Supporting Information

Phosphorus-Containing Tetrahedranes: Synthesis and Reactivity Studies

Dissertation

Zur Erlangung des Doktorgrades der Naturwissenschaften
Dr. rer. nat.
an der Fakultät Chemie und Pharmazie der Universität Regensburg

vorgelegt von:
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aus Kelheim

Regensburg, April 2021

Chapter 3

Aggregation and Degradation of White Phosphorus Mediated by N Heterocyclic Carbene Nickel(0) Complexes

S1 NMR Spectra

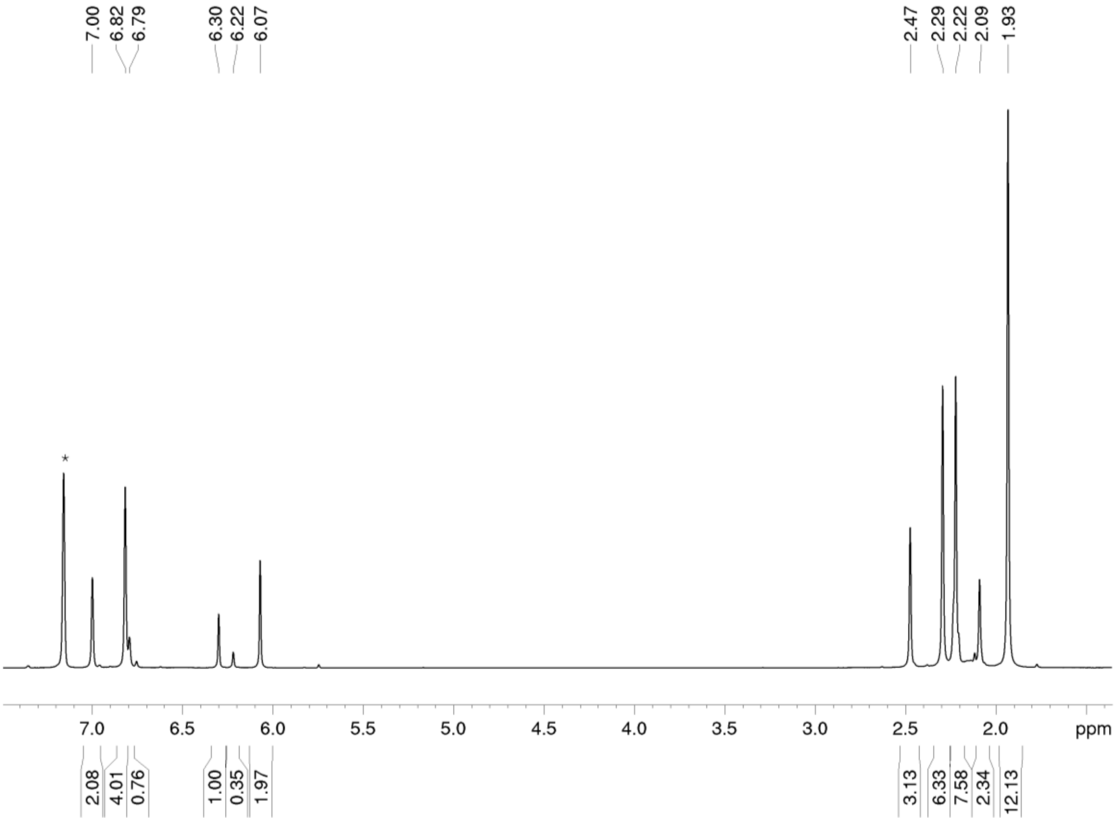


Figure S1. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **1**; *C_6D_6.

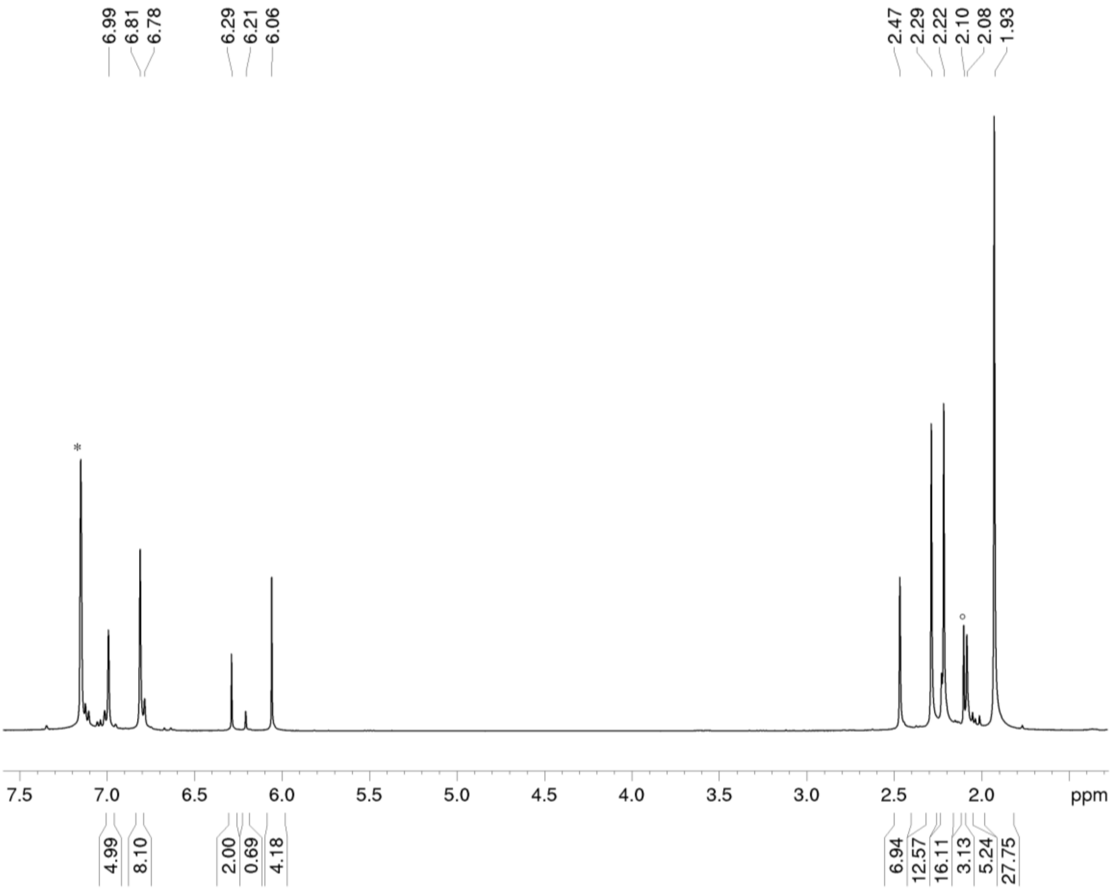


Figure S2. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **1**·toluene; *C_6D_6; °toluene-CH_3.

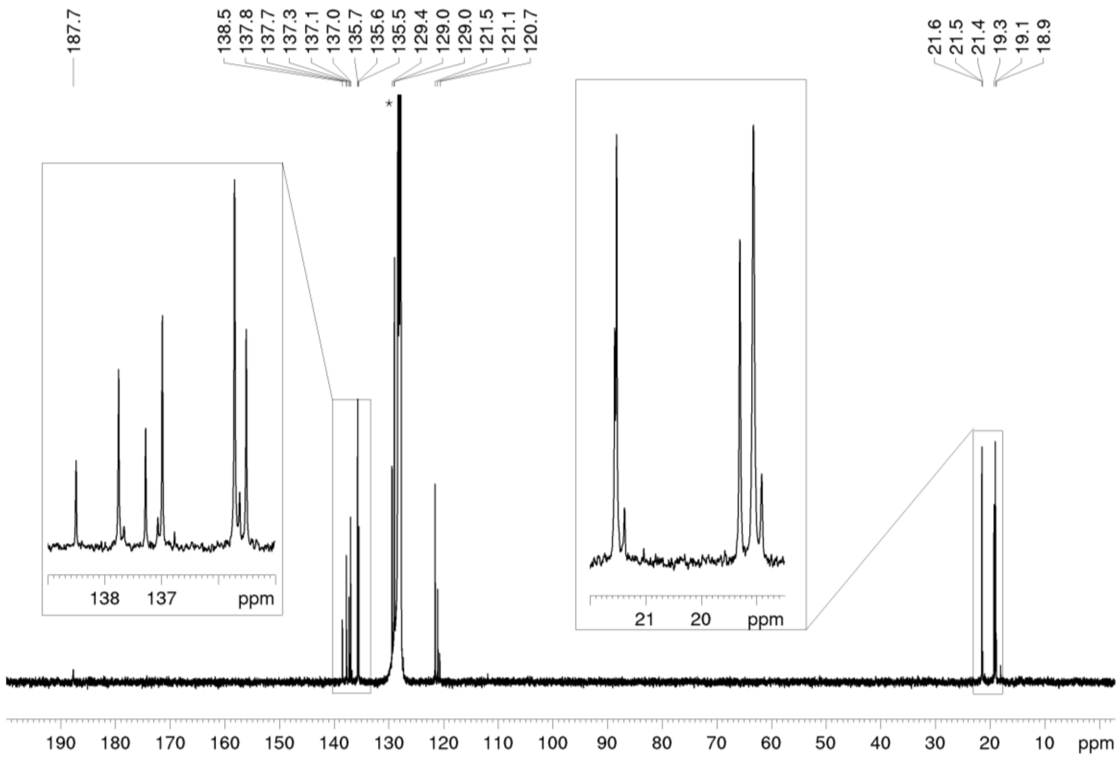


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **1**; $^{*}C_6D_6$.

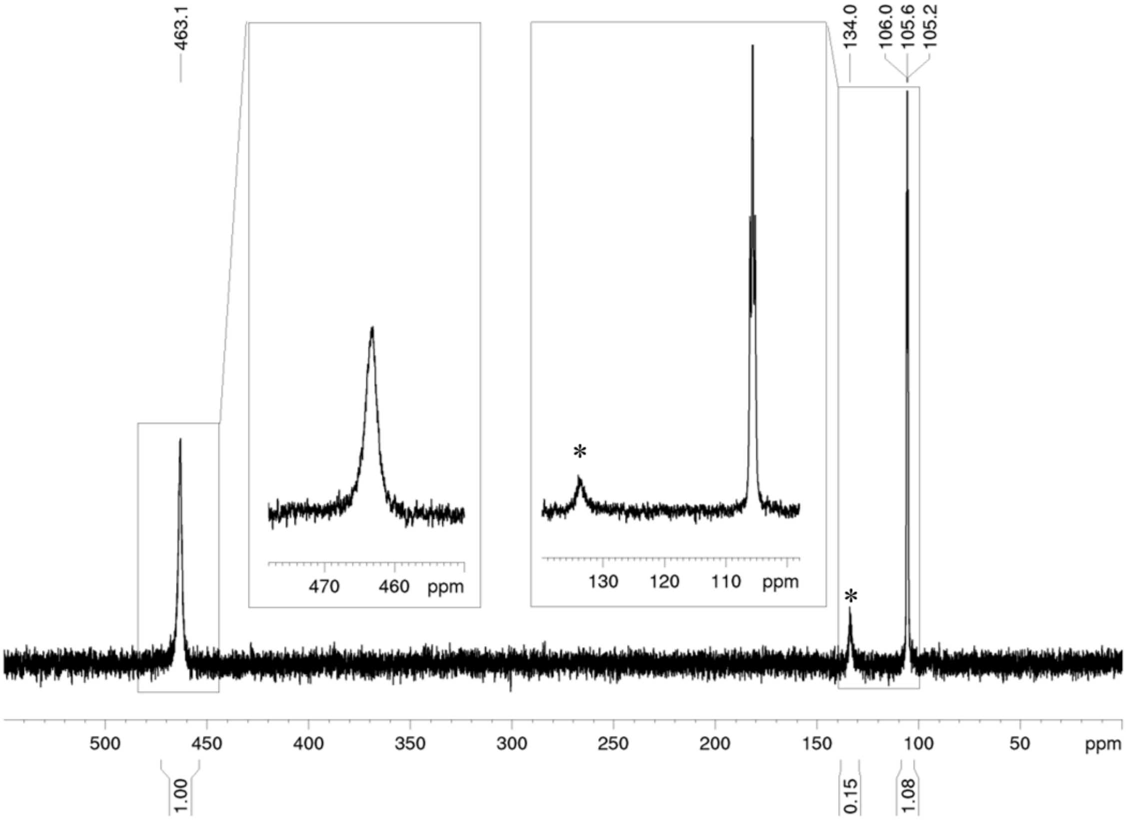


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **1**; *isomer in solution.

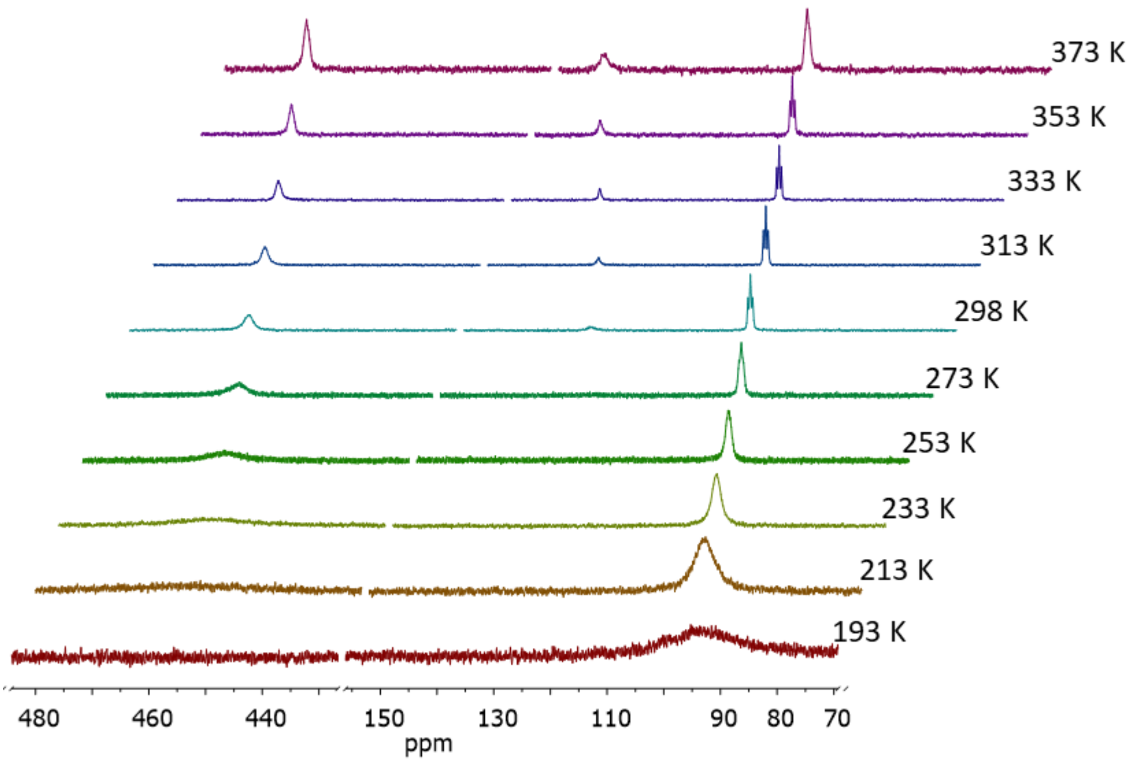


Figure S5. Variable temperature $^{31}P\{^{1}H\}$ NMR (162 MHz, 193-373 K, toluene-d^{8}) of **1**.

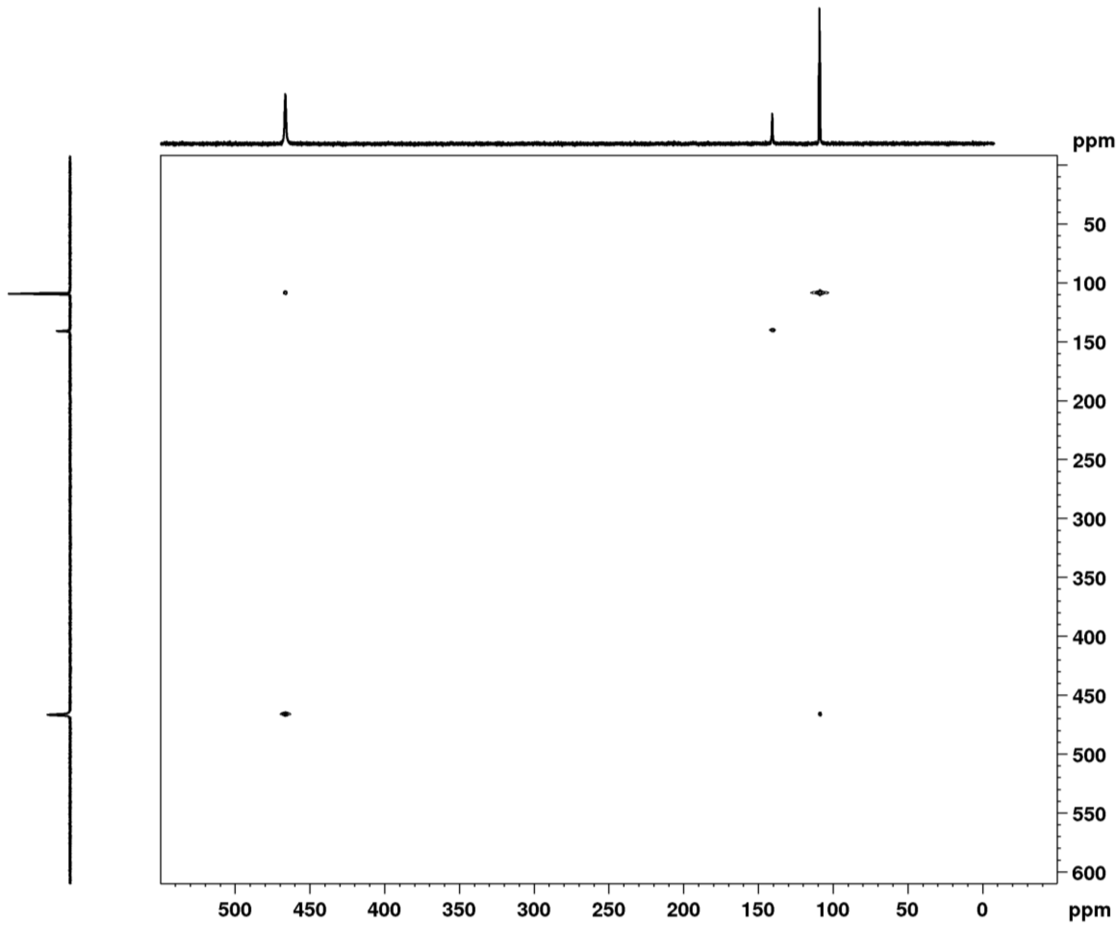


Figure S6. $^{31}P\{^{1}H\}$-$^{31}P\{^{1}H\}$ COSY NMR (162 MHz, 333 K, toluene-d^{8}) of **1**.

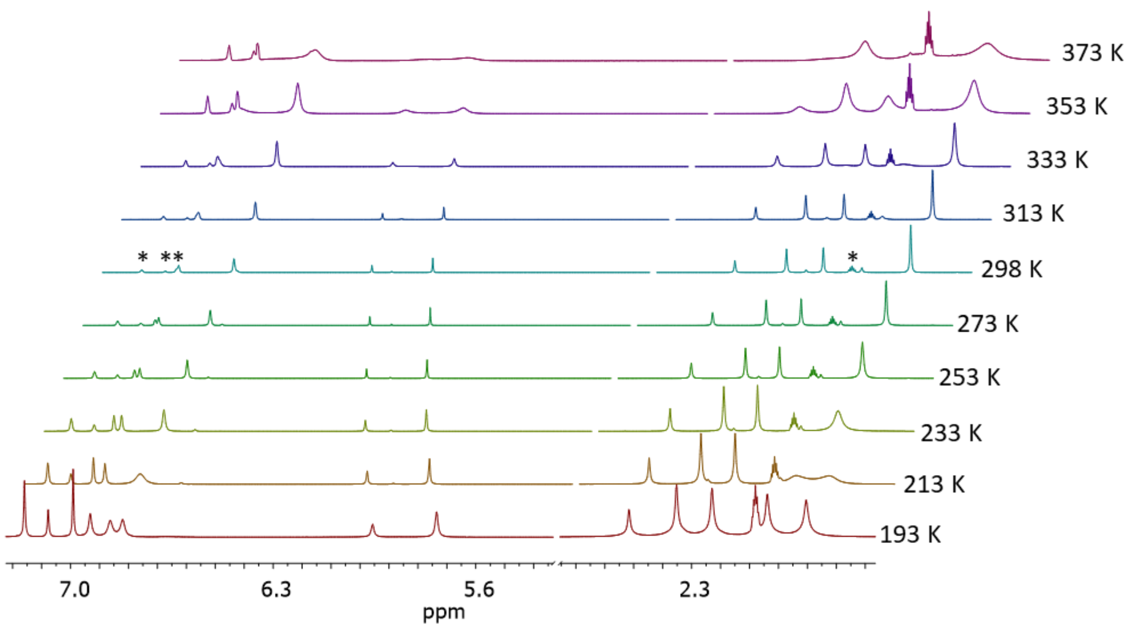


Figure S7. Variable temperature ^{1}H NMR (400 MHz, 193-373 K, toluene-d^{8}) of **1**, *toluene-d^{8}.

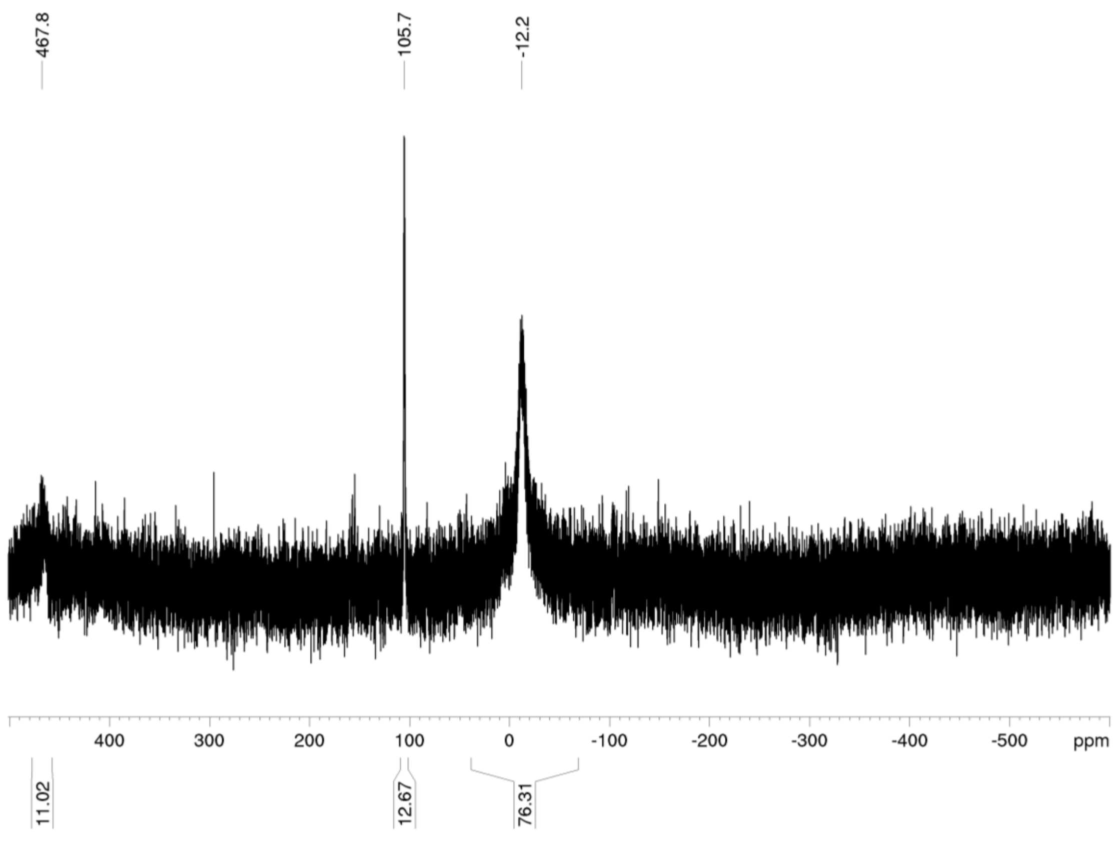


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(IMes)$_2$Ni] + 0.5 eq. P_4 (in THF).

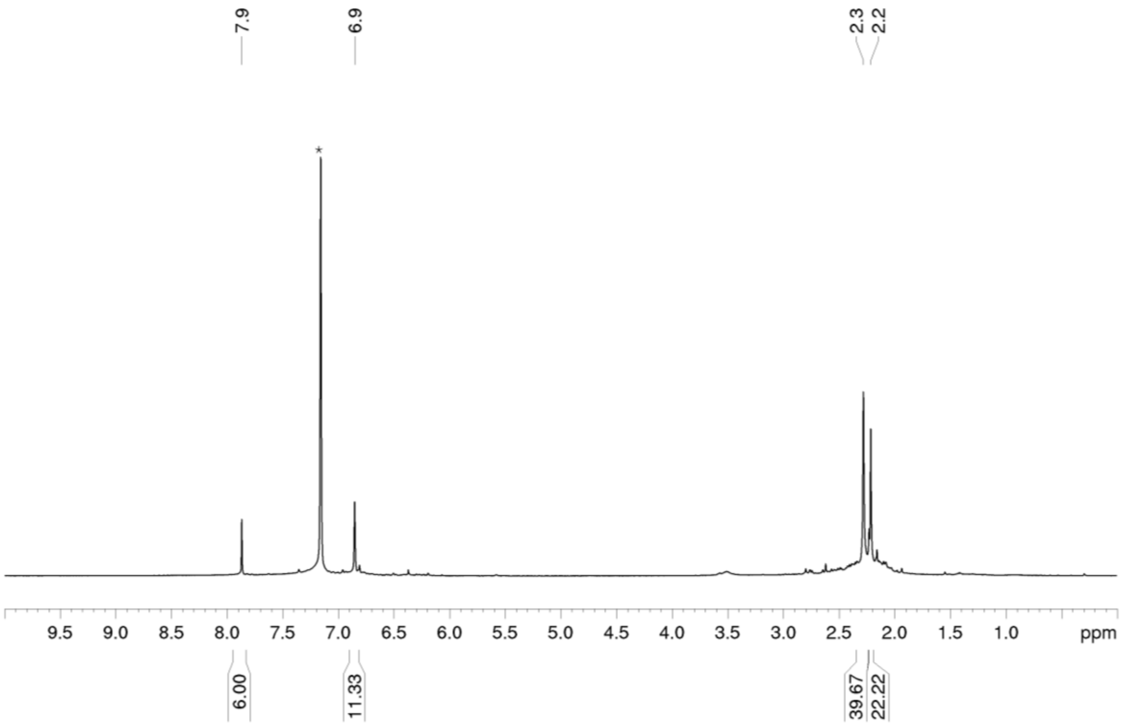


Figure S9. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **2**, *C_6D_6.

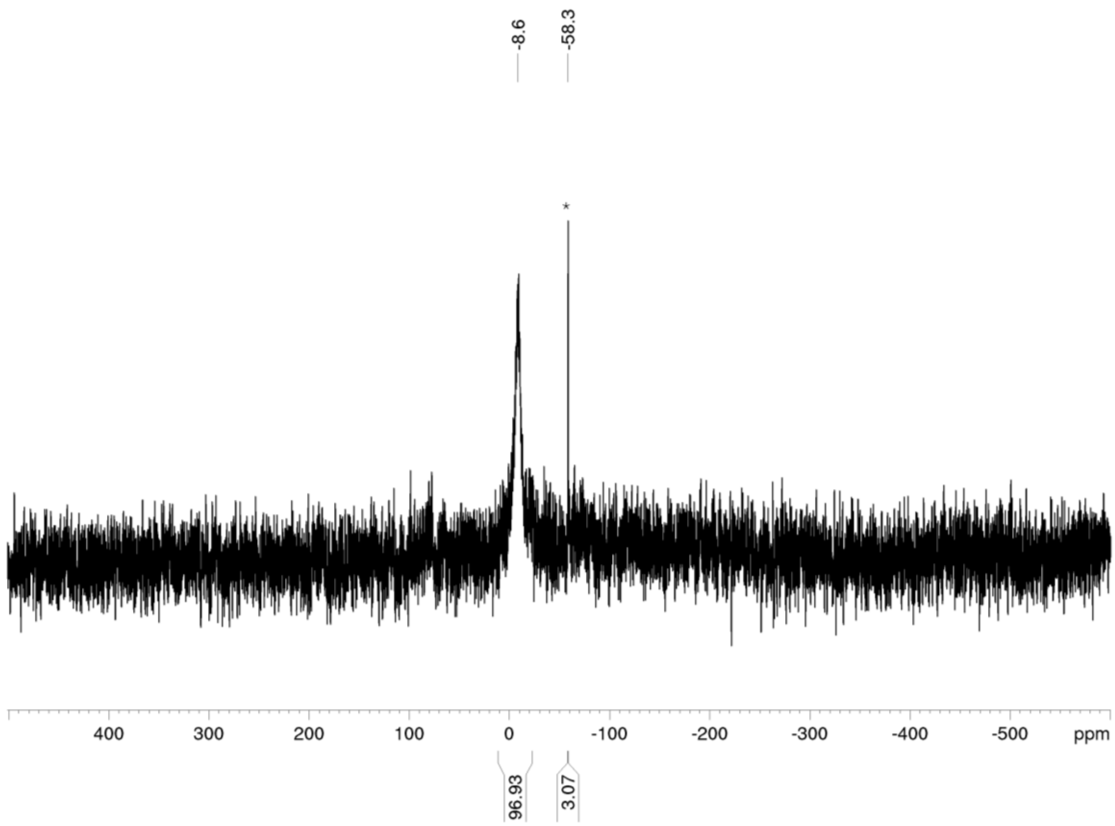


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **2**, * unknown impurity.

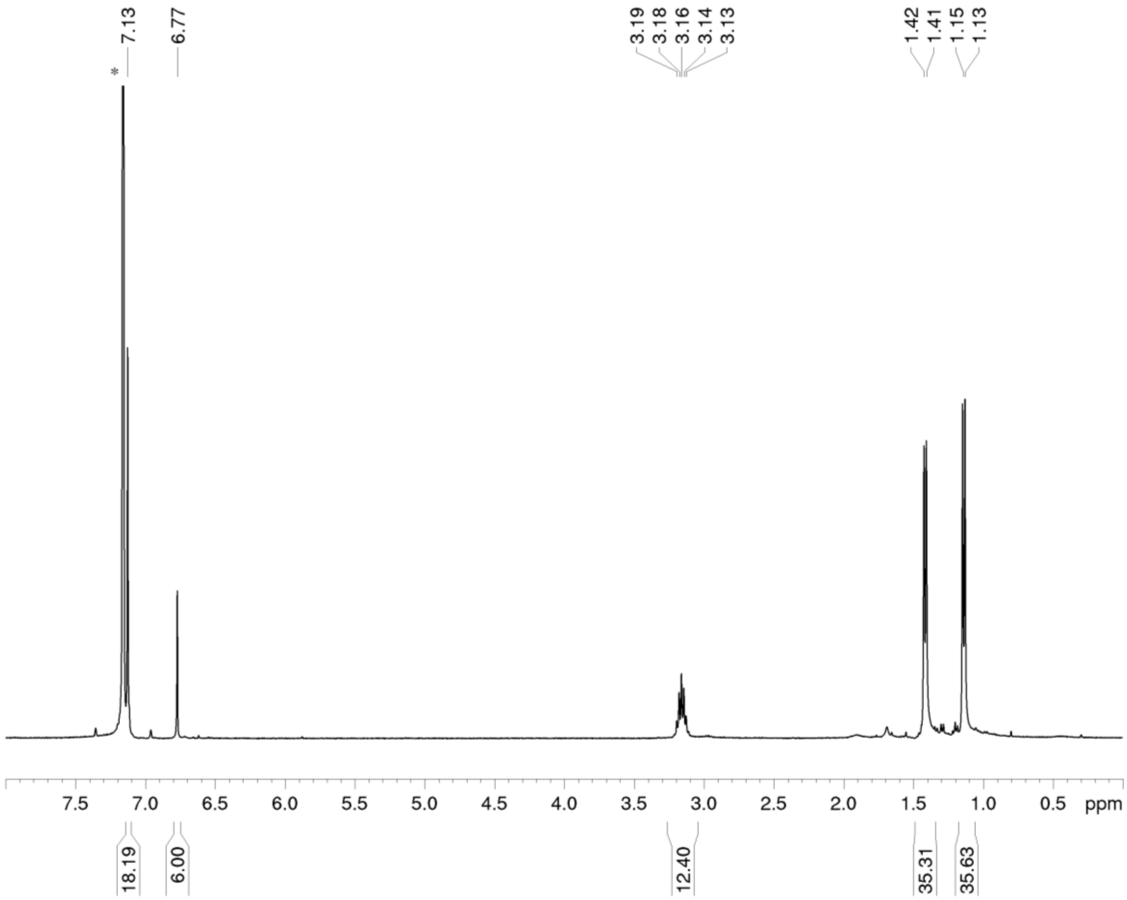


Figure S11. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **4**, *C_6D_6.

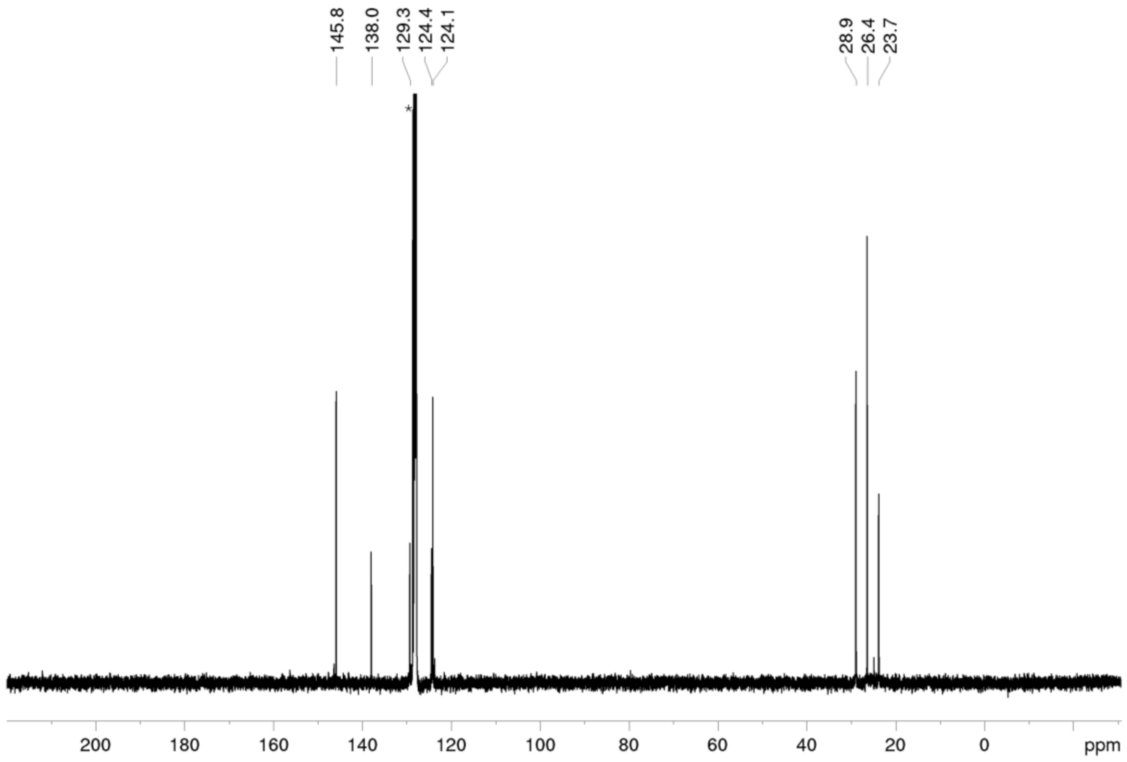


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **4**; *C_6D_6.

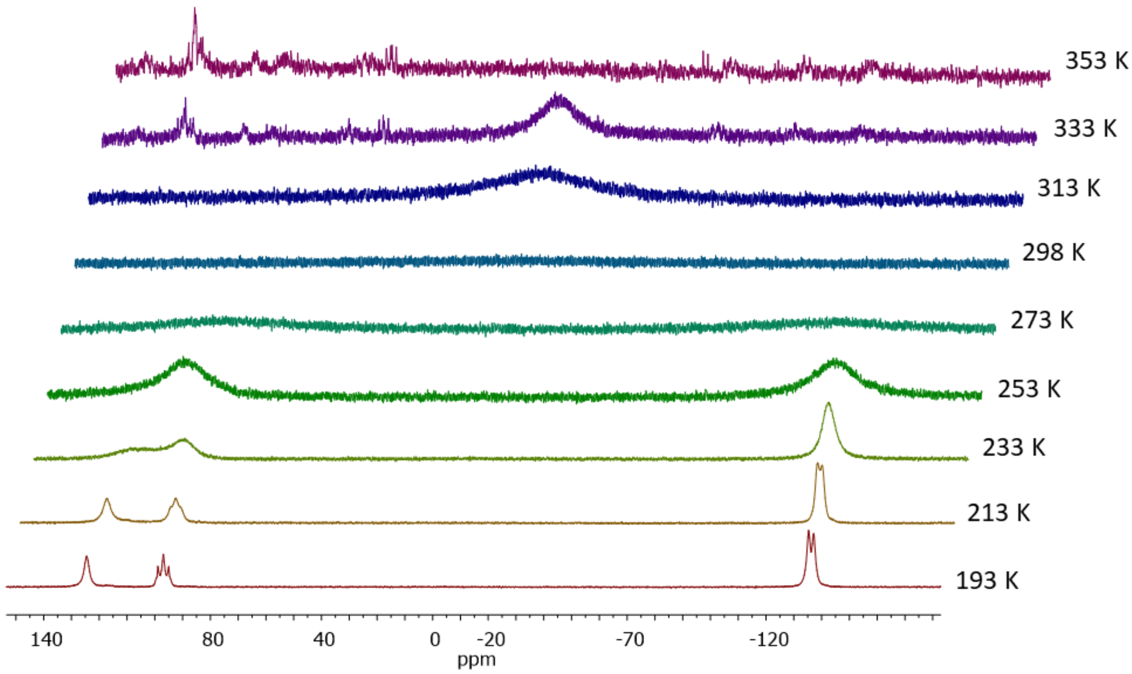


Figure S13. Variable temperature $^{31}P\{^1H\}$ NMR (162 MHz, 193-353 K, toluene-d^8) of **4**. Thermal decomposition of **4** starts at 333 K.

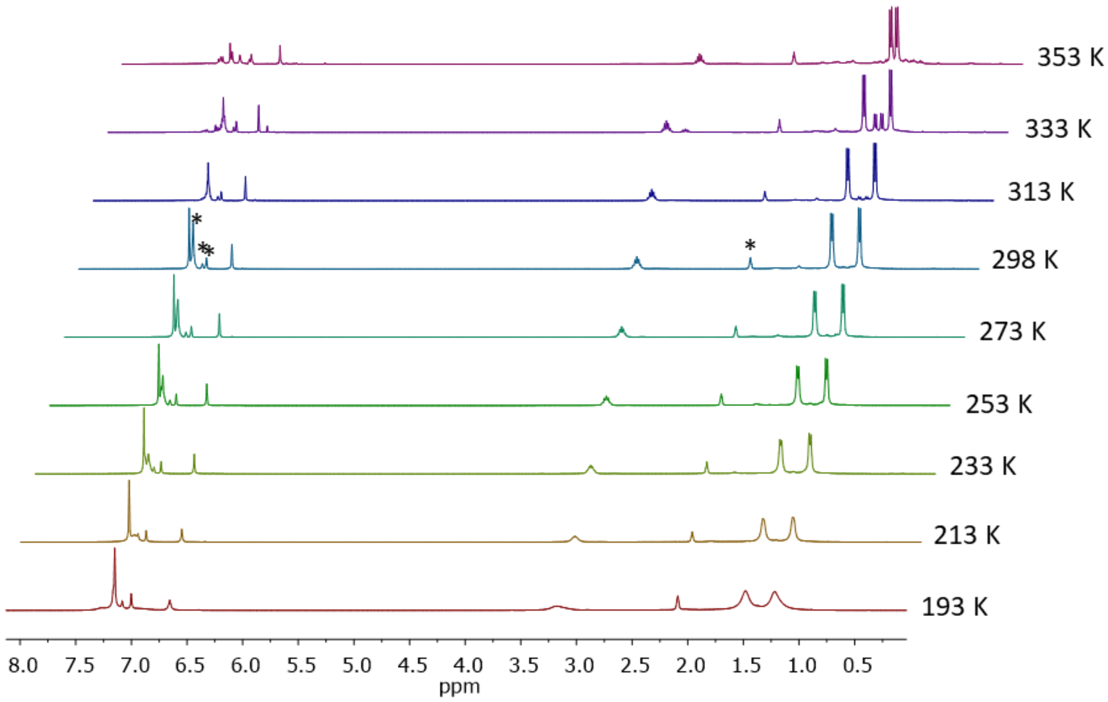


Figure S14. Variable temperature ^1H NMR (400 MHz, 193-353 K, toluene-d^8) of **4**. Note that thermal decomposition of **4** starts at 333 K

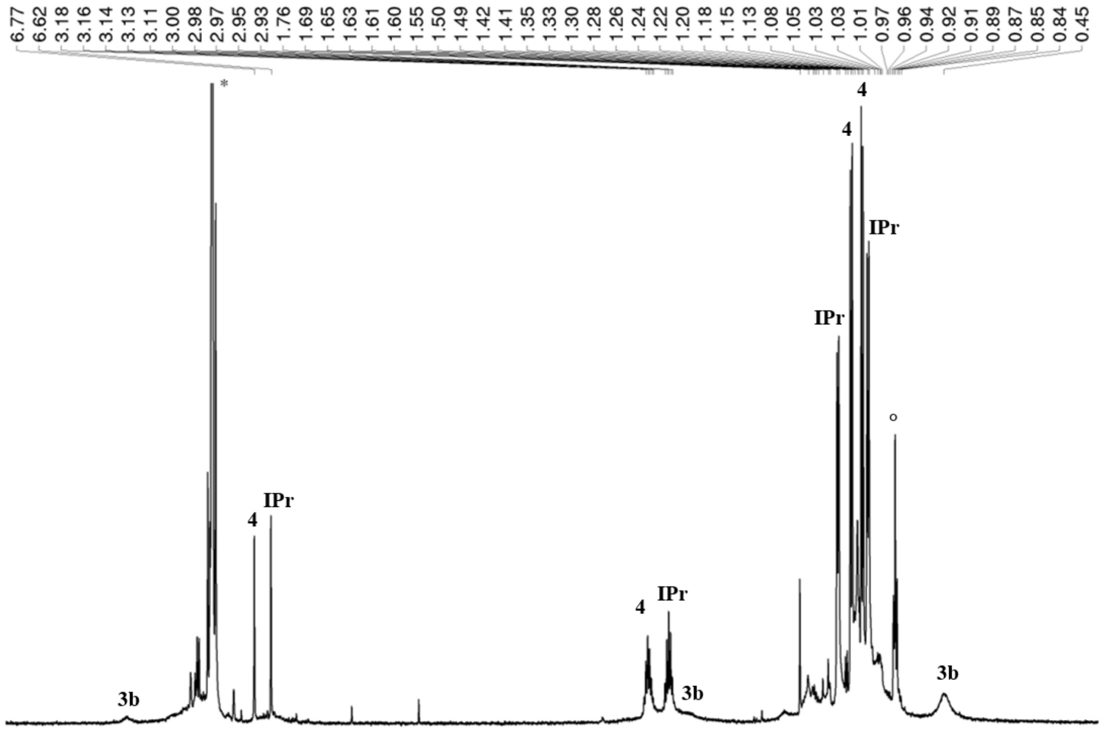


Figure S15. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of a mixture of free IPr, **4** and **3b** *C_6D_6, °*n*-hexane.

S2 UV/Vis Spectra

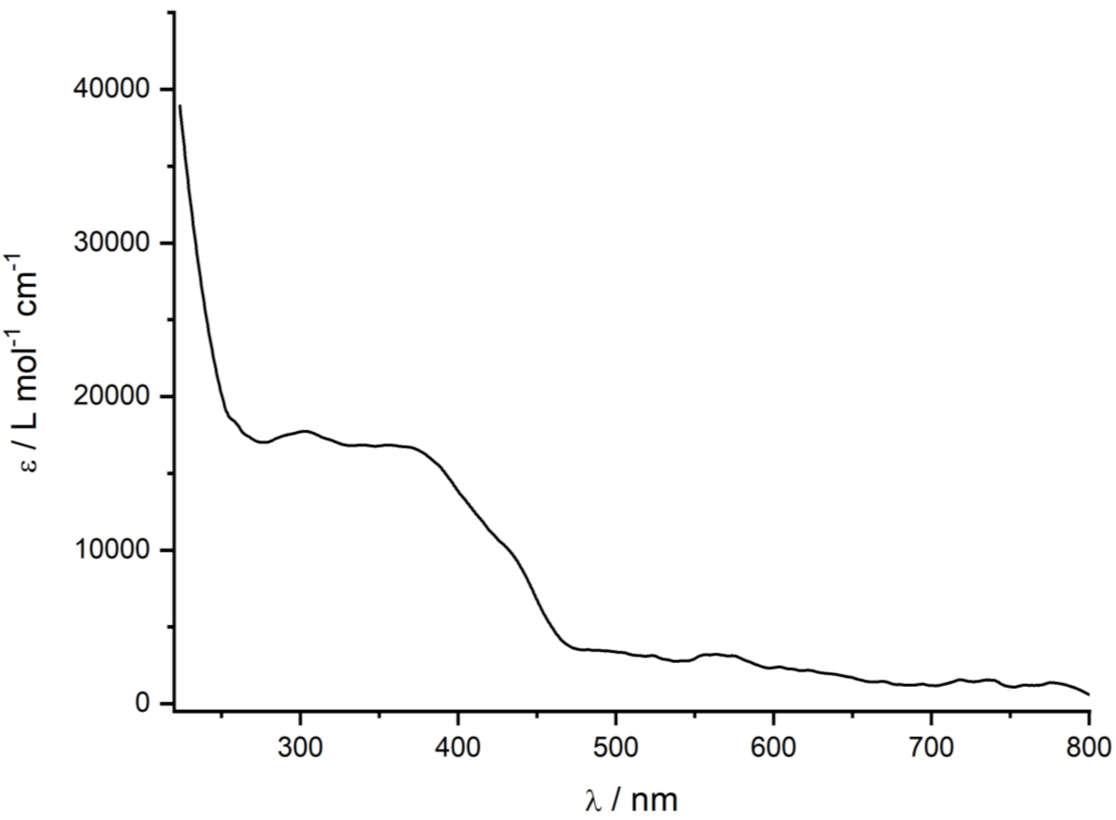


Figure S16. UV/Vis spectrum of **1** recorded in THF.

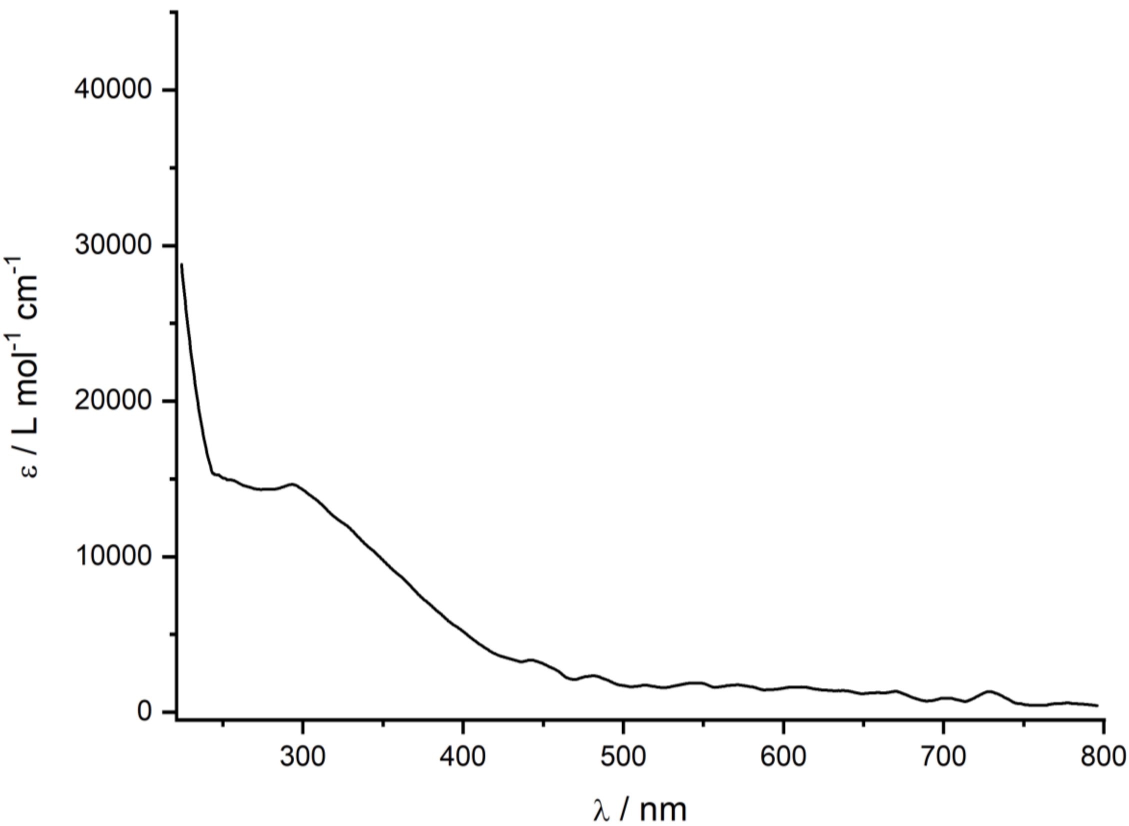


Figure S17. UV/Vis spectrum of **4** recorded in THF.

S3 Cyclic Voltammetry

Cyclic voltammetry experiments were performed in a single-compartment cell inside a nitrogen-filled glovebox using a CH Instruments CHI600E potentiostat. The cell was equipped with a platinum disc working electrode (2 mm diameter) polished with 0.05 µm alumina paste, a platinum wire counter electrode and a silver/silver nitrate reference electrode. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate, was dried in vacuo at 110 °C for three days. All redox potentials are reported versus the ferrocene/ferrocenium (Fc/Fc^{+}) couple. The scan rate is v = 100 $mV \cdot s^{-1}$ unless stated otherwise.

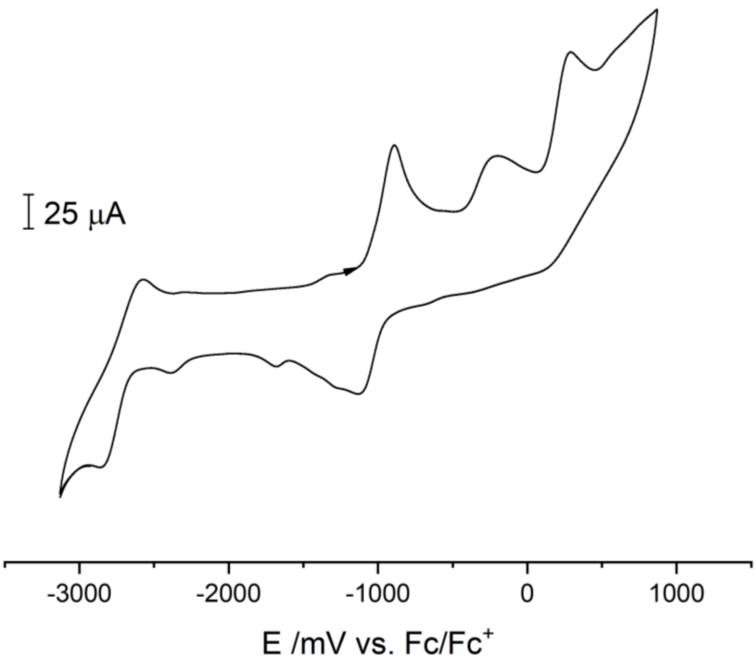


Figure S18. Cyclic voltammogram of **1** recorded in THF/TBAH.

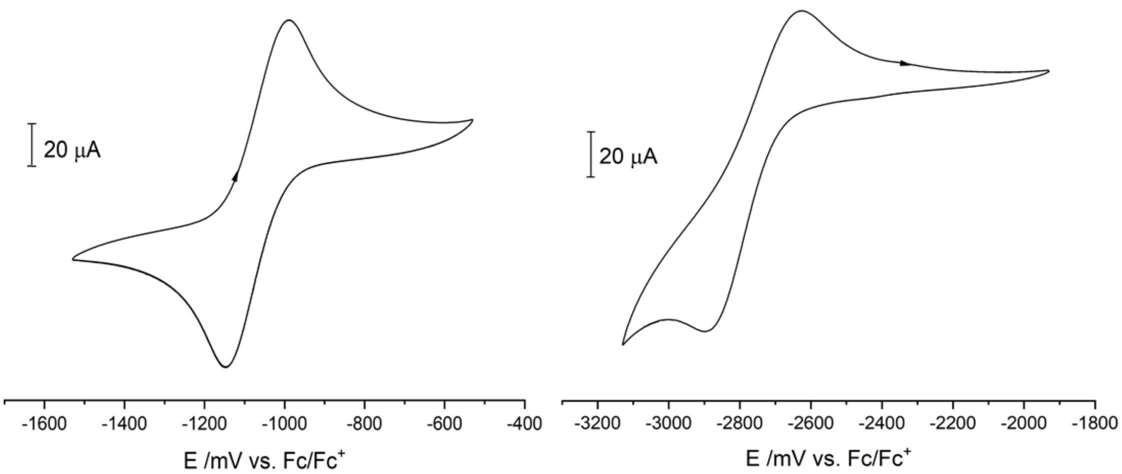


Figure S19. Cyclic voltammograms of **1** recorded in THF/TBAH at two different E ranges.

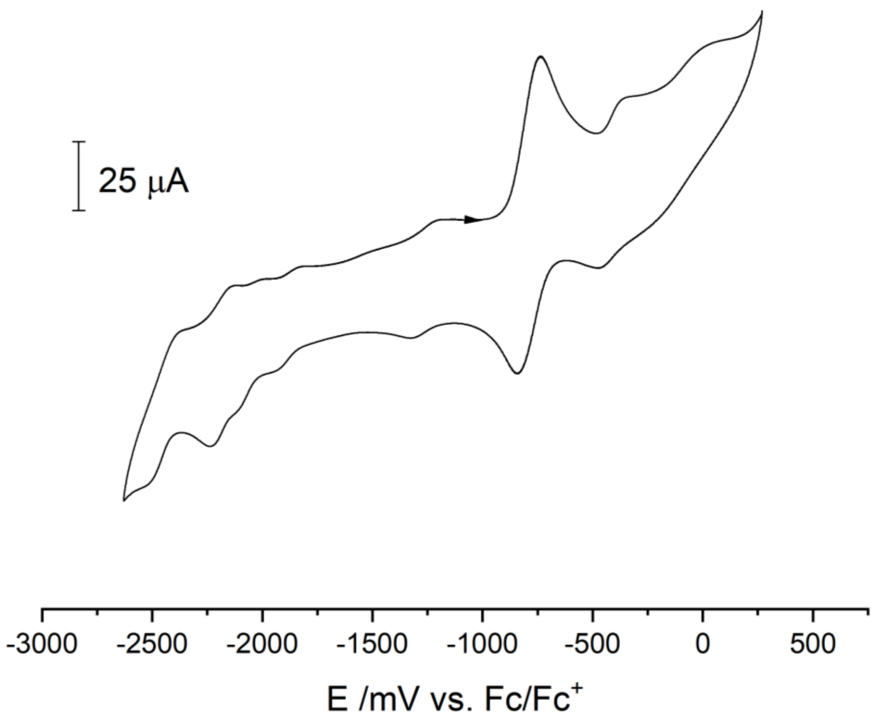


Figure S20. Cyclic voltammogram of **4** recorded in THF/TBAH.

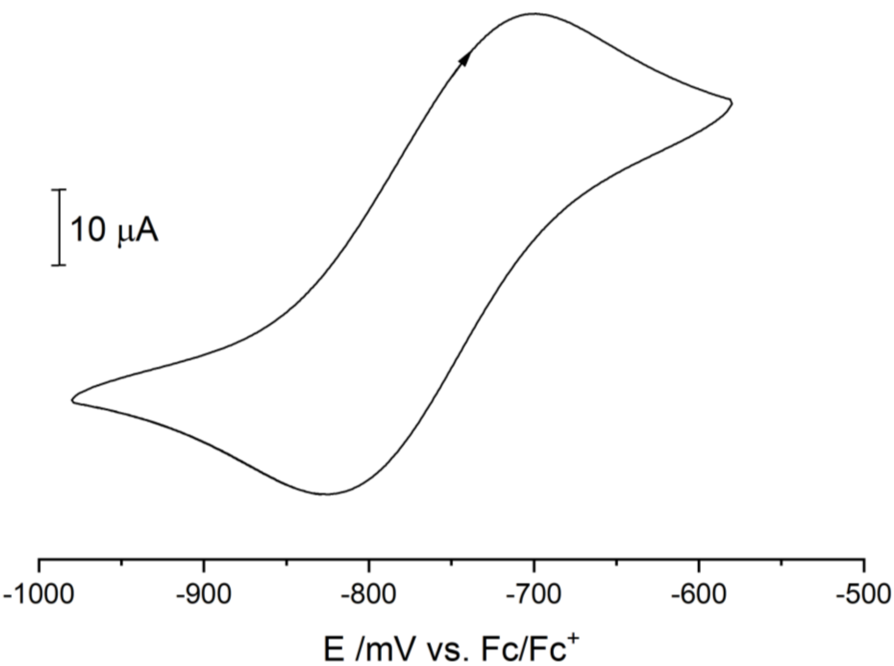


Figure S21. Cyclic voltammogram of **4** recorded in THF/TBAH at a different E range.

S4 EPR Spectroscopy

General method

Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten) equipped with a Helium temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed by iteration of the anisotropic g-values, hyperfine coupling interactions and line widths using the EPR simulation program W95EPR developed by Prof. Dr. Frank Neese.

Experimental and simulated EPR spectra

[$(IMes)_2Ni_2P_5$] (3a)

A crystalline sample containing **2** and **3a** was used for the measurement. This sample was contaminated with another S = ½ system giving rise to the broad resonances. Nevertheless, an axial spectrum displaying hyperfine interaction with a P_5^- ring was observed. Based on the g-values, this spectrum arises from a nickel-centered radical. The sample was measured in toluene glass at 20K using a microwave frequency of 9.650672 GHz, a power of 0.6325 mW and a modulation amplitude 4.000 G. The simulation parameters were: $g_{11} = g_{22} = 2.1535$, $g_{33} = 1.990$, W_{11} = 15 MHz, W_{22} = 12 MHz, W_{33} = 4.5 MHz, $A^{31P}{}_{33}$ = 30.0 MHz.

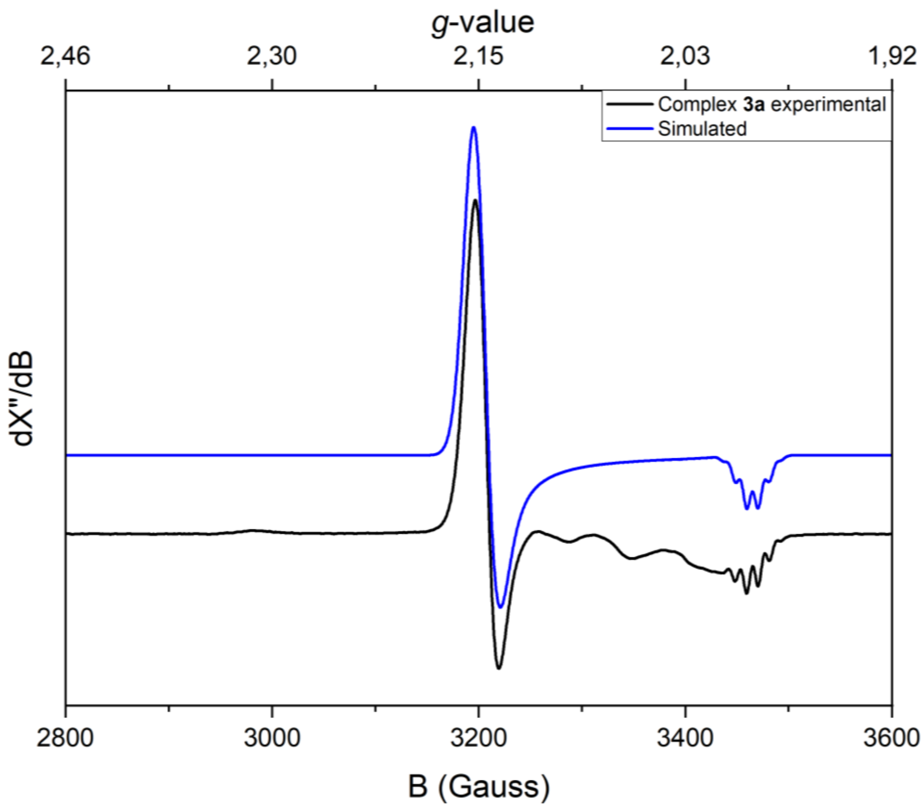


Figure S22. Experimental and simulated X-band EPR spectrum of **3a** contaminated by another paramagnetic species in frozen toluene.

[(IPr)$_2$Ni$_2$P$_5$] (3b) (see Doctoral Thesis)

The spectrum was measured in toluene glass at 20K using a microwave frequency of 9.650846 GHz, a power of 0.6325 mW and a modulation amplitude of 4.000 G. The simulation parameters were: $g_{11} = g_{22} = 2.186$, $g_{33} = 1.987$, $W_{11} = 15$ MHz, $W_{22} = 13$ MHz, $W_{33} = 4.5$ MHz, $A^{31P}{}_{33} = 30.0$ MHz.

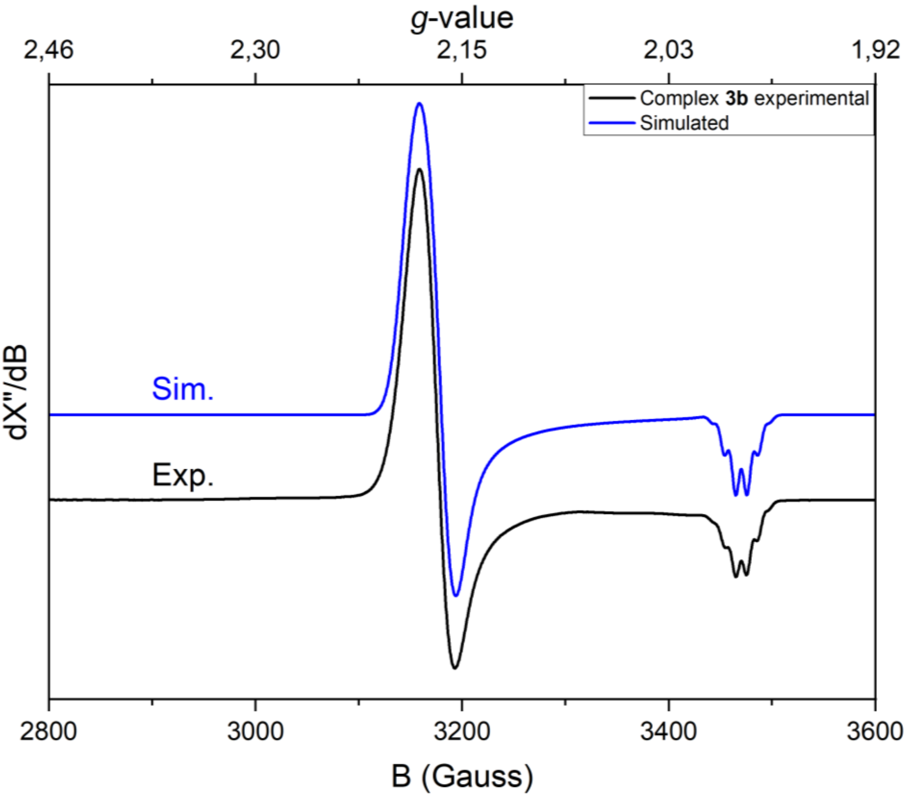


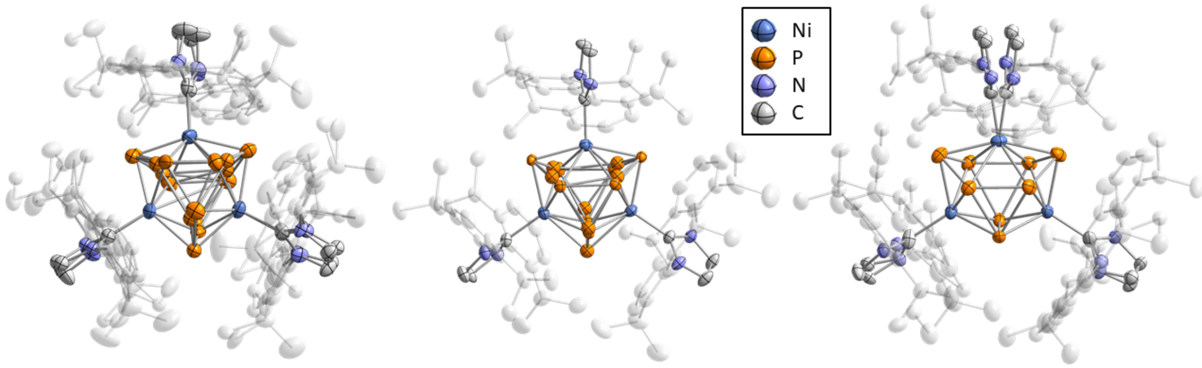
Figure S23. Experimental and simulated X-band EPR spectrum of **3b** in frozen toluene.

S5 Single Crystal X-ray Diffraction Data

Additional Refinement Details

The crystal of **2** contained several disordered molecules of *n*-hexane which were refined by using the solvent mask command. A solvent mask was calculated and 408.0 electrons were found in a volume of 3086.0 Å^3 in a single void. This is consistent with the presence of one *n*-hexane per formula unit which accounts for 400.0 electrons.

The molecular structure of **4** was determined by single crystal X-ray crystallography several times using different solvents for the crystallisations. In each case, a saturated solution of **4** was cooled from ambient temperature to −30 °C. The structure obtained from a crystal grown from *n*-hexane features disorder in the P_8 framework and the IPr ligand. Several samples grown by this method were investigated. All of the data sets feature the same disorder pattern. The structure obtained from a crystal grown from *n*-heptane features disorder in the P_8 framework and is therefore less suitable for interpretation of bond metric data. The structure obtained from a crystal grown from toluene features disorder in the IPr ligand. Bond lengths and angles reported in the manuscript are from this data set. Moreover, the crystal structure of **4** from a crystal grown from Et_2O as solvent was determined and disorder over the P_8 framework was indicated by residual electron density in the cluster core (not included in Figure S24).



crystal obtained from *n*-hexane R_1 = 9.05%

crystal obtained from *n*-heptane R_1 = 5.12%

crystal obtained from toluene R_1 = 6.77%

Figure S24. Molecular structures of **4** in the solid state depending on the solvent of crystallisation. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvents molecules are omitted for clarity. Depending on the solvent of crystallisation, disorder in the P_8 framework (middle), the IPr ligand (right) or both (left) were observed.

Additional Figures (not depicted in the Doctoral Thesis)

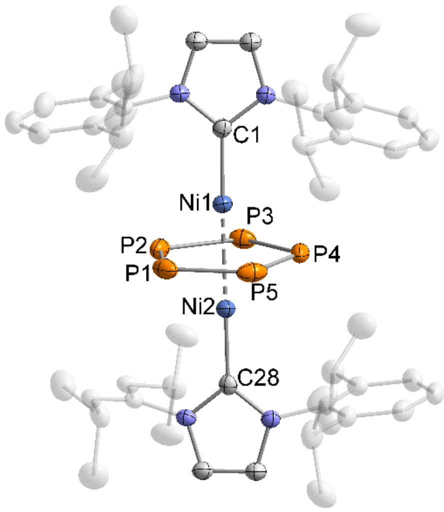


Figure S25. Molecular structure of **3b** in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **3b**: Ni1−Ni2 2.6813(6), P1−P2 2.1978(11), P2−P3 2.2155(10), P3−P4 2.2160(10), P4−P5 2.2053(11), P5−P1 2.2250(11), P2−P1−P5 107.94(4), P1−P2−P3 107.73(4), P2−P3−P4 108.68(4), P5−P4−P3 107.17(4), P4−P5−P1 108.46(4).

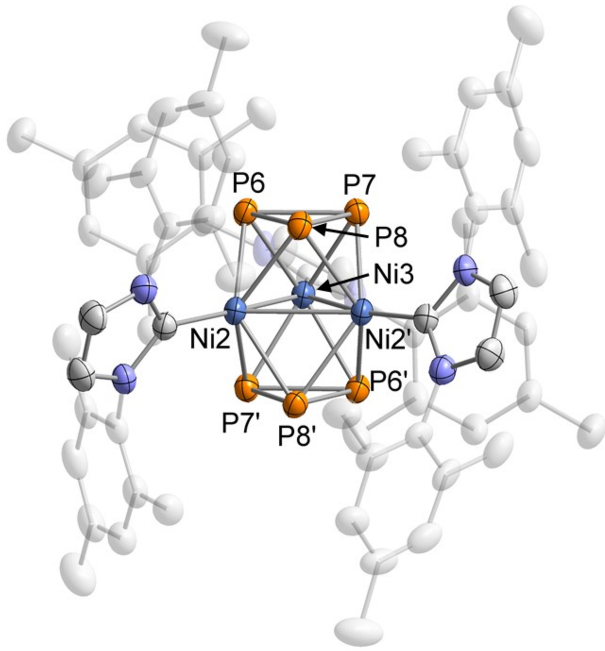


Figure S26. Molecular structure of **2** as part of **2·3a** in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and the molecule of **3a** are omitted for clarity. Selected bond lengths [Å] and angles [°] for **2** (values obtained from the crystal structure of **2** in brackets: Ni2−Ni3 2.4978(10) [2.4834(3), 2.4883(3)], Ni2−Ni2′ 2.6167(12) [2.6432(3)], P7−P8 2.1938(13) [P1−P2 2.2087(5), 2.2049(5)], P7−P6 2.2901(12) [P2−P3 2.2698(5), 2.2822(5)], P6−P8 2.1984(14) [P1−P3 2.2156(5), 2.2116(5)], Ni3−Ni2−Ni2 58.411(18) [57.974(9), 57.793(9)], Ni2−Ni3−Ni2 63.18(3) [64.233(10)], P8−P6−P7 58.48(4) [58.744(16), 58.985(16)] 59.285(16)], P8−P7−P6 58.68(4) [59.030(16), 59.285(16)], P7−P8−P6 62.85(4) [62.226(16), 61.729(16)]

Table S1. Crystallographic data and structure refinement for compounds **1**, **2**, **2·3a**, **3b**, and **4**.

Compound	**1**	**2**	**2·3a**	**3b**	**4**
CCDC	1989656	1989653	1989654	1989652	1989655
Empirical formula	$C_{70}H_{80}N_6Ni_3P_4$	$C_{63}H_{72}N_6Ni_3P_6$	$C_{105}H_{120}N_{10}Ni_5P_{11}$	$C_{54}H_{72}N_4Ni_2P_5$	$C_{98.5}H_{128}N_6Ni_3P_8$
Formula weight	1305.41	1275.21	2156.32	1049.42	1819.68
Temperature/K	123.0(1)	123.0(1)	123.0(1)	123.0(1)	89.9(4)
Crystal system	triclinic	monoclinic	tetragonal	triclinic	tetragonal
Space group	*P*-1	*I*2/*a*	*P*4₁2₁2	*P*-1	*P*-4*n*2
a/Å	11.9677(2)	22.7801(4)	15.54130(10)	10.3749(6)	24.2943(3)
b/Å	16.7171(3)	13.3087(3)	15.54130(10)	14.4469(8)	24.2943(3)
c/Å	17.0685(3)	47.3928(7)	44.4242(3)	19.0051(10)	16.2469(3)
α/°	88.270(2)	90	90	103.126(5)	90
β/°	76.7620(10)	95.1000(10)	90	95.163(5)	90
γ/°	89.6720(10)	90	90	96.316(5)	90
Volume/Å^3	3322.55(10)	14311.4(5)	10729.87(16)	2737.8(3)	9589.1(3)
Z	2	8	4	2	4
ρ_{calc}g/cm^3	1.305	1.184	1.335	1.273	1.260
μ/mm^{-1}	2.238	2.477	2.898	2.521	2.307
F(000)	1372.0	5328.0	4500.0	1110.0	3859.0
Crystal size/mm^3	0.289 × 0.268 × 0.194	0.447 × 0.128 × 0.067	0.805 × 0.432 × 0.317	0.208 × 0.169 × 0.052	0.288 × 0.087 × 0.042
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.392 to 148.476	6.9 to 147.354	6.942 to 147.918	8.636 to 147.736	7.278 to 148.2
Index ranges	-14 ≤ h ≤ 11, -20 ≤ k ≤ 20, -21 ≤ l ≤ 20	-28 ≤ h ≤ 18, -16 ≤ k ≤ 16, -53 ≤ l ≤ 58	-19 ≤ h ≤ 17, -19 ≤ k ≤ 18, -54 ≤ l ≤ 49	-9 ≤ h ≤ 12, -17 ≤ k ≤ 17, -22 ≤ l ≤ 23	-30 ≤ h ≤ 18, -24 ≤ k ≤ 30, -19 ≤ l ≤ 19
Reflections collected	30320	43060	52935	17586	32746
Independent reflections	13196 [R_{int} = 0.0226, R_{sigma} = 0.0235]	14180 [R_{int} = 0.0260, R_{sigma} = 0.0252]	10776 [R_{int} = 0.0549, R_{sigma} = 0.0313]	10530 [R_{int} = 0.0332, R_{sigma} = 0.0628]	9451 [R_{int} = 0.0522, R_{sigma} = 0.0478]
Data/restraints/parameters	13196/0/820	14180/6/731	10776/0/629	10530/0/602	9451/446/785
Goodness-of-fit on F^2	1.040	1.029	1.106	1.095	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0783	R_1 = 0.0286, wR_2 = 0.0750	R_1 = 0.0448, wR_2 = 0.1195	R_1 = 0.0438, wR_2 = 0.1041	R_1 = 0.0677, wR_2 = 0.1655
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0794	R_1 = 0.0317, wR_2 = 0.0774	R_1 = 0.0455, wR_2 = 0.1199	R_1 = 0.0568, wR_2 = 0.1180	R_1 = 0.0791, wR_2 = 0.1730
Largest diff. peak/hole / e Å^{-3}	0.30/-0.40	0.31/-0.24	0.98/-0.28	0.79/-0.45	0.82/-0.38
Flack parameter			0.009(10)		0.016(13)

S6 Quantum Chemical Calculations

General Methods

All calculations were performed with the ORCA program package.[1] All calculations were conducted in the gas phase. The RI approximation was used for GGA calculations,[2] whereas the RIJCOSX approximation was used for hybrid-DFT calculations.[3] Geometry optimisations have been carried out at the BP86-D3BJ/def2-TZVP level of theory.[4–8] Thereby, the aryl substituents at the NHC moieties were truncated to phenyl rings [NHC = 1,3-diphenylimidazolin-2-ylidene (IPh)]. The transition state for the fluxional process of **1** in solution was located using relaxed surface scans followed by a saddle-point optimisation.

Intrinsic bond orbitals (IBOs) have been constructed from the occupied BP86 orbitals according to Knizia *et al*.[9] To estimate the electron count within the clusters, the composition and shape of the respective IBOs was analysed. Thereby, an IBO with a Ni contribution greater than 65% are identified as occupied 3d orbitals. This criterion ensures that only significant bonding interactions between the cluster atoms are taken into account when determining the number of cluster electrons. Orbitals with a comparably low Ni contribution (65% to 80%) may indicate back-bonding from Ni in P-based orbitals, offering additional stabilisation.

Orbital Pictures and Compositions

$[(IPh)_3Ni_3P_4]$ (**1′**):

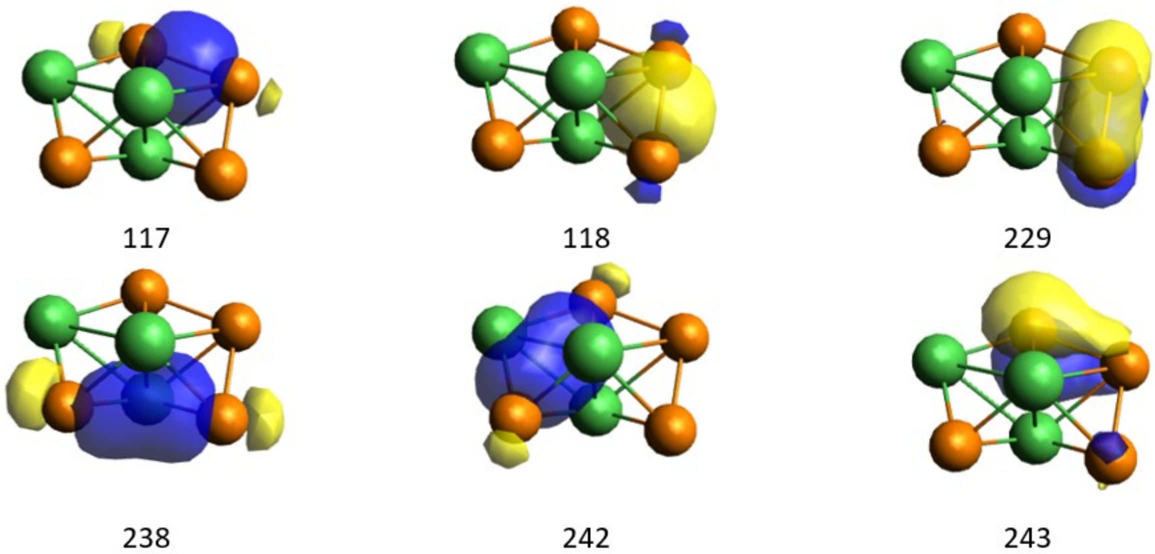


Figure S27. Intrinsic Bond orbitals of **1′** showing significant bonding interactions between the cluster atoms. Surface isovalue = 0.06. NHC groups at the Ni atoms have been omitted for clarity.

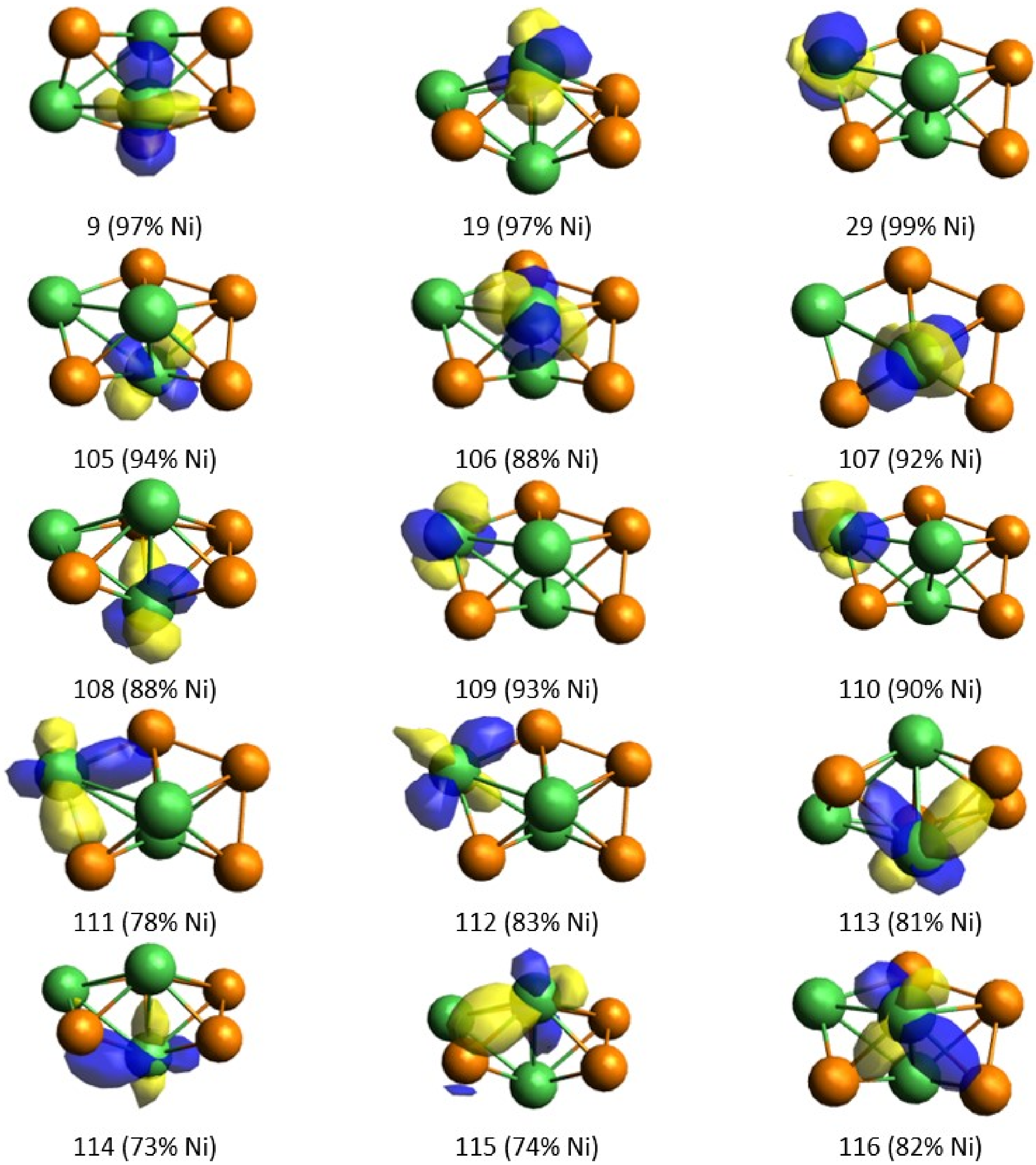


Figure S28. Intrinsic bond orbitals of **1′** showing the filled 3d-orbitals at the Ni atoms (highest contribution of a single Ni atom is given in parentheses). Surface isovalue = 0.06. NHC groups at the Ni atoms have been omitted for clarity.

$[(IPh)_3Ni_3P_6]$ (**2′**):

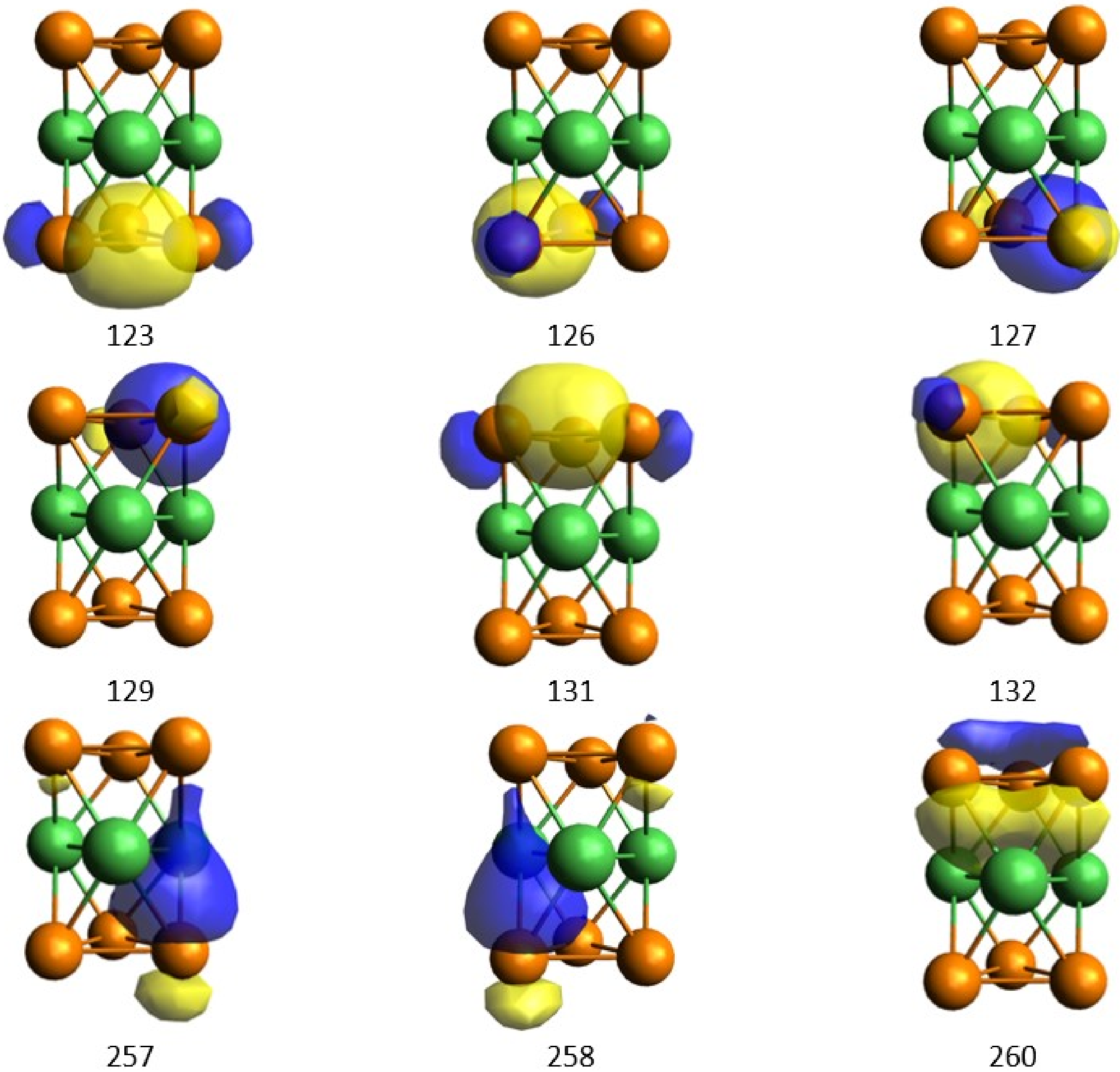


Figure S29. Intrinsic Bond orbitals of **2′** showing significant bonding interactions between the cluster atoms. Surface isovalue = 0.06. NHC groups at the Ni atoms have been omitted for clarity.

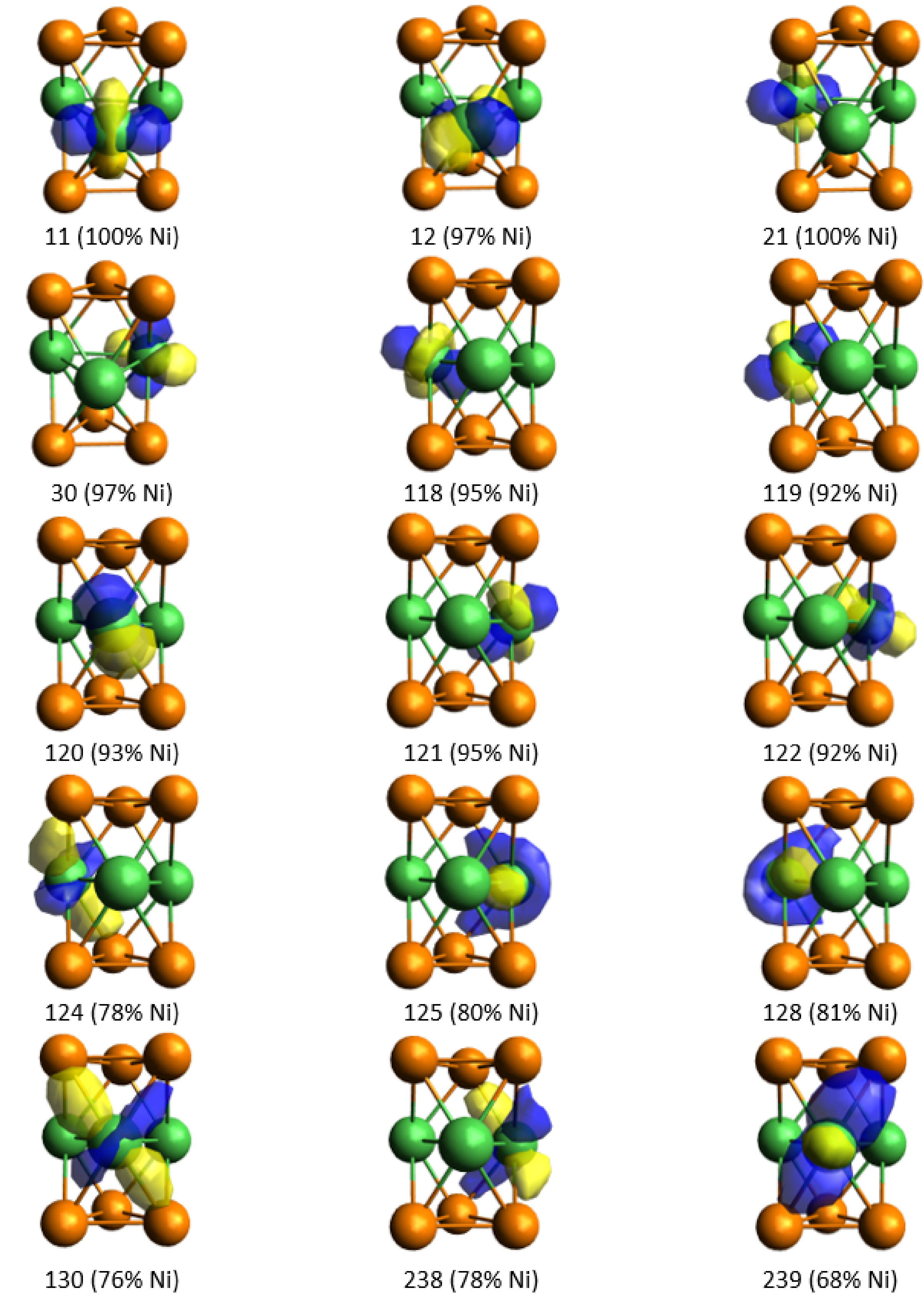


Figure S30. Intrinsic bond orbitals of **2′** showing the filled 3d-orbitals at the Ni atoms (highest contribution of a single Ni atom is given in parentheses). Surface isovalue = 0.06. NHC groups at the Ni atoms have been omitted for clarity.

$[(IPh)_3Ni_3P_8]$ (**4′**):

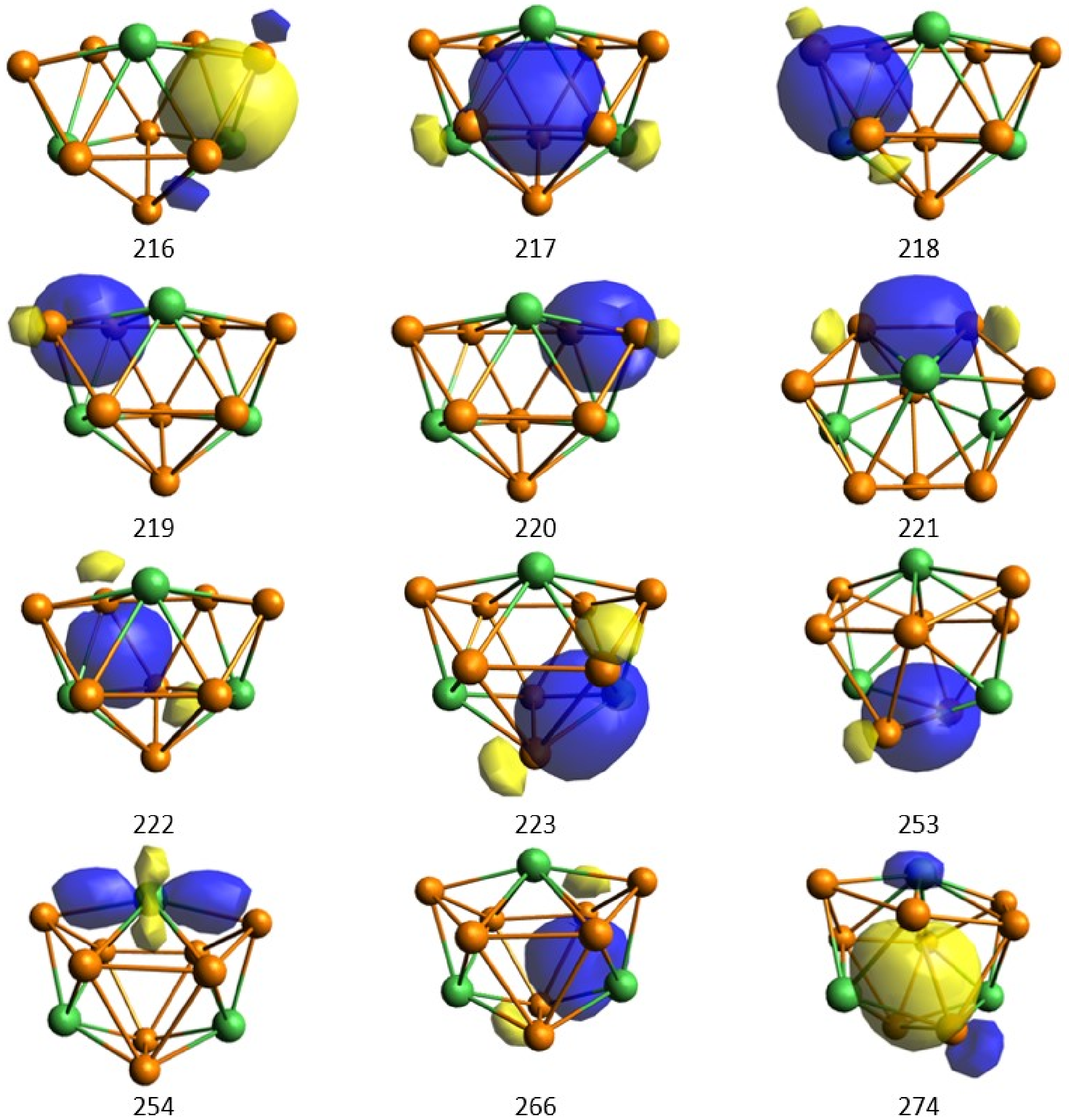


Figure S31. Intrinsic Bond orbitals of **4′** showing significant bonding interactions between the cluster atoms. Surface isovalue = 0.06. NHC groups at the Ni atoms have been omitted for clarity.

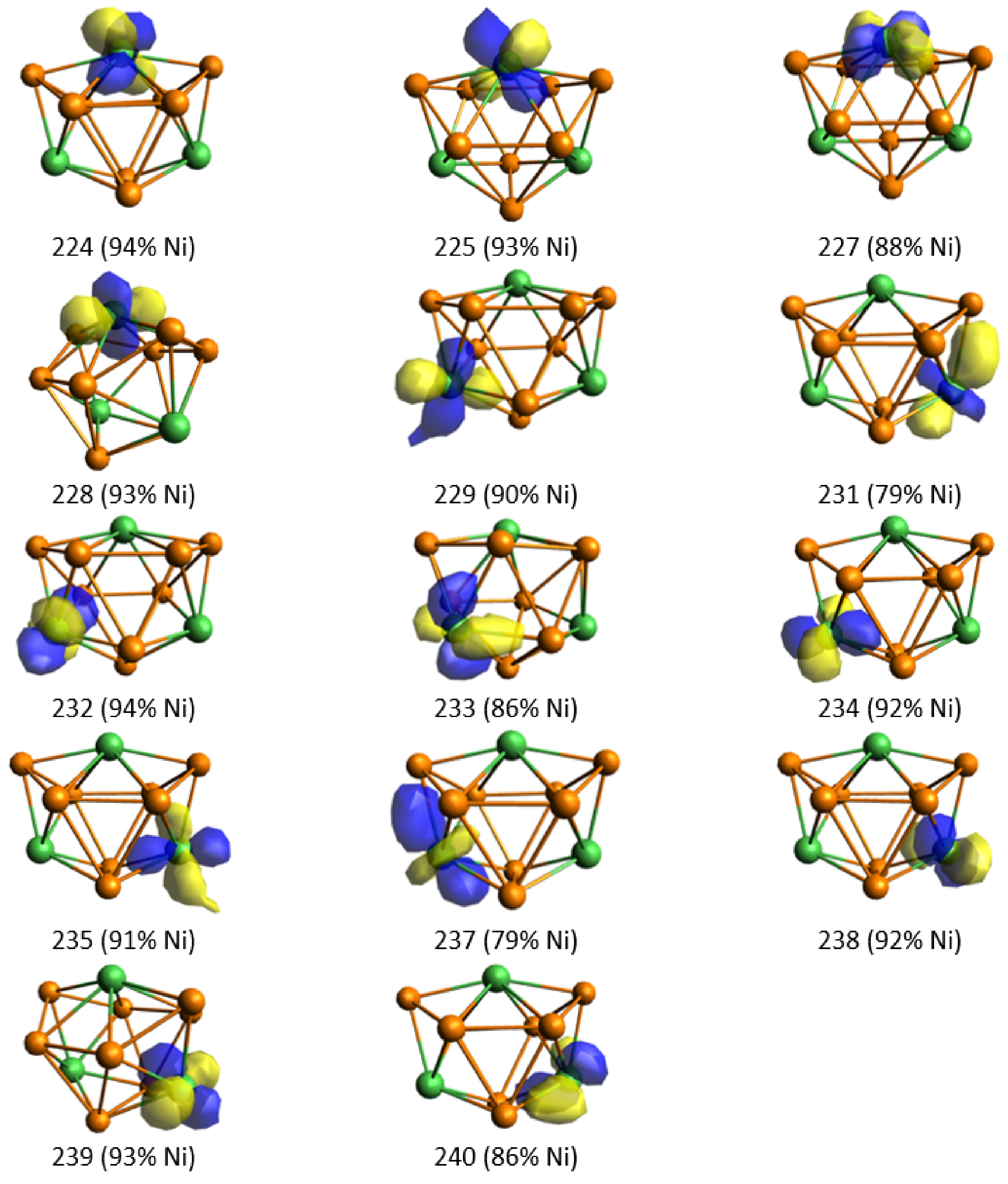


Figure S32. Intrinsic bond orbitals of **4′** showing the filled 3d-orbitals at the Ni atoms (highest contribution of a single Ni atom is given in parentheses). Surface isovalue = 0.06. NHC groups at the Ni atoms have been omitted for clarity.

Fluxional behaviour of 1 in solution

DFT calculations at the BP86/def2-TZVP level of theory gave more insights into the fluxional behaviour of **1** in solution. The presence of only two major signals in $^{31}P\{^{1}H\}$ NMR can be attributed to either an exchange process between the phosphorus atoms or the formation of a symmetrical isomer. Starting from the asymmetrical isomer $[(IPh)_3Ni_3P_4]$ (**1′**), the symmetrical isomer **1*** can form (Figure S33, left side). This symmetrical isomer is slightly (0.3 kcal/mol) more stable in energy compared to **1′**. Moreover, **1′** can undergo a change in connectivity via a transition state that is 2.6 kcal/mol higher in energy than **1′**.

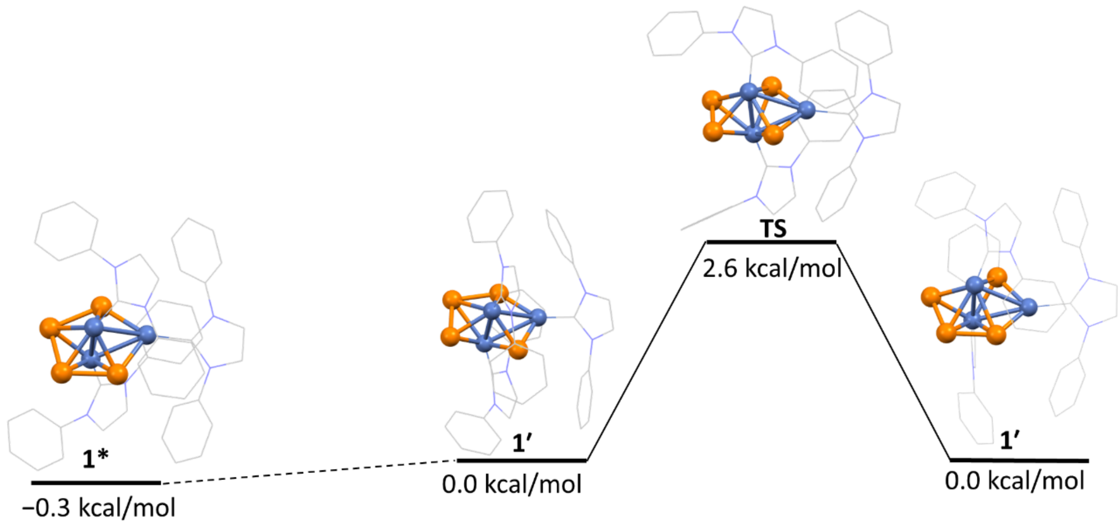


Figure S33. Isomerisation of the asymmetrical isomer **1′** to the symmetrical isomer **1*** (left) and connectivity change in **1′** (right). Note that solid lines are transformations with a found transition state, and the dashed line indicates a transformations for which no transition state was found.

Cartesian Coordinates of Optimised Structures

$[(IPh)_3Ni_3P_4]$ (**1′**, unsymmetrical isomer resembling crystal structure)

Ni	13.40254838552172	14.49878132866253	13.25542264117263
Ni	13.27923858827665	12.42766449516554	12.03247448859933
Ni	10.99031961685278	13.33797674984631	13.16098287077068
P	12.62425224740829	12.57151180937054	14.31255211168585
P	12.10851354131078	14.15530912200754	11.55522723942295
P	14.78696274259674	12.51453407106275	13.96863788990859
P	15.14983331403212	13.63922075651268	12.13535334001406
N	8.55098912436172	12.47075086961428	14.46744784423685
N	8.24985760154552	12.46542992046274	12.32526347038900
N	12.53708551998850	11.26947275802396	9.43655486919104
N	13.45159392484180	16.95771795873294	14.93756879233807
N	11.71968584992447	10.14565406508542	11.08921873459813
N	13.17672659925197	17.36774785407717	12.83379223048311
C	8.05590590561257	11.55646666501145	10.06847411148383
C	8.45548118665200	12.58872398795793	10.92473608613295

C	9.17746021428511	12.83187570424171	13.28714933047962
C	10.70218169778488	8.96264923565387	14.99411577153180
C	12.97802752801767	17.20663947517704	11.42862210131686
C	7.12510398231665	11.86658415480065	12.89522200815618
H	6.27450681177024	11.55392849502686	12.30331981182616
C	9.06302446685090	13.73809541891843	10.40974186435422
C	12.93582638726670	16.78934449718794	17.31734596837483
C	7.31821996747825	11.86866160289894	14.23998721143582
H	6.67042523295314	11.55079652335151	15.04689780437356
C	14.00573645830513	16.68435093304871	10.64056316709328
C	11.73717938121495	17.52715223775747	10.87454336514642
C	13.40029970916043	16.32187950839247	13.70730127413558
C	10.03627878690448	9.59299623220840	12.75616802337356
C	13.26484815941090	12.20138160014134	8.64382953060401
C	14.70140400739550	13.93306612343024	6.99636315241958
C	9.69888215554111	9.20598057571736	14.05274146322677
H	8.64719958884950	9.12087209134370	14.32824464243476
C	12.60014373056699	11.17284765631316	10.81328486738966
C	9.16101312089273	12.62592453372233	15.74411426805077
C	12.61764720873132	12.85548112004611	7.59230650417697
C	8.26461235906504	11.67868213604687	8.69381521344570
H	7.95401685080917	10.87162245476669	8.02934651731264
C	12.39103350490898	9.46604155092139	13.33221963313015
C	14.62242374973163	12.42264890351818	8.89238257819330
C	9.91142247660450	13.77619532753831	16.00925926743267
C	13.34126346632135	13.71567559414477	6.76434284522927
H	12.83684992453742	14.22131912499493	5.93987600016023
C	9.29061147387334	13.84048014394541	9.03867888728912
H	9.78956574543822	14.72880261786077	8.65070504661985
C	14.41375891214246	15.16529847696743	16.28366052834721
C	12.04404812460123	9.09345326788833	14.63119198625696
H	12.83067423688958	8.92139384885464	15.36565541253513
C	11.62863708163822	10.35997029524156	8.89566982158951
H	11.47035412766304	10.27262912886893	7.82927710142772
C	9.05413804401602	11.61171654710858	16.69815391376336
C	14.53218458913133	14.50631242413233	17.50666066775784
H	15.14805196601202	13.60847142790965	17.56321490985498
C	13.77156612997106	16.44922476618025	9.28778519832848
H	14.55311052452792	16.00124109777468	8.67689404236948
C	13.60444402909129	16.29977033298099	16.18788208495650
C	8.88773007704812	12.81655247563876	8.17601374272588
C	11.51634150357274	17.30141525935600	9.51372966836268
H	10.54407759196476	17.53680704455358	9.07891754196589
C	15.33370409468058	13.29267165238888	8.06753468548808
H	16.39268451806390	13.46437205291303	8.26287320159884
C	11.11555582778616	9.65477501513741	9.93432883818988
H	10.41748587291342	8.82852478374045	9.95842409244030
C	11.38155213072236	9.71519436628365	12.40180722935320
C	12.52720554291136	16.74712306273459	8.72557159695482
C	13.87838570726415	14.99231664425644	18.64121172095514
C	10.57787118162849	13.89430787225441	17.22638040123270
H	11.19033405211202	14.77387175263972	17.41799365739264
C	13.08834749530943	16.14190534848015	18.54480955947718
H	12.56442968451550	16.52491371108792	19.42138819466606
C	9.71596675890646	11.74475109672382	17.92088997012486
H	9.64457216828862	10.94613977025692	18.66032425258349

C	13.24821077427716	18.33394849707302	14.81445049128096
H	13.30473229360054	19.00414220820696	15.66173946138918
C	13.07066124233057	18.58782989244656	13.49359348681423
H	12.92189676625412	19.51733507916859	12.95912434237504
C	10.48722619255119	12.87995175199121	18.18199930449617
H	8.49156895358548	10.70712103647646	16.46865234539106
H	11.02335264542193	12.97340274654082	19.12705585018604
H	9.99332058019833	14.55038507176491	15.24551472190706
H	7.59870486797370	10.65485305176035	10.47791002129475
H	9.35895893650163	14.53369214176118	11.08915503320874
H	9.05262479928678	12.90628538145203	7.10130274015629
H	15.26694995486820	14.60376654685408	6.34804017088388
H	12.34752074003028	16.53908797277592	7.67042736660657
H	14.94318690731779	14.80390677137685	15.40385911416805
H	14.95481917995649	16.42059141445787	11.10444530576373
H	10.94273119895807	17.90496423361543	11.51870797788532
H	10.43937076424185	8.68162428290480	16.01414966190593
H	12.27633673126722	17.65329355223411	17.23222725184360
H	13.98208650772995	14.47825010953237	19.59733936534850
H	13.43225669126073	9.58708923653894	13.03947027957496
H	11.54920657923699	12.70150811448795	7.44414700988496
H	15.10210344848175	11.91621100394475	9.72689707315775
H	9.26495897613322	9.83633839557234	12.02643276463803

$[(IPh)_3Ni_3P_4]$ (**1***, symmetrical isomer)

Ni	13.52061533126539	14.69864224947701	13.31043067031789
Ni	13.61127426906433	12.26600149531655	12.16150826674840
Ni	11.31531535282302	13.67871931629193	12.22541603097969
P	12.47577745098996	12.87783647373341	13.99845085297506
P	13.24501585654460	14.23249121624232	11.15085268978842
P	14.79736783269966	12.82470760394243	14.09972681979870
P	15.33964343808701	13.81246578514062	12.21112975326833
N	8.62083763678387	13.19208075647942	13.44621535310505
N	8.64016586245040	12.87665932955404	11.30495676757638
N	12.96629361234433	10.82744644702528	9.71894787476033
N	13.41694663245016	16.61177332645234	15.49838640518565
N	11.65888527074766	10.18720270301035	11.31728684074294
N	11.88725290085424	17.08668089263850	14.05005667110248
C	8.51218364477837	11.71207455718691	9.16074929093443
C	9.07961616437330	12.70564724692854	9.96694477836620
C	9.47566609467056	13.24478556897576	12.35437114114985
C	9.80145985573038	9.61340809776977	15.05087220138551
C	11.03087210610926	17.06314443344253	12.91171243805254
C	7.34548834149371	12.60342980018800	11.73895623830557
H	6.54226240397489	12.35414681895355	11.05802025062951
C	10.09534935097310	13.52454150131745	9.46435514972894
C	14.34997326837318	15.49269796572877	17.45475357860399
C	7.33510512255036	12.80117437513310	13.08097458482758
H	6.52066336229177	12.75362603124098	13.79176658485812
C	11.57987230549724	17.00193030025212	11.62911024341733
C	9.64328284670112	17.07090928477849	13.09200048024158
C	12.95546434074818	16.22653863902821	14.25520665805649
C	9.64414650762471	10.00910930961245	12.66927632027266
C	14.01172629159339	11.44856467776305	8.98082284975779
C	16.04605158816923	12.71064827426479	7.55127616981357

C	9.02798456667962	9.81230922121785	13.90477372695340
H	7.93944976785808	9.83391513635713	13.96812970846885
C	12.75408679117958	10.99604510493433	11.07657698806461
C	8.99683271534875	13.44969833488654	14.79317312415468
C	13.75532633466892	11.94039618353710	7.69835998516146
C	8.96120711234766	11.54588183958519	7.84929194609056
H	8.51762434589152	10.76973578777235	7.22470756348592
C	11.81905160918491	9.76985007557184	13.71844153578199
C	15.28553425376572	11.56202655950039	9.54362797450221
C	9.97108705602109	14.41059705734697	15.07004431869510
C	14.77669414408144	12.56975971806583	6.98498898050376
H	14.57293342907334	12.96480839573297	5.98887888327521
C	10.55695402725793	13.33359786369756	8.16413559846749
H	11.36374859334538	13.96639328049718	7.79330277990080
C	15.71685478568329	15.80983066896182	15.47086982370303
C	11.19440084118022	9.58976493536966	14.95231337130610
H	11.80505638144215	9.43841729081161	15.84243646358641
C	12.01355541801755	9.98790796795552	9.14628444694293
H	12.03336613391946	9.72387456660028	8.09781446440363
C	8.39953180353340	12.73233174033038	15.83523885767407
C	16.76988431823411	15.14620554907319	16.09864618655920
H	17.70451187280695	14.99576292590434	15.55863341211271
C	10.73162465009910	16.93768638249723	10.52310542973911
H	11.16526876635450	16.88150424207597	9.52433945396270
C	14.51127049608698	15.97523385632171	16.15522799628209
C	9.98787418722400	12.35091072018350	7.34898945311132
C	8.80359655661745	16.99470909857128	11.97979349914119
H	7.72280479439154	16.97633384494228	12.12310147149303
C	16.29629453650125	12.20134915937508	8.82865433813891
H	17.28226223109446	12.30818250430127	9.28088891649575
C	11.19382028879025	9.58678531057590	10.14812941921291
H	10.35961203805710	8.89836796785324	10.15028245569428
C	11.03810722890535	9.99096769347137	12.58147015541385
C	9.34503369318538	16.92409916051269	10.69360320739960
C	16.62318543528581	14.66450224682426	17.40282048554949
C	10.34932484926140	14.65394030321994	16.38904813258647
H	11.11789595384138	15.40001898447942	16.58904805567535
C	15.41576806939917	14.84186032918453	18.08089495599380
H	15.29147690440668	14.45411181227418	19.09251123602598
C	8.77869216643054	12.98633982354409	17.15401866452860
H	8.31822442576855	12.41809815904777	17.96303510309938
C	12.65231521103761	17.63506775203704	16.05062560074263
H	12.88836679460357	18.08036980678528	17.00882430293454
C	11.68873830775642	17.93375682197464	15.14013133158070
H	10.91880314853274	18.69436000208638	15.14441790325885
C	9.75545986276697	13.94593873613447	17.43558353056266
H	7.66868543789514	11.95497110300577	15.61612819758658
H	10.05556901877532	14.13360455715569	18.46717043103285
H	10.43690036388949	14.93368910334155	14.23865930782608
H	7.73954543951169	11.05536525561733	9.56203965444372
H	10.51150187420283	14.31527473718335	10.09099784345457
H	10.33909818687201	12.21408748249823	6.32514187547517
H	16.83874615817929	13.21576503887814	6.99835455414503
H	8.68809246445077	16.85167542460916	9.82635445938518
H	15.80629174060738	16.17331472182697	14.44861214708520
H	12.66117605074960	16.99796998752161	11.51054656342339

H	9.22799396262120	17.08795904342691	14.09967753167848
H	9.32048910290294	9.47922007571172	16.01999383175490
H	13.38771070436928	15.59931087714254	17.95665160360177
H	17.44753805968634	14.13905896309555	17.88594638116660
H	12.90340414041574	9.76210298618714	13.62828189192635
H	12.75241138251659	11.85950814699348	7.28179675729658
H	15.46543641456535	11.16907454578834	10.54339066164447
H	9.04953755711257	10.20499855016434	11.77758711390496

[(IPh)$_2$Ni$_2$P$_5$] (**3′**)

Ni	6.35153355909917	3.51035264259057	3.92821775530809
Ni	7.26827636922801	1.57596381903156	5.49824776115351
P	6.29604726150640	1.23333799145857	3.40146764796528
P	5.02783979569714	1.99453314657066	5.08184432802988
P	6.22225552853812	3.50799171206316	6.25405555570411
P	8.27217218984466	2.27840374933312	3.52833189412974
P	8.22605028279849	3.68976028381575	5.28794720484267
N	9.22374260700717	0.35151347566716	7.32616733163511
N	4.79066258302546	4.65564104339115	1.70912713141137
N	4.90424313584551	6.01328990290763	3.37767702026691
N	8.21822530888984	-1.13805785604697	6.13848072473882
C	9.91063242700632	-0.84462143904014	7.52478348300187
H	10.74679764119922	-0.92336035894489	8.20803776514746
C	3.95652413151919	6.53926605089410	2.50171966840692
H	3.46248568874924	7.48480170912806	2.68635389010003
C	9.27565940444046	-1.78524082166664	6.77529512970270
H	9.44644100687463	-2.84948169866664	6.67348695144428
C	7.31396998289450	-1.75318351696913	5.22464805524593
C	8.17737723753667	0.20548728963900	6.44138428220471
C	3.88493708763850	5.68221011536585	1.44816516903127
H	3.31651187875225	5.72985324908517	0.52794900298524
C	5.42265016004854	4.82021276572375	2.92263742721896
C	9.58227310061523	1.60658276896107	7.89905695131228
C	5.00619761299893	3.52277903695160	0.87162376250794
C	5.93980984838164	-1.57537236393662	5.40105350657206
C	5.26310926865815	6.58346993038300	4.63396165809079
C	3.92064690729576	2.75397039867994	0.44858934452347
C	6.31254182173117	3.16996158069056	0.52509004368986
C	7.80868293205788	-2.48231552617442	4.14200621291755
C	5.45120935942691	1.25255145780358	-0.67561161154723
H	5.62677079559718	0.35624428195237	-1.27125961958777
C	8.93625300764128	3.61714818548114	9.05779608529757
H	8.16909635383612	4.21501977949651	9.54986939030311
C	10.88334305528179	2.09122175951115	7.75292249704999
C	4.14800810320927	1.61945947264565	-0.33338818216588
H	3.30360276679777	1.00938067897207	-0.65573110923267
C	10.23598444570331	4.11233496874464	8.91751120483654
H	10.48917462984687	5.09948222192119	9.30556842578847
C	6.61329741813297	6.77944138746992	4.93229010686409
C	11.20884206219755	3.34595511078633	8.27177055081986
H	12.22026151238621	3.73426869654170	8.14820083421704
C	8.60655342184875	2.35950572706473	8.55587067668186
C	4.27134217712444	6.88975129324532	5.56750932412197
C	6.91436074494965	-3.04185682685619	3.22693100734662
H	7.29720528782643	-3.60204191774505	2.37326050411548

C	6.53090336694332	2.02871533107373	-0.24428696250762
H	7.55116295395402	1.74076820282221	-0.49810367302700
C	5.98745335494982	7.58324794056033	7.12779042562547
H	6.27183057930869	7.96328195698277	8.10956429687823
C	5.53929034422267	-2.85996619173462	3.38862892446957
H	4.84407055081674	-3.28286718170863	2.66280934151120
C	5.05532640667471	-2.12578656660318	4.47537320636490
H	3.98359193512392	-1.97059804680069	4.60007010756664
C	4.63891479100114	7.39784476423201	6.81507510477643
H	3.86837252465043	7.62564542523331	7.55223080403646
C	6.97211016789676	7.27300691994016	6.18524485701900
H	8.02683455699193	7.40393814872872	6.42715671778281
H	3.22568108080701	6.69372277223685	5.32832099693400
H	7.36656758597691	6.51215284267662	4.19335338380946
H	11.61963840424911	1.50369076527137	7.20361497265853
H	8.88599159193971	-2.57660637998137	4.00187368946160
H	5.58254772048485	-0.98318939599879	6.24177131491674
H	7.59474183246612	1.96637576930007	8.63695442103235
H	2.91205167054975	3.02540321458265	0.76191734870725
H	7.14193667930760	3.77451435126549	0.88797397778610

$[(IPh)_3Ni_3P_4]$ (**1′ → 1*** transition state)

Ni	13.35602435330095	14.49323448929582	13.15805868699094
Ni	13.27789651026949	12.32136494070568	12.10397037777389
Ni	10.91095281602255	13.36569261837839	12.68278265132808
P	12.42638293220335	12.73755316332853	14.12615189735589
P	12.34460424344972	14.12698886791475	11.23245111257291
P	15.03098277481012	12.88074086453457	13.50702494208402
P	14.98349450673357	13.84693431001975	11.61401178474657
N	8.01834903561892	13.65198915478147	13.24646977020044
N	8.42071836990310	13.66668326238726	11.12063363101300
N	13.29244151686880	10.25059300762158	10.02681337585437
N	13.95236879461364	16.50639009500177	15.15352020529531
N	11.78163929203415	9.84830424663224	11.51322197518138
N	12.03016375550509	16.91195646116720	14.25794308206285
C	10.00762239199934	12.53662813636293	9.65462706261303
C	9.06590713045997	13.54959487923370	9.85795524909363
C	9.06363705190183	13.54833744540653	12.33900887624818
C	9.34828291050941	10.16171141353811	14.93895640627397
C	10.88600227013084	16.90621706477373	13.40783084741458
C	7.04957157265548	13.86029313432332	11.27113844155189
H	6.38357056519895	13.96594042908793	10.42437557088783
C	8.75247775897286	14.44297702786101	8.83083316825230
C	15.49516694485376	15.38108455825201	16.67309991744530
C	6.79544035149993	13.84290514263648	12.60419536531612
H	5.86795112744844	13.97998569831304	13.14400702553790
C	11.05128394447181	16.93676830896579	12.02170881055187
C	9.60799990598796	16.89330050078649	13.97372498494792
C	13.12609486345771	16.07818140651030	14.13662940952615
C	9.58669602827634	10.17863987662535	12.53190576680422
C	14.38558450043453	10.82110942250579	9.29849763284688
C	16.51842565130811	11.90323914012235	7.88062924110016
C	8.78485783942757	10.29405116580371	13.66900080210037
H	7.72375144256854	10.51840106644763	13.55923269151558
C	12.79703367049052	10.73808254018386	11.21778690331498

C	8.16837754363545	13.51890257249855	14.65116310935934
C	14.28235906409455	12.11523139009553	8.78754175241017
C	10.62539881711230	12.41130345946365	8.41155847512979
H	11.35284468811864	11.61486755644464	8.25650009774900
C	11.51882002909320	9.75889771094565	13.93966742191417
C	15.54241395036055	10.06294766995503	9.11146249811891
C	9.36832767169999	13.89661753854001	15.26181609410962
C	15.35639583102710	12.65296936633306	8.07774966884289
H	15.28591575952820	13.67030285870649	7.69253837138244
C	9.38427627598218	14.31721890331839	7.59131896436846
H	9.14918275297067	15.02239397549627	6.79334039830810
C	16.20435902322971	15.94020618724548	14.41750516756536
C	10.71122712529405	9.88763809333122	15.07144629947712
H	11.15807920315753	9.79677150993662	16.06136334726540
C	12.60867639994104	9.11255258759011	9.60355972514255
H	12.85974196730528	8.60285050859630	8.68203868403505
C	7.13152406937076	12.97147729224309	15.41747914245016
C	17.44867356200808	15.36618130925004	14.67213080984717
H	18.19975634396370	15.34337774081493	13.88259767107929
C	9.92689888766203	16.93335959550758	11.19766548679683
H	10.05960827887220	16.93280284579262	10.11584985561322
C	15.23600121429555	15.94263442659164	15.42253998300776
C	10.32060883352390	13.30173450490845	7.37885125535921
C	8.48802088672622	16.89755184057967	13.14086581159267
H	7.49077823407801	16.86740807672593	13.58062545189507
C	16.61087186970266	10.60770743347741	8.39601856285306
H	17.52094614159723	10.02360195067573	8.25548549714988
C	11.65207680930044	8.86422382657457	10.53640498541198
H	10.91066811893651	8.07905200806991	10.61044574977688
C	10.95048317247053	9.91578288339715	12.67622249862779
C	8.64564951746764	16.91330555347749	11.75332916806788
C	17.72243872757405	14.80471518168368	15.92233701444819
C	9.54159944389843	13.69116305525266	16.62950164262456
H	10.49427547004357	13.96204026362746	17.08592377641055
C	16.74678924071236	14.81436059777888	16.92164040653496
H	16.95096300825028	14.36155277043443	17.89244942238359
C	7.30427631745527	12.79429351773100	16.79085792348740
H	6.49690394702232	12.35909862318997	17.38102689122560
C	13.37284914819807	17.52485626797409	15.90392470908173
H	13.89008636669234	17.99488895290055	16.73064152427924
C	12.16386680591238	17.78192781612924	15.34060218831935
H	11.41530223318281	18.52926038605531	15.56965914901757
C	8.51379304260278	13.14354684183317	17.40065818473325
H	6.20725326987075	12.64750980837263	14.93842567184339
H	8.65220109921652	12.98678031120185	18.47101276864249
H	10.16670652107697	14.32905337685194	14.65398610245835
H	10.25968817787867	11.87366752654566	10.47865335330456
H	8.03825007319766	15.24671727911936	9.01185581951619
H	10.81439739976946	13.20714270090507	6.41119170181031
H	17.35822472352321	12.33233687533526	7.33269599832566
H	7.76671520653807	16.90294120997787	11.10789632437167
H	15.96186540891513	16.35376035257120	13.44006884104598
H	12.05621804263032	16.94902844437233	11.60577395727733
H	9.49457979640825	16.84502790952573	15.05658164755358
H	8.72878297486894	10.29579232820443	15.82572163511489
H	14.70899387447138	15.36044218939274	17.42838011541513

H	18.69355228651362	14.34696944892244	16.11362871855891
H	12.58837304459680	9.57586116956228	14.02560974471817
H	13.38246275423924	12.69741380307440	8.97567270742818
H	15.60703830176622	9.06429074761692	9.54493350553746
H	9.16246442706108	10.30935322776460	11.53640888402172

$[(IPh)_3Ni_3P_6]$ (**2′**)

Ni	13.60461323459110	8.54196784608361	16.06698235003657
Ni	14.38106217959208	6.17685342724423	15.86925526319302
Ni	14.11378836737850	7.30774711104430	18.17696119400860
P	15.45680529456928	9.16206616416978	17.19139763574527
P	12.07358322389422	7.01750393998754	15.42943374647581
P	11.95407984450658	7.93050151168315	17.55720616700534
P	12.56171326305027	5.83708159404472	17.20375117074995
P	16.13608045939462	7.08265053584091	17.14706007769775
P	15.66915452464935	8.00127811014225	15.19632163590679
N	12.56339743641803	10.30386078593512	13.92101187830941
N	15.72882668191001	3.53338346712427	16.29719429788791
N	12.99872499888881	11.42131837217254	15.70713608233392
N	14.47786517925872	5.18707164277170	20.26765092316701
N	13.78652227436041	3.29591740838080	15.40823247993337
N	15.93602301775521	6.75370686661648	20.46318605099900
C	14.70993113458522	4.27804808824819	15.73239124883983
C	13.03675149827262	10.13812733634229	15.20509711164955
C	13.31697061546023	4.43841262617986	19.91872905939471
C	12.05386303612915	4.96376095936899	20.19747711301967
C	14.77108387898692	6.44604267276907	19.77731817997591
C	12.42772099762030	9.26737363691894	12.94555377846313
C	13.54733004659769	8.53807408016666	12.54465044949674
C	13.36125600296357	11.80248458571064	17.03646440670323
C	10.91794839012455	4.23783057760691	19.84127995561713
H	9.93003492949518	4.65543627038055	20.03534578235579
C	17.32613709441406	3.95672228307822	18.09233346072941
C	16.96644021823611	4.07583435464661	16.74903559594799
C	17.79892904907775	4.73252345141494	15.84079003118275
C	11.04489281675331	2.99064709063469	19.22407689851046
C	12.24344192037828	11.63304906784310	13.64589000282287
H	11.87075374586882	11.94438292481706	12.67848017453719
C	14.19866350458967	2.02662534922998	15.80286283407509
H	13.60817648009415	1.14174778505943	15.60228981175748
C	12.52623196045107	12.33936634833427	14.76981033899741
H	12.41814870974888	13.39121229004323	15.00142421479899
C	13.45413627591949	3.19864561299690	19.29255460492230
C	11.17490066541094	9.02851163262769	12.37660290990055
C	13.40732667178419	7.55731068425873	11.56311807134585
H	14.28083864576109	6.98267754364451	11.25346017463640
C	15.42663587794042	2.17386768231301	16.36413085452423
H	16.12820574997181	1.44650536873961	16.75306094639055
C	19.00232443351298	5.27715485563654	16.28710271428153
H	19.64348919767021	5.81153050941695	15.58611584070100
C	12.52737940223606	3.54973466927371	14.79404494275271
C	12.46065053364791	4.34597842506335	13.64887481837203
C	11.21823419686460	4.59817308691202	13.06758997172294
H	11.16288451807015	5.24344355762559	12.19264099324977
C	18.53822401786557	4.49188886232743	18.52807680163614

H	18.81538715329360	4.40389658889951	19.57924694320156
C	16.66086225826585	7.96895125765928	20.30536546812228
C	12.69322647926131	11.24395552181153	18.12641681951191
C	10.05501279792983	4.05663349147268	13.61914714321705
C	14.35780554130727	12.76315740832259	17.22131522530254
C	12.16279848418425	7.32497512451816	10.97066192053642
C	11.04703116899408	8.06065968647652	11.37883803957871
H	10.07038592006346	7.87156409314206	10.93207215762494
C	12.31310647306823	2.47217804217315	18.95253113075054
H	12.42150788787821	1.50631194049501	18.45770915073039
C	11.36906616630943	3.01277731036970	15.36056840802174
C	18.03288962734065	7.91939527845155	20.04890374491965
C	10.13199625621607	3.26414372864301	14.76649131876915
H	9.22525632946792	2.85974236524353	15.21763856644879
C	19.37643589306679	5.15361043864385	17.62789468813073
C	15.99120216962095	9.19163741746244	20.38580172162232
C	15.43859180610073	4.72371224007682	21.16557979726368
H	15.34609314052243	3.76712559329028	21.66449130063571
C	16.35965008189918	5.71465583819797	21.28609988980668
H	17.23822358475461	5.79861439053425	21.91301209519053
C	18.74527488582211	9.10789626965262	19.88546073872388
H	19.81324412948474	9.07069076547673	19.66801514648710
C	13.03028374966148	11.65371362495257	19.41609912317737
H	12.51283112851465	11.21346164080256	20.26904011997027
C	14.67416950715811	13.18432547316728	18.51408047748272
H	15.45176483201146	13.93434271444123	18.66241515141359
C	16.71107207785590	10.37352563718023	20.21257562418342
H	16.18474785441462	11.32589965570581	20.24498216790067
C	18.08552202043431	10.33598238667178	19.96742037102744
C	14.01018748534739	12.63111533963994	19.61211877807002
H	12.06247947305757	6.56912168903573	10.19024839959640
H	10.30838032710133	9.58740929720047	12.73081996568122
H	14.51409592259028	8.73915201484516	13.00504218542443
H	20.31680636624152	5.58498277270097	17.97271546955670
H	16.64448083026662	3.48085284878666	18.79666525013311
H	17.47522388251754	4.84030501836412	14.80641305331616
H	18.63878422389154	11.26429341629746	19.82146249252706
H	18.52022704317658	6.95264878169681	19.92985039226149
H	10.15329118323034	2.42884904046924	18.94351406307027
H	9.08646855259703	4.26825739167032	13.16495577884262
H	13.37379291435987	4.78093908748846	13.24431271942225
H	11.44063486887998	2.44693532442049	16.28833401656926
H	14.91496860995511	9.20290621911477	20.55388597135403
H	14.44584552792954	2.82329237692322	19.04158891409173
H	11.97828214638028	5.94917138682378	20.65533346958309
H	14.25684261006375	12.96162152452372	20.62225473034116
H	14.88973738536271	13.15918298089092	16.35590997487093
H	11.92208504542837	10.49277451230195	17.95826487877487

$[(IPh)_2Ni_2P_5]$ (**3′**)

Ni	6.35153355909917	3.51035264259057	3.92821775530809
Ni	7.26827636922801	1.57596381903156	5.49824776115351
P	6.29604726150640	1.23333799145857	3.40146764796528
P	5.02783979569714	1.99453314657066	5.08184432802988
P	6.22225552853812	3.50799171206316	6.25405555570411

P	8.27217218984466	2.27840374933312	3.52833189412974
P	8.22605028279849	3.68976028381575	5.28794720484267
N	9.22374260700717	0.35151347566716	7.32616733163511
N	4.79066258302546	4.65564104339115	1.70912713141137
N	4.90424313584551	6.01328990290763	3.37767702026691
N	8.21822530888984	-1.13805785604697	6.13848072473882
C	9.91063242700632	-0.84462143904014	7.52478348300187
H	10.74679764119922	-0.92336035894489	8.20803776514746
C	3.95652413151919	6.53926605089410	2.50171966840692
H	3.46248568874924	7.48480170912806	2.68635389010003
C	9.27565940444046	-1.78524082166664	6.77529512970270
H	9.44644100687463	-2.84948169866664	6.67348695144428
C	7.31396998289450	-1.75318351696913	5.22464805524593
C	8.17737723753667	0.20548728963900	6.44138428220471
C	3.88493708763850	5.68221011536585	1.44816516903127
H	3.31651187875225	5.72985324908517	0.52794900298524
C	5.42265016004854	4.82021276572375	2.92263742721896
C	9.58227310061523	1.60658276896107	7.89905695131228
C	5.00619761299893	3.52277903695160	0.87162376250794
C	5.93980984838164	-1.57537236393662	5.40105350657206
C	5.26310926865815	6.58346993038300	4.63396165809079
C	3.92064690729576	2.75397039867994	0.44858934452347
C	6.31254182173117	3.16996158069056	0.52509004368986
C	7.80868293205788	-2.48231552617442	4.14200621291755
C	5.45120935942691	1.25255145780358	-0.67561161154723
H	5.62677079559718	0.35624428195237	-1.27125961958777
C	8.93625300764128	3.61714818548114	9.05779608529757
H	8.16909635383612	4.21501977949651	9.54986939030311
C	10.88334305528179	2.09122175951115	7.75292249704999
C	4.14800810320927	1.61945947264565	-0.33338818216588
H	3.30360276679777	1.00938067897207	-0.65573110923267
C	10.23598444570331	4.11233496874464	8.91751120483654
H	10.48917462984687	5.09948222192119	9.30556842578847
C	6.61329741813297	6.77944138746992	4.93229010686409
C	11.20884206219755	3.34595511078633	8.27177055081986
H	12.22026151238621	3.73426869654170	8.14820083421704
C	8.60655342184875	2.35950572706473	8.55587067668186
C	4.27134217712444	6.88975129324532	5.56750932412197
C	6.91436074494965	-3.04185682685619	3.22693100734662
H	7.29720528782643	-3.60204191774505	2.37326050411548
C	6.53090336694332	2.02871533107373	-0.24428696250762
H	7.55116295395402	1.74076820282221	-0.49810367302700
C	5.98745335494982	7.58324794056033	7.12779042562547
H	6.27183057930869	7.96328195698277	8.10956429687823
C	5.53929034422267	-2.85996619173462	3.38862892446957
H	4.84407055081674	-3.28286718170863	2.66280934151120
C	5.05532640667471	-2.12578656660318	4.47537320636490
H	3.98359193512392	-1.97059804680069	4.60007010756664
C	4.63891479100114	7.39784476423201	6.81507510477643
H	3.86837252465043	7.62564542523331	7.55223080403646
C	6.97211016789676	7.27300691994016	6.18524485701900
H	8.02683455699193	7.40393814872872	6.42715671778281
H	3.22568108080701	6.69372277223685	5.32832099693400
H	7.36656758597691	6.51215284267662	4.19335338380946
H	11.61963840424911	1.50369076527137	7.20361497265853
H	8.88599159193971	-2.57660637998137	4.00187368946160

H	5.58254772048485	-0.98318939599879	6.24177131491674
H	7.59474183246612	1.96637576930007	8.63695442103235
H	2.91205167054975	3.02540321458265	0.76191734870725
H	7.14193667930760	3.77451435126549	0.88797397778610

$[(IPh)_3Ni_3P_8]$ (**4′**)

C	15.86196837396580	-1.41078262793282	5.57813802696483
C	13.91566154257561	-1.52600673290628	6.78203925569156
H	13.08929651110481	-1.13816073266393	7.36410766746857
C	14.20422044311361	-2.78725189935525	6.35756180274681
H	13.69096442479797	-3.72846370972299	6.50841446749722
C	15.02941243814228	0.71191985195777	6.47977158577774
C	15.34627791442833	1.22569267020191	7.73768751561384
C	15.50910582538239	2.60394855642685	7.88882621043730
H	15.77201187224979	3.01263800123297	8.86493161554037
C	15.37298686717125	3.45074594678784	6.78581538290343
H	15.52707268769900	4.52403166465747	6.90260813172198
C	15.05953030762538	2.92356504474756	5.53072439198595
H	14.98039964604530	3.57564235392014	4.66107073662418
C	14.87628547720330	1.54983562563474	5.37475368745488
C	16.08305895775317	-3.78790333899501	5.01256951308174
C	17.28527051078770	-4.22943055732107	5.56581325345632
C	18.00495417353359	-5.23370800316600	4.91838353259506
H	18.96437767086223	-5.55168147441463	5.32597078128958
C	17.51280061525072	-5.79997756032897	3.74002869469415
H	18.08336484549862	-6.57731135481298	3.23054565680585
C	16.30136262903903	-5.35887217203977	3.20139685028740
H	15.92636617692627	-5.78650019475729	2.27111562821267
C	15.58402145576022	-4.34153236098911	3.83300484519937
C	22.14956196736879	0.71020012414789	5.87635412222189
C	24.37954512737577	0.33784643086477	6.29902259295839
H	25.24209693037875	-0.22565428026317	6.63227835857639
C	24.26242988825634	1.62148093480538	5.86287727452085
H	25.00363436397862	2.40204558164050	5.74639845769434
C	22.74946960816986	-1.53840829411315	6.64432192475952
C	23.26462565582983	-2.58731539226316	5.88131387141494
C	22.88060835773295	-3.89800234381160	6.17222493906497
H	23.26905592897365	-4.71927238123708	5.56916319327258
C	21.97894796700340	-4.15160103206990	7.20778813368753
H	21.66927934323057	-5.17500158928711	7.42269925648863
C	21.45946789384651	-3.09227988500030	7.95735624021538
H	20.74061846446262	-3.28307990433816	8.75448655434623
C	21.84633345195344	-1.78153636649912	7.68145095370787
C	22.34035942174162	3.02245841520660	5.07423267003168
C	22.91408399235758	3.60480331057039	3.94197719310700
C	22.30334302980193	4.71679871875577	3.35790482296491
H	22.74357101821918	5.16666533592891	2.46716355900686
C	21.12000417203143	5.22988490796360	3.89312733627228
H	20.63858613637650	6.08988452390421	3.42582316951202
C	20.55493233329382	4.64099630686709	5.02846186041554
H	19.62382378376810	5.02577112473353	5.44443345647639
C	21.16729340822188	3.54269983927697	5.62853723055189
C	19.31671526185175	0.33336756725477	0.15614153258124
C	19.90131888088784	1.71079083715298	-1.58892330824907
H	19.86209827046858	2.60517547108481	-2.19809635331846

C	20.60346946373083	0.55450836395729	-1.73735794356979
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C	18.28255875668328	2.55795558077590	0.13484603149088
C	18.86659736838827	3.63202792973988	0.80838693043278
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C	16.65644394938960	4.44515744038076	1.36929397601359
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C	16.08286960094445	3.35876647032247	0.70364563136037
H	14.99950924298336	3.23888359384828	0.67994075575194
C	16.89606746641581	2.40780027839369	0.08639539041485
C	20.79313666803949	-1.55081231630382	-0.39448862325587
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C	22.17526658001546	-1.73695816559958	-0.47755173677443
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N	15.39120949435817	-2.69735732978935	5.63181056591351
N	23.09051106862369	-0.19148733643675	6.31945699290573
N	22.90513850591636	1.83962489679848	5.62970257239910
N	19.11796408513624	1.55235773334709	-0.44792464809495
N	20.22775399803549	-0.27688145658271	-0.68258285356276
P	18.77395360829301	-0.38352844947824	6.58838059526002
P	19.59862792347383	-1.87642940995649	5.12375924605559
P	18.58530479186575	-2.14055742672265	3.07198307979964
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P	17.41702215370523	1.17523401185953	3.23913667913362
P	18.37523890476776	1.41700833769066	5.32278604353547
P	19.82644251442610	1.44207062096850	3.30961107431588
P	20.65983846461906	-0.79422403563748	3.21532037608960
Ni	17.42190617432741	-0.77618097029382	4.74719940518499
Ni	20.42301204277537	0.31646785812802	5.18301536123647
Ni	18.90053691482148	-0.11179748992615	1.95645240798967
H	23.80530397993504	3.16011491033143	3.49819136842266
H	20.72802608689189	3.05706518485942	6.49796923873971
H	21.43376673797481	-0.94078233671742	8.23718982918707
H	22.81677649571533	-0.90584900640570	-0.77205161431441
H	15.50049256439546	0.54373035901583	8.57396137632277
H	14.65572086543162	1.11724670875649	4.40018685396652
H	14.66414991851153	-3.94673138066876	3.40178425259686
H	16.47239963038953	1.53390329608760	-0.40751429272022
H	19.95142090670077	3.69344855566639	0.88732866987242
H	23.92578140320175	-2.36708210221906	5.04310837106661
H	18.88479440989488	-2.41356269133135	0.09293316892683
H	17.66611289440625	-3.75694758665421	6.4700257288058

Chapter 4

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

S1 Additional Experiments

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.
$^{31}P\{^1H\}$ (162 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 (Figure S68).

Detection of 1b

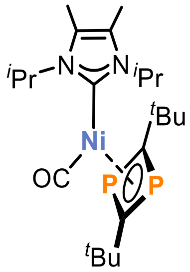
To a solution of [(IMes)Ni(CO)$_3$] (20.0 mg, 0.045 mmol, 1.0 eq.) in C_6D_6 (0.5 mL) was added AdCP (8.5 mg, 0.048 mmol, 1.1 eq.). The reaction mixture was stirred at ambient temperature for 18 hours. Subsequently, the sample was subjected to NMR spectroscopic studies.
$^{31}P\{^1H\}$ (162 MHz, 300 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 Figure S69 and Figure S70).

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 S71.

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.
$^{31}P\{^1H\}$ (162 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 S72).
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 below and 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 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} (162 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 S75). The main signal at δ = −52.4 ppm most probably corresponds to complex **6**.

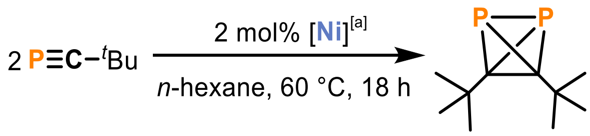
Upon further storage of the supernatant solution at −30 °C, more crystals of **6** along with some dark brown crystals of **7** were obtained. The crystals of **7** were suitable for structure elucidation of by X-ray crystallography (see below). However, the small amount of crystals precluded further 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 Figure S76, Figure S77 and Figure S78.

S2 Catalyst Screening

The screening reactions for the dimerisation 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 S2. Screening of different nickel catalysts for the dimerisation of *t*BuCP.



Entry	Catalyst	Yield [%] of **1a***
1	no catalyst	0
2	$[Ni(CO)_4]$	9
3	$[(i\text{Pr}_2\text{Im}^{\text{Me}})\text{Ni(CO)}_3]$	3
4	$[(\text{IMes})\text{Ni(CO)}_3]$	67
5	$[(\text{IPr})\text{Ni(CO)}_3]$	49
6	$[\{(\text{IMes})\text{NiP(CO)}\}_2]$	57
7	$[\text{IMesNi(vinyl-TMS)}_2]$	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.[a] For the dinuclear complex $[\{(\text{IMes})\text{NiP(CO)}\}_2]$ only 1 mol% was used.

S3 Kinetic Data

Two methods were required to extract the relevant kinetic information of the dimerisation 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.

A. 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 S34). 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]

Figure S34. Picture of the set-up used for kinetic analysis with air sensitive samples in an argon-filled glove box.

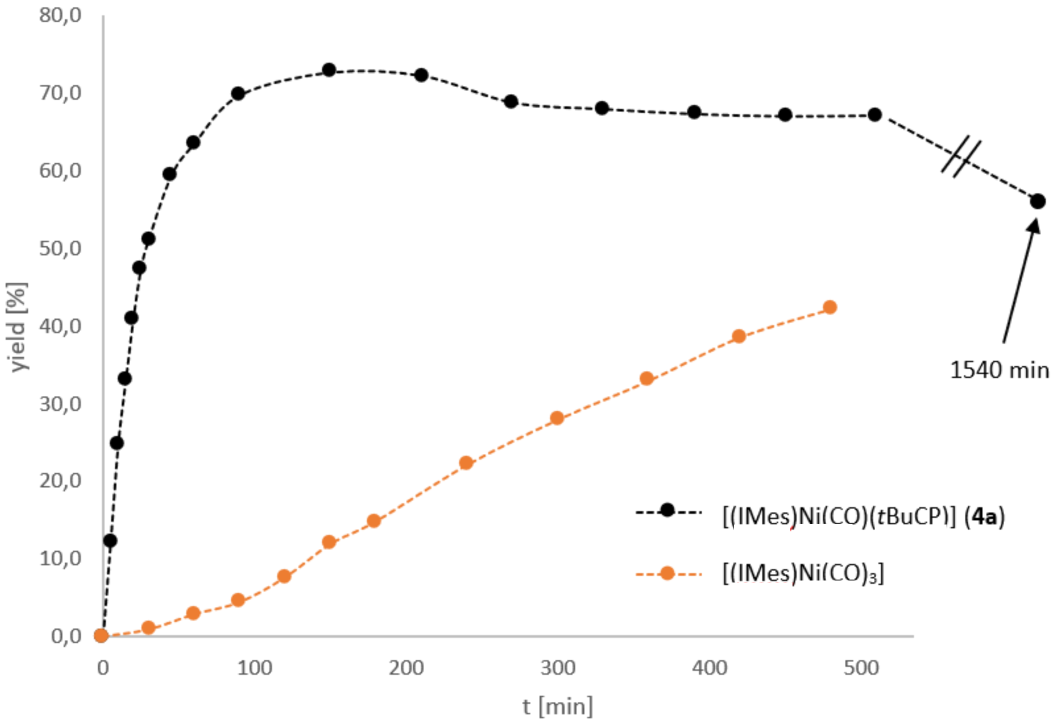


Figure S35. Plot of yield [%] of **1a** over time for the dimerisation of *t*BuCP using nickel-catalysts **4a** (black, 2mol%) and [(IMes)Ni(CO)3] (orange, 2 mol%) for the dimerisation of *t*BuCP. Yields were determined by GC-FID using *n*-pentadecane as internal standard.

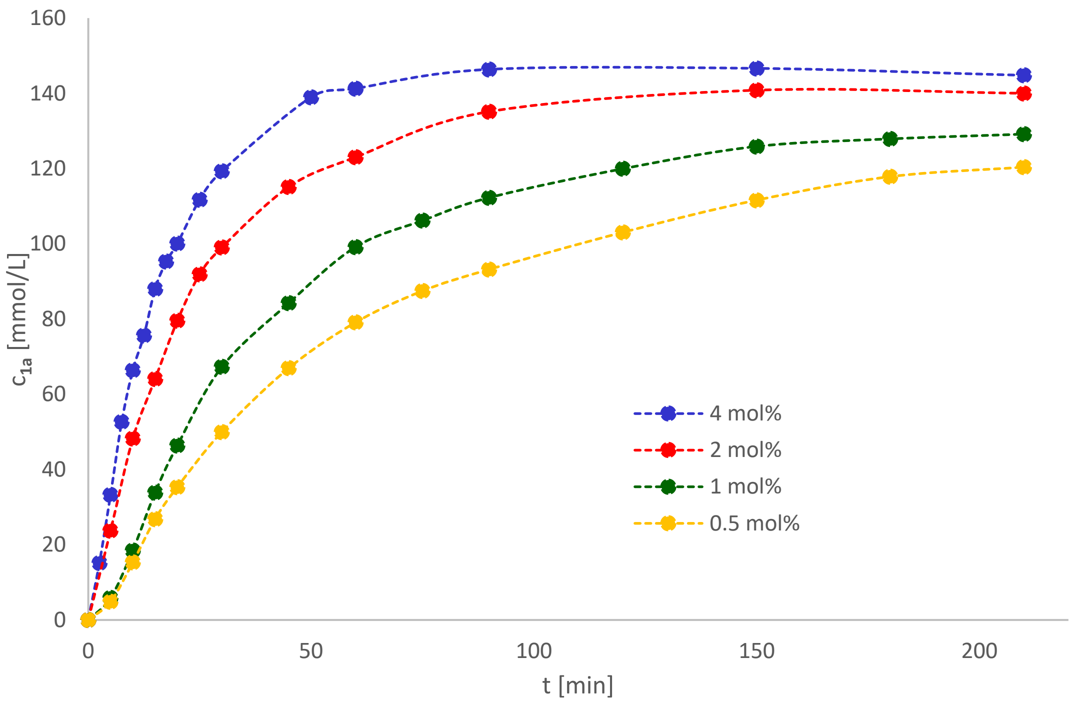


Figure S36. Plots of the concentration of **1a** over time using 0.5-4 mol% of **4a** as catalyst. Concentrations were determined by GC-FID using *n*-pentadecane as internal standard.

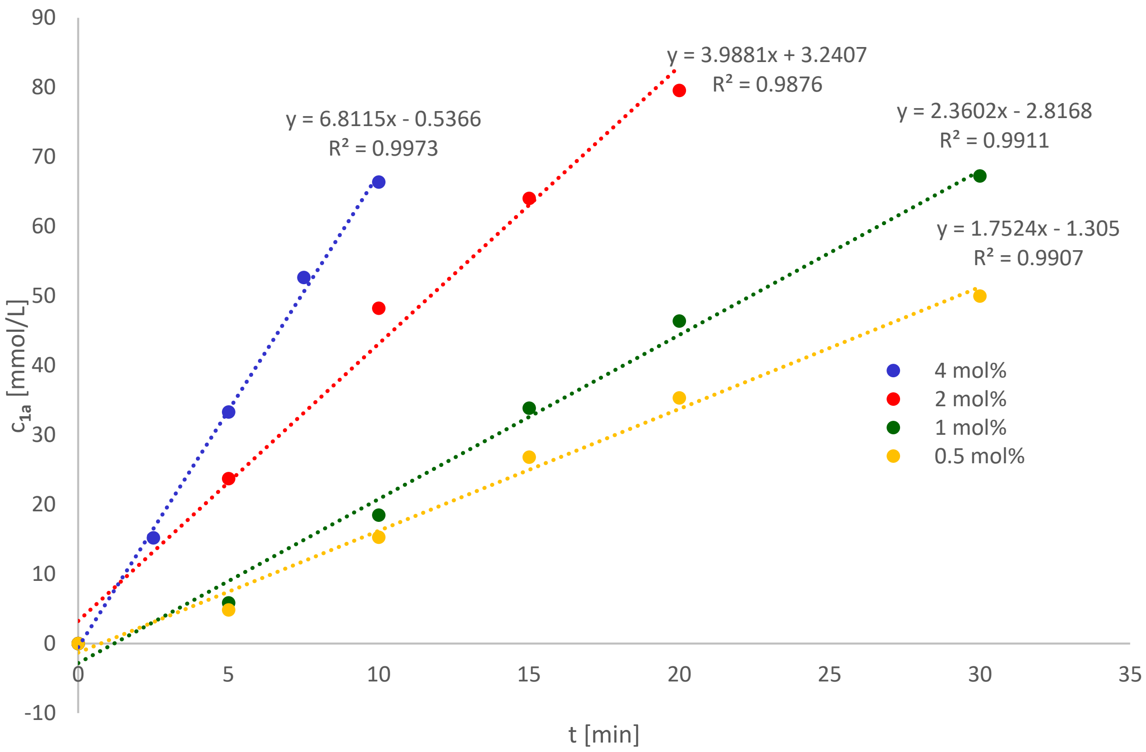


Figure S37. Plots of the concentration of **1a** over time using 0.5-4 mol% of **4a** as catalyst as used for determination of k_{obs} including lines of best fit.

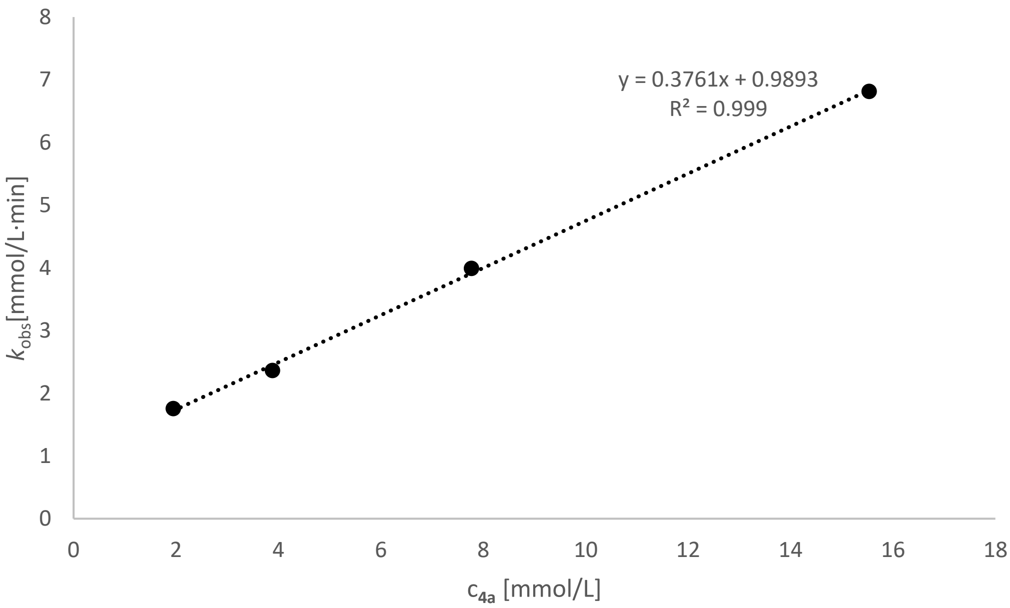


Figure S38. Plot of k_{obs} versus c_{4a} including line of best fit.

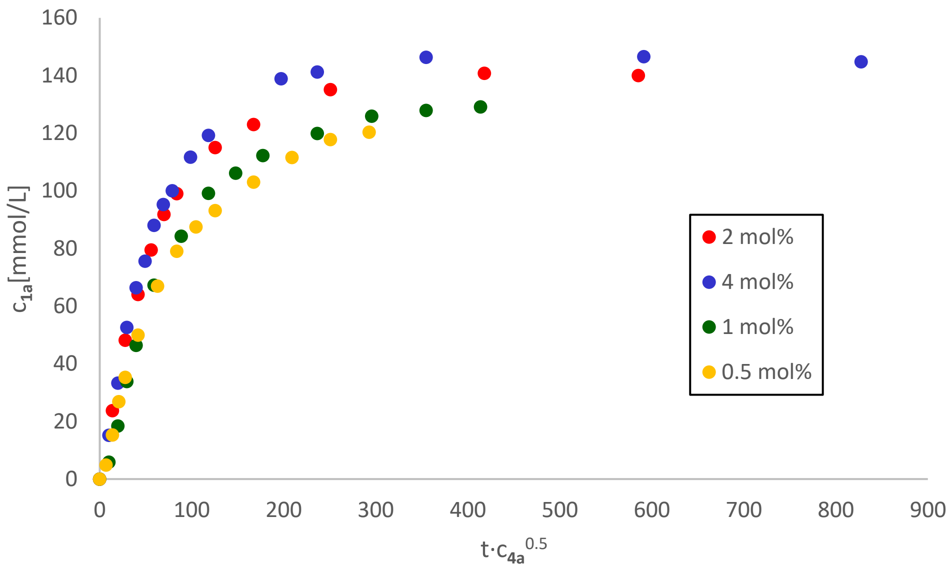


Figure S39. Time normalization plot for order of **4a** = 0.5. A poor overlay of the data points is observed, which suggests that the reaction order of 0.5 for **4a** is not in agreement with the kinetic data.

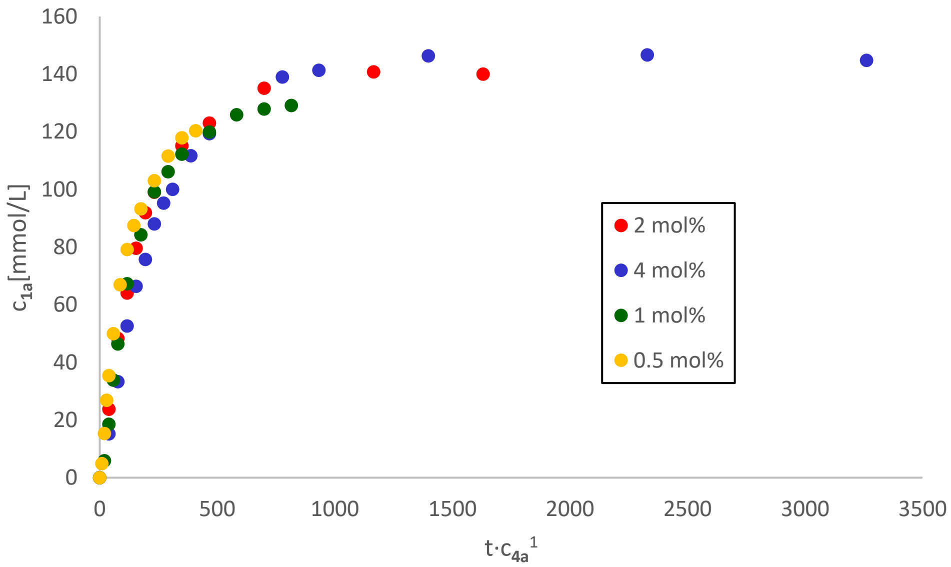


Figure S40. Time normalization plot for order of **4a** = 1. A good overlay of the data points suggests that the reaction order of 1 for **4a** is in agreement with the kinetic data.

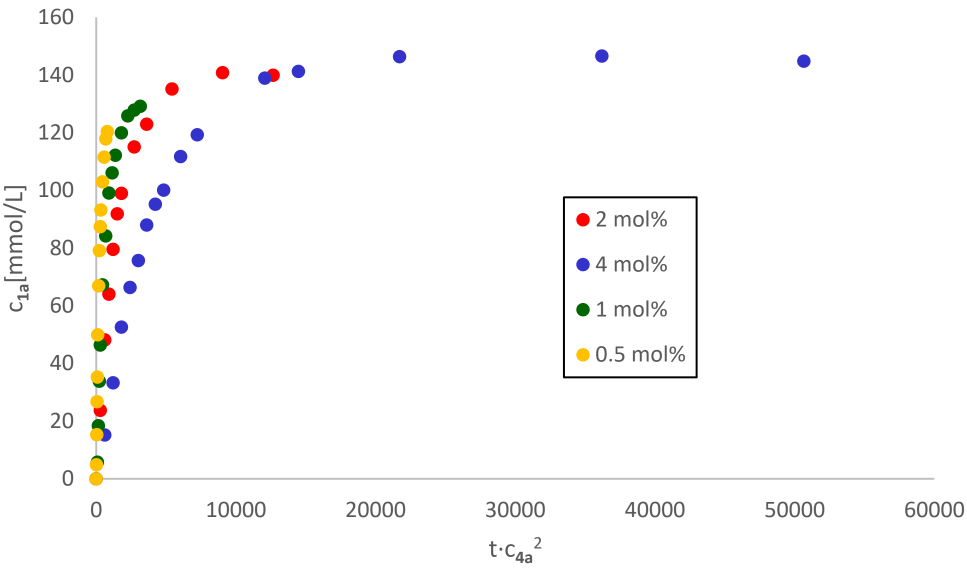


Figure S41. Time normalization plot for order of **4a** = 2. A poor overlay of the data points is observed, which suggests that the reaction order of 2 for **4a** is not in agreement with the kinetic data.

B. 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.

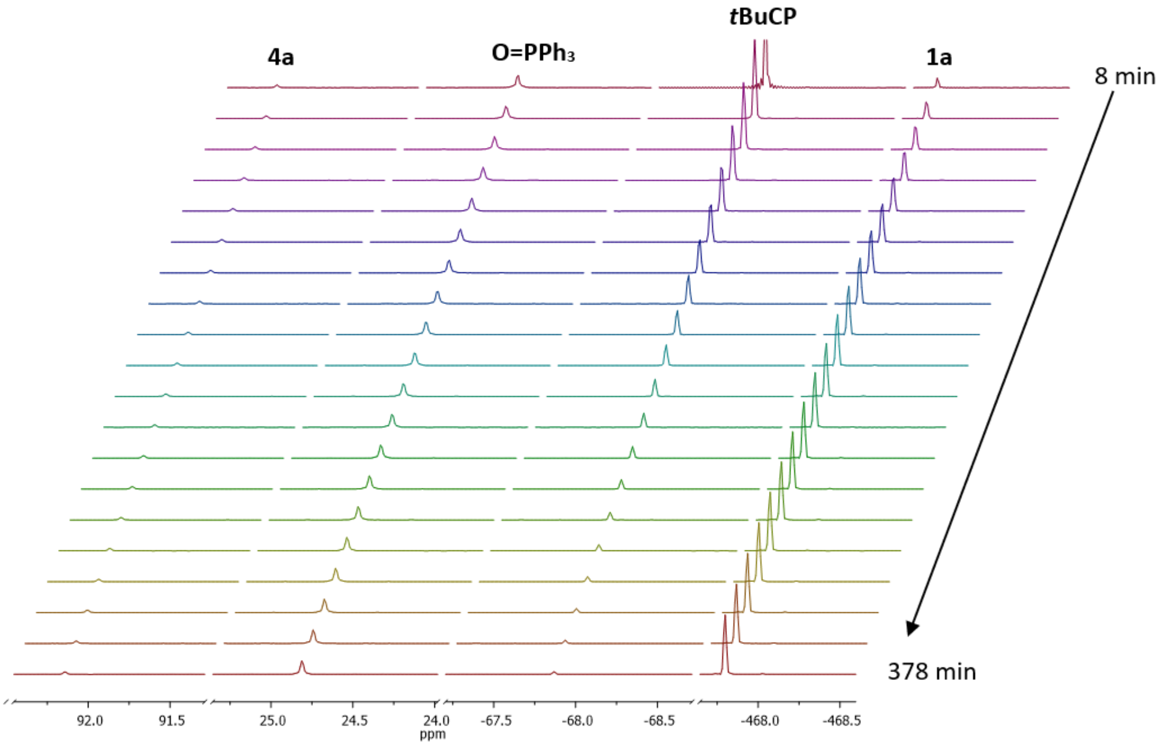


Figure S42. Stacked plot of $^{31}P\{^1H\}$ NMR spectra (161.98 MHz, 333 K, C_6D_6) for the reaction of *t*BuCP (0.1 mL, 2.6 M in $O(SiMe_3)_2$, 0.26 mmol) with catalyst **4a** (2 mol%) in C_6D_6.

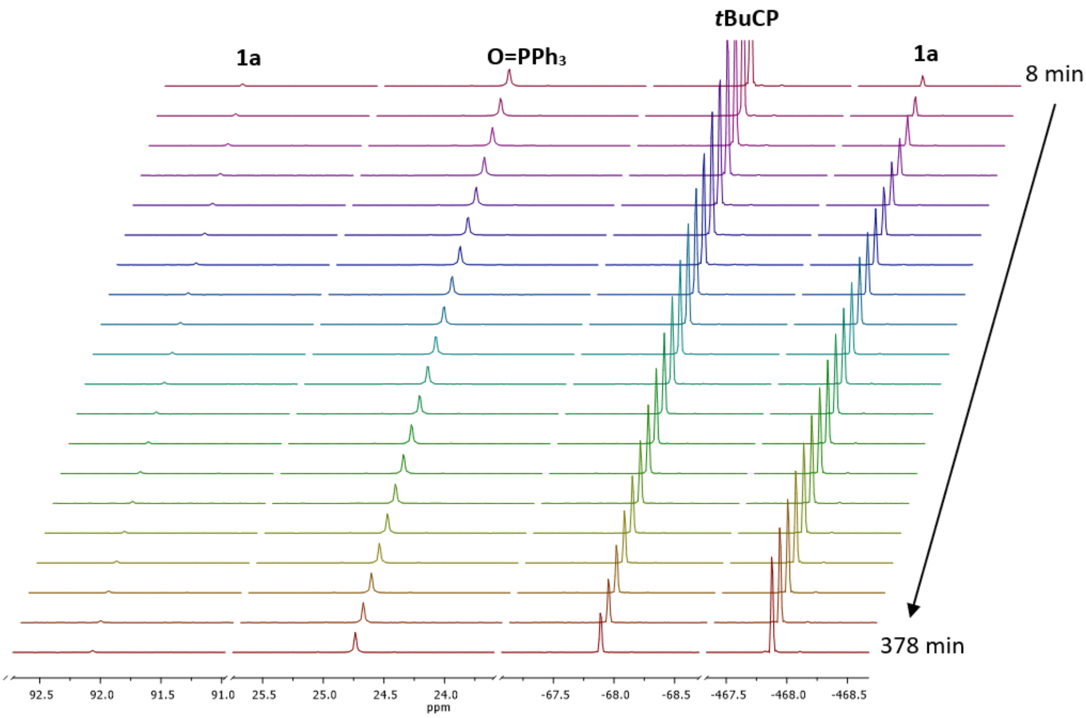


Figure S43. Stacked plot of $^{31}P\{^1H\}$ NMR spectra (161.98 MHz, 333 K, C_6D_6) for the reaction of *t*BuCP (0.1 mL, 2.6 M in $O(SiMe_3)_2$, 0.26 mmol) with catalyst **4a** (1 mol%) in C_6D_6.

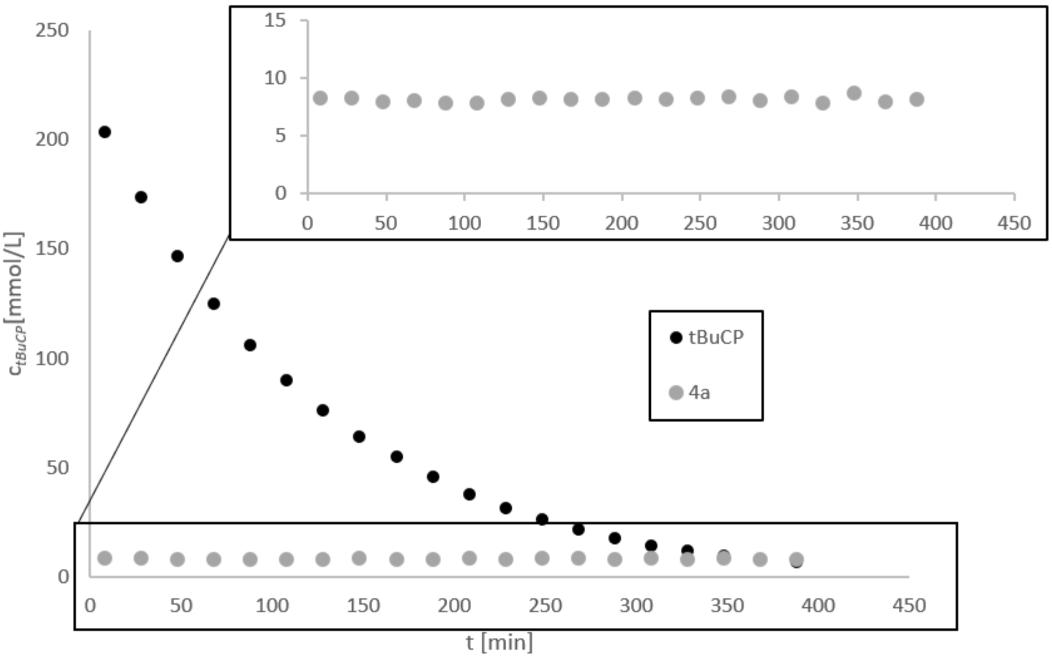


Figure S44. Example plot of c(*t*BuCP) [mmol/L] over time using 2 mol% of **4a** as catalyst. c(*t*BuCP) was determined via integration versus $O{=}PPh_3$ as internal standard.

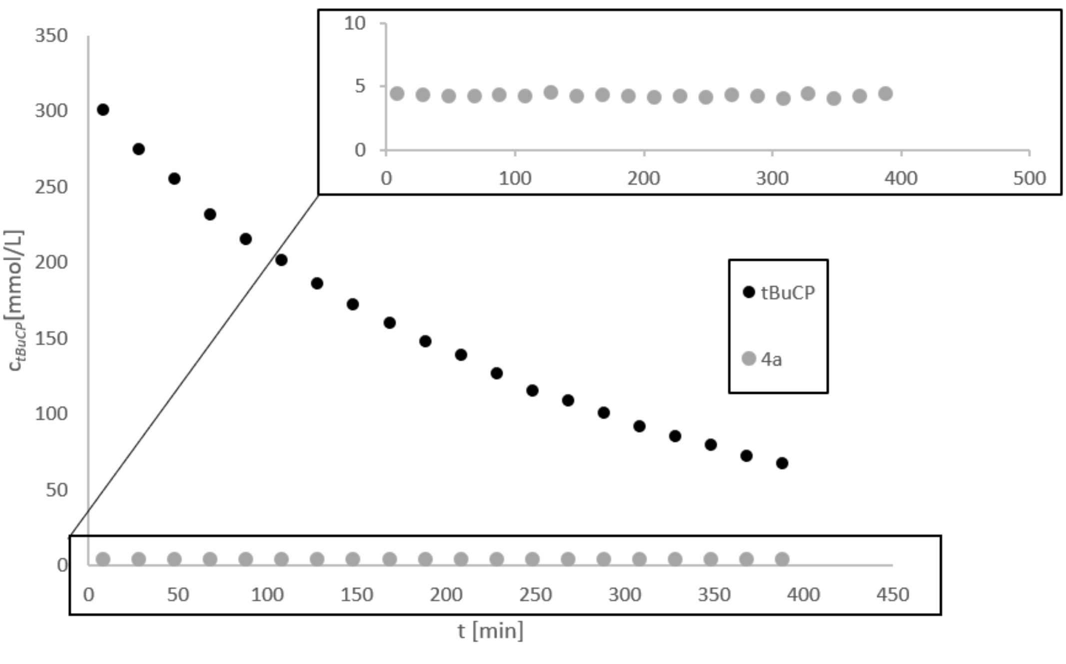


Figure S45. Example plot of c(*t*BuCP) [mmol/L] over time using 1 mol% of **4a** as catalyst. c(*t*BuCP) was determined via integration versus $O{=}PPh_3$ as internal standard.

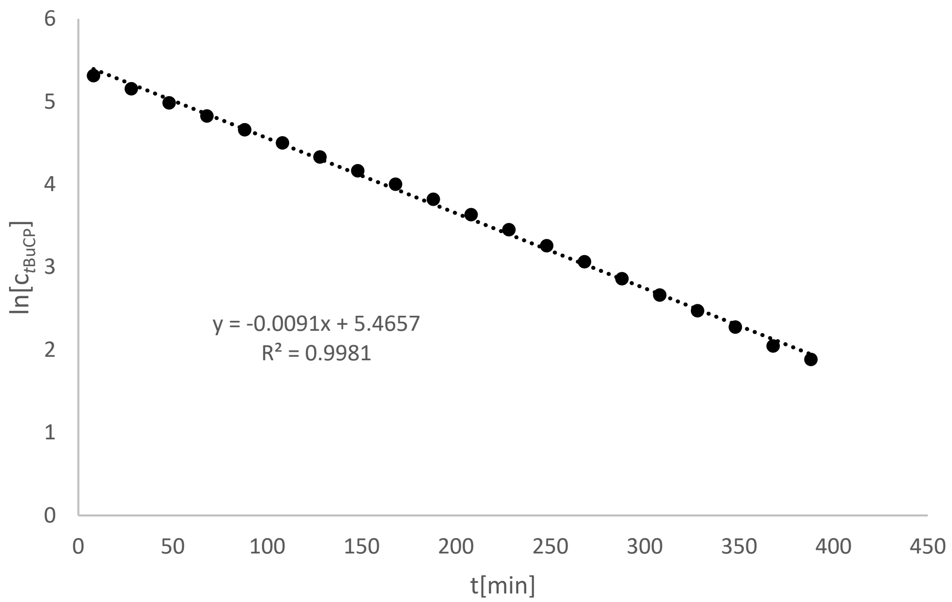


Figure S 46. Example plot of ln[c(*t*BuCP)] over time using 2 mol% of **4a** as catalyst.

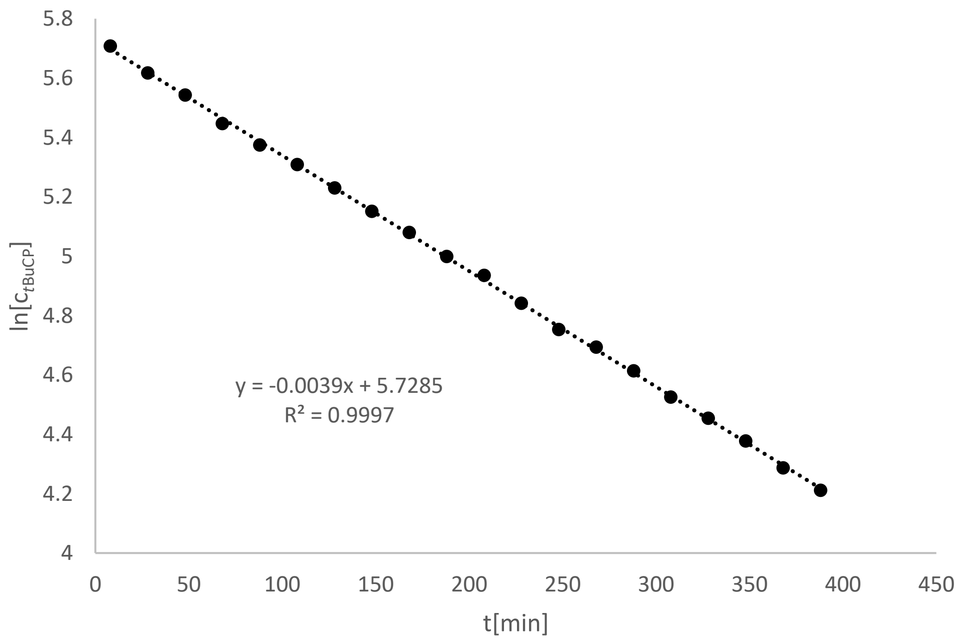


Figure S47. Example plot of ln[c(tBuCP)] over time using 1 mol% of **4a** as catalyst.

S4 NMR Spectra

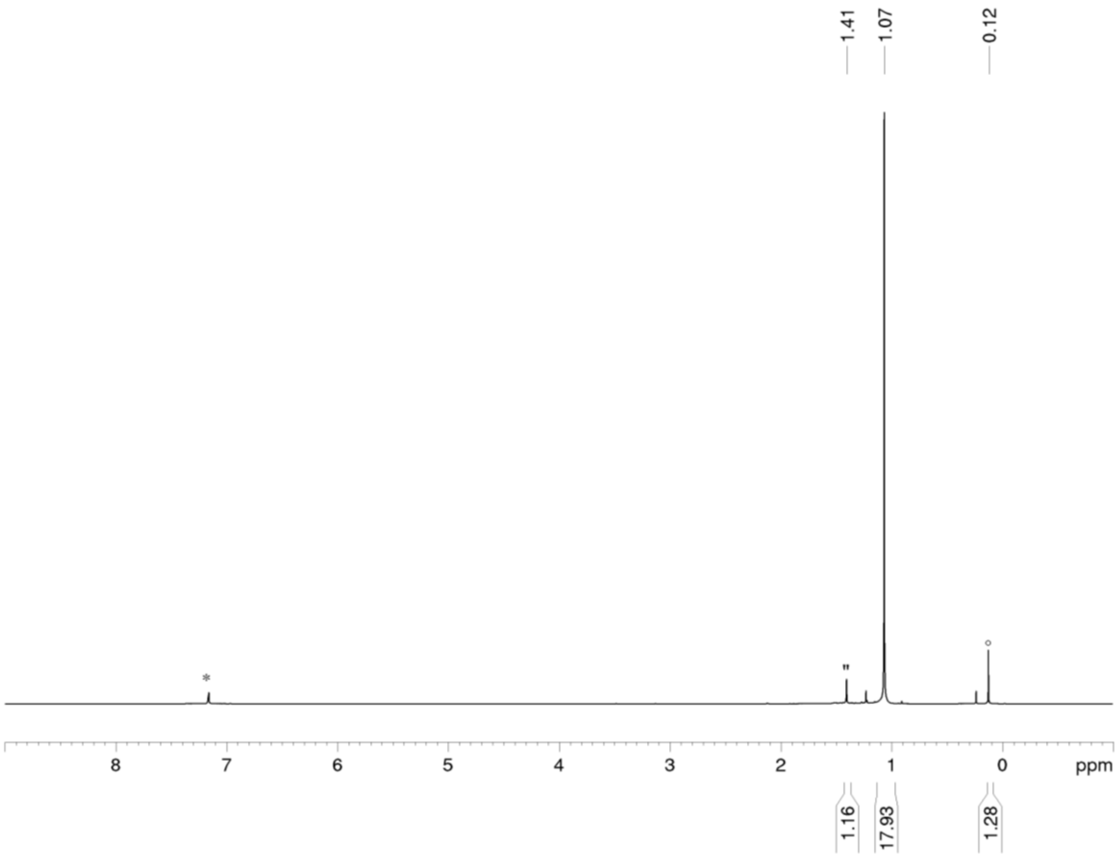


Figure S48. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **1a**; *C_6D_6, °$O(SiMe_3)_2$, ”**2a**.

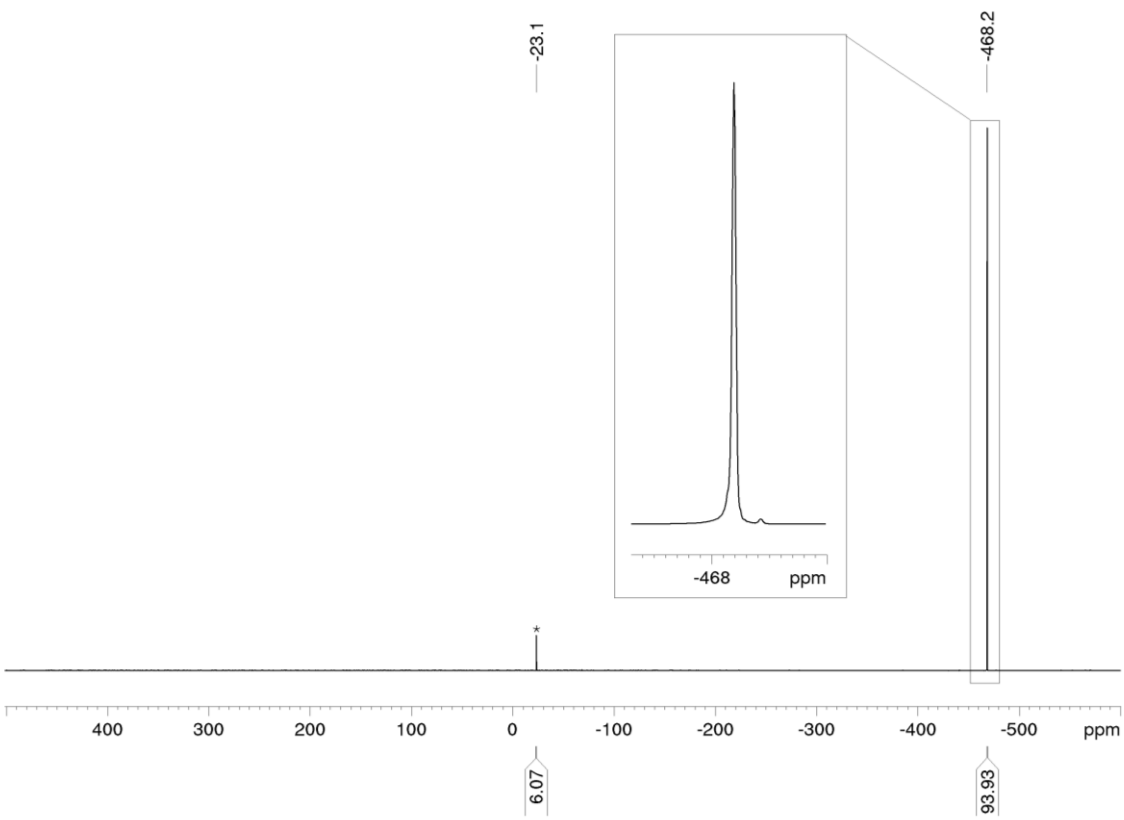


Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **1a**; ***2a**.

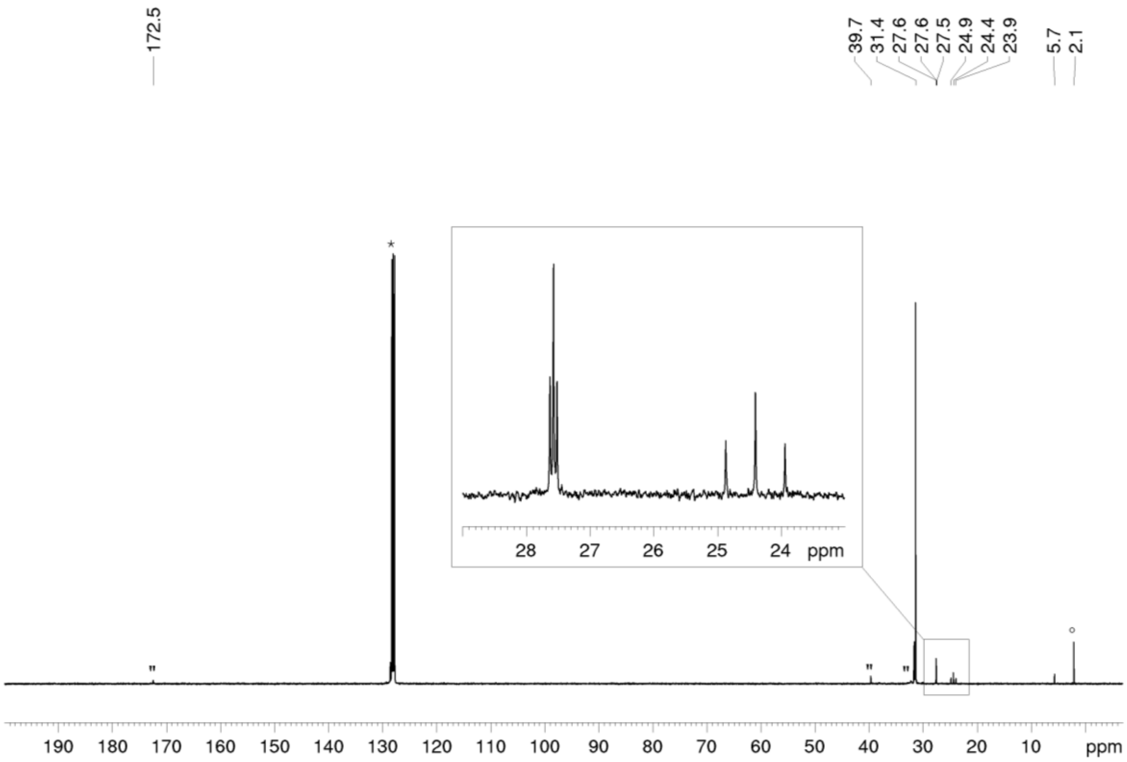


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **1a** *C_6D_6, °$O(SiMe_3)_2$, ″**2a**.

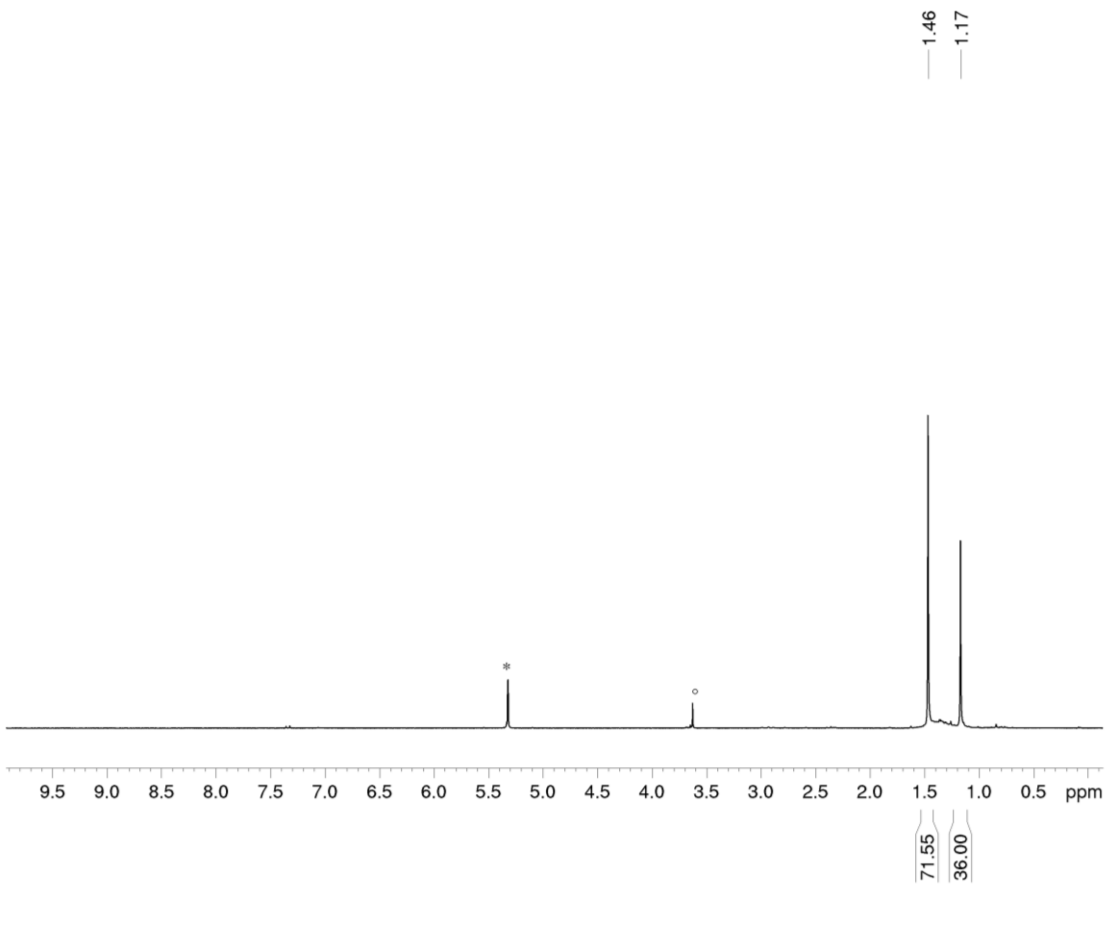


Figure S51. ^{1}H NMR spectrum (400 MHz, 300 K, CD_2Cl_2) of **3**; *CD_2Cl_2, ° unknown impurity.

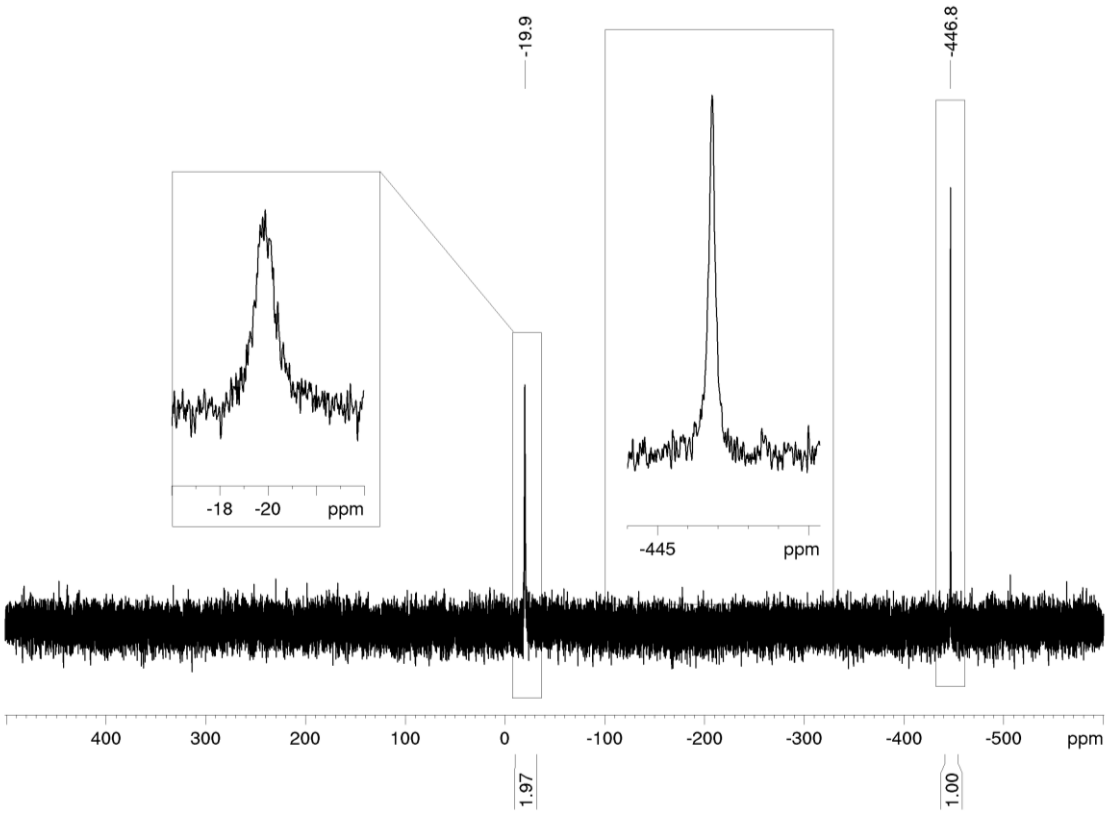


Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **3.**

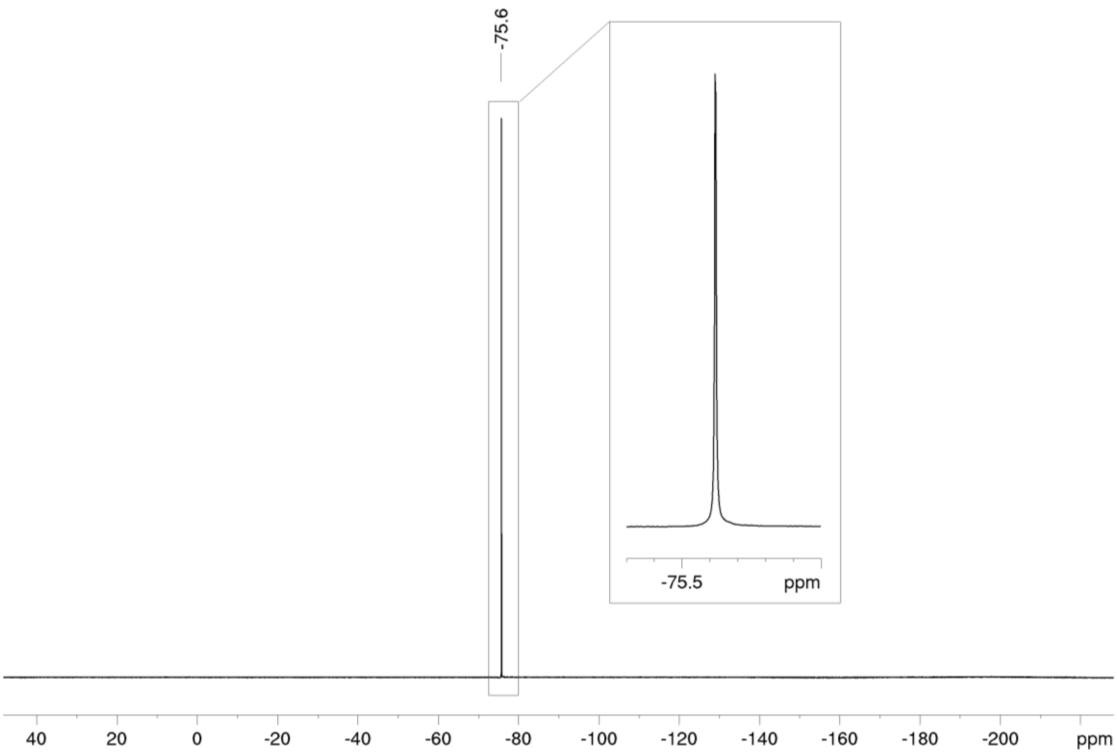


Figure S53. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz, 300 K, CD_2Cl_2) of **3**.

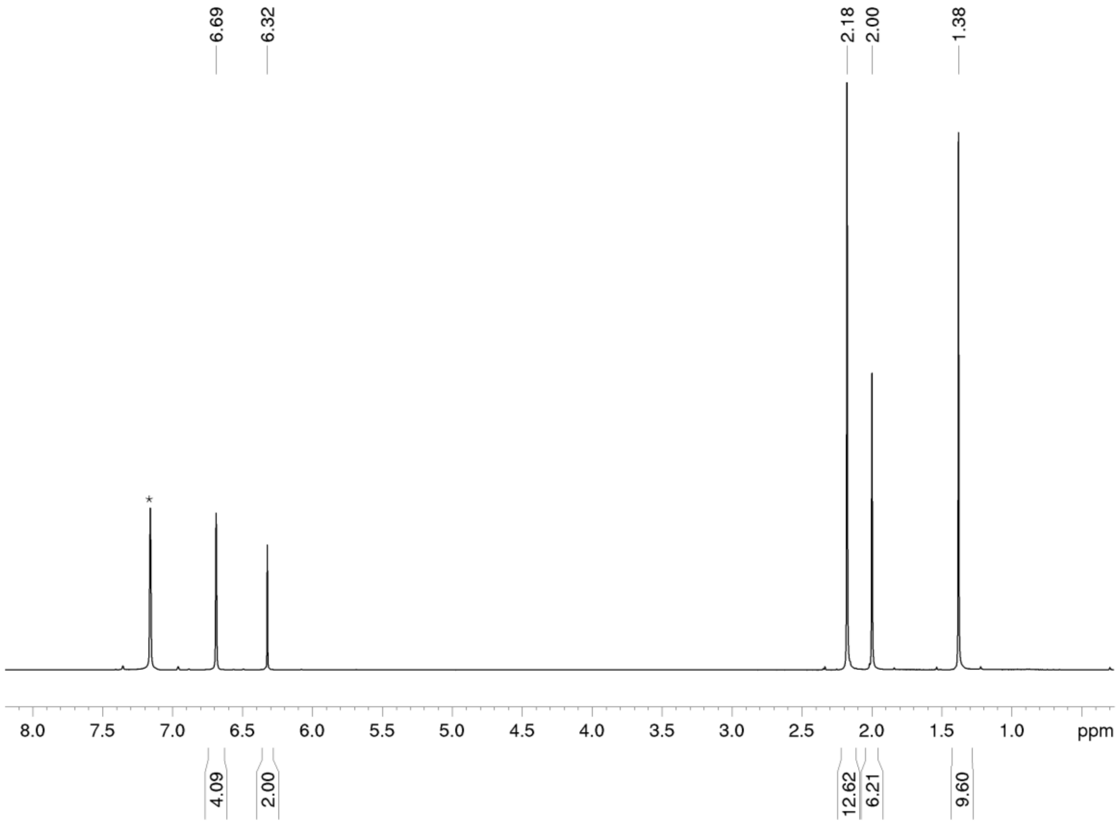


Figure S54. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **4a**; *C_6D_6.

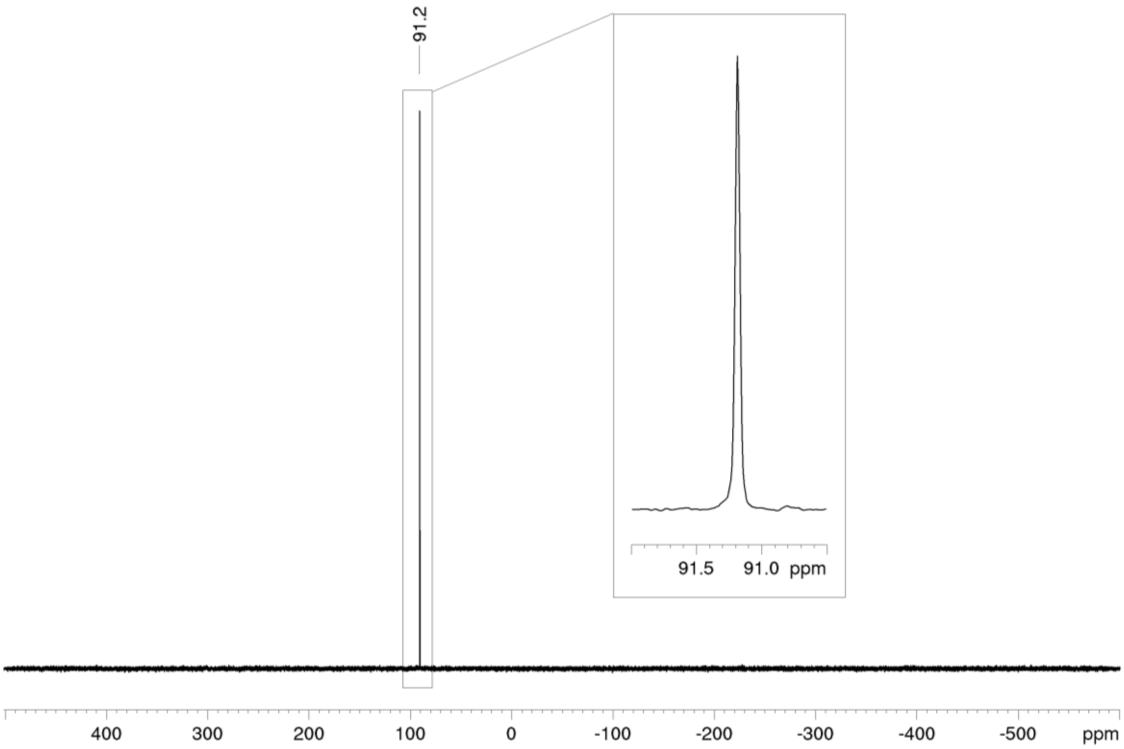


Figure S55. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **4a**.

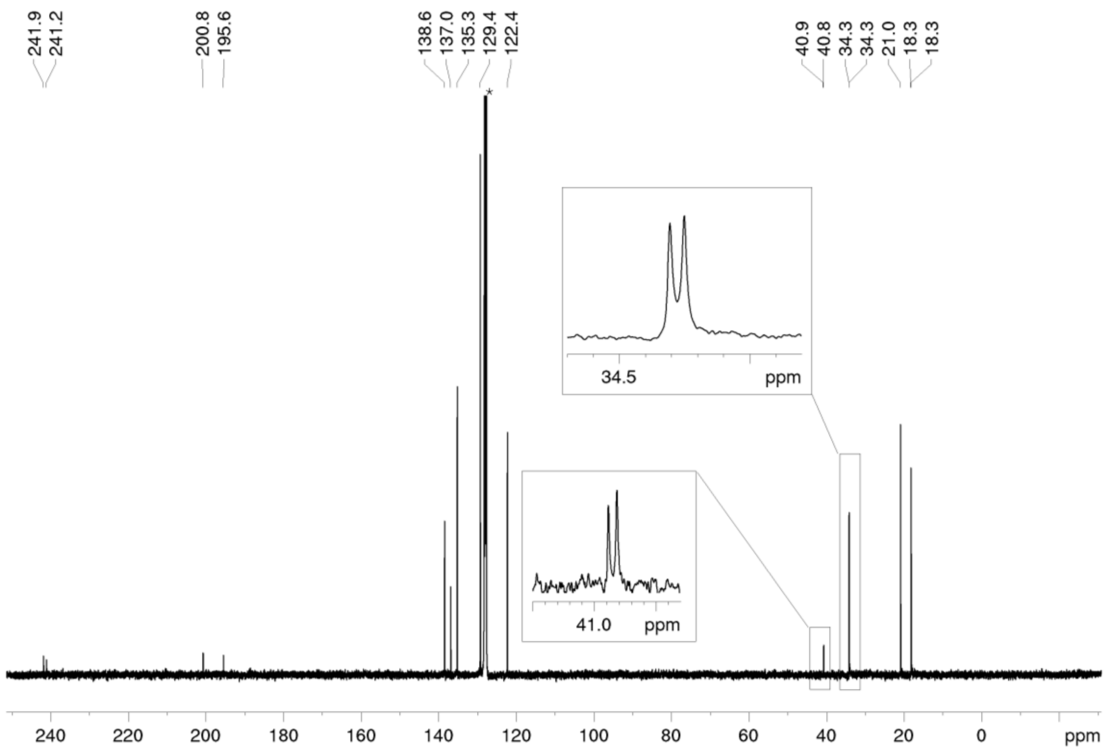


Figure S56. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **4a**; *C_6D_6.

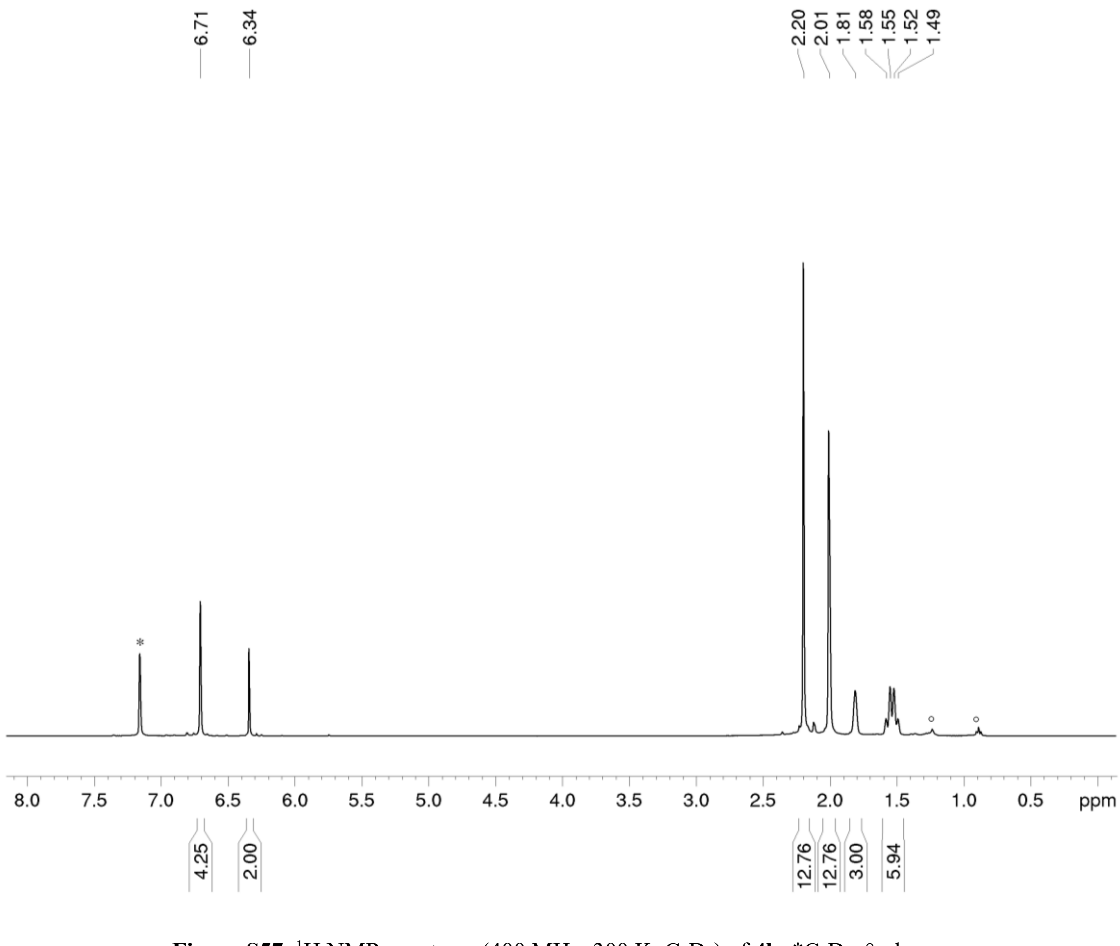


Figure S57. ^1H NMR spectrum (400 MHz, 300 K, C_6D_6) of **4b**; *C_6D_6, °*n*-hexane.

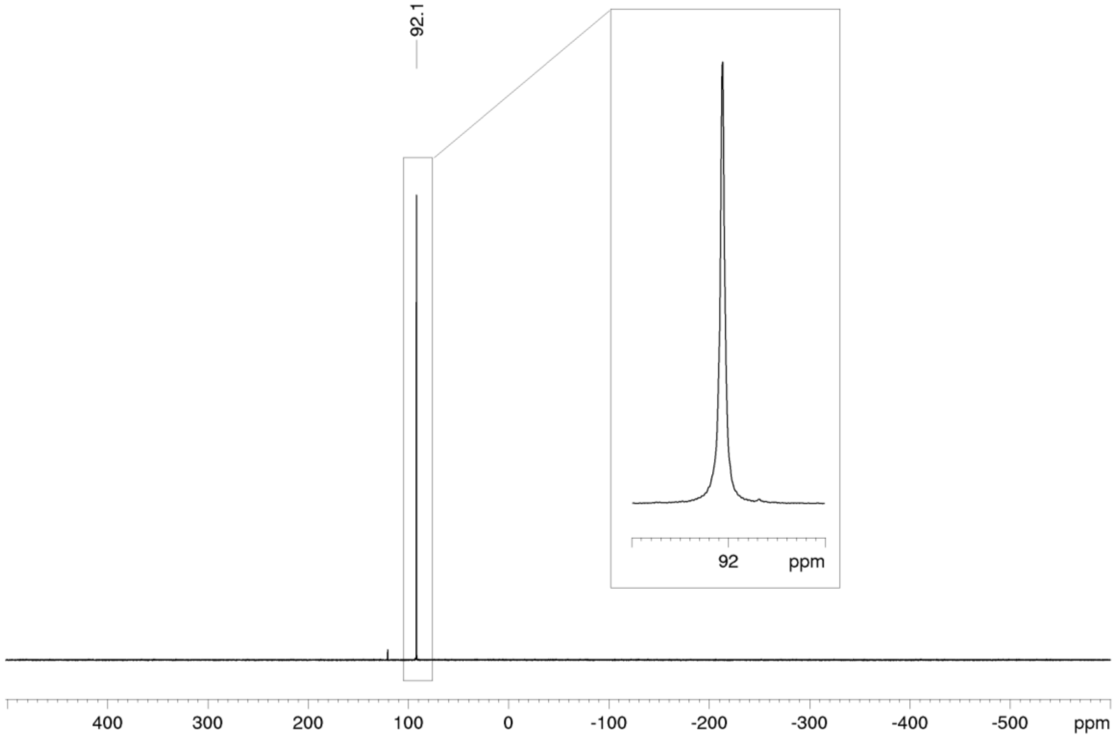


Figure S58. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **4b**.

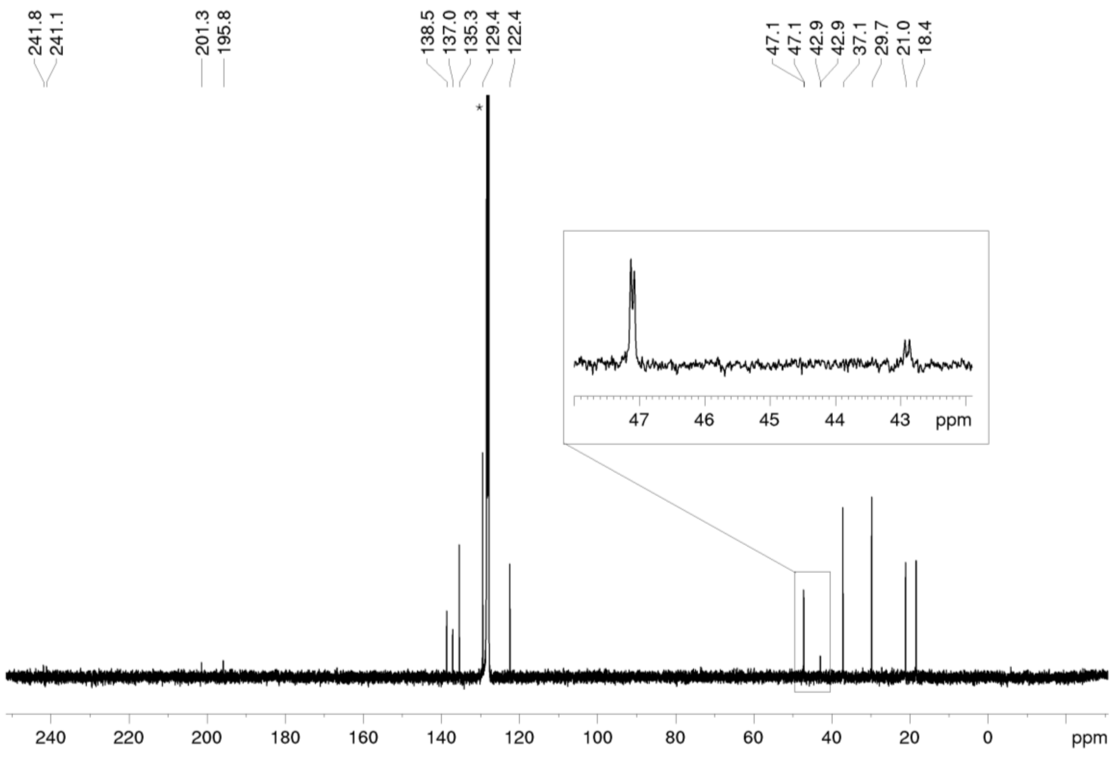


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **4b**; *C_6D_6

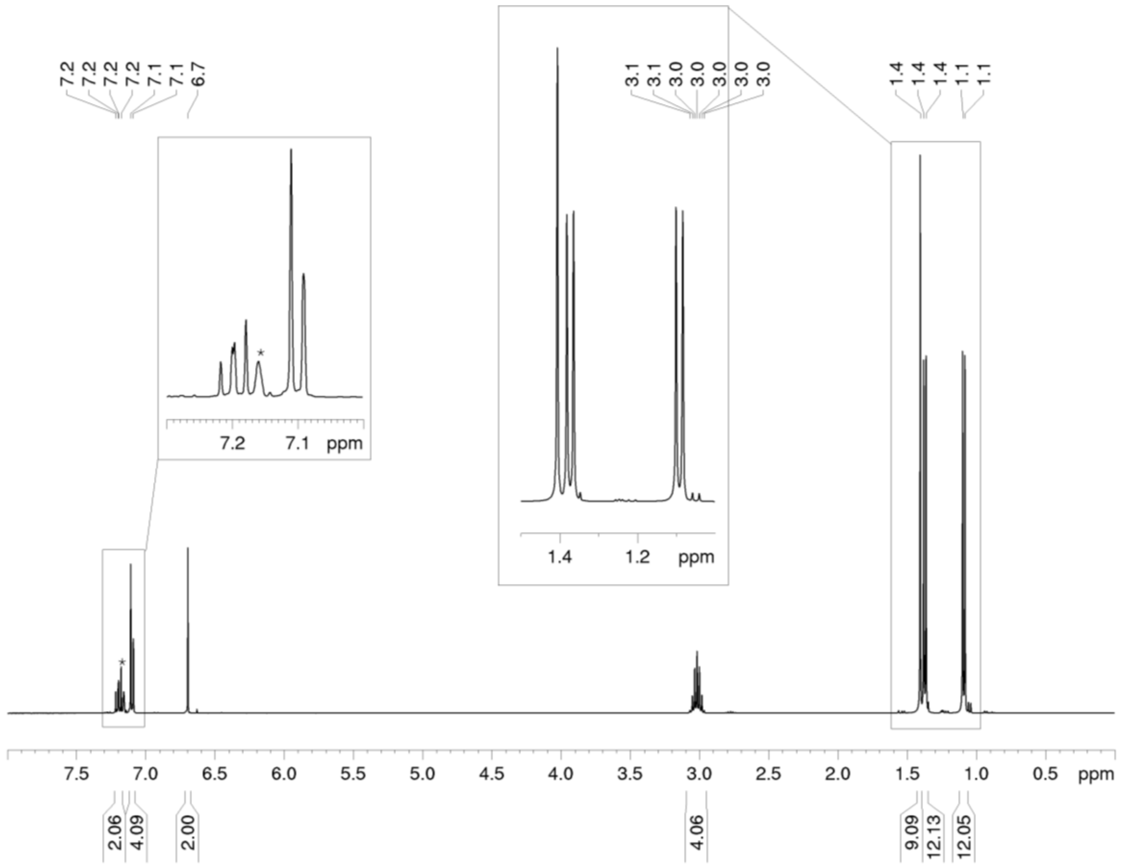


Figure S60. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **4c**; *C_6D_6.

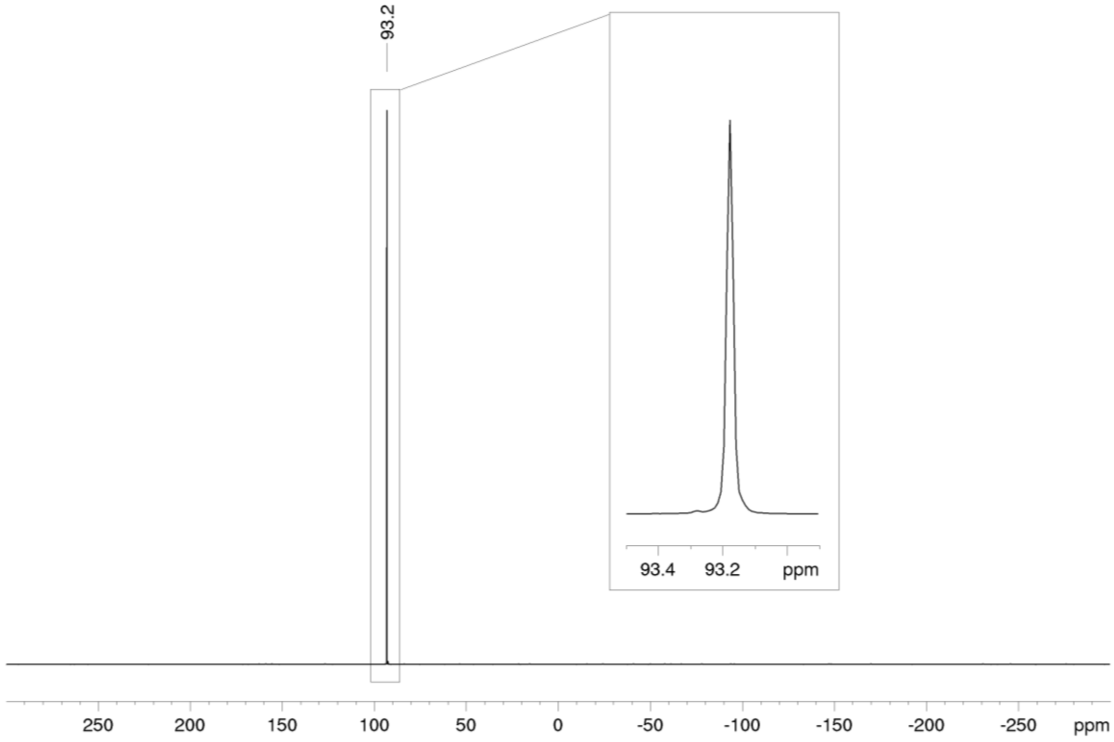


Figure S61. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **4c**.

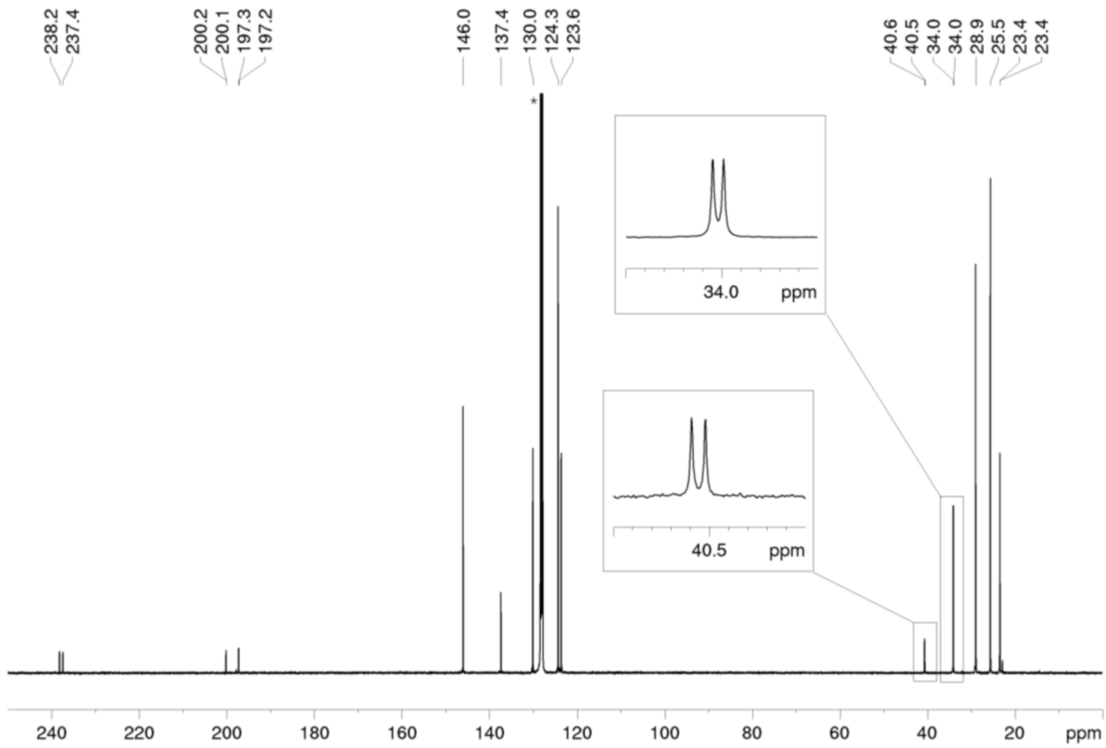


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **4c**; *C_6D_6

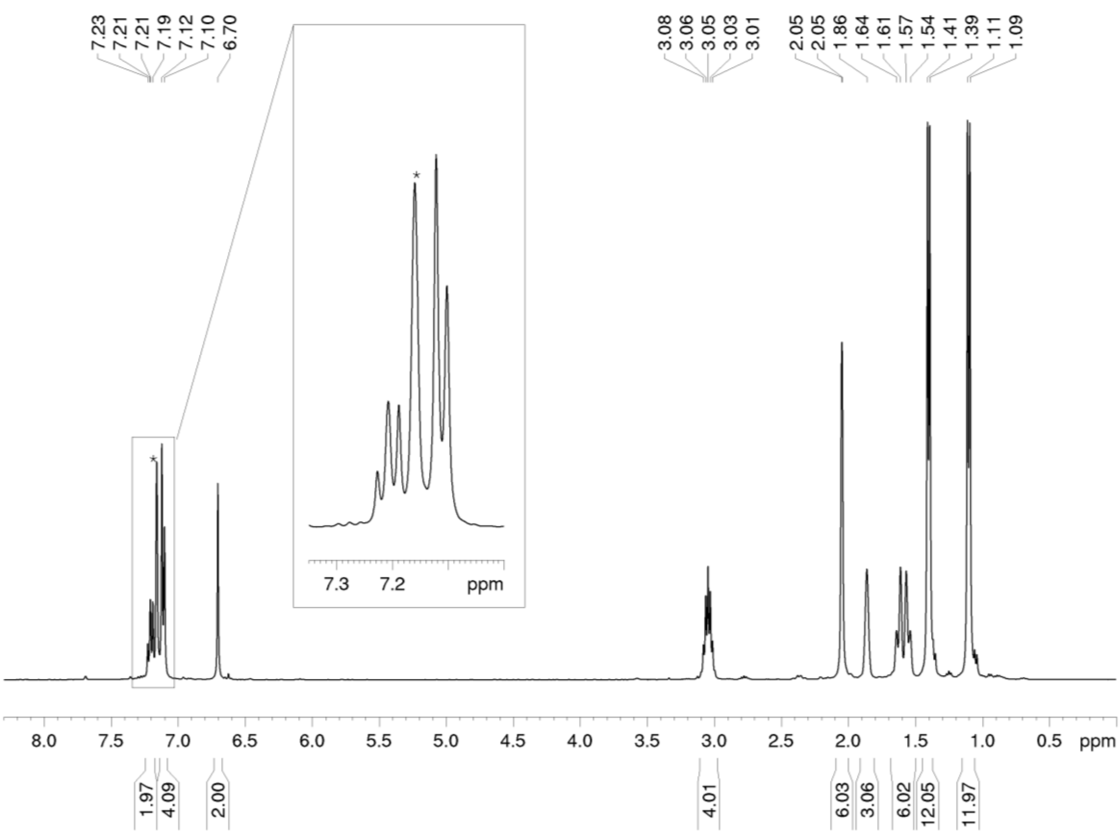


Figure S 63. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **4d**; *C_6D_6.

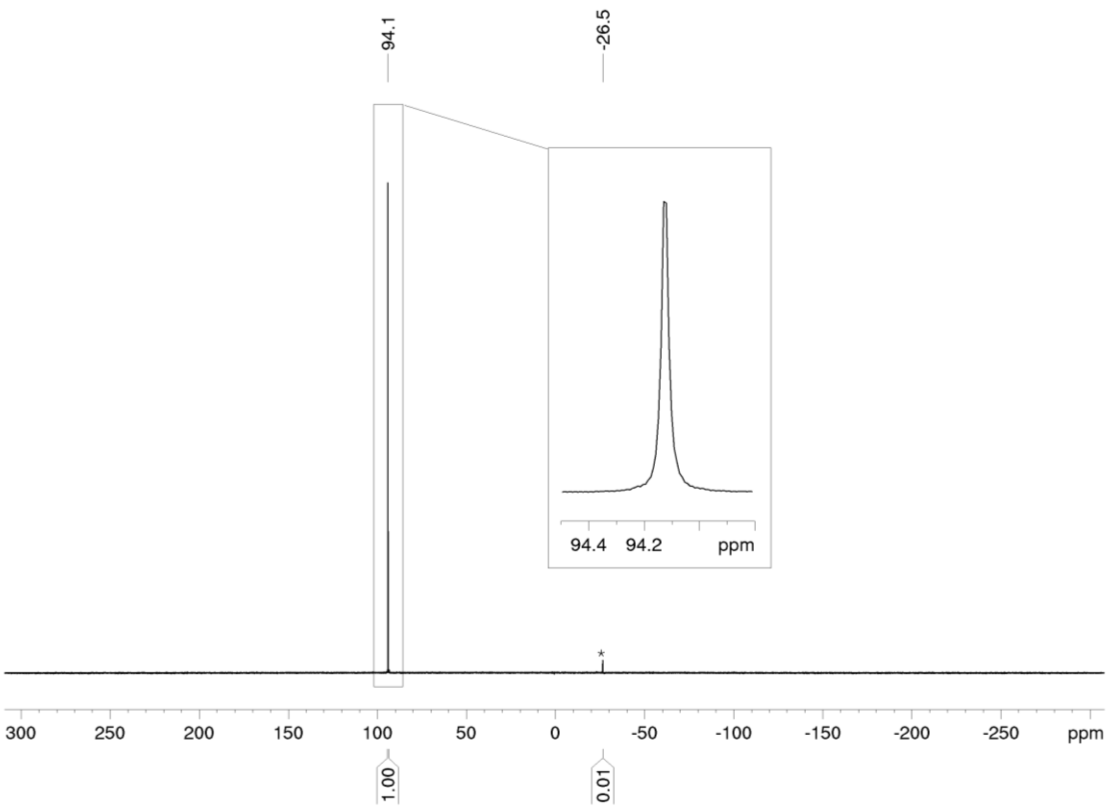


Figure S64. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **4d**; *minor impurity of (tBuCP)$_4$ **2b**.

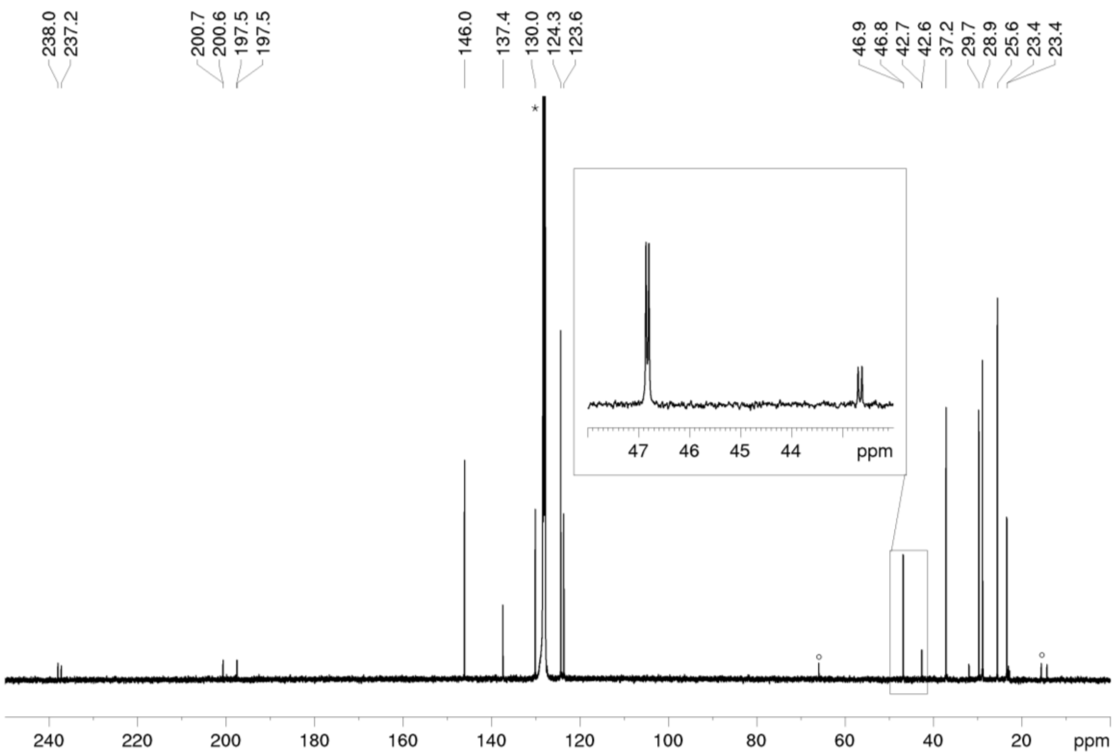


Figure S65. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **4d**; *C_6D_6, ° traces of Et_2O

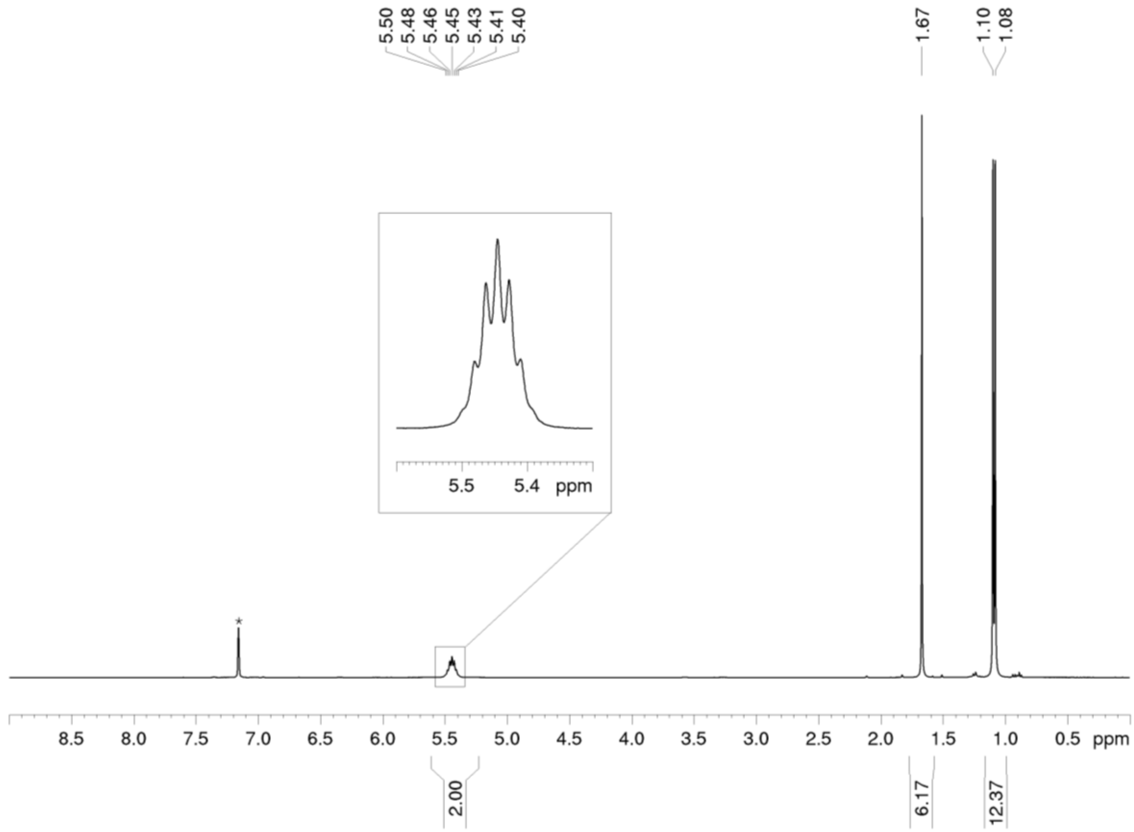


Figure S66. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of [(*i*Pr_2Im^{Me})$Ni(CO)_3$], *C_6D_6.

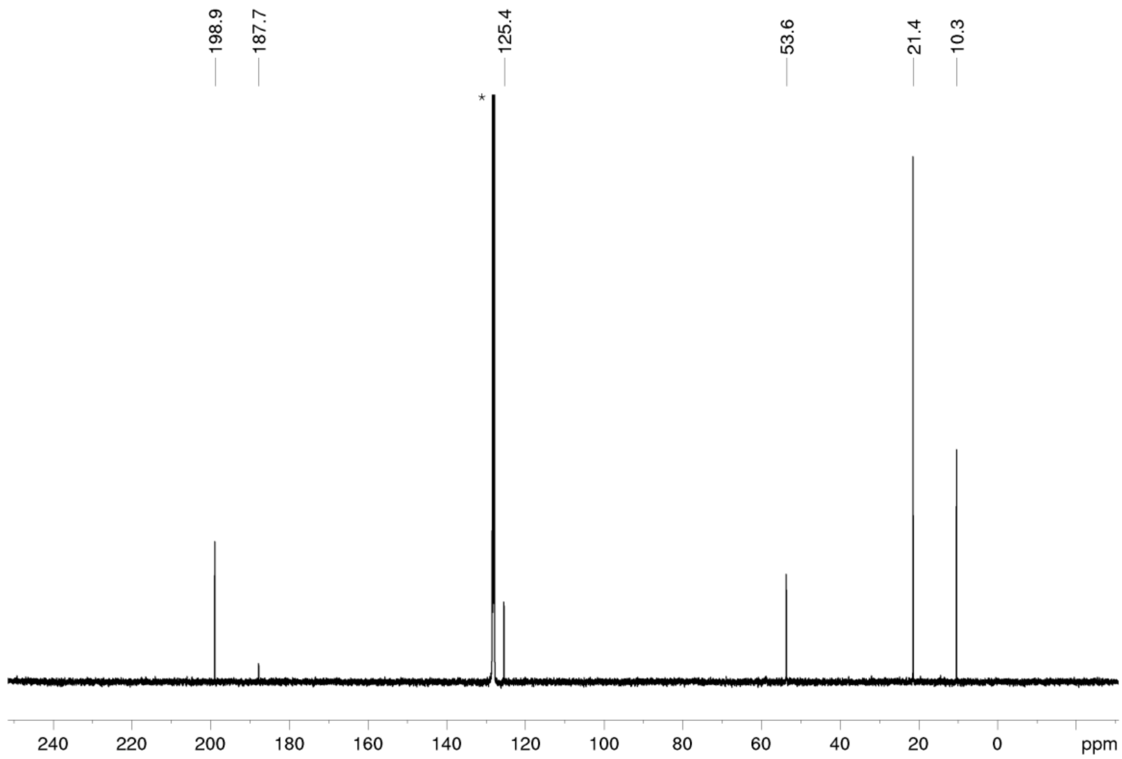


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of [(*i*Pr_2Im^{Me})$Ni(CO)_3$]; *C_6D_6.

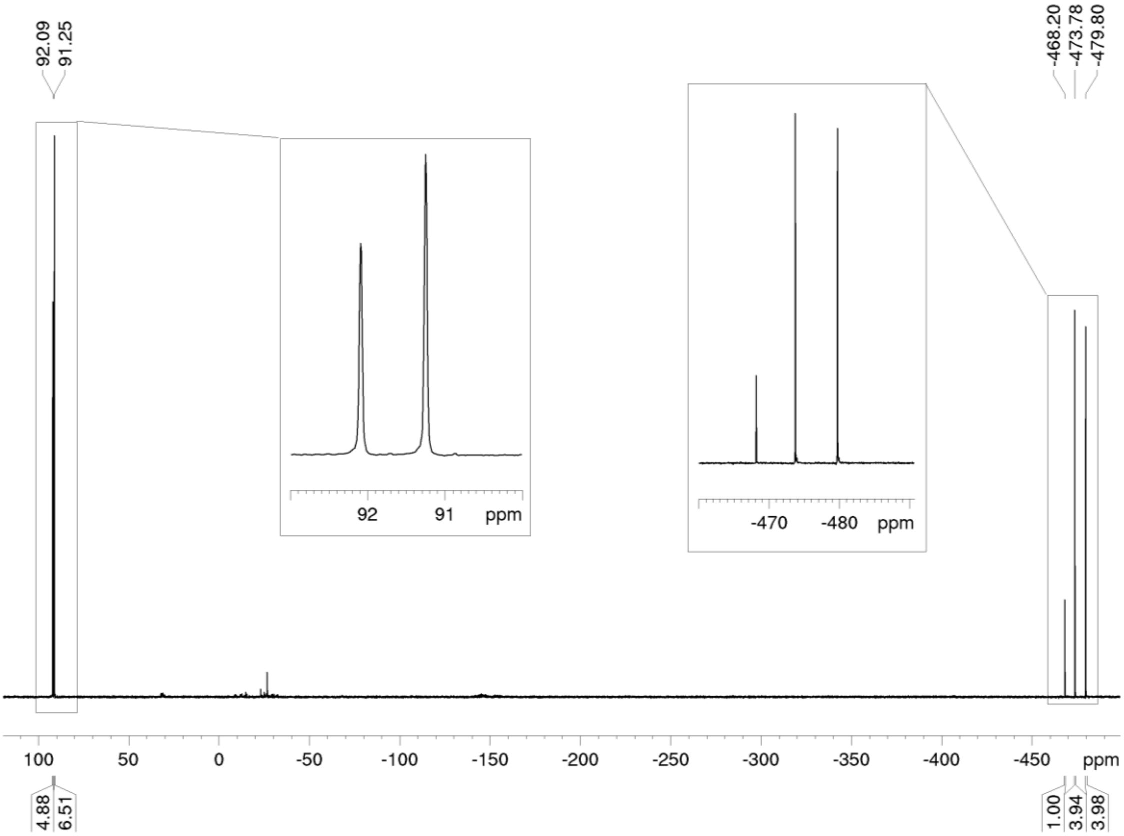


Figure S68. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **4a** with AdCP.

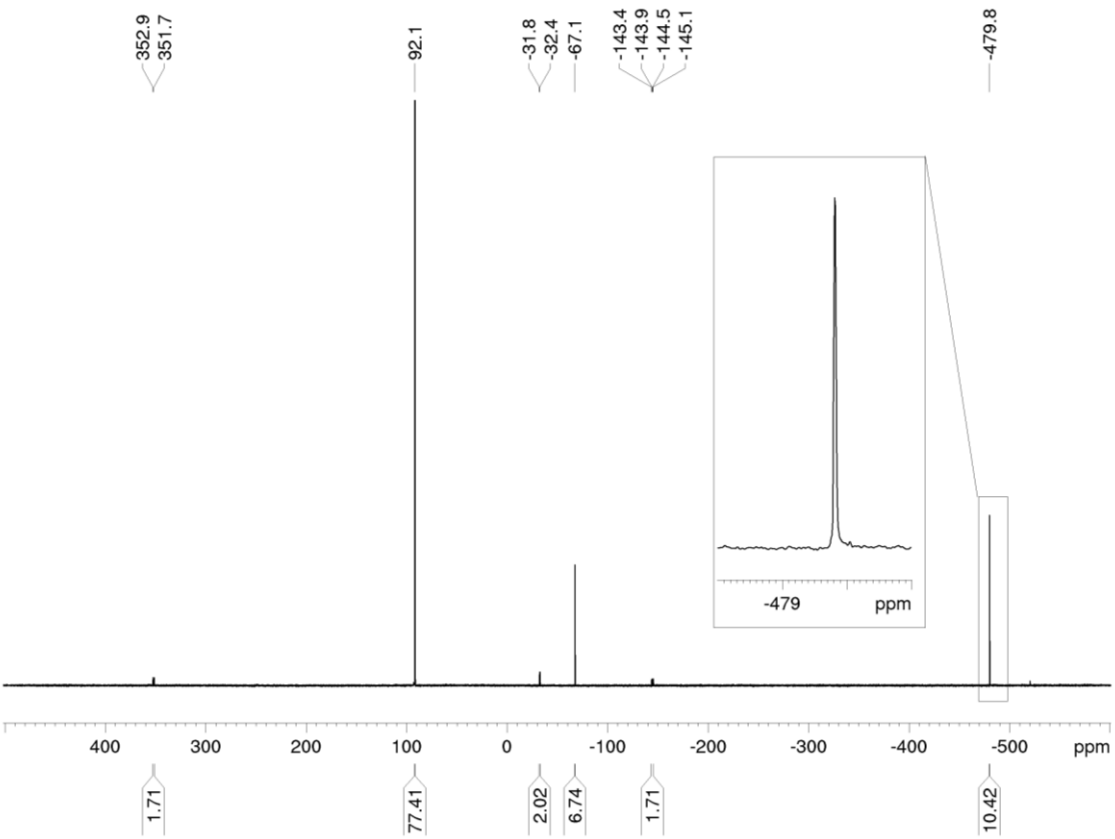


Figure S69. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(IMes)Ni(CO)$_3$] with 1.0 eq. AdCP.

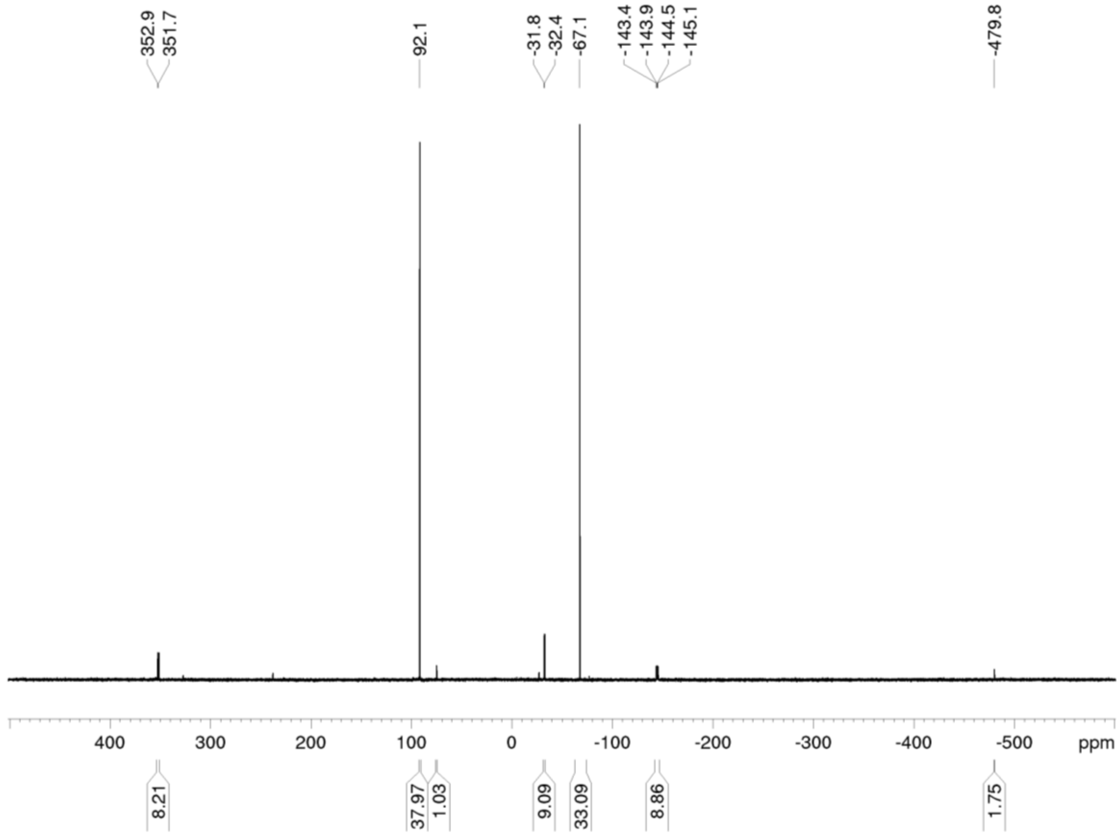


Figure S70. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(IMes)Ni(CO)$_3$] with 3.0 eq. AdCP.

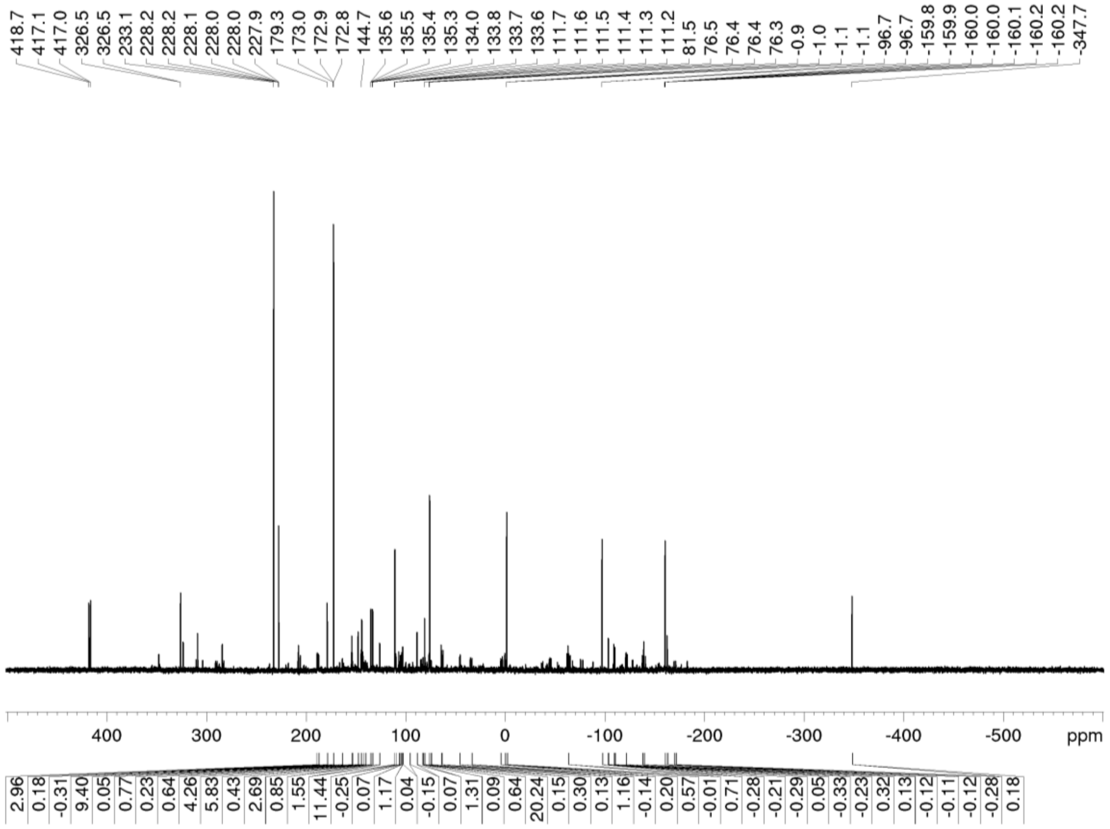


Figure S71. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [Ni(CO)$_4$] with 1.1 eq. *t*BuCP.

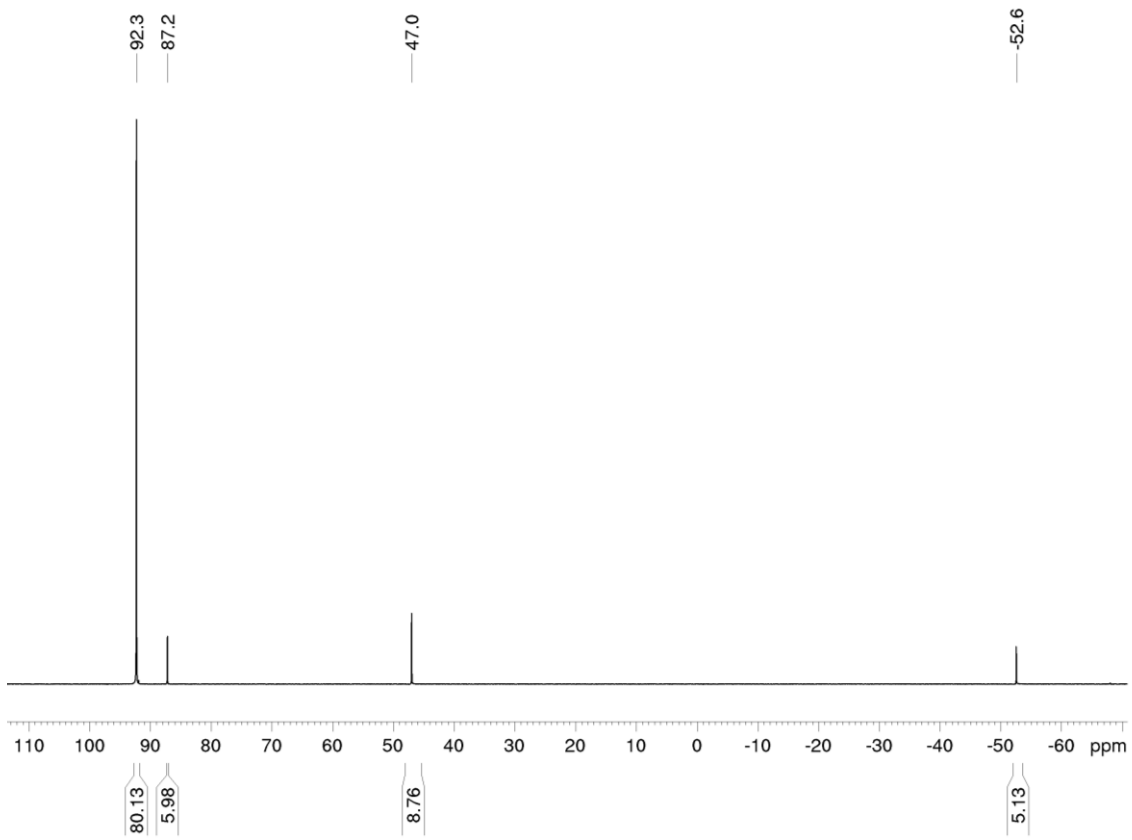


Figure S72. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr_2Im^{Me})$Ni(CO)_3$] with 1.5 eq. *t*BuCP.

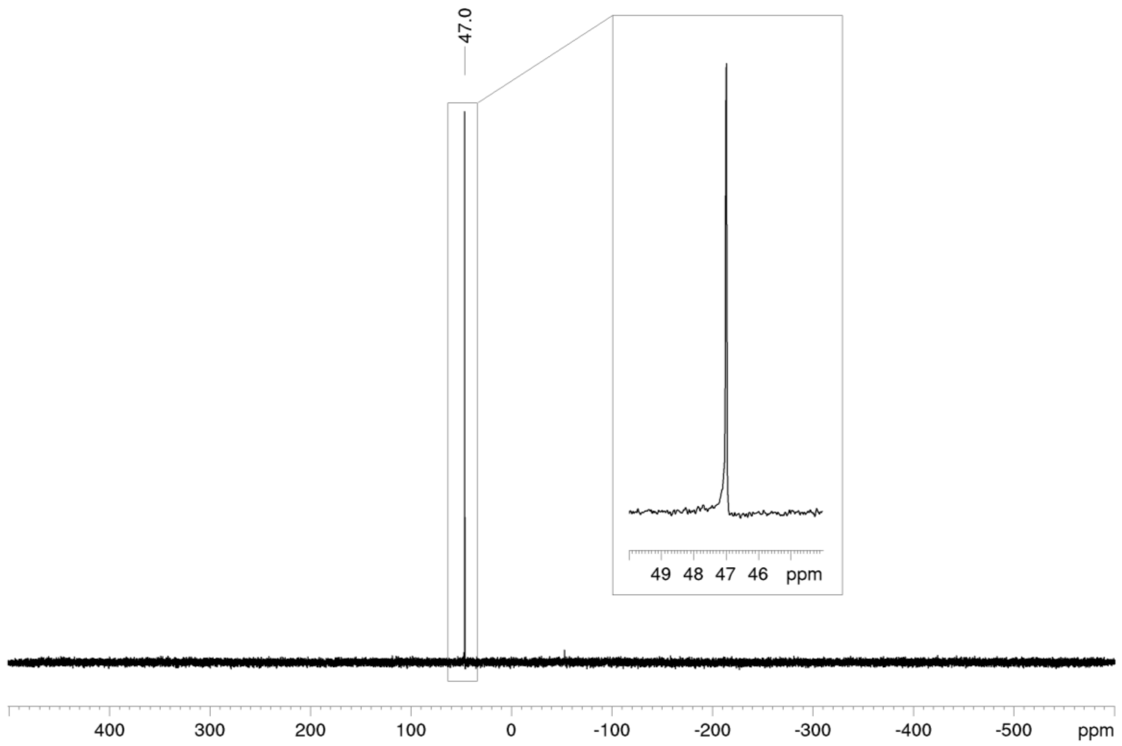


Figure S73. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **5**.

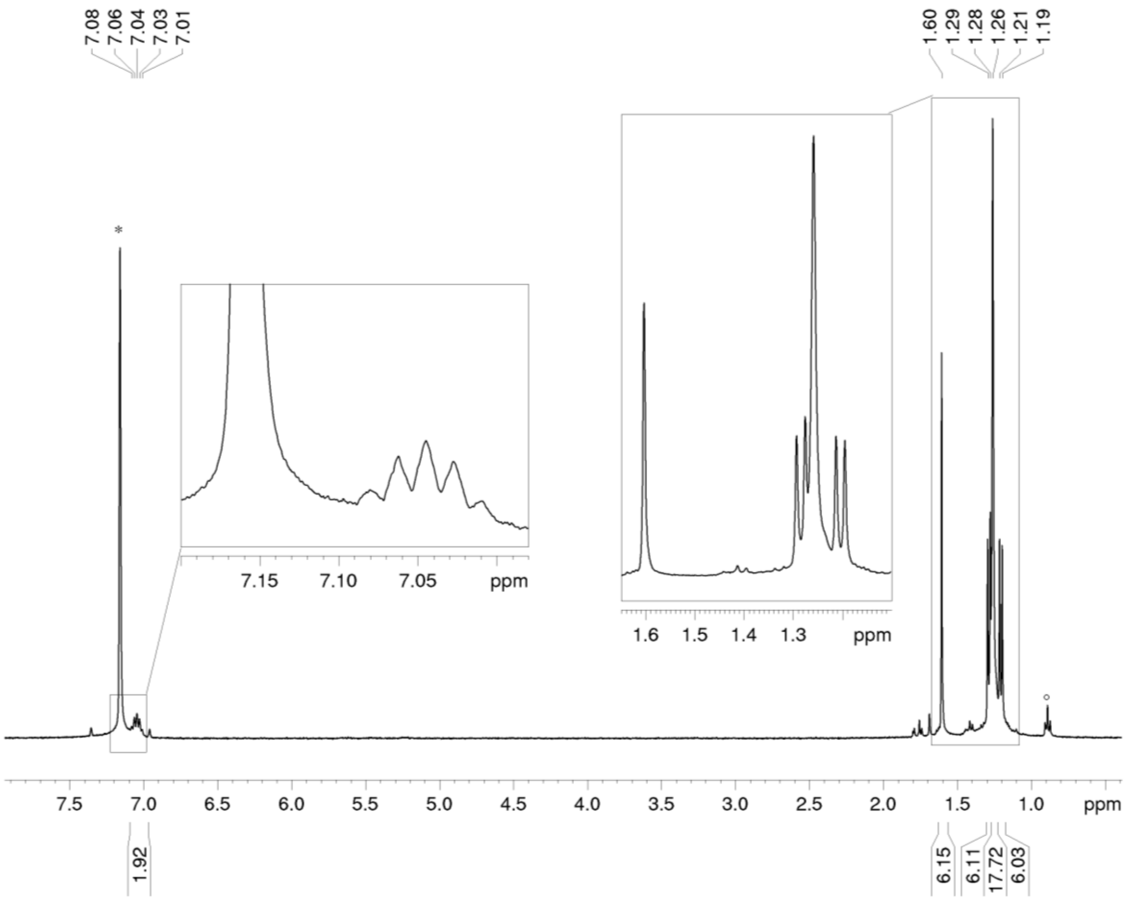


Figure S74. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **5**, *C_6D_6, °*n*-hexane.

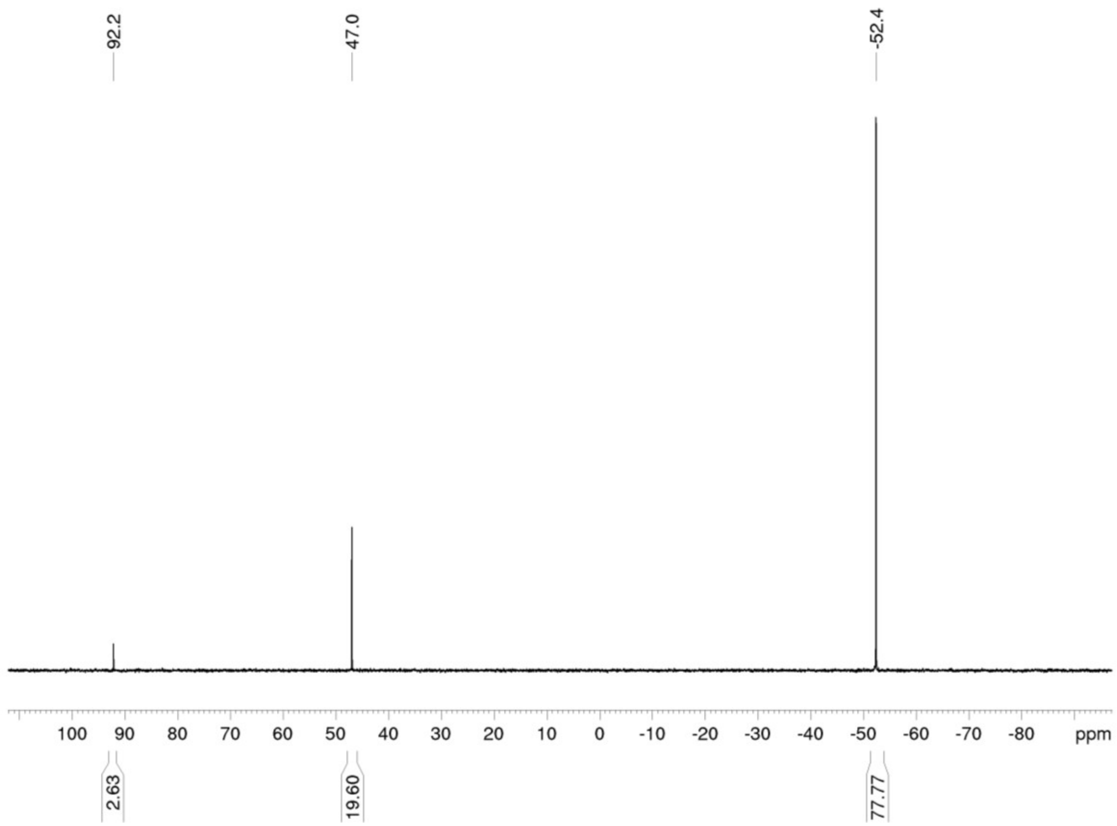


Figure S75. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of crystals of **6** re-dissolved in C_6D_6.

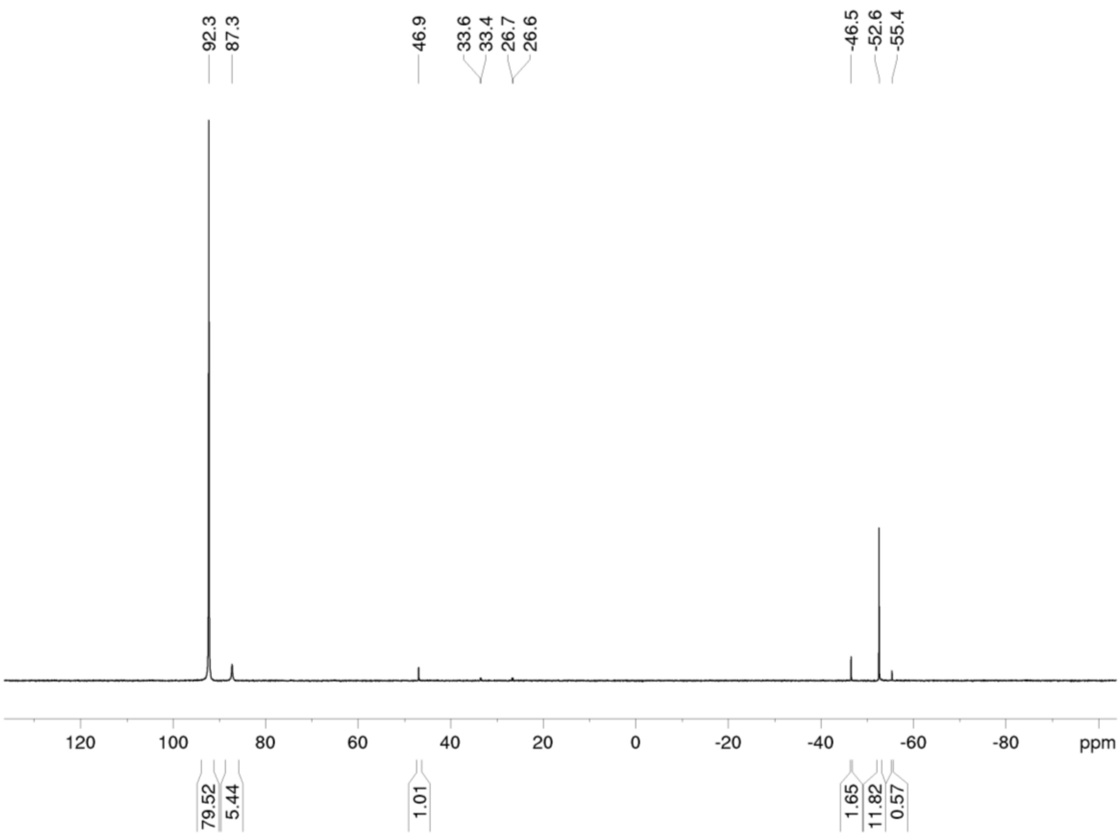


Figure S76. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr_2Im^{Me})$Ni(CO)_3$] with 1.0 eq. *t*BuCP.

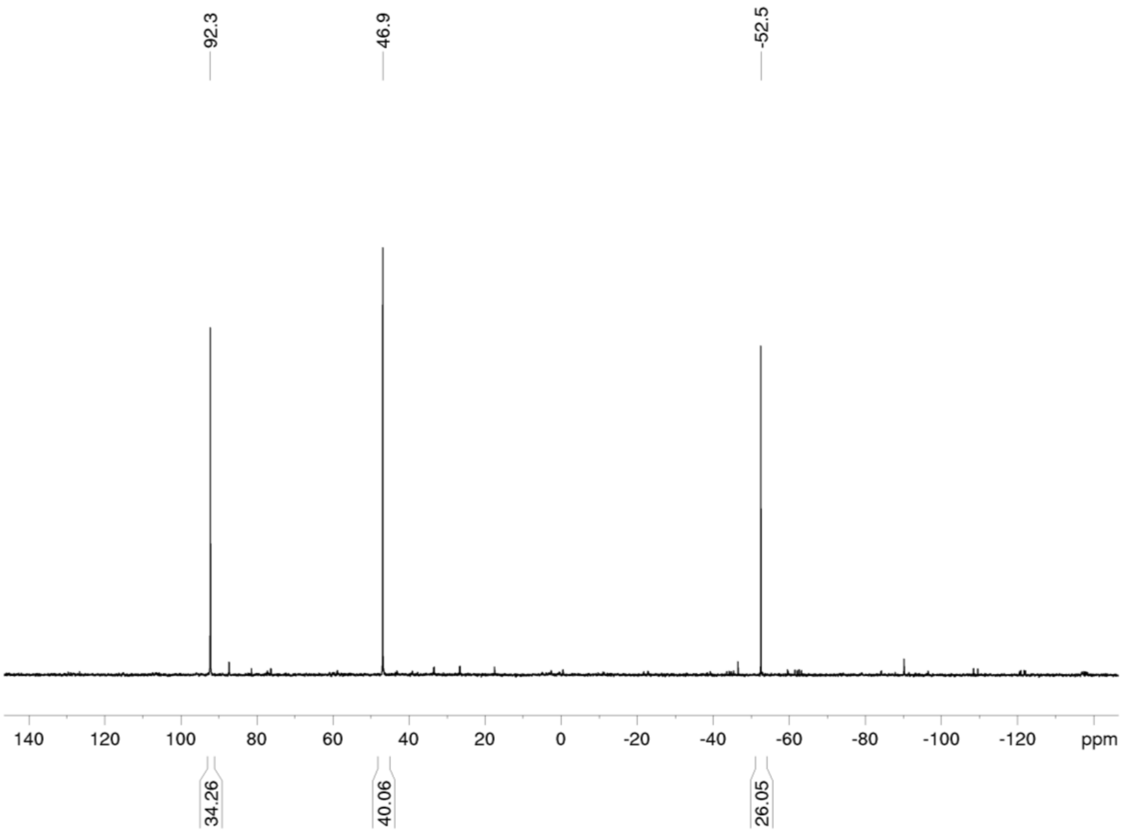


Figure S77. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(*i*Pr_2Im^{Me})$Ni(CO)_3$] with 2.1 eq. *t*BuCP.

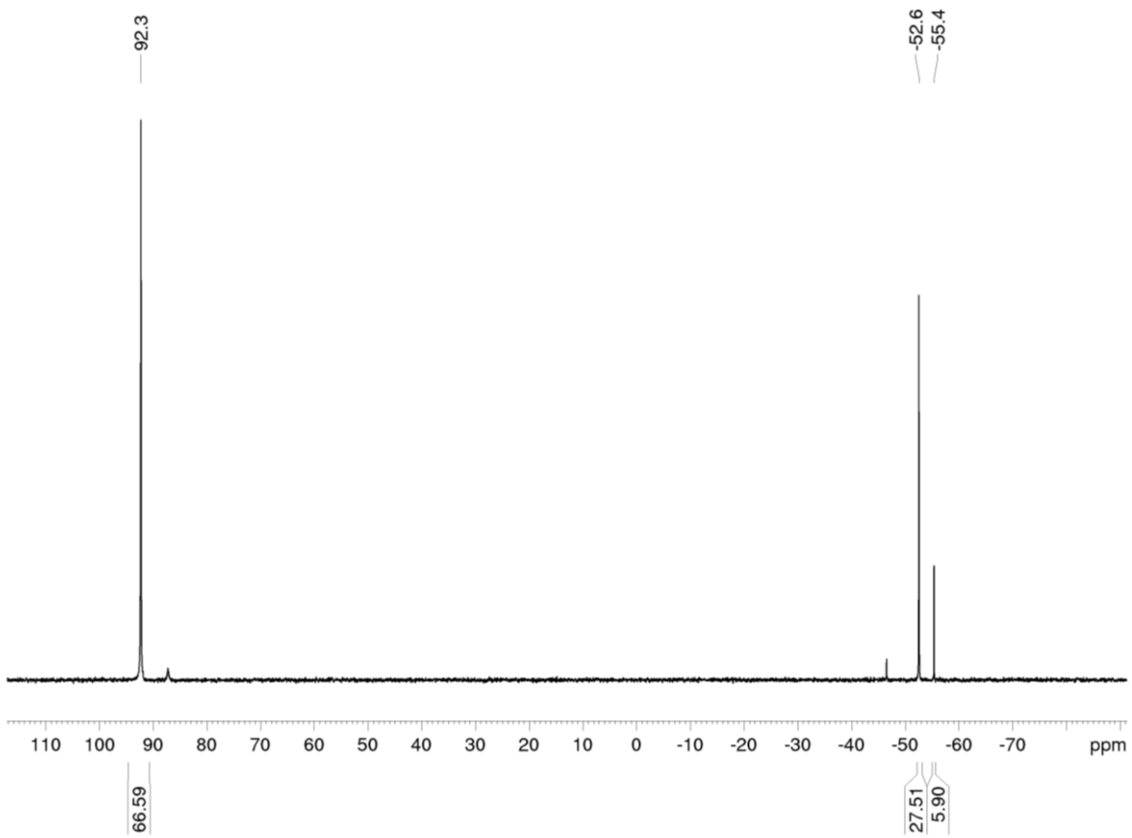


Figure S78. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [(iPr$_2$Im^{Me})Ni(CO)$_3$] with 0.5 eq. *t*BuCP.

S5 UV/Vis Spectra

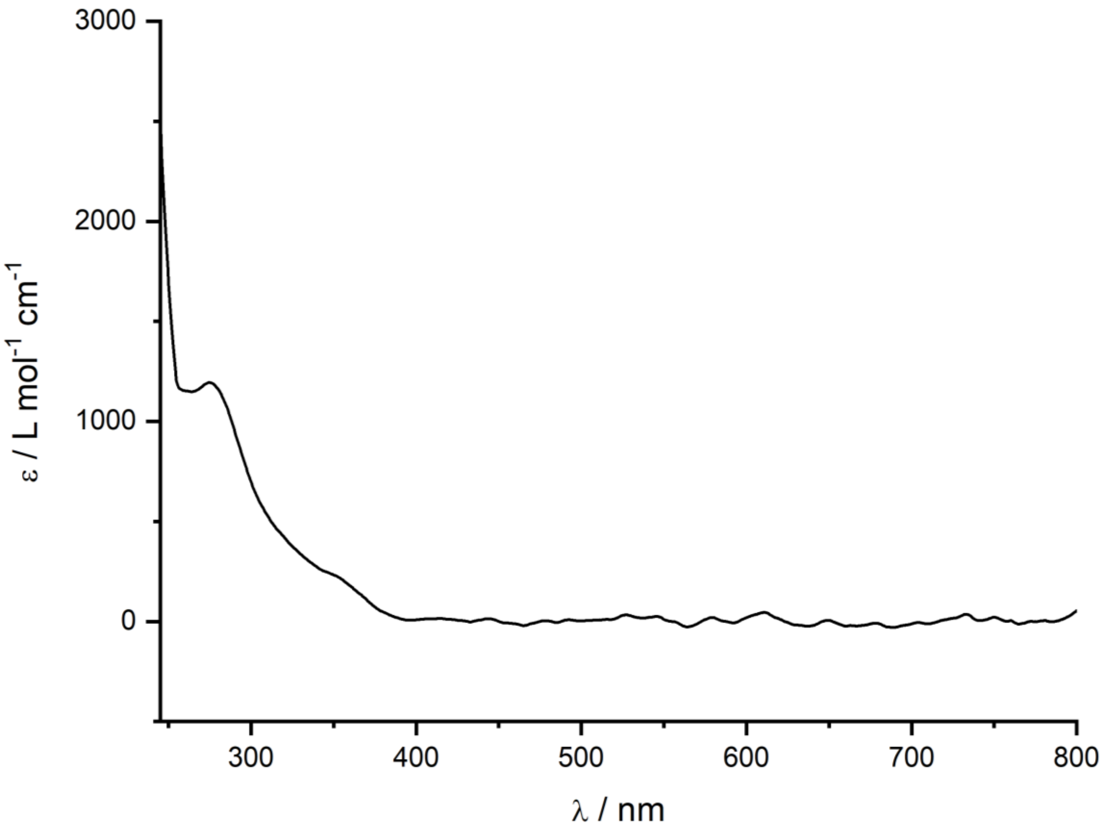


Figure S79. UV/Vis spectrum (*n*-hexane) of **1a**.

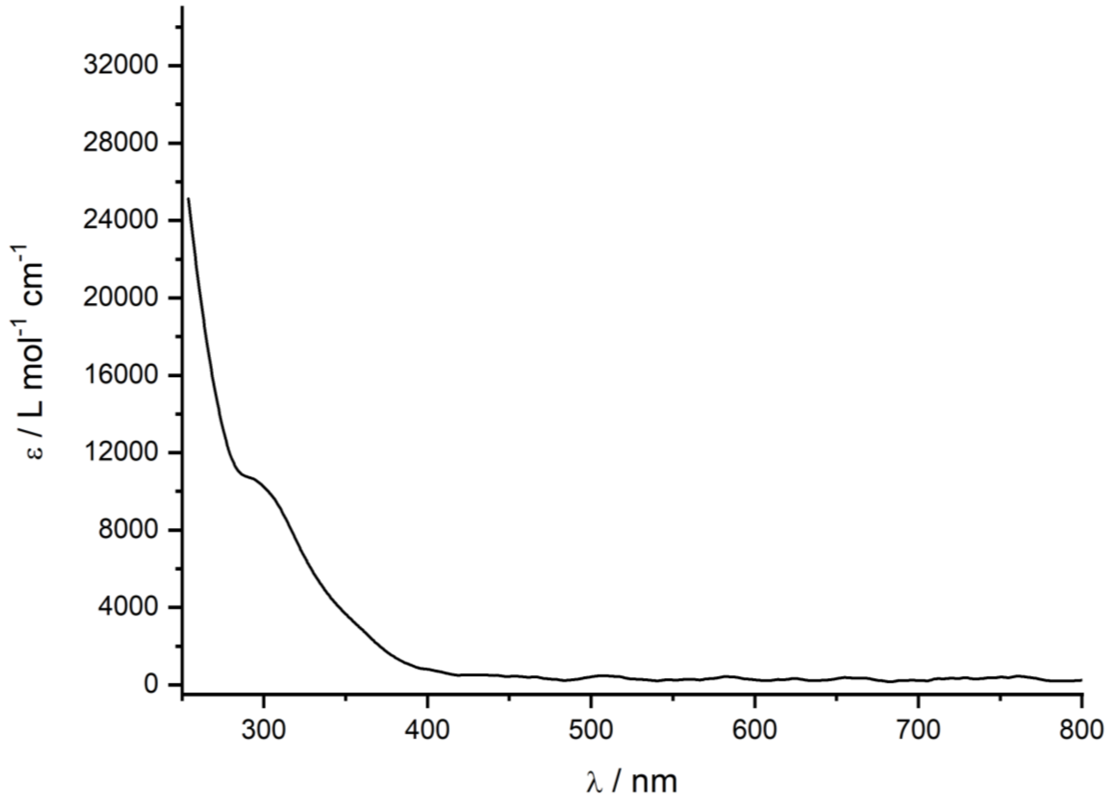


Figure S80. UV/Vis spectrum (CH_2Cl_2) of **3**.

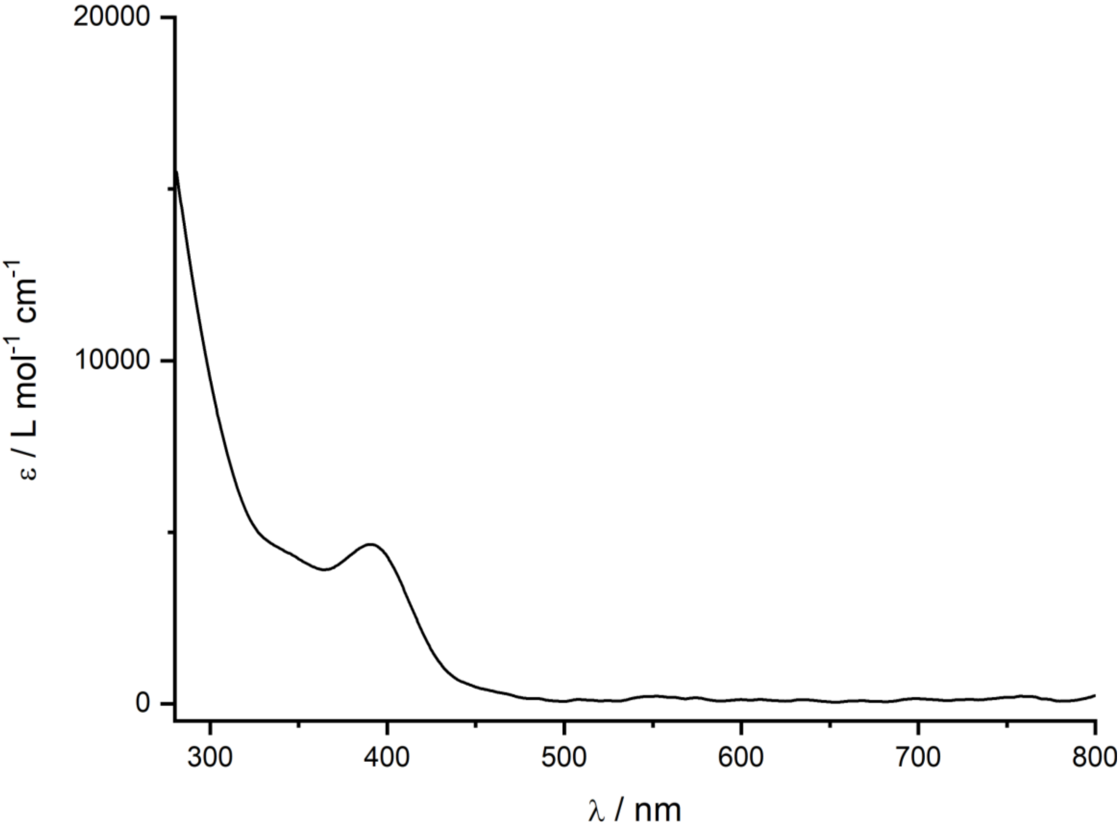


Figure S81. UV/Vis spectrum (THF) of **4a**.

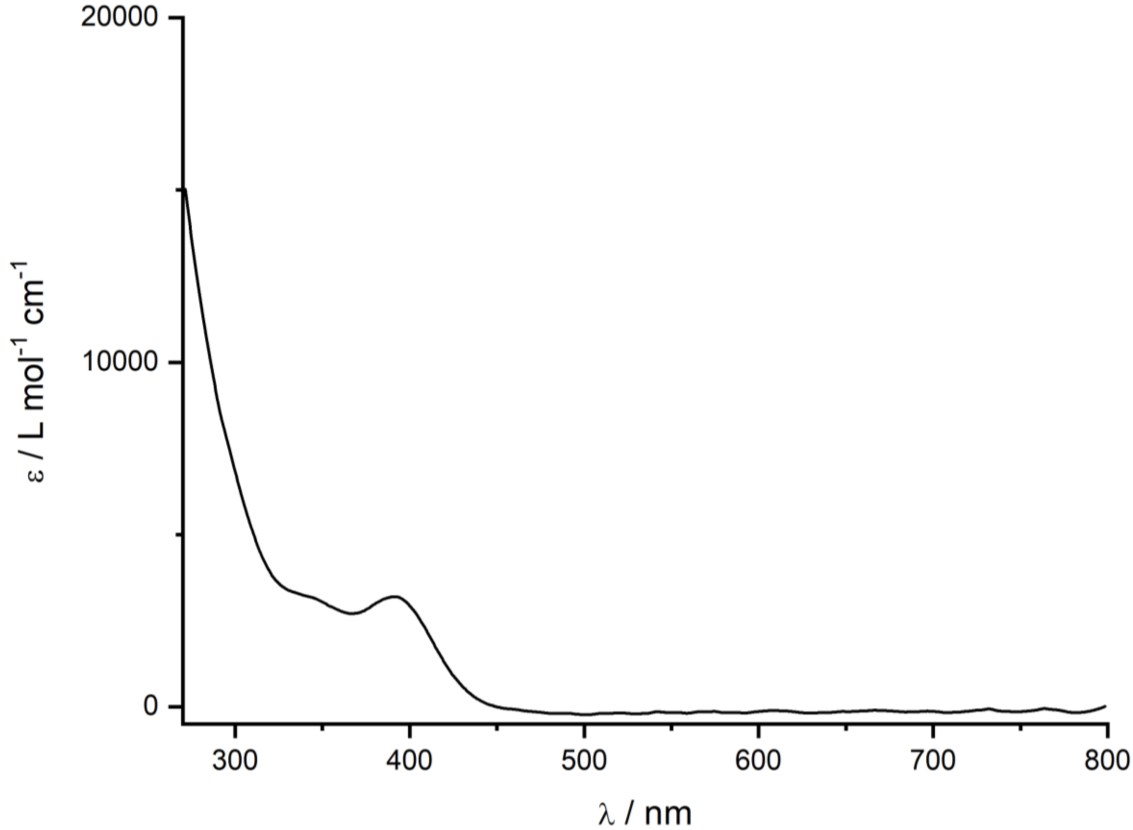


Figure S82. UV/Vis spectrum (THF) of **4b**.

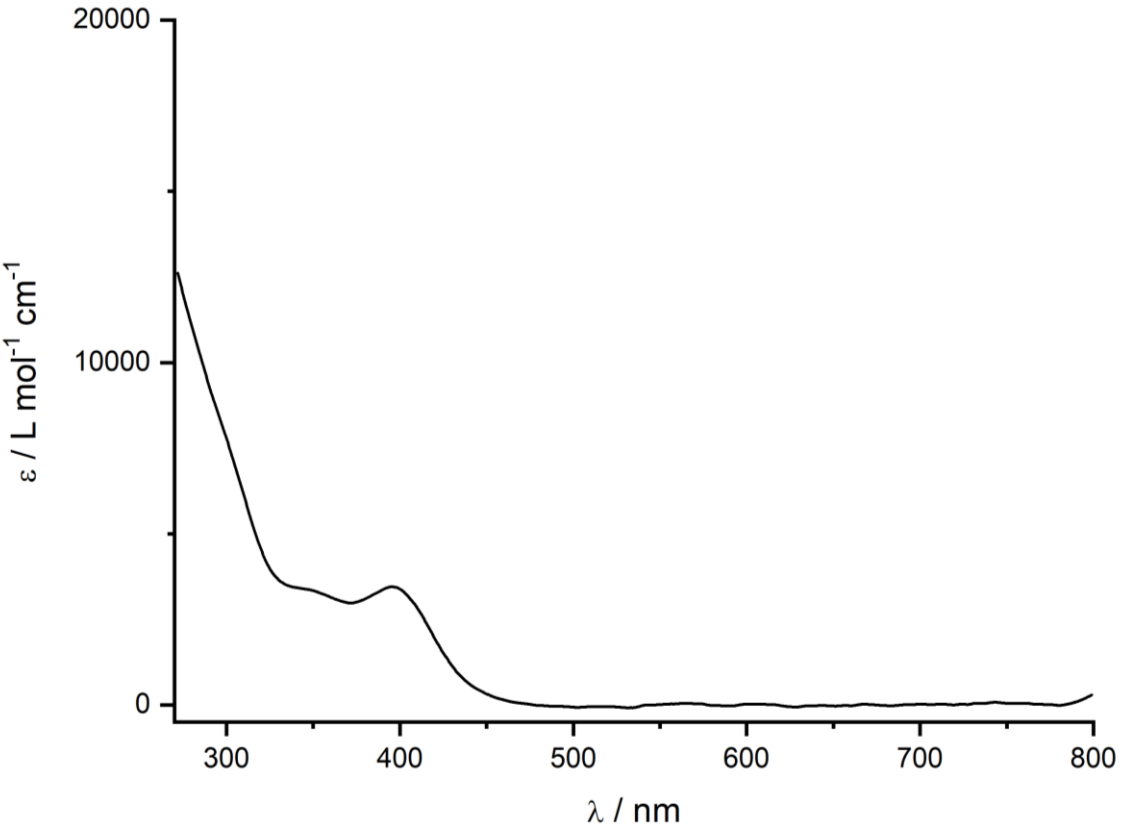


Figure S83. UV/Vis spectrum (THF) of **4c**.

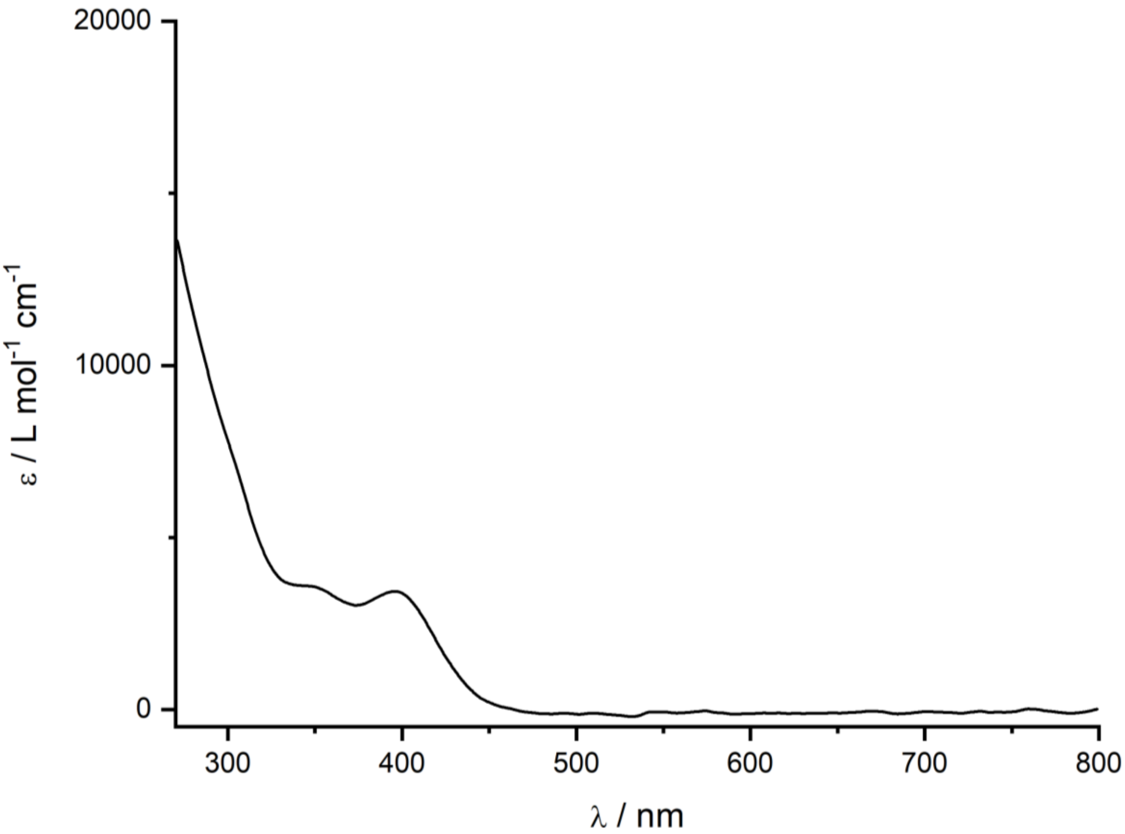


Figure S84. UV/Vis spectrum (THF) of **4d**.

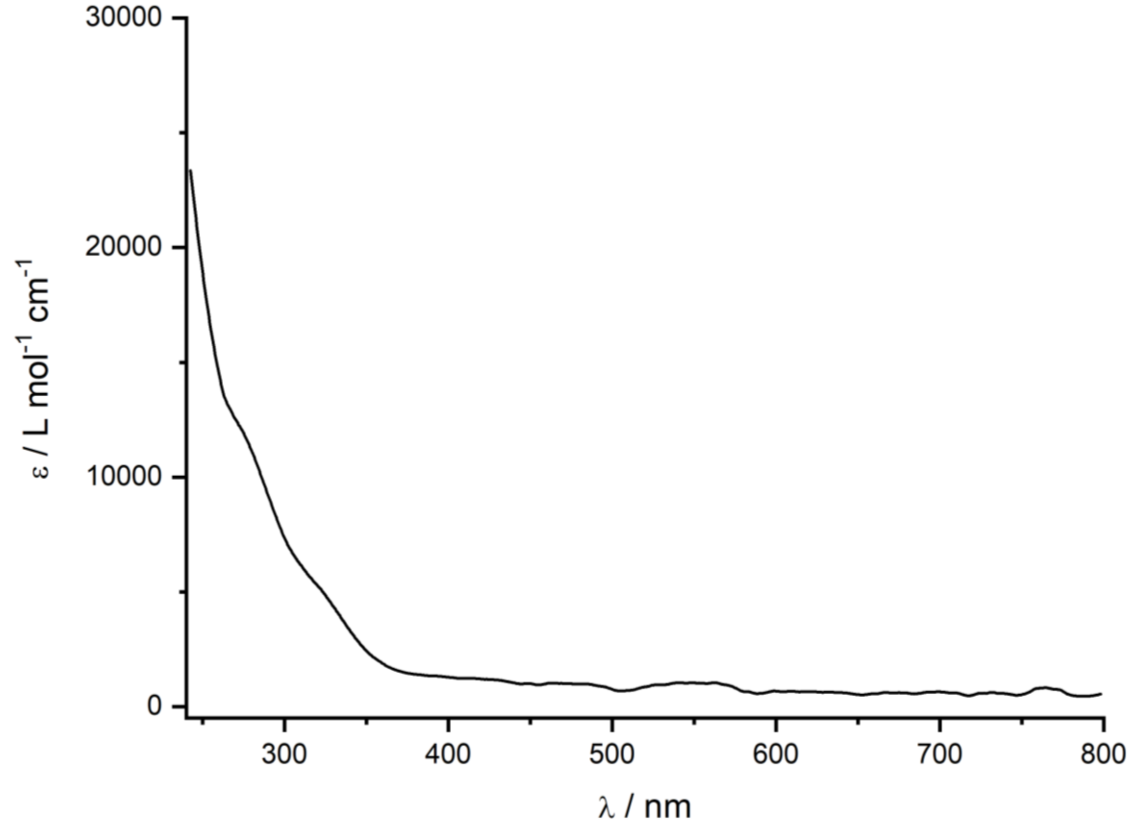


Figure S85. UV/Vis spectrum (THF) of [iPr$_2$Im^{Me}Ni(CO)$_3$].

S6 IR Spectra

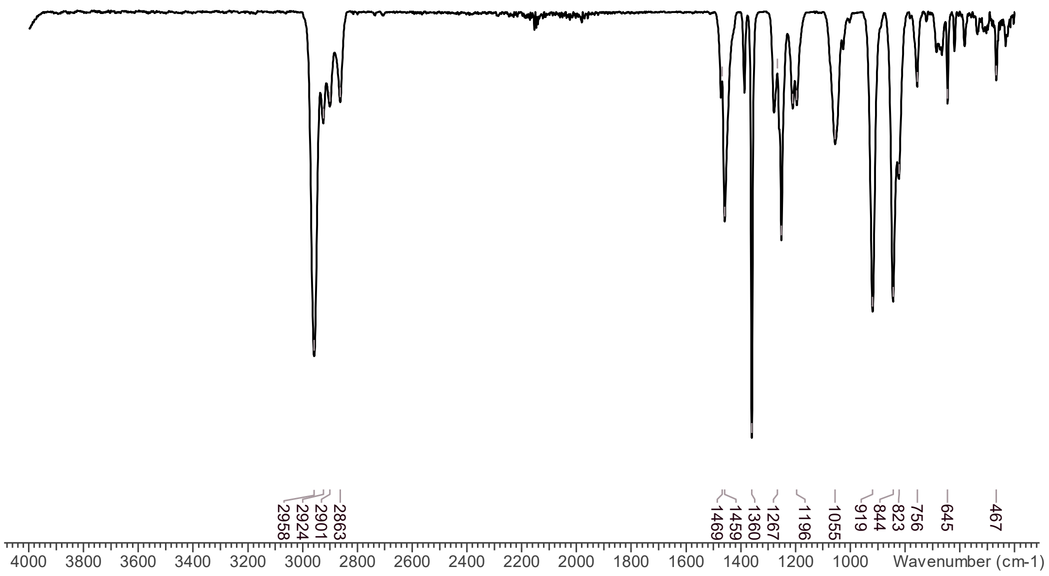


Figure S86. IR spectrum (ATR) of **1a**.

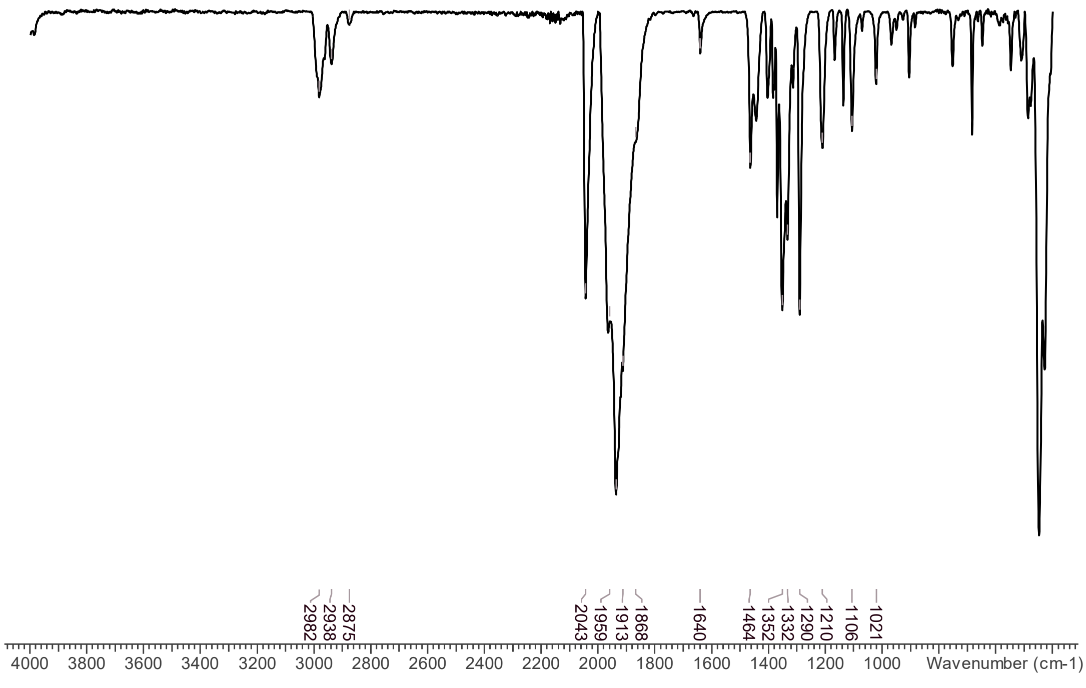


Figure S87. IR spectrum (ATR) of (iPrIm^{Me})Ni(CO)$_3$.

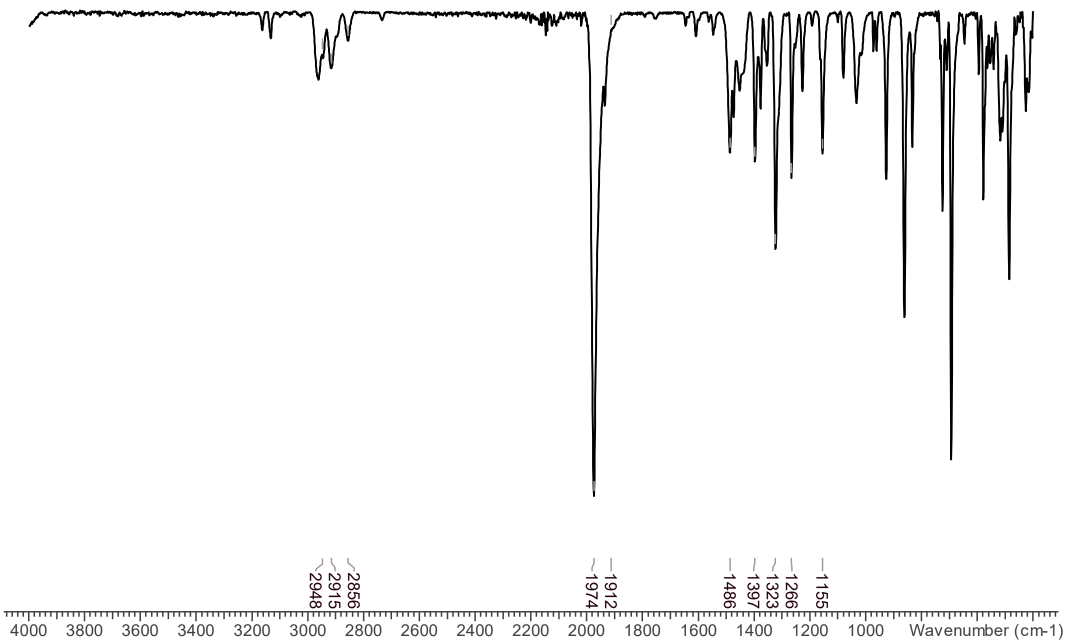


Figure S88. IR spectrum (ATR) of **4a**.

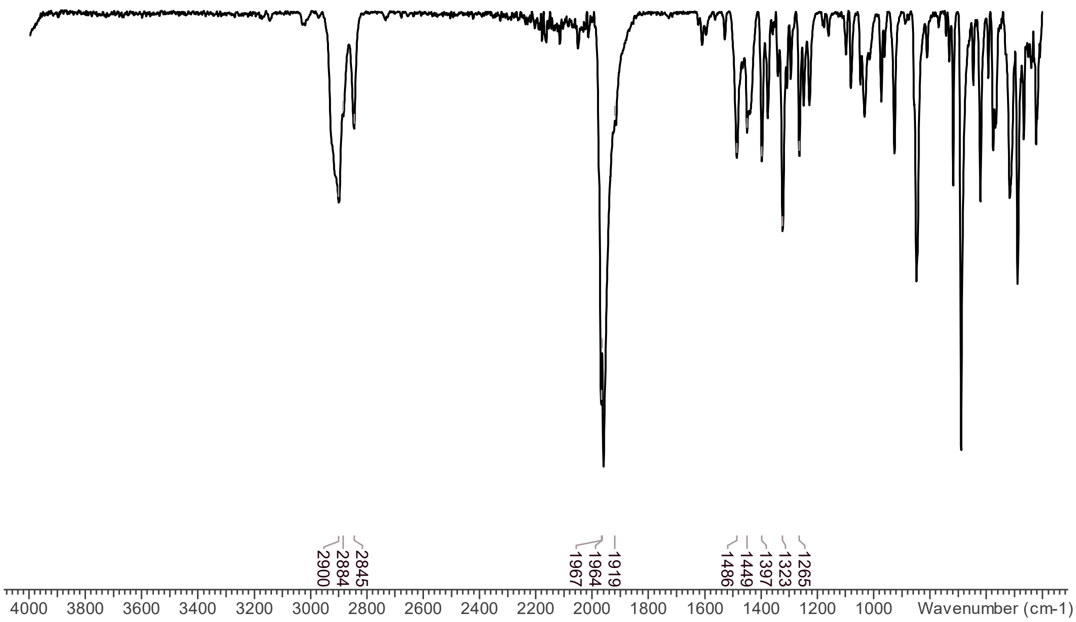


Figure S89. IR spectrum (ATR) of **4b**.

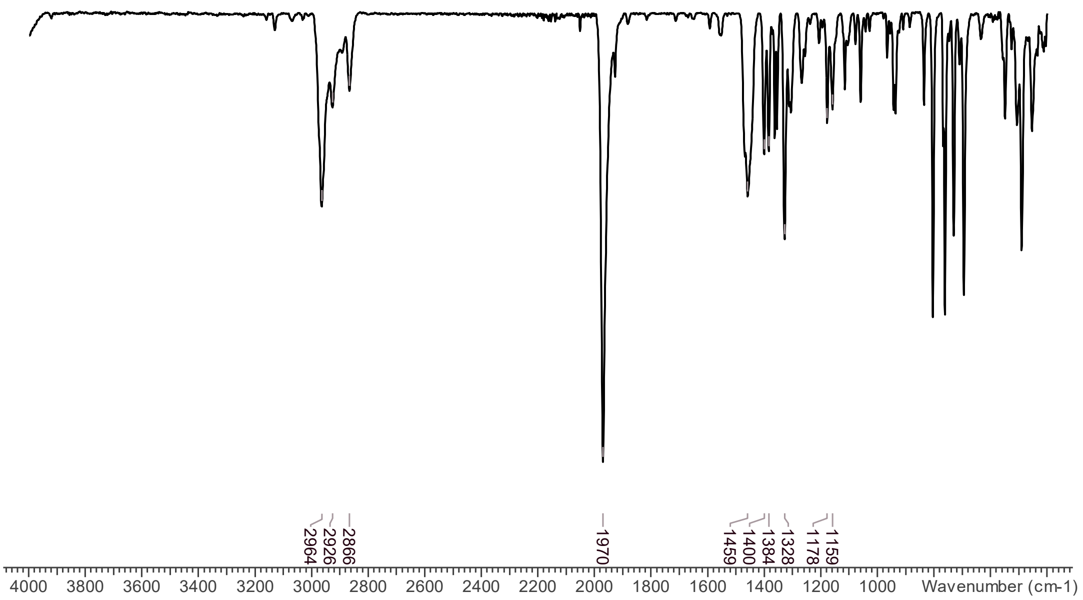


Figure S90. IR spectrum (ATR) of **4c**.

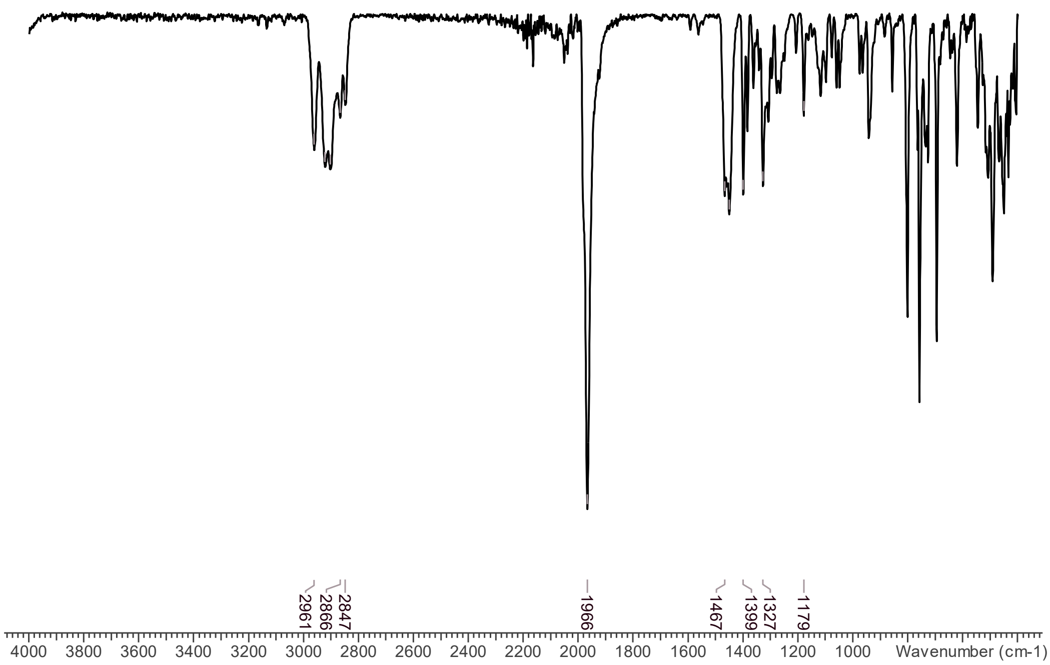


Figure S91. IR spectrum (ATR) of **4d**.

S7 Single Crystal X-ray Diffraction Data

Additional Refinement Details

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 S92) and only weakly diffracting, especially at higher resolution. Additionally, the crystals decompose in the X-ray beam (see Figure S93). 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 $2\sigma(I)$.

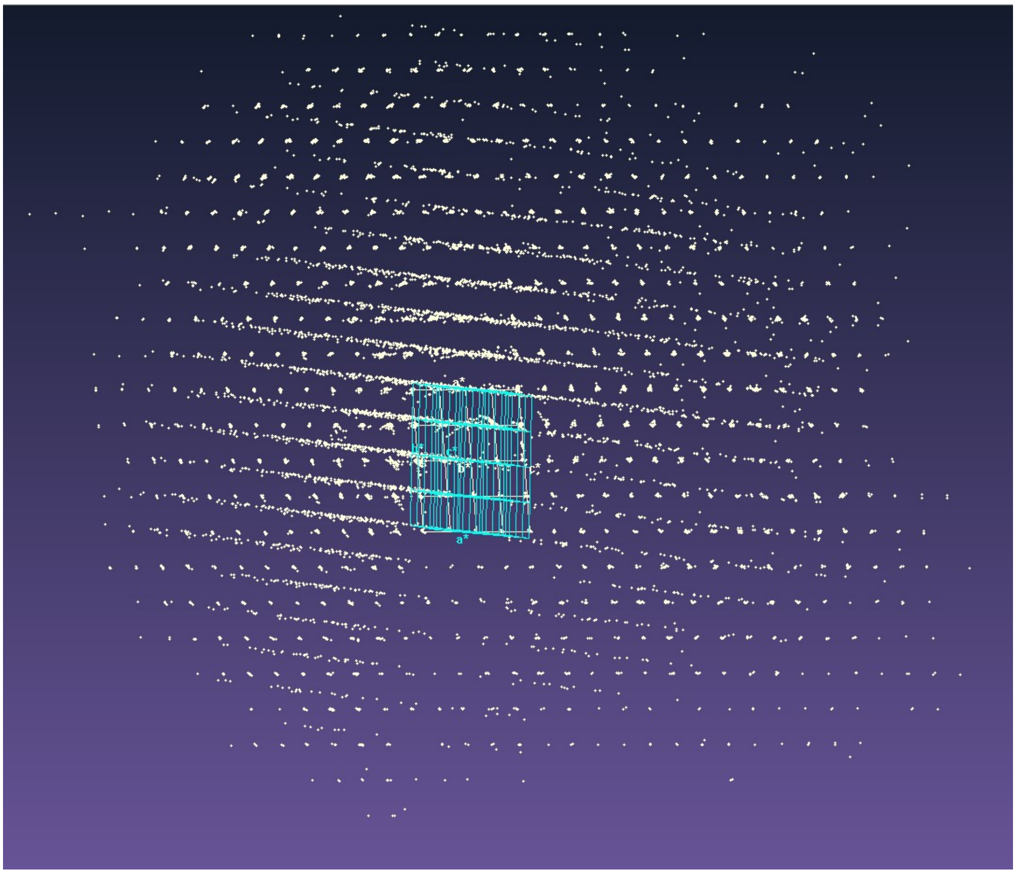


Figure S92. Reciprocal space view along b* of the main component.

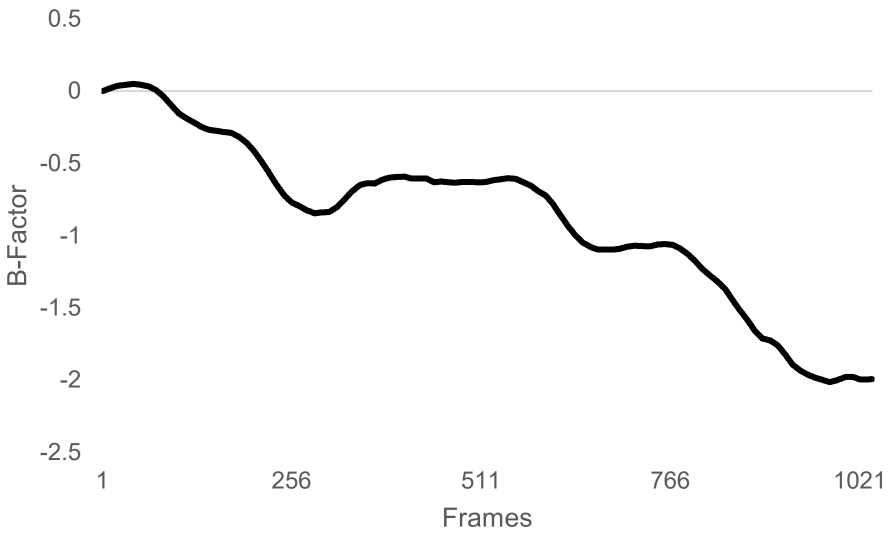


Figure S93. Decomposition of **3**. B-factor of scaling $\boldsymbol{S} = \boldsymbol{e}^{-2\boldsymbol{B}\left(\frac{\sin\theta}{\lambda}\right)^2}$ plotted against the frames of the diffraction experiment (10 frames averaged).

Additional Figures (not depicted in the Doctoral Thesis)

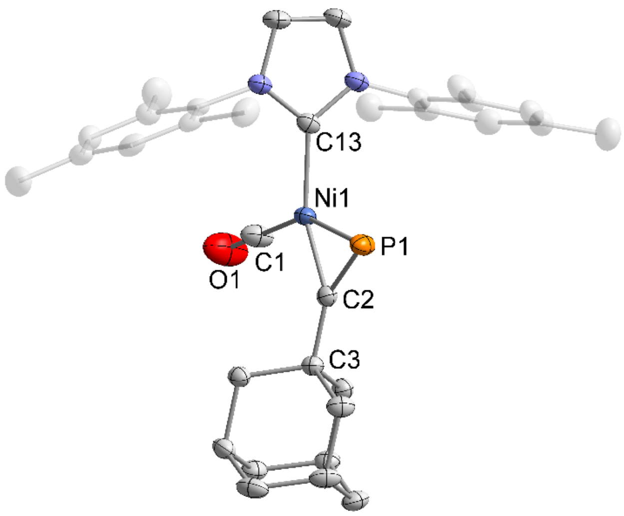


Figure S94. Molecular structure **4c** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles: Ni1─C1 1.753(2), Ni1─C13 1.9284(19), Ni1─P1 2.2189(6), Ni1─C2 1.8950(19), C1─O1 1.136(3), P1─C2 1.6273(19), C3−C2−P1 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).

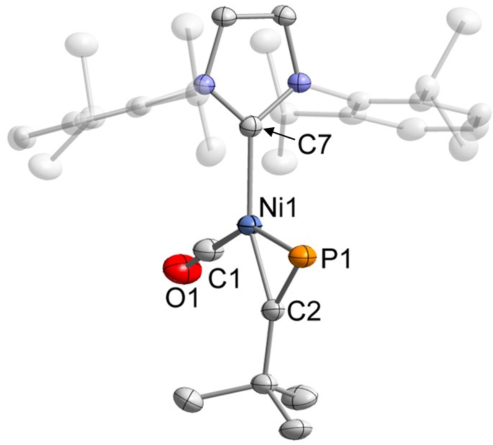


Figure S95. Molecular structure **4c** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles: Ni1─C1 1.760(2), Ni1─C7 1.947(2), Ni1─P1 2.2201(7), Ni1─C2 1.900(2), C1─O1 1.137(3), P1─C2 1.626(2), C3−C2−P1 146.13(18), 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)

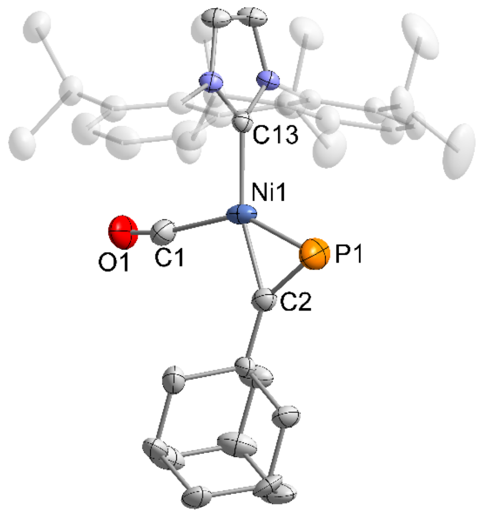


Figure S96. Molecular structure **4d** in the solid state**.** Ellipsoids are set at 50% probability level. The second component and hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] with data for the second part of the molecule in brackets: Ni1─C1 1.86(2) [1.796(13)], 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)].

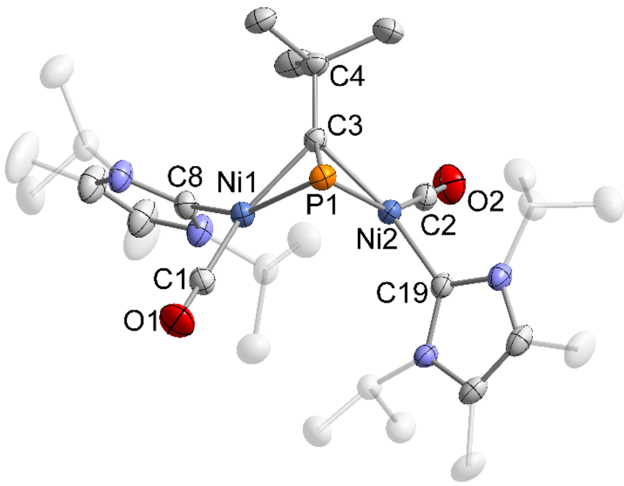


Figure S97. Molecular structure **6** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1—Ni2 2.7907(4), Ni1—P1 2.2123(5), Ni1—C1 1.757(2), Ni1—C8 1.9435(18), Ni1—C3 1.9703(18), C1—O1 1.141(3), C2—O2 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).

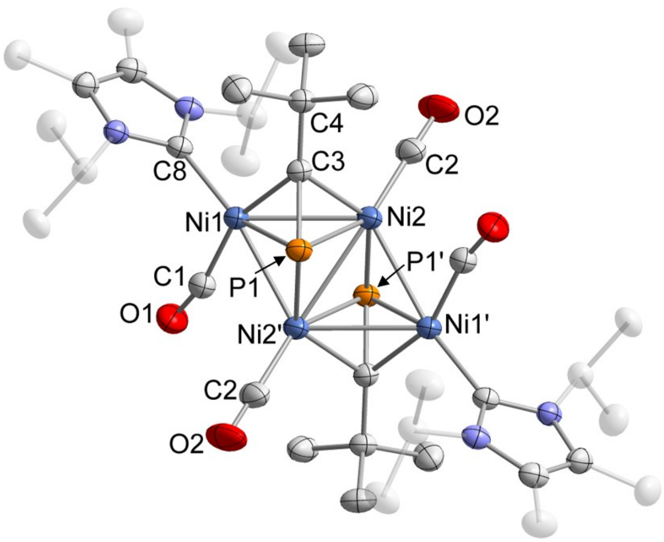


Figure S98. Molecular structure **7** in the solid state**.** Ellipsoids are set at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1—P1 2.3142(6), Ni1—C3 1.969(2), Ni1—C1 1.784(2), Ni1—C8 1.923(2), C1—O1 1.150(3), C2—O2 1.139(3), P1—C3 1.702(2), 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).

Table S3. Crystallographic data and structure refinement for compounds **3-7** and [(iPr$_2$Im^{Me})Ni(CO)$_3$].

Compound	**[(iPr$_2$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	123.0(1)	122.9(3)	123.0(1)	123.0(1)	123.0(1)	123.0(1)	123.0(1)	123.0(1)	123.0(1)
Crystal System	triclinic	triclinic	triclinic	monoclinic	ortho-rhombic	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	CuKα	CuKα	CuKα	CuKα	CuKα	CuKα	CuKα	CuKα	CuKα
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

S8 Quantum Chemical Calculations

General Methods

All calculations were carried out with ORCA 4.1.[11] Geometry optimizations were performed at the TPSS-D3BJ/def2-TZVP level of theory in the gas phase.[6–8,12] 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),[13] were used for density functional theory (DFT) calculations, whereas the RIJCOSX approximation was used for DLPNO-CCSD(T)/def2-QZVPP calculations.[3,8,14]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, tBu)

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.[15] 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 dimerisation reaction

For the sake of computational cost, the complete reaction mechanism for the phosphaalkyne dimerisation 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 Figure S99. 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 $\Delta G = -41.6$ 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 $i\text{Pr}_2\text{Im}^{\text{Me}}$ 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_2Im^{Me}. The red line in Figure S99 displays the reaction profile for the dimerisation of *t*Bu−C≡P catalysed 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 figures in main text of the thesis).

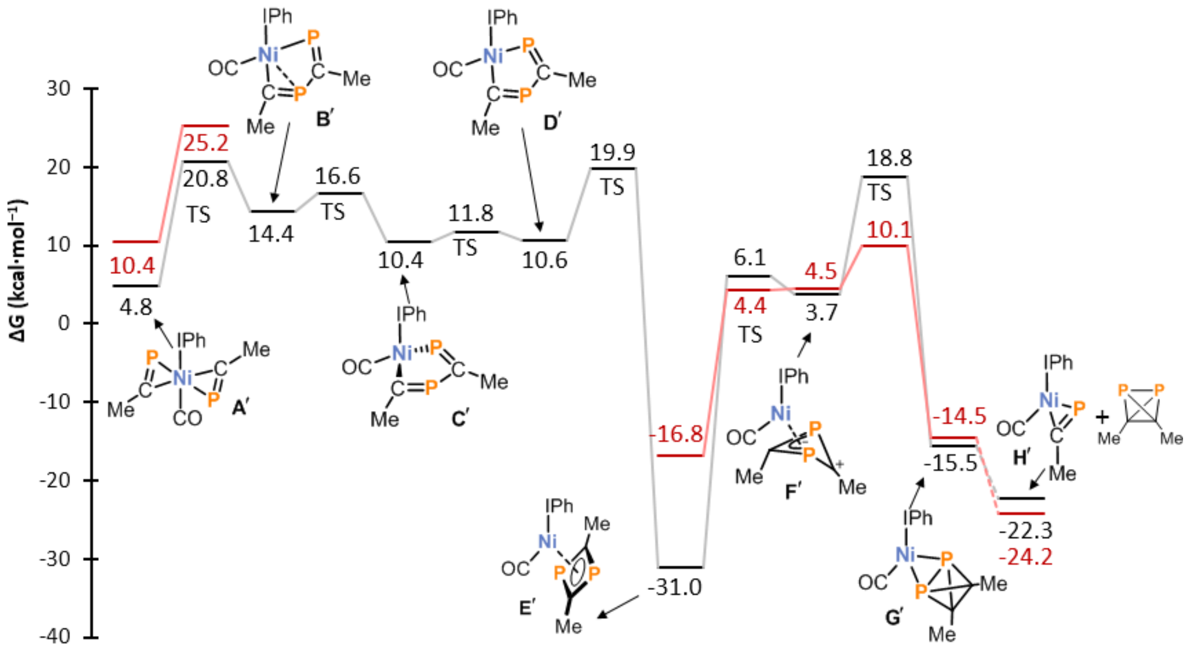


Figure S99. Gibbs energies (in kcal·mol^{-1}at 298 K) and schematic drawings of intermediates for the dimerisation of Me−C≡P catalysed by [(IPh)Ni(PCMe)] (black, IPh (=1,3-diphenylimidazolin-2-ylidene). For comparison the graph for the dimerisation of *t*Bu−C≡P catalysed by [(IXy)Ni(PCtBu)], (red, IXy = 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 S100). The initial step of this mechanism is the transformation of **A′** into a 1,4-diphosphabutadiene complex **B″** (ΔG‡ = 17.9 kcal·mol^{-1} and ΔG = 12.1 kcal·mol^{-1}). Next, an intermediate **C″** (ΔG‡ = 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′** (ΔG‡ = 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 S100 appears to be kinetically disfavored compared to the pathway shown in Figure S99.

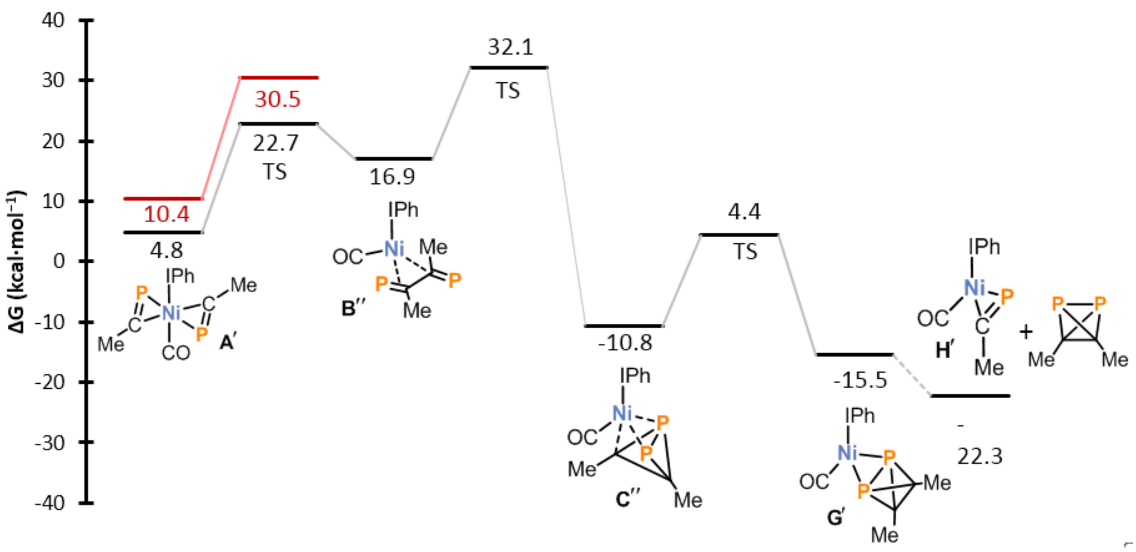


Figure S100. Gibbs energies (in kcal·mol^{-1}at 298 K) and schematic drawings of transition states and intermediates for an alternative dimerisation pathway of Me−C≡P catalysed by [(IPh)Ni(PCMe)]. For comparison, the red line demonstrates the increased ΔG‡ when increasing the size of the substituents (*t*Bu−C≡P and [(IXy)Ni(PCtBu)], 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**

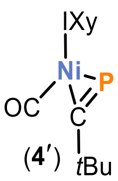
C	-7.22769137413322	1.80924719317750	0.00024851421473
C	-5.76258587380059	1.75828102158799	0.00272945512880
C	-7.70773616906694	2.78329129599880	1.10418249745131
C	-7.78946578697890	0.39272023534112	0.27574266519012
C	-7.71998813183538	2.30535694684890	-1.38167575365641
P	-4.21122440152084	1.70447601158052	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

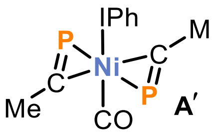
4′ (NHC = IXy, R = *t*Bu)



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

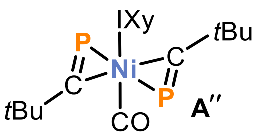
H	-4.74480303788721	5.49524264187132	8.60052931535652
C	-4.10963923533110	3.69340359948650	9.73482489291606
H	-4.72199968683197	3.57134258176227	10.61352149902893
C	-2.65390335534664	5.32989456462747	4.33652102207082
H	-2.87082824763517	4.95755274903154	3.33885838086288
C	-1.71420698275772	7.02456452295438	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

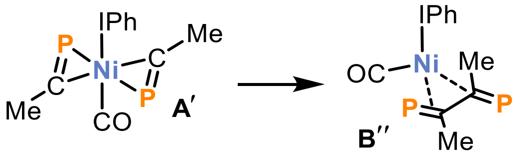
A″ [(IXy)Ni(CO)(PC*t*Bu)$_2$]



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

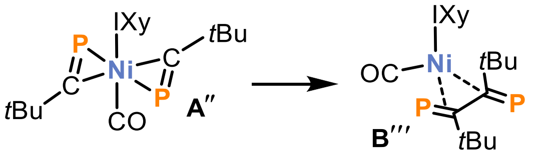
C	-2.73172749761487	5.06916201401510	6.71412917272881
C	-2.06924166987893	6.28885922495786	6.91185693748873
C	-3.03166338959111	4.56292001217550	5.44272211178625
C	-2.72109376653781	1.64860345528012	10.19557562935413
C	-4.11803093396544	4.63226095235853	8.75635359667505
H	-4.74480303788721	5.49524264187132	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

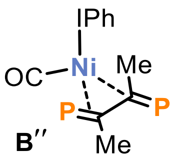
Transition State for A″ → B‴ (NHC = IXy, R = *t*Bu)



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

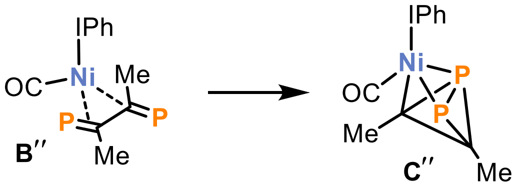
B′′ (NHC = IPh, R = Me)



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

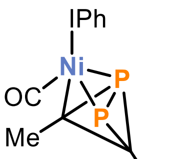
Transition state for B″ → C″ (NHC = IPh, R = Me)



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)

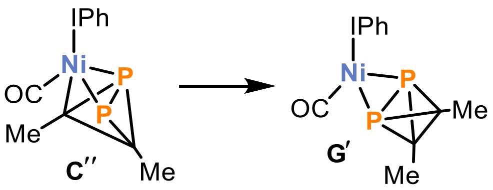


C″

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

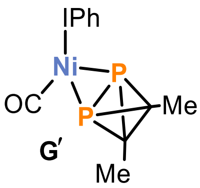
Transition State for C′′ → G′ (NHC = IPh, R = Me)



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

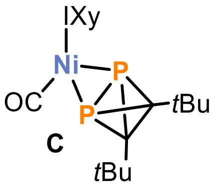
[(IPh)Ni(CO)($P_2C_2Me_2$)] (G′)



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)($P_2C_2t Bu_2$)] (C)

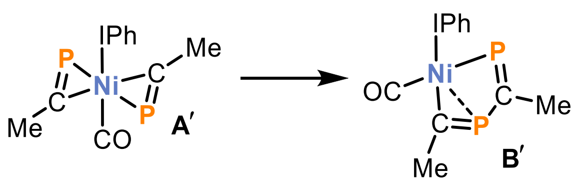


C

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

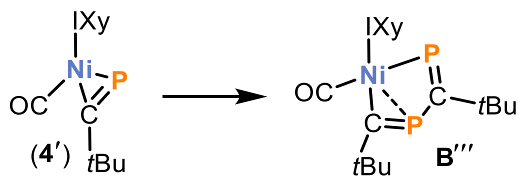
Transition State for A′ → B′ (NHC = IPh, R = Me)



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)

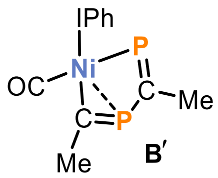


C	0.92179078653434	-5.63813959274923	1.91817097373715
C	1.89774856424580	-3.89078854281032	-0.82760864240766
Ni	0.87347314978076	-3.74594488893684	1.49023996127770
N	-2.22044297469722	-3.94645331640729	1.20396799264234
N	-1.49621949040511	-2.01161258489863	1.78454750180673
C	-1.04041907030841	-3.26317171244802	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

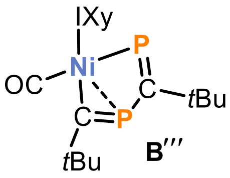
B′ (NHC = IPh, R = Me)



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

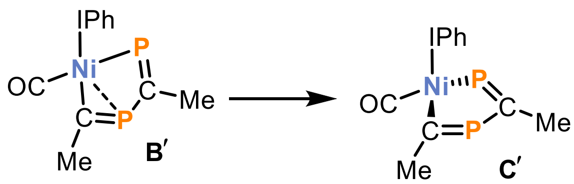
B′′′ (NHC = IXy, R = *t*Bu)



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

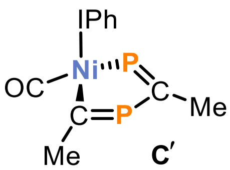
Transition State for B′ → C′ (NHC = IPh, R = Me)



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)

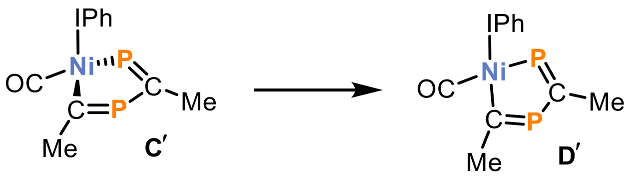


C′

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	-3.83282222284694	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

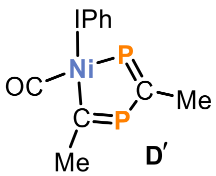
Transition State C′ → D′ (NHC = IPh, R = Me)



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

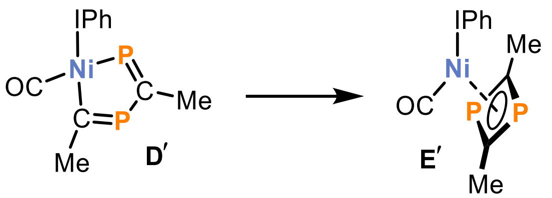
D′ (NHC = IPh, R = Me)



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

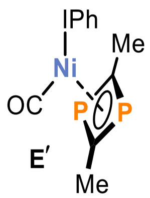
Transition state D′ → E′ (NHC = IPh, R = Me)



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

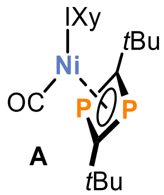
E′ (NHC = IPh, R = Me)



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

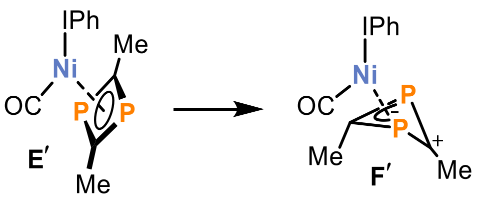
A (NHC = IXy, R = *t*Bu)



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

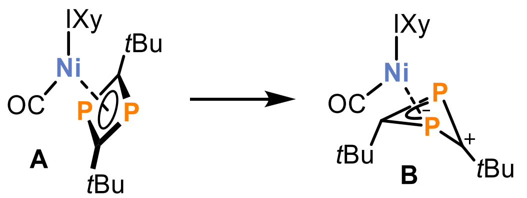
Transition State E′ → F′ (NHC = IPh, R = Me)



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)

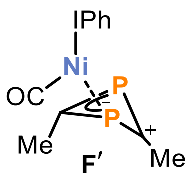


Ni	-0.65039595606173	-0.69052281030555	-0.39510346812471
N	-1.57369134266931	1.86157988049859	0.91139127002900
N	-2.22755280396392	0.09346630473170	1.94351762252048

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

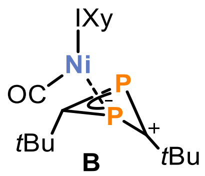
F′ (NHC = IPh, R = Me)



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)



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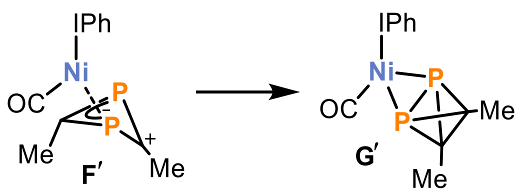
Transition State F′ → G′ (NHC = IPh, R = Me)



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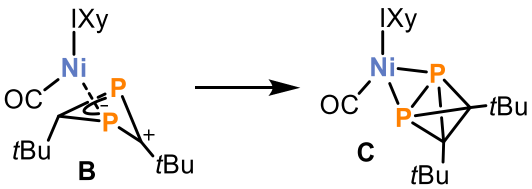
Transition State B → C (NHC = IXy, R = *t*Bu)



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Chapter 6

Di-tert-butyldiphosphatetrahedrane as a Building Block for Phosphaalkenes and Phosphinophosphirenes

S1 Additional Experiments

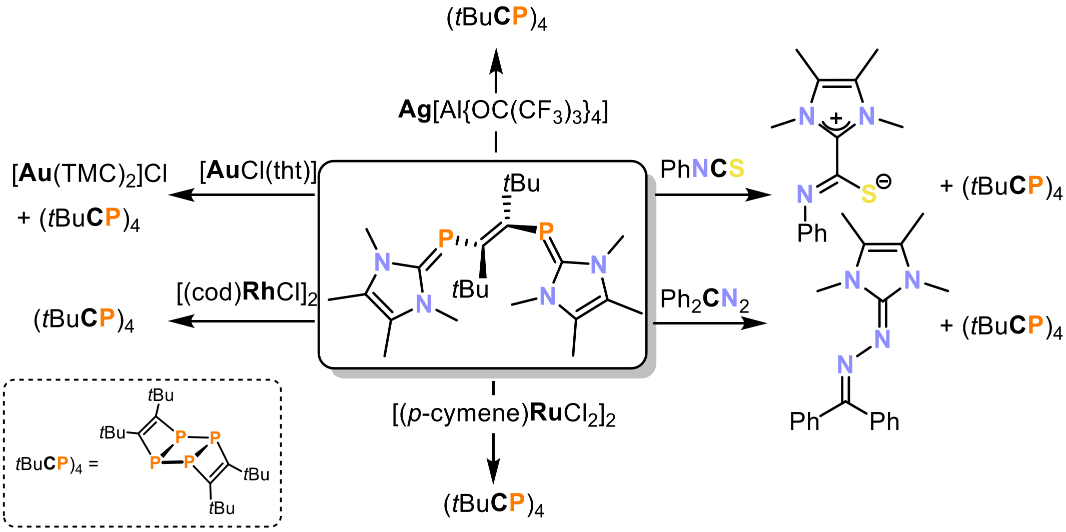

Figure S101. Reactivity of **2** toward transition metal complexes and heterocumulenes.

Reaction of 2 with [AuCl(tht)]

[AuCl(tht)] (11 mg, 33 µmol, 1.0 eq.) was dissolved in THF (1.0 mL) and added to a yellow solution of **2** (15 mg, 33 µmol, 1.0 eq.) in THF (1.5 mL) at – 30 °C. The orange solution turned cloudy whilst stirring overnight and was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S122). Subsequently, the solvent was removed *in vacuo* and the residue was recrystallised from dichloromethane. Colourless crystals formed upon storage at −30 °C overnight were identified as $[(TMC)_2Au]Cl(DCM)$ by single crystal X-ray crystallography.[16]

Reaction of 2 with Ag[Al{OC(CF3)3}4]

A colourless solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (28 mg, 22 µmol, 0.5 eq.) in dichloromethane (1.5 mL) was added to **2** (20 mg, 45 µmol, 1.0 eq.) in tetrahydrofurane (3 mL) at –30 °C The solution turned intense orange while stirring overnight and was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S123).

Reaction of 2 with [(*p*-cymene)RuCl2]2

An orange solution of [*p*-cymeneRuCl$_2$]$_2$ (14 mg, 22 µmol, 0.5 eq.) in THF (7 mL) was added to **2** (20 mg, 45 µmol, 1.0 eq.) in THF (3 mL). The reaction mixture turned red whilst stirring overnight and was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S124).

Reaction of 2 with [(cod)RhCl]2

A solution of [(cod)RuCl]$_2$ (13 mg, 27 µmol, 0.8 eq.) in THF (1 mL) was added to an orange solution of **2** (15.0 mg, 33.4 µmol, 1.0 eq.) in THF (1 mL) at –30 °C. The reaction mixture was stirred overnight whilst turning brown and was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (Figure S125).

Reaction of 1 with ^{Ment}CAAC

To a solution of ^{Ment}CAAC (50 mg, 0.13 mmol, 1.0 eq) in toluene (10 mL) was added $(t\text{BuCP})_2$ (0.59 M in toluene, 0.5 mL, 0.3 mmol, 2.3 eq.). After stirring at ambient temperature in the dark for two weeks, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy revealed the presence of starting material (**1** + ^{Ment}CAAC) and $(t\text{BuCP})_4$ (see Figure S126). Stirring at ambient temperature for another two weeks did not result in any further change of the integral ratios.

Reaction of 1 with and $i\text{Pr}_2\text{Im}^{Me}$

To a solution of $i\text{Pr}_2\text{Im}^{Me}$ (30 mg, 0.17 mmol, 1.0 eq) in toluene (10 mL) was added $(t\text{BuCP})_2$ (0.59 M in toluene, 0.5 mL, 0.3 mmol, 2.4 eq.). After stirring at ambient temperature in the dark for two weeks, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy revealed the presence of starting material (**1** + $i\text{Pr}_2\text{Im}^{Me}$) and $(t\text{BuCP})_4$ and two other, unidentified species (see ^{31}P{^{1}H} NMR spectrum in Figure S127). Stirring at ambient temperature for another two weeks did not result in any further change of the integral ratios.

S2 NMR Spectra

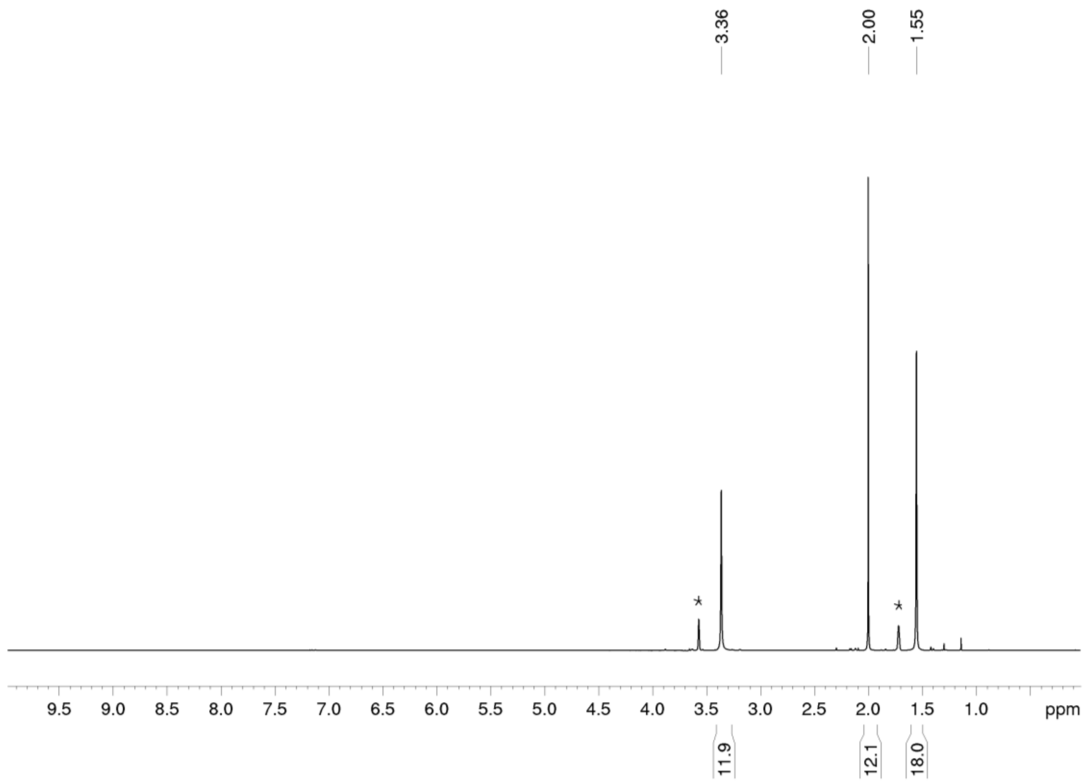

Figure S102. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **2**; *THF-d_8.

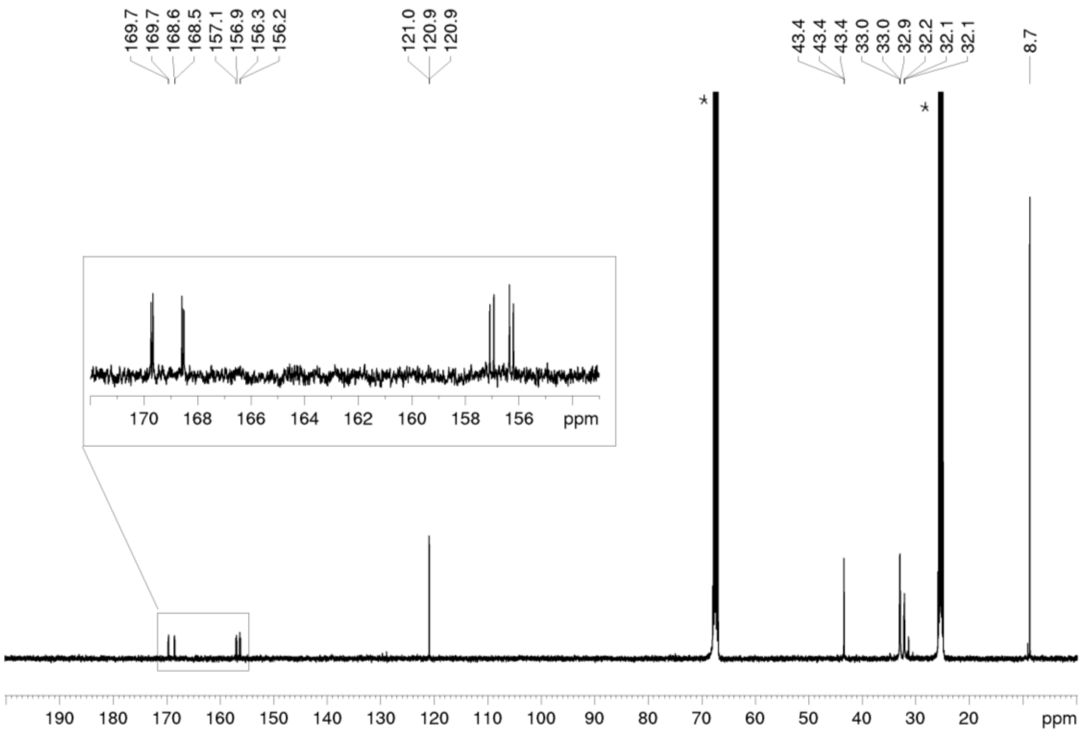

Figure S103. ^{13}C{^{1}H} NMR spectrum (100 MHz, 300 K, THF-d_8) of **2**; *THF-d_8.

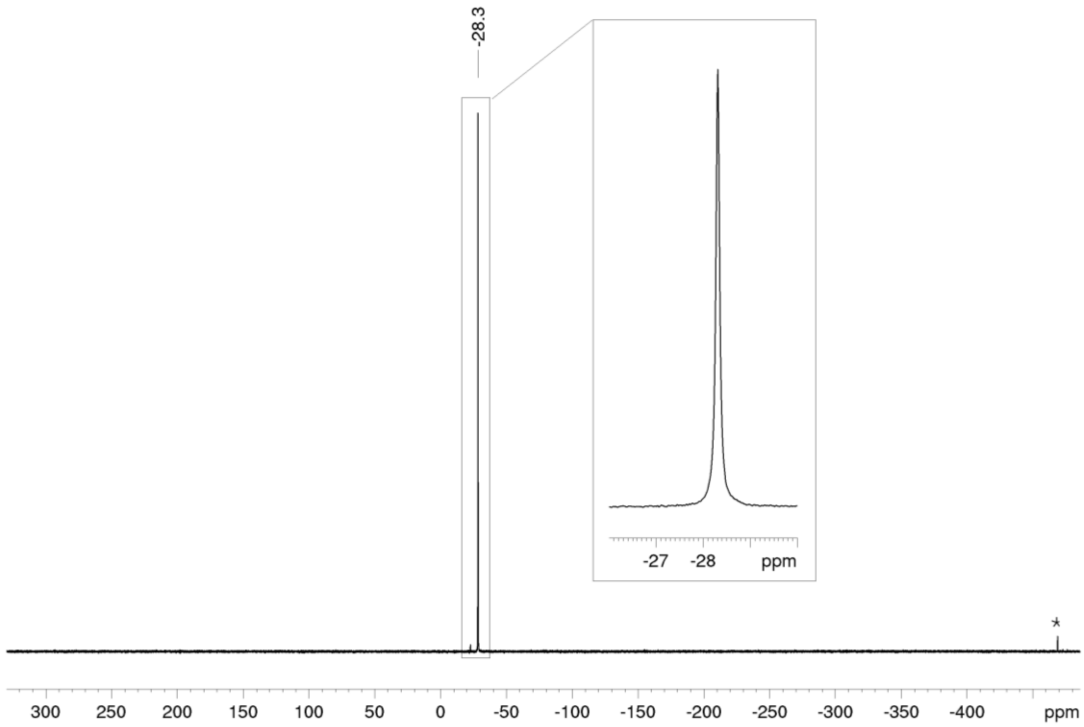

Figure S104. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d$_8$) of **2**; *minor amount of **1** (*t*BuCP)$_2$.

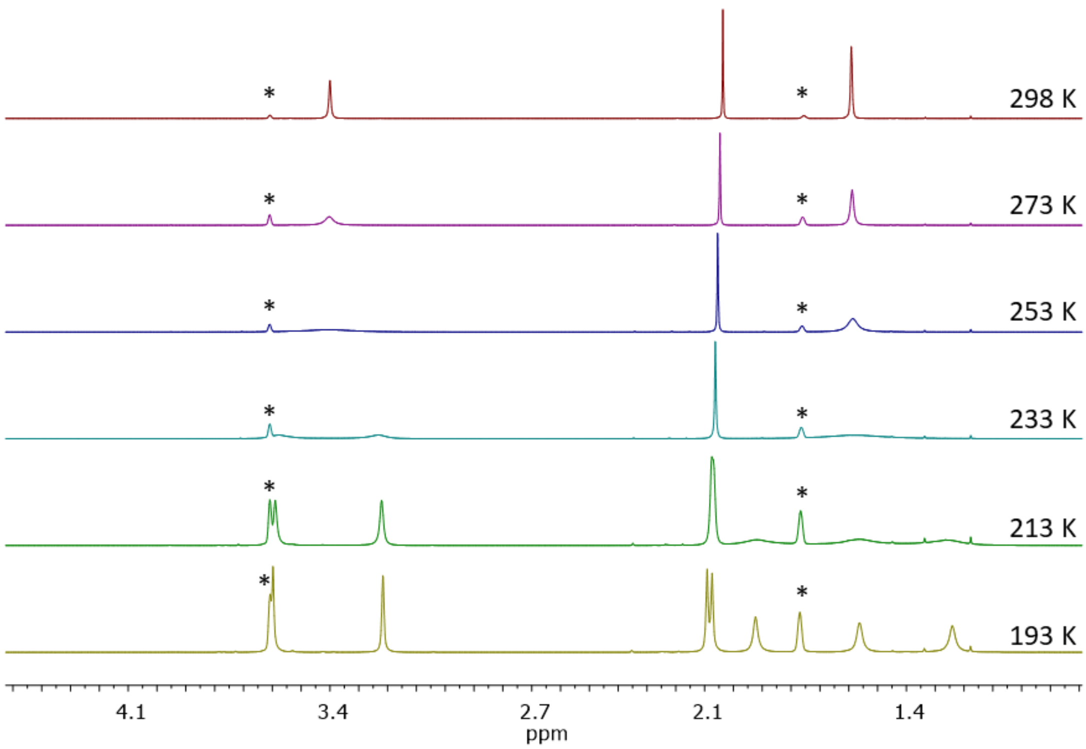

Figure S105. Variable Temperature ^{1}H NMR spectra (400 MHz, THF-d$_8$) of **2**; *THF-d$_8$.

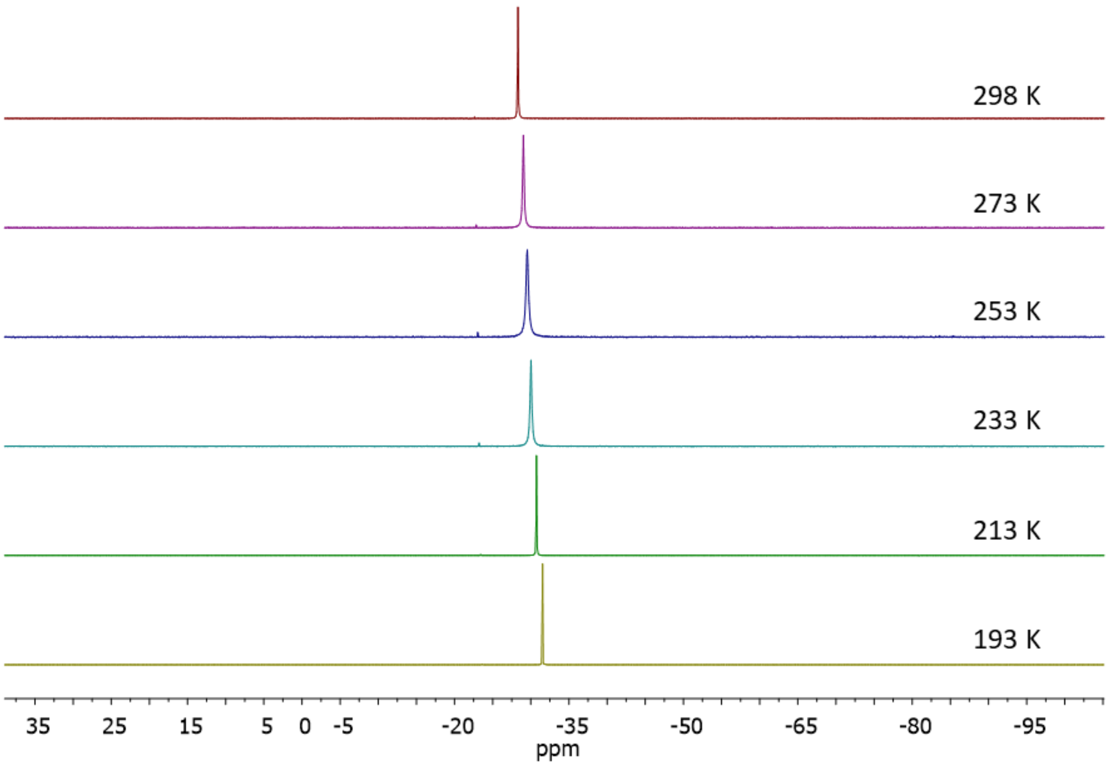

Figure S106. Variable Temperature $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, THF-d_8) of **2**.

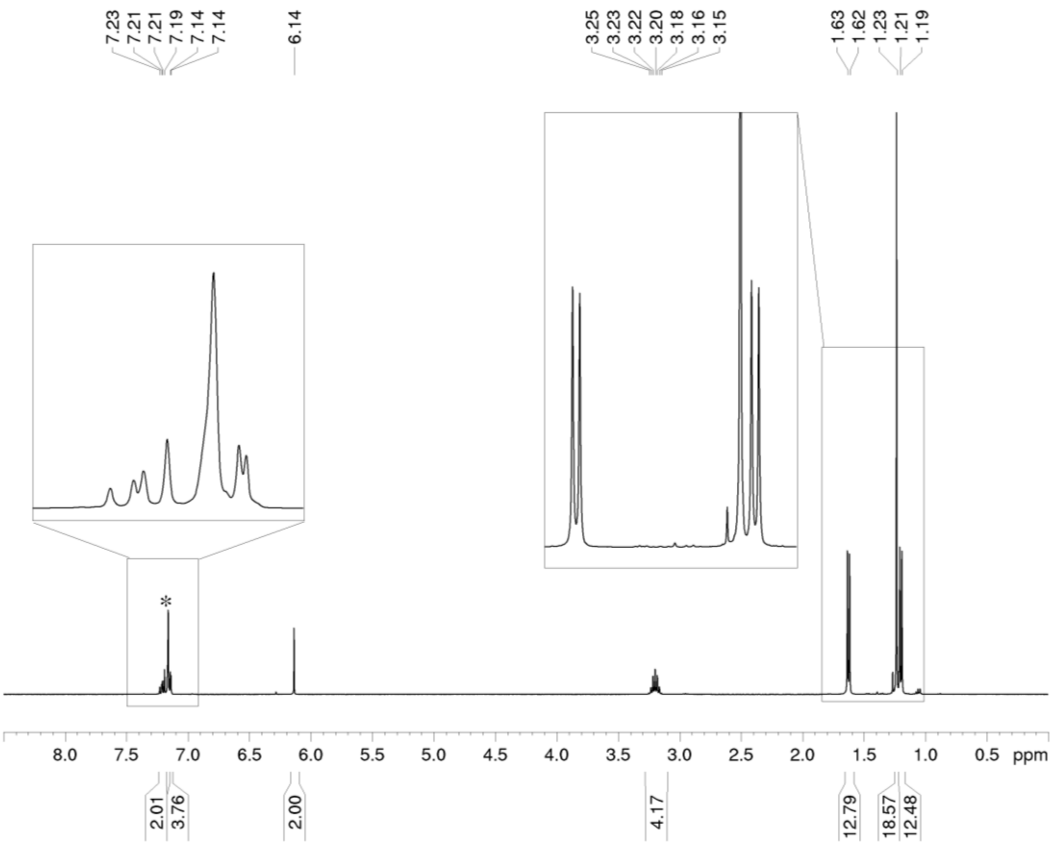

Figure S107. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **3a**; *C_6D_6.

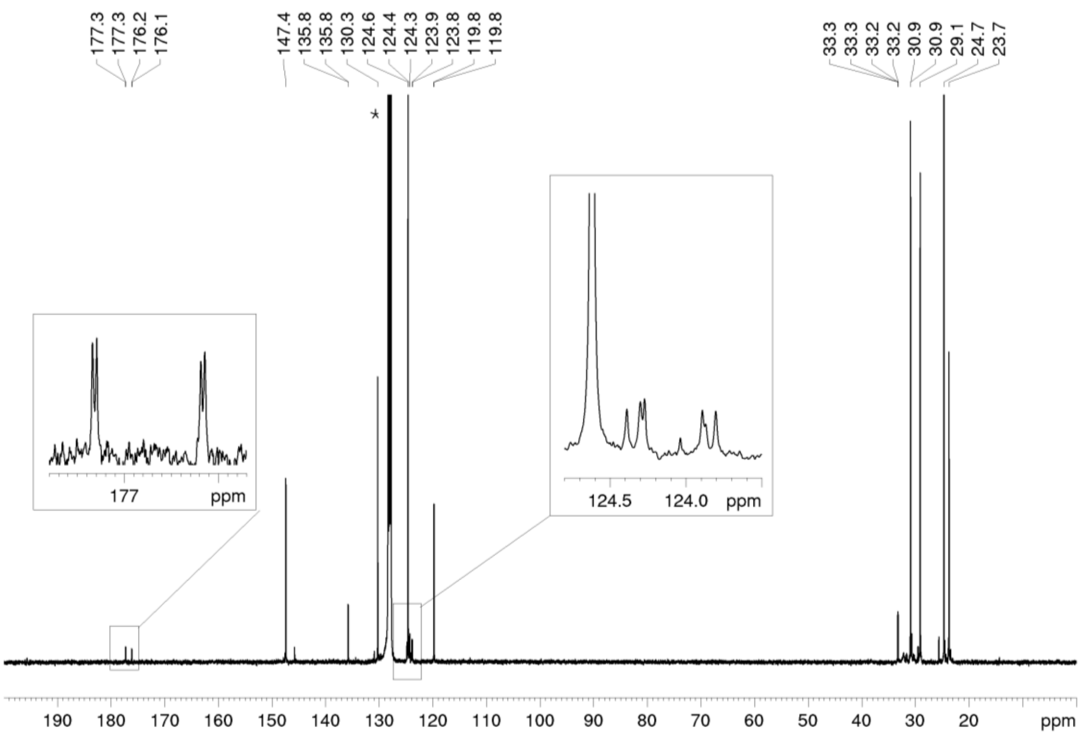

Figure S108. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **3a**; *C_6D_6.

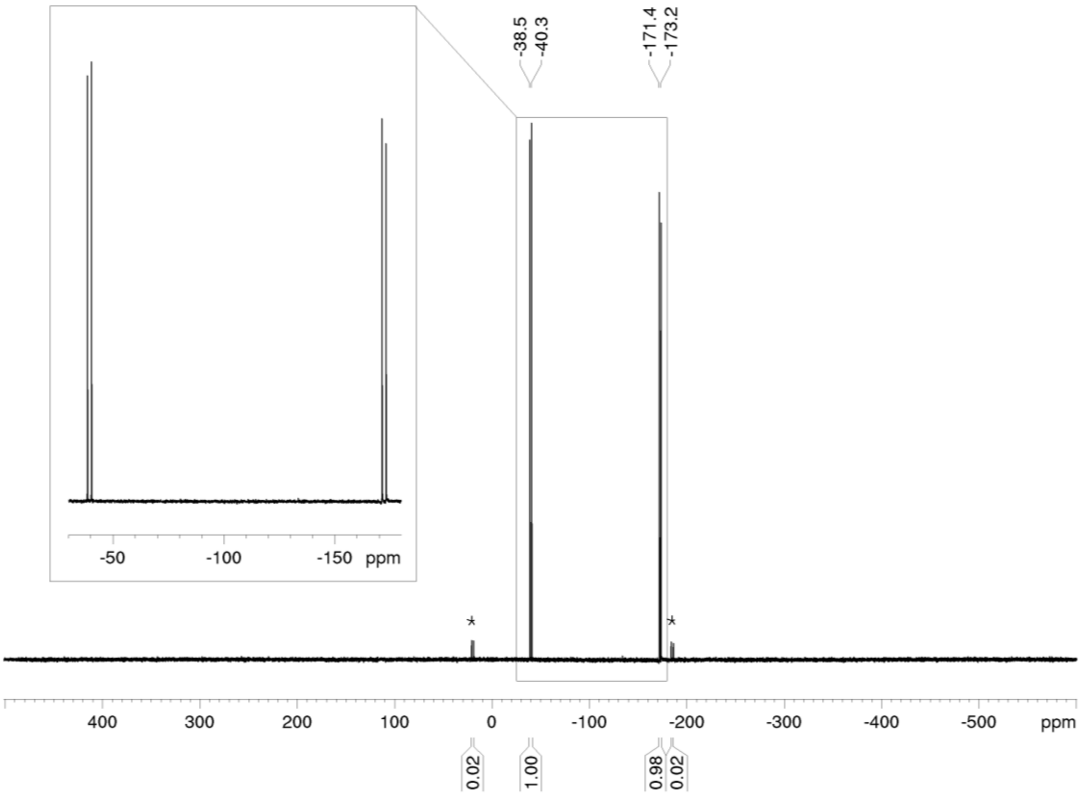

Figure S109. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **3a**; *minor unknown impurity (<2%).

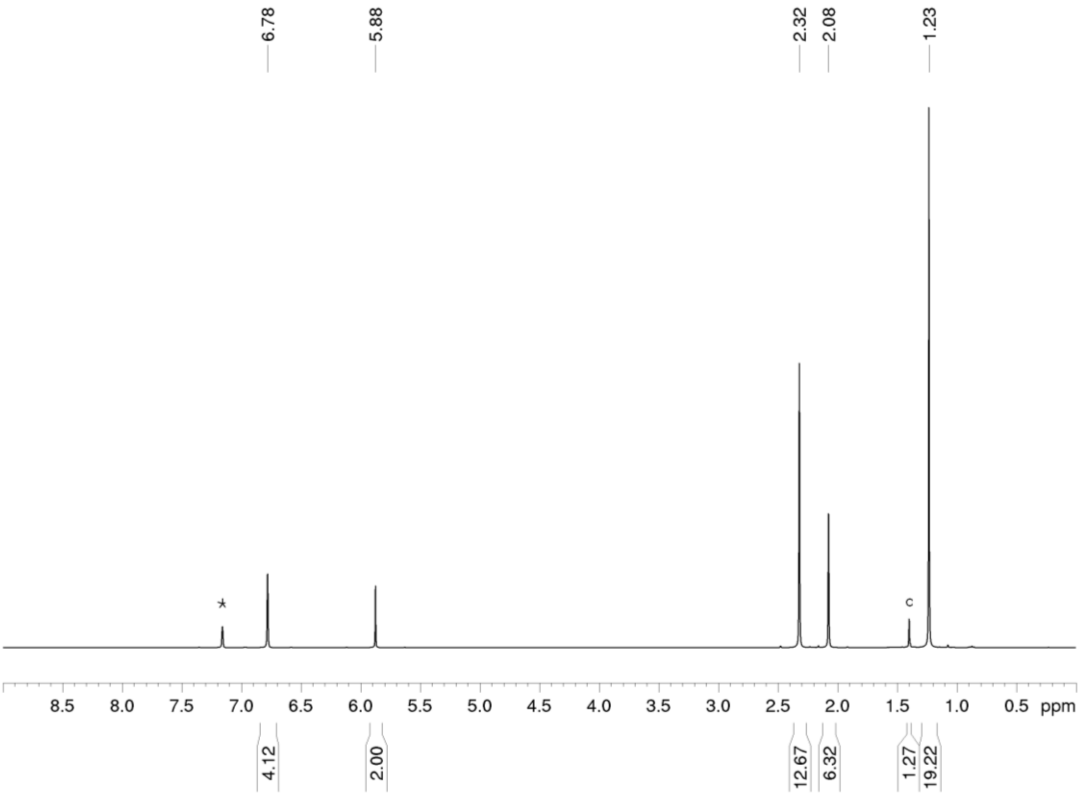

Figure S 110. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **3b**; *C_6D_6; °minor amount of (*t*BuCP)$_4$ (<3%).

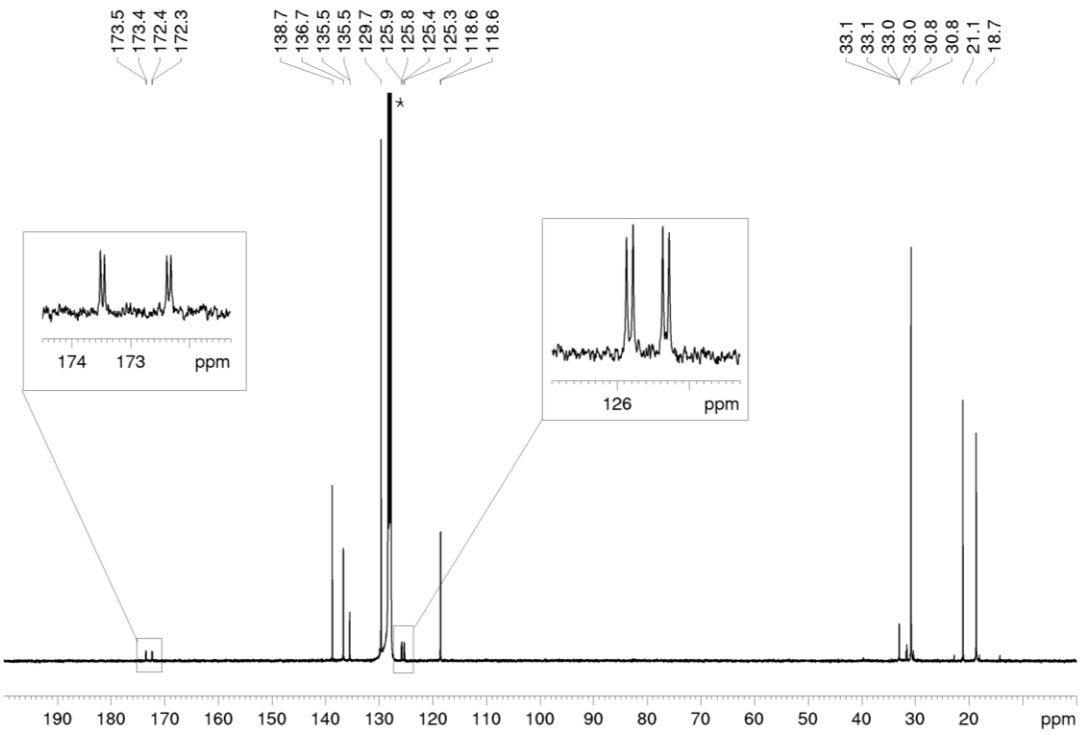

Figure S111. ^{13}C{^{1}H} NMR spectrum (100 MHz, 300 K, C_6D_6) of **3b**; *C_6D_6.

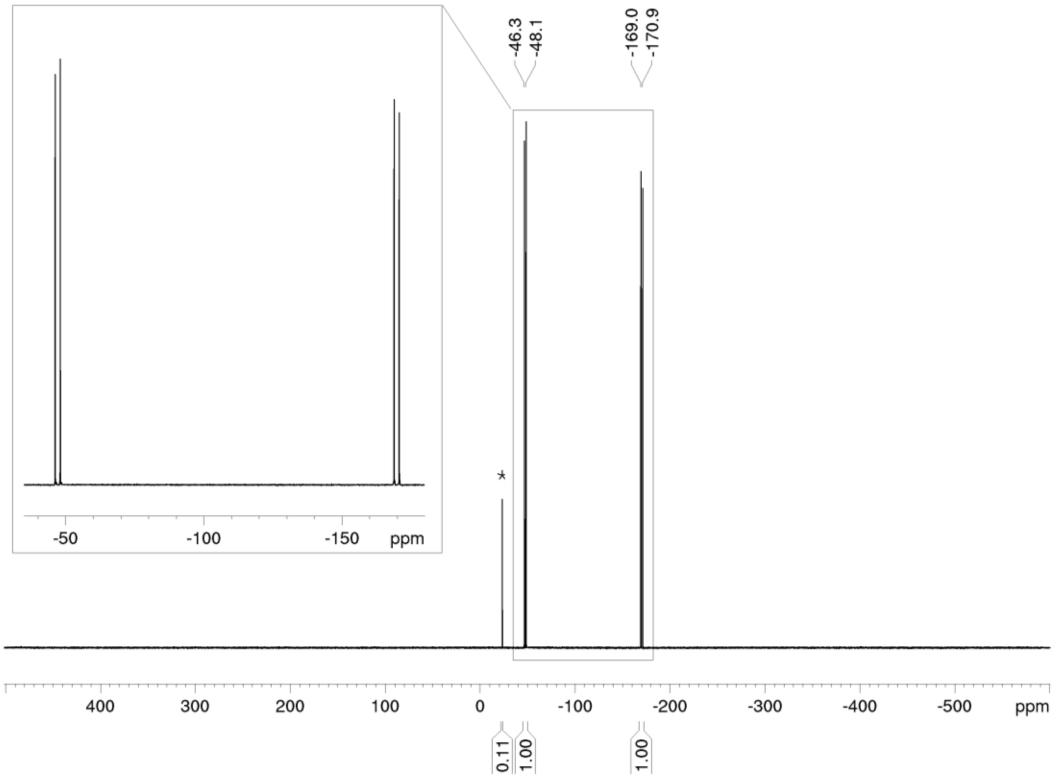

Figure S112. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **3b**; *minor amount of **1** (tBuCP)$_4$ (<3%).

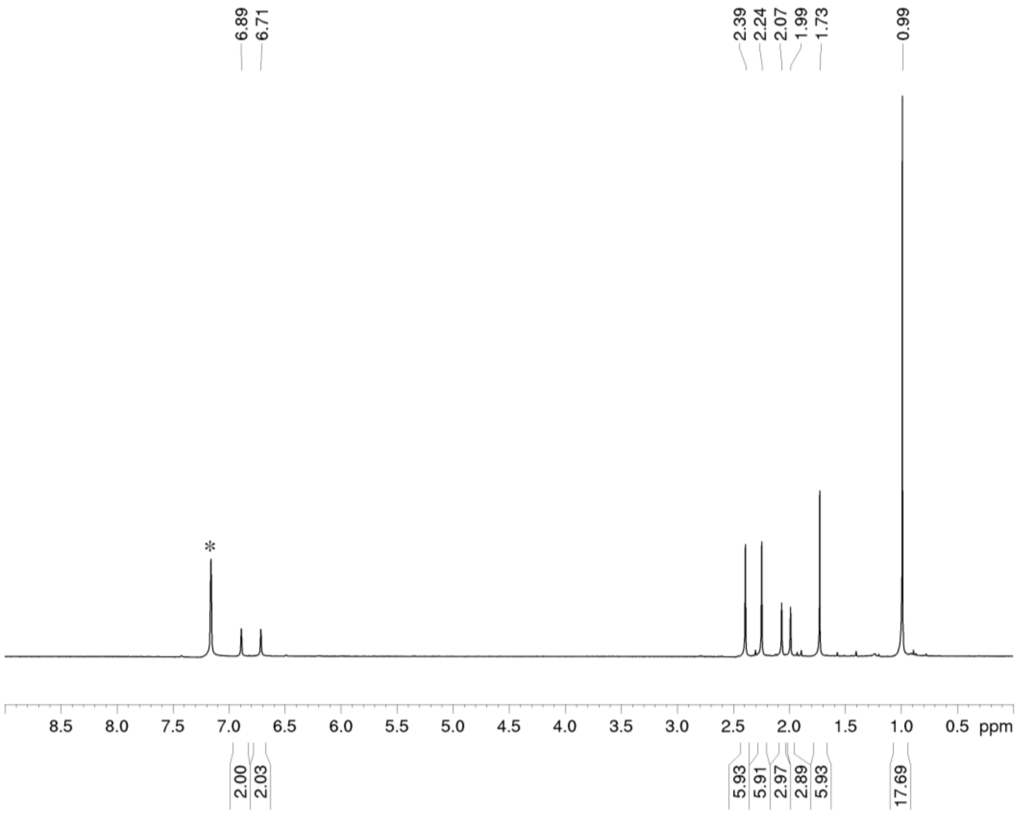

Figure S113. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **3c**; *C_6D_6.

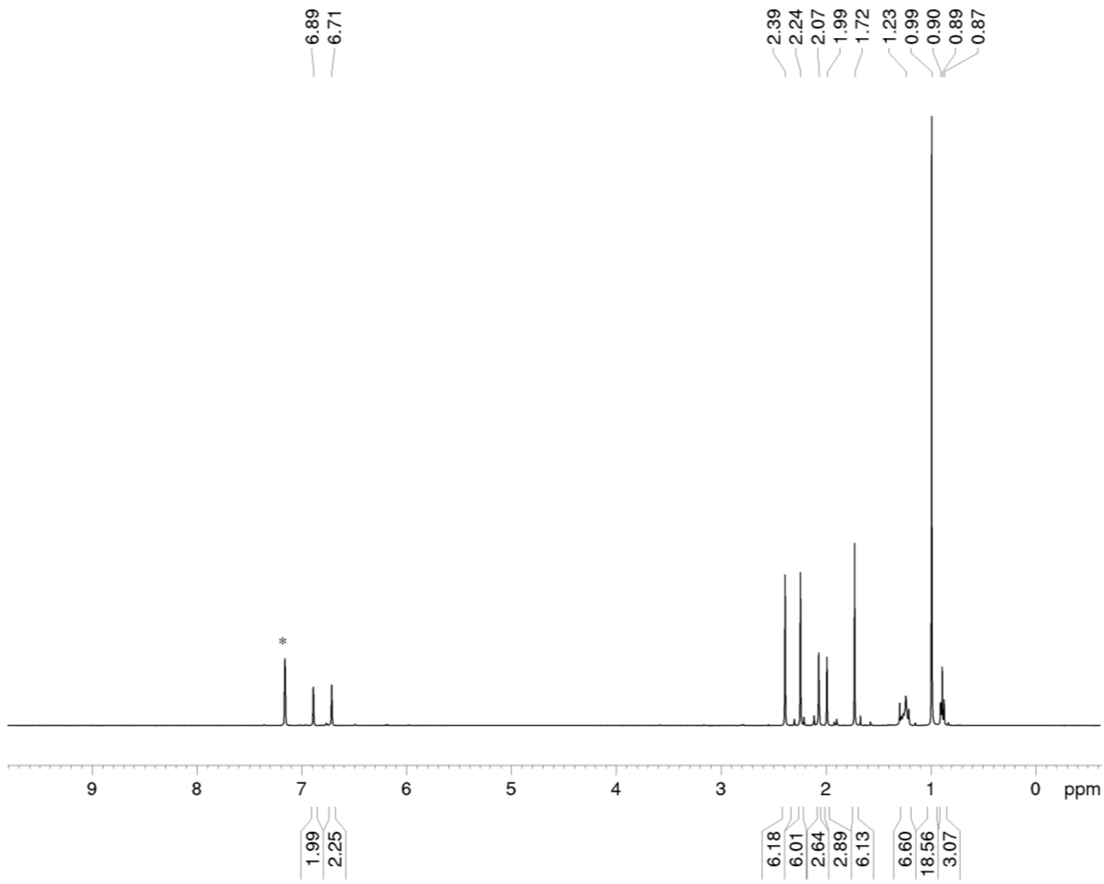

Figure S114. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **3c** (*0.5 hex); *C_6D_6.

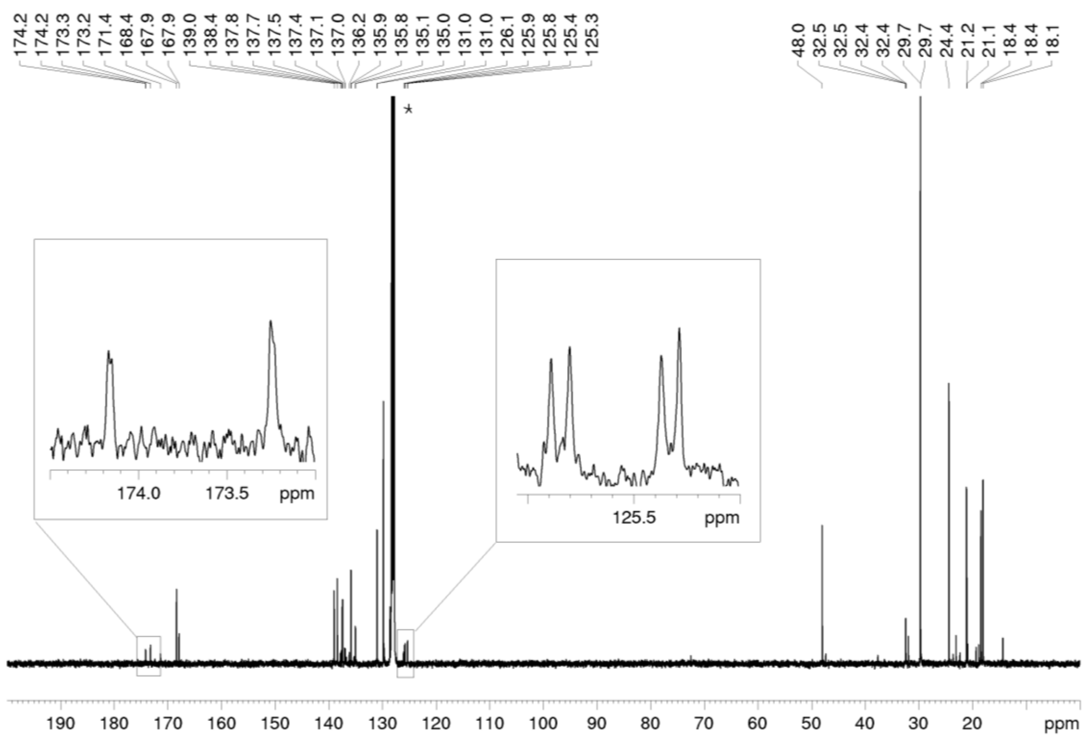

Figure S115. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **3c**; *C_6D_6.

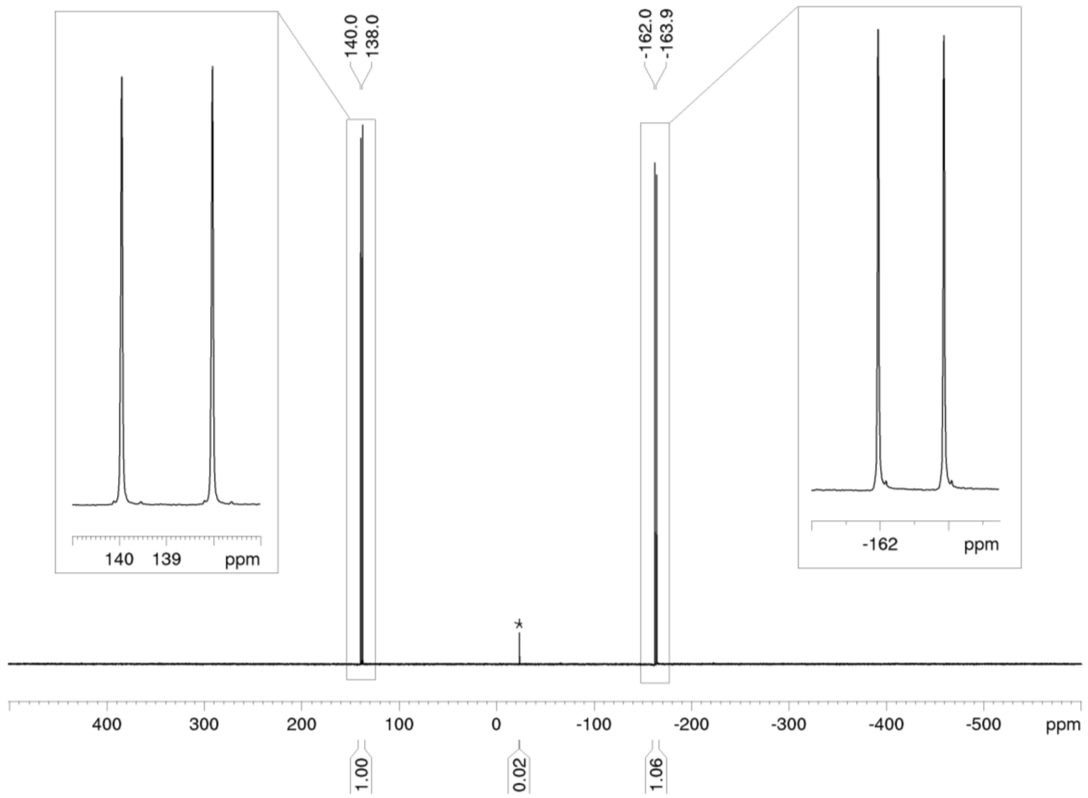

Figure S116. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **3c**; *minor amount of (*t*BuCP)$_4$ (<1%).

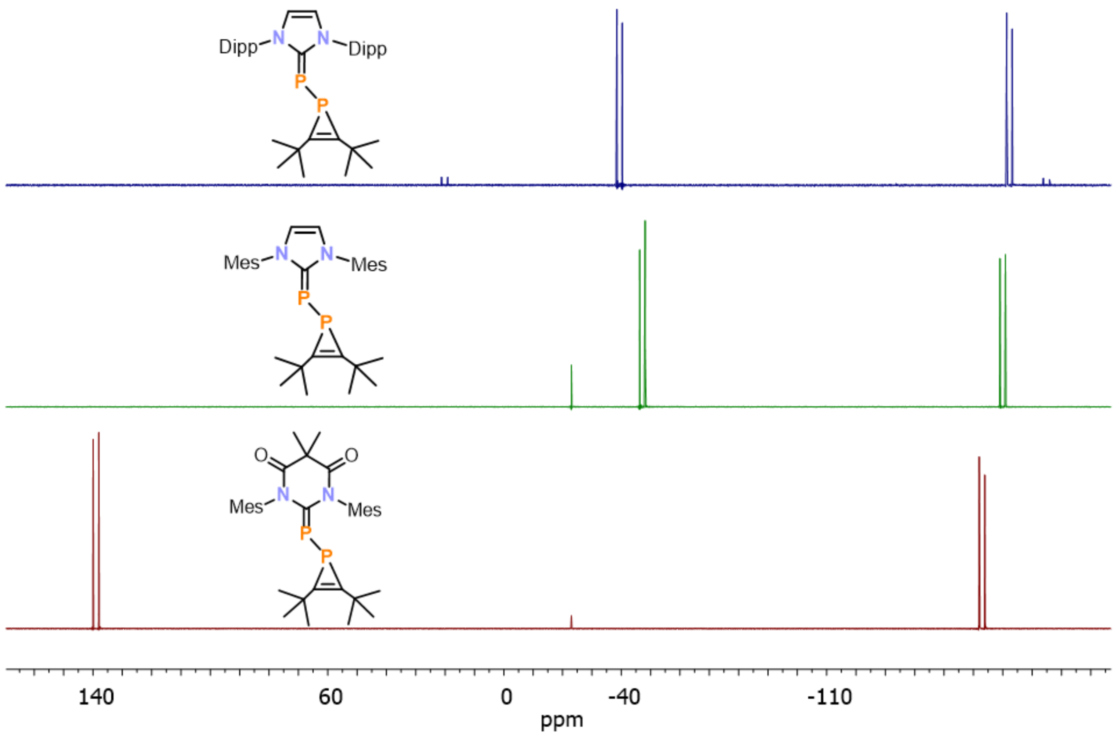

Figure S117. $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, 300K, C_6D_6) of **3a** (top), **3b** (middle) and **3c** (bottom).

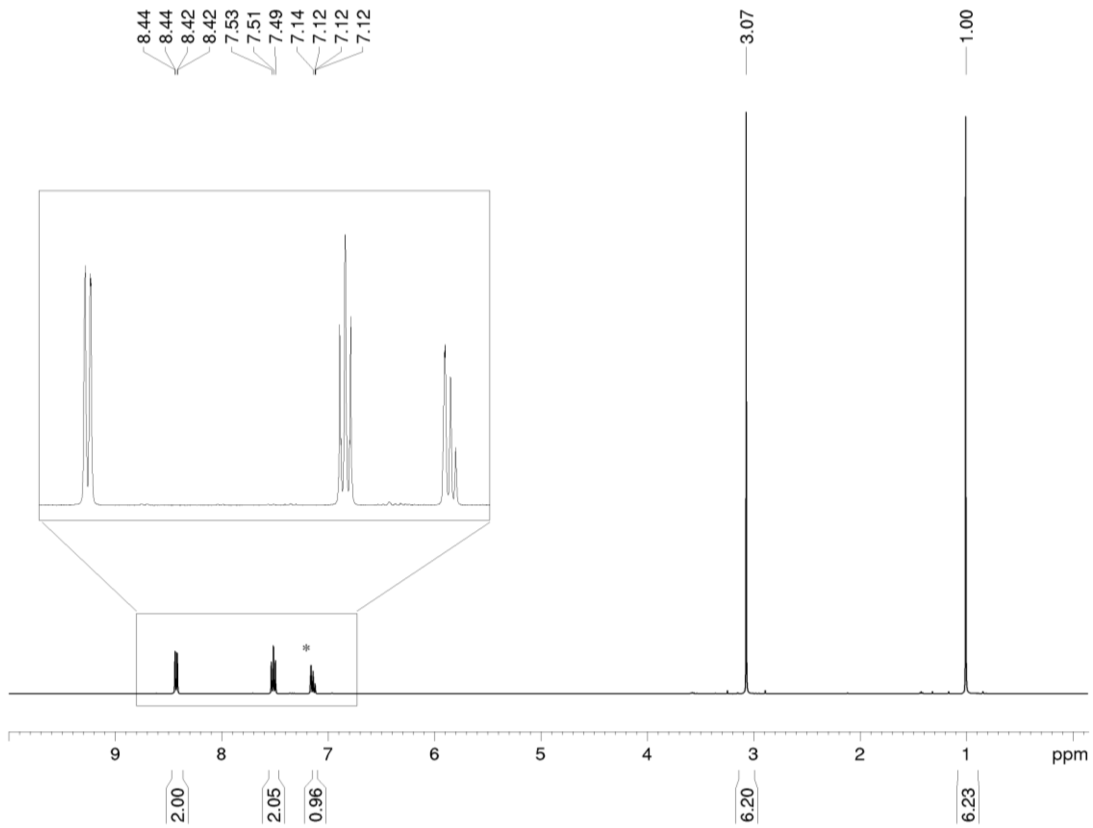

Figure S118. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of [(TMC)=C(S)(NPh)]; *C_6D_6.

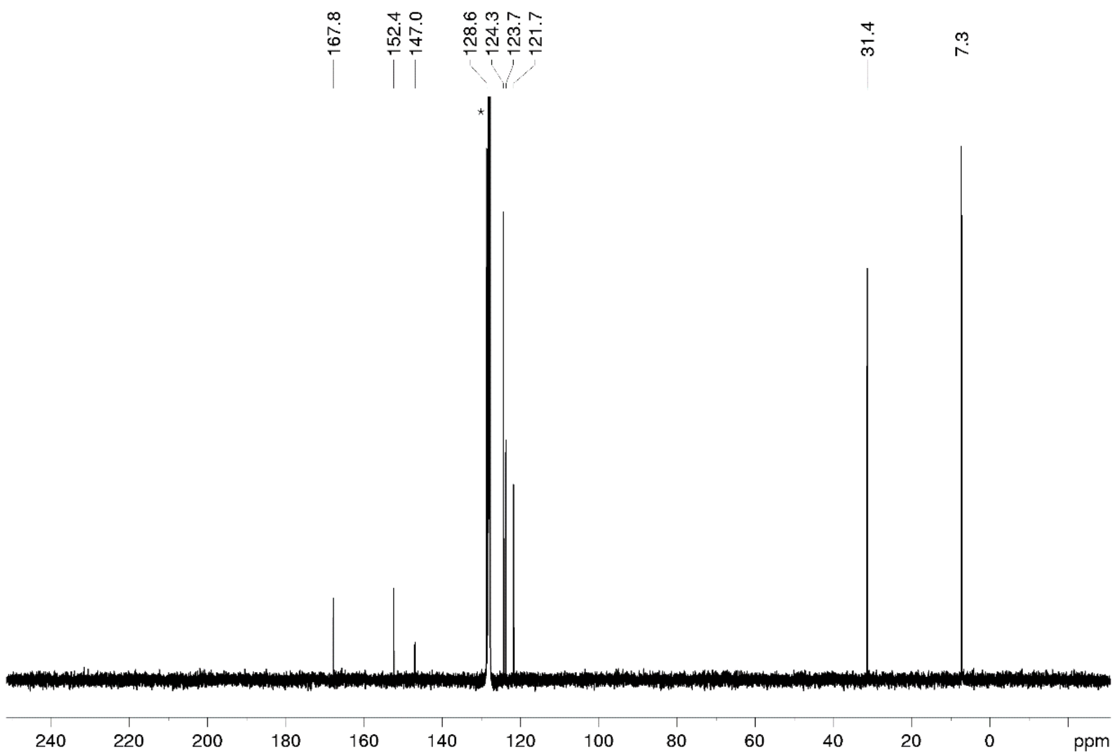

Figure S119. ^{13}C{^{1}H} NMR spectrum (100 MHz, 300 K, C_6D_6) of [(TMC)=C(S)(NPh)]; *C_6D_6.

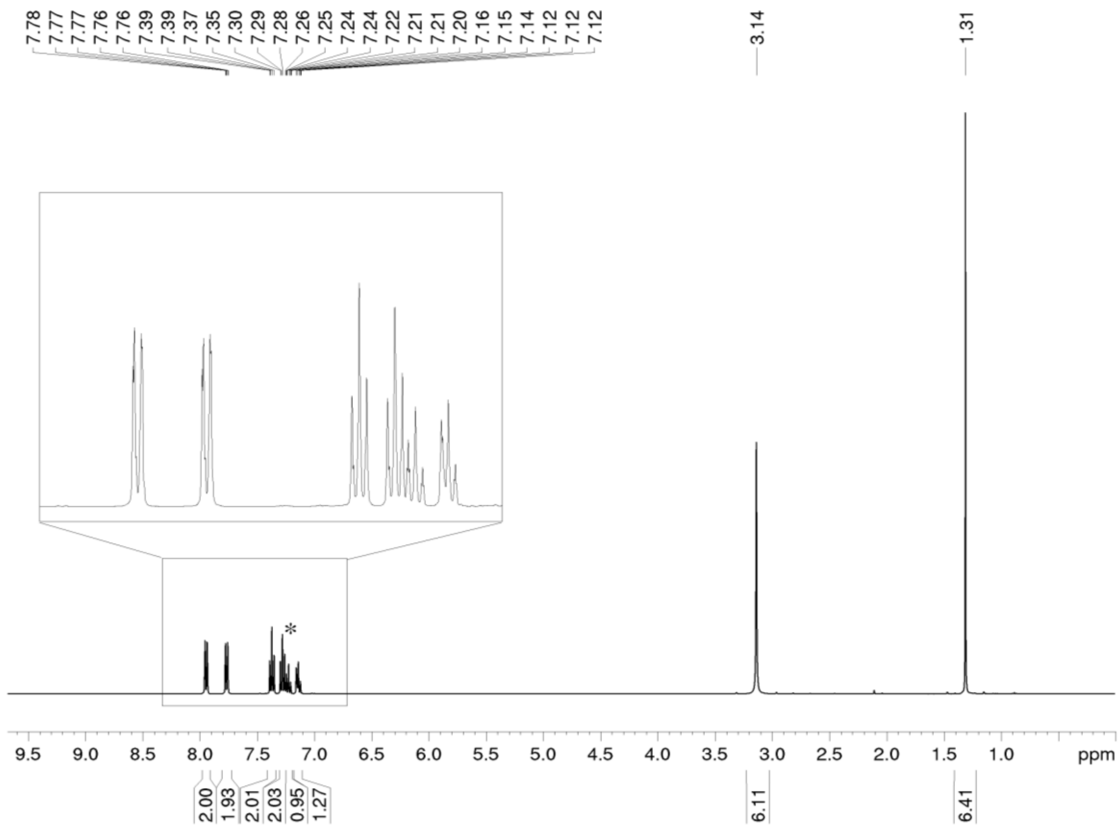

Figure S120: ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of [(TMC)-N=N-CPh$_2$]; *C_6D_6.

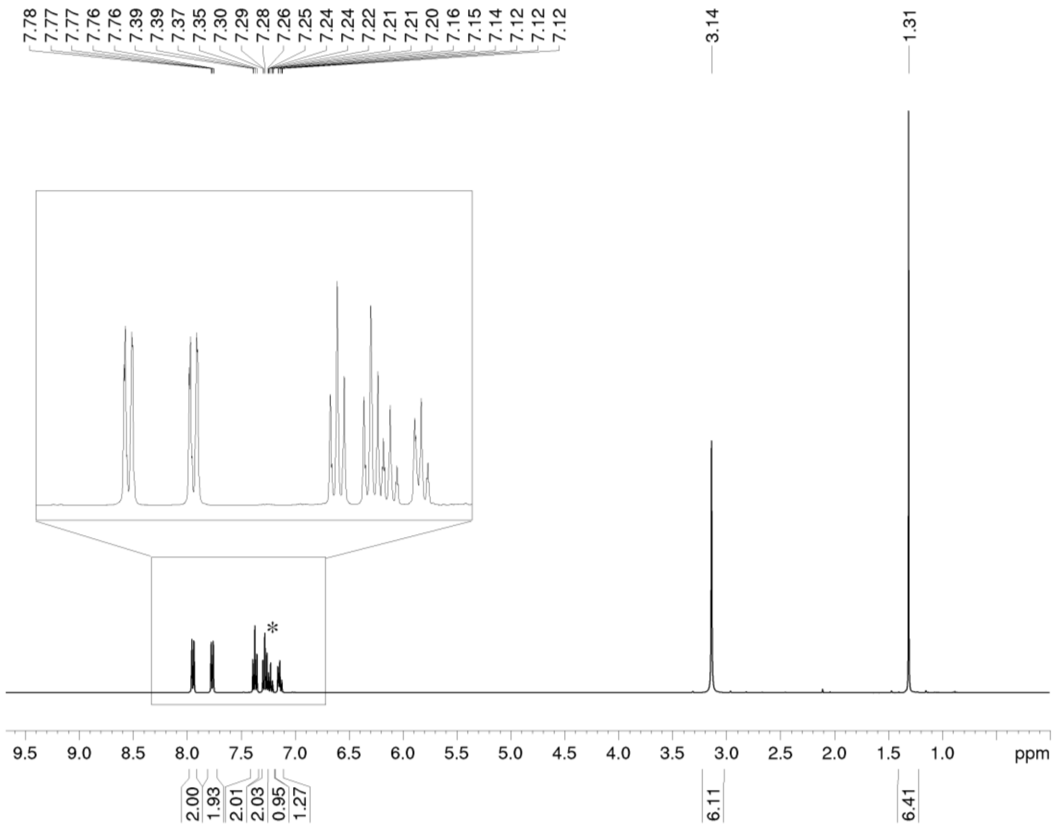

Figure S121. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of [(TMC)-N=N-CPh$_2$]; *C_6D_6.

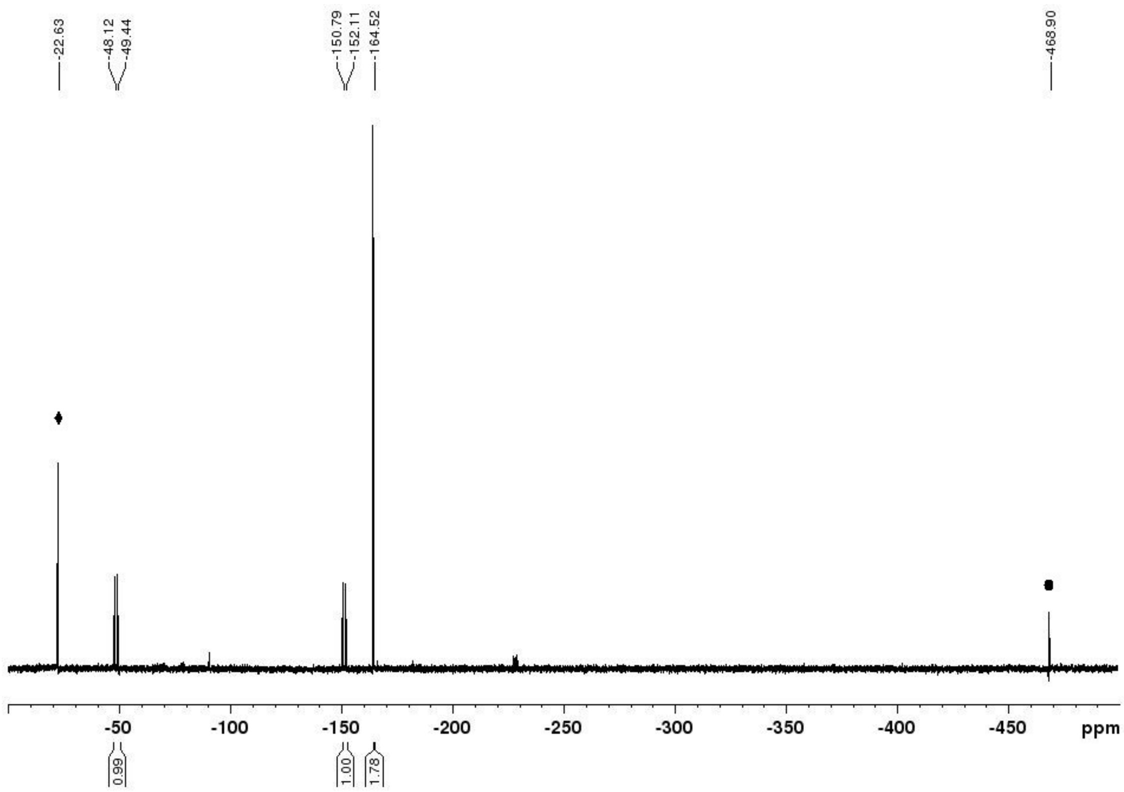

Figure S122. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **2** with AuCl(tht). ◆(*t*BuCP)$_4$, ● (*t*BuCP)$_2$

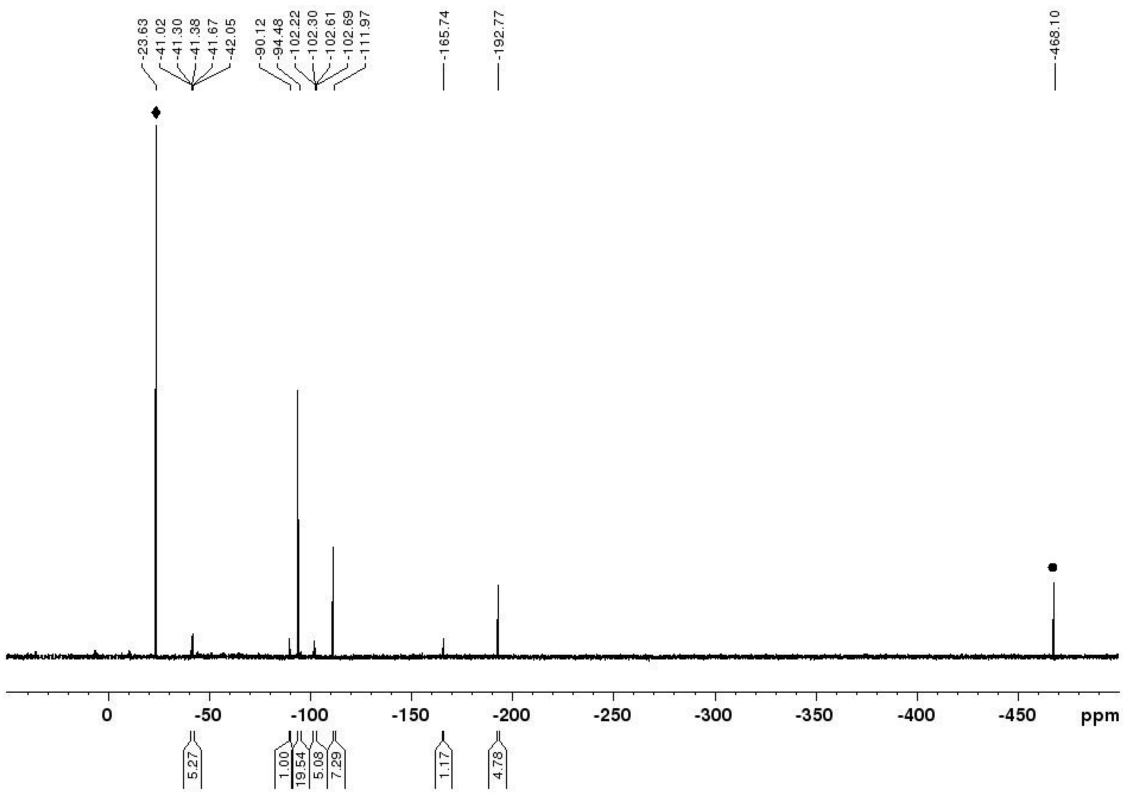

Figure S123. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **2** with Ag[Al{OC(CF_3)$_3$}$_4$]; ◆(*t*BuCP)$_4$, ●*t*BuCP)$_2$.

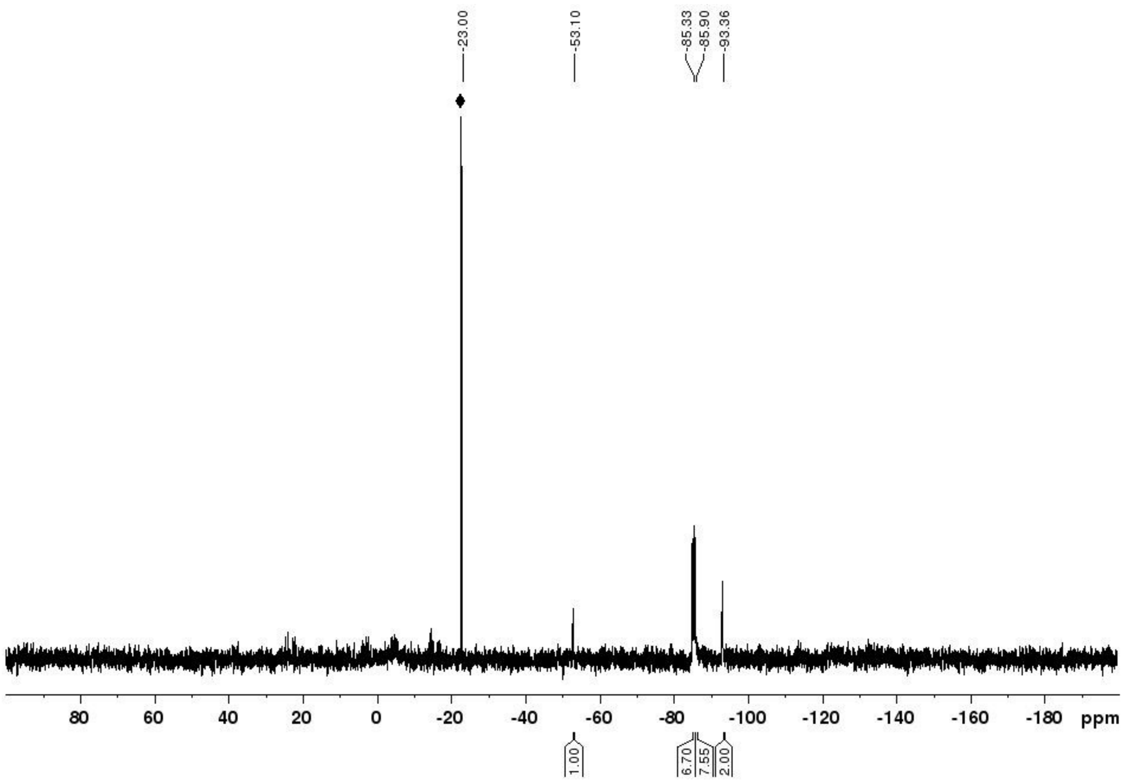

Figure S124. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **2** with [(*p*-cymene)$RuCl_2]_2$; ◆ (*t*BuCP)$_4$.

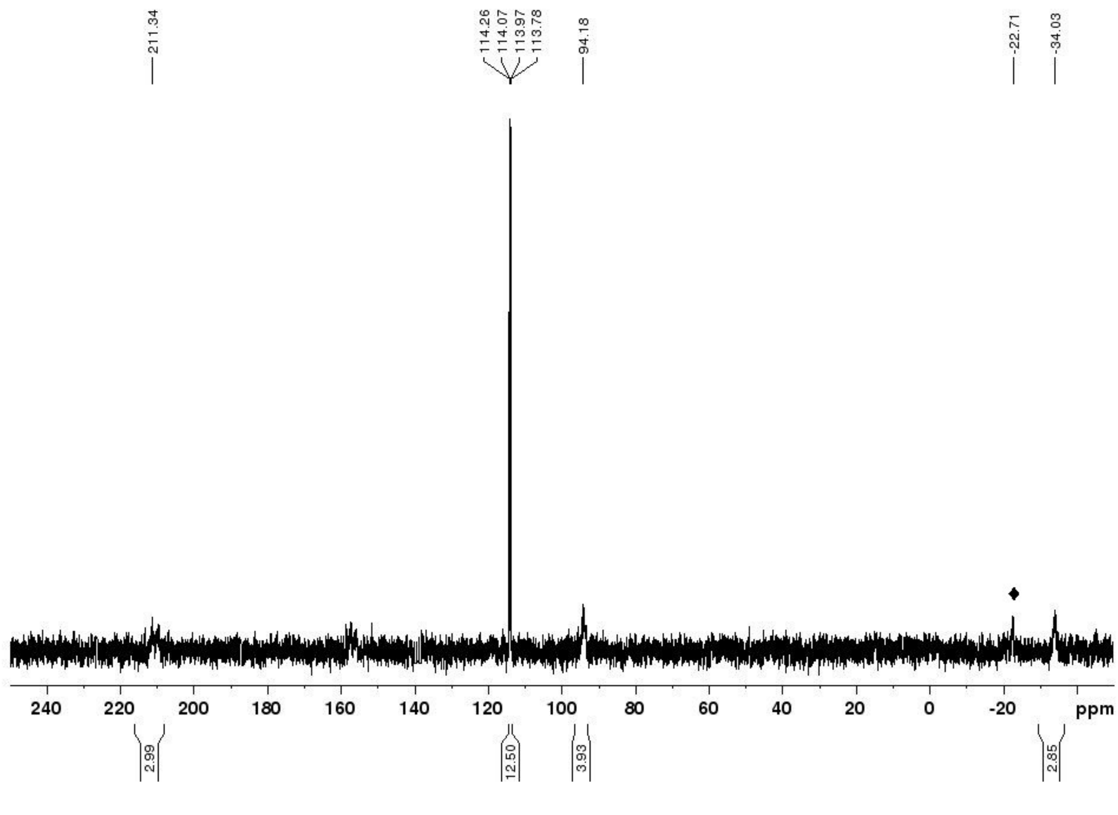

Figure S125. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **2** with [(cod)RuCl]$_2$; ◆ (*t*BuCP)$_4$.

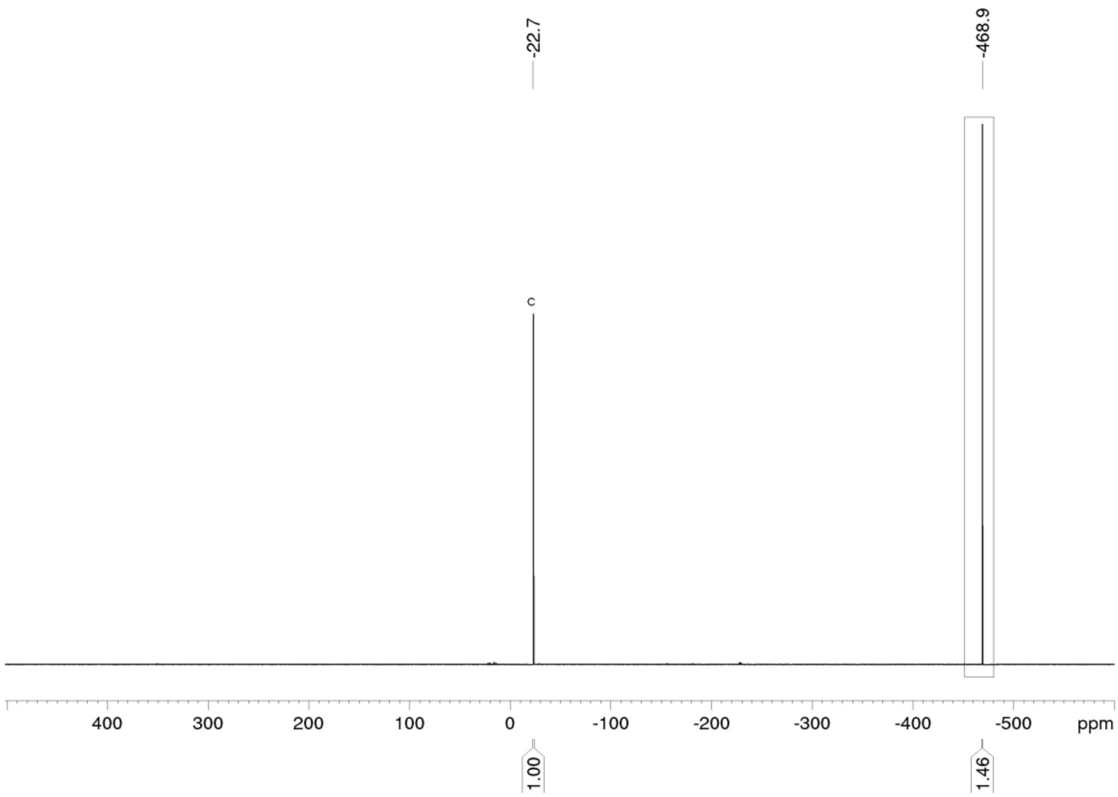

Figure S 126. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **1** with ^{Ment}CAAC; ° (tBuCP)$_4$.

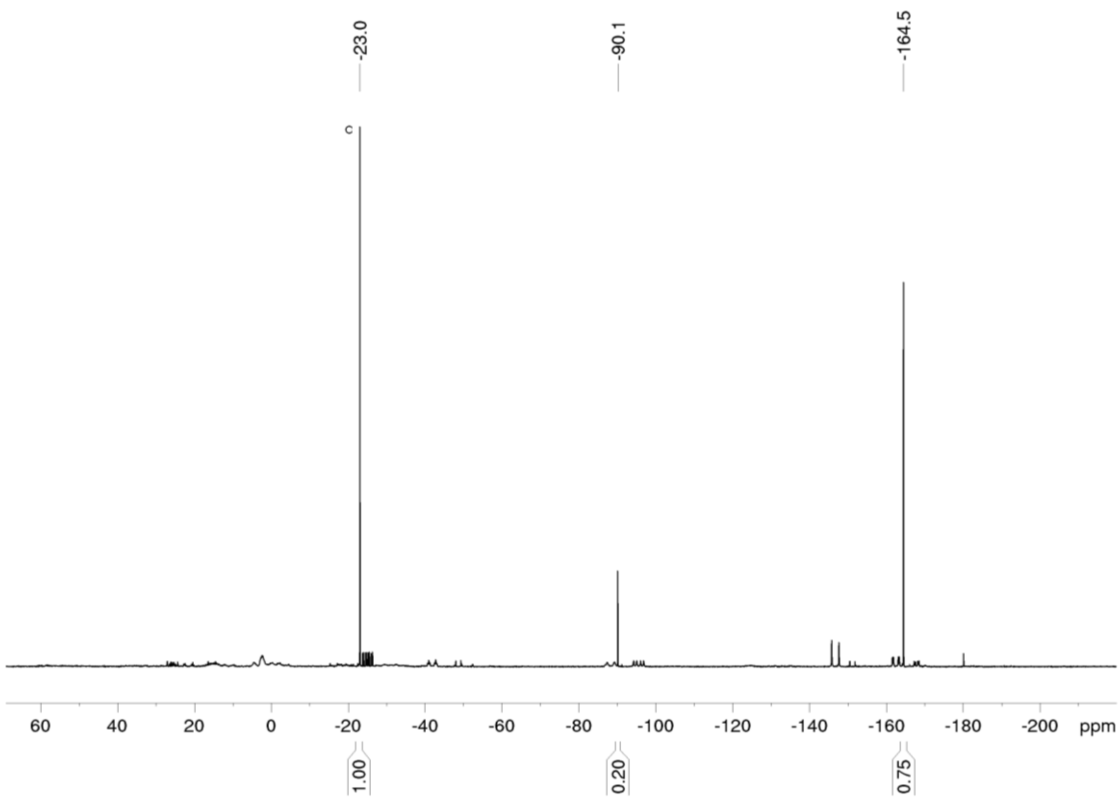

Figure S 127. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **1** with iPr$_2$Im^{Me}; ° (tBuCP)$_4$.

S3 UV/Vis Spectra

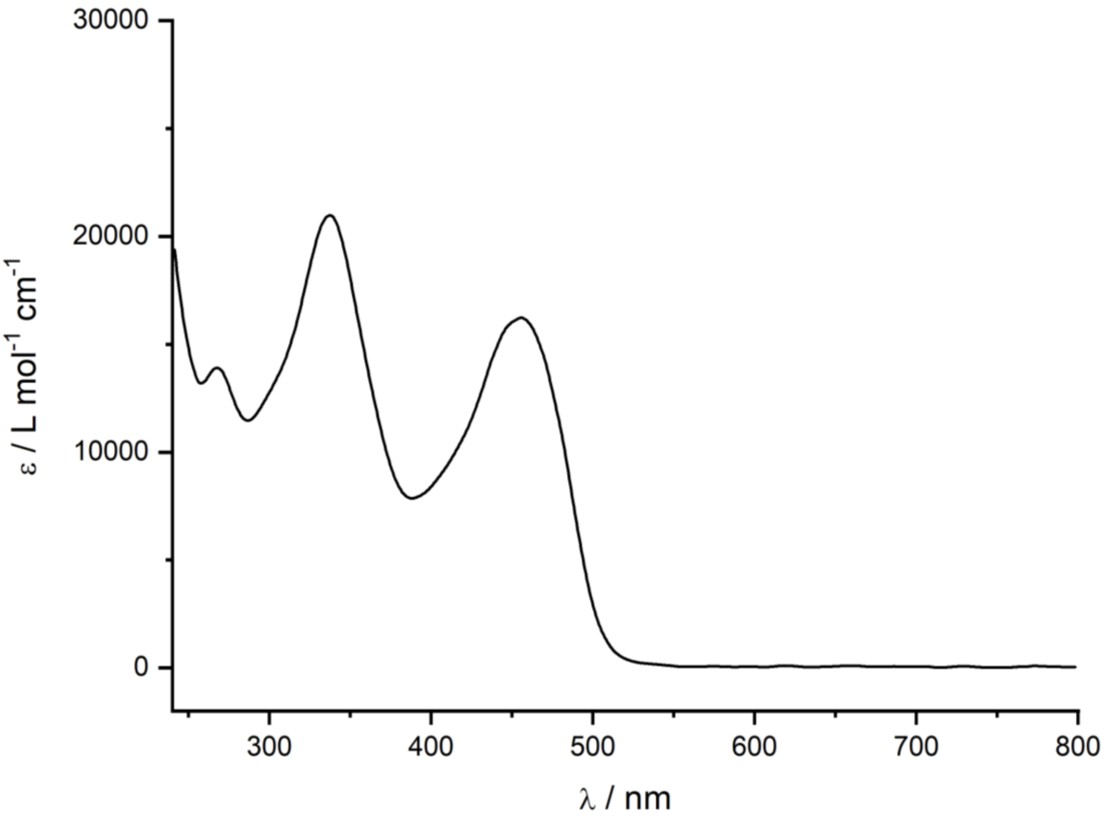

Figure S128. UV/Vis spectrum of **2** recorded in THF.

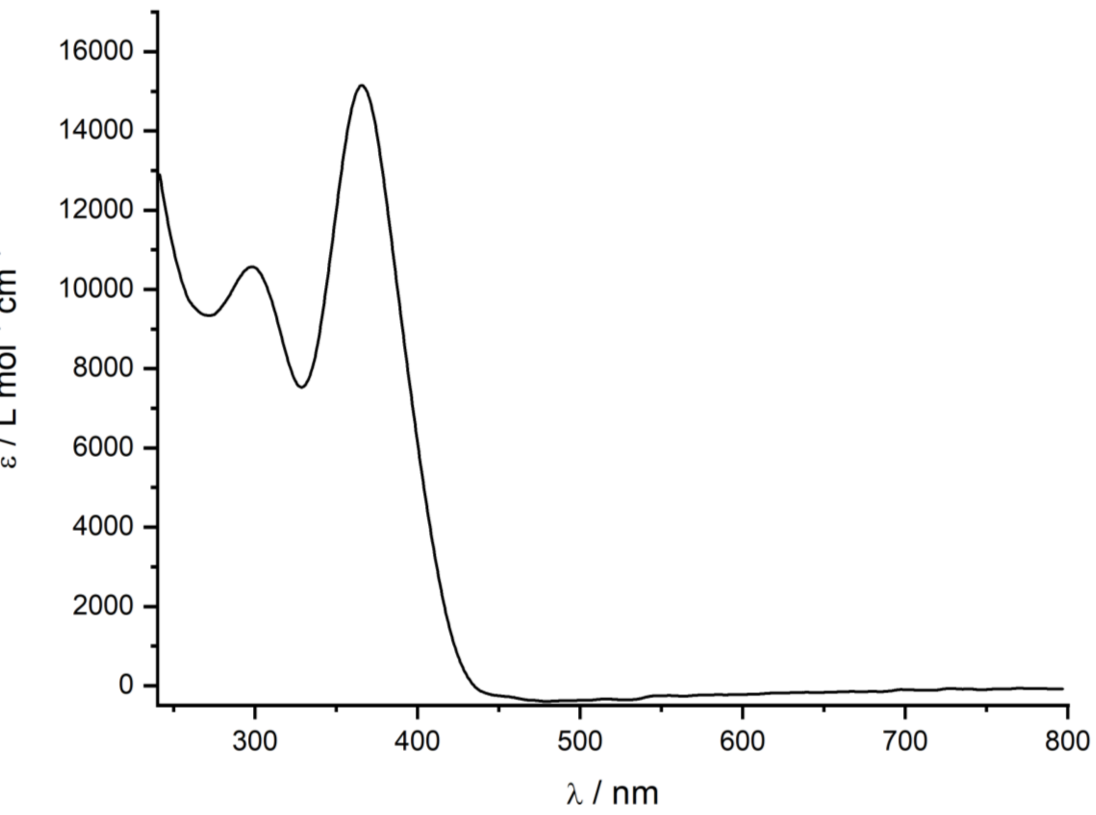

Figure S129. UV/Vis spectrum of **3a** recorded in THF.

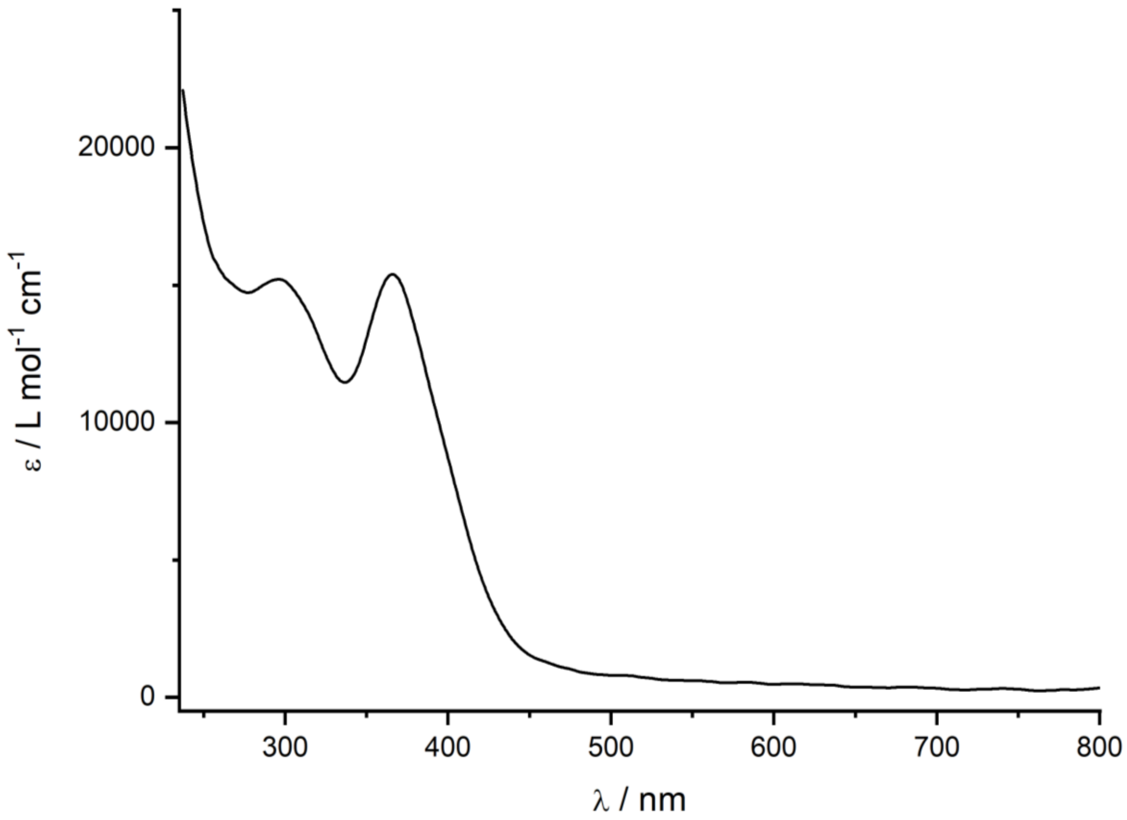

Figure S130. UV/Vis spectrum of **3b** recorded in THF.

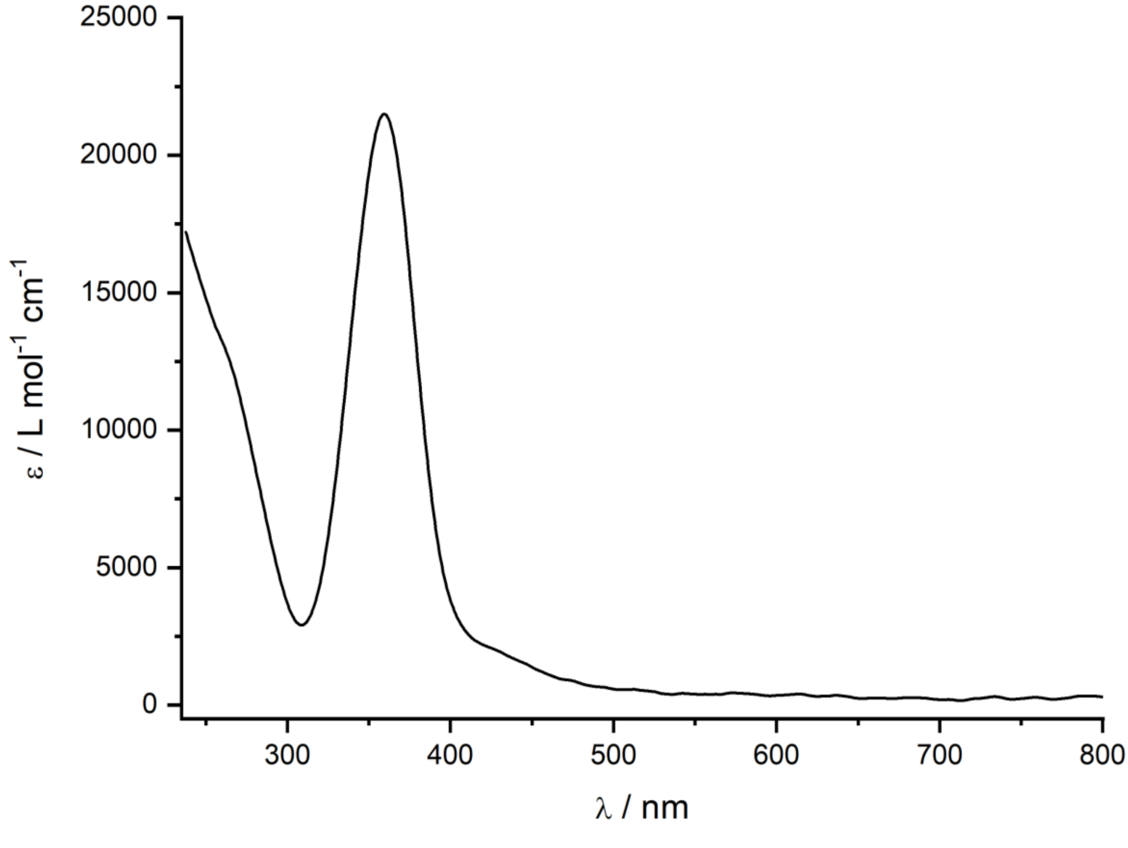

Figure S131. UV/Vis spectrum of **3c** recorded in THF.

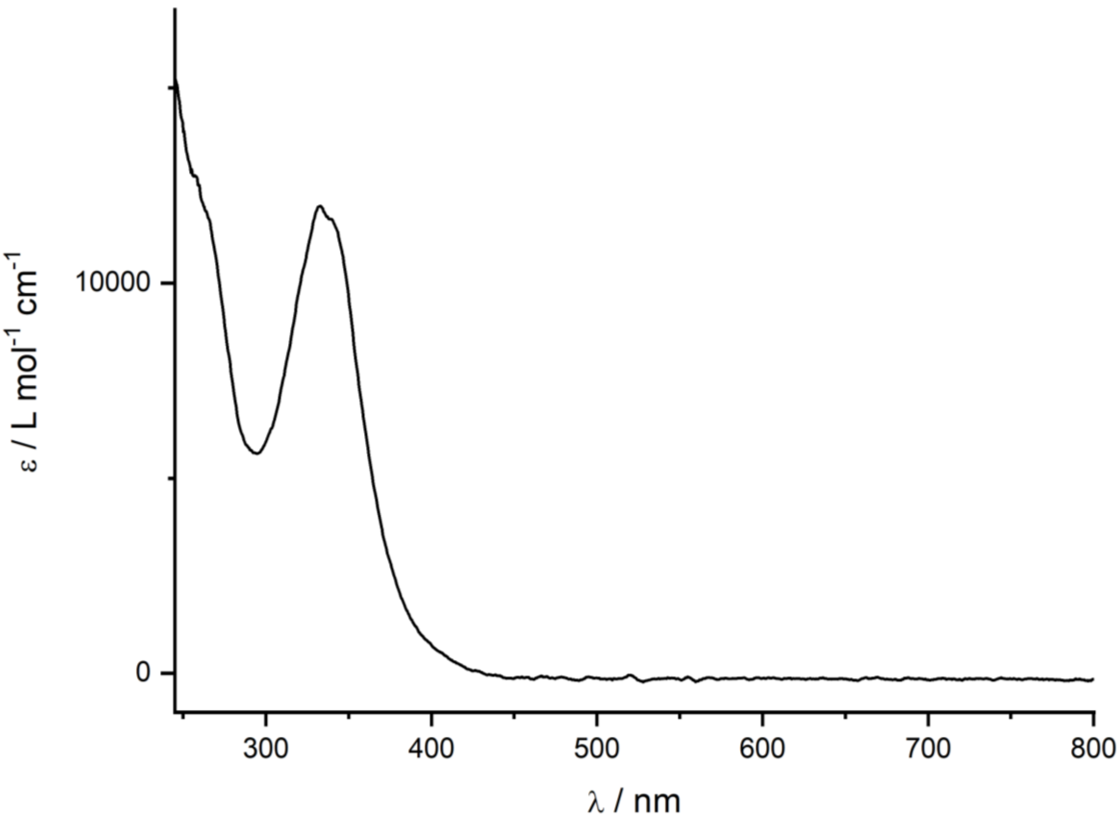

Figure S132. UV/Vis spectrum of [(TMC)=C(S)(NPh)] recorded in THF.

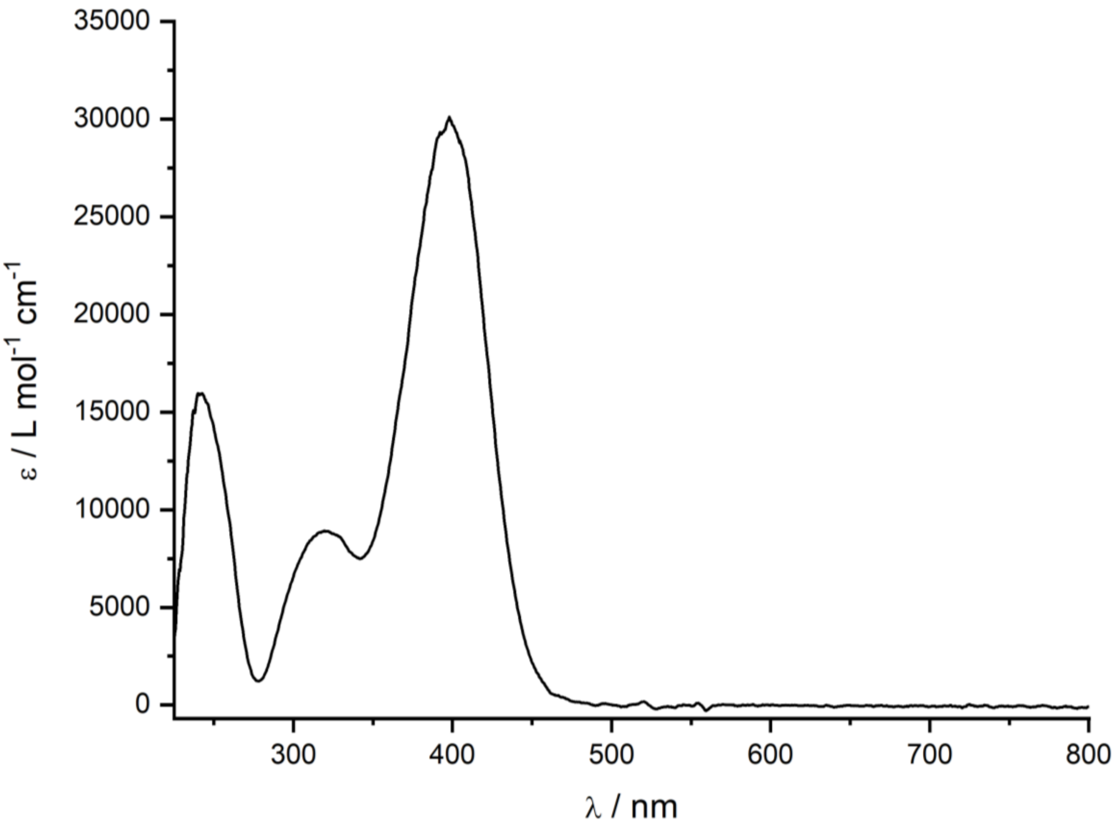

Figure S133. UV/Vis spectrum of [(TMC)-N=N-CPh_2] recorded in THF.

S4 Single Crystal X-ray Diffraction Data

Additional Comments

The disorder in **3a**, **3c** and (TMC)=N-N=CPh_2 were treated with soft displacement parameters and geometrical restraints.

Despite numerous crystallisation attempts, only poor quality crystals could be obtained of compound **3c**. Numerous samples were tested for diffraction, but most crystals turned out to be twinned or only weakly diffracting, especially at higher resolution. Moreover, positional disorder over two positions in the phosphirene moiety was found. The presented dataset was tailored to the best compromise between completeness, frame exposure and total dose time.

Additional Figures (not depicted in the Doctoral Thesis)

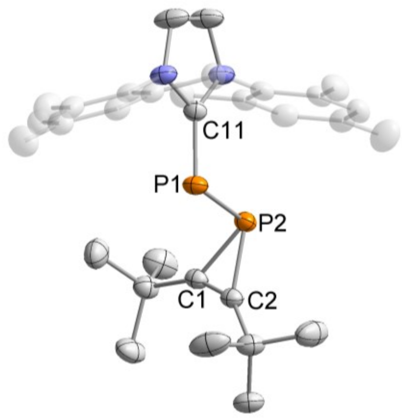

Figure S134. Molecular structure of **3b** in the solid state. H atoms and the second, crystallographically independent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1−P2 2.2225(8), P2−C1 1.835(2), P2−C2 1.841(2), P1−C11 1.768(2), C1−C2 1.297(3), C1−P2−C2 41.31(10), C1−P2−P1 99.19(7), C2−P2−P1 99.40(7), C2−C1−P2 69.59(14), C1−C2−P2 69.10(13), C11−P1−P2 105.30(7).

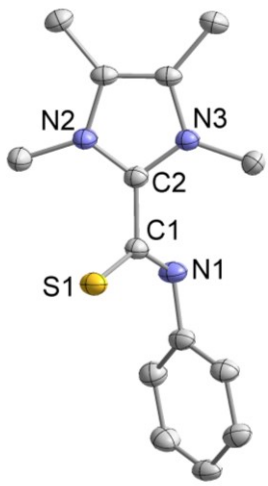

Figure S135. Molecular structure of (TMC)C(S)(NPh) in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and the second, crystallographically independent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1−C1 1.7118(15), N1−C1 1.2923(19), C1−C2 1.4918(19), N2−C2 1.3378(19), N3−C2 1.3409(19), N1−C1−S1 131.91(11), N1−C1−C2 113.33(13), C2−C1−S1 114.68(10), N2−C2−N3 107.41(12).

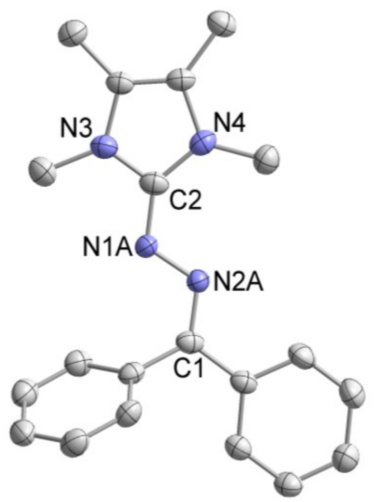

Figure S 136. Molecular structure of (TMC)=N−N=CPh_2 in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and a minor disordered component of N1/N2 are omitted for clarity. Selected bond lengths [Å] and angles [°]:N2A−N1A 1.361(2), N2A−C1 1.315(2), N1A−C2 1.340(2), N3−C2 1.345(2), N4−C2 1.375(2), C1−N2A−N1A 113.09(16), C2−N1A−N2A 115.28(16), N3−C2−N4 106.21(15).

Table S4. Crystallographic data and structure refinement for compounds **2**, **3a-c**, (TMC)C(S)(NPh) and (TMC)=N-N=CPh_2.

Compound	**2**	**3a**	**3b**	**3c**	**(TMC)C(S)(NPh)**	**(TMC)=N-N=CPh_2)**
CCDC	2040302	2040304	2040303	2040305	2040306	2040301
Empirical formula	$C_{24}H_{42}N_4P_2$	$C_{37}H_{54}N_2P_2$	$C_{31}H_{42}N_2P_2$	$C_{34}H_{46}N_2O_2P_2$	$C_{14}H_{17}N_3S$	$C_{20}H_{23}N_4$
Formula weight	448.55	588.76	504.60	574.48	259.36	319.42
Temperature/K	290(13)	123.0(1)	123.0(1)	123.0(1)	123.0(1)	151(4)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1	$P2_1/n$	P-1	P-1
a/Å	15.7329(4)	11.8598(2)	8.5803(2)	18.4310(12)	7.5819(2)	8.0986(3)
b/Å	8.3859(2)	18.0388(3)	10.6253(2)	8.6721(7)	12.0396(4)	9.9827(4)
c/Å	19.9061(4)	17.3344(2)	35.5315(8)	20.5999(13)	15.5332(6)	11.1882(4)
α/°	90	90	93.857(2)	90	87.680(3)	87.935(3)
β/°	94.152(2)	92.7130(10)	95.926(2)	94.086(6)	88.235(3)	77.417(4)
γ/°	90	90	110.711(2)	90	72.214(3)	73.219(3)
Volume/Å^3	2619.41(11)	3704.30(10)	2995.00(12)	3284.2(4)	1348.79(8)	844.85(6)
Z	4	4	4	4	4	2
ρ_{calc}g/cm^3	1.137	1.056	1.119	1.162	1.277	1.256
μ/mm^{-1}	1.624	1.238	1.458	1.436	2.004	0.593
F(000)	976.0	1280.0	1088.0	1235.0	552.0	342.0
Crystal size/mm^3	0.207 × 0.112 × 0.033	0.702 × 0.372 × 0.279	0.143 × 0.119 × 0.044	0.345 × 0.298 × 0.052	0.413 × 0.244 × 0.084	0.567 × 0.404 × 0.145
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.908 to 148.138	7.076 to 146.798	7.552 to 147.074	8.606 to 134.134	7.716 to 145.492	9.256 to 145.362
Index ranges	-19 ≤ h ≤ 18, -10 ≤ k ≤ 10, -24 ≤ l ≤ 22	-14 ≤ h ≤ 14, -21 ≤ k ≤ 22, -20 ≤ l ≤ 21	-10 ≤ h ≤ 10, -10 ≤ k ≤ 13, -44 ≤ l ≤ 43	-22 ≤ h ≤ 20, -9 ≤ k ≤ 10, -17 ≤ l ≤ 24	-9 ≤ h ≤ 7, -14 ≤ k ≤ 13, -19 ≤ l ≤ 18	-9 ≤ h ≤ 9, -12 ≤ k ≤ 8, -13 ≤ l ≤ 13
Reflections collected	11361	16465	20271	9705	9306	5328
Independent reflections	5186 [R_{int} = 0.0246, R_{sigma} = 0.0273]	7280 [R_{int} = 0.0179, R_{sigma} = 0.0205]	11591 [R_{int} = 0.0299, R_{sigma} = 0.0484]	5526 [R_{int} = 0.0783, R_{sigma} = 0.1153]	5154 [R_{int} = 0.0241, R_{sigma} = 0.0314]	3156 [R_{int} = 0.0189, R_{sigma} = 0.0220]
Data/restraints/para-meters	5186/0/285	7280/39/414	11591/0/655	5526/169/482	5154/0/333	3156/36/240
Goodness-of-fit on F^2	1.024	1.045	1.026	1.042	1.037	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.1067	R_1 = 0.0363, wR_2 = 0.0964	R_1 = 0.0500, wR_2 = 0.1221	R_1 = 0.0830, wR_2 = 0.1821	R_1 = 0.0364, wR_2 = 0.0961	R_1 = 0.0556, wR_2 = 0.1558
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1143	R_1 = 0.0390, wR_2 = 0.0987	R_1 = 0.0647, wR_2 = 0.1317	R_1 = 0.1502, wR_2 = 0.2086	R_1 = 0.0404, wR_2 = 0.1003	R_1 = 0.0592, wR_2 = 0.1597
Largest diff. peak/hole / e Å^{-3}	0.21/-0.23	0.27/-0.29	0.37/-0.33	0.30/-0.37	0.28/-0.30	0.54/-0.31

S5 Quantum Chemical Calculations

General Methods

All calculations were performed with the ORCA program package.[1] All calculations were conducted in the gas phase. The RI[2] approximation was used for GGA calculations whereas the RIJCOSX[3] approximation was used for hybrid-DFT calculations. Geometry optimisations have been carried out at the BP86-D3BJ/def2-TZVP[4–8] level of theory. Thereby, the aryl substituents at the NHC moieties were truncated to phenyl rings (NHC = IPh (1,3-diphenylimidazolin-2-ylidene)). Intrinsic bond orbitals (IBOs) have been constructed from the occupied BP86 orbitals according to Knizia *et al*.[9] TD-DFT calculations were performed on the wB97X-D3/def2-SVP[17] level of theory and GaussSum[18] was used to visualise the results.

Density difference plots

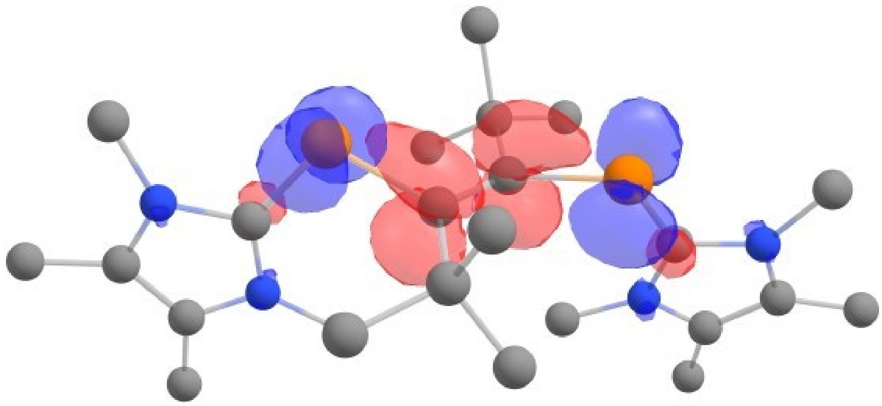

Figure S137: Density difference plot (isosurface value 0.01) for the transition at 450 nm caused mainly by a HOMO-LUMO transition (n_P → π^*_{CC}) for **2**. The transition occurs from blue → red.

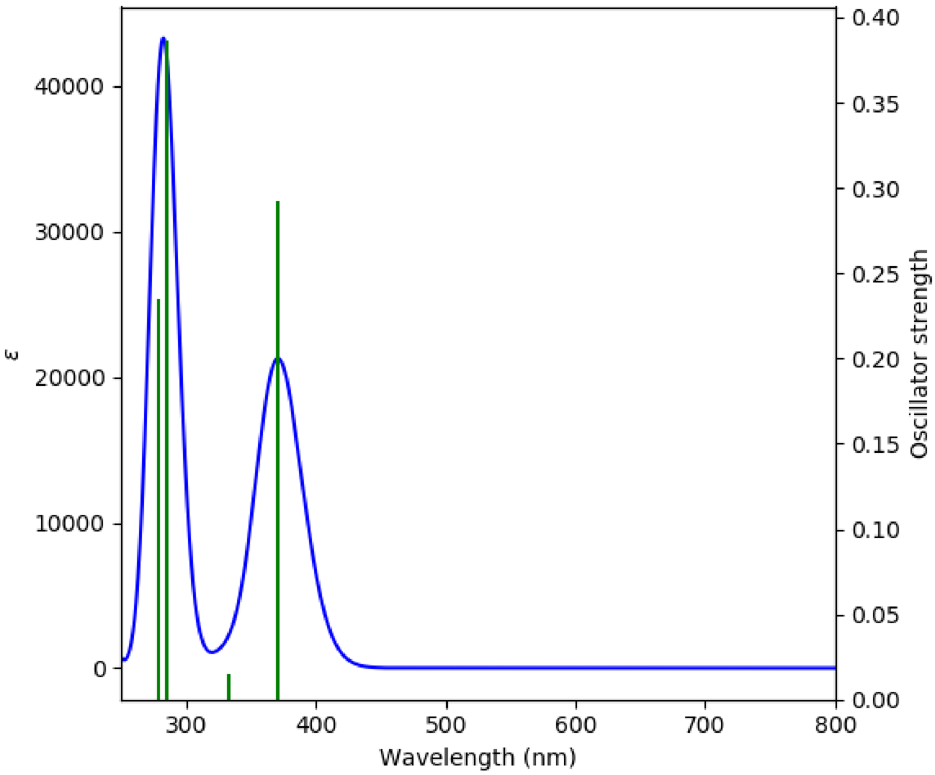

Figure S138: Calculated UV/Vis Spectrum for **2** as visualised by GaussSum.

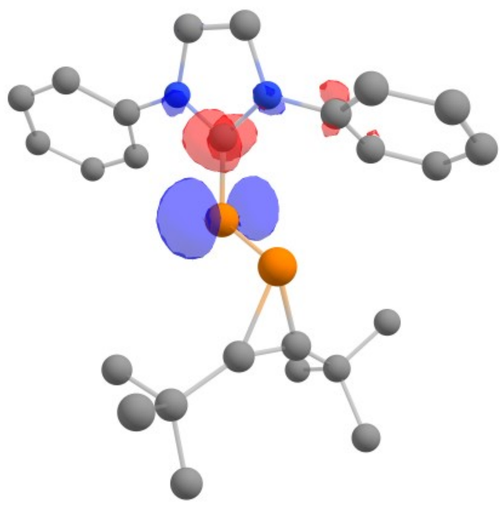

Figure S139: Density difference plot (isosurface value 0.01) for the transition at 360 nm caused mainly by a HOMO-LUMO transition for (IPh)PP(C*t*Bu)$_2$. The transition occurs from blue → red.

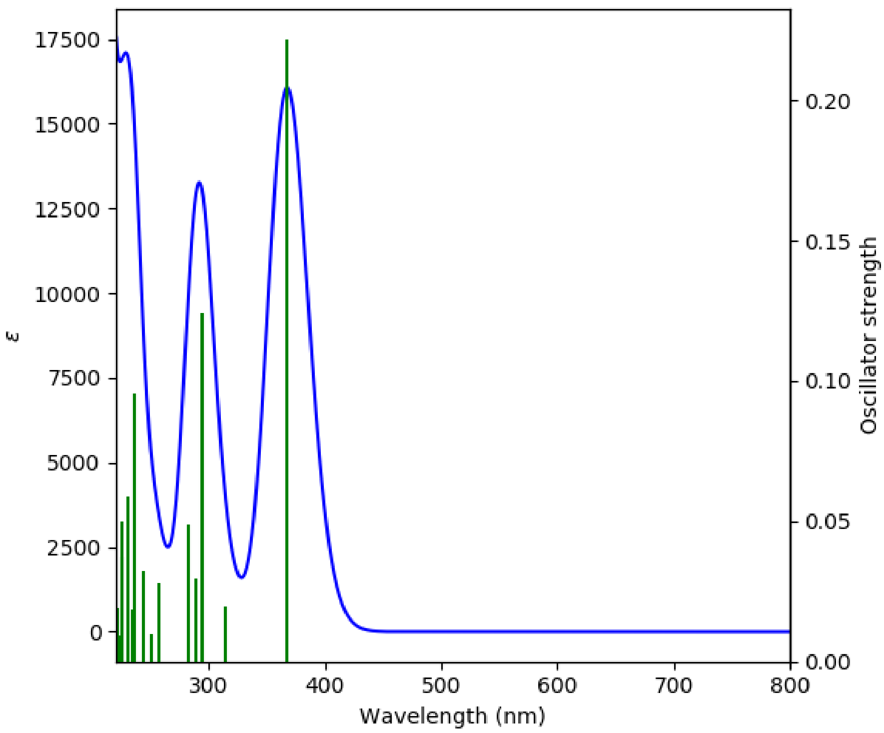

Figure S140: Calculated UV/Vis Spectrum for (IPh)PP(C*t*Bu)$_2$ as visualised by GaussSum.

Cartesian Coordinates for Optimised Structures

2

P	4.52516715511791	2.48065643079355	3.39236715085063
P	2.91112346262265	2.62083834140304	7.52923813787542
N	5.00888339384399	5.22270354511455	2.52178032859559
N	5.63187548011858	3.63212636781320	1.15938588114814
N	1.89969992450498	5.31489348951829	8.00661830306115
N	1.57552256307653	3.84577781192967	9.59122599573389
C	5.07405440980034	3.84189293596235	2.41251979108958
C	5.50763353561199	5.83791766478722	1.36352757011603
C	2.09841122065270	3.97713806175743	8.31261557640173
C	4.28806635567537	3.12583935810668	5.12272061817684
C	3.04431297377538	3.04741342463565	5.72207517710754
C	5.88501828960876	4.84311313550106	0.50876747113664
C	5.63004025099947	3.34563315341792	5.91671021099667
C	1.27877146480482	5.98266867966557	9.07310693596211
C	1.08829614544149	5.06661642912846	10.06669110943350
C	1.69618586230946	2.88903335212317	4.92397302962304
C	5.86210516496124	2.30588059738929	0.63281114549536
H	6.32945902695700	1.68889836174668	1.41672976143283
H	6.51860542634570	2.36535815963926	-0.24180732355543
H	4.91374063730109	1.82101228363322	0.35007447747707
C	5.56717009521720	7.31674222707925	1.22172188643552
H	4.57036128830776	7.78073961098635	1.29324265465154
H	5.98843318053989	7.58494419905281	0.24539085771354
H	6.19931476290186	7.77960621061721	1.99654940758512
C	6.03674571896595	2.01131313984368	6.58035735450738
H	5.29721923440082	1.69247180882098	7.32600864255358

H	7.01179653341212	2.11996161471612	7.08278273808805
H	6.12721915171246	1.22767367771056	5.81358671032045
C	1.60012013708163	2.59024437646264	10.30696773419743

(IPh)PP(C*t*Bu)$_2$

P	2.87186623820695	4.87741704658394	11.90864259877218
P	3.97079430196542	6.80468619211665	11.52531694387042
N	2.70256314664553	9.30966612384833	11.84185948426615
N	1.94317170920530	7.83568264021944	13.28644248679334
C	2.62162742108278	10.75774417718113	9.88893676124389
C	3.35518023052869	9.93028322768038	10.75109445921696
C	2.87541231507736	7.97764070307693	12.25709840272294
C	4.71991442204510	9.71286058680685	10.52404842762294
C	1.87705617452494	6.76066361674719	14.21966569521741
C	0.63896512998081	6.18597659087902	14.51672832368624
C	4.25735431543161	3.69205699894395	11.65014030830400
C	3.59858828280957	3.88328622467979	10.52949424696750
C	1.67524810354612	9.91618235920368	12.56661354373359
H	1.41641646817981	10.95624251391938	12.41994315863684
C	3.25611145159723	11.37111178825715	8.80975311357452
H	2.67843134969555	12.00808597935160	8.13893485711227
C	5.34118599511710	10.32281978765113	9.43325769620516
H	6.40394679286489	10.14955301488048	9.26032173016405
C	1.20160133833675	9.00703364493121	13.44882475071079
H	0.45507540181053	9.09639055415736	14.22705517005674
C	3.03887842028685	6.32844503111504	14.86665578170123
C	4.61734940890980	11.15308101568269	8.57506070583166
H	5.10905852091531	11.62593529345006	7.72439698792020
C	2.95669578433825	5.29533665769881	15.79707495533607
H	3.86196384871094	4.95144184666615	16.29789291306349
C	0.56589681631561	5.15834984954988	15.45827972637895
H	-0.39795110752395	4.69925667124310	15.68052156137903
C	5.46510209466534	3.10705807796427	12.31951020026804
C	1.72350884467169	4.70428850464797	16.09304657138793
H	1.66701566709926	3.89125798801846	16.81748869781741
C	3.48985156263782	3.65224578794483	9.05769079267893
C	2.00651890315075	3.45912924485665	8.69131345467375
H	1.58967075174268	2.57387501430049	9.19270182165805
H	1.89414158442403	3.32862744287471	7.60468573179754
H	1.41864117445629	4.33390451805653	9.00202433192563
C	4.30125801194928	2.41036237756488	8.65001485146952
H	5.36395259318671	2.53594575446298	8.90104181685716
H	4.22551763449434	2.24491294248258	7.56468548022276
H	3.92906126299269	1.51136237032945	9.16138053408416
C	4.03820376270199	4.90103410413775	8.33324762072342
H	3.49696294956997	5.80382297764392	8.64616577883255
H	3.93136242980816	4.77747253249528	7.24430571879657
H	5.10057095584639	5.05412656526030	8.56792423540883
C	6.72221588214685	3.72801311767304	11.67385044129591
C	5.43142641614828	3.45431542151179	13.81623756853068
C	5.47236627067199	1.57796884677979	12.13202377335237
H	5.42865016496124	4.54485099179936	13.95070547199805
H	6.30938918319680	3.03677860454278	14.33122674119087
H	4.52244138416219	3.05587072158711	14.28757336717011
H	5.50623915986180	1.31148942906826	11.06750482533628

H	4.57084597606333	1.12675300887442	12.56994184053215
H	6.35317785259191	1.13975372900901	12.62574583638078
H	6.77695518278076	3.47918889591537	10.60497149989481
H	7.63096643347916	3.34797201638978	12.16628045152224
H	6.70235848207707	4.82262559277510	11.76878354923495
H	1.55157128506228	10.89273231835745	10.04788959179648
H	5.28641764485399	9.08225308560299	11.20721314642112
H	3.99326659433725	6.78582924083338	14.60885642702599
H	-0.25155037639713	6.52117863971796	13.98438303922634

Chapter 7

Activation of Di-tert-butyldiphosphatetrahedrane: Access to (tBuCP)$_n$ (n = 2, 4) Ligand Frameworks by P–C Bond Cleavage

S1 Additional Experiments

Reaction of 1 with 1.5 eq. [CpNi(IPr)]

To a solution of [CpNi(IPr)] (50 mg, 0.1 mmol, 1.0 eq.) in THF (3 mL) was added (*t*BuCP)$_2$ (0.2 mL, c = 0.36 M in toluene, 0.07 mmol, 0.7 eq.) at ambient temperature. The colour of the reaction mixture immediately changed from yellow to deep red. After stirring at ambient temperature for 18 h, the reaction mixture was analysed by $^{31}P\{^{1}H\}$ NMR spectroscopy (see Figure S163).

Reaction of [CpNi(IPr)] with 1.0 eq. 1

To a solution of [CpNi(IPr)] (40 mg, 0.08 mmol, 1.0 eq.) in toluene (0.5 mL) was added (*t*BuCP)$_2$ (0.054 mL, c = 1.5 M in toluene, 0.08 mmol, 1.0 eq.) at −30 °C. The colour of the reaction mixture immediately changed from yellow to deep red. The reaction mixture was analysed by $^{31}P\{^{1}H\}$ NMR spectroscopy (see Figure S164).

Reaction of [CpNi(IPr)] with 10 eq. 1

A solution of [CpNi(IPr)] (30 mg, 0.06 mmol, 1.0 eq.) in toluene (0.5 mL) was added to (*t*BuCP)$_2$ (0.4 mL, c = 1.5 M in toluene, 0.6 mmol, 10.0 eq.) at −30 °C. The colour of the reaction mixture immediately changed from yellow to deep red. The reaction mixture was analysed by $^{31}P\{^{1}H\}$ NMR spectroscopy (see Figure S165).

Detection of di-*tert*-butylacetylene by elimination from 4

To a solution of [(IMes)$_2$Ni] (80.0 mg, 0.12 mmol, 1.0 eq.) in C_6D_6 (0.8 mL) in a J. Young NMR tube was added (*t*BuCP)$_2$ (0.12 mL, c = 1.2 M in toluene, 0.14 mmol, 1.2 eq.). The solution was heated for 3 hours to 60 °C. Subsequently, the sample was subjected to NMR spectroscopic studies (see Figure S166 and Figure S167).

Reaction of 4 with CO gas

A deep brown solution of [{(IMes)Ni}$_2$(P$_4$C$_4$*t*Bu$_4$)] (6 mg, 0.005 mmol) in C_6D_6 (0.5 mL) was degassed (3 x freeze-pump-thaw). Subsequently, an atmosphere of CO gas (1 bar) was added. The colour of the reaction mixture immediately changed from brown to pale beige and was subjected to NMR spectroscopy (see Figure S168 and Figure S169).

Reaction of 4 with C_2Cl_6: Synthesis of [{(IMes)NiCl}$_2$(μ-*t*Bu$_2$C$_2$P$_2$)] (7) and [(IMes)NiCl(μ-Cl)]$_2$:

To a deep brown solution of [{(IMes)Ni}$_2$(P$_4$C$_4$*t*Bu$_4$)] (7 mg, 0.006 mmol, 1.0 eq.) in toluene (0.5 mL) was added Cl_2Cl_6 (1.3 mg, 0.006 mmol, 1.0 eq.) at −30 °C. The solution turned red immediately and was analysed by NMR spectroscopy (see Figure S170, Figure S171 and Figure S172). Subsequently, the solvent was removed *in vacuo* and the dark red residue was dissolved in *n*-hexane. Storage at −30 °C overnight afforded brown crystals of [{(IMes)NiCl}$_2$(*t*Bu$_2$C$_2$P$_2$)] and violet crystals of [(IMes)NiCl(μ-Cl)]$_2$.

Reaction of [(IPr)$_2$Ni] with 1:

To a deep blue solution of [(IPr)$_2$Ni] (50 mg, 0.06 mmol, 1.0 eq.) in toluene (0.5 mL) was added (*t*BuCP)$_2$ (0.3 mL, c = 0.2 M in toluene, 0.006 mmol, 1.0 eq.) at −30 °C. The solution turned orange immediately and was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S173).

Reaction of [(IPr)Ni(η^6-toluene)] with 1:

To a brown solution of [(IPr)Ni(η^6-toluene)] (40 mg, 0.07 mmol, 1.0 eq.) in toluene (0.5 mL) was added (*t*BuCP)$_2$ (0.15 mL, c = 0.57 M in toluene, 0.085 mmol, 1.2 eq.) at −30 °C. No colour change was observed and the sample was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S174).

Control experiments [Cp^{x}Ni(IPr)] + 1:

General procedure:

To a solution of [(Cp^x)Ni(IPr)] (0.02 - 0.04 mmol, 1.0 eq.) in toluene (0.5 mL) was added (*t*BuCP)$_4$ (1.0 eq.) at −30 °C. No colour change was observed and the sample was analysed by $^{31}P\{^1H\}$ NMR spectroscopy. Only starting material (*t*BuCP)$_4$ was observed in the spectrum (δ = −22.6 ppm).

Example for Cp^x = C_5H_5:

To a mixture of [(Cp^x)Ni(IPr)] (11.5 mg, 0.023 mmol, 1.0 eq.) and (*t*BuCP)$_4$ (9.0 mg, 0.023 mmol, 1.0 eq.) was added cold (−30 °C) toluene (0.5 mL). No colour change was observed and the sample was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S175).

S2 NMR Spectra

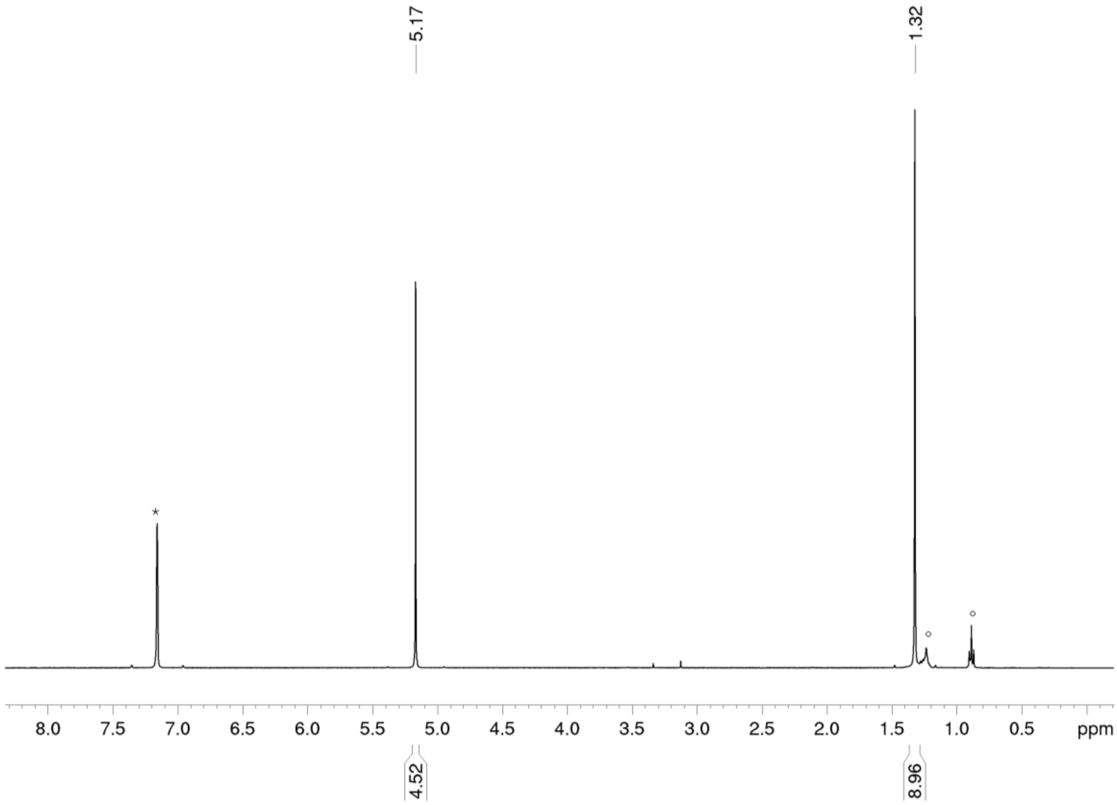

Figure S141. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **2** *C_6D_6, °residual *n*-hexane.

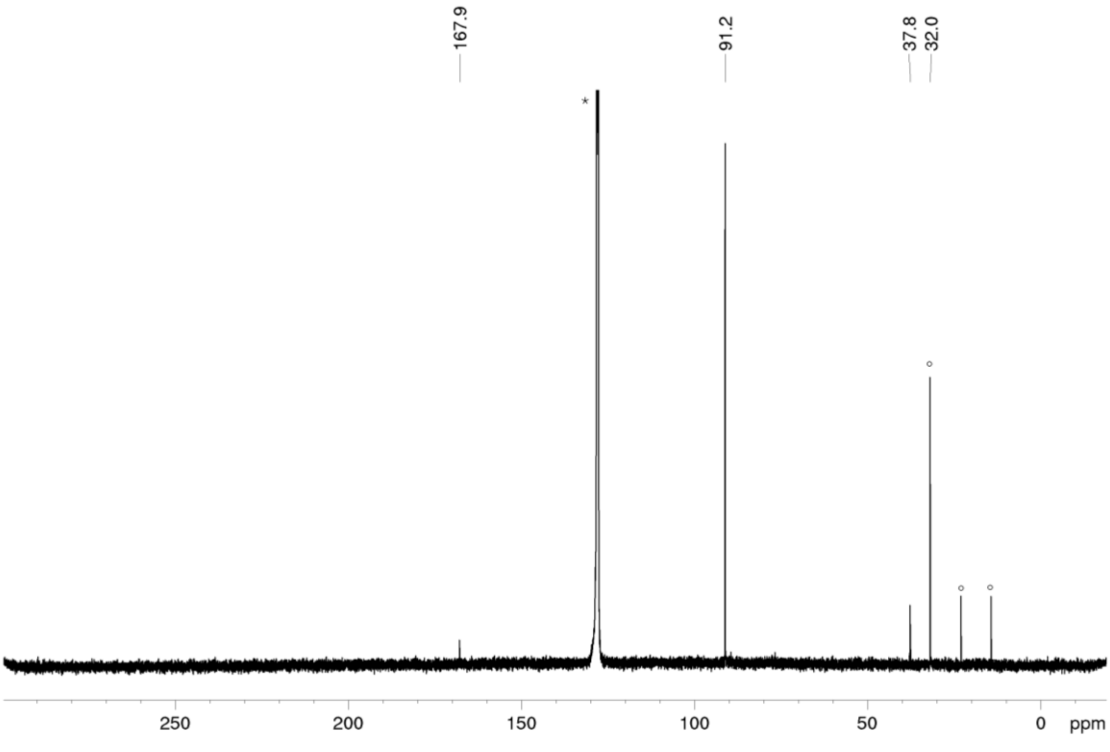

Figure S142. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **2**; *C_6D_6, ° residual *n*-hexane (overlap with C^3 signal).

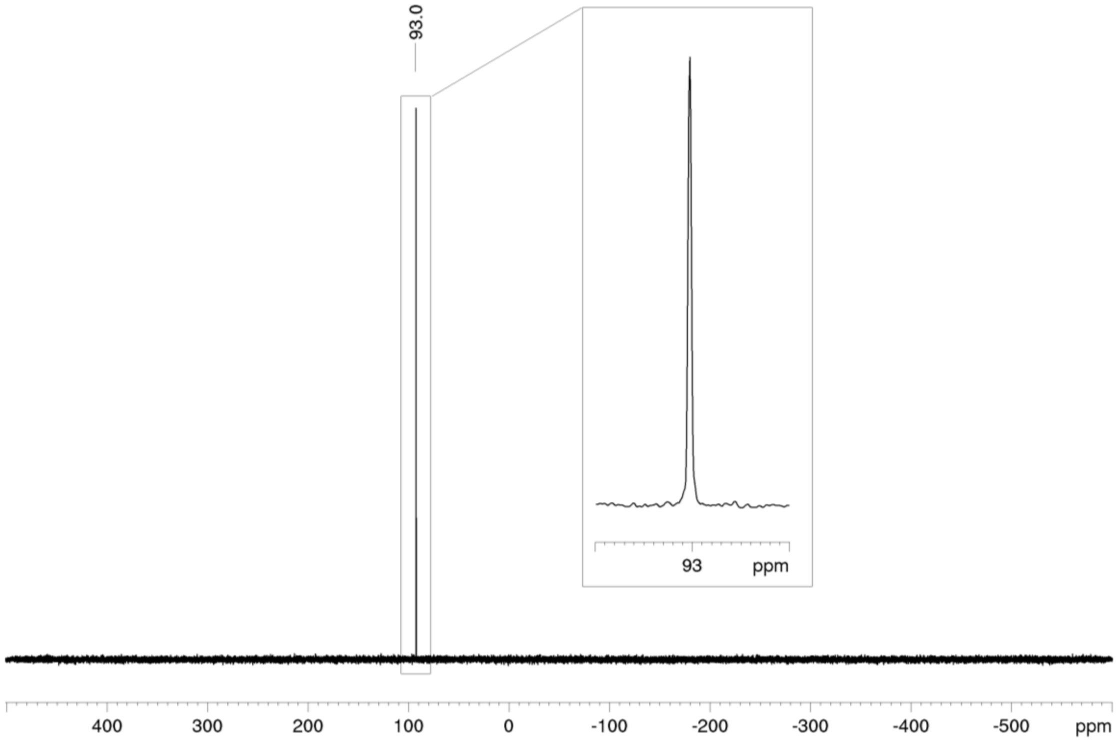

Figure S143. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **2**.

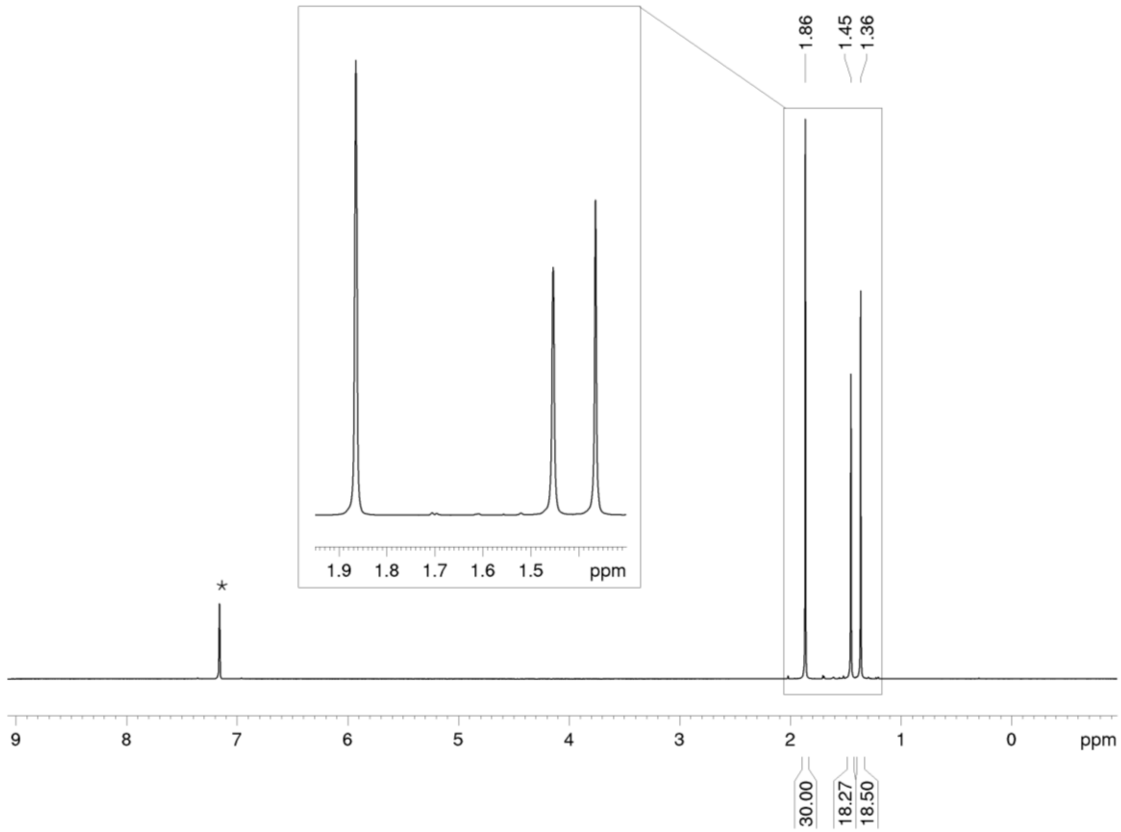

Figure S144. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **3a** *C_6D_6.

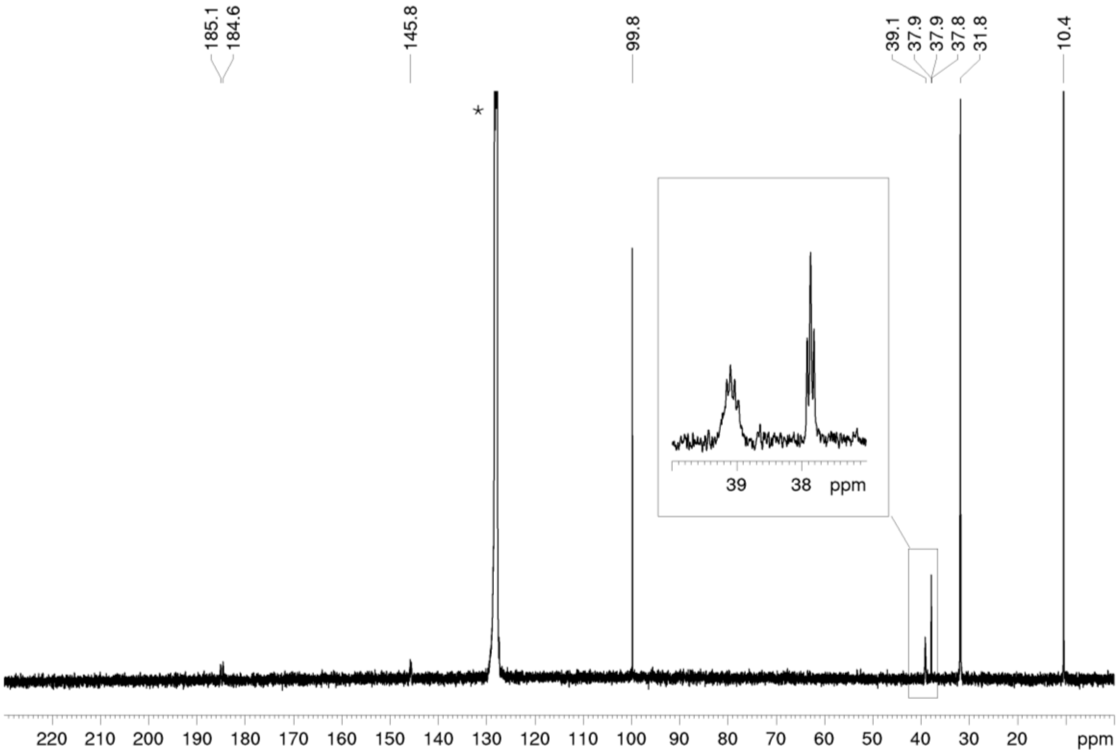

Figure S145. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **3a**; *C_6D_6.

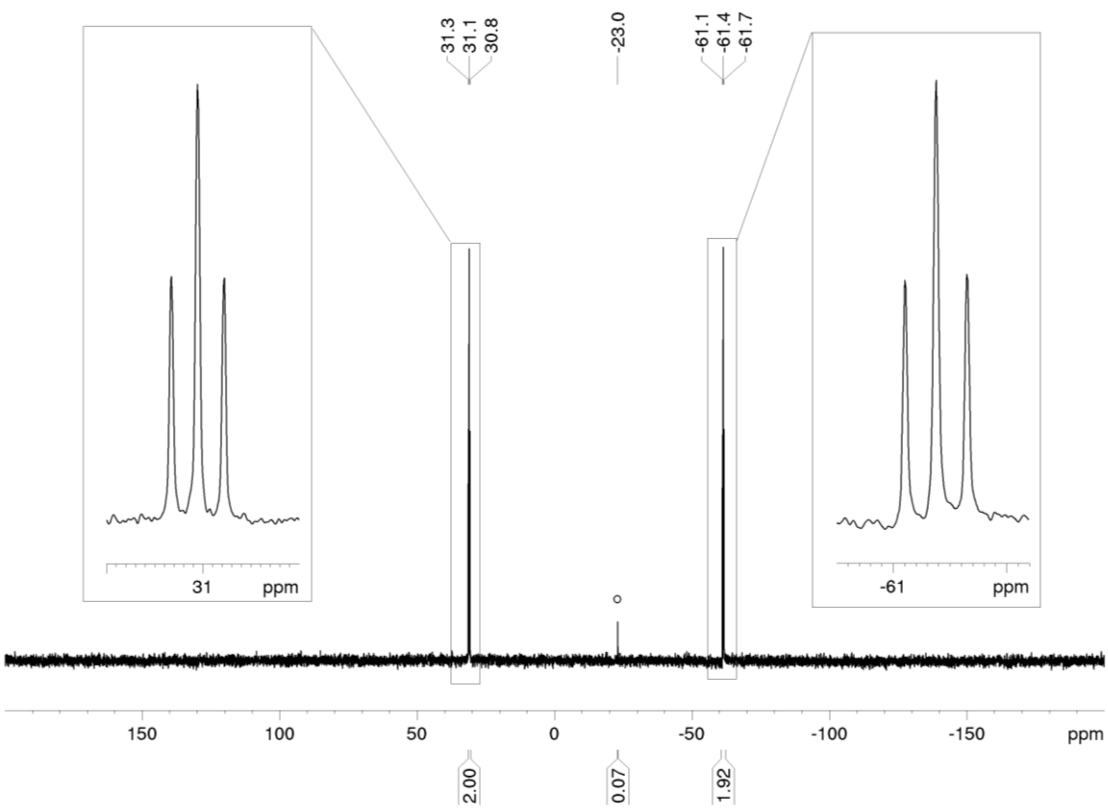

Figure S146. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **3a**, °minor amount of (*t*BuCP)$_4$ (<2%).

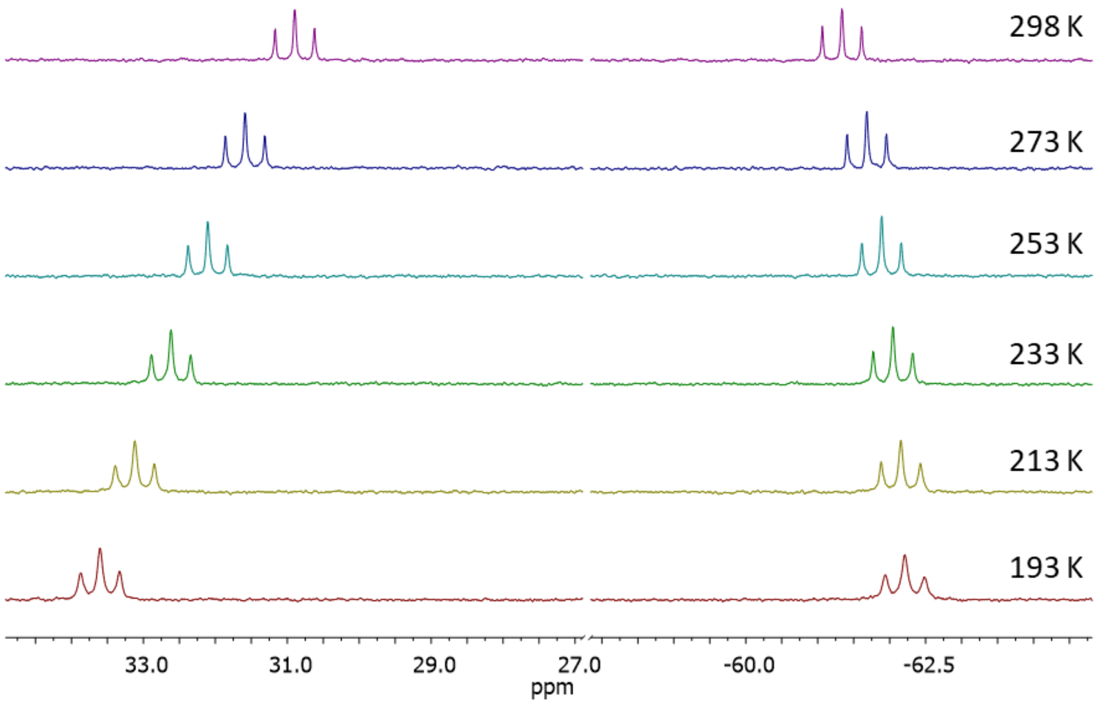

Figure S147. Variable Temperature $^{31}P\{^1H\}$ NMR spectra (162 MHz, tol-d^8) of **3a**.

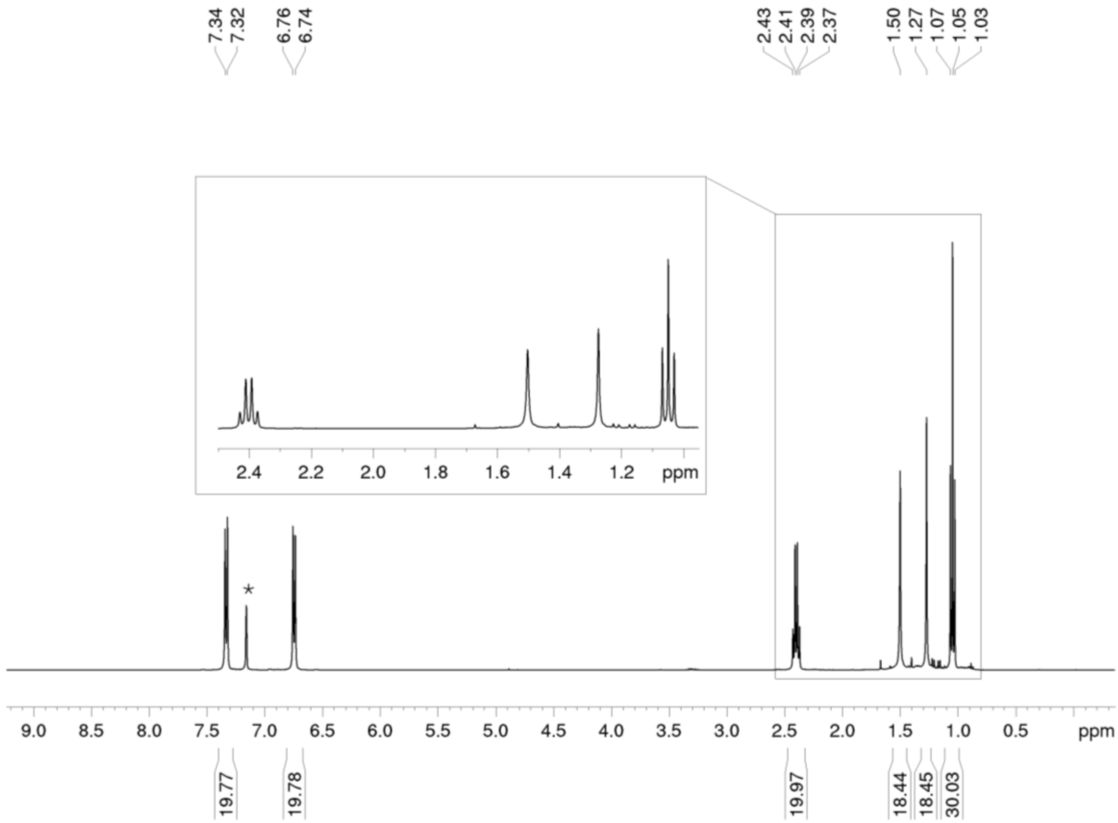

Figure S148. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **3b** *C_6D_6.

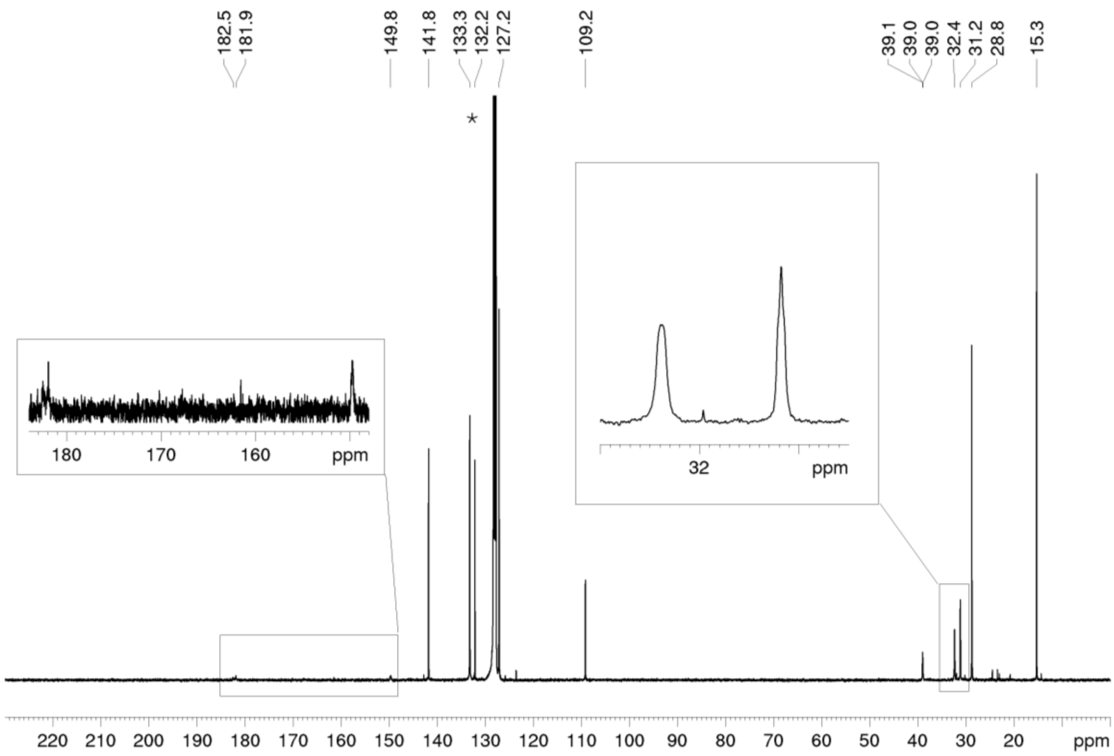

Figure S149. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **3b**; *C_6D_6.

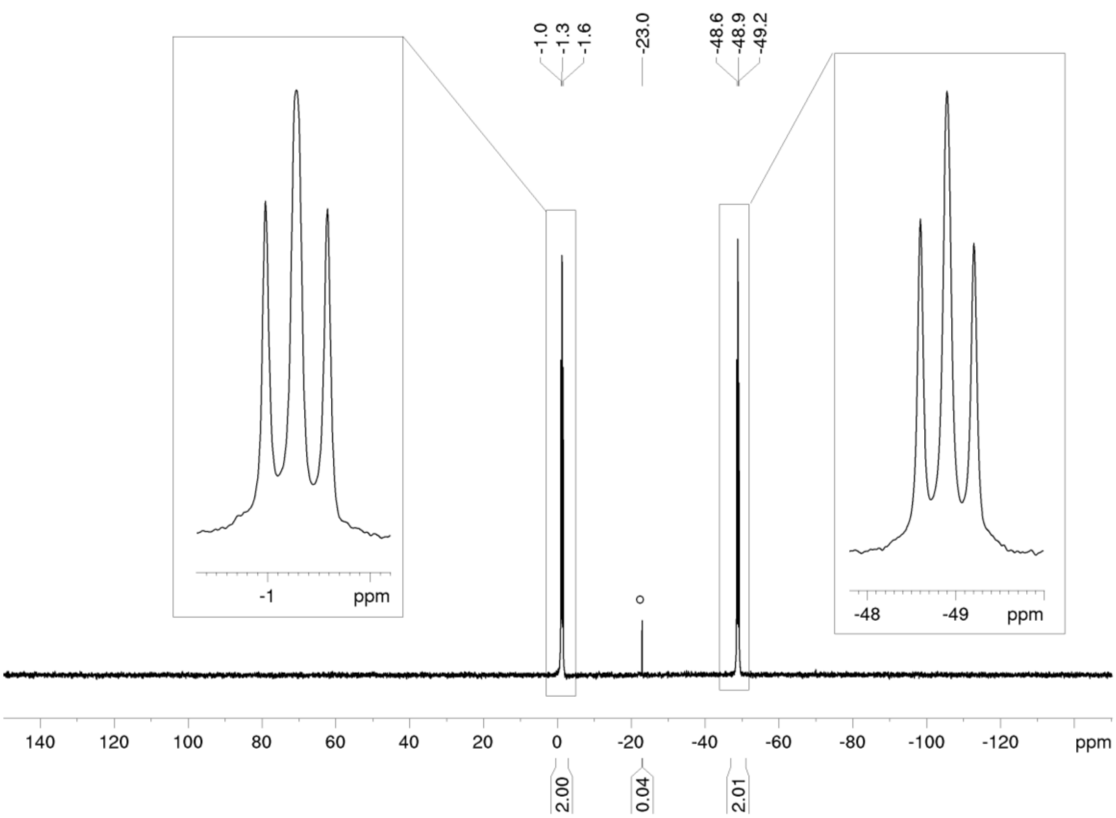

Figure S150. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **3b**, °minor amount of (*t*BuCP)$_4$ (ca. 1%).

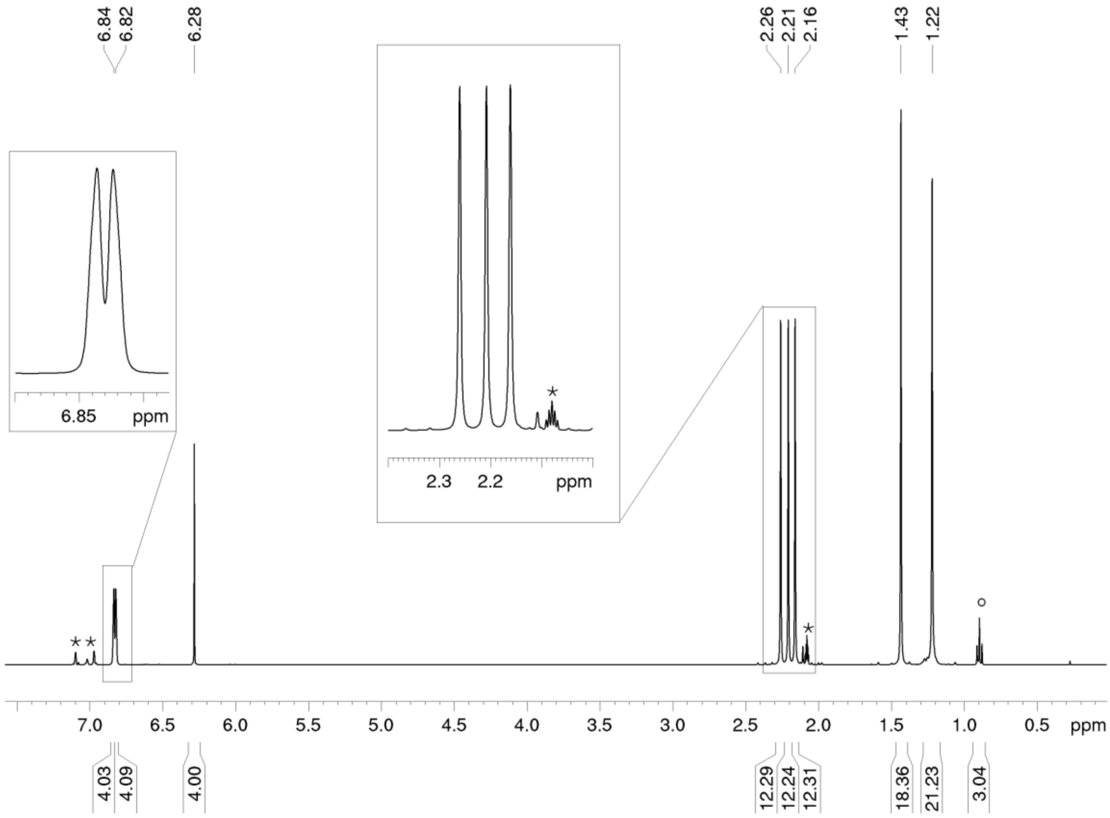

Figure S151. ^{1}H NMR spectrum (400 MHz, 273 K, tol-d^8) of **4** *tol-d^8; °*n*-hexane.

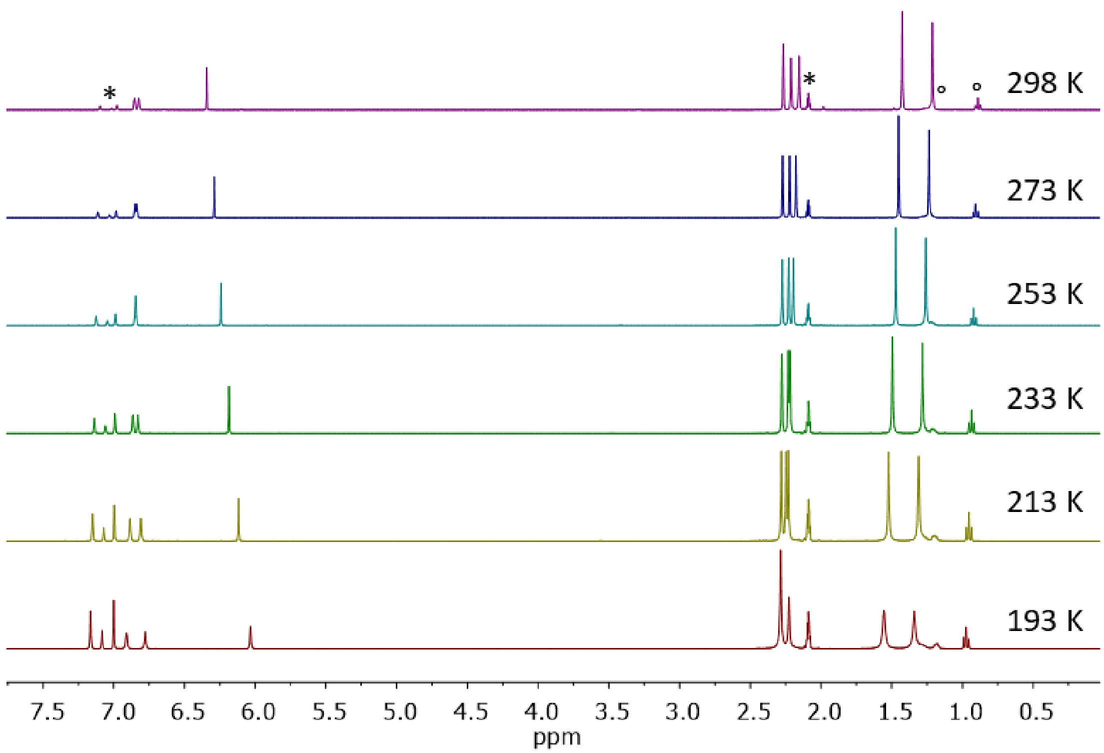

Figure S152. Variable temperature ^{1}H NMR spectrum (400 MHz, tol-d^8) of **4** *tol-d^8; °*n*-hexane.

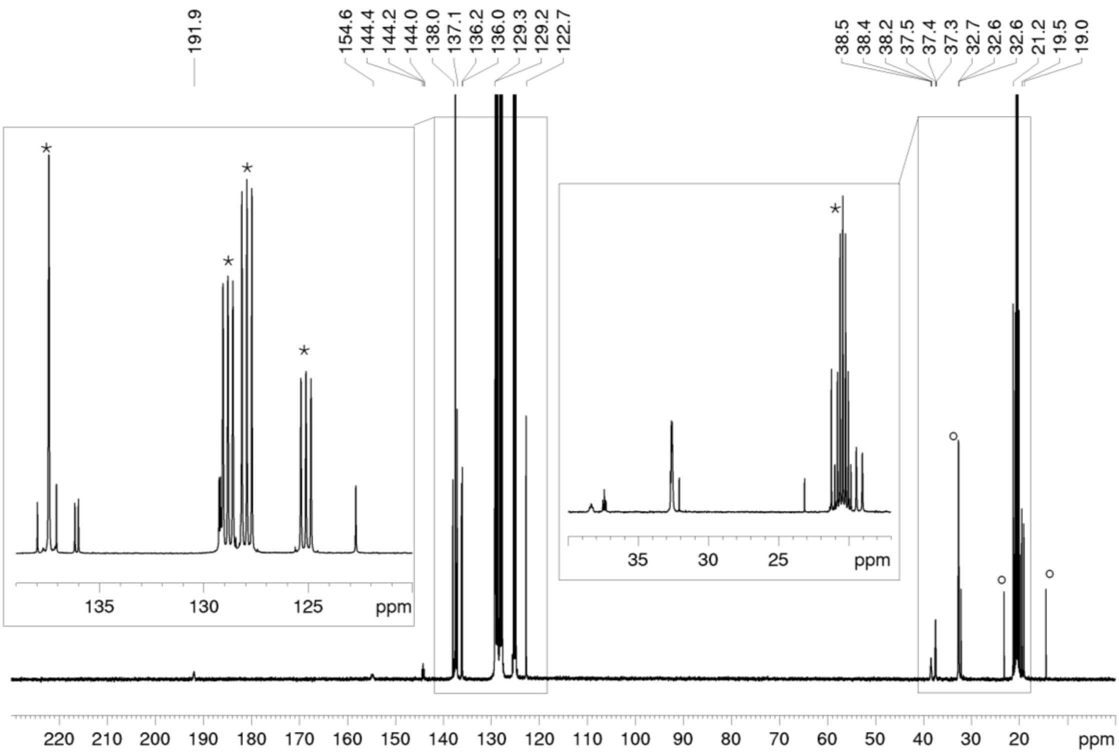

Figure S153. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 273 K, tol-d^8) of **4**; *tol-d^8, °*n*-hexane.

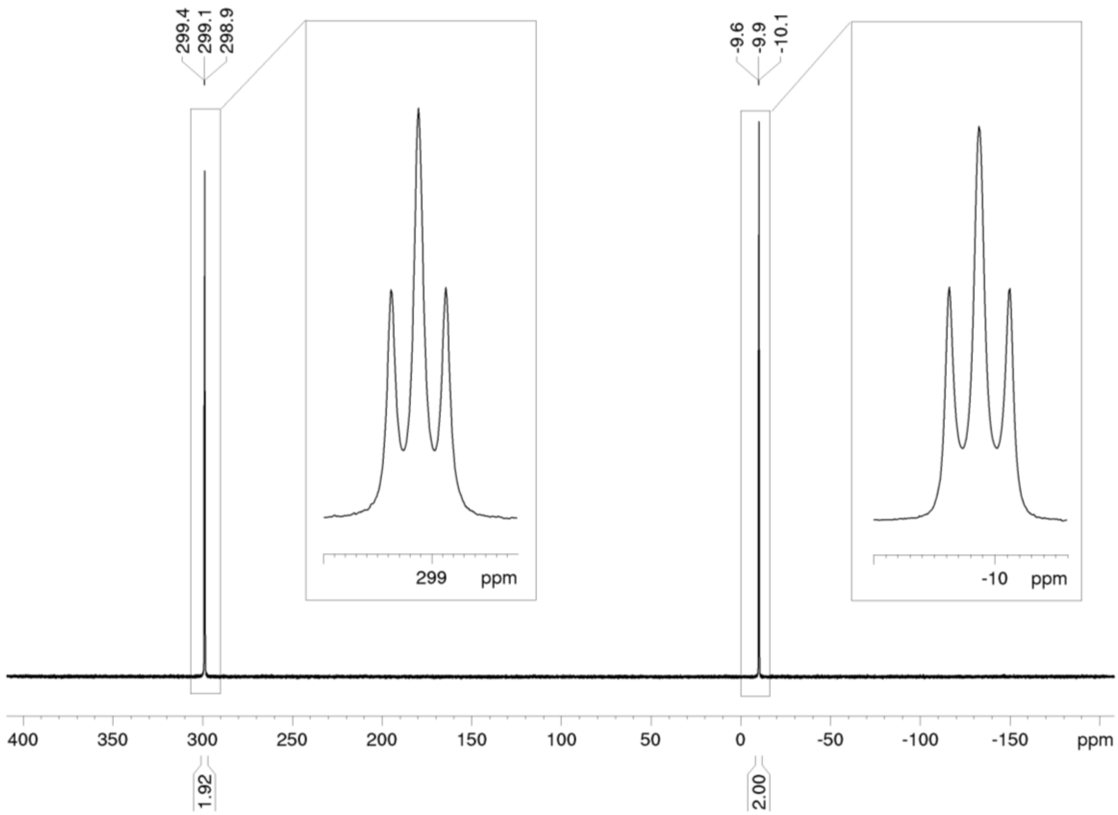

Figure S154. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 273 K, tol-d^8) of **4**.

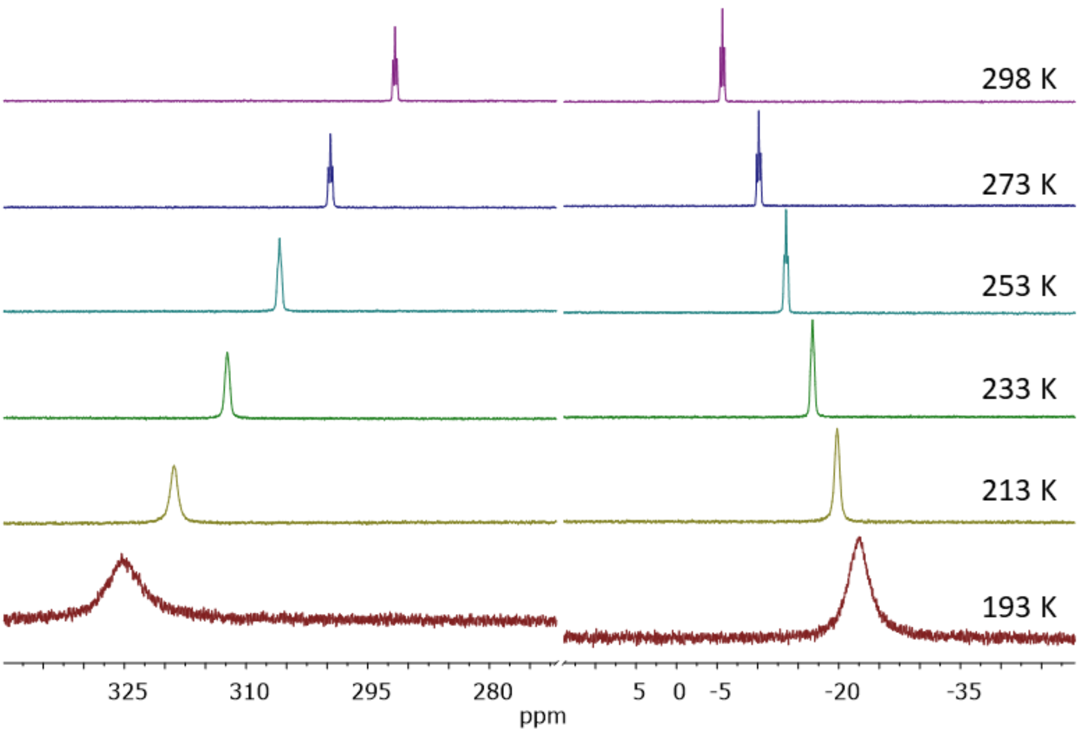

Figure S155. Variable temperature $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, tol-d^8) of **4**.

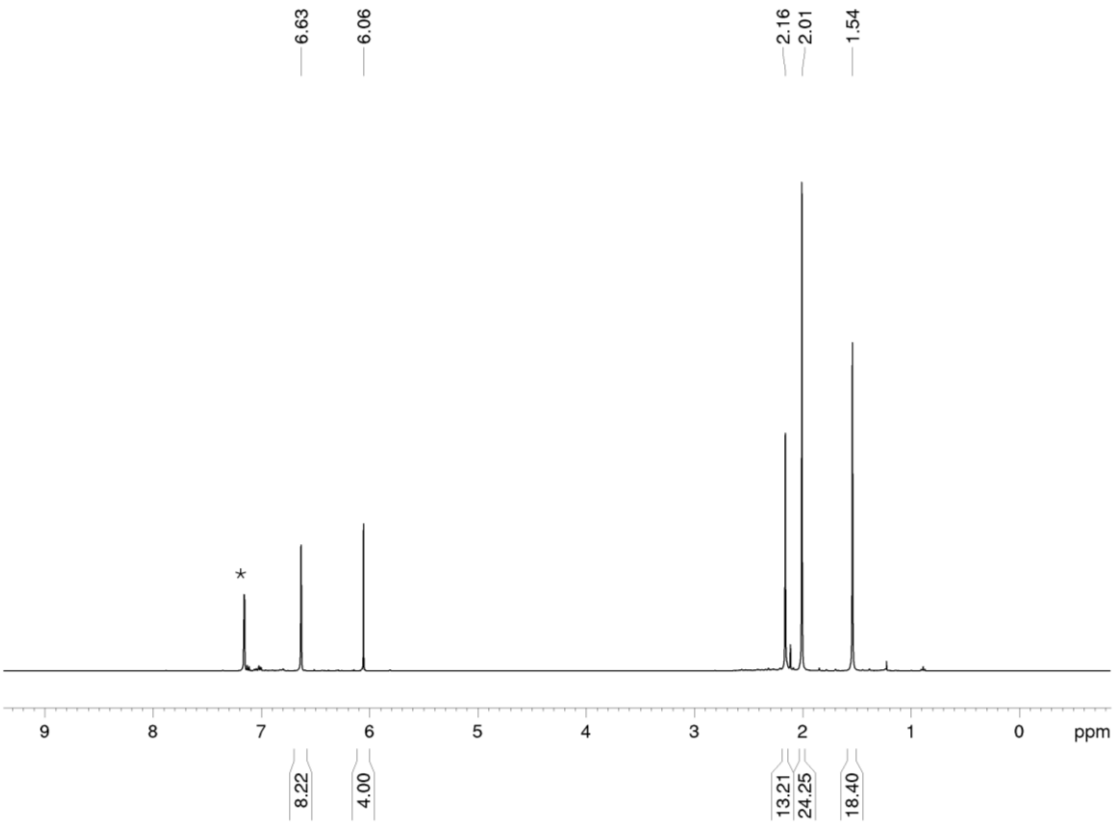

Figure S156. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **5** *C_6D_6.

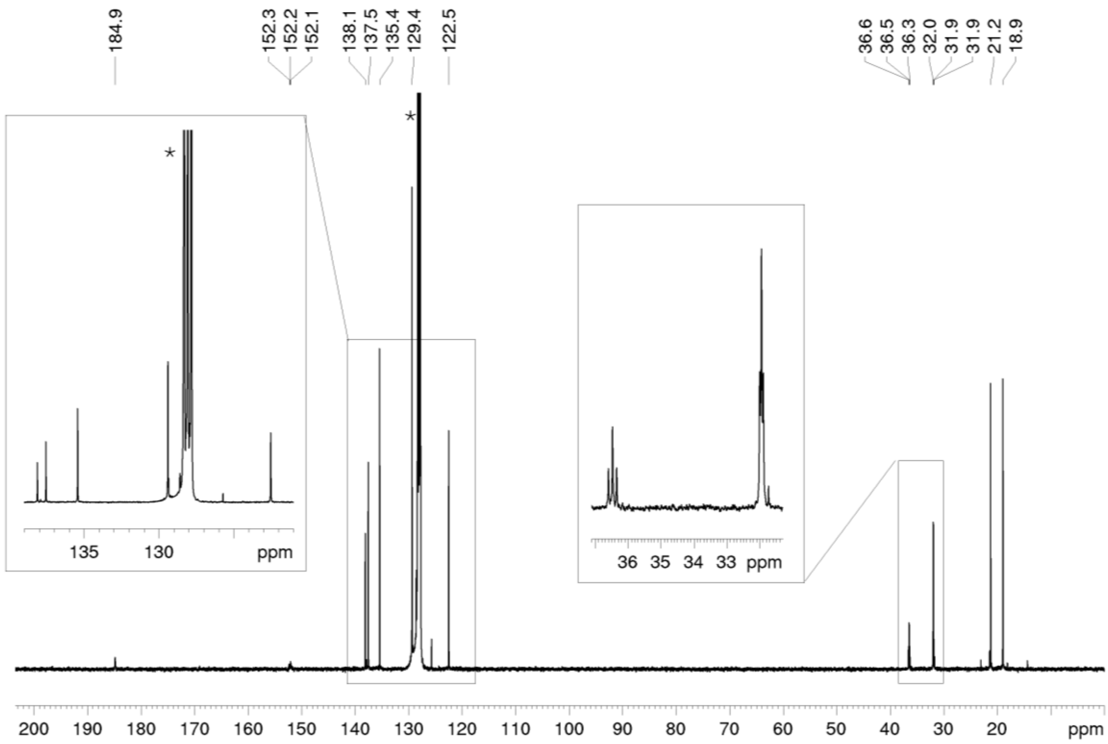

Figure S157. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **5**; *C_6D_6.

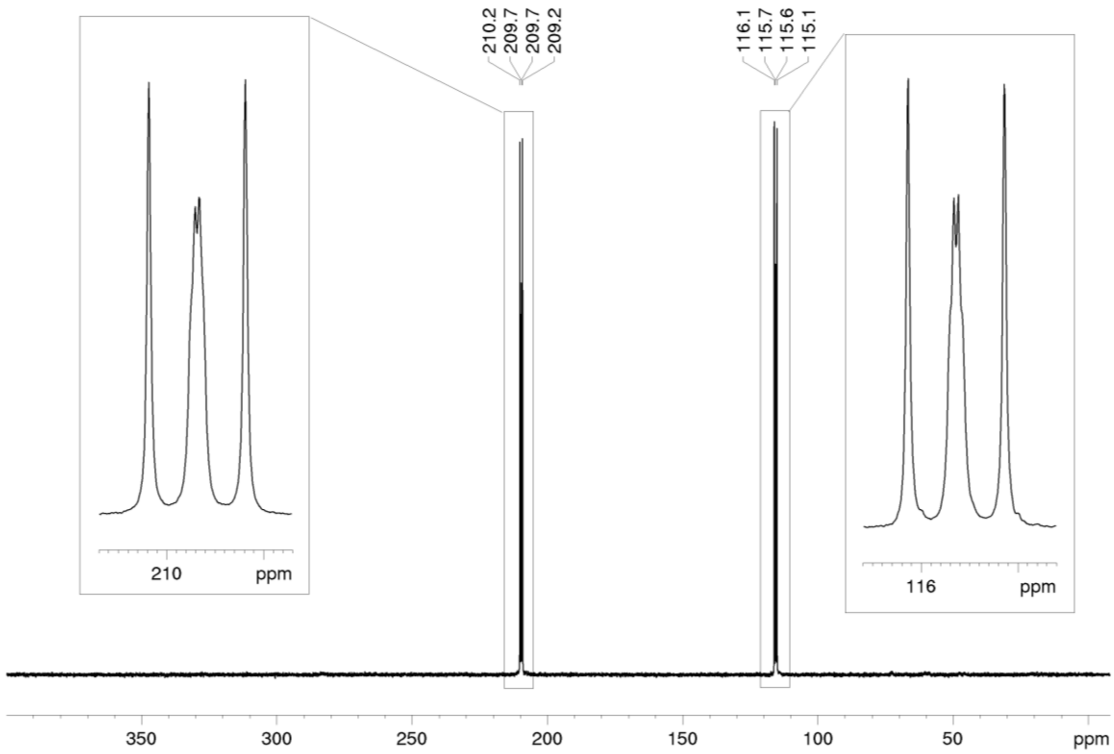

Figure S158. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **5**.

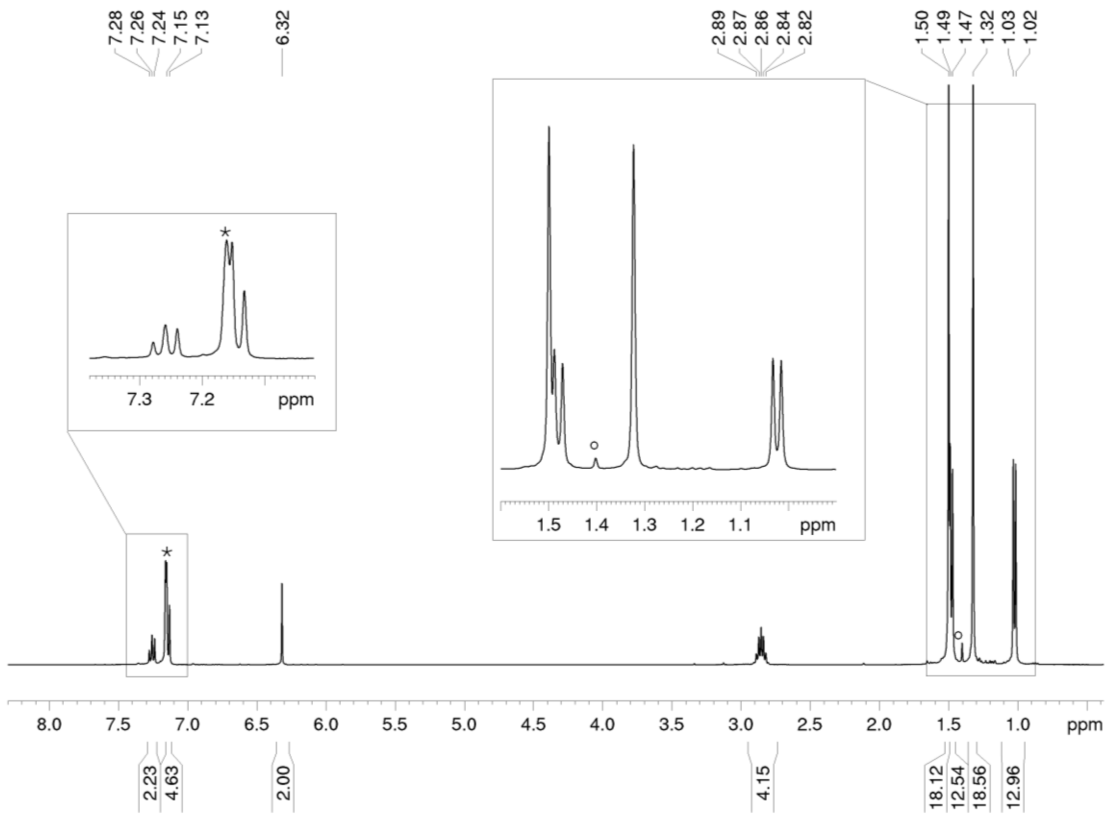

Figure S159. ^{1}H NMR spectrum (400 MHz,300 K, C_6D_6) of **8** *C_6D_6, °minor amount of (*t*BuCP)$_4$ (<3%).

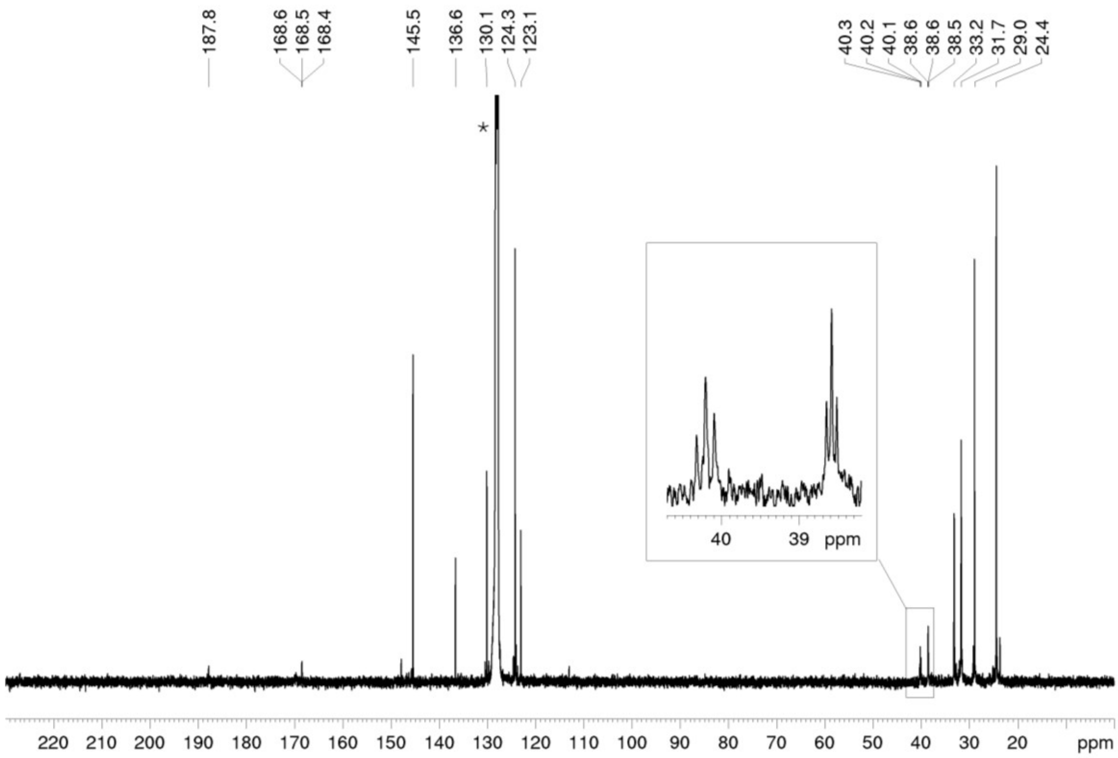

Figure S160. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **8**; *C_6D_6.

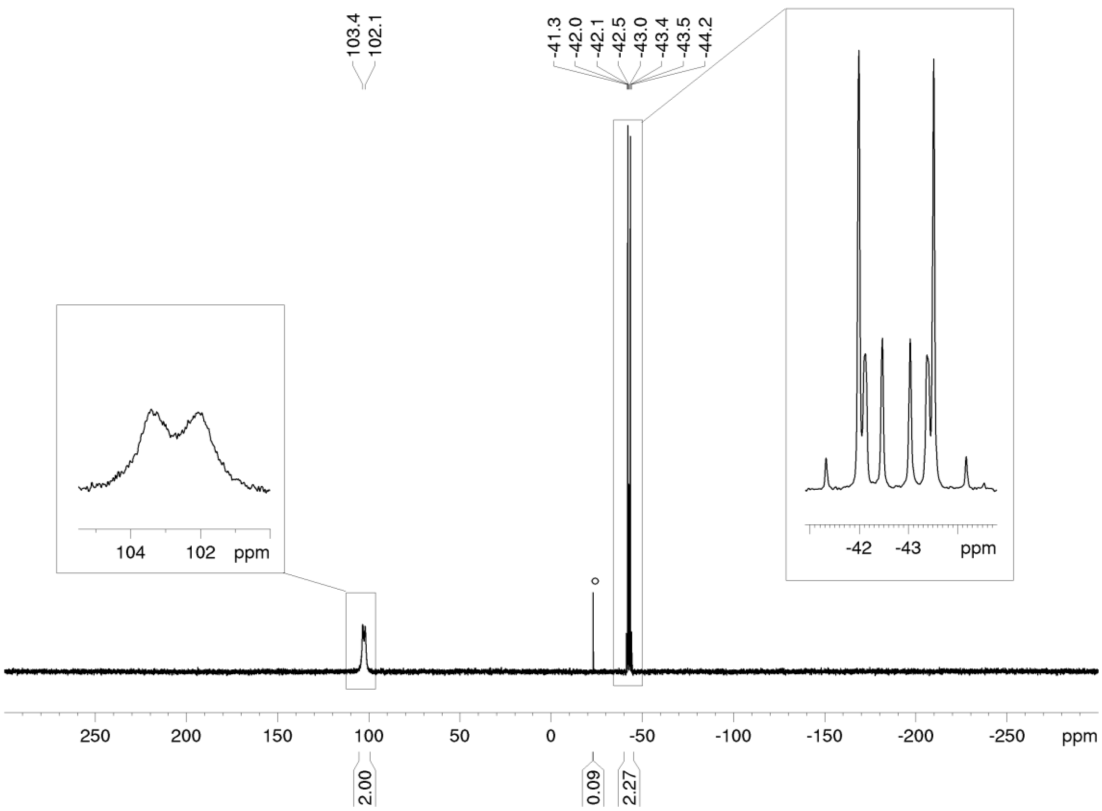

Figure S161. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **8**, °minor amount of (*t*BuCP)$_4$ (<3%).

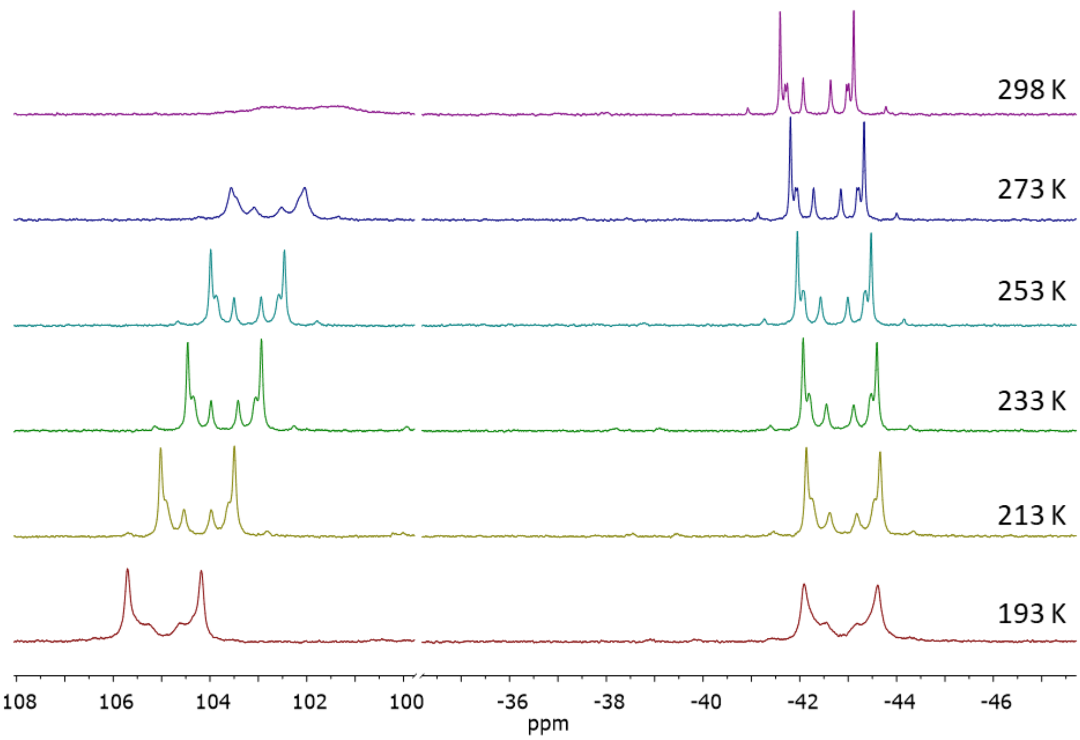

Figure S162. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra (162 MHz, tol-d$_8$) of **8**.

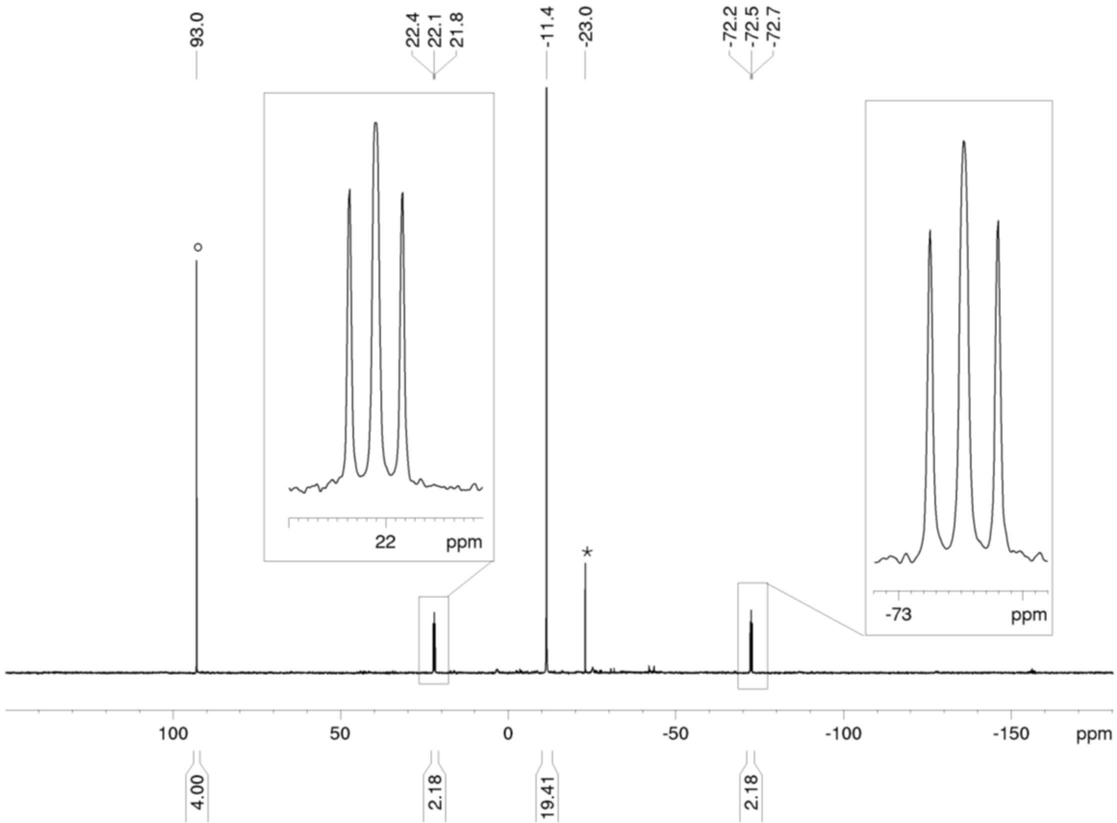

Figure S163. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **1** with 1.5 eq. [CpNi(IPr)]; ° **2**; *(*t*BuCP)$_4$.

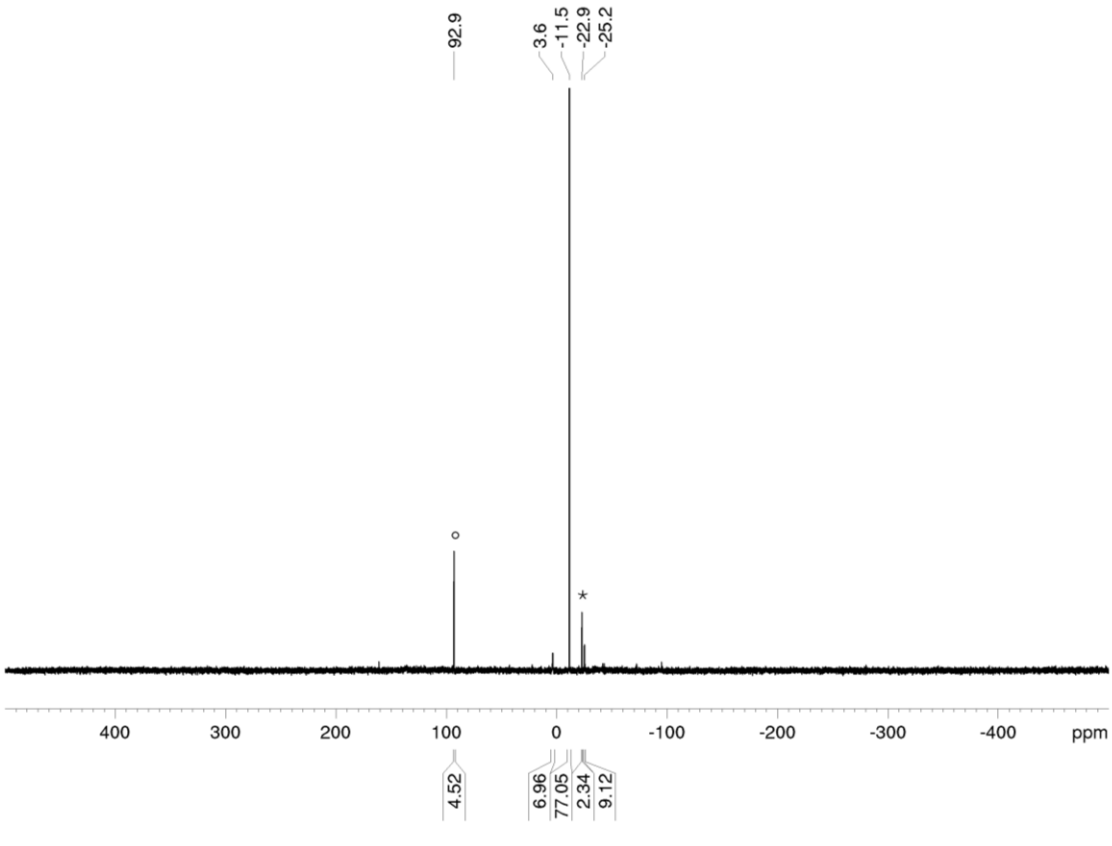

Figure S164. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **1** with 1.0 eq. [CpNi(IPr)]; ° **2**; *(*t*BuCP)$_4$.

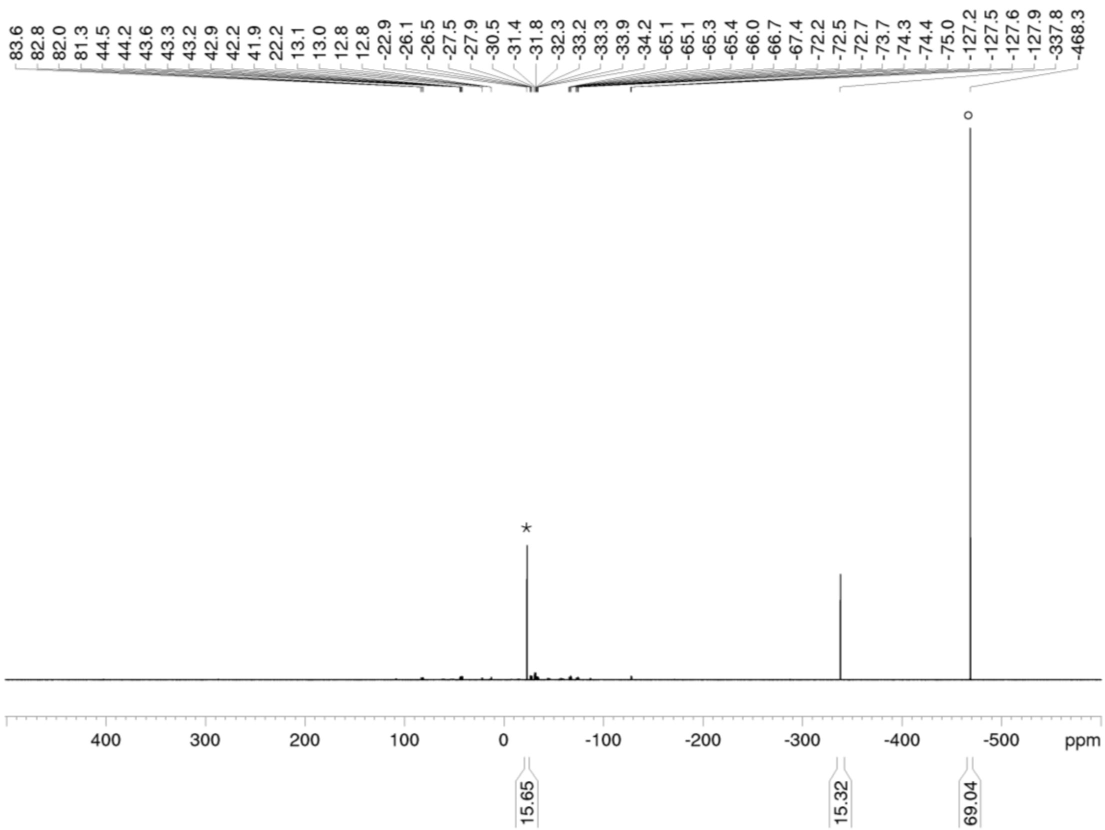

Figure S165. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of [CpNi(IPr)] with 10.0 eq. **1**; ° unreacted **1**; *(*t*BuCP)$_4$.

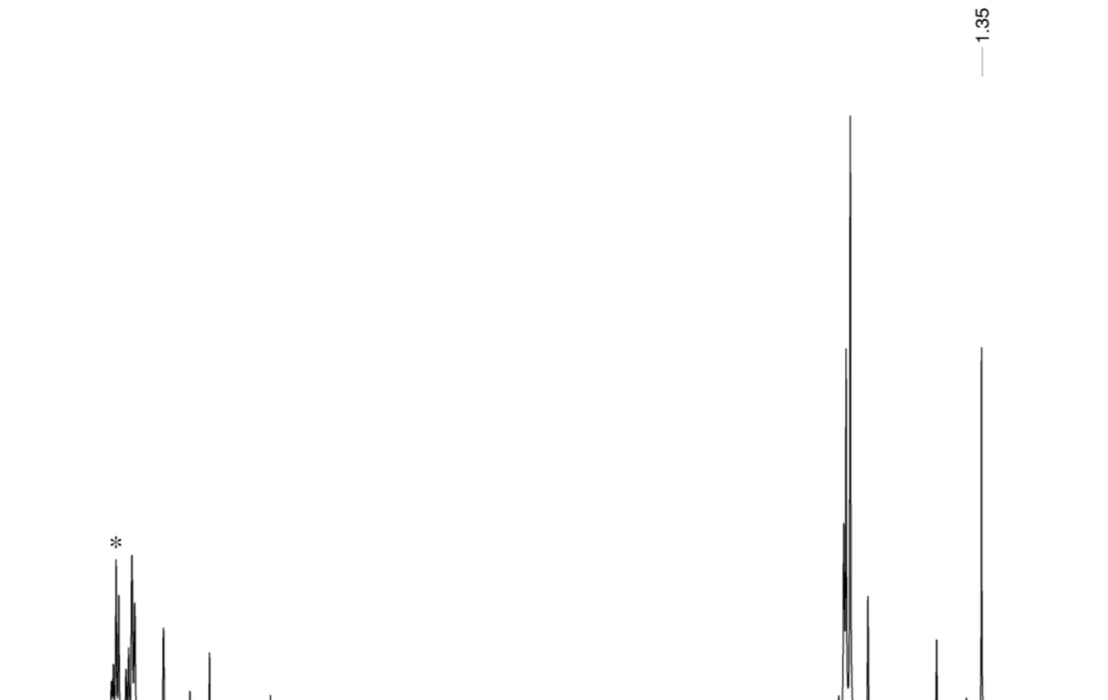

Figure S166. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of the reaction of [(IMes)$_2$Ni] with (*t*BuCP)$_2$ (3h, 60 °C); the signal at 1.35 ppm corresponds to *t*BuC≡C*t*Bu; *C_6D_6.

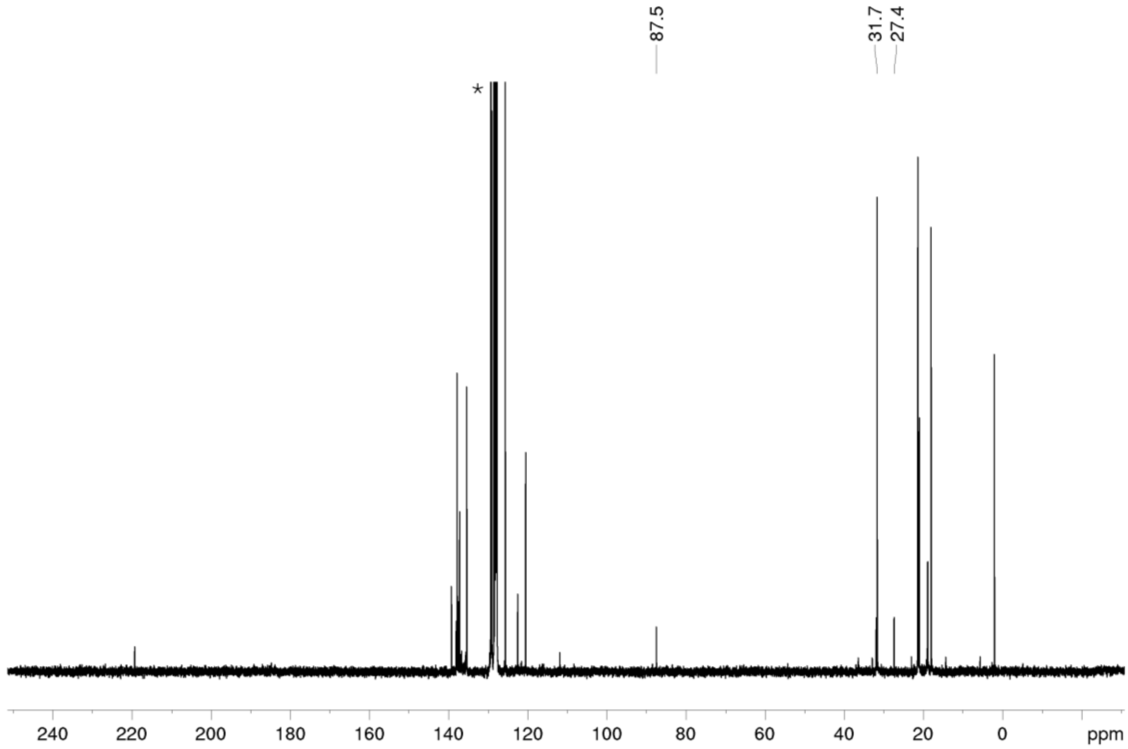

Figure S167. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of the reaction of [(IMes)$_2$Ni] with (*t*BuCP)$_2$ (3h, 60 °C); the marked signals correspond to *t*BuC≡C*t*Bu; *C_6D_6.

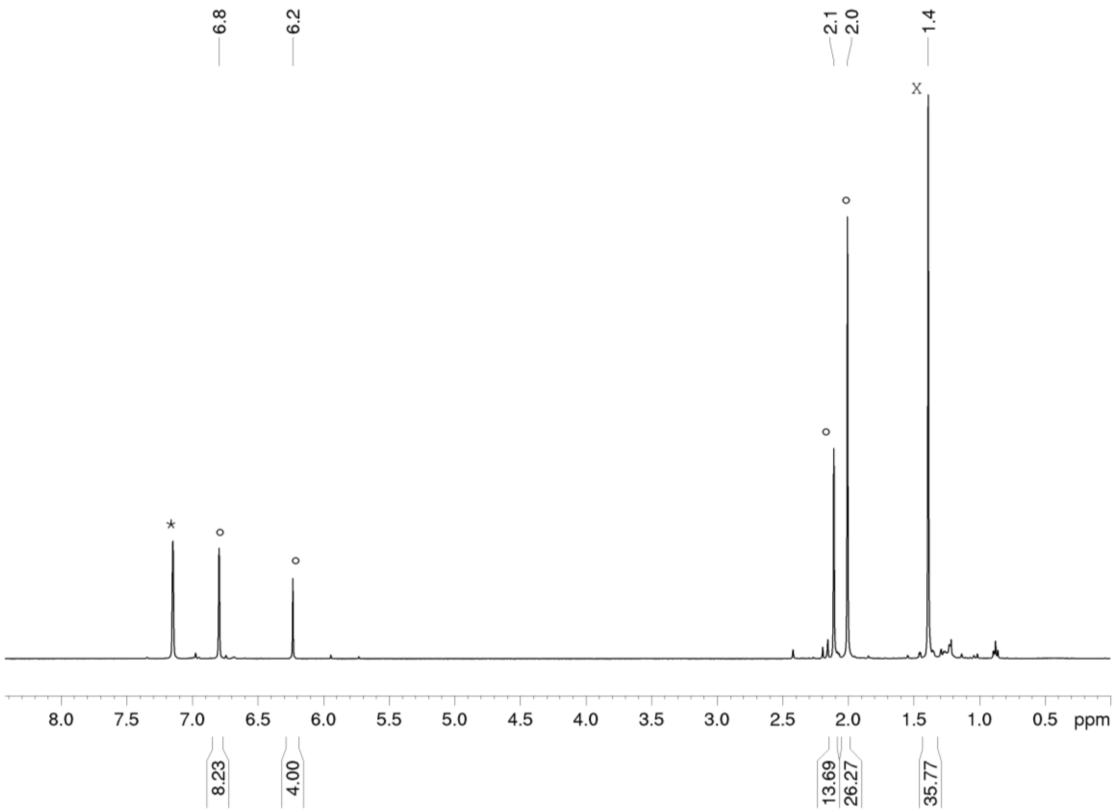

Figure S168. ^1H NMR spectrum (400 MHz,300 K, C_6D_6) of the reaction of **4** with CO gas; * C_6D_6, ° [(IMes)Ni(CO)$_3$], x (*t*BuCP)$_4$.

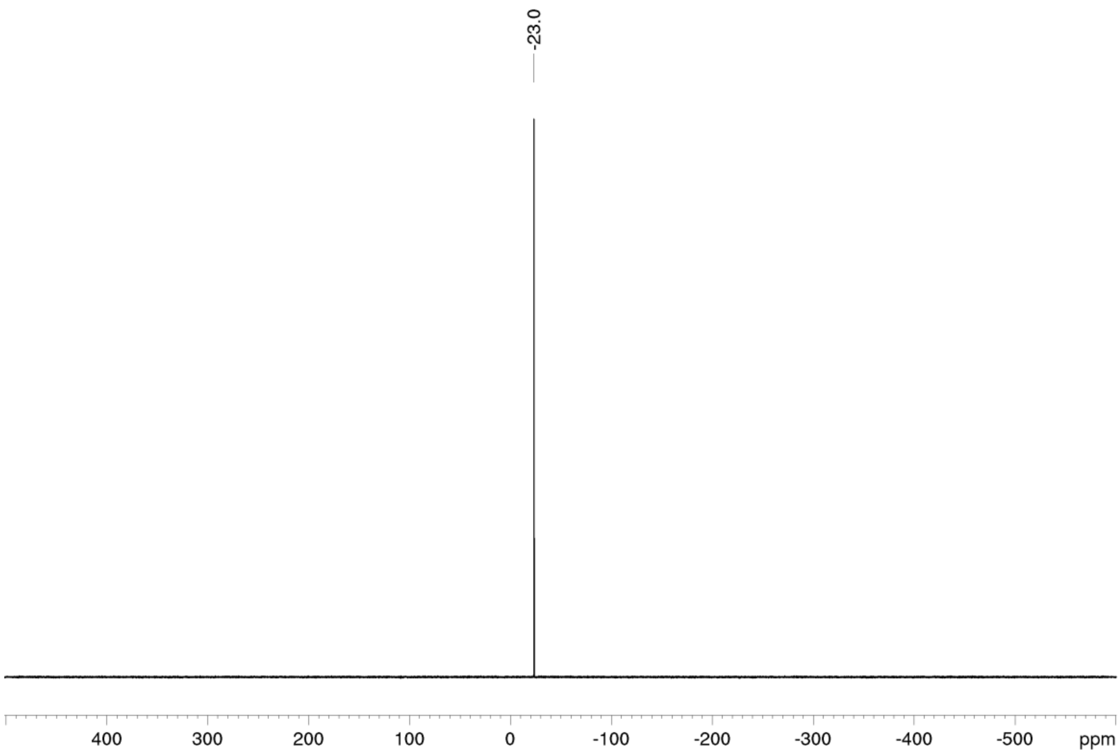

Figure S169. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **4** with CO. The signal corresponds to (tBuCP)$_4$ (**6**).[19]

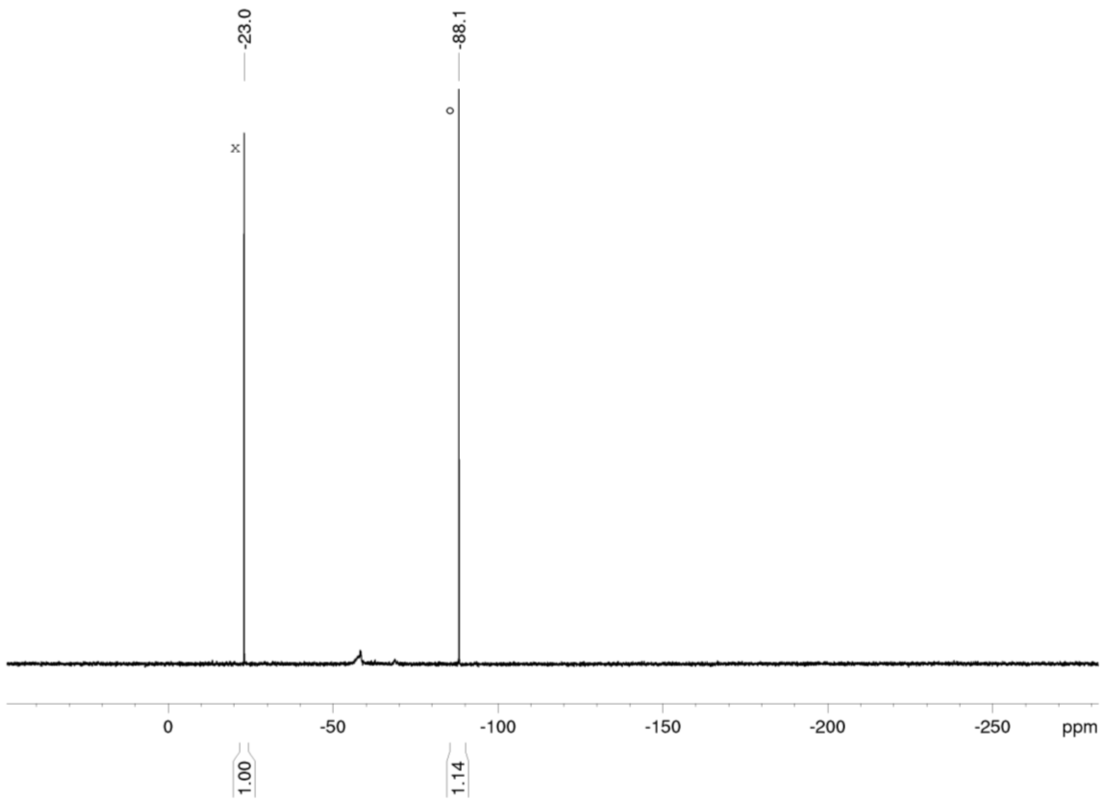

Figure S170. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction of **4** with C_2Cl_6; ° (tBuCP)$_4$, x [{(IMes)NiCl}$_2$(μ-tBu$_2$C$_2$P$_2$)] (**7**).[19]

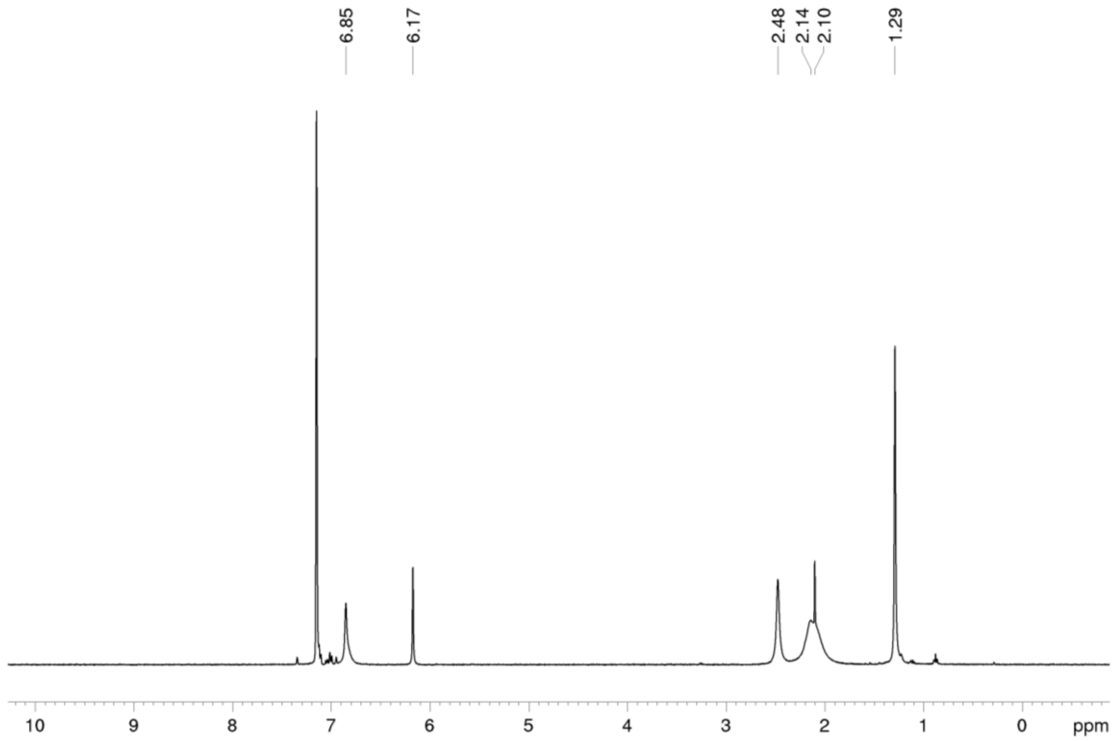

Figure S171. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of a mixture of [{(IMes)NiCl}$_2$(μ-*t*$Bu_2C_2P_2$)] (**7**) and [(IMes)NiCl(μ-Cl)]$_2$; * C_6D_6.

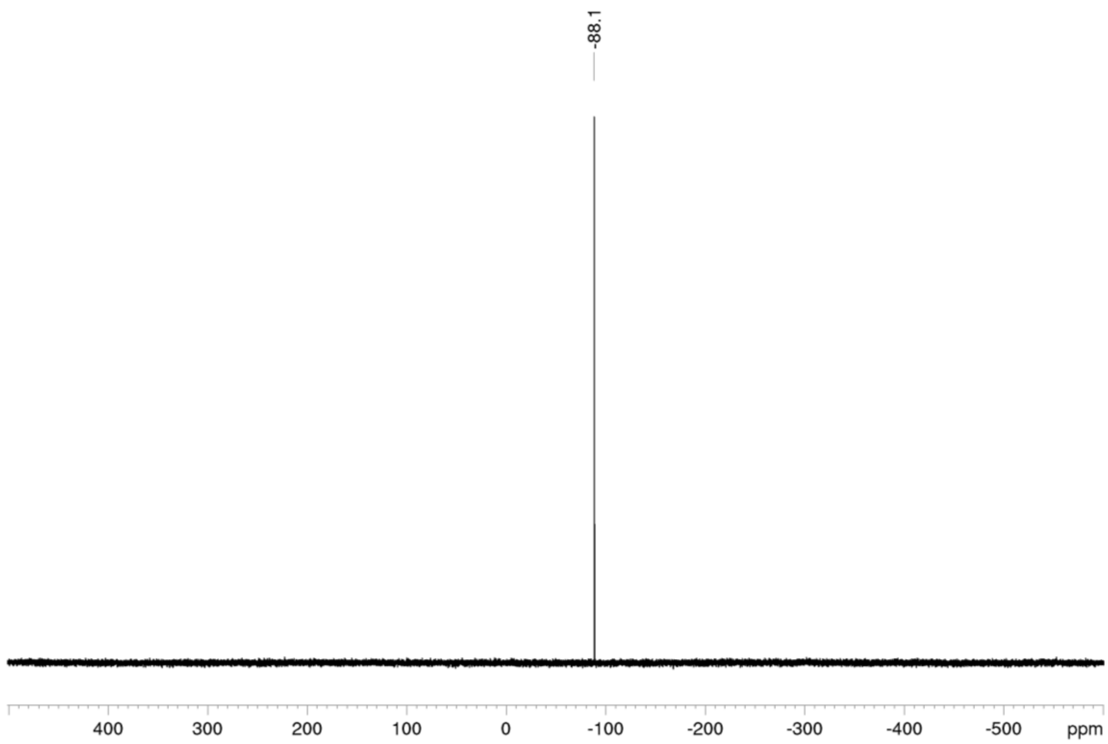

Figure S172. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, C_6D_6) of a mixture of [{(IMes)NiCl}$_2$(μ-*t*$Bu_2C_2P_2$)] (**7**) and [(IMes)NiCl(μ-Cl)]$_2$; * C_6D_6.

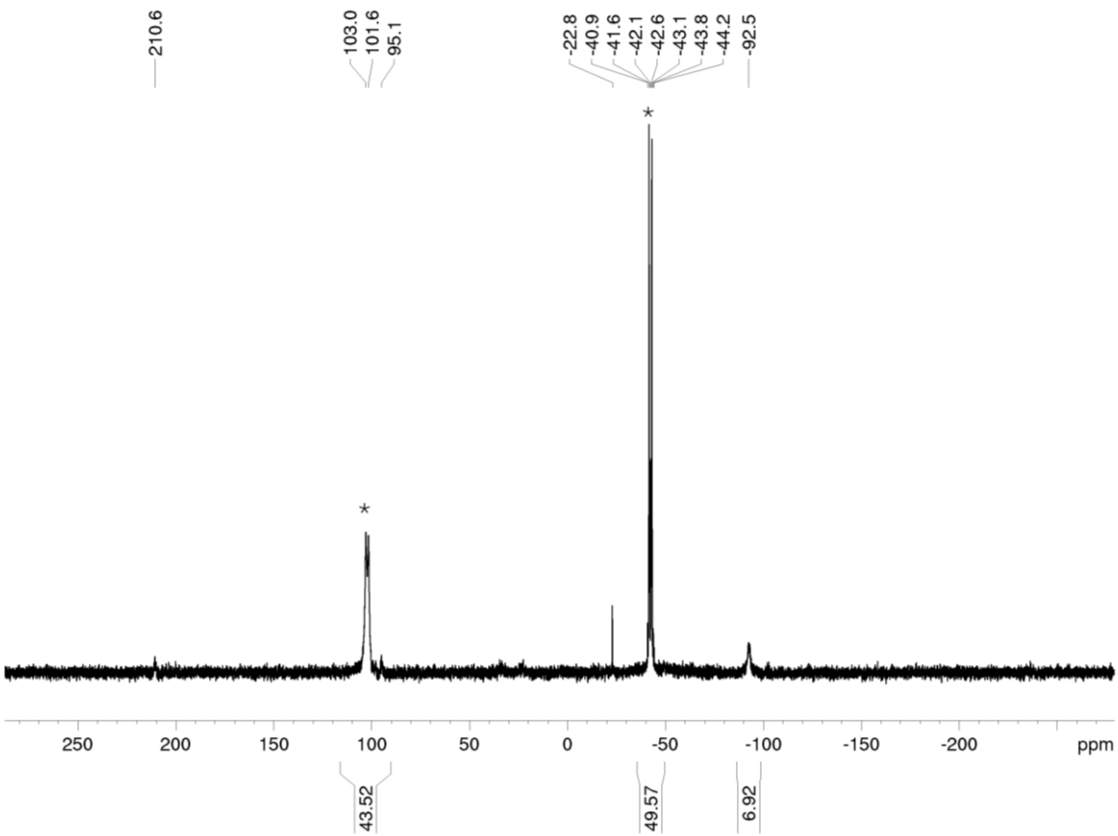

Figure S173. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of a mixture of [(IPr)$_2$Ni] and **1**; ***8**.

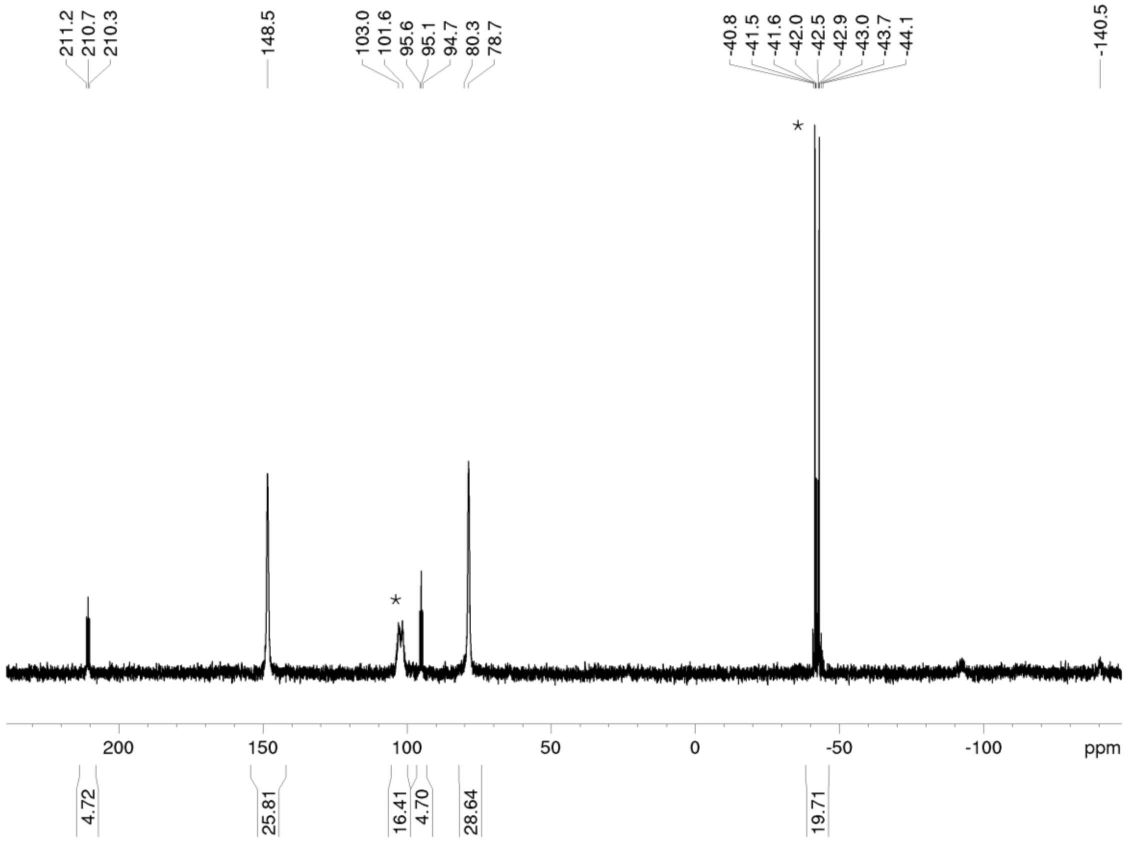

Figure S174. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of a mixture of [(IPr)Ni(η^6-toluene)] and **1**; ***8**.

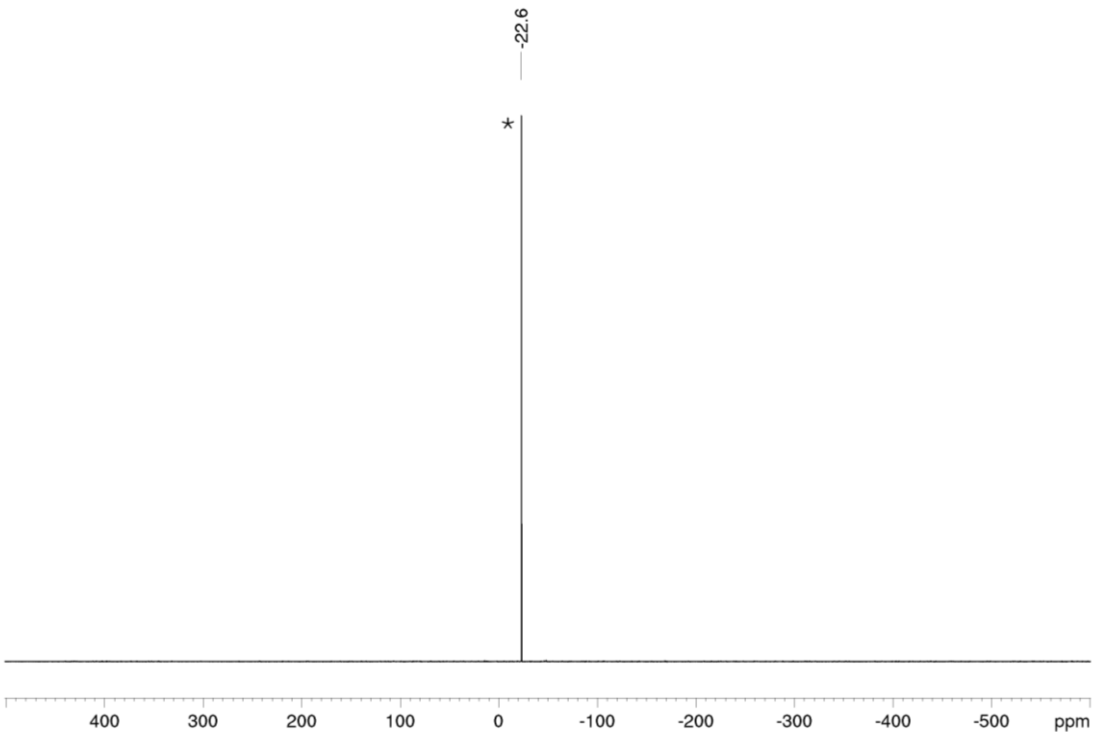

Figure S175. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of a mixture of [CpNi(IPr)] and **6**; *unreacted **6**.

S3 UV/Vis Spectra

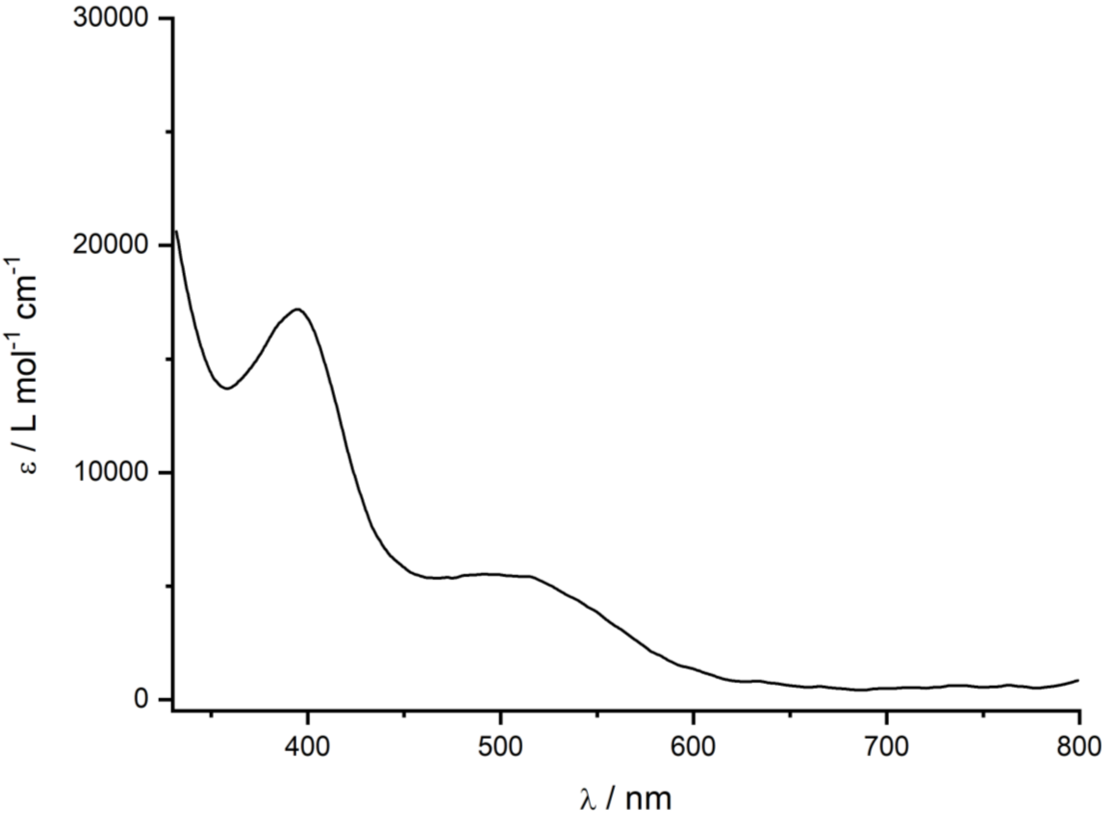

Figure S176. UV/Vis spectrum of **2** recorded in THF.

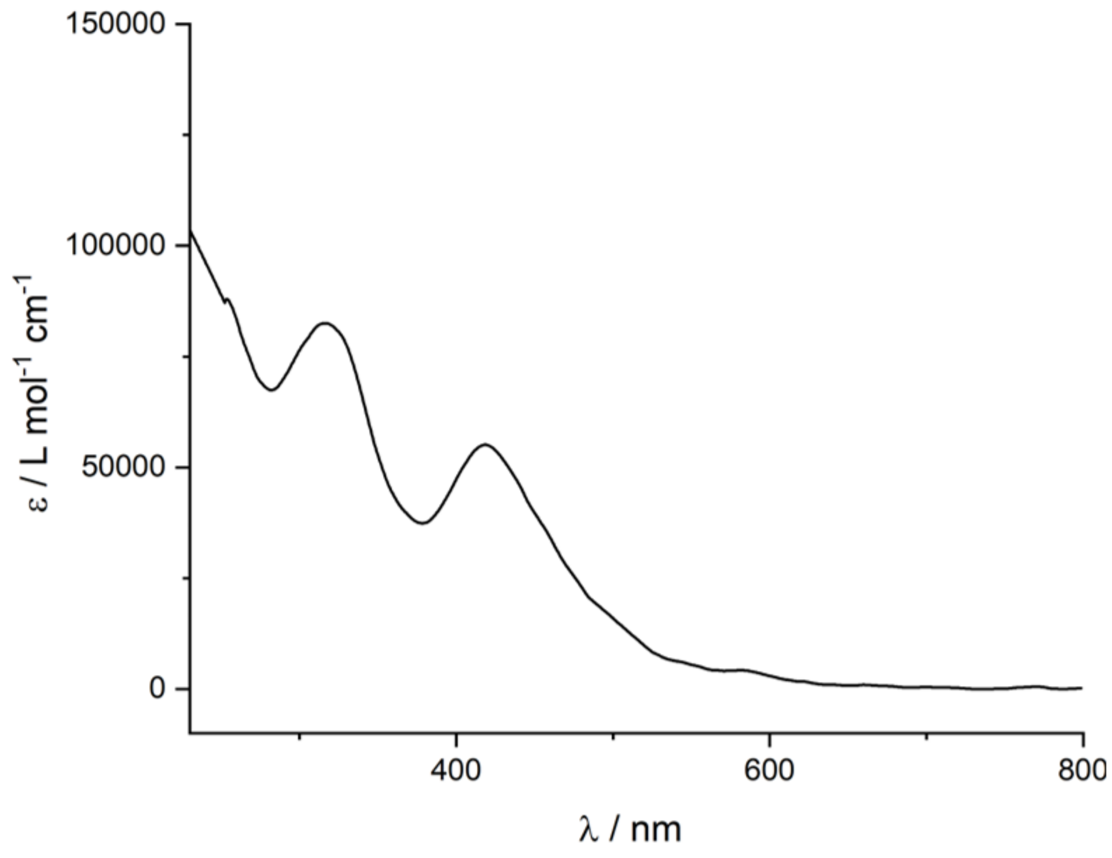

Figure S177. UV/Vis spectrum of **3a** recorded in THF.

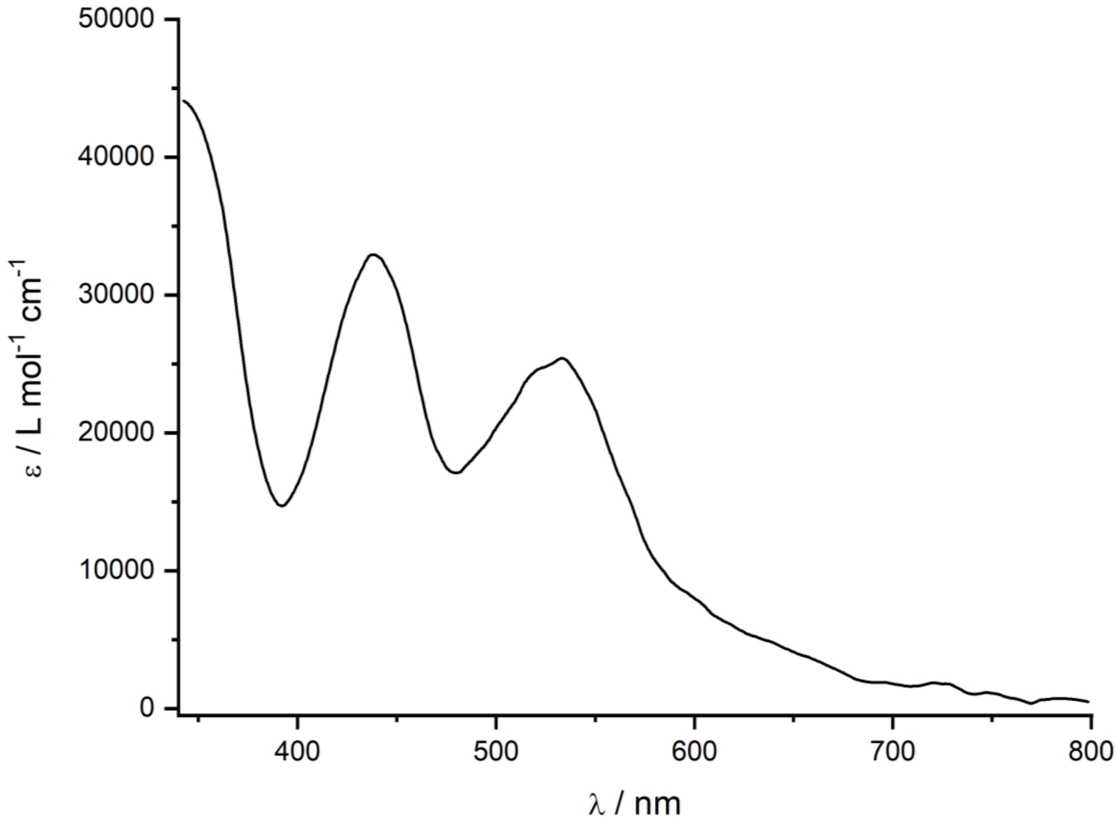

Figure S178. UV/Vis spectrum of **3b** recorded in THF.

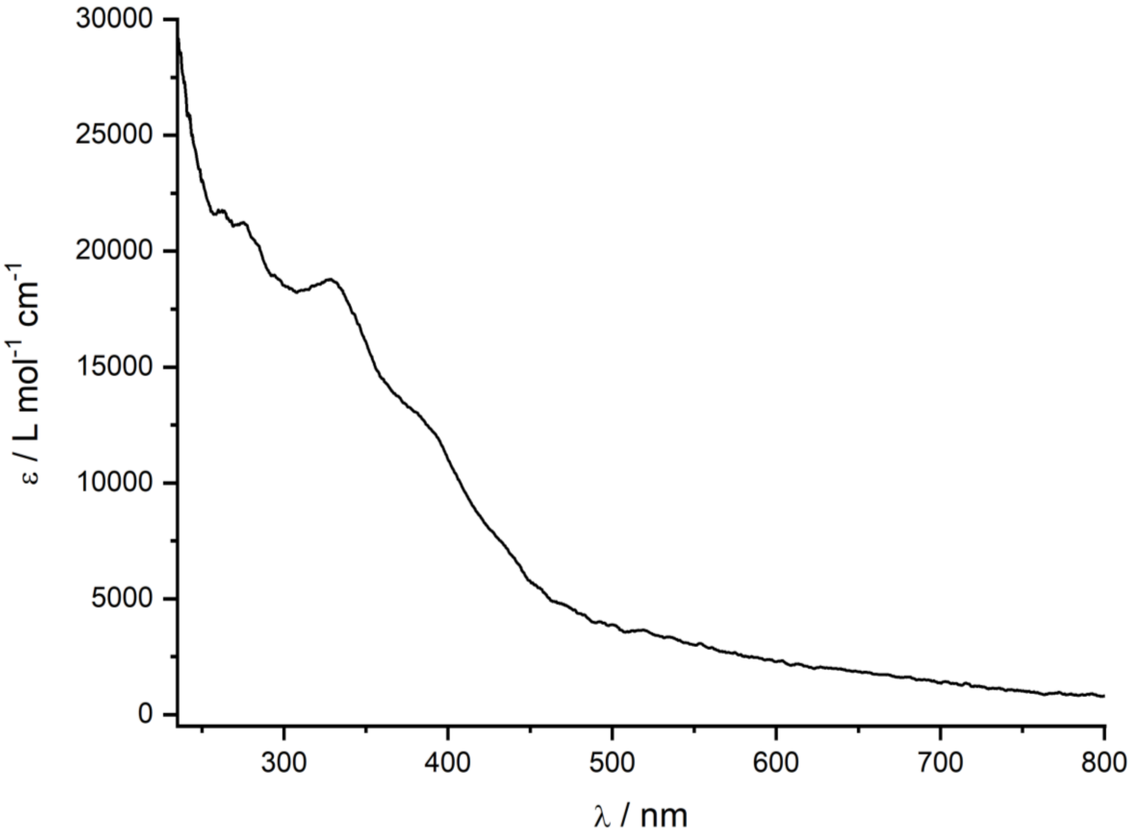

Figure S179. UV/Vis spectrum of **4** recorded in THF.

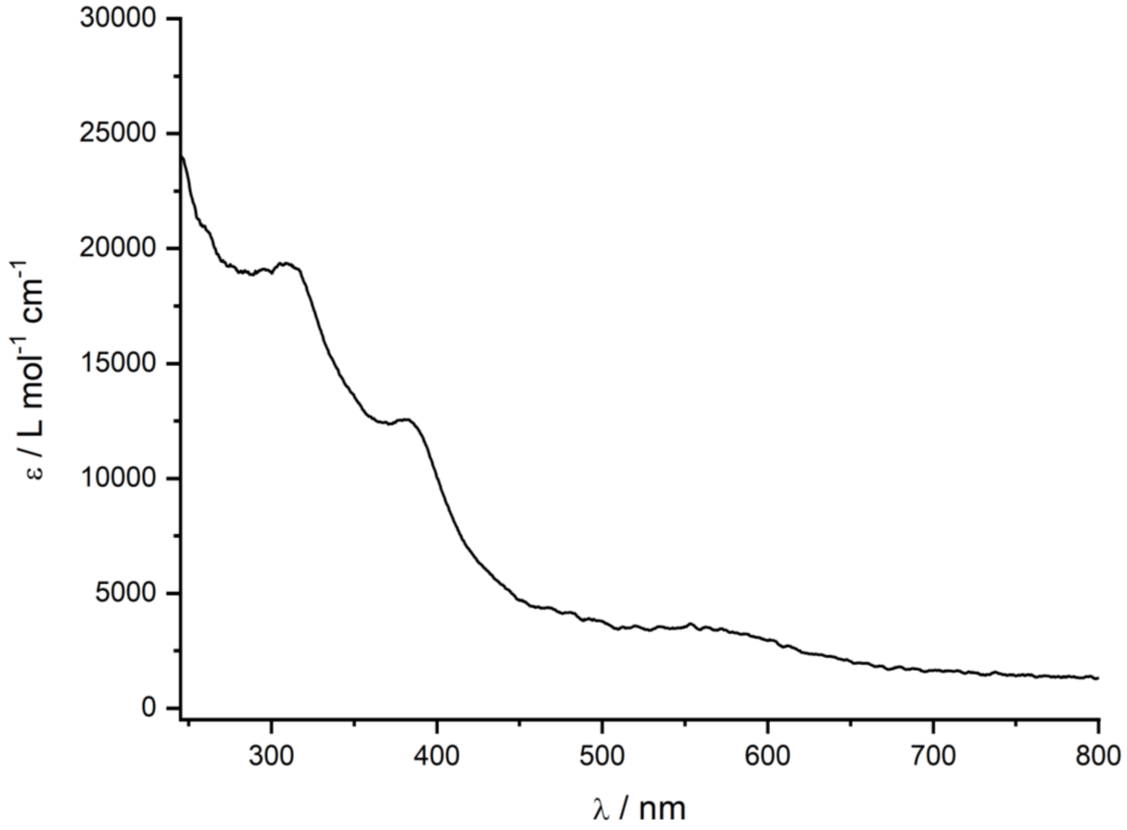

Figure S180. UV/Vis spectrum of **5** recorded in THF.

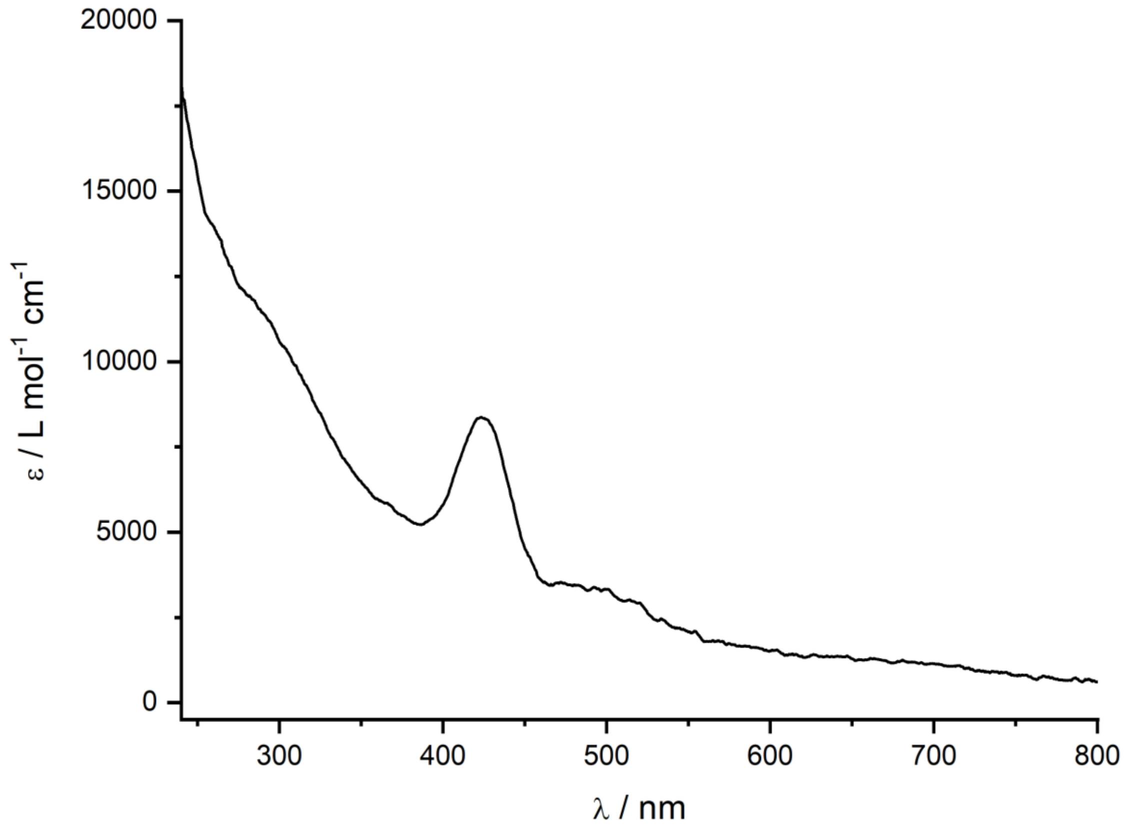

Figure S181. UV/Vis spectrum of **6** recorded in THF.

S4 Single Crystal X-ray Diffraction Data

Additional Comments

The disorder in **3b** and **8** was treated with soft displacement parameters and geometrical restraints. Several crystals of [(IMes)NiCl(μ-Cl)]$_2$ were screened and all of them turned out to be non-merohedrally twinned. The twinning was identified with the Crysalis Pro Software (Version 41.21). Two components with 59.7% and 49.6% were identified which were refined with the hklf5 command of SHELXL. X-ray diffraction data on **8** was collected using Cu-Kβ radiation.

Additional Figures (not depicted in the Doctoral Thesis)

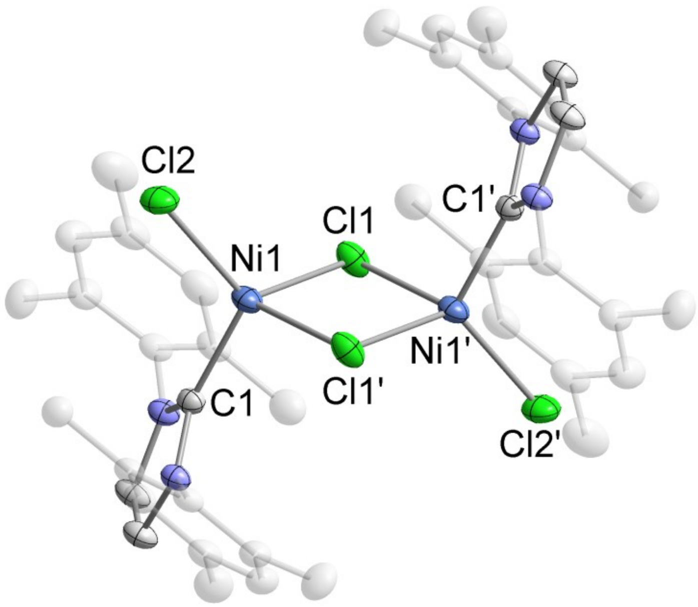

Figure S182. Molecular structure of [(IMes)Ni(Cl)(μ-Cl)]$_2$ in the solid state. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1−Cl1 2.3101(6), Ni1−Cl1′ 2.3244(7), Ni1−Cl2 2.1976(6), Ni1−C1 1.985(2), Cl1−Ni1−Cl1′ 91.20(2), Cl2−Ni1−Cl1 117.67(3), Cl2−Ni1−Cl1′ 116.88(3), C1−Ni1−Cl1′ 106.65(6), C1−Ni1−Cl1 106.56(6), C1−Ni1−Cl2 114.97(6).

Table S5. Crystallographic data and structure refinement for compounds **2-8** and [(IMes)Ni(Cl)(μ-Cl)]$_2$

Compound	**2**	**3a**	**3b**	**4**	**5**	**7**	**8**	**[(IMes)Ni(Cl)(μ-Cl)]$_2$**
CCDC	2043979	2043974	2043977	2043978	2043975	2043976	2043980	2043981
Empirical formula	$C_{40}H_{56}Ni_4P_4$	$C_{40}H_{66}Ni_2P_4$	$C_{117}H_{134}Ni_2P_4$	$C_{65}H_{91}N_4Ni_2P_4$	$C_{73}H_{90}N_6Ni_2P_4$	$C_{69.5}H_{86}Cl_2N_4Ni_2P_2$	$C_{47}H_{72}N_2NiP_4$	$C_{42}H_{48}Cl_4N_4Ni_2$
Formula weight	895.56	788.22	1781.53	1169.71	1292.80	1227.68	847.65	868.06
Temperature/K	123(1)	123(1)	123(1)	123(1)	123(1)	123(1)	123(1)	123()
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	19.10330(10)	19.4033(4)	16.9618(6)	11.0853(3)	22.7881(2)	11.6535(6)	12.5093(2)	11.3439(6)
b/Å	17.29460(10)	11.8450(2)	17.9713(6)	12.2194(2)	16.53850(10)	11.6641(3)	17.0633(3)	17.5861(7)
c/Å	23.8473(2)	19.9590(4)	18.7714(6)	25.0997(8)	18.5835(2)	24.9113(8)	22.4968(3)	11.3670(6)
α/°	90	90	76.289(3)	93.614(2)	90	77.735(3)	90	90
β/°	90	115.663(2)	83.095(3)	97.125(2)	103.7000(10)	86.603(3)	93.818(2)	114.446(6)
γ/°	90	90	63.886(3)	111.282(2)	90	78.811(3)	90	90
Volume/Å^3	7878.77(9)	4134.72(15)	4990.7(3)	3122.04(15)	6804.50(11)	3245.4(2)	4791.28(13)	2064.4(2)
Z	8	4	2	2	4	2	4	2
ρ_{calc}g/cm^3	1.510	1.266	1.186	1.244	1.262	1.256	1.175	1.397
μ/mm^{-1}	3.878	2.774	1.429	2.027	1.922	2.265	3.619	3.776
F(000)	3744.0	1688.0	1904.0	1250.0	2744.0	1302.0	1824.0	904.0
Crystal size/mm^3	0.341 × 0.173 × 0.138	0.389 × 0.152 × 0.062	0.434 × 0.198 × 0.142	0.38 × 0.103 × 0.055	0.686 × 0.119 × 0.077	0.266 × 0.225 × 0.153	0.22 × 0.135 × 0.075	0.216 × 0.063 × 0.053
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKβ (λ = 1.39222)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.894 to 147.264	8.44 to 147.746	7.496 to 147.468	7.148 to 145.528	7.248 to 147.726	7.894 to 145.836	5.874 to 120.326	8.562 to 145.988
Index ranges	$-23 \le h \le 23$, $-15 \le k \le 21$, $-29 \le l \le 29$	$-18 \le h \le 24$, $-13 \le k \le 14$, $-24 \le l \le 22$	$-19 \le h \le 20$, $-22 \le k \le 21$, $-23 \le l \le 19$	$-13 \le h \le 13$, $-12 \le k \le 14$, $-30 \le l \le 31$	$-28 \le h \le 28$, $-19 \le k \le 15$, $-16 \le l \le 23$	$-14 \le h \le 14$, $-13 \le k \le 14$, $-30 \le l \le 22$	$-15 \le h \le 11$, $-10 \le k \le 20$, $-21 \le l \le 27$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-13 \le l \le 13$
Reflections collected	64756	18027	40245	23135	26507	22273	18385	7045
Independent reflections	13233 [R_{int} = 0.0241, R_{sigma} = 0.0171]	8159 [R_{int} = 0.0236, R_{sigma} = 0.0246]	19581 [R_{int} = 0.0257, R_{sigma} = 0.0371]	12018 [R_{int} = 0.0258, R_{sigma} = 0.0374]	13358 [R_{int} = 0.0198, R_{sigma} = 0.0214]	12421 [Rint = 0.0176, Rsigma = 0.0222]	9352 [R_{int} = 0.0233, R_{sigma} = 0.0349]	7045 [R_{sigma} = 0.0258]
Data/restraints/para-meters	13233/1/889	8159/0/437	19581/810/1461	12018/0/720	13358/0/790	12421/120/743	9352/72/580	7045/0/242
Goodness-of-fit on F^2	1.038	1.028	1.052	1.041	1.023	1.082	1.034	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0202, wR_2 = 0.0510	R_1 = 0.0289, wR_2 = 0.0740	R_1 = 0.0598, wR_2 = 0.1676	R_1 = 0.0364, wR_2 = 0.0883	R_1 = 0.0281, wR_2 = 0.0727	R_1 = 0.0334, wR_2 = 0.0877	R_1 = 0.0347, wR_2 = 0.0843	R_1 = 0.0362, wR_2 = 0.0985
Final R indexes [all data]	R_1 = 0.0211, wR_2 = 0.0516	R_1 = 0.0307, wR_2 = 0.0755	R_1 = 0.0685, wR_2 = 0.1760	R_1 = 0.0426, wR_2 = 0.0926	R_1 = 0.0303, wR_2 = 0.0744	R_1 = 0.0356, wR_2 = 0.0893	R_1 = 0.0424, wR_2 = 0.0888	R_1 = 0.0434, wR_2 = 0.1014
Largest diff. peak/hole / e Å^{-3}	0.52/–0.26	0.41/–0.27	1.29/–0.51	0.51/–0.38	0.31/–0.31	0.33/–0.31	0.38/–0.27	0.47/–0.43
Flack parameter	0.003(6)	/	/	/	/		/	

S5 Quantum Chemical Calculations

General Methods

All calculations were performed with the ORCA program package.[1] All calculations were conducted in the gas phase with the he RI[2] approximation. Geometry optimisations for **3a** and **4′** have been carried out at the BP86-D3BJ/def2-TZVP[4–8] level of theory. Aryl substituents at the NHC moieties were truncated to phenyl rings (NHC = IPh (1,3-diphenylimidazolin-2-ylidene).

Thermochemistry for different bond-cleavage reactions of 1

In order to evaluate the thermodynamic feasibility of different bond cleavage reactions (P−P vs. P−C bond cleavage) possible in **1**, the hypothetical reaction between **1** and two methyl radicals was analysed by means of DFT computations on the TPSS-D3BJ/def2-TZVP level of theory (geometry optimisation and frequency analysis). While the formation of both the cyclobutene and the butterfly (*t*BuCP)$_2$Me$_2$ compounds are energetically favourable, the formation of the cyclobutene structural motif is strongly preferred (ΔΔG = −22.7 kcal·mol^{-1}, ΔΔH = 22.5 kcal·mol^{-1}).

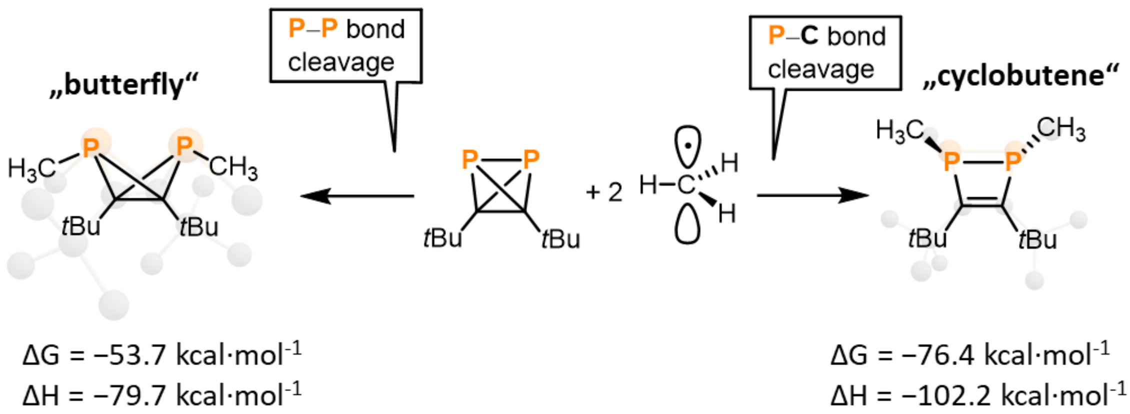

Figure S183. Thermochemistry of the reaction of **1** with methyl radicals.

Similarly, the reaction between **1** and two nickel radicals [CpNi(IPh)] (IPh = 1,3-diphenylimidazolin-2-ylidene) was analysed on the BP86-D3BJ/def2-SVP level of theory (geometry optimisation and frequency analysis). Again, the formation of the observed cyclobutene complex **2** and the butterfly type compound are energetically favourable (ΔG and ΔH < 0). However, in this reaction, entropy effects play a crucial role. While the reaction enthalpy is more negative for the butterfly type product (ΔΔH = −17.4 kcal·mol^{-1}) the Gibbs free energy is more negative for the cyclobutene structural motif, presumably due to the release of two equivalents of IPh (ΔΔG = −4.6 kcal·mol^{-1}).

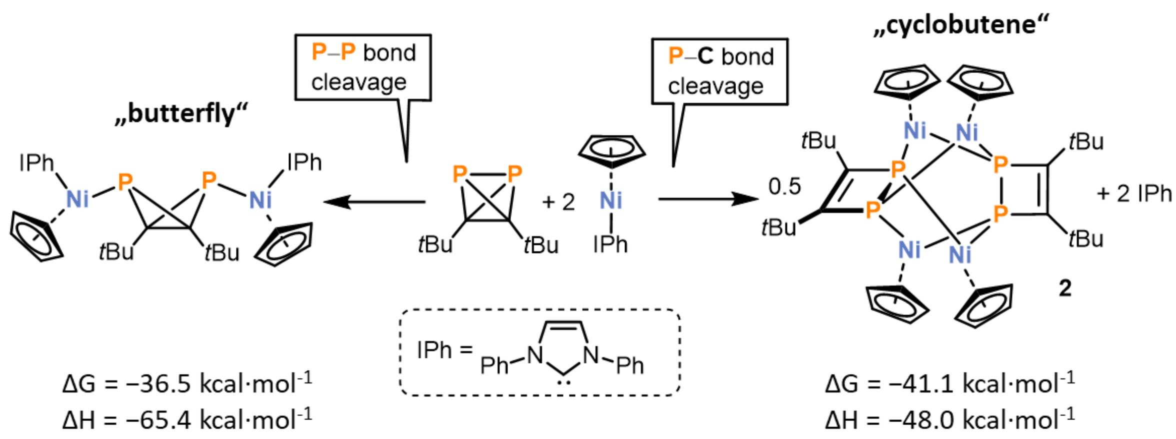

Figure S184. Thermochemistry of the reaction of **1** with [CpNi(IPh)].

IBO calculations

Intrinsic bond orbitals (IBOs) have been constructed from the occupied BP86 orbitals according to Knizia *et al*.[9]

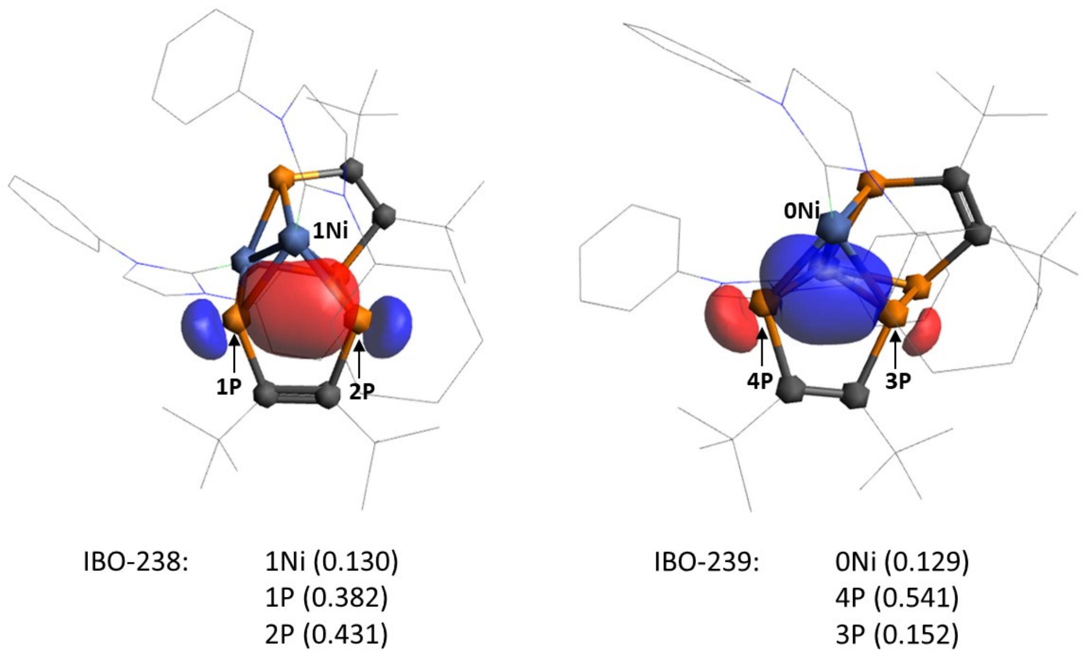

Figure S185. Depiction of the IBOs of **4′** featuring multicentre bonds between Ni/P/P; isosurface value = 0.06.

Calculation of NMR chemical shieldings

NMR calculations were performed using TPSS pcSseg-2 using the ladderane phosphaalkyne tetramer (*t*BuCP)$_4$ as reference.[20]

Cartesian Coordinates for Optimised Structures

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

P	-5.12137832703673	0.39967110787853	0.28610674290692
C	-3.36123164803409	-0.12777579742836	0.51961271592198
C	-3.52096875319146	0.90274648436491	-0.49937032603757
P	-3.51492408218759	1.57802241335179	1.22541092933580
C	-2.63937317624284	-1.39840158727862	0.87945355077558
C	-3.06896514466104	1.36866977599835	-1.85722489911349
C	-1.55467122655552	1.64533694749302	-1.83409093464056
C	-3.82459916566125	2.66582586810054	-2.19279423191146
C	-3.39573007974418	0.29439103049284	-2.91045642154347
C	-2.96815063539180	-2.49260540870536	-0.15250571791444
C	-3.11953307987220	-1.84223285910460	2.27176474747998
C	-1.12187762318037	-1.14133284518135	0.91544066015956
H	-4.20243003307666	-2.00417524998187	2.27068054335077
H	-2.88632080051612	-1.07753926251677	3.01988076100569
H	-2.62836918685772	-2.77665622361916	2.56454111663207
H	-0.75362943071672	-0.81396333921413	-0.06137250159896
H	-0.59108353031774	-2.05932874492669	1.19121772609456
H	-0.88154498621655	-0.36665077170327	1.65084632574252
H	-1.22464333501927	2.01497854993938	-2.81131051187287
H	-0.99107464475818	0.73609126705160	-1.60460095074362
H	-1.31382740364564	2.39954758227026	-1.07784334696888
H	-3.52266404785936	3.03884406820338	-3.17755027514009
H	-3.61030912176894	3.43873382118150	-1.44742733638409
H	-4.90504236318560	2.48868654529508	-2.20421186283261
H	-3.09741722953879	0.64054645997889	-3.90629433455861
H	-4.47005140723202	0.08364536486144	-2.92319583822258
H	-2.86473279710153	-0.63876267060706	-2.69982256165200
H	-2.64784733451359	-2.19756044157232	-1.15618508221975
H	-4.04580379629062	-2.68428593315495	-0.17817987747476
H	-2.45521560962589	-3.42434615146702	0.11058119142437

CH_3-radical

C	5.51540515575140	0.19062620870951	11.56078599215377
H	5.51474101311520	1.26513114851447	11.69819843915670
H	5.51574121345342	-0.46601606076934	12.42238530290536
H	5.51574261767997	-0.22805129645464	10.56166026578414

(*t*BuCP)$_2$Me$_2$ (cyclobutene):

P	-5.73660308596140	1.40455480954609	-0.11816995247545
C	-3.79225437385552	-0.08052139842522	0.53240933252105
C	-4.06262772254005	0.73008251440175	-0.53691974480447
P	-5.07183469798290	0.44264665677513	1.76654259024555
C	-2.67973595669894	-1.06558894521791	0.90043806477913
C	-3.40788030072205	0.99877530121749	-1.89431802456373
C	-1.87979402960199	1.17411869858145	-1.82653954269126
C	-3.98114411952391	2.30424826370592	-2.48425303246861
C	-3.78404084631379	-0.14513427567955	-2.86560246397600
C	-2.29034333240023	-2.02051604955157	-0.24304222853158
C	-3.15101949534302	-1.94646952242699	2.07636214968543
C	-1.44755733315954	-0.26959006062817	1.39149373678561

H	-3.98348054897943	-2.59273420712689	1.78232338928707
H	-3.46827946591046	-1.33127023541723	2.92747234082246
H	-2.32630293553803	-2.58383897448639	2.41310440907354
H	-1.03596848955360	0.36424385784660	0.60398925408298
H	-0.66577839814772	-0.96206324425850	1.72674451742554
H	-1.72553209334368	0.37086191306320	2.23510708545248
H	-1.50166210093088	1.45275903055742	-2.81716609120756
H	-1.36370240500801	0.26325340424800	-1.52088128244423
H	-1.61442039361239	1.97155296812445	-1.12474736492133
H	-3.59538151486563	2.45040082905749	-3.49896055530943
H	-3.69710400933254	3.17277289250719	-1.88251275879903
H	-5.07570894881305	2.26227874243004	-2.54481414754099
H	-3.38244399019832	0.06608949698120	-3.86421386941102
H	-4.87307080714903	-0.22999943503958	-2.94282390816510
H	-3.39083887852764	-1.10604932567747	-2.52888020876916
H	-1.84095178247817	-1.50204608675641	-1.09084426075706
H	-3.16737946189248	-2.56906119886860	-0.60184528545303
H	-1.55942665366932	-2.74996619030988	0.12514957571706
C	-5.49079437987271	3.21307512694272	0.28829421725564
H	-6.25832422207729	3.48693764996575	1.02016026016340
H	-5.63692023594034	3.82663647837439	-0.60470566073399
H	-4.50562335103646	3.41537680317103	0.71715515897993
C	-6.28484943565957	-0.97359042562982	1.90308820097439
H	-7.26090696111563	-0.54149594056767	2.14869843035481
H	-5.99451850703706	-1.64421953292532	2.71623666694808
H	-6.37351473520666	-1.54037038850416	0.97231100246892

(*t*BuCP)$_2$Me$_2$ (butterfly)

P	-5.20164922080453	0.38983119747275	0.10729421243038
C	-3.43350399858577	-0.03079105370468	0.54256757099734
C	-3.54080423603821	1.06019059475742	-0.45488496342895
P	-3.22178377787787	1.68293363973269	1.27850867037013
C	-2.72788571310143	-1.34382978854867	0.86233268984471
C	-3.06937527826209	1.53031792176580	-1.82583935542900
C	-1.63406746889404	2.08466494561477	-1.77717713320409
C	-4.01293812447820	2.66620953554262	-2.26590244570521
C	-3.10450302507655	0.39972561971379	-2.87243581355488
C	-3.33271061577927	-2.52194263316127	0.07742176442861
C	-2.92592863864708	-1.61171385505959	2.36674412015089
C	-1.22128109563853	-1.28825163684977	0.54375461433447
H	-3.99235387796596	-1.64692519289571	2.61222898026138
H	-2.46702024055009	-0.81774308882521	2.96466034469704
H	-2.47132050780511	-2.56804162272806	2.64913483242886
H	-1.04912680930984	-0.98761016775116	-0.49501747331206
H	-0.78316835928005	-2.28271999743998	0.68657457329964
H	-0.69384189856307	-0.59495850717389	1.20056326438881
H	-1.35518860647455	2.44899161971518	-2.77237390883296
H	-0.91397151626045	1.31250817356799	-1.48883040079816
H	-1.55488043421299	2.91806029547135	-1.07427864962996
H	-3.70112130898337	3.06909383827718	-3.23616245979171
H	-4.00296714571386	3.47842376061850	-1.53176993529618
H	-5.04159211333876	2.30213040281730	-2.35389422172484
H	-2.65154819142296	0.75437901789720	-3.80529835723235
H	-4.12567038209072	0.08743696152418	-3.09583050892551
H	-2.53776991978685	-0.47260534624647	-2.53013384314839

H	-3.19217450441135	-2.40114519479020	-1.00126380622029
H	-4.40136693347702	-2.62751594271959	0.28198632068472
H	-2.83297325993106	-3.44955108644684	0.37871963398787
C	-5.70633036160452	-0.80498053032077	-1.23931397257021
H	-6.27980163394856	-0.24462294270637	-1.98634399617828
H	-6.38273039957808	-1.53887599662022	-0.78775280386258
H	-4.89076964091176	-1.33084354119290	-1.73211539334902
C	-1.37070085076677	1.90537312146065	1.42200242210514
H	-1.16898996819075	2.98199274261134	1.40299813295430
H	-0.77693171602046	1.42043652012773	0.64963450492712
H	-1.06342822621736	1.53044821649291	2.40481278990323

[(CpNi)$_2$(tBu$_2$C$_2$P$_2$)]$_2$ (2)

Ni	18.83494637164867	8.77602790724377	6.50360876098817
Ni	17.48084164460913	6.56933832260051	8.99217334801557
Ni	20.14698311441895	10.79481242206452	8.83774445909183
Ni	18.98013147034237	8.87495617432404	11.40916935921497
P	20.21126245695243	8.71919531441910	8.18900423715125
P	17.44573669309370	8.57601038966471	8.16460038281119
P	18.30026291832711	10.01963337997347	9.69096510498933
P	19.29189348302982	7.43497507267283	9.81282145581114
C	21.54745043856868	7.47037572796978	8.57422322525554
C	16.06233701283481	9.80038025788341	8.42943247247514
C	20.97604579670341	6.67328542391380	9.55307415465042
C	20.00682869224500	9.31522287297910	4.82930464542596
H	21.08533976139516	9.50585921048993	4.84922172015528
C	17.98157829741615	8.21903346706982	4.62582542215576
H	17.21273080711971	7.44850675321176	4.49525593264892
C	16.59348868397418	10.70019334573819	9.33875627807523
C	18.99044916918355	10.19797811032141	13.05413398293455
H	18.62894369269437	11.23156237687619	13.04040164065689
C	22.93773152110194	7.54386141816788	7.92979010033802
C	17.73814263751275	9.62562856272931	4.92004578029448
H	16.75363301059717	10.09634863000723	5.02372658467535
C	16.49675372776853	13.12350000534442	8.83088850434994
H	17.55506812791139	13.02793816433287	8.52342782627450
H	16.33076747651228	14.14668575830902	9.22892867596053
H	15.87491550140114	12.99540435065676	7.92503505459751
C	20.34623438837522	9.79132122225571	12.81312136307850
H	21.17926584936457	10.44257712099020	12.52854191249143
C	21.15527986099129	4.21546814969017	9.24972679620686
H	20.11544770863383	4.23664188565245	8.87215659038773
H	21.33682034386906	3.23345316132861	9.73501978532013
H	21.82764771120010	4.30383329410052	8.37723710767233
C	16.15623139652297	12.05797540944011	9.90408621570993
C	20.37513972758484	8.37438027598966	12.90338738457785
H	21.25721513814067	7.74592780247588	12.73575158938063
C	17.42005737860512	4.53362504507844	9.57989390615861
H	18.17998084685697	4.01456009729141	10.17432460449661
C	21.37306051971037	11.96038902703860	7.51909170219852
H	21.66189479965599	11.65687647385925	6.50586289872730
C	22.09594998563770	11.63474935914760	8.74186800128272
H	23.03482104395364	11.07115214727794	8.79144584475494
C	18.98735299529718	10.30748970530323	4.97771352529328
H	19.13921982939430	11.37297678237725	5.17944551076536

C	16.97714444712527	12.35219300643700	11.17772743725208
H	16.71949186160523	11.63249848001254	11.97879555485142
H	16.76799139180659	13.37742801292501	11.54538451096092
H	18.06517774358396	12.26817447157060	10.98672562722332
C	19.38371944953461	8.02924767094011	4.56958223914668
H	19.90965616144319	7.08636840693310	4.38014600615715
C	13.63688005639414	9.26049373744872	8.80053407056459
H	13.95971767606808	8.34731215842403	9.33907132287147
H	12.66257270488618	9.05188133484674	8.31081522205768
H	13.48342827403001	10.05235704101389	9.55309218544608
C	14.67263005638144	12.15909634132330	10.31256704942279
H	13.97968118586605	12.07013072891852	9.45779442527605
H	14.48821465772516	13.14802207703467	10.78096724647124
H	14.41174424247902	11.37958750653566	11.05616093823806
C	19.05049856712280	7.90479668670397	13.29815332025664
H	18.76605002111712	6.86045059589166	13.47145891548822
C	15.53184934640576	5.71429176162070	9.00445555865342
H	14.59351869084748	6.27876814928976	9.05347082927497
C	18.20282549066146	9.03575642940684	13.40754428567931
H	17.14201437126412	9.03397240377396	13.68294636154852
C	23.91907110143251	8.13897278216605	8.97002063544899
H	23.52422553384394	9.09804700264747	9.35952011384593
H	24.91103099229093	8.32658444160027	8.50789724006102
H	24.05976212012683	7.46459070206446	9.83353069217423
C	14.69645483611671	9.65436554609581	7.74216648453409
C	21.37799040562465	5.37011896895011	10.26072919061732
C	16.23158474608207	5.33642673226550	7.78262433493717
H	15.91706918645152	5.58226737043207	6.76142411573588
C	20.23592118216489	12.85451862330509	9.31379607251016
H	19.49407971448819	13.40916965359350	9.90020058808975
C	20.45909507010711	5.12966593711710	11.48209848090393
H	20.71339264333548	5.80904168093116	12.31543137600742
H	20.57776831066540	4.08941509707870	11.84773251491508
H	19.39181190558161	5.28863481215228	11.23494273489646
C	22.82409832786177	5.35422488210502	10.80088437151608
H	23.58864205753779	5.39109594049735	10.00522589868850
H	22.99369920414952	4.42120177205511	11.37721687752718
H	22.99859605727677	6.20934929685162	11.48497529665276
C	16.24771746792993	5.18550494646222	10.10944058851692
H	15.98789712071162	5.29032423502995	11.16882400579813
C	17.37774157691198	4.58119642274616	8.14012373981127
H	18.11220658907573	4.14749153436608	7.45208726851281
C	22.87849097068550	8.49494181938548	6.71601898482135
H	22.23531388739212	8.06768548783158	5.92345521618608
H	23.89266390066495	8.65165285770671	6.29593630863996
H	22.46266172240533	9.48154100058864	6.99746755779007
C	14.28284605735889	10.93203201427443	6.97904397040669
H	14.11610390503647	11.79732133847089	7.64491513609685
H	13.33926598456051	10.75250078987726	6.42310734893492
H	15.06329850030215	11.21709670033727	6.24483005772057
C	14.75911321228292	8.50883396203901	6.70815305806701
H	15.47190921847415	8.73466989123140	5.89509663511456
H	13.75984772272306	8.34360510170288	6.25734874355902
H	15.08462068750804	7.56795667363193	7.18439495120031
C	20.23820508092825	12.72843387018079	7.87128925247983
H	19.48447479088227	13.13411876338713	7.18680058409454

C	23.44540633119141	6.18701816864311	7.39543231229272
H	23.61218344870226	5.44109720056150	8.19197010684651
H	24.41186071836449	6.33111952371846	6.86926664337873
H	22.72358000650016	5.75961826174023	6.67045757410024
C	21.42262165797315	12.23822612846965	9.83924062777388
H	21.72458761878726	12.20488468639410	10.89155535445159

[{CpNi(IPh)}$_2$(*t*BuCP)$_2$] (butterfly)

C	6.95511370077627	5.15887728906238	2.85465111049625
C	8.80024120654942	6.54355233169522	2.91359413757941
H	9.54422191345112	7.19990756524553	3.37171263844536
C	8.57206488639791	6.22779896632131	1.60380240838196
H	9.09869189558093	6.51665762478583	0.69010307746510
C	4.80591580779655	3.12970844956022	5.18962588923846
C	4.12338933803326	2.63850656618043	4.01946000483931
H	3.04565453042125	2.70913255859522	3.83330953691213
C	5.07169191234884	1.93943636573343	3.19033513354481
H	4.85094880726344	1.44415711973442	2.23742313978076
C	6.34564001661558	2.08376282290166	3.79960006189928
H	7.29877004149366	1.69460171183023	3.41850575113110
C	6.18035445545143	2.81209974397799	5.04159524306196
C	6.92776385224625	4.79235955755108	0.39020551528536
C	6.81898987930247	3.39297101560826	0.30677466621904
C	6.22330394871018	2.82026748419431	-0.82577828622300
H	6.12416521667308	1.72617121866839	-0.89182802200833
C	5.75512083491926	3.63589425176378	-1.87154558487718
H	5.28217001855584	3.18338397777098	-2.75616278171902
C	5.89476302743493	5.03089840864495	-1.79103181193202
H	5.51205780960743	5.67336989580195	-2.59718921236312
C	6.48941155975738	5.61231219669399	-0.66278914574335
C	7.75148066306376	5.93825439813811	5.08984507355538
C	8.94136532049914	5.95552257626713	5.84052079732190
C	8.87927886345747	6.00350394446372	7.24296493944988
H	9.81243478383194	6.01128270855603	7.82627749707935
C	7.63621802883590	6.02261583899073	7.89586901552678
H	7.58977038026346	6.05347651313432	8.99489517309179
C	6.45241700835777	5.99980386754409	7.13746643264092
H	5.47283293725878	6.01754190173623	7.63868916798878
C	6.50282492196620	5.95948835343233	5.73799668508507
N	7.46463914673346	5.37981361546710	1.58206951498743
N	7.81898371554171	5.88689538417750	3.66472517267142
Ni	5.53426515759055	4.07866003077317	3.32674513432907
P	4.23613339505168	5.00920292341639	1.76573570182843
P	2.76878336746086	6.26600085786251	0.25037770892956
C	2.67381361916448	6.01009880320833	2.13145744078580
C	3.79427841291362	6.86594332291580	1.73139549527332
C	1.58979999826318	5.84202913298893	3.17531895508932
C	4.42292825914310	8.19169542520937	2.11558270857117
C	4.94900278301083	8.14855635510009	3.56024032217655
C	3.38684251791223	9.32303398011314	1.97185583650154
C	5.60549167989282	8.49140508487224	1.17561602874599
H	2.53307079553696	9.17137660356817	2.66140336360724
H	2.98919125834122	9.35214042894207	0.93995991384163
H	3.84676489284535	10.30519418857647	2.20980902309056
H	4.13341886170135	7.95388935353778	4.28318832300402

H	5.43040444546177	9.11043884725743	3.83541540652819
H	5.69657424958038	7.34402453607590	3.66365289803315
H	6.40963845845052	7.74470385727120	1.31137030242915
H	6.03294072165116	9.49388183788168	1.38587379392815
H	5.27827241468386	8.46721466598067	0.11727499562754
C	0.55313057563431	6.97816667493800	3.12110925877121
C	2.22361875485568	5.79511548936023	4.58238079862848
C	0.86478877244973	4.51650957884600	2.86704676893663
H	1.02724909347567	7.96526031629196	3.29138970760774
H	-0.22074688656375	6.83352704273025	3.90387371143558
H	0.05472443610843	6.99514066644225	2.13547010148041
H	0.42026235310212	4.55366369473657	1.85326936929060
H	0.05915873477455	4.31728049730980	3.60428443898534
H	1.57505122720018	3.66709361059139	2.87897972781425
H	2.59610777959795	6.79597609422217	4.87936830750767
H	3.08415204114671	5.10000517506093	4.59858257518858
H	1.47920888263429	5.47204981119728	5.34004773609211
H	0.61704238178716	9.50641514726187	-3.04992581633943
H	4.74594625909314	10.78164509557619	-1.54170192038726
H	2.13534065810093	1.80417448494649	0.43579440090004
H	1.68592409455783	10.43575482454352	-0.73704138439048
C	0.36949753519006	9.16054472811414	-2.03833848821046
C	4.36069609311656	10.29718227168643	-2.45171893205805
C	3.90550581353835	8.97333225534118	-2.38402181774507
C	0.94037124438993	9.63830685695222	-0.83185757203956
C	1.53027314049042	2.49810110593386	-0.16593851482886
C	2.16918058892097	3.38087326096963	-1.04971014881897
C	4.33312747119819	10.99603892570732	-3.67206386078940
Ni	1.39718831082806	7.50884447406353	-0.99926596051518
C	-0.59596608576719	8.12585817597019	-1.71424366318840
H	4.69085556685011	12.03564884458477	-3.72080750913880
C	3.41262363405833	8.35437049459761	-3.54726532896802
C	2.13686828457114	6.55080084732480	-2.43566677304410
C	0.13344729448410	2.53578921327846	-0.01899012243376
N	2.94133520964750	7.00988574194079	-3.46043468784820
C	1.39110222911366	4.28064089440285	-1.79868094694444
N	2.05348298970461	5.19735288364933	-2.68071954067962
C	0.39202175631064	8.84724949473120	0.23975780531173
C	3.33921746999454	5.97174587366843	-4.31144047411444
C	2.78385398874122	4.82519949086956	-3.80845700395058
H	-1.20379427938140	7.57640269825891	-2.44403659409100
H	3.99477196156780	6.14016419021538	-5.17022489122199
H	2.82237707821629	3.78953232574860	-4.15719497731873
H	0.60703116206197	8.98146399442076	1.30299223565526
C	-0.60434746621974	7.95078598353765	-0.30962922949413
C	3.85115778183383	10.36475503107288	-4.83096660779958
C	3.38329535739350	9.04049254638389	-4.77192602305082
C	-0.63076395426531	3.45833113925408	-0.75431359981011
C	-0.00195477166796	4.33942772940440	-1.64929801235078
H	3.82443531779193	10.90854990109660	-5.78724608973731
H	-1.22501897869023	7.24706291748824	0.25719344838498
H	-1.72336791449024	3.49567247106344	-0.62988936149731
H	-0.36251270137253	1.85347618307845	0.68784773431197
H	2.97544223758271	8.54692195184685	-5.66666886700781
H	3.90343189291362	8.40841410232186	-1.44075274535439
H	-0.57492182263401	5.07630685454995	-2.22773883250535

H	3.26413977514594	3.41152998637702	-1.12859178378958
H	5.58872316112712	5.91567722357990	5.13166737220196
H	9.91446811677576	5.90326376548777	5.33070730634842
H	6.55720664486803	6.70278546470366	-0.56936886576575
H	7.17250972008040	2.77711138043440	1.14290138693287
H	6.98482704777083	3.07496876125933	5.73875854514005
H	4.34536722240029	3.65871290078932	6.03186791916754

[CpNi(IPh)]

C	8.10673472195380	1.80953135080954	4.60176839951706
C	9.38139522638244	-0.04478309565770	5.15547588089027
H	9.98728248829883	-0.69389158343572	5.79324390674760
C	9.05484520454821	-0.15091192902932	3.83290091932081
H	9.27675309417188	-0.93439216917980	3.10277231229482
C	7.46497987361109	5.46628439311648	3.96575247330081
H	8.36578898276348	5.94133934782881	3.55899225185775
C	6.54335618495929	4.64481065781165	3.24365803847958
H	6.61718227456915	4.36981782341940	2.18523802258274
C	5.49464094125946	4.24438978698859	4.14849368877381
H	4.62375877235426	3.62756388971417	3.89370004251079
C	5.77194460418970	4.80971563544248	5.43074623296538
H	5.15910797090867	4.70580833565517	6.33420553892102
C	6.99227166223586	5.56422490353210	5.31680876826112
H	7.47760951062927	6.12371910814109	6.12747410494648
C	7.70157185419948	1.18464782965762	2.22765218311230
C	6.34907274513526	1.55749615204206	2.12856735679166
C	5.78021307607582	1.76732647831957	0.86464139698214
H	4.72214919707143	2.06098624800206	0.78947314933509
C	6.54948205808697	1.59635179532067	-0.29974257935967
H	6.09850541229494	1.76119099770634	-1.28981029320611
C	7.89739997921851	1.21320985030655	-0.19388415762508
H	8.50835346120192	1.08345127596145	-1.10009337147395
C	8.47906007465753	1.01122032283581	1.06731687238908
C	8.83586975461668	1.65897036281067	6.92569448139921
C	8.92072301567207	0.82648326832193	8.05585185716378
C	8.83598145178871	1.39410332828025	9.33729346454009
H	8.89158157349392	0.74146445131175	10.22162447464005
C	8.65223588583590	2.78151380013614	9.49508684543353
H	8.57329290549796	3.21544045832903	10.50323298736031
C	8.58297570066969	3.60902720857598	8.36364830421010
H	8.46857839379024	4.69788127487540	8.47580266824605
C	8.68258195748102	3.05631461047338	7.07622817425477
N	8.27736055447289	0.96748094620523	3.50995958263299
N	8.80533206537454	1.14163545007505	5.61251285012703
Ni	7.40202350402203	3.50089817281768	4.89900614904132
H	5.76548458533447	1.68036275167429	3.05010309023133
H	9.54206776247807	0.74309465563646	1.15792710515720
H	9.01000260705948	-0.26339264281160	7.93743529365261
H	8.82023891163451	3.71518449797912	6.18286153359381

IPh

C	8.38456579755661	1.72699963009782	4.60728102992709
C	8.17880323616632	-0.33222753432169	5.65002416649944
H	8.25268013624957	-1.05864377326649	6.46400363375457

C	7.85007090114046	-0.51155331329579	4.33662941950135
H	7.58720961514953	-1.42459915627632	3.79551776694613
C	7.71908389738422	1.00673505657269	2.34887949741198
C	6.90052265509891	0.14380503301861	1.59587652986161
C	6.66668736857997	0.41346628540935	0.23781404803911
H	6.02388268500641	-0.26459110581503	-0.34401953052576
C	7.23400305249975	1.54362783080259	-0.37136184121759
H	7.04602950648890	1.75280586287842	-1.43517175225841
C	8.04029953915614	2.40798896095820	0.39085525868008
H	8.48838453556449	3.29841872647664	-0.07619923194344
C	8.28845526657436	2.14449486484710	1.74411008275509
C	8.88606804666681	1.64304094367872	7.01614388237130
C	8.53010767447340	1.07043028802786	8.25181604906469
C	8.93480831999532	1.68601235135353	9.44725668083055
H	8.65109626625015	1.23424991083491	10.41001987677822
C	9.68135320804275	2.87432825832599	9.41831304278764
H	9.99420360736315	3.35511705459654	10.35734040367492
C	10.02176514666162	3.44738810969188	8.17969002071231
H	10.60518612749325	4.38024139908842	8.14611485711649
C	9.63191893444563	2.83726256860152	6.98036547864734
N	7.98030375289457	0.74532836814054	3.72808944301169
N	8.49569169116380	1.02703674063536	5.78881881347026
H	6.42282532562559	-0.72633622455201	2.06787194389349
H	7.91713963031996	0.15866507431192	8.28768278690405
H	9.87951233689696	3.26430961877138	5.99890289129496
H	8.91058173909103	2.80292817040730	2.36551475201059

[(Cp*Ni)$_2$(*t*Bu$_4$C$_4$P$_4$)] (3a)

Ni	-0.22623222907222	6.04030900531030	10.99624162507714
Ni	2.64767565801279	2.77219373357584	9.19249359949213
P	0.69435352298460	5.47290379596270	9.20750806789595
P	0.62330132107212	3.28660583158644	9.31522151137857
P	-0.38551477626412	3.82983461753494	11.24780065737791
P	2.88265431305919	4.98570064205976	9.06153535520524
C	-1.70630641568259	3.19638685681611	10.10716509246037
C	2.33974441487615	5.54932179573538	7.37813604096426
C	-1.07246972844116	2.71132357331015	8.97795967392733
C	-3.17478433731120	3.40021885598168	10.48496668033506
C	1.03862837570682	6.00085164035472	7.49902326648228
C	-0.66057317528609	8.11734252566977	11.23868434696662
C	3.70302216963401	1.95483812367526	10.86759562507351
C	0.76309193607349	7.85220711140001	11.44089081101992
C	-1.38838986624648	7.39139736479198	12.21629824171769
C	4.23489336919594	1.41952651569822	8.63739120920382
C	3.07454152520066	0.68902690628471	9.00328860605811
C	3.27542332697347	5.34848079845965	6.18474515194292
C	-0.42324405587857	6.64437681344296	13.00610148437530
C	2.73759682946380	1.02755573080483	10.38576915825624
C	4.60020140321357	2.24359189617609	9.77626031451511
C	-0.02034490934201	6.65130229939322	6.60938394104219
C	-1.46245134082313	2.00327220655928	7.68071347322410
C	0.90347370370906	6.97745996214393	12.55614818089789
C	-3.28115839535843	3.63946965113816	12.00337734406844
H	-2.94004506399159	2.76385838863586	12.57301275548531
H	-4.32499258242206	3.85071699797042	12.27930691104457

H	-2.66678658337193	4.50015790078361	12.30195787664000
C	-0.24388108751392	2.00229301717235	6.73583953277401
H	0.08555405976782	3.02823040860102	6.51636235678398
H	-0.50269694149819	1.51325507212371	5.78545689113395
H	0.61096336993862	1.47452385364480	7.17708409838523
C	-1.37416522554764	6.60581473568344	7.34645301049626
H	-1.66329795172978	5.56987280433113	7.57483199936828
H	-2.16074189733077	7.05366057725020	6.72184267001056
H	-1.33694409783042	7.14786017544686	8.29994324315926
C	-3.67236213990187	4.67584236614773	9.76864618833103
H	-3.01638578840447	5.52080354243186	10.02609199502566
H	-4.70110351277507	4.91215756416074	10.08191234612010
H	-3.65943582721714	4.55801887446782	8.67853359361359
C	5.00008741620544	1.28607536187081	7.35936629567419
H	4.34062990539095	1.01680776245756	6.52310341136651
H	5.77406044792332	0.50296190990030	7.43467742223484
H	5.50895205535758	2.22014253394985	7.08785609715984
C	-2.60501451788260	2.71020627022369	6.92528279910703
H	-3.54098971270781	2.74117986443741	7.49222656430622
H	-2.80471346098584	2.18276364486791	5.98002497511742
H	-2.32326508476263	3.74352250142145	6.68043276252978
C	3.30679014461631	6.54816445400263	5.22222921768805
H	2.34536360525130	6.72672914533237	4.73070723177588
H	4.05292630491987	6.36656773778037	4.43380616773751
H	3.59455122275107	7.46499821560043	5.75636609579455
C	4.71494240991590	5.14161348068833	6.69318646990756
H	5.08419981946996	6.02771653676207	7.22792553648804
H	5.38698088145828	4.93941097505078	5.84596957710416
H	4.76148871152247	4.28528780196776	7.37982032822226
C	-4.07274466886528	2.19513118874396	10.15648756889107
H	-4.14453885456913	1.99455347146950	9.08277494095487
H	-5.09193562716321	2.38664349938513	10.52529628742018
H	-3.69907180564686	1.28737712713976	10.65138797179451
C	-0.22225352399714	5.91453139269150	5.27043058051117
H	0.66552886594240	5.93767103741558	4.63030164511493
H	-1.04776456593927	6.38183246140328	4.71232064743540
H	-0.48597239518350	4.86226786808546	5.44543827712625
C	2.38492821454498	-0.35044092159664	8.17986857854372
H	1.31634559537449	-0.41814969090979	8.42404997620481
H	2.82071510263340	-1.34855894882443	8.35648206096730
H	2.46957302628275	-0.14075615000296	7.10490624729073
C	-1.83580471005689	0.53530615261749	7.97704391383012
H	-1.00529097078698	0.02697901258194	8.48769702886170
H	-2.04086742064480	-0.00287648191442	7.03874750332641
H	-2.72027495010589	0.45834126558546	8.61959280656710
C	5.78949645110925	3.14331229104842	9.86664676306438
H	6.21135278638395	3.35843881308660	8.87688334836981
H	6.58366325490720	2.67914642411548	10.47364700752532
H	5.53218668373176	4.10556554880254	10.33373819139063
C	3.74598805875337	2.57680672545078	12.22759529203536
H	4.13866159404521	3.60189532771400	12.18142876683848
H	4.38854031947692	2.00737681039686	12.92044518141923
H	2.74206849961378	2.62773554494607	12.67169162013227
C	-2.86128958933087	7.46864825239013	12.46358075688037
H	-3.41537747007897	7.66863389349590	11.53643909386249
H	-3.10590062835285	8.27630793963925	13.17476083411024

H -3.25529495785588 6.53503233767401 12.88580049231956
C 2.84487942216171 4.05709491756332 5.45378726554322
H 2.83627796955500 3.21830090705531 6.16529770152428
H 3.55037583907421 3.82729359534612 4.64025596832862
H 1.83983733109407 4.14924017696832 5.02591926877620
C 0.34012259057618 8.13176847269520 6.36413411582413
H 0.44569522948069 8.66133166926834 7.32200839465404
H -0.45432962720574 8.62750038167403 5.78525202646739
H 1.28422010751190 8.23849189111433 5.81787348716996
C -1.22690172549083 9.08752797269804 10.25251155828671
H -0.61422349269907 9.14749151136880 9.34296047623127
H -1.27479083134610 10.10440586487690 10.67795232777752
H -2.24560712109946 8.80945016596691 9.94964436095249
C -0.73545353568517 5.77246008048269 14.17826564006537
H -1.79239406959880 5.47789700251972 14.19500443584519
H -0.52105129574696 6.29756924887824 15.12329496168652
H -0.13597979125712 4.85044491074410 14.16510518139443
C 1.59950339164682 0.45171220279317 11.16687449084645
H 1.20947390067496 1.17387767339996 11.89804478731716
H 1.90931206415848 -0.45238309019890 11.71650409123056
H 0.76393721349177 0.17011993670932 10.51186411436208
C 1.88046670533821 8.44616458747323 10.64311066333887
H 2.72055030272211 7.74349301137381 10.54407044756487
H 2.26340718091786 9.36522414764207 11.11637809595848
H 1.55408483087642 8.70865376761276 9.62790454258666
C 2.18557462260229 6.43587631697513 13.10568626171962
H 2.04386632400244 5.42970544040294 13.52338964048125
H 2.59228485837925 7.07329460084488 13.90901161735116
H 2.95049377355812 6.36132771408902 12.32005481438339

[{(IPh)Ni}$_2$(P$_4$C$_4$*t*Bu$_4$)] (4′)

Ni 3.01632642393276 3.43246857635610 6.29094153032754
Ni 2.68075027781760 1.09057898862293 5.79884405303595
P 1.52840143767394 2.61905788441786 4.80880981675818
P 3.85461401101610 1.96200011148561 7.60269035519875
P 4.63489293644233 2.49952089154792 5.10438019636439
P 3.44236846320267 1.15561671471305 3.71487941433360
N 1.85577396382875 -1.73101533807317 5.51263390666058
N 3.49007700768805 6.22063426260409 6.55574376269967
N 1.67702895781299 5.78665104526605 7.64455749915401
N 1.78775392092414 -1.12643009458249 7.57747495143716
C 5.76090195651211 5.35337215844487 6.53793102346023
C 2.08300358732189 -0.63763367828343 6.32109602567827
C 4.72577085544476 6.00576347009574 5.86490502548695
C 2.64279727318680 5.17764733022393 6.86108275086206
C 1.86180791241160 -1.69690115910634 4.08194379690785
C 1.77554429530614 -0.33876617249258 8.76675552204191
C 0.56270361960383 5.13585640167193 8.24218975356323
C 2.45609965255854 -0.78813655969229 9.89959930927237
C -0.13545307487390 4.14405685507091 7.54692267603553
C 6.05449307605977 6.11675110872412 3.86121111978215
H 6.16165529988276 6.39853898370248 2.81360490461266
C 7.09745552756293 5.46924464658505 4.52542679027462
C 4.86064098587974 6.39112344848550 4.53400548941189
C 2.75589909227605 -2.49212904465797 3.36885466639400

C	0.96330875920306	-0.85215693050364	3.42595895256986
C	5.93419821899384	1.48516663737470	5.97920939214536
C	1.09870113942474	0.88255408383004	8.77204410155619
C	6.95246591100953	5.09294599488842	5.86475924780237
H	7.75897128320341	4.57304904782137	6.38017283360437
C	1.14611020900141	1.68328040311819	9.91106044304580
H	0.64833986797654	2.65128817406544	9.90534770005157
C	0.14869155498911	5.51932988008148	9.52432968675010
C	1.43354889975622	-2.47184884826530	7.54577047668726
H	1.14294011189590	-3.01149202842705	8.43798526408978
C	-1.68765131091249	3.94274353034347	9.40084503747653
C	2.88976103598542	2.49708731338209	2.54636014256972
C	1.84327525250141	1.25404438248518	11.04305464147405
C	5.63903337454157	1.51384275223367	7.31611335652159
C	1.47908014403398	-2.85402556274652	6.24197181931753
H	1.24404986621320	-3.79637930742484	5.76365659501690
C	2.48746057820332	0.01448045580276	11.04107322843493
H	3.03916366802254	-0.32049066591891	11.91996740563085
C	1.92338114643244	3.26825527228169	3.13225423487396
C	-1.25606813360359	3.55413603383649	8.12884144250278
H	-1.79609698821488	2.78368564951453	7.57693970714733
C	1.93811734014174	7.15274830190235	7.80954985287875
H	1.27103143492746	7.80456167005487	8.35784415505949
C	6.39470686038974	1.14950156759125	8.60729974740226
C	2.74927145991962	-2.44305400323217	1.97239401259347
H	3.45381782402897	-3.05361055738407	1.40705211147732
C	3.07532401732770	7.42268249197629	7.11923199874626
H	3.62154609109734	8.34626745281067	6.97516011345681
C	7.10609881013226	0.89748704320193	5.17386807831703
C	-0.97812994435696	4.92493155907385	10.09650072331833
H	-1.29212464540313	5.22354605239512	11.09738688104754
C	0.97039813107866	-0.80100113052941	2.03334476170173
H	0.28703375433560	-0.12645230411608	1.51760916197239
C	1.85988928097439	-1.59815923666879	1.30586564253935
C	3.60787133540705	2.54545877457229	1.18584947525159
C	1.08401548734969	4.47851951924334	2.67637881527819
C	8.36356110616060	1.79067466637035	5.26076892106738
H	8.14552314180675	2.77259236561120	4.81956808724480
H	9.18521417743492	1.33509508850743	4.68519581892668
H	8.70813631352655	1.94697347387544	6.28596131403645
C	7.92150091305860	1.31861064170121	8.55821666339448
H	8.41137050193609	0.64480730668646	7.84895977713363
H	8.33978068985808	1.10661479530624	9.55417772546343
H	8.19077425756733	2.35217390724056	8.29771995255556
C	7.40631331821526	-0.54859510454549	5.61389849181833
H	7.75223175099292	-0.61836814509169	6.64989505615938
H	8.18570373997016	-0.98443206115305	4.96931326035822
H	6.49879880525345	-1.16217898395799	5.52120917606168
C	4.34571416642424	1.21903467782994	0.90643024516838
H	5.12867772870615	1.01818879109455	1.64755324806118
H	4.82731903275394	1.27862251924325	-0.08167768168386
H	3.65670418093492	0.36444539544261	0.90922567687099
C	6.75416212115410	0.82709379769301	3.67662759552473
H	5.90670391735582	0.15346164491805	3.49180793439108
H	7.62334963624345	0.45961736061212	3.11040778816558
H	6.49452372920720	1.82126559740426	3.28274468834165

C	0.47291704068371	5.19194461251019	3.90217627039755
H	-0.16628725680980	4.51380045513545	4.48712702821011
H	-0.15629243838094	6.02851337460460	3.56371198265431
H	1.25240281327540	5.58289241987654	4.56865258876777
C	4.68145951837437	3.65709492012922	1.22582675046918
H	4.23954653284984	4.65189474468214	1.34001199958083
H	5.27993292803177	3.64361360609459	0.30089134286396
H	5.35493274088035	3.49863388994129	2.08022590069689
C	5.90825361503784	2.07520472459009	9.74860467260616
H	6.12824123948826	3.12817158884675	9.51880765831901
H	6.42138009857995	1.81043073011874	10.68565477727057
H	4.82450914709575	1.98235387377693	9.91140726228822
C	6.03795801890783	-0.30256010645204	8.99385257841635
H	4.94783434362420	-0.40563719744171	9.07795098870941
H	6.48911651490096	-0.56387025482845	9.96465978592310
H	6.39069790813898	-1.01865759886152	8.24054297302612
C	-0.09406425331394	3.97400242305350	1.81344440551426
H	0.24902530125378	3.46438190721376	0.90618329975610
H	-0.73900309302242	4.81647117032636	1.51692873931839
H	-0.70157688253700	3.26258341339089	2.39178353740162
C	1.89205379807763	5.55783785985158	1.93299704657968
H	2.74824895364315	5.87246335568090	2.54485644093171
H	1.25543918830504	6.43836151560166	1.75594501657717
H	2.27422906861831	5.22948240783538	0.96227386979208
C	2.64591374628720	2.73864272950722	-0.00190240435813
H	1.91181148443373	1.92004903837291	-0.03004359577293
H	3.21178742184501	2.71909741853043	-0.94619237697457
H	2.09540041216912	3.68250968185719	0.03315519482890
H	0.58479359252811	1.21437818311904	7.87073858558700
H	2.99328395922357	-1.73647903131812	9.86844626659925
H	1.88834721296580	1.88979207351320	11.92800921206480
H	3.46825371020189	-3.11860254955190	3.90635114963448
H	0.30111915976859	-0.21641730629653	4.01196115786402
H	1.86556824973892	-1.55315309816144	0.21623196836962
H	8.02457375476179	5.24771643291713	3.99524121159089
H	0.21435290132974	3.83245034090061	6.56285338342926
H	-2.56321634372452	3.47535602525463	9.85214456186841
H	0.71938174727345	6.26418271196777	10.07954611352396
H	4.02618803425353	6.87705057176997	4.02890790203639
H	5.60583359720131	5.02559690735798	7.56476543451540

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