Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Di-*tert*-butyldiphosphatetrahedrane: Catalytic Synthesis of the Elusive Phosphaalkyne Dimer

*Gabriele Hierlmeier, Peter Coburger, Michael Bodensteiner, and Robert Wolf**

anie_201910505_sm_miscellaneous_information.pdf

The Supporting Information contains:

1 Synthetic Procedures

1.1 General Synthetic Methods

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H_2O and <0.1 ppm O_2).*t*BuCP,[1,2] AdCP,[3] [(NHC)Ni(CO)$_3$] (NHC = IMes, IPr, *i*Pr$_2$Im^{Me})[4,5], [(IMes)NiP(CO)]$_2$[6], [(IMes)Ni(H_2CCHTMS)$_2$][7] and [Ag(CH_2Cl_2)(pftb)][8] were prepared according to procedures previously reported in the chemical literature. $Ni(CO)_4$ in toluene (c = 0.96 M) was kindly provided by the group of Manfred Scheer.

Solvents were dried and degassed with a MBraun SPS800solvent purification system. All dry solvents except *n*-hexane and *n*-pentane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane and *n*-pentane were stored over a potassium mirror.

1.2 Analytical Techniques

NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers at 300 K unless otherwise noted and internally referenced to residual solvent resonances (^{1}H NMR: [D_8]-THF: 1.72 ppm, C_6D_6: 7.16 ppm, ^{13}C{^{1}H} NMR: [D_8]-THF: 25.31 ppm, C_6D_6: 128.06 ppm,). Chemical shifts δ are given in ppm referring to external standards of tetramethylsilane (^{1}H, ^{13}C{^{1}H}), 85% phosphorus acid (^{31}P and ^{31}P{^{1}H} spectra). ^{1}H and ^{13}C NMR signals were assigned based on 2D NMR spectra (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMQC).

UV-Vis spectra were recorded on a Varian Cary 50 spectrometer. IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit. High resolution mass spectra were recorded by the analytical department at the University of Regensburg using a Jeol AccuTOF GCX.

Yields of the catalytic and kinetic studies were determined using Gas chromatography with FID detector (GC-FID) by Shimadzu GC2010plus. H_2 was used as carrier gas. A Restek Rxi® (30m x 0.25 mm x 0.25 µm) column was used. The standard heating procedure was: 50°C (2 min), 25°C/min → 280°C (5 min). **1a** was calibrated with *n*-pentadecane on the GC-FID after determination of the concentration via NMR with triphenylphosphine.

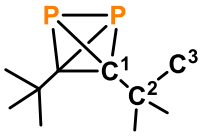
1a was also analyzed via GC-MS. An Agilent 7820A GC system with mass detector 5977B was used with. H_2 as carrier gas and a HP-5MS (30m x 0.25 mm x 0.25 µm) column were used. The standard heating procedure was: 50°C → 300°C.

1.3 Synthesis of Compounds

(*t*BuCP)$_2$ (1a):

To a solution of [(IMes)Ni(CO)$_3$] (100 mg, 0.224 mmol, 1.0 eq.) was added *n*-hexane (25 mL) and *t*BuCP (4.4 mL, 2.56 M in O(SiMe$_3$)$_2$, 11.2 mmol, 50.0 eq.). A color change from colorless to yellow was observed. The solution was heated to 60 °C for 18 h. Subsequently, the reaction flask was connected to a short connection tube with a Schlenk flask. The solvent was condensed into the Schlenk flask under full vacuum ($p < 1 \cdot 10^{-3}$ mbar) with the reaction flask at room temperature and the collection flask cooled to −30 °C. The condensate contains minor amounts of **1a**, *n*-hexane, O(SiMe$_3$)$_2$, residual *t*BuCP and (*t*BuCP)$_4$ (**2a**) in varying ratios. Subsequently, a new collection flask was attached to the connection tube and the collection flask was cooled to 77 K using liquid nitrogen. The reaction flask was heated to 60 °C and the product was condensed under full vacuum ($p < 1 \cdot 10^{-3}$ mbar) as a yellow liquid. The concentration of **1a** was determined using PPh$_3$ as an internal standard via $^{31}P\{^1H\}$ NMR and ^1H NMR spectroscopy. The concentration was found to be between 3.0 and 3.5 mol/L.

1a is a yellow, pyrophoric liquid (see Figure S2). It starts smoking on contact with air and ignites organic materials (e.g. tissue paper). Neat **1a** can be stored in the freezer at −80 °C for several weeks. **1a** slowly decomposes at room temperature to **2a** within a few hours. Single crystals suitable for X-ray diffraction of **2a** were obtained by leaving the sample at room temperature for 1 week.[9]



$C_{10}H_{18}P_2$, MW = 200.20 g/mol

Yield: 623 mg, 0.9 mL (55% yield, determined by measurement of concentration (3.4 M)

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.07 (s, 18H, C^3H_3) ppm.

$^{13}C\{^1H\}$ NMR (100.61 MHz, 300 K, C_6D_6) δ = 24.4 (t, $^1J_{CP}$ = 46.7 Hz, C^1), 25.6 (t, $^2J_{CP}$ = 5.7 Hz, C^2), 31.4 (s, C^3) ppm.

$^{31}P\{^1H\}$ (161.98 MHz, 300 K, C_6D_6) δ = −468.2 (s) ppm.

Elemental Analysis calcd. C 59.99, H 9.06; found C 59.66, H 8.96.

IR (ATR, cm^{-1}) ν = 2958 (vs), 2924 (w), 2901 (w), 1469 (s), 1459 (s), 1360 (s), 1267 (w), 1196 (s), 1055 (m), 919 (s), 855 (s), 823 (m), 756 (w), 645 (w), 467 (w).

melting point −32 °C.

UV/vis (*n*-hexane): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 275 (1200), 350 (sh, 300).

HRMS (EI-MS) m/z = 200.0879 (M^+, calculated 200.0878), 185.0648 (M^+-CH_3), 123.1172 ($M^+-CH_3-P_2$), 81.0705 (M^+-P_2-C*t*Bu), 57.0704 (*t*Bu).

GC-MS: Using GC-MS, **1a** was detected in the chromatogram with a retention time of 6.0 minutes. The tetrameric species **2a** was detected at 15.6 min (see Figure S1).

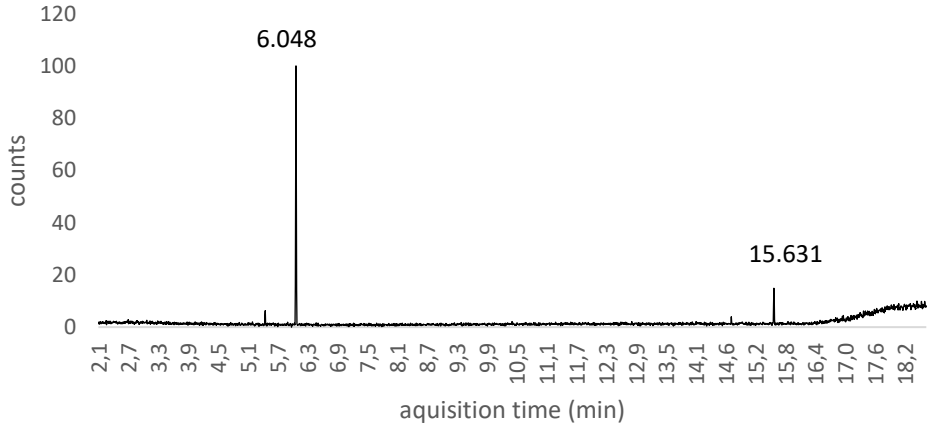


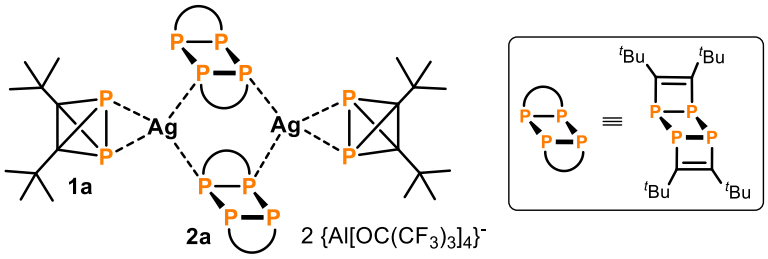
Figure S1. Chromatogram of a solution of **1a** in $O(SiMe_3)_2$.

Figure S2. Photograph of **1a** at ambient temperature in a Schlenk flask.

Upon prolonged air contact, the sample solidified. Elemental analysis of the solid formed were lower in carbon and hydrogen, possibly due to the formation of oxides [found C 58.85, H 8.82].

[Ag(1a)(2a)]$_2$[pftb]$_2$ (3):

To a solution of [Ag(CH$_2$Cl$_2$)$_2$(pftb)] (0.108 g, 0.09 mmol, 1.0 eq.) in dichloromethane (2 ml) was added a solution of **1a** in toluene (40 ml, 5.0 mM, 0.200 mmol, 2.3 eq.) at room temperature. The reaction mixture was stirred for 20 min under the exclusion of light. Subsequently, the solvent was removed *in vacuo*. The beige solid was washed with *n*-hexane (3 x 10 ml) and dried under reduced pressure. The residue was dissolved in dichloromethane (1 mL) and stored at −30 °C overnight to afford colorless crystals of **3** suitable for X-ray crystallography. The crystals were isolated by decanting the supernatant solution and dried *in vacuo* to afford a colorless solid.



$C_{92}H_{108}Ag_2Al_2F_{72}O_8P_{12}$, MW = 3351.14 g/mol

Yield: 43 mg, 29 %

^{1}H NMR (400.13 MHz, 300 K, CD_2Cl_2) δ = 1.17 (s, 36H, Ag-**1a**-H), 1.46 (s, 72H, Ag-**2a**-H) ppm.

^{31}P{^{1}H} (161.98 MHz, 300 K, CD_2Cl_2) δ = −446.8 (brs, Ag-**1a**-P), −19.9 (brs, Ag-**2a**-P) ppm.

^{19}F{^{1}H} (376.62 MHz, 300 K, CD_2Cl_2) δ = −75.6 (s, CF_3) ppm.

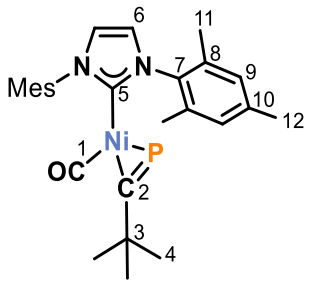
A **^{13}C{^{1}H} NMR** could not be obtained due to slow decomposition and the low solubility of **3** in CD_2Cl_2.

UV/vis (CH_2Cl_2): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 300 (10000).

Elemental Analysis calcd. C 32.97, H 3.25; found C 33.73, H 3.24.

[(IMes)Ni(CO)(PC*t*Bu)] (4a):

To a solution of [(IMes)Ni(CO)$_3$] (50.0 mg, 0.11 mmol, 1.0 eq.) in *n*-hexane (5 mL) was added *t*BuCP (2.56 M in O(SiMe$_3$)$_2$, 44 µL, 0.12 mmol, 1.05 eq.). Gas evolution and a color change from colorless to intense yellow were observed. After a few minutes, a yellow precipitate formed. The suspension was stirred at ambient temperature for two days. Subsequently, the solid was isolated by filtration, washed with cold hexane (−30 °C, 2 x 1 mL) and dried under reduced pressure, yielding a bright yellow powder. Crystals suitable for X-ray crystallography were grown by slow diffusion of *n*-hexane into a saturated solution of [IMesNi(CO)(PC*t*Bu)] in toluene.



$C_{27}H_{33}N_2NiOP$, MW = 491.24 g/mol

Yield: 48 mg (87%)

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.38 (s, 9H, C^4H), 1.20 (s, 6H, $C^{12}H$), 2.18 (s, 12H, $C^{11}H$), 6.32 (s, 2H, C^6H), 6.69 (s, 4H, C^9H) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, 300 K, C_6D_6) δ = 18.30 (s, C^{11}), 18.31 (s, C^{11}), 21.0 (s, C^{12}), 34.26 (d, $^3J_{CP}$ = 5.2 Hz, C^4), 40.82 (d, $^2J_{CP}$ = 6.9 Hz, C^3), 122.4 (s, C^6), 129.4 (s, C^9), 135.3 (s, C^8), 137.0 (s, C^7), 138.6 (s, C^{10}), 195.6 (d, $^2J_{CP}$ = 3.1 Hz, C^5), 200.8 (d, $^2J_{CP}$ = 3.4 Hz, C^1), 241.6 (d, $^1J_{CP}$ = 78.1 Hz, C^2) ppm.

^{31}P{^{1}H} (161.98 MHz, 300 K, C_6D_6) δ = 91.2 (s) ppm.

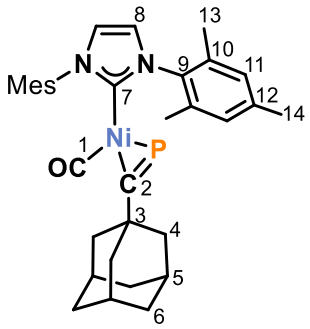
Elemental Analysis calcd. C 66.02, H 6.77, N 5.70; found C 66.47, H 6.50, N 5.64.

IR (ATR, cm^{-1}) 2948 (w), 2915 (w), 2856 (w), 1974 (vs), 1912 (w), 1486 (m), 1397 (m), 1323 (m), 1266 (m), 1155 (m).

UV/vis (THF): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 350 (4400sh), 390 (4600).

[(IMes)Ni(CO)(PCAd)] (4b):

To a solution of [(IMes)Ni(CO)$_3$] (50.0 mg, 0.11 mmol, 1.0 eq.) in *n*-hexane (5 mL) was added AdCP (21.0 mg, 0.12 mmol, 1.05 eq.). Gas evolution and a color change from colorless to intense yellow were observed. After a few minutes, a yellow precipitate formed. The suspension was stirred at ambient temperature for two days. Subsequently, the solvent was removed and the orange residue was dried *in vacuo*. *n*-Pentane (2 mL) was added and the suspension was stored at −30 °C in order to complete precipitation. The solid was isolated by filtration, washed with cold *n*-pentane (−30 °C, 2 x 1 mL) and dried under reduced pressure, yielding a yellow powder. A second crop of crystalline compound was obtained after reducing the volume of the filtrate further to half the volume and storing the solution at −35 °C overnight. Crystals suitable for X-ray crystallography were grown by cooling a saturated solution of [(IMes)Ni(CO)(PCAd)] in toluene from ambient temperature to −30 °C.



$C_{33}H_{39}N_2NiOP$, MW = 569.36 g/mol

Yield: 52 mg (81%)

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.54 (m, 6H, C^6H), 1.81 (s, 3H, C^5), 2.01 (overlapping s, 12H, $C^{14}H$ + C^4H), 2.20 (s, 12H, $C^{13}H$), 6.34 (s, ^{2}H, C^8H), 6.71 (s, 4H, $C^{11}H$) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, 300 K, C_6D_6) δ = 18.3 (s, C^{13}), 18.4 (s, C^{13}), 21.0 (s, C^{14}), 29.7 (s, C^5), 37.1 (s, C^6), 42.9 (d, $^2J_{CP}$ = 6.8 Hz, C^3) 47.1 (d, $^3J_{CP}$ = 5.3 Hz, C^4), 122.4 (s, C^8), 129.4 (s, C^{11}), 135.3 (s, C^{10}), 137.0 (s, C^9), 138.6 (s, C^{12}), 195.8 (d, $^2J_{CP}$ = 2.5 Hz, C^7), 201.3 (d, $^2J_{CP}$ = 2.5 Hz, C^1), 241.4 (d, $^1J_{CP}$ = 77.8 Hz, C^2) ppm.

^{31}P{^{1}H} (161.98 MHz, 300 K, C_6D_6) δ = 92.1 (s) ppm.

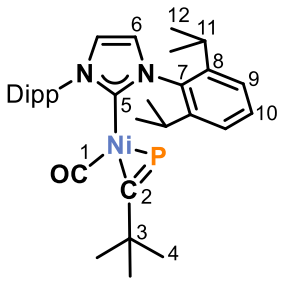
Elemental Analysis calcd. C 69.62, H 6.99, N 4.92; found C 69.92, H 7.01, N 4.76.

IR (ATR, cm^{-1}) 2900 (m), 2884 (m), 2845 (w), 1967 (m), 1964 (vs), 1919 (w), 1486 (w), 1449 (w), 1397 (w), 1323 (m), 1265 (w).

UV/vis (THF): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 340 (3200sh), 390 (3200).

[(IPr)Ni(CO)(PC*t*Bu)] (4c):

To a solution of [(IPr)Ni(CO)$_3$] (100.0 mg, 0.188 mmol, 1.0 eq.) in *n*-hexane (5 mL) was added *t*BuCP (2.56 M in O(SiMe$_3$)$_2$, 77 µL, 1.05 eq.). Gas evolution and a color change from colorless to intense yellow were observed. The yellow solution was stirred at ambient temperature for two days. Subsequently, the solution was concentrated to ca. 2 mL. Storage at −30 °C for two days afforded large yellow blocks which were isolated by filtration and dried under reduced pressure. A second crop of crystalline compound was obtained after reducing the volume of the filtrate to 1 mL and storing the solution at −35 °C overnight. Crystals suitable for X-ray crystallography were grown by cooling a saturated solution of [(IPr)Ni(CO)(PC*t*Bu)] from ambient temperature to −30 °C.



$C_{33}H_{45}N_2NiOP$, MW = 575.40 g/mol

Yield: 51 mg (47%)

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.09 (d, $^3J_{HH}$ = 7.0 Hz, 12H, C^{12}H), 1.37 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C^{12}H), 1.41 (s, 9H, C^{4}H), 3.02 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C^{11}H), 6.70 (s, 2H, C^{6}H), 7.10 (d, $^3J_{HH}$ = 7.6 Hz, 4H, C^{9}H), 7.20 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 7.6 Hz, 2H, C^{10}H) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, 300 K, C_6D_6) δ = 23.4 (s, C^{12}), 25.5 (s, C^{12}), 28.9 (s, C^{11}), 34.0 (d, $^3J_{CP}$ = 5.7 Hz, C^4), 40.6 (d, $^3J_{CP}$ = 7.2 Hz, C^3), 124.0 (s, C^6), 124.3 (s, C^9), 130.1 (s, C^{10}), 137.4 (s, C^7), 146.0 (s, C^8), 197.3 (d, $^2J_{CP}$ = 3.1 Hz, C^5), 200.1 (d, $^2J_{CP}$ = 2.9 Hz, C^1), 237.8 (d, $^1J_{CP}$ = 77.7 Hz, C^2) ppm.

^{31}P{^{1}H} (161.98 MHz, 300 K, C_6D_6) δ = 93.2 (s) ppm.

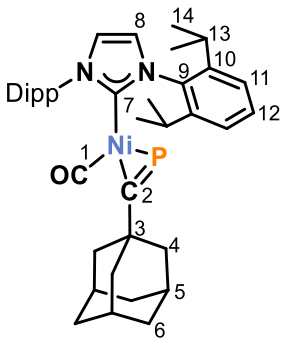
Elemental Analysis calcd. C 68.88, H 7.88, N 4.87; found C 68.95, H 7.51, N 4.81.

IR (ATR, cm^{-1}) 2964 (m), 2926 (w), 2866 (w), 1970 (vs) 1459 (m) 1400 (m) 1384 (m) 1328 (m) 1178 (w), 1159 (w).

UV/vis (THF): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 350 (3400sh), 400 (3500).

[(IPr)Ni(CO)(PCAd)] (4d):

To a solution of [(IPr)Ni(CO)$_3$] (100.0 mg, 0.19 mmol, 1.0 eq.) in *n*-hexane (5 mL) was added AdCP (35.2 mg, 0.20 mmol, 1.05 eq.). Gas evolution and a color change from colorless to intense yellow were observed. The yellow solution was stirred at ambient temperature for two days. Subsequently, the solution was concentrated to ca. 2 mL. Storage at −30 °C for two days afforded yellow crystals which were isolated by filtration and dried under reduced pressure. A second crop of crystalline compound was obtained after reducing the volume of the filtrate to 1 mL and storing the solution at −35 °C overnight. Crystals suitable for X-ray crystallography were grown by cooling a saturated solution of [(IPr)Ni(CO)(PCAd)] in *n*-hexane from ambient temperature to −30 °C.



$C_{39}H_{51}N_2NiOP$, MW = 653.52 g/mol

Yield: 42 mg (34%)

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 12H, C^{14}H), 1.40 (d, $^3J_{HH}$ = 6.9 Hz), 1.59 (m, 6H, C^{6}H), 1.86 (s, 3H, C^{5}H), 2.04 (d, $^4J_{HP}$ = 2.6 Hz, 6H, C^{4}H), 3.05 (sept, $^3J_{HH}$ = 6.9 Hz, C^{13}H), 6.71 (s, 2H, C^{8}H), 7.11 (d, $^3J_{HH}$ = 7.6 Hz, 4H, C^{11}H), 7.21 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 8.4 Hz, 2H, C^{12}H) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, 300 K, C_6D_6) δ = 23.4 (s, C^{14}), 25.5 (s, C$^{14'}$), 28.9 (s, C^{13}), 29.7 (s, C^5), 37.2 (s, C^6), 42.7 (d, $^2J_{CP}$ = 7.7 Hz, C^3), 46.8 (d, $^3J_{CP}$ = 5.8 Hz, C^4), 123.6 (s, C^8), 124.3 (s, C^{11}), 130.0 (s, C^{12}), 137.4 (s, C^9), 146.0 (s, C^{10}), 197.5 (d, $^2J_{CP}$ = 3.0 Hz, C^7), 200.7 (d, $^2J_{CP}$ = 2.8 Hz, C^1), 237.6 (d, $^1J_{CP}$ = 78.0 Hz, C^2) ppm.

^{31}P{^{1}H} (161.98 MHz, 300 K, C_6D_6) δ = 94.1(s) ppm.

Elemental Analysis calcd. C 71.68, H 7.87, N 4.29; found C 72.02, H 7.50, N 4.23.

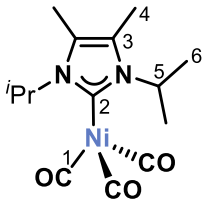
IR (ATR, cm^{-1}) 2961 (w), 2866 (w), 2847 (w), 1966 (vs), 1467 (m) 1399 (m) 1327 (m) 1179 (m)

UV/vis (THF): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 350 (3600sh), 400 (3400).

[(*i*Pr$_2$Im^{Me})Ni(CO)$_3$]:

The compound was prepared analogous to the procedure for the synthesis of [(NHC)Ni(CO)$_3$] (NHC = IMes, IPr) reported by *Nolan* and co-workers.[3a] An independent preparation was recently reported by *Radius* and co-workers.[3b]

A cold (−60 °C) THF solution (20 mL) of *i*Pr$_2$Im^{Me} (600.0 mg, 3.33 mmol, 1.0 eq.) was added dropwise to a cold (−60 °C) THF solution (20 mL) of a [Ni(CO)$_4$] stock solution in toluene (0.96 M, 4.16 mL, 3.99 mmol, 1.2 eq.). A color change from yellow to red and then finally to pale orange and evolution of CO gas were observed. The pale orange solution was stirred at room temperature for one hour. Subsequently, the volatiles were removed *in vacuo*. The brown solid was washed with cold *n*-pentane (−30 °C, 3 × 15 mL), and dried in vacuo to give a beige solid. Crystals suitable for X-ray crystallography were grown by cooling a saturated solution of [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$] in toluene from ambient temperature to −30 °C.



$C_{14}H_{20}N_2NiO_3$, MW = 323.03 g/mol

yield: 420 mg (39%)

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.09 (d, 12H, $^3J_{CH}$ = 7.2 Hz, C^{6}H), 1.67 (s, 6H, C^{4}H), 5.45 (sept, $^3J_{CH}$ = 5.45 Hz, 2H, C^{5}H) ppm.

^{13}C{^{1}H} NMR (100.61 MHz, 300 K, C_6D_6) δ = 10.3 (s, C^4), 21.4 (s, C^6), 53.6 (s, C^5), 125.4 (s, C^3), 187.7 (s, C^2), 198.9 (s, C^1) ppm.

Elemental Analysis calcd. C 52.06, H 6.24, N 8.67; found C 52.58, H 6.26, N 8.76.

UV/vis (THF): λ_{max} (nm, ε_{max} /L·mol^{-1}·cm^{-1}) 280 (12 000sh), 320 (5000sh).

IR (ATR, cm^{-1}) 2982 (w), 2938 (w), 2875 (w), 2043 (s), 1959 (s), 1913 (vs), 1868 (m), 1640 (w), 1464 (m) 1352 (w), 1332 (w), 1290 (m), 1210 (m), 1106 (w) 1021 (w)

1.4 Procedures for Other Reactions

Crossover experiment:

To a solution of **4a** (15.0 mg, 0.030 mmol, 1.0 eq.) in C_6D_6 (0.5 mL) was added AdCP (6.0 mg, 0.033 mmol, 1.1 eq.). The reaction was stirred at ambient temperature for 1 hour. A $^{31}P\{^1H\}$ NMR spectrum of the solution was recorded.

$^{31}P\{^1H\}$ (161.98 MHz, 300 K, C_6D_6) δ = −479.8 (s, **1b**, 4P), −473.8 (s, **1c**, 4P), −468.2 (s, **1a**, 1P), 91.3 (s, **4a**, 7P), 92.1 (s, **4b**, 5P) ppm (see Figure S37).

Detection of 1b:

To a solution of [(IMes)Ni(CO)$_3$] (20.0 mg, 0.045 mmol, 1.0 eq.) in C_6D_6 (0.5 mL) was added AdCP (8.5 mg, 0.048 mmol, 1.1 eq.). The reaction mixture was stirred at ambient temperature for 18 hours. Subsequently, the sample was subjected to NMR spectroscopic studies.

$^{31}P\{^1H\}$ (161.98 MHz, 300 K, C_6D_6) δ = −479.8 (s, **1b**), 92.1 (s, **4b**) ppm.

More AdCP (17.0 mg, 0.096 mmol, 2.0 eq.) was added and the reaction mixture was stirred for 6 hours. The sample was again subjected to NMR spectroscopic analysis. The intensity of the signal at −479.8 significantly decreased from 10.4% of the overall intensity of $^{31}P\{^1H\}$ signals to 1.8% (see Figures S38, S39).

Reaction of [Ni(CO)$_4$] with *t*BuCP:

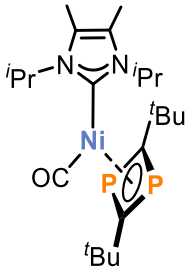
To a solution of [Ni(CO)$_4$] (0.048 mmol, 0.96 M in Toluene, 0.05 mL, 1.0 eq.) in toluene (1 mL) was added *t*BuCP (0.058 mmol, 3.88 M in O(SiMe$_3$)$_2$, 0.015 mL, 1.2 eq.). The color of the reaction mixture immediately changed from colorless to dark brown. Subsequently, the solution was subjected to $^{31}P\{^1H\}$ NMR spectroscopy. More than 10 different species were observed in the $^{31}P\{^1H\}$ NMR spectrum, see Figure S40.

Reaction of [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$] with *t*BuCP:

To a solution of [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$] (30.0 mg, 0.093 mmol, 1.0 eq.) in *n*-hexane (0.5 mL) was added *t*BuCP (0.05 mL, 2.6 M in O(SiMe$_3$)$_2$, 0.05 mL, 1.5 eq.). Gas evolution and a color change from colorless to intense yellow were observed. The yellow solution was stirred at ambient temperature for 18 hours. Subsequently, a $^{31}P\{^1H\}$ NMR spectrum of the solution was recorded.

$^{31}P\{^1H\}$ (161.98 MHz, 300 K, C_6D_6) δ = −52.6 (s, **6**), 47.0 (s, **5**), 87.2 (s, not assigned), 92.3 (s, not assigned) ppm (see Figure S41).

The solvent was removed *in vacuo* and the residue was extracted with *n*-hexane (ca. 2 mL). Upon storage of the solution at −30 °C overnight, the blue crystals of **5** along with orange crystals of **6** was formed. Both crystals were suitable for X-ray crystallography (see Figures S67 and Figure 3 in the main text). The crystals of **5** were separated manually from crystals of **6** and re-dissolved in C_6D_6 for spectroscopic characterization.



$C_{23}H_{38}N_2NiOP_2$, MW = 479.21 g/mol

^{1}H NMR (400.13 MHz, 300 K, C_6D_6) δ = 1.20 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *i*Pr-CH_3), 1.26 (s, 18H, *t*Bu), 1.29 (d, $^3J_{HH}$ = 7.1 Hz, 6H, *i*Pr-CH_3), 1.60 (s, 6H, NCCH_3), 7.04 (sept, $^3J_{HH}$ = 7.0 Hz) ppm.

^{31}P{^{1}H} (161.98 MHz, 300 K, C_6D_6) δ = 47.0 (s) ppm.

Crystals of **6** were re-dissolved in C_6D_6 and subjected to NMR spectroscopic studies. However, three species were detected in ^{31}P{^{1}H} NMR spectroscopy (see Figure S44). The main signal at δ = −52.4 ppm most probably corresponds to complex **6**.

Upon further storage of the supernatant solution at −30 °C, more crystals of **6** along with some dark brown crystals of **7** were obtained. The crystals of **7** were suitable for structure elucidation of by X-ray crystallography (see Figure S68). However, the small amount of crystals precluded further spectroscopic analysis.

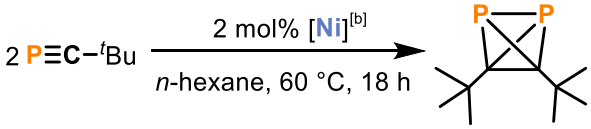
^{31}P{^{1}H} NMR spectra of analogous reaction mixtures prepared with 1.0, 2.0 and 0.5 equivalents of *t*BuCP are shown in Figures S45-S47.

2 Catalyst Screening

General procedure:

The screening reactions for the dimerization of *t*BuCP to **1a** were performed in test tubes with a ground glass joint and magnetic stirring bar in an argon-filled glovebox. To a test tube was added pre-catalyst (2 mol% for all entries except 6, 1 mol% for entry 6), *n*-pentadecane (50 µL), *n*-hexane (0.5 mL). Subsequently, *t*BuCP (0.1 mL, 2.6 M in $O(SiMe_3)_2$, 0.26 mmol) was added. The test tube was placed in a pre-heated oil bath at 60 °C and stirred for 18 h. The reaction was quenched with QuadraSil® MP metal scavenger (1.0-1.4 mmol/g loading), diluted with n-hexane (1 mL) and filtered through a Whatman® glass fiber filter. The reaction mixture was analyzed by quantitative GC-FID analysis vs internal standard *n*-pentadecane.

Table S1. Screening of different nickel catalysts for the dimerization of *t*BuCP.



Entry	Catalyst	Yield [%] of **1a***
1	no catalyst	0
2	$[Ni(CO)_4]$	9
3	$[(iPr_2Im^{Me})Ni(CO)_3]$	3
4	[(IMes)Ni(CO)$_3$]	67
5	[(IPr)Ni(CO)$_3$]	49
6	$[\{(IMes)NiP(CO)\}_2]$	57
7	$[IMesNi(vinyl\text{-}TMS)_2]$	32
8	[(IMes)Ni(CO)(PC*t*Bu)]	58
9	[(IPr)Ni(CO)(PC*t*Bu)]	66

* Note that conversions of *t*BuCP could not be determined due to the high volatility of *t*BuCP.

3 Kinetic Studies

Two methods were required to extract the relevant kinetic information of the dimerization reaction of *t*BuCP. In both cases, [(IMes)Ni(CO)(PC*t*Bu)] (**4a**) was used as catalyst. The rate constant and the order in catalyst were obtained by GC-FID detection (*n*-pentadecane as internal standard). However, due to the high volatility of *t*BuCP, this method was unsuitable to monitor the consumption of *t*BuCP. Therefore, quantitative high temperature $^{31}P\{^{1}H\}$ NMR spectroscopy (using triphenylphosphine oxide as internal standard) was used to monitor the consumption of *t*BuCP and to determine the order in *t*BuCP.

3.1 Kinetic Analysis by GC-FID Monitoring

General procedure for GC-FID monitoring:

The reactions were performed in glass vials equipped with a PTFE septum and a magnetic stirring bar placed in a metal block that was kept at 60 °C inside an argon filled glove box (see Figure S3). To a glass vial was added **4a** (0.5-4 mol%), *n*-pentadecane (150 µL) and *n*-hexane (2.5 mL). The vial was placed in a pre-heated metal block and heated to 60 °C for 30 min. Before the addition of *t*BuCP, the pressure was equalized by piercing the septum with a needle for five seconds. Subsequently, *t*BuCP (0.6 mL, 2.1 M in $O(SiMe_3)_2$, 1.26 mmol) was added and aliquots (*ca*. 0.1 mL each) were taken *via* syringe over a period of 4 hours. The aliquots were quenched with QuadraSil® MP metal scavenger (1.0-1.4 mmol/g loading), diluted with *n*-hexane (1 mL) and filtered through a Whatman® glass fiber filter in a GC vial with a septum lid. The samples were analyzed by quantitative GC-FID analysis vs internal standard *n*-pentadecane.

The rate constant was calculated using the initial concentration c^0_{tBuCP} = 387.7 mmol/L as k = 0.97 $L \cdot mol^{-1} \cdot min^{-1}$. The order in catalyst was determined using both initial rate plots and time normalization methods.[10,11]

Figure S3. Picture of the set-up used for kinetic analysis with air sensitive samples in an argon-filled glove box.

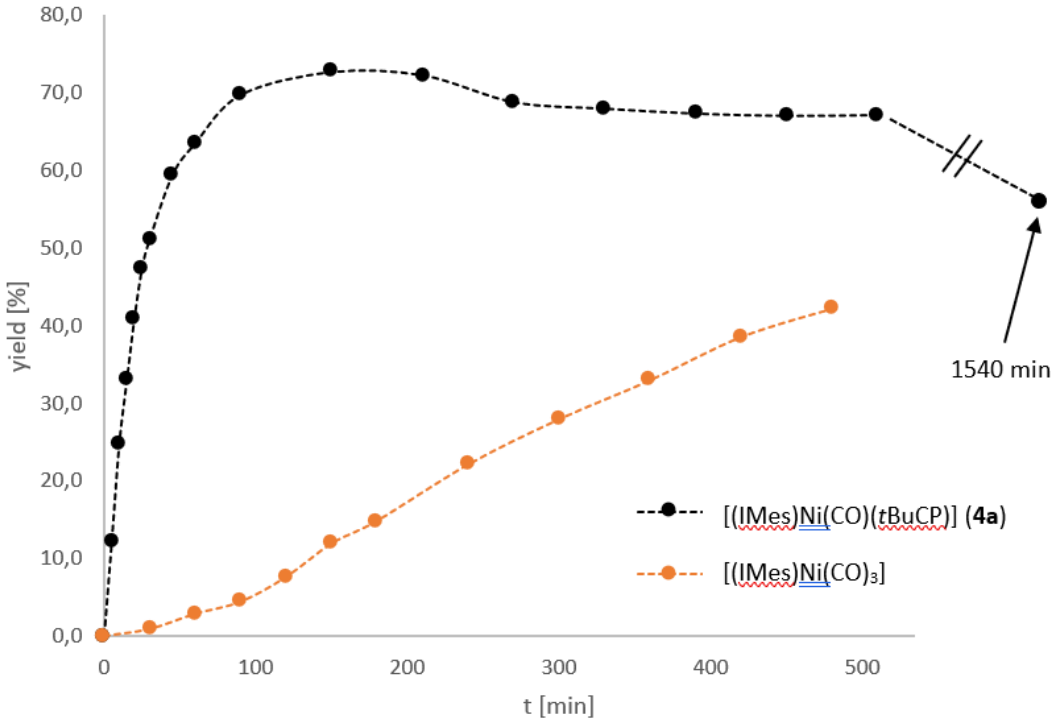


Figure S4. Plot of yield [%] of **1a** over time for the dimerization of *t*BuCP using nickel-catalysts **4a** (black, 2mol%) and [(IMes)Ni(CO)$_3$] (orange, 2 mol%) for the dimerization of *t*BuCP. Yields were determined by GC-FID using *n*-pentadecane as internal standard.

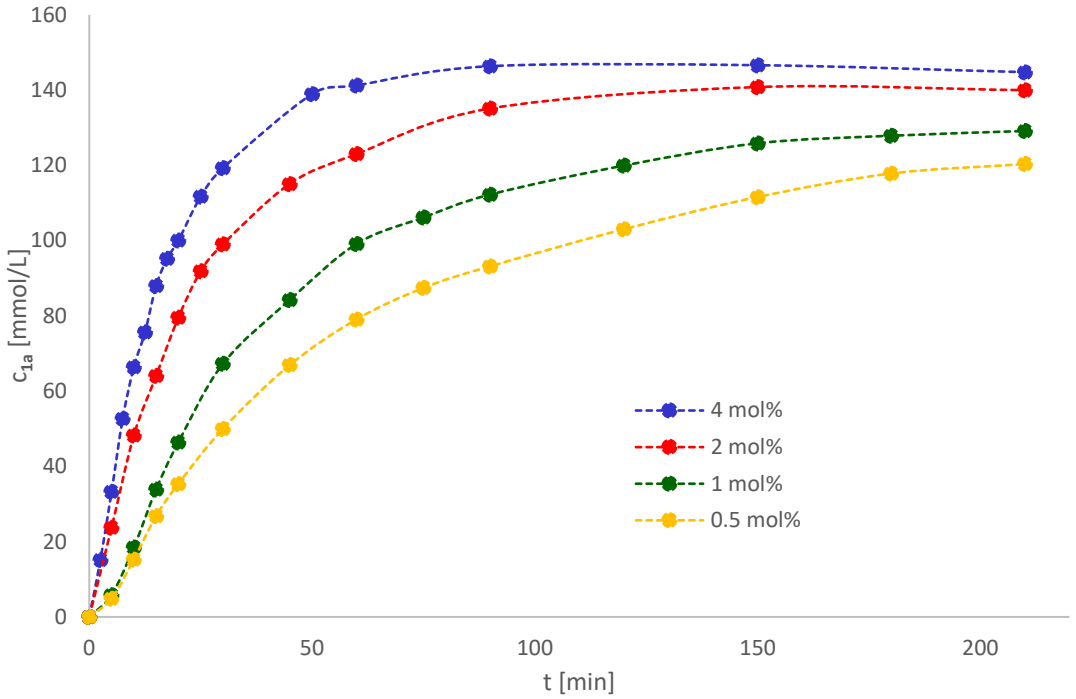


Figure S5. Plots of the concentration of **1a** over time using 0.5-4 mol% of **4a** as catalyst. Concentrations were determined by GC-FID using *n*-pentadecane as internal standard.

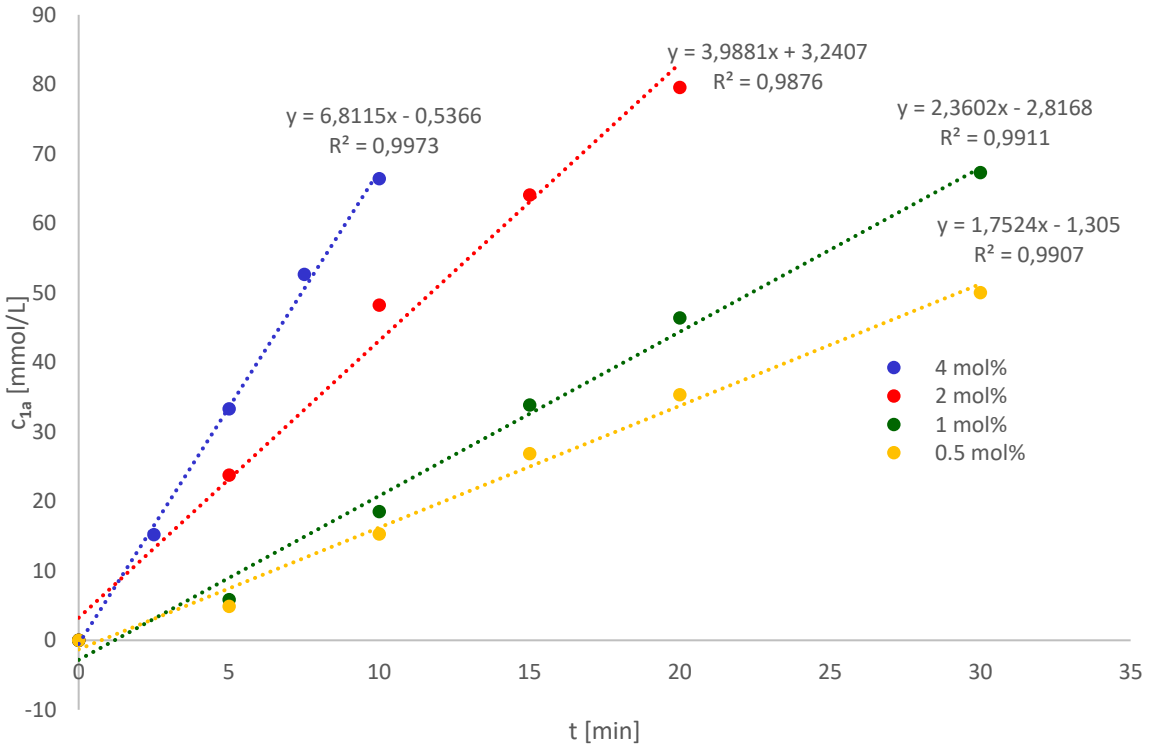


Figure S6. Plots of the concentration of **1a** over time using 0.5-4 mol% of **4a** as catalyst as used for determination of k_{obs} including lines of best fit.

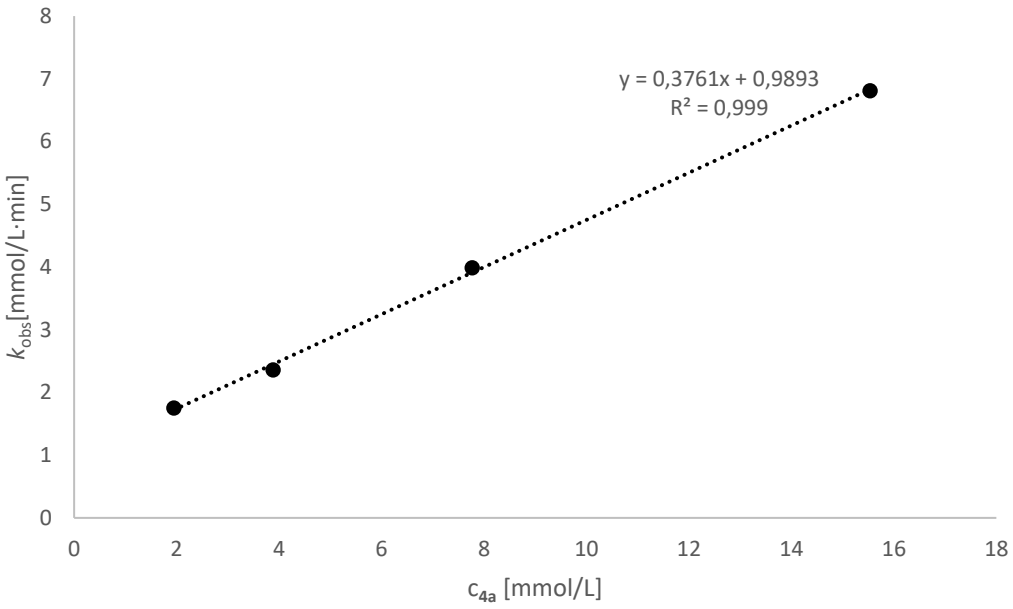


Figure S7. Plot of k_{obs} versus c_{4a} including line of best fit.

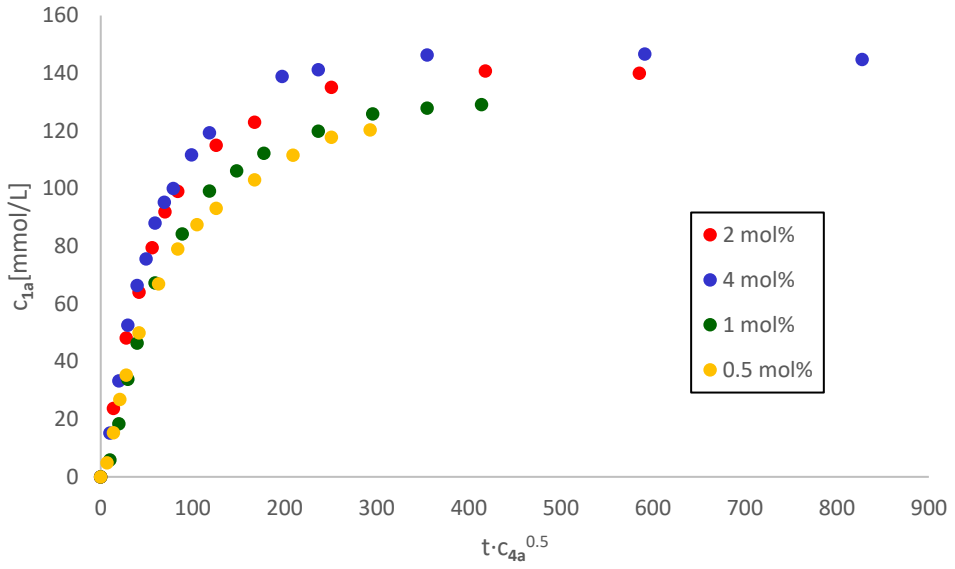


Figure S8. Time normalization plot for order of **4a** = 0.5. A poor overlay of the data points is observed, which suggests that the reaction order of 0.5 for **4a** is not in agreement with the kinetic data.

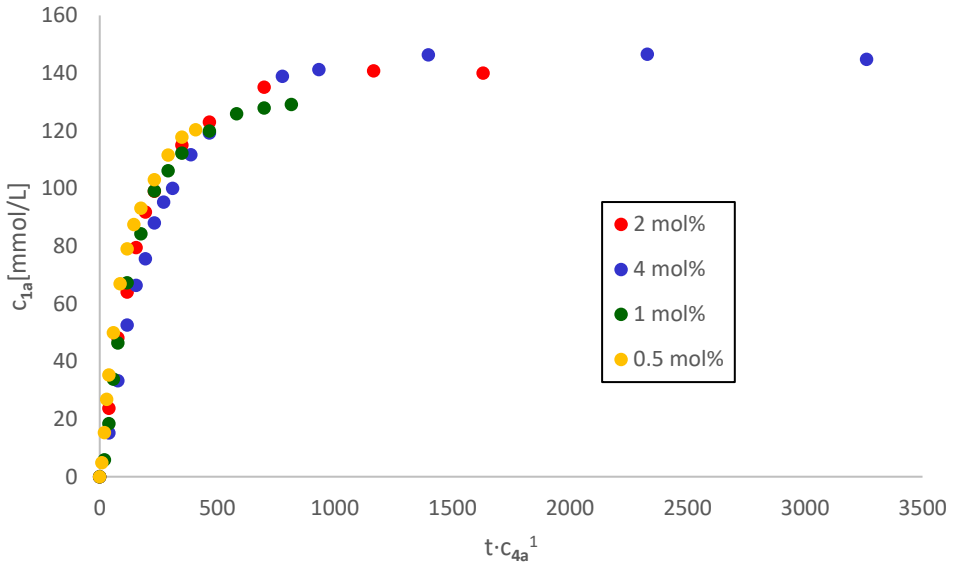


Figure S9. Time normalization plot for order of **4a** = 1. A good overlay of the data points suggests that the reaction order of 1 for **4a** is in agreement with the kinetic data.

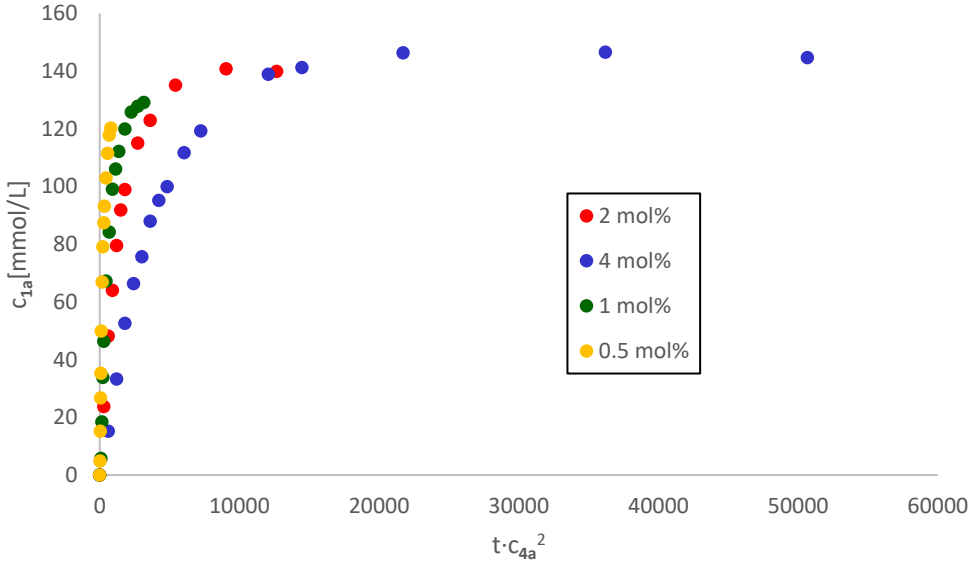


Figure S10. Time normalization plot for order of **4a** = 2. A poor overlay of the data points is observed, which suggests that the reaction order of 2 for **4a** is not in agreement with the kinetic data.

The best overlay was achieved for the plot shown in Figure S9, corresponding to an order of 1 in catalyst **4a.**

3.2 Kinetic Analysis by $^{31}P\{^{1}H\}$ NMR Reaction Monitoring

In order to monitor the concentration of *t*BuCP over time, quantitative $^{31}P\{^{1}H\}$ NMR spectroscopy was used. Spectra were recorded at 60 °C with triphenylphosphine oxide as an internal standard. Triphenylphosphine oxide does not react with any of the compounds present in the reaction mixture. First, the t_1 relaxation times of all species in the reaction mixture (tBuCP, **4a**, **1a**, $O{=}PPh_3$) were determined. **1a** was found to have the longest t_1 time (t_1 = 2.16 s). Therefore, a delay time of 10 seconds was used for all experiments. The concentration of **1a** was found to be significantly lower than expected. The hard pulses used in the NMR experiment have a sinc shaped excitation profile. Hence, they do not excite uniformly over the desired frequency range and especially **4a** with its high field-shift is only excited partially, accounting for its low intensity in the experiments.

General procedure for NMR monitoring experiments:

To a J. Young NMR tube was added **4a** (0.5-4 mol%), $O{=}PPh_3$ (*ca.* 20 mg), 0.5 mL C_6D_6 and *t*BuCP (0.1 mL, 2.6 M in $O(SiMe_3)_2$, 0.26 mmol). The NMR tube was then sealed and subjected to the pre-heated (60 °C) 400 MHz NMR spectrometer. NMR spectra were acquired over the course of 6 hours using the method described above.

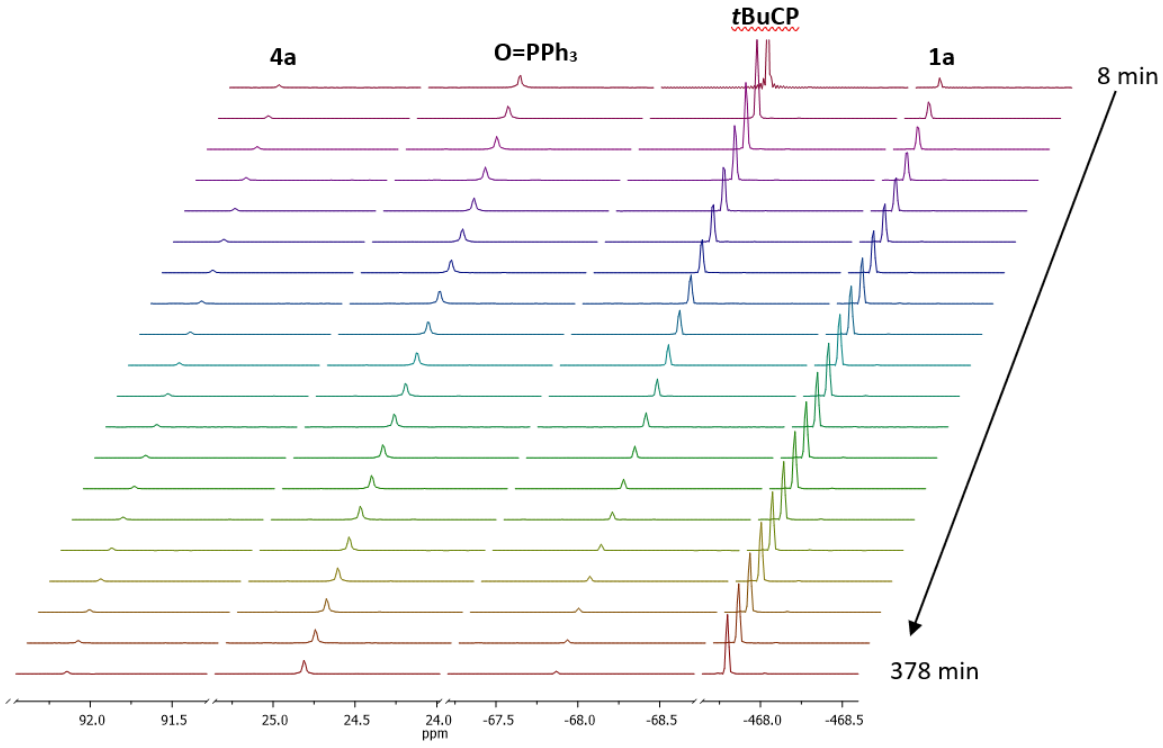


Figure S11. Stacked plot of $^{31}P\{^{1}H\}$ NMR spectra (161.98 MHz, 333 K, C_6D_6) for the reaction of *t*BuCP (0.1 mL, 2.6 M in $O(SiMe_3)_2$, 0.26 mmol) with catalyst **4a** (2 mol%) in C_6D_6.

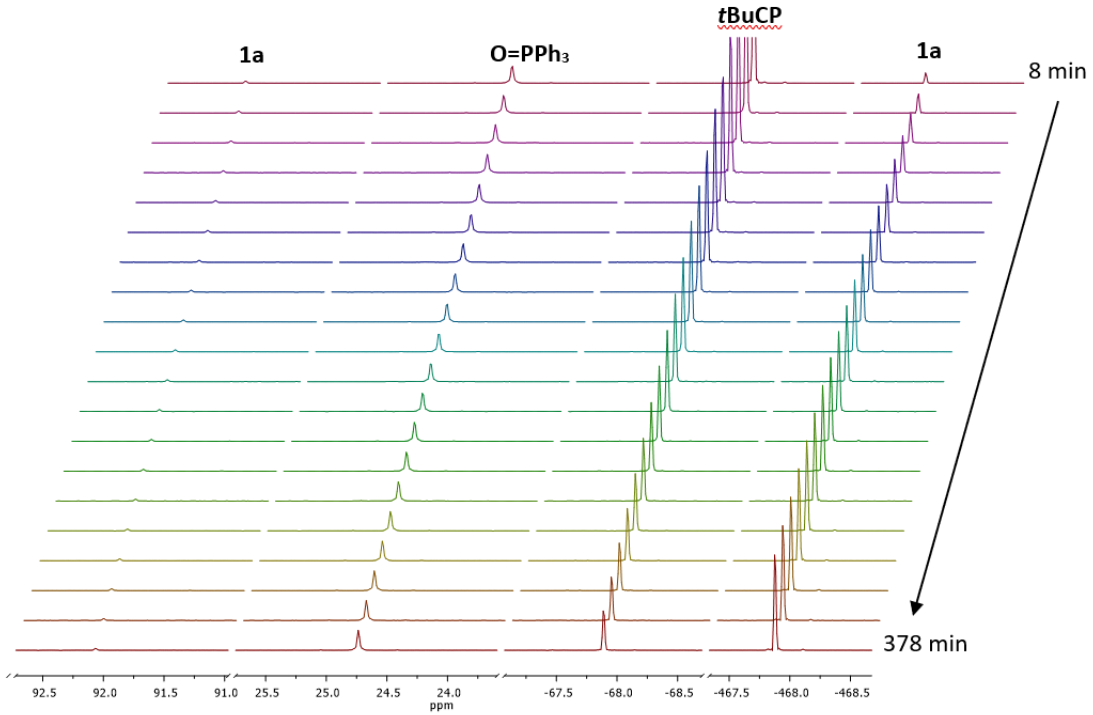


Figure S12. Stacked plot of $^{31}P\{^{1}H\}$ NMR spectra (161.98 MHz, 333 K, C_6D_6) for the reaction of *t*BuCP (0.1 mL, 2.6 M in $O(SiMe_3)_2$, 0.26 mmol) with catalyst **4a** (1 mol%) in C_6D_6.

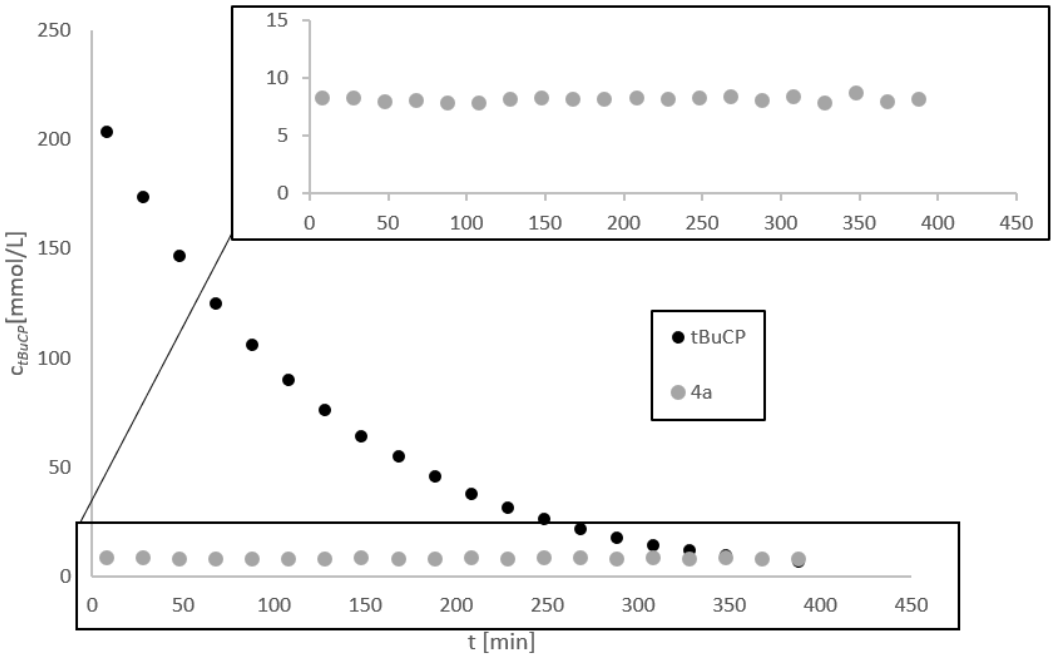


Figure S13. Example plot of c(*t*BuCP) [mmol/L] over time using 2 mol% of **4a** as catalyst. c(*t*BuCP) was determined via integration versus $O=PPh_3$ as internal standard.

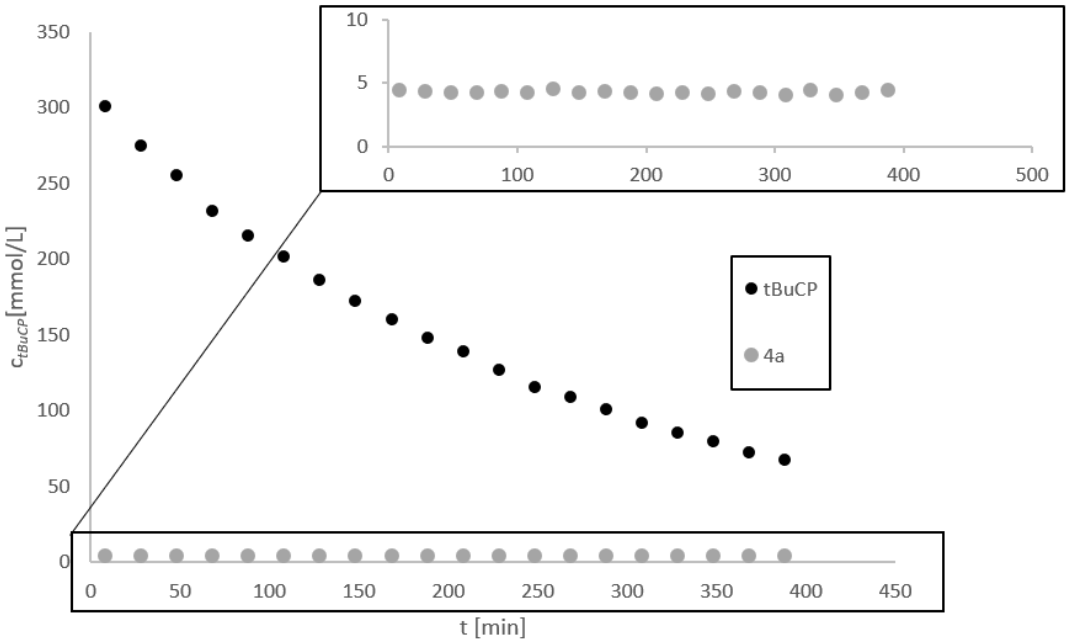


Figure S14. Example plot of c(*t*BuCP) [mmol/L] over time using 1 mol% of **4a** as catalyst. c(*t*BuCP) was determined via integration versus $O=PPh_3$ as internal standard.

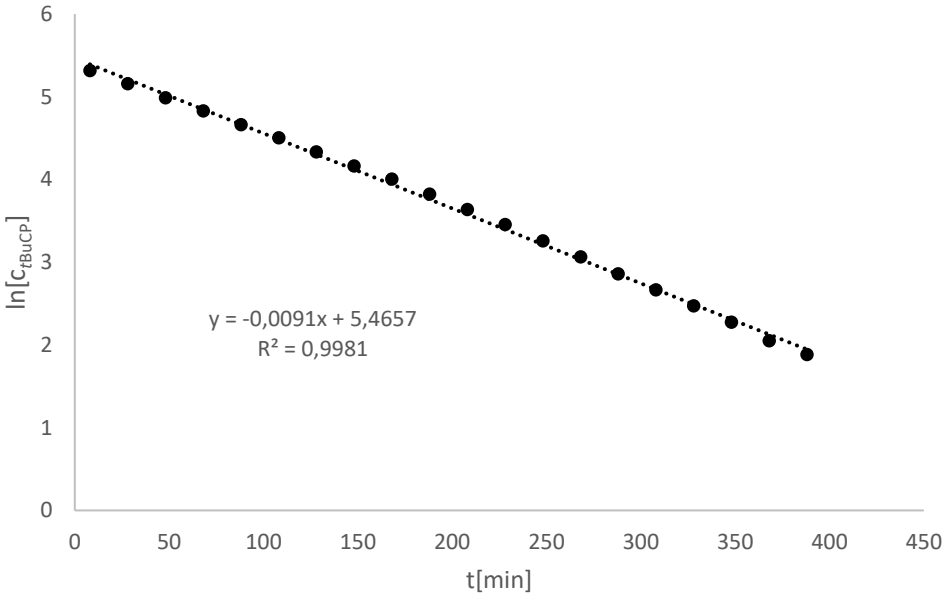


Figure S 15. Example plot of ln[c(*t*BuCP)] over time using 2 mol% of **4a** as catalyst.

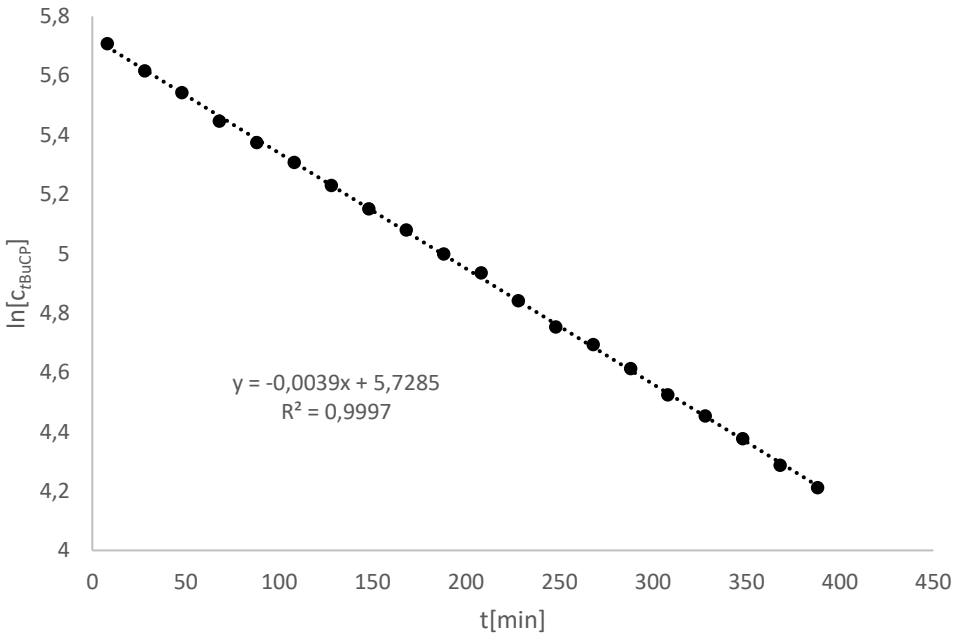


Figure S16. Example plot of ln[c(*t*BuCP)] over time using 1 mol% of **4a** as catalyst.

4 NMR Spectra

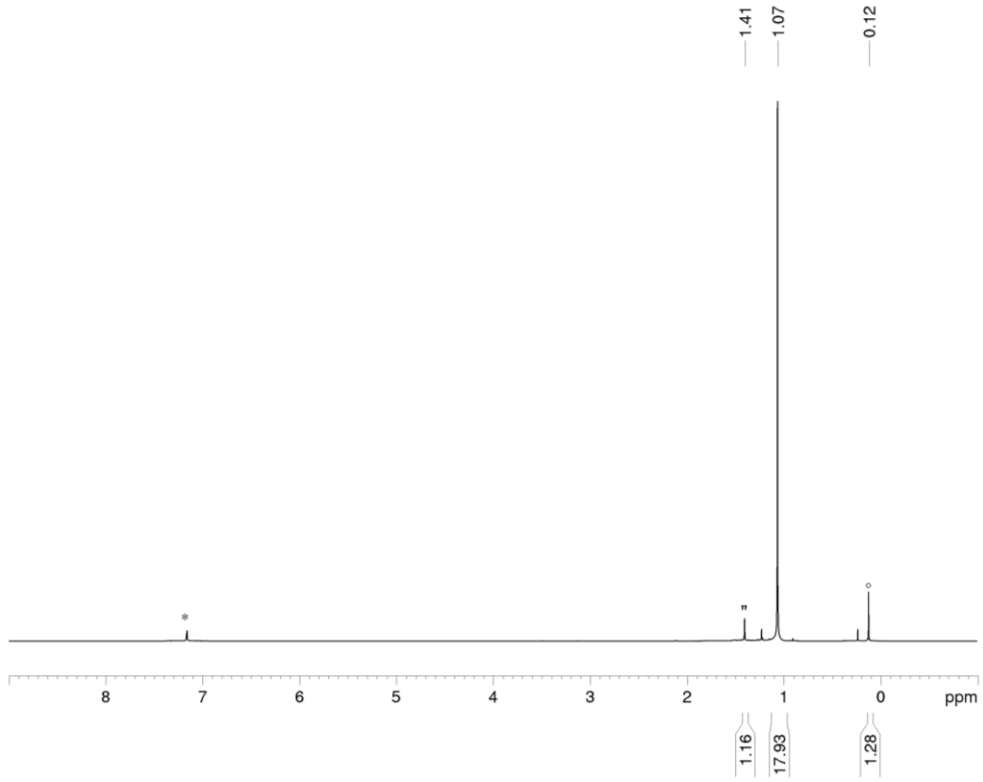


Figure S17. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **1a**; *C_6D_6, °$O(SiMe_3)_2$, ”**2a**.

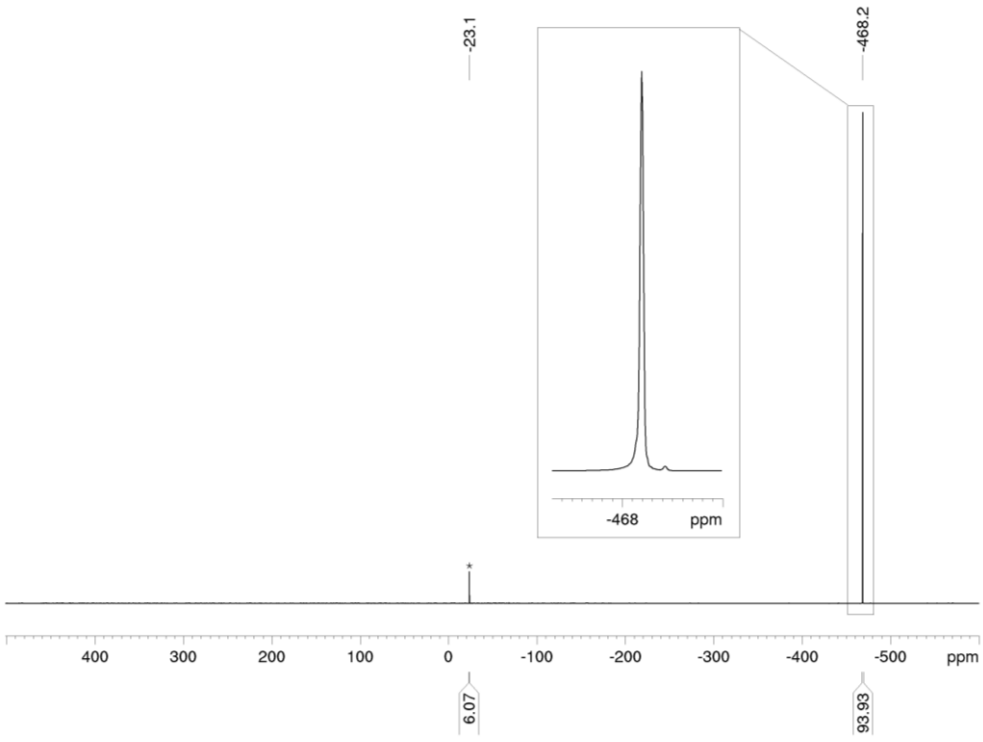


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **1a**; ***2a**.

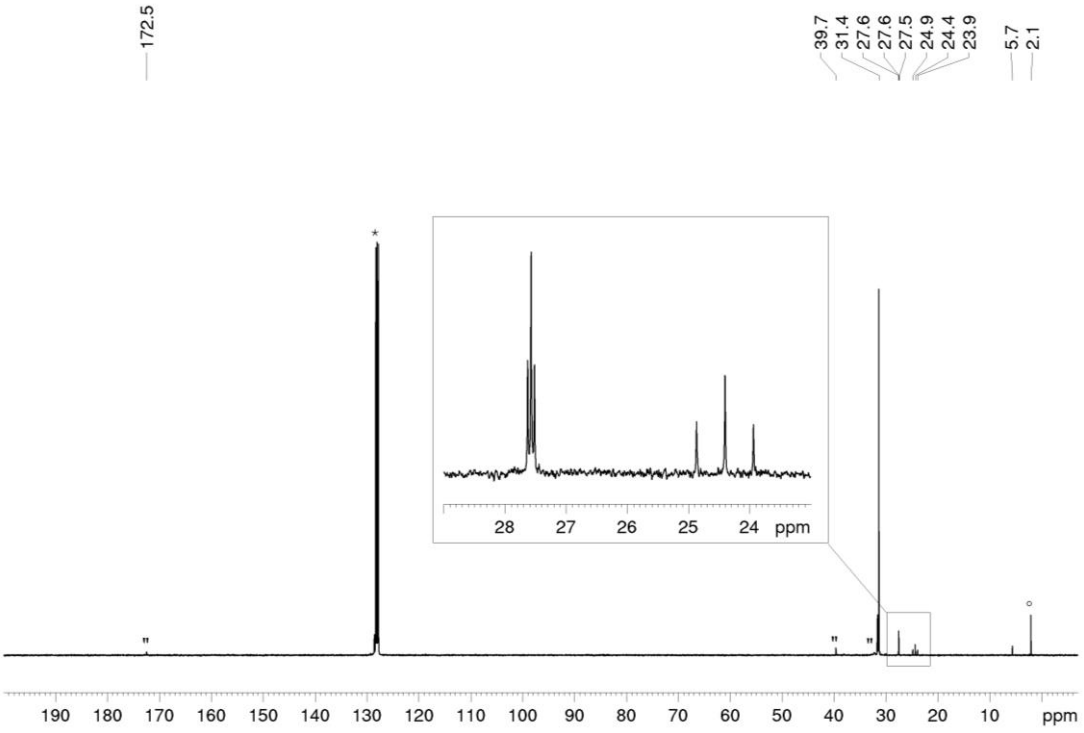


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **1a** *C_6D_6, °$O(SiMe_3)_2$, "**2a**.

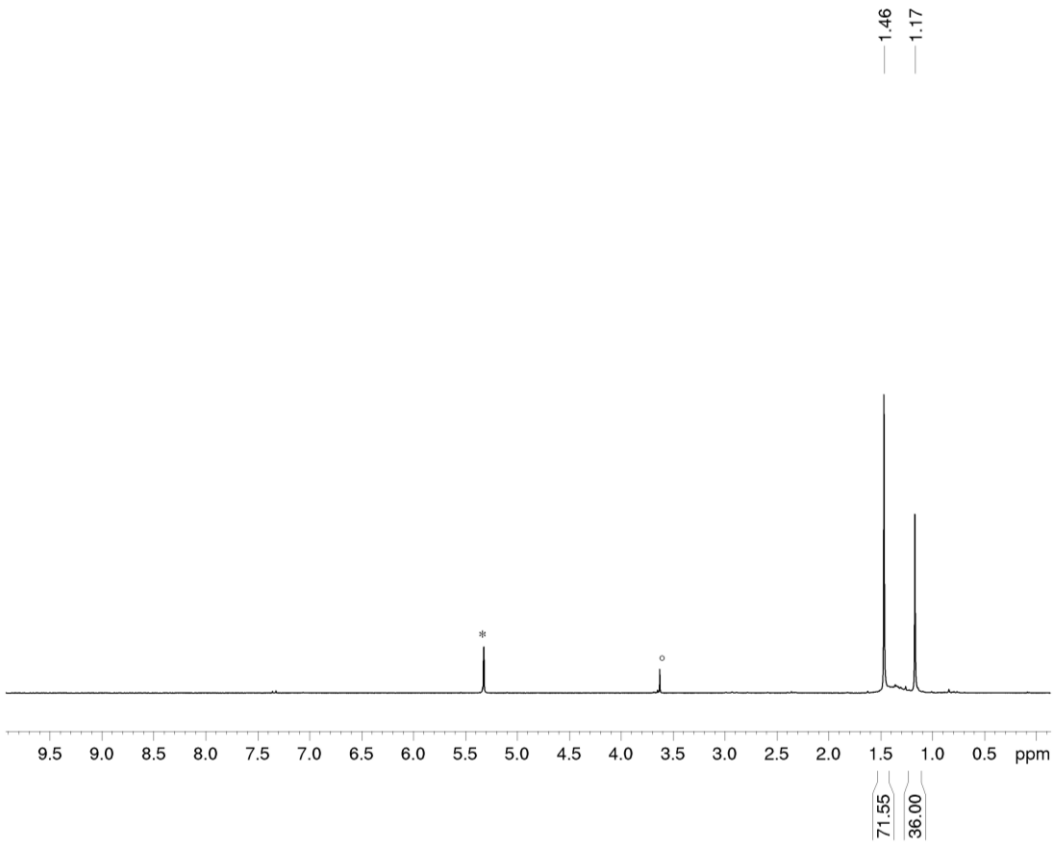


Figure S20. ^{1}H NMR spectrum (400.13 MHz, 300 K, CD_2Cl_2) of **3**; *CD_2Cl_2, ° unknown impurity.

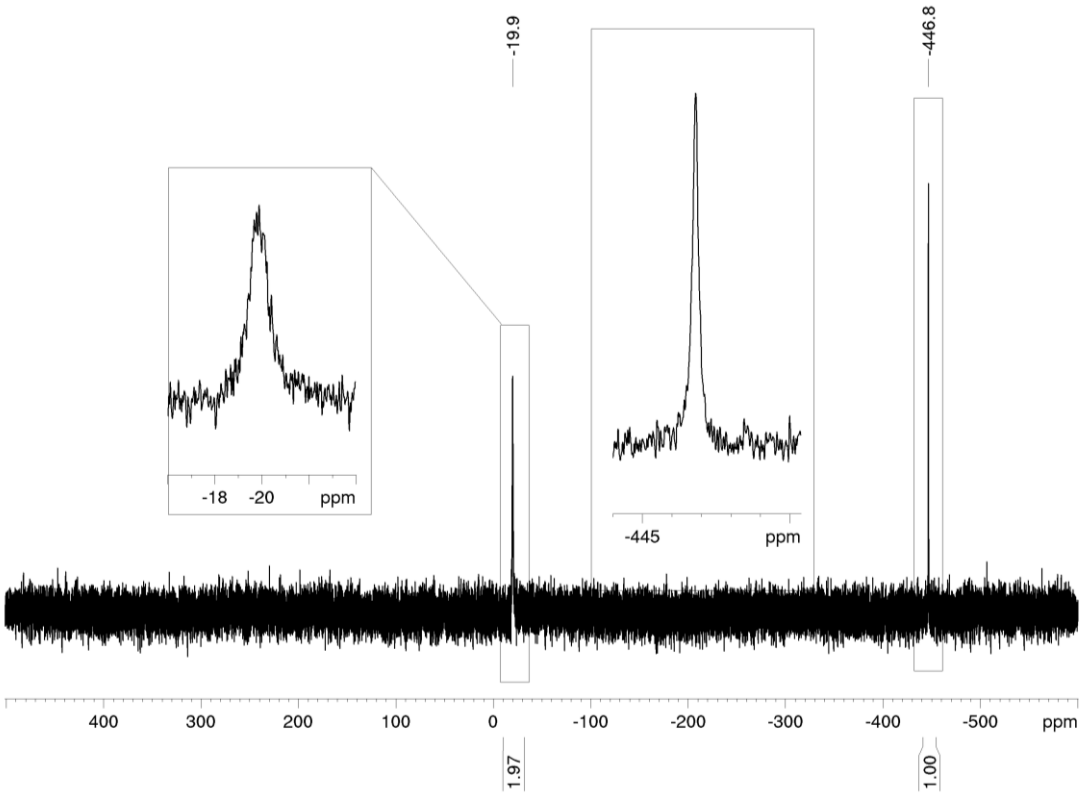


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **3.**

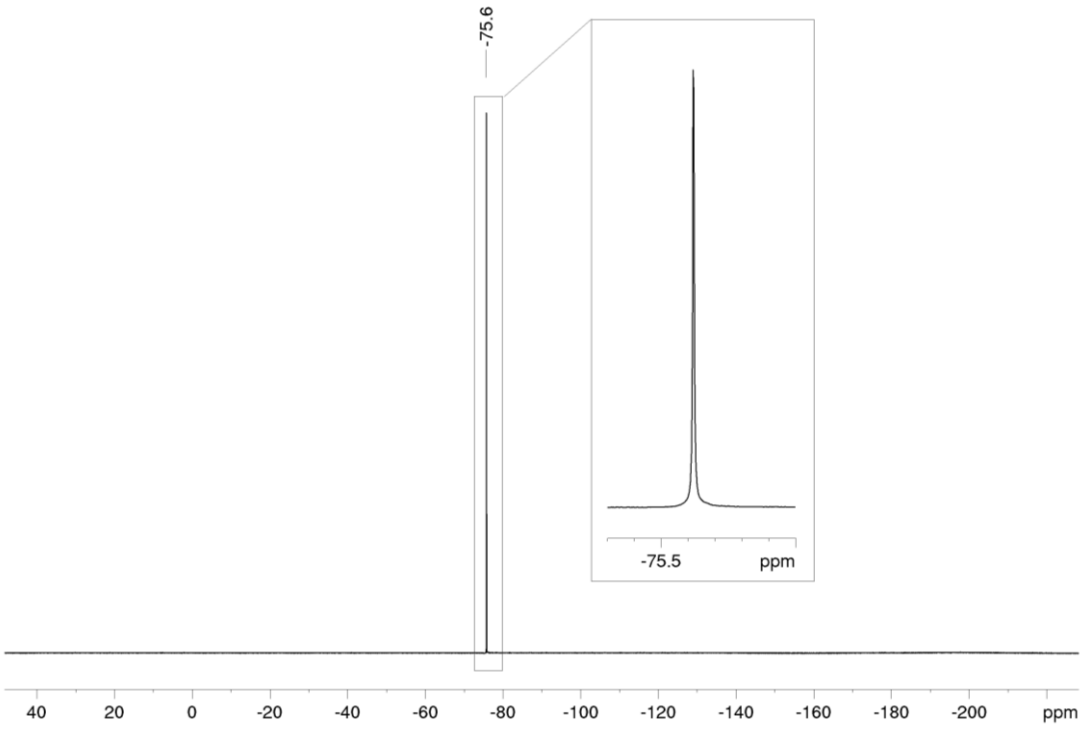


Figure S22. $^{19}F\{^{1}H\}$ NMR spectrum (376.62 MHz, 300 K, CD_2Cl_2) of **3**.

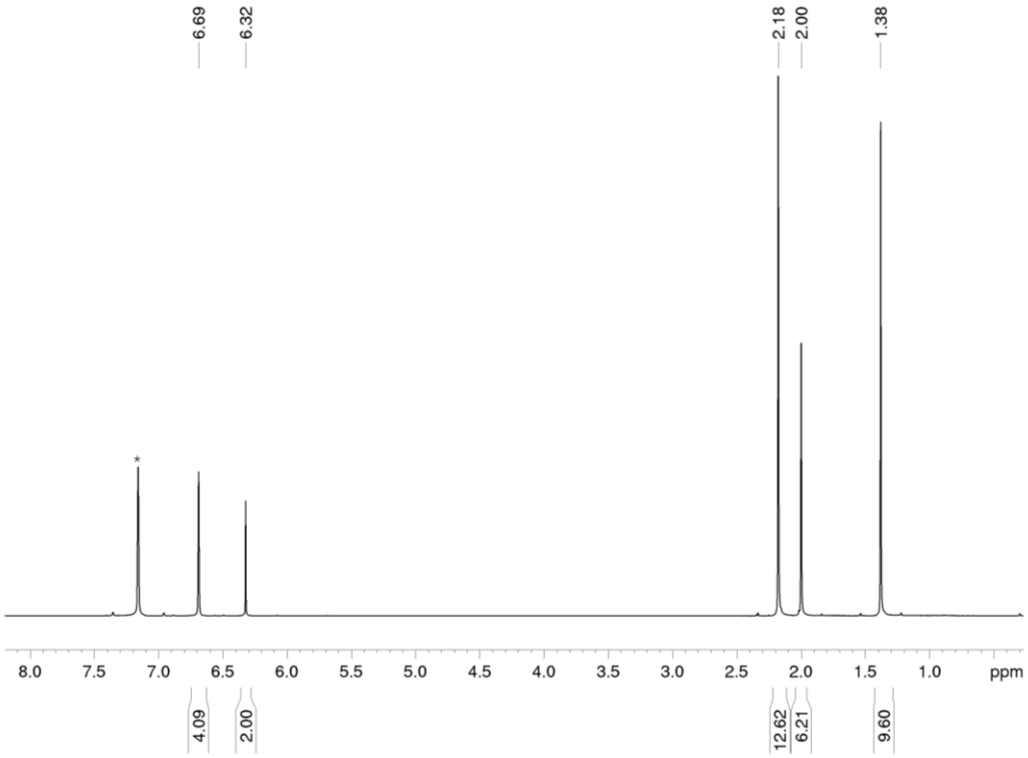


Figure S23. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **4a**; *C_6D_6.

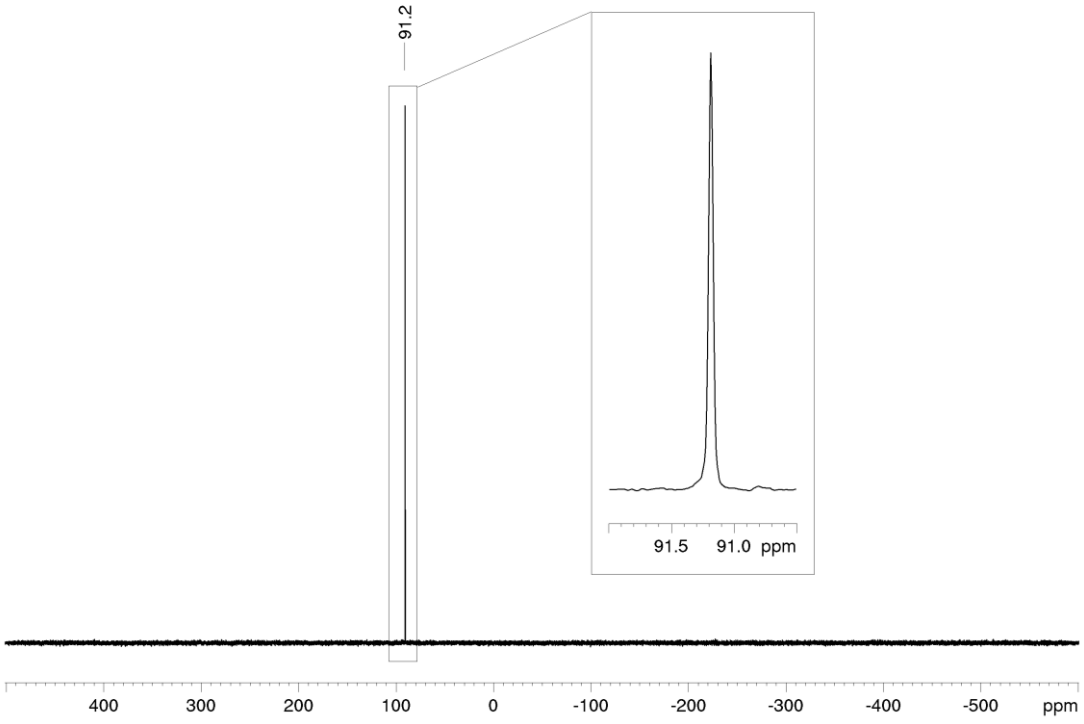


Figure S24. ^{31}P{^{1}H} NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **4a**.

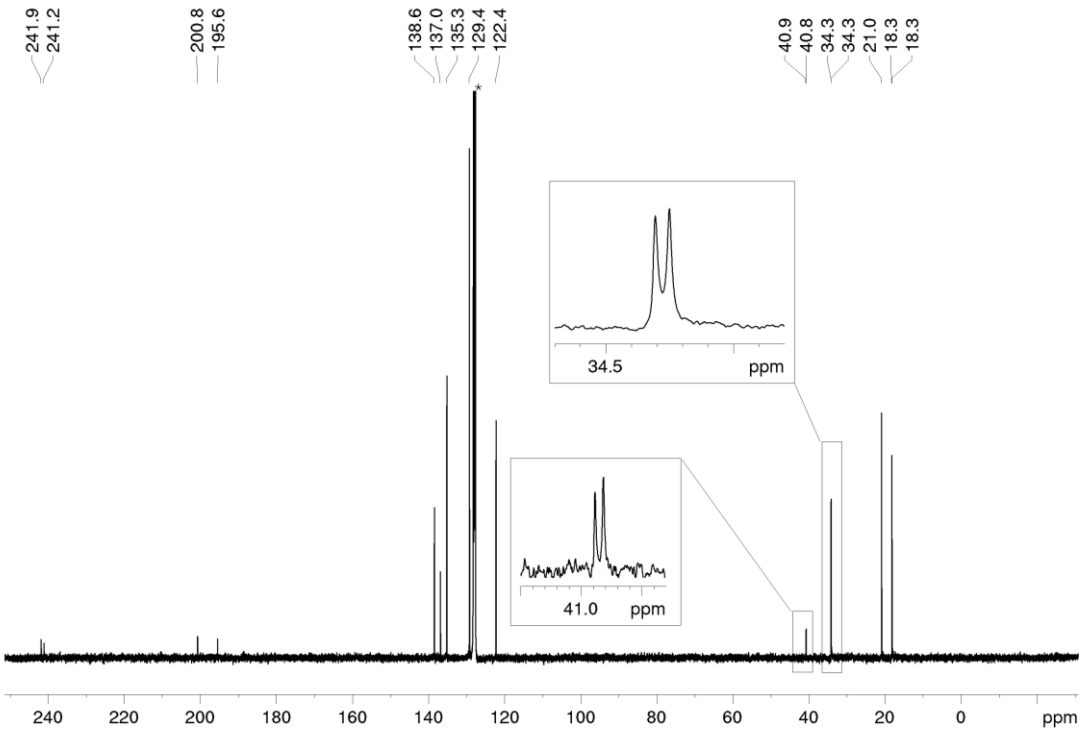


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **4a**; *C_6D_6.

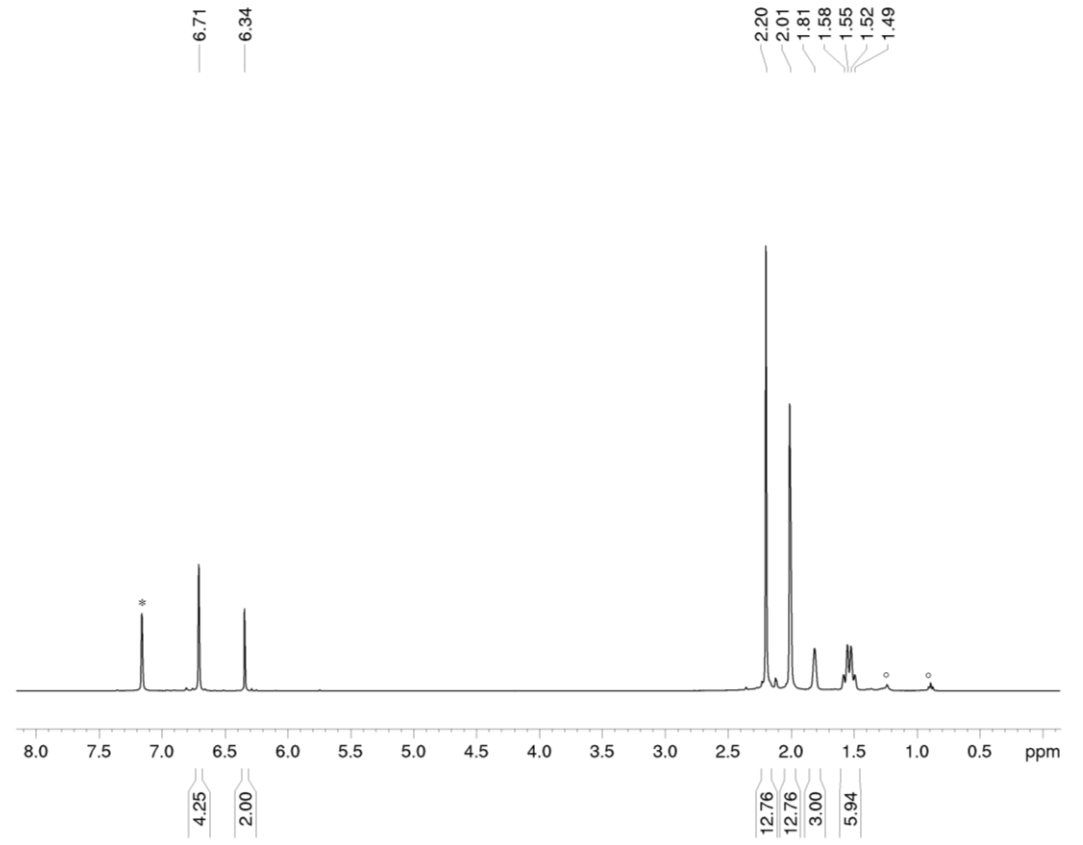


Figure S26. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **4b**; *C_6D_6, °*n*-hexane.

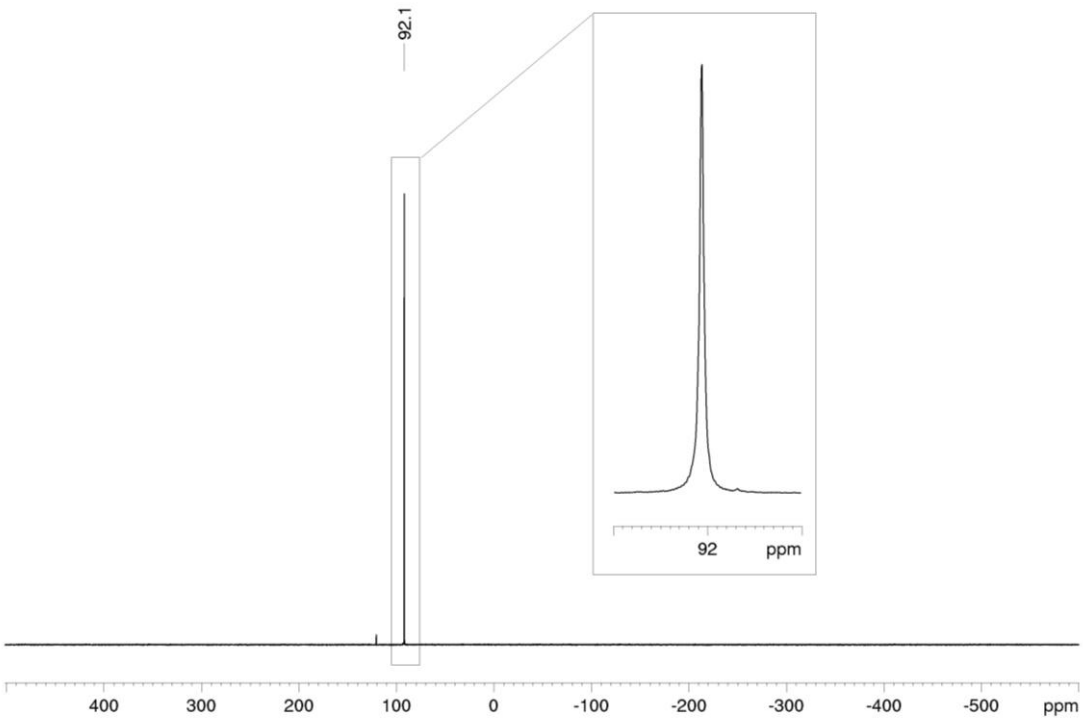


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **4b**.

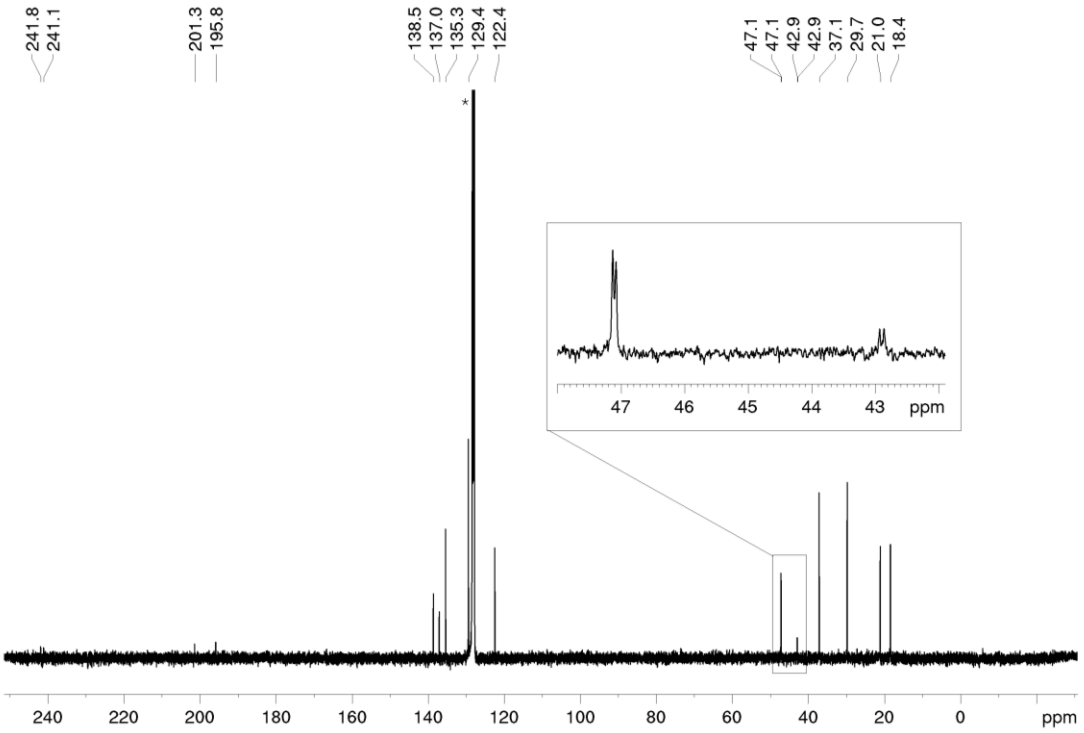


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **4b**; *C_6D_6

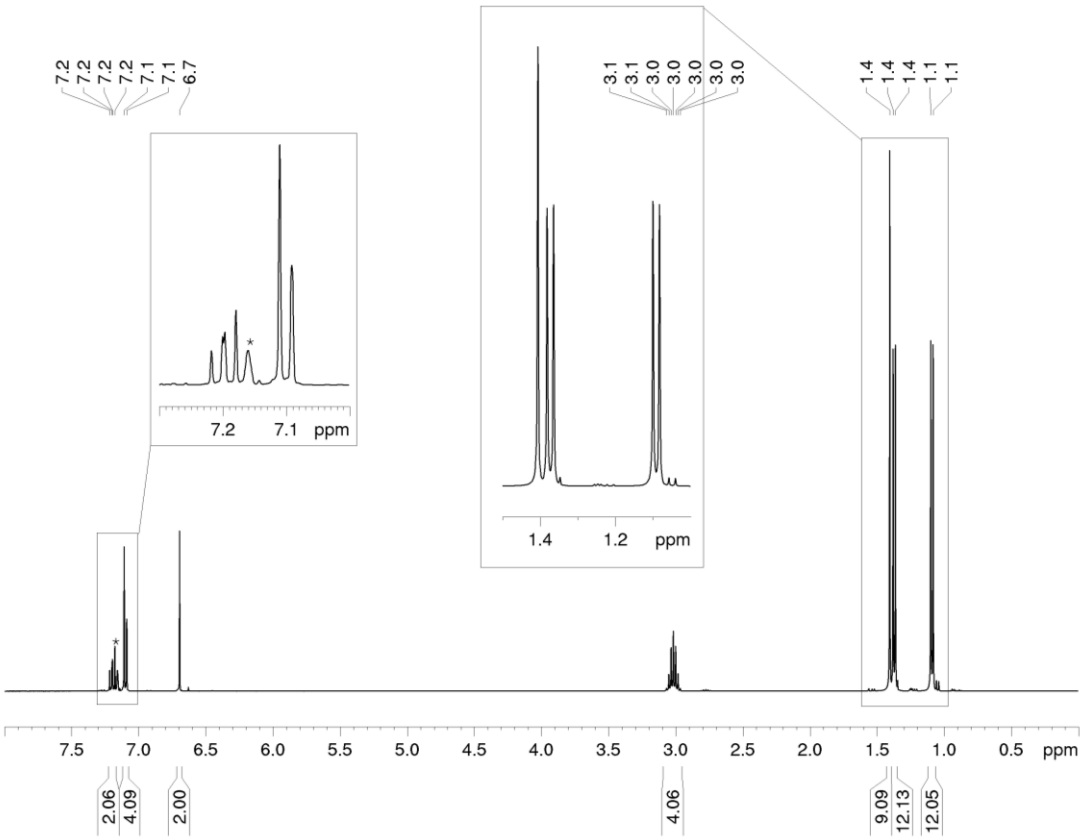


Figure S29. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **4c**; *C_6D_6.

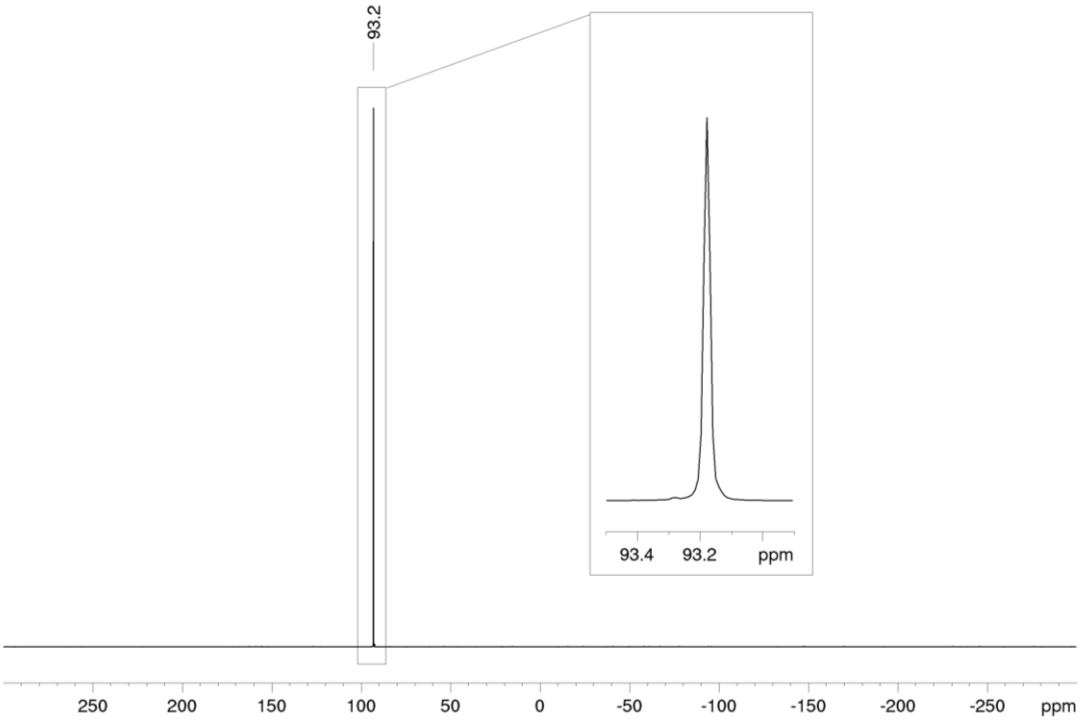


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **4c**.

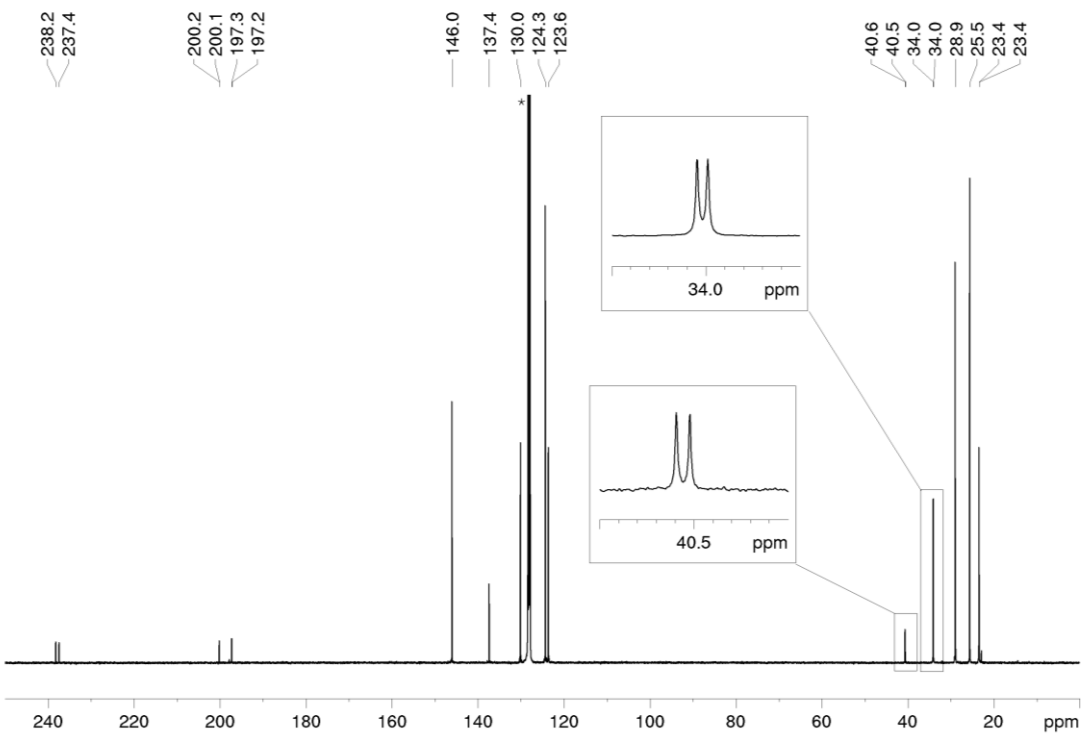


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **4c**; *C_6D_6

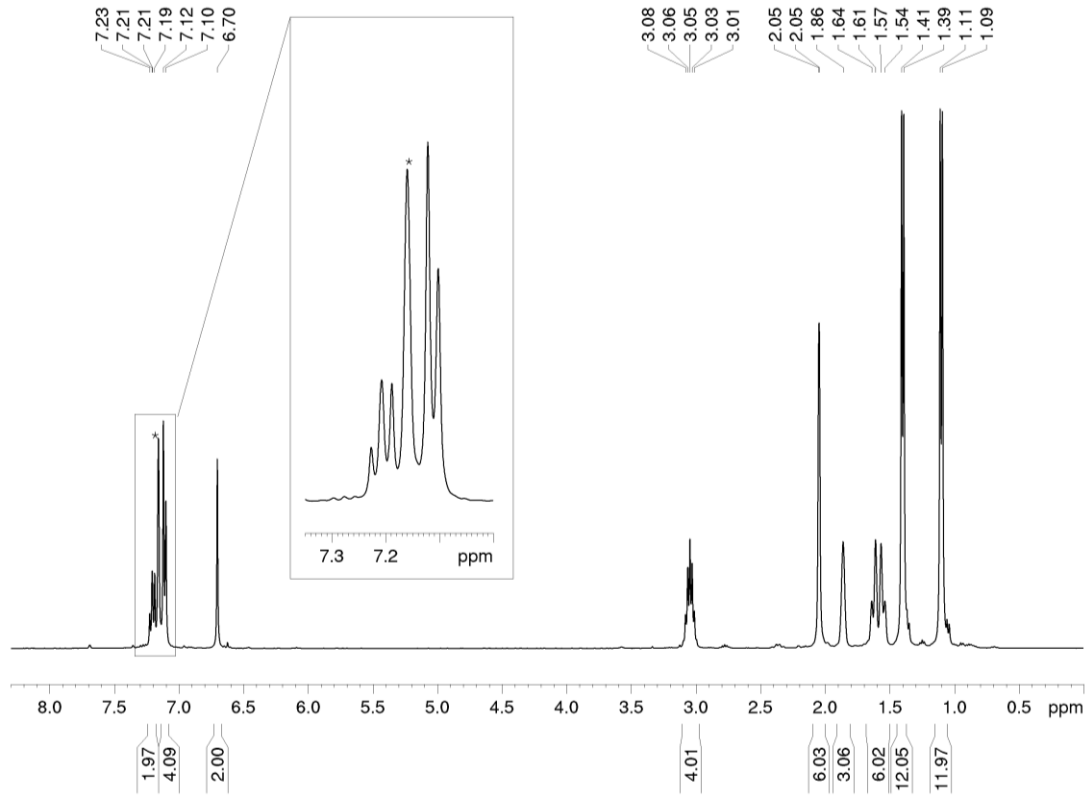


Figure S 32. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **4d**; *C_6D_6.

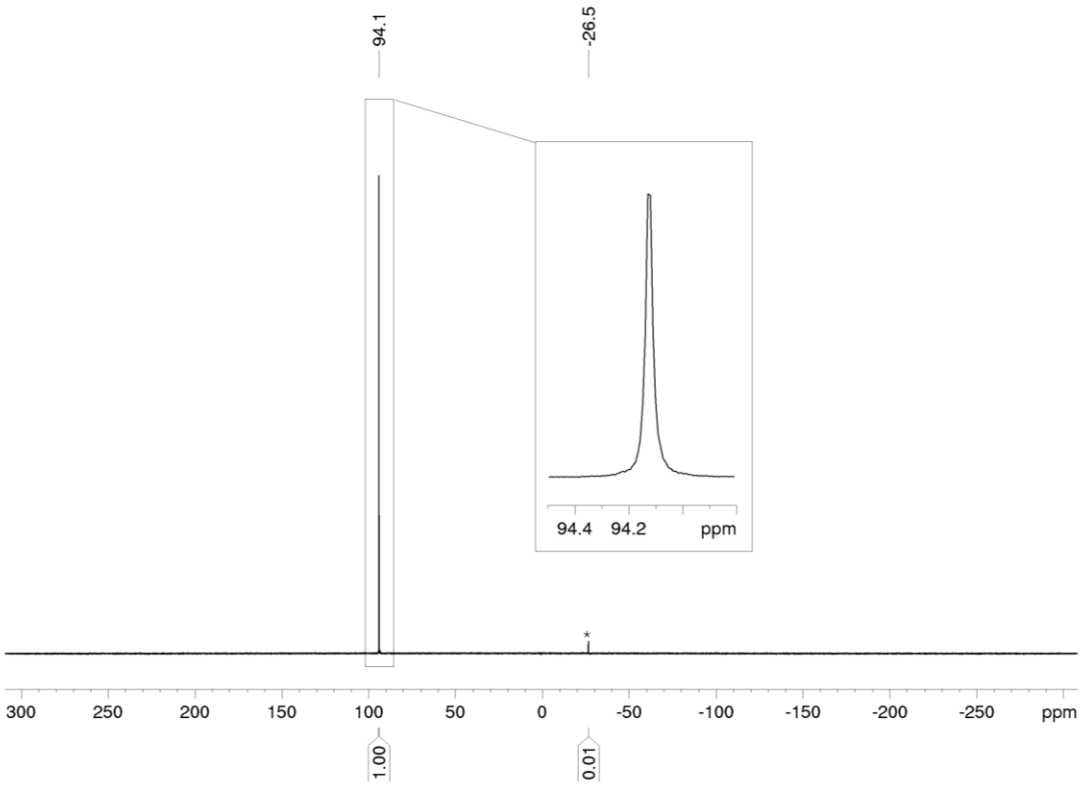


Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **4d**; *minor impurity of (*t*BuCP)$_4$ **2b**.

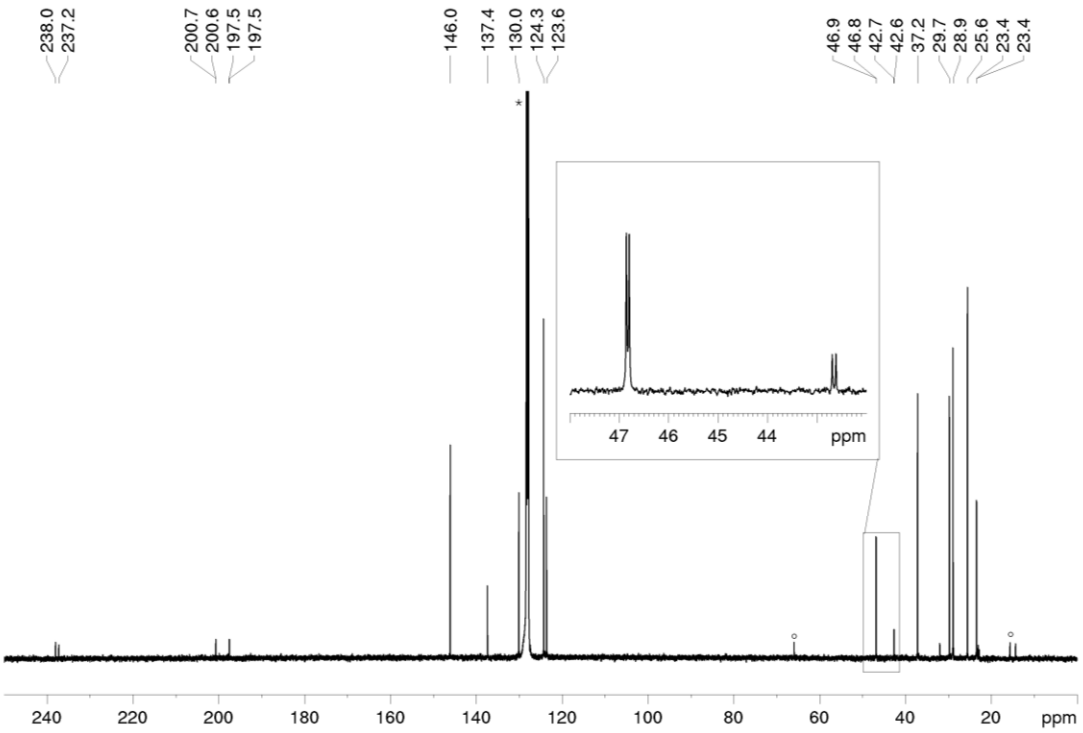


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of **4d**; *C_6D_6, ° traces of Et_2O

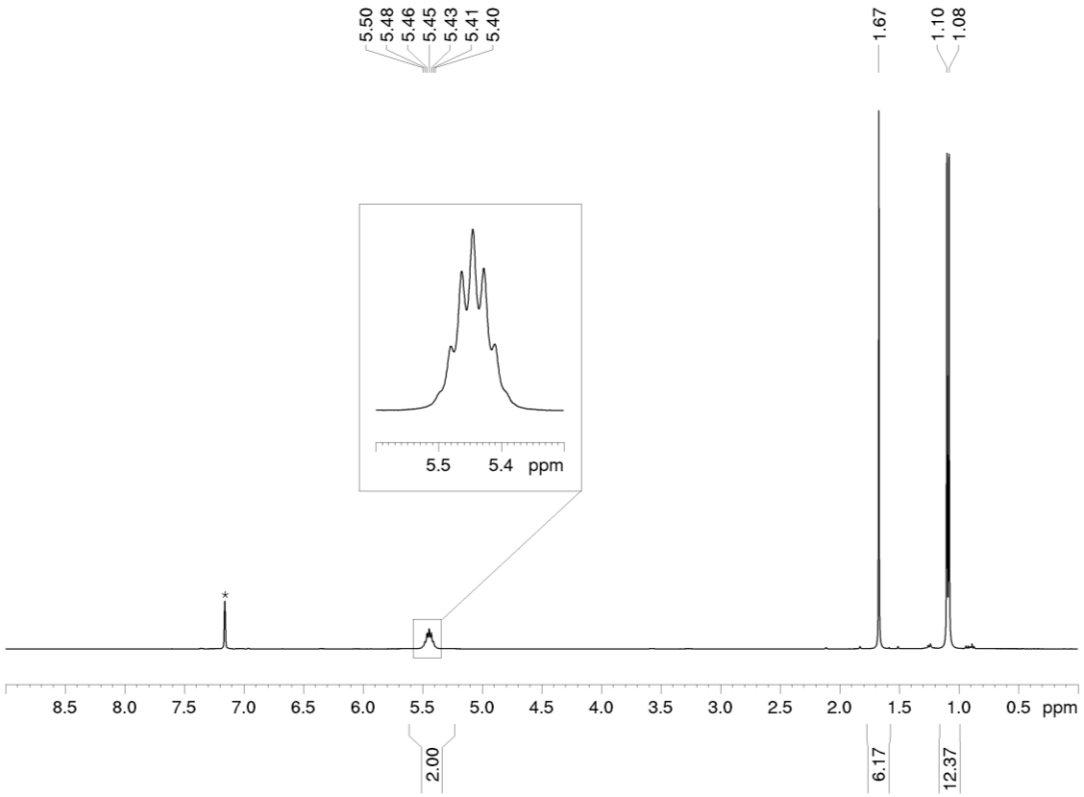


Figure S35. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of [(*i*Pr_2Im^{Me})$Ni(CO)_3$], *C_6D_6.

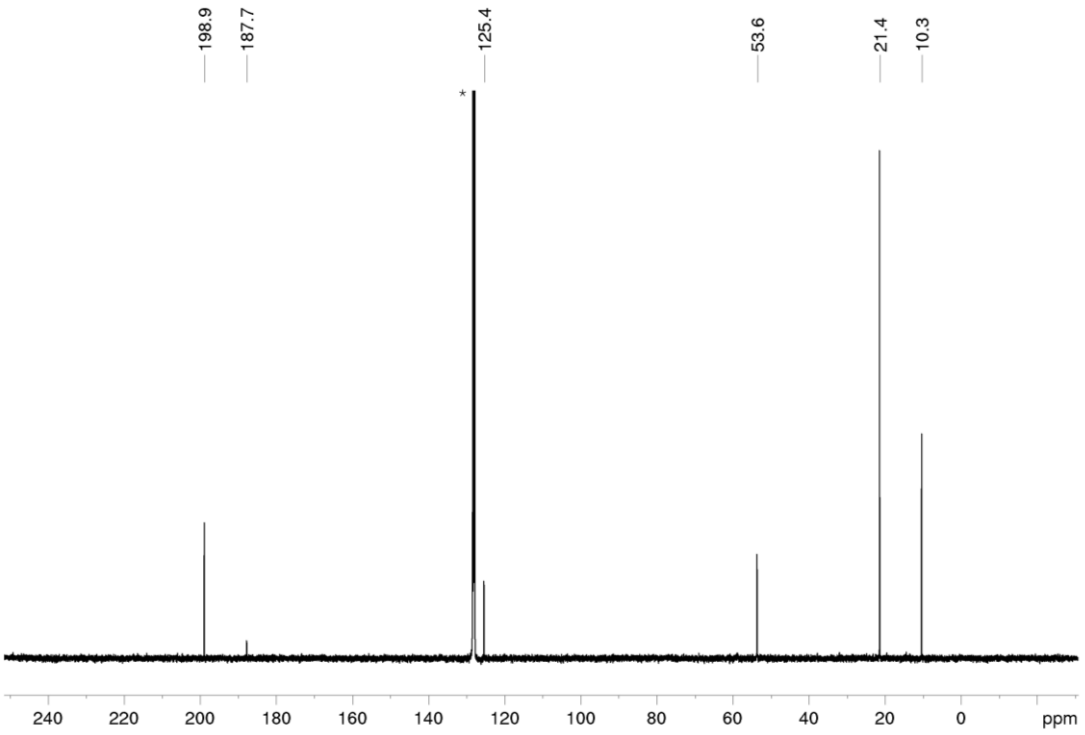


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, 300 K, C_6D_6) of [(*i*Pr_2Im^{Me})$Ni(CO)_3$]; *C_6D_6.

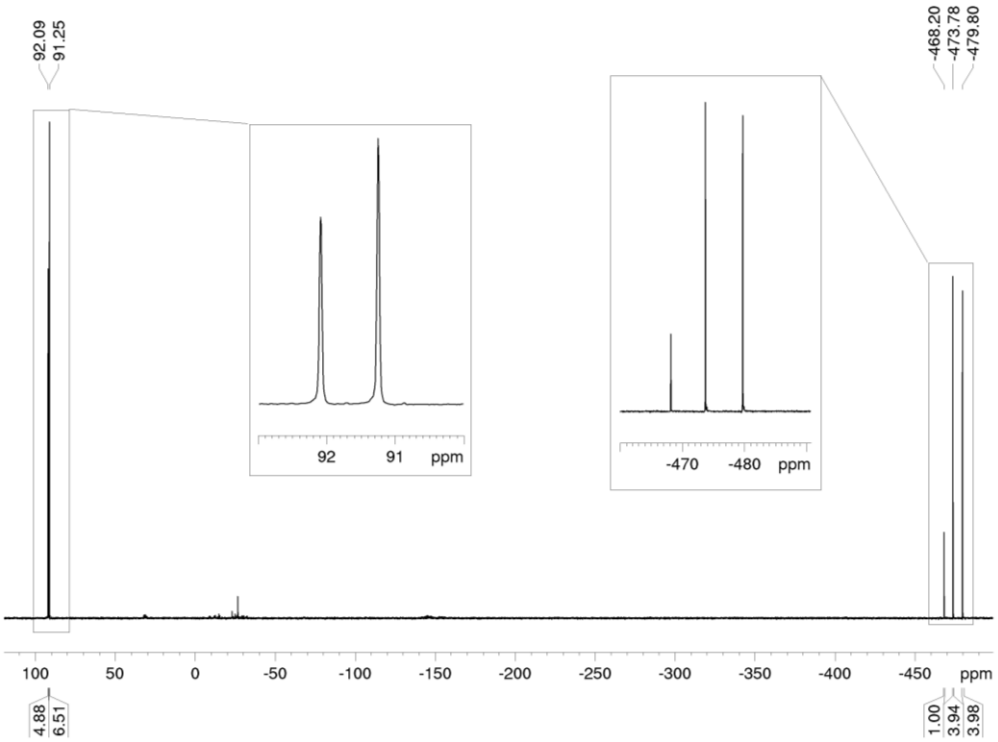


Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of **4a** with AdCP.

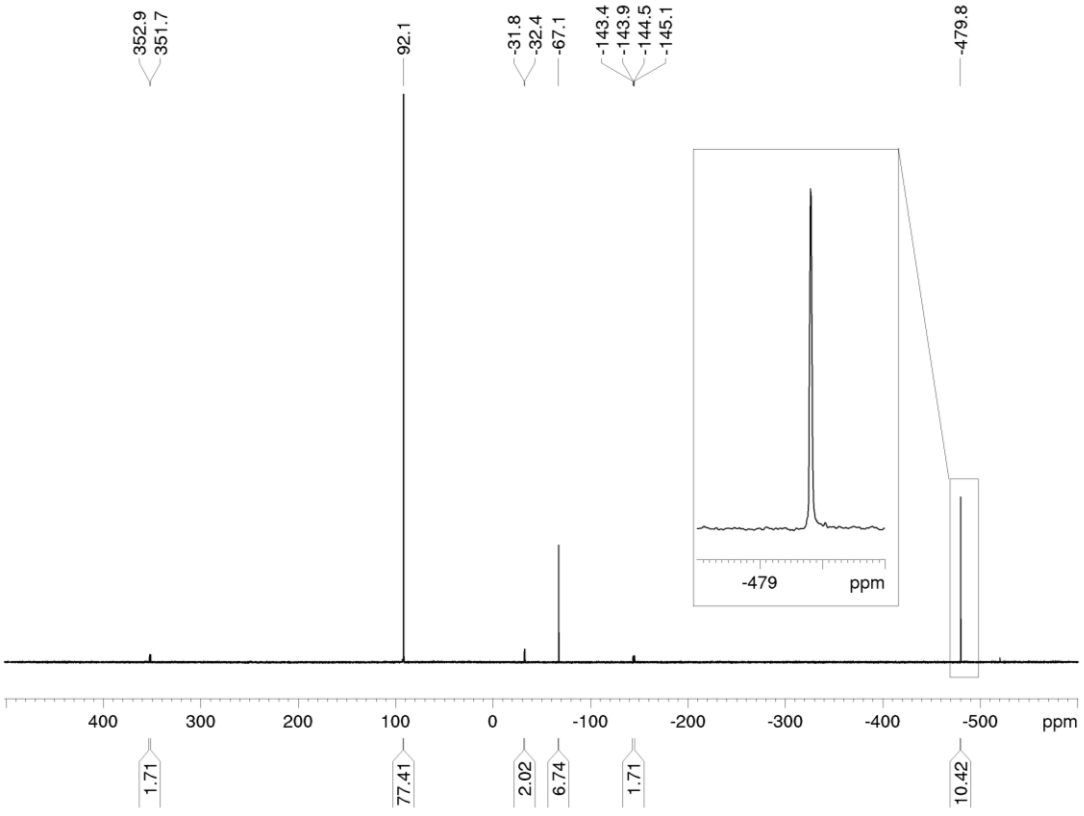


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(IMes)Ni(CO)$_3$] with 1.0 eq. AdCP.

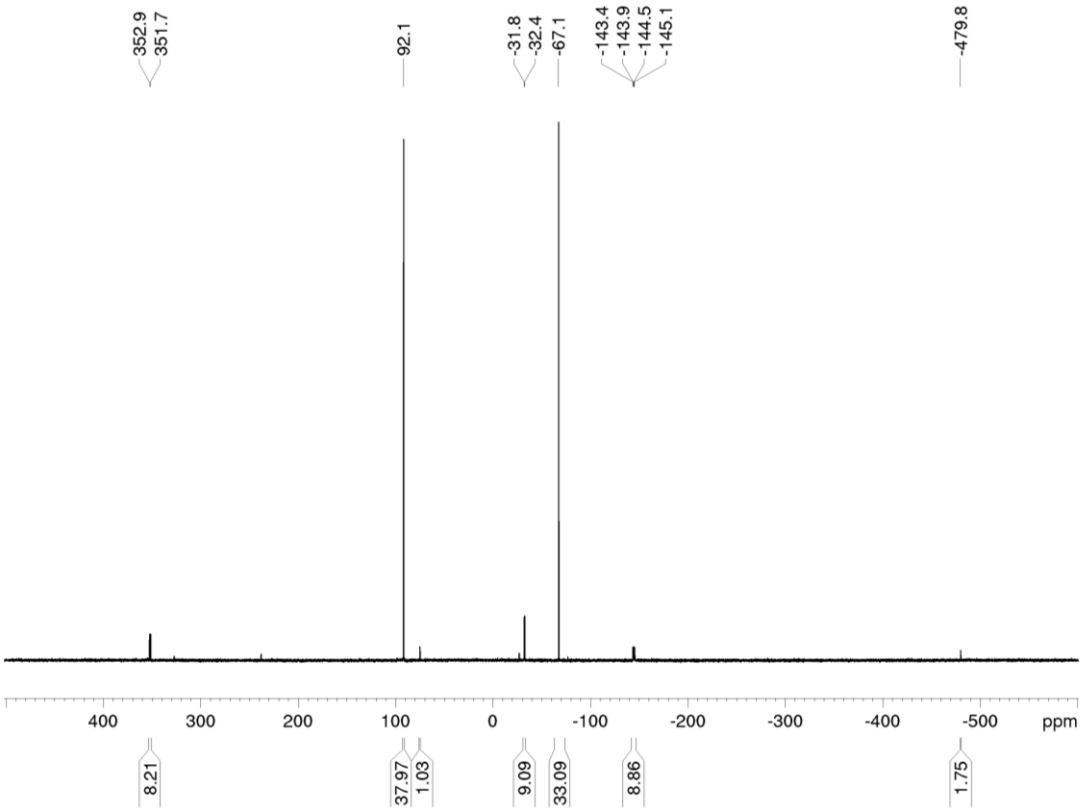


Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(IMes)Ni(CO)$_3$] with 3.0 eq. AdCP.

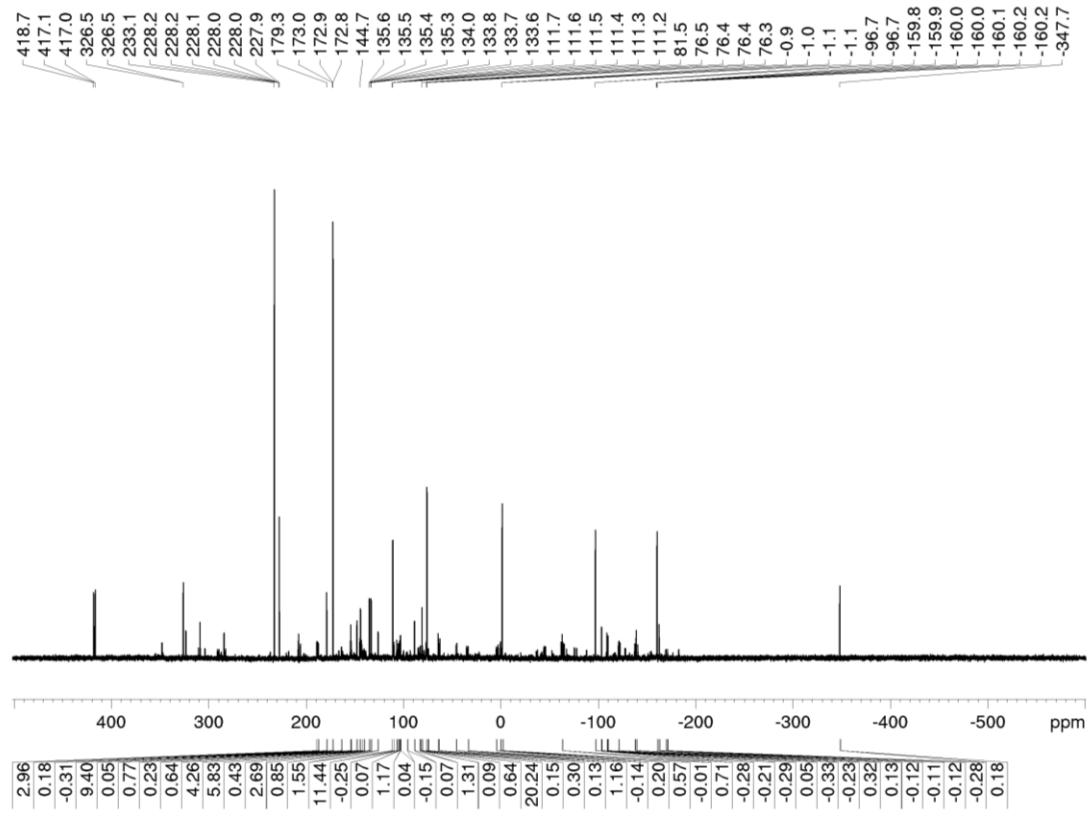


Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [Ni(CO)$_4$] with 1.1 eq. *t*BuCP.

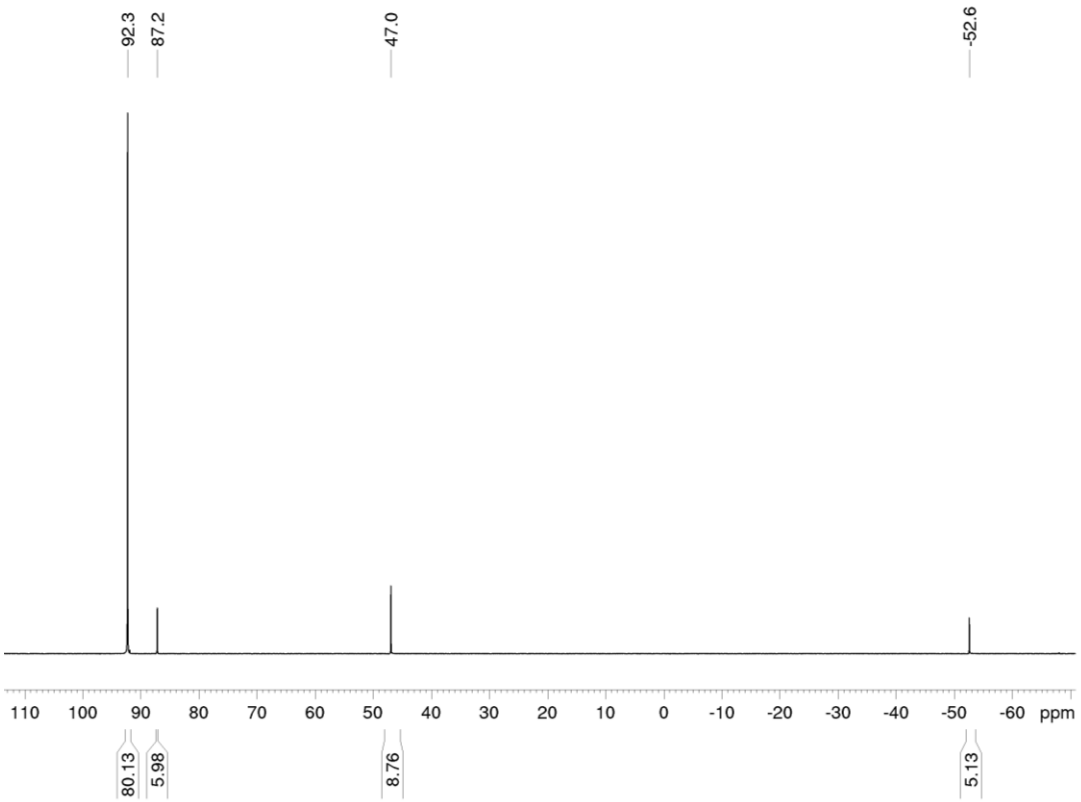


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr_2Im^{Me})Ni(CO)$_3$] with 1.5 eq. *t*BuCP.

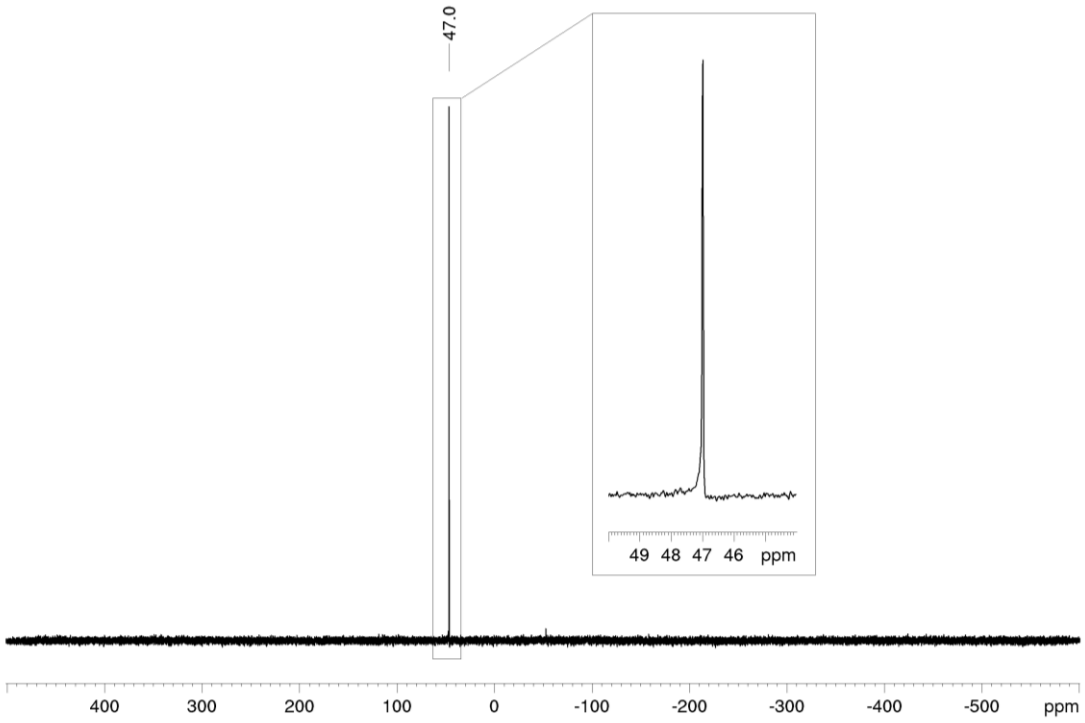
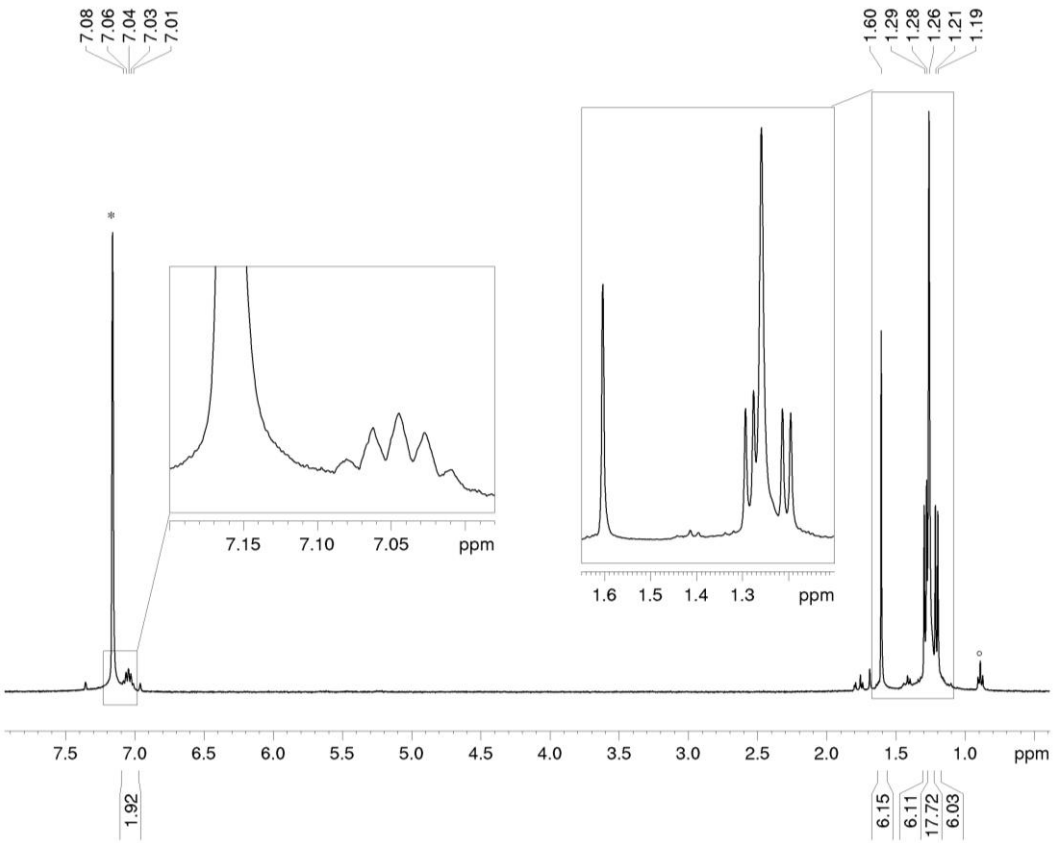


Figure S42. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of **5**.



FigureS43. ^{1}H NMR spectrum (400.13 MHz, 300 K, C_6D_6) of **5**, *C_6D_6, °*n*-hexane.

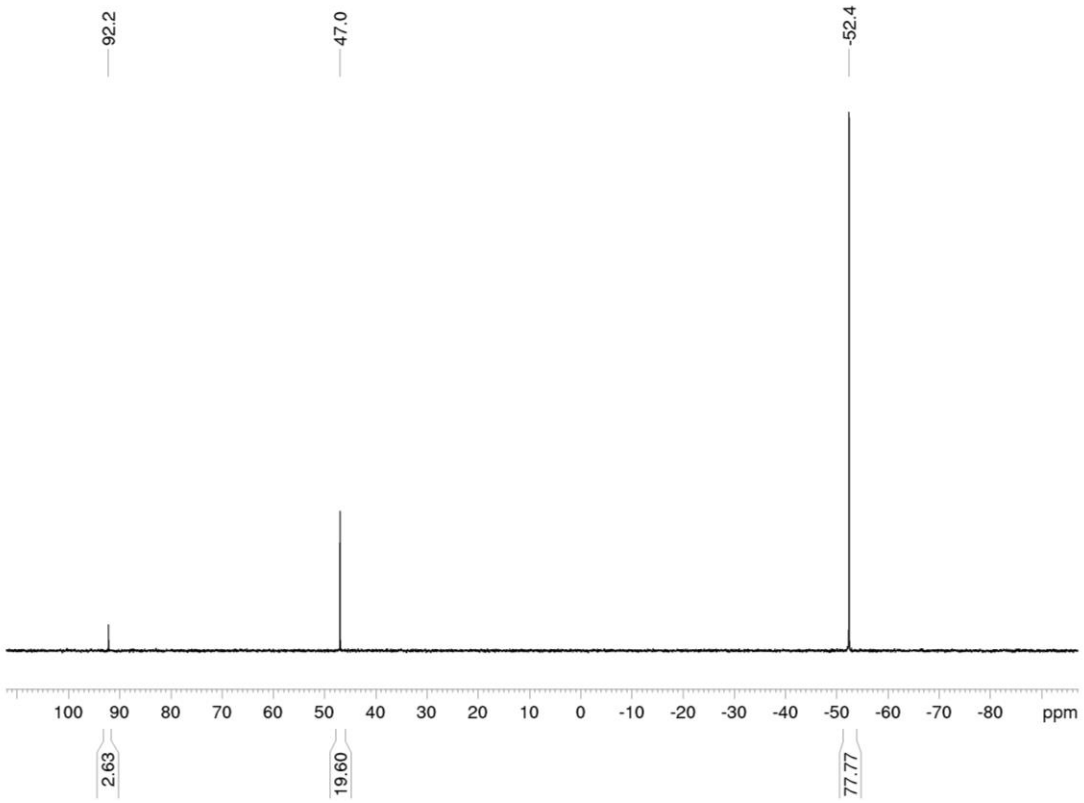


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of crystals of **6** re-dissolved in C_6D_6.

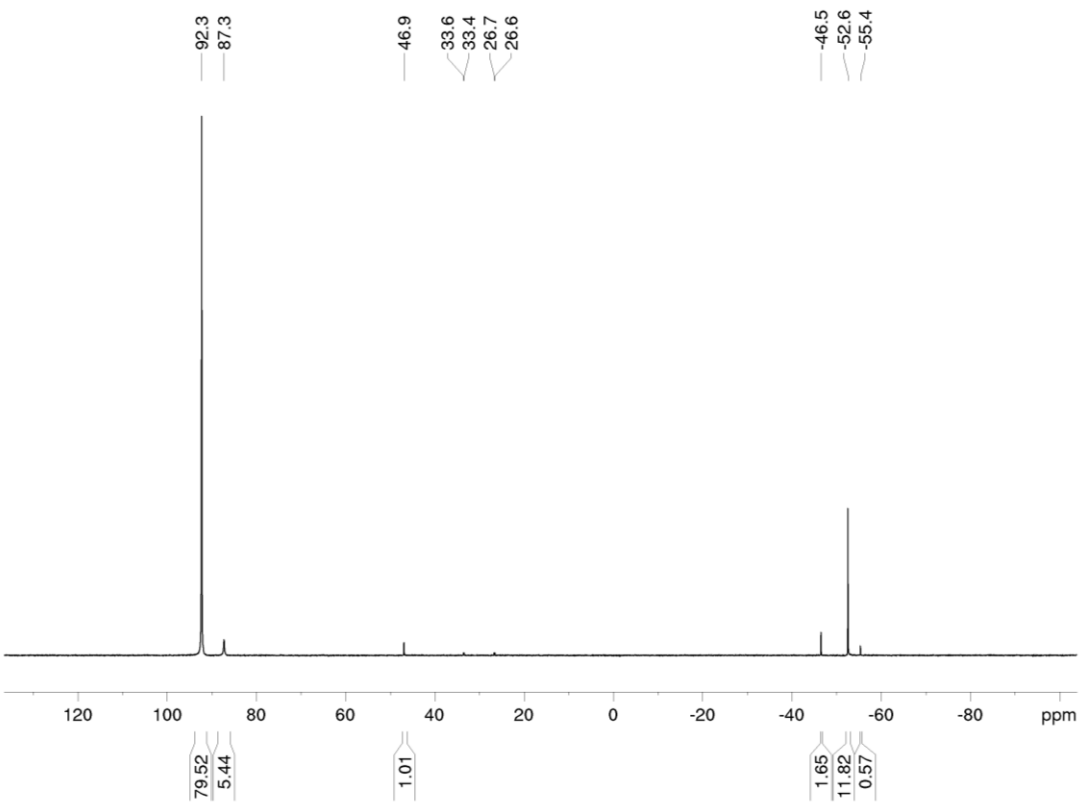


Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$] with 1.0 eq. *t*BuCP.

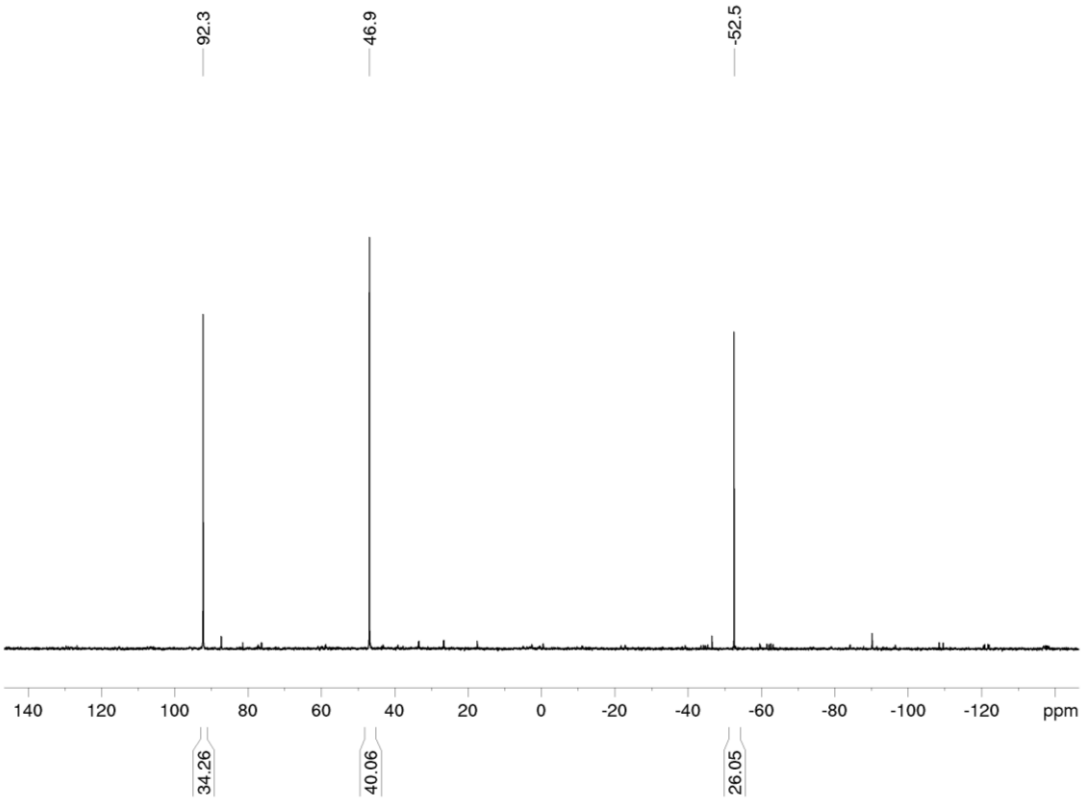


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$] with 2.1 eq. *t*BuCP.

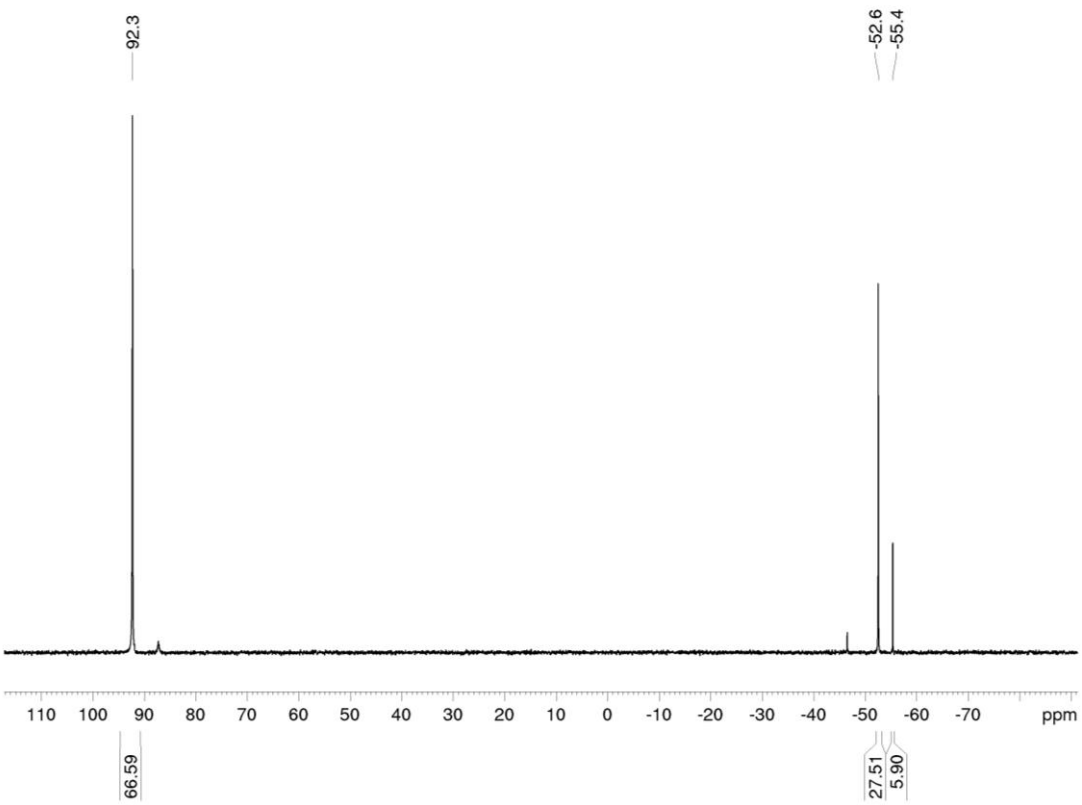


Figure S47. $^{31}P\{^{1}H\}$ NMR spectrum (161.98 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr_2Im^{Me})Ni$(CO)_3$] with 0.5 eq. *t*BuCP.

5 UV-Vis, IR and Mass Spectra

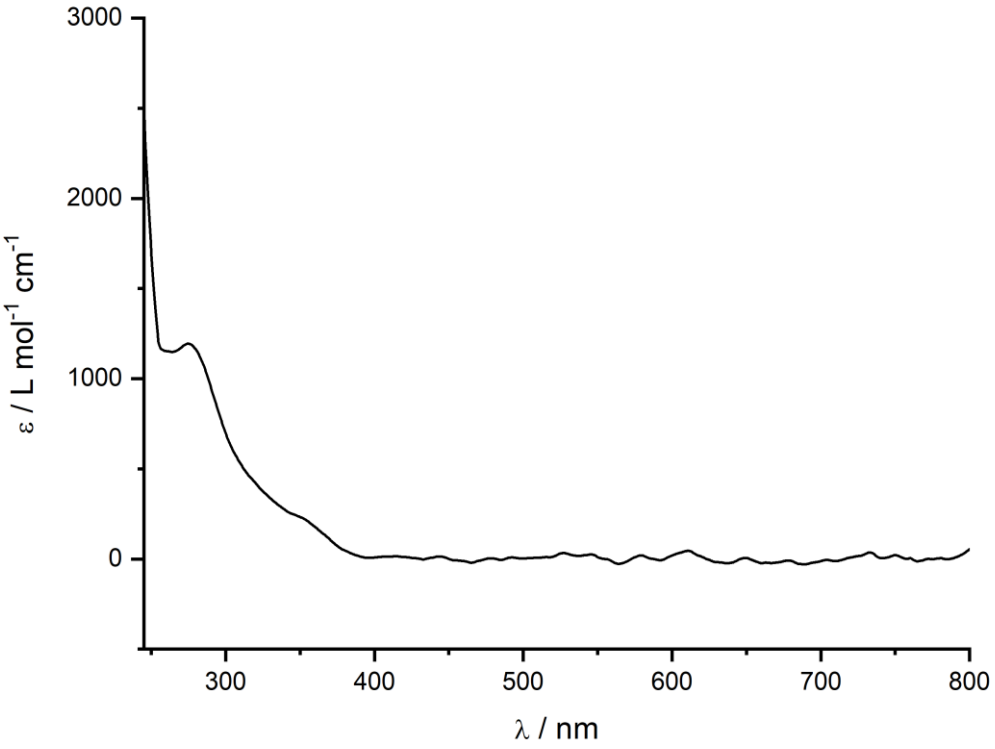


Figure S48. UV/VIS spectrum (*n*-hexane) of **1a**.

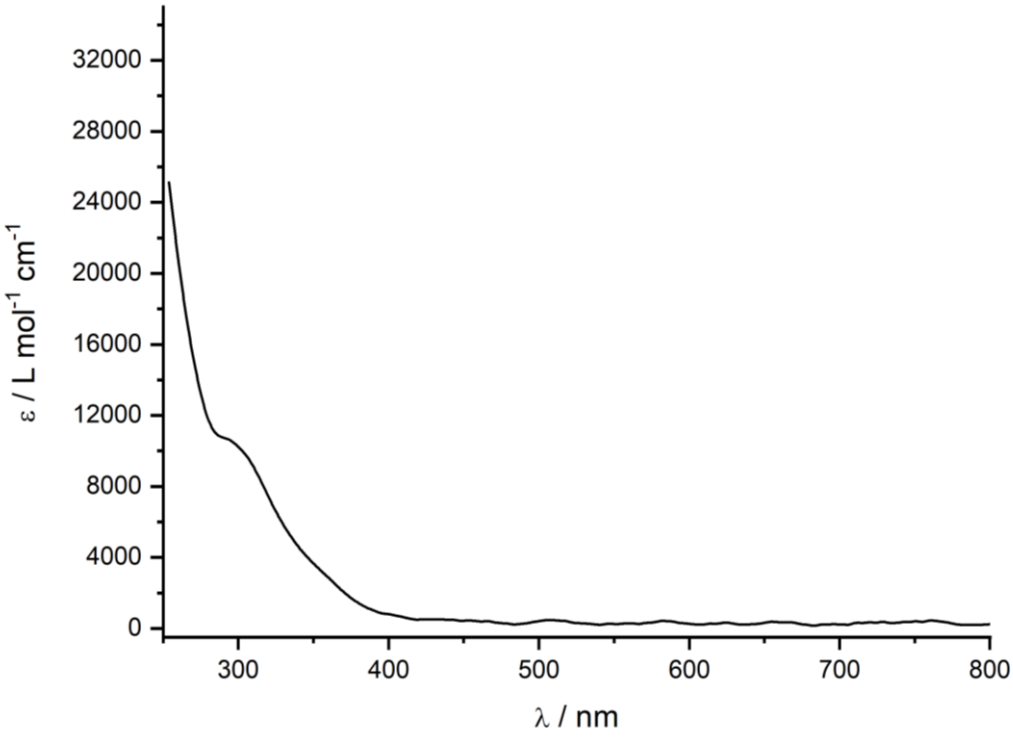


Figure S49. UV/VIS spectrum (CH_2Cl_2) of **3**.

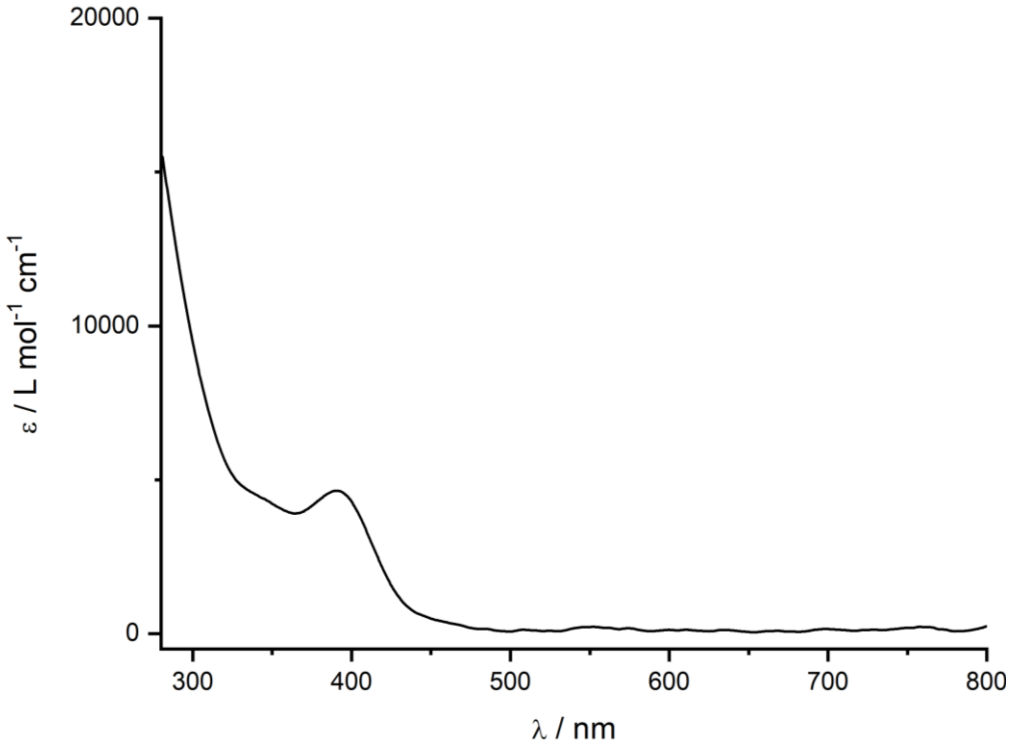


Figure S50. UV/VIS spectrum (THF) of **4a**.

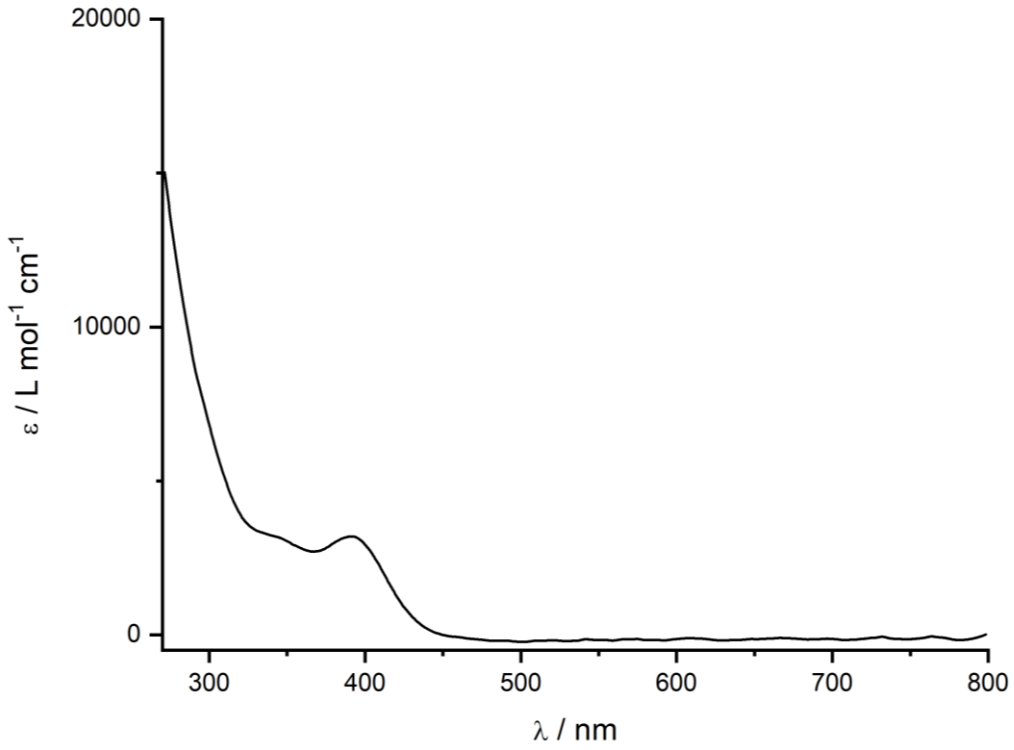


Figure S51. UV/VIS spectrum (THF) of **4b**.

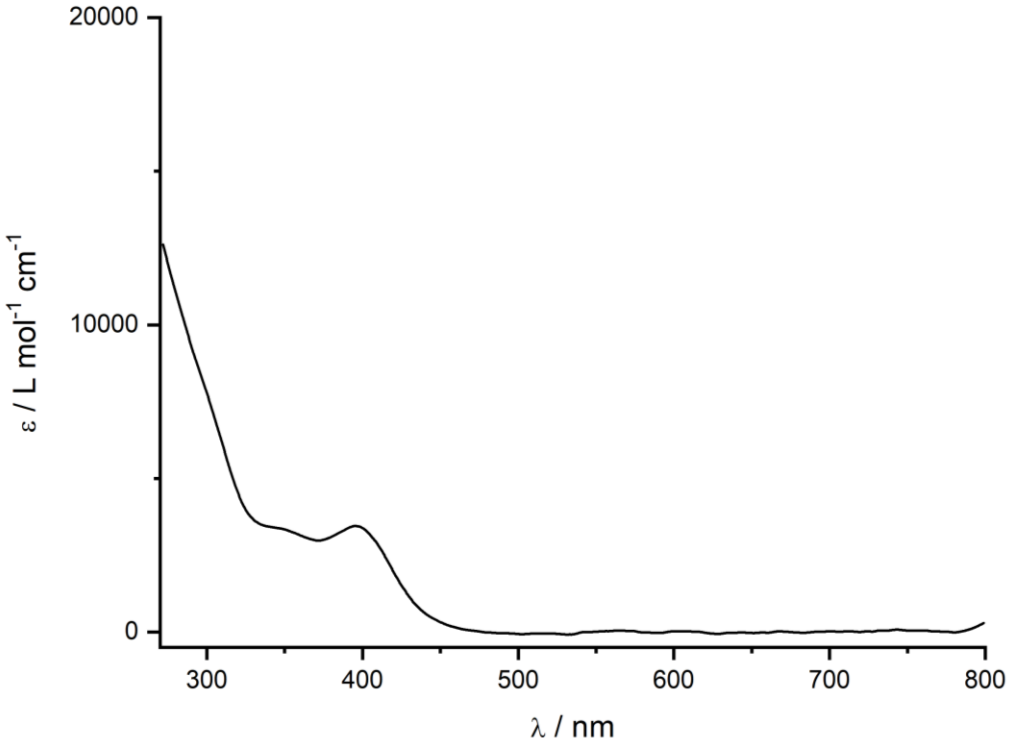


Figure S52. UV/VIS spectrum (THF) of **4c**.

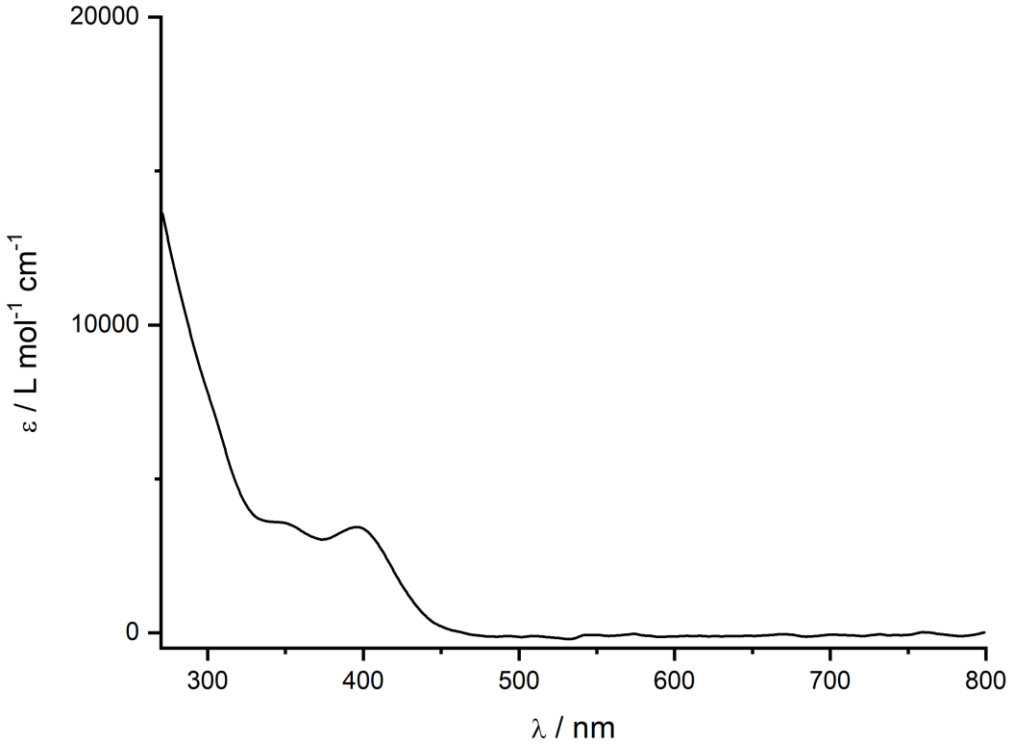


Figure S53. UV/VIS spectrum (THF) of **4d**.

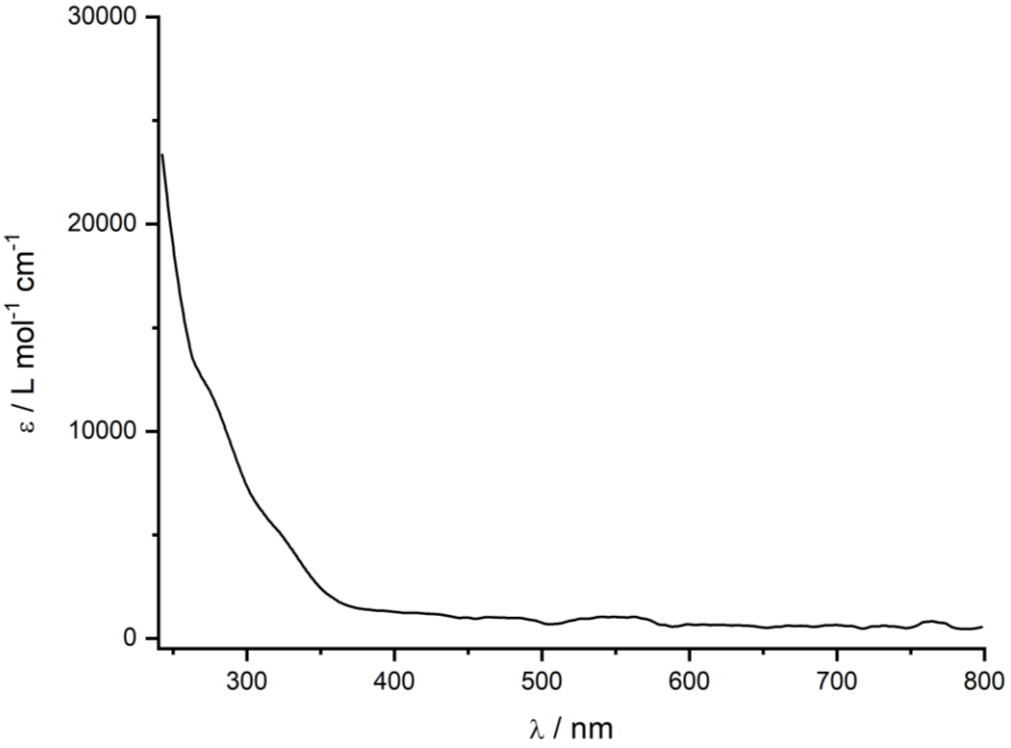


Figure S54. UV/VIS spectrum (THF) of [*i*Pr$_2$Im^{Me}Ni(CO)$_3$].

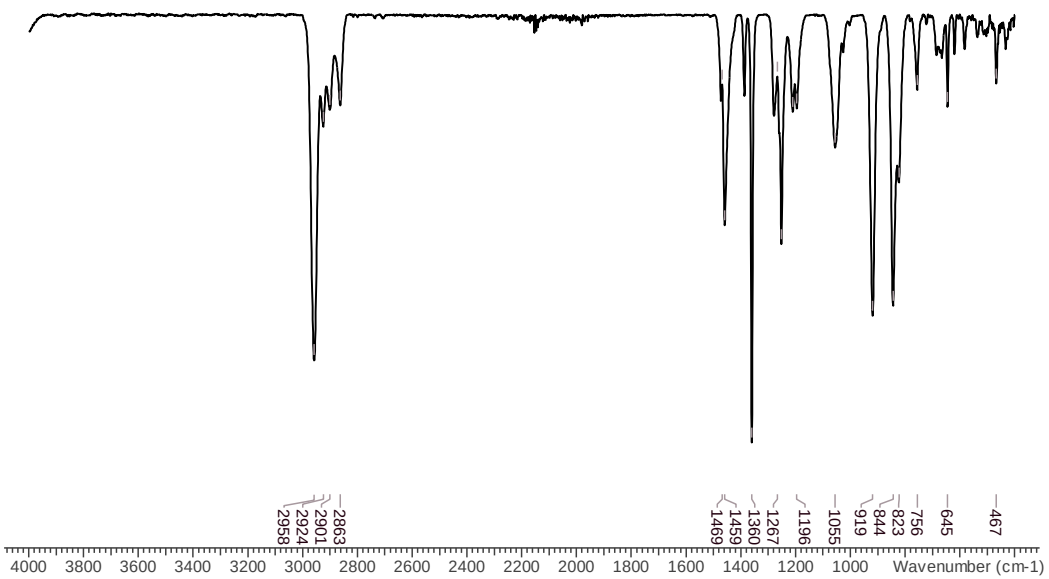


Figure S55. IR spectrum (ATR) of **1a**.

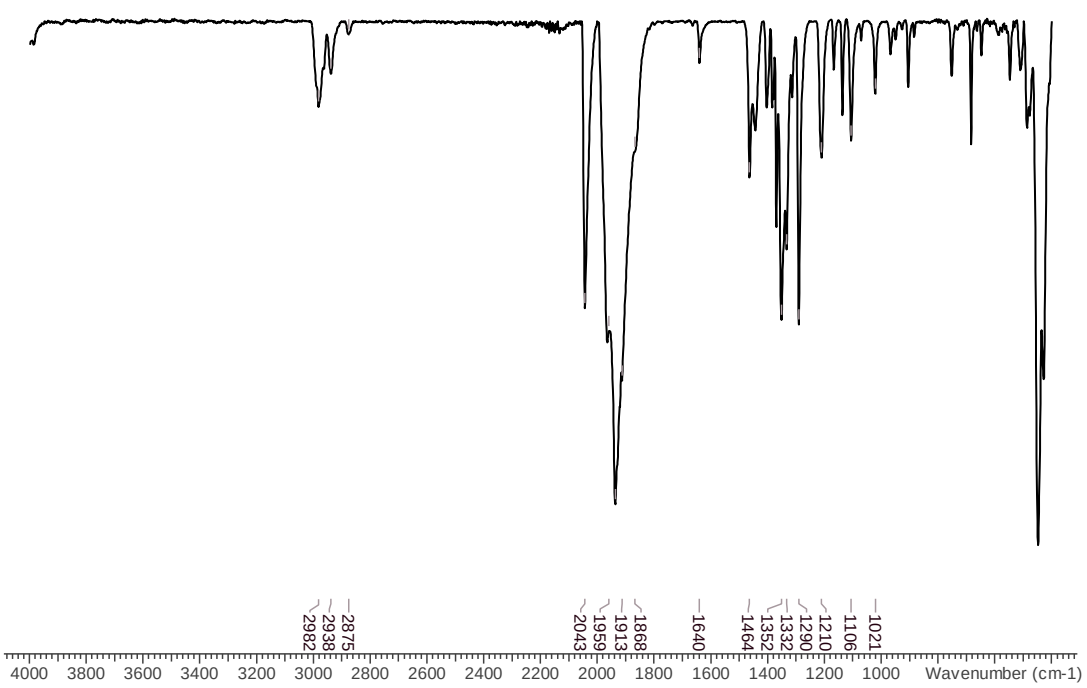


Figure S56. IR spectrum (ATR) of (*i*PrIm^{Me})Ni(CO)$_3$.

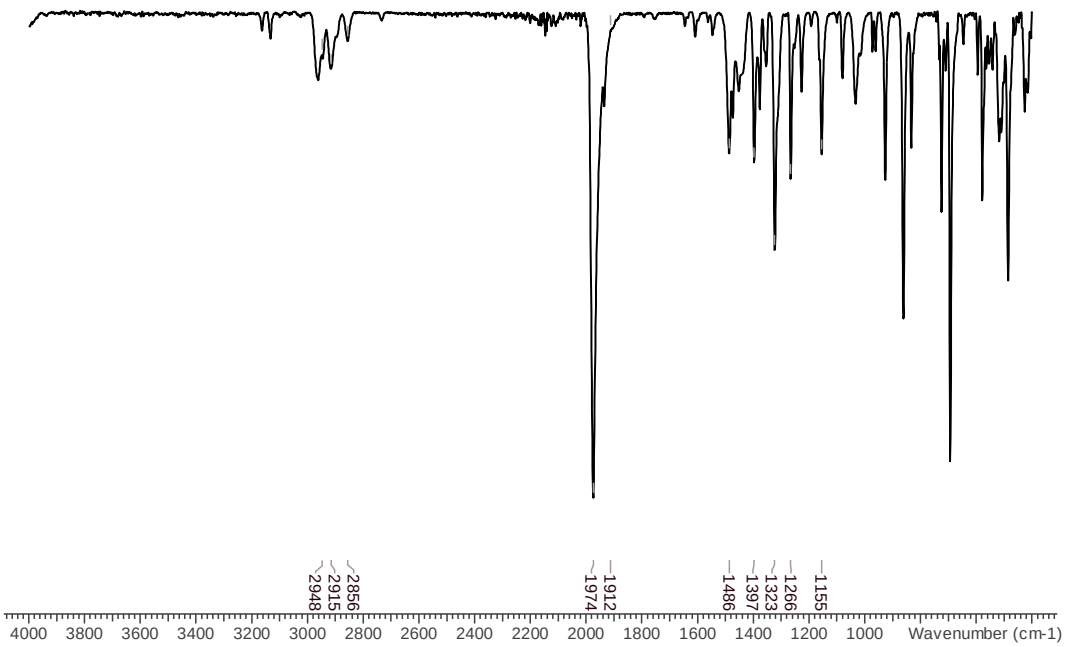


Figure S57. IR spectrum (ATR) of **4a**.

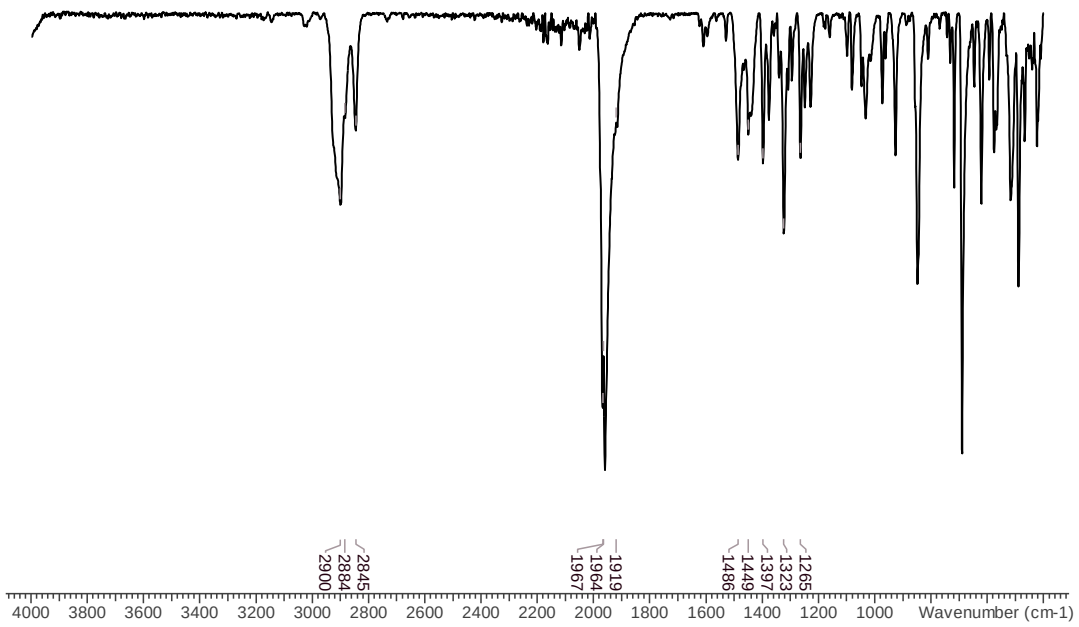


Figure S58. IR spectrum (ATR) of **4b**.

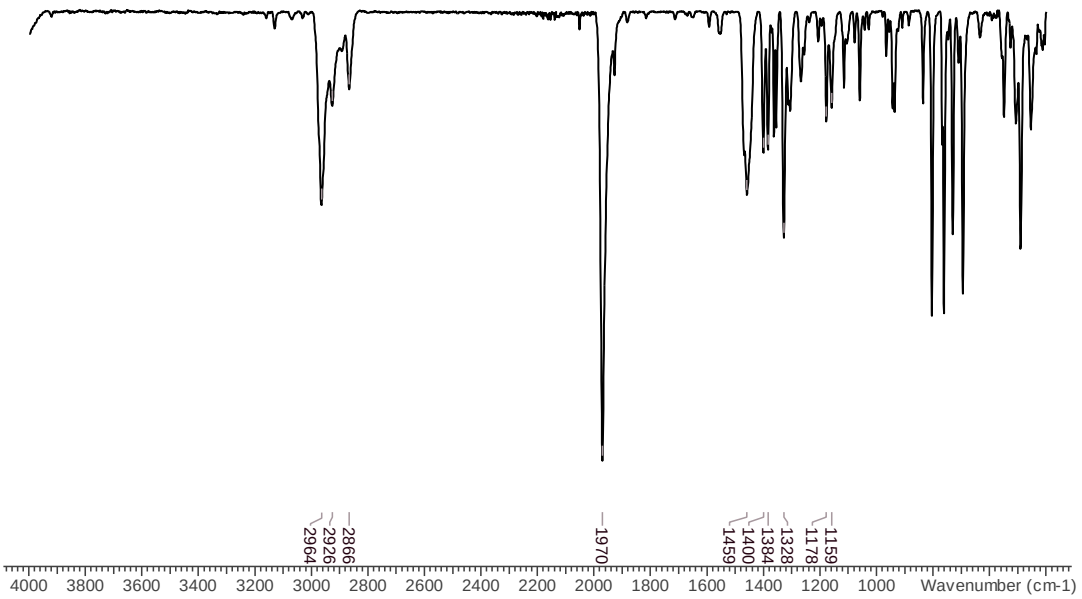


Figure S59. IR spectrum (ATR) of **4c**.

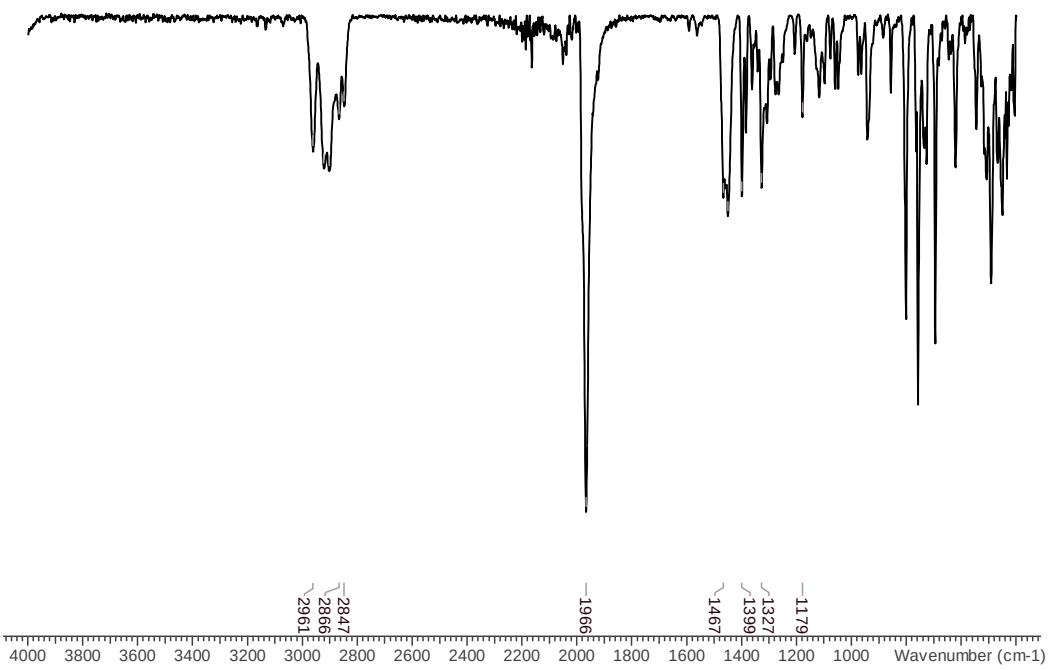


Figure S60. IR spectrum (ATR) of **4d**.

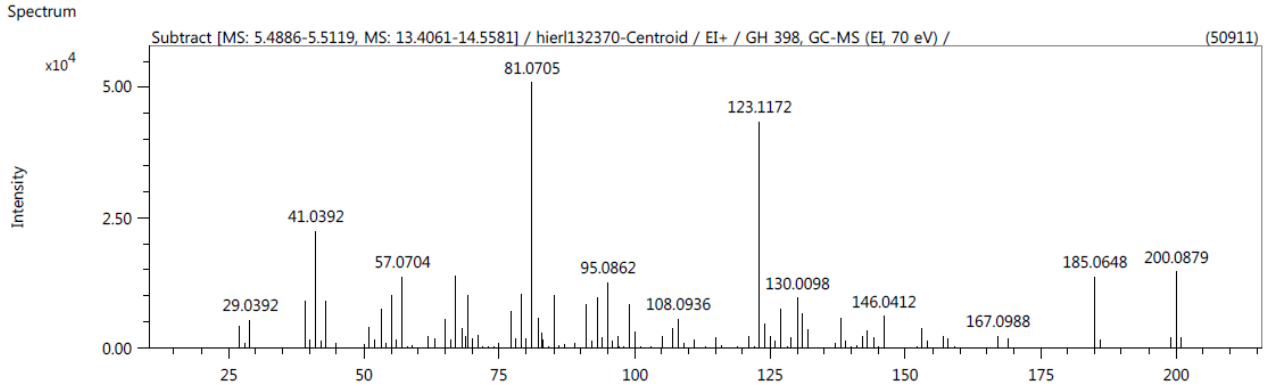


Figure S61. Mass spectrum of **1a**.

6 Single Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku Oxford Diffraction SuperNova Atlas or GV1000 Titan[S2] diffractometers with Cu-K_α radiation (λ= 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[12,13] or analytical ones[14] were applied to the data. The structures were solved with SHELXT[15] solution program using dual methods and by using Olex2 as the graphical interface.[16] The models were refined with ShelXL[18] using full matrix least squares minimization on F^2.[17] The hydrogen atoms were located in idealized positions and refined isotropically with a riding model. The disorder in **4a** and **4d** were treated with soft displacement parameter and geometrical restraints.

Several crystallization efforts only led to poor quality crystals of **3**. Numerous samples were tested for diffraction, but all crystals turned out to be twinned (see Figure S62) and only weakly diffracting, especially at higher resolution. Additionally, the crystals decompose in the X-ray beam (see Figure S63). Hence, the experiment strategy was tailored to the best compromise between twin completeness, frame exposure and total dose time. From the thus acquired full experiments the best dataset was taken for the structure determination. The chosen individual revealed the largest amount of non-overlapping, relatively strong major and only weak minor component reflections (major:minor 79:21). All fully overlapping and minor component reflections were omitted to allow for a good structure determination. A decay model was applied during scaling. The model was refined against data to $2\theta \leq 116°$, since the reflections at higher resolutions were below $2\sigma(I)$.

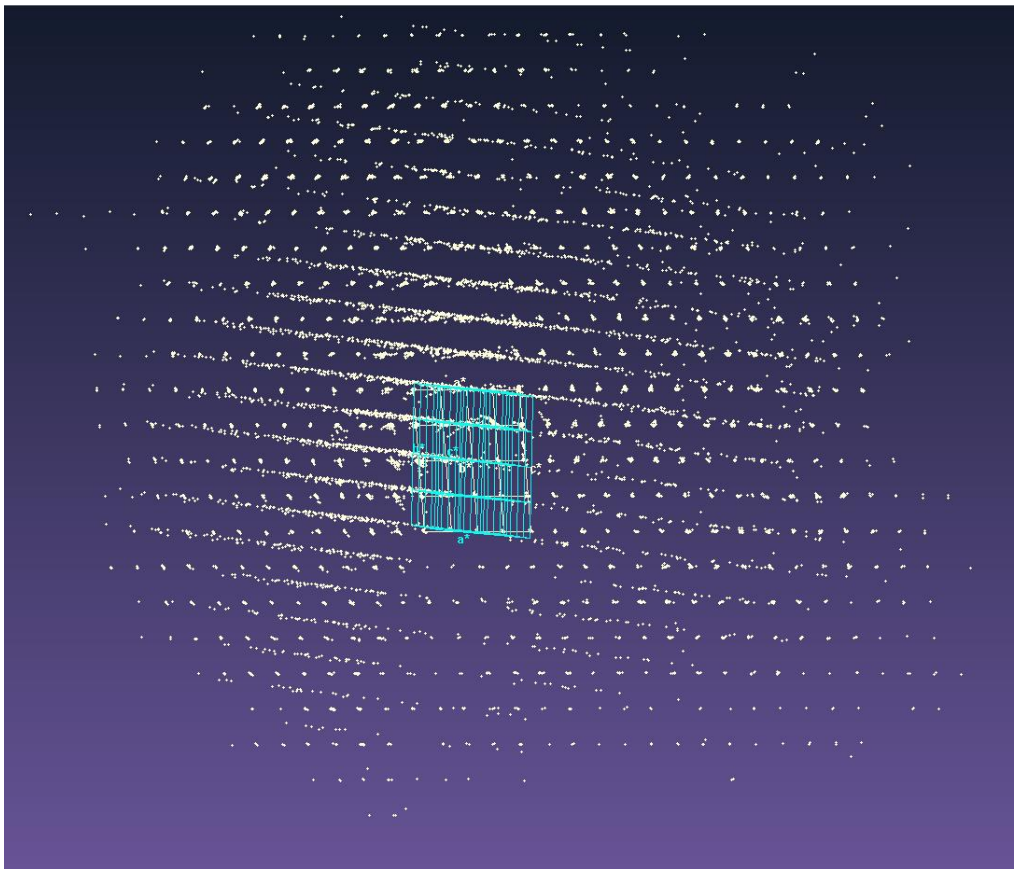


Figure S62: Reciprocal space view along b* of the main component.

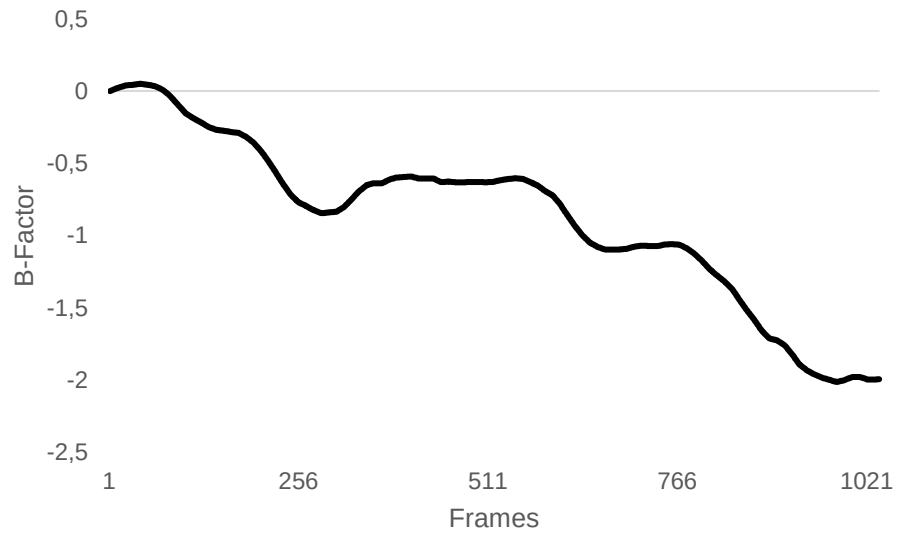


Figure S63: Decomposition of **3.** B-factor of scaling $S = e^{-2B\left(\frac{\sin\theta}{\lambda}\right)^2}$ plotted against the frames of the diffraction experiment (10 frames averaged).

Table S2: Crystallographic data and structure refinement for compounds **3-7** and [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$]

Compound	**[(*i*Pr$_2$Im^{Me})Ni(CO)$_3$]**	**3**	**4a**	**4b**	**4c**	**4d**	**5**	**6**	**7**
CCDC	1947631	1947632	1947633	1947634	1947635	1947636	1947637	1947638	1947639
Formula	$C_{14}H_{20}N_2NiO_3$	$C_{92}H_{108}Ag_2Al_2F_{72}O_8P_{12}$	$C_{27}H_{33}N_2NiOP$	$C_{33}H_{39}N_2NiOP$	$C_{33}H_{45}N_2NiOP$	$C_{39}H_{54.5}N_2NiOP$	$C_{22}H_{38}N_2NiOP_2$	$C_{29}H_{49}N_4Ni_2O_2P$	$C_{36}H_{58}N_4Ni_4O_4P_2$
$D_{calc.}$/ g cm^{-3}	1.375	1.734	1.254	1.279	1.170	1.216	1.228	1.286	1.449
μ/mm^{-1}	1.869	5.423	1.805	1.662	1.504	1.430	2.402	2.118	3.074
Formula Weight	323.03	3351.12	491.23	569.34	575.39	657.02	467.19	634.11	907.64
Colour	clear colourless	clear colourless	clear yellow	clear yellow	clear yellow	clear yellow	clear violet	clear orange	dark brown
Shape	block	block	plate	block	block	plate	needle	block	block
Size/mm^3	0.44×0.25×0.12	0.16×0.11×0.08	0.229×0.19×0.062	0.24×0.11×0.08	0.42×0.36×0.27	0.27×0.21×0.05	0.37×0.09×0.07	0.27×0.15×0.10	0.18×0.11×0.07
T/K	123.00(10)	122.9(3)	123.01(10)	123.00(10)	123.00(10)	123.00(10)	123.01(10)	123.01(10)	123.01(10)
Crystal System	triclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
Space Group	*P*-1	*P*-1	P-1	$P2_1/n$	*Pnma*	$P2_1/c$	*P*-1	$P2_1/c$	$P2_1/n$
a/Å	8.7124(3)	12.6272(7)	11.5266(7)	16.8246(3)	20.5418(2)	11.4259(2)	10.0766(2)	11.3105(3)	9.9904(3)
b/Å	9.3283(4)	16.4361(8)	15.8276(8)	18.0464(3)	14.94490(18)	32.4011(3)	10.6066(3)	19.8290(5)	20.1893(6)
c/Å	11.3805(4)	16.9899(11)	15.8972(8)	19.5061(3)	10.64474(13)	10.26580(10)	12.7392(4)	14.6276(4)	10.9108(4)
α/°	69.893(4)	66.156(5)	95.601(4)	90	90	90	100.397(2)	90	90
β/°	78.027(3)	85.584(5)	110.034(5)	93.2020(10)	90	109.172(2)	108.743(2)	93.492(2)	108.984(4)
γ/°	64.205(4)	84.822(4)	103.357(5)	90	90	90	91.220(2)	90	90
V/Å^3	780.17(6)	3208.8(3)	2601.0(3)	5913.26(17)	3267.88(7)	3589.73(9)	1263.57(6)	3274.53(15)	2081.00(13)
Z	2	1	4	8	4	4	2	4	2
Z'	1	0.5	2	2	0.5	1	1	1	0.5
Wavelength/Å	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	CuK□	Cu K□	Cu K□	CuK□	CuK□	CuK□	CuK□	CuK□	CuK□
Θ_{min}/°	4.146	3.518	3.774	3.595	5.101	4.096	3.738	3.760	4.813
Θ_{max}/°	74.057	58.003	74.737	73.631	73.506	73.680	74.670	74.378	73.554
Measured Refl.	4910	16718	17640	22355	24967	28521	9263	12803	7056
Unique Refl.	2997	8447	10130	11469	3399	7155	5012	6423	3996
Refl. with I > 2(I)	2852	6032	8443	9750	3241	6654	4715	5364	3545
R_{int}	0.0170	0.0651	0.0305	0.0254	0.0208	0.0245	0.0167	0.0289	0.0171
Parameters	187	902	693	697	195	510	265	358	235
Restraints	0	0	82	0	0	234	0	0	0
Largest Peak	0.309	1.245	1.11	0.569	1.368	0.602	0.282	0.381	0.524
Deepest Hole	-0.221	-0.952	-0.62	-0.360	-0.391	-0.393	-0.183	-0.381	-0.341
GooF	1.049	1.045	1.046	1.064	1.095	1.052	1.040	1.024	1.029
wR_2 (all data)	0.0714	0.2125	0.1583	0.1104	0.1050	0.1217	0.0631	0.0872	0.0993
wR_2	0.0706	0.1955	0.1495	0.1043	0.1040	0.1196	0.0616	0.0824	0.0950
R_1 (all data)	0.0276	0.1024	0.0680	0.0511	0.0385	0.0481	0.0257	0.0422	0.0398
R_1	0.0264	0.0760	0.0576	0.0419	0.0373	0.0453	0.0239	0.0327	0.0347

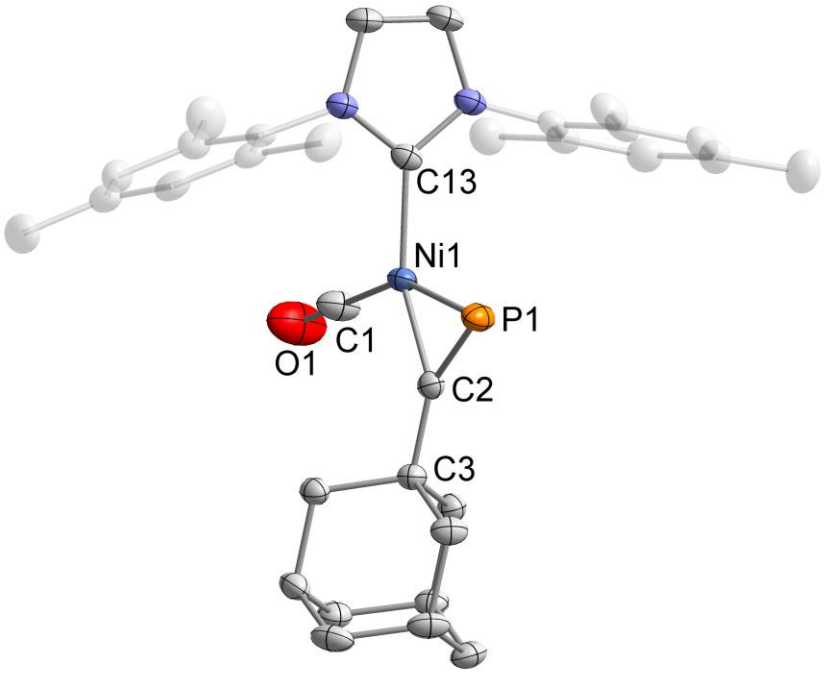


Figure S64. Molecular structure **4c** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles: Ni1─C1 1.753(2), Ni1─C13 1.9284(19), Ni1─P1 2.2189(6), Ni1─C2 1.8950(19), C1─O1 1.136(3), P1─C2 1.6273(19), C3-C2-P1 144.85(15), C13-Ni1-P1 102.47(6), C2-Ni1-P1 45.77(6), C2-Ni1-C13 148.16(8), C2-P1-Ni1 56.55(7), O1-C1-Ni1 179.5(3).

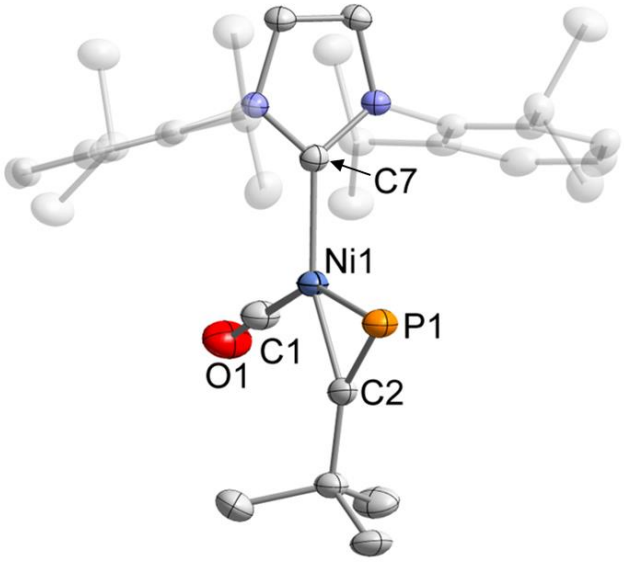


Figure S65. Molecular structure **4c** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles: Ni1─C1 1.760(2), Ni1─C7 1.947(2), Ni1─P1 2.2201(7), Ni1─C2 1.900(2), C1─O1 1.137(3), P1─C2 1.626(2), C3-C2-P1 146.13(18), C7-Ni1-P1 102.80(6), C2-Ni1-P1 45.67(7), C2-Ni1-C7 148.47(9), C2-P1-Ni1 56.71(8), O1-C1-Ni1 176.8(2)

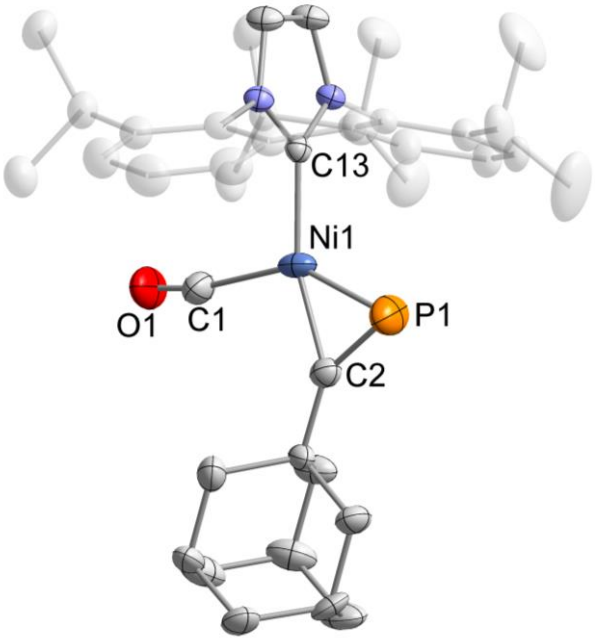


Figure S66. Molecular structure **4d** in the solid state**.** Ellipsoids are set at 50% probability level. The second component and hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] with data for the second part of the molecule in brackets: Ni1─C1 1.86(2) [1.796(13)], Ni1─C13 1.9204(17), Ni1─P1 2.092(2) [2.049(4)], Ni1─C2 1.862(4) [1.796(4)], C1─O1 1.170(19) [1.245(13)], P1─C2 1.638(4) [1.643(5)], C3-C2-P1 146.5(3) [142.9(3)], C13-Ni1-P1 111.97(7) [102.96(9)], C2-Ni1-P1 48.53(12) [50.05(14)], C2-Ni1-C13 160.49(12) [152.83(13)], C2-P1-Ni1 58.39(14) [56.97(17)], O1-C1-Ni1 169.7(15) [170.1(13)].

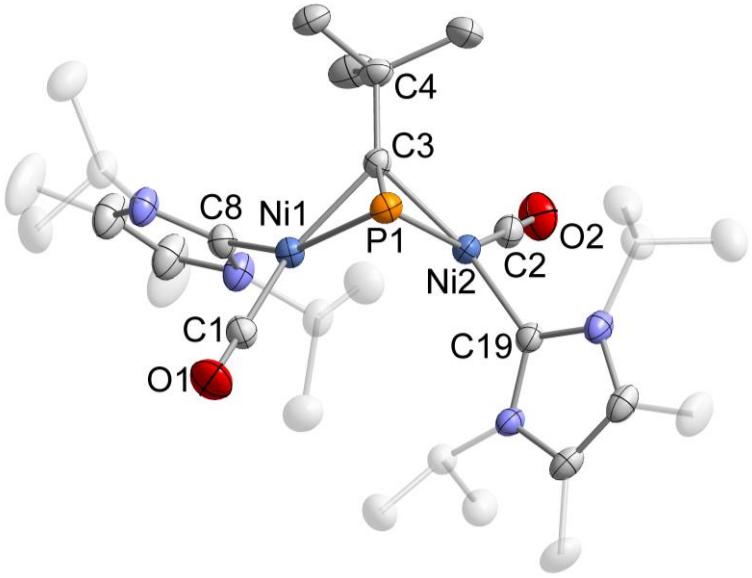


Figure S67. Molecular structure **6** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1─Ni2 2.7907(4), Ni1─P1 2.2123(5), Ni1─C1 1.757(2), Ni1─C8 1.9435(18), Ni1─C3 1.9703(18), C1─O1 1.141(3), C2─O2 1.150(3), P1─C3 1.7087(17), Ni2─P1 2.2382(5), Ni2─C2 1.740(2), Ni2─C19 1.9337(18), Ni2─C3 1.9579(17), C4-C3-P1 135.17(14), Ni2-C3-Ni1 90.54(7), Ni1-P1-Ni2 77.664(18), O1-C1-Ni1 174.26(19), O2-C2-Ni2 177.34(19), plane-to-plane fold angle Ni1-P1-C3/Ni2-P1-C3: 84.834(2).

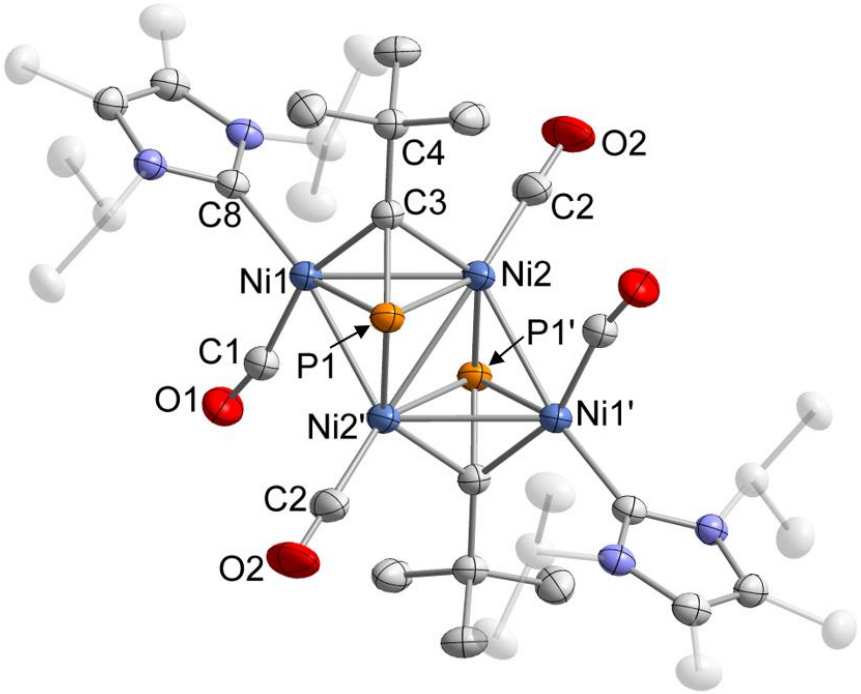


Figure S68. Molecular structure **7** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1─P1 2.3142(6), Ni1─C3 1.969(2), Ni1─C1 1.784(2), Ni1─C8 1.923(2), C1─O1 1.150(3), C2─O2 1.139(3), P1─C3 1.702(2), Ni1─Ni2 2.6388(5), Ni1─Ni2' 2.4800(5), Ni2─Ni2' 2.6201(7), Ni2─C3 2.010(2), Ni2─P1 2.3335(6), Ni2─C2 1.766(2), C4-C3-P1 133.57(15), Ni2-Ni1-Ni2' 61.483(15), Ni1-Ni2-Ni1' 118.517(15), Ni1-Ni2-Ni2 62.246(16), Ni2-Ni2-Ni1 56.272(15), Ni1-P1-Ni2 69.189(19), Ni1-C3-Ni2 83.08(8), O1-C1-Ni1 166.2(2), O2-C2-Ni2 178.3(2).

7 Quantum Chemical Calculations

General Methods

All calculations were carried out with ORCA 4.1.[19,20] Geometry optimizations were performed at the TPSS-D3BJ/def2-TZVP level of theory in the gas phase.[21–24] Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimizations. Density fitting techniques, also called resolution-of-identity approximation (RI),[25] were used for density functional theory (DFT) calculations, whereas the RIJCOSX approximation was used for DLPNO-CCSD(T)/def2-QZVPP calculations.[24,26–28]Approximate transition states were generated using the nudged elastic band (NEB) method implemented in ORCA, followed by a saddle-point optimization.

Investigations on $(RCP)_2$ isomers (R = Me, *t*Bu)

Geometries of the four $(RCP)_2$ isomers were optimized for R = Me and R = *t*Bu on the DFT level. Subsequent energy evaluations were performed at the accurate DLPNO-CCSD(T)/def2-QZVPP level of theory. The results for R = Me agree well with earlier studies by *Boldyrev* and *Bozhenko*, who calculated the minima for R = H and predicted the 1,2-diphospha-4,4-dimethyltriafulvene to be the global minimum using coupled cluster methods.[29] The situation, however, changes when large substituents (R = *t*Bu) are attached to the carbon atoms. In this case, di-*tert*-butyldiphosphatetrahedrane (**1a**) is the global minimum, presumably due to steric repulsion in the 1,2-diphospha-4,4-dimethyltriafulvene isomer.

Mechanism of the catalytic phosphaalkyne dimerization reaction

For the sake of computational cost, the complete reaction mechanism for the phosphaalkyne dimerization was initially calculated for a small model system with methyl groups at the phosphaalkyne and phenyl groups at the NHC moiety. The results are shown in in Figure S69. In the first step, a phosphaalkyne molecule binds to the active catalyst [(IPh)Ni(CO)(PCMe)] to give **A′**. This step is slightly endergonic ($\Delta G = 4.8$ kcal·mol^{-1}) and is apparently an activation-barrier free process. Next, the formation of the metalla-2,4-diphosphacyclopentadiene **B′** take place ($\Delta G^{\ddagger} = 16.0$ kcal·mol^{-1} and $\Delta G = 9.5$ kcal·mol^{-1}). **B′** then adopts a reactive conformation *via* a spontaneous and slightly exergonic two-step process (a first step forms **C′**: $\Delta G^{\ddagger} = 2.3$ kcal·mol^{-1} and $\Delta G = -4.0$ kcal·mol^{-1}; a second step converts **C′** into **D′**: $\Delta G^{\ddagger} = 0.2$ kcal·mol^{-1} and $\Delta G = 1.4$ kcal·mol^{-1}). Subsequently, the 1,3-diphosphacyclobutadiene complex **E′** is

formed in a highly exergonic reaction ($\Delta G^{\ddagger}$ = 9.3 kcal·mol^{-1} and ΔG = −41.6 kcal·mol^{-1}). From there on, the reaction follows the same steps as discussed for the large model system in the main text. Note that the activation barrier for the conversion of **E′** into **F′** ($\Delta G^{\ddagger}$ = +49.8 kcal·mol^{-1}) is too high to be accessible under experimental conditions. In addition to this kinetic stability, **E′** also constitutes the thermodynamic minimum of the small model system. In agreement with this, an analogous complex **5** carrying the small N-heterocyclic carbene *i*Pr$_2$Im^{Me} has been isolated during our experimental studies.

It is important to note that the calculations clearly indicate that catalytic turnover is not feasible with small substituents on the N-heterocyclic carbene and on the phosphaalkyne. Indeed, this is in line with our experimental investigations using the small carbene *i*Pr$_2$Im^{Me}. The red line in Figure S69 displays the reaction profile for the dimerization of *t*Bu−C≡P catalyzed by [(IXy)Ni(PCMe)]. These calculations show that the intermediate **E′** is strongly destabilized for the bulkier substituents, resulting in a calculated overall activation barrier is 26.9 kcal mol^{-1}, which is in good agreement with the experimental observations (see also Figure 5 of the main text).

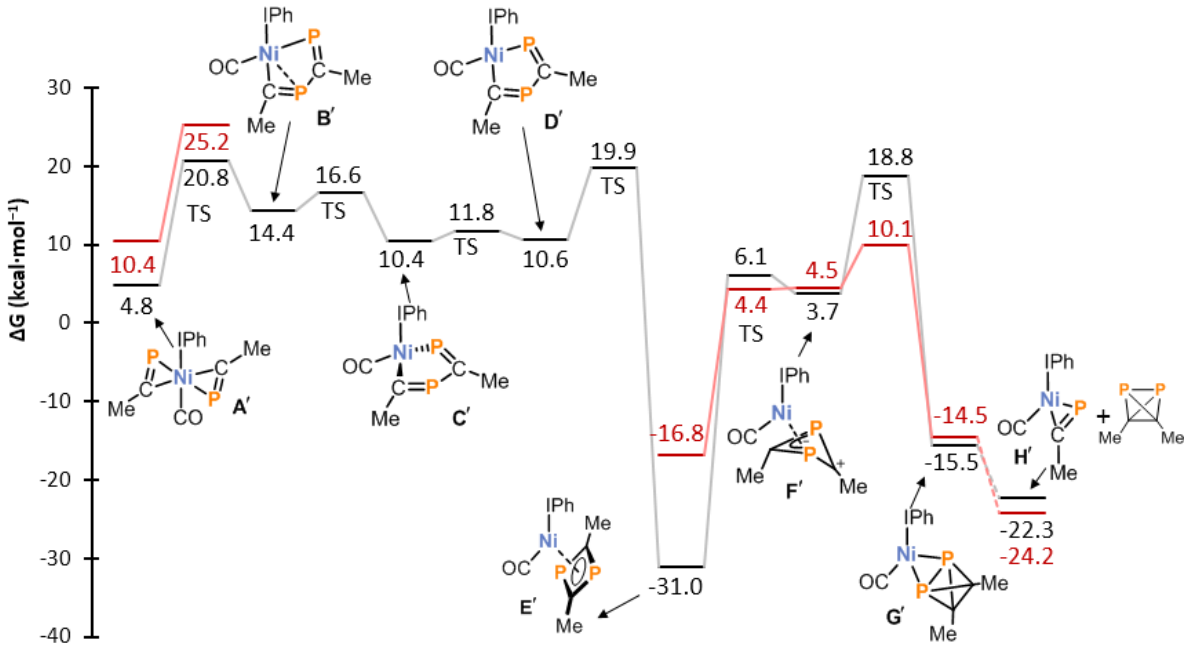


Figure S69. Gibbs energies (in kcal·mol^{-1}at 298 K) and schematic drawings of intermediates for the dimerization of Me−C≡P catalyzed by [(IPh)Ni(PCMe)] (black, IPh (=1,3-diphenylimidazolin-2-ylidene). For comparison the graph for the dimerization of *t*Bu−C≡P catalyzed by [(IXy)Ni(PC*t*Bu)], (red, IXy = 1,3-bis(2,6-dimethylphenyl)imidazolin-2-ylidene)) as discussed in the main text is shown. Solid lines connect intermediates and transition states, dashed lines connect intermediates.

The calculations with the small model system additionally indicate a potential alternative pathway for the formation of tetrahedrane **1a** (Figure S70). The initial step of this mechanism is the transformation of **A′** into a 1,4-diphosphabutadiene complex **B″** ($\Delta G^{\ddagger}$ = 17.9 kcal·mol^{-1}

and ΔG = 12.1 kcal·mol^{-1}). Next, an intermediate **C″** ($\Delta G^{\ddagger}$ = 15.1 kcal·mol^{-1} and ΔG = −27.7 kcal·mol^{-1}) is formed, in which C−P and P−P bond formation has occurred. Finally, **C″** can be directly converted into the tetrahedrane complex **G′** ($\Delta G^{\ddagger}$ = 15.1 kcal·mol^{-1} and ΔG = −4.8 kcal·mol^{-1}). Note that the reaction barrier for the second process was calculated to be 32.1 kcal·mol^{-1} (formation of intermediate **C″** is rate limiting). This barrier is much higher than the reaction barrier for the pathway described in Figure S69, for which the formation of **E′** is rate limiting with a barrier 20.8 kcal·mol^{-1}, and also for the large model shown in Figure 5 revealing a barrier of +26.8 kcal·mol^{-1}. As shown in Figure S70, the calculated rate-limiting barrier for the alternative pathway is *at least* 30.5 kcal·mol^{-1} when larger substituents are introduced.

In conclusion, the alternative pathway shown in Figure S70 appears to be kinetically disfavored compared to the pathway shown in Figure 5 and Figure S69.

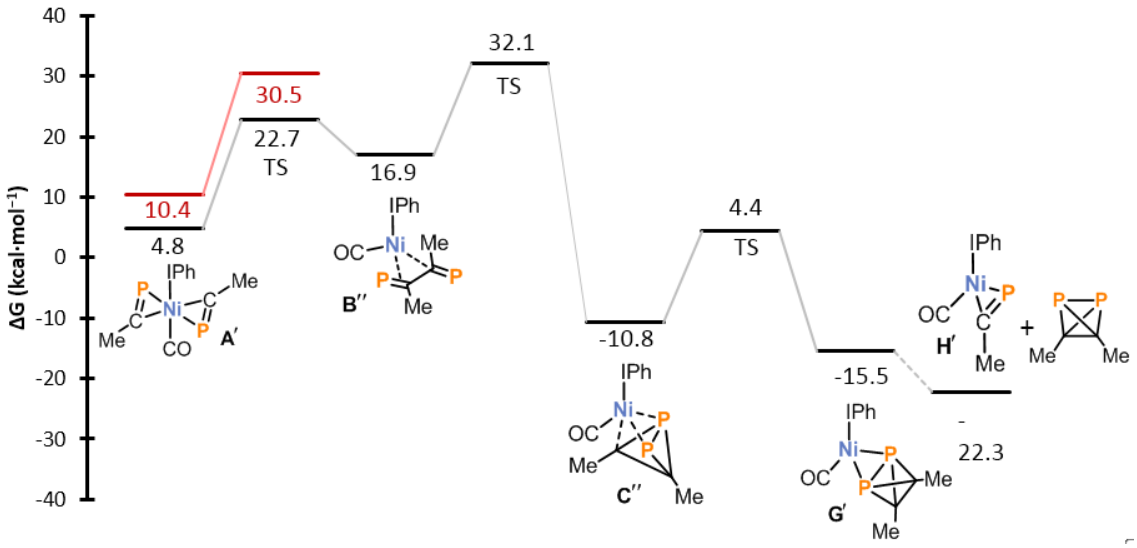


Figure S70. Gibbs energies (in kcal·mol^{-1}at 298 K) and schematic drawings of transition states and intermediates for an alternative dimerization pathway of Me−C≡P catalyzed by [(IPh)Ni(PCMe)]. For comparison, the red line demonstrates the increased $\Delta G^{\ddagger}$ when increasing the size of the substituents (*t*Bu−C≡P and [(IXy)Ni(PC*t*Bu)], IXy = 1,3-bis(2,6-dimethylphenyl)imidazolin-2-ylidene). Solid lines connect intermediates and transition states, dashed lines connect intermediates.

Cartesian Coordinates of Optimized Structures

1,2-Diphosphacyclobutadiene (R = Me)

C	-7.68843642514963	1.65779367000223	0.28592460568119
C	-6.32083175021577	1.53995941204171	-0.29567051989961
P	-8.27794001916265	0.07027905683960	0.42733890224925
C	-8.34775991656728	2.94841096495540	0.64971797920274
P	-6.04615577668809	-0.12206737838487	-0.51954842603114
C	-5.42426939999596	2.69675233737087	-0.59692046605474
H	-9.34968647542934	2.78211689289284	1.05561457190333
H	-8.42981119248383	3.60532854135315	-0.22714758497192
H	-7.75359935368689	3.49190859678981	1.39733223335569
H	-4.47061139622933	2.36181391638399	-1.01481719075872
H	-5.22246900398356	3.28071161281381	0.31163946299736
H	-5.89874929040766	3.38128237694145	-1.31357356767343

1,3-Diphosphacyclobutadiene (R = Me)

C	-7.86726899591022	1.73426806473078	0.41332949024796
P	-6.05677061511099	1.85909030949062	-0.21268819569307
P	-8.07332455231083	0.06638552686379	0.27845239787945
C	-8.75579128035494	2.82845492275555	0.86459287650931
C	-6.26169824273563	0.19122192883105	-0.34774487658397
H	-9.74327769583770	2.46555005398378	1.16929032420058
H	-8.88462911939459	3.57317713797507	0.06494363495965
H	-8.30223543828262	3.36886374174702	1.70888270271490
C	-5.37400422822414	-0.90337025663911	-0.79957518060990
H	-5.82830894834811	-1.44305927303097	-1.64383781705443
H	-5.24521358060652	-1.64781282422154	0.00032452761427
H	-4.38623730288370	-0.54099933248603	-1.10412988418474

1,2-Diphosphatriafulvene (R = Me)

C	-7.74275362987707	2.30277159363213	-0.38633443176604
P	-6.67912367846133	3.60715306415782	-1.03241316723017
P	-7.26791856626089	1.96497567786877	-2.09237579755477
C	-8.43443155167832	1.86838546195247	0.67109966883942
C	-8.47435074405619	2.64328593267023	1.96347518549155
C	-9.21375141667366	0.57864580844288	0.63201111415125
H	-7.88275949380530	3.56029116078990	1.89672109654487
H	-8.08511616735194	2.03935637847827	2.79490601074666
H	-9.50626916787386	2.91478144133375	2.22604082589500
H	-9.12582055725793	0.08917865208076	-0.34165277663394
H	-10.27872940037745	0.75776284790987	0.83511282853376
H	-8.85766562632607	-0.11799801931686	1.40363944298241

Diphosphatetrahedrane (R = Me)

P	-5.17003525290904	0.44133548384166	0.33722499922210
C	-3.41582948260242	-0.08324757658390	0.57430152120227
C	-3.57739464241726	0.94664587380540	-0.44744152286558
P	-3.54723892996764	1.62122619369476	1.27086205490887
C	-2.63184328925898	-1.33146153989883	0.78854166768298
C	-3.03993323930629	1.27699138813880	-1.79667497672525
H	-1.95375839846542	1.42038816188612	-1.75434298014486
H	-3.49186973938333	2.19617624349717	-2.18077495056980
H	-3.25279316286549	0.46779935103951	-2.50523067055675
H	-2.85297642998351	-2.06449914844177	0.00375650852483
H	-2.87421864220684	-1.78133931291122	1.75575984376545

H	-1.55639879063380	-1.11914511806768	0.76826850555574

1,2-Diphosphacyclobutadiene (R = *t*Bu)

C	-7.577056	1.844621	0.324396
C	-6.395818	1.745967	-0.323523
P	-8.033573	-0.026708	0.497916
C	-8.463936	2.956188	0.867396
P	-6.308019	-0.167302	-0.592381
C	-5.308116	2.691026	-0.814317
C	-9.896852	2.402204	1.034024
C	-8.556834	4.166183	-0.082846
C	-7.953376	3.391381	2.260256
C	-4.008139	1.879674	-1.013713
C	-4.988664	3.812221	0.193926
C	-5.716827	3.284646	-2.182061
H	-10.291770	2.033369	0.080582
H	-10.560228	3.195649	1.394939
H	-9.925593	1.578935	1.755586
H	-4.134857	1.102815	-1.775081
H	-3.697171	1.395177	-0.081185
H	-3.202107	2.546901	-1.337760
H	-4.156180	4.416954	-0.183886
H	-4.692270	3.386014	1.157793
H	-5.834503	4.480070	0.361953
H	-6.961906	3.845636	2.197536
H	-7.892041	2.528636	2.932372
H	-8.644697	4.119334	2.701844
H	-8.926866	3.853183	-1.064505
H	-7.597059	4.664954	-0.223351
H	-9.257692	4.901395	0.329155
H	-5.939964	2.484167	-2.895693
H	-4.895104	3.885836	-2.589728
H	-6.601973	3.918613	-2.093355

1,3-Diphosphacyclobutadiene (R = *t*Bu)

C	-7.86501691902840	1.72887737639406	0.39065953715346
P	-6.05244760128809	1.86701046984555	-0.22953115198881
P	-8.06604028622960	0.05742650963649	0.26524704307317
C	-8.76069406852207	2.83279372364472	0.83653313537457
C	-6.25338365125661	0.19557176573899	-0.35478685371235
C	-10.13967636138706	2.29598353709621	1.25174795653021
C	-8.91083433852300	3.84023360291198	-0.32954813238583
C	-8.08744960926871	3.55041828385600	2.03260344183368
C	-5.35718759939165	-0.90856715374765	-0.79944771700107
C	-6.03067205569075	-1.63114917397631	-1.99209794692038
C	-5.20296709043564	-1.91159417226381	0.37020306553526
C	-3.97976822175373	-0.37016464321174	-1.21819157271484
H	-4.59092731455239	-2.76231200182321	0.04966065316592
H	-6.17857817519837	-2.29168502254811	0.69214882342183
H	-4.71889319072818	-1.43347822423922	1.22713126519040
H	-4.07704801506150	0.34207382243610	-2.04472422208573
H	-3.33128538015766	-1.19042284784022	-1.54481305796043
H	-3.49285190600189	0.14157844676372	-0.38099962958086
H	-10.62695406694602	1.78863501825427	0.41209628116688
H	-10.78642550504367	3.11651838237185	1.58105416820971
H	-10.04507526710261	1.58022730063055	2.07557207563556
H	-7.09378481133781	3.92115028182421	1.75851177690790
H	-7.97933558411076	2.86764723758312	2.88075722274616
H	-8.69970527885368	4.40445431570148	2.34381389324799
H	-6.14212403034235	-0.95103612956904	-2.84196270304425
H	-7.02288233187935	-2.00378817596960	-1.71530870956961
H	-5.41674311836800	-2.48440921438833	-2.30209798668409
H	-9.38587571929517	3.36346377392053	-1.19226909509649

H	-7.93433263365842	4.22572926847528	-0.64209845931184
H	-9.52939986858689	4.68637364249211	-0.00962310113614

1,2-Diphosphatriafulvene (R = *t*Bu)

C	-7.739888	2.307981	-0.401516
P	-6.740874	3.652112	-1.092065
P	-7.197046	1.943964	-2.090824
C	-8.430626	1.870046	0.664093
C	-8.514881	2.760666	1.935990
C	-9.133238	0.484536	0.601517
C	-7.391361	3.817964	1.976037
C	-8.364241	1.968085	3.254831
C	-9.850563	3.544652	1.955615
C	-9.323402	-0.001706	-0.850546
C	-10.554183	0.488594	1.210819
C	-8.270968	-0.590518	1.308683
H	-7.261490	-0.600683	0.884400
H	-8.718387	-1.580037	1.152446
H	-8.188699	-0.425978	2.383863
H	-9.812367	0.758036	-1.470262
H	-9.956753	-0.896030	-0.842902
H	-8.376862	-0.277956	-1.322715
H	-7.381918	1.487900	3.310195
H	-9.128487	1.202551	3.394070
H	-8.443918	2.668135	4.094477
H	-7.531168	4.600910	1.226041
H	-6.405196	3.364883	1.825969
H	-7.398625	4.303707	2.958410
H	-11.211694	1.167991	0.658731
H	-10.576908	0.770384	2.264192
H	-10.971998	-0.521691	1.131974
H	-9.965906	4.113211	1.026872
H	-9.847865	4.253191	2.793317
H	-10.719290	2.894589	2.068979

Di-*tert*-butyldiphosphatetrahedrane (1a)

P	-5.12137783907350	0.39967169899593	0.28610730456242
C	-3.36123120451169	-0.12777555265565	0.51961291438714
C	-3.52096836044728	0.90274670987689	-0.49937014088859
P	-3.51492315387866	1.57802271846826	1.22541110778401
C	-2.63937305697805	-1.39840157122337	0.87945358653299
C	-3.06896509627181	1.36866978257099	-1.85722489925801
C	-1.55467122620358	1.64533729916710	-1.83409127302251
C	-3.82459943934436	2.66582564439220	-2.19279439363964
C	-3.39573008025164	0.29439066822668	-2.91045603237571
C	-2.96815054867160	-2.49260499465574	-0.15250610247847
C	-3.11953344476288	-1.84223309442971	2.27176455062166
C	-1.12187746672834	-1.14133310885331	0.91544111385900
H	-4.20243044037764	-2.00417522611600	2.27068000610061
H	-2.88632122512431	-1.07753972235598	3.01988080510128
H	-2.62836987628463	-2.77665664897664	2.56454083109457
H	-0.75362899305131	-0.81396346293761	-0.06137189847398
H	-0.59108359125682	-2.05932915261062	1.19121811488813
H	-0.88154486021968	-0.36665121662777	1.65084698347044
H	-1.22464358534788	2.01497873535823	-2.81131100229442
H	-0.99107438692460	0.73609181588207	-1.60460113717272
H	-1.31382743729788	2.39954818014916	-1.07784391156855
H	-3.52266457872926	3.03884371290288	-3.17755056817381
H	-3.61030944224891	3.43873379333851	-1.44742769205442
H	-4.90504260439551	2.48868610804622	-2.20421178046073
H	-3.09741755572110	0.64054586080336	-3.90629412481847
H	-4.47005136962059	0.08364479535850	-2.92319508753355
H	-2.86473257216999	-0.63876286643911	-2.69982200847138

H	-2.64784696408911	-2.19755976463992	-1.15618529965970
H	-4.04580376188614	-2.68428518098336	-0.17818056658930
H	-2.45521583813124	-3.42434596003219	0.11058060053172

Methylphosphaalkyne

C	-7.32456077152292	1.81265554713336	0.00000418113423
C	-5.86683114264374	1.76144048047523	0.00006264123886
H	-7.69201493990222	2.49712905012893	0.77465549511437
H	-7.75095559797229	0.82058316815608	0.19387978327425
H	-7.70374058267616	2.16151228851557	-0.96856609965725
P	-4.31743696528267	1.70739946559082	-0.00003600110446

***tert*-Butylphosphaalkyne**

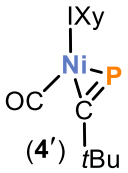
C	-7.22769137413322	1.80924719317750	0.00024851421473
C	-5.76258587380059	1.75828102158799	0.00272945512880
C	-7.70773616906694	2.78329129599880	1.10418249745131
C	-7.78946578697890	0.39272023534112	0.27574266519012
C	-7.71998813183538	2.30535694684890	-1.38167575365641
P	-4.21122440152084	1.70447601158052	0.00506701897428
H	-7.30301705310478	3.78542898485375	0.93781475457245
H	-7.38504755004598	2.43779556680532	2.09027570084943
H	-8.80222013698944	2.83801492736061	1.09029994429873
H	-7.44550089628019	-0.31416686747146	-0.48439627961252
H	-8.88470994738118	0.42586812395322	0.25690422207517
H	-7.46478710732274	0.03322930279713	1.25615644136490
H	-7.37219898170151	1.64073986356666	-2.17736623279968
H	-7.34792214929904	3.31350150703237	-1.58450520607503
H	-8.81564444053924	2.32484588656757	-1.39162774197627

H′ (NHC = IPh, R = Me)

Ni	-0.90746384980435	2.25690990794517	7.38258511973940
P	0.72101073339251	3.77888076579121	7.64625585034881
N	-3.04702705062397	4.30237790063003	7.87758984634649
N	-3.07247531339888	2.76299417264896	9.38305577408324
C	-2.40753650128227	3.13912998961575	8.23925929000382
C	-2.69002146125519	5.08629123836626	6.74057231026809
C	-2.72109690126348	6.47894572327622	6.82475202396505
C	-2.29423845825044	4.45219406653252	5.56210631135806
C	-2.75956957470176	1.59272429273284	10.13736751129565
C	-4.06735204183663	4.63186551442091	8.76989038811195
H	-4.69019681494522	5.50051849240078	8.63443338057177
C	-4.08634156152142	3.66280891480005	9.71381981399010
H	-4.69887701993992	3.54039658046232	10.59174474814246
C	-1.91744403981466	5.22371020691395	4.46588329443732
H	-1.60256455613389	4.73064618520215	3.55125233243903
C	-2.35376923926707	7.24121662351337	5.71726859950810
H	-2.36873692084292	8.32501592929156	5.78568408794272
C	1.85607834396430	1.41370239760574	6.19136322936365
C	0.94218367223154	2.34367594409413	6.89956898669957
C	-3.79126588151461	0.83290932566618	10.69097683355657
C	-1.42589341245665	1.21601449658174	10.30640854964068
C	-1.94780956900587	6.61682155420352	4.53769032864429
O	-1.67042732981804	-0.40795723027192	6.47636463935713
C	-1.39227686461889	0.65886008764967	6.83218106407594
C	-2.15425752877156	-0.70737756470939	11.58327095331478
C	-1.13105936708010	0.05911165952622	11.02413973125781
H	-0.09429039188552	-0.23639542635508	11.15330201824775
C	-3.48283656865681	-0.31498093449666	11.41913757142125
H	-4.28534970817329	-0.91105262715405	11.84325490222073

H	-0.63937025443910	1.83018108102482	9.87673981494151
H	-1.91813051164891	-1.60695592437430	12.14366703137274
H	-4.82532469402462	1.12114545037625	10.52937768027142
H	-2.99803597436790	6.96163747397642	7.75733199611765
H	-2.27876438465555	3.36684643236333	5.52025952733031
H	-1.65333935624520	7.21385863633307	3.67994180383585
H	1.89599703370962	0.44819293707188	6.71038596022082
H	2.87421849389019	1.81143849678422	6.11212913089356
H	1.48129482505654	1.20896722956012	5.18079756466397

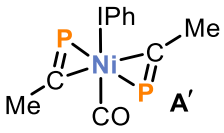
4′ (NHC = IXy, R = *t*Bu)



Ni	-0.95143480742273	2.23258817242079	7.42864813524673
P	0.54820661973527	3.88180817597940	7.27423737660429
N	-3.09518563368997	4.29549131371393	7.87208288428698
N	-3.08415927463719	2.80530342157368	9.41947768905522
C	-2.43772309816990	3.15671471988230	8.26364847666741
C	-2.73172749761487	5.06916201401510	6.71412917272881
C	-2.06924166987893	6.28885922495786	6.91185693748873
C	-3.03166338959111	4.56292001217550	5.44272211178625
C	-2.72109376653781	1.64860345528012	10.19557562935413
C	-4.11803093396544	4.63226095235853	8.75635359667505
H	-4.74480303788721	5.49524264187132	8.60052931535652
C	-4.10963923533110	3.69340359948650	9.73482489291606
H	-4.72199968683197	3.57134258176227	10.61352149902893
C	-2.65390335534664	5.32989456462747	4.33652102207082
H	-2.87082824763517	4.95755274903154	3.33885838086288
C	-1.71420698275772	7.02456452295438	5.77779702417600
H	-1.18715845487410	7.96651484610693	5.90377139921309
C	1.79296910892421	1.41158363987417	6.11292577730280
C	0.82701500658890	2.35402777005882	6.75459000087918
C	-3.49427667735696	0.48779255839943	10.06274331636242
C	-1.59705965272418	1.72771779275102	11.02900144832903
C	-2.00420238498194	6.55065994910770	4.50083686913697
O	-1.77465738715627	-0.55096809898321	7.14581599479267
C	-1.44338377356283	0.55668307704597	7.24691725793354
C	-2.00629710679367	-0.58308293966053	11.65104949672260
C	-1.25431384277568	0.58461495602445	11.75769358062217
H	-0.38483521945381	0.61582238448389	12.40889187674315
C	-3.11570299732524	-0.63094596930662	10.81016355334373
H	-3.68952390990012	-1.54878771440953	10.71498173294215
C	-0.77511218692269	2.98679084052400	11.11153002939728
H	-1.72184464845069	-1.46309474872639	12.22092734411552
C	-4.66360236411145	0.43848669495665	9.11330840291490
C	-1.70103391037361	6.76143409415751	8.29456320966834
C	-3.70369495721468	3.22633011618974	5.27296923455803
H	-1.71437145292032	7.13131170943820	3.62967326272932
C	2.10417489460127	0.26121767841432	7.09552802380415
C	3.09841371634263	2.15352286905695	5.75746899947127
C	1.16381244248629	0.82935301869431	4.82875624664429
H	2.81714887966924	-0.43468331876812	6.63764637597157
H	1.19272357886365	-0.28612774360980	7.35037328644301
H	2.54112589311614	0.65247731221770	8.01965590075504
H	3.81377466294702	1.46912267295728	5.28551097752863
H	3.55624948720844	2.57173891726529	6.65936364626777
H	2.89303064068970	2.97679752218764	5.06610895299715
H	1.86814906836429	0.13975282443111	4.34845705779941
H	0.92093123147658	1.62949320894737	4.12236466317842
H	0.24444535391668	0.28587144143767	5.06307010499430

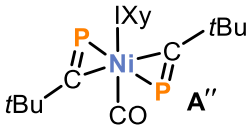
H	-1.04720053648201	7.63477684920982	8.23497463587653
H	-1.17584703411743	5.97116788678389	8.84199768693269
H	-2.58371253681118	7.03619685970266	8.88345660350878
H	-3.99795501493213	3.07506703082009	4.23142337004335
H	-4.59322644448624	3.14041479074443	5.90644686974903
H	-3.01972160993661	2.41979392073512	5.56681792217237
H	-4.36397916485666	0.76516451816804	8.11201001374571
H	-5.47798747195730	1.09632468595553	9.43850716337644
H	-5.05413434139319	-0.57931664429137	9.04279046511720
H	-1.40328551447633	3.86398287267311	11.30191564858738
H	-0.25198891296704	3.16399211798452	10.16327188390501
H	-0.03353045831826	2.90805562815948	11.91034556911864

A′ (NHC = IPh, R = *t*Bu)



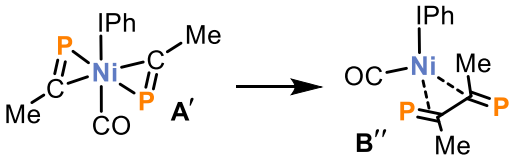
Ni	-1.26477869701795	1.95777836759585	7.43539651610263
P	-0.67021346559133	1.75017841413221	5.35942506475735
N	-3.05189574518153	4.46621438623756	7.86055408791726
N	-3.16779933086739	2.85161419981130	9.28314550523804
C	-2.54445672790815	3.20710661001050	8.09724919503366
C	-2.72402786272382	5.27758825796258	6.73422743756083
C	-2.54697912568266	6.65279816452870	6.90291689452246
C	-2.59228543122644	4.69068036591915	5.47595575937911
C	-2.86819398362841	1.59461328937014	9.85045006237320
C	-3.94593355207168	4.85894294547014	8.85993769929058
H	-4.46112722475448	5.80496168644799	8.82474141245715
C	-4.02371684758405	3.84193826977567	9.75208315165737
H	-4.58688476618016	3.74730281000664	10.66608189515276
C	-2.27012658985601	5.49002087684322	4.38195605802263
H	-2.16012565878062	5.03153057288635	3.40391664271727
C	-2.23892603757484	7.44467758221116	5.79831350857890
H	-2.09552596020773	8.51317607056917	5.92954086384499
C	0.90599704365737	-0.22923377300527	6.98220926462088
C	-0.02526339751159	0.85049296479299	6.56598649209906
C	-3.78794646219424	0.88737627189141	10.62039501745085
C	-1.62391024539619	1.03050225033478	9.51027510838499
C	-2.09614621326914	6.86608320876792	4.53671034588735
C	-2.23929958911902	-0.97527547183580	10.72020513425559
C	-1.31938938054087	-0.25989738907106	9.95689001886212
H	-0.35350668923147	-0.69142492542507	9.71652343192568
C	-3.46508247949369	-0.39658679106685	11.06087781046536
H	-4.18329038402090	-0.95283084785282	11.65556013587470
H	-0.78574178828804	1.69019087853744	9.16855505699900
H	-1.99918594563581	-1.97798057591066	11.06057019013418
H	-4.76205768641787	1.31506043075591	10.83815426014477
H	-2.62401671447712	7.09315995052464	7.89268487789926
H	-2.73732489456729	3.62208023496092	5.37255696184119
H	-1.84735854775866	7.48454472291332	3.67952654120562
H	1.51707289827765	0.08105844733530	7.83916444954910
H	1.57926544813760	-0.53790690853358	6.17398026266174
H	0.33342203468658	-1.11106554789186	7.30076288513236

A″ [(IXy)Ni(CO)(PC*t*Bu)$_2$]



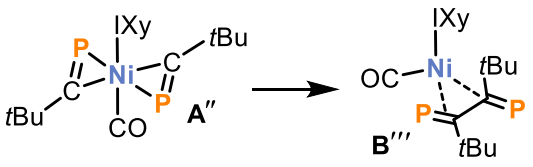
Ni	-0.95143480742273	2.23258817242079	7.42864813524673
P	0.54820661973527	3.88180817597940	7.27423737660429
N	-3.09518563368997	4.29549131371393	7.87208288428698
N	-3.08415927463719	2.80530342157368	9.41947768905522
C	-2.43772309816990	3.15671471988230	8.26364847666741
C	-2.73172749761487	5.06916201401510	6.71412917272881
C	-2.06924166987893	6.28885922495786	6.91185693748873
C	-3.03166338959111	4.56292001217550	5.44272211178625
C	-2.72109376653781	1.64860345528012	10.19557562935413
C	-4.11803093396544	4.63226095235853	8.75635359667505
H	-4.74480303788721	5.49524264187132	8.60052931535652
C	-4.10963923533110	3.69340359948650	9.73482489291606
H	-4.72199968683197	3.57134258176227	10.61352149902893
C	-2.65390335534664	5.32989456462747	4.33652102207082
H	-2.87082824763517	4.95755274903154	3.33885838086288
C	-1.71420698275772	7.02456452295438	5.77779702417600
H	-1.18715845487410	7.96651484610693	5.90377139921309
C	1.79296910892421	1.41158363987417	6.11292577730280
C	0.82701500658890	2.35402777005882	6.75459000087918
C	-3.49427667735696	0.48779255839943	10.06274331636242
C	-1.59705965272418	1.72771779275102	11.02900144832903
C	-2.00420238498194	6.55065994910770	4.50083686913697
O	-1.77465738715627	-0.55096809898321	7.14581599479267
C	-1.44338377356283	0.55668307704597	7.24691725793354
C	-2.00629710679367	-0.58308293966053	11.65104949672260
C	-1.25431384277568	0.58461495602445	11.75769358062217
H	-0.38483521945381	0.61582238448389	12.40889187674315
C	-3.11570299732524	-0.63094596930662	10.81016355334373
H	-3.68952390990012	-1.54878771440953	10.71498173294215
C	-0.77511218692269	2.98679084052400	11.11153002939728
H	-1.72184464845069	-1.46309474872639	12.22092734411552
C	-4.66360236411145	0.43848669495665	9.11330840291490
C	-1.70103391037361	6.76143409415751	8.29456320966834
C	-3.70369495721468	3.22633011618974	5.27296923455803
H	-1.71437145292032	7.13131170943820	3.62967326272932
C	2.10417489460127	0.26121767841432	7.09552802380415
C	3.09841371634263	2.15352286905695	5.75746899947127
C	1.16381244248629	0.82935301869431	4.82875624664429
H	2.81714887966924	-0.43468331876812	6.63764637597157
H	1.19272357886365	-0.28612774360980	7.35037328644301
H	2.54112589311614	0.65247731221770	8.01965590075504
H	3.81377466294702	1.46912267295728	5.28551097752863
H	3.55624948720844	2.57173891726529	6.65936364626777
H	2.89303064068970	2.97679752218764	5.06610895299715
H	1.86814906836429	0.13975282443111	4.34845705779941
H	0.92093123147658	1.62949320894737	4.12236466317842
H	0.24444535391668	0.28587144143767	5.06307010499430
H	-1.04720053648201	7.63477684920982	8.23497463587653
H	-1.17584703411743	5.97116788678389	8.84199768693269
H	-2.58371253681118	7.03619685970266	8.88345660350878
H	-3.99795501493213	3.07506703082009	4.23142337004335
H	-4.59322644448624	3.14041479074443	5.90644686974903
H	-3.01972160993661	2.41979392073512	5.56681792217237
H	-4.36397916485666	0.76516451816804	8.11201001374571
H	-5.47798747195730	1.09632468595553	9.43850716337644
H	-5.05413434139319	-0.57931664429137	9.04279046511720
H	-1.40328551447633	3.86398287267311	11.30191564858738
H	-0.25198891296704	3.16399211798452	10.16327188390501
H	-0.03353045831826	2.90805562815948	11.91034556911864

Transition State for A′ → B″ (NHC = IPh, R = Me)



C	1.10270723086364	2.37386192412106	6.61480624734287
C	0.69369195414290	1.95110414834879	8.41856007771615
Ni	-0.80304118745859	2.12384682239358	7.13317625005552
N	-2.50562437387321	4.40343277258924	8.24972663218132
N	-2.56459724321449	2.68923457070276	9.53757769823494
C	-2.10476764686736	3.08647751335219	8.30250548929692
C	-2.32211623721974	5.27344503334369	7.13227838426005
C	-1.83878785958008	6.56438067177622	7.33954431640856
C	-2.63518433907826	4.82317894399294	5.85030881421469
C	-2.49946791321229	1.35595857556467	10.04773073485174
C	-3.14655516655284	4.80790075277974	9.41975003798566
H	-3.54924207836284	5.80069935337188	9.53638692035882
C	-3.18338353625997	3.72753245117409	10.23266488345916
H	-3.62498694397938	3.57960775431048	11.20472944473991
C	-2.44451285443067	5.67394076659918	4.76489268227088
H	-2.67606729888630	5.32264354122196	3.76408754858259
C	-1.66094072109645	7.41239015110259	6.24742637299058
H	-1.27198849018509	8.41395093237093	6.40422222150085
C	2.01064836596053	1.35291201031672	6.00920085656790
C	-2.95818205084795	0.29879813260702	9.26083529141250
C	-2.01963344056156	1.13428220830169	11.33812533816323
C	-1.95765167859054	6.96786038836031	4.95951627719182
O	-2.22901312503691	0.73963718991479	4.93357203700706
C	-1.67290625866633	1.29010525587761	5.78541984776923
C	-2.43514042400840	-1.23010235205209	11.06081048118526
C	-1.99222100986439	-0.16446615308248	11.84365308288223
H	-1.60855194037140	-0.34311864512904	12.84353435935579
C	-2.91696496448482	-0.99595913205018	9.77182735177852
H	-3.26086397481784	-1.82336725986566	9.15896293428407
H	-1.65071610369407	1.96888481330527	11.92679636736132
H	-2.40313996589811	-2.24195545085556	11.45320922560710
H	-3.32424796491659	0.50169321508760	8.26102370244957
H	-1.57229605249451	6.88703665216346	8.34146421547798
H	-3.00604115769862	3.81383003693985	5.71758279901169
H	-1.80658276422551	7.62593028249924	4.10921145389319
H	1.68168069830142	0.34470427204654	6.29408295145762
H	3.04128920510016	1.47971837726762	6.36449140339356
H	2.00937412817136	1.44777618435042	4.91845209941977
C	1.15972947080524	3.00656917085830	9.36890828279551
H	0.63602079209715	2.90996531057716	10.32640396905061
H	0.97138074314068	4.00048202106600	8.94251212268643
H	2.23674202532667	2.92149704527439	9.56047160027533
P	0.16065548358483	0.38226797844260	8.44833090295370
P	0.56244866894049	3.91006976866244	6.30915229011806

Transition State for A″ → B‴ (NHC = IXy, R = *t*Bu)

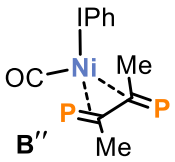


C	1.01004863391845	2.36799519650617	6.61907452984858
C	1.00850335895251	2.21496378422081	8.54315944459534

Ni	-0.75014572501422	2.12846947591151	7.48799501012285
N	-2.91554757587915	4.21818003861448	8.21953319494805
N	-3.06743229087327	2.44285595878668	9.41178834034268
C	-2.28876669255908	3.00699813892573	8.42618208468346
C	-2.54355601768858	5.21070405902671	7.24520363108791
C	-1.99765267037380	6.42355019943366	7.68857250034437
C	-2.79730902787451	4.94730439176445	5.88936593233998
C	-2.88856888173840	1.10939548676922	9.92555367855521
C	-4.02500632356079	4.38575886835483	9.04557401312277
H	-4.63055787435465	5.27659475916919	9.00786763672031
C	-4.12101404778462	3.26463833582310	9.79792043559844
H	-4.82856336550620	2.96712637153136	10.55507580396740
C	-2.42815442781355	5.92127029495222	4.95870928674445
H	-2.59984575133233	5.73031653614408	3.90292281075741
C	-1.63654774447528	7.36651878899776	6.71971417396574
H	-1.18717353706110	8.30322523983194	7.03925777906459
C	1.88727722052373	1.38743037394346	5.84255915880766
C	-3.50697024636783	0.04880344385875	9.25081182429769
C	-2.13996002275415	0.93214422181069	11.09729607507975
C	-1.83974634413631	7.11590696146866	5.36674701866186
O	-1.86539261138115	-0.20893230675730	6.01316272685397
C	-1.50128384790402	0.76720393586758	6.51929587005654
C	-2.53008947512502	-1.45237468832361	10.88964824909929
C	-1.96953831847619	-0.37336272652513	11.56786288828700
H	-1.37577480485013	-0.53843785272031	12.46263992363907
C	-3.29830740264236	-1.24172961449553	9.74695389439847
H	-3.74439066160232	-2.08502788930266	9.22671086556077
C	-1.55606291592932	2.11282034476046	11.82527083532768
H	-2.37122448445366	-2.46264382429935	11.25570011846280
C	-4.40001698914736	0.29185450109123	8.06190093896494
C	-1.81984957772837	6.73916362932062	9.15268883686409
C	-3.42413068847625	3.65484947309535	5.44602878973097
H	-1.54537426421744	7.85571107351517	4.62791527388714
C	2.01663504944289	-0.00626258950640	6.46291724100532
C	3.29754261934660	1.98649902780206	5.65521025075813
C	1.24676625327118	1.23899857137725	4.43948048264573
C	1.73297221052281	3.34995713844036	9.26915360918817
C	0.77930898013602	4.53778553734305	9.44816322755365
C	3.00389794889664	3.83961734701389	8.55108567513294
C	2.15997925046826	2.82341968853416	10.65740676240604
P	0.35527146179769	0.76033807093441	9.00376941603352
P	0.27831252487301	3.81274448428852	6.21403519494768
H	-1.00538289667123	2.75680745543319	11.13486010725590
H	-0.87428147398862	1.78102295447138	12.61167774308129
H	-2.34236190872941	2.72271854631145	12.28694170840346
H	0.43095788755774	4.89688354837185	8.47096134107068
H	1.29290941330828	5.36105915781068	9.95919562693316
H	-0.09596045456858	4.24258929822348	10.03246916864616
H	2.77184090919971	4.23618719011982	7.56096899870083
H	3.72832808057577	3.02713031323326	8.44622821317506
H	3.46736621893172	4.63345210951638	9.14874860985937
H	2.83393385958656	1.96762240404989	10.55038655336421
H	1.29110149586273	2.50120996625557	11.23650535080102
H	2.68178624804274	3.61454127493672	11.21003804119083
H	1.84139758943181	0.54459233475141	3.83378038798488
H	1.21071819620922	2.21072987760868	3.93833942326539
H	0.22846864375093	0.84967032991299	4.51469403107870
H	2.53385552632595	-0.66520853163528	5.75512680673983
H	1.03273012269551	-0.44041641803595	6.67230090042072
H	2.58912831735441	0.01597075033808	7.39367280289757
H	3.86866089196223	1.36307484365986	4.95732038127698
H	3.83985217142197	2.02404684879251	6.60226549638141
H	3.23375119228427	3.00041290030514	5.24787809786385
H	-4.50415273410711	-0.61775965364375	7.46645210304108
H	-4.00885034399483	1.08409578771490	7.42001418826944
H	-5.40034131862687	0.59960534903790	8.39276060872636
H	-0.94897393833215	7.38354013705409	9.30029102160808
H	-1.69045443764792	5.83752780194685	9.75240882222285
H	-2.69570686546772	7.27402426802808	9.54223144790460
H	-3.71094600947858	3.71046922245653	4.39299887946250

H	-4.31294600726571	3.41678576039308	6.04062061470820
H	-2.71429927869120	2.82908191528185	5.57743708920511

B″ (NHC = IPh, R = Me)

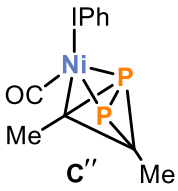


C	1.20347229718996	2.36537946907346	6.81891755809722
C	0.89641129242270	2.05934660712591	8.26303369461874
Ni	-0.76839186748328	2.10816688659560	7.13815358629546
N	-2.46859117702456	4.39656378644848	8.26928272595508
N	-2.55765714844456	2.67353382773482	9.54231368686925
C	-2.07667624950416	3.07763922098561	8.31704181879918
C	-2.27591300040922	5.26986509081285	7.15509969871802
C	-1.77056614648230	6.55190527216564	7.36592153430171
C	-2.61281536434722	4.83328813502195	5.87433392625377
C	-2.49748041086771	1.33780362584911	10.04790121995845
C	-3.12537055354160	4.79632837878051	9.43166308221846
H	-3.52327968693111	5.79100091735197	9.54963219424004
C	-3.18088944205328	3.70985575744241	10.23591191309823
H	-3.63581143929058	3.55831467088726	11.20128354836426
C	-2.42330951349723	5.68907727315532	4.79268744624421
H	-2.67238494320726	5.34894667320795	3.79222958197448
C	-1.59418910704256	7.40503424154623	6.27764101198778
H	-1.18803002093705	8.39946651554171	6.43609713719516
C	1.91959900370450	1.33265680564142	5.98779052568064
C	-2.94732942372472	0.28298051183661	9.25237887157884
C	-2.03103744027254	1.11147235071816	11.34290787152228
C	-1.91470837019243	6.97412928478817	4.99064844432751
O	-2.15437883026689	0.58433831254703	4.99360478488622
C	-1.60327602542753	1.18502092589293	5.81336666916640
C	-2.43576230406650	-1.25261793348399	11.04957802688901
C	-2.00495122690458	-0.18951696051508	11.84249499964705
H	-1.63052377342046	-0.37185442227101	12.84518502829387
C	-2.90640686530157	-1.01366986099471	9.75701689622190
H	-3.24208193201620	-1.83926060069429	9.13713267671790
H	-1.66918929104627	1.94400445714998	11.93880482891937
H	-2.40367242423493	-2.26641144203810	11.43700355797994
H	-3.30360657780310	0.48941906888770	8.24979815985472
H	-1.48814826497649	6.86285780218766	8.36719821062447
H	-2.99862788668692	3.82949987007498	5.73995053331509
H	-1.76518882866703	7.63618616282043	4.14315111634894
H	1.65897745168845	0.33776298265057	6.39461262951563
H	3.00812997182403	1.46054019994614	6.06026179703419
H	1.62973036815254	1.38176543114897	4.93483224888378
C	1.06677280524326	3.13372480952780	9.30578675527942
H	0.36079965458996	3.01481915572869	10.13251993414256
H	0.89867795166381	4.10873685107522	8.81462244547759
H	2.08608534997986	3.12266479092940	9.71396098033075
P	0.22184168341433	0.48835578715017	8.51601557700735
P	0.54069970619832	3.84951730956826	6.23815706516497

Transition state for B″ → C″ (NHC = IPh, R = Me)

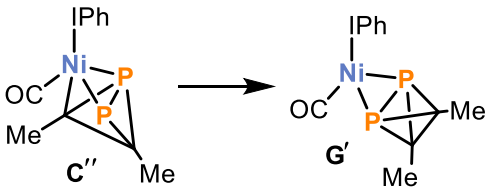
P	1.50110125849291	-2.23602413331024	0.24199939100427
C	2.56220752896982	-0.67313536193300	-1.42210714042655
C	1.90948547747163	-0.58582960679834	-0.05575922357875
Ni	0.18767516167266	-0.90451354749483	-1.19334380987253
N	-1.12594979768772	1.52075881959154	0.17435861395509
N	-1.25101210844169	-0.22133922181845	1.41806778502133
C	-0.92872948109242	0.15981912895023	0.13928038264983
C	-0.91095125109503	2.39338351183047	-0.93439644109544
C	-0.28489744789918	3.62296016444670	-0.73161677822188
C	-1.32037079771246	2.00043213902816	-2.20859998430866
C	-1.21383320497417	-1.57202384075665	1.88336828125273
C	-1.52244737300499	1.96205269538849	1.43668314766227
H	-1.75397938739427	2.99514676890264	1.63808438666305
C	-1.59941810811739	0.86229710427912	2.22277724220245
H	-1.91069628442078	0.73863820718677	3.24750170654752
C	-1.10001621037827	2.85342675042507	-3.28674709957901
H	-1.41254562785973	2.54808979025752	-4.28051030208093
C	-0.07312802000134	4.47198158047791	-1.81777277516712
H	0.42105148034448	5.42647286194783	-1.66323189742663
C	3.90416131734273	-1.33674763176429	-1.63192502789628
C	-1.87012034691366	-2.56603887324061	1.15864503251740
C	-0.53358767193424	-1.87411123060308	3.06436704651833
C	-0.47808338068983	4.08856933298888	-3.09572948874905
O	-1.67705544148977	-2.58647981451343	-2.71891444758042
C	-0.91344227536431	-1.93792794992294	-2.13586799548582
C	-1.15423609640452	-4.19377902034785	2.79906021616993
C	-0.51408377220753	-3.19041012361949	3.52482659030159
H	0.02077427452843	-3.43139002042633	4.43836634535963
C	-1.82914882348297	-3.87951537566759	1.61742213249340
H	-2.32894639710779	-4.65897039121376	1.05073197665302
H	-0.00979665828818	-1.08860523237985	3.60068803675352
H	-1.12685611484623	-5.22029225357729	3.15192147850242
H	-2.39133046971325	-2.30221445094395	0.24618028120376
H	0.05699231709952	3.90034749089212	0.26110279415461
H	-1.79238122513017	1.03376049228524	-2.33894514586137
H	-0.30570905138558	4.74769239012703	-3.94118464882323
H	4.30205649291269	-1.71810643090848	-0.68621824877687
H	4.59934172735841	-0.59724722395014	-2.05359286128788
H	3.84803601382331	-2.16559706904817	-2.34355985265094
C	2.07671389347434	0.64242959801850	0.79682763145254
H	1.39099035200587	0.63569643645737	1.64886007855949
H	1.89658032267396	1.54227520350359	0.19744415333590
H	3.10302582743424	0.69172300288847	1.18492449033151
P	1.55256037943244	0.10234233436516	-2.60346405239627

C″ (NHC = IPh, R = Me)



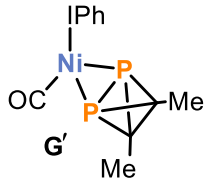
P	1.66702955100544	-2.38585958577446	-0.41912004956387
C	2.51426132347186	-1.05868595541915	-1.48794581221141
C	1.55282950528759	-0.40054111712083	-0.61823304100523
Ni	-0.19190928109775	-0.94462598792694	-1.18281902989653
N	-1.23009118750318	1.48316253821680	0.18252428098609
N	-1.40369220729892	-0.25756854596618	1.43732043659434
C	-1.03432270420508	0.12400329914802	0.17380321145560
C	-0.86102843696065	2.35589212065554	-0.88767147204054
C	-0.25653543790595	3.57835530354453	-0.59064795560128
C	-1.07810503802303	1.96927783674979	-2.21009075424264
C	-1.28328674356979	-1.59138130981564	1.94770391753041
C	-1.69338522766568	1.92674810015517	1.42130408618292
H	-1.94229853888527	2.95904682384711	1.60315809188449
C	-1.79933512003981	0.83266497133154	2.21147679130927
H	-2.15181301372421	0.71467732267278	3.22308307574823
C	-0.67622878007925	2.81671798848191	-3.24062834887769
H	-0.83881727230431	2.51370144922608	-4.27034901676824
C	0.13074442287703	4.42353473336440	-1.62980617730779
H	0.60758850416868	5.37139950923713	-1.39920096347398
C	3.99015295427191	-0.86304340322360	-1.65095087752936
C	-1.86235888878385	-2.65585367264366	1.26015720250355
C	-0.57144427376150	-1.80007565021139	3.12786354932418
C	-0.07304856448708	4.04211002179322	-2.95599699914898
O	-2.49801236496766	-1.99009425471506	-2.65229890605159
C	-1.59166677614493	-1.60306606428803	-2.04093123326733
C	-0.99991064533332	-4.17052005019405	2.93791712322580
C	-0.43480641218554	-3.09585146917825	3.62369734706792
H	0.12796291227951	-3.26426468824915	4.53683366361242
C	-1.71291123411163	-3.94749647330408	1.75914321241430
H	-2.15604100977727	-4.78096322905310	1.22301329157999
H	-0.10640269431841	-0.95919844078271	3.63367413193153
H	-0.88301653071650	-5.18022889924018	3.31971239922614
H	-2.41544002166265	-2.46888565200439	0.34823889657872
H	-0.06175353074492	3.85129254042664	0.44198263544748
H	-1.54738251594858	1.01622320583553	-2.41957234405611
H	0.23814730489759	4.69707798898678	-3.76426762206999
H	4.48668365796528	-0.69154792676839	-0.68950169016496
H	4.18445074762065	0.00489002854783	-2.29508395057784
H	4.44335251769010	-1.74253614847516	-2.11921727416072
C	1.95361727548569	0.56641619303298	0.46588465307765
H	1.26318155155640	0.54251369857475	1.31375913780606
H	1.95219572177789	1.58840015759301	0.06511379139877
H	2.96339929105242	0.35764459627158	0.84381556388558
P	1.27944321079868	-1.88346290333870	-2.57684697275536

Transition State for C″ → G′ (NHC = IPh, R = Me)



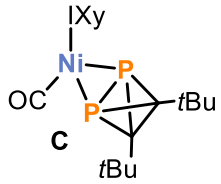
P	1.61453668851430	-1.71345769002937	0.22256607782799
C	2.70308987534487	-1.42702314475252	-1.29047268352038
C	1.88843833399107	-0.27128320225511	-0.82857549395762
Ni	-0.09376496842369	-0.95694677930773	-1.11644776496157
N	-1.26236635592625	1.44675444544117	0.33486877356942
N	-1.42630225485261	-0.33178026752557	1.53126509150344
C	-1.00035591654205	0.09491561577196	0.29833519041222
C	-0.93189753525114	2.37444417985105	-0.70195761861795
C	-0.46039597238788	3.64299497489098	-0.35586690299943
C	-1.06008683961625	2.00526846708241	-2.04018040039316
C	-1.33896923738877	-1.67879811298303	2.00970912375303
C	-1.81792796912869	1.83482607890848	1.55436275159505
H	-2.12403361414575	2.84930000149285	1.74878146641422
C	-1.91951616883240	0.71554660609524	2.30707690616815
H	-2.32921683628269	0.55342487574944	3.29055886317933
C	-0.69301957530581	2.90907894958439	-3.03497445112621
H	-0.78314714713258	2.61561205409510	-4.07640358061391
C	-0.11175268932432	4.54487757032386	-1.35917515373329
H	0.26211702993498	5.52765182781845	-1.08824040487474
C	4.19450342268914	-1.49412678250675	-1.37160601875289
C	-1.80029308485009	-2.73071434374049	1.22078593336228
C	-0.78992958273012	-1.91350080693060	3.26962596036325
C	-0.21993600695195	4.17810377425602	-2.70091523251981
O	-2.36774173856973	-1.96576753033963	-2.70129059353961
C	-1.47915978330768	-1.51982678395230	-2.10562817675707
C	-1.15216234244392	-4.28256818368417	2.96028074173347
C	-0.70155343580237	-3.22114495532540	3.74467492440090
H	-0.26452181541911	-3.40863195072509	4.72079685495963
C	-1.69997521787824	-4.03414105592216	1.70095856546782
H	-2.05207534506694	-4.85685534719072	1.08640297091441
H	-0.40701794812143	-1.08295678929458	3.85491051952255
H	-1.07388071372054	-5.30126080457621	3.32802480622061
H	-2.22466284645921	-2.52360523598841	0.24655417029374
H	-0.33396288232429	3.91016110088642	0.68882802453271
H	-1.42499351446236	1.01655663436069	-2.28980298314404
H	0.06316744206313	4.87809225573604	-3.48121952604884
H	4.64934248609149	-1.13600119223400	-0.43865487779446
H	4.56963831443566	-0.87231182519102	-2.19581896420433
H	4.53393826444322	-2.52131007830942	-1.54042617759282
C	2.28658712560820	1.16654763680401	-0.74042417660325
H	1.60622401053642	1.73475108618533	-0.10296249023547
H	2.28859580762918	1.63550686432732	-1.73009382521720
H	3.29878105463286	1.24610044174982	-0.32010238602126
P	1.38566048273435	-1.63650157864676	-2.50812783296489

[(IPh)Ni(CO)($P_2C_2Me_2$)] (G′)



Ni	-2.75667590133618	1.68144760412631	6.63864069912235
N	-2.24574344120257	4.15567630778368	8.27934567616136
N	-2.69101425725431	2.46959967338541	9.54435627089621
C	-2.61979993384324	2.82856593927463	8.21304954128602
C	-2.00775362177326	4.97176519108546	7.13635252332074
C	-0.98207825771726	5.91880100983487	7.16064843591667
C	-2.79523624958202	4.80742774933739	5.99571572169673
C	-3.01387627219227	1.15826531539040	9.99757466710991
C	-2.08089073723218	4.58757546454240	9.59632815777383
H	-1.83379735824622	5.60754854410922	9.84043270034416
C	-2.36010766637461	3.52948444533267	10.39008142413302
H	-2.40418293751640	3.44416173633463	11.46328946387118
C	-2.54517740813654	5.59129264890923	4.87276468179591
H	-3.15575545755736	5.45814558365297	3.98480853146035
C	-0.74803983827865	6.70624019445313	6.03460867691525
H	0.05491195056043	7.43727654989568	6.05161226568446
P	-0.81344239324143	1.80086780810550	5.49041083091913
C	-3.95923871913167	0.40203529907936	9.30295441715930
C	-2.37420277307880	0.63560178015759	11.12325423356401
C	-1.52471537491116	6.54328556665916	4.88741818689936
O	-4.92625097817910	0.87329071366497	4.82939095655480
C	-4.12219028319060	1.23648837379795	5.58476937789924
C	-3.62491009804542	-1.41847526834936	10.86180284611783
C	-2.68749673417506	-0.65227895707873	11.55469557916813
H	-2.18400022877939	-1.06098689800394	12.42581989457459
C	-4.25584859207909	-0.88739257260210	9.73592354703798
H	-4.98788388453792	-1.47587716624400	9.19108696340198
H	-1.61722067809267	1.21875533867265	11.63876301389856
H	-3.85984868845770	-2.42452625079566	11.19592317026371
H	-4.44467761096353	0.83180634038997	8.43135084225585
H	-0.35402474551263	6.01806752943845	8.04073717348272
H	-3.58858579786919	4.06529512602806	6.00192078462463
H	-1.33361375936887	7.15276678672319	4.00936744937815
C	1.71854017025951	0.90720054339306	7.09497469995036
C	0.36380383601798	0.77886780393538	6.48391436804573
H	1.69432711022577	1.57748592515404	7.96031665495223
H	2.43509977142881	1.31212252492733	6.36973919129669
H	2.08849016630047	-0.06966575612162	7.42993756922636
P	-1.26675564035754	-0.00097562448693	6.87181538788510
C	-0.23019590953069	0.05408964760503	5.34318942357921
C	0.25156301231056	-0.87898631523588	4.28372896282723
H	1.02577394180631	-0.40281944248137	3.66980149916599
H	-0.56993186449156	-1.17847127612688	3.62573647207876
H	0.68031413332731	-1.78425553765338	4.73063706630417

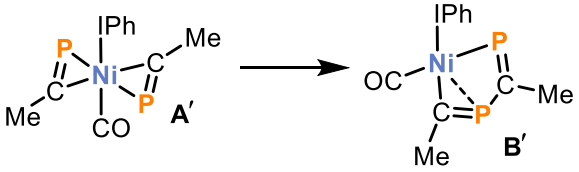
[(IXy)Ni(CO)(P$_2$C$_2$*t*Bu$_2$)] (C)



Ni	-2.25220661369226	1.85801341219794	6.55755330292866
N	-2.77540974112329	4.28827138429092	8.21458400241174
N	-3.11504103659542	2.50983141726647	9.36925739191209
C	-2.71839751081446	2.91990980911554	8.11852312073803
C	-2.45948411075013	5.14824511646956	7.10533956084010
C	-1.14412453099246	5.60907627835481	6.97008001011327
C	-3.47508198313902	5.45870425259737	6.19155364737317
C	-3.19674978434318	1.12281717967668	9.73947927449575
C	-3.18770302359565	4.71040692183359	9.47721651420629
H	-3.29151507171140	5.75416377273889	9.72668324479756
C	-3.40302164935570	3.58704026646231	10.20613624326978
H	-3.73479315085217	3.44874787431801	11.22259945200712
C	-3.14175650998233	6.27927286931807	5.10964510049990
H	-3.90871906376671	6.53226709570986	4.38243048195584
C	-0.85309801936738	6.42674102785189	5.87440103790408
H	0.16169919326765	6.79236999091573	5.74169457735093
P	-0.20169360320083	1.84946775431727	5.61784569108290
C	-4.32278400229061	0.38784041157055	9.34645235868437
C	-2.12573863535481	0.55616264007426	10.44239070906066
C	-1.84365204799581	6.76042794775600	4.95312929749661
O	-4.03021057885171	1.06734937030022	4.36007735646307
C	-3.36953636179372	1.42606571298606	5.24596024623964
C	-3.31136370741865	-1.55820660793850	10.38783660467701
C	-2.20376004674079	-0.80167634850298	10.76378317738444
H	-1.37952632596084	-1.26747218970588	11.29741092874006
C	-4.35987330052267	-0.96827617445586	9.68564267229088
H	-5.21920127698825	-1.56314501840358	9.38773504445246
C	-0.91739510212399	1.38162678637881	10.79608713748021
H	-3.35474519898980	-2.61457671523009	10.63749526634847
C	-5.43828467283538	1.03626700580868	8.56964206327651
C	-0.08351469509754	5.19964968623341	7.95702122789269
C	-4.86280656577684	4.89886811106095	6.36216299280986
H	-1.60099790470072	7.39350521662303	4.10428032856844
C	2.20338762294094	0.82089755522396	7.38535064192887
C	0.87520500923468	0.76240951123265	6.67107383265733
C	2.24259687148036	2.07971333259261	8.26757632230060
C	3.34984373472414	0.88877070389892	6.35995259719556
C	2.36547283800363	-0.42947732734045	8.27091226706643
P	-0.84551671026233	0.17664503495241	7.06416330864512
C	0.21932105027503	0.04734829525753	5.55840964123510
C	0.45503867044692	-0.97222526110935	4.47395621128107
C	1.39577283235285	-0.39733792392500	3.39873330393385
C	-0.90615101975827	-1.29941409655388	3.83229990155629
C	1.06164049159833	-2.25025038426412	5.08098055133346
H	1.15757237791230	-3.02620286091404	4.31290864932303
H	0.42281530472590	-2.63457500402031	5.88338132748734
H	2.05656558454319	-2.05533386253071	5.49422816836342
H	1.53929190054697	-1.12858656272016	2.59485382145620
H	2.37580812509258	-0.15030612430966	3.81659305587945
H	0.96701428511769	0.51335245167714	2.96815687402330
H	3.40403299575144	-0.03237997661054	5.77228414272451
H	4.30909313152433	1.02311810323423	6.87333652657270
H	3.20489418049050	1.72938845567810	5.67315266531624
H	2.31835116677275	-1.34416010768107	7.67250311907089
H	1.56703911921198	-0.47120275951460	9.01889159652669
H	3.33142299000147	-0.40560214175884	8.78905443095713
H	2.17580576561070	2.98051876111996	7.65028341180904
H	3.17672563017789	2.11708209537763	8.84000498520989

H	1.40693202969807	2.08319950352856	8.97337860852199
H	-0.54282433405398	1.90226373995757	9.90909710568265
H	-0.12090065196911	0.74757600671455	11.19286207464008
H	-1.15263251363623	2.14670521930620	11.54522747587226
H	0.88747511503341	5.61179369923764	7.67191678554519
H	-0.00241426638532	4.10861039323095	7.99360270414044
H	-0.32069399449356	5.54218852963453	8.97084725376491
H	-0.78102006502093	-2.02760704909307	3.02272610567007
H	-1.36404394458670	-0.39519784586472	3.41985077271683
H	-1.59099920600986	-1.71671878393886	4.57716659008415
H	-6.25337629264085	0.32739162399175	8.40484800747377
H	-5.07207930650290	1.38493497936815	7.59723159705152
H	-5.83651280839796	1.90981343304279	9.09811419027451
H	-5.52229351823236	5.25820826424550	5.56852911036880
H	-5.29414211745353	5.18336452236297	7.32868965887035
H	-4.83492144040734	3.80375759929310	6.32822053971634

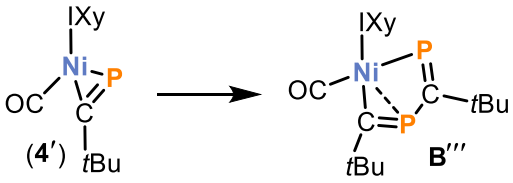
Transition State for A′ → B′ (NHC = IPh, R = Me)



P	2.46792329675017	0.73606038749325	-1.55024037817434
C	1.33490527831405	-0.37905024400232	-1.91989450495473
C	2.61999271815344	0.89210495048825	0.83152590287115
Ni	1.10913600035453	-0.77184690173880	-0.03793788201447
N	-1.32620785633728	1.03329160720407	-0.18473566481268
N	-1.67899230167929	-0.75581452162397	0.94374024052592
C	-0.69567116911909	-0.11971388121125	0.21751959395282
C	-0.69814449937031	2.09379718400508	-0.92205107953361
C	0.17413134169320	2.95692492739452	-0.26400553790636
C	-0.98294624947095	2.24977859608423	-2.27568470384762
C	-1.50655748432378	-2.00955781245872	1.61342640852519
C	-2.63978343422463	1.10878189819883	0.27666018088665
H	-3.27293870730593	1.95200348350391	0.05297010284750
C	-2.85970073352789	-0.01896316124754	0.99323727126591
H	-3.73474193118560	-0.37958501281096	1.50894492191732
C	-0.37012084510856	3.27931920075712	-2.98812018808770
H	-0.57793567873268	3.39955901561143	-4.04709811456828
C	0.78457261312287	3.98206474148724	-0.98439102181612
H	1.47281394129190	4.65541041896473	-0.48257909162408
C	0.63516617736553	-1.00852804751719	-3.06702510906274
C	-1.20903922437590	-3.15176264584075	0.87385877502581
C	-1.64669526099160	-2.06540062890289	2.99889875206625
C	0.51636871127247	4.14210915293986	-2.34449573044935
O	2.07510843749584	-3.53943089579366	0.04775858110100
C	1.75507813766086	-2.42444041088096	0.03265009080739
C	-1.17678288086534	-4.43478092852529	2.92261611916197
C	-1.48415136996049	-3.28648228257295	3.65241829996237
H	-1.58235897702239	-3.33495753072472	4.73274995741315
C	-1.03912620953806	-4.36563946042063	1.53547445633239
H	-0.79148190726206	-5.25580754627495	0.96595810185317
H	-1.85604510239729	-1.15658977462899	3.55489803899998
H	-1.03950350155081	-5.38240432230182	3.43481264784561
H	-1.10250185512750	-3.07529897549961	-0.20215605417606
H	0.38778443176887	2.79980156103612	0.78727396957190
H	-1.66153907951510	1.55772167063303	-2.76444041424867
H	1.00013694861275	4.93792227908250	-2.90287334291475
H	0.86114100038197	-2.08202133895231	-3.09644082894503
H	0.91084655833721	-0.56579622676317	-4.03135739423149
H	-0.45160903519254	-0.92551664643466	-2.93777909036424
C	3.66088313081980	1.96312627707738	0.78232909401669

H	3.32696883130916	2.81457448176812	0.17561473940673
H	4.58173631297262	1.58913541105010	0.31729172614635
H	3.89497763294678	2.31374444743918	1.79340679483724
P	1.81490379356110	0.03215750490916	1.95727136439194

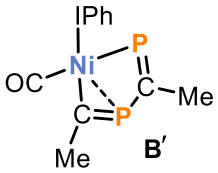
Transition State for 4′ → B‴ (NHC = IXy, R = *t*Bu)



C	0.92179078653434	-5.63813959274923	1.91817097373715
C	1.89774856424580	-3.89078854281032	-0.82760864240766
Ni	0.87347314978076	-3.74594488893684	1.49023996127770
N	-2.22044297469722	-3.94645331640729	1.20396799264234
N	-1.49621949040511	-2.01161258489863	1.78454750180673
C	-1.04041907030841	-3.26317171244802	1.42465840231047
C	-2.33817752031715	-5.28445702296579	0.68882578831577
C	-1.99348880533255	-5.50125427772554	-0.65446777982891
C	-2.86245434717111	-6.29514230903719	1.50363405972367
C	-0.64827186229849	-0.87671770000454	2.04262709629426
C	-3.34169059213531	-3.14781847897199	1.42207966296108
H	-4.34160367721493	-3.52666421793167	1.28569098582599
C	-2.88354496411365	-1.92887441004560	1.79079234424006
H	-3.39871431539636	-1.01908563266062	2.05367349746686
C	-2.95876401246569	-7.58289291311037	0.95983680347472
H	-3.34457633855765	-8.38806690220470	1.58004755158119
C	-2.10068640474284	-6.80056600756018	-1.15342830943387
H	-1.82252213110904	-6.99244044054728	-2.18609906770535
C	0.83102403717870	-6.35568255388467	3.23671879927156
C	-0.13973197289013	-0.68664589685648	3.33292801559310
C	-0.40129538133404	0.01187658689267	0.98681015848897
C	-2.56448476584867	-7.83903021424092	-0.34828413022108
O	2.71597909688967	-2.67678034484311	3.48404078336910
C	2.02675049532429	-3.12820418451805	2.66564629979675
C	0.97449851827832	1.30542751837227	2.50949745483215
C	0.42778064189752	1.10752697894071	1.24379891702332
H	0.65143369134413	1.80095348738297	0.43753810970112
C	0.68707033463930	0.41990538158927	3.54560396724325
H	1.11383587619134	0.57713580607577	4.53233428973767
C	-1.01135289510937	-0.20819563353792	-0.37345632644697
H	1.62761968467469	2.15456465786719	2.68954971550090
C	-0.48340550966402	-1.63908739735168	4.44636961280831
C	-1.55428251797000	-4.36349907226746	-1.53215668370394
C	-3.35546122775071	-6.03581891901876	2.90584147027259
H	-2.63509052779607	-8.84643867612599	-0.74838127968848
C	2.28273351134316	-6.53746389120251	3.74754664306350
C	0.19266042463291	-7.74780349906664	3.04917963011804
C	0.04669858345084	-5.54653466368571	4.28284326908957
C	2.58186722488585	-4.49959284130343	-2.03081913303151
C	1.65842064966021	-5.42560487607065	-2.84813866173779
C	3.84921378509463	-5.26965480760965	-1.59597470035441
C	3.01723146582539	-3.33050496549267	-2.94706867177204
P	1.65091722599925	-2.42314558946477	-0.17859396299988
P	1.31168424492557	-5.99835716857776	0.37139367289181
H	-0.55586749530016	0.45892157009334	-1.10895108942357
H	-2.09169906241635	-0.01815128543158	-0.35986911943369
H	-0.86652034340889	-1.24108675350753	-0.70727722500419
H	1.27546666029571	-6.25149716997071	-2.24298150957433
H	2.22159578832956	-5.84498078235462	-3.68972937371030
H	0.80951840955883	-4.86325815782747	-3.24677473235199
H	3.59635088161704	-6.12850490631225	-0.96823539565390
H	4.51604289587910	-4.61322369931074	-1.02918417869332

H	4.37773503963495	-5.63071297049391	-2.48636957537020
H	3.70468877112969	-2.66402421759562	-2.41846357040432
H	2.14745407230122	-2.74837231888393	-3.26593883830838
H	3.52174295276243	-3.72905959895357	-3.83577549251633
H	-0.06888573573650	-6.12925805777958	5.20466188167974
H	-0.94412396290899	-5.28046880999857	3.91078874316206
H	0.58021353931572	-4.62277101356417	4.52095923339879
H	2.26346141890137	-7.02333681396934	4.73087853664007
H	2.78337900712072	-5.57060841937827	3.84634632062034
H	2.85634310904885	-7.15737981290889	3.05314109440897
H	0.15301378417927	-8.27827575680282	4.00849825912505
H	0.78195955322881	-8.34107208769270	2.34301656225228
H	-0.82046060744022	-7.66047586817137	2.65022637348591
H	0.14873597923756	-1.45604204988892	5.31821160295560
H	-0.34701925654621	-2.67440161549544	4.12381450993389
H	-1.53144365878810	-1.52478015615997	4.75070975357581
H	-1.52986936576041	-4.67947303420501	-2.57767140132884
H	-0.55572108971182	-4.01158601649558	-1.24996942756069
H	-2.23865123434064	-3.51245559851004	-1.44115139430089
H	-3.06572465099032	-6.85237215269953	3.57371067853525
H	-4.45111617577268	-5.97446706078116	2.91981454494213
H	-2.96802991158769	-5.10076965593619	3.31283814779130

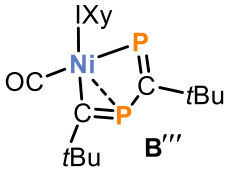
B′ (NHC = IPh, R = Me)



P	1.08043398670091	3.46284306916378	6.50473351623148
C	-0.13215220122183	2.31390661859376	6.21706838563215
C	1.33619817767084	3.65948625402988	8.34579551191324
Ni	-0.53176544964075	1.81549775333957	8.00105998787549
N	-2.59358539730510	4.00847607135095	8.21304437113094
N	-3.09143763245701	2.21925081452618	9.30226232972233
C	-2.12669110694381	2.74490325587479	8.46565701101934
C	-1.94960844677118	4.97477273961159	7.36534131061612
C	-1.09120158649756	5.91530629729022	7.92667361506166
C	-2.21407475326627	4.96024262622104	5.99854213994921
C	-3.02576007495581	0.91308531619276	9.86787251616304
C	-3.79263100372866	4.26312280221372	8.87651034445222
H	-4.30314988222324	5.20703374234332	8.77699689456543
C	-4.10612141211835	3.13800538621450	9.56094068910943
H	-4.96105791425644	2.88805503326079	10.16732259011891
C	-1.59564551536654	5.89790139699003	5.17490063655401
H	-1.78591912879236	5.88522564006885	4.10610955759364
C	-0.47477319320899	6.84932145098858	7.09474903402667
H	0.20498194749384	7.58151662657050	7.51964309414148
C	-0.57522210490887	1.88662680365340	4.85619140526024
C	-2.64462802843595	-0.16156990755981	9.06389753437277
C	-3.32494946521389	0.72723931270956	11.21747622633653
C	-0.72264304674370	6.83796319894342	5.72196538776275
O	0.93195404449199	-0.68714675287287	8.26875103307211
C	0.40511116847175	0.33797002660383	8.16529638238483
C	-2.84390963521910	-1.63068654818587	10.97449212131662
C	-3.23886661453989	-0.55142734751762	11.76600158020207
H	-3.46121662987105	-0.69829127122111	12.81860829523656
C	-2.54635216011602	-1.43283742585256	9.62591559132203
H	-2.23836146655368	-2.26877812218803	9.00556234701834
H	-3.58993126136719	1.57940822368533	11.83594113998441
H	-2.76595649475126	-2.62276624753949	11.40874355635985
H	-2.44107496302952	0.00939503851069	8.01098225782662
H	-0.88957382609268	5.88836417424741	8.99189823740345

H	-2.88369155717468	4.20945632251949	5.59209305989187
H	-0.23162411272822	7.56082824917623	5.07745191721086
H	-0.36762713830832	0.81713208989887	4.71841821147855
H	-0.09402504536292	2.43959356643244	4.03904202954468
H	-1.66365913279926	1.99817094333998	4.75982668038099
C	2.38665307800467	4.73695242168385	8.57955084917170
H	2.08241565801011	5.67724658927253	8.10118422241551
H	3.34276127598772	4.44124888566909	8.12922110183595
H	2.54479003290265	4.91730233128602	9.64741275420552
P	0.60454201223564	2.85928955046041	9.64678254212832

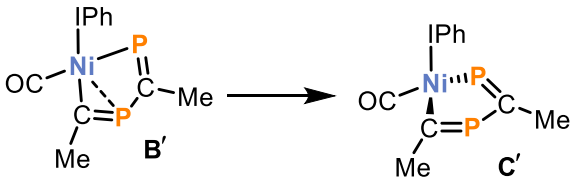
B‴ (NHC = IXy, R = *t*Bu)



P	1.09589572921527	3.31558771522170	6.44465666277576
C	-0.03244346299130	2.04114459549522	6.39385508458309
C	1.37076224135882	3.94950495564208	8.18238218917300
Ni	-0.54078932148829	2.07958636945947	8.20372891763325
N	-2.72575166316445	4.20206305244903	8.39979239445841
N	-3.25998326790990	2.24921302219155	9.12914053330790
C	-2.22210304608735	2.93143512733640	8.53471724289564
C	-2.05849896733158	5.32703092992980	7.79417709052869
C	-1.57443696249233	6.34871417220843	8.62390136195710
C	-2.01490388076662	5.39826088735950	6.39580856746038
C	-3.21397682845011	0.84495163257896	9.44227708874131
C	-4.03118790865064	4.29448024790902	8.88454441726297
H	-4.58265603246769	5.21974452911191	8.84359554815636
C	-4.36625158410485	3.06532416645914	9.34249490855361
H	-5.27156750098599	2.69015202527820	9.79139426455444
C	-1.43656196756523	6.53361666171807	5.82067442336764
H	-1.38102439342240	6.60565800361007	4.73805858588338
C	-1.02163241722785	7.47430061496842	8.00562068072946
H	-0.63555444265331	8.27906029345811	8.62561703421312
C	-0.21616808314895	1.14704507055540	5.19104210228641
C	-3.79283778623826	-0.05580078298476	8.53811888113972
C	-2.60704258156409	0.44095359394982	10.63967799398574
C	-0.95168276463812	7.56684253630361	6.61729517915833
O	0.67219371647022	-0.33392196499876	9.27753911558616
C	0.25341854922800	0.65710689342171	8.84754633566261
C	-3.08772927667280	-1.85278064848865	10.00746445524692
C	-2.55082171527525	-0.93047235744676	10.90276700441646
H	-2.07144649282879	-1.27257492710468	11.81576516832727
C	-3.71048228235796	-1.41881643441858	8.83990263044066
H	-4.13598089456987	-2.14013885696752	8.14716622700360
C	-2.03530604812478	1.44885809148136	11.60055696637171
H	-3.02309640496342	-2.91545831263180	10.22294380554916
C	-4.49902590030386	0.42934984522417	7.29832901316986
C	-1.63151858959750	6.23691412680936	10.12376368922640
C	-2.60945299738134	4.30629141943626	5.55040849739821
H	-0.51137758531518	8.44594591487469	6.15539187319794
C	0.80847117874965	-0.00685881781632	5.33572325209723
C	0.04153766740158	1.87884159837829	3.85726312403491
C	-1.62879384428999	0.53564884970696	5.17974955108336
C	2.51984527101296	4.99409169780383	8.20194301340319
C	2.36956975377712	6.03463686568449	7.07772116687766
C	3.84812903132455	4.22974920377664	8.00598348181654
C	2.56068777862780	5.73688895767972	9.54718543897198
P	0.62869954376135	3.39554662115582	9.59831043267926
H	-4.60415513734223	-0.38199724775311	6.57394156599738
H	-3.95513654704084	1.25019899113515	6.82553787818256

H	-5.50416225475135	0.79759219972309	7.53959525104244
H	-1.21541945001804	2.00525737314507	11.13339702992042
H	-1.65441735332472	0.95108927928691	12.49538336185682
H	-2.79217820469809	2.18099059747882	11.90464839288143
H	-2.46426173040798	4.52012171904014	4.48901273516379
H	-3.68506439098303	4.20413255017393	5.74005575817906
H	-2.13819366022628	3.34778365754945	5.78608508914499
H	-1.22534159266427	7.13847240265162	10.58892413007676
H	-1.04084741887045	5.37563682852175	10.46241599038164
H	-2.65530616685298	6.09220169821719	10.48536859145274
H	3.39063960856067	6.45394326593380	9.54787432078148
H	2.70446215971494	5.04093509337548	10.38055141180404
H	1.62774121801557	6.28410813193643	9.71634192397290
H	2.37658447582794	5.56544029320637	6.08887754075111
H	3.20785892623702	6.74047328156269	7.12500510137267
H	1.43495165857962	6.58904007638425	7.18676437827400
H	3.84361796641895	3.68746233000236	7.05439442126270
H	3.99623139011996	3.50612062951511	8.81365451268539
H	4.68819691776834	4.93538250336032	8.00067666946632
H	-1.72865246403619	-0.17678830845714	4.35169105020548
H	-2.39121953092304	1.31046497850320	5.05465049481772
H	-1.81703856558372	0.01521799299335	6.12310571975502
H	-0.09112757465299	1.18928438347661	3.01485634358258
H	1.06119506290718	2.27586788248433	3.82617635676305
H	-0.65338798691981	2.71522741464310	3.73404439146534
H	0.68800438845356	-0.70898671860756	4.50152258179020
H	0.65194735061097	-0.54754188711248	6.27328932754678
H	1.82879534018405	0.38690142186037	5.32847228405630

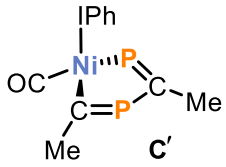
Transition State for B′ → C′ (NHC = IPh, R = Me)



C	1.97279965131612	-1.45613036494534	0.22346154422572
C	0.69213759493459	-2.11991845282103	-2.16437980240024
Ni	1.10478585383944	0.16437654609297	-0.38567836457235
C	2.20833750586237	0.90879794447868	-1.55216007831063
N	-0.61535947394936	1.96373644269265	1.01757127978882
N	-1.84398280651505	0.28378281282608	0.44584862956422
C	-0.54987529465698	0.73587870649457	0.38231637324747
C	0.52597736228867	2.79182541865788	1.16510382554059
C	1.77663766031495	2.18117805360286	1.30080812924114
C	0.41550096730233	4.18220189507172	1.13203221869625
C	-2.29339846518750	-0.99965837439321	0.00144445189477
C	-1.91066104188907	2.26118695402199	1.43446881241695
H	-2.15010619393544	3.15886383032060	1.98014991119662
C	-2.68067819871144	1.20850928059883	1.07421154035711
H	-3.72442447026903	1.00216590572692	1.24455038850819
C	1.56862290763479	4.95986055987407	1.22703838324703
H	1.48523777031439	6.04188526681789	1.19186662802093
C	2.92443882689399	2.96782700851462	1.37358838806693
H	3.89381803243778	2.48870732753319	1.46862208810689
C	2.88731044398845	-1.66561614094727	1.40383798420747
C	-3.49436474924538	-1.10451303113888	-0.70174737277597
C	-1.53356188856998	-2.12720602889584	0.30078503367583
C	2.82348824600371	4.35820919274940	1.33822884670615
O	3.03165133292981	1.41152349067151	-2.19376584843563
C	-3.17689005874736	-3.49878676919484	-0.82484626401302
C	-1.97707422780917	-3.37644679642436	-0.12312551072723
H	-1.37150959203192	-4.25193885755555	0.09112291606567
C	-3.93428528278244	-2.36162198906812	-1.11118128773010

H	-4.86242445769983	-2.44913371420541	-1.66809221079403
H	-0.58972635473775	-2.01444804053972	0.82322070232755
H	-3.51934881119481	-4.47562921102425	-1.15327589292043
H	-4.05772855740668	-0.21085517603686	-0.95319705606973
H	1.83976947208695	1.09344006553970	1.41663934613150
H	-0.55469908917628	4.65030057299439	0.99814207420402
H	3.71732863893369	4.97128575025765	1.39681936247300
H	2.37942576503864	-1.39305336127757	2.33987263230235
H	3.75327381226120	-0.99253375558045	1.32370359456939
H	3.27042041589635	-2.69129194396658	1.50661108235968
C	0.25056526711993	-3.12460907967766	-3.21523643149254
H	1.12358094350228	-3.59143251435050	-3.68707194921092
H	-0.35946433993922	-2.65948693193763	-3.99709267336962
H	-0.33888228494256	-3.92262317856607	-2.74720670628569
P	0.15382112334840	-0.52190606405596	-2.28623797092783
P	1.73951604514845	-2.77670324893505	-0.83776874710634

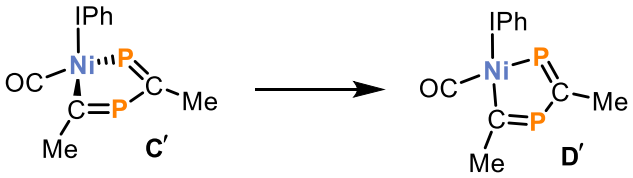
C′ (NHC = IPh, R = Me)



C	-0.03929119742260	0.81654782454329	7.55188314299178
C	-1.13538724592954	1.10394421097351	5.29409825573500
Ni	-0.02491318614384	2.62950419867424	7.92186835493093
C	1.34463133659341	3.77123784579348	7.63414219015022
N	-1.80143166351031	4.73771572675612	9.16021560454911
N	-2.83530596976310	2.87650911043945	8.89429303481932
C	-1.57768767998006	3.42033889144543	8.83536911153167
C	-0.78203753523745	5.73780129458008	9.24527198701245
C	0.30615044646923	5.53874554139168	10.09389148550459
C	-0.89604493267499	6.89871721164544	8.48307417212953
C	-3.13755042394426	1.49964594270315	8.61704965046999
C	-3.15113814575915	5.00083849561309	9.37342613571293
H	-3.50517674552973	5.97938581773800	9.65409845151267
C	-3.80272188798123	3.82255433373620	9.20893830731233
H	-4.84389127988994	3.56171849162477	9.30785824077312
C	0.09655295945472	7.87381596364704	8.57334187368946
H	0.01874847133424	8.77529944343210	7.97328054158530
C	1.29631183694496	6.51474715039744	10.17107554294780
H	2.15028821482027	6.36201789403669	10.82379130177610
C	0.62610907307955	0.56282793796176	8.86783056912930
C	-3.83282228284694	1.17473349851636	7.45517976865700
C	-2.75945613610918	0.51976864522964	9.53181352915449
C	1.19313730317364	7.68236521516479	9.41340162500817
O	2.23110170929599	4.43706769874539	7.31277236973954
C	-3.76062613878162	-1.15254890967292	8.10782568768421
C	-3.07486495956351	-0.81198470909173	9.27369124591103
H	-2.77815320255503	-1.58310492021906	9.97802418773996
C	-4.14042009204976	-0.16096490391511	7.20343368950592
H	-4.66307682311124	-0.42802087344874	6.29015802597370
H	-2.22486644509411	0.80918325154190	10.43093481784750
H	-3.99202278398896	-2.19251810049331	7.89941702082855
H	-4.09116576659814	1.95541964917466	6.74822441299908
H	0.36783505228067	4.62416769106952	10.67338816643710
H	-1.73781020629007	7.01872346617918	7.80798516859463
H	1.96956387676472	8.43885299335394	9.47343151128783
H	0.75301611083369	1.52380229012758	9.44552020808483
H	1.63564791139932	0.15137959409417	8.75522173090748
H	0.02883486218598	-0.08516525765975	9.52128151785967
C	-1.80485863503604	0.88509078022895	3.96101355594601
H	-1.14526007593981	0.34727018891516	3.26793292072960

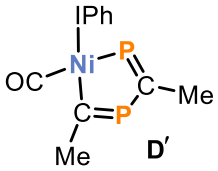
H	-2.08702428881547	1.83662734311498	3.49502357443530
H	-2.71309822671972	0.27678657652162	4.07344031398909
P	-0.92181692910756	2.67715210974061	5.92184631239283
P	-0.54302727825708	-0.24218164435092	6.32294568402295

Transition State C′ → D′ (NHC = IPh, R = Me)



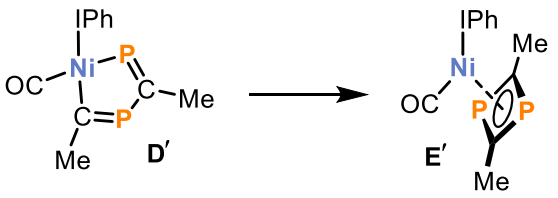
C	0.03083559131156	0.73261756719179	7.50122284942881
C	-1.07342005388992	1.49237667072012	5.27882370433676
Ni	-0.16917360623978	2.48297366837164	8.19668459736934
C	1.52974182524152	2.95412200572399	8.64446638660185
N	-1.90349478586765	4.80968479888596	9.17574477827731
N	-2.92842031467494	2.92416794506362	9.08375262506491
C	-1.68035843939757	3.47533921040818	8.95694009512721
C	-0.89124861924204	5.81985968901772	9.10319211661758
C	0.24821879755102	5.70977304505064	9.89767453870134
C	-1.06234247397522	6.89625865273819	8.23425806601285
C	-3.18395104381503	1.53650931264371	8.81885886548817
C	-3.25450147905872	5.07788074655812	9.39127859403798
H	-3.61105629029475	6.07362555142313	9.59854606418076
C	-3.89967741012369	3.88564459849114	9.33714750981442
H	-4.93620576553532	3.62694860759118	9.48039498017904
C	-0.07551541345758	7.87833440242270	8.16426684632454
H	-0.19882882082626	8.71477086161853	7.48305745818841
C	1.23469035042790	6.68918599007465	9.81048970232524
H	2.12931051161169	6.60331334312031	10.41934948848817
C	0.57042103259145	-0.05791630047372	8.66448190346418
C	-3.88944174980738	1.18188530944009	7.67080834526809
C	-2.69353068386846	0.57111413460944	9.69446454076813
C	1.07408413892127	7.77423109968858	8.94755107834660
O	2.63126500071488	3.30114343613142	8.61754112145189
C	-3.60423211227648	-1.14532800761605	8.26141771549377
C	-2.90974762874081	-0.77621896603570	9.41262111237129
H	-2.52531923217006	-1.53541308320886	10.08663475417103
C	-4.09406739314179	-0.16773349480164	7.39445025697477
H	-4.61811026523038	-0.45650833270055	6.48873563920923
H	-2.14820355668446	0.88137728346065	10.58009063382608
H	-3.75575957467564	-2.19570213217759	8.03287356536329
H	-4.22700474337042	1.95379363381303	6.98764019114224
H	0.35337882887223	4.86147065525117	10.56429916456929
H	-1.94390029864820	6.94345708622200	7.60247511337507
H	1.84605432305202	8.53494113336423	8.88227337407081
H	0.26706813463978	0.38084095226524	9.63019894044151
H	1.66819817144720	-0.06099826164900	8.66004379500653
H	0.21160919416264	-1.09728534386721	8.64982839845901
C	-1.60578035592540	1.51062176158314	3.86788266136654
H	-0.86109473641677	1.12425484945146	3.16018040585745
H	-1.88576376277617	2.52302435449181	3.55564508023872
H	-2.49259782852795	0.86838944519535	3.77670105002328
P	-0.97581136440764	2.90088776371372	6.22160470773306
P	-0.48133509747867	-0.01590064326645	6.06211218444343

D′ (NHC = IPh, R = Me)



C	0.20130894348058	0.69059692303594	7.55625484586401
C	-1.05027730541937	1.76082895418668	5.43460054189067
Ni	-0.34590624122009	2.33020160772726	8.42280612044255
N	-1.95733747187874	4.88109473329263	9.11440723436045
N	-3.01009013224251	3.00292847836029	9.10924622506091
C	-1.75600214134740	3.53436498277006	8.99029642373994
C	-0.93122672400275	5.86179069766125	8.94931899904013
C	0.30491958318564	5.67945992845943	9.56679952993590
C	-1.17715547313303	6.98041681630659	8.15276434294118
C	-3.22373335535079	1.60489682990925	8.86832011594791
C	-3.31445654933385	5.17477081420244	9.27488183115657
H	-3.66312887753960	6.18332257296637	9.42423301830779
C	-3.97628723244220	3.99116730157999	9.26670811331000
H	-5.02084258449148	3.75611782259275	9.39099213923906
C	-0.17172700256719	7.92913182897337	7.98037233702213
H	-0.35651354187525	8.79619984522314	7.35348837855490
C	1.30836438196170	6.62649311466387	9.37472191276129
H	2.27391208970329	6.48359557367368	9.85007743964628
C	0.88966720541033	-0.36249087121036	8.38794544400927
C	-3.98493434183384	1.20362182480370	7.77295842332819
C	-2.58488556581797	0.67519495160821	9.68918806539081
C	1.07280770540621	7.75301623056988	8.58607904669993
O	1.66998847446811	2.30976651787052	10.55368076640861
C	0.77914185970054	2.20619592900844	9.82424277982287
C	-3.46504939704032	-1.09787174300668	8.30603058058693
C	-2.71482669494729	-0.68282433360797	9.40488171675296
H	-2.21654188092006	-1.41349132006683	10.03405310100826
C	-4.10105302320109	-0.15665843204769	7.49506728713821
H	-4.66955278207551	-0.48009158355151	6.62870578940871
H	-2.00125749070487	1.02128197790547	10.53593815545645
H	-3.54649076273477	-2.15491258751090	8.07306274102644
H	-4.42917152150960	1.95007865467489	7.12281385235853
H	0.46928425792343	4.81170859895139	10.19358365562150
H	-2.13118459380723	7.08401608546066	7.64565780490836
H	1.85748892034749	8.48900754359615	8.43983799419800
H	0.39289163516265	-0.48247582152258	9.36211288892554
H	1.92810175999029	-0.07613139706189	8.60263420445657
H	0.90077206393785	-1.34320016995469	7.89017151644287
C	-1.56550405074336	1.83045172501100	4.01644582346979
H	-0.83398938271847	1.41223443614360	3.31209851334798
H	-1.79205177296226	2.86002407955511	3.71972716962287
H	-2.48140688544765	1.23303993423547	3.90744277268230
P	-0.93568280044475	3.14874847329426	6.40159034481249
P	-0.42540030092480	0.18019747126731	6.06246501289381

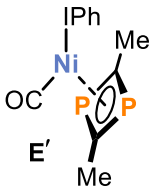
Transition state D′ → E′ (NHC = IPh, R = Me)



C	0.50677146219823	0.86861571398258	7.57323308679925

C	-0.60191384147734	2.40428012736221	5.64216342277167
Ni	-0.19985192806687	2.27920891670905	8.43617538174427
N	-2.03216590204514	4.68229140691270	8.83914704396174
N	-3.08994187258361	2.81041438713262	8.88081760881174
C	-1.81778143367931	3.32569092599945	8.79864630649978
C	-1.00844808641505	5.67646216167853	8.75069657417684
C	0.13292825994295	5.56977868182382	9.54229801867036
C	-1.17096233991339	6.74366009558662	7.86701125978198
C	-3.40123991266488	1.41527880039936	8.86415467528452
C	-3.38931007797205	4.99166564081591	8.91201565250160
H	-3.73788291260739	6.00881470733399	8.98265685981613
C	-4.05527693353080	3.81374798486233	8.93571898342928
H	-5.10531153610247	3.59024193988523	9.02860571206269
C	-0.17261185129038	7.70992553336205	7.77131630751416
H	-0.28982821878274	8.53431042675778	7.07450627652014
C	1.13435569073653	6.53104298305177	9.42524320893613
H	2.03083653288009	6.44325184987181	10.03131545240804
C	1.49908415657788	-0.18365001569299	7.89254006034235
C	-4.41453288545292	0.95023365100390	8.02767167831473
C	-2.68292284710990	0.53957479381926	9.67688468377328
C	0.98485512261732	7.60109712317185	8.54270498586566
O	1.46676099739288	2.25583307280218	10.87369015786696
C	0.76072652424827	2.21767503991645	9.95539377247985
C	-3.98744772677257	-1.29921534219338	8.79956999800039
C	-2.97547453842076	-0.82070779670346	9.63387973497698
H	-2.41262680851691	-1.50807911914068	10.25813738585977
C	-4.70988718038132	-0.41188271879976	8.00341049901109
H	-5.49084414912670	-0.77934580772266	7.34468962760333
H	-1.89731563742437	0.92762805168568	10.31544358798784
H	-4.20997328054811	-2.36152266013077	8.76858486017547
H	-4.94144817808744	1.64395145986533	7.37956692911743
H	0.22890962844140	4.74290058316265	10.23422237793882
H	-2.05209067591684	6.79079289963005	7.23466282319504
H	1.76892841129598	8.34697448762383	8.45410360493472
H	1.94626560081385	-0.06208023219626	8.88387457702573
H	2.30996430386030	-0.16766659019681	7.14921741088500
H	1.03439893407405	-1.17977142990310	7.82242511862189
C	-1.07743568481772	2.60464429942578	4.22960839667425
H	-0.70333425252350	1.81274973422151	3.56577787345743
H	-0.74473967446500	3.57409704250042	3.84065569984498
H	-2.17446374060808	2.57095923941304	4.17268733079370
P	0.25535262691345	3.53853863255515	6.57450414021248
P	-0.89212014468933	0.82622631835416	6.51830085335049

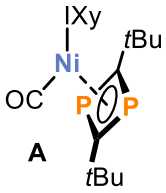
E′ (NHC = IPh, R = Me)



Ni	-2.32692654688879	1.47743173138861	6.56001016798455
N	-2.30458636362833	4.12469550400826	7.93115425890417
N	-2.46619654657716	2.51344533332383	9.35230560204337
C	-2.36090683044377	2.75144584027433	8.00100262143405
C	-2.08136805937267	4.88429611620032	6.73757578550509
C	-1.16749591451882	5.93908394983955	6.77678845311621
C	-2.74773041182186	4.56029111006815	5.55722818578892
C	-2.44916788456516	1.22062531328071	9.96853196211132
C	-2.37393195687867	4.70974097802669	9.19450003200677
H	-2.38970908939212	5.77876670245089	9.32779610541021
C	-2.47554356515258	3.69826407698933	10.08665122045463
H	-2.59809401927864	3.70475500072774	11.15704376245210
C	-2.47310817536228	5.28884433433911	4.40096368991662

H	-2.98008510940394	5.02690317058499	3.47761726888874
C	-0.91389617178721	6.67240298152402	5.61933417277220
H	-0.19639032170711	7.48685721668046	5.64742217814811
C	0.53216939268290	2.87229062600487	6.00753294263330
C	-0.35250740675474	1.66661667840059	5.89007461626491
C	-3.18622357808687	0.16884993876760	9.42740217567322
C	-1.66291678460342	1.03193371489193	11.10675415636005
C	-1.55920929681024	6.34240482999215	4.42697115816951
O	-5.12666505177385	1.13239328359286	5.84408931573603
C	-4.00993605154206	1.26775360503842	6.12700530080013
C	-2.32683767522363	-1.29065684998963	11.15868615659404
C	-1.60986118281873	-0.22545352467767	11.70499822463966
H	-0.99141918636540	-0.37458047623210	12.58491078627861
C	-3.11168205574932	-1.08915309200083	10.02326982376376
H	-3.67322264457150	-1.91244912828649	9.59307105499314
H	-1.07084105698959	1.85350949574204	11.49863193625603
H	-2.27331168056119	-2.27377234667901	11.61661057443574
H	-3.78971461938744	0.33311809052800	8.54488968198154
H	-0.63414740715791	6.15989542407145	7.69652467186971
H	-3.45242073648080	3.73977898354029	5.54523790948915
H	-1.34990241006304	6.90455414386186	3.52184927093316
H	0.49419270498202	3.30419669220991	7.01441727521928
H	0.24432285462298	3.64530478289726	5.28986969441004
H	1.57670670172562	2.59531539536631	5.80901124875454
C	0.29322206331660	0.46258418414295	8.14615219576823
C	-0.45980525559166	0.58061760430822	6.85402470720119
H	0.30674731733522	1.41157398943837	8.69496023036873
H	1.33727512895610	0.18224227110786	7.95043089041346
H	-0.14803346070282	-0.30209098104404	8.79122010143952
P	-1.49475758895661	-0.60946859617055	6.03581881585552
P	-1.32680406665148	1.10556190147041	4.51443961676070

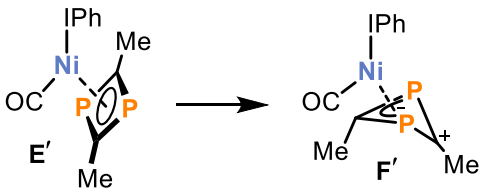
A (NHC = IXy, R = *t*Bu)



Ni	-1.87235638588750	1.69311247431248	6.49057665367764
N	-2.50572684672247	4.15356318344520	8.24190023780060
N	-3.11696146997430	2.25481748140556	9.04957893784821
C	-2.41103645999748	2.79809043712349	7.99840755415619
C	-1.88431130831564	5.22862525147132	7.50870280702487
C	-0.91575849272077	6.00132556075037	8.17719407167172
C	-2.31151140209524	5.52915698595883	6.20500935749347
C	-3.30455611430919	0.84233182655409	9.27756049550050
C	-3.24978114459473	4.42057259382963	9.39102346600099
H	-3.43091120198773	5.42975198395905	9.72176490439057
C	-3.63084103354900	3.22650193336819	9.89875299256851
H	-4.21351371145665	2.96963396375001	10.76828819927971
C	-1.69735580108301	6.60414224167826	5.55262881220720
H	-2.00925605382321	6.84433007503796	4.53988008088279
C	-0.33272414705936	7.06430020741928	7.48148390209228
H	0.43308759633016	7.65668549163612	7.97529175744522
P	-0.52603955249279	1.61351037654763	4.61582358753377
C	-4.52681634759871	0.25208159061802	8.93424523954074
C	-2.26526276082747	0.13409614253388	9.90014431118577
C	-0.71204514425004	7.36135368801273	6.17668560016920
O	-4.57068692034360	1.45704613972441	5.42109860943496
C	-3.49398971572958	1.50981118312256	5.85174157029450
C	-3.62899296122664	-1.86347464994226	9.71892464178216
C	-2.44476064247407	-1.23504851132103	10.10119500459391
H	-1.64463043355393	-1.80914253612265	10.56011172468899

C	-4.66342140514928	-1.12380789829395	9.15677089081975
H	-5.59344396673235	-1.61207323016371	8.87743605511273
C	-1.02053911287951	0.83902965935653	10.36333007504922
H	-3.74789737158402	-2.93261584932686	9.86991992103632
C	-5.68453309123341	1.05035117922499	8.38987308367064
C	-0.50010641950101	5.74536421256401	9.60666274421668
C	-3.38552208530198	4.75023273711685	5.50059039246907
H	-0.24320049687181	8.18636482568836	5.64830178544777
C	1.28628324539257	2.83603244311759	6.61082316742999
C	0.23692167815505	1.83637084655636	6.19873087894922
C	1.13914694791117	4.14208508022753	5.81850108438003
C	2.66067255992327	2.20263644955012	6.27892592105023
C	1.22035915741879	3.09315335022211	8.12189851745222
P	-0.16175210784741	0.22314239983598	6.99299536389123
C	-1.06339138169902	0.06524848403774	5.46794208963050
C	-1.74487981945817	-1.16245722869739	4.90846844773938
C	-2.58098897883263	-0.83648095905007	3.65941920582950
C	-2.60984767674366	-1.84351165711456	5.98232513001539
C	-0.60824762172063	-2.12996878120442	4.48944830431151
H	1.41107367609160	2.16702531586065	8.67593900920738
H	0.22921708625283	3.45767065555949	8.39688396819350
H	1.96895235739323	3.83366820231597	8.42650504005031
H	2.74478408206292	2.01720057261821	5.20370369217927
H	2.78385417265183	1.24969748036097	6.80404866311591
H	3.46895572697401	2.87827633332813	6.58471851439337
H	1.20444412796427	3.94247410545828	4.74263374721485
H	1.93585332103947	4.84639772604945	6.08399343573903
H	0.17651803612100	4.61482202078078	6.01762221911347
H	0.55250579307102	6.00824567378847	9.74162909178928
H	-0.63571337008303	4.70399103819898	9.90309566779908
H	-1.08479424711246	6.36424835613637	10.29899863937986
H	-0.56636809695267	1.39766849748068	9.54150468610063
H	-0.28907875031208	0.11942186576766	10.73753123074977
H	-1.25104556156699	1.55019853541070	11.16697177355112
H	-3.88516741363069	5.38280350595188	4.76147212265806
H	-4.13308255270351	4.36434473069961	6.19833003346473
H	-2.94624036314648	3.88855490824359	4.98498869801845
H	-6.40106551520313	1.27104907249941	9.19144147445077
H	-6.21363375266106	0.48557792973159	7.61815955087203
H	-5.36543175918306	1.99964746565917	7.95876270578226
H	-2.96092146143576	-1.76196197076260	3.21144343369027
H	-1.96925985166043	-0.32230936003234	2.90945072182055
H	-3.43607492848082	-0.20079904172935	3.89729946703268
H	-3.00127897996041	-2.79926007267119	5.61339465349415
H	-3.45039729584819	-1.20472856505677	6.26658253931561
H	-2.02164598401025	-2.03768056524888	6.88597780555906
H	-1.03242393492265	-3.03282335121879	4.03379761924931
H	-0.01164965755457	-2.41828241776158	5.36035839355855
H	0.05550149930308	-1.65196982593892	3.76137382469079

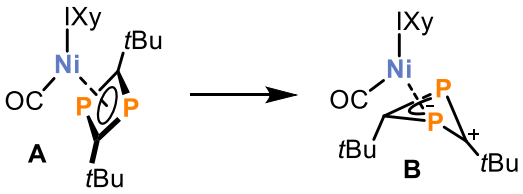
Transition State E′ → F′ (NHC = IPh, R = Me)



Ni	-0.60913992651547	-0.58322410483615	-0.95337380629648
N	-0.51019475364026	1.89850331141843	0.69138733055757
N	-0.77851687625699	0.15672590015161	1.92713036570571
C	-0.67327717232449	0.53216545851581	0.60469092057295
C	-0.32359618132083	2.77461176514506	-0.42137082745766
C	0.69120134207675	3.72971002662126	-0.37195489227714
C	-1.15126218427643	2.66804134331489	-1.53877829397345

C	-0.93320094503186	-1.18629233369751	2.38867147268837
C	-0.48882877134770	2.33920379721911	2.01380427640017
H	-0.40317771217827	3.38346508401391	2.26536124954208
C	-0.65737278849261	1.24469717173246	2.79034683023832
H	-0.74894374231902	1.13773346833414	3.85864957336296
C	-0.94667557933711	3.52116748211558	-2.61981732683186
H	-1.58478786210589	3.43563829240602	-3.49411773284694
C	0.88117541536830	4.58652520932461	-1.45606289476916
H	1.67710446432260	5.32454433938155	-1.42289799663688
P	1.35881166276783	0.16909043082800	-2.01239877654854
C	-1.87425784366284	-2.02461102308594	1.79146921055986
C	-0.13427117557465	-1.64090540240405	3.43721266208677
C	0.06736006994273	4.48053586296505	-2.58274145331703
O	-3.25316342048412	-1.00964725839316	-2.12664455793966
C	-2.19848488848322	-0.84338448973794	-1.66237864986173
C	-1.20672679754796	-3.80183543675484	3.29343406779531
C	-0.27762289919361	-2.95192534310311	3.89124309057567
H	0.35041798559893	-3.31025882200213	4.70144891017080
C	-2.00230151760966	-3.33458431081253	2.24521733013269
H	-2.72903838627686	-3.99175152288781	1.77735374087155
H	0.61212890821281	-0.98280736219850	3.87212125651704
H	-1.30925588859803	-4.82567689230062	3.64034293115575
H	-2.47825595526827	-1.64892264953424	0.97452878255439
H	1.34355822352807	3.78036695412051	0.49477674000590
H	-1.92826770261079	1.91348061515165	-1.55464414368986
H	0.22379911820482	5.14062748132327	-3.43063038233842
C	3.68263756575220	-1.20732888086255	-0.90388189092105
C	2.19139729646075	-0.99737114235069	-0.93057849643423
H	4.21598089470007	-0.25718434294309	-1.01114982747320
H	3.97959734488957	-1.84769078000682	-1.74444553947232
H	3.99283738888338	-1.71088597650819	0.01750194408528
P	0.99553955296030	-2.19781122612914	-0.33656424473470
C	0.61191213557146	-1.54647813208819	-2.04862827289675
C	0.58566145450917	-2.41352589296720	-3.27875716143531
H	0.18457513927242	-1.85223573538120	-4.12807118346319
H	-0.03880439864733	-3.29526620697884	-3.10600863163286
H	1.59372940608210	-2.75523072611856	-3.54079470233070

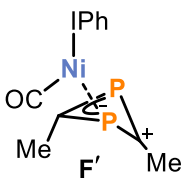
Transition State A → B (NHC = IXy, R = *t*Bu)



Ni	-0.65039595606173	-0.69052281030555	-0.39510346812471
N	-1.57369134266931	1.86157988049859	0.91139127002900
N	-2.22755280396392	0.09346630473170	1.94351762252048
C	-1.46773794281836	0.48768355751769	0.86406266104891
C	-0.92709969706691	2.78781653888701	0.02361907142672
C	0.16789333699109	3.51289530520022	0.51466860789371
C	-1.44040605507757	2.96717301965288	-1.26886650191486
C	-2.43048658483925	-1.27881689683364	2.32662636504506
C	-2.37080581964353	2.28766244060780	1.97339976101114
H	-2.56708989073568	3.33256070932263	2.15042072080638
C	-2.78302560566263	1.17291818188411	2.62153923808176
H	-3.41212148389178	1.03910490425836	3.48659813372832
C	-0.79979165825747	3.89627225409449	-2.09449730131451
H	-1.16728804026857	4.04123348810656	-3.10665316759892
C	0.77518592288290	4.43456890510463	-0.34383812387163
H	1.63331957561509	5.00069415233391	0.00952035239828
P	0.76010583615549	0.57364796347244	-1.72848502900744
C	-3.58963431758581	-1.93132592239345	1.88928862352026
C	-1.47410209981706	-1.88914374542847	3.14954093904808

C	0.29756766664927	4.62316718960099	-1.63904965385651
O	-2.74559924132507	-2.53022057613071	-1.30580969393761
C	-1.91552636319426	-1.80913681494143	-0.92226767364795
C	-2.80649294088336	-3.91412463317150	3.04785030814458
C	-1.67960822568001	-3.22695754334435	3.49583856847970
H	-0.94588014789080	-3.72962816752364	4.12043356415134
C	-3.75636789859756	-3.26924405585352	2.25994530371116
H	-4.63470068235331	-3.80726326223930	1.91372339344722
C	-0.28054741821314	-1.11849928319992	3.64547355447160
H	-2.94625774698401	-4.95711391276081	3.31779813023899
C	-4.61930528460539	-1.21537077730739	1.05351674016710
C	0.68198149979211	3.28769150092245	1.91408994448906
C	-2.61003074251701	2.15716766376702	-1.75344722877291
H	0.78441525668204	5.33767134636364	-2.29663155970348
C	3.49830949720790	0.59431007599993	-0.61086055317612
C	2.05504630100356	0.08989439924932	-0.57907103591497
C	3.50293743869727	1.69223730791642	0.48450097132794
C	3.87188491776942	1.24722155290654	-1.95080947020037
C	4.53062138442956	-0.47751406391118	-0.22685339795252
P	1.45162289843973	-1.28229594993728	0.42732816191214
C	0.93895386728380	-1.24581302678228	-1.36004884294815
C	1.20745765105785	-2.34067223842034	-2.39137152758332
C	0.32210525517942	-2.08659900529263	-3.62475086493648
C	0.86863744498263	-3.70593619190187	-1.76542707890937
C	2.68352569386929	-2.33972674143245	-2.81803065453143
H	4.61395076427320	-1.24358000756533	-1.00106564429391
H	4.25512044779379	-0.97005735294577	0.71047929820699
H	5.51381679577697	-0.00890858362338	-0.10217232168753
H	4.50760505776933	2.12519288278385	0.55058257746342
H	3.23797549014692	1.27422838787074	1.46052004552555
H	2.79482274695662	2.48629083395803	0.23562001450134
H	3.87911348066408	0.51389646168403	-2.76175237099096
H	4.87215105787528	1.69017185456250	-1.87786001787444
H	3.15938792048288	2.03456887400670	-2.21506211851666
H	1.05367083096948	-4.50537818301524	-2.49177815133015
H	-0.17998792872820	-3.74852379141271	-1.46112786059801
H	1.49253555550491	-3.88276583117019	-0.88252079244550
H	0.48317014283024	-2.87385204613766	-4.36975129924655
H	0.56852722123089	-1.11959747255440	-4.07679897559828
H	-0.73572715660249	-2.07965901795926	-3.34897428265042
H	2.84822460011935	-3.10668650730301	-3.58279718542037
H	3.32764438308119	-2.56140579474744	-1.96290745898359
H	2.96467443201634	-1.36884919419370	-3.23635199763733
H	-2.92443575487331	2.48845557951248	-2.74605246444644
H	-3.46173679319218	2.23777466029781	-1.06867751931446
H	-2.33181669410918	1.09513592780897	-1.79928164167819
H	1.64248715711867	3.78919807688149	2.05429280375273
H	0.81081670997502	2.21944924919844	2.11502334436449
H	-0.01455106852351	3.67571808559874	2.66636019027865
H	-5.27162620588040	-1.93433418331060	0.55284064563080
H	-4.14742804742984	-0.58796482228095	0.29285346477312
H	-5.24440885640206	-0.56302488961889	1.67648832216911
H	0.28594337859447	-0.70912467564433	2.80143183499456
H	0.37907517456479	-1.76389656772534	4.23042949190784
H	-0.58901929608817	-0.27518197624320	4.27518788994850

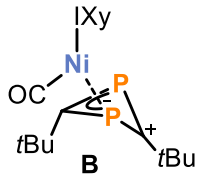
F′ (NHC = IPh, R = Me)



Ni	-0.55494996911815	-0.58042706748092	-0.89478550822481

N	-0.59318851675479	1.91015230408035	0.70400999852406
N	-0.85984162066737	0.17325022025505	1.95125673196282
C	-0.70015846090616	0.53679068126779	0.63008166957433
C	-0.37890220436843	2.78177850236712	-0.40739840384480
C	0.62350008251662	3.74789651621467	-0.32777338293522
C	-1.16904087703548	2.66352384376928	-1.55078722027184
C	-0.98422505529085	-1.16749695154456	2.42837738228855
C	-0.65768062908607	2.36691886498313	2.01990225746700
H	-0.62407137475832	3.41689080153367	2.25941910242228
C	-0.82495799482885	1.27717367477337	2.80243735327592
H	-0.96754077148446	1.17969706448313	3.86596883332127
C	-0.93836398401500	3.51623637174239	-2.62698771825969
H	-1.54675599763616	3.42174480231623	-3.52122780612564
C	0.83872529866623	4.60493485008829	-1.40717385312230
H	1.62477385184394	5.35189583725178	-1.35005372169228
P	1.33672882188119	0.24330263747202	-1.91503399511489
C	-1.88681919549364	-2.04315871605149	1.82486768971084
C	-0.19598409515970	-1.58089806602500	3.50181693852456
C	0.06308097563549	4.48720927809350	-2.55908642315198
O	-3.24903834071641	-0.94210789730678	-2.01590785922798
C	-2.17377772000100	-0.81918250997936	-1.58678830281141
C	-1.20141817355430	-3.77443763325299	3.37197919563986
C	-0.31156470639072	-2.88781529973916	3.97564452348405
H	0.30803004721602	-3.21376871389973	4.80567164982628
C	-1.98609047070717	-3.34884271871670	2.29800078264921
H	-2.68225864983711	-4.03502819399786	1.82551061249430
H	0.51985974491875	-0.89305734543455	3.94190123825828
H	-1.28166067560057	-4.79501177711346	3.73388099284069
H	-2.48364818938695	-1.69976155052961	0.98884872142231
H	1.24564989603098	3.80781360196168	0.56024670712317
H	-1.93798664606369	1.90187394851243	-1.59031694282415
H	0.23959525095460	5.14695295546950	-3.40321892834324
C	3.60718785269358	-1.48716007387182	-1.27422122105015
C	2.17040680222343	-1.08712892763714	-1.02241803743157
H	4.23071527484113	-1.02859899632079	-0.49780753578613
H	3.96275740816871	-1.12759067950436	-2.24472302616205
H	3.74129277943226	-2.57159399918470	-1.21356354467531
P	0.97288581275777	-2.15259882741062	-0.18914331605398
C	0.81822723919699	-1.54805525638981	-1.94609700911223
C	0.78583227469287	-2.42833608884753	-3.17549503687492
H	0.38201227254013	-1.87761299569865	-4.02899121943703
H	0.16017893733004	-3.30713724945027	-2.99906146037648
H	1.79439569532063	-2.77111222124752	-3.43391690789971

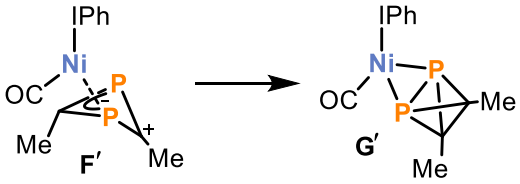
B (NHC = IXy, R = *t*Bu)



Ni	-0.44933573247858	-0.64245286094817	-0.99765690664168
N	-0.86642698023925	1.84288031037207	0.55771637708279
N	-1.11512979105295	0.10028568368579	1.79280466290400
C	-0.78801934876431	0.46988144872499	0.50791935349157
C	-0.54138088579341	2.71665359631690	-0.53874739508959
C	0.76749970492638	3.21003278493801	-0.62025867496148
C	-1.54115070026183	3.05524927707126	-1.45761534673600
C	-1.10845638875222	-1.25427313314223	2.27888314627568
C	-1.22319739019336	2.30046528411485	1.82375421669097
H	-1.33350313246729	3.35126299937149	2.03770903226199
C	-1.37989610109557	1.20261018732268	2.60197738982777
H	-1.65615870809293	1.09332064995541	3.63823412738505

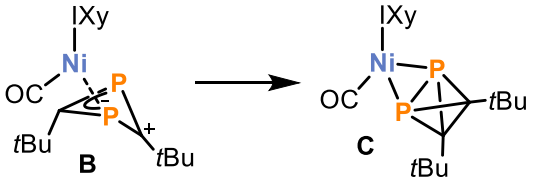
C	-1.18781119981881	3.90353717404016	-2.51180712175180
H	-1.94222154389223	4.17389880175501	-3.24591251090296
C	1.07848775432303	4.05592727773774	-1.68818763719730
H	2.09141212559714	4.43793957638345	-1.78316079185861
P	1.49020018840550	0.17537093450982	-1.96045834134696
C	-2.26181445095446	-2.03409875254904	2.13620140321058
C	0.05694980563767	-1.72461044178375	2.89889860760813
C	0.10986791493149	4.39609892173362	-2.62969102003121
O	-3.02757023977171	-1.14978398440894	-2.30269239950544
C	-1.99739528774771	-0.95090850289251	-1.79233926665294
C	-1.06864887012834	-3.84629450483041	3.22732662928681
C	0.05839929086809	-3.04039528437316	3.36961283752049
H	0.95645942878596	-3.43381585694586	3.83833770323586
C	-2.21780646249974	-3.34563574392135	2.61960720490478
H	-3.09633706655331	-3.97629662160893	2.51214080316217
C	1.26853147069672	-0.83981260277560	3.02626755896800
H	-1.05111942737546	-4.86989736951388	3.59058203994413
C	-3.49444839426938	-1.47833594645989	1.47598525906348
C	1.80022497947578	2.81775943362823	0.40270849492774
C	-2.93917654006693	2.51715334279282	-1.31387957708463
H	0.36742727039215	5.04848626828697	-3.45921626441376
C	3.83067117909423	-1.25255725097266	-0.82795043924292
C	2.31215572905610	-1.06972581024495	-0.94016320308373
C	4.20851523578681	-0.33384463072045	0.36278192068023
C	4.60241925821798	-0.76616137003034	-2.06525464096065
C	4.23669307595076	-2.69205173552507	-0.47516747886797
P	1.08247252635403	-2.20894948389680	-0.27024371172988
C	0.93152891940994	-1.59605374920499	-2.02107677979831
C	0.83142166738343	-2.47257466067957	-3.27306262935295
C	0.21282742768437	-1.63887965692855	-4.41003060690399
C	-0.06631924095608	-3.68266734877097	-2.95863279040177
C	2.21409159506491	-2.97046930653855	-3.71888379736248
H	3.99129260213489	-3.38568828951914	-1.28354397480383
H	3.72245993589561	-3.03536875420397	0.42755782985320
H	5.31815332803433	-2.73618516679321	-0.30035158946465
H	5.28619603302095	-0.40950755426021	0.54621163060379
H	3.68055785339177	-0.63089759114215	1.27330913056630
H	3.96626063291184	0.70972564968063	0.14245055179504
H	4.44302818596517	-1.42742473638129	-2.91954887425769
H	5.67571131298354	-0.74970777205163	-1.84219308463876
H	4.28756818071478	0.24177618762844	-2.35161551861843
H	-0.18278518975566	-4.30523009170216	-3.85280938337511
H	-1.05652842462060	-3.35535543269253	-2.63017982152133
H	0.37750333080105	-4.29008018421284	-2.16236568918669
H	0.12836260744183	-2.24893779941954	-5.31642524366644
H	0.84241695331984	-0.76949949488094	-4.62914099405656
H	-0.78309474556470	-1.28232231007645	-4.13566650575412
H	2.10559281970468	-3.62438275124604	-4.59118186584638
H	2.69943174647533	-3.54020136403647	-2.92143631395515
H	2.85307797896081	-2.12881107842396	-3.99851013636634
H	-3.58376085303399	2.90591034195104	-2.10588015325336
H	-3.37380059549971	2.79334226427994	-0.34621791807716
H	-2.93916920237749	1.42487955019821	-1.36990509278353
H	2.78992310010195	3.17299152519957	0.10536486772686
H	1.83391224032735	1.72851588734507	0.51190916822941
H	1.56800161097854	3.23512794999369	1.38971059908973
H	-4.30159877203952	-2.21473529751296	1.48667775226798
H	-3.28365040638043	-1.20712966815268	0.43737389600302
H	-3.84400763305149	-0.57232966519918	1.98423780994962
H	1.51090298776880	-0.38447114743400	2.06028790527088
H	2.13047022252501	-1.41632880892419	3.37111131248807
H	1.09745949404889	-0.02151174108570	3.73589026922837

Transition State F′ → G′ (NHC = IPh, R = Me)



Ni	-0.98202263971050	-0.85452616192529	-0.67927292833178
N	-0.16163854502796	1.68105724210451	0.70916547172579
N	-0.67579480694096	0.06647984382581	2.04717593242769
C	-0.62659881710601	0.38111536598051	0.69642642740377
C	-0.03764000488507	2.53842091689509	-0.42706801138225
C	1.15489923530987	3.22930532554815	-0.63943987073588
C	-1.12708140705772	2.71134414010296	-1.28293591427616
C	-1.08460139581512	-1.19827784480558	2.55338716237737
C	0.09718224893333	2.12843744589225	2.00449266974559
H	0.43209462027692	3.13404326489221	2.19934478265264
C	-0.23104911084104	1.11791183410759	2.84209845872966
H	-0.23399028552393	1.06258543741272	3.91820758716216
C	-1.00646644749523	3.57168834669712	-2.37096819785415
H	-1.84792963570110	3.70170537415770	-3.04445820702052
C	1.26000193416072	4.10023544149410	-1.72421226157476
H	2.19019569699890	4.63380913033540	-1.89500253398516
P	0.26643988496295	0.09382833637897	-2.36728732546395
C	-2.15687847440662	-1.85825810143532	1.94961594010517
C	-0.39720880475259	-1.77791416959458	3.61981011546983
C	0.18361669857718	4.26875978524402	-2.59294236772269
O	-2.97585150969349	-2.54049424166142	-2.03248415791069
C	-2.12719242616323	-1.90739380183066	-1.55638456302612
C	-1.85254170468194	-3.70499015552066	3.48217637737674
C	-0.78969604852585	-3.03139698803022	4.08687381465721
H	-0.25039898999169	-3.48858565611266	4.91096662641720
C	-2.53248513900422	-3.11710316054776	2.41562452878114
H	-3.36160798807652	-3.63477128362963	1.94311375975469
H	0.45771568032141	-1.26939116424279	4.05528307780052
H	-2.14877665614307	-4.68571947828088	3.84212155531053
H	-2.69442689575411	-1.36970569692689	1.14289250914803
H	1.99511413552477	3.07076592247114	0.02963739450886
H	-2.03926996047271	2.15556119748103	-1.09771015630026
H	0.27119477599593	4.93746644564389	-3.44378826871968
C	3.05324607537079	0.02485815532498	-1.29395747940549
C	1.63587962498475	-0.49031209299985	-1.31049964423523
H	3.18639516834074	0.70091511395342	-0.44142587861201
H	3.29019835510427	0.58151188813144	-2.20622672231046
H	3.76856145704239	-0.79663431481545	-1.17824968388283
P	1.01070426444477	-1.98334085753137	-0.42322969672829
C	0.94195224516690	-1.59714158223485	-2.22141789160969
C	1.44877502730888	-2.47223521755713	-3.34151493510739
H	1.73667774373788	-1.87926377195764	-4.21515507942526
H	0.65505362489535	-3.16294279913679	-3.64742533888406
H	2.30524919631196	-3.07140741329756	-3.01535807704981

Transition State B → C (NHC = IXy, R = *t*Bu)



Ni	-0.76793286155443	-0.50394657735313	-0.15514592644276
N	-1.43343045381394	2.22420444627777	0.84331424151084
N	-1.79351791822182	0.66981105319711	2.29160424612797
C	-1.32755446062934	0.86521894162017	1.01500879579519
C	-1.00267051760977	2.93484332075050	-0.33150294731582
C	0.20192000739069	3.65179619327418	-0.25985900473775
C	-1.79434968772541	2.89307624368695	-1.48776509857134
C	-1.81754078580728	-0.61006305576825	2.95194418937408
C	-1.95088708620271	2.84585510276883	1.97886794846488
H	-2.11057030961344	3.91109265966017	2.01784301927245
C	-2.17872753100453	1.86760496427579	2.88815118413757
H	-2.57536590301990	1.90002604037696	3.88976657778856
C	-1.33421333651242	3.58981597521814	-2.60943147047402
H	-1.92576129841214	3.56681829790566	-3.52076868944406
C	0.61633401597338	4.34333229375940	-1.40139299022258
H	1.55341011031437	4.89282980788836	-1.37424369786399
P	1.12485715499091	0.52227290302115	-0.74329043461946
C	-3.03092356223498	-1.30107839395158	3.04175653141801
C	-0.61640659365602	-1.09586655235946	3.48847645838528
C	-0.14216648709922	4.30985784865179	-2.56816265493120
O	-3.33589639036039	-1.86709558270668	-0.61617181202512
C	-2.33584097207947	-1.28761262561974	-0.49166630278306
C	-1.83805001253206	-3.06559366963523	4.20492451559724
C	-0.64995054217845	-2.34142265399831	4.11807364508986
H	0.26848093148776	-2.74789498625395	4.53299336635657
C	-3.01684473270802	-2.54825349697026	3.67633997687437
H	-3.94089070493639	-3.11628661289450	3.74406501163380
C	0.66095133030464	-0.31027975702361	3.36382094117547
H	-1.84368022248497	-4.03881254792249	4.68758336292196
C	-4.30928348022950	-0.72621566653789	2.48641795251737
C	1.04038948276098	3.64474005962553	0.99248758898955
C	-3.08184416443074	2.11739187385567	-1.52753653477017
H	0.19804471323172	4.84439206662248	-3.45052329240944
C	3.43760880438202	-1.35417001665641	-0.44347860490623
C	1.93827949650943	-1.07053960559342	-0.37434810712652
C	3.90795747029205	-1.32167438837708	1.02888172187973
C	4.20750163798766	-0.27208212225027	-1.21844807500599
C	3.72845198033282	-2.75290195715810	-1.01391449148338
P	0.64379984520488	-2.23189135292084	0.17406025771590
C	0.74436566496715	-1.11178590659227	-1.45087829715958
C	0.58677792786309	-1.51012528400296	-2.92207580372735
C	-0.64576106472251	-0.77791422618179	-3.48620287793226
C	0.38408215328769	-3.02833422124557	-3.05047986837378
C	1.80687897449026	-1.06976333817224	-3.75213185429275
H	3.51677220313360	-2.80349401750654	-2.08524962952461
H	3.11111929899082	-3.50426606510153	-0.51071607247731
H	4.78488595059127	-3.00333721419862	-0.86382124849266
H	4.99000536605031	-1.48748132418876	1.08492425738977
H	3.40290819045441	-2.10174222804755	1.60801442885103
H	3.68066089843303	-0.35228447518375	1.48593656474863
H	3.91741368383849	-0.23843634242353	-2.27094569425671
H	5.28402199563559	-0.47232498343897	-1.16603337090481
H	4.02348005401900	0.71724384425064	-0.78504742633418
H	0.25352232266675	-3.29890296940458	-4.10522021734432
H	-0.50406115060818	-3.34414948810568	-2.49503131890285
H	1.24155694063647	-3.57504116440041	-2.64864662366912

H	-0.75816062315515	-1.00741301935636	-4.55260814190556
H	-0.53511204985454	0.30590257119742	-3.36887846088581
H	-1.55410656874621	-1.08397382512513	-2.96131301197250
H	1.62788083575705	-1.28544435390141	-4.81152271488225
H	2.71316052390792	-1.59876600982913	-3.45002021230609
H	1.97612693678643	0.00651185500654	-3.64050860423853
H	-3.63368994303850	2.33611945157296	-2.44499477293845
H	-3.71891760310567	2.35561780911347	-0.66882673679859
H	-2.87140959178422	1.04190551076858	-1.48546518501586
H	2.02776857025916	4.06643828753894	0.79012516076476
H	1.16874564188788	2.62424104906062	1.37019679865441
H	0.57771835471837	4.23027416643386	1.79581420071010
H	-5.03288730343378	-1.52190624020496	2.29385712446004
H	-4.13591844556200	-0.18533082476064	1.55339559158705
H	-4.76368582104575	-0.02225399913225	3.19547650632974
H	0.94589335407930	-0.23802224747274	2.30709037028863
H	1.46901137977223	-0.80157808325446	3.91138792758200
H	0.54526597672428	0.70851883580337	3.75166781507606

8 References

(1) *Synthetic Methods of Organometallic and Inorganic Chemistry;* W. Rösch, T. Allspach, U. Bergsträßer, M. Regitz, W. A. Herrmann, Ed., Vol.3; Thieme: Stuttgart, 1996.

(2) G. Becker, G. Gresser, W.Uhl. Acyl- and Alkylidenephosphines, XV 2,2-Dimethylpropvlidynephosphine, a Stable Compound with a Phosphorus Atom of Coordination Number 1. *Z. Naturforsch. B* **1981**, *36*, 16–19.

(3) T. Allspach, M. Regitz, G. Becker, W. Becker. Unusually Coordinated Phosphorus Compounds; 7[1]. Adamant-1-ylmethylidynephosphine, A New, Stable Phosphaalkyne. *Synthesis* **1986**, 31–36.

(4) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. Steric and electronic properties of N-heterocyclic carbenes (NHC): A detailed study on their interaction with Ni(CO)4. *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.

(5) Berthel, J. H. J.; Kuntze-Fechner, M. W.; Radius, U. $[Ni_3(iPr_2Im)_3(\mu^2\text{-}CO)_3(\mu^3\text{-}CO)]$ - A CO-Stabilized NHC Analogue of the Parent Neutral Nickel Chini-Type Cluster. *Eur. J. Inorg. Chem.* **2019**, *2019*, 2618–2623.

(6) Hierlmeier, G.; Hinz, A.; Wolf, R.; Goicoechea, J. M. Synthesis and Reactivity of Nickel-Stabilised $\mu^2{:}\eta^2,\eta^2\text{-}P_2$, As_2 and PAs Units. *Angew. Chem. Int. Ed.* **2018**, *57*, 431–436.

(7) Elsby, M. R.; Liu, J.; Zhu, S.; Hu, L.; Huang, G.; Johnson, S. A. Influence of N - Heterocyclic Carbene Steric Bulk on Selectivity in Nickel Catalyzed C–H Bond Silylation, Germylation, and Stannylation. *Organometallics* **2018,** DOI: 10.1021/acs.organomet.8b00786.

(8) Krossing, I. $Ag(P_4)^{2+}$: The First Homoleptic Metal−Phosphorus Cation. *J. Am. Chem. Soc.* **2001**, *123*, 4603–4604.

(9) Geissler, B.; Barth, S.; Bergsträsser, U.; Slany, M.; Durkin, J.; Hitchcock, P. B.; Hofmann, M.; Binger, P.; Nixon, J. F.; Ragué Schleyer, P. von *et al.* Tetraphosphatricyclo[4.2.0.$0^{2,5}$]octadienes; New Phosphaalkyne Cyclotetramers Derived from $\lambda^3\sigma^2$-Diphosphetes. *Angew. Chem. Int. Ed.* **1995**, *34*, 484–487.

(10) Burés, J. A Simple Graphical Method to Determine the Order in Catalyst. *Angew. Chem. Int. Ed.* **2016**, *55*, 2028–2031.

(11) Nielsen, C. D.-T.; Burés, J. Visual kinetic analysis. *Chem. Sci.* **2019**, *10*, 348–353.

(12) Sheldrick, G. M. SADABS, Bruker AXS, Madison, USA, **2007**.

(13) CrysAlisPro, Scale3 Abspack, Rigaku Oxford Diffraction, **2019**.

(14) Clark, R. C.; Reid, J. S. The analytical calculation of absorption in multifaceted crystals. *Acta Crystallogr. A* **1995**, *51*, 887–897.

(15) Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015**, *71*, 3–8.

(16) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J Appl Crystallogr* **2009**, *42*, 339–341.

(17) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122.

(18) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta crystallographica. Section C, Structural chemistry* **2015**, *71*, 3–8.

(19) Neese, F. The ORCA program system. *WIREs Comput Mol Sci* **2012**, *2*, 73–78.

(20) Neese, F. Software update: The ORCA program system, version 4.0. *WIREs Comput Mol Sci* **2018**, *8*, e1327.

(21) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(22) S. Grimme, S. Ehrlich, L. Goerigk. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

(23) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(24) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(25) Whitten, J. L. Coulombic potential energy integrals and approximations. *J. Chem. Phys.* **1973**, *58*, 4496–4501.

(26) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange. *Chem. Phys.* **2009**, *356*, 98–109.

(27) Liakos, D. G.; Sparta, M.; Kesharwani, M. K.; Martin, J. M. L.; Neese, F. Exploring the Accuracy Limits of Local Pair Natural Orbital Coupled-Cluster Theory. *J. Chem. Theory Comput.* **2015**, *11*, 1525–1539.

(28) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* **2013**, *139*, 134101.

(29) Ivanov, A. S.; Bozhenko, K. V.; Boldyrev, A. I. Peculiar Transformations in the $C_xH_xP_{4-x}$ (x = 0-4) Series. *J. Chem. Theory Comput.* **2012**, *8*, 135–140.