Supplementary Information for the paper

Synthesis and reactivity of the cyclobutadiene nickel bromide

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Contents

Synthetic procedures

General remarks

All reactions were carried out under an argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. Isolation of all products was carried out in air. ^{1}H, ^{11}B and ^{13}C NMR spectra were measured with a Bruker Avance 400 spectrometer at 20 °C. Chemical shifts are reported in ppm using the residual signals of the solvents as internal standards. Most of reagents were purchased from Acros, Aldrich or Vekton and used as received. Column chromatography was carried out using Macherey-Nagel silica gel 60 (0.04−0.063 mm particle size).

Synthesis of tetraethylcyclobutadiene nickel dibromide (**1**)

[(C_4Et_4)$NiBr_2$]$_2$ (**1**)

The suspension of $NiBr_2$ (436 mg, 2.0 mmol) in 0.7 ml THF and 0.7 ml C_2H_5OH was stirred at 75 ºC for 15 minutes. Then 3-hexyne (0.23 ml, 2.0 mmol) was added to the hot, dark-green solution. Magnesium powder (30 mg, 1.3 mmol) was added immediately afterwards. The color of the mixture changed to dark purple within 10-30 seconds. The mixture was held at 75 ºC for 24 hours. After cooling, concentrated HBr (0.3 ml) was added, the mixture was vigorously shaken and the solvent was evaporated. Purple residue was washed by c.a. 20 ml of petroleum ether to remove the hexaethylbenzene. The product was extracted by toluene. Toluene solution was filtered from the precipitate of unreacted $NiBr_2$ and the solvent was removed in vacuum. Recrystallization from CH_2Cl_2/ petroleum ether at −32 ºC gives 97 mg of product as purple crystals (24% yield based on alkyne).

In our hands dark magnesium powder that was stored in a common bottle in air for more than 35 years typically gave the highest yields of **1** (25−30%). However, fresh magnesium powder and commercially available magnesium chips (6-35 mesh, >99% purity, Aldrich product) were also suitable and typically gave ca. 15−20% yield of **1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.02 (q, *J* = 7.5 Hz, 8H, CH_2), 1.17 (t, *J* = 7.5 Hz, 12H, CH_3). ^{13}C NMR δ: 111.12, 21.60, 10.95. Cf. G. Guerch, P. Mauret, J. Jaud, J. Galy, *Acta Cryst.*, **1977**, *B33*, 3747-3751.

Figure S0. Photo of the reaction mixture after the complex **1** was formed.

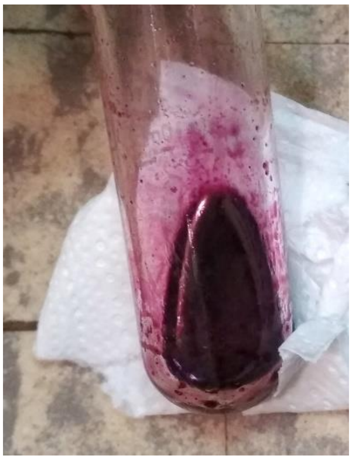


Figure S1. ^{1}H NMR spectra of $[(C_4Et_4)NiBr_2]_2$ (**1**).

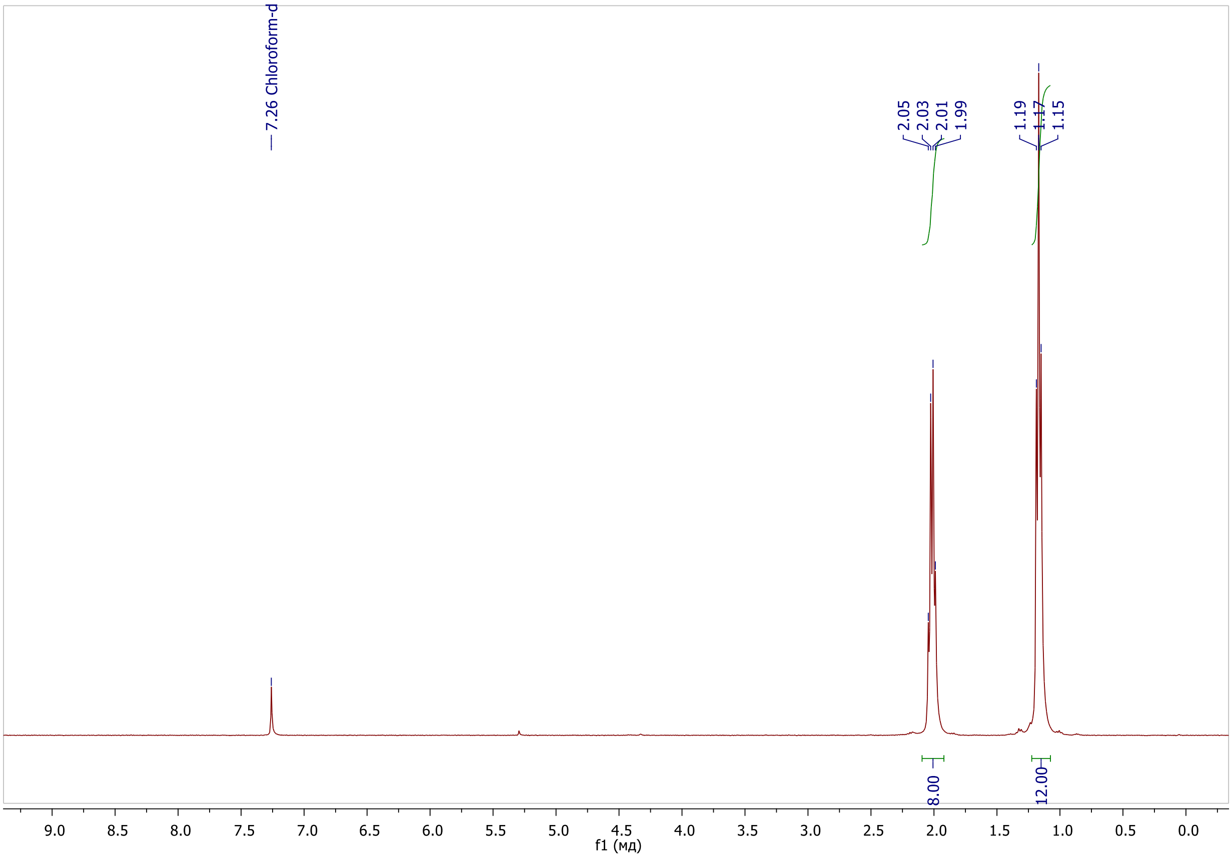


Figure S2. ^{13}C NMR spectra of $[(C_4Et_4)NiBr_2]_2$ (**1**).

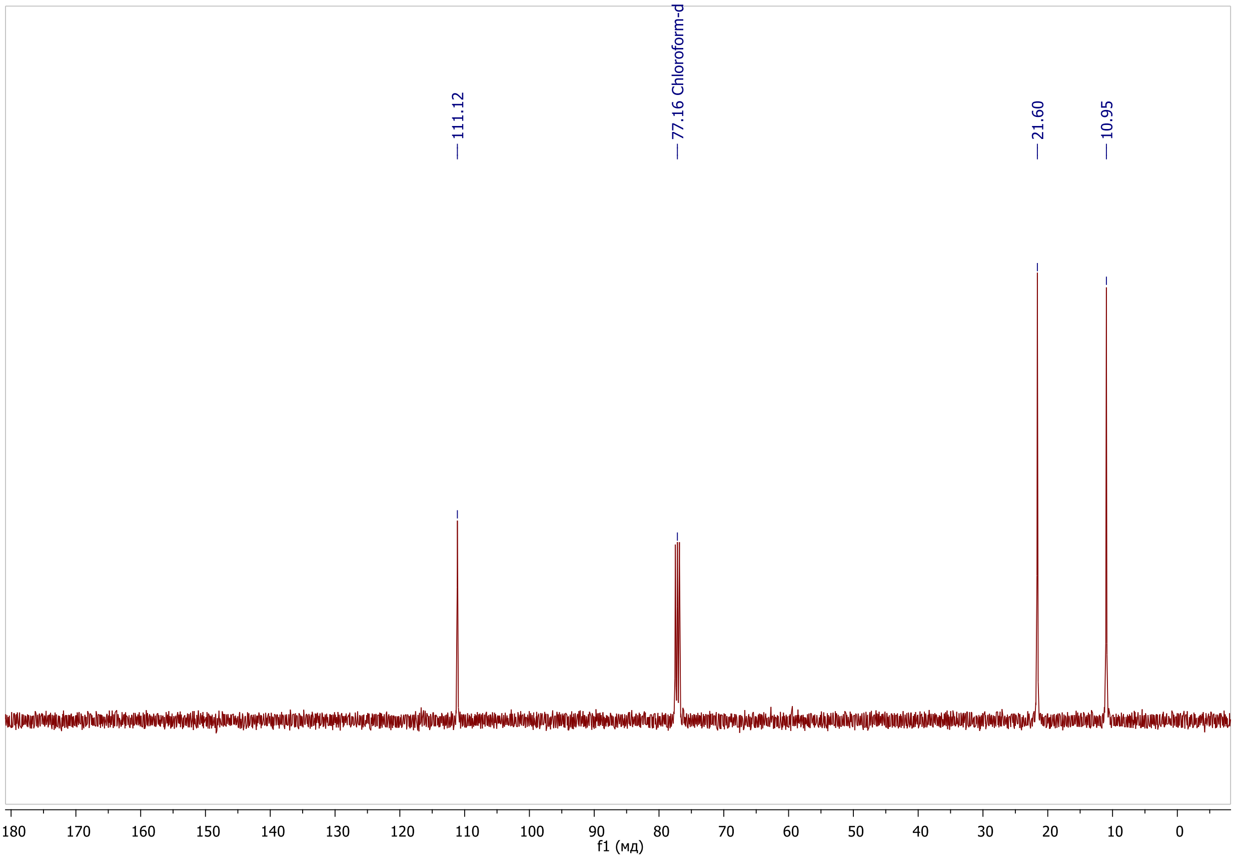


Table S1. *Optimization of reaction conditions for synthesis of* $[(C_4Et_4)NiBr_2]_2$ (**1**).

Entry	Additive	Activation of magnesium	T, ºC	Solvent	Yield*, %
1	–	–	85	THF or EtOH	0
2	Mg	–	75	THF	0[a]
3	Mg	I_2	75	THF	traces
4	Mg	Na	75	THF	traces
5	Mg	ultrasound	75	THF	traces
6	Mg	CH_3I	75	THF	0–15%, non-reproducible
7	–	$SnCl_2$	75	THF	0
8	Mg	MeOH	80	MeOH	0
9	Mg, 63 mol.%	EtOH	75	EtOH	8
10	Mg, 25 mol%	EtOH	75	THF	8
11	Mg, 45 mol%	EtOH	75	THF	10

12	Mg, 63 mol%	EtOH	75	THF	24
13	Mg, 110 mol%	EtOH	75	THF	16
14	Mg	EtOH	75	THF	0[b]
15	Mg, 83 mol%	EtOH	75	THF	15[c]
16	Mg, 45 mol%	EtOH	75	THF	10[d]
17	Mg, 63 mol%	EtOH	75	THF	traces[e]
18	Mg, 45 mol%	EtOH	85	THF	8
19	Mg, 110 mol%	EtOH	75	THF	25[f]
20	Al	EtOH	75	THF	traces
21	Zn	EtOH	75	THF	5

Standard conditions: 436 mg of $NiBr_2$, 0.23 ml of 3-hexyne, additive, activator, 75 °C, 24 hours.
* Isolated yield based on alkyne amount.
a) (dimetoxyethane)$NiBr_2$ was used as a nickel source; b) 100 mg $NiBr_2$ was used; c) stepwise addition of magnesium; d) 0.5 ml of 3-hexyne was used; e) 0.11 ml of 3-hexyne was used; f) 120 hours.

Note: According to our observations, the most important factors affecting the reaction yield are the presence of ethanol and the high concentration of nickel bromide (with less 100 mg of $NiBr_2$ the reaction does not start, see entry 14). The optimal amount of magnesium depends on its grade (fresh magnesium can be used in smaller amounts). The purify of ethanol does not significantly affect the reaction outcome.

*Synthesis and characterization of complexes **2-4**.*

$(C_4Et_4)NiBr_2(PPh_3)$ (**2a**)

The solution of $[(C_4Et_4)NiBr_2]_2$ (19 mg, 0.025 mmol) and PPh_3 (26 mg, 0.1 mmol) in 1 ml THF was stirred for 8 hours. The color of the solution changed to dark red with the gradual formation of a red precipitate of the product. Petroleum ether (4 ml) was added and solution was decanted. Precipitate of the product was washed with cold Et_2O (2x5 ml) and dried in vacuum. Yield – 25 mg (78%). The crystals of complex for X-ray analysis were grown from CH_2Cl_2/petroleum ether mixture at −32 °C. Anal. calc. for $C_{30}H_{35}Br_2NiP$: C 55.86, H 5.47. Found: C 55.59, H 5.57.

^{1}H NMR (300 MHz, $CDCl_3$, 240 K) δ: 7.84 (brs, 6H), 7.51 (brs, 6H), 7.31 (brs, 3H), 1.99 (brs, 8H), 1.15 (brs, 12H). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.84 (brs, 6H), 7.45 (brs, 9H), 2.04 (brs, 8H), 1.18 (brs, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ: 134.81, 130.37, 128.26, 110.17, 20.31, 11.28. ^{31}P NMR (121 MHz, $CDCl_3$, 240 K) δ: 19.31. ^{31}P NMR (162 MHz, $CDCl_3$, 298 K) δ: 29.27, 19.37.

Figure S3. ^{1}H NMR spectra of $(C_4Et_4)NiBr_2(PPh_3)$ (**2a**) at 240 K.

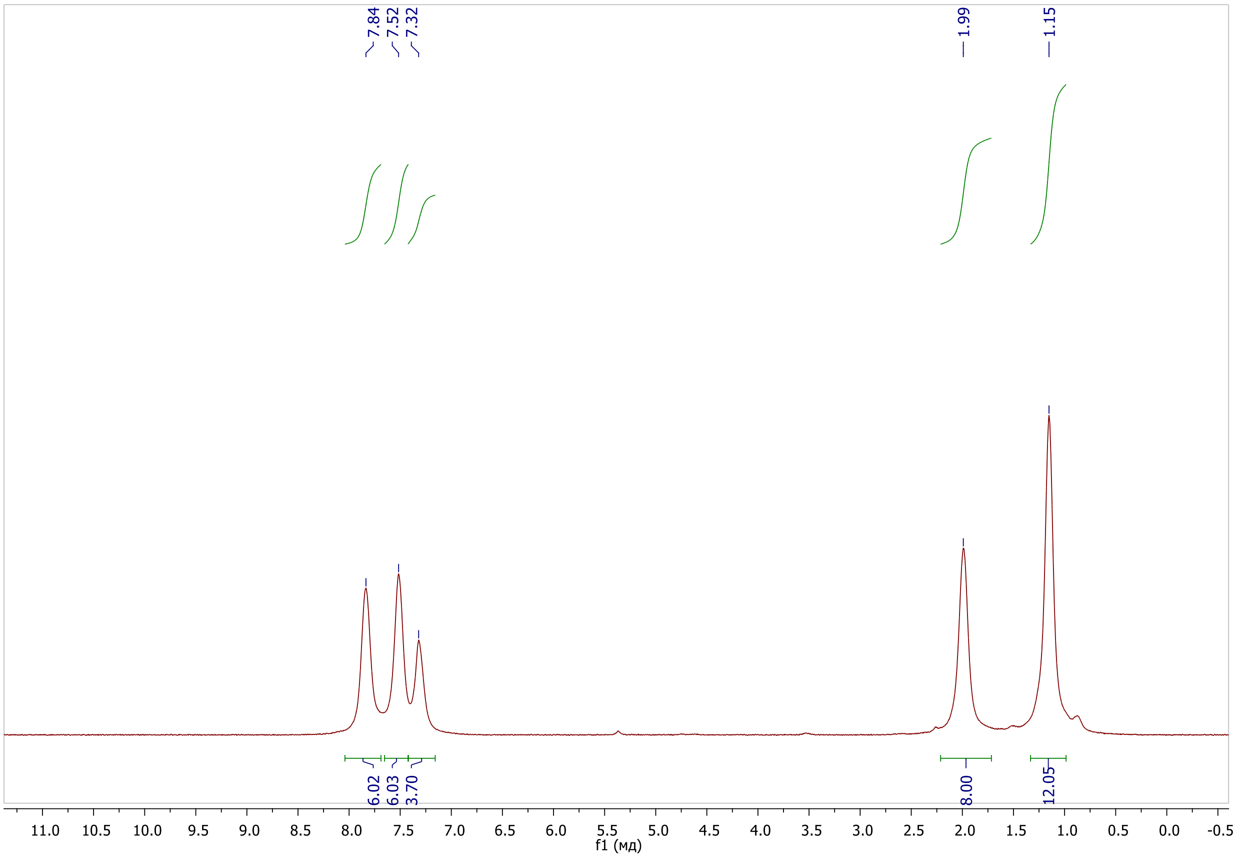


Figure S4. ^{1}H NMR spectra of $(C_4Et_4)NiBr_2(PPh_3)$ (**2a**) at 298 K.

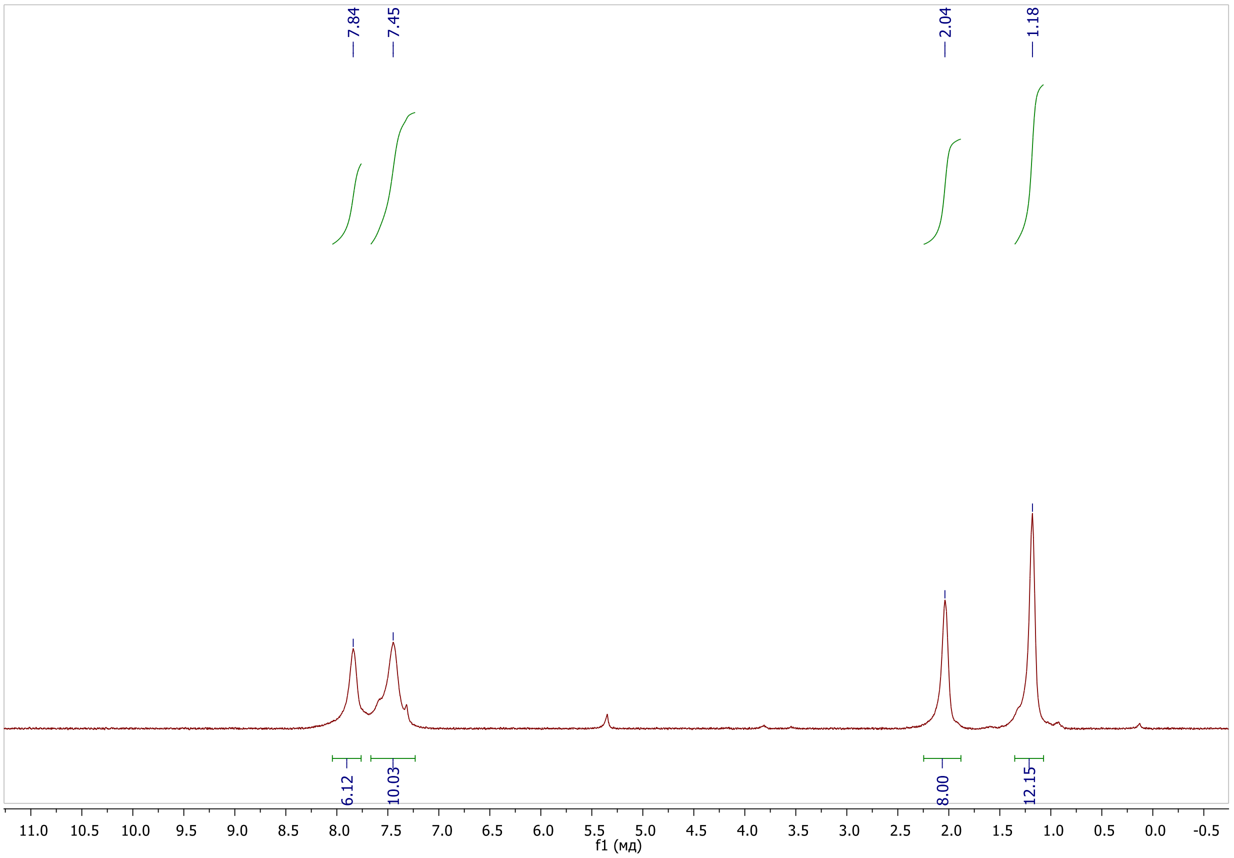


Figure S5. ^{13}C NMR spectra of $(C_4Et_4)NiBr_2(PPh_3)$ (**2a**) at 298 K.

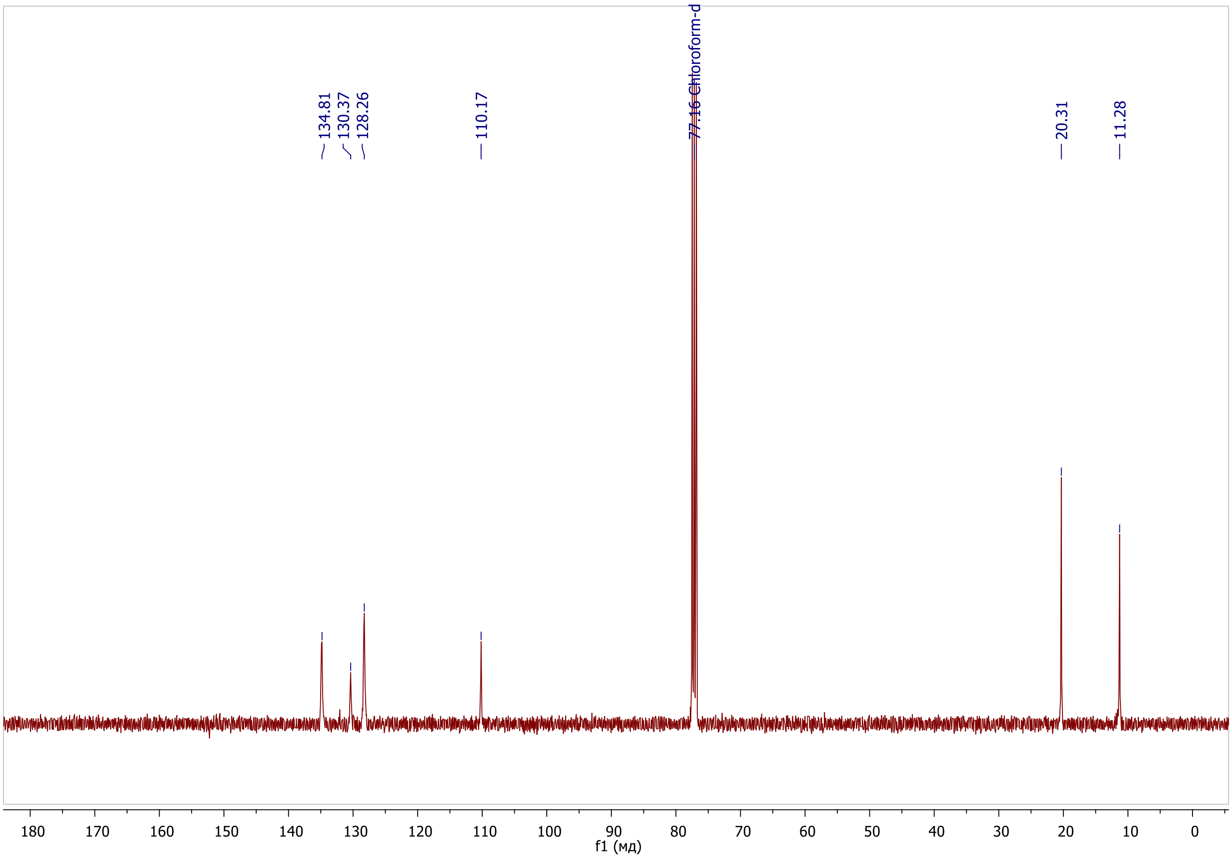


Figure S6. ^{31}P NMR spectra of $(C_4Et_4)NiBr_2(PPh_3)$ (**2a**) at 240 K.

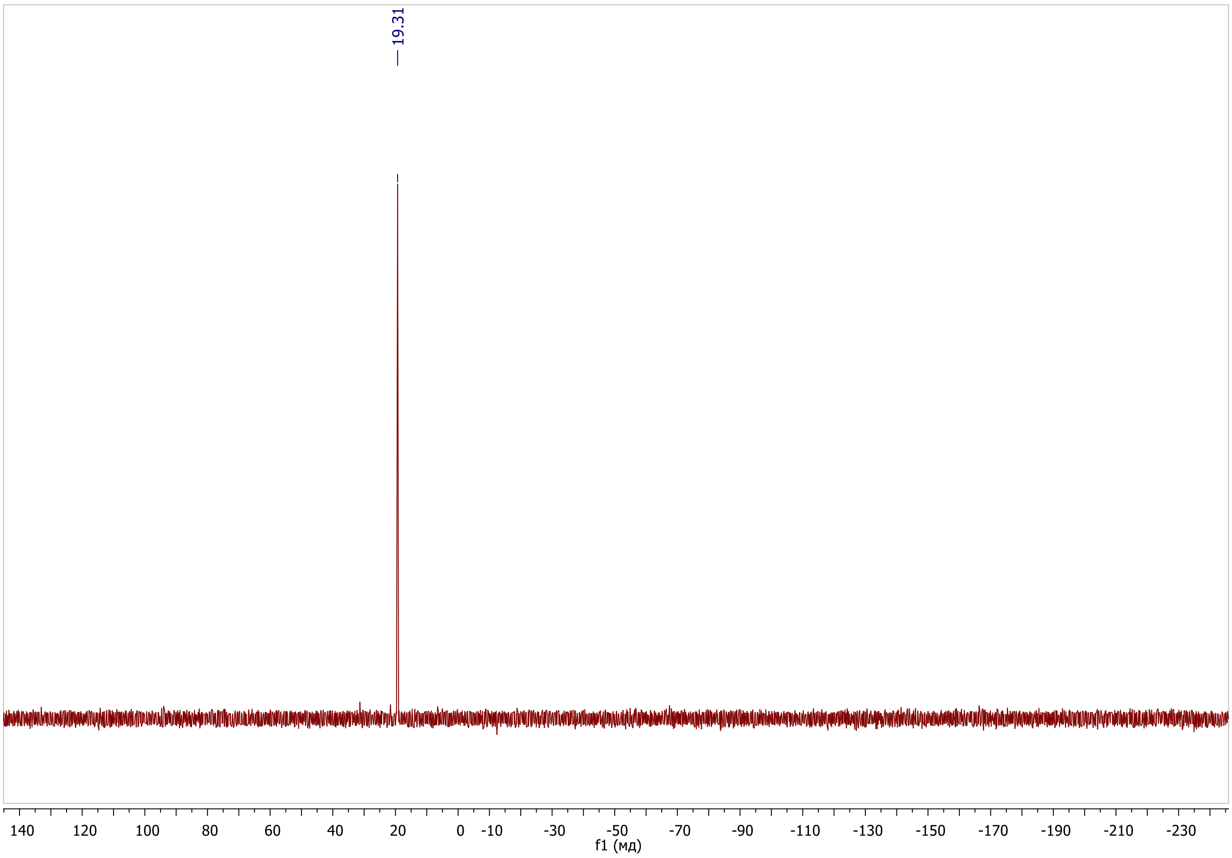
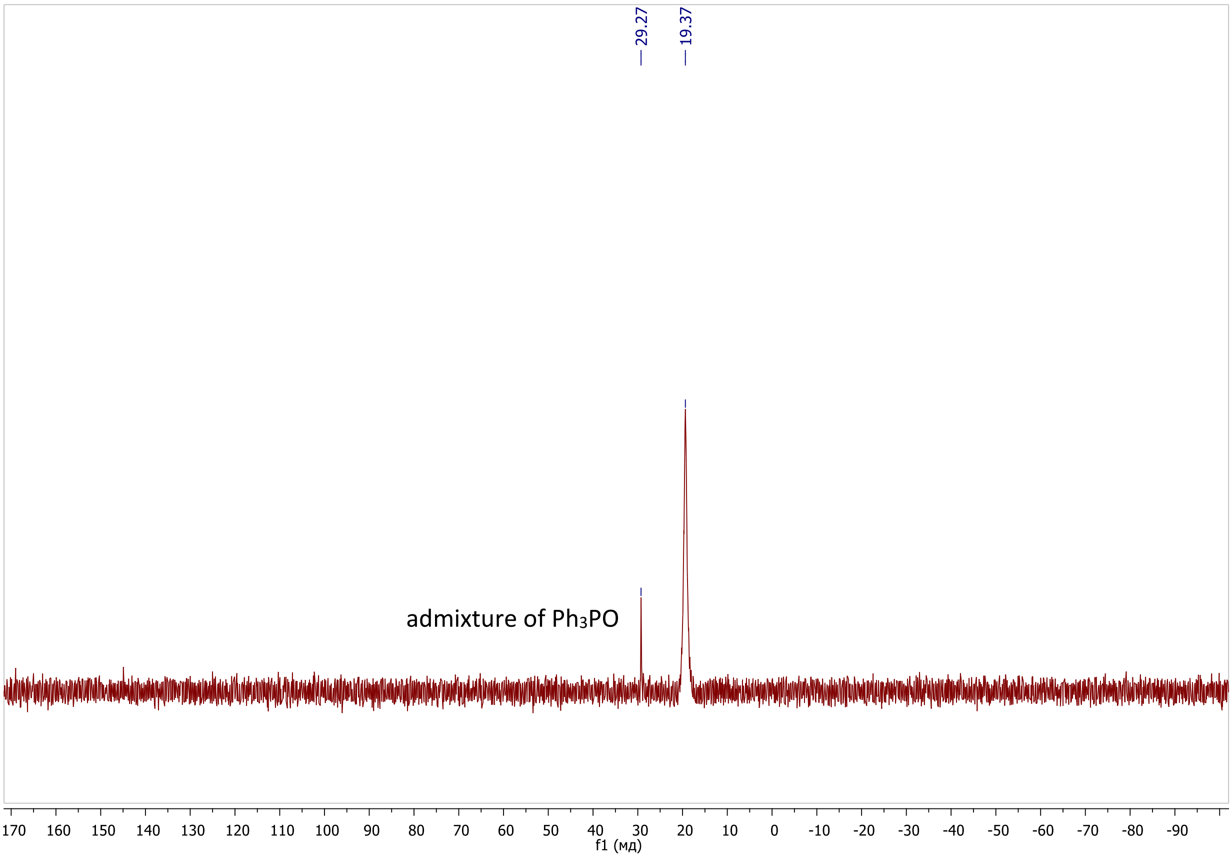


Figure S7. ^{31}P NMR spectra of (C_4Et_4)$NiBr_2$(PPh_3) (**2a**) at 298 K.



(C_4Et_4)$NiBr_2$($P(OMe)_3$) (**2b**)

To the solution of [(C_4Et_4)$NiBr_2$]$_2$ (40 mg, 0.052 mmol) in 1 ml THF was added $P(OMe)_3$ (13 mg, 0.105 mmol) as 0.117 ml of stock solution in THF. The color immediately changed to dark red and mixture was stirred for 8 hours. The solvent was evaporated and residue thoroughly dried in vacuum for 2 hours. Yield – 51 mg (96%). The crystals of complex for X-ray analysis were grown from CH_2Cl_2/petroleum ether mixture at −32 °C. Anal. calc. for $C_{15}H_{29}Br_2NiO_3P$: C 35.54, H 5.77. Found: C 35.34, H 5.74.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.85 (d, J = 8.7 Hz, 9H, OMe), 2.19 (brs, 8H, CH_2), 1.20 (brs, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 111.52, 54.72 (d, J=6.3 Hz), 20.26, 11.16. ^{31}P NMR (162 MHz, $CDCl_3$, 298K) δ: 127.97.

Figure S8. ^{1}H NMR spectra of $(C_4Et_4)NiBr_2(P(OMe)_3)$ (**2b**).

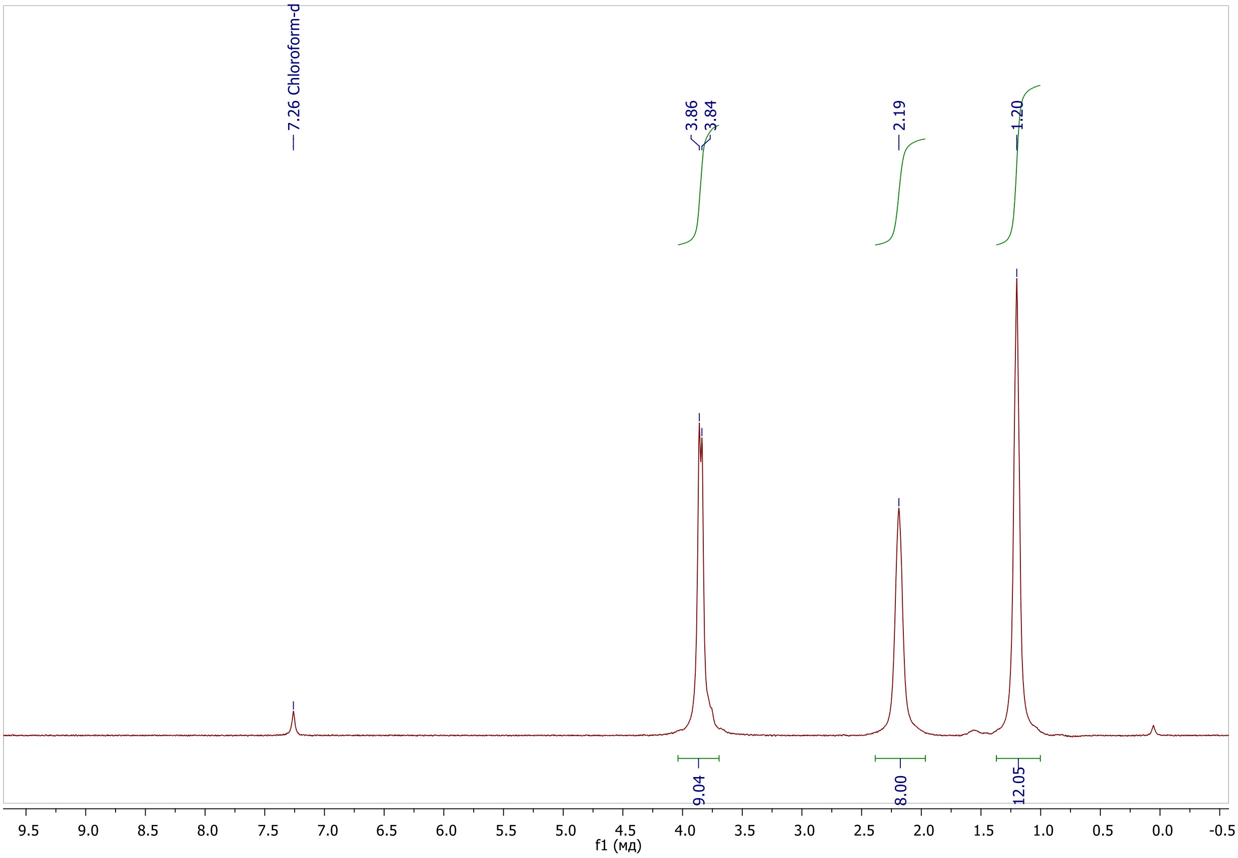


Figure S9. ^{13}C NMR spectra of $(C_4Et_4)NiBr_2(P(OMe)_3)$ (**2b**).

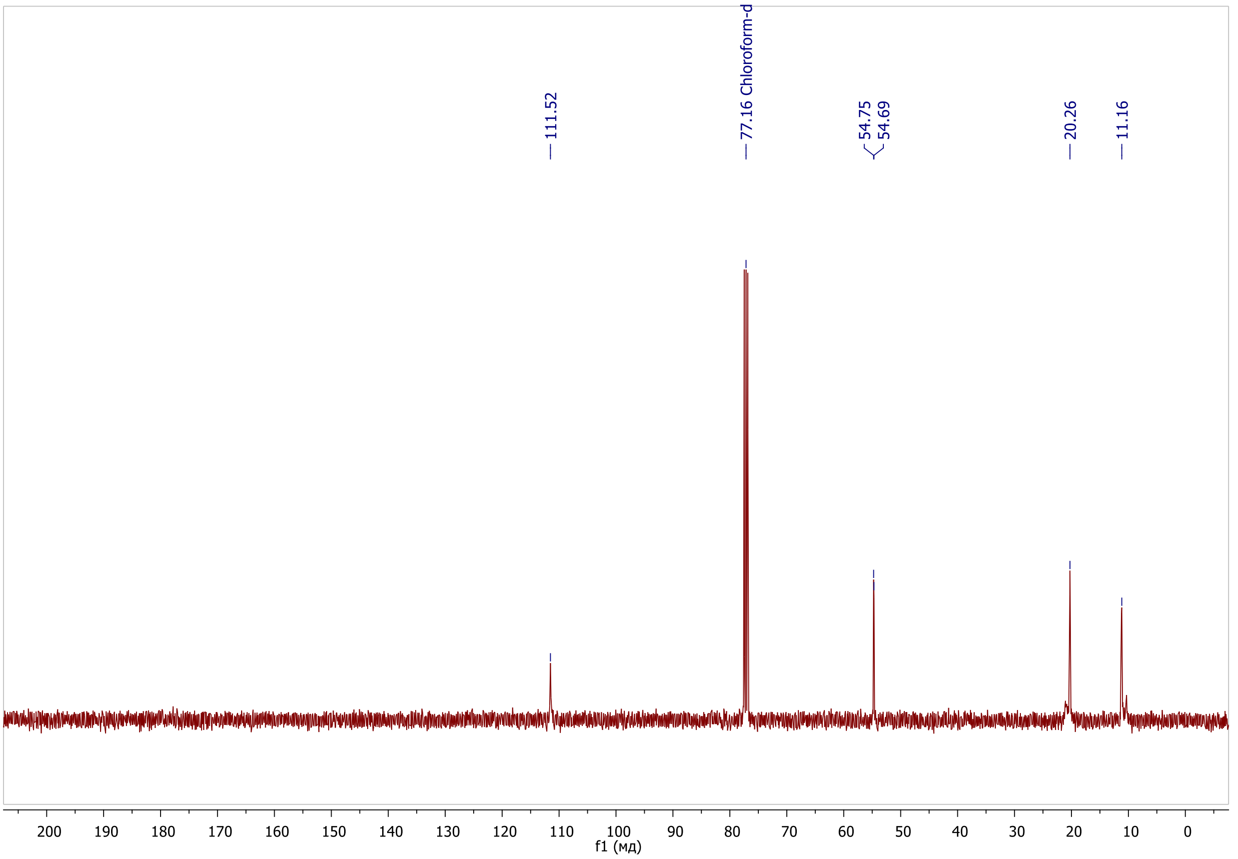
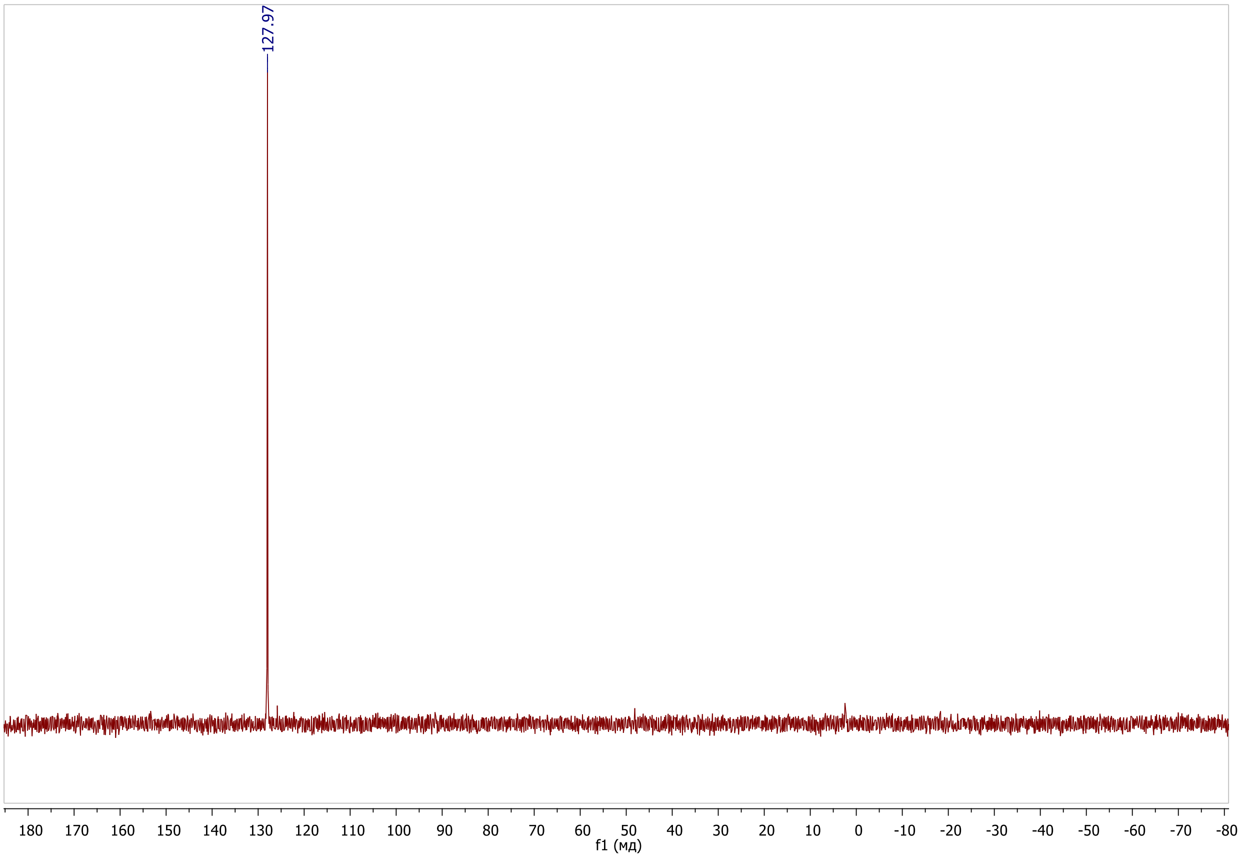


Figure S10. ^{31}P NMR spectra of $(C_4Et_4)NiBr_2(P(OMe)_3)$ (**2b**) at 298 K.



$(C_4Et_4)NiBr_2(py)$ (**2c**)

To the solution of $[(C_4Et_4)NiBr_2]_2$ (24 mg, 0.031mmol) in 1 ml THF was added pyridine (7.5 mg, 0.095 mmol) as 0.107 ml of stock solution in THF. The color of the solution changed to dark red with the gradual formation of a red precipitate of the product. The mixture was stirred for 8 hours. The diethyl ester (5 ml) was added and solution was decanted. Red precipitate of the product washed with cold Et_2O (2x5 ml) and dried in vacuum. Yield – 28 mg (97%). The crystals of complex for X-ray analysis were grown from CH_2Cl_2/Et_2O mixture at −32 °C. Anal. calc. for $C_{17}H_{25}Br_2NNi$: C 44.21, H 5.46, N 3.03. Found: C 44.12, H 5.31, N 3.22.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.48 (bs, 2H, py), 8.2-6.9 (bs, 3H, py), 1.91 (m, 8H, CH_2), 1.17 (t, J =6.5 Hz, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 109.15, 20.71, 10.46.

Figure S11. ^{1}H NMR spectra of $(C_4Et_4)NiBr_2(py)$ (**2c**).

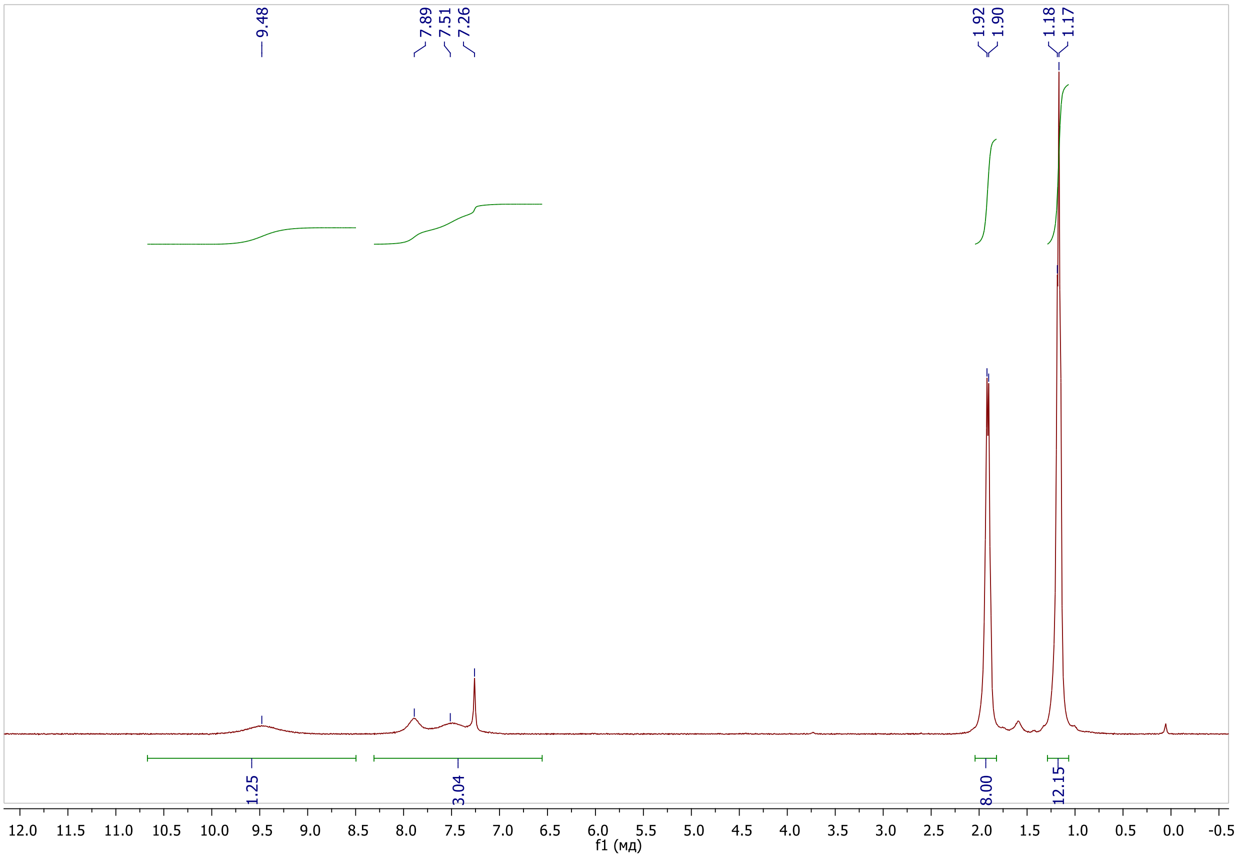
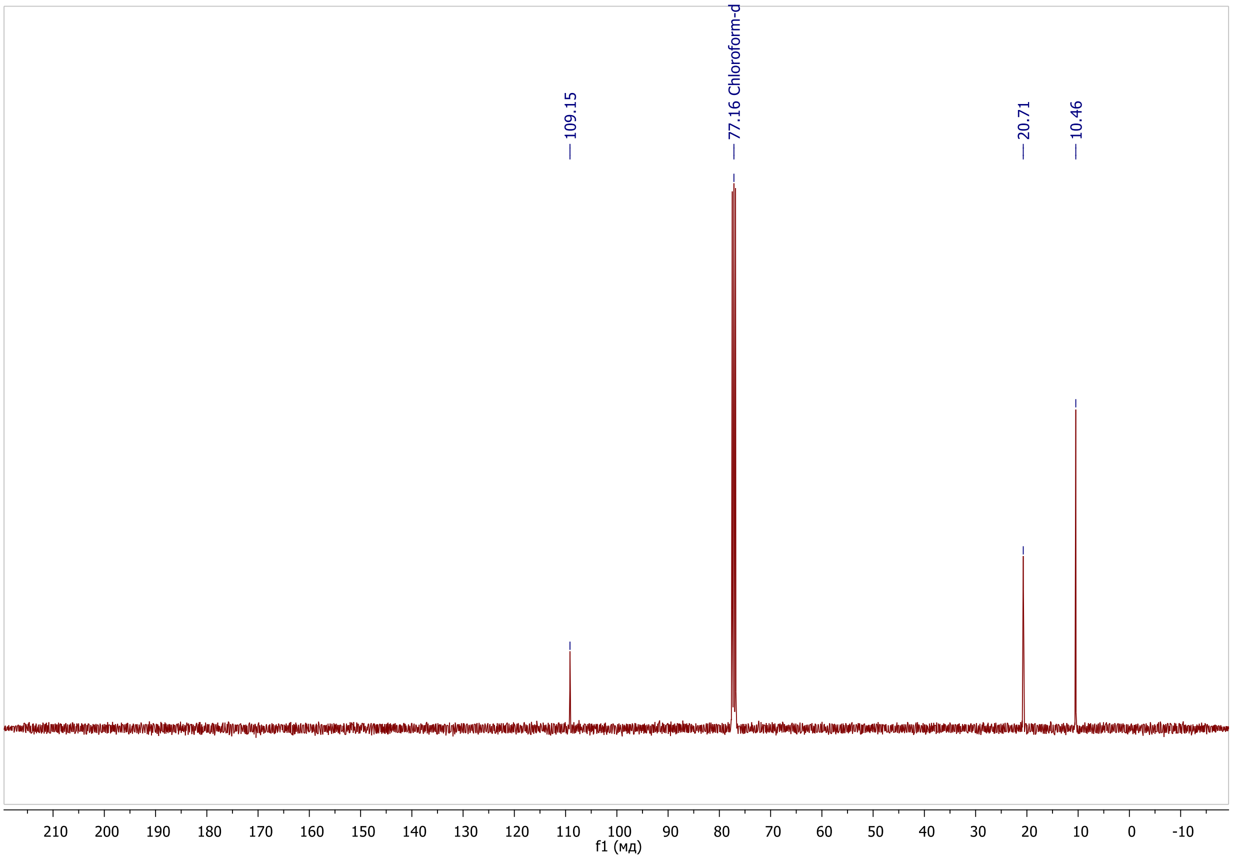


Figure S12. ^{13}C NMR spectra of $(C_4Et_4)NiBr_2(py)$ (**2c**).



$((C_4Et_4)NiBr_2)_2$(dppe) (**2d**)

The solution of $[(C_4Et_4)NiBr_2]_2$ (29 mg, 0.038 mmol) and 1,2-bis(diphenylphosphino)ethane (17 mg, 0.043 mmol) in 1 ml THF was stirred for 8 hours. The color of the solution changed to dark red with the gradual formation of a red precipitate of the product. The diethyl ester (5 ml) was added and solution was decanted. Red precipitate of the product washed with cold Et_2O (2x5 ml) and dried in vacuum. Yield – 37 mg (84%). The crystals of complex for X-ray analysis were grown from CH_2Cl_2/ Et_2O mixture at −32 °C. Anal. calc. for $C_{50}H_{64}Br_4Ni_2P_2$: C 51.59, H 5.54. Found: C 51.31, H 5.49.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (t, J=8.2 Hz, 8H), 7.39 (d, J = 6.8 Hz, 4H), (m,12H), 7.34 (m, 8H), 2.67 (s, 4H), 1.83 (m, 16H), 1.01 (t, *J* = 7.1 Hz, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 134.42, 130.50, 128.49, 109.68, 20.04, 11.30. ^{31}P NMR (162 MHz, $CDCl_3$) δ: 65.72.

Figure S13. ^{1}H NMR spectra of $((C_4Et_4)NiBr_2)_2$(dppe) (**2d**).

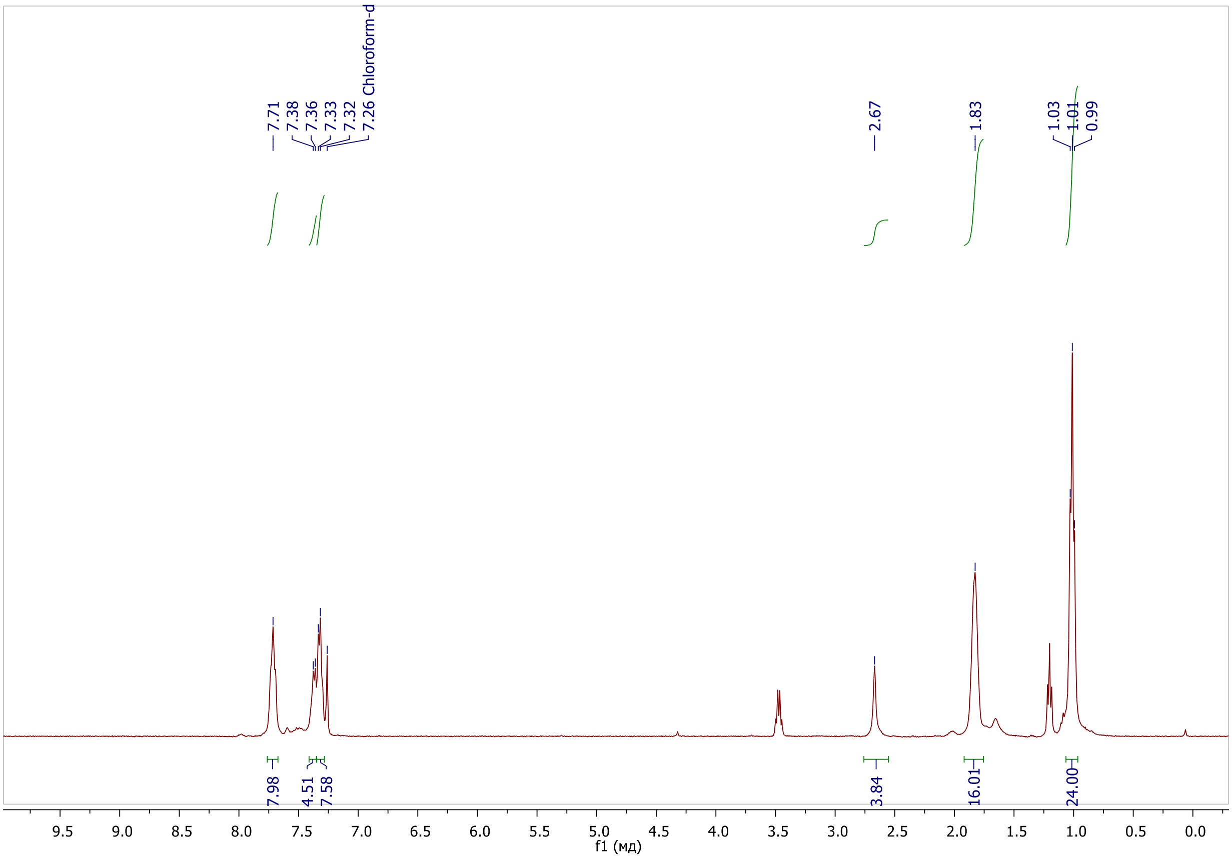


Figure S14. ^{13}C NMR spectra of $((C_4Et_4)NiBr_2)_2$(dppe) (**2d**).

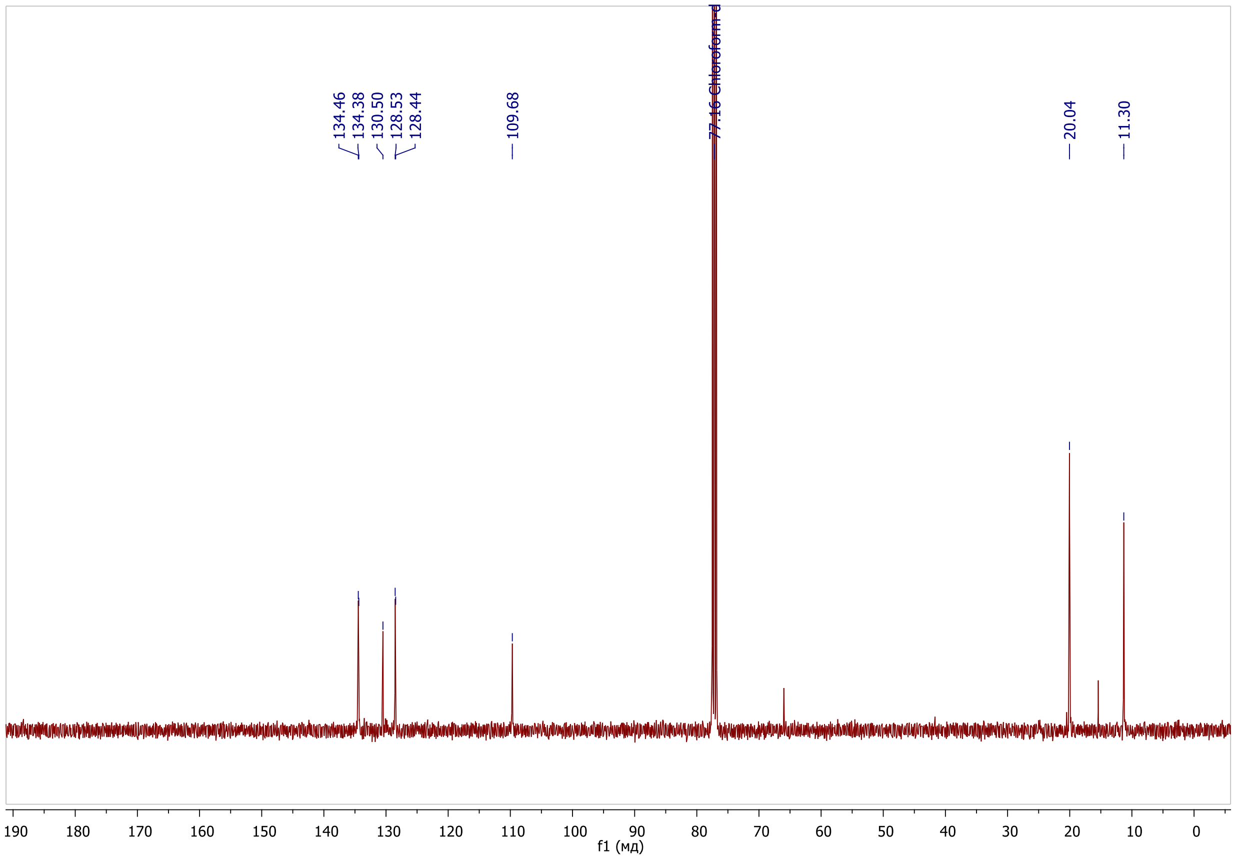
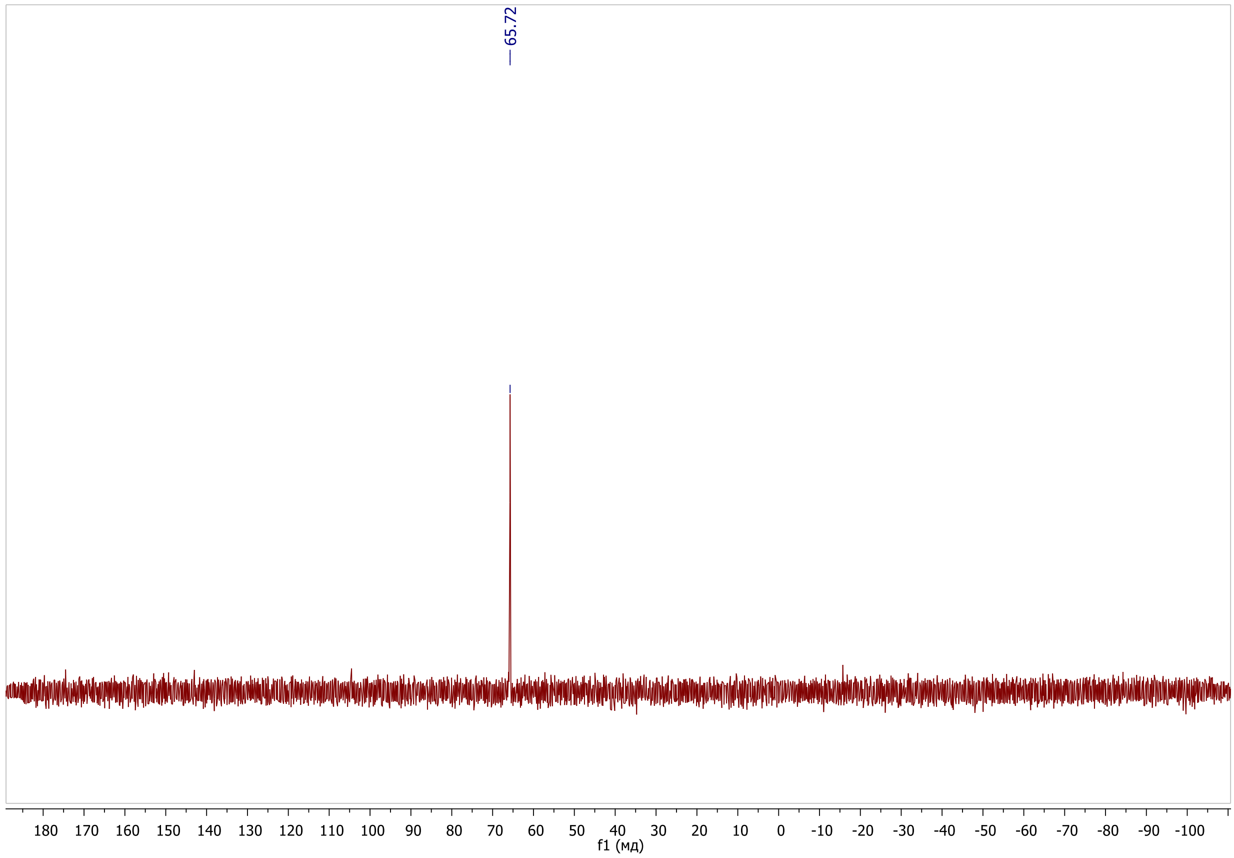


Figure S15. ^{31}P NMR spectra of $((C_4Et_4)NiBr_2)_2$(dppe) (**2d**) at 298 K.



[$(C_4Et_4)NiBr(bipy)$]PF_6 (**3a**)

The mixture of [$(C_4Et_4)NiBr_2$]$_2$ (27 mg, 0.035mmol), $TlPF_6$ (24.5 mg, 0.07 mmol), and 2,2′-bipyridine (11 mg, 0.07 mmol) in 1ml THF was stirred for 8 hours at the room temperature. The solvent was evaporated, orange residue was washed with Et_2O (1x5 ml). The product was extracted with acetone and the solvent was removed in vacuum. Crude product was reprecipitated several times from acetone by Et_2O. Yield – 35 mg (82%). The crystals of complex for X-ray analysis were grown from acetone/ Et_2O mixture. Anal. calc. for $C_{22}H_{28}BrF_6N_2NiP$: C 43.75, H 4.67, N 4.64. Found: C 43.94, H 4.91, N 4.62.

^{1}H NMR (400 MHz, acetone-*d*$_6$) δ: 9.40 (d, *J* = 5.3 Hz, 2H, bipy), 8.67 (d, *J* = 8.1 Hz, 2H, bipy), 8.39 (t, *J* = 7.6 Hz, 2H, bipy), 7.98 (m, 2H, bipy), 2.16 (q, *J* = 7.5 Hz, 8H, CH_2), 1.21 (t, *J* = 7.5 Hz, 12H, CH_3). ^{13}C NMR (101 MHz, acetone-*d*$_6$) δ: 153.93, 153.18, 141.65, 129.28, 124.24, 113.42, 20.28, 10.55.

Figure S16. ^{1}H NMR spectra of [$(C_4Et_4)NiBr(bipy)$]PF_6 (**3a**).

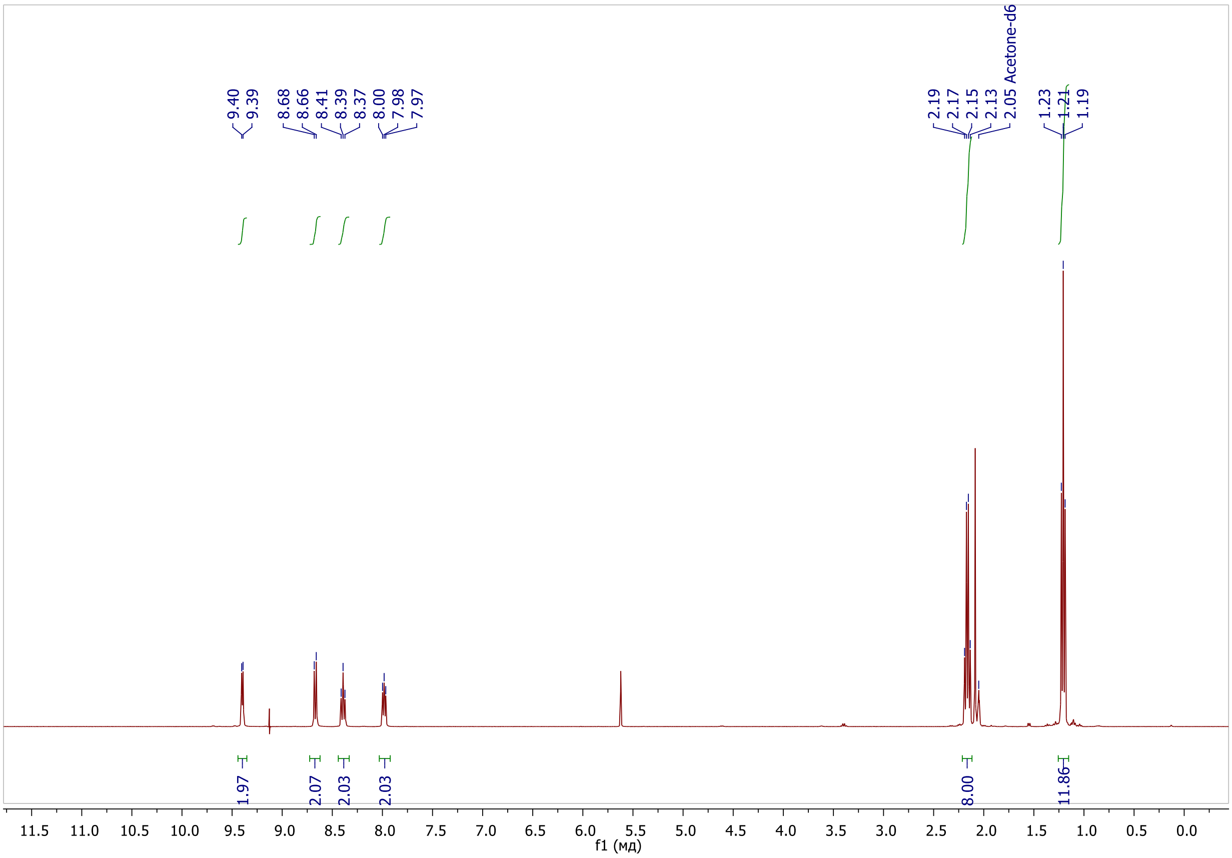
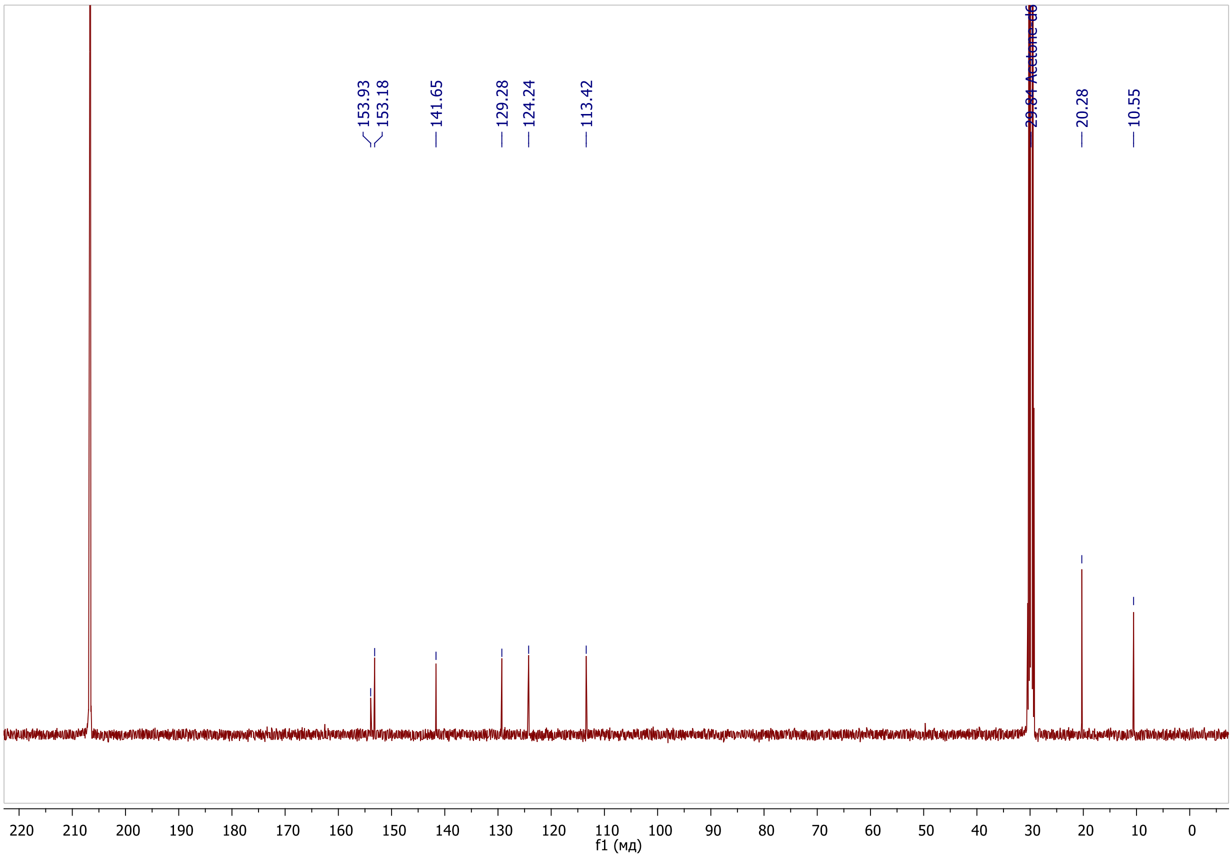


Figure S17. ^{13}C NMR spectra of [$(C_4Et_4)NiBr(bipy)]PF_6$ (**3a**).



[$(C_4Et_4)NiBr(phen)]PF_6$ (**3b**)

The mixture of [$(C_4Et_4)NiBr_2]_2$ (27 mg, 0.035 mmol), $TlPF_6$ (24.5 mg, 0.07 mmol), and 1,10-phenanthroline (12.6 mg, 0.07 mmol) in 1ml THF was stirred for 8 hours at the room temperature. The solvent was evaporated, orange residue was washed with Et_2O (1x5 ml). The product was extracted with acetone and the solvent was removed in vacuum. Crude product was reprecipitated several times from acetone by Et_2O. Yield – 37 mg (84%). The crystals of complex for X-ray analysis were grown from acetone/Et_2O mixture. Anal. calc. for $C_{24}H_{28}BrF_6N_2NiP$: C 45.90, H 4.49, N 4.46. Found: C 45.74, H 4.44, N 4.53.

^1H NMR (400 MHz, acetone-d_6) δ: 9.77 (d, J = 4.7 Hz, 2H), 8.96 (d, J = 8.0 Hz, 2H), 8.31(bs, 4H), 2.23 (q, J = 6.9 Hz, 8H), 1.22 (t, J = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, acetone-d_6) δ: 153.60, 144.89, 140.23, 131.02, 128.54, 128.01, 113.75, 20.46, 10.61.

Figure S18. ^{1}H NMR spectra of [(C$_4$Et$_4$)NiBr(phen)]PF$_6$ (**3b**).

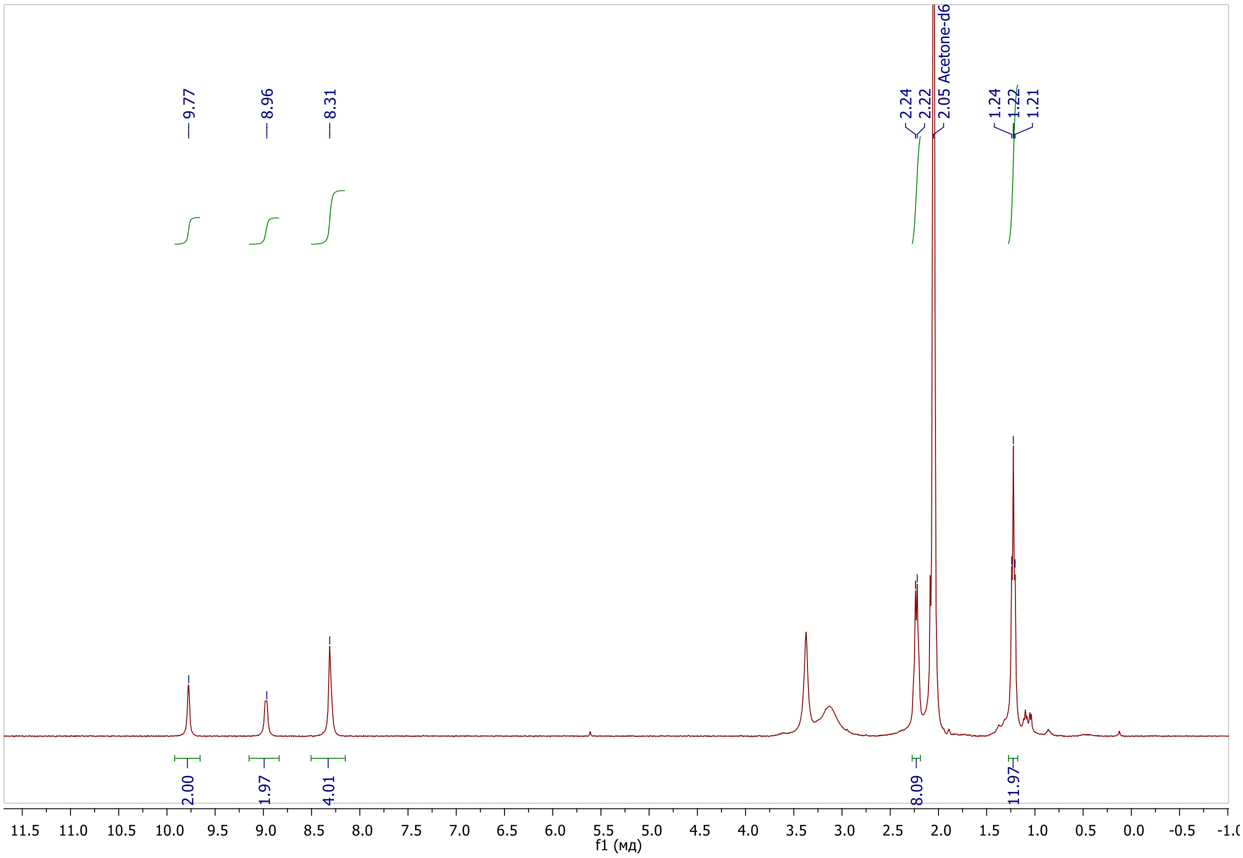
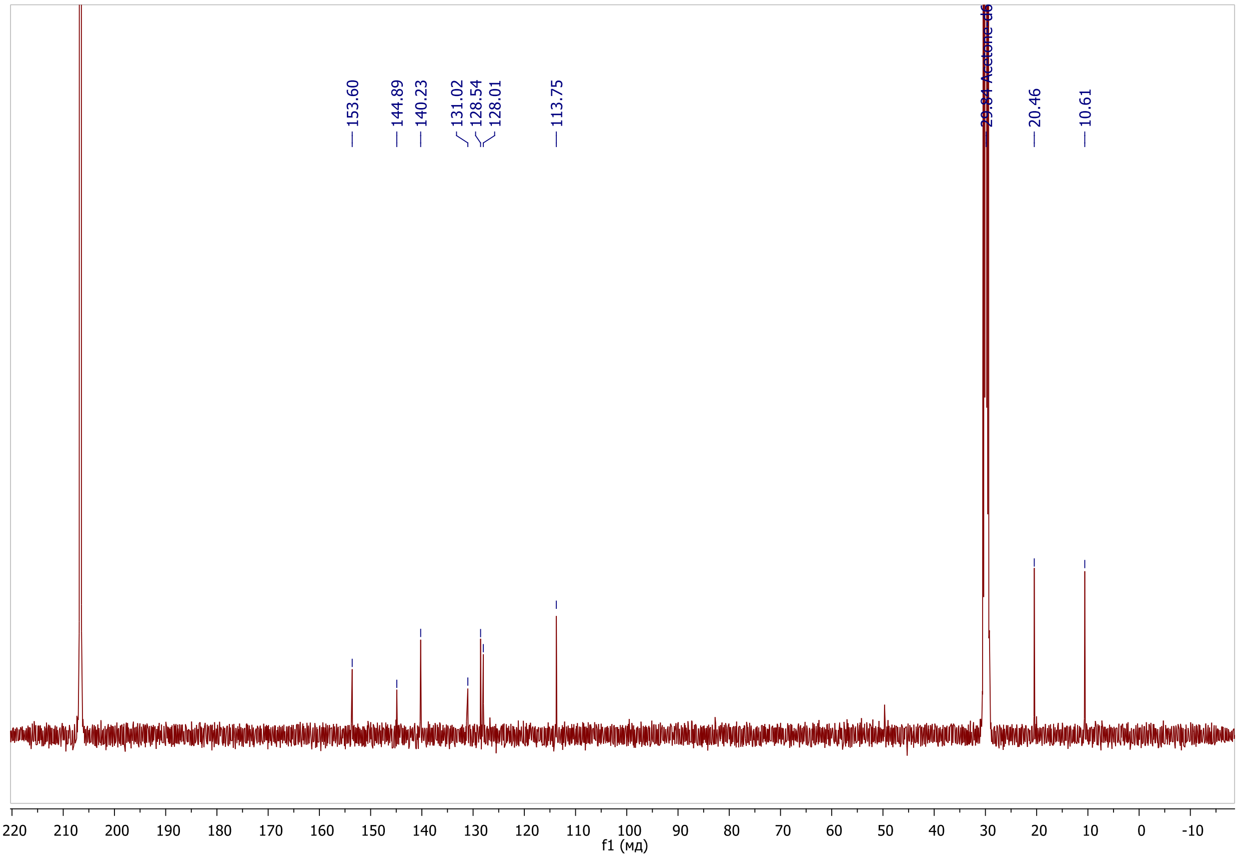


Figure S19. ^{13}C NMR spectra of [(C$_4$Et$_4$)NiBr(phen)]PF$_6$ (**3b**).



[$(C_4Et_4)Ni(C_2B_9H_{11})$] (**4**)

The mixture of [$(C_4Et_4)NiBr_2]_2$ (59 mg, 0.077 mmol) and thallium dicarbollide (127 mg, 0.23 mmol) in acetonitrile (2 ml) was stirred for 24 hours at the room temperature. The color of the solution almost immediately changed to yellow with the formation of a white precipitate of TlBr. The solvent was evaporated and the yellow product was extracted with CH_2Cl_2. The product was purified by column chromatography (eluent: CH_2Cl_2/petroleum ether (5:2), $R_f \approx 0.9$). Yield − 39 mg (71%). HRMS (ESI): calc. for $C_{14}H_{35}B_9NNi$ $[M+NH_4]^+$ = 373.3005. Found: 373.2998.

^1H NMR (400 MHz, $CDCl_3$) δ: 2.68 (bs, 2H, CH), 2.44 (q, J = 7.6 Hz, CH_2), 1.28 (t, J = 7.6 Hz, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 109.87, 19.68, 12.79. Signal of carbon atoms of the cluster is not observed due to its low intensity.

^{11}B NMR (128 MHz, $CDCl_3$) δ: 4.58 (1B), −7.20 (2+1B), −8.11 (2B), −18.01 (2B), −21.64 (1B).

Figure S20. ^1H NMR spectra of [$(C_4Et_4)Ni(C_2B_9H_{11})$] (**4**).

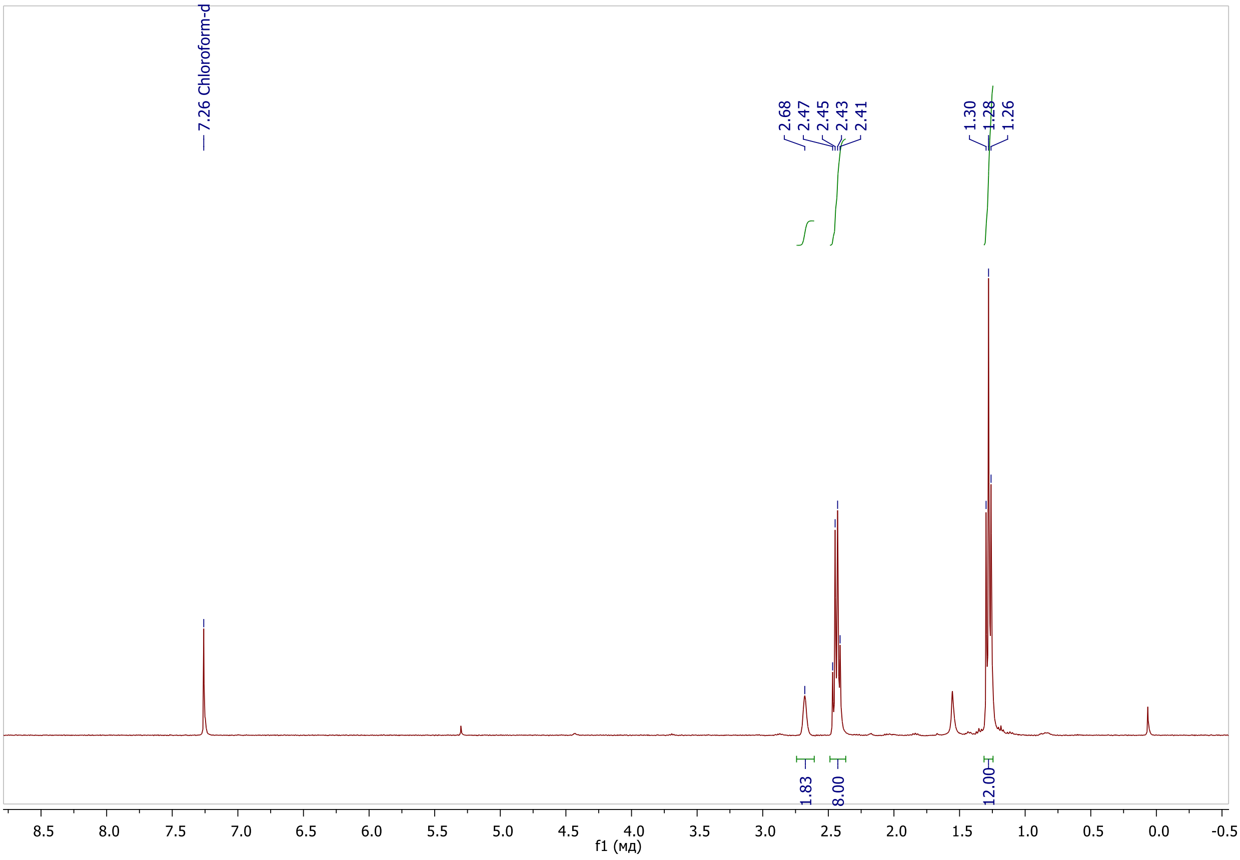


Figure S21. ^{13}C NMR spectra of [(C$_4$Et$_4$)Ni(C$_2$B$_9$H$_{11}$)] (**4**).

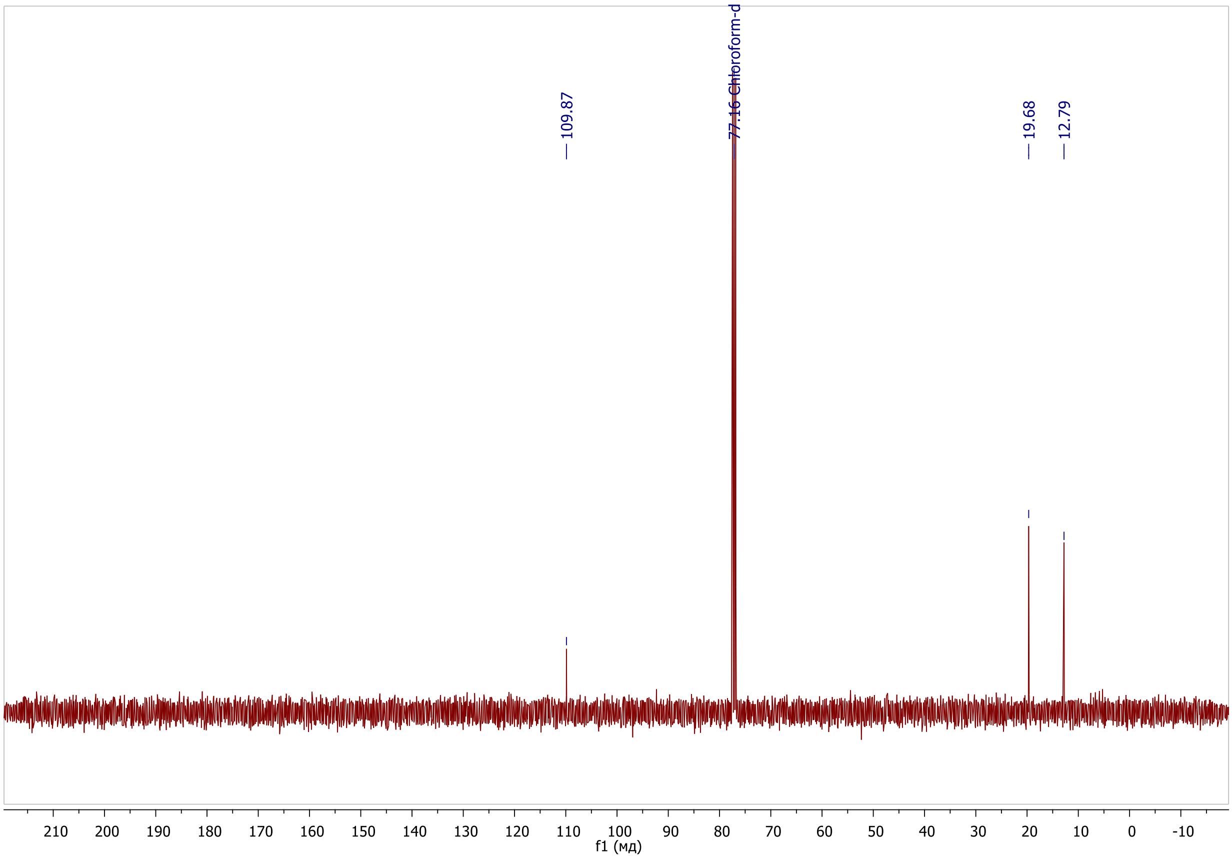


Figure S22. ^{11}B{1H} NMR spectrum of [(C$_4$Et$_4$)Ni(C$_2$B$_9$H$_{11}$)] (**4**).

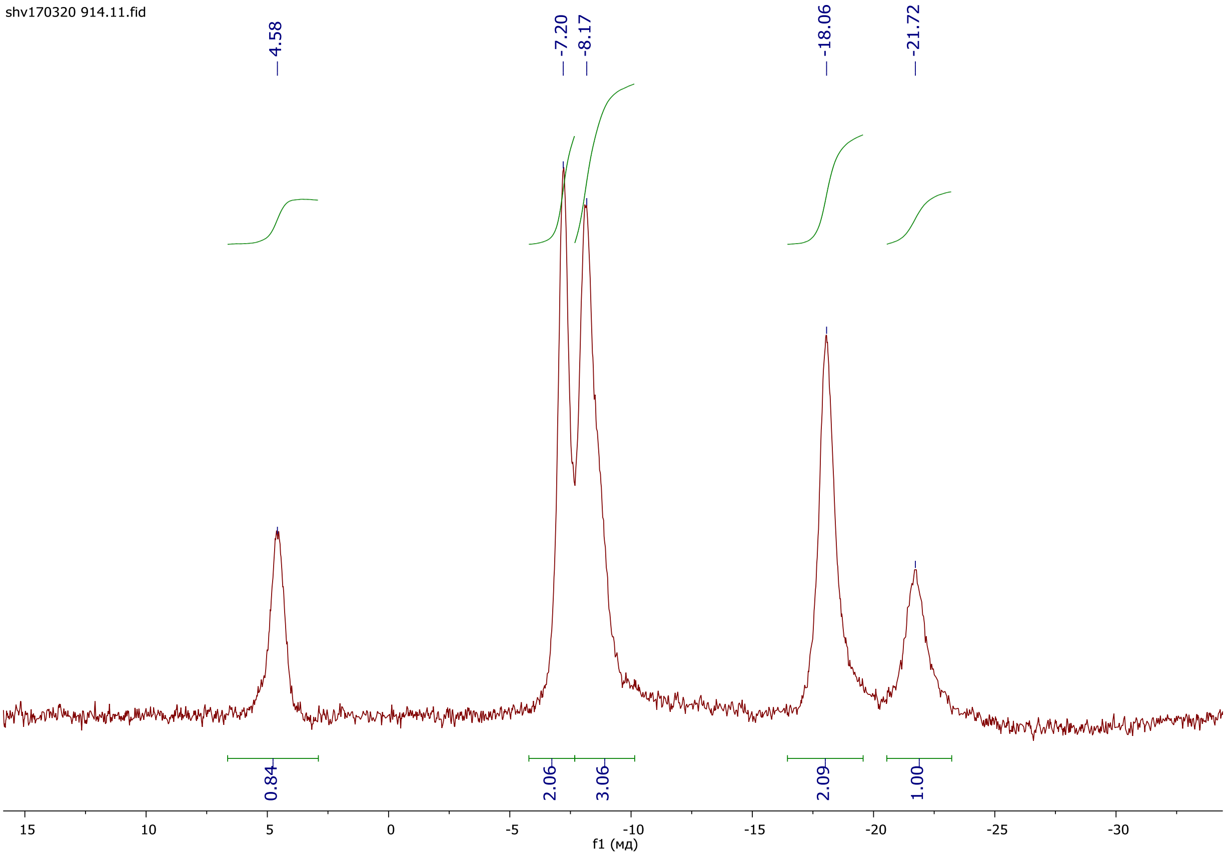
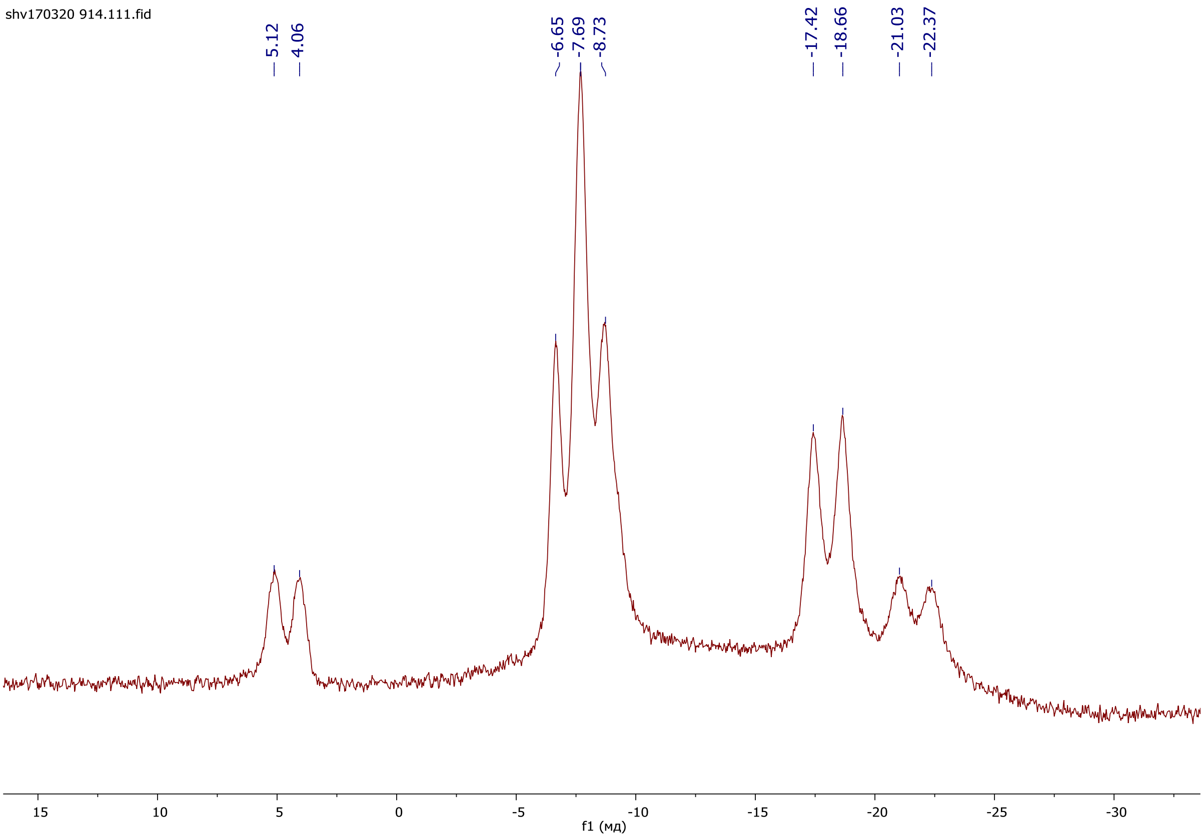


Figure S23. ^{11}B NMR spectrum of [(C$_4$Et$_4$)Ni(C$_2$B$_9$H$_{11}$)] (**4**).



Details of X-ray diffraction experiments.

X-ray diffraction data for **2a**, **2d**, **3a**, **3b** and **4** were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using the graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) for **2a**, **2d** and **4** and Cu-Kα radiation (λ = 1.54178 Å) for **3a** and **3b**. Using Olex2 (see O.V. Dolomanov, L.J. Bourhis, R.J Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341), the structures were solved with the ShelXT (see G.M. Sheldrick, *Acta Cryst.*, **2015**, *A71*, 3-8) structure solution program using Intrinsic Phasing and refined against F^2 in the anisotropic-isotropic approximation with the olex2.refine (see L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, *Acta Cryst.*, **2015**, *A71*, 59-75) refinement package using Least-Squares minimization. Hydrogen atoms of BH groups of the dicarbollide moiety in **4** were found in the difference Fourier synthesis, the positions of other hydrogen atoms were calculated, and they all were refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Table S1. CCDC 1990251, 1990252, 1990253, 1991640 and 1991641 contain the supplementary crystallographic information for **2a**, **2d**, **3a**, **3b** and **4**, respectively.

Table S2. Crystal data and structure refinement parameters for **2a**, **2d**, **3a**, **3b** and **4**.

	2a	**2d**	**3a**	**3b**	**4**
Formula unit	$C_{30}H_{35}Br_2NiP$	$C_{50}H_{64}Br_4Ni_2P_2$	$C_{25}H_{34}BrF_6N_2NiOP$	$C_{24}H_{28}BrF_6N_2NiP$	$C_{14}H_{31}B_9Ni$
Formula weight	645.08	1164.01	662.13	628.07	355.39
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	Pnma	$P2_1/c$	P-1
Z	4	2	4	4	2
a, Å	16.6563(12)	14.5260(9)	19.2163(3)	8.7709(5)	7.9405(4)
b, Å	14.3947(11)	16.9081(11)	12.0734(2)	16.2919(9)	9.2273(5)
c, Å	17.3244(15)	17.1531(11)	12.3104(2)	17.2763(9)	13.9856(7)
α, °	90	90	90	90	83.8180(10)
β, °	139.294(2)	143.6071(10)	90	96.782(4)	80.4720(10)
γ, °	90	90	90	90	70.0340(10)
V, Å^3	2709.0(4)	2499.6(3)	2856.09(8)	2451.4(2)	948.39(8)
D_{calc} (g cm^{-1})	1.582	1.547	1.540	1.702	1.244
Linear absorption, μ (cm^{-1})	37.43	40.47	36.90	42.34	10.14
F(000)	1312	1180	1352	12732	376
2Θ$_{max}$, °	56	54	135	135	56
Reflections measured	30951	26339	39248	32362	11045

Independent reflections	6538	5456	2709	4325	4575
Observed reflections [$I > 2\sigma(I)$]	5039	4474	2406	3565	3995
Parameters	311	266	181	320	221
R1	0.0567	0.0544	0.0346	0.0345	0.0336
wR2	0.0800	0.1721	0.0919	0.0900	0.0790
GOF	1.022	1.057	1.058	1.022	1.036
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.922/-0.418	2.116/-2.281	0.986/-0.506	0.680/-0.388	0.393/-0.295

Figure S24. Crystal structure of the complex **2d** in representation of atoms via 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

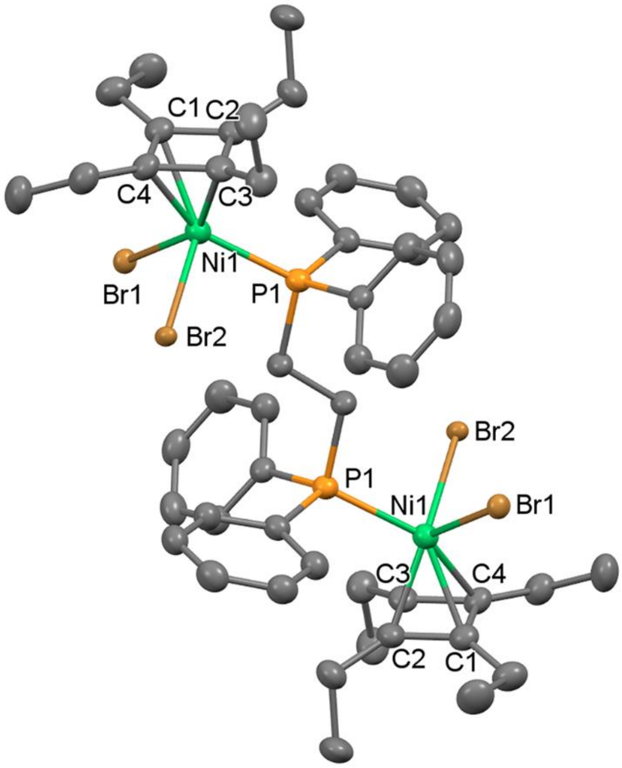
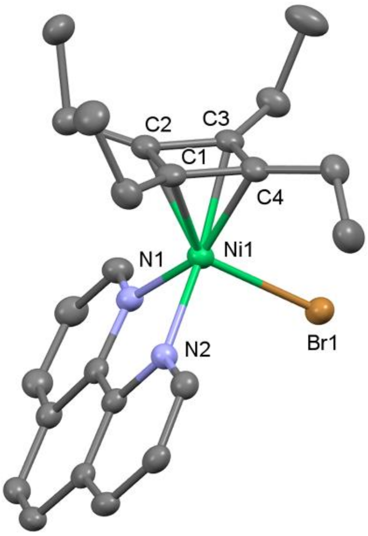


Figure S25. Crystal structure of the complex **3b** in representation of atoms via 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



Details of DFT calculations

Geometry optimizations were performed without symmetry constraints using PBE exchange-correlation functional and all-electron triple-ζ basis set 3z (similar to TZP) implemented in Priroda 16 software (D. N. Laikov and Y. A. Ustynyuk, *Russ. Chem. Bull.*, 2005, **54**, 820–826). Frequency calculations were performed to confirm the nature of the stationary points. The scaling factor of 1.006 was used to obtain frequency values. Noteworthy, less than 1 cm^{-1} deviation between calculated and experimental values was observed for $Ni(CO)_4$, $Ni(P(OMe)_3)_2(CO)_2$ and $(dppe)Ni(CO)_2$ (G. R. van Hecke and W. W. Horrocks, Jr., *Inorg. Chem.*, 1966, **5**, 1960−1968; experimental data was not available of other compounds).

The ChemCraft software (http://www.chemcraftprog.com) was used for molecular modelling. The supplemental file “Optimized structures.xyz” contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis.