Electronic Supplementary Material (ESI) for Dalton Transactions.

Lewis and Brønsted Basicity of Phosphine-Diazomethane Derivatives

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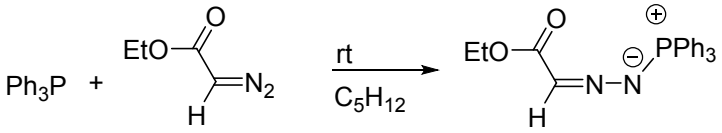
Supporting Information

Content

General Considerations

All manipulations were carried out under an atmosphere of dry, O_2-free N_2 conditions in a VAC glovebox. All glass devices used for the synthesis were oven-dried and cooled under vacuum before use. Oxygen-free and dry solvents were prepared using an Innovative Technologies solvent purification system. Deuterated chloroform ($CDCl_3$) purchased from Cambridge Isotope Laboratories Inc. was degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were used without further purification unless indicated otherwise. NMR spectra were recorded at 298 K on a Bruker AvanceIII 400 MHz spectrometer. Chemical shifts are reported in ppm and coupling constants as scalar values in Hertz (Hz).

Syntheses and Spectroscopic Data
Synthesis of EtO(=O)CHNNPPh$_3$ (1)



A 20 mL vial was charged with Ph_3P (0.100g, 0.392 mmol) in pentane (5 mL) and a solution of EtOC(=O)CH(N_2) (0.050 g, ≥13 wt% dichloromethane) diluted in further pentane (0.5 mL) was added, in a dropwise fashion. The resulting pale yellow solution was stored in the glovebox and crystals precipitated over the next 4 hours. The solvent was carefully taken out and the solid was dried *in vacuo*.

white to pale yellow solid, 0.142 g (86%)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.77 (d, $^4J_{H\text{-}P}$ = 2.3 Hz, 1H, CH), 7.71 – 7.42 (m, 15H, $(C_6H_5)_3$), 4.20 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2), 1.27 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, CH_3) ppm.

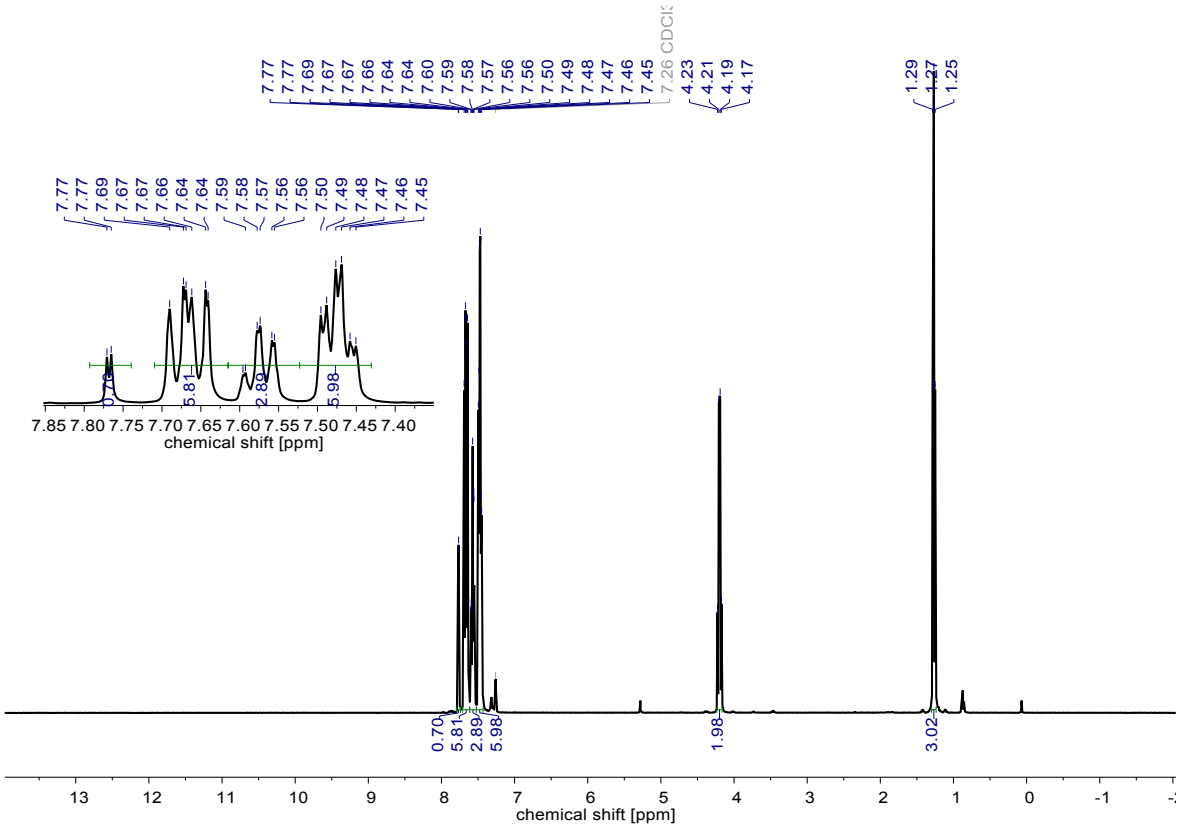
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 165.6 (s, C=O), 138.3 (d, $^3J_{C\text{-}P}$ = 47.9 Hz, N-CH), 133.7 (d, $^2J_{C\text{-}P}$ = 8.4 Hz, *o*-$(C_6H_5)_3$), 132.6 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, *p*-$(C_6H_5)_3$), 128.9 (d, $^3J_{C\text{-}P}$ = 11.8 Hz, *m*-$(C_6H_5)_3$), 127.9 (d, $^1J_{C\text{-}P}$ = 93.9 Hz, P-qC), 59.8 (s, CH_2), 14.6 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 22.7 (s) ppm.

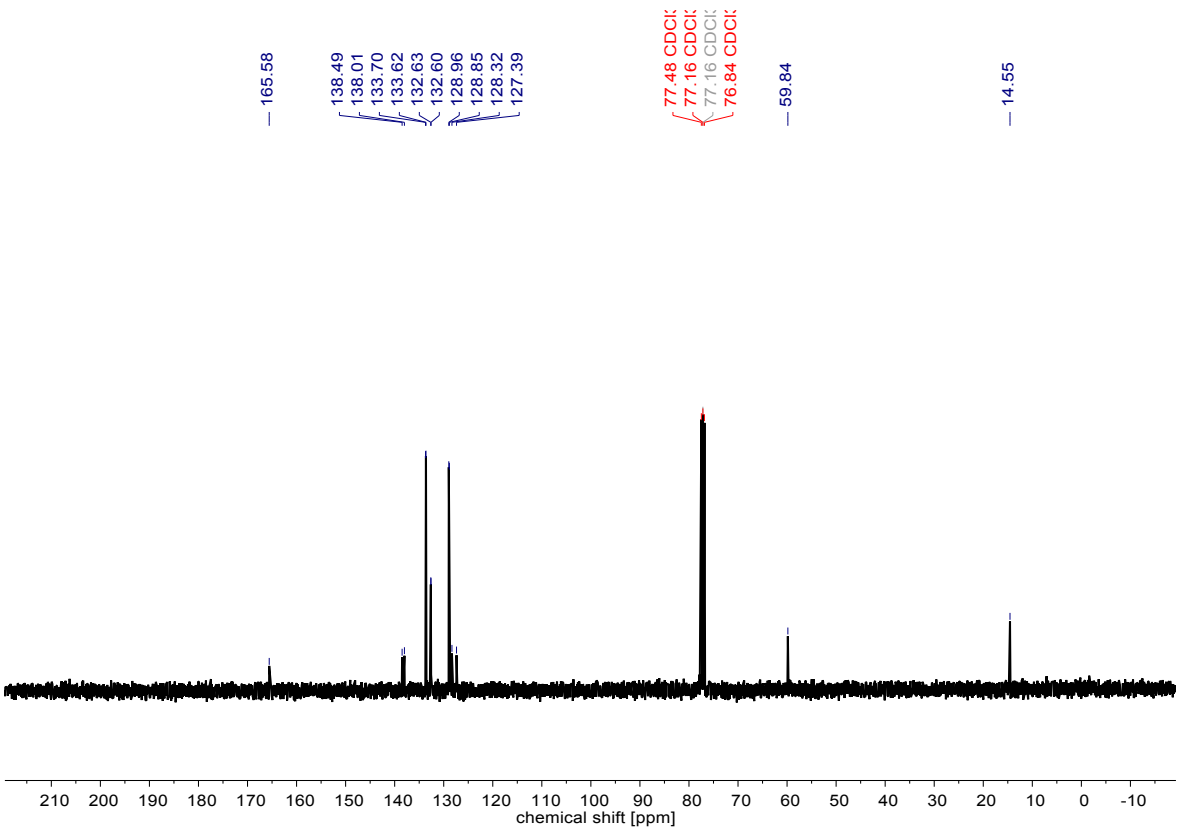
HR-MS (ESI+): calculated for $C_{22}H_{21}N_2O_2P$: 376.13
found $C_{22}H_{21}N_2O_2P$: 377.14 (+ H^+)

Data is in consistence with literature.[1]

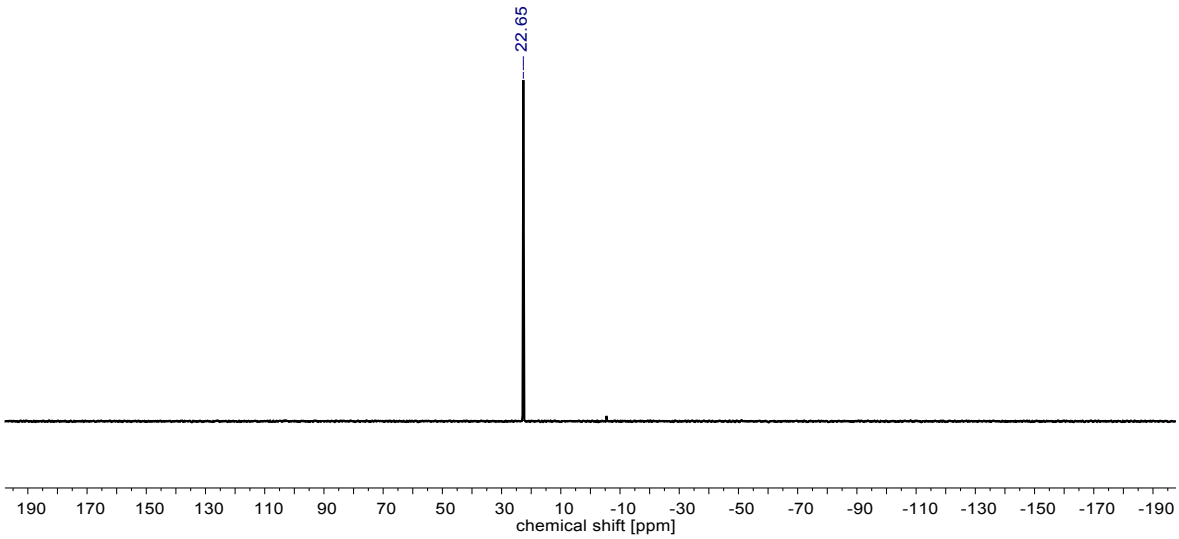
[1] F. M. Pedro, A. M. Santos, W. Baratta, F. E. Kühn, *Organometallics* **2007**, *26*, 302–309.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $EtO(=O)CHNNPPh_3$.

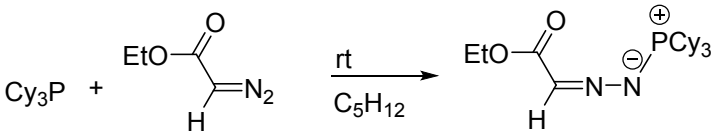


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of $EtO(=O)CHNNPPh_3$.



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of $EtO(=O)CHNNPPh_3$.

Synthesis of $EtOC(=O)CHNNPCy_3$ (2)



A 20 mL vial was charged with Cy_3P (0.110g, 0.392 mmol) and filled with pentane (5 mL). $EtOC(=O)CH(N_2)$ (0.050 g, ≥13 wt% dichloromethane), diluted in further pentane (1 mL) was added, in a dropwise fashion. The resulting pale yellow solution was stored in the glovebox and a solid precipitated over the next hour. The solvent was carefully taken out and the solid was dried *in vacuo*.

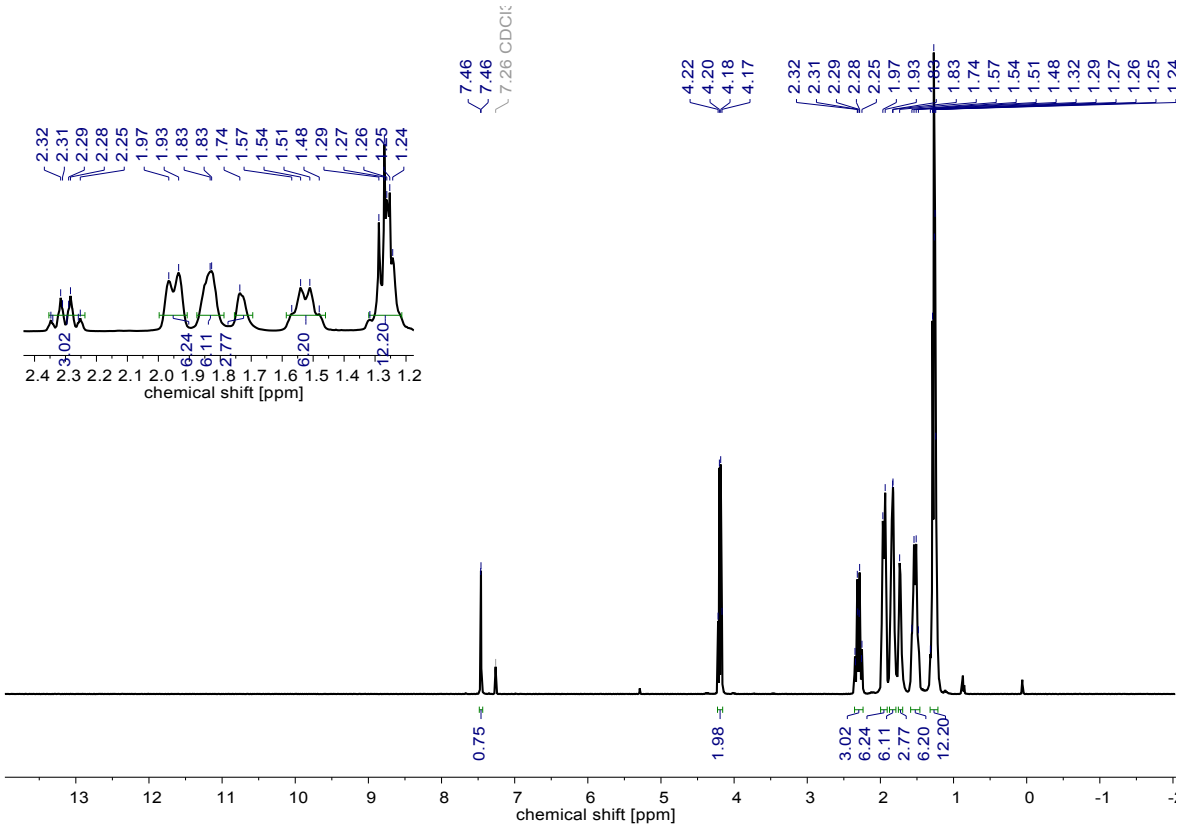
pale yellow solid 0.108 g (70 %)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.46 (d, $^{4}J_{H-P}$ = 1.7 Hz, 1H, N-CH), 4.19 (q, $^{3}J_{H-H}$ = 7.1 Hz, 2H, CH_2), 2.35 – 2.24 (m, 3H, P-CH), 1.95 (d, $^{3}J_{H-H}$ = 12.8 Hz, 6H, C_6H_{11}), 1.88 – 1.79 (m, 6H, C_6H_{11}), 1.74 (bs, 3H, C_6H_{11}), 1.53 (q, $^{3}J_{H-H}$ = 11.8 Hz, 6H, C_6H_{11}), 1.32 – 1.21 (m, 12H, CH_3 and C_6H_{11}) ppm.

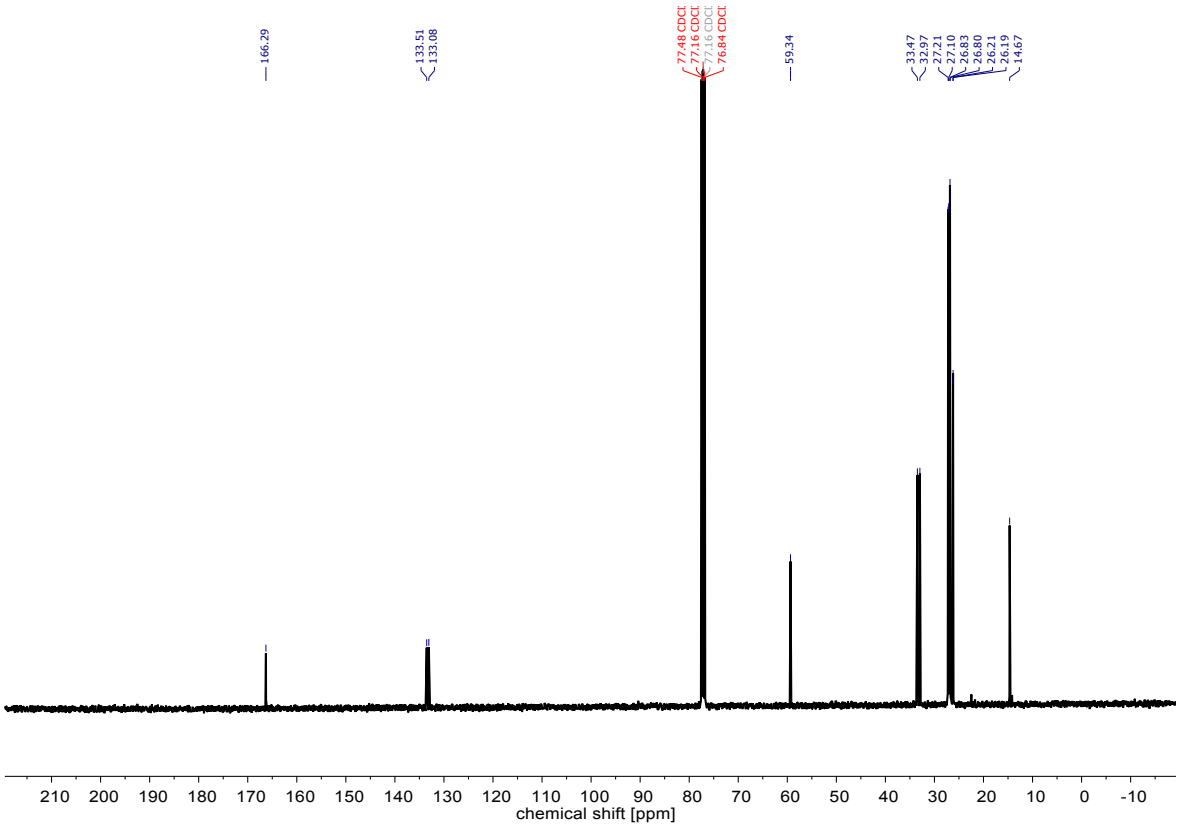
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 166.3 (s, C=O), 133.3 (d, $^{3}J_{C-P}$= 44.0 Hz, N-CH), 59.3 (s, CH_2), 33.2 (d, $^{1}J_{C-P}$ 51.1 Hz, P-CH), 27.2 (d, $^{2}J_{C-P}$ = 10.9 Hz, C_6H_{11}), 26.8 (d, $^{3}J_{C-P}$ = 3.5 Hz, C_6H_{11}), 26.2 (d, $^{4}J_{C-P}$ = 1.4 Hz, C_6H_{11}),14.7 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 41.7 (s) ppm.

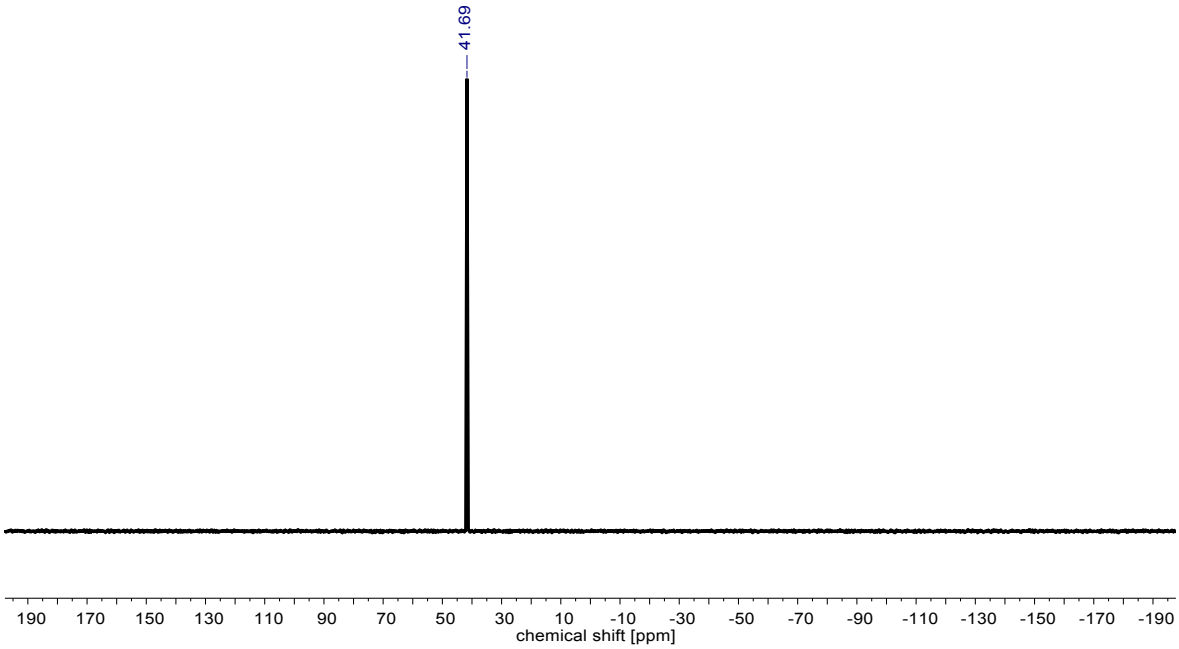
HR-MS (ESI+): calculated for $C_{22}H_{39}N_2O_2P$ 394.27
found for $C_{22}H_{39}N_2O_2P$ 395.28 (+ H^+)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $EtOC(=O)CHNNPCy_3$

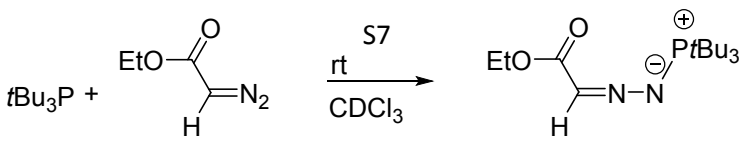


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of $EtOC(=O)CHNNPCy_3$



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of EtOC(=O)CHNNPCy$_3$.

Synthesis of EtOC(=O)CHNN*t*Bu$_3$ (3)



A 20 mL vial was charged with *t*Bu_3P (0.032g, 0.158 mmol) and filled with $CDCl_3$ (0.4 mL). EtOC(=O)CH(N_2) (0.020 g, ≥13 wt% dichloromethane), diluted in further $CDCl_3$ (0.3 mL) was added, in a dropwise fashion. A yellow solution was obtained and the product formed immediately.

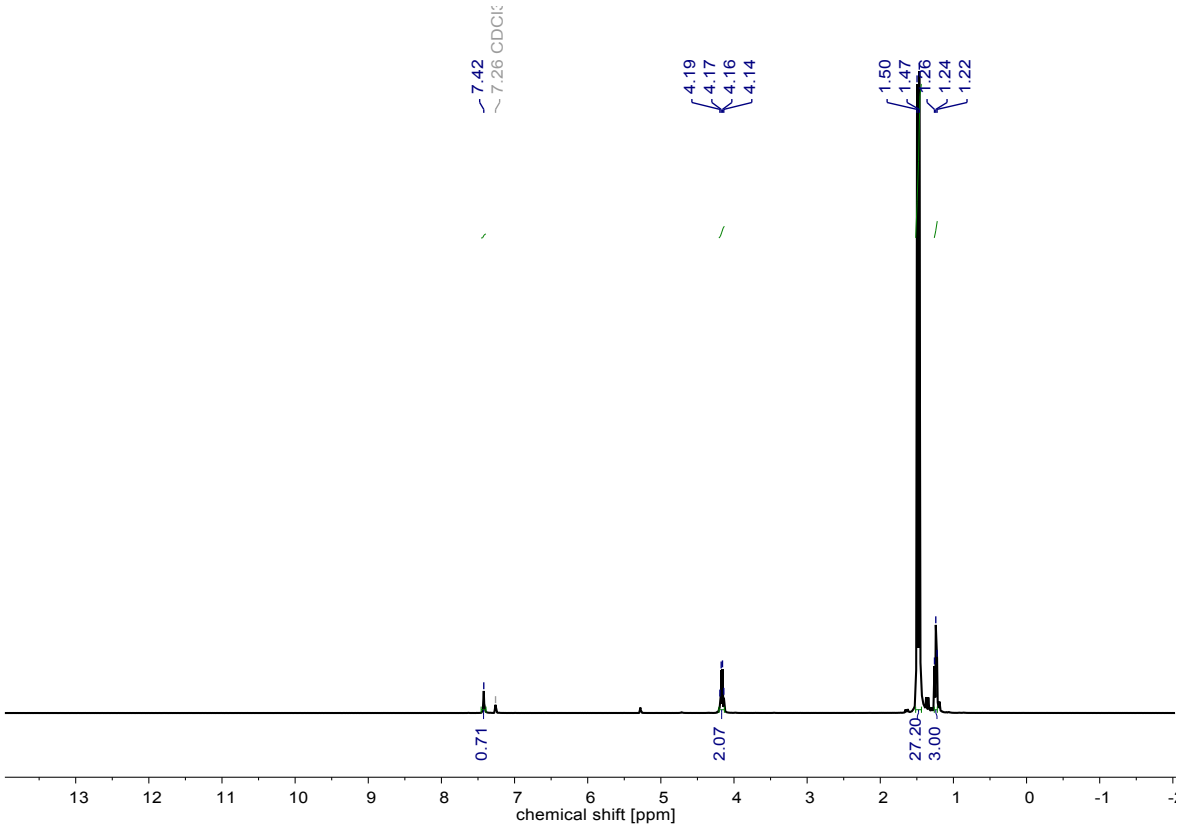
Yield (by NMR): 98%

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.42 (s, 1H, N-CH), 4.17 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 1.48 (d, $^3J_{H-P}$ = 12.5 Hz, 27H, 9 CH_3, *t*Bu_3), 1.24 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3) ppm.

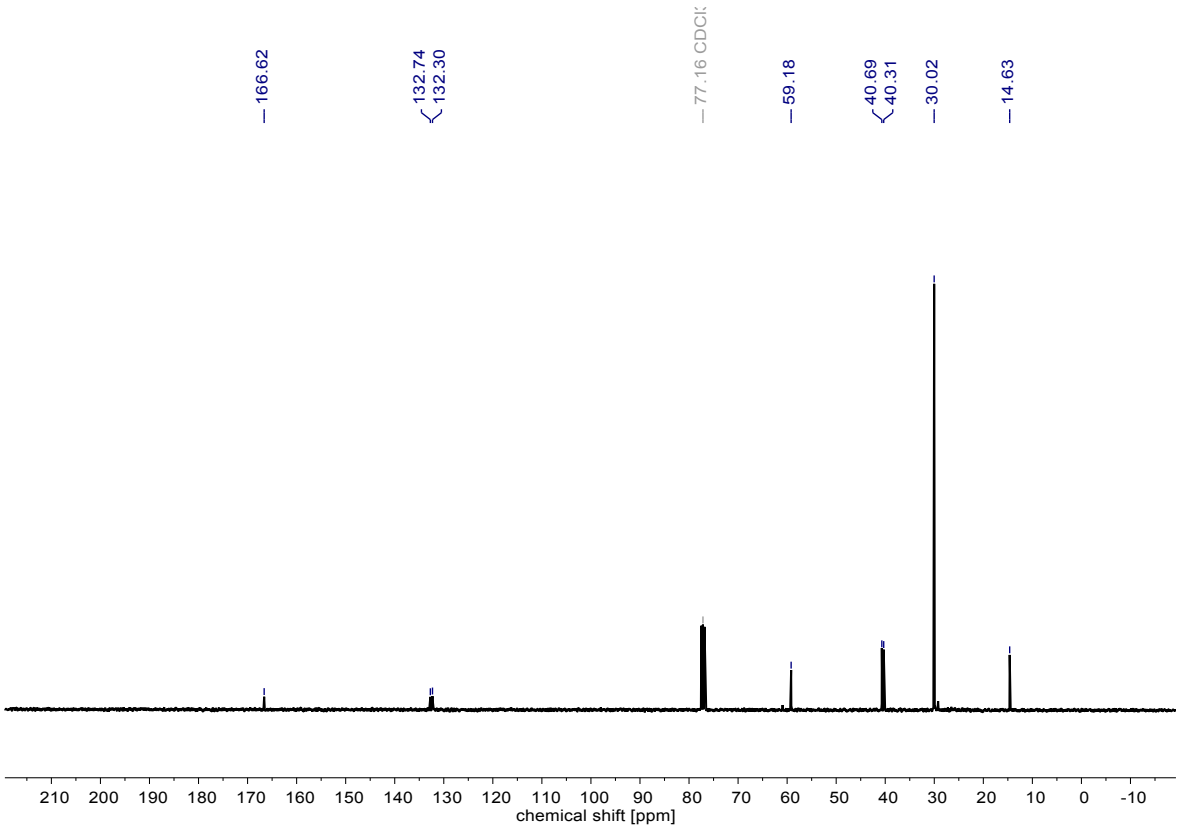
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 166.6 (s, C=O), 132.5 (d, $^3J_{C-P}$ = 44.4 Hz, N-CH), 59.2 (s, CH_2), 40.5 (d, $^1J_{C-P}$ = 38.9 Hz, P-qC (*t*Bu_3)), 30.0 (s, 9 CH_3 (*t*Bu_3)), 14.6 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 53.1 (s) ppm.

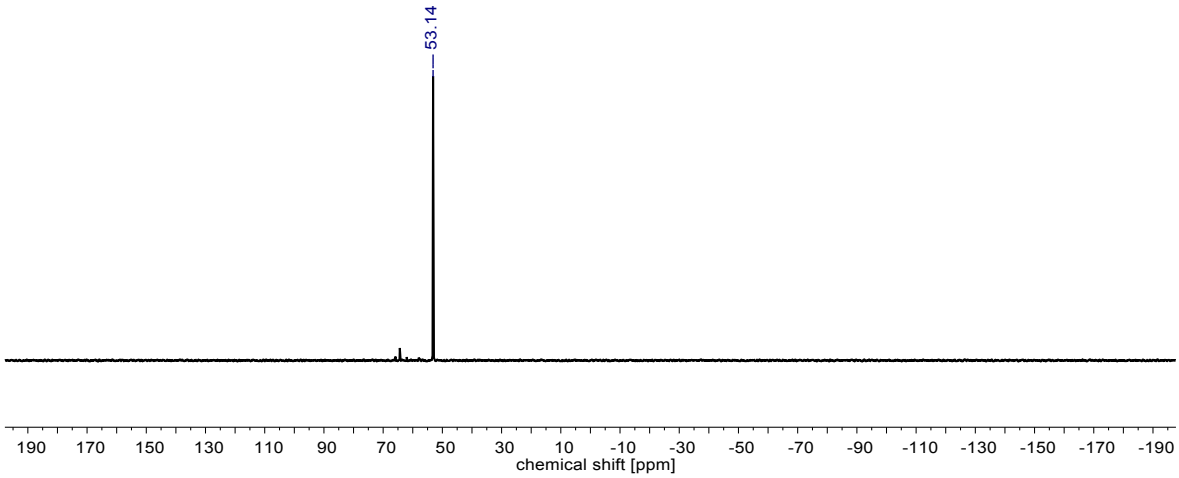
HR-MS (ESI+, $CDCl_3$) calculated for $C_{16}H_{33}N_2O_2P$: 316.23
found for $C_{16}H_{33}N_2O_2P$: 317.2357 (+ H^+)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of EtOC(=O)CHN*t*Bu_3.

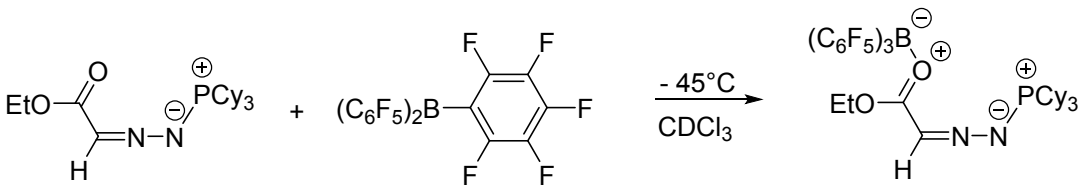


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of EtOC(=O)CHN*t*Bu_3.



^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) spectrum of EtOC(=O)CHN*t*Bu_3.

Synthesis of EtOC(=O(B(C_6F_5)$_3$))CHNNPCy_3 (5)



A 20 mL vial was charged with EtOC(=O)CHNNPCy_3 (0.031g, 0.078 mmol) in $CDCl_3$ (0.4 mL). The reaction was cooled to -45 °C where a pre-cooled solution of B(C_6F_5)$_3$ (0.040 g, 0.078 mmol), diluted in further $CDCl_3$ (0.3 mL), was added in a dropwise fashion. The resulting yellow solution was stirred at -45 °C for a period of 30 minutes and was warmed to room temperature.

Yield (by NMR): >99%

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.10 (s, 1H, N-CH), 4.36 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 2.40 – 2.24 (m, 3H, P-CH), 1.90 – 1.80 (m, 12H, *o*-C_6H_{11}), 1.77 (s, 3H, *p*-C_6H_{11}), 1.48 – 1.36 (m, 6H, *m*-C_6H_{11}), 1.31 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 1.28 – 1.22 (m, 9H, C_6H_{11}) ppm.

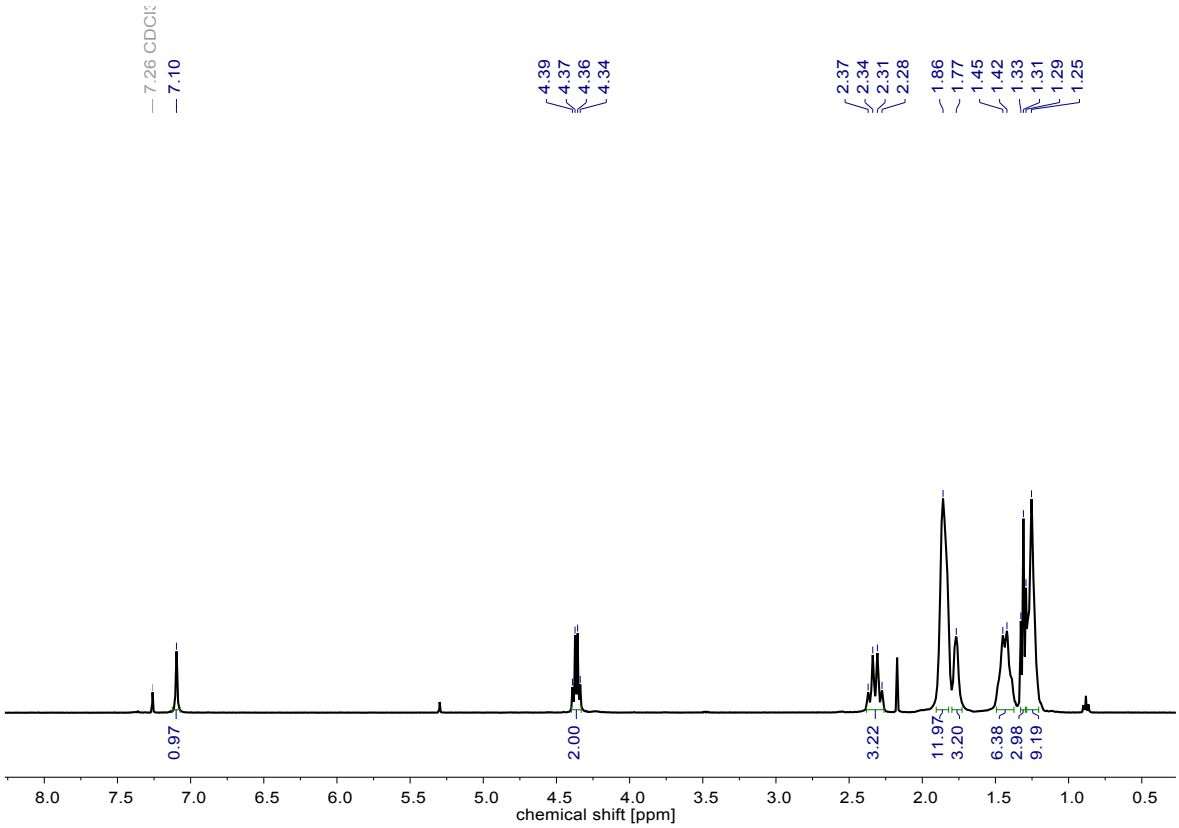
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 172.8 (s, C=O), 149.1 (bs, C_6F_5), 146.8 (bs, C_6F_5), 138.2 (bs, C_6F_5)135.7 (bs, C_6F_5), 125.4 (d, $^3J_{C-P}$ = 48.8 Hz, N-CH), 66.0 (s, CH_2), 32.6 (d, $^1J_{C-P}$ = 48.1 Hz, P-CH), 26.9 (d, $^2J_{C-P}$ = 11.2 Hz, C_6H_{11}), 26.4 (d, $^3J_{C-P}$ = 3.8 Hz, C_6H_{11}), 25.9 (s, C_6H_{11}), 14.1 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 45.4 (s) ppm.

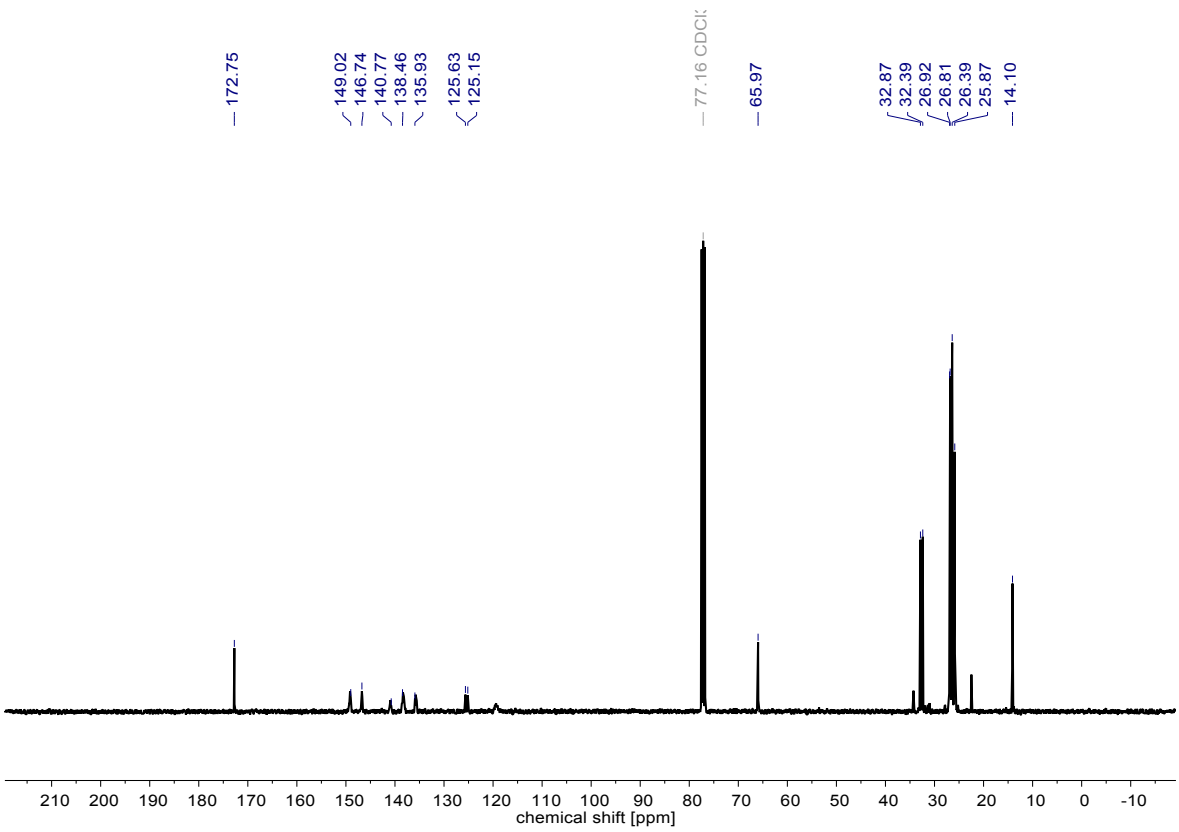
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -134.2 (d, $^3J_{F-F}$ = 21.5 Hz, 6F, *o*-C_6F_5), -159.1 (t, $^3J_{F-F}$ = 20.2 Hz, *p*-C_6F_5), -165.0 (bt, $^3J_{F-F}$ = 20.2 Hz, *m*-C_6F_5) ppm.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K): δ – 1.4 (bs) ppm.

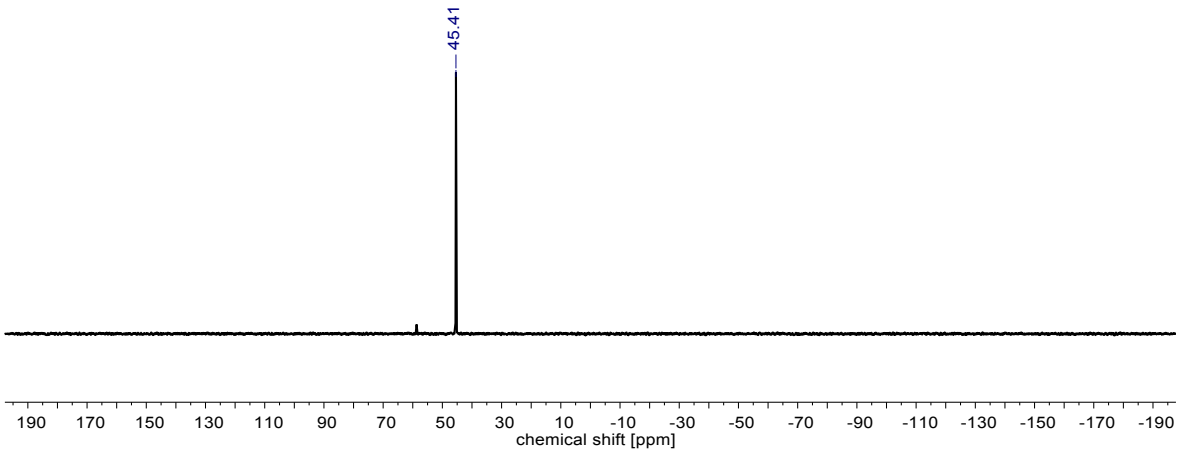
HR-MS (ESI, $CDCl_3$) hydrolysation occurred through measurements



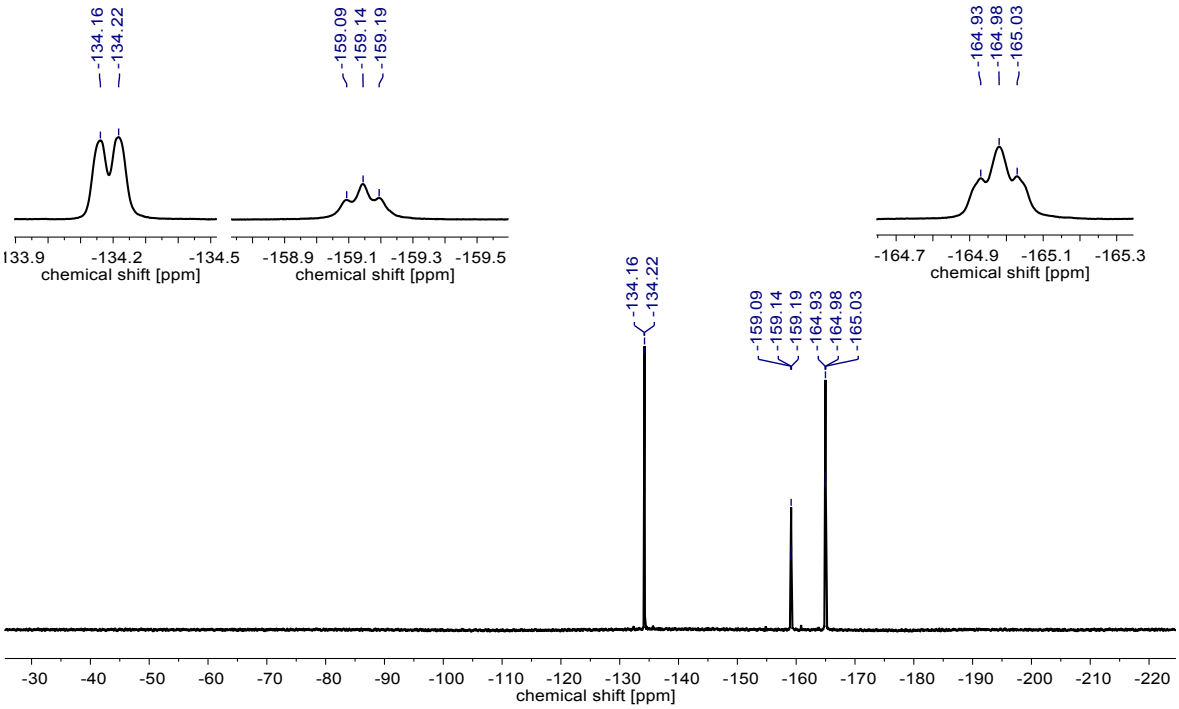
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of EtOC(=O(B(C_6F_5)$_3$))CHNNPCy$_3$.



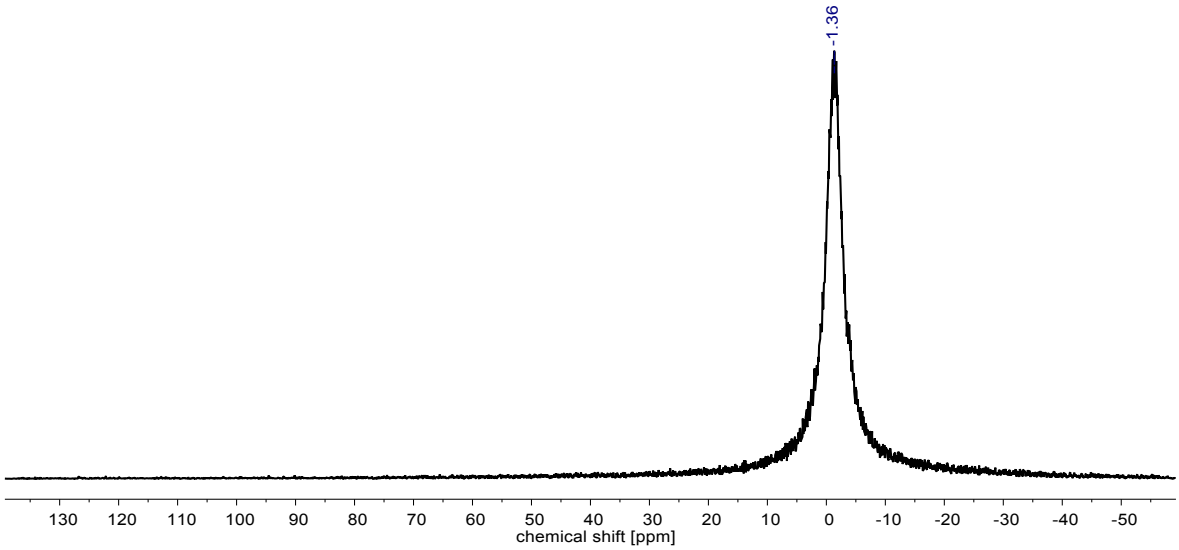
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of EtOC(=O(B(C_6F_5)$_3$))CHNNPCy$_3$



^{31}P NMR (162 MHz, $CDCl_3$) spectrum of $EtOC(=O(B(C_6F_5)_3))CHNNPCy_3$.

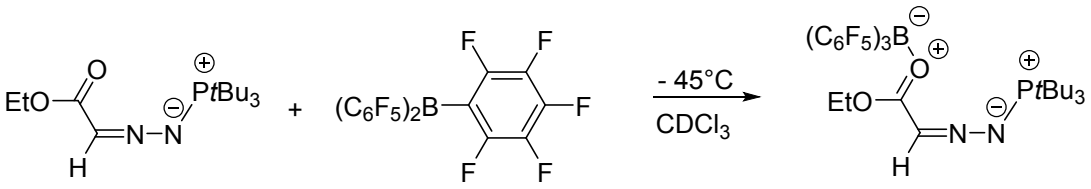


$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) spectrum of $EtOC(=O(B(C_6F_5)_3))CHNNPCy_3$.



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) spectrum of $EtOC(=O(B(C_6F_5)_3))CHNNPCy_3$.

Synthesis of EtOC(=O(B(C_6F_5)$_3$))CHNNP*t*Bu$_3$ (6)



A 20 mL vial with the product solution from EtOC(=O)CHNN*t*Bu$_3$ (0.078 mmol) in $CDCl_3$ (0.4 mL) was cooled to -45 °C where a cooled solution of B(C_6F_5)$_3$ (0.040 g, 0.078 mmol), diluted in further $CDCl_3$ (0.3 mL) was added, in a dropwise fashion. The resulting yellow solution was stirred at -45 °C for a period of 30 minutes and was warmed to room temperature where the reaction was stirred for further 20 minutes.

Yield (by NMR): >99%

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.07 (s, 1H, N-CH), 4.37 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 1.44 (d, $^3J_{H-P}$ = 12.8 Hz, 27H, 9 CH_3 (*t*Bu$_3$)), 1.30 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3) ppm.

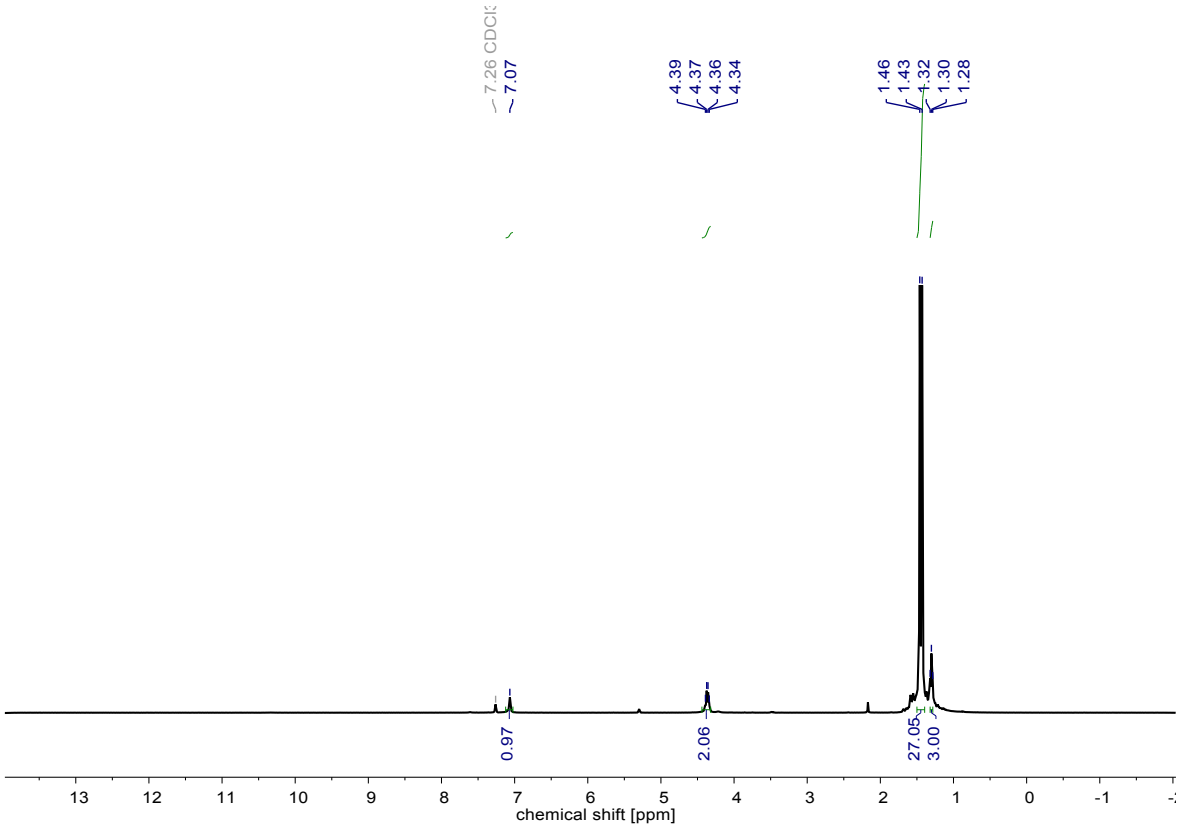
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 172.9 (s, C=O), 149.1 (bm, C_6F_5), 148.7 (bm, C_6F_5), 140.9 (m, C_6F_5), 138.3 (bm, C_6F_5), 135.8 (bm, C_6F_5), 125.8 (d, $^3J_{C-P}$ = 45.3 Hz, N-CH), 119.1 (bm, C_6F_5), 65.9 (s, CH_2), 40.8 (d, $^1J_{C-P}$ = 35.0 Hz, P-qC), 29.7 (s, 9 CH_3 (tBu_3), 14.1 (s, CH_3) ppm..

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 55.2 (s) ppm.

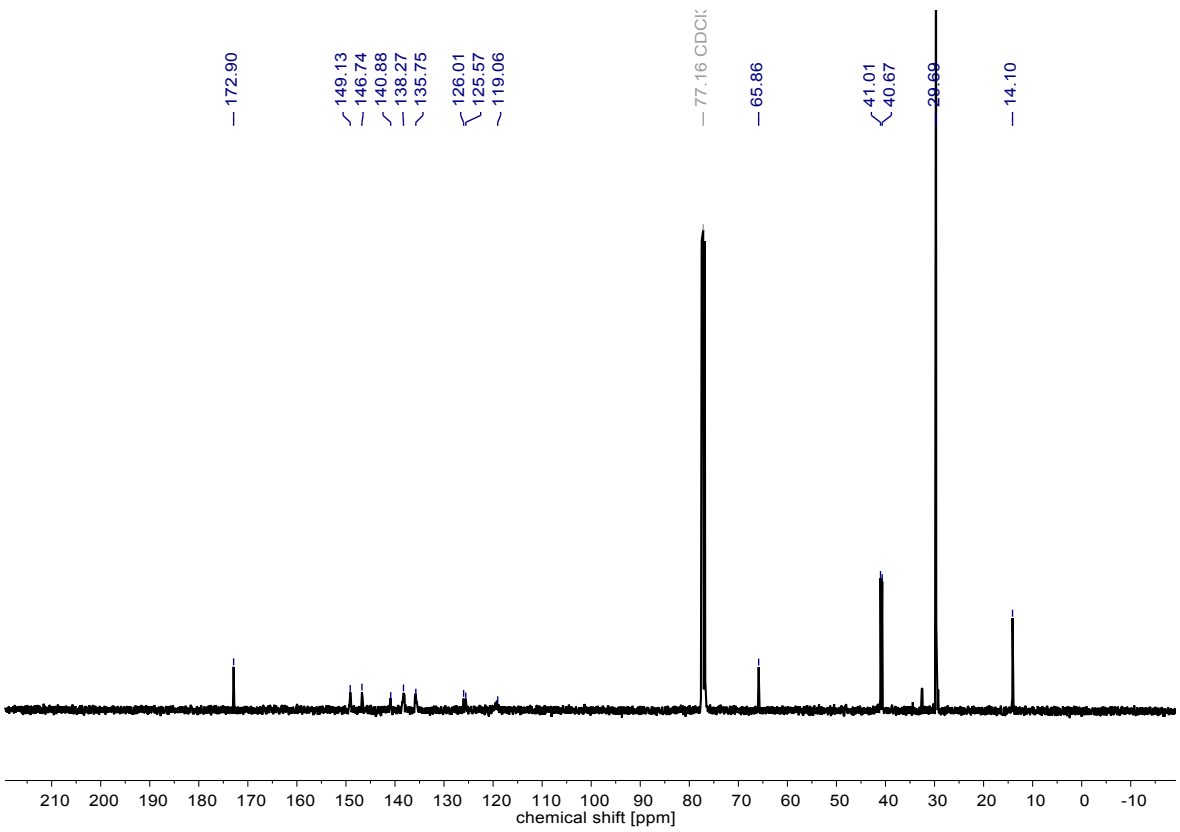
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -134.2 (d, $^3J_{F-F}$ = 20.0 Hz, *o*-C_6F_5), -159.1 (bs, *p*-C_6F_5), -165.0 (bs, *m*-C_6F_5) ppm.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K): δ – 1.3 (bs) ppm.

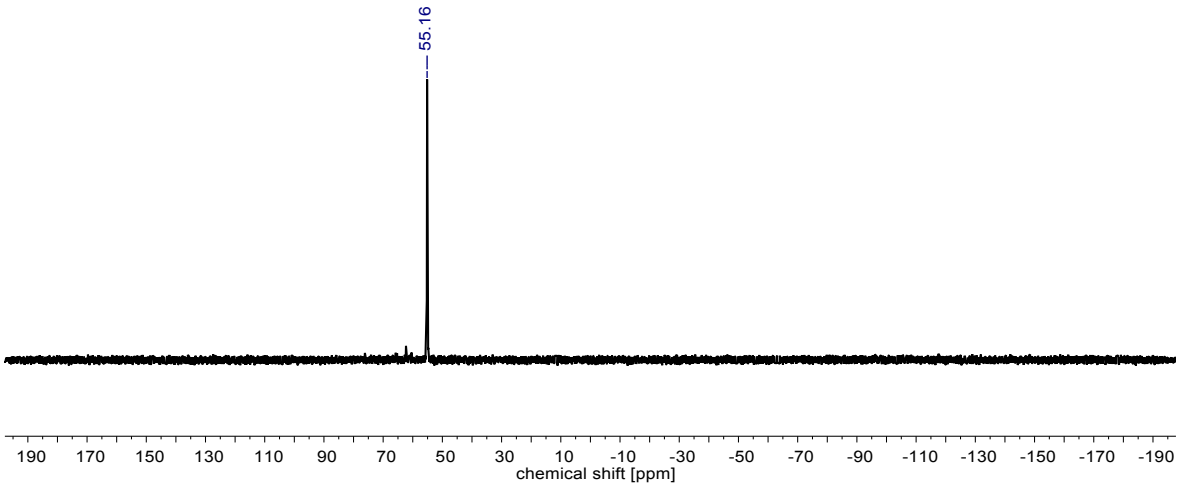
HR-MS (ESI, $CDCl_3$) hydrolysation occurred through measurements



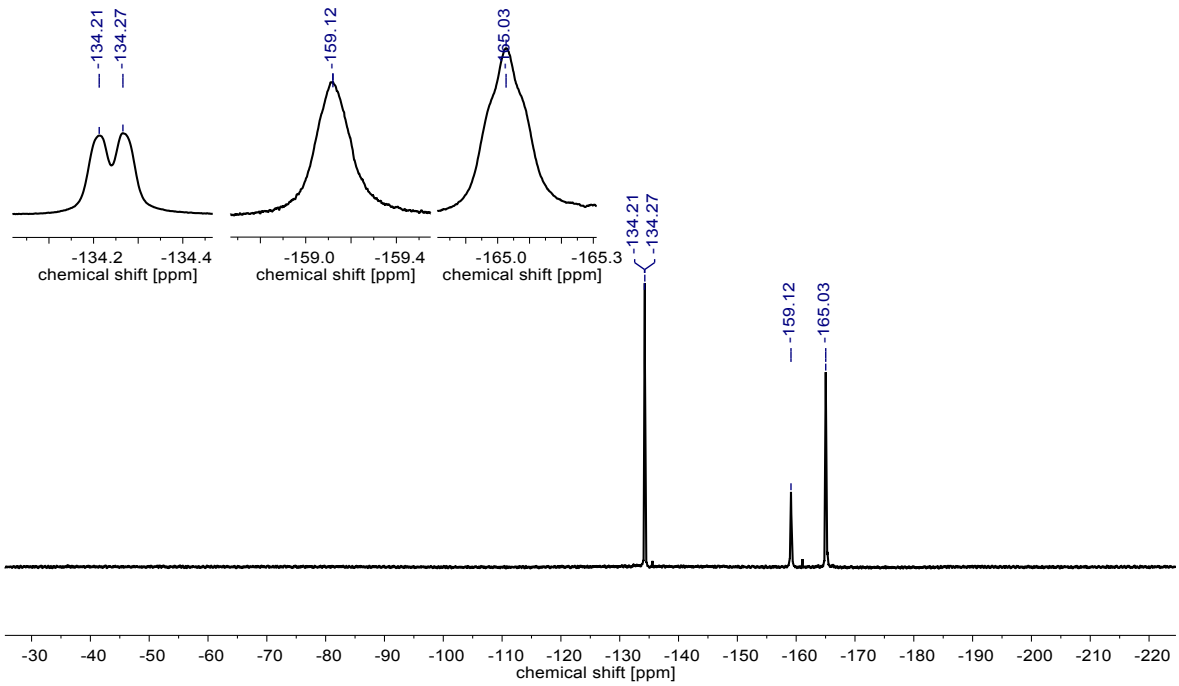
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of EtOC(=O(B(C_6F_5)$_3$))CHNNP*t*Bu$_3$.



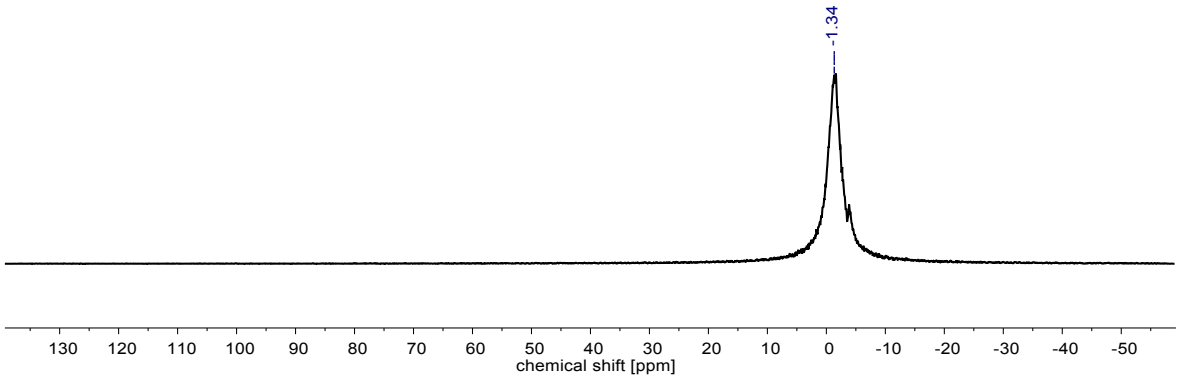
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of EtOC(=O(B(C_6F_5)$_3$))CHNNP*t*Bu$_3$.



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of EtOC(=O(B(C_6F_5)$_3$))CHNNP*t*Bu$_3$.

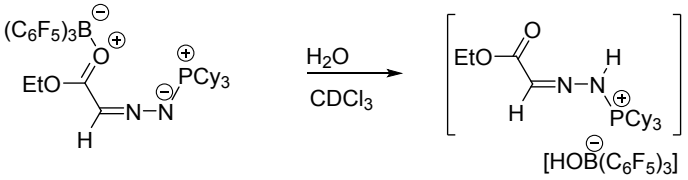


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of EtOC(=O(B(C_6F_5)$_3$))CHNNP*t*Bu$_3$.



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) spectrum of $EtOC(=O(B(C_6F_5)_3))CHNNP\textit{t}Bu_3$.

Synthesis of [EtOC(=O)CHNNHPCy$_3$] [HOB(C$_6$F$_5$)$_3$] (7)



To the 20 mL vial with a pre-cooled (-45°C) reaction product of EtOC(=O(B(C$_6$F$_5$)$_3$))CHNNPCy$_3$. (0.078 mmol) degassed H_2O was added (0.3 mL). The water freezes immediately. The ice containing solution was stirred for further 10 min before it was allowed to warm to room temperature and the ice started to melt. It was stirred for further 30min and the solution is turning colorless over this process.

Yield (by NMR): 97%

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 11.88 (bs, 1H, NH), 7.27 (s, 1H, N-CH), 4.21 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 2.53 (bs, 1H, OH), 2.42 (q, *J* = 12.3 Hz, 3H, qC, C_6H_{11}), 1.91 – 1.76 (m, 15H, C_6H_{11}), 1.52-1.41 (m, 6H, C_6H_{11}), 1.31 – 1.20 (m, 12H, 3H CH_3, 9H C_6H_{11}) ppm.

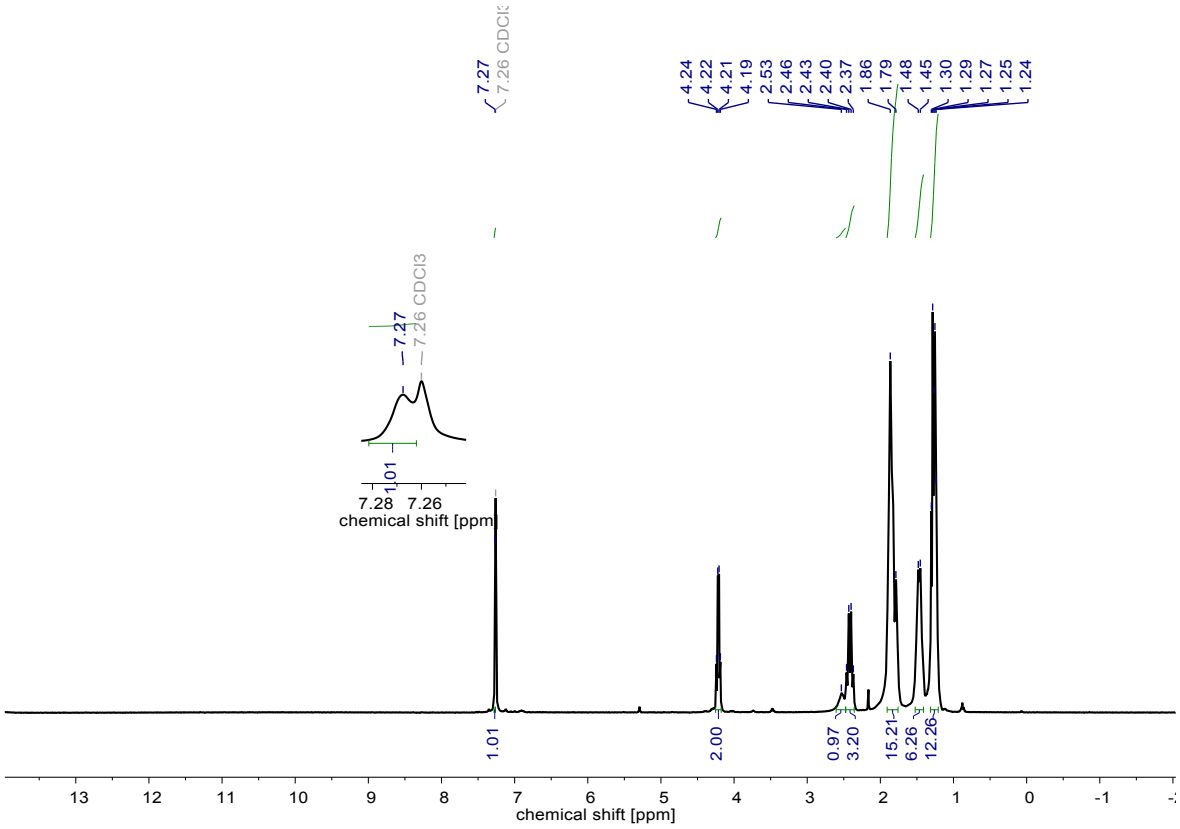
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K): δ 162.3 (s, C=O), 149.2 (bs, C_6F_5), 146.9 (bs, C_6F_5), 139.6 (d, $^3J_{C-P}$ = 16.2 Hz, N-CH), 137.9 (bs, C_6F_5), 135.6 (bs, C_6F_5), 61.4 (s, CH_2), 32.1 (d, $^1J_{C-P}$ = 48.7 Hz, P-CH), 26.5 (d, $^2J_{C-P}$ = 12.6 Hz, C_6H_{11}), 26.2 (d, $^3J_{C-P}$ = 3.4 Hz, C_6H_{11}), 25.5 (s, C_6H_{11}), 14.0 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K): δ 57.2 (bs) ppm.

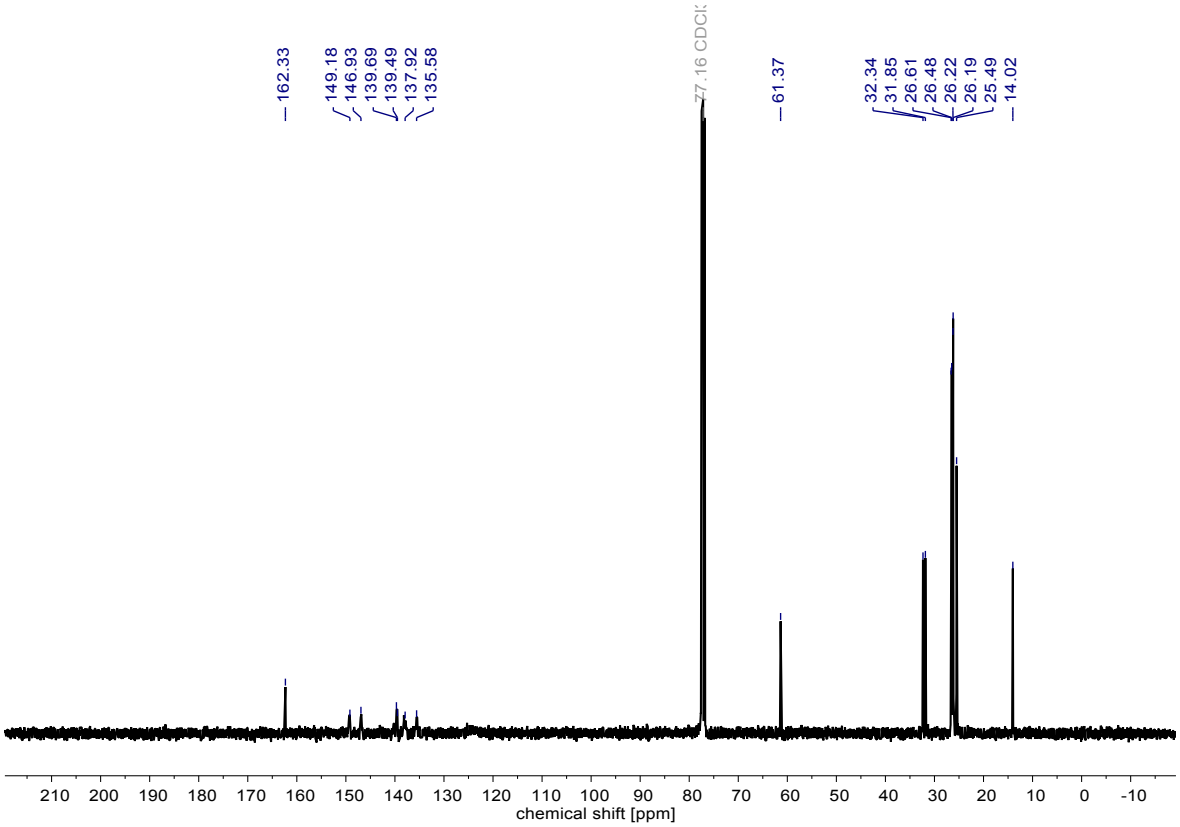
^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$, 298 K): δ -135.6 (d, $^3J_{F-F}$ = 19.2 Hz, *o*-C_6F_5), -160.9 (t, $^3J_{F-F}$ = 20.3 Hz, *p*-C_6F_5), -165.2 (t, $^3J_{F-F}$ = 18.6 Hz, *m*-C_6F_5) ppm.

^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$, 298 K): δ – 3.8 (bs) ppm.

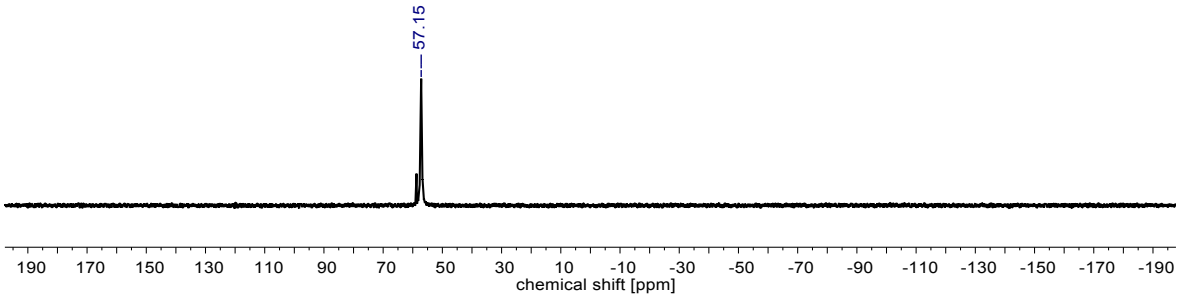
HR-MS (ESI+, CDCl$_3$) calculated for $C_{22}H_{40}N_2O_2P^+$: 395.28
found for $C_{22}H_{40}N_2O_2P^+$: 395.28
HR-MS (ESI-, CDCl$_3$) calculated for $C_{18}HBF_{15}O^-$: 528.99
found for $C_{18}HBF_{15}O^-$: 528.94



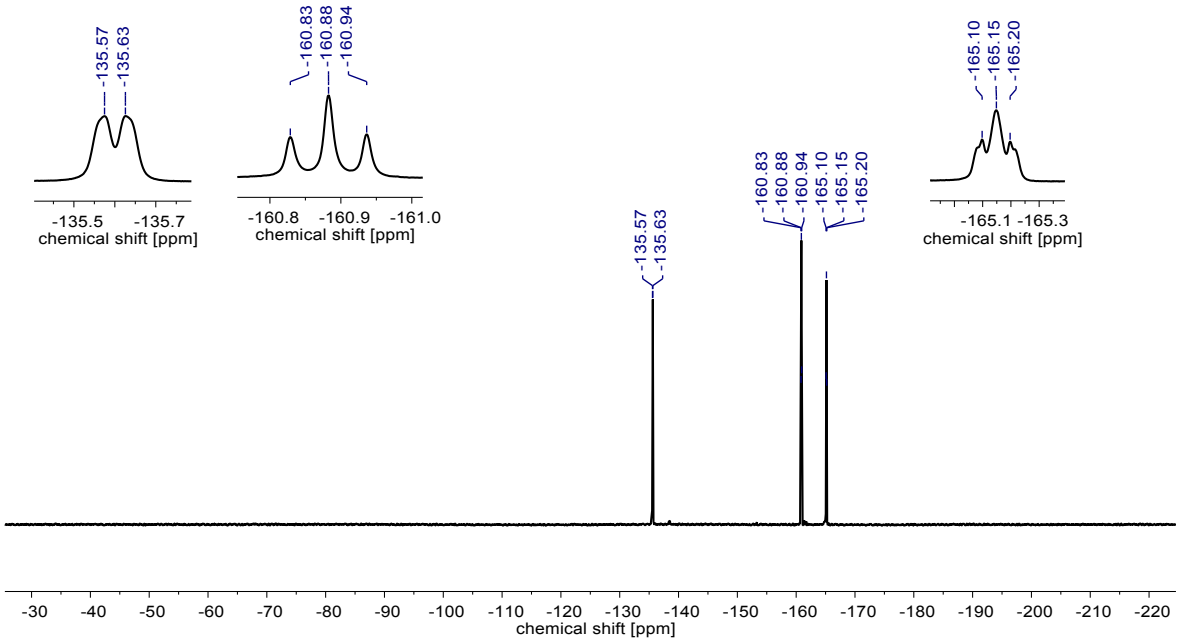
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPCy_3][HOB(C_6F_5)_3]$.



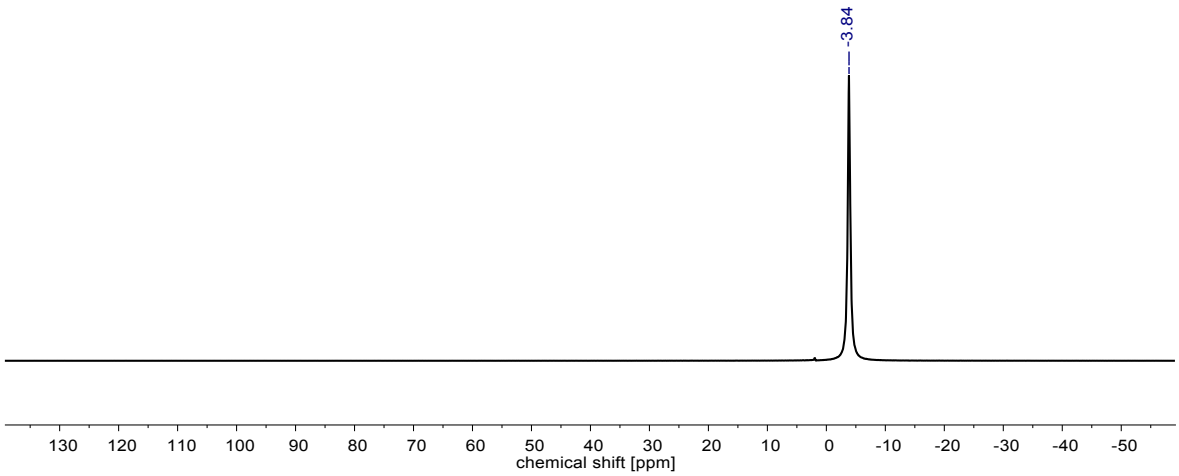
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPCy_3][HOB(C_6F_5)_3]$.



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPCy_3][HOB(C_6F_5)_3]$.

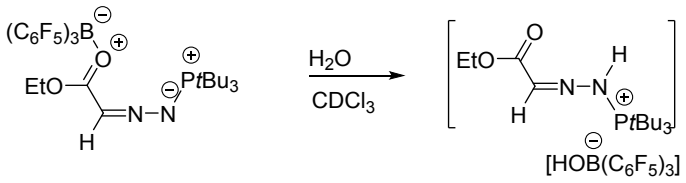


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPCy_3][HOB(C_6F_5)_3]$.



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPCy_3][HOB(C_6F_5)_3]$.

Synthesis of [EtOC(=O)CHNNHP*t*Bu$_3$] [HOB(C$_6$F$_5$)$_3$] (8)



To the 20 mL vial with a pre-cooled (-45°C) reaction product of EtOC(=O(B(C$_6$F$_5$)$_3$))CHNNP*t*Bu$_3$ (0.078 mmol) degassed H_2O was added (0.3 mL). The water freezes immediately. The ice containing solution was stirred for further 10 min before it was allowed to warm to room temperature and the ice started to melt. It was stirred for further 30min and the solution is turning colorless over this process.

Yield (by NMR): >99%

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 11.20 (d, $^2J_{H\text{-}P}$ = 25.4 Hz, 1H, NH), 7.65 (s, 1H, N-CH), 4.19 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2), 2.76 (bs, 1H, OH), 1.55 (d, $^3J_{H\text{-}P}$ = 14.6 Hz, 27H, *t*Bu$_3$), 1.26 (t, $^3J_{H\text{-}H}$ = 7.1, 3H, CH_3) ppm.

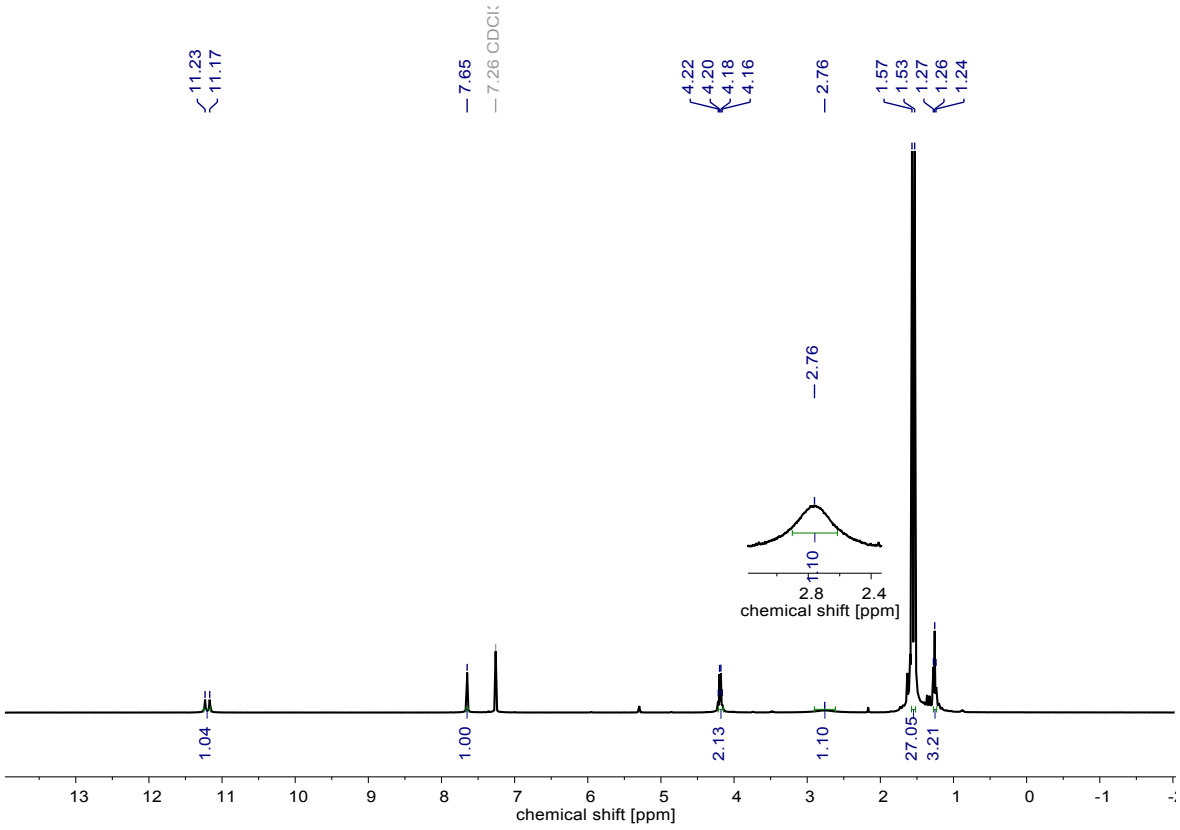
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 298 K): δ 162.2 (s, C=O), 149.2 (bs, C_6F_5), 146.9 (bs, C_6F_5), 140.2 (d, $^3J_{C\text{-}P}$ = 13.9 Hz, N-CH), 137.8 (bs, C_6F_5), 135.6 (bs, C_6F_5), 61.5 (s, CH_2), 41.5 (d, $^1J_{C\text{-}P}$ = 34.3 Hz, qC, *t*Bu$_3$), 29.5 (s,9Me, *t*Bu$_3$), 13.9 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 298 K): δ 72.9 (bs) ppm.

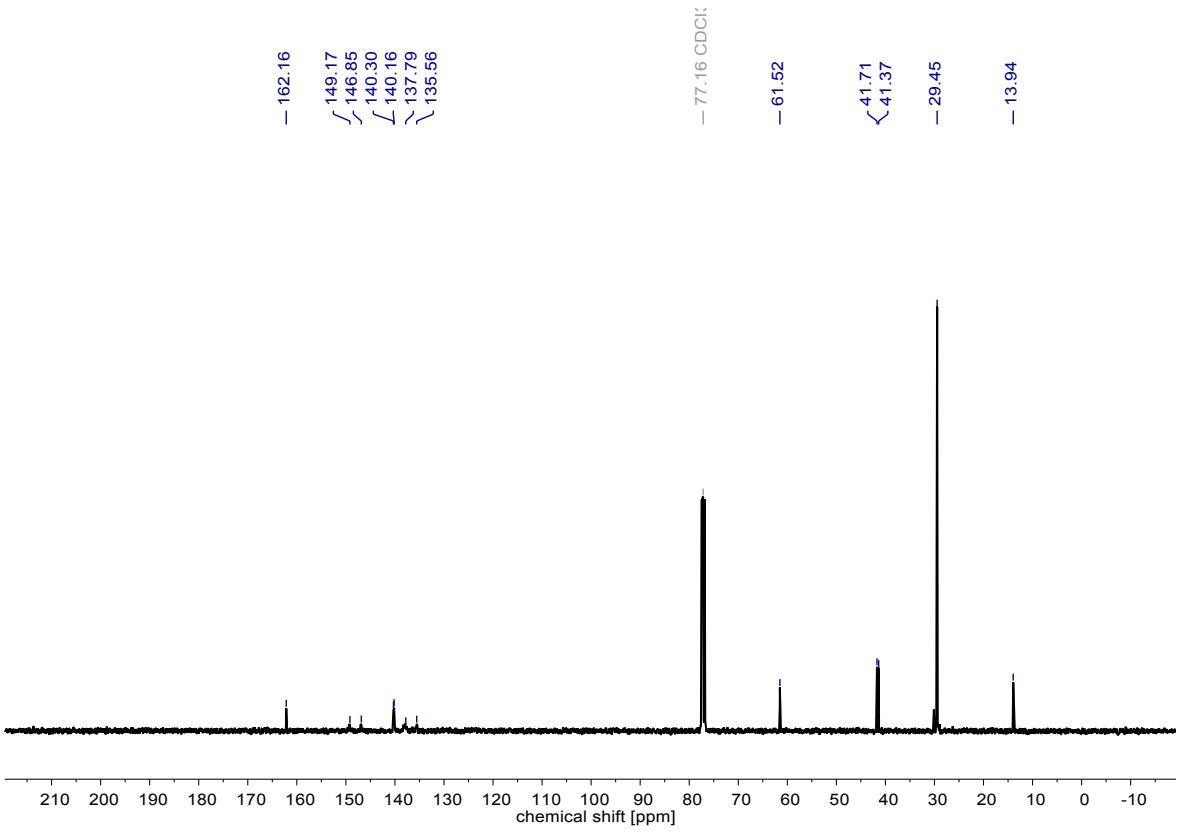
^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$, 298 K): δ -135.6 (d, $^3J_{F\text{-}F}$ = 19.4 Hz, *o*-C_6F_5), -161.0 (t, $^3J_{F\text{-}F}$ = 19.7 Hz, *p*-C_6F_5), -165.3 (t, $^3J_{F\text{-}F}$ = 18.6 Hz, *m*-C_6F_5) ppm.

^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$, 298 K): δ – 3.8 (bs) ppm.

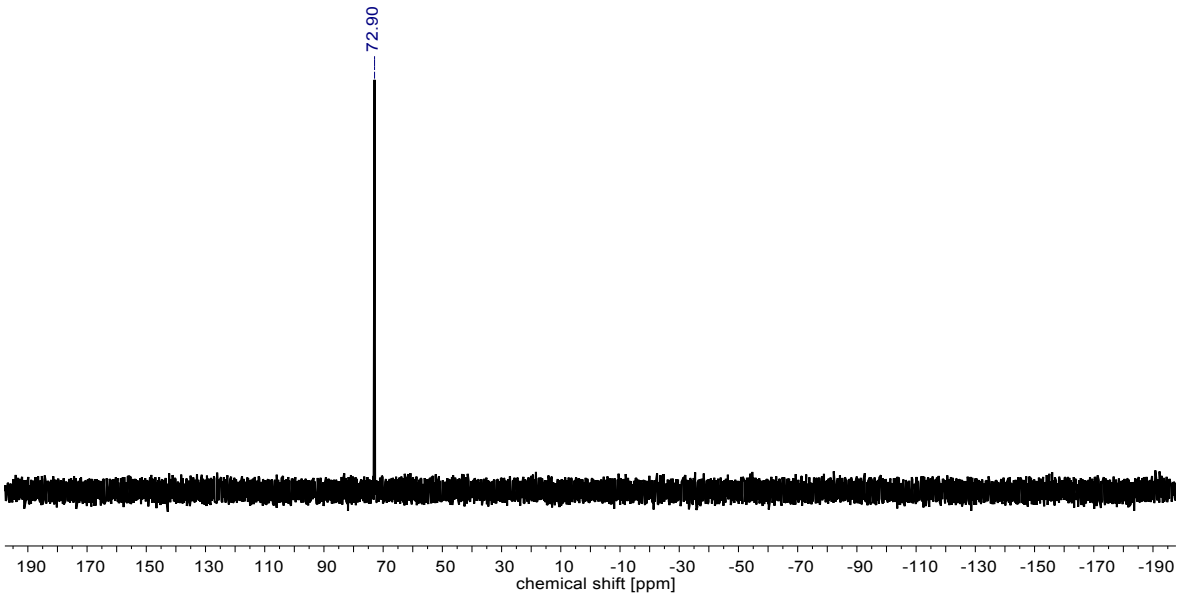
HR-MS (ESI+, CDCl$_3$) calculated for $C_{16}H_{34}N_2O_2P^+$: 317.24
found for $C_{16}H_{34}N_2O_2P^+$: 317.24
HR-MS (ESI-, CDCl$_3$) calculated for $C_{18}HBF_{15}O^-$: 528.99
found for $C_{18}HBF_{15}O^-$: 529.01



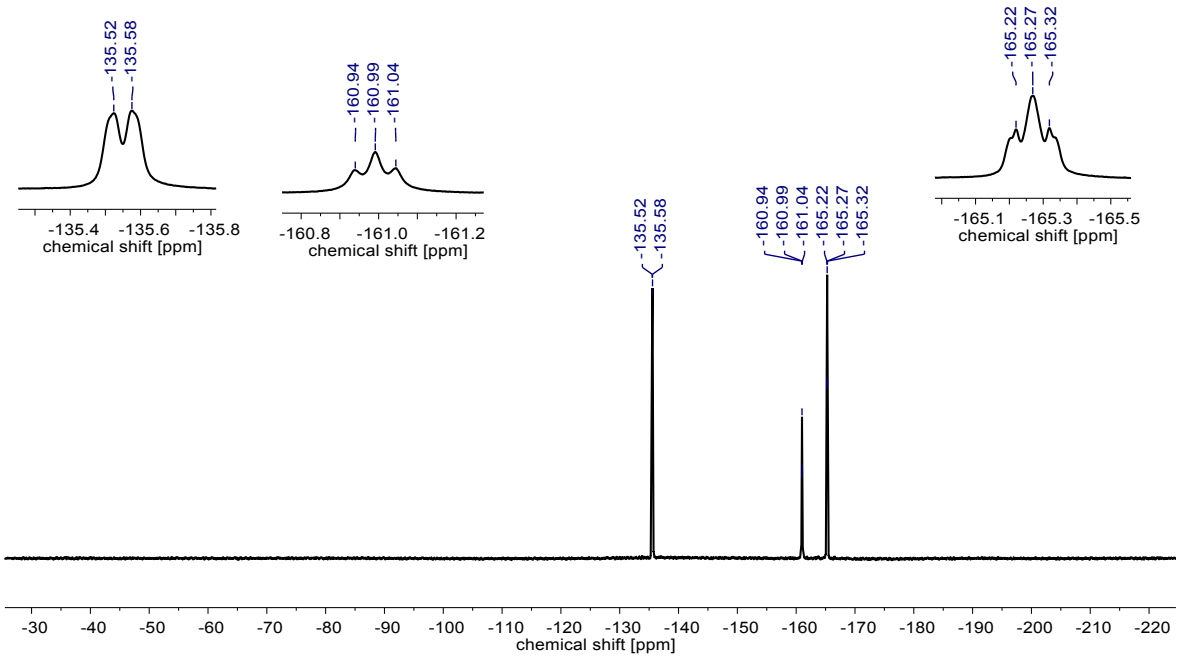
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu$_3$] [HOB(C_6F_5)$_3$].



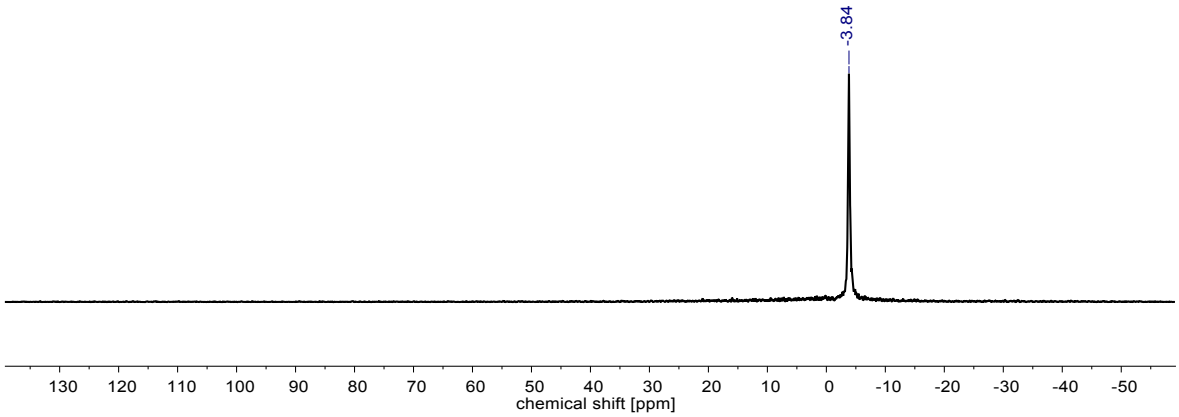
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu$_3$] [HOB(C_6F_5)$_3$].



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu$_3$] [HOB(C_6F_5)$_3$].

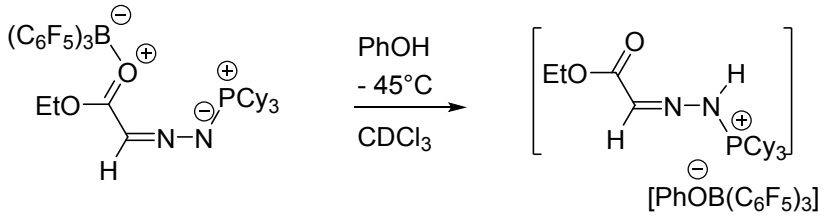


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu$_3$] [HOB(C_6F_5)$_3$].



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu_3] [$HOB(C_6F_5)_3$].

Synthesis of [EtOC(=O)CHNNHPCy$_3$] [PhOB(C$_6$F$_5$)$_3$] (9)



To the 20 mL vial with the reaction product of EtOC(=O(B(C$_6$F$_5$)$_3$))CHNNPCy$_3$ (0.071 g, 0.078 mmol) a solution of phenol (0.007 g, 0.078 mmol), diluted in $CDCl_3$ (0.3 mL) was added, in a dropwise fashion. The yellow solution was stirred at -45 °C for a period of 30 minutes and turned to a colorless solution over time.

Yield (by NMR): 98%

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.86 (bs, 1H, NH), 7.83 (s, 1H, CH), 6.94 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, C_6H_5), 6.69 – 6.59 (m, 3H, C_6H_5), 4.21 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 2.47 (q, $^2J_{H-P}$ = 12.5, 2.8 Hz, 3H, P-CH), 1.88 – 1.71 (m, 15H, C_6H_{11}), 1.52-1.39 (m, 6H, C_6H_{11}), 1.29 – 1.19 (m, 12H, 3H CH_3, 9H C_6H_{11}) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 161.9 (s, C=O), 159.7 (s, qC-O), 149.2 (bs, C_6F_5), 146.8 (bs, C_6F_5) 141.6 (d, $^3J_{C-P}$ = 14.1 Hz, N-CH), 140.1 (bs, C_6F_5), 138.0 (m, C_6F_5), 135.5 (m, C_6F_5) 129.8 (s, C_6H_5), 128.8 (s, C_6H_5), 119.9 (s, C_6H_5), 119.7 (s, C_6H_5), 115.4 (s, C_6H_5), 61.6 (s, CH_2), 32.1 (d, $^1J_{C-P}$ = 47.7 Hz, P-CH), 26.7 (d, $^2J_{C-P}$ = 12.8 Hz, C_6H_{11}), 26.0 (d, $^3J_{C-P}$ = 3.3 Hz, C_6H_{11}), 25.4 (bs, C_6H_{11}), 13.9 (s, CH_3) ppm.

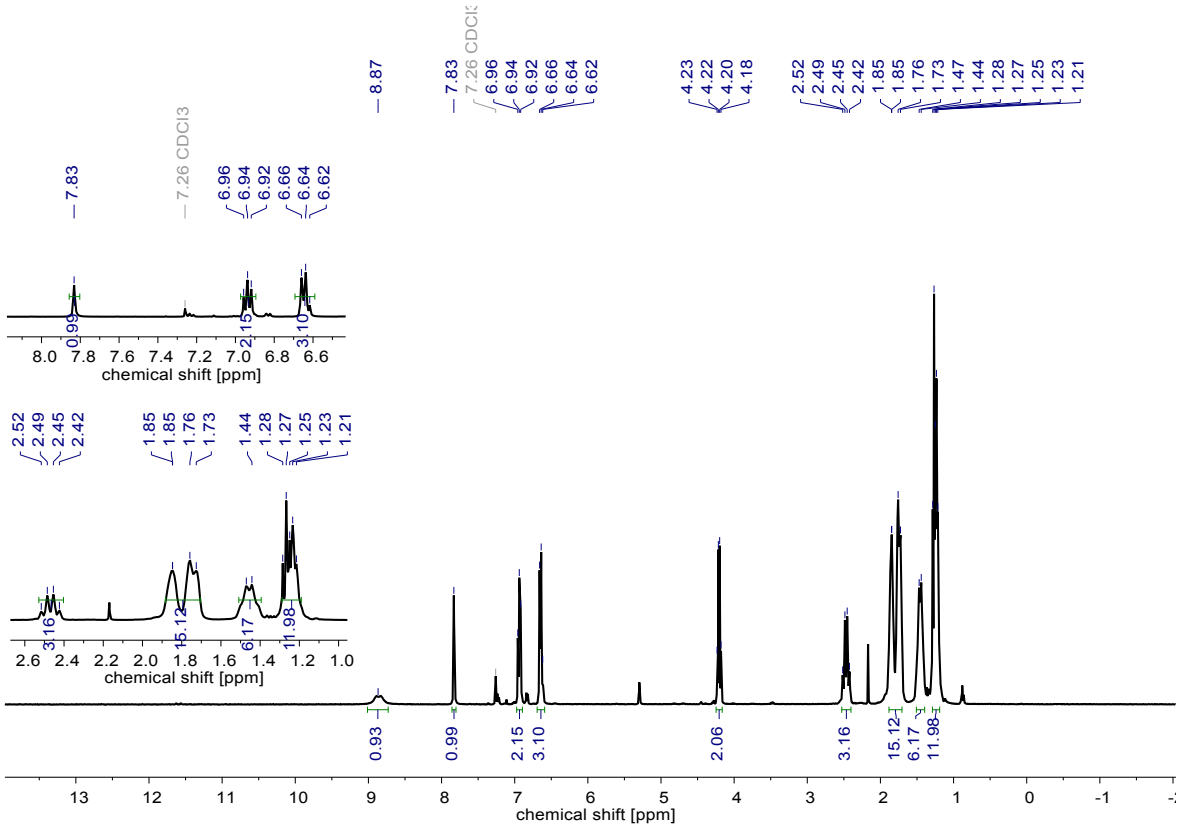
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 60.4 (s) ppm.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -133.9 (d, $^3J_{F-F}$ = 23.6 Hz, *o*-C_6F_5), -160.9 (t, $^3J_{F-F}$ = 20.4 Hz, *p*-C_6F_5), -165.8 (bt, $^3J_{F-F}$ = 24.5 Hz, *m*-C_6F_5) ppm.

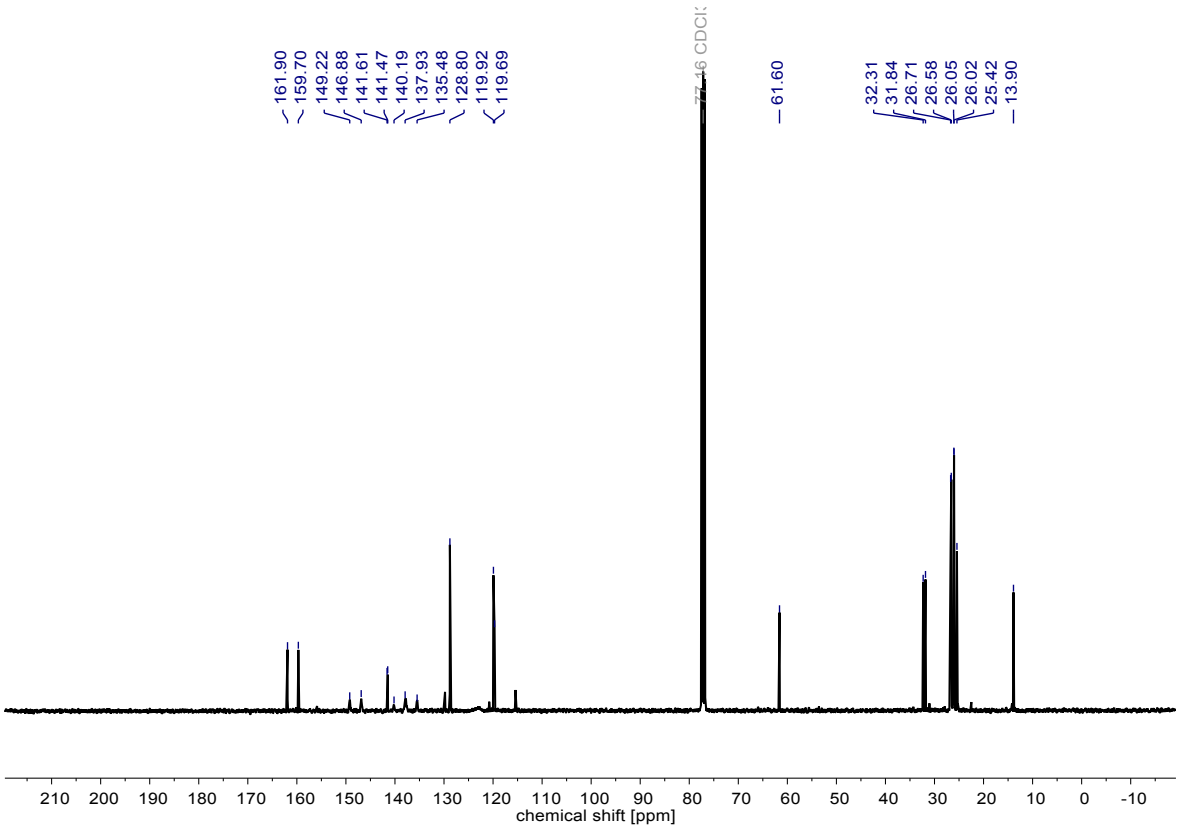
^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K): δ – 2.6 (s) ppm.

HR-MS (ESI+, $CDCl_3$) calculated for $C_{22}H_{40}N_2O_2P^+$: 395.28

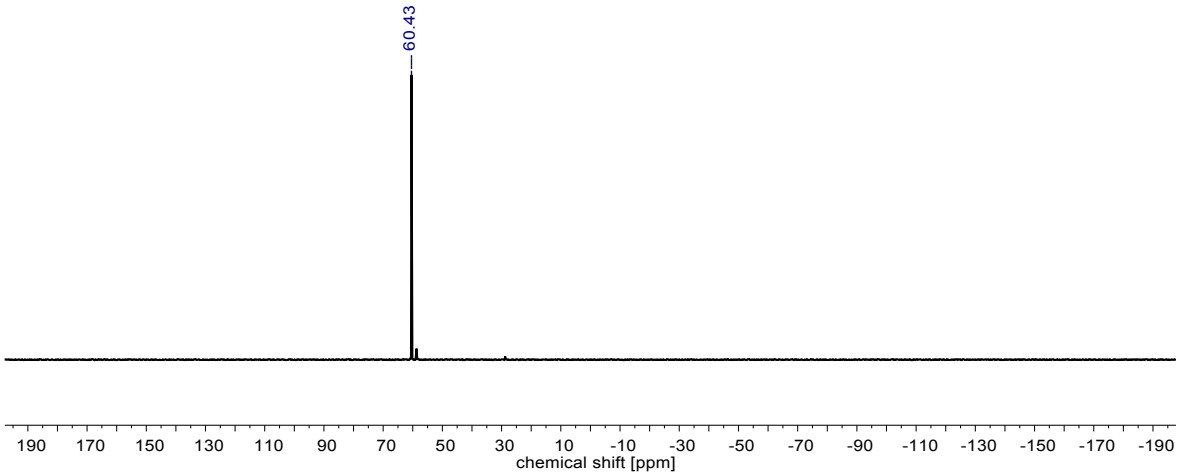
found for $C_{22}H_{40}N_2O_2P^+$: 395.28



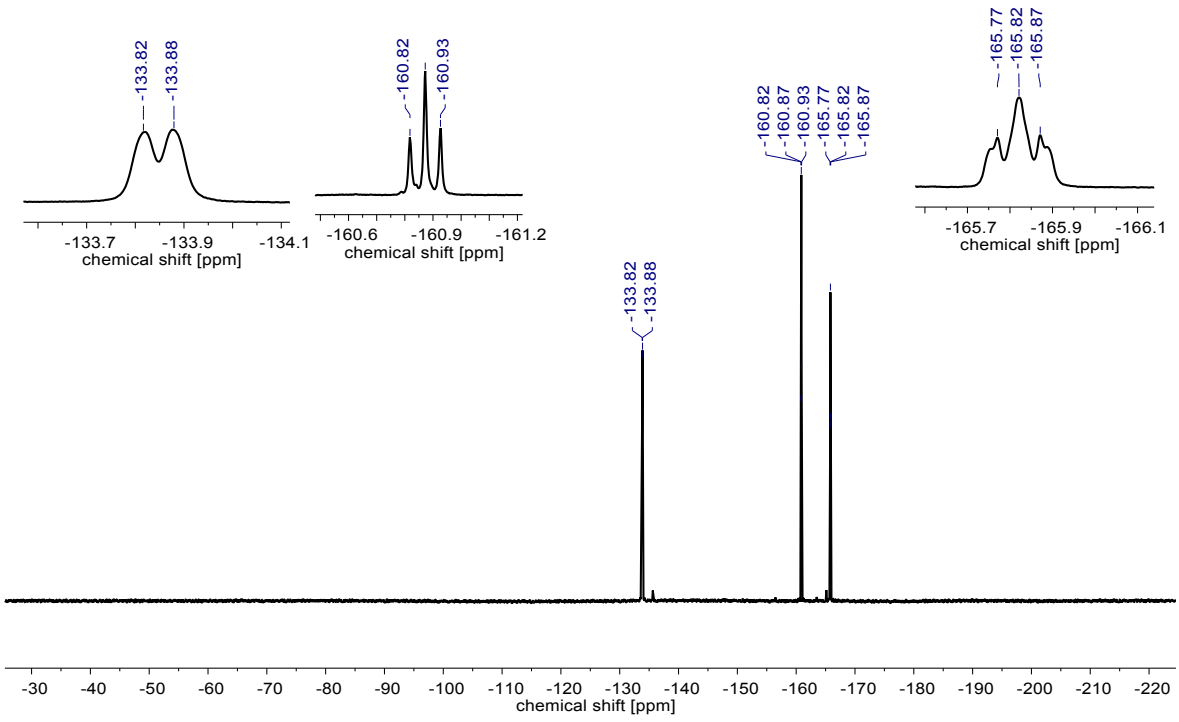
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHPCy$_3$] [PhOB(C_6F_5)$_3$].



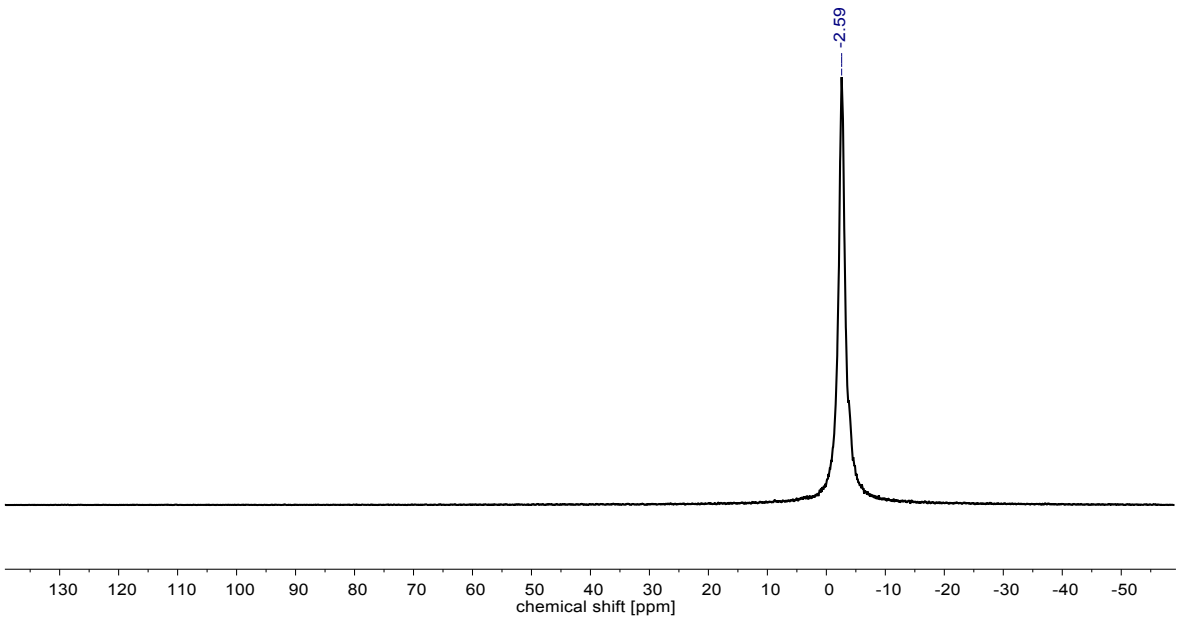
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHPCy$_3$] [PhOB(C_6F_5)$_3$].



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHPCy$_3$] [PhOB(C_6F_5)$_3$].

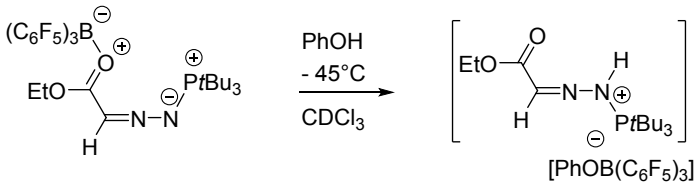


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHPCy$_3$] [PhOB(C_6F_5)$_3$].



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPCy_3]$ $[PhOB(C_6F_5)_3]$.

Synthesis of [EtOC(=O)CHNNHP*t*Bu$_3$] [PhOB(C$_6$F$_5$)$_3$] (10)



To the 20 mL vial with the pre-cooled reaction product of EtOC(=O(B(C$_6$F$_5$)$_3$))CHNNP*t*Bu$_3$ (0.078 mmol), a solution of phenol (0.007 g, 0.078 mmol), diluted in $CDCl_3$ (0.3 mL) was added, in a dropwise fashion. The yellow solution was stirred at -45 °C for a period of 30 minutes and turned to a colorless solution over time.

Yield (by NMR): >99%

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.26 (d, $^2J_{H\text{-}P}$ = 24.2 Hz, 1H, NH), 7.80 (s, 1H, CH), 6.97 – 6.92 (m, 2H, C_6H_5), 6.68 – 6.57 (m, 3H, C_6H_5), 4.19 (q, $^3J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2), 1.56 (d, $^3J_{H\text{-}P}$ = 14.9 Hz, 27H, *t*Bu$_3$), 1.27 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, 3H, CH_3) ppm.

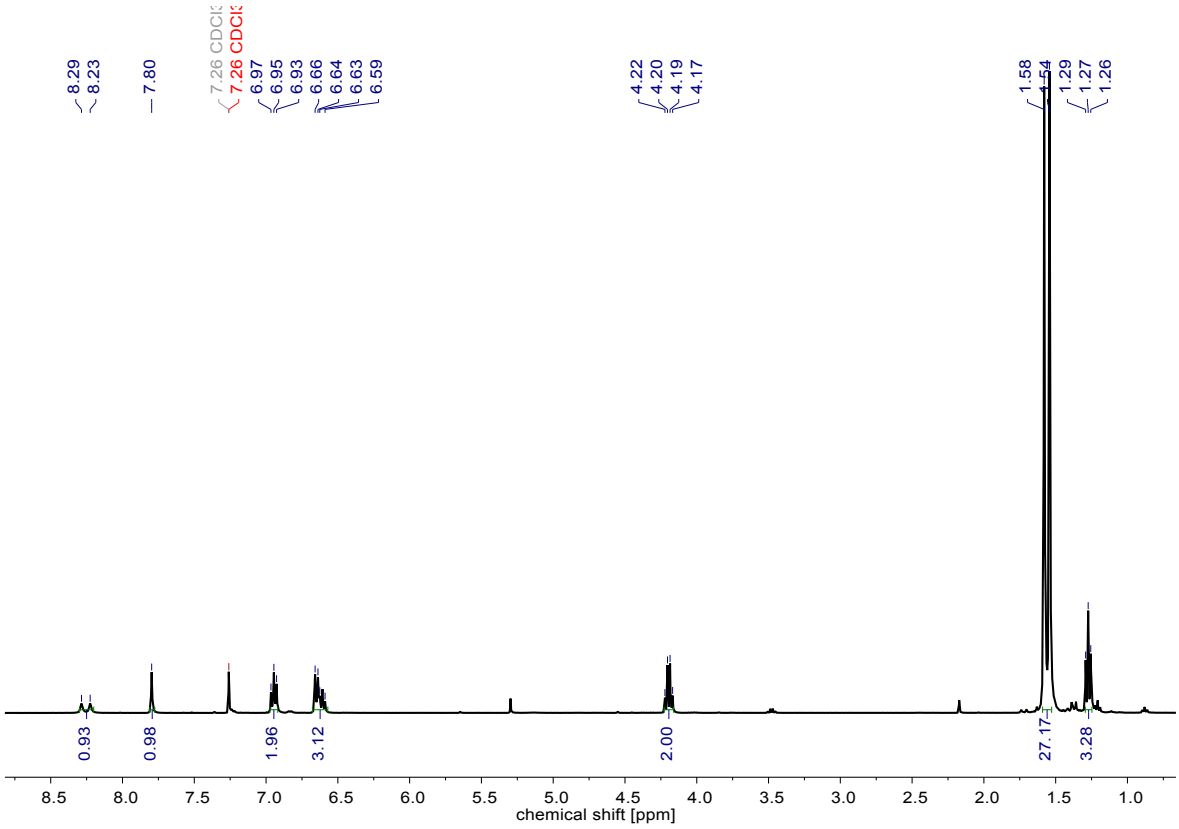
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 161.8 (s, C=O), 160.3 (s, C-O), 149.3 (bs, C_6F_5), 146.8 (bs, C_6F_5), 141.1 (d, $^3J_{C\text{-}P}$ = 12.3 Hz N-CH), 140.0 (bs, C_6F_5), 137.8 (bs, C_6F_5), 135,5 (bs, C_6F_5), 128.8 (s, C_6H_5), 119.7 (s, C_6H_5), 119.0 (s, C_6H_5), 61.8 (s, CH_2), 41.6 (d, $^1J_{C\text{-}P}$ = 33.1 Hz, qC, *t*Bu$_3$), 29.3 (s,9Me, *t*Bu$_3$), 13.8 (s, CH_3) ppm.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 74.0 (bs) ppm.

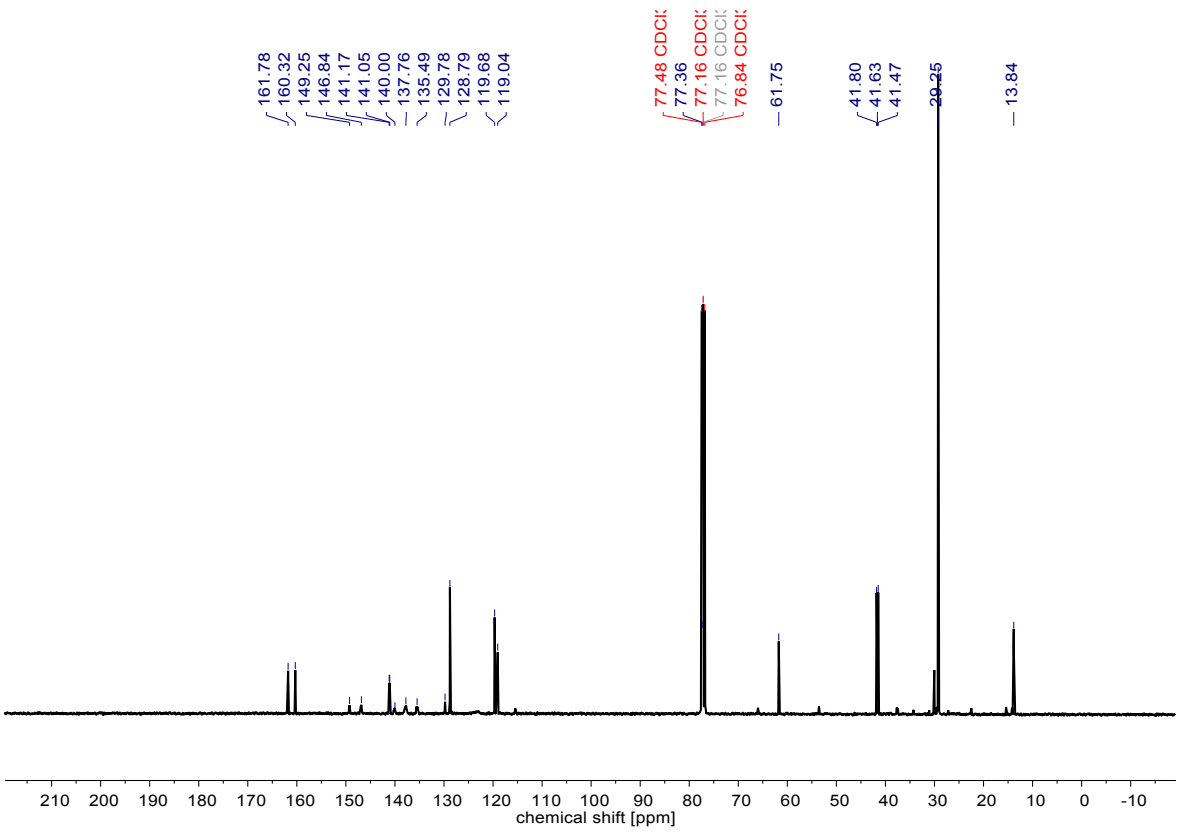
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K): δ -133.4 (d, $^3J_{F\text{-}F}$ = 21.5 Hz, *o*-C_6F_5), -161.2 (t, $^3J_{F\text{-}F}$ = 20.4 Hz, *p*-C_6F_5), -165.9 (bt, $^3J_{F\text{-}F}$ = 20.3 Hz, *m*-C_6F_5) ppm.

^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K): δ – 2.8 (s) ppm.

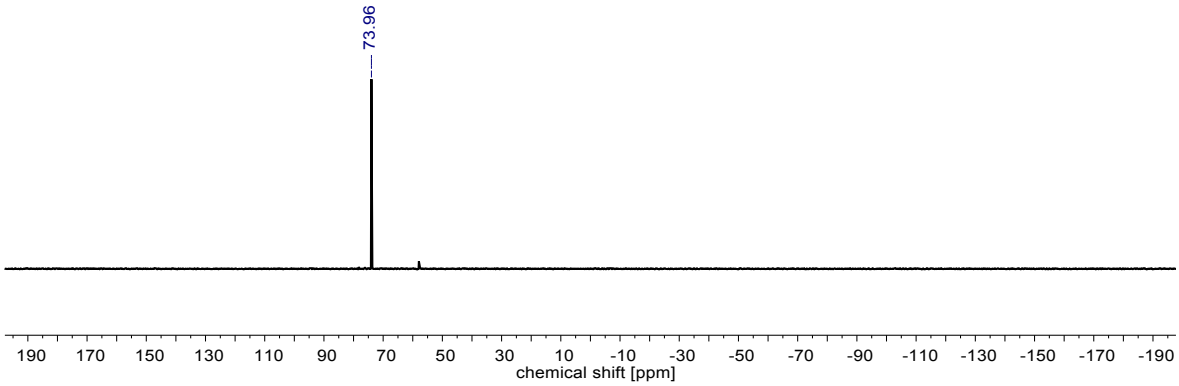
HR-MS (ESI+, $CDCl_3$) calculated for $C_{16}H_{34}N_2O_2P^+$: 317.24
found for $C_{16}H_{34}N_2O_2P^+$: 317.24



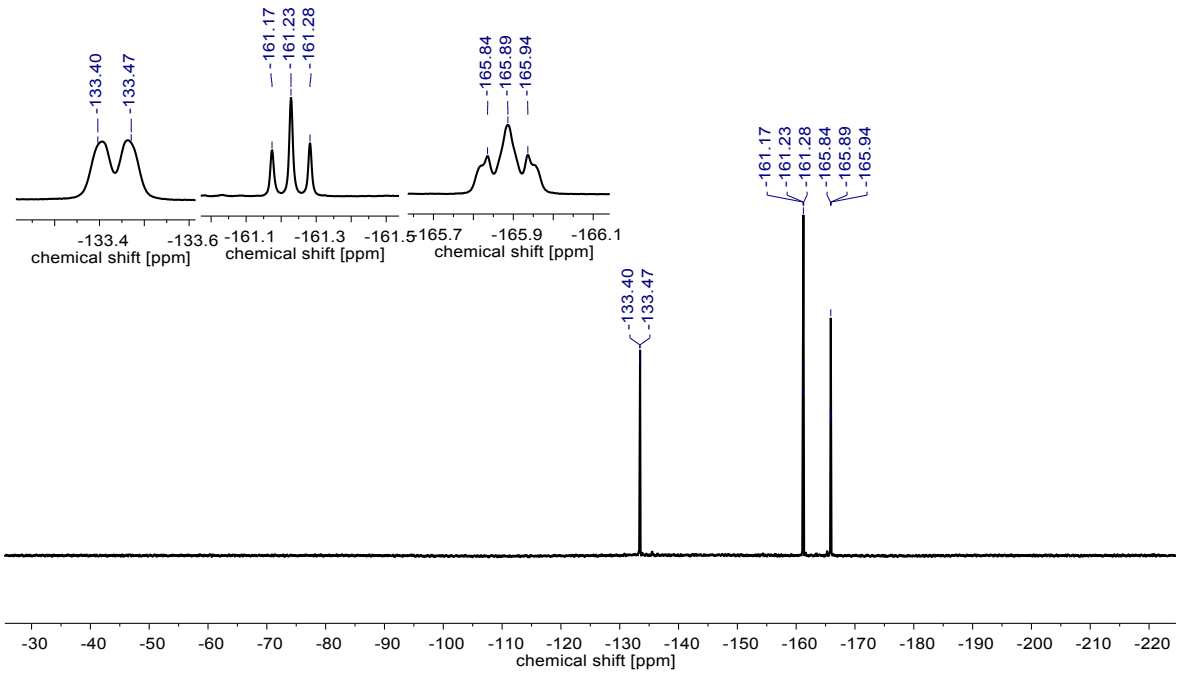
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu$_3$] [PhOB(C_6F_5)$_3$].



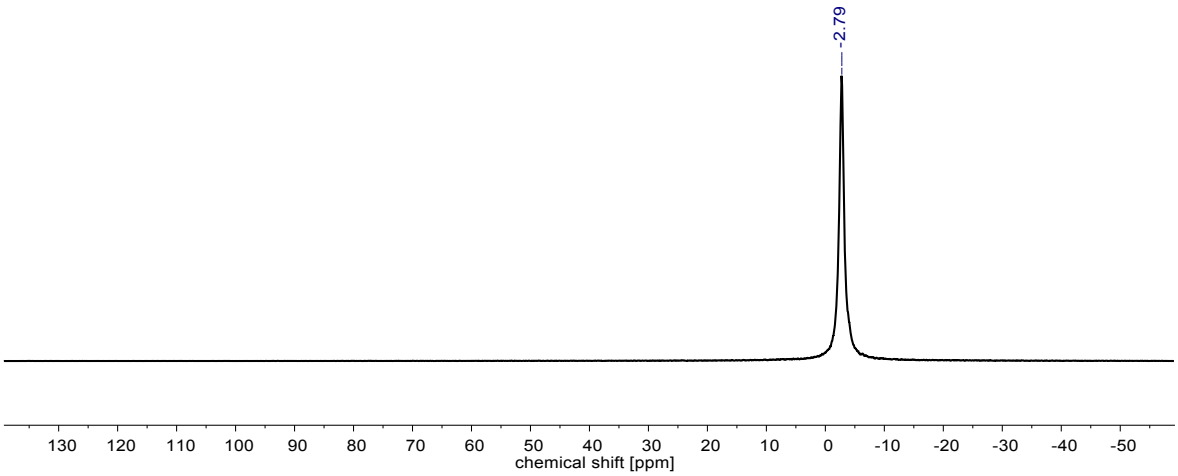
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu$_3$] [PhOB(C_6F_5)$_3$].



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPtBu_3][PhOB(C_6F_5)_3]$.

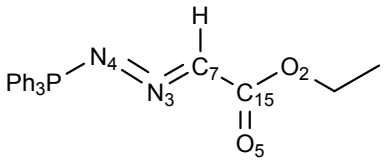


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of $[EtOC(=O)CHNNHPtBu_3][PhOB(C_6F_5)_3]$.



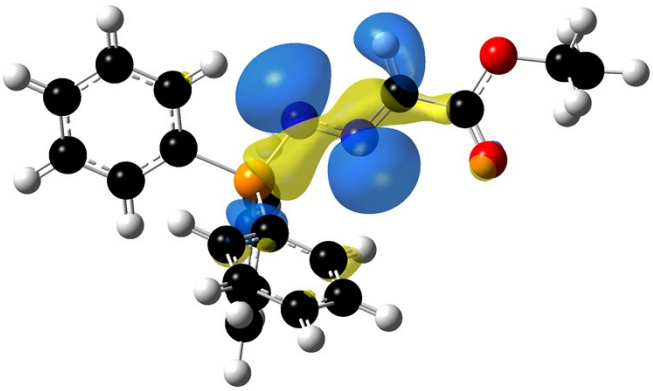
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) spectrum of [EtOC(=O)CHNNHP*t*Bu_3] [PhOB(C_6F_5)$_3$].

Surface contour plot Compound 1

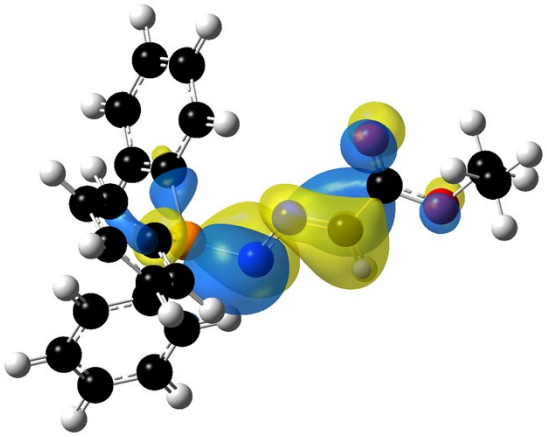


ChemDraw

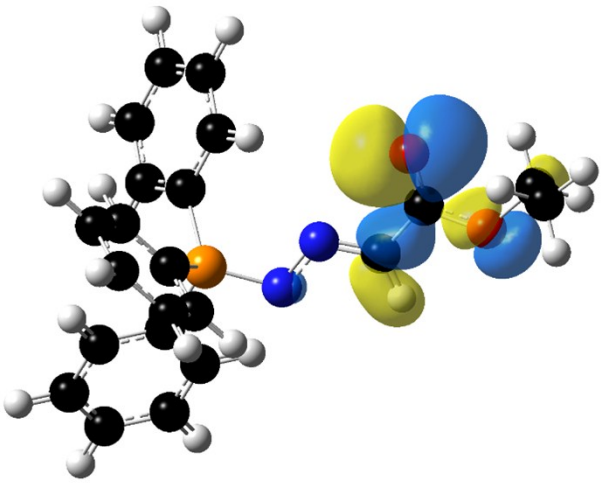
a)



b)

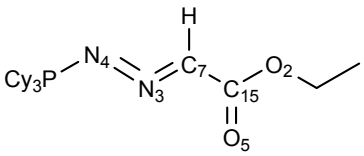


c)



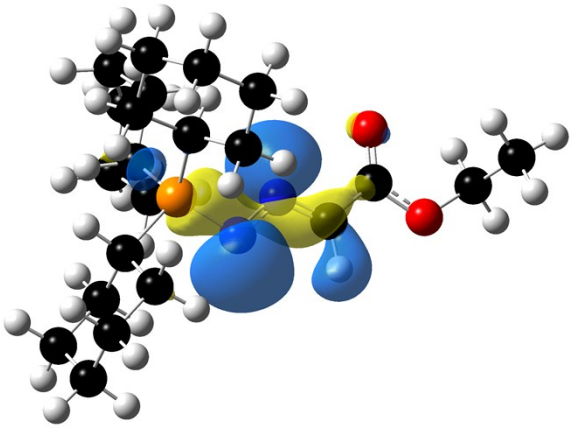
Surface contour plot (isovalue 0.03) of a) the HOMO, b) HOMO-1 and c) the HOMO-2 of compound 1, featuring significant contribution from the O lone pairs.

Surface contour plot Compound 2

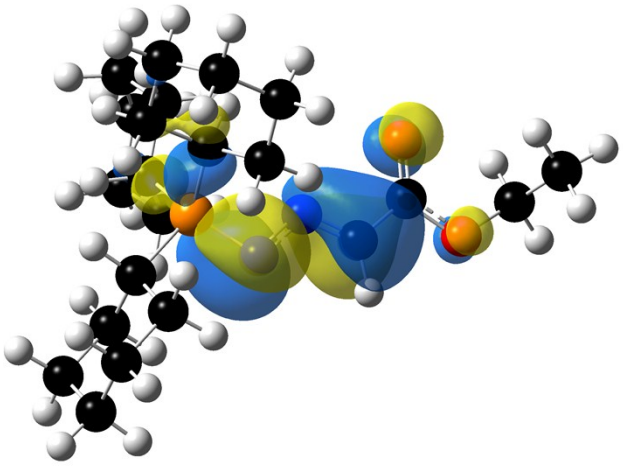


ChemDraw

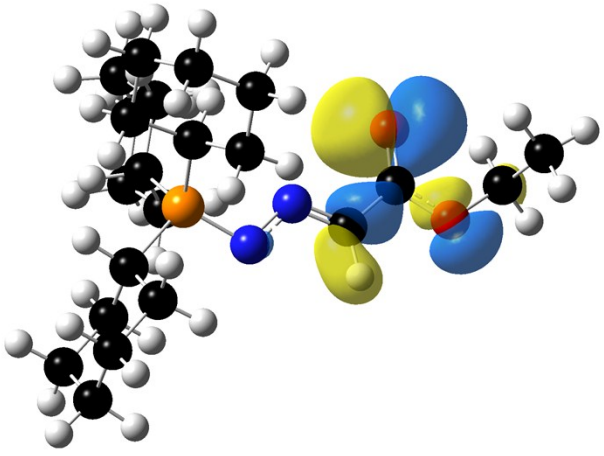
a)



b)

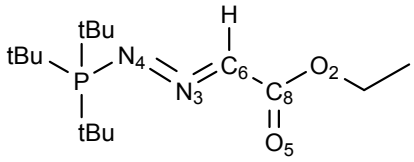


c)



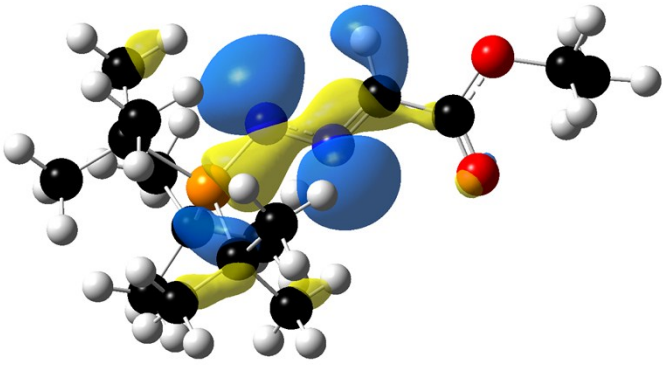
Surface contour plot (isovalue 0.03) of a)the HOMO, b) the HOMO-1 and c) the HOMO-2 of compound 2, featuring significant contribution from the O lone pairs.

Surface contour plot Compound 3

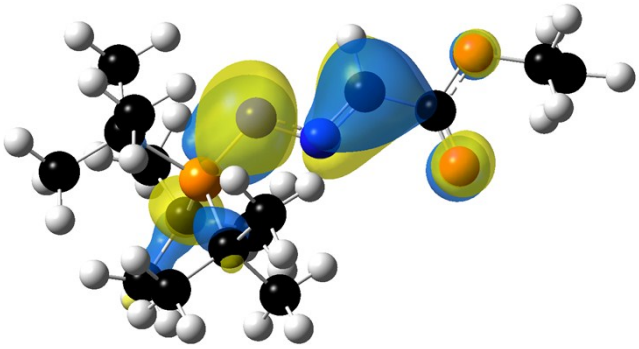


ChemDraw

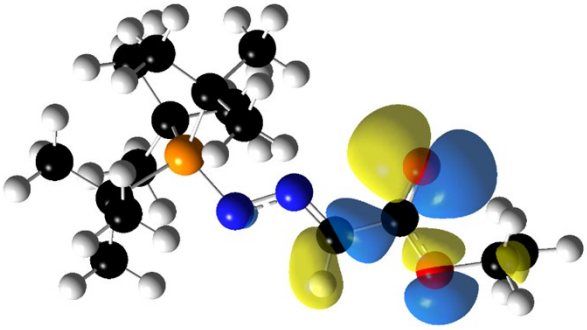
a)



b)



c)



Surface contour plot (isovalue 0.03) of a)the HOMO, b) the HOMO-1 and c) the HOMO-2 of compound 3, featuring significant contribution from the O lone pairs.

Computational Details

Electronic structure calculations, including geometry optimization, frequency calculations, and energy calculations, were performed using Gaussian 16[i] using the BP86 functional and the def2-TZVPP basis set[ii,iii,iv,v]. Natural bond orbital and natural population analyses were performed using Gaussian 09[vi] on optimized structures using NBO 6.0[vii]. X-ray coordinates were used as the starting geometry for the compounds 1-3 and the published electronic structure was used for the starting geometry for Ph3PNNPPh3[viii]. The Cartesian coordinates of the optimized structures are collected in tables 1-3. The absence of any imaginary frequency with an absolute magnitude greater than 10 cm^{-1} confirmed that each optimized structure was indeed located at a minimum on its potential energy hypersurface.

Table 1. Cartesian coordinates for the optimized structure of compound 1.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.570895	6.031243	3.328888
2	8	0	-0.740962	10.124569	2.557730
3	7	0	1.835502	7.804067	3.205424
4	7	0	2.298724	6.710540	2.538220
5	8	0	0.625978	10.092997	4.396713
6	6	0	3.249702	5.547981	5.055756
7	6	0	0.842325	8.431307	2.651533
8	1	0	0.405299	8.107869	1.697389
9	6	0	3.953387	4.546619	2.362601
10	6	0	2.828763	6.545691	5.958499
11	1	0	2.731878	7.578538	5.620950
12	6	0	5.070460	7.073039	3.362074
13	6	0	2.936959	3.949326	1.597540
14	1	0	1.950764	4.413096	1.574081
15	6	0	0.283175	9.611797	3.328595
16	6	0	5.238250	3.980035	2.381737
17	1	0	6.036080	4.450897	2.958546
18	6	0	2.496276	6.197281	7.269092
19	1	0	2.162774	6.971928	7.961146
20	6	0	2.993973	3.874232	6.796435
21	1	0	3.057148	2.834173	7.120418
22	6	0	3.322505	4.210499	5.480206
23	1	0	3.633424	3.431180	4.783221
24	6	0	5.303178	7.910737	2.257496
25	1	0	4.582182	7.931991	1.438675
26	6	0	5.980107	7.063513	4.431453
27	1	0	5.794016	6.431417	5.300903
28	6	0	2.582449	4.866122	7.691433
29	1	0	2.323329	4.601160	8.717864
30	6	0	4.489202	2.226909	0.888783
31	1	0	4.698396	1.324408	0.312076
32	6	0	3.210529	2.793546	0.862370
33	1	0	2.421431	2.335703	0.263955
34	6	0	5.502399	2.820783	1.647926
35	1	0	6.502988	2.386280	1.663362
36	6	0	-1.398262	11.302835	3.086633
37	1	0	-1.412407	11.238160	4.183440
38	1	0	-2.425657	11.241634	2.702340
39	6	0	6.438717	8.721496	2.222776
40	1	0	6.611566	9.375065	1.366469
41	6	0	7.116753	7.876508	4.390253
42	1	0	7.818554	7.868960	5.225711
43	6	0	7.346891	8.703794	3.287214
44	1	0	8.231168	9.342582	3.260144
45	6	0	-0.708695	12.579018	2.624617
46	1	0	-1.269094	13.456878	2.979751
47	1	0	-0.658955	12.624019	1.527697
48	1	0	0.310404	12.636497	3.028724

Table 2. Cartesian coordinates for the optimized structure of compound 2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.358199	5.981144	3.304006
2	8	0	-0.900863	10.170641	3.058144
3	7	0	1.681305	7.778935	3.355757
4	7	0	1.990023	6.642449	2.668466
5	8	0	0.770409	10.168675	4.627218
6	6	0	0.624573	8.425658	2.955828
7	1	0	0.018339	8.078785	2.108418
8	6	0	0.230867	9.651433	3.660608
9	6	0	-1.415846	11.394580	3.635545
10	1	0	-1.230783	11.381531	4.718680
11	1	0	-2.497845	11.355753	3.448080
12	6	0	-0.786617	12.622251	2.991109
13	1	0	-1.247064	13.536078	3.395917
14	1	0	-0.936680	12.615202	1.902409
15	1	0	0.290473	12.659497	3.200336
16	6	0	3.636759	4.429032	2.344021
17	6	0	2.562563	3.355717	2.636750
18	6	0	3.729594	4.701638	0.824963
19	1	0	4.612338	4.044209	2.695971
20	6	0	2.813813	2.070719	1.830776
21	1	0	1.573629	3.768806	2.380149
22	1	0	2.542187	3.114179	3.709380
23	6	0	3.967357	3.407798	0.029121
24	1	0	2.792706	5.181601	0.501101
25	1	0	4.538330	5.415085	0.612122
26	6	0	2.897403	2.350452	0.325605
27	1	0	2.015400	1.343534	2.045759
28	1	0	3.758027	1.607065	2.168516
29	1	0	3.992081	3.641389	-1.046648
30	1	0	4.962096	2.999194	0.282737
31	1	0	3.111598	1.421879	-0.226000
32	1	0	1.917966	2.711629	-0.033101
33	6	0	4.849156	7.087948	3.165748
34	6	0	6.198280	6.357126	3.324692
35	6	0	4.842484	7.988175	1.911855
36	1	0	4.716958	7.762625	4.030049
37	6	0	7.363289	7.361783	3.367421
38	1	0	6.346316	5.672559	2.471634
39	1	0	6.207599	5.732859	4.232819
40	6	0	6.006868	8.990390	1.972591
41	1	0	4.941444	7.376149	1.001122
42	1	0	3.881741	8.514148	1.836288
43	6	0	7.359834	8.283536	2.139531
44	1	0	8.319656	6.820382	3.440775
45	1	0	7.277300	7.972716	4.282947
46	1	0	6.008482	9.610795	1.062978
47	1	0	5.845433	9.679559	2.819775
48	1	0	8.172035	9.022733	2.218660
49	1	0	7.570830	7.684109	1.235945
50	6	0	3.225727	5.501655	5.114854
51	6	0	3.839279	6.516588	6.104784
52	6	0	1.746792	5.241741	5.491357
53	1	0	3.786713	4.550577	5.201918
54	6	0	3.705709	6.025593	7.557156
55	1	0	3.320910	7.482709	5.989582
56	1	0	4.902573	6.690199	5.883959
57	6	0	1.621359	4.738762	6.937839
58	1	0	1.193750	6.186633	5.377362
59	1	0	1.280218	4.529136	4.797885
60	6	0	2.249156	5.724602	7.931082
61	1	0	4.130091	6.780421	8.237490
62	1	0	4.312575	5.111188	7.686649
63	1	0	0.558902	4.576253	7.177386
64	1	0	2.117306	3.755646	7.032318
65	1	0	2.192320	5.328152	8.956905
66	1	0	1.670739	6.664197	7.922686

Table 3. Cartesian coordinates for the optimized structure of compound 3.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	3.331677	-0.576582	0.026990
2	8	0	-1.092243	3.428923	-0.891066
3	7	0	1.495319	1.158768	-0.105163
4	7	0	2.135482	0.192801	-0.811181
5	8	0	-0.047185	3.207713	1.136861
6	6	0	0.568776	1.815516	-0.742311
7	1	0	0.326689	1.612552	-1.794054
8	6	0	-0.174631	2.860722	-0.027839
9	6	0	-1.904054	4.492585	-0.336152
10	1	0	-2.092282	4.278524	0.725085
11	1	0	-2.849040	4.438989	-0.894109
12	6	0	-1.236354	5.850108	-0.507533
13	1	0	-1.905071	6.645134	-0.144720
14	1	0	-1.011137	6.046775	-1.565079
15	1	0	-0.303170	5.897816	0.068772
16	6	0	4.925478	0.508726	0.078598
17	6	0	3.596687	-2.125494	-1.060270
18	6	0	2.790689	-1.044885	1.818711
19	6	0	2.896137	0.179791	2.755753
20	1	0	2.330314	1.034089	2.363119
21	1	0	2.453062	-0.106978	3.723639
22	1	0	3.931811	0.481160	2.954203
23	6	0	1.292744	-1.430059	1.788067
24	1	0	0.988091	-1.655910	2.822834
25	1	0	0.678183	-0.596763	1.428346
26	1	0	1.077880	-2.314020	1.180245
27	6	0	3.611481	-2.203547	2.419447
28	1	0	3.270711	-2.362928	3.455635
29	1	0	3.466944	-3.150461	1.883792
30	1	0	4.687290	-1.989423	2.459697
31	6	0	4.914926	-2.866701	-0.763908
32	1	0	4.999269	-3.193461	0.280167
33	1	0	4.952150	-3.769146	-1.394629
34	1	0	5.799314	-2.265730	-1.009930
35	6	0	2.415003	-3.099099	-0.852568
36	1	0	2.518783	-3.916697	-1.583294
37	1	0	2.401892	-3.554352	0.144906
38	1	0	1.452419	-2.604193	-1.035177
39	6	0	3.560550	-1.721156	-2.554321
40	1	0	3.557796	-2.648669	-3.149445
41	1	0	2.654722	-1.148168	-2.783168
42	1	0	4.430976	-1.134604	-2.863392
43	6	0	6.026244	-0.022947	1.016707
44	1	0	6.903370	0.639929	0.933998
45	1	0	5.720186	-0.020783	2.070097
46	1	0	6.357395	-1.036368	0.755149
47	6	0	4.523464	1.940178	0.503939
48	1	0	5.420255	2.575758	0.422233
49	1	0	3.749596	2.355957	-0.151804
50	1	0	4.160249	2.006875	1.532952
51	6	0	5.501489	0.633517	-1.348288
52	1	0	6.294587	1.397999	-1.326853
53	1	0	5.956793	-0.296073	-1.711149
54	1	0	4.739371	0.963367	-2.066499

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