Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Two complimentary approaches for the synthesis and isolation of stable phosphanylphosphaalkenes

Aleksandra Ziółkowska, Natalia Szynkiewicz, Łukasz Ponikiewski*

Department of Inorganic Chemistry, Chemical Faculty, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk

KEYWORDS: Stable phosphanylphosphaalkenes; phospha-Wittig reaction; phospha-Peterson reaction; organophosphorus compounds.

PART A. Experimental section

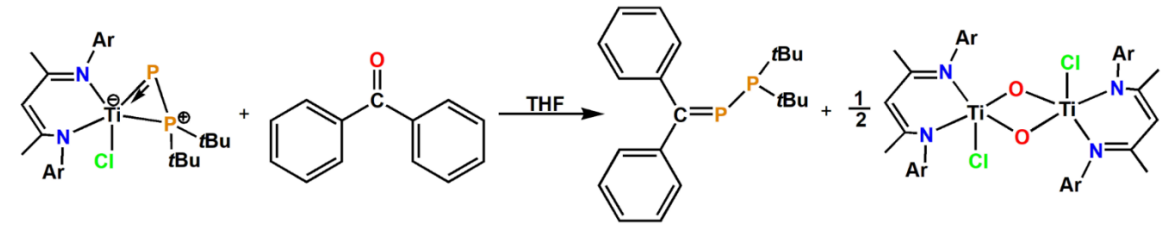
A.1. Materials and method

All synthetic procedures were performed under inert gas (Ar) and were carried out using mBraun glovebox and standard Schlenk techniques. All spectra in solution were recorded on Bruker AV400 MHz spectrometer (external standard tetramethylsilane for ^{1}H, ^{13}C; 85% H_3PO_4 for ^{31}P). Melting point of the all crystalline products were measured on the Stuart SMP 30 apparatus. Elemental analysis for solid and liquid samples were recorded on Elementary Vario El Cube CHNS. [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**) and *t*Bu$_2$P-P(SiMe$_3$)Li·3THF (**2**), were prepared according to procedures in the literature.[1-3] All ketones and aldehydes were commercially purchased. THF and toluene were dried over Na/Ph_2CO, while pentane was dried over Na/K alloy. All solvents were distilled under argon atmosphere. Elemental analysis were recorded on Elementary Vario El Cube CHNS.

A.2. General method for the phospha-Wittig reaction of [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (1) with selected ketones and aldehydes

To the [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**) (0.400 g, 0.591 mmol) dissolved in 15 mL of THF the appropriate amount of ketone or aldehyde in 5 mL of THF was dropwise added. The initial green solution of the titanium complex, after the right time for each reaction was changed. In the next step the solvent was evaporated and in results a slightly oily residue for each reaction was obtained.

A.2.1. Reaction of **1** with benzophenone



(1)

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

(3a)

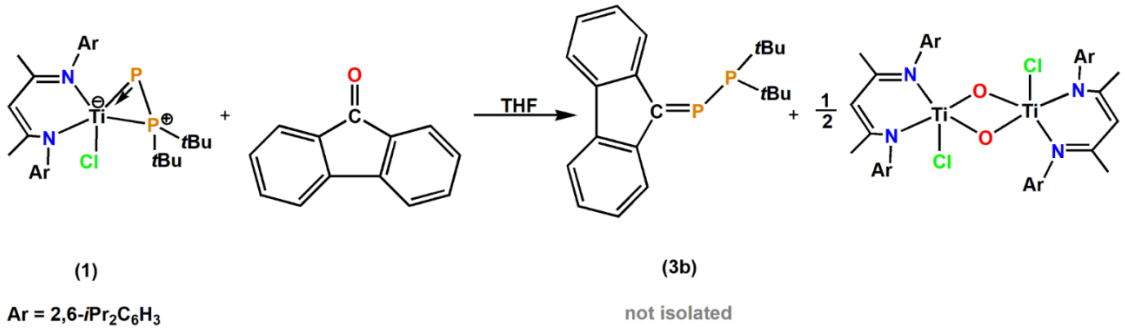
not isolated

Benzophenone (0.108 g, 0.591 mmol); deep orange reaction solution after 3 months. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

$^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) δ: 277.32 (d, $J_{P\text{-}P}$ = 228.9 Hz, $(Ph)_2C$=**P**-P*t*Bu$_2$, **3a**), 27.39 (d, $J_{P\text{-}P}$ = 228.9 Hz, $(Ph)_2C$=P-**P***t*Bu$_2$, **3a**) ppm.

$^{31}P\{^{1}H\}$, ^{1}H, $^{13}C\{^{1}H\}$-NMR spectra of isolated $(Ph)_2C$=P-P*t*Bu$_2$ (**3a**) see point A.3.1. page 20.

A.2.2. Reaction of **1** with 9-fluorenone

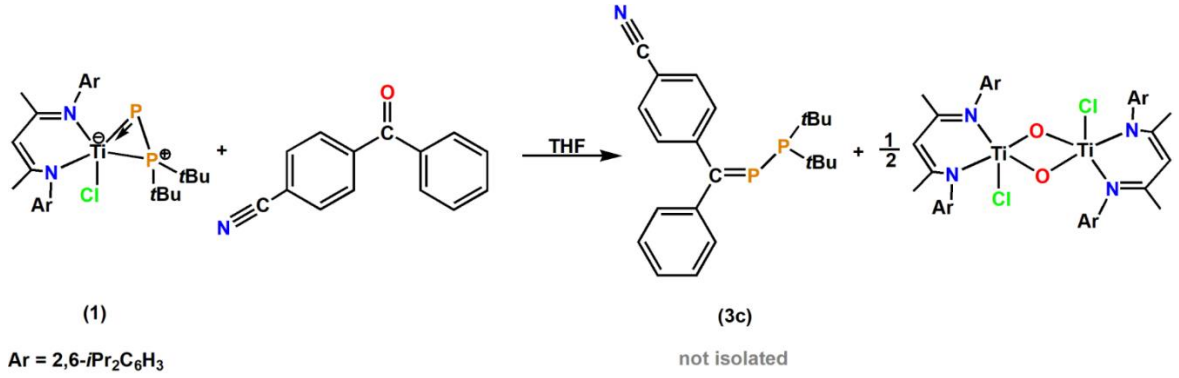


9-fluorenone (0.106 g, 0.591 mmol); red reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) δ: 297.84 (d, $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=**P**-P*t*Bu$_2$, **3b**), 19.50 (s, *t*Bu$_2$PH), 9.61 (d, $J_{P\text{-}P}$ = 228.9 Hz, (fluorenyl)C=P-**P***t*Bu$_2$, **3b**) ppm.

$^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ NMR spectra of isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**) see point A.3.2. page 21.

A.2.3. Reaction of **1** with 4-cyanobenzophenone

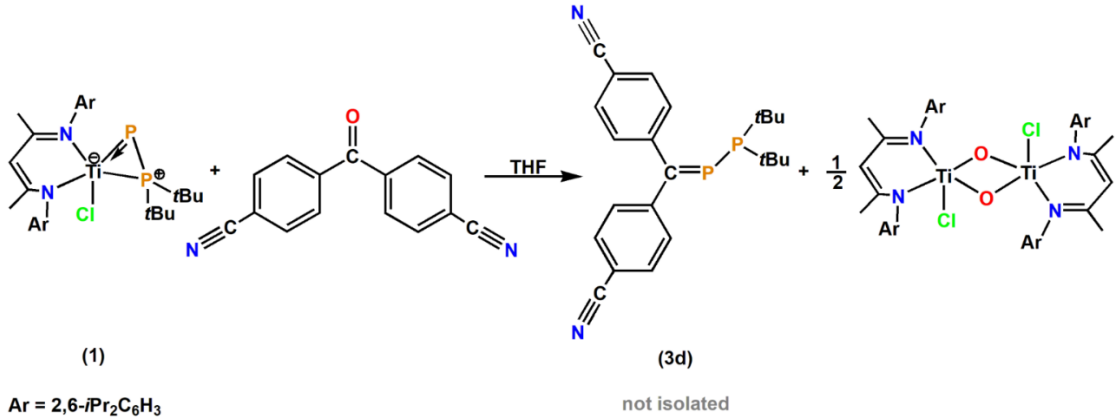


4-cyanobenzophenone (0.122 g, 0.591 mmol); yellow-red reaction solution after 3 months. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) δ: 843.47 (d, $J_{P\text{-}P}$ = 450.5 Hz, unreacted [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}]), 302.86 (d $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$, ***E*-3c**), 285.73 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$, ***Z*-3c**), 143.57 (d $J_{P\text{-}P}$ = 450.5 Hz, unreacted [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}]), 28.98 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$, ***E*-3c**), 27.81 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$, ***Z*-3c**) ppm.

$^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ NMR spectra of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) see point A.3.3. page 22.

A.2.4. Reaction of **1** with 4,4'-dicyanobenzophenone



(1) (3d)

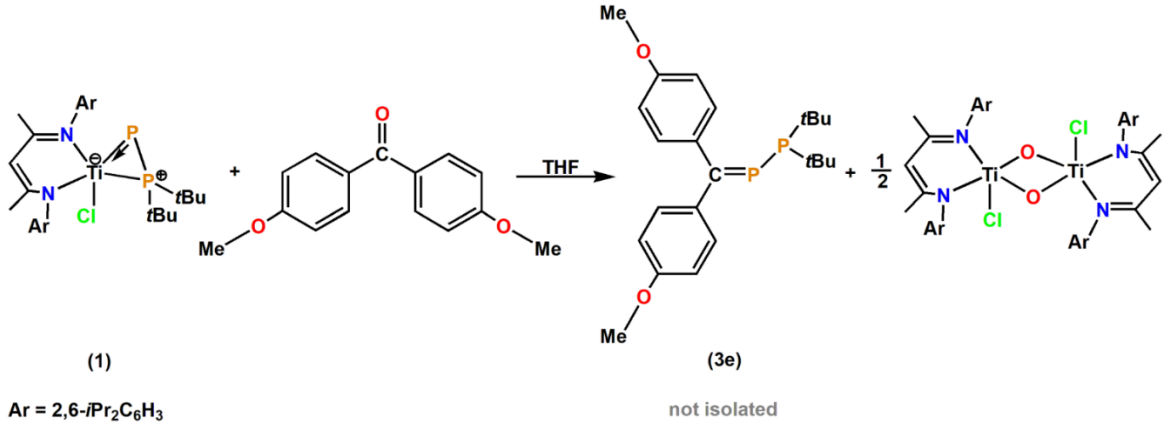
Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ not isolated

4,4'-dicyanobenzophenone (0.137 g, 0.591 mmol); yellow-red reaction solution after 3 months. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 843.85 (d, $J_{P\text{-}P}$ = 450.5 Hz, unreacted [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}]), 312.22 (d, $J_{P\text{-}P}$ = 232.5 Hz, (4-CN-Ph)$_2$C=**P**-P*t*Bu$_2$, **3d**), 143.56 (d, $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}]), 29.54 (d, $J_{P\text{-}P}$ = 232.5 Hz, (4-CN-Ph)$_2$C=P-**P***t*Bu$_2$, **3d**), 19.51 (s, *t*Bu$_2$PH) ppm.

^{31}P{^{1}H}, ^{1}H, ^{13}C{^{1}H} NMR spectra of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) see point A.3.4. page 23.

A.2.5. Reaction of **1** with 4,4'-dimethoxybenzophenone

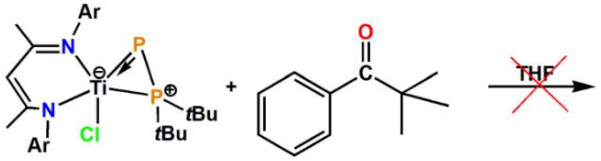


4,4'-dimethoxybenzophenone (0.143 g, 0.591 mmol); yellow-red reaction solution after 3 months. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 844.38 (d, $J_{P\text{-}P}$ = 450.5 Hz, unreacted [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}]), 257.68 (d, $J_{P\text{-}P}$ = 228.9 Hz, (4-MeO-Ph)$_2$C=**P**-P*t*Bu$_2$, **3e**), 143.78 (d, $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}]), 28.38 (d, $J_{P\text{-}P}$ = 228.9 Hz, (4-MeO-Ph)$_2$C=P-**P***t*Bu$_2$, **3e**), 19.66 (s, *t*Bu$_2$PH) ppm.

^{31}P{^{1}H}, ^{1}H, ^{13}C{^{1}H} NMR spectra of isolated (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) see point A.3.5. page 24.

A.2.6. Reaction of **1** with *tert*-butyl phenyl ketone



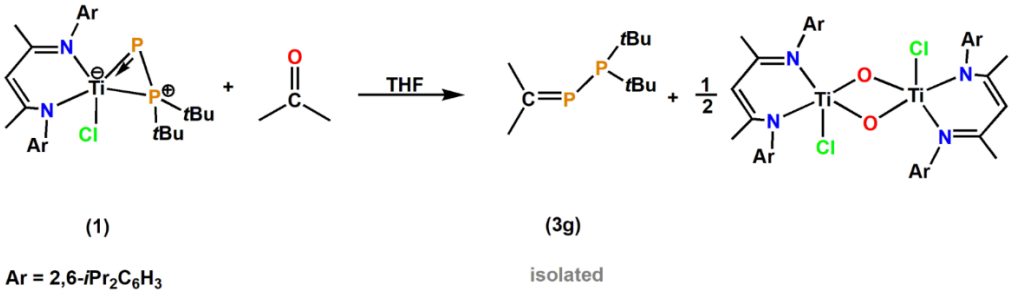
(1)

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

Tert-butyl phenyl ketone (0.099 mL, 0.591 mmol, 0.970 g/mL); still green reaction solution after 3 months. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 838.89 (d, $J_{P\text{-}P}$ = 450.5 Hz, unreacted [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}]), 142.05 (d, $J_{P\text{-}P}$ = 450.5 Hz, unreacted [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}]), 19.56 (s, *t*Bu$_2$PH) ppm.

A.2.7. Reaction of **1** with acetone



(1)

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

(3g)

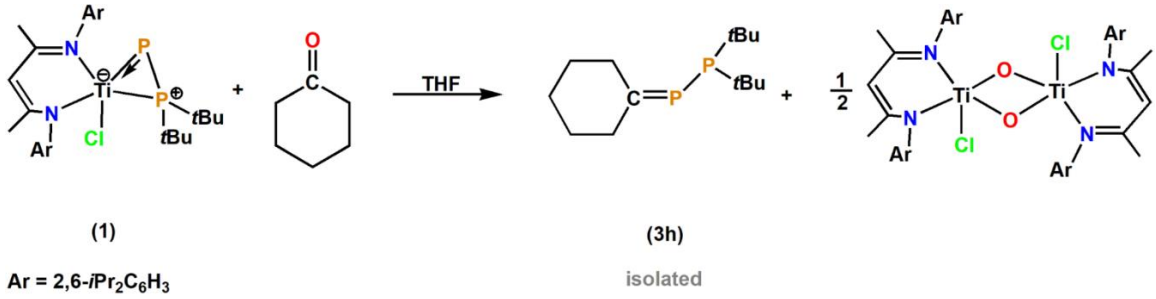
isolated

Acetone (0.044 mL, 0.591 mmol, 0.784 g/mL); dark yellow reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (125°C, 0.01 Torr), finally resulting clear yellow oil characterized as (Me)$_2$C=P-P*t*Bu$_2$ (**3g**) (0.100 g, yield: 72%).

^{31}P{^{1}H} NMR data from the reaction mixture (400 MHz, C_6D_6, 298 K) δ: 234.73 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Me)$_2$C=**P**-P*t*Bu$_2$), 23.14 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Me)$_2$C=P-**P***t*Bu$_2$) ppm.

The ^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H}-NMR shifts of isolated **3g** are analogical to these presented in our earlier publication.[4]

A.2.8. Reaction of **1** with cyclohexanone



(1)

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

(3h)

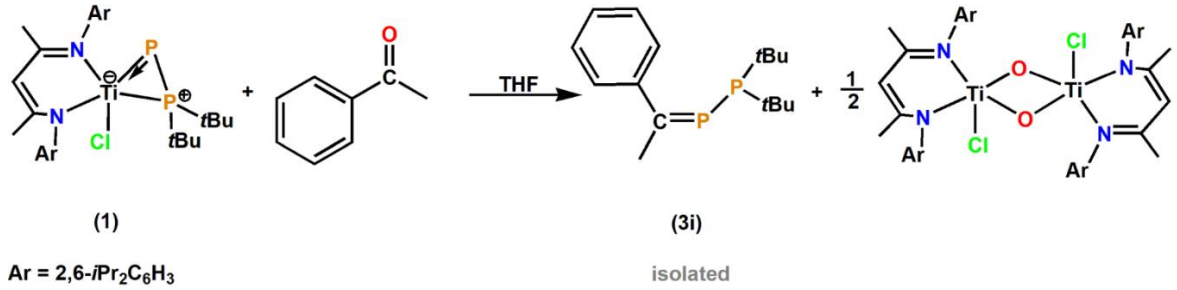
isolated

Cyclohexanone (0.061 mL, 0.591 mmol, 0.948 g/mL); dark yellow reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (130°C, 0.01 Torr) finally resulting clear yellow oil characterized as $(CH_2)_5C$=P-P*t*Bu$_2$ (**3h**) (0.09 g, yield: 55%).

^{31}P{^{1}H} NMR data from the reaction mixture (400 MHz, C_6D_6, 298 K) δ: 221.02 (d, $J_{P\text{-}P}$ = 228.8 Hz, $(CH_2)_5C$=**P**-P*t*Bu$_2$), 19.51 (s, *t*Bu$_2$PH), 17.76 (d, $J_{P\text{-}P}$ = 228.8 Hz, $(CH_2)_5C$=P-**P***t*Bu$_2$) ppm.

The ^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H}-NMR shifts of isolated **3h** are analogical to these presented in our earlier publication.[5]

A.2.9. Reaction of **1** with acetophenone



(1)

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

(3i)

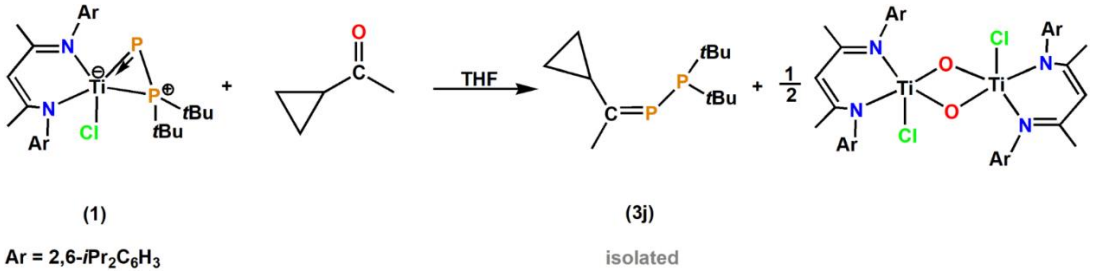
isolated

Acetophenone (0.069 mL, 0.591 mmol, 1.030 g/mL); dark yellow reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (160°C, 0.01 Torr) finally resulting yellow oil characterized as (Ph)MeC=P–P*t*Bu$_2$ (**3i**) (0.09 g, yield: 55%).

^{31}P{^{1}H} NMR data from the reaction mixture (400 MHz, C_6D_6, 298 K) δ: 263.63 (d, $J_{P\text{-}P}$ = 234.9 Hz, (Ph)MeC=**P**–P*t*Bu$_2$, ***E*-3i**), 253.06 (d, $J_{P\text{-}P}$ = 222.8 Hz, (Ph)MeC=**P**–P*t*Bu$_2$, ***Z*-3i**), 24.65 (d, $J_{P\text{-}P}$ = 222.8 Hz, (Ph)MeC=P–**P***t*Bu$_2$, ***Z*-3i**), 21.91 (d, $J_{P\text{-}P}$ = 234.9 Hz, (Ph)MeC=P–**P***t*Bu$_2$, ***E*-3i**), 19.65 (s, *t*Bu$_2$PH) ppm.

The ^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H}-NMR shifts of isolated **3i** are analogical to these presented in our earlier publication.[5]

A.2.10. Reaction of **1** with cyclopropyl methyl ketone



(1) (3j)

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ isolated

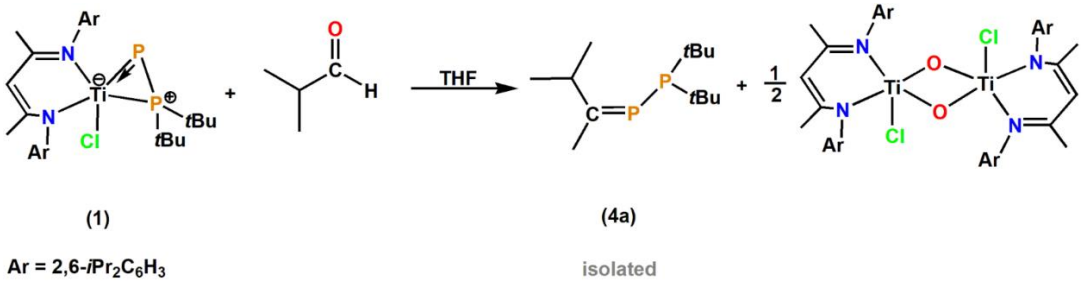
Cyclopropyl methyl ketone (0.059 mL, 0.591 mmol, 0.849 g/mL); orange reaction solution after 24 hours An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (140°C, 0.01 Torr) finally resulting clear dark yellow oil characterized as (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P*t*Bu$_2$ (**3j**) (0.094 g, yield: 61%) . Calculated elemental analysis (%) for $C_{13}H_{26}P_2$: C, 63.91; H, 10.73 N. Found (conducted for oil): C, 63.65; H, 10.94.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 3.64 (broad m, 1H, (*cyclo*-CH$_2$CH$_2$C**H**)(Me)C=P-P*t*Bu$_2$, ***Z*-3j**), 2.29 (ddd, 3H, $J_{P\text{-}H}$ = 10.8 Hz, $J_{H\text{-}H}$ = 1.3 Hz, $J_{P\text{-}H}$ = 0.4 Hz, (*cyclo*-CH$_2$CH$_2$CH)(**Me**)C=P-P*t*Bu$_2$, ***E*-3j**), 2.04 (broad m, 1H, (*cyclo*-CH$_2$CH$_2$C**H**)(Me)C=P-P*t*Bu$_2$, ***E*-3j**), 1.73 (dd, 3H, $J_{P\text{-}H}$ = 21.9 Hz, J_{PH} = 1.6 Hz, (*cyclo*-CH$_2$CH$_2$CH)(**Me**)C=P-P*t*Bu$_2$, ***Z*-3j**), 1.24 (d, 18H, $J_{P\text{-}H}$ = 11.2 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P***t*Bu$_2$**, ***E*-3j**), 1.17 (d, 18H, $J_{P\text{-}H}$ = 11.2 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P***t*Bu$_2$**, ***Z*-3j**), 0.74 (broad m, 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu$_2$, ***Z*-3j**), 0.60 (broad m, 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu$_2$, ***Z*-3j**), 0.53 ppm, (broad m, 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu$_2$, ***E*-3j**), 0.50 (broad m, 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu$_2$, ***E*-3j**) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 213.28 (dd, $J_{P\text{-}C}$ = 53.6 Hz, $J_{P\text{-}C}$ = 14.5 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)**C**=P-P*t*Bu$_2$, ***E*-3j**), 210.41 (dd, $J_{P\text{-}C}$ = 55.4 Hz, $J_{P\text{-}C}$ = 11.8 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)**C**=P-P*t*Bu$_2$, ***Z*-3j**), 33.36 (dd, $J_{P\text{-}C}$ = 9.1 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P{**C**(CH$_3$)$_3$}$_2$, ***E*-3j**), 33.36 (dd, $J_{P\text{-}C}$ = 9.1 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P{**C**(CH$_3$)$_3$}$_2$, ***E*-3j**), 31.15 (dd, $J_{P\text{-}C}$ = 10.9 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P{C(**C**H$_3$)$_3$}$_2$, ***Z*-3j**), 31.01 (dd, $J_{P\text{-}C}$ = 10.9 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-P{C(**C**H$_3$)$_3$}$_2$, ***Z*-3j**), 26.45 (dd), $J_{P\text{-}C}$ = 45.4 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (*cyclo*-CH$_2$CH$_2$**C**H)(Me)C=P-P*t*Bu$_2$, ***E*-3j**), 25.19 (dd, $J_{P\text{-}C}$ = 29.1 Hz, $J_{P\text{-}C}$ = 15.4 Hz, (*cyclo*-CH$_2$CH$_2$CH)(**C**H$_3$)C=P-P*t*Bu$_2$, ***E*-3j**), 24.43 (dd, $J_{P\text{-}C}$ = 38.1 Hz, $J_{P\text{-}C}$ = 17.2 Hz, (*cyclo*-CH$_2$CH$_2$CH)(**C**H$_3$)C=P-P*t*Bu$_2$, ***Z*-3j**), 23.63 (dd, $J_{P\text{-}C}$ = 45.4 Hz, $J_{P\text{-}C}$ = 3.6 Hz, (*cyclo*-CH$_2$CH$_2$**C**H)(Me)C=P-P*t*Bu$_2$, ***Z*-3j**), 9.52 (d, $J_{P\text{-}C}$ = 2.7 Hz, (*cyclo*-**C**H$_2$**C**H$_2$CH)(Me)C=P-P*t*Bu$_2$, ***Z*-3j**), 9.37 (d, $J_{P\text{-}C}$ = 12.7 Hz, (*cyclo*-**C**H$_2$**C**H$_2$CH)(Me)C=P-P*t*Bu$_2$, ***E*-3j**) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 232.48 (d, $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=**P**-P*t*Bu$_2$, ***Z*-3j**), 225.87 (d, $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=**P**-P*t*Bu$_2$, ***E*-3j**) 18.52 (d, $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-**P***t*Bu$_2$, ***Z*-3j**),17.00 (d, $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH$_2$CH$_2$CH)(Me)C=P-**P***t*Bu$_2$, ***E*-3j**) ppm.

A.2.11. Reaction of **1** with isobutyraldehyde



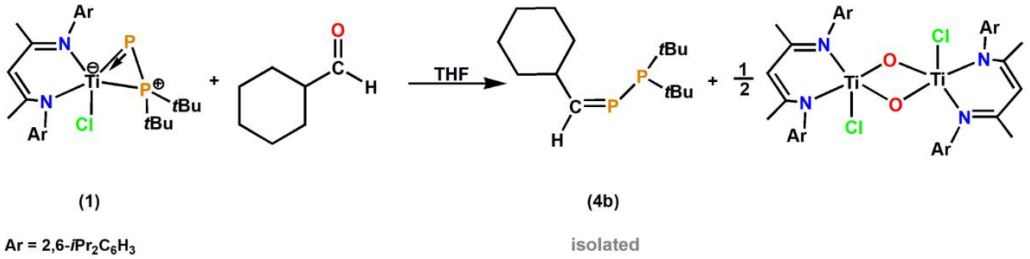
Isobutyraldehyde (0.054 mL, 0.591 mmol, 0.790 g/mL); pale orange reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (160°C, 0.01 Torr) finally resulting clear yellow oil characterized as {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$ (**4a**) (0.110 g, yield: 58%). Calculated elemental analysis (%) for $C_{12}H_{26}P_2$: C, 62.05; H, 11.28 N. Found (conducted for oil): C, 61.95; H, 11.51.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 9.49 (ddd, 1H, $J_{P\text{-}H}$ = 24.1 Hz, $J_{P\text{-}H}$ = 12.0 Hz, $J_{P\text{-}H}$ = 8.1 Hz, {(Me)$_2$CH}(**H**)C=P-P*t*Bu$_2$, ***E*-4a**), 8.42 (ddd, 1H, $J_{P\text{-}H}$ = 36.1 Hz, $J_{H\text{-}H}$ = 20.9 Hz, $J_{P\text{-}H}$ = 8.0 Hz, {(Me)$_2$CH}(**H**)C=P-P*t*Bu$_2$, ***Z*-4a**), 4.12 (br. m, 1H, $J_{H\text{-}H}$ = 6.7 Hz, {(Me)$_2$C**H**}(H)C=P-P*t*Bu$_2$, ***Z*-4a**), 3.55 (q, THF protons), 2.77 (br. m, 1H, $J_{H\text{-}H}$ = 6.7 Hz, {(Me)$_2$C**H**}(H)C=P-P*t*Bu$_2$, ***E*-4a**), 1.39 (q, THF protons), 1.25 (d, 18H, $J_{P\text{-}H}$ = 11.3 Hz, {(Me)$_2$CH}(H)C=P-P***t*Bu**$_2$, ***E*-4a**), 1.23 (d, 18H, $J_{P\text{-}H}$ = 11.2 Hz, {(Me)$_2$CH}(H)C=P-P***t*Bu**$_2$, ***Z*-4a**), 1.04 (dd, 6H, $J_{H\text{-}H}$ = 6.7 Hz, $J_{P\text{-}H}$ = 0.8 Hz, {(**Me**)$_2$CH}(H)C=P-P*t*Bu$_2$, ***E*-4a**), 0.94 (br. d, 6H, $J_{H\text{-}H}$ = 6.7 Hz, {(**Me**)$_2$CH}(H)C=P-P*t*Bu$_2$, ***Z*-4a**) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 213.12 (dd, $J_{P\text{-}C}$ = 49.0 Hz, $J_{P\text{-}C}$ = 33.6 Hz, {(Me)$_2$CH}(H)**C**=P-P*t*Bu$_2$, ***E*-4a**), 38.50 (dd, $J_{P\text{-}C}$ = 19.9 Hz, $J_{P\text{-}C}$ = 13.6 Hz, {(Me)$_2$**C**H}(H)C=P-P*t*Bu$_2$, ***E*-4a**), 32.51 (dd, $J_{P\text{-}C}$ = 28.2 Hz, $J_{P\text{-}C}$ = 2.7 Hz, {(Me)$_2$CH}(H)C=P-P{**C**(CH$_3$)$_3$}$_2$, ***E*-4a**), 31.04 (dd, $J_{P\text{-}C}$ = 19.9 Hz, $J_{P\text{-}C}$ = 5.4 Hz, {(Me)$_2$CH}(H)C=P-P{C(**C**H$_3$)$_3$}$_2$, ***E*-4a**), 23.02 (d , $J_{P\text{-}C}$ = 12.7 Hz, {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$, ***E*-4a**) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 254.39 (d, $J_{P\text{-}P}$ = 220.8 Hz, {(Me)$_2$CH}(H)C=**P**-P*t*Bu$_2$, ***E*-4a**), 249.40 (d, $J_{P\text{-}P}$ = 212.8 Hz, {(Me)$_2$CH}(H)C=**P**-P*t*Bu$_2$, ***Z*-4a**), 52.83 (d, $J_{P\text{-}P}$ = 220.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$, ***E*-4a**), 12.85 (d, $J_{P\text{-}P}$ = 212.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$, ***Z*-4a**) ppm.

4bA.2.12. Reaction of **1** with cyclohexanecarboxaldehyde



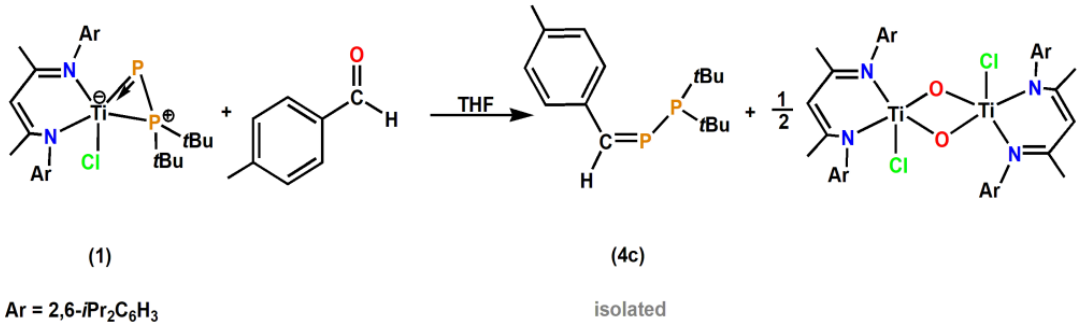
Cyclohexanecarboxaldehyde (0.072 mL, 0.591 mmol, 0.926 g/mL); orange reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (165°C, 0.01 Torr) finally resulting clear yellow oil characterized as {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2 (**4b**) (0.085 g, yield: 53%). Calculated elemental analysis (%) for $C_{15}H_{30}P_2$: C, 66.15; H, 11.10 N. Found (conducted for oil): C, 66.03; H, 11.19.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 9.44 (ddd, 1H, $J_{P\text{-}H}$ = 22.7 Hz, $J_{P\text{-}H}$ = 14.2 Hz, $J_{H\text{-}H}$ = 8.4 Hz, {*cyclo*-$(CH_2)_4CH$}(**H**)C=P-P*t*Bu_2, ***E*-4b**), 8.49 (ddd, 1H, $J_{P\text{-}H}$ = 31.9 Hz, $J_{P\text{-}H}$ = 21.5 Hz, $J_{H\text{-}H}$ = 10.9 Hz, {*cyclo*-$(CH_2)_4CH$}(**H**)C=P-P*t*Bu_2, ***Z*-4b**), 2.51 (broad m, 1H, {*cyclo*-$(CH_2)_4$C**H**}(H)C=P-P*t*Bu_2, ***E*-4b**), 1.83 (broad m, 2H, {*cyclo*-(C**H**$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**), 1.65, (broad m, 2H, {*cyclo*-(C**H**$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**), 1.29 (d, 18H, $J_{P\text{-}H}$ = 11.1 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P***t*Bu$_2$** ***E*-4b**), 1.19 (broad m, 6H, {*cyclo*-(C**H**$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 211.64 (dd, $J_{P\text{-}C}$ = 48.2 Hz, $J_{P\text{-}C}$ = 34.6 Hz, {*cyclo*-$(CH_2)_4CH$}(H)**C**=P-P*t*Bu_2, ***E*-4b**), 203.01 (dd, $J_{P\text{-}C}$ = 55.7 Hz, $J_{P\text{-}C}$ = 14.2 Hz, {*cyclo*-$(CH_2)_4CH$}(H)**C**=P-P*t*Bu_2, ***Z*-4b**), 48.07 (dd, $J_{P\text{-}C}$ = 18.6 Hz, $J_{P\text{-}C}$ = 13.4 Hz, {*cyclo*-$(CH_2)_4$**C**H}(H)C=P-P*t*Bu_2, ***E*-4b**), 33.98 (s, {*cyclo*-(**C**H$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**), 33.85 (s, {*cyclo*-(**C**H$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**), 33.27 (s, {*cyclo*-(**C**H$_2)_4$CH}(H)C=P-P*t*Bu_2, ***Z*-4b**), 33.18 (s, {*cyclo*-(**C**H$_2)_4$CH}(H)C=P-P*t*Bu_2, ***Z*-4b**), 32.46 (dd, $J_{P\text{-}C}$ = 28.2 Hz, $J_{P\text{-}C}$ = 2.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P{**C**$(CH_3)_3$}$_2$, ***E*-4b**), 31.02 (dd, $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 5.0 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P{C(**C**H$_3)_3$}$_2$, ***E*-4b**), 30.18 (dd, $J_{P\text{-}C}$ = 14.8 Hz, $J_{P\text{-}C}$ = 5.42 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P{**C**$(CH_3)_3$}$_2$, ***Z*-4b**), 25.86 (s, {*cyclo*-(**C**H$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**), 25.84 (s, {*cyclo*-(**C**H$_2)_4$CH}(H)C=P-P*t*Bu_2, ***E*-4b**) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 256.25 (d, J_{PP} = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2, ***E*-4b**), 251.24 (d, J_{PP} = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2, ***Z*-4b**), 52.23 (d, J_{PP} = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-**P***t*Bu_2, ***E*-4b**), 13.17 (d, J_{PP} = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-**P***t*Bu_2, ***Z*-4b**) ppm.

A.2.13. Reaction of **1** with *p*-tolualdehyde



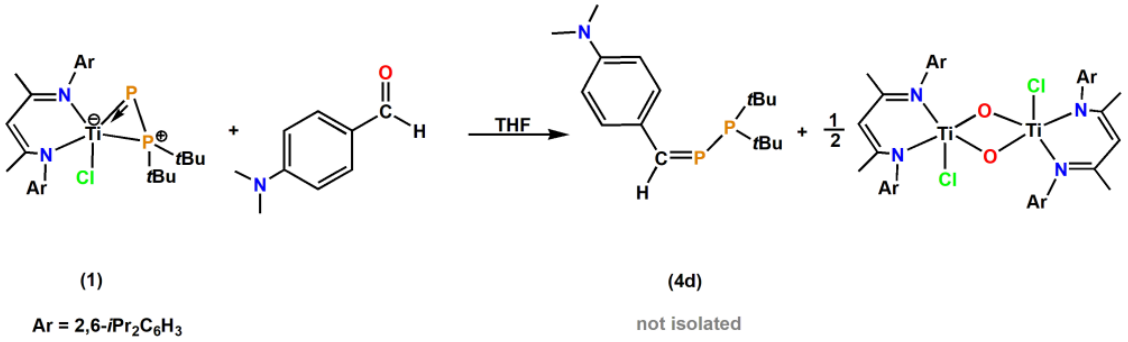
p-Tolualdehyde (0.065 mL, 0.591 mmol, 1.019 g/mL); pale orange reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was distilled using the Kugelrohr apparatus (150°C, 0.01 Torr) finally resulting clear yellow oil characterized as (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**) (0.115 g; yield: 69%). Calculated elemental analysis (%) for $C_{16}H_{26}P_2$: C, 68.55 H, 9.35 N. Found (conducted for oil): C, 68.45; H, 9.58.

^{1}H NMR (400 MHz, 298 K, C_6D_6) only *E* isomer visible; δ: 10.16 (dd, 1H, $J_{P\text{-}H}$ = 22.7 Hz, $J_{P\text{-}H}$ = 13.6 Hz, (*p*-Me-Ph)(**H**)C=P-P*t*Bu$_2$, ***E*-4c**), 7.56 (dd, 2H, $J_{P\text{-}H}$ = 7.6 Hz, $J_{P\text{-}H}$ = 2.7 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$, *o*-H$_{Ar}$, ***E*-4c**) 6.83 (d, 2H, $J_{P\text{-}H}$ = 7.9 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$, *m*-H$_{Ar}$, ***E*-4c**), 1.97 (d, 3H, $J_{P\text{-}H}$ = 1.9 Hz, (*p*-**Me**-Ph)(H)C=P-P*t*Bu$_2$, ***E*-4c**), 1.28 (d, 18H, $J_{P\text{-}H}$ = 11.1 Hz, (*p*-Me-Ph)(H)C=P-P***t*Bu**$_2$, ***E*-4c**) ppm;

^{13}C{^{1}H} NMR (400 MHz, 298 K, C_6D_6) only *E* isomer visible; δ: 197.67 (dd, $J_{P\text{-}C}$ = 45.1 Hz, $J_{P\text{-}C}$ = 39.2 Hz, (*p*-Me-Ph)(H)**C**=P-P*t*Bu$_2$, ***E*-4c**), 129.30 (d, $J_{P\text{-}C}$ = 2.6 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***E*-4c**), 126.73 (d, $J_{P\text{-}C}$ = 19.5 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$, *o*-C$_{Ar}$, ***E*-4c**), 33.10 (dd, $J_{P\text{-}C}$ = 27.7 Hz, $J_{P\text{-}C}$ = 2.5 Hz, (*p*-Me-Ph)(H)C=P-P{**C**(CH$_3$)$_3$}$_2$, ***E*-4c**), 31.15 (dd, $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 5.1 Hz, (*p*-Me-Ph)(H)C=P-P{C(**C**H$_3$)$_3$}$_2$, ***E*-4c**), 20.95 (d, $J_{P\text{-}C}$ = 1.0 Hz, (*p*-**Me**-Ph)(H)C=P-P*t*Bu$_2$, ***E*-4c**) ppm;

^{31}P{^{1}H} NMR (400 MHz, 298 K, C_6D_6) only *E* isomer visible; δ: 266.61 (d, $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=**P**-P*t*Bu$_2$, ***E*-4c**), 56.72 (d, $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=P-**P***t*Bu$_2$, ***E*-4c**) ppm.

A.2.14. Reaction of **1** with 4-(dimethylamino)benzaldehyde

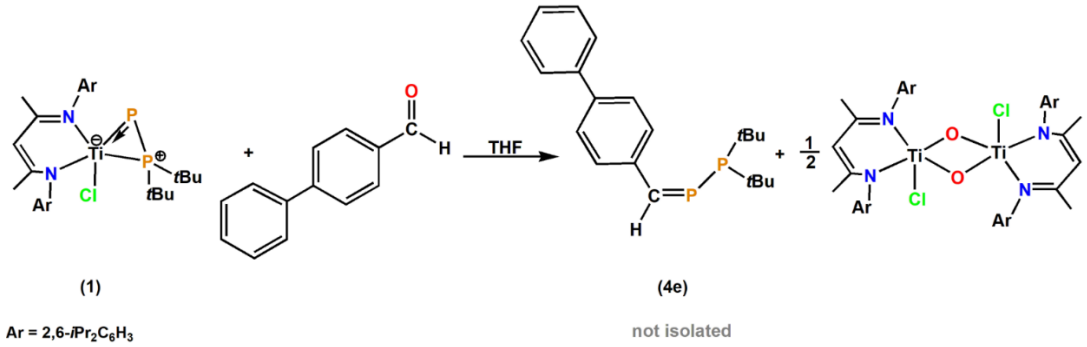


4-(dimethylamino)benzaldehyde (0.088 g, 0.591 mmol); orange-red reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) only *E* isomer visible; δ: 230.63 (d, $J_{P\text{-}P}$ = 224.9 Hz, {$(Me)_2$N-Ph}(H)C=**P**-P*t*Bu_2, ***E*-4d**), 57.72 (d, $J_{P\text{-}P}$ = 224.9 Hz, {4-$(Me)_2$N-Ph}(H)C=P-**P***t*Bu_2, ***E*-4d**), 19.56 (s, *t*Bu_2PH) ppm.

$^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ NMR spectra of isolated {4-$(Me)_2$N-Ph}(H)C=P-**P***t*Bu_2 (**4d**) see point A.3.14. page 33.

A.2.15. Reaction of **1** with biphenyl-4-carboxaldehyde



Biphenyl-4-carboxaldehyde (0.108 g, 0.591 mmol); dark orange reaction solution after 24 hours. An oily residue obtained after evaporation of the solvent was dissolved in C_6D_6 and investigated by NMR spectroscopy.

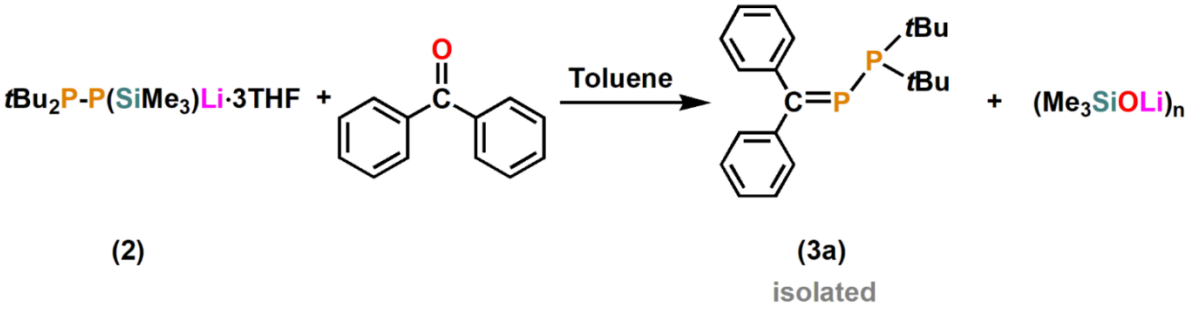
^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) only *E* isomer visible; δ: 274.76 (d, $J_{P\text{-}P}$ = 224.9 Hz, PhPh(H)C=**P**-P*t*Bu$_2$, ***E*-4e**), 57.13 (d, $J_{P\text{-}P}$ = 224.9 Hz, PhPh(H)C=P-**P***t*Bu$_2$, ***E*-4e**), 19.57 (s, *t*Bu$_2$PH) ppm.

^{31}P{^{1}H}, ^{1}H, ^{13}C{^{1}H} NMR spectra of isolated PhPh(H)C=P-**P***t*Bu$_2$ (**4e**) see point A.3.15. page 34.

A.3. General method for the phospha-Peterson reaction of *t*Bu$_2$P-P(SiMe$_3$)Li·3THF (2) with selected ketones and aldehydes

Lithium salt of diphosphane *t*Bu$_2$P-P(SiMe$_3$)Li·3THF (**2**) (0.200 g; 0.424 mmol) was dissolved in 5 mL of toluene, and was added to following amount of the ketone or aldehyde solution in 5 mL of toluene. Each of the presented below reaction was conducted only 1 hour, and the solution was evaporated.

A.3.1. Reaction of **2** benzophenone



(2) **(3a)** isolated

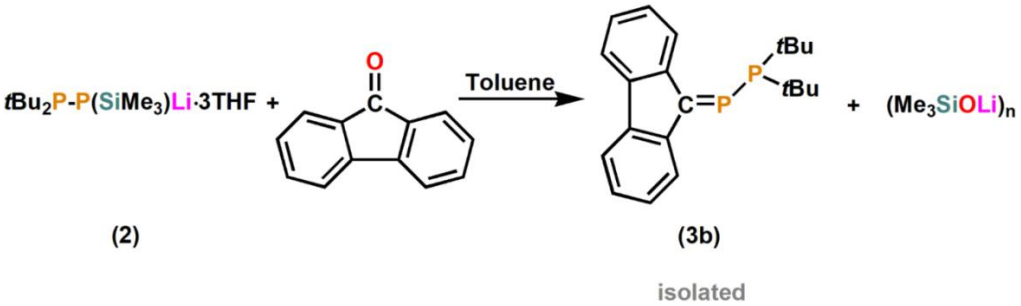
Benzophenone (0.077 g, 0.424 mmol). The solid residue was treated with petroleum ether (10 mL), the resulting solution was filtered, and concentrated by about half its volume. The solution was placed in -30°C, and after three hours dark orange crystals of (Ph)$_2$C=P-P*t*Bu$_2$ (**3a**) appeared (0.109 g; yield: 75 %). M$_P$ at 85-86°C. Calculated elemental analysis (%) for C$_{21}$H$_{28}$P$_2$ (**3a**): C, 73.45; H, 8.51. Found: C, 73.41; H, 8.50.

^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ: 7.70 – 7.00 (10H, (**Ph**)$_2$C=P-P*t*Bu$_2$), 1.20 (d, 18H, J_{P-H} = 10.9 Hz, (Ph)$_2$C=P-P***t*Bu**$_2$) ppm;

^{13}C{^{1}H} NMR (400 MHz, C$_6$D$_6$, 298 K) δ: 207.29 (dd, J_{P-C} = 54.5 Hz, J_{P-C} = 16.8 Hz, (Ph)$_2$**C**=P-P*t*Bu$_2$), 146.53 (dd, J_{P-C} = 23.2 Hz, J_{P-C} = 4.3 Hz, (**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), 145.61 (dd, J_{P-C} = 13.9 Hz, J_{P-C} = 5.9 Hz, (**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), 129.70 (dd, J_{P-C} = 10.6 Hz, J_{P-C} = 6.5 Hz, (Ph)$_2$C=P-P*t*Bu$_2$, *o*-C$_{Ar}$), 129.29 (d, J_{P-C} = 4.8 Hz, (**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-C$_{Ar}$), 128.04 (d, J_{P-C} = 1.1 Hz, (**Ph**)$_2$C=P-P*t*Bu$_2$, *p*-C$_{Ar}$), 127.32 (s, (**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-C$_{Ar}$), 127.20 (s, (**Ph**)$_2$C=P-P*t*Bu$_2$, *p*-C$_{Ar}$), 127.13 (s, (**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-Ar), 33.92 (dd, J_{P-C} = 30.1 Hz, J_{PC} = 4.3 Hz, (**Ph**)$_2$C=P-P{**C**(Me$_3$)}$_2$), 31.08 (dd, J_{P-C} = 14.4 Hz, J_{PC} = 5.4 Hz, (**Ph**)$_2$C=P-P{C(**Me**$_3$)}$_2$) ppm;

^{31}P{^{1}H} NMR (400 MHz, C$_6$D$_6$, 298 K) δ: 277.32 (d, J_{P-P} = 228.9 Hz, (Ph)$_2$C=**P**-P*t*Bu$_2$), 27.39 (d, J_{P-P} = 228.9 Hz, (Ph)$_2$C=P-**P***t*Bu$_2$) ppm.

A.3.2. Reaction of **2** with 9-fluorenone



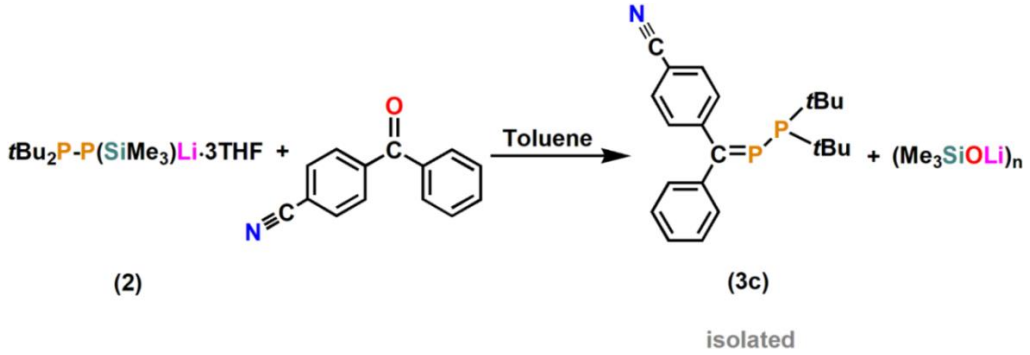
9-fluorenone (0.076 g, 0.424 mmol). The oily, red residue was treated with petroleum ether (10 mL), and the resulting solution was filtered. In the next step, from the obtained filtrate, the solvent was evaporated to dryness and red oil (0.128 g; yield 89 %) was NMR investigated. Calculated elemental analysis (%) for $C_{21}H_{26}P_2$: C, 74.10; H, 7.70 N. Found (conducted for oil): C, 73.90; H, 7.84.

^{1}H NMR (400 MHz, Toluene-d_8, 298 K) δ: 9.43 – 6.76 ((**fluorenyl**)C=P-P*t*Bu_2), 1.07 (d, 18H, J_{PH} = 11.9 Hz, (fluorenyl)C=P-P***t*Bu**$_2$) ppm;

^{13}C{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 189.46 (dd, $J_{P\text{-}C}$ = 54.5 Hz, $J_{P\text{-}C}$ = 10.9 Hz, (fluorenyl)**C**=P-P*t*Bu_2), 143.81 (dd, $J_{P\text{-}C}$ = 26.3 Hz, $J_{P\text{-}C}$ = 8.2 Hz, (**fluorenyl**)C=P-P*t*Bu_2), 141.36 (d, $J_{P\text{-}C}$ = 9.1 Hz, (fluorenyl)C=P-P*t*Bu_2), 140.52 (dd, $J_{P\text{-}C}$ = 18.6 Hz, $J_{P\text{-}C}$ = 1.3 Hz, (fluorenyl)C=P-P*t*Bu_2), 138.34 (d, $J_{P\text{-}C}$ = 13.6 Hz, (fluorenyl)C=P-P*t*Bu_2), 129.72 (dd, $J_{P\text{-}C}$ = 59.0 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (fluorenyl)C=P-P*t*Bu_2), 129.65 (dd, $J_{P\text{-}C}$ = 5.7 Hz, $J_{P\text{-}C}$ = 3.9 Hz, (fluorenyl)C=P-P*t*Bu_2), 121.38 (d, $J_{P\text{-}C}$ = 25.4 Hz, (fluorenyl)C=P-P*t*Bu_2), 34.99 (dd, $J_{P\text{-}C}$ = 27.9 Hz, $J_{P\text{-}C}$ = 3.1 Hz, (fluorenyl)C=P-P{**C**$(Me_3)\}_2$), 30.77 (dd, $J_{P\text{-}C}$ = 14.1 Hz, $J_{P\text{-}C}$ = 5.3 Hz, (fluorenyl)C=P-P{C(**Me**$_3)\}_2$) ppm;

^{31}P{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 297.17 (d, $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=**P**-P*t*Bu_2), 9.57 (d, $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=P-**P***t*Bu_2) ppm.

A.3.3. Reaction of **2** with 4-cyanobenzophenone



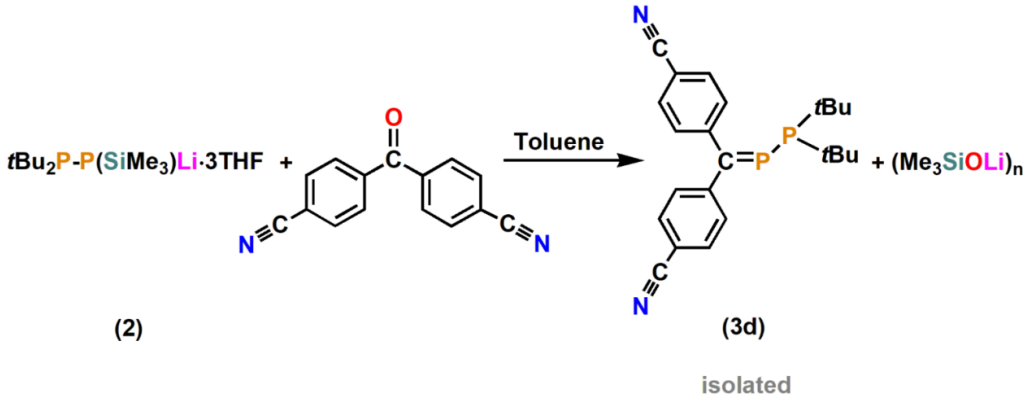
4-cyanobenzophenone 0.088 g, 0.424 mmol. The solid residue was treated with toluene (10 mL), and the resulting solution was filtered. During concentrating on the Schlenk appeared pale red crystals; therefore, the solution was left at room temperature for 24 hours. After this time a lot of crystals appeared, and were characterized as (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) (0.100 g; yield: 65 %). M$_P$ at 92-93°C. Calculated elemental analysis (%) for $C_{22}H_{27}NP_2$ (**3c**): C, 71.72; H, 7.66; N, 3.80. Found: C, 71.68 ; H, 7.61; N, 3.82.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 7.50 - 6.70 (10H, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$), 1.14 (d, 18H, J_{P-H} = 10.9 Hz, (Ph)(4-CN-Ph)C=P-P***t*Bu**$_2$, ***E*-3c**), 1.10 (d, 18H, J_{PH} = 10.9 Hz, (Ph)(4-CN-Ph)C=P-P***t*Bu**$_2$, ***Z*-3c**) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 204.62 (dd, J_{P-C} = 54.4 Hz, J_{P-C} = 16.8 Hz, (Ph)(4-CN-Ph)**C**=P-P*t*Bu$_2$, ***E*-3c**), 204.40 (dd, J_{P-C} = 55.5 Hz, J_{P-C} = 17.1 Hz, (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$, ***Z*-3c**), 149.57 (dd, J_{P-C} = 24.1 Hz, J_{P-C} = 3.7 Hz, (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), ***Z*-3c**), 149.34 (dd, J_{P-C} = 13.7 Hz, J_{P-C} = 6.2 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *i*-C$_{Ar}$, ***E*-3c**), 145.21 (dd, J_{P-C} = 22.1 Hz, J_{P-C} = 4.2 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *i*-C$_{Ar}$, ***E*-3c**), 144.56 (dd, J_{P-C} = 20.1 Hz, J_{P-C} = 5.6 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *i*-C$_{Ar}$, ***Z*-3c**), 131.58 (d, J_{P-C} = 1.0 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *p*-Ar, ***Z*-3c**), 131.24 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *o*-C$_{Ar}$, ***E*-3c**), 130.00 (dd, J_{P-C} = 6.6 Hz, J_{P-C} = 4.1 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *o*-C$_{Ar}$, ***Z*-3c**), 129.72 (d, J_{P-C} = 4.8 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *o*-C$_{Ar}$, ***E*-3c**), 129.44 (dd, J_{P-C} = 6.5 Hz, J_{P-C} = 4.2 Hz, (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$, *o*-C$_{Ar}$, ***E*-3c**), 128.24 (d, J_{P-C} = 0.9 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *p*-C$_{Ar}$, ***E*-3c**), 127.33 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***Z*-3c**), 127.13 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***Z*-3c**), 126.93 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***E*-3c**), 126.73 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***E*-3c**), 118.64 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***Z*-3c**), 110.67 (s, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***E*-3c**), 34.15 (dd, J_{P-C} = 30.2 Hz, J_{P-C} = 4.1 Hz, (Ph)(4-CN-Ph)C=P-P{**C**(Me$_3$)}$_2$, ***E*-3c**), 34.04 (dd, J_{P-C} = 29.5 Hz, J_{P-C} = 4.1 Hz, (Ph)(4-CN-Ph)C=P-P{**C**(Me$_3$)}$_2$, ***Z*-3c**), 30.99 (dd, J_{P-C} = 14.3 Hz, J_{P-C} = 5.6 Hz, (Ph)(4-CN-Ph)C=P-P{C(**Me**$_3$)}$_2$, ***E*-3c**), 30.98 (dd, J_{P-C} = 14.2 Hz, J_{P-C} = 5.3 Hz, (Ph)(4-CN-Ph)C=P-P{C(**Me**$_3$)}$_2$, ***Z*-3c**) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 303.89 (d, J_{P-P} = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$, ***E*-3c**), 286.27 (d, J_{P-P} = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$, ***Z*-3c**), 28.96 (d, J_{P-P} = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$**, *E*-3c**), 27.77 (d, J_{P-P} = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$, ***Z*-3c**) ppm.

A.3.4. Reaction of **2** with 4,4'-dicyanobenzophenone



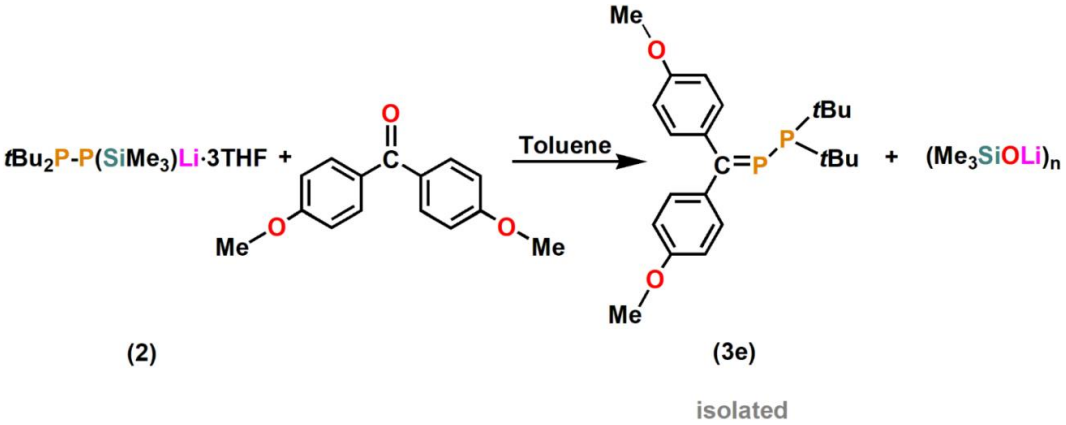
4,4'-dicyanobenzophenone (0.098 g, 0.424 mmol). The solid residue was treated with toluene (10 mL), and the resulting solution was filtered. The solution was concentrated to 2 mL, and 0.5 mL of pentane was added. The solution was stored at +4 °C for 24 hours. During this time dark red crystals appeared and were characterized as (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) (0.118 g; yield: 71 %). M_P at 158-159°C. Calculated elemental analysis (%) for $C_{26.5}H_{30}N_2P_2$ (**3d**): C, 71.92; H, 7.41; N, 3.81. Found: C, 71.84; H,7.36; N, 3.88.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 7.13 (broad s, aromatic protons of toluene), 7.10 – 6.55 ppm (8H, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$), 1.05 (d, 18H, J_{P-H} = 11.4 Hz, (4-CN-Ph)$_2$C=P-P***t*Bu**$_2$) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 201.99 (dd, J_{P-C} = 55.6 Hz, J_{P-C} = 17.6 Hz, (4-CN-Ph)$_2$**C**=P-P*t*Bu$_2$), 147.89 (dd, J_{P-C} = 23.0 Hz, J_{P-C} = 4.0 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C_{Ar}), 137.53 (s, toluene, *i*-C_{Ar}), 131.67 (d, J_{P-C} = 1.0 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-C_{Ar}), 131.36 (s, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-C_{Ar}), 129.67 (dd, J_{P-C} = 6.7 Hz, J_{P-C} = 4.2 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-C_{Ar}), 129.47 (s, toluene, *o*-C_{Ar}), 128.20 (toluene, *m*-C_{Ar}), 126.75 (d, J_{P-C} = 20.2 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-C_{Ar}), 125.33 (s, toluene, *p*-C_{Ar}), 118.27 (s, (4-**C**N-Ph)$_2$C=P-P*t*Bu$_2$), 111.64 (s, (4-CN-Ph)$_2$C=P-P*t*Bu$_2$, *o*-C_{Ar}), 34.26 (dd, J_{P-C} = 29.4 Hz, J_{P-C} = 3.9 Hz, (4-CN-Ph)$_2$C=P-P{**C**(Me)$_3$}$_2$), 30.91 (dd, J_{P-C} = 14.2 Hz, J_{P-C} = 5.3 Hz, (4-CN-Ph)$_2$C=P-P{C(**Me**)$_3$}$_2$), 21.06 (s, methyl group of toluene) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 311.26 (d, J_{P-P} = 232.5 Hz, (4-CN-Ph)$_2$C=**P**-P*t*Bu$_2$), 29.40 (d, J_{P-P} = 232.5 Hz, (4-CN-Ph)$_2$C=P-**P***t*Bu$_2$) ppm.

A.3.5. Reaction of **2** with 4,4'-dimethoxybenzophenone



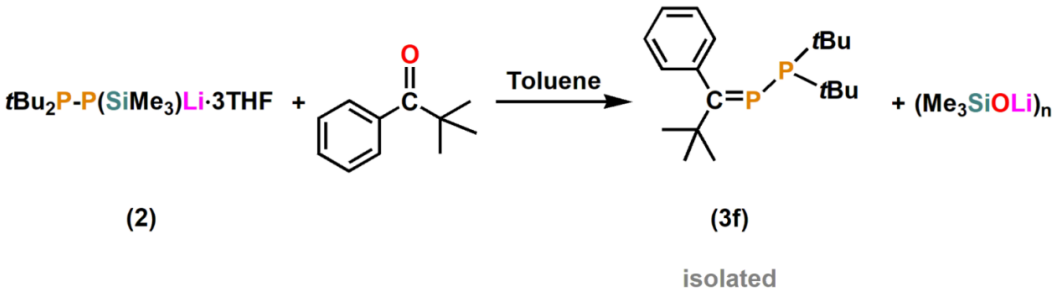
4,4'-dimethoxybenzophenone (0.143 g, 0.591 mmol). The slightly oily residue was treated with pentane (15 mL), and the resulting mixture was filtered. The solution was concentrated to 5 mL and stored at -23 °C for 24 hours. During this time orange crystals grown and were characterized as (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) (0.119 g; yield: 70 %). M_P at 32-33°C. Calculated elemental analysis (%) for $C_{26.5}H_{30}N_2P_2$ (**3e**): C, 71.92; H, 7.41; N, 3.81. Found: C, 71.84; H,7.36; N, 3.88.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 7.65 (dd, 2H, J_{P-H} = 8.9 Hz, J_{P-H} = 2.69 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-H$_{Ar}$), 7.18 (dd, 2H, J_{P-H} = 8.9 Hz, J_{P-H} = 1.13 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-H$_{Ar}$), 6.75 (d, 2H, J_{P-H} = 8.7 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-H), 6.64 (d, 2H, J_{P-H} = 9.3 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-H$_{Ar}$), 3.23 (s, 3H, (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$), 3.20 (s, 3H, (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$), 1.24 (d, 18H, J_{P-H} = 11.8 Hz, (4-MeO-Ph)$_2$C=P-P***t*Bu**$_2$) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 206.36 (dd, J_{P-C} = 55.0 Hz, J_{P-C} = 16.1 Hz, (4-MeO-Ph)$_2$**C**=P-P*t*Bu$_2$), 161.39 (d, J_{P-C} = 4.4 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), 159.31 (s, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), 140.25 (dd, J_{P-C} = 24.2 Hz, J_{P-C} = 4.4 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), 138.47 (dd, J_{P-C} = 13.9 Hz, J_{P-C} = 5.1 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *i*-C$_{Ar}$), 131.40 (dd, J_{P-C} = 5.8 Hz, J_{P-C} = 4.5 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-C$_{Ar}$), 128.98 (d, J_{P-C} = 19.8 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *o*-C$_{Ar}$)), 113.44 (s, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-C$_{Ar}$), 112.86 (s, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$, *m*-C$_{Ar}$), 54.49 (s, (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$), 54.32 (s, (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$), 33.96 (dd, J_{P-C} = 30.1 Hz, J_{P-C} = 4.4 Hz, (4-MeO-Ph)$_2$C=P-P{**C**(CH$_3$)}$_2$), 31.13 (dd, J_{P-C} = 14.7 Hz, J_{P-C} = 5.1 Hz, (4-MeO-Ph)$_2$C=P-P{C(**CH$_3$**)}$_2$) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 258.28 (d, J_{P-P} = 228.9 Hz, (4-MeO-Ph)$_2$C=**P**-P*t*Bu$_2$), 28.28 (d, J_{P-P} = 228.9 Hz, (4-MeO-Ph)$_2$C=P-**P***t*Bu$_2$) ppm.

A.3.6. Reaction of **2** with *tert*-butyl phenyl ketone



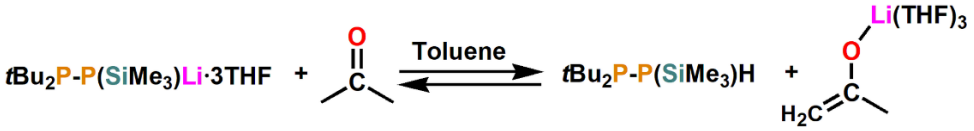
tert-butyl phenyl ketone (0.071 mL, 0.424 mmol, 0.970 g/mL). The yellow oily residue was treated with pentane (10 mL), and the resulting solution was filtered. From the resulting filtrate, the solvent was evaporated under reduced pressure to give an intensive yellow oil characterized as *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**). After 1 month the oil crystalized and the yellow crystals of **3f** were isolated (0.098 g; yield: 72 %). Calculated elemental analysis (%) for $C_{19}H_{32}P_2$ (**3f**): C, 70.78; H, 10.00; Found: C, 70.69; H, 10.22.

^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) δ: 7.57 – 6.81 (5H, *t*Bu(**Ph**)C=P-P*t*Bu$_2$), 1.29 (d, 9H, $J_{P\text{-}H}$ = 1.9 Hz, ***t*Bu**(Ph)C=P-P*t*Bu$_2$, ***Z*-3f**); 1.17 (d, 18H, $J_{P\text{-}H}$ = 10.7 Hz, *t*Bu(Ph)C=P-P***t*Bu**$_2$, ***Z*-3f**) ppm;

^{13}C{^{1}H} NMR (400 MHz, Toluene-d$_8$, 298 K) δ: 225.56 (dd, $J_{P\text{-}C}$ = 62.0 Hz, $J_{P\text{-}C}$ = 16.5 Hz, *t*Bu(Ph)**C**=P-P*t*Bu$_2$, ***Z*-3f**), 145.71 (dd, $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 8.9 Hz, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*i*-C$_{Ar}$), ***Z*-3f**), 129.42, (s, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*p*-C$_{Ar}$), ***Z*-3f**), 128.08 (dd, $J_{P\text{-}C}$ = 8.2 Hz, $J_{P\text{-}C}$ = 2.7 Hz, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*o*-C$_{Ar}$), ***Z*-3f**), 127.00 (s, $J_{P\text{-}C}$ = 3.6 Hz, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$), ***Z*-3f**), 44. 18 (dd, $J_{P\text{-}C}$ = 21.6 Hz, J_{PC} = 3.2 Hz, {(CH$_3$)$_3$**C**}(Ph)C=P-P{C(CH$_3$)$_3$}$_2$, ***Z*-3f**), 32.93 (dd, $J_{P\text{-}C}$ = 30.2 Hz, J_{PC} = 5.0 Hz, {(CH$_3$)$_3$C}(Ph)C=P-P{**C**(CH$_3$)$_3$}$_2$, ***Z*-3f**), 31.19 (dd, $J_{P\text{-}C}$ = 14.53 Hz, $J_{P\text{-}C}$ = 5.3 Hz, {(CH$_3$)$_3$C}(Ph)C=P-P{C(**C**H$_3$)$_3$}2, ***Z*-3f**), 30.66 (d, $J_{P\text{-}C}$ = 15.0 Hz, {(**C**H$_3$)$_3$C}(Ph)C=P-P{C(CH$_3$)$_3$}$_2$, ***Z*-3f**) ppm;

^{31}P{^{1}H} NMR (400 MHz, Toluene-d$_8$, 298 K) δ: 265.96 (d, $J_{P\text{-}P}$ = 216.9 Hz, *t*Bu(Ph)C=**P**-P*t*Bu$_2$, ***Z*-3f**), 261.05 (d, $J_{P\text{-}P}$ = 230.4 Hz, *t*Bu(Ph)C=**P**-P*t*Bu$_2$, ***E*-3f**), 21.31 (d), $J_{P\text{-}P}$ = 216.9 Hz, *t*Bu(Ph)C=P-**P***t*Bu$_2$, ***Z*-3f**), 16.15 (d, $J_{P\text{-}P}$ = 230.4 Hz, *t*Bu(Ph)C=**P**-P*t*Bu$_2$, ***E*-3f**) ppm.

A.3.7. Reaction of **2** with acetone



(2)

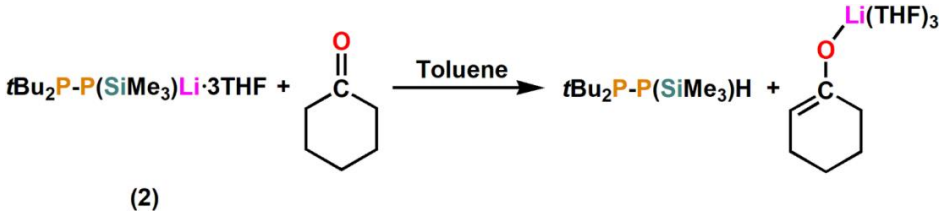
Acetone (0.031 mL, 0.424 mmol, 0.784 g/mL). The pale yellow oily residue was treated with C_6D_6 and NMR investigated.

^{1}H NMR (400 MHz, Toluene-d_8, 298 K) δ: 3.86 and 3.82 (broad t, 2H, (Me)(**C**H_2=)C-OLi(THF)$_3$), 3.51 (quint., THF protons), 2.40 (d, 3 H, $J_{P\text{-}H}$ = 10.5 Hz, (**Me**)$_2$C=P-P*t*Bu$_2$), 2.13 (d, 3 H, $J_{P\text{-}H}$ = 20.4 Hz, (**Me**)$_2$C=P-P*t*Bu$_2$, **3g**), 1.94 (broad s, 3H, (**Me**)(CH$_2$=)**C**-OLi(THF)$_3$), 1.86 (s, 6H, **Me**$_2$C=O), 1.43 (broad d, 18 H, $J_{P\text{-}H}$ = 10.4 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)Li), 1.39 (quint., THF protons), 1.38 (dd, 1H, $J_{P\text{-}H}$ = 187.2 Hz, $J_{P\text{-}H}$ = 2.5 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**), 1.16 (d, 18 H, $J_{P\text{-}H}$ = 14.2 Hz, (Me)$_2$C=P-P***t*Bu**$_2$, **3g**), 1.09 (dd, 18 H, $J_{P\text{-}H}$ = 11.2 Hz, $J_{P\text{-}H}$ = 0.5 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)H), 0.46 (broad s, 9 H, *t*Bu$_2$P-P(Si**Me**$_3$)Li), 0.20 (dd, 9 H, $J_{P\text{-}H}$ = 4.1 Hz, $J_{P\text{-}H}$ = 0.6 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)H) ppm.

^{13}C{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 164.47 (s, (Me)(CH$_2$=)**C**-OLi(THF)$_3$), 137.06, 128.45, 127.55, 124.71 and 20.03 (Tolene-d_8), 81.81 (s, (Me)(**C**H$_2$=)C-OLi(THF)$_3$), 67.59 (s, THF), 34.57 (s, **Me**$_2$C=O), 32.23 (broad dd, $J_{P\text{-}C}$ = 29.8 Hz, $J_{P\text{-}C}$ = 9.9 Hz, {(CH$_3$)$_3$**C**}P-P(SiMe$_3$)Li), 31.80 (dd, $J_{P\text{-}C}$ = 14.9 Hz, $J_{P\text{-}C}$ = 2.5 Hz, {(**C**H$_3$)$_3$C}P-P(SiMe$_3$)Li), 30.82 (broad dd, $J_{P\text{-}C}$ = 22.4 Hz, $J_{P\text{-}C}$ = 9.9 Hz, {(CH$_3$)$_3$**C**}P-P(SiMe$_3$)H), 30.19 (dd, $J_{P\text{-}C}$ = 14.9 Hz, $J_{P\text{-}C}$ = 7.5 Hz, {(**C**H$_3$)$_3$C}P-P(SiMe$_3$)H), 26.06 (s, (**Me**)(CH$_2$=)**C**-OLi(THF)$_3$), 25.34 (s, THF), 5.66 (broad dd, $J_{P\text{-}C}$ = 9.9 Hz, $J_{P\text{-}C}$ = 7.5 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)Li), 1.03 (dd, $J_{P\text{-}C}$ = 9.9 Hz, $J_{P\text{-}C}$ = 4.9 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)H) ppm.

^{31}P{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 235.53 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Me)$_2$C=**P**-P*t*Bu$_2$, **3g**), 46.57 (d, $J_{P\text{-}P}$ = 278.4 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)Li), 23.07 (d, $J_{P\text{-}P}$ = 228.9 Hz, (Me)$_2$C=P-**P***t*Bu$_2$, **3g**), and 19.02 (d, $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H), -197.35 (d, $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H), -245.14 (d, $J_{P\text{-}P}$ = 278.4 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)Li) ppm.

A.3.8. Reaction of **2** with cyclohexanone



(2)

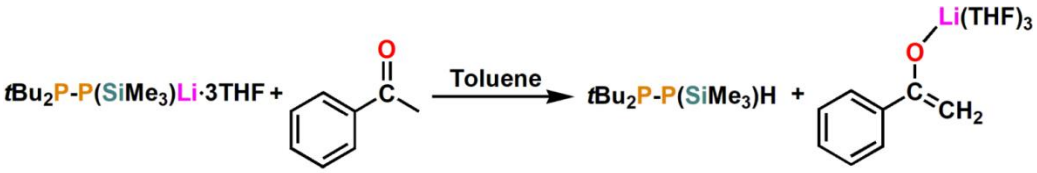
Cyclohexanone (0.044 mL, 0.424 mmol, 0.948 g/mL). The almost colorless oily residue was treated with C_6D_6 and NMR investigated.

^{1}H NMR (400 MHz, Toluene-d_8, 298 K) δ: 4.49 (broad s, (*cyclo*-$CH_2CH_2CH_2CH_2C$**H**=C)OLi(THF)$_3$), 3.63 (quintet, 12H, (*cyclo*-$CH_2CH_2CH_2CH_2CH$=C)OLi(**THF**)$_3$), 1.85 (broad m, 2 H, (*cyclo*-$CH_2CH_2CH_2C$**H**$_2$CH=C)OLi(THF)$_3$), 1.74 (broad m, 2H, (*cyclo*-C**H**$_2CH_2CH_2CH_2CH$=C)OLi(THF)$_3$), 1.52 , (quintet, 12H, (*cyclo*-$CH_2CH_2CH_2CH_2CH$=C)OLi(**THF**)$_3$), 1.48 (dd, 1H, $J_{P\text{-}H}$ = 188.4 Hz, $J_{P\text{-}H}$ = 2.5 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**), 1.30 (broad m, 4H, (*cyclo*-CH_2C**H**$_2C$**H**$_2CH_2CH$=C)OLi(THF)$_3$), 1.20 (d, 18H, $J_{P\text{-}H}$ = 11.4 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)H), 0.31 (dd, 9H, $J_{P\text{-}H}$ = 4.2 Hz, $J_{P\text{-}H}$ = 0.6 Hz, *t*Bu$_2$P-P(Si**M**e$_3$)H) ppm;

^{13}C{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 159.32 (s, (*cyclo*-$CH_2CH_2CH_2CH_2CH$=**C**)OLi(THF)$_3$, 137.06, 128.45, 127.55 (toluene-d_8), 89.53 (broad s, (*cyclo*-$CH_2CH_2CH_2CH_2$**C**H=C)OLi(THF)$_3$), 33.56 (s, (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$), 31.21 (dd, $J_{P\text{-}C}$ = 32.3 Hz, $J_{P\text{-}C}$ = 13.7 Hz, {(CH$_3$)$_3$C}$_2$P-P(Si**M**e$_3$)H), 30.18 ppm, (dd, $J_{P\text{-}C}$ = 14.9 Hz, $J_{P\text{-}C}$ = 6.2 Hz, {(CH$_3$)$_3$C}$_2$P-P(Si**M**e$_3$)H), 25.59 (s, (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$), 24.95 (s, (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$), 24.41 (s, (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$), 20.03 (toluene-d_8), 1.01 (dd, $J_{P\text{-}C}$ = 9.9 Hz, $J_{P\text{-}C}$ = 4.9 Hz, *t*Bu$_2$P-P(Si**M**e$_3$)H) ppm;

^{31}P{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 19.06 (d, $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H), -197.24 (d, $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H) ppm.

A.3.9. Reaction of **2** with acetophenone



(2)

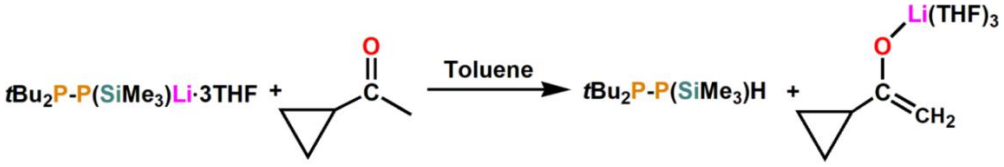
Acetophenone (0.050 mL, 0.424 mmol, 1.030 g/mL). The pale yellow oily residue was treated with C_6D_6 and NMR investigated.

^{1}H NMR (400 MHz, Toluene-d_8, 298 K) δ: 7.93 (dd, 2H, $J_{H\text{-}H}$ = 9.2 Hz, $J_{H\text{-}H}$ = 1.1 Hz, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *m*-H_{Ar}), 7.15 (t, 2H, $J_{H\text{-}H}$ = 7.5 Hz, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *o*-H_{Ar}), 7.00 (t, 1H, $J_{H\text{-}H}$ = 7.5 Hz, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *p*-H_{Ar}), 4.59, 4.29 (s, 2H, (Ph)(C**H**$_2$=)C-OLi(THF)$_3$), 3.44 (quintet, 12H, (Ph)(CH_2=)C-OLi(**THF**)$_3$), 1.38 (dd, 1H, $J_{P\text{-}H}$ = 187.2 Hz, $J_{P\text{-}H}$ = 2.4 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**), 1.28 (quintet, 12H, (Ph)(CH_2=)C-OLi(**THF**)$_3$), 1.09 (d, 18H, $J_{P\text{-}H}$ = 11.2 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)H), 0.21 (d, 9H, $J_{P\text{-}H}$ = 4.2 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)H ppm;

^{13}C{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 165.92 (s, (Ph)(CH_2=)**C**-OLi(THF)$_3$, *i*-C_{Ar}), 144.23 (s, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *i*-C_{Ar}), 137.06, 128.46, 127.56 (toluene-d_8), 127.56, (s, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *o*-C_{Ar}), 126.29 (s, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *p*-C_{Ar}), 125.98 (s, (**Ph**)(CH_2=)C-OLi(THF)$_3$, *m*-C_{Ar}), 124.72 (toluene-d_8), 80.39 (s, (Ph)(**C**H_2=)C-OLi(THF)$_3$), 67.47 ((Ph)(CH_2=)C-OLi(**THF**)$_3$), 25.23 ((Ph)(CH_2=)C-OLi(**THF**)$_3$), 20.04 (toluene-d_8), 4.67 (dd, $J_{P\text{-}C}$ = 10.4 Hz, $J_{P\text{-}C}$ = 5.2 Hz, {(CH_3)C}$_2$P-P(Si**Me**$_3$)H) ppm;

^{31}P{^{1}H} NMR (400 MHz, 298 K, Toluene-d_8) δ: 263.61 (d, $J_{P\text{-}P}$ = 234.9 Hz, (Ph)MeC=**P**-P*t*Bu$_2$, ***E*-3i**), 21.89 (d, $J_{P\text{-}P}$ = 234.9 Hz, (Ph)MeC=**P**-P*t*Bu$_2$, ***E*-3i**), 19.07 (d, $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H), -197.30 (d, $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H) ppm.

A.3.10. Reaction of **2** with cyclopropyl methyl ketone



(2)

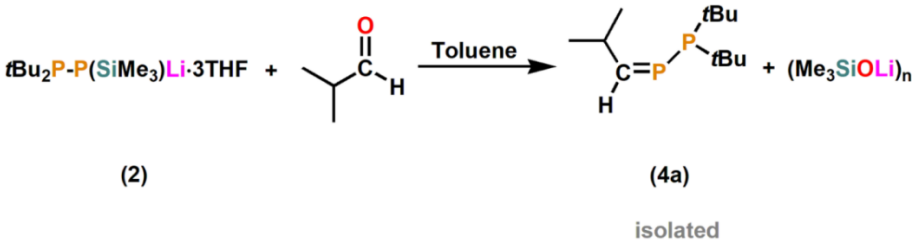
Cyclopropyl methyl ketone (0.042 mL, 0.424 mmol, 0.849 g/mL). The almost colorless, oily residue, was treated with C_6D_6 and NMR investigated.

^{1}H NMR (400 MHz, Toluene-d_8, 298 K) δ: 3.79 (broad s, 2H, (*cyclo*-CH_2CH_2CH)(C**H**$_2$=)C-OLi(THF)$_3$), 3.76 (quintet, 12H, (*cyclo*-CH_2CH_2CH)(CH_2=)C-OLi(**THF**)$_3$) 2.13 (sept., 1H, (*cyclo*-CH_2CH_2C**H**)(CH_2=)C-OLi(THF)$_3$), 1.52 (quintet, 12H, (*cyclo*-CH_2CH_2CH)(CH_2=)C-OLi(**THF**)$_3$), 1.50 (dd, 1H, $J_{P\text{-}H}$ = 188.3 Hz, $J_{P\text{-}H}$ = 2.7 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**), 1.21 (d, 18H, 1H, $J_{P\text{-}H}$ = 11.4 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)$_3$), 0.79 (broad m, 2H, (*cyclo*-CH_2C**H**$_2$CH)(CH_2=)C-OLi(THF)$_3$), 0.55 (broad m, 2H, (*cyclo*-C**H**$_2CH_2CH$)(CH_2=)C-OLi(THF)$_3$) ppm;

^{13}C{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 174.14 (s, (*cyclo*-CH_2CH_2CH)(CH_2=)**C**-OLi(THF)$_3$), 142.07, 133.46, 132.56, 129.72 (toluene-d_8), 80.4 (s, (*cyclo*-CH_2CH_2CH)(**C**H$_2$=)C-OLi(THF)$_3$), 72.49 (s, (*cyclo*-CH_2CH_2CH)(CH_2=)C-OLi(**THF**)$_3$), 37.02 (broad d, $J_{P\text{-}C}$ = 34.5 Hz, {(CH_3)**C**}$_2$P-P(SiMe$_3$)H), 35.18 (dd, $J_{P\text{-}C}$ = 30.2 Hz, $J_{P\text{-}C}$ = 5.4 Hz, {(**C**H$_3$)C}$_2$P-P(SiMe$_3$)H), 30.40 (s, (*cyclo*-CH_2CH_2CH)(CH_2=)C-OLi(**THF**)$_3$), 25.03 (tolene-d_8), 22.93 (s, (*cyclo*-CH_2CH_2**C**H)(CH_2=)C-OLi(THF)$_3$), 10.10 (s, (*cyclo*-**C**H$_2$**C**H$_2$CH)(CH_2=)C-OLi(THF)$_3$), 7.82 ppm, (dd, $J_{P\text{-}C}$ = 10.4 Hz, $J_{P\text{-}C}$ = 5.1 Hz, {(**C**H$_3$)C}$_2$P-P(Si**Me**$_3$)H) ppm;

^{31}P{^{1}H} NMR (400 MHz, Toluene-d_8, 298 K) δ: 19.01 (d, $J_{P\text{-}P}$ = 188.9 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H), -197.35 (d, $J_{P\text{-}P}$ = 188.9 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H) ppm.

A.3.11. Reaction of **2** with isobutyraldehyde

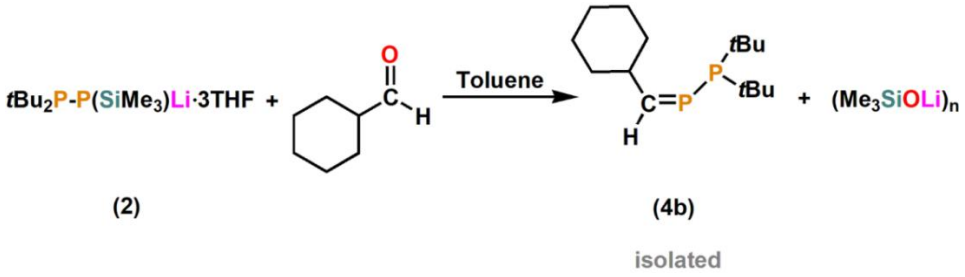


Isobutyraldehyde (0.039 mL, 0.424 mmol, 0.790 g/mL). The yellow oily residue was treated with pentane (10 mL), and the resulting solution was filtered. From the resulting filtrate, the solvent was evaporated under reduced pressure to give a yellow oil characterized as {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$ (**4a**) (0.075 g; 76 %).

^{31}P{^{1}H} NMR (400 MHz, Toluene-d$_8$, 298 K) δ: 254.78 (d, J_{P-P} = 220.8 Hz, {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$, ***E*-4a**), 249.85 (d, J_{P-P} = 212.8 Hz, {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$, ***Z*-4a**), 52.83 (d, J_{P-P} = 220.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$, ***E*-4a**), 19.47 (s, *t*Bu$_2$PH), 18.98 (d, J_{P-P} = 188.7 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H), 12.65 (d, J_{P-P} = 212.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$, ***Z*-4a**), -197.35 (d, J_{P-P} = 188.7 Hz, *t*Bu$_2$P-P(SiMe$_3$)H) ppm.

The ^{1}H and ^{13}C{^{1}H} NMR were analogical to these obtained in the reaction of **1** with isobutyraldehyde (see point A.2.11. page 15).

A.3.12. Reaction of **2** with cyclohexanecarbaldehyde

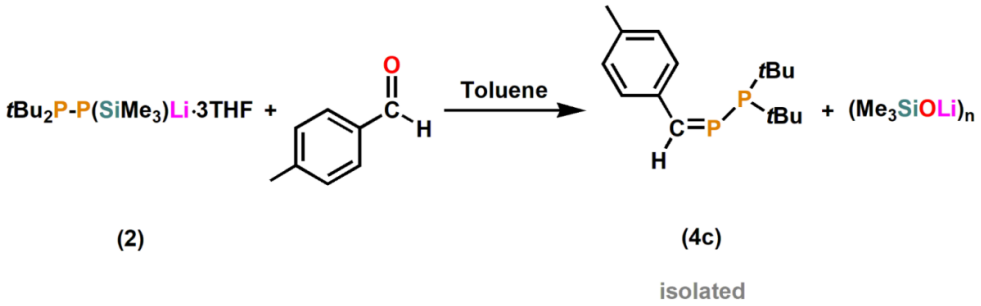


Cyclohexanecarbaldehyde (0.051 mL, 0.424 mmol, 0.926 g/mL). The yellow oily residue was treated with pentane (10 mL), and the resulting solution was filtered. From the resulting filtrate, the solvent was evaporated under reduced pressure to give a yellow oil characterized as {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**) (0.072 g; 62 %).

$^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) δ: 256.37 (d, $J_{P\text{-}P}$ = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2, ***E*-4b**), 251.56 (d, $J_{P\text{-}P}$ = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2, ***Z*-4b**), 53.16 (d, $J_{P\text{-}P}$ = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-**P***t*Bu_2, ***E*-4b**), 13.03 (d, $J_{P\text{-}P}$ = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2, ***Z*-4b**) ppm.

The ^1H and $^{13}C\{^1H\}$ NMR were analogical to these obtained in the reaction of **1** with cyclohexanecarbaldehyde (see point A.2.12. page 16).

A.3.13. Reaction of **2** with *p*-tolualdehyde

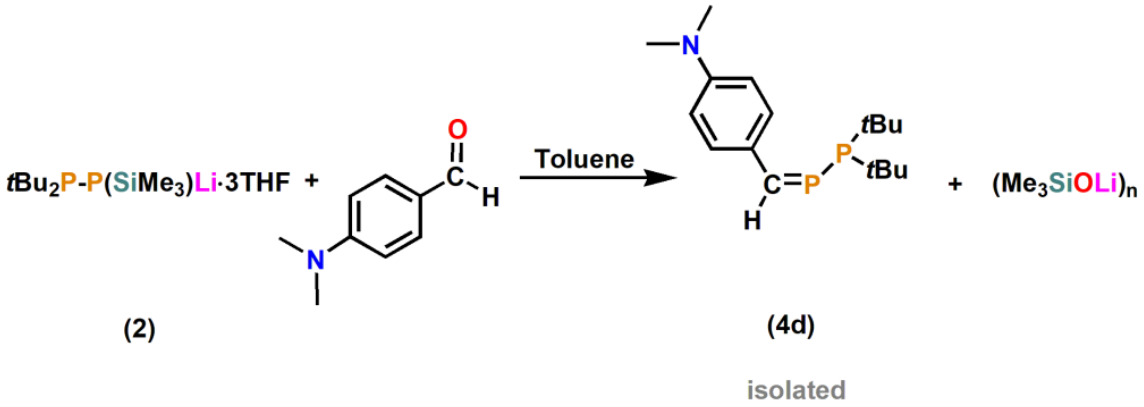


p-Tolualdehyde (0.050 mL, 0.424 mmol, 1.019 g/mL). The yellow oily residue was treated with pentane (10 mL), and the resulting solution was filtered. From the resulting filtrate, the solvent was evaporated under reduced pressure to give an intensive yellow oil characterized as (*p*-Me-Ph)(H)C=**P**-P*t*Bu$_2$ (***E*-4c**) (0.089 g; 75 %).

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 266.64 (d $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=**P**-P*t*Bu$_2$, **4c_*E***), 56.69 (d, $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=**P**-P*t*Bu$_2$, **4c_*E***), 19.13 (d, $J_{P\text{-}P}$ = 188.9 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H, -197.20 (d, $J_{P\text{-}P}$ = 188.9 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H) ppm.

The ^{1}H and ^{13}C{^{1}H} NMR were analogical to these obtained in the reaction of **1** with *p*-Tolualdehyde (see point A.2.13. page 17).

A.3.14. Reaction of **2** with 4-(dimethylamino)benzaldehyde



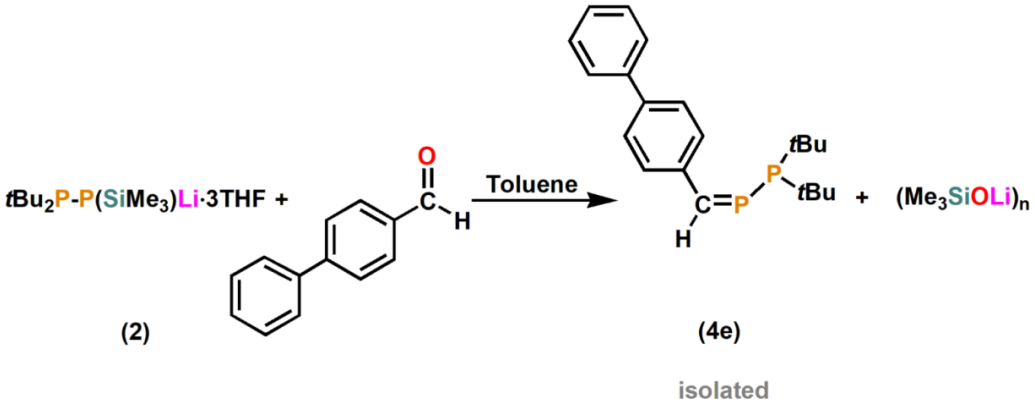
4-(dimethylamino)benzaldehyde (0.063 g, 0.424 mmol). The solid, intensive yellow residue was treated with pentane (15 mL), and the resulting solution was filtered. The solution was concentrated to 10 mL. The solution was stored at room temperature for 24 hours. During this time bright yellow crystals appeared and were characterized as {4-(Me)$_2$N-Ph}(H)C=P-P*t*Bu$_2$ (***E*-4d**) (0.100 g; yield: 76 %). M$_P$ at 115-116°C. Calculated elemental analysis (%) for $C_{17}H_{29}NP_2$ (***E*-4d**): C, 66.00; H, 8.45; N, 4.53. Found: C, 65.92; H, 9.38; N, 4.59.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 10.14, (dd, 1H, J_{P-H} = 21.8 Hz, J_{P-H} = 14.4 Hz, {4-(Me)$_2$N-Ph}(**H**)C=P-P*t*Bu$_2$, ***E*-4d**), 7.60, (dd, 2H, J_{P-H} = 9.2 Hz, J_{P-H} = 2.6 Hz, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$, *o*-H$_{Ar}$, ***E*-4d**), 6.21, (d, 2H, J_{P-H} = 8.9 Hz, {4-(Me)$_2$N-Ph}(**H**)C=P-P*t*Bu$_2$, *m*-H$_{Ar}$, ***E*-4d**), 2.22 (s, 6H, {4-(**Me**)$_2$N-Ph}(H)C=P-P*t*Bu$_2$, ***E*-4d**), 1.25 (d, 18H, J_{P-H} = 11.1 Hz, {4-(Me)$_2$N-Ph}(H)C=P-P***t*Bu**$_2$, ***E*-4d**) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 197.40 (dd, J_{P-C} = 46.3 Hz, J_{P-C} = 39.9 Hz, {4-(Me)$_2$N-Ph}(H)**C**=P-P*t*Bu$_2$, ***E*-4d**), 151.20 (d, J_{P-C} = 5.5 Hz, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$, *p*-C$_{Ar}$, ***E*-4d**), 131.49 (dd, J_{P-C} = 16.3 Hz, J_{P-C} = 11.8 Hz, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$, *i*-C$_{Ar}$, ***E*-4d**), 128.56 (d, J_{P-C} = 19.9 Hz, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$, *o*-C$_{Ar}$, ***E*-4d**), 111.60 (d, J_{P-C} = 19.9 Hz, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$, *m*-C$_{Ar}$, ***E*-4d**), 39.22 (s, {4-(**Me**)$_2$N-Ph}(H)C=P-P*t*Bu$_2$, ***E*-4d**), 33.04 (dd, J_{P-C} = 22.7 Hz, J_{P-C} = 1.8 Hz, {4-(Me)$_2$N-Ph}(H)C=P-P{**C**(Me)$_3$}$_2$, ***E*-4d**), 31.32 (dd, J_{P-C} = 13.6 Hz, J_{P-C} = 5.5 Hz, {4-(Me)$_2$N-Ph}(H)C=P-P{C(**Me**)$_3$}$_2$, ***E*-4d**) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 231.17 (d, J_{P-P} = 224.9 Hz, {4-(Me)$_2$N-Ph}(H)C=**P**-P*t*Bu$_2$, ***E*-4d**), 57.73 (d, J_{P-P} = 224.9 Hz, {4-(Me)$_2$N-Ph}(H)C=P-**P***t*Bu$_2$, ***E*-4d**) ppm.

A.3.15. Reaction of **2** with biphenyl-4-carboxaldehyde



Biphenyl-4-carboxaldehyde (0.077 g, 0.424 mmol). The solid, residue was treated with pentane (15 mL), and the resulting solution was filtered. The solution was concentrated to 8 mL. The solution was stored at +4°C for 24 hours. During this time orange crystals appeared and were characterized as PhPh(H)C=P-P*t*Bu$_2$ (***E*-4e**) (0.122 g; yield: 84 %). M_P at 134-135°C. Calculated elemental analysis (%) for $C_{21}H_{28}P_2$ (**4e**): C, 73.66; H, 8.24. Found: C, 73.61; H, 8.18.

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 10.16 (dd, 1H, J_{PH} = 22.5 Hz, J_{P-H} = 13.4 Hz, PhPh(**H**)C=P-P*t*Bu$_2$), 7.67 – 7.04 (9H, aromatic protons, **PhPh**(H)C=P-P*t*Bu$_2$, ***E*-4e**), 1.28 (d, 18 H, J_{P-H} = 11.1 Hz, PhPh(H)C=P-P***t*Bu**$_2$, ***E*-4e**) ppm;

^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 196.94 (dd, J_{P-C} = 44.9 Hz, J_{P-C} = 39.5 Hz, PhPh(H)**C**=P-P*t*Bu$_2$, ***E*-4e**), 142.24 (d, J_{P-C} = 7.18 Hz, **PhPh**(H)C=P-P*t*Bu$_2$, *i*-C_{Ar}, ***E*-4e**), 140.47 (d, J_{P-C} = 1.5 Hz, **PhPh**(H)C=P-P*t*Bu$_2$, *i*-C_{Ar}, ***E*-4e**), 140.46 (dd, J_{P-C} = 15.8 Hz, J_{P-C} = 12.4 Hz, **PhPh**(H)C=P-P*t*Bu$_2$, *i*-C_{Ar}, ***E*-4e**), 128.72 (s, **PhPh**(H)C=P-P*t*Bu$_2$, ***E*-4e**), 127.34 (s, **PhPh**(H)C=P-P*t*Bu$_2$, *o*-C_{Ar}, ***E*-4e**), 127.28 (d, J_{P-C} = 2.6 Hz, **PhPh**(H)C=P-P*t*Bu$_2$, *o*-C_{Ar}, ***E*-4e**), 126.90 (s, **PhPh**(H)C=P-P*t*Bu$_2$, *m*-C_{Ar}, ***E*-4e**), 33.21 (dd, J_{P-C} = 27.7 Hz, J_{P-C} = 2.27 Hz, PhPh(H)C=P-P{**C**$(CH_3)_3$}$_2$, ***E*-4e**), 31.18 (dd, J_{P-C} = 13.8 Hz, J_{P-C} = 5.0 Hz, PhPh(H)C=P-P{C(**C**$H_3)_3$}$_2$, ***E*-4e**) ppm;

^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) δ: 274.72 (d, J_{P-P} = 224.9 Hz, PhPh(H)C=**P**-P*t*Bu$_2$, ***E*-4e**), 57.13 (d, J_{P-P} = 224.9 Hz, PhPh(H)C=P-**P***t*Bu$_2$, ***E*-4e**) ppm.

PART B. NMR Spectra

B.1. Reaction of [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (1) with selected ketones and aldehydes

B.1.1. Benzophenone

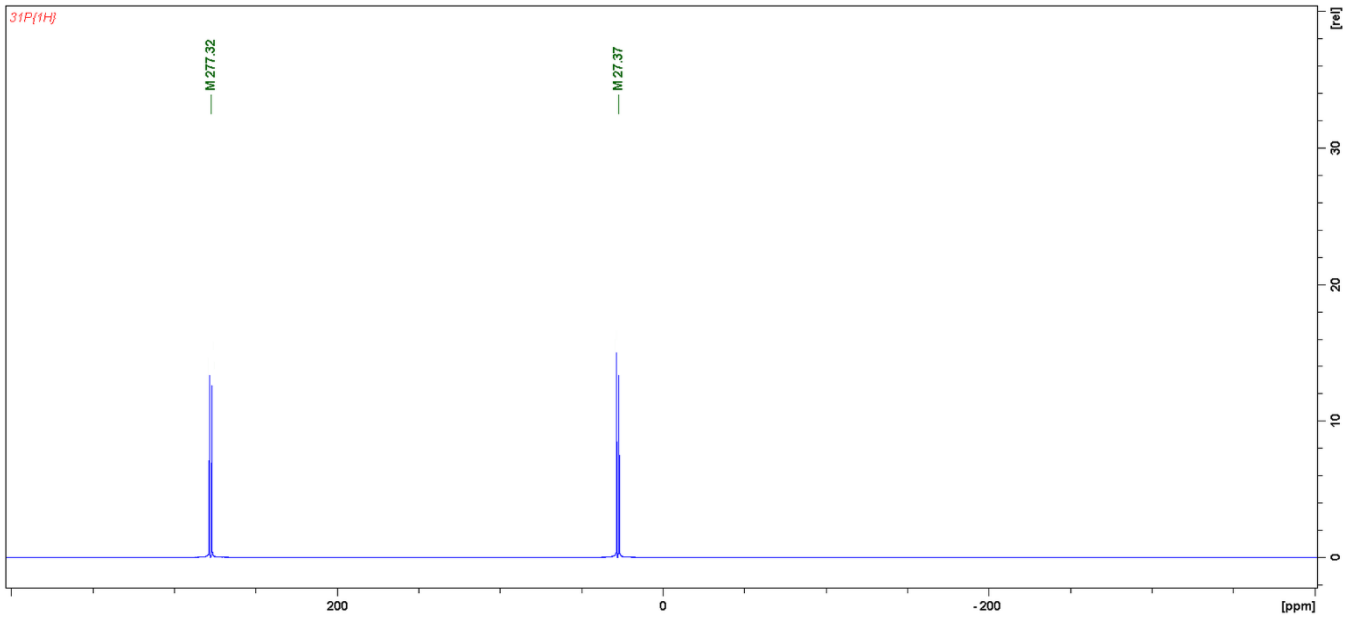


Figure S1. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 3 months after starting the reaction of [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**) with benzophenone.

- 277.32 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Ph)_2C$=**P**-P*t*Bu$_2$;
- 27.39 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Ph)_2C$=P-**P***t*Bu$_2$;

B.1.2. 9-fluorenone

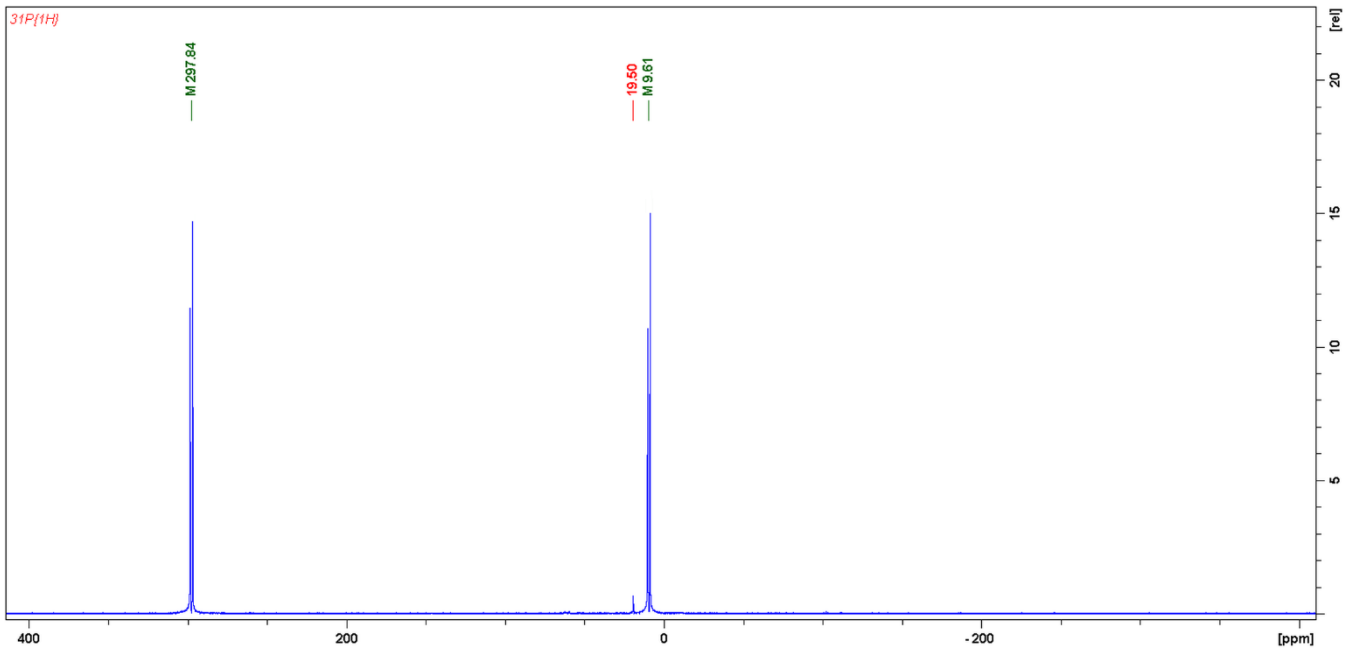


Figure S2. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 24 hours after starting the reaction of 1 with 9-fluorenone.

- 297.84 ppm, (d), $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=**P**-P*t*Bu$_2$;
- 19.50 ppm, (s), *t*Bu$_2$**P**H;
- 9.61 ppm, (d), $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=P-**P***t*Bu$_2$;

B.1.3. 4-cyanobenzophenone

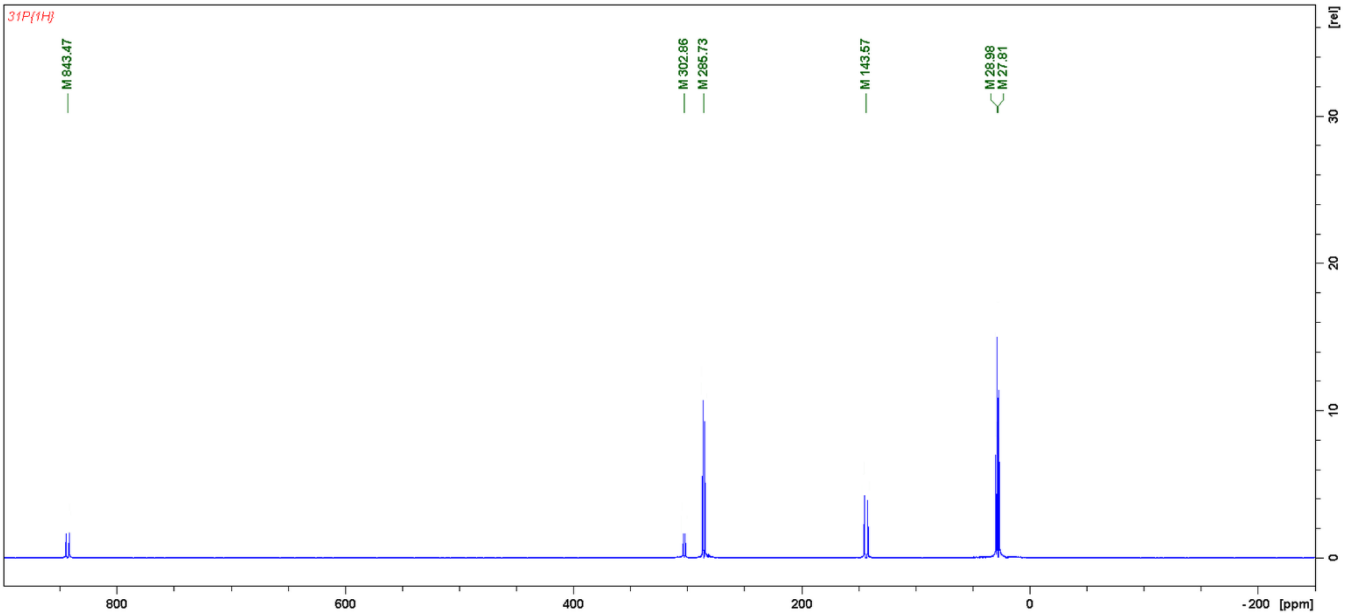


Figure S3. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 3 months after starting the reaction of **1** with 4-cyanobenzophenone.

- 843.47 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}];
- 302.86 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 285.73 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$ – *Z* isomer;
- 143.57 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}];
- 28.98 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$ – *E* isomer;
- 27.81 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$ – *Z* isomer;

B.1.4. 4,4'-dicyanobenzophenone

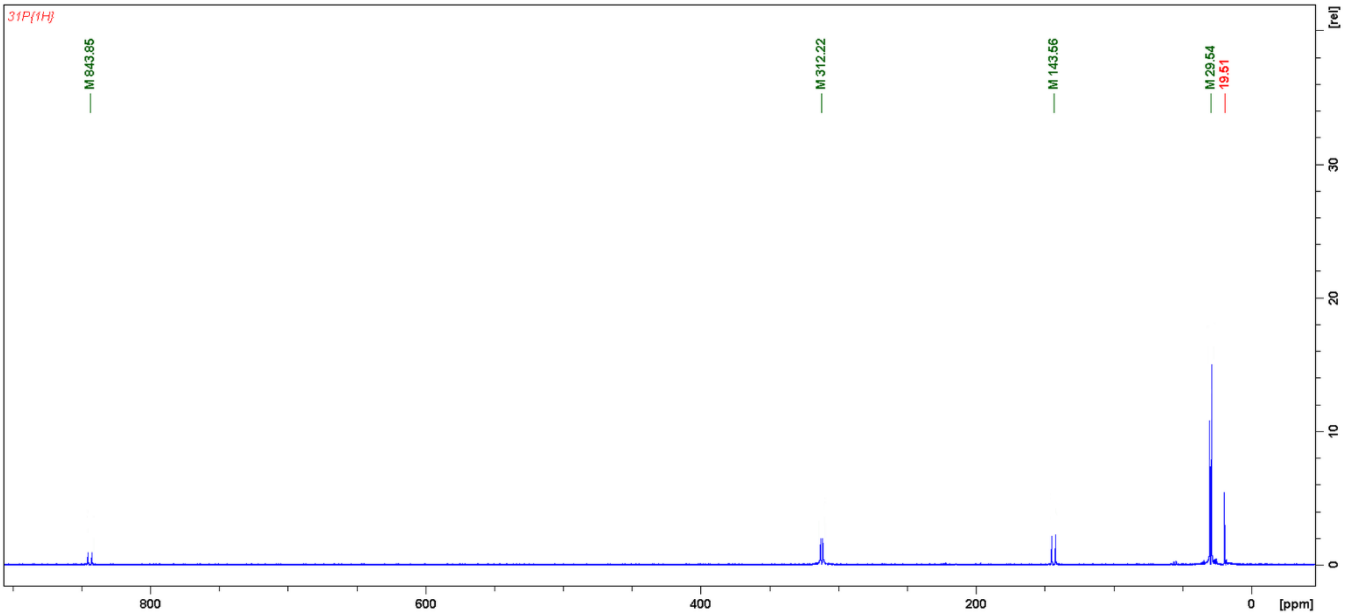


Figure S4. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 3 months after starting the reaction of **1** with 4,4'-dicyanobenzophenone.

- 843.85 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}];
- 312.22 ppm, (d), $J_{P\text{-}P}$ = 232.5 Hz, (4-CN-Ph)$_2$C=**P**-P*t*Bu$_2$;
- 143.56 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}];
- 29.54 ppm, (d), $J_{P\text{-}P}$ = 232.5 Hz, (4-CN-Ph)$_2$C=P-**P***t*Bu$_2$;
- 19.51 ppm, (s), *t*Bu$_2$PH;

B.1.5. 4,4'-dimethoxybenzophenone

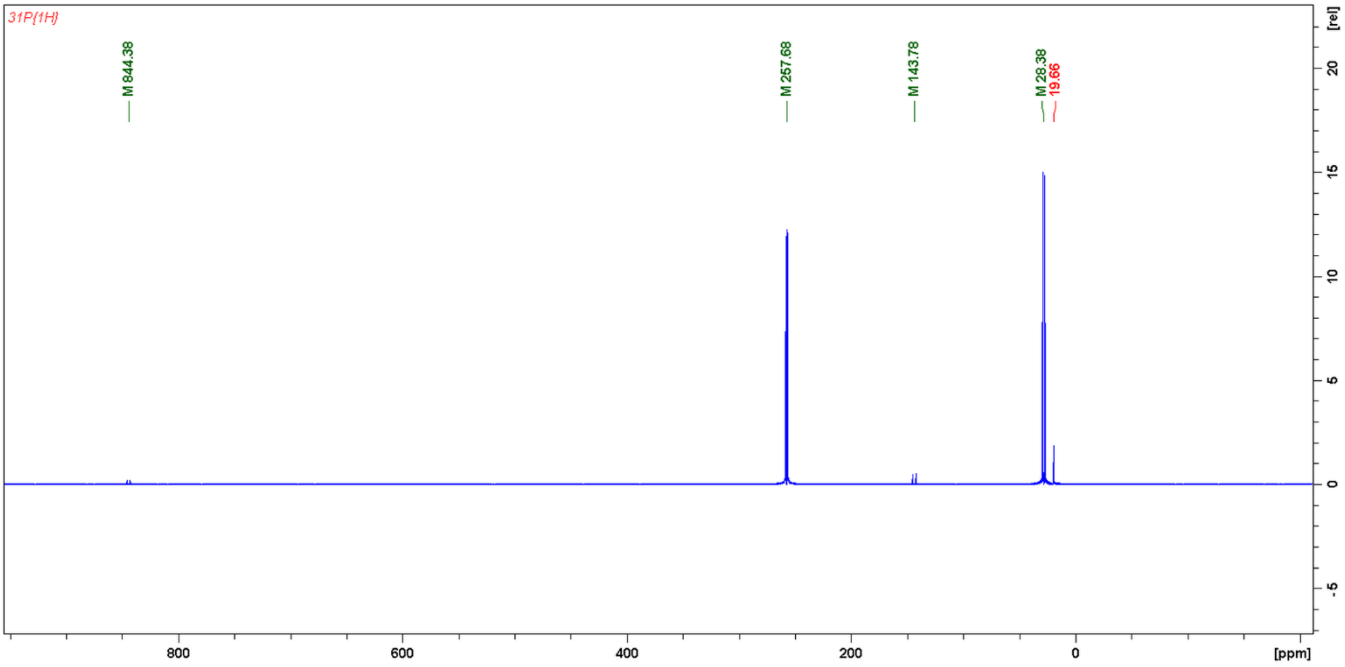


Figure S5. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 3 months after starting the reaction of **1** with 4,4'-dimethoxybenzophenone.

- 844.38 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-**P**-P*t*Bu$_2$}];
- 257.68 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (4-MeO-Ph)$_2$C=**P**-P*t*Bu$_2$;
- 143.78 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-**P***t*Bu$_2$}];
- 28.38 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (4-MeO-Ph)$_2$C=P-**P***t*Bu$_2$;
- 19.66 ppm, (s), *t*Bu$_2$**P**H;

B.1.6. *Tert*-butyl phenyl ketone

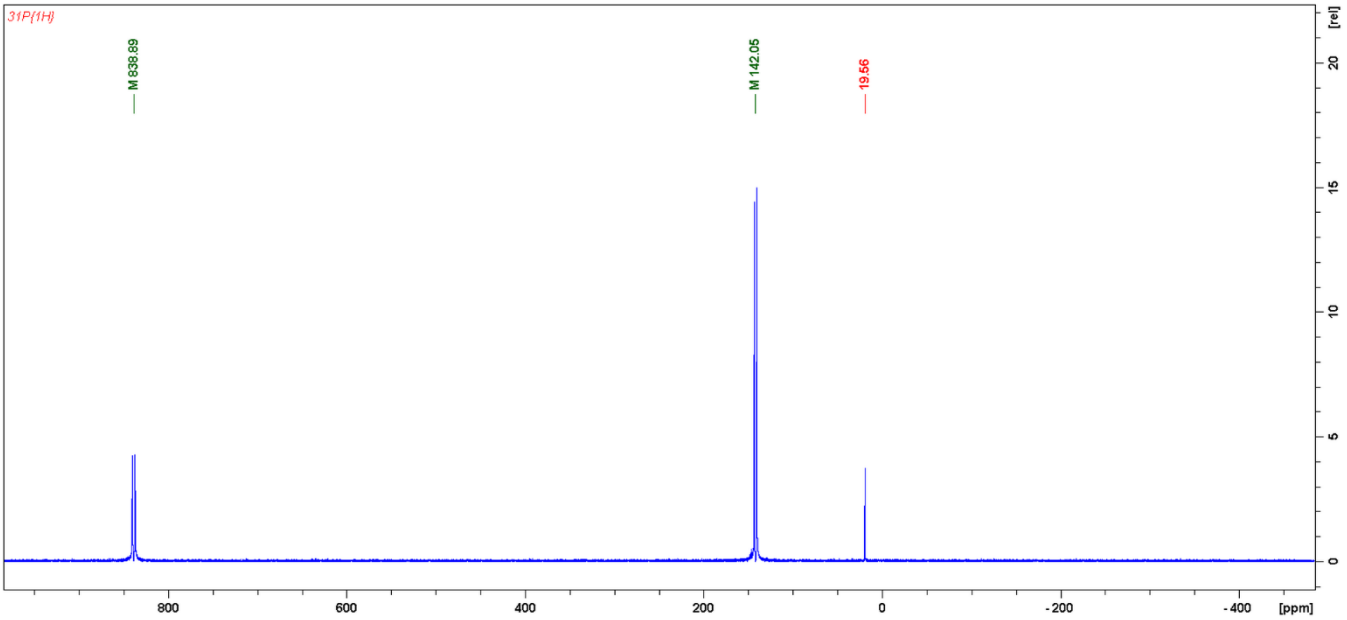


Figure S6. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 3 months after starting the reaction of **1** with *tert*-butyl phenyl ketone.

- 838.89 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}];
- 142.05 ppm, (d), $J_{P\text{-}P}$ = 450.5 Hz, [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}];
- 19.56 ppm, (s), *t*Bu$_2$PH;

B.1.7. Acetone

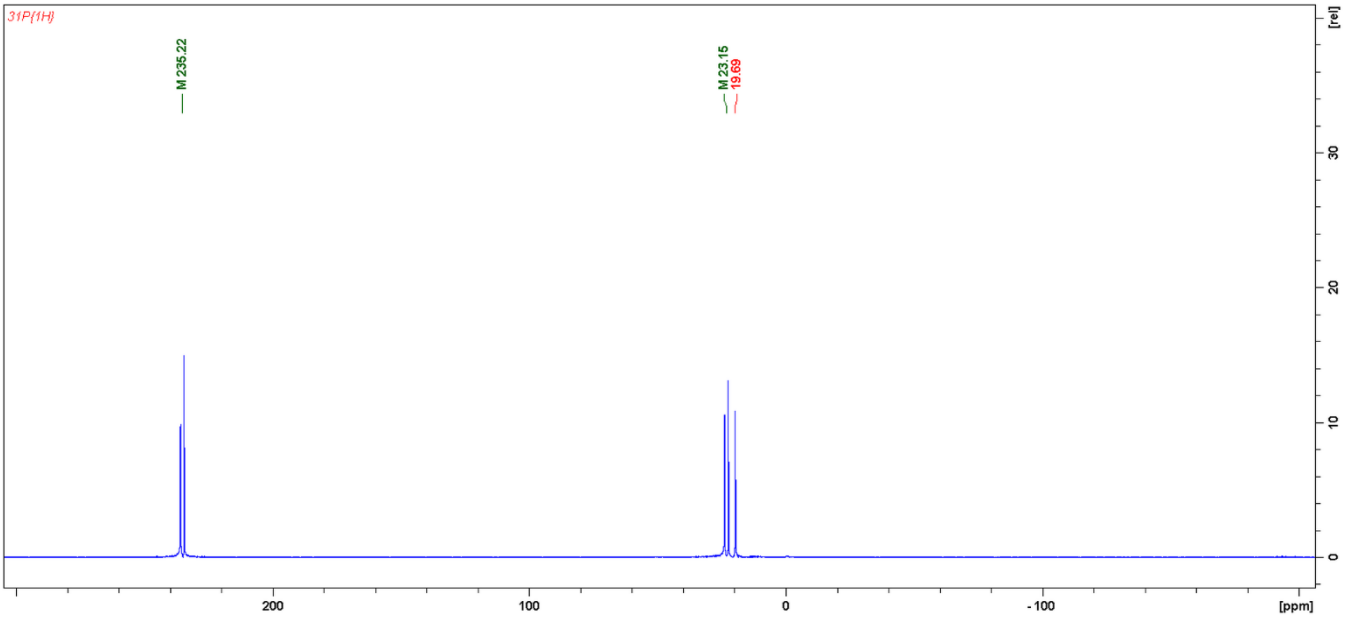


Figure S7. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with acetone.

- 234.73 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Me)_2C$=**P**-P*t*Bu_2;
- 23.14 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Me)_2C$=P-**P***t*Bu_2;
- 19.69 ppm, (s), *t*Bu_2PH;

B.1.8. Cyclohexanone

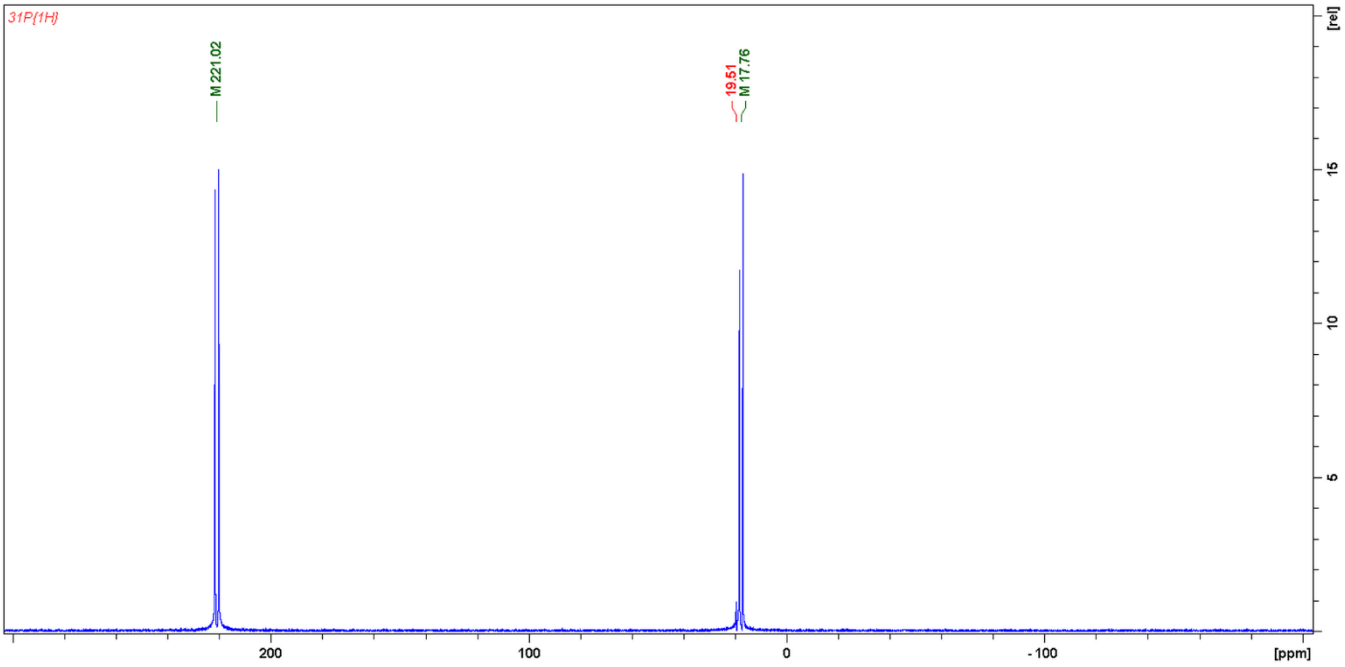


Figure S8. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with cyclohexanone.

- 221.02 ppm, (d), $J_{P\text{-}P}$ = 228.8 Hz, $(CH_2)_5C$=**P**-P*t*Bu_2;
- 19.51 ppm, (s), *t*Bu_2PH;
- 17.76 ppm, (d), $J_{P\text{-}P}$ = 228.8 Hz, $(CH_2)_5C$=P-**P***t*Bu_2;

B.1.9. Acetophenone

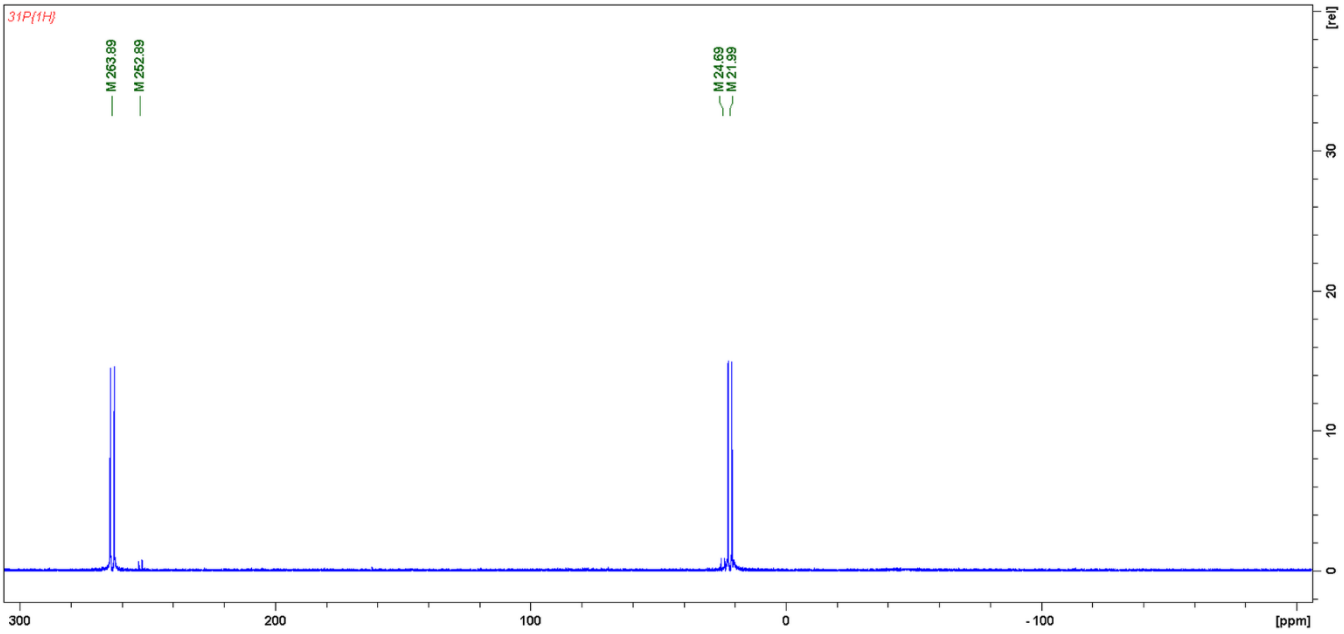


Figure S9. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with acetophenone.

- 263.63 ppm, (d), $J_{P\text{-}P}$ = 234.9 Hz, (Ph)(Me)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 253.06 ppm, (d), $J_{P\text{-}P}$ = 222.8 Hz, (Ph)(Me)C=**P**-P*t*Bu$_2$ – *Z* isomer;
- 24.65 ppm, (d), $J_{P\text{-}P}$ = 222.8 Hz, (Ph)(Me)C=P-**P***t*Bu$_2$ – *Z* isomer;
- 21.91 ppm, (d), $J_{P\text{-}P}$ = 234.9 Hz, (Ph)(Me)C=P-**P***t*Bu$_2$ – *E* isomer;
- 19.65 *t*Bu$_2$PH;

B.1.10. Cyclopropyl methyl ketone

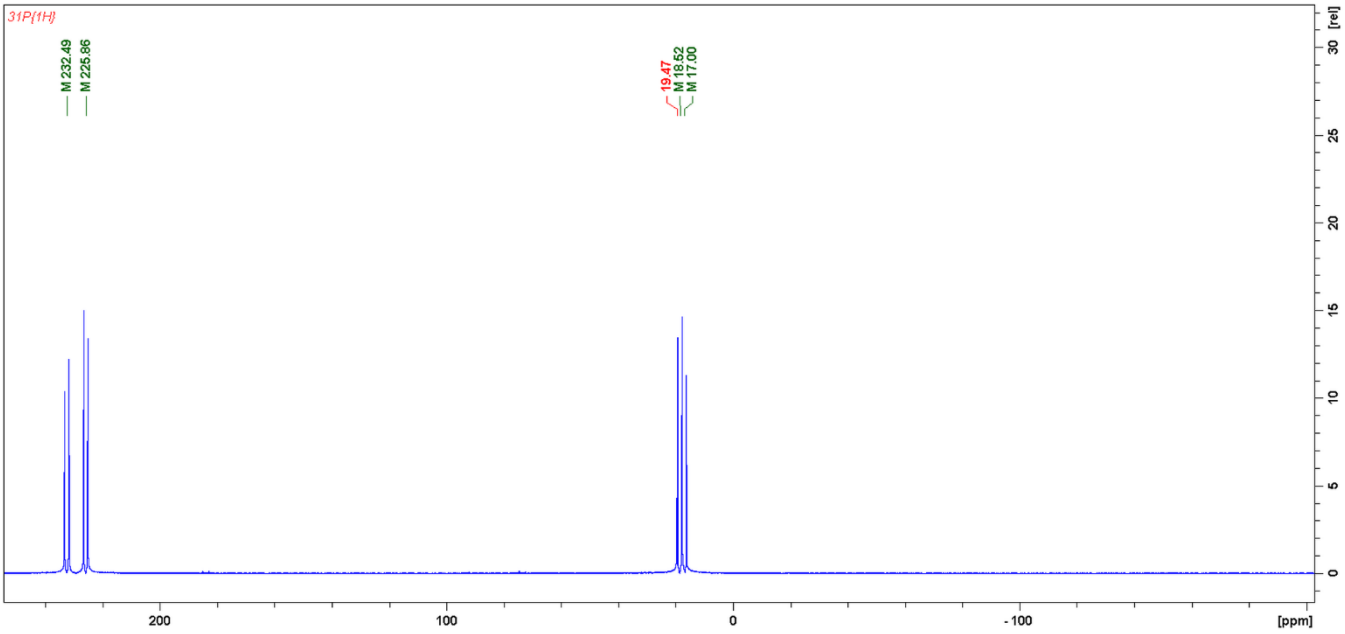


Figure S10. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with cyclopropyl methyl ketone.

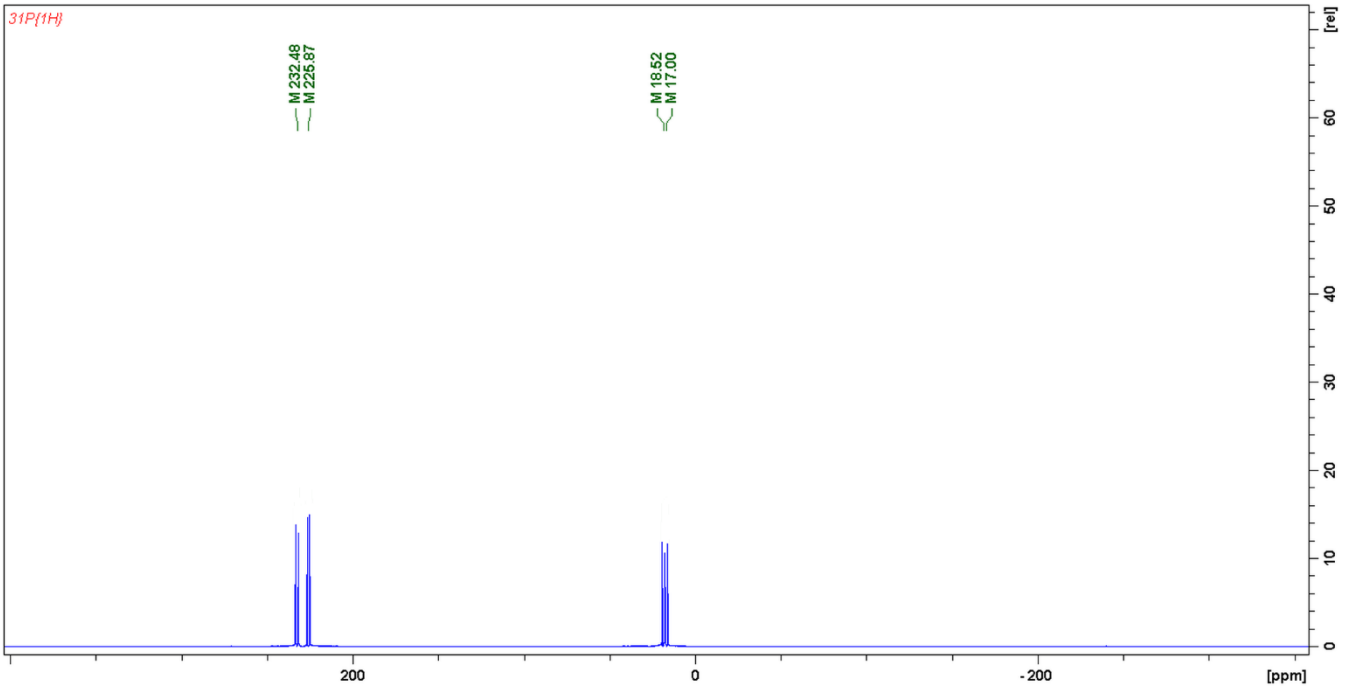


Figure S11. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*cyclo*-CH_2CH_2CH)(Me)C=P-P*t*Bu_2 (**3j**).

- 232.48 ppm, (d), $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=**P**-P*t*Bu_2 – *Z* isomer;
- 225.87 ppm, (d), $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=**P**-P*t*Bu_2 – *E* isomer;
- 18.52 ppm, (d), $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=P-**P***t*Bu_2 – *Z* isomer;
- 17.00 ppm, (d), $J_{P\text{-}P}$ = 232.9 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=P-**P***t*Bu_2 – *E* isomer;

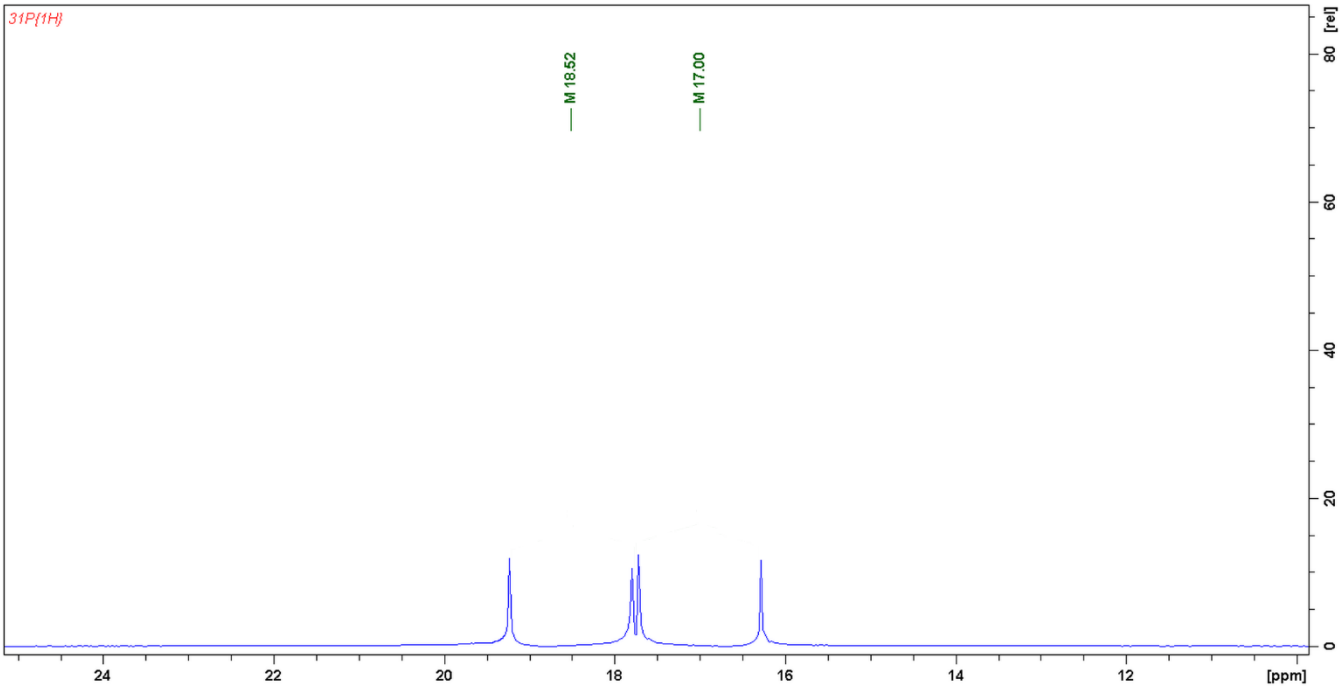


Figure S12. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*cyclo*-CH_2CH_2CH)(Me)C=P-P*t*Bu_2 (**3j**) in the range from 25 ppm to 10 ppm.

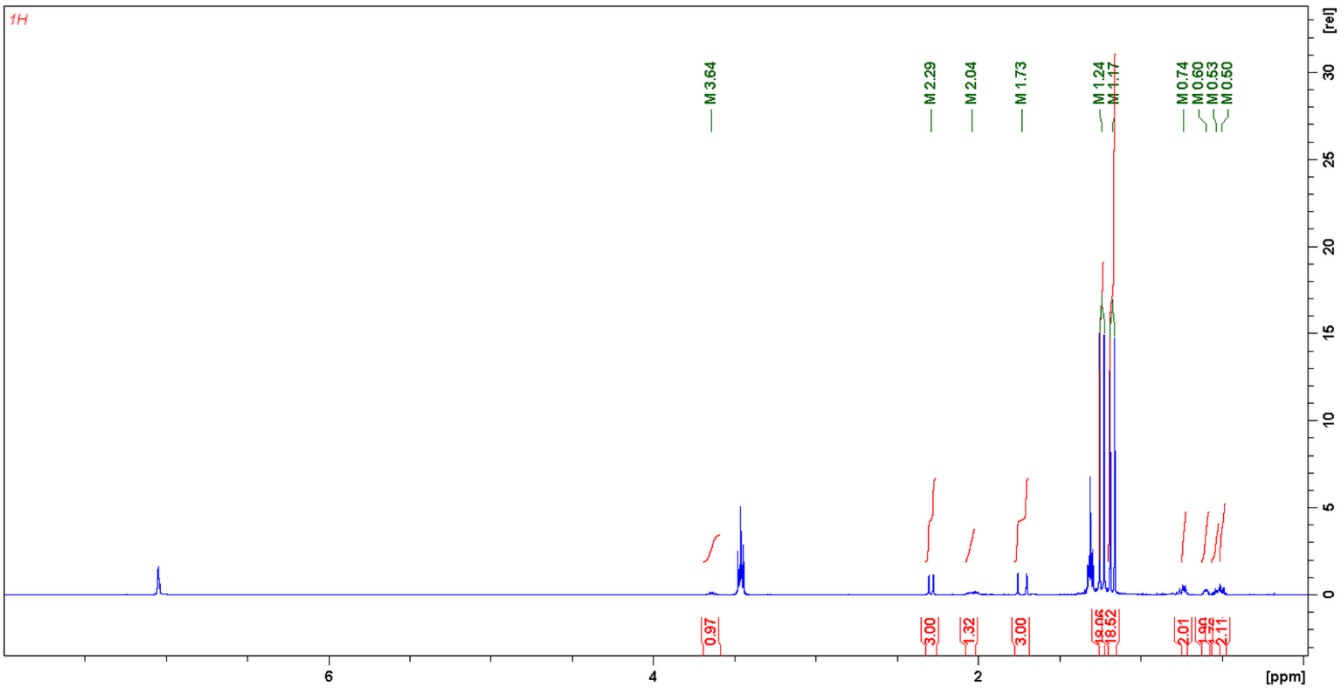


Figure S13. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*cyclo*-CH_2CH_2CH)(Me)C=P-P*t*Bu_2 (**3j**).

- 3.64 ppm, (broad m), 1H, (*cyclo*-CH_2CH_2C**H**)(Me)C=P-P*t*Bu_2 – *Z* isomer;
- 2.29 ppm, (ddd), $J_{P\text{-}H}$ = 10.8 Hz, J_{HH} = 1.3 Hz, J_{PH} = 0.4 Hz, 3H, (*cyclo*-CH_2CH_2CH)(**Me**)C=P-P*t*Bu_2 – *E* isomer;
- 2.04 ppm, (broad m), 1H,(*cyclo*-CH_2CH_2C**H**)(Me)C=P-P*t*Bu_2 – *E* isomer;
- 1.73 ppm, (dd), $J_{P\text{-}H}$ = 21.9 Hz, J_{PH} = 1.6 Hz, 3H, (*cyclo*-CH_2CH_2CH)(**Me**)C=P-P*t*Bu_2 – *Z* isomer;
- 1.24 ppm, (d), $J_{P\text{-}H}$ = 11.2 Hz, 18H, (CH_2CH_2CH)(*cyclo*-CH_3)C=P-P***t*Bu**$_2$ – *E* isomer;
- 1.17 ppm, (d), $J_{P\text{-}H}$ = 11.2 Hz, 18H, (*cyclo*-CH_2CH_2CH)(Me)C=P-P***t*Bu**$_2$ – *Z* isomer;
- 0.74 ppm, (broad m), 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu_2 – *Z* isomer;
- 0.60 ppm, (broad m), 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu_2 – *Z* isomer;
- 0.53 ppm, (broad m), 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu_2 – *E* isomer;
- 0.50 ppm, (broad m), 2H, (*cyclo*-C**H**$_2$C**H**$_2$CH)(Me)C=P-P*t*Bu_2 – *E* isomer;

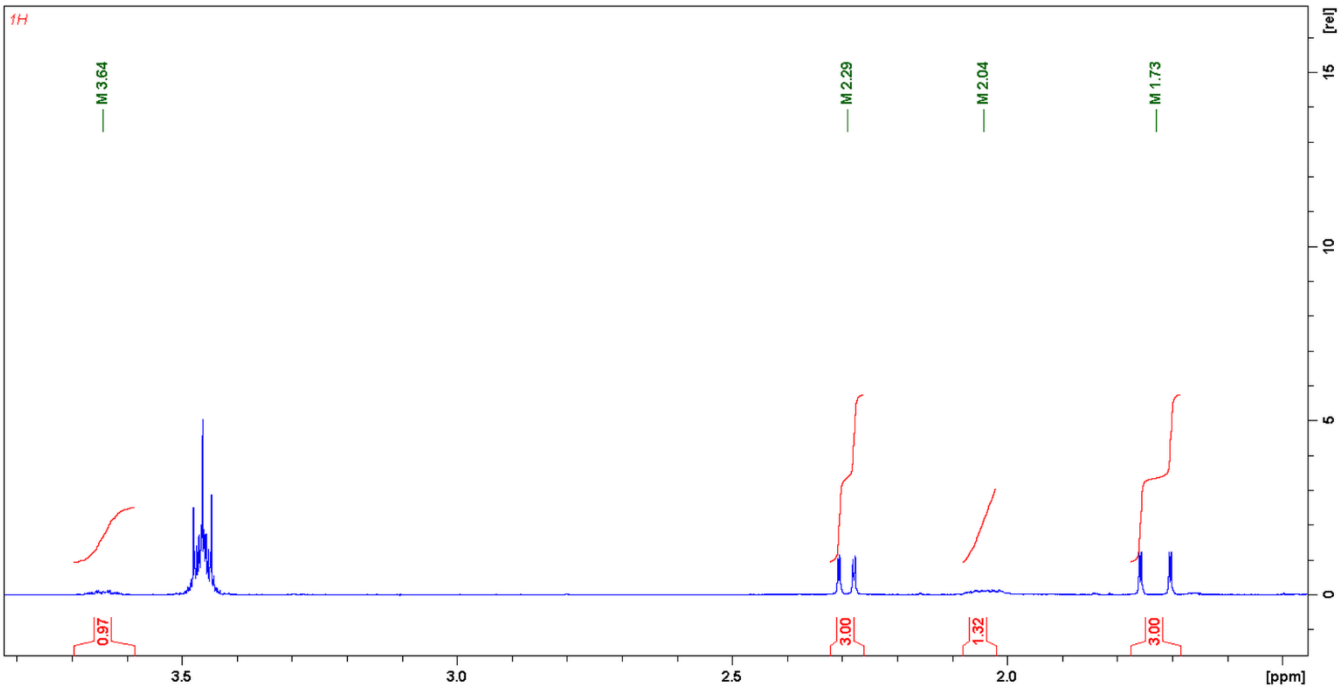


Figure S14. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*cyclo*-CH_2CH_2CH)(Me)C=P-P*t*Bu_2 (**3j**) in the range from 4 ppm to 1.5 ppm.

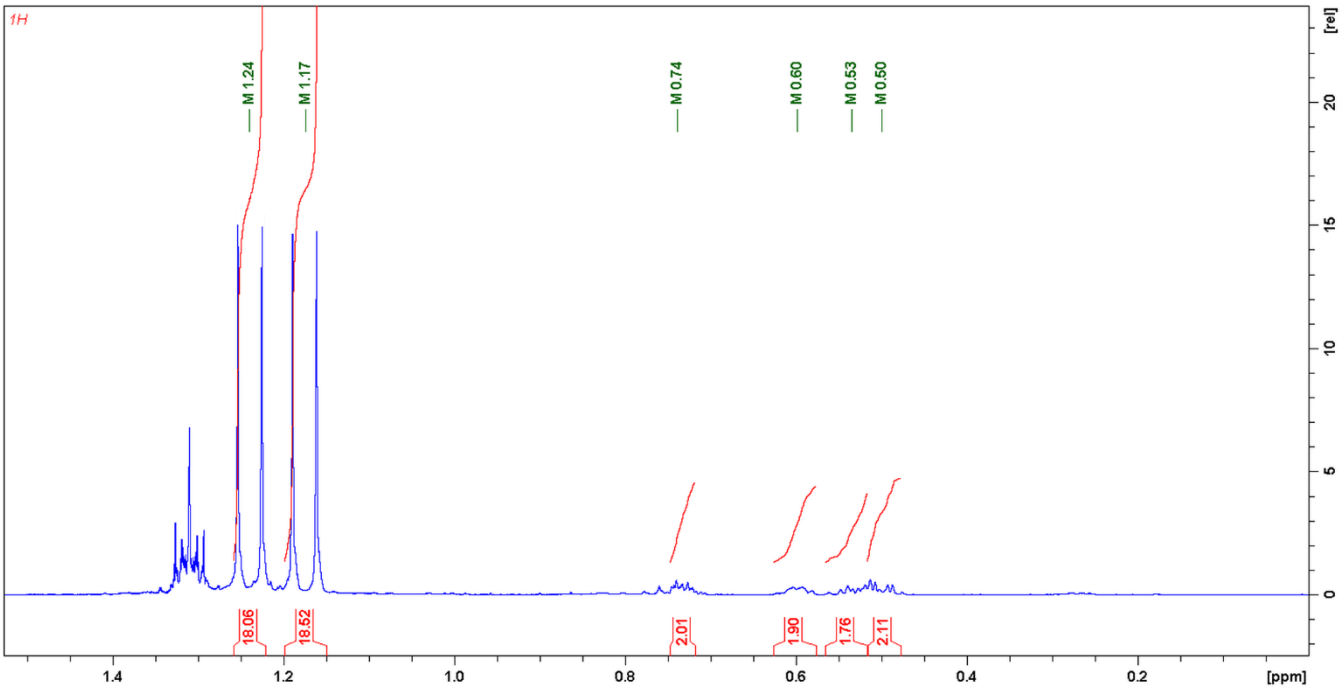


Figure S15. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*cyclo*-CH_2CH_2CH)(Me)C=P-P*t*Bu_2 (**3j**) in the range from 1.5 ppm to 0 ppm.

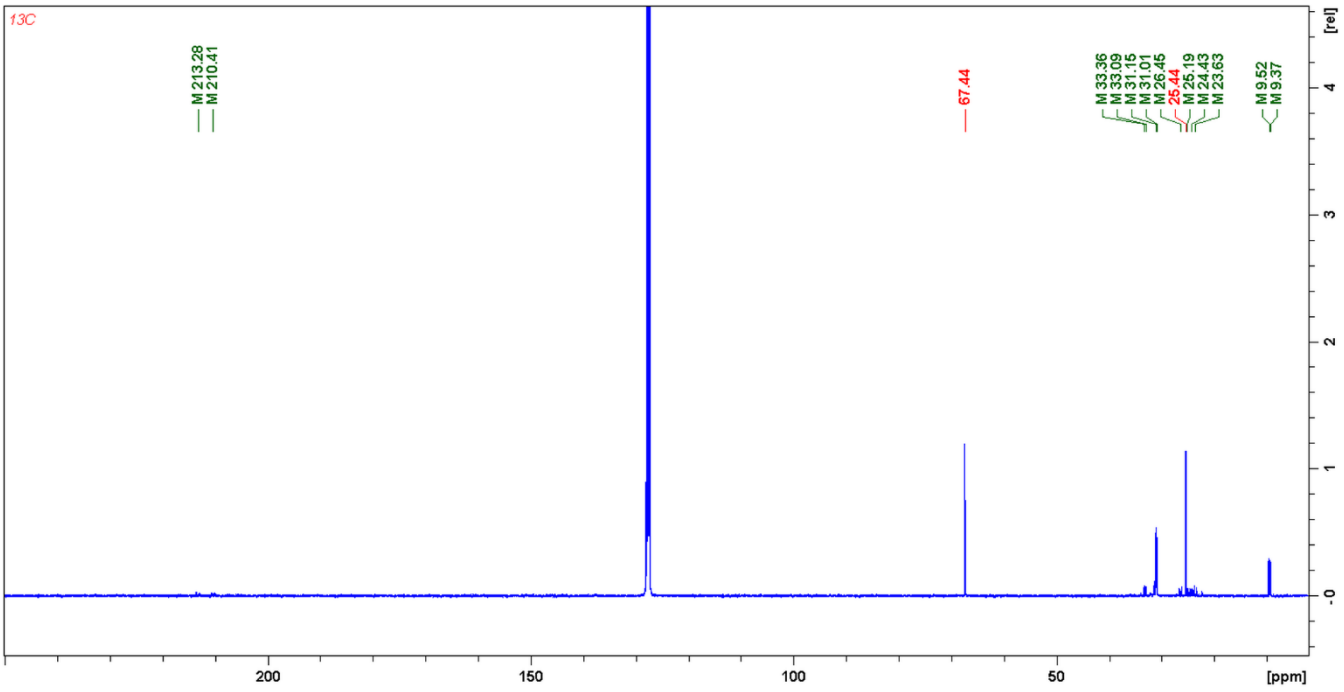


Figure S16. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*cyclo*-CH_2CH_2CH)(Me)C=P-P*t*Bu_2 (**3j**).

- 213.28 ppm, (dd), $J_{P\text{-}C}$ = 53.6 Hz, $J_{P\text{-}C}$ = 14.5 Hz, (*cyclo*-CH_2CH_2CH)(Me)**C**=P-P*t*Bu_2 – *E* isomer;
- 210.41 ppm, (dd), $J_{P\text{-}C}$ = 55.4 Hz, $J_{P\text{-}C}$ = 11.8 Hz, (*cyclo*-CH_2CH_2CH)(Me)**C**=P-P*t*Bu_2 – *Z* isomer;
- 33.36 ppm, (dd), $J_{P\text{-}C}$ = 9.1 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=P-P{**C**$(CH_3)_3$}$_2$ – *E* isomer;
- 33.36 ppm, (dd), $J_{P\text{-}C}$ = 9.1 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=P-P{**C**$(CH_3)_3$}$_2$ – *Z* isomer;
- 31.15 ppm, (dd), $J_{P\text{-}C}$ = 10.9 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=P-P{C(**C**$H_3)_3$}$_2$ – *E* isomer;
- 31.01 ppm, (dd), $J_{P\text{-}C}$ = 10.9 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (*cyclo*-CH_2CH_2CH)(Me)C=P-P{C(**C**$H_3)_3$}$_2$ – *Z* isomer;
- 26.45 ppm, (dd), $J_{P\text{-}C}$ = 45.4 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (*cyclo*-CH_2CH_2**C**H)(Me)C=P-P*t*Bu_2 – *E* isomer;
- 25.19 ppm, (dd), $J_{P\text{-}C}$ = 29.1 Hz, $J_{P\text{-}C}$ = 15.4 Hz, (*cyclo*-CH_2CH_2CH)(**C**H_3)C=P-P*t*Bu_2 – *E* isomer;
- 24.43 ppm, (dd), $J_{P\text{-}C}$ = 38.1 Hz, $J_{P\text{-}C}$ = 17.2 Hz, (*cyclo*-CH_2CH_2CH)(**C**H_3)C=P-P*t*Bu_2 – *Z* isomer;
- 23.63 ppm, (dd), $J_{P\text{-}C}$ = 45.4 Hz, $J_{P\text{-}C}$ = 3.6 Hz, (*cyclo*-CH_2CH_2**C**H)(Me)C=P-P*t*Bu_2 – *Z* isomer;
- 9.52 ppm, (d), $J_{P\text{-}C}$ = 2.7 Hz, (*cyclo*-**C**H_2**C**H_2CH)(Me)C=P-P*t*Bu_2 – *Z* isomer;
- 9.37 ppm, (d), $J_{P\text{-}C}$ = 12.7 Hz, (*cyclo*-**C**H_2**C**H_2CH)(Me)C=P-P*t*Bu_2 – *E* isomer;

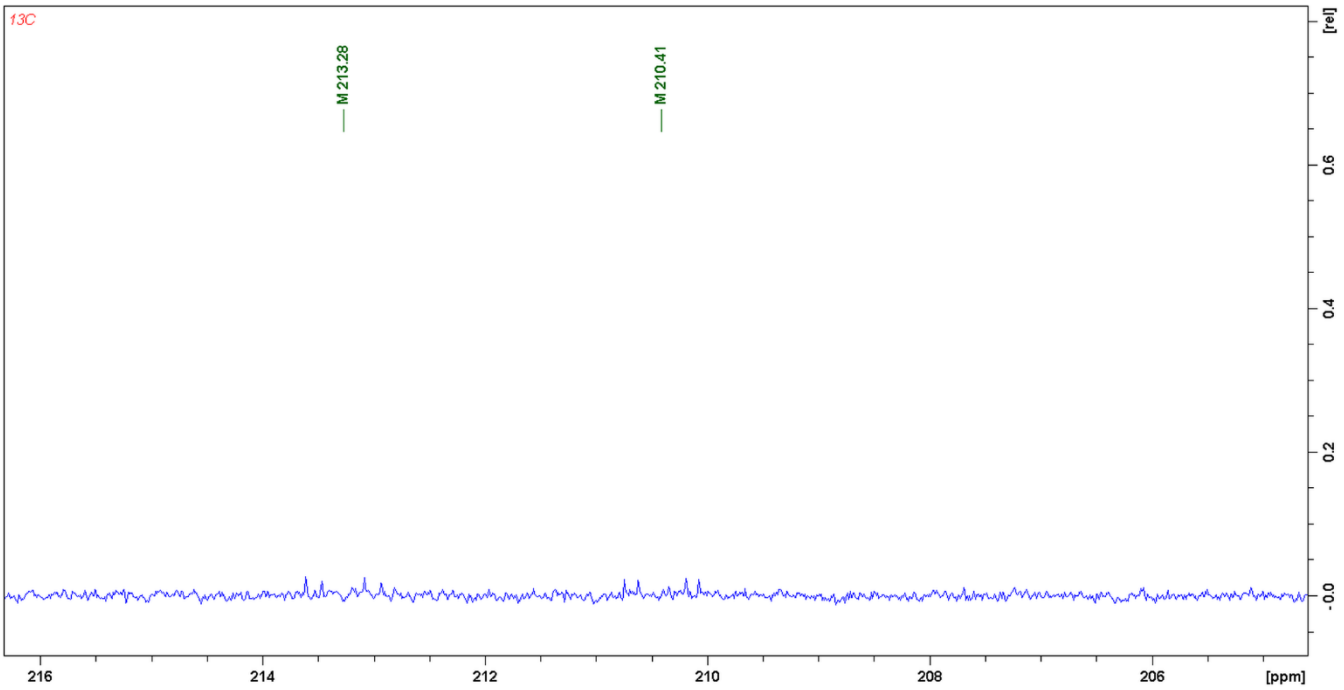


Figure S17. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(CH_2CH_2CH)(Me)C{=}P\text{-}PtBu_2$ (**3j**) in the range from 216 ppm to 205 ppm.

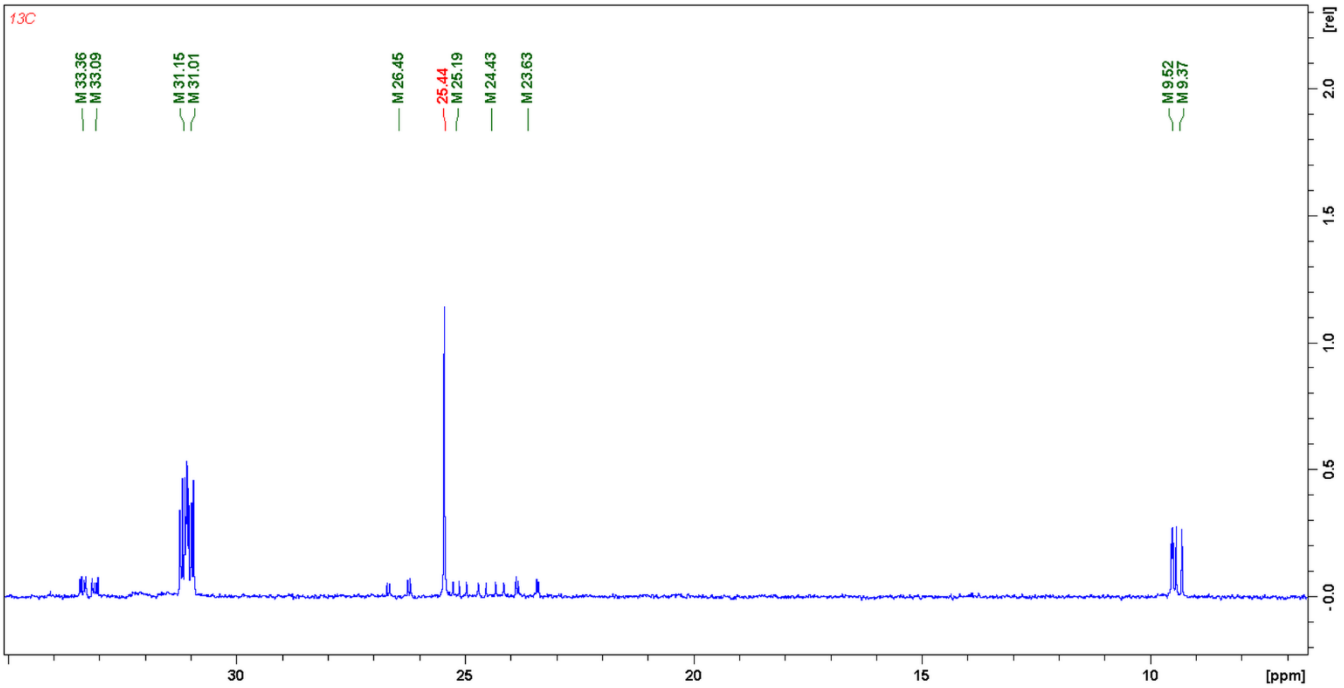


Figure S18. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(CH_2CH_2CH)(Me)C{=}P\text{-}PtBu_2$ (**3j**) in the range from 35 ppm to 5 ppm.

B.1.11. Isobutyraldehyde

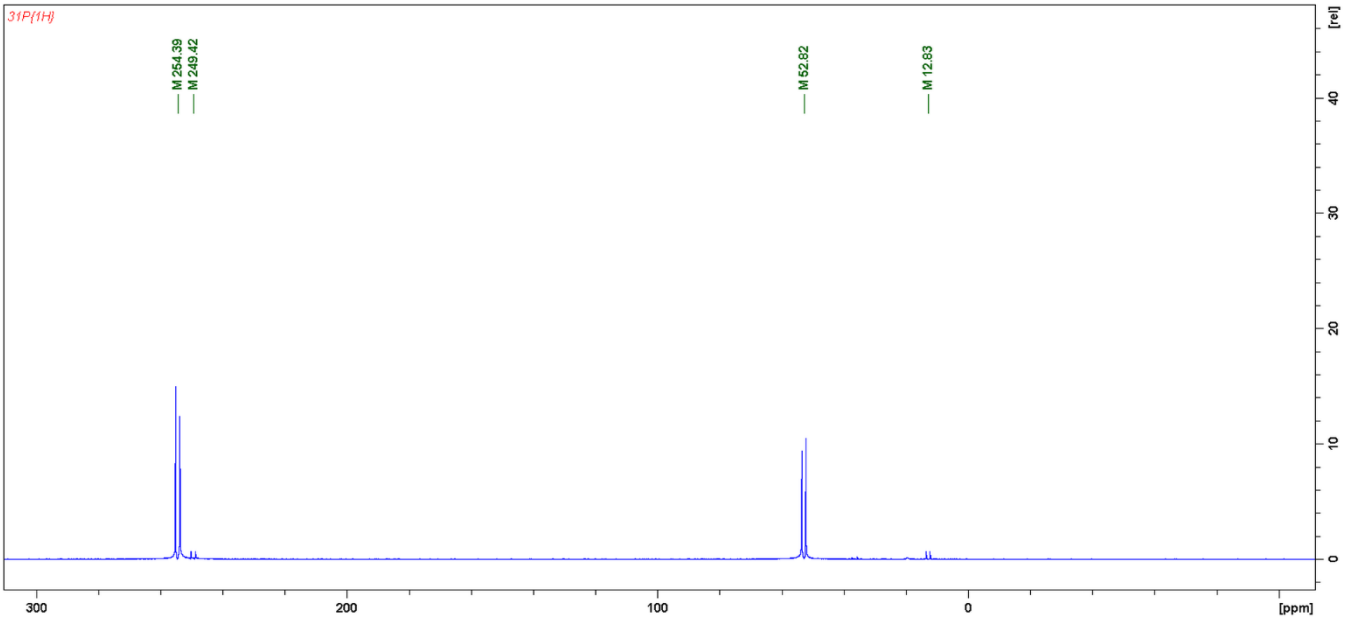


Figure S19. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with isobutyraldehyde.

- 254.39 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {(Me)$_2$CH}(H)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 249.42 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {(Me)$_2$CH}(H)C=**P**-P*t*Bu$_2$ – *Z* isomer;
- 52.82 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$ – *E* isomer;
- 12.83 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$ – *Z* isomer;

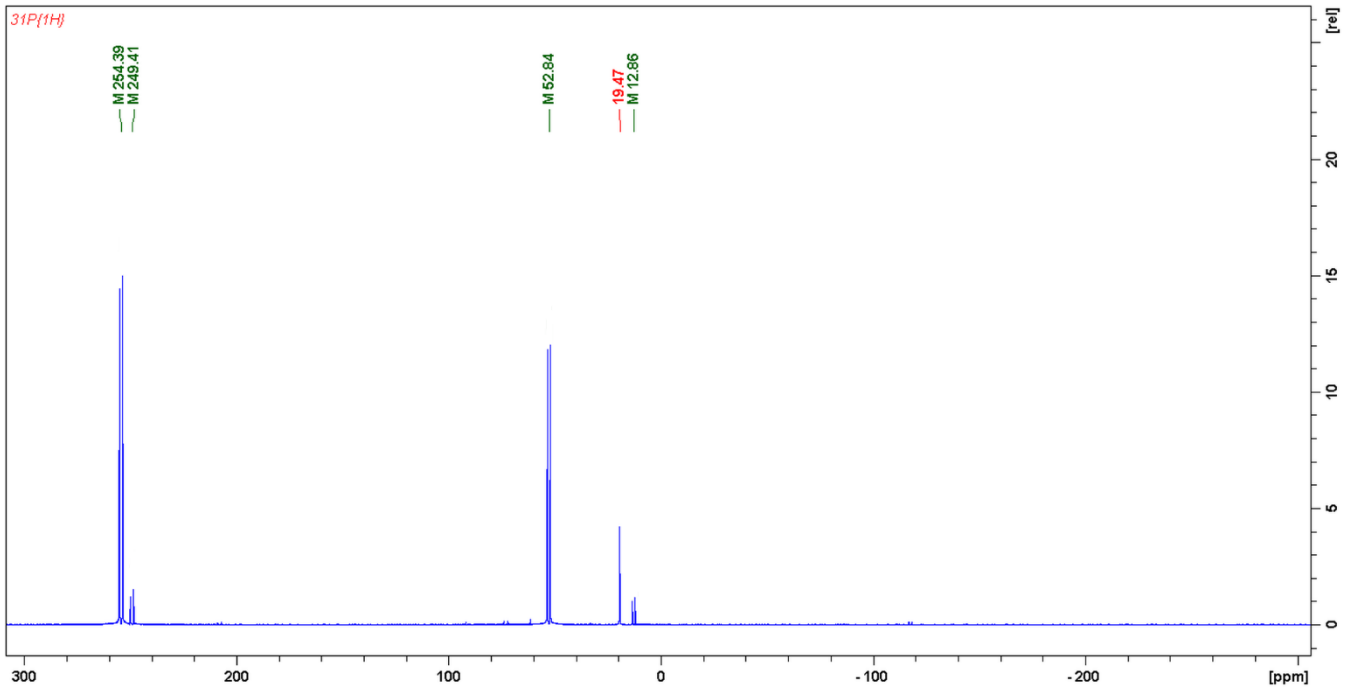


Figure S20. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $\{(Me)_2CH\}(H)C=P\text{-}PtBu_2$ (**4a**).

- 254.39 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, $\{(Me)_2CH\}(H)C=\mathbf{P}\text{-}PtBu_2$ – *E* isomer;
- 249.40 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, $\{(Me)_2CH\}(H)C=\mathbf{P}\text{-}PtBu_2$ – *Z* isomer;
- 52.83 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, $\{(Me)_2CH\}(H)C=P\text{-}\mathbf{P}tBu_2$ – *E* isomer;
- 12.85 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, $\{(Me)_2CH\}(H)C=P\text{-}\mathbf{P}tBu_2$ – *Z* isomer;
- 19.47 ppm, (s), $t\text{Bu}_2\mathbf{P}H$;

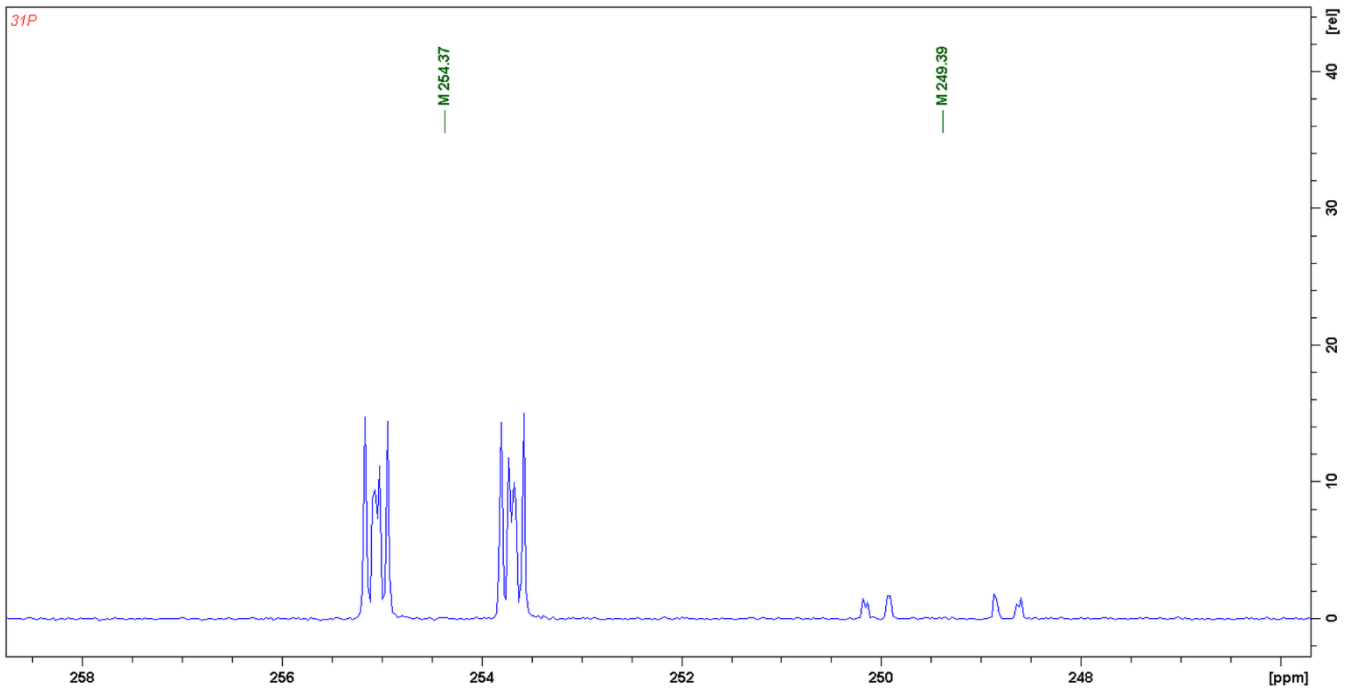


Figure S21. ^{31}P NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $\{(Me)_2CH\}(H)C=P\text{-}PtBu_2$ (**4a**) in the range from 258 ppm to 247 ppm.

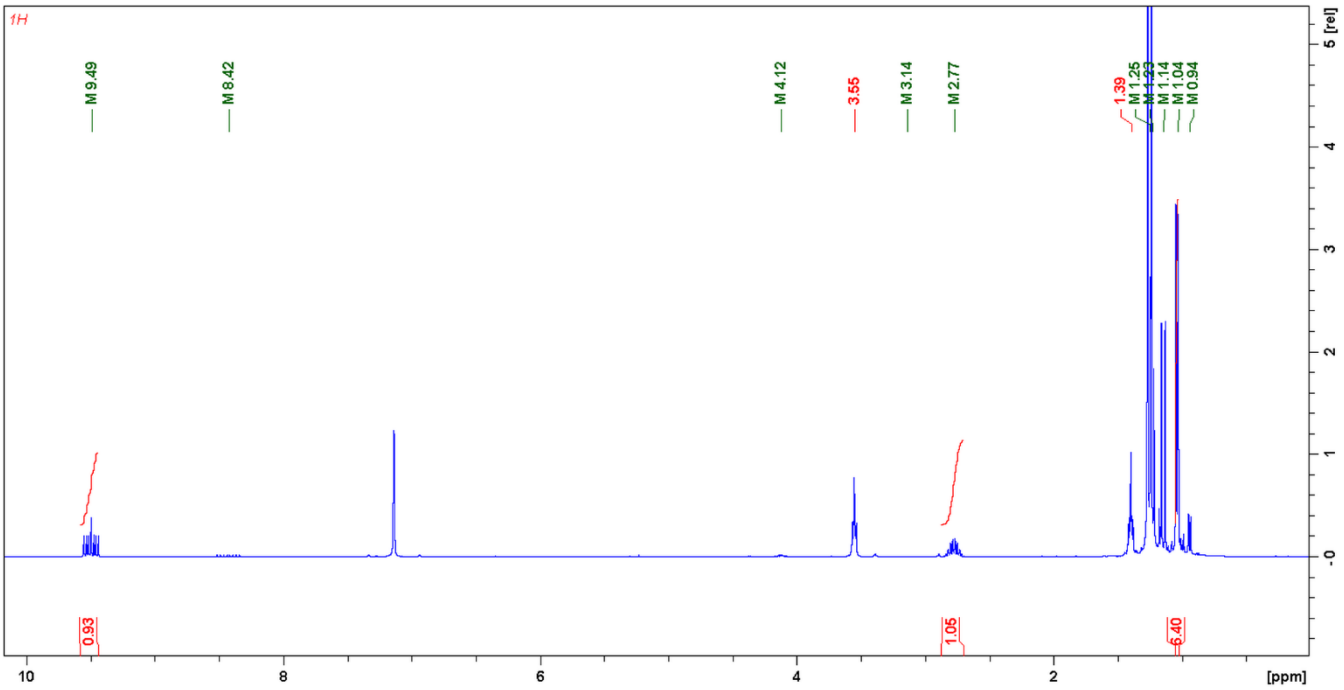


Figure S22. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$ (**4a**).

- 9.49 ppm, (ddd), 1H, $J_{P\text{-}H}$ = 24.1 Hz, $J_{P\text{-}H}$ = 12.0 Hz, $J_{P\text{-}H}$ = 8.1 Hz, {(Me)$_2$CH}(**H**)C=P-P*t*Bu$_2$ – *E* isomer;
- 8.42 ppm, (ddd), 1H, $J_{P\text{-}H}$ = 36.1 Hz, $J_{H\text{-}H}$ = 20.9 Hz, $J_{P\text{-}H}$ = 8.0 Hz, {(Me)$_2$CH}(**H**)C=P-P*t*Bu$_2$ – *Z* isomer;
- 4.12 ppm, (br. m), 1H, $J_{H\text{-}H}$ = 6.7 Hz, {(Me)$_2$C**H**}(H)C=P-P*t*Bu$_2$ – *Z* isomer;
- 3.55 ppm, (m), 4H, THF;
- 3.14 ppm, (d), 1H, $J_{P\text{-}H}$ = 197.8 Hz, *t*Bu$_2$P**H**;
- 2.77 ppm, (br. m), 1H, $J_{H\text{-}H}$ = 6.7 Hz, {(Me)$_2$C**H**}(H)C=P-P*t*Bu$_2$ – *E* isomer;
- 1.39 ppm, (m), 4H, THF;
- 1.25 ppm, (d), 18H, $J_{P\text{-}H}$ = 11.3 Hz, {(Me)$_2$CH}(H)C=P-P***t*Bu$_2$** – *E* isomer;
- 1.23 ppm, (d), 18H, $J_{P\text{-}H}$ = 11.2 Hz, {(Me)$_2$CH}(H)C=P-P***t*Bu$_2$** – *Z* isomer;
- 1.14 ppm, (d), $J_{P\text{-}H}$ = 11.4 Hz, ***t*Bu$_2$**PH;
- 1.04 ppm, (dd), 6H, $J_{H\text{-}H}$ = 6.7 Hz, $J_{P\text{-}H}$ = 0.8 Hz, {(**Me**)$_2$CH}(H)C=P-P*t*Bu$_2$ – *E* isomer;
- 0.94 ppm, (br. d), 6H, $J_{H\text{-}H}$ = 6.7 Hz, {(**Me**)$_2$CH}(H)C=P-P*t*Bu$_2$ – *Z* isomer;

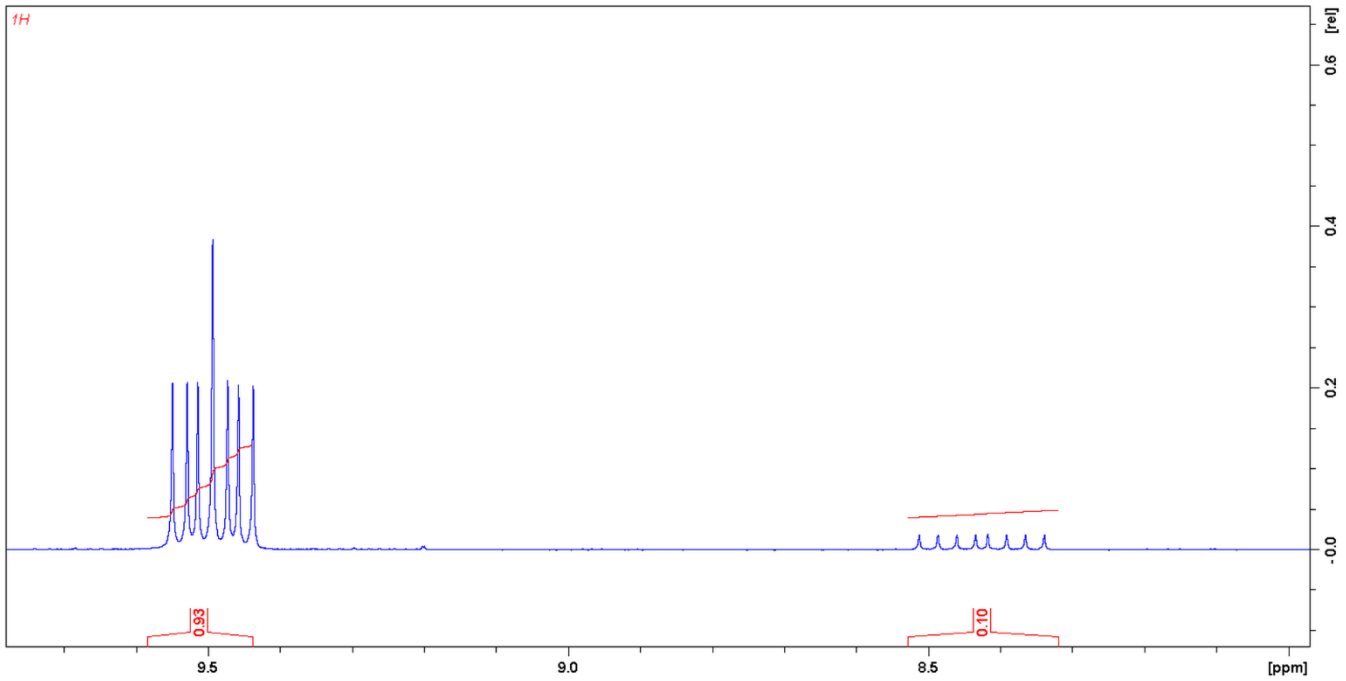


Figure S23. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$ (**4a**) in the aldehyde proton range. The integration shows the ratio of two isomers *E* : *Z* (90 % : 10 %).

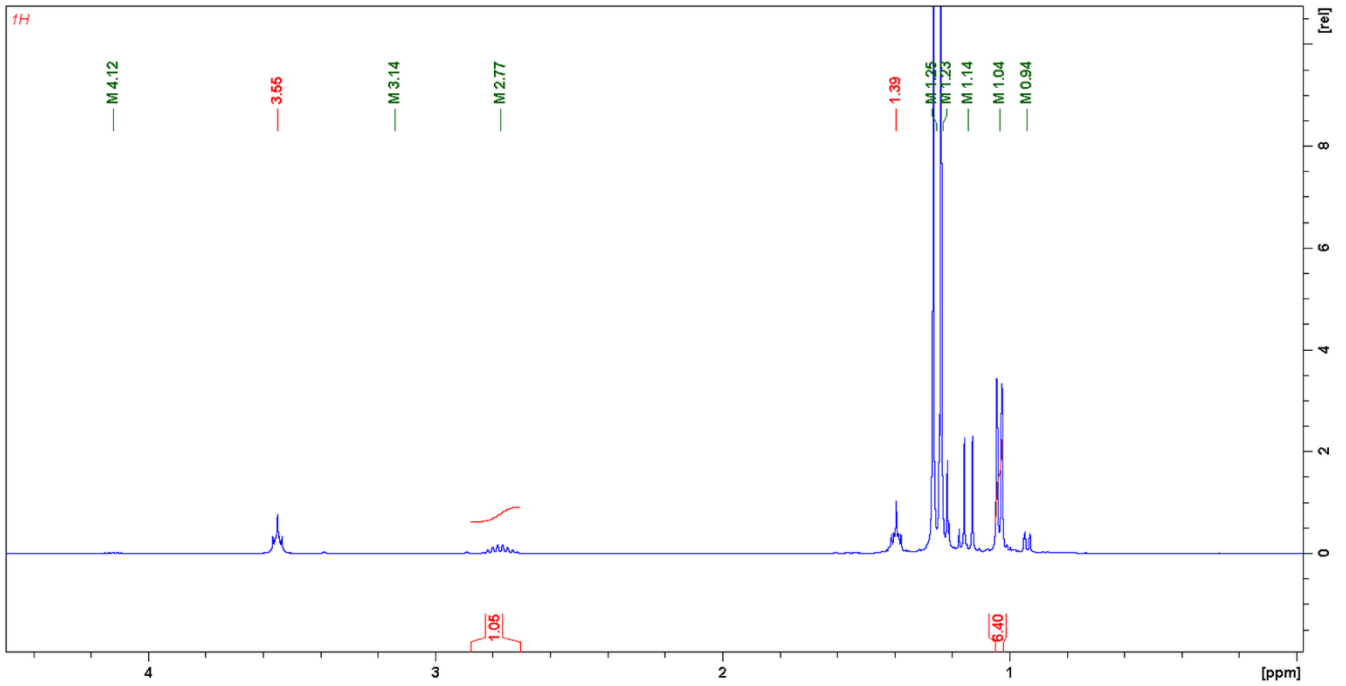


Figure S24. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {(Me)$_2$CH}(H)C=P-P*t*Bu$_2$ (**4a**) in the range of 4.5 ppm to 0 ppm.

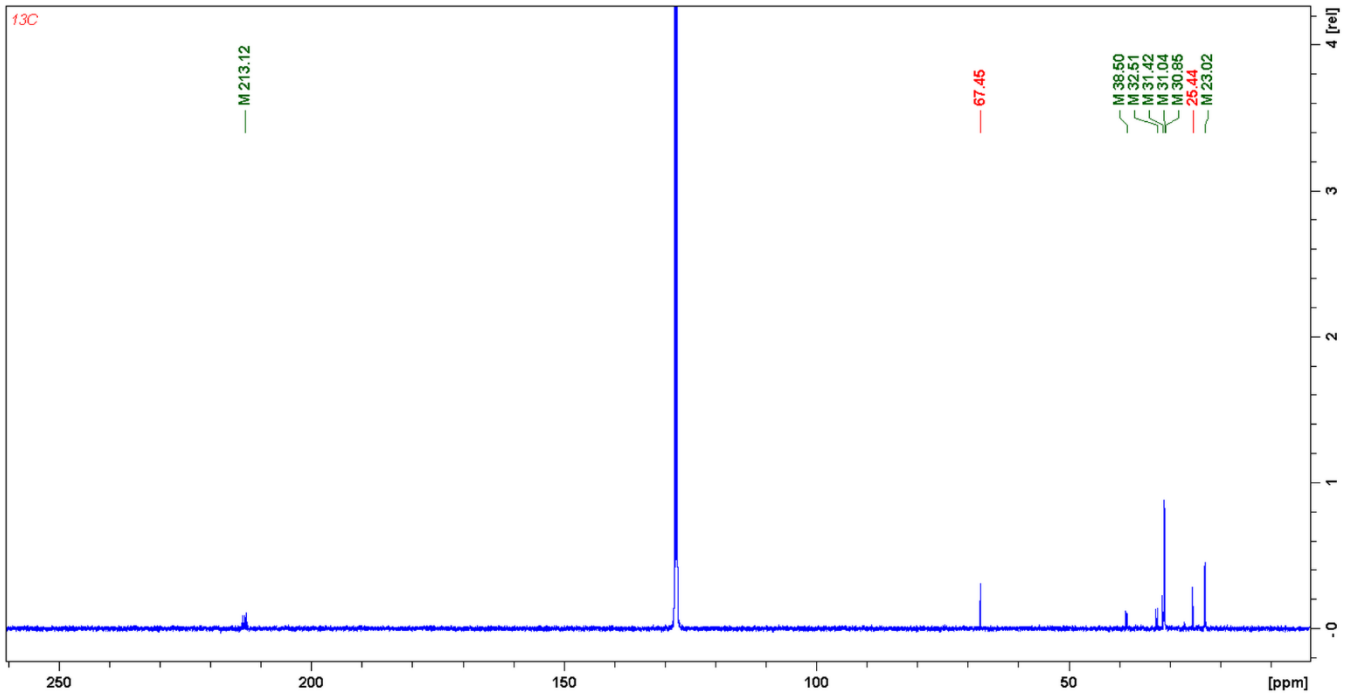


Figure S25. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $\{(Me)_2CH\}(H)C{=}P\text{-}PtBu_2$ (**4a**).

Only *E* isomer was visible, the weak signals of the *Z* isomer were not visible.

- 213.12 ppm, (dd), $J_{P\text{-}C}$ = 49.0 Hz, $J_{P\text{-}C}$ = 33.6 Hz, $\{(Me)_2CH\}(H)\mathbf{C}{=}P\text{-}PtBu_2$;
- 38.50 ppm, (dd), $J_{P\text{-}C}$ = 19.9 Hz, $J_{P\text{-}C}$ = 13.6 Hz, $\{(Me)_2\mathbf{C}H\}(H)C{=}P\text{-}PtBu_2$;
- 32.51 ppm, (dd), $J_{P\text{-}C}$ = 28.2 Hz, $J_{P\text{-}C}$ = 2.7 Hz Hz, $\{(Me)_2CH\}(H)C{=}P\text{-}P\{\mathbf{C}(CH_3)_3\}_2$;
- 31.04 ppm, (dd), $J_{P\text{-}C}$ = 19.9 Hz, $J_{P\text{-}C}$ = 5.4 Hz, $\{(Me)_2CH\}(H)C{=}P\text{-}P\{C(\mathbf{C}H_3)_3\}_2$;
- 23.02 ppm, (d) , $J_{P\text{-}C}$ = 12.7 Hz, $\{(\mathbf{Me})_2CH\}(H)C{=}P\text{-}PtBu_2$
- 31.42 ppm, (d), $J_{P\text{-}C}$ = 13.6 Hz, $\{(CH_3)_3\mathbf{C}\}_2PH$;
- 30.85 ppm, (d), $J_{P\text{-}C}$ = 4.5 Hz, $\{(\mathbf{C}H_3)_3C\}_2PH$;

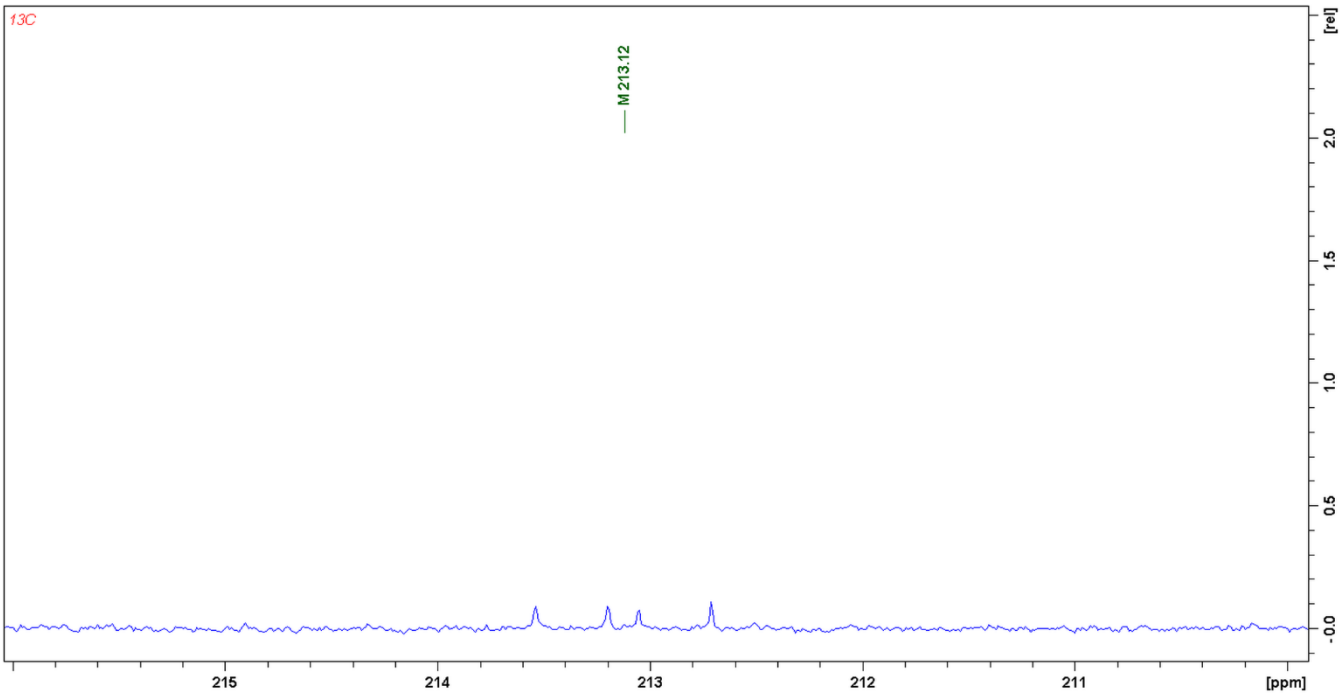


Figure S26. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $\{(Me)_2CH\}(H)C{=}P\text{-}PtBu_2$ (**4a**) in the range from 216 ppm to 210 ppm.

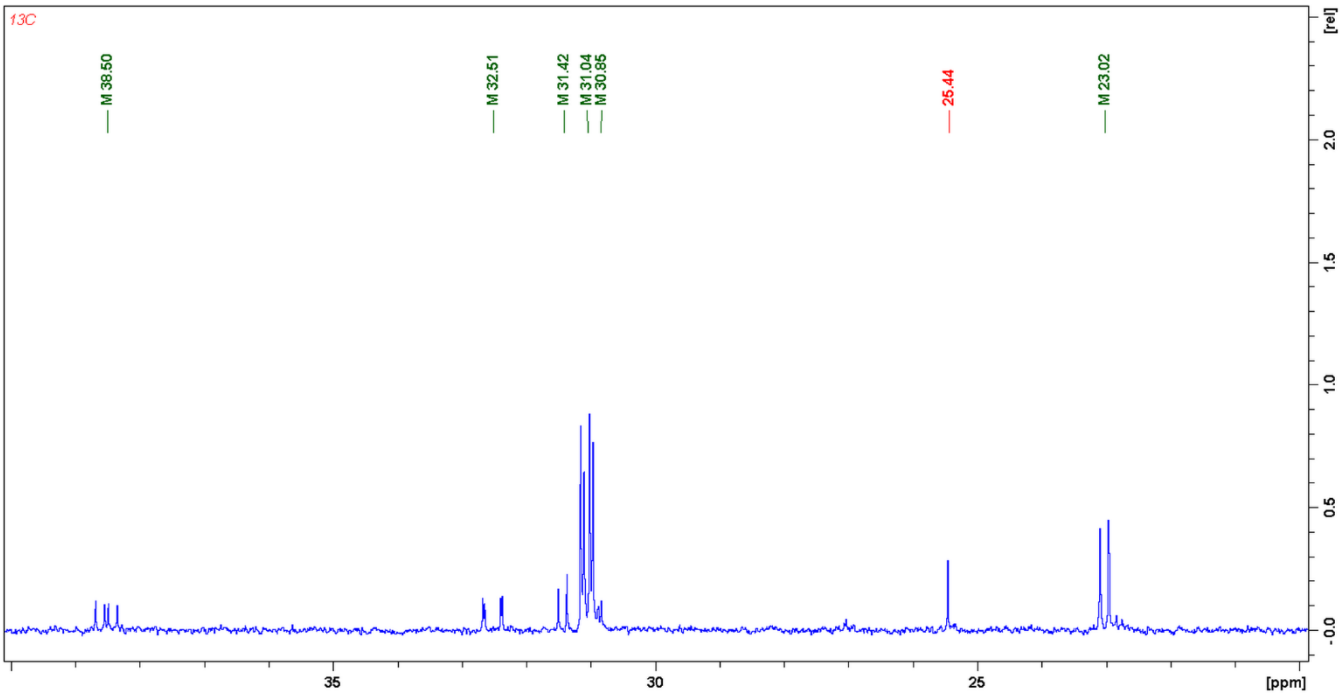


Figure S27. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $\{(Me)_2CH\}(H)C{=}P\text{-}PtBu_2$ (**4a**) in the range from 40 ppm to 20 ppm.

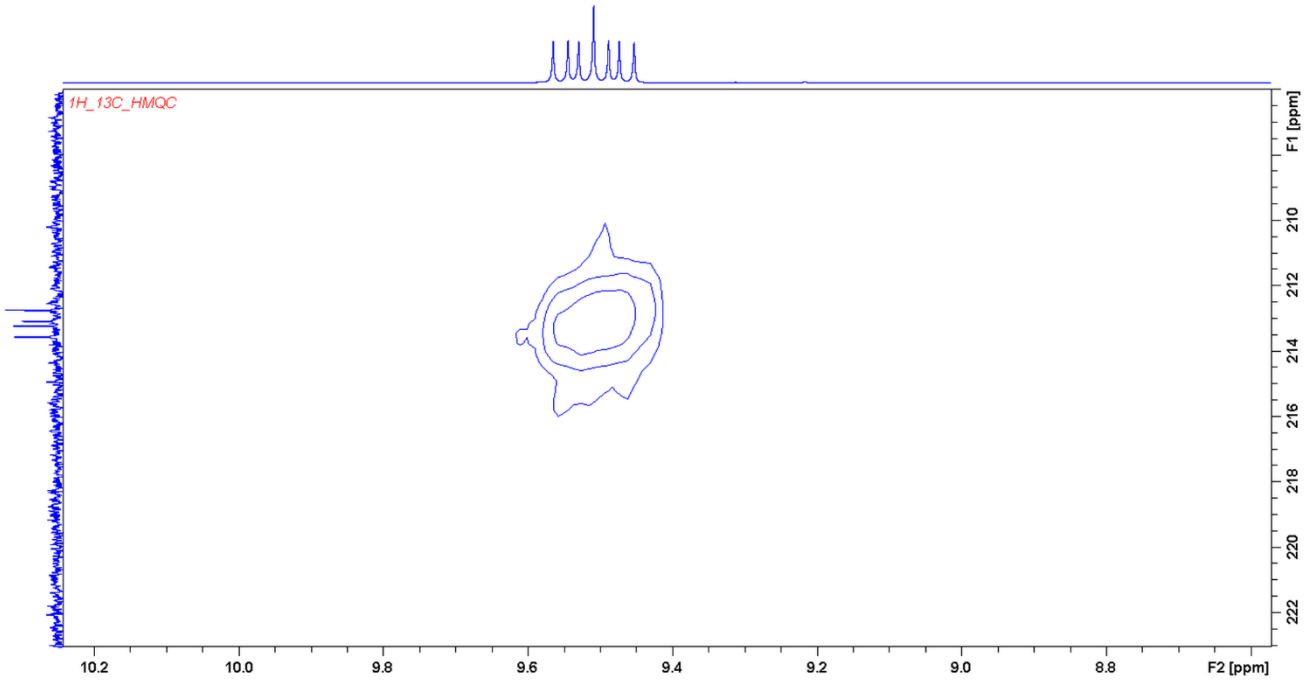


Figure S28. $^{13}C\{^{1}H\}/^{1}H$-HMQC (400 MHz, C_6D_6, 298 K) spectrum of isolated $\{(Me)_2CH\}(H)C{=}P\text{-}PtBu_2$ (**4a**).

B.1.12. Cyclohexanecarboxaldehyde

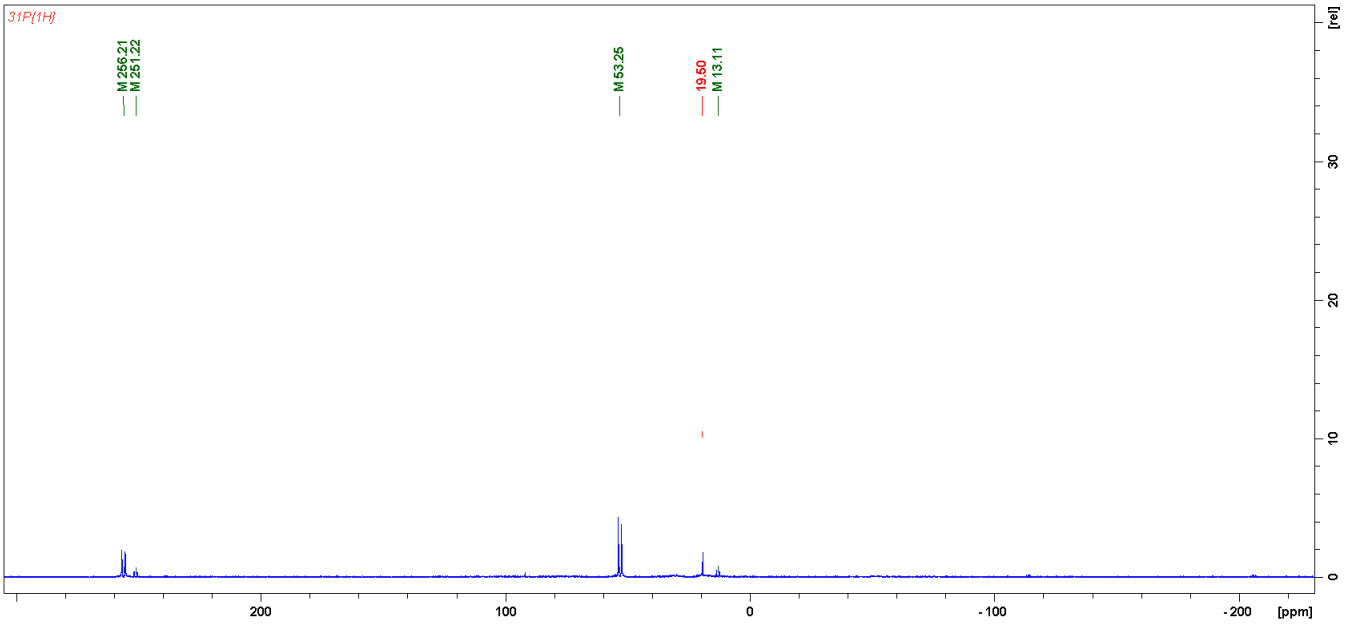


Figure S29. $^{31}P\{^{1}H\}$-NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with cyclohexanecarboxaldehyde.

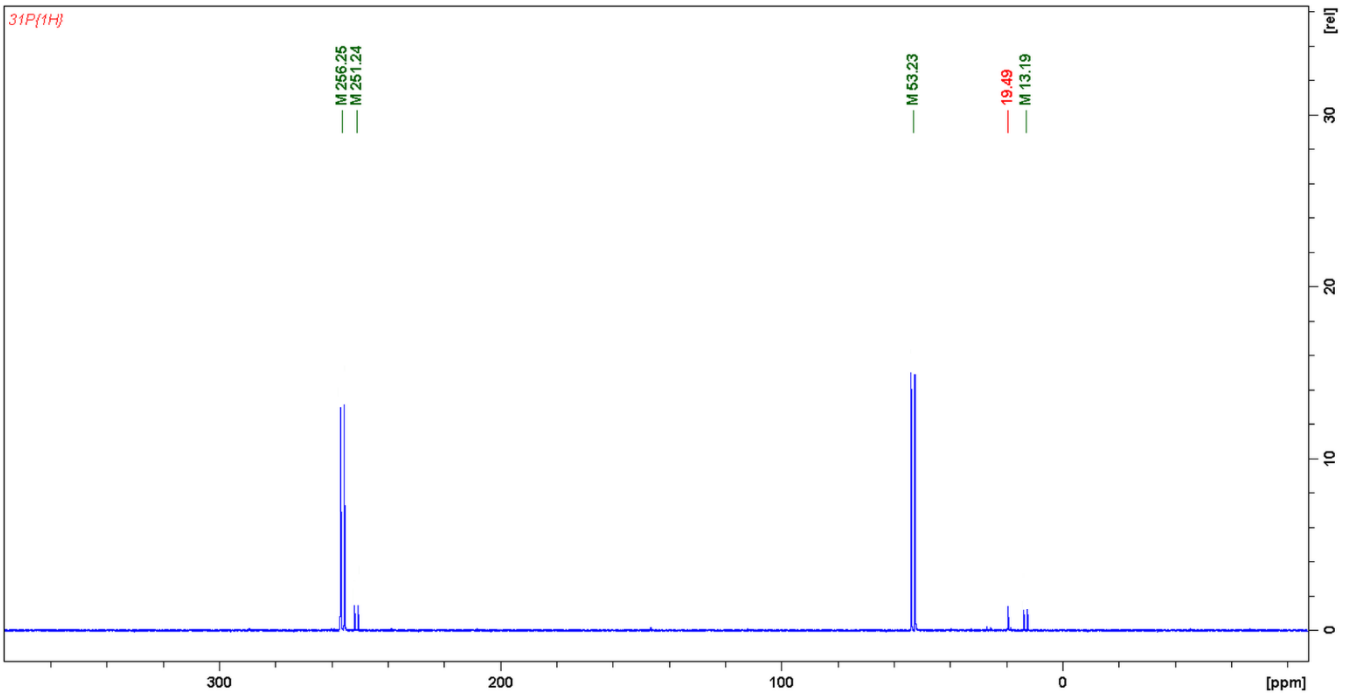


Figure S30. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**).

- 256.25 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2 – *E* isomer;
- 251.24 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2 – *Z* isomer;
- 53.23 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-**P***t*Bu_2 – *E* isomer;
- 13.17 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2 – *Z* isomer;
- 19.49 ppm, (s), *t*Bu_2**P**H;

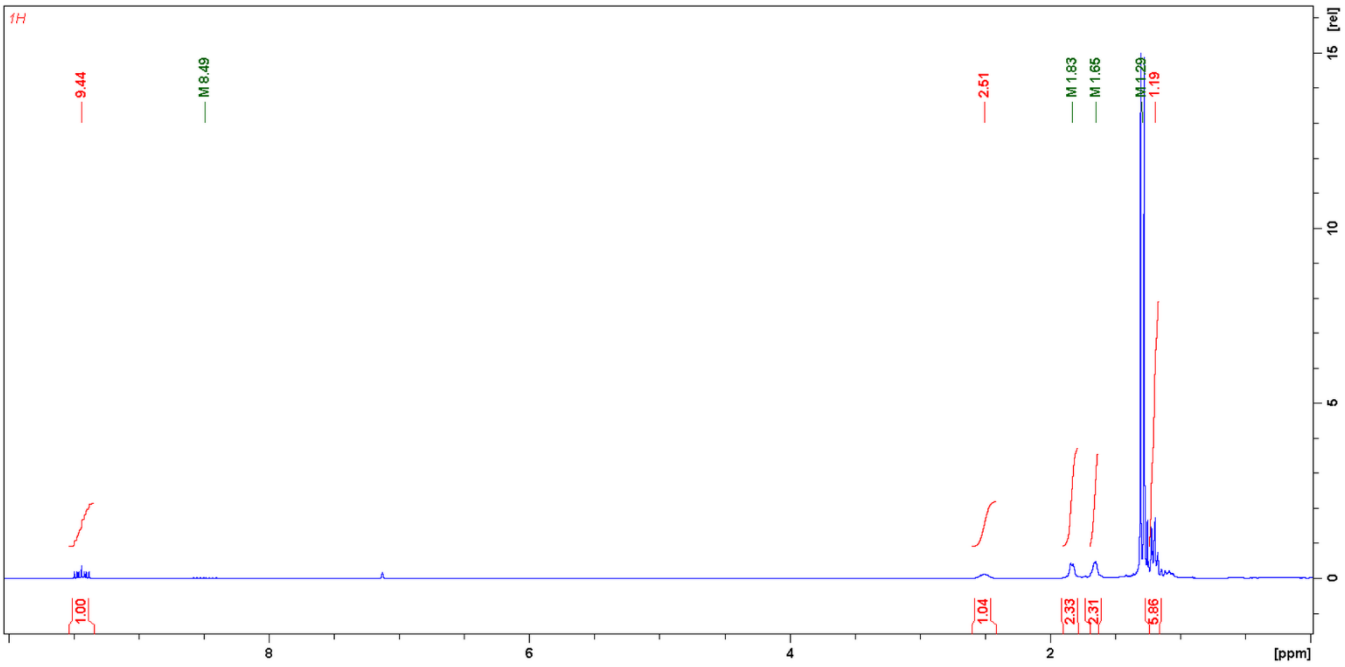


Figure S31. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**).

- 9.44 ppm, (ddd), 1H, $J_{P\text{-}H}$ = 22.7 Hz, $J_{P\text{-}H}$ = 14.2 Hz, $J_{H\text{-}H}$ = 8.4 Hz, {*cyclo*-$(CH_2)_4CH$}(**H**)C=P-P*t*Bu_2 – *E* isomer;
- 8.49 ppm, (ddd), 1H, $J_{P\text{-}H}$ = 31.9 Hz, $J_{P\text{-}H}$ = 21.5 Hz, $J_{H\text{-}H}$ = 10.9 Hz, {*cyclo*-$(CH_2)_4CH$}(**H**)C=P-P*t*Bu_2 – *Z* isomer;
- 2.51 ppm, (broad m), 1H, {*cyclo*-$(CH_2)_4C$**H**}(H)C=P-P*t*Bu_2 – *E* isomer;
- 1.83 ppm, (broad m), 2H, {*cyclo*-$(C$**H**$_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;
- 1.65 ppm, (broad m), 2H, {*cyclo*-$(C$**H**$_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;
- 1.29 ppm, (d), $J_{P\text{-}H}$ = 11.1 Hz, {*cyclo*-$(C$**H**$_2)_4CH$}(H)C=P-P***t*****Bu$_2$** – *E* isomer;
- 1.19 ppm, (broad m), 6H, {*cyclo*-$(C$**H**$_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;

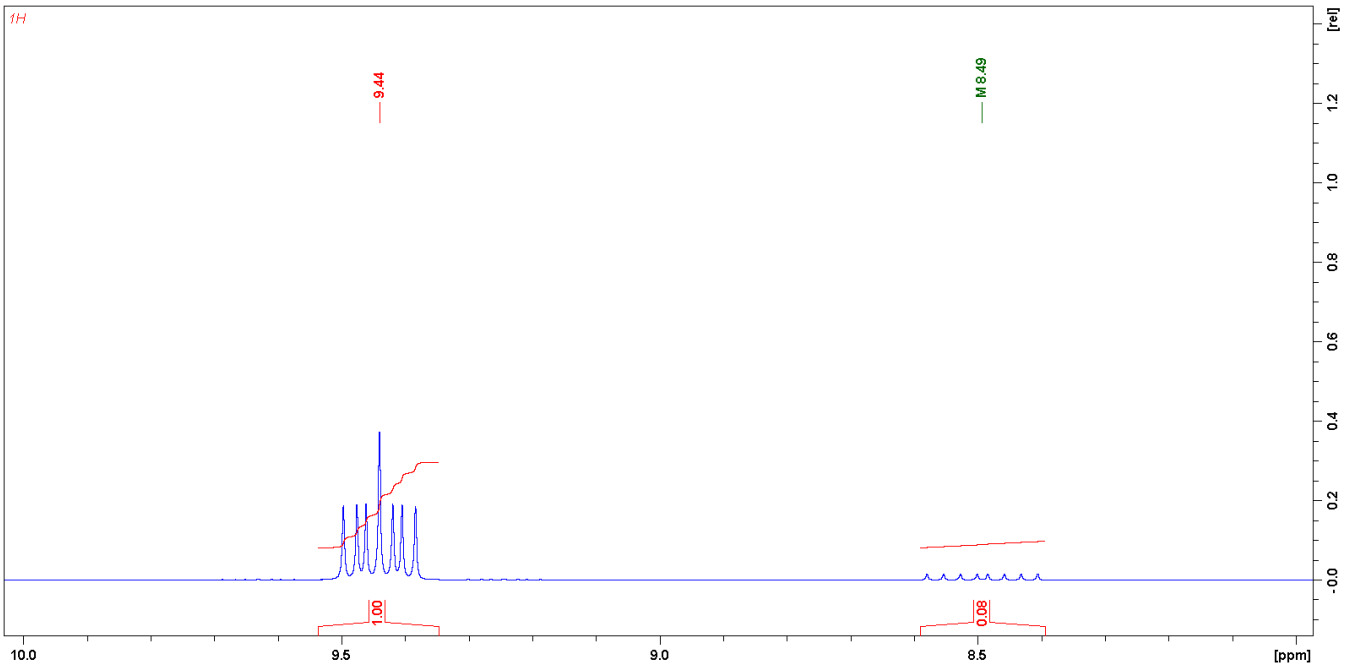


Figure S32. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**) with aldehyde proton of *Z* isomer and with integration (ratio of isomers *E* : *Z* = 93 % : 7 %)

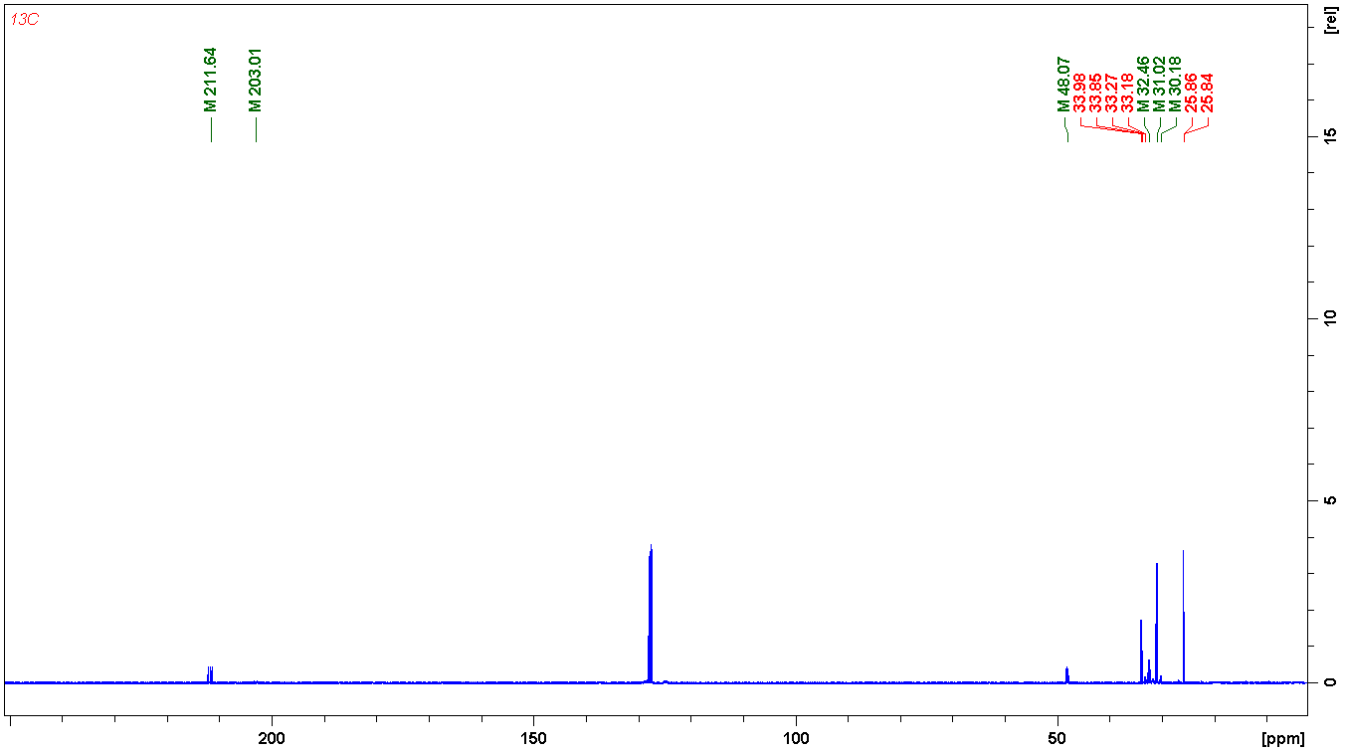


Figure S33. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**).

E isomer:

- 211.64 ppm, (dd), $J_{P\text{-}C}$ = 48.2 Hz, $J_{P\text{-}C}$ = 34.6 Hz, {*cyclo*-$(CH_2)_4CH$}(H)**C**=P-P*t*Bu_2 – *E* isomer;
- 48.07 ppm, (dd), $J_{P\text{-}C}$ = 18.6 Hz, $J_{P\text{-}C}$ = 13.4 Hz, {*cyclo*-$(CH_2)_4$**C**H}(H)C=P-P*t*Bu_2 – *E* isomer;
- 33.98 ppm, (s), {*cyclo*-(**C**$H_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;
- 33.85 ppm, (s), {*cyclo*-(**C**$H_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;
- 32.46 ppm, (dd), $J_{P\text{-}C}$ = 28.2 Hz, $J_{P\text{-}C}$ = 2.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P{**C**$(CH_3)_3$}$_2$ – *E* isomer;
- 31.02 ppm, (dd), $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 5.0 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P{C(**C**$H_3)_3$}$_2$ – *E* isomer;
- 25.86 ppm, (s), {*cyclo*-(**C**$H_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;
- 25.84 ppm, (s), {*cyclo*-(**C**$H_2)_4CH$}(H)C=P-P*t*Bu_2 – *E* isomer;

Z isomer: only few signals are visible

- 203.01 ppm, (dd), $J_{P\text{-}C}$ = 55.7 Hz, $J_{P\text{-}C}$ = 14.2 Hz, {*cyclo*-$(CH_2)_4CH$}(H)**C**=P-P*t*Bu_2 – *Z* isomer;
- 33.27 ppm, (s), {*cyclo*-(**C**$H_2)_4CH$}(H)C=P-P*t*Bu_2 – *Z* isomer;
- 33.18 ppm, (s), {*cyclo*-(**C**$H_2)_4CH$}(H)C=P-P*t*Bu_2 – *Z* isomer;
- 30.18 ppm, (dd), $J_{P\text{-}C}$ = 14.8 Hz, $J_{P\text{-}C}$ = 5.42 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-P{**C**$(CH_3)_3$}$_2$ – *Z* isomer;

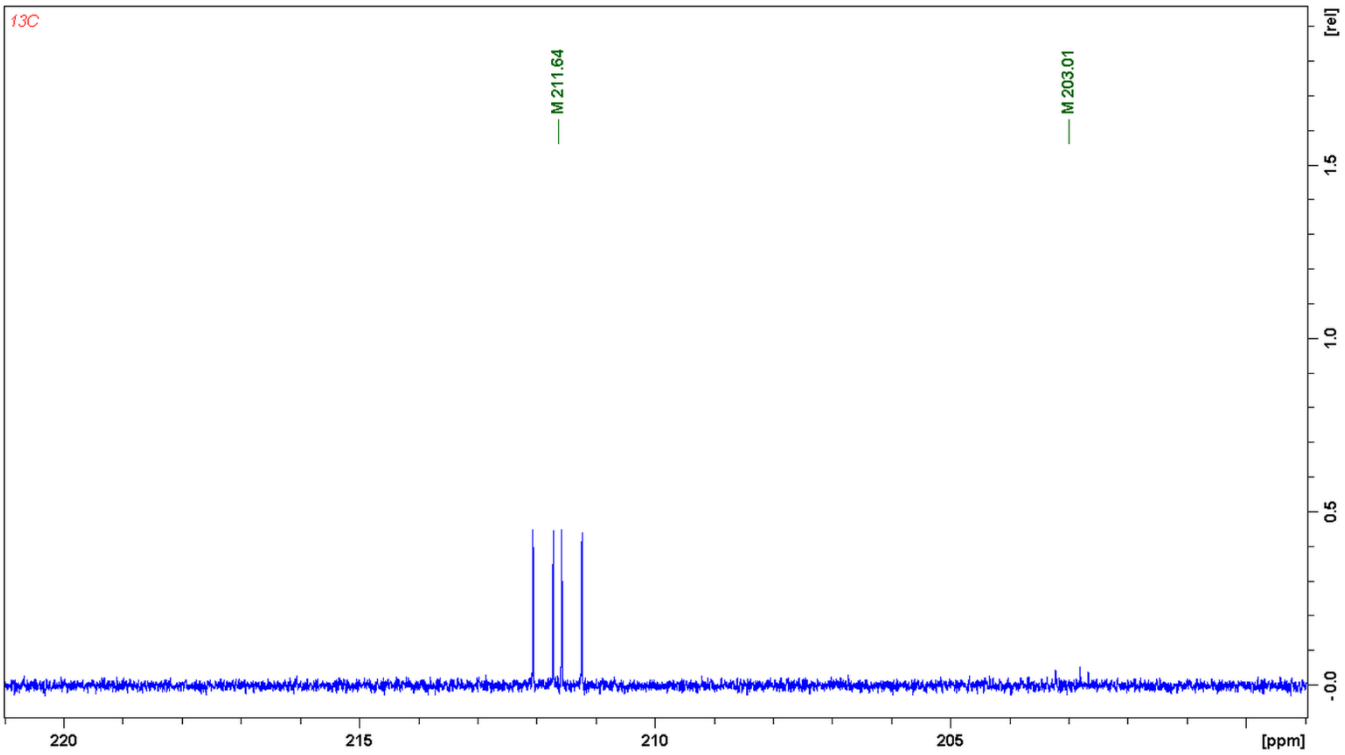


Figure S34. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**) in the range of 220 ppm to 200 ppm.

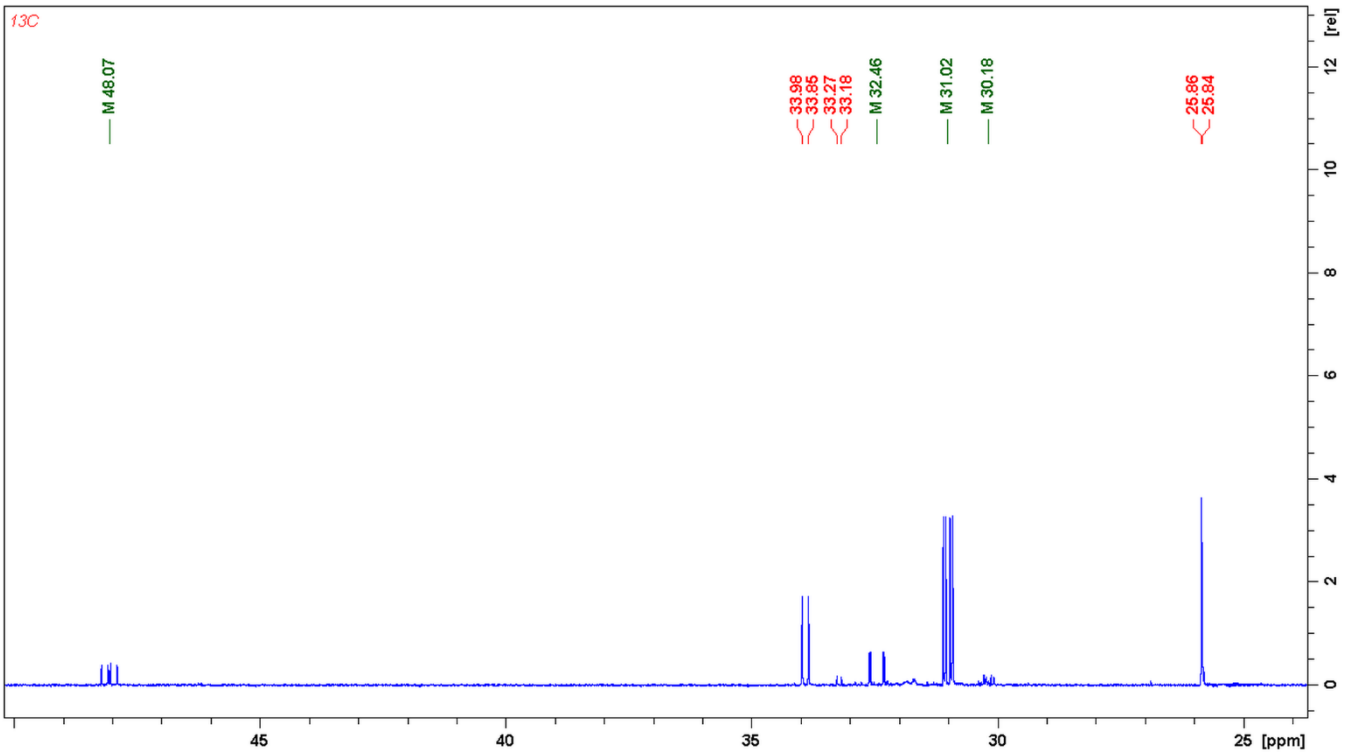


Figure S35. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2 (**4b**) in the range of 50 ppm to 25 ppm.

B.1.13. *p*-Tolualdehyde

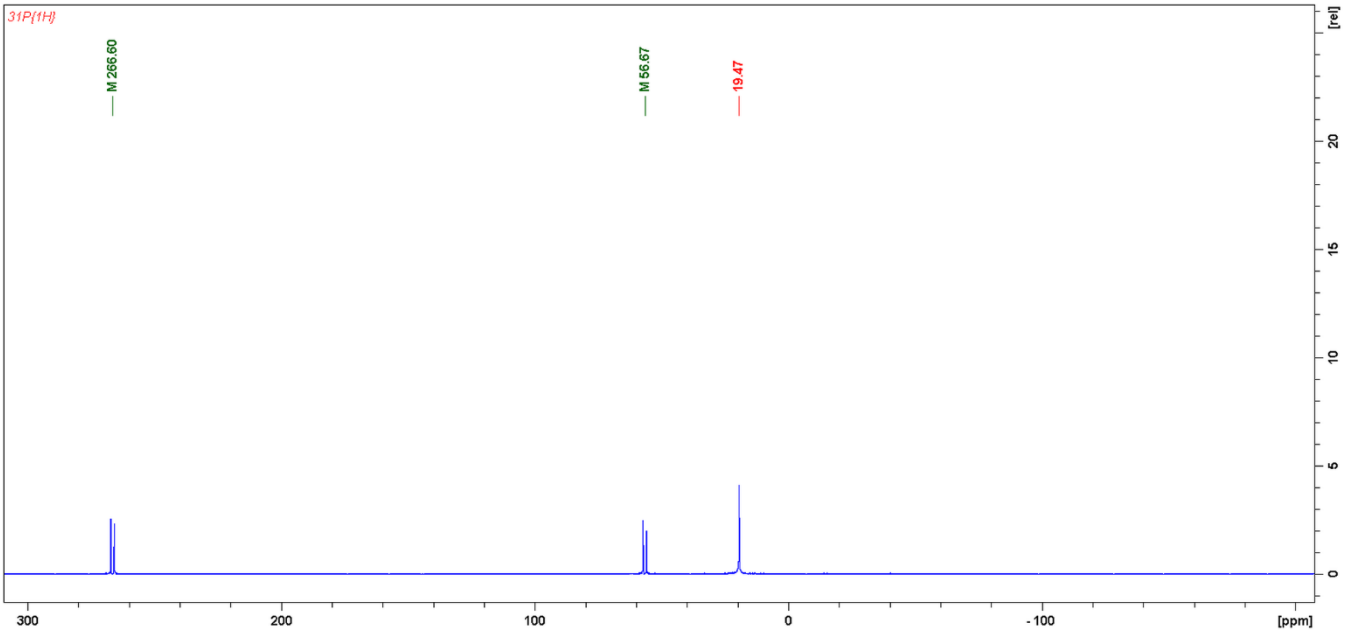


Figure S36. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with *p*-Tolualdehyde.

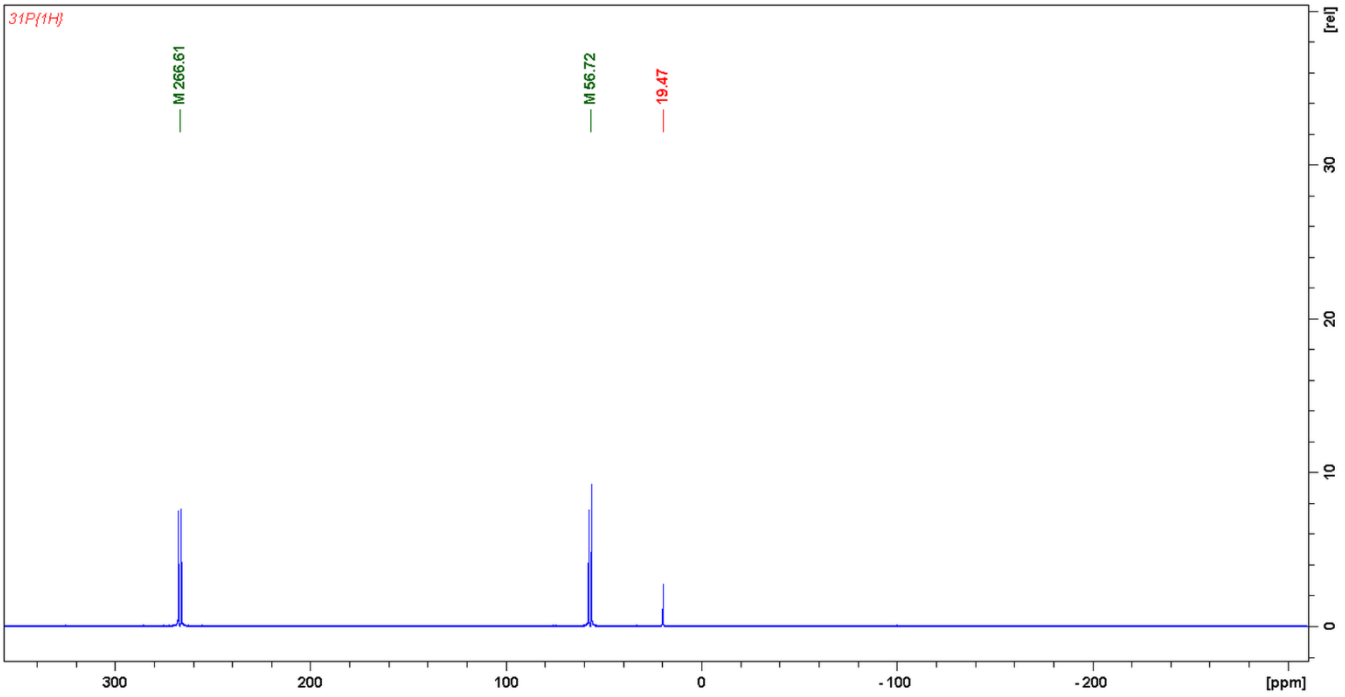


Figure S37. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**).

Visible only one *E* isomer:

- 266.61 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=**P**-P*t*Bu$_2$;
- 56.72 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=P-**P***t*Bu$_2$;

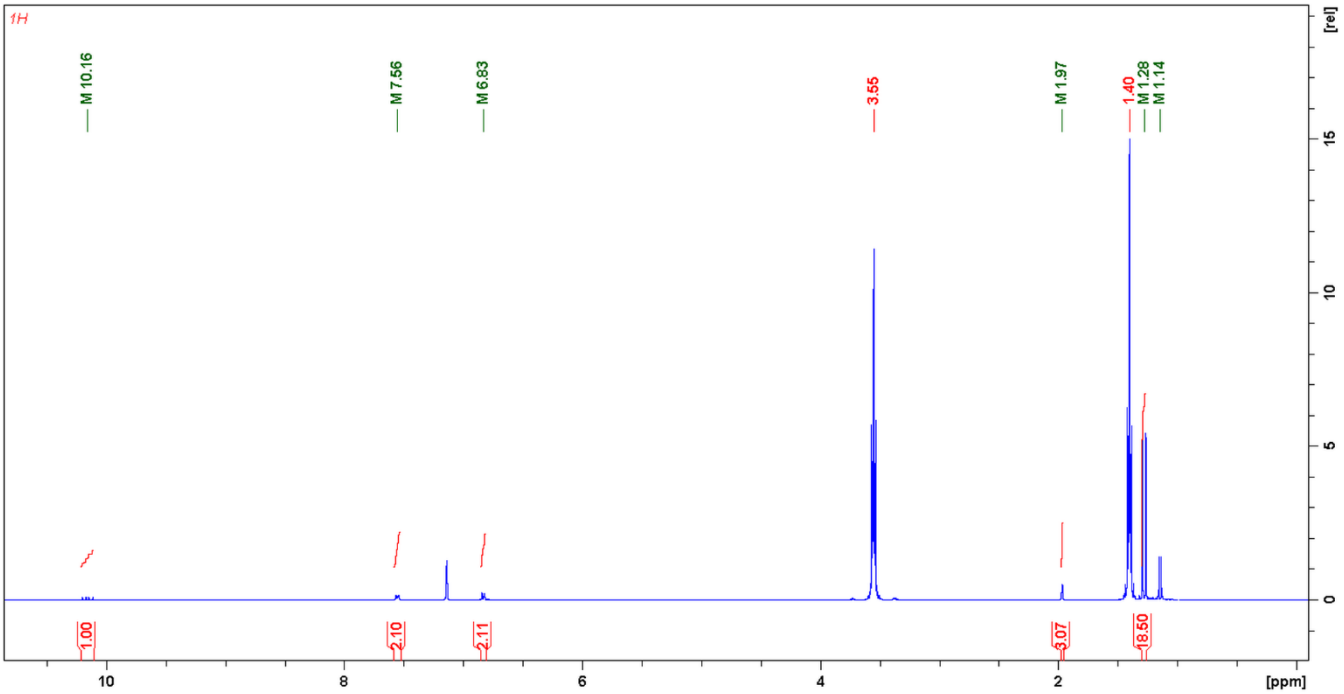


Figure S38. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**).

Visible only one *E* isomer:

- 10.16 ppm, (dd), 1H, $J_{P\text{-}H}$ = 22.7 Hz, $J_{P\text{-}H}$ = 13.6 Hz (*p*-Me-Ph)(**H**)C=P-P*t*Bu$_2$;
- 7.56 ppm, (dd), $J_{P\text{-}H}$ = 7.6 Hz, $J_{P\text{-}H}$ = 2.7 Hz (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$ (*o*-H$_{Ar}$);
- 6.83 ppm, (d), $J_{P\text{-}H}$ = 7.9 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$ (*m*-H$_{Ar}$);
- 1.97 ppm, (d), $J_{P\text{-}H}$ = 1.9 Hz, (*p*-**Me**-Ph)(H)C=P-P*t*Bu$_2$;
- 1.28 ppm, (d), $J_{P\text{-}H}$ = 11.1 Hz, (*p*-Me-Ph)(H)C=P-P***t*Bu$_2$**;

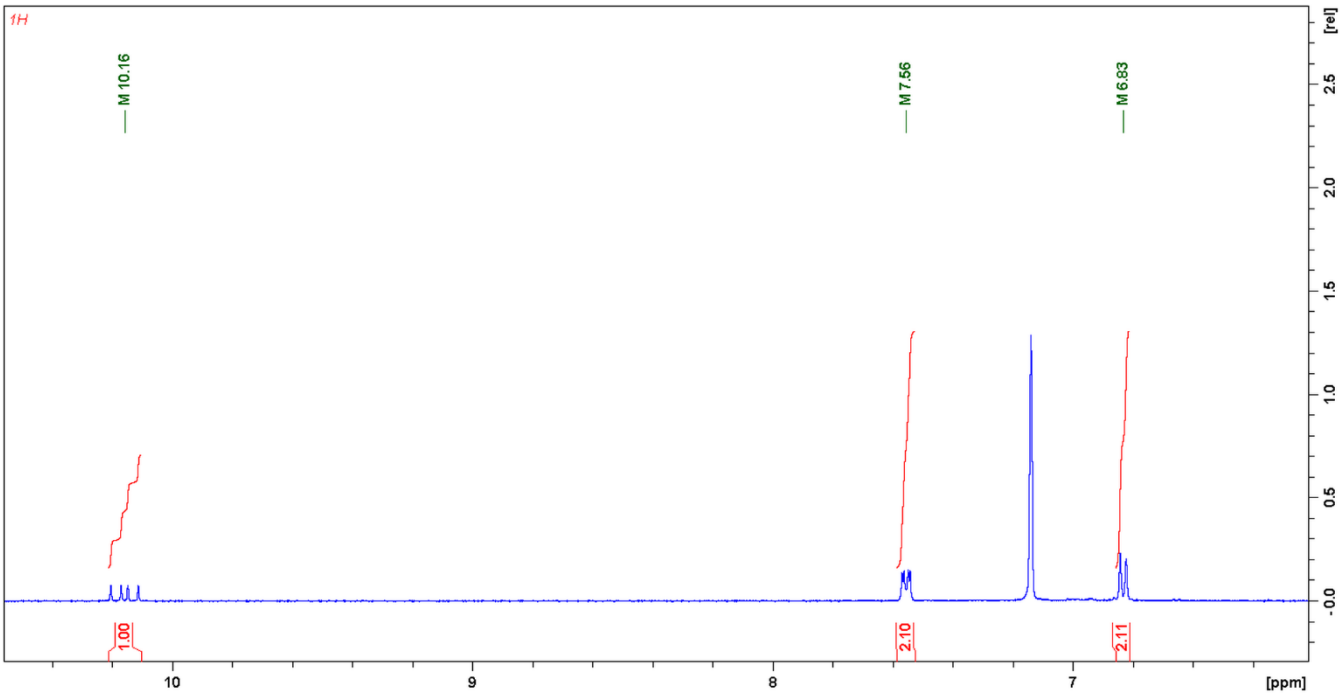


Figure S39. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**) in the range from 10.5 ppm to 6 ppm.

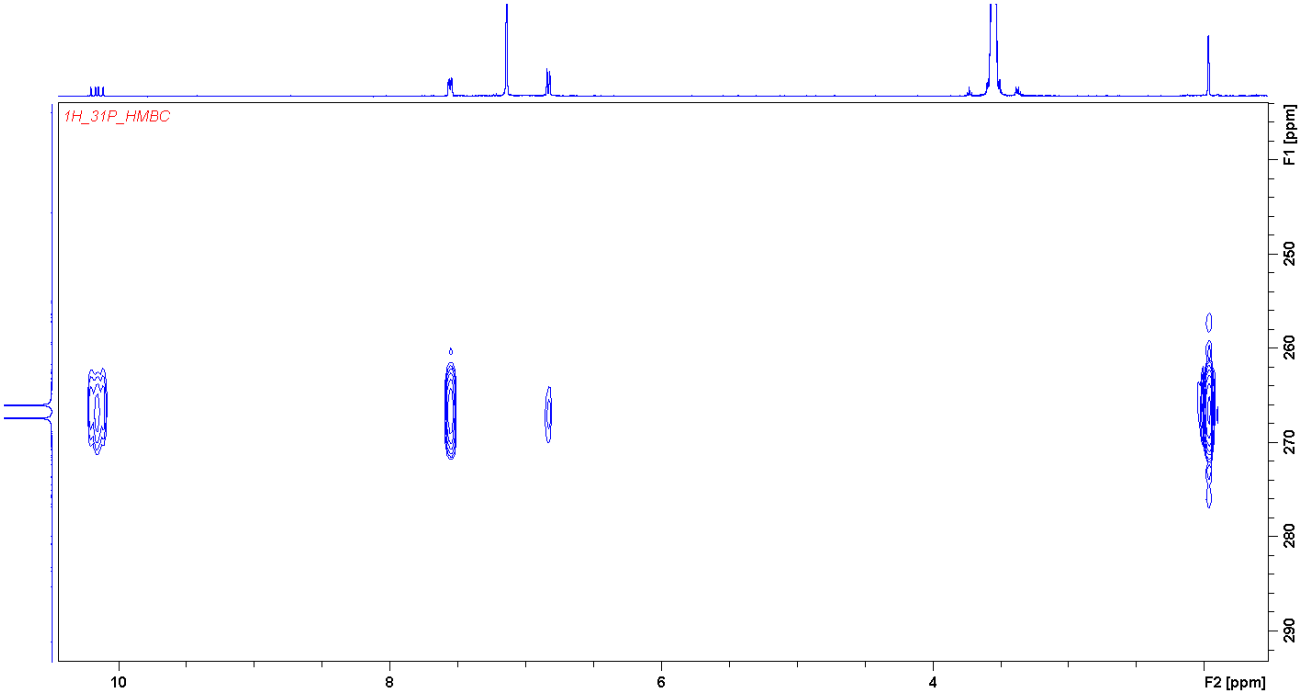


Figure S40. ^{31}P{^{1}H}/^{1}H-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**).

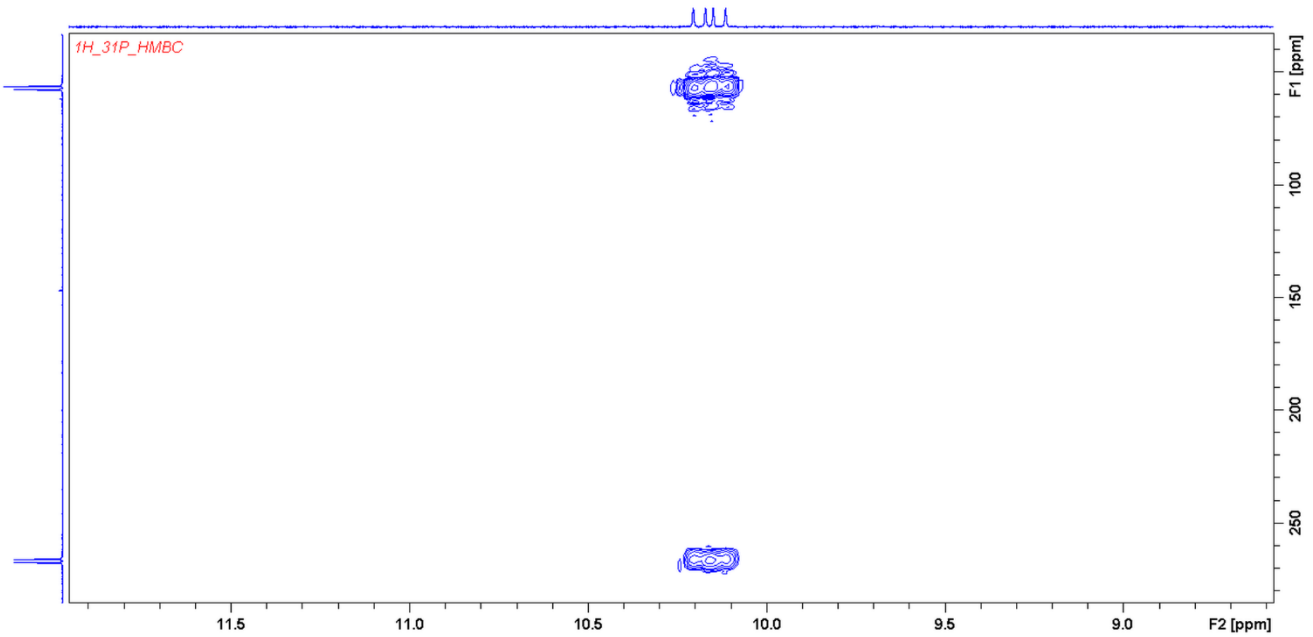


Figure S41. ^{31}P{^{1}H}/^{1}H-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**).

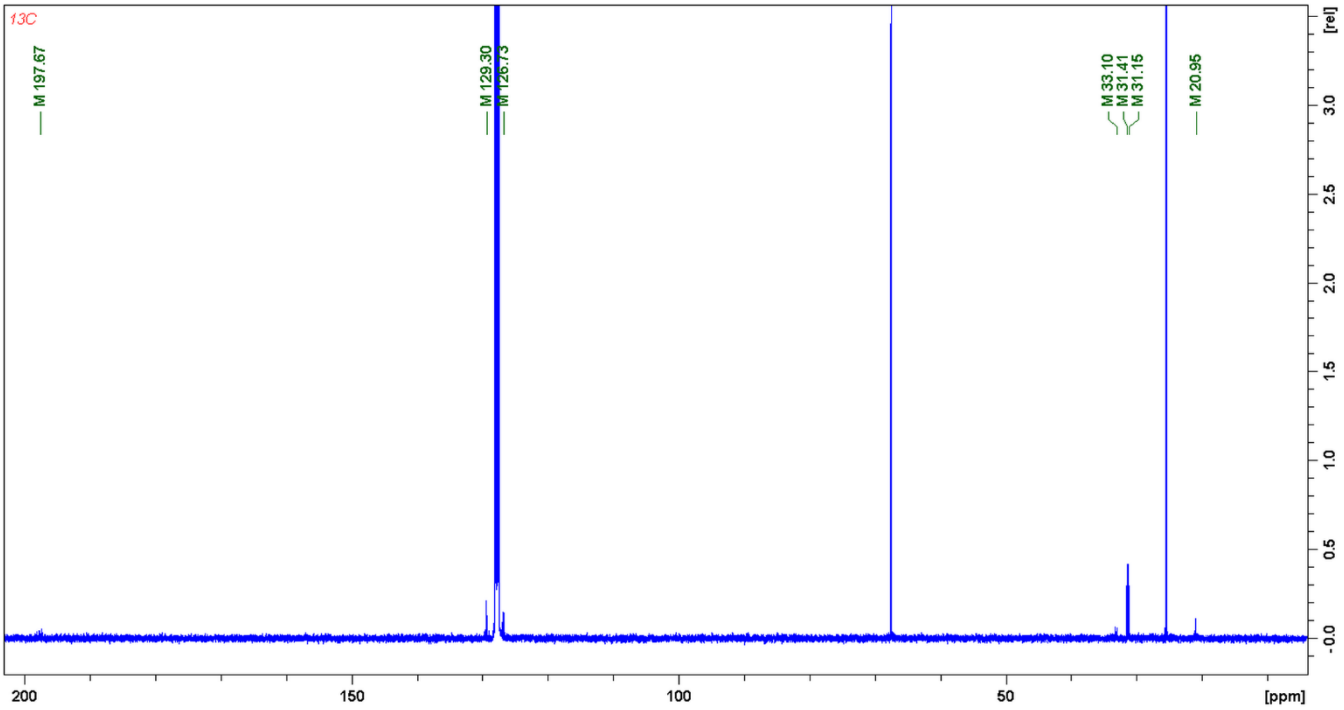


Figure S42. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**).

Visible only *E* isomer:

- 197.67 ppm, (dd), $J_{P\text{-}C}$ = 45.1 Hz, $J_{P\text{-}C}$ = 39.2 Hz, (*p*-Me-Ph)(H)**C**=P-P*t*Bu$_2$;
- 129.30 ppm, (d), $J_{P\text{-}C}$ = 2.6 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$ (*m*-C_{Ar});
- 126.73 ppm, (d), $J_{P\text{-}C}$ = 19.5 Hz, (*p*-Me-**Ph**)(H)C=P-P*t*Bu$_2$ (*o*-C_{Ar});
- 33.10 ppm, (dd), $J_{P\text{-}C}$ = 27.7 Hz, $J_{P\text{-}C}$ = 2.5 Hz, (*p*-Me-Ph)(H)C=P-P{**C**$(CH_3)_3$}$_2$;
- 31.15 ppm, (dd), $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 5.1 Hz, (*p*-Me-Ph)(H)C=P-P{C(**C**$H_3)_3$}$_2$;
- 20.95 ppm, (d), $J_{P\text{-}C}$ = 1.0 Hz, (*p*-**Me**-Ph)(H)C=P-P*t*Bu$_2$;

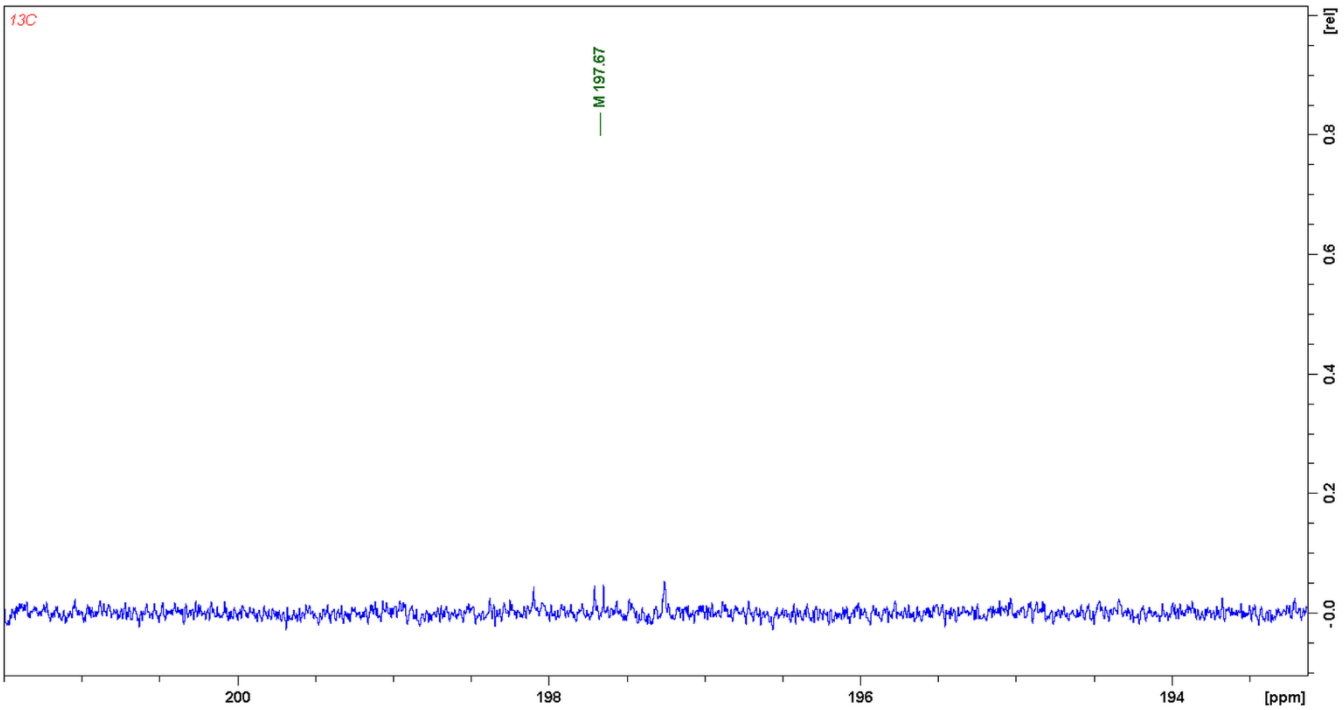


Figure S43. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**) in the range from 202 ppm to 192 ppm.

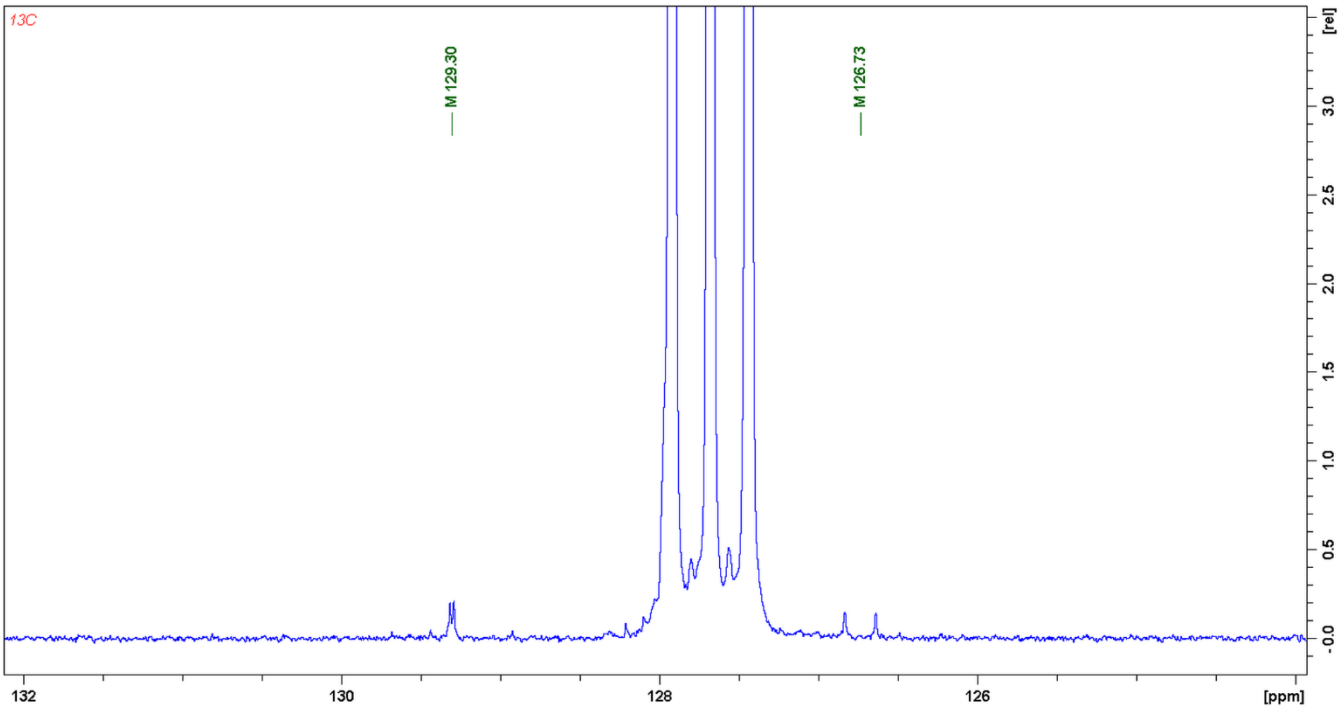


Figure S44. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**) in the range from 132 ppm to 124 ppm.

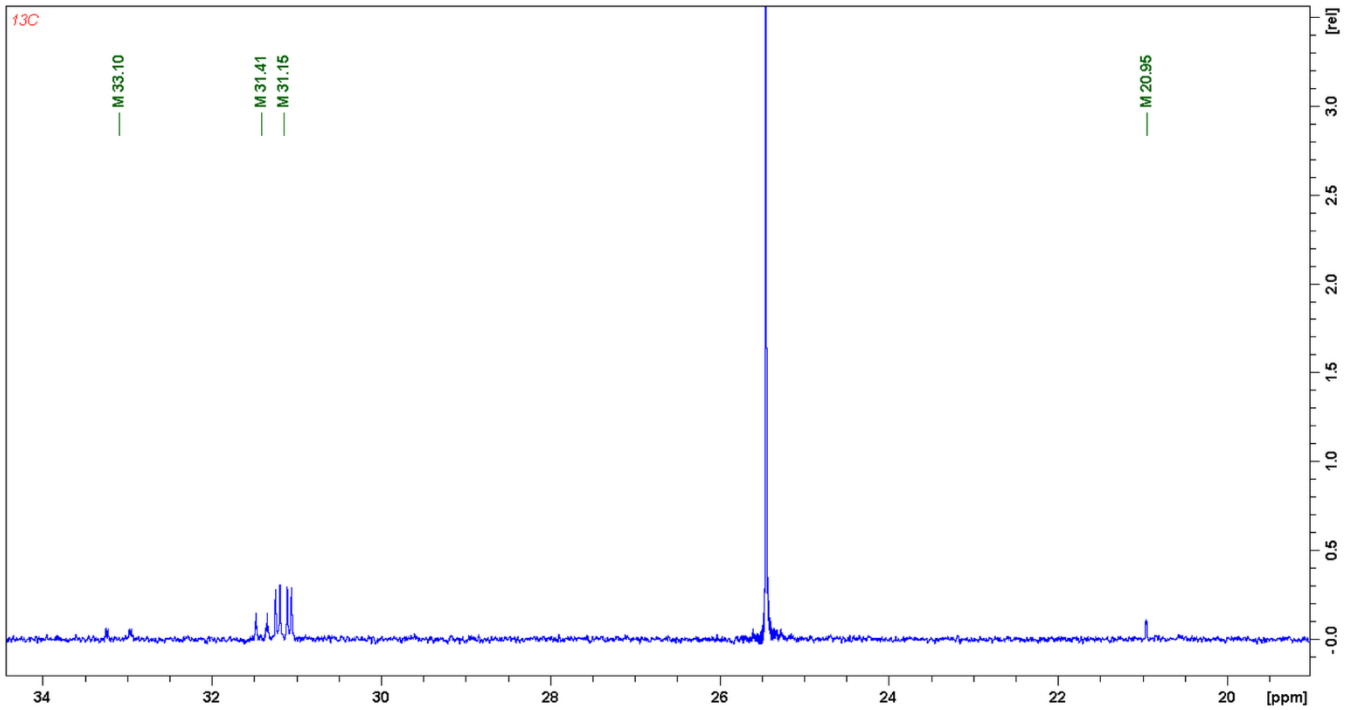


Figure S45. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (*p*-Me-Ph)(H)C=P-P*t*Bu$_2$ (**4c**) in the range from 34 ppm to 20 ppm.

B.1.14. 4-(dimethylamino)benzaldehyde

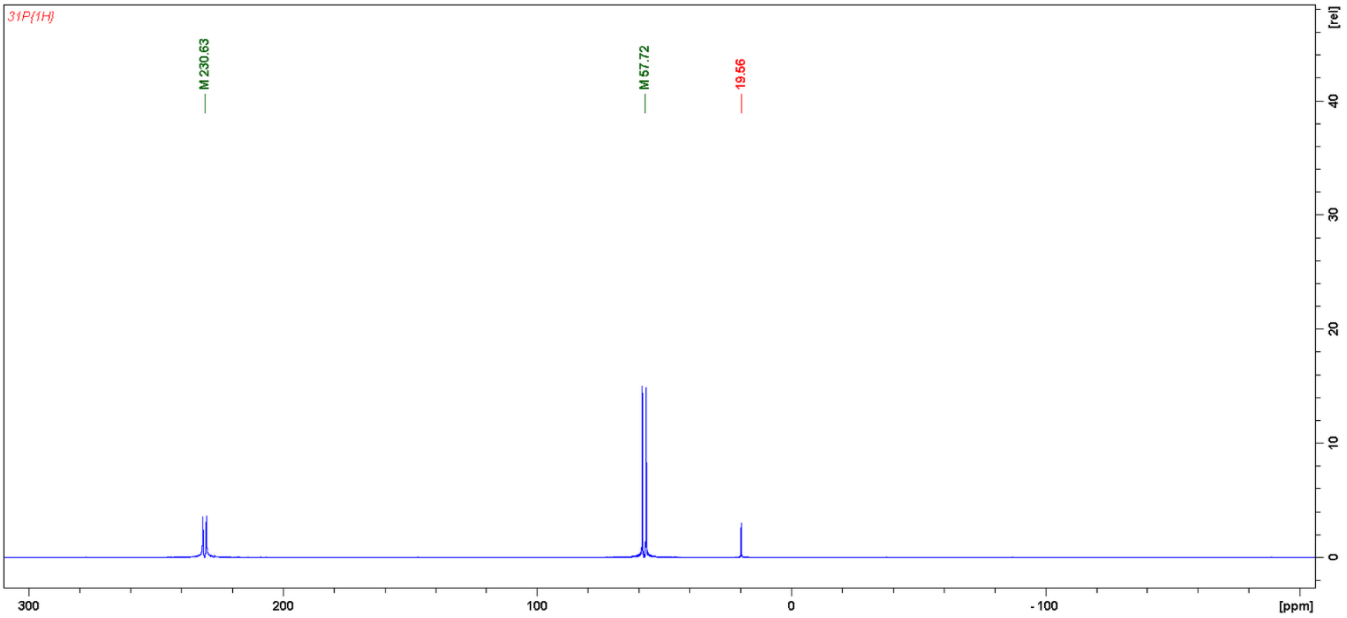


Figure S46. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of the reaction mixture conducted 24 hours after starting the reaction of **1** with 4-(dimethylamino)benzaldehyde.

- 230.63 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, {4-(Me)$_2$N-Ph}(H)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 57.72 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, {4-(Me)$_2$N-Ph}(H)C=P-**P***t*Bu$_2$ – *E* isomer;
- 19.56 ppm, (s), *t*Bu$_2$PH;

B.1.15. Biphenyl-4-carboxaldehyde

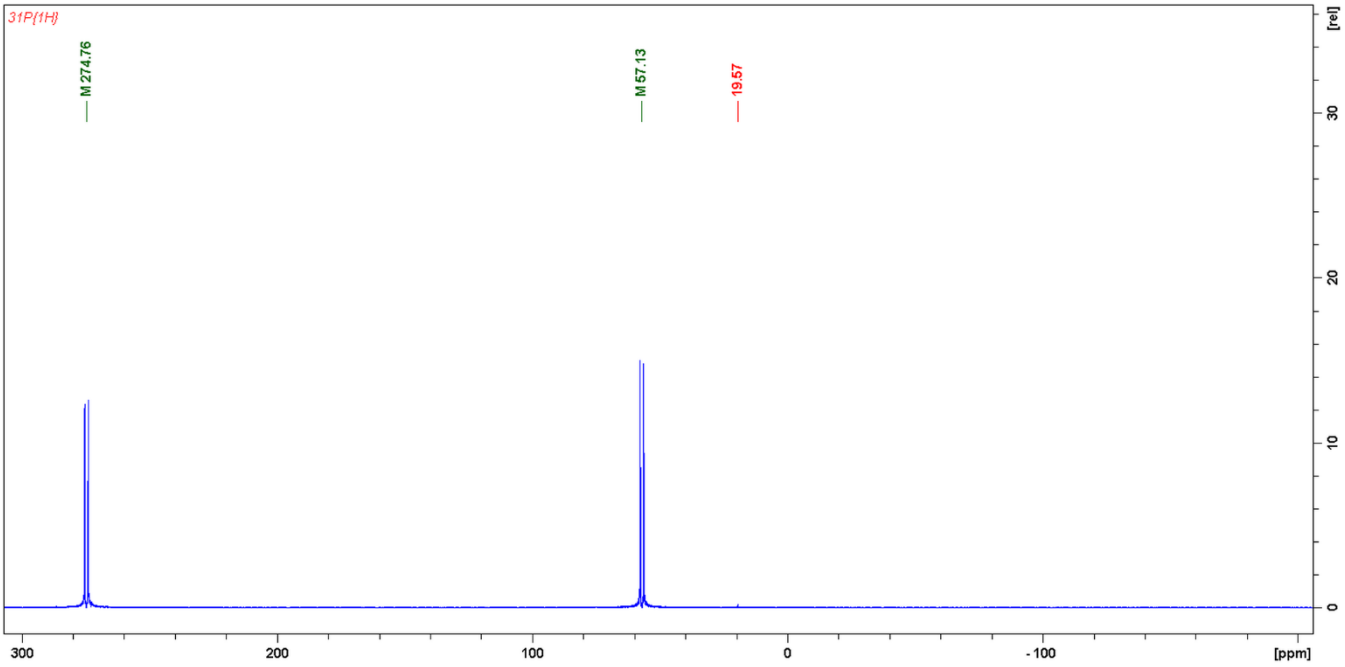


Figure S47. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture conducted 24 hours after starting the reaction of **1** with biphenyl-4-carboxaldehyde.

- 274.76 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, PhPh(H)C=**P**-P*t*Bu$_2$;
- 57.13 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, PhPh(H)C=P-**P***t*Bu$_2$;
- 19.57 ppm, (s), *t*Bu$_2$PH;

B.2. Phospha-Peterson reaction of *t*Bu$_2$P-P(SiMe$_3$)Li·3THF (2) with selected ketones and aldehydes

B.2.1. Benzophenone

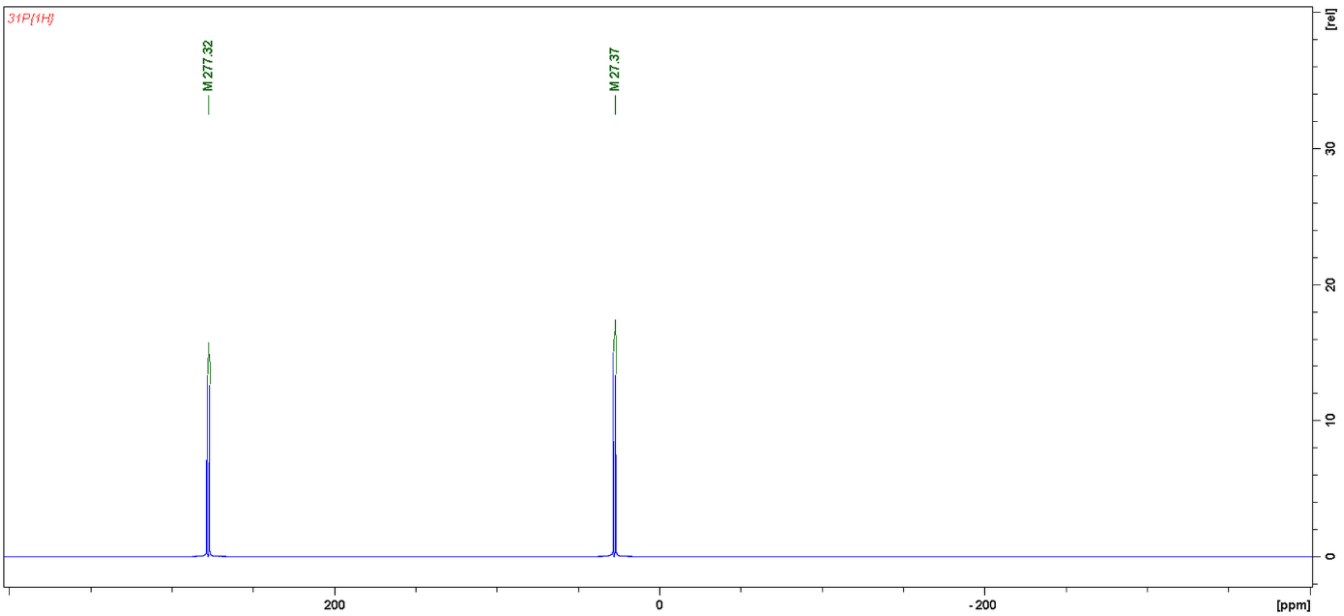


Figure S48. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C$=P-P*t*Bu$_2$ (**3a**).

- 277.32 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Ph)_2C$=**P**-P*t*Bu$_2$;
- 27.37 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Ph)_2C$=P-**P***t*Bu$_2$;

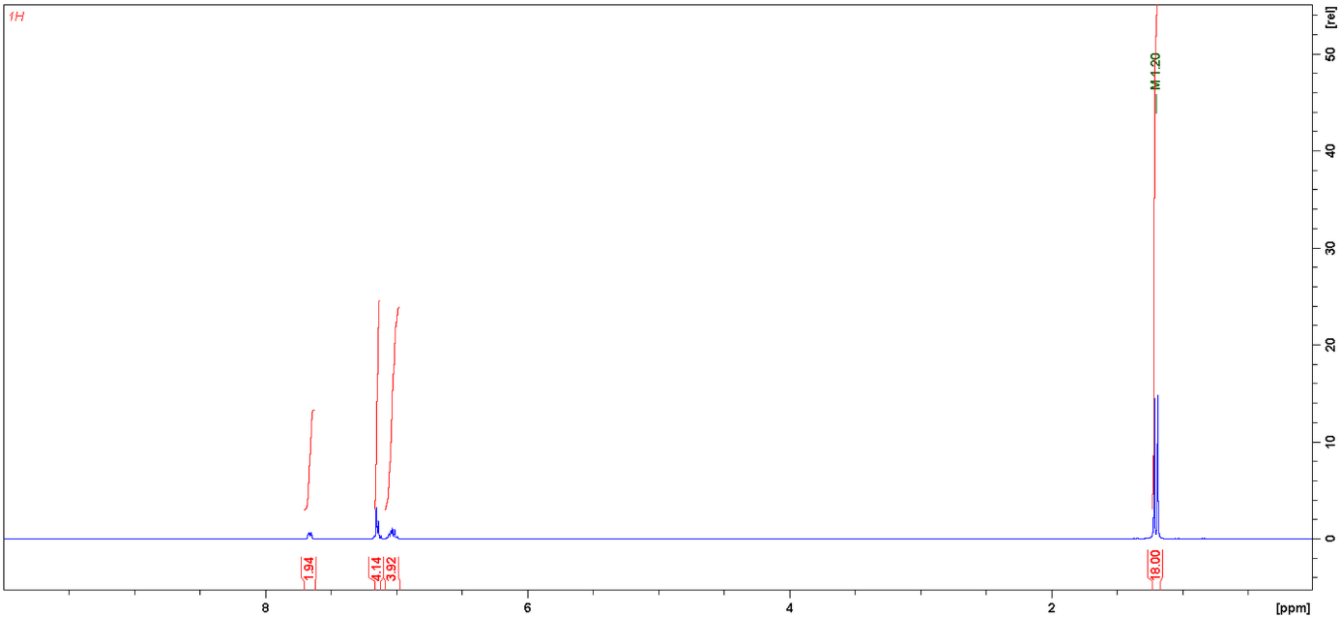


Figure S49. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C$=P-P*t*Bu$_2$ (**3a**).

- 7.70 ppm – 7.00 ppm, 10H, (**Ph**)$_2$C=P-P*t*Bu$_2$;
- 1.20 ppm, (d), $J_{P\text{-}H}$ = 10.9 Hz, 18H, $(Ph)_2C$=P-P***t*Bu**$_2$;

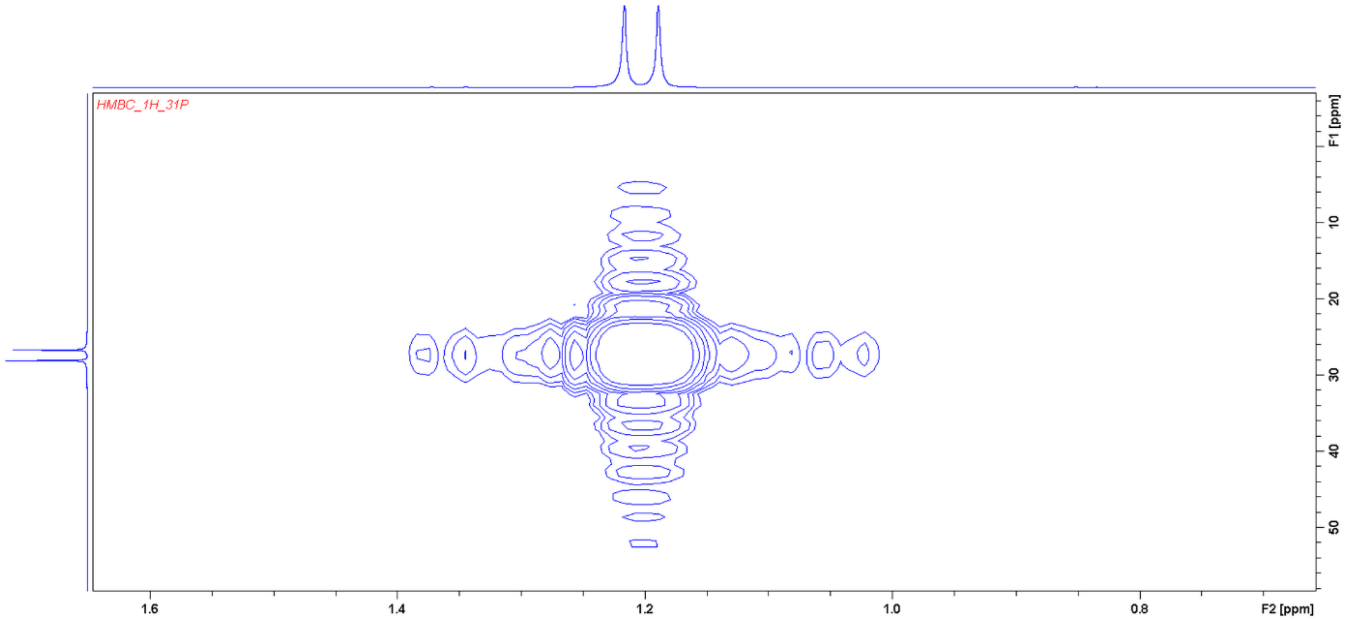


Figure S50. $^{31}P\{^{1}H\}/^{1}H$-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) (correlation of *tert*-butyl groups).

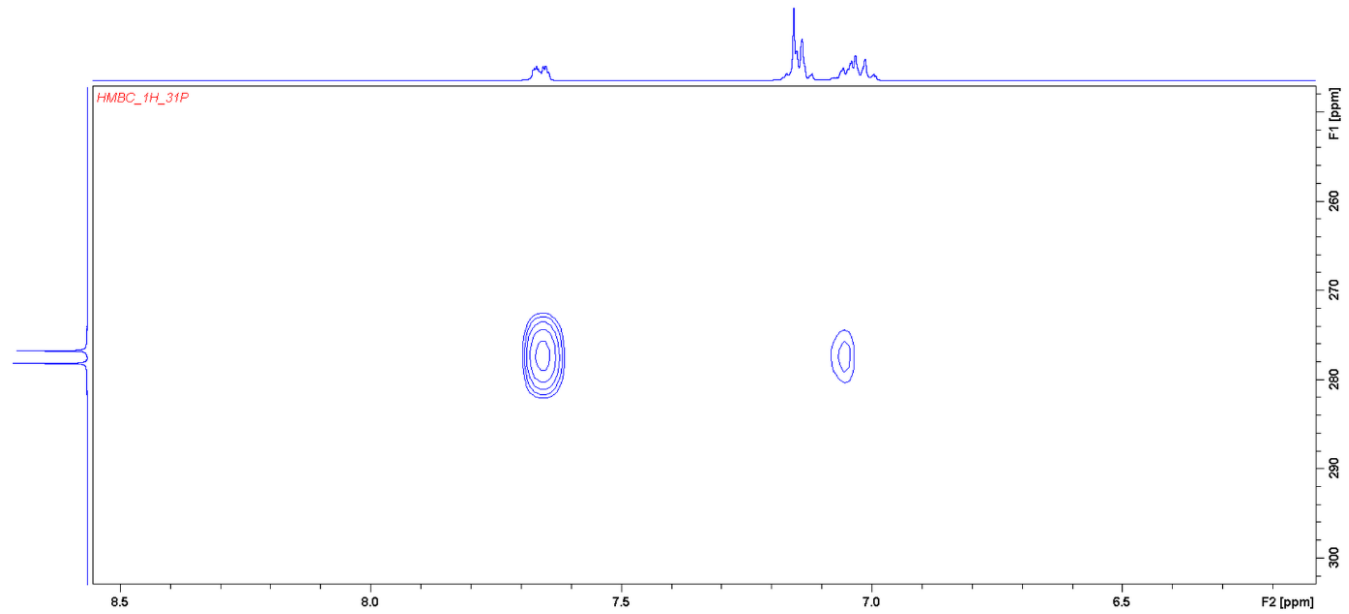


Figure S51. $^{31}P\{^{1}H\}/^{1}H$-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) (correlation of aromatic protons).

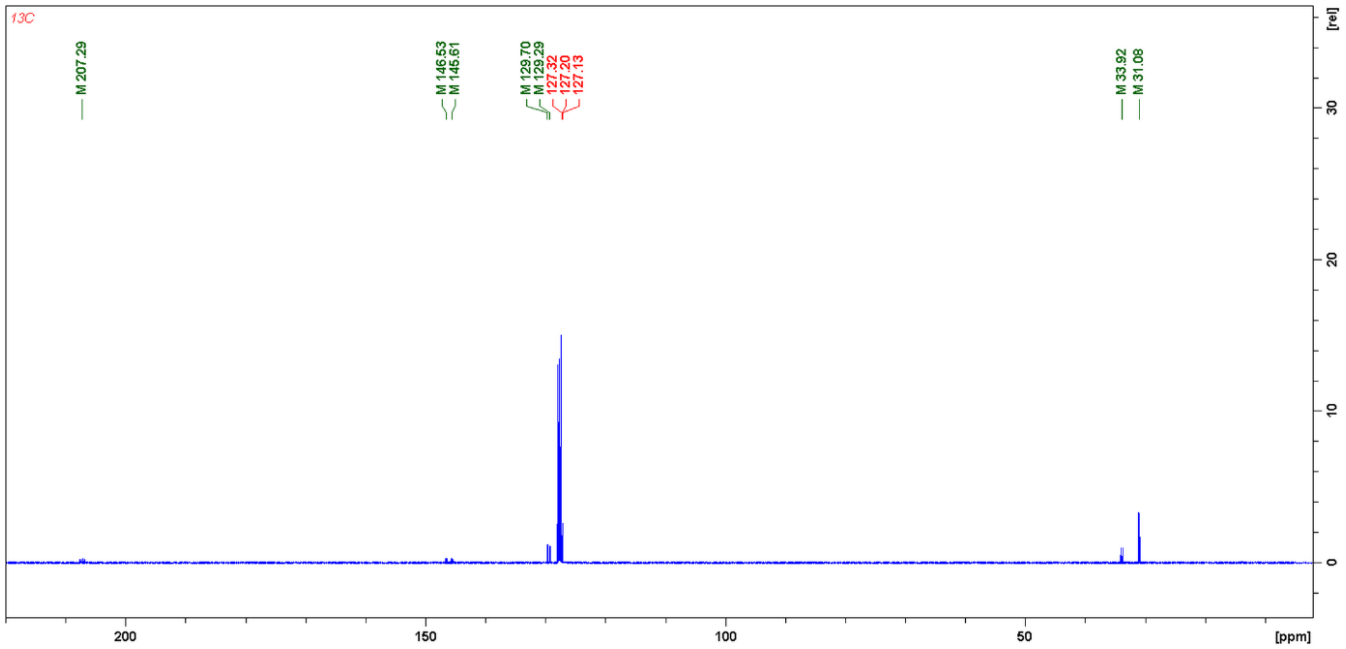


Figure S52. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**).

- 207.29 ppm, (dd), $J_{P\text{-}C}$ = 54.5 Hz, $J_{P\text{-}C}$ = 16.8 Hz, $(Ph)_2\mathbf{C}{=}P\text{-}PtBu_2$;
- 146.53 ppm, (dd), $J_{P\text{-}C}$ = 23.2 Hz, $J_{P\text{-}C}$ = 4.3 Hz, $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (i-C_{Ar});
- 145.61 ppm, (dd), $J_{P\text{-}C}$ = 13.9 Hz, $J_{P\text{-}C}$ = 5.9 Hz, $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (i-C_{Ar});
- 129.70 ppm, (dd), $J_{P\text{-}C}$ = 10.6 Hz, $J_{P\text{-}C}$ = 6.5 Hz, $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (o-C_{Ar});
- 129.29 ppm, (d), $J_{P\text{-}C}$ = 4.8 Hz, $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (o-C_{Ar});
- 128.04 ppm, (d), $J_{P\text{-}C}$ = 1.1 Hz, $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (p-C_{Ar});
- 127.32 ppm, (s), $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (m-C_{Ar});
- 127.20 ppm, (s), $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (p-C_{Ar});
- 127.13 ppm, (s), $(\mathbf{Ph})_2C{=}P\text{-}PtBu_2$ (m-C_{Ar});
- 33.92 ppm, (dd), $J_{P\text{-}C}$ = 30.1 Hz, $J_{P\text{-}C}$ = 4.3 Hz, - $(Ph)_2C{=}P\text{-}P\{\mathbf{C}(Me_3)\}_2$;
- 31.08 ppm, (dd), $J_{P\text{-}C}$ = 14.4 Hz, $J_{P\text{-}C}$ = 5.4 Hz, $(Ph)_2C{=}P\text{-}P\{\mathbf{C}(\mathbf{Me}_3)\}_2$;

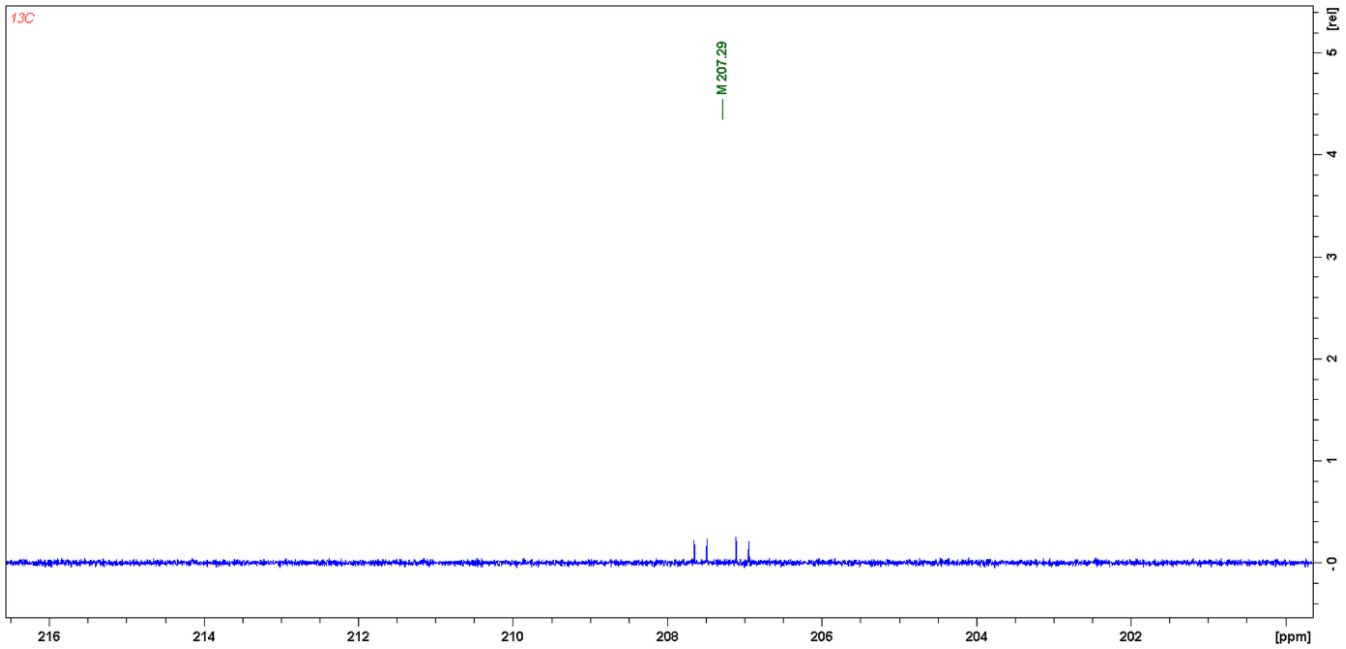


Figure S53. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) in the range from 216 to 201 ppm.

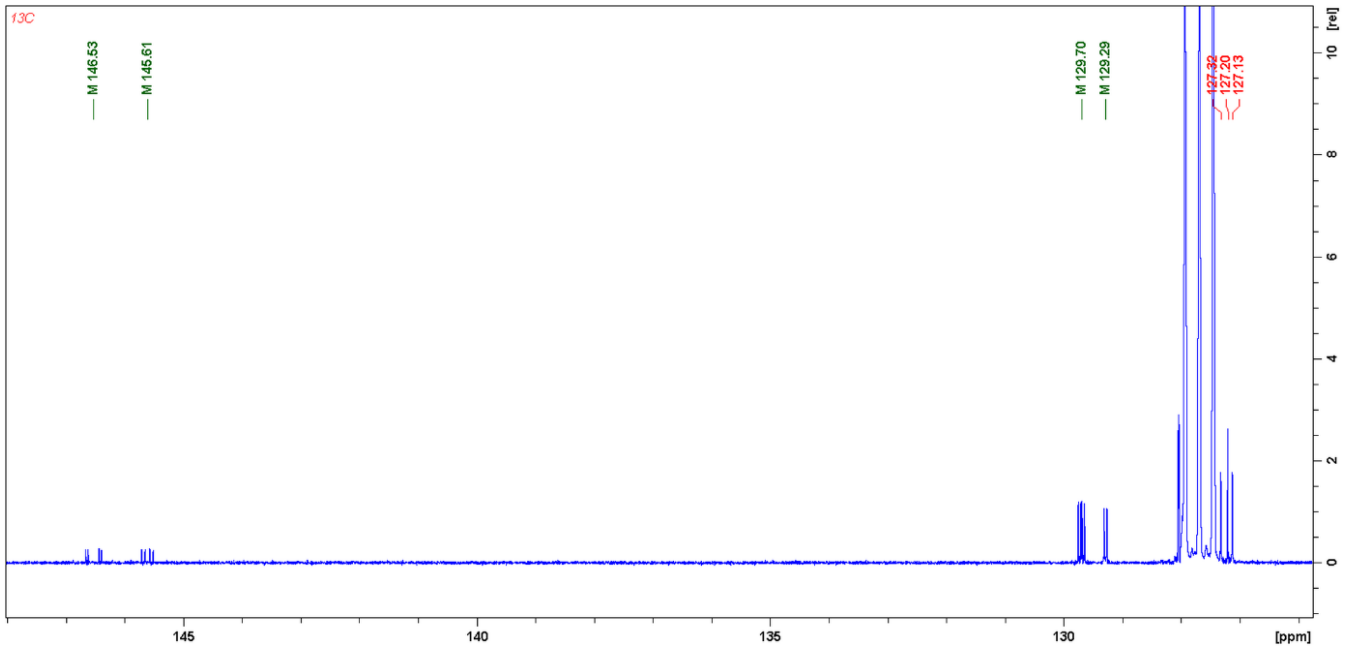


Figure S54. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) in the range from 146 to 125 ppm.

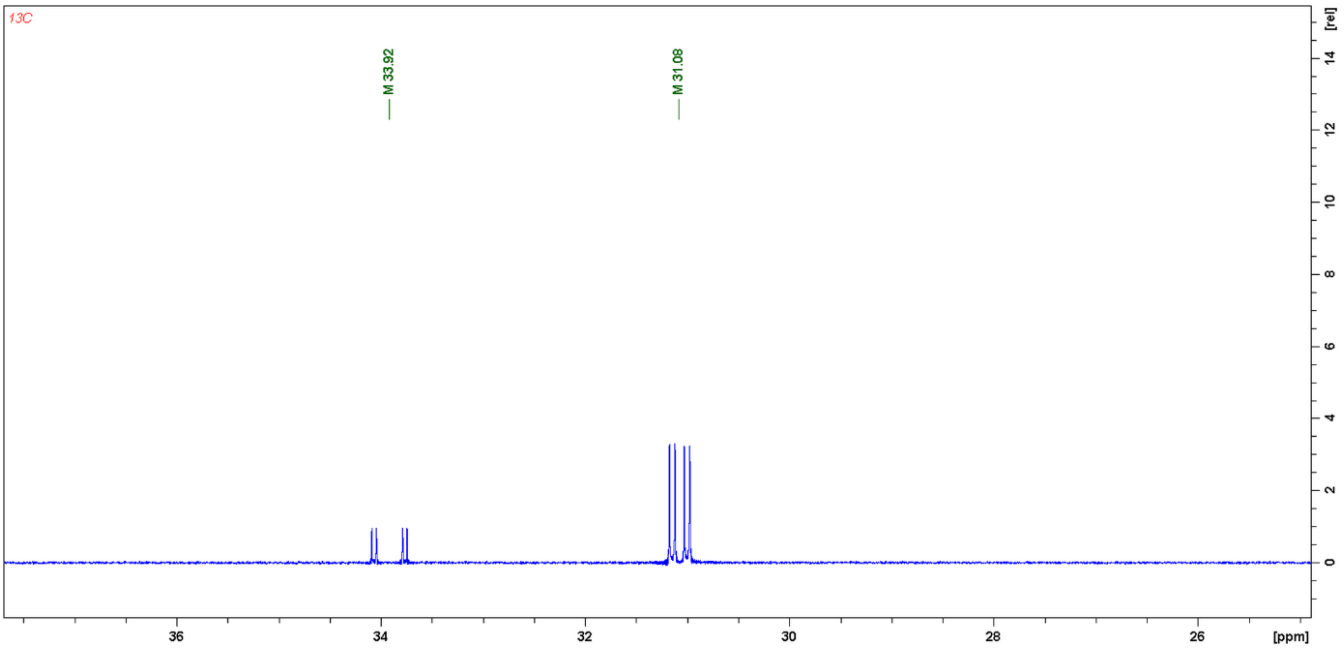


Figure S55. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) in the range from 37 to 25 ppm.

B.2.2. 9-fluorenone

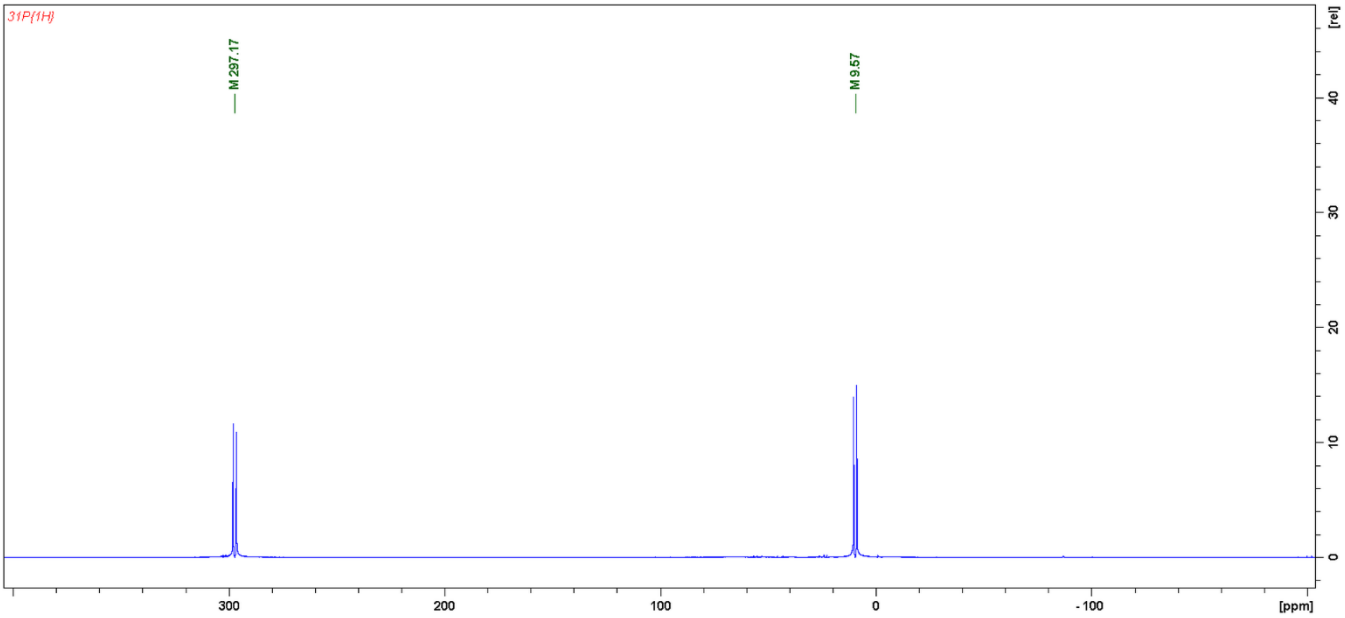


Figure S56. $^{31}P\{^{1}H\}$ NMR(400 MHz, Toluene-d_8, 298 K) spectrum isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**).

- 297.17 ppm, (d), $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=**P**-P*t*Bu$_2$;
- 9.57 ppm, (d), $J_{P\text{-}P}$ = 228.4 Hz, (fluorenyl)C=**P**-P*t*Bu$_2$;

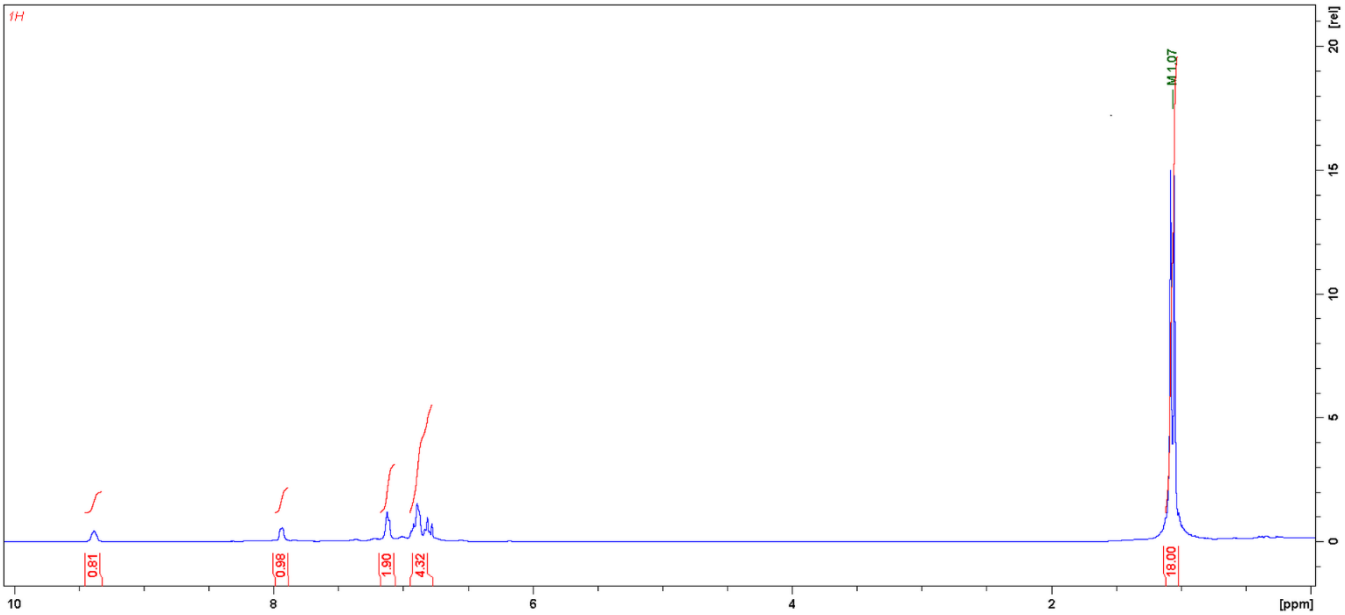


Figure S57. ^{1}H NMR (400 MHz, Toluene-d_8, 298 K) spectrum of isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**).

- 9.43 – 6.76 ppm, aromatic protons of fluorenyl;
- 1.07 ppm, (d), $J_{P\text{-}H}$ = 11.9 Hz, (fluorenyl)C=P-P***t*Bu**$_2$;

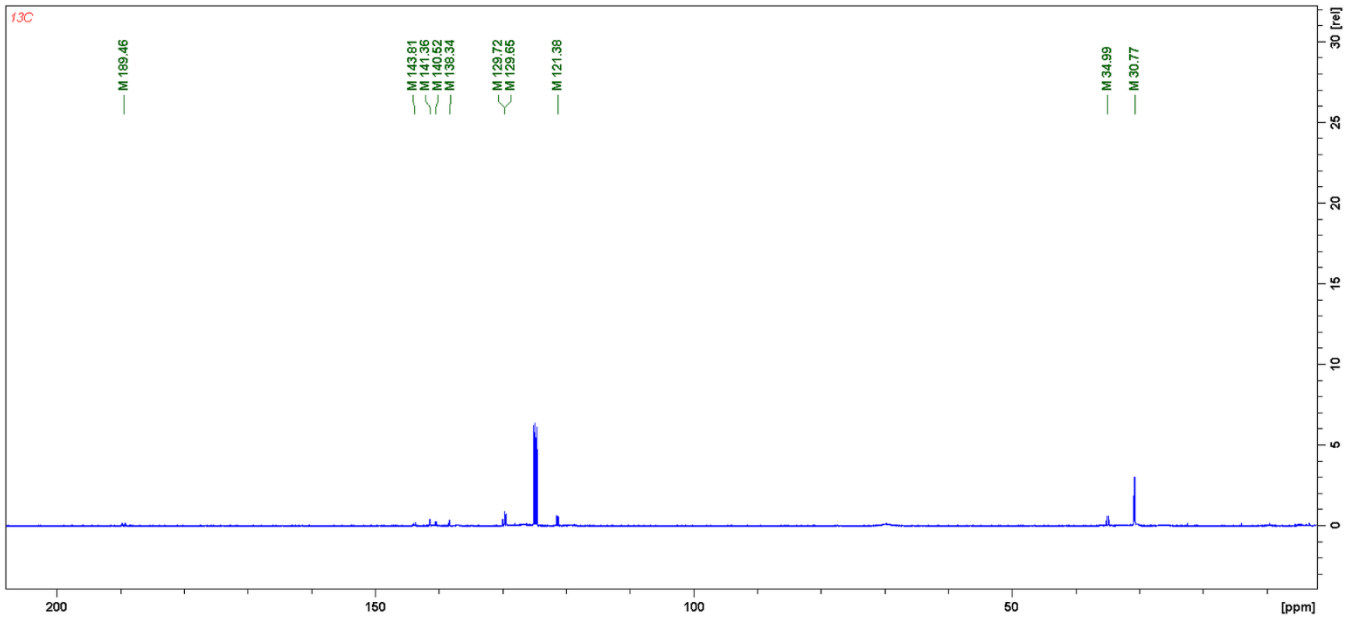


Figure S58. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**).

- 189.46 ppm, (dd), $J_{P\text{-}C}$ = 54.5 Hz, $J_{P\text{-}C}$ = 10.9 Hz, (fluorenyl)**C**=P-P*t*Bu$_2$;
- 143.81 ppm, (dd), $J_{P\text{-}C}$ = 26.3 Hz, $J_{P\text{-}C}$ = 8.2 Hz, (**fluorenyl**)C=P-P*t*Bu$_2$;
- 141.36 ppm, (d), $J_{P\text{-}C}$ = 9.1 Hz, (**fluorenyl**)C=P-P*t*Bu$_2$;
- 140.52 ppm, (dd), $J_{P\text{-}C}$ = 18.6 Hz, $J_{P\text{-}C}$ = 1.3 Hz, (**fluorenyl**)C=P-P*t*Bu$_2$;
- 138.34 ppm, (d), $J_{P\text{-}C}$ = 13.6 Hz, (**fluorenyl**)C=P-P*t*Bu$_2$;
- 129.72 ppm, (dd), $J_{P\text{-}C}$ = 59.0 Hz, $J_{P\text{-}C}$ = 5.4 Hz, (**fluorene**)C=P-P*t*Bu$_2$;
- 129.65 ppm, (dd), $J_{P\text{-}C}$ = 5.7 Hz, $J_{P\text{-}C}$ = 3.9 Hz, (**fluorenyl**)C=P-P*t*Bu$_2$;
- 121.38 ppm, (d), $J_{P\text{-}C}$ = 25.4 Hz, (**fluorenyl**)C=P-P*t*Bu$_2$;
- 34.99 ppm, (dd), $J_{P\text{-}C}$ = 27.9 Hz, $J_{P\text{-}C}$ = 3.1 Hz, (fluorenyl)C=P-P{**C**$(CH_3)_3$}$_2$;
- 30.77 ppm, (dd), $J_{P\text{-}C}$ = 14.1 Hz, $J_{P\text{-}C}$ = 5.3 Hz, (fluorenyl)C=P-P{C(**C**$H_3)_3$}$_2$;

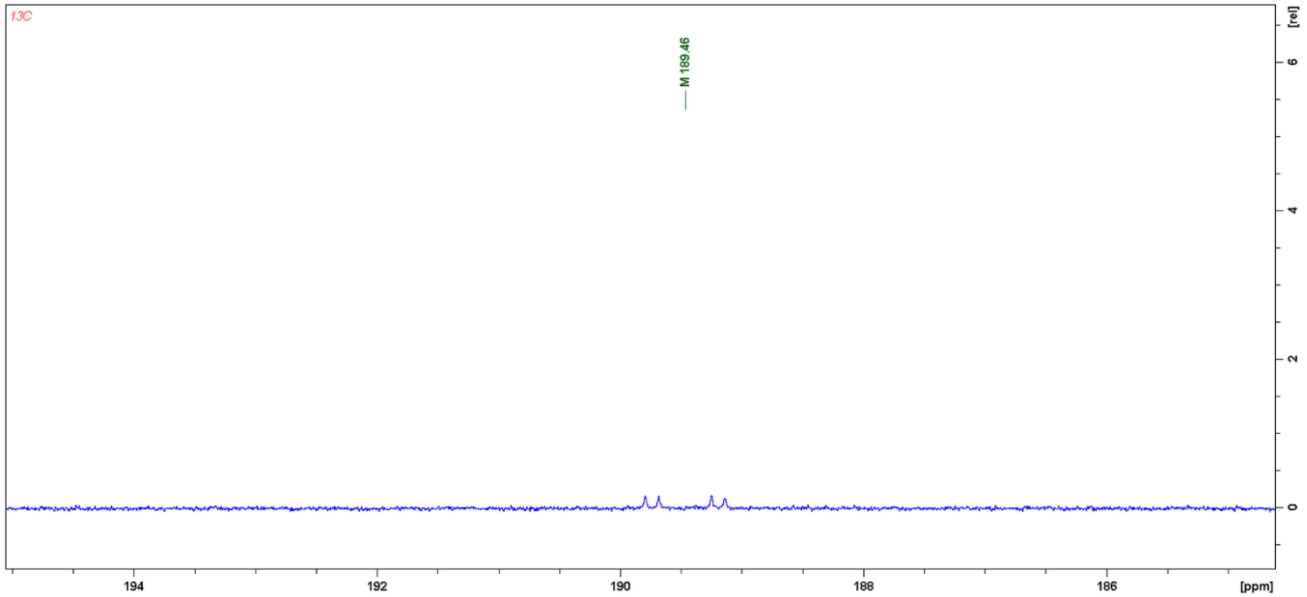


Figure S59. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**) in the range from 195 ppm to 185 ppm.

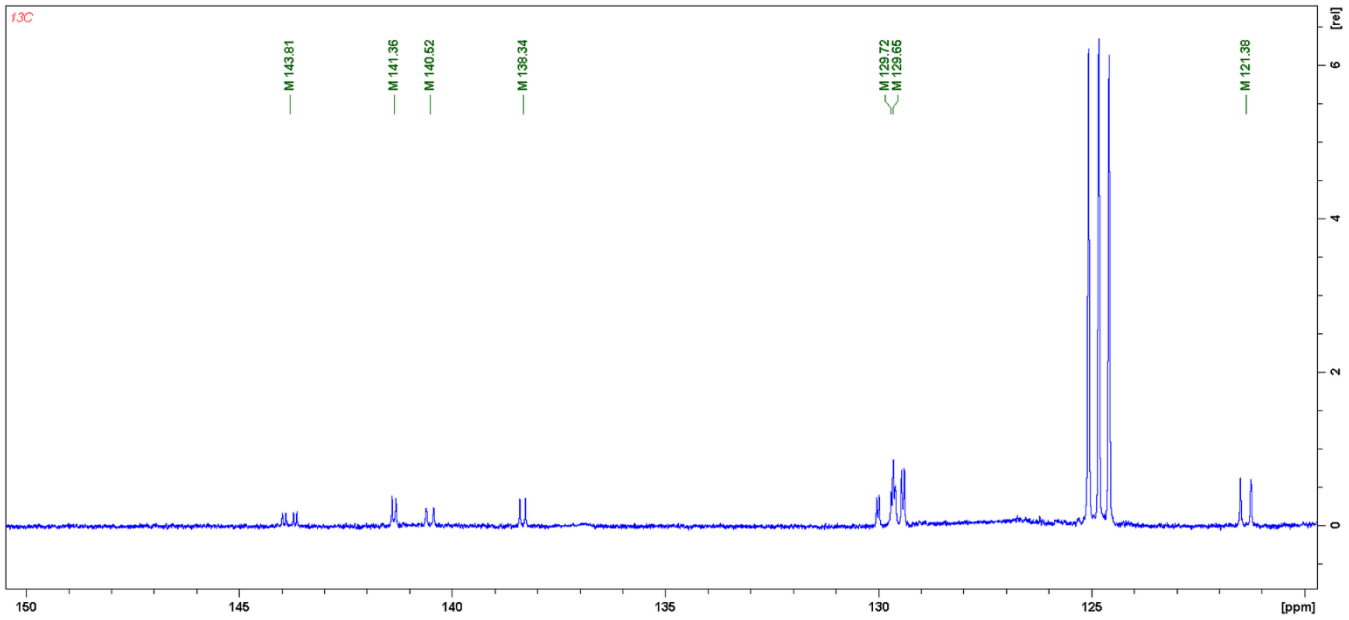


Figure S60. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**) in the range from 150 ppm to 120 ppm.

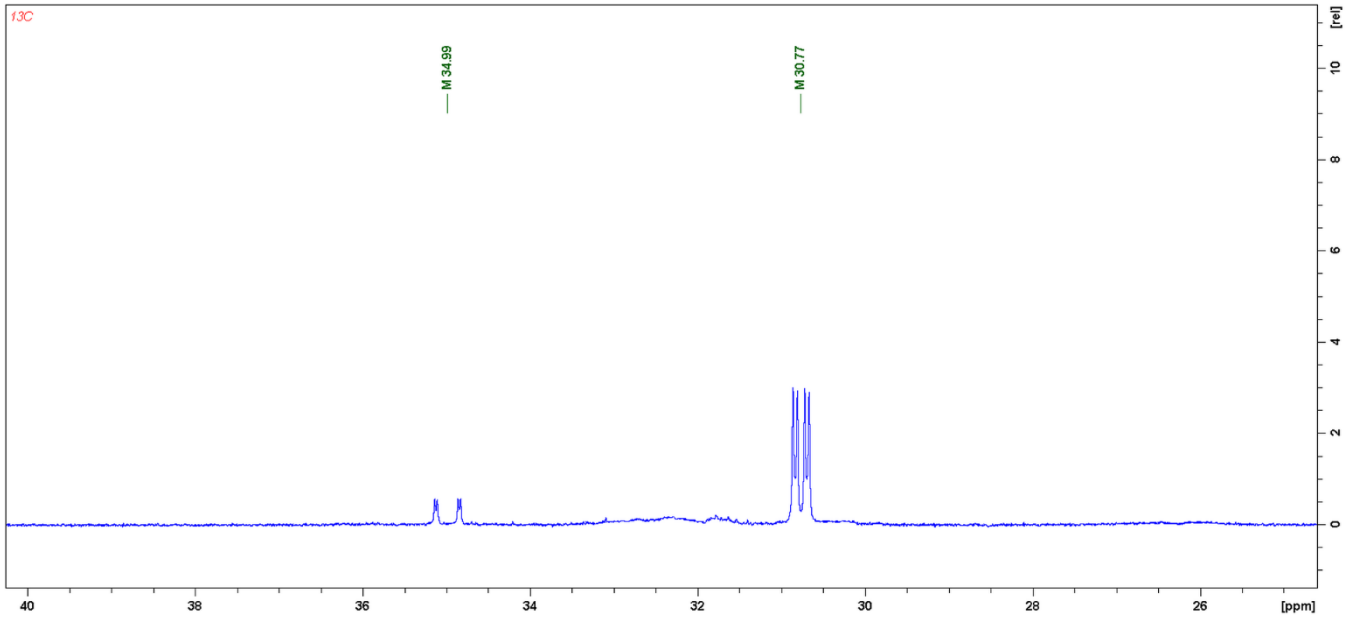


Figure S61. $^{13}C\{^{1}H\}$ NMR(400 MHz, Toluene-d_8, 298 K) spectrum of isolated (fluorenyl)C=P-P*t*Bu$_2$ (**3b**) in the range from 40 ppm to 25 ppm.

B.2.3. 4-cyanobenzophenone

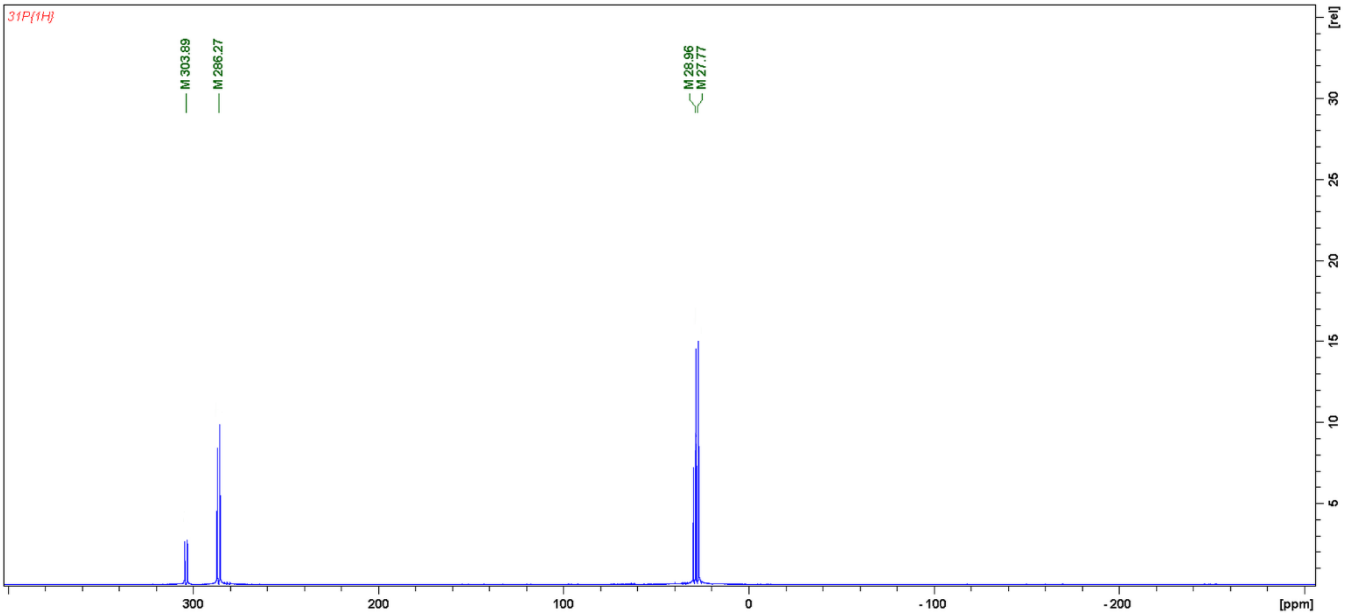


Figure S62. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**).

- 303.89 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 286.27 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=**P**-P*t*Bu$_2$ – *Z* isomer;
- 28.96 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$ – *E* isomer;
- 27.77 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, (Ph)(4-CN-Ph)C=P-**P***t*Bu$_2$ – *Z* isomer;

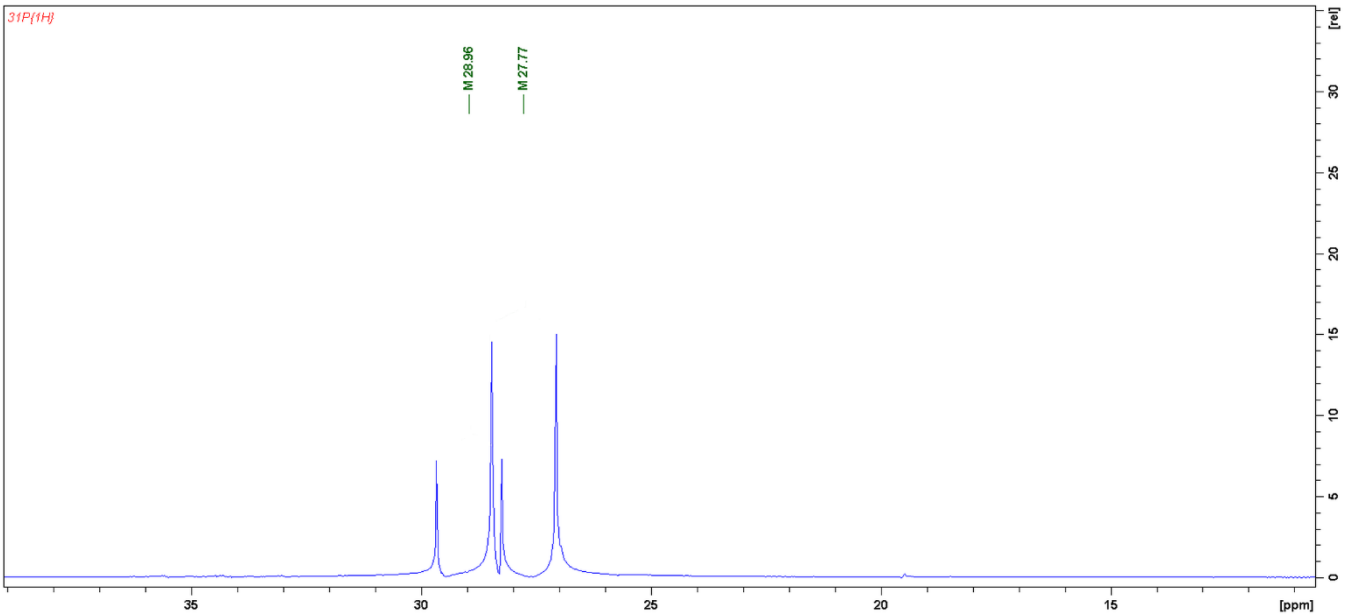


Figure S63. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) in the range from 40 ppm to 10 ppm.

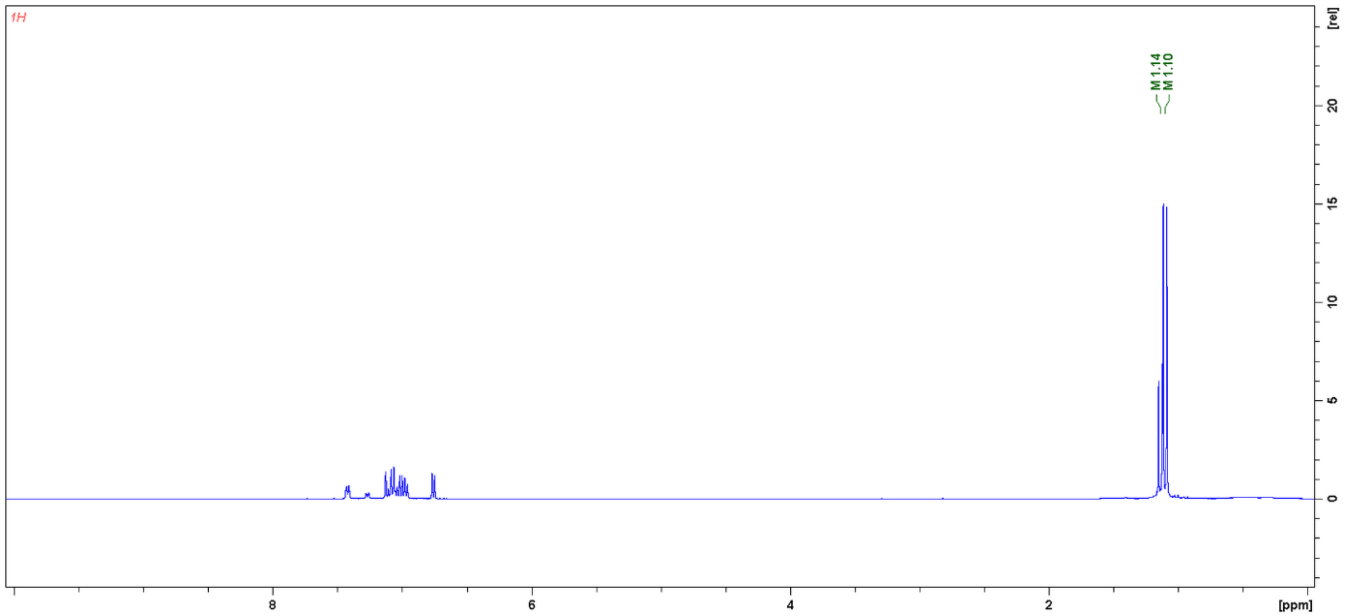


Figure S64. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**).

- 7.50 ppm – 6.70 ppm, 10H, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$;
- 1.14 ppm, (d), $J_{P\text{-}H}$ = 10.9 Hz, 18H, (Ph)(4-CN-Ph)C=P-P***t*Bu**$_2$ – *E* isomer ;
- 1.10 ppm, (d), $J_{P\text{-}H}$ = 10.9 Hz, 18H, (Ph)(4-CN-Ph)C=P-P***t*Bu**$_2$ – *Z* isomer;

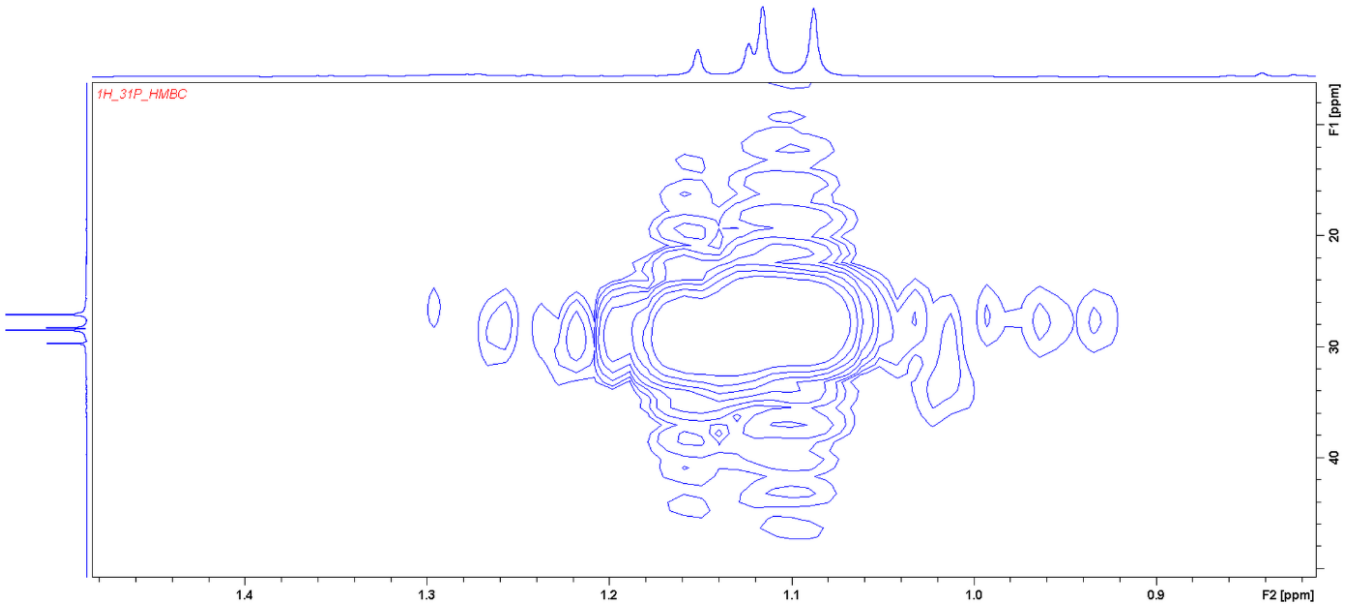


Figure S65. ^{31}P{^{1}H}/^{1}H-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**).

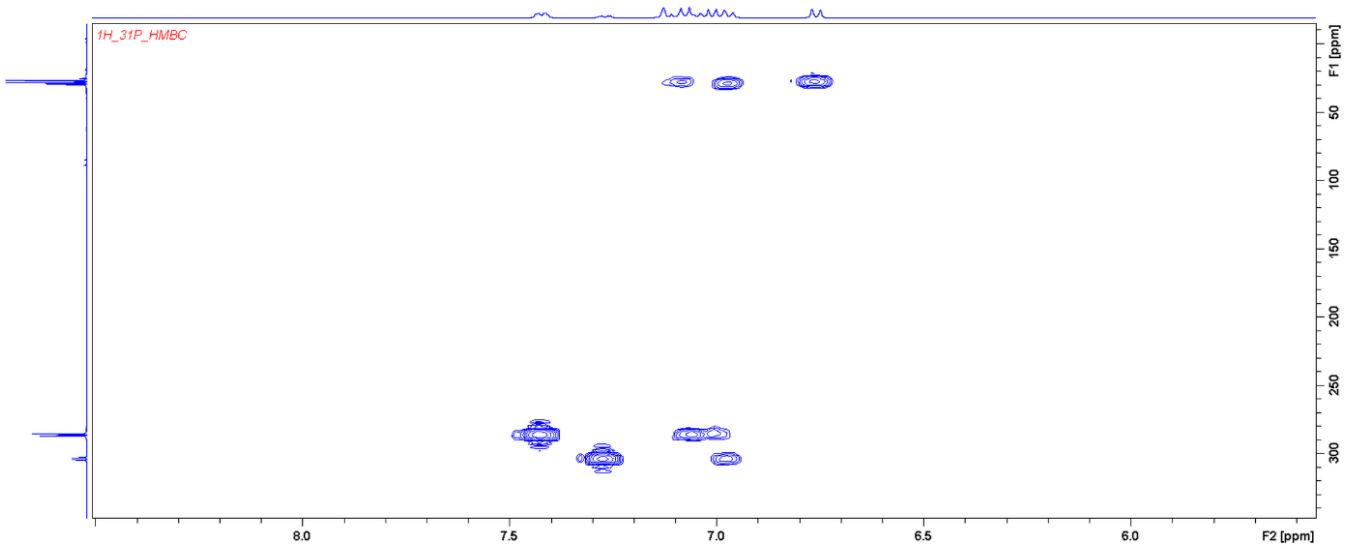


Figure S66. $^{31}P\{^{1}H\}/^{1}H$-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) (correlation of aromatic protons).

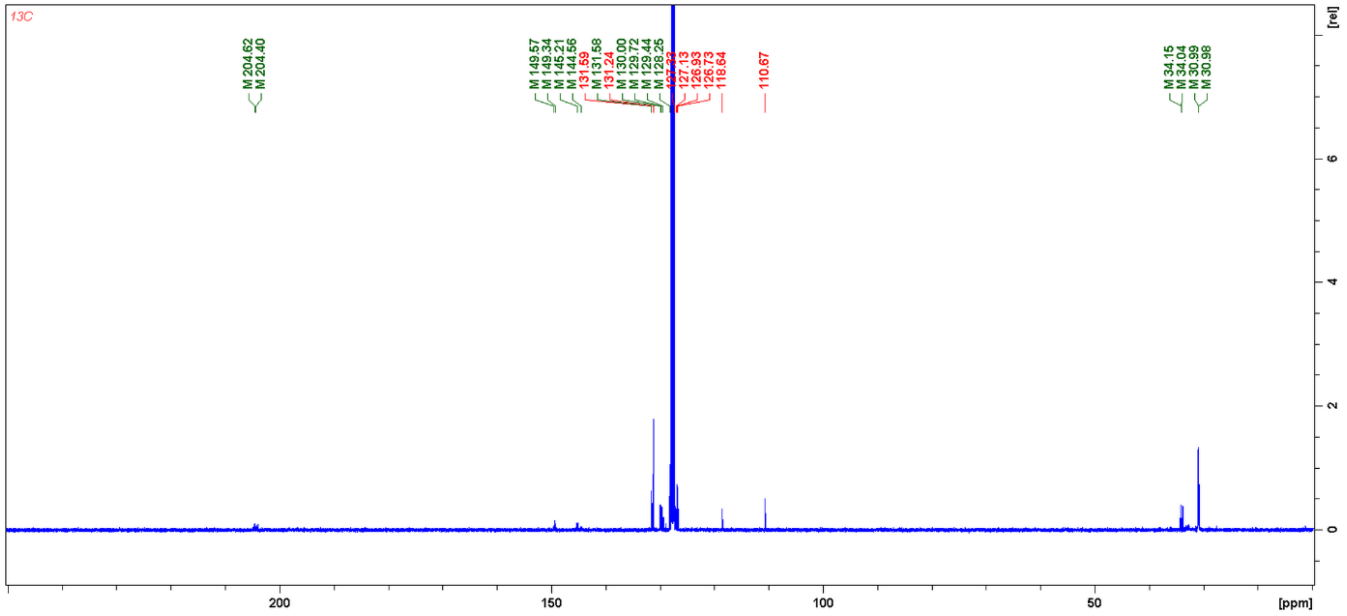


Figure S67. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**).

- 204.62 ppm, (dd), $J_{P\text{-}C}$ = 54.4 Hz, $J_{P\text{-}C}$ = 16.8 Hz, (Ph)(4-CN-Ph)**C**=P-P*t*Bu$_2$ – *E* isomer;
- 204.40 ppm, (dd), $J_{P\text{-}C}$ = 55.5 Hz, $J_{P\text{-}C}$ = 17.1 Hz, (Ph)(4-CN-Ph)**C**=P-P*t*Bu$_2$ – *Z* isomer;
- 149.57 ppm, (dd), $J_{P\text{-}C}$ = 24.1 Hz, $J_{P\text{-}C}$ = 3.7 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*i*-C$_{Ar}$) – *Z* isomer;
- 149.34 ppm, (dd), $J_{P\text{-}C}$ = 13.7 Hz, $J_{P\text{-}C}$ = 6.2 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*i*-C$_{Ar}$) – *E* isomer;
- 145.21 ppm, (dd), $J_{P\text{-}C}$ = 22.1 Hz, $J_{P\text{-}C}$ = 4.2 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*i*-C$_{Ar}$) – *E* isomer;
- 144.56 ppm, (dd), $J_{P\text{-}C}$ = 20.1 Hz, $J_{P\text{-}C}$ = 5.6 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*i*-C$_{Ar}$) – *Z* isomer;
- 131.58 ppm, (d), $J_{P\text{-}C}$ = 1.0 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*p*-C$_{Ar}$) – *Z* isomer;
- 131.24 ppm, (s), (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*o*-C$_{Ar}$) – *E* isomer;
- 130.00 ppm, (dd), $J_{P\text{-}C}$ = 6.6 Hz, $J_{P\text{-}C}$ = 4.1 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*o*-C$_{Ar}$) – *Z* isomer;

- 129.72 ppm, (d), $J_{P\text{-}C}$ = 4.8 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*o*-C$_{Ar}$) – *E* isomer;
- 129.44 ppm, (dd), $J_{P\text{-}C}$ = 6.5 Hz, $J_{P\text{-}C}$ = 4.2 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*o*-C$_{Ar}$) – *E* isomer;
- 128.24 ppm, (d, $J_{P\text{-}C}$ = 0.9 Hz, (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*p*-C$_{Ar}$) – *E* isomer;
- 127.33 ppm, (s), (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$) – *Z* isomer;
- 127.13 ppm, (s), (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$) – *Z* isomer;
- 126.93 ppm, (s), (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$) – *E* isomer;
- 126.73 ppm, (s), (**Ph**)(4-CN-**Ph**)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$) – *E* isomer;
- 118.64 ppm, (s), (Ph)(4-**C**N-Ph)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$) – *Z* isomer;
- 110.67 ppm, (s), (Ph)(4-**C**N-Ph)C=P-P*t*Bu$_2$ (*m*-C$_{Ar}$) – *E* isomer;
- 34.15 ppm, (dd), $J_{P\text{-}C}$ = 30.2 Hz, $J_{P\text{-}C}$ = 4.1 Hz, (Ph)(4-CN-Ph)C=P-P{**C**(CH$_3$)$_3$}$_2$ - *E* isomer;
- 34.04 ppm, (dd), $J_{P\text{-}C}$ = 29.5 Hz, $J_{P\text{-}C}$ = 4.1 Hz, (Ph)(4-CN-Ph)C=P-P{**C**(CH$_3$)$_3$}$_2$ - *Z* isomer;
- 30.99 ppm, (dd), $J_{P\text{-}C}$ = 14.3 Hz, $J_{P\text{-}C}$ = 5.6 Hz, (Ph)(4-CN-Ph)C=P-P{C(**C**H$_3$)$_3$}$_2$ - *E* isomer;
- 30.98 ppm, (dd), $J_{P\text{-}C}$ = 14.2 Hz, $J_{P\text{-}C}$ = 5.3 Hz, (Ph)(4-CN-Ph)C=P-P{C(**C**H$_3$)$_3$}$_2$ - *Z* isomer;

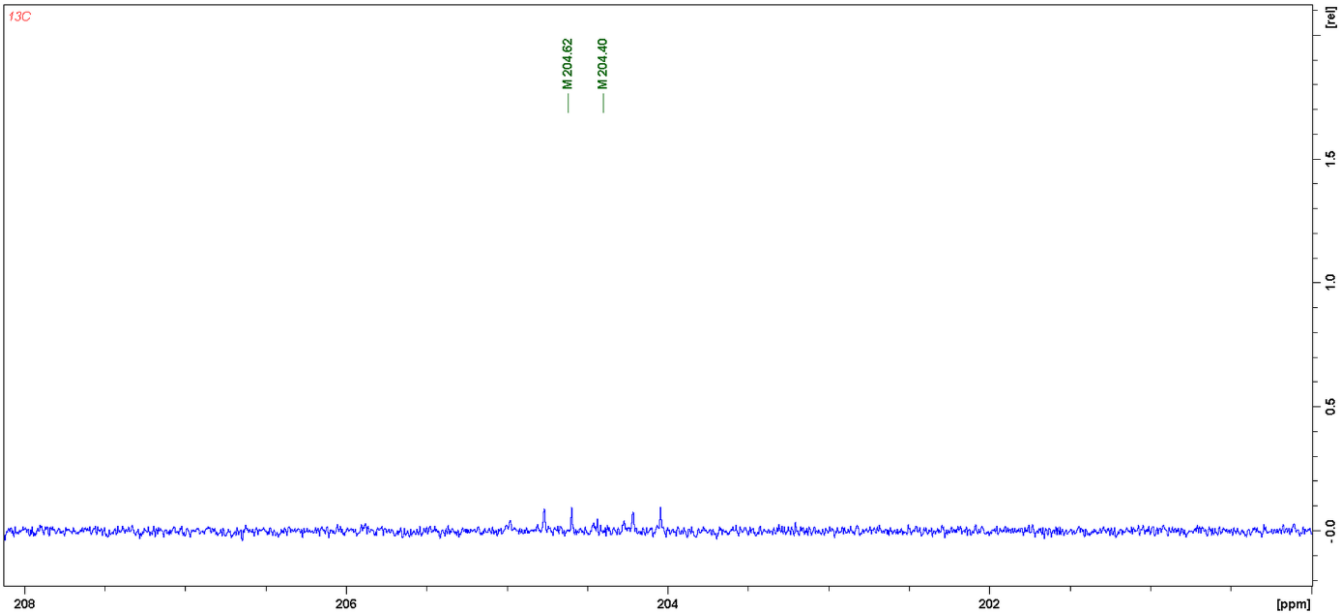


Figure S68. $^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) in the range from 208 to 201 ppm.

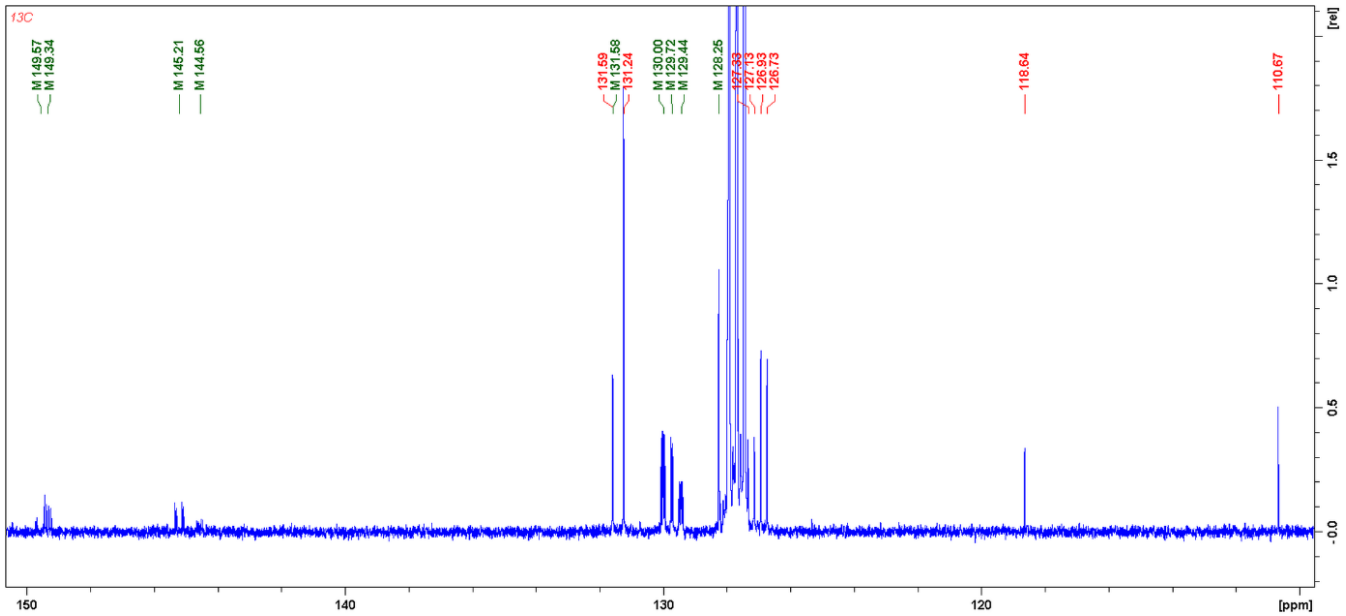


Figure S69. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) in the range from 150 to 110 ppm.

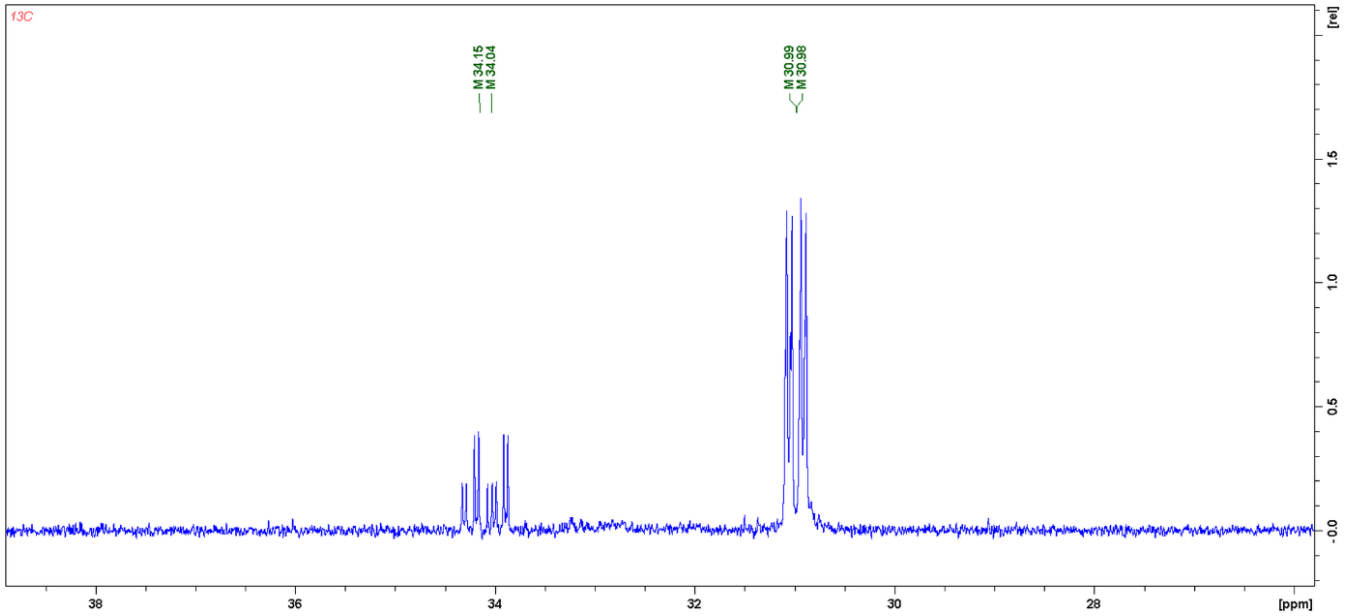


Figure S70. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) in the range from 38 to 27 ppm.

B.2.4. 4,4'-dicyanobenzophenone

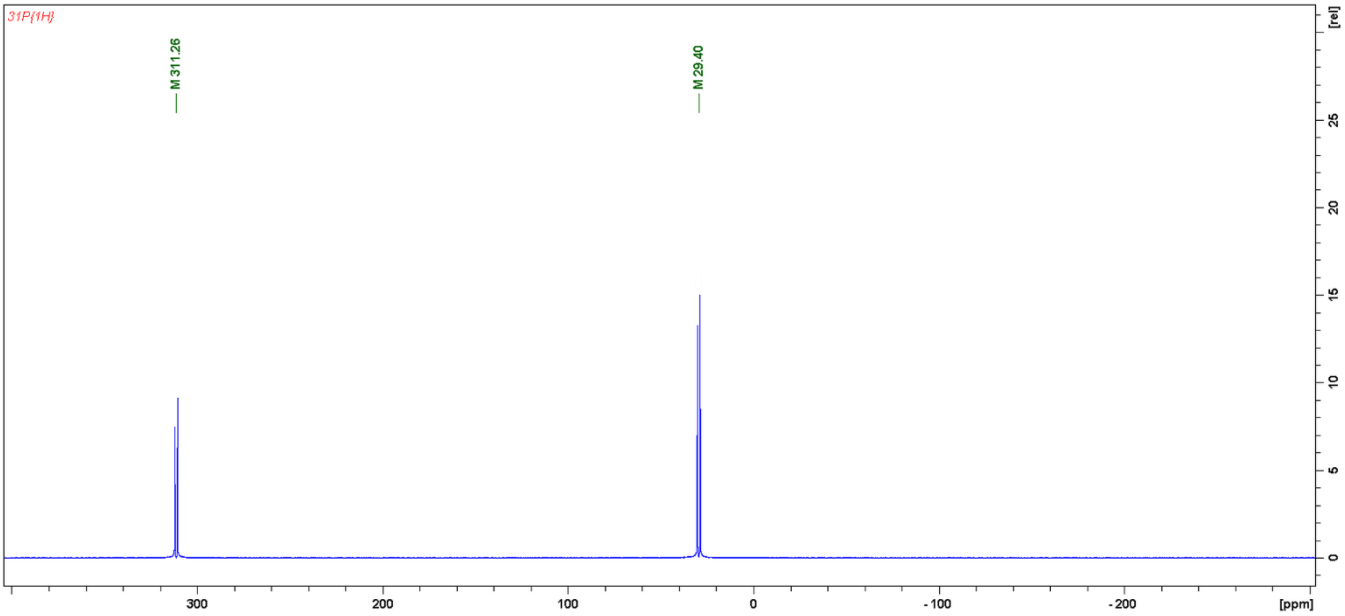


Figure S71. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**).

- 311.26 ppm, (d), $J_{P\text{-}P}$ = 232.5 Hz, (4-CN-Ph)$_2$C=**P**-P*t*Bu$_2$;
- 29.40 ppm, (d), $J_{P\text{-}P}$ = 232.5 Hz, (4-CN-Ph)$_2$C=P-**P***t*Bu$_2$;

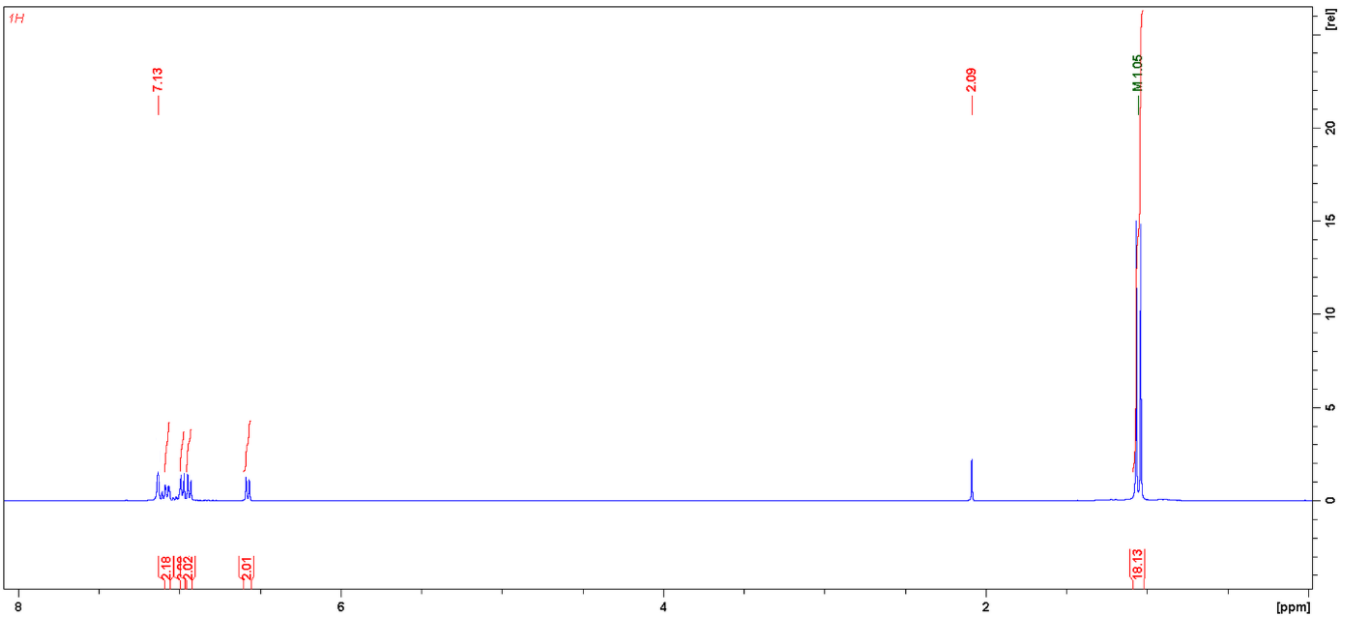


Figure S72. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**).

- 7.13 ppm, (broad s), aromatic protons of toluene (toluene molecule is present in the unit cell with two molecules of phosphanylphosphaalkenes);
- 7.10 ppm – 6.55 ppm, 8H, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$;
- 1.05 ppm, (d), $J_{P\text{-}H}$ = 11.4 Hz, 18H, (4-CN-Ph)$_2$C=P-P***t*Bu**$_2$;

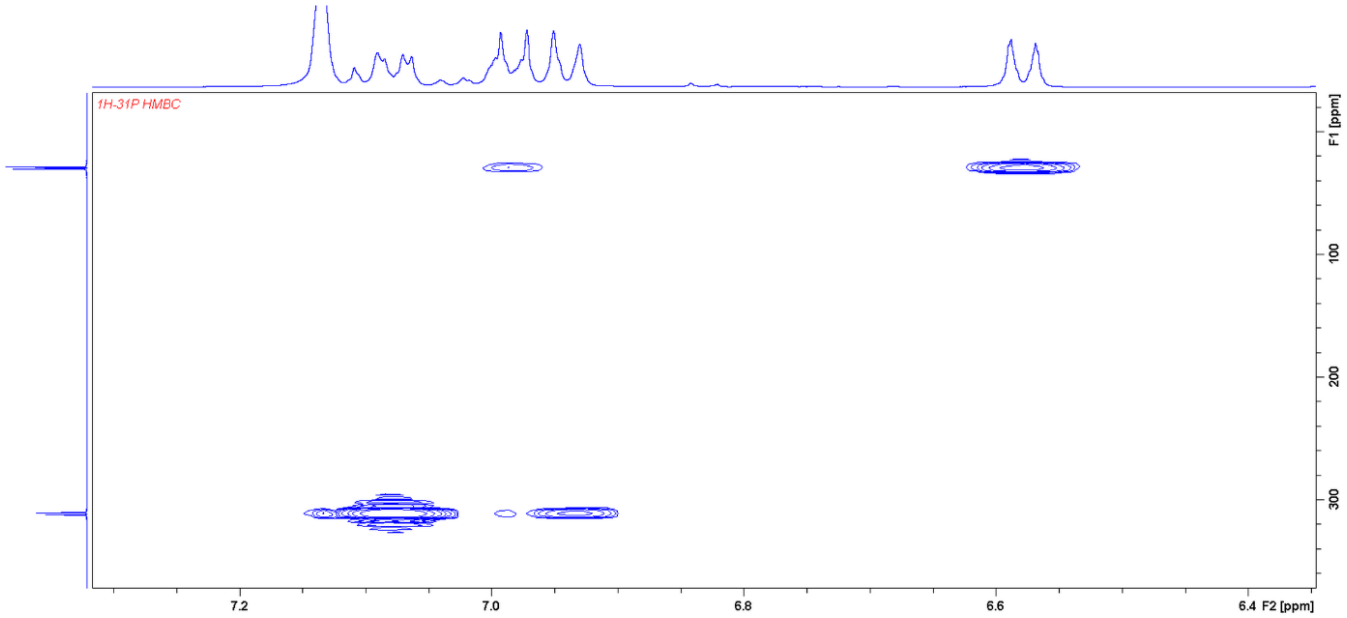


Figure S73. $^{31}P\{^{1}H\}/^{1}H$-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) (correlation of aromatic protons).

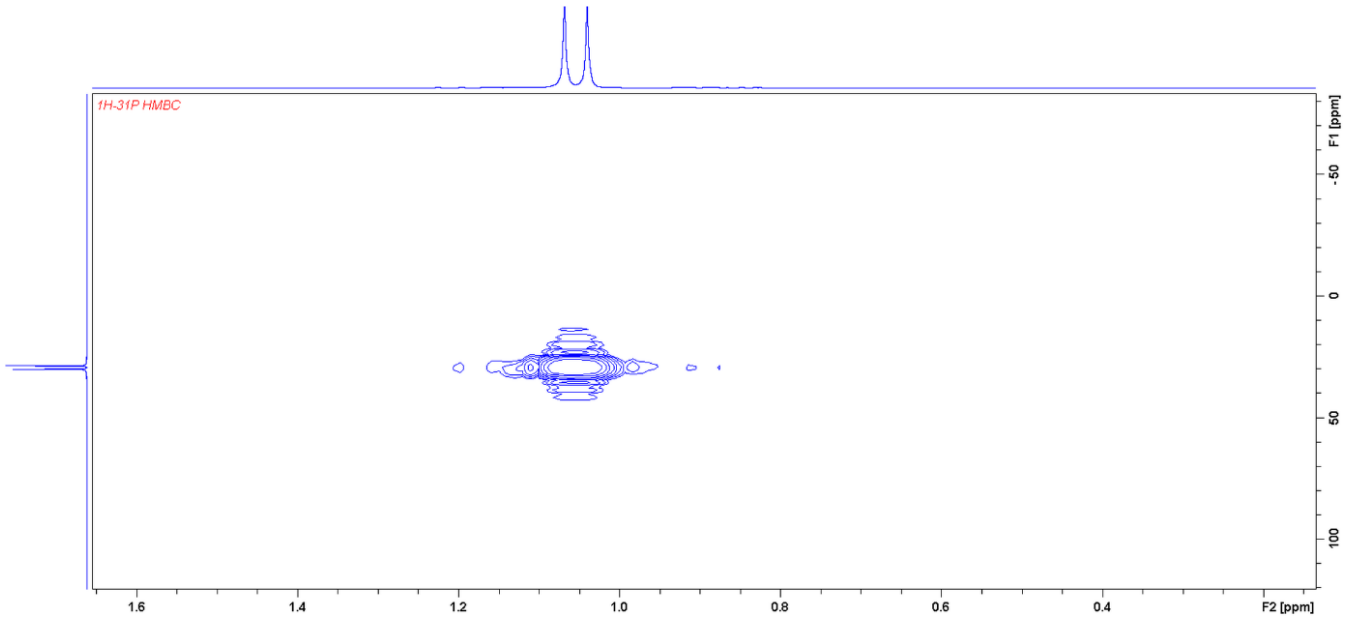


Figure S74. $^{31}P\{^{1}H\}/^{1}H$-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) (correlation of *tert*-butyl groups protons).

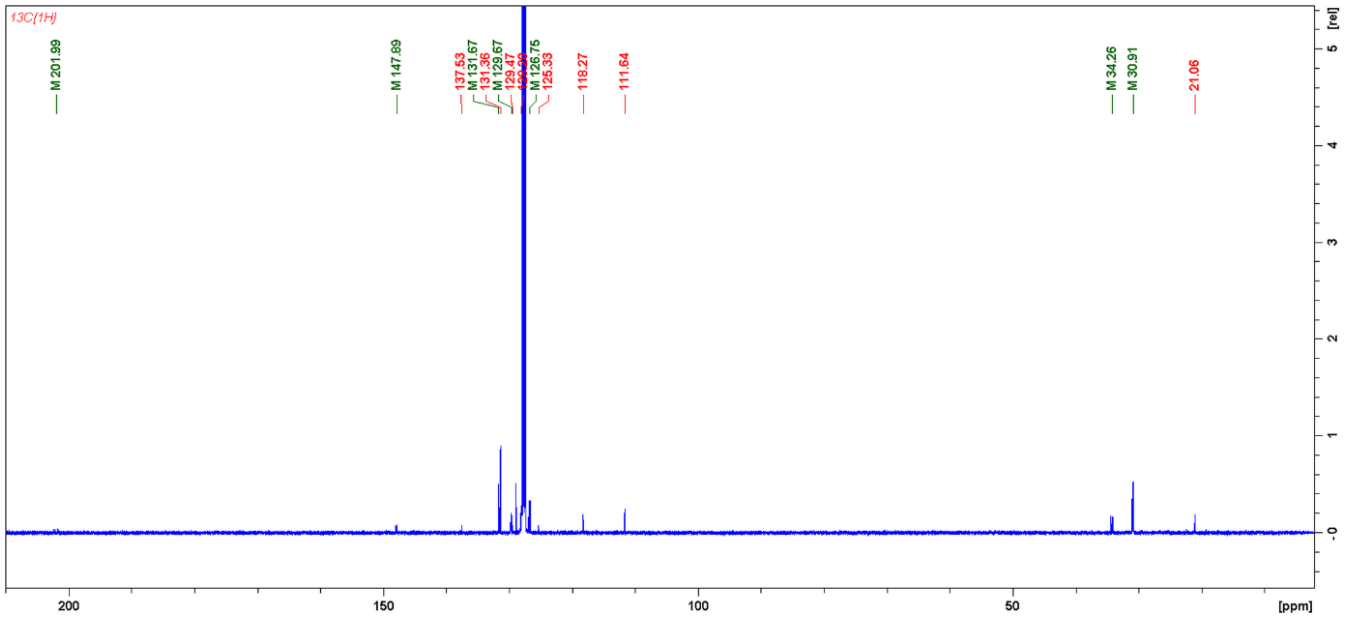


Figure S75. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**).

- 201.99 ppm, (dd), $J_{P\text{-}C}$ = 55.6 Hz, $J_{P\text{-}C}$ = 17.6 Hz, (4-CN-Ph)$_2$**C**=P-P*t*Bu$_2$;
- 147.89 ppm, (dd), $J_{P\text{-}C}$ = 23.0 Hz, $J_{P\text{-}C}$ = 4.0 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$ (*i*-C_{Ar});
- 137.53 ppm, (s), toluene (*i*-C_{Ar});
- 131.67 ppm, (d), $J_{P\text{-}C}$ = 1.0 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$ (*m*-C_{Ar});
- 131.36 ppm, (s), (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$ – (*m*-C_{Ar});
- 129.67 ppm, (dd), $J_{P\text{-}C}$ = 6.7 Hz, $J_{P\text{-}C}$ = 4.2 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$ (*o*-C_{Ar});
- 129.47 ppm, (s), toluene (*o*-C_{Ar});
- 128.20 ppm, toluene (*m*-C_{Ar});
- 126.75 ppm, (d), $J_{P\text{-}C}$ = 20.2 Hz, (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$ (*o*-C_{Ar});
- 125.33 ppm, (s), toluene (*p*-C_{Ar});
- 118.27 ppm, (s), (4-**C**N-Ph)$_2$C=P-P*t*Bu$_2$;
- 111.64 ppm, (s), (4-CN-**Ph**)$_2$C=P-P*t*Bu$_2$ (*o*-C_{Ar});
- 34.26 ppm, (dd), $J_{P\text{-}C}$ = 29.4 Hz, $J_{P\text{-}C}$ = 3.9 Hz, (4-CN-Ph)$_2$C=P-P{**C**(CH$_3$)$_3$}$_2$;
- 30.91 ppm, (dd), $J_{P\text{-}C}$ = 14.2 Hz, $J_{P\text{-}C}$ = 5.3 Hz, (4-CN-Ph)$_2$C=P-P{C(**C**H$_3$)$_3$}$_2$;
- 21.06 ppm, (s), methyl group of toluene;

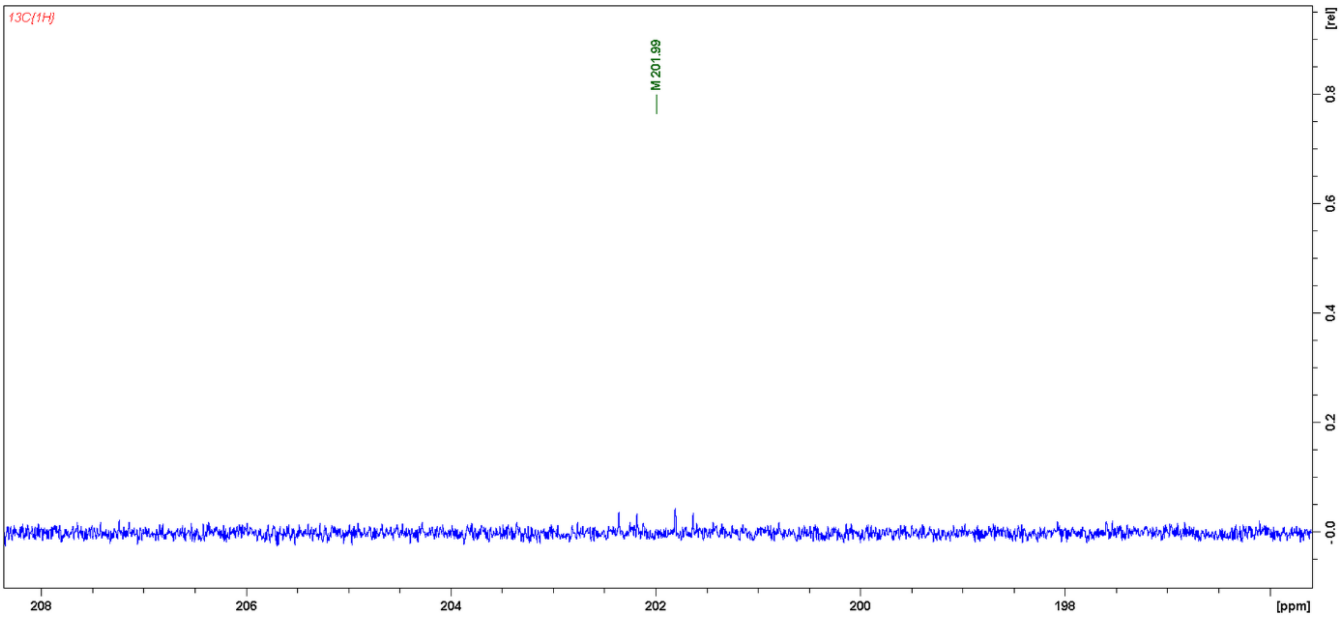


Figure S76. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) in the range from 208 ppm to 196 ppm.

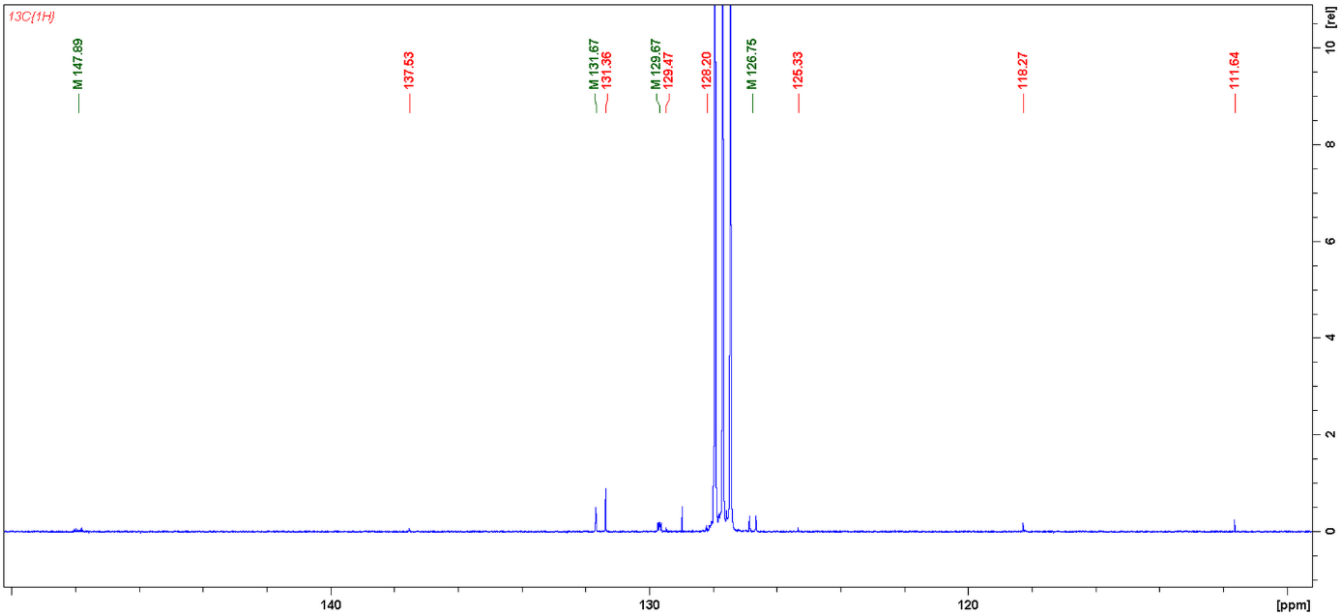


Figure S77. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) in the range from 150 ppm to 110 ppm.

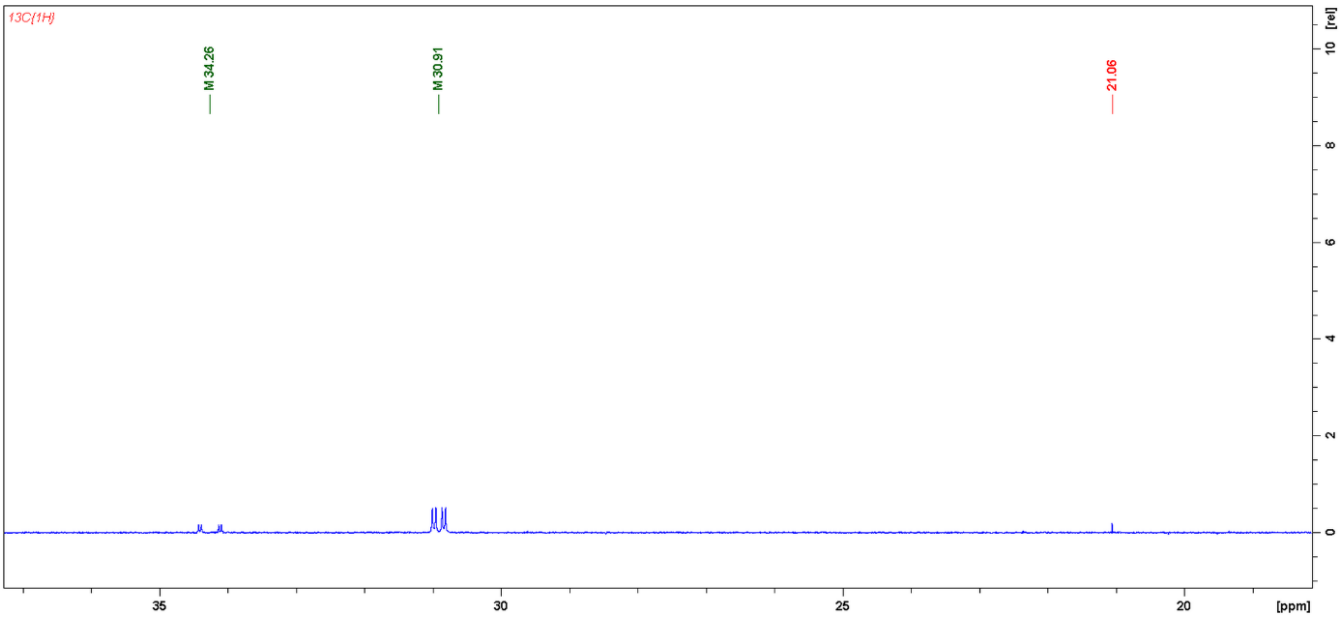


Figure S78. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) in the range from 40 ppm to 25 ppm.

B.2.5. 4,4'-dimethoxybenzophenone

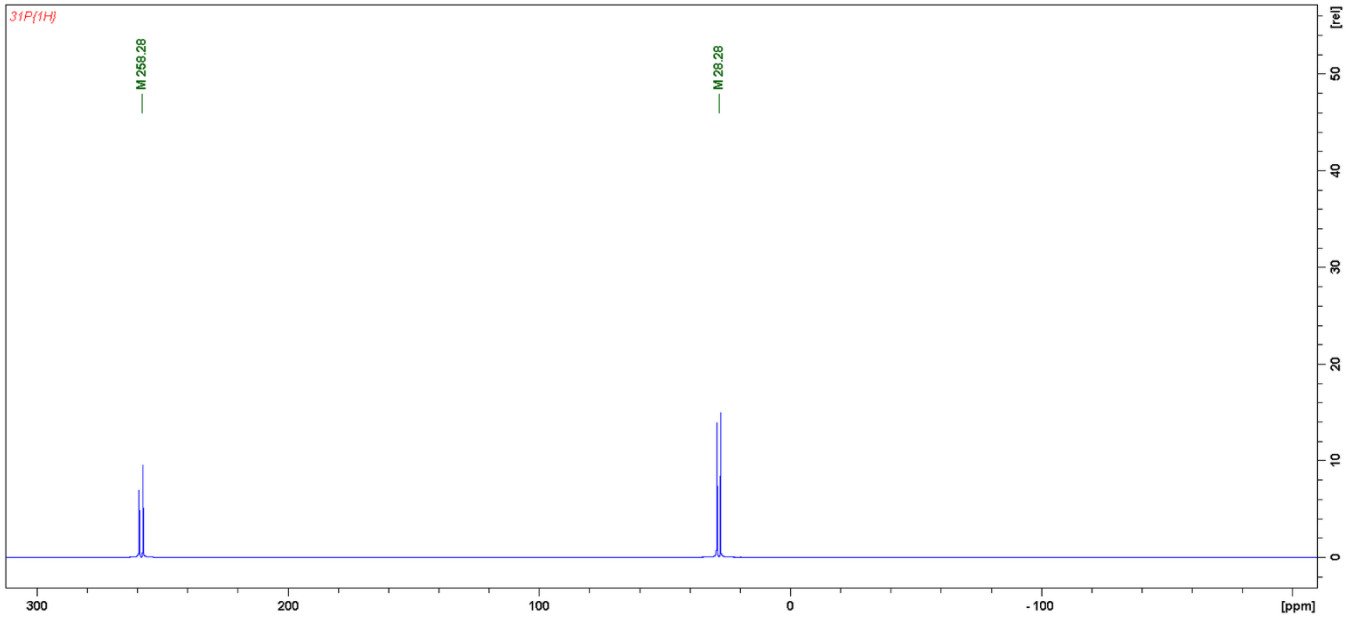


Figure S79. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated $(4\text{-MeO-Ph})_2C{=}P\text{-}PtBu_2$ (**3e**).

- 258.28 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(4\text{-MeO-Ph})_2C{=}\mathbf{P}\text{-}PtBu_2$;
- 28.28 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(4\text{-MeO-Ph})_2C{=}P\text{-}\mathbf{P}tBu_2$;

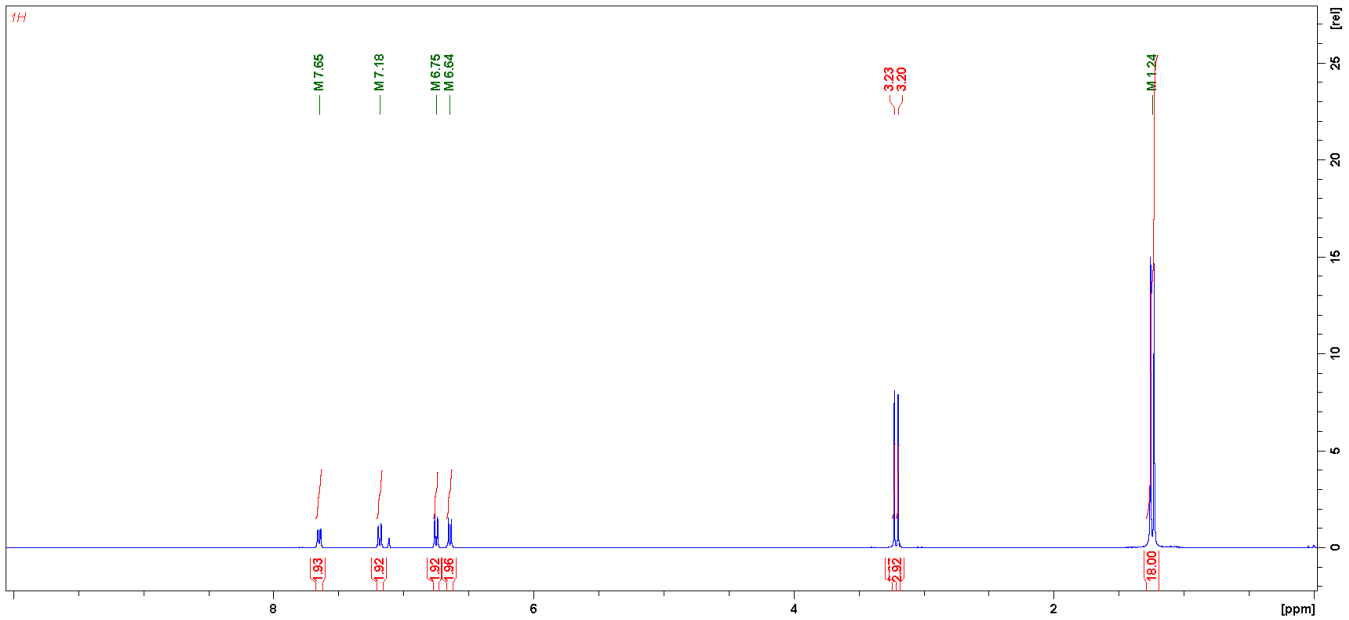


Figure S80. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**).

- 7.65 ppm, (dd), 2H, $J_{P\text{-}H}$ = 8.9 Hz, $J_{P\text{-}H}$ = 2.69 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$ (*o*-H$_{Ar}$);
- 7.18 ppm, (dd), 2H, $J_{P\text{-}H}$ = 8.9 Hz, $J_{P\text{-}H}$ = 1.13 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$ (*o*-H$_{Ar}$);
- 6.75 ppm, (d), 2H, $J_{P\text{-}H}$ = 8.7 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$ (*m*-H$_{Ar}$);
- 6.64 ppm, (d), 2H, $J_{P\text{-}H}$ = 9.3 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$ (*m*-H$_{Ar}$);
- 3.23 ppm, (s), 3H, (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$;
- 3.20 ppm, (s), 3H, (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$;
- 1.24 ppm, (d), 18H, $J_{P\text{-}H}$ = 11.8 Hz, (4-MeO-Ph)$_2$C=P-P***t*Bu**$_2$;

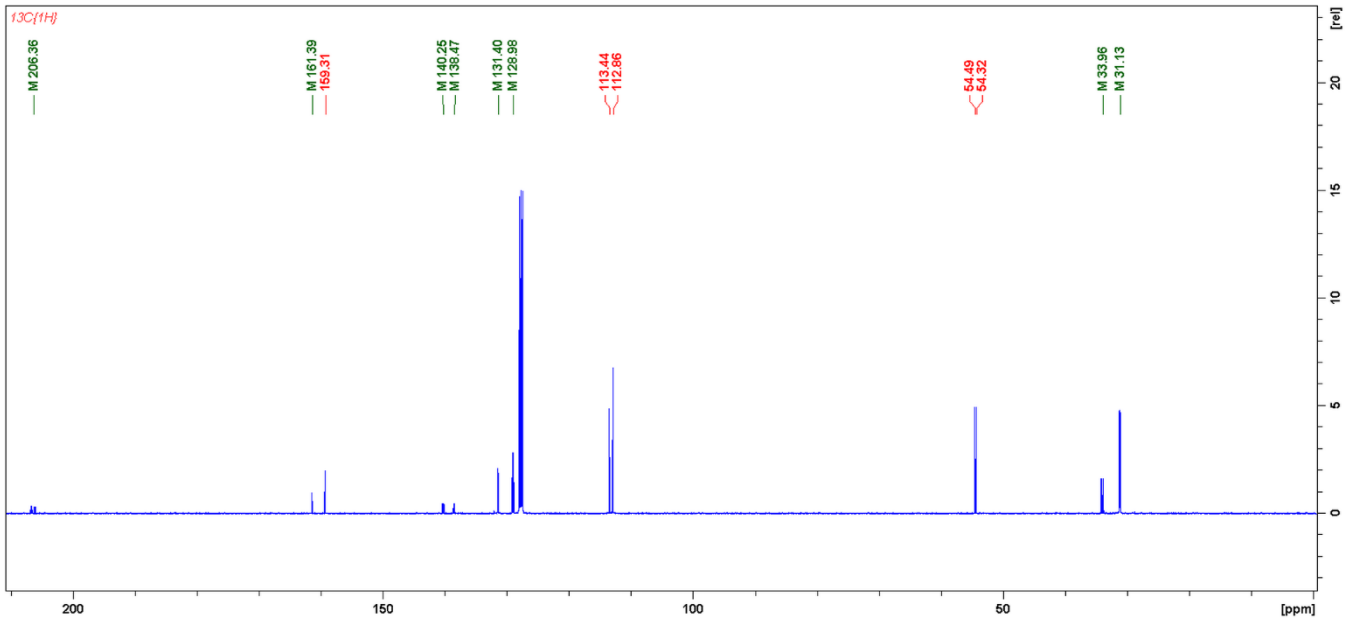


Figure S81. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**).

- 206.36 ppm, (dd), $J_{P\text{-}C}$ = 55.0 Hz, $J_{P\text{-}C}$ = 16.1 Hz, (4-MeO-Ph)$_2$**C**=P-P*t*Bu$_2$;
- 161.39 ppm, (d), $J_{P\text{-}C}$ = 4.4 Hz, (4-MeO-**Ph**)$_2$C=P-P*t*Bu$_2$ (*i*-C_{Ar});
- 159.31 ppm, (s), (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*i*-C_{Ar});
- 140.25 ppm, (dd), $J_{P\text{-}C}$ = 24.2 Hz, $J_{P\text{-}C}$ = 4.4 Hz, (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*i*-C_{Ar});
- 138.47 ppm, (dd), $J_{P\text{-}C}$ = 13.9 Hz, $J_{P\text{-}C}$ = 5.1 Hz, (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*i*-C_{Ar});
- 131.40 ppm, (dd), $J_{P\text{-}C}$ = 5.8 Hz, $J_{P\text{-}C}$ = 4.5 Hz, (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*o*-C_{Ar});
- 128.98 ppm, (d), $J_{P\text{-}C}$ = 19.8 Hz, (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*o*-C_{Ar});
- 113.44 ppm, (s), (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*m*-C_{Ar});
- 112.86 ppm, (s), (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (*m*-C_{Ar});
- 54.49 ppm, (s), (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$;
- 54.32 ppm, (s), (4-**Me**O-Ph)$_2$C=P-P*t*Bu$_2$;
- 33.96 ppm, (dd), $J_{P\text{-}C}$ = 30.1 Hz, $J_{P\text{-}C}$ = 4.4 Hz, (4-MeO-Ph)$_2$**C**=P-P{**C**(CH$_3$)}$_2$;
- 31.13 ppm, (dd), $J_{P\text{-}C}$ = 14.7 Hz, $J_{P\text{-}C}$ = 5.1 Hz, (4-MeO-Ph)$_2$**C**=P-P{C(**C**H$_3$)}$_2$;

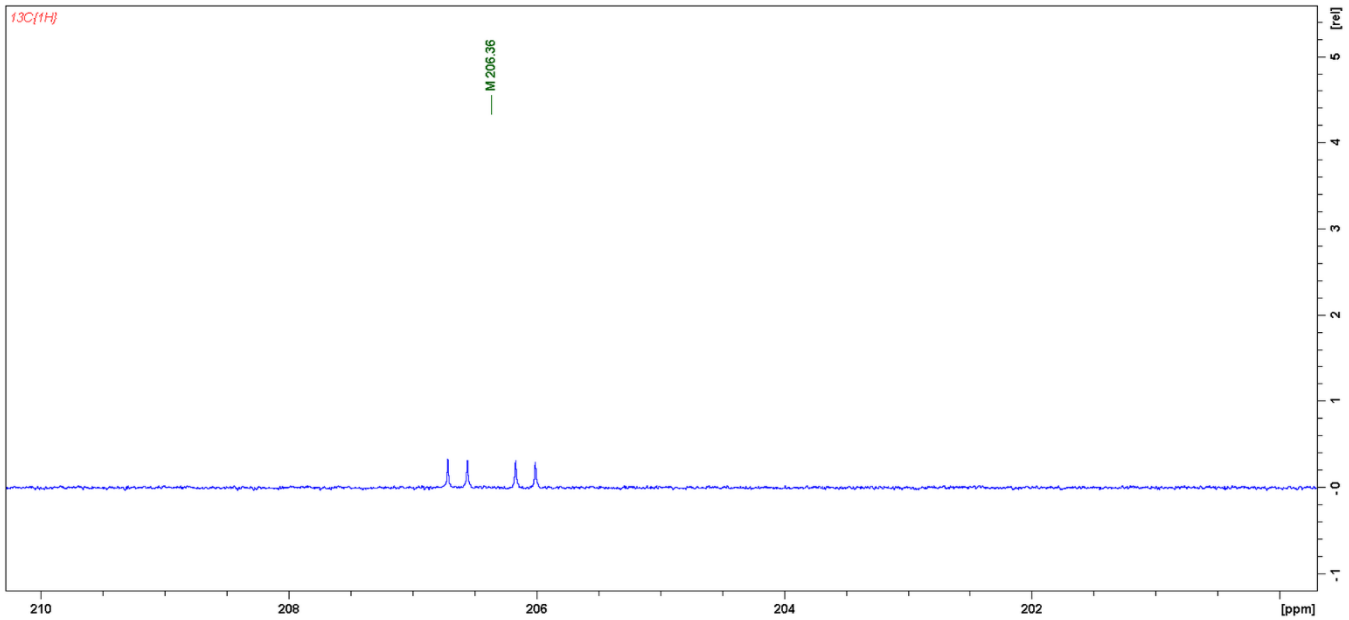


Figure S82. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) in the range from 210 ppm to 200 ppm.

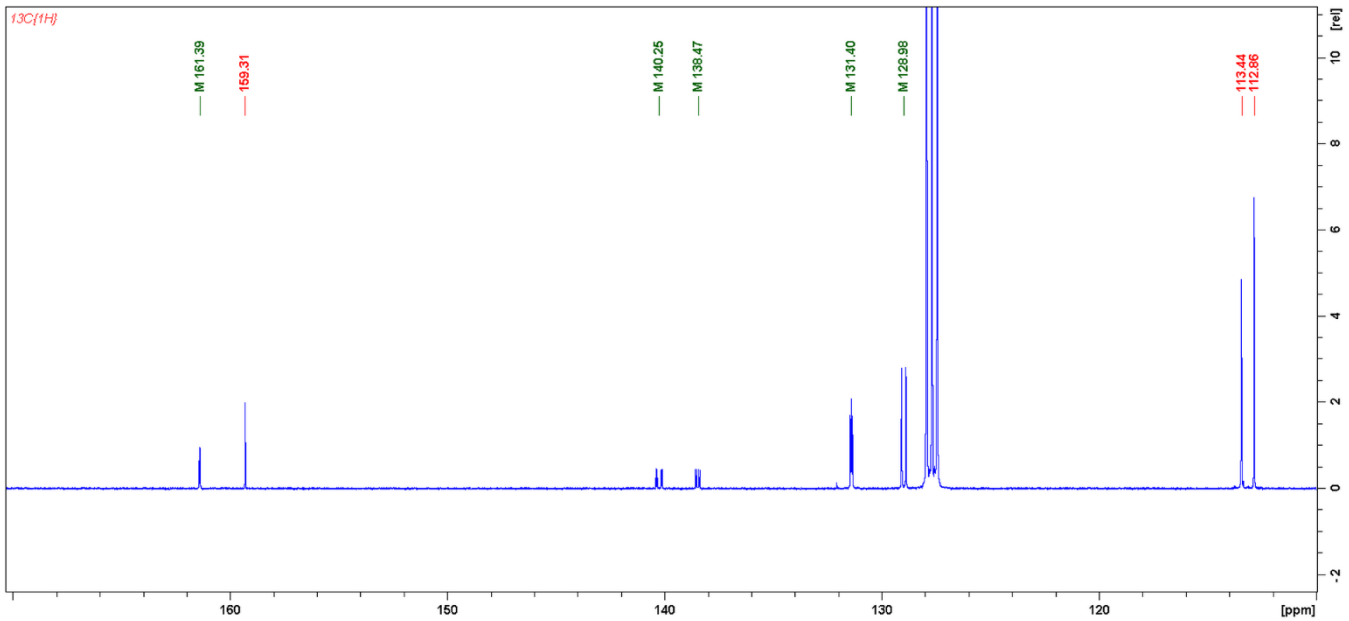


Figure S83. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) in the range from 170 ppm to 110 ppm.

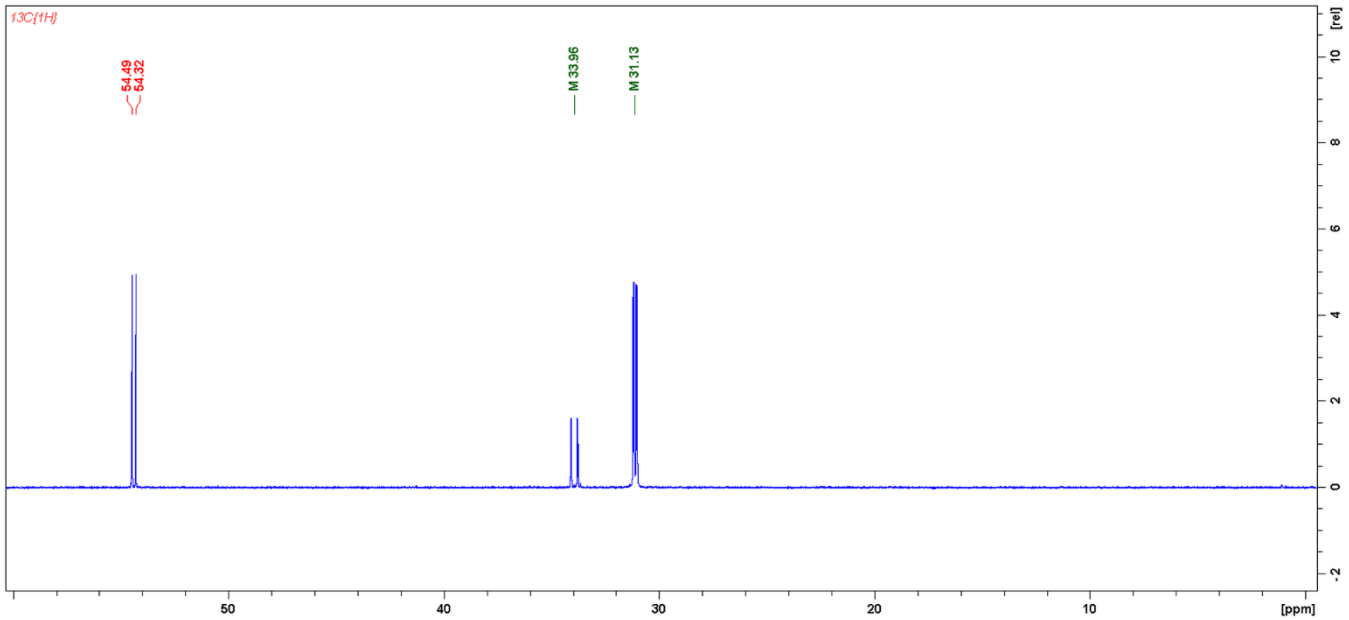


Figure S84. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) in the range from 60 ppm to 0 ppm.

B.2.6. *Tert*-butyl phenyl ketone

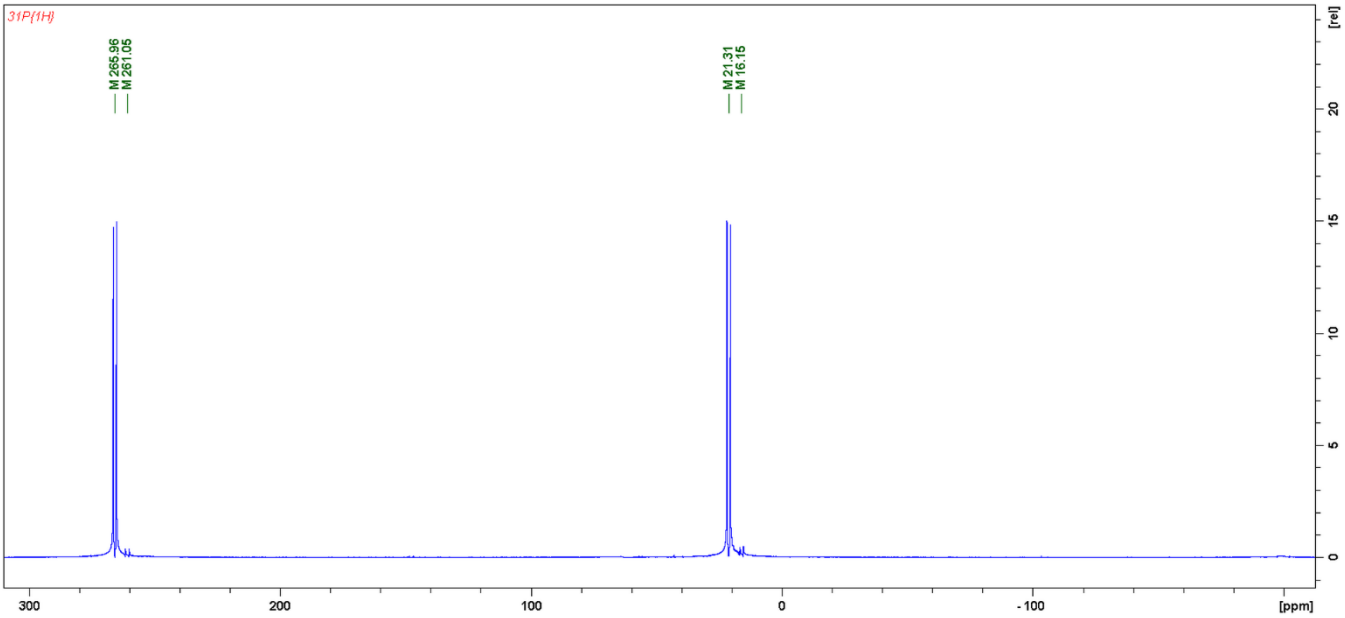


Figure S85. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of isolated *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**).

- 265.96 ppm, (d), $J_{P\text{-}P}$ = 216.9 Hz, *t*Bu(Ph)C=**P**-P*t*Bu$_2$ – *Z* isomer;
- 261.05 ppm, (d), $J_{P\text{-}P}$ = 230.4 Hz, *t*Bu(Ph)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 21.31 ppm, (d), $J_{P\text{-}P}$ = 216.9 Hz, *t*Bu(Ph)C=P-**P***t*Bu$_2$ – *Z* isomer;
- 16.15 ppm, (d), $J_{P\text{-}P}$ = 230.4 Hz, *t*Bu(Ph)C=P-**P***t*Bu$_2$ – *E* isomer;

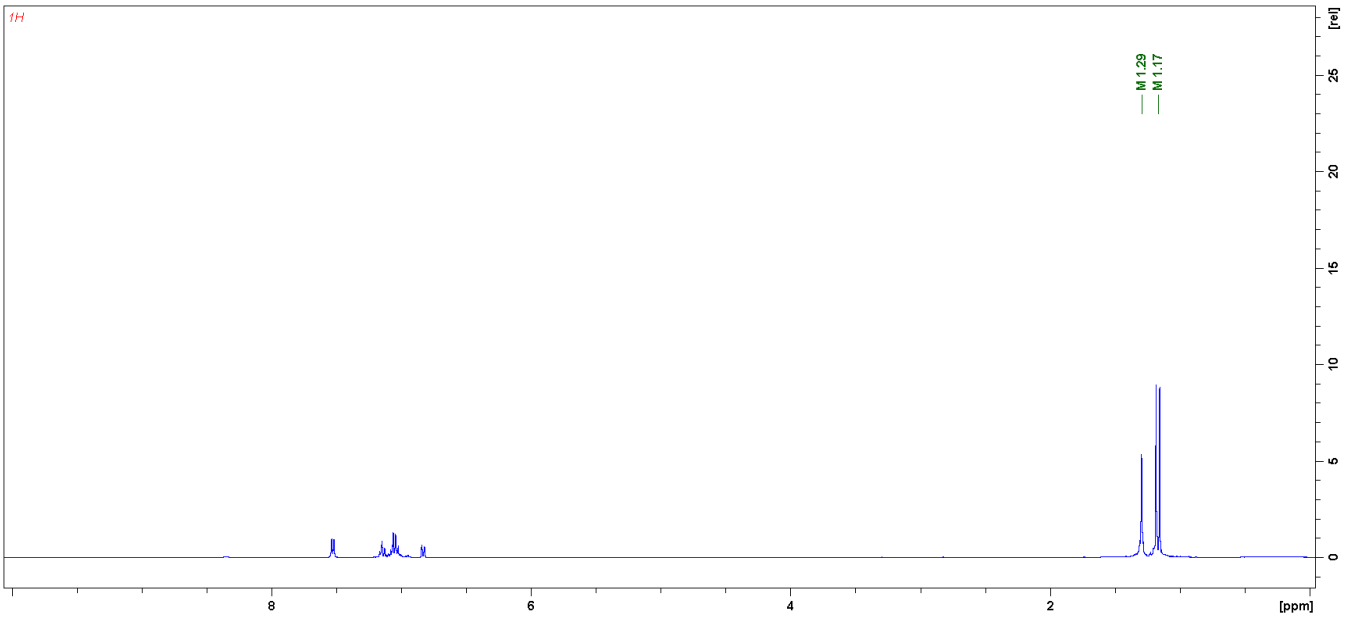


Figure S86. ^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) spectrum of of isolated *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**).

- 7.57 – 6.81 ppm, aromatic protons;
- 1.29 ppm, (d), $J_{P\text{-}H}$ = 1.9 Hz, ***t*Bu**(Ph)C=P-P*t*Bu$_2$ – *Z* isomer;
- 1.17 ppm, (d), $J_{P\text{-}H}$ = 10.7 Hz, *t*Bu(Ph)C=P-P***t*Bu**$_2$ – *Z* isomer;

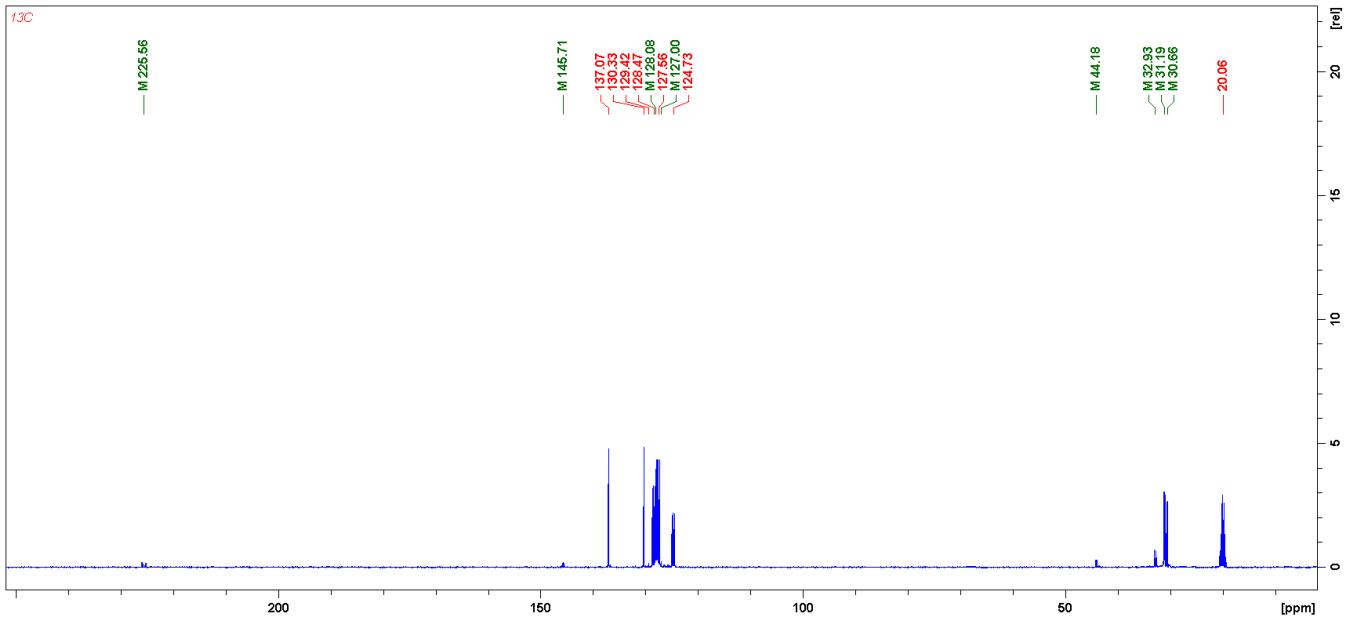


Figure S87. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of of isolated *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**).

- 225.56 ppm, (dd), $J_{P\text{-}C}$ = 62.0 Hz, $J_{P\text{-}C}$ = 16.5 Hz, *t*Bu(Ph)**C**=P-P*t*Bu$_2$ – *Z* isomer;
- 145.71 ppm, (dd), $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 8.9 Hz, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*i*-C_{Ar}) – *Z* isomer;
- 129.42 ppm, (s), *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*p*-C_{Ar}) – *Z* isomer;
- 128.08 ppm, (dd), $J_{P\text{-}C}$ = 8.2 Hz, $J_{P\text{-}C}$ = 2.7 Hz, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*o*-C_{Ar}) – *Z* isomer;
- 127.00 ppm, (s), $J_{P\text{-}C}$ = 3.6 Hz, *t*Bu(**Ph**)C=P-P*t*Bu$_2$ (*m*-C_{Ar}) – *Z* isomer;
- 44. 18 ppm, (dd), $J_{P\text{-}C}$ = 21.6 Hz, $J_{P\text{-}C}$ = 3.2 Hz, {$(CH_3)_3$**C**}(Ph)C=P-P{C$(CH_3)_3\}_2$ – *Z* isomer;
- 32.93 ppm, (dd), $J_{P\text{-}C}$ = 30.2 Hz, $J_{P\text{-}C}$ = 5.0 Hz, {$(CH_3)_3$C}(Ph)C=P-P{**C**$(CH_3)_3\}_2$ – *Z* isomer;
- 31.19 ppm, (dd,) $J_{P\text{-}C}$ = 14.53 Hz, $J_{P\text{-}C}$ = 5.3 Hz, {$(CH_3)_3$C}(Ph)C=P-P{C(**C**$H_3)_3\}_2$ – *Z* isomer;
- 30.66 ppm, (d), $J_{P\text{-}C}$ = 15.0 Hz, {(**C**$H_3)_3$C}(Ph)C=P-P{C$(CH_3)_3\}_2$ – *Z* isomer;

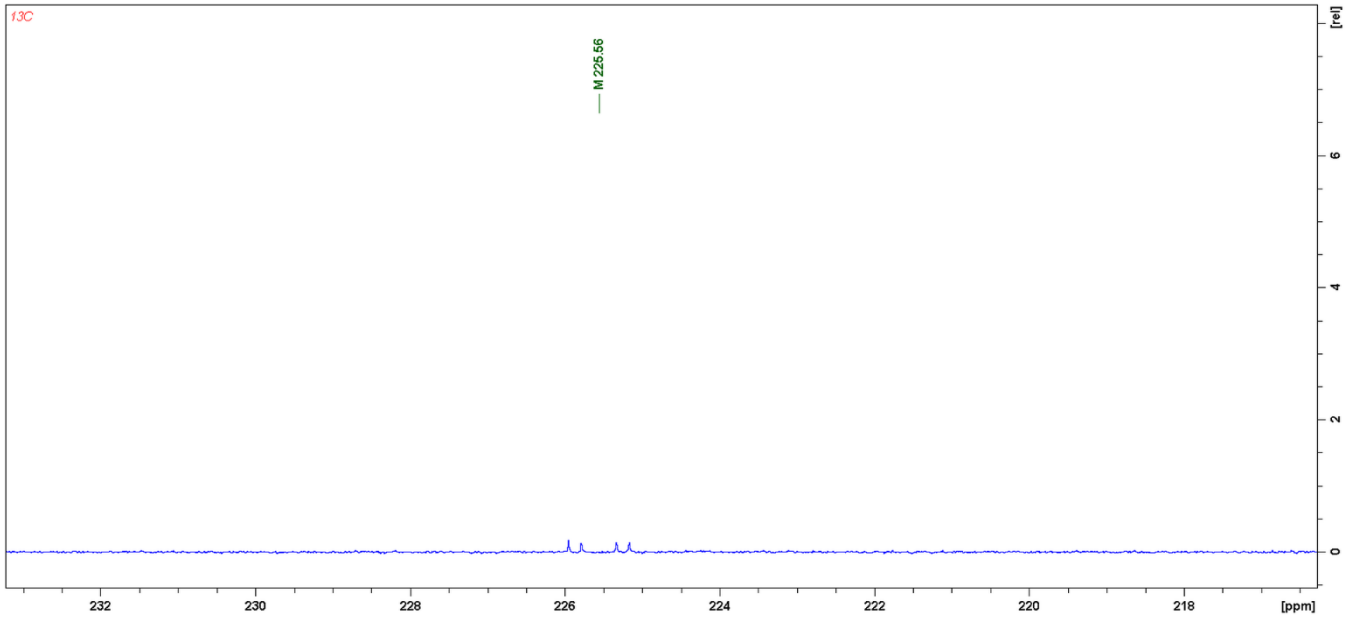


Figure S88. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of of isolated *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**) in the range from 235 ppm to 210 ppm.

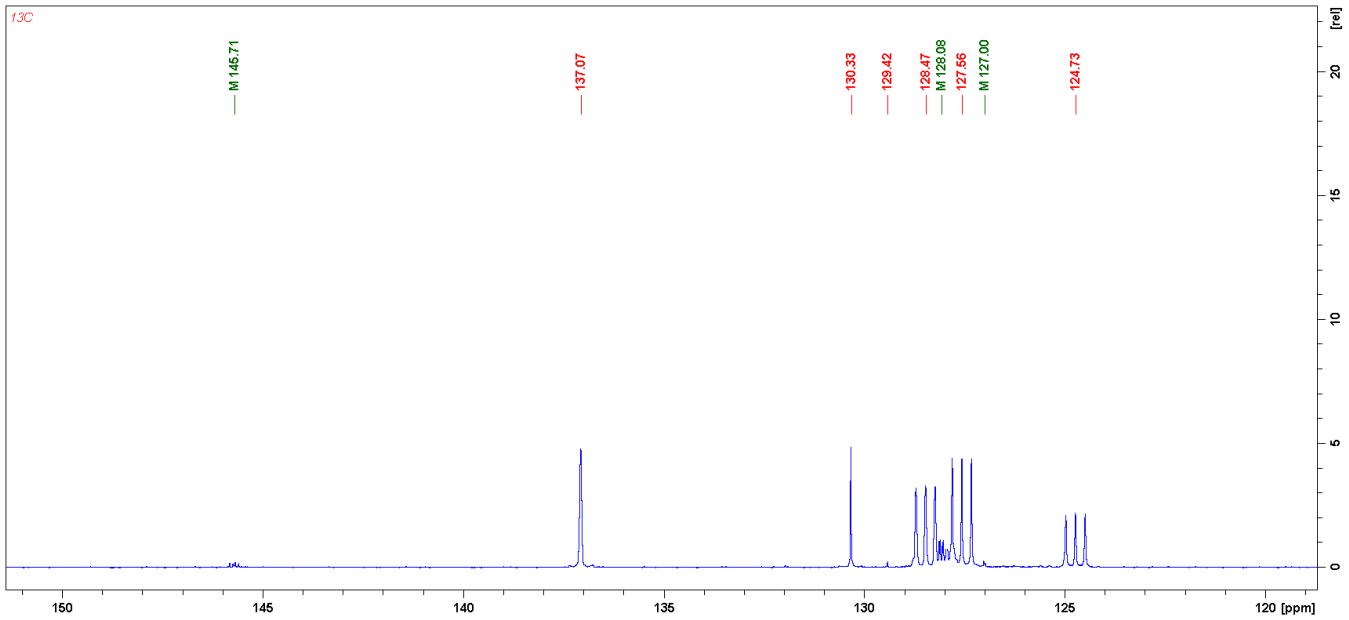


Figure S89. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of of isolated *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**) in the range from 140 ppm to 120 ppm.

- 127.07, 130.33 128.47, 127.56, 124.73 ppm, toluene-d_8;

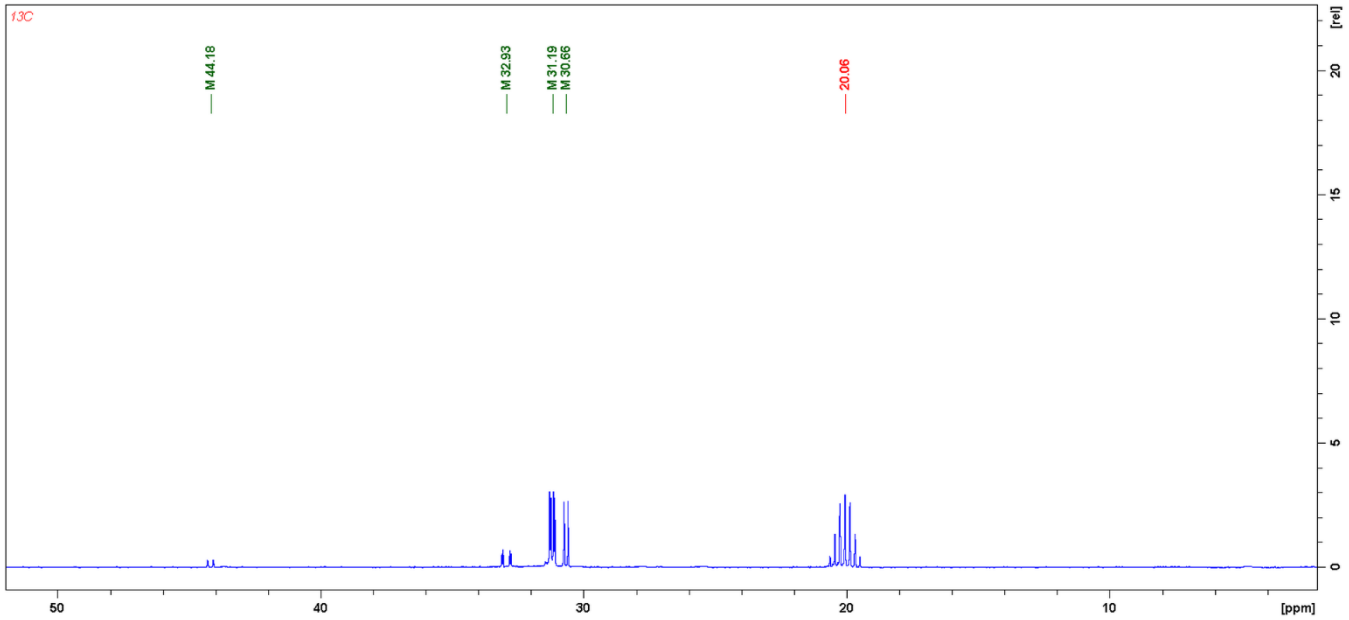


Figure S90. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of of isolated *t*Bu(Ph)C=P-P*t*Bu$_2$ (**3f**) in the range from 50 ppm to 0 ppm.

- 20.06 ppm, methyl group of toluene-d_8;

B.2.7. Acetone

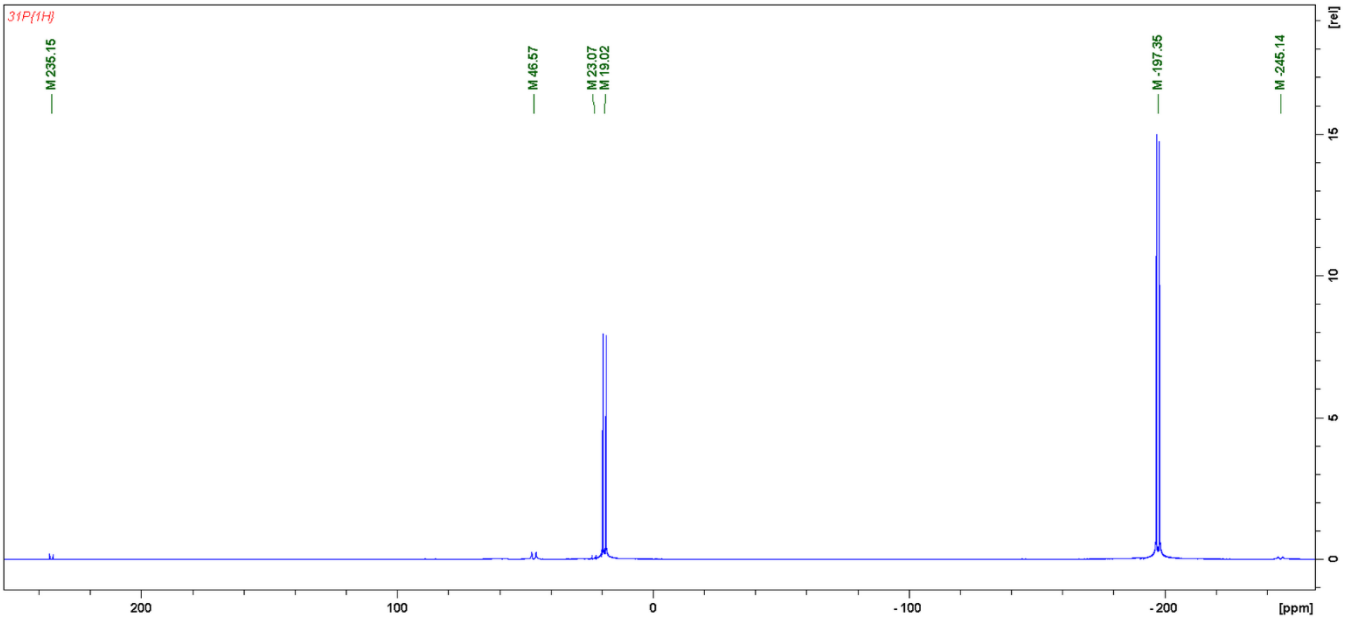


Figure S91. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetone.

- 235.53 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Me)_2C$=**P**-P*t*Bu_2;
- 46.57 ppm, (d), $J_{P\text{-}P}$ = 278.4 Hz, *t*Bu_2**P**-P($SiMe_3$)Li;
- 23.07 ppm, (d), $J_{P\text{-}P}$ = 228.9 Hz, $(Me)_2C$=P-**P***t*Bu_2;
- 19.02 ppm, (d), $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu_2**P**-P($SiMe_3$)H;
- -197.35 ppm, (d), $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu_2P-**P**($SiMe_3$)H;
- -245.14 ppm, (d), $J_{P\text{-}P}$ = 278.4 Hz, *t*Bu_2**P**-P($SiMe_3$)Li;

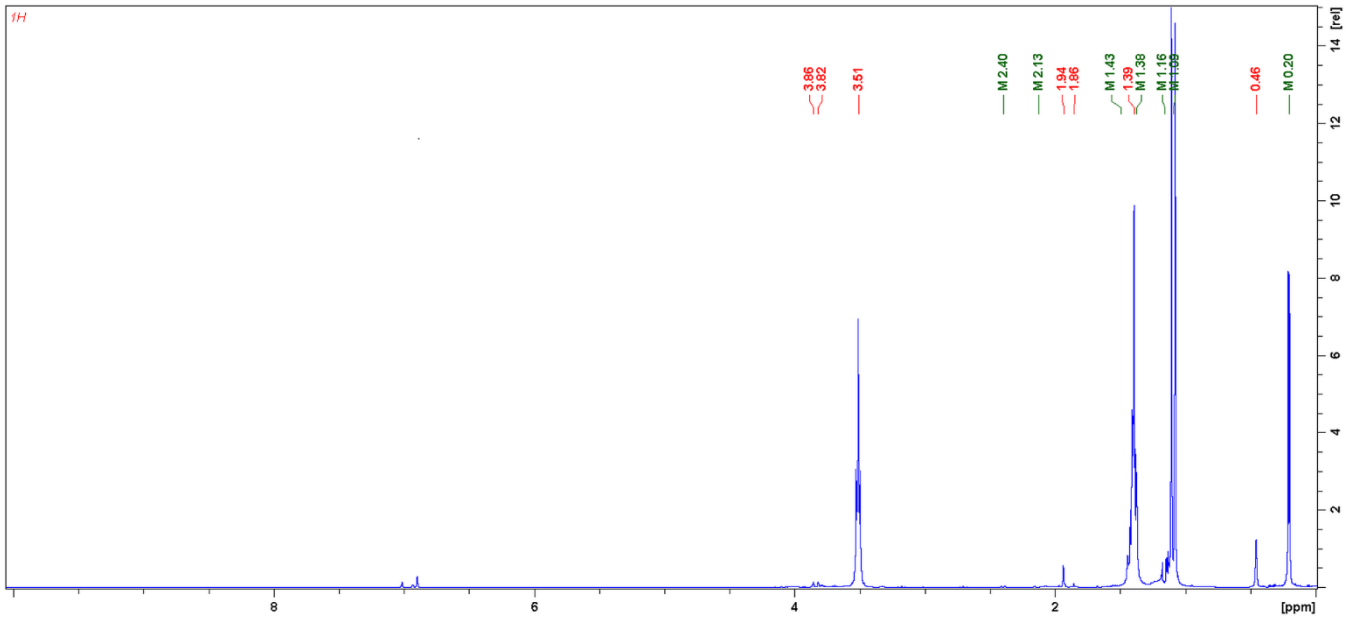


Figure S92. ^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) spectrum of reaction mixture of **2** with acetone.

- 3.86 ppm and 3.82 ppm (brad t), (Me)(**C**H$_2$=)**C**-OLi(THF)$_3$;
- 3.51 ppm, THF;
- 2.40 ppm, (d), 3 H, $J_{P\text{-}H}$ = 10.5 Hz, (**Me**)$_2$C=P-P*t*Bu$_2$;
- 2.13 ppm, (d), 3 H, $J_{P\text{-}H}$ = 20.4 Hz, (**Me**)$_2$C=P-P*t*Bu$_2$;
- 1.94 ppm, (broad s), 3H, (**Me**)(CH$_2$=)**C**-OLi(THF)$_3$;
- 1.86 ppm, (s), **Me**$_2$C=O;
- 1.43 ppm, (broad d), 18 H, $J_{P\text{-}H}$ = 10.4 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)Li;
- 1.39 ppm, THF;
- 1.38 ppm, (dd), 1H, $J_{P\text{-}H}$ = 187.2 Hz, $J_{P\text{-}H}$ = 2.5 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**;
- 1.16 ppm, (d), 18 H, $J_{P\text{-}H}$ = 14.2 Hz, (Me)$_2$C=P-P***t*Bu**$_2$;
- 1.09 ppm, (dd) 18 H, $J_{P\text{-}H}$ = 11.2 Hz, $J_{P\text{-}H}$ = 0.5 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)H;
- 0.46 ppm, (broad s), 9 H, *t*Bu$_2$P-P(Si**Me**$_3$)Li;
- 0.20 ppm, (dd) 9 H, $J_{P\text{-}H}$ = 4.1 Hz, $J_{P\text{-}H}$ = 0.6 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)H;

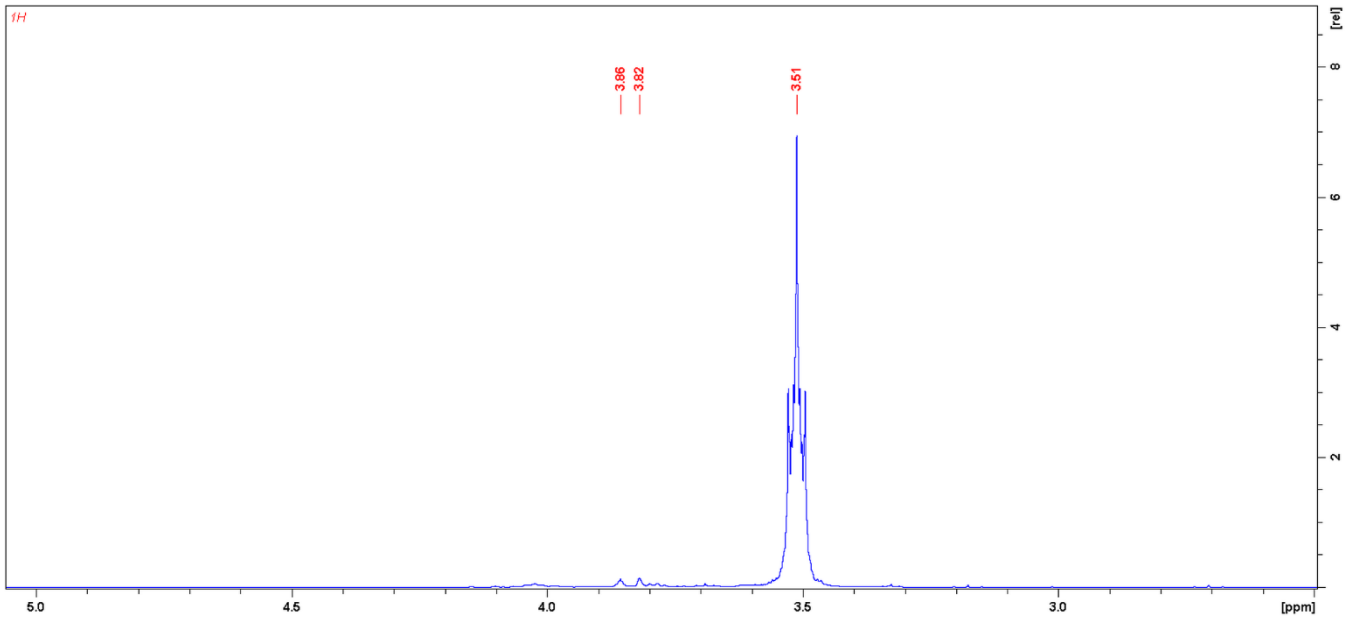


Figure S93. ^{1}H NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetone in the range from 5 ppm to 2 ppm.

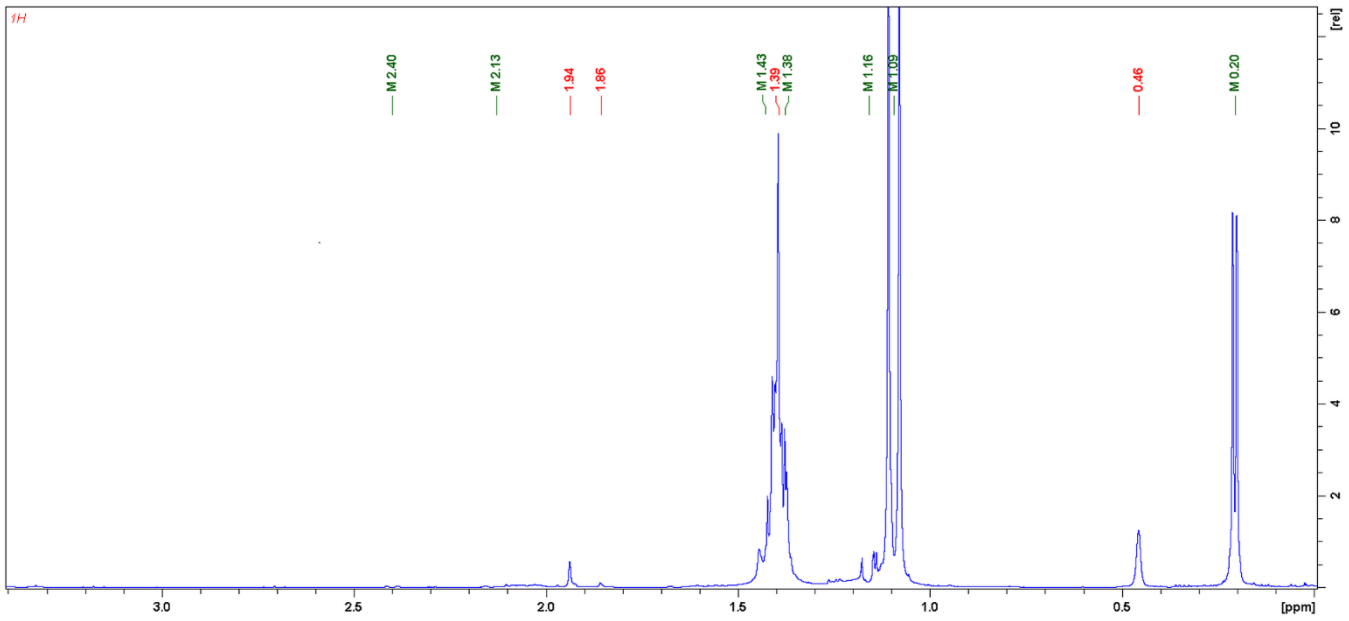


Figure S94. ^{1}H NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetone in the range from 3 ppm to 0 ppm.

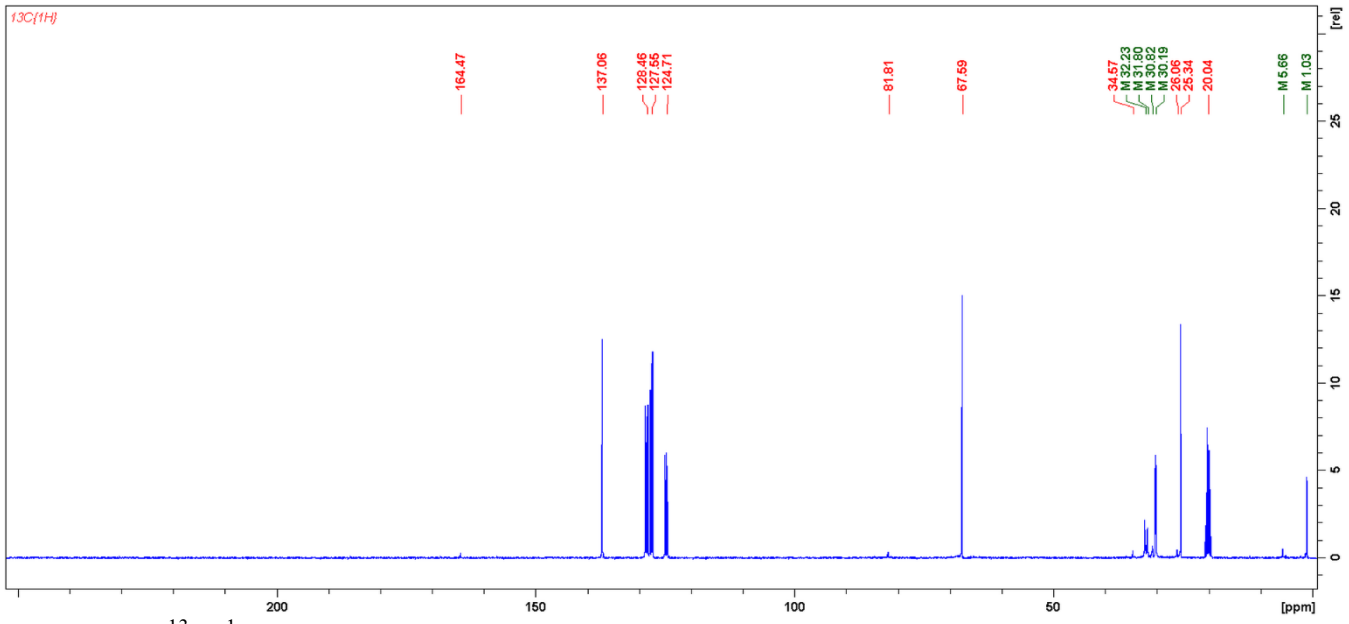


Figure S95. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetone.

- 164.47 ppm, (s), (Me)(CH_2=)**C**-OLi(THF)$_3$;
- 137.06 ppm, 128.45 ppm, 127.55 ppm, 124.71 ppm and 20.03 ppm, Tolene-d_8;
- 81.81 ppm, (s), (Me)(**C**H_2=)C-OLi(THF)$_3$;
- 67.59 ppm, (s), THF;
- 34.57 ppm, **Me**$_2$C=O
- 32.23 ppm, (broad dd), $J_{P\text{-}C}$ = 29.8 Hz, $J_{P\text{-}C}$ = 9.9 Hz, {(CH_3)$_3$**C**}P-P($SiMe_3$)Li;
- 31.80 ppm, (dd), $J_{P\text{-}C}$ = 14.9 Hz, $J_{P\text{-}C}$ = 2.5 Hz, {(**C**H_3)$_3$C}P-P($SiMe_3$)Li;
- 30.82 ppm, (broad dd), $J_{P\text{-}C}$ = 22.4 Hz, $J_{P\text{-}C}$ = 9.9 Hz, {(CH_3)$_3$**C**}P-P($SiMe_3$)H;
- 30.19 ppm, (dd), $J_{P\text{-}C}$ = 14.9 Hz, $J_{P\text{-}C}$ = 7.5 Hz, {(**C**H_3)$_3$C}P-P($SiMe_3$)H;
- 26.06 ppm, (s), (**Me**)(CH_2=)**C**-OLi(THF)$_3$;
- 25.34 ppm, (s), THF;
- 5.66 ppm, (broad dd), $J_{P\text{-}C}$ = 9.9 Hz, $J_{P\text{-}C}$ = 7.5 Hz, *t*Bu_2P-P(Si**Me**$_3$)Li;
- 1.03 ppm, (dd), $J_{P\text{-}C}$ = 9.9 Hz, $J_{P\text{-}C}$ = 4.9 Hz, *t*Bu_2P-P(Si**Me**$_3$)H;

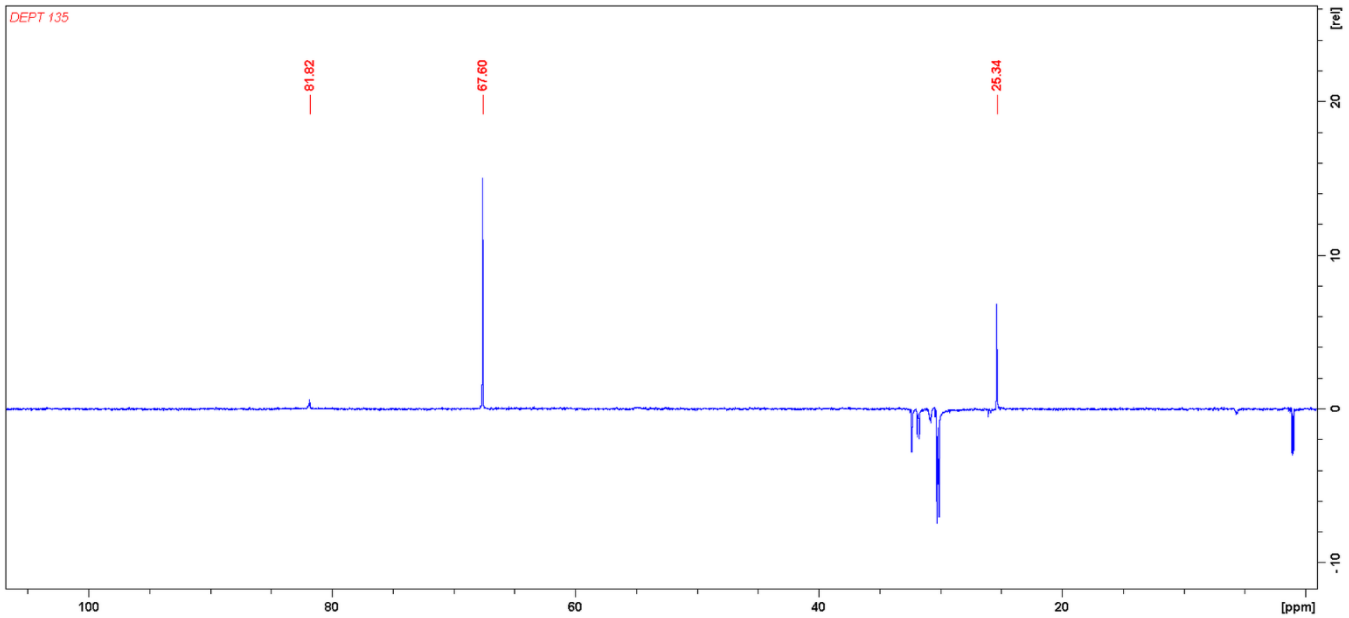


Figure S96. $^{13}C\{^{1}H\}$ NMR-DEPT 135 (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetone in the range from 100 ppm to 0 ppm.

B.2.8. Cyclohexanone

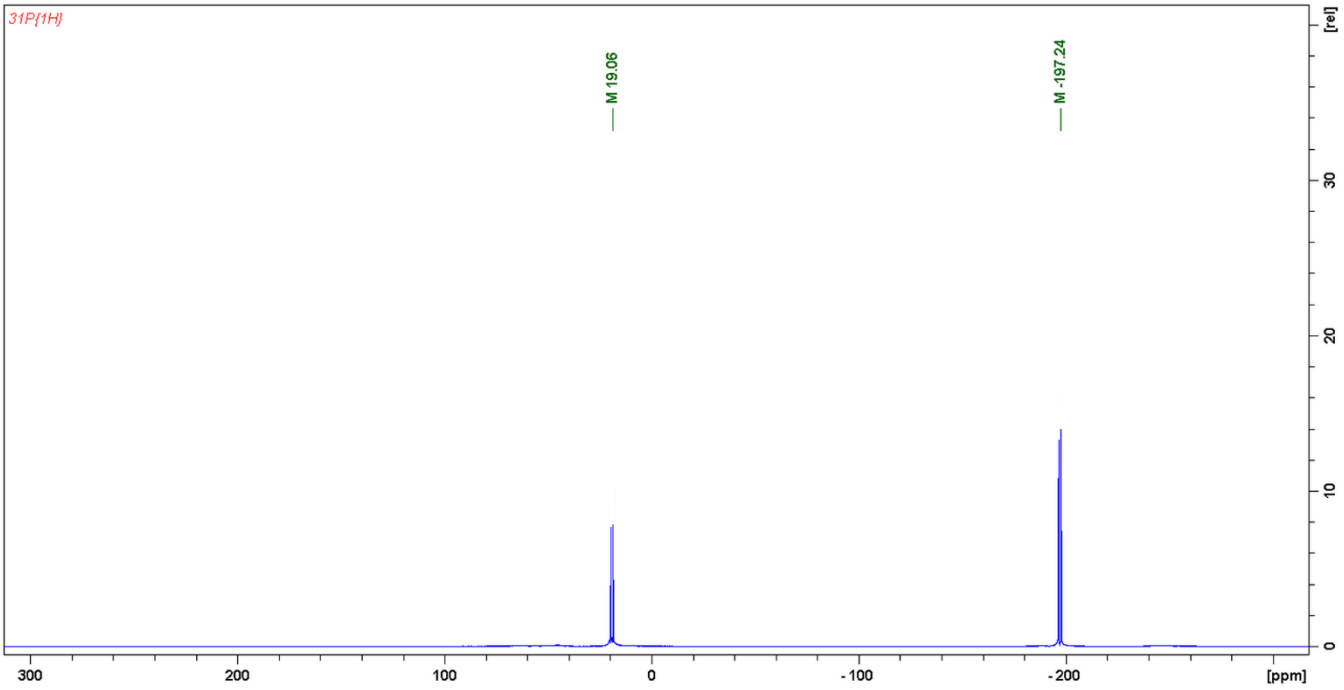


Figure S97. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclohexanone.

- 19.06 ppm, (d), $J_{P\text{-}P}$ = 188.7 Hz, tBu$_2$**P**-P(SiMe$_3$)H;
- -197.24 ppm, (d), $J_{P\text{-}P}$ = 188.7 Hz, tBu$_2$P-**P**(SiMe$_3$)H;

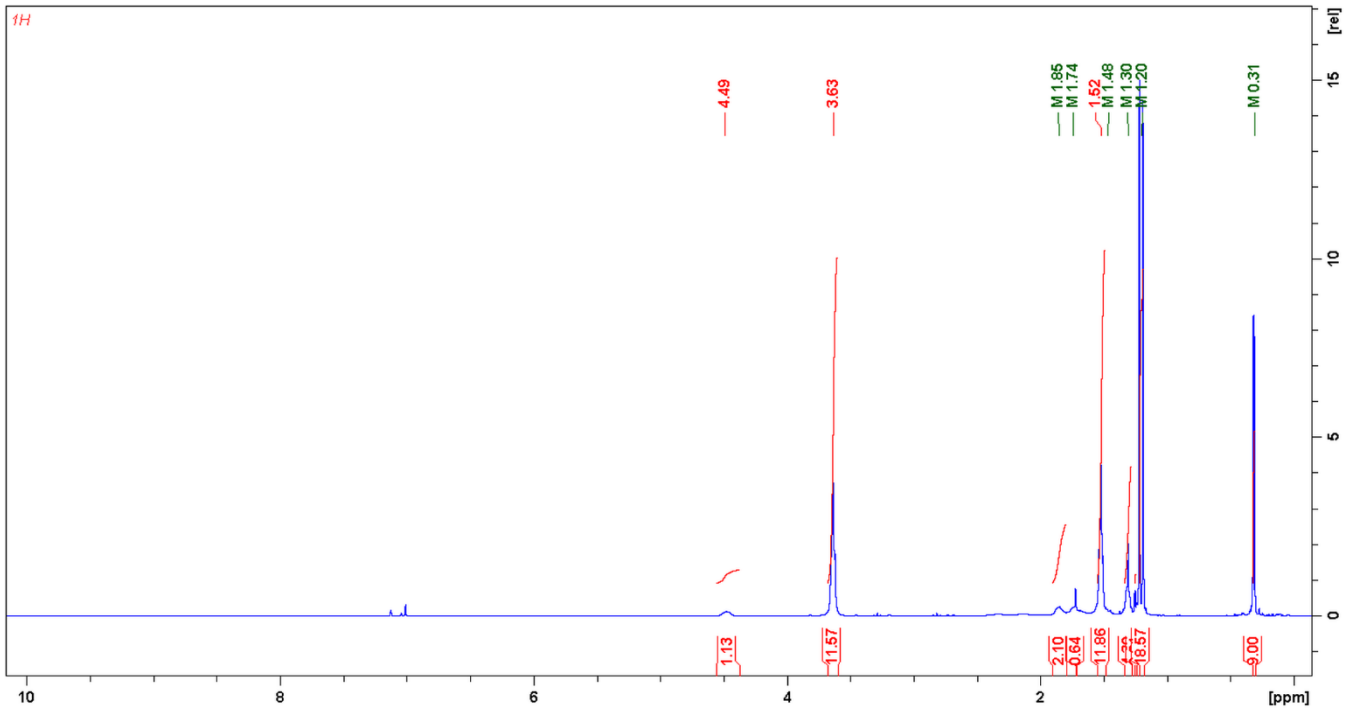


Figure S98. ^{1}HNMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclohexanone.

- 4.49 ppm, (broad s), (*cyclo*-$CH_2CH_2CH_2CH_2C\mathbf{H}$=C)OLi(THF)$_3$;
- 3.63 ppm and 1.52 ppm, (quintet), 24H, (*cyclo*-$CH_2CH_2CH_2CH_2CH$=C)OLi(**THF**)$_3$;
- 1.85 ppm, (broad m), 2 H, (*cyclo*-$CH_2CH_2CH_2C\mathbf{H}_2CH$=C)OLi(THF)$_3$;
- 1.74 ppm, (broad m), 2H, (*cyclo*-$C\mathbf{H}_2CH_2CH_2CH_2CH$=C)OLi(THF)$_3$;
- 1.48 ppm, (dd), 1H, $J_{P\text{-}H}$ = 188.4 Hz, $J_{P\text{-}H}$ = 2.5 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**;
- 1.30 ppm, (broad m), 4H, (*cyclo*-$CH_2C\mathbf{H}_2C\mathbf{H}_2CH_2CH$=C)OLi(THF)$_3$;
- 1.20 ppm, (d), 18H, $J_{P\text{-}H}$ = 11.4 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)H;
- 0.31 ppm, (dd), 9H, $J_{P\text{-}H}$ = 4.2 Hz, J_{PH} = 0.6 Hz, *t*Bu$_2$P-P(Si**M**e$_3$)H;

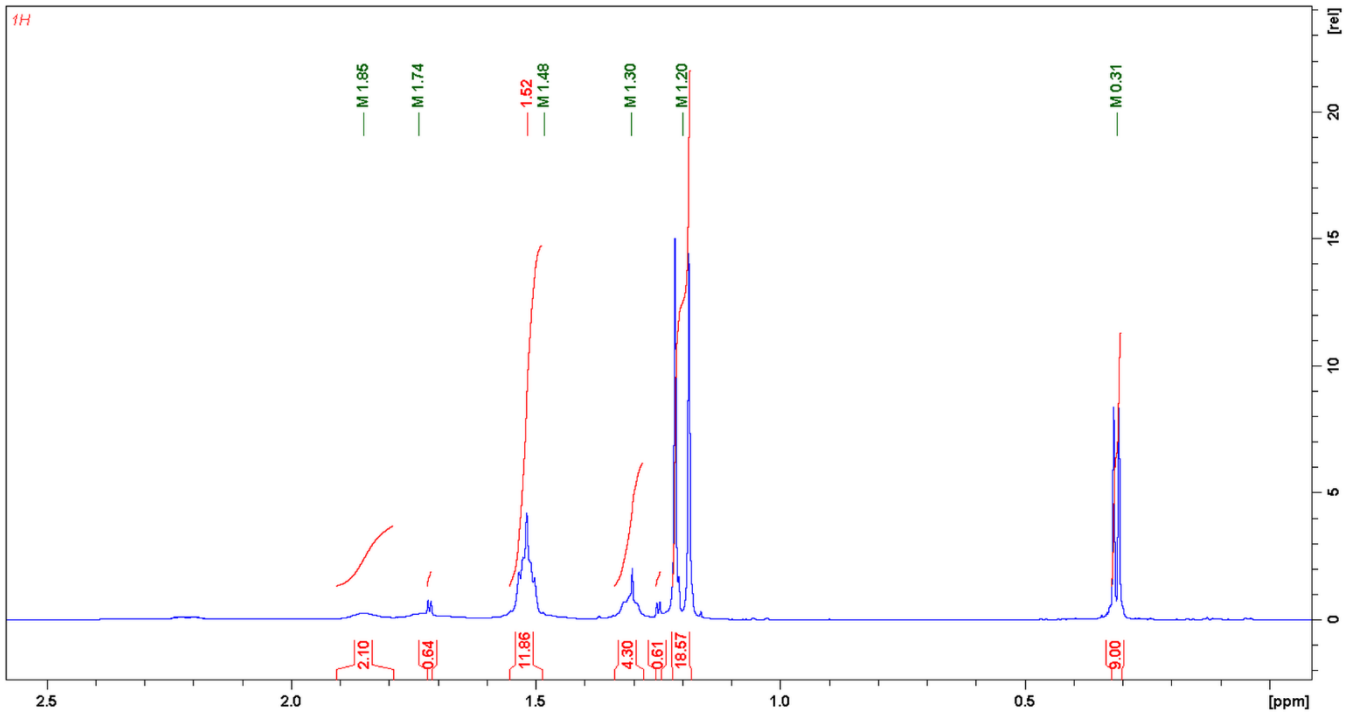


Figure S99. ^{1}H NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclohexanone in the range from 2.5 ppm to 0 ppm.

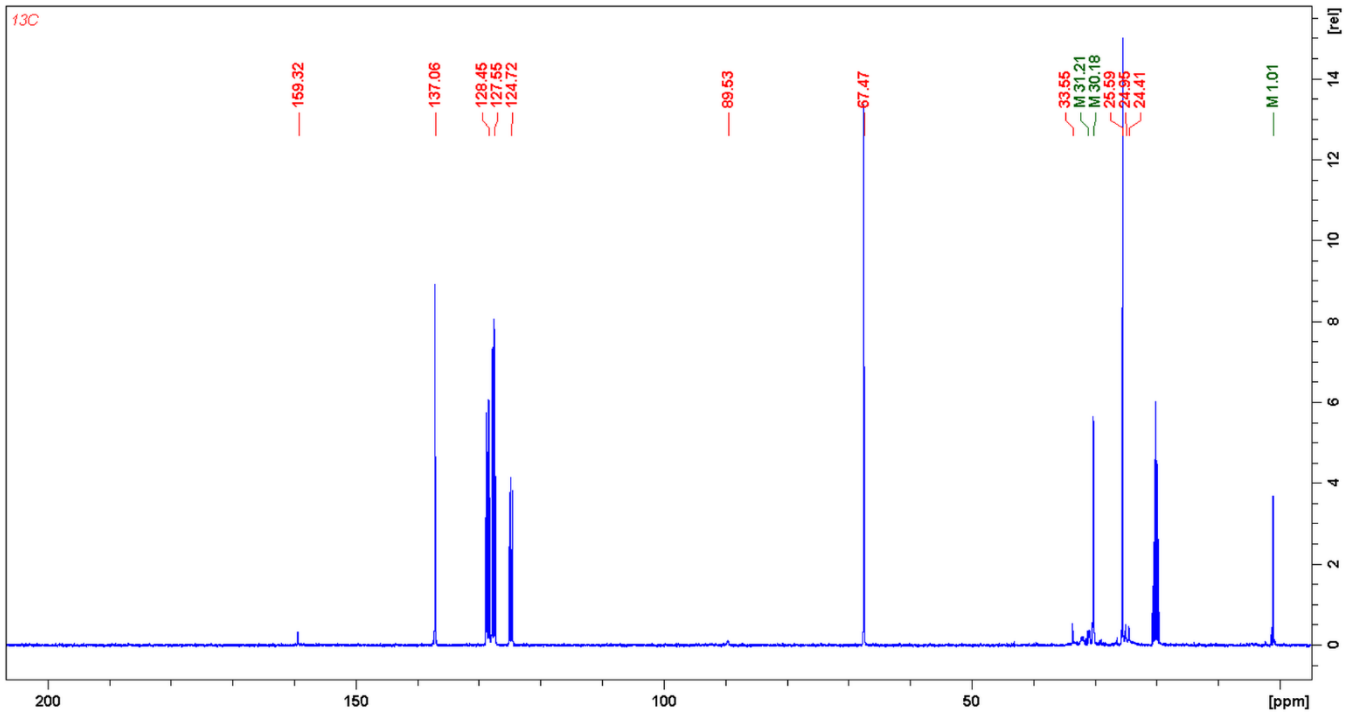


Figure S100. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclohexanone.

- 159.32 ppm, (s), (*cyclo*-$CH_2CH_2CH_2CH_2CH$=**C**)OLi(THF)$_3$;
- 137.06, 128.45, 127.55, 20.03 ppm, toluene-d_8;
- 89.53 ppm, (broad s), (*cyclo*-$CH_2CH_2CH_2CH_2$**C**H=C)OLi(THF)$_3$;
- 33.56 ppm, (s), (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$;
- 31.21 ppm, (dd), $J_{P\text{-}C}$ = 32.3 Hz, J_{PC} = 13.7 Hz, {$(CH_3)_3C$}$_2$P-P(Si**M**e$_3$)H;
- 30.18 ppm, (dd), $J_{P\text{-}C}$ = 14.9 Hz, J_{PC} = 6.2 Hz, {$(CH_3)_3C$}$_2$P-P(Si**M**e$_3$)H;
- 25.59 ppm, (s), (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$;
- 24.95 ppm, (s), (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$;
- 24.41 ppm, (s), (*cyclo*-$CH_2CH_2CH_2$**C**H_2CH=C)OLi(THF)$_3$;
- 1.01ppm, (dd), $J_{P\text{-}C}$ = 9.9 Hz, $J_{P\text{-}C}$ = 4.9 Hz, *t*Bu$_2$P-P(Si**M**e$_3$)H;

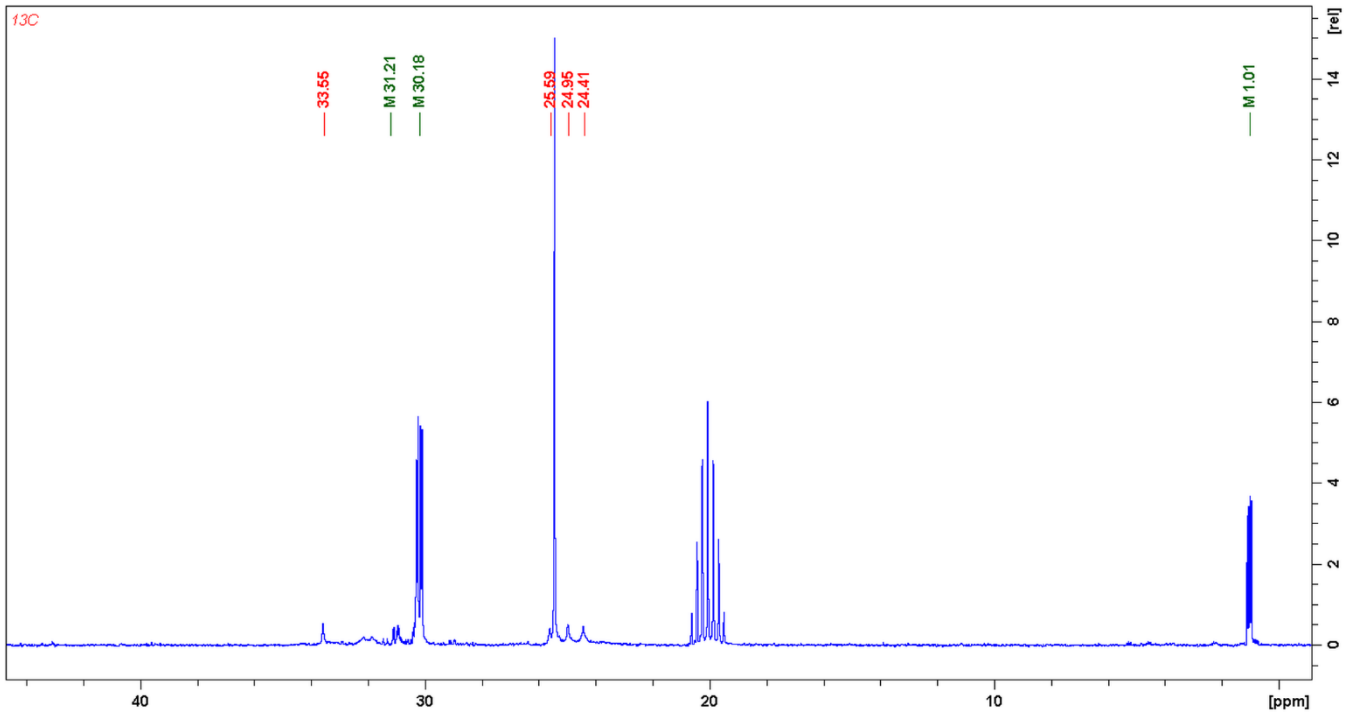


Figure S101. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclohexanone in the range from 45 ppm to 0 ppm.

B.2.9. Acetophenone

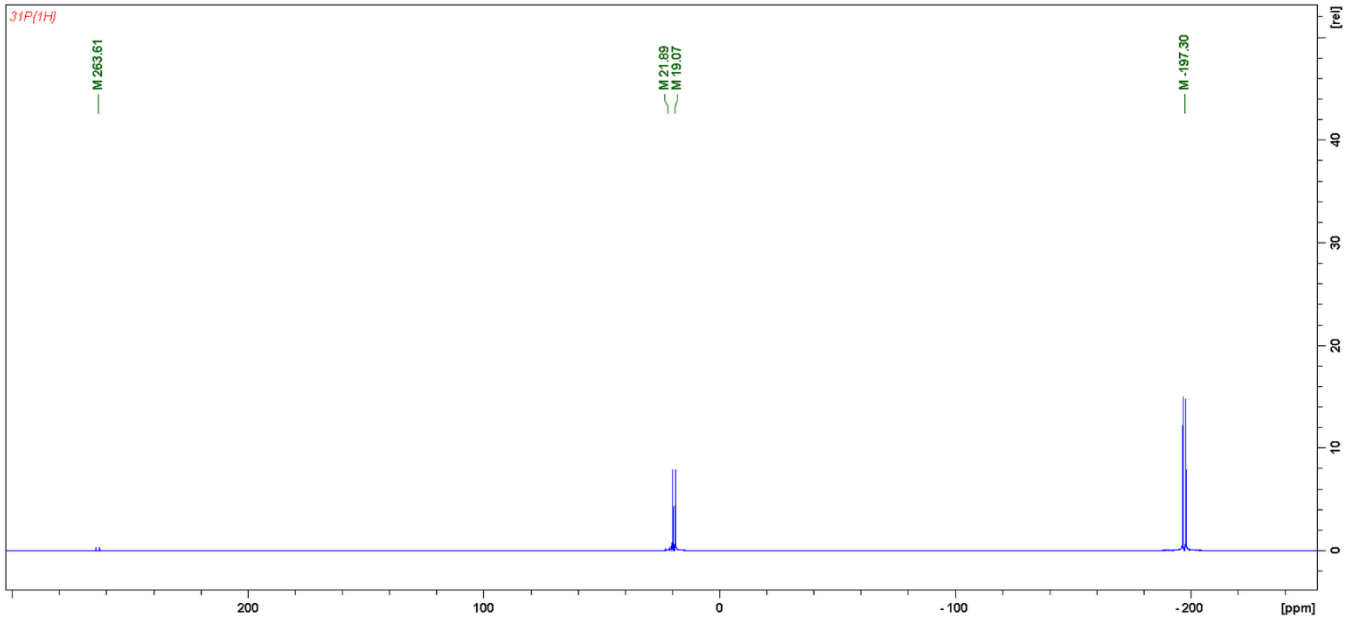


Figure S102. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetophenone.

- 263.61 ppm, (d), $J_{P\text{-}P}$ = 234.9 Hz, (Ph)MeC=**P**-P*t*Bu$_2$ – *E* isomer;
- 21.89 ppm, (d), $J_{P\text{-}P}$ = 234.9 Hz, (Ph)MeC=P-**P***t*Bu$_2$ – *E* isomer;
- 19.07 ppm, (d), 188.7 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H;
- -197.30 ppm, (d), 188.7 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H;

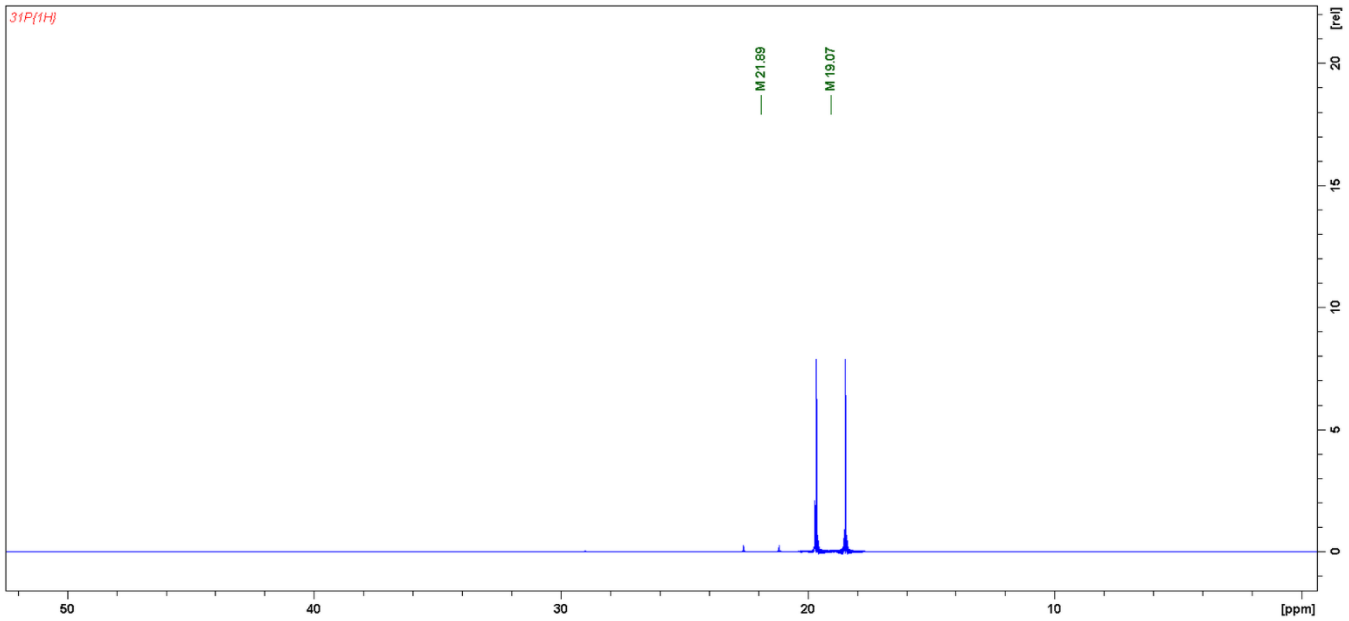


Figure S103. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetophenone in the range from 50 ppm to 0 ppm.

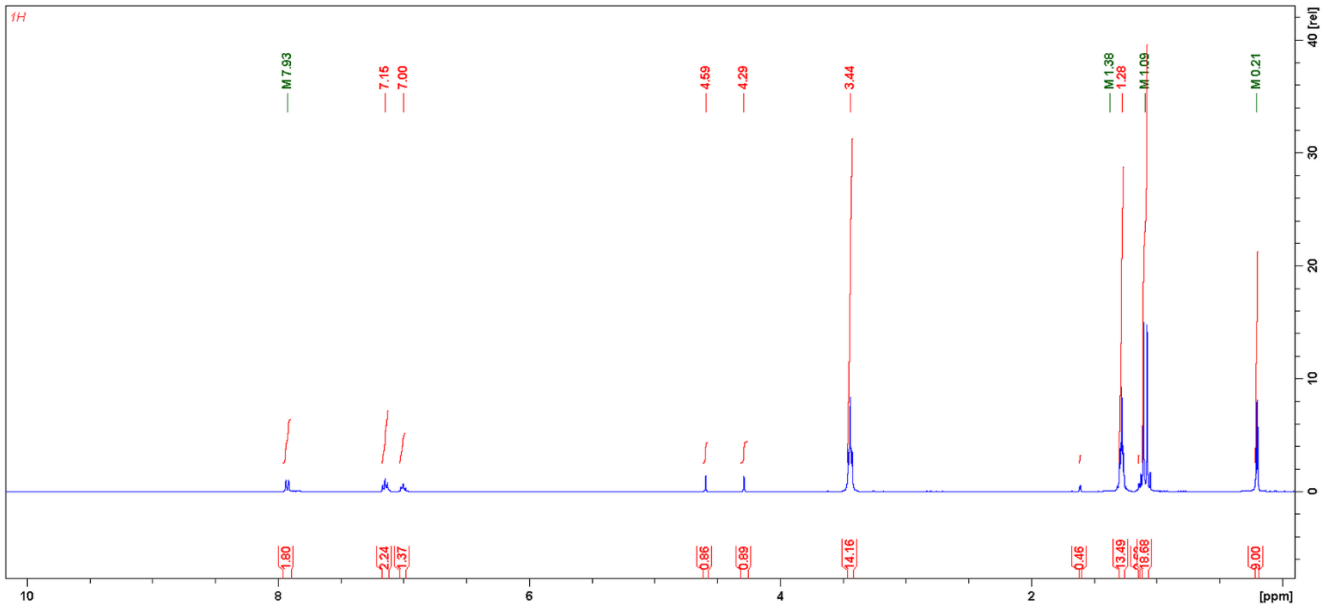


Figure S104. ^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) spectrum of reaction mixture of **2** with acetophenone.

- 7.93 ppm, (dd), 2H, $J_{H\text{-}H}$ = 9.2 Hz, $J_{H\text{-}H}$ = 1.1 Hz, (**Ph**)(CH$_2$=)C-OLi(THF)$_3$, (*m*-H$_{Ar}$);
- 7.15 ppm, (t), 2H, $J_{H\text{-}H}$ = 7.5 Hz, (**Ph**)(CH$_2$=)C-OLi(THF)$_3$, (*o*-H$_{Ar}$);
- 7.00 ppm, (t), 1H, $J_{H\text{-}H}$ = 7.5 Hz, (**Ph**)(CH$_2$=)C-OLi(THF)$_3$, (*p*-H$_{Ar}$);
- 4.59 ppm and 4.29 ppm, (s), 2H, (Ph)(C**H**$_2$=)C-OLi(THF)$_3$;
- 3.44 ppm and 1.28 ppm, (quintet), 24H of 3 THF molecules;
- 1.38 ppm, (dd), 1H, $J_{P\text{-}H}$ = 187.2 Hz, $J_{P\text{-}H}$ = 2.4 Hz, *t*Bu$_2$P-P(SiMe$_3$)**H**;
- 1.09 ppm, (d), 18H, $J_{P\text{-}H}$ = 11.2 Hz, ***t*Bu**$_2$P-P(SiMe$_3$)H;
- 0.21 ppm, (d), 9H, $J_{P\text{-}H}$ = 4.2 Hz, *t*Bu$_2$P-P(Si**Me**$_3$)H;

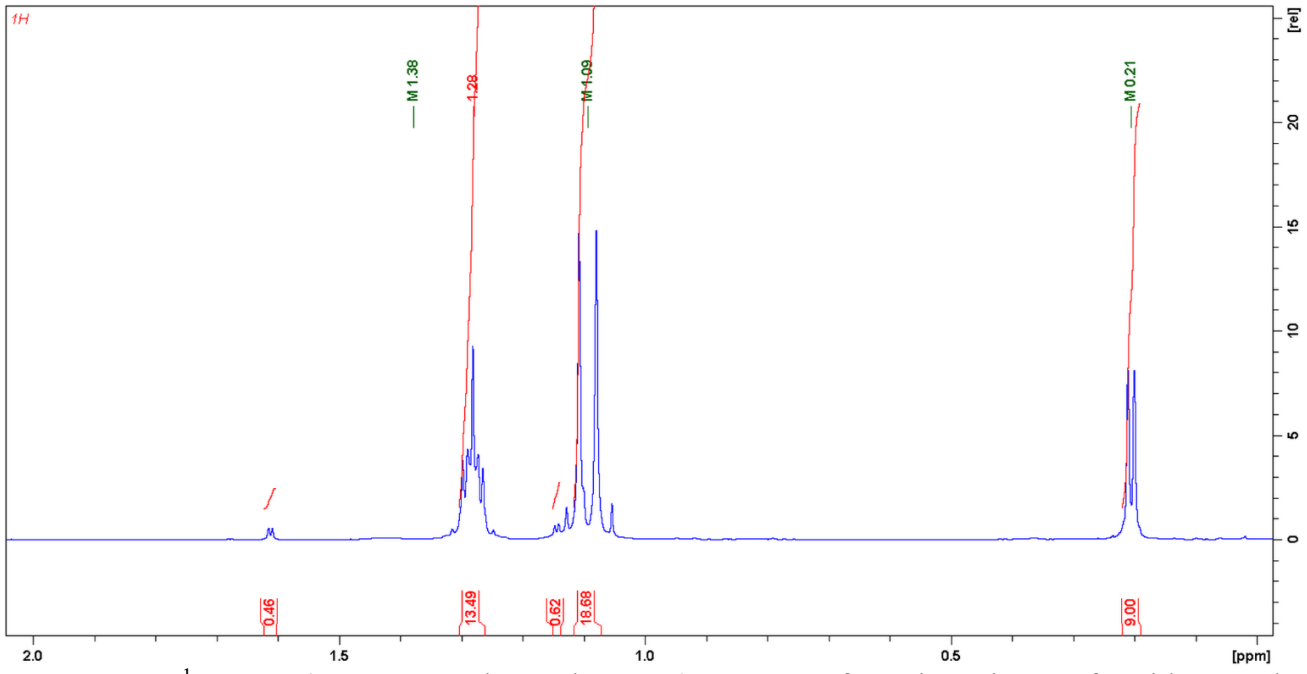


Figure S105. ^{1}H NMR (400 MHz, Toluene-d$_8$, 298 K) spectrum of reaction mixture of **2** with acetophenone in the range from 2 ppm to 0 ppm.

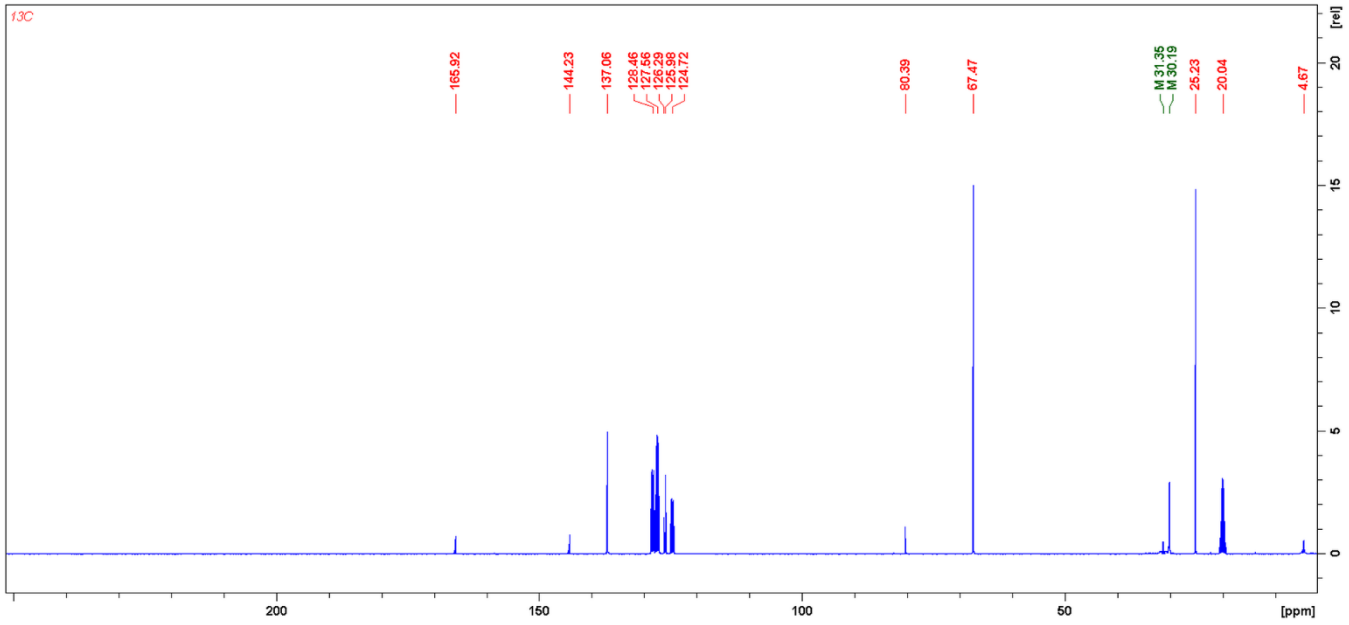


Figure S106. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with aceto-phenone.

- 165.92 ppm, (s), (Ph)(CH_2=)**C**-OLi(THF)$_3$, (*i*-C_{Ar});
- 144.23 ppm, (s), (**Ph**)(CH_2=)C-OLi(THF)$_3$, (*i*-C_{Ar});
- 127.56 ppm, (s), (**Ph**)(CH_2=)C-OLi(THF)$_3$, (*o*-C_{Ar});
- 126.29 ppm, (s), (**Ph**)(CH_2=)C-OLi(THF)$_3$, (*p*-C_{Ar});
- 125.98 ppm, (s), (**Ph**)(CH_2=)C-OLi(THF)$_3$, (*m*-C_{Ar});
- 80.39 ppm, (s) (Ph)(**C**H_2=)C-OLi(THF)$_3$;
- 67.47 ppm and 25.23 ppm, (Ph)(CH_2=)C-OLi(**THF**)$_3$;
- 137.06, 128.46, 127.56, 124.72 and 20.04 ppm, Toluene-d_8;
- 31.35 ppm, (dd), $J_{P\text{-}C}$ = 34.2 Hz, $J_{P\text{-}C}$ = 5.9 Hz, {(CH_3)**C**}$_2$P-P($SiMe_3$)H;
- 30.19 ppm, (dd), $J_{P\text{-}C}$ = 14.5 Hz, $J_{P\text{-}C}$ = 5.5 Hz, {(**C**H_3)C}$_2$P-P($SiMe_3$)H;
- 4.67 ppm, (dd), $J_{P\text{-}C}$ = 10.4 Hz, $J_{P\text{-}C}$ = 5.2 Hz, {(CH_3)C}$_2$P-P(Si**Me**$_3$)H;

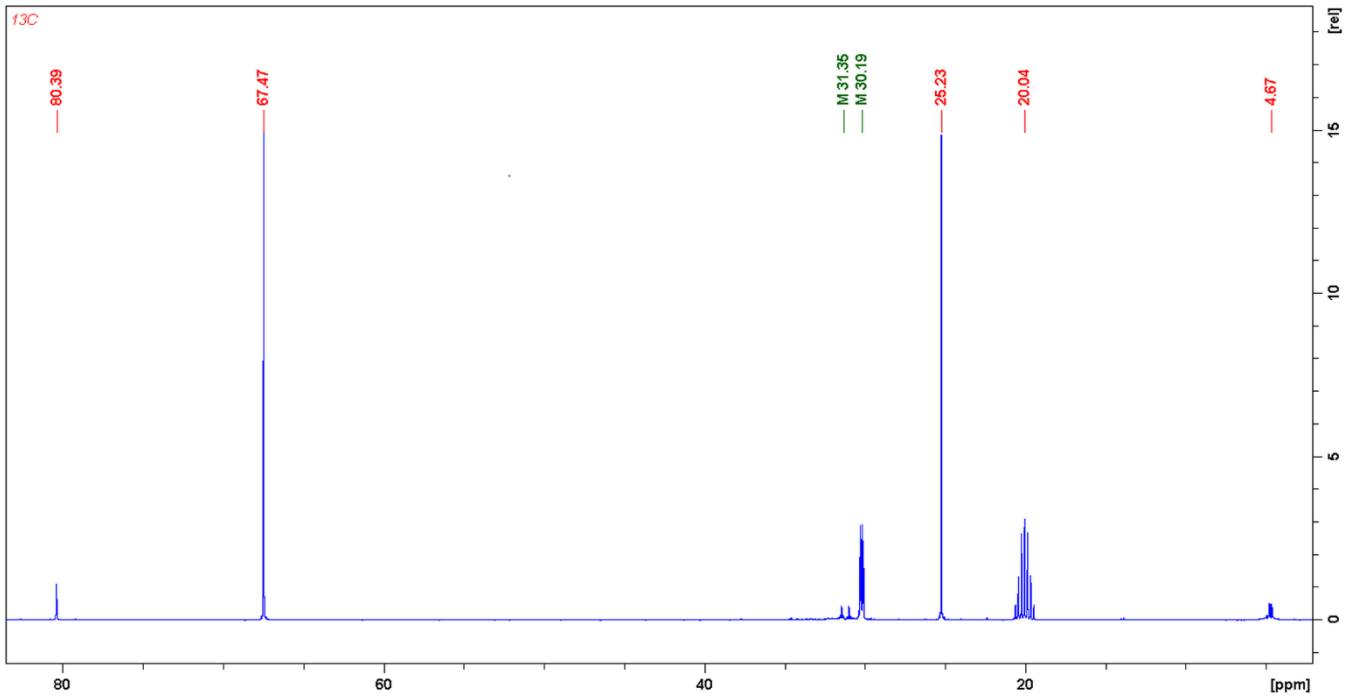


Figure S107. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with acetophenone in the range of 85 ppm to 0 ppm.

B.2.10. Cyclopropyl methyl ketone

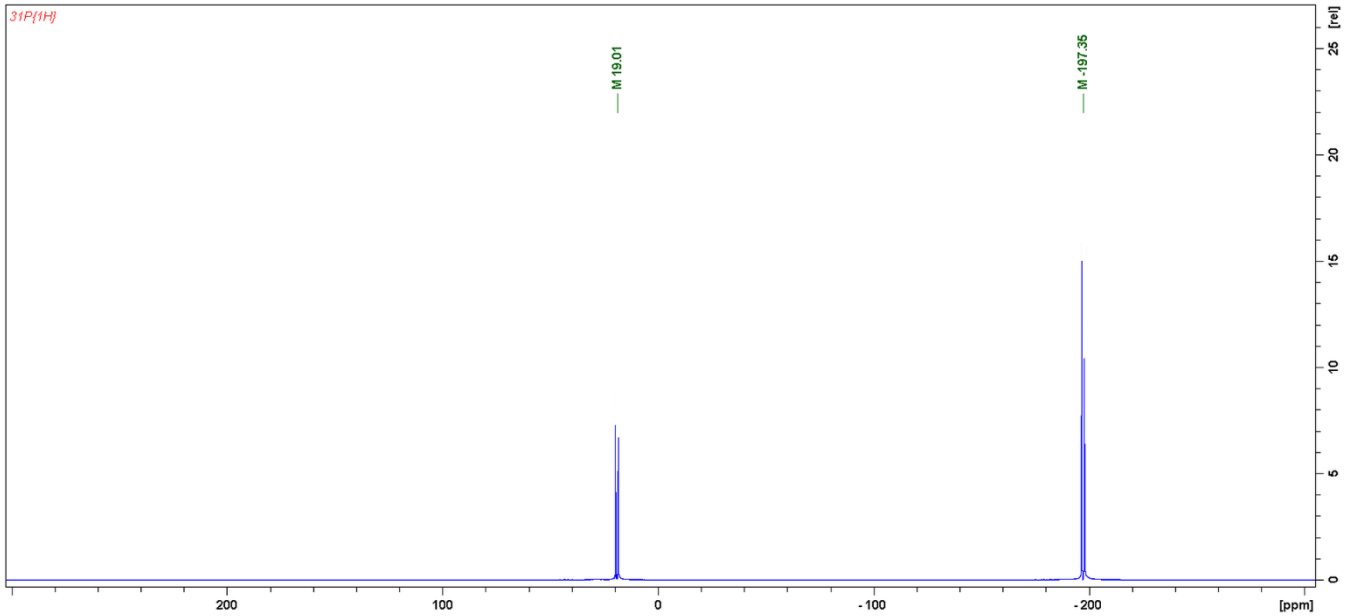


Figure S108. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclopropyl methyl ketone.

- 19.01 ppm, (d), $J_{P\text{-}P}$ = 188.9 Hz, tBu$_2$P-P(SiMe$_3$)H;
- -197.35 ppm, (d), $J_{P\text{-}P}$ = 188,9 Hz, tBu$_2$P-P(SiMe$_3$)H;

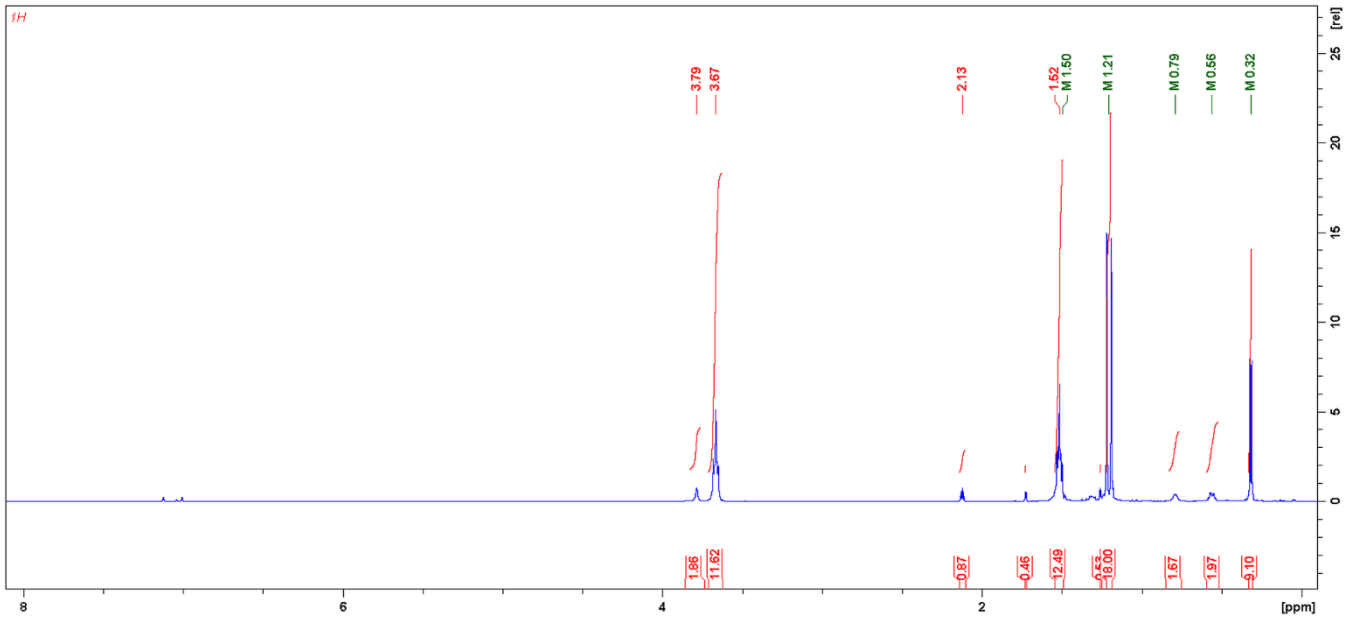


Figure S109. ^{1}H NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclopropyl methyl ketone.

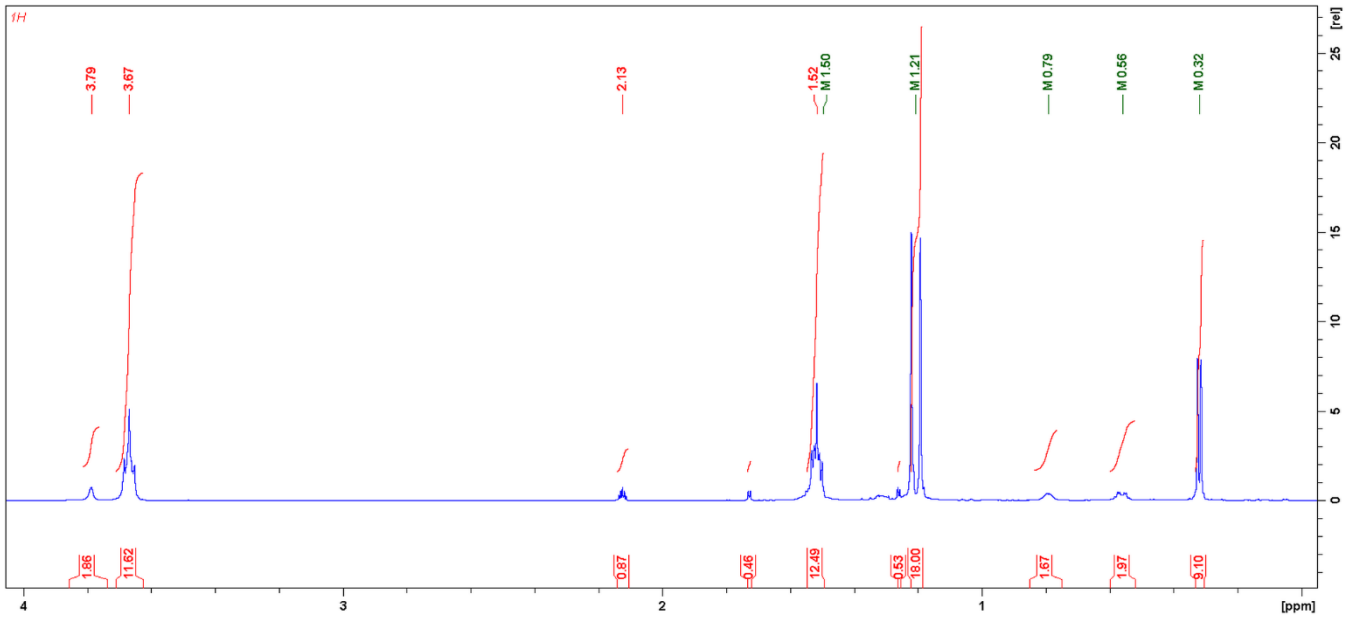


Figure S110. ^{1}H NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclopropyl methyl ketone in the range from 4 ppm to 0 ppm.

- 3.79 ppm, (broad s), 2H, $(CH_2CH_2CH)(C\mathbf{H}_2{=})C\text{-}OLi(THF)_3$;
- 3.76 and 1.52 ppm, (quinted), 24H, $(CH_2CH_2CH)(CH_2{=})C\text{-}OLi(\mathbf{THF})_3$;
- 2.13 ppm, (sept.), 1H, $(CH_2CH_2C\mathbf{H})(CH_2{=})C\text{-}OLi(THF)_3$;
- 1.50 ppm, (dd), 1H, $J_{P\text{-}H}$ = 188.3 Hz, $J_{P\text{-}H}$ = 2.7 Hz, tBu$_2$P-P(SiMe$_3$)**H**;
- 1.21 ppm, (d), 18H, 1H, $J_{P\text{-}H}$ = 11.4 Hz, tBu$_2$P-P(SiMe$_3$)**H;**
- 0.79 ppm, (broad m), 2H, $(CH_2C\mathbf{H}_2CH)(CH_2{=})C\text{-}OLi(THF)_3$;
- 0.55 ppm, (broad m), 2H, $(C\mathbf{H}_2CH_2CH)(CH_2{=})C\text{-}OLi(THF)_3$;

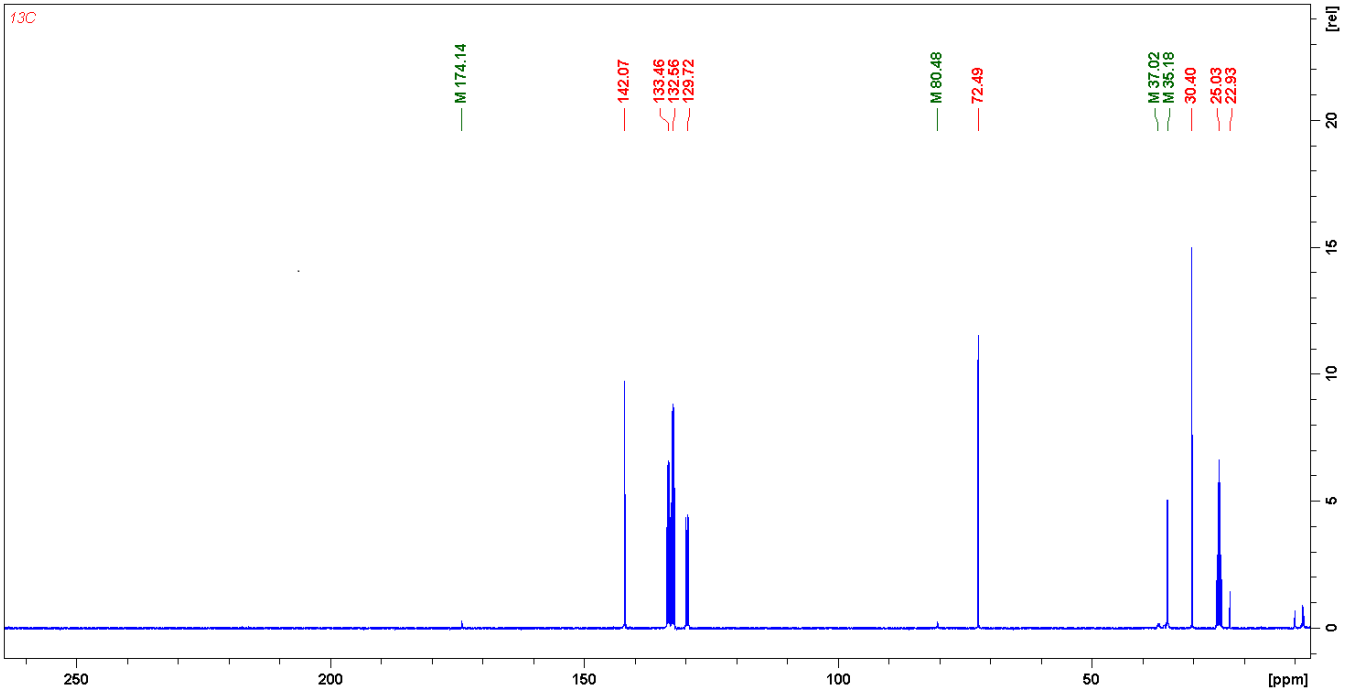


Figure S111. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclopropyl methyl ketone.

- 142.07, 133.46, 132.56, 129.72, 25.03 ppm, tolene-d_8;
- 174.14 ppm, (s), $(CH_2CH_2CH)(CH_2=)$**C**-OLi$(THF)_3$;
- 80.48 ppm, (s), $(CH_2CH_2CH)($**C**$H_2=)$C-OLi$(THF)_3$;
- 72.49, 30.40 ppm, (s), $(CH_2CH_2CH)(CH_2=)$C-OLi(**THF**)$_3$;
- 37.02 ppm, (broad d), $J_{P\text{-}C}$ = 34.5 Hz, $\{(CH_3)$**C**$\}_2$P-P$(SiMe_3)$H;
- 35.18 ppm, (dd), $J_{P\text{-}C}$ = 30.2 Hz, $J_{P\text{-}C}$ = 5.4 Hz, $\{($**C**$H_3)C\}_2$P-P$(SiMe_3)$H;
- 22.93 ppm, (s), $(CH_2CH_2$**C**$H)(CH_2=)$C-OLi$(THF)_3$;
- 10.10 ppm, (s), (**C**H_2**C**$H_2CH)(CH_2=)$C-OLi$(THF)_3$;
- 7.82 ppm, (dd), $J_{P\text{-}C}$ = 10.4 Hz, $J_{P\text{-}C}$ = 5.1 Hz, $\{($**C**$H_3)C\}_2$P-P(Si**Me**$_3)$H;

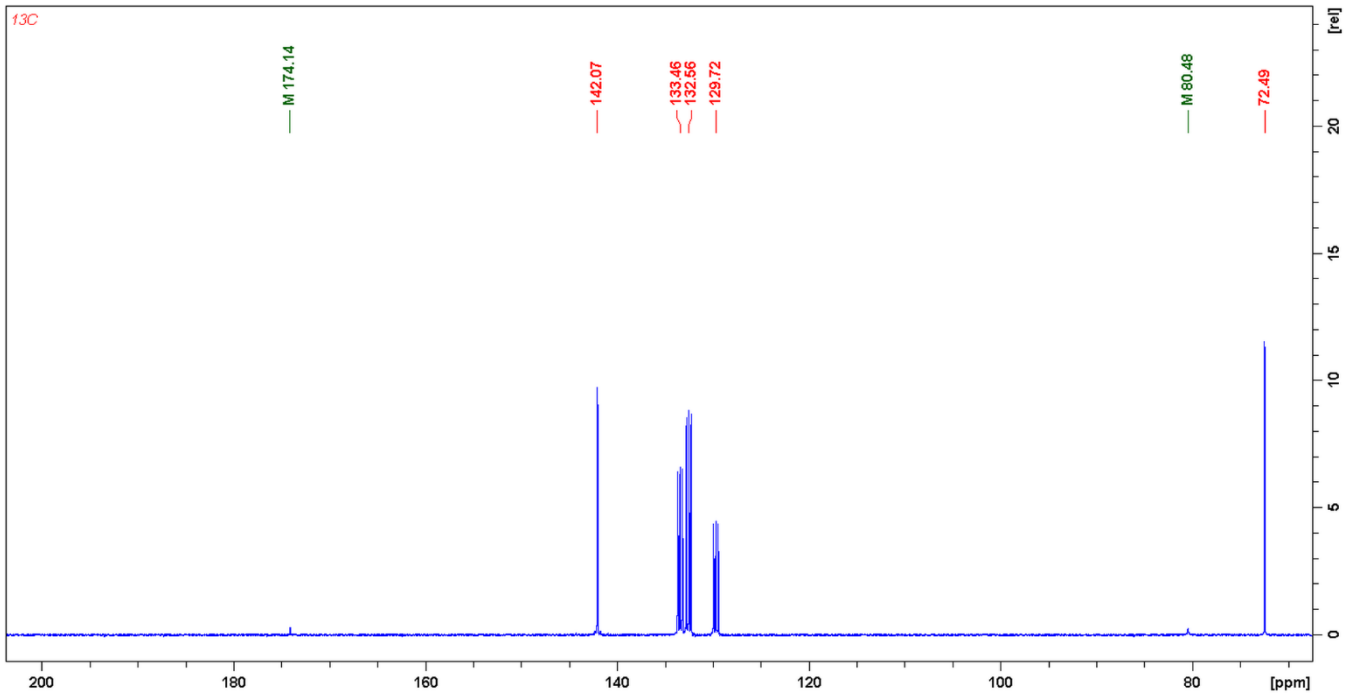


Figure S112. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclopropyl methyl ketone in the range of 200 ppm to 70 ppm.

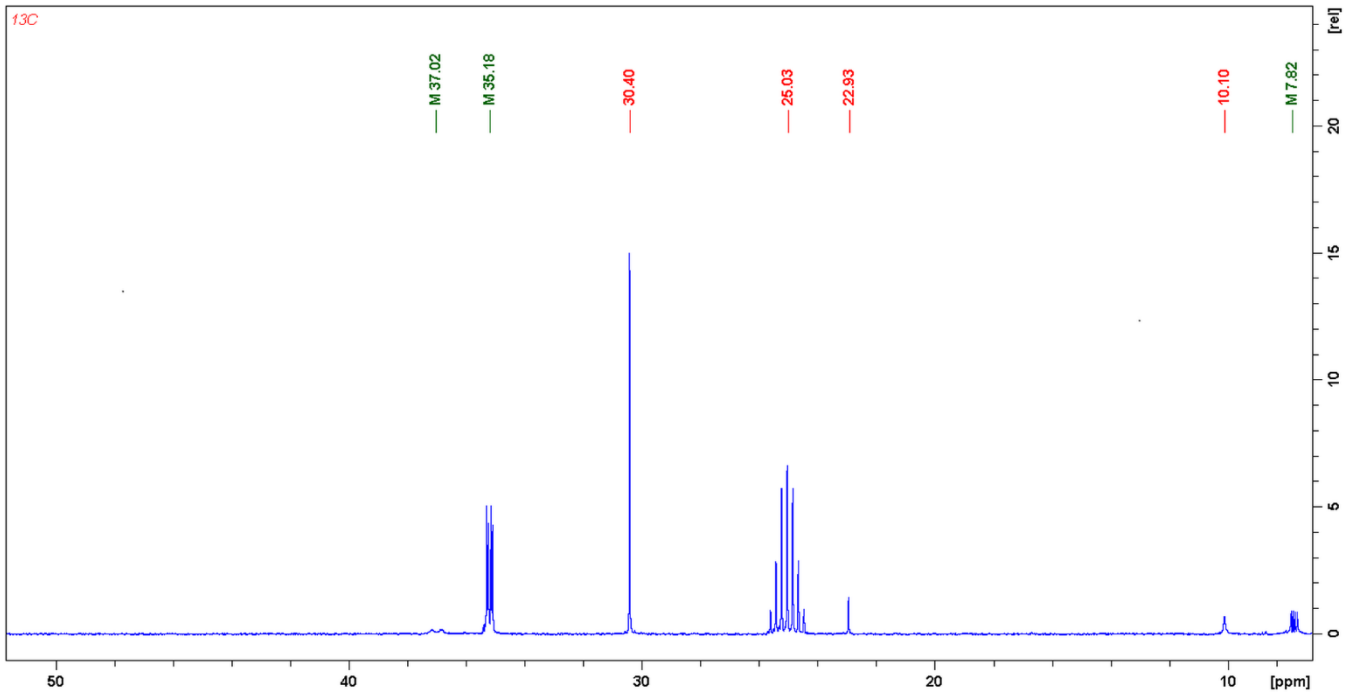


Figure S113. $^{13}C\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with cyclopropyl methyl ketone in the range of 50 ppm to 0 ppm.

B.2.11. Isobutyraldehyde

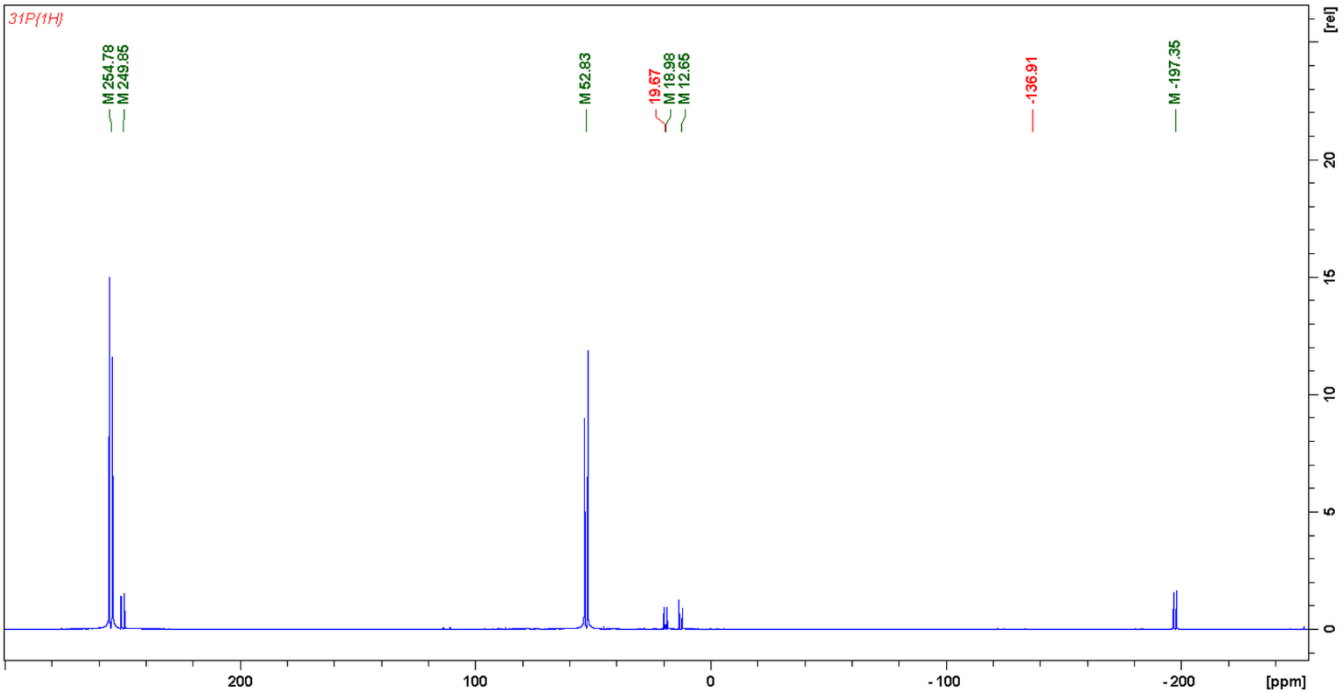


Figure S114. $^{31}P\{^{1}H\}$ NMR (400 MHz, Toluene-d_8, 298 K) spectrum of reaction mixture of **2** with isobutyraldehyde.

- 254.78 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {(Me)$_2$CH}(H)C=**P**-P*t*Bu$_2$ – *E* isomer;
- 249.85 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {(Me)$_2$CH}(H)C=**P**-P*t*Bu$_2$ – *Z* isomer;
- 52.83 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$ – *E* isomer;
- 19.47 ppm, (s), *t*Bu$_2$PH;
- 18.98 ppm, (d), $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$P-P(SiMe$_3$)H;
- 12.65 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {(Me)$_2$CH}(H)C=P-**P***t*Bu$_2$ – *Z* isomer;
- -197.35 ppm, (d), $J_{P\text{-}P}$ = 188.7 Hz, *t*Bu$_2$P-P(SiMe$_3$)H;

B.2.12. Cyclohexanecarboxaldehyde

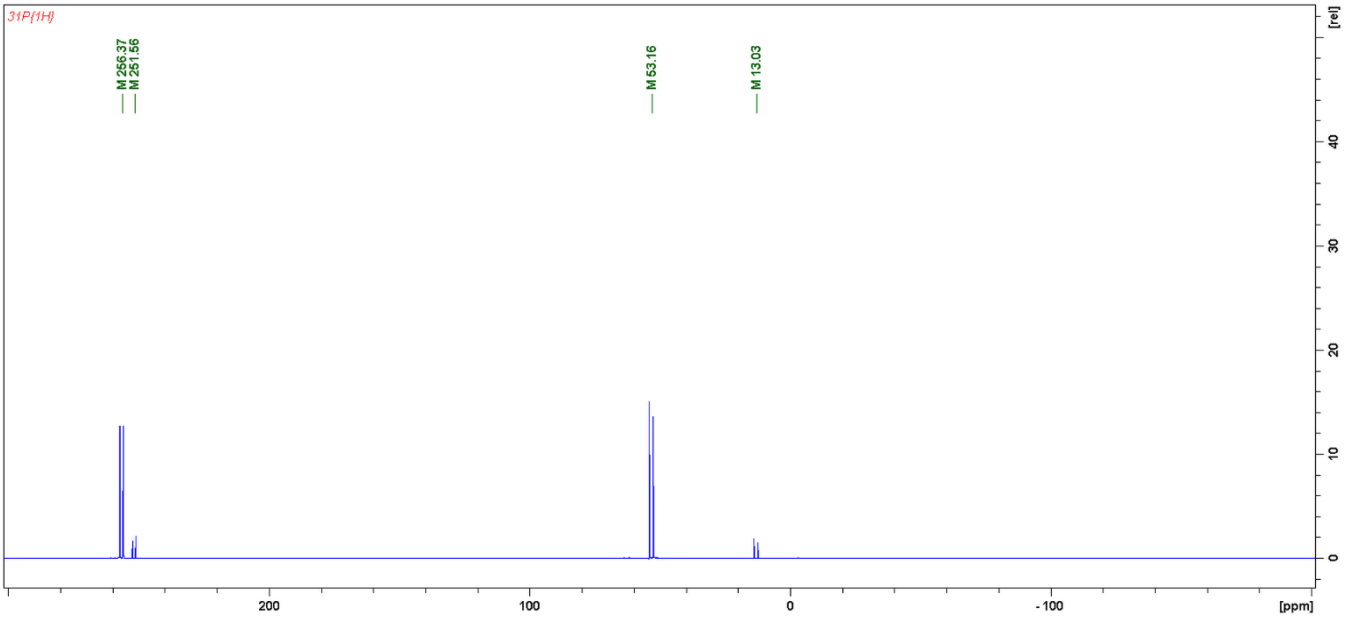


Figure S115. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {*cyclo*-$(CH_2)_4CH$}(H)C=P-P*t*Bu_2.

- 256.37 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2 – *E* isomer;
- 251.56 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=**P**-P*t*Bu_2 – *Z* isomer;
- 53.16 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-**P***t*Bu_2 – *E* isomer;
- 13.03 ppm, (d), $J_{P\text{-}P}$ = 212.8 Hz, {*cyclo*-$(CH_2)_4CH$}(H)C=P-**P***t*Bu_2 – *Z* isomer;

B.2.13. *p*-Tolualdehyde

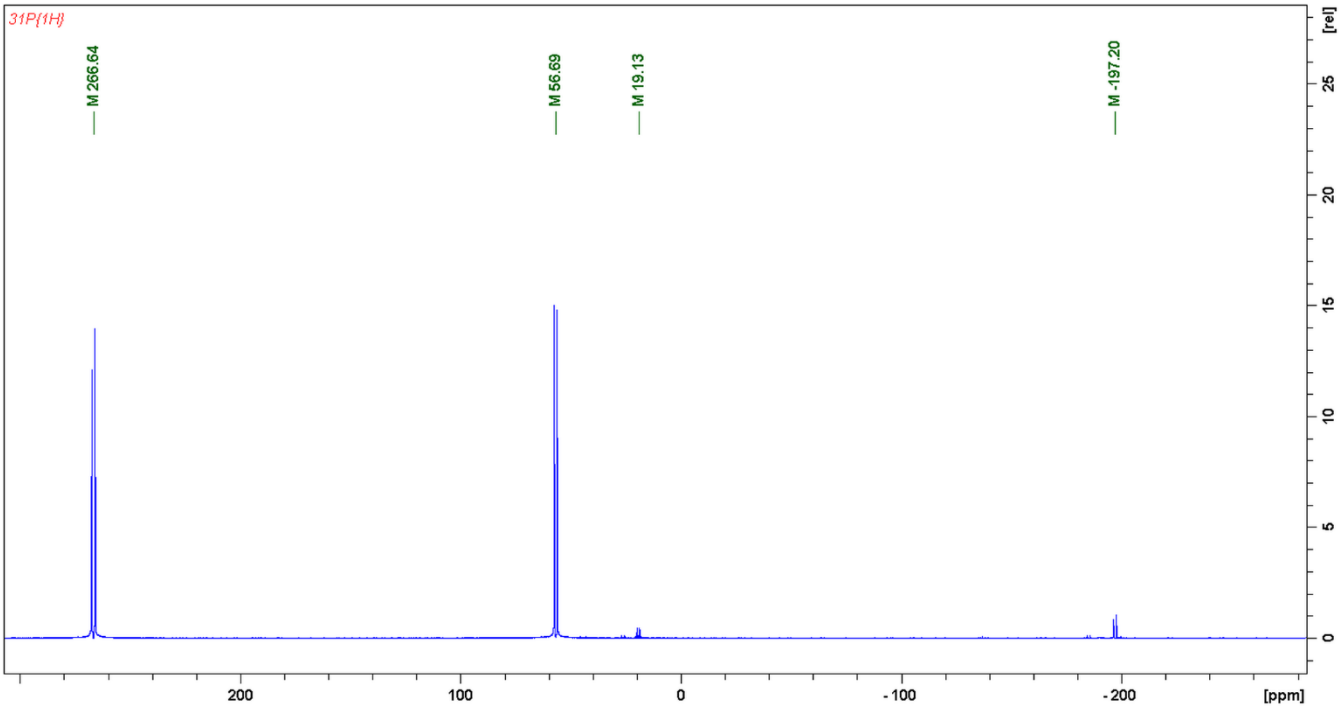


Figure S116. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of reaction mixture of **2** with *p*-Tolualdehyde.

Visible only one *E* isomer

- 266.64 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=**P**-P*t*Bu$_2$;
- 56.69 ppm, (d), $J_{P\text{-}P}$ = 220.8 Hz, (*p*-Me-Ph)(H)C=P-**P***t*Bu$_2$;
- 19.13 ppm, (d), $J_{P\text{-}P}$ = 188.9 Hz, *t*Bu$_2$**P**-P(SiMe$_3$)H;
- -197.20 ppm, (d), $J_{P\text{-}P}$ = 188.9 Hz, *t*Bu$_2$P-**P**(SiMe$_3$)H;

B.2.14. 4-(dimethylamino)benzaldehyde

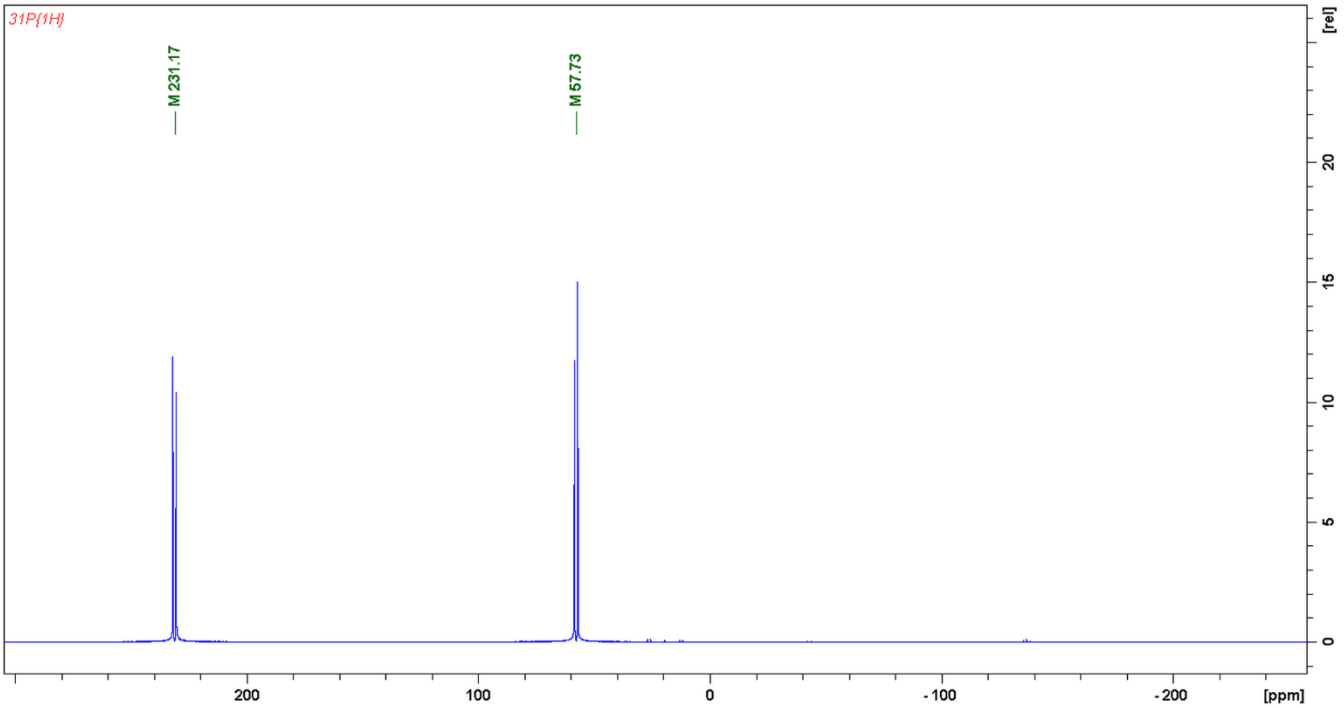


Figure S117. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**).

Visible only one *E* isomer

- 231.17 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, {4-$(Me)_2$N-Ph}(H)C=**P**-P*t*Bu_2;
- 57.73 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, {4-$(Me)_2$N-Ph}(H)C=P-**P***t*Bu_2;

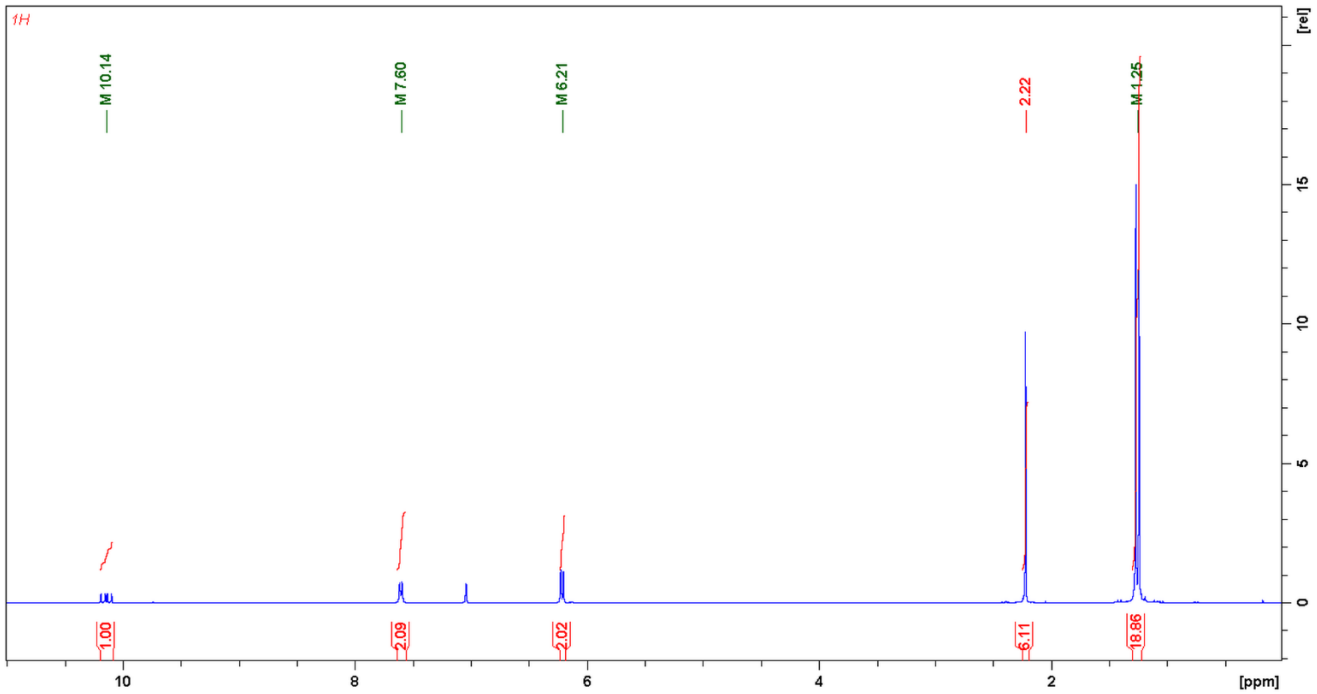


Figure S118. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-(Me)$_2$N-Ph}(H}C=P-P*t*Bu$_2$ (**4d**).

Visible only one *E* isomer

- 10.14 ppm, (dd), $J_{P\text{-}H}$ = 21.8 Hz, $J_{P\text{-}H}$ = 14.4 Hz, 1H, {4-(Me)$_2$N-Ph}(**H**)C=P-P*t*Bu$_2$;
- 7.60 ppm, (dd), $J_{P\text{-}H}$ = 9.2 Hz, $J_{P\text{-}H}$ = 2.6 Hz, 2H, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$ (*o*-H);
- 6.21 ppm, (d), $J_{P\text{-}H}$ = 8.9 Hz, 2H, {4-(Me)$_2$N-**Ph**}(H)C=P-P*t*Bu$_2$ (*m*-H);
- 2.22 ppm, (s), 6H, {4-(**Me**)$_2$N-Ph}(H)C=P-P*t*Bu$_2$;
- 1.25 ppm, (d), $J_{P\text{-}H}$ = 11.1 Hz, 18H, {4-(Me)$_2$N-Ph}(H)C=P-P***t*Bu$_2$**;

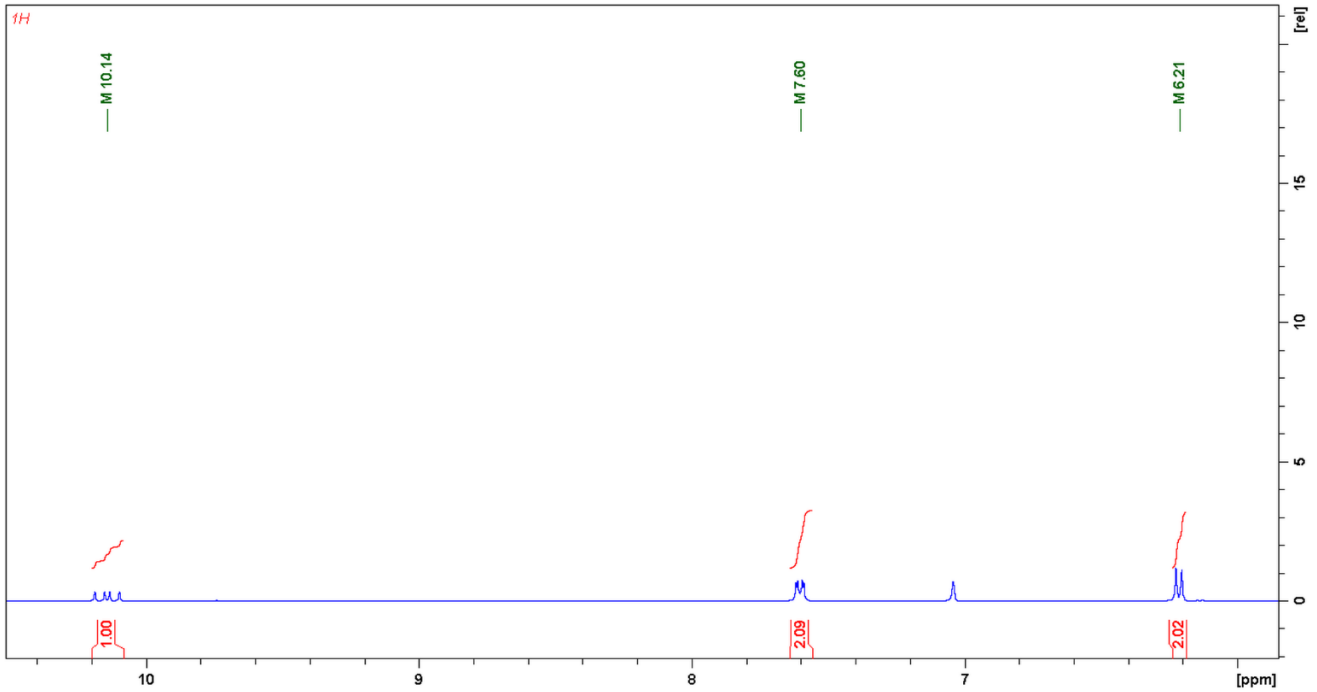


Figure S119. ^{31}P{^{1}H} NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-(Me)$_2$N-Ph}(H)C=P-P*t*Bu$_2$ (**4d**) in the range from 10.5 ppm to 6 ppm.

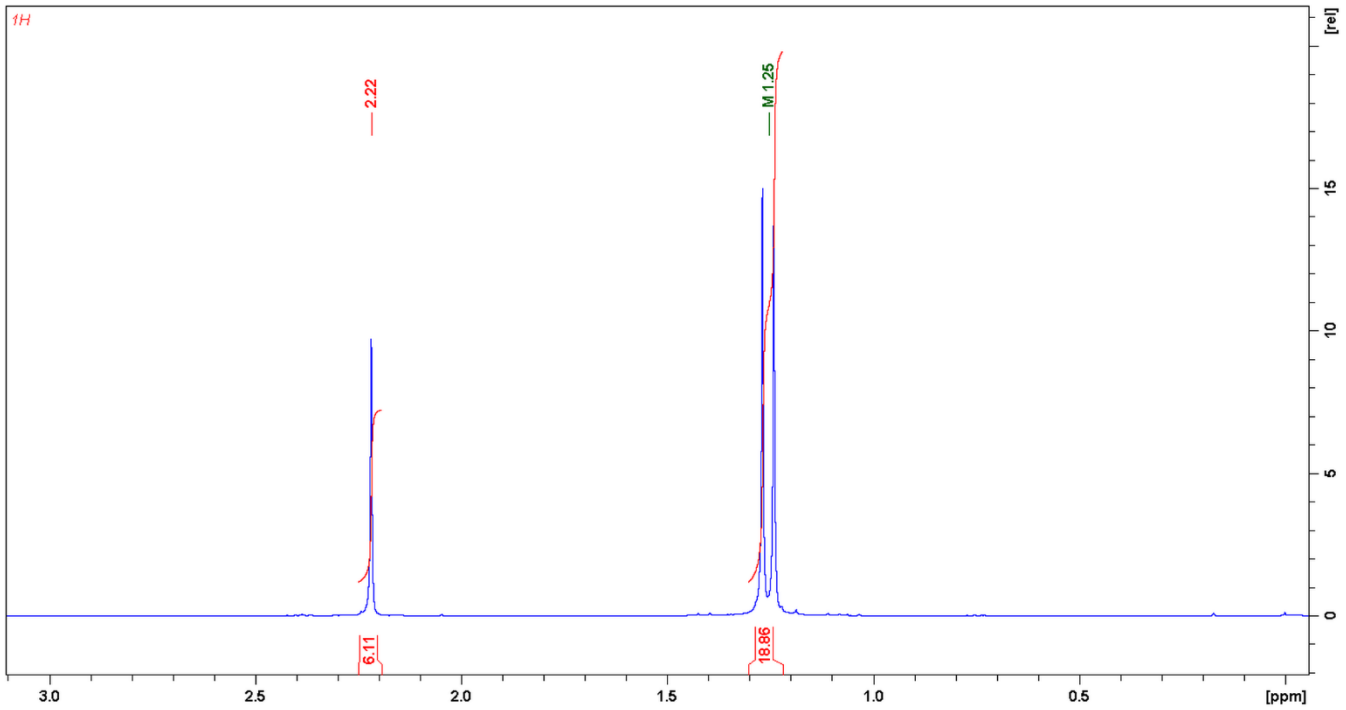


Figure S120. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**) in the range from 3 ppm to 0 ppm.

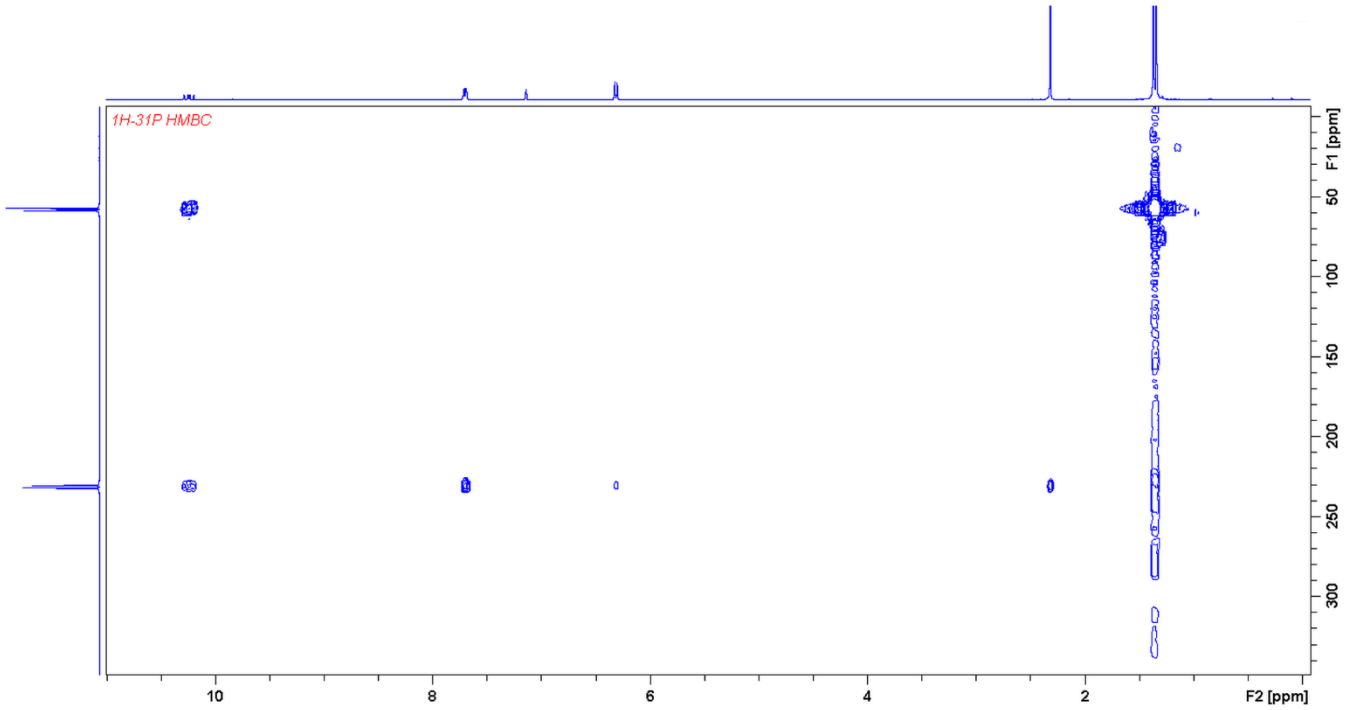


Figure S121. $^{31}P\{^{1}H\}/^{1}H$-HMBC (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**).

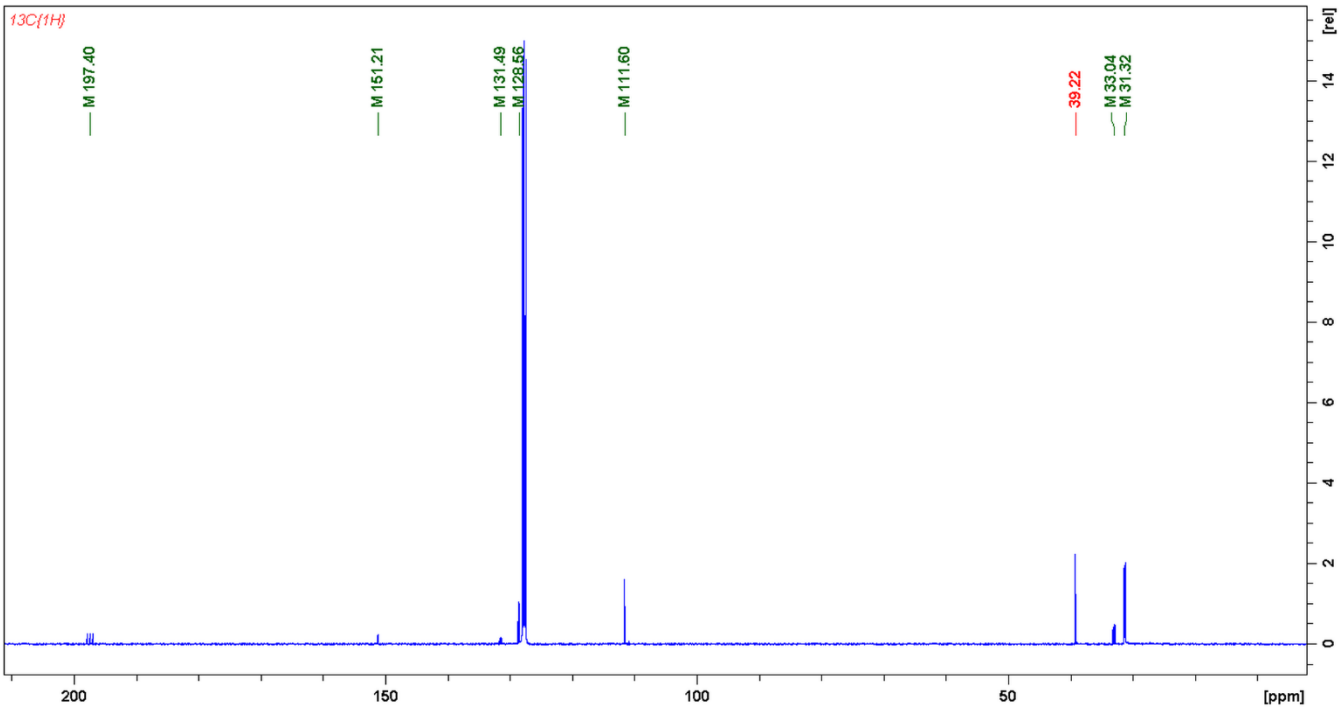


Figure S122. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**).

Visible only one *E* isomer

- 197.40 ppm, (dd), $J_{P\text{-}C}$ = 46.3 Hz, $J_{P\text{-}C}$ = 39.9 Hz, {4-$(Me)_2$N-Ph}(H)**C**=P-P*t*Bu_2;
- 151.20 ppm, (d), $J_{P\text{-}C}$ = 5.5 Hz, {4-$(Me)_2$N-**Ph**}(H)C=P-P*t*Bu_2 (*p*-C_{Ar});
- 131.49 ppm, (dd), $J_{P\text{-}C}$ = 16.3 Hz, J_{PC} = 11.8 Hz, {4-$(Me)_2$N-**Ph**}(H)C=P-P*t*Bu_2 (*i*-C_{Ar});
- 128.56 ppm, (d), $J_{P\text{-}C}$ = 19.9 Hz, {4-$(Me)_2$N-**Ph**}(H)C=P-P*t*Bu_2 (*o*-C_{Ar});
- 111.60 ppm, (d), $J_{P\text{-}C}$ = 19.9 Hz, {4-$(Me)_2$N-**Ph**}(H)C=P-P*t*Bu_2 (*m*-C_{Ar});
- 39.22 ppm, (s), {4-(**Me**)$_2$N-Ph}(H)C=P-P*t*Bu_2;
- 33.04 ppm, (dd), $J_{P\text{-}C}$ = 22.7 Hz, $J_{P\text{-}C}$ = 1.8 Hz, {4-$(Me)_2$N-Ph}(H)C=P-P{**C**$(CH_3)_3$}$_2$;
- 31.32 ppm, (dd), $J_{P\text{-}C}$ = 13.6 Hz, $J_{P\text{-}C}$ = 5.5 Hz, {4-$(Me)_2$N-Ph}(H)C=P-P{C(**C**$H_3)_3$}$_2$;

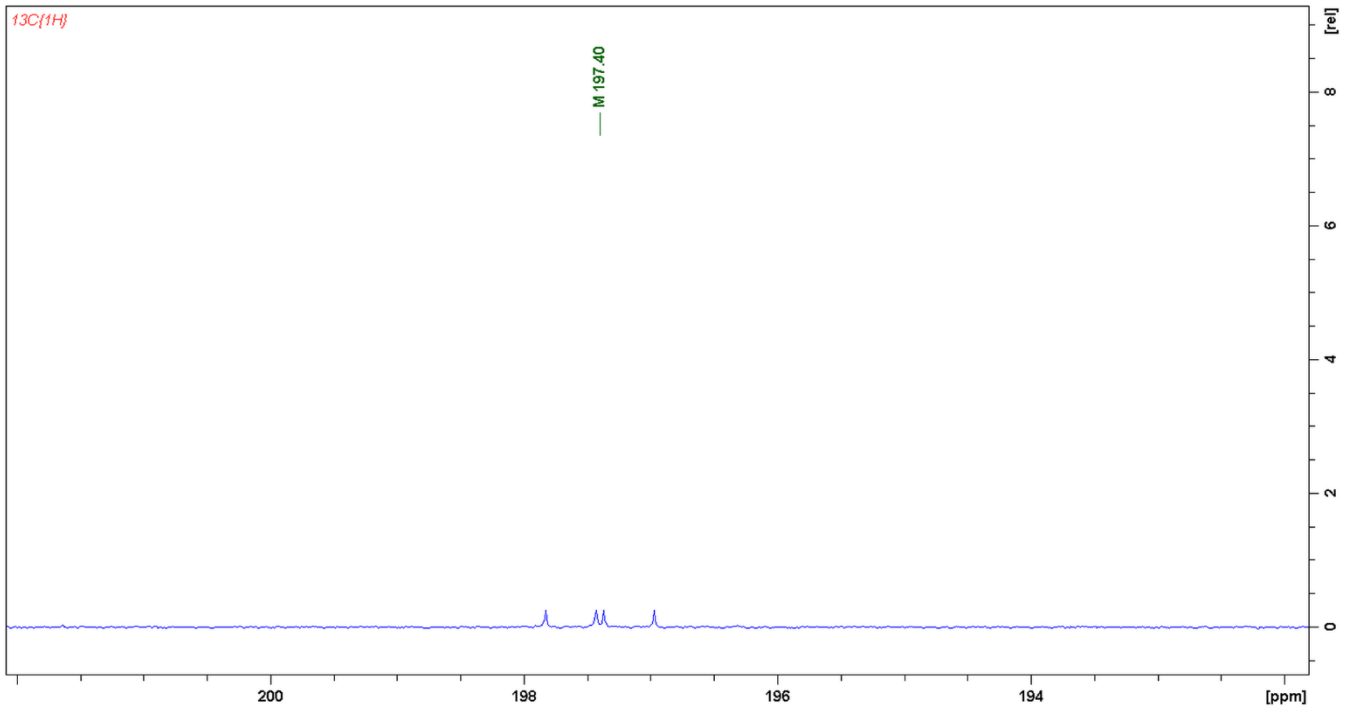


Figure S123. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**) in the range from 202 ppm to 192 ppm.

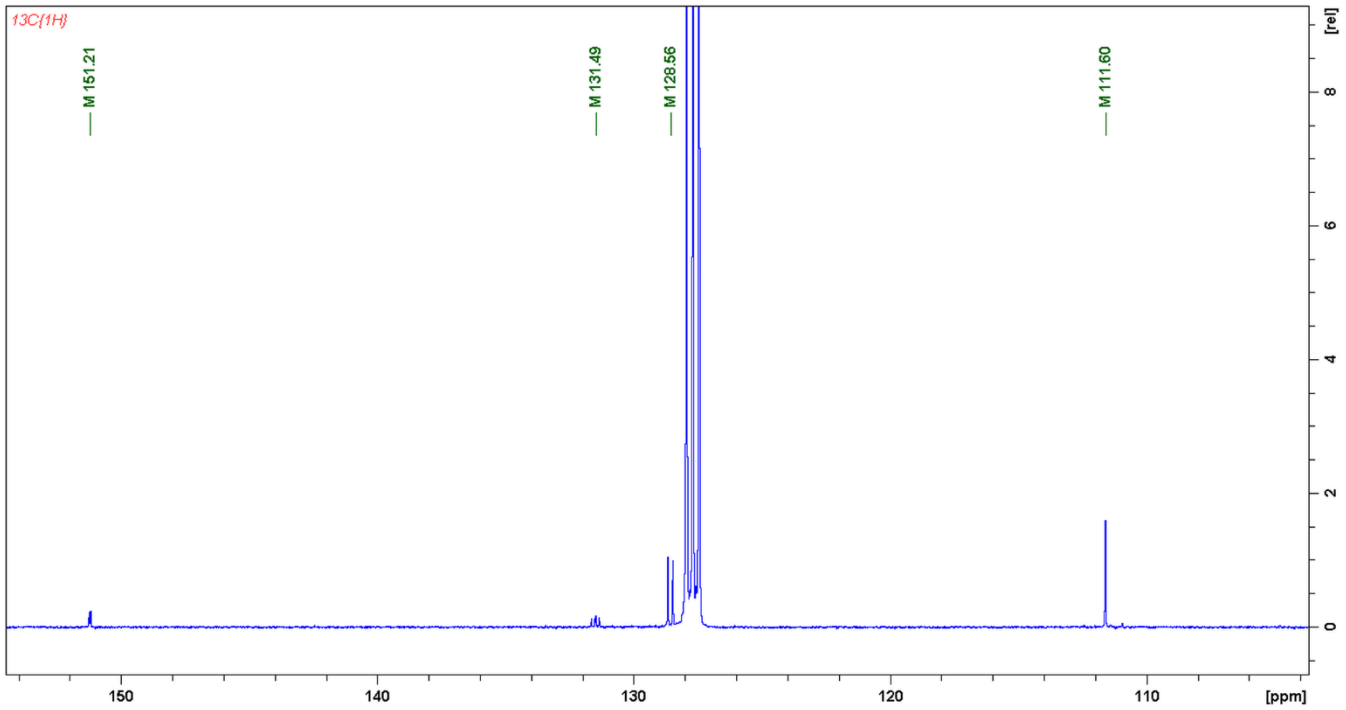


Figure S124. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**) in the range from 155 ppm to 105 ppm.

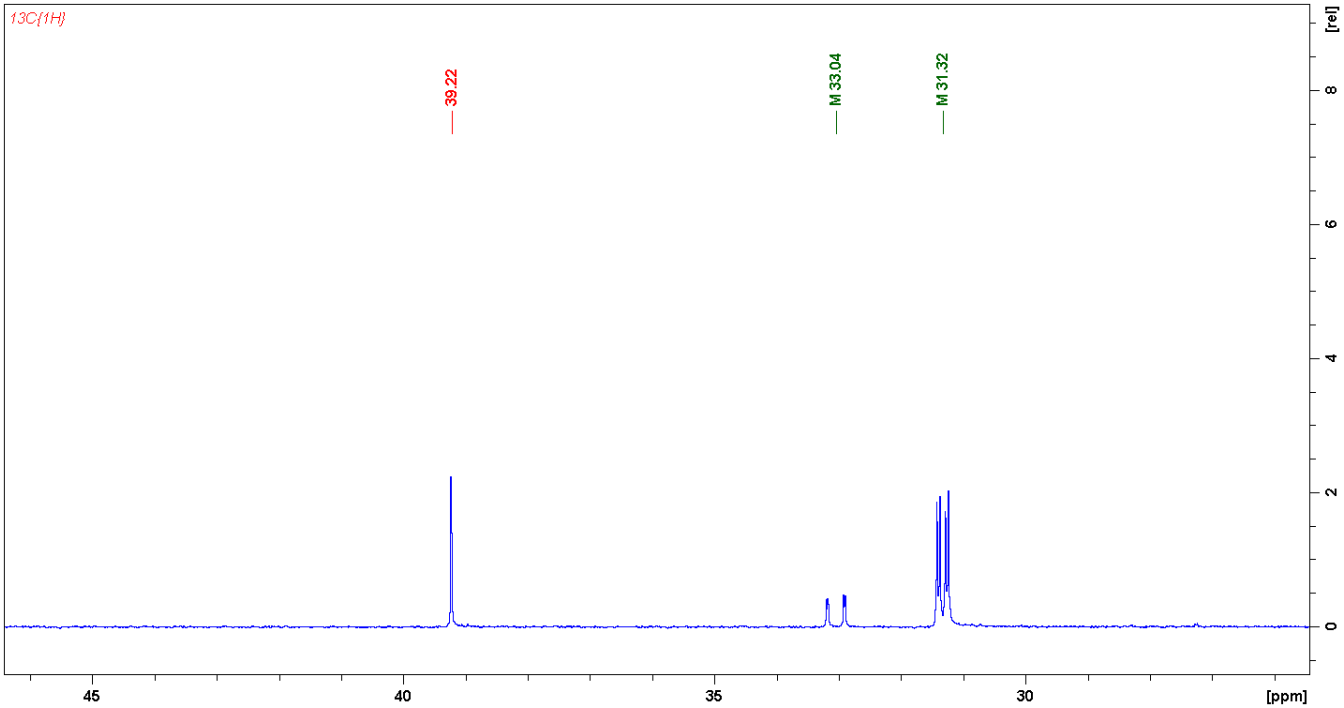


Figure S125. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated {4-$(Me)_2$N-Ph}(H)C=P-P*t*Bu_2 (**4d**) in the range from 45 ppm to 25 ppm.

B.2.15. Biphenyl-4-carboxaldehyde

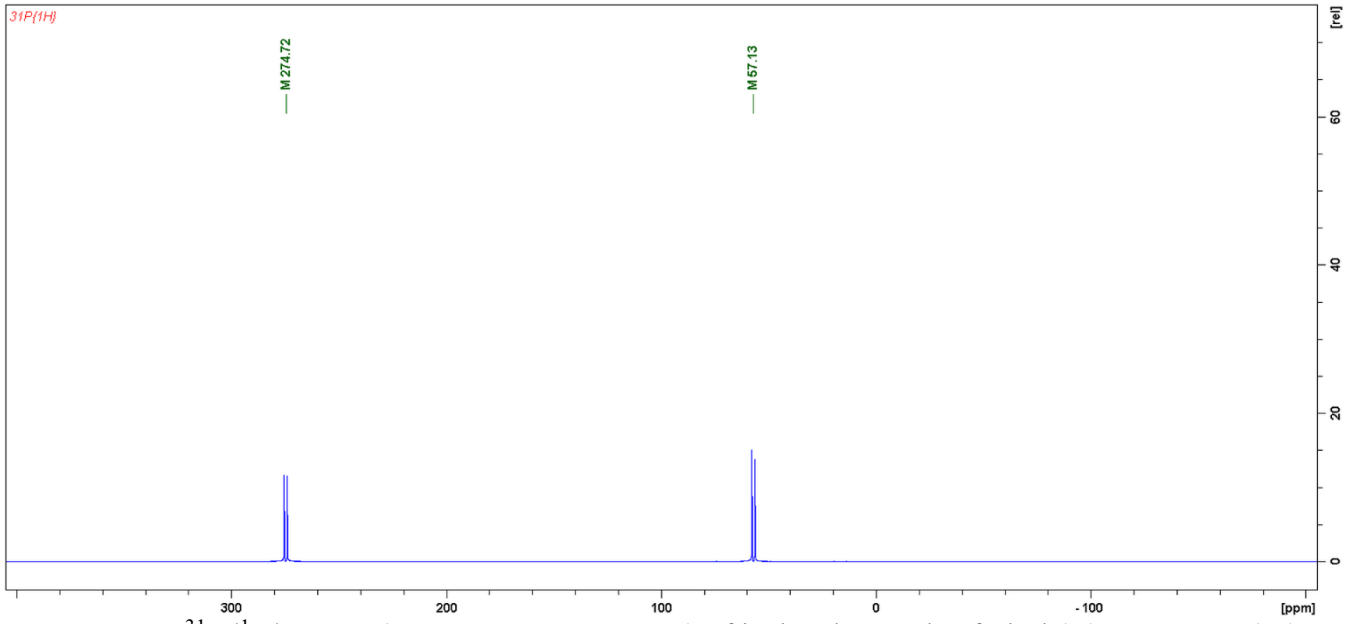


Figure S126. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) of isolated crystals of PhPh(H)C=P-P*t*Bu$_2$ (**4e**).

- 274.72 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, PhPh(H)C=**P**-P*t*Bu$_2$;
- 57.13 ppm, (d), $J_{P\text{-}P}$ = 224.9 Hz, PhPh(H)C=P-**P***t*Bu$_2$;

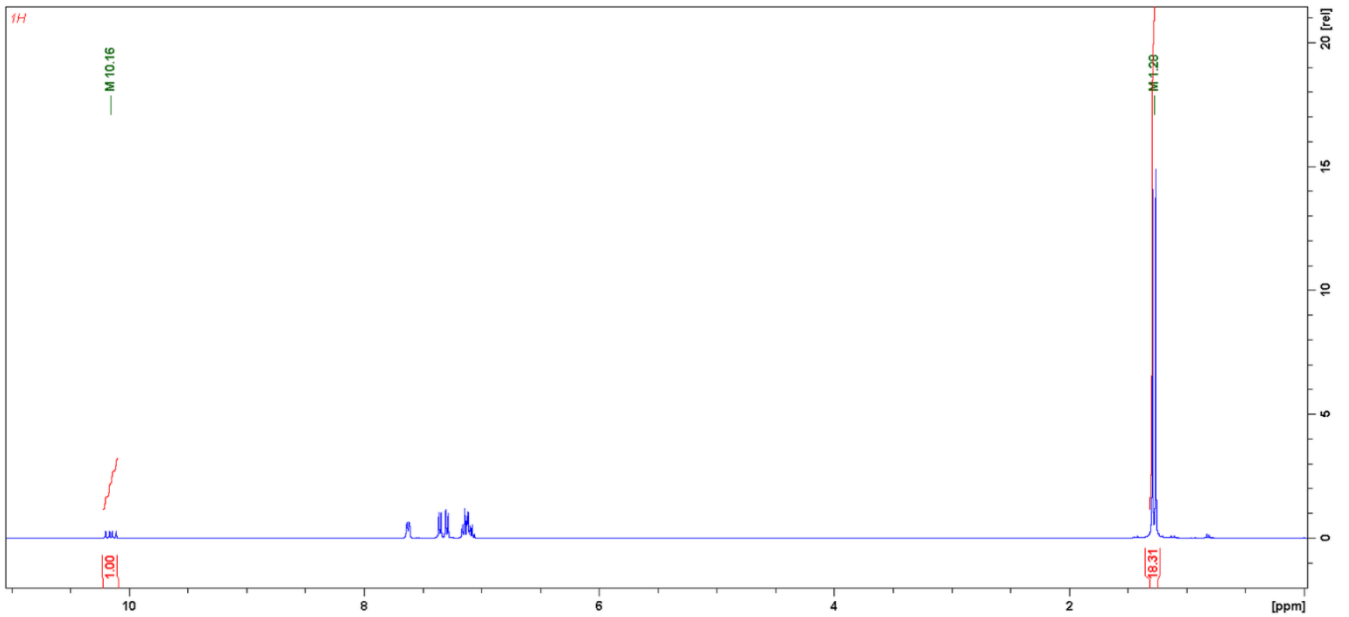


Figure S127. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated crystals of PhPh(H)C=P-P*t*Bu$_2$ (**4e**).

- 10.16 ppm, (dd), 1H, $J_{P\text{-}H}$ = 22.5 Hz, $J_{P\text{-}H}$ = 13.4 Hz, PhPh(**H**)C=P-P*t*Bu$_2$;
- 7.67 – 7.04 ppm, 9H, aromatic protons, **PhPh**(H)C=P-P*t*Bu$_2$
- 1.28 ppm, (d), 18 H, $J_{P\text{-}H}$ = 11.1 Hz, PhPh(H)C=P-P***t*Bu**$_2$;

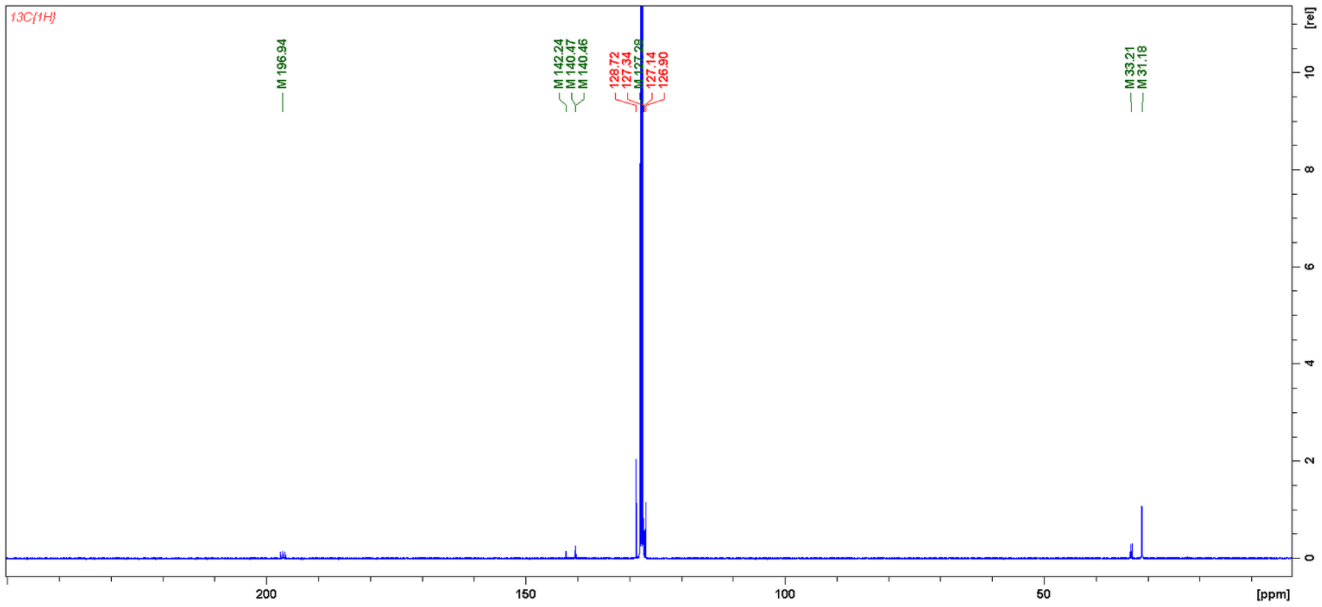


Figure S128. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated crystals of PhPh(H)C=P-P*t*Bu$_2$ (**4e**).

- 196.94 ppm, (dd), $J_{P\text{-}C}$ = 44.9 Hz, $J_{P\text{-}C}$ = 39.5 Hz, PhPh(H)**C**=P-P{C(CH$_3$)$_3$}$_2$;
- 142.24 ppm, (d), $J_{P\text{-}C}$ = 7.18 Hz, **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*i*-C$_{Ar}$);
- 140.47 ppm, (d), $J_{P\text{-}C}$ = 1.5 Hz, **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*i*-C$_{Ar}$)
- 140.46 ppm, (dd), $J_{P\text{-}C}$ = 15.8 Hz, $J_{P\text{-}C}$ = 12.4 Hz, **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*i*-C$_{Ar}$);
- 128.72 ppm, (s), **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*o*-C$_{Ar}$);
- 127.34 ppm, (s), **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*o*-C$_{Ar}$);
- 127.28 ppm, (d), $J_{P\text{-}C}$ = 2.6 Hz, **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*m*-C$_{Ar}$);
- 126.90 ppm, (s), **PhPh**(H)C=P-P{C(CH$_3$)$_3$}$_2$ (*m*-C$_{Ar}$);
- 33.21 ppm, (dd), $J_{P\text{-}C}$ = 27.7 Hz, $J_{P\text{-}C}$ = 2.27 Hz, PhPh(H)C=P-P{**C**(CH$_3$)$_3$}$_2$;
- 31.18 ppm, (dd), $J_{P\text{-}C}$ = 13.8 Hz, $J_{P\text{-}C}$ = 5.0 Hz, PhPh(H)C=P-P{C(**C**H$_3$)$_3$}$_2$;

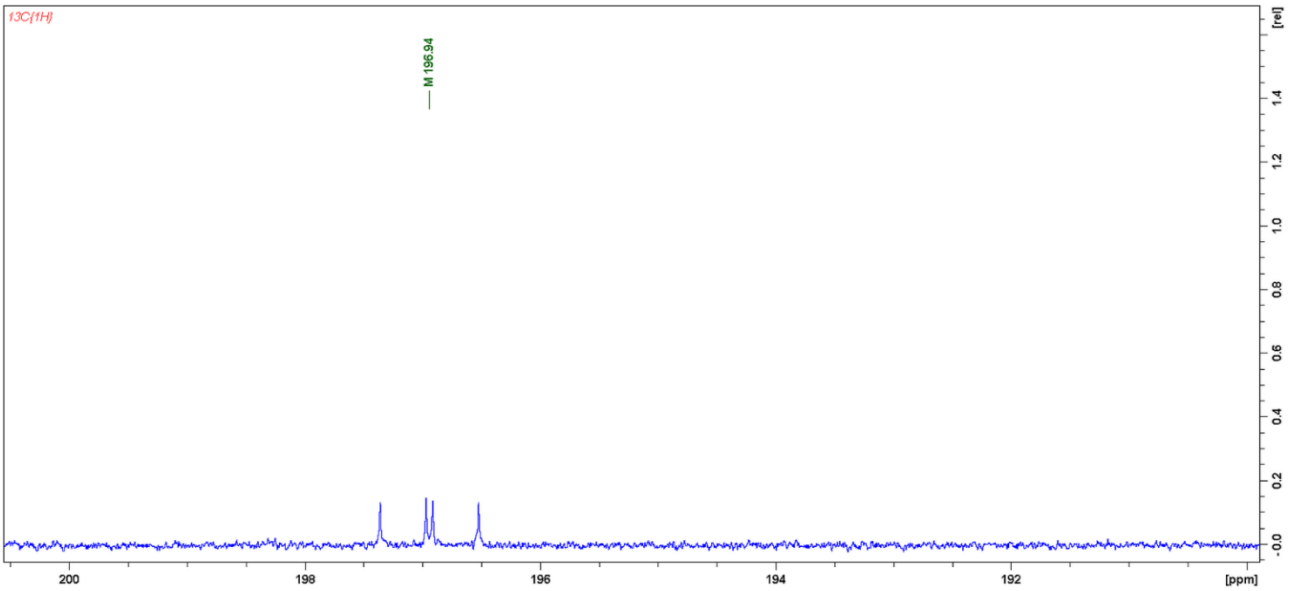


Figure S129. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated crystals of PhPh(H)C=P-P*t*Bu$_2$ (**4e**) in the range from 200 ppm to 190 ppm.

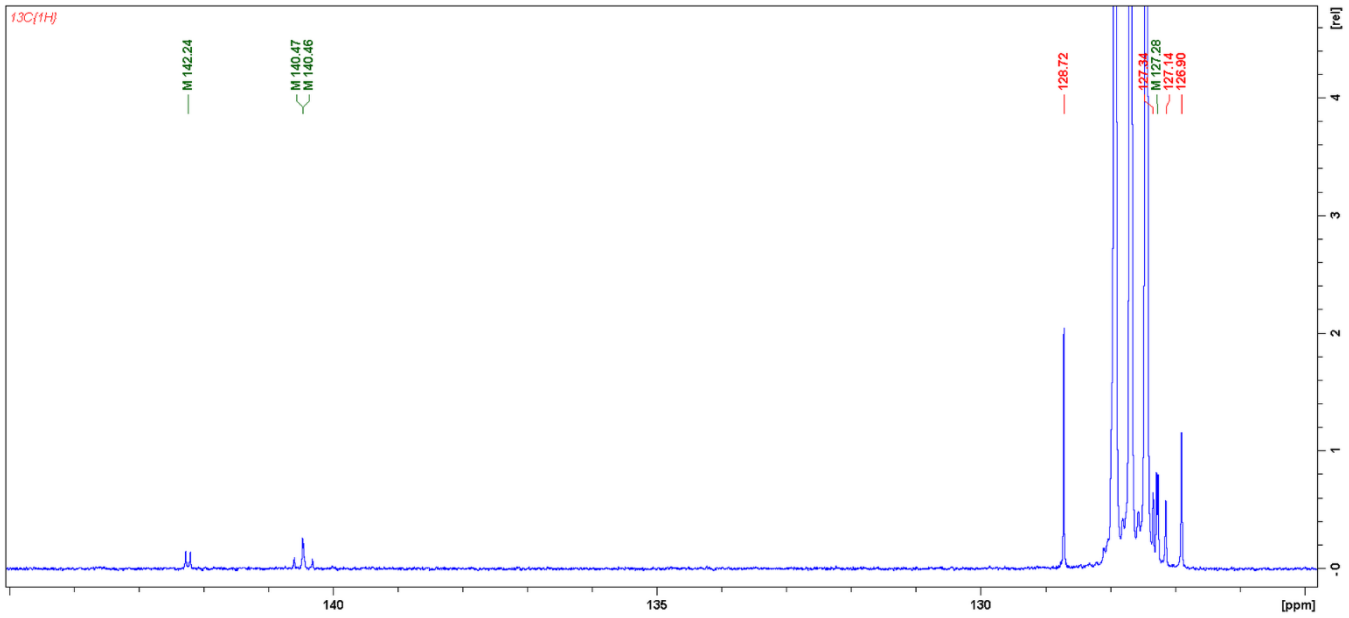


Figure S130. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated crystals of PhPh(H)C=P-P*t*Bu$_2$ (**4e**) in the range from 145 ppm to 125 ppm.

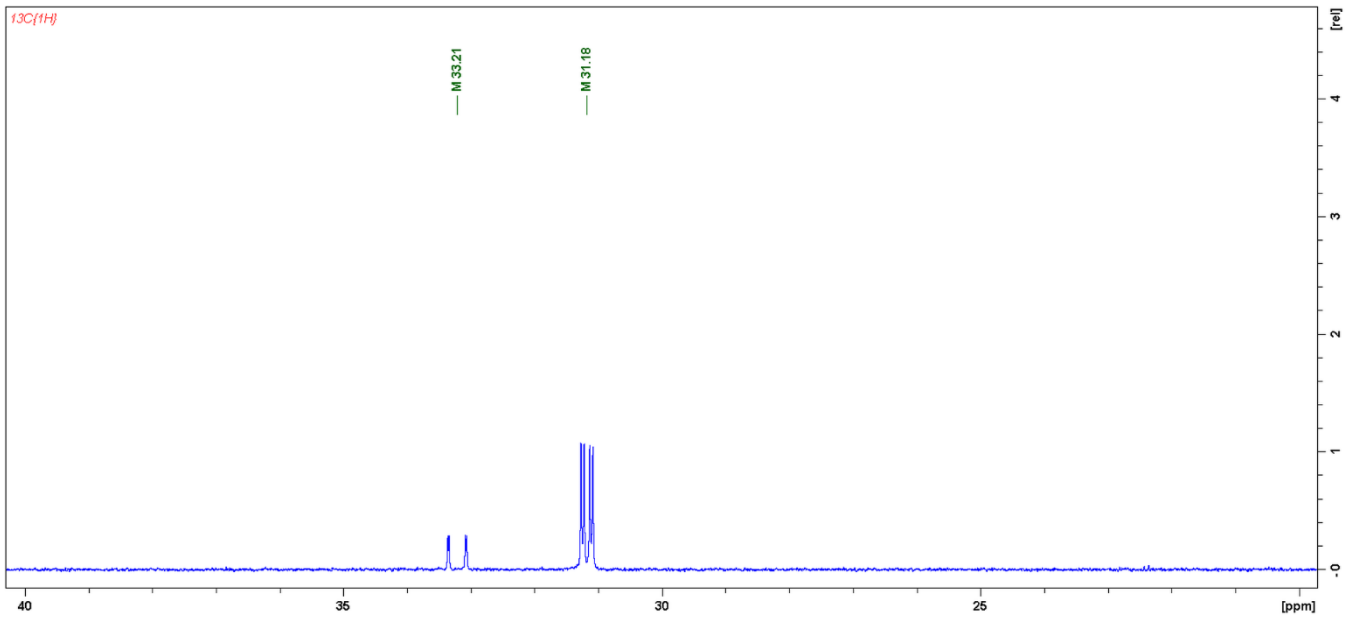


Figure S131. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of isolated crystals of PhPh(H)C=P-P*t*Bu$_2$ (**4e**) in the range from 40 ppm to 20 ppm.

B.3. Decomposition of the isolated crystals of phosphanylphosphaalkenes

B.3.1. $(Ph)_2C$=P-P*t*Bu_2 (**3a**)

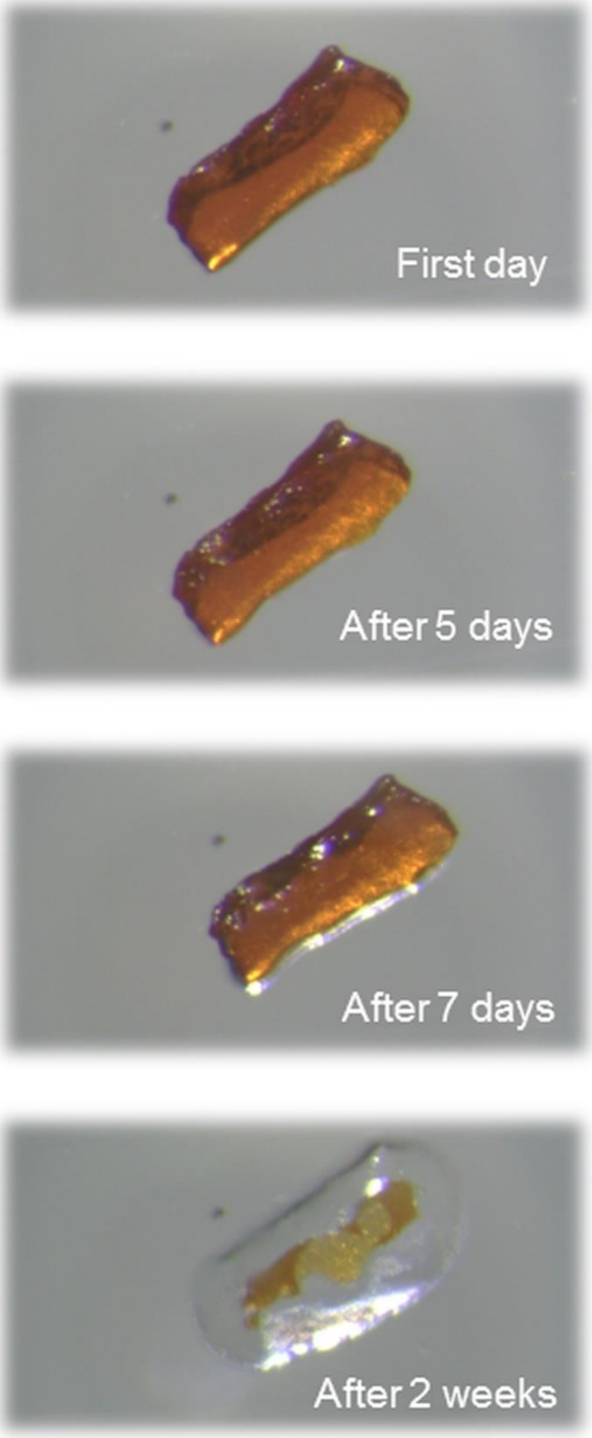


Figure S132. Decomposition of crystal 3a over time.

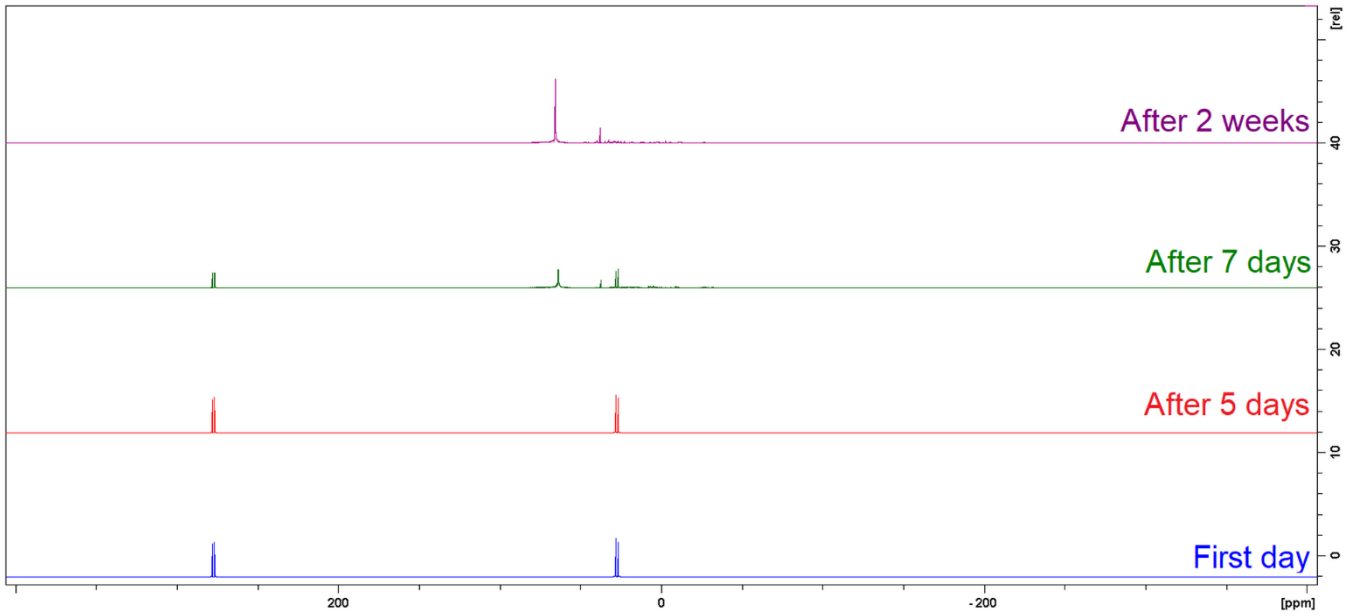


Figure S133. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of decomposition of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) dissolved in C_6D_6 and measured immediately after dissolving, after 5, 7 days and 2 weeks.

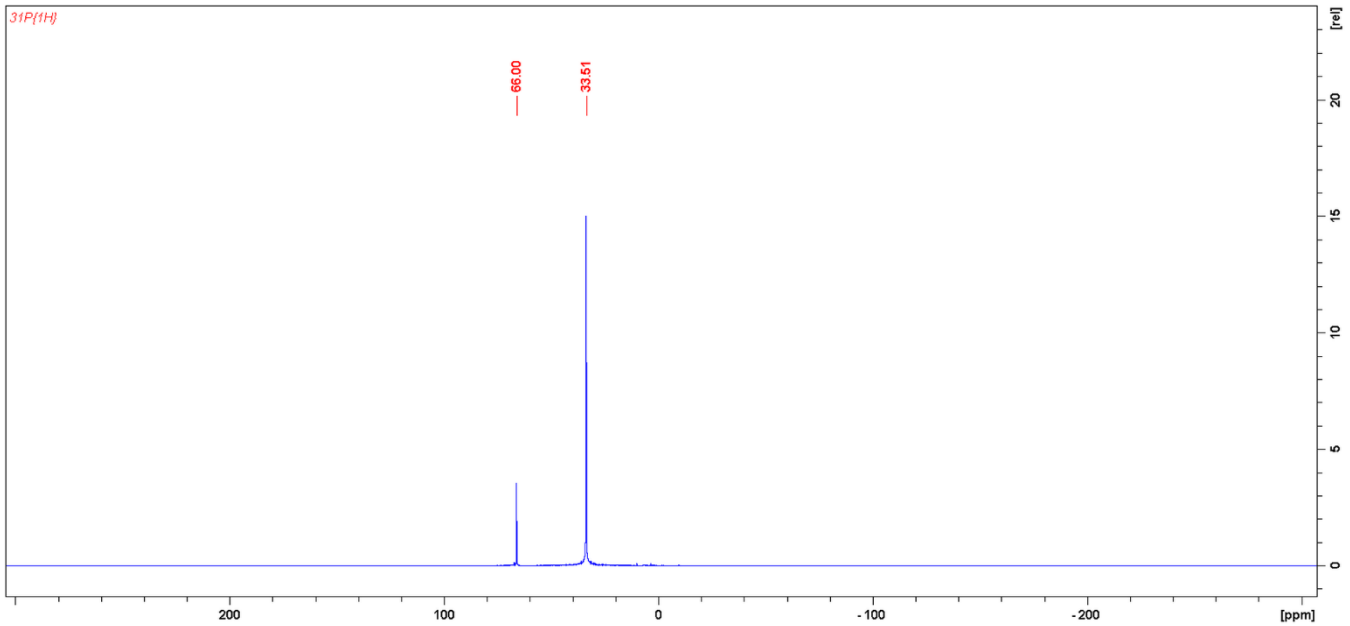


Figure S134. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) crystals after 2 weeks in the air conditions.

- 66.00 ppm, (s), tBu_2**P**H(=O);
- 33.51 ppm, (s), Ph_2(H)C-**P**H(=O)(OH);

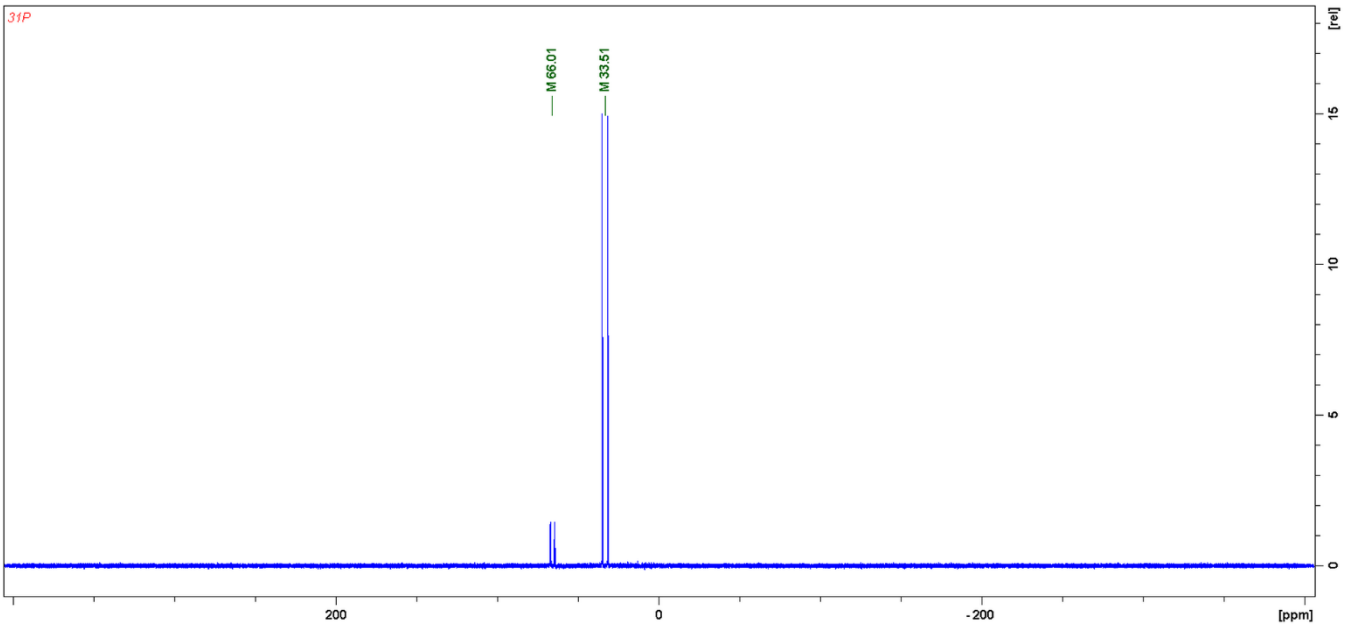


Figure S135. ^{31}P NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C$=P-P*t*Bu_2 (**3a**) crystals after 2 weeks in the air conditions.

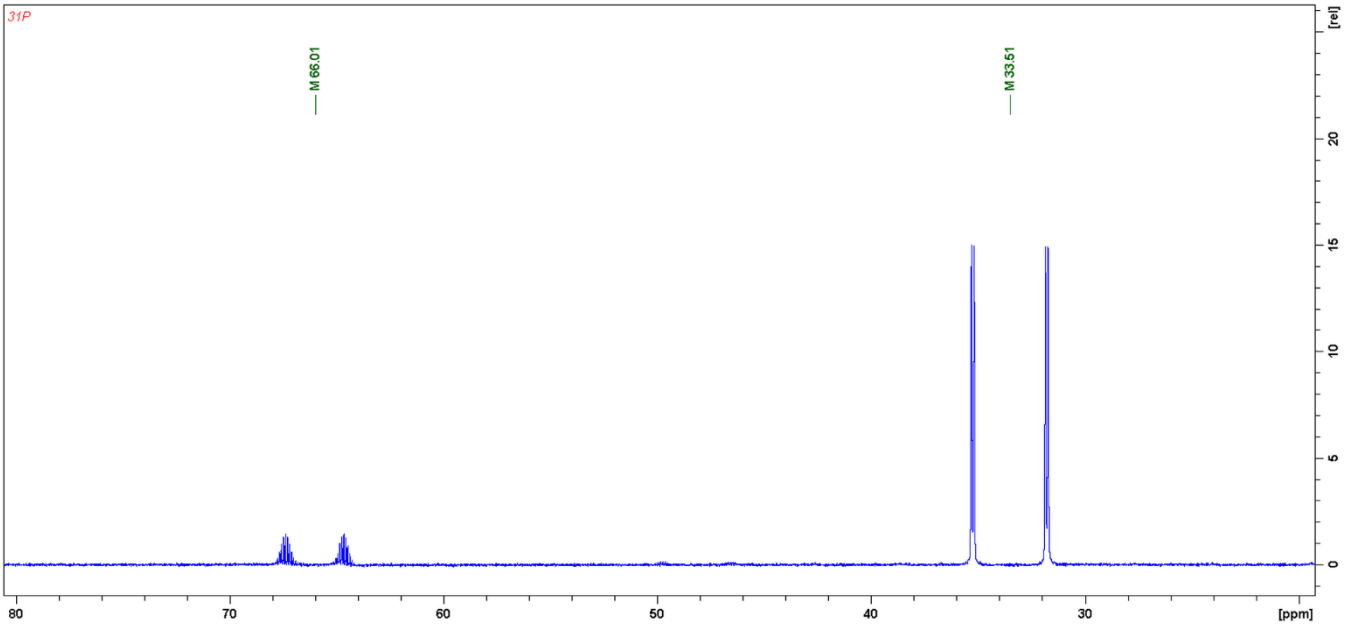


Figure S136. ^{31}P NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C$=P-P*t*Bu_2 (**3a**) crystals after 2 weeks in the air conditions in the range from 80 ppm to 20 ppm.

- 66.01 ppm, (doublet of multiplets), $J_{P\text{-}H}$ = 441.7 Hz, *t*Bu_2**P**H(=O);
- 33.51 ppm, (dd), J_{PH} = 560.2 Hz, $J_{P\text{-}H}$ = 19.4 Hz, Ph_2(H)C-**P**H(=O)(OH).

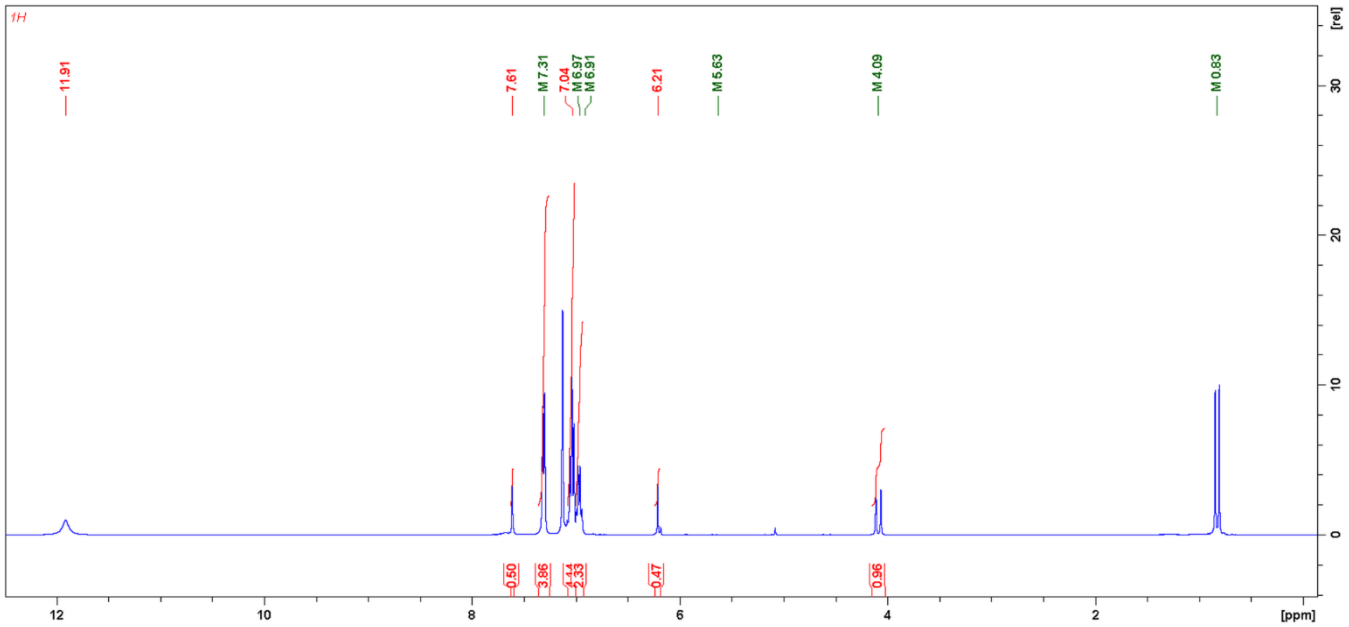


Figure S137. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) crystals after 2 weeks in the air conditions.

- 11.91 ppm, (broad s), $Ph_2(H)C\text{-}PH(=O)(O\mathbf{H})$;
- 7.31 ppm, (d), 4H, $J_{H\text{-}H}$ = 7.6 Hz, $\mathbf{Ph}_2(H)C\text{-}PH(=O)(OH)$, *o*-$H_{Ar}$;
- 7.04 ppm, (t), 4H, $J_{H\text{-}H}$ = 7.6 Hz, $\mathbf{Ph}_2(H)C\text{-}PH(=O)(OH)$, *m*-$H_{Ar}$;
- 6.97 ppm, (q), 2H, $J_{H\text{-}H}$ = 6.7 Hz, $\mathbf{Ph}_2(H)C\text{-}PH(=O)(OH)$, *p*-$H_{Ar}$;
- 6.91 ppm, (d), 1H, $J_{P\text{-}H}$ = 560.2 Hz, $Ph_2(H)C\text{-}P\mathbf{H}(=O)(OH)$;
- 5.63 ppm, (d), 1H, $J_{P\text{-}H}$ = 441.7 Hz, $tBu_2P\mathbf{H}(=O)$;
- 4.09 ppm, (d), 1H, $J_{P\text{-}H}$ = 19.4 Hz, $Ph_2(\mathbf{H})C\text{-}PH(=O)(OH)$;
- 0.83 ppm, (d), 18H, $J_{P\text{-}H}$ = 15.3 Hz, $\mathbf{\textit{t}Bu}_2PH(=O)$;

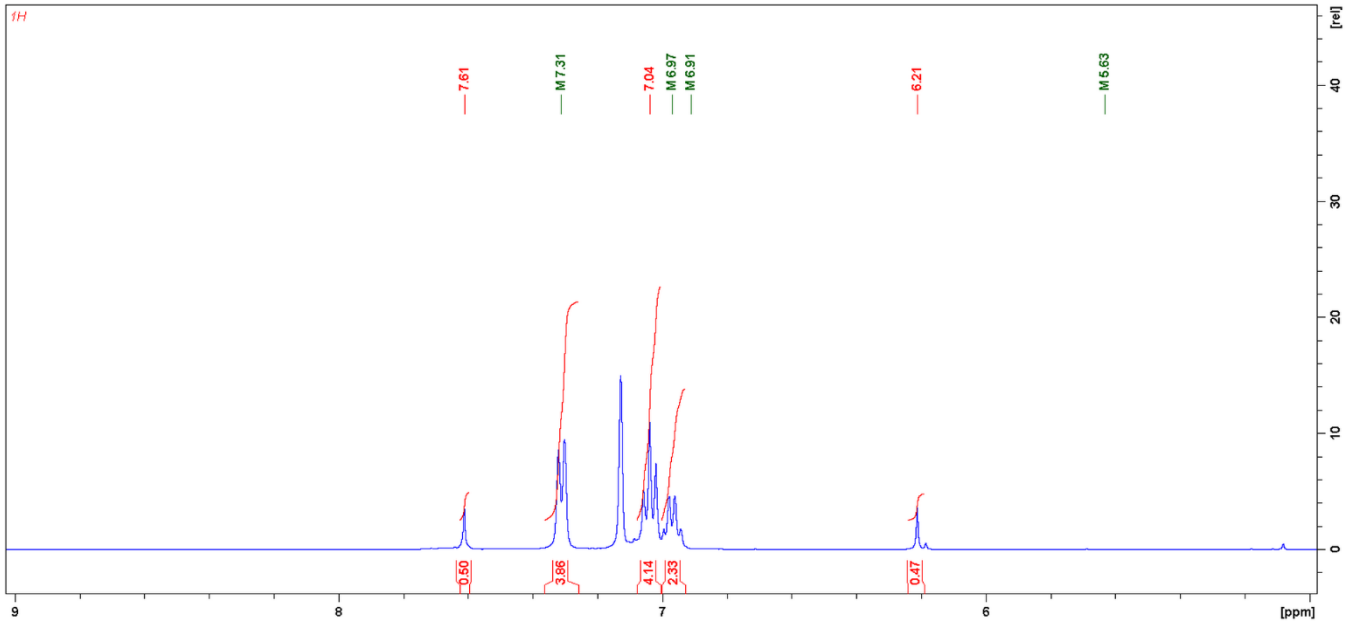


Figure S138. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) crystals after 2 weeks in the air conditions in the range from 9 ppm to 5 ppm.

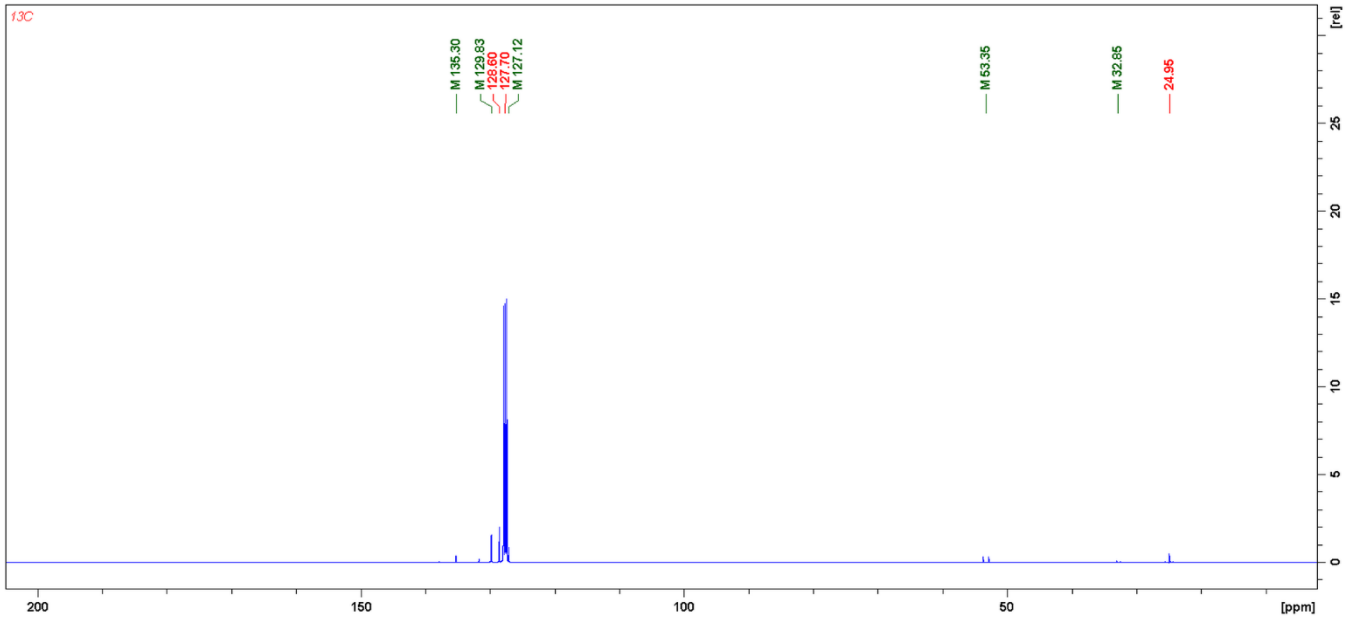


Figure S139. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) crystals after 2 weeks in the air conditions.

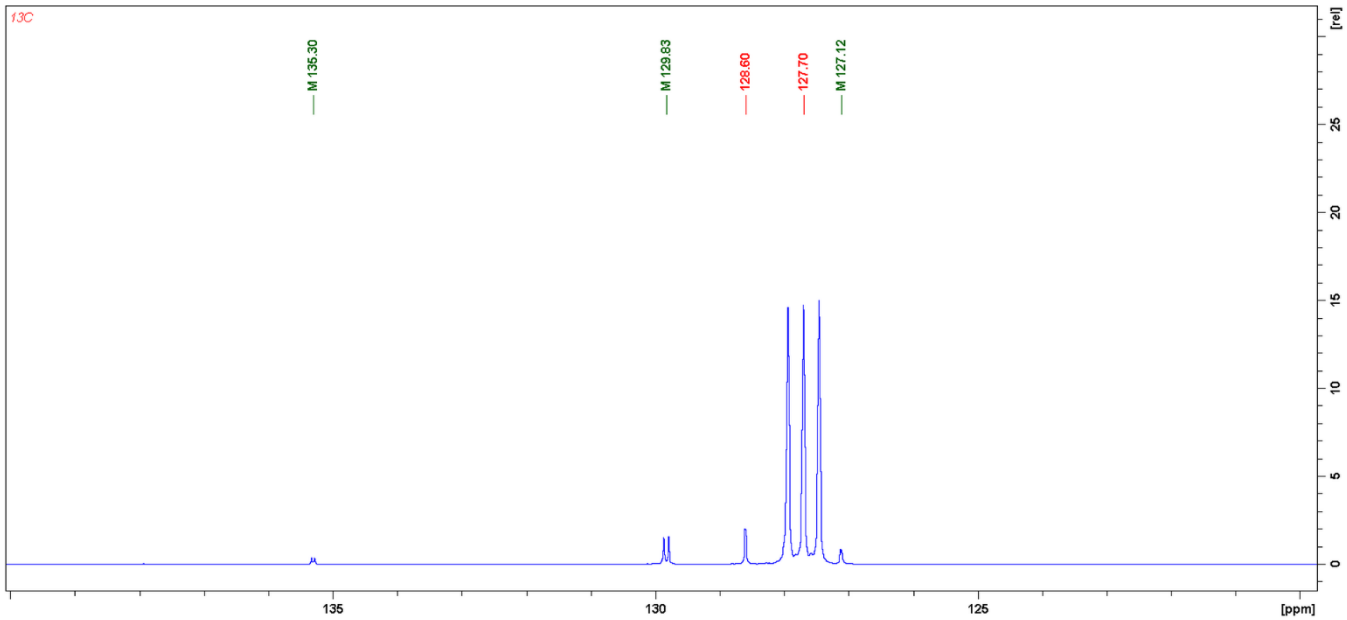


Figure S140. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) crystals after 2 weeks in the air conditions in the range from 140 ppm to 120 ppm.

- 135.30 ppm, (d), $J_{P\text{-}C}$ = 4.7 Hz, **Ph**$_2$(H)C-PH(=O)(OH), *i*-C_{Ar};
- 129.83 ppm, (d), $J_{P\text{-}C}$ = 8.4 Hz, **Ph**$_2$(H)C-PH(=O)(OH), *o*-C_{Ar};
- 128.60 ppm, (s), **Ph**$_2$(H)C-PH(=O)(OH), *m*-C_{Ar};
- 127.12 ppm, (d), $J_{P\text{-}C}$ = 1.4 Hz, **Ph**$_2$(H)C-PH(=O)(OH), *p*-C_{Ar};

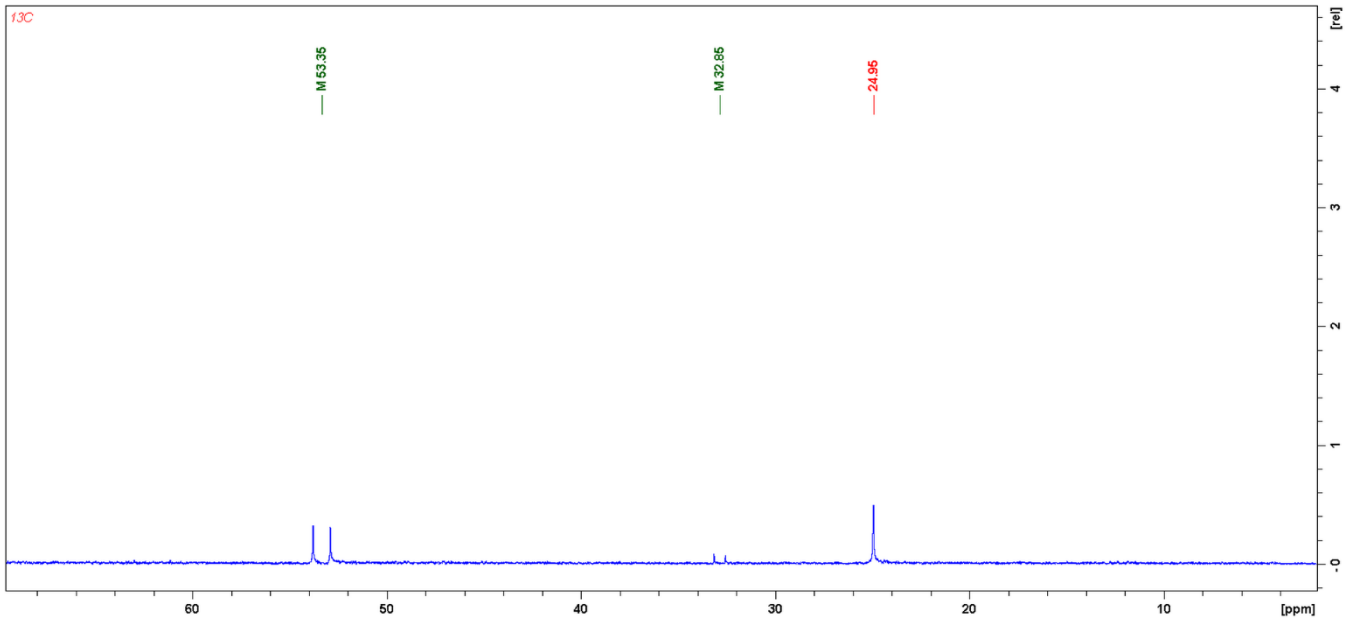


Figure S141. $^{13}C\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of $(Ph)_2C{=}P\text{-}PtBu_2$ (**3a**) crystals after 2 weeks in the air conditions in the range from 70 ppm to 0 ppm.

- 53.35 ppm, (d), $J_{P\text{-}C}$ = 90.46 Hz, $Ph_2(H)\mathbf{C}\text{-}PH(=O)(OH)$;
- 32.85 ppm, (d), $J_{P\text{-}C}$ = 60.1 Hz, $\{CH_3)_3\mathbf{C}\}_2PH(=O)$;
- 24.95 ppm, (d), $J_{P\text{-}C}$ = 1.8 Hz, $\{\mathbf{C}H_3)_3C\}_2PH(=O)$;

B.3.2. (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**)

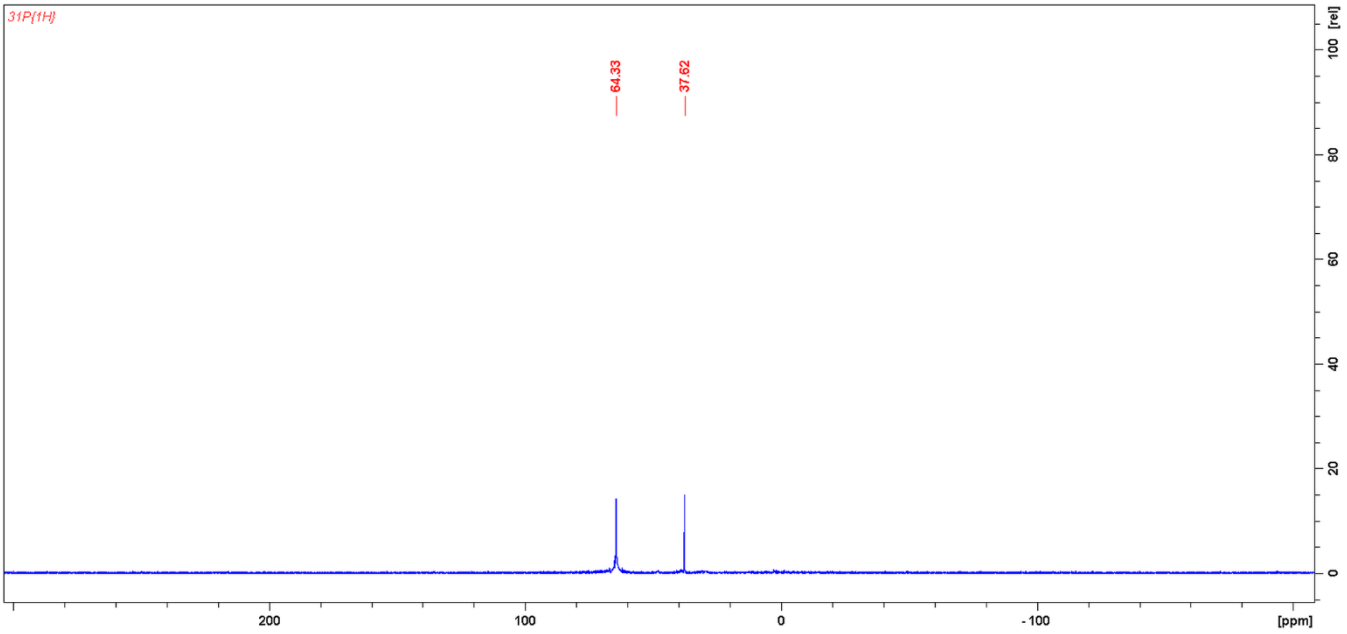


Figure S142. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) crystals after 2 weeks in the air condition.

- 64.33 ppm, (s), *t*Bu$_2$**P**H(=O);
- 37.52 ppm, (s), (Ph)(4-CN-Ph)HC-**P**H(=O)(OH);

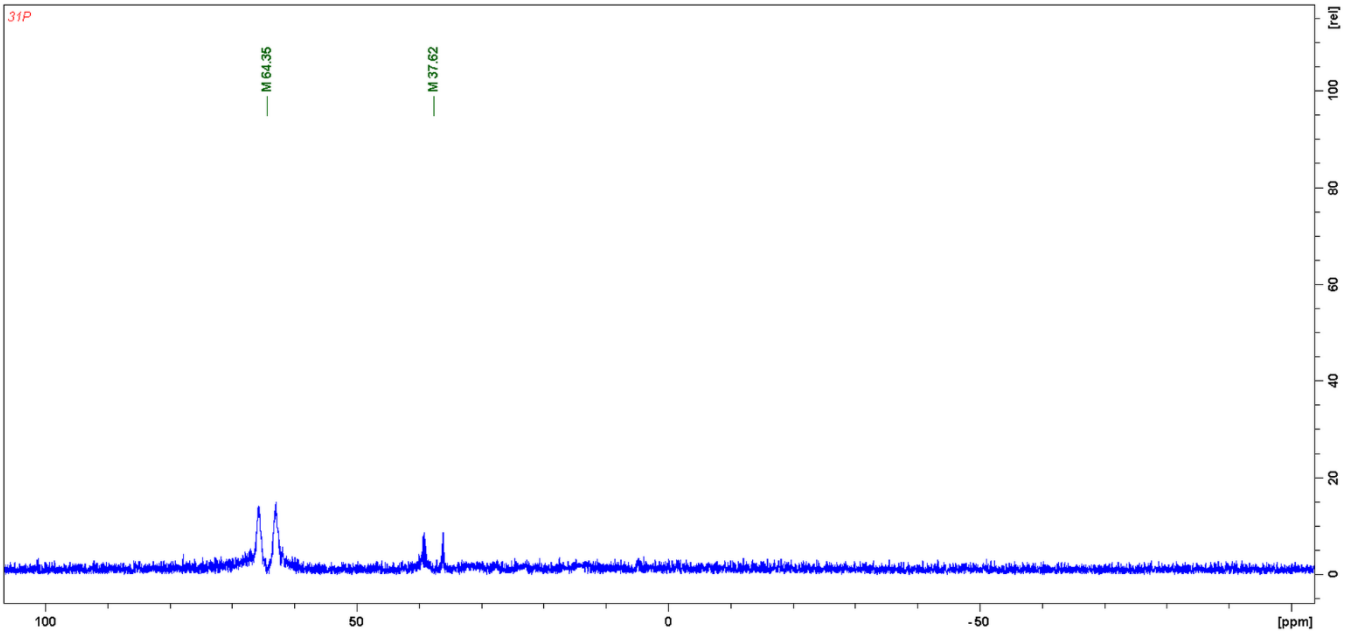


Figure S143. ^{31}P NMR (400 MHz, C_6D_6, 298 K) spectrum of (Ph)(4-CN-Ph)C=P-P*t*Bu$_2$ (**3c**) crystals after 2 weeks in the air condition.

- 64.33 ppm, (doublet of multiplets), $J_{P\text{-}H}$ = 445.7 Hz, *t*Bu$_2$**P**H(=O);
- 37.52 ppm, (doublet of multiplets), $J_{P\text{-}H}$ = 505.9 Hz, (Ph)(4-CN-Ph)HC-**P**H(=O)(OH);

B.3.3. (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**)

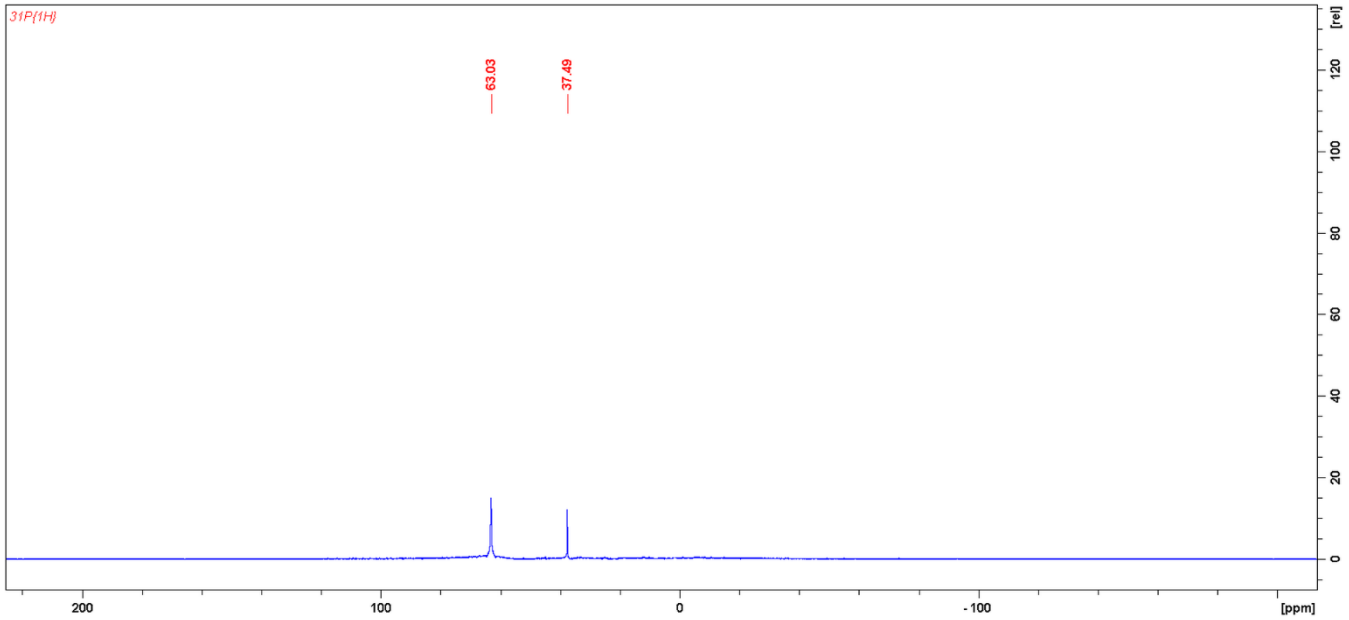


Figure S144. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) crystals after 2 weeks in the air conditions.

- 63.03 ppm, (s), *t*Bu$_2$**P**H(=O);
- 37.49 ppm, (s), (4-CN-Ph)$_2$(H)C-**P**H(=O)(OH);

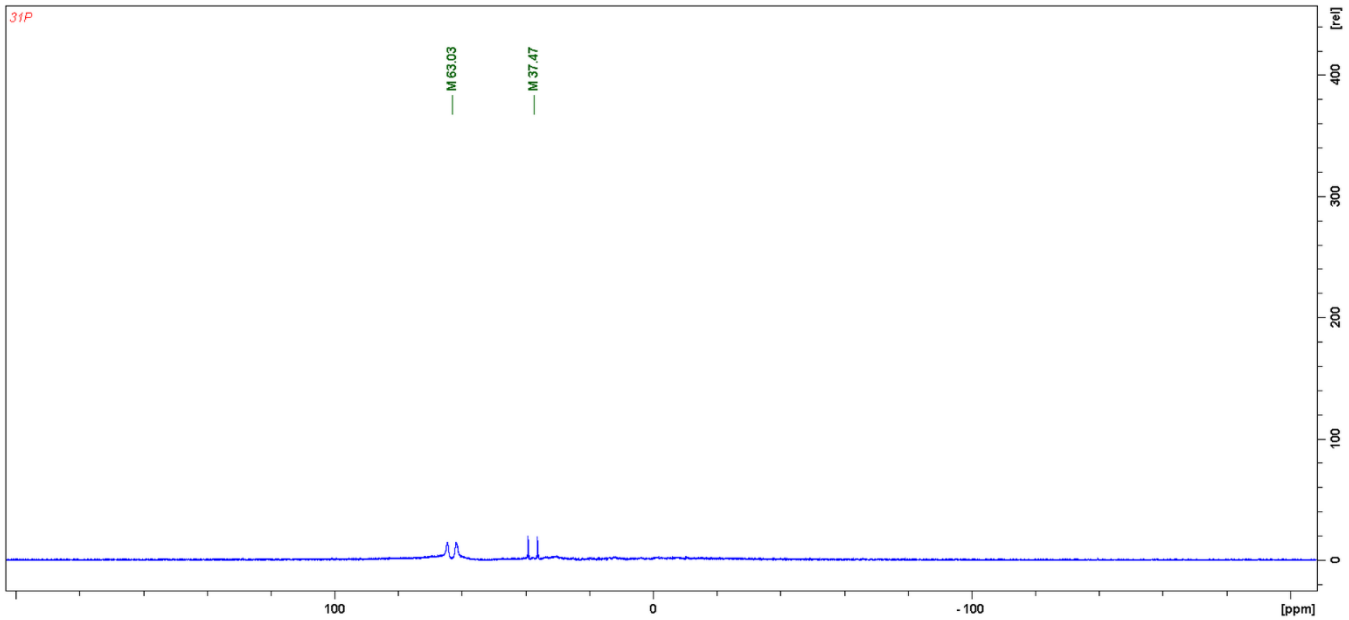


Figure S145. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of (4-CN-Ph)$_2$C=P-P*t*Bu$_2$ (**3d**) crystals after 2 weeks in the air conditions.

- 63.03 ppm, (d), $J_{P\text{-}H}$ = 440.9 Hz, *t*Bu$_2$**P**H(=O);
- 37.49 ppm, (dd), $J_{P\text{-}H}$ = 560.3 Hz, J_{PH} = 16.1 Hz, (4-CN-Ph)$_2$(H)C-**P**H(=O)(OH);

B.3.4. (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**)

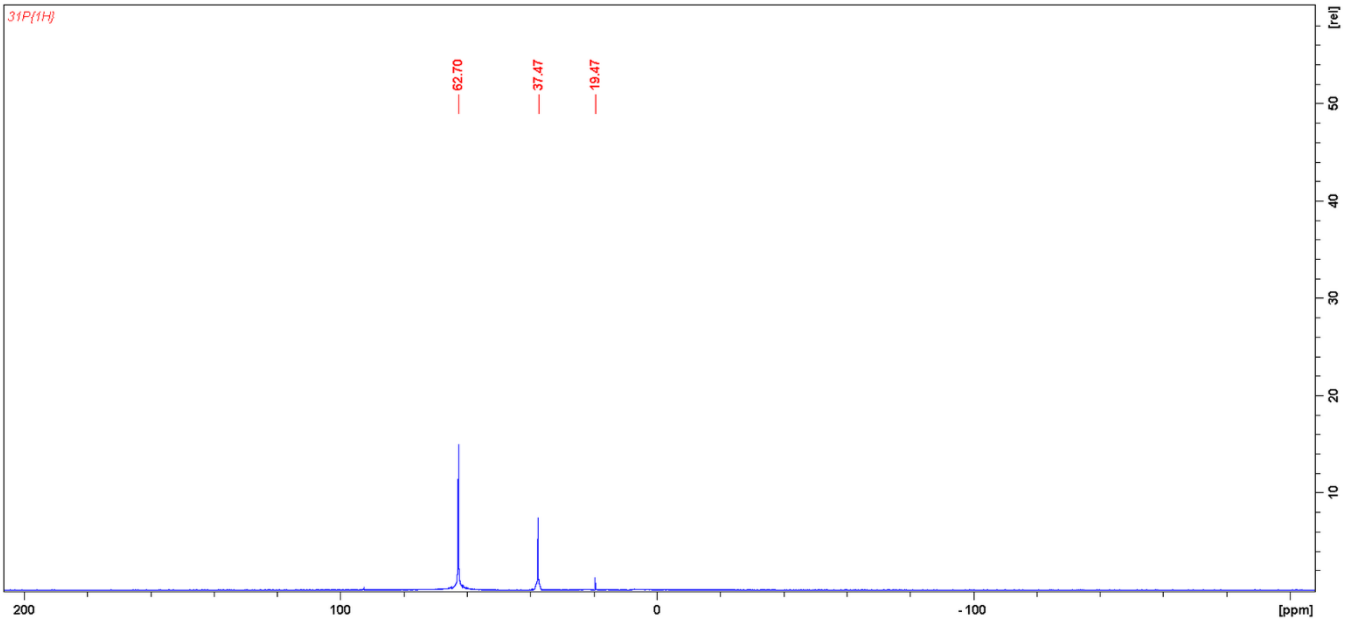


Figure S146. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum of (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) crystals after 2 weeks in the air conditions.

- 62.70 ppm, (s), *t*Bu$_2$**P**H(=O);
- 37.47 ppm, (s), (4-MeO-Ph)$_2$(H)C-**P**H(=O)(OH);
- 19.47 ppm, (s), *t*Bu$_2$**P**H;

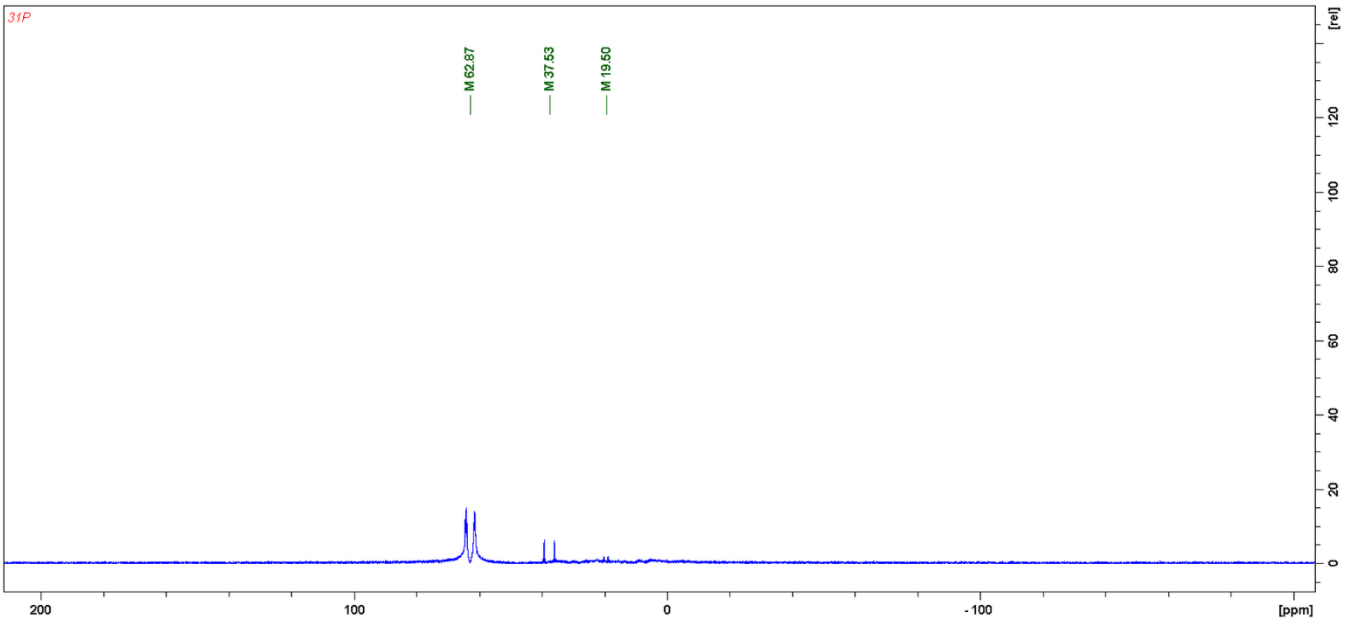


Figure S147. $^{31}P\{^{1}H\}$-NMR (400 MHz, C_6D_6, 298 K) spectrum of (4-MeO-Ph)$_2$C=P-P*t*Bu$_2$ (**3e**) crystals after 2 weeks in the air conditions.

- 62.87 ppm, (doublet of multiplets), $J_{P\text{-}H}$ = 425.6 Hz, *t*Bu$_2$**P**H(=O);
- 37.53 ppm, (dd), J_{PH} = 507.2 Hz, $J_{P\text{-}H}$ = 18.4 Hz, (4-MeO-Ph)$_2$(H)C-**P**H(=O)(OH);
- 19.5 ppm, (doublet of multiplets), $J_{P\text{-}H}$ = 188.7 Hz, *t*Bu$_2$**P**H;

B.3.5. {(Me)$_2$N-Ph}(H)C=P-P*t*Bu$_2$ (**4d**)

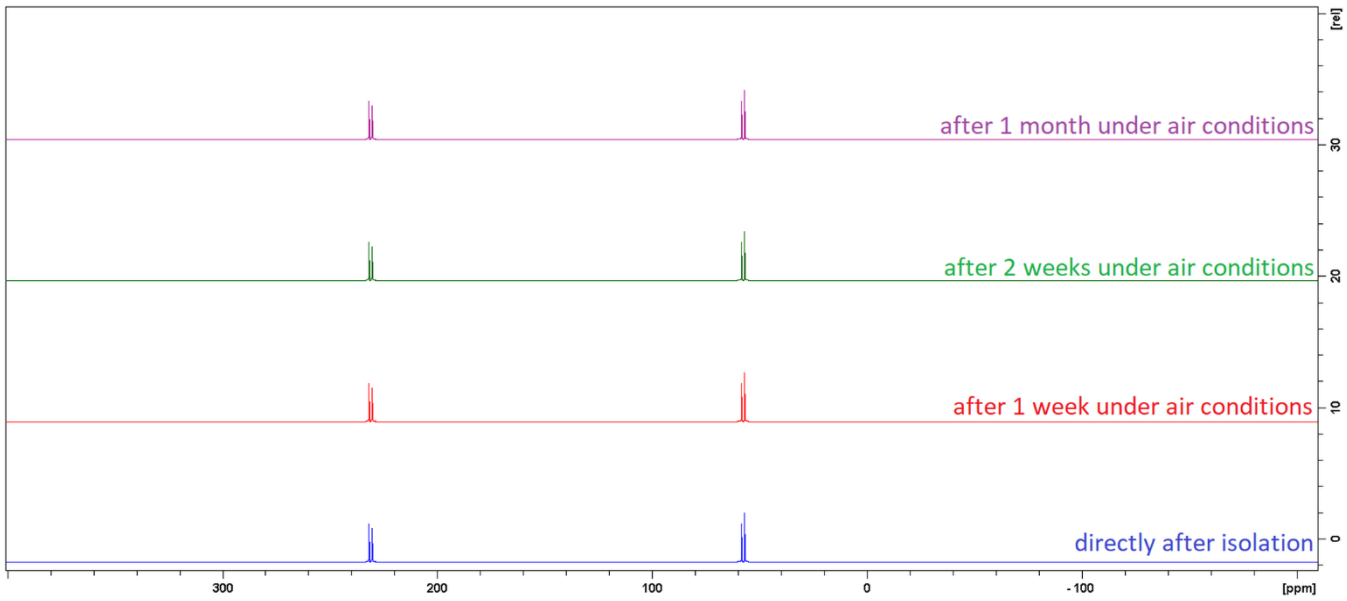


Figure S148. $^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum presented stability investigation of {(Me)$_2$N-Ph}(H)C=P-P*t*Bu$_2$ (**4d**) under air conditions.

B.3.6. PhPh(H)C=P-P*t*Bu$_2$ (**4e**)

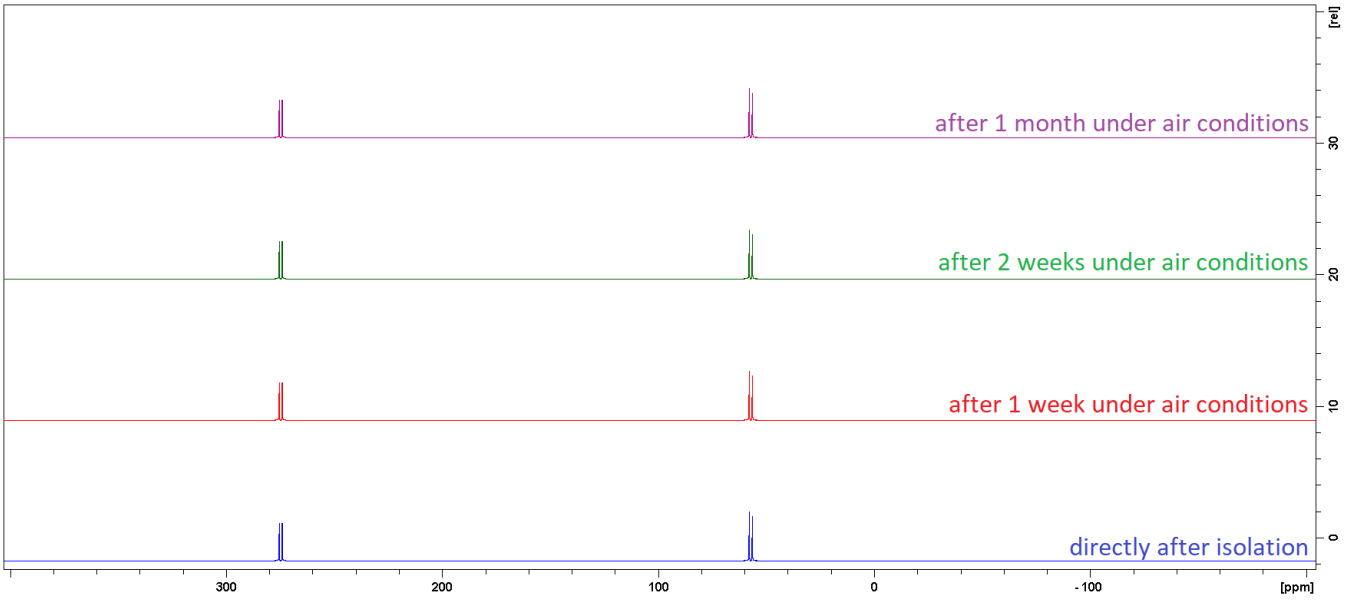


Figure S149. $^{31}P\{^{1}H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum presented stability investigation of PhPh(H)C=P-P*t*Bu$_2$ (**4e**) under air conditions.

B.3.7. Stability of $(Ph)_2C=P\text{-}PtBu_2$ (**3a)** in water

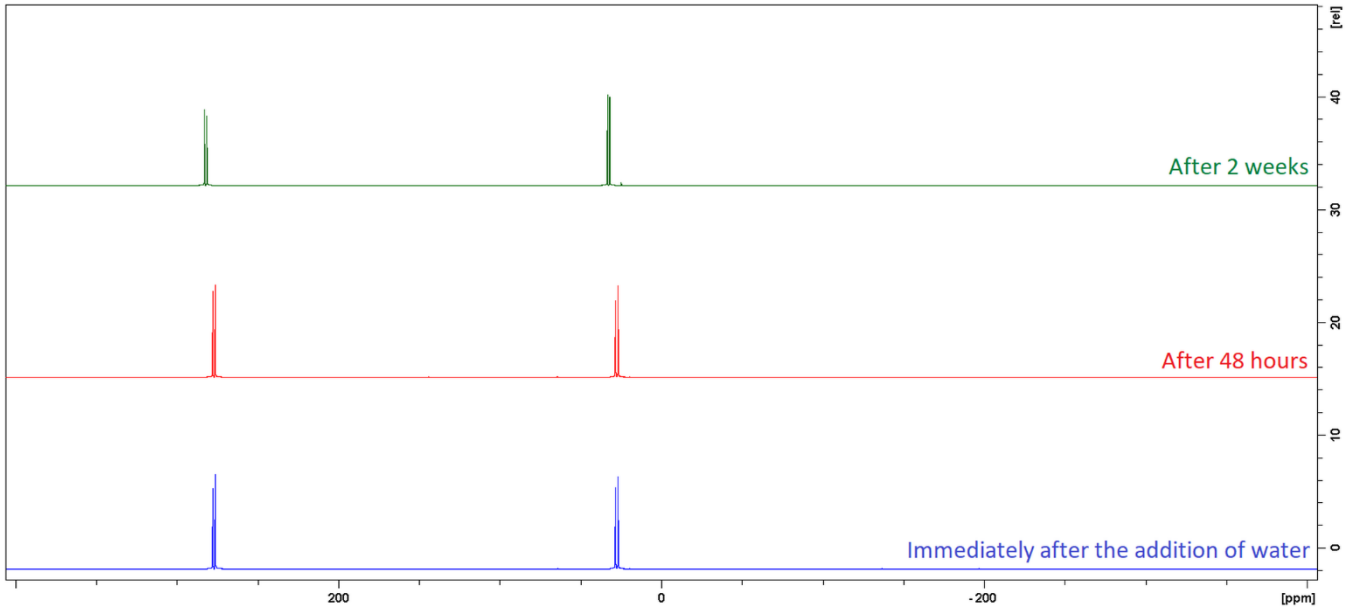


Figure S150. $^{31}P\{^1H\}$ NMR (400 MHz, C_6D_6, 298 K) spectrum presented stability investigation of $(Ph)_2C=P\text{-}PtBu_2$ (**3a**) in water.

PART C. Crystallographic data

The X-ray intensity data for **3a**, **3c**, **3d**, **3e**, **4d**, **4e**, and **5** were measured with an IPDS2T diffractometer equipped with an IPDS2T STOE image plate detector system and microfocus X-ray sources providing Kα radiation by high-grade multilayer X-ray mirror optics for Mo (λ = 0.71073 Å, **3e**, **3f** and **4e**) and Cu (λ = 1.54186 Å, **3a**, **3c**, **3d**, **4d**, **5**) wavelengths. The all measurements were carried out at 120 K. The structures of the compounds were solved by direct methods and refined against F^2 with the Shelxs-2008 and Shelxl-2008 programs[6] run under WinGX.[7] Non-hydrogen atoms were refined with anisotropic displacement parameters. The isotropic displacement parameters of all hydrogens were fixed to 1.2 U_{eq} for CH and CH_2 (1.5 times for methyl groups).

The crystallographic data for the structures of **3a**, **3c**, **3d**, **3e**, **3f**, **4d**, **4e**, and **5** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 2077813-2077819 and 2087482. Copies of the data can be obtained free of charge upon application to the 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 **3a**, **3c**, **3d**, and **3e**.

	3a	**3c**	**3d**	**3e**
Empirical formula	$C_{21}H_{28}P_2$	$C_{22}H_{27}N_1P_2$	$C_{53}H_{60}N_4P_4$	$C_{23}H_{32}O_2P_2$
Formula weight	684.74	367.38	876.93	402.42
Radiation source	Cu-*K*α	Cu-*K*α	Cu-*K*α	Mo-*K*α
Crystallographic System	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*C*2/*c*	Pbcn	$P2_1/c$	$P2_1/n$
a [Å]	15.2838(7)	24.4705(11)	16.0860(3)	10.1084(14)
b [Å]	10.1380(4)	9.0836(3)	16.7747(3)	20.209(3)
c [Å]	26.3114(11)	18.7680(7)	18.1220(4)	11.8485(17)
α [°]	90	90	90	90
β [°]	101.444(4)	90	93.719(2)	110.326(10)
γ [°]	90	90	90	90
V [Å^3]	3995.8(3)	4171.8(3)	4879.70(19)	2269.7(6)
Z	8	8	4	4
Calculated Density [g·cm^{-1}]	1.138	1.170	1.194	1.178
T [K]	120(2)	120(2)	120(2)	120(2)
μ [mm^{-1}]	1.935	1.904	1.723	0.2060
Final R indices	0.0410	0.0686	0.0430	0.7070
[*I*>2σ(I)]	0.1054	0.1708	0.1049	0.1759
R indices (all data)	0.0496	0.1064	0.0500	0.1332
[*I*>2σ(I)] (all data)	0.1107	0.2090	0.1089	0.2019
CCDC	2077813	2077814	2077816	2077815

Table S2. Crystallographic data for **3f**, **4d**, **4e**, and **5**.

	3f	**4d**	**4e**	**5**
Empirical formula	$C_{19}H_{32}P_2$	$C_{34}H_{55}N_2P_4$	$C_{21}H_{28}P_2$	$C_{24}H_{72}Li_8O_8Si_8$
Formula weight	322.38	618.7	342.37	769.05
Radiation source	Mo-*K*α	Cu-*K*α	Mo-*K*α	Cu-*K*α
Crystallographic System	Orthorhombic	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_12_12_1$	*C*2/*c*	I2/a	*I*-4
a [Å]	10.1040(2)	40.670(2)	23.6882(16)	13.6438(4)
b [Å]	12.2845(4)	6.1403(2)	5.9485(2)	13.6438(4)
c [Å]	15.8640(4)	35.368(2)	29.8384(19)	13.3861(4)
α [°]	90	90	90	90
β [°]	90	122.345(4)	111.433(5)	90
γ [°]	90	90	90	90
V [Å^3]	1969.08(9)	7462.0(7)	3913.7(4)	2491.87(16)
Z	4	8	8	2
Calculated Density [g·cm^{-1}]	1.087	1.101	1.162	1.025
T [K]	120(2)	120(2)	120(2)	120(2)
μ [mm^{-1}]	0.215	2.033	0.221	2.283
Final R indices	0.0319	0.0812	0.0686	0.0790
[*I*>2σ(I)]	0.0831	0.1899	0.2010	0.2049
R indices (all data)	0.0354	0.1802	0.1111	0.0862
[*I*>2σ(I)] (all data)	0.0848	0.2331	0.2208	0.2209
CCDC	2087482	2077817	2077818	2077819

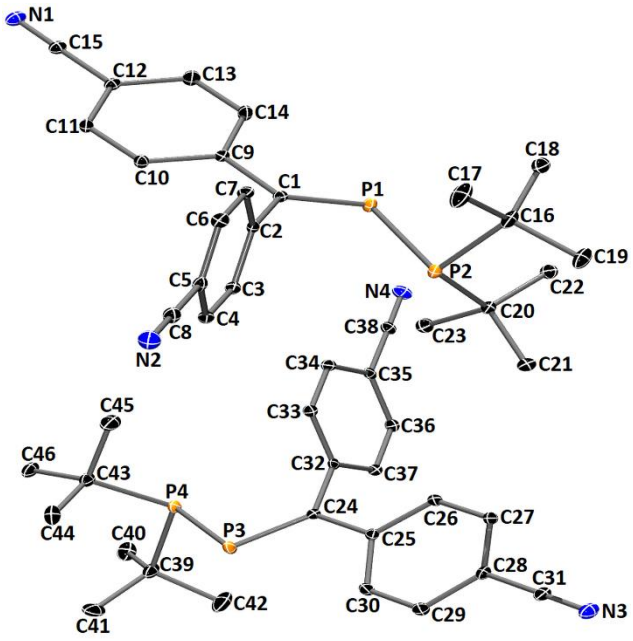


Figure S151. X-ray crystal structure of (4-CN-Ph)$_2$C=P-*t*Bu$_2$ (**3d**) (the independent part of the unit cell; ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted and carbon atoms are drawn as sphere for clarity). Important distances (Å) and angles (deg): C1-P1 1.697(2), P1-P2 2.222(8), C24-P3 1.691(2), P3-P4 2.2184(8); C1-P1-P2 104.90(7), C24-P3-P4 103.92(7).

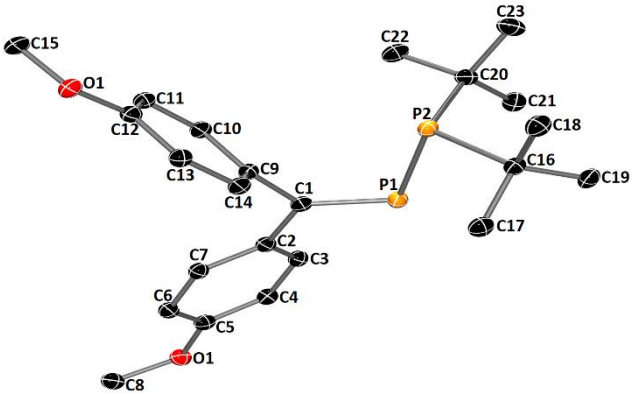


Figure S152. X-ray crystal structure of (4-MeO-Ph)$_2$C=P-*t*Bu$_2$ (**3e**) (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted and carbon atoms are drawn as sphere for clarity). Important distances (Å) and angles (deg): C1-P1 1.707(3), P1-P2 2.2114(12); C1-P1-P2 103.65(12).

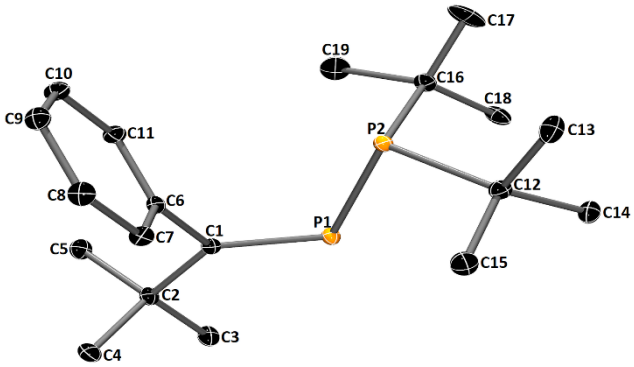


Figure S153. X-ray crystal structure of *t*Bu(Ph)C=P-*t*Bu$_2$ (**3e**) (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted and carbon atoms are drawn as sphere for clarity). Important distances (Å) and angles (deg): C1-P1 1.6936(16), P1-P2 2.2245(6); C1-P1-P2 103.38(6).

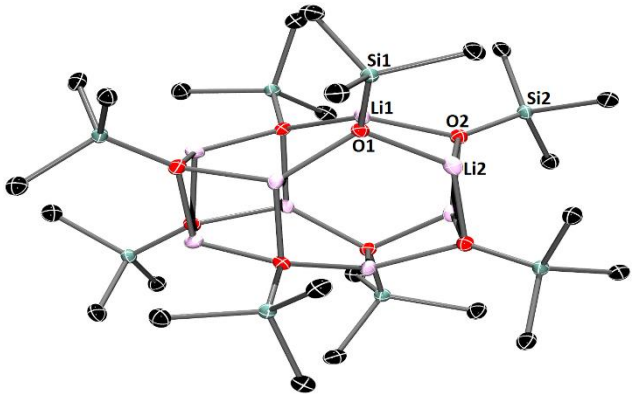


Figure S154. X-ray crystal structure of [LiOSiMe$_3$]$_8$ (**5**) (ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted and carbon atoms are drawn as sphere for clarity). Important distances (Å) and angles (deg): O1-Si1 1.615(6), O2-Si2 1.606(7), O1-Li1 1.896(19), O1-Li2 1.903(18), O2-Li1 1.91(2), O2-Li2 1.876(17); Li1-O1-Li2 79.0(7), Li1-O2-Li2 80.3(8).

PART E. DFT calculations

E.1. General methods

All calculations presented in the paper were performed using the Gaussian 09[8] program package. Molecular geometries of all compounds were optimized using density functional theory at the TPSSTPSS functional by Tao *et al*[9] with 6-31+G(d,p) basis set for: C, H, N, Cl, O, Si, Li, P, and LANL2DZ basis set for Ti. The TPSSTPSS exchange-correlation functional has been chosen, as it has good overall performance for the description of kinetic and thermodynamic parameters of reactions. By adding GD3BJ keyword that includes D3 version of Grimme dispersion with Becke-Johnson[10] damping into calculations 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. Nature of the final gas-phase geometries as local minima (no imaginary frequencies) or transition states (one imaginary frequency) on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Values of calculated energies, enthalpies and Gibbs free-energies derived from thermochemical calculations were corrected for the zero-point energy (ZPE). Scans of potential energy surface along the *t*Bu$_2$P**P**/RR'**C**=O, **Ti/O=**CRR' and **C=O** bonds were performed to establish local minima corresponding to transition products and confirm proposed mechanism of the reaction. Local maxima related to transition states were also established and validated by IRC calculations (to confirm that a located saddle points lie on the minimum energy path between assumed minima) and used to determine energy barriers between respective transformations. Values of energy barriers $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ of reactions **3a-3j** were determined as the difference between energy of rate-determining transition state and rate-determining intermediate as described.[11]

Molecular geometries of [(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**), **3a-3j** and respective ketones were re-optimized and geometries of **4a-4e** and [(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] were optimized using density functional theory at the ωB97XD functional[10, 12, 13] with 6-31+G(d,p) basis set before calculating properties of these species (NMR shifts and Fukui Functions). Theoretical ^{31}P NMR shifts of **3a-3j** and **4a-4e** were determined by calculating NMR shielding tensors using Gauge-Independent Atomic Orbital (GIAO)[14] method at the MN12SX[15]/cc-pvdz level of theory including presence of a solvent (benzene) using the CPCM polarizable conductor calculation model.[16] Condensed Fukui functions[17] and dual descriptors[17, 18] were determined using optimized structures to single point calculations on **1**, [(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] and ketones for *N*, *N-1* and *N+1* electron states at ωB97XD/DefTZVP[19, 20] for **1**, [(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] and ωB97XD/6-31+G(d,p) level of theory for ketones. Condensed to atom parameters were calculated using partial charges derived *via* Hirshfeld population analysis.

Table S3. Experimental and calculated $^{31}P\{^{1}H\}$ NMR shifts for the formed phosphanylphosphaalkenes.

Phosphanylphosphaalkenes	$^{31}P\{^{1}H\}$ NMR-exp.			$^{31}P\{^{1}H\}$ NMR-theor.	
	P(1) [ppm]	P(2) [ppm]	$J_{P\text{-}P}$ [Hz]	P(1) [ppm]	P(2) [ppm]
3a	277.32	27.39	228.9	278.26	30.99
3b	297.17	9.57	228.4	297.43	2.07
3c_*E*	303.89	28.98	228.9	306.88	28.83
3c_*Z*	286.27	27.77	228.9	288.40	27.19
3d	311.26	29.40	232.5	321.03	30.26
3e	258.28	28.28	228.9	254.30	30.93
3f_*E*	265.96	21.31	216.9	268.83	20.12
3f_*Z*	261.05	16.15	230.4	256.58	16.70
3g	234.73	23.14	228.9	236.65	22.11
3h	221.02	19.51	228.8	219.62	16.76
3i_*E*	263.63	21.91	234.9	262.57	23.52
3i_*Z*	253.06	24.65	222.8	255.49	24.02
3j_*E*	225.87	17.00	232.9	224.88	17.18
3j_*Z*	232.48	18.52	232.9	232.63	19.50
4a_*E*	254.39	52.82	220.8	254.39	50.63
4a_*Z*	249.40	12.85	212.8	249.21	12.63
4b_*E*	256.25	52.23	220.8	255.34	50.08
4b_*Z*	251.24	13.17	212.8	251.29	16.16
4c_*E*	266.61	56.72	220.8	264.64	52.49
4c_Z	not observed	not observed	not observed	268.00	12.09
4d_E	231.17	57.73	224.9	230.41	63.45
4d_Z	not observed	not observed	not observed	229.63	19.85
4e_E	274.72	57.13	224.9	281.10	58.14
4e_Z	not observed	not observed	not observed	228.31	18.14

Table S4. Selected computational parameters obtained for considered systems (in atomic units A.U.): **ε_0 -** electronic energy; **$\varepsilon_{0+...}$ -** sum of electronic and: **E_{zpe} -** zero-point energies, **E_{therm} -** thermal energies, **H –** thermal enthalpies, **G -** thermal free energies calculated at TPSSTPSS//6-31+G(d,p) [TPSSTPSS//LANL2DZ for Ti] level of theory. Values of **ΔH** and **ΔG** were calculated as the difference between energy of given transition state/intermediate or products and substrates (**1** and respective ketone).

Substrates							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
1	-2756.748730	-2755.870773	-2755.818193	-2755.817249	-2755.952186	-	-
$(Ph)_2C=O$ (3a)	-576.804227	-576.615676	-576.604657	-576.603713	-576.653632	-	-
9-fluorenone (3b)	-575.607850	-575.440898	-575.431082	-575.430138	-575.476274	-	-
(Ph)(4-CN-Ph)C=O (3c)	-669.067353	-668.880585	-668.867673	-668.866729	-668.921430	-	-
$(4\text{-CN-Ph})_2C=O$ (3d)	-761.329100	-761.144129	-761.129331	-761.128386	-761.187795	-	-
$(4\text{-MeO-Ph})_2C=O$ (3e)	-805.909108	-805.656488	-805.640181	-805.639237	-805.701418	-	-
*t*Bu(Ph)C=O (3f)	-502.981595	-502.762110	-502.749873	-502.748929	-502.801997	-	-
$Me_2C=O$ (3g)	-193.205228	-193.122707	-193.117135	-193.116190	-193.151963	-	-
Cyclohexanone (3h)	-309.979720	-309.830773	-309.824136	-309.823192	-309.861339	-	-
Me(Ph)C=O (3i)	-385.005760	-384.869848	-384.861830	-384.860886	-384.902834	-	-
cyclo-PrMeC=O (3j)	-270.622260	-270.504781	-270.498094	-270.497150	-270.535365	-	-
$[(BDI^*)Ti(Cl)(\mu_2\text{-}O)]_2$	-3667.011357	-3665.739078	-3665.661895	-3665.660951	-3665.846223	-	-
Formation of 3a							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3333.543647	-3332.475563	-3332.411768	-3332.410824	-3332.566603	6.49	25.11
I1	-3333.566908	-3332.498405	-3332.435040	-3332.434096	-3332.589349	-8.41	10.55
TS2	-3333.550495	-3332.483334	-3332.419367	-3332.418423	-3332.575538	1.63	19.39
3a	-1500.108057	-1499.678736	-1499.653113	-1499.652169	-1499.734600	-39.50	-33.23
Formation of 3b							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3332.345641	-3331.300647	-3331.236919	-3331.235975	-3331.394539	7.31	21.72
I1	-3332.387966	-3331.343114	-3331.278745	-3331.277801	-3331.439957	-19.48	-7.36
TS2	-3331.061988	-3331.306390	-3331.242609	-3331.241665	-3331.401609	3.66	17.19
3b	-1498.916061	-1498.507926	-1498.483457	-1498.482513	-1498.561712	-42.01	-36.09
Formation of *Z*-3c							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3425.801373	-3424.736391	-3424.669843	-3424.668899	-3424.833818	9.66	25.49
I1	-3425.832789	-3424.766083	-3424.700728	-3424.699784	-3424.859765	-10.12	8.87
TS2	-3425.816070	-3424.750788	-3424.684755	-3424.683811	-3424.846532	0.11	17.34
Z-3c	-1592.373550	-1591.946022	-1591.918434	-1591.917490	-1592.008632	-40.98	-37.22
Formation of *E*-3c							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3425.801416	-3424.736298	-3424.669830	-3424.668886	-3424.833410	9.66	25.75
I1	-3425.834087	-3424.767168	-3424.700973	-3424.700029	-3424.864483	-10.28	5.85
TS2	-3425.817367	-3424.751839	-3424.685943	-3424.684999	-3424.847081	-0.65	16.99

E-3c	-1592.373062	-1591.945502	-1591.917949	-1591.917005	-1592.004427	-40.66	-34.53
Formation of 3d							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3518.064129	-3517.000819	-3516.932399	-3516.931455	-3517.100871	9.08	25.04
I1	-3518.099878	-3517.034963	-3516.966781	-3516.965836	-3517.133998	-12.94	3.83
TS2	-3518.082024	-3517.018253	-3516.950417	-3516.949473	-3517.116290	-2.46	15.17
3d	-1684.637380	-1684.211522	-1684.182081	-1684.181137	-1684.273200	-42.25	-36.07
Formation of 3e							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3562.643329	-3561.512310	-3561.442535	-3561.441591	-3561.613514	9.54	25.67
I1	-3562.667753	-3561.535290	-3561.466506	-3561.465562	-3561.633290	-5.81	13.01
TS2	-3562.650177	-3561.518739	-3561.449394	-3561.448450	-3561.619847	5.15	21.62
3e	-1729.211092	-1728.717918	-1728.686886	-1728.685942	-1728.781542	-38.38	-32.69
Formation of *Z*-3f							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3259.710657	-3258.613782	-3258.547802	-3258.546858	-3258.710307	12.37	28.10
I1	-3259.745009	-3258.646559	-3258.580852	-3258.579908	-3258.743156	-8.79	7.06
TS2	-3259.721157	-3258.624271	-3258.558637	-3258.557693	-3258.719743	5.43	22.05
Z-3f	-1426.284266	-1425.823812	-1425.797217	-1425.796273	-1425.879964	-38.79	-31.31
Formation of *E*-3f							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3259.709289	-3258.611816	-3258.546029	-3258.545085	-3258.707911	13.51	29.63
I1	-3259.750650	-3258.651891	-3258.586596	-3258.585652	-3258.745580	-12.47	5.51
TS2	-3259.709324	-3258.613192	-3258.547310	-3258.546366	-3258.709311	12.69	28.73
E-3f	-1426.276102	-1425.815444	-1425.788971	-1425.788027	-1425.870835	-33.51	-25.46
Formation of 3g							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-2949.941184	-2948.979370	-2948.921003	-2948.920059	-2949.066336	8.57	24.21
I1	-2949.976905	-2949.012292	-2948.954440	-2948.953496	-2949.097690	-12.84	4.14
TS2	-2949.954136	-2948.991811	-2948.933817	-2948.932873	-2949.078147	0.36	16.65
3g	-1116.504264	-1116.179412	-1116.160195	-1116.159251	-1116.224752	-36.04	-27.99
Formation of 3h							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3066.720932	-3065.693363	-3065.633362	-3065.632418	-3065.782222	5.14	20.05
I1	-3065.643079	-3065.726890	-3065.666875	-3065.665931	-3065.815357	-16.32	-1.17
TS2	-3066.734289	-3065.706151	-3065.646546	-3065.645602	-3065.793980	-3.30	12.52
3h	-1233.281831	-1232.891297	-1232.870388	-1232.869444	-1232.940059	-38.09	-31.79
Formation of *Z*-3i							
Compound	E_{electr} [A.U.]			ε_0 + H [A.U.]	ε_0 + G [A.U.]		

		$\varepsilon_0 + E_{ZPE}$ [A.U.]	$\varepsilon_0 + E_{therm}$ [A.U.]			ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3141.741552	-3140.726565	-3140.665373	-3140.664429	-3140.816754	8.78	24.50
I1	-3141.775999	-3140.759481	-3140.698448	-3140.697504	-3140.848972	-12.40	3.87
TS2	-3141.753018	-3140.738392	-3140.677367	-3140.676422	-3140.827716	1.10	17.48
Z-3i	-1308.303326	-1307.926242	-1307.903806	-1307.902862	-1307.977266	-35.35	-29.05
Formation of *E*-3i							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3141.738647	-3140.726033	-3140.663718	-3140.662774	-3140.820871	9.84	21.87
I1	-3141.779931	-3140.765400	-3140.703694	-3140.702750	-3140.858301	-15.76	-2.10
TS2	-3141.741103	-3140.728468	-3140.666462	-3140.665518	-3140.823623	8.08	20.11
E-3i	-1308.304831	-1307.927558	-1307.905167	-1307.904222	-1307.978895	-36.22	-30.09
Formation of *Z*-3j							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3027.360404	-3026.363588	-3026.303963	-3026.303019	-3026.451866	7.29	22.85
I1	-3027.387622	-3026.389660	-3026.329937	-3026.328993	-3026.478119	-9.35	6.04
TS2	-3027.367428	-3026.370859	-3026.311326	-3026.310381	-3026.458934	2.57	18.33
Z-3j	-1193.919416	-1193.560030	-1193.539316	-1193.538372	-1193.607826	-34.87	-27.78
Formation of *E*-3j							
Compound	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.]	ΔH [kcal mol^{-1}]	ΔG [kcal mol^{-1}]
TS1	-3027.359489	-3026.362673	-3026.303048	-3026.302104	-3026.450951	7.87	23.44
I1	-3027.380572	-3026.383537	-3026.324367	-3026.323423	-3026.473032	-5.78	9.30
TS2	-3027.361618	-3026.366779	-3026.307433	-3026.306489	-3026.455933	5.07	20.25
E-3j	-1193.918065	-1193.558825	-1193.538062	-1193.537118	-1193.606958	-34.06	-27.23

Table S5. Selected computational parameters obtained for considered systems (in atomic units A.U.): **ε_0 -** electronic energy; **$\varepsilon_{0+...}$ -** sum of electronic and: **E_{zpe} -** zero-point energies, **E_{therm} -** thermal energies, **H –** thermal enthalpies, **G -** thermal free energies calculated at TPSSTPSS//6-31+G(d,p).

Reaction of acetone with *t*Bu_2P-P$SiMe_3$($LiTHF_3$)									
Compound	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.]	ΔH_{298K} [kJ mol^{-1}]	ΔG_{298K} [kJ mol^{-1}]	K_{298K}	α [%]
CH_3COCH_3	-193.205228	-193.122707	-193.117135	-193.116190	-193.151963	5.60	-4.03	5.09	83.57
tBu_2PP($SiMe_3$)H	-1408.490128	-1408.126216	-1408.103133	-1408.102189	-1408.176256				
$CH_2C(OLiTHF_3)CH_3$	-897.791336	-897.366748	-897.341144	-897.340200	-897.430294				
tBu_2PP($SiMe_3$)Li·3THF	-2113.086524	-2112.378529	-2112.335690	-2112.334946	-2112.453052				

E.2. Philicity of selected atoms in 1, [(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}] and ketones

Table S6. Values of nucleophilic (f_N), electrophilic(f_E) Fukui functions and dual descriptors (Δf) calculated using partial charges derived via Hirshfeld Population Analysis.

[(BDI*)Ti(Cl){η^2-P-P*t*Bu$_2$}] (**1**)								
*t*Bu$_2$**P**			P			**Ti**(IV)		
f_N	f_E	Δf	f_N	f_E	Δf	f_N	f_E	Δf
0.048	0.045	-0.003	0.241	0.158	-0.083	0.067	0.148	0.081
[(BDI*)Ti(Cl){η^2-P(SiMe$_3$)-P*t*Bu$_2$}]								
*t*Bu$_2$**P**			Me$_3$Si**P**			**Ti**(III)		
f_N	f_E	Δf	f_N	f_E	Δf	f_N	f_E	Δf
0.030	0.024	-0.006	0.069	0.036	-0.033	0.137	0.203	0.066

Table S7. Values of nucleophilic (f_N), electrophilic(f_E) Fukui functions and dual descriptors (Δf) calculated using partial charges derived via Hirshfeld Population Analysis.

Compound	C			O		
	f_N	f_E	Δf	f_N	f_E	Δf
(Ph)$_2$C=O	0.057	0.127	0.070	0.266	0.141	-0.125
9-fluorenone	0.077	0.113	0.036	0.311	0.142	-0.169
(Ph)(4-CN-Ph)C=O	0.055	0.101	0.046	0.255	0.121	-0.134
(4-CN-Ph)$_2$C=O	0.053	0.106	0.053	0.245	0.124	-0.120
(4-MeO-Ph)$_2$C=O	0.027	0.130	0.103	0.139	0.141	0.002
*t*Bu(Ph)C=O	0.078	0.121	0.043	0.295	0.136	-0.159
Me$_2$C=O	0.121	0.213	0.092	0.386	0.228	-0.159
Cyclohexanone	0.109	0.109	-0.001	0.341	0.134	-0.207
Me(Ph)C=O	0.086	0.123	0.037	0.342	0.147	-0.194
cyclo-PrMeC=O	0.097	0.192	0.094	0.349	0.186	-0.163

E.3. Optimized structures and Cartesian coordinates

E.3.1. Substrates and by-products

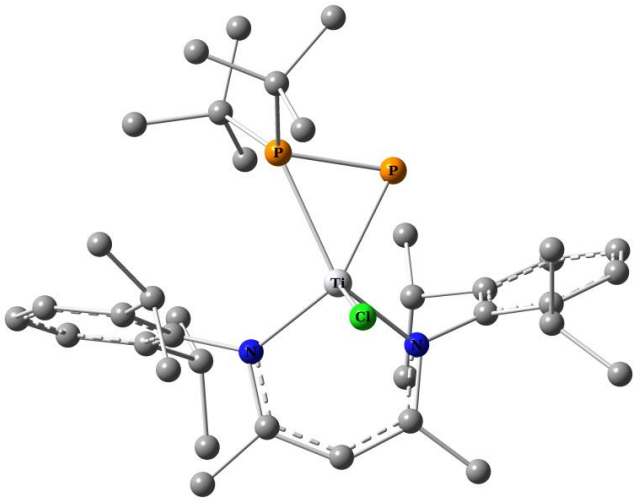


Figure S155. Optimized structure of **1**.

Below are presented xyz coordinates for optimized geometry of **1**:

C	-3.12142900	-0.43821000	0.21235000
C	-3.18317000	-1.08400800	1.47197200
C	-4.30821200	-0.85662700	2.27879200
H	-4.37722600	-1.34288600	3.24957700
C	-5.33314700	0.00231700	1.86335500
H	-6.19604900	0.17278100	2.50510000
C	-5.23283100	0.65688400	0.63396500
H	-6.01724400	1.34724100	0.32732700
C	-4.13090600	0.45450700	-0.21788100
C	-2.04603600	-1.98798600	1.92913000
H	-1.12887400	-1.56972900	1.48867900
C	-2.22643800	-3.42775600	1.39737800
H	-1.42235500	-4.07676700	1.76836600
H	-2.20472000	-3.45874100	0.30167100
H	-3.18491400	-3.84422700	1.73578300
C	-1.86369800	-1.99921100	3.45753400
H	-0.93068800	-2.51642300	3.71520900
H	-2.68389100	-2.52824400	3.96237400
H	-1.81485500	-0.97802600	3.85445600
C	-4.03573400	1.24035400	-1.52133100
H	-3.19252900	0.84771600	-2.10185200
C	-3.73396600	2.72864500	-1.22932700
H	-3.60853200	3.27985300	-2.17024200
H	-2.81417100	2.82993400	-0.64182800
H	-4.55881400	3.18336500	-0.66315100
C	-5.31234100	1.11509600	-2.38199900
H	-5.15744100	1.60514300	-3.35202700
H	-6.16961300	1.60118200	-1.89727300
H	-5.58538500	0.06714200	-2.56388700
C	2.28606900	-1.34560700	-0.69375400
C	3.31609900	-0.53661400	-1.23931900
C	4.64624600	-0.91804800	-0.98830400
H	5.45857500	-0.32346700	-1.39940900
C	4.94865700	-2.03800000	-0.20603800
H	5.98683200	-2.31263300	-0.02700600
C	3.91653000	-2.78298800	0.37193100
H	4.15991600	-3.62952600	1.01095400
C	2.56835700	-2.45699900	0.14175200
C	3.00411900	0.73447100	-2.02817300
H	2.13231500	1.19471400	-1.53163200
C	4.15432000	1.75759000	-1.96480900

H	3.80434900	2.72793400	-2.33795200
H	5.00070400	1.45003800	-2.59473800
H	4.52242000	1.88997000	-0.94029800
C	2.61587700	0.49839000	-3.50380800
H	2.50907500	1.46557300	-4.01105800
H	1.65518700	-0.01578400	-3.59566200
H	3.39280300	-0.08031400	-4.02339500
C	1.45469400	-3.28136200	0.79332800
H	0.56883500	-2.63494800	0.84919400
C	1.06383300	-4.53710700	-0.02514500
H	0.52035300	-4.28162800	-0.93990800
H	0.40966400	-5.18186400	0.57598300
H	1.95750700	-5.11705000	-0.29396300
C	1.82513000	-3.72503100	2.22579800
H	0.93413900	-4.12007900	2.73052500
H	2.22135700	-2.89593700	2.82083300
H	2.57480700	-4.52783000	2.21283600
C	-3.40151500	-2.15363100	-1.99533600
H	-3.95124700	-2.45291200	-1.09566100
H	-3.27872200	-3.01779500	-2.65486300
H	-4.01271900	-1.40213200	-2.51032700
C	-2.05501400	-1.56600800	-1.62727200
C	-0.93172500	-1.99744500	-2.36892200
H	-1.15800300	-2.62499200	-3.22643400
C	0.43834000	-1.86338100	-2.06879700
C	1.40368000	-2.67892200	-2.91558200
H	1.91057200	-3.44238700	-2.31593300
H	2.18897900	-2.04208800	-3.33390600
H	0.86607000	-3.17116800	-3.73137700
C	1.46070700	3.69069900	0.78103700
C	1.00696500	4.05259100	-0.64694400
H	1.55826800	3.48725000	-1.40770700
H	1.18418700	5.12558500	-0.81629500
H	-0.06100100	3.85095900	-0.78680600
C	2.96411100	3.99619800	0.92468000
H	3.56757100	3.39753500	0.23429200
H	3.32833000	3.82880300	1.94440800
H	3.13218200	5.05683300	0.68406000
C	0.64787900	4.54242100	1.77850600
H	0.94556000	4.36484100	2.81700000
H	-0.42405800	4.32713600	1.68602600
H	0.80980700	5.60795600	1.55328200
C	2.02514000	1.10927700	2.51500000
C	3.49898400	0.83120400	2.15082600
H	3.57075200	0.12633500	1.31626900
H	4.00505600	0.38248500	3.01946000
H	4.04349000	1.74264100	1.88295000
C	1.92133400	2.01959000	3.75410400
H	0.87310500	2.24677000	3.98588100
H	2.46631500	2.96182500	3.62811800
H	2.35961100	1.49732800	4.61866600
C	1.33520300	-0.22671800	2.83542100
H	1.30117000	-0.87206100	1.95025500
H	0.30671900	-0.07011700	3.17746100
H	1.90096800	-0.74169700	3.62595800
N	-1.95843100	-0.68148600	-0.61513100
N	0.91405100	-1.08634100	-1.05627400
P	-1.02153600	1.58697800	1.28097100
P	1.07305300	1.81644300	1.01259200
Cl	-0.60720200	1.66425900	-2.58709900
Ti	-0.31140100	0.52119200	-0.65254500

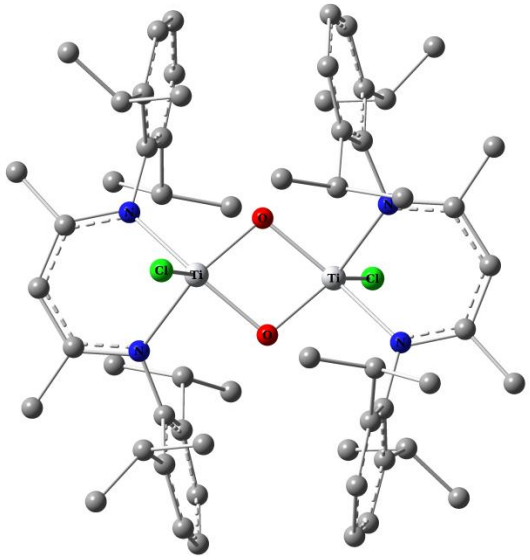


Figure S156. Optimized structure of **[(BDI*)Ti(Cl)(μ_2-O)]$_2$**.

Below are presented xyz coordinates for optimized geometry of **[(BDI*)Ti(Cl)(μ_2-O)]$_2$**:

Ti	0.03786200	-1.13036000	0.85773300
Cl	-0.09655100	-0.78669600	3.06756200
O	-1.27494700	-0.08854600	0.05561800
N	1.60592600	-2.55724800	0.88484900
N	-1.20605200	-2.81811700	0.66290900
C	2.75602600	-4.49116000	1.95150200
H	3.38779000	-4.70083600	1.08133900
H	2.48583100	-5.43403000	2.43569400
H	3.36191200	-3.89697600	2.64486200
C	1.50748700	-3.72985400	1.54790500
C	0.27704500	-4.32952700	1.85162500
H	0.31809900	-5.25946500	2.40998900
C	-0.97501900	-3.97662600	1.32369100
C	-2.08115300	-5.00500500	1.48791500
H	-2.88853600	-4.61438000	2.11655000
H	-1.68202600	-5.91308400	1.94897100
H	-2.52822400	-5.25860800	0.51967300
C	-2.51890200	-2.75202400	0.04881800
C	-3.64410400	-2.43398200	0.84577500
C	-4.91706300	-2.54397000	0.25981900
H	-5.79749600	-2.29722200	0.85089800
C	-5.07227800	-2.99274300	-1.05516900
H	-6.06841900	-3.09833700	-1.48267300
C	-3.94414600	-3.27985800	-1.83052900
H	-4.07189700	-3.59520000	-2.86395100
C	-2.64847100	-3.13875000	-1.30574800
C	-3.50072600	-2.00227200	2.30161100
H	-2.49305400	-2.27327300	2.63866900
C	-3.63352500	-0.47196500	2.41543700
H	-2.93756000	0.03339100	1.74014200
H	-3.42852000	-0.14581900	3.44336000
H	-4.64980700	-0.16164500	2.14700600
C	-4.51751300	-2.68750500	3.24017500
H	-5.54231300	-2.34950000	3.03493000
H	-4.28784400	-2.42939400	4.28213500
H	-4.50245100	-3.78180100	3.14688000
C	-1.42075700	-3.44090400	-2.16058200
H	-0.58952700	-2.84675900	-1.75512000
C	-1.02713000	-4.93315100	-2.06084800
H	-0.74252300	-5.20984000	-1.03900000
H	-0.17495600	-5.14880800	-2.71844500
H	-1.86758400	-5.56945200	-2.37022500
C	-1.60799700	-3.03787300	-3.63582100

H	-0.66601100	-3.17397600	-4.17948900
H	-1.90246600	-1.98751100	-3.72429800
H	-2.36612000	-3.65917800	-4.13163900
C	2.93534600	-2.25362800	0.39609400
C	3.84787500	-1.56449300	1.22928300
C	5.13045000	-1.29610100	0.72422700
H	5.83762300	-0.73985800	1.33742700
C	5.52307500	-1.75798600	-0.53625100
H	6.52685700	-1.55177700	-0.90523000
C	4.62814900	-2.49962200	-1.31333700
H	4.94423500	-2.88004000	-2.28425100
C	3.31825800	-2.75177700	-0.87163200
C	3.48716600	-1.18871800	2.66117500
H	2.55843700	-1.71175000	2.91844900
C	4.57533900	-1.62172900	3.66921000
H	4.83897300	-2.68252700	3.56426700
H	4.21923500	-1.45422500	4.69425200
H	5.49541300	-1.03646400	3.53753400
C	3.21462300	0.31661200	2.80430200
H	4.13052000	0.89191900	2.62456500
H	2.85359200	0.53147000	3.81839200
H	2.46288700	0.64696400	2.08204100
C	2.38118300	-3.60907500	-1.71887800
H	1.43085700	-3.70048700	-1.17967600
C	2.08437400	-2.96774700	-3.08927800
H	1.52783200	-2.03128800	-2.97877100
H	1.48884400	-3.65466200	-3.70439400
H	3.01315600	-2.75075400	-3.63290400
C	2.95473400	-5.03223400	-1.90888000
H	3.89835200	-5.00582700	-2.47051000
H	2.24517600	-5.65573100	-2.46887700
H	3.14988700	-5.52042700	-0.94615700
Ti	-0.14719100	1.10286800	-0.79356800
Cl	-0.19696000	0.56784100	-2.97041400
O	1.16297600	0.09342900	0.04265800
N	-1.63329100	2.60541100	-0.69695900
N	1.20216400	2.74927500	-0.85068900
C	-2.77918700	4.63665300	-1.57637900
H	-3.17430700	4.94154600	-0.59955200
H	-2.52141100	5.53024000	-2.15190400
H	-3.58627300	4.10188100	-2.08699000
C	-1.55373400	3.75860900	-1.39872200
C	-0.35667700	4.25161400	-1.93780700
H	-0.43588900	5.15448500	-2.53515300
C	0.94198000	3.85685300	-1.58021000
C	2.06152100	4.79837300	-1.98856900
H	2.74247500	4.30996100	-2.69338900
H	1.64659100	5.69257900	-2.46263400
H	2.66050200	5.09588000	-1.12032800
C	2.56796300	2.66734200	-0.36823600
C	3.58756800	2.20410200	-1.23278500
C	4.91106500	2.20776800	-0.75983200
H	5.70575100	1.83410300	-1.40330800
C	5.22397900	2.70796500	0.50584100
H	6.25753400	2.72253100	0.84913000
C	4.20429600	3.19024700	1.33364200
H	4.45662900	3.57335800	2.31974800
C	2.85950300	3.16287600	0.92701900
C	3.28757800	1.73304000	-2.65172500
H	2.27105400	2.05275200	-2.90948500
C	3.31746100	0.19857700	-2.72768700
H	2.66697200	-0.24138600	-1.96696200
H	2.98660100	-0.13899200	-3.71771800
H	4.33440600	-0.17052000	-2.55200600
C	4.25767500	2.32444600	-3.69870300
H	5.27204200	1.92279100	-3.57288800
H	3.91912600	2.05601200	-4.70801100
H	4.32478900	3.41890400	-3.63806600

C	1.75240600	3.68073600	1.84529600
H	0.89206600	3.00806500	1.71554300
C	1.29942000	5.11071600	1.46277000
H	0.82376500	5.14746700	0.47809200
H	0.57235400	5.48092400	2.19714000
H	2.15972800	5.79397100	1.46269600
C	2.13965300	3.67485600	3.33632600
H	1.26153600	3.92785400	3.94312400
H	2.51008600	2.69797900	3.66104900
H	2.91010200	4.42855600	3.55081200
C	-2.92855500	2.38239500	-0.08111500
C	-3.97556800	1.82524400	-0.85449400
C	-5.24005600	1.69096200	-0.25640400
H	-6.05424900	1.25106300	-0.83046200
C	-5.47640400	2.13365700	1.04888100
H	-6.46662100	2.03106400	1.49057900
C	-4.43621000	2.70895900	1.78372600
H	-4.62255900	3.05673400	2.79909900
C	-3.14854800	2.84339500	1.23649600
C	-3.77180100	1.41837500	-2.30924300
H	-2.81125900	1.82568800	-2.64747200
C	-4.87838600	1.96308100	-3.23987100
H	-5.01221300	3.04842400	-3.13980600
H	-4.62178600	1.74444400	-4.28471300
H	-5.84587500	1.48759100	-3.02984400
C	-3.69823900	-0.11161100	-2.42741500
H	-4.64324300	-0.56208700	-2.10349500
H	-3.51406800	-0.40562700	-3.46887000
H	-2.90048500	-0.51631800	-1.79856800
C	-2.04601500	3.50866500	2.05091600
H	-1.17322100	3.62188200	1.39691800
C	-1.63723800	2.62164800	3.24421300
H	-1.27294200	1.64722200	2.90471500
H	-0.84291400	3.10350400	3.82864400
H	-2.49257500	2.44772500	3.91104500
C	-2.46037400	4.91736600	2.52853600
H	-3.32260700	4.87061200	3.20684600
H	-1.63353300	5.39125300	3.07364500
H	-2.72931300	5.56462700	1.68380500

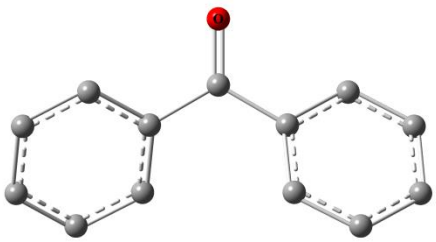


Figure S157. Optimized structure of **(Ph)$_2$C=O**.

Below are presented xyz coordinates for optimized geometry of (**Ph)$_2$C=O**:

C	0.00000000	1.10715600	0.00000000
O	0.00000000	2.34656600	0.00000000
C	1.29659500	0.35624100	0.02798300
C	1.42569400	-0.90362700	0.64710900
C	2.43651300	0.97562300	-0.52315300
C	2.67477700	-1.53495800	0.70574300
H	0.55813600	-1.37236900	1.10694900
C	3.67683500	0.33319000	-0.48434200
H	2.32368900	1.95831000	-0.97583300
C	3.79837700	-0.92366800	0.13122500
H	2.77117400	-2.49983300	1.20018000
H	4.54983900	0.80976800	-0.92648200

H	4.76632600	-1.42041200	0.16829700
C	-1.29659500	0.35624100	-0.02798300
C	-1.42569400	-0.90362700	-0.64710900
C	-2.43651300	0.97562300	0.52315300
C	-2.67477600	-1.53495800	-0.70574400
H	-0.55813600	-1.37236900	-1.10694900
C	-3.67683500	0.33319000	0.48434200
H	-2.32368900	1.95831000	0.97583400
C	-3.79837700	-0.92366800	-0.13122600
H	-2.77117400	-2.49983300	-1.20018100
H	-4.54984000	0.80976700	0.92648200
H	-4.76632600	-1.42041200	-0.16829800

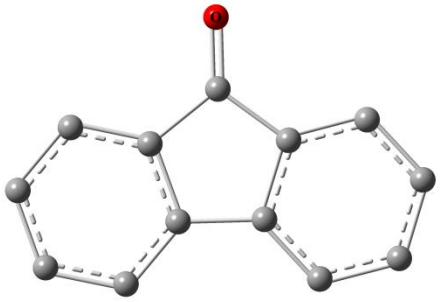


Figure S158. Optimized structure of **9-fluorenone**.

Below are presented xyz coordinates for optimized geometry of **9-fluorenone**.

C	-3.03859900	-1.40130600	0.00014300
C	-3.47892000	-0.06759300	0.00014400
C	-2.54877700	0.98809300	0.00009200
C	-1.19208700	0.67063400	0.00004000
C	-0.74200500	-0.67233700	0.00003900
C	-1.66579600	-1.71893900	0.00009100
H	-3.77170900	-2.20607400	0.00018400
H	-4.54568100	0.14700900	0.00018500
H	-2.86859300	2.02832000	0.00009200
H	-1.34426100	-2.75895100	0.00009100
C	0.00000000	1.58195900	-0.00002000
C	1.19208700	0.67063400	-0.00005800
C	2.54877700	0.98809300	-0.00011800
C	3.47892000	-0.06759300	-0.00014200
C	3.03859900	-1.40130600	-0.00010700
C	1.66579600	-1.71893900	-0.00004600
C	0.74200500	-0.67233700	-0.00002200
H	2.86859300	2.02832000	-0.00014500
H	4.54568100	0.14700900	-0.00018900
H	3.77170900	-2.20607400	-0.00012600
H	1.34426100	-2.75895100	-0.00001900
O	0.00000000	2.81312500	-0.00003700

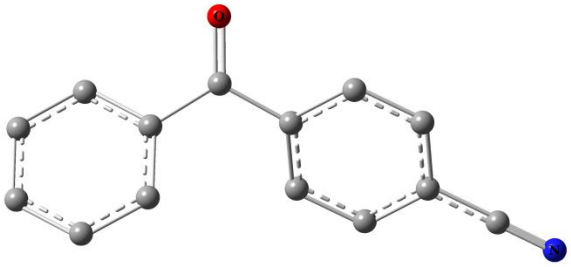


Figure S159. Optimized structure of **(4-CN-Ph)PhC=O**.

Below are presented xyz coordinates for optimized geometry of **(4-CN-Ph)PhC=O**:

C	-0.81686400	1.21435200	-0.02051500
O	-0.97366300	2.44190700	-0.06268800
C	0.57612500	0.64968500	-0.01366500
C	0.89476000	-0.57738100	-0.62908200
C	1.60336600	1.42514800	0.56031900
C	2.21554200	-1.03012700	-0.66342100
H	0.11336100	-1.16484000	-1.10552300
C	2.92128500	0.97280500	0.55402700
H	1.34461400	2.38238300	1.00655500
C	3.23378600	-0.26159500	-0.06026400
H	2.46758800	-1.96844400	-1.15069100
H	3.71346300	1.56001800	1.01121000
C	-1.99388300	0.29385200	0.01786800
C	-3.21061900	0.74673200	-0.53228300
C	-1.94279900	-0.96991700	0.64162200
C	-4.34809200	-0.06295300	-0.48675900
H	-3.23720500	1.73294700	-0.99030500
C	-3.09081300	-1.76927900	0.70605500
H	-1.01850200	-1.31176200	1.10289900
C	-4.29013800	-1.32235000	0.13312100
H	-5.28042100	0.28473200	-0.92743500
H	-3.05020500	-2.73625300	1.20362100
C	4.58827200	-0.73198100	-0.07602400
N	5.69654500	-1.11806700	-0.08706000
H	-5.17877700	-1.94950300	0.17460000

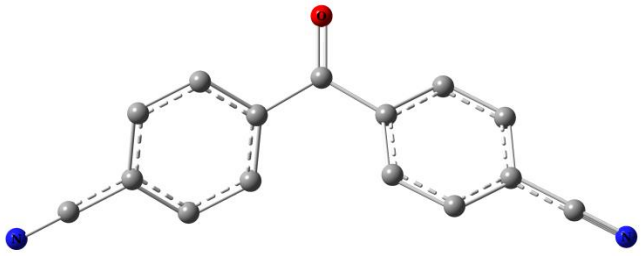


Figure S160. Optimized structure of **(4-CN-Ph)$_2$C=O**.

Below are presented xyz coordinates for optimized geometry of **(4-CN-Ph)$_2$C=O**.

C	0.00000000	1.48264500	0.00000000
O	0.00000000	2.71966300	0.00000000
C	1.29820600	0.73235900	0.00206700
C	2.42431300	1.35577400	-0.57279500
C	1.44070600	-0.52549000	0.62223600
C	3.66588500	0.72392500	-0.56123000
H	2.30219500	2.33724500	-1.02451400
C	2.68526800	-1.15761500	0.66087400
H	0.58604100	-0.99707600	1.10182700
C	3.80152000	-0.53992100	0.05775400
H	4.53310800	1.19320100	-1.01824900
H	2.80324300	-2.11999100	1.15183700

C	-1.29820600	0.73235900	-0.00206700
C	-1.44070500	-0.52549000	-0.62223600
C	-2.42431300	1.35577400	0.57279500
C	-2.68526800	-1.15761500	-0.66087400
H	-0.58604100	-0.99707600	-1.10182600
C	-3.66588500	0.72392500	0.56123000
H	-2.30219500	2.33724500	1.02451400
C	-3.80152000	-0.53992100	-0.05775400
H	-2.80324300	-2.11999100	-1.15183600
H	-4.53310800	1.19320100	1.01824800
C	5.07742700	-1.19402900	0.07857800
N	6.12123300	-1.72999800	0.09387400
C	-5.07742700	-1.19402900	-0.07857800
N	-6.12123200	-1.72999900	-0.09387400

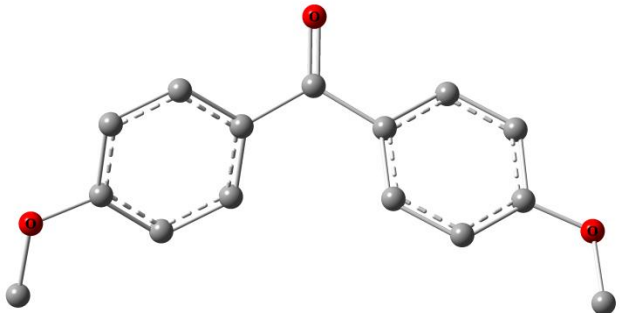


Figure S161. Optimized structure of **(4-MeO-Ph)$_2$C=O**.

Below are presented xyz coordinates for optimized geometry of **(4-MeO-Ph)$_2$C=O**:

C	-0.00000100	1.65786000	0.00000300
C	1.29189700	0.91119900	-0.04836600
C	2.41276100	1.54330300	-0.63438100
H	2.28055700	2.53457400	-1.06219900
C	3.65247600	0.91680100	-0.66622800
H	4.51601600	1.38756600	-1.13020400
C	3.81041700	-0.35681100	-0.07944200
C	2.71601100	-0.99103000	0.53596900
H	2.82471500	-1.95957500	1.01585000
C	1.46699500	-0.35582600	0.53791600
H	0.63041500	-0.84195700	1.03558100
C	5.28486400	-2.18118100	0.43270800
H	5.08534900	-2.15824700	1.51301600
H	6.33814900	-2.40712700	0.25413500
H	4.65243600	-2.94015900	-0.04851900
C	-1.29189700	0.91119700	0.04837400
C	-1.46699000	-0.35583500	-0.53789600
H	-0.63040400	-0.84197300	-1.03554500
C	-2.71600600	-0.99103800	-0.53595400
H	-2.82470500	-1.95958800	-1.01582600
C	-3.81041800	-0.35681200	0.07943900
C	-3.65248000	0.91680400	0.66621700
H	-4.51602300	1.38757300	1.13018200
C	-2.41276500	1.54330600	0.63437500
H	-2.28056600	2.53458100	1.06218600
C	-5.28486300	-2.18118300	-0.43271700
H	-5.08533200	-2.15825200	-1.51302100
H	-6.33815200	-2.40712300	-0.25415700
H	-4.65244600	-2.94016200	0.04852200
O	5.07053800	-0.88896700	-0.15506400
O	-5.07053900	-0.88896600	0.15505500
O	-0.00000100	2.90110100	-0.00000300

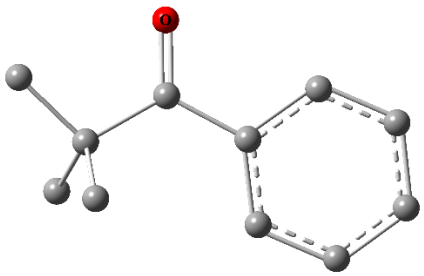


Figure S162. Optimized structure of ***t*Bu(Ph)C=O**.

Below are presented xyz coordinates for optimized geometry of ***t*Bu(Ph)C=O**:

C	-0.72455300	0.73163300	-0.09963600
O	-0.93529800	1.94051000	-0.24709900
C	0.70972800	0.26100000	-0.05103600
C	1.13324500	-1.08215700	-0.13086700
C	1.69330000	1.26746100	0.07078500
C	2.49552400	-1.40611500	-0.09306200
H	0.41305700	-1.88649100	-0.23637100
C	3.05116800	0.94459600	0.12073500
H	1.35850900	2.30064400	0.12453600
C	3.45828300	-0.39632600	0.03724300
H	3.79267000	1.73493300	0.22298300
H	2.80241300	-2.44794900	-0.16510500
C	-1.92934300	-0.23163300	0.04692900
H	4.51599400	-0.65137200	0.07243400
C	-2.05554900	-1.12499900	-1.21717100
H	-1.20335700	-1.79695000	-1.36041900
H	-2.96049000	-1.74114400	-1.12862500
H	-2.15334100	-0.50411500	-2.11657500
C	-1.80304000	-1.09345300	1.32934600
H	-2.71237200	-1.69844800	1.44496800
H	-0.94473200	-1.77192000	1.31155300
H	-1.70857400	-0.45287900	2.21568400
C	-3.21389300	0.61676400	0.15818900
H	-4.07945300	-0.05166300	0.25927200
H	-3.17570000	1.27765500	1.03183700
H	-3.35146900	1.24499200	-0.72810400

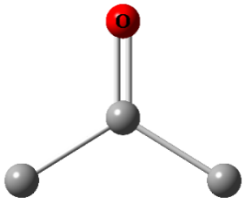


Figure S163. Optimized structure of **Me_2C=O**.

Below are presented xyz coordinates for optimized geometry of **Me_2C=O**:

C	0.00000000	0.18160500	0.00000000
O	0.00000000	1.40979000	-0.00000100
C	1.29645500	-0.61714500	-0.00000100
H	1.33828900	-1.27081900	0.88261400
H	1.33828800	-1.27081800	-0.88261800
H	2.15400000	0.06052800	-0.00000100
C	-1.29645500	-0.61714500	0.00000200
H	-1.33828900	-1.27082000	-0.88261300
H	-1.33828800	-1.27081700	0.88261900
H	-2.15400000	0.06052800	0.00000100

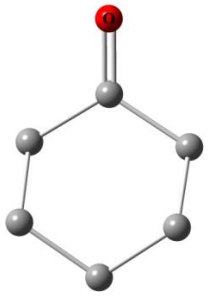


Figure S164. Optimized structure of **$(CH_2)_5C=O$**.

Below are presented xyz coordinates for optimized geometry of **$(CH_2)_5C=O$**:

O	1.32607100	1.91126900	0.00000000
C	0.42288000	1.07707200	0.00000000
C	-0.16922300	0.51375000	1.28679400
C	-0.16922300	0.51375000	-1.28679400
C	-0.16922300	-1.03570200	1.26819200
H	-1.21197700	0.86514300	1.35846300
H	0.38791500	0.91623300	2.13963000
C	-0.16922300	-1.03570200	-1.26819200
H	-1.21197700	0.86514300	-1.35846300
H	0.38791500	0.91623300	-2.13963000
C	-0.85049300	-1.57945800	0.00000000
H	-0.66970600	-1.41222000	2.17046300
H	0.87076200	-1.39371400	1.30568800
H	-0.66970600	-1.41222000	-2.17046300
H	0.87076200	-1.39371400	-1.30568800
H	-0.82300500	-2.67785200	0.00000000
H	-1.91252100	-1.28544000	0.00000000

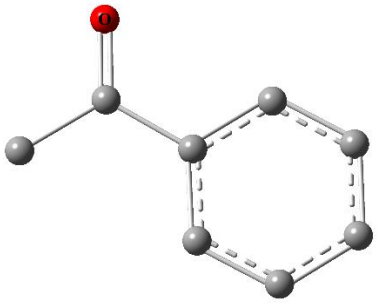


Figure S165. Optimized structure of **Me(Ph)C=O**.

Below are presented xyz coordinates for optimized geometry of **Me(Ph)C=O**.

C	-1.70055800	-0.20033000	0.00000200
O	-2.22492300	-1.31807000	0.00000000
C	-0.20772800	-0.05735100	0.00000100
C	0.43019900	1.19954800	0.00000000
C	0.57785900	-1.22826700	0.00000000
C	1.82823400	1.28339500	-0.00000100
H	-0.15923700	2.11396900	0.00000100
C	1.97220000	-1.14382200	-0.00000100
H	0.06678000	-2.18849200	0.00000000
C	2.60043300	0.11281000	-0.00000100
H	2.57214900	-2.05201400	-0.00000100
H	2.31353100	2.25759800	-0.00000100
C	-2.56101600	1.05584100	0.00000000
H	-2.35289900	1.67181800	0.88552200
H	-2.35289800	1.67181700	-0.88552100
H	-3.61281900	0.76025400	0.00000000

H	3.68704300	0.17866000	-0.00000200

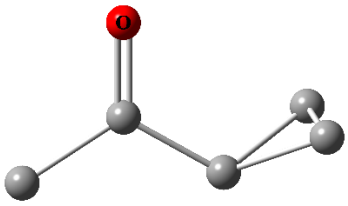


Figure S166. Optimized structure of ***cyclo*-PrMeC=O**.

Below are presented xyz coordinates for optimized geometry of ***cyclo*-PrMeC=O**:

O	0.78662900	1.38691400	0.00000300
C	0.79486600	0.15303400	-0.00000100
C	2.09270400	-0.63822100	-0.00000200
H	2.13496400	-1.29111900	-0.88343500
H	2.94764500	0.04274500	0.00000200
H	2.13496200	-1.29112400	0.88342800
C	-0.47381600	-0.63565700	-0.00000200
C	-1.66981200	-0.03792200	0.74636500
C	-1.66981400	-0.03791900	-0.74636300
H	-0.37692500	-1.71996400	-0.00000400
H	-1.47534700	0.90885700	1.24546500
H	-2.31387400	-0.73673400	1.27504900
H	-2.31387700	-0.73672800	-1.27505000
H	-1.47534900	0.90886300	-1.24546000

E.3.2. Reaction of **1** with benzophenone leading to **3a**

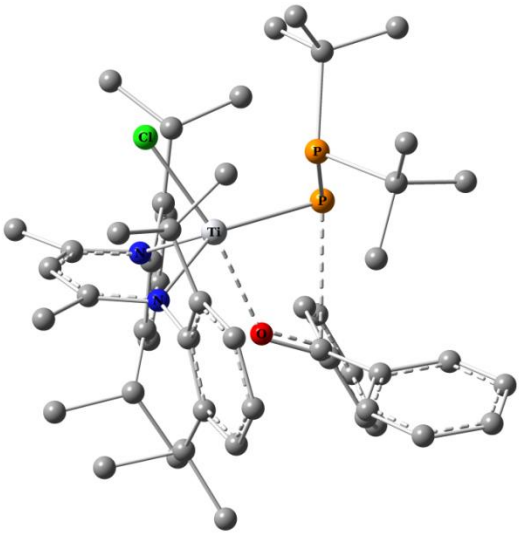


Figure S167. Optimized structure of **3a$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of **3a$_{TS1}$**:

C	2.96003400	0.66014800	-1.05213900
C	3.58137600	1.84825500	-0.59348900
C	4.93676800	1.77980200	-0.21604800
H	5.43674400	2.69042800	0.11138400
C	5.65597700	0.58285900	-0.26297600
H	6.70338400	0.55923600	0.03444200
C	5.01157100	-0.58764200	-0.67136400
H	5.55820500	-1.52962200	-0.68051800
C	3.66572200	-0.57195300	-1.07110400
C	2.88068900	3.20080800	-0.52945200
H	1.82163800	3.05305700	-0.77865800

C	2.97570000	3.78253700	0.89841800
H	2.41360500	4.72052400	0.95934800
H	2.56166700	3.08341100	1.63450700
H	4.01886700	4.00028800	1.16656100
C	3.48410900	4.21435000	-1.53173900
H	3.12204600	5.22533900	-1.30402900
H	4.58061800	4.22401900	-1.46471000
H	3.21575900	3.98140600	-2.56781000
C	3.00110300	-1.85990700	-1.53929300
H	1.91903000	-1.70292700	-1.48208400
C	3.36105200	-3.08201400	-0.64017500
H	2.45063200	-3.52733800	-0.22417500
H	3.87470000	-3.86444600	-1.21484200
H	4.00270000	-2.80481200	0.20259100
C	3.37280900	-2.15460500	-3.01456200
H	2.92928300	-1.42453200	-3.70102500
H	4.46397300	-2.13348800	-3.14363400
H	3.01517400	-3.15105000	-3.30331900
C	-2.15198900	-1.49345200	-1.66225300
C	-1.91098500	-2.86353700	-1.37435400
C	-3.01534300	-3.67361600	-1.05244700
H	-2.85712300	-4.72571200	-0.82569100
C	-4.31442400	-3.15385800	-1.00647900
H	-5.15004900	-3.79586200	-0.73162800
C	-4.53688500	-1.82099500	-1.35722500
H	-5.55378800	-1.42947200	-1.37847000
C	-3.47425100	-0.97731200	-1.72628800
C	-0.49711500	-3.44436200	-1.47197300
H	0.17998900	-2.67928200	-1.07378700
C	-0.28119400	-4.75867100	-0.66849100
H	0.67748900	-4.71408700	-0.13793500
H	-1.05711100	-4.94656900	0.08017800
H	-0.24007000	-5.63066300	-1.33441400
C	-0.11183500	-3.69171100	-2.95705500
H	0.72936700	-4.39465700	-3.01438900
H	-0.95463800	-4.12545400	-3.51127800
H	0.19436900	-2.76705000	-3.45636400
C	-3.79756100	0.39166600	-2.32476900
H	-2.85982800	0.86125200	-2.63692200
C	-4.45013000	1.35454300	-1.31817300
H	-4.79174600	2.26245500	-1.83242500
H	-5.31700300	0.88940600	-0.82799900
H	-3.71988600	1.65182900	-0.55718000
C	-4.72065200	0.23047700	-3.57142000
H	-4.44172200	0.95444600	-4.34829400
H	-4.66484900	-0.77636900	-4.00250900
H	-5.77010900	0.41899500	-3.30648700
C	2.68162600	1.29278100	-3.76560300
H	2.62608300	0.96393300	-4.80783900
H	2.57896100	2.38614700	-3.74601700
H	3.66590000	1.04503500	-3.35884000
C	1.54496900	0.70181000	-2.95273000
C	0.43918700	0.24737000	-3.67904000
H	0.50815600	0.37446300	-4.75680300
C	-0.71264200	-0.44712700	-3.23983800
C	-1.58437200	-0.98950300	-4.36201800
H	-0.96334100	-1.30768400	-5.20608700
H	-2.20969200	-1.82485800	-4.03971300
H	-2.24400300	-0.18632100	-4.71605200
C	0.76504500	-1.40924000	1.65092100
C	-1.84116100	4.00767700	1.35718300
C	-1.91729500	4.41860300	2.84210800
H	-2.86375500	4.13606600	3.31568500
H	-1.09181600	3.97232200	3.41060200
H	-1.82663200	5.51436500	2.90924500
C	-0.55064000	4.63849100	0.78179700
H	-0.11708900	4.04956200	-0.03005600
H	-0.78657700	5.63971100	0.39238900

H	0.19839900	4.74669700	1.57330200
C	-3.03791500	1.28860400	2.37721300
C	-3.07110600	-0.17129900	1.89449500
H	-2.05783400	-0.57168300	1.83199100
H	-3.64078200	-0.79458300	2.59872800
H	-3.52966800	-0.25895800	0.90270900
C	-4.46435900	1.86271400	2.26272800
H	-4.51309300	2.92841000	2.51090500
H	-4.89222600	1.71257600	1.26697200
H	-5.10254100	1.32919100	2.98455700
Cl	-0.80492400	2.56811200	-1.96266400
N	1.61816800	0.64914900	-1.59294900
N	-1.04274300	-0.61173800	-1.94537400
O	0.52460000	-1.10658600	0.44249600
P	0.18709600	1.38692100	1.69984700
P	-1.75207900	2.09224300	1.17156500
Ti	-0.16587900	0.79048200	-0.55557000
C	-2.58165000	1.33684000	3.85766000
H	-2.91965800	2.25027800	4.35845400
H	-3.00518800	0.47654200	4.39744000
H	-1.48890300	1.28002400	3.94193400
C	-3.06138200	4.53712200	0.56938300
H	-2.99738100	4.23007900	-0.48170200
H	-4.01442000	4.18367900	0.97501600
H	-3.06831100	5.63735800	0.60766500
C	-0.24227200	-2.03368200	2.54426000
C	-0.19372600	-1.81895600	3.94018700
C	-1.25306800	-2.84993800	2.00824600
C	-1.13687500	-2.42364700	4.77442200
H	0.56148100	-1.15417000	4.35229600
C	-2.16643200	-3.49281400	2.84882800
H	-1.32401200	-2.95414800	0.93288100
C	-2.11107100	-3.28109800	4.23397400
H	-1.11263000	-2.23026000	5.84518100
H	-2.93268500	-4.13493200	2.41883200
H	-2.83151200	-3.76686100	4.88999000
C	2.16633900	-1.39075400	2.16790500
C	2.63661400	-2.48419400	2.93273000
C	3.02217500	-0.29693400	1.94046900
C	3.93880400	-2.48386100	3.44288600
H	1.98805800	-3.34089300	3.10174700
C	4.30550900	-0.27750300	2.49316100
H	2.66385200	0.55212400	1.36882800
C	4.77149000	-1.37211100	3.23622000
H	4.29783400	-3.34128700	4.00911800
H	4.93772200	0.59240300	2.33301900
H	5.77694400	-1.35915400	3.65395100

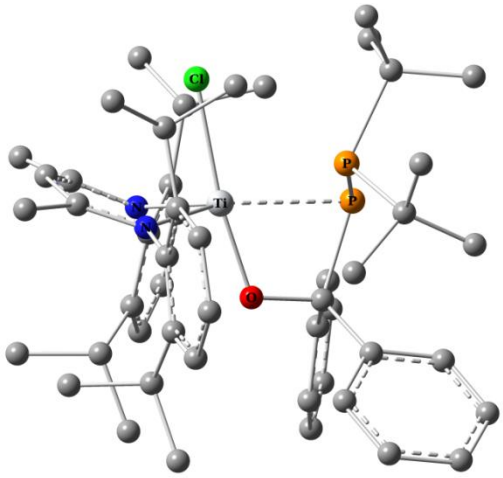


Figure S168. Optimized structure of **3a$_I$**.

Below are presented xyz coordinates for optimized geometry of **3a$_I$**:

C	-2.84869200	-1.42574400	0.23664800
C	-3.59325500	-1.27322400	1.43048900
C	-4.93225900	-0.85892800	1.31596900
H	-5.52817200	-0.73558300	2.21937800
C	-5.50797600	-0.60100300	0.07015600
H	-6.54233900	-0.26759000	0.00590000
C	-4.75415100	-0.76508100	-1.09750300
H	-5.21359000	-0.56744600	-2.06391700
C	-3.41843200	-1.18868000	-1.04108400
C	-3.02034700	-1.59973600	2.80660000
H	-2.02960600	-2.04887400	2.66514300
C	-2.82747200	-0.32760500	3.65799500
H	-2.43746100	-0.59221700	4.64969900
H	-2.11110200	0.35226700	3.18311500
H	-3.78201700	0.20096900	3.79322600
C	-3.91082700	-2.60612500	3.57137800
H	-3.40243000	-2.93025200	4.48898000
H	-4.86568500	-2.14836200	3.86373900
H	-4.13965200	-3.49378100	2.96874300
C	-2.64001300	-1.51310600	-2.31350700
H	-1.57505000	-1.50414800	-2.05305000
C	-2.85796100	-0.49803600	-3.44828600
H	-2.25062300	-0.78087000	-4.31795500
H	-3.90565500	-0.46863600	-3.77705800
H	-2.56757900	0.50662500	-3.13273700
C	-3.00401900	-2.93464100	-2.80599300
H	-2.77432800	-3.69639200	-2.05289200
H	-4.07616300	-2.99703600	-3.03823900
H	-2.43912700	-3.17753300	-3.71592700
C	2.45417600	-1.45489200	-1.39815400
C	2.35255600	-0.84698400	-2.67653900
C	3.53563300	-0.40062300	-3.29103200
H	3.48273600	0.07936900	-4.26509200
C	4.78438100	-0.57414100	-2.68406300
H	5.68590500	-0.21273200	-3.17601300
C	4.86794400	-1.23052100	-1.45440400
H	5.84231900	-1.39279100	-0.99553800
C	3.71622700	-1.69438700	-0.79366800
C	1.01474000	-0.76795300	-3.41147200
H	0.26071400	-0.41719400	-2.69283900
C	1.03023500	0.19199200	-4.61825900
H	0.00446600	0.34654000	-4.97470700
H	1.45545800	1.17214700	-4.37322500
H	1.61132400	-0.22827200	-5.45129800
C	0.58269600	-2.16709200	-3.91663700
H	-0.31227300	-2.07708100	-4.54574700

H	1.38048500	-2.61875100	-4.52169100
H	0.34148400	-2.84453100	-3.09265000
C	3.87977700	-2.46122500	0.51642700
H	2.90251300	-2.85665100	0.81628600
C	4.33858000	-1.52599800	1.64627500
H	4.41110300	-2.07320700	2.59477800
H	5.32213400	-1.08995800	1.42056300
H	3.60940800	-0.71953600	1.76964500
C	4.87441200	-3.63693600	0.37501300
H	4.85411800	-4.25222600	1.28424200
H	4.64260000	-4.27748900	-0.48405100
H	5.90157700	-3.26957500	0.24691300
C	-2.46457900	-4.19735900	0.58870600
H	-2.28105300	-5.20413000	0.20135200
H	-2.53955800	-4.25678900	1.68274000
H	-3.42496300	-3.83088000	0.21257500
C	-1.32356500	-3.26924900	0.23009000
C	-0.11493500	-3.84765600	-0.16121800
H	-0.09410700	-4.93465100	-0.17618900
C	1.01621700	-3.22208000	-0.73584600
C	1.95313400	-4.19969900	-1.43387400
H	1.36024700	-4.90418900	-2.02829800
H	2.67566900	-3.70447500	-2.08487400
H	2.50069800	-4.78195400	-0.68194500
C	-0.85825000	1.86601900	-0.24626100
C	1.89816100	1.32993200	3.64202300
C	2.12278200	2.80099900	4.05246700
H	3.08503700	3.20115400	3.72087100
H	1.31867500	3.44083200	3.66818600
H	2.10475200	2.85494500	5.15164900
C	0.61565200	0.87147000	4.37553500
H	0.30277300	-0.13354800	4.08667000
H	0.84287200	0.86952300	5.45294500
H	-0.21497300	1.56681500	4.21078900
C	3.03301300	2.36998800	0.90069500
C	3.13706200	1.86502700	-0.55272500
H	2.15758000	1.75503200	-1.02058700
H	3.71652100	2.58377000	-1.15064200
H	3.64272200	0.89637800	-0.58781500
C	4.43700900	2.21590200	1.52913700
H	4.50025600	2.60803600	2.54924600
H	4.77374700	1.17433600	1.52880600
H	5.14078100	2.79228400	0.90925800
Cl	0.62413300	-1.90350400	2.43794800
N	-1.49197900	-1.92738700	0.26603300
N	1.25060700	-1.89521400	-0.72600300
O	-0.50337200	0.57237600	-0.79089400
P	-0.38282500	1.70853100	1.61426300
P	1.75463200	1.16607000	1.69878000
Ti	0.05165300	-0.63380100	0.53304400
C	2.61761500	3.85122000	0.92673200
H	2.61223000	4.26515100	1.93907500
H	3.34030300	4.42735000	0.32828600
H	1.62887000	3.99656300	0.48904500
C	3.05879600	0.43998000	4.13491600
H	2.83403400	-0.61593200	3.95211500
H	4.01517900	0.68494300	3.66193400
H	3.17306000	0.58549900	5.21992800
C	-0.22025000	3.00720700	-1.02137400
C	-0.42997000	4.33229700	-0.59121300
C	0.45135300	2.78168500	-2.22755300
C	0.05374400	5.40622900	-1.34377900
H	-0.97595600	4.51063300	0.33477700
C	0.94514400	3.85750200	-2.98170500
H	0.57771600	1.75788800	-2.56209700
C	0.75106000	5.17283400	-2.54223700
H	-0.11046000	6.42528500	-0.99720900
H	1.47457600	3.66440300	-3.91403900

H	1.13099700	6.00916600	-3.12648000
C	-2.38696300	2.10120100	-0.35863500
C	-2.91403400	2.47852200	-1.61080100
C	-3.25481400	2.06833400	0.74290900
C	-4.26283600	2.81510000	-1.75604900
H	-2.24929200	2.54984200	-2.46877200
C	-4.60396500	2.42764100	0.60585200
H	-2.87870400	1.78257500	1.72170900
C	-5.11387100	2.80577700	-0.64061900
H	-4.64237000	3.10629300	-2.73444200
H	-5.25230000	2.40396900	1.47999600
H	-6.16017600	3.08914000	-0.74418100

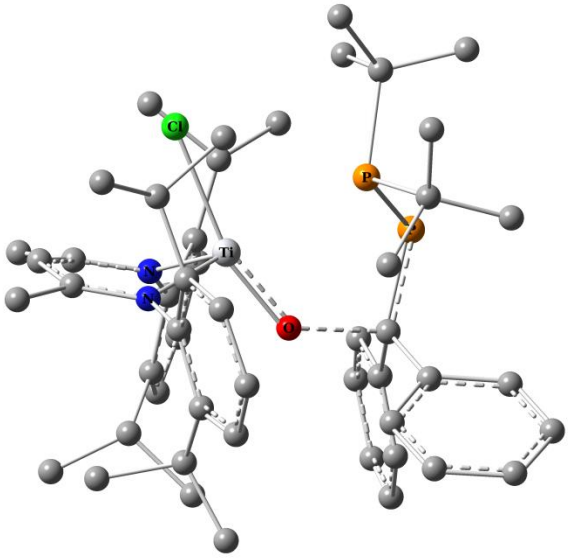


Figure S169. Optimized structure of **3a**$_{TS2}$.

Below are presented xyz coordinates for optimized geometry of **3a**$_{TS2}$:

C	-2.93998400	0.88846000	-0.85747600
C	-3.47940000	0.03888300	-1.85527000
C	-4.84011400	-0.29959500	-1.75812400
H	-5.28924800	-0.92676300	-2.52459000
C	-5.62668500	0.14249200	-0.68831400
H	-6.67946900	-0.13140500	-0.63648200
C	-5.04703500	0.89792200	0.33285900
H	-5.64734000	1.19550400	1.19164100
C	-3.69983300	1.29109600	0.26610400
C	-2.61970400	-0.48105700	-3.00388700
H	-1.61549200	-0.65991000	-2.58614700
C	-3.12950400	-1.82349700	-3.56003700
H	-2.42542800	-2.20012200	-4.30996200
H	-3.22577800	-2.58038900	-2.77148700
H	-4.10280900	-1.71051000	-4.05685400
C	-2.46906300	0.53700900	-4.15499600
H	-1.88936900	0.08726600	-4.97141700
H	-3.45489600	0.82421200	-4.54786800
H	-1.93043700	1.43264700	-3.83279200
C	-3.09861800	2.11685600	1.39875700
H	-2.06983200	2.37420600	1.12044100
C	-3.04240700	1.27093600	2.68801800
H	-2.64452300	1.86937300	3.51821400
H	-4.04322200	0.92024400	2.97218700
H	-2.40572200	0.39286600	2.54625000
C	-3.87098800	3.43000800	1.65126100
H	-3.90189000	4.06497600	0.75739700
H	-4.90582500	3.23024700	1.95991300

H	-3.38708700	4.00160500	2.45407500
C	2.04661000	2.23630900	0.86503100
C	1.82988000	2.11456300	2.26567000
C	2.95375300	1.93169300	3.08698900
H	2.81926400	1.82234400	4.16022600
C	4.24883900	1.89821600	2.55385000
H	5.10320200	1.74444000	3.21103300
C	4.44229500	2.08180700	1.18440800
H	5.45239500	2.07925000	0.77738300
C	3.35311600	2.25900300	0.31115400
C	0.42808700	2.25168300	2.86019600
H	-0.24093700	1.61334800	2.26491900
C	0.33574800	1.82003000	4.33623400
H	-0.71185700	1.84923600	4.65756700
H	0.70401200	0.80294100	4.50375000
H	0.89828300	2.50493800	4.98626500
C	-0.07716200	3.71188100	2.75404500
H	-1.04914700	3.80478500	3.25570000
H	0.62713600	4.39701800	3.24491500
H	-0.20919300	4.03020500	1.71633100
C	3.62090000	2.50129500	-1.17314400
H	2.67129200	2.73613300	-1.66592000
C	4.16796700	1.24125600	-1.86959400
H	4.36329900	1.44997900	-2.92911600
H	5.10320900	0.90553500	-1.40037100
H	3.43206500	0.43112500	-1.82239700
C	4.59349500	3.68520000	-1.38064000
H	4.65958600	3.92895900	-2.44906200
H	4.26947400	4.58167700	-0.83790900
H	5.60466100	3.43336800	-1.03377600
C	-2.94904100	3.33092000	-2.07538200
H	-3.48384100	2.59327600	-2.67958300
H	-3.63145500	3.64521800	-1.27614200
H	-2.71294800	4.20670700	-2.68862300
C	-1.66912000	2.75805900	-1.48981300
C	-0.59814100	3.65988200	-1.34785000
H	-0.75279300	4.64815700	-1.77347300
C	0.55492600	3.51154300	-0.55975300
C	1.37401500	4.76213500	-0.30491900
H	0.71166400	5.62410800	-0.17027700
H	2.01262300	4.65609100	0.57627700
H	2.01610900	4.96483200	-1.17207000
C	-0.53251900	-2.14371000	1.00014000
C	1.66552900	-2.49740700	-3.11033200
C	1.97647300	-4.01083400	-3.13132300
H	2.97301800	-4.24374700	-2.74292000
H	1.23632400	-4.57591600	-2.55053600
H	1.93681800	-4.36233500	-4.17385800
C	0.29823500	-2.29266100	-3.79436900
H	0.02601900	-1.23307500	-3.81909800
H	0.37725100	-2.65213900	-4.83208700
H	-0.49271800	-2.85693700	-3.29097900
C	3.21514600	-2.36876300	-0.40392200
C	3.43630700	-1.32929400	0.71049800
H	2.55479100	-1.20366100	1.33933000
H	4.26656300	-1.65242200	1.35669600
H	3.69444700	-0.35373500	0.28949500
C	4.47977100	-2.35605300	-1.28957300
H	4.47303000	-3.13940900	-2.05423200
H	4.64823000	-1.38929500	-1.77161600
H	5.33966000	-2.55008700	-0.62943500
Cl	0.83323900	1.11413200	-2.95221400
N	-1.63144300	1.47906500	-1.04419200
N	0.90408400	2.32865500	-0.01368800
O	-0.21787900	-0.33089700	0.69440700
P	-0.23323900	-2.89689300	-0.64392700
P	1.56669700	-1.82863300	-1.30073600
Ti	0.19345000	0.56371600	-0.73027200

C	3.06265400	-3.78068000	0.19154900
H	2.92527800	-4.53847000	-0.58756900
H	3.97652900	-4.02617100	0.75525900
H	2.21429500	-3.84087100	0.87530100
C	2.71058700	-1.71759700	-3.94212400
H	2.51031800	-0.64191700	-3.91141700
H	3.73763200	-1.90077200	-3.62009100
H	2.62800000	-2.05024500	-4.98820400
C	0.39950500	-2.40880000	2.15950900
C	0.57619800	-3.75530900	2.54628000
C	0.99333600	-1.40603500	2.93977800
C	1.34574700	-4.08412800	3.66779900
H	0.10221100	-4.53725000	1.95507500
C	1.78081900	-1.73570900	4.05256400
H	0.85253100	-0.37319800	2.64230200
C	1.96053100	-3.07383200	4.42407200
H	1.47112800	-5.12974900	3.94440400
H	2.26046800	-0.94113800	4.62256400
H	2.57125300	-3.32823900	5.28866900
C	-1.97327400	-2.21702500	1.43529700
C	-2.31874900	-2.24900300	2.80680800
C	-3.01542100	-2.29307100	0.48745900
C	-3.65273400	-2.37502200	3.20983300
H	-1.53938000	-2.18671100	3.56126200
C	-4.34334600	-2.45216100	0.88989700
H	-2.76436800	-2.24014600	-0.56835500
C	-4.67102600	-2.48965400	2.25328800
H	-3.89281800	-2.39410500	4.27183300
H	-5.12375000	-2.52934800	0.13722000
H	-5.70839100	-2.60205600	2.56523400

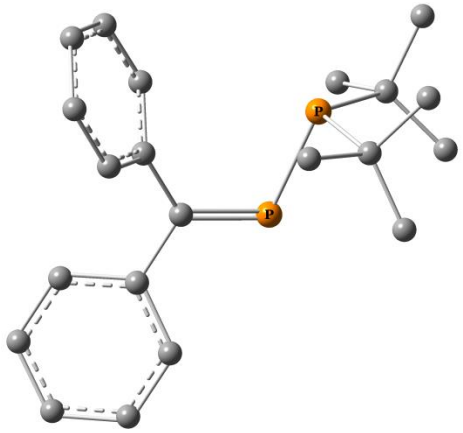


Figure S170. Optimized structure of **3a**.

Below are presented xyz coordinates for optimized geometry of **3a**:

C	-0.66538800	3.44050400	-1.20975300
C	-0.63070100	2.04241500	-1.23825000
C	-1.26497400	1.28762200	-0.22994200
C	-1.94599200	1.97227000	0.80048300
C	-1.95842500	3.37087400	0.84213900
C	-1.31881800	4.11011500	-0.16439000
H	-0.17910700	4.00721000	-2.00177800
H	-2.47205200	3.88236200	1.65441700
C	-1.24260500	-0.19701200	-0.23992100
P	0.14604900	-1.21381400	-0.38854600
P	1.86778500	0.19610200	-0.15547900
C	2.24261100	-0.09056000	1.71724200
C	1.22492700	0.83201200	2.42891400
C	2.06774700	-1.52202500	2.26102400
C	3.67010300	0.40901000	2.01717000
H	1.31400300	1.87095800	2.08821100
H	0.19505700	0.50121300	2.24395700

H	1.40143500	0.80172200	3.51505900
H	2.75955800	-2.23277200	1.79878200
H	2.25742900	-1.52043100	3.34594200
H	1.04533400	-1.88841100	2.10019500
H	3.81053000	0.47214400	3.10720800
H	4.42964600	-0.27822900	1.62508900
H	3.84807500	1.40628200	1.59338900
C	3.13972700	-0.74955300	-1.24330000
C	4.40873400	0.12732700	-1.35383000
C	3.52105800	-2.17055400	-0.79102800
C	2.49067500	-0.81579200	-2.64674900
H	4.15832400	1.14283300	-1.68661800
H	4.94512300	0.20249400	-0.40189800
H	5.09518900	-0.31693400	-2.09093900
H	2.63531000	-2.80388700	-0.65466100
H	4.16066700	-2.64075700	-1.55445900
H	4.08711400	-2.15515900	0.14808000
H	3.22449800	-1.20133800	-3.37055100
H	1.61810400	-1.48282700	-2.66096400
H	2.16885500	0.17886300	-2.98510200
H	-0.12632200	1.52061700	-2.04767700
H	-2.44924600	1.39728900	1.57602700
H	-1.33674400	5.19821900	-0.13882700
C	-2.56288500	-0.86585700	-0.13153900
C	-2.71143200	-2.11498800	0.51635100
C	-3.71237700	-0.26795100	-0.70283200
C	-3.95418500	-2.75385700	0.56647200
H	-1.84378500	-2.56316000	0.99713600
C	-4.95350600	-0.90968900	-0.65210500
H	-3.61650800	0.69356600	-1.20269200
C	-5.08064300	-2.15573300	-0.01879700
H	-4.04789000	-3.71027500	1.07793200
H	-5.82241000	-0.43801200	-1.10787900
H	-6.04961300	-2.64937700	0.02883100

E.3.3. Reaction of **1** with 9-fluorenone leading to **3b**

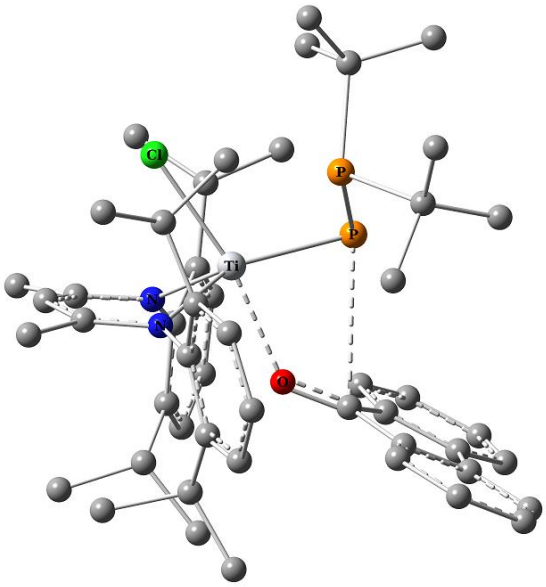


Figure S171. Optimized structure of **3b$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of **3b$_{TS1}$**:

C	2.81007344	-1.18331452	1.04310428
C	3.49013281	-2.00797421	0.11009133
C	4.86200552	-1.76823823	-0.09942062
H	5.40744042	-2.40047690	-0.79774152

C	5.53961954	-0.74662387	0.57325874
H	6.60262508	-0.58755727	0.39806140
C	4.84157791	0.07950066	1.46014774
H	5.36456512	0.89093575	1.96386647
C	3.47229402	-0.11484398	1.70640509
C	2.80623088	-3.15359764	-0.62838303
H	1.72056990	-3.01145777	-0.54009071
C	3.16133809	-3.15878978	-2.12844506
H	2.61639273	-3.96596530	-2.63266833
H	2.88235103	-2.20898276	-2.60006296
H	4.23374205	-3.33395625	-2.29102558
C	3.16131561	-4.52044840	-0.00103551
H	2.63858759	-5.32350215	-0.53675863
H	4.24246762	-4.70881011	-0.06531179
H	2.86906488	-4.56975707	1.05254922
C	2.73699087	0.80416797	2.67749252
H	1.66335902	0.62611327	2.54573321
C	3.01372709	2.29242398	2.38081606
H	2.39373377	2.92257678	3.03098232
H	4.06318091	2.55383570	2.57226255
H	2.78819956	2.54084003	1.33833374
C	3.10687000	0.48286563	4.14348854
H	2.84736291	-0.54790935	4.40729388
H	4.18531826	0.61573508	4.30775728
H	2.57065073	1.15450179	4.82685436
C	-2.36556278	0.58161930	1.89101832
C	-2.13455405	1.94256280	2.23764675
C	-3.21205503	2.84158806	2.13532787
H	-3.05579122	3.88918338	2.38309329
C	-4.48107361	2.41944040	1.72168064
H	-5.29426863	3.13827754	1.63277745
C	-4.70535172	1.06572392	1.46370423
H	-5.70497984	0.72709341	1.19351333
C	-3.66983991	0.11972040	1.56927019
C	-0.77874925	2.41452332	2.76775077
H	-0.01336863	1.94188311	2.14064116
C	-0.58462892	3.94330381	2.70971009
H	0.45291720	4.18626853	2.97015080
H	-0.78327923	4.35812085	1.71576270
H	-1.23146827	4.45676934	3.43534744
C	-0.54530220	1.95815224	4.22897603
H	0.37398688	2.41841290	4.61557041
H	-1.37927062	2.27129240	4.87170476
H	-0.42863680	0.87413827	4.30852501
C	-4.01231992	-1.36409583	1.43953466
H	-3.10957186	-1.94811621	1.65038032
C	-4.46578211	-1.74873112	0.02128864
H	-4.76071379	-2.80548239	-0.00801945
H	-5.32362259	-1.14134961	-0.30094148
H	-3.63890405	-1.60972130	-0.68356936
C	-5.11242529	-1.75833097	2.45540213
H	-5.23152863	-2.84989371	2.46874660
H	-4.87812539	-1.42063986	3.47184491
H	-6.08006245	-1.32037824	2.17482447
C	2.28120405	-2.90118362	3.21966646
H	3.29219935	-2.60976700	2.92457176
H	2.20014668	-2.87156682	4.31126351
H	2.11933658	-3.94056175	2.90081386
C	1.21053756	-2.03887641	2.57407264
C	0.00016402	-1.93748857	3.26398824
H	-0.06106143	-2.51413005	4.18438746
C	-1.10538927	-1.08801215	3.02197154
C	-2.12516439	-1.05992963	4.15075169
H	-1.61825332	-1.10683168	5.12068005
H	-2.76026285	-0.17159404	4.12024188
H	-2.76678914	-1.94745438	4.06749711
C	0.91261246	1.95530282	-0.65849698
C	-1.65793435	-2.94169633	-3.12114542

C	-1.65451188	-2.67116119	-4.64070607
H	-2.53075560	-2.11295855	-4.98443902
H	-0.75077077	-2.12147659	-4.93327726
H	-1.65073433	-3.63781649	-5.16816024
C	-0.42403689	-3.81762172	-2.82413252
H	-0.31594709	-4.02693684	-1.75686440
H	-0.53929593	-4.77129990	-3.36281693
H	0.48782724	-3.32558986	-3.17968961
C	-2.57878599	0.07294464	-2.94473219
C	-2.74270514	1.09944379	-1.81199329
H	-1.76297360	1.33523550	-1.38390336
H	-3.17824783	2.03162936	-2.20210793
H	-3.38435790	0.72302875	-1.00875712
C	-3.98044128	-0.40075256	-3.38000652
H	-3.95450128	-1.08709996	-4.23243520
H	-4.52203255	-0.88407756	-2.56035202
H	-4.56185483	0.48260772	-3.68698771
Cl	-0.90886344	-3.18797301	0.52021030
N	1.43187202	-1.42554361	1.38334582
N	-1.26666532	-0.35372434	1.90853085
O	0.55194031	1.10838582	0.20663242
P	0.51504642	-0.66266341	-2.10465003
P	-1.50736332	-1.30808863	-2.11342975
Ti	-0.15415135	-0.98052527	0.13870426
C	-1.84661766	0.74163739	-4.12463626
H	-1.69819492	0.05264689	-4.96300518
H	-2.44342623	1.59577414	-4.48199574
H	-0.86362439	1.11173894	-3.80667958
C	-2.93506251	-3.68971128	-2.68423099
H	-2.89212524	-3.92338186	-1.61420541
H	-3.84376288	-3.10833333	-2.87936503
H	-3.01349808	-4.63460936	-3.24417474
C	0.14599821	3.16259742	-1.05552437
C	-1.12049990	3.59461857	-0.65798002
C	0.92528797	3.91893691	-1.97159978
C	-1.62231883	4.79130191	-1.19755400
H	-1.70918196	3.01532358	0.04715396
C	0.42603271	5.10560341	-2.50632401
C	-0.85865881	5.53408382	-2.11178287
H	-2.61083747	5.13979704	-0.90507201
H	1.00772142	5.69481913	-3.21290245
H	-1.26264104	6.45775204	-2.52293490
C	2.20800058	2.03549573	-1.38691214
C	2.20970065	3.21927261	-2.17467532
C	3.30336542	1.16951160	-1.39396291
C	3.30704894	3.53589453	-2.97323014
C	4.41084135	1.49444082	-2.19325792
H	3.28605163	0.25263406	-0.81846127
C	4.41326071	2.66113627	-2.97401700
H	3.31689600	4.43524690	-3.58657363
H	5.26807937	0.82516965	-2.20866656
H	5.27871764	2.89391218	-3.59218271

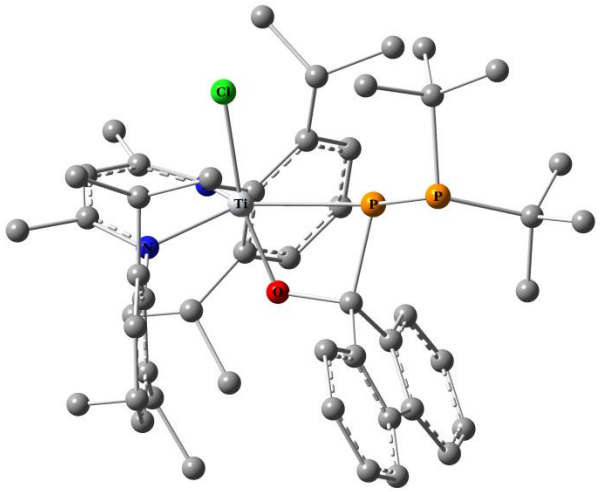


Figure S172. Optimized structure of **3b$_I$**.

Below are presented xyz coordinates for optimized geometry of **3b$_I$**:

C	1.16768200	2.95685700	-0.79879000
C	0.07243700	3.59217800	-1.44030700
C	-0.36116000	4.82514200	-0.92413800
H	-1.19658100	5.33515900	-1.39710100
C	0.25635900	5.40889900	0.18886800
H	-0.09593400	6.36741000	0.56685400
C	1.30839400	4.74674600	0.82424400
H	1.76579700	5.18595000	1.70953500
C	1.77679900	3.50627200	0.35600900
C	-0.60020300	2.97812200	-2.66313700
H	-0.60183700	1.88841000	-2.52098100
C	-2.06914400	3.40684400	-2.81853700
H	-2.52726000	2.84493900	-3.64058400
H	-2.63632500	3.19960900	-1.90263800
H	-2.16163500	4.47489600	-3.05964000
C	0.19102900	3.26065900	-3.95853200
H	-0.33208300	2.82056200	-4.81711000
H	0.29293000	4.34171200	-4.12716400
H	1.19080600	2.81698300	-3.91773800
C	2.88967300	2.79538000	1.11771500
H	3.05937800	1.82053900	0.64526100
C	2.47059900	2.53980900	2.58091200
H	3.28728700	2.04308500	3.12010500
H	2.25100800	3.48124600	3.10126400
H	1.57872400	1.90786600	2.62527400
C	4.21173000	3.59434600	1.07326600
H	4.52597000	3.80550600	0.04447000
H	4.10424600	4.55556400	1.59411300
H	5.01135500	3.02862200	1.56982100
C	2.34138000	-2.37209800	-0.03161800
C	2.67334600	-2.31868500	1.34771400
C	2.67056400	-3.52075700	2.07308900
H	2.91514700	-3.50190700	3.13209900
C	2.33671100	-4.73733900	1.46983200
H	2.33247100	-5.65475000	2.05645400
C	1.99532800	-4.76620700	0.11707100
H	1.72106500	-5.71067700	-0.35068300
C	1.99373800	-3.59340500	-0.65985600
C	3.04326300	-1.00735400	2.03051500
H	2.48259300	-0.21670800	1.52065400
C	2.62772500	-0.98794500	3.51436600
H	2.76296400	0.01820600	3.92652100
H	1.57397100	-1.26650000	3.63008600
H	3.23843900	-1.67266700	4.11931800
C	4.55244400	-0.70781900	1.88024300

H	4.80392700	0.23429300	2.38608300
H	5.15649300	-1.50901000	2.32819400
H	4.83994300	-0.60892200	0.82627100
C	1.56699800	-3.67654100	-2.11928500
H	1.74514300	-2.70384000	-2.59226300
C	0.05113400	-3.95272100	-2.19309800
H	-0.29581100	-3.93412500	-3.23337300
H	-0.18649100	-4.93443400	-1.76040200
H	-0.51294400	-3.19415200	-1.63745900
C	2.34718900	-4.74839700	-2.91066300
H	2.07117200	-4.70133500	-3.97206000
H	3.43260200	-4.60676600	-2.82912300
H	2.11628500	-5.75996100	-2.55090600
C	3.46692900	2.91132000	-2.52119900
H	4.45374200	3.07114700	-2.07066300
H	3.61428400	2.79587200	-3.60288000
H	2.84576700	3.79081100	-2.33762600
C	2.83522900	1.64499300	-1.97003800
C	3.56257200	0.45039600	-2.16625700
H	4.45232900	0.55611300	-2.78252200
C	3.40730400	-0.81244300	-1.55335700
C	4.51655500	-1.82407400	-1.75364400
H	5.42166200	-1.33914300	-2.13074500
H	4.74285900	-2.34677500	-0.81781100
H	4.19861700	-2.58302800	-2.48015900
C	-3.80726100	-1.21332700	-2.40803800
C	-3.53004100	0.12415800	-3.12065800
H	-4.11112700	0.94942600	-2.69844500
H	-2.46567600	0.38175600	-3.06280000
H	-3.79060000	0.02854900	-4.18711200
C	-2.89318700	-2.29446000	-3.02142800
H	-3.06160200	-3.27345400	-2.55441000
H	-3.10359900	-2.38174300	-4.09889500
H	-1.84040000	-2.02274700	-2.91115400
C	-4.82086800	-0.27498700	0.38846400
C	-4.27332000	0.04830700	1.79358000
H	-3.51026000	0.83263200	1.75106200
H	-5.09398300	0.41865000	2.42676000
H	-3.84108800	-0.83671500	2.27747100
C	-6.01699400	-1.23908600	0.57100800
H	-6.51572900	-1.48581900	-0.37081400
H	-5.69511700	-2.17501400	1.04639200
H	-6.76054400	-0.76184400	1.22800100
Cl	0.28561700	-0.54202400	-3.26766500
N	1.66167200	1.69865800	-1.30390200
N	2.34014800	-1.13777400	-0.79178500
O	0.46812200	0.19486400	0.77717100
P	-1.75538300	0.24832700	-0.43364000
P	-3.41235100	-1.24081500	-0.51823900
Ti	0.66076900	-0.02449600	-1.04855400
C	-5.26601600	1.04117200	-0.27221400
H	-5.76584100	0.87929200	-1.23426900
H	-5.97796700	1.55983600	0.38938700
H	-4.40429100	1.70336700	-0.43033100
C	-5.26946100	-1.64328200	-2.64892000
H	-5.50758000	-2.58154400	-2.13058400
H	-5.98873300	-0.87747200	-2.33870600
H	-5.40857200	-1.81111000	-3.72792400
C	-0.88615100	0.07183600	1.27101300
C	-1.02051100	-1.19350100	2.09457200
C	-1.15198800	1.16429000	2.29106300
C	-0.86763000	-2.51595700	1.68775400
C	-1.28104100	-0.86812100	3.44851900
C	-1.18056600	2.54179200	2.08938900
C	-1.36246000	0.59908500	3.57056600
C	-0.98059300	-3.53392800	2.64984200
H	-0.66506800	-2.75825200	0.64707400
C	-1.40287300	-1.88462400	4.40508000

C	-1.41874200	3.37396800	3.19705100
H	-1.02480700	2.95842800	1.09647300
C	-1.60885000	1.43008400	4.67155000
C	-1.24899000	-3.21978200	3.99309800
H	-0.85799600	-4.57251600	2.34962300
H	-1.60615500	-1.65038100	5.44913700
C	-1.63146200	2.82173000	4.47274800
H	-1.43986400	4.45428200	3.06359100
H	-1.78233600	1.01330300	5.66279200
H	-1.33813200	-4.02139400	4.72479100
H	-1.82071300	3.48098000	5.31870300

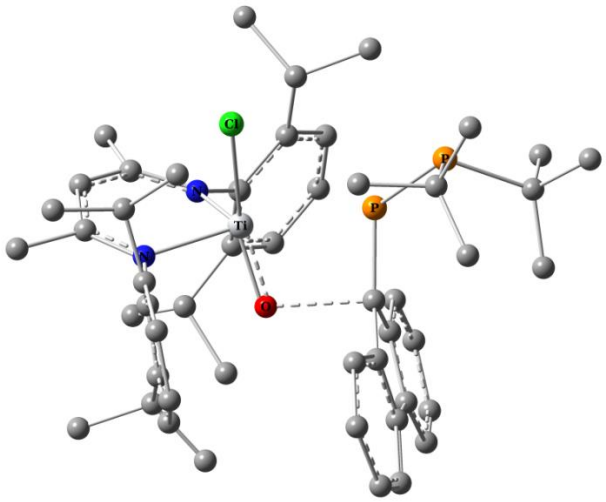


Figure S173. Optimized structure of **3b**$_{TS2}$.

Below are presented xyz coordinates for optimized geometry of **3b**$_{TS2}$:

C	0.87085600	2.99791900	-0.96926000
C	-0.18307700	3.35986500	-1.85158400
C	-0.89880200	4.53600000	-1.56553600
H	-1.70690700	4.83906600	-2.22764300
C	-0.59521800	5.32042800	-0.44574700
H	-1.16180500	6.22970700	-0.24868600
C	0.42403400	4.92566400	0.42551400
H	0.64119400	5.52425000	1.30943200
C	1.17029400	3.75833500	0.18848200
C	-0.52209500	2.52532100	-3.08329400
H	-0.26954000	1.48147800	-2.85839300
C	-2.02097900	2.56609200	-3.43366500
H	-2.24001300	1.79605100	-4.18327600
H	-2.63589000	2.36046200	-2.55022400
H	-2.31762200	3.53784000	-3.85442700
C	0.32464500	2.92896700	-4.31179400
H	0.00201900	2.34866700	-5.18589500
H	0.20303600	3.99740600	-4.54004900
H	1.38818200	2.72286700	-4.15335600
C	2.24908000	3.33914400	1.18088000
H	2.72723700	2.43014500	0.79627300
C	1.62456000	2.99558200	2.55025600
H	2.41609600	2.72724200	3.26249800
H	1.07817700	3.85576500	2.95972200
H	0.93382900	2.15228500	2.45690600
C	3.33311700	4.42753500	1.34767500
H	3.77432200	4.71770700	0.38618700
H	2.91553100	5.33248700	1.80983500
H	4.13728400	4.05946800	1.99869600
C	2.72774600	-1.99528900	0.25731000
C	2.75090600	-1.88108400	1.67620500
C	2.61694000	-3.04890400	2.44176600

H	2.62291900	-2.97659900	3.52690400
C	2.47264400	-4.30257600	1.83782200
H	2.35829400	-5.19586700	2.45067900
C	2.50074800	-4.40351400	0.44639600
H	2.42389200	-5.38317600	-0.02334300
C	2.63871900	-3.26707000	-0.37373900
C	3.00630100	-0.54279600	2.36031300
H	2.65180800	0.24201000	1.68392900
C	2.23445300	-0.39722400	3.68378600
H	2.38227900	0.60878700	4.09362200
H	1.16240000	-0.54797300	3.51943200
H	2.58120700	-1.11201000	4.44319200
C	4.52408700	-0.34124400	2.57929700
H	4.71353100	0.63835100	3.04005100
H	4.93121700	-1.11808600	3.24152000
H	5.07241800	-0.38325800	1.63004800
C	2.75825300	-3.47798600	-1.88070900
H	2.80393300	-2.49648300	-2.36591200
C	1.53624400	-4.21938000	-2.46096300
H	1.63381900	-4.30314200	-3.55109100
H	1.45604100	-5.23467200	-2.04736200
H	0.61526500	-3.67414300	-2.24735600
C	4.04190600	-4.27669600	-2.21720200
H	4.17585500	-4.32867500	-3.30615100
H	4.93984300	-3.82754700	-1.77822400
H	3.96707600	-5.30530500	-1.83840400
C	3.31864300	3.30009300	-2.34259300
H	3.99811200	3.16628300	-3.19125800
H	2.47161500	3.92070400	-2.64590400
H	3.86356700	3.84178500	-1.55853100
C	2.87700300	1.94669700	-1.81490200
C	3.82234700	0.91183300	-1.85457100
H	4.75385400	1.14655700	-2.36444600
C	3.80110400	-0.32841500	-1.16822500
C	5.09905900	-1.11140500	-1.15755600
H	5.94461800	-0.43661000	-0.98164100
H	5.09126800	-1.89057600	-0.39018900
H	5.24981000	-1.58794700	-2.13490100
C	-4.91981800	-0.25451200	-0.63310000
C	-4.88588700	-0.46799200	0.89203300
H	-4.78463700	-1.52056500	1.17059900
H	-4.06217200	0.09206700	1.34760900
H	-5.82239600	-0.08810400	1.33061100
C	-4.96582800	1.26677500	-0.91343200
H	-5.01740700	1.47433500	-1.98976300
H	-5.85812700	1.69536200	-0.43182800
H	-4.07953000	1.77042100	-0.50716500
C	-3.38504800	-2.83918600	-1.57203500
C	-1.93472800	-3.23654500	-1.90408600
H	-1.23375800	-2.91005100	-1.12821600
H	-1.86826300	-4.33081000	-1.99955800
H	-1.59803600	-2.78086100	-2.84265600
C	-4.27827300	-3.32506200	-2.74280000
H	-5.33668300	-3.08861900	-2.58748800
H	-3.96040600	-2.87804300	-3.69284800
H	-4.18816500	-4.41896500	-2.82873700
Cl	0.68221500	-0.94929600	-2.88651300
N	1.65408900	1.81895900	-1.25114600
N	2.72485100	-0.77666200	-0.51961000
O	0.56335500	0.24407800	0.95961000
P	-1.74730300	0.13470400	-0.70748200
P	-3.42477300	-0.91839000	-1.64676400
Ti	0.82555900	0.06400500	-0.72512300
C	-3.84365600	-3.50949400	-0.26625600
H	-4.91352100	-3.35317800	-0.08345500
H	-3.67695100	-4.59602300	-0.34083100
H	-3.28908600	-3.14385800	0.60336600
C	-6.20036900	-0.89246800	-1.22070200

H	-6.23905900	-0.78814200	-2.31293400
H	-6.28480800	-1.95561700	-0.96732300
H	-7.07849100	-0.38091200	-0.79858300
C	-1.57188300	0.00656000	1.08646600
C	-1.54230200	-1.13194500	2.02610200
C	-1.72549000	1.21050000	1.93723300
C	-1.23536700	-2.47266300	1.78723600
C	-1.69770800	-0.64965600	3.35875500
C	-1.83811900	2.54993300	1.55722900
C	-1.83935000	0.81787900	3.29985400
C	-1.15669900	-3.35637100	2.87657300
H	-1.02154300	-2.81674700	0.77963500
C	-1.62683400	-1.52952400	4.43860300
C	-2.03823200	3.51294000	2.56021900
H	-1.75751600	2.83355400	0.50947900
C	-2.05293000	1.77662800	4.29055800
C	-1.36657000	-2.89172900	4.18413200
H	-0.91252500	-4.40219100	2.70413300
H	-1.74292900	-1.17535600	5.46160100
C	-2.14590000	3.13065400	3.90737600
H	-2.10877200	4.56341300	2.28691800
H	-2.15635100	1.49411300	5.33704100
H	-1.29971400	-3.58814100	5.01839600
H	-2.31231000	3.89045100	4.66936200

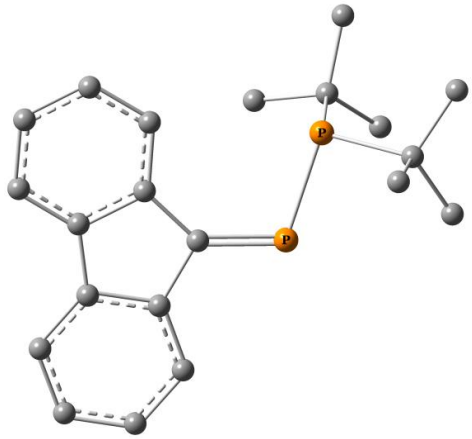


Figure S174. Optimized structure of **3b**.

Below are presented xyz coordinates for optimized geometry of **3b**:

C	-3.03859900	-1.40130600	0.00014300
C	-3.47892000	-0.06759300	0.00014400
C	-2.54877700	0.98809300	0.00009200
C	-1.19208700	0.67063400	0.00004000
C	-0.74200500	-0.67233700	0.00003900
C	-1.66579600	-1.71893900	0.00009100
H	-3.77170900	-2.20607400	0.00018400
H	-4.54568100	0.14700900	0.00018500
H	-2.86859300	2.02832000	0.00009200
H	-1.34426100	-2.75895100	0.00009100
C	0.00000000	1.58195900	-0.00002000
C	1.19208700	0.67063400	-0.00005800
C	2.54877700	0.98809300	-0.00011800
C	3.47892000	-0.06759300	-0.00014200
C	3.03859900	-1.40130600	-0.00010700
C	1.66579600	-1.71893900	-0.00004600
C	0.74200500	-0.67233700	-0.00002200
H	2.86859300	2.02832000	-0.00014500
H	4.54568100	0.14700900	-0.00018900
H	3.77170900	-2.20607400	-0.00012600
H	1.34426100	-2.75895100	-0.00001900

O	0.00000000	2.81312500	-0.00003700

E.3.4. Reaction of **1** with 4-cyanobenzophenone leading to ***Z*-3c**

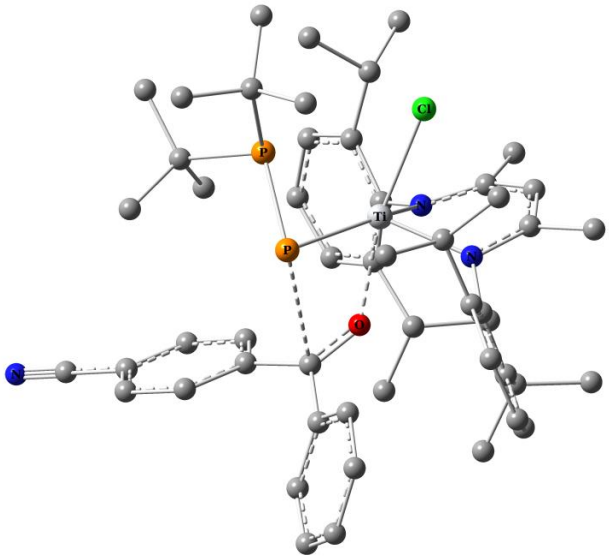


Figure S175. Optimized structure of ***Z*-3c$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3c$_{TS1}$**:

C	3.31363500	-0.43850500	0.25474400
C	3.96047400	-0.86060700	-0.93334400
C	5.17966500	-0.24199200	-1.27011700
H	5.71197900	-0.57386700	-2.16026500
C	5.72836100	0.77405700	-0.48210300
H	6.67868000	1.22821300	-0.75903500
C	5.04031800	1.21854100	0.65113200
H	5.45357900	2.03113100	1.24683700
C	3.82647900	0.62956500	1.03851800
C	3.41162500	-1.96933400	-1.82586200
H	2.37405800	-2.16590400	-1.52168200
C	3.39422700	-1.53670700	-3.30638600
H	3.00185300	-2.35076100	-3.92747900
H	2.75285700	-0.65869200	-3.45161400
H	4.40309500	-1.30059400	-3.67057000
C	4.20897900	-3.28261000	-1.66930400
H	3.77658000	-4.06067600	-2.31172300
H	5.25928500	-3.13916100	-1.95980000
H	4.18725200	-3.64617800	-0.63689000
C	3.12006700	1.10659200	2.30487100
H	2.11903300	0.66031100	2.30725300
C	2.95672100	2.63978600	2.32890400
H	2.38227700	2.93860400	3.21552100
H	3.92855100	3.14909000	2.38000200
H	2.43272400	2.99589300	1.43702600
C	3.86769600	0.63974300	3.57499300
H	3.92771700	-0.45241400	3.63119900
H	4.89157600	1.03846600	3.58954200
H	3.34843100	0.99779000	4.47383100
C	-1.78664800	-0.53292600	2.40090700
C	-1.86914800	0.76772100	2.97122500
C	-3.14601500	1.27613500	3.27235300
H	-3.23631400	2.27279200	3.69905400
C	-4.30390200	0.52616700	3.03347600
H	-5.28299300	0.94771000	3.25564800
C	-4.19328900	-0.77919800	2.54942400
H	-5.09146400	-1.38125500	2.41658900
C	-2.94089500	-1.34733700	2.25378000

C	-0.60861600	1.57443000	3.29888400
H	0.08097000	1.44799100	2.45332700
C	-0.86770200	3.08239200	3.49811500
H	0.09304900	3.60583700	3.57625400
H	-1.42692300	3.53248200	2.66970100
H	-1.42126500	3.27339600	4.42806500
C	0.09835100	1.03775000	4.56766300
H	0.91901400	1.71220500	4.84552100
H	-0.60362700	0.98869100	5.41085900
H	0.52773400	0.04496500	4.40977000
C	-2.86382200	-2.83743400	1.91488400
H	-1.80773600	-3.11961200	1.84057200
C	-3.50830900	-3.19895900	0.56498900
H	-3.49380900	-4.28747200	0.42427300
H	-4.55280100	-2.85948900	0.51718600
H	-2.94166000	-2.74676100	-0.25646200
C	-3.52695700	-3.67565900	3.03613500
H	-3.31113900	-4.74092500	2.88019000
H	-3.17193700	-3.38961300	4.03320700
H	-4.61821000	-3.55118400	3.02415400
C	3.79974100	-2.57562900	2.00477600
H	3.95413500	-2.85823200	3.05094200
H	3.86630300	-3.48774100	1.39524600
H	4.60136300	-1.90297400	1.68949200
C	2.41856600	-1.97854100	1.80584000
C	1.44109500	-2.34807500	2.73293100
H	1.76503300	-3.04459300	3.50275500
C	0.12953600	-1.84864000	2.89899700
C	-0.54155300	-2.28553900	4.19245100
H	0.18806400	-2.29399200	5.00946800
H	-1.38112000	-1.64358400	4.46813500
H	-0.91468900	-3.31101700	4.07023100
C	0.35666600	2.13140500	-0.49768300
C	-1.28459200	-2.94836200	-3.31286700
C	-1.71922100	-2.48124900	-4.71816300
H	-2.78479400	-2.24297700	-4.78648500
H	-1.14230200	-1.59983100	-5.02651800
H	-1.51473500	-3.29049600	-5.43627800
C	0.20450400	-3.33276600	-3.41517500
H	0.61524500	-3.64913900	-2.45310200
H	0.29931700	-4.16418400	-4.13089300
H	0.79112300	-2.48603400	-3.78740000
C	-3.12448800	-0.59551500	-2.31843200
C	-3.39164300	0.08569200	-0.96562200
H	-2.48578200	0.57837800	-0.59739000
H	-4.17420300	0.85098700	-1.07290400
H	-3.71229400	-0.63385500	-0.20803800
C	-4.32699400	-1.51026600	-2.63195000
H	-4.26334100	-1.98214200	-3.61746100
H	-4.45178300	-2.29389700	-1.87702800
H	-5.23744700	-0.89145200	-2.62163500
Cl	0.28665700	-3.42379200	0.02113100
N	2.16253400	-1.14109000	0.76642700
N	-0.49789100	-1.05463600	2.01092300
O	0.51606900	1.15447400	0.30121000
P	0.14369300	-0.16820600	-2.20417600
P	-1.46852600	-1.54077400	-2.01346300
Ti	0.25696400	-1.06543400	-0.00981600
C	-2.96951700	0.47758000	-3.41415900
H	-2.77957400	0.03625200	-4.39850800
H	-3.89476700	1.07185600	-3.47399000
H	-2.13745200	1.15101200	-3.17555300
C	-2.09861500	-4.17300300	-2.84254900
H	-1.74459700	-4.51227600	-1.86214900
H	-3.17079100	-3.95787400	-2.77225900
H	-1.96808000	-4.99511100	-3.56315600
C	-0.96913400	2.74630400	-0.75109700
C	-1.21763600	3.48811100	-1.93062600

C	-1.97617300	2.66136300	0.22706600
C	-2.43888900	4.12770800	-2.11893800
H	-0.46032400	3.52324600	-2.70966400
C	-3.19131200	3.32351100	0.06645100
H	-1.80074900	2.05651000	1.10851900
C	-3.43171700	4.06392200	-1.11013100
H	-2.63996600	4.67603500	-3.03562600
H	-3.95780800	3.25324900	0.83415900
C	1.52943900	2.86507100	-1.04960100
C	1.56915400	4.27579100	-0.96075500
C	2.60594800	2.17968600	-1.64048700
C	2.67799800	4.98118100	-1.43951800
H	0.74524500	4.81016100	-0.49170400
C	3.68939000	2.89199200	-2.16088200
H	2.56583900	1.09881000	-1.72105100
C	3.73458100	4.29017700	-2.05248100
H	2.71213200	6.06484600	-1.34446700
H	4.50035800	2.35065400	-2.64118400
C	-4.68444600	4.73277900	-1.29369500
N	-5.71327800	5.27912000	-1.44400600
H	4.58812800	4.83978800	-2.44582700

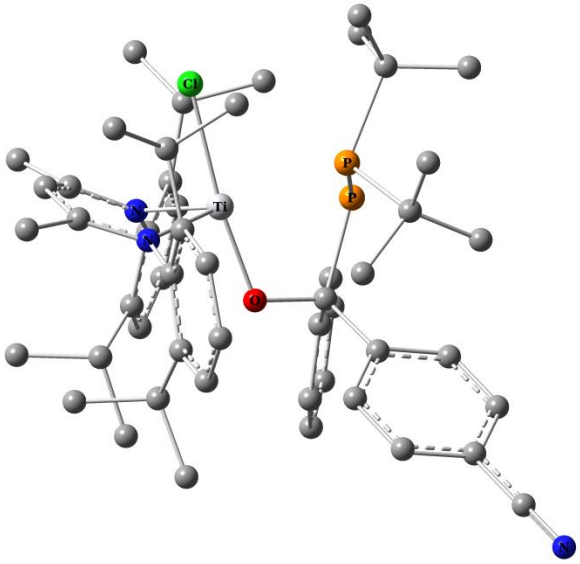


Figure S176. Optimized structure of ***Z*-3c$_{I}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3c$_{I}$**:

C	-3.26556000	-0.60207100	-0.19214300
C	-4.02042900	-0.55799300	1.00421900
C	-5.15038000	0.27937900	1.03397100
H	-5.74961700	0.32739000	1.94236600
C	-5.51501300	1.04663600	-0.07355500
H	-6.38579700	1.69814600	-0.02369300
C	-4.75745000	0.98267100	-1.24863700
H	-5.05113300	1.58158700	-2.10803500
C	-3.62963900	0.15401500	-1.33758100
C	-3.70069700	-1.42377300	2.21895400
H	-2.85145200	-2.07033400	1.96464200
C	-3.28798000	-0.56639900	3.43339400
H	-3.07785000	-1.21069100	4.29708300
H	-2.38344200	0.01031900	3.21152500
H	-4.09204300	0.12920200	3.71256900
C	-4.90075500	-2.31929100	2.60731500
H	-4.60049400	-3.02478300	3.39318700
H	-5.73118800	-1.71605000	2.99873300
H	-5.28157900	-2.89216300	1.75348700

C	-2.88465600	-0.02119100	-2.65827800
H	-1.87376400	-0.37006100	-2.41486300
C	-2.76197000	1.27728300	-3.47461400
H	-2.15269200	1.09444900	-4.36894400
H	-3.74196100	1.63661500	-3.81718800
H	-2.29165300	2.06955400	-2.88769700
C	-3.57583200	-1.10338300	-3.52312600
H	-3.59553800	-2.07699800	-3.02275100
H	-4.61174900	-0.81079300	-3.74303300
H	-3.04210000	-1.22431300	-4.47518900
C	1.89968500	-1.76537400	-1.79641700
C	2.08237500	-0.78189500	-2.80446100
C	3.39256400	-0.52802200	-3.24668000
H	3.56133200	0.22963100	-4.00806100
C	4.48461800	-1.24643400	-2.74687900
H	5.49027900	-1.02853400	-3.10230900
C	4.27320100	-2.25820900	-1.80838900
H	5.11910200	-2.83896900	-1.44307300
C	2.98576700	-2.54506100	-1.31953100
C	0.88815300	-0.09835700	-3.47256800
H	0.19853600	0.21777100	-2.67801200
C	1.26873600	1.13767500	-4.31260500
H	0.35650800	1.66856600	-4.61095900
H	1.90573100	1.84444200	-3.76843900
H	1.79809900	0.84671900	-5.23068500
C	0.13964600	-1.09100500	-4.39679700
H	-0.63299000	-0.56022300	-4.96779000
H	0.83657400	-1.54913500	-5.11141300
H	-0.35482100	-1.88537800	-3.83090000
C	2.81447500	-3.69906600	-0.33376400
H	1.74384800	-3.85461200	-0.15786400
C	3.43924200	-3.36140200	1.03043700
H	3.28455900	-4.18525800	1.73874500
H	4.51986500	-3.18487200	0.93391600
H	2.96559500	-2.46388500	1.44051400
C	3.43022800	-5.01032700	-0.87585700
H	3.15949500	-5.84774800	-0.21935200
H	3.09046600	-5.24071000	-1.89235300
H	4.52653600	-4.94874000	-0.89897300
C	-3.75629000	-3.34356300	-0.70821500
H	-3.86523500	-4.16746400	-1.42008400
H	-3.90593800	-3.74172600	0.30453500
H	-4.53589300	-2.59761000	-0.89050000
C	-2.36820800	-2.74572200	-0.78491000
C	-1.35769800	-3.52105900	-1.35720800
H	-1.66044400	-4.50299900	-1.71285200
C	-0.04543500	-3.13431600	-1.71929900
C	0.61951300	-4.08824100	-2.70154400
H	-0.09779400	-4.35996300	-3.48429400
H	1.51078100	-3.66298600	-3.16643400
H	0.90302700	-5.01066500	-2.17890900
C	-0.29272600	1.82953700	0.38230100
C	1.63575100	-0.74684600	3.94512500
C	2.22095800	0.36374300	4.84395100
H	3.29132000	0.52723800	4.69314800
H	1.69036800	1.31122400	4.68684100
H	2.07838500	0.06446800	5.89333000
C	0.19011500	-0.97788400	4.44355300
H	-0.36445700	-1.68149500	3.82038800
H	0.26034100	-1.39393100	5.46043300
H	-0.36839100	-0.03726100	4.50682300
C	3.38683700	0.67570100	1.76284200
C	3.54933700	0.61032000	0.23059200
H	2.64286400	0.91577700	-0.29327000
H	4.36564000	1.27608200	-0.08533000
H	3.78785900	-0.40834900	-0.08655800
C	4.59091900	-0.08293500	2.36801900
H	4.62376200	-0.04529100	3.46119400

H	4.62077700	-1.12932000	2.04902700
H	5.50476600	0.40320000	1.99377300
Cl	-0.32085500	-2.86562100	1.68842600
N	-2.13254400	-1.49363500	-0.32598100
N	0.56925700	-2.01685400	-1.28561400
O	-0.27546800	0.72721400	-0.54636000
P	-0.13373500	0.98278200	2.10991600
P	1.71106600	-0.23381900	2.06432100
Ti	-0.30072400	-0.93291500	0.33687900
C	3.40803800	2.13375600	2.25452100
H	3.38505800	2.20261100	3.34608100
H	4.33615500	2.61050000	1.90365900
H	2.56620800	2.70328500	1.85893600
C	2.41275300	-2.06969500	4.11829300
H	1.92694200	-2.87434800	3.55616200
H	3.45632100	-1.99458300	3.79658400
H	2.40847000	-2.34164200	5.18466800
C	0.75958800	2.87055800	0.04693400
C	0.87548700	4.02204600	0.85365200
C	1.53865900	2.76863900	-1.11182800
C	1.77633900	5.03181000	0.52723900
H	0.25118900	4.11525700	1.74093300
C	2.45331600	3.76967400	-1.45093600
H	1.41856300	1.89169300	-1.73821100
C	2.58349600	4.90788400	-0.62963500
H	1.86904600	5.91511500	1.15421800
H	3.06499800	3.67908200	-2.34578500
C	-1.64374700	2.58125500	0.29978500
C	-1.87170000	3.40292100	-0.82265600
C	-2.59579400	2.57806100	1.32907100
C	-3.01401000	4.20354300	-0.91011100
H	-1.12631700	3.44037800	-1.61465200
C	-3.73571100	3.39239500	1.25171000
H	-2.44431800	1.95534100	2.20710400
C	-3.94765000	4.21114200	0.13737000
H	-3.16519700	4.83348800	-1.78537000
H	-4.45645500	3.37821600	2.06723800
C	3.52434500	5.93436600	-0.96559900
N	4.29867000	6.77385000	-1.24047800
H	-4.82935600	4.84756000	0.08272000

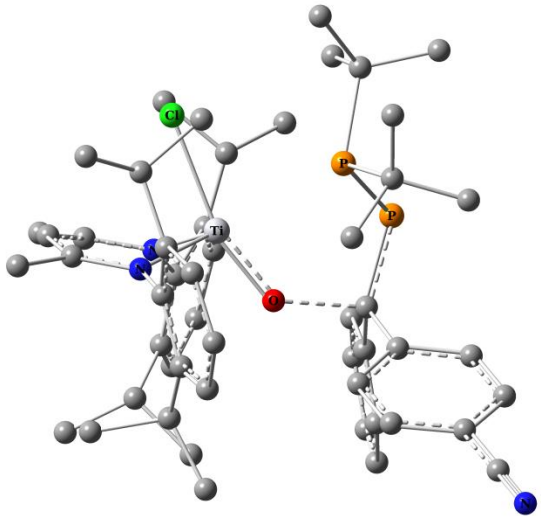


Figure S177. Optimized structure of ***Z*-3c$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3c$_{TS2}$**:

C	-3.32126800	-0.20750500	-0.19902100
C	-3.94111500	-0.12013000	1.07247400

C	-5.10113700	0.66619400	1.18019900
H	-5.61510200	0.72956100	2.13631700
C	-5.60178000	1.38041900	0.08579500
H	-6.50380300	1.98093700	0.19374300
C	-4.91799100	1.35380600	-1.13111900
H	-5.27960700	1.95171900	-1.96661800
C	-3.77323900	0.55685500	-1.30045400
C	-3.38060800	-0.86401400	2.28122500
H	-2.28265400	-0.83300200	2.18552500
C	-3.74447600	-0.18285300	3.61346100
H	-3.23915700	-0.69716900	4.43798100
H	-3.43905300	0.87092300	3.62964400
H	-4.82370800	-0.23671000	3.81107500
C	-3.80050800	-2.34927000	2.32515000
H	-3.41276600	-2.81512800	3.24021800
H	-4.89601900	-2.44029900	2.32800000
H	-3.39102500	-2.90939600	1.47986400
C	-3.05140100	0.55201200	-2.64397500
H	-2.23646800	-0.17949900	-2.58800100
C	-2.42606300	1.93856200	-2.90407400
H	-1.93684800	1.95676700	-3.88676400
H	-3.19301000	2.72401500	-2.89311600
H	-1.68689100	2.17926200	-2.13449600
C	-3.97680300	0.15349900	-3.81416000
H	-4.41806500	-0.83985100	-3.66738200
H	-4.79743200	0.87305600	-3.93514300
H	-3.40789800	0.13441100	-4.75290500
C	1.54914400	-1.74568400	-2.06968800
C	1.79266800	-0.65439600	-2.94954900
C	3.12360100	-0.39208400	-3.31177500
H	3.34327800	0.43992200	-3.97627400
C	4.17680700	-1.19036500	-2.84649800
H	5.20121900	-0.95928100	-3.13345800
C	3.90779900	-2.29218100	-2.03406100
H	4.72700900	-2.92507900	-1.69613300
C	2.59472600	-2.59957200	-1.63148100
C	0.63740000	0.15729400	-3.53646400
H	-0.03566300	0.41254100	-2.70496900
C	1.08352000	1.46028900	-4.22715400
H	0.19889700	2.03144500	-4.53122100
H	1.68200300	2.10349100	-3.57399300
H	1.66664200	1.25033300	-5.13451200
C	-0.16307700	-0.68144400	-4.56321200
H	-0.93840500	-0.05778600	-5.02672400
H	0.50023500	-1.04840500	-5.35783600
H	-0.66084100	-1.53762900	-4.09980300
C	2.34889500	-3.84806100	-0.78582100
H	1.26823100	-3.98685600	-0.67312700
C	2.91579900	-3.70151500	0.63897800
H	2.73641200	-4.62012200	1.21187900
H	3.99759500	-3.50978500	0.61645400
H	2.41723700	-2.88070800	1.16594500
C	2.94265100	-5.10532100	-1.46278600
H	2.63269800	-6.00426900	-0.91414300
H	2.61567100	-5.20289100	-2.50517400
H	4.04040300	-5.07567800	-1.45984400
C	-4.21426400	-2.60886700	-1.15265300
H	-4.67099200	-2.03878900	-1.97099200
H	-4.36461000	-3.67477700	-1.35257300
H	-4.74038100	-2.32959000	-0.23595300
C	-2.72720900	-2.31174100	-1.06135400
C	-1.87641400	-3.19329800	-1.75354300
H	-2.35489500	-4.06487900	-2.19294000
C	-0.53448700	-2.98938800	-2.11619700
C	0.04411400	-3.93061500	-3.15441400
H	-0.71104700	-4.16321500	-3.91293400
H	0.92592900	-3.50503200	-3.64107300
H	0.33781000	-4.87297700	-2.67385500

C	0.11037600	2.12340500	0.88877600
C	0.98259900	-1.17573700	4.07980100
C	1.58226400	-0.31569200	5.21472700
H	2.67506400	-0.26650700	5.17681400
H	1.18738900	0.70796800	5.18829000
H	1.30448400	-0.76605100	6.17997300
C	-0.53903700	-1.26453500	4.31519500
H	-1.02117500	-1.87677700	3.54686700
H	-0.70719100	-1.74353600	5.29206400
H	-1.00250000	-0.27331900	4.33091000
C	3.22195100	-0.03258600	2.23182900
C	3.55278000	-0.06155700	0.72752100
H	2.86686900	0.54815400	0.13927900
H	4.57072300	0.32305400	0.56391800
H	3.51014900	-1.08238600	0.33904500
C	4.12676600	-1.08517500	2.90812500
H	4.05307000	-1.07320800	4.00015300
H	3.93448000	-2.09987200	2.54906100
H	5.16673200	-0.83437100	2.64719400
Cl	-0.49426800	-3.12431100	1.28293700
N	-2.28811200	-1.19563000	-0.43027500
N	0.20144800	-1.98090800	-1.60531500
O	-0.07919000	0.62313100	-0.20567800
P	0.07195300	1.42644600	2.58179600
P	1.30243200	-0.37592300	2.35141400
Ti	-0.31018600	-1.06132100	0.12989600
C	3.55580300	1.34310600	2.83871300
H	3.35660500	1.37122100	3.91551300
H	4.62566600	1.54960200	2.67945000
H	2.97950600	2.14302800	2.37089100
C	1.53751700	-2.61826400	4.14026600
H	1.14097500	-3.22443600	3.31959100
H	2.62836900	-2.65857900	4.12169900
H	1.20640000	-3.06935000	5.08805500
C	1.38289600	2.71682700	0.33368700
C	1.94998700	3.80036900	1.04283300
C	1.97223300	2.33080600	-0.88000000
C	3.08560300	4.45641100	0.57079400
H	1.48694700	4.11606000	1.97574000
C	3.12116500	2.96666800	-1.35725200
H	1.53263400	1.50497800	-1.42686900
C	3.69018500	4.03484200	-0.63539400
H	3.51530700	5.28426700	1.12933600
H	3.58693800	2.63366200	-2.28168000
C	-1.07686900	2.99229700	0.56996800
C	-0.98060000	4.04255200	-0.37289800
C	-2.31138500	2.79899500	1.22482700
C	-2.07105600	4.88079100	-0.62958800
H	-0.04686900	4.21215400	-0.90226700
C	-3.38990800	3.65447900	0.99040400
H	-2.40471000	1.97673600	1.92890300
C	-3.27784900	4.69807900	0.05962300
H	-1.97246900	5.68080500	-1.36152300
H	-4.32362900	3.49475000	1.52341300
C	4.87208900	4.68295600	-1.12082000
N	5.84189900	5.21034100	-1.52200200
H	-4.12371800	5.35723800	-0.12951900

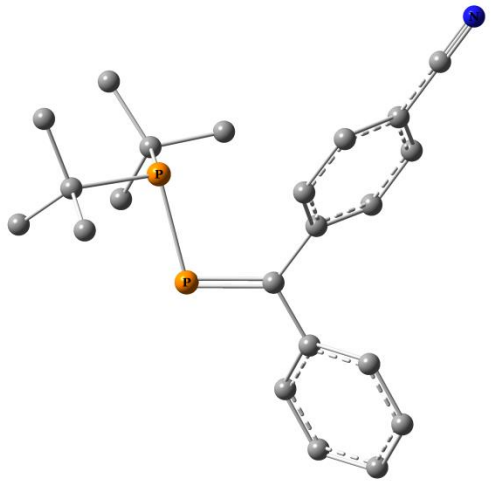


Figure S178. Optimized structure of ***Z*-3c**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3c**:

C	-1.16907500	2.86625900	-1.19620800
C	-0.87147800	1.50476900	-1.23062900
C	-1.33606800	0.63571500	-0.22078100
C	-2.12501000	1.16942200	0.82244800
C	-2.40868900	2.53333100	0.88297400
C	-1.93043300	3.39344100	-0.13001700
H	-0.81524300	3.52819800	-1.98236500
H	-2.99995300	2.93987800	1.69957800
C	-1.02329300	-0.81541300	-0.23887500
P	0.54433700	-1.52616900	-0.37603200
P	1.93778600	0.21044900	-0.15787600
C	2.36746000	0.02162700	1.71527200
C	1.18526100	0.72047800	2.42730200
C	2.49131700	-1.41237000	2.26642000
C	3.66340800	0.80568800	2.00388700
H	1.05661300	1.75301200	2.07979500
H	0.24512600	0.18131500	2.25387000
H	1.37031100	0.73660300	3.51201900
H	3.31056900	-1.96980200	1.80247100
H	2.68307700	-1.36586600	3.34971200
H	1.56402600	-1.98063300	2.11502100
H	3.79179800	0.90338700	3.09259700
H	4.54610900	0.28616900	1.61209000
H	3.63142500	1.81554600	1.57408200
C	3.37202600	-0.45877100	-1.24765000
C	4.43014700	0.66234700	-1.37050600
C	4.04092900	-1.76598800	-0.78669300
C	2.74357200	-0.66914000	-2.64617700
H	3.97323500	1.60149500	-1.70775300
H	4.94391800	0.85348500	-0.42247100
H	5.18999600	0.36513300	-2.10918800
H	3.30730200	-2.56976600	-0.64507300
H	4.76389500	-2.09702200	-1.54837600
H	4.59168600	-1.62658200	0.15103300
H	3.53718500	-0.90295400	-3.37141000
H	2.02664100	-1.50163100	-2.65047200
H	2.22390400	0.23542300	-2.99124200
H	-0.28633300	1.09662500	-2.04999500
H	-2.50020500	0.50446400	1.59763600
C	-2.18671100	-1.72921400	-0.13273600
C	-2.08460300	-2.98683900	0.50770700
C	-3.43251700	-1.36500800	-0.69890200
C	-3.17772000	-3.85692000	0.55597800
H	-1.14461500	-3.25922400	0.98414700
C	-4.52366600	-2.23774000	-0.64945200
H	-3.53015000	-0.40218000	-1.19618800

C	-4.40147600	-3.48767400	-0.02326800
H	-3.08058400	-4.81598400	1.06149000
H	-5.46932100	-1.94326400	-1.10090500
C	-2.22712100	4.79432800	-0.08197700
N	-2.46932400	5.94256400	-0.04193200
H	-5.25453600	-4.16193900	0.02334300

E.3.5. Reaction of **1** with 4-cyanobenzophenone leading to ***E*-3c**

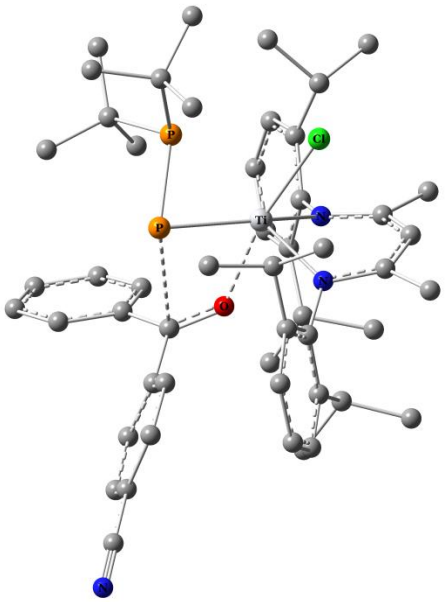


Figure S179. Optimized structure of ***E*-3c$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3c$_{TS1}$**:

C	2.40957400	1.23150400	-1.45734300
C	2.98356800	2.36174600	-0.82265200
C	4.38709700	2.41563300	-0.72451600
H	4.85148800	3.29042500	-0.27132600
C	5.19706900	1.38375800	-1.20889800
H	6.28072100	1.45402200	-1.12777600
C	4.60663300	0.25230000	-1.78056300
H	5.23801500	-0.56071900	-2.13602100
C	3.21257900	0.15182100	-1.91477400
C	2.15309100	3.52756600	-0.29360100
H	1.09730500	3.22335500	-0.29887800
C	2.53888400	3.87759300	1.15863800
H	1.94362700	4.73060800	1.50635100
H	2.34473900	3.03387800	1.83246200
H	3.59774300	4.15801000	1.23865300
C	2.29510700	4.78035500	-1.18663500
H	1.66073900	5.58837500	-0.79974800
H	3.33532700	5.13495400	-1.19877600
H	1.99416600	4.57720700	-2.21945000
C	2.59992900	-1.06757800	-2.59975000
H	1.51930600	-1.03494300	-2.41920400
C	3.13915400	-2.39055200	-2.02065400
H	2.63134100	-3.23925200	-2.49696500
H	4.21564800	-2.50531900	-2.20567700
H	2.97186900	-2.44705700	-0.94122300
C	2.84224400	-1.03066200	-4.12643300
H	2.39863300	-0.14080500	-4.58529000
H	3.91871100	-1.02725900	-4.34686700
H	2.39794900	-1.91506600	-4.60202300
C	-2.45503300	-1.41373300	-1.57228200
C	-2.02865800	-2.77104500	-1.56454100

C	-2.96464500	-3.75425800	-1.19522300
H	-2.65940000	-4.79809900	-1.17035200
C	-4.28122400	-3.41801500	-0.85863300
H	-4.98340300	-4.19427200	-0.55820200
C	-4.69923600	-2.08881200	-0.95154600
H	-5.73815400	-1.83558300	-0.74304300
C	-3.81217800	-1.06747200	-1.33686400
C	-0.61319400	-3.16442700	-1.99799900
H	0.07259700	-2.43313600	-1.55004800
C	-0.19033200	-4.57568900	-1.53957600
H	0.87534600	-4.72028500	-1.75585700
H	-0.33863300	-4.73686400	-0.46562700
H	-0.74282300	-5.35489000	-2.08328600
C	-0.44552000	-3.08973300	-3.53565000
H	0.53079700	-3.50363800	-3.82063200
H	-1.22504500	-3.67661400	-4.03979000
H	-0.48644300	-2.06142300	-3.90436400
C	-4.36681800	0.33319000	-1.60322300
H	-3.55836300	0.95384100	-2.00516300
C	-4.87413500	1.04332300	-0.33582900
H	-5.32996800	2.00546100	-0.60296200
H	-5.62835800	0.43776600	0.18674700
H	-4.03735300	1.24466600	0.34213800
C	-5.51128500	0.26868500	-2.64481100
H	-5.78273800	1.28448900	-2.96134800
H	-5.23175200	-0.31060800	-3.53268900
H	-6.40772000	-0.19687300	-2.21325800
C	1.57565200	2.30411300	-3.91425600
H	1.41012300	2.09194400	-4.97525200
H	1.31879400	3.35776100	-3.73619000
H	2.63534600	2.17337800	-3.68034000
C	0.67135900	1.44933900	-3.04552700
C	-0.50354700	0.98331800	-3.63954400
H	-0.66168200	1.29356800	-4.66984800
C	-1.45505800	0.06059700	-3.14606400
C	-2.45259500	-0.41869300	-4.18982700
H	-1.94963500	-0.56447100	-5.15201700
H	-2.95034000	-1.34692700	-3.90064900
H	-3.21805000	0.35631500	-4.32956400
C	1.07327600	-1.46987400	1.15619700
C	-2.19944100	3.42839800	2.31087500
C	-2.12964600	3.57133800	3.84602600
H	-2.93028100	3.03910300	4.36814100
H	-1.16435800	3.20973800	4.22311300
H	-2.21828800	4.63806300	4.10406900
C	-1.07104400	4.30568200	1.73294100
H	-1.02532000	4.25273100	0.64242500
H	-1.25959100	5.34944800	2.02889000
H	-0.10164600	3.99938400	2.14068100
C	-2.85567700	0.41641300	2.95671200
C	-2.98642700	-0.87389800	2.12927700
H	-2.02593600	-1.13845600	1.67491700
H	-3.29427600	-1.71005900	2.77382900
H	-3.71970400	-0.76618800	1.32556800
C	-4.27805400	0.88816500	3.32494300
H	-4.28490400	1.76388100	3.98168100
H	-4.87634000	1.11436700	2.43575500
H	-4.78042100	0.06937900	3.86306400
Cl	-1.57261700	2.75609700	-1.28894500
N	0.99848400	1.17859400	-1.75358700
N	-1.50073600	-0.37296000	-1.87355400
O	0.62289400	-1.03440100	0.04855700
P	0.16440600	1.16528500	1.86167200
P	-1.91321100	1.60479900	1.76239800
Ti	-0.50882300	0.85238800	-0.38998600
C	-2.03944500	0.12788300	4.23185000
H	-1.91667300	1.02144200	4.85347400
H	-2.55694300	-0.64039100	4.82759700

H	-1.04252800	-0.24787400	3.97153300
C	-3.55672500	3.91104100	1.75584800
H	-3.56743200	3.84135400	0.66196200
H	-4.39801100	3.33106700	2.15173100
H	-3.71197900	4.96362400	2.03891200
C	0.28940100	-2.33505400	2.06187100
C	0.64850000	-2.47614400	3.42362700
C	-0.78871500	-3.08501100	1.55648800
C	-0.05652300	-3.35496100	4.24761800
H	1.45208100	-1.86710600	3.83140900
C	-1.47245400	-3.98813000	2.37489500
H	-1.08647500	-2.94213500	0.52415900
C	-1.10818100	-4.12724300	3.72151900
H	0.20973700	-3.44007800	5.29931500
H	-2.29719000	-4.56556700	1.96133400
H	-1.64574700	-4.82233000	4.36413400
C	2.53596900	-1.36166300	1.46273100
C	3.25023500	-2.53736400	1.78622600
C	3.21848800	-0.13561500	1.39754800
C	4.62571300	-2.49252900	2.01458700
H	2.72743400	-3.49013900	1.83208000
C	4.58269000	-0.07102400	1.67335900
H	2.66733800	0.76840100	1.16374500
C	5.29809800	-1.25201600	1.96696900
H	5.18053800	-3.40062300	2.23612700
H	5.09865400	0.88350400	1.64905400
C	6.70930200	-1.19011300	2.21150300
N	7.86631100	-1.13669400	2.40381300

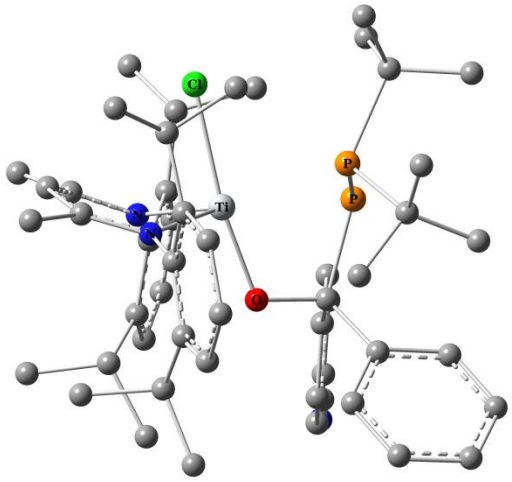


Figure S180. Optimized structure of ***E*-3c$_{I}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3c$_{I}$**:

C	-2.37207300	-1.92175500	0.21458300
C	-3.10434100	-1.98304900	1.42473900
C	-4.49605500	-1.79394500	1.35462800
H	-5.08553600	-1.84212700	2.26917200
C	-5.13575700	-1.54798300	0.13659600
H	-6.21321900	-1.39461000	0.10660300
C	-4.39032500	-1.49741200	-1.04704000
H	-4.89995000	-1.32150200	-1.99291000
C	-3.00106400	-1.69403400	-1.03622300
C	-2.44859800	-2.30648800	2.76456600
H	-1.41295000	-2.61120300	2.57027400
C	-2.38946800	-1.06786300	3.68273600
H	-1.94035400	-1.33452600	4.64840600
H	-1.77527300	-0.27899600	3.23283000
H	-3.39789600	-0.67149500	3.86992200

C	-3.17091000	-3.46272100	3.49285400
H	-2.58939900	-3.76816800	4.37246900
H	-4.16518200	-3.15424700	3.84304800
H	-3.30438800	-4.33717000	2.84368900
C	-2.21672400	-1.81506600	-2.34086100
H	-1.15159100	-1.76109600	-2.08838000
C	-2.51236900	-0.69297500	-3.35111100
H	-1.99398200	-0.89969100	-4.29658100
H	-3.58406800	-0.60788400	-3.57407600
H	-2.15957900	0.26786600	-2.96874500
C	-2.48792900	-3.19744700	-2.98180300
H	-2.22425500	-4.01526500	-2.30116100
H	-3.55014900	-3.30204900	-3.24187600
H	-1.89522900	-3.31380600	-3.89896600
C	2.82972400	-1.02188900	-1.48941900
C	2.60810300	-0.38092400	-2.73560500
C	3.69378600	0.27270700	-3.34429400
H	3.54711100	0.78027700	-4.29435300
C	4.96497800	0.27591700	-2.75972000
H	5.78800900	0.79807400	-3.24469100
C	5.17478000	-0.41093100	-1.56216100
H	6.17107400	-0.43565100	-1.12287100
C	4.12529300	-1.08533300	-0.91251900
C	1.25736000	-0.47338000	-3.44403300
H	0.47587600	-0.28717900	-2.69373400
C	1.09625800	0.54528000	-4.59047100
H	0.05029900	0.56388800	-4.92013700
H	1.37876800	1.56167400	-4.29208000
H	1.71158500	0.26626600	-5.45732600
C	1.03405100	-1.89217000	-4.02407000
H	0.11677700	-1.90935800	-4.62665000
H	1.87355700	-2.17700500	-4.67248700
H	0.92801100	-2.64504700	-3.23774100
C	4.43720900	-1.88458800	0.35018300
H	3.54159900	-2.44569100	0.64068900
C	4.76785900	-0.95031700	1.52400200
H	4.94376800	-1.52838500	2.44007900
H	5.66675100	-0.35418100	1.31196300
H	3.92472900	-0.27559300	1.69900400
C	5.60165300	-2.87809800	0.12861400
H	5.69806700	-3.53804100	1.00083100
H	5.45619800	-3.49881700	-0.76329200
H	6.55478600	-2.34549800	0.00973000
C	-1.56611000	-4.61194500	0.35826000
H	-1.21901100	-5.55533200	-0.07345400
H	-1.65122700	-4.73957700	1.44550700
H	-2.56655300	-4.38293200	-0.02261700
C	-0.58238200	-3.49850000	0.06829500
C	0.69576200	-3.85569100	-0.36328500
H	0.88598900	-4.92281800	-0.44668600
C	1.70353800	-3.02625900	-0.90861800
C	2.77163700	-3.80236700	-1.66847600
H	2.28830600	-4.56355600	-2.29133600
H	3.39108100	-3.16498600	-2.30163600
H	3.42142400	-4.32439200	-0.95475500
C	-0.96732600	1.66272900	-0.10457900
C	2.00095500	1.43257700	3.65455600
C	2.00566500	2.90662500	4.11150800
H	2.88404400	3.46097100	3.76844300
H	1.10017900	3.42530500	3.77309200
H	2.01561600	2.92208600	5.21188900
C	0.83830900	0.74728900	4.41097900
H	0.68283900	-0.28581900	4.09440100
H	1.10370900	0.74794900	5.47948800
H	-0.10054400	1.30134700	4.30036500
C	2.82583800	2.73999400	0.91098100
C	2.90923400	2.32406100	-0.57154800
H	1.92732100	2.09377900	-0.98885800

H	3.34061900	3.14671800	-1.16046000
H	3.54542600	1.44298100	-0.68732600
C	4.27246800	2.77331700	1.45410900
H	4.33515200	3.11860900	2.49132000
H	4.76048500	1.79646900	1.37541800
H	4.84392800	3.48121200	0.83459900
Cl	1.16482300	-1.92380000	2.34444100
N	-0.95334900	-2.20341100	0.19388100
N	1.72324300	-1.68086400	-0.82783300
O	-0.44048600	0.47067000	-0.72823100
P	-0.38738600	1.50575200	1.72534400
P	1.80878700	1.31270500	1.71030500
Ti	0.36515800	-0.69396800	0.50992800
C	2.19317300	4.13682300	1.04125400
H	2.22064600	4.51360500	2.06735300
H	2.76018500	4.83682100	0.40843300
H	1.15699100	4.14099400	0.69898200
C	3.30704500	0.72840600	4.07864400
H	3.24636500	-0.34585800	3.87610200
H	4.19323200	1.13354900	3.57935500
H	3.43927300	0.86689000	5.16241300
C	-0.57575200	2.92574200	-0.85367800
C	-0.95198100	4.17977900	-0.33503500
C	0.01760900	2.86128000	-2.11948500
C	-0.70795500	5.34868100	-1.06243300
H	-1.43601100	4.22976400	0.64020400
C	0.27139000	4.03327100	-2.84822800
H	0.27256200	1.88592500	-2.51940900
C	-0.08798100	5.28068900	-2.32212800
H	-0.99857100	6.31259900	-0.64809800
H	0.74210000	3.96756000	-3.82833400
H	0.10501000	6.19107800	-2.88676600
C	-2.52005000	1.63967400	-0.13528500
C	-3.17717500	2.00037400	-1.33086600
C	-3.30440000	1.36679700	0.99584800
C	-4.56569600	2.07706900	-1.40294500
H	-2.58947300	2.25682400	-2.20800100
C	-4.69779600	1.46184600	0.94931400
H	-2.82909700	1.09093600	1.93267600
C	-5.34083100	1.81563200	-0.25210400
H	-5.05578000	2.35198200	-2.33383300
H	-5.28911700	1.25221000	1.83669400
C	-6.77039900	1.87441900	-0.31140100
N	-7.94375400	1.90083900	-0.36113100

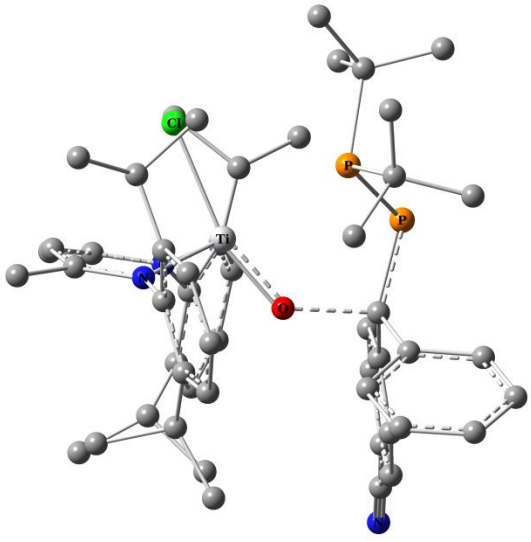


Figure S181. Optimized structure of ***E*-3c$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3c$_{TS2}$**:

C	-2.47922000	-1.44405100	1.09442700
C	-2.96876200	-0.81328800	2.26586900
C	-4.36006800	-0.65437800	2.38830200
H	-4.76758700	-0.20165000	3.28914700
C	-5.23272500	-1.05198500	1.36841100
H	-6.30674100	-0.91496900	1.48338700
C	-4.71799900	-1.58320200	0.18409400
H	-5.39601800	-1.84353900	-0.62749600
C	-3.33821100	-1.80094700	0.02799200
C	-2.02305400	-0.33727000	3.36530900
H	-1.11920200	0.04084300	2.85929600
C	-2.60916600	0.82641200	4.18611400
H	-1.85445500	1.19516400	4.88905100
H	-2.91792800	1.66357600	3.54747100
H	-3.47526200	0.50365100	4.77957700
C	-1.58228800	-1.47134900	4.31613600
H	-0.94883200	-1.05960900	5.11228900
H	-2.45792500	-1.94607000	4.78112400
H	-0.99186800	-2.22935700	3.79395200
C	-2.81434600	-2.39943200	-1.27371600
H	-1.73485700	-2.55774500	-1.16416400
C	-3.03132500	-1.40403900	-2.43234400
H	-2.70077600	-1.84656000	-3.38103800
H	-4.09319900	-1.14401000	-2.53285400
H	-2.47054500	-0.48118500	-2.25768800
C	-3.46978100	-3.75717700	-1.60815700
H	-3.32084000	-4.49255700	-0.80826300
H	-4.55034300	-3.64808000	-1.76921700
H	-3.03396000	-4.16698400	-2.52873900
C	2.33423000	-1.82405200	-1.40807000
C	1.90252700	-1.55543500	-2.73652900
C	2.86282400	-1.10611300	-3.65674200
H	2.56159300	-0.88145900	-4.67685800
C	4.20622500	-0.95104400	-3.29089000
H	4.92974300	-0.59049400	-4.02018600
C	4.61802700	-1.27904400	-1.99883100
H	5.66789300	-1.18131000	-1.72661400
C	3.69912100	-1.72672900	-1.03151700
C	0.45806700	-1.81798400	-3.16251600
H	-0.19231700	-1.37746400	-2.39302700
C	0.09293400	-1.20256900	-4.52680100
H	-0.97687800	-1.34748600	-4.71600500
H	0.29400100	-0.12750900	-4.57300300
H	0.63972200	-1.69404300	-5.34363200
C	0.16817100	-3.33808400	-3.22540700
H	-0.84948300	-3.50643900	-3.60086600
H	0.87068200	-3.83363300	-3.90884400
H	0.24136000	-3.81419300	-2.24374700
C	4.20891700	-2.12337000	0.35290100
H	3.37919800	-2.56006700	0.91902200
C	4.68767700	-0.90277600	1.16101800
H	5.05745200	-1.22222400	2.14358000
H	5.49693200	-0.37537500	0.63715200
H	3.85747500	-0.20796100	1.32981500
C	5.34336700	-3.16922400	0.25260800
H	5.59408800	-3.54245700	1.25412400
H	5.06002100	-4.02191400	-0.37648300
H	6.25333800	-2.72771400	-0.17512400
C	-2.01184600	-4.00539500	1.93139400
H	-2.74379000	-4.32848300	1.18102800
H	-1.57979300	-4.89892200	2.39375600
H	-2.55743100	-3.43004100	2.68380900
C	-0.91048500	-3.18455900	1.28269400
C	0.23383800	-3.89593900	0.87714300
H	0.26677600	-4.94320400	1.16670100
C	1.23520100	-3.48045000	-0.01635300

C	2.16089400	-4.55406800	-0.55407800
H	1.60121800	-5.47897200	-0.73013300
H	2.64628300	-4.24290900	-1.48309100
H	2.94223900	-4.77073800	0.18609600
C	-0.72087900	2.12880000	-0.53593300
C	1.96586000	2.23585600	3.27314300
C	2.09208400	3.75992500	3.49279400
H	2.98750300	4.18262400	3.02627000
H	1.21413900	4.29110900	3.10343400
H	2.15879600	3.95391700	4.57427100
C	0.74152100	1.74792600	4.07509600
H	0.60188000	0.66844700	3.96236400
H	0.92222700	1.96196800	5.13976200
H	-0.17345900	2.26406400	3.76858000
C	3.12604700	2.70043400	0.41132200
C	3.31911000	1.86789200	-0.86969100
H	2.38137200	1.70191300	-1.40021100
H	4.00166400	2.39650000	-1.55226000
H	3.75721500	0.89250200	-0.64147200
C	4.49269600	2.74900600	1.12792000
H	4.49454500	3.41037200	2.00011800
H	4.84632500	1.75958700	1.43031500
H	5.22122600	3.15402100	0.40836600
Cl	1.55588600	-1.40927500	2.66059200
N	-1.09465800	-1.86565900	1.02982200
N	1.35143500	-2.19746300	-0.41719500
O	-0.17684600	0.35295200	-0.54703800
P	-0.28505400	2.70916700	1.14327400
P	1.69840000	1.81397800	1.40733400
Ti	0.54225500	-0.67344400	0.64961100
C	2.71512700	4.14336400	0.06246300
H	2.57859600	4.75688200	0.95963600
H	3.51048400	4.59736900	-0.54930900
H	1.78686000	4.17103300	-0.51113500
C	3.20301900	1.50062600	3.83996900
H	3.13153800	0.42251200	3.66473200
H	4.14523500	1.86869900	3.42930800
H	3.22843600	1.66821600	4.92747000
C	-0.01052700	2.66369700	-1.75780000
C	-0.06316200	4.05869900	-1.97039400
C	0.58532800	1.85918300	-2.74046000
C	0.48614900	4.62919500	-3.12423500
H	-0.53854000	4.68696900	-1.21874100
C	1.15317800	2.43240400	-3.88759600
H	0.62332800	0.78826800	-2.57582600
C	1.10549000	3.81762000	-4.08753800
H	0.43708900	5.70767800	-3.26487300
H	1.64114400	1.79097800	-4.62006200
H	1.54545500	4.26068100	-4.97924100
C	-2.20827900	2.04349500	-0.76741500
C	-2.74972300	2.14403900	-2.07066200
C	-3.10008100	1.86577900	0.31109300
C	-4.12471400	2.06762100	-2.28987200
H	-2.08758300	2.28276500	-2.92051400
C	-4.47648100	1.82938800	0.11202600
H	-2.69210900	1.76546200	1.31304400
C	-5.00206500	1.91046000	-1.19611900
H	-4.52537700	2.12811400	-3.29889500
H	-5.14920200	1.71217700	0.95535100
C	-6.41392900	1.80075700	-1.40711100
N	-7.57177000	1.69171800	-1.57389600

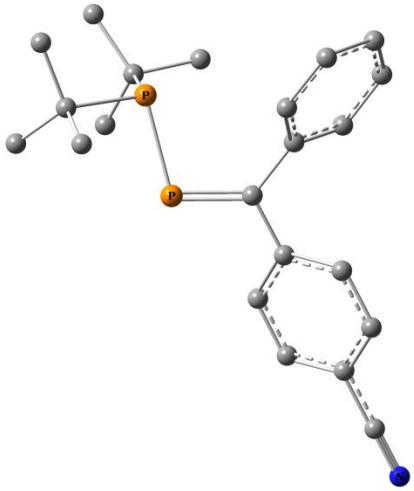


Figure S182. Optimized structure of ***E*-3c**.

Below are presented xyz coordinates for optimized geometry of ***E*-3c**:

C	0.42445000	3.60122200	-1.26892400
C	0.20748100	2.21933400	-1.27260400
C	-0.55176000	1.61007100	-0.25243900
C	-1.09855200	2.42430600	0.76378600
C	-0.86052400	3.80301400	0.77954300
C	-0.09855800	4.39628800	-0.23822200
H	1.00385300	4.05681800	-2.06977300
H	-1.27410200	4.41314200	1.58051700
C	-0.79737000	0.14534700	-0.23623700
P	0.37840500	-1.11366000	-0.36083200
P	2.33654500	-0.05123700	-0.18024600
C	2.64704300	-0.30997200	1.70892200
C	1.84359100	0.83560800	2.36777600
C	2.18395200	-1.64719200	2.31956500
C	4.14825300	-0.09993700	1.99106700
H	2.13971400	1.81621400	1.97540600
H	0.76680700	0.71282900	2.19712600
H	2.01772400	0.82488600	3.45447600
H	2.70362900	-2.50759000	1.88748500
H	2.38496800	-1.63709000	3.40212800
H	1.10479400	-1.79671400	2.18193900
H	4.30254800	-0.01329500	3.07738800
H	4.74898100	-0.94669700	1.63801100
H	4.52523600	0.81772700	1.52056400
C	3.39697800	-1.28244300	-1.20748000
C	4.81065300	-0.67243200	-1.35367400
C	3.49831700	-2.72396600	-0.67768200
C	2.74288000	-1.29558400	-2.61013800
H	4.75977000	0.35396200	-1.73901900
H	5.35524600	-0.65435100	-0.40368400
H	5.39532100	-1.27741700	-2.06327600
H	2.50779100	-3.16958100	-0.52070100
H	4.03790100	-3.34655200	-1.40819700
H	4.05467500	-2.76780900	0.26622700
H	3.38536000	-1.85437900	-3.30689500
H	1.75771400	-1.78172700	-2.59685900
H	2.61938000	-0.27712600	-3.00339300
H	0.60985600	1.60175600	-2.07145800
H	-1.69493500	1.96444400	1.55023100
C	-2.21707300	-0.27116500	-0.13100200
C	-2.59435000	-1.47163000	0.51843700
C	-3.23711700	0.52563900	-0.70732500
C	-3.92615900	-1.87749700	0.56879400
H	-1.82693300	-2.07236400	1.00198200
C	-4.57222900	0.12960500	-0.66384600

H	-2.96758700	1.45257300	-1.20770000
C	-4.92916800	-1.07878400	-0.02448900
H	-4.20352600	-2.79734700	1.07735000
H	-5.34440200	0.74362000	-1.12044400
H	0.07879100	5.47013200	-0.23271700
C	-6.30163500	-1.48346400	0.03598000
N	-7.42677900	-1.81611700	0.08437100

E.3.6. Reaction of **1** with 4,4'-dicyanobenzophenone leading to **3d**

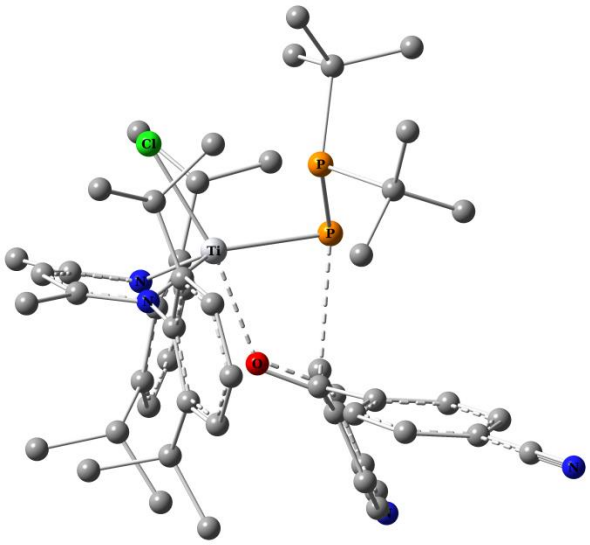


Figure S183. Optimized structure of **3d$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of **3d$_{TS1}$**:

C	2.73143998	-1.66339801	0.40012997
C	3.34842836	-2.08529310	-0.80406942
C	4.73364929	-1.87130850	-0.93956428
H	5.23619196	-2.21944878	-1.84075348
C	5.48012250	-1.24051420	0.06045770
H	6.55214759	-1.09639352	-0.06494882
C	4.83871802	-0.77791233	1.21379395
H	5.41729995	-0.26398552	1.97996284
C	3.46194058	-0.97534437	1.40621197
C	2.58916356	-2.79378475	-1.92184983
H	1.51359441	-2.68694683	-1.72291333
C	2.88195646	-2.14966862	-3.29269565
H	2.33872976	-2.68612053	-4.07977060
H	2.55884335	-1.10134918	-3.31224882
H	3.95079557	-2.19410641	-3.54046173
C	2.91744747	-4.30242513	-1.96952826
H	2.33735542	-4.78581677	-2.76621136
H	3.98516519	-4.46338426	-2.17413843
H	2.67383812	-4.79818001	-1.02437802
C	2.80115051	-0.51044577	2.70189893
H	1.71668721	-0.58707866	2.56175220
C	3.13581215	0.95900199	3.02677002
H	2.60440543	1.26959483	3.93566089
H	4.20947242	1.09941396	3.20965513
H	2.84066962	1.62171062	2.20812336
C	3.20534038	-1.41207624	3.89111250
H	2.91395785	-2.45473242	3.72609916
H	4.29262026	-1.38308572	4.04648364
H	2.71857548	-1.06494967	4.81212894
C	-2.33178272	-0.34246527	2.16337857
C	-2.05013938	0.80642948	2.95354043
C	-3.11482871	1.67416750	3.25810575

H	-2.92357671	2.56549882	3.85174674
C	-4.41688332	1.41351052	2.81431311
H	-5.22216763	2.10856121	3.04669141
C	-4.68412148	0.23777352	2.10964991
H	-5.70705673	0.00987602	1.81243607
C	-3.66228845	-0.67626313	1.79478058
C	-0.64608675	1.06613976	3.50765980
H	0.06445039	0.83254033	2.70338782
C	-0.41308702	2.52292474	3.95911489
H	0.64846524	2.66099452	4.19806045
H	-0.68089971	3.25586701	3.18931522
H	-0.98574859	2.75644831	4.86741371
C	-0.32767836	0.13542362	4.70354087
H	0.62814250	0.42965763	5.15660792
H	-1.10794448	0.21248540	5.47244394
H	-0.23860469	-0.91027412	4.39771356
C	-4.03958329	-2.02918889	1.18776060
H	-3.13566284	-2.64538886	1.12879488
C	-4.59422743	-1.93004121	-0.24463997
H	-4.92020160	-2.92041686	-0.58755794
H	-5.45508723	-1.24819644	-0.29366056
H	-3.81377379	-1.57832185	-0.92862850
C	-5.07530610	-2.74913368	2.08677693
H	-5.20620730	-3.78463209	1.74600350
H	-4.77084149	-2.76383947	3.13987599
H	-6.05384775	-2.25353091	2.03099037
C	2.27472878	-4.09912124	1.72505428
H	2.21145754	-4.57418469	2.70912051
H	2.09752282	-4.87317434	0.96510774
H	3.28392951	-3.70717691	1.57614228
C	1.20219868	-3.03747225	1.56796210
C	0.05343366	-3.19100705	2.34833049
H	0.03557723	-4.06993531	2.98852720
C	-1.03140793	-2.30343378	2.52792661
C	-1.96279920	-2.67883045	3.66967204
H	-1.38292179	-3.05764190	4.51830547
H	-2.57937355	-1.84060858	4.00149206
H	-2.62683372	-3.48677463	3.33476050
C	0.92653779	1.85520137	-0.02670749
C	-1.95587541	-1.83511294	-3.86897254
C	-2.03067744	-1.02403513	-5.17994394
H	-2.93685783	-0.41680377	-5.26346877
H	-1.15761283	-0.36599556	-5.27724281
H	-2.02364407	-1.72586153	-6.02816098
C	-0.67820708	-2.69371269	-3.94811372
H	-0.52403003	-3.28682199	-3.04306409
H	-0.77239695	-3.37695529	-4.80628476
H	0.19933010	-2.05771345	-4.10584899
C	-3.02018440	0.81560241	-2.53588994
C	-3.21665651	1.30716110	-1.09206200
H	-2.25357391	1.37671314	-0.57459521
H	-3.67594726	2.30633252	-1.09043788
H	-3.85647469	0.63142092	-0.51935675
C	-4.40694781	0.44463896	-3.10175360
H	-4.37838702	0.15697754	-4.15739257
H	-4.87717184	-0.36381573	-2.53168067
H	-5.05613894	1.32980888	-3.01958556
Cl	-1.06227766	-3.36509275	-0.58581801
N	1.36124746	-2.00645090	0.69553322
N	-1.24814624	-1.21236200	1.76860559
O	0.64551870	0.76958355	0.56645455
P	0.15524370	0.05507565	-2.13232076
P	-1.82280192	-0.68541973	-2.33362504
Ti	-0.31226631	-1.17785627	-0.16123628
C	-2.37912761	1.93636852	-3.37853265
H	-2.20376867	1.62463265	-4.41382687
H	-3.04883647	2.81040821	-3.38891363
H	-1.41811869	2.23891516	-2.94484199

C	-3.18262244	-2.75696642	-3.69829327
H	-3.08807476	-3.35225948	-2.78268378
H	-4.12237961	-2.19522869	-3.65505062
H	-3.24226388	-3.44485916	-4.55564361
C	-0.06209445	2.93625292	-0.24109810
C	0.13110502	3.91957194	-1.24139961
C	-1.17965812	3.03561183	0.60798250
C	-0.77057211	4.96970743	-1.38333656
H	0.96870521	3.82932869	-1.92859918
C	-2.07229738	4.09894887	0.49758121
H	-1.34651247	2.26186344	1.34827276
C	-1.87410437	5.07583566	-0.50116627
H	-0.63719989	5.71043445	-2.16745724
H	-2.92759472	4.16618995	1.16524596
C	2.34776500	2.18885834	-0.34619185
C	2.88032144	3.42888583	0.07279603
C	3.17035653	1.27684066	-1.02931662
C	4.21929030	3.74086098	-0.16274634
H	2.24922766	4.13512037	0.60821003
C	4.49579082	1.59883536	-1.31296797
H	2.75523540	0.33156857	-1.36176434
C	5.03283084	2.82592800	-0.86659072
H	4.63856573	4.68199412	0.18354410
H	5.12004420	0.90264558	-1.86411785
C	6.40767766	3.13906180	-1.12511692
N	7.53610307	3.38803736	-1.33248114
C	-2.79776321	6.16173603	-0.63513984
N	-3.55857710	7.04967412	-0.74501313

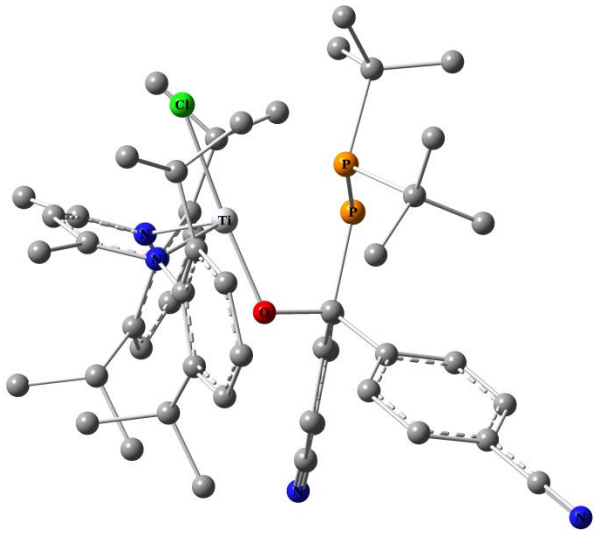


Figure S184. Optimized structure of **3dI**.

Below are presented xyz coordinates for optimized geometry of **3dI**:

C	-2.89295675	-1.43938407	0.16264202
C	-3.34902948	-1.43866206	1.50661922
C	-4.65954224	-0.99448621	1.75057754
H	-5.04464619	-1.00326256	2.76765841
C	-5.47558451	-0.52627810	0.71505408
H	-6.48337070	-0.17459436	0.92941071
C	-4.98704961	-0.48951075	-0.59321892
H	-5.62208701	-0.10800930	-1.39146746
C	-3.69756145	-0.95514605	-0.90125058
C	-2.47519344	-1.94812596	2.64930732
H	-1.43508745	-1.67396602	2.40900756
C	-2.80817647	-1.29197415	4.00134864
H	-2.07330610	-1.60769233	4.75061780

H	-2.78262629	-0.19692072	3.94016996
H	-3.79832895	-1.59530753	4.36758321
C	-2.51970403	-3.48467077	2.78295019
H	-1.93047023	-3.79877108	3.65409441
H	-3.55280527	-3.83476113	2.91428934
H	-2.08582527	-3.96849702	1.90444604
C	-3.24382514	-1.00240076	-2.35987185
H	-2.19740072	-1.32872617	-2.38037526
C	-3.31732471	0.37726212	-3.04145651
H	-3.06282692	0.28228737	-4.10491820
H	-4.32604408	0.80552821	-2.97584844
H	-2.62006961	1.07658131	-2.57568336
C	-4.08788069	-2.01673116	-3.16729378
H	-4.08815110	-3.00962413	-2.70655882
H	-5.13110398	-1.68036088	-3.23809633
H	-3.69034770	-2.10834277	-4.18689240
C	2.04326789	-1.10975135	-2.15260143
C	1.75225994	-0.06847090	-3.07451505
C	2.83431456	0.63950447	-3.62567191
H	2.64063759	1.45294642	-4.32153789
C	4.15819751	0.30500401	-3.31450391
H	4.98020236	0.87204785	-3.74821782
C	4.41902648	-0.77858677	-2.47332333
H	5.45012884	-1.06336782	-2.26712203
C	3.37534951	-1.51203264	-1.88029109
C	0.31927968	0.19422949	-3.54183368
H	-0.32794155	0.11647989	-2.66043090
C	0.11152878	1.58373309	-4.17487768
H	-0.95617436	1.73443078	-4.37495439
H	0.44974922	2.39710906	-3.52324077
H	0.63767523	1.67271518	-5.13549717
C	-0.11459355	-0.88196431	-4.56741361
H	-1.11040466	-0.64397970	-4.96337658
H	0.58873300	-0.91878966	-5.41028728
H	-0.16643728	-1.87755893	-4.11693258
C	3.71327128	-2.73746256	-1.03068702
H	2.77766599	-3.24018098	-0.76077680
C	4.40185501	-2.36182638	0.29346878
H	4.63450820	-3.26658394	0.86970972
H	5.33933095	-1.81769538	0.11104149
H	3.73444496	-1.73648879	0.89634527
C	4.60602277	-3.72872169	-1.81435111
H	4.70942267	-4.66463545	-1.24951191
H	4.19580762	-3.96217028	-2.80390876
H	5.61328323	-3.31666113	-1.96164340
C	-2.81703823	-4.17514668	-0.62933888
H	-3.07442955	-4.60505143	-1.60319534
H	-2.54006700	-5.00703621	0.03268546
H	-3.69391585	-3.67761427	-0.21006432
C	-1.62167609	-3.24589449	-0.75039892
C	-0.54605942	-3.71280417	-1.51366194
H	-0.66468505	-4.71155740	-1.92841505
C	0.58193844	-2.99871287	-1.97774277
C	1.35868139	-3.69151745	-3.08545850
H	0.66494160	-4.16148920	-3.79114703
H	2.01285348	-3.00458323	-3.62697265
H	1.97665152	-4.48687834	-2.64829494
C	-0.35733092	1.58246980	0.47984219
C	2.15922782	-0.79203984	3.79761647
C	2.48254068	0.32316119	4.81601415
H	3.46473865	0.77873891	4.66872425
H	1.71933225	1.11104263	4.78278559
H	2.47219641	-0.11789097	5.82404676
C	0.82474113	-1.41570713	4.26517546
H	0.47430389	-2.20487106	3.59727866
H	0.99867498	-1.85487553	5.25941807
H	0.04287221	-0.65478786	4.36836017
C	3.49350497	1.17857216	1.75715698

C	3.68798586	1.24734875	0.22663503
H	2.74301781	1.24917596	-0.31878851
H	4.23929519	2.16066595	-0.03861495
H	4.25973332	0.38463553	-0.12418757
C	4.83932297	0.68898078	2.34199169
H	4.86616911	0.68486911	3.43544160
H	5.11101676	-0.30649591	1.97700498
H	5.61462352	1.38960060	1.99635829
Cl	0.79682452	-3.14608887	1.35325975
N	-1.61177001	-2.02341955	-0.16226583
N	0.94755022	-1.79284881	-1.50492192
O	-0.15223001	0.55110490	-0.49319449
P	0.01139838	0.73818378	2.18152345
P	2.04967284	-0.09051130	1.98823221
Ti	0.14369517	-1.12448898	0.33581374
C	3.16572188	2.56419610	2.34106115
H	3.04676851	2.53389001	3.42854718
H	3.99249357	3.25174598	2.10583414
H	2.25186021	2.97575389	1.91084331
C	3.23398769	-1.90187274	3.80916981
H	2.95665000	-2.70939691	3.12250056
H	4.22680609	-1.53215056	3.53640523
H	3.29881201	-2.31937335	4.82524672
C	0.44188858	2.83397746	0.15980440
C	0.29980449	3.97798712	0.97305065
C	1.24220071	2.90593681	-0.98697646
C	0.97035173	5.15850027	0.66355822
H	-0.33638612	3.93086395	1.85565428
C	1.92808974	4.08064188	-1.30792126
H	1.33175450	2.02553589	-1.61566745
C	1.80029927	5.21592877	-0.48214521
H	0.86520855	6.03710421	1.29508090
H	2.55989276	4.12405733	-2.19216280
C	-1.83828195	2.01626314	0.42537918
C	-2.27456617	2.69350190	-0.73131956
C	-2.74319252	1.82789877	1.47854757
C	-3.58402534	3.15357876	-0.84551301
H	-1.57039550	2.86965222	-1.54176183
C	-4.05847736	2.29071136	1.38535719
H	-2.41886392	1.32051040	2.38356629
C	-4.49065974	2.94917450	0.21807530
H	-3.91474208	3.66575303	-1.74570315
H	-4.75440726	2.13296732	2.20453802
C	-5.85276279	3.37653099	0.10035558
N	-6.97630299	3.70333410	-0.00078622
C	2.50718057	6.42059523	-0.80072399
N	3.09124311	7.40556610	-1.06187281

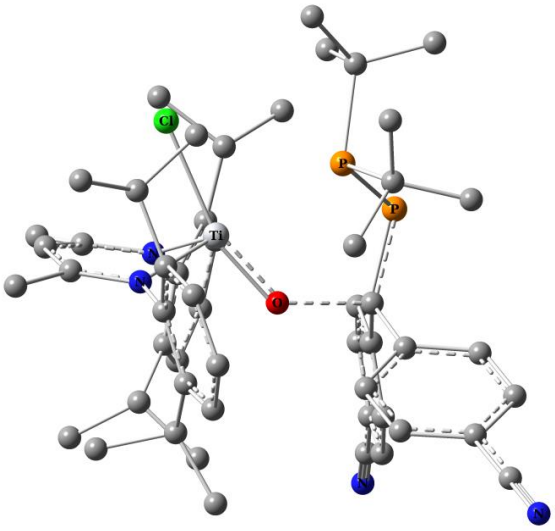


Figure S185. Optimized structure of **3d**$_{TS2}$.

Below are presented xyz coordinates for optimized geometry of **3d**$_{TS2}$:

C	-3.07767330	-0.99077479	-0.24535521
C	-3.62788530	-1.33013572	1.01631124
C	-4.92334143	-0.86904982	1.30813470
H	-5.38415180	-1.13855256	2.25548506
C	-5.62852036	-0.05722995	0.41185371
H	-6.62958320	0.29101494	0.66086758
C	-5.02597874	0.34154406	-0.78299489
H	-5.55718593	1.01478292	-1.45431936
C	-3.74881127	-0.12408693	-1.14036709
C	-2.85180030	-2.17979866	2.01911607
H	-1.79416823	-1.87880783	1.93340204
C	-3.28489491	-1.92090398	3.47412004
H	-2.63099559	-2.47595188	4.15520584
H	-3.22630677	-0.85710045	3.73675067
H	-4.31112961	-2.26760715	3.65554616
C	-2.93040838	-3.69226972	1.71783379
H	-2.40042479	-4.25213196	2.49901135
H	-3.97716120	-4.02712805	1.70215211
H	-2.45515811	-3.93998292	0.76464162
C	-3.12858997	0.32308098	-2.46024494
H	-2.17326181	-0.20136527	-2.58159208
C	-2.83452491	1.83685115	-2.41190363
H	-2.42959458	2.17728656	-3.37367113
H	-3.74969696	2.40850063	-2.20971635
H	-2.11155481	2.06301767	-1.62270459
C	-4.01905771	-0.00820408	-3.67767000
H	-4.23219327	-1.08154064	-3.74976012
H	-4.97811611	0.52358020	-3.62544882
H	-3.51625898	0.29871820	-4.60404586
C	1.89858357	-0.92451582	-2.42817260
C	1.84519414	0.36304228	-3.03095150
C	3.06303547	0.99639849	-3.32596528
H	3.05622889	1.98377223	-3.78112676
C	4.29072770	0.37582225	-3.05980535
H	5.22119286	0.89272967	-3.28806866
C	4.31758094	-0.91190246	-2.52366173
H	5.27394797	-1.40042309	-2.34340442
C	3.12932737	-1.59393160	-2.20143845
C	0.50801315	1.00029309	-3.40982132
H	-0.15928459	0.89547798	-2.54186031
C	0.61416258	2.49399635	-3.77214196
H	-0.39033125	2.90112993	-3.93432422
H	1.08778020	3.08880314	-2.98438198

H	1.18055791	2.63864885	-4.70240129
C	-0.13872397	0.25870746	-4.60588361
H	-1.05796383	0.77579202	-4.90978933
H	0.54605387	0.24690509	-5.46426600
H	-0.40602215	-0.77215680	-4.35772416
C	3.21236965	-3.02412948	-1.67041751
H	2.19718132	-3.42827133	-1.59449414
C	3.80692509	-3.07975755	-0.25049962
H	3.86278394	-4.12013253	0.09387134
H	4.81800746	-2.65006504	-0.22852443
H	3.16954212	-2.53212224	0.45262760
C	4.03356128	-3.92503655	-2.62199286
H	3.96081012	-4.97134935	-2.29795324
H	3.68087556	-3.85554357	-3.65820548
H	5.09578591	-3.64691391	-2.61262796
C	-3.47271937	-3.26173734	-1.72153850
H	-3.99842685	-3.31090895	-0.76441593
H	-4.08643305	-2.64997900	-2.39401816
H	-3.39404838	-4.26617387	-2.15000616
C	-2.08580440	-2.66129442	-1.57213957
C	-1.10120403	-3.14700573	-2.45209458
H	-1.39902736	-3.98277119	-3.08010395
C	0.14090971	-2.56675783	-2.76109309
C	0.85532281	-3.09165563	-3.99053222
H	0.12964395	-3.31489953	-4.77991780
H	1.59138795	-2.37663998	-4.36786121
H	1.37797482	-4.02461093	-3.74216303
C	-0.15384411	1.72068586	1.37081421
C	1.58037467	-1.92981212	3.69494135
C	2.03872673	-1.24706260	5.00294204
H	3.09157530	-0.94862616	4.97945706
H	1.43113565	-0.35971699	5.22217396
H	1.91524605	-1.96004142	5.83229456
C	0.12700890	-2.40497554	3.89951090
H	-0.25457335	-2.90404289	3.00339767
H	0.11739749	-3.13054934	4.72721532
H	-0.53591004	-1.57427573	4.16039354
C	3.41975882	0.08016345	2.16826568
C	3.67311659	0.47574171	0.70145122
H	2.85008070	1.05206238	0.27929726
H	4.58314610	1.09095061	0.63664730
H	3.81750190	-0.40921419	0.07650000
C	4.56288416	-0.87270513	2.57912202
H	4.54130943	-1.13225212	3.64210100
H	4.57764354	-1.79231242	1.98774914
H	5.50963679	-0.34346590	2.39010323
Cl	0.39742808	-3.46050239	0.51377651
N	-1.86755749	-1.64424329	-0.70215882
N	0.66329541	-1.56021491	-2.02998469
O	-0.09628843	0.51399339	-0.04322837
P	0.05669221	0.67854616	2.85707083
P	1.63056724	-0.70312523	2.20427757
Ti	0.05846940	-1.21118698	-0.12922015
C	3.47545829	1.31876410	3.08255554
H	3.31393987	1.05672419	4.13373636
H	4.47038966	1.78132280	2.99005203
H	2.72585413	2.06138678	2.80302957
C	2.43493078	-3.18700234	3.40897000
H	2.13516088	-3.65880533	2.46783485
H	3.50628298	-2.97911626	3.38059386
H	2.25980712	-3.90775300	4.22195616
C	0.91779306	2.70010054	0.95572850
C	1.27188102	3.70050184	1.88949353
C	1.50375640	2.73696937	-0.31916689
C	2.20356859	4.68747636	1.57053665
H	0.80912659	3.68722700	2.87447099
C	2.45240026	3.70875393	-0.64723794
H	1.22719631	1.97359267	-1.03695609

C	2.81281454	4.69237464	0.29538875
H	2.47225420	5.44724634	2.30019387
H	2.92459201	3.70351133	-1.62664078
C	-1.52389346	2.33670941	1.25994980
C	-1.72895800	3.53830811	0.54168599
C	-2.64064616	1.72615086	1.86842814
C	-2.99701859	4.10851423	0.43369103
H	-0.88968796	4.03179476	0.05982134
C	-3.90423063	2.30389958	1.80157981
H	-2.49670155	0.79079365	2.40202669
C	-4.09809901	3.49342600	1.06556469
H	-3.14266611	5.02282206	-0.13631886
H	-4.74941960	1.83078043	2.29068613
C	-5.41221226	4.04737885	0.93726077
N	-6.49639131	4.48443652	0.82136109
C	3.79191398	5.68387534	-0.03844505
N	4.59667548	6.49267893	-0.31661433

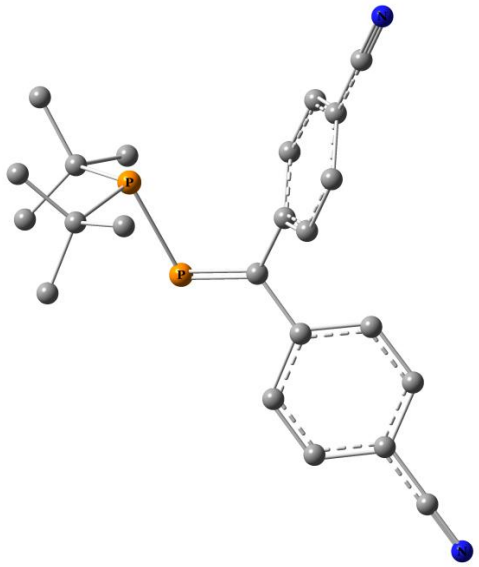


Figure S186. Optimized structure of **3d**.

Below are presented xyz coordinates for optimized geometry of **3d**:

C	0.83046700	-0.21403700	-0.22837900
C	2.26553700	-0.57308900	-0.13155800
C	2.69049700	-1.77126200	0.49205600
H	1.94849900	-2.41332600	0.96193700
C	4.03755400	-2.12343500	0.53466700
H	4.35197300	-3.04205200	1.02332300
C	5.00731600	-1.27179800	-0.04012500
C	4.60237000	-0.06538100	-0.65339300
H	5.34886700	0.58923200	-1.09583100
C	3.25209200	0.27666600	-0.69012300
H	2.94747400	1.20191600	-1.17348100
C	6.39502700	-1.62233700	0.01277700
C	0.52439200	1.23928700	-0.21928200
C	1.01922400	2.05397200	0.82320700
H	1.62564600	1.60557300	1.60764100
C	0.72176200	3.41554300	0.87326300
H	1.09007900	4.03251600	1.68886600
C	-0.05954400	3.99905900	-0.14809300
C	-0.53238600	3.20098600	-1.21274500
H	-1.12034200	3.65619300	-2.00543100
C	-0.24765600	1.83643200	-1.23800800
H	-0.61033100	1.22130500	-2.05671200
C	-0.36233800	5.39910600	-0.10962900
C	-3.31386500	-1.72867900	-1.23328800

C	-2.64558300	-1.69643700	-2.62893800
H	-2.54339200	-0.66751100	-3.00049700
H	-1.64919000	-2.15978600	-2.61632500
H	-3.26704300	-2.25576700	-3.34371700
C	-4.73900900	-1.14575100	-1.37897900
H	-4.70778700	-0.11043600	-1.74165000
H	-5.30375100	-1.74766000	-2.10674100
H	-5.29193200	-1.16069900	-0.43387700
C	-3.38751400	-3.18305700	-0.73493700
H	-3.95070400	-3.25978700	0.20266100
H	-3.90732600	-3.80059700	-1.48349300
H	-2.38906800	-3.61122900	-0.57941200
C	-2.60634400	-0.80034800	1.71089000
C	-4.11372100	-0.62729500	1.98591900
H	-4.50661400	0.29265900	1.53353500
H	-4.69424300	-1.47824600	1.61037200
H	-4.27666800	-0.56788800	3.07257400
C	-2.11852500	-2.14048700	2.29545900
H	-1.03513500	-2.26412900	2.16404600
H	-2.32786300	-2.15856000	3.37610400
H	-2.61614400	-3.00207300	1.84072700
C	-1.83178900	0.34764500	2.39941200
H	-2.14522900	1.33007700	2.02541200
H	-2.01470700	0.31152800	3.48381800
H	-0.75098600	0.24835300	2.23730200
N	7.53225600	-1.91111900	0.05514500
N	-0.61198300	6.54577800	-0.07711700
P	-0.30661100	-1.50667100	-0.35775000
P	-2.29164000	-0.49760000	-0.17014300

E.3.7. Reaction of **1** with 4,4'-dimethoxybenzophenone leading to **3e**

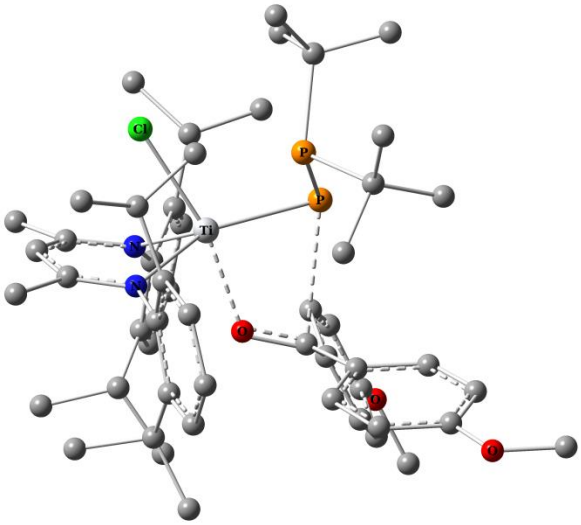


Figure S187. Optimized structure of **3e**$_{TS1}$.

Below are presented xyz coordinates for optimized geometry of **3e**$_{TS1}$:

C	2.74840109	-1.81396357	0.29003696
C	3.37723933	-2.17377388	-0.92864729
C	4.76660759	-1.97340603	-1.03363276
H	5.27548132	-2.27066132	-1.94968208
C	5.50744931	-1.41333540	0.01170660
H	6.58251882	-1.27438282	-0.09290415
C	4.85641621	-1.00869289	1.18126894
H	5.42978926	-0.54540025	1.98310538
C	3.47454028	-1.19547948	1.34231053
C	2.61851716	-2.78550362	-2.10306671
H	1.54345624	-2.69436091	-1.89659764

C	2.91658566	-2.02883472	-3.41464043
H	2.36746311	-2.49207090	-4.24345798
H	2.60284988	-0.98007933	-3.34634880
H	3.98572365	-2.06177494	-3.66469215
C	2.94433149	-4.28473863	-2.28264099
H	2.36487770	-4.69460769	-3.12016796
H	4.01233679	-4.42950341	-2.49885964
H	2.69771162	-4.86282342	-1.38612043
C	2.79571235	-0.78567938	2.64614311
H	1.71395916	-0.83496718	2.47827873
C	3.14790238	0.66117243	3.04632901
H	2.57284031	0.95105401	3.93574014
H	4.21344353	0.76393076	3.29430732
H	2.91583064	1.36092417	2.23774411
C	3.15853040	-1.75457866	3.79482699
H	2.83031214	-2.77714390	3.57891446
H	4.24520239	-1.77141090	3.95861513
H	2.67677640	-1.43422247	4.72807396
C	-2.37713544	-0.63181275	2.13561531
C	-2.11068391	0.41242354	3.06528855
C	-3.18142165	1.23669942	3.45721271
H	-2.99949155	2.04955249	4.15706031
C	-4.47574538	1.03734771	2.96262118
H	-5.28414153	1.70232880	3.26312778
C	-4.73025379	-0.04320203	2.11538492
H	-5.74810904	-0.23286738	1.77568810
C	-3.70262764	-0.91488841	1.71224378
C	-0.71430671	0.61182910	3.66490042
H	0.00356043	0.49294338	2.84273455
C	-0.50263227	2.00220124	4.30004983
H	0.55473863	2.11729826	4.56924743
H	-0.76657008	2.82422626	3.62465927
H	-1.08917277	2.11431462	5.22302711
C	-0.39021653	-0.45677990	4.73724326
H	0.55561659	-0.20341564	5.23460770
H	-1.17868116	-0.49231086	5.50128798
H	-0.27634272	-1.45333081	4.30289209
C	-4.06880143	-2.18959165	0.95034747
H	-3.15992755	-2.78865659	0.82550896
C	-4.61455613	-1.92278463	-0.46260663
H	-4.93243893	-2.86530912	-0.92703070
H	-5.47829114	-1.24292726	-0.43588941
H	-3.82884428	-1.48697512	-1.08923290
C	-5.10750624	-3.01395334	1.75072783
H	-5.23318532	-4.00236819	1.28881651
H	-4.80970758	-3.15298017	2.79667603
H	-6.08734422	-2.51703202	1.74784196
C	2.26282913	-4.31070261	1.43123586
H	2.12053783	-4.91516356	2.33253844
H	2.18188940	-4.97457688	0.55969398
H	3.27258457	-3.89109372	1.43497586
C	1.18437067	-3.24670166	1.32470758
C	0.01884027	-3.47018647	2.05885084
H	-0.00885127	-4.40397821	2.61566856
C	-1.07681185	-2.60654471	2.30046115
C	-2.02212712	-3.10594992	3.38443296
H	-1.45294445	-3.57252580	4.19592363
H	-2.64801945	-2.31136647	3.79679635
H	-2.67703647	-3.87511352	2.95335295
C	0.75959992	1.66777772	0.07852699
C	-1.94105148	-1.55854549	-3.96313221
C	-2.02377604	-0.65260540	-5.21032709
H	-2.93411314	-0.04745331	-5.25015207
H	-1.15473981	0.01615291	-5.25813137
H	-2.01216636	-1.29110964	-6.10746404
C	-0.66547359	-2.40873555	-4.12804883
H	-0.49605974	-3.06845589	-3.27406568
H	-0.77796792	-3.02364507	-5.03488242

H	0.21074930	-1.76329489	-4.25411913
C	-3.00247502	1.00275241	-2.48224399
C	-3.19737664	1.41071584	-1.01126711
H	-2.23515558	1.45450088	-0.49336976
H	-3.65943538	2.40688067	-0.94713353
H	-3.83109075	0.69838766	-0.47527537
C	-4.39315541	0.67401982	-3.06594257
H	-4.36990599	0.44371621	-4.13577304
H	-4.87073175	-0.15947332	-2.54033179
H	-5.03445297	1.55950875	-2.93338730
Cl	-1.03418934	-3.31475882	-0.87030428
N	1.36873927	-2.14998447	0.54230516
N	-1.29025649	-1.44955806	1.65504837
O	0.47741772	0.57082440	0.71541076
P	0.21082772	0.16398563	-2.20639249
P	-1.81327151	-0.51225399	-2.34506299
Ti	-0.24797292	-1.14892050	-0.26133781
C	-2.36158696	2.16734345	-3.26085726
H	-2.22579059	1.92823955	-4.32127146
H	-3.01105852	3.05430325	-3.18606081
H	-1.38137846	2.41793856	-2.83908961
C	-3.16603509	-2.49143282	-3.85664526
H	-3.06229479	-3.15732097	-2.99222775
H	-4.10539321	-1.93525895	-3.75990460
H	-3.23304087	-3.10859857	-4.76618237
C	-0.19270965	2.78898659	0.03798586
C	-0.06350068	3.82141680	-0.91719826
C	-1.22826917	2.88468881	0.99120522
C	-0.92910027	4.91556873	-0.91826366
H	0.69843590	3.73818791	-1.68903494
C	-2.07814595	3.98293528	1.02560992
H	-1.36573223	2.07046248	1.69188949
C	-1.93579804	5.00521036	0.06715034
H	-0.82523905	5.67704774	-1.68587210
H	-2.87340880	4.05259738	1.76390246
C	2.17126891	2.01284960	-0.24872038
C	2.68404285	3.24592104	0.21184814
C	3.04554348	1.14804316	-0.94014043
C	4.02396700	3.60009449	0.01628049
H	2.03771619	3.92253203	0.76633196
C	4.36340214	1.50702338	-1.18630366
H	2.66940986	0.20644381	-1.32193619
C	4.86748447	2.72737376	-0.69456546
H	4.38932291	4.54228853	0.41493488
H	5.02220066	0.84977630	-1.74561459
O	-2.83142229	6.03524605	0.15916389
O	6.18831737	2.97323811	-0.96064423
C	-2.74132036	7.09044532	-0.81214064
H	-2.90120529	6.70192240	-1.82725417
H	-3.53881216	7.78923778	-0.55106162
H	-1.76701172	7.59481419	-0.75256595
C	6.74511892	4.20631850	-0.48076903
H	6.68811519	4.26133533	0.61543736
H	7.78992181	4.19374041	-0.79855990
H	6.22919731	5.06870666	-0.92565803

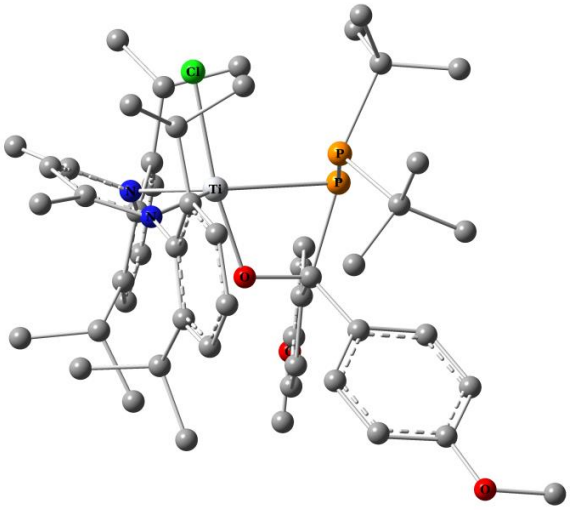


Figure S188. Optimized structure of **3e$_I$**.

Below are presented xyz coordinates for optimized geometry of **3e$_I$**:

C	-2.19084190	-2.33427757	-0.18158541
C	-2.87045996	-2.74803015	0.98911442
C	-4.27177442	-2.63541682	1.00398499
H	-4.82038817	-2.94669108	1.89187152
C	-4.97116043	-2.12498570	-0.09253242
H	-6.05469569	-2.02786631	-0.05062181
C	-4.27730317	-1.72705119	-1.24082807
H	-4.83047984	-1.34128336	-2.09561492
C	-2.88043500	-1.83339271	-1.31489709
C	-2.14358941	-3.35226453	2.18730415
H	-1.10080417	-3.53011896	1.89711399
C	-2.11808535	-2.37972705	3.38497349
H	-1.61420742	-2.84793400	4.24087716
H	-1.57054836	-1.46457983	3.13125181
H	-3.13905009	-2.10923341	3.69058464
C	-2.76796037	-4.69832571	2.61966901
H	-2.13641245	-5.17308867	3.38201896
H	-3.76484752	-4.55301676	3.05760348
H	-2.87419596	-5.39142280	1.77555416
C	-2.14087786	-1.56057391	-2.62224471
H	-1.07295757	-1.49463458	-2.38483368
C	-2.54790470	-0.24202781	-3.30147309
H	-2.02643069	-0.14460495	-4.26293839
H	-3.62634631	-0.19728996	-3.50436753
H	-2.27873057	0.60966043	-2.67259599
C	-2.34421008	-2.74891495	-3.59248712
H	-1.99383419	-3.69080517	-3.15447748
H	-3.40773130	-2.86618480	-3.84262140
H	-1.78756501	-2.57950941	-4.52397735
C	2.89088823	-0.70517518	-1.71966230
C	2.58713701	0.21035650	-2.76060781
C	3.60957640	1.06562400	-3.20744830
H	3.39866957	1.78419501	-3.99545275
C	4.89894458	1.00694215	-2.66730541
H	5.67124300	1.68762669	-3.02169593
C	5.19242894	0.05804297	-1.68584224
H	6.20375978	-0.00951926	-1.28707494
C	4.20852726	-0.82450297	-1.20481700
C	1.21949179	0.20891118	-3.44259167
H	0.45539026	0.15953122	-2.65369139
C	0.96385995	1.46237576	-4.30376074
H	-0.09236739	1.49583296	-4.59770232
H	1.20006755	2.39229389	-3.77374769
H	1.56373705	1.43843959	-5.22450835

C	1.05236209	-1.03761736	-4.34672888
H	0.11826265	-0.96089147	-4.91826895
H	1.88442109	-1.10711967	-5.06046465
H	1.01021774	-1.96351092	-3.76617654
C	4.61285585	-1.89096944	-0.18993101
H	3.76116632	-2.56122789	-0.02659478
C	4.93801870	-1.25784851	1.17140103
H	5.17978699	-2.03265290	1.91008992
H	5.79485647	-0.57355796	1.09303851
H	4.06712543	-0.70081415	1.52890062
C	5.82060447	-2.72280477	-0.68111165
H	5.98883776	-3.57002597	-0.00309083
H	5.67385878	-3.11241172	-1.69529292
H	6.73704474	-2.11737605	-0.68808869
C	-1.22922047	-4.91285435	-0.74918085
H	-0.84542064	-5.69157752	-1.41506365
H	-1.26739227	-5.31772754	0.27080477
H	-2.25417601	-4.65842495	-1.03763840
C	-0.32078896	-3.70136784	-0.76551235
C	0.95944965	-3.85809876	-1.29938245
H	1.20496877	-4.85627679	-1.65356550
C	1.90131920	-2.85826890	-1.63638076
C	2.98455077	-3.35273400	-2.58711649
H	2.52262656	-3.95807391	-3.37534480
H	3.54953451	-2.54045217	-3.04758279
H	3.68285155	-3.99950395	-2.04095815
C	-1.00003801	1.31503603	0.37371401
C	2.11272341	0.32528996	3.89104287
C	2.05514228	1.63261740	4.70908858
H	2.89161634	2.30679616	4.50296826
H	1.11310220	2.16550173	4.52966753
H	2.09977215	1.36932068	5.77691558
C	1.01541142	-0.59745366	4.47232685
H	0.90277765	-1.52322698	3.90489917
H	1.31925586	-0.85278330	5.49952505
H	0.04576084	-0.09023259	4.52654235
C	2.77250148	2.33331367	1.56042873
C	2.82989650	2.31824680	0.01966778
H	1.84669405	2.15776026	-0.42573858
H	3.20918745	3.28490642	-0.34330196
H	3.49928719	1.52877371	-0.33093248
C	4.23294910	2.31664806	2.06619659
H	4.31310359	2.38854966	3.15599026
H	4.77073805	1.42446081	1.72952801
H	4.74300301	3.19339146	1.63839132
Cl	1.42372898	-2.64079474	1.79794231
N	-0.76039148	-2.50782652	-0.30685656
N	1.84987104	-1.57741692	-1.22100776
O	-0.42487467	0.33815345	-0.53558041
P	-0.34312322	0.74000644	2.09156615
P	1.85827947	0.69039063	1.98469332
Ti	0.48160159	-1.03723538	0.34938776
C	2.06928892	3.60940369	2.05580933
H	2.11824728	3.71780403	3.14290771
H	2.56967286	4.48090676	1.60547527
H	1.02137024	3.63054751	1.75166325
C	3.46779621	-0.38396086	4.09517768
H	3.45560636	-1.37290617	3.62545318
H	4.31319430	0.18666530	3.69716857
H	3.63102174	-0.51788544	5.17548742
C	-0.67887017	2.73473345	-0.05828090
C	-1.07881305	3.81303179	0.74683760
C	-0.13306308	3.01081132	-1.31941863
C	-0.90425703	5.13793397	0.32889071
H	-1.53614364	3.61388602	1.71576042
C	0.05390563	4.32550851	-1.75482507
H	0.14291435	2.17650615	-1.95461505
C	-0.32426083	5.39646250	-0.92794065

H	-1.21579021	5.94781451	0.98287502
H	0.48718111	4.54088484	-2.72939324
C	-2.54361617	1.21083430	0.38245970
C	-3.27471592	1.83446653	-0.64431846
C	-3.27408835	0.60261306	1.41954462
C	-4.67439095	1.83747622	-0.66388297
H	-2.74588009	2.35683513	-1.43788649
C	-4.66891017	0.62295404	1.43703107
H	-2.75242406	0.11673227	2.23939711
C	-5.37791833	1.22875994	0.38886829
H	-5.19268282	2.32511375	-1.48525615
H	-5.22252348	0.15153000	2.24531767
O	-0.09435345	6.65719372	-1.43323407
O	-6.75136355	1.16717525	0.47681041
C	-0.46745539	7.77096666	-0.61289664
H	0.08402830	7.76296497	0.33857658
H	-0.19797036	8.65902593	-1.18952224
H	-1.54899449	7.77067796	-0.41363582
C	-7.50254540	1.78081902	-0.57743734
H	-7.28063225	1.30996794	-1.54644939
H	-8.55186477	1.61945322	-0.31905451
H	-7.29450335	2.85901558	-0.63510695

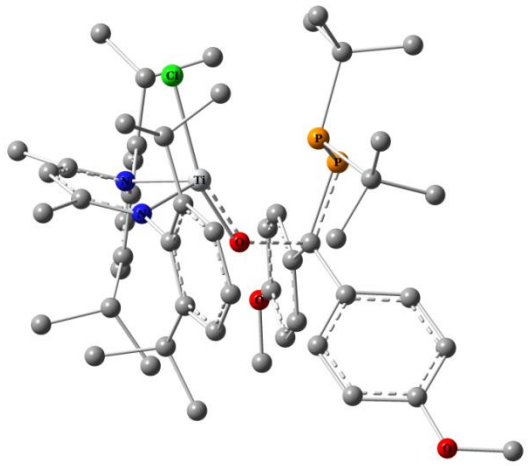


Figure S189. Optimized structure of **3e**$_{TS2}$.

Below are presented xyz coordinates for optimized geometry of **3e**$_{TS2}$:

C	-2.04453318	-2.36940073	-0.43136161
C	-2.71122661	-2.98880102	0.65306470
C	-4.11667898	-3.01855539	0.62563243
H	-4.65225343	-3.50047851	1.44250188
C	-4.83803586	-2.44304665	-0.42433250
H	-5.92639995	-2.47052572	-0.41948592
C	-4.15807011	-1.81057527	-1.46971093
H	-4.72344020	-1.36018077	-2.28442532
C	-2.75520154	-1.76983606	-1.50040007
C	-1.95941905	-3.63896833	1.81056267
H	-0.89925449	-3.70634087	1.53439518
C	-2.05086308	-2.75869104	3.07457733
H	-1.52892914	-3.24020248	3.91181461
H	-1.58847524	-1.77841300	2.90542903
H	-3.10079025	-2.60793071	3.36514845
C	-2.47556664	-5.05956208	2.13140754
H	-1.81401554	-5.53568060	2.86664220
H	-3.48464217	-5.02891151	2.56459024
H	-2.51729719	-5.69874605	1.23998954
C	-2.02504380	-1.22605415	-2.72476203
H	-0.96358210	-1.14600615	-2.46339653
C	-2.51052248	0.17260303	-3.14311396

H	-1.95633626	0.51015067	-4.02933905
H	-3.57875169	0.17568683	-3.39904415
H	-2.35206877	0.89154965	-2.33470576
C	-2.15667197	-2.22311602	-3.90019133
H	-1.72977420	-3.20045951	-3.64481669
H	-3.21268476	-2.37204215	-4.16451432
H	-1.63107788	-1.84464097	-4.78661366
C	2.95326440	-0.47378421	-1.79351830
C	2.62505130	0.58310752	-2.68297745
C	3.60542914	1.55587802	-2.93869009
H	3.37803037	2.38342208	-3.60528872
C	4.87466236	1.48235483	-2.35287294
H	5.61293784	2.25648015	-2.55547115
C	5.19428751	0.40795969	-1.52116620
H	6.18984357	0.34087876	-1.08512257
C	4.25295117	-0.59651011	-1.23287593
C	1.27092929	0.62494178	-3.38525361
H	0.50343323	0.44324642	-2.61821049
C	0.98360710	1.97708542	-4.06273874
H	-0.06537841	2.01572421	-4.38114119
H	1.16943817	2.81979879	-3.38908009
H	1.60666026	2.11192704	-4.95810409
C	1.15547014	-0.49288017	-4.44973075
H	0.22132006	-0.37187711	-5.01321789
H	1.99159660	-0.43304491	-5.15949741
H	1.14565239	-1.49017781	-4.00080624
C	4.67477976	-1.77558924	-0.36100129
H	3.86165562	-2.50953696	-0.34393353
C	4.88758628	-1.33249251	1.09549394
H	5.13064138	-2.19558195	1.72770628
H	5.70625970	-0.60284191	1.16947157
H	3.96933660	-0.88179348	1.48294215
C	5.95286040	-2.45761378	-0.90065534
H	6.14891490	-3.37800818	-0.33518263
H	5.86786101	-2.71328251	-1.96378674
H	6.82829252	-1.80444675	-0.78522180
C	-1.08580690	-4.79176667	-1.32460141
H	-0.63612539	-5.53632629	-1.98790295
H	-1.25191148	-5.25263141	-0.34342422
H	-2.06796596	-4.50491440	-1.71576977
C	-0.16817069	-3.59325616	-1.17467123
C	1.10437931	-3.70683431	-1.76127672
H	1.32777769	-4.66478823	-2.22334072
C	2.04107878	-2.69054348	-2.00481084
C	3.15248969	-3.03485515	-2.98080239
H	2.74451053	-3.62507049	-3.80872644
H	3.63892769	-2.14236636	-3.38207715
H	3.91292505	-3.64619182	-2.47864245
C	-1.19134077	1.47850775	0.84440127
C	1.83357597	-0.13141837	4.04018136
C	1.80588881	1.00413657	5.08753348
H	2.64366395	1.70060308	4.97550218
H	0.86741468	1.57038015	5.03796088
H	1.88325615	0.55322985	6.08881601
C	0.74889525	-1.15928140	4.43193409
H	0.65668901	-1.94700982	3.67955773
H	1.05232627	-1.62253242	5.38388678
H	-0.22931882	-0.68839592	4.57557082
C	2.57823518	2.13030530	1.99880361
C	2.62611224	2.31377020	0.46947123
H	1.62801707	2.37504980	0.03150915
H	3.16168021	3.24414728	0.22737325
H	3.16155782	1.48270265	-0.00134963
C	4.03097741	1.96841466	2.49083913
H	4.10425338	1.90023115	3.58135250
H	4.52558484	1.10113325	2.04557832
H	4.58957598	2.86452621	2.17791167
Cl	1.69683814	-2.77852443	1.44837875

N	-0.60592369	-2.46833749	-0.56714973
N	1.94633097	-1.45757910	-1.46269132
O	-0.22936011	0.35421893	-0.25509537
P	-0.66284688	0.95369913	2.53395542
P	1.46871950	0.55493186	2.26749611
Ti	0.73398500	-1.04305160	0.13749350
C	1.97074324	3.37686723	2.66643762
H	2.01664169	3.32182134	3.75875804
H	2.54094448	4.26219051	2.34335937
H	0.92864292	3.51771495	2.37441077
C	3.19132553	-0.86553867	4.09117338
H	3.17854445	-1.74360295	3.43847109
H	4.03598602	-0.22851226	3.81545602
H	3.35513409	-1.20764571	5.12473140
C	-0.79159602	2.82654760	0.29547155
C	-0.98090187	3.95082554	1.11716028
C	-0.42539950	3.04637527	-1.04592749
C	-0.77628710	5.25446446	0.64363080
H	-1.30505573	3.79762964	2.14545666
C	-0.21238589	4.33633429	-1.53397557
H	-0.30097957	2.18659402	-1.69522467
C	-0.37916001	5.44875846	-0.68960580
H	-0.92681202	6.09309056	1.31799233
H	0.07891451	4.50814700	-2.56745275
C	-2.65513932	1.22404666	0.61303913
C	-3.40980596	2.01817697	-0.27780241
C	-3.36061342	0.25847478	1.37067649
C	-4.79333307	1.86287486	-0.41963561
H	-2.91818636	2.78983180	-0.86350229
C	-4.73984173	0.13011990	1.28466942
H	-2.80731808	-0.37978967	2.05189428
C	-5.46640050	0.91971413	0.37469678
H	-5.32734461	2.49103924	-1.12752916
H	-5.27175462	-0.60054984	1.88746339
O	-0.13652452	6.67683016	-1.26139625
O	-6.81888178	0.68663210	0.32960758
C	-0.29479049	7.83076280	-0.42597879
H	0.39401824	7.79440812	0.43032735
H	-0.05125879	8.68497399	-1.06203914
H	-1.32992474	7.91777395	-0.06527411
C	-7.59163765	1.46419166	-0.59524303
H	-7.25928421	1.28975553	-1.62867772
H	-8.62147158	1.12081095	-0.47301819
H	-7.52475999	2.53577255	-0.35995335

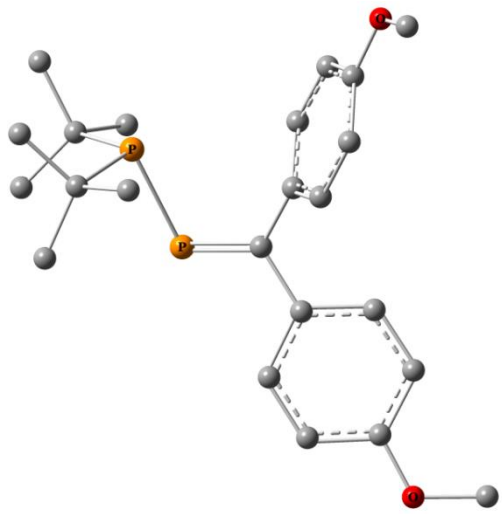


Figure S190. Optimized structure of **3e**.

Below are presented xyz coordinates for optimized geometry of **3e**:

C	0.67517900	-0.34372500	-0.26478100
C	2.07967800	-0.77813600	-0.10231900
C	2.42059100	-1.97881400	0.57283800
H	1.62771900	-2.56025500	1.03954900
C	3.73992000	-2.40708800	0.67220800
H	3.99835700	-3.31967300	1.20420400
C	4.77442100	-1.64035200	0.09987200
C	4.46911500	-0.43753200	-0.56384000
H	5.24932900	0.16938600	-1.01483100
C	3.13744200	-0.01834700	-0.65171900
H	2.90738200	0.90463500	-1.17958400
C	7.12801600	-1.38188800	-0.29460300
H	7.02604600	-1.28583000	-1.38458000
H	8.02836800	-1.95148000	-0.05472200
H	7.18277100	-0.38476500	0.16435600
C	0.44554000	1.11804400	-0.31665600
C	1.01636900	1.96167300	0.65726600
H	1.63121300	1.52444800	1.44216000
C	0.78653500	3.34329700	0.66040500
H	1.22449800	3.95568300	1.44373400
C	-0.00435100	3.91126900	-0.35445800
C	-0.55480300	3.09095200	-1.35840200
H	-1.14717400	3.55203500	-2.14506200
C	-0.34140600	1.71650000	-1.32829100
H	-0.76675400	1.08679100	-2.10530800
C	0.25643400	6.12251200	0.54097500
H	-0.11585300	5.85433600	1.53983200
H	-0.08990800	7.12283900	0.27214400
H	1.35530900	6.09327700	0.53342100
C	-3.57325000	-1.65618100	-1.20112500
C	-2.95354300	-1.64574200	-2.61918100
H	-3.62604100	-2.16966800	-3.31534400
H	-1.97915200	-2.15169300	-2.64090400
H	-2.81636900	-0.61913300	-2.98625700
C	-4.97549300	-1.01137400	-1.29791700
H	-5.59054000	-1.58198800	-2.01090900
H	-4.90891400	0.02462000	-1.65435600
H	-5.49811200	-1.00818400	-0.33540200
C	-3.69714500	-3.10983500	-0.71024700
H	-4.23797400	-3.16726700	0.24209300
H	-2.71337000	-3.57885100	-0.58222700
H	-4.26279900	-3.70122200	-1.44759800
C	-2.75200700	-0.77748200	1.72279600
C	-2.33405200	-2.14440900	2.29872700
H	-1.27113300	-2.34657100	2.11284900
H	-2.91506500	-2.97034300	1.87691100
H	-2.49210800	-2.14026100	3.38886400
C	-1.88857100	0.31939800	2.39001900
H	-2.03927200	0.29109600	3.48029500
H	-2.15396100	1.31948400	2.02498000
H	-0.82177600	0.15712600	2.19020600
C	-4.23686100	-0.51129800	2.04080500
H	-4.36797600	-0.43846500	3.13156400
H	-4.87819500	-1.32666400	1.68444900
H	-4.58507700	0.42895400	1.59280000
O	6.04188100	-2.14073300	0.25673800
O	-0.28720800	5.25120300	-0.46001400
P	-0.52429700	-1.58908800	-0.39861900
P	-2.45552900	-0.48523200	-0.16373800

E.3.8. Reaction of **1** with *tert*-butyl phenyl ketone leading to ***Z*-3f**

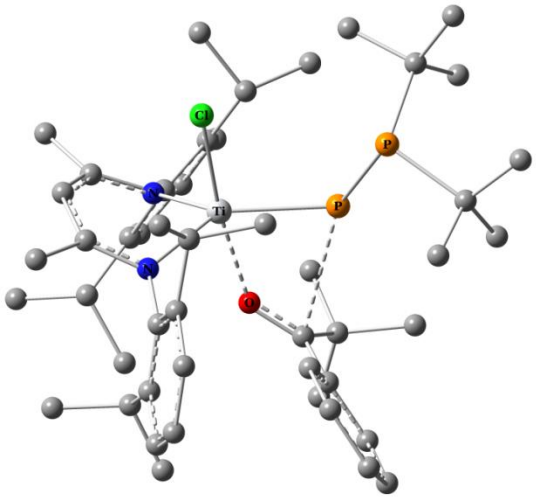


Figure S191. Optimized structure of ***Z*-3f$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3f $_{TS1}$**:

C	-2.63003400	-2.22985400	-0.16124500
C	-2.02580300	-3.50164100	0.00713400
C	-2.68534000	-4.44397000	0.81394900
H	-2.24011900	-5.42518600	0.95740700
C	-3.89853800	-4.14569500	1.44316800
H	-4.39082100	-4.89333800	2.06300200
C	-4.46641600	-2.87979000	1.28313000
H	-5.39865000	-2.63994800	1.79299100
C	-3.84962100	-1.90055400	0.48542800
C	-0.70164500	-3.84011400	-0.66223300
H	-0.06933400	-2.93322900	-0.60108400
C	0.06637200	-4.95857900	0.06420800
H	1.06755000	-5.05782100	-0.36680900
H	0.17592300	-4.73785300	1.13348300
H	-0.43608800	-5.93027200	-0.04231600
C	-0.87914600	-4.18417400	-2.15685600
H	0.08792100	-4.46077700	-2.59441400
H	-1.57234300	-5.02836000	-2.27914700
H	-1.25935100	-3.32626300	-2.72090200
C	-4.47483100	-0.50873200	0.41994500
H	-3.92876300	0.08974400	-0.31855900
C	-4.31572500	0.18631900	1.78884600
H	-4.80234200	1.16967600	1.78301400
H	-4.77233000	-0.41511800	2.58626500
H	-3.25472400	0.32209500	2.01903600
C	-5.96424200	-0.53605100	0.01292600
H	-6.12377800	-1.07239000	-0.93048400
H	-6.57880200	-1.02412100	0.78105700
H	-6.33625000	0.48967600	-0.10949300
C	-0.55750100	2.87109200	-1.19180700
C	-1.28056800	3.59637200	-0.21350500
C	-0.89587600	4.92222600	0.04734200
H	-1.43796100	5.49722800	0.79506300
C	0.17924000	5.51046600	-0.62569100
H	0.46421000	6.53850100	-0.40692300
C	0.89403700	4.76998900	-1.57252800
H	1.73569200	5.22764300	-2.08966400
C	0.54034600	3.44419600	-1.87943600
C	-2.46408300	2.97255800	0.51596500
H	-2.30330600	1.88782500	0.51306000
C	-2.55956100	3.44083300	1.98207300
H	-3.31007900	2.84612800	2.51692500
H	-1.59837300	3.32909300	2.49682600

H	-2.86750800	4.49307900	2.05260000
C	-3.78550400	3.26756100	-0.23212200
H	-4.64159000	2.86596900	0.32575700
H	-3.93028900	4.35068700	-0.34612300
H	-3.79232900	2.81255800	-1.22956700
C	1.34993700	2.64650500	-2.89325500
H	0.74014900	1.79846100	-3.22713600
C	2.59621700	2.05783500	-2.20354700
H	3.16239400	1.41727800	-2.88948800
H	3.25114100	2.86124900	-1.83819900
H	2.31620800	1.42881100	-1.34790500
C	1.74293900	3.46417400	-4.13970200
H	2.21076400	2.80272700	-4.87980800
H	0.86997000	3.94174800	-4.60509900
H	2.46879800	4.25215600	-3.89762000
C	-3.70597700	-1.94123500	-2.69405800
H	-3.75069000	-1.87131100	-3.78624900
H	-3.48075200	-2.96983700	-2.39924100
H	-4.69963800	-1.69550400	-2.29958800
C	-2.66581000	-0.96893100	-2.16454900
C	-2.48855300	0.21206500	-2.91039600
H	-3.04739100	0.24885900	-3.84187800
C	-1.81691000	1.40649700	-2.57295600
C	-2.06718000	2.60020500	-3.47703900
H	-2.88560200	2.39015300	-4.17161000
H	-2.30656000	3.49698400	-2.89512700
H	-1.16350100	2.82739600	-4.05754000
C	-0.17327200	0.35050400	2.30754600
C	3.91207700	-2.97939300	-0.82540500
C	3.80830500	-3.79902100	0.47194900
H	4.63985100	-3.57915000	1.15311500
H	2.86543400	-3.58732100	0.99326700
H	3.84365200	-4.87653600	0.24099000
C	2.81559100	-3.42484600	-1.81478900
H	2.91652600	-2.90732500	-2.77661000
H	2.89744800	-4.50928600	-1.99154400
H	1.81916400	-3.20023200	-1.42249400
C	4.76479200	-0.40052000	0.77147800
C	4.62293600	1.13246200	0.63441400
H	3.58138600	1.43921000	0.78856100
H	5.24088200	1.63223100	1.39758700
H	4.94538000	1.47670100	-0.35650800
C	6.23090200	-0.78394200	0.48895800
H	6.43147500	-1.83119500	0.74493500
H	6.50117800	-0.62175300	-0.56320300
H	6.89269100	-0.15997000	1.11043000
Cl	0.63654500	-0.89112100	-2.87848800
N	-2.01135100	-1.24183500	-1.00556000
N	-0.98574600	1.52579900	-1.51060400
O	-0.74622100	0.22911800	1.17860500
P	1.66710700	-0.94553600	0.42552400
P	3.60688500	-1.08493500	-0.62536400
Ti	-0.19182600	-0.29770300	-0.86974700
C	4.40320600	-0.78559700	2.21873200
H	4.42647100	-1.86905900	2.37938900
H	5.12529500	-0.32119600	2.91045600
H	3.40029700	-0.42270900	2.47210900
C	5.27291800	-3.23043100	-1.51435900
H	5.39580700	-2.58299400	-2.39293200
H	6.12269200	-3.06884600	-0.84454000
H	5.31315100	-4.27731800	-1.85509300
C	0.59978900	1.59009700	2.58486300
C	1.13569000	2.30240000	1.49003500
C	0.81193500	2.11097400	3.88303200
C	1.85911600	3.47951200	1.67343800
H	1.02639100	1.87926100	0.49904000
C	1.51698800	3.30530600	4.06813000
H	0.41210700	1.60654200	4.75449700

C	2.04750000	3.99135100	2.96598700
H	2.27328600	3.98976100	0.80810700
H	1.65470000	3.69511900	5.07491800
H	2.60837300	4.91271200	3.11400100
C	-0.40245700	-0.72868700	3.38324800
C	0.92244600	-1.11076100	4.09243200
H	1.61023900	-1.54913800	3.36103300
H	1.42320700	-0.26300200	4.56938700
H	0.69795000	-1.85887000	4.86476400
C	-0.96373500	-1.99899500	2.72263500
H	-1.03653000	-2.79178800	3.47824200
H	-1.95846300	-1.83002900	2.30386400
H	-0.29566600	-2.33260500	1.92022500
C	-1.46012700	-0.23925700	4.42103500
H	-1.70883000	-1.08833800	5.07082800
H	-1.10775900	0.57790000	5.05735800
H	-2.37970100	0.08533200	3.92263900

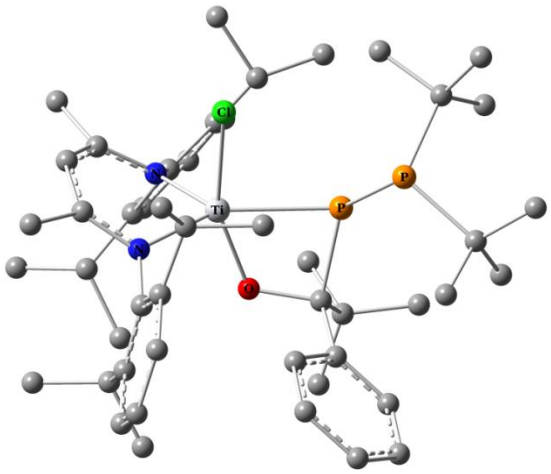


Figure S192. Optimized structure of ***Z*-3f$_I$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3f$_I$**

C	-2.83337100	-2.11862300	-0.01734700
C	-2.28363500	-3.41838100	-0.14920400
C	-2.84531600	-4.44745700	0.62551800
H	-2.44447800	-5.45454700	0.54349000
C	-3.89963100	-4.20255300	1.51211400
H	-4.31562800	-5.01743000	2.10240000
C	-4.39982300	-2.90629600	1.65294500
H	-5.19838500	-2.71132700	2.36750400
C	-3.88045400	-1.84207200	0.89613400
C	-1.10793600	-3.69195600	-1.08067500
H	-0.43761800	-2.81958900	-1.00761900
C	-0.28834200	-4.92364800	-0.65395400
H	0.61834200	-4.99271200	-1.26411400
H	0.01364700	-4.85901400	0.39902500
H	-0.85260800	-5.85556200	-0.79817000
C	-1.53074900	-3.81309000	-2.56040500
H	-0.65349300	-4.04940200	-3.17587600
H	-2.27452700	-4.61193500	-2.69007200
H	-1.94522400	-2.87206800	-2.93563100
C	-4.40039700	-0.42887000	1.14657500
H	-3.96293000	0.24247500	0.39791500
C	-3.92698700	0.04978100	2.53689700
H	-4.33069300	1.04586600	2.75793300
H	-4.26908100	-0.63767700	3.32187400
H	-2.83381300	0.09982700	2.57399900
C	-5.93711500	-0.32796900	1.03881500
H	-6.30451300	-0.69910200	0.07381200

H	-6.43263500	-0.90613900	1.83003700
H	-6.25100200	0.71880800	1.14439200
C	-0.80473400	3.04950500	-0.86799800
C	-1.33847900	3.69456400	0.27180900
C	-0.91776500	5.00698800	0.54647300
H	-1.32623000	5.52794800	1.41020500
C	0.02457500	5.64811900	-0.26374900
H	0.33556600	6.66707400	-0.03815400
C	0.59039100	4.96568400	-1.34620300
H	1.35004500	5.45557300	-1.95235400
C	0.19292100	3.65650800	-1.67052400
C	-2.34565100	2.99504700	1.17518900
H	-2.25967100	1.91936500	0.98113600
C	-2.02558100	3.22528200	2.66591900
H	-2.69174000	2.61927900	3.29164400
H	-0.98998600	2.94073900	2.88525600
H	-2.16638500	4.27524700	2.95613400
C	-3.78636800	3.43531600	0.83054700
H	-4.51086000	2.94011900	1.49031100
H	-3.89997700	4.52127700	0.95251500
H	-4.04193700	3.17929700	-0.20571200
C	0.86697800	2.90000800	-2.80785600
H	0.19923100	2.09018900	-3.12672100
C	2.15674000	2.23280900	-2.28217500
H	2.64257600	1.64955000	-3.07284900
H	2.85987800	2.98862000	-1.90578300
H	1.94385200	1.53308500	-1.46385900
C	1.16671900	3.77893800	-4.03789100
H	1.53100700	3.14843500	-4.85865700
H	0.27111100	4.31276900	-4.38400800
H	1.94438800	4.52538400	-3.82684900
C	-4.30501200	-1.53340000	-2.27536600
H	-4.57518700	-1.32268800	-3.31520600
H	-4.06701600	-2.59483800	-2.16292900
H	-5.18134500	-1.32754500	-1.64761300
C	-3.14311400	-0.65050600	-1.85622700
C	-3.02616300	0.58229200	-2.52718100
H	-3.71140100	0.71480400	-3.35975000
C	-2.27976000	1.72775300	-2.18344000
C	-2.62038000	3.00657400	-2.92572800
H	-3.49215000	2.85477600	-3.56825500
H	-2.82641300	3.82246200	-2.22288300
H	-1.77431500	3.32702600	-3.54659300
C	0.84154300	-0.26072700	1.79014900
C	3.69313700	-2.77458500	-1.43681900
C	3.79762300	-3.81401300	-0.30836200
H	4.71972600	-3.69222500	0.27318800
H	2.93842800	-3.73560800	0.37127600
H	3.80595400	-4.82923000	-0.73651800
C	2.46219900	-3.08565900	-2.31523300
H	2.39394300	-2.39557900	-3.16369100
H	2.54979800	-4.11277400	-2.70296900
H	1.52936600	-3.00798300	-1.74750300
C	4.80325200	-0.52607200	0.43843000
C	4.77691800	1.01694900	0.52842700
H	3.79814800	1.39075400	0.83864400
H	5.51849800	1.35429100	1.26827800
H	5.02297800	1.46760000	-0.44177700
C	6.19468500	-0.93962800	-0.08606500
H	6.35026800	-2.02278900	-0.02665100
H	6.36152800	-0.61224000	-1.12039300
H	6.95750500	-0.45972600	0.54638400
Cl	0.18228200	-0.58514600	-2.82423300
N	-2.34009900	-1.03557600	-0.83427200
N	-1.32506500	1.74450600	-1.22315900
O	-0.39587400	0.14889500	1.14530800
P	1.46893100	-1.22593300	0.19321000
P	3.45164300	-0.94097200	-0.86469500

Ti	-0.53679100	-0.08806500	-0.69804400
C	4.58978900	-1.13436300	1.83103900
H	4.60208600	-2.22898500	1.80949100
H	5.38710300	-0.79333200	2.51116800
H	3.63526600	-0.80994000	2.24687800
C	4.92474500	-2.85621800	-2.37114400
H	4.91571700	-2.04340600	-3.10973600
H	5.87512500	-2.82529900	-1.83185100
H	4.88534600	-3.81021100	-2.91921400
C	1.60917100	0.99750200	2.17717300
C	1.49072600	2.13067100	1.35385500
C	2.44793900	1.11200100	3.30499600
C	2.16085200	3.32591800	1.62878800
H	0.85833500	2.07951200	0.47713800
C	3.12864700	2.30463200	3.58823400
H	2.58572600	0.27581400	3.97995400
C	2.98786100	3.42224200	2.75637000
H	2.03229300	4.17034300	0.95680100
H	3.76971300	2.35217500	4.46728000
H	3.51630800	4.34764200	2.97872400
C	0.45859700	-1.24550700	2.96844800
C	1.64775900	-2.10666500	3.44994500
H	2.07828400	-2.65745800	2.60282900
H	2.45148400	-1.54518800	3.93521100
H	1.27530400	-2.83924400	4.17881400
C	-0.60083400	-2.24852100	2.46706100
H	-0.81772000	-2.97360300	3.26235500
H	-1.53254600	-1.74970600	2.19588600
H	-0.23385400	-2.79788800	1.59247200
C	-0.17659200	-0.44843900	4.13483800
H	-0.63804700	-1.14884600	4.84445900
H	0.54708900	0.16340900	4.68251600
H	-0.95987000	0.21691900	3.75252600

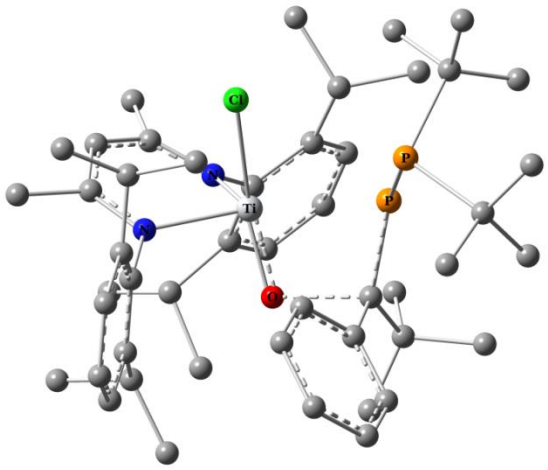


Figure S193. Optimized structure of ***Z*-3f$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3f$_{TS2}$**:

C	-2.75071500	-2.19933600	-0.12513000
C	-2.14363200	-3.46765200	-0.31369800
C	-2.66253500	-4.55402900	0.41130500
H	-2.22084500	-5.53941000	0.28459900
C	-3.72748900	-4.39216100	1.30502400
H	-4.11040500	-5.24997500	1.85571600
C	-4.28086100	-3.12515400	1.50635800
H	-5.08844300	-2.99755100	2.22625600
C	-3.80416600	-2.00650600	0.80183300
C	-0.95265700	-3.64817300	-1.25078300
H	-0.33846800	-2.73888500	-1.15620200

C	-0.05944800	-4.83605000	-0.84940300
H	0.85818000	-4.82410400	-1.44775000
H	0.22454500	-4.78448200	0.20901200
H	-0.55839300	-5.79826100	-1.03106000
C	-1.35234100	-3.75219100	-2.73860100
H	-0.46268800	-3.97372200	-3.34184100
H	-2.08689100	-4.55464200	-2.89515700
H	-1.76590300	-2.80746100	-3.10489600
C	-4.37936500	-0.62623700	1.10454000
H	-3.89669900	0.09978300	0.43908300
C	-4.03605600	-0.23211000	2.55749200
H	-4.45378100	0.75451700	2.79427100
H	-4.45387500	-0.95636700	3.26960300
H	-2.95123200	-0.19447500	2.69736000
C	-5.90455400	-0.55315900	0.87657500
H	-6.17839400	-0.82835700	-0.14927500
H	-6.44089300	-1.22570800	1.55955000
H	-6.26188000	0.46846000	1.06141500
C	-0.89721700	3.00281400	-0.66426800
C	-1.34099200	3.52163400	0.57868000
C	-0.84985900	4.76882700	0.99769600
H	-1.18383700	5.17998400	1.94777900
C	0.04989200	5.49565200	0.21273200
H	0.41526600	6.46413600	0.55128100
C	0.48094500	4.96710500	-1.00547600
H	1.18693700	5.52941200	-1.61547000
C	0.03097900	3.71655000	-1.46953700
C	-2.39074300	2.79402900	1.40823200
H	-2.30378500	1.72713100	1.17639300
C	-2.15926800	2.96180200	2.92184900
H	-2.83565400	2.30362800	3.48032400
H	-1.12764300	2.70189100	3.18648700
H	-2.35599400	3.98993900	3.25607500
C	-3.80689500	3.26619600	1.00552000
H	-4.56994000	2.74611700	1.60022300
H	-3.91922700	4.34638500	1.17288800
H	-4.00646700	3.06204900	-0.05384500
C	0.56527900	3.20494800	-2.80382100
H	0.01097900	2.30080600	-3.07685600
C	2.05360400	2.80239700	-2.68679600
H	2.42067900	2.44829400	-3.65886300
H	2.66519200	3.66404200	-2.38133000
H	2.20494500	1.98808000	-1.97079800
C	0.40110000	4.24848100	-3.93306200
H	0.65457900	3.79136900	-4.89847700
H	-0.62333000	4.63732100	-3.99136900
H	1.07254300	5.10563900	-3.78684700
C	-4.18266200	-1.62928400	-2.43162700
H	-4.48202500	-1.35641300	-3.44859900
H	-3.85313900	-2.67189800	-2.41339400
H	-5.06595200	-1.55935500	-1.78436900
C	-3.09832700	-0.68679200	-1.94145900
C	-3.04615700	0.58188500	-2.52323900
H	-3.72633500	0.73957800	-3.35646400
C	-2.37387600	1.74750200	-2.06842500
C	-2.81373600	3.04610800	-2.71958100
H	-3.86522900	2.97950000	-3.01760500
H	-2.67683600	3.90279800	-2.05372400
H	-2.21739500	3.22462400	-3.62377400
C	1.09056600	-0.47044100	1.80132000
C	3.68407500	-2.41562200	-1.69953500
C	3.89807700	-3.65915700	-0.81368400
H	4.81666700	-3.60152000	-0.21976200
H	3.05263500	-3.80077900	-0.12808300
H	3.97174200	-4.55217100	-1.45480000
C	2.43051200	-2.64686000	-2.56889400
H	2.29539100	-1.84515700	-3.30005300
H	2.55311400	-3.59992000	-3.10758500

H	1.51436900	-2.70574500	-1.97405700
C	4.86757000	-0.68023900	0.58680600
C	5.06163500	0.81460300	0.92978800
H	4.19893400	1.23333600	1.44697800
H	5.93518900	0.92056100	1.59215300
H	5.24121900	1.40853500	0.02450300
C	6.20757800	-1.14798300	-0.02255200
H	6.24196100	-2.22538300	-0.21003000
H	6.43884800	-0.61626500	-0.95397100
H	7.00504500	-0.91364000	0.69953200
Cl	0.32993500	-0.16884900	-2.66026000
N	-2.30344600	-1.07118400	-0.90527000
N	-1.44303300	1.73537900	-1.10832000
O	-0.66215100	0.24690100	1.20588700
P	1.55020400	-1.48952100	0.34212100
P	3.43045600	-0.74103100	-0.73236500
Ti	-0.59115800	-0.10412000	-0.48750200
C	4.59456900	-1.46172000	1.88047000
H	4.38394700	-2.52042300	1.69310000
H	5.47102300	-1.39400800	2.54526900
H	3.74070300	-1.03388600	2.41234500
C	4.85330700	-2.24419200	-2.70224300
H	4.75548600	-1.30315200	-3.25933600
H	5.83904200	-2.27029700	-2.23324700
H	4.81030800	-3.07142200	-3.42749000
C	1.73335400	0.85664500	2.02547300
C	1.79915200	1.76339500	0.94489300
C	2.29082800	1.26635500	3.25531200
C	2.35568600	3.03232100	1.08616500
H	1.41696600	1.46123400	-0.03074200
C	2.86423700	2.53740100	3.39946000
H	2.31011400	0.58973600	4.10175400
C	2.88482000	3.43175000	2.32243800
H	2.37622200	3.70244200	0.23311800
H	3.29623200	2.82086400	4.35755500
H	3.31928100	4.42297300	2.43773300
C	0.49404900	-1.27522100	2.99561700
C	1.64921200	-2.04024800	3.70611700
H	2.12498400	-2.74241700	3.01171200
H	2.42245300	-1.38221700	4.11623700
H	1.21351400	-2.60782100	4.53929300
C	-0.49094800	-2.35874800	2.50232500
H	-0.78802500	-2.98197500	3.35566900
H	-1.38742300	-1.90583400	2.07443700
H	-0.03070700	-3.00797300	1.74824700
C	-0.26393300	-0.39040000	4.01461500
H	-0.80455900	-1.04480700	4.71139600
H	0.39247400	0.25370100	4.60658700
H	-0.98574600	0.24136700	3.49139900

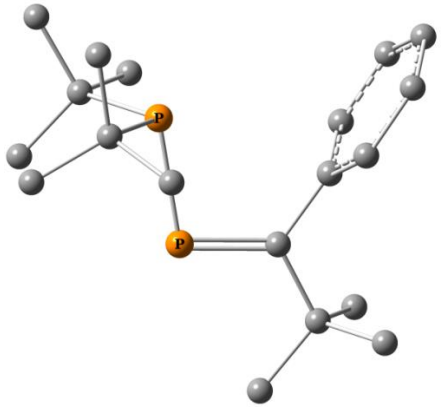


Figure S194. Optimized structure of ***Z*-3f**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3f**:

C	-1.99480300	2.83724900	-1.25165200
C	-1.82118100	1.44804100	-1.23926400
C	-1.76088000	0.74128800	-0.02182400
C	-1.88164600	1.46136900	1.18236300
C	-2.05209300	2.85146000	1.16939400
C	-2.11068800	3.54530500	-0.04714900
H	-2.02973900	3.36636600	-2.20267300
H	-2.13126200	3.39171400	2.11147900
C	-1.52869400	-0.73437100	-0.01681700
P	0.02755900	-1.44416900	-0.03456900
P	1.37896000	0.34857500	-0.01856900
C	2.34029700	-0.04344100	1.60707900
C	1.38402200	0.46527900	2.71249600
C	2.68017600	-1.51867000	1.90018300
C	3.63020200	0.80129200	1.63718600
H	1.12881200	1.52245200	2.56729600
H	0.45054800	-0.11397300	2.72205800
H	1.86376400	0.35037400	3.69651200
H	3.36091400	-1.94569000	1.15768000
H	3.16877900	-1.58638900	2.88509500
H	1.77712500	-2.14178200	1.93177600
H	4.06147000	0.77311000	2.64966300
H	4.38550600	0.40900700	0.94526600
H	3.43278700	1.85056300	1.38023600
C	2.46883000	-0.08672300	-1.54475400
C	3.39389800	1.12340000	-1.81153400
C	3.30075300	-1.37852300	-1.46400900
C	1.47712200	-0.19028100	-2.72767700
H	2.81400400	2.05192800	-1.88934800
H	4.14337700	1.25393000	-1.02354300
H	3.92931900	0.97060900	-2.76145300
H	2.67584200	-2.24780000	-1.22268200
H	3.78391100	-1.56655600	-2.43591900
H	4.09498300	-1.30008600	-0.71194900
H	2.03988200	-0.26222100	-3.67069500
H	0.83819200	-1.07969000	-2.64457300
H	0.82872100	0.69460100	-2.78079100
H	-1.71098300	0.90181000	-2.17402300
H	-1.81581600	0.92959900	2.12917100
H	-2.23857800	4.62613400	-0.05644900
C	-2.78365300	-1.62911200	-0.00990500
C	-3.62820200	-1.31682900	1.25363800
H	-3.05208000	-1.51883100	2.16594100
H	-3.95537700	-0.27103000	1.26924600
H	-4.52040500	-1.95748600	1.25978300
C	-3.63524200	-1.31138400	-1.26792700
H	-3.06554900	-1.51445000	-2.18397500
H	-4.53062200	-1.94760400	-1.26958800
H	-3.95607800	-0.26351400	-1.28010700
C	-2.44113600	-3.13230700	-0.01364700
H	-1.86380200	-3.41100300	-0.90438800
H	-1.85584500	-3.41310200	0.87127900
H	-3.37206400	-3.71532300	-0.01033800

E.3.9. Reaction of **1** with *tert*-butyl phenyl ketone leading to ***E*-3f**

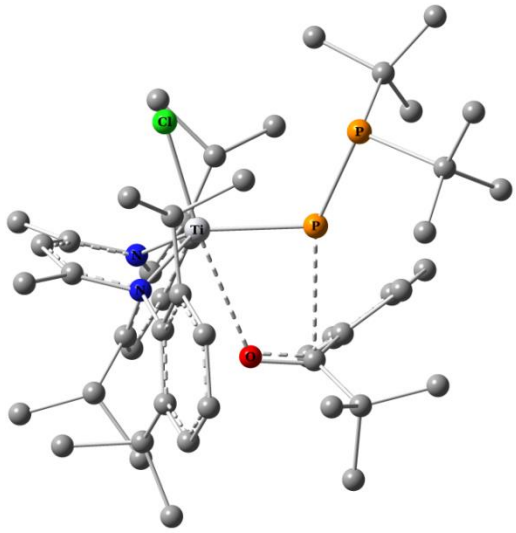


Figure S195. Optimized structure of ***E*-3f** $_{TS1}$.

Below are presented xyz coordinates for optimized geometry of ***E*-3f** $_{TS1}$:

C	-2.47064154	-1.56074602	-1.08415463
C	-1.89284093	-2.79980985	-1.45448211
C	-2.64020382	-3.96736449	-1.22879791
H	-2.22403446	-4.93000756	-1.51406155
C	-3.90614259	-3.91851450	-0.63565455
H	-4.47185619	-4.83613962	-0.48112377
C	-4.42641824	-2.69235916	-0.21455589
H	-5.39444744	-2.66074817	0.28461482
C	-3.72300994	-1.49291037	-0.42183983
C	-0.52025798	-2.86512145	-2.11353362
H	0.11388037	-2.10097722	-1.62045795
C	0.17434382	-4.22185543	-1.90153177
H	1.20176698	-4.16955413	-2.27588310
H	0.20388355	-4.49495843	-0.84040861
H	-0.33610088	-5.02119085	-2.45688894
C	-0.58503472	-2.53693634	-3.62155118
H	0.41529667	-2.61422374	-4.06539836
H	-1.24998577	-3.24560984	-4.13482318
H	-0.94425528	-1.51917548	-3.80228862
C	-4.31172616	-0.18664205	0.10851513
H	-3.64161172	0.63248676	-0.17601340
C	-4.38051012	-0.21929327	1.65205914
H	-4.84559991	0.70145361	2.02777504
H	-4.98824128	-1.06624528	1.99900236
H	-3.37689221	-0.30272213	2.07983877
C	-5.71875587	0.11070027	-0.45650220
H	-5.73125477	0.13925335	-1.55218802
H	-6.44219945	-0.65022884	-0.13429846
H	-6.07068906	1.08373451	-0.08930479
C	-0.32432967	3.37248832	0.14470188
C	-1.11709235	3.64464937	1.29130702
C	-0.66699636	4.63948507	2.17593949
H	-1.24755310	4.86176231	3.06784612
C	0.52226346	5.33950337	1.94404692
H	0.85900830	6.09256140	2.65478112
C	1.26571778	5.07776184	0.79191804
H	2.17905512	5.63889764	0.59976811
C	0.84888614	4.11131300	-0.14066552
C	-2.42662588	2.89928076	1.55780404
H	-2.25163562	1.84574664	1.29964220
C	-2.87223566	2.96854493	3.03322755
H	-3.71546649	2.28639786	3.19302234

H	-2.07053898	2.68429934	3.72416770
H	-3.21337070	3.97850521	3.30086935
C	-3.58442587	3.43389308	0.67956714
H	-4.52552866	2.94581103	0.96669896
H	-3.70596631	4.51655170	0.82053023
H	-3.42475971	3.23796188	-0.38511696
C	1.65087737	3.91809829	-1.42314254
H	1.08561725	3.25355154	-2.08701332
C	2.99712809	3.22907895	-1.13661778
H	3.54483846	3.04607820	-2.06927332
H	3.61990523	3.85149547	-0.47835637
H	2.83699178	2.25947365	-0.65483608
C	1.87476562	5.25412654	-2.16699657
H	2.33895074	5.06157434	-3.14308372
H	0.93442978	5.79694213	-2.32929517
H	2.54704285	5.91527811	-1.60400474
C	-3.41229511	-0.28936423	-3.37257628
H	-3.19432213	-1.35434776	-3.49063095
H	-4.43139693	-0.20531793	-2.97773025
H	-3.38742903	0.20413262	-4.35025004
C	-2.41638267	0.37945535	-2.44207778
C	-2.18661405	1.75529101	-2.64812997
H	-2.67454224	2.17694368	-3.52347409
C	-1.52723818	2.69209963	-1.82280133
C	-1.69270471	4.15469979	-2.18463965
H	-2.59056822	4.30194626	-2.79243537
H	-1.74724118	4.78338656	-1.29084350
H	-0.82206502	4.48423520	-2.76717258
C	-0.42574141	-0.91190725	2.22896645
C	3.92171181	-2.13301860	-1.29709337
C	3.29244414	-3.24423244	-0.43839610
H	3.78620603	-3.34783789	0.53288235
H	2.23039405	-3.03868728	-0.26184972
H	3.37573018	-4.20915776	-0.96422633
C	3.20881692	-2.10589279	-2.66677449
H	3.64197326	-1.34747523	-3.33035037
H	3.30335665	-3.09134780	-3.15014740
H	2.14465105	-1.87546857	-2.54940628
C	4.81277304	-0.15530356	0.95166977
C	4.28096268	1.06797581	1.73061554
H	3.27277678	0.88521684	2.12039585
H	4.95012354	1.27357573	2.58077723
H	4.24457996	1.96428929	1.10036470
C	6.24609948	0.18572034	0.47761454
H	6.72233233	-0.64492996	-0.05348473
H	6.23930768	1.05832998	-0.18828958
H	6.87037258	0.42593168	1.35273700
Cl	1.00103682	0.67698431	-3.07345660
N	-1.81399471	-0.33361700	-1.45276235
N	-0.75619348	2.33213584	-0.76611095
O	-1.13123682	-0.24598230	1.44407574
P	1.67633777	-0.36616472	0.25812480
P	3.71029817	-0.33336946	-0.62866609
Ti	0.01663622	0.46970478	-1.07175120
C	4.84032143	-1.36578705	1.90020392
H	5.34526546	-2.22957943	1.45200354
H	5.38409402	-1.10419291	2.82220853
H	3.82259705	-1.66533154	2.18067982
C	5.41632364	-2.43005917	-1.53804562
H	5.90184844	-1.62560914	-2.10656425
H	5.96527115	-2.57689864	-0.60032968
H	5.50636035	-3.35903838	-2.12266925
C	-0.41001809	-2.41200115	2.10938025
C	0.76378376	-3.19130157	2.12722668
C	-1.65697217	-3.05733449	2.01026084
C	0.68770360	-4.58585116	2.05069203
H	1.73112097	-2.70044204	2.14653730
C	-1.73262319	-4.45518561	1.97197119

H	-2.56229516	-2.45841544	1.96403177
C	-0.56169005	-5.22408221	1.98945741
H	1.60473769	-5.17256070	2.03361579
H	-2.70580805	-4.93696478	1.90724641
H	-0.61884464	-6.31047684	1.94235263
C	0.13447479	-0.24568496	3.50348707
C	-1.04101391	-0.37541496	4.52095922
H	-1.94076166	0.12554310	4.14361962
H	-1.27940482	-1.42814300	4.72146206
H	-0.74647130	0.09943437	5.46645838
C	0.42856622	1.23886562	3.23917126
H	0.68204271	1.74358484	4.18106669
H	1.26278137	1.34716055	2.53776458
H	-0.43559636	1.73101675	2.79428312
C	1.38224519	-0.91908420	4.10355834
H	1.67455180	-0.36791110	5.00780631
H	1.20014528	-1.96236792	4.38651274
H	2.21969554	-0.87900728	3.39783267

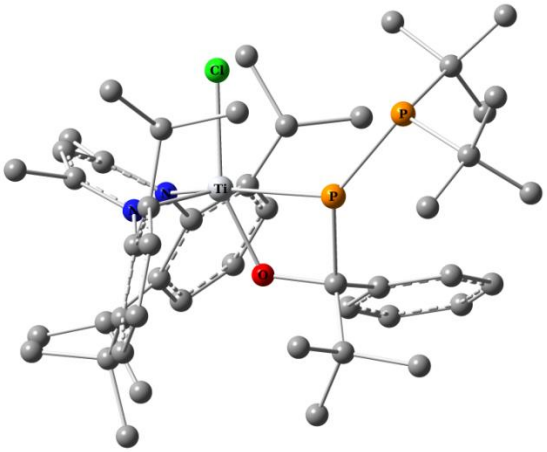


Figure S196. Optimized structure of ***E*-3f$_{I}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3f$_{I}$**:

C	-2.24298400	-2.29787700	-0.84143200
C	-1.30415300	-3.29182500	-1.21036400
C	-1.59130200	-4.62504100	-0.87667300
H	-0.89248500	-5.40782100	-1.15918200
C	-2.74191500	-4.96290000	-0.15575300
H	-2.94275700	-6.00357200	0.09406800
C	-3.60782600	-3.95612800	0.27762600
H	-4.47341500	-4.21427700	0.88637800
C	-3.37654900	-2.60888200	-0.05171000
C	-0.01809600	-2.92817200	-1.94281000
H	0.34971800	-1.97134100	-1.51457200
C	1.10138200	-3.96059400	-1.72410400
H	2.02927100	-3.59596500	-2.17458600
H	1.27736600	-4.14211800	-0.65755500
H	0.85776100	-4.91607400	-2.20888400
C	-0.26028600	-2.70835200	-3.45050100
H	0.67936000	-2.44326500	-3.95004400
H	-0.65229000	-3.63005600	-3.90265300
H	-0.96817900	-1.89327200	-3.62975800
C	-4.28236300	-1.52948500	0.53213300
H	-4.00658200	-0.56683900	0.08572300
C	-4.02357500	-1.43331800	2.05251200
H	-4.66227000	-0.66330300	2.50359000
H	-4.24544600	-2.38963900	2.54476100
H	-2.97573200	-1.18158100	2.24908000
C	-5.78113100	-1.77539000	0.25921600
H	-5.99159700	-1.87621200	-0.81281600

H	-6.13359800	-2.68853500	0.75702700
H	-6.37414900	-0.93568300	0.64487200
C	-1.43980800	3.09043300	0.09984200
C	-2.13406500	3.17992700	1.33421300
C	-1.91271300	4.31138900	2.13635200
H	-2.43023600	4.40155600	3.08832300
C	-1.01658500	5.31220900	1.74539700
H	-0.84711300	6.17411500	2.38889800
C	-0.33829700	5.19879200	0.53031300
H	0.35937200	5.97871100	0.22861900
C	-0.54198500	4.10020800	-0.32435800
C	-3.08928500	2.07534500	1.78325700
H	-2.65499100	1.12280000	1.44710700
C	-3.24929400	2.01577800	3.31510300
H	-3.79856900	1.10991500	3.59676300
H	-2.27777600	1.99647700	3.82147000
H	-3.82047600	2.87510700	3.69277100
C	-4.48130400	2.22623900	1.12494800
H	-5.16538200	1.45500300	1.50357800
H	-4.91129000	3.20918400	1.36057600
H	-4.43205900	2.12222000	0.03576500
C	0.19704800	4.05207600	-1.65714200
H	-0.16752400	3.18718300	-2.22327100
C	1.71079500	3.85000200	-1.43994600
H	2.22328800	3.74281600	-2.40414600
H	2.14379900	4.70957000	-0.90788000
H	1.89972900	2.94382000	-0.85668800
C	-0.04859900	5.32594800	-2.49831500
H	0.39629000	5.20400000	-3.49453000
H	-1.11733900	5.54470900	-2.62016700
H	0.41682200	6.20425200	-2.03093200
C	-3.75166100	-1.42035500	-3.01012600
H	-4.07284500	-0.94872700	-3.94435700
H	-3.20894900	-2.34556800	-3.23020500
H	-4.64741500	-1.69783200	-2.44100000
C	-2.88862700	-0.46009200	-2.21421400
C	-3.05491800	0.91453500	-2.46827100
H	-3.72721400	1.15709200	-3.28685200
C	-2.59479400	2.02185200	-1.72224200
C	-3.18306200	3.37208800	-2.07779700
H	-4.11330800	3.24992700	-2.64042000
H	-3.37226400	3.97243200	-1.18215800
H	-2.47083000	3.92801000	-2.70075600
C	0.81392100	-0.57630100	1.64477000
C	4.30023400	-1.04775500	-1.53125600
C	4.18045700	-2.30206300	-0.65687800
H	4.80941600	-2.24465700	0.23828100
H	3.14470300	-2.45193500	-0.34107000
H	4.49496000	-3.18780000	-1.23279400
C	3.38931200	-1.20727800	-2.76855500
H	3.49326200	-0.35847400	-3.45519500
H	3.65973000	-2.13007600	-3.30569300
H	2.33535800	-1.26488300	-2.47634400
C	4.93301500	1.20771400	0.58191100
C	4.21334500	2.30397000	1.39728000
H	3.40893300	1.89034000	2.01263100
H	4.94182800	2.79448900	2.06120800
H	3.77516900	3.06669500	0.74163600
C	6.10079400	1.89818900	-0.16767600
H	6.70927000	1.19448900	-0.74333900
H	5.72418100	2.66892400	-0.85194900
H	6.75915800	2.38372100	0.56925900
Cl	0.35569500	0.63920100	-2.86689700
N	-2.04336300	-0.93823800	-1.26958100
N	-1.68386500	1.92721000	-0.72769600
O	-0.45714400	-0.34996200	0.99616600
P	1.72281700	0.42250700	0.21129900
P	3.68552700	0.59299300	-0.74502800

Ti	-0.48372300	0.27868000	-0.76439700
C	5.48589100	0.13144500	1.53227500
H	6.08219200	-0.61746000	0.99792900
H	6.13741700	0.60023800	2.28685800
H	4.67792400	-0.38602400	2.06233800
C	5.75530800	-0.88276300	-2.01951200
H	5.88714000	0.03206600	-2.61182400
H	6.47114200	-0.87258400	-1.18877700
H	6.00806500	-1.73984300	-2.66257100
C	1.06680300	-2.06195700	1.77581700
C	2.36145900	-2.56062900	2.00688300
C	-0.00926500	-2.96944700	1.77337000
C	2.58147200	-3.92423000	2.23255200
H	3.20330500	-1.87417200	1.99304800
C	0.20672200	-4.33493700	2.00478700
H	-1.01376600	-2.59839900	1.59420900
C	1.50106700	-4.82013700	2.23638700
H	3.59565900	-4.28572100	2.39641200
H	-0.64204200	-5.01566900	1.99518200
H	1.66841900	-5.88174600	2.41132700
C	0.78843700	0.13802800	3.05229300
C	-0.36101900	-0.46995100	3.89007100
H	-1.32033700	-0.34371900	3.37651700
H	-0.20240600	-1.53893000	4.07668300
H	-0.41784100	0.04405500	4.85950500
C	0.52990000	1.64575500	2.88297000
H	0.36735600	2.10445900	3.86832300
H	1.37028200	2.15315300	2.39805200
H	-0.35677000	1.82138500	2.27022600
C	2.11340400	-0.05796100	3.81293900
H	2.09818300	0.55984700	4.72113100
H	2.26633100	-1.10108500	4.11304000
H	2.97093000	0.26050200	3.20782400

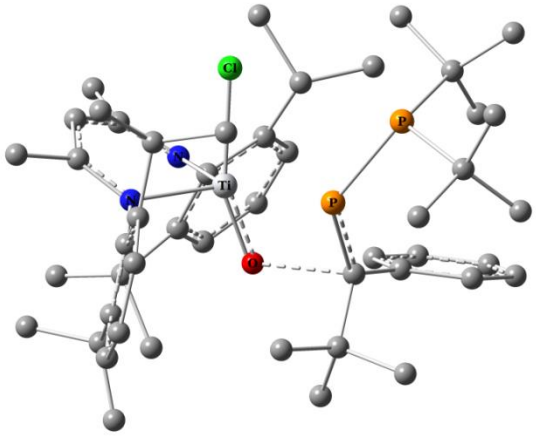


Figure S197. Optimized structure of ***E*-3f** $_{TS2}$.

Below are presented xyz coordinates for optimized geometry of ***E*-3f** $_{TS2}$:

C	1.79999200	2.70738000	-0.69893600
C	0.74532200	3.56707400	-1.10196300
C	0.77432900	4.89802600	-0.65050100
H	-0.01162200	5.58210000	-0.95976800
C	1.78442800	5.36007400	0.20116400
H	1.78572400	6.39707900	0.53371600
C	2.77025700	4.47686000	0.64522000
H	3.53101600	4.82391200	1.34345700
C	2.79457800	3.13953200	0.21224900
C	-0.39715400	3.06857700	-1.98355800
H	-0.68674400	2.07147700	-1.60319400
C	-1.64085400	3.97249600	-1.91226700

H	-2.46408200	3.50168100	-2.45843100
H	-1.96548100	4.13992500	-0.87862600
H	-1.44987300	4.94653800	-2.38410300
C	0.02352100	2.88462600	-3.45777100
H	-0.84426800	2.57672000	-4.05423800
H	0.40768400	3.83156900	-3.86294200
H	0.78155400	2.10465900	-3.56595900
C	3.83735800	2.19018300	0.79101500
H	3.70472300	1.20862000	0.32078900
C	3.58747400	2.02555000	2.30617900
H	4.33371300	1.35066800	2.74383800
H	3.66401900	2.99164100	2.82288300
H	2.58806800	1.61413500	2.48315200
C	5.28529800	2.66104100	0.53580400
H	5.49370400	2.78300500	-0.53407200
H	5.48296600	3.62259200	1.02850300
H	5.99549200	1.92636300	0.93763700
C	2.11286700	-2.72140600	0.01475800
C	2.76295800	-2.75868600	1.27693600
C	2.70275800	-3.94824600	2.02030700
H	3.19187100	-3.99864600	2.99004100
C	2.00184400	-5.06302700	1.54669300
H	1.95518000	-5.97220300	2.14433700
C	1.36010700	-5.00303700	0.30853200
H	0.81361200	-5.87128800	-0.05689800
C	1.40710400	-3.84491900	-0.48923500
C	3.49784300	-1.53249700	1.81133200
H	2.90495800	-0.65507500	1.51484700
C	3.61389900	-1.52999800	3.34758100
H	4.01728900	-0.56986800	3.68895600
H	2.63722100	-1.67636300	3.82376000
H	4.29516400	-2.31513800	3.70373700
C	4.90221800	-1.40007900	1.17738500
H	5.42469300	-0.52748600	1.59186800
H	5.50539300	-2.29316300	1.39032800
H	4.84524200	-1.27136100	0.09103000
C	0.72036900	-3.86442800	-1.85135800
H	0.91516600	-2.91009700	-2.35374300
C	-0.81022200	-3.99215300	-1.70357600
H	-1.29074500	-3.93074300	-2.68778800
H	-1.07878600	-4.95373500	-1.24208300
H	-1.20966200	-3.18407500	-1.08398000
C	1.25152900	-5.01463800	-2.73920800
H	0.83682100	-4.92325900	-3.75163100
H	2.34631600	-5.01534200	-2.81079700
H	0.94652700	-5.99197400	-2.34070800
C	3.49155600	2.28017100	-2.87054200
H	3.92218300	1.93927500	-3.81766700
H	2.79239000	3.10053800	-3.05874500
H	4.30336700	2.68138800	-2.25103900
C	2.80920500	1.12331800	-2.16461500
C	3.25554500	-0.17468700	-2.47878200
H	3.96458900	-0.24190600	-3.29971800
C	3.03965300	-1.37432700	-1.77071000
C	3.87552600	-2.56614600	-2.19201800
H	4.81237900	-2.23123000	-2.64817200
H	4.09569900	-3.22264300	-1.34454400
H	3.32492800	-3.15435900	-2.93704900
C	-1.38317500	0.08748800	1.75770400
C	-4.21855000	0.54766800	-1.61486600
C	-4.14936300	1.72496300	-0.63459800
H	-4.74034100	1.53834400	0.26730700
H	-3.11687800	1.92323300	-0.33100500
H	-4.54561200	2.63192600	-1.11840600
C	-3.38006100	0.86756200	-2.87193300
H	-3.44786000	0.06121100	-3.61209000
H	-3.75805500	1.79497100	-3.32994800
H	-2.32108300	0.99489900	-2.62895900

C	-4.71214900	-2.01627500	0.18103800
C	-3.93974200	-3.19087200	0.82755200
H	-3.17969500	-2.84410100	1.53584100
H	-4.65468700	-3.83189000	1.36601800
H	-3.43285700	-3.79995100	0.06841500
C	-5.79687400	-2.65353800	-0.72584100
H	-6.48663800	-1.91715600	-1.14624400
H	-5.34006600	-3.21357800	-1.55190100
H	-6.39012100	-3.35762900	-0.12258200
Cl	-0.15931600	-0.49931200	-2.74933200
N	1.87761300	1.36478700	-1.22116200
N	2.17001200	-1.49112200	-0.74527600
O	0.66380100	0.41483900	1.10048200
P	-1.64304400	-0.94337100	0.26373000
P	-3.46510100	-1.09930900	-0.96775000
Ti	0.65570500	-0.14109700	-0.53003500
C	-5.37038000	-1.17200300	1.28270100
H	-5.93584100	-0.32528100	0.87615100
H	-6.06596700	-1.79279700	1.86970300
H	-4.61015600	-0.78148000	1.96777900
C	-5.68045400	0.33924800	-2.06407400
H	-5.78251700	-0.50860900	-2.75288500
H	-6.36125400	0.19527000	-1.21693800
H	-6.00522000	1.24503100	-2.59876300
C	-1.90512000	1.47351200	1.94682100
C	-3.20087600	1.69737400	2.46032900
C	-1.09702500	2.59545100	1.66292000
C	-3.67404200	2.99731900	2.67534000
H	-3.85731600	0.85785300	2.66110200
C	-1.57599300	3.89223200	1.88210800
H	-0.09224100	2.43301300	1.28899900
C	-2.86494500	4.10438200	2.38920200
H	-4.68324700	3.13727300	3.05966300
H	-0.92556100	4.73342500	1.65087600
H	-3.23398700	5.11459300	2.55705800
C	-0.90778200	-0.62110300	3.04284100
C	-0.03497700	0.29464600	3.92918700
H	0.90041800	0.52850500	3.41416600
H	-0.55068100	1.23191000	4.16901400
H	0.19002700	-0.22729900	4.86895500
C	-0.17381200	-1.94387400	2.77036800
H	0.12469200	-2.38872100	3.72902000
H	-0.80346100	-2.66337600	2.23426100
H	0.72192300	-1.76741500	2.17428800
C	-2.20442300	-0.96986800	3.84534900
H	-1.89947100	-1.60109800	4.69000000
H	-2.69279600	-0.07582100	4.24535100
H	-2.91797500	-1.53659500	3.23613500

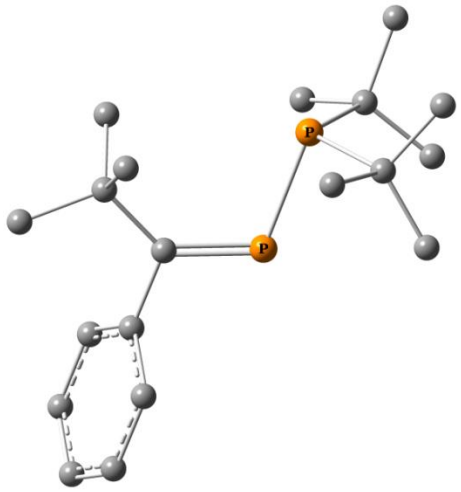


Figure S198. Optimized structure of ***E*-3f**.

Below are presented xyz coordinates for optimized geometry of ***E*-3f**:

C	4.31729300	1.85781000	-0.91533200
C	3.09460000	1.51357000	-0.32184500
C	2.65917600	0.17367600	-0.29521800
C	3.47098800	-0.81154400	-0.89714800
C	4.68633600	-0.46553100	-1.49798000
C	5.11787300	0.87016300	-1.50373900
H	4.63748900	2.89833300	-0.92315100
H	5.29289200	-1.23740800	-1.96885800
C	1.34733300	-0.19338600	0.34106400
P	0.04570300	0.33421800	-0.63896400
P	-1.89652700	-0.21842100	0.35719500
C	-2.67420300	1.54886800	0.43114500
C	-2.05691600	2.17022500	1.70646200
C	-2.39200200	2.50029100	-0.74986000
C	-4.19721400	1.41423300	0.63415600
H	-2.27325900	1.56467400	2.59585100
H	-0.96717700	2.26972100	1.61329000
H	-2.47629000	3.17578200	1.86231200
H	-2.80532700	2.13266700	-1.69338800
H	-2.85332900	3.47733500	-0.53674200
H	-1.31578100	2.66168800	-0.89047300
H	-4.61406800	2.39466300	0.91115000
H	-4.70118500	1.08900900	-0.28388000
H	-4.43793100	0.70338000	1.43581200
C	-2.68388100	-1.20806300	-1.09942900
C	-4.00749600	-1.81937400	-0.58444500
C	-2.93540000	-0.42751600	-2.40196600
C	-1.70899200	-2.37291800	-1.39113900
H	-3.84496000	-2.39140400	0.33796900
H	-4.76752400	-1.05671000	-0.38422000
H	-4.41181700	-2.50338900	-1.34656800
H	-2.02224200	0.06167700	-2.76370600
H	-3.27984100	-1.12352200	-3.18284200
H	-3.71405000	0.33357100	-2.27377300
H	-2.16272800	-3.04435500	-2.13561900
H	-0.75357100	-2.01283400	-1.79545700
H	-1.50037100	-2.95964600	-0.48753900
H	2.46603900	2.27930900	0.12873200
H	3.13197000	-1.84606600	-0.91093100
H	6.06449600	1.13716700	-1.96978300
C	1.40782000	-0.93615700	1.69760300
C	2.86210900	-1.13854400	2.18815700
H	3.43408300	-1.80290600	1.53063200
H	3.40182500	-0.18599700	2.25747300
H	2.83426800	-1.59298000	3.18745000

C	0.66680100	-0.09585400	2.76953100
H	0.76176700	-0.58868500	3.74728200
H	1.10080600	0.90946500	2.84469500
H	-0.39650900	-0.00805800	2.52751000
C	0.73137800	-2.32460700	1.57751900
H	1.20002700	-2.92147600	0.78447000
H	0.83630600	-2.86682100	2.52777300
H	-0.33527900	-2.21518100	1.35585300

E.3.10. Reaction of **1** with acetone leading to **3g**

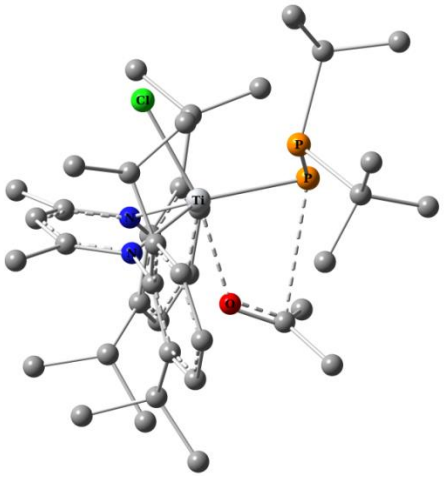


Figure S199. Optimized structure of **3g**$_{TS1}$.

Below are presented xyz coordinates for optimized geometry of **3g**$_{TS1}$:

C	3.17002400	0.38580500	-0.30319100
C	3.57770500	1.74453500	-0.25903200
C	4.75722400	2.05542200	0.44401300
H	5.09102800	3.09063300	0.48502100
C	5.51195900	1.06456200	1.07942900
H	6.42498600	1.32943800	1.61050900
C	5.08792700	-0.26865500	1.03202800
H	5.67663500	-1.03560700	1.53372100
C	3.91123200	-0.63319700	0.35760600
C	2.82135500	2.84771700	-0.99267600
H	1.81782200	2.47030100	-1.23038100
C	2.65370600	4.11986200	-0.13936500
H	2.01679700	4.83591200	-0.67371200
H	2.17519400	3.89175500	0.81994600
H	3.61835800	4.61071300	0.05124100
C	3.52186900	3.20310500	-2.32455900
H	2.94326800	3.96774400	-2.85917300
H	4.52952500	3.60037800	-2.13688900
H	3.61813200	2.32964300	-2.97714200
C	3.46358500	-2.09432400	0.33262600
H	2.41599700	-2.10942600	0.00916800
C	3.53989000	-2.76048100	1.72204000
H	3.15449200	-3.78612600	1.66366500
H	4.57287200	-2.81835000	2.08991400
H	2.94266300	-2.21783200	2.46283300
C	4.29527900	-2.92284100	-0.67381200
H	4.22243000	-2.51836400	-1.68803600
H	5.35572300	-2.92807400	-0.38547200
H	3.93909300	-3.96171200	-0.69412000
C	-1.70605800	-2.21815900	-0.38406200
C	-1.53437000	-3.13338000	0.68946600
C	-2.68101900	-3.70928900	1.26359900
H	-2.57099900	-4.39928200	2.09728100
C	-3.96184100	-3.42635600	0.77645400

H	-4.83722300	-3.87440700	1.24388600
C	-4.10426400	-2.59007100	-0.33255900
H	-5.09645900	-2.40282400	-0.74148200
C	-2.99079700	-1.98483100	-0.94316100
C	-0.14211500	-3.56223100	1.14615800
H	0.49347300	-2.67117600	1.12454200
C	-0.11322500	-4.14761100	2.57140300
H	0.92659000	-4.25084900	2.90683800
H	-0.64445200	-3.51312000	3.29135500
H	-0.56881000	-5.14712700	2.60657300
C	0.46198300	-4.59901800	0.16807100
H	1.42610000	-4.96130300	0.55031800
H	-0.20763300	-5.46261600	0.05579500
H	0.63815000	-4.16600500	-0.82100300
C	-3.21247500	-1.15716400	-2.20627500
H	-2.23839800	-0.82168300	-2.57979500
C	-4.03842800	0.10692700	-1.91693300
H	-4.17043600	0.69524000	-2.83390100
H	-5.03334100	-0.15010800	-1.52612500
H	-3.51569000	0.72788100	-1.18283700
C	-3.91369200	-1.99157600	-3.30507200
H	-3.93518700	-1.42533100	-4.24578100
H	-3.41038200	-2.94838400	-3.48635200
H	-4.95286000	-2.21150700	-3.02486100
C	3.35779700	-0.43695900	-3.04087200
H	3.58041800	-1.32536600	-3.64107200
H	3.16049000	0.39449200	-3.73238000
H	4.23291200	-0.17561400	-2.43903600
C	2.11821200	-0.64423100	-2.19175600
C	1.13613200	-1.49864700	-2.69356800
H	1.35070200	-1.93749300	-3.66580100
C	-0.03418100	-1.99935400	-2.06545600
C	-0.67306500	-3.15883500	-2.81748000
H	0.10292400	-3.85001900	-3.16588800
H	-1.39645400	-3.70707900	-2.21023600
H	-1.18812100	-2.76787100	-3.70483600
C	1.13608200	-0.18582900	2.65195000
C	0.30805900	-0.64214500	3.82562800
H	-0.23490200	0.23027100	4.21448400
H	-0.40472400	-1.41347100	3.53387100
H	0.96394500	-1.00453100	4.62957800
C	2.32155000	0.68678600	2.96598200
H	2.08847200	1.36533800	3.79316400
H	3.14127300	0.02328100	3.28747600
H	2.65831800	1.24340800	2.09064600
C	-2.48802100	3.64327600	-0.17777600
C	-2.94832400	4.58842200	0.95114200
H	-3.87006800	4.25621400	1.44044200
H	-2.16404200	4.69866400	1.71061800
H	-3.14443200	5.58127700	0.51706500
C	-1.26827600	4.30511800	-0.85384500
H	-0.83580300	3.66900800	-1.63070000
H	-1.60141600	5.24928500	-1.31275900
H	-0.48915500	4.53217600	-0.11703700
C	-3.11616500	1.39781900	1.96288900
C	-2.80386000	-0.10063200	2.14676400
H	-1.72324000	-0.26916000	2.21832000
H	-3.27493400	-0.47388900	3.06893400
H	-3.17984000	-0.68902700	1.30515200
C	-4.60666100	1.53507100	1.58960200
H	-4.92176500	2.57846300	1.47964000
H	-4.83765000	1.00128400	0.66085400
H	-5.21480600	1.08840800	2.39142000
Cl	-0.40875900	1.30745900	-2.40438300
N	1.97794100	-0.00069600	-1.00677500
N	-0.55321100	-1.52938000	-0.91913000
O	0.91328900	-0.63458000	1.50318500
P	0.01513700	2.18107500	1.30838400

P	-1.94336900	1.92315500	0.52255700
Ti	0.11134100	0.46130700	-0.28893700
C	-2.81558400	2.13922700	3.27966500
H	-3.08854000	3.19821000	3.23452200
H	-3.38847500	1.67372000	4.09732100
H	-1.74534800	2.07652700	3.51867500
C	-3.60166600	3.46413700	-1.22939600
H	-3.23234900	2.88645800	-2.08366300
H	-4.48626600	2.96017700	-0.82244800
H	-3.91602900	4.45475300	-1.59304000

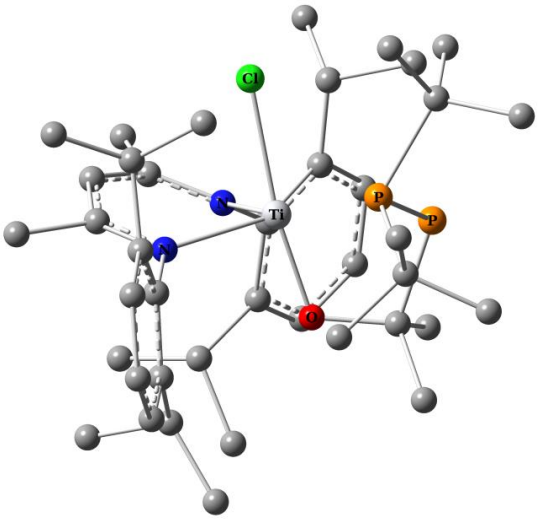


Figure S200. Optimized structure of **3g**ı.

Below are presented xyz coordinates for optimized geometry of **3g**ı:

C	-3.25901000	0.00889300	0.22188000
C	-3.87659900	1.26022200	0.46176900
C	-5.01624500	1.58650900	-0.29774800
H	-5.50073600	2.54875700	-0.13801200
C	-5.54009800	0.69770600	-1.24021500
H	-6.42391500	0.96961900	-1.81521000
C	-4.92972400	-0.54705300	-1.43915100
H	-5.34985200	-1.23825700	-2.16786000
C	-3.77877800	-0.91276300	-0.72492900
C	-3.38140400	2.23018600	1.52876500
H	-2.51765800	1.77374500	2.02718600
C	-2.91345500	3.56523400	0.91239300
H	-2.51976100	4.22317000	1.69818000
H	-2.12207800	3.39792500	0.17361300
H	-3.74755600	4.08344800	0.41829300
C	-4.47394200	2.49723600	2.59029000
H	-4.06209200	3.10741900	3.40492700
H	-5.32025200	3.04565100	2.15426100
H	-4.86660900	1.56684700	3.01856600
C	-3.13153900	-2.27849800	-0.93231300
H	-2.11552100	-2.21961400	-0.52505600
C	-3.01850900	-2.66203600	-2.41975600
H	-2.52985300	-3.63966000	-2.51659300
H	-4.00292900	-2.74073900	-2.90006500
H	-2.41957900	-1.92488600	-2.96485000
C	-3.89938400	-3.37103700	-0.15234100
H	-3.93000900	-3.15057200	0.92100200
H	-4.93427100	-3.45105800	-0.51299000
H	-3.41138000	-4.34600900	-0.28538000
C	1.87900400	-2.06313600	0.43454100
C	1.89314900	-2.84255100	-0.74865700
C	3.12512500	-3.34320900	-1.20347000
H	3.15382400	-3.94086700	-2.11205200
C	4.31273600	-3.08977100	-0.50945800

H	5.25886600	-3.47979000	-0.88131300
C	4.27554000	-2.33725900	0.66766200
H	5.19841300	-2.15000000	1.21499200
C	3.06766000	-1.82106800	1.17102400
C	0.59675800	-3.20026500	-1.46544200
H	-0.10407000	-2.37374900	-1.30668500
C	0.77255200	-3.36732100	-2.98635100
H	-0.21060400	-3.46390800	-3.46289900
H	1.28074000	-2.49984900	-3.42438500
H	1.34939100	-4.26815400	-3.23808800
C	-0.01055000	-4.48164000	-0.84738300
H	-0.92835500	-4.76666000	-1.37822100
H	0.69866800	-5.31810600	-0.91569500
H	-0.26513200	-4.33287900	0.20847200
C	3.09075600	-1.03879700	2.48082500
H	2.05752700	-0.83046000	2.78273500
C	3.77622200	0.32293600	2.27583600
H	3.74696300	0.91401100	3.20006700
H	4.82682900	0.19271500	1.97903600
H	3.25202200	0.87961800	1.49294200
C	3.79886700	-1.81581200	3.61432500
H	3.67024600	-1.28409300	4.56626700
H	3.40797800	-2.83402300	3.72926500
H	4.87753000	-1.89567800	3.42295000
C	-3.52770300	-1.11413600	2.81218000
H	-3.58690200	-1.96442000	3.49828300
H	-3.60877000	-0.18893200	3.39857500
H	-4.37821000	-1.14097300	2.12290500
C	-2.20750900	-1.10594100	2.07262600
C	-1.16370200	-1.88479200	2.57713600
H	-1.38847100	-2.44548000	3.48104200
C	0.07758900	-2.20170700	1.97265900
C	0.77671300	-3.39663800	2.60641000
H	0.02939800	-4.13851700	2.90788400
H	1.49922600	-3.86505400	1.93451400
H	1.30927300	-3.07604000	3.51077600
C	-0.67936000	0.82348600	-2.41297500
C	0.05529100	0.43807700	-3.69792200
H	0.02670100	1.27534800	-4.40662300
H	1.09541800	0.16152100	-3.52815000
H	-0.45972500	-0.42074400	-4.15286900
C	-2.14159500	1.15006800	-2.77736800
H	-2.15702600	1.97042200	-3.50640400
H	-2.61915400	0.26964600	-3.22392800
H	-2.72190800	1.45436800	-1.90163900
C	2.11479800	3.66700100	0.26647500
C	2.59784900	4.65658800	-0.81506700
H	3.59489200	4.42219900	-1.20004600
H	1.89078800	4.69510200	-1.65305000
H	2.64714900	5.65956600	-0.36449300
C	0.81136800	4.25981000	0.85098600
H	0.33392200	3.59107800	1.57006300
H	1.08087700	5.19445000	1.36694800
H	0.09151900	4.50750700	0.06297000
C	3.21372000	1.53802800	-1.77555300
C	3.14279900	0.00658900	-1.96892500
H	2.12141600	-0.36024800	-2.10314200
H	3.73698800	-0.28755400	-2.84686800
H	3.55227100	-0.50298100	-1.09214700
C	4.61869700	1.84057300	-1.20631300
H	4.81007800	2.91090000	-1.07874900
H	4.78050600	1.33611000	-0.24696600
H	5.36509600	1.45215000	-1.91619900
Cl	0.06811700	1.28911600	2.36664700
N	-2.06927500	-0.38142200	0.94094000
N	0.61401000	-1.55418000	0.91997800
O	-0.64370900	-0.27448600	-1.47173700
P	-0.14711000	2.33229300	-1.36222200

P	1.82444000	1.89321400	-0.49113600
Ti	-0.26961900	0.28093200	0.26698100
C	3.02495000	2.27961900	-3.11471100
H	3.25147000	3.34602900	-3.02382200
H	3.71072500	1.85099200	-3.86186400
H	2.00233100	2.18797500	-3.49192300
C	3.13953700	3.56859400	1.41577400
H	2.72901000	2.98107200	2.24360400
H	4.08993300	3.12237300	1.10422000
H	3.34918300	4.58371500	1.78590200

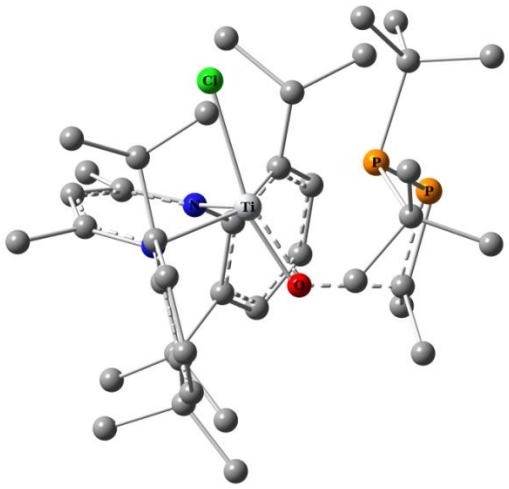


Figure S201. Optimized structure of **3g**$_{TS2}$.

Below are presented xyz coordinates for optimized geometry of **3g**$_{TS2}$:

C	3.10014900	-0.00403100	-0.37937900
C	3.55048500	1.31692300	-0.63598300
C	4.76628400	1.71631900	-0.05397100
H	5.14047500	2.72007300	-0.23877900
C	5.50031900	0.85475600	0.77063800
H	6.43812500	1.18988400	1.21096600
C	5.01610600	-0.42717500	1.04000800
H	5.57701200	-1.08738500	1.70091100
C	3.81218100	-0.88240600	0.47347000
C	2.75031800	2.27170900	-1.51834500
H	1.68936700	2.10807800	-1.27739000
C	3.05726600	3.75053100	-1.22781200
H	2.37278800	4.38260700	-1.80547800
H	2.92219300	3.98149200	-0.16388400
H	4.08015100	4.02133400	-1.52538000
C	2.92319000	1.97941300	-3.02496600
H	2.38212600	2.73509600	-3.60877200
H	3.98397700	2.01217500	-3.31165500
H	2.50572100	1.00499700	-3.29422600
C	3.30809800	-2.28247400	0.81721300
H	2.37915100	-2.45887500	0.26190500
C	2.97947200	-2.38688300	2.32235600
H	2.68634000	-3.41356600	2.57717000
H	3.85271700	-2.12587200	2.93555100
H	2.15341300	-1.71636500	2.58137400
C	4.32491600	-3.37883900	0.42787500
H	4.60919400	-3.31587800	-0.62903200
H	5.24280700	-3.29574900	1.02547600
H	3.89442400	-4.37269300	0.60930900
C	-1.85935200	-2.26133600	-0.20637500
C	-1.78184800	-2.87913300	1.06986300
C	-2.97979900	-3.24853000	1.70233100
H	-2.94311600	-3.71689600	2.68306300
C	-4.22043800	-3.02807700	1.09337000

H	-5.13776600	-3.31932800	1.60265600
C	-4.27729500	-2.43210400	-0.16819500
H	-5.24406600	-2.25928000	-0.63860300
C	-3.10871400	-2.03489100	-0.84339900
C	-0.43173300	-3.18929700	1.70281800
H	0.25115400	-2.38091200	1.41547900
C	-0.48628500	-3.23260800	3.24059100
H	0.52873600	-3.31735400	3.64617300
H	-0.94170100	-2.32038200	3.64513700
H	-1.05690600	-4.09710000	3.60747400
C	0.12399400	-4.51847300	1.13944600
H	1.09210200	-4.75460400	1.60044100
H	-0.56653500	-5.34720300	1.34805100
H	0.27346300	-4.45905300	0.05505900
C	-3.23753100	-1.35291600	-2.20078500
H	-2.23617400	-1.22391600	-2.62659100
C	-3.82382700	0.06079600	-2.02280300
H	-3.86925500	0.58266200	-2.98663000
H	-4.83683100	0.01378500	-1.59838500
H	-3.18458700	0.64900500	-1.35542600
C	-4.10091200	-2.16813300	-3.18884500
H	-4.06558700	-1.70367400	-4.18279200
H	-3.75565700	-3.20586000	-3.27793400
H	-5.15232300	-2.19474800	-2.87217600
C	3.42620600	-1.46080800	-2.73787900
H	4.05938400	-0.58699600	-2.56940700
H	3.95545800	-2.34176000	-2.35342000
H	3.28069800	-1.60463400	-3.81487300
C	2.07102900	-1.32502200	-2.06364200
C	1.06368000	-2.19574300	-2.52817600
H	1.32860500	-2.79975300	-3.39270400
C	-0.14964200	-2.52736100	-1.90336800
C	-0.89144100	-3.73804500	-2.43505700
H	-0.18564800	-4.44852100	-2.87708900
H	-1.46324700	-4.23679100	-1.64611800
H	-1.59843300	-3.43266800	-3.21692400
C	0.87081800	1.39404300	2.50316300
C	0.12912900	0.82827700	3.69591500
H	0.26418200	1.52357500	4.53906900
H	-0.93807600	0.70525200	3.52720200
H	0.55896500	-0.14088000	3.98070200
C	2.37376900	1.33246000	2.72633700
H	2.61085200	1.80327000	3.69274000
H	2.69705500	0.28868300	2.78331800
H	2.93976500	1.83032100	1.93546200
C	-1.78722600	3.74169800	-0.52549000
C	-2.22641000	4.91938500	0.37312200
H	-3.20457100	4.75672300	0.83774300
H	-1.49038000	5.10797600	1.16493300
H	-2.30246500	5.82448800	-0.24855000
C	-0.48411000	4.15962000	-1.24439200
H	-0.07844500	3.33855000	-1.84363600
H	-0.72537200	4.99448100	-1.92044000
H	0.27947100	4.50070500	-0.53806500
C	-2.95487400	1.86651900	1.71693900
C	-2.95076800	0.34388600	1.99227000
H	-1.95973200	-0.05337900	2.22776500
H	-3.62873100	0.11476200	2.82790400
H	-3.31117800	-0.19850400	1.11067600
C	-4.33145700	2.18779300	1.09476000
H	-4.47623200	3.25585500	0.90386800
H	-4.50175400	1.63368100	0.16657200
H	-5.10395800	1.87284000	1.81361900
Cl	-0.48149400	0.86817500	-2.52794400
N	1.90292300	-0.48958300	-1.02074700
N	-0.63554700	-1.83930200	-0.84854000
O	0.43243100	-0.10387300	1.32883600
P	0.41953200	2.79991600	1.47868000

P	-1.44958100	2.16527800	0.52935800
Ti	0.01654100	0.01715200	-0.34240800
C	-2.80472000	2.69232900	3.01215000
H	-2.95611900	3.75986800	2.81694300
H	-3.56590100	2.36659200	3.73804400
H	-1.81673500	2.58343200	3.46799700
C	-2.84235900	3.46264400	-1.61815100
H	-2.48871100	2.68229500	-2.29935400
H	-3.81448900	3.16951300	-1.21262200
H	-2.98804300	4.38657000	-2.19835900

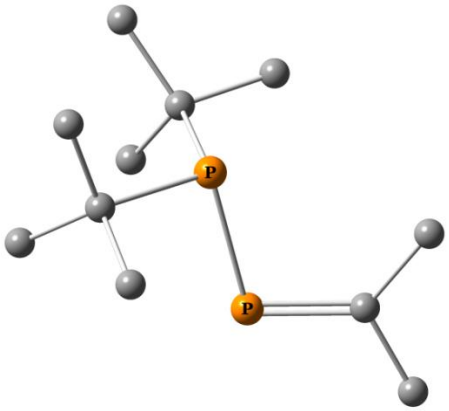


Figure S202. Optimized structure of **3g**.

Below are presented xyz coordinates for optimized geometry of **3g**:

C	-2.70485400	-0.37712000	-0.09323100
P	-1.27887000	-0.64425200	0.80697000
P	0.33995100	-0.03112000	-0.60980000
C	0.75718800	1.71251600	0.10097700
C	-0.32004900	2.62826000	-0.52741000
C	0.69367000	1.86981000	1.63344900
C	2.14470000	2.15003200	-0.40993800
H	-0.29653300	2.58296600	-1.62370300
H	-1.32547000	2.34362000	-0.18962800
H	-0.14254100	3.66949000	-0.21814600
H	1.42692600	1.24162500	2.14805600
H	0.90199500	2.91870800	1.89714600
H	-0.30211100	1.61766800	2.02054200
H	2.28954700	3.22033100	-0.19739400
H	2.95098400	1.60164000	0.09188600
H	2.24323800	2.00214600	-1.49351200
C	1.68855700	-1.29933700	-0.09672400
C	2.86740000	-1.16387700	-1.08841900
C	2.20458600	-1.20684900	1.35056300
C	1.04051000	-2.68673800	-0.32021700
H	2.51977800	-1.23998800	-2.12658900
H	3.39913000	-0.21312600	-0.97452800
H	3.58926200	-1.97507200	-0.90735800
H	1.38318300	-1.25527600	2.07655000
H	2.88572700	-2.04852100	1.55173700
H	2.76712700	-0.28093700	1.52016900
H	1.80674600	-3.46795300	-0.20382000
H	0.24170900	-2.88433700	0.40680300
H	0.61508600	-2.77202200	-1.32930600
C	-4.01824300	-0.68333600	0.59949800
H	-4.64926900	0.21826800	0.63755200
H	-4.57837600	-1.43951900	0.02773600
H	-3.87416000	-1.05138400	1.62164500
C	-2.85603300	0.14077000	-1.50097800
H	-3.32696500	1.13665600	-1.48609200
H	-1.89601400	0.21789300	-2.02142700
H	-3.52980800	-0.51709000	-2.07128600

E.3.11. Reaction of **1** with cyclohexanone leading to **3h**

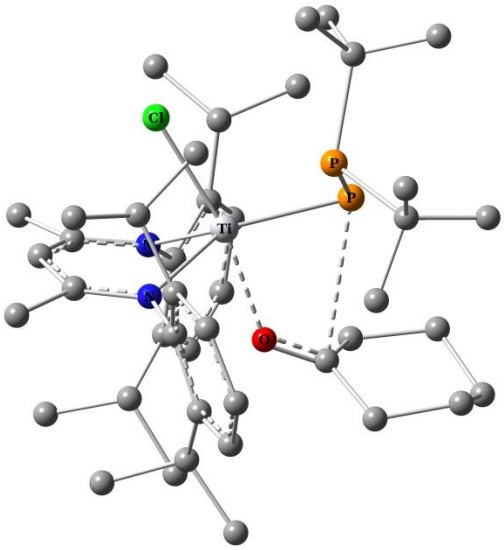


Figure S203. Optimized structure of **3h$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of **3h$_{TS1}$**:

C	-3.04715900	-0.14244400	-0.89818400
C	-3.47943800	-1.48621800	-1.04088300
C	-4.73374600	-1.83565600	-0.50564100
H	-5.08773700	-2.85944900	-0.61168000
C	-5.53462700	-0.89654100	0.15144100
H	-6.50459200	-1.18923600	0.55073600
C	-5.08121400	0.41953600	0.30006500
H	-5.70356800	1.14410200	0.82380900
C	-3.83267000	0.81912600	-0.20361100
C	-2.65666800	-2.52859500	-1.79080800
H	-1.62306600	-2.16159300	-1.85268400
C	-2.62376100	-3.88822900	-1.06746100
H	-1.93994900	-4.56514500	-1.59439600
H	-2.26220100	-3.77724900	-0.03854200
H	-3.61424100	-4.36393900	-1.04888000
C	-3.17693300	-2.71136900	-3.23464800
H	-2.55011300	-3.43664600	-3.76964000
H	-4.21101200	-3.08436800	-3.22908300
H	-3.15808900	-1.76905400	-3.79139700
C	-3.34983300	2.25560500	-0.00376200
H	-2.27356300	2.27012000	-0.21339700
C	-3.55613900	2.74970600	1.44330600
H	-3.13146300	3.75496100	1.55737200
H	-4.62082100	2.81062700	1.70515000
H	-3.06448300	2.09144000	2.16799200
C	-4.04908800	3.23155300	-0.97780200
H	-3.87579300	2.95378700	-2.02197800
H	-5.13414000	3.23890500	-0.80356600
H	-3.66983200	4.25161400	-0.82849800
C	1.86565600	2.23997700	-0.15144400
C	1.61695100	2.99836100	1.02546000
C	2.71931700	3.40956400	1.79513700
H	2.55141400	3.97525600	2.70867500
C	4.03147700	3.11648400	1.40709700
H	4.86894900	3.42996100	2.02829300
C	4.25816100	2.45056400	0.20096500
H	5.27997800	2.26651900	-0.12884400
C	3.19280200	2.01982700	-0.60996100
C	0.20289800	3.44051300	1.39770900

H	-0.45882300	2.58456300	1.22548600
C	0.06175900	3.88564600	2.86638100
H	-1.00091000	4.01205700	3.11069000
H	0.48989200	3.15786100	3.56593300
H	0.55460400	4.85216600	3.04206500
C	-0.27344800	4.59686700	0.48476700
H	-1.24678400	4.97155600	0.82968700
H	0.44139300	5.43057700	0.50932700
H	-0.39250100	4.27104400	-0.55233500
C	3.51196800	1.41034800	-1.97303700
H	2.56896200	1.18236600	-2.48240300
C	4.27873900	0.08483800	-1.84923600
H	4.46471700	-0.34187400	-2.84308000
H	5.24799500	0.23059300	-1.35134000
H	3.68510600	-0.63072700	-1.27366100
C	4.33179700	2.39755200	-2.83943900
H	4.42731700	2.00612000	-3.86114200
H	3.87288200	3.39162100	-2.88901100
H	5.34512300	2.52033800	-2.43338200
C	-2.93243400	1.00995800	-3.51939800
H	-3.06595300	1.96935000	-4.03012600
H	-2.68761600	0.25542900	-4.28051000
H	-3.87268300	0.71643300	-3.04375600
C	-1.78308900	1.06728600	-2.53126000
C	-0.73474300	1.94395600	-2.81772200
H	-0.83638900	2.51081800	-3.74090200
C	0.36970800	2.32055600	-2.01139300
C	1.10376100	3.55149300	-2.52464700
H	0.37986600	4.31740900	-2.82613200
H	1.78366900	3.97409800	-1.78167300
H	1.68436700	3.27856600	-3.41540400
C	2.48366600	-3.58424000	-0.72675000
C	2.95685000	-4.67882200	0.25033500
H	3.88589700	-4.41618600	0.76791900
H	2.18450800	-4.90162300	0.99668300
H	3.14862400	-5.59797700	-0.32513300
C	1.25186000	-4.14170400	-1.47109800
H	0.80863600	-3.40040600	-2.14171600
H	1.57483900	-5.00956400	-2.06758500
H	0.48475500	-4.47224000	-0.76144200
C	3.05009900	-1.70685800	1.76631900
C	2.65808700	-0.29951800	2.25499500
H	1.58267900	-0.26027900	2.46013300
H	3.20007200	-0.06213500	3.18307000
H	2.89446200	0.46636900	1.51039900
C	4.55240600	-1.70676600	1.41824800
H	4.89910400	-2.67778600	1.04653800
H	4.78691400	-0.94350400	0.66879400
H	5.12921200	-1.47410500	2.32675100
Cl	0.68553800	-0.94300100	-2.73201300
N	-1.78135200	0.28038100	-1.42921600
N	0.75432900	1.68714900	-0.89052600
O	-1.00336800	0.52946900	1.18721100
P	-0.05264700	-2.20923600	0.83536900
P	1.95601800	-1.96314000	0.19711900
Ti	-0.00938700	-0.32837500	-0.57773800
C	2.75064600	-2.71197100	2.89660500
H	3.13536200	-3.71335600	2.68318000
H	3.22499100	-2.35956300	3.82625700
H	1.66797400	-2.78682300	3.06503500
C	3.59125000	-3.27022100	-1.75282000
H	3.22991300	-2.56083500	-2.50496000
H	4.48925500	-2.85391700	-1.27990300
H	3.88172000	-4.20095300	-2.26474000
C	-1.36937400	0.02309700	2.27653800
C	-0.73516800	0.47956600	3.56735500
C	-2.56814900	-0.88394900	2.38590600
C	-0.57414500	-0.67330400	4.58327000

H	-1.41823900	1.23665800	3.99192400
H	0.21061400	0.97981000	3.34356300
C	-2.44132100	-1.96791000	3.47949200
H	-3.40758500	-0.21049800	2.63879600
H	-2.79446100	-1.31273000	1.40635700
C	-1.91131300	-1.39850800	4.80503300
H	-0.18302400	-0.26577400	5.52499300
H	0.16914800	-1.38187300	4.19356200
H	-3.42333400	-2.43857700	3.62012300
H	-1.75088900	-2.73857700	3.11085200
H	-1.78096200	-2.21064500	5.53316500
H	-2.64456200	-0.69635600	5.23472100

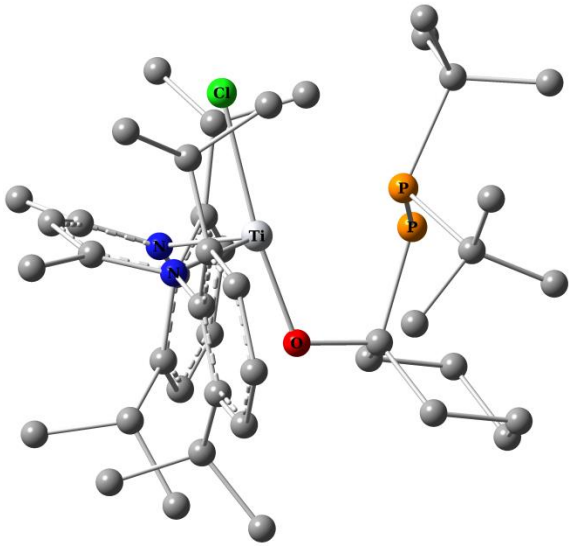


Figure S204. Optimized structure of **3h$_I$**.

Below are presented xyz coordinates for optimized geometry of **3h$_I$**:

C	3.10278300	-0.61273000	-0.63769800
C	3.80146500	0.41185400	-1.32118800
C	5.04083300	0.82454600	-0.79652900
H	5.58912800	1.62087700	-1.29802100
C	5.58146100	0.22739000	0.34540300
H	6.54277800	0.56108900	0.73319600
C	4.88813600	-0.80743500	0.98551400
H	5.32074600	-1.27489700	1.86849000
C	3.63827200	-1.24064300	0.51753500
C	3.27995400	1.04767800	-2.60493700
H	2.33402800	0.55794800	-2.86625600
C	2.98970600	2.55143200	-2.41577900
H	2.57630000	2.97320400	-3.34129000
H	2.26403500	2.70982900	-1.61028100
H	3.90962800	3.10075900	-2.16980200
C	4.27394100	0.84734800	-3.77251500
H	3.83033800	1.21408500	-4.70754000
H	5.20307200	1.40751200	-3.59913900
H	4.54253600	-0.20778800	-3.90678000
C	2.89475000	-2.37809500	1.21114700
H	1.84865100	-2.32375500	0.88771900
C	2.91859800	-2.25621900	2.74659700
H	2.35893500	-3.08658000	3.19496400
H	3.94048500	-2.29833300	3.14661100
H	2.45409300	-1.31809000	3.06913900
C	3.46173100	-3.74864600	0.77296300
H	3.38635900	-3.88534300	-0.31201700
H	4.51989700	-3.83928700	1.05502400
H	2.90469200	-4.56194100	1.25740700
C	-2.18742800	-2.02735600	0.22286400

C	-2.14525600	-2.36965800	1.59668000
C	-3.36189600	-2.55066200	2.27678800
H	-3.34736200	-2.81101500	3.33304300
C	-4.58883600	-2.40317700	1.62169800
H	-5.52130900	-2.53800400	2.16747500
C	-4.60967700	-2.08795500	0.25998800
H	-5.56488500	-1.98702200	-0.25357800
C	-3.42058800	-1.90858900	-0.46959700
C	-0.81704700	-2.61937400	2.30035900
H	-0.06567300	-1.98656200	1.81643400
C	-0.84256200	-2.24042200	3.79280700
H	0.17329900	-2.29053100	4.20360100
H	-1.21885700	-1.22029600	3.93521600
H	-1.46918700	-2.92485300	4.38144500
C	-0.39915000	-4.09804300	2.12245600
H	0.54134600	-4.29873200	2.65207500
H	-1.16970400	-4.76938300	2.52600900
H	-0.24942100	-4.34466400	1.06475200
C	-3.50862800	-1.61242800	-1.96393800
H	-2.49756700	-1.64192100	-2.38692400
C	-4.04272100	-0.18926300	-2.19696700
H	-4.05651000	0.04844700	-3.26832100
H	-5.06406900	-0.08396800	-1.80383700
H	-3.39082500	0.53049100	-1.69258300
C	-4.39424400	-2.63602300	-2.71055600
H	-4.31881100	-2.47280300	-3.79369800
H	-4.10557600	-3.67159500	-2.49399200
H	-5.45038900	-2.52136700	-2.43136200
C	2.98851800	-2.51045400	-2.73139200
H	2.88959900	-3.52573600	-3.12710000
H	3.09930500	-1.81748500	-3.57618400
H	3.90083700	-2.44076600	-2.12957100
C	1.76173200	-2.11779800	-1.93694200
C	0.60925000	-2.89278700	-2.07881500
H	0.68707700	-3.73426500	-2.76291400
C	-0.57866100	-2.85871900	-1.30836500
C	-1.43023800	-4.11328600	-1.45225800
H	-0.77759300	-4.99294700	-1.47988800
H	-2.15425600	-4.22755100	-0.64304900
H	-1.97849900	-4.07907100	-2.40243800
C	-1.92623000	3.42600600	-1.51521700
C	-2.24250800	4.75641600	-0.79946100
H	-3.21681400	4.75673600	-0.30123300
H	-1.46444500	4.99896200	-0.06490300
H	-2.25926700	5.55665200	-1.55492600
C	-0.63951700	3.66761400	-2.33914000
H	-0.27482500	2.75817100	-2.82098600
H	-0.88714600	4.40262300	-3.12075000
H	0.16191100	4.08951100	-1.72271700
C	-3.00066600	2.20248300	1.17923600
C	-3.01333900	0.82800300	1.88300600
H	-2.00913100	0.44985900	2.09575900
H	-3.56572300	0.90059700	2.83173200
H	-3.51164300	0.08679300	1.25280000
C	-4.42237700	2.42205300	0.61412400
H	-4.55082000	3.40201700	0.14305600
H	-4.69293000	1.64435500	-0.10860900
H	-5.13450400	2.36021100	1.45136400
Cl	-0.31082900	0.30170900	-2.83553800
N	1.80900000	-1.06169700	-1.09503000
N	-0.94281300	-1.85033700	-0.49326400
O	0.63833100	0.00270700	1.24840500
P	0.37684200	2.46945400	0.30843200
P	-1.70104200	1.98014800	-0.22461500
Ti	0.15213000	-0.00928300	-0.54737100
C	-2.66004900	3.32331400	2.17953800
H	-2.77194700	4.31821000	1.73938600
H	-3.34450700	3.25426600	3.03933900

H	-1.63555200	3.23509100	2.54923500
C	-3.05087000	3.05861100	-2.50580000
H	-2.75829300	2.19523800	-3.11236300
H	-4.00162900	2.83583600	-2.01016600
H	-3.21487100	3.91263600	-3.18049400
C	0.90086000	1.33325200	1.75525200
C	0.30200500	1.49288000	3.15903600
C	2.43322600	1.53148500	1.85205600
C	0.67847700	2.83886600	3.80740100
H	0.70570100	0.66650500	3.76775900
H	-0.78288900	1.36932600	3.13631800
C	2.82608800	2.86983300	2.49985400
H	2.82864800	0.69963800	2.45153600
H	2.88005800	1.45145400	0.85574800
C	2.20296100	3.01350000	3.89684000
H	0.21560600	2.90423600	4.80220700
H	0.26575900	3.66269200	3.20421300
H	3.92235800	2.93134200	2.54916700
H	2.48491300	3.69863200	1.85994200
H	2.45079000	3.99156100	4.33289600
H	2.62125200	2.24406800	4.56623600

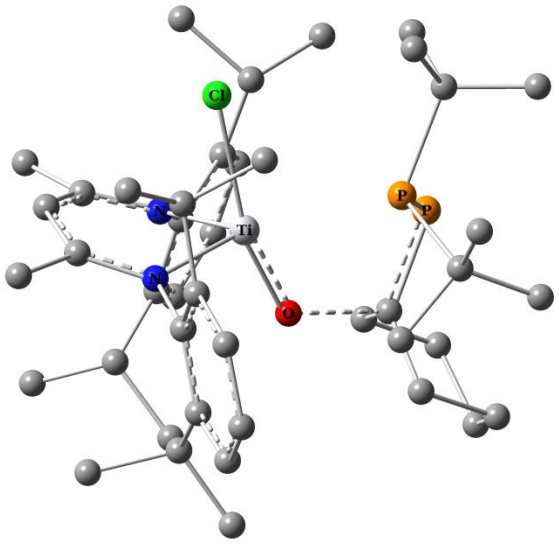


Figure S205. Optimized structure of **3h**$_{TS2}$.

Below are presented xyz coordinates for optimized geometry of **3h**$_{TS2}$:

C	2.78528700	-0.89954600	-0.94413700
C	3.40505300	0.18995000	-1.60985800
C	4.75199200	0.45859900	-1.30879900
H	5.25461500	1.28322300	-1.80776800
C	5.45634500	-0.30121000	-0.36669900
H	6.49775200	-0.06941200	-0.14858600
C	4.81269000	-1.34320800	0.30436800
H	5.35517800	-1.91740900	1.05492400
C	3.47142200	-1.66477400	0.03033500
C	2.64015800	1.04374400	-2.61790100
H	1.62672700	1.17638300	-2.21069100
C	3.24470700	2.44730000	-2.79039100
H	2.58940800	3.04737900	-3.43244300
H	3.34009100	2.95813400	-1.82422500
H	4.23082500	2.41068300	-3.27460400
C	2.49029000	0.35648900	-3.99275400
H	1.99406000	1.04151400	-4.69211700
H	3.47296000	0.08852800	-4.40655100
H	1.86865000	-0.54097000	-3.92597500
C	2.80279100	-2.79684100	0.80708600
H	1.78258300	-2.92052300	0.42460600

C	2.69871400	-2.43941400	2.30552000
H	2.28410600	-3.28479700	2.86990400
H	3.68787800	-2.20908600	2.72450000
H	2.04510500	-1.57230800	2.44608900
C	3.55124800	-4.13850000	0.64130100
H	3.67872400	-4.40863600	-0.41366400
H	4.54988000	-4.09271600	1.09648600
H	2.99300900	-4.94388700	1.13696000
C	-2.39345400	-1.92666000	0.43503700
C	-2.20879200	-2.21588300	1.81313400
C	-3.32590200	-2.14877900	2.66107300
H	-3.20477300	-2.35996100	3.72094200
C	-4.59291500	-1.81639000	2.16838900
H	-5.44528000	-1.76582600	2.84412100
C	-4.75905000	-1.54849800	0.80809600
H	-5.74555600	-1.28824200	0.42744800
C	-3.67313300	-1.59521100	-0.08524500
C	-0.84725700	-2.64693200	2.34188100
H	-0.09168400	-2.10333800	1.76259600
C	-0.64279000	-2.29493000	3.82637800
H	0.39599100	-2.49282300	4.11578800
H	-0.85430600	-1.23477300	4.01266300
H	-1.28481800	-2.89734300	4.48402600
C	-0.64124400	-4.16192800	2.10688400
H	0.33552100	-4.47967100	2.49502100
H	-1.41992200	-4.74393200	2.61887200
H	-0.67440600	-4.40661400	1.03876500
C	-3.91226500	-1.25934800	-1.55291200
H	-2.99133600	-1.45441400	-2.11361800
C	-4.20786800	0.24504700	-1.70541600
H	-4.32262500	0.50918400	-2.76393900
H	-5.12861200	0.51968500	-1.17118500
H	-3.37470100	0.83196900	-1.30409600
C	-5.05882600	-2.09326200	-2.16653900
H	-5.11614700	-1.90677300	-3.24677200
H	-4.91616700	-3.16943200	-2.00704500
H	-6.02896300	-1.81927700	-1.73035100
C	2.44609300	-2.93761400	-2.81172800
H	2.90465200	-3.74560700	-2.22776100
H	2.09438300	-3.36722900	-3.75661500
H	3.21840700	-2.19204500	-3.01454100
C	1.26717800	-2.34761000	-2.05607800
C	0.05737000	-3.06754700	-2.14156000
H	0.06047900	-3.90910700	-2.83005900
C	-1.07255800	-2.96470900	-1.31344200
C	-2.09706900	-4.07874400	-1.40281000
H	-1.61205800	-5.01473400	-1.69797900
H	-2.61723100	-4.22321900	-0.45066700
H	-2.85137800	-3.83495300	-2.16178800
C	-1.31901400	3.65366300	-1.50591600
C	-1.38929000	5.08016200	-0.91678300
H	-2.29028200	5.24776400	-0.31716900
H	-0.51049500	5.29439500	-0.29534300
H	-1.40719900	5.80142500	-1.74800800
C	-0.10646800	3.59930700	-2.46295500
H	0.04449000	2.58950400	-2.85674400
H	-0.31398400	4.27283400	-3.30886100
H	0.81376000	3.93555900	-1.97460400
C	-2.38372200	2.67660000	1.28873700
C	-2.58255900	1.30709200	1.98047600
H	-1.64406800	0.79781900	2.21440900
H	-3.15134800	1.44129800	2.91270600
H	-3.15815100	0.63814100	1.33032000
C	-3.77447600	3.10543500	0.77206700
H	-3.76960100	4.09472600	0.30360800
H	-4.19229800	2.37967100	0.06763000
H	-4.45261900	3.15276900	1.63843100
Cl	-0.90593200	0.16768000	-2.80099300

N	1.42917500	-1.26239300	-1.27541600
N	-1.24336800	-1.95072000	-0.43940300
O	0.46836900	-0.01729200	1.03849200
P	1.00643900	2.77483500	0.39155600
P	-1.08094400	2.34597300	-0.11100200
Ti	-0.19631700	-0.21166300	-0.54074600
C	-1.87803000	3.75595500	2.26880700
H	-1.89963800	4.74845400	1.80518300
H	-2.53360300	3.77762300	3.15314600
H	-0.85075400	3.57626000	2.59837300
C	-2.57781600	3.34488800	-2.34567200
H	-2.48344600	2.36729700	-2.82901700
H	-3.50112800	3.36657600	-1.76045000
H	-2.66274100	4.11122600	-3.13122600
C	1.37355500	1.59375200	1.69644900
C	0.77594900	1.53341800	3.08865000
C	2.85961400	1.26727200	1.74870000
C	1.47558500	2.57905900	3.99601100
H	0.95225300	0.52790700	3.49854600
H	-0.29908800	1.70704100	3.08206800
C	3.60148100	2.28303400	2.65858400
H	2.98092200	0.26272300	2.17017400
H	3.29904200	1.26729100	0.74825100
C	2.98918000	2.31938100	4.06760600
H	1.02350600	2.53836700	4.99735600
H	1.29128600	3.58517900	3.58985800
H	4.66417800	2.00487700	2.69999200
H	3.54027900	3.28100400	2.20010600
H	3.48059200	3.09067300	4.67776600
H	3.16566700	1.35234100	4.56577700

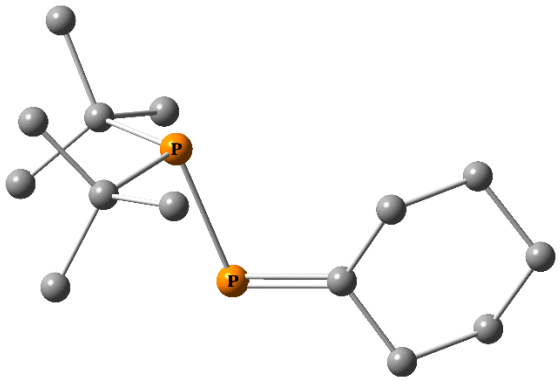


Figure S206. Optimized structure of **3h**.

Below are presented xyz coordinates for optimized geometry of **3h**:

P	0.99216900	0.04771900	-0.53444800
P	-0.46935200	0.20509800	1.15506600
C	2.10148800	1.55817900	-0.11291300
C	3.10947300	1.74421900	-1.27085900
C	2.84838900	1.50832200	1.23211000
H	2.59338300	1.79424800	-2.23815200
H	3.65991000	2.68654600	-1.12569700
H	3.84397900	0.93297800	-1.31663000
H	2.16157100	1.33260400	2.06968500
H	3.61550100	0.72467000	1.23858200
H	3.35702800	2.46964600	1.40565200
C	1.88082500	-1.59256700	-0.04732100
C	3.23060400	-1.67962300	-0.78746000
C	0.93702500	-2.68958800	-0.59555600
H	3.97093900	-0.99355600	-0.35854500
H	3.63167000	-2.70055600	-0.69463800
H	3.12213700	-1.45268400	-1.85637800
H	-0.04335800	-2.65099700	-0.10191000

H	0.78459800	-2.58357200	-1.67728900
H	1.37404900	-3.68092200	-0.40145000
C	-1.93443400	-0.30246700	0.44467000
C	-2.21943900	-0.71264400	-0.98013800
C	-3.17349700	-0.29184200	1.32234600
C	-3.31135400	0.20054100	-1.59597000
H	-2.59276900	-1.75169100	-0.97704700
H	-1.30839400	-0.68402600	-1.58804300
C	-4.26275600	0.62757700	0.71411200
H	-3.57474100	-1.31869500	1.37874000
H	-2.92790200	0.02357100	2.34483100
C	-4.58426300	0.21960600	-0.73337600
H	-3.53745400	-0.14428000	-2.61462000
H	-2.90588200	1.21987600	-1.67943800
H	-5.16572900	0.58760500	1.33942400
H	-3.89671800	1.66501700	0.73285300
H	-5.32546300	0.90679400	-1.16554200
H	-5.03930000	-0.78416900	-0.73489900
C	1.14400300	2.77396100	-0.12089600
H	0.55566400	2.81348300	-1.04772200
H	0.44704600	2.74792600	0.72718400
H	1.73322700	3.70061200	-0.04887400
C	2.09562800	-1.84395200	1.45848700
H	2.55775500	-2.83411100	1.59694700
H	2.75345400	-1.09863000	1.91576500
H	1.14339500	-1.83827200	2.00453300

E.3.12. Reaction of **1** with acetophenone leading to ***Z*-3i**

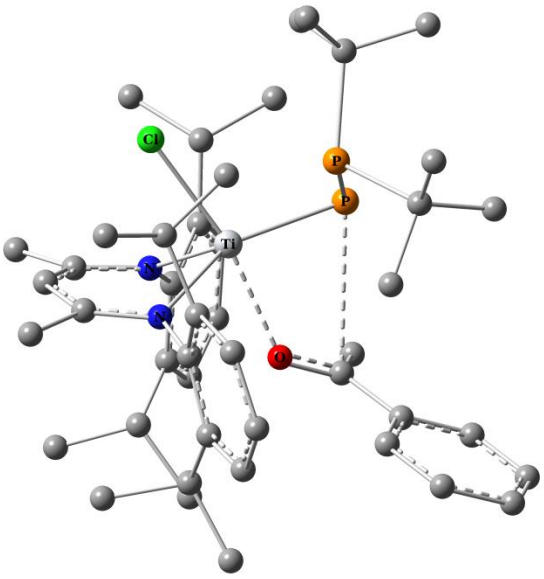


Figure S207. Optimized structure of ***Z*-3i$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3i$_{TS1}$**:

C	3.28744800	0.17459100	-0.08180300
C	3.83421100	1.35696900	0.48355300
C	4.89767600	1.21813800	1.39486600
H	5.33223400	2.11131000	1.83957100
C	5.41802200	-0.03611500	1.72908500
H	6.24644600	-0.11454200	2.43152700
C	4.87186200	-1.18837000	1.15397700
H	5.28102200	-2.16333400	1.41525600
C	3.79656200	-1.11091900	0.25392400
C	3.36323500	2.75173200	0.08140400
H	2.37159600	2.65479400	-0.38061100
C	3.23395200	3.70427600	1.28579100
H	2.81824400	4.66237900	0.95003000

H	2.56378100	3.28877600	2.04731800
H	4.21034500	3.91197400	1.74547800
C	4.32211000	3.37323300	-0.96139200
H	3.94920600	4.35871400	-1.27007100
H	5.32617400	3.50267400	-0.53299200
H	4.41331300	2.74817100	-1.85474400
C	3.21859900	-2.38894000	-0.35112700
H	2.25413800	-2.13134200	-0.80486500
C	2.96826200	-3.48556000	0.70418700
H	2.54650000	-4.37497600	0.21981900
H	3.89823000	-3.79345600	1.20010700
H	2.26239300	-3.15430800	1.47313800
C	4.14383700	-2.94849900	-1.45673800
H	4.31056000	-2.21629700	-2.25276500
H	5.12212900	-3.22203400	-1.03743300
H	3.69875400	-3.84655400	-1.90565200
C	-1.68554300	-1.58154900	-1.63067300
C	-1.68761100	-2.88082000	-1.04701000
C	-2.92997100	-3.50170200	-0.82107500
H	-2.95672600	-4.48771600	-0.36271800
C	-4.13382100	-2.88565000	-1.18221700
H	-5.08311000	-3.38063900	-0.98290400
C	-4.10418800	-1.65362600	-1.83755400
H	-5.03607800	-1.19759200	-2.17015700
C	-2.89055900	-0.99144700	-2.09669800
C	-0.38523100	-3.62384300	-0.73336700
H	0.27639800	-2.90784800	-0.22928800
C	-0.57449500	-4.85041200	0.18246300
H	0.40856500	-5.24302800	0.46935900
H	-1.11931800	-4.61509600	1.10308600
H	-1.10916400	-5.65720500	-0.33869400
C	0.32667500	-4.10312200	-2.02283800
H	1.17453800	-4.74940200	-1.75823600
H	-0.36069700	-4.68507700	-2.65147200
H	0.72040500	-3.27020900	-2.61066300
C	-2.91433500	0.27685900	-2.94812200
H	-1.88217100	0.60994600	-3.10440200
C	-3.65641500	1.43521500	-2.26118900
H	-3.69012300	2.30970200	-2.92340000
H	-4.68873500	1.15337300	-2.00939000
H	-3.12779400	1.72355400	-1.34655400
C	-3.56583300	-0.00464300	-4.32443000
H	-3.43667000	0.86542000	-4.98193100
H	-3.13140600	-0.88182600	-4.81796300
H	-4.64417700	-0.18469300	-4.21632500
C	3.83188700	0.29250000	-2.88541000
H	4.61547100	0.22866500	-2.12555200
H	4.06434400	-0.39445900	-3.70598800
H	3.83315800	1.31306200	-3.29395000
C	2.45188300	0.01770100	-2.31699400
C	1.48353300	-0.43618600	-3.21504800
H	1.80882100	-0.51859000	-4.25000200
C	0.18410900	-0.94172900	-2.95954300
C	-0.46865800	-1.60359800	-4.16396500
H	0.27403300	-2.17082300	-4.73566500
H	-1.28899500	-2.26799200	-3.88260700
H	-0.86706400	-0.81961900	-4.82201400
C	0.59317700	-1.10452800	2.21773600
C	-1.66376700	4.20260400	0.42337800
C	-2.13386600	4.88301600	1.72623300
H	-3.16181800	4.62835800	2.00216100
H	-1.47066600	4.61915700	2.55984800
H	-2.08920200	5.97452300	1.58740600
C	-0.25162300	4.74646300	0.12314400
H	0.18789800	4.28226000	-0.76312000
H	-0.33053500	5.83187000	-0.04644900
H	0.41631500	4.57561600	0.97485600
C	-3.06124500	1.66858400	1.68388300

C	-3.09593600	0.16505100	1.35902100
H	-2.10281200	-0.27134800	1.51152100
H	-3.80128100	-0.35419500	2.02519300
H	-3.39254700	-0.02141600	0.32161000
C	-4.41406900	2.28474700	1.27132400
H	-4.49389000	3.34755300	1.52187300
H	-4.60756800	2.16492500	0.20021900
H	-5.21404000	1.75769000	1.81438100
Cl	0.17969300	2.23411200	-2.18428500
N	2.18627500	0.23735800	-1.00506600
N	-0.44012100	-0.86645700	-1.77306800
O	0.45162900	-1.05960200	0.96217600
P	0.23620400	1.82829500	1.65907400
P	-1.56468600	2.28798900	0.62899900
Ti	0.26896400	0.69961800	-0.40141800
C	-2.82747200	1.84814300	3.19621700
H	-2.80785900	2.90326700	3.48951600
H	-3.64063500	1.35213300	3.74968700
H	-1.87423400	1.39211500	3.49326300
C	-2.59965400	4.53830500	-0.75636500
H	-2.21353200	4.10107600	-1.68433600
H	-3.62016900	4.17138500	-0.59517400
H	-2.65071700	5.63106900	-0.88186600
C	-0.42743400	-1.79400900	3.03785800
C	-1.51733400	-2.41789100	2.39557700
C	-0.34311100	-1.84553700	4.44849500
C	-2.50050900	-3.07418500	3.13708300
H	-1.58284800	-2.36842500	1.31314600
C	-1.33067800	-2.49892400	5.19064600
H	0.48347500	-1.36805000	4.96737700
C	-2.41121500	-3.11467800	4.53707700
H	-3.33658100	-3.54482300	2.62311000
H	-1.26220700	-2.52623000	6.27625000
H	-3.18010600	-3.62047600	5.11864200
C	1.84878600	-0.60501200	2.88768600
H	2.47428300	-1.47120700	3.15388000
H	2.41098200	0.03961700	2.21395600
H	1.61335800	-0.05534100	3.80354200

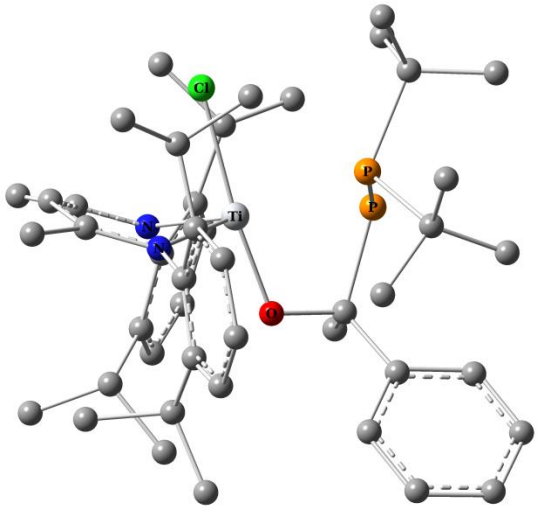


Figure S208. Optimized structure of ***Z*-3i$_I$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3i$_I$**:

C	-3.33340200	-0.00581800	-0.40097400
C	-3.77962300	-1.17971500	-1.06214600
C	-4.92189100	-1.82138100	-0.55275300
H	-5.29099900	-2.71979700	-1.04205200

C	-5.57445400	-1.34411200	0.59034200
H	-6.45212600	-1.86318000	0.97226800
C	-5.08173000	-0.21757700	1.25561100
H	-5.57363700	0.12884600	2.16390600
C	-3.95525300	0.47360000	0.77779700
C	-3.02367100	-1.75522300	-2.25682400
H	-1.95886200	-1.52754200	-2.09891200
C	-3.12772000	-3.28845300	-2.34531300
H	-2.43241900	-3.65317300	-3.11123900
H	-2.85993300	-3.75880200	-1.39111000
H	-4.13676500	-3.61784100	-2.63039800
C	-3.42434800	-1.10008400	-3.59501400
H	-2.90688600	-1.60221300	-4.42237400
H	-4.50798900	-1.17902700	-3.76215200
H	-3.13259300	-0.04538000	-3.62268800
C	-3.42050700	1.67712100	1.55028900
H	-2.54135100	2.05592900	1.01592700
C	-2.96317800	1.26560700	2.96730700
H	-2.62699500	2.14969500	3.52498200
H	-3.78628600	0.80718500	3.53200400
H	-2.13424400	0.55408400	2.91217800
C	-4.46289600	2.81349500	1.64839200
H	-4.81473300	3.13561800	0.66107100
H	-5.33949600	2.49445400	2.22840300
H	-4.02341000	3.68380900	2.15356600
C	1.61953500	2.40735500	0.07700000
C	1.64494900	2.67410800	1.47075800
C	2.88037400	2.99178100	2.06106800
H	2.92733100	3.18881000	3.12907400
C	4.05444500	3.06416200	1.30335600
H	5.00242300	3.29764800	1.78522400
C	3.99799000	2.85382000	-0.07573800
H	4.90562300	2.94078400	-0.67162100
C	2.78656000	2.54234000	-0.71916600
C	0.35896500	2.69180700	2.29494600
H	-0.23007000	1.81144300	2.00206400
C	0.61162800	2.63959600	3.81498400
H	-0.33351800	2.45522400	4.34041300
H	1.31774800	1.84816000	4.09223900
H	1.01278600	3.59452700	4.18291500
C	-0.48342300	3.95372000	1.98455200
H	-1.35916900	3.99172900	2.64601200
H	0.11098200	4.86210400	2.15238000
H	-0.84603600	3.96046000	0.95250800
C	2.77762700	2.40591400	-2.23901900
H	1.74213400	2.27524300	-2.57344800
C	3.54186400	1.14882300	-2.68086000
H	3.48959900	1.02794700	-3.77034200
H	4.60001600	1.20661900	-2.38845300
H	3.09052400	0.26823100	-2.21464500
C	3.37625400	3.65341300	-2.92973700
H	3.22436300	3.58638600	-4.01522200
H	2.92282700	4.58526000	-2.57181900
H	4.45770800	3.72062300	-2.74976800
C	-3.91298600	2.12878800	-2.09229200
H	-4.48641600	2.60521200	-1.28737400
H	-3.89669500	2.81272900	-2.94743600
H	-4.44056200	1.21092900	-2.36572500
C	-2.49512900	1.84674900	-1.63330300
C	-1.53147800	2.83269500	-1.86801900
H	-1.86304700	3.68403700	-2.45796300
C	-0.26559400	2.98697000	-1.25531600
C	0.32241200	4.38207300	-1.42017500
H	-0.46657300	5.12958300	-1.28087300
H	1.13254600	4.58306300	-0.71648500
H	0.71018800	4.49641100	-2.44049100
C	-0.55717200	-1.69118800	1.48200200
C	2.14242800	-2.82487700	-2.30795000

C	2.79982300	-4.13633300	-1.82930300
H	3.81629000	-3.99011700	-1.45091100
H	2.19477200	-4.61858400	-1.05157000
H	2.86282900	-4.82216000	-2.68785000
C	0.82022200	-3.22116000	-3.00781700
H	0.23698600	-2.35131200	-3.31920900
H	1.08787400	-3.80047100	-3.90514600
H	0.19883800	-3.85877300	-2.36890200
C	3.31647800	-1.74228400	0.41866100
C	3.11805600	-0.51986800	1.33940000
H	2.12217900	-0.50022600	1.78848500
H	3.85418700	-0.55522200	2.15610900
H	3.26412900	0.40980300	0.78257100
C	4.66344800	-1.55590400	-0.31449000
H	4.91794500	-2.40191900	-0.96213400
H	4.67817900	-0.63740600	-0.91042000
H	5.45366200	-1.47196700	0.44715900
Cl	-0.05284900	0.08393100	-3.03027900
N	-2.21248900	0.72644000	-0.93480700
N	0.36691400	2.03323100	-0.54269800
O	-0.58383800	-0.28966100	1.13876500
P	-0.05157700	-2.55626800	-0.15192600
P	1.83549800	-1.62200000	-0.80295900
Ti	-0.32070600	0.00729200	-0.68921500
C	3.35128800	-3.03393000	1.25451700
H	3.60037300	-3.91345900	0.65420900
H	4.12096900	-2.92637200	2.03438700
H	2.39520400	-3.21149700	1.75147900
C	3.03363600	-2.12653800	-3.35570800
H	2.51295800	-1.26658400	-3.78912200
H	3.99095700	-1.79027900	-2.94331400
H	3.24797500	-2.84260700	-4.16371400
C	0.21949900	-1.94749800	2.75947800
C	0.55263600	-0.88932200	3.61615600
C	0.50033300	-3.26535900	3.16723100
C	1.18247800	-1.13338000	4.84481300
H	0.31713800	0.12127500	3.30113300
C	1.12417400	-3.51328700	4.39533700
H	0.24350300	-4.09527500	2.50829500
C	1.47369600	-2.44619400	5.23905200
H	1.44191600	-0.29708700	5.49296300
H	1.34421700	-4.53804500	4.69094000
H	1.96431600	-2.63873200	6.19161600
C	-1.99882600	-2.19605800	1.73651900
H	-2.44812600	-1.62352000	2.55554700
H	-2.62082500	-2.09646500	0.84451000
H	-1.96466500	-3.25281900	2.02560300

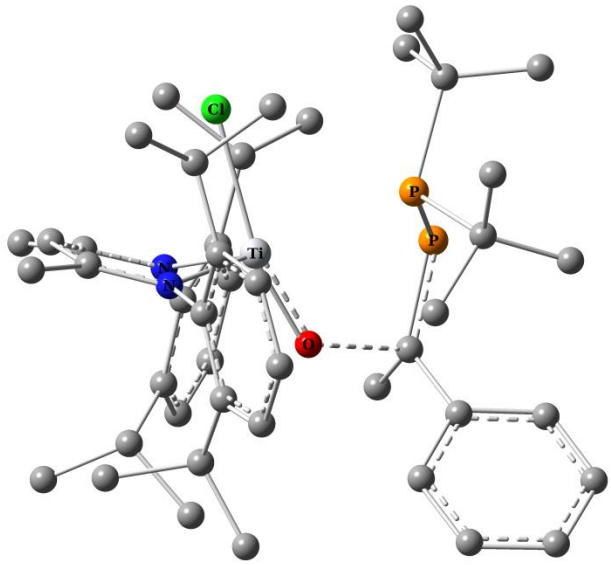


Figure S209. Optimized structure of ***Z*-3i$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3i$_{TS2}$**:

C	-3.21316100	-0.03810900	-0.35964500
C	-3.60958000	-1.17791500	-1.10669200
C	-4.70410800	-1.92077100	-0.62969500
H	-5.03545600	-2.79576700	-1.18324400
C	-5.36613500	-1.56962400	0.55355300
H	-6.20783500	-2.16508100	0.90369700
C	-4.93111900	-0.46622200	1.29148900
H	-5.43359300	-0.20950300	2.22363300
C	-3.85272400	0.32149700	0.85148100
C	-2.87416200	-1.58896500	-2.38013200
H	-1.80537500	-1.40545300	-2.19600000
C	-3.02859400	-3.08593700	-2.69877200
H	-2.37889000	-3.34505000	-3.54298000
H	-2.73931200	-3.70594500	-1.84133700
H	-4.05823500	-3.33776100	-2.98987100
C	-3.27400200	-0.74117200	-3.60762600
H	-2.77219800	-1.13375600	-4.50137600
H	-4.35996600	-0.77779300	-3.77474100
H	-2.96010400	0.30040200	-3.49413200
C	-3.40161500	1.51307000	1.69335900
H	-2.56655900	1.99935700	1.17519600
C	-2.88830700	1.04932400	3.07313800
H	-2.62113000	1.91701500	3.69025300
H	-3.65743900	0.47913700	3.61137900
H	-2.00158300	0.41799100	2.96076400
C	-4.53117100	2.55067800	1.88079000
H	-4.94136000	2.88683400	0.92143500
H	-5.35850900	2.13023900	2.46845500
H	-4.14962900	3.42950600	2.41759700
C	1.52999100	2.56985500	0.24428800
C	1.57800000	2.65610600	1.66251600
C	2.82874200	2.85024900	2.26983300
H	2.89447500	2.90922300	3.35315600
C	3.99779000	2.96874000	1.50829900
H	4.95809500	3.10593700	2.00278400
C	3.92599500	2.92115000	0.11553800
H	4.83401700	3.03134700	-0.47546000
C	2.69896600	2.73182300	-0.54659300
C	0.30023800	2.58869800	2.49218900
H	-0.29420300	1.75531700	2.09178800
C	0.56473500	2.33107900	3.98706300
H	-0.38038200	2.11160700	4.49842600

H	1.24262200	1.48378800	4.14035400
H	1.00488700	3.21330700	4.47303200
C	-0.52825800	3.88770300	2.34269600
H	-1.41686800	3.84276200	2.98625300
H	0.06760500	4.75994700	2.64421100
H	-0.86984500	4.03775100	1.31402400
C	2.67800900	2.72800000	-2.07148700
H	1.63770300	2.66086300	-2.40798200
C	3.39475800	1.48386900	-2.62382700
H	3.33004500	1.45806800	-3.71873600
H	4.45536300	1.47804200	-2.33505500
H	2.91386400	0.57886000	-2.23999700
C	3.31195700	4.01172200	-2.65425800
H	3.16804200	4.03607500	-3.74241200
H	2.87165200	4.91978300	-2.22467300
H	4.39268600	4.04287400	-2.46071600
C	-3.97283600	2.17219400	-1.86813400
H	-4.50755700	2.74007800	-1.09641700
H	-3.99603100	2.76257000	-2.79135500
H	-4.50677100	1.23226600	-2.02337500
C	-2.52827200	1.95157800	-1.45011200
C	-1.66380700	3.04987500	-1.63026800
H	-2.08890400	3.90265300	-2.15444500
C	-0.40474600	3.26077800	-1.04684200
C	0.15814800	4.66704500	-1.13164000
H	-0.64824900	5.40055300	-1.02424300
H	0.91511400	4.84795200	-0.36328200
H	0.62315700	4.82205700	-2.11371600
C	-0.48769700	-2.24717400	1.40344800
C	1.89157300	-2.72078200	-2.58261400
C	2.59019400	-4.07751800	-2.34442300
H	3.62277700	-3.96352700	-1.99719600
H	2.03870400	-4.68736400	-1.61759800
H	2.62149900	-4.62487500	-3.29882400
C	0.53263100	-3.00286600	-3.26396700
H	-0.05309900	-2.08620400	-3.38296100
H	0.73743900	-3.41416900	-4.26448900
H	-0.05905600	-3.73800800	-2.70818000
C	3.22655500	-1.83886500	0.12602300
C	3.06454000	-0.69933400	1.15475800
H	2.16010700	-0.80947800	1.75635000
H	3.93063600	-0.69893100	1.83348000
H	3.02810000	0.27530800	0.65369100
C	4.48473100	-1.53018100	-0.71259000
H	4.72600500	-2.32800900	-1.42313000
H	4.40065500	-0.58358400	-1.25372900
H	5.33295400	-1.44012500	-0.01643400
Cl	0.08148200	0.48162800	-3.00444500
N	-2.15175800	0.80490300	-0.85179000
N	0.26577500	2.28752600	-0.39523500
O	-0.30124300	-0.31570900	0.97999900
P	-0.11549500	-2.97381200	-0.19470500
P	1.59372700	-1.79954200	-0.91397600
Ti	-0.15220100	0.30652000	-0.62266500
C	3.42975800	-3.18557700	0.84242100
H	3.63429500	-3.99821900	0.13803100
H	4.29129900	-3.09746200	1.52251400
H	2.55701900	-3.45736900	1.43826000
C	2.72129100	-1.85647600	-3.55756600
H	2.18316500	-0.93760500	-3.80900200
H	3.70864400	-1.59684500	-3.16605800
H	2.87041300	-2.43368900	-4.48290200
C	0.35419300	-2.31722500	2.64415400
C	0.49231900	-1.23705600	3.53483600
C	0.86838600	-3.57398700	3.02545400
C	1.16644900	-1.39532000	4.75115800
H	0.09494000	-0.27247300	3.23712800
C	1.53409600	-3.73467700	4.24819300

H	0.73210900	-4.42164800	2.35515400
C	1.69410600	-2.64389000	5.11344800
H	1.27904700	-0.54183600	5.41821500
H	1.92987300	-4.71239900	4.51861600
H	2.21817600	-2.76527000	6.05988700
C	-1.95704300	-2.38830700	1.77653800
H	-2.24278100	-1.58829500	2.46634400
H	-2.61150100	-2.37092200	0.90329400
H	-2.08810300	-3.33967500	2.31355400

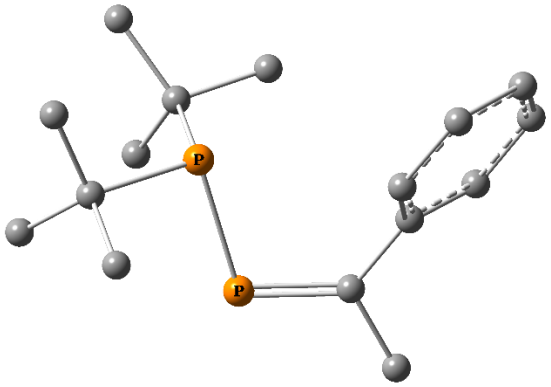


Figure S210. Optimized structure of ***Z*-3i**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3i**:

C	2.95083100	0.11804800	2.18617700
C	2.13664300	-0.61612200	1.31754600
C	2.30964300	-0.52808800	-0.08046700
C	3.33152800	0.31016000	-0.57862400
C	4.13041300	1.06202700	0.29085300
C	3.94424100	0.96771800	1.67759700
H	2.80582500	0.02940900	3.26139800
H	4.89851500	1.71828600	-0.11493700
C	1.45901400	-1.31090400	-1.00971200
P	-0.24976000	-1.36463200	-1.10575400
P	-0.95158700	0.13293000	0.40743500
C	-1.26555300	1.63637100	-0.75985200
C	0.13748800	2.27094200	-0.90968000
C	-1.81610500	1.33019800	-2.16654000
C	-2.19491900	2.63701900	-0.04388700
H	0.57486600	2.52092800	0.06484500
H	0.82629900	1.59020900	-1.42532200
H	0.05986700	3.19236500	-1.50698500
H	-2.81260900	0.87908400	-2.13613400
H	-1.88674400	2.26930900	-2.73761700
H	-1.15158800	0.65231400	-2.71804600
H	-2.19196200	3.59111800	-0.59292200
H	-3.23029500	2.27661600	-0.01291100
H	-1.86248700	2.83550400	0.98369000
C	-2.61680200	-0.71074100	0.86943000
C	-3.23662400	0.08438800	2.04201400
C	-3.65011400	-0.87284300	-0.25982300
C	-2.22138900	-2.10752300	1.40602300
H	-2.51709400	0.20130900	2.86254800
H	-3.57095300	1.08151900	1.73628800
H	-4.11287500	-0.45926200	2.42750900
H	-3.22458400	-1.39318800	-1.12722000
H	-4.50443500	-1.46430300	0.10538300
H	-4.03948200	0.09723400	-0.59126000
H	-3.10588900	-2.59339300	1.84490300
H	-1.83954100	-2.75795200	0.60759300
H	-1.45167500	-2.03242900	2.18649300
H	1.36651700	-1.27328800	1.71213600

H	3.47859400	0.39853700	-1.65377600
H	4.57046200	1.54581300	2.35467400
C	2.21453600	-2.15792900	-2.01992100
H	1.53175700	-2.72433100	-2.66344700
H	2.84755100	-1.52619900	-2.66050800
H	2.88518800	-2.85600900	-1.49839200

E.3.13. Reaction of **1** with acetophenone leading to ***E*-3i**

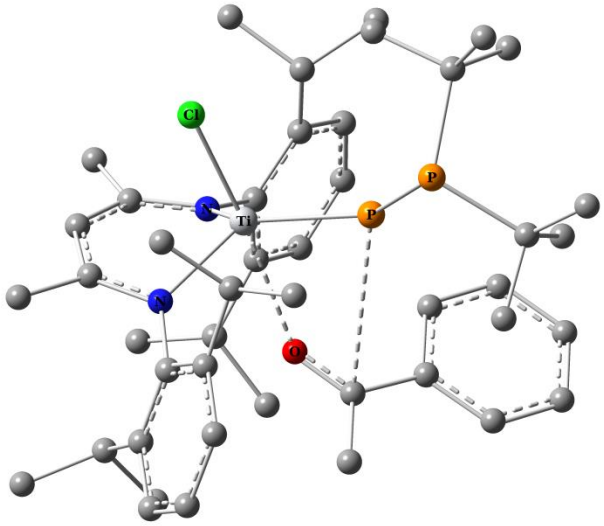


Figure S211. Optimized structure of ***E*-3i$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3i$_{TS1}$**:

C	-0.80386500	-2.82156400	-0.68075500
C	0.38841700	-3.44022400	-1.14154700
C	0.74394800	-4.67930600	-0.58208100
H	1.64960900	-5.17597700	-0.92184900
C	-0.04380400	-5.28946100	0.40068000
H	0.24539200	-6.25618400	0.81019500
C	-1.18641000	-4.64016900	0.87314300
H	-1.77337000	-5.09941300	1.66623500
C	-1.58057600	-3.39020000	0.36295700
C	1.26574700	-2.78320300	-2.20082600
H	1.27741300	-1.70247600	-1.97527100
C	2.72922100	-3.25340600	-2.14011100
H	3.34096800	-2.63104400	-2.80314600
H	3.13183600	-3.16805700	-1.12325900
H	2.83740700	-4.29544400	-2.47295400
C	0.70674000	-2.95187300	-3.62835000
H	1.40229100	-2.51018400	-4.35318600
H	0.57136900	-4.01460800	-3.87314900
H	-0.25011600	-2.43451700	-3.74029400
C	-2.78531700	-2.67351800	0.97090000
H	-2.71101300	-1.61687900	0.68785400
C	-2.75671700	-2.75408000	2.51322000
H	-3.54774300	-2.12394300	2.93640800
H	-2.93336300	-3.77939600	2.86506000
H	-1.79285100	-2.41953200	2.91112700
C	-4.12986200	-3.23264900	0.45319500
H	-4.23833100	-3.10499100	-0.62837600
H	-4.21620700	-4.30446600	0.67993300
H	-4.96569200	-2.71285100	0.94129200
C	-2.32432000	2.36346500	-0.09137300
C	-3.47577800	2.34364700	0.74007500
C	-3.70112800	3.44261400	1.58966600
H	-4.58024400	3.44128200	2.23317500
C	-2.81154800	4.51795600	1.64108900

H	-3.00030600	5.35527200	2.31086800
C	-1.66943500	4.50870300	0.83043800
H	-0.97609300	5.34484900	0.87659600
C	-1.40555200	3.44487000	-0.04584300
C	-4.44893800	1.16801500	0.79429900
H	-4.12288100	0.40948700	0.07376900
C	-4.42565800	0.50990400	2.19056900
H	-5.10350000	-0.35399400	2.21350800
H	-3.41612400	0.16800100	2.43557700
H	-4.75269000	1.21693100	2.96500200
C	-5.89082000	1.59110800	0.43380000
H	-6.54662600	0.71057700	0.40476900
H	-6.29468400	2.28455800	1.18380100
H	-5.93776800	2.08960400	-0.54088500
C	-0.19927700	3.48025600	-0.97515900
H	0.25312700	2.46373100	-0.99859200
C	0.92751600	4.40630900	-0.49088600
H	1.81629600	4.25516600	-1.11171700
H	0.63051700	5.46255400	-0.56148700
H	1.20617200	4.18473700	0.54564600
C	-0.62545900	3.85471900	-2.41003300
H	0.23900200	3.81588300	-3.08334700
H	-1.38042600	3.16306700	-2.79621100
H	-1.04082400	4.87198500	-2.42025000
C	-2.76054600	-2.85884400	-2.77122500
H	-2.42725900	-3.74481100	-2.22581400
H	-3.85239400	-2.87118700	-2.85655700
H	-2.34740500	-2.91062700	-3.78790300
C	-2.28489300	-1.57274500	-2.11503700
C	-2.96206900	-0.39311300	-2.48702500
H	-3.69180300	-0.51418900	-3.28546500
C	-2.91763900	0.89825200	-1.91633600
C	-3.88994500	1.91582000	-2.48607600
H	-4.89526700	1.49080200	-2.58314600
H	-3.93486200	2.82288300	-1.87887700
H	-3.54514600	2.18865600	-3.49363300
C	-0.50383900	0.15306400	2.49003500
C	4.54913600	0.76865200	-1.59638000
C	5.19746800	-0.53297200	-1.09714000
H	5.93507000	-0.34298800	-0.30775700
H	4.43968300	-1.22414500	-0.70980000
H	5.72256200	-1.02845500	-1.92960200
C	3.68442500	0.47003700	-2.83819500
H	3.18522400	1.37394800	-3.20913200
H	4.32588200	0.07397800	-3.64113500
H	2.90314900	-0.26263600	-2.61184600
C	4.14420100	1.58596900	1.41615400
C	3.18871800	2.45958000	2.26262800
H	2.17635900	2.03409900	2.25686300
H	3.54479600	2.49398500	3.30417000
H	3.13660200	3.48632500	1.87776100
C	5.53456800	2.25289700	1.39151100
H	6.28201100	1.61279700	0.90718900
H	5.51273400	3.22021100	0.87135600
H	5.87105000	2.43017300	2.42485000
Cl	0.17401900	0.61469900	-3.31979600
N	-1.22981200	-1.57608800	-1.26343100
N	-2.04298200	1.25052600	-0.94453700
O	-0.99768500	-0.11245600	1.37733200
P	1.68028200	0.28831600	-0.05717100
P	3.36403300	1.63451100	-0.35192900
Ti	-0.28521700	0.21498400	-1.13883700
C	4.23646300	0.19618400	2.07440000
H	4.94012800	-0.46251800	1.55598500
H	4.57923900	0.30698700	3.11552500
H	3.25464000	-0.29196400	2.08752000
C	5.63650100	1.78941800	-2.00690100
H	5.18373400	2.72171900	-2.36893100

H	6.31579000	2.03473800	-1.18354700
H	6.24015100	1.36329100	-2.82348000
C	0.50243100	-0.74765700	3.09910900
C	1.08299100	-0.48090300	4.35788700
C	0.92597400	-1.87986800	2.36787900
C	2.05893900	-1.33575100	4.88005300
H	0.77936300	0.39558200	4.92625500
C	1.89802400	-2.73477200	2.89355800
H	0.48264000	-2.07094800	1.39655900
C	2.46617000	-2.46353900	4.14800800
H	2.50623000	-1.12291000	5.84917100
H	2.21521300	-3.60289900	2.31965700
H	3.22931100	-3.12553200	4.55451200
C	-0.88873400	1.43441500	3.20039900
H	-1.26537700	1.23325100	4.21230800
H	-0.00396300	2.07861800	3.29797200
H	-1.64867800	1.96045600	2.62044600

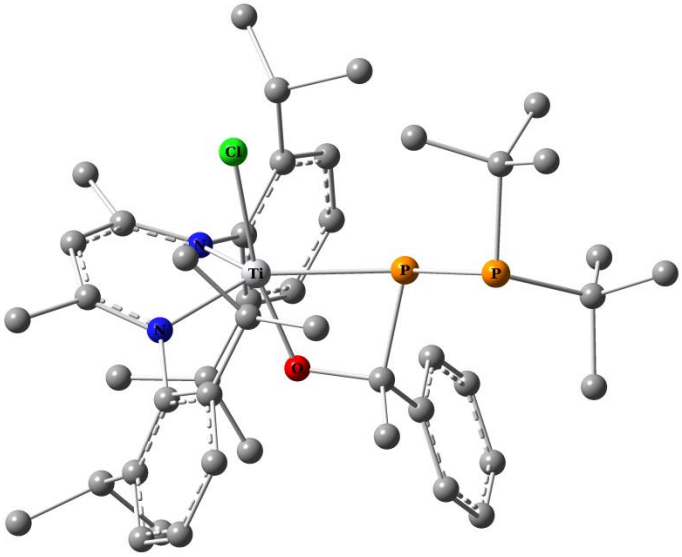


Figure S212. Optimized structure of ***E*-3i$_{I}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3i$_{I}$**:

C	-1.03988500	-2.66711600	-0.99992700
C	-0.08537600	-3.29389800	-1.83875800
C	0.41649600	-4.54721900	-1.44342500
H	1.15949400	-5.03957000	-2.06932800
C	-0.02732900	-5.17115400	-0.27531900
H	0.36881300	-6.14497800	0.00921700
C	-0.97839500	-4.53798300	0.53252700
H	-1.30606100	-5.02129900	1.44952900
C	-1.49182900	-3.27371100	0.20169200
C	0.40189100	-2.67475900	-3.14391300
H	-0.15827800	-1.74865000	-3.31415400
C	1.89625400	-2.29508000	-3.05761700
H	2.20735900	-1.77778600	-3.97443400
H	2.07814900	-1.63154600	-2.20468800
H	2.52061000	-3.19171900	-2.93619800
C	0.15861400	-3.61506300	-4.34615400
H	0.41832400	-3.10092200	-5.28092500
H	0.78064500	-4.51774000	-4.27655000
H	-0.88861000	-3.93781400	-4.40686300
C	-2.50866800	-2.57924600	1.10248100
H	-2.30653300	-1.50384600	1.02800800
C	-2.36538600	-2.98546900	2.58154900
H	-3.02828900	-2.36979400	3.20023400
H	-2.65242500	-4.03386300	2.74443700

H	-1.33857300	-2.84620400	2.93581200
C	-3.95640800	-2.83650400	0.62240800
H	-4.12685700	-2.44901200	-0.38836400
H	-4.17912100	-3.91247800	0.62063100
H	-4.66983700	-2.34088700	1.29506500
C	-2.31964600	2.49386800	0.25391500
C	-3.30248300	2.39936400	1.26941300
C	-3.41853600	3.46324200	2.18185600
H	-4.16900100	3.40704700	2.96916900
C	-2.57192200	4.57134900	2.11435300
H	-2.67655400	5.38577200	2.82920600
C	-1.56315000	4.61515500	1.14459100
H	-0.88156900	5.46164600	1.12328400
C	-1.40707800	3.57989800	0.20960100
C	-4.14205600	1.14447600	1.48416200
H	-3.98413200	0.46649400	0.63672200
C	-3.64127800	0.42210400	2.75615300
H	-4.22329000	-0.49280500	2.92595700
H	-2.58313100	0.15706500	2.65760200
H	-3.75995300	1.06773800	3.63691900
C	-5.65368600	1.43660500	1.59746900
H	-6.21260200	0.49425900	1.66713600
H	-5.87913200	2.02382700	2.49764600
H	-6.03173400	1.99634500	0.73261900
C	-0.29447900	3.63186200	-0.83373800
H	0.13244500	2.61041300	-0.93577500
C	0.88609600	4.53330400	-0.43047900
H	1.68884400	4.43603300	-1.16966200
H	0.58866200	5.59053800	-0.40678000
H	1.29711400	4.25800800	0.54768900
C	-0.83838500	4.04455100	-2.21651300
H	-0.02992200	4.04376500	-2.95731400
H	-1.60728000	3.34904800	-2.56681800
H	-1.26855900	5.05397900	-2.15904400
C	-3.12516500	-2.41234800	-2.92782400
H	-2.53135200	-2.52239500	-3.84543500
H	-3.01512000	-3.33612900	-2.35092800
H	-4.17368100	-2.27732200	-3.21035600
C	-2.61618800	-1.21554900	-2.15166000
C	-3.29090900	0.01344200	-2.34086300
H	-4.08613900	-0.00611500	-3.08174000
C	-3.17513900	1.21700900	-1.61481600
C	-4.23218500	2.27905600	-1.84186400
H	-5.05172000	2.16655800	-1.12121200
H	-3.81432900	3.28265800	-1.71081000
H	-4.65123000	2.18151200	-2.84868100
C	0.77356300	0.16059100	1.59785100
C	4.28076700	1.56941700	-1.47372600
C	4.98982700	0.29737900	-1.97540600
H	5.89552400	0.06728000	-1.40330600
H	4.31975000	-0.56975800	-1.93554600
H	5.29048600	0.44623700	-3.02454900
C	3.13368900	1.88374700	-2.45172800
H	2.50084500	2.70635400	-2.09789500
H	3.55459400	2.17267100	-3.42719200
H	2.48985600	1.01381700	-2.60517600
C	4.69571800	0.43275500	1.39761800
C	4.17805800	0.60963900	2.84309900
H	3.21156900	0.11577200	2.98644000
H	4.88937300	0.14128400	3.54077600
H	4.08195200	1.67027600	3.11112200
C	6.10857200	1.05251000	1.33232800
H	6.59691600	0.88019700	0.36688700
H	6.08399600	2.13394000	1.52427900
H	6.73548800	0.58707200	2.10832500
Cl	-0.01768900	0.85473700	-3.06138300
N	-1.55468500	-1.35668100	-1.33169500
N	-2.19446900	1.43407300	-0.71008300

O	-0.52476300	0.00201800	0.96122500
P	1.81223400	0.07190600	-0.02228000
P	3.50488700	1.48676800	0.28520300
Ti	-0.52576100	0.31829000	-0.86733300
C	4.75748000	-1.07646200	1.09376700
H	5.16623000	-1.28853500	0.10172000
H	5.40219400	-1.56665500	1.84053000
H	3.76102400	-1.53013500	1.15602100
C	5.25715800	2.77098700	-1.48103300
H	4.74237900	3.69364900	-1.18328700
H	6.11268300	2.62771200	-0.81295300
H	5.64654100	2.90895600	-2.50159500
C	0.98356600	-1.02726400	2.53248700
C	0.90159000	-0.90008300	3.93145800
C	1.23207700	-2.30229400	1.98893400
C	1.08897700	-2.01257500	4.76601500
H	0.70303100	0.07044900	4.38046400
C	1.42072400	-3.41336500	2.81767500
H	1.28156100	-2.41383500	0.90661300
C	1.35562100	-3.27242900	4.21246900
H	1.03042300	-1.89095600	5.84667400
H	1.61256000	-4.38730200	2.37130300
H	1.50796900	-4.13468400	4.85977500
C	0.75555200	1.52587600	2.28615000
H	-0.08692100	1.57912000	2.98898300
H	1.69052400	1.72882000	2.81801000
H	0.61643900	2.30580600	1.53281500

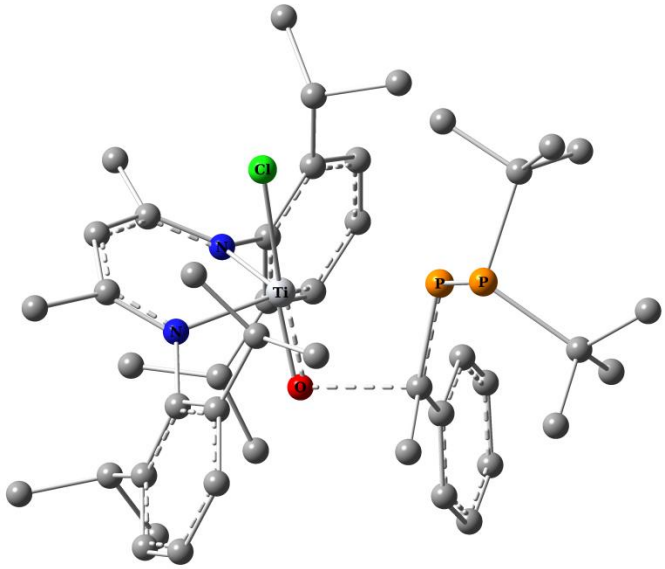


Figure S213. Optimized structure of ***E*-3i$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3i$_{TS2}$**.

C	-2.13803000	-2.18331800	-0.72456100
C	-1.50549400	-3.26492400	-1.39132100
C	-1.63947200	-4.55225500	-0.83753500
H	-1.15826200	-5.39299400	-1.33550400
C	-2.38133500	-4.76940500	0.32449100
H	-2.47842100	-5.77484500	0.73226600
C	-2.99714100	-3.68928000	0.96756000
H	-3.56148000	-3.86408400	1.88018300
C	-2.88314000	-2.38255800	0.46931500
C	-0.70781100	-3.09830000	-2.67946000
H	-0.73761100	-2.04261000	-2.97287200
C	0.77362400	-3.47121200	-2.45854900
H	1.35279100	-3.27177800	-3.36880200

H	1.20469800	-2.88448000	-1.63945500
H	0.87791800	-4.53705400	-2.20996200
C	-1.29590600	-3.94941300	-3.82843800
H	-0.76839900	-3.72598500	-4.76507400
H	-1.17862000	-5.02268700	-3.62477300
H	-2.36506900	-3.75568300	-3.97813800
C	-3.55605200	-1.21216400	1.17608800
H	-2.89855200	-0.34456600	1.03737100
C	-3.70885800	-1.44932000	2.68943200
H	-4.07334200	-0.53673800	3.17438500
H	-4.43573000	-2.24475000	2.90718800
H	-2.74968200	-1.71911100	3.14416500
C	-4.92823600	-0.89062000	0.53982600
H	-4.82928300	-0.61057200	-0.51496100
H	-5.59999700	-1.75773900	0.60577800
H	-5.40087500	-0.05034800	1.06643800
C	-1.04672800	3.09980500	-0.11826100
C	-2.02885500	3.47935800	0.83004000
C	-1.75464600	4.56949000	1.67448600
H	-2.50559000	4.88165800	2.39936100
C	-0.53267900	5.24237300	1.61226300
H	-0.33541600	6.08468300	2.27360500
C	0.44857100	4.81377800	0.71052500
H	1.40777500	5.32473900	0.68720900
C	0.22146400	3.73671200	-0.16295500
C	-3.33806000	2.71767200	1.00142500
H	-3.32701600	1.86009800	0.31862900
C	-3.44438200	2.16608100	2.43938400
H	-4.37943300	1.60373500	2.55835400
H	-2.60123500	1.50091600	2.65569500
H	-3.44959600	2.98003800	3.17678100
C	-4.56714100	3.59035700	0.66479800
H	-5.48750100	2.99726500	0.75174200
H	-4.64581900	4.44010700	1.35676600
H	-4.51075600	3.99120000	-0.35378100
C	1.30465000	3.28599100	-1.14015700
H	1.34216200	2.18129600	-1.12766300
C	2.71235000	3.78325900	-0.76913500
H	3.44875600	3.29619800	-1.41697900
H	2.79967800	4.87060900	-0.90682500
H	2.97628300	3.53856100	0.26719800
C	0.96941300	3.70165700	-2.58850700
H	1.77186600	3.38071600	-3.26397300
H	0.04568000	3.22952700	-2.93202300
H	0.86535100	4.79384100	-2.65351100
C	-3.72660700	-1.31738900	-2.94777900
H	-3.18834600	-1.75554300	-3.79873500
H	-4.05342200	-2.13781600	-2.30079800
H	-4.60162700	-0.78588100	-3.33494800
C	-2.80436000	-0.36597800	-2.21403000
C	-2.83712500	0.98880500	-2.60044100
H	-3.50231300	1.21870600	-3.42961200
C	-2.23324200	2.10730900	-1.98428600
C	-2.66458400	3.47429800	-2.48391600
H	-2.23045100	3.63352900	-3.48094600
H	-3.75446600	3.52796300	-2.58363000
H	-2.31863400	4.27582400	-1.82673200
C	1.09384100	-0.25361800	1.70212900
C	4.49610000	-0.89144800	-1.47088700
C	4.65207600	-2.36396200	-1.04097200
H	5.36393100	-2.49319600	-0.21826200
H	3.68880200	-2.78594300	-0.72837400
H	5.01972200	-2.95139600	-1.89682900
C	3.50250700	-0.82422600	-2.64619400
H	3.36152000	0.20324700	-3.00037300
H	3.89495100	-1.42850900	-3.47866900
H	2.51605400	-1.21386100	-2.38255800
C	4.84653100	0.05259000	1.49645200

C	4.83754700	1.42461500	2.21788200
H	3.83511600	1.77773600	2.46511200
H	5.41038400	1.34626400	3.15502100
H	5.31299200	2.18934500	1.59028200
C	6.33268700	-0.21756700	1.16982800
H	6.49928200	-1.19633600	0.71062200
H	6.75308800	0.55851700	0.51941100
H	6.89559200	-0.19570700	2.11574600
Cl	0.44963500	0.30466200	-2.88121600
N	-2.00959900	-0.83625400	-1.23171600
N	-1.32462100	1.99647000	-1.00089700
O	-0.75520600	0.34158700	1.04879300
P	1.89834600	-0.90380500	0.21106900
P	3.78532200	0.31043300	-0.12731000
Ti	-0.38990200	0.21460400	-0.63061100
C	4.34554700	-1.06553400	2.42968800
H	4.33178000	-2.03633600	1.92034800
H	5.01783700	-1.13996100	3.29904800
H	3.33504300	-0.88029200	2.80868800
C	5.83798700	-0.32697400	-1.99944200
H	5.75925200	0.74813700	-2.20911300
H	6.67619600	-0.48893200	-1.31793800
H	6.07711600	-0.83758800	-2.94452900
C	0.46165500	-1.24373000	2.62254100
C	0.08328400	-0.86580400	3.93046100
C	0.26373200	-2.58725900	2.23285200
C	-0.43794200	-1.80555100	4.82703100
H	0.19902500	0.16465400	4.25483900
C	-0.28159200	-3.51842700	3.11887500
H	0.54563900	-2.89742600	1.22821800
C	-0.62182900	-3.13680000	4.42624700
H	-0.70785600	-1.49484700	5.83488900
H	-0.43570000	-4.54304400	2.78801000
H	-1.03024000	-3.86731200	5.12254800
C	1.42260900	1.10798300	2.27376800
H	0.51278800	1.58562900	2.65055000
H	2.13257300	1.00142200	3.10412500
H	1.85974600	1.75503700	1.50806800

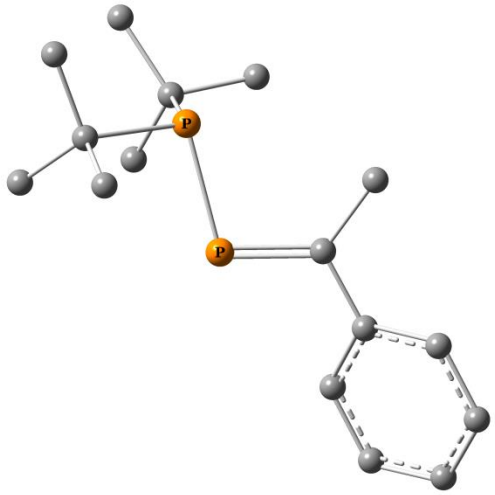


Figure S214. Optimized structure of ***E*-3i**.

Below are presented xyz coordinates for optimized geometry of ***E*-3i**:

C	-4.49558700	0.07540800	1.61193800
C	-3.17662700	0.15969300	1.15843400
C	-2.85383100	-0.04546800	-0.20578800
C	-3.92038600	-0.30688300	-1.09952400
C	-5.24080200	-0.39139400	-0.64425300

C	-5.53679500	-0.20350100	0.71339200
H	-4.71351100	0.24436000	2.66509200
H	-6.03943600	-0.60590900	-1.35243500
C	-1.44730200	0.01293800	-0.67928400
P	-0.22894500	-0.47625100	0.43568400
P	1.67309900	-0.05297000	-0.65398500
C	2.13314200	1.64551500	0.14127700
C	1.29925200	2.66589500	-0.66915300
C	1.80002600	1.82366100	1.63574600
C	3.63127800	1.92255000	-0.09597900
H	1.52587700	2.60877300	-1.74145300
H	0.22300000	2.49636700	-0.53184200
H	1.52703700	3.68438000	-0.31985600
H	2.35251400	1.12651800	2.27281300
H	2.06353300	2.84744100	1.94450100
H	0.72807400	1.68071000	1.82424800
H	3.84909300	2.97360000	0.14803200
H	4.26446500	1.29664200	0.54431400
H	3.91458500	1.75085800	-1.14284900
C	2.75267800	-1.45521800	0.09248700
C	4.10636500	-1.45796400	-0.65517500
C	2.99073900	-1.40532900	1.61255000
C	2.01267200	-2.76612800	-0.26658200
H	3.95667600	-1.50714100	-1.74125900
H	4.70620000	-0.56912900	-0.43222200
H	4.68834900	-2.34045600	-0.34818300
H	2.04584000	-1.35774400	2.16840800
H	3.52613000	-2.31384900	1.92976400
H	3.60751800	-0.54418300	1.89636900
H	2.65234900	-3.62463700	-0.01223000
H	1.07158200	-2.86783800	0.29003500
H	1.78408800	-2.81569300	-1.33978900
H	-2.37702700	0.40858300	1.85383400
H	-3.71589700	-0.47044900	-2.15475800
H	-6.56550300	-0.26072900	1.06428800
C	-1.24223700	0.45825700	-2.11052200
H	-1.74435800	-0.23455700	-2.80182100
H	-1.68724100	1.45091900	-2.27069700
H	-0.18178200	0.48926800	-2.37519000

E.3.14. Reaction of **1** with cyclopropyl methyl ketone leading to ***Z*-3j**

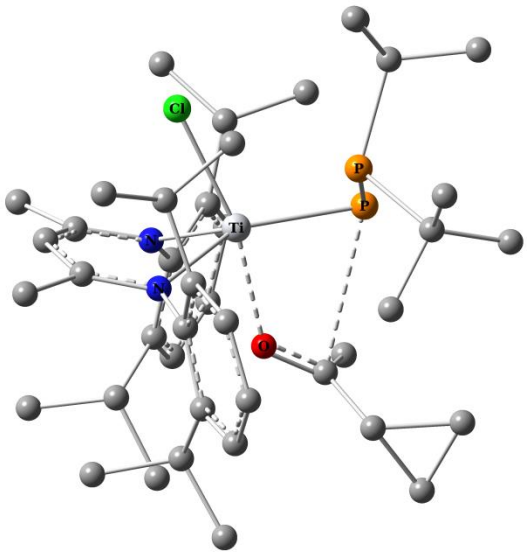


Figure S215. Optimized structure of ***Z*-3j$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3j$_{TS1}$**:

C	3.13777400	0.50134600	-0.51721500
C	3.50835500	1.86592800	-0.39506500
C	4.69290500	2.16731000	0.30360500
H	4.99885300	3.20722300	0.40237200
C	5.48780900	1.16146600	0.86193100
H	6.40476500	1.41926100	1.38986300
C	5.09852700	-0.17787500	0.74180900
H	5.71763800	-0.95697000	1.18509200
C	3.91798400	-0.53409100	0.06944300
C	2.70423800	2.98823900	-1.04418800
H	1.70260800	2.59924200	-1.27172900
C	2.53188800	4.20719900	-0.11786100
H	1.86467100	4.93583100	-0.59500800
H	2.08355500	3.91496600	0.83877000
H	3.48974600	4.71028000	0.07536500
C	3.35305700	3.43062400	-2.37594700
H	2.74135800	4.20948500	-2.84971400
H	4.35811600	3.83941800	-2.19911100
H	3.44484300	2.59541900	-3.07746300
C	3.50623000	-2.00314000	-0.02812500
H	2.45496600	-2.02720800	-0.33876300
C	3.61712700	-2.73945300	1.32342600
H	3.26518000	-3.77288200	1.21249800
H	4.65509100	-2.78304400	1.67937000
H	3.00909700	-2.25922000	2.09778900
C	4.34455000	-2.75652400	-1.08660900
H	4.24823900	-2.30143100	-2.07713700
H	5.40865300	-2.75048400	-0.81189100
H	4.01369800	-3.80159200	-1.15738900
C	-1.66797700	-2.20994900	-0.62196200
C	-1.45487800	-3.16828300	0.40695500
C	-2.57885800	-3.78169100	0.98753900
H	-2.43844300	-4.50643300	1.78639100
C	-3.87654200	-3.49346000	0.55017400
H	-4.73304200	-3.96991000	1.02451100
C	-4.05990400	-2.61707600	-0.52105200
H	-5.06516400	-2.42732600	-0.89550000
C	-2.97080700	-1.97606600	-1.13883700
C	-0.04517500	-3.60117500	0.80608600
H	0.57184700	-2.69698600	0.84742500
C	0.02147900	-4.30794700	2.17461200
H	1.06902600	-4.41172400	2.48445700
H	-0.51265000	-3.75627400	2.95854500
H	-0.40938800	-5.31790300	2.12641800
C	0.56690300	-4.54097000	-0.26144500
H	1.53763800	-4.92167200	0.08428100
H	-0.09182900	-5.40072100	-0.44484700
H	0.73287900	-4.02131700	-1.20926300
C	-3.23431500	-1.11527800	-2.37168100
H	-2.27464500	-0.75020200	-2.75429600
C	-4.07639000	0.12474700	-2.03282800
H	-4.23061500	0.73817400	-2.92961600
H	-5.06173100	-0.15997600	-1.63681700
H	-3.55257200	0.73115200	-1.28781800
C	-3.94206900	-1.93306400	-3.47900500
H	-3.99360200	-1.34180200	-4.40306200
H	-3.42511600	-2.87483500	-3.69686900
H	-4.97098000	-2.18009400	-3.18376500
C	3.28839400	-0.17596800	-3.29859100
H	3.51872200	-1.02885900	-3.94567400
H	3.05963100	0.68355400	-3.94467800
H	4.16932300	0.07579000	-2.70105000
C	2.07071000	-0.45203600	-2.43685300
C	1.09708300	-1.30356100	-2.96150800
H	1.29959700	-1.68706000	-3.95945400
C	-0.04354300	-1.86705500	-2.33283100
C	-0.66887100	-3.00654700	-3.12631700
H	0.11667900	-3.66293900	-3.51805800

H	-1.36752600	-3.59923400	-2.53173500
H	-1.20897100	-2.58983600	-3.98653500
C	1.19691000	-0.31528300	2.42207700
C	-2.57910200	3.60840200	-0.15678700
C	-3.10721600	4.48894400	0.99410100
H	-4.03380500	4.10717400	1.43599700
H	-2.35346600	4.59262700	1.78458800
H	-3.32146800	5.49249500	0.59436500
C	-1.36024700	4.33798800	-0.76082000
H	-0.87749700	3.74844400	-1.54486100
H	-1.71019200	5.28757700	-1.19566900
H	-0.61740000	4.56209700	0.01334400
C	-3.16507000	1.27398300	1.89993100
C	-2.77719200	-0.20684700	2.07679800
H	-1.69831300	-0.30025200	2.24099900
H	-3.30035000	-0.62935700	2.94896600
H	-3.04382600	-0.79840700	1.19639200
C	-4.65300400	1.34321000	1.50029300
H	-5.01008400	2.37140700	1.37497700
H	-4.84346300	0.79339500	0.57213000
H	-5.25635700	0.87761600	2.29510100
Cl	-0.50277300	1.44187200	-2.48253200
N	1.94220700	0.12775700	-1.21965700
N	-0.54493200	-1.47179400	-1.15128000
O	0.96848200	-0.65206600	1.22784500
P	-0.04765400	2.12318400	1.27680700
P	-2.00060000	1.87284300	0.48133300
Ti	0.08292400	0.49659500	-0.41593000
C	-2.92217100	2.00859800	3.23255100
H	-3.26917800	3.04600300	3.20917200
H	-3.46617500	1.48778600	4.03705800
H	-1.85165200	2.01009400	3.47599200
C	-3.65442900	3.44349500	-1.24970200
H	-3.24450400	2.90949400	-2.11373900
H	-4.53701600	2.90145900	-0.88908600
H	-3.98436500	4.43971100	-1.58341800
C	2.35181300	0.58631400	2.77129200
H	3.23264200	-0.04953500	2.95111200
H	2.58441100	1.25060300	1.93789700
H	2.15623300	1.17170900	3.67515300
C	0.41331500	-0.95166800	3.48864800
C	0.99781200	-1.15189300	4.89448200
C	-0.04530400	-0.10895700	4.69074400
H	-0.29256400	-1.69362500	3.13121200
H	2.02607600	-0.83650700	5.05464800
H	0.72215000	-2.08469600	5.38108900
H	-1.06377100	-0.30283400	5.01639500
H	0.24085300	0.93950300	4.68189400

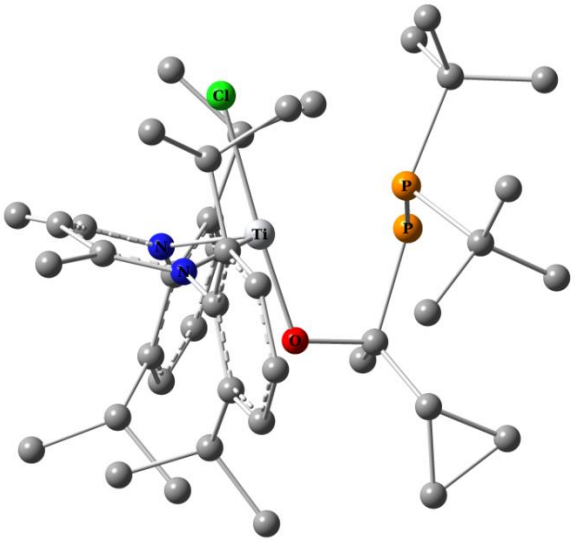


Figure S216. Optimized structure of ***Z*-3jI**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3jI**:

C	-3.22408800	-0.11888800	-0.55899600
C	-3.62913500	-1.45862500	-0.79537400
C	-4.83677700	-1.88971300	-0.21978700
H	-5.17434200	-2.90946000	-0.38938600
C	-5.59989600	-1.03947300	0.58934700
H	-6.52866500	-1.39717400	1.03105800
C	-5.15501400	0.26001200	0.84817600
H	-5.73695700	0.90672300	1.50405500
C	-3.96268000	0.74703600	0.28534000
C	-2.77102000	-2.41107600	-1.62340600
H	-1.71946000	-2.15186900	-1.42259600
C	-2.93587200	-3.88331100	-1.20791400
H	-2.18571700	-4.49106000	-1.72806100
H	-2.78750300	-4.00890500	-0.12814500
H	-3.92535800	-4.27855000	-1.47721800
C	-2.98890500	-2.23994700	-3.14087600
H	-2.39678900	-2.98502900	-3.68723200
H	-4.04826500	-2.37527900	-3.40128700
H	-2.65903900	-1.25230400	-3.47826300
C	-3.48905400	2.15683700	0.63317000
H	-2.55799500	2.34843100	0.08647800
C	-3.17486200	2.27150600	2.14175400
H	-2.90141200	3.30490800	2.39210400
H	-4.05051400	2.00101100	2.74781200
H	-2.34036400	1.61647100	2.40833400
C	-4.52379200	3.23321100	0.23438000
H	-4.79595800	3.17158500	-0.82613300
H	-5.44627600	3.12956900	0.82172900
H	-4.11513900	4.23446500	0.42469600
C	1.79303600	2.21502000	-0.33118800
C	1.69050600	2.89649200	0.90696200
C	2.86410800	3.41090100	1.48446200
H	2.80408600	3.93171400	2.43778800
C	4.10448100	3.27497800	0.85233800
H	5.00343900	3.67700800	1.31701800
C	4.18065200	2.62673900	-0.38338600
H	5.14429300	2.53278700	-0.88238100
C	3.03665700	2.09267900	-1.00365100
C	0.33158500	3.14544600	1.55073000
H	-0.31805200	2.30675700	1.27945300
C	0.39497400	3.20506500	3.08789200
H	-0.62103300	3.22075700	3.50034500
H	0.91253400	2.32868200	3.49527400
H	0.90966800	4.10861900	3.44369100

C	-0.28976000	4.44454700	0.98542300
H	-1.26006800	4.64270000	1.45979400
H	0.36769100	5.30420700	1.17578900
H	-0.45236700	4.37069100	-0.09627300
C	3.18371800	1.41715100	-2.36354600
H	2.18424600	1.18283600	-2.74797300
C	3.92530000	0.07721100	-2.21536700
H	3.99075500	-0.43776900	-3.18224800
H	4.94451600	0.23310000	-1.83357300
H	3.37845500	-0.56655300	-1.51881000
C	3.91896100	2.31351400	-3.38590400
H	3.87891500	1.85225000	-4.38146900
H	3.48056600	3.31677700	-3.44972000
H	4.97769700	2.43158500	-3.11805600
C	-3.50153400	1.34384000	-2.92969600
H	-4.13427900	2.07929100	-2.41762200
H	-3.34818500	1.68772800	-3.95819900
H	-4.04517400	0.39485500	-2.93679600
C	-2.16379900	1.21595100	-2.22673600
C	-1.13080300	2.06457800	-2.63795200
H	-1.35265700	2.68931800	-3.50002800
C	0.07233700	2.38366200	-1.96271700
C	0.75112900	3.64299200	-2.48364900
H	-0.00883800	4.37910600	-2.76704900
H	1.42789900	4.08808700	-1.75091500
H	1.33174300	3.40217500	-3.38338900
C	-0.74305400	-0.98095400	2.13618400
C	2.21407300	-3.51366000	-0.67848200
C	2.66843700	-4.60258300	0.31705600
H	3.64053800	-4.39276000	0.77311100
H	1.92414300	-4.73775100	1.11177200
H	2.76032300	-5.55292900	-0.23045200
C	0.94292100	-4.05799200	-1.37249800
H	0.49811600	-3.32936300	-2.05391700
H	1.24295300	-4.94329500	-1.95445000
H	0.18830400	-4.37350500	-0.64351200
C	3.22646700	-1.56625600	1.58241000
C	3.15826600	-0.05241700	1.88505000
H	2.13679100	0.31301400	2.02020300
H	3.73175400	0.17116600	2.79689800
H	3.58937500	0.52100800	1.05922300
C	4.65024500	-1.83686500	1.04521200
H	4.84294700	-2.89609500	0.84824700
H	4.85354100	-1.26538800	0.13290600
H	5.36888200	-1.50624800	1.81089600
Cl	0.32405900	-0.95931000	-2.67498100
N	-2.02236800	0.37773200	-1.17830900
N	0.58812000	1.68561900	-0.93176600
O	-0.70502500	0.17389400	1.26268000
P	-0.11237200	-2.40489600	1.01091600
P	1.86685000	-1.83104900	0.24144600
Ti	-0.21310800	-0.24539000	-0.48817100
C	2.98384900	-2.40144400	2.85486700
H	3.16772400	-3.46628400	2.68201800
H	3.67445100	-2.06226800	3.64307100
H	1.95903600	-2.29447400	3.22128800
C	3.27901700	-3.28291100	-1.77115600
H	2.89506900	-2.60375600	-2.53966300
H	4.21512100	-2.87511100	-1.37579100
H	3.50712900	-4.24839700	-2.24790900
C	-2.20998300	-1.36920100	2.39707700
H	-2.77223100	-0.51130200	2.77963300
H	-2.69253200	-1.70400900	1.47586400
H	-2.26317700	-2.19102200	3.12133300
C	-0.00259000	-0.65374700	3.42091800
C	-0.70092400	-0.09729400	4.64973500
C	-0.12515900	-1.49776400	4.67138700
H	0.98636800	-0.24445000	3.24877700

H	-1.78346300	0.00268400	4.63544900
H	-0.18604500	0.68350100	5.20597000
H	0.78069600	-1.67976800	5.24672700
H	-0.82187600	-2.33349100	4.66225200

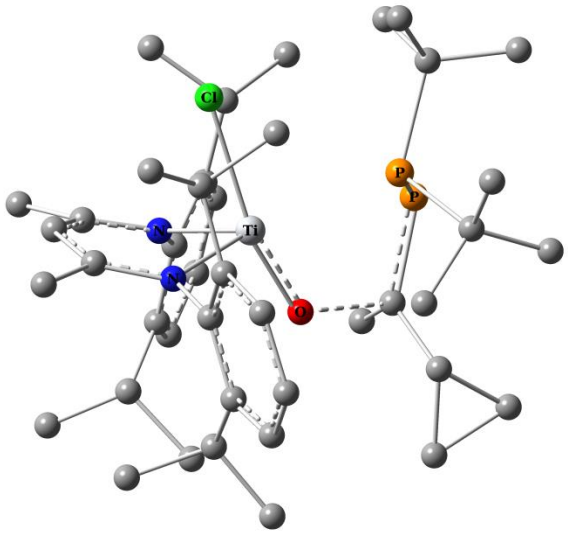


Figure S217. Optimized structure of ***Z*-3j$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3j$_{TS2}$**:

C	3.07511900	-0.08833800	-0.62847300
C	3.52904300	1.20230200	-1.00569000
C	4.76318700	1.63611300	-0.49056600
H	5.13974500	2.61776200	-0.76710300
C	5.51274400	0.83780900	0.38251500
H	6.46431100	1.19901300	0.76962400
C	5.02852700	-0.41502300	0.76563600
H	5.60367600	-1.02556700	1.46122400
C	3.80664700	-0.90383300	0.26952700
C	2.71168700	2.08965800	-1.94109100
H	1.65711800	1.94803300	-1.66386600
C	3.02813200	3.58528600	-1.77107700
H	2.32737900	4.17428200	-2.37443800
H	2.92348800	3.89602600	-0.72408000
H	4.04240100	3.83137800	-2.11614400
C	2.84934800	1.68204600	-3.42457200
H	2.30218100	2.39722000	-4.05215700
H	3.90344500	1.68098500	-3.73696400
H	2.41616400	0.69485500	-3.60954500
C	3.30485000	-2.26979600	0.73380200
H	2.36895700	-2.48896500	0.20613200
C	2.99278300	-2.25112300	2.24620700
H	2.71085400	-3.25564100	2.58780600
H	3.87187700	-1.93564800	2.82516600
H	2.16357500	-1.56825400	2.45892300
C	4.31512200	-3.39658700	0.42221500
H	4.59010800	-3.41726800	-0.63893700
H	5.23870100	-3.27123200	1.00349100
H	3.88319900	-4.37162300	0.68436600
C	-1.90095600	-2.28342600	-0.15993100
C	-1.79179500	-2.82164300	1.14989100
C	-2.97402200	-3.13866400	1.83816700
H	-2.91267700	-3.54535600	2.84484800
C	-4.23006200	-2.94527100	1.25203800
H	-5.13457200	-3.19494100	1.80456300
C	-4.31834900	-2.43153200	-0.04346800
H	-5.29674100	-2.28227000	-0.49772900

C	-3.16654600	-2.08958900	-0.77535600
C	-0.42683600	-3.10614800	1.76256300
H	0.25178700	-2.31870300	1.41414000
C	-0.44226300	-3.06426000	3.30077900
H	0.58263200	-3.12296400	3.68519600
H	-0.88883400	-2.13032400	3.66206600
H	-1.00181200	-3.90758400	3.72914800
C	0.10966200	-4.46717300	1.26035500
H	1.08918000	-4.68009200	1.70867000
H	-0.57695200	-5.28025700	1.53366500
H	0.23090600	-4.46972700	0.17098000
C	-3.32903400	-1.50449600	-2.17353200
H	-2.33866700	-1.40904000	-2.63267600
C	-3.90803800	-0.08012900	-2.08123100
H	-3.97622500	0.37291100	-3.07795100
H	-4.91063700	-0.09324100	-1.63029600
H	-3.25087800	0.55000200	-1.47204100
C	-4.21944600	-2.38465800	-3.07852600
H	-4.20900300	-1.99205800	-4.10358100
H	-3.87883700	-3.42739700	-3.10253800
H	-5.26233900	-2.38451200	-2.73367700
C	3.32436700	-1.72498200	-2.86357400
H	3.86272300	-2.56327300	-2.40348200
H	3.15396400	-1.97701500	-3.91659300
H	3.96243100	-0.84081600	-2.79918300
C	1.98575400	-1.51931900	-2.17328500
C	0.95931400	-2.40905100	-2.55266100
H	1.19854400	-3.07592700	-3.37751900
C	-0.24054700	-2.68281100	-1.87776800
C	-1.00636100	-3.91932800	-2.30641800
H	-0.31683700	-4.67129600	-2.70336000
H	-1.57373100	-4.34975100	-1.47533000
H	-1.71950500	-3.66258400	-3.10012500
C	0.92125000	1.51107200	2.19648100
C	-1.82329300	3.64234600	-0.93020700
C	-2.22673900	4.88425300	-0.10380600
H	-3.19848000	4.77085200	0.38782600
H	-1.47190300	5.11274300	0.65918600
H	-2.30015900	5.74608600	-0.78441300
C	-0.53745200	4.00042400	-1.71007800
H	-0.14183500	3.13446900	-2.24909700
H	-0.79712100	4.77785200	-2.44525300
H	0.24011000	4.40066700	-1.05115500
C	-2.93149500	1.97270600	1.49914200
C	-2.93179800	0.47864700	1.90588000
H	-1.93785100	0.08543400	2.13777300
H	-3.58128500	0.33207300	2.78191600
H	-3.32927500	-0.13285300	1.08769000
C	-4.32716900	2.25092200	0.89774700
H	-4.47044300	3.29865200	0.61522300
H	-4.53316500	1.61713000	0.02955600
H	-5.07695600	2.01056800	1.66768100
Cl	-0.55707000	0.64815100	-2.71977200
N	1.85355900	-0.60906900	-1.18994500
N	-0.69288000	-1.91673700	-0.86280700
O	0.44050000	-0.06437500	1.19153000
P	0.45146000	2.80815000	1.02306700
P	-1.47497700	2.14073300	0.22916900
Ti	-0.01251000	-0.03616100	-0.48075000
C	-2.72708000	2.91135800	2.70778100
H	-2.91123500	3.95449200	2.42763300
H	-3.44258700	2.64125800	3.50028700
H	-1.71361100	2.86026100	3.11629700
C	-2.91143600	3.29852700	-1.96981500
H	-2.57660400	2.47939500	-2.61388900
H	-3.86849400	3.02737100	-1.51542900
H	-3.07941300	4.18630500	-2.59839900
C	2.43285000	1.45508200	2.33830600

H	2.76514500	0.41785700	2.42652900
H	2.93446100	1.90282700	1.47764700
H	2.75033600	1.98803100	3.24633400
C	0.16822900	1.14154000	3.42974500
C	0.78392200	0.35415500	4.57018500
C	0.50389900	1.82564000	4.75482300
H	-0.89001700	0.97764700	3.28033700
H	1.82246800	0.04454100	4.48138400
H	0.14290100	-0.36294700	5.07815100
H	-0.33836000	2.13089800	5.37254500
H	1.34739200	2.51238600	4.77310400

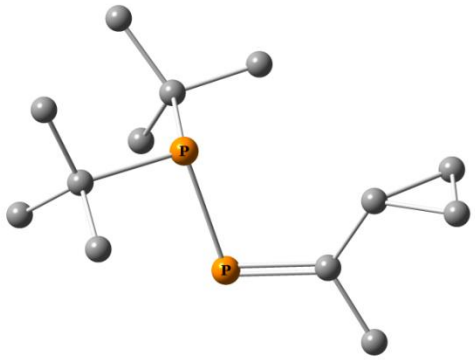


Figure S218. Optimized structure of ***Z*-3j**.

Below are presented xyz coordinates for optimized geometry of ***Z*-3j**:

C	-2.18833400	-0.65029300	0.51988600
P	-0.59282000	-0.84730200	1.12170900
P	0.67845800	-0.01540900	-0.52067400
C	1.08041300	1.72237800	0.21106000
C	-0.16942500	2.56238700	-0.14497400
C	1.29813600	1.79698300	1.73539300
C	2.30374200	2.31324900	-0.51836400
H	-0.34472300	2.57979300	-1.22851800
H	-1.06811100	2.16342900	0.34324700
H	-0.02581400	3.59765700	0.20017900
H	2.16931700	1.21992600	2.06000100
H	1.46012200	2.84701100	2.02595000
H	0.42124600	1.42691600	2.28189200
H	2.39446900	3.38167100	-0.26921000
H	3.23451100	1.82220100	-0.20954200
H	2.20742900	2.22538800	-1.60871400
C	2.19541300	-1.18082900	-0.35385200
C	3.15579400	-0.88179400	-1.52841300
C	2.96172400	-1.12349600	0.98016100
C	1.63103100	-2.60730300	-0.55737400
H	2.62919400	-0.93093200	-2.49006100
H	3.62171500	0.10576600	-1.44336700
H	3.96125900	-1.63221100	-1.53894000
H	2.29430700	-1.28211700	1.83662100
H	3.72933400	-1.91308000	0.99669700
H	3.47536300	-0.16326200	1.11000600
H	2.46639100	-3.31940800	-0.63616300
H	0.99739100	-2.91720900	0.28385200
H	1.03564300	-2.67431200	-1.47799800
C	-3.30009100	-1.13836600	1.42977700
H	-2.90565200	-1.46595000	2.39779600
H	-4.04706100	-0.35118300	1.61167700
H	-3.82602100	-1.98716100	0.96850400
C	-2.57535500	-0.05821100	-0.77732500
C	-3.91952200	-0.35286800	-1.44318600
C	-3.67749600	1.00857100	-0.86119700

H	-1.74175400	0.10726300	-1.45847500
H	-4.61476000	-1.01025300	-0.92639600
H	-3.90528600	-0.46875700	-2.52484100
H	-3.48584300	1.84552500	-1.52918200
H	-4.19339300	1.27151700	0.05988900

E.3.15. Reaction **1** with cyclopropyl methyl ketone leading to ***E*-3j**

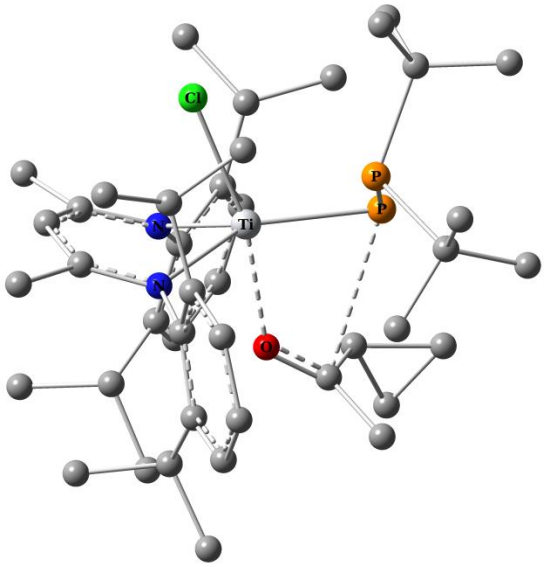


Figure S219. Optimized structure of ***E*-3j$_{TS1}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3j$_{TS1}$**:

C	-3.04797800	-0.13778000	-0.72382600
C	-3.51771100	-1.47484200	-0.80096000
C	-4.76610900	-1.76946300	-0.22058900
H	-5.14790600	-2.78731700	-0.27518900
C	-5.52840200	-0.78296600	0.41270300
H	-6.49553300	-1.03367000	0.84604300
C	-5.04190600	0.52745000	0.48974400
H	-5.63650200	1.29047800	0.99077400
C	-3.79563500	0.87337200	-0.05778900
C	-2.74774900	-2.56603300	-1.53852900
H	-1.70858300	-2.22913200	-1.65249600
C	-2.72381000	-3.89981500	-0.76775000
H	-2.07554300	-4.61238100	-1.29287200
H	-2.32507800	-3.76315800	0.24412100
H	-3.72472100	-4.34867000	-0.69973300
C	-3.32980500	-2.78958300	-2.95326900
H	-2.74042800	-3.54804300	-3.48489600
H	-4.37016000	-3.13953400	-2.89224500
H	-3.31533300	-1.86943300	-3.54591700
C	-3.27958300	2.30762200	0.05962100
H	-2.20987300	2.28997500	-0.18046100
C	-3.43512100	2.87727900	1.48525900
H	-3.00712900	3.88672800	1.52980200
H	-4.49020100	2.95525000	1.77969500
H	-2.91691300	2.26008200	2.22720900
C	-3.98853000	3.24774300	-0.94253800
H	-3.85385400	2.91274900	-1.97557900
H	-5.06727400	3.28864800	-0.73647900
H	-3.58356700	4.26534100	-0.85805100
C	1.92567100	2.19244500	-0.18511400
C	1.70611800	3.02946900	0.94345800
C	2.82543600	3.47908200	1.66571300
H	2.67858400	4.10794000	2.54098600

C	4.12816600	3.14940100	1.27513000
H	4.97948100	3.49699000	1.85825800
C	4.32664300	2.40095500	0.11339400
H	5.34058500	2.18315200	-0.22014200
C	3.24278800	1.92598600	-0.64709800
C	0.30437900	3.51552200	1.30793600
H	-0.37378700	2.66270500	1.19490900
C	0.18968100	4.05048800	2.74928600
H	-0.86762300	4.19444000	3.00524100
H	0.62883400	3.36704100	3.48700700
H	0.69022000	5.02294900	2.85773400
C	-0.16615600	4.62400000	0.33461700
H	-1.13079800	5.03166100	0.66637600
H	0.56050000	5.44726300	0.30386700
H	-0.29988600	4.23978200	-0.68048800
C	3.53344300	1.20688200	-1.96190000
H	2.58054000	0.96597600	-2.44623600
C	4.26377700	-0.12593900	-1.73435800
H	4.43878900	-0.63359100	-2.69141900
H	5.23585000	0.03185700	-1.24551800
H	3.64906300	-0.77830500	-1.10690600
C	4.37098400	2.09924900	-2.90956000
H	4.44721000	1.62470700	-3.89704600
H	3.93553600	3.09729100	-3.03579100
H	5.39095100	2.22891200	-2.52264500
C	-2.95656000	0.88804200	-3.39905000
H	-3.08259800	1.82948400	-3.94402100
H	-2.74163900	0.10021100	-4.13503200
H	-3.89232000	0.63195800	-2.89383000
C	-1.78657200	0.96197300	-2.43612700
C	-0.72309500	1.79539800	-2.78645200
H	-0.82855300	2.31373500	-3.73733800
C	0.40603200	2.18840800	-2.02199000
C	1.16125100	3.36649300	-2.62270400
H	0.45139800	4.12411900	-2.97414600
H	1.85488800	3.82620100	-1.91527100
H	1.73103800	3.01961400	-3.49468500
C	-1.26770200	0.15887900	2.40920500
C	2.40605100	-3.69103600	-0.41671200
C	2.79117300	-4.74482400	0.64159500
H	3.70811600	-4.49222400	1.18473100
H	1.97844400	-4.88795100	1.36460600
H	2.96459200	-5.70454400	0.13005900
C	1.18609700	-4.24548100	-1.18291100
H	0.80064800	-3.52845700	-1.91273000
H	1.50068100	-5.15778000	-1.71396900
H	0.37721800	-4.50656600	-0.49086700
C	3.00262800	-1.68046300	1.95492400
C	2.70437100	-0.20774400	2.29658000
H	1.62541900	-0.05364700	2.40512400
H	3.19232300	0.06257500	3.24616700
H	3.07164100	0.46624100	1.51747200
C	4.50686800	-1.81259200	1.64146600
H	4.80147800	-2.84151800	1.40712400
H	4.79885800	-1.16820800	0.80506300
H	5.08298500	-1.49616700	2.52492400
Cl	0.64969200	-1.10180900	-2.56733700
N	-1.78346400	0.22791200	-1.29797700
N	0.79523900	1.61299200	-0.87260000
O	-0.93363900	0.62253400	1.28438600
P	-0.11358100	-2.20658300	1.03833000
P	1.90289700	-2.00888700	0.40257900
Ti	-0.01449900	-0.37781300	-0.43611300
C	2.61751700	-2.55376000	3.16470800
H	2.89431500	-3.60364600	3.02946600
H	3.13762300	-2.17939100	4.06123200
H	1.53489400	-2.50400000	3.34000000
C	3.56422200	-3.47434600	-1.41153400

H	3.25311400	-2.80791100	-2.22321900
H	4.45393000	-3.04977600	-0.93094500
H	3.84862900	-4.44377400	-1.84970500
C	-0.45795300	0.45070400	3.64523700
H	0.31493700	-0.32868800	3.73292600
H	0.04752600	1.41297800	3.55332100
H	-1.07196800	0.43380800	4.55110800
C	-2.37104800	-0.80861600	2.46543100
C	-2.42689800	-1.88973400	3.55454100
C	-3.37205400	-0.74164000	3.63120500
H	-2.78745700	-1.05584300	1.49485900
H	-1.59802500	-1.93046200	4.25722100
H	-2.79915700	-2.85754100	3.22641100
H	-4.41025200	-0.88573700	3.34433900
H	-3.20453000	0.04119400	4.36628300

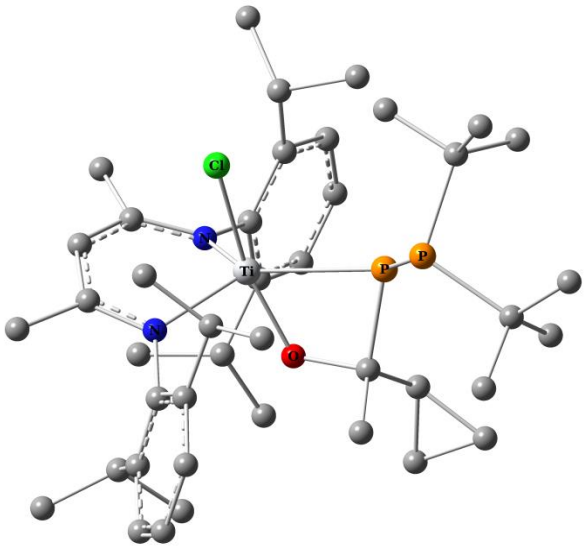


Figure S220. Optimized structure of ***E*-3j$_I$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3j$_I$**:

C	-2.16128000	-2.47004300	0.12108400
C	-1.59613100	-3.71313500	-0.25277600
C	-1.81009400	-4.81898300	0.59068200
H	-1.37892700	-5.78126200	0.31831700
C	-2.55756400	-4.70421800	1.76303700
H	-2.71489900	-5.57253100	2.40098200
C	-3.09519700	-3.46279300	2.12243400
H	-3.66439600	-3.37789700	3.04488600
C	-2.90617400	-2.32444400	1.32176300
C	-0.74565700	-3.89788300	-1.50306900
H	-0.73545900	-2.95400200	-2.06076500
C	0.71021600	-4.22365400	-1.10316000
H	1.34550000	-4.28375000	-1.99548800
H	1.11329900	-3.45194300	-0.43671700
H	0.76088800	-5.18852500	-0.57937400
C	-1.29631100	-5.00400800	-2.43092700
H	-0.70950500	-5.03841100	-3.35810400
H	-1.22802100	-5.99134400	-1.95433900
H	-2.34813900	-4.83584700	-2.69455600
C	-3.48918100	-0.97497800	1.73346900
H	-2.75459000	-0.21389900	1.43986200
C	-3.70458100	-0.87200700	3.25540800
H	-3.95151600	0.15974100	3.52950300
H	-4.53673000	-1.50697700	3.59034100
H	-2.80292700	-1.16424600	3.80455200
C	-4.82166700	-0.67465000	1.00684900

H	-4.68944400	-0.59604200	-0.07745400
H	-5.55925700	-1.46302300	1.21079400
H	-5.23564200	0.27940200	1.36103100
C	-1.05452600	2.86639900	-0.72968100
C	-1.97079000	3.52668700	0.12452700
C	-1.64507700	4.81792500	0.57663300
H	-2.33818500	5.33985900	1.23519400
C	-0.44395600	5.43043600	0.21404500
H	-0.20946400	6.43185100	0.57128500
C	0.47139400	4.74013400	-0.58916700
H	1.41909300	5.20918300	-0.84113900
C	0.19619200	3.44761000	-1.06432900
C	-3.23854900	2.85869900	0.64536600
H	-3.35676300	1.89259600	0.14040800
C	-3.08256100	2.57803000	2.15701400
H	-3.99617800	2.11623600	2.55268400
H	-2.23805200	1.90424800	2.33648100
H	-2.91172900	3.51269300	2.70819600
C	-4.50801700	3.70034800	0.39087800
H	-5.39857500	3.13965800	0.70412000
H	-4.48468900	4.63666600	0.96435100
H	-4.62279900	3.96267000	-0.66818200
C	1.21464700	2.69592700	-1.91638000
H	1.24463700	1.64616400	-1.56436300
C	2.64874500	3.23300000	-1.77322200
H	3.34212600	2.54696000	-2.27036600
H	2.75048300	4.22454900	-2.23730100
H	2.95381500	3.30172200	-0.72226900
C	0.80662900	2.67268200	-3.40451700
H	1.55733800	2.12828700	-3.98975200
H	-0.15293400	2.16810300	-3.55192600
H	0.73431100	3.69970100	-3.78905900
C	-3.80425000	-2.17598400	-2.15489700
H	-3.25592400	-2.92926800	-2.73510000
H	-4.23026100	-2.68343600	-1.28273300
H	-4.61086600	-1.77634200	-2.77634600
C	-2.85143700	-1.07586000	-1.73551200
C	-2.92854300	0.14511900	-2.44155700
H	-3.63414600	0.15241800	-3.26822300
C	-2.34018300	1.39613600	-2.14886200
C	-2.87751300	2.60612400	-2.88710000
H	-3.70792500	3.05495300	-2.32755600
H	-2.10539800	3.37261700	-3.00564900
H	-3.25632900	2.30705500	-3.87003300
C	0.76671200	0.36259400	1.83943200
C	4.39751200	-1.55915000	-0.93595400
C	4.51562800	-2.74423300	0.03970800
H	5.27788700	-2.57452500	0.80940100
H	3.55616500	-2.93550400	0.53735400
H	4.80144200	-3.65028200	-0.51776000
C	3.39508200	-1.92139300	-2.04903200
H	3.29329900	-1.10876800	-2.77790900
H	3.75224300	-2.81968700	-2.57641000
H	2.40054800	-2.13504300	-1.65088600
C	4.77630100	0.44142900	1.42444300
C	4.66729600	1.97099300	1.63827100
H	3.63293800	2.31449900	1.70736200
H	5.18487200	2.25206100	2.56888800
H	5.14090500	2.50794300	0.80612100
C	6.27588900	0.14964200	1.20254000
H	6.49115300	-0.92232200	1.14339700
H	6.66033300	0.64132400	0.30026400
H	6.83279100	0.55130500	2.06356600
Cl	0.41391100	-0.65886500	-2.78631500
N	-1.99148300	-1.29875900	-0.71374500
N	-1.37279400	1.55171400	-1.22207700
O	-0.48388800	0.36258400	1.10692300
P	1.73871100	-0.72290400	0.55229500

P	3.73188700	0.08780400	-0.17072200
Ti	-0.35794300	-0.11184400	-0.68142600
C	4.30255900	-0.32320100	2.67122900
H	4.39655000	-1.40645500	2.53524600
H	4.91234800	-0.03081600	3.54162500
H	3.25548300	-0.11354500	2.90296100
C	5.74995600	-1.28622600	-1.63823700
H	5.69607700	-0.38275700	-2.26047700
H	6.58530600	-1.17909900	-0.94200500
H	5.97627700	-2.13755700	-2.29847900
C	1.15978400	1.82454900	2.03255500
H	0.30544800	2.37841500	2.44425900
H	2.00829200	1.92837700	2.71550400
H	1.41830600	2.28014000	1.07186400
C	0.52165800	-0.40926300	3.13078300
C	1.23684000	-0.11992900	4.43614900
C	-0.23008700	0.21392000	4.29372800
H	0.29765700	-1.45930600	2.94357100
H	1.93275100	0.71509700	4.47890200
H	1.52711500	-0.97203800	5.04752100
H	-0.95852200	-0.40307800	4.81427900
H	-0.50142500	1.26535000	4.22423100

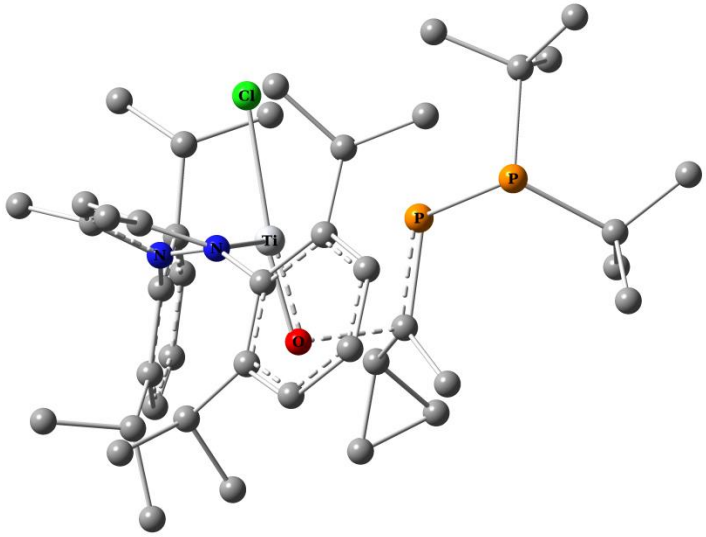


Figure S221. Optimized structure of ***E*-3j$_{TS2}$**.

Below are presented xyz coordinates for optimized geometry of ***E*-3j$_{TS2}$**.

C	-2.79125400	-1.72688900	-0.28913500
C	-2.47579000	-2.98972700	-0.85303500
C	-2.87943800	-4.14566700	-0.15701200
H	-2.63232300	-5.12268800	-0.56991400
C	-3.59890700	-4.06009600	1.03527800
H	-3.90854100	-4.96552700	1.55538100
C	-3.93146300	-2.80314800	1.55769600
H	-4.50087800	-2.74776100	2.48250600
C	-3.52942400	-1.61769500	0.92299500
C	-1.75673600	-3.14664900	-2.18785900
H	-1.57937200	-2.14870600	-2.60276700
C	-0.37631300	-3.81431600	-2.01345300
H	0.13477700	-3.87337700	-2.98296300
H	0.25933400	-3.23665400	-1.33219000
H	-0.47846800	-4.83333800	-1.61299500
C	-2.61516300	-3.94938200	-3.19240200
H	-2.13084000	-3.94931900	-4.17773100
H	-2.72803600	-4.99489700	-2.87416600
H	-3.62090400	-3.52387200	-3.30007700

C	-3.87680000	-0.25145600	1.50832700
H	-2.98230300	0.37192700	1.37690000
C	-4.21173000	-0.30635100	3.01023000
H	-4.36350900	0.71021000	3.39097900
H	-5.14113000	-0.86199800	3.19831900
H	-3.40565400	-0.76865500	3.59034400
C	-5.05404800	0.41747300	0.75933400
H	-4.81973900	0.60566000	-0.29254200
H	-5.95275000	-0.21262500	0.80907800
H	-5.28810400	1.38475400	1.22503200
C	-0.18107800	3.04802400	-0.15961600
C	-0.84453500	3.70655100	0.90446700
C	-0.16588500	4.73901800	1.57479800
H	-0.66242200	5.25697000	2.39450800
C	1.13413700	5.09937800	1.21562600
H	1.64613800	5.90236300	1.74365700
C	1.78710300	4.41111100	0.18655900
H	2.80709200	4.68500500	-0.06902300
C	1.15641900	3.37076800	-0.51766000
C	-2.23244200	3.29833800	1.38405100
H	-2.60727800	2.51082200	0.71916800
C	-2.13722400	2.70770300	2.80890800
H	-3.13710000	2.45069400	3.18029100
H	-1.51818800	1.80431300	2.80210800
H	-1.69829400	3.43740400	3.50280400
C	-3.23428500	4.47375700	1.36047000
H	-4.23647600	4.11837300	1.63481200
H	-2.94754400	5.25330900	2.07914000
H	-3.29543300	4.94077000	0.36977900
C	1.89295400	2.62975900	-1.63459300
H	1.72569600	1.54970700	-1.48178400
C	3.41414700	2.86014400	-1.61123200
H	3.88669100	2.20161900	-2.35004200
H	3.66585700	3.89489200	-1.88524100
H	3.84567500	2.62685600	-0.63169700
C	1.34705900	2.97197900	-3.03860900
H	1.95800700	2.47099900	-3.80003500
H	0.32026700	2.62195900	-3.17130100
H	1.39133800	4.05624100	-3.21399700
C	-4.16161000	-0.62595500	-2.56211100
H	-3.76920700	-1.23008500	-3.39153000
H	-4.66619600	-1.30283300	-1.86506100
H	-4.88572300	0.08629700	-2.97014300
C	-3.00849000	0.09537000	-1.89708700
C	-2.71506600	1.40185000	-2.33984800
H	-3.34582500	1.77620800	-3.14195900
C	-1.80954600	2.33532500	-1.79257400
C	-1.96696200	3.78238300	-2.21836000
H	-2.66635300	4.29583000	-1.54594800
H	-1.01523800	4.31989600	-2.18068800
H	-2.37734000	3.83123800	-3.23244100
C	0.80787600	-1.04781700	1.81844400
C	4.30719400	-1.31188900	-1.33851800
C	4.47922100	-2.83186300	-1.14109000
H	5.25197600	-3.08308900	-0.40667900
H	3.53601100	-3.29367600	-0.82257700
H	4.77318800	-3.28627000	-2.10025200
C	3.27709200	-1.09653300	-2.46327700
H	3.05581300	-0.03541800	-2.62417000
H	3.68198900	-1.50546000	-3.40181300
H	2.32748100	-1.60135600	-2.26200500
C	4.70729100	-0.93058300	1.72941200
C	4.69095700	0.24267400	2.74167000
H	3.69050800	0.51066900	3.08259200
H	5.28698100	-0.03333200	3.62560200
H	5.14015100	1.13847300	2.29395300
C	6.19572000	-1.09849700	1.34662500
H	6.37682600	-1.95105500	0.68598100

H	6.59680500	-0.19214500	0.87649500
H	6.76659900	-1.27073000	2.27227700
Cl	0.14548800	-0.29432900	-2.78239800
N	-2.32290900	-0.51042500	-0.91055700
N	-0.87388000	2.00778100	-0.88132800
O	-0.65138900	0.18744500	1.23173000
P	1.68788500	-1.48726300	0.29577700
P	3.64408700	-0.33478200	0.20150500
Ti	-0.42031600	0.07061700	-0.47282300
C	4.21686100	-2.23551400	2.38221800
H	4.26999700	-3.07621800	1.68151000
H	4.84844700	-2.47104800	3.25372900
H	3.17906500	-2.16607000	2.72454100
C	5.62980900	-0.66265400	-1.81368300
H	5.52095500	0.42510600	-1.91028600
H	6.47625000	-0.86695200	-1.15380700
H	5.87833000	-1.06766300	-2.80653900
C	1.28338100	-0.06662400	2.85738800
H	0.44468000	0.28380400	3.46680400
H	2.01987000	-0.54852700	3.51413200
H	1.75109700	0.79636800	2.37568000
C	-0.09620100	-2.15051100	2.24967400
C	0.29708100	-2.96426300	3.49072700
C	-0.94099600	-2.10496200	3.50042300
H	-0.49010100	-2.75025800	1.42913000
H	1.15635700	-2.62690700	4.06608000
H	0.19879200	-4.04456300	3.41221800
H	-1.90855800	-2.59481200	3.43881100
H	-0.92398700	-1.19660000	4.09805100

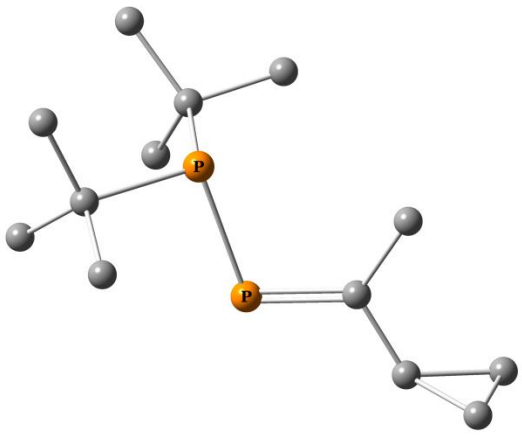


Figure S222. Optimized structure of ***E*-3j**.

Below are presented xyz coordinates for optimized geometry of ***E*-3j**:

C	-2.17675600	-0.12616400	-0.12142900
P	-0.77556600	-0.47936400	0.80789500
P	0.89936800	-0.03470000	-0.60208000
C	1.47775000	1.67091700	0.08713000
C	0.48087400	2.67171500	-0.54478300
C	1.43857700	1.84998400	1.61794000
C	2.89475800	1.97923400	-0.43702900
H	0.48941300	2.60992000	-1.64058800
H	-0.54239800	2.48277400	-0.19340000
H	0.75415200	3.69684100	-0.25187700
H	2.12766300	1.17495200	2.13449800
H	1.72669700	2.88332600	1.86775800
H	0.42988900	1.67566600	2.01391000
H	3.13333200	3.03592000	-0.24131600
H	3.65361200	1.37056200	0.06938400
H	2.97373000	1.80741300	-1.51872800

C	2.12217400	-1.41782900	-0.07243000
C	3.31408500	-1.39880300	-1.05763600
C	2.63686600	-1.36125900	1.37715600
C	1.35203100	-2.74225100	-0.28966000
H	2.96683100	-1.45317900	-2.09732200
H	3.92902400	-0.49905300	-0.94904800
H	3.95869200	-2.27014300	-0.86459400
H	1.81066100	-1.32150000	2.09819800
H	3.23187100	-2.26300700	1.59109000
H	3.28602200	-0.49275000	1.54076700
H	2.04400000	-3.58854800	-0.16284400
H	0.53391700	-2.85953400	0.43289400
H	0.92638700	-2.79619400	-1.30085300
C	-2.23610600	0.39429300	-1.53665400
H	-3.00563600	-0.12791400	-2.12283900
H	-2.49959900	1.46294100	-1.53597100
H	-1.26937100	0.28804500	-2.03920400
C	-3.46793800	-0.33708600	0.58503000
C	-4.71147300	0.49675300	0.27056400
C	-4.68267200	-0.95409800	-0.11705000
H	-3.36101000	-0.62740500	1.63012400
H	-4.63210900	1.23501600	-0.52423200
H	-5.32355000	0.80321000	1.11612800
H	-5.26385900	-1.66550900	0.46544500
H	-4.58840400	-1.20332200	-1.17151700

E.3.16. Reaction of acetone with *t*Bu_2P-P($SiMe_3$)Li($THF)_3$

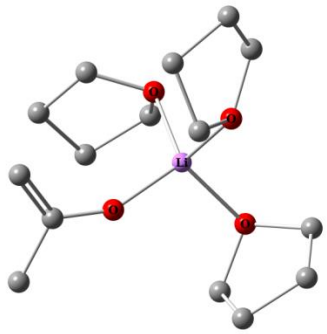


Figure S223. Optimized structure of **CH_2=C(OLiTHF_3)CH_3**.

Below are presented xyz coordinates for optimized geometry of **CH_2=C(OLiTHF_3)CH_3**:

Li	-0.12488800	0.17092700	-0.38264700
O	-0.43231600	2.05614100	-0.99368500
O	0.86901900	-0.81452500	-1.80412100
O	-1.90132000	-0.68231200	-0.20190500
C	-1.81032800	2.48112800	-1.14082900
H	-2.36056600	1.64070600	-1.57230200
H	-1.84054600	3.33870600	-1.83178000
C	-2.27003800	2.87652600	0.27860400
H	-2.93127500	3.75070500	0.25238100
H	-2.81419400	2.04980000	0.74735300
C	-0.93820500	3.15970700	1.03884300
H	-0.77656800	2.41587300	1.82572800
H	-0.91514500	4.16045200	1.48580900
C	0.14801900	2.98698500	-0.03521400
H	0.37415700	3.92923000	-0.55972900
H	1.05654100	2.51380600	0.34472700
C	1.68120400	-1.82741000	-1.12527100
H	1.69646300	-2.73013400	-1.75303600
H	1.19209600	-2.03687300	-0.16970500
C	3.08967100	-1.21479300	-0.94005100
H	3.34501500	-1.16020600	0.12270600
H	3.84550000	-1.82231300	-1.45302100

C	1.79229200	0.03463800	-2.53462400
H	1.25631900	0.96136000	-2.76017700
H	2.08225100	-0.46800000	-3.47230400
C	-2.09939500	-1.18180000	1.15936400
H	-3.06267300	-0.80348400	1.53652700
H	-1.26777400	-0.78777100	1.75267200
C	-2.38158200	-1.67473100	-1.16110900
H	-3.17971400	-1.21716600	-1.76037700
H	-1.53786300	-1.92483900	-1.81589000
C	2.97887300	0.19214700	-1.58041600
H	2.73372400	0.93324100	-0.81129800
H	3.89721200	0.49991900	-2.09485700
C	-2.11314800	-2.70027500	1.00313600
H	-1.08503500	-3.07500400	0.92005800
H	-2.60079400	-3.20741900	1.84333900
C	-2.86903100	-2.87550400	-0.32936100
H	-2.65641600	-3.83034400	-0.82354600
H	-3.95206500	-2.81210500	-0.16048700
O	0.78473100	0.21975100	1.13998000
C	1.52153000	-0.29336200	2.10436200
C	1.44907700	-1.58625100	2.55741100
H	2.08639600	-1.93764400	3.36529800
H	0.73271400	-2.29237600	2.13861200
C	2.51998600	0.67937800	2.72512500
H	3.20189800	1.05964400	1.94922900
H	1.98465100	1.54778400	3.13628900
H	3.11589400	0.22092100	3.52374400

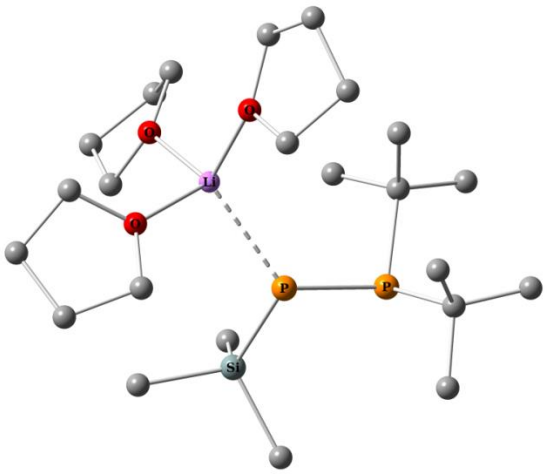


Figure S224. Optimized structure of ***t*Bu$_2$P-P(SiMe$_3$)LiTHF$_3$**.

Below are presented xyz coordinates for optimized geometry of ***t*Bu$_2$P-P(SiMe$_3$)LiTHF$_3$**:

Li	1.30893300	0.66414000	0.00905200
Si	-0.29051500	-2.94786600	-0.24978300
P	-0.59111300	-0.78535200	-0.66381900
P	-2.62093800	-0.72008600	0.19278700
O	2.66853900	0.16736100	-1.31761800
O	1.14300100	2.58647400	-0.35399400
O	2.33836300	0.43031200	1.67261600
C	-0.43422500	-3.47632900	1.58283100
H	-0.23209200	-4.55268200	1.69844900
H	-1.45751500	-3.28402300	1.93374900
H	0.24960400	-2.92792000	2.24549200
C	1.45064600	-3.45065900	-0.87035200
H	1.70081600	-4.47329700	-0.55070100
H	2.23756400	-2.77780200	-0.50299800
H	1.48101500	-3.43124400	-1.96924300
C	-1.53379400	-4.05180600	-1.17726600
H	-1.35367300	-5.11926600	-0.97607900

H	-1.46996400	-3.88793400	-2.26180800
H	-2.55810700	-3.81193700	-0.86153300
C	-3.63328100	0.06436600	-1.25703700
C	-2.92820700	1.18499000	-2.04159300
H	-3.53591300	1.46683700	-2.91718500
H	-1.95065900	0.83223100	-2.39682100
H	-2.78044800	2.08484400	-1.43321100
C	-3.84534500	-1.12880200	-2.21873900
H	-4.42060300	-0.79864700	-3.09865100
H	-4.39589000	-1.94208900	-1.72820500
H	-2.87906300	-1.52228200	-2.56018900
C	-5.00904900	0.55684300	-0.76834100
H	-5.66147800	0.74763000	-1.63524300
H	-4.92732600	1.49634000	-0.20684300
H	-5.50241700	-0.18894600	-0.13051800
C	-2.50908300	0.56523500	1.63352700
C	-1.46133400	-0.02269900	2.60161100
H	-1.35360000	0.64000400	3.47661900
H	-0.49240600	-0.12926800	2.09609700
H	-1.76332100	-1.01686200	2.95607800
C	-2.05991900	1.97250800	1.21393900
H	-1.85297300	2.59185100	2.10438400
H	-2.83239000	2.48616200	0.62805500
H	-1.14381600	1.91217400	0.61042600
C	-3.85431400	0.62835000	2.38999000
H	-3.72730900	1.19963400	3.32409800
H	-4.20140300	-0.37997600	2.65126300
H	-4.64002300	1.11873000	1.80680800
C	4.07095800	0.50175500	-1.27170100
H	4.32760200	0.66795200	-0.22141700
H	4.24201500	1.43149100	-1.84065900
C	4.76160800	-0.70182300	-1.93262600
H	5.71577500	-0.42704300	-2.39696800
H	4.95780600	-1.47863800	-1.18422200
C	3.70823200	-1.20075000	-2.96740400
H	3.52445000	-2.27298800	-2.84802900
H	4.03386400	-1.02396100	-3.99890500
C	2.43837500	-0.38128500	-2.64212800
H	2.30907300	0.45612400	-3.34655400
H	1.50653000	-0.95014500	-2.58372600
C	1.11822200	3.79333000	0.46012100
H	2.12721500	3.95104700	0.85981300
H	0.41781200	3.63011600	1.29045100
C	0.64008700	4.91457000	-0.47240000
H	0.09771800	5.69770600	0.06909700
H	1.49272100	5.37696100	-0.98725900
C	0.54558200	2.85272000	-1.66236800
H	-0.06136100	1.97783900	-1.91803300
H	1.35911400	2.96829400	-2.39435300
C	2.64390100	-0.98725100	1.88773600
H	3.49475500	-1.23710600	1.24536400
H	1.76744000	-1.56803800	1.57415600
C	2.05792300	1.07113300	2.95452400
H	2.88246300	1.76599300	3.17041100
H	1.12349000	1.63388900	2.85286000
C	-0.24221500	4.14879300	-1.47824800
H	-1.22574300	3.93452200	-1.04313300
H	-0.38675600	4.68767500	-2.42130900
C	2.92623300	-1.11872000	3.38408900
H	2.72469600	-2.13088200	3.75207200
H	3.97240500	-0.86817700	3.60547200
C	1.97541400	-0.06362400	3.98139500
H	0.95378500	-0.45827100	4.02775900
H	2.26997300	0.26441900	4.98470900

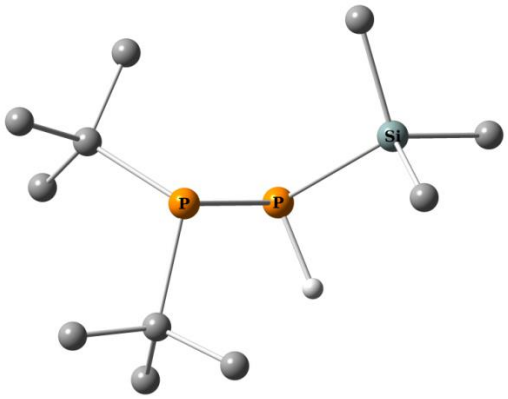


Figure S225. Optimized structure of ***t*Bu$_2$P-P(SiMe$_3$)LiTHF$_3$**.

Below are presented xyz coordinates for optimized geometry of ***t*Bu$_2$P-P(SiMe$_3$)LiTHF$_3$**:

P	-0.80996300	0.02474400	1.20938300
P	0.69873700	0.00060100	-0.47066500
C	1.74181600	-1.56083200	-0.04393800
C	1.67918100	1.59185000	-0.02016100
C	-2.77030800	1.60528300	-1.07436300
C	-2.65940400	-1.47584900	-1.30231100
C	-4.16799400	-0.15680300	1.06915500
C	0.62301700	2.72124500	0.02162700
C	2.44083900	1.56762200	1.31549600
C	2.64591700	1.90044000	-1.18706400
C	2.05217300	-1.82882600	1.44169200
C	0.90998000	-2.73963600	-0.60365600
C	3.06681800	-1.48486800	-0.83427100
H	-3.70683600	1.64920700	-1.64874200
H	-2.73523200	2.48306400	-0.41590500
H	-1.93595800	1.67427700	-1.78458400
H	-3.54987600	-1.45962100	-1.94778200
H	-2.64696100	-2.43538400	-0.76795000
H	-1.77025100	-1.43042000	-1.94442100
H	-4.20637300	0.68849300	1.76909600
H	-5.10803900	-0.16794700	0.49863100
H	-4.12536300	-1.08136000	1.66106300
H	1.13374100	3.68751500	0.14764400
H	0.04286000	2.76365500	-0.90907100
H	-0.07122200	2.59641900	0.86294200
H	2.84032400	2.57119700	1.52958600
H	3.29094100	0.87566400	1.28409500
H	1.78070700	1.28116700	2.14426800
H	2.11350000	1.91548800	-2.14688200
H	3.09782800	2.89166800	-1.03059400
H	3.46004800	1.17175500	-1.25865800
H	2.61104200	-2.77398300	1.52449000
H	2.66292400	-1.03806100	1.88638100
H	1.13995700	-1.93216200	2.04026500
H	1.46642600	-3.67836000	-0.46237900
H	0.70962600	-2.61344700	-1.67502800
H	-0.05247000	-2.83989300	-0.08593300
H	2.89724900	-1.22828600	-1.88832800
H	3.75446000	-0.74929800	-0.40063400
H	3.56500000	-2.46542600	-0.79883000
H	-0.83746300	-1.38154000	1.42766600
Si	-2.68031500	-0.01373700	-0.09888800

E.3.17. Optimized structures of **4a-4e**

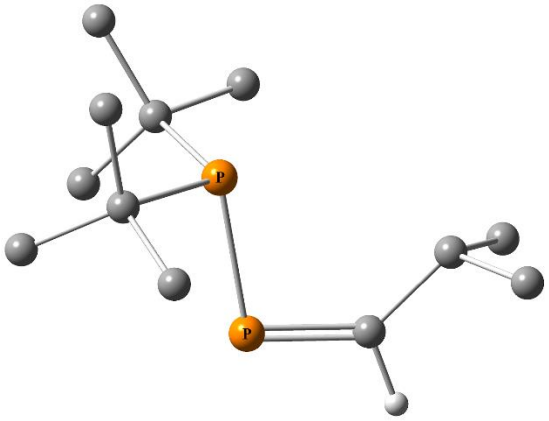


Figure S226. Optimized structure of ***Z*-4a**.

Below are presented xyz coordinates for optimized geometry of ***Z*-4a**:

C	-2.27856300	-0.53384700	0.90967500
H	-2.99303400	-0.77080100	1.70524800
P	-0.68497000	-0.59820400	1.42095900
P	0.45805400	-0.09990700	-0.43008300
C	0.90181100	1.72731700	-0.08966400
C	-0.35548700	2.50930000	-0.51375400
C	1.23362400	2.10161400	1.36252000
C	2.06525900	2.14691600	-1.00005800
H	-0.61358600	2.32295100	-1.56122000
H	-1.21968800	2.24423600	0.10459200
H	-0.17900200	3.58503900	-0.39063100
H	2.10680600	1.56961700	1.74404000
H	1.44820500	3.17674400	1.41807500
H	0.39525700	1.90053000	2.03653100
H	2.16951800	3.23886400	-0.97649900
H	3.01637300	1.72244600	-0.66648200
H	1.89829200	1.84885000	-2.04069900
C	1.98426700	-1.21366800	-0.18180700
C	2.81644500	-1.16852000	-1.47653900
C	2.88275900	-0.89400800	1.01858300
C	1.43870100	-2.64700200	-0.03331700
H	2.20718200	-1.42557400	-2.34878700
H	3.26358300	-0.18797300	-1.65358100
H	3.63513700	-1.89614600	-1.40837500
H	2.32002800	-0.87023500	1.95714800
H	3.65660300	-1.66670300	1.11301600
H	3.39518600	0.06458200	0.89813500
H	2.27289100	-3.35800000	-0.07351800
H	0.92391700	-2.79690700	0.92105900
H	0.74271300	-2.90054600	-0.84071100
C	-2.93760800	-0.24267900	-0.41089700
C	-3.57355800	-1.52989400	-0.95820900
C	-3.98971900	0.86303800	-0.25061800
H	-2.17897400	0.09122500	-1.12521000
H	-4.31910500	-1.92757100	-0.25973900
H	-2.81428000	-2.29962200	-1.12237900
H	-4.77733200	0.55537900	0.44728800
H	-3.54472800	1.78741200	0.12941800
H	-4.07510400	-1.33023200	-1.91101800
H	-4.46068800	1.08269000	-1.21431800

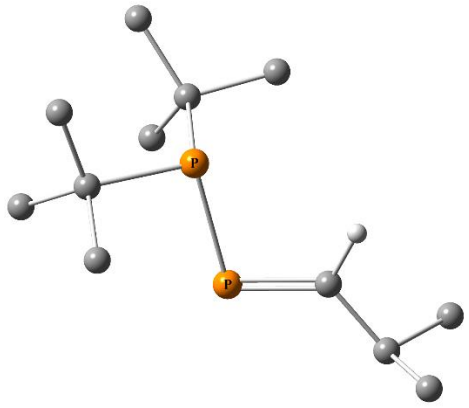


Figure S227. Optimized structure of ***E*-4a**.

Below are presented xyz coordinates for optimized geometry of ***E*-4a**:

C	-2.20672300	-0.23143600	-0.20095900
H	-2.05954400	0.03792600	-1.25014900
P	-0.90274800	-0.51477300	0.81015300
P	0.75113300	-0.08302300	-0.61513800
C	1.23968600	1.68474300	-0.07255200
C	0.23053300	2.60085300	-0.79046800
C	1.17875400	1.98522000	1.43248500
C	2.64529500	2.01105400	-0.59888000
H	0.27964100	2.47903600	-1.87714800
H	-0.79792700	2.40033600	-0.47137600
H	0.45327600	3.64853900	-0.55256300
H	1.85090500	1.35227200	2.01467500
H	1.47119300	3.02916700	1.60481500
H	0.16741000	1.85980400	1.83136200
H	2.83121600	3.08713100	-0.49287900
H	3.42418400	1.48979900	-0.03539100
H	2.75427500	1.75660200	-1.65864800
C	2.06388400	-1.33594000	-0.03435200
C	3.21486800	-1.33049300	-1.05728100
C	2.62782600	-1.13634100	1.37742900
C	1.38571100	-2.71746900	-0.11035100
H	2.84374300	-1.50040000	-2.07297400
H	3.77452900	-0.39277900	-1.05415400
H	3.92044300	-2.13549700	-0.81559700
H	1.83607200	-1.09542800	2.13235300
H	3.28694600	-1.97665600	1.63104700
H	3.22389200	-0.22268700	1.45293000
H	2.14039900	-3.50010400	0.03448000
H	0.62422800	-2.84743500	0.66538600
H	0.91215800	-2.88337800	-1.08423600
C	-3.64559000	-0.30988300	0.23225500
C	-4.30729300	1.07054900	0.10220500
C	-4.39281100	-1.35768400	-0.60536100
H	-3.68482000	-0.61363900	1.28611900
H	-4.27627600	1.41930600	-0.93666100
H	-3.79746900	1.81154600	0.72474700
H	-4.37222900	-1.09112600	-1.66848500
H	-3.93929200	-2.34670900	-0.49485100
H	-5.44068400	-1.42137700	-0.29392500
H	-5.35688500	1.02365400	0.41087500

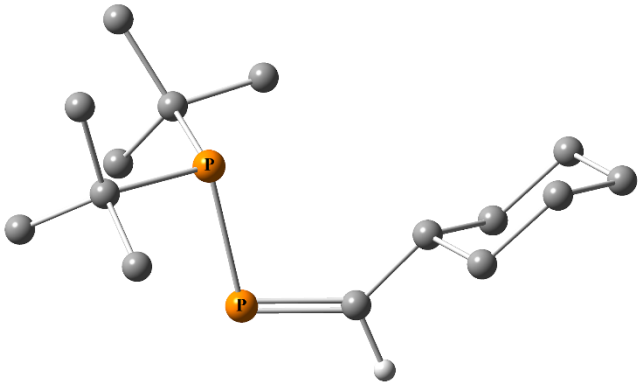


Figure S228. Optimized structure of ***Z*-4b**.

Below are presented xyz coordinates for optimized geometry of ***Z*-4b**

C	-1.27300500	-0.47352400	1.55403700
H	-1.80576900	-0.67421000	2.48933500
P	0.39239600	-0.53799300	1.72125300
P	1.12005100	-0.12357600	-0.34829300
C	1.59200600	1.72238000	-0.19961500
C	0.26199100	2.47402900	-0.39533800
C	2.20769700	2.17493900	1.13266300
C	2.53701500	2.10055200	-1.34956700
H	-0.20478500	2.22809100	-1.35473300
H	-0.45084700	2.24079000	0.40243900
H	0.44336600	3.55570200	-0.37013100
H	3.14852300	1.66796000	1.35361800
H	2.41238000	3.25253900	1.08831600
H	1.52787700	2.00588700	1.97337300
H	2.62565200	3.19285000	-1.40263700
H	3.54329300	1.69996600	-1.19801500
H	2.16500800	1.74741300	-2.31731100
C	2.68469500	-1.21105400	-0.36840200
C	3.23110300	-1.22567900	-1.80797500
C	3.80566400	-0.82443300	0.60350400
C	2.20762300	-2.63940800	-0.04203100
H	2.45941400	-1.53072000	-2.52182900
H	3.61547300	-0.25252000	-2.12097100
H	4.05846800	-1.94348300	-1.87572800
H	3.44811400	-0.75727200	1.63588300
H	4.59577900	-1.58576000	0.57291400
H	4.26563400	0.13047600	0.33399300
H	3.02771800	-3.34507400	-0.22239700
H	1.90601000	-2.74592800	1.00475700
H	1.36324700	-2.93797100	-0.67323700
C	-2.18429600	-0.21940900	0.39054100
C	-2.92746400	-1.51393300	0.00470500
C	-3.19387300	0.89735700	0.71232500
H	-1.58961100	0.08986000	-0.47686200
C	-3.89170600	-1.27550100	-1.16078700
H	-3.48671100	-1.88248700	0.87699700
H	-2.19537100	-2.28598500	-0.25548700
C	-4.15246500	1.13648800	-0.45695000
H	-3.77030400	0.61268700	1.60475000
H	-2.66087800	1.82118000	0.96348800
C	-4.88271700	-0.15023400	-0.85111000
H	-4.42805000	-2.20181400	-1.39466600
H	-3.31161400	-1.01116800	-2.05546500
H	-4.87301800	1.91893200	-0.19428200
H	-3.58157100	1.50849500	-1.31900600
H	-5.53255300	0.03114600	-1.71432400
H	-5.53519200	-0.46146200	-0.02318700

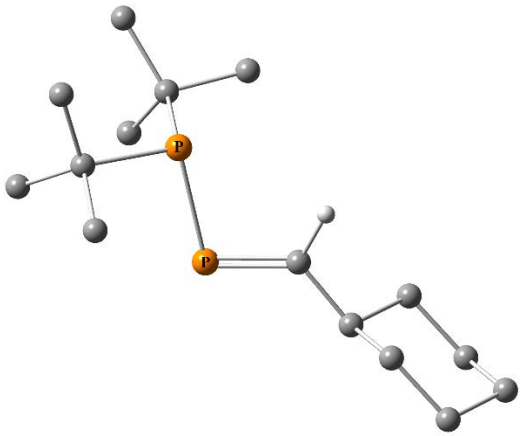


Figure S229. Optimized structure of ***E*-4b**.

Below are presented xyz coordinates for optimized geometry of ***E*-4b**:

C	-1.29195100	-0.21235000	-0.19835600
H	-1.14145700	0.04011200	-1.25103300
P	0.01003400	-0.49962500	0.81451300
P	1.66654600	-0.10707800	-0.61816800
C	2.15488900	1.67510700	-0.12376300
C	1.14837100	2.57175800	-0.86940900
C	2.09022400	2.01785700	1.37208800
C	3.56210700	1.98542800	-0.65546400
H	1.19935100	2.41907700	-1.95211400
H	0.11908400	2.38177900	-0.54657500
H	1.37219500	3.62547200	-0.66086000
H	2.76088600	1.40167800	1.97368900
H	2.38221000	3.06629500	1.51564000
H	1.07779200	1.90354400	1.77154800
H	3.74893100	3.06384800	-0.57870300
H	4.33915900	1.47914500	-0.07598400
H	3.67330300	1.70170200	-1.70753300
C	2.97763400	-1.34372500	-0.00039000
C	4.13021400	-1.36844200	-1.02120500
C	3.53960800	-1.10408700	1.40595600
C	2.29849600	-2.72637400	-0.03775600
H	3.76044300	-1.56648700	-2.03228100
H	4.69091000	-0.43159500	-1.04366100
H	4.83455900	-2.16706000	-0.75582700
H	2.74665700	-1.04167200	2.15815400
H	4.19842600	-1.93676900	1.68437400
H	4.13539100	-0.18846400	1.45620700
H	3.05211500	-3.50508100	0.13179900
H	1.53473000	-2.83277700	0.73934000
H	1.82729000	-2.92018000	-1.00763100
C	-2.72630500	-0.26099200	0.23922000
C	-3.37563600	1.13155000	0.11209600
C	-3.51407900	-1.29437500	-0.58826700
H	-2.77234100	-0.56079700	1.29642200
C	-4.85678900	1.10237600	0.49901800
H	-3.27583000	1.47567300	-0.92770800
H	-2.82910000	1.84658600	0.73698600
C	-4.99470100	-1.32028800	-0.19917100
H	-3.42107800	-1.03980900	-1.65408000
H	-3.06497300	-2.28505000	-0.45888700
C	-5.63030500	0.06709400	-0.32183500
H	-5.29464600	2.09805700	0.36768400
H	-4.94519400	0.85703500	1.56638800
H	-5.53070800	-2.04208400	-0.82527100
H	-5.08899100	-1.67106100	0.83784300
H	-6.67757000	0.03478300	-0.00176300
H	-5.63089700	0.37143000	-1.37790400

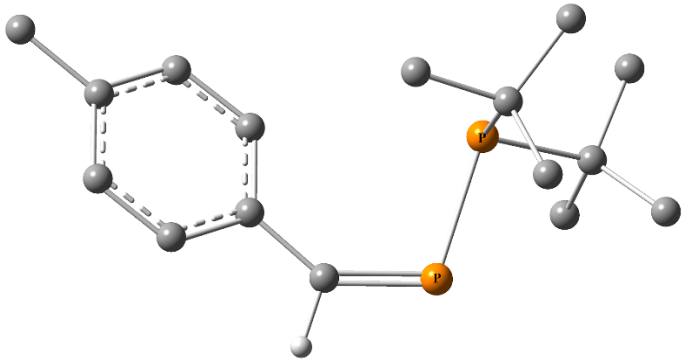


Figure S230. Optimized structure of ***Z*-4c**.

Below are presented xyz coordinates for optimized geometry of ***Z*-4c**:

C	3.23333600	0.14659500	1.35470900
C	2.08977000	-0.39468500	0.78514600
C	2.11668900	-0.92187200	-0.51552500
C	3.34039900	-0.89934400	-1.20214300
C	4.47902600	-0.34148500	-0.63158900
C	4.44601400	0.19482500	0.65712200
H	3.18437400	0.54088300	2.36673200
H	5.40860300	-0.33117100	-1.19458500
C	0.95898600	-1.52766500	-1.18592000
H	1.26307400	-2.20106700	-1.99190600
P	-0.72095300	-1.46515700	-1.12951600
P	-1.31288900	0.00858200	0.43746900
C	-1.38930600	1.61658300	-0.59592800
C	0.06546300	2.12039200	-0.64243600
C	-1.90235500	1.49034500	-2.03798600
C	-2.23875500	2.65431900	0.15300500
H	0.47283200	2.27650800	0.36129100
H	0.72300900	1.42083100	-1.16754800
H	0.10129300	3.07657400	-1.17942000
H	-2.92500400	1.11264800	-2.08960000
H	-1.88873100	2.48066700	-2.51125200
H	-1.26756200	0.83222300	-2.63873300
H	-2.09794900	3.63820200	-0.31159300
H	-3.30614400	2.42146100	0.10314400
H	-1.94947600	2.73741100	1.20606900
C	-3.06965600	-0.63611500	0.80327900
C	-3.60843000	0.13749000	2.02093300
C	-4.08505100	-0.56289000	-0.34313900
C	-2.89971400	-2.10642800	1.23239900
H	-2.91668400	0.07697400	2.86710400
H	-3.78575300	1.19282900	1.80367500
H	-4.56532800	-0.29923400	2.33373600
H	-3.72052200	-1.06145700	-1.24684400
H	-5.01516600	-1.06075000	-0.04031900
H	-4.33809200	0.47052400	-0.59604100
H	-3.84996000	-2.47664500	1.63614100
H	-2.62436400	-2.75429800	0.39445900
H	-2.13931900	-2.21462600	2.01377300
C	5.66820500	0.81911600	1.27915500
H	5.59613200	1.91233400	1.26286900
H	5.78058900	0.51371700	2.32373300
H	6.57778800	0.53749200	0.74225400
H	1.16496200	-0.40878200	1.34999700
H	3.39731900	-1.31970200	-2.20293200

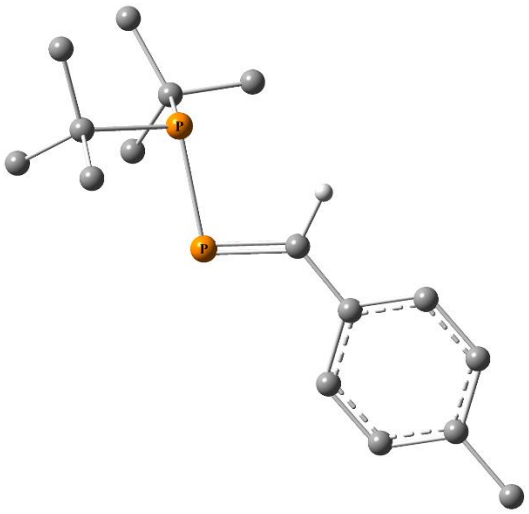


Figure S231. Optimized structure of ***E*-4c**.

Below are presented xyz coordinates for optimized geometry of ***E*-4c**:

C	-4.75947600	0.26544400	-1.17166400
C	-3.37715500	0.28375000	-1.33424000
C	-2.51765100	-0.04093000	-0.27646500
C	-3.09888100	-0.37886100	0.95854900
C	-4.47511200	-0.39667100	1.11490100
C	-5.33320700	-0.07510300	0.05343100
H	-5.39960300	0.52054000	-2.01195300
H	-4.89892000	-0.66203300	2.08027000
C	-1.06980800	-0.02049600	-0.50004800
H	-0.77516000	0.31105200	-1.49656400
P	0.12432900	-0.46131800	0.60480400
P	1.90368600	0.00024100	-0.64277500
C	2.47303900	1.65131600	0.13634700
C	1.58258400	2.71675400	-0.53065600
C	2.32405200	1.78193300	1.65945300
C	3.93191000	1.92680500	-0.25706800
H	1.70266400	2.71676400	-1.61866700
H	0.52260600	2.55920600	-0.30450800
H	1.85732300	3.71059400	-0.15576200
H	2.90886600	1.03842300	2.20401400
H	2.67232100	2.77473300	1.97256100
H	1.28034100	1.68737900	1.97490900
H	4.18241600	2.96674600	-0.01323000
H	4.63062400	1.28752500	0.28977700
H	4.09972800	1.78639800	-1.33032900
C	3.07913600	-1.40936100	-0.13155200
C	4.29968600	-1.37480600	-1.06996100
C	3.55030000	-1.41678600	1.32746400
C	2.31544100	-2.71689700	-0.41640500
H	3.99332000	-1.39839000	-2.12059900
H	4.92109400	-0.48971400	-0.91845800
H	4.92835400	-2.25419200	-0.88108500
H	2.70986200	-1.39984400	2.02876600
H	4.12769600	-2.32998900	1.52126200
H	4.20248800	-0.56771000	1.54981500
H	3.00259400	-3.56619100	-0.31840200
H	1.49206600	-2.87614300	0.28719000
H	1.90351600	-2.73305000	-1.43137600
C	-6.82744300	-0.09434600	0.24664500
H	-7.35327300	0.14310900	-0.68153900
H	-7.16655400	-1.07881400	0.58518200
H	-7.13370600	0.63512900	1.00384700
H	-2.46020900	-0.62664800	1.80163700
H	-2.95517900	0.55079900	-2.29958000

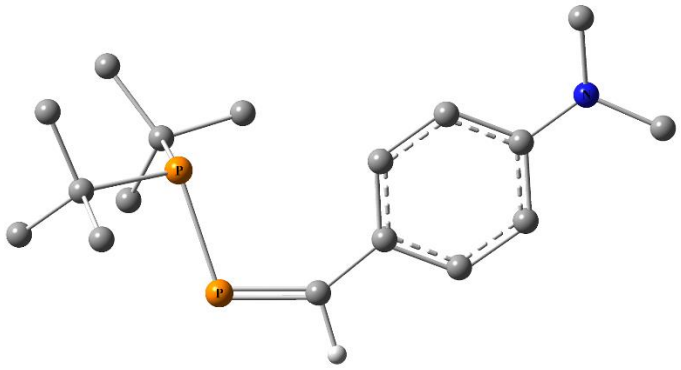


Figure S232. Optimized structure of ***Z*-4d**.

Below are presented xyz coordinates for optimized geometry of ***Z*-4d**:

C	-2.74970500	0.53509700	-0.71656900
C	-1.54006600	-0.08555900	-0.46219100
C	-1.45309700	-1.24332800	0.32955900
C	-2.66323700	-1.74792400	0.83746600
C	-3.88195300	-1.13480800	0.60240300
C	-3.95856100	0.03913500	-0.17785400
H	-2.74926500	1.41811300	-1.34369400
H	-4.77514500	-1.57758100	1.02528600
C	-0.22341300	-1.96848200	0.62804700
H	-0.43402000	-2.93245100	1.10047100
P	1.45165300	-1.80113000	0.50648200
P	1.89811700	0.19868900	-0.37312300
C	2.12487400	1.24350700	1.21327000
C	0.69279800	1.63150200	1.62751900
C	2.80072600	0.55414300	2.40774700
C	2.89585400	2.52661300	0.86990900
H	0.18002200	2.18942000	0.83762300
H	0.08624300	0.75286000	1.86968300
H	0.73139900	2.26525600	2.52249000
H	3.81766600	0.22705100	2.18415000
H	2.85480500	1.26068200	3.24628700
H	2.23303700	-0.31699300	2.74747200
H	2.82386000	3.22787300	1.71082400
H	3.95850200	2.33066400	0.70059400
H	2.48866400	3.02414300	-0.01689100
C	3.58860200	-0.18297900	-1.16764600
C	4.00101900	1.03934800	-2.00841500
C	4.72832800	-0.55841600	-0.21332700
C	3.34366700	-1.35049700	-2.14285400
H	3.21705800	1.31204900	-2.72207100
H	4.22054700	1.91622800	-1.39561400
H	4.90863600	0.79956200	-2.57699600
H	4.45687600	-1.39290000	0.44090300
H	5.60782300	-0.86298700	-0.79530100
H	5.02960000	0.28762500	0.41087000
H	4.23586100	-1.49506200	-2.76452700
H	3.14839300	-2.29157200	-1.61974000
H	2.49843200	-1.14896600	-2.81022900
H	-0.63910500	0.33307800	-0.89621800
H	-2.64794700	-2.65354600	1.43900000
N	-5.15923200	0.67540500	-0.40357200
C	-5.22210400	1.77252600	-1.34756300
H	-4.92381400	1.46874700	-2.36147600
H	-6.24431300	2.14915200	-1.39124800
H	-4.57840000	2.60168600	-1.03318600
C	-6.39188400	0.05187700	0.03132200
H	-6.39895600	-0.09270500	1.11756200
H	-7.23040400	0.70254500	-0.21804000
H	-6.55907200	-0.92372000	-0.44831200

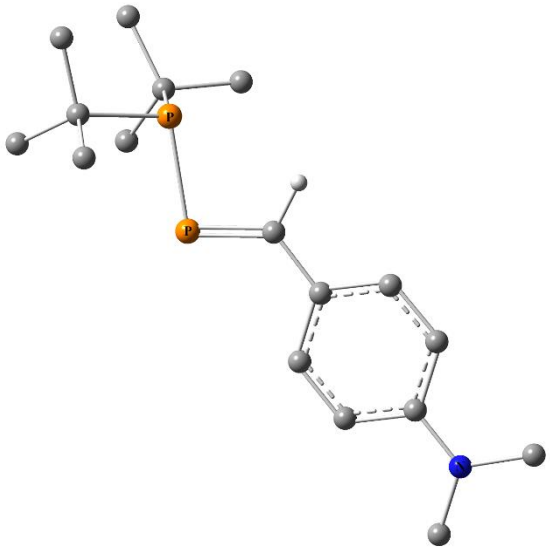


Figure S233. Optimized structure of ***E*-4d**.

Below are presented xyz coordinates for optimized geometry of ***E*-4d**:

P	0.82516200	-0.42614500	0.61066400
P	2.61129400	0.03515400	-0.62539600
N	-6.01675300	-0.12779800	0.08721300
C	-0.36143500	-0.00420400	-0.51733500
H	-0.04881600	0.32391800	-1.50989900
C	-1.80513600	-0.03215100	-0.32400900
C	-2.41852900	-0.38185500	0.89142700
H	-1.79950000	-0.63467000	1.74785900
C	-3.79271200	-0.40799300	1.03485400
H	-4.20632600	-0.67981900	1.99807200
C	-4.64642000	-0.08373500	-0.04620600
C	-4.03648300	0.28382400	-1.26447500
H	-4.63738300	0.55702300	-2.12286100
C	-2.65638500	0.30285700	-1.38780000
H	-2.22217600	0.58780800	-2.34287900
C	-6.60453800	-0.35609300	1.39129600
H	-6.30199700	-1.32800500	1.79722400
H	-7.69072300	-0.36379500	1.29805900
H	-6.32774200	0.42292600	2.11643800
C	-6.85581700	0.35980900	-0.98770400
H	-6.67578700	1.42209500	-1.20826300
H	-7.90273000	0.24278700	-0.70699700
H	-6.69466700	-0.21479000	-1.90701000
C	3.23519100	1.63653400	0.21300000
C	3.10868000	1.70824900	1.74199800
H	2.06786800	1.61597700	2.06693600
H	3.47749300	2.68202800	2.08996200
H	3.68880800	0.93421000	2.24779700
C	2.36167300	2.74926200	-0.39703200
H	2.46934200	2.79255900	-1.48556300
H	2.66257400	3.72027600	0.01608200
H	1.30112500	2.60391200	-0.16525300
C	4.69496500	1.89504200	-0.18804200
H	5.38519400	1.21794000	0.32310900
H	4.97320800	2.91816700	0.09448900
H	4.84612600	1.79446200	-1.26829200
C	3.75773600	-1.42294400	-0.18607700
C	4.97174000	-1.37805300	-1.13247900
H	4.65650300	-1.35176800	-2.18046700
H	5.58173800	-2.27845500	-0.98496500
H	5.61428500	-0.51392800	-0.95091900

C	2.96186800	-2.69950500	-0.51816500
H	2.13934300	-2.86645900	0.18424800
H	3.62986200	-3.56785000	-0.46145300
H	2.54181800	-2.66304900	-1.52933200
C	4.24007000	-1.50289100	1.26713600
H	4.91626400	-0.68082100	1.51782500
H	4.79455200	-2.43817800	1.41884800
H	3.40537800	-1.49195100	1.97537700

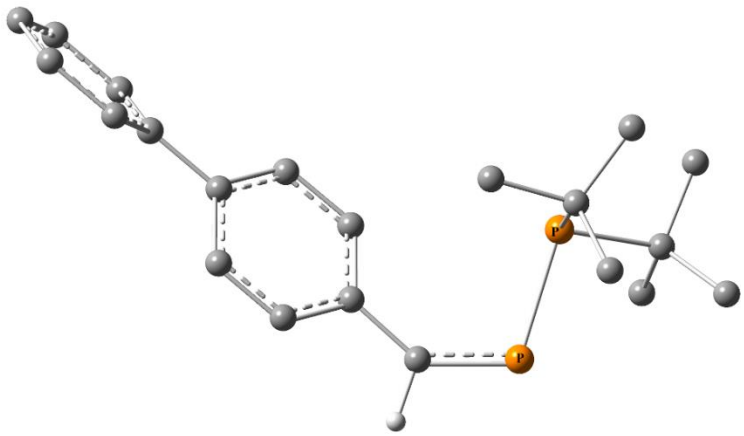


Figure S234. Optimized structure of ***Z*-4e**.

Below are presented xyz coordinates for optimized geometry of ***Z*-4e**:

C	-0.79639300	2.27711500	0.42117700
C	0.52210400	1.65938500	0.21753400
C	0.79045100	0.70062000	-0.76932300
H	-0.00613400	0.36776400	-1.42385000
C	2.06042900	0.15747400	-0.90452300
H	2.23454200	-0.59888700	-1.66431100
C	3.11053900	0.54342400	-0.06188200
C	2.84913400	1.51323900	0.91278600
H	3.65244000	1.85690300	1.55780800
C	1.58313000	2.06919400	1.03974100
H	1.40852000	2.83157700	1.79436400
C	4.46315100	-0.05100800	-0.20328600
C	5.02265100	-0.26742600	-1.46853100
H	4.46824000	0.02503500	-2.35555500
C	6.29115700	-0.82491800	-1.60010700
H	6.71148900	-0.97770800	-2.58934200
C	7.02366400	-1.17572400	-0.46796500
H	8.01306300	-1.61021600	-0.57032200
C	6.47757600	-0.96498300	0.79640200
H	7.03722300	-1.24258800	1.68431200
C	5.20864000	-0.40824300	0.92696000
H	4.78032200	-0.26925800	1.91544100
C	-2.44259400	-1.20501500	1.27553200
C	-3.19319900	-0.54651000	2.44237400
H	-4.25990600	-0.42794300	2.24412400
H	-3.08847000	-1.17495800	3.33620300
H	-2.78226200	0.43780400	2.68604400
C	-0.95012200	-1.29091100	1.64670800
H	-0.51540900	-0.30226300	1.82131000
H	-0.84001900	-1.86939500	2.57251600
H	-0.36404500	-1.78258500	0.86416200
C	-2.97421300	-2.63220500	1.07413400
H	-4.05946200	-2.64972700	0.94047700
H	-2.50908400	-3.12484700	0.21365400
H	-2.74616900	-3.23005600	1.96527600
C	-4.23716400	-0.30388100	-1.13741600
C	-4.43009000	-1.65050800	-1.85912500
H	-3.63104200	-1.82931900	-2.58556300

H	-4.45626800	-2.49702800	-1.16993200
H	-5.38410300	-1.63809600	-2.40122600
C	-4.25654800	0.79955800	-2.21305600
H	-3.41087600	0.70664300	-2.90353600
H	-5.17892800	0.71510200	-2.80043900
H	-4.23542300	1.80369500	-1.77810700
C	-5.39686800	-0.07212100	-0.16175000
H	-5.50411800	-0.89935000	0.54534700
H	-5.27640800	0.85574300	0.40634200
H	-6.33766000	0.00052800	-0.72234600
P	-2.41257200	1.83789300	0.27919100
P	-2.47750100	-0.28637300	-0.40209000
H	-0.72156100	3.29129300	0.82231600

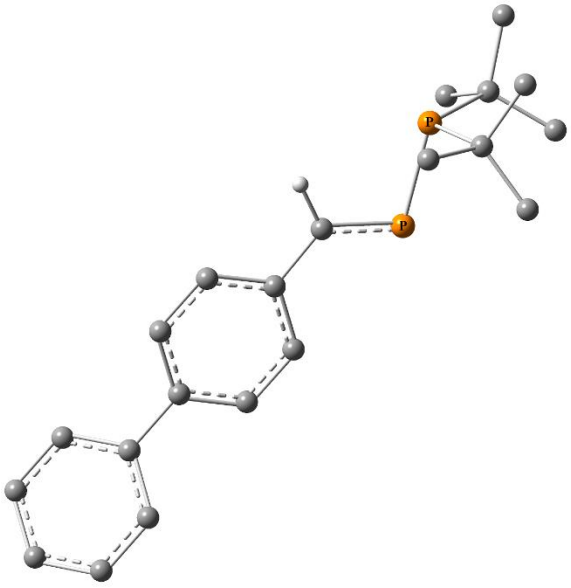


Figure S235. Optimized structure of ***E*-4e**.

Below are presented xyz coordinates for optimized geometry of ***E*-4e**:

C	0.44909700	-0.09787500	-0.56315900
C	-1.00434300	-0.07647000	-0.37814800
C	-1.61943000	-0.20785300	0.87802700
H	-1.00530200	-0.32608600	1.76615100
C	-2.99959400	-0.19534100	1.00042900
H	-3.44943600	-0.32281900	1.98066000
C	-3.82597400	-0.04604400	-0.12322200
C	-3.21727700	0.09118700	-1.37513700
H	-3.83265800	0.23449500	-2.25837200
C	-1.83365200	0.07695900	-1.49890100
H	-1.38358300	0.19225700	-2.48131100
C	-5.30364300	-0.03027400	0.01354900
C	-5.91873000	0.66483600	1.06208800
H	-5.30680700	1.21732600	1.76925500
C	-7.30457400	0.67996200	1.18990300
H	-7.76355400	1.23117600	2.00483700
C	-8.10075900	-0.00002300	0.27065900
H	-9.18154700	0.01163200	0.37005900
C	-7.50027100	-0.69531300	-0.77686400
H	-8.11179100	-1.23526900	-1.49318300
C	-6.11435400	-0.71035900	-0.90362300
H	-5.65327000	-1.27495600	-1.70886800
C	3.96523000	1.64732000	-0.10249800
C	3.75990700	2.02554900	1.37183600
H	4.32164600	1.38361500	2.05284200
H	4.09879300	3.05748600	1.53043700

H	2.70472500	1.98088400	1.65875300
C	3.10037100	2.58327100	-0.96780900
H	2.03271900	2.45953000	-0.75727500
H	3.36162700	3.62673000	-0.75193100
H	3.26029700	2.40496900	-2.03587100
C	5.43779500	1.86257500	-0.48231300
H	6.11534100	1.32458800	0.18655100
H	5.64483000	1.55002600	-1.51149500
H	5.67979000	2.92966600	-0.40254400
C	4.58509200	-1.41162900	0.15690200
C	5.83716300	-1.52330700	-0.73270700
H	5.56724300	-1.72163300	-1.77484300
H	6.45175800	-0.62100900	-0.70807100
H	6.46001100	-2.35524600	-0.38051900
C	3.83319800	-2.75343000	0.06546100
H	3.45790800	-2.93988400	-0.94671600
H	4.51713700	-3.57017200	0.32654800
H	2.98547900	-2.80035200	0.75654800
C	5.00568200	-1.17528600	1.61224800
H	5.64729100	-0.29563500	1.71365200
H	4.14166200	-1.05072000	2.27284400
H	5.57875800	-2.03928000	1.97265300
P	1.60711700	-0.37851000	0.62822400
P	3.42637800	-0.11357200	-0.61899600
H	0.77290000	0.07917900	-1.58953300

PART F. Experimental and theoretical UV-VIS spectra of phosphaalkenes isolated in the solid state form

UV-VIS Solution electronic spectra were recorded in the range 250-650 nm on a Unicam SP300 spectrometer. Quartz cuvettes and pentane as solvent were used. TD-DFT calculations for **3a**, **3c**, **3d**, **3e**, **3f**, **4d** and **4e** were carried out using CAM-B3LYP functional with 6-31+G(d,p) basis set including presence of a solvent (pentane) using the CPCM polarizable conductor calculation model.[16]

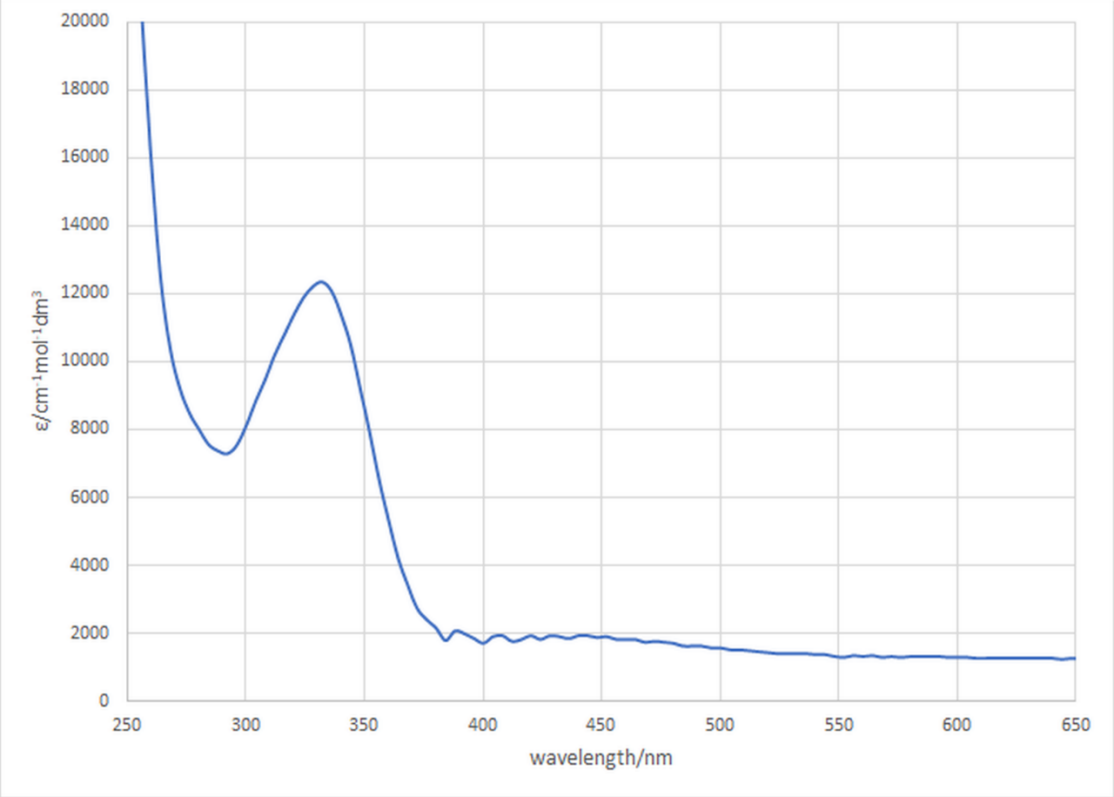


Figure S236. UV-VIS spectrum for phosphanylphosphaalkene **3a** in pentane.

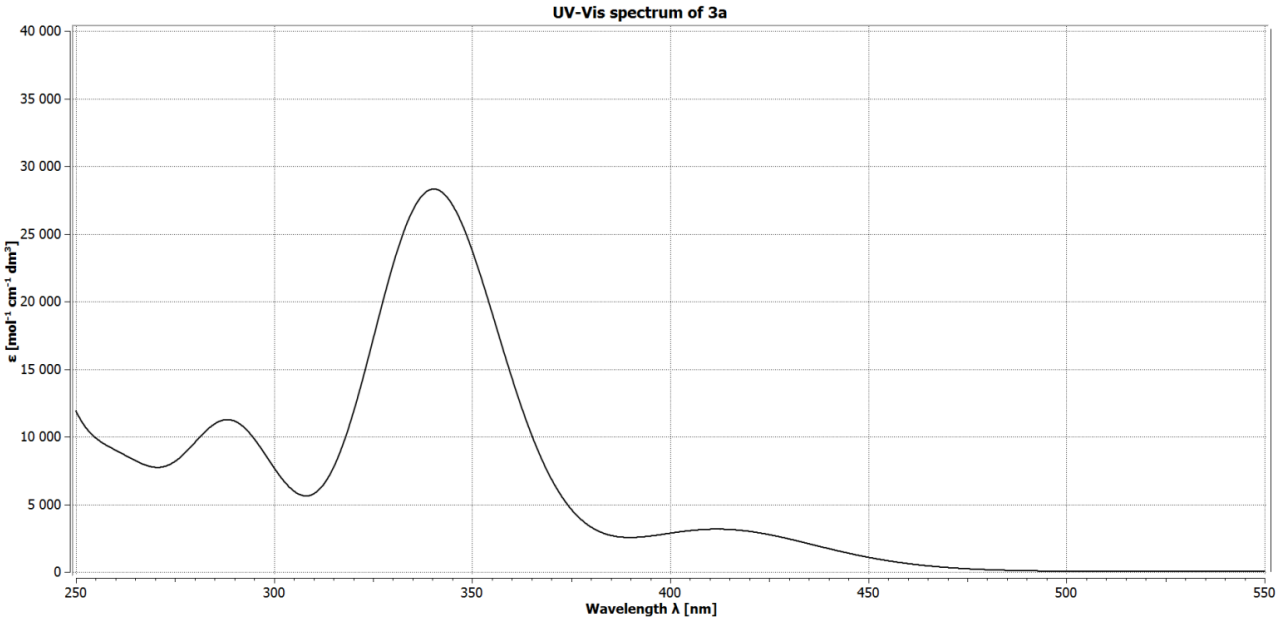


Figure S237. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **3a**.

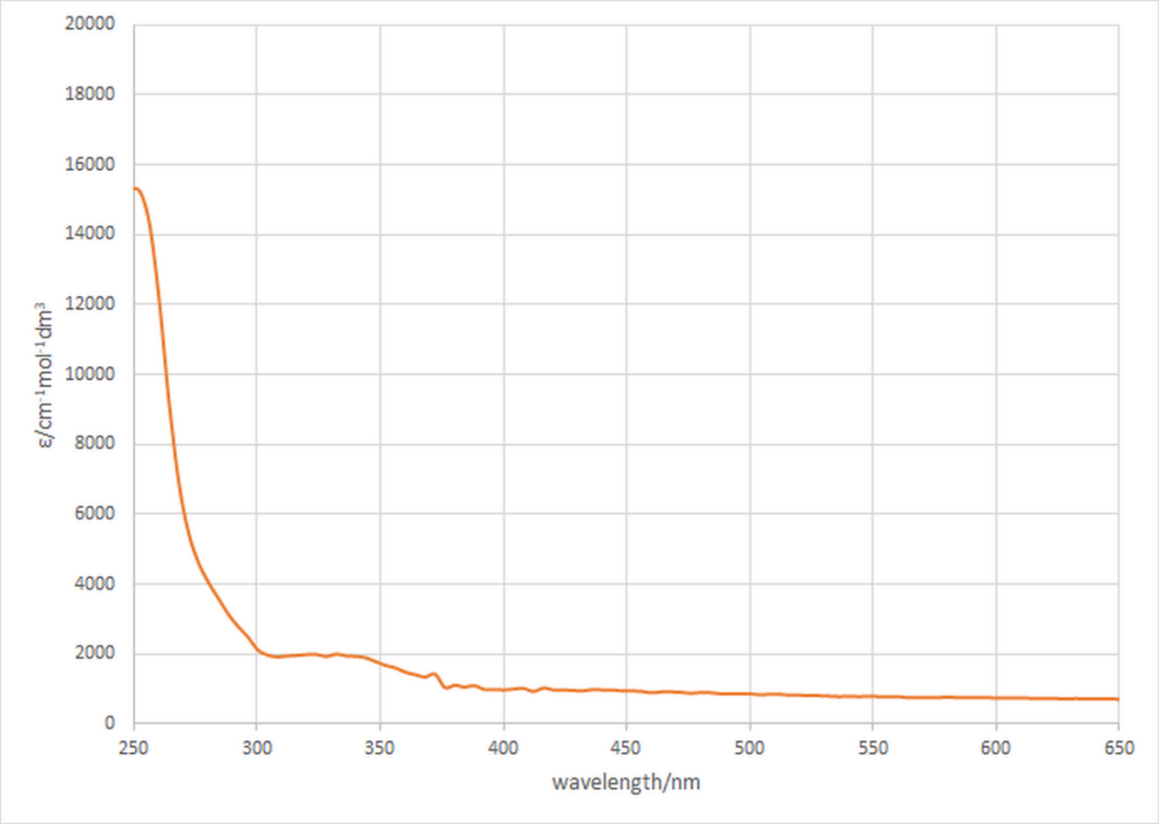


Figure S238. UV-VIS spectrum for phosphanylphosphaalkene **3c** in pentane.

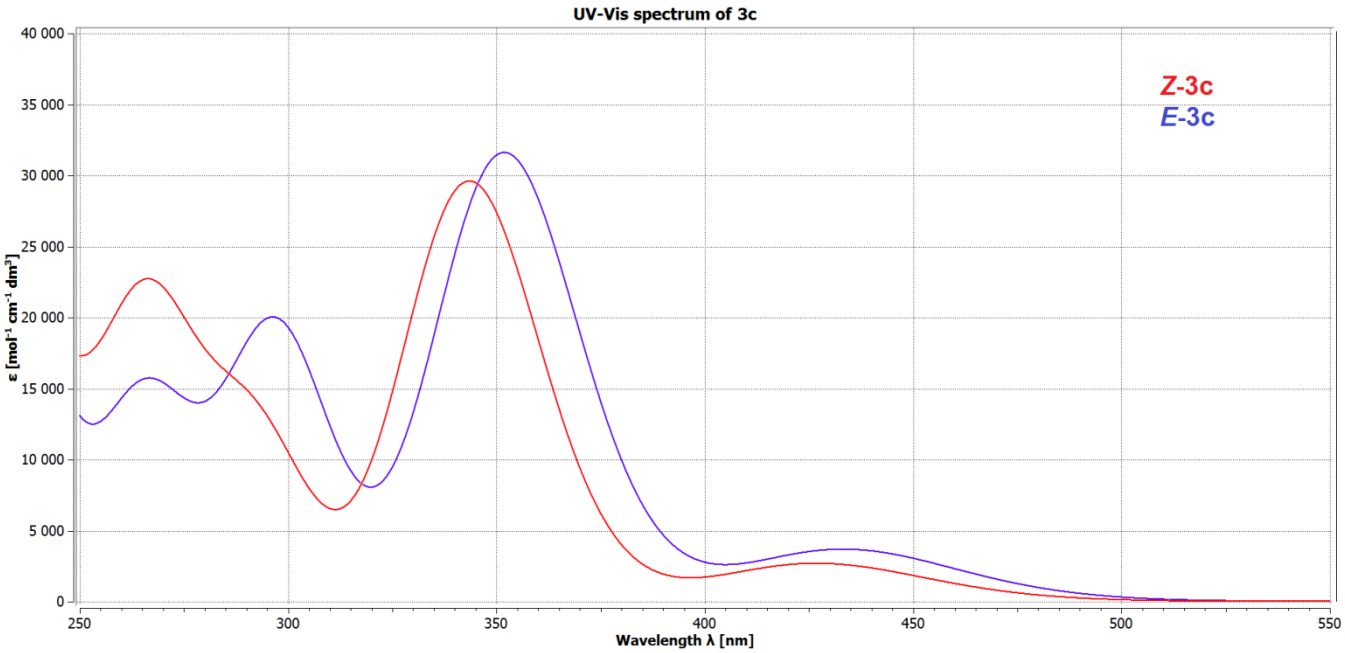


Figure S239. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **3c**.

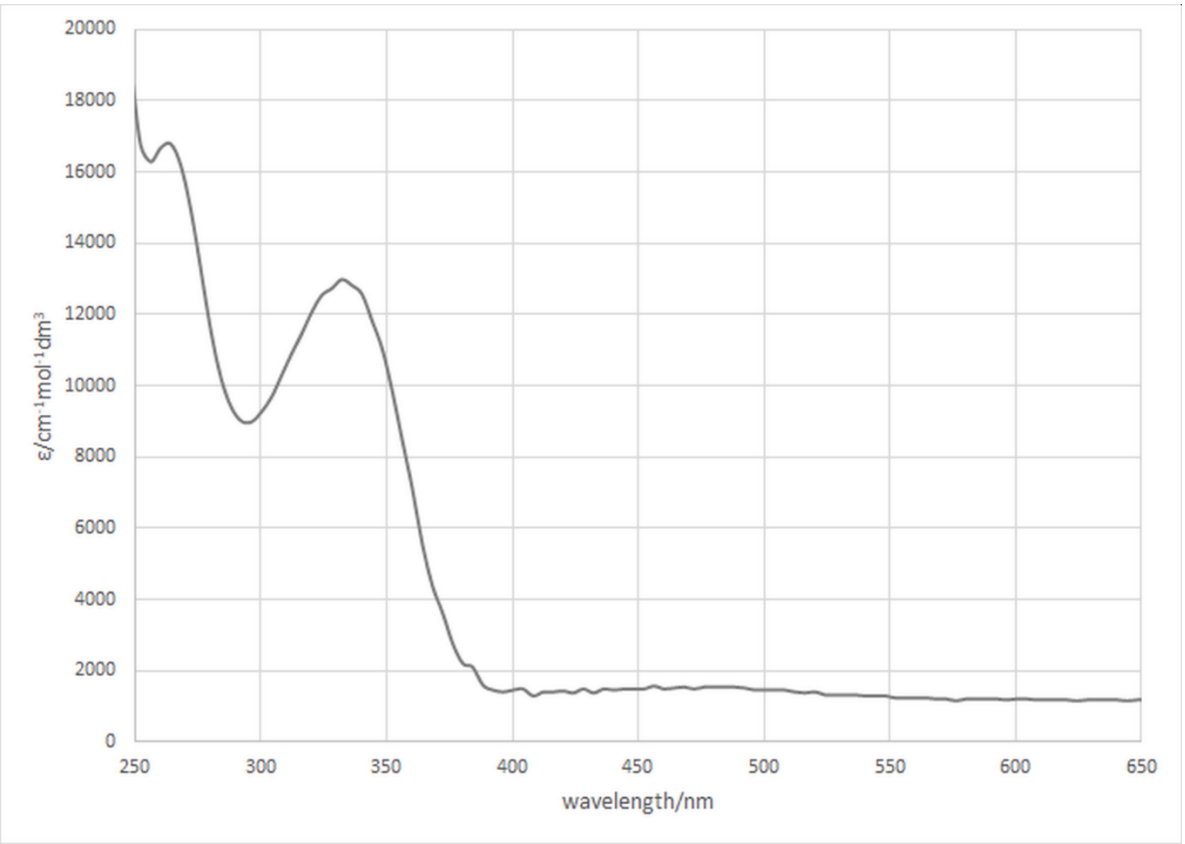


Figure S240. UV-VIS spectrum for phosphanylphosphaalkene **3d** in pentane.

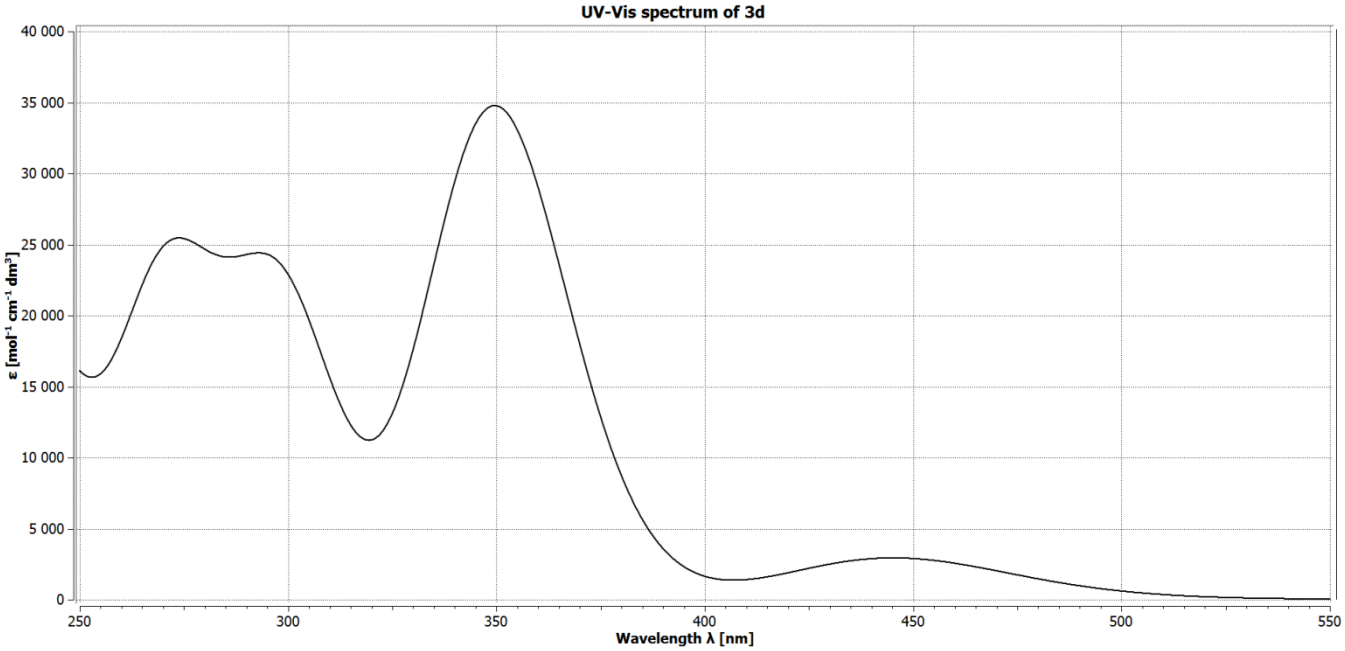


Figure S241. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **3d**.

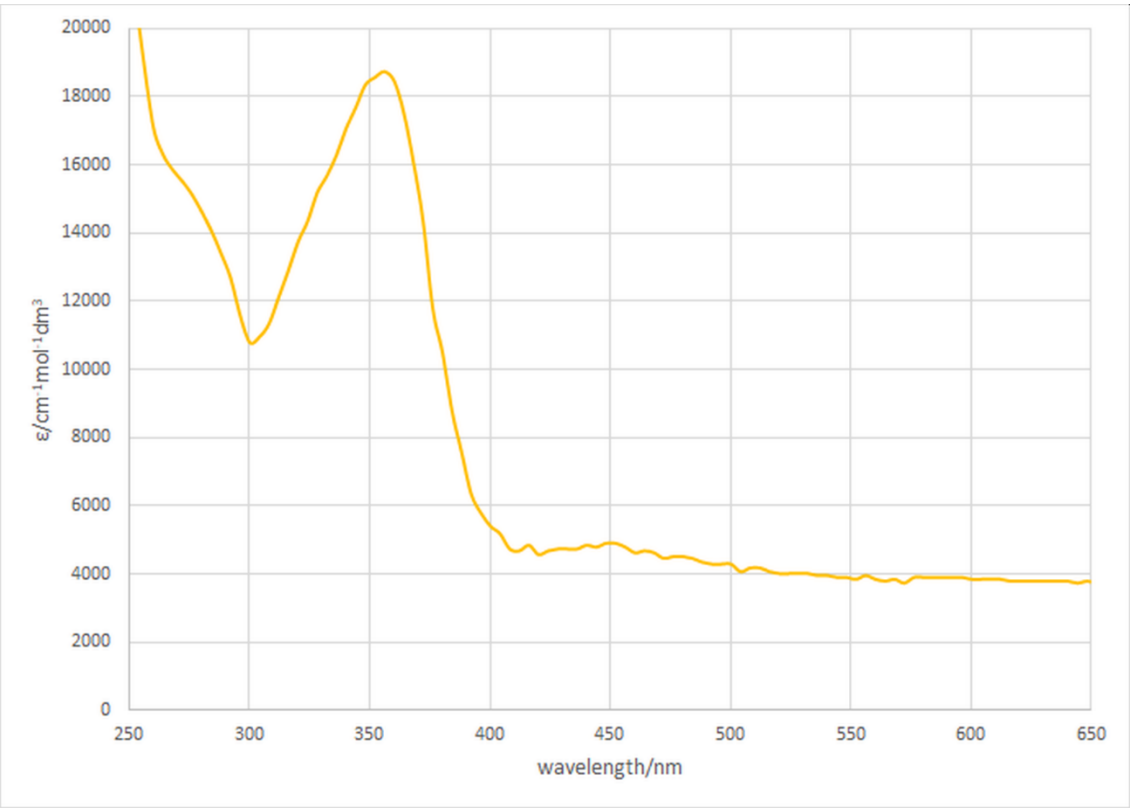


Figure S242. UV-VIS spectrum for phosphanylphosphaalkene **3e** in pentane.

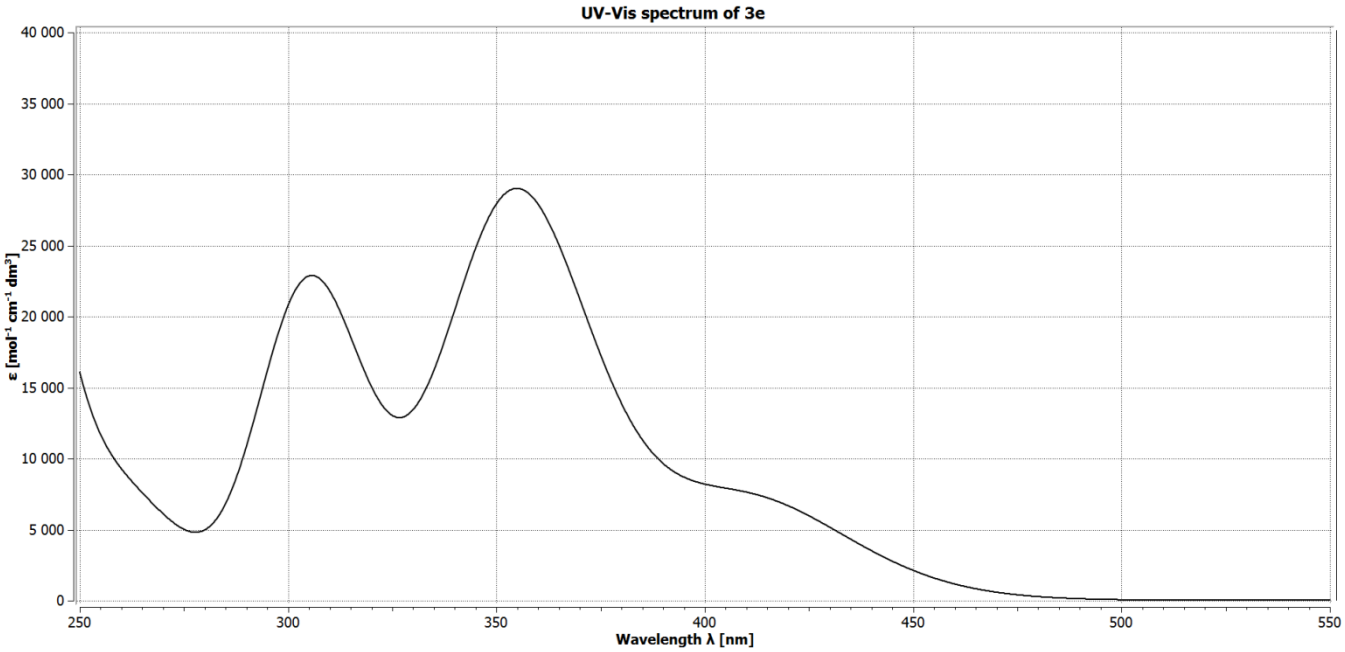


Figure S243. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **3e**.

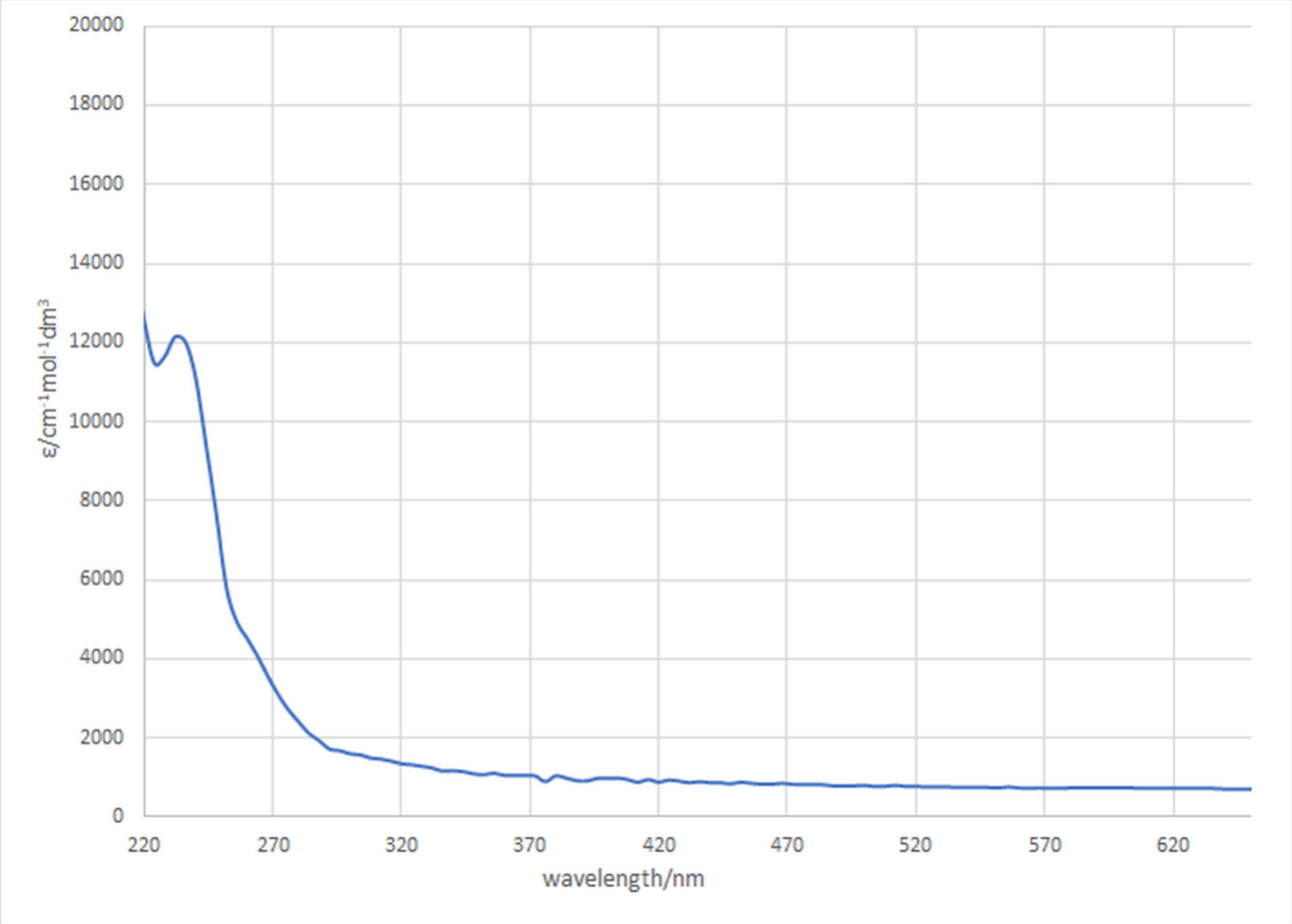


Figure S244. UV-VIS spectrum for phosphanylphosphaalkene **3f** in pentane.

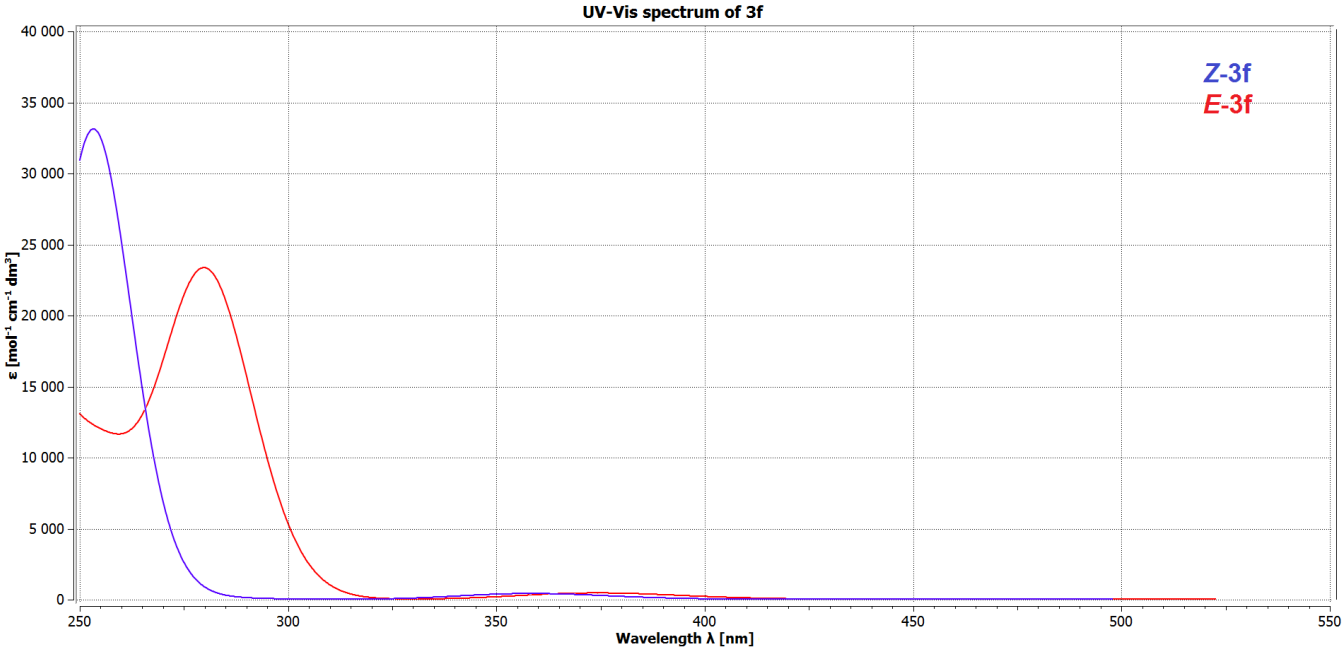


Figure S245. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **3f**.

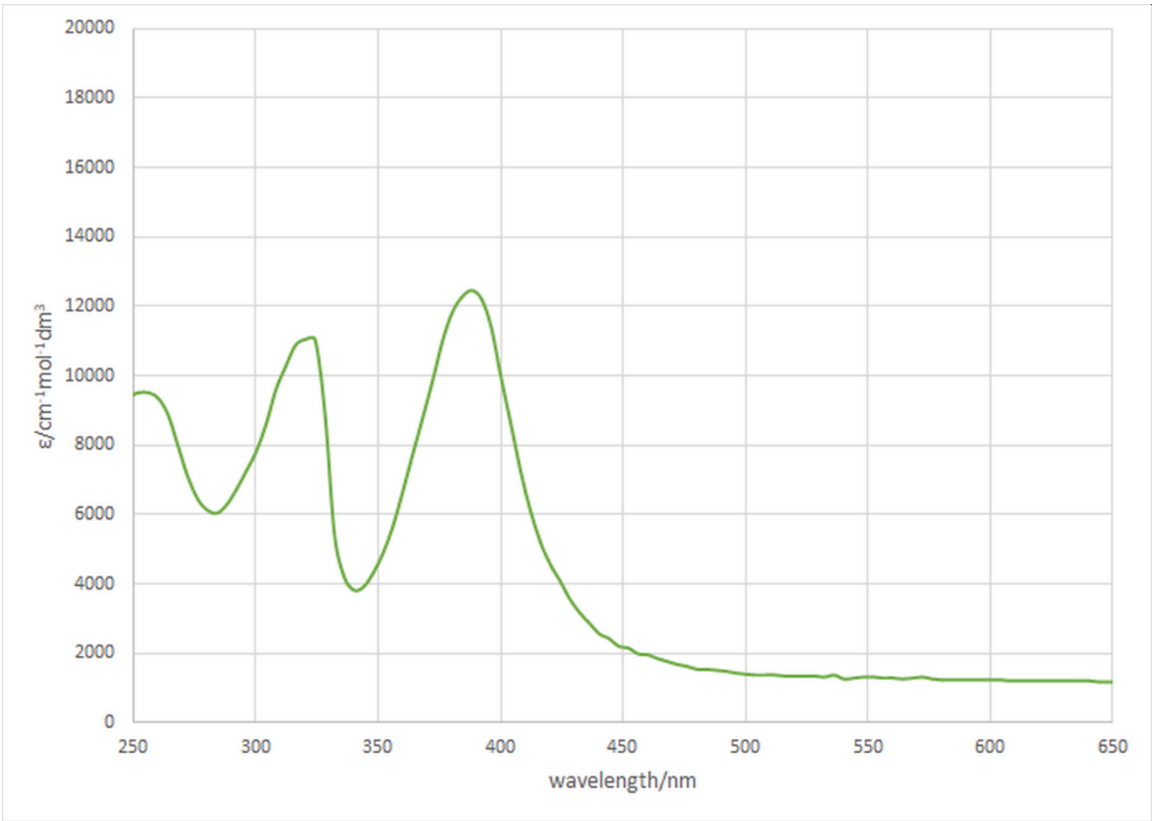


Figure S246. UV-VIS spectrum for phosphanylphosphaalkene **4d** in pentane.

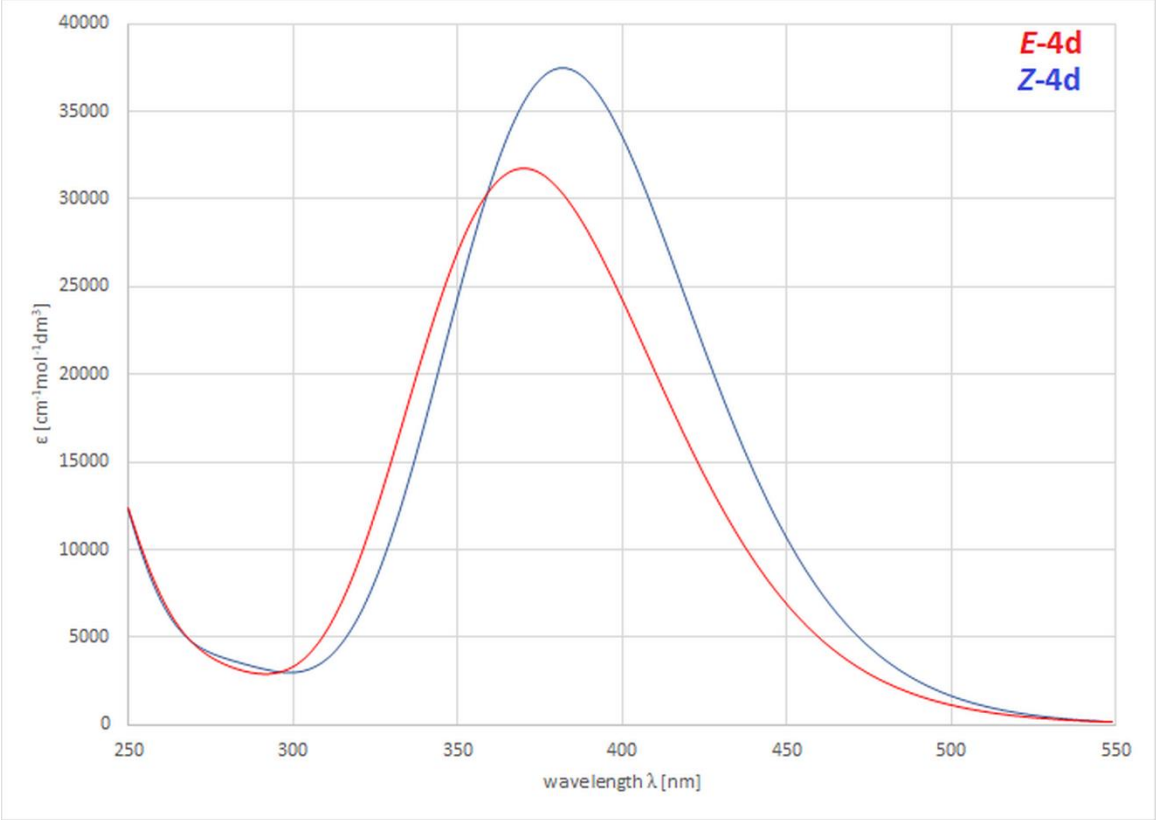


Figure S247. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **4d**.

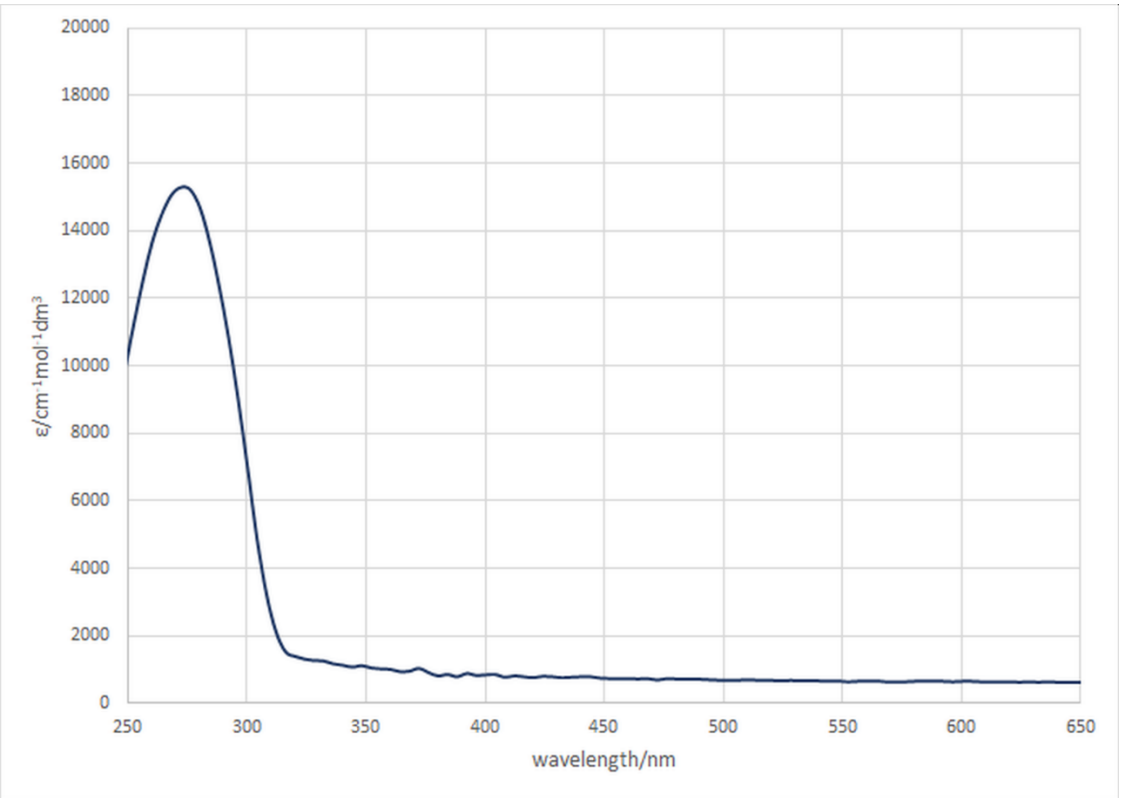


Figure S248. UV-VIS spectrum for phosphanylphosphaalkene **4e** in pentane.

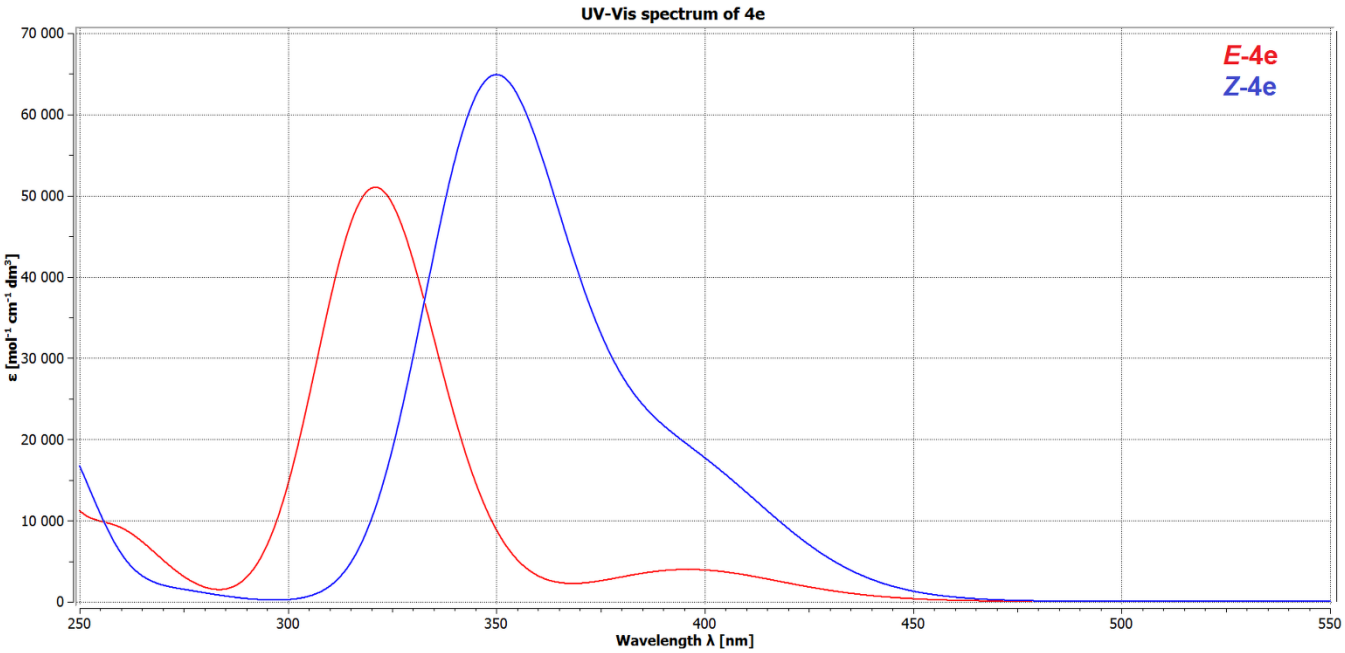


Figure S249. Theoretical UV-VIS spectrum for phosphanylphosphaalkene **4e**.

Table S8. UV-VIS spectroscopic data of **3a**, **3c**, **3d**, **3e**, **3f**, **4c** and **4d** in pentane at room temperature.

	Experimental		**Theoretical**	
	π -π* [λ/nm (log ε)	n- π* [λ/nm (log ε)	π -π* [λ/nm (log ε)	n- π* [λ/nm (log ε)
3a	322 (4.09)	440 (3.28)	340 (4.45)	412 (3.49)
3c	320 (3.29) not visible	not visible not visible	351 (4.49)_*E* 343 (4.47)_*Z*	433 (3.56)_*E* 426 (3.42)_*Z*
3d	332 (4.11)	480 (3.18)	349 (4.54)	445 (3.46)
3e	356 (4.27)	456 (3.69)	354 (4.46)	410 (3.87)
3f	264 (3.93) not visible	not visible not visible	280 (4.36)_*E* 253 (4.51)_*Z*	374 (2.65)_*E* 358 (2.61)_Z
4d	316 (4.04)_*E* 388 (4.06)_*Z*	not visible not visible	369 (4.51)_*E* 380 (4.64)_*Z*	391 (4.31)_*E* 359 (4.22)_*Z*
4e	277 (4.18) not visible	not visible not visible	320 (4.7)_*E* 349 (4.7)_*Z*	395 (3,65)_*E* 400 (4.32)_*Z*

PART G. References

1. W. Domanska-Babul, J. Chojnacki, E. Matern and J. Pikies, Reactions of R_2P-P($SiMe_3$)Li with [$(R_3P)_2PtCl_2$]. A general and efficient entry to phosphanylphosphinidene complexes of platinum. Syntheses and structures of [(η^2-P=P*i*Pr_2)Pt(p-$Tol_3P)_2$], [(η^2-P=P*t*Bu_2)Pt(p-$Tol_3P)_2$], [{η^2-P=P(N*i*$Pr_2)_2$}Pt(p-$Tol_3P)_2$] and [{($Et_2PhP)_2$Pt}$_2P_2$], *Dalton Trans.*, 2009, 146-151.
2. Ł. Ponikiewski, A. Ziółkowska and J. Pikies, Reactions of Lithiated Diphosphanes R_2P–P($SiMe_3$)Li (R = *t*Bu and *i*Pr) with [^{Me}NacnacTiCl_2·THF] and [^{Me}NacnacTiCl_3]. Formation and Structure of TitaniumIII and TitaniumIV β-Diketiminato Complexes Bearing the Side-on Phosphanylphosphido and Phosphanylphosphinidene Functionalities, *Inorg. Chem.*, 2017, **56**, 1094-1103.
3. E. Sattler, E. Matern, A. Rothenberger, A. Okrut, P. Bombicz, I. Fernández and I. Kovács, From Neutral to Ionic Species: Syntheses and X-ray Crystallographic and Multinuclear NMR Spectroscopic Studies of Li···P($SiMe_3$)–P*t*Bu_2 and Its Solvent Complexes, *Eur. J. Inorg. Chem.*, 2014, **2014**, 221-232.
4. A. Ziółkowska, N. Szynkiewicz and Ł. Ponikiewski, Molecular Structures of the Phospha-Wittig Reaction Intermediate: Initial Step in the Synthesis of Compounds with a C═P–P Bond as Products in the Phospha-Wittig Reaction, *Organometallics*, 2019, **38**, 2873-2877.
5. A. Ziółkowska, N. Szynkiewicz, J. Pikies and Ł. Ponikiewski, Synthesis of compounds with C–P–P and C=P–P bond systems based on the phospha-Wittig reaction, *Dalton Transactions*, 2020, **49**, 13635-13646.
6. G. Sheldrick, A short history of SHELX, *Acta Crystallogr. A*, 2008, **64**, 112-122.
7. L. Farrugia, WinGX and ORTEP for Windows: an update, *J. Appl. Cryst.*, 2012, **45**, 849-854.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. B.01.*Journal*, 2016.
9. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, Climbing the Density Functional Ladder: Nonempirical Meta--Generalized Gradient Approximation Designed for Molecules and Solids, *Phys. Rev. Lett.*, 2003, **91**, 146401.
10. S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
11. S. Kozuch and S. Shaik, How to Conceptualize Catalytic Cycles? The Energetic Span Model, *Acc. Chem. Res.*, 2011, **44**, 101-110.
12. S. Grimme, Density functional theory with London dispersion corrections, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2011, **1**, 211-228.
13. Y.-S. Lin, G.-D. Li, S.-P. Mao and J.-D. Chai, Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections, *J. Chem. Theory Comput.*, 2013, **9**, 263-272.
14. K. Wolinski, J. F. Hinton and P. Pulay, Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations, *J. Am. Chem. Soc.*, 1990, **112**, 8251-8260.
15. R. Peverati and D. G. Truhlar, Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16187-16191.
16. V. Barone and M. Cossi, Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, *J. Phys. Chem. A.*, 1998, **102**, 1995-2001.
17. R. G. Parr and W. Yang, Density functional approach to the frontier-electron theory of chemical reactivity, *J. Am. Chem. Soc.*, 1984, **106**, 4049-4050.
18. C. Morell, A. Grand and A. Toro-Labbé, New Dual Descriptor for Chemical Reactivity, *J. Phys. Chem. A.*, 2005, **109**, 205-212.
19. F. Weigend, Accurate Coulomb-fitting basis sets for H to Rn, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
20. F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.