Electronic Supplementary Information

Acetylacetonato-based pincer-type nickel(II) complexes: Synthesis and catalysis in cross-couplings of aryl chlorides with aryl Grignard reagents

Erika Asano, [a] Yuki Hatayama, [a] Nobutaka Kurisu, [a] Atsufumi Ohtani, [a] Toru Hashimoto, [a] Youji Kurihara, [a] Kazuyoshi Ueda, [a] Shinji Ishihara, [b] Hirotaka Nagao [c] and Yoshitaka Yamaguchi [a,*]

[a] *Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[b] *Instrumental Analysis Center, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[c] *Department of Materials and Life Science, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan*

Corresponding author
Tel: +81-45-339-3932; fax: +81-45-339-3932
e-mail: yamaguchi-yoshitaka-hw@ynu.ac.jp

Table of Contents

General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were performed under an atmosphere of nitrogen, which was dried with SICAPENT (Merck Co., Inc.), using standard Schlenk tube or high vacuum techniques. All solvents were distilled over appropriate drying agents prior to use. 2-(Diphenylphosphino)ethylamine,[1] **1a-H**,[2] **1b-H**,[3] 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one,[4] [$NiCl_2$(2,4-lutidine)$_2$],[5] and [$NiCl_2(PPh_3)_2$][6] were prepared according to literature reported procedures. The other reagents employed in this work were commercially available and used without further purification. ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on BRUKER DRX-300, DRX-500, or JEOL ECX-400 spectrometers at ambient temperature. The ^1H, $^1H\{^{31}P\}$, and $^{13}C\{^1H\}$ NMR chemical shifts were recorded in ppm relative to Me_4Si as an internal standard. The $^{31}P\{^1H\}$ NMR chemical shifts were recorded in ppm relative to H_3PO_4 as an external standard. All coupling constants were recorded in Hz. Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet), dt (doublet of triplets), dq (doublet of quartets) and m (multiplet). Thin layer chromatography was performed using Merck silica gel 60F-254 plates and examined under UV (254 nm) irradiation. Column chromatography was performed using Silica Gel 60N (spherical, neutral, 63–210 μm, Kanto Chemical Co., Inc.). High-resolution mass spectra (HRMS) were recorded using fast atom bombardment (FAB) ionization with a JEOL JMS-700 mass spectrometer. Elemental analyses were performed on a Vario EL elemental analyzer. GLC were recorded on a Shimadzu GC-17A gas chromatograph using a ULBON HR-1 capillary column (0.25 ID × 25 m, Shinwa Chemical Industries Ltd.).

Spectroscopic data of 1b-H

^1H NMR (δ, $CDCl_3$): 1.80 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 2.34 (m, 2H, NCH_2CH_2P), 3.31 (m, 2H, NCH_2CH_2P), 4.93 (s, 1H, CH), 7.34 (m, 6H, PPh_2), 7.42 (m, 4H, PPh_2), 10.93 (broad s, 1H, NH). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 18.7 (s, CCH_3), 28.8 (s, CCH_3), 29.7 (d, J = 13.7 Hz, NCH_2CH_2P), 40.2 (d, J = 25.7 Hz, NCH_2CH_2P), 95.5 (s, OCCCN), 128.6 (d, J = 6.4 Hz, P-*m*-C_6H_5), 129.0 (s, P-*p*-C_6H_5), 132.7 (d, J = 18.3 Hz, P-*o*-C_6H_5), 137.5 (d, J = 11.9 Hz, P-*ε*-C_6H_5), 162.4 (s, OCCCN), 195.0 (s, OCCCN). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): -20.8. HRMS (FAB^+) *m*/*z* $[M+H]^+$ Calc. for $C_{19}H_{23}NOP$: 312.1517; Found 312.1516.

Preparation of 1c-H

4-((2,4,6-Trimethylphenyl)amino)pent-3-en-2-one (1240 mg, 5.71 mmol), *N*,*N*-diethylethylenediamine (992 mg, 1.20 mL, 8.54 mmol), and toluene (60 mL) were put in a round-bottom flask. A few drops of H_2SO_4 and molecular sieves 4Å (ca. 10 g) were added to the reaction mixture. The mixture was refluxed for 48 h and then cooled to room temperature. After neutralization with aq. KOH, the reaction mixture was extracted with CH_2Cl_2. The combined organic extracts were dried with Na_2SO_4, filtered, and concentrated in vacuo to obtain **1c-H** as a brown liquid (1300 mg, 4.12 mmol, 72%). ^{1}H NMR (*δ*, $\mathrm{CDCl_3}$): 0.97 (t, *J* = 7.3 Hz, 6H, $\mathrm{NCH_2C}H_3$), 1.59 (s, 3H, $\mathrm{NCCH_3}$), 2.00 (s, 9H, *o*-$(\mathrm{C}H_3)\mathrm{C_6H_2}$ + *p*-$(\mathrm{C}H_3)\mathrm{C_6H_2}$, overlapped), 2.26 (s, 3H, $\mathrm{NCCH_3}$), 2.51 (q, *J* = 7.3 Hz, 4H, $\mathrm{NC}H_2\mathrm{CH_3}$), 2.54 (m, 2H, $\mathrm{NC}H_2\mathrm{CH_2N}$), 3.30 (m, 2H, $\mathrm{NCH_2C}H_2\mathrm{N}$), 4.62 (s, 1H, CH), 6.84 (s, 2H, N-*m*-$(\mathrm{CH_3})_3\mathrm{C_6}H_2$), 10.69 (broad s, 1H, NH). ^{13}C{^{1}H} NMR (*δ*, $\mathrm{CDCl_3}$): 11.9 (s, $\mathrm{NCH_2}C\mathrm{H_3}$), 18.3 (s, N-*o*-$(C\mathrm{H_3})_3\mathrm{C_6H_2}$), 19.4 (s, N-*p*-$(C\mathrm{H_3})_3\mathrm{C_6H_2}$), 20.7 (s, $\mathrm{NC}C\mathrm{H_3}$), 21.1 (s, $\mathrm{NC}C\mathrm{H_3}$), 41.9 (s, $\mathrm{NCH_2}C\mathrm{H_2N}$), 47.5 (s, $\mathrm{N}C\mathrm{H_2CH_3}$), 53.8 (s, $\mathrm{NCH_2}C\mathrm{H_2N}$), 93.1 (s, $\mathrm{NC}C\mathrm{CN}$), 127.6 (s, N-*m*-$(\mathrm{CH_3})_3C_6\mathrm{H_2}$), 128.2 (s, N-*o*-$(\mathrm{CH_3})_3C_6\mathrm{H_2}$), 130.8 (s, N-*p*-$(\mathrm{CH_3})_3C_6\mathrm{H_2}$), 147.2 (s, N-*ε*-$(\mathrm{CH_3})_3C_6\mathrm{H_2}$), 155.3 (s, $\mathrm{N}C\mathrm{CCN}$), 166.0 (s, $\mathrm{NCC}C\mathrm{N}$). HRMS (FAB$^+$) *m*/*z* $[\mathrm{M+H}]^+$ Calc. for $\mathrm{C_{20}H_{34}N_3}$: 316.2753; Found 316.2750.

Preparation of 2a

A solution of $[\mathrm{NiCl_2(2,4\text{-}lutidine)_2}]$ (1240 mg, 3.61 mmol) in THF (15 mL) was prepared and cooled to –78 °C. To this solution, a THF solution of the lithiated ligand (**1a-Li**), which was prepared by the reaction of **1a-H** (718 mg, 3.62 mmol) with *n*-butyllithium (1.40 mL of the 2.67 M hexane solution, 3.74 mmol) at –78 °C, was added. The reaction mixture was allowed to warm to room temperature. After 18 h, the volatiles were removed under reduced pressure. The residual solid was extracted with $\mathrm{CH_2Cl_2}$ (30 mL) and the volatiles were removed under reduced pressure. The resulting purple solid was washed with hexane and dried in vacuo to yield **2a** (1040 mg, 3.57 mmol, 99%). Analytically pure sample of **2a** was obtained by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. Anal. Calc. for $\mathrm{C_{11}H_{21}ClN_2NiO}$: C, 45.33; H, 7.26; N, 9.61%. Found: C, 45.35; H, 7.33; N, 9.53%. ^{1}H NMR (*δ*, $\mathrm{CDCl_3}$): 1.75 (s, 3H, $\mathrm{CH_3}$), 1.78 (t, *J* = 7.2 Hz, 6H, $\mathrm{NCH_2C}H_3$), 1.90 (s, 3H, $\mathrm{CH_3}$), 2.14 (t, *J* = 6.4 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_2N}$), 2.46 (dq, *J* = 13.2, 7.2 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.06 (t, *J* = 6.4 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_2N}$), 3.18 (dq, *J* = 13.2, 7.2 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.92 (s, 1H, CH). ^{13}C{^{1}H} NMR (*δ*, $\mathrm{CDCl_3}$): 11.1 (s, $\mathrm{NCH_2}C\mathrm{H_3}$), 21.2 (s, $\mathrm{CH_3}$), 24.0 (s, $\mathrm{CH_3}$), 50.2 (s, $\mathrm{NC}H_2\mathrm{CH_2N}$), 52.0 (s, $\mathrm{NCH_2C}H_2\mathrm{N}$ + $\mathrm{NC}H_2\mathrm{CH_3}$, overlapped), 99.6 (s, CH), 164.6 (s, $C\mathrm{CH_3}$), 176.8 (s, $C\mathrm{CH_3}$).

Preparation of 2b

Compound **1b-H** (191 mg, 0.61 mmol), $[\mathrm{NiCl_2(PPh_3)_2}]$ (405 mg, 0.62 mmol), and THF (20 mL) were mixed in a Schlenk tube. After stirring the reaction mixture for 1 h, $\mathrm{NEt_3}$ (0.10 mL, 73 mg, 0.72 mmol) was added to the mixture and the solution was stirred for another 4 h at room temperature. Subsequently, the solution was filtered through a Celite pad and the filtrate was evaporated to dryness in vacuo. The residual solid was washed with $\mathrm{Et_2O}$ and dried in vacuo to yield **2b** as an orange solid (237 mg, 0.59 mmol, 97%). An analytically pure sample of **2b** was obtained by recrystallization from $\mathrm{CH_2Cl_2}$/hexane. Anal. Calc. for $\mathrm{C_{19}H_{21}ClNNiOP}$: C, 56.42; H, 5.23; N, 3.46%. Found: C, 56.14; H, 5.27; N, 3.37%. ^{1}H NMR (*δ*, $\mathrm{C_6D_6}$): 1.27 (dt, *J* = 10.9, 6.8 Hz, 2H, $\mathrm{NCH_2C}H_2\mathrm{P}$), 1.35 (s, 3H, $\mathrm{NCCH_3}$), 1.99 (s, 3H, $\mathrm{OCCH_3}$), 2.41 (dt, *J* = 25.2, 6.8 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_2P}$), 4.92 (s, 1H, CH), 6.98-7.08 (m, 6H, P-*p*-$\mathrm{C_6H_5}$ + P-*m*-$\mathrm{C_6H_5}$), 7.93-8.01 (m, 4H, P-*o*-$\mathrm{C_6H_5}$). ^{1}H{^{31}P} NMR (*δ*, $\mathrm{C_6D_6}$): 1.27 (t, *J* = 6.7 Hz, 2H, $\mathrm{NCH_2C}H_2\mathrm{P}$), 1.35 (s, 3H, $\mathrm{NCCH_3}$), 1.99 (s, 3H, $\mathrm{OCCH_3}$), 2.42 (t, *J* = 6.7 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_2P}$), 4.92 (s, 1H, CH), 6.99-7.09 (m, 6H, P-*p*-$\mathrm{C_6H_5}$ + P-*m*-$\mathrm{C_6H_5}$), 7.97 (d, J = 7.0 Hz, 4H, P-*o*-$\mathrm{C_6H_5}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (δ, $\mathrm{C_6D_6}$): 23.1 (s, $\mathrm{NC}C\mathrm{H_3}$), 25.2 (d, $^4J_{\mathrm{PC}}$ = 6.4 Hz, $\mathrm{OC}C\mathrm{H_3}$), 30.6 (d, $^1J_{\mathrm{PC}}$ = 25.7 Hz, $\mathrm{NCH_2}C\mathrm{H_2P}$), 52.0 (d, $^2J_{\mathrm{PC}}$ = 8.2 Hz, $\mathrm{N}C\mathrm{H_2CH_2P}$), 99.8 (s, $\mathrm{OC}C\mathrm{CN}$), 128.7 (d, $^3J_{\mathrm{PC}}$ = 11.0 Hz, P-*m*-$\mathrm{C_6H_5}$), 129.6 (d, $^1J_{\mathrm{PC}}$ = 52.2 Hz, P-*ε*-$\mathrm{C_6H_5}$), 131.1 (d, $^4J_{\mathrm{PC}}$ = 2.7 Hz, P-*p*-$\mathrm{C_6H_5}$), 133.7 (d, $^2J_{\mathrm{PC}}$ = 9.2 Hz, P-*o*-$\mathrm{C_6H_5}$), 165.1 (s, $\mathrm{OCC}C\mathrm{N}$), 178.8 (d, $^3J_{\mathrm{PC}}$ = 2.7 Hz, $\mathrm{O}C\mathrm{CCN}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (δ, $\mathrm{C_6D_6}$): 37.5.

Preparation of 2c

This complex was prepared from **1c-H** (302 mg, 0.96 mmol), [$\mathrm{NiCl_2}$(2,4-lutidine)$_2$] (225 mg, 0.65 mmol), and $\mathrm{NEt_3}$ (0.10 mL, 73 mg, 0.72 mmol) with THF (10 mL) as the solvent in the same manner as that described for **2b**. Complex **2c** was isolated as a red solid (246 mg, 0.60 mmol, 92%). An analytically pure sample of **2c** was obtained by recrystallization from $\mathrm{Et_2O}$/hexane. Anal. Calc. for $\mathrm{C_{20}H_{32}ClN_3Ni}$: C, 58.79; H, 7.89; N, 10.28%. Found: C, 58.48; H, 7.97; N, 10.12%. ^{1}H NMR (δ, $\mathrm{CDCl_3}$): 1.23 (s, 3H, $\mathrm{NCCH_3}$), 1.67 (t, J = 7.2 Hz, 6H, $\mathrm{NCH_2C}H_3$), 1.92 (s, 3H, $\mathrm{NCCH_3}$), 2.21 (s, 3H, N-*p*-$\mathrm{(C}H_3\mathrm{)_3C_6H_2}$), 2.22 (t, J = 6.4 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_2N}$), 2.46 (dq, J = 12.8, 7.2 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_3}$), 2.49 (s, 6H, N-*o*-$\mathrm{(C}H_3\mathrm{)_3C_6H_2}$), 3.25 (dq, J = 12.8, 7.2 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.39 (t, J = 6.4 Hz, 2H, $\mathrm{NCH_2C}H_2\mathrm{N}$), 4.56 (s, 1H, CH). 6.75 (s, 2H, N-*m*-$\mathrm{(CH_3)_3C_6}H_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (δ, $\mathrm{CDCl_3}$): 11.2 (s, $\mathrm{NCH_2}C\mathrm{H_3}$), 19.3 (s, N-*o*-$\mathrm{(}C\mathrm{H_3)_3C_6H_2}$), 21.0 (s, N-*p*-$\mathrm{(}C\mathrm{H_3)_3C_6H_2}$), 22.8 (s, $\mathrm{NC}C\mathrm{H_3}$), 23.4 (s, $\mathrm{NC}C\mathrm{H_3}$), 49.9 (s, $\mathrm{N}C\mathrm{H_2CH_2N}$), 51.3 (s, $\mathrm{N}C\mathrm{H_2CH_3}$), 52.1 (s, $\mathrm{N}C\mathrm{H_2CH_2N}$), 99.3 (s, $\mathrm{NC}C\mathrm{CN}$), 127.8 (s, N-*m*-$\mathrm{(CH_3)_3}C_6\mathrm{H_2}$), 132.7 (s, N-*o*-$\mathrm{(CH_3)_3}C_6\mathrm{H_2}$), 133.2 (s, N-*p*-$\mathrm{(CH_3)_3}C_6\mathrm{H_2}$), 149.1 (s, N-*ε*-$\mathrm{(CH_3)_3}C_6\mathrm{H_2}$), 157.7 (s, $\mathrm{N}C\mathrm{CCN}$), 158.0 (s, $\mathrm{N}C\mathrm{CCN}$).

Experimental procedure for X-ray crystallography

Suitable single crystals were obtained by recrystallization from solvent mixtures of toluene/hexane (for **1b-H**), CH_2Cl_2/hexane (for **2a** and **2b**), or CH_2Cl_2/Et_2O (for **2c**) at room temperature and were individually mounted on glass fibers. Diffraction measurements of all compounds were made on a Rigaku Mercury 70 diffractometer using graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å). The data were collected at –50 ± 1 °C to a maximum 2θ value of 60°. A total of 744 oscillation images were collected. The crystal-to-detector distance was 45.00 mm. Readout was performed in the 0.068 mm pixel mode. Data were collected using CrystalClear[7] and processed using CrysAlisPro.[8] In the reduction of the data, an empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Crystallographic data and the results of measurements are summarized in Table S1. The structure was solved by direct methods (SHELXT)[9] for all complexes, and expanded using Fourier techniques. Least-square refinements were carried out using SHELXL.[10] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at the ideal positions and refined using the riding model. In compound **1b-H**, the hydrogen atom (H1) bonded to the nitrogen atom (N1) was located at the place determined from difference Fourier maps and refined isotropically. All calculations were performed using the CrystalStructure crystallographic software package.[11]

Table S1. Summary of crystal data for **1b-H**, **2a**, **2b**, and **2c**.

	1b-H	**2a**	**2b**	**2c**
Empirical formula	$C_{19}H_{22}NOP$	$C_{11}H_{21}ClN_2NiO$	$C_{19}H_{21}ClNNiOP$	$C_{20}H_{32}ClN_3Ni$
Formula weight	311.36	291.45	404.51	408.65
Temperature (°C)	-50(1)	-50(1)	-50(1)	-50(1)
Crystal color, habit	colorless, plate	purple, needle	orange, plate	red, plate
Crystal dimensions (mm)	0.400 × 0.050 × 0.025	0.500 × 0.200 × 0.200	0.400 × 0.300 × 0.100	0.500 × 0.300 × 0.050
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/c$ (#14)	$Pca2_1$ (#29)	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)
Lattice parameters				
a (Å)	9.4204(9)	11.6387(3)	9.6206(2)	15.2771(10)
b (Å)	9.3731(7)	10.5076(2)	11.6272(2)	10.0576(5)
c (Å)	20.8127(15)	10.8961(2)	16.5733(3)	15.8197(10)
β (°)	98.482(8)	90	90	115.809(8)
V (Å^3)	1817.6(3)	1332.54(5)	1853.90(6)	2188.2(3)
Z	4	4	4	4
D_c (g cm^{-3})	1.138	1.453	1.449	1.240
F_{000}	664.00	616.00	840.00	872.00
μ(Mo-$K\alpha$) (cm^{-1})	1.527	16.388	12.819	10.158
Reflection measured	13831	9291	14071	16353
Independent reflections	4163	2591	4232	5014
R_{int}	0.0653	0.0191	0.0343	0.0525
No. variables	205	149	219	233
Reflection/parameter ratio	20.31	17.39	19.32	21.52
Residuals: R; w$R2$	0.1356; 0.1371	0.0211; 0.0530	0.0246; 0.0550	0.0834; 0.1189
Residuals: $R1$ [$I > 2.00\sigma(I)$]	0.0553	0.0196	0.0210	0.0463
Goodness-of-fit (GOF) on F^2	1.000	1.036	1.076	1.017
Flack parameter	–	-0.017(11)	-0.015(5)	–
Parsons' quotients	–	912	1723	–
$\delta\rho_{max, min}$ (e$^-$ Å^{-3})	0.17, -0.22	0.19, -0.25	0.25, -0.17	0.44, -0.41
CCDC number	1585437	1585438	1585439	1585440

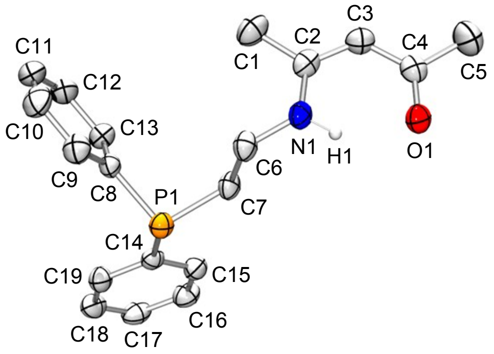


Figure S1. ORTEP drawing of **1b-H** (30% probability of thermal ellipsoids) showing the numbering system. All hydrogen atoms except for H1 have been omitted for clarity.

Table S2. Bond lengths (Å) and bond angles (°) for **1b-H**

P1-C7	1.837(2)	P1-C8	1.829(2)	P1-C14	1.831(2)
O1-C4	1.241(3)	N1-C2	1.324(4)	N1-C6	1.454(3)
C1-C2	1.507(4)	C2-C3	1.374(4)	C3-C4	1.408(4)
C4-C5	1.511(4)	C6-C7	1.526(4)	C8-C9	1.384(4)
C8-C13	1.378(3)	C9-C10	1.385(5)	C10-C11	1.363(5)
C11-C12	1.363(5)	C12-C13	1.384(4)	C14-C15	1.379(3)
C14-C19	1.387(3)	C15-C16	1.388(4)	C16-C17	1.368(4) C17-
C18	1.370(4)	C18-C19	1.379(4)	N1-H1	0.90(3)

C7-P1-C8	100.00(11)	C7-P1-C14	101.66(11)	C8-P1-C14	101.56(10)
C2-N1-C6	127.4(2)	N1-C2-C1	117.7(2)	N1-C2-C3	122.3(2)
C1-C2-C3	120.0(3)	C2-C3-C4	124.5(3)	O1-C4-C3	123.2(2)
O1-C4-C5	118.5(3)	C3-C4-C5	118.3(3)	N1-C6-C7	111.7(2)
P1-C7-C6	111.33(16)	P1-C8-C9	118.35(18)	P1-C8-C13	123.54(19)
C9-C8-C13	118.1(2)	C8-C9-C10	120.6(3)	C9-C10-C11	120.6(3)
C10-C11-C12	119.4(3)	C11-C12-C13	120.6(3)	C8-C13-C12	120.7(3)
P1-C14-C15	124.00(18)	P1-C14-C19	118.73(18)	C15-C14-C19	117.1(2)
C14-C15-C16	121.4(2)	C15-C16-C17	120.3(3)	C16-C17-C18	119.2(3)
C17-C18-C19	120.3(2)	C14-C19-C18	121.6(2)	C2-N1-H1	112.3(15)
C6-N1-H1	119.8(15)				

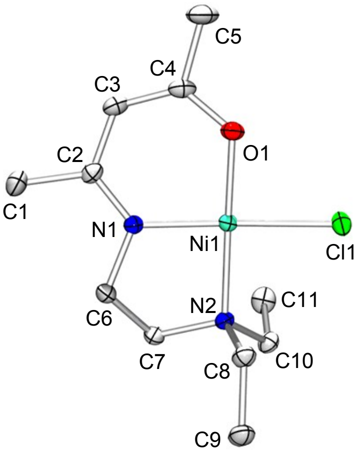


Figure S2. ORTEP drawings of complex **2a** (30% probability of thermal ellipsoids) showing the numbering system. All hydrogen atoms have been omitted for clarity.

Table S3. Bond lengths (Å) and bond angles (°) for **2a**

Ni1-Cl1	2.2399(6)	Ni1-O1	1.8395(18)	Ni1-N1	1.8696(18)
Ni1-N2	1.980(2)	O1-C4	1.296(3)	N1-C2	1.316(3)
N1-C6	1.470(3)	N2-C7	1.499(3)	N2-C8	1.494(3)
N2-C10	1.506(3)	C1-C2	1.511(4)	C2-C3	1.408(3)
C3-C4	1.366(4)	C4-C5	1.506(4)	C6-C7	1.505(4)
C8-C9	1.526(4)	C10-C11	1.511(4)		
Cl1-Ni1-O1	87.40(6)	Cl1-Ni1-N1	177.20(7)	Cl1-Ni1-N2	91.74(6)
O1-Ni1-N1	93.68(9)	O1-Ni1-N2	178.36(9)	N1-Ni1-N2	87.11(9)
Ni1-O1-C4	126.49(16)	Ni1-N1-C2	127.51(17)	Ni1-N1-C6	112.80(16)
C2-N1-C6	119.49(19)	Ni1-N2-C7	106.23(14)	Ni1-N2-C8	106.36(15)
Ni1-N2-C10	115.15(14)	C7-N2-C8	110.92(18)	C7-N2-C10	108.15(18)
C8-N2-C10	109.97(18)	N1-C2-C1	120.7(2)	N1-C2-C3	121.7(2)
C1-C2-C3	117.6(2)	C2-C3-C4	123.9(2)	O1-C4-C3	125.5(2)
O1-C4-C5	114.5(2)	C3-C4-C5	120.0(2)	N1-C6-C7	105.93(19)
N2-C7-C6	109.2(2)	N2-C8-C9	116.7(2)	N2-C10-C11	114.0(2)

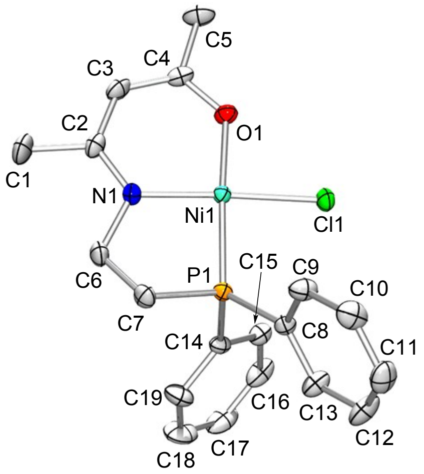


Figure S3. ORTEP drawings of complex **2b** (30% probability of thermal ellipsoids) showing the numbering system. All hydrogen atoms have been omitted for clarity.

Table S4. Bond lengths (Å) and bond angles (°) for **2b**

Ni1-Cl1	2.1732(7)	Ni1-P1	2.1292(6)	Ni1-O1	1.8665(18)
Ni1-N1	1.896(2)	P1-C7	1.813(3)	P1-C8	1.810(2)
P1-C14	1.807(3)	O1-C4	1.282(3)	N1-C2	1.321(3)
N1-C6	1.478(4)	C1-C2	1.517(4)	C2-C3	1.403(4)
C3-C4	1.369(4)	C4-C5	1.505(4)	C6-C7	1.516(4)
C8-C9	1.388(4)	C8-C13	1.385(4)	C9-C10	1.377(4)
C10-C11	1.387(5)	C11-C12	1.360(5)	C12-C13	1.388(4)
C14-C15	1.392(4)	C14-C19	1.396(4)	C15-C16	1.387(5)
C16-C17	1.366(6)	C17-C18	1.390(7)	C18-C19	1.380(6)
Cl1-Ni1-P1	87.92(3)	Cl1-Ni1-O1	88.80(6)	Cl1-Ni1-N1	174.50(6)
P1-Ni1-O1	174.16(5)	P1-Ni1-N1	88.10(6)	O1-Ni1-N1	95.48(8)
Ni1-P1-C7	100.02(9)	Ni1-P1-C8	122.12(9)	Ni1-P1-C14	112.99(8)
C7-P1-C8	107.08(12)	C7-P1-C14	108.28(12)	C8-P1-C14	105.50(11)
Ni1-O1-C4	126.94(17)	Ni1-N1-C2	123.64(18)	Ni1-N1-C6	118.64(15)
C2-N1-C6	117.4(2)	N1-C2-C1	120.2(3)	N1-C2-C3	124.1(2)
C1-C2-C3	115.7(2)	C2-C3-C4	125.9(2)	O1-C4-C3	123.9(2)
O1-C4-C5	114.6(2)	C3-C4-C5	121.6(2)	N1-C6-C7	110.6(2)
P1-C7-C6	106.16(18)	P1-C8-C9	118.28(19)	P1-C8-C13	122.32(19)
C9-C8-C13	119.4(2)	C8-C9-C10	120.4(3)	C9-C10-C11	119.9(3)
C10-C11-C12	119.9(3)	C11-C12-C13	120.9(3)	C8-C13-C12	119.6(3)
P1-C14-C15	118.8(2)	P1-C14-C19	121.6(2)	C15-C14-C19	119.6(3)
C14-C15-C16	120.3(3)	C15-C16-C17	119.7(3)	C16-C17-C18	120.8(4)
C17-C18-C19	120.0(3)	C14-C19-C18	119.6(3)		

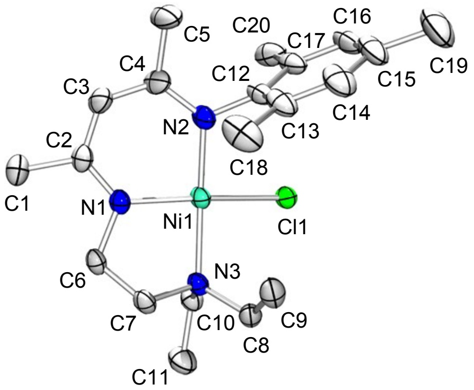


Figure S4. ORTEP drawings of complex **2c** (30% probability of thermal ellipsoids) showing the numbering system. All hydrogen atoms have been omitted for clarity.

Table S5. Bond lengths (Å) and bond angles (°) for **2c**

Ni1-Cl1	2.2154(8)	Ni1-N1	1.860(2)	Ni1-N2	1.891(3)
Ni1-N3	1.994(3)	N1-C2	1.321(4)	N1-C6	1.475(5)
N2-C4	1.339(4)	N2-C12	1.440(5)	N3-C7	1.483(4)
N3-C8	1.498(4)	N3-C10	1.505(3)	C1-C2	1.504(5)
C2-C3	1.384(5)	C3-C4	1.381(5)	C4-C5	1.527(5)
C6-C7	1.490(4)	C8-C9	1.511(4)	C10-C11	1.521(5)
C12-C13	1.394(5)	C12-C17	1.394(6)	C13-C14	1.383(6)
C13-C18	1.502(6)	C14-C15	1.375(8)	C15-C16	1.387(7)
C15-C19	1.515(8)	C16-C17	1.398(6)	C17-C20	1.494(5)

Cl1-Ni1-N1	163.43(6)	Cl1-Ni1-N2	93.20(8)	Cl1-Ni1-N3	90.34(7)
N1-Ni1-N2	93.27(11)	N1-Ni1-N3	86.08(10)	N2-Ni1-N3	169.29(9)
Ni1-N1-C2	127.1(2)	Ni1-N1-C6	114.36(16)	C2-N1-C6	117.8(3)
Ni1-N2-C4	125.1(2)	Ni1-N2-C12	117.48(19)	C4-N2-C12	116.9(3)
Ni1-N3-C7	104.47(16)	Ni1-N3-C8	115.2(2)	Ni1-N3-C10	108.76(19)
C7-N3-C8	108.6(2)	C7-N3-C10	110.4(2)	C8-N3-C10	109.24(19)
N1-C2-C1	120.2(3)	N1-C2-C3	121.6(3)	C1-C2-C3	118.1(3)
C2-C3-C4	125.8(3)	N2-C4-C3	123.2(3)	N2-C4-C5	119.4(3)
C3-C4-C5	117.3(3)	N1-C6-C7	106.9(3)	N3-C7-C6	109.0(3)
N3-C8-C9	114.1(2)	N3-C10-C11	116.7(3)	N2-C12-C13	118.4(3)
N2-C12-C17	120.3(3)	C13-C12-C17	121.3(4)	C12-C13-C14	118.0(4)
C12-C13-C18	120.9(4)	C14-C13-C18	121.1(4)	C13-C14-C15	123.0(4)
C14-C15-C16	117.7(5)	C14-C15-C19	122.4(5)	C16-C15-C19	119.9(5)
C15-C16-C17	122.1(4)	C12-C17-C16	117.8(4)	C12-C17-C20	121.7(4)
C16-C17-C20	120.4(4)				

Experimental procedure for cyclic voltammetry

Cyclic voltammograms were recorded on a BAS 100B/W electrochemical analyzer in CH_2Cl_2 containing 0.1 M Bu_4NClO_4 as a supporting electrolyte by using a conventional three-electrode system of Pt (ϕ = 1.6 mm, working electrode), Pt wire (counter electrode), and Ag/AgCl (reference electrode) at 100 mV/s scan rate. Potentials are given vs. Fc/Fc$^+$.

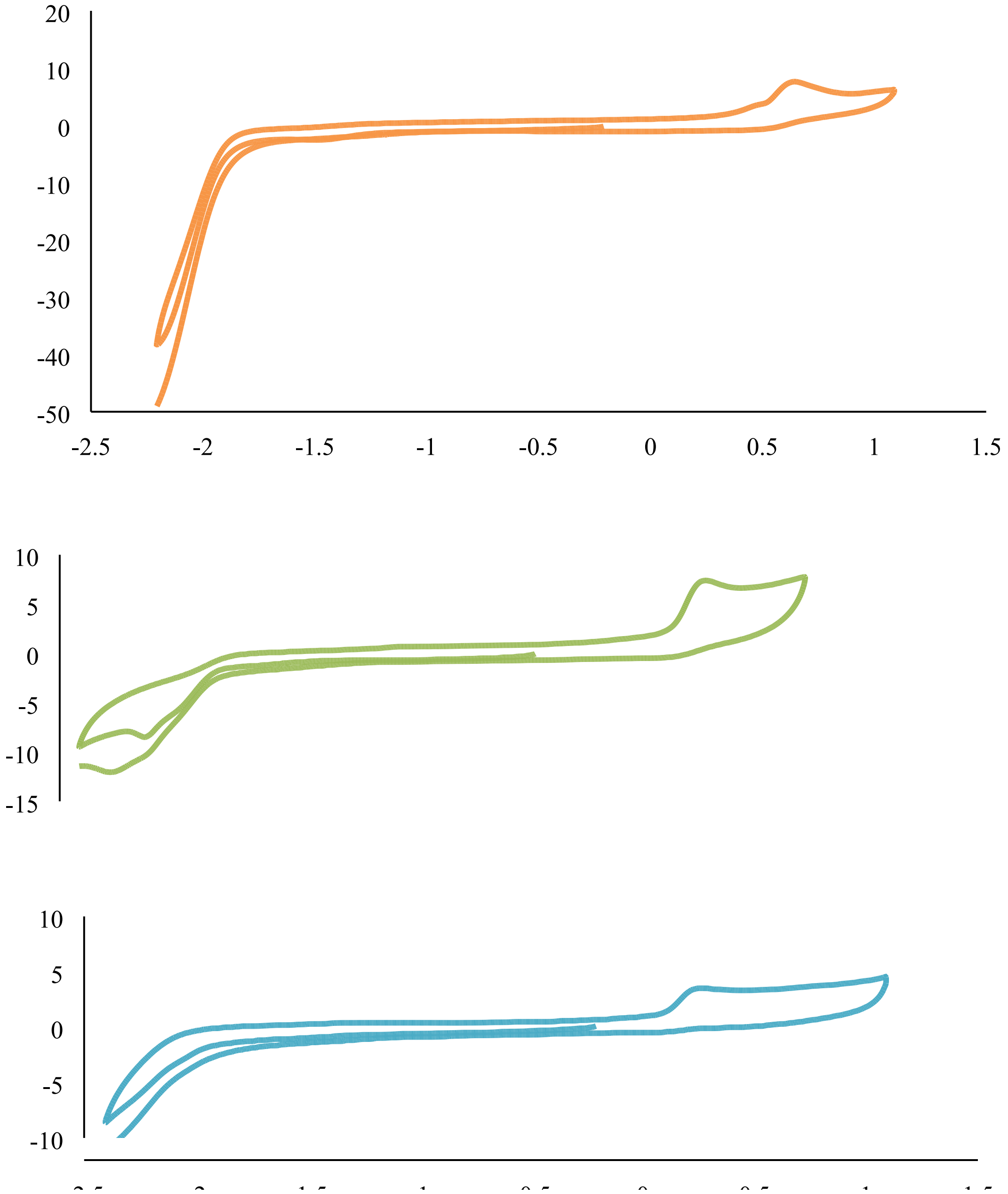


Figure S5. Cyclic voltammograms of **2a** (upper), **2b** (middle), and **2c** (bottom).

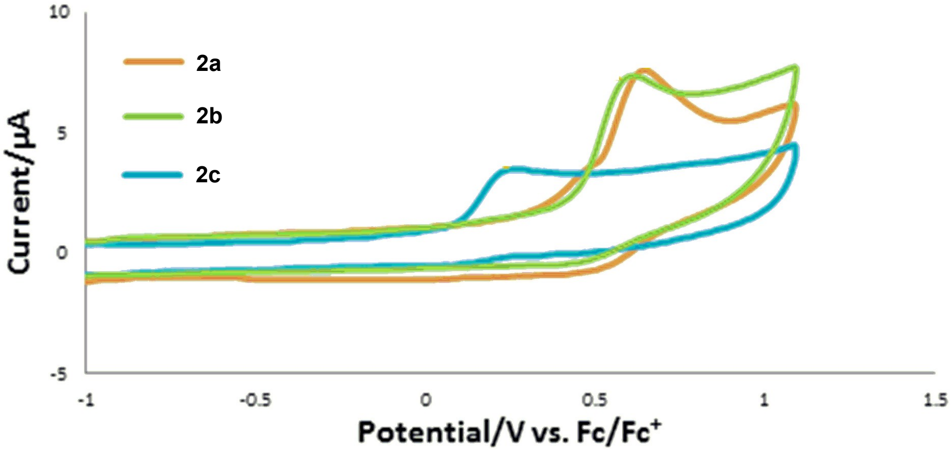


Figure S6. Cyclic voltammograms of **2a**, **2b**, and **2c** (on the scan between -1.00 V and 1.50 V).

DFT calculations

All geometry optimizations were carried out using Gaussian 09[12] at B3LYP[13] level of density functional theory (DFT)[14] with LANL2DZ basis set[15] for the nickel atom and 6-311++G(d,p) basis set for other atoms. The LANL2DZ pseudo-potential was used for the nickel center.

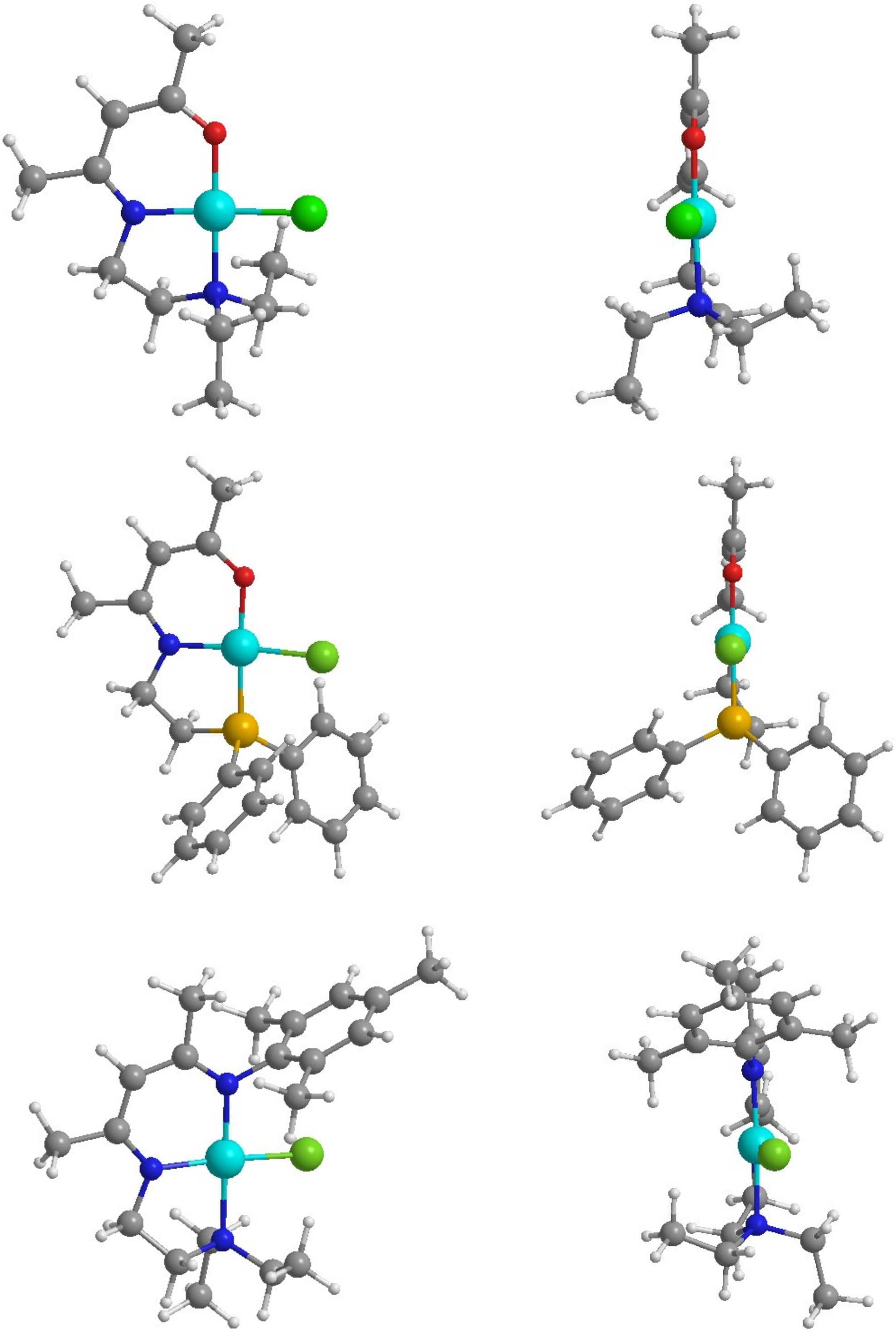


Figure S7. Optimized molecular structures of nickel complexes **2a** (upper), **2b** (middle), and **2c** (bottom) at B3LYP functional level with LANL2DZ and the pseudo potential in this basis set for Ni, and 6-311++G(d,p) for the rest (left: side view, right: front view).

White = hydrogen, gray = carbon, blue = nitrogen, red = oxygen, orange = phosphorus, green = chlorine, and light blue = nickel.

Table S6. Selected bond lengths (Å) and angles (°) for complexes **2a**, **2b** and **2c**.

	2a			**2b**			**2c**	
	Calculated	Experimental		Calculated	Experimental		Calculated	Experimental
				Bond lengths				
Ni1-Cl1	2.254	2.2399(6)	Ni1-Cl1	2.243	2.1732(7)	Ni1-Cl1	2.261	2.2154(8)
Ni1-N1	1.907	1.8696(18)	Ni1-N1	1.933	1.896(2)	Ni1-N1	1.916	1.860(2)
Ni1-O1	1.866	1.8395(18)	Ni1-O1	1.887	1.8665(18)	Ni1-N2	1.942	1.891(3)
Ni1-N2	2.015	1.980(2)	Ni1-P1	2.207	2.1292(6)	Ni1-N3	2.066	1.994(3)
N1-C2	1.323	1.316(3)	N1-C2	1.329	1.321(3)	N1-C2	1.328	1.321(4)
O1-C4	1.275	1.296(3)	O1-C4	1.270	1.282(3)	N2-C4	1.329	1.339(4)
C1-C2	1.516	1.511(4)	C1-C2	1.519	1.517(4)	C1-C2	1.517	1.504(5)
C2-C3	1.408	1.408(3)	C2-C3	1.408	1.403(4)	C2-C3	1.394	1.384(5)
C3-C4	1.394	1.366(4)	C3-C4	1.395	1.369(4)	C3-C4	1.404	1.381(5)
C4-C5	1.510	1.506(4)	C4-C5	1.511	1.505(4)	C4-C5	1.519	1.527(5)
				Bond angles				
Cl1-Ni1-N1	173.70	177.20(7)	Cl1-Ni1-N1	175.93	174.50(6)	Cl1-Ni1-N1	168.90	163.43(6)
O1-Ni1-N2	178.04	178.36(9)	O1-Ni1-P1	176.90	174.16(5)	N2-Ni1-N3	176.25	169.29(9)
N1-Ni1-O1	93.68	93.68(9)	N1-Ni1-O1	94.92	95.48(8)	N1-Ni1-N2	93.86	93.27(11)
N1-Ni1-N2	86.85	87.11(9)	N1-Ni1-P1	88.09	88.10(6)	N1-Ni1-N3	85.09	86.08(10)
Cl1-Ni1-O1	87.91	87.40(6)	Cl1-Ni1-O1	88.93	88.80(6)	Cl1-Ni1-N2	93.52	93.20(8)
Cl1-Ni1-N2	91.76	91.74(6)	Cl1-Ni1-P1	88.08	87.92(3)	Cl1-Ni1-N3	88.08	90.34(7)
Ni1-N1-C2	126.25	127.51(17)	Ni1-N1-C2	123.48	123.64(18)	Ni-N1-C2	126.67	127.1(2)
Ni1-N1-C6	112.96	112.80(16)	Ni1-N1-C6	118.05	118.64(15)	Ni-N1-C6	114.35	114.36(16)
C2-N1-C6	120.39	119.49(19)	C2-N1-C6	118.05	117.4(2)	C2-N1-C6	118.46	117.8(3)
C2-C3-C4	124.02	123.9(2)	C2-C3-C4	125.16	125.9(2)	C2-C3-C4	126.18	125.8(3)
Ni1-O1-C4	127.71	126.49(16)	Ni1-O1-C4	127.15	126.94(17)	Ni1-N2-C4	124.81	125.1(2)

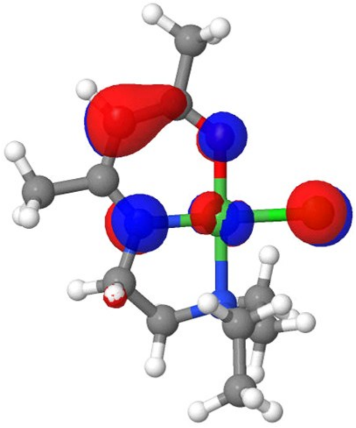
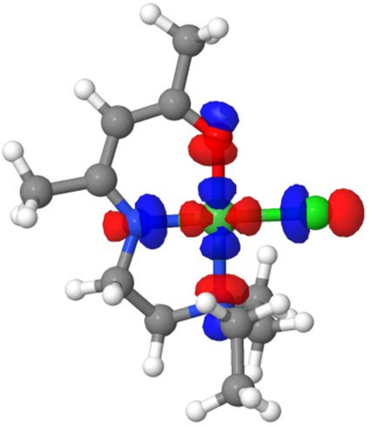
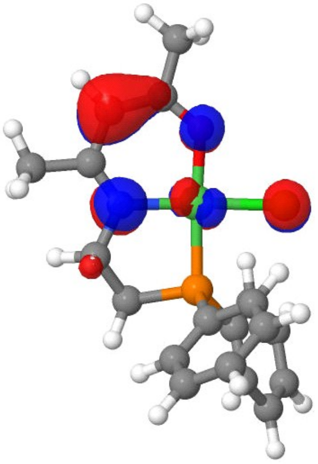
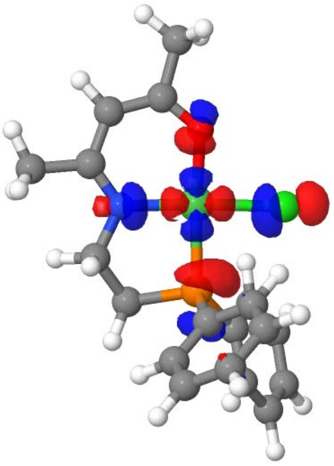
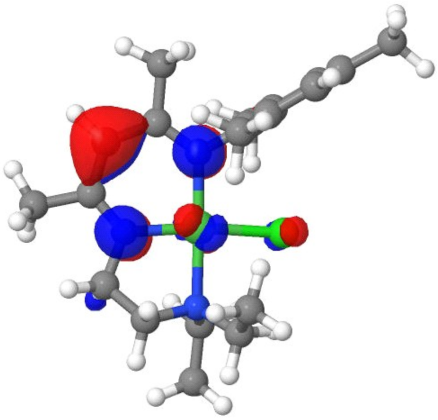
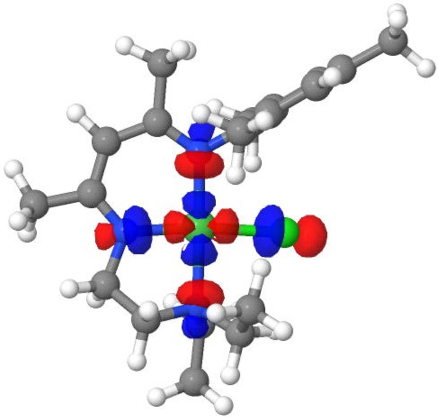
HOMO	LUMO
 **2a** (*E* = -5.68 eV)	 **2a** (*E* = -1.84 eV)
 **2b** (*E* = -5.61 eV)	 **2b** (*E* = -1.86 eV)
 **2c** (*E* = -5.23 eV)	 **2c** (*E* = -1.80 eV)

Figure S8. HOMO and LUMO orbitals for nickel complexes using the Jmol software.[16] Values in the parentheses represent the energies of HOMO and LUMO.

Table S7. Cartesian coordinates of the optimized molecular structure of **2a**.

Ni	-0.065398	-0.511683	-0.064117
Cl	0.854154	-2.527593	-0.475548
O	-1.738844	-1.332722	-0.154540
N	-0.797683	1.242646	0.085232
N	1.748012	0.351609	0.098231
C	-2.507497	3.012806	0.097937
C	-2.082052	1.558535	0.063454
C	-3.107711	0.595070	0.009558
C	-2.884167	-0.777358	-0.089234
C	-4.048076	-1.738892	-0.137781
C	0.222285	2.290329	0.063020
C	1.483641	1.703998	0.664967
C	2.270690	0.419679	-1.312967
C	3.625646	1.102124	-1.519212
C	2.719897	-0.384580	0.976735
C	2.151981	-0.831755	2.319228
H	-3.590818	3.093687	0.027203
H	-2.068134	3.575735	-0.730493
H	-2.192270	3.497361	1.027127
H	-4.129945	0.944349	0.033890
H	-5.009532	-1.226147	-0.097433
H	-3.974182	-2.436781	0.700486
H	-3.988659	-2.330859	-1.054681
H	-0.065635	3.169271	0.646643
H	0.397268	2.635157	-0.965277
H	1.329247	1.580866	1.736017
H	2.345331	2.364746	0.524256
H	1.508604	0.920856	-1.912976
H	2.308897	-0.613967	-1.655632
H	3.632012	2.151602	-1.214128
H	3.858495	1.075629	-2.586969
H	4.434774	0.586596	-0.998817
H	3.592364	0.261277	1.132750
H	3.033009	-1.264076	0.417462
H	1.850933	0.000101	2.960491
H	2.927132	-1.387499	2.854086
H	1.302274	-1.499450	2.173438

Table S8. Cartesian coordinates of the optimized molecular structure of **2b**.

Ni	-1.187266	-0.346589	-0.435045
Cl	-0.193615	-1.221252	-2.245841
P	0.822533	0.032507	0.393145
O	-2.862841	-0.733713	-1.211052
N	-1.925359	0.470589	1.153930
C	-3.728216	1.350698	2.598642
C	-3.229802	0.616152	1.365430
C	-4.234683	0.127452	0.508177
C	-4.009530	-0.514196	-0.709992
C	-5.174023	-0.995262	-1.544467
C	-0.992368	1.109189	2.103644
C	0.337695	0.361642	2.141489
C	1.658360	1.540106	-0.240844
C	2.206835	2.511924	0.606052
C	2.831062	3.639715	0.074526
C	2.916541	3.805101	-1.305949
C	2.370595	2.842554	-2.154136
C	1.739356	1.717748	-1.629874
C	2.093787	-1.283370	0.478310
C	3.436935	-0.981777	0.731548
C	4.368567	-2.007862	0.875821
C	3.966015	-3.337862	0.767116
C	2.631026	-3.641225	0.504690
C	1.696738	-2.619571	0.353720
H	-3.326333	2.366162	2.650729
H	-3.438261	0.833808	3.518453
H	-4.814438	1.417652	2.582183
H	-5.260409	0.276009	0.813909
H	-5.089265	-2.075345	-1.691529
H	-5.124288	-0.531808	-2.533197
H	-6.136616	-0.768035	-1.085155
H	-1.405104	1.128482	3.113347
H	-0.821346	2.153171	1.807502
H	0.202172	-0.623904	2.595414
H	1.091312	0.895457	2.724341
H	2.155301	2.402707	1.682595
H	3.250267	4.385582	0.740614
H	3.402404	4.682197	-1.718569
H	2.428618	2.968567	-3.229318
H	1.303576	0.975570	-2.289186
H	3.762471	0.049618	0.802663
H	5.408393	-1.766833	1.066180
H	4.693040	-4.135035	0.874849
H	2.317500	-4.673510	0.398930
H	0.668805	-2.853711	0.106104

Table S9. Cartesian coordinates of the optimized molecular structure of **2c**.

Ni	-0.854963	-0.087923	-0.055443
Cl	0.238207	-1.971930	-0.662423
N	-2.018041	1.417108	0.175263
N	-2.579168	-1.216743	0.084970
N	0.758105	0.993411	-0.062072
C	-2.755693	3.769968	0.126054
C	-1.681715	2.699635	0.092635
C	-0.361883	3.136373	-0.006912
C	0.781187	2.321939	-0.027489
C	2.110185	3.057194	0.005608
C	-3.436503	1.073446	0.274739
C	-3.531224	-0.336379	0.807719
C	-2.474732	-2.529606	0.806104
C	-1.756611	-2.471710	2.149637
C	-2.990531	-1.450460	-1.344002
C	-4.342303	-2.131483	-1.578340
C	2.040416	0.334819	-0.032892
C	2.593719	-0.038205	1.200970
C	3.851842	-0.645136	1.217604
C	4.567929	-0.890677	0.046294
C	3.989437	-0.509825	-1.166004
C	2.733090	0.093243	-1.231226
C	1.849929	0.203184	2.490849
C	5.910867	-1.580598	0.082794
C	2.124584	0.442573	-2.565225
H	-3.512423	3.605138	-0.646254
H	-2.314702	4.752493	-0.034659
H	-3.273176	3.787881	1.090412
H	-0.199802	4.203886	-0.031102
H	2.733522	2.800203	-0.852627
H	2.681585	2.788868	0.897362
H	1.945909	4.134234	0.009939
H	-3.933055	1.158443	-0.702263
H	-3.975578	1.736532	0.958099
H	-3.235466	-0.331937	1.856084
H	-4.554434	-0.724766	0.749178
H	-1.932533	-3.204085	0.147138
H	-3.490459	-2.920113	0.944847
H	-1.709717	-3.484256	2.560147
H	-2.267307	-1.848272	2.887141
H	-0.734271	-2.116176	2.022265
H	-2.186317	-2.041104	-1.781202
H	-2.974111	-0.481923	-1.846508
H	-4.489410	-2.230939	-2.657132
H	-5.186463	-1.556251	-1.189851
H	-4.384616	-3.135692	-1.152404

H	4.280293	-0.933252	2.173530
H	4.525406	-0.697740	-2.092158
H	0.872829	-0.288062	2.478943
H	1.661618	1.267562	2.664142
H	2.416456	-0.181641	3.341198
H	6.573379	-1.207281	-0.702529
H	5.802260	-2.660456	-0.068549
H	6.409222	-1.433489	1.044117
H	2.817460	0.212423	-3.377141
H	1.857512	1.501041	-2.637835
H	1.207632	-0.132818	-2.719349

Nickel catalyzed cross-coupling reaction

Typical procedure for the cross-coupling reaction (Table 2, entry 15): GLC analysis

Complex **2b** (10.2 mg, 0.025mmol), octadecane (145.8 mg, 0.57 mmol), THF (5 mL), and 4-chlorotoluene (130.1 mg, 0.122 mL, 1.03 mmol) were placed in a Schlenk tube. Phenylmagnesium bromide (1.5 mL of the 1.0 M THF solution, 1.5 mmol) was added at once to the reaction mixture. After stirring for 24 h at 25 °C, 1 M hydrochloric acid (5 mL) was added to quench the reaction. The products were extracted with Et_2O and the yields of the products were determined by GLC analysis using octadecane as an internal standard.

Typical procedure for the cross-coupling reaction (Table 3, entry 2): ^{1}H NMR analysis

Complex **2b** (10.1 mg, 0.025mmol), octadecane (120.6 mg, 0.47 mmol), THF (5 mL), and 4-chlorobenzotrifluoride (175.9 mg, 0.130 mL, 0.97 mmol) were mixed together in a Schlenk tube. Phenylmagnesium bromide (1.5 mL of the 1.0 M THF solution, 1.5 mmol) was added at once to the reaction mixture. After stirring for 5 min at 25 °C, the reaction was quenched with 1 M hydrochloric acid and then extracted with Et_2O. The organic layer was washed with brine and distilled water, dried with Na_2SO_4, filtered, and evaporated to dryness. The yields of products were determined by ^{1}H NMR using pyrazine as an internal standard. The products were characterized by comparison with the previously reported ^{1}H NMR data: 4-trifluoromethylbiphenyl,[17] 4-methoxybiphenyl,[17] and 2,4,6-trimethylbiphenyl.[18]

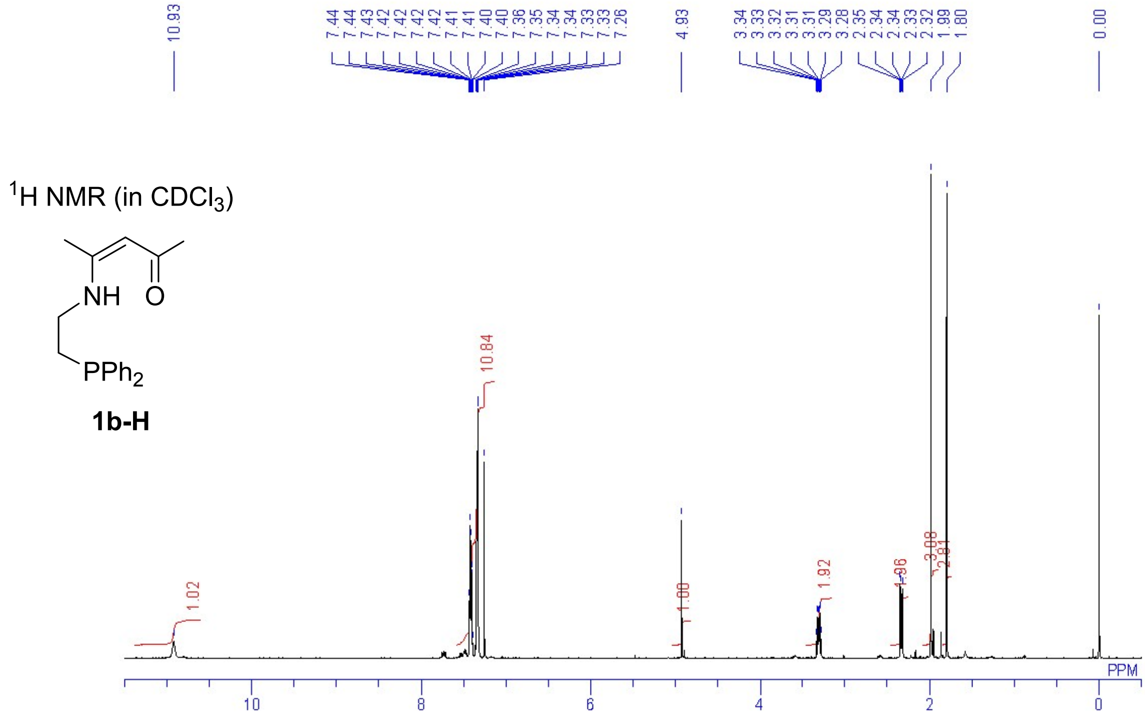
Typical procedure for the cross-coupling reaction (Table 4, entry 1): Isolation of product

Complex **2b** (10.0 mg, 0.025mmol), 1,4-dichlorobenzene (148.1 mg, 1.01 mmol), and THF (5 mL) were put in a Schlenk tube. Phenylmagnesium bromide (2.5 mL of the 1.0 M THF solution, 2.5 mmol) was added at once to the reaction mixture. After stirring for 5 min at 25 °C, the reaction was quenched with 1 M hydrochloric acid and then extracted with CH_2Cl_2. The organic layer was washed with brine and distilled water, dried with Na_2SO_4, filtered, and evaporated to dryness. The residual solid was washed with hexane and dried in vacuo to yield *p*-terphenyl as colorless solid (187.0 mg, 0.81 mmol, 80%), which was characterized by the comparison of the reported NMR data.[17]

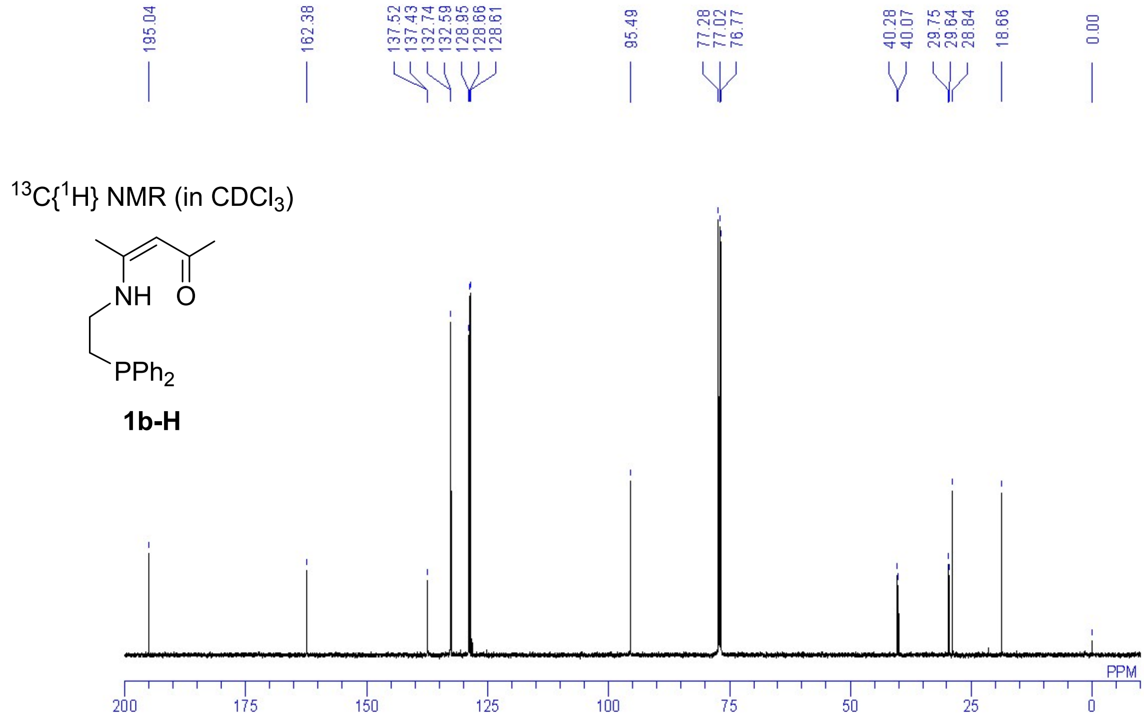
***p*-Terphenyl:** ^{1}H NMR (δ, $CDCl_3$): 7.34–7.39 (m, 2H), 7.44–7.48 (m, 4H), 7.63–7.66 (m, 4H), 7.68 (s, 4H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 127.2, 127.5, 127.6, 129.0, 140.2, 140.8.

***m*-Terphenyl:** ^{1}H NMR (δ, $CDCl_3$): 7.34–7.38 (m, 2H), 7.44–7.52 (m, 5H), 7.56–7.58 (m, 2H), 7.63–7.66 (m, 4H), 7.80–7.81 (m, 1H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 126.3 (overlapped), 127.4, 127.5, 129.0, 129.3, 141.3, 141.9.

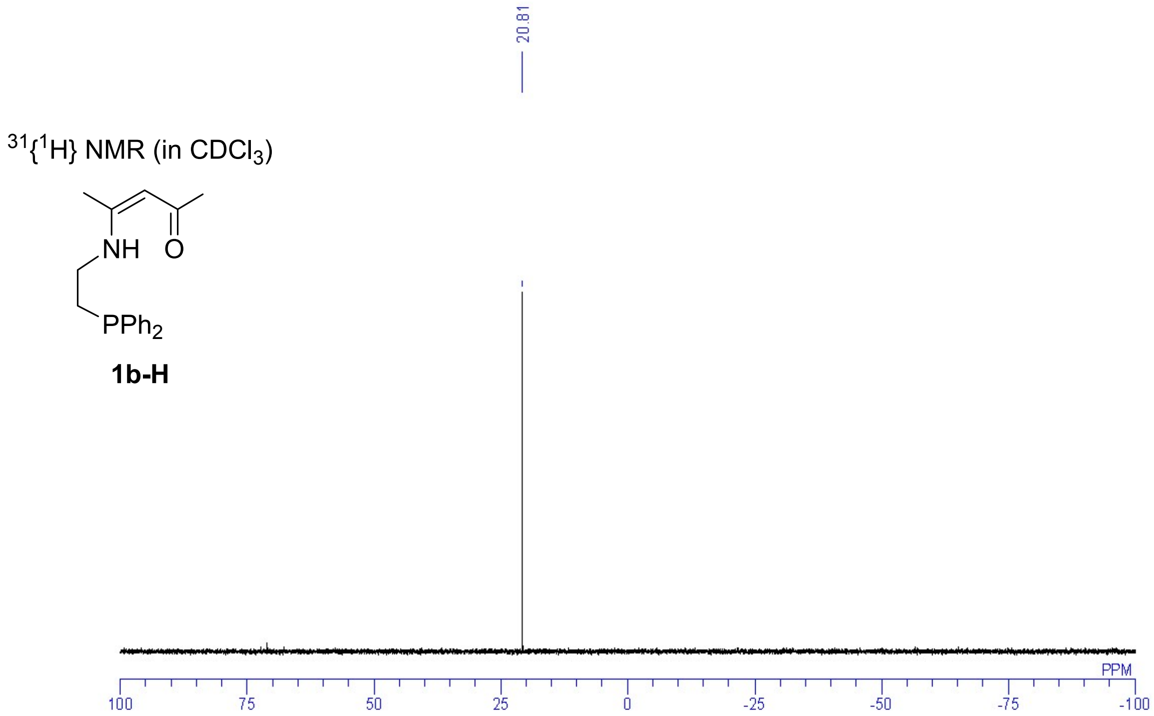
***o*-Terphenyl:** ^{1}H NMR (δ, $CDCl_3$): 7.12–7.14 (m, 4H), 7.18–7.22 (m, 6H), 7.39–7.44 (m, 4H). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 126.6, 127.6, 128.0, 130.0, 130.7, 140.7, 141.6.



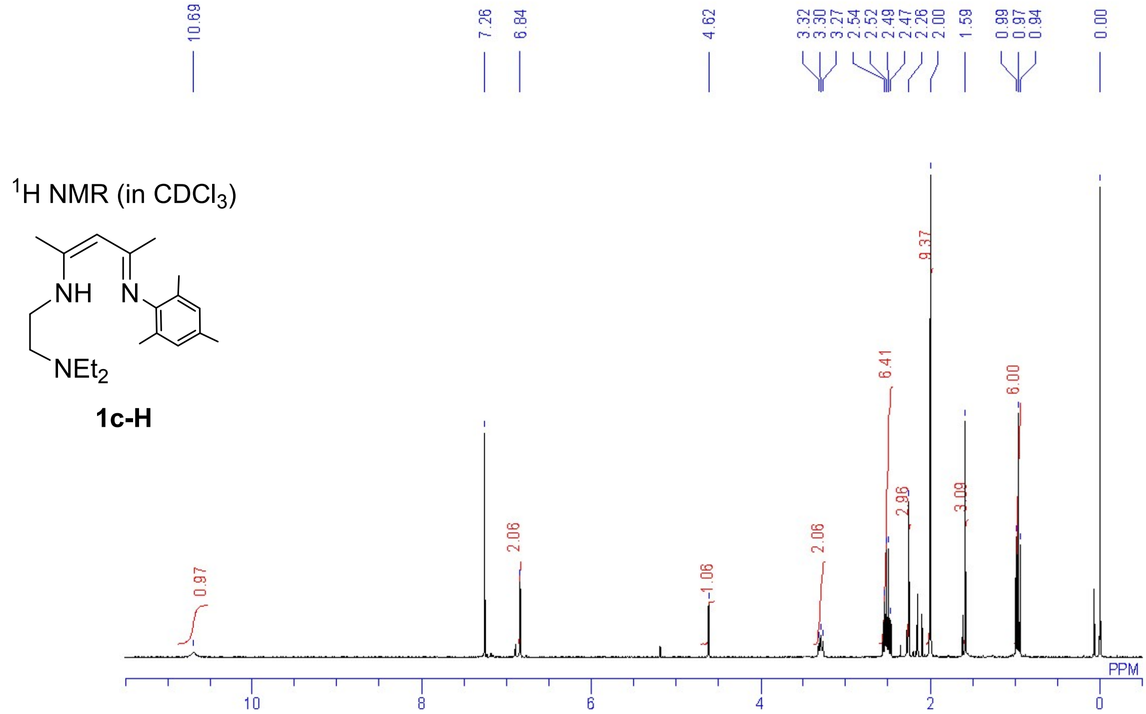
^{1}H NMR spectrum of **1b-H** (in CDCl$_3$)



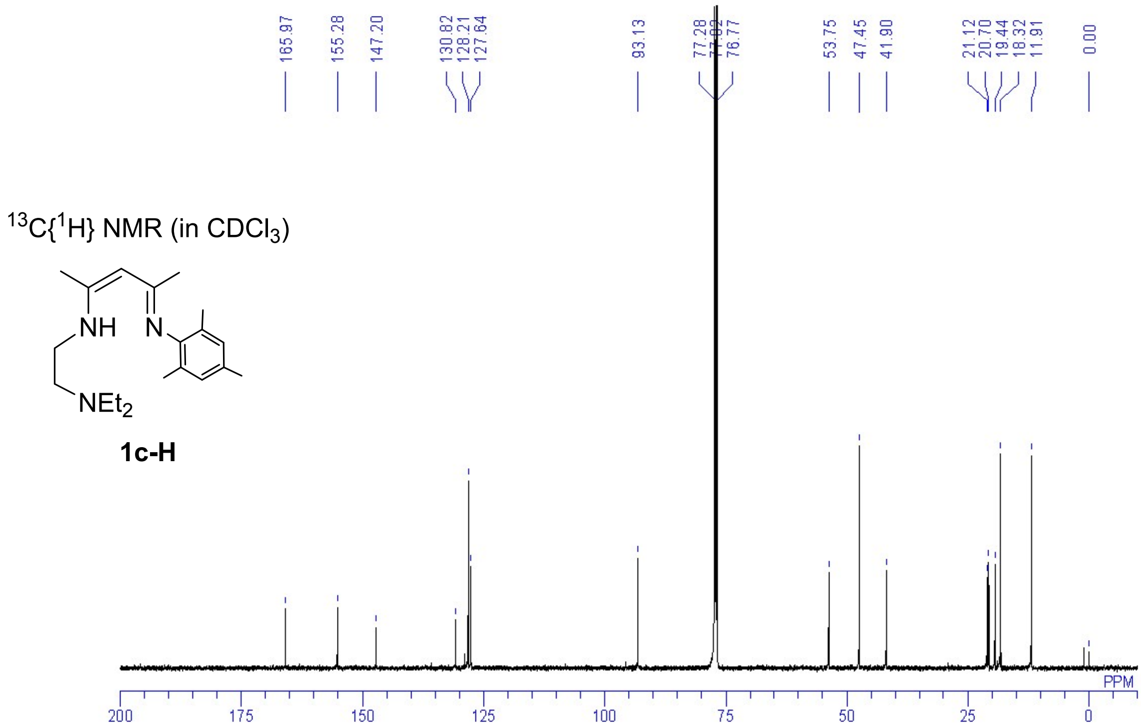
^{13}C{^{1}H} NMR spectrum of **1b-H** (in CDCl$_3$)



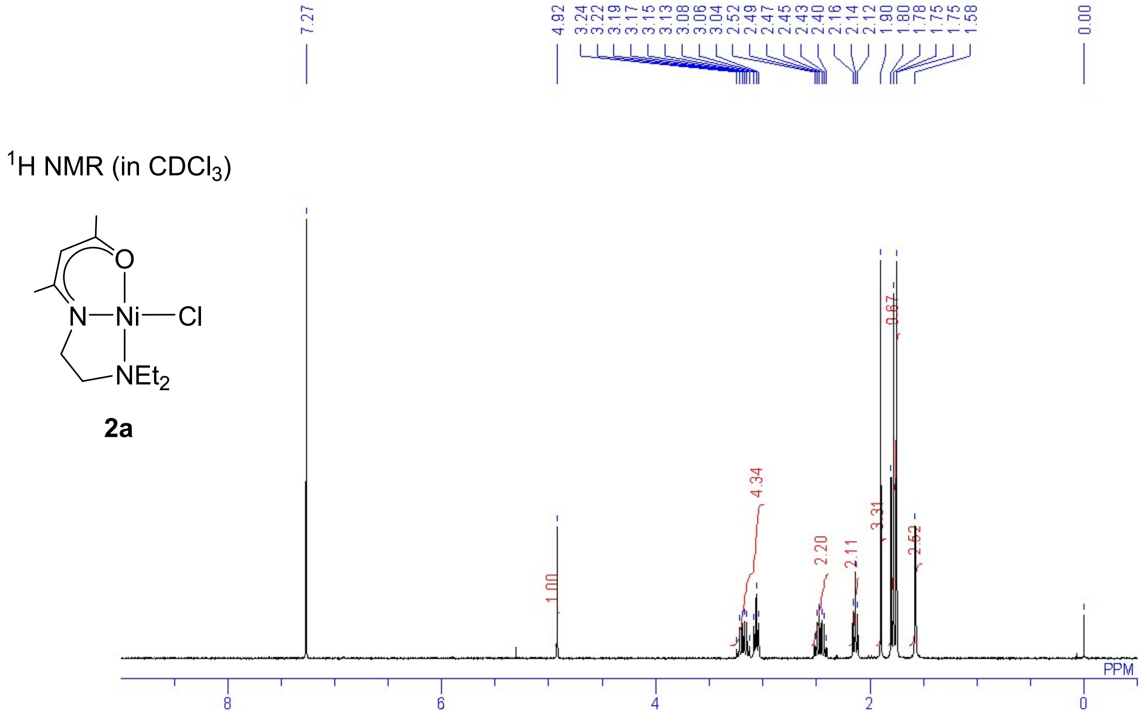
$^{31}P\{^1H\}$ NMR spectrum of **1b-H** (in $CDCl_3$)



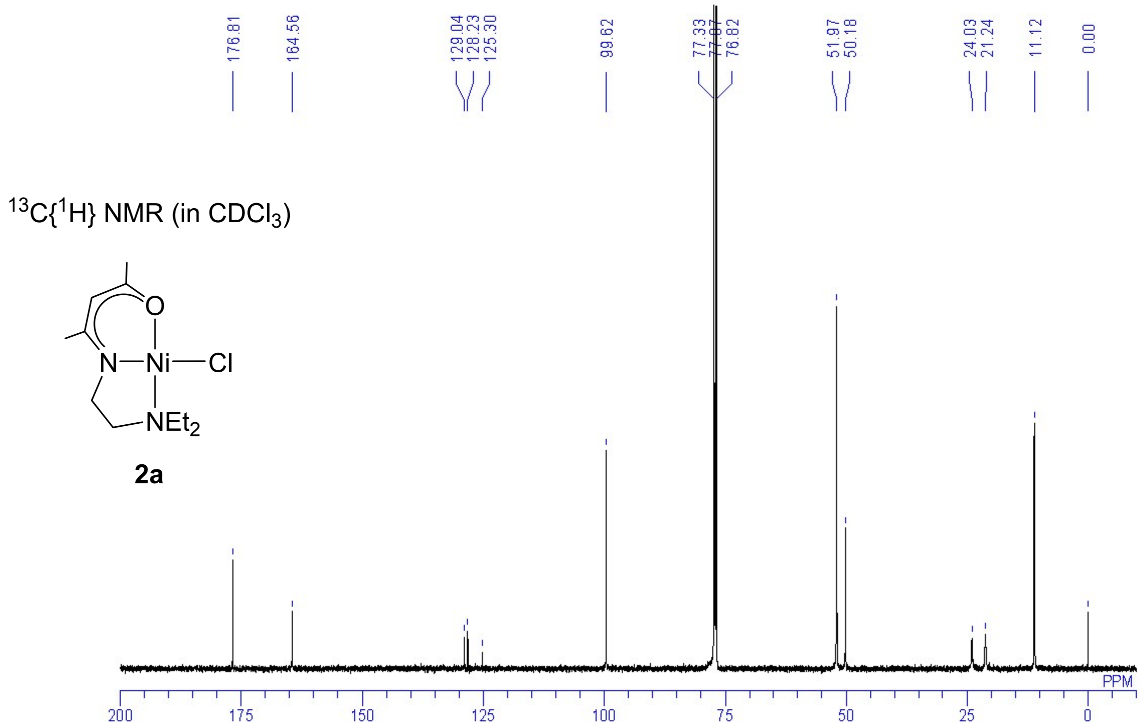
^{1}H NMR spectrum of **1c-H** (in CDCl$_3$)



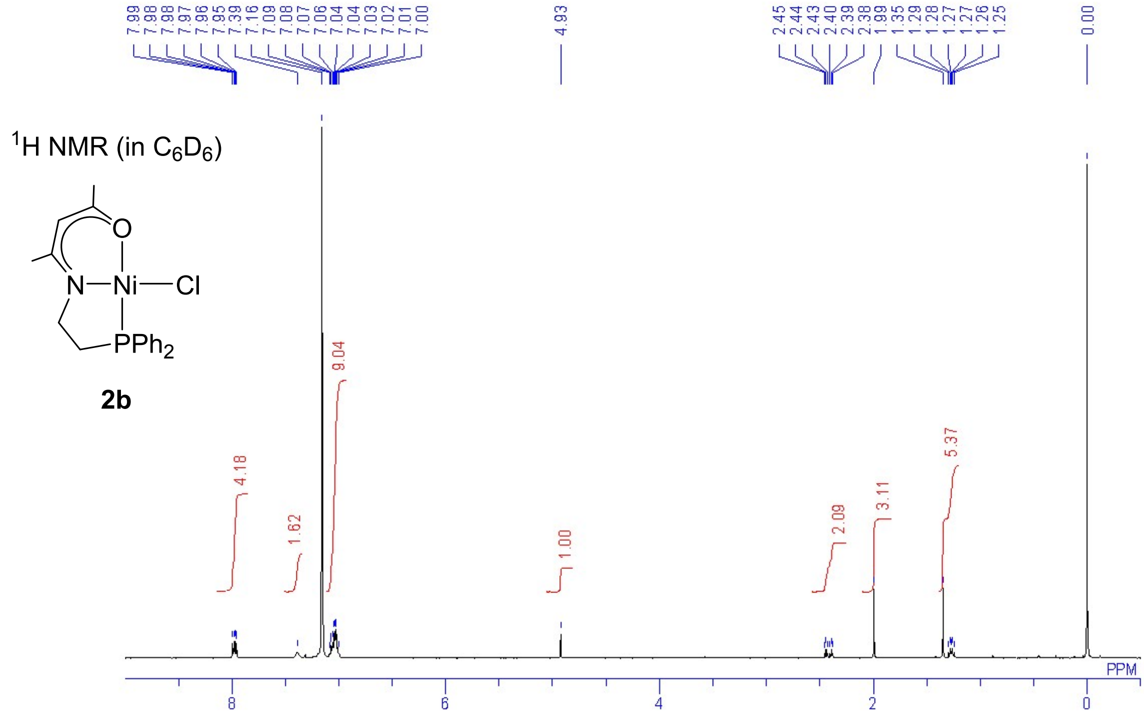
^{13}C{^{1}H} NMR spectrum of **1c-H** (in CDCl$_3$)



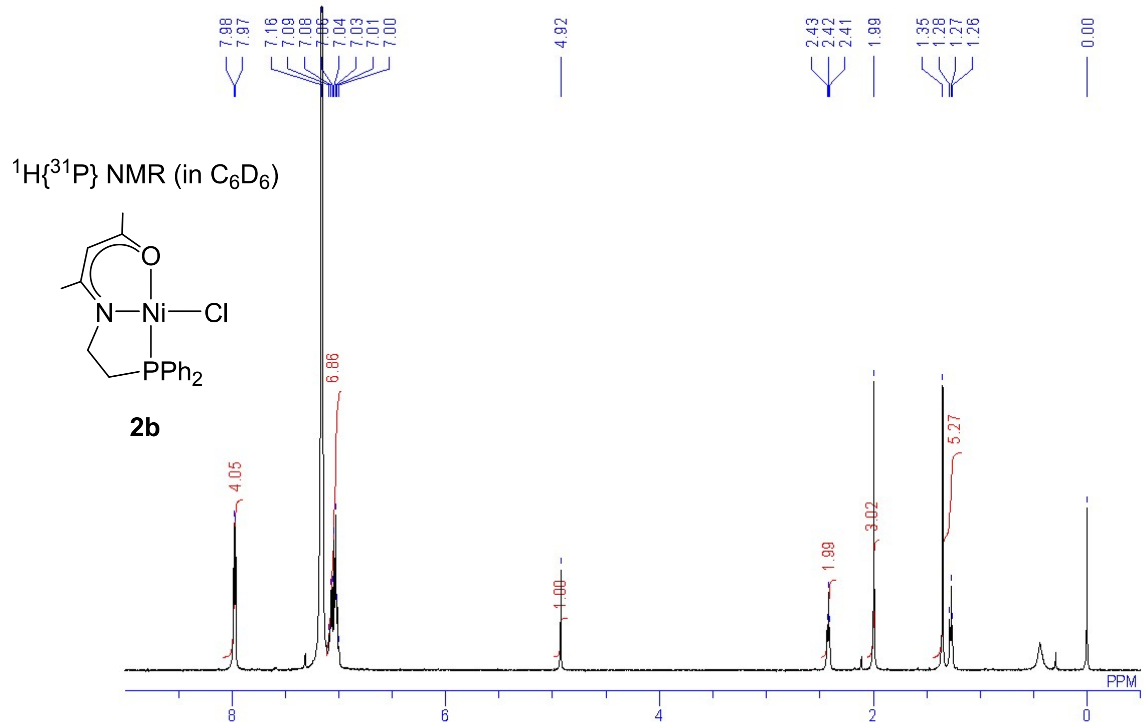
^{1}H NMR spectrum of **2a** (in CDCl$_3$)



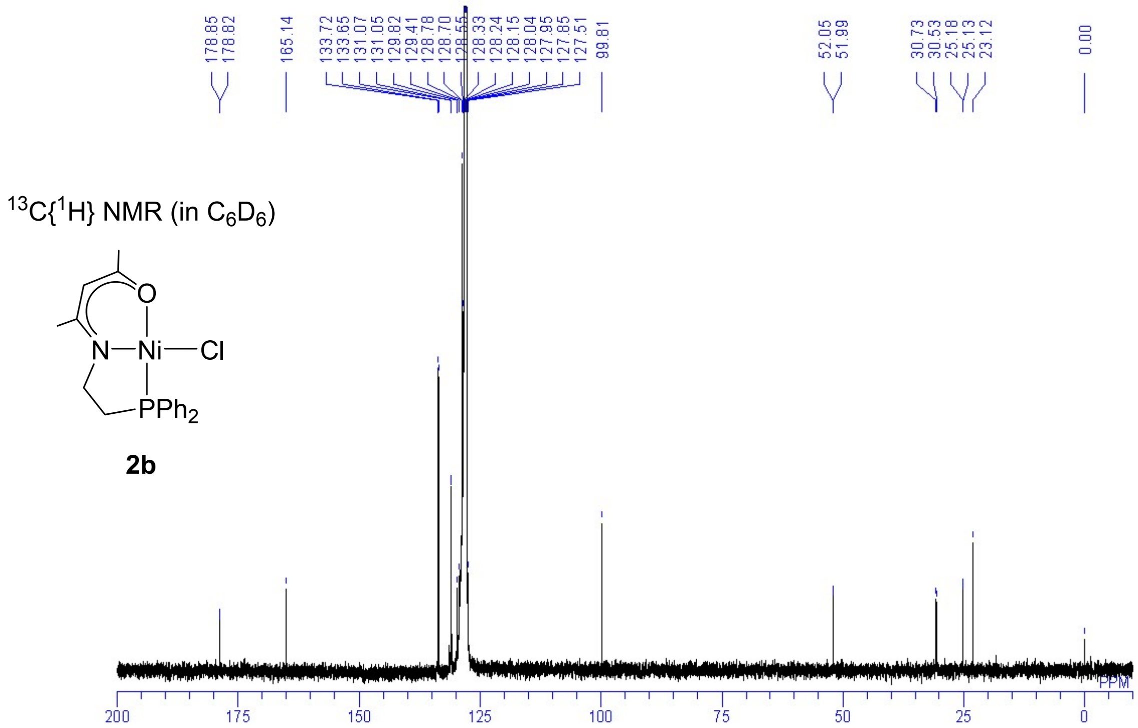
^{13}C{^{1}H} NMR spectrum of **2a** (in CDCl$_3$)



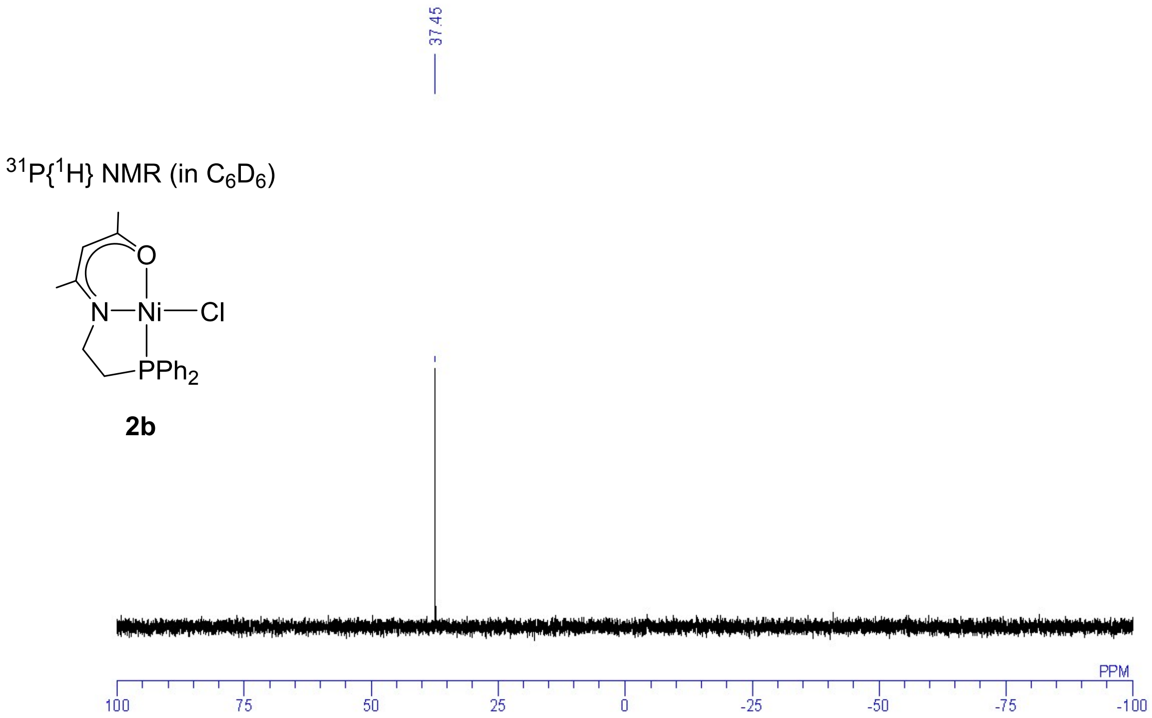
¹H NMR spectrum of **2b** (in C_6D_6)



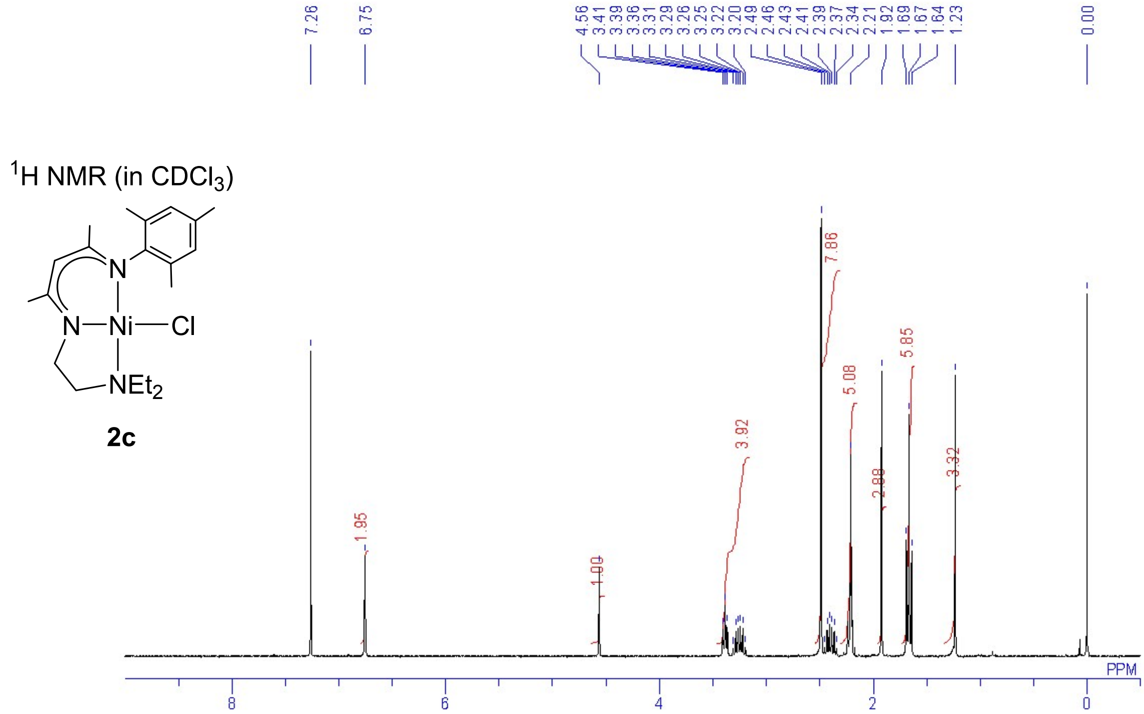
$^1H\{^{31}P\}$ NMR spectrum of **2b** (in C_6D_6)



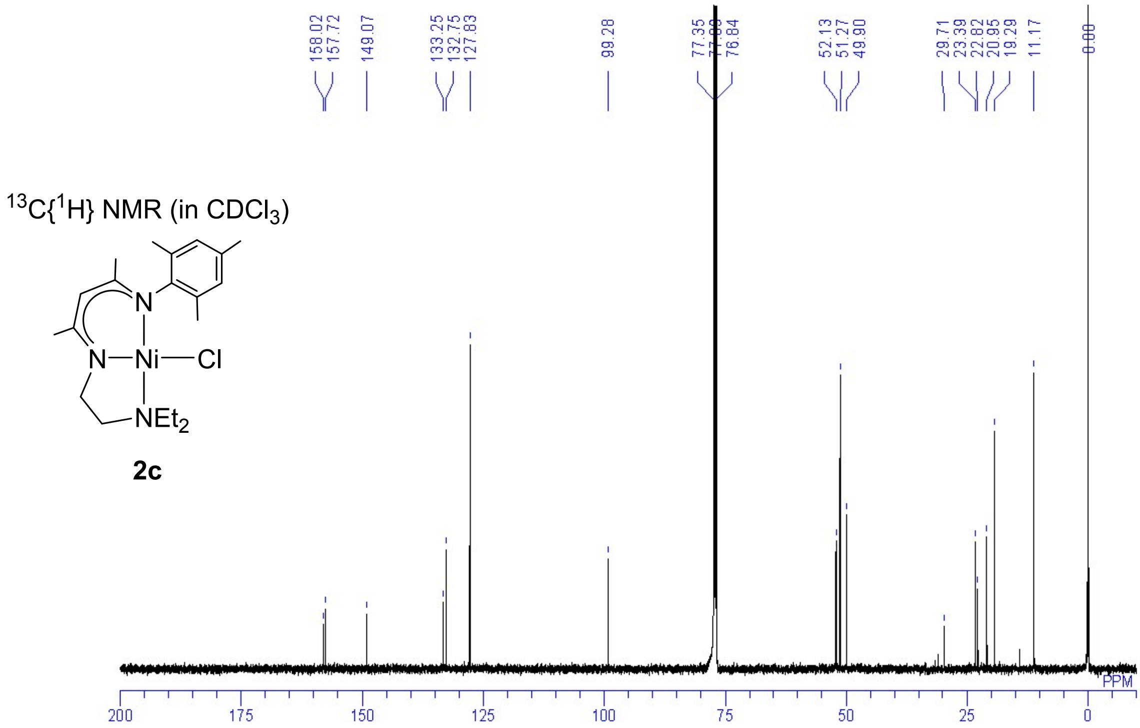
$^{13}C\{^{1}H\}$ NMR spectrum of **2b** (in C_6D_6)



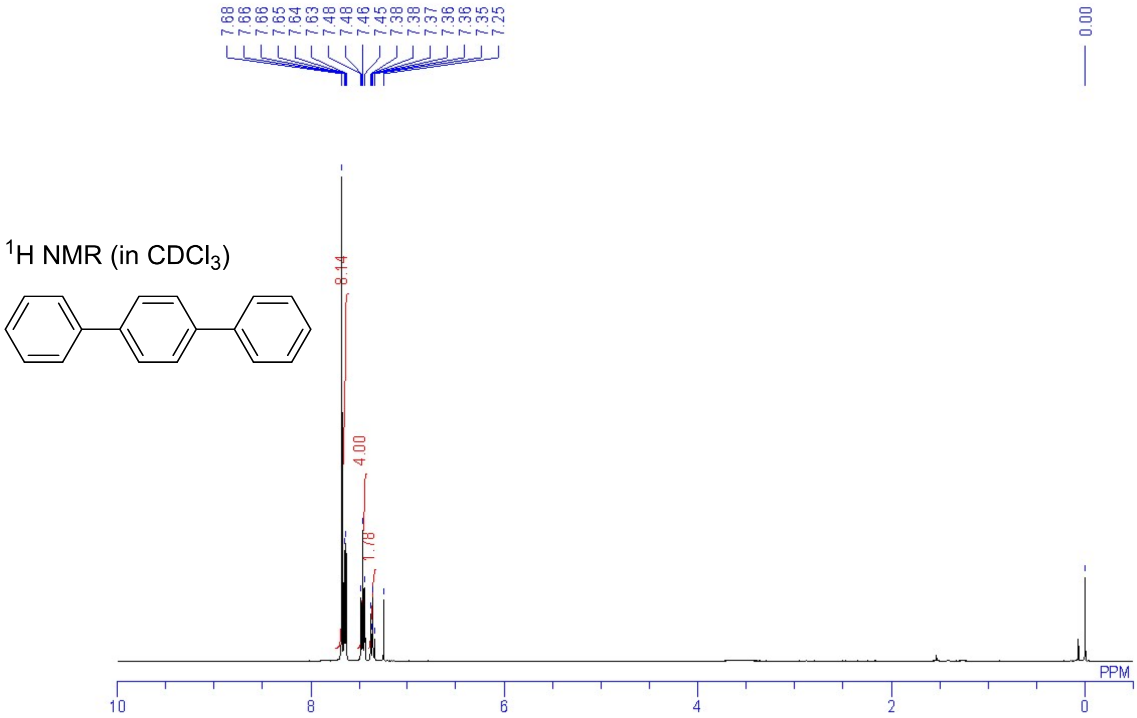
$^{31}P\{^{1}H\}$ NMR spectrum of **2b** (in C_6D_6)



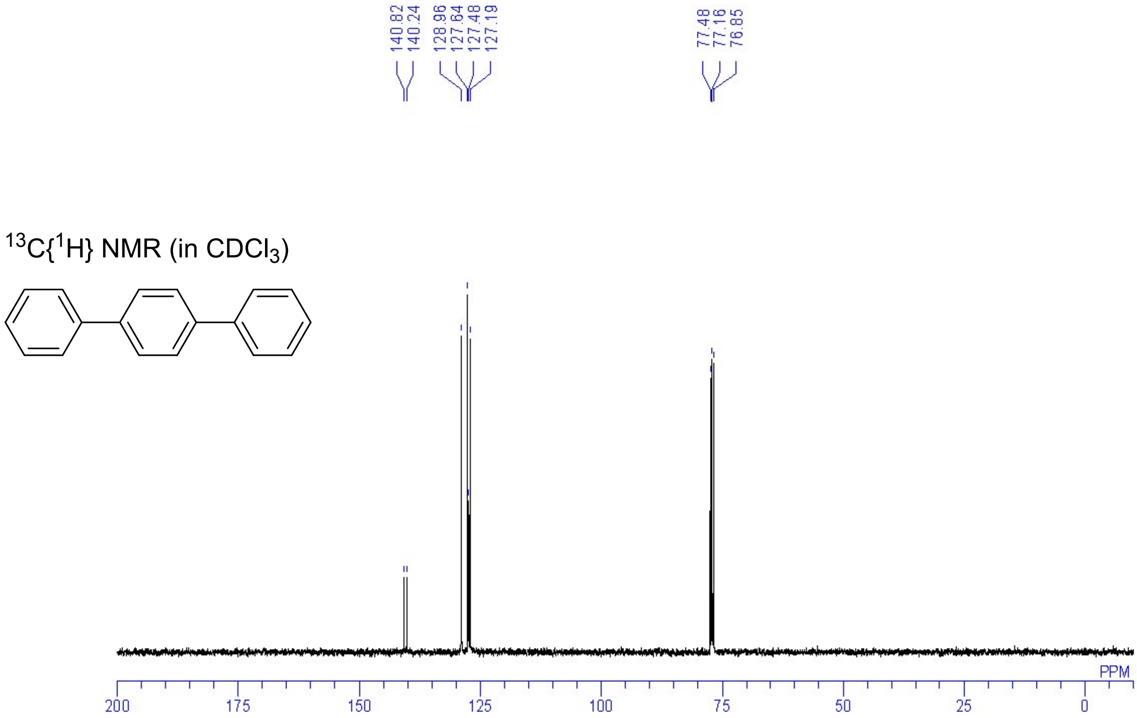
^{1}H NMR spectrum of **2c** (in CDCl$_3$)



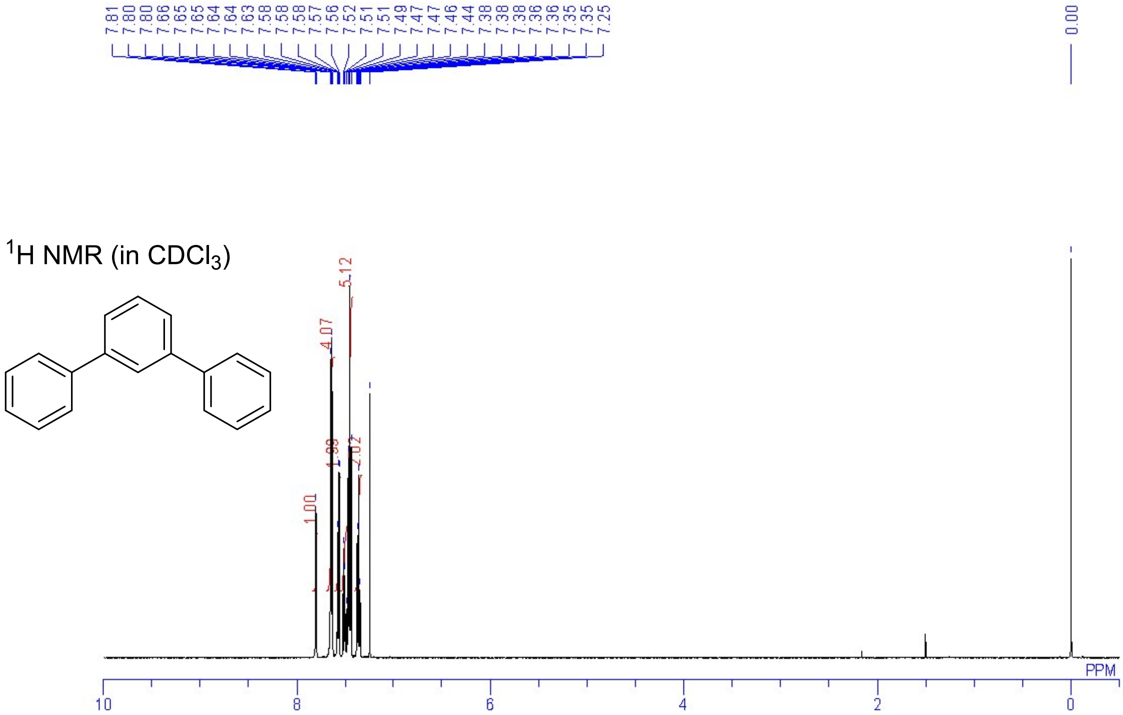
^{13}C{^{1}H} NMR spectrum of **2c** (in CDCl$_3$)



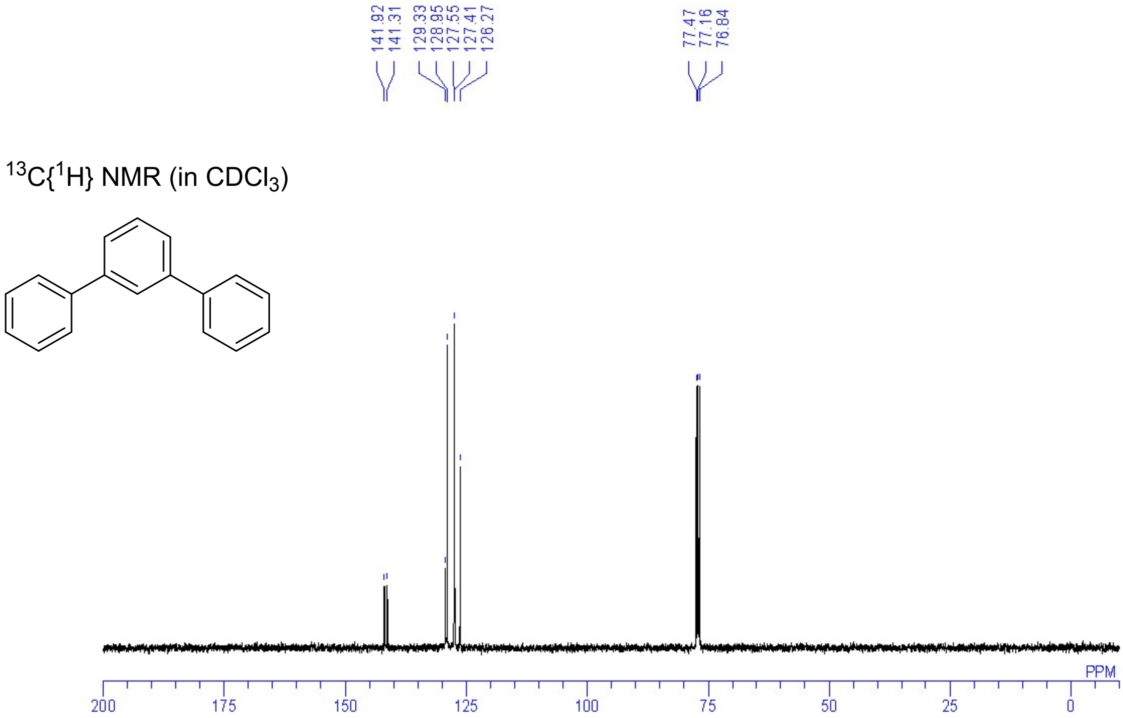
^{1}H NMR spectrum of *p*-terphenyl (in CDCl$_3$)



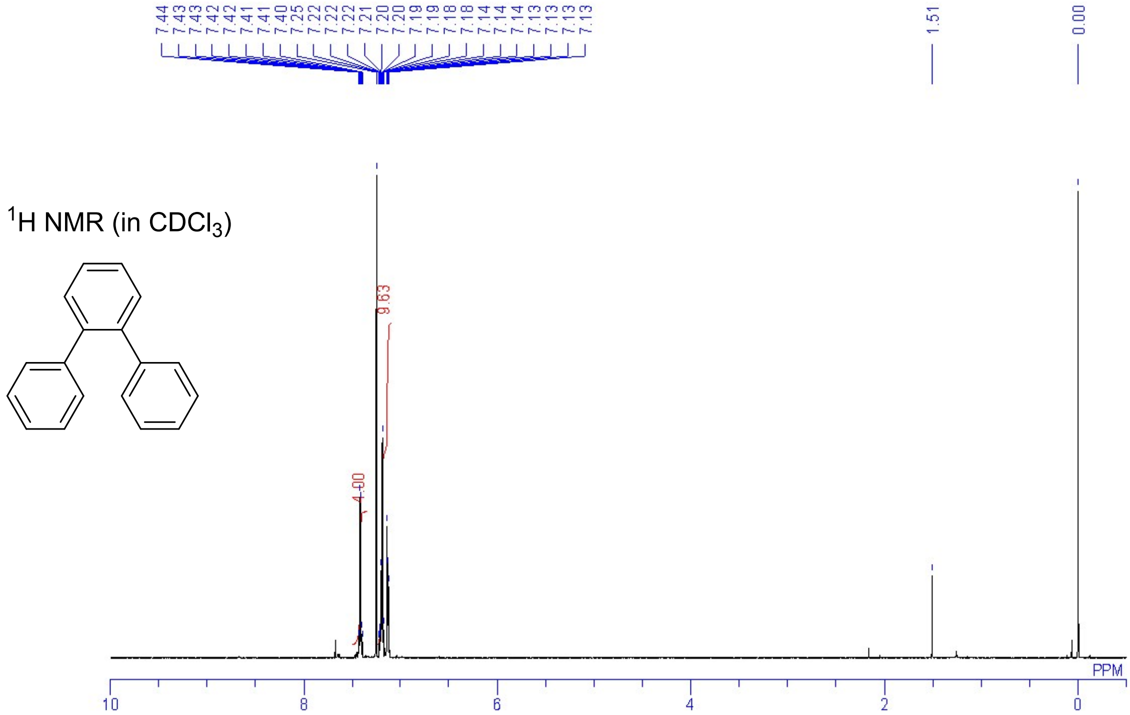
^{13}C{^{1}H} NMR spectrum of *p*-terphenyl (in CDCl$_3$)



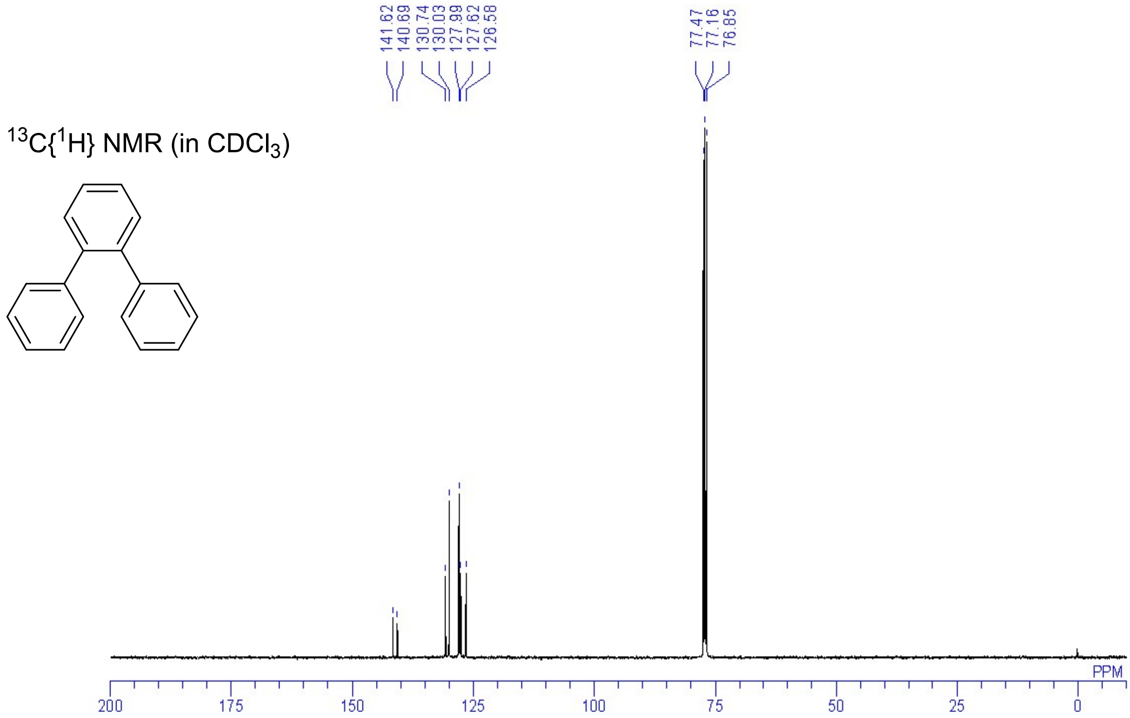
^{1}H NMR spectrum of *m*-terphenyl (in CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of *m*-terphenyl (in CDCl$_3$)



^{1}H NMR spectrum of *o*-terphenyl (in CDCl$_3$)



^{13}C{^{1}H} NMR spectrum of *o*-terphenyl (in CDCl$_3$)

References

1. D. Spasyuk and D. G. Gusev, *Organometallics*, 2012, **31**, 5239–5242.
2. Y. Yamaguchi, H. Ando, M. Nagaya, H. Hinago, T. Ito and M Asami, *Chem. Lett.*, 2011, **40**, 983–985.
3. K. Hiraki, T. Masumoto, Y. Fuchita and Y. Zegi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1044–1047.
4. D. M. Granum, P. J. Riedel, J. A. Crawford, T. K. Mahle, C. M. Wyss, A. K. Begej, N. Arulsamy, B. S. Pierce, and M. P. Mehn, *Dalton Trans.*, 2011, **40**, 5881–5890.
5. H. L. Wiencko, E. Kogut and T. H. Warren, *Inorg. Chim. Acta*, 2003, **345**, 199–208.
6. L. M. Venanzi, *J. Chem. Soc.*, 1958, 719–724.
7. CrytalClear: Data Collection and Processing Software, Rigaku Corporation (1998–2014). Tokyo 196-8666, Japan.
8. CrysAlisPro: Data Collection and Processing Software, Rigaku Corporation (2015). Tokyo 196-8666, Japan.
9. SHELXT Version 2014/5: G. M. Sheldrick, *Acta Cryst.,* 2014, **A70**, C1437.
10. SHELXL Version2014/7: G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112–122.
11. CrystalStructure 4.2.1: Crystal Structure Analysis Package, Rigaku Corporation (2000–2016). Tokyo 196-8666, Japan.
12. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
13. A. D. Beck, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
14. R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
15. (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270–283;
    (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284–298;
    (c) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299–310.
16. Jmol: An open-source Java viewer for chemical structures in 3D. http://www.jmol.org
17. L. Liu, Y. Zhang and B. Xin, *J. Org. Chem.*, 2006, **71**, 3944–3997.
18. L.-C. Liang, P.-S. Chien and M.-H. Huang, *Organometallics*, 2005, **24**, 353–357.