Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Intramolecular C−N Bond Activation by Geometrically Constrained P^{III}-Centre

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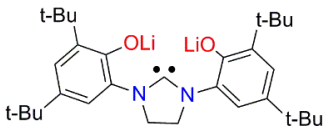
1. General experimental considerations: All preparations were carried out under an anhydrous N_2 atmosphere using standard Schlenk and glove box techniques. All glassware was oven dried and cooled under vacuum before use. Commercial reagents were purchased from Sigma Aldrich, Strem or Apollo Scientific and used without further purification unless indicated otherwise. **1** was prepared following the reported procedures.[1] NMR spectra were recorded at room temperature using a Bruker AvanceIII-400 MHz spectrometer. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), assignment.

2. X-ray Crystallography:

Single crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a MoKα X-ray source (α = 0.710 73 Å). The crystals were mounted on a cryoloop with Paratone oil, and all data were collected at 100(2) K. Unit cell determination and refinement and data collection were done using the Bruker APPEX-II suite,[2] data reduction and integration were performed using SAINT v8.34A (Bruker, 2013)[3] and absorption corrections and scaling were done using SADABS-2014/5 (Bruker,2014/5)[4]. All the crystal structures were solved through OLEX2[5] package using SHELXT[6] and the structures were refined using SHELXL[6]. All non-hydrogen atoms were refined anisotropically. All the figures were generated using Mercury 3.10.2. CCDC no (2097389, 2097391, 2097392 and 2097395) for the X-ray structures.

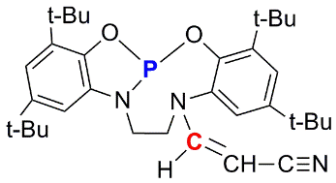
3. Experimental Procedures

Synthesis of 1-Li_2C:



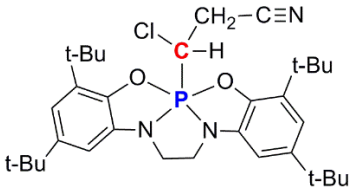
3.3 eq. *n*BuLi (0.474 mL, 2.5M in hexane, 1.185 mmol) was added to a 4 mL THF solution of **1** (185 mg, 0.3591 mmol) at -80 ^{o}C. The solution was allowed to warm temperature and stirred for 2h. The solution was concentrated up to 0.5 mL. The NMR of this solution showed exclusive formation of compound **1-Li_2C:**. **^{1}H NMR (400 MHz, in THF); δ** = 6.50 (m, 4H, Ar-*H*), 3.32 (s, 4H, -CH_2), 1.06 (s, 18H, -C(CH_3)$_3$), 0.86 (s, 18H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, in THF); δ** = 228.72 (N-*C*-N), 159.27, 136.78, 133.75, 130.70, 118.53, 117.08, 51.30 (-*C*H_2), 34.97 (-*C*(CH$_3$)$_3$), 31.25 (-C(*C*H$_3$)$_3$), 29.02 (-C(*C*H$_3$)$_3$).

Synthesis of 7:



3.3 eq. *n*BuLi (3.75 mL, 6 mmol, 1.6 M in hexanes) was added to a 35 mL THF solution of **1** (940 mg, 1.82 mmol) and acetonitrile (95 µL, 1.82 mmol) at -80 °C. The solution was allowed to warm to RT and stirred for 24h. PCl_3 (0.16 mL, 1.82 mmol) was added at -80 °C followed by the addition of Et_3N (0.26 mL, 1.82 mmol) after 5 min. The mixture was stirred for 15 min at this temperature and then allowed to warm to RT. The mixture was stirred for 18h. The solution was filtered and all the volatiles were evaporated that afforded a red solid. This solid was extracted with 80 mL hexane and further concentrated to 5 mL. Few drops of DCM were added. Slow evaporation of this solution at room temperature gave orange crystals after 3 days. Yield: 631 mg (63.2 %). **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 7.26 (s, 1H, Ar-*H*), 7.19 (d, 1H, *J* = 12 Hz, -CH=C*H*-CN), 6.93 (s, 1H, Ar-*H*), 6.85 (s, 1H, Ar-*H*), 6.60 (s, 1H, Ar-*H*), 4.34 (d, 1H, *J* = 12 Hz, -C*H*=CH-CN), 3.95 (m, 2H, -CH_2), 3.70 (m, 1H, -CH_2), 3.56 (m, 1H, -CH_2), 1.48 (s, 9H, -C(CH_3)$_3$), 1.30 (s, 9H, -C(CH_3)$_3$), 1.29 (s, 9H, -C(CH_3)$_3$), 1.21 (s, 9H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**; δ = 153.99 (-*C*H=CH-CN), 145.30, 145.16, 140.96, 134.44, 133.89, 131.91, 124.11, 121.24, 119.72 (-*C*N), 114.28, 103.86, 72.89 (-CH=*C*H-CN), 52.77 (d, *J* = 6 Hz, -*C*H_2), 40.85 (-*C*H_2), 35.42 (-*C*(CH$_3$)$_3$), 34.89 (-*C*(CH$_3$)$_3$), 34.66 (-*C*(CH$_3$)$_3$), 34.47 (-*C*(CH$_3$)$_3$), 31.88 (-C(*C*H$_3$)$_3$), 31.49 (-C(*C*H$_3$)$_3$), 29.94 (-C(*C*H$_3$)$_3$), 29.69 (-C(*C*H$_3$)$_3$). **^{31}P NMR (162 MHz, $CDCl_3$); *δ*** = 126.44 ppm. **HRMS** (APPI$^+$): Calculated for $C_{33}H_{46}N_3O_2P$: 547.3328 $[M]^+$; Obs: 547.3333.

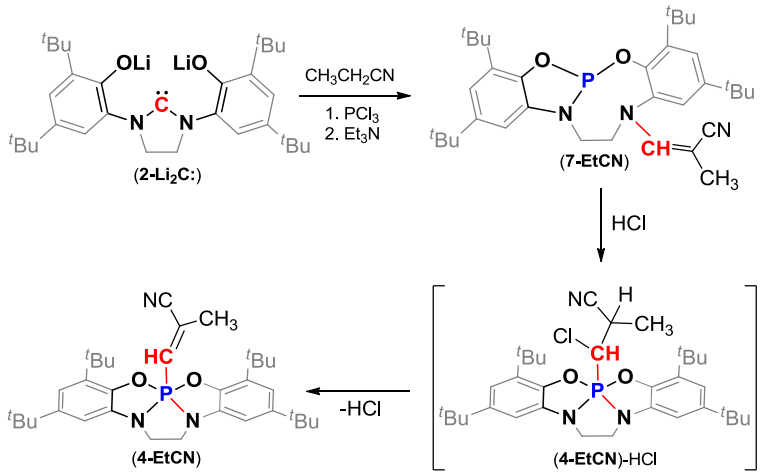
Synthesis of 4: Compound **4** could be obtained in absence of Et_3N (scavenger for HCl) during the synthesis of **7** in THF. In this process, after the addition of PCl_3 the mixture was stirred for overnight. All the volatiles were evaporated and the solid obtained was extracted with 50 mL hexane. The solution was fruther concentrated up to 20 mL that on slow evapoartion at room temperature after one week afforded colorless crystals (Yield: 450 mg, 42.4 %).



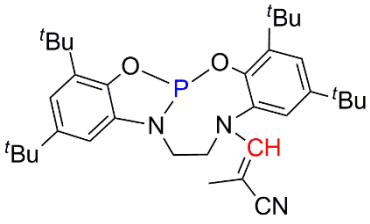
Alternative route: 1 equivalent HCl (0.5 mL, 2.0 M in Et_2O, 1.0 mmol) was added to a $CHCl_3$ (10 mL) solution of compound **7** (548 mg, 1 mmol) at -80 °C. The reaction mixture was allowed to warm to RT and stirred for 2h. All the volatiles were evaporated and the solid obtained was extracted with 20 mL hexane. Concentrating the solution to 10 mL and keeping for slow evaporation after one week afforded

colorless crystals (Yield: 305 mg, 52.2 %). ^{1}H NMR (400 MHz, $CDCl_3$); δ 6.82 (s, 2H, Ar-*H*), 6.60 (d, 2H, *J* = 8 Hz, Ar-*H*), 4.35 (m, 1H, P-C*H*), 3.86 (m, 2H, N-CH_2), 3.58 (s, 2H, N-CH_2), 3.12 (m, 1H, CN-CH_2), 2.74 (m, 1H, CN-CH_2), 1.43 (s, 18H, -C(CH_3)$_3$), 1.34 (s, 18H, -C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$); δ 144.55 (d, $J_{C\text{-}P}$ = 9 Hz), 139.92 (s), 133.40 (d, $J_{C\text{-}P}$ = 19 Hz), 132.80 (d, $J_{C\text{-}P}$ = 20 Hz), 132.50 (d, $J_{C\text{-}P}$ = 9 Hz), 132.20 (d, $J_{C\text{-}P}$ = 8 Hz), 116.80 (d, $J_{C\text{-}P}$ = 18 Hz), 114.02 (d, $J_{C\text{-}P}$ = 9 Hz, Ar-*C*H), 104.21 (t, $J_{C\text{-}P}$ = 9 Hz, Ar-*C*H), 55.88 (d, $J_{C\text{-}P}$ = 197 Hz, P-*C*H), 38.45 (d, $J_{C\text{-}P}$ = 20 Hz, N-*C*H_2), 37.52 (d, $J_{C\text{-}P}$ = 12 Hz, N-*C*H_2), 35.01 (-*C*(CH$_3$)$_3$), 34.41 (-*C*(CH$_3$)$_3$), 31.92 (-C(*C*H$_3$)$_3$), 29.84 (-C(*C*H$_3$)$_3$), 29.76 (-C(*C*H$_3$)$_3$), 24.34 (*C*H_2-CN). ^{31}P NMR (162 MHz, $CDCl_3$); δ -24.81 ppm. HRMS (ES^+): Calculated for $C_{33}H_{48}ClN_3O_2P$: 584.3173 $[M+H]^+$; Obs: 584.3163.

Synthesis of 7-EtCN:



*n*BuLi (4 mL, 6.4 mmol, 1.6 M in hexanes) was added to a 35 mL THF solution containing mixture of **1** (1 g, 1.94 mmol) and EtCN (139 µL, 1.94 mmol) at -80 °C. The solution was allowed to

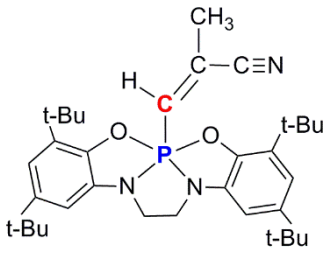


warm to room temperature and stirred for 24 h. PCl_3 (0.22 mL, 2.52 mmol) was added at -80 °C, followed by addition of Et_3N (0.35 mL, 2.52 mmol). The light orange mixture was stirred for 15 min at this temperature and then allowed to warm to room temperature and further stirred for 16 h. All the volatiles were evaporated and the solid left was extracted with 80 mL hexane. A white precipitate was obtained after concentrating this hexane solution up to 5 mL. This precipitate was further washed with 2×5 mL cold hexane that afforded pure compound as an

isomeric mixture (3:1). Yield: 650 mg, 59 %. ***1st Isomer (major):*** **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 7.20 (d, 1H, *J* = 4 Hz, Ar-*H*), 6.98 (d, 1H, *J* = 4 Hz, Ar-H), 6.85 (d, 1H, *J* = 4 Hz, Ar-*H*), 6.79 (s, 1H, -C*H*=C-CN), 6.61 (d, 1H, *J* = 4 Hz, Ar-*H*), 3.87-3.75 (m, 3H, -CH_2), 3.40 (m, 1H, -CH_2), 1.48 (s, 9H, -C(CH_3)$_3$), 1.32 (s, 9H, -C(CH_3)$_3$), 1.29 (s, 3H, -CH_3), 1.28 (s, 9H, -C(CH_3)$_3$), 1.23 (s, 9H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**; δ = 148.03 (-*C*H=CH-CN), 145.0, 144.51, 140.76, 134.51, 133.98 (d, *J* = 5 Hz), 132.63 (d, *J* = 5Hz), 123.40 (-*C*N), 123.17, 121.52, 114.23, 103.93, 87.63 (-CH=*C*H-CN) 57.12 (d, *J* = 7 Hz, -*C*H_2), 43.64 (-*C*H_2), 35.41 (-*C*(CH$_3$)$_3$), 34.98 (-*C*(CH$_3$)$_3$), 34.55 (-*C*(CH$_3$)$_3$), 31.97 (-C(*C*H$_3$)$_3$), 31.52 (-C(*C*H$_3$)$_3$), 29.96 (-C(*C*H$_3$)$_3$), 29.70 (-C(*C*H$_3$)$_3$), 14.27 (-*C*H$_3$). **^{31}P NMR (162 MHz, $CDCl_3$); *δ*** = 126.12 ppm. **HRMS** (APPI$^+$): Calculated for $C_{34}H_{48}N_3O_2P$: 561.3484 $[M]^+$; Obs: 561.3489.

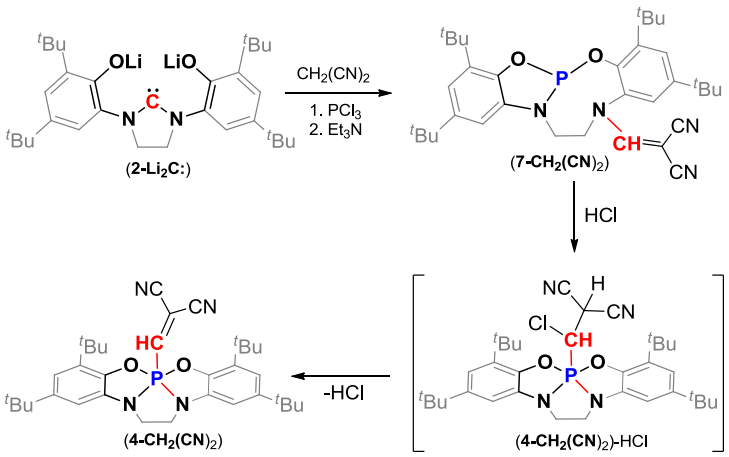
2nd Isomer (minor): **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 7.25 (d, 0.3H, *J* = 4 Hz, Ar-*H*), 6.95 (d, 0.3H, *J* = 4 Hz, Ar-H), 6.64 (d, 0.3H, *J* = 4 Hz, Ar-*H*), 6.49 (s, 0.3H, -C*H*=C-CN), 4.53 (m, 0.3H, -CH_2), 4.05 (m, 0.3H, -CH_2), 3.47 (m, 0.3H, -CH_2), 1.48 (s, 3H, -C(CH_3)$_3$), 1.32 (s, 3H, -C(CH_3)$_3$), 1.30 (s, 9H, -C(CH_3)$_3$), 1.23 (s, 3H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**; δ = 146.69 (-CH=*C*H-CN), 123.78, 121.82, 114.08, 52.16 (d, *J* = 6 Hz, -*C*H_2), 41.91 (-*C*H_2), 29.78 (-C(*C*H$_3$)$_3$), other signals could not be distinguished from major isomer. **^{31}P NMR (162 MHz, $CDCl_3$); *δ*** = 126.81 ppm.

Synthesis of 4-EtCN: 1 equivalent HCl (0.2 mL, 2.0 M in Et_2O, 0.4 mmol) was added to a $CHCl_3$ (2 mL) solution of compound **7-EtCN** (228 mg, 0.4 mmol) at -80 °C. The reaction mixture was allowed to warm to RT and stirred for overnight. All the volatiles were evaporated and the solid obtained was dissolved in 5 mL hexane. On keeping this solution for slow evaporation after one week afforded crystalline product (Yield: 150 mg, 65.8 %). ^{1}H NMR (400 MHz, $CDCl_3$); *δ* 6.84 (s, 2H, Ar-*H*), 6.65 (s, 2H, Ar-*H*), 6.58 (d, 1H, *J* = 12 Hz, P-C*H*), 4.07-4.02 (m, 2H, N-CH_2), 3.56 (m, 2H, N-CH_2), 1.97 (s, 3H, -CH_3), 1.45 (s, 18H, -C(CH_3)$_3$), 1.35 (s, 18H, -C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$); *δ* 145.0 (d, $J_{C\text{-}P}$ = 225 Hz, P-*C*H), 144.01, 139.91, 133.14

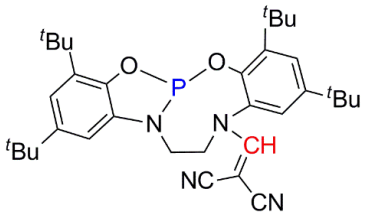


(d, $J_{C\text{-}P}$ = 20 Hz), 132.39 (d, $J_{C\text{-}P}$ = 9 Hz), 117.97 (d, $J_{C\text{-}P}$ = 12 Hz, -*C*N), 116.29, (-CH=*C*-CN), 113.92 (Ar-*C*H), 104.92 (d, $J_{C\text{-}P}$ = 11 Hz, Ar-*C*H), 38.75 (d, $J_{C\text{-}P}$ = 12 Hz, N-*C*H_2), 34.98 (-*C*$(CH_3)_3$), 34.44 (-*C*$(CH_3)_3$), 31.95 (-C(*C*$H_3)_3$), 29.71 (-C(*C*$H_3)_3$), 23.73 (d, *J* = 21 Hz, -*C*H_3). ^{31}P NMR (162 MHz, $CDCl_3$); ***δ*** -32.30 ppm. HRMS (AP^+): Calculated for $C_{34}H_{49}N_3O_2P$: 562.3562 $[M+H]^+$; Obs: 562.3564.

Synthesis of 7-$CH_2(CN)_2$:



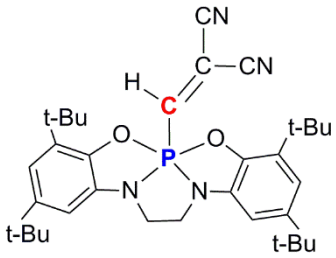
*n*BuLi (4 mL, 6.4 mmol, 1.6 M in hexanes) was added to a 35 mL THF solution containing mixture



of **1** (1 g, 1.94 mmol) and $CH_2(CN)_2$ (128 mg, 1.94 mmol) at -80 °C. The solution was allowed to warm to room temperature and stirred for 24 h. PCl_3 (0.22 mL, 2.52 mmol) was added at -80 °C, followed by addition of Et_3N (0.35 mL, 2.52 mmol). The dark red mixture was stirred for 15 min at this temperature and then allowed to warm to room temperature and further stirred for 16 h. All the volatiles were evaporated and the solid left was extracted with 50 mL hexane. The solution was concentrated up to 5 mL and kept for crystallization. An off white precipitate was obtained next day. This precipitate was further washed with 2×10 mL cold hexane that afforded pure compound as an isomeric mixture (2:1.3:0.5). Yield: 430 mg, 38.7 %. ***1st Isomer (major):*** **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 7.55 (s, 1H, -C*H*=C(CN)$_2$), 7.39 (s, 2H Ar-*H*), 6.91 (s, 2H, Ar-H), 4.32 (br, 1H, -C*H*$_2$), 3.86 (br, 3H, -C*H*$_2$), 1.50 (s, 18H, -C(C*H*$_3)_3$), 1.32 (s, 9H, -C(C*H*$_3)_3$), 1.23 (s,

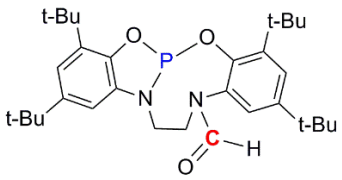
9H, -C(CH_3)$_3$) ppm. ***2nd Isomer:*** **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 7.38 (s, 0.65H, -C*H*=C(CN)$_2$), 7.05 (s, 0.65H Ar-*H*), 6.93 (s, 0.65H, Ar-H), 6.74 (s, 0.65H, Ar-H), 6.61 (s, 0.65H, Ar-H), 4.32 (m, 0.65H, -CH_2), 4.12-3.99 (m, 2H, -CH_2), 3.86 (br, 1H, -CH_2) ppm; -C(CH_3)$_3$ signals could not be distinguished from 1st isomer. ***3rd Isomer:*** **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 7.59 (s, 0.25H Ar-*H*), 7.10 (s, 0.25H, Ar-H), 6.80 (s, 0.25H, Ar-H), 6.69 (s, 0.25H, -C*H*=C(CN)$_2$), 4.80 (br, 0.5H, -CH_2) ppm; -C(CH_3)$_3$ signals could not be distinguished from 1st isomer. **^{13}C NMR (100 MHz, $CDCl_3$)**; δ = 160.30 (-*C*H=C(CN)$_2$, 1st isomer), 158.34 (-*C*H=C(CN)$_2$, 2nd isomer), 157.43 (-*C*H=C(CN)$_2$, 3rd isomer), 59.73 (-CH=*C*(CN)$_2$, 3rd isomer); other signals could not be distinguished among all three isomers. **^{31}P NMR (162 MHz, $CDCl_3$); *δ*** = 131.09 (3rd isomer), 128.35 (2nd isomer), 126.41 (1st isomer) ppm. **HRMS** (APPI$^+$): Calculated for $C_{34}H_{45}N_4O_2P$: 572.3280 [M]$^+$; Obs: 572.3278.

Synthesis of 4-$CH_2(CN)_2$: 1 equivalent HCl (0.2 mL, 2.0 M in Et_2O, 0.4 mmol) was added to a



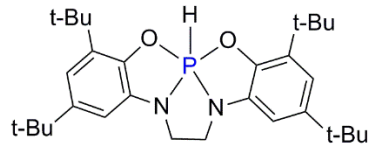
$CHCl_3$ (5 mL) solution of compound **7- $CH_2(CN)_2$** (229 mg, 0.4 mmol) at -80 °C. The reaction mixture was allowed to warm to RT and stirred for overnight. All the volatiles were evaporated and the solid obtained was dissolved in 5 mL hexane. On keeping this solution for slow evaporation after one week afforded red precipitate (Yield: 210 mg, 91.7 %). ^{1}H NMR (400 MHz, $CDCl_3$); *δ* 7.64 (d, 1H, *J* = 8 Hz, P-C*H*), 6.94 (s, 2H, Ar-*H*), 6.73 (s, 2H, Ar-*H*), 4.10-4.04 (m, 2H, N-CH_2), 3.67 (m, 2H, N-CH_2), 1.49 (s, 18H, -C(CH_3)$_3$), 1.38 (s, 18H, -C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$); *δ* 162.75 (d, $J_{C\text{-}P}$ = 220 Hz, P-*C*H), 145.09, 139.33, 133.30 (d, $J_{C\text{-}P}$ = 9 Hz), 132.19 (d, $J_{C\text{-}P}$ = 20 Hz), 114.98 (Ar-*C*H), 112.55 (d, $J_{C\text{-}P}$ = 28 Hz, -*C*N), 111.55 (d, $J_{C\text{-}P}$ = 9 Hz), 105.33 (d, $J_{C\text{-}P}$ = 12 Hz, Ar-*C*H), 91.94 (d, $J_{C\text{-}P}$ = 6 Hz, -CH=*C*-CN), 38.50 (d, $J_{C\text{-}P}$ = 12 Hz, N-*C*H_2), 35.04 (-*C*(CH_3)$_3$), 34.49 (-*C*(CH_3)$_3$), 31.86 (-C(*C*H_3)$_3$), 29.72 (-C(*C*H_3)$_3$). ^{31}P NMR (162 MHz, $CDCl_3$); *δ* -35.89 ppm. HRMS (AP$^+$): Calculated for $C_{34}H_{46}N_4O_2P$: 573.3358 [M+H]$^+$; Obs: 573.3364.

Synthesis of 9:



3.3 eq. *n*BuLi (3.75 mL, 6 mmol, 1.6 M in hexanes) was added to a 35 mL THF solution of **1** (940 mg, 1.82 mmol) and H_2O (33 µL, 1.82 mmol) at -80 °C. The solution was allowed to warm to RT and stirred for 24h. PCl_3 (0.16 mL, 1.82 mmol) was added at -80 °C followed by the addition of Et_3N (0.26 mL, 1.82 mmol) after 5 min. The mixture was stirred for 15 min at this temperature and then allowed to warm to RT. The mixture was stirred for 18h. The solution was filtered and all the volatiles were evaporated that afforded a red solid. This solid was extracted with 40 mL hexane and fruther concentrated to 5 mL. Few drops of DCM were added. Slow evaporation of the DCM-hexane mixtutre at room temperature after 2 days afforded transparent crystals. Yield: 660 mg (69.2 %). **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 8.49 (s, O=C*H*-), 7.34 (s, 1H, Ar-*H*), 6.93 (s, 1H, -C=C*H*), 6.86 (s, 1H, Ar-*H*), 6.68 (s, 1H, Ar-*H*), 4.37 (m, 2H, -CH_2), 3.93 (t, *J* = 12 Hz, 1H, -CH_2), 3.27 (t, *J* = 12 Hz, 1H, -CH_2), 1.49 (s, 9H, -C(CH_3)$_3$), 1.34 (s, 9H, -C(CH_3)$_3$), 1.32 (s, 9H, -C(CH_3)$_3$), 1.30 (s, 9H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**; ***δ*** = 166.07 (O=*C*H-), 146.51, 145.21 (d, *J* = 14 Hz), 143.68 (d, *J* = 12 Hz), 141.42, 134.68, 133.82, 130.90, 124.55, 123.04, 114.13, 103.72, 49.22 (d, *J* = 8 Hz, -*C*H_2), 40.67 (-*C*H_2), 35.60 (-*C*(CH$_3$)$_3$), 35.03 (-*C*(CH$_3$)$_3$), 34.67 (-*C*(CH$_3$)$_3$), 34.59 (-*C*(CH$_3$)$_3$), 31.99 (-C(*C*H$_3$)$_3$), 31.54 (-C(*C*H$_3$)$_3$), 30.08 (-C(*C*H$_3$)$_3$), 29.98 (-C(*C*H$_3$)$_3$). **^{31}P NMR (162 MHz, $CDCl_3$); *δ*** = 127.13 ppm. **HRMS** (APCI$^+$): Calculated for $C_{31}H_{46}N_2O_3P$: 525.3241 $[M+H]^+$; Obs:525.3209.

Synthesis of 5:

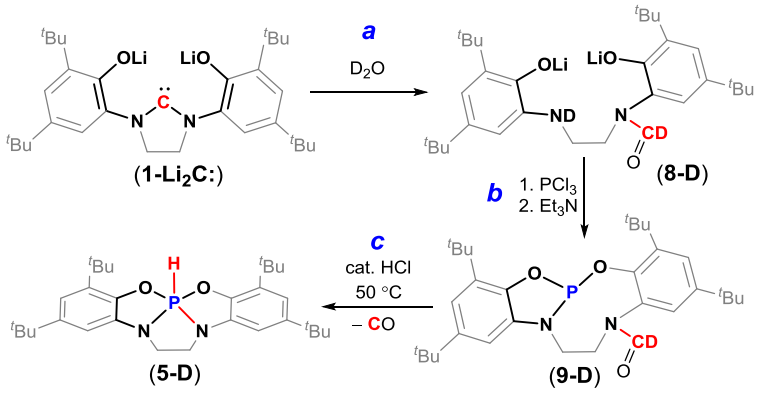


Catalytic amount of HCl (10 µL, 2.0 M in Et_2O, 0.02 mmol) was added to **9** (524 mg, 1mmol) dissolved in 5 mL chloroform solution and heated for 48 h at 50 °C. All the volatiles were evaporated that afforded a white solid which was crystallized by slow evaporation of hexane-DCM mixture at room temperature. Yield: 410 mg (82.5 %). **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 8.43 (d, $J_{H\text{-}P}$ = 788 Hz, -P*H*), 6.82 (s, 2H, Ar-*H*), 6.62 (s, 2H, Ar-*H*), 3.72 (m, 2H, -CH_2), 3.52 (m, 2H, -CH_2), 1.43 (s, 18H, -C(CH_3)$_3$), 1.32 (s, 18H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$); *δ*** = 143.83, 140.82, 132.93 (d, *J* = 18 Hz), 132.49 (d, *J* = 9 Hz), 114.11, 104.52 (d, *J* = 9 Hz), 38.33 (d, *J* = 10 Hz, -*C*H_2), 34.81 (-*C*(CH$_3$)$_3$), 34.34 (-*C*(CH$_3$)$_3$), 31.77 (-C(*C*H$_3$)$_3$), 29.56 (-

C(CH_3)$_3$). **^{31}P NMR (162 MHz, $CDCl_3$); δ** = -39.43 (d, J_{P-H} = 790 Hz) ppm. **HRMS** (ES^+): Calculated for $C_{30}H_{46}N_2O_2P$: 497.3297 $[M]^+$; Obs: 497.3293.

Note: The formation of **5** could be expedite by equimolar reaction of **9** with HCl at room temperature.

Deuterium labelling experiment: *A deuterium labelling experiment was conducted in an attempt to understand the origin of 'H/D' in the P-H moiety in compound* ***5****.*



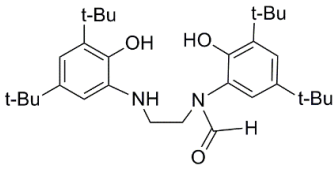
Synthesis of 9-D: 3.2 eq. *n*BuLi (3.8 mL, 6.2 mmol, 1.6 M in hexanes) was added to a 35 mL THF solution of **1** (1 g, 1.94 mmol) at -80 °C. The solution was allowed to warm to RT and stirred for 3h. D_2O (35 µL, 1.94 mmol) was added at -80 °C. The solution was allowed to warm to RT and stirred for 24h. PCl_3 (0.23 mL, 2.5 mmol) was added at -80 °C followed by the addition of Et_3N (0.35 mL, 2.5 mmol) after 5 min. The mixture was stirred for 15 min at this temperature and then allowed to warm to RT. The mixture was stirred for 12h. All the volatiles were evaporated and the off-white solid obtained was extracted with 40 mL hexane and further concentrated to 5 mL that yielded a crystalline solid. Washing this solid with 3×3 mL hexane gave pure compound. Yield: 230 mg (22.5 %). **^{1}H NMR (400 MHz, $CDCl_3$)**; δ = 7.38 (s, 1H, Ar-*H*), 6.97 (s, 1H, -C=C*H*), 6.90 (s, 1H, Ar-*H*), 6.73 (s, 1H, Ar-*H*), 4.40 (m, 2H, -CH_2), 3.97 (t, *J* = 12 Hz, 1H, -CH_2), 3.31 (m, 1H, -CH_2), 1.52 (s, 9H, -C(CH_3)$_3$), 1.38 (s, 9H, -C(CH_3)$_3$), 1.36 (s, 9H, -C(CH_3)$_3$), 1.34 (s, 9H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**; δ = 165.77 (t, J_{C-D} = 32 Hz, O=*C*D-), 146.50, 145.17 (d, *J* = 13 Hz), 143.68 (d, *J* = 11 Hz), 141.39, 134.63, 133.82, 130.90, 124.50, 122.99, 114.10, 103.71, 49.13 (d, *J* = 8 Hz, -CH_2), 40.66 (-CH_2), 35.58 (-*C*(CH$_3$)$_3$), 35.00 (-*C*(CH$_3$)$_3$), 34.63 (-*C*(CH$_3$)$_3$), 34.56 (-*C*(CH$_3$)$_3$), 31.98 (-C(*C*H$_3$)$_3$), 31.53 (-C(*C*H$_3$)$_3$), 30.08 (-C(*C*H$_3$)$_3$), 29.97 (-C(*C*H$_3$)$_3$). **^{31}P NMR (162 MHz, $CDCl_3$)**; δ = 127.17 ppm.

Synthesis of 5-D: Catalytic amount of HCl (5 μL, 2.0 M in Et_2O, 0.01 mmol) was added to **9-D** (105 mg, 0.2 mmol) dissolved in 0.5 mL chloroform solution and heated for 48 h at 50 °C. ^{31}P NMR spectra of this reaction showed formation of a PH (**5**) compound as major product. Formation of a small amount of P-D (**5-D**) product could also be seen by a triplet (-37.59 ppm, $J_{P\text{-}D}$ = 123 Hz) in ^{31}P NMR spectrum.

Reaction of 1-Li_2C: with PCl_3 in presence of other molecules: We screened various new substrates such as Cl-CH_2CN, CH_3CH_2CN, $CH_2(CN)_2$, $PhCH_2CN$, CH_3NO_2, NH_2CN, EtOAc. Interestingly, the reaction of reaction of PCl_3 with **1-Li_2C:** in presence of equivalent amount of $ClCH_2CN$ produced phosphine **7** that was also obtained from the acetonitrile (CH_3CN) route (already mentioned in manuscript). The reaction performed in the presence of $PhCH_2CN$ lead the formation of its corresponding phosphine (**7-$PhCH_2CN$**) however its very high solubility in all organic solvents precluded its purification. Nevertheless, formation of a desired C-N activated (P^V) product was not observed clearly when **7-$PhCH_2CN$** (crude compound) was treated with HCl, rather a complex mixture was formed. In case when the reaction was performed in presence of equivalent amount of CH_3NO_2 or NH_2CN, formation of multiple products was observed that could not be purified. A complex mixture was also observed in case when the reaction was performed in presence of equivalent amount of EtOAc, perhaps this could be explaining by the presence of two reactive sites (C-H and O-H bonds) in ethyl acetate that can react with carbene center.

Decarbonylation attempt from 8-OH promoted by HCl:

Synthesis of quenched compound 8-OH from 8: 5 mL THF solution of **8** (104 mg, 0.2 mmol) was



quenched dropwise with excess H_2O (2-3mL). The solution was filtered, dried under vaccum and then extracted with DCM (5 mL). A white precipitate was obtained after 1 day by the slow evaporation. Yield: 45 mg (45 %). **^{1}H NMR (400 MHz, $CDCl_3$); *δ*** = 10.38 (s, -OH), 8.28 (s, O=C*H*-), 7.50 (s, 1H, Ar-*H*), 7.35, 7.26 (s, 1H, Ar-*H*), 7.05 (s, 1H, Ar-*H*), 4.94 (br, 4H, -CH_2), 1.46 (s, 9H, -C(CH_3)$_3$), 1.44 (s, 9H, -C(CH_3)$_3$), 1.35 (s, 9H, -C(CH_3)$_3$), 1.30 (s, 9H, -C(CH_3)$_3$) ppm. **^{13}C NMR (100 MHz, $CDCl_3$); *δ*** = 164.56 (O=*C*H-), 163.32, 151.32, 148.42, 142.86, 142.86, 139.95, 134.20, 128.74, 124.97, 122.92, 119.96, 113.81, 44.80 (-*C*H_2), 35.69 (-*C*(CH$_3$)$_3$), 34.53 (-*C*(CH$_3$)$_3$), 31.93 (-C(*C*H$_3$)$_3$), 31.65 (-C(*C*H$_3$)$_3$), 30.08 (-C(*C*H$_3$)$_3$), 29.82 (-C(*C*H$_3$)$_3$).

Decarbonylation attempts of 8-OH: 32 % HCl in H_2O (10 µL) was added to a 0.5 mL $CDCl_3$ solution of 8-OH (45 mg, 0.09 mmol). The formation of CO gas was not observed on heating this mixture at 50 °C for 48 h. The formamide group remained untouched.

4. Selected spectra:

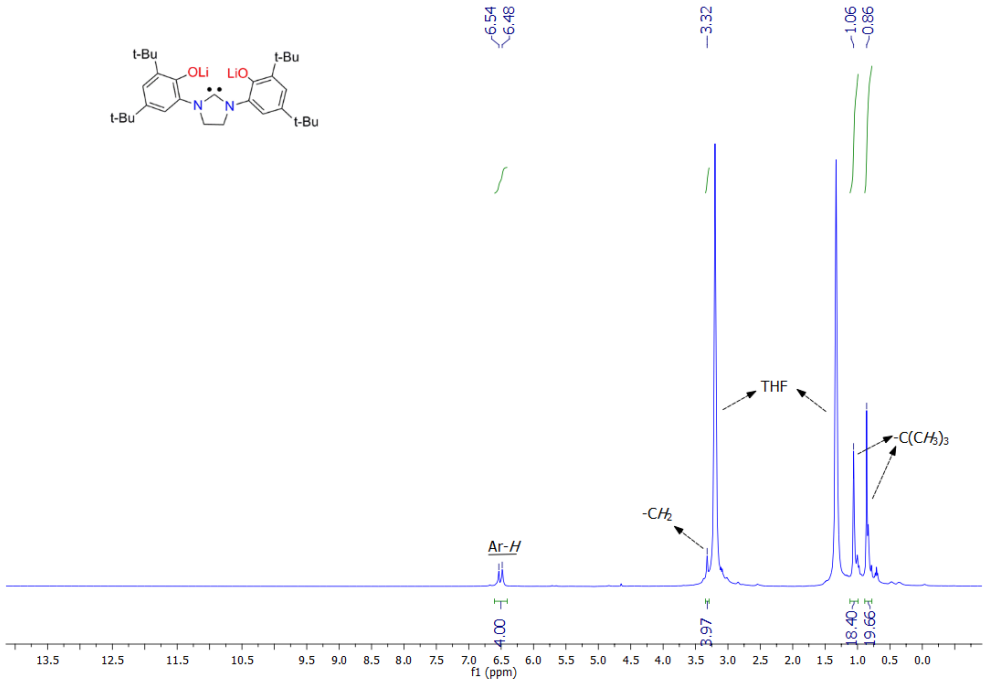


Figure S1. ^{1}H NMR spectrum (400 MHz, in THF reaction mixture) of **1-Li$_2$C:**.

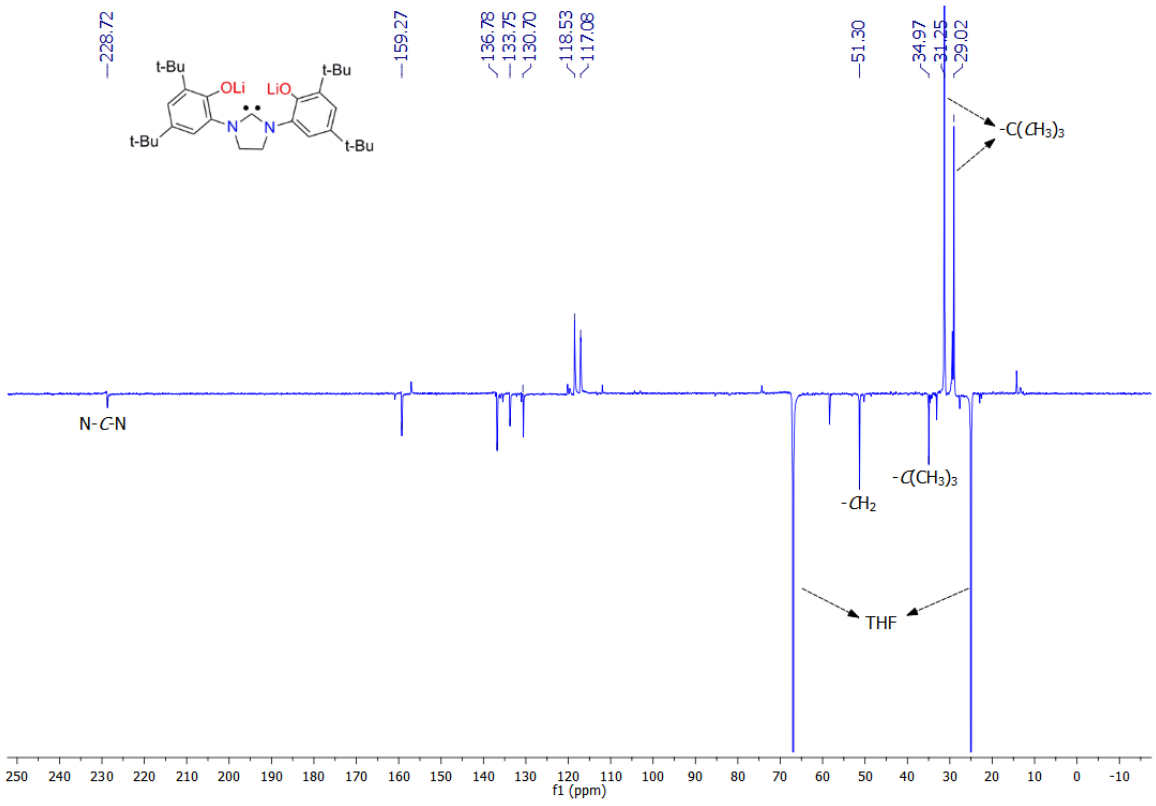


Figure S2. ^{13}C-JMOD NMR spectrum (100 MHz, in THF reaction mixture) of **1-Li$_2$C:**

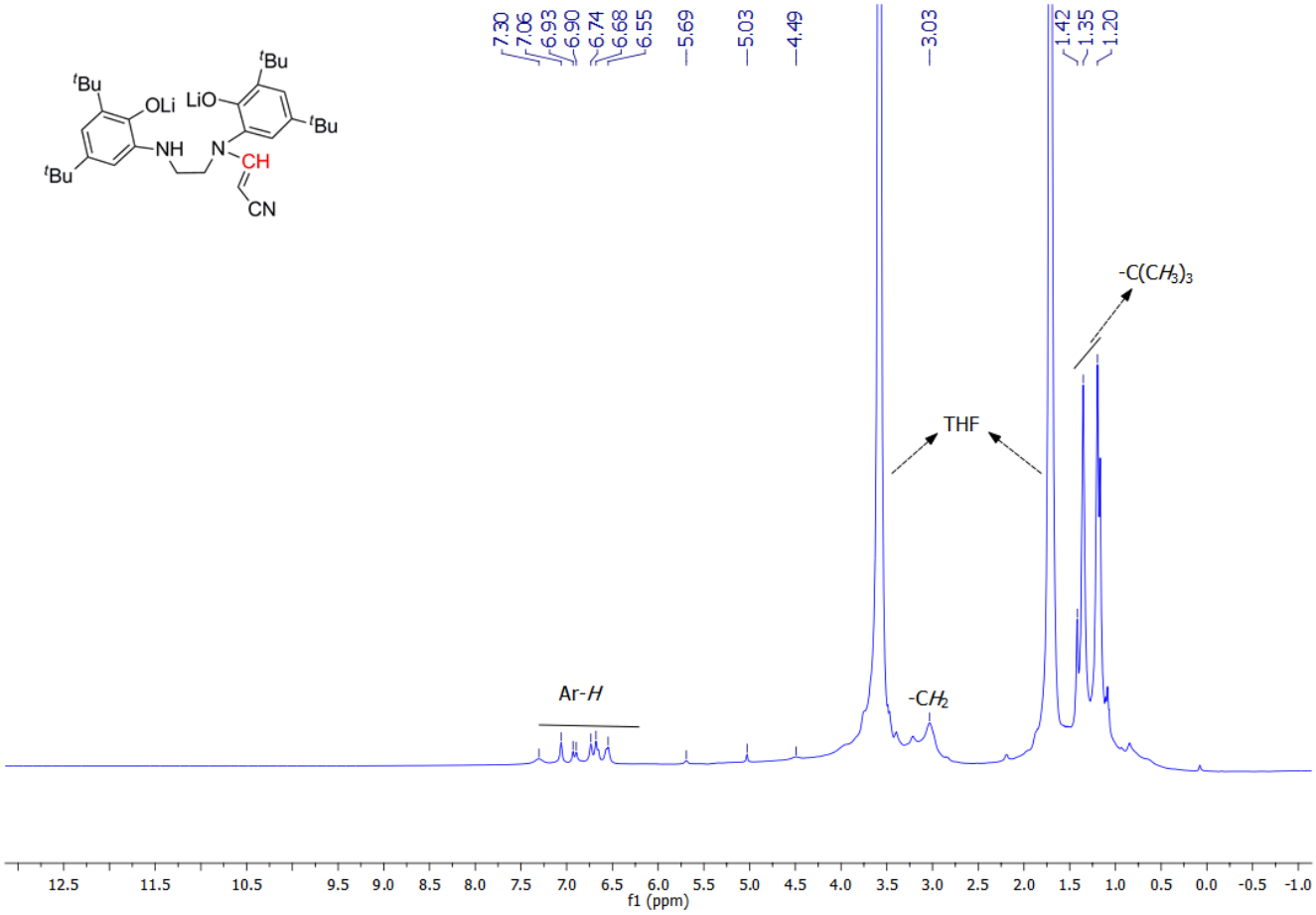


Figure S3. ^{1}H NMR spectrum (400 MHz, in THF reaction mixture) of **6**.

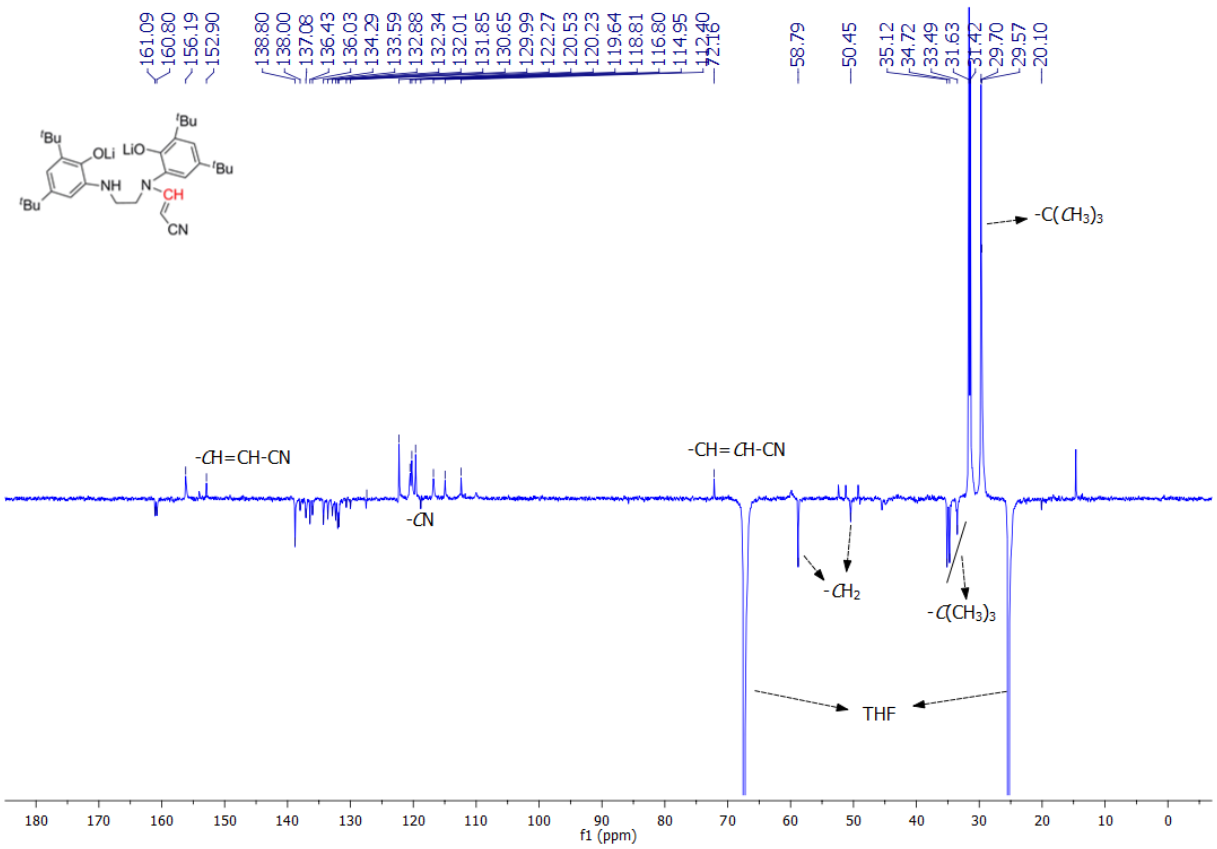


Figure S4. ^{13}C-JMOD NMR spectrum (100 MHz, in THF reaction mixture) of **6**.

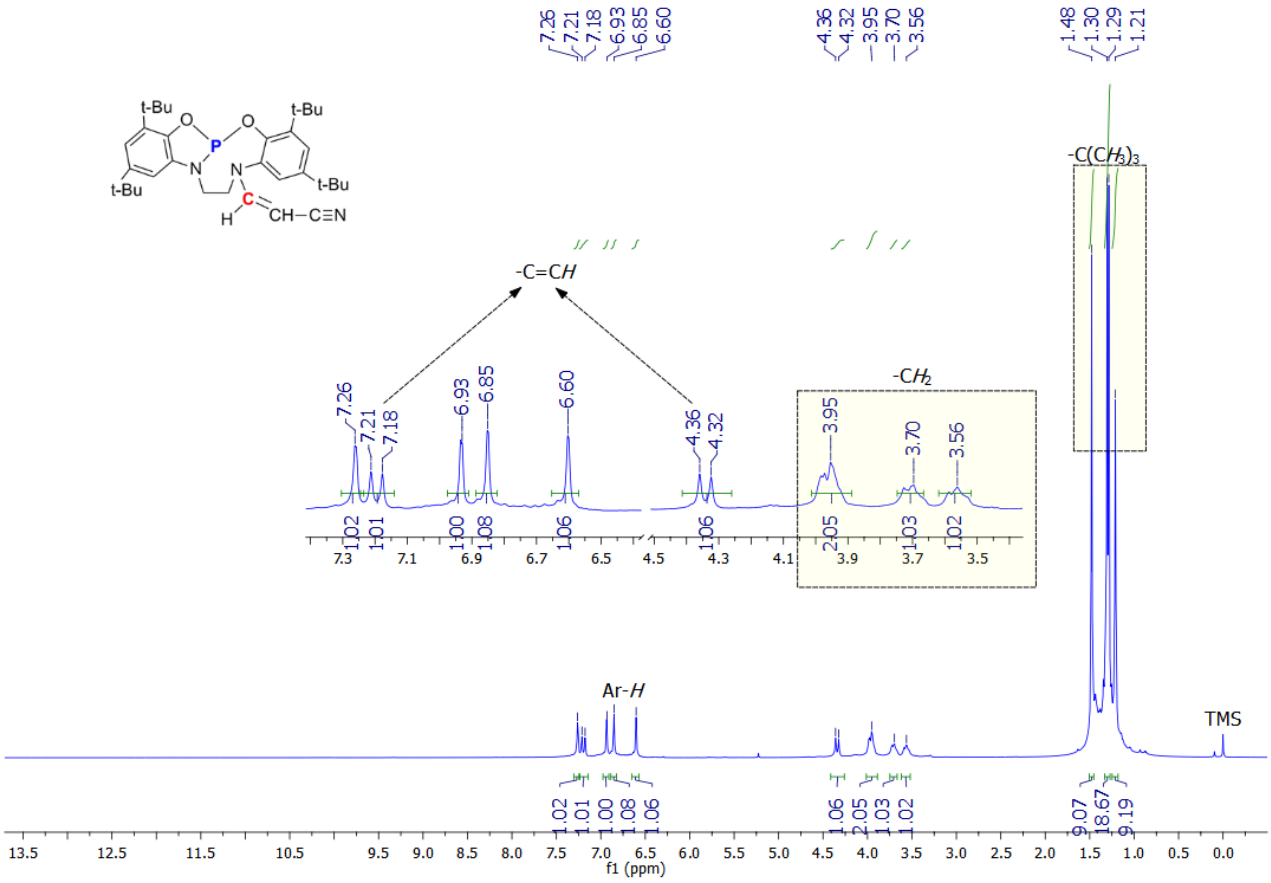


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7**.

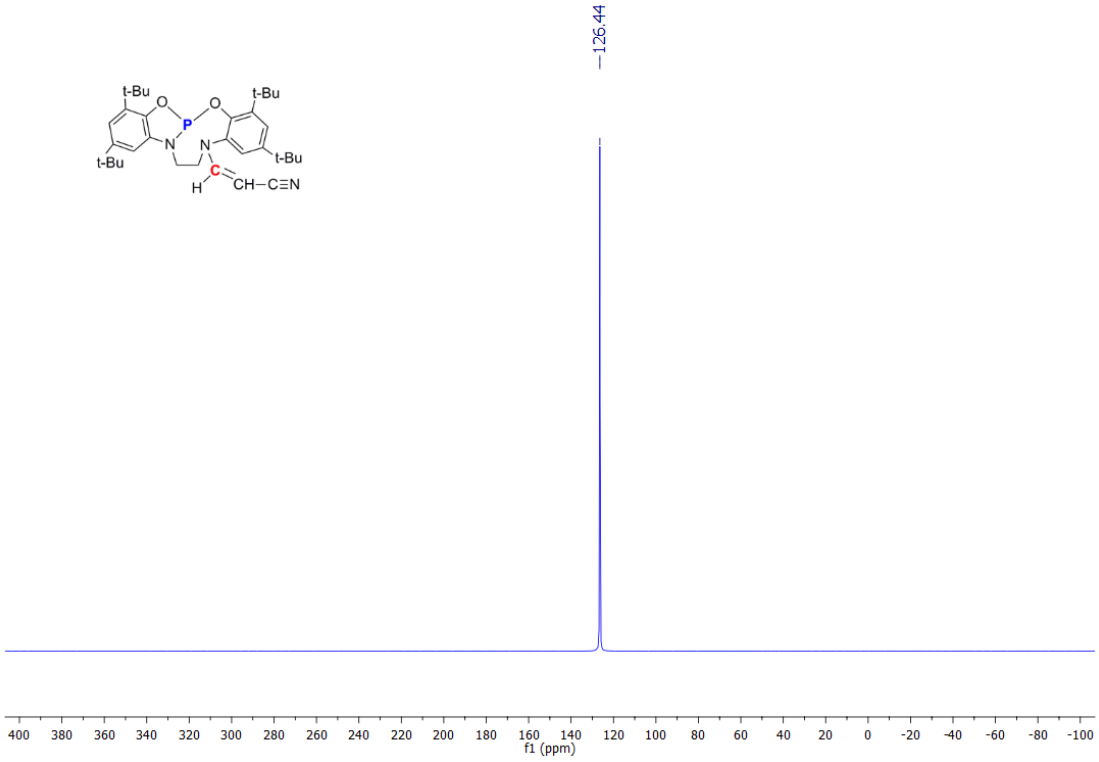


Figure S6. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **7**.

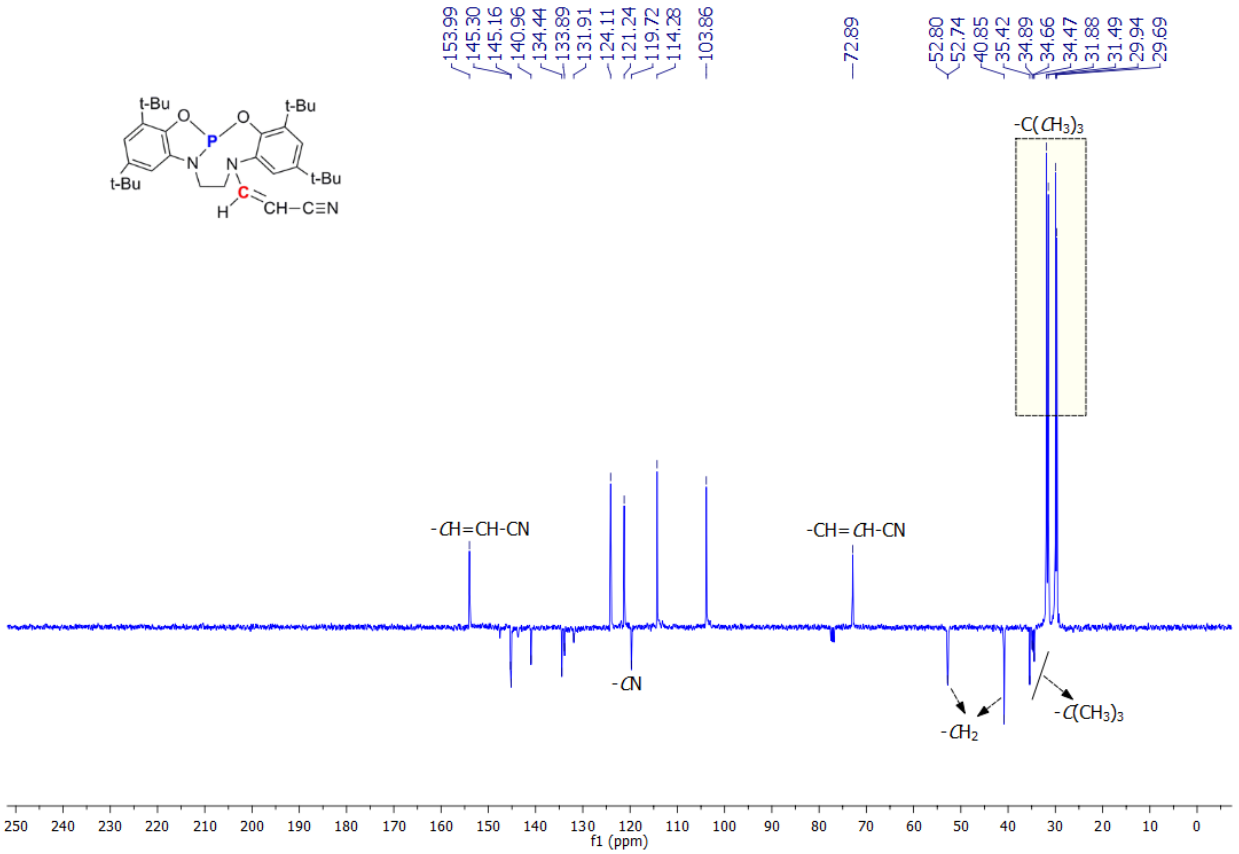


Figure S7. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **7**.

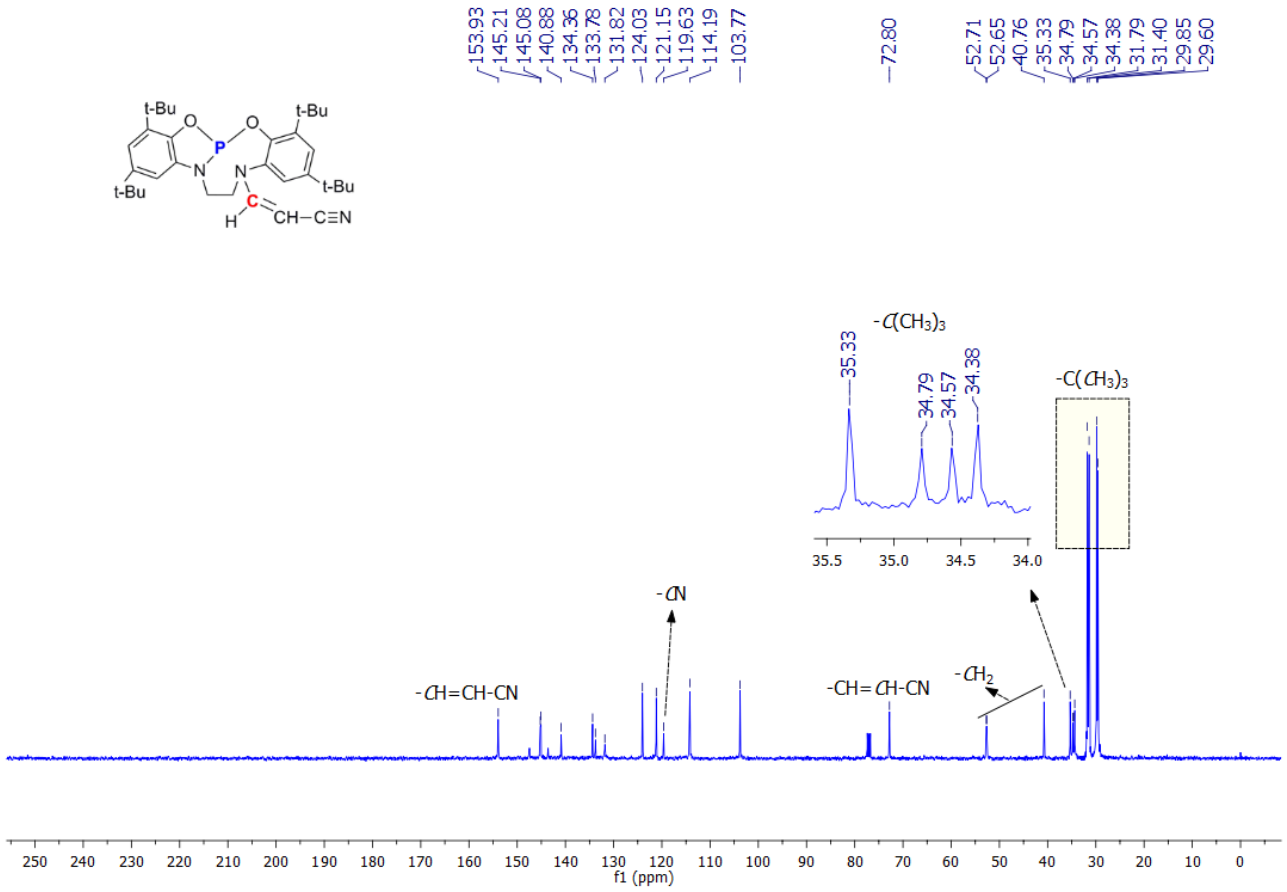


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **7**.

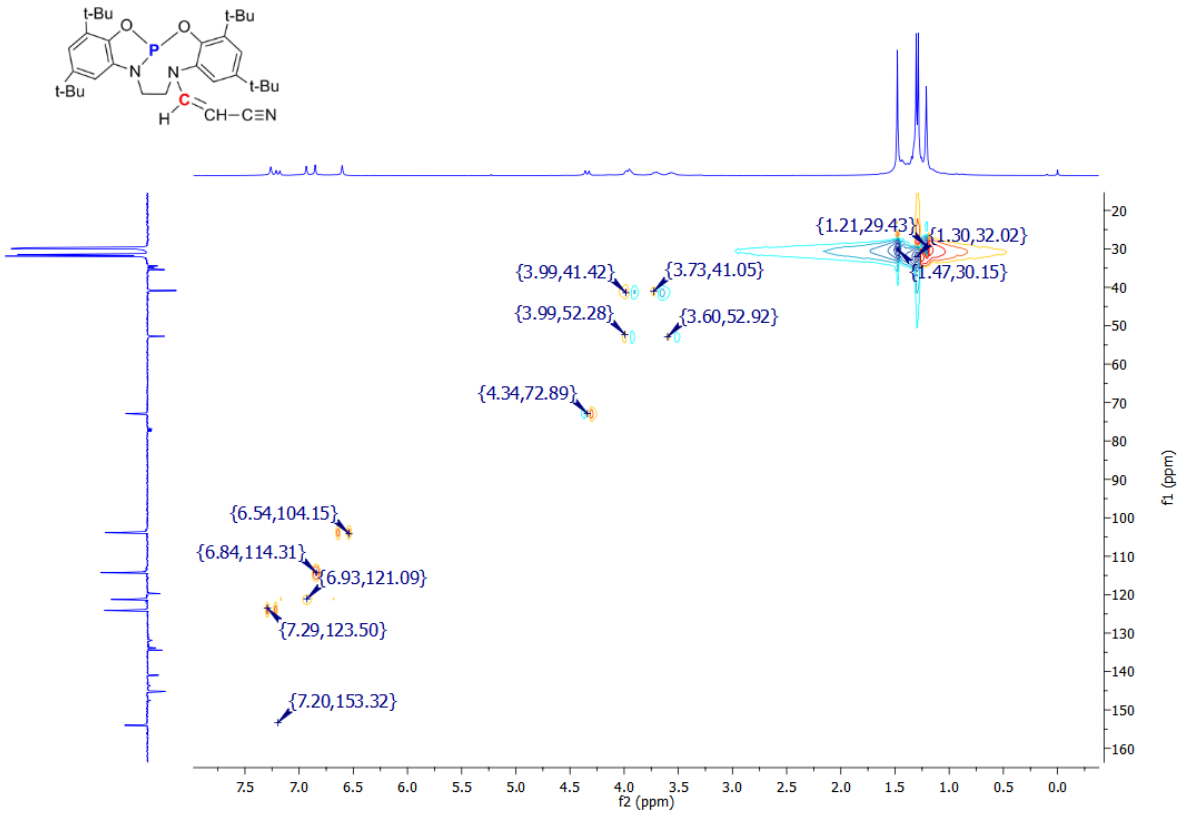


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) of **7**.

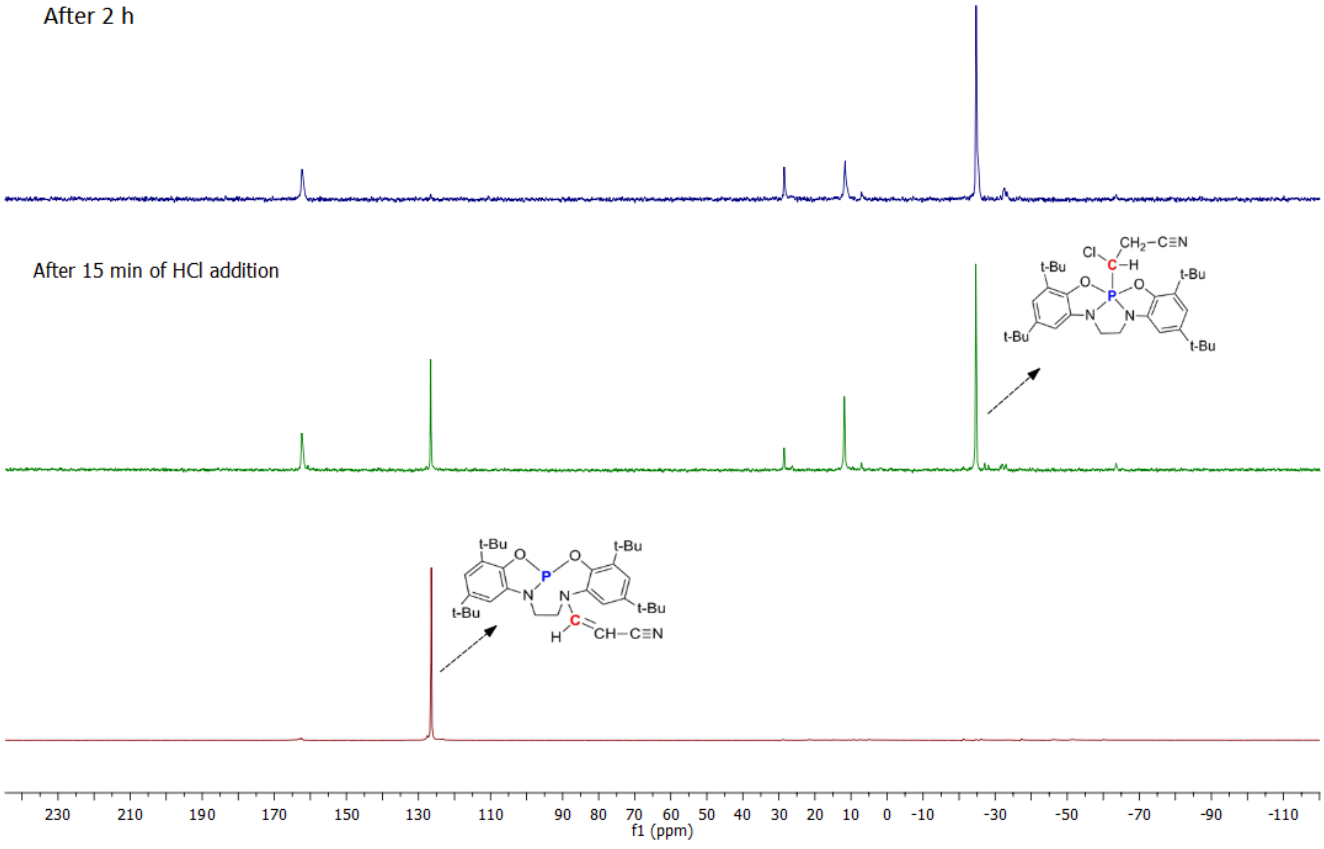


Figure S10. Stacked ^{31}P NMR spectra (162 MHz, in $CDCl_3$) of **7** with different intervals to show the formation of **4**.

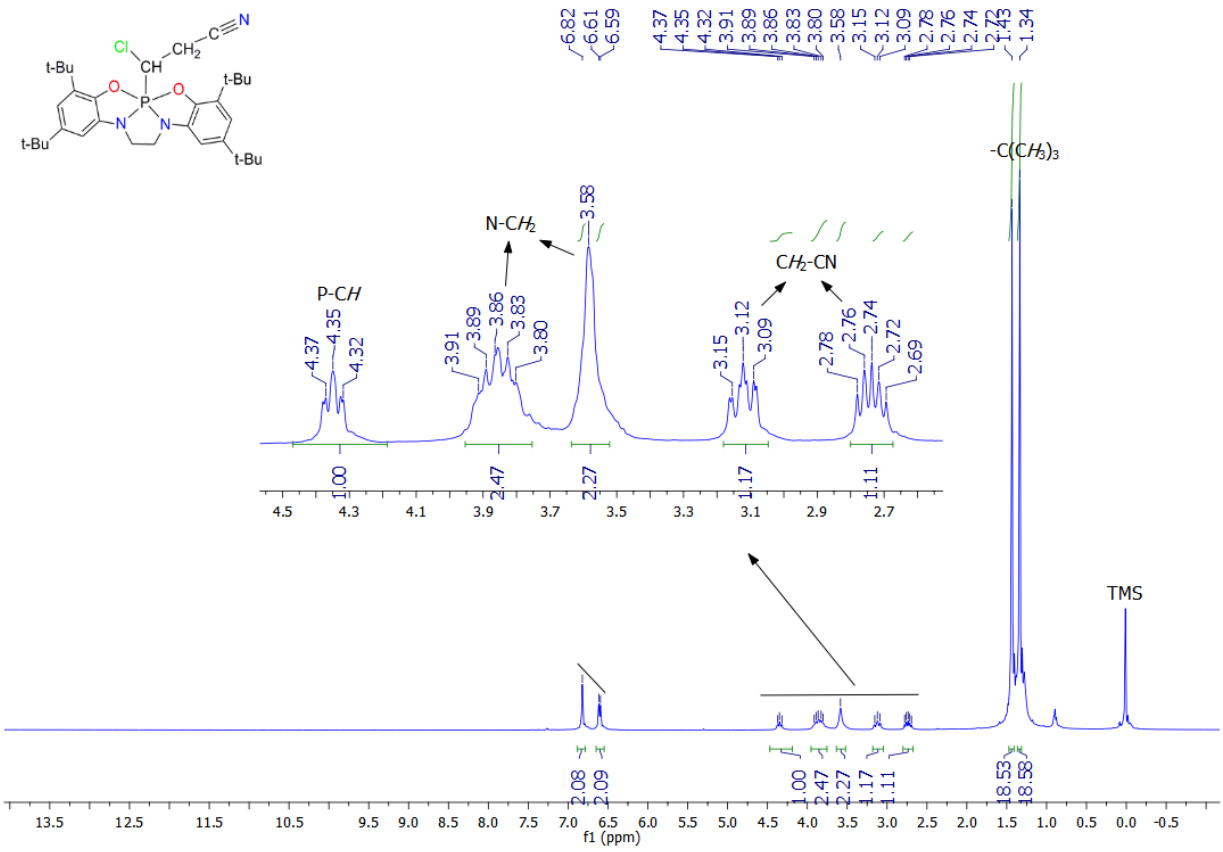


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

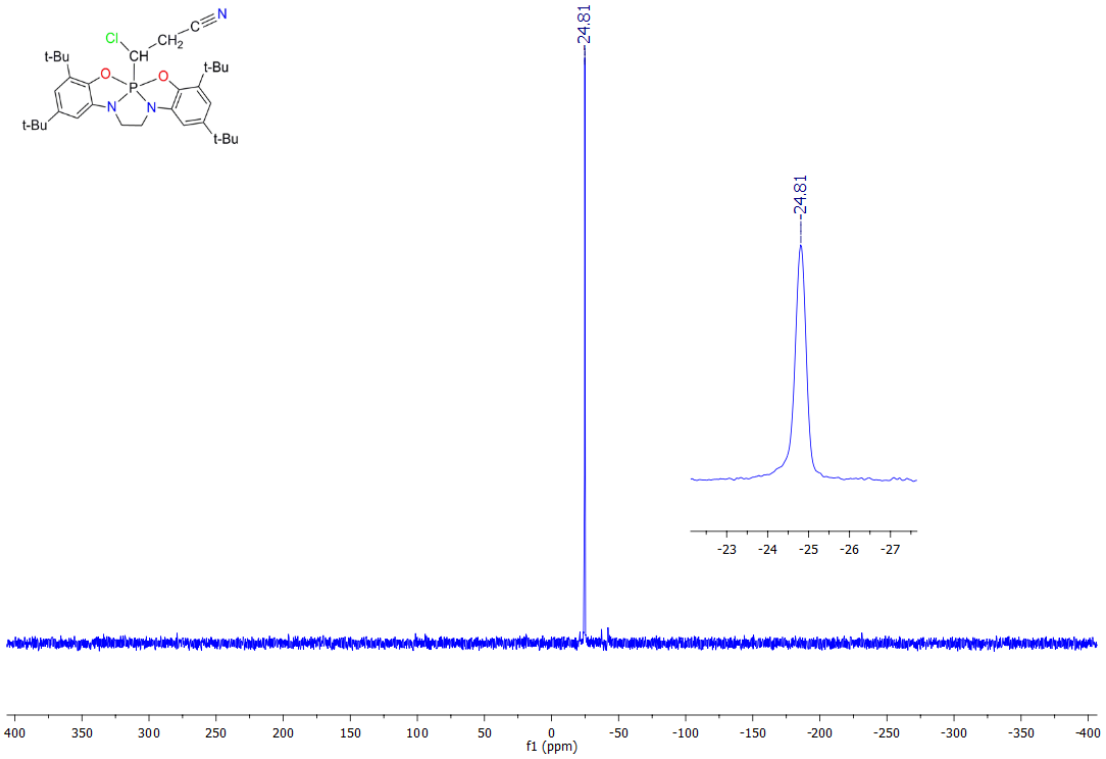


Figure S12. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4**.

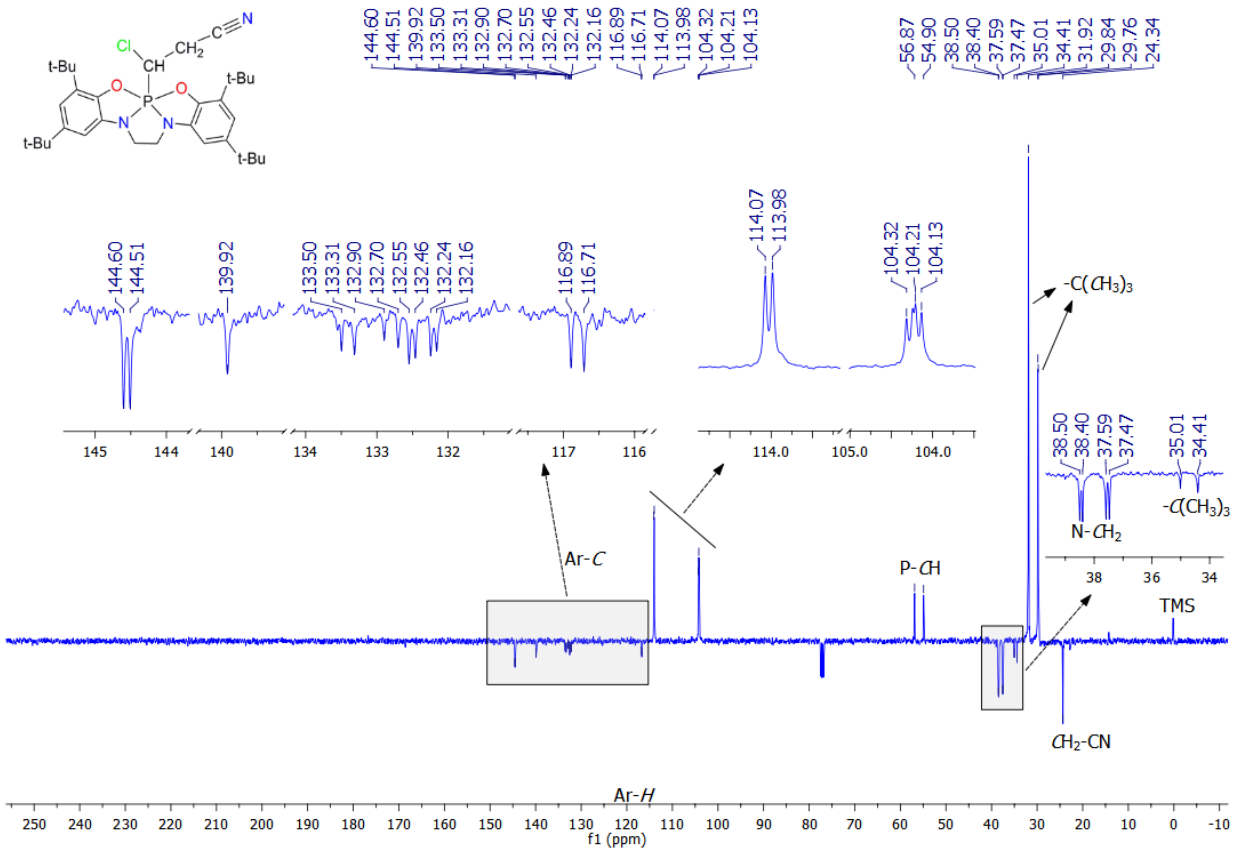


Figure S13. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **4**.

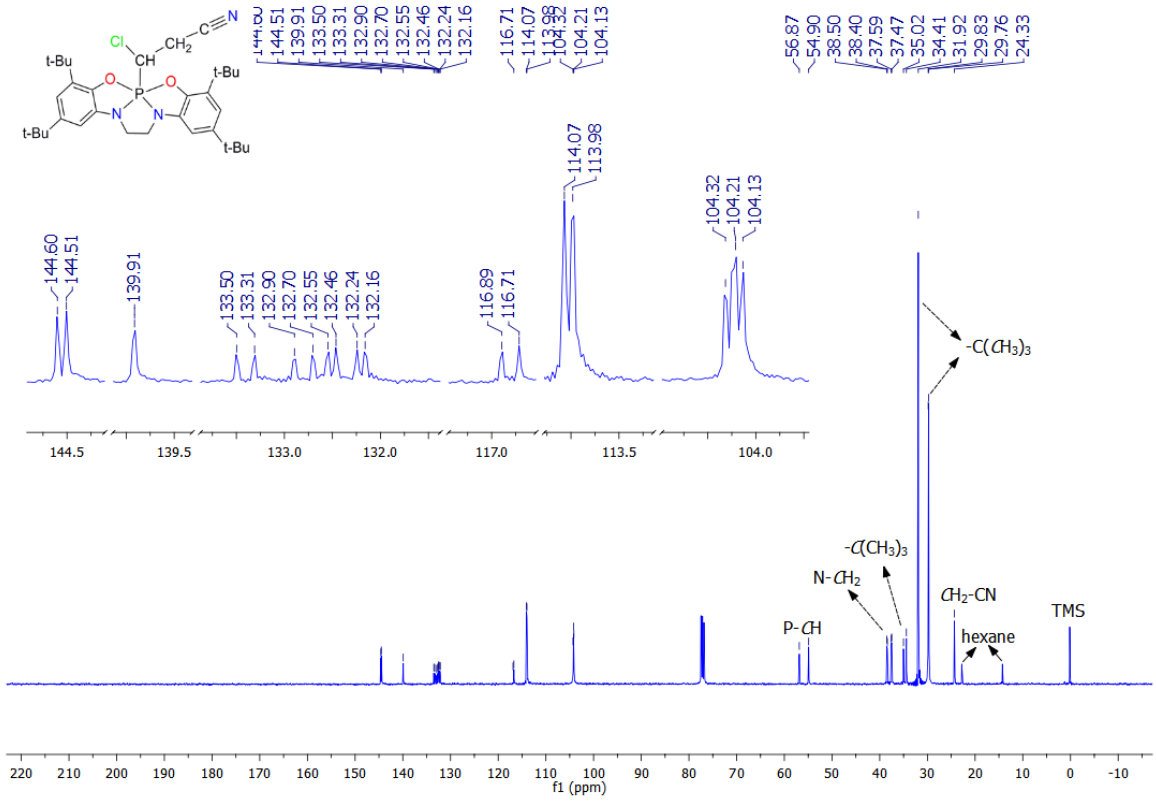


Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **4**.

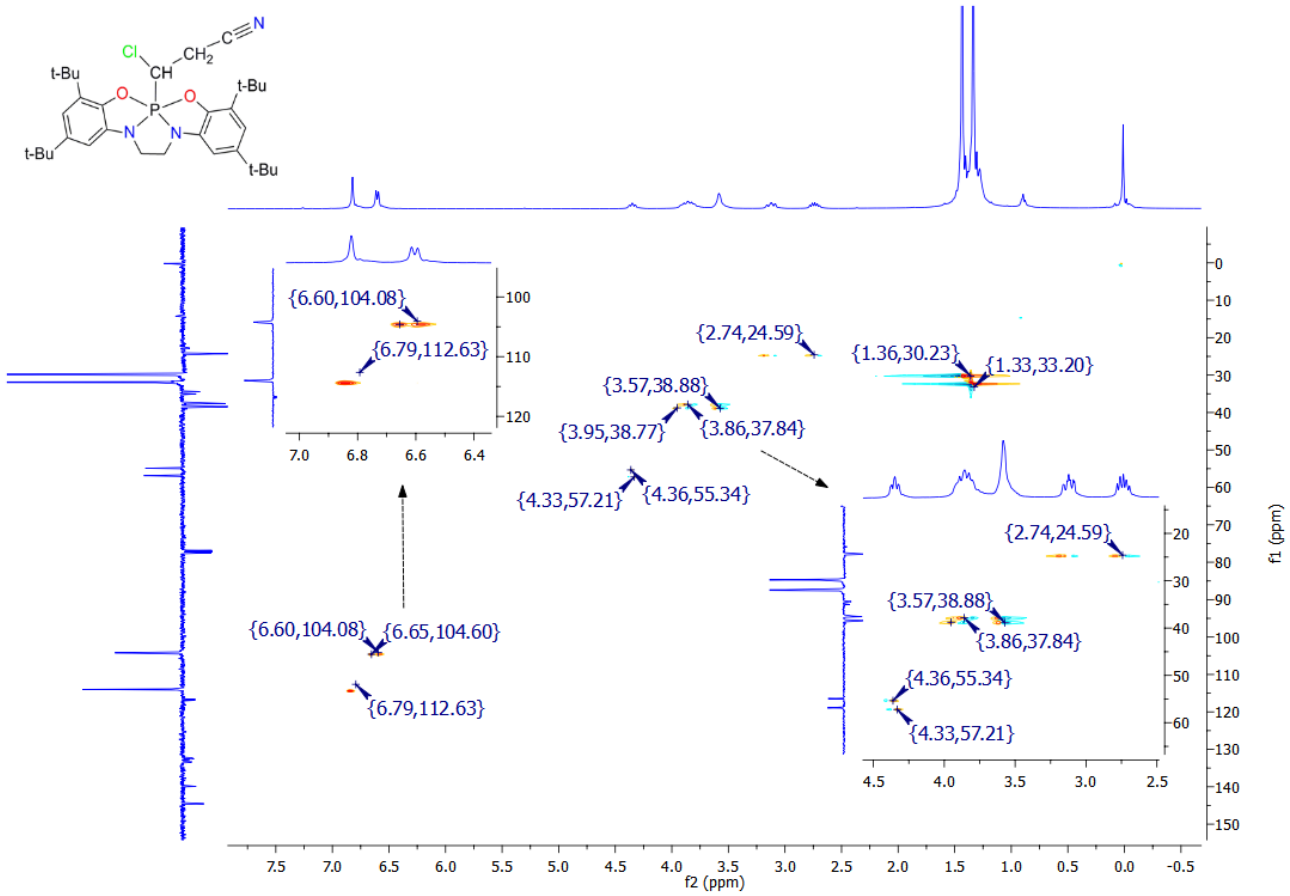


Figure S15. ^{1}H-^{13}C HSQC NMR spectrum ($CDCl_3$) of **4**.

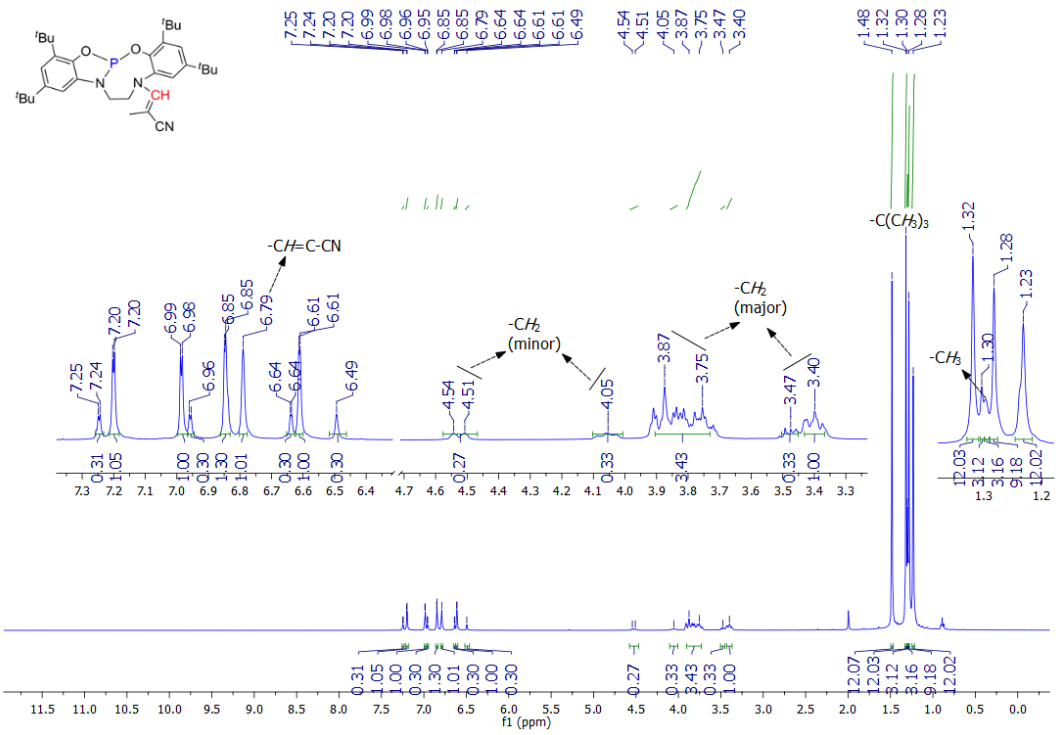


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7-EtCN**.

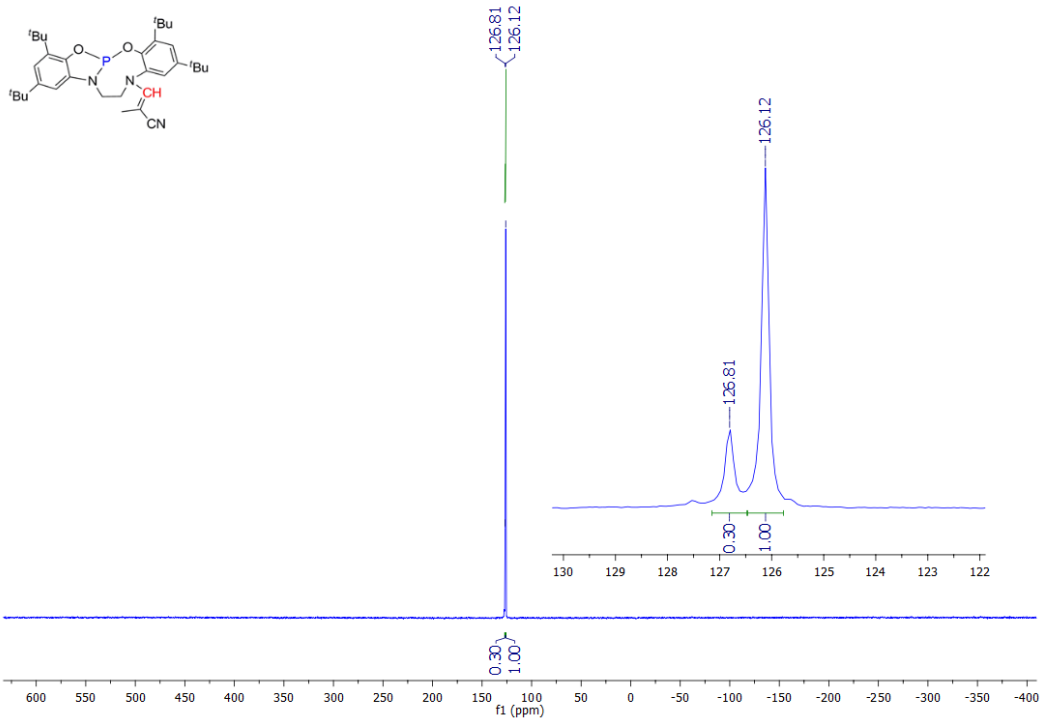


Figure S17. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **7-EtCN**.

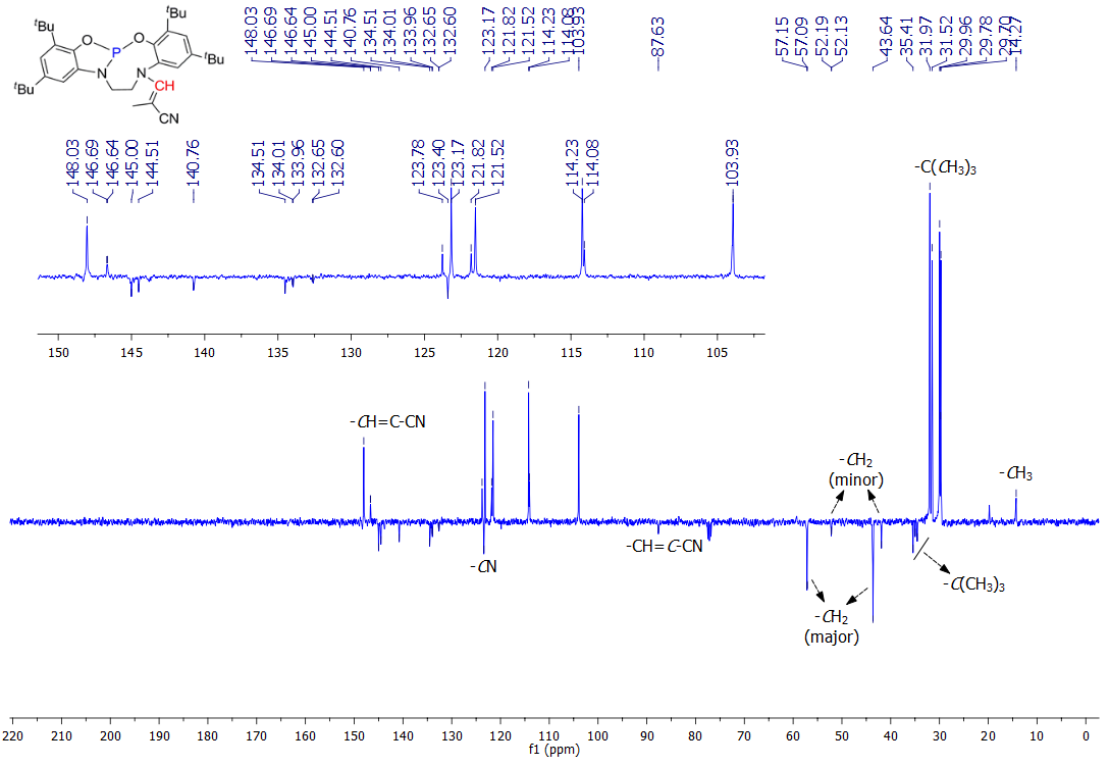


Figure S18. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **7-EtCN**.

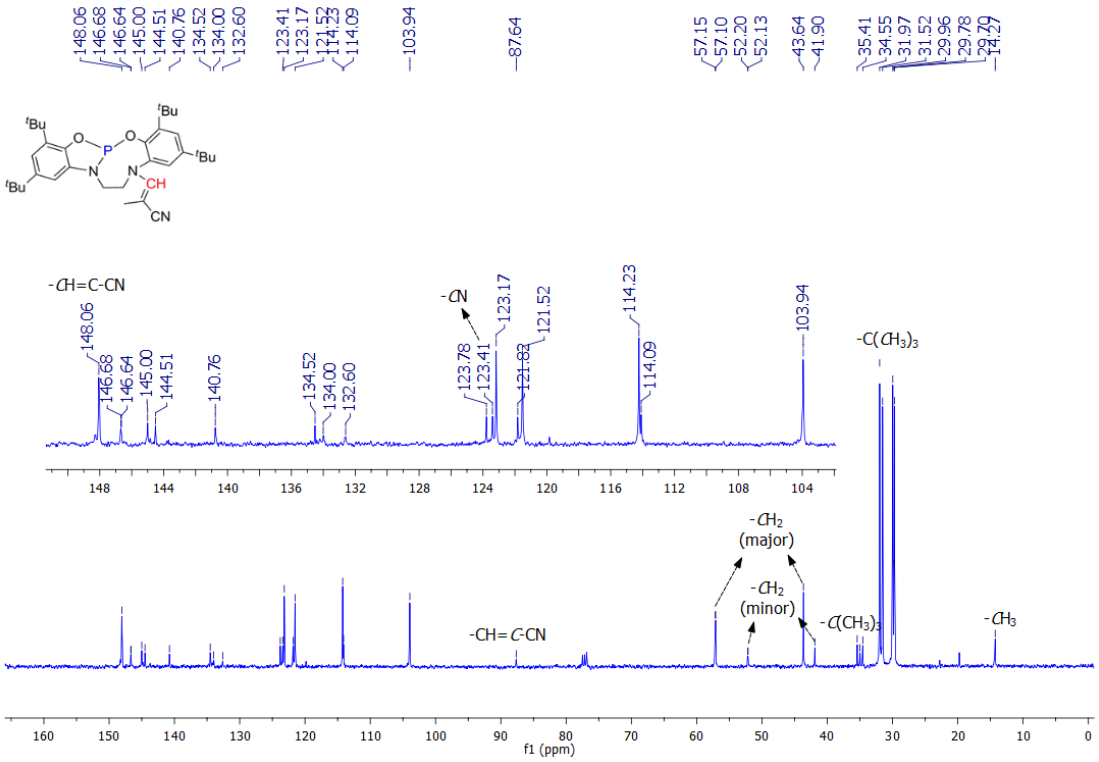


Figure S19. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **7-EtCN**.

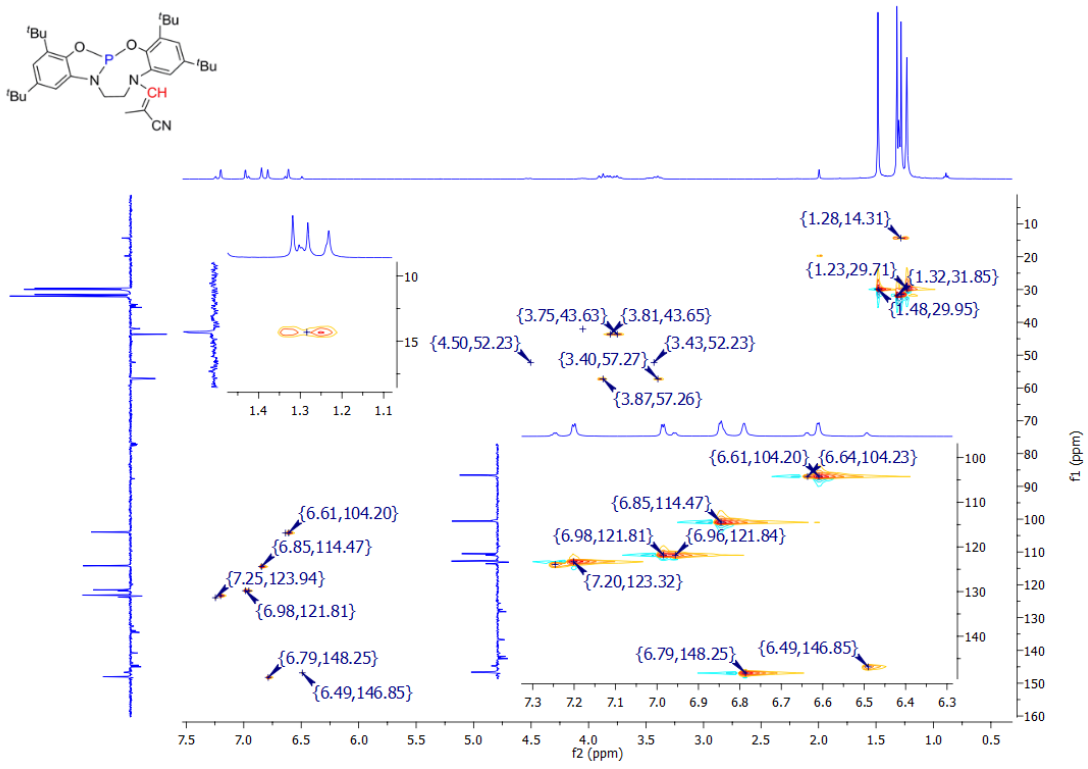


Figure S20. ^{1}H-^{13}C-HSQC NMR spectrum ($CDCl_3$) of **7-EtCN**.

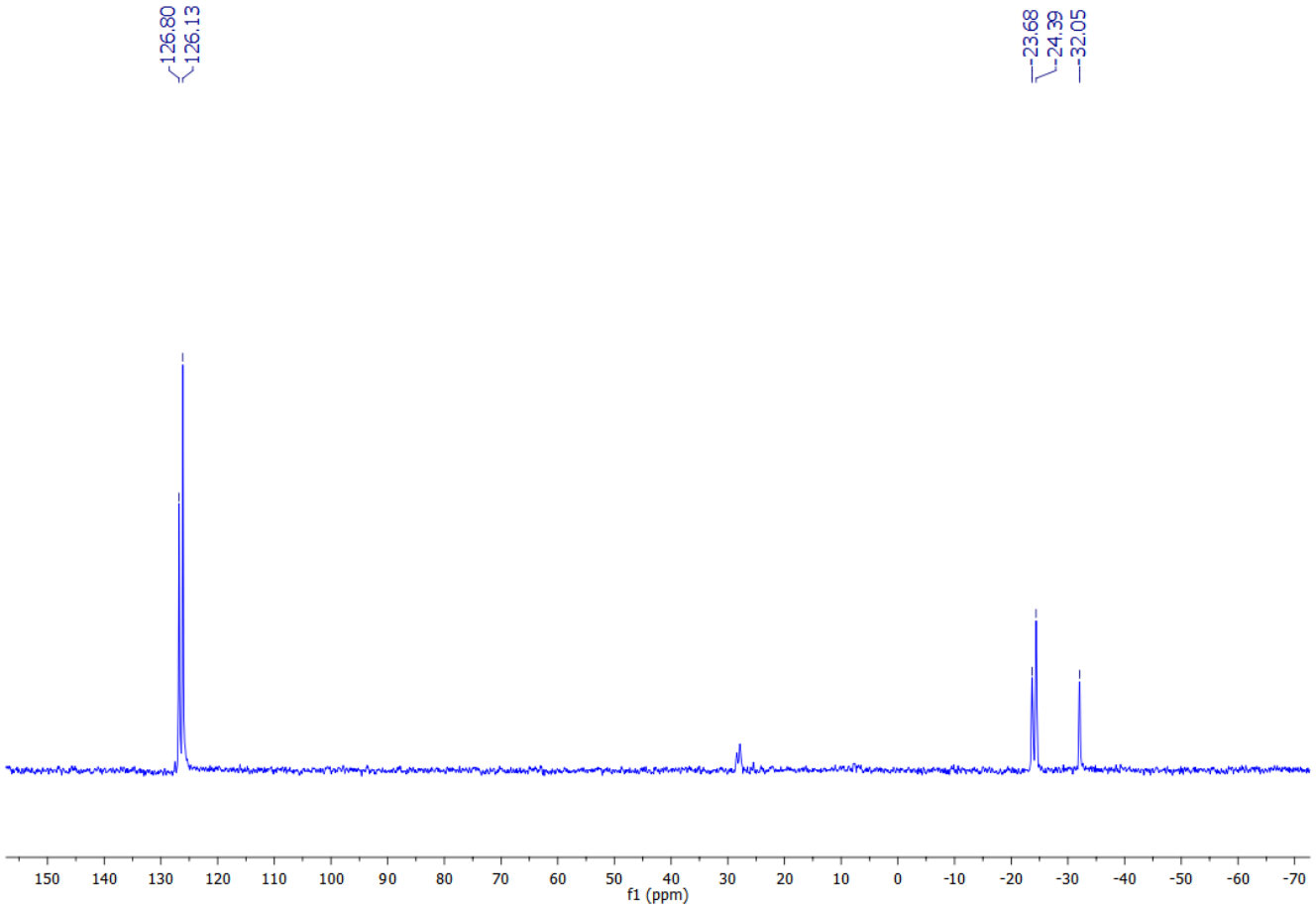


Figure S21. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) after few minutes of HCl addition to **7-EtCN**.

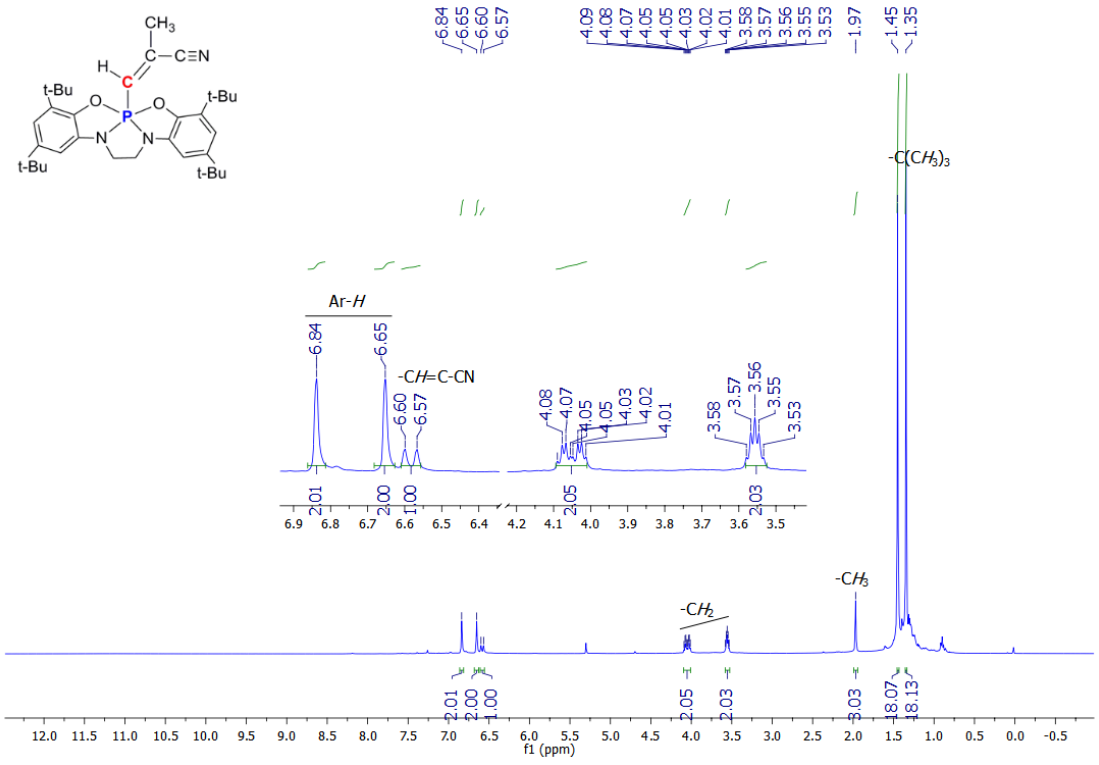


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4-EtCN**.

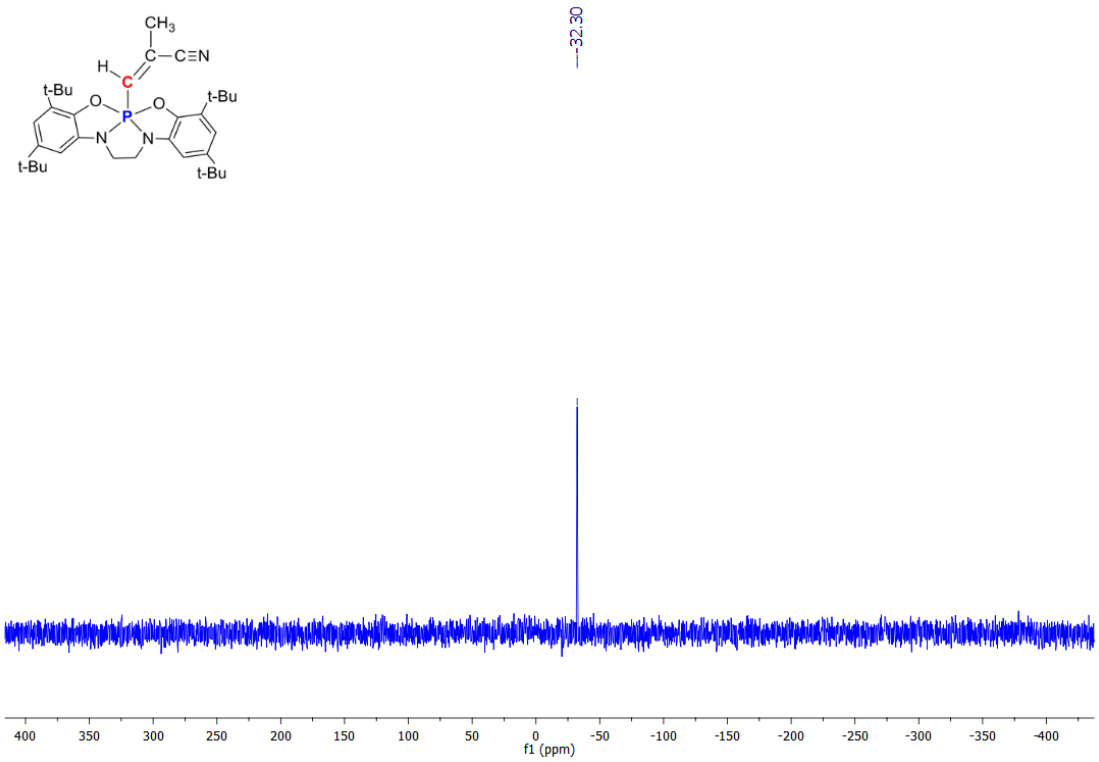


Figure S23. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4-EtCN**.

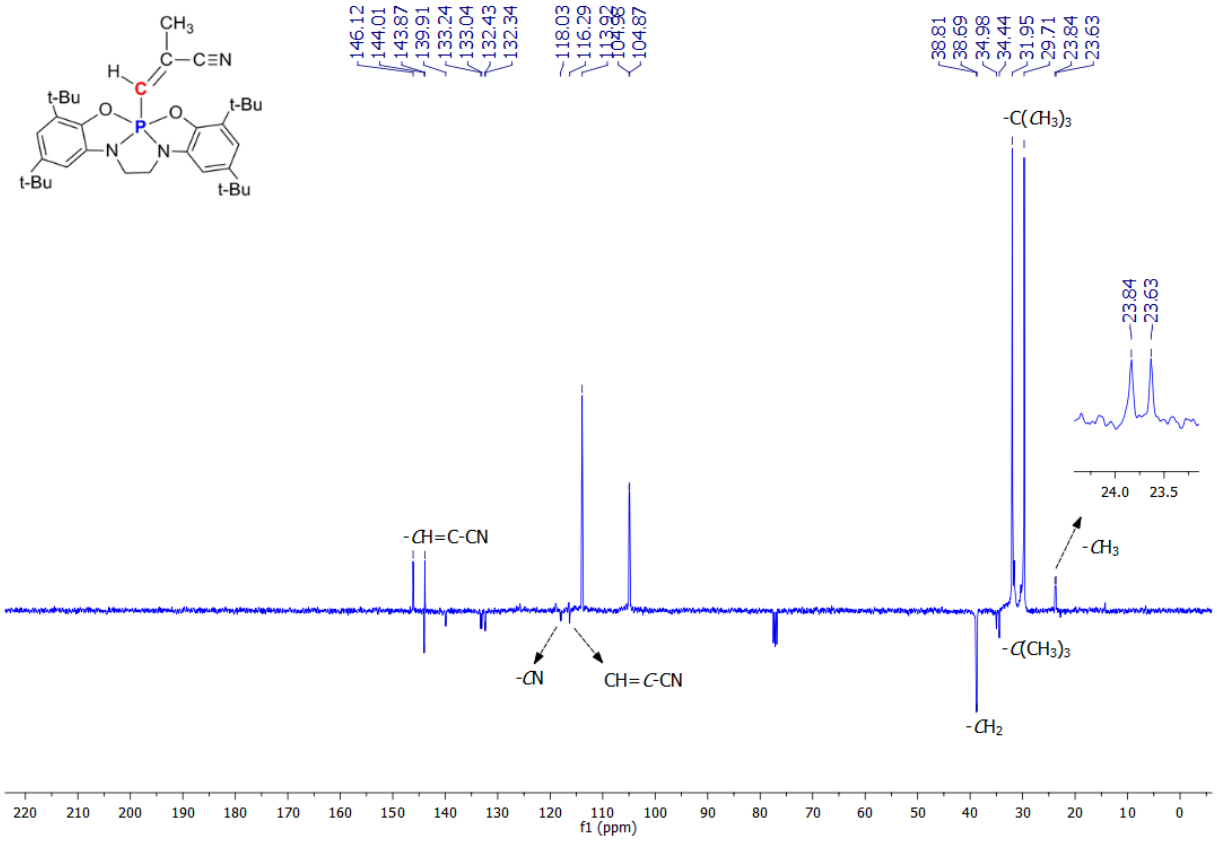


Figure S24. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **4-EtCN**.

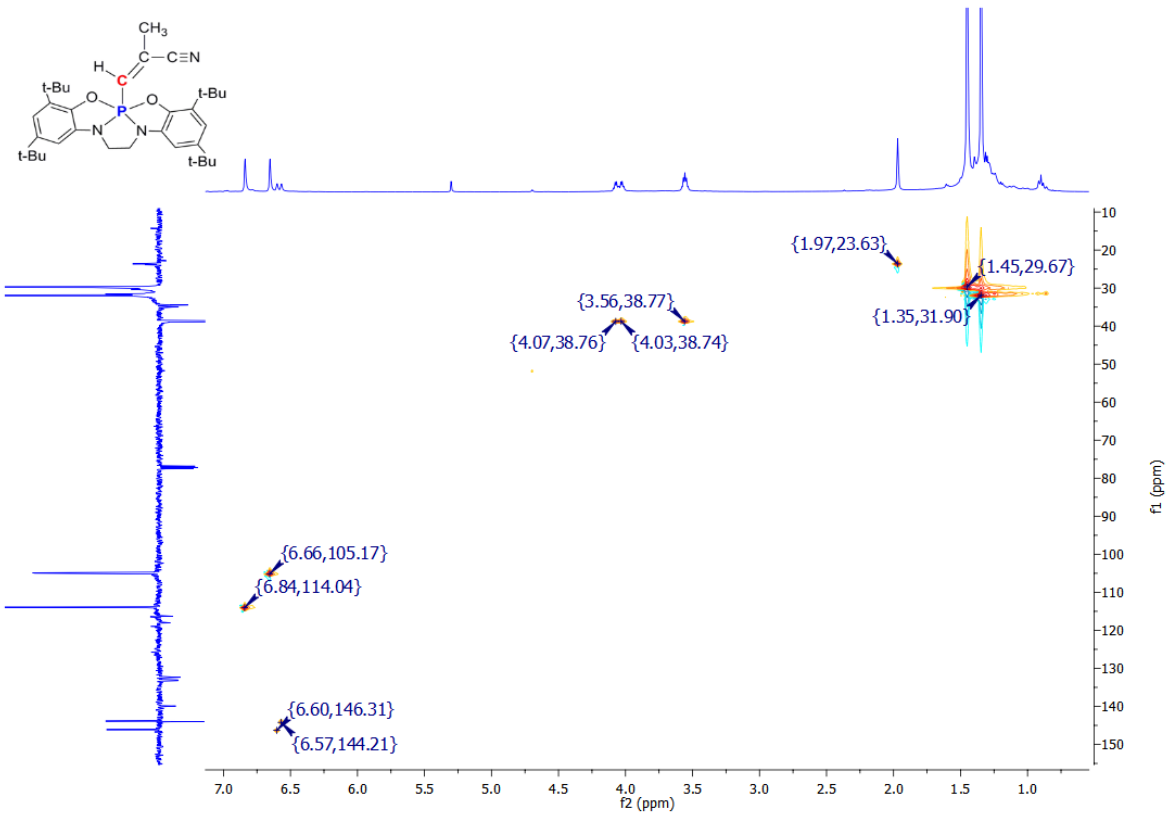


Figure S25. ^{1}H-^{13}C-HSQC NMR spectrum ($CDCl_3$) of **4-EtCN**.

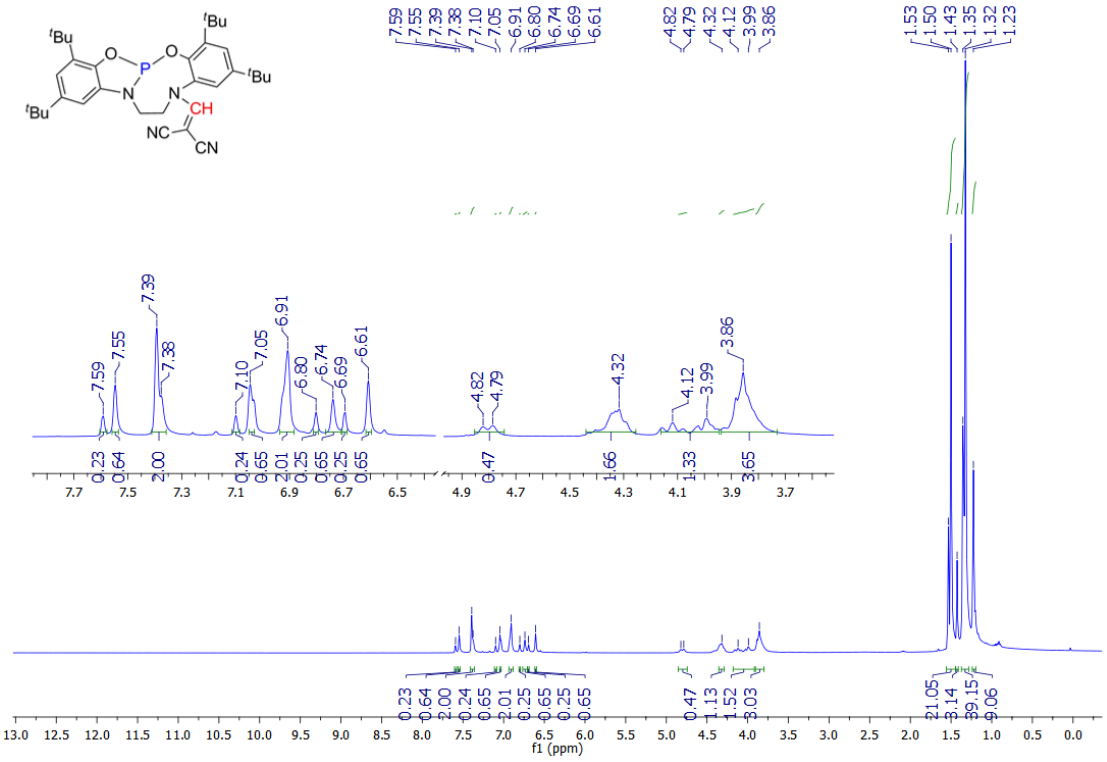


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7-$CH_2(CN)_2$**.

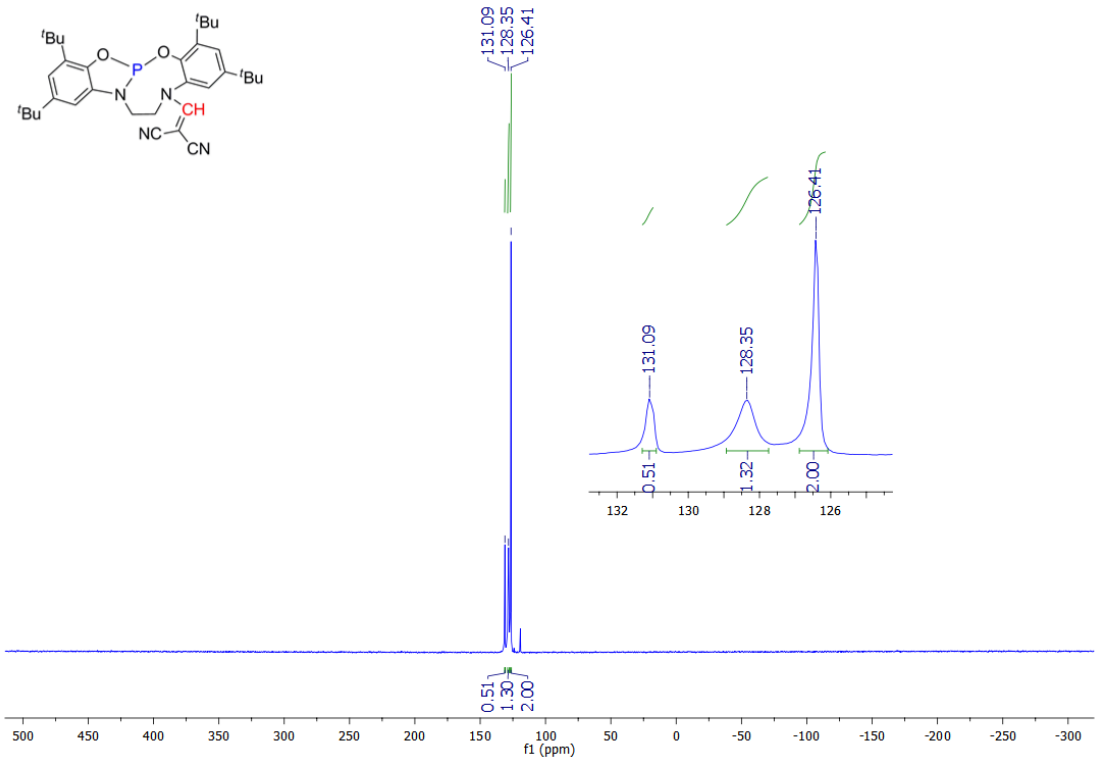


Figure S27. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **7-$CH_2(CN)_2$**.

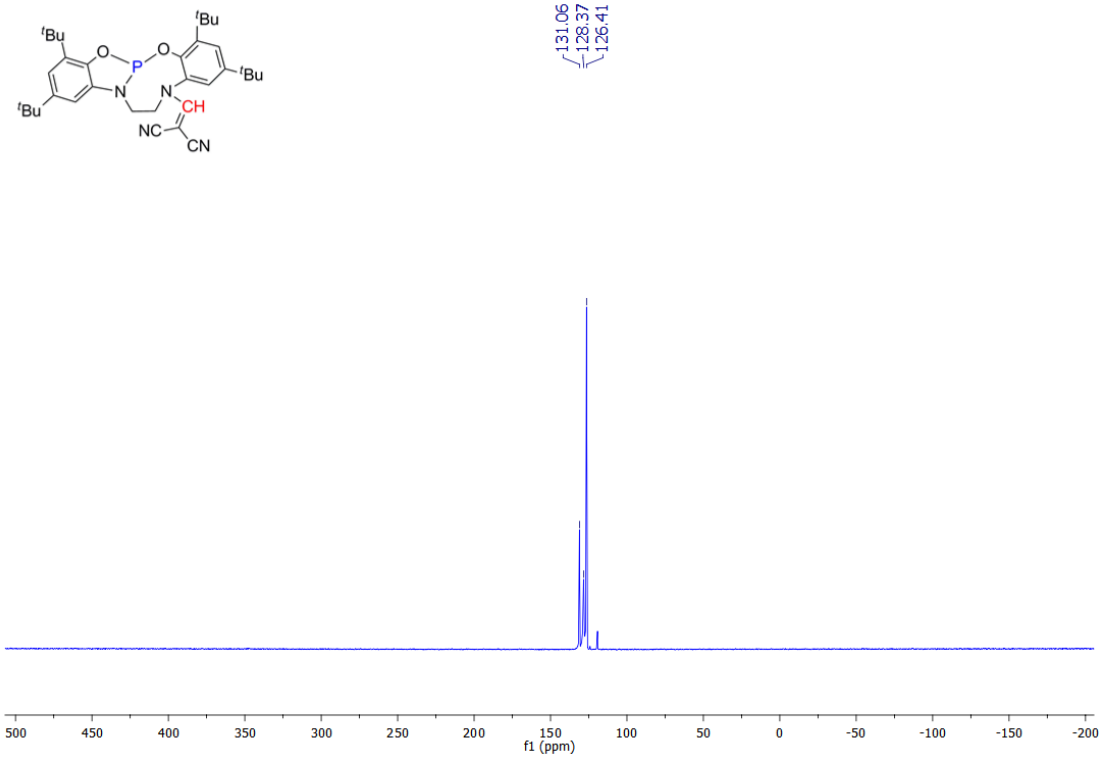


Figure S28. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **7-$CH_2(CN)_2$**.

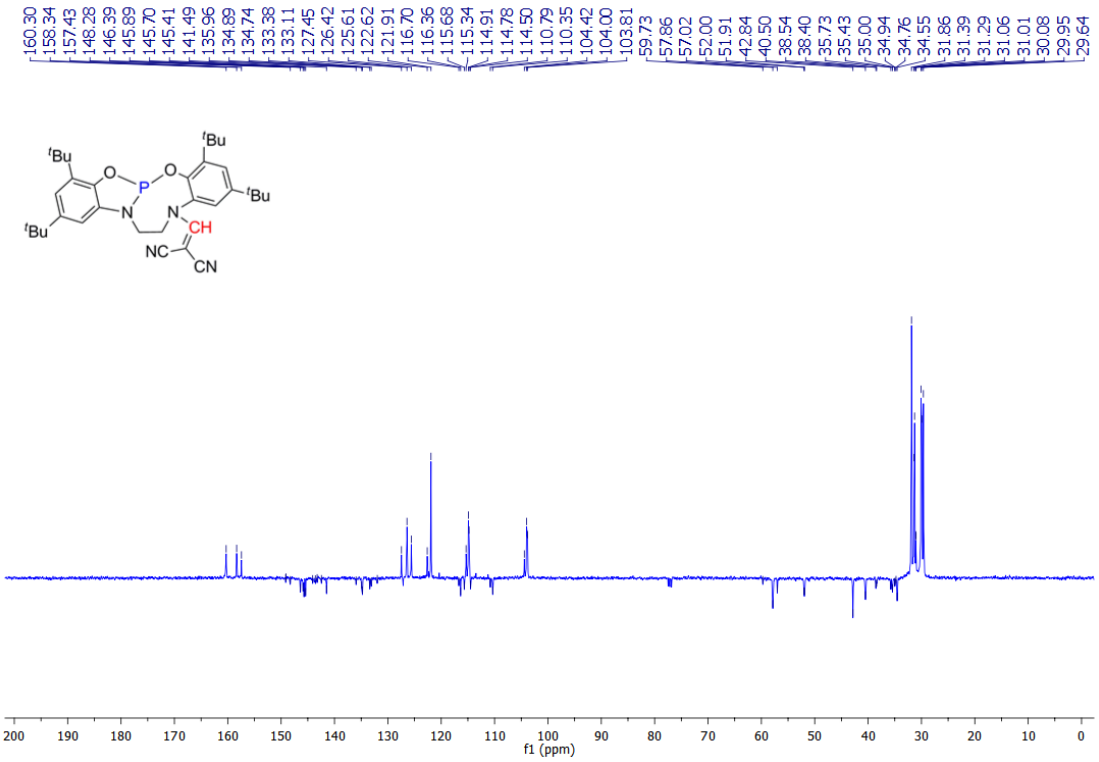


Figure S29. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **7-$CH_2(CN)_2$**.

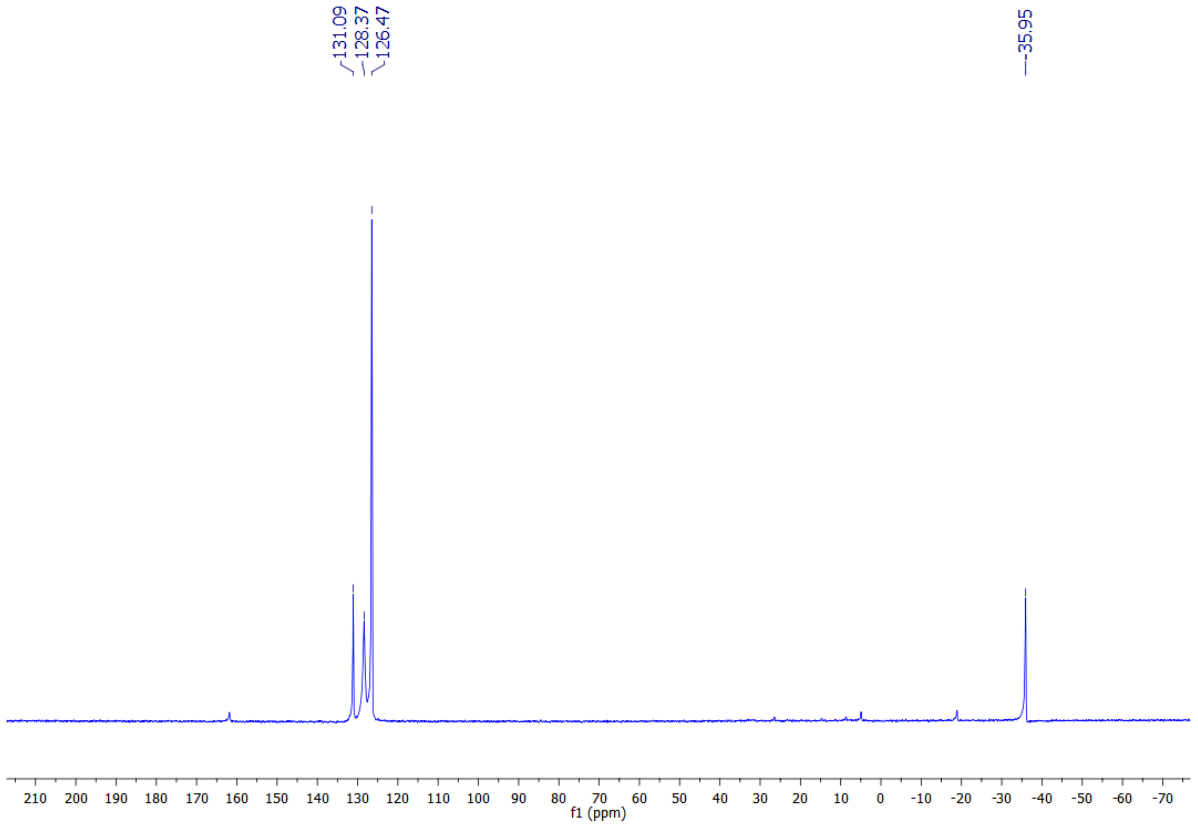


Figure S30. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) after few minutes of HCl addition to **7-$CH_2(CN)_2$**.

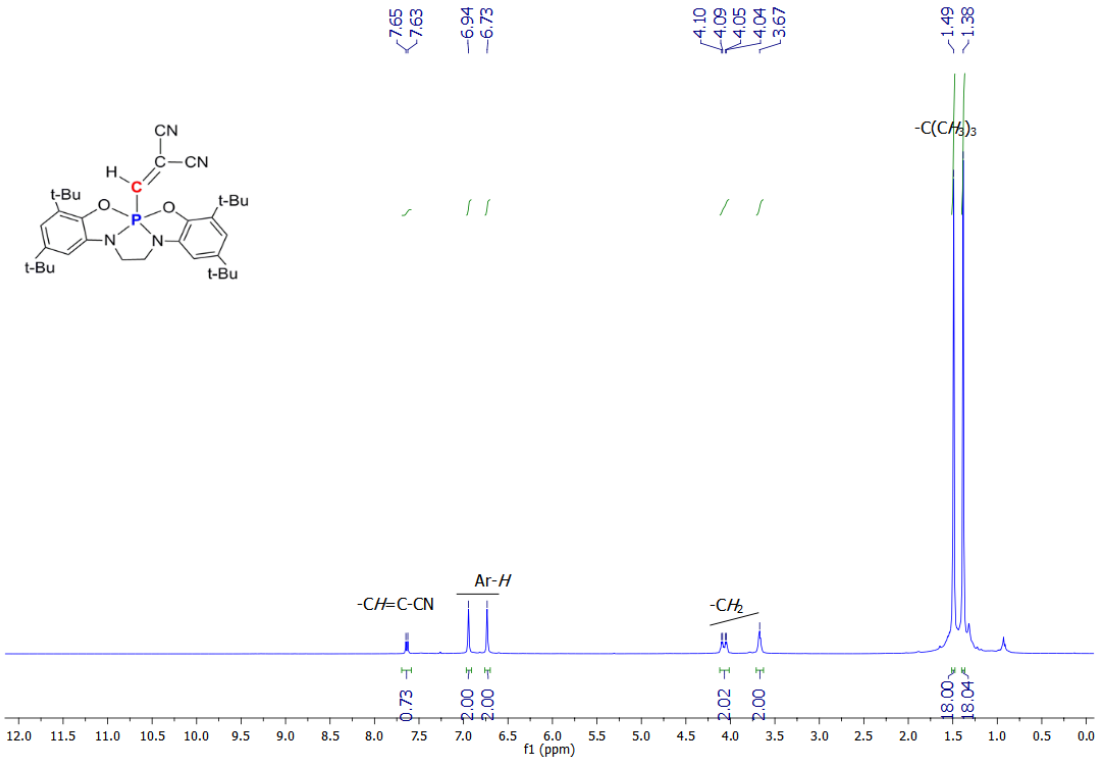


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4-CH_2(CN)$_2$**.

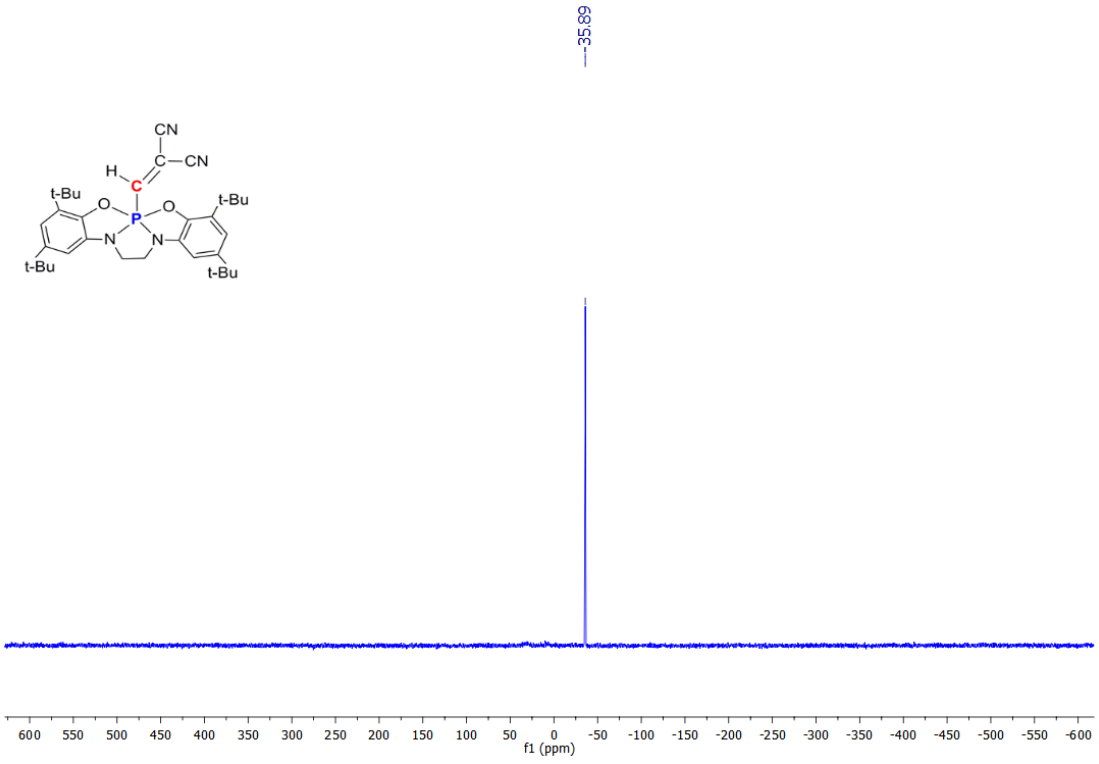


Figure S32. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4-CH_2(CN)$_2$**.

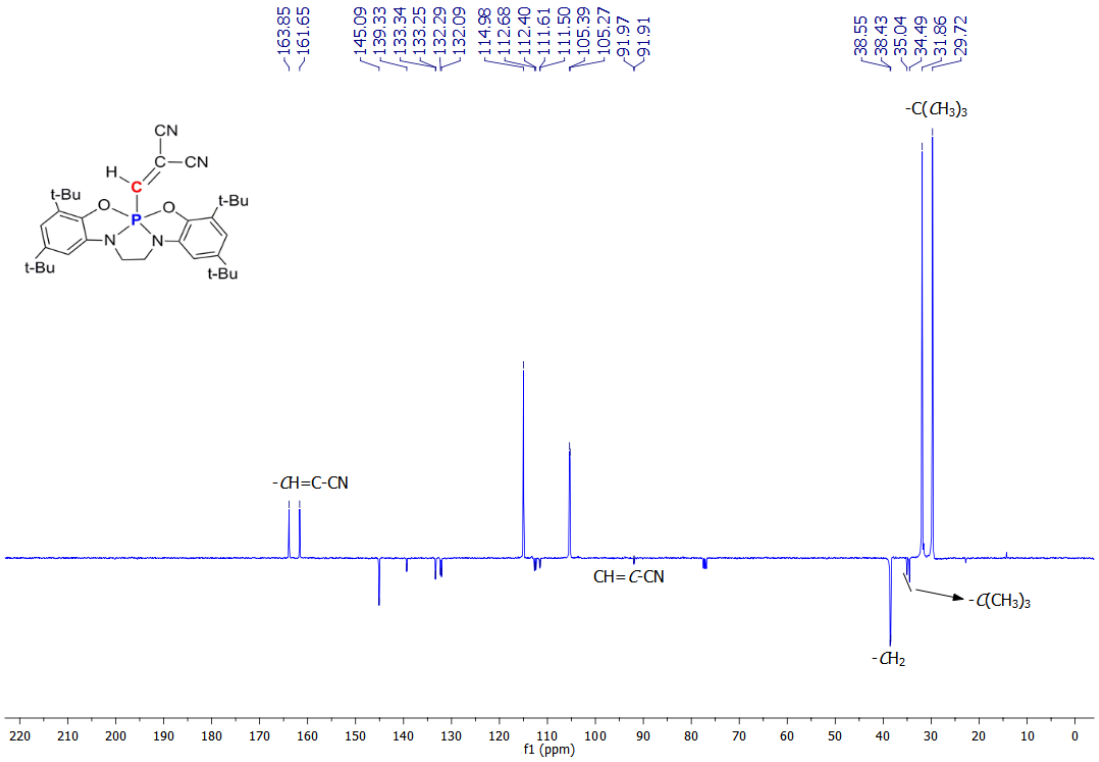


Figure S33. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **4-CH_2(CN)$_2$**.

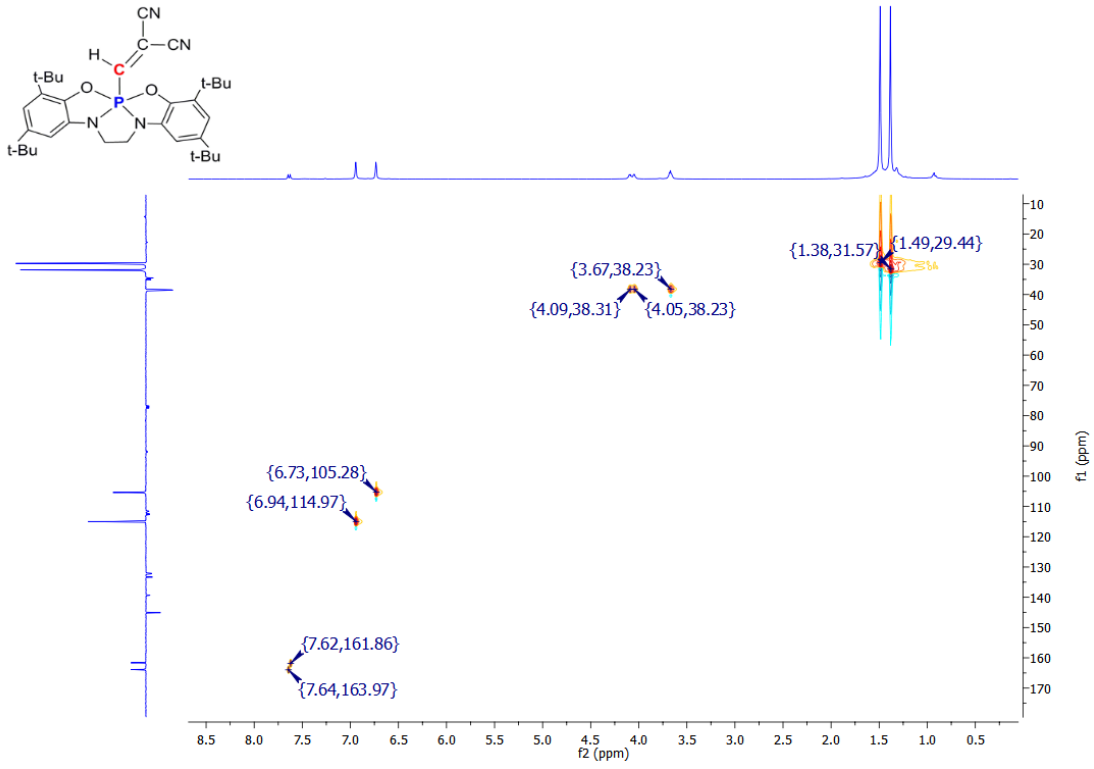


Figure S34. ^{1}H-^{13}C-HSQC NMR spectrum ($CDCl_3$) of **4-CH_2(CN)$_2$**.

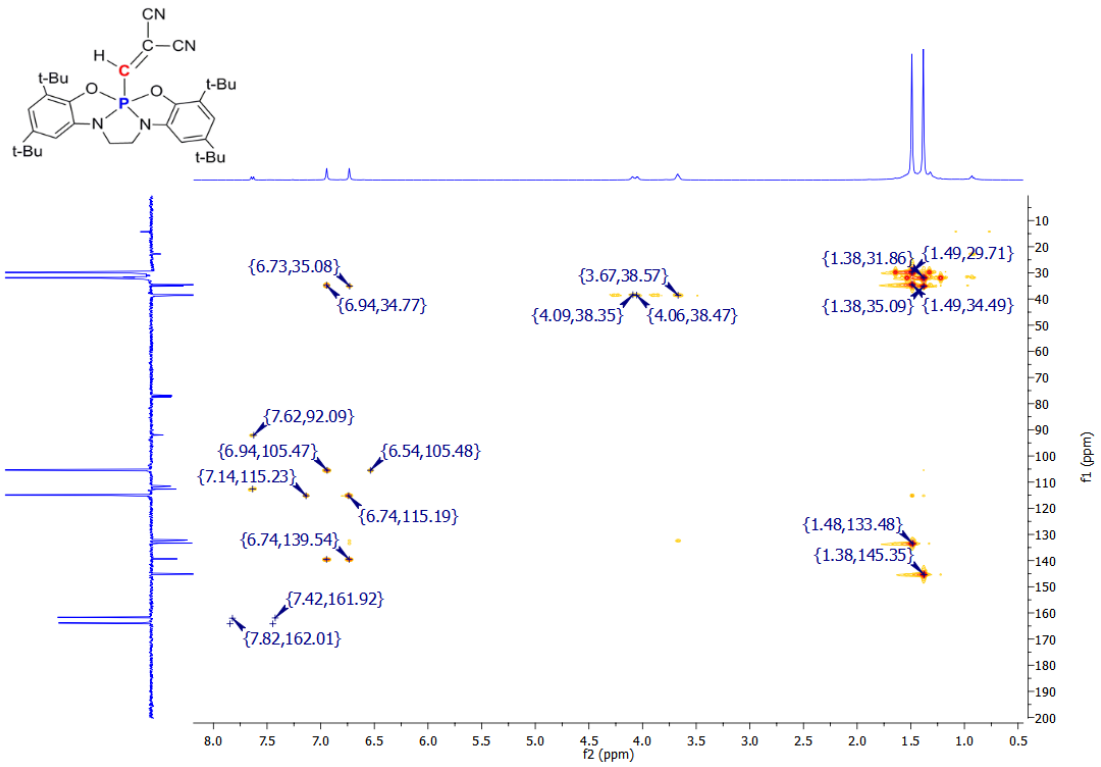


Figure S35. ^{1}H-^{13}C-HMBC NMR spectrum ($CDCl_3$) of **4-$CH_2(CN)_2$**.

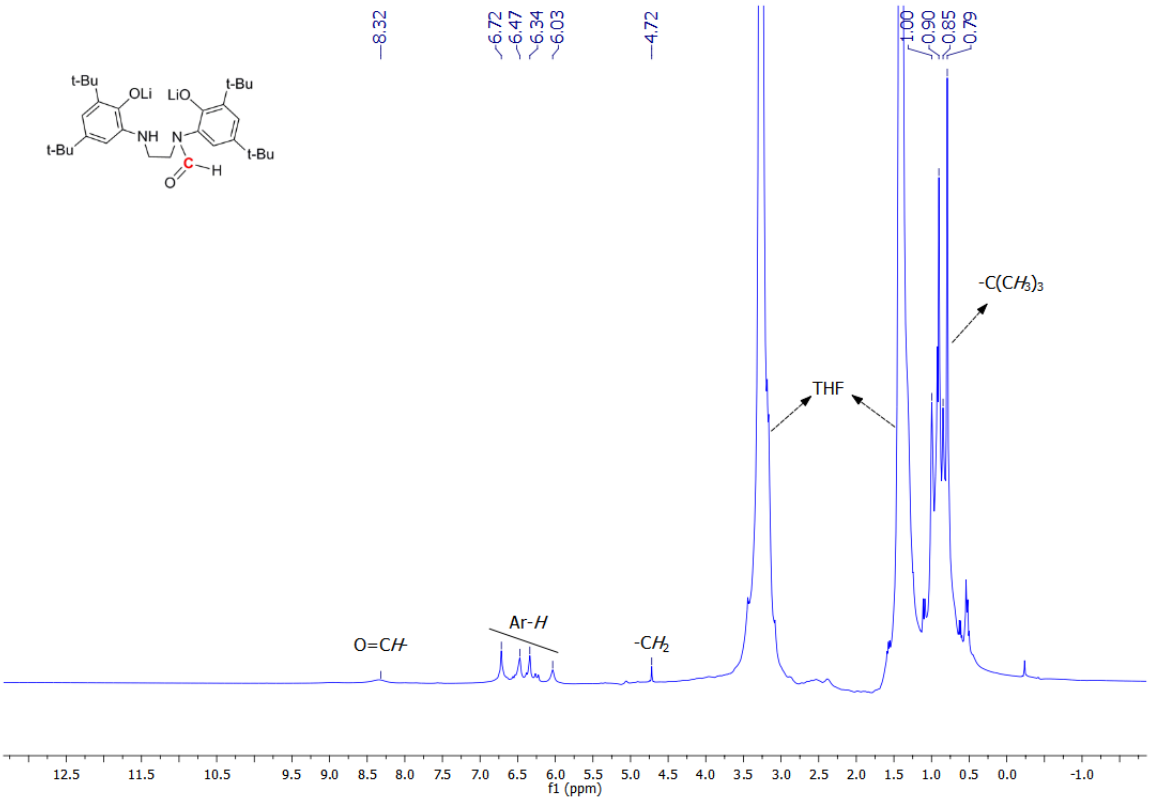


Figure S36. ^{1}H NMR spectrum (400 MHz, in THF reaction mixture) of **8**.

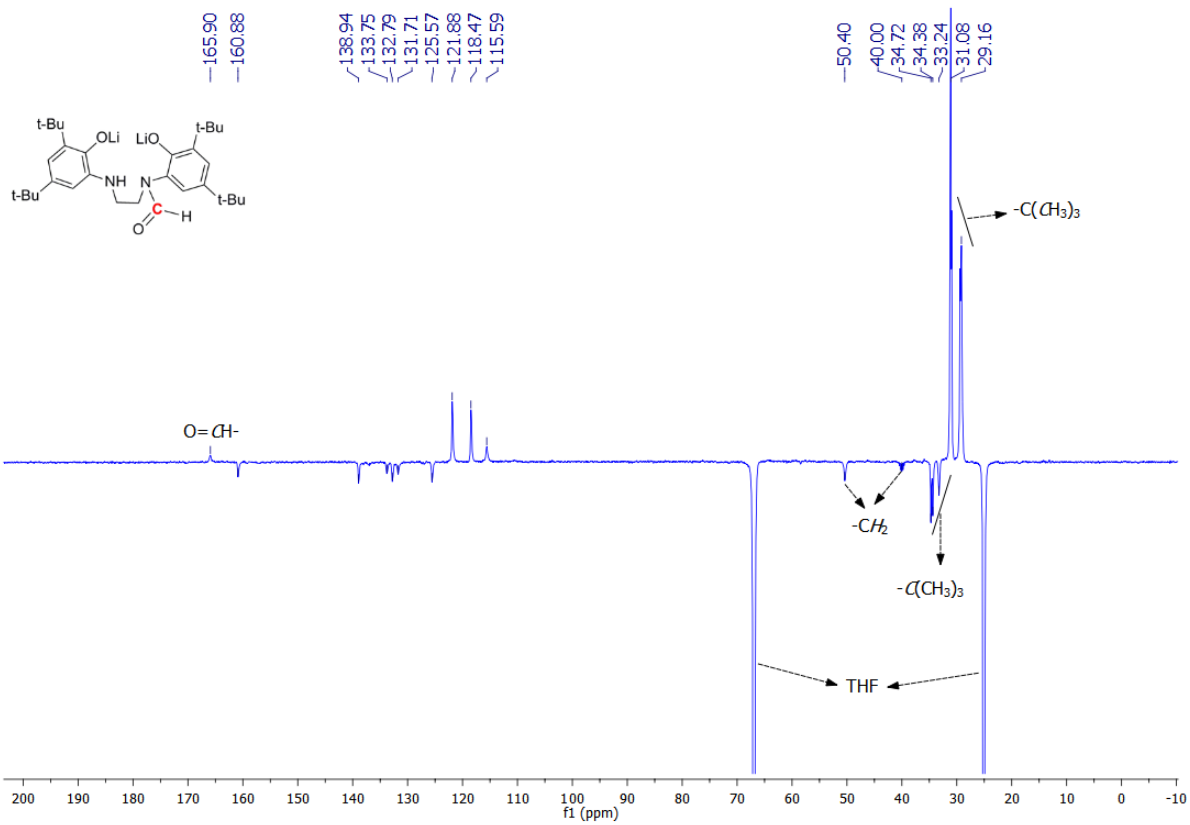


Figure S37. ^{13}C-JMOD NMR spectrum (100 MHz, in THF reaction mixture) of **8**.

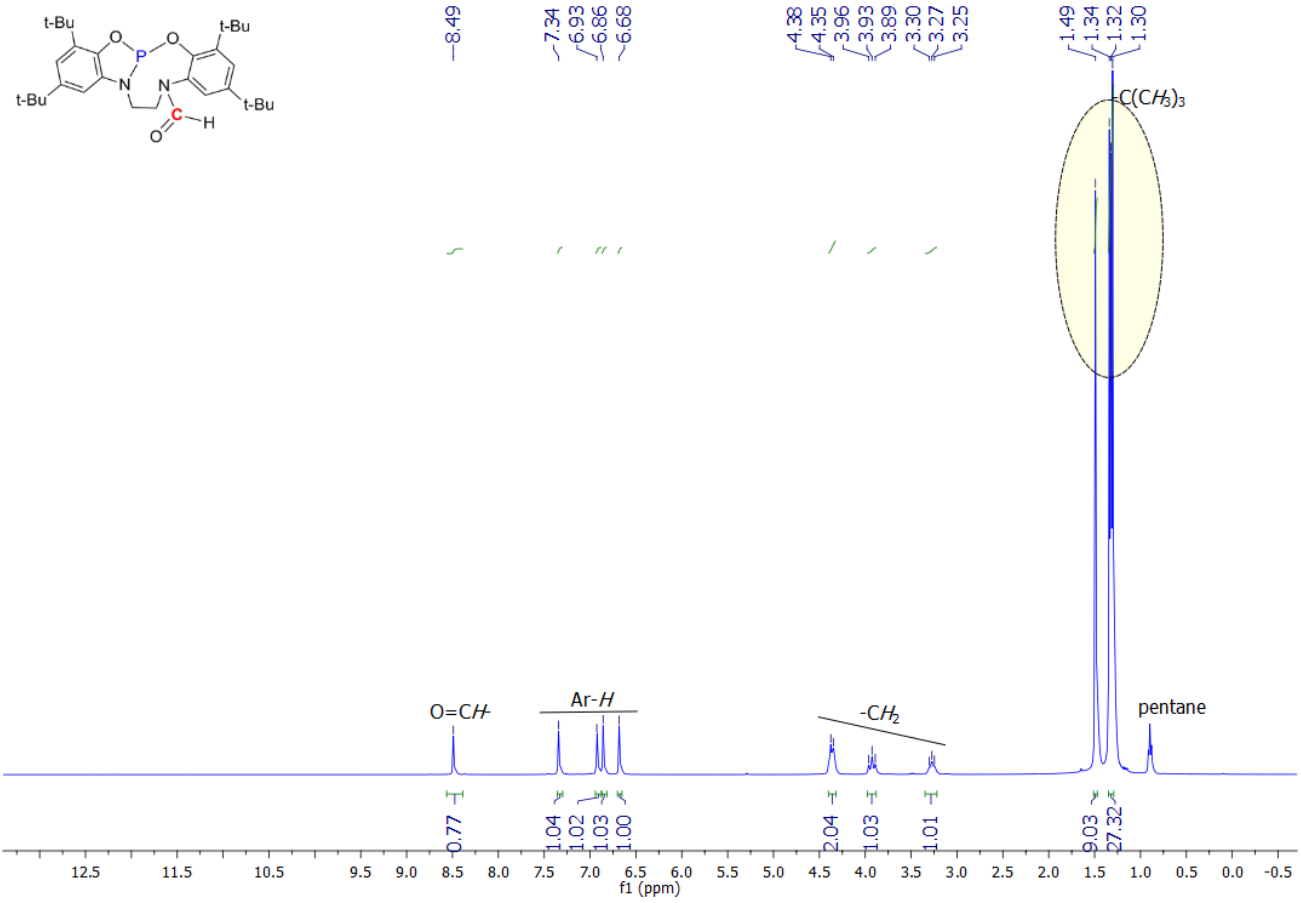


Figure S38. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9**.

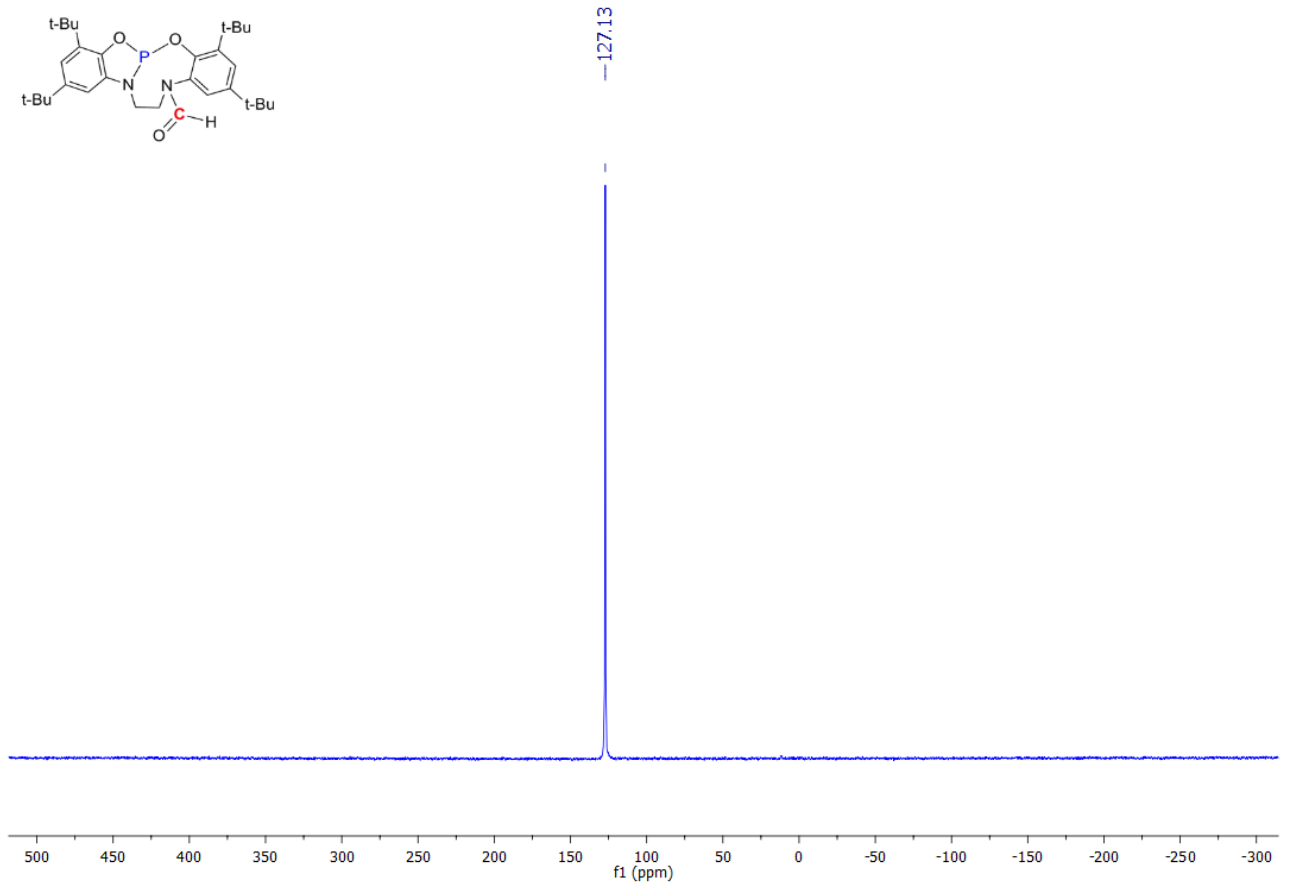


Figure S39. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **9**.

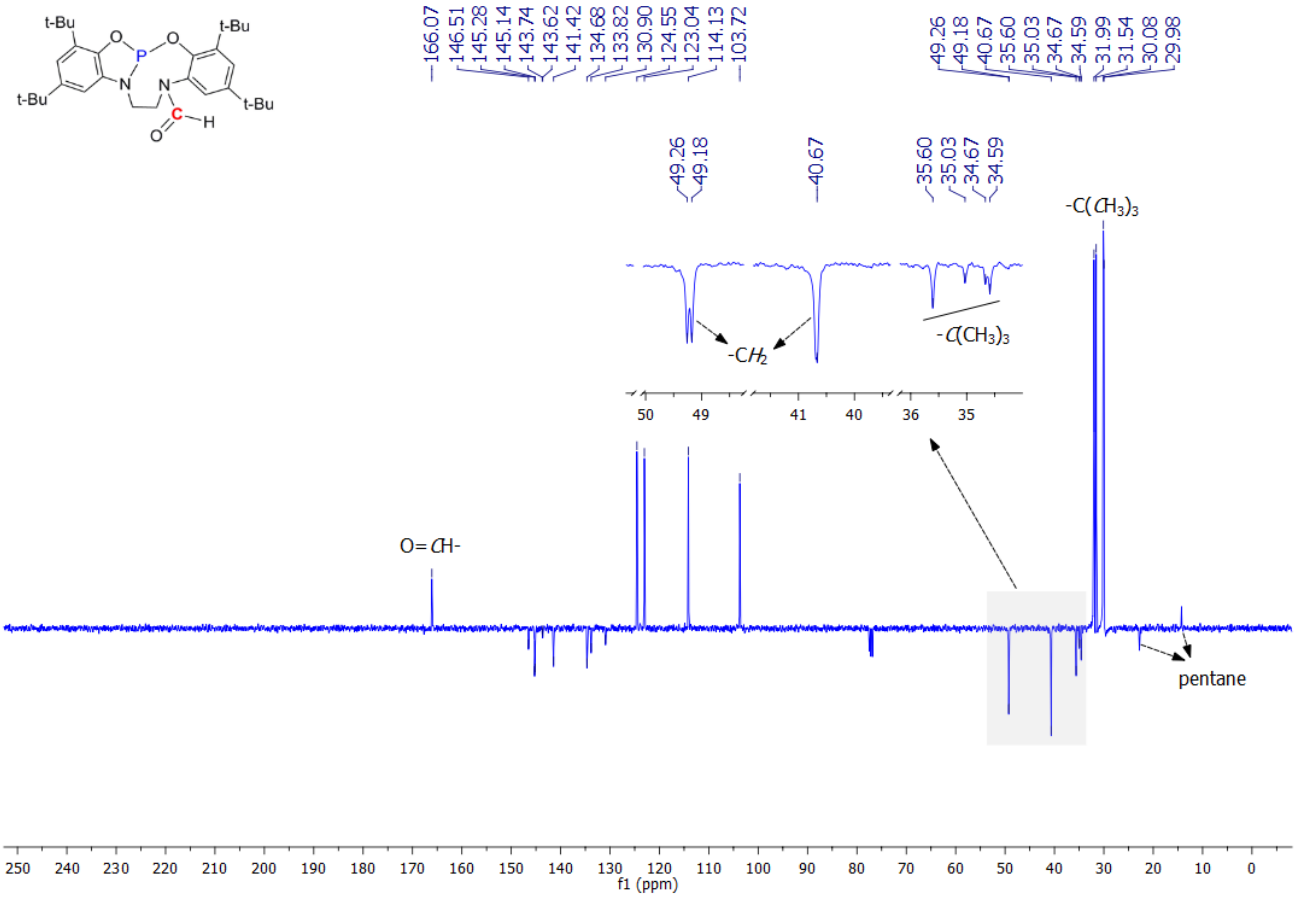


Figure S40. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **9**.

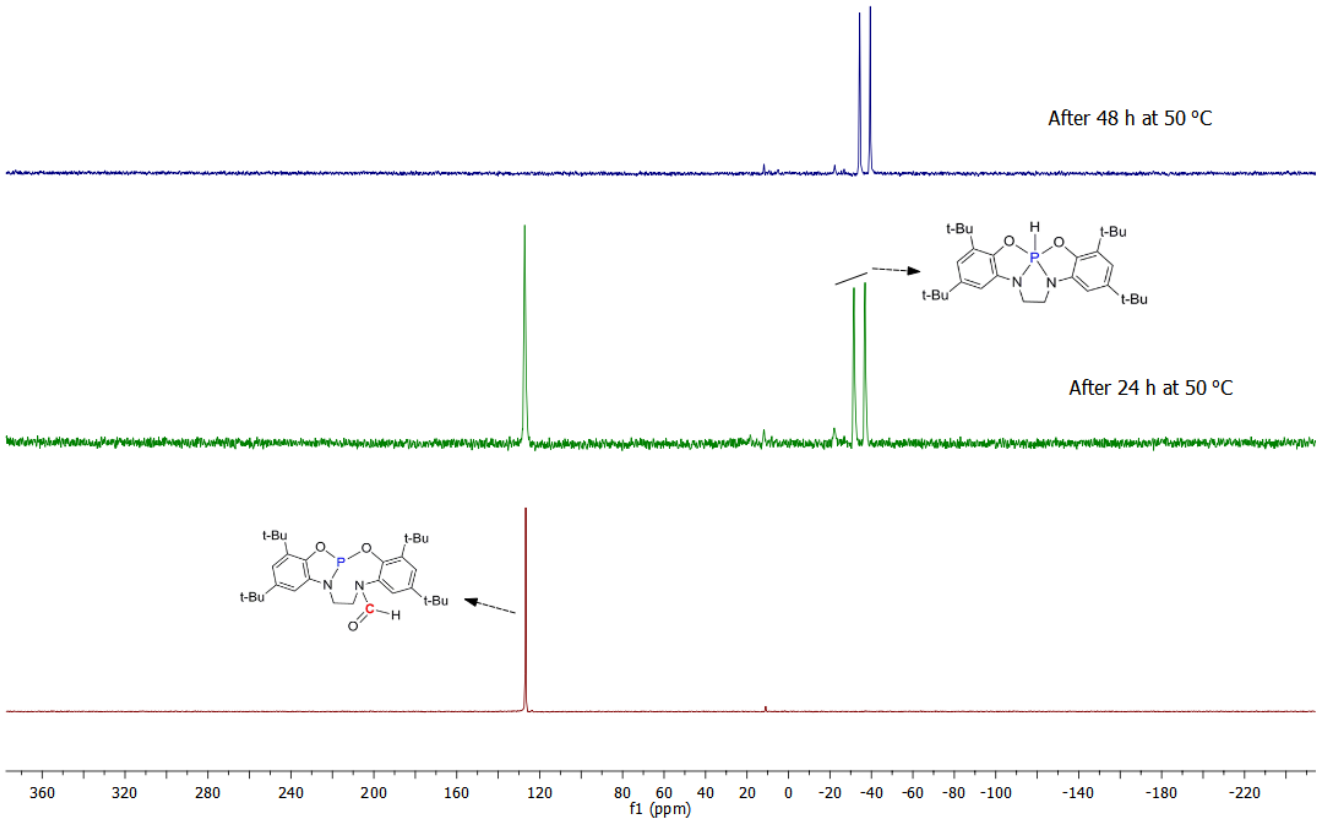


Figure S41. Stacked ^{31}P NMR spectra (162 MHz, in $CDCl_3$) of **9** at 50 ˚C with different intervals to show the formation of **5**.

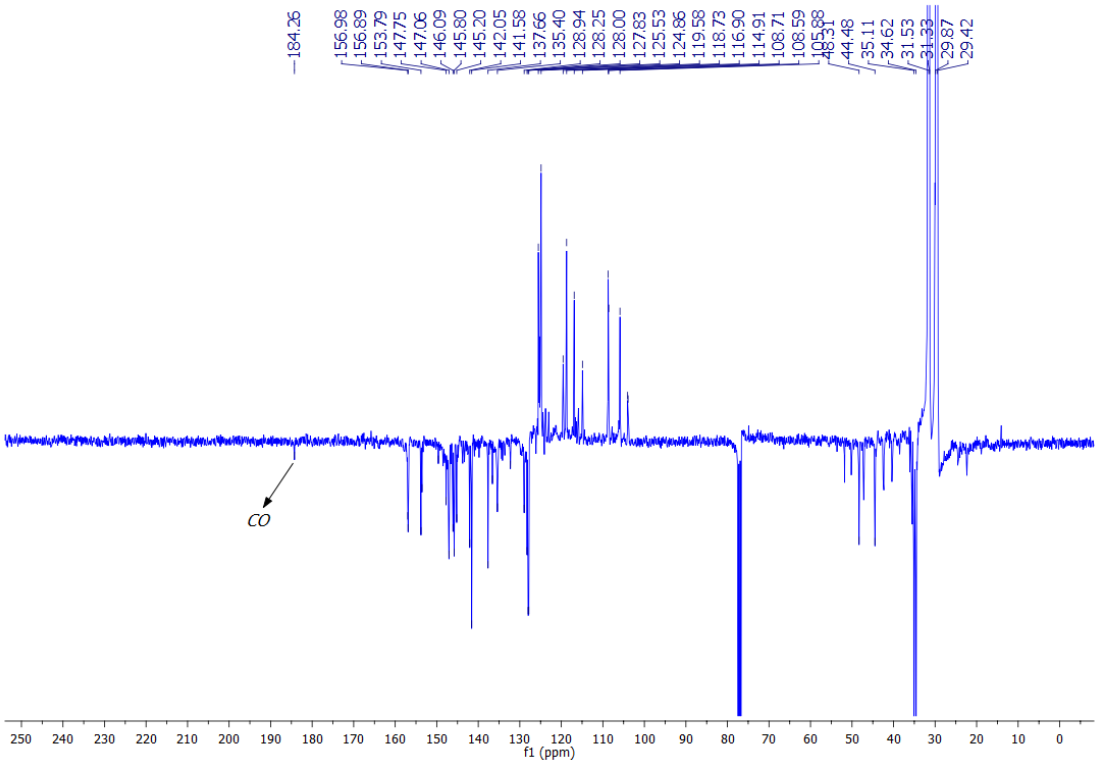


Figure S42. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) to show the formation of CO gas during conversion of on **9** to **5**.

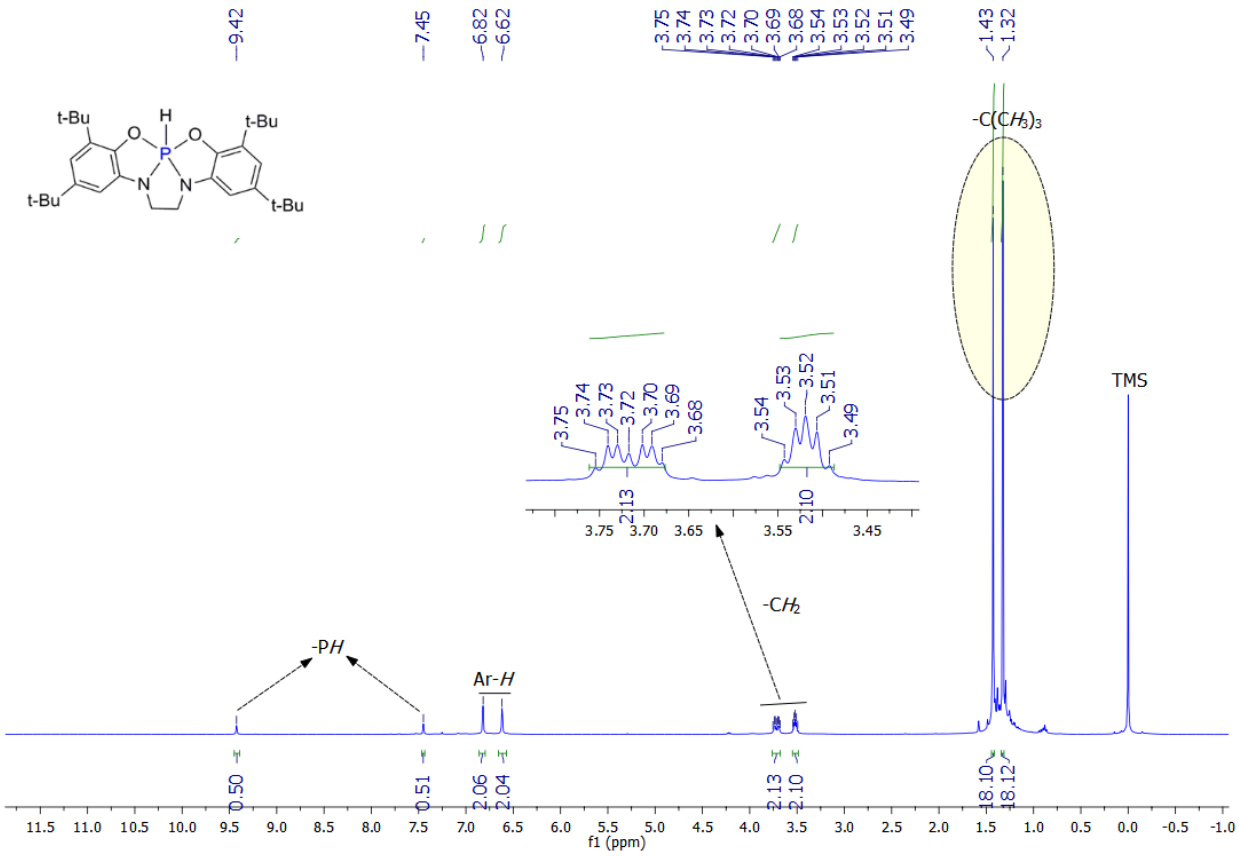


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**.

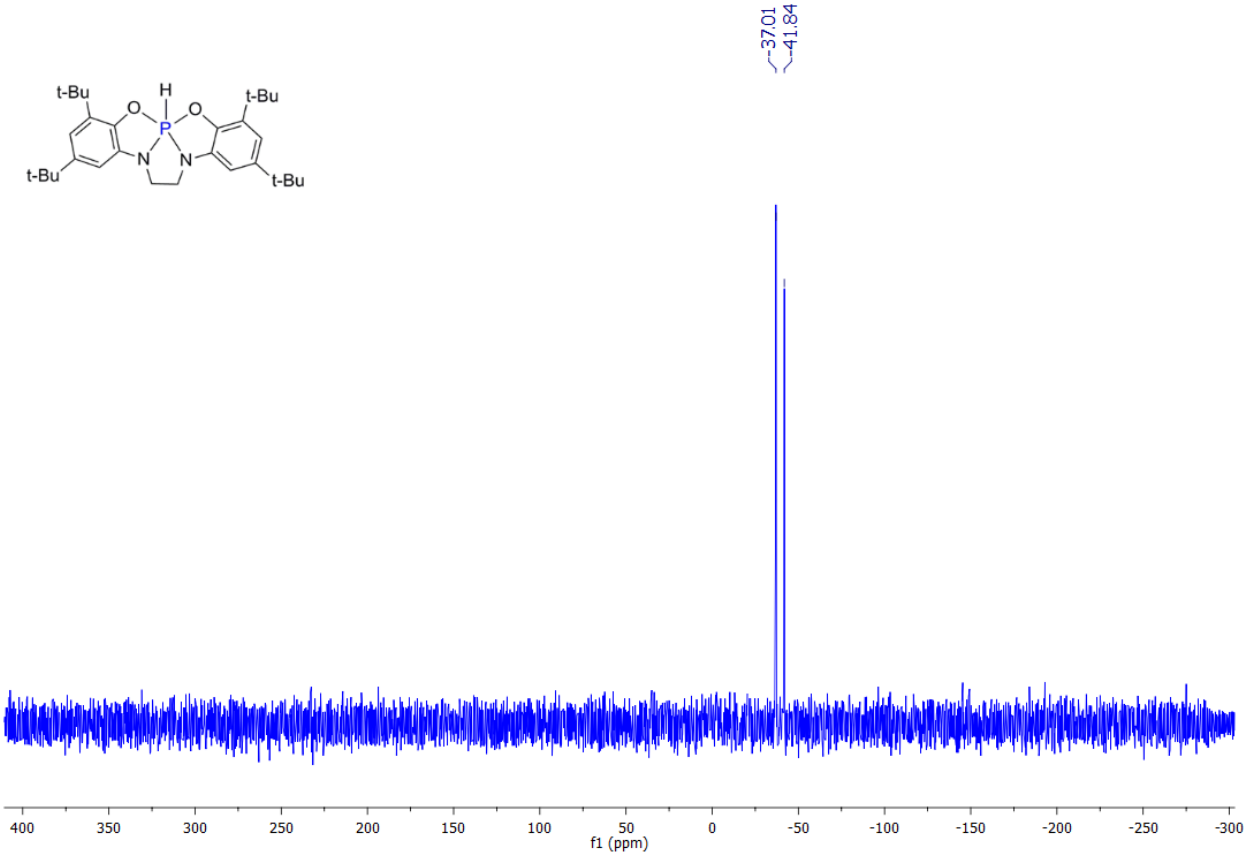


Figure S44. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **5**.

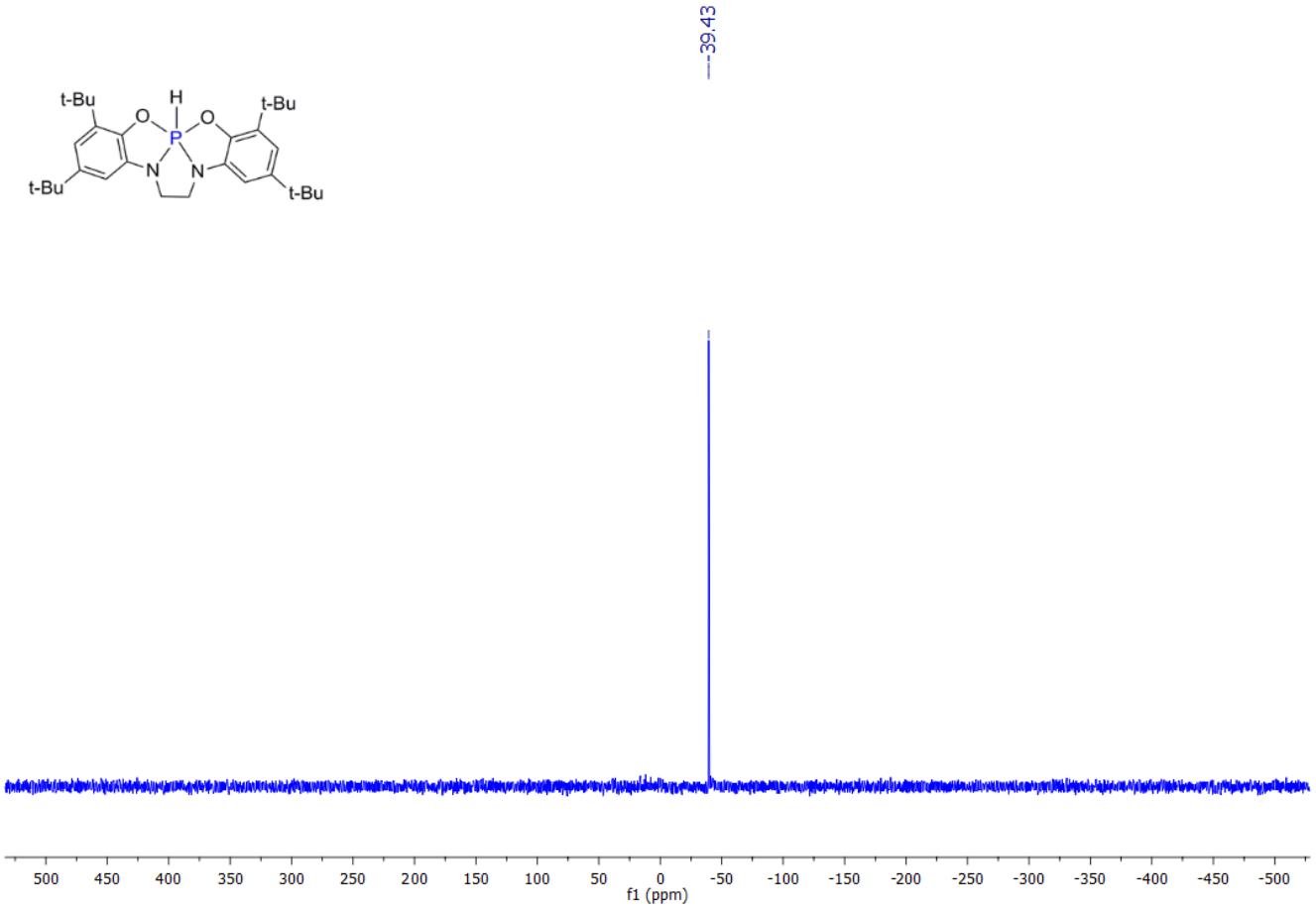


Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5**.

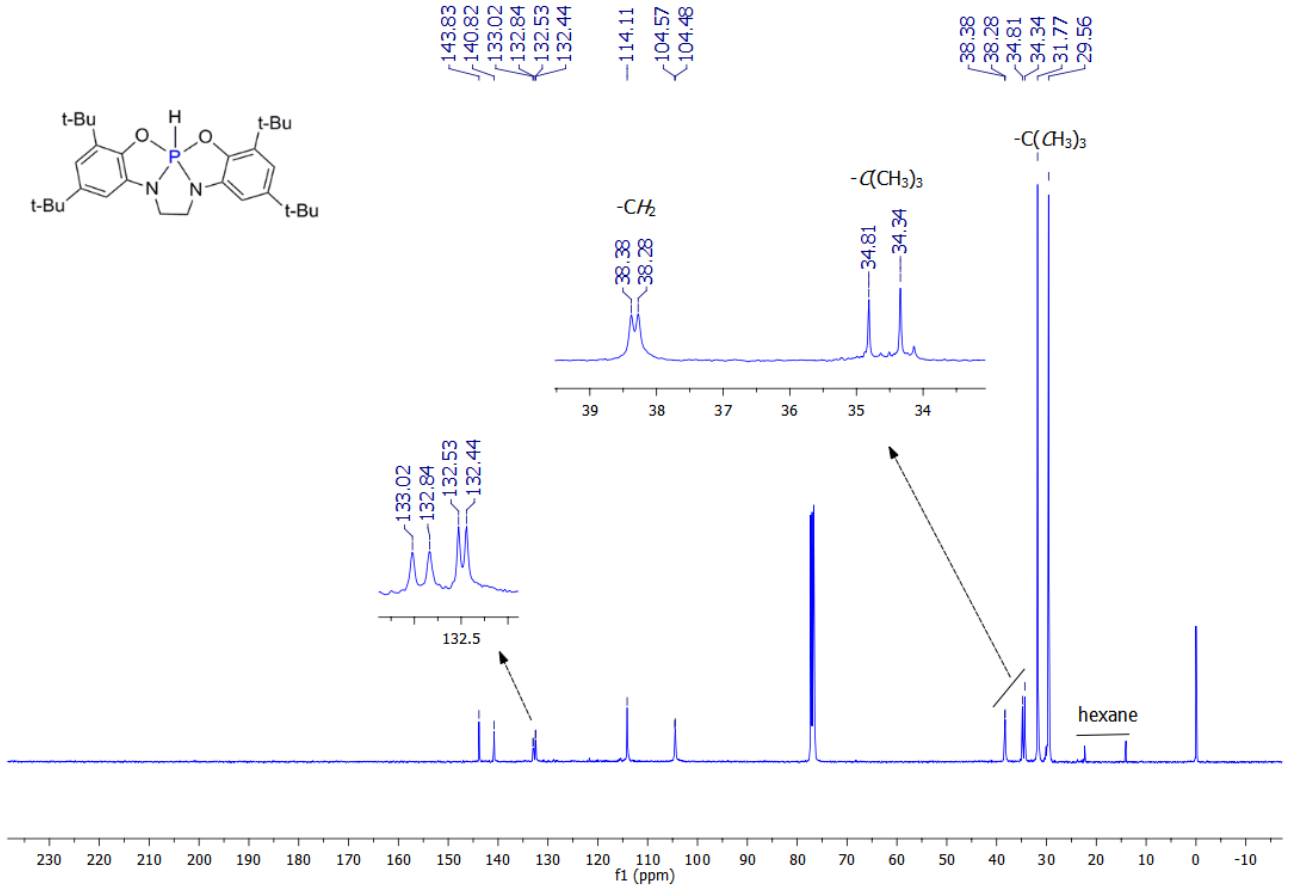


Figure S46. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **5**.

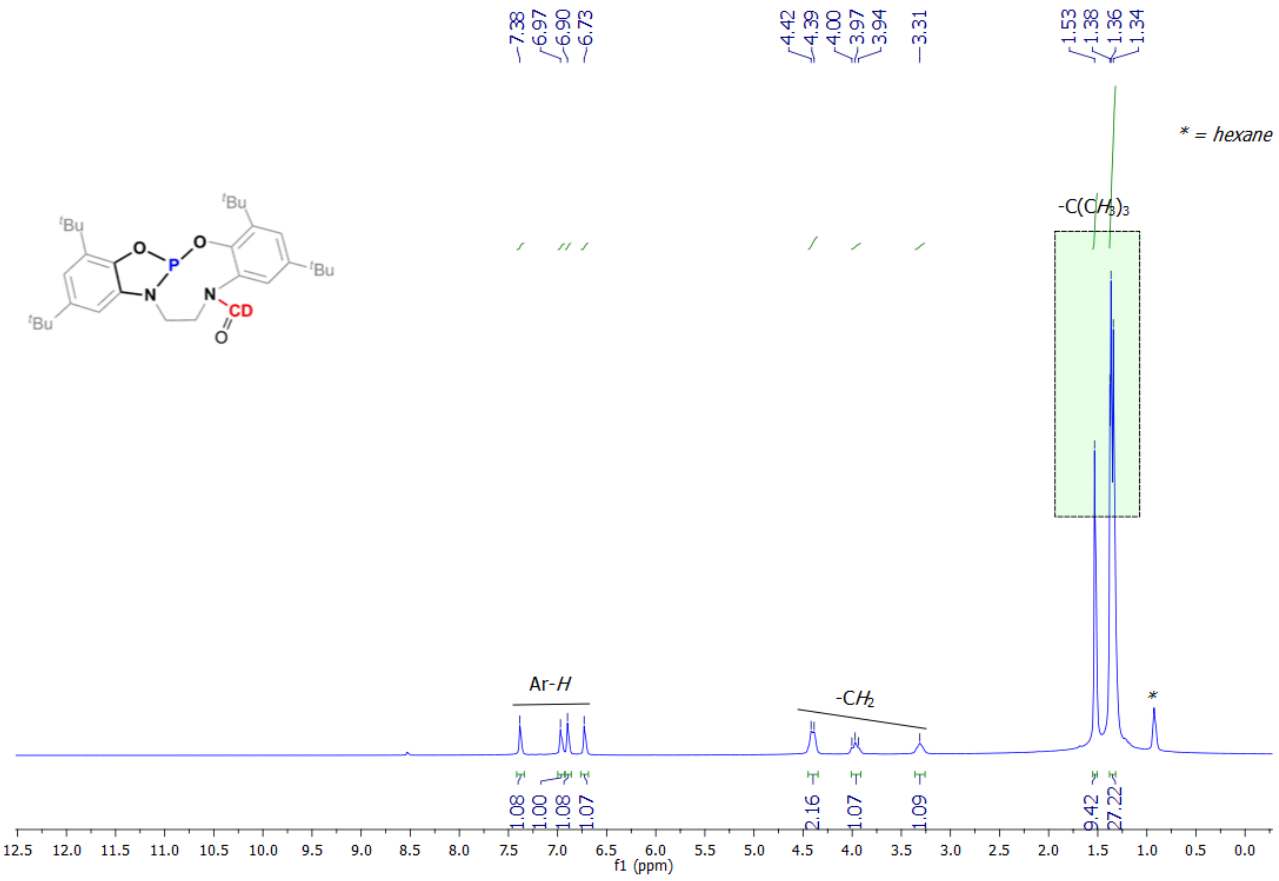


Figure S47. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9-D**.

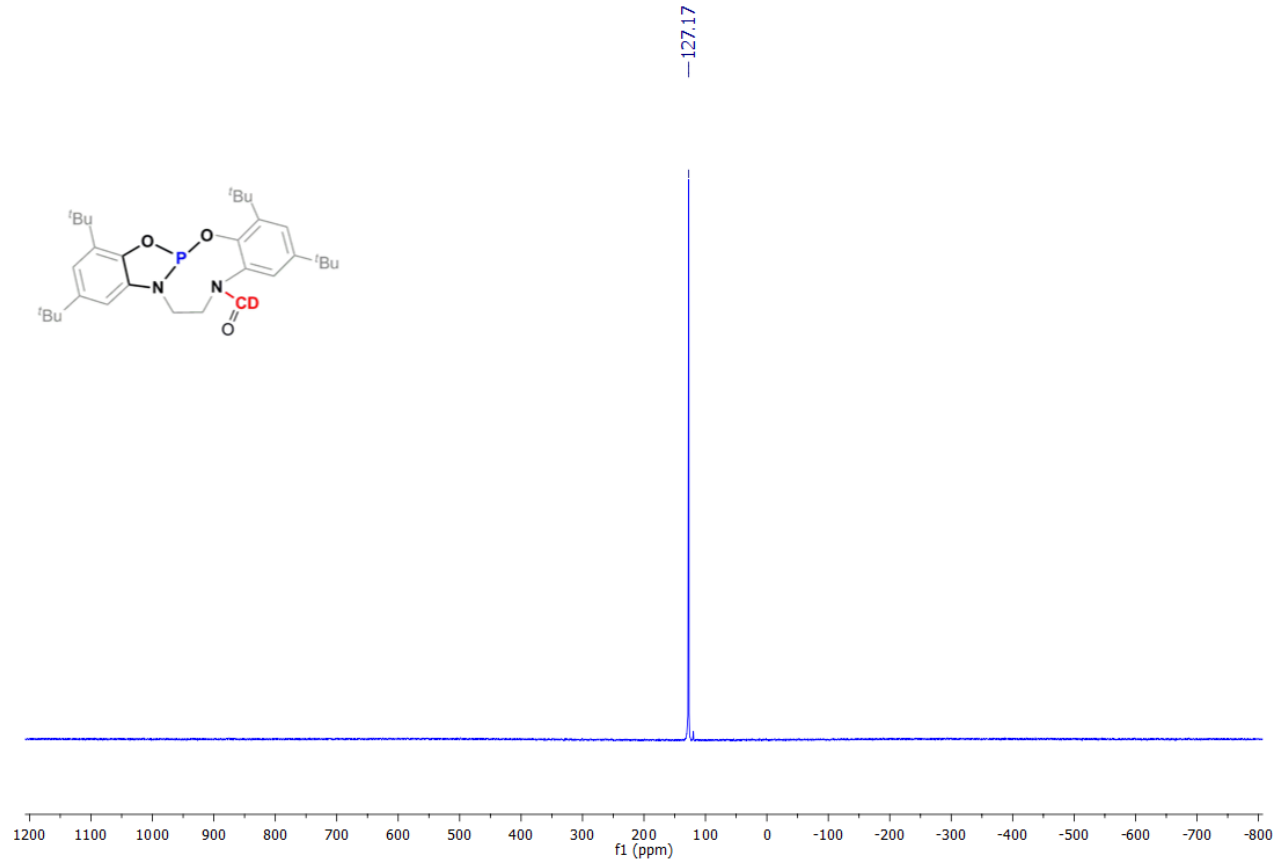


Figure S48. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **9-D**.

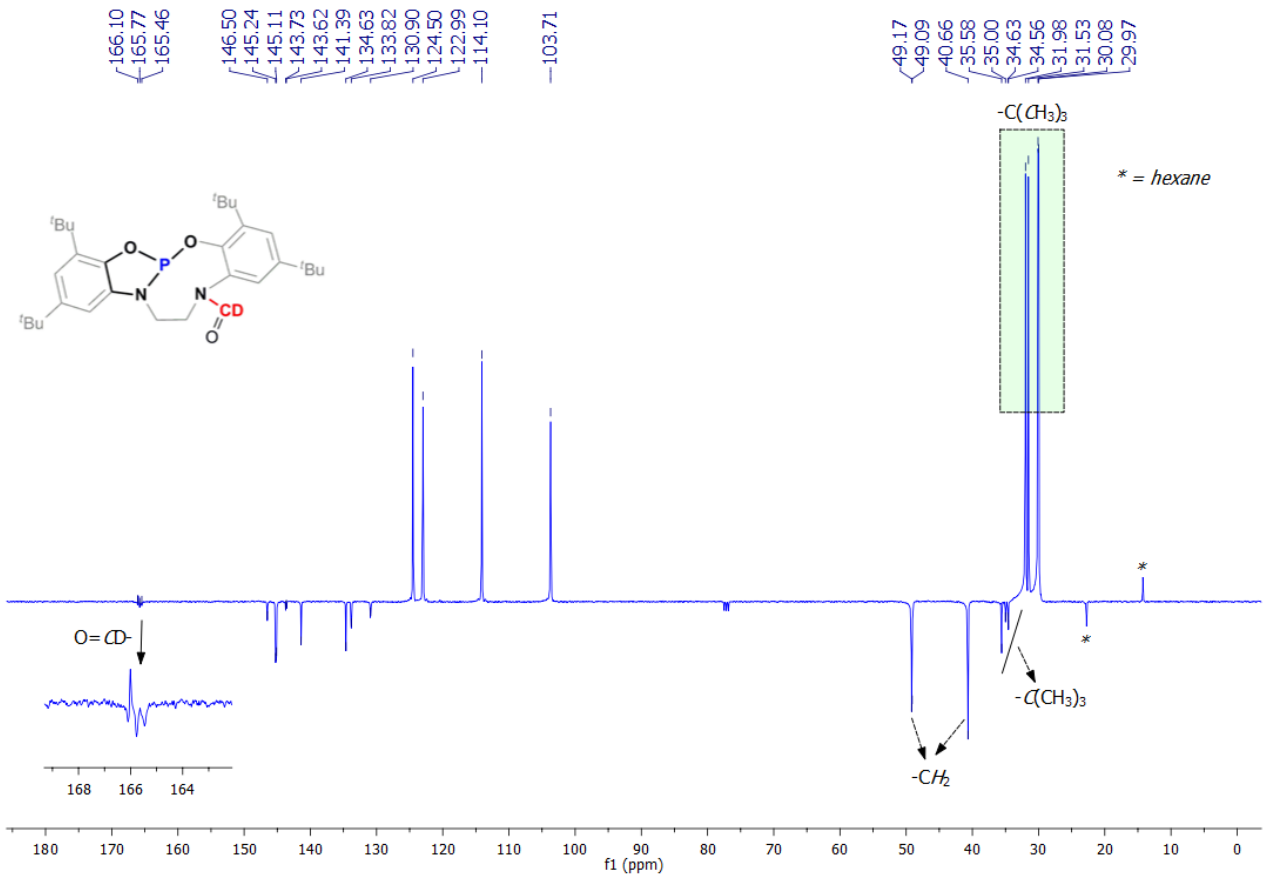


Figure S49. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) of **9-D**.

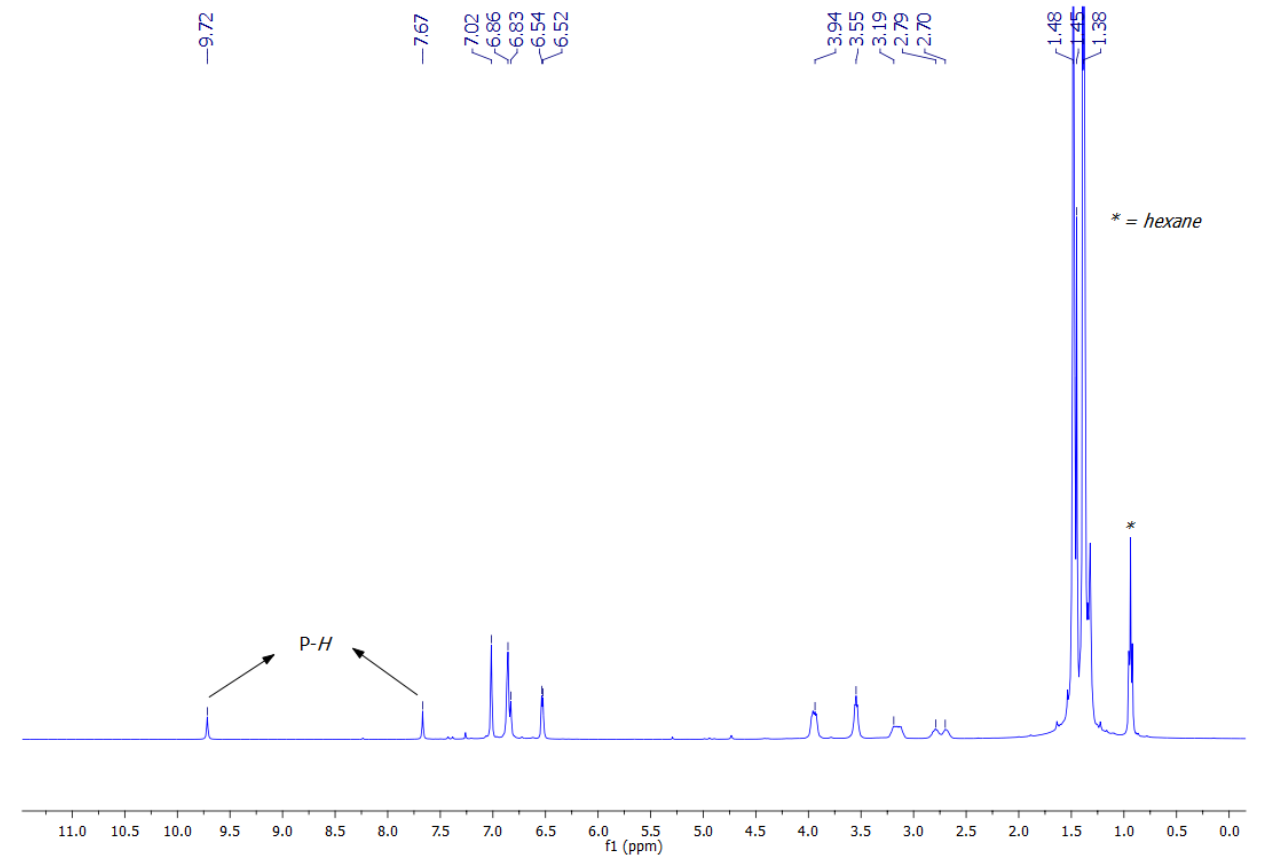


Figure S50. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) after heating **9-D** at 50 °C (to see the formation of **5-D**).

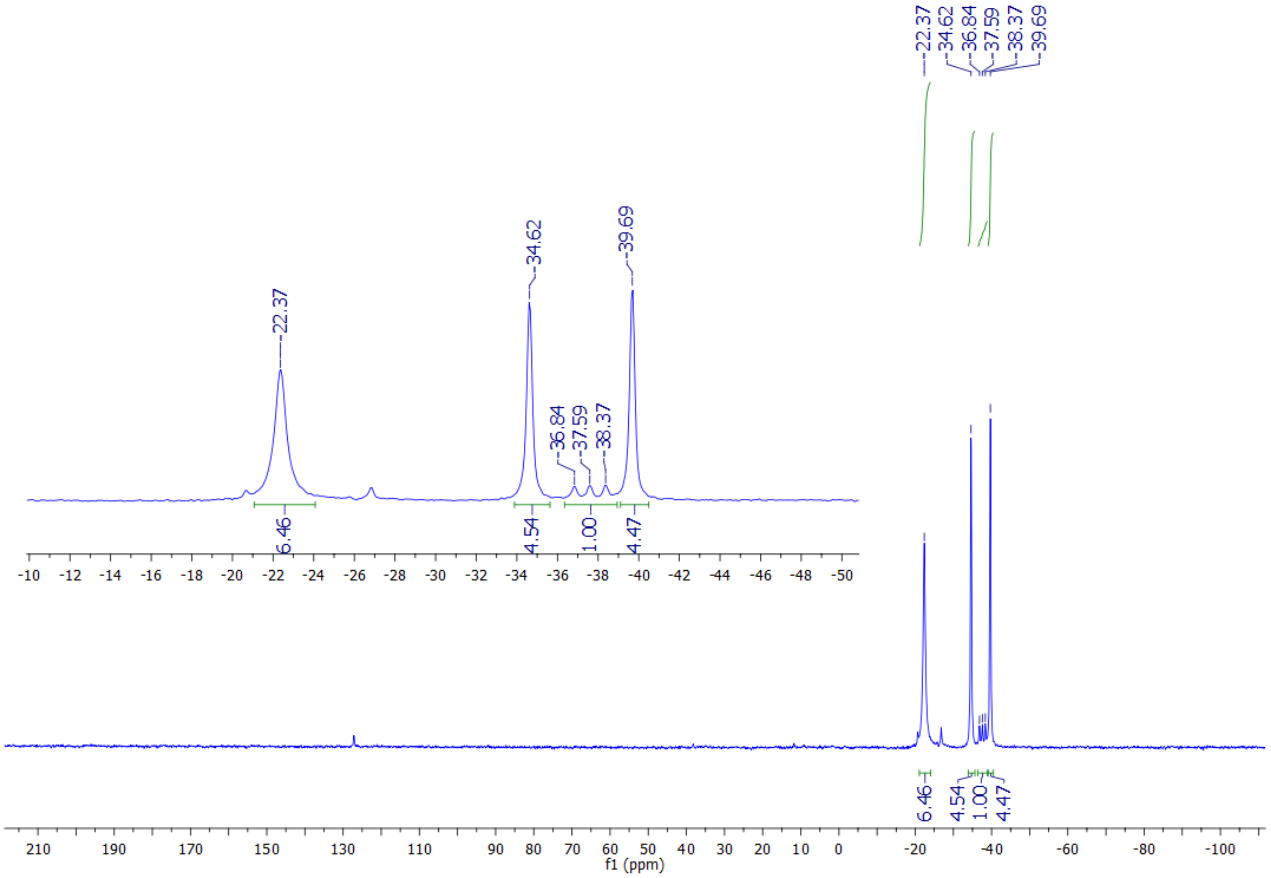


Figure S51. ^{31}P NMR spectrum (162 MHz, $CDCl_3$) after heating **9-D** at 50 °C (to see the formation of **5-D**).

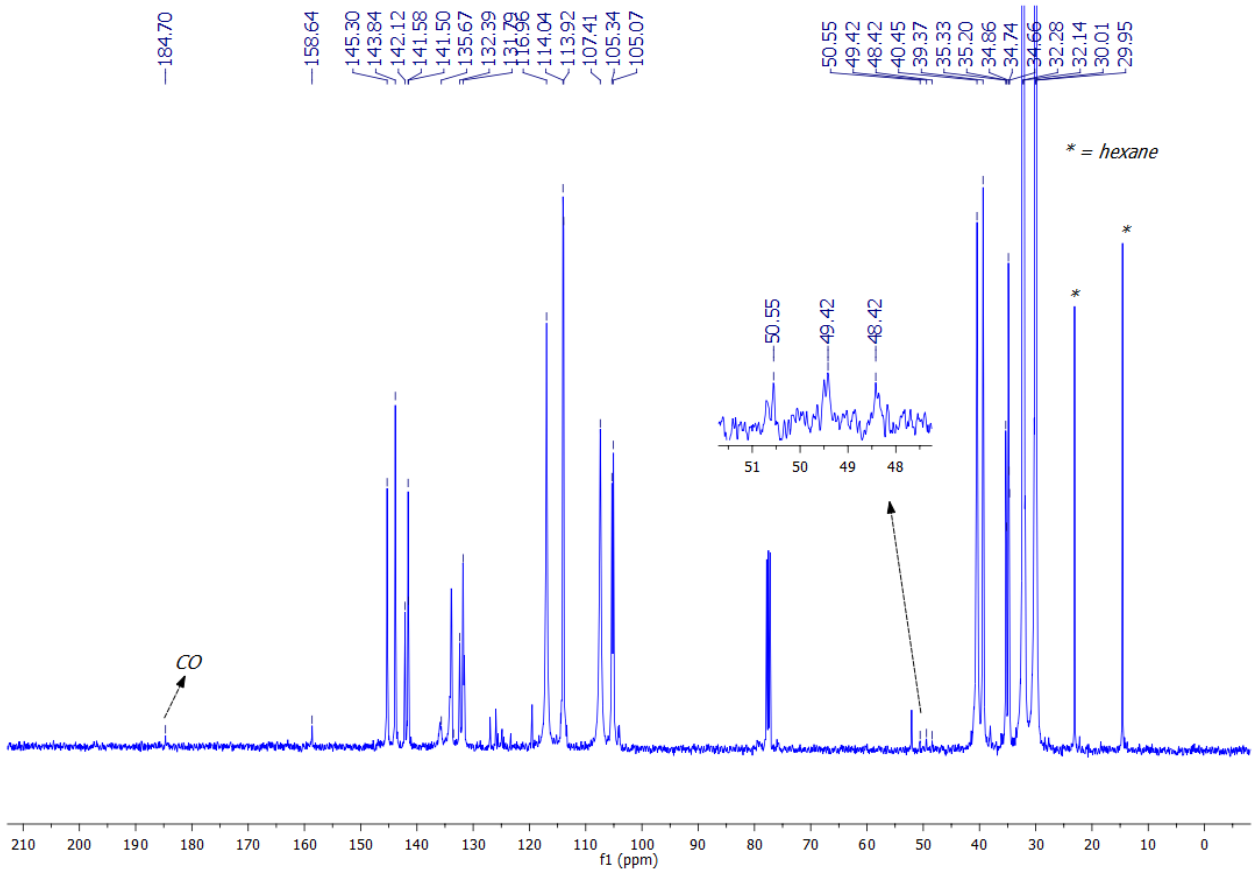


Figure S52. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) after heating **9-D** at 50 °C (to see the formation of **5-D**).

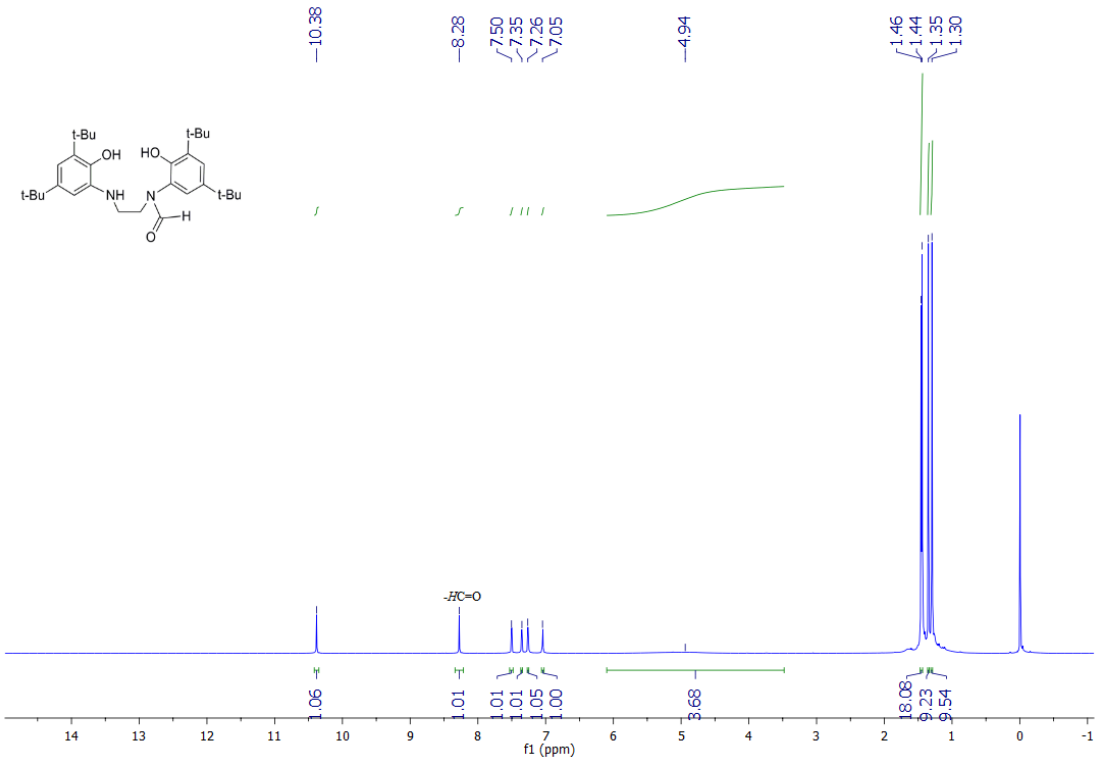


Figure S53. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8-OH**.

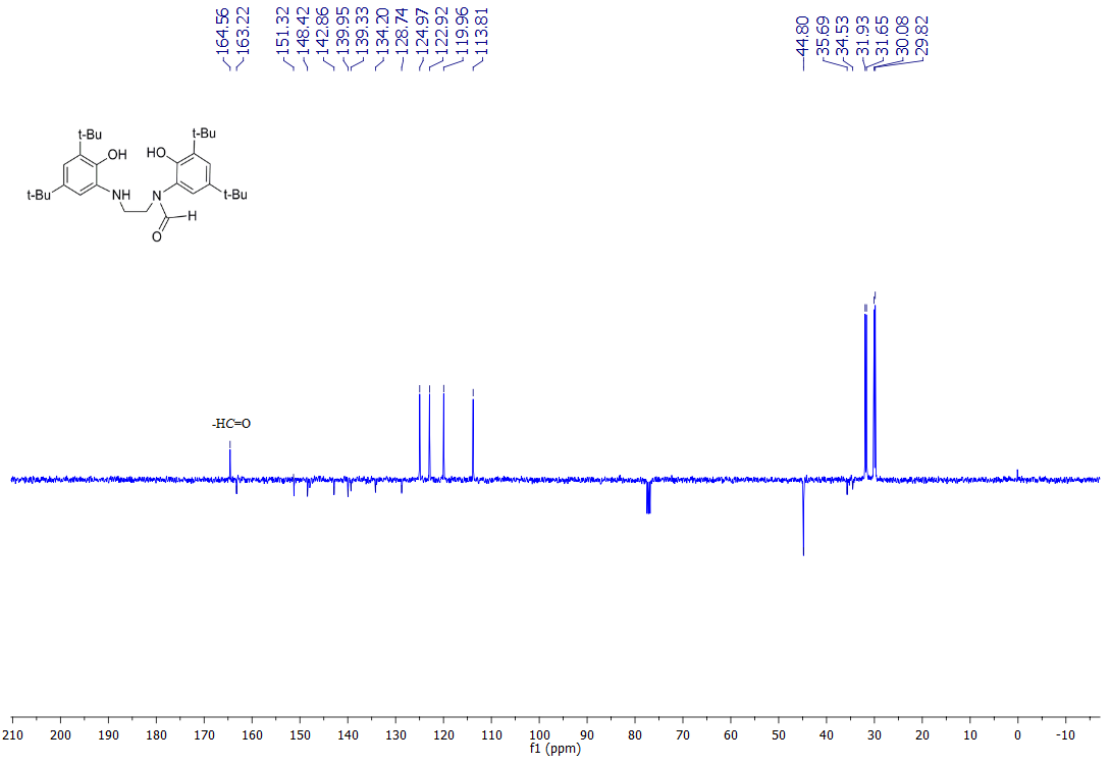


Figure S54. ^{13}C-JOMD NMR spectrum (100 MHz, $CDCl_3$) of **8-OH**.

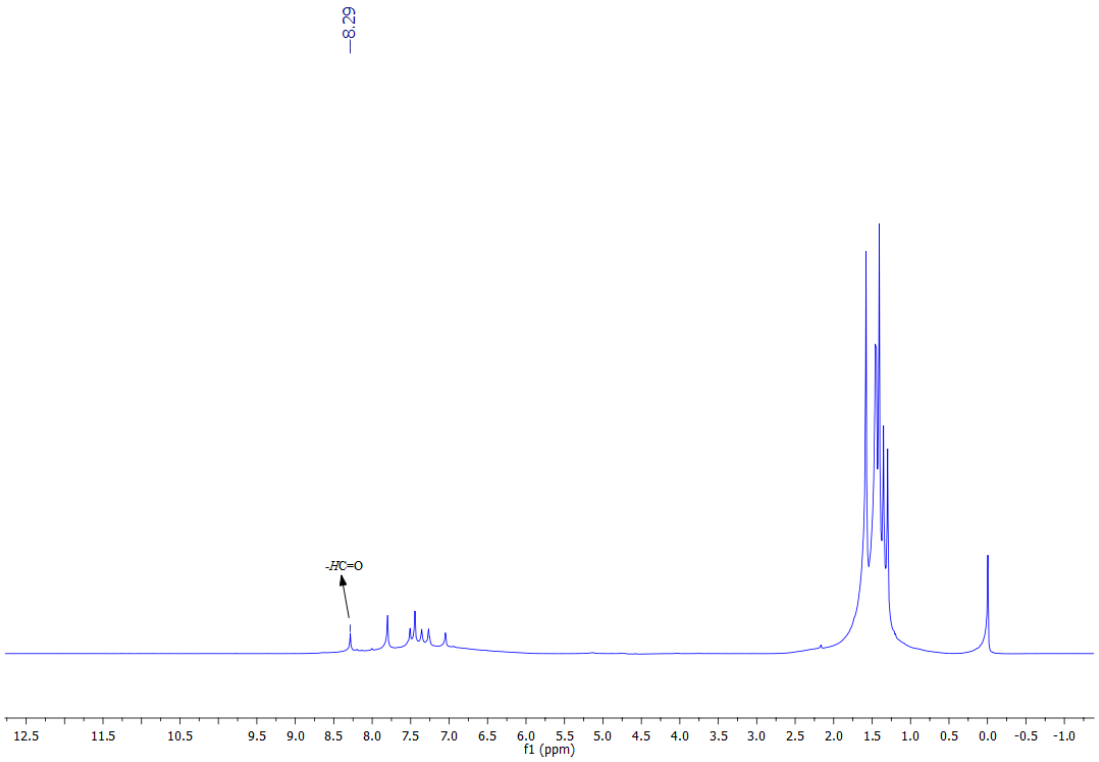


Figure S55. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) after (48 h) heating **8-OH** with 32 % HCl.

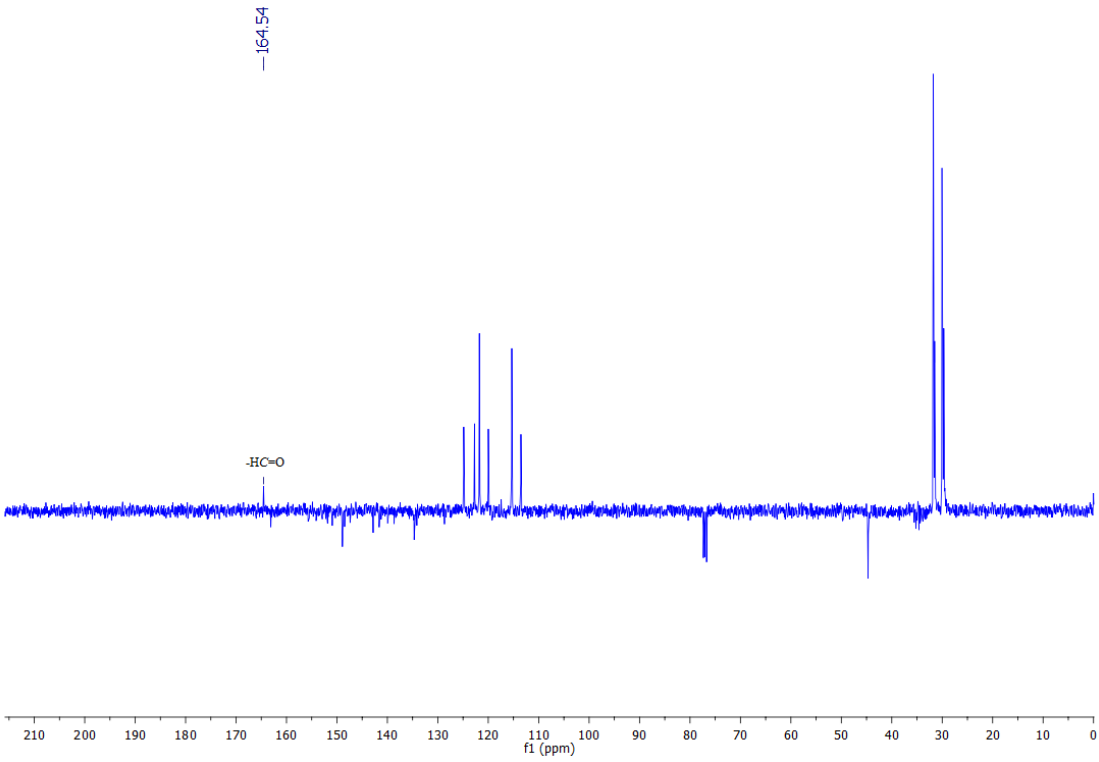
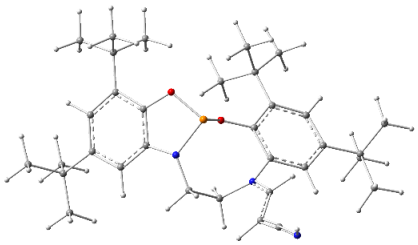


Figure S56. ^{13}C-JMOD NMR spectrum (100 MHz, $CDCl_3$) after (48 h) heating **8-OH** with 32 % HCl.

5. DFT Computations

DFT calculations were performed using Gaussian 09.2.[7] Geometry optimization of all the molecules were carried out using the BP86-D3 method[8] with Ahlrichs' def2TZVP basis set,[9] implemented in the Gaussian 09 software. Conductor-like polarizable continuum model (CPCM)[10] was used to account for the effect of chloroform. Thermal energy corrections were extracted from the results of frequency analysis performed at the same level of theory. Frequency analysis of all the molecules and intermediates contained no imaginary frequency showing that these are energy minima. The transition states geometries gave one imaginary frequency at expected reaction coordinates confirming that it is a first-order saddle point. IRC (Intrinsic Reaction Coordinate) calculations and subsequent geometry optimizations were also used to ensure the minima are related to the isolated transition states.

7a:



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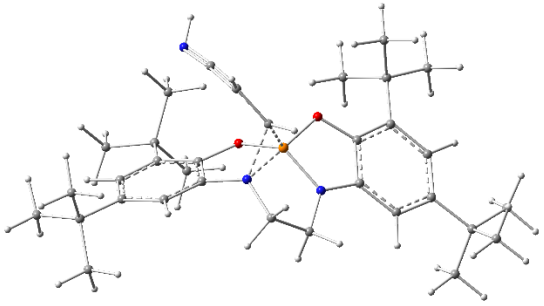

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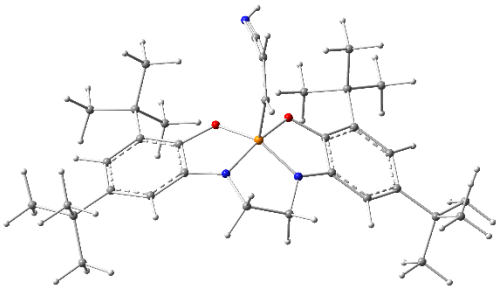
H	1.97984500	0.92503500	3.56111600
C	5.98898000	-3.00173100	0.89057400
H	5.58643600	-2.99515700	1.92480200
H	6.98923300	-3.48286800	0.91192200
H	5.32571300	-3.63859700	0.26968000
C	6.65531000	-1.60361100	-1.11577400
H	6.01653300	-2.21177300	-1.78888600
H	7.67014300	-2.05367900	-1.12308300
H	6.72712300	-0.58204100	-1.54348300
C	-6.29507600	-3.08085200	-0.07397900
H	-6.55745000	-2.62400200	-1.05094800
H	-7.15502300	-3.69934100	0.25958300
H	-5.43621200	-3.76378900	-0.23773600
C	4.03463100	2.58872500	2.71476500
H	4.39246700	1.80364800	3.41256100
H	3.76198300	3.47452500	3.32386100
H	4.87846800	2.88397300	2.05729900
N	2.64769800	2.68303300	-2.22724000
H	2.29790700	3.64147500	-2.37807100
C	2.10387300	1.68905200	-2.66308400
C	1.63090800	0.52058700	-3.14274200
H	2.03670900	0.19231300	-4.11498100

Zero-point correction= 0.716384 (Hartree/Particle)
Thermal correction to Energy= 0.754888
Thermal correction to Enthalpy= 0.755832
Thermal correction to Gibbs Free Energy= 0.652378
Sum of electronic and zero-point Energies= -1941.712122
Sum of electronic and thermal Energies= -1941.673618

Sum of electronic and thermal Enthalpies= -1941.672674
Sum of electronic and thermal Free Energies= -1941.776128

7-T:



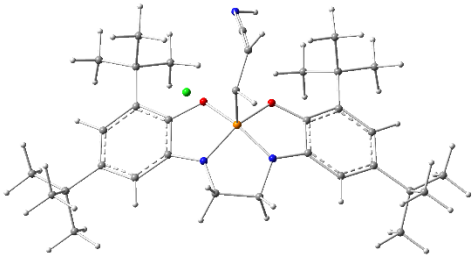
P	-0.22557700	0.50259800	-1.72930000
O	-1.59899600	-0.40161000	-1.90224000
O	0.41807200	-0.42935100	-0.43877000
N	-1.06380500	1.68095800	-0.79659000
N	1.99939900	1.90964100	-0.07546000
C	-3.72982400	-0.80085900	-0.68369300
C	-2.57120800	-0.06481500	-0.94392100
C	-2.25690700	1.12781500	-0.28078100
C	-3.09742700	1.62754100	0.71515100
H	-2.83999100	2.54700900	1.23763900
C	-4.27061800	0.92229800	1.02574500
C	-4.55580000	-0.26147000	0.31987900
H	-5.46898800	-0.79900500	0.56931000
C	-4.06115200	-2.09882800	-1.43283600
C	-5.39527600	-2.70795900	-0.96547100
H	-5.37330700	-2.97474500	0.10202600
H	-5.58947500	-3.62942800	-1.53417400
H	-6.24159100	-2.02572900	-1.13711300
C	-2.94272500	-3.13635200	-1.17952500
H	-1.96758400	-2.77503700	-1.52758900
H	-3.17188600	-4.07281900	-1.71158300
H	-2.85963000	-3.36280100	-0.10624000
C	-4.17079800	-1.80307200	-2.94778000
H	-4.96179800	-1.06266400	-3.14144200
H	-4.42608500	-2.72635300	-3.49062400
H	-3.22779100	-1.41677500	-3.35574300
C	-5.24870200	1.40397300	2.11177600
C	-5.38130600	0.31368600	3.20104200
H	-5.76733100	-0.62916000	2.78753400
H	-6.07584500	0.64641000	3.98801900
H	-4.40561400	0.10702900	3.66644900
C	-6.63317300	1.66232100	1.47247100
H	-6.56336300	2.43527700	0.69206600
H	-7.34663500	2.00718300	2.23712900

H	-7.04518800	0.75234300	1.01308700
C	-4.77956700	2.70546400	2.78747800
H	-3.80659100	2.57940000	3.28709600
H	-5.50936600	3.00418400	3.55450600
H	-4.69766000	3.53443900	2.06774300
C	1.72575000	-0.55495900	-0.06521500
C	2.26337400	-1.84301100	0.18175400
C	3.59819200	-1.90461000	0.59697000
H	4.02739300	-2.88709300	0.78418900
C	4.42403100	-0.78183900	0.79438100
C	3.86050100	0.47098200	0.56554300
H	4.42256700	1.38719000	0.74569600
C	2.52899800	0.58308300	0.13958300
C	1.41974600	-3.11910800	-0.00871800
C	0.16451400	-3.06818100	0.89744800
H	0.45640100	-2.98068300	1.95511300
H	-0.40995500	-3.99893800	0.77724100
H	-0.49438300	-2.22990300	0.64536400
C	2.21137800	-4.38645700	0.36959600
H	3.10018100	-4.52475500	-0.26438000
H	1.56508300	-5.26453900	0.22693500
H	2.52833200	-4.37552800	1.42342500
C	1.00518300	-3.25872400	-1.49336100
H	0.37914600	-2.42459600	-1.82962400
H	0.42686500	-4.18544000	-1.62897600
H	1.89384400	-3.31167000	-2.14022000
C	5.87293700	-0.97088000	1.26652500
C	6.63523600	-1.82652900	0.22736200
H	6.17756200	-2.81786600	0.09974200
H	7.67543900	-1.97669400	0.55450100
H	6.65072700	-1.32858200	-0.75392400
C	5.87208000	-1.69727700	2.63217700
H	5.33227900	-1.10705600	3.38803500
H	6.90514300	-1.84434000	2.98251000
H	5.39544500	-2.68617000	2.56828300
C	6.61145900	0.36921000	1.42784800
H	6.66205200	0.92542800	0.47898100
H	7.64381300	0.18087300	1.75641400
H	6.13557400	1.01082400	2.18531700
C	-0.36395600	2.79737500	-0.17848200
H	-1.06819400	3.36660000	0.44177600
H	-0.02364900	3.48250800	-0.96867800
C	0.82219000	2.37543400	0.71203300
H	1.14976600	3.21770700	1.34014300
H	0.53395100	1.55363500	1.37626900
C	2.71308400	2.74984300	-0.81767400

H	3.50994700	2.28670800	-1.40193300
C	2.53863600	4.14301300	-0.88944700
H	1.80995600	4.69460500	-0.29439700
C	3.30904900	4.87094600	-1.73117800
N	4.07270000	5.53817300	-2.35886600
H	4.02600700	5.87800400	-3.32197800

Zero-point correction= 0.718931 (Hartree/Particle)
Thermal correction to Energy= 0.761198
Thermal correction to Enthalpy= 0.762143
Thermal correction to Gibbs Free Energy= 0.645927
Sum of electronic and zero-point Energies= -1941.728189
Sum of electronic and thermal Energies= -1941.685922
Sum of electronic and thermal Enthalpies= -1941.684978
Sum of electronic and thermal Free Energies= -1941.801194

(7-TCl)



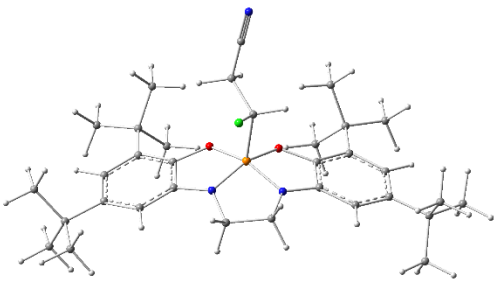
P	0.06076100	-0.24615100	0.72135800
C	0.01247600	0.30526700	2.51657400
H	0.65344800	-0.38711200	3.07335900
O	1.22804200	0.81668100	0.08996900
O	-1.09408300	0.84408600	0.08998200
N	1.29255000	-1.49659400	0.76978400
N	-1.07876000	-1.50572900	0.48884500
C	4.75340500	0.14234400	-0.77083700
H	5.63906400	0.62596000	-1.17363400
C	4.82405600	-1.21894300	-0.44068900
C	3.59142000	0.93345300	-0.61239200
C	3.56052700	2.43505900	-0.93390200
C	2.48487200	0.26869800	-0.08292300
C	2.52694200	-1.08622900	0.28631300
C	-2.32002900	0.27797900	-0.19703600
C	-3.43640700	0.94937000	-0.69475400
C	-4.57318600	0.13948200	-0.93256000
H	-5.46582600	0.62823300	-1.31310800
C	3.68180200	-1.84136200	0.10258800
H	3.68877600	-2.89546300	0.38313100
C	6.10279100	-2.05104200	-0.64522400

C	-4.61683600	-1.24151800	-0.69624000
C	-3.45139500	2.47177000	-0.89244100
C	-3.46282200	-1.87581300	-0.19088900
H	-3.45038100	-2.94511500	0.02359900
C	-5.87920900	-2.08352400	-0.95367800
C	7.25352300	-1.22592100	-1.24857300
H	6.98697400	-0.81504200	-2.23419100
H	8.13551500	-1.87018200	-1.38289200
H	7.54707500	-0.39180700	-0.59311300
C	3.43487300	3.19867600	0.40560400
H	2.58260700	2.82944700	0.99166800
H	3.30874500	4.27873700	0.22687200
H	4.33950600	3.05599800	1.01586200
C	-2.32947300	-1.10722400	0.04383300
C	0.85470200	-2.88245900	0.67105700
H	1.31478100	-3.50511500	1.45249300
H	1.14628600	-3.29380100	-0.31144700
C	-0.68140900	-2.85423900	0.82810000
H	-1.15697900	-3.58108500	0.15407700
H	-0.98399300	-3.09030900	1.86302900
C	2.36384100	2.77940700	-1.85242800
H	2.42891100	2.22115000	-2.79885200
H	2.37547000	3.85475800	-2.08983200
H	1.40160000	2.53945200	-1.38357300
C	5.80089800	-3.22621400	-1.60459600
H	5.01409900	-3.88456600	-1.20835300
H	6.70527500	-3.83624800	-1.75678100
H	5.46848300	-2.85207500	-2.58492300
C	-3.36708500	3.13335800	0.50298000
H	-4.24120400	2.85678300	1.11215600
H	-3.34585200	4.23041100	0.40520100
H	-2.45946000	2.82254100	1.03420700
C	4.84487900	2.90837200	-1.63967300
H	5.73850600	2.76184500	-1.01483500
H	4.76515800	3.98498100	-1.85313000
H	4.99994200	2.38601900	-2.59610200
C	-7.04027600	-1.24794800	-1.52162900
H	-7.35080600	-0.45312100	-0.82654500
H	-7.91090000	-1.89892400	-1.69312300
H	-6.77505100	-0.78348700	-2.48353500
C	-2.25246400	2.92177700	-1.76052500
H	-1.29362700	2.67365800	-1.28956900
H	-2.29037200	4.01230100	-1.91006800
H	-2.28830700	2.43952800	-2.74972600
C	-5.55338700	-3.20329400	-1.96977200
H	-5.21793500	-2.77393600	-2.92621500

H	-6.44767400	-3.81704200	-2.16210600
H	-4.76107900	-3.87107900	-1.60135600
C	-6.34837100	-2.71999600	0.37569700
H	-5.57545400	-3.37105500	0.80949700
H	-7.25065500	-3.33030200	0.21107200
H	-6.58928700	-1.94078000	1.11488500
C	6.57515600	-2.61193700	0.71663500
H	6.80154200	-1.79281100	1.41619900
H	7.48700100	-3.21604300	0.58549000
H	5.81083500	-3.25255500	1.17993200
C	-4.74087400	2.95600800	-1.58158800
H	-4.86862000	2.50139900	-2.57620100
H	-4.69103900	4.04734700	-1.71401300
H	-5.63745500	2.73761200	-0.98216300
Cl	-1.69000600	-0.07158200	3.21870400
N	-0.01005100	3.75046600	1.36249100
H	0.68976800	4.05091800	0.67109000
C	0.22996700	2.74927900	2.01951300
C	0.40530200	1.70547900	2.81500000
H	0.85419800	1.90728500	3.79051500

Zero-point correction= 0.720911 (Hartree/Particle)
Thermal correction to Energy= 0.764482
Thermal correction to Enthalpy= 0.765426
Thermal correction to Gibbs Free Energy= 0.646474
Sum of electronic and zero-point Energies= -2402.192587
Sum of electronic and thermal Energies= -2402.149015
Sum of electronic and thermal Enthalpies= -2402.148071
Sum of electronic and thermal Free Energies= -2402.267024

4:



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H	-1.09640900	-3.27843800	-0.98363400
H	-1.18335700	-3.50122900	0.78571500
C	0.80275500	-2.89155400	0.07545900
H	1.13607700	-3.35383000	1.01863700
H	1.24614800	-3.45564600	-0.75963200
N	1.21036000	-1.50289500	0.01823600

N	-1.16073000	-1.49925000	0.12673900
C	2.48844600	-1.02729100	-0.22438000
C	2.45185400	0.37338800	-0.36363800
C	3.68182500	-1.72925600	-0.35507000
C	3.59180600	1.12647700	-0.63644500
C	4.86476900	-1.01003500	-0.62489500
H	3.68849900	-2.81386500	-0.24050300
C	4.79121200	0.38470100	-0.75448300
H	5.70625500	0.93597200	-0.95152300
C	-2.43603400	-1.02978400	-0.14885500
C	-3.61702100	-1.75441100	-0.31027100
C	-2.40900200	0.36374400	-0.30145800
C	-4.79572400	-1.05387400	-0.61836400
H	-3.60455000	-2.83635100	-0.18900500
C	-3.54886600	1.10134800	-0.63232800
C	-4.73071600	0.34404200	-0.76769200
H	-5.65009000	0.87597300	-1.00661200
O	-1.13432500	0.87969800	-0.15047100
O	1.16846200	0.87904400	-0.23951300
P	0.03564500	-0.27816000	0.28883800
C	3.53149800	2.65322900	-0.78871300
C	6.19070200	-1.78013100	-0.75679200
C	4.91768400	3.26257400	-1.06776300
H	5.35526800	2.87660600	-2.00101000
H	4.81873800	4.35347300	-1.17269000
H	5.62416700	3.06870900	-0.24635900
C	2.98525300	3.27882800	0.51681000
H	1.96779300	2.92818000	0.73236500
H	3.62931600	3.02050200	1.37095300
H	2.95724500	4.37600300	0.42660000
C	2.59959600	3.01538000	-1.97024300
H	2.98167700	2.58547700	-2.90874400
H	1.57970400	2.64242100	-1.80901000
H	2.55175000	4.10936400	-2.08917400
C	7.38700100	-0.85345200	-1.03937700
H	8.30455900	-1.45510000	-1.12332900
H	7.26295800	-0.30236100	-1.98402500
H	7.54011000	-0.12350800	-0.22985200
C	6.08141100	-2.79268100	-1.92104800
H	7.02307600	-3.35405300	-2.02745600
H	5.27343700	-3.52029700	-1.75467600
H	5.88047100	-2.27328400	-2.87041700
C	6.47335200	-2.54271400	0.55911000
H	6.55244200	-1.84206200	1.40425500
H	5.67710100	-3.26496100	0.79025800
H	7.42073700	-3.09925600	0.48190100

C	-3.49653000	2.61923800	-0.85709100
C	-2.96130900	3.32243700	0.41179500
H	-1.92803600	3.02374700	0.62575900
H	-2.97556100	4.41453300	0.27166100
H	-3.58378300	3.08068200	1.28673400
C	-2.55667200	2.92101200	-2.04943600
H	-1.53839900	2.55544700	-1.86070800
H	-2.93192200	2.44417000	-2.96767300
H	-2.50597700	4.00765100	-2.22288500
C	-4.88440700	3.20378000	-1.17671700
H	-5.59620000	3.04059600	-0.35314400
H	-4.79236400	4.28947400	-1.32981800
H	-5.31084400	2.77351300	-2.09549600
C	-6.14694600	-1.76920500	-0.79641600
C	-6.03267800	-3.29182600	-0.60007000
H	-5.34635000	-3.74716100	-1.33050300
H	-5.68270400	-3.54766700	0.41180500
H	-7.02050400	-3.75658100	-0.73764500
C	-6.68372400	-1.50657200	-2.22319200
H	-7.65230700	-2.01147700	-2.36618400
H	-6.83220100	-0.43333300	-2.41064000
H	-5.98084900	-1.88876100	-2.97915500
C	-7.15808100	-1.22434100	0.23956500
H	-7.32470900	-0.14456900	0.11590200
H	-8.12974600	-1.73091100	0.12707600
H	-6.79557600	-1.39680500	1.26443700
C	0.24989700	0.07717200	2.12096600
H	1.33460400	0.16301500	2.27833600
C	-0.45231400	1.36221900	2.57983400
H	-1.54408700	1.26368700	2.48777900
H	-0.14196300	2.18216000	1.91231900
C	-0.11503400	1.72909800	3.95190400
Cl	-0.26944000	-1.34435500	3.11422100
N	0.16636200	2.01540300	5.04335700

Zero-point correction= 0.722761 (Hartree/Particle)
Thermal correction to Energy= 0.766286
Thermal correction to Enthalpy= 0.767230
Thermal correction to Gibbs Free Energy= 0.647285
Sum of electronic and zero-point Energies= -2402.224696
Sum of electronic and thermal Energies= -2402.181171
Sum of electronic and thermal Enthalpies= -2402.180227
Sum of electronic and thermal Free Energies= -2402.300172

Cl anion:

Cl	0.00000000	0.00000000	0.00000000

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.015023
Sum of electronic and zero-point Energies=	-460.409502
Sum of electronic and thermal Energies=	-460.408086
Sum of electronic and thermal Enthalpies=	-460.407142
Sum of electronic and thermal Free Energies=	-460.424525

Alternative path to form 4 by addition of HCl to alkene bond of 7: in gas phase

To compare the path discussed in main paper, an alternative path was DFT calculated in solvent ($CHCl_3$) phase using BP86-D3/def2-TZVP level of theory that show the formation of **4** from **7**, through the additionof HCl molecule across the C=C (alkene part of acrylonitrile group) double bond. The initial point for these caclulation could be undrestood as the formation of HCl addition product (**7-HCl**). The conversion of **7-HCl** to **4** was found exothermic (ΔH = -16.6 Kcal/mol) and exergonic (ΔG = -16.5 Kcal/mol) through a transition state (**TS''**) with very high energy barrier (ΔH = 46.2 Kcal/mol , ΔG = 46.8 Kcal/mol).

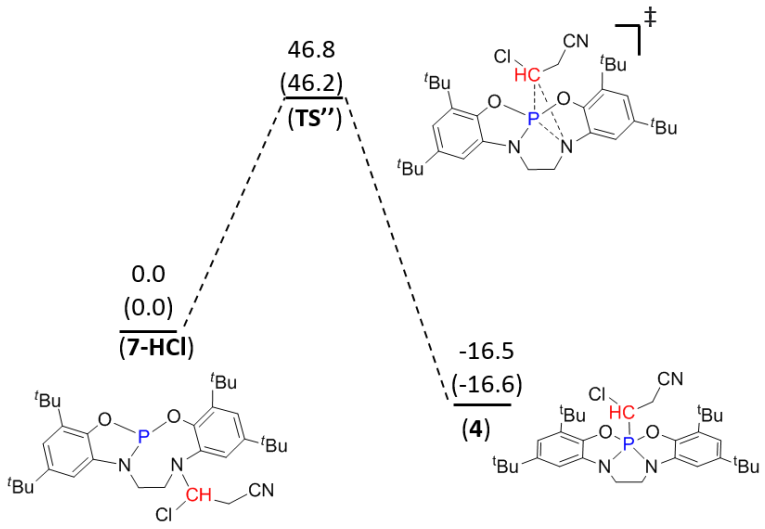
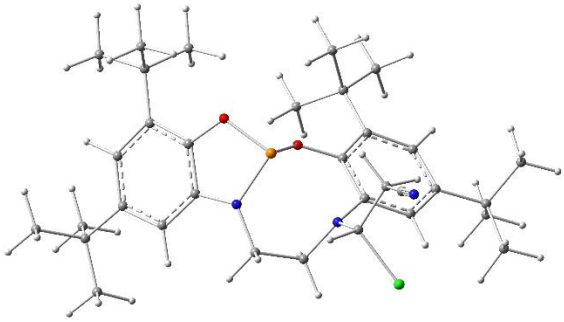


Fig 57: Alternative path to form **4** by addition of HCl to alkene bond of **7**. Gibbs free energies (enthalpies) in kcal·mol^{-1} are given relatively to **7-HCl**.

7-HCl



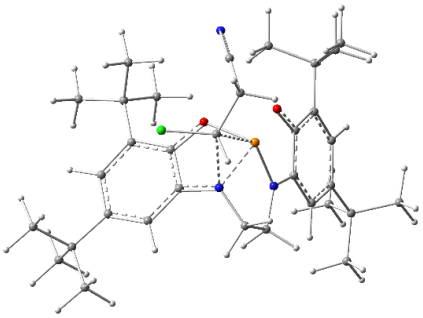
P	-0.30686500	0.34366000	-1.56658900
O	-1.72612300	-0.50459600	-1.77581800
O	0.27321200	-0.62796200	-0.28050800
N	-1.12841600	1.54992500	-0.63948300
N	1.92747300	1.64593400	0.11984300
N	4.66712900	5.38199100	-1.22473200
C	-3.91198600	-0.80595600	-0.64098800
C	-2.71197200	-0.12388700	-0.85917000
C	-2.36723700	1.05581600	-0.18513900
C	-3.23166000	1.59682000	0.77039300
H	-2.95778600	2.50814400	1.29875300
C	-4.44971900	0.94997000	1.03149400
C	-4.75846300	-0.22561200	0.32246700
H	-5.70503400	-0.71977600	0.53445400
C	-4.26256500	-2.09756400	-1.39317400
C	-5.63640700	-2.65281200	-0.97595000
H	-5.66826700	-2.90620000	0.09462200
H	-5.84066000	-3.57396400	-1.54210400
H	-6.44943500	-1.94243600	-1.19006000
C	-3.19521600	-3.17401000	-1.08645800
H	-2.19415800	-2.85186600	-1.39693700
H	-3.43719300	-4.10709400	-1.61938200
H	-3.16324500	-3.39251800	-0.00856700
C	-4.30000700	-1.81415900	-2.91385200
H	-5.05510700	-1.04751000	-3.14563400
H	-4.56589100	-2.73308100	-3.45957500
H	-3.32782100	-1.46466600	-3.28450200
C	-5.45283800	1.48859000	2.06724800
C	-5.68407500	0.42041500	3.16182600
H	-6.08657900	-0.51206400	2.74047400
H	-6.40230400	0.79111500	3.91011300
H	-4.74117200	0.18114100	3.67671400
C	-6.79550200	1.80050600	1.36506500
H	-6.65780200	2.56286800	0.58319000
H	-7.52730400	2.18153300	2.09480200
H	-7.22454700	0.90502600	0.89289600
C	-4.95799700	2.77699500	2.74943200

H	-4.01527600	2.61519600	3.29452500
H	-5.70816100	3.11886200	3.47821900
H	-4.80477800	3.59078800	2.02407500
C	1.59215400	-0.80678000	0.05294100
C	2.08727300	-2.12217000	0.23858600
C	3.42612300	-2.24931200	0.62442200
H	3.82879000	-3.25103700	0.76223800
C	4.28477700	-1.15874700	0.85091400
C	3.75337800	0.11946100	0.68837500
H	4.35774300	1.00197600	0.89687200
C	2.42333600	0.30915300	0.28151600
C	1.19699900	-3.36086700	0.01085000
C	-0.04050000	-3.31062800	0.94105700
H	0.27235900	-3.28627400	1.99628900
H	-0.65385100	-4.21159100	0.78632600
H	-0.66806800	-2.43513600	0.74151400
C	1.95046800	-4.67050700	0.31844700
H	2.82030600	-4.81273100	-0.34066200
H	1.27041500	-5.51959100	0.15560900
H	2.29220500	-4.71358400	1.36382600
C	0.74890800	-3.42508200	-1.46917100
H	0.13754200	-2.56133900	-1.75351400
H	0.14514000	-4.33101400	-1.63488900
H	1.62286900	-3.46835000	-2.13658100
C	5.73872100	-1.40822900	1.28172300
C	6.45499700	-2.23802000	0.19012900
H	5.96670300	-3.21035100	0.03221400
H	7.49917400	-2.42900200	0.48315700
H	6.45868700	-1.69905300	-0.76940500
C	5.75238600	-2.19284600	2.61441000
H	5.24972500	-1.62067800	3.40895700
H	6.78921000	-2.38574900	2.93117700
H	5.24345200	-3.16338100	2.52114400
C	6.52009500	-0.09766400	1.48232200
H	6.56474100	0.49776500	0.55740100
H	7.55401200	-0.32770400	1.77919900
H	6.07772700	0.52426700	2.27570600
C	-0.40675400	2.61457800	0.05588200
H	-1.10735600	3.14507800	0.71357500
H	-0.04955000	3.34648500	-0.68285200
C	0.76636800	2.10256900	0.91017700
H	1.08278000	2.90001400	1.60273200
H	0.43819800	1.25725300	1.52715400
C	3.85847100	4.74157300	-0.68882300
C	2.86865400	3.93789200	0.01839100
H	3.21121500	3.81140400	1.06036700

H	1.92061500	4.49397100	0.04487100
C	2.69190900	2.54662200	-0.60381600
H	3.64445700	2.10272800	-0.89630600
Cl	1.98903100	2.93212300	-2.44184300

Zero-point correction= 0.721979 (Hartree/Particle)
Thermal correction to Energy= 0.765775
Thermal correction to Enthalpy= 0.766719
Thermal correction to Gibbs Free Energy= 0.646639
Sum of electronic and zero-point Energies= -2402.198421
Sum of electronic and thermal Energies= -2402.154625
Sum of electronic and thermal Enthalpies= -2402.153681
Sum of electronic and thermal Free Energies= -2402.273761

TS''



P	0.07086000	-1.04379500	-1.35085000
C	-2.24890700	-2.21300500	-2.54295100
H	-2.39481300	-1.70387800	-3.49466800
O	1.52521500	-1.53491300	-0.34358000
O	-0.84012800	-1.14384200	0.15575000
N	0.93363700	0.48238400	-1.57351000
N	-1.42414000	0.02214000	-1.92096100
C	4.53313300	0.42112800	0.42099900
H	5.47703400	0.36945600	0.96214000
C	4.24503100	1.61119900	-0.28282100
C	3.68314300	-0.69570900	0.47397400
C	4.02225500	-1.96810500	1.26281700
C	2.47563100	-0.58437400	-0.24451800
C	2.16201000	0.59993300	-0.95634500
C	-1.81849500	-0.22407700	0.32125200
C	-2.43331200	0.05948300	1.55640900
C	-3.42991400	1.04326100	1.52037700
H	-3.95804800	1.26492100	2.44708400
C	3.03174900	1.69719500	-0.97807500
H	2.74971500	2.59376900	-1.52828800
C	5.26903300	2.75887700	-0.26745600
C	-3.80285500	1.76899800	0.36044800

N	-0.88539400	-4.60129700	-0.32173500
C	-2.02517800	-0.68840400	2.83193100
C	-3.14476900	1.49006700	-0.83626000
H	-3.39013700	2.01369300	-1.75900900
C	-4.91847900	2.82121800	0.46414300
C	5.53403000	3.20086500	1.19111800
H	4.60449500	3.54803300	1.66739000
H	6.26272200	4.02682100	1.21270900
H	5.93994600	2.37927200	1.79871700
C	4.10350600	-3.16821100	0.28878500
H	3.15186400	-3.31766200	-0.23731700
H	4.34132900	-4.08951400	0.84404100
H	4.89420900	-3.00537100	-0.46002500
C	-2.16057000	0.48532700	-0.85694700
C	0.32997000	1.53176000	-2.37860200
H	1.02130700	1.87504200	-3.16532600
H	0.05991700	2.39573300	-1.74491400
C	-0.96814300	0.91623000	-2.96595500
H	-1.69870900	1.69201500	-3.22984400
H	-0.73729800	0.32613800	-3.86702400
C	2.91976500	-2.22891800	2.31722200
H	2.84672800	-1.38277100	3.01761000
H	3.15973100	-3.13459100	2.89663900
H	1.93992600	-2.37038000	1.84411000
C	4.78186300	3.98694500	-1.05783800
H	4.60741900	3.74711400	-2.11797300
H	5.54551700	4.77827000	-1.01731100
H	3.85146200	4.39965500	-0.63815900
C	-2.27083200	-2.20493600	2.64042400
H	-3.33814600	-2.40096400	2.45444700
H	-1.97678500	-2.74785100	3.55240400
H	-1.69434700	-2.60856500	1.79852800
C	5.37004900	-1.85304600	1.99763100
H	6.20829500	-1.70156100	1.30017500
H	5.56165800	-2.78481000	2.55098500
H	5.36990400	-1.02656000	2.72498300
C	-4.51342800	3.89980800	1.49657500
H	-4.35216800	3.46942300	2.49548100
H	-5.30505200	4.66068600	1.58207000
H	-3.58341200	4.40194100	1.18942200
C	-0.52486300	-0.42825800	3.11462400
H	0.10890400	-0.77106300	2.28750900
H	-0.21773000	-0.96443700	4.02620400
H	-0.34284700	0.64609700	3.27178300
C	-5.18812700	3.51835900	-0.88104800
H	-4.29779000	4.05013900	-1.25039100

H	-5.99143000	4.25972900	-0.75712000
H	-5.51160300	2.80335600	-1.65294500
C	-6.22546900	2.13369700	0.92529900
H	-6.53241000	1.35937100	0.20588200
H	-7.03753900	2.87349500	1.00424500
H	-6.10820700	1.65584300	1.90857900
C	6.59275900	2.27096100	-0.90169100
H	7.01502800	1.41737600	-0.35164800
H	7.34023700	3.08030600	-0.89669700
H	6.43038800	1.95662300	-1.94393700
C	-1.17749300	-4.12905700	-1.34310500
C	-2.83290300	-0.22260100	4.05633800
H	-2.68772400	0.84924900	4.26141000
H	-2.49699300	-0.77999800	4.94337200
H	-3.91053600	-0.41161900	3.93315100
Cl	-3.63372000	-2.14543600	-1.52319500
C	-1.56373400	-3.55851700	-2.63089200
H	-0.66516800	-3.45831500	-3.25752100
H	-2.23667100	-4.28542100	-3.13298300

Zero-point correction= 0.717518 (Hartree/Particle)
Thermal correction to Energy= 0.761181
Thermal correction to Enthalpy= 0.762125
Thermal correction to Gibbs Free Energy= 0.643022
Sum of electronic and zero-point Energies= -2402.124628
Sum of electronic and thermal Energies= -2402.080965
Sum of electronic and thermal Enthalpies= -2402.080020
Sum of electronic and thermal Free Energies= -2402.199123

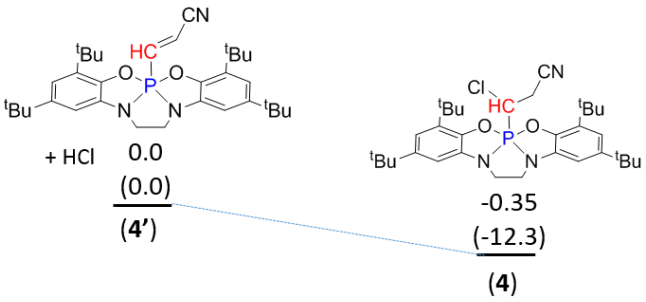
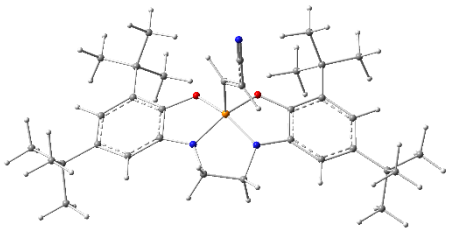


Fig S58: Comparision of energies for **4'** and **4**. Gibbs free energies (enthalpies) in kcal·mol^{-1} are given relatively to **4'** + HCl.

4':



P	-0.03866900	-0.25553000	0.51343600
O	1.12210700	0.96049600	0.21470100
O	-1.18531800	0.94563900	0.16652500
N	1.15022400	-1.45015100	0.11077400
N	-1.23343400	-1.44075900	0.11866100
C	4.69038300	0.54419900	-0.61196000
H	5.59903800	1.11642400	-0.77810500
C	4.74658400	-0.85191500	-0.74472000
C	3.51725200	1.25930700	-0.27820200
C	3.47355500	2.78920100	-0.15379300
C	2.38248500	0.47586800	-0.06326800
C	2.40902600	-0.92682800	-0.16255700
C	-2.45997500	0.46730300	-0.07554900
C	-3.58533400	1.25429100	-0.31165300
C	-4.78171800	0.53786200	-0.55479300
H	-5.68696900	1.11291400	-0.72868700
C	3.57376100	-1.59972400	-0.51551700
H	3.56668500	-2.68721200	-0.59975000
C	6.03997400	-1.58968400	-1.13243500
C	-4.86541900	-0.86235000	-0.57845400
N	0.61904900	-1.02110600	5.67461100
C	-3.51318000	2.78810200	-0.30212600
C	-3.69513100	-1.61471200	-0.34806300
H	-3.71019300	-2.70531400	-0.35067000
C	-6.18870900	-1.60356400	-0.83965900
C	7.23276900	-0.63371800	-1.31211700
H	7.05026300	0.10176400	-2.11026300
H	8.12745400	-1.21116200	-1.58922200
H	7.46201400	-0.08846600	-0.38385900
C	3.02440100	3.17133800	1.27711100
H	2.02603500	2.77456300	1.50290700
H	2.99206300	4.26730600	1.38196300
H	3.73148300	2.77606100	2.02238400
C	-2.50503200	-0.93889600	-0.10091200
C	0.69299300	-2.75139100	-0.35634400
H	1.25243200	-3.56336100	0.13068600
H	0.83969500	-2.83479900	-1.44726800
C	-0.80435700	-2.81895200	0.01921300
H	-1.38158300	-3.35195500	-0.74994800

H	-0.94512200	-3.34192700	0.98136200
C	2.47163600	3.36206900	-1.18535100
H	2.77722600	3.09705200	-2.20912200
H	2.44254600	4.46055600	-1.11022100
H	1.45658500	2.97981700	-1.01651900
C	5.81757300	-2.33867400	-2.46759500
H	5.00305500	-3.07360000	-2.39132200
H	6.73226800	-2.87799200	-2.76055500
H	5.56247800	-1.63114900	-3.27126700
C	-3.02251100	3.27266700	1.08328900
H	-3.71502400	2.94817800	1.87497600
H	-2.97281500	4.37281700	1.10047800
H	-2.02347000	2.88050600	1.31370000
C	4.84826600	3.43134000	-0.41425300
H	5.60653900	3.08553400	0.30476900
H	4.76235600	4.52330800	-0.30900800
H	5.21247400	3.22125500	-1.43141000
C	-7.36968300	-0.64297700	-1.06617700
H	-7.55105200	-0.00350000	-0.18891900
H	-8.28546200	-1.22533300	-1.24827100
H	-7.20723200	0.00503000	-1.94080900
C	-2.52673200	3.26101100	-1.39731500
H	-1.51578000	2.86911800	-1.22513100
H	-2.47266200	4.36117100	-1.40438100
H	-2.86416600	2.92815900	-2.39081000
C	-6.04058400	-2.48834500	-2.09992000
H	-5.79933300	-1.87295000	-2.98003000
H	-6.98085600	-3.02554200	-2.30185900
H	-5.24490500	-3.23829600	-1.98155100
C	-6.52353400	-2.49884700	0.37668100
H	-5.74074600	-3.24942900	0.55903700
H	-7.47041600	-3.03535200	0.20655400
H	-6.63026600	-1.89137800	1.28831200
C	6.40528400	-2.60979100	-0.02835400
H	6.56057200	-2.10085400	0.93517100
H	7.33377800	-3.14064700	-0.29168800
H	5.61676100	-3.36392500	0.11021900
C	0.62923800	-1.02759600	4.50682000
C	-4.88282400	3.43392000	-0.58008800
H	-5.27713000	3.14927400	-1.56746200
H	-4.77593700	4.52900700	-0.56629100
H	-5.62803400	3.16185200	0.18285100
C	-0.04353800	-0.19530200	2.32263200
H	-0.66817300	0.57467200	2.78310300
C	0.66377700	-1.05481700	3.08475800
H	1.30417700	-1.81659200	2.63028300

Zero-point correction= 0.707951 (Hartree/Particle)
Thermal correction to Energy= 0.750208
Thermal correction to Enthalpy= 0.751152
Thermal correction to Gibbs Free Energy= 0.633364
Sum of electronic and zero-point Energies= -1941.347498
Sum of electronic and thermal Energies= -1941.305241
Sum of electronic and thermal Enthalpies= -1941.304297
Sum of electronic and thermal Free Energies= -1941.422085

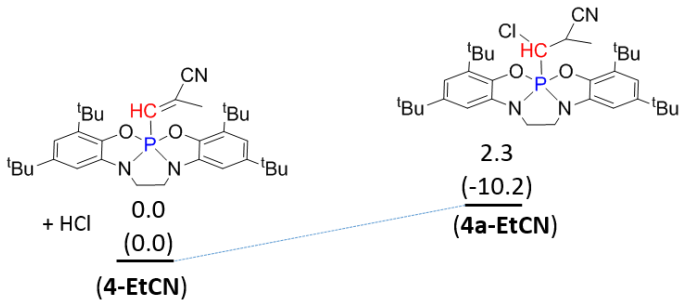
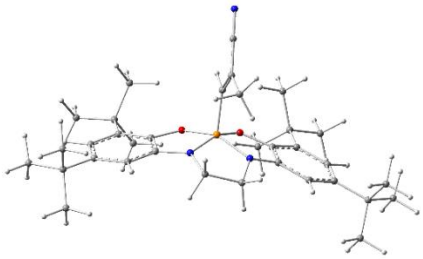


Fig S59: Comparision of energies for **4-EtCN** and **4a-EtCN**. Gibbs free energies (enthalpies) in kcal·mol^{-1} are given relatively to **4-EtCN** + HCl.

4'-EtCN:



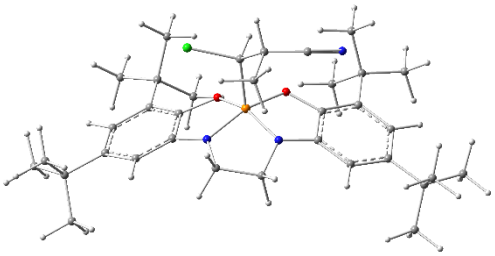
P	-0.00571500	-0.23985000	0.46572900
O	1.16915300	0.98292400	0.20160600
O	-1.13754500	0.98017900	0.09298900
N	1.18306400	-1.42466100	0.03470800
N	-1.20300500	-1.41801000	0.04333400
C	4.73221000	0.57341000	-0.63937700
H	5.64221000	1.14611900	-0.79705700
C	4.78555900	-0.82072800	-0.79344500
C	3.56103400	1.28621000	-0.29497000
C	3.51973100	2.81428100	-0.14915200
C	2.42383400	0.50256700	-0.09075400
C	2.44744700	-0.89715300	-0.21448100
C	-2.40860200	0.51221300	-0.16895300
C	-3.52640200	1.30828000	-0.41767800
C	-4.71956700	0.60209000	-0.69840400
H	-5.61774100	1.18416000	-0.88556600
C	3.61033800	-1.56830500	-0.57684300
H	3.60052300	-2.65433100	-0.67833800

C	6.07763900	-1.55586700	-1.19063500
C	-4.80867000	-0.79749100	-0.74922600
N	-0.12737900	-0.22012900	5.71181800
C	-3.44588700	2.84132200	-0.38778200
C	-3.64803900	-1.55806800	-0.50018700
H	-3.66685000	-2.64852100	-0.52090900
C	-6.12572100	-1.52706600	-1.06719900
C	7.27044200	-0.59883700	-1.36427500
H	7.08574700	0.14472400	-2.15441900
H	8.16408200	-1.17382900	-1.64974800
H	7.50278200	-0.06291300	-0.43137200
C	3.07655700	3.17711800	1.28863100
H	2.07888000	2.77765000	1.51278100
H	3.04506000	4.27153400	1.40905900
H	3.78636900	2.77112000	2.02548700
C	-2.46198600	-0.89231200	-0.20833900
C	0.74015400	-2.68986900	-0.53783100
H	1.25108200	-3.53829000	-0.05815500
H	0.98211800	-2.71353300	-1.61403600
C	-0.78672600	-2.76387700	-0.29872900
H	-1.30944600	-3.10079200	-1.20678900
H	-1.02779500	-3.47080400	0.51042700
C	2.51431200	3.40241800	-1.16866600
H	2.81587100	3.15170600	-2.19723900
H	2.48612600	4.49974900	-1.07803400
H	1.49966300	3.01833900	-1.00142000
C	5.85297300	-2.29331500	-2.53172700
H	5.03876000	-3.02905700	-2.46028700
H	6.76709800	-2.83012000	-2.83104400
H	5.59628500	-1.57905500	-3.32892100
C	-2.97925900	3.30498900	1.01291400
H	-3.69081400	2.97798500	1.78641400
H	-2.91926100	4.40431700	1.04419700
H	-1.98916200	2.89992300	1.25900400
C	4.89400500	3.45860000	-0.40612100
H	5.65447900	3.10298800	0.30578400
H	4.80941300	4.54921400	-0.28665700
H	5.25443300	3.26112000	-1.42716400
C	-7.30095700	-0.55712000	-1.28350600
H	-7.49949400	0.05037100	-0.38740000
H	-8.21330100	-1.13061700	-1.50615500
H	-7.11932400	0.12207100	-2.13022900
C	-2.43608400	3.32300500	-1.45767500
H	-1.43023300	2.92492200	-1.27034000
H	-2.37756600	4.42296800	-1.45038000
H	-2.75495500	3.00345800	-2.46166000

C	-5.94723000	-2.36181600	-2.35741500
H	-5.69048500	-1.71141200	-3.20747800
H	-6.88030800	-2.89465700	-2.60029300
H	-5.14986900	-3.11170300	-2.25074000
C	-6.49039000	-2.46922100	0.10443200
H	-5.71477000	-3.23002900	0.27489200
H	-7.43446400	-2.99511900	-0.10881900
H	-6.61647200	-1.89865100	1.03719100
C	6.44422500	-2.58561100	-0.09598900
H	6.60298300	-2.08468200	0.87115600
H	7.37099500	-3.11624300	-0.36592700
H	5.65417900	-3.33894000	0.03852500
C	-0.06687500	-0.54994500	4.59300800
C	-4.80638500	3.49847600	-0.68346800
H	-5.18214600	3.23090000	-1.68277800
H	-4.69435500	4.59266600	-0.65080400
H	-5.56808100	3.21883400	0.06022400
C	-0.04349800	-0.05088400	2.26367100
H	-0.12917000	0.99924200	2.55610200
C	0.00903900	-0.99368500	3.23334500
C	0.11585200	-2.48646000	3.03210900
H	-0.88465000	-2.92235400	2.88972000
H	0.72669600	-2.71185800	2.15006100
H	0.57055000	-2.97013400	3.90572800

Zero-point correction=	0.735408 (Hartree/Particle)
Thermal correction to Energy=	0.779140
Thermal correction to Enthalpy=	0.780084
Thermal correction to Gibbs Free Energy=	0.658875
Sum of electronic and zero-point Energies=	-1980.651271
Sum of electronic and thermal Energies=	-1980.607539
Sum of electronic and thermal Enthalpies=	-1980.606595
Sum of electronic and thermal Free Energies=	-1980.727804

4a-EtCN:



P	-0.06040600	-0.24203300	0.54452200
O	1.14262100	0.96740700	0.35583400
O	-1.16707100	0.97002400	0.12438400
N	1.13303500	-1.42068000	0.09957100

N	-1.26024100	-1.42018900	0.13221100
C	4.58475700	0.61063200	-0.90408800
H	5.47227400	1.19210400	-1.13910900
C	4.62538400	-0.77864700	-1.09664500
C	3.45485700	1.30686300	-0.41689600
C	3.42551700	2.82781200	-0.21202100
C	2.35203400	0.51047600	-0.11369200
C	2.36264000	-0.88160400	-0.27990000
C	-2.43134800	0.50837800	-0.19718000
C	-3.52179900	1.31312500	-0.51593500
C	-4.70821600	0.61627400	-0.84736200
H	-5.58720700	1.20576700	-1.09288100
C	3.48034300	-1.53821900	-0.77955500
H	3.46523500	-2.62158000	-0.90449100
C	5.87316700	-1.50007600	-1.63630000
C	-4.81094300	-0.78242800	-0.87321300
N	3.34404100	-0.23522300	2.86904900
C	-3.42559800	2.84509800	-0.49008400
C	-3.67668700	-1.55214300	-0.54019900
H	-3.71451300	-2.64214200	-0.53084200
C	-6.11747700	-1.50423200	-1.24735200
C	7.04808900	-0.53782300	-1.88595900
H	6.79764600	0.22607600	-2.63756900
H	7.91331500	-1.10425900	-2.26221000
H	7.35911800	-0.02693700	-0.96203400
C	3.16022900	3.13507500	1.28117400
H	2.19538700	2.72666300	1.60875000
H	3.14887100	4.22440800	1.44448000
H	3.94654000	2.69535900	1.91224900
C	-2.49762500	-0.89543900	-0.20511600
C	0.66574500	-2.70067700	-0.42202300
H	1.22939000	-3.53458300	0.02226600
H	0.81488400	-2.72999200	-1.51503100
C	-0.83218200	-2.78889300	-0.05682700
H	-1.40396600	-3.26385900	-0.86695400
H	-0.98473600	-3.38026100	0.86144300
C	2.30150500	3.44445200	-1.07933700
H	2.48005000	3.23986500	-2.14618000
H	2.27577900	4.53689300	-0.93990900
H	1.31701600	3.04045500	-0.80939700
C	5.52371500	-2.19196500	-2.97501700
H	4.71202600	-2.92453300	-2.85528500
H	6.40288800	-2.72408900	-3.37202800
H	5.20345100	-1.44999800	-3.72247300
C	-3.04047600	3.30798100	0.93552700
H	-3.80382900	2.99420800	1.66374900

H	-2.96593900	4.40643500	0.96691000
H	-2.07501500	2.88830300	1.24663100
C	4.75634500	3.49132900	-0.61000900
H	5.59728500	3.11943800	-0.00512700
H	4.68247700	4.57717300	-0.44702800
H	4.99374700	3.32864700	-1.67247000
C	-7.25350000	-0.52470600	-1.59442600
H	-7.50722500	0.12579700	-0.74355600
H	-8.15818500	-1.09161600	-1.86127600
H	-6.99413700	0.11361800	-2.45280700
C	-2.34965700	3.31398500	-1.49925300
H	-1.36023400	2.90635200	-1.25420600
H	-2.28024200	4.41333400	-1.49003400
H	-2.61241200	2.99587100	-2.51987700
C	-5.86886200	-2.40746500	-2.47830800
H	-5.52831500	-1.80938500	-3.33728500
H	-6.79737500	-2.92607700	-2.76516700
H	-5.10572500	-3.17300800	-2.27451100
C	-6.58167200	-2.37874600	-0.05863400
H	-5.83121600	-3.13856800	0.20370600
H	-7.51732100	-2.90235400	-0.31135100
H	-6.76279500	-1.75840400	0.83229300
C	6.33548200	-2.56591100	-0.61490600
H	6.58272900	-2.09814000	0.35016200
H	7.23242900	-3.08585800	-0.98701000
H	5.55910200	-3.32357500	-0.43446500
C	2.22694200	-0.51154100	3.03802000
C	-4.75954000	3.51464300	-0.86741700
H	-5.07994300	3.24580700	-1.88551100
H	-4.63867800	4.60789300	-0.83319100
H	-5.56525600	3.24606800	-0.16734300
C	0.65174100	-2.41232100	3.22840900
H	-0.40578600	-2.66065700	3.38456200
H	0.97898900	-2.80661800	2.26061300
H	1.24426400	-2.89427400	4.01629000
C	-0.13150600	-0.04927900	2.41352000
H	0.07617100	1.01745900	2.57031800
C	0.83302900	-0.88403900	3.29751700
H	0.62905600	-0.56026800	4.33351400
Cl	-1.82193200	-0.29053500	3.03683600

Zero-point correction= 0.749731 (Hartree/Particle)
Thermal correction to Energy= 0.794674
Thermal correction to Enthalpy= 0.795619
Thermal correction to Gibbs Free Energy= 0.673260
Sum of electronic and zero-point Energies= -2441.525076

Sum of electronic and thermal Energies= -2441.480133
Sum of electronic and thermal Enthalpies= -2441.479189
Sum of electronic and thermal Free Energies= -2441.601548

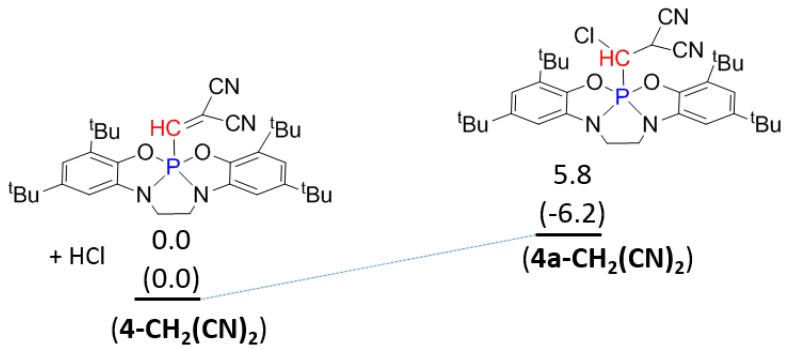
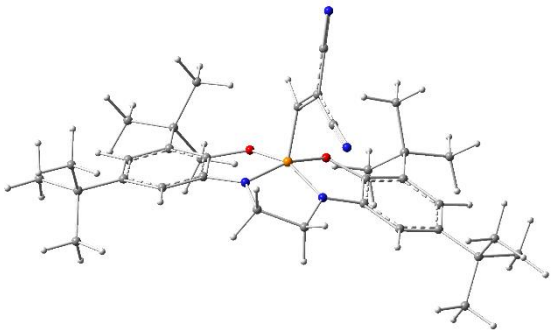


Fig S60: Comparision of energies for **4-CH$_2$(CN)$_2$** and **4a-CH$_2$(CN)$_2$**. Gibbs free energies (enthalpies) in kcal·mol^{-1} are given relatively to **4-CH$_2$(CN)$_2$** + HCl.

4-CH$_2$(CN)$_2$



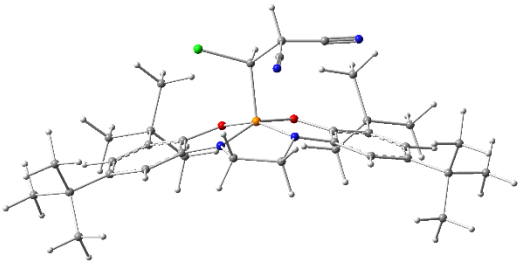
P	-0.08056300	-0.20277300	0.35194600
O	1.07296100	1.05519300	0.19751800
O	-1.23653100	1.00820600	0.13241500
N	1.09322500	-1.31062400	-0.23327500
N	-1.27969600	-1.37473900	-0.05982400
C	4.63594000	0.75115400	-0.68263800
H	5.54531000	1.33895800	-0.77404300
C	4.69356500	-0.61984700	-0.98275800
C	3.46409000	1.42060700	-0.26548500
C	3.41723200	2.92319200	0.04293000
C	2.32969800	0.61504200	-0.15192400
C	2.35561500	-0.76275700	-0.43169100
C	-2.51365800	0.54119300	-0.12568200
C	-3.64433700	1.33966200	-0.28512500
C	-4.83861400	0.63638200	-0.56636700
H	-5.74851300	1.21797300	-0.68657300
C	3.52047600	-1.39047100	-0.85666300
H	3.51447900	-2.45979900	-1.07012800
C	5.99487700	-1.30956300	-1.42806000
C	-4.91636800	-0.75978300	-0.69378400

N	0.48746200	-0.88478600	5.55016300
C	-3.57919300	2.86786200	-0.15198800
C	-3.74301300	-1.52211600	-0.52637900
H	-3.75404500	-2.60989700	-0.60419700
C	-6.23818200	-1.48332500	-1.00604700
C	7.17520900	-0.32786800	-1.53924000
H	6.97880300	0.46678500	-2.27513300
H	8.07360200	-0.87172800	-1.86745200
H	7.40722000	0.14402600	-0.57242100
C	2.96497200	3.13267100	1.50858500
H	1.96604600	2.71403200	1.68800800
H	2.93230700	4.20870600	1.74099500
H	3.67140400	2.65326900	2.20330800
C	-2.55310500	-0.85951900	-0.24234700
C	0.65079300	-2.58047700	-0.78958700
H	1.24010100	-3.40784300	-0.36910300
H	0.77891100	-2.57315800	-1.88456600
C	-0.83708800	-2.71745200	-0.38895000
H	-1.43434900	-3.12197700	-1.21868900
H	-0.95036600	-3.38713900	0.47791000
C	2.41683400	3.61329700	-0.91581400
H	2.73007100	3.48029400	-1.96261200
H	2.37911200	4.69337800	-0.70373800
H	1.40329100	3.20673600	-0.80330900
C	5.78138800	-1.96548200	-2.81224700
H	4.98065300	-2.71858100	-2.78658600
H	6.70438500	-2.46765800	-3.14221400
H	5.51282600	-1.20856000	-3.56488800
C	-3.06921500	3.23674800	1.26225100
H	-3.74559100	2.83780500	2.03354800
H	-3.02934500	4.33169400	1.37408800
H	-2.06273900	2.83782600	1.44421300
C	4.79163200	3.59298200	-0.13411300
H	5.54688800	3.16369600	0.54168400
H	4.70399200	4.66436400	0.09992600
H	5.15994800	3.50682700	-1.16770500
C	-7.42378100	-0.51192900	-1.14710100
H	-7.60473000	0.04967000	-0.21799300
H	-8.33760800	-1.08065100	-1.37540000
H	-7.26684300	0.20896400	-1.96383300
C	-2.61322200	3.43641700	-1.21928100
H	-1.59752100	3.03814800	-1.09782600
H	-2.56387800	4.53336800	-1.13441900
H	-2.96590900	3.18691500	-2.23163000
C	-6.09167100	-2.26068300	-2.33527900
H	-5.86423400	-1.57321300	-3.16422100

H	-7.02764800	-2.79033900	-2.57306100
H	-5.28658300	-3.00774900	-2.28296700
C	-6.56375100	-2.47598200	0.13477900
H	-5.77924000	-3.23793600	0.25149100
H	-7.51043800	-2.99866600	-0.07415900
H	-6.66691900	-1.94573000	1.09374800
C	6.37010600	-2.40018800	-0.39689900
H	6.52115400	-1.95687000	0.59908700
H	7.30319400	-2.90311800	-0.69616500
H	5.58614500	-3.16669500	-0.31170500
C	0.49435700	-1.02744800	4.39256600
C	-4.95642000	3.52518500	-0.35231000
H	-5.36478100	3.32283700	-1.35405800
H	-4.85437100	4.61557100	-0.24689800
H	-5.68718900	3.18446200	0.39686000
C	-0.01171900	-0.22813700	2.15819600
H	-0.40533900	0.67171500	2.63793600
C	0.50572400	-1.19521800	2.96990100
C	1.08402900	-2.42475100	2.51389900
N	1.56560100	-3.44595100	2.22067600

Zero-point correction= 0.707233 (Hartree/Particle)
Thermal correction to Energy= 0.750876
Thermal correction to Enthalpy= 0.751820
Thermal correction to Gibbs Free Energy= 0.631865
Sum of electronic and zero-point Energies= -2033.623279
Sum of electronic and thermal Energies= -2033.579637
Sum of electronic and thermal Enthalpies= -2033.578693
Sum of electronic and thermal Free Energies= -2033.698648

4a-$CH_2(CN)_2$



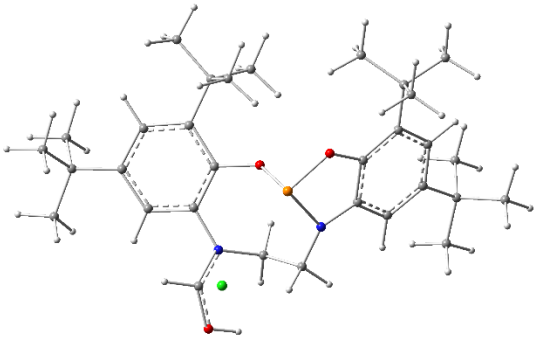
P	-0.07612200	-0.20380100	0.38071600
O	1.08369500	1.02895300	0.22031400
O	-1.22757300	1.02509000	0.15756500
N	1.15099700	-1.36593200	-0.04162400
N	-1.23698800	-1.33631000	-0.17640700
C	4.59223400	0.76056300	-0.87616600

H	5.47527300	1.36468900	-1.06609900
C	4.67754000	-0.62687200	-1.06939400
C	3.42334100	1.42689600	-0.44258400
C	3.34608300	2.94604200	-0.23626200
C	2.32957400	0.59987200	-0.19724400
C	2.38073000	-0.79032300	-0.36712800
C	-2.48761200	0.56849500	-0.18151000
C	-3.61971600	1.36465700	-0.33590400
C	-4.79521300	0.67159300	-0.70985000
H	-5.70539100	1.25293800	-0.83062900
C	3.53812800	-1.41638100	-0.81274800
H	3.55481800	-2.49961900	-0.93815500
C	5.97116800	-1.31468900	-1.53992100
C	-4.85217400	-0.71387000	-0.92466700
N	3.36696500	-0.06550300	2.78706800
C	-3.57602800	2.87939400	-0.09159200
C	-3.67693300	-1.47556400	-0.75558100
H	-3.67488000	-2.55724400	-0.89515600
C	-6.15238000	-1.42986300	-1.33075700
C	7.12792300	-0.31990400	-1.74102300
H	6.88952700	0.43318200	-2.50737400
H	8.02495100	-0.86277100	-2.07474900
H	7.38282400	0.20334100	-0.80689600
C	2.98989000	3.24372600	1.23993800
H	2.01893600	2.81041100	1.51269900
H	2.94067400	4.33205600	1.40251200
H	3.75181600	2.82475200	1.91354300
C	-2.50823800	-0.82111200	-0.38527600
C	0.71368300	-2.62050600	-0.64788200
H	1.21713100	-3.47645400	-0.17686600
H	0.96096200	-2.61187600	-1.72274400
C	-0.81177100	-2.69910900	-0.42141300
H	-1.31948100	-3.10571800	-1.30789900
H	-1.05035500	-3.33965400	0.44305700
C	2.25846700	3.53668200	-1.16593200
H	2.50175300	3.33721500	-2.22083300
H	2.19935100	4.62796500	-1.02877100
H	1.26954300	3.11040200	-0.95214000
C	5.70983700	-2.02904900	-2.88662000
H	4.91675300	-2.78578100	-2.79900100
H	6.62369700	-2.53677900	-3.23368900
H	5.40480100	-1.30452200	-3.65715600
C	-3.14018400	3.14498000	1.36997400
H	-3.85650000	2.69436600	2.07371900
H	-3.10441400	4.22897400	1.56221400
H	-2.14611600	2.72675000	1.57533400

C	4.68095300	3.64228300	-0.55746500
H	5.49489600	3.28872000	0.09355800
H	4.57125600	4.72523900	-0.39605200
H	4.98141500	3.48939600	-1.60518200
C	-7.33977300	-0.46086800	-1.47219000
H	-7.56595000	0.04929200	-0.52350900
H	-8.23784500	-1.02216400	-1.77075400
H	-7.15322300	0.30405300	-2.24130000
C	-2.56452900	3.53105700	-1.06489600
H	-1.55220000	3.13115300	-0.92249600
H	-2.53041900	4.61923500	-0.89821800
H	-2.86393900	3.35388200	-2.10921000
C	-5.94398700	-2.13719700	-2.69039900
H	-5.68749600	-1.40700500	-3.47310200
H	-6.86458100	-2.65982800	-2.99478700
H	-5.13543500	-2.88083400	-2.64197600
C	-6.51634200	-2.48246900	-0.25713500
H	-5.72927200	-3.24280500	-0.14719300
H	-7.44869400	-3.00109400	-0.53120000
H	-6.66356500	-2.00267300	0.72247100
C	6.41137500	-2.35624600	-0.48401600
H	6.59432200	-1.87133200	0.48689900
H	7.34149000	-2.85254200	-0.80312700
H	5.64955100	-3.13520200	-0.33493100
C	2.29479300	-0.50438600	2.86469200
C	-4.94777500	3.54198600	-0.31105200
H	-5.30600000	3.40905200	-1.34322500
H	-4.86076300	4.62278500	-0.12402500
H	-5.71037600	3.14441500	0.37583300
C	-0.13290700	-0.18722700	2.26663200
H	0.00613800	0.86309300	2.55473500
C	0.93317900	-1.03337100	3.02639200
H	0.69463100	-0.95173200	4.10342800
Cl	-1.75845200	-0.67331600	2.89107300
C	0.88420400	-2.46478900	2.69102400
N	0.81926600	-3.60586500	2.48298400

Zero-point correction= 0.721026 (Hartree/Particle)
Thermal correction to Energy= 0.766097
Thermal correction to Enthalpy= 0.767041
Thermal correction to Gibbs Free Energy= 0.645110
Sum of electronic and zero-point Energies= -2494.490957
Sum of electronic and thermal Energies= -2494.445885
Sum of electronic and thermal Enthalpies= -2494.444941
Sum of electronic and thermal Free Energies= -2494.566873

9a



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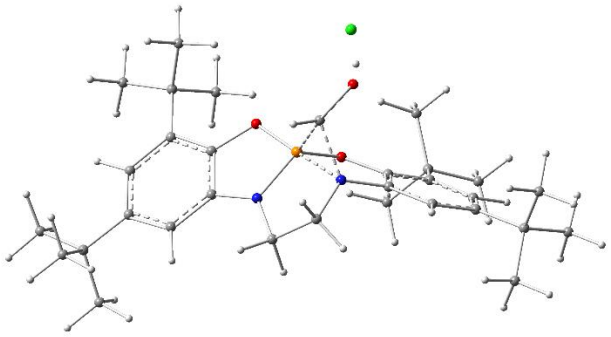
O	1.56562400	0.76688100	1.72776200
C	2.54593800	0.33036900	0.83106700
C	3.65545600	1.07727600	0.42662100
C	3.91421400	2.49694000	0.95092900
C	2.72983900	3.41440500	0.56781000
H	1.78599200	3.06153400	1.00086500
H	2.60909200	3.45579400	-0.52495000
H	2.91421100	4.43728000	0.93194000
C	5.20081700	3.10285500	0.36203700
H	5.34412400	4.11386400	0.77169500
H	5.14885500	3.19109900	-0.73391700
H	6.09006100	2.50843300	0.62165800
C	4.06483100	2.45164800	2.49037200
H	3.15662000	2.06995700	2.97436200
H	4.26091600	3.46373500	2.87787900
H	4.90861100	1.80557500	2.77696200
C	4.50696100	0.42568300	-0.48568700
H	5.38314400	0.96516900	-0.84127600
C	4.28760200	-0.87705900	-0.97115000
C	5.28241400	-1.48174800	-1.97851900
C	4.88552700	-2.90324500	-2.41698700
H	4.85488500	-3.60049100	-1.56561900
H	5.62730600	-3.28681700	-3.13331300
H	3.90371800	-2.91917900	-2.91493500
C	6.68589100	-1.55213400	-1.33155000
H	6.66777300	-2.18135200	-0.42870100
H	7.04982600	-0.55560600	-1.04306700
H	7.41023600	-1.98453800	-2.03986100
C	5.34563900	-0.58913600	-3.24032400
H	4.35688900	-0.52173500	-3.71921600
H	6.05448400	-1.01130300	-3.97008800
H	5.67670500	0.43156800	-3.00108600
C	3.16549000	-1.58875300	-0.51835900
H	2.96245500	-2.59814000	-0.87045700
C	2.30449400	-0.97991100	0.39844400
N	1.16504100	-1.51647900	1.03245300
C	0.52386100	-2.73347500	0.55015900
H	0.07686800	-3.24594000	1.41634500
H	1.29452200	-3.39839000	0.13789600
C	-0.55455400	-2.49007900	-0.53361700

H	-0.25118000	-1.68431000	-1.21069500
H	-0.67878600	-3.39314700	-1.15594600
N	-1.87951200	-2.13226300	0.02484700
C	-2.50194600	-0.85698900	-0.20881900
C	-3.83355200	-0.85267800	-0.65161900
H	-4.31493100	-1.81106100	-0.84230900
C	-4.51081900	0.34264800	-0.87978700
C	-5.97227800	0.39489400	-1.35052300
C	-6.59384000	-1.00702500	-1.47719300
H	-6.58672100	-1.54341600	-0.51599300
H	-6.06889700	-1.62240300	-2.22400000
H	-7.64111000	-0.91599700	-1.80149900
C	-6.80464800	1.20540400	-0.32907700
H	-6.76445100	0.73801100	0.66635800
H	-7.85745900	1.24782000	-0.64868300
H	-6.44070300	2.23878500	-0.23476600
C	-6.03882100	1.08696800	-2.73221000
H	-7.08142500	1.13331200	-3.08379700
H	-5.44812300	0.53016600	-3.47541600
H	-5.65106000	2.11500200	-2.69031300
C	-3.79204700	1.53617000	-0.68964000
H	-4.30527700	2.47546400	-0.88592900
C	-2.45551800	1.58953400	-0.28087600
C	-1.71638500	2.93656400	-0.14393600
C	-2.62504200	4.12659300	-0.51567000
H	-3.49933100	4.20345100	0.14857300
H	-2.97871100	4.06862600	-1.55630400
H	-2.04934400	5.05826300	-0.41283300
C	-1.25497200	3.15775000	1.31596000
H	-2.11317000	3.12504000	2.00378300
H	-0.77906600	4.14653700	1.40645800
H	-0.52272800	2.41034000	1.64000700
C	-0.50136400	2.96673200	-1.10293600
H	0.22827600	2.18388500	-0.86715100
H	0.00686900	3.93975600	-1.02317900
H	-0.83241700	2.83694700	-2.14478300
C	-1.80788500	0.35538900	-0.01477700
O	-0.48329000	0.34438200	0.32685900
O	-2.36141400	-4.34629200	0.64456700
H	-1.48083200	-4.56659100	0.28199500
C	-2.56032400	-3.03442000	0.75006400
H	-3.55547200	-2.76761600	1.08859900
Cl	-1.92649800	-2.67579700	3.08948500

Zero-point correction= 0.700342 (Hartree/Particle)
Thermal correction to Energy= 0.742290
Thermal correction to Enthalpy= 0.743234
Thermal correction to Gibbs Free Energy= 0.627835
Sum of electronic and zero-point Energies= -2345.874640
Sum of electronic and thermal Energies= -2345.832693
Sum of electronic and thermal Enthalpies= -2345.831749
Sum of electronic and thermal Free Energies= -2345.947147

TS1'

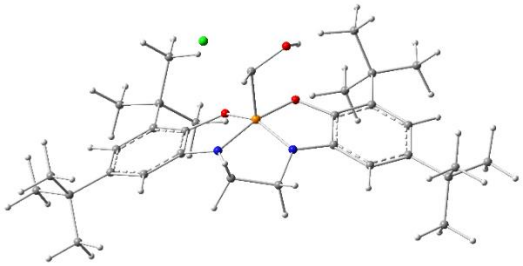


P	0.11740500	-0.05064600	-0.87595000
O	-0.86089400	0.66578600	0.21535200
O	1.38181200	0.98318900	-0.71009600
N	-1.30025800	-1.28046500	-1.30853500
N	1.05422300	-1.40143200	-0.55046600
C	-4.40371500	0.09817300	1.07156800
H	-5.18369800	0.47596500	1.72703700
C	-4.72226700	-0.96126700	0.20625100
C	-3.13590600	0.71063200	1.15590500
C	-2.82017300	1.83608600	2.15233900
C	-2.17718200	0.19041900	0.28178200
C	-2.45002200	-0.88275400	-0.57529500
C	2.55220300	0.32739000	-0.31258000
C	3.76243600	0.95629400	-0.03978200
C	4.80765100	0.08472300	0.34501100
H	5.77522600	0.52869600	0.56227000
C	-3.71107200	-1.45919900	-0.63319700
H	-3.89279400	-2.28452200	-1.32274400
C	-6.12607500	-1.58561000	0.14545300
C	4.66944800	-1.30625500	0.46267800
C	3.92937400	2.47739400	-0.15737600
C	3.41669400	-1.89026600	0.18094000
H	3.25738400	-2.96517900	0.26810000
C	5.83398300	-2.21745600	0.88897900
C	-7.11157900	-0.91489700	1.11888100
H	-6.78816600	-1.01819400	2.16587500
H	-8.09750200	-1.39415700	1.02695500
H	-7.24002000	0.15541700	0.89744900
C	-2.42385700	3.11480300	1.38112100
H	-1.57446700	2.95064000	0.70660100
H	-2.15939100	3.91019200	2.09555800
H	-3.26495900	3.47073300	0.76753000
C	2.37542700	-1.06125300	-0.21064000
C	-0.82376500	-2.66868300	-1.37396000
H	-0.61130900	-2.92978000	-2.42041100
H	-1.59514400	-3.35042700	-0.99549900
C	0.46694300	-2.74019200	-0.51864600
H	0.24994700	-3.03779900	0.51954500
H	1.17440800	-3.46222400	-0.94947500
C	-1.65801200	1.39111700	3.07428700
H	-1.92140900	0.46922200	3.61528000

H	-1.45511400	2.17788600	3.81710800
H	-0.73362200	1.21224500	2.51109000
C	-6.03012200	-3.08607200	0.50864200
H	-5.38171200	-3.63470700	-0.19006300
H	-7.02842600	-3.54964000	0.47406800
H	-5.62464200	-3.21583100	1.52357800
C	3.63115200	2.91659000	-1.61157400
H	4.31275100	2.41402000	-2.31485300
H	3.77843500	4.00328300	-1.70945100
H	2.59787700	2.68912300	-1.90423300
C	-4.03070500	2.16723900	3.04481400
H	-4.88975200	2.52362200	2.45646800
H	-3.75013000	2.97195400	3.74008600
H	-4.35135700	1.30260500	3.64605800
C	7.13269400	-1.43252600	1.14883500
H	7.47480800	-0.89922500	0.24896800
H	7.92853500	-2.13276000	1.44382800
H	7.01463100	-0.70124100	1.96281300
C	2.94738600	3.17922500	0.81200300
H	1.90225900	2.94037400	0.57649300
H	3.07080100	4.27091400	0.74000900
H	3.14888400	2.87949100	1.85182800
C	5.45031900	-2.96053700	2.19019800
H	5.24794700	-2.24455700	3.00121400
H	6.27306800	-3.61957900	2.50868500
H	4.55372600	-3.58302600	2.05551200
C	6.11075400	-3.24921500	-0.22953500
H	5.23341700	-3.88207600	-0.42769300
H	6.94295200	-3.90976000	0.05995600
H	6.38286500	-2.74216700	-1.16763700
C	-6.68543900	-1.43731500	-1.28906600
H	-6.75978400	-0.37606500	-1.57030700
H	-7.69046800	-1.88252400	-1.35166700
H	-6.04787700	-1.94114500	-2.02996700
C	5.35871500	2.92529400	0.19608400
H	5.62729700	2.66472300	1.23128200
H	5.42752200	4.01875600	0.09930200
H	6.10589500	2.48291500	-0.48034100
O	-1.57590100	0.63157400	-3.03216400
H	-1.46821000	1.63261300	-2.62278400
C	-0.71172000	-0.19062300	-2.48248800
H	-0.17650000	-0.87415700	-3.16132500
Cl	-1.05497400	3.22272800	-2.05319700

Zero-point correction= 0.697532 (Hartree/Particle)
Thermal correction to Energy= 0.738283
Thermal correction to Enthalpy= 0.739227
Thermal correction to Gibbs Free Energy= 0.626046
Sum of electronic and zero-point Energies= -2345.871917
Sum of electronic and thermal Energies= -2345.831166
Sum of electronic and thermal Enthalpies= -2345.830222
Sum of electronic and thermal Free Energies= -2345.943403

9b

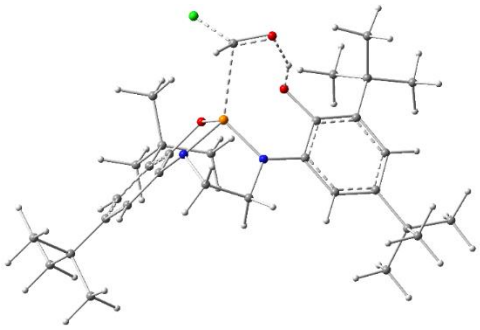


P	0.01519200	-0.25983500	0.69043700
O	1.22906200	0.91603700	0.32618600
O	-1.05817400	0.83135200	0.00800700
N	1.18379700	-1.48990700	0.42074400
N	-1.20514600	-1.48922500	0.58473100
C	4.76385000	0.32284100	-0.54536100
H	5.68294900	0.85174300	-0.78206600
C	4.78494700	-1.07923300	-0.52586400
C	3.61182300	1.09880400	-0.27559000
C	3.59853500	2.63265900	-0.34216300
C	2.46702800	0.37266900	0.04837300
C	2.45488000	-1.03214400	0.08601400
C	-2.34253000	0.33680400	-0.17380200
C	-3.42094500	1.07424900	-0.65316600
C	-4.62912800	0.35047500	-0.79405600
H	-5.50077900	0.89128600	-1.15270200
C	3.59533400	-1.76872800	-0.21123500
H	3.56129600	-2.85847200	-0.18650500
C	6.05734800	-1.89000200	-0.82919500
C	-4.76119400	-1.01325000	-0.49292000
C	-3.29131800	2.56593300	-0.99396700
C	-3.63603700	-1.71482300	-0.01177300
H	-3.69528800	-2.77224200	0.24954200
C	-6.09418400	-1.76552200	-0.65548600
C	7.27018600	-0.99320800	-1.13700600
H	7.09964800	-0.36350800	-2.02346000
H	8.14892300	-1.62362900	-1.34071600
H	7.51970700	-0.33807500	-0.28853300
C	3.15505600	3.21425400	1.02148800
H	2.11062600	2.95649700	1.24550600
H	3.22376600	4.31299200	1.00475600
H	3.79744800	2.84270600	1.83417500
C	-2.43616400	-1.02914800	0.14581900
C	0.71849500	-2.85254500	0.19823400
H	1.31298100	-3.56391200	0.78933800
H	0.82217100	-3.11617300	-0.86833000
C	-0.76273400	-2.86840700	0.64752900
H	-1.36832300	-3.49872500	-0.01942200
H	-0.85445800	-3.26677400	1.67186500
C	2.60907400	3.08434100	-1.44348500
H	2.92283800	2.69918500	-2.42557800
H	2.58271500	4.18414400	-1.49829200
H	1.59121800	2.72565800	-1.23963600
C	5.80547300	-2.79895400	-2.05517300

H	4.97915400	-3.50275800	-1.87716900
H	6.70687600	-3.38901900	-2.28459100
H	5.55306100	-2.19610600	-2.94077700
C	-2.85736100	3.34497600	0.27078100
H	-3.60772600	3.23498700	1.06849600
H	-2.75966600	4.41680800	0.03592500
H	-1.89562500	2.98555400	0.65837400
C	4.98741300	3.20811300	-0.67434900
H	5.73329600	2.94628000	0.09162500
H	4.92350400	4.30559600	-0.71853400
H	5.35470600	2.85750300	-1.65072400
C	-7.21376300	-0.86965000	-1.21451700
H	-7.43120900	-0.02255500	-0.54648000
H	-8.13742400	-1.45882200	-1.31761700
H	-6.95864900	-0.47115400	-2.20826100
C	-2.23209100	2.75034800	-2.10747800
H	-1.24668100	2.38432800	-1.79125100
H	-2.13621800	3.81803700	-2.36044800
H	-2.52920500	2.20769300	-3.01802000
C	-5.89966600	-2.95273400	-1.62811000
H	-5.57468400	-2.59577000	-2.61731600
H	-6.84604100	-3.50239100	-1.75355300
H	-5.14582100	-3.66319400	-1.25947800
C	-6.54924200	-2.30349300	0.72179300
H	-5.80722600	-2.98967800	1.15527700
H	-7.49926600	-2.85228600	0.62281600
H	-6.70043800	-1.47529700	1.43075200
C	6.40851400	-2.76876400	0.39478000
H	6.58602800	-2.14387300	1.28332100
H	7.32051300	-3.35358600	0.19595100
H	5.60141800	-3.47647700	0.63330100
C	-4.61953500	3.16274100	-1.49271000
H	-4.97072800	2.67016300	-2.41218500
H	-4.47427900	4.22962400	-1.71948200
H	-5.41257200	3.08779700	-0.73317800
O	1.21603700	0.53220400	3.05260200
H	1.51372500	1.24713000	2.45051000
C	0.04618400	0.00688300	2.55185800
H	-0.12708500	-0.96631500	3.02880500
Cl	-1.45132400	1.00981500	3.06583200

Zero-point correction= 0.700379 (Hartree/Particle)
Thermal correction to Energy= 0.741911
Thermal correction to Enthalpy= 0.742855
Thermal correction to Gibbs Free Energy= 0.628207
Sum of electronic and zero-point Energies= -2345.896365
Sum of electronic and thermal Energies= -2345.854833
Sum of electronic and thermal Enthalpies= -2345.853889
Sum of electronic and thermal Free Energies= -2345.968537

TS2'

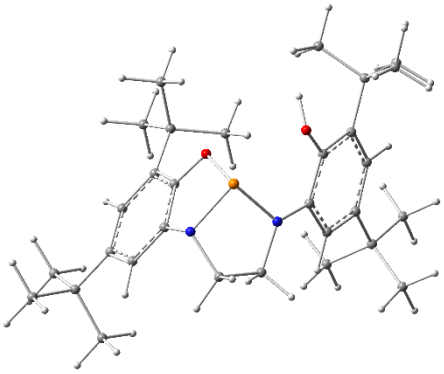


P	-0.28195600	-0.90728900	-1.48480600
O	-1.01738300	-1.22662900	-0.01852100
N	0.65534400	0.54912100	-1.43456600
N	-1.68310300	-0.04476400	-2.10273900
C	4.25803100	0.88097200	0.66933300
H	5.18432900	0.95855900	1.23090300
C	3.74637100	2.02874700	0.05132500
C	3.62235700	-0.37515800	0.60239900
C	4.18715300	-1.60844200	1.33255300
C	2.44093800	-0.44255800	-0.14723600
C	1.88005400	0.69435600	-0.76871500
C	-2.20115800	-0.50431100	0.13961900
C	-2.93409600	-0.45409600	1.32568000
C	-4.11220200	0.32232000	1.26878900
H	-4.72103800	0.38354600	2.16711600
C	2.54417500	1.92344500	-0.66413800
H	2.11489400	2.80646300	-1.13547500
C	4.44274200	3.39793800	0.14416300
C	-4.53506300	1.01544300	0.12372600
C	-2.46709200	-1.18504300	2.59297600
C	-3.74916900	0.93532700	-1.04231500
H	-4.04291600	1.45248500	-1.95696900
C	-5.82964400	1.84731500	0.09670900
C	5.76294100	3.33528800	0.93314500
H	5.60367300	3.01534100	1.97410900
H	6.22103400	4.33531700	0.95948400
H	6.48520000	2.64889700	0.46567600
C	4.51637600	-2.73262700	0.32101800
H	3.62028500	-3.13462900	-0.16839800
H	5.00516900	-3.57090400	0.84179500
H	5.20262700	-2.36730500	-0.45765600
C	-2.58502700	0.17372700	-1.02629400
C	-0.02082000	1.71036600	-2.03573700
H	0.67082300	2.25911100	-2.69198700
H	-0.38023300	2.39597200	-1.24827000
C	-1.18962300	1.12608100	-2.84957200
H	-1.99181800	1.85917800	-2.99740600
H	-0.84161900	0.79589200	-3.83952200
C	3.15194000	-2.11155200	2.36821900
H	2.93988000	-1.32741200	3.11099000
H	3.55239700	-2.98846100	2.90088100
H	2.20745400	-2.39875100	1.89010700

C	3.50134100	4.39953800	0.85401300
H	2.55563300	4.52648500	0.30714300
H	3.98295700	5.38714400	0.92974900
H	3.26148500	4.05320100	1.87083700
C	-2.40148100	-2.70626500	2.31590700
H	-3.39537300	-3.09202400	2.04188200
H	-2.06523100	-3.23712300	3.22051100
H	-1.70258100	-2.93950700	1.50224200
C	5.48727800	-1.27967900	2.09214700
H	6.28913100	-0.95044700	1.41385000
H	5.83880200	-2.18511500	2.60851000
H	5.33256100	-0.50131800	2.85433300
C	-6.56903100	1.83031700	1.44687700
H	-6.86677300	0.81075600	1.73541400
H	-7.48480200	2.43570500	1.37109900
H	-5.95465600	2.25477300	2.25539000
C	-1.06514600	-0.66744300	3.00002500
H	-0.32020500	-0.85144700	2.21520000
H	-0.73036000	-1.17885400	3.91606200
H	-1.09633200	0.41396600	3.20337400
C	-5.48963100	3.31617300	-0.24913700
H	-4.81669600	3.74790800	0.50739900
H	-6.40786800	3.92352300	-0.28129400
H	-4.99723200	3.40041200	-1.22881800
C	-6.78173200	1.27473300	-0.97966400
H	-6.33057500	1.30736800	-1.98193400
H	-7.71599100	1.85727800	-1.01175600
H	-7.03538200	0.22741700	-0.75562700
C	4.75780600	3.91151900	-1.28036900
H	5.42778400	3.21399100	-1.80583600
H	5.25323700	4.89382100	-1.23026000
H	3.84648700	4.02657400	-1.88513900
C	-3.42512700	-0.95359200	3.77558200
H	-3.50015500	0.11213100	4.04029300
H	-3.04713700	-1.49126200	4.65789800
H	-4.43689100	-1.33113700	3.56277600
O	1.78144400	-2.94970700	-2.54310700
O	1.68806700	-1.61112200	-0.26264200
H	2.01421300	-2.18009100	-1.01403700
C	0.57475600	-2.96852800	-2.71618300
H	0.03953100	-2.66605600	-3.62699700
Cl	-0.47473000	-4.20816100	-1.82231300

Zero-point correction= 0.696111 (Hartree/Particle)
Thermal correction to Energy= 0.738069
Thermal correction to Enthalpy= 0.739014
Thermal correction to Gibbs Free Energy= 0.620183
Sum of electronic and zero-point Energies= -2345.854048
Sum of electronic and thermal Energies= -2345.812089
Sum of electronic and thermal Enthalpies= -2345.811145
Sum of electronic and thermal Free Energies= -2345.929975

9c



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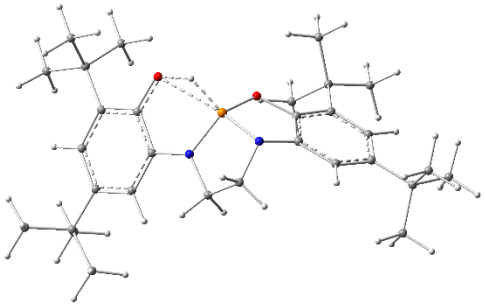
N	-0.47100200	-0.05044200	2.30647100
N	1.84840000	-1.01778900	2.56622400
C	-3.45882000	0.93437400	-0.47102100
H	-4.20620500	1.16987400	-1.22252100
C	-2.62645500	1.95572100	-0.00149000
C	-3.37961800	-0.39193300	-0.00133800
C	-4.32667000	-1.48963600	-0.52918500
C	-2.39938100	-0.66451800	0.96340000
C	-1.50346900	0.32522500	1.43414600
C	1.66888800	-1.29376400	0.22871800
C	2.00868600	-1.09398300	-1.11222300
C	3.20352700	-0.37493700	-1.33395800
H	3.50977000	-0.20852500	-2.36326000
C	-1.65760600	1.63652800	0.96209600
H	-0.98872900	2.41359500	1.32871100
C	-2.71162100	3.39987300	-0.52623500
C	4.00131700	0.14592500	-0.30371600
C	1.08690500	-1.54675000	-2.25420200
C	3.58816700	-0.04751000	1.02775000
H	4.16569300	0.36023800	1.85900800
C	5.29446200	0.93426900	-0.57811000
C	-3.83133800	3.58319400	-1.56623300
H	-3.67125400	2.95316900	-2.45444700
H	-3.85293700	4.63118600	-1.90110200
H	-4.82070800	3.34580300	-1.14628300
C	-5.16728700	-2.07256300	0.63376700
H	-4.55162800	-2.50205000	1.43467100
H	-5.83423400	-2.86351900	0.25698300
H	-5.79026500	-1.28342800	1.08092700
C	2.42135800	-0.76110700	1.28723100
C	0.49714500	0.96309000	2.75124800
H	0.02532200	1.66972900	3.45159100
H	0.89892900	1.53344300	1.89296300
C	1.63974900	0.17470000	3.41366900
H	2.55729700	0.77098900	3.49011500
H	1.36168800	-0.15503100	4.42636000
C	-3.52092400	-2.60826100	-1.23811100
H	-2.93174300	-2.19199700	-2.06676200
H	-4.20689300	-3.36803400	-1.64256200

H	-2.81245700	-3.15421600	-0.59277600
C	-1.36744700	3.77552500	-1.19430600
H	-0.52987000	3.71827100	-0.48395700
H	-1.40883100	4.80416200	-1.58642200
H	-1.14747500	3.09499200	-2.03111000
C	0.82459700	-3.06827300	-2.17174500
H	1.76820800	-3.62893000	-2.25678100
H	0.16623900	-3.37887200	-2.99831100
H	0.34266700	-3.34484900	-1.22615400
C	-5.31822800	-0.94175400	-1.57515200
H	-5.95465800	-0.14890200	-1.15575000
H	-5.97691900	-1.75746500	-1.90824200
H	-4.80285500	-0.54492400	-2.46245800
C	5.60840900	1.04830000	-2.08111700
H	5.74678200	0.06006800	-2.54543300
H	6.54144500	1.61540400	-2.21832100
H	4.81310900	1.57944800	-2.62578900
C	-0.24998300	-0.77545000	-2.13068700
H	-0.75162400	-0.97318200	-1.17438800
H	-0.93236700	-1.06974300	-2.94390400
H	-0.08057300	0.30969400	-2.20414200
C	5.15429800	2.36427700	-0.00545500
H	4.31499700	2.89347400	-0.48201000
H	6.07461200	2.94106900	-0.18888700
H	4.97557400	2.35242100	1.07954600
C	6.48315200	0.22200500	0.10921400
H	6.34413000	0.15767200	1.19821600
H	7.41901900	0.77161900	-0.07909300
H	6.59951700	-0.80122700	-0.27913900
C	-2.98536700	4.36316200	0.65211500
H	-3.93815100	4.11484700	1.14407600
H	-3.04368100	5.40246900	0.29175000
H	-2.18978000	4.31485100	1.40944600
C	1.68777000	-1.24255300	-3.63875300
H	1.84614100	-0.16422700	-3.79073000
H	0.99199300	-1.58805000	-4.41809400
H	2.64723100	-1.76000900	-3.79275100
O	-2.21115900	-1.90589900	1.56016700
H	-2.41444800	-2.61669800	0.92177900

Zero-point correction= 0.676893 (Hartree/Particle)
Thermal correction to Energy= 0.714791
Thermal correction to Enthalpy= 0.715735
Thermal correction to Gibbs Free Energy= 0.609866
Sum of electronic and zero-point Energies= -1771.630232
Sum of electronic and thermal Energies= -1771.592335
Sum of electronic and thermal Enthalpies= -1771.591390
Sum of electronic and thermal Free Energies= -1771.697260

TS3



C	0.11142500	-2.26625700	-0.98503500
H	-0.20663400	-2.41438000	0.06058500
H	0.80975400	-3.06796000	-1.25946300
C	-1.08138300	-2.23795200	-1.95498000
H	-0.76271700	-2.50746800	-2.97143600
H	-1.87931800	-2.92251600	-1.64471600
N	-1.59214500	-0.84560800	-1.96230000
N	0.77722600	-0.95780900	-1.15769100
C	-2.64312200	-0.47083000	-1.07668400
C	-2.34567900	0.69164900	-0.35139400
C	-3.85267800	-1.12886600	-0.89196500
C	-3.21808400	1.24662000	0.58393600
C	-4.77351500	-0.61522700	0.04142100
H	-4.07090200	-2.02921400	-1.46782900
C	-4.43629500	0.55115400	0.74521900
H	-5.14948700	0.94911600	1.46188400
C	2.09016500	-0.70986100	-0.65323100
C	2.78825200	-1.69602500	0.05299400
C	2.62542500	0.59351600	-0.86659500
C	4.05556400	-1.42775800	0.58183200
H	2.33148300	-2.67337000	0.19802300
C	3.90464300	0.88511200	-0.29766000
C	4.57460000	-0.13571200	0.38838600
H	5.56018600	0.08266100	0.79904200
O	1.91822200	1.49068500	-1.54943300
O	-1.08640000	1.22237900	-0.67920500
P	-0.26972700	0.21982500	-1.71030600
C	-2.86364400	2.50960300	1.38086000
C	-6.10825400	-1.34897200	0.25816500
C	-3.98091900	2.90129900	2.36567800
H	-4.16758200	2.11292300	3.11078200
H	-3.67812300	3.80806100	2.91000200
H	-4.92706100	3.12366900	1.84915700
C	-2.64626200	3.68938000	0.40360300
H	-1.82342000	3.49030100	-0.29495000
H	-3.55951300	3.88057600	-0.18019700
H	-2.40245800	4.60275500	0.96807400
C	-1.57265400	2.25799900	2.19726900
H	-1.71460100	1.42001400	2.89661500
H	-0.71859600	2.02688700	1.54813800

H	-1.32214700	3.15540500	2.78403300
C	-7.00903600	-0.63937400	1.28548000
H	-7.94819200	-1.20149200	1.39720400
H	-6.53458200	-0.58386300	2.27690600
H	-7.26743900	0.38155500	0.96573900
C	-5.82208700	-2.77968000	0.77201000
H	-6.76650200	-3.32276000	0.93375400
H	-5.22078100	-3.35652200	0.05433500
H	-5.27505500	-2.74819300	1.72660700
C	-6.87625900	-1.42932100	-1.08190400
H	-7.08888800	-0.42167000	-1.46998700
H	-6.30681200	-1.97510800	-1.84805000
H	-7.83422500	-1.95322300	-0.93931600
C	4.51984000	2.28735600	-0.45513200
C	4.71718900	2.60859900	-1.95617300
H	3.76133400	2.57179800	-2.49334200
H	5.15107000	3.61483400	-2.07538500
H	5.40620300	1.88298900	-2.41646200
C	3.58370000	3.33936100	0.18782700
H	2.59117300	3.31981200	-0.27926800
H	3.46864300	3.14296000	1.26543200
H	4.01018000	4.34870200	0.06821000
C	5.89350200	2.40607400	0.23282600
H	6.63438300	1.71649400	-0.20076900
H	6.27537000	3.43000300	0.10062300
H	5.82935100	2.21124500	1.31459600
C	4.87064300	-2.47165400	1.36336300
C	4.14297000	-3.82384400	1.46831700
H	3.18156400	-3.72960700	1.99659300
H	3.95189200	-4.26143900	0.47617400
H	4.76380900	-4.53594700	2.03311700
C	5.13150000	-1.95253200	2.79704400
H	5.72205800	-2.68422800	3.37163000
H	5.68614400	-1.00291800	2.78776300
H	4.18140400	-1.78275700	3.32666400
C	6.22512300	-2.70823400	0.65491500
H	6.81478200	-1.78219200	0.58994500
H	6.82362800	-3.45168900	1.20575700
H	6.06813000	-3.08132700	-0.36877700
H	0.67023400	1.08537300	-2.38615800

Zero-point correction= 0.672757 (Hartree/Particle)
Thermal correction to Energy= 0.710480
Thermal correction to Enthalpy= 0.711424
Thermal correction to Gibbs Free Energy= 0.604290
Sum of electronic and zero-point Energies= -1771.596478
Sum of electronic and thermal Energies= -1771.558755
Sum of electronic and thermal Enthalpies= -1771.557811
Sum of electronic and thermal Free Energies= -1771.664945

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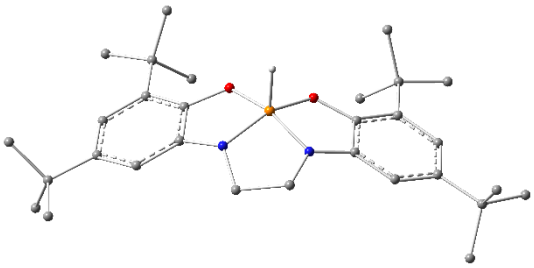

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H	0.93073200	-3.00691400	0.66756300
H	1.24628300	-3.60390200	-0.98389000
C	-0.79326200	-2.85771500	-0.69576700
H	-0.99729100	-3.33307200	-1.67075700
H	-1.33195900	-3.42354400	0.07897600
N	-1.21050600	-1.47179700	-0.70155400
N	1.17831300	-1.49837600	-0.78399800
C	-2.46506000	-0.98160200	-0.38106700
C	-2.40836200	0.42192500	-0.27924600
C	-3.64989100	-1.66948600	-0.13904200
C	-3.51553300	1.18781600	0.08141900
C	-4.80329700	-0.93544100	0.20923400
H	-3.67586700	-2.75619500	-0.22998800
C	-4.70839300	0.46000200	0.30938200
H	-5.59932000	1.02360000	0.57250100
C	2.43638200	-1.00917400	-0.44358900
C	3.58954100	-1.72779500	-0.12470300
C	2.41794200	0.39284200	-0.40038500
C	4.75325400	-1.01721400	0.21728700
H	3.56930300	-2.81631600	-0.15319400
C	3.54486900	1.14208500	-0.04710500
C	4.70129000	0.38861800	0.23982700
H	5.60973700	0.92973000	0.50032800
O	1.17225300	0.91335100	-0.67455500
O	-1.14145600	0.91440800	-0.52313300
P	-0.01756700	-0.26278700	-1.02518200
C	-3.42952900	2.71526700	0.21586400
C	-6.12078600	-1.69172400	0.45706200
C	-4.77841300	3.33739600	0.62012800
H	-5.13124800	2.95888600	1.59172100
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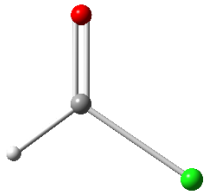
C	-3.00554200	3.32995600	-1.13924800
H	-2.02298200	2.95971600	-1.45936600
H	-3.74070800	3.08430000	-1.92091000
H	-2.94902700	4.42681900	-1.05449900
C	-2.38759500	3.07724800	1.30172700

H	-2.68055900	2.65296200	2.27443000
H	-1.39000900	2.69735000	1.04512500
H	-2.32222900	4.17141400	1.41107900
C	-7.28378500	-0.74965800	0.81892100
H	-8.19777700	-1.34136100	0.97950600
H	-7.08368500	-0.18818000	1.74423300
H	-7.49115400	-0.02822800	0.01395100
C	-5.92915400	-2.68885400	1.62386900
H	-6.86414500	-3.23940800	1.81392800
H	-5.14327600	-3.42634600	1.40407700
H	-5.64767200	-2.15787100	2.54600300
C	-6.51323600	-2.46923900	-0.82124700
H	-6.64884400	-1.77960900	-1.66836300
H	-5.74484000	-3.20405400	-1.10205300
H	-7.45819000	-3.01314200	-0.66397400
C	3.50125500	2.67491100	0.02855800
C	3.10803400	3.25144100	-1.35224000
H	2.11937600	2.89606300	-1.67028600
H	3.07951800	4.35164000	-1.30606100
H	3.84456200	2.95995500	-2.11671700
C	2.45921000	3.10544200	1.08928400
H	1.45452600	2.74113100	0.83774200
H	2.73267200	2.71239000	2.08061600
H	2.42165000	4.20447500	1.15466200
C	4.86349300	3.27277400	0.42392500
H	5.64651200	3.02569700	-0.30917600
H	4.77943500	4.36910600	0.46628600
H	5.19352900	2.92526700	1.41488200
C	6.07387600	-1.72669800	0.56872300
C	5.95427700	-3.25962400	0.49136900
H	5.19997200	-3.64650800	1.19369200
H	5.69117400	-3.59851000	-0.52241200
H	6.91971400	-3.71703900	0.75539300
C	6.49248600	-1.34942500	2.00907000
H	7.43876000	-1.84695700	2.27478100
H	6.63873000	-0.26509700	2.11746500
H	5.72351600	-1.66191000	2.73204500
C	7.17809000	-1.27978100	-0.41793600
H	7.35531100	-0.19577300	-0.36534800
H	8.12734100	-1.78866100	-0.18601700
H	6.89788800	-1.52778000	-1.45305300
H	-0.07453500	-0.07528800	-2.42188600

Zero-point correction=	0.677327 (Hartree/Particle)
Thermal correction to Energy=	0.714884
Thermal correction to Enthalpy=	0.715828

Thermal correction to Gibbs Free Energy= 0.609977
Sum of electronic and zero-point Energies= -1771.657786
Sum of electronic and thermal Energies= -1771.620229
Sum of electronic and thermal Enthalpies= -1771.619285
Sum of electronic and thermal Free Energies= -1771.725136

HC(=O)Cl:



C	0.00000000	0.81228800	0.00000000
H	-0.90432100	1.44622900	0.00000000
Cl	-0.48036900	-0.92471500	0.00000000
O	1.13382400	1.17502500	0.00000000

Zero-point correction= 0.018274 (Hartree/Particle)
Thermal correction to Energy= 0.021583
Thermal correction to Enthalpy= 0.022527
Thermal correction to Gibbs Free Energy= -0.007000
Sum of electronic and zero-point Energies= -574.222104
Sum of electronic and thermal Energies= -574.218795
Sum of electronic and thermal Enthalpies= -574.217850
Sum of electronic and thermal Free Energies= -574.247377

CO:

O	0.00000000	0.00000000	0.48711700
C	0.00000000	0.00000000	-0.64948900

Zero-point correction= 0.004833 (Hartree/Particle)
Thermal correction to Energy= 0.007194
Thermal correction to Enthalpy= 0.008138
Thermal correction to Gibbs Free Energy= -0.014303
Sum of electronic and zero-point Energies= -113.354863
Sum of electronic and thermal Energies= -113.352502
Sum of electronic and thermal Enthalpies= -113.351558
Sum of electronic and thermal Free Energies= -113.373999

HCl:

Cl	0.00000000	0.00000000	0.07182400
H	0.00000000	0.00000000	-1.22101000

Zero-point correction=	0.006486 (Hartree/Particle)
Thermal correction to Energy=	0.008846
Thermal correction to Enthalpy=	0.009790
Thermal correction to Gibbs Free Energy=	-0.011412
Sum of electronic and zero-point Energies=	-460.859626
Sum of electronic and thermal Energies=	-460.857265
Sum of electronic and thermal Enthalpies=	-460.856321
Sum of electronic and thermal Free Energies=	-460.877523

PES for the formation of 5: When the energies of CO and HCl were considered instead of HC(=O) Cl: *When instead of HC(=O)Cl, the energies of its decomposed products CO and HCl were considerd, slightly lower energies were observed for* ***9c***, ***TS3'*** *and* ***5****.*

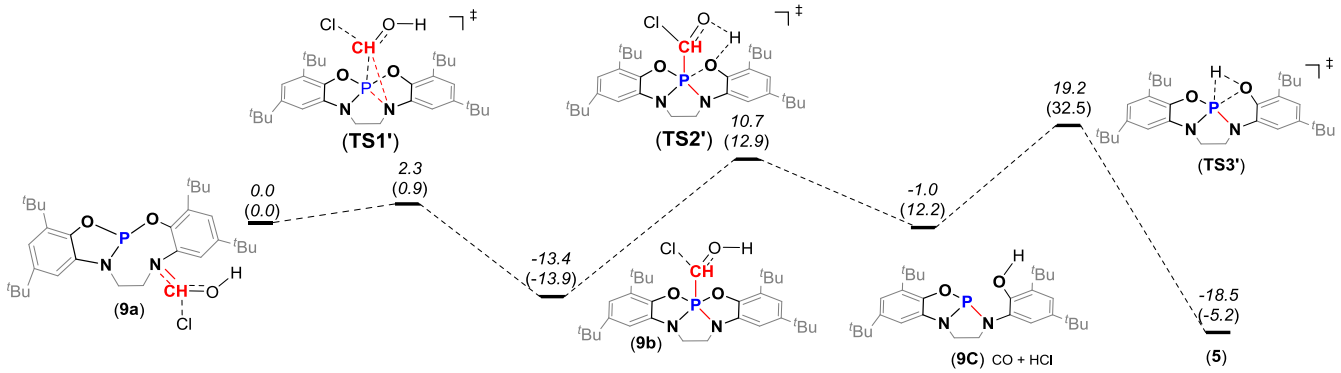


Figure 61. PES for the transformation of **9a** to **5**, Gibbs free energies (enthalpies) in kcal·mol^{-1} are given relatively to **9a**.

Alternative mecahnism for the formation of 5:

The transformation of **9** to **5** could possibly start with protonation of HCO- group in **9** leading to an intermediate **9a'**. The potential energy surface (PES) for this suggested mechanism was DFT calculated using BP86-D3/def2TZVP level of theory in $CHCl_3$. To avoid the comparison of the calculated ionic species with the neutral ones, the mechanism was divided into two parts:

a) insertion of the P^{III} center into C-N bond: This part of reaction involves the insertion of the P^{III}-centre into the polarized C–N bond through a transition state (**TS1"**) ($\Delta G^{\ddagger}$ = 12.7 kcal·mol^{-1}) leading to an intermediate **9b"** (ΔG = 10.4 and ΔH = 11.7 kcal·mol^{-1}).

b) decarbonylation reaction: This part involves the decarbonylation process that began with the nucleophilic attack of the Cl^- at a C=O unit in **9b'** to produce a neutral molecule **9b** (ΔG = 0.0 and ΔH = 0.0 kcal·mol^{-1}). **9b** further undergo transfer of a hydrogen (O-H) with simultaneous elimination of a formyl chloride molecule by a slightly endergonic and endothermic transition state **TS2'** (ΔG = 24.1 and ΔH = 26.8 kcal·mol^{-1}) and produced **9c** (ΔG = 15.0 and ΔH = 28.0 kcal·mol^{-1}). This step could explain the necessity of prolong heating, moreover CO is then formed from the decomposition of formyl chloride, which is well established process. The last step of this transformation involves insertion of P-center into O-H bond of **9c** that proceeds through an endergonic and endothermic transition state **TS3'** (ΔG = 35.2 and ΔH = 49.0 kcal·mol^{-1}) and produce a stable product **5** (ΔG = −2.5 and ΔH = -10.5 kcal·mol^{-1}).

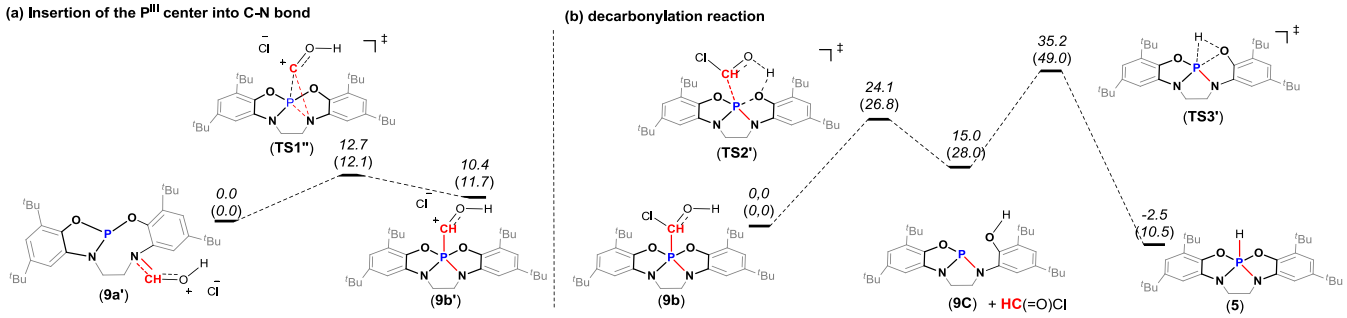
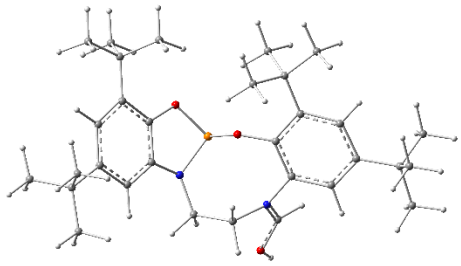


Figure 62. PES for the transformation of **9a'** to **9b'** and **9b** to **5**, Gibbs free energies (enthalpies) in kcal·mol^{-1} are given relatively to (a) **9a'** and (b) **9b**.

9a':



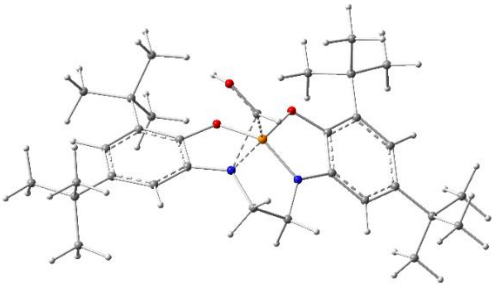
P	-0.18875400	-0.28570500	-1.94462900
O	-1.46849500	0.75018500	-1.82529400
C	-2.43788400	0.28503800	-0.91785300
C	-3.51575900	1.03657800	-0.44398800
C	-3.74347800	2.49554300	-0.86232800
C	-2.52367700	3.34732500	-0.43908800
H	-1.59862200	2.99792300	-0.91354000
H	-2.38387400	3.31004200	0.65139800
H	-2.68154800	4.39756900	-0.72953800
C	-4.99833700	3.09441800	-0.20163800
H	-5.12102200	4.13423800	-0.53863100
H	-4.91832300	3.10735100	0.89592900
H	-5.91061700	2.54487300	-0.47883700
C	-3.92718200	2.56701500	-2.39720800
H	-3.04220200	2.19651900	-2.93046300
H	-4.09928800	3.61033200	-2.70391700
H	-4.79676300	1.97002500	-2.71142000
C	-4.36294100	0.34967700	0.44511700
H	-5.21747000	0.88792800	0.85064200
C	-4.17001200	-0.98543900	0.84726800
C	-5.16860800	-1.62645100	1.82721500
C	-4.78447500	-3.07082900	2.19617400
H	-4.76554700	-3.72874300	1.31372900
H	-5.52698000	-3.47998800	2.89700700
H	-3.80095600	-3.11896100	2.68887700

C	-6.57172400	-1.65057600	1.17554700
H	-6.55976100	-2.23913200	0.24552400
H	-6.92337800	-0.63783500	0.93166000
H	-7.30177700	-2.10587300	1.86291600
C	-5.22216300	-0.79413000	3.12959200
H	-4.23151200	-0.75307000	3.60718400
H	-5.92967000	-1.24833600	3.84055500
H	-5.55178900	0.23757900	2.94132100
C	-3.07362200	-1.69518700	0.33328300
H	-2.89054300	-2.72886700	0.62059900
C	-2.21716800	-1.05040200	-0.56052300
N	-1.09733800	-1.56874900	-1.24898900
C	-0.49594900	-2.86013700	-0.94803000
H	-0.26363600	-3.38560400	-1.88442600
H	-1.22963500	-3.48333500	-0.42058500
C	0.75911800	-2.77546300	-0.05899700
H	0.58821800	-2.13016000	0.80896600
H	1.04243200	-3.77825100	0.29041000
N	1.94805900	-2.20916200	-0.77781600
C	2.52248800	-2.87887200	-1.74414800
H	3.36796400	-2.43306300	-2.27401500
C	2.62014400	-1.02271200	-0.28851700
C	3.96260500	-1.14066500	0.09582800
H	4.43585400	-2.12082100	0.03856900
C	4.64849000	-0.03007300	0.58245100
C	6.11815800	-0.08559500	1.02416100
C	6.72175600	-1.49091000	0.85651500
H	6.70267500	-1.82192000	-0.19343600
H	6.19573500	-2.23847200	1.47013400
H	7.77252000	-1.47881300	1.17980800
C	6.93922500	0.90630400	0.16710600
H	6.88573800	0.63973100	-0.89926500
H	7.99554300	0.88523700	0.47564000
H	6.57758100	1.93846700	0.27900900
C	6.21630900	0.31539100	2.51489100
H	7.26574100	0.28347000	2.84497800
H	5.63542500	-0.37559000	3.14416400
H	5.84096800	1.33393600	2.68981400
C	3.93033100	1.17661400	0.68197000
H	4.45658400	2.04524000	1.07381300
C	2.58729200	1.33507400	0.32187100
C	1.86338900	2.68637800	0.47811100
C	2.78446500	3.75699800	1.09519400
H	3.66223500	3.96448300	0.46443900
H	3.13244900	3.47188900	2.09960400
H	2.22052800	4.69562400	1.19452700

C	1.40904600	3.20531900	-0.90730400
H	2.27300900	3.32886000	-1.57738500
H	0.92187000	4.18523200	-0.79126700
H	0.68979200	2.53156300	-1.38658500
C	0.64327800	2.52632400	1.41935100
H	-0.10311600	1.83238900	1.01672800
H	0.15708200	3.50408900	1.55638300
H	0.96435400	2.16313200	2.40744800
C	1.92120300	0.19443100	-0.19306700
O	0.59979800	0.27068200	-0.51821300
O	2.08773500	-4.07784000	-2.05088400
H	2.58177200	-4.45008400	-2.81000200

Zero-point correction= 0.700538 (Hartree/Particle)
Thermal correction to Energy= 0.740346
Thermal correction to Enthalpy= 0.741290
Thermal correction to Gibbs Free Energy= 0.631415
Sum of electronic and zero-point Energies= -1885.424395
Sum of electronic and thermal Energies= -1885.384587
Sum of electronic and thermal Enthalpies= -1885.383643
Sum of electronic and thermal Free Energies= -1885.493518

TS1":



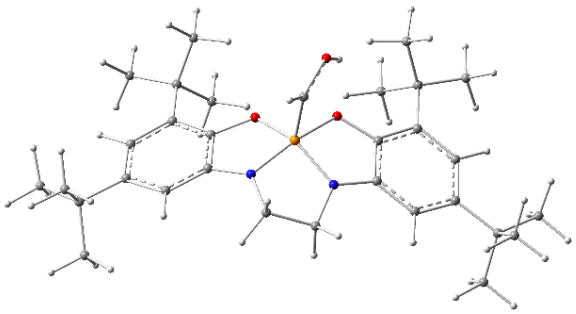
P	0.06297400	-0.17055500	0.82913100
C	-0.62284300	-0.35550800	2.48151300
H	-0.26924600	-1.16459900	3.12668300
O	1.29231500	0.93126000	0.82398600
O	-0.97737500	0.87867900	0.09501400
N	1.07007800	-1.40716800	0.34183900
N	-1.28284900	-1.40125000	0.94819700
C	4.78234200	0.31003200	-0.22191300
H	5.73446000	0.81571500	-0.35743300
C	4.70711300	-1.05971500	-0.51931400
C	3.69587300	1.08733100	0.23852100
C	3.79902000	2.59035200	0.52975600
C	2.50617300	0.38264000	0.39957600
C	2.39257700	-0.98420200	0.10958000

C	-2.29347700	0.41074200	-0.05894000
C	-3.31875400	1.15833400	-0.63740800
C	-4.56304500	0.49553800	-0.69508000
H	-5.39607100	1.03839100	-1.13360200
C	3.47334600	-1.72057400	-0.35191200
H	3.35774600	-2.78037900	-0.57959500
C	5.92159400	-1.85984700	-1.02000700
C	-4.79651100	-0.80778800	-0.22161800
C	-3.09921300	2.58404800	-1.16054500
C	-3.72732700	-1.51007700	0.36108300
H	-3.85273800	-2.51806700	0.75735800
C	-6.17771500	-1.47801400	-0.30872500
C	7.17496000	-0.98193900	-1.18632100
H	7.01440400	-0.17427000	-1.91658100
H	8.00790900	-1.60038200	-1.55177100
H	7.48980600	-0.53133000	-0.23287900
C	3.43893800	2.85487700	2.01120800
H	2.41423800	2.53650800	2.24297300
H	3.51960000	3.93123800	2.22789300
H	4.12904400	2.31844000	2.67986600
C	-2.48446000	-0.89163200	0.42460200
C	0.52810500	-2.74280400	0.09701600
H	1.21807500	-3.49839200	0.49560300
H	0.40312800	-2.91079700	-0.98328800
C	-0.82801400	-2.79438500	0.84657100
H	-1.57094700	-3.38835700	0.30043200
H	-0.70909900	-3.22584100	1.84931000
C	2.82006600	3.35554000	-0.39393500
H	3.06801300	3.17896100	-1.45148600
H	2.89389200	4.43688500	-0.20054400
H	1.77874000	3.04964400	-0.22768800
C	5.58943100	-2.49243200	-2.39188000
H	4.73696900	-3.18454700	-2.32917100
H	6.45457000	-3.06206100	-2.76488600
H	5.34394300	-1.71528000	-3.13136300
C	-2.61056500	3.48549800	-0.00035200
H	-3.34275300	3.49345500	0.82137300
H	-2.48888200	4.51866900	-0.35897800
H	-1.64153700	3.15320600	0.39525700
C	5.21892100	3.12856400	0.27690400
H	5.96332200	2.64170600	0.92492100
H	5.24026600	4.20614000	0.49671600
H	5.52783600	2.99578900	-0.77081400
C	-7.23045800	-0.57011200	-0.96893600
H	-7.38523000	0.35973900	-0.40094300
H	-8.19359900	-1.09944600	-1.00692900

H	-6.95492000	-0.30757700	-2.00152800
C	-2.04180700	2.55816600	-2.29037000
H	-1.07294800	2.18220100	-1.93666900
H	-1.88985800	3.57661900	-2.67906400
H	-2.37986100	1.92179800	-3.12186200
C	-6.05951500	-2.77357100	-1.14517100
H	-5.70943000	-2.54981700	-2.16410800
H	-7.04153700	-3.26519200	-1.21842600
H	-5.35939500	-3.49066100	-0.69261000
C	-6.66152600	-1.82716000	1.11856400
H	-5.97843500	-2.52602400	1.62314800
H	-7.65351200	-2.30204200	1.07482800
H	-6.74112200	-0.92070200	1.73737400
C	6.24391900	-2.97979600	-0.00273000
H	6.48068700	-2.55344000	0.98381200
H	7.11260000	-3.56446900	-0.34307100
H	5.39914000	-3.67338600	0.11980400
C	-4.39570600	3.19025300	-1.72674900
H	-4.78330100	2.60803900	-2.57603900
H	-4.18762500	4.20719800	-2.08934500
H	-5.18383300	3.26286300	-0.96223900
O	-1.50943000	0.43727500	3.05409000
H	-1.69046300	1.23922000	2.51568400

Zero-point correction=	0.699448 (Hartree/Particle)
Thermal correction to Energy=	0.738572
Thermal correction to Enthalpy=	0.739516
Thermal correction to Gibbs Free Energy=	0.630522
Sum of electronic and zero-point Energies=	-1885.404328
Sum of electronic and thermal Energies=	-1885.365205
Sum of electronic and thermal Enthalpies=	-1885.364261
Sum of electronic and thermal Free Energies=	-1885.473255

9b':



P	-0.02183500	-0.26915100	0.76560800
C	0.09049200	-0.12634900	2.54597600
H	-0.15037800	-0.97704900	3.19091800

O	1.13742200	0.90513400	0.36465700
O	-1.16949600	0.89627600	0.37123300
N	1.17413800	-1.48902600	0.52791300
N	-1.21261100	-1.48421900	0.55514300
C	4.69119000	0.39961700	-0.44235000
H	5.59584600	0.94613100	-0.69376200
C	4.76697700	-1.00490800	-0.35900000
C	3.51930100	1.15306100	-0.22219500
C	3.46257000	2.68042400	-0.35740300
C	2.39814700	0.39668100	0.11891400
C	2.43559300	-1.00762700	0.21015600
C	-2.43188800	0.39613400	0.12547200
C	-3.55055900	1.16143400	-0.20732800
C	-4.72562700	0.41582400	-0.42993700
H	-5.62648500	0.96611700	-0.68648500
C	3.60592800	-1.72230200	-0.02966800
H	3.60677900	-2.80971800	0.04451100
C	6.07514000	-1.77269300	-0.61325600
C	-4.80645000	-0.98789500	-0.33963500
C	-3.48573500	2.69011700	-0.31671700
C	-3.64939100	-1.71297400	-0.00579100
H	-3.66324000	-2.79915700	0.08383600
C	-6.11925700	-1.75004400	-0.58726500
C	7.25310500	-0.83842600	-0.94422400
H	7.07202400	-0.25681900	-1.86084100
H	8.15872000	-1.44071100	-1.10810000
H	7.46543800	-0.13795900	-0.12228600
C	2.98051300	3.30837300	0.97175500
H	1.94107600	3.02931300	1.19256800
H	3.01667200	4.40588000	0.90218300
H	3.61864200	2.99463400	1.81096300
C	-2.47370200	-1.00666600	0.22562200
C	0.74397100	-2.86961800	0.35946300
H	1.23813500	-3.52114600	1.09287600
H	1.02436200	-3.20897600	-0.64970300
C	-0.79478900	-2.87619000	0.54486900
H	-1.28651500	-3.41033200	-0.28045900
H	-1.07845100	-3.36643600	1.48835500
C	2.47977500	3.04924400	-1.49513600
H	2.81729800	2.62349500	-2.45180900
H	2.43015300	4.14340900	-1.60499300
H	1.46567000	2.68028100	-1.29033100
C	5.87220000	-2.73954400	-1.80360500
H	5.07794600	-3.47375100	-1.60363500
H	6.80149400	-3.29591900	-1.99995000
H	5.60298100	-2.18544100	-2.71538900

C	-3.05712200	3.28383100	1.04668300
H	-3.77637600	3.00866400	1.83270600
H	-3.02500900	4.38219100	0.98102800
H	-2.06166000	2.93285200	1.34930700
C	4.84154000	3.27665100	-0.69331600
H	5.58066600	3.06996800	0.09544000
H	4.74867800	4.36835400	-0.78694500
H	5.23338400	2.89483200	-1.64800300
C	-7.29141800	-0.81235600	-0.92957300
H	-7.50109200	-0.10270700	-0.11491100
H	-8.20025400	-1.41095400	-1.08954500
H	-7.10493000	-0.24044800	-1.85118400
C	-2.46015600	3.08425200	-1.40729700
H	-1.45030700	2.72685400	-1.16610300
H	-2.42105400	4.18030300	-1.50197100
H	-2.75185200	2.66689700	-2.38285800
C	-5.92220000	-2.73073400	-1.76736900
H	-5.64858400	-2.18769300	-2.68452000
H	-6.85512200	-3.28285100	-1.95883600
H	-5.13284000	-3.46789600	-1.55930200
C	-6.49201700	-2.54491100	0.68669100
H	-5.71885200	-3.28092000	0.95046600
H	-7.43478600	-3.09088500	0.52889300
H	-6.62534900	-1.86740700	1.54357100
C	6.44065200	-2.58317800	0.65289600
H	6.57738900	-1.91580100	1.51714100
H	7.37988100	-3.13373600	0.49052000
H	5.66240700	-3.31699800	0.90775800
C	-4.84931100	3.29510000	-0.69592200
H	-5.20490700	2.92929800	-1.67109700
H	-4.75149800	4.38823500	-0.76639400
H	-5.61876000	3.07744300	0.06009700
O	0.47788000	0.93901700	3.20082100
H	0.71820400	1.66714700	2.57801400

Zero-point correction= 0.699131 (Hartree/Particle)
Thermal correction to Energy= 0.739269
Thermal correction to Enthalpy= 0.740213
Thermal correction to Gibbs Free Energy= 0.628322
Sum of electronic and zero-point Energies= -1885.406029
Sum of electronic and thermal Energies= -1885.365891
Sum of electronic and thermal Enthalpies= -1885.364947
Sum of electronic and thermal Free Energies= -1885.476838

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