Supplementary Information

Facile Synthesis of Pd(II) and Ni(II) Pincer Carbene Complexes by the Double C-H Bond Activation of a New Hexahydropyrimidine-Based Bis(phosphine): Catalysis of C–N Couplings.

Vasudevan Subramaniyan, Bidisa Dutta, Anbarasu Govindaraj and Ganesan Mani*[a]

[a] Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur, India 721 302. Fax: 91 3222 282252; Tel: 91 3222 282320; E-mail: gmani@chem.iitkgp.ac.in

1. **NMR: ^{1}H, ^{13}C, and ^{31}P**
2. **ATR**
3. **X-ray structures and refinement data**
4. **DFT: Coordinates of optimized structures**

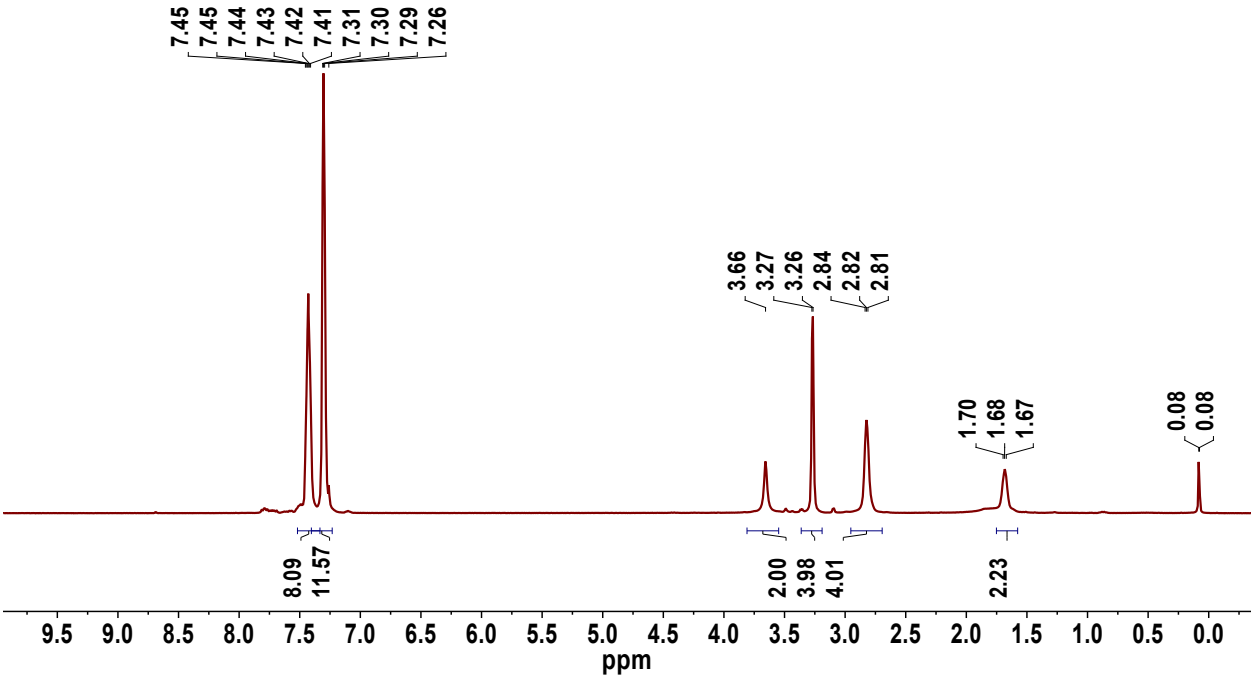


Figure S1. ^{1}H NMR (400 MHz) spectrum of 1,3-bis(diphenylphosphanylmethyl)hexahydropyrimidine **1** in $CDCl_3$.

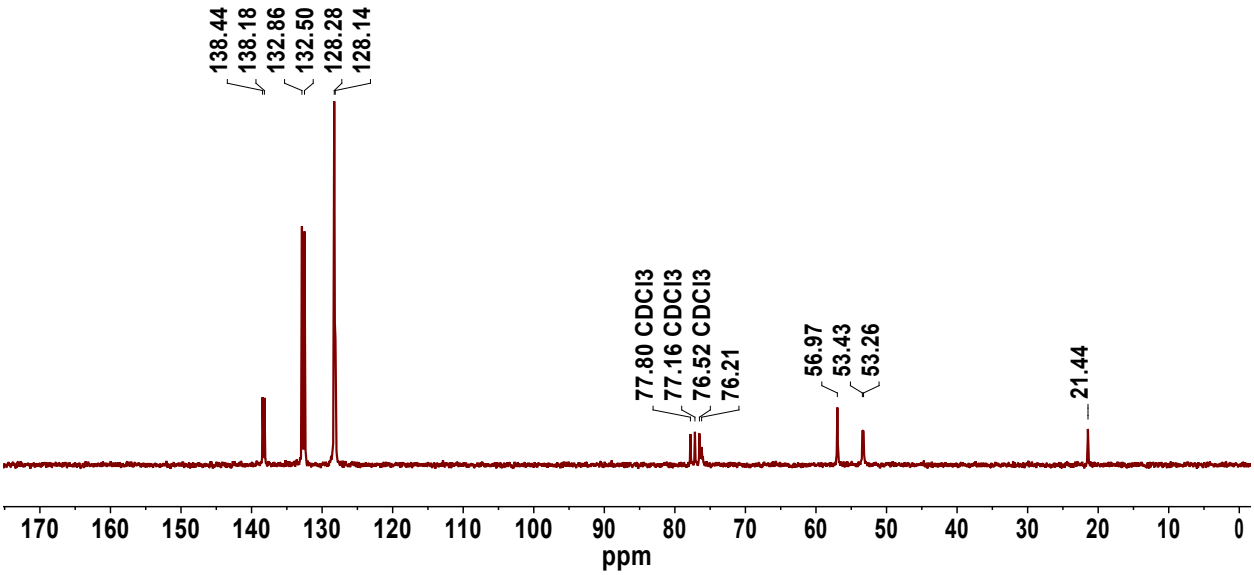


Figure S2. ^{13}C NMR (100.6 MHz) spectrum of 1,3-bis(diphenylphosphanylmethyl)hexahydropyrimidine **1** in $CDCl_3$.

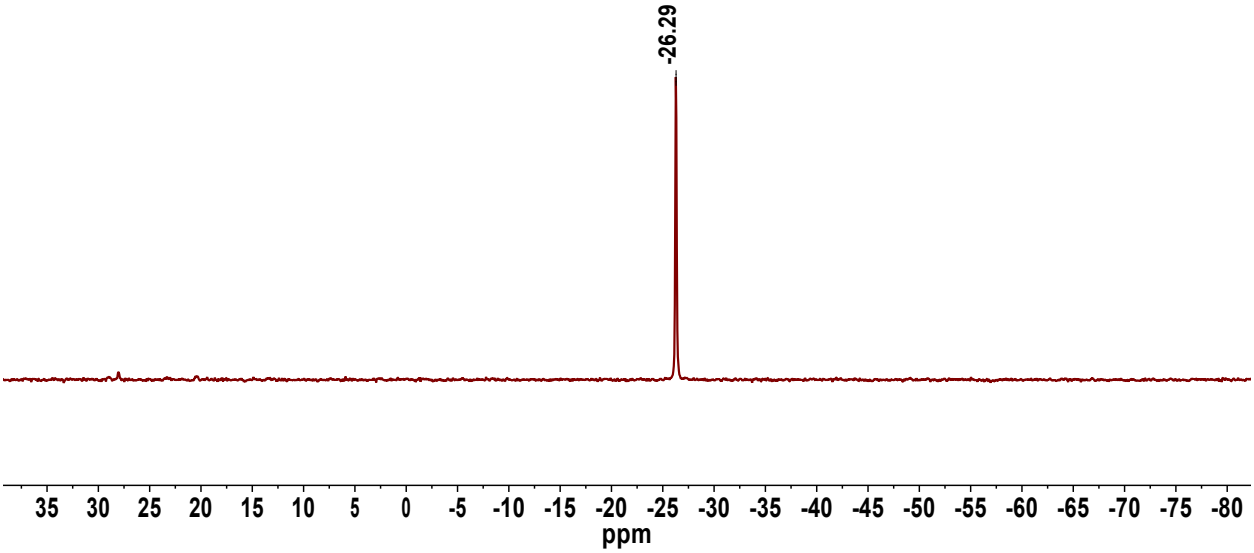


Figure S3. ^{31}P NMR (161.9 MHz) spectrum of 1,3-bis(diphenylphosphanylmethyl)hexahydropyrimidine **1** in $CDCl_3$.

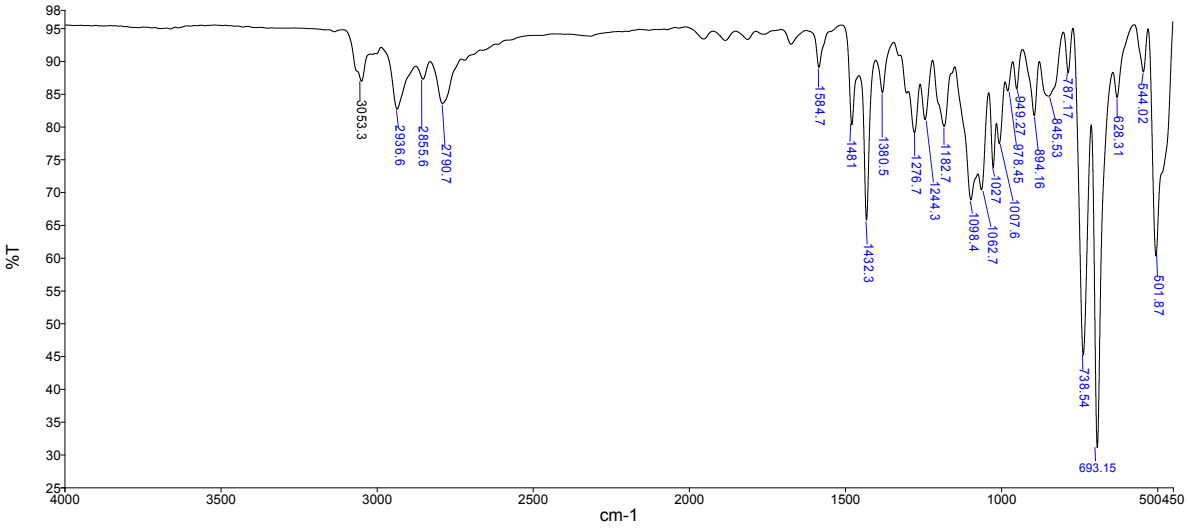


Figure S4. FTIR-ATR spectrum of 1,3-bis(diphenylphosphanylmethyl)hexahydropyrimidine **1**.

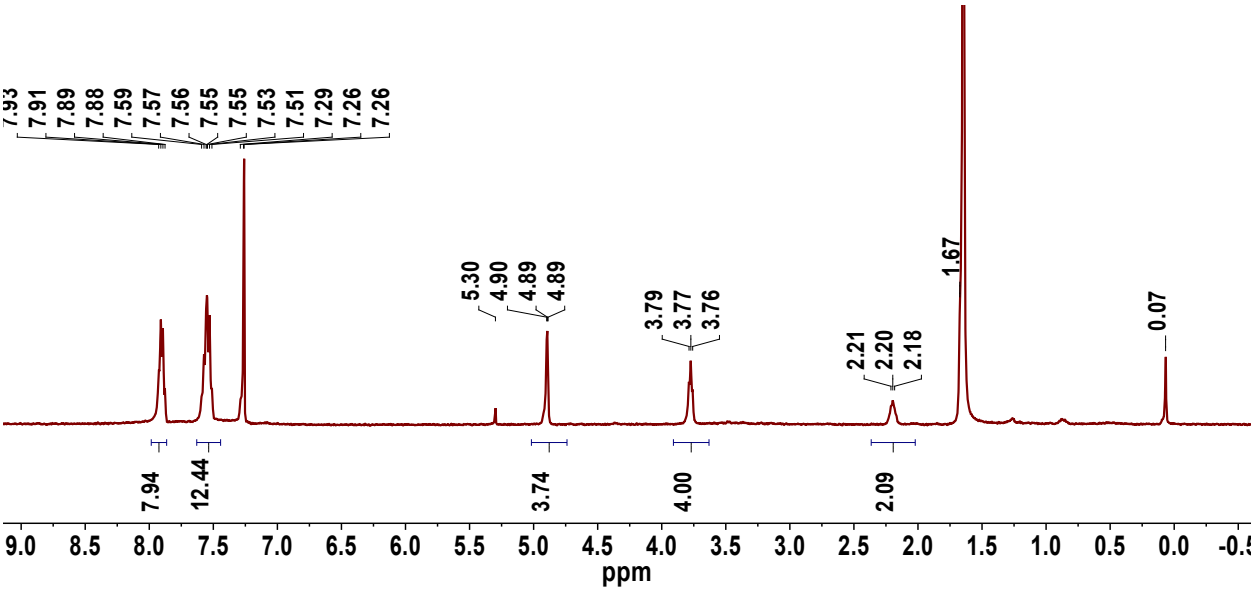


Figure S5. ^{1}H NMR (400 MHz) spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **2a** in CDCl$_3$.

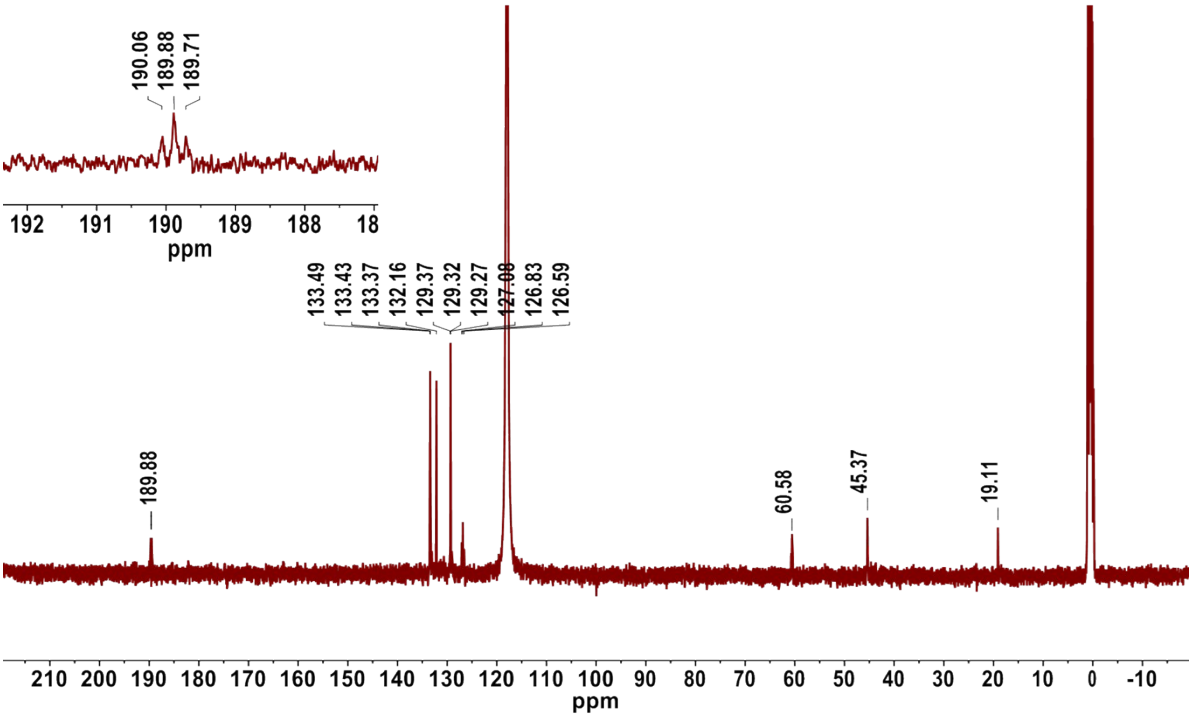


Figure S6. ^{13}C NMR (100.6 MHz) spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **2a** in CD$_3$CN.

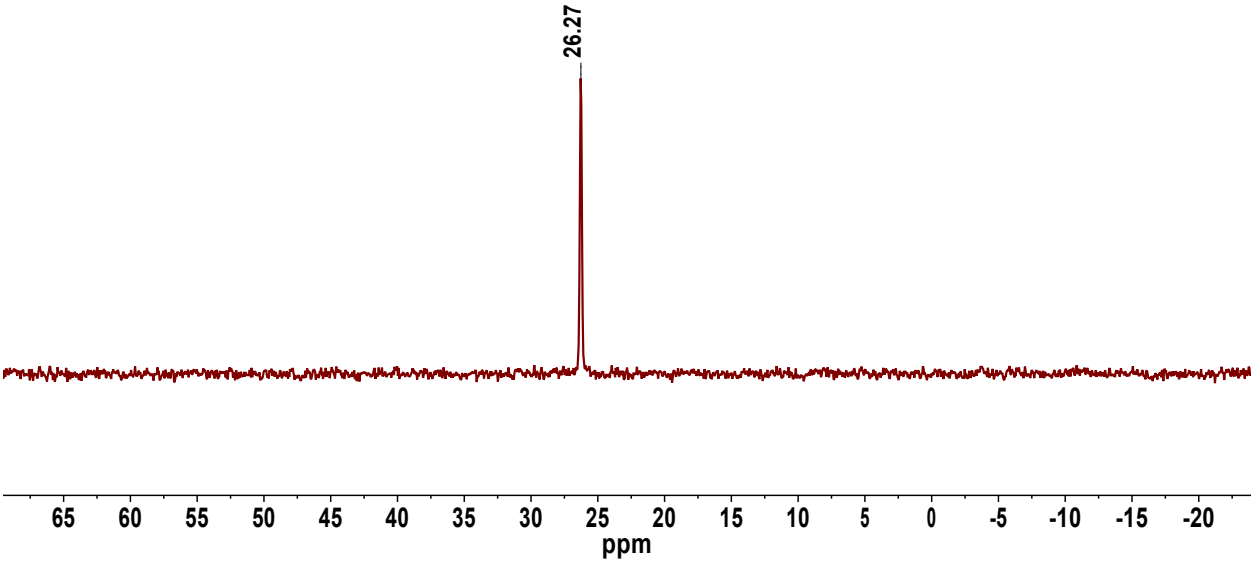


Figure S7. ^{31}P NMR (161.9 MHz) spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **2a** in CDCl$_3$.

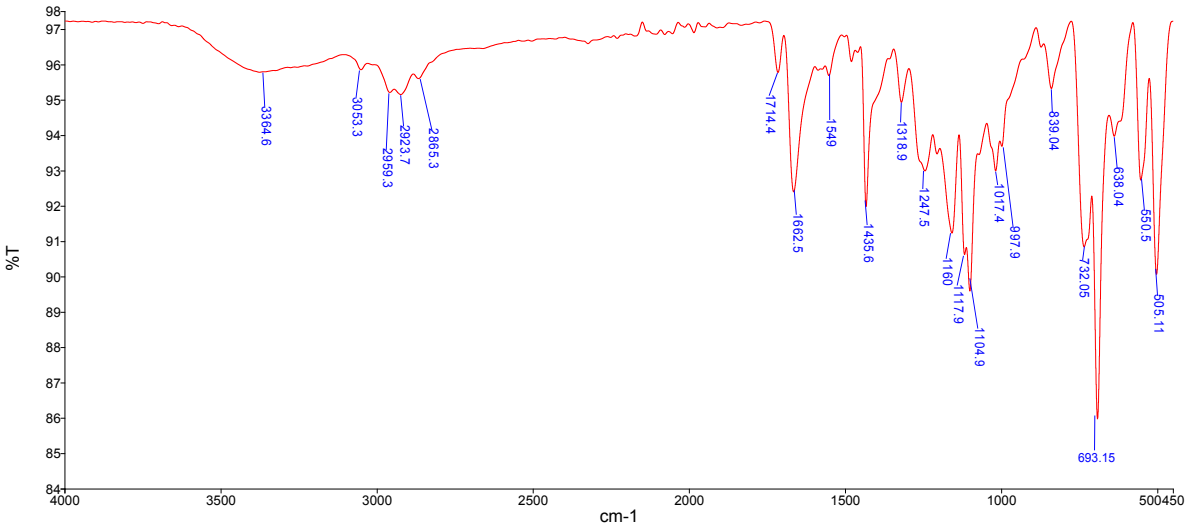


Figure S8. FTIR-ATR spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **2a**.

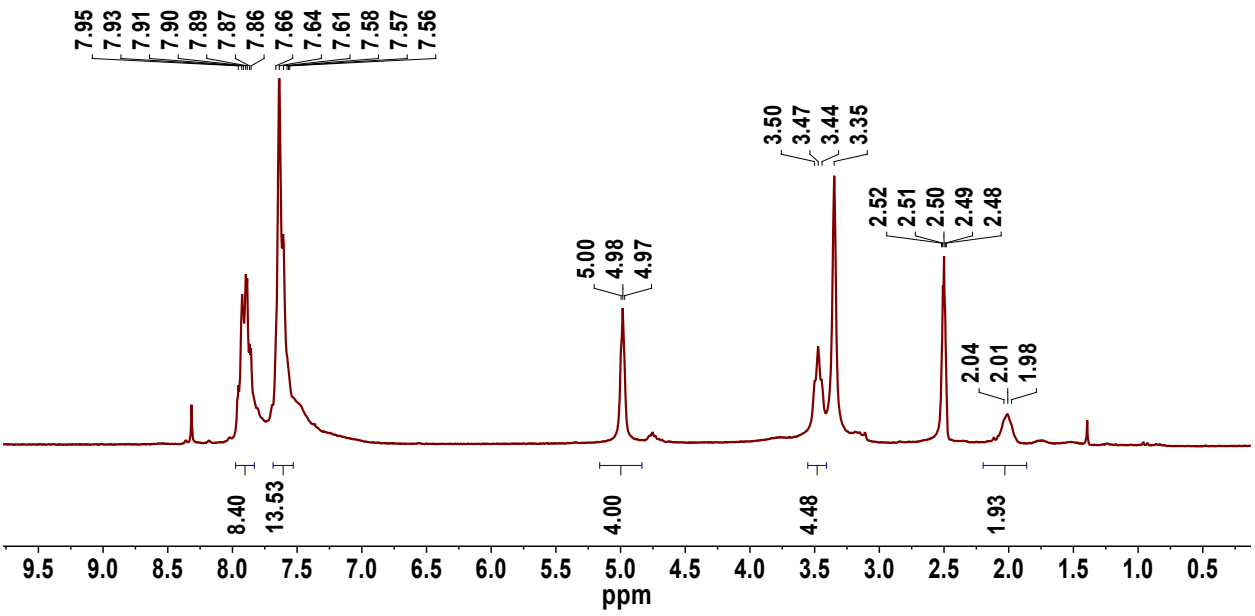


Figure S9. ^{1}H NMR (400 MHz) spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **2b** in DMSO-d_6.

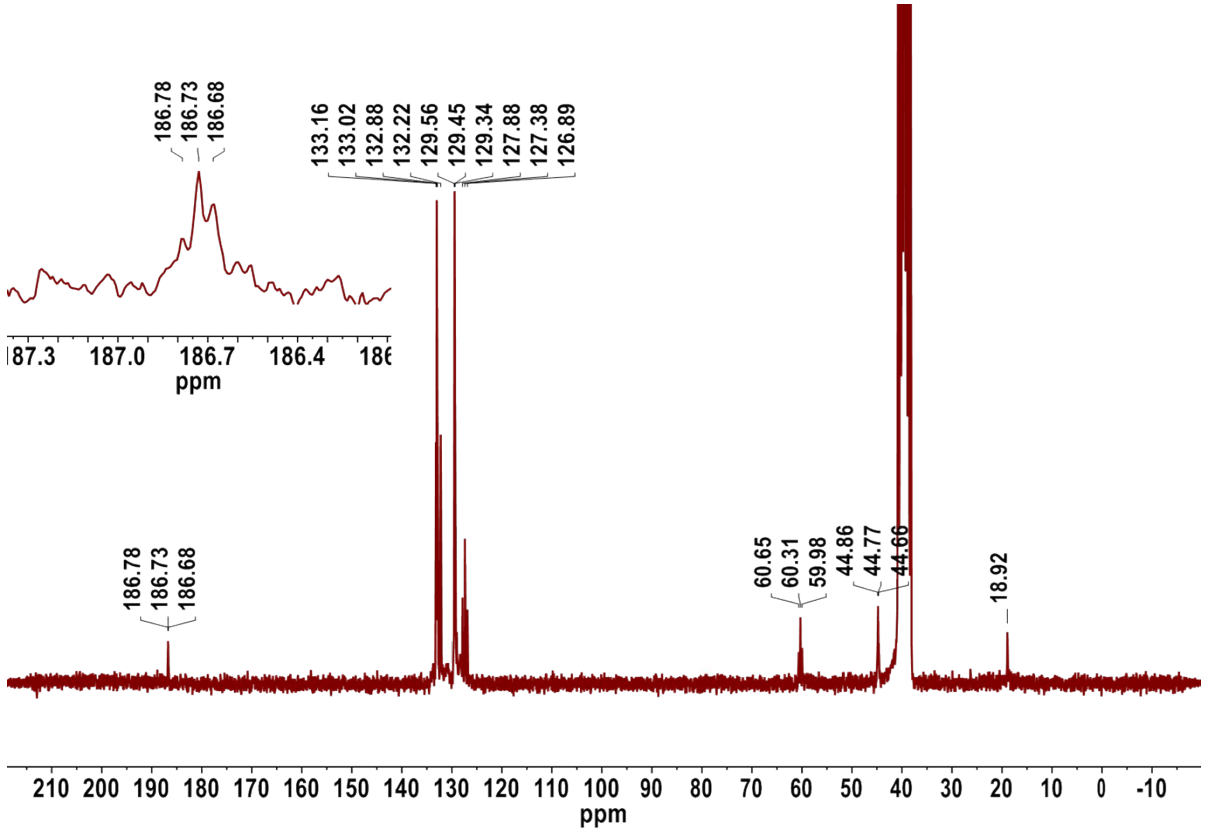


Figure S10. ^{13}C NMR (100.6 MHz) spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **2b** in DMSO-d_6.

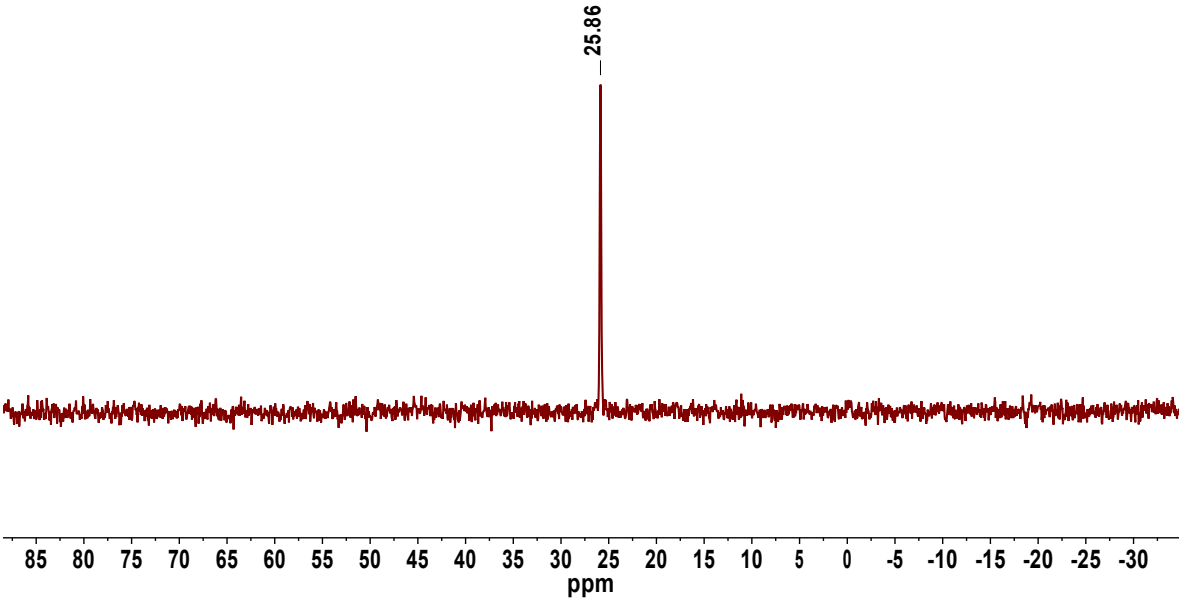


Figure S11. ^{31}P NMR (161.9 MHz) spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **2b**, CDCl$_3$.

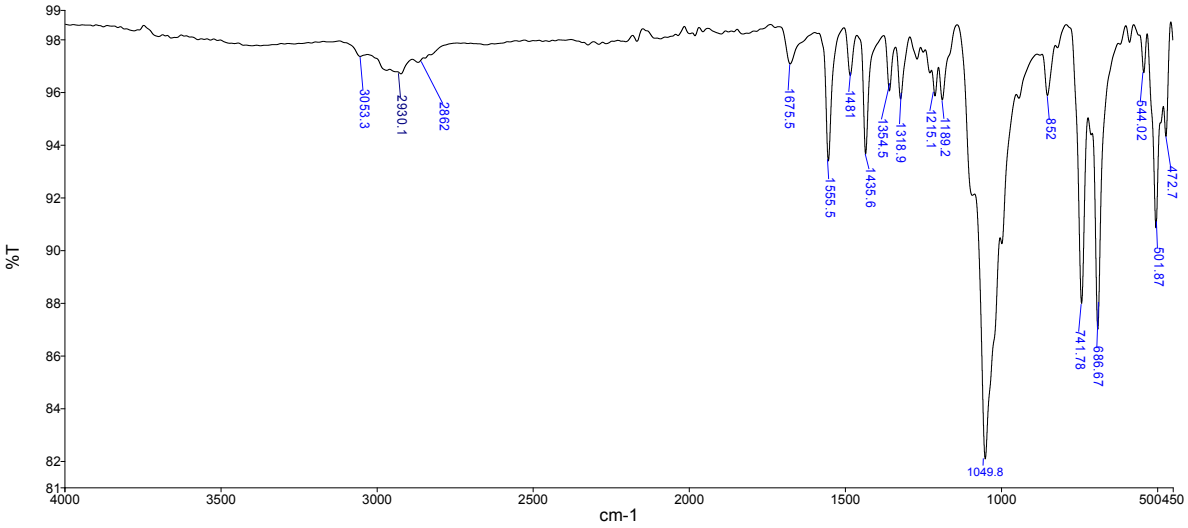


Figure S12. FTIR-ATR spectrum of [PdCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **2b**.

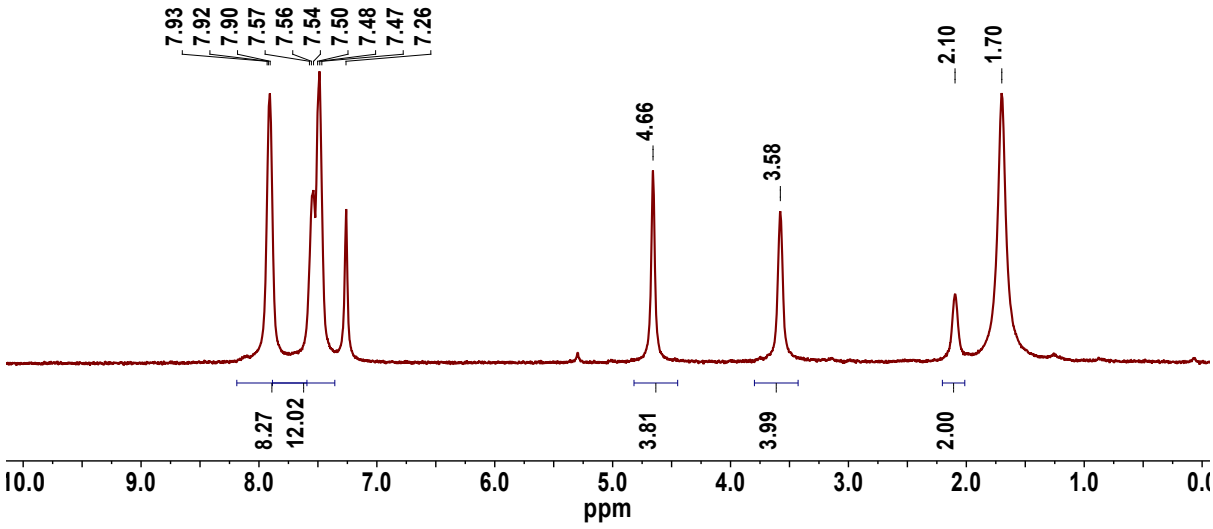


Figure S13. ^{1}H NMR (400 MHz) spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **3a** in CDCl$_3$.

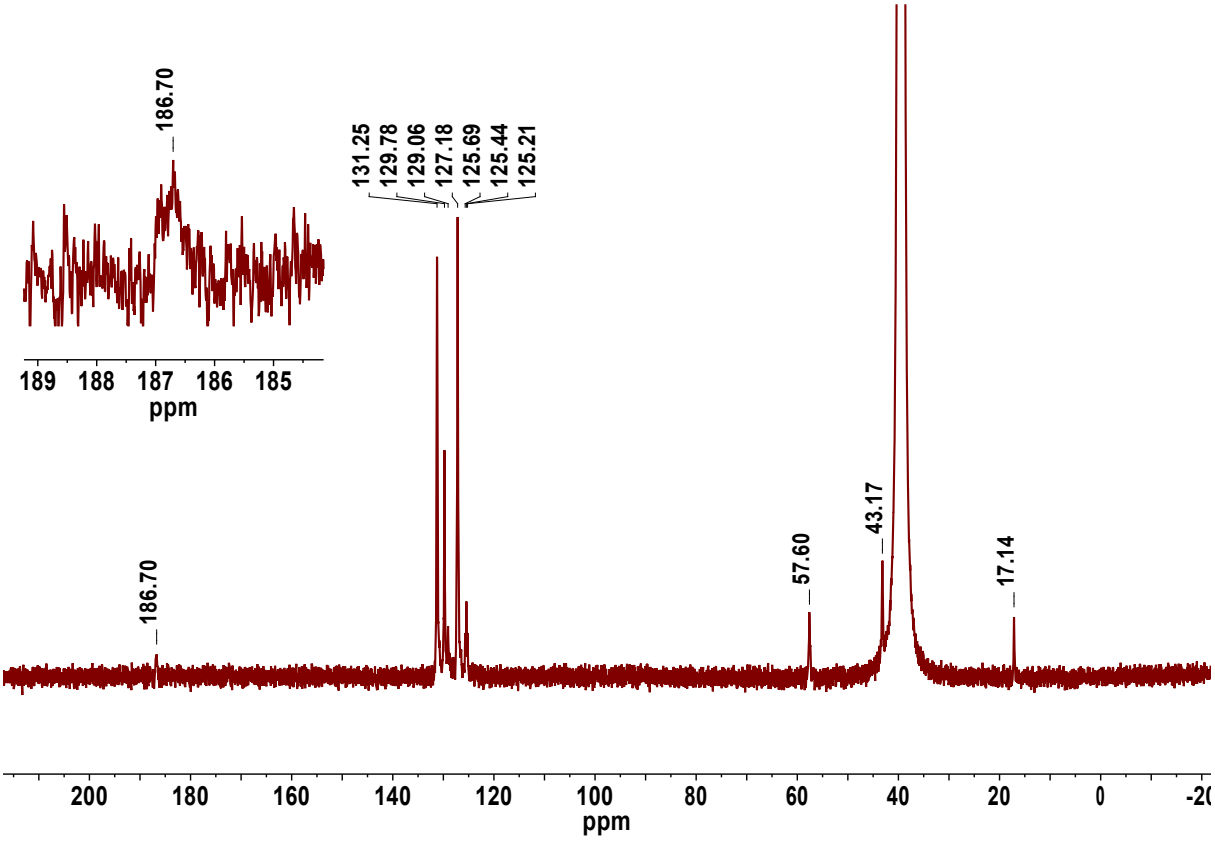


Figure S14. ^{13}C NMR (100.6 MHz) spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **3a** in DMSO-d_6.

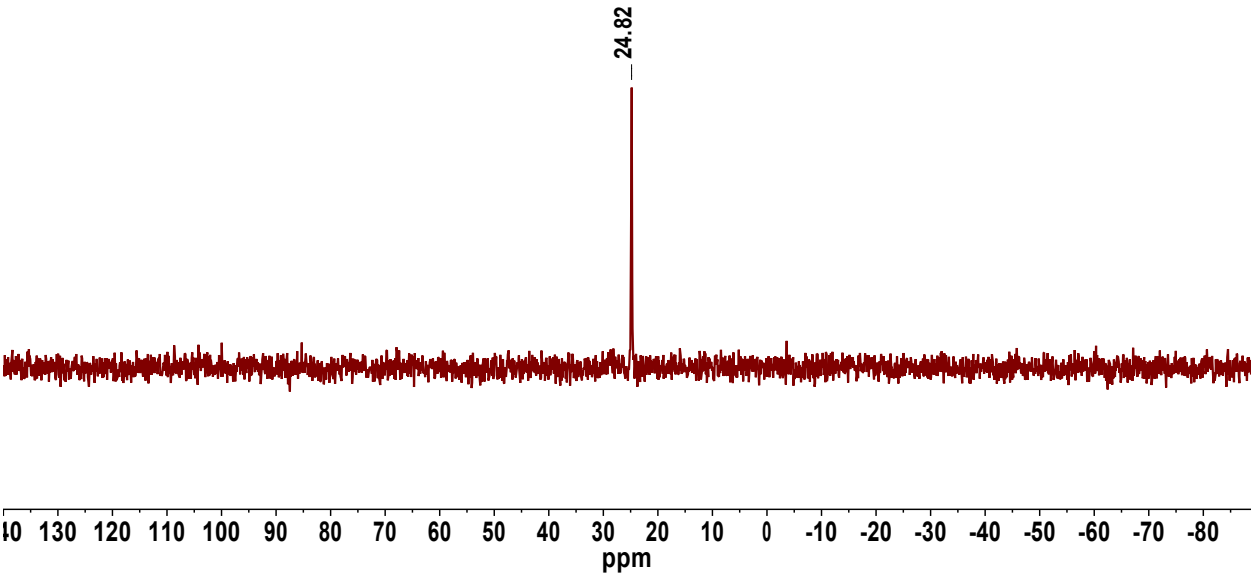


Figure S15. ^{31}P NMR (161.9 MHz) spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **3a** in CDCl$_3$.

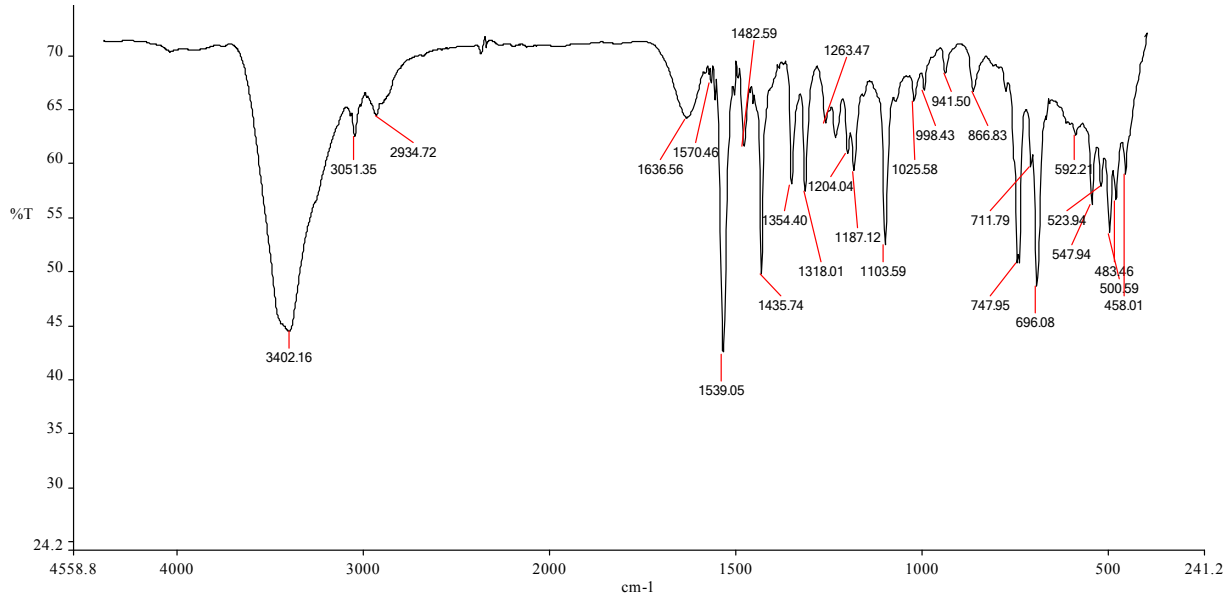


Figure S16. FTIR spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]Cl, **3a**.

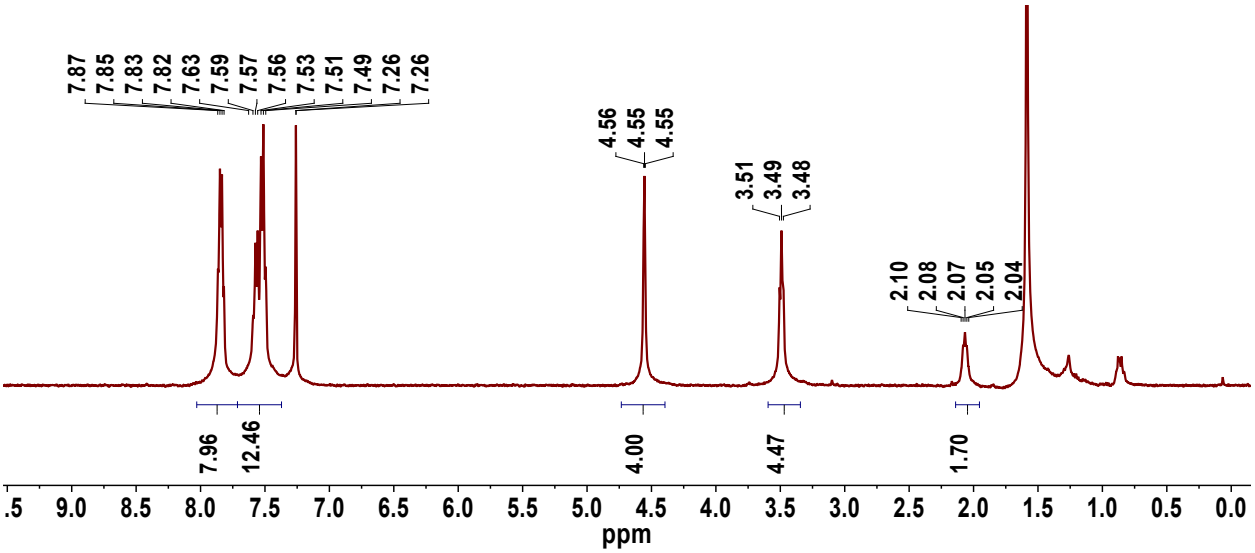


Figure S17. ^{1}H NMR (400 MHz) spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **3b** in CDCl$_3$.

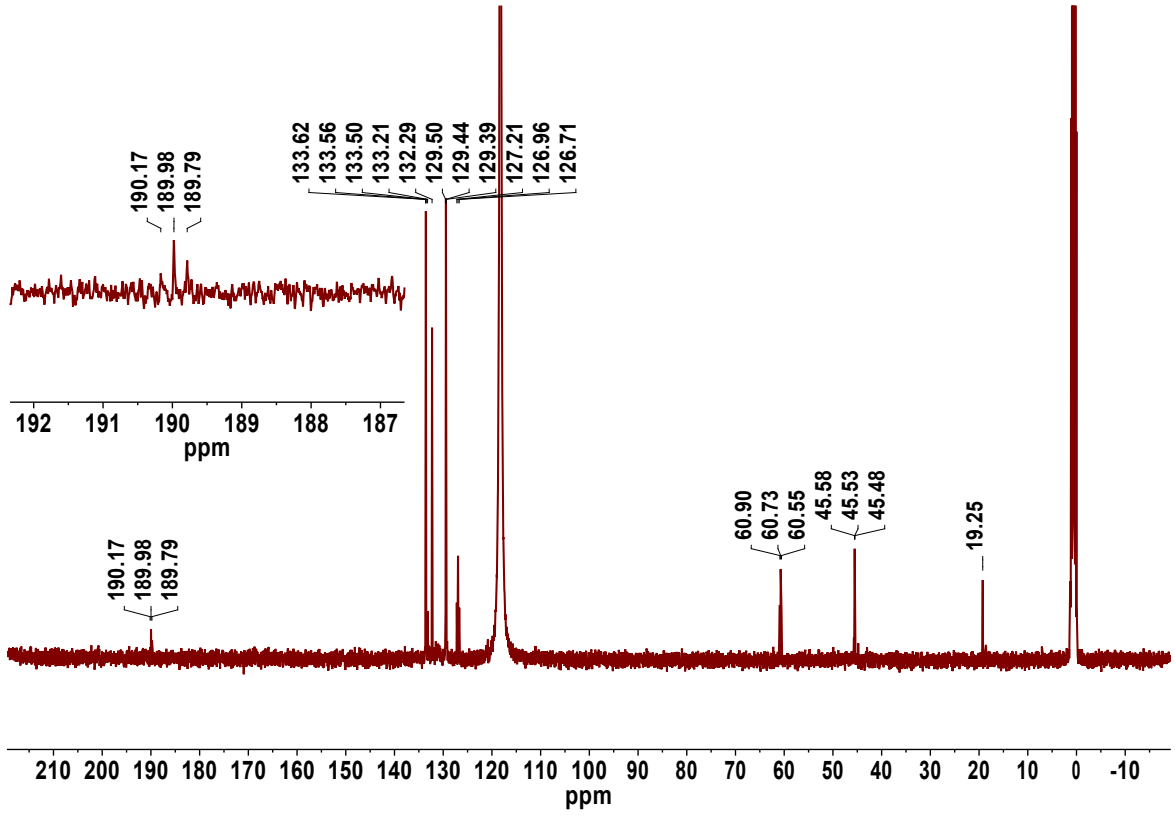


Figure S18. ^{13}C NMR (100.6 MHz) spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **3b** in CD$_3$CN.

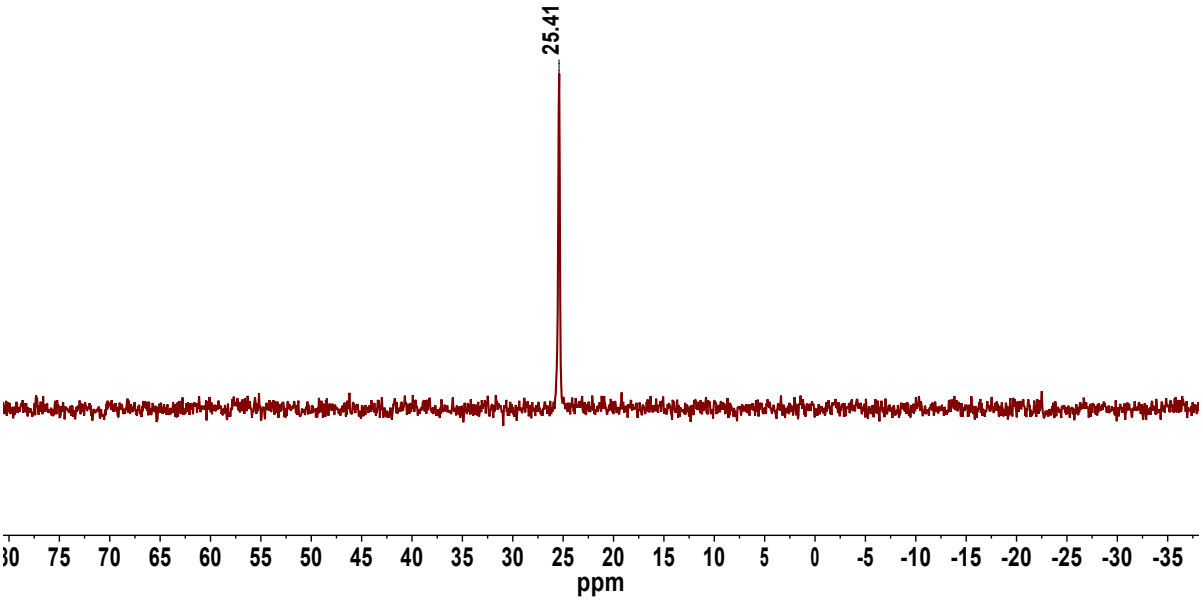


Figure S19. ^{31}P NMR (161.9 MHz) spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **3b** in CDCl$_3$.

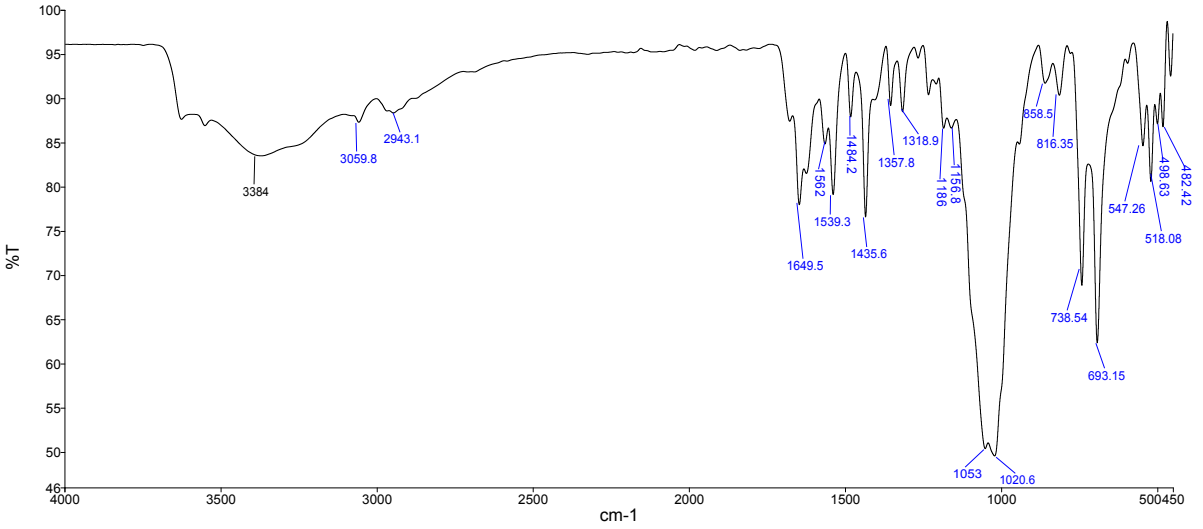


Figure S20. FTIR spectrum of [NiCl{C(NCH$_2$PPh$_2$)$_2$(CH$_2$)$_3$-κ^3*P,C,P*}]BF$_4$, **3b** recorded in ATR mode.

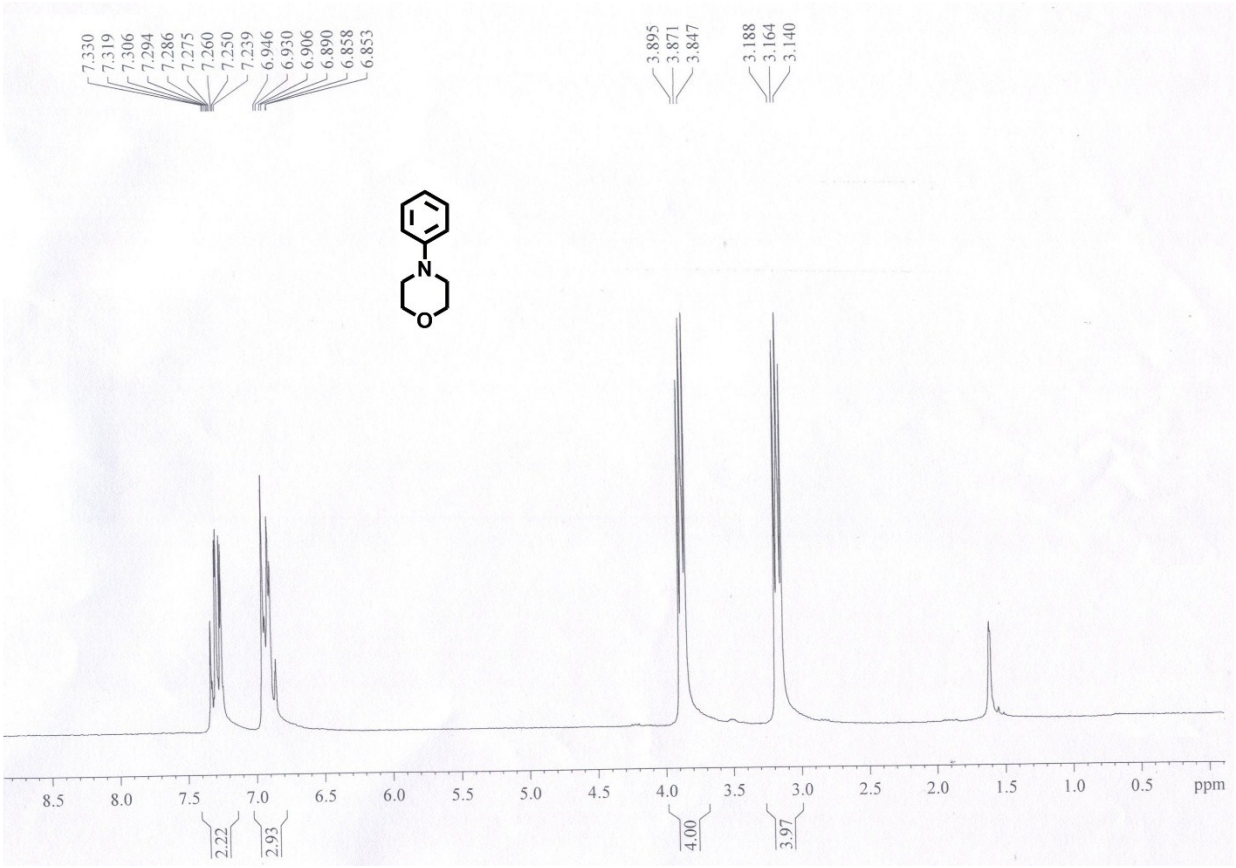


Figure S21. ^{1}H NMR (200 MHz) spectrum of isolated 4-phenyl morpholine (Table 1: entry 9) in $CDCl_3$.

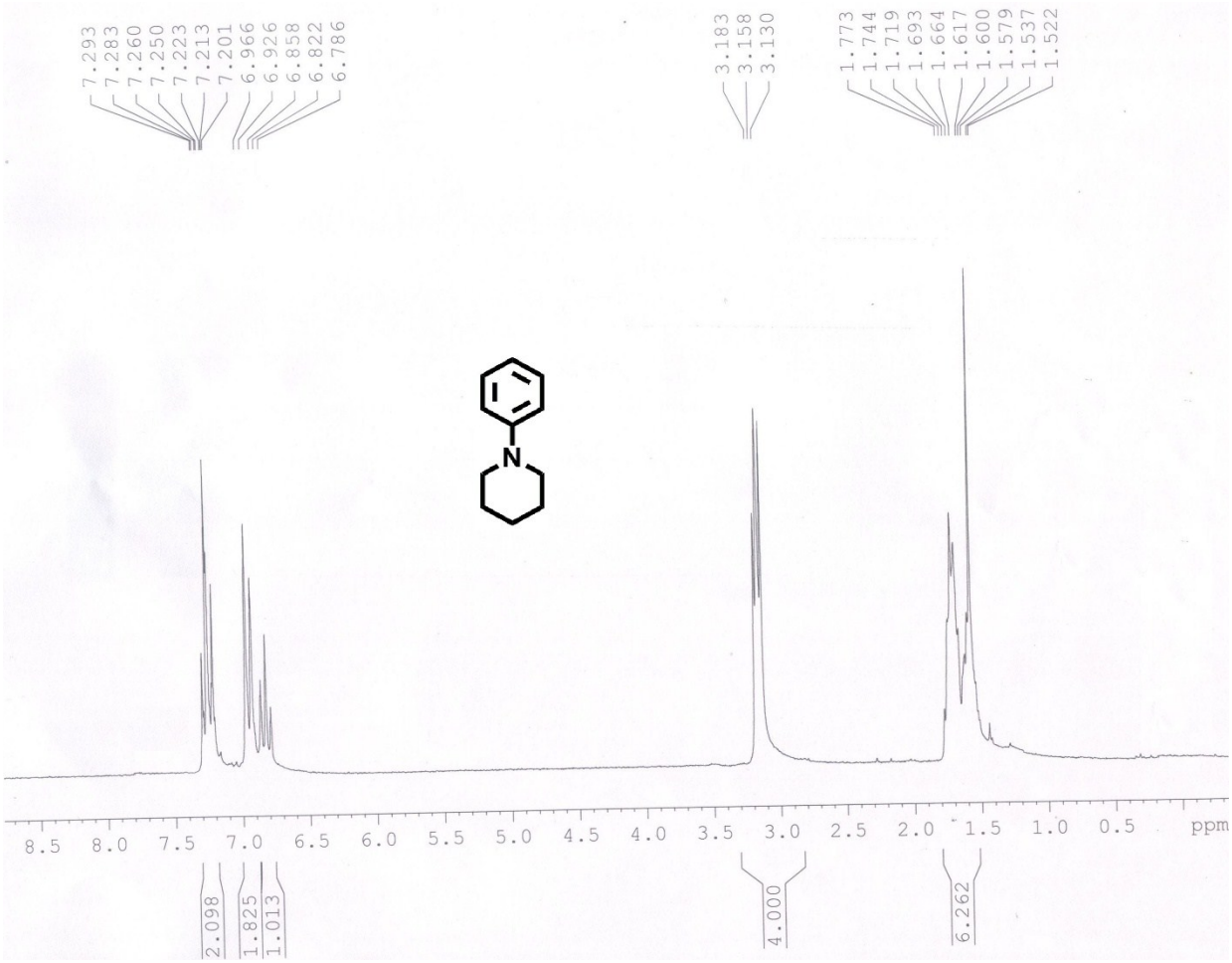


Figure S22. ^{1}H NMR (200 MHz) spectrum of isolated 1-phenylpiperidine (**table 2**: entry 1) in $CDCl_3$.

Figure S23. ^{1}H NMR (200 MHz) spectrum of isolated 1-phenylpyrrolidine (**table 2**: entry 2) in $CDCl_3$.

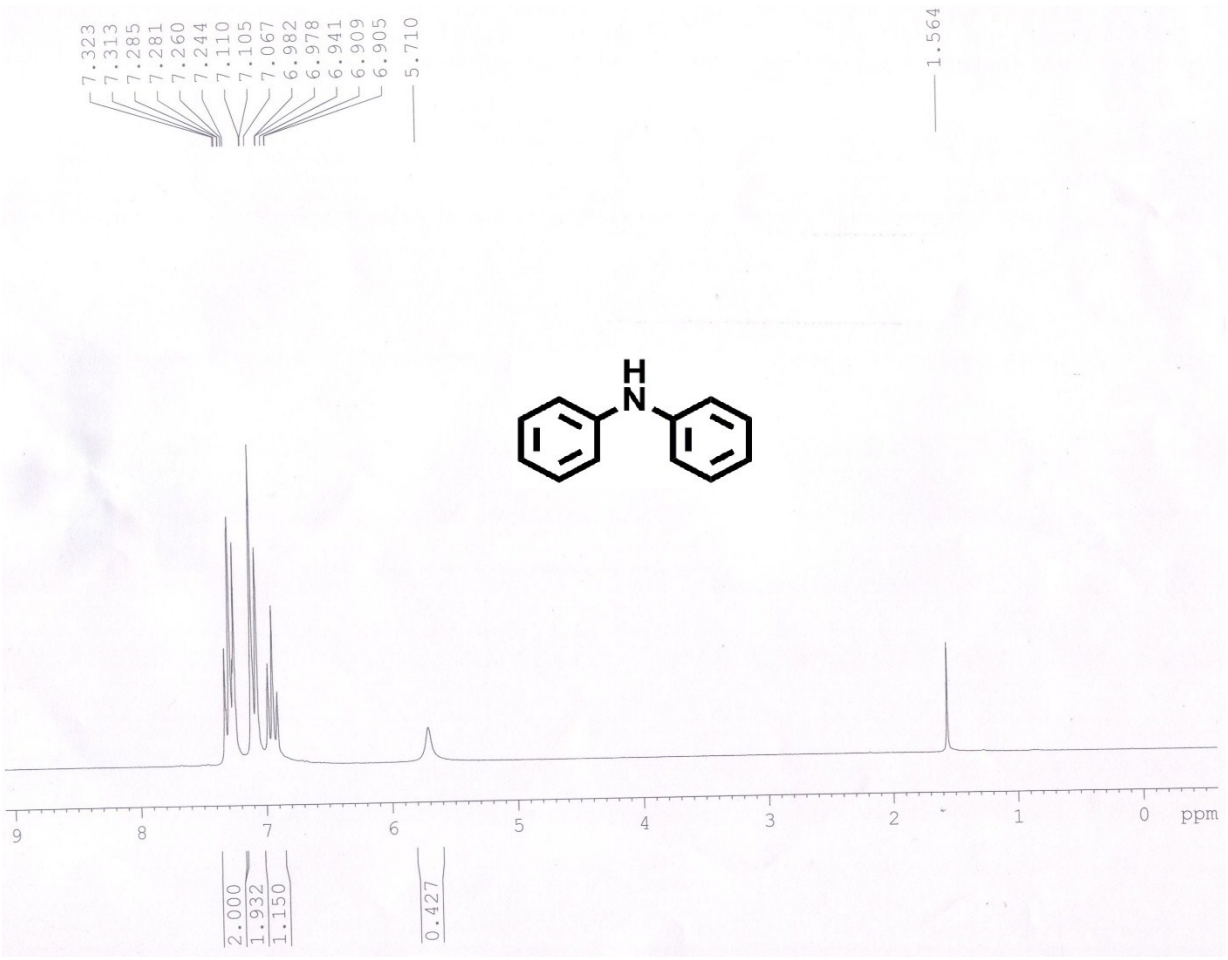


Figure S24. ^{1}H NMR (200 MHz) spectrum of isolated diphenylamine (**table 2**: entry 3) in $CDCl_3$.

X-ray crystallography

Table 1. Crystallographic data for 2a, 2b, 3a and 3b

	2a·CH_2Cl_2	**2b**	**3a**·$(H_2O)_{1.5}$	**3b**
Empirical formula	$C_{31}H_{32}Cl_4N_2P_2Pd$	$C_{30}H_{30}B_{0.7}Cl_{1.3}F_{2.8}N_2P_2Pd$	$C_{30}H_{33}Cl_2N_2NiO_{1.5}P_2$	$C_{30}H_{30}BClF_4N_2NiP_2$
Formula weight	742.72	693.75	637.13	661.47
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	293.15(2)	100(2)	100(2)	297.75(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	C2/c	P-1	C2/c	*P*-1
a/Å	36.962(4)	9.4114(14)	28.845(3)	8.974(3)
b/Å	10.2290(11)	12.154(2)	9.0434(10)	12.154(3)
c/Å	16.7982(18)	15.368(2)	23.141(3)	15.103(4)
α/degree	90.00	70.883(8)	90	95.040(18)
β/degree	99.294(5)	88.024(8)	101.366(3)	106.082(18)
γ/degree	90.00	71.058(7)	90	103.084(17)
Volume (Å^3)	6267.8(12)	1566.0(4)	5918.2(11)	1521.5(8)
Z	8	2	8	2
D_{calcd}, g cm^{-3}	1.574	1.471	1.430	1.444
μ/mm^{-1}	1.060	0.845	0.973	0.879
F(000)	3008.0	702.0	2648.0	680.0
θ range (degree)	2.068 to 24.993	3.371 to 24.999	1.44 to 24.997	1.719 to 24.997
Limiting Indices	-43 ≤ h ≤ 35, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19	-11 ≤ h ≤ 11, -14 ≤ k ≤ 9, -18 ≤ l ≤ 18	-29 ≤ h ≤ 34, -10 ≤ k ≤ 10, -27 ≤ l ≤ 27	-10 ≤ h ≤ 10, -14 ≤ k ≤ 13, -17 ≤ l ≤ 17
Total/ unique no. of reflns	34963 / 5496	12684 / 5481	30717 / 5177	13262 / 5234
R_{int}	0.0656	0.0252	0.0651	0.0736
Data / restr./params.	5496/2/380	5481/44/406	5177/17/367	5234/11/411
GOF (F^2)	1.060	1.050	1.006	1.068
R1, *wR2*	0.0324, 0.0766	0.0370, 0.0962	0.0334, 0.0862	0.0710, 0.1477
R indices (all data) *R1*, *wR2*	0.0403, 0.0803	0.0493, 0.1021	0.0464, 0.0936	0.1295, 0.1760
Largest different peak and hole (e Å^{-3})	0.69, –0.81	0.74, -0.37	0.58/-0.33	0.73/-0.85

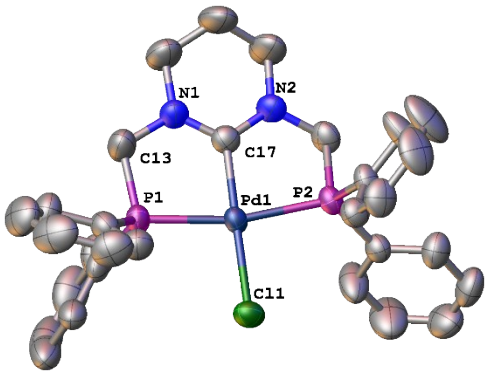


Figure S25. Crystal structure of **2b** (50% displacement ellipsoids). Hydrogen atoms and BF_4^- anion are omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–Pd1 2.2783(10), P2–Pd1 2.2727(10), Cl1–Pd1 2.3351(10), C17–Pd1 1.997(4), N1–C17 1.337(5), N2–C17 1.344(5), C17–Pd1–P2 83.49(12), C17–Pd1–P1 84.19(12), P2–Pd1–P1 167.48(4), C17–Pd1–Cl1 179.06(12), P2–Pd1–Cl1 95.61(4), P1–Pd1–Cl1 96.72(4).

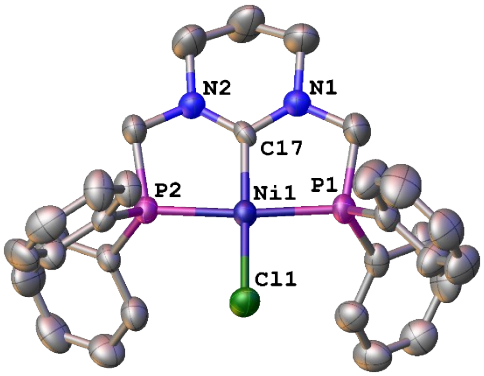


Figure S26. Crystal structure of 3**b** (50% displacement ellipsoids). Hydrogen atoms and BF_4^- anion are omitted for clarity. Selected bond lengths (Å) and bond angles (°): P1–Ni1 2.1678(19), P2–Ni1 2.1653(18), Cl1–Ni1 2.1985(19), C17–Ni1 1.905(6), N1–C17 1.346(7), N2–C17 1.348(7), C17–Ni1–P2 86.72(18), C17–Ni1–P1 86.10(18), P2–Ni1–P1 171.68(8), C17–Ni1–Cl1 175.28(17), P2–Ni1–Cl1 93.10(7), P1–Ni1–Cl1 94.40(7).

DFT: Coordinates of optimized structures

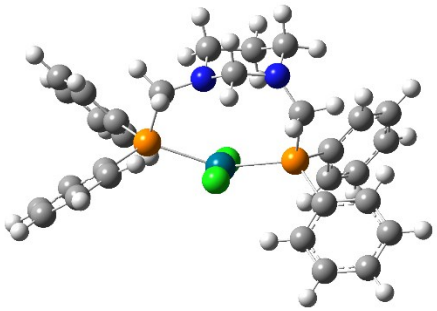


Figure S27. Optimized geometry of the hexahydropyrimidine based neutral coordination $PdCl_2$ complex (**A**) in scheme 3.

The coordinates of the optimized hexahydropyrimidine based neutral coordination $PdCl_2$ complex.

	Coordinates (Angstroms)		
Type	X	Y	Z
C	-0.08529400	-0.11508600	3.10957500
C	-1.57794700	-2.03521700	2.94849100
C	-0.57313800	-2.75661600	2.01518400
C	0.86250900	-2.23674200	2.25681000
H	0.15511100	-0.36778300	4.16353100
H	-0.02253000	0.96655600	2.97627500
H	-1.37669600	-2.32950300	3.99205800
H	-2.60411000	-2.33718800	2.71933500
H	-0.60754700	-3.83953700	2.20215300
H	-0.83863900	-2.58874200	0.96578200
H	1.23091800	-2.60019700	3.24085200
H	1.53138500	-2.63700900	1.48700900
C	2.16000800	-0.11002600	1.95338200
H	3.02162800	-0.65774900	2.36473100
H	2.15818800	0.89956100	2.37241900
N	0.88791200	-0.76339500	2.19888300
N	-1.45561800	-0.56570200	2.86182200
C	-2.37423000	0.23108100	2.09522200
H	-3.40985400	-0.00649500	2.36726800
H	-2.20256800	1.29213200	2.29714800
P	2.43855400	0.12586000	0.03530000
P	-2.34247600	0.22238200	0.10097200
C	-3.44142700	1.69535400	-0.32311600
C	-4.82126300	1.65760000	-0.01750800
C	-2.89957800	2.84108500	-0.94195100
C	-5.64520900	2.75771400	-0.31692400
H	-5.26420300	0.77039000	0.42829400
C	-3.72918300	3.93678600	-1.24794100
H	-1.83941900	2.88413000	-1.16686700
C	-5.10073800	3.90079000	-0.93393900
H	-6.70535000	2.71773200	-0.07771200
H	-3.30114600	4.81377200	-1.72717900

H	-5.73871800	4.74920200	-1.17078500
C	-3.42271500	-1.21054600	-0.47554600
C	-3.44886600	-1.51732800	-1.85424700
C	-4.25256800	-1.93987600	0.40253600
C	-4.29149600	-2.53126900	-2.34204800
H	-2.79923100	-0.98365200	-2.53976800
C	-5.09244300	-2.95953100	-0.08579500
H	-4.26997600	-1.72296200	1.46621400
C	-5.11497900	-3.25778700	-1.46012500
H	-4.29561100	-2.75793300	-3.40518700
H	-5.72585600	-3.51137500	0.60493000
H	-5.76243200	-4.04530000	-1.83867000
C	3.64908200	1.56132700	-0.15020900
C	4.68603900	1.48681000	-1.10867700
C	3.50372200	2.74203900	0.61293400
C	5.57030900	2.56564400	-1.28877100
H	4.81082600	0.59247700	-1.71224800
C	4.39709800	3.81506000	0.43651800
H	2.68031600	2.84779200	1.31021400
C	5.43299600	3.73212000	-0.51250400
H	6.36086100	2.49283200	-2.03190700
H	4.27195500	4.71671600	1.03115100
H	6.11806400	4.56542600	-0.65026400
C	3.52566600	-1.33595300	-0.45631700
C	4.67219900	-1.64134100	0.31522500
C	3.23628400	-2.10931000	-1.59844900
C	5.50789500	-2.71302600	-0.04380900
H	4.93358600	-1.03496400	1.17967600
C	4.07964300	-3.17995200	-1.95930300
H	2.34943700	-1.89597400	-2.18451400
C	5.21237000	-3.48732000	-1.18432500
H	6.38680500	-2.93617400	0.55646600
H	3.84312900	-3.77099200	-2.84058600
H	5.85951300	-4.31551900	-1.46404900
Cl	-0.12598600	-1.68216600	-1.80160800
Cl	0.07950300	2.45192700	0.72565000
Pd	0.01362300	0.31099000	-0.45999500

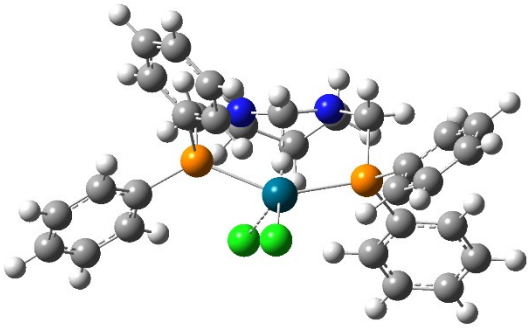


Figure S28. Optimized geometry of the transition state of hydride abstraction step (**B**) in scheme 3.

The coordinates of the optimized hydride abstraction step (B) in scheme 3.

Type	Coordinates (Angstroms) X	Y	Z
C	-0.01642300	-0.57587200	2.15372300
C	-1.68803600	-2.21762900	2.97561600
C	-0.69029300	-3.25284400	2.42171100
C	0.78357900	-2.87401600	2.67419300
H	0.23840000	0.48159900	2.17630000
H	-0.10860200	-0.76523800	0.75588700
H	-1.71143400	-2.24117700	4.07488500
H	-2.69533800	-2.44476200	2.61023700
H	-0.88788300	-4.22539000	2.88829600
H	-0.81720600	-3.35639500	1.33918300
H	1.08625500	-3.09244500	3.70833500
H	1.40047400	-3.45649500	1.98106500
C	2.34561000	-0.98748900	1.93354000
H	2.98698200	-1.86047500	1.79960300
H	2.81006500	-0.29422800	2.64346100
N	1.03688300	-1.42642500	2.42010000
N	-1.32484900	-0.84143000	2.54694700
C	-2.31957200	0.08892500	2.03686500
H	-3.31366900	-0.21974100	2.36886600
H	-2.12029900	1.10807000	2.39003900
P	2.34672100	0.00698100	0.19829300
P	-2.33678700	0.27085500	0.04726500
C	-3.26608600	1.88947700	-0.14210900
C	-4.28512400	2.29296600	0.75200200
C	-2.91501600	2.72701000	-1.22410300
C	-4.94763300	3.51980800	0.56460700
H	-4.57132800	1.66689700	1.59432900
C	-3.58916400	3.94914100	-1.41182000
H	-2.11399700	2.43472300	-1.90013400
C	-4.60391300	4.34828300	-0.52150500
H	-5.72840400	3.82280500	1.25820300
H	-3.31367200	4.58593500	-2.24854000
H	-5.11935700	5.29449600	-0.66875900
C	-3.51493000	-1.08055100	-0.52206700
C	-2.94948400	-2.29413400	-0.97385000
C	-4.91819000	-0.91644400	-0.50856400
C	-3.79393600	-3.34323400	-1.38735000
H	-1.86794200	-2.42720000	-1.02090300
C	-5.75296200	-1.96920500	-0.92592500
H	-5.36372100	0.02681600	-0.20549500

C	-5.19247900	-3.18677400	-1.36156500
H	-3.34967900	-4.27039900	-1.74005100
H	-6.83220600	-1.83489000	-0.92225200
H	-5.83947300	-3.99682200	-1.69064900
C	2.89960900	1.71820100	0.77846300
C	2.22794500	2.84667100	0.25867500
C	3.95112200	1.90653200	1.70610800
C	2.59520200	4.14222700	0.67427500
H	1.44016400	2.71348900	-0.47973500
C	4.30995300	3.20042900	2.12500100
H	4.50994800	1.05572700	2.09112100
C	3.62960800	4.32264500	1.61100900
H	2.07514000	5.00257800	0.26069500
H	5.11997900	3.33143600	2.83859600
H	3.90919600	5.32353900	1.93173300
C	3.85787900	-0.68583300	-0.68311700
C	4.96083300	0.13712300	-1.00185800
C	3.85156700	-2.04081000	-1.08714300
C	6.06363200	-0.39887000	-1.69228000
H	4.96459900	1.18784500	-0.72951100
C	4.96193200	-2.56848100	-1.77133300
H	2.96904900	-2.65484000	-0.91427100
C	6.07107100	-1.75422400	-2.07196300
H	6.90609600	0.24327200	-1.93797800
H	4.94601800	-3.60912700	-2.08577400
H	6.92275500	-2.16585900	-2.60889700
Cl	0.55778100	-2.95999000	-0.70643700
Cl	0.21861300	1.52963500	-2.57336700
Pd	0.01482300	0.10907700	-0.59030400

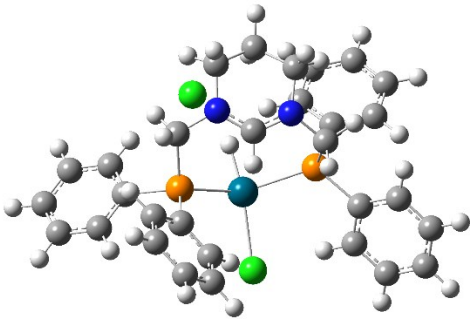


Figure S29. Optimized geometry of the tetrahydropyrimidinium cationic palladium hydride intermediate (**C**) in scheme 3.

The coordinates of the optimized dihydroperimidine based cationic Pd complex.

	Coordinates (Angstroms)		
Type	X	Y	Z
C	0.06693300	-0.56314400	2.08188800

C	-1.72913700	-2.02853800	2.93289400
C	-0.81011200	-3.18452200	2.50236300
C	0.68249600	-2.85827900	2.69522800
H	0.34909200	0.42220600	1.73874500
H	0.03000600	-1.29313800	-0.44674200
H	-1.79647400	-1.94809900	4.02682100
H	-2.73679600	-2.19169400	2.53914400
H	-1.05878200	-4.07901300	3.08515700
H	-0.95830800	-3.40905900	1.44212800
H	0.98155700	-2.89795500	3.75229400
H	1.26905100	-3.58131200	2.12327300
C	2.33712900	-1.29659000	1.52908200
H	2.62430700	-2.25675900	1.09559200
H	3.07716000	-0.98591400	2.27339300
N	1.01172200	-1.50027400	2.16966200
N	-1.22981800	-0.73102300	2.40070000
C	-2.18153600	0.28167200	1.91176900
H	-3.16080900	0.08221000	2.35264800
H	-1.86157500	1.28847500	2.20253700
P	2.35297800	-0.02218200	0.05646300
P	-2.29473100	0.29844000	-0.04699600
C	-3.34166000	1.84298100	-0.29115600
C	-4.30381900	2.27503100	0.65216500
C	-3.14724000	2.58894300	-1.47344800
C	-5.06673300	3.43186800	0.41134500
H	-4.47122800	1.72748400	1.57694400
C	-3.92199700	3.73959400	-1.71568900
H	-2.36438200	2.30710200	-2.17106000
C	-4.88222200	4.16296500	-0.77840300
H	-5.80095600	3.75626300	1.14510600
H	-3.75690300	4.30885700	-2.62651100
H	-5.47347600	5.05622200	-0.96628600
C	-3.47082000	-1.13886700	-0.39761200
C	-2.91855600	-2.35461700	-0.85690400
C	-4.86888600	-1.03003100	-0.21883700
C	-3.75930800	-3.45653300	-1.11281100
H	-1.84833600	-2.45985300	-1.02004500
C	-5.70308300	-2.13234200	-0.47979900
H	-5.31563200	-0.08928200	0.08898000
C	-5.14955800	-3.35044200	-0.92346400
H	-3.31902100	-4.38468000	-1.46764000
H	-6.77866500	-2.03642500	-0.35008500
H	-5.79675200	-4.19962500	-1.13106800
C	3.06339500	1.49707600	0.93138000
C	2.46190800	2.75656800	0.72380000
C	4.18566400	1.39600700	1.78830100

C	2.96681000	3.89510700	1.38603900
H	1.62964500	2.85468800	0.02819400
C	4.68375300	2.53319400	2.44737500
H	4.69237600	0.44339200	1.92984200
C	4.07021700	3.78757400	2.25124200
H	2.49925700	4.86090600	1.21149700
H	5.54884400	2.44310000	3.10012700
H	4.45679700	4.66851700	2.75869400
C	3.78698200	-0.68063600	-0.97405400
C	4.90190100	0.13122600	-1.27429800
C	3.68711300	-1.97532400	-1.53341400
C	5.92517800	-0.35850300	-2.10752600
H	4.97439800	1.13947200	-0.87784800
C	4.71934800	-2.45848600	-2.35844300
H	2.80347000	-2.58775900	-1.35765400
C	5.84070000	-1.65624200	-2.64584500
H	6.77773600	0.27562100	-2.33874500
H	4.63410000	-3.45414500	-2.78681000
H	6.63127400	-2.03191400	-3.29145700
Cl	0.53454100	-3.35039000	-0.64084400
Cl	0.24005300	2.49598500	-1.94976600
Pd	0.04901600	0.24939000	-0.79026800

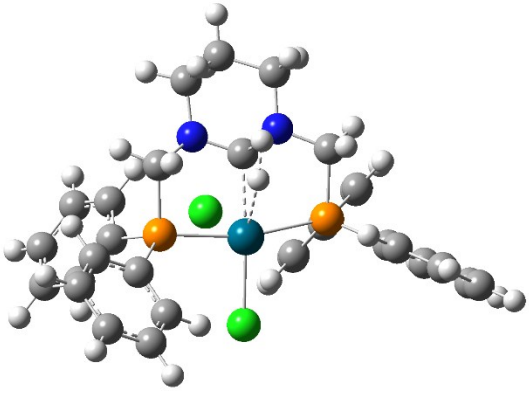


Figure S30. Optimized geometry of the transition state of hydrogen evolution (**D**) in scheme 3.

The coordinates of the optimized transition state of hydrogen evolution (**D**) in **scheme 3**.

Type	Coordinates (Angstroms) X	Y	Z
C	1.41029900	0.85688100	0.08979000
C	2.60429300	2.40775300	-1.37446600
C	3.92744000	0.88544600	0.00673300
C	2.68048100	-0.00593100	0.10460700
H	1.37322900	1.49695600	0.98784300
H	0.51728400	0.22945300	0.05633800

H	4.83232100	0.27962100	-0.07564400
H	4.00481700	1.53714600	0.89336400
H	2.65983600	-0.69664000	-0.74288300
H	2.71686800	-0.58350900	1.03352900
H	2.60165800	3.62052400	-1.36551000
C	0.17898300	2.51175900	-1.30753000
H	-0.68507300	1.87903600	-1.10083200
H	0.14904100	3.38255700	-0.62748900
C	5.03055800	2.54285200	-1.49882000
H	5.91584800	1.91685500	-1.37448400
H	5.10300800	3.41728000	-0.82853200
P	0.14713700	3.17672900	-3.10097600
P	4.89550500	3.18959000	-3.29350300
Pd	2.52308200	3.43872200	-3.34396900
Cl	2.48854900	4.34813300	-5.55348200
C	5.56919000	1.82993400	-4.35265800
C	6.39580900	2.13195000	-5.43955400
C	5.19591000	0.50477800	-4.08620800
C	6.86351400	1.09909100	-6.25450900
H	6.67442700	3.15823300	-5.64553400
C	5.67136000	-0.51951200	-4.90394500
H	4.54053600	0.28361400	-3.25152100
C	6.50483700	-0.22377200	-5.98709400
H	7.50590300	1.32958100	-7.09559400
H	5.39024400	-1.54573800	-4.69964200
H	6.86966200	-1.02186900	-6.62222400
C	6.02159400	4.65010400	-3.41211300
C	7.33771100	4.57991600	-2.93184700
C	5.53531000	5.83374100	-3.98148700
C	8.16046600	5.70329600	-3.00957100
H	7.72487600	3.65744200	-2.51306700
C	6.36920800	6.95179700	-4.06024500
H	4.52783100	5.86744600	-4.38139500
C	7.67533300	6.88873200	-3.57123300
H	9.17698700	5.65284200	-2.63857600
H	5.99785700	7.86590900	-4.50701300
H	8.31850500	7.75831500	-3.63232100
C	-0.52849000	1.80512600	-4.15068600
C	0.06950200	1.56667700	-5.39495800
C	-1.61243900	1.02398900	-3.72586100
C	-0.42074000	0.54468400	-6.21109400
H	0.89480900	2.18654200	-5.72775200
C	-2.09457400	0.00435900	-4.54689700
H	-2.08972000	1.20953700	-2.76989200
C	-1.49757200	-0.23645200	-5.78824000
H	0.03917600	0.36443100	-7.17500800

H	-2.93411500	-0.59771800	-4.22074300
H	-1.87517100	-1.02860300	-6.42346300
C	-1.08444800	4.55916700	-3.06846500
C	-2.28296800	4.47540800	-3.78400800
C	-0.78015000	5.71284200	-2.33195100
C	-3.18656200	5.53940300	-3.74338500
H	-2.50697800	3.59132800	-4.36759000
C	-1.68853400	6.76905000	-2.29181600
H	0.16610600	5.79819000	-1.80652200
C	-2.89330900	6.68165800	-2.99629100
H	-4.11448000	5.47591200	-4.29854000
H	-1.45414100	7.66085400	-1.72343800
H	-3.59503400	7.50638400	-2.97005900
N	1.40764900	1.72343300	-1.12854800
N	3.82933000	1.73470100	-1.22099600
H	2.64609600	3.44281600	-0.23612100
Cl	2.30623400	0.38663100	-4.68036700

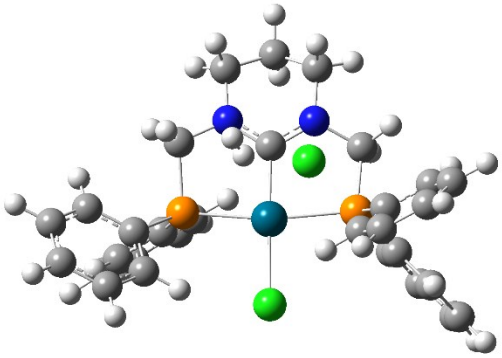


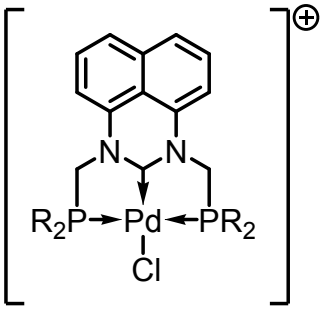
Figure S31. Optimized geometry of the hexahydroperimidine based carbene Pd complex with evolved H_2 molecule (**2a**) in scheme 3.

The coordinates of the optimized hexahydroperimidine based carbene Pd complex with evolved H_2 molecule (**2a**) in scheme 3.

	Coordinates (Angstroms)		
Type	X	Y	Z
C	-1.14277000	-1.43513700	3.71993400
C	0.03703200	-0.44570600	1.74891400
C	1.35194900	-1.32483700	3.71489300
C	0.14411800	-2.23311700	3.95248100
H	-1.28042400	-0.64928000	4.47696100
H	-2.00433300	-2.10663500	3.75765300
H	2.26657000	-1.92695200	3.65708400
H	1.47718100	-0.59619900	4.53113000
H	0.15977100	-3.06864100	3.24187500
H	0.16947500	-2.61928100	4.97845300
H	0.23990800	3.02238500	2.06532000

C	-2.37307000	-0.97433300	1.60769400
H	-2.43153700	-2.02985100	1.30415300
H	-3.22053200	-0.70096600	2.24461900
C	2.47008700	0.00801100	1.93466900
H	3.30235200	-0.66122700	2.17704300
H	2.65061900	0.98313200	2.40773300
P	-2.33602000	0.08104900	0.03477300
P	2.37809000	0.29559100	0.05127900
Pd	0.00578700	0.38375200	-0.11732500
Cl	-0.11708900	1.52286700	-2.27000000
C	3.19680900	-1.20241000	-0.71432700
C	4.40647200	-1.09965800	-1.43426800
C	2.55066900	-2.45144600	-0.57370200
C	4.98170000	-2.25401900	-1.99777600
H	4.89300400	-0.13769600	-1.56970400
C	3.14009100	-3.59922700	-1.13542400
H	1.59171700	-2.56742400	-0.06398300
C	4.35303300	-3.50539800	-1.84501600
H	5.91021400	-2.17279800	-2.55803600
H	2.63027000	-4.55214800	-1.02318000
H	4.79808000	-4.39467300	-2.28578000
C	3.49873500	1.76095200	-0.22901200
C	4.73356100	1.87233900	0.45063000
C	3.09991100	2.76810000	-1.13337700
C	5.55971100	2.98945000	0.23395300
H	5.06031900	1.09577400	1.13952800
C	3.93521500	3.88158700	-1.35013700
H	2.15141800	2.67988000	-1.65804100
C	5.16137700	3.99597800	-0.66860900
H	6.50744500	3.07051700	0.76044800
H	3.62439300	4.65380100	-2.04905900
H	5.80163500	4.85845800	-0.83803300
C	-3.24286600	-0.91297600	-1.25845900
C	-2.87666700	-2.26224800	-1.46782100
C	-4.23309700	-0.30690000	-2.06035000
C	-3.53220700	-3.00215300	-2.46900200
H	-2.09062000	-2.73647300	-0.87552300
C	-4.87687000	-1.05728700	-3.06084600
H	-4.50022900	0.73651700	-1.91718400
C	-4.53036500	-2.40676800	-3.26461700
H	-3.25066400	-4.04015300	-2.62639200
H	-5.63776800	-0.58756300	-3.67940100
H	-5.02704500	-2.98512200	-4.04042900
C	-3.36448900	1.60539700	0.37142900
C	-2.87212500	2.86283400	-0.03678100
C	-4.62206600	1.51621100	1.00870400

C	-3.63067300	4.02480000	0.20427200
H	-1.91712900	2.92806100	-0.55225200
C	-5.37367600	2.67993100	1.25157300
H	-5.02710400	0.55043300	1.30431200
C	-4.87753800	3.93701500	0.85130100
H	-3.24780700	4.99042000	-0.11590500
H	-6.34072400	2.60543500	1.74282600
H	-5.46045100	4.83589500	1.03778500
N	-1.11747300	-0.80173400	2.36581300
N	1.21568600	-0.58760400	2.42438500
H	0.46025200	3.46984600	2.61858400
Cl	-0.48732000	-3.64629200	0.79215500



Structure of the model dihydroperimidine based cationic Pd complex.

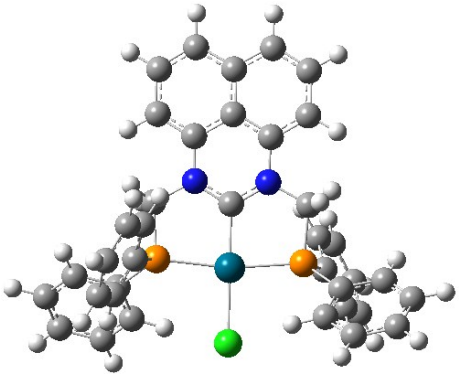


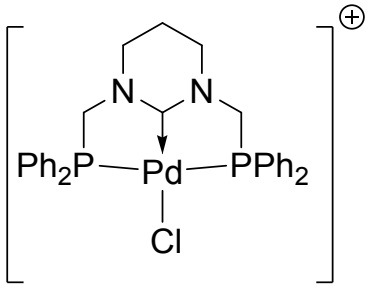
Figure S32. Optimized geometry of the dihydroperimidine based cationic Pd complex.

The coordinates of the optimized dihydroperimidine based cationic Pd complex.

	Coordinates (Angstroms)		
Type	X	Y	Z
P	-2.355313	0.674140	0.079513
Cl	-0.000038	3.289866	-0.000135
P	2.355370	0.673997	-0.079643
N	1.141024	-1.860348	-0.284509
N	-1.141027	-1.860273	0.284484
C	-3.269330	0.772111	-1.542133
C	-3.987054	1.944183	-1.863192
C	3.391500	1.533903	-1.365781

C	3.269237	0.771984	1.542097
C	0.000015	-1.155109	-0.000022
C	-2.416044	-1.158930	0.580656
C	2.792850	2.475125	-2.228317
C	3.986792	1.944137	1.863232
C	-3.183397	-0.281783	-2.477971
C	-4.764686	1.220312	1.490968
C	4.764840	1.220004	-1.490995
C	-4.633746	2.048357	-3.108085
C	-3.391309	1.534054	1.365767
C	-5.531284	1.839142	2.493170
C	3.570627	3.092559	-3.227106
C	4.561604	0.991765	4.035873
C	-2.792522	2.475070	2.228433
C	4.934372	2.773749	-3.363515
C	5.531539	1.838892	-2.493081
C	-4.933979	2.773787	3.363733
C	-3.570195	3.092446	3.227336
C	4.633359	2.048382	3.108188
C	-4.561935	0.991765	-4.035797
C	-3.834871	-0.172456	-3.719133
C	3.183351	-0.281933	2.477914
C	2.416078	-1.159085	-0.580664
C	3.834714	-0.172545	3.719126
H	-2.618697	-1.201003	1.656915
H	-3.228713	-1.662372	0.049145
H	3.228701	-1.662505	-0.049054
H	2.618813	-1.201276	-1.656903
H	2.611907	-1.181786	2.259226
H	3.771432	-0.987686	4.434932
H	5.062626	1.075714	4.996446
H	5.186450	2.951314	3.351272
H	4.044731	2.768357	1.157446
H	5.239996	0.515759	-0.811142
H	6.586881	1.599138	-2.590433
H	5.531007	3.254272	-4.134408
H	3.112051	3.824133	-3.886373
H	1.747814	2.744411	-2.106294
H	-4.045037	2.768374	-1.157378
H	-5.186971	2.951222	-3.351116
H	-5.063055	1.075677	-4.996322
H	-3.771548	-0.987585	-4.434948
H	-2.611831	-1.181573	-2.259342
H	-5.239950	0.516225	0.811028
H	-6.586653	1.599503	2.590507
H	-5.530529	3.254271	4.134716
H	-3.111514	3.823864	3.886704
H	-1.747460	2.744256	2.106411

H	0.000036	0.883368	-0.000052
H	-1.176433	-3.300434	0.394010
H	-0.000065	-4.008303	0.000007
H	-2.299875	-3.994711	0.838775
H	1.176345	-3.300506	-0.394002
H	-0.000102	-5.442689	0.000027
H	-2.283890	-5.418652	0.863618
H	-3.194184	-3.485295	1.173618
H	2.299754	-3.994854	-0.838738
H	1.171609	-6.131179	-0.442311
H	-1.171846	-6.131104	0.442390
H	-3.168209	-5.943614	1.212692
H	2.283692	-5.418797	-0.863550
H	3.194096	-3.485497	-1.173583
H	1.176199	-7.217436	-0.446988
H	-1.176497	-7.217361	0.447096
H	3.167986	-5.943812	-1.212606



Structure of the model hexahydropyrimidine based cationic Pd complex.

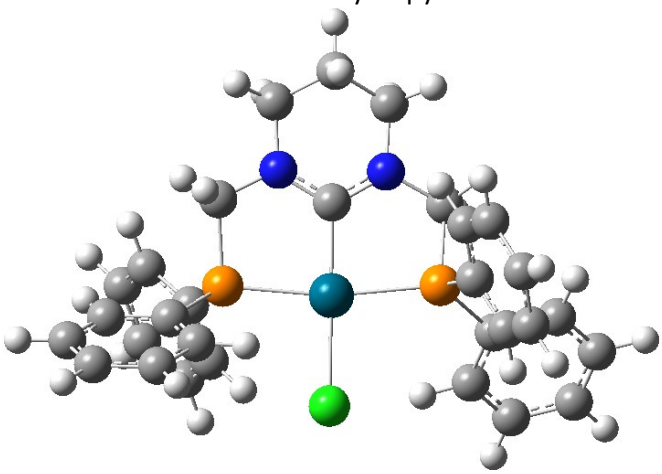


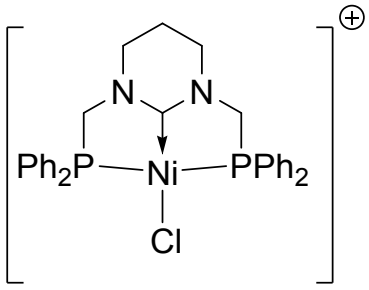
Figure S33. Optimized geometry of the hexahydropyrimidine based cationic Pd(II) complex **2**.

The coordinates of the optimized hexahydropyrimidine based cationic Pd complex.

C	-3.33847	-1.24902	-1.1335
C	-2.62991	-2.03793	-2.06391
H	-1.54749	-1.97188	-2.12782

C	-3.33747	-2.8792	-2.94267
H	-2.79329	-3.47948	-3.66643
C	-4.74371	-2.92698	-2.89882
H	-5.28729	-3.57276	-3.58339
C	-5.44878	-2.12347	-1.9808
H	-6.53491	-2.14662	-1.95744
C	-4.74977	-1.27933	-1.09943
H	-5.30562	-0.64348	-0.41478
C	-3.31671	1.41648	0.29335
C	-4.33036	1.57346	1.26252
H	-4.59892	0.76494	1.93846
C	-5.0206	2.79581	1.36534
H	-5.80085	2.91292	2.11268
C	-4.70706	3.8598	0.49821
H	-5.24388	4.80137	0.57736
C	-3.69877	3.70067	-0.47219
H	-3.45536	4.518	-1.14534
C	-2.99991	2.48457	-0.57644
H	-2.22161	2.3671	-1.32691
C	-2.4026	-1.13062	1.69746
H	-3.2395	-0.82059	2.33146
H	-2.53542	-2.19207	1.4525
C	-1.2159	-1.32449	3.88646
H	-1.94439	-2.13651	3.97949
H	-1.58912	-0.46922	4.4666
C	0.15623	-1.78094	4.39314
H	0.12468	-1.91336	5.47974
H	0.41672	-2.74806	3.94651
C	1.21418	-0.73438	4.0289
H	1.07287	0.18789	4.61064
H	2.21857	-1.11256	4.24633
C	-0.00077	-0.50109	1.83692
C	2.37497	0.19861	2.01912
H	3.24899	-0.34032	2.40043
H	2.45244	1.24945	2.32654
C	3.33385	1.67058	-0.38726
C	2.71453	2.70104	-1.12396
H	1.68277	2.59786	-1.44722
C	3.45541	3.84819	-1.46903
H	2.98163	4.63851	-2.04451
C	4.80296	3.96642	-1.08161
H	5.37105	4.8528	-1.35151
C	5.42136	2.9303	-0.35205
H	6.46457	3.01548	-0.06023
C	4.69172	1.77975	-0.00716
H	5.18431	0.97664	0.53718
C	3.32448	-1.33386	-0.38413
C	4.06543	-1.31696	-1.58503

H	4.10409	-0.42068	-2.19823
C	4.76146	-2.46919	-1.99405
H	5.33177	-2.45117	-2.9186
C	4.71765	-3.63985	-1.2134
H	5.25684	-4.52768	-1.53248
C	3.9694	-3.65933	-0.02006
H	3.92843	-4.56302	0.58234
C	3.26835	-2.51233	0.39194
H	2.67971	-2.5506	1.30642
N	-1.13931	-0.93504	2.44457
N	1.14553	-0.41196	2.57241
P	-2.37457	-0.17667	0.04969
P	2.34556	0.1739	0.1144
Cl	-0.07208	0.73382	-2.44066
Pd	-0.01722	0.04375	-0.12904



Structure of the model hexahydropyrimidine based cationic Ni complex **3**.

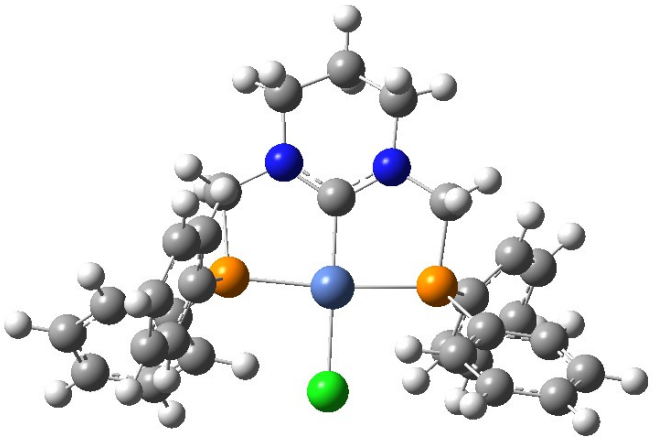


Figure S34. Optimized geometry of the hexahydropyrimidine based cationic Ni complex **3**.

The coordinates of the optimized hexahydropyrimidine based cationic Ni complex.

C	3.2382	-1.43414	-0.87555
C	2.58396	-2.31056	-1.76524
H	1.51658	-2.21692	-1.93917
C	3.33019	-3.28212	-2.45938
H	2.82718	-3.95142	-3.15177

C	4.72121	-3.37833	-2.26854
H	5.29427	-4.12753	-2.80843
C	5.37435	-2.49503	-1.38526
H	6.44963	-2.56095	-1.24326
C	4.63706	-1.52094	-0.68975
H	5.15292	-0.83251	-0.02395
C	3.1544	1.42966	0.0356
C	3.1943	2.28181	1.16037
H	2.73187	1.98846	2.10076
C	3.8312	3.53272	1.07331
H	3.86581	4.18305	1.94339
C	4.41934	3.94305	-0.13884
H	4.91052	4.91009	-0.20548
C	4.36651	3.09913	-1.26473
H	4.81247	3.41405	-2.20404
C	3.73314	1.84585	-1.18275
H	3.69168	1.20628	-2.06015
C	2.3769	-0.79669	1.8971
H	2.56056	-1.87809	1.87816
H	3.20735	-0.31415	2.42515
C	-0.01745	-0.1588	1.90545
C	1.15975	-0.69306	4.07632
H	1.55003	0.22358	4.54089
H	1.8682	-1.50082	4.28872
C	-0.22855	-1.04049	4.62364
H	-0.51086	-2.05374	4.31385
H	-0.212	-1.01811	5.71834
C	-1.2544	-0.03104	4.09793
H	-2.2706	-0.35099	4.35142
H	-1.09711	0.96137	4.54506
C	-2.36411	0.60582	1.94021
H	-2.41336	1.69804	2.03732
H	-3.25961	0.18339	2.40556
C	-3.15223	1.59996	-0.75338
C	-2.41595	2.71368	-1.21
H	-1.33238	2.72536	-1.13355
C	-3.0877	3.79391	-1.81056
H	-2.51998	4.64742	-2.17067
C	-4.48695	3.75923	-1.96552
H	-5.00253	4.5913	-2.43778
C	-5.21712	2.63804	-1.52534
H	-6.29505	2.60259	-1.65806
C	-4.55287	1.55503	-0.92109
H	-5.12271	0.68469	-0.60567
C	-3.19412	-1.36981	-0.22013
C	-4.18149	-1.8646	0.65776
H	-4.43052	-1.34547	1.57996
C	-4.87123	-3.05132	0.34505

H	-5.63176	-3.42745	1.02414
C	-4.58293	-3.74333	-0.84642
H	-5.11954	-4.65697	-1.08796
C	-3.5997	-3.24763	-1.72483
H	-3.37559	-3.77664	-2.64705
C	-2.90141	-2.06687	-1.41484
H	-2.14228	-1.68943	-2.09554
N	-1.16005	0.07481	2.61344
N	1.10629	-0.50502	2.59542
P	2.24602	-0.19744	0.10237
P	-2.24413	0.208	0.09
Cl	0.02846	0.16578	-2.26931
Ni	0.00311	-0.0058	-0.02832