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Electronic Supporting Information for:

Ni(II) Phosphine and Phosphide Complexes Supported by a PNP-Pyrrole Pincer Ligand

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1 X-ray data for compounds 2-6

X−Ray crystal structure of [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (2). Single crystals were obtained as orange blocks from a concentrated solution of tetrahydrofuran/dichloromethane layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **2**: $C_{30}H_{45}F_6NNiP_4$; M_r = 716.26; monoclinic; space group $P2_1/n$; a = 16.313(2) Å; b = 10.5410(16) Å; c = 19.493(3) Å; α = 90°; β = 94.416(2)°; γ = 90°; V = 3341.9(9) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.827 mm^{-1}; d_{calc} = 1.424 g·cm^{-3}; 57265 reflections collected; 5886 unique (R_{int} = 0.0405); giving R_1 = 0.0250, wR_2 = 0.0588 for 5158 data with [I>2σ(I)] and R_1 = 0.0314, wR_2 = 0.0608 for all 5886 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.417/−0.579.

X−Ray crystal structure of [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (3). Single crystals were obtained as orang blocks from a concentrated solution of dichloromethane layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **3**: $C_{21}H_{43}F_6NNiP_4$; M_r = 606.15; monoclinic; space group $P2_1/n$; a = 8.2850(17) Å; b = 15.792(3) Å; c = 21.433(4) Å; α = 90°; β = 94.379(3)°; γ = 90°; V = 2796.0(10) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.974 mm^{-1}; d_{calc} = 1.440 g·cm^{-3}; 40751 reflections collected; 4861 unique (R_{int} = 0.0936); giving R_1 = 0.0649, wR_2 = 0.1642 for 3825 data with [I>2σ(I)] and R_1 = 0.0839, wR_2 = 0.1713 for all 4861 data. Residual electron density (e$^-$·Å^{-3}) max/min: 1.930/−1.440.

X−Ray crystal structure of [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (4). Single crystals were obtained as orange blocks from a concentrated solution of dichloromethane layered with hexanes at −35 °C in the glovebox. Crystal and refinement data for **4**: $C_{21}H_{43}F_6NNiO_3P_4$; M_r = 654.15; triclinic; space group $P\bar{1}$; a = 14.4915(6) Å; b = 15.0549(6) Å; c = 16.2395(6) Å; α = 109.950(2)°; β = 107.078(2)°; γ = 107.074(2)°; V = 2861.4(2) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.965 mm^{-1}; d_{calc} = 1.518 g·cm^{-3}; 71121 reflections collected; 10079 unique (R_{int} = 0.0777); giving R_1 = 0.0358, wR_2 = 0.0735 for 7500 data with [I>2σ(I)] and R_1 = 0.0620, wR_2 = 0.0803 for all 10079 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.428/−0.382.

X−Ray crystal structure of [(PN^{pyr}P)Ni(PPh$_2$)] (5). Single crystals were obtained as red blocks from a concentrated solution of diethyl ether layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **5**: $C_{30}H_{44}NNiP_3$; M_r = 570.28; triclinic; space group $P\bar{1}$; a = 9.2144(8) Å; b = 9.2591(8) Å; c = 19.2579(16) Å; α = 86.080(3)°; β = 84.872(3)°; γ = 63.320(2)°; V = 1461.5(2) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 0.847 mm^{-1}; d_{calc} = 1.296 g·cm^{-3}; 34813 reflections collected; 5134 unique (R_{int} = 0.0275); giving R_1 = 0.0234, wR_2 = 0.0588 for 4769 data with [I>2σ(I)] and R_1 = 0.0258, wR_2 = 0.0598 for all 5134 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.421/−0.629.

X−Ray crystal structure of [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (6). Single crystals were obtained as yellow/orange dichroic needles from a concentrated solution of *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **6**: $C_{21}H_{42}NNiP_3$; M_r = 460.18; monoclinic; space group $P2_1/c$; a = 7.6605(16) Å; b = 11.777(2) Å; c = 27.694(6) Å; α = 90°; β = 92.670(3)°; γ = 90°; V = 2495.8(9) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.976 mm^{-1}; d_{calc} = 1.225 g·cm^{-3}; 44437 reflections collected; 4387 unique (R_{int} = 0.0923); giving R_1 = 0.0417, wR_2 = 0.0878 for 3351 data with [I>2σ(I)] and R_1 = 0.0651, wR_2 = 0.0940 for all 4387 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.733/−1.365.

2 NMR Spectra

2.1 NMR Spectra for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (2)

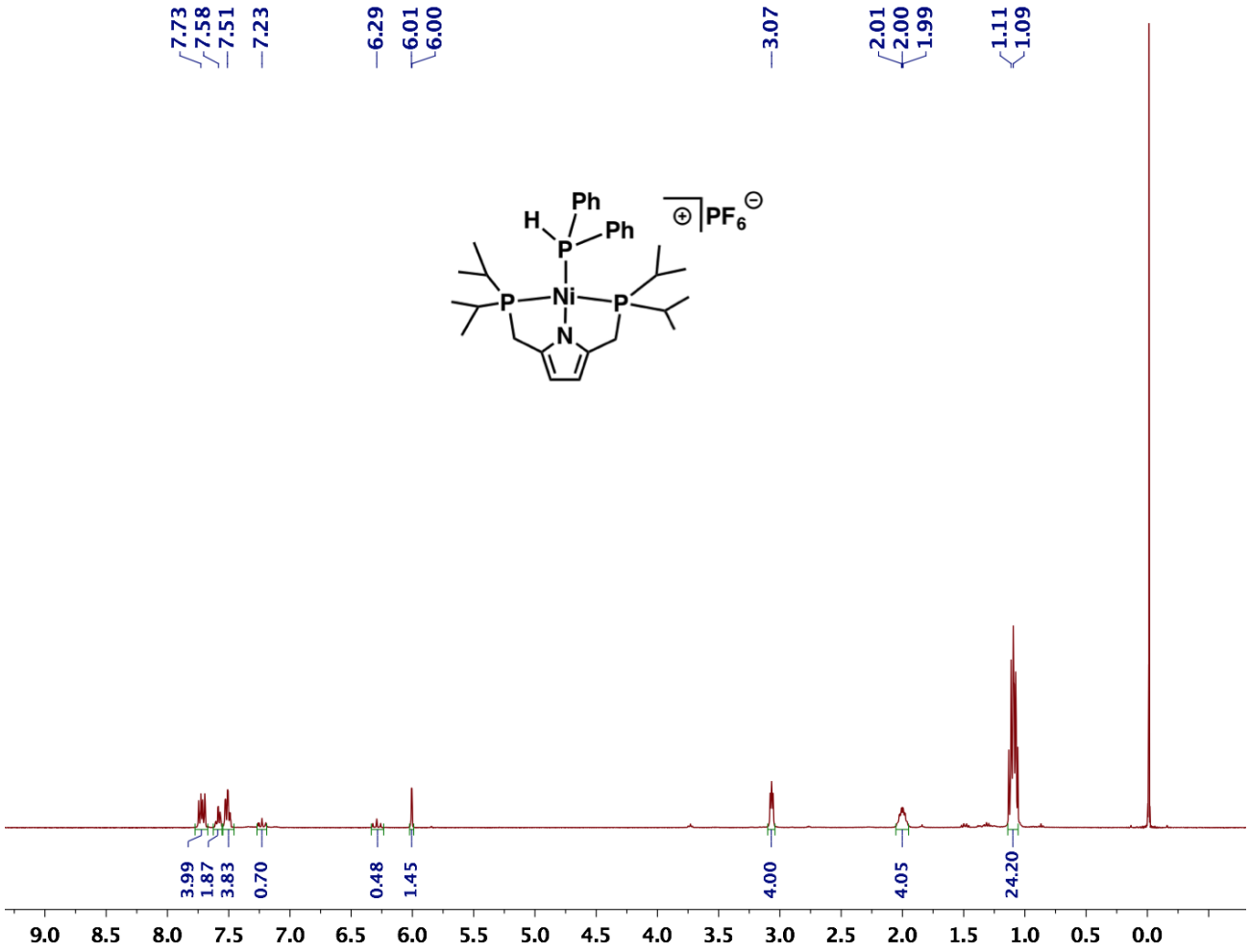

Figure S1. ^{1}H NMR spectrum for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**).

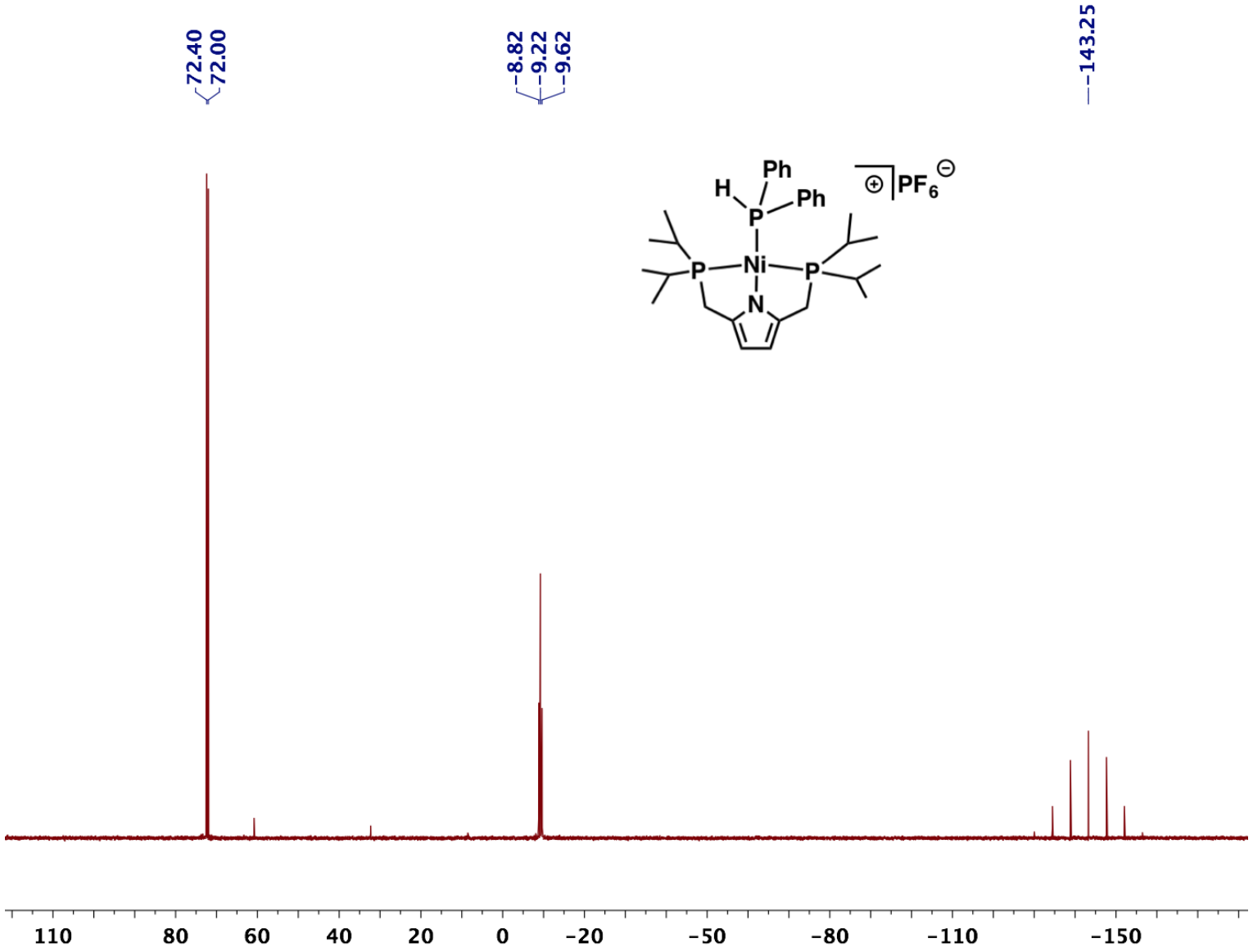

Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni(PHPh_2)][PF_6]$ (**2**).

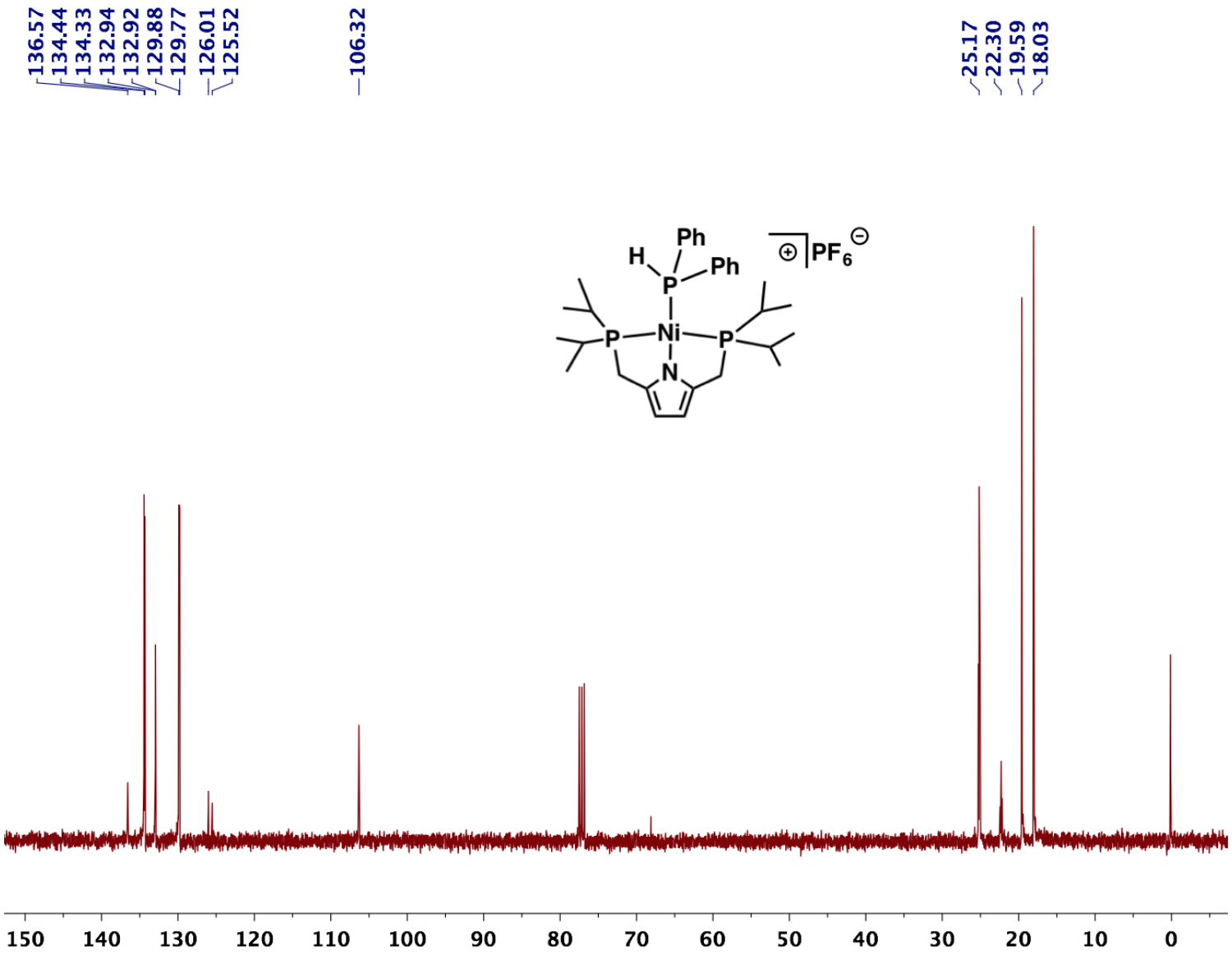

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni(PHPh_2)][PF_6]$ (**2**).

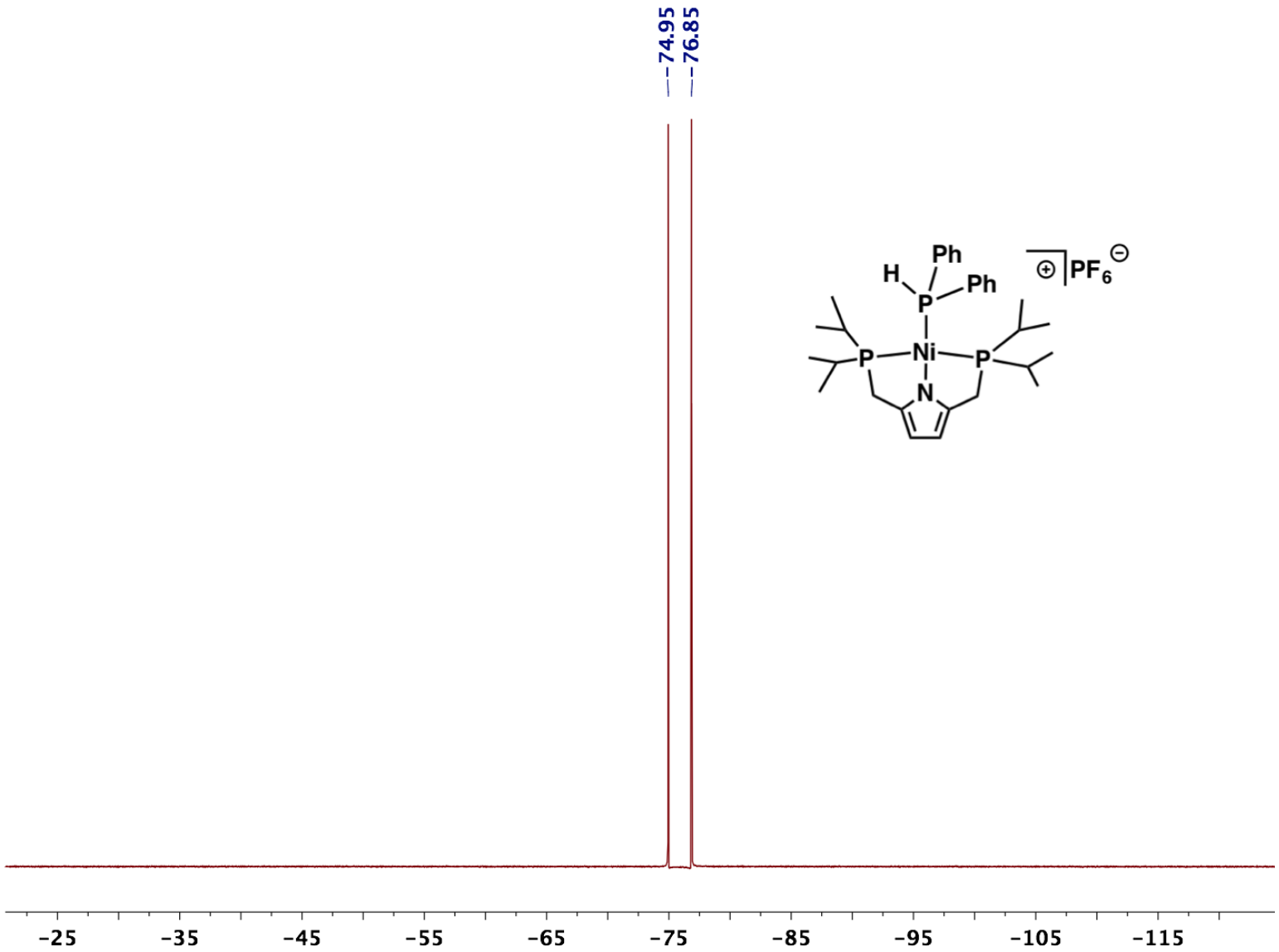

Figure S4. ^{19}F NMR spectrum for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**).

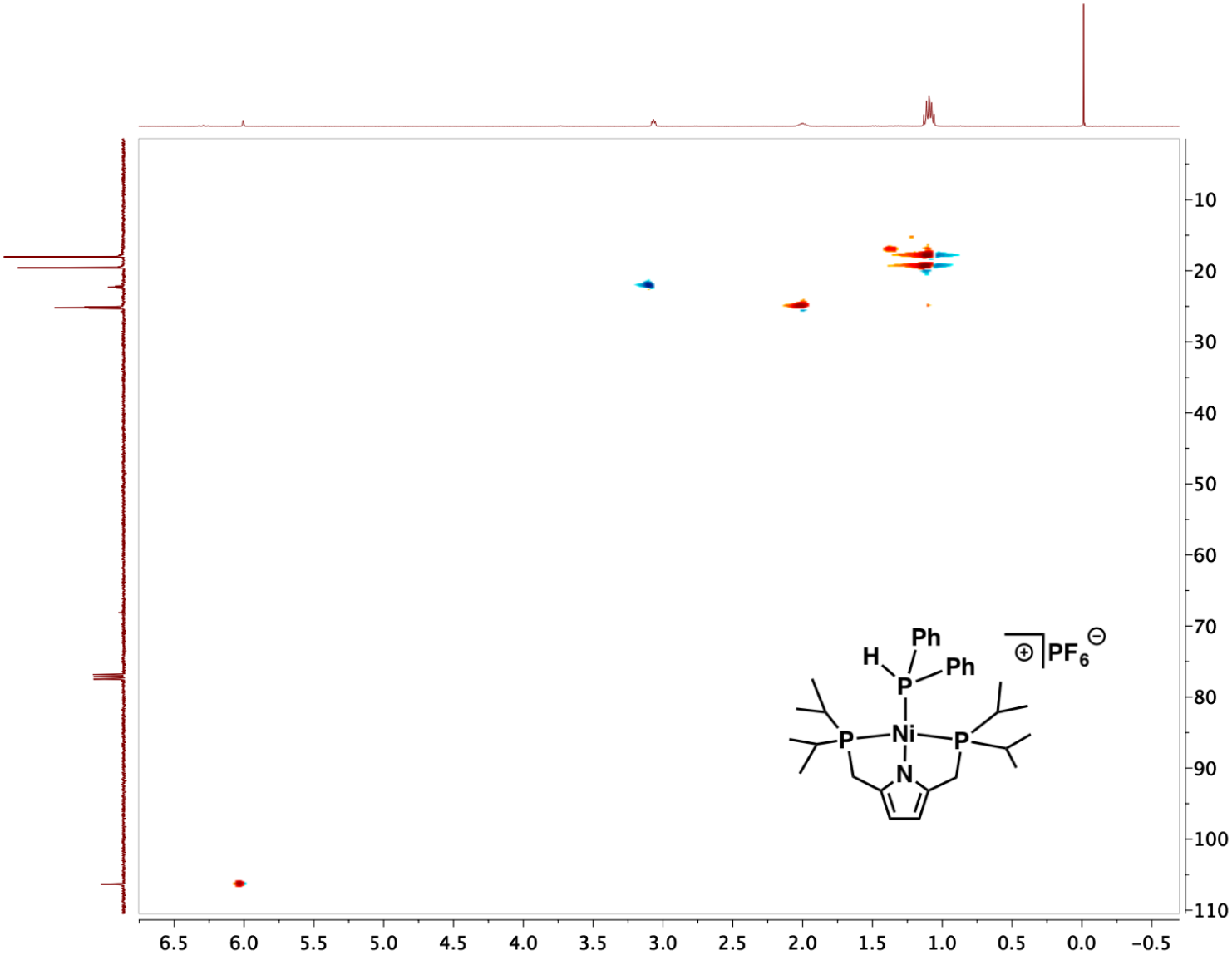

Figure S5. ^{1}H-^{13}C HSQC NMR spectrum for $[(PN^{pyr}P)Ni(PHPh_2)][PF_6]$ (**2**).

2.2 NMR Spectra for [(PN^{pyr}P)Ni(PMe$_3$)][PF$_6$] (3)

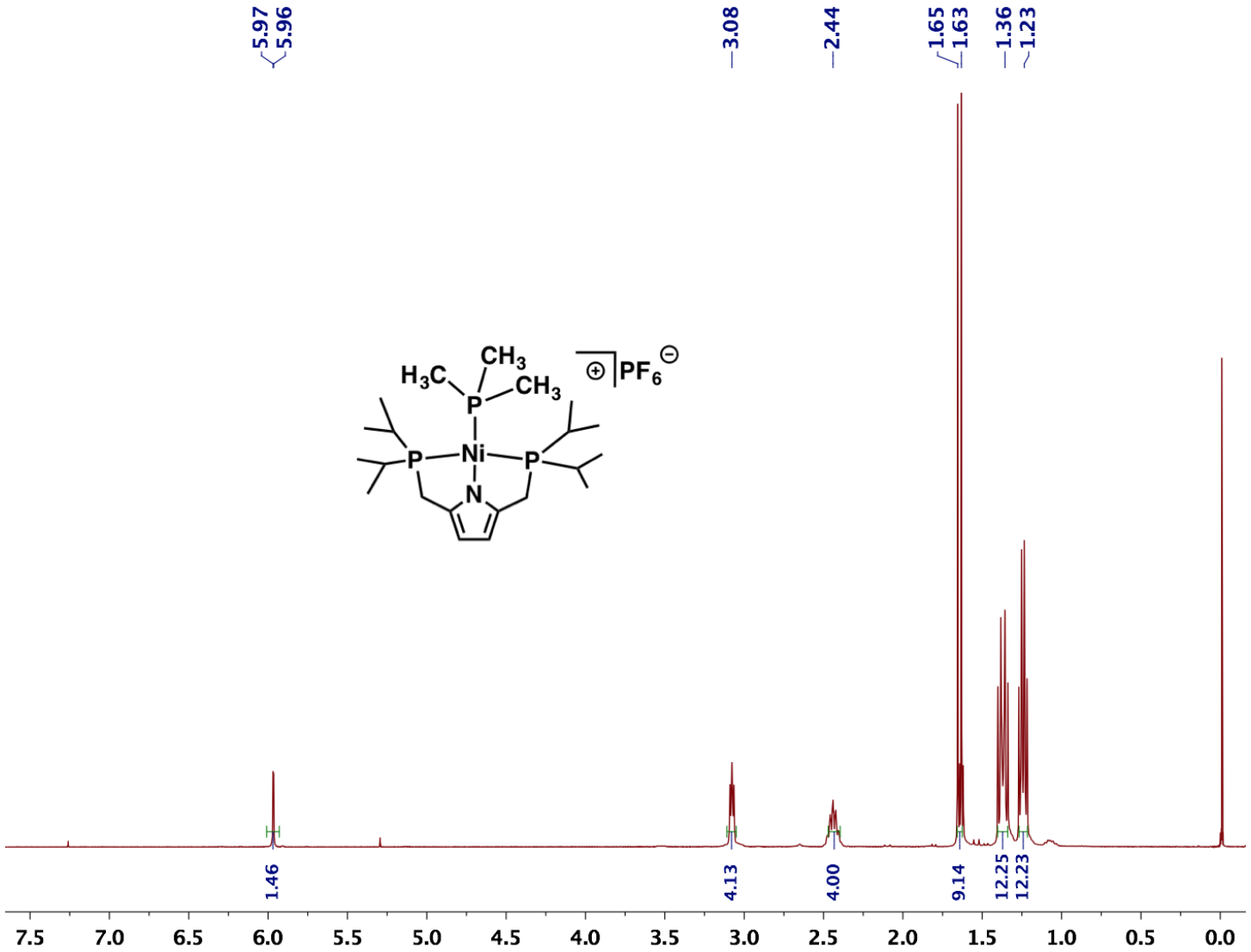

Figure S6. ^{1}H NMR spectrum for [(PN^{pyr}P)Ni(PMe$_3$)][PF$_6$] (**3**).

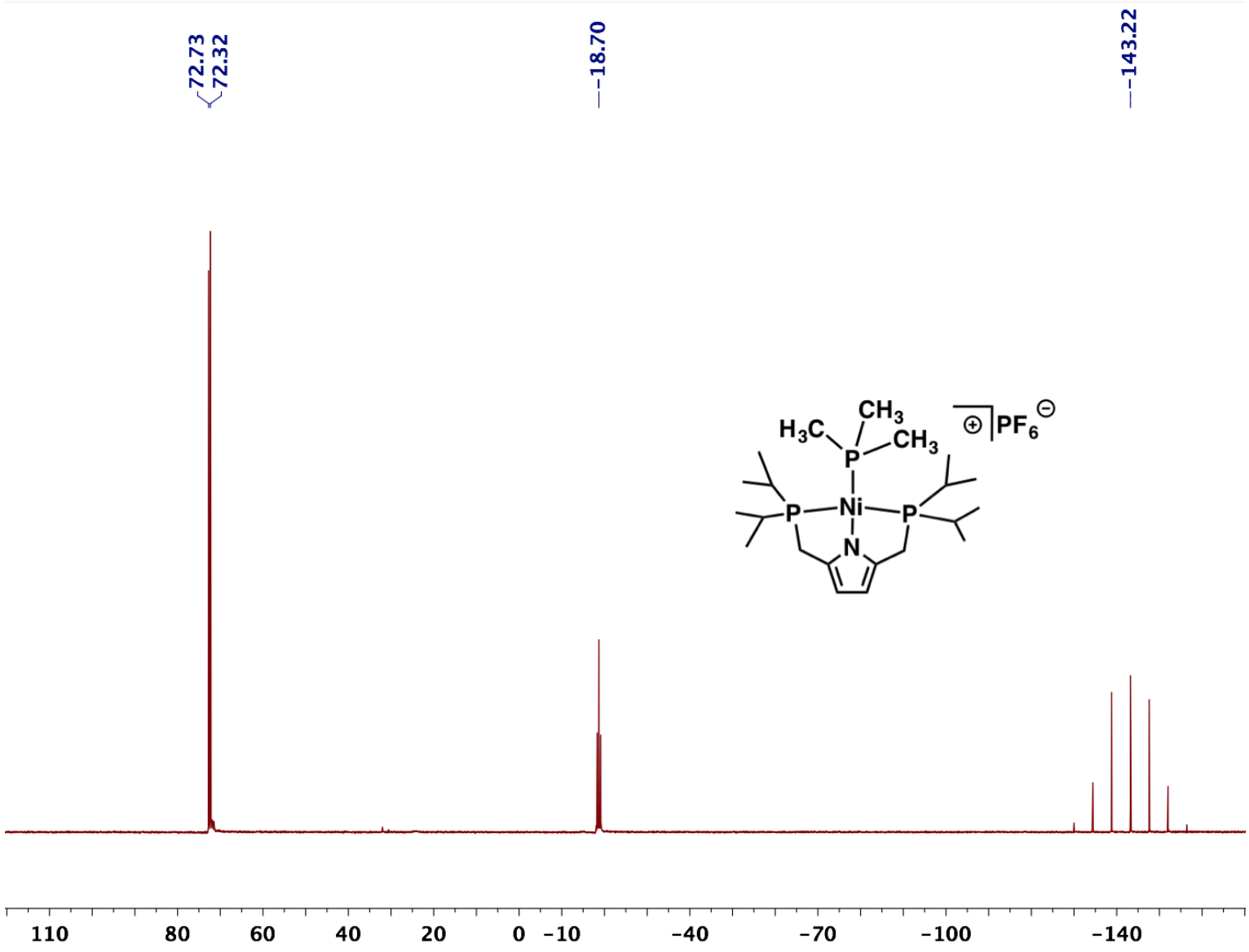

Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni(PMe_3)][PF_6]$ (**3**).

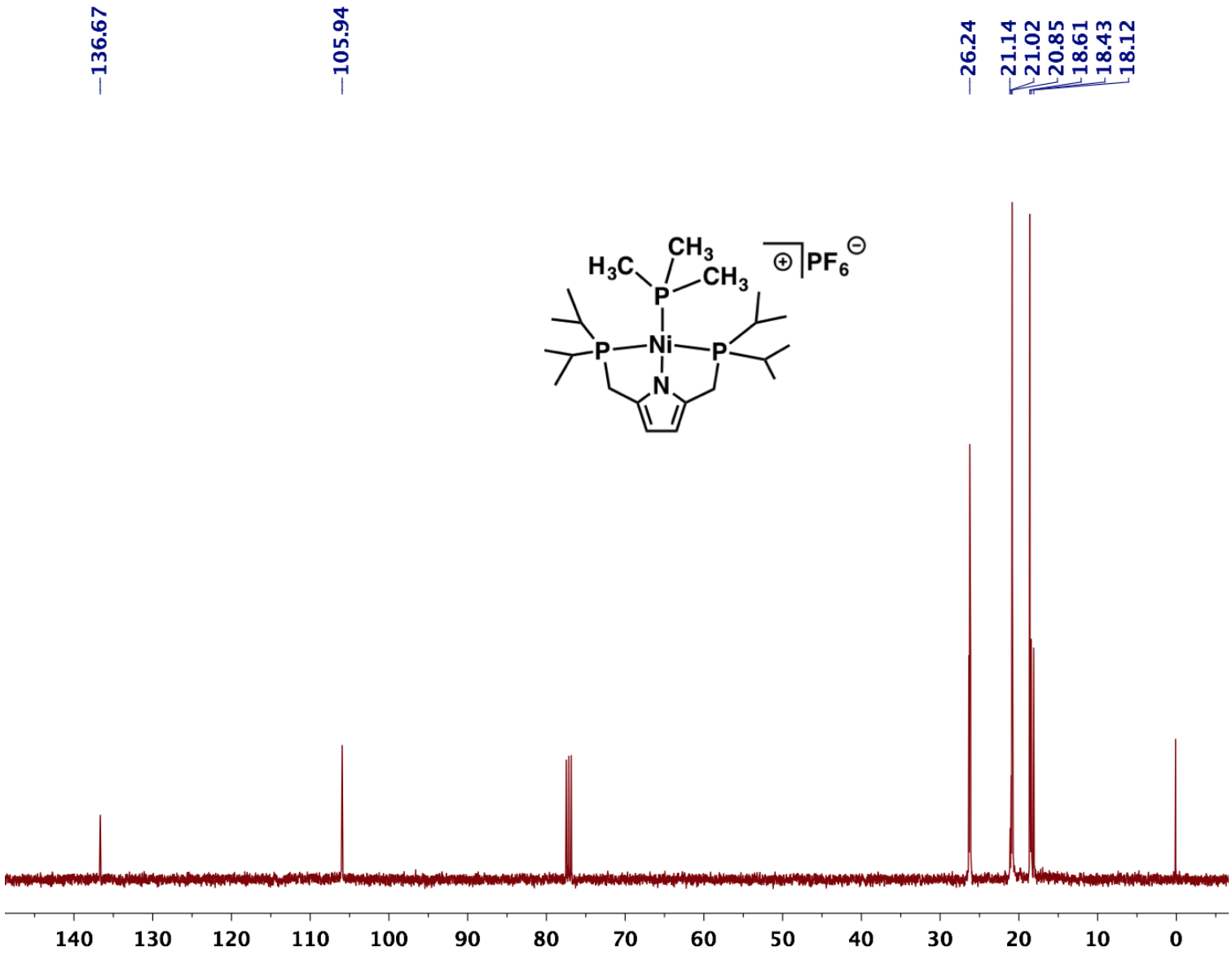

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni(PMe_3)][PF_6]$ (**3**).

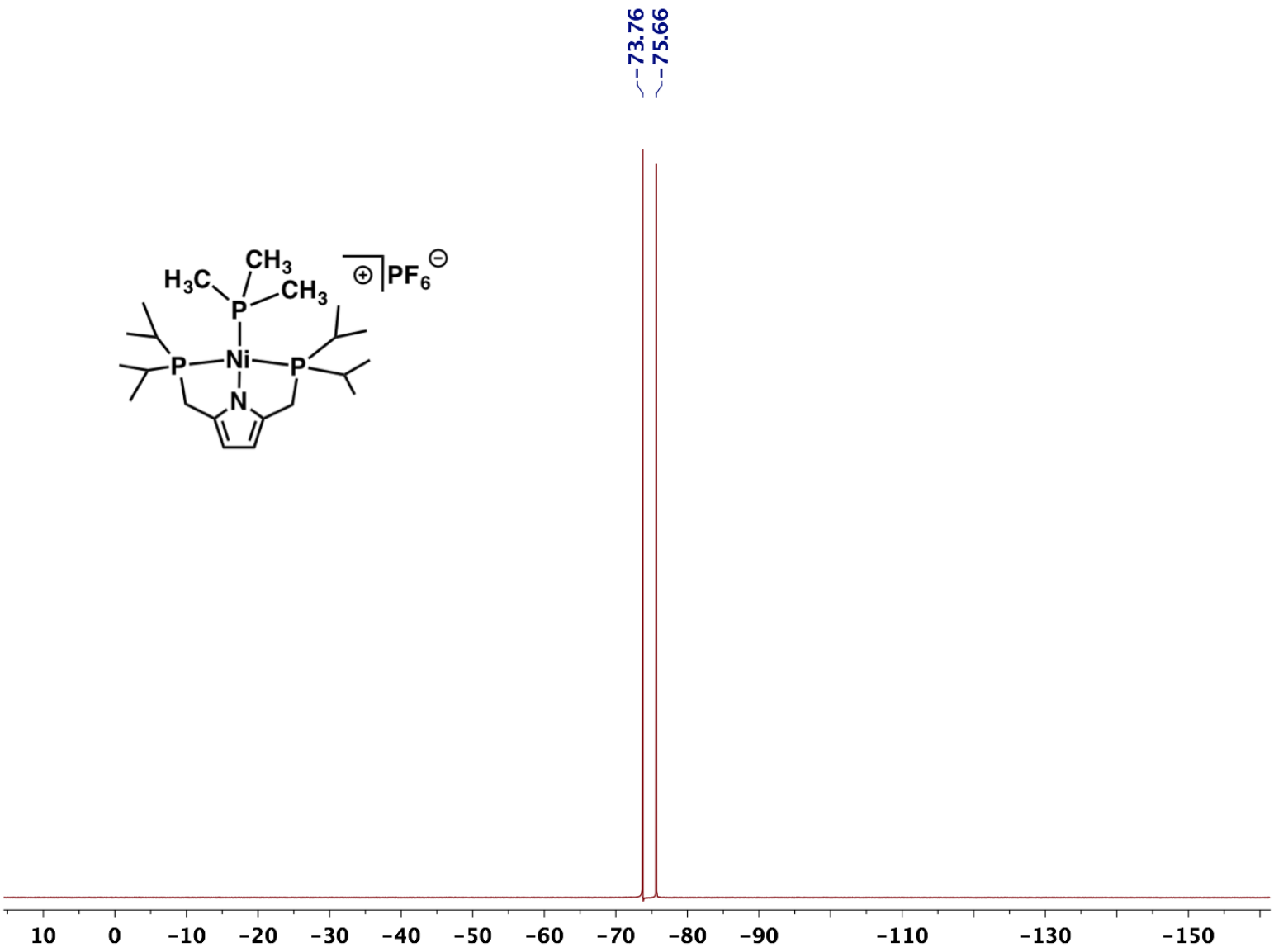

Figure S9. ^{19}F NMR spectrum for $[(PN^{pyr}P)Ni(PMe_3)][PF_6]$ (**3**).

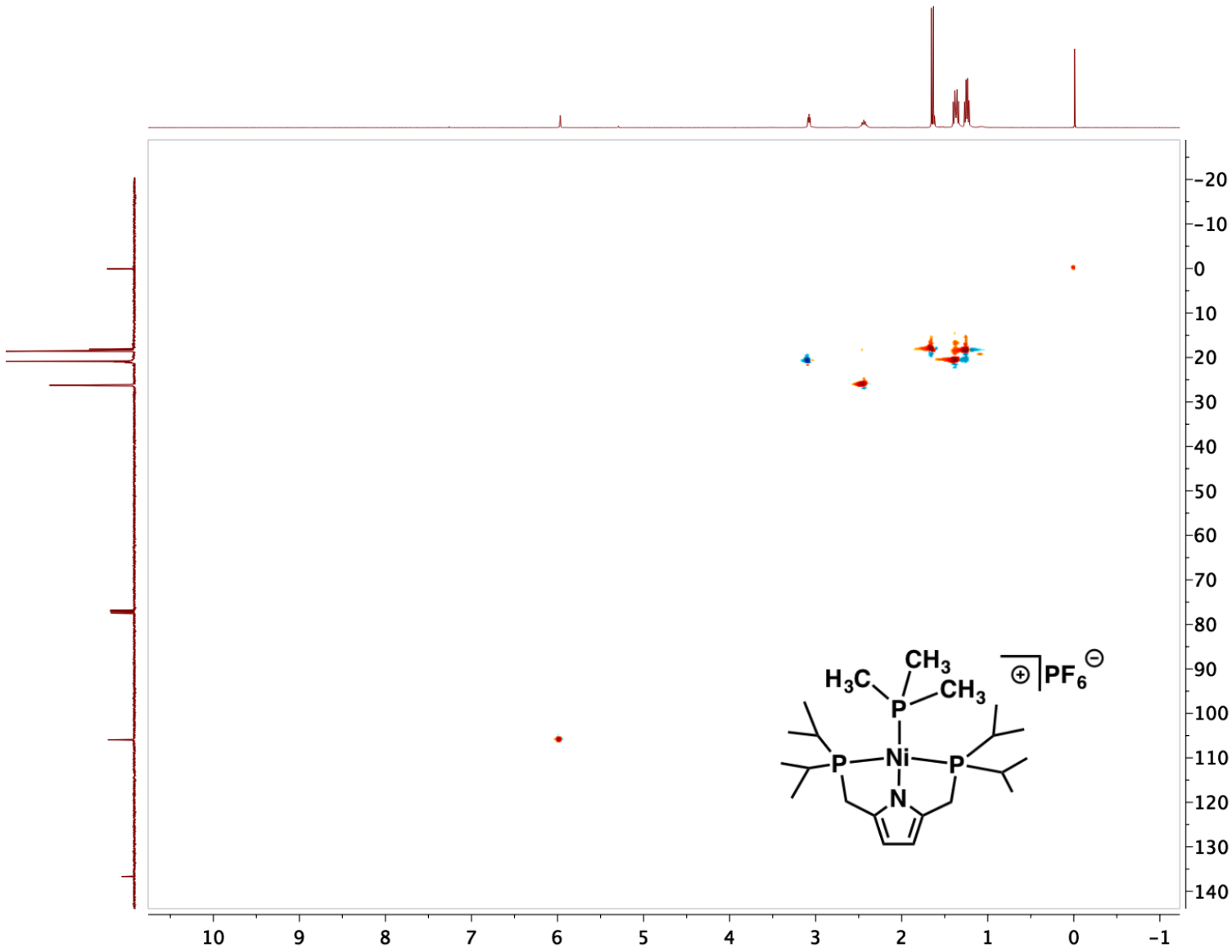

Figure S10. ^{1}H-^{13}C HSQC NMR spectrum for $[(PN^{pyr}P)Ni(PMe_3)][PF_6]$ (**3**).

2.3 NMR Spectra for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (4)

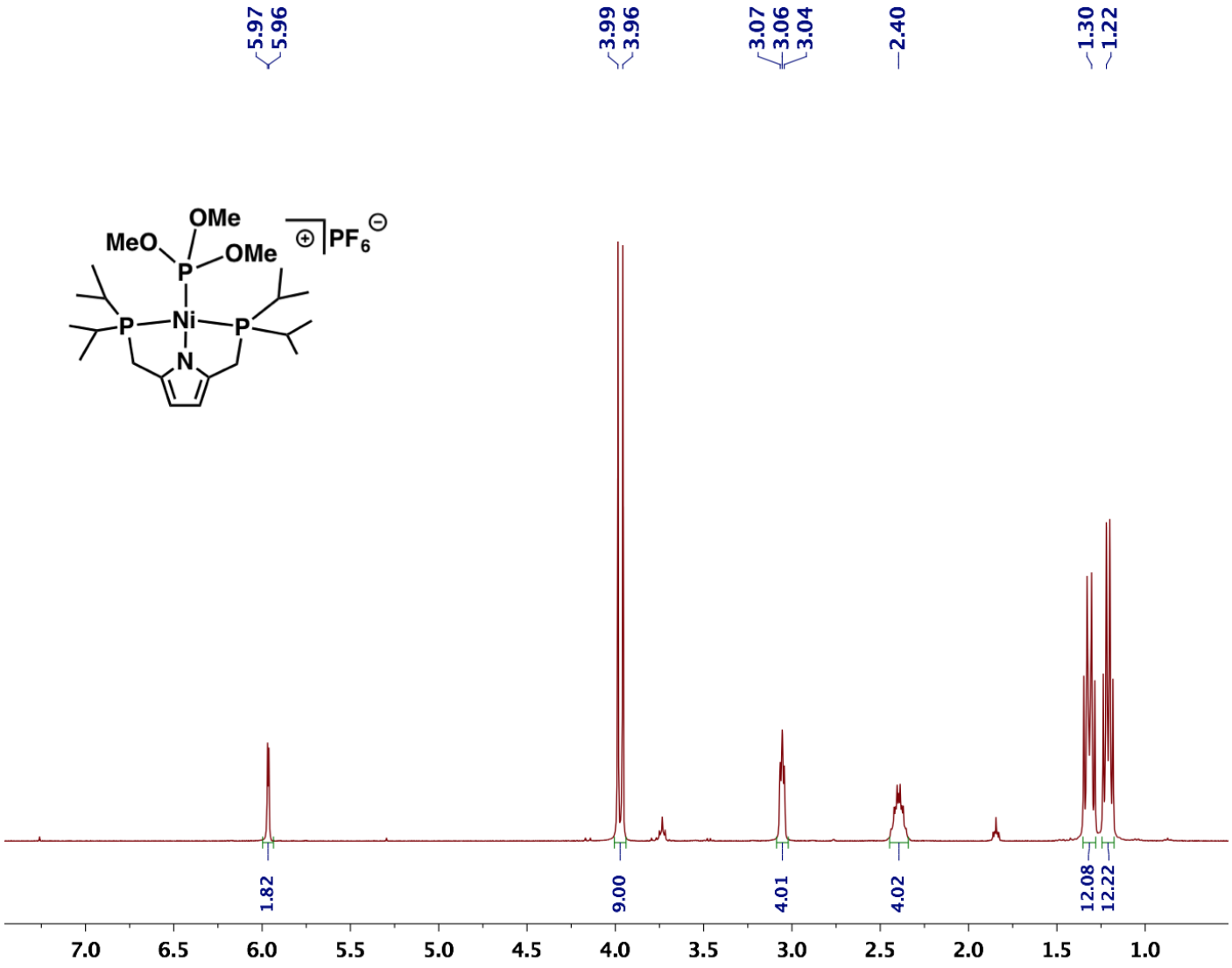

Figure S11. ^{1}H NMR spectrum for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**).

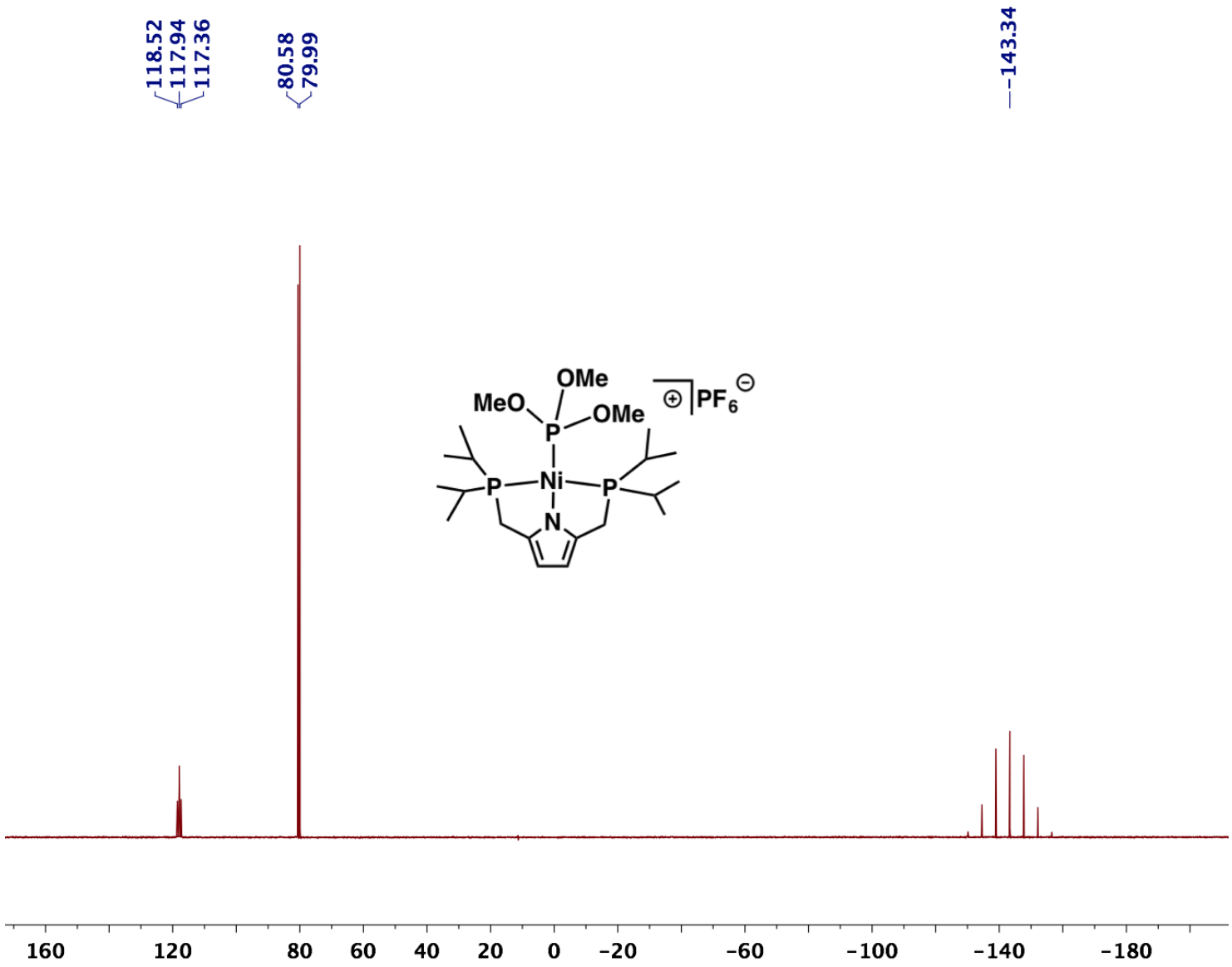

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni\{P(OMe)_3\}][PF_6]$ (**4**).

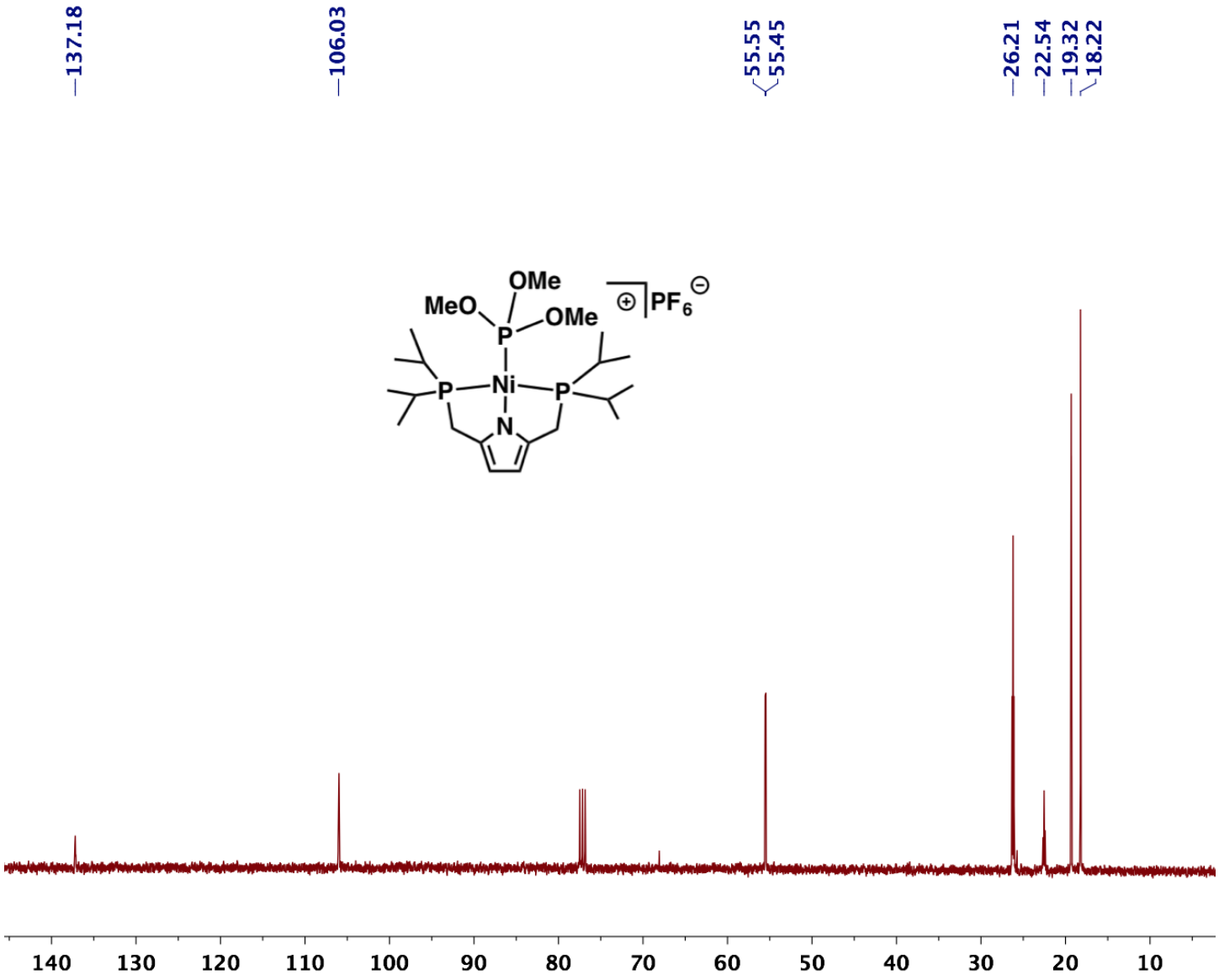

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni\{P(OMe)_3\}][PF_6]$ (**4**).

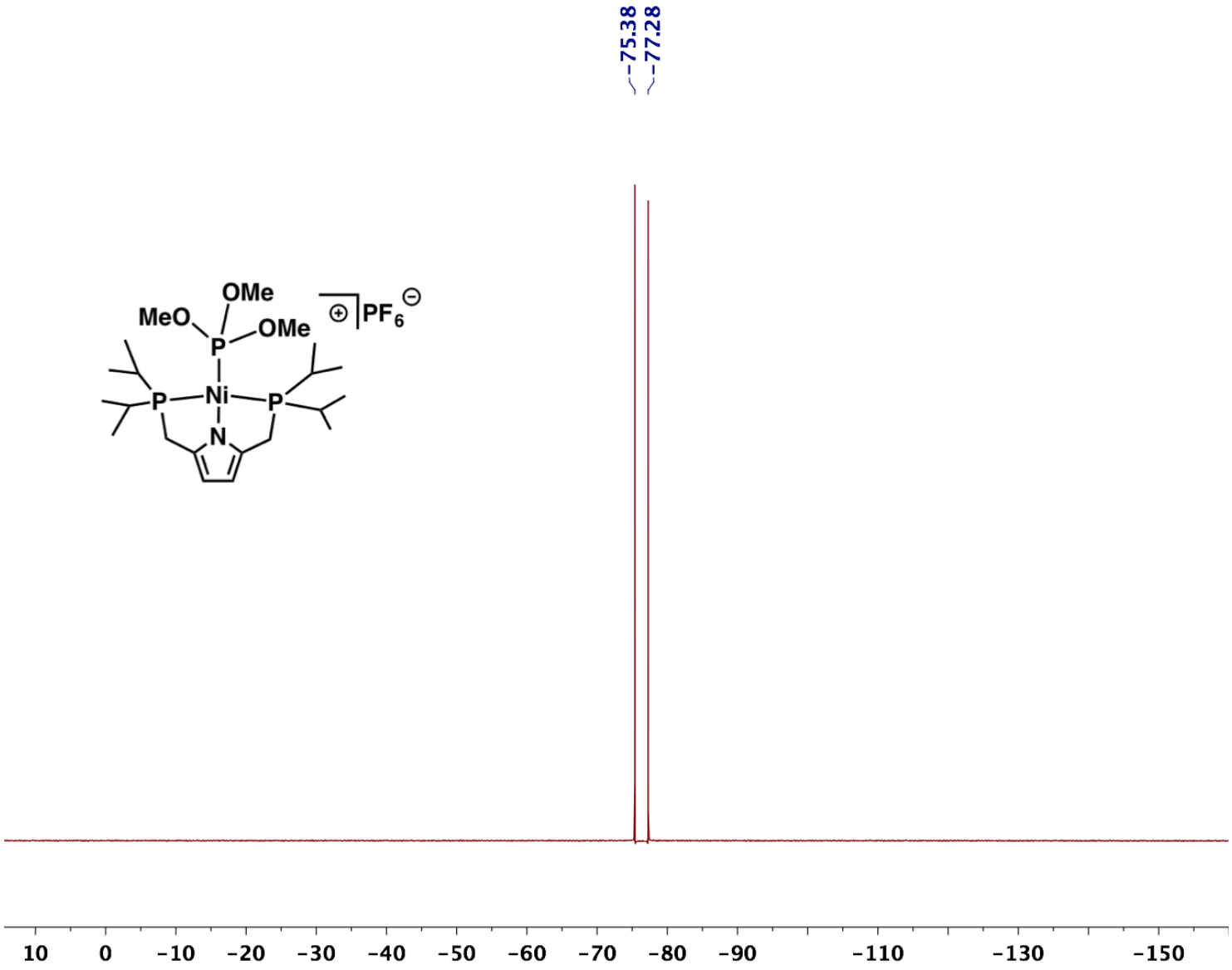

Figure S14. ^{19}F NMR spectrum for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**).

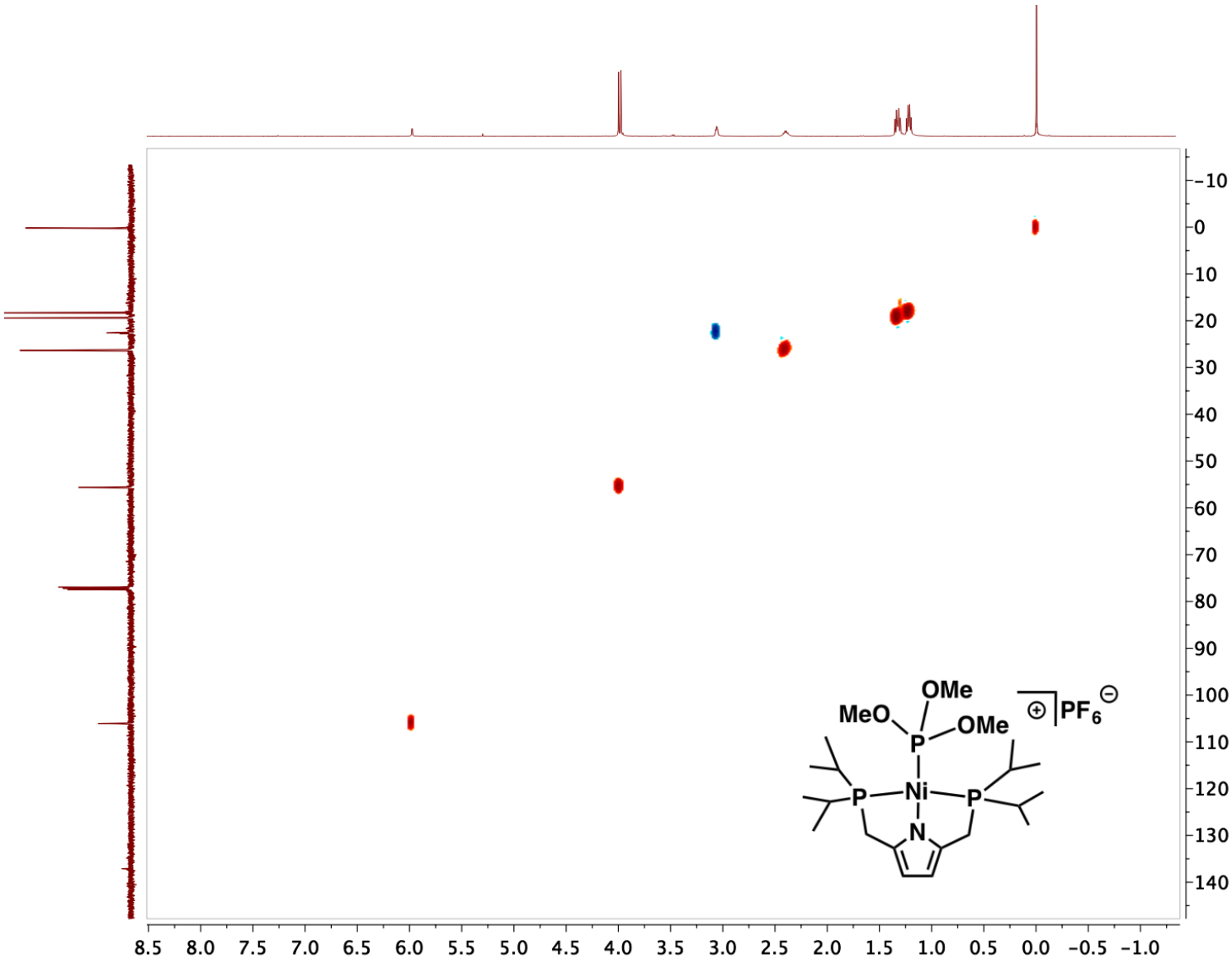

Figure S15. ^{1}H-^{13}C HSQC NMR spectrum for $[(PN^{pyr}P)Ni\{P(OMe)_3\}][PF_6]$ (**4**).

2.4 NMR Spectra for [(PN^{pyr}P)Ni(PPh$_2$)] (5)

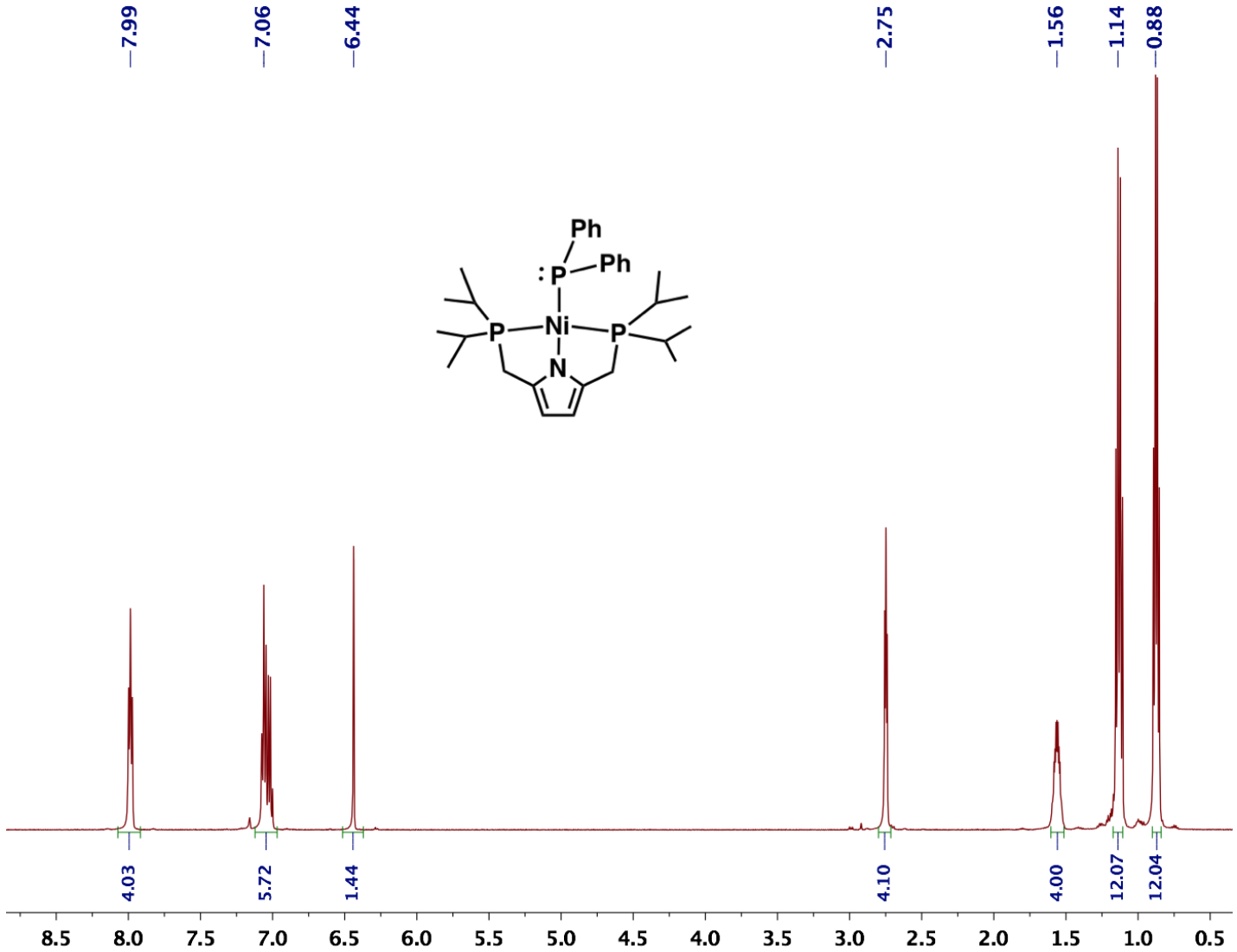

Figure S16. ^{1}H NMR spectrum for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

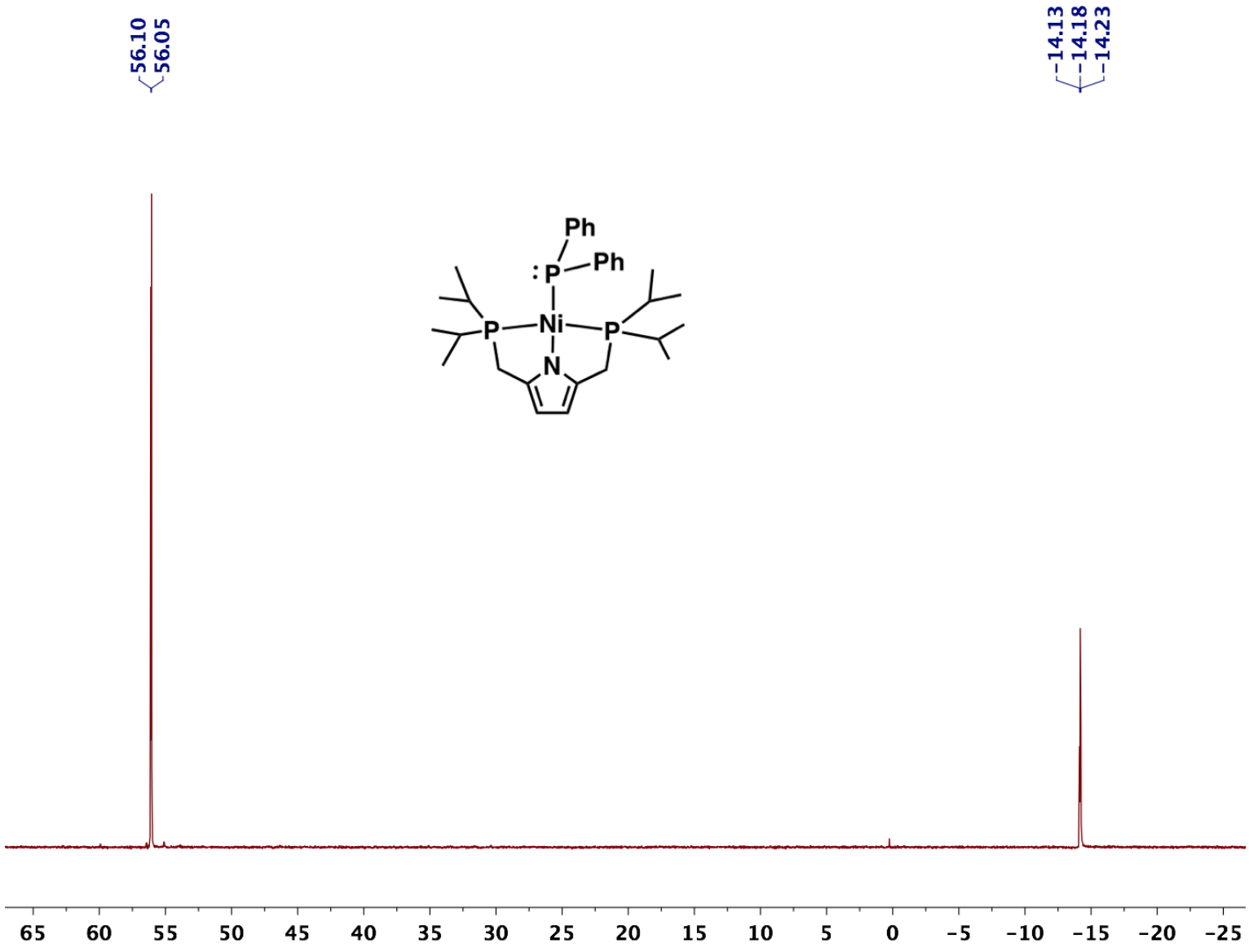

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

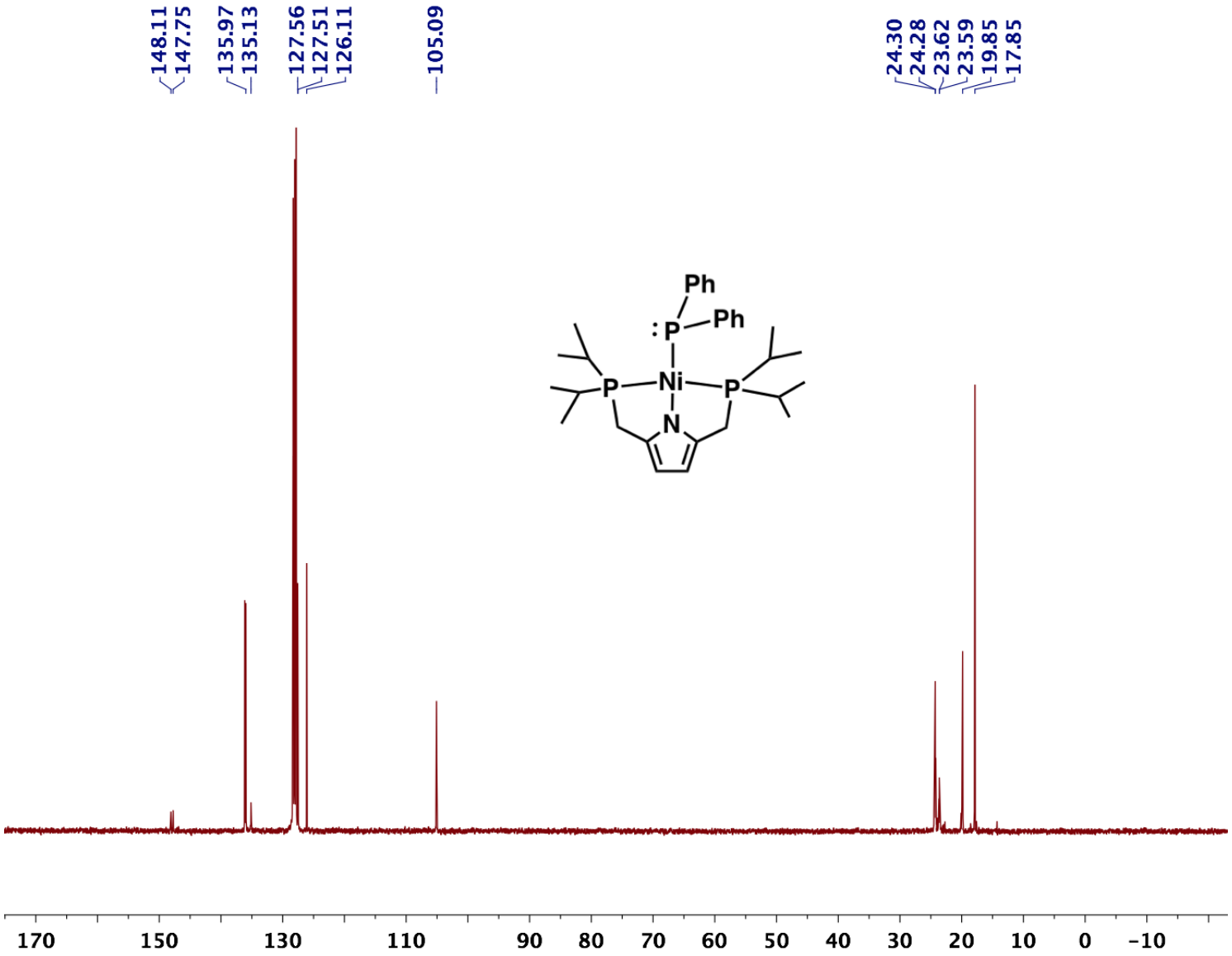

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

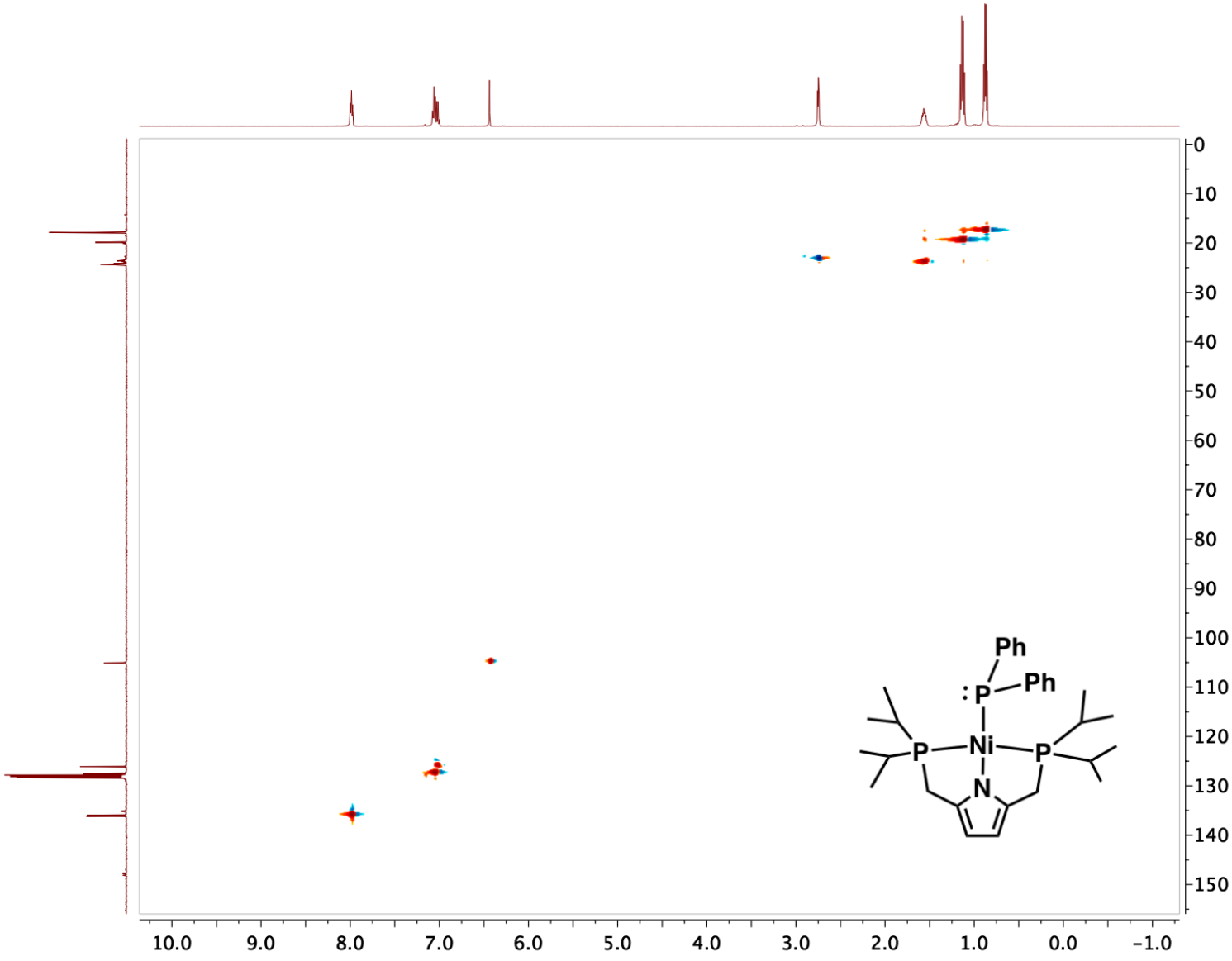

Figure S19. ^{1}H-^{13}C HSQC NMR spectrum for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

2.5 NMR Spectra for [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (6)

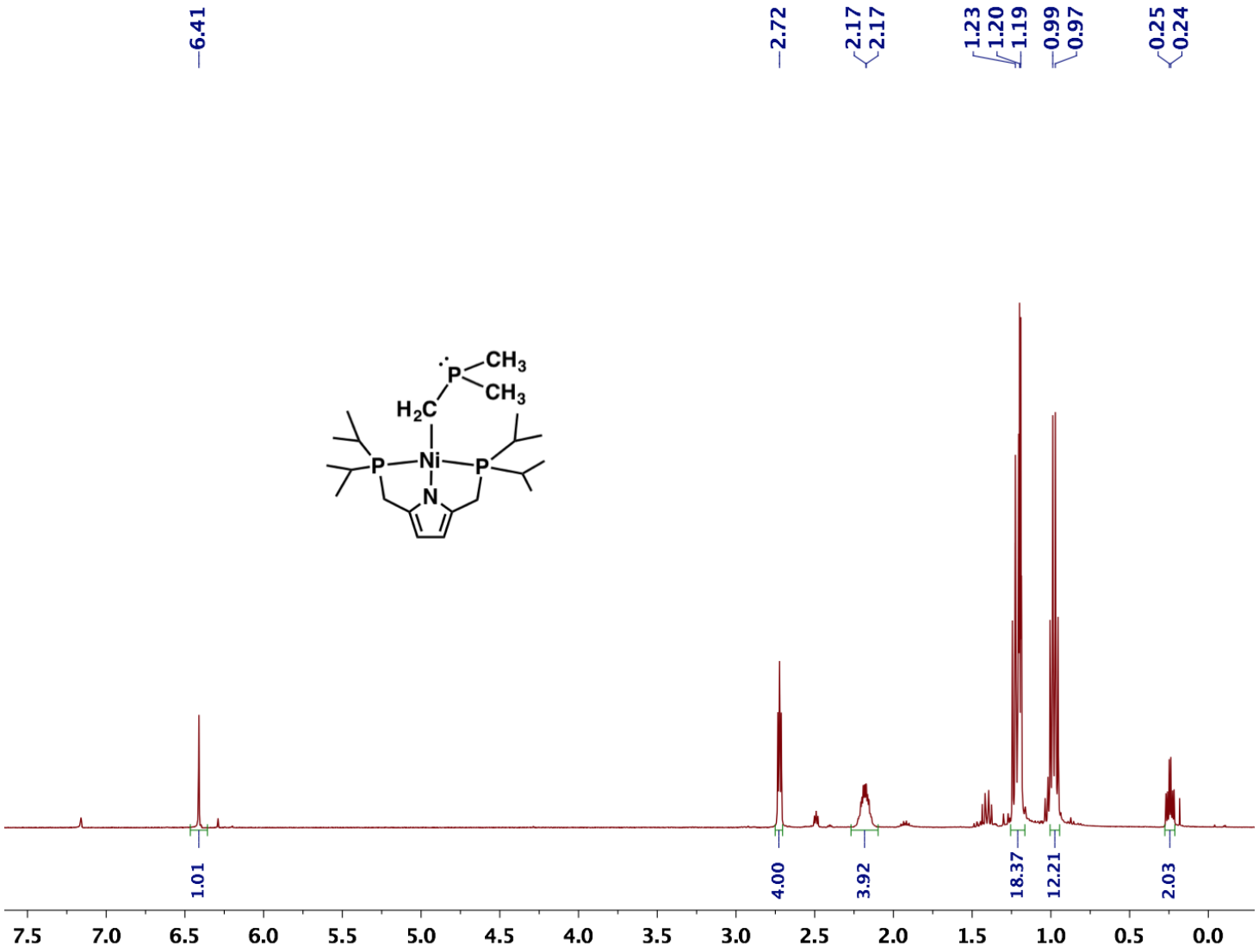

Figure S20. ^{1}H NMR spectrum for [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (**6**).

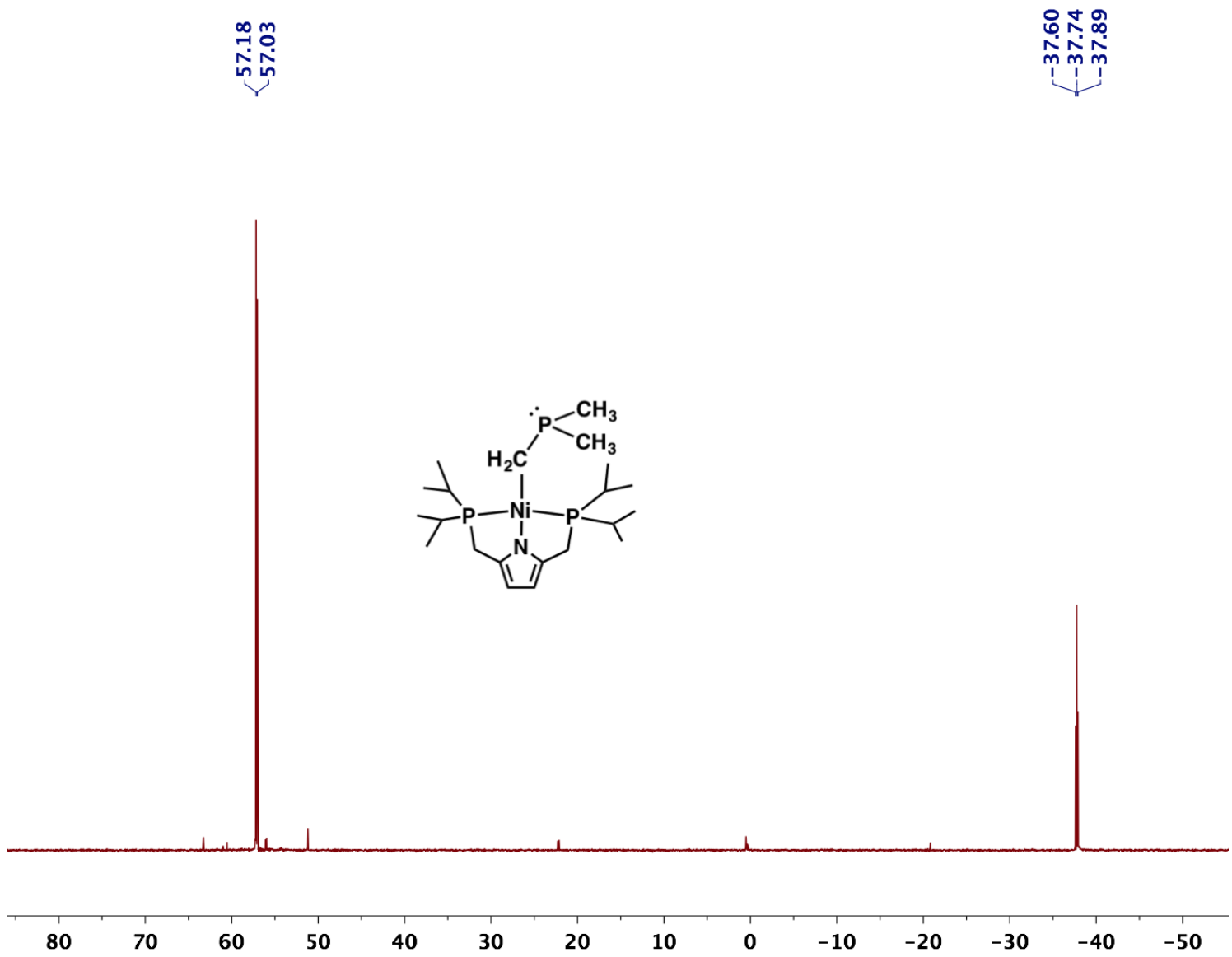

Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum for $[(PN^{pyr}P)Ni(CH_2PMe_2)]$ (**6**).

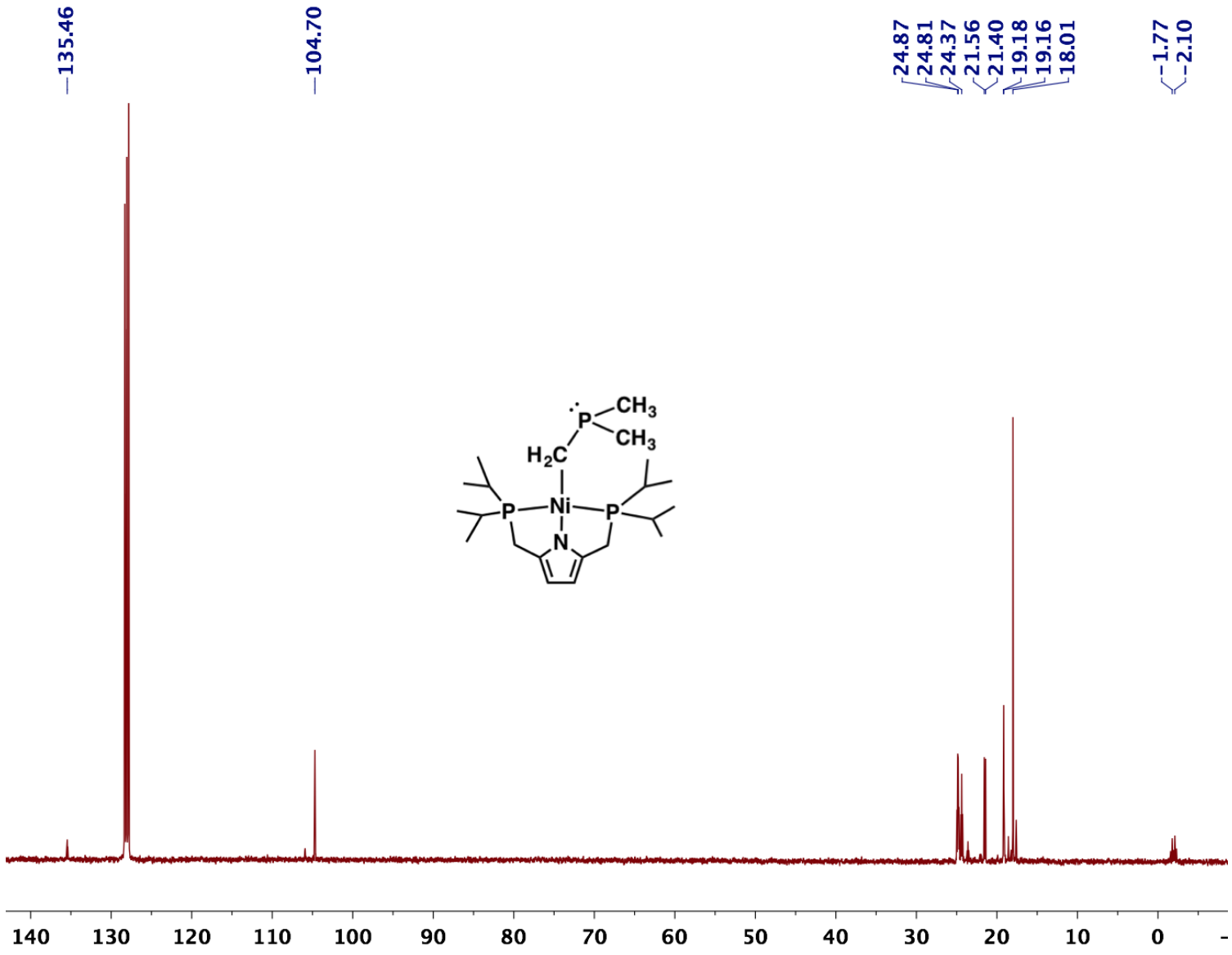

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum for [(PN^{pyr}P)Ni(CH_2PMe_2)] (**6**).

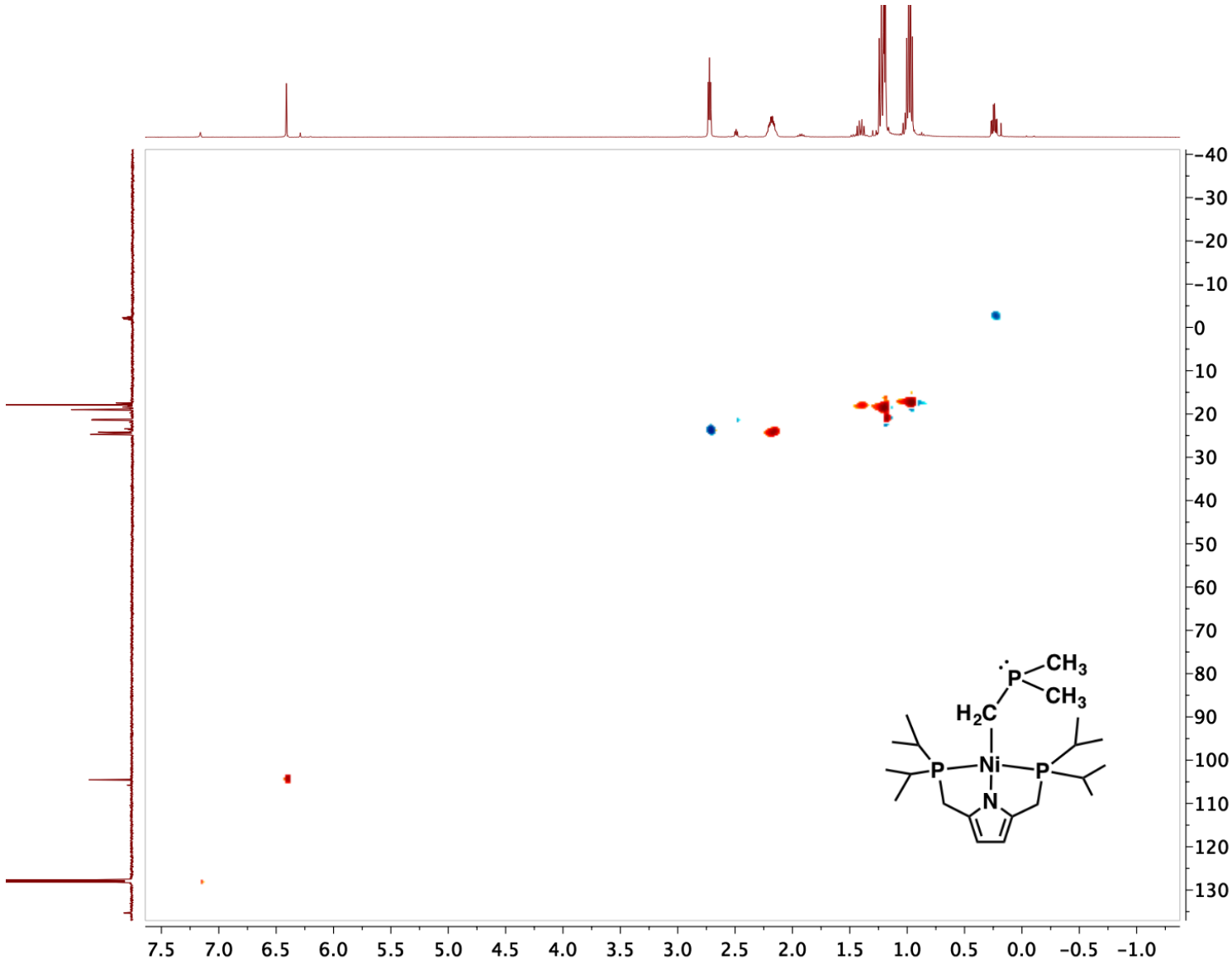

Figure S23. ^{1}H-^{13}C HSQC NMR spectrum for [(PN^{pyr}P)Ni(CH_2PMe_2)] (**6**).

3 Crystallographic tables

3.1 Crystal data for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (2)

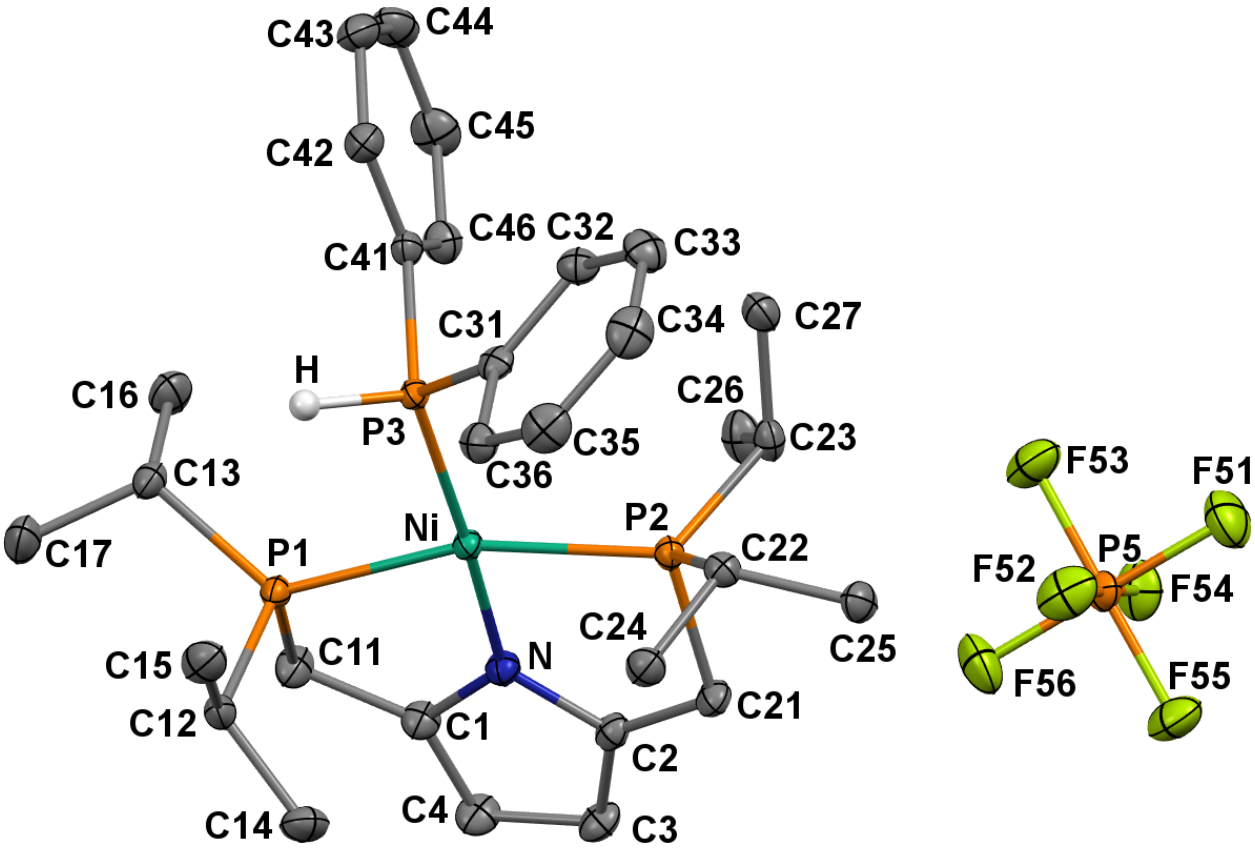

Figure S24. Thermal-ellipsoid representation of [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S1. Crystal data and structure refinement for $[(PN^{pyr}P)Ni(PHPh_2)][PF_6]$ (**2**).

Identification code:	jk2_68	
Empirical formula:	$C_{30}H_{45}F_6NNiP_4$	
Formula weight:	716.26	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	monoclinic	
Space group:	$P2_1/n$	
Unit cell dimensions:	a = 16.313(2) Å	α = 90°
	b = 10.5410(16) Å	β = 94.416(2)°
	c = 19.493(3) Å	γ = 90°
Volume:	3341.9(9) $Å^3$	
Z:	4	
Density (calculated):	1.424 $g \cdot cm^{-3}$	
Absorption coefficient (μ):	0.827 mm^{-1}	
F(000):	1496	
Crystal size:	$0.10 \times 0.09 \times 0.07$ mm^3	
θ range for data collection:	1.57 to 24.99°	
Index ranges:	$-19 \leq h \leq 19$, $-12 \leq k \leq 12$, $-23 \leq l \leq 23$	
Reflections collected:	57265	
Independent reflections:	5886 [R_{int} = 0.0405]	
Completeness to θ = 24.99°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6715	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	5886 / 0 / 385	
Goodness-of-fit on F^2:	1.038	
Final R indices [$I>2\sigma(I)$]:	R_1 = 0.0250, wR_2 = 0.0588	
R indices (all data):	R_1 = 0.0314, wR_2 = 0.0608	
Largest diff. peak and hole:	0.417 and −0.579 $e^- \cdot Å^{-3}$	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Ni	0.28363(1)	0.90376(2)	0.45587(1)	0.012(1)
C(1)	0.40365(11)	1.10768(17)	0.47114(9)	0.018(1)
P(1)	0.27669(3)	1.04382(4)	0.54027(2)	0.014(1)
C(2)	0.39850(10)	1.01903(17)	0.36713(9)	0.016(1)
P(2)	0.30296(3)	0.81143(4)	0.35527(2)	0.013(1)
C(3)	0.45371(11)	1.11669(18)	0.36717(9)	0.020(1)
P(3)	0.19122(3)	0.77873(4)	0.49445(2)	0.012(1)
C(4)	0.45716(11)	1.17329(18)	0.43319(9)	0.021(1)
C(11)	0.37777(11)	1.11962(18)	0.54280(9)	0.021(1)
P(5)	0.53160(3)	0.66333(4)	0.19326(2)	0.018(1)
C(17)	0.23803(14)	1.1194(2)	0.67321(10)	0.030(1)
C(16)	0.32670(13)	0.92680(19)	0.66493(10)	0.027(1)
C(15)	0.11420(12)	1.11514(19)	0.50617(10)	0.026(1)
C(14)	0.22148(13)	1.22945(19)	0.44474(10)	0.026(1)
C(13)	0.25613(11)	1.00382(17)	0.62933(9)	0.018(1)
C(12)	0.20182(11)	1.16754(17)	0.51256(9)	0.019(1)
C(21)	0.36397(11)	0.93067(17)	0.31258(9)	0.017(1)
C(23)	0.36838(11)	0.66889(17)	0.35513(9)	0.018(1)
C(22)	0.21321(10)	0.78305(16)	0.29427(9)	0.016(1)
C(27)	0.32639(12)	0.55038(17)	0.38049(10)	0.022(1)
C(26)	0.44995(11)	0.69505(19)	0.39640(10)	0.025(1)
C(25)	0.23792(12)	0.74668(17)	0.22263(9)	0.020(1)
C(24)	0.15830(11)	0.90079(17)	0.29000(9)	0.021(1)
N	0.36696(9)	1.01207(14)	0.43097(7)	0.015(1)
C(36)	0.05250(11)	0.76502(18)	0.40310(9)	0.019(1)
C(35)	−0.00217(11)	0.7074(2)	0.35458(10)	0.025(1)
C(34)	0.00604(12)	0.57957(19)	0.33987(10)	0.026(1)
C(33)	0.06801(12)	0.50914(18)	0.37423(10)	0.023(1)
C(32)	0.12303(11)	0.56663(17)	0.42225(9)	0.019(1)
C(31)	0.11634(10)	0.69558(17)	0.43646(9)	0.015(1)
C(41)	0.23641(11)	0.65860(16)	0.55231(9)	0.016(1)
C(42)	0.18710(12)	0.57615(17)	0.58733(9)	0.020(1)
C(43)	0.22325(13)	0.48567(18)	0.63132(10)	0.026(1)
C(44)	0.30814(13)	0.47780(19)	0.64172(10)	0.029(1)
C(45)	0.35714(12)	0.55969(19)	0.60788(10)	0.027(1)
C(46)	0.32155(11)	0.64978(18)	0.56297(9)	0.021(1)
F(51)	0.53493(8)	0.53523(11)	0.14954(6)	0.038(1)
F(52)	0.43365(7)	0.66657(12)	0.18015(6)	0.034(1)
F(53)	0.52330(7)	0.58224(12)	0.26150(6)	0.035(1)

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
F(54)	0.62949(6)	0.66147(12)	0.20673(6)	0.031(1)
F(55)	0.53925(7)	0.74309(12)	0.12428(6)	0.034(1)
F(56)	0.52835(7)	0.79177(11)	0.23643(6)	0.037(1)
H(3)	0.4841	1.1419	0.3298	0.024
H(4)	0.4903	1.2435	0.4484	0.025
H(11A)	0.3741	1.2099	0.5562	0.025
H(11B)	0.4173	1.0760	0.5760	0.025
H	0.1407(11)	0.8360(17)	0.5322(9)	0.019(5)
H(17A)	0.2290	1.0917	0.7200	0.045
H(17B)	0.1887	1.1625	0.6531	0.045
H(17C)	0.2848	1.1778	0.6747	0.045
H(16A)	0.3723	0.9837	0.6794	0.041
H(16B)	0.3455	0.8634	0.6329	0.041
H(16C)	0.3075	0.8839	0.7053	0.041
H(15A)	0.1027	1.0729	0.5492	0.039
H(15B)	0.1085	1.0540	0.4682	0.039
H(15C)	0.0752	1.1849	0.4970	0.039
H(14A)	0.1805	1.2952	0.4322	0.039
H(14B)	0.2202	1.1650	0.4085	0.039
H(14C)	0.2763	1.2679	0.4502	0.039
H(13)	0.2061	0.9488	0.6269	0.021
H(12)	0.2045	1.2350	0.5487	0.022
H(21A)	0.4089	0.8891	0.2896	0.021
H(21B)	0.3287	0.9775	0.2776	0.021
H(23)	0.3808	0.6529	0.3064	0.021
H(22)	0.1809	0.7113	0.3122	0.019
H(27A)	0.3623	0.4768	0.3760	0.034
H(27B)	0.2744	0.5368	0.3529	0.034
H(27C)	0.3156	0.5614	0.4289	0.034
H(26A)	0.4397	0.7146	0.4441	0.038
H(26B)	0.4772	0.7673	0.3762	0.038
H(26C)	0.4853	0.6200	0.3953	0.038
H(25A)	0.2712	0.6691	0.2259	0.029
H(25B)	0.2701	0.8156	0.2043	0.029
H(25C)	0.1884	0.7320	0.1920	0.029
H(24A)	0.1486	0.9292	0.3366	0.031
H(24B)	0.1056	0.8801	0.2649	0.031
H(24C)	0.1854	0.9685	0.2658	0.031
H(36)	0.0463	0.8523	0.4136	0.023
H(35)	−0.0452	0.7555	0.3315	0.030
H(34)	−0.0308	0.5403	0.3062	0.031
H(33)	0.0728	0.4211	0.3649	0.028

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Table S2. – continued from previous page

atom	x	y	x	U(eq)
H(32)	0.1655	0.5179	0.4456	0.022
H(42)	0.1289	0.5822	0.5810	0.024
H(43)	0.1897	0.4287	0.6545	0.032
H(44)	0.3326	0.4159	0.6722	0.034
H(45)	0.4153	0.5545	0.6153	0.032
H(46)	0.3555	0.7056	0.5394	0.025

Table S3. Anisotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.0121(1)	0.0118(1)	0.0126(1)	−0.0007(1)	0.0027(1)	−0.0009(1)
C(1)	0.0157(9)	0.0192(9)	0.0182(9)	−0.0016(7)	0.0007(7)	−0.0045(7)
P(1)	0.0161(2)	0.0137(2)	0.0115(2)	−0.0011(2)	0.0023(2)	−0.0018(2)
C(2)	0.0126(9)	0.0193(9)	0.0154(9)	0.0011(7)	0.0036(7)	0.0016(7)
P(2)	0.0138(2)	0.0137(2)	0.0130(2)	−0.0019(2)	0.0029(2)	0.0005(2)
C(3)	0.0147(9)	0.0262(10)	0.0192(9)	0.0033(8)	0.0042(7)	−0.0034(8)
P(3)	0.0121(1)	0.0118(1)	0.0126(1)	−0.0007(1)	0.0027(1)	−0.0009(1)
C(4)	0.0172(9)	0.0234(10)	0.0218(10)	−0.0011(8)	0.0003(7)	−0.0083(8)
C(11)	0.0212(10)	0.0229(10)	0.0176(9)	−0.0035(8)	0.0016(8)	−0.0085(8)
P(5)	0.0153(2)	0.0197(2)	0.0193(2)	−0.0002(2)	0.0045(2)	0.0023(2)
C(17)	0.0430(13)	0.0306(11)	0.0170(10)	−0.0013(8)	0.0067(9)	0.0083(10)
C(16)	0.0359(12)	0.0286(11)	0.0166(10)	0.0023(8)	−0.0003(8)	0.0060(9)
C(15)	0.0234(10)	0.0285(11)	0.0270(11)	0.0068(8)	0.0057(8)	0.0097(9)
C(14)	0.0313(11)	0.0206(10)	0.0255(11)	0.0083(8)	0.0029(8)	0.0034(8)
C(13)	0.0198(9)	0.0208(9)	0.0132(9)	0.0003(7)	0.0035(7)	−0.0023(7)
C(12)	0.0271(10)	0.0144(9)	0.0141(9)	−0.0015(7)	0.0027(7)	0.0036(8)
C(21)	0.0170(9)	0.0189(9)	0.0170(9)	0.0000(7)	0.0063(7)	−0.0018(7)
C(23)	0.0176(9)	0.0198(9)	0.0160(9)	−0.0041(7)	0.0013(7)	0.0050(7)
C(22)	0.0147(9)	0.0157(9)	0.0166(9)	−0.0003(7)	0.0009(7)	−0.0006(7)
C(27)	0.0286(11)	0.0175(9)	0.0212(10)	−0.0019(8)	0.0023(8)	0.0048(8)
C(26)	0.0186(10)	0.0308(11)	0.0255(10)	−0.0061(9)	−0.0007(8)	0.0068(8)
C(25)	0.0235(10)	0.0194(9)	0.0155(9)	−0.0025(7)	−0.0014(7)	−0.0003(8)
C(24)	0.0196(10)	0.0216(10)	0.0204(10)	0.0021(8)	0.0023(8)	0.0038(8)
N	0.0143(7)	0.0160(7)	0.0158(7)	−0.0008(6)	0.0030(6)	−0.0022(6)
C(36)	0.0156(9)	0.0196(9)	0.0223(10)	0.0006(8)	0.0044(7)	0.0021(8)
C(35)	0.0149(10)	0.0332(11)	0.0275(11)	0.0025(9)	−0.0015(8)	0.0019(8)
C(34)	0.0188(10)	0.0332(11)	0.0248(10)	−0.0042(9)	−0.0024(8)	−0.0079(9)
C(33)	0.0240(10)	0.0191(9)	0.0270(10)	−0.0034(8)	0.0009(8)	−0.0044(8)
C(32)	0.0170(9)	0.0182(9)	0.0207(10)	0.0018(7)	0.0008(7)	−0.0008(7)
C(31)	0.0123(9)	0.0175(9)	0.0161(9)	0.0011(7)	0.0039(7)	−0.0035(7)
C(41)	0.0195(9)	0.0149(9)	0.0129(9)	−0.0017(7)	0.0012(7)	0.0017(7)
C(42)	0.0220(10)	0.0204(10)	0.0177(9)	0.0007(7)	0.0032(8)	−0.0003(8)
C(43)	0.0376(12)	0.0222(10)	0.0193(10)	0.0046(8)	0.0035(9)	−0.0027(9)
C(44)	0.0405(13)	0.0219(10)	0.0221(10)	0.0027(8)	−0.0063(9)	0.0069(9)
C(45)	0.0220(10)	0.0289(11)	0.0292(11)	0.0003(9)	−0.0046(8)	0.0066(9)
C(46)	0.0199(10)	0.0215(10)	0.0213(10)	−0.0012(8)	0.0018(8)	0.0005(8)
F(51)	0.0437(8)	0.0290(7)	0.0417(7)	−0.0139(6)	0.0062(6)	−0.0026(6)
F(52)	0.0160(6)	0.0465(8)	0.0381(7)	0.0103(6)	0.0020(5)	0.0004(5)
F(53)	0.0321(7)	0.0446(7)	0.0281(6)	0.0150(6)	0.0072(5)	0.0078(6)
F(54)	0.0157(6)	0.0425(7)	0.0353(7)	−0.0049(5)	0.0040(5)	0.0045(5)

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Table S3. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(55)	0.0329(7)	0.0398(7)	0.0298(7)	0.0134(5)	0.0098(5)	0.0006(6)
F(56)	0.0362(7)	0.0298(7)	0.0452(8)	−0.0150(6)	0.0098(6)	0.0048(6)

Table S4. Distances [Å] for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**).

atom – atom	distance	atom – atom	distance
Ni – N	1.8678(14)	Ni – P(3)	2.1793(5)
Ni – P(1)	2.2199(5)	Ni – P(2)	2.2333(5)
C(1) – C(4)	1.374(3)	C(1) – N	1.384(2)
C(1) – C(11)	1.495(2)	P(1) – C(11)	1.8295(18)
P(1) – C(12)	1.8392(18)	P(1) – C(13)	1.8422(17)
C(2) – C(3)	1.368(2)	C(2) – N	1.385(2)
C(2) – C(21)	1.491(2)	P(2) – C(22)	1.8383(17)
P(2) – C(21)	1.8412(18)	P(2) – C(23)	1.8430(18)
C(3) – C(4)	1.416(3)	C(3) – H(3)	0.9500
P(3) – C(41)	1.8140(18)	P(3) – C(31)	1.8236(18)
P(3) – H	1.296(18)	C(4) – H(4)	0.9500
C(11) – H(11A)	0.9900	C(11) – H(11B)	0.9900
P(5) – F(53)	1.5957(12)	P(5) – F(56)	1.5971(12)
P(5) – F(54)	1.5983(12)	P(5) – F(55)	1.5988(12)
P(5) – F(52)	1.5990(12)	P(5) – F(51)	1.5999(12)
C(17) – C(13)	1.530(3)	C(17) – H(17A)	0.9800
C(17) – H(17B)	0.9800	C(17) – H(17C)	0.9800
C(16) – C(13)	1.531(3)	C(16) – H(16A)	0.9800
C(16) – H(16B)	0.9800	C(16) – H(16C)	0.9800
C(15) – C(12)	1.529(3)	C(15) – H(15A)	0.9800
C(15) – H(15B)	0.9800	C(15) – H(15C)	0.9800
C(14) – C(12)	1.530(2)	C(14) – H(14A)	0.9800
C(14) – H(14B)	0.9800	C(14) – H(14C)	0.9800
C(13) – H(13)	1.0000	C(12) – H(12)	1.0000
C(21) – H(21A)	0.9900	C(21) – H(21B)	0.9900
C(23) – C(27)	1.525(3)	C(23) – C(26)	1.526(2)
C(23) – H(23)	1.0000	C(22) – C(24)	1.529(2)
C(22) – C(25)	1.532(2)	C(22) – H(22)	1.0000
C(27) – H(27A)	0.9800	C(27) – H(27B)	0.9800
C(27) – H(27C)	0.9800	C(26) – H(26A)	0.9800
C(26) – H(26B)	0.9800	C(26) – H(26C)	0.9800
C(25) – H(25A)	0.9800	C(25) – H(25B)	0.9800
C(25) – H(25C)	0.9800	C(24) – H(24A)	0.9800
C(24) – H(24B)	0.9800	C(24) – H(24C)	0.9800
C(36) – C(35)	1.389(3)	C(36) – C(31)	1.392(2)
C(36) – H(36)	0.9500	C(35) – C(34)	1.386(3)
C(35) – H(35)	0.9500	C(34) – C(33)	1.385(3)
C(34) – H(34)	0.9500	C(33) – C(32)	1.385(3)
C(33) – H(33)	0.9500	C(32) – C(31)	1.393(2)
C(32) – H(32)	0.9500	C(41) – C(46)	1.392(3)
C(41) – C(42)	1.397(3)	C(42) – C(43)	1.384(3)

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Table S4. – continued from previous page

atom – atom	distance	atom – atom	distance
C(42) – H(42)	0.9500	C(43) – C(44)	1.386(3)
C(43) – H(43)	0.9500	C(44) – C(45)	1.379(3)
C(44) – H(44)	0.9500	C(45) – C(46)	1.388(3)
C(45) – H(45)	0.9500	C(46) – H(46)	0.9500

Table S5. Angles [°] for [(PN^{pyr}P)Ni(PHPh$_2$)][PF$_6$] (**2**).

atom – atom – atom	angle	atom – atom – atom	angle
N – Ni – P(3)	174.83(5)	N – Ni – P(1)	82.28(5)
P(3) – Ni – P(1)	94.035(19)	N – Ni – P(2)	83.30(5)
P(3) – Ni – P(2)	100.82(2)	P(1) – Ni – P(2)	163.600(19)
C(4) – C(1) – N	109.09(15)	C(4) – C(1) – C(11)	134.23(17)
N – C(1) – C(11)	116.67(15)	C(11) – P(1) – C(12)	105.96(9)
C(11) – P(1) – C(13)	107.68(8)	C(12) – P(1) – C(13)	105.91(8)
C(11) – P(1) – Ni	102.31(6)	C(12) – P(1) – Ni	108.93(6)
C(13) – P(1) – Ni	124.72(6)	C(3) – C(2) – N	109.23(15)
C(3) – C(2) – C(21)	133.10(16)	N – C(2) – C(21)	117.50(15)
C(22) – P(2) – C(21)	104.48(8)	C(22) – P(2) – C(23)	107.39(8)
C(21) – P(2) – C(23)	102.86(8)	C(22) – P(2) – Ni	118.66(6)
C(21) – P(2) – Ni	102.54(6)	C(23) – P(2) – Ni	118.53(6)
C(2) – C(3) – C(4)	107.33(16)	C(2) – C(3) – H(3)	126.3
C(4) – C(3) – H(3)	126.3	C(41) – P(3) – C(31)	105.70(8)
C(41) – P(3) – Ni	112.21(6)	C(31) – P(3) – Ni	121.66(6)
C(41) – P(3) – H	102.6(8)	C(31) – P(3) – H	98.7(8)
Ni – P(3) – H	113.6(8)	C(1) – C(4) – C(3)	107.15(16)
C(1) – C(4) – H(4)	126.4	C(3) – C(4) – H(4)	126.4
C(1) – C(11) – P(1)	104.88(12)	C(1) – C(11) – H(11A)	110.8
P(1) – C(11) – H(11A)	110.8	C(1) – C(11) – H(11B)	110.8
P(1) – C(11) – H(11B)	110.8	H(11A) – C(11) – H(11B)	108.8
F(53) – P(5) – F(56)	90.37(7)	F(53) – P(5) – F(54)	90.25(7)
F(56) – P(5) – F(54)	89.83(7)	F(53) – P(5) – F(55)	179.21(8)
F(56) – P(5) – F(55)	90.30(7)	F(54) – P(5) – F(55)	90.17(6)
F(53) – P(5) – F(52)	89.81(6)	F(56) – P(5) – F(52)	89.59(7)
F(54) – P(5) – F(52)	179.42(8)	F(55) – P(5) – F(52)	89.78(6)
F(53) – P(5) – F(51)	90.03(7)	F(56) – P(5) – F(51)	179.60(8)
F(54) – P(5) – F(51)	90.16(7)	F(55) – P(5) – F(51)	89.30(7)
F(52) – P(5) – F(51)	90.42(7)	C(13) – C(17) – H(17A)	109.5
C(13) – C(17) – H(17B)	109.5	H(17A) – C(17) – H(17B)	109.5
C(13) – C(17) – H(17C)	109.5	H(17A) – C(17) – H(17C)	109.5
H(17B) – C(17) – H(17C)	109.5	C(13) – C(16) – H(16A)	109.5
C(13) – C(16) – H(16B)	109.5	H(16A) – C(16) – H(16B)	109.5
C(13) – C(16) – H(16C)	109.5	H(16A) – C(16) – H(16C)	109.5
H(16B) – C(16) – H(16C)	109.5	C(12) – C(15) – H(15A)	109.5
C(12) – C(15) – H(15B)	109.5	H(15A) – C(15) – H(15B)	109.5
C(12) – C(15) – H(15C)	109.5	H(15A) – C(15) – H(15C)	109.5
H(15B) – C(15) – H(15C)	109.5	C(12) – C(14) – H(14A)	109.5
C(12) – C(14) – H(14B)	109.5	H(14A) – C(14) – H(14B)	109.5
C(12) – C(14) – H(14C)	109.5	H(14A) – C(14) – H(14C)	109.5
H(14B) – C(14) – H(14C)	109.5	C(17) – C(13) – C(16)	109.84(15)

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(17) – C(13) – P(1)	113.69(13)	C(16) – C(13) – P(1)	111.32(13)
C(17) – C(13) – H(13)	107.2	C(16) – C(13) – H(13)	107.2
P(1) – C(13) – H(13)	107.2	C(15) – C(12) – C(14)	109.91(15)
C(15) – C(12) – P(1)	111.31(13)	C(14) – C(12) – P(1)	112.18(13)
C(15) – C(12) – H(12)	107.8	C(14) – C(12) – H(12)	107.8
P(1) – C(12) – H(12)	107.8	C(2) – C(21) – P(2)	106.96(12)
C(2) – C(21) – H(21A)	110.3	P(2) – C(21) – H(21A)	110.3
C(2) – C(21) – H(21B)	110.3	P(2) – C(21) – H(21B)	110.3
H(21A) – C(21) – H(21B)	108.6	C(27) – C(23) – C(26)	111.85(15)
C(27) – C(23) – P(2)	113.12(13)	C(26) – C(23) – P(2)	109.47(12)
C(27) – C(23) – H(23)	107.4	C(26) – C(23) – H(23)	107.4
P(2) – C(23) – H(23)	107.4	C(24) – C(22) – C(25)	110.35(14)
C(24) – C(22) – P(2)	109.71(12)	C(25) – C(22) – P(2)	112.21(12)
C(24) – C(22) – H(22)	108.2	C(25) – C(22) – H(22)	108.2
P(2) – C(22) – H(22)	108.2	C(23) – C(27) – H(27A)	109.5
C(23) – C(27) – H(27B)	109.5	H(27A) – C(27) – H(27B)	109.5
C(23) – C(27) – H(27C)	109.5	H(27A) – C(27) – H(27C)	109.5
H(27B) – C(27) – H(27C)	109.5	C(23) – C(26) – H(26A)	109.5
C(23) – C(26) – H(26B)	109.5	H(26A) – C(26) – H(26B)	109.5
C(23) – C(26) – H(26C)	109.5	H(26A) – C(26) – H(26C)	109.5
H(26B) – C(26) – H(26C)	109.5	C(22) – C(25) – H(25A)	109.5
C(22) – C(25) – H(25B)	109.5	H(25A) – C(25) – H(25B)	109.5
C(22) – C(25) – H(25C)	109.5	H(25A) – C(25) – H(25C)	109.5
H(25B) – C(25) – H(25C)	109.5	C(22) – C(24) – H(24A)	109.5
C(22) – C(24) – H(24B)	109.5	H(24A) – C(24) – H(24B)	109.5
C(22) – C(24) – H(24C)	109.5	H(24A) – C(24) – H(24C)	109.5
H(24B) – C(24) – H(24C)	109.5	C(1) – N – C(2)	107.19(14)
C(1) – N – Ni	126.15(12)	C(2) – N – Ni	126.45(12)
C(35) – C(36) – C(31)	120.40(17)	C(35) – C(36) – H(36)	119.8
C(31) – C(36) – H(36)	119.8	C(34) – C(35) – C(36)	119.92(18)
C(34) – C(35) – H(35)	120.0	C(36) – C(35) – H(35)	120.0
C(33) – C(34) – C(35)	119.98(18)	C(33) – C(34) – H(34)	120.0
C(35) – C(34) – H(34)	120.0	C(34) – C(33) – C(32)	120.20(18)
C(34) – C(33) – H(33)	119.9	C(32) – C(33) – H(33)	119.9
C(33) – C(32) – C(31)	120.31(17)	C(33) – C(32) – H(32)	119.8
C(31) – C(32) – H(32)	119.8	C(36) – C(31) – C(32)	119.15(16)
C(36) – C(31) – P(3)	118.56(14)	C(32) – C(31) – P(3)	122.23(14)
C(46) – C(41) – C(42)	119.39(16)	C(46) – C(41) – P(3)	119.52(14)
C(42) – C(41) – P(3)	121.08(14)	C(43) – C(42) – C(41)	119.84(18)
C(43) – C(42) – H(42)	120.1	C(41) – C(42) – H(42)	120.1
C(42) – C(43) – C(44)	120.33(18)	C(42) – C(43) – H(43)	119.8
C(44) – C(43) – H(43)	119.8	C(45) – C(44) – C(43)	120.13(18)

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(45) – C(44) – H(44)	119.9	C(43) – C(44) – H(44)	119.9
C(44) – C(45) – C(46)	120.02(18)	C(44) – C(45) – H(45)	120.0
C(46) – C(45) – H(45)	120.0	C(45) – C(46) – C(41)	120.27(18)
C(45) – C(46) – H(46)	119.9	C(41) – C(46) – H(46)	119.9

3.2 Crystal data for [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (3)

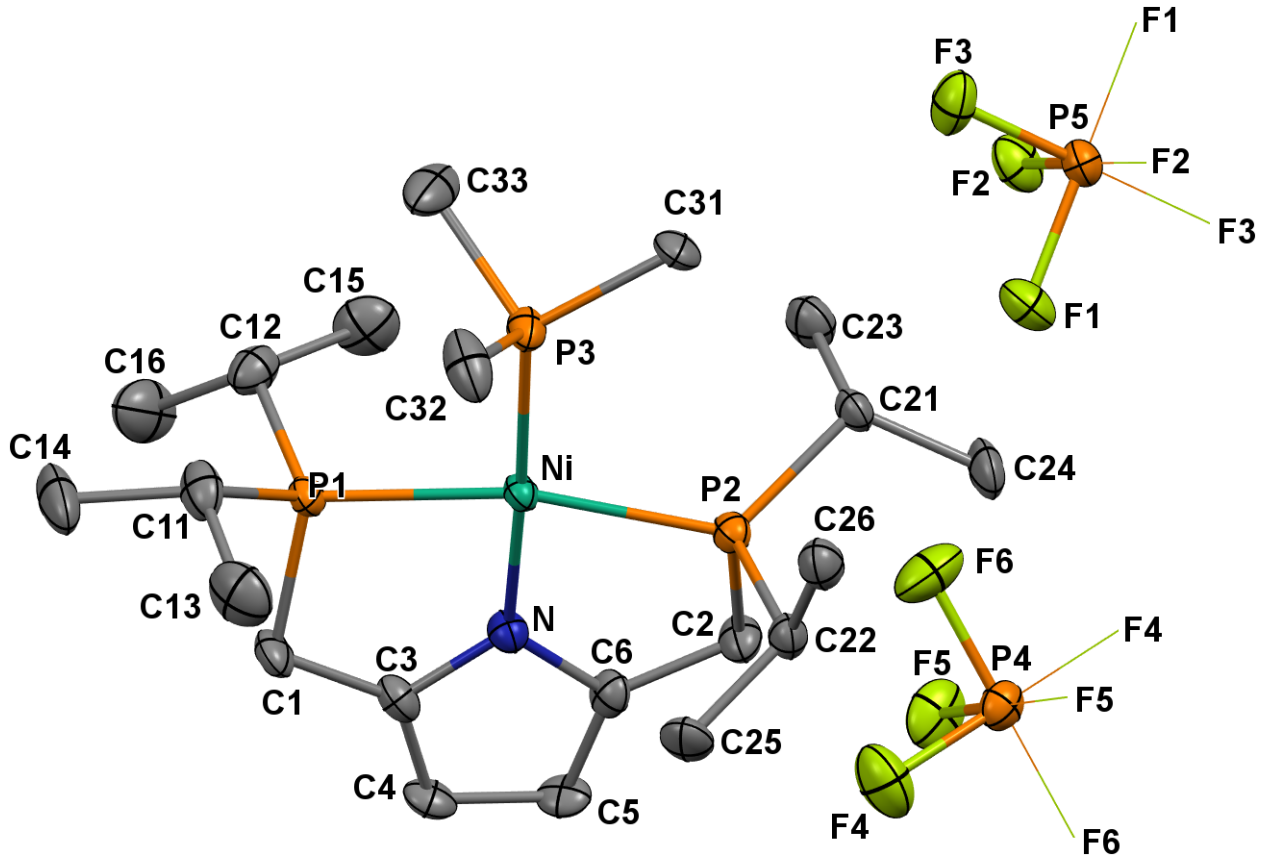

Figure S25. Thermal-ellipsoid representation of [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (**3**) at 50% probability. Hydrogen atoms were omitted for clarity.

Table S6. Crystal data and structure refinement for $[(PN^{pyr}P)NiP(Me_3)][PF_6]$ (**3**).

$C_{21}H_{43}F_6NNiP_4$ Identification code:	jk2_58	
Empirical formula:	$C_{21}H_{43}F_6NNiP_4$	
Formula weight:	606.15	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	monoclinic	
Space group:	$P2_1/n$	
Unit cell dimensions:	a = 8.2850(17) Å	α = 90°
	b = 15.792(3) Å	β = 94.379(3)°
	c = 21.433(4) Å	γ = 90°
Volume:	2796.0(10) $Å^3$	
Z:	4	
Density (calculated):	1.440 $g{\cdot}cm^{-3}$	
Absorption coefficient (μ):	0.974 mm^{-1}	
F(000):	1272	
Crystal size:	$0.12 \times 0.10 \times 0.09$ mm^3	
θ range for data collection:	1.60 to 25.00°	
Index ranges:	$-9 \leq h \leq 9$, $-18 \leq k \leq 18$, $-25 \leq l \leq 25$	
Reflections collected:	40751	
Independent reflections:	4861 [R_{int} = 0.0936]	
Completeness to θ = 25.00°:	98.8 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6732	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	4861 / 0 / 312	
Goodness-of-fit on F^2:	1.081	
Final R indices [$I>2\sigma(I)$]:	R_1 = 0.0649, wR_2 = 0.1642	
R indices (all data):	R_1 = 0.0839, wR_2 = 0.1713	
Largest diff. peak and hole:	1.930 and −1.440 $e^{-}{\cdot}Å^{-3}$	

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (**3**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Ni	0.38187(8)	0.17841(4)	0.24940(3)	0.016(1)
F(1)	0.1833(4)	0.0045(2)	0.48131(17)	0.033(1)
C(1)	0.5668(8)	0.2658(4)	0.1403(3)	0.025(1)
P(1)	0.39082(18)	0.19686(9)	0.14638(7)	0.019(1)
P(2)	0.41815(18)	0.18760(9)	0.35377(7)	0.019(1)
C(2)	0.5122(8)	0.2921(4)	0.3657(3)	0.026(1)
F(2)	−0.0335(4)	0.0924(2)	0.47058(16)	0.032(1)
P(3)	0.21570(19)	0.06889(10)	0.24118(7)	0.022(1)
F(3)	−0.0540(5)	−0.0415(2)	0.43384(16)	0.036(1)
C(3)	0.6021(7)	0.3052(4)	0.2036(3)	0.022(1)
N	0.5234(6)	0.2722(3)	0.2524(2)	0.019(1)
P(4)	0.5000	0.5000	0.5000	0.024(1)
F(4)	0.6138(5)	0.4743(3)	0.4468(2)	0.049(1)
C(4)	0.7039(7)	0.3684(4)	0.2256(3)	0.024(1)
P(5)	0.0000	0.0000	0.5000	0.022(1)
F(5)	0.4772(5)	0.5925(2)	0.47024(18)	0.041(1)
C(5)	0.6908(7)	0.3746(4)	0.2903(3)	0.025(1)
C(6)	0.5802(7)	0.3159(4)	0.3059(3)	0.022(1)
F(6)	0.6534(5)	0.5328(2)	0.54307(19)	0.043(1)
C(11)	0.4243(9)	0.1090(4)	0.0933(3)	0.031(2)
C(12)	0.2074(8)	0.2553(4)	0.1147(3)	0.029(1)
C(13)	0.5748(9)	0.0606(5)	0.1170(4)	0.045(2)
C(14)	0.4324(10)	0.1357(5)	0.0249(3)	0.047(2)
C(15)	0.1258(9)	0.2996(5)	0.1678(3)	0.041(2)
C(16)	0.2391(10)	0.3216(5)	0.0652(4)	0.049(2)
C(23)	0.1187(8)	0.2479(4)	0.3820(3)	0.031(2)
C(22)	0.5784(7)	0.1144(4)	0.3853(3)	0.022(1)
C(21)	0.2543(7)	0.1874(4)	0.4067(3)	0.021(1)
C(31)	0.1216(7)	0.0302(4)	0.3093(3)	0.025(1)
C(26)	0.5201(8)	0.0247(4)	0.3958(3)	0.028(1)
C(25)	0.7167(7)	0.1135(4)	0.3419(3)	0.031(2)
C(24)	0.3140(9)	0.2085(4)	0.4740(3)	0.034(2)
C(32)	0.3056(10)	−0.0293(4)	0.2129(3)	0.039(2)
C(33)	0.0364(9)	0.0812(5)	0.1878(3)	0.045(2)
H(1A)	0.6609	0.2325	0.1284	0.030
H(1B)	0.5425	0.3102	0.1082	0.030
H(2A)	0.4306	0.3342	0.3767	0.031
H(2B)	0.5991	0.2897	0.4000	0.031
H(4)	0.7712	0.4020	0.2015	0.029

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Table S7. – continued from previous page

atom	x	y	x	U(eq)
H(5)	0.7483	0.4128	0.3182	0.030
H(11)	0.3304	0.0695	0.0949	0.037
H(12)	0.1292	0.2130	0.0952	0.035
H(13A)	0.5747	0.0048	0.0971	0.067
H(13B)	0.5757	0.0537	0.1625	0.067
H(13C)	0.6713	0.0921	0.1068	0.067
H(14A)	0.4546	0.0859	−0.0004	0.070
H(14B)	0.5190	0.1774	0.0220	0.070
H(14C)	0.3288	0.1607	0.0095	0.070
H(15A)	0.1933	0.3470	0.1837	0.061
H(15B)	0.1126	0.2591	0.2018	0.061
H(15C)	0.0194	0.3208	0.1519	0.061
H(16A)	0.2822	0.2938	0.0291	0.073
H(16B)	0.3179	0.3631	0.0830	0.073
H(16C)	0.1377	0.3505	0.0518	0.073
H(23A)	0.1554	0.3066	0.3876	0.047
H(23B)	0.0228	0.2388	0.4052	0.047
H(23C)	0.0914	0.2370	0.3375	0.047
H(22)	0.6225	0.1372	0.4267	0.027
H(21)	0.2079	0.1290	0.4065	0.025
H(31A)	0.0538	0.0748	0.3253	0.038
H(31B)	0.2057	0.0140	0.3417	0.038
H(31C)	0.0545	−0.0193	0.2976	0.038
H(26A)	0.4871	−0.0015	0.3554	0.043
H(26B)	0.4277	0.0262	0.4217	0.043
H(26C)	0.6080	−0.0084	0.4171	0.043
H(25A)	0.6757	0.0941	0.3002	0.047
H(25B)	0.8020	0.0751	0.3588	0.047
H(25C)	0.7609	0.1708	0.3388	0.047
H(24A)	0.3586	0.2660	0.4757	0.050
H(24B)	0.3983	0.1681	0.4886	0.050
H(24C)	0.2235	0.2050	0.5007	0.050
H(32A)	0.2267	−0.0755	0.2137	0.058
H(32B)	0.4024	−0.0437	0.2399	0.058
H(32C)	0.3354	−0.0209	0.1699	0.058
H(33A)	0.0687	0.0897	0.1452	0.067
H(33B)	−0.0258	0.1303	0.2003	0.067
H(33C)	−0.0306	0.0301	0.1890	0.067

Table S8. Anisotropic displacement parameters (Å^2) for [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.0179(4)	0.0153(4)	0.0147(4)	0.0002(3)	0.0040(3)	−0.0033(3)
F(1)	0.029(2)	0.034(2)	0.038(2)	0.0045(17)	0.0140(16)	−0.0005(16)
C(1)	0.031(3)	0.027(3)	0.020(3)	0.002(2)	0.010(3)	−0.010(3)
P(1)	0.0204(8)	0.0203(7)	0.0162(7)	0.0025(6)	0.0035(6)	−0.0035(6)
P(2)	0.0205(8)	0.0186(7)	0.0176(7)	−0.0027(6)	0.0031(6)	−0.0026(6)
C(2)	0.032(3)	0.023(3)	0.021(3)	−0.004(2)	0.003(3)	−0.010(3)
F(2)	0.037(2)	0.0270(19)	0.034(2)	0.0104(16)	0.0111(16)	0.0017(16)
P(3)	0.0278(9)	0.0223(8)	0.0173(8)	−0.0003(6)	0.0030(6)	−0.0104(6)
F(3)	0.045(2)	0.041(2)	0.0224(19)	−0.0059(16)	−0.0007(16)	0.0093(18)
C(3)	0.025(3)	0.020(3)	0.023(3)	0.003(2)	0.009(2)	0.000(2)
N	0.023(3)	0.016(2)	0.019(2)	−0.0011(19)	0.004(2)	−0.0025(19)
P(4)	0.0284(12)	0.0206(11)	0.0227(11)	0.0040(9)	−0.0016(9)	0.0003(9)
F(4)	0.056(3)	0.050(3)	0.045(3)	0.000(2)	0.024(2)	0.009(2)
C(4)	0.022(3)	0.017(3)	0.034(3)	0.004(2)	0.007(3)	−0.006(2)
P(5)	0.0243(12)	0.0214(11)	0.0193(11)	0.0015(9)	0.0051(9)	0.0004(9)
F(5)	0.058(3)	0.0231(19)	0.040(2)	0.0129(17)	−0.0073(19)	−0.0001(18)
C(5)	0.025(3)	0.015(3)	0.033(3)	−0.006(2)	0.001(3)	−0.007(2)
C(6)	0.025(3)	0.022(3)	0.019(3)	−0.006(2)	0.003(2)	0.003(2)
F(6)	0.043(2)	0.034(2)	0.049(2)	0.0008(18)	−0.0209(19)	−0.0041(18)
C(11)	0.045(4)	0.026(3)	0.022(3)	−0.007(3)	0.008(3)	−0.008(3)
C(12)	0.031(4)	0.026(3)	0.029(3)	0.004(3)	−0.005(3)	−0.005(3)
C(13)	0.046(5)	0.043(4)	0.048(5)	−0.010(4)	0.016(4)	0.007(3)
C(14)	0.068(5)	0.052(5)	0.023(4)	−0.011(3)	0.019(4)	−0.026(4)
C(15)	0.038(4)	0.035(4)	0.049(4)	−0.001(3)	0.001(3)	0.012(3)
C(16)	0.044(5)	0.053(5)	0.049(5)	0.027(4)	−0.002(4)	0.002(4)
C(23)	0.029(4)	0.036(4)	0.030(4)	−0.001(3)	0.009(3)	0.006(3)
C(22)	0.023(3)	0.026(3)	0.017(3)	0.000(2)	0.003(2)	0.003(2)
C(21)	0.021(3)	0.025(3)	0.018(3)	−0.001(2)	0.008(2)	0.000(2)
C(31)	0.022(3)	0.028(3)	0.026(3)	0.004(3)	0.007(2)	−0.009(3)
C(26)	0.029(3)	0.032(3)	0.024(3)	0.004(3)	0.004(3)	0.003(3)
C(25)	0.018(3)	0.043(4)	0.033(4)	0.002(3)	0.006(3)	0.008(3)
C(24)	0.045(4)	0.041(4)	0.017(3)	−0.006(3)	0.013(3)	−0.007(3)
C(32)	0.066(5)	0.023(3)	0.030(4)	−0.004(3)	0.020(3)	−0.009(3)
C(33)	0.045(4)	0.052(5)	0.036(4)	0.018(3)	−0.010(3)	−0.030(4)

Table S9. Distances [Å] for [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (**3**).

atom – atom	distance	atom – atom	distance
Ni – N	1.887(5)	Ni – P(3)	2.2093(16)
Ni – P(1)	2.2340(16)	Ni – P(2)	2.2388(16)
F(1) – P(5)	1.601(3)	C(1) – C(3)	1.502(8)
C(1) – P(1)	1.833(6)	C(1) – H(1A)	0.9900
C(1) – H(1B)	0.9900	P(1) – C(11)	1.829(6)
P(1) – C(12)	1.861(6)	P(2) – C(2)	1.834(6)
P(2) – C(21)	1.834(6)	P(2) – C(22)	1.849(6)
C(2) – C(6)	1.486(8)	C(2) – H(2A)	0.9900
C(2) – H(2B)	0.9900	F(2) – P(5)	1.605(3)
P(3) – C(31)	1.812(6)	P(3) – C(33)	1.815(7)
P(3) – C(32)	1.843(7)	F(3) – P(5)	1.595(3)
C(3) – C(4)	1.367(8)	C(3) – N	1.377(7)
N – C(6)	1.389(7)	P(4) – F(4)#1	1.586(4)
P(4) – F(4)	1.586(4)	P(4) – F(5)#1	1.599(3)
P(4) – F(5)	1.599(3)	P(4) – F(6)#1	1.599(4)
P(4) – F(6)	1.599(4)	C(4) – C(5)	1.404(8)
C(4) – H(4)	0.9500	P(5) – F(3)#2	1.595(4)
P(5) – F(1)#2	1.601(3)	P(5) – F(2)#2	1.605(3)
C(5) – C(6)	1.363(8)	C(5) – H(5)	0.9500
C(11) – C(13)	1.516(10)	C(11) – C(14)	1.530(9)
C(11) – H(11)	1.0000	C(12) – C(16)	1.528(9)
C(12) – C(15)	1.536(9)	C(12) – H(12)	1.0000
C(13) – H(13A)	0.9800	C(13) – H(13B)	0.9800
C(13) – H(13C)	0.9800	C(14) – H(14A)	0.9800
C(14) – H(14B)	0.9800	C(14) – H(14C)	0.9800
C(15) – H(15A)	0.9800	C(15) – H(15B)	0.9800
C(15) – H(15C)	0.9800	C(16) – H(16A)	0.9800
C(16) – H(16B)	0.9800	C(16) – H(16C)	0.9800
C(23) – C(21)	1.537(8)	C(23) – H(23A)	0.9800
C(23) – H(23B)	0.9800	C(23) – H(23C)	0.9800
C(22) – C(26)	1.518(8)	C(22) – C(25)	1.530(8)
C(22) – H(22)	1.0000	C(21) – C(24)	1.525(8)
C(21) – H(21)	1.0000	C(31) – H(31A)	0.9800
C(31) – H(31B)	0.9800	C(31) – H(31C)	0.9800
C(26) – H(26A)	0.9800	C(26) – H(26B)	0.9800
C(26) – H(26C)	0.9800	C(25) – H(25A)	0.9800
C(25) – H(25B)	0.9800	C(25) – H(25C)	0.9800
C(24) – H(24A)	0.9800	C(24) – H(24B)	0.9800
C(24) – H(24C)	0.9800	C(32) – H(32A)	0.9800

Symmetry transformations used to generate equivalent atoms:
#1: $-x+1, -y+1, -z+1$; #2: $-x, -y, -z+1$

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Table S9. – continued from previous page

atom – atom	distance	atom – atom	distance
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800		

Symmetry transformations used to generate equivalent atoms:
#1: $-x+1, -y+1, -z+1$; #2: $-x, -y, -z+1$

Table S10. Angles [°] for [(PN^{pyr}P)NiP(Me$_3$)][PF$_6$] (**3**).

atom – atom – atom	angle	atom – atom – atom	angle
N – Ni – P(3)	177.41(15)	N – Ni – P(1)	82.20(14)
P(3) – Ni – P(1)	95.21(6)	N – Ni – P(2)	83.05(15)
P(3) – Ni – P(2)	99.54(6)	P(1) – Ni – P(2)	165.24(6)
C(3) – C(1) – P(1)	106.4(4)	C(3) – C(1) – H(1A)	110.4
P(1) – C(1) – H(1A)	110.4	C(3) – C(1) – H(1B)	110.4
P(1) – C(1) – H(1B)	110.4	H(1A) – C(1) – H(1B)	108.6
C(11) – P(1) – C(1)	104.3(3)	C(11) – P(1) – C(12)	107.9(3)
C(1) – P(1) – C(12)	108.1(3)	C(11) – P(1) – Ni	122.3(2)
C(1) – P(1) – Ni	103.59(19)	C(12) – P(1) – Ni	109.7(2)
C(2) – P(2) – C(21)	104.0(3)	C(2) – P(2) – C(22)	103.1(3)
C(21) – P(2) – C(22)	108.5(3)	C(2) – P(2) – Ni	102.7(2)
C(21) – P(2) – Ni	124.6(2)	C(22) – P(2) – Ni	111.25(19)
C(6) – C(2) – P(2)	107.0(4)	C(6) – C(2) – H(2A)	110.3
P(2) – C(2) – H(2A)	110.3	C(6) – C(2) – H(2B)	110.3
P(2) – C(2) – H(2B)	110.3	H(2A) – C(2) – H(2B)	108.6
C(31) – P(3) – C(33)	99.3(3)	C(31) – P(3) – C(32)	101.0(3)
C(33) – P(3) – C(32)	102.4(4)	C(31) – P(3) – Ni	120.2(2)
C(33) – P(3) – Ni	116.2(2)	C(32) – P(3) – Ni	114.8(2)
C(4) – C(3) – N	109.3(5)	C(4) – C(3) – C(1)	133.3(5)
N – C(3) – C(1)	117.3(5)	C(3) – N – C(6)	106.8(5)
C(3) – N – Ni	126.9(4)	C(6) – N – Ni	126.1(4)
F(4)#1 – P(4) – F(4)	180.000(1)	F(4)#1 – P(4) – F(5)#1	90.3(2)
F(4) – P(4) – F(5)#1	89.7(2)	F(4)#1 – P(4) – F(5)	89.7(2)
F(4) – P(4) – F(5)	90.3(2)	F(5)#1 – P(4) – F(5)	180.0(3)
F(4)#1 – P(4) – F(6)#1	90.4(2)	F(4) – P(4) – F(6)#1	89.6(2)
F(5)#1 – P(4) – F(6)#1	90.0(2)	F(5) – P(4) – F(6)#1	90.0(2)
F(4)#1 – P(4) – F(6)	89.6(2)	F(4) – P(4) – F(6)	90.4(2)
F(5)#1 – P(4) – F(6)	90.0(2)	F(5) – P(4) – F(6)	90.0(2)
F(6)#1 – P(4) – F(6)	180.000(1)	C(3) – C(4) – C(5)	107.4(5)
C(3) – C(4) – H(4)	126.3	C(5) – C(4) – H(4)	126.3
F(3)#2 – P(5) – F(3)	180.000(1)	F(3)#2 – P(5) – F(1)	89.8(2)
F(3) – P(5) – F(1)	90.2(2)	F(3)#2 – P(5) – F(1)#2	90.2(2)
F(3) – P(5) – F(1)#2	89.8(2)	F(1) – P(5) – F(1)#2	180.0(2)
F(3)#2 – P(5) – F(2)	90.24(19)	F(3) – P(5) – F(2)	89.76(19)
F(1) – P(5) – F(2)	90.04(18)	F(1)#2 – P(5) – F(2)	89.96(18)
F(3)#2 – P(5) – F(2)#2	89.76(19)	F(3) – P(5) – F(2)#2	90.24(19)
F(1) – P(5) – F(2)#2	89.96(18)	F(1)#2 – P(5) – F(2)#2	90.04(18)
F(2) – P(5) – F(2)#2	180.0(2)	C(6) – C(5) – C(4)	107.4(5)
C(6) – C(5) – H(5)	126.3	C(4) – C(5) – H(5)	126.3

Symmetry transformations used to generate equivalent atoms:
#1: $-x+1, -y+1, -z+1$; #2: $-x, -y, -z+1$

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Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(5) – C(6) – N	109.1(5)	C(5) – C(6) – C(2)	133.6(5)
N – C(6) – C(2)	117.3(5)	C(13) – C(11) – C(14)	111.4(6)
C(13) – C(11) – P(1)	109.5(5)	C(14) – C(11) – P(1)	114.0(5)
C(13) – C(11) – H(11)	107.2	C(14) – C(11) – H(11)	107.2
P(1) – C(11) – H(11)	107.2	C(16) – C(12) – C(15)	108.1(6)
C(16) – C(12) – P(1)	114.5(5)	C(15) – C(12) – P(1)	110.4(4)
C(16) – C(12) – H(12)	107.9	C(15) – C(12) – H(12)	107.9
P(1) – C(12) – H(12)	107.9	C(11) – C(13) – H(13A)	109.5
C(11) – C(13) – H(13B)	109.5	H(13A) – C(13) – H(13B)	109.5
C(11) – C(13) – H(13C)	109.5	H(13A) – C(13) – H(13C)	109.5
H(13B) – C(13) – H(13C)	109.5	C(11) – C(14) – H(14A)	109.5
C(11) – C(14) – H(14B)	109.5	H(14A) – C(14) – H(14B)	109.5
C(11) – C(14) – H(14C)	109.5	H(14A) – C(14) – H(14C)	109.5
H(14B) – C(14) – H(14C)	109.5	C(12) – C(15) – H(15A)	109.5
C(12) – C(15) – H(15B)	109.5	H(15A) – C(15) – H(15B)	109.5
C(12) – C(15) – H(15C)	109.5	H(15A) – C(15) – H(15C)	109.5
H(15B) – C(15) – H(15C)	109.5	C(12) – C(16) – H(16A)	109.5
C(12) – C(16) – H(16B)	109.5	H(16A) – C(16) – H(16B)	109.5
C(12) – C(16) – H(16C)	109.5	H(16A) – C(16) – H(16C)	109.5
H(16B) – C(16) – H(16C)	109.5	C(21) – C(23) – H(23A)	109.5
C(21) – C(23) – H(23B)	109.5	H(23A) – C(23) – H(23B)	109.5
C(21) – C(23) – H(23C)	109.5	H(23A) – C(23) – H(23C)	109.5
H(23B) – C(23) – H(23C)	109.5	C(26) – C(22) – C(25)	110.1(5)
C(26) – C(22) – P(2)	114.2(4)	C(25) – C(22) – P(2)	109.5(4)
C(26) – C(22) – H(22)	107.6	C(25) – C(22) – H(22)	107.6
P(2) – C(22) – H(22)	107.6	C(24) – C(21) – C(23)	111.4(5)
C(24) – C(21) – P(2)	112.5(4)	C(23) – C(21) – P(2)	110.0(4)
C(24) – C(21) – H(21)	107.6	C(23) – C(21) – H(21)	107.6
P(2) – C(21) – H(21)	107.6	P(3) – C(31) – H(31A)	109.5
P(3) – C(31) – H(31B)	109.5	H(31A) – C(31) – H(31B)	109.5
P(3) – C(31) – H(31C)	109.5	H(31A) – C(31) – H(31C)	109.5
H(31B) – C(31) – H(31C)	109.5	C(22) – C(26) – H(26A)	109.5
C(22) – C(26) – H(26B)	109.5	H(26A) – C(26) – H(26B)	109.5
C(22) – C(26) – H(26C)	109.5	H(26A) – C(26) – H(26C)	109.5
H(26B) – C(26) – H(26C)	109.5	C(22) – C(25) – H(25A)	109.5
C(22) – C(25) – H(25B)	109.5	H(25A) – C(25) – H(25B)	109.5
C(22) – C(25) – H(25C)	109.5	H(25A) – C(25) – H(25C)	109.5
H(25B) – C(25) – H(25C)	109.5	C(21) – C(24) – H(24A)	109.5
C(21) – C(24) – H(24B)	109.5	H(24A) – C(24) – H(24B)	109.5

Symmetry transformations used to generate equivalent atoms:
#1: $-x+1, -y+1, -z+1$; #2: $-x, -y, -z+1$

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Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(21) – C(24) – H(24C)	109.5	H(24A) – C(24) – H(24C)	109.5
H(24B) – C(24) – H(24C)	109.5	P(3) – C(32) – H(32A)	109.5
P(3) – C(32) – H(32B)	109.5	H(32A) – C(32) – H(32B)	109.5
P(3) – C(32) – H(32C)	109.5	H(32A) – C(32) – H(32C)	109.5
H(32B) – C(32) – H(32C)	109.5	P(3) – C(33) – H(33A)	109.5
P(3) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
P(3) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5		

Symmetry transformations used to generate equivalent atoms:
#1: $-x+1, -y+1, -z+1$; #2: $-x, -y, -z+1$

3.3 Crystal data for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (4)

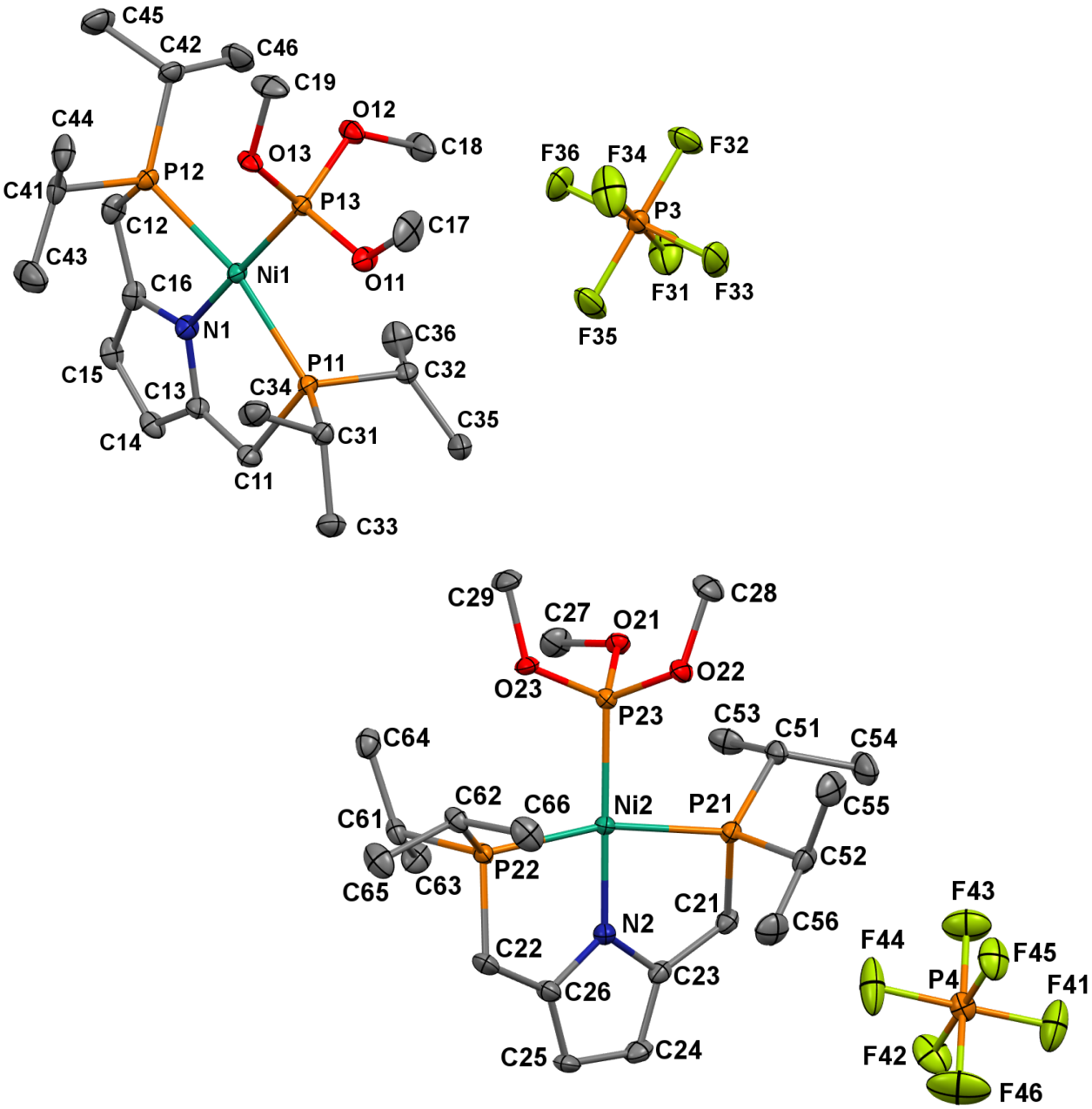

Figure S26. Thermal-ellipsoid representation of both crystallographically independent molecules of [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**) at 50% probability. Hydrogen atoms were omitted for clarity.

Table S11. Crystal data and structure refinement for $[(PN^{pyr}P)Ni\{P(OMe)_3\}][PF_6]$ (**4**).

Identification code:	JK4_165_0m	
Empirical formula:	$C_{21}H_{43}F_6NNiO_3P_4$	
Formula weight:	654.15	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 14.4915(6) Å	α = 109.950(2)°
	b = 15.0549(6) Å	β = 107.078(2)°
	c = 16.2395(6) Å	γ = 107.074(2)°
Volume:	2861.4(2) $Å^3$	
Z:	4	
Density (calculated):	1.518 $g \cdot cm^{-3}$	
Absorption coefficient (μ):	0.965 mm^{-1}	
F(000):	1368	
Crystal size:	$0.140 \times 0.100 \times 0.090$ mm^3	
θ range for data collection:	1.484 to 24.998°	
Index ranges:	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$	
Reflections collected:	71121	
Independent reflections:	10079 [R_{int} = 0.0777]	
Completeness to θ = 25.000°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7455 and 0.6838	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	10079 / 0 / 671	
Goodness-of-fit on F^2:	1.096	
Final R indices [I>2σ(I)]:	R_1 = 0.0358, wR_2 = 0.0735	
R indices (all data):	R_1 = 0.0620, wR_2 = 0.0803	
Extinction coefficient:	n/a	
Largest diff. peak and hole:	0.428 and −0.382 $e^- \cdot Å^{-3}$	

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Ni(1)	0.22439(3)	0.23161(3)	0.00771(2)	0.012(1)
N(1)	0.11929(18)	0.09622(17)	−0.07778(16)	0.016(1)
Ni(2)	0.75400(3)	0.21304(3)	0.49970(2)	0.012(1)
N(2)	0.74155(18)	0.18089(17)	0.59723(16)	0.015(1)
P(3)	0.72002(6)	0.28963(6)	0.03215(6)	0.019(1)
P(4)	0.24072(6)	0.27519(6)	0.51700(6)	0.019(1)
P(11)	0.29607(6)	0.15531(6)	0.08544(5)	0.014(1)
C(11)	0.1854(2)	0.0244(2)	0.0288(2)	0.020(1)
O(11)	0.43800(15)	0.39137(14)	0.18722(13)	0.020(1)
P(12)	0.11847(6)	0.27179(6)	−0.08739(5)	0.015(1)
C(12)	0.0332(2)	0.1455(2)	−0.1972(2)	0.021(1)
O(12)	0.41840(15)	0.42873(14)	0.04535(14)	0.019(1)
P(13)	0.35177(6)	0.38436(6)	0.09604(5)	0.013(1)
C(13)	0.1092(2)	0.0077(2)	−0.0657(2)	0.017(1)
O(13)	0.31907(15)	0.47518(14)	0.13586(13)	0.016(1)
C(14)	0.0242(2)	−0.0779(2)	−0.1455(2)	0.019(1)
C(15)	−0.0213(2)	−0.0422(2)	−0.2102(2)	0.019(1)
C(19)	0.3748(3)	0.5837(2)	0.1574(2)	0.029(1)
C(18)	0.4837(3)	0.3801(2)	0.0147(2)	0.031(1)
C(17)	0.5245(3)	0.4894(2)	0.2665(2)	0.038(1)
C(16)	0.0382(2)	0.0635(2)	−0.1669(2)	0.017(1)
P(21)	0.75911(6)	0.36221(6)	0.59362(5)	0.014(1)
C(21)	0.8000(2)	0.3634(2)	0.71174(19)	0.017(1)
O(21)	0.89634(15)	0.35634(14)	0.43892(13)	0.015(1)
P(22)	0.72729(6)	0.04755(6)	0.42599(5)	0.014(1)
C(22)	0.6736(2)	−0.0069(2)	0.4956(2)	0.021(1)
O(22)	0.70616(15)	0.30704(15)	0.36005(14)	0.019(1)
P(23)	0.78307(6)	0.26065(6)	0.39785(5)	0.013(1)
C(24)	0.7491(2)	0.1990(2)	0.7419(2)	0.021(1)
C(25)	0.7142(2)	0.0914(2)	0.6795(2)	0.020(1)
C(26)	0.7096(2)	0.0830(2)	0.5920(2)	0.018(1)
C(27)	0.9938(2)	0.3440(2)	0.4725(2)	0.026(1)
C(28)	0.7185(3)	0.3648(3)	0.3057(2)	0.029(1)
C(29)	0.8103(3)	0.1868(2)	0.2360(2)	0.024(1)
C(31)	0.3408(2)	0.2051(2)	0.2170(2)	0.016(1)
F(31)	0.71787(15)	0.18740(14)	−0.04240(14)	0.043(1)
C(32)	0.4070(2)	0.1418(2)	0.0588(2)	0.016(1)
F(32)	0.79178(14)	0.35897(14)	−0.00033(13)	0.037(1)
C(33)	0.3306(2)	0.1193(2)	0.2488(2)	0.023(1)

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
F(33)	0.82573(14)	0.30801(15)	0.11495(13)	0.038(1)
C(34)	0.2787(3)	0.2635(2)	0.2518(2)	0.025(1)
F(34)	0.72085(15)	0.39145(15)	0.10678(14)	0.047(1)
C(35)	0.4599(2)	0.0856(2)	0.1041(2)	0.024(1)
F(35)	0.64769(14)	0.22040(15)	0.06490(13)	0.040(1)
C(36)	0.3709(3)	0.0905(2)	−0.0513(2)	0.027(1)
F(36)	0.61354(14)	0.27140(15)	−0.05035(12)	0.035(1)
C(41)	0.0234(2)	0.3025(2)	−0.0433(2)	0.020(1)
F(41)	0.22938(16)	0.37069(15)	0.58726(13)	0.045(1)
C(42)	0.1685(2)	0.3658(2)	−0.1295(2)	0.020(1)
F(42)	0.32547(15)	0.28114(14)	0.60962(12)	0.037(1)
C(43)	−0.0254(3)	0.2234(3)	−0.0123(3)	0.037(1)
F(43)	0.33642(15)	0.35681(15)	0.51352(14)	0.044(1)
C(44)	0.0704(2)	0.4146(2)	0.0373(2)	0.027(1)
F(44)	0.25377(16)	0.18168(15)	0.44691(13)	0.049(1)
C(45)	0.0781(3)	0.3794(3)	−0.1932(2)	0.031(1)
F(45)	0.15703(14)	0.26990(14)	0.42467(12)	0.034(1)
C(46)	0.2338(3)	0.3353(3)	−0.1826(2)	0.031(1)
F(46)	0.14690(16)	0.19450(17)	0.52115(15)	0.061(1)
C(51)	0.8514(2)	0.4904(2)	0.6168(2)	0.018(1)
C(52)	0.6256(2)	0.3599(2)	0.5662(2)	0.021(1)
C(53)	0.9671(2)	0.5058(2)	0.6628(2)	0.025(1)
C(54)	0.8370(3)	0.5811(2)	0.6799(2)	0.032(1)
C(55)	0.5832(3)	0.3805(3)	0.4803(2)	0.031(1)
C(56)	0.5456(2)	0.2569(2)	0.5509(2)	0.029(1)
C(61)	0.8466(2)	0.0245(2)	0.4396(2)	0.017(1)
C(62)	0.6287(2)	−0.0371(2)	0.2985(2)	0.017(1)
C(63)	0.9319(2)	0.0946(2)	0.5455(2)	0.024(1)
C(64)	0.8914(2)	0.0387(2)	0.3688(2)	0.022(1)
C(65)	0.6028(3)	−0.1529(2)	0.2675(2)	0.027(1)
C(66)	0.5282(2)	−0.0196(2)	0.2811(2)	0.028(1)
C(23)	0.7652(2)	0.2518(2)	0.6902(2)	0.016(1)
O(23)	0.77642(15)	0.17079(14)	0.30729(13)	0.017(1)
H(11A)	0.2126	−0.0298	0.0178	0.024
H(11B)	0.1493	0.0199	0.0714	0.024
H(12A)	−0.0416	0.1365	−0.2243	0.025
H(12B)	0.0598	0.1409	−0.2474	0.025
H(14)	−0.0003	−0.1485	−0.1559	0.022
H(15)	−0.0819	−0.0842	−0.2721	0.023
H(19A)	0.3228	0.6127	0.1454	0.044
H(19B)	0.4112	0.5865	0.1156	0.044
H(19C)	0.4279	0.6251	0.2259	0.044

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
H(18A)	0.5213	0.4176	−0.0132	0.046
H(18B)	0.4374	0.3065	−0.0345	0.046
H(18C)	0.5364	0.3833	0.0711	0.046
H(17A)	0.5691	0.4756	0.3145	0.057
H(17B)	0.4949	0.5343	0.2975	0.057
H(17C)	0.5685	0.5250	0.2414	0.057
H(21A)	0.8788	0.4036	0.7507	0.020
H(21B)	0.7650	0.3960	0.7487	0.020
H(22A)	0.5942	−0.0436	0.4613	0.025
H(22B)	0.7010	−0.0577	0.5042	0.025
H(24)	0.7595	0.2288	0.8076	0.026
H(25)	0.6971	0.0355	0.6956	0.024
H(27A)	1.0559	0.4132	0.5103	0.039
H(27B)	1.0012	0.3008	0.4163	0.039
H(27C)	0.9904	0.3095	0.5137	0.039
H(28A)	0.7178	0.4324	0.3389	0.043
H(28B)	0.6592	0.3240	0.2399	0.043
H(28C)	0.7869	0.3772	0.3016	0.043
H(29A)	0.8387	0.1368	0.2124	0.036
H(29B)	0.8664	0.2588	0.2661	0.036
H(29C)	0.7488	0.1757	0.1811	0.036
H(31)	0.4183	0.2564	0.2504	0.020
H(32)	0.4638	0.2147	0.0865	0.019
H(33A)	0.3669	0.1519	0.3201	0.035
H(33B)	0.3639	0.0767	0.2210	0.035
H(33C)	0.2545	0.0744	0.2257	0.035
H(34A)	0.3033	0.2891	0.3221	0.038
H(34B)	0.2019	0.2158	0.2177	0.038
H(34C)	0.2912	0.3233	0.2378	0.038
H(35A)	0.5171	0.0813	0.0848	0.037
H(35B)	0.4061	0.0146	0.0815	0.037
H(35C)	0.4905	0.1248	0.1753	0.037
H(36A)	0.4335	0.0956	−0.0644	0.040
H(36B)	0.3356	0.1267	−0.0791	0.040
H(36C)	0.3204	0.0164	−0.0808	0.040
H(41)	−0.0365	0.2943	−0.0998	0.024
H(42)	0.2176	0.4355	−0.0705	0.024
H(43A)	−0.0812	0.2363	0.0049	0.056
H(43B)	0.0307	0.2305	0.0443	0.056
H(43C)	−0.0571	0.1521	−0.0661	0.056
H(44A)	0.0134	0.4275	0.0525	0.040
H(44B)	0.1019	0.4641	0.0157	0.040

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
H(44C)	0.1261	0.4243	0.0958	0.040
H(45A)	0.1075	0.4261	−0.2182	0.047
H(45B)	0.0446	0.4101	−0.1543	0.047
H(45C)	0.0242	0.3107	−0.2479	0.047
H(46A)	0.2730	0.3943	−0.1909	0.046
H(46B)	0.1855	0.2741	−0.2466	0.046
H(46C)	0.2850	0.3178	−0.1444	0.046
H(51)	0.8372	0.4900	0.5526	0.021
H(52)	0.6326	0.4176	0.6249	0.026
H(53A)	1.0125	0.5534	0.6469	0.037
H(53B)	0.9694	0.4378	0.6372	0.037
H(53C)	0.9936	0.5362	0.7337	0.037
H(54A)	0.8916	0.6477	0.6934	0.047
H(54B)	0.8446	0.5798	0.7414	0.047
H(54C)	0.7653	0.5746	0.6456	0.047
H(55A)	0.5162	0.3864	0.4744	0.046
H(55B)	0.5696	0.3222	0.4203	0.046
H(55C)	0.6366	0.4462	0.4910	0.046
H(56A)	0.4775	0.2604	0.5443	0.043
H(56B)	0.5743	0.2454	0.6070	0.043
H(56C)	0.5335	0.1988	0.4916	0.043
H(61)	0.8257	−0.0502	0.4267	0.021
H(62)	0.6608	−0.0161	0.2574	0.020
H(63A)	0.9955	0.0815	0.5538	0.036
H(63B)	0.9029	0.0786	0.5889	0.036
H(63C)	0.9518	0.1686	0.5617	0.036
H(64A)	0.9534	0.0226	0.3789	0.034
H(64B)	0.9139	0.1115	0.3801	0.034
H(64C)	0.8359	−0.0089	0.3017	0.034
H(65A)	0.5526	−0.1953	0.1982	0.041
H(65B)	0.5701	−0.1759	0.3060	0.041
H(65C)	0.6691	−0.1615	0.2786	0.041
H(66A)	0.4783	−0.0609	0.2116	0.041
H(66B)	0.5477	0.0552	0.3014	0.041
H(66C)	0.4937	−0.0416	0.3189	0.041

Table S13. Anisotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	0.0115(2)	0.0106(2)	0.0122(2)	0.0050(2)	0.0028(2)	0.0040(2)
N(1)	0.0147(14)	0.0110(13)	0.0130(13)	0.0023(11)	0.0020(11)	0.0036(11)
Ni(2)	0.0138(2)	0.0120(2)	0.0120(2)	0.0068(2)	0.0067(2)	0.0062(2)
N(2)	0.0177(14)	0.0150(13)	0.0149(13)	0.0079(11)	0.0085(11)	0.0083(11)
P(3)	0.0159(4)	0.0217(5)	0.0174(4)	0.0106(4)	0.0064(4)	0.0067(4)
P(4)	0.0162(4)	0.0165(4)	0.0194(4)	0.0067(4)	0.0040(4)	0.0059(4)
P(11)	0.0124(4)	0.0127(4)	0.0157(4)	0.0076(3)	0.0044(3)	0.0052(3)
C(11)	0.0163(17)	0.0140(16)	0.0239(18)	0.0096(14)	0.0047(14)	0.0035(14)
O(11)	0.0153(12)	0.0132(11)	0.0176(11)	0.0052(9)	−0.0017(9)	0.0009(9)
P(12)	0.0151(4)	0.0155(4)	0.0133(4)	0.0069(3)	0.0042(3)	0.0072(3)
C(12)	0.0183(17)	0.0230(18)	0.0148(16)	0.0058(14)	0.0025(14)	0.0083(14)
O(12)	0.0216(12)	0.0171(11)	0.0246(12)	0.0106(10)	0.0160(10)	0.0098(9)
P(13)	0.0119(4)	0.0117(4)	0.0145(4)	0.0062(3)	0.0047(3)	0.0042(3)
C(13)	0.0154(17)	0.0135(16)	0.0217(17)	0.0087(14)	0.0083(14)	0.0060(14)
O(13)	0.0182(11)	0.0087(10)	0.0224(11)	0.0062(9)	0.0117(9)	0.0051(9)
C(14)	0.0170(17)	0.0123(16)	0.0185(17)	0.0025(13)	0.0071(14)	0.0022(14)
C(15)	0.0136(17)	0.0180(17)	0.0126(16)	−0.0003(13)	0.0019(13)	0.0024(14)
C(19)	0.041(2)	0.0130(17)	0.038(2)	0.0128(15)	0.0231(17)	0.0104(16)
C(18)	0.037(2)	0.0263(19)	0.050(2)	0.0225(18)	0.0338(19)	0.0210(17)
C(17)	0.0189(19)	0.024(2)	0.033(2)	0.0013(16)	−0.0111(16)	−0.0003(16)
C(16)	0.0155(17)	0.0181(17)	0.0105(15)	0.0022(13)	0.0035(13)	0.0066(14)
P(21)	0.0151(4)	0.0140(4)	0.0136(4)	0.0059(3)	0.0071(3)	0.0072(3)
C(21)	0.0179(17)	0.0198(17)	0.0131(16)	0.0064(13)	0.0076(13)	0.0095(14)
O(21)	0.0126(11)	0.0147(11)	0.0183(11)	0.0085(9)	0.0074(9)	0.0045(9)
P(22)	0.0166(4)	0.0117(4)	0.0140(4)	0.0067(3)	0.0064(3)	0.0066(3)
C(22)	0.0261(19)	0.0167(17)	0.0274(18)	0.0152(15)	0.0156(15)	0.0096(14)
O(22)	0.0207(12)	0.0242(12)	0.0246(12)	0.0182(10)	0.0131(10)	0.0155(10)
P(23)	0.0143(4)	0.0127(4)	0.0135(4)	0.0071(3)	0.0065(3)	0.0066(3)
C(24)	0.0242(18)	0.0304(19)	0.0158(17)	0.0135(15)	0.0115(14)	0.0141(15)
C(25)	0.0265(19)	0.0250(18)	0.0250(18)	0.0201(15)	0.0174(15)	0.0143(15)
C(26)	0.0205(17)	0.0165(16)	0.0225(17)	0.0129(14)	0.0111(14)	0.0081(14)
C(27)	0.0155(18)	0.0305(19)	0.033(2)	0.0164(16)	0.0111(15)	0.0092(15)
C(28)	0.036(2)	0.036(2)	0.032(2)	0.0270(17)	0.0170(17)	0.0223(17)
C(29)	0.036(2)	0.0218(18)	0.0164(17)	0.0088(14)	0.0172(15)	0.0100(16)
C(31)	0.0165(17)	0.0185(16)	0.0159(16)	0.0087(13)	0.0075(13)	0.0089(14)
F(31)	0.0358(12)	0.0289(11)	0.0524(13)	0.0056(10)	0.0183(11)	0.0152(10)
C(32)	0.0158(16)	0.0141(16)	0.0190(16)	0.0080(13)	0.0078(13)	0.0070(13)
F(32)	0.0309(12)	0.0456(12)	0.0408(12)	0.0319(10)	0.0182(10)	0.0078(10)
C(33)	0.0270(19)	0.0254(18)	0.0249(18)	0.0171(15)	0.0135(15)	0.0133(15)
F(33)	0.0184(11)	0.0612(14)	0.0331(11)	0.0312(11)	0.0037(9)	0.0112(10)

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Table S13. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(34)	0.034(2)	0.0304(19)	0.0262(19)	0.0180(16)	0.0189(16)	0.0200(17)
F(34)	0.0367(13)	0.0351(12)	0.0479(13)	−0.0026(10)	0.0183(11)	0.0144(10)
C(35)	0.0200(18)	0.0274(19)	0.037(2)	0.0212(16)	0.0166(16)	0.0136(15)
F(35)	0.0241(11)	0.0578(14)	0.0390(12)	0.0347(11)	0.0129(9)	0.0051(10)
C(36)	0.027(2)	0.0280(19)	0.0192(18)	0.0045(15)	0.0112(15)	0.0111(16)
F(36)	0.0223(11)	0.0509(13)	0.0306(11)	0.0249(10)	0.0035(9)	0.0167(10)
C(41)	0.0117(16)	0.0238(18)	0.0213(17)	0.0087(15)	0.0040(13)	0.0091(14)
F(41)	0.0425(13)	0.0464(13)	0.0331(12)	0.0015(10)	0.0105(10)	0.0302(11)
C(42)	0.0191(18)	0.0213(17)	0.0192(17)	0.0135(14)	0.0037(14)	0.0068(14)
F(42)	0.0346(12)	0.0355(11)	0.0250(11)	0.0139(9)	−0.0033(9)	0.0132(10)
C(43)	0.042(2)	0.035(2)	0.059(3)	0.027(2)	0.039(2)	0.0230(19)
F(43)	0.0304(12)	0.0462(13)	0.0435(13)	0.0235(11)	0.0144(10)	0.0013(10)
C(44)	0.0207(18)	0.0284(19)	0.0294(19)	0.0075(16)	0.0116(15)	0.0156(16)
F(44)	0.0542(14)	0.0399(12)	0.0304(12)	−0.0034(10)	−0.0012(10)	0.0354(11)
C(45)	0.030(2)	0.032(2)	0.0272(19)	0.0206(17)	0.0022(16)	0.0100(17)
F(45)	0.0330(12)	0.0392(12)	0.0260(11)	0.0121(9)	0.0027(9)	0.0237(10)
C(46)	0.030(2)	0.040(2)	0.0285(19)	0.0228(17)	0.0171(16)	0.0112(17)
F(46)	0.0355(13)	0.0608(15)	0.0552(15)	0.0332(13)	0.0086(11)	−0.0150(11)
C(51)	0.0249(18)	0.0129(16)	0.0153(16)	0.0060(13)	0.0097(14)	0.0082(14)
C(52)	0.0206(18)	0.0276(18)	0.0221(17)	0.0110(15)	0.0126(14)	0.0156(15)
C(53)	0.0204(18)	0.0190(17)	0.0224(18)	0.0094(15)	0.0042(14)	−0.0011(14)
C(54)	0.048(2)	0.0162(18)	0.0275(19)	0.0074(15)	0.0169(17)	0.0140(17)
C(55)	0.024(2)	0.047(2)	0.034(2)	0.0236(18)	0.0138(16)	0.0253(18)
C(56)	0.0165(18)	0.038(2)	0.035(2)	0.0185(17)	0.0128(16)	0.0126(16)
C(61)	0.0208(17)	0.0136(16)	0.0165(16)	0.0067(13)	0.0054(14)	0.0100(14)
C(62)	0.0183(17)	0.0128(16)	0.0143(16)	0.0056(13)	0.0037(13)	0.0053(13)
C(63)	0.0208(18)	0.034(2)	0.0187(17)	0.0129(15)	0.0057(14)	0.0153(16)
C(64)	0.0239(18)	0.0257(18)	0.0204(17)	0.0105(15)	0.0088(14)	0.0154(15)
C(65)	0.030(2)	0.0164(17)	0.0194(18)	0.0041(14)	0.0005(15)	0.0057(15)
C(66)	0.0194(18)	0.0254(19)	0.0297(19)	0.0132(16)	0.0028(15)	0.0072(15)
C(23)	0.0161(17)	0.0219(17)	0.0140(16)	0.0089(14)	0.0078(13)	0.0112(14)
O(23)	0.0253(12)	0.0152(11)	0.0150(11)	0.0081(9)	0.0141(9)	0.0081(9)

Table S14. Distances [Å] for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**).

atom – atom	distance	atom – atom	distance
Ni(1) – N(1)	1.845(2)	Ni(1) – P(13)	2.1106(8)
Ni(1) – P(12)	2.2131(8)	Ni(1) – P(11)	2.2163(8)
N(1) – C(16)	1.376(3)	N(1) – C(13)	1.384(3)
Ni(2) – N(2)	1.848(2)	Ni(2) – P(23)	2.1137(8)
Ni(2) – P(21)	2.2075(8)	Ni(2) – P(22)	2.2174(8)
N(2) – C(26)	1.372(3)	N(2) – C(23)	1.385(3)
P(3) – F(32)	1.5842(18)	P(3) – F(31)	1.5854(19)
P(3) – F(33)	1.5870(18)	P(3) – F(34)	1.591(2)
P(3) – F(35)	1.5912(18)	P(3) – F(36)	1.5929(18)
P(4) – F(46)	1.571(2)	P(4) – F(44)	1.5820(19)
P(4) – F(45)	1.5872(18)	P(4) – F(41)	1.5891(19)
P(4) – F(43)	1.5904(19)	P(4) – F(42)	1.5929(18)
P(11) – C(11)	1.829(3)	P(11) – C(32)	1.831(3)
P(11) – C(31)	1.832(3)	C(11) – C(13)	1.490(4)
C(11) – H(11A)	0.9900	C(11) – H(11B)	0.9900
O(11) – C(17)	1.441(3)	O(11) – P(13)	1.5794(19)
P(12) – C(12)	1.826(3)	P(12) – C(42)	1.829(3)
P(12) – C(41)	1.831(3)	C(12) – C(16)	1.488(4)
C(12) – H(12A)	0.9900	C(12) – H(12B)	0.9900
O(12) – C(18)	1.454(3)	O(12) – P(13)	1.5873(19)
P(13) – O(13)	1.5715(19)	C(13) – C(14)	1.360(4)
O(13) – C(19)	1.453(3)	C(14) – C(15)	1.421(4)
C(14) – H(14)	0.9500	C(15) – C(16)	1.358(4)
C(15) – H(15)	0.9500	C(19) – H(19A)	0.9800
C(19) – H(19B)	0.9800	C(19) – H(19C)	0.9800
C(18) – H(18A)	0.9800	C(18) – H(18B)	0.9800
C(18) – H(18C)	0.9800	C(17) – H(17A)	0.9800
C(17) – H(17B)	0.9800	C(17) – H(17C)	0.9800
P(21) – C(21)	1.826(3)	P(21) – C(51)	1.829(3)
P(21) – C(52)	1.841(3)	C(21) – C(23)	1.483(4)
C(21) – H(21A)	0.9900	C(21) – H(21B)	0.9900
O(21) – C(27)	1.449(3)	O(21) – P(23)	1.5898(19)
P(22) – C(22)	1.825(3)	P(22) – C(61)	1.828(3)
P(22) – C(62)	1.829(3)	C(22) – C(26)	1.487(4)
C(22) – H(22A)	0.9900	C(22) – H(22B)	0.9900
O(22) – C(28)	1.446(3)	O(22) – P(23)	1.5667(19)
P(23) – O(23)	1.5763(19)	C(24) – C(23)	1.361(4)
C(24) – C(25)	1.416(4)	C(24) – H(24)	0.9500
C(25) – C(26)	1.364(4)	C(25) – H(25)	0.9500
C(27) – H(27A)	0.9800	C(27) – H(27B)	0.9800
C(27) – H(27C)	0.9800	C(28) – H(28A)	0.9800

Continued on next page

Table S14. – continued from previous page

atom – atom	distance	atom – atom	distance
C(28) – H(28B)	0.9800	C(28) – H(28C)	0.9800
C(29) – O(23)	1.448(3)	C(29) – H(29A)	0.9800
C(29) – H(29B)	0.9800	C(29) – H(29C)	0.9800
C(31) – C(34)	1.525(4)	C(31) – C(33)	1.530(4)
C(31) – H(31)	1.0000	C(32) – C(35)	1.522(4)
C(32) – C(36)	1.529(4)	C(32) – H(32)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(43)	1.516(4)	C(41) – C(44)	1.523(4)
C(41) – H(41)	1.0000	C(42) – C(46)	1.521(4)
C(42) – C(45)	1.528(4)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(54)	1.517(4)	C(51) – C(53)	1.530(4)
C(51) – H(51)	1.0000	C(52) – C(56)	1.523(4)
C(52) – C(55)	1.525(4)	C(52) – H(52)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(55) – H(55C)	0.9800	C(56) – H(56A)	0.9800
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800
C(61) – C(64)	1.521(4)	C(61) – C(63)	1.532(4)
C(61) – H(61)	1.0000	C(62) – C(66)	1.518(4)
C(62) – C(65)	1.529(4)	C(62) – H(62)	1.0000
C(63) – H(63A)	0.9800	C(63) – H(63B)	0.9800
C(63) – H(63C)	0.9800	C(64) – H(64A)	0.9800
C(64) – H(64B)	0.9800	C(64) – H(64C)	0.9800
C(65) – H(65A)	0.9800	C(65) – H(65B)	0.9800
C(65) – H(65C)	0.9800	C(66) – H(66A)	0.9800
C(66) – H(66B)	0.9800	C(66) – H(66C)	0.9800

Table S15. Angles [°] for [(PN^{pyr}P)Ni{P(OMe)$_3$}][PF$_6$] (**4**).

atom – atom – atom	angle	atom – atom – atom	angle
N(1) – Ni(1) – P(13)	174.34(8)	N(1) – Ni(1) – P(12)	83.01(7)
P(13) – Ni(1) – P(12)	96.75(3)	N(1) – Ni(1) – P(11)	83.88(7)
P(13) – Ni(1) – P(11)	96.66(3)	P(12) – Ni(1) – P(11)	166.38(3)
C(16) – N(1) – C(13)	107.0(2)	C(16) – N(1) – Ni(1)	126.57(19)
C(13) – N(1) – Ni(1)	126.40(19)	N(2) – Ni(2) – P(23)	174.60(8)
N(2) – Ni(2) – P(21)	82.54(7)	P(23) – Ni(2) – P(21)	95.33(3)
N(2) – Ni(2) – P(22)	83.58(7)	P(23) – Ni(2) – P(22)	98.99(3)
P(21) – Ni(2) – P(22)	164.94(3)	C(26) – N(2) – C(23)	107.3(2)
C(26) – N(2) – Ni(2)	126.56(19)	C(23) – N(2) – Ni(2)	126.17(18)
F(32) – P(3) – F(31)	90.04(11)	F(32) – P(3) – F(33)	89.63(10)
F(31) – P(3) – F(33)	90.66(11)	F(32) – P(3) – F(34)	90.51(11)
F(31) – P(3) – F(34)	179.35(12)	F(33) – P(3) – F(34)	89.68(11)
F(32) – P(3) – F(35)	179.71(12)	F(31) – P(3) – F(35)	90.21(11)
F(33) – P(3) – F(35)	90.51(10)	F(34) – P(3) – F(35)	89.24(11)
F(32) – P(3) – F(36)	90.68(10)	F(31) – P(3) – F(36)	89.66(10)
F(33) – P(3) – F(36)	179.55(12)	F(34) – P(3) – F(36)	89.99(11)
F(35) – P(3) – F(36)	89.18(10)	F(46) – P(4) – F(44)	90.37(13)
F(46) – P(4) – F(45)	90.32(11)	F(44) – P(4) – F(45)	89.56(10)
F(46) – P(4) – F(41)	90.74(13)	F(44) – P(4) – F(41)	178.89(13)
F(45) – P(4) – F(41)	90.39(10)	F(46) – P(4) – F(43)	179.50(13)
F(44) – P(4) – F(43)	89.57(12)	F(45) – P(4) – F(43)	90.17(11)
F(41) – P(4) – F(43)	89.32(11)	F(46) – P(4) – F(42)	90.14(11)
F(44) – P(4) – F(42)	90.43(10)	F(45) – P(4) – F(42)	179.54(13)
F(41) – P(4) – F(42)	89.61(10)	F(43) – P(4) – F(42)	89.37(11)
C(11) – P(11) – C(32)	108.60(14)	C(11) – P(11) – C(31)	105.56(13)
C(32) – P(11) – C(31)	107.64(13)	C(11) – P(11) – Ni(1)	102.30(9)
C(32) – P(11) – Ni(1)	110.43(9)	C(31) – P(11) – Ni(1)	121.52(9)
C(13) – C(11) – P(11)	106.78(19)	C(13) – C(11) – H(11A)	110.4
P(11) – C(11) – H(11A)	110.4	C(13) – C(11) – H(11B)	110.4
P(11) – C(11) – H(11B)	110.4	H(11A) – C(11) – H(11B)	108.6
C(17) – O(11) – P(13)	122.98(18)	C(12) – P(12) – C(42)	105.68(14)
C(12) – P(12) – C(41)	103.29(14)	C(42) – P(12) – C(41)	107.84(14)
C(12) – P(12) – Ni(1)	102.35(10)	C(42) – P(12) – Ni(1)	123.20(10)
C(41) – P(12) – Ni(1)	112.29(10)	C(16) – C(12) – P(12)	106.21(19)
C(16) – C(12) – H(12A)	110.5	P(12) – C(12) – H(12A)	110.5
C(16) – C(12) – H(12B)	110.5	P(12) – C(12) – H(12B)	110.5
H(12A) – C(12) – H(12B)	108.7	C(18) – O(12) – P(13)	119.44(17)
O(13) – P(13) – O(11)	106.93(10)	O(13) – P(13) – O(12)	99.99(10)
O(11) – P(13) – O(12)	104.85(11)	O(13) – P(13) – Ni(1)	115.90(8)
O(11) – P(13) – Ni(1)	111.65(8)	O(12) – P(13) – Ni(1)	116.26(8)
C(14) – C(13) – N(1)	109.2(2)	C(14) – C(13) – C(11)	133.8(3)

Continued on next page

Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
N(1) – C(13) – C(11)	116.9(2)	C(19) – O(13) – P(13)	126.32(18)
C(13) – C(14) – C(15)	107.1(3)	C(13) – C(14) – H(14)	126.4
C(15) – C(14) – H(14)	126.4	C(16) – C(15) – C(14)	107.0(2)
C(16) – C(15) – H(15)	126.5	C(14) – C(15) – H(15)	126.5
O(13) – C(19) – H(19A)	109.5	O(13) – C(19) – H(19B)	109.5
H(19A) – C(19) – H(19B)	109.5	O(13) – C(19) – H(19C)	109.5
H(19A) – C(19) – H(19C)	109.5	H(19B) – C(19) – H(19C)	109.5
O(12) – C(18) – H(18A)	109.5	O(12) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	O(12) – C(18) – H(18C)	109.5
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5
O(11) – C(17) – H(17A)	109.5	O(11) – C(17) – H(17B)	109.5
H(17A) – C(17) – H(17B)	109.5	O(11) – C(17) – H(17C)	109.5
H(17A) – C(17) – H(17C)	109.5	H(17B) – C(17) – H(17C)	109.5
C(15) – C(16) – N(1)	109.6(2)	C(15) – C(16) – C(12)	133.3(3)
N(1) – C(16) – C(12)	117.0(2)	C(21) – P(21) – C(51)	105.22(13)
C(21) – P(21) – C(52)	103.59(14)	C(51) – P(21) – C(52)	107.77(13)
C(21) – P(21) – Ni(2)	101.95(9)	C(51) – P(21) – Ni(2)	122.70(10)
C(52) – P(21) – Ni(2)	113.37(10)	C(23) – C(21) – P(21)	105.87(19)
C(23) – C(21) – H(21A)	110.6	P(21) – C(21) – H(21A)	110.6
C(23) – C(21) – H(21B)	110.6	P(21) – C(21) – H(21B)	110.6
H(21A) – C(21) – H(21B)	108.7	C(27) – O(21) – P(23)	119.71(17)
C(22) – P(22) – C(61)	103.95(13)	C(22) – P(22) – C(62)	105.75(14)
C(61) – P(22) – C(62)	107.19(13)	C(22) – P(22) – Ni(2)	101.52(10)
C(61) – P(22) – Ni(2)	116.94(10)	C(62) – P(22) – Ni(2)	119.53(9)
C(26) – C(22) – P(22)	106.88(19)	C(26) – C(22) – H(22A)	110.3
P(22) – C(22) – H(22A)	110.3	C(26) – C(22) – H(22B)	110.3
P(22) – C(22) – H(22B)	110.3	H(22A) – C(22) – H(22B)	108.6
C(28) – O(22) – P(23)	126.05(19)	O(22) – P(23) – O(23)	108.64(11)
O(22) – P(23) – O(21)	100.20(10)	O(23) – P(23) – O(21)	104.72(10)
O(22) – P(23) – Ni(2)	112.61(8)	O(23) – P(23) – Ni(2)	113.74(7)
O(21) – P(23) – Ni(2)	115.79(7)	C(23) – C(24) – C(25)	107.2(3)
C(23) – C(24) – H(24)	126.4	C(25) – C(24) – H(24)	126.4
C(26) – C(25) – C(24)	107.1(3)	C(26) – C(25) – H(25)	126.5
C(24) – C(25) – H(25)	126.5	C(25) – C(26) – N(2)	109.4(3)
C(25) – C(26) – C(22)	134.1(3)	N(2) – C(26) – C(22)	116.4(2)
O(21) – C(27) – H(27A)	109.5	O(21) – C(27) – H(27B)	109.5
H(27A) – C(27) – H(27B)	109.5	O(21) – C(27) – H(27C)	109.5
H(27A) – C(27) – H(27C)	109.5	H(27B) – C(27) – H(27C)	109.5
O(22) – C(28) – H(28A)	109.5	O(22) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	O(22) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
O(23) – C(29) – H(29A)	109.5	O(23) – C(29) – H(29B)	109.5

Continued on next page

Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(29A) – C(29) – H(29B)	109.5	O(23) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
C(34) – C(31) – C(33)	109.0(2)	C(34) – C(31) – P(11)	110.61(19)
C(33) – C(31) – P(11)	113.6(2)	C(34) – C(31) – H(31)	107.8
C(33) – C(31) – H(31)	107.8	P(11) – C(31) – H(31)	107.8
C(35) – C(32) – C(36)	110.8(2)	C(35) – C(32) – P(11)	115.6(2)
C(36) – C(32) – P(11)	110.1(2)	C(35) – C(32) – H(32)	106.6
C(36) – C(32) – H(32)	106.6	P(11) – C(32) – H(32)	106.6
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(43) – C(41) – C(44)	111.1(3)	C(43) – C(41) – P(12)	110.2(2)
C(44) – C(41) – P(12)	114.1(2)	C(43) – C(41) – H(41)	107.0
C(44) – C(41) – H(41)	107.0	P(12) – C(41) – H(41)	107.0
C(46) – C(42) – C(45)	110.7(2)	C(46) – C(42) – P(12)	111.3(2)
C(45) – C(42) – P(12)	112.1(2)	C(46) – C(42) – H(42)	107.5
C(45) – C(42) – H(42)	107.5	P(12) – C(42) – H(42)	107.5
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(54) – C(51) – C(53)	110.6(2)	C(54) – C(51) – P(21)	113.2(2)
C(53) – C(51) – P(21)	109.45(19)	C(54) – C(51) – H(51)	107.8
C(53) – C(51) – H(51)	107.8	P(21) – C(51) – H(51)	107.8
C(56) – C(52) – C(55)	110.9(3)	C(56) – C(52) – P(21)	110.6(2)

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Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(55) – C(52) – P(21)	113.6(2)	C(56) – C(52) – H(52)	107.1
C(55) – C(52) – H(52)	107.1	P(21) – C(52) – H(52)	107.1
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5
C(64) – C(61) – C(63)	111.4(2)	C(64) – C(61) – P(22)	114.26(19)
C(63) – C(61) – P(22)	108.94(19)	C(64) – C(61) – H(61)	107.3
C(63) – C(61) – H(61)	107.3	P(22) – C(61) – H(61)	107.3
C(66) – C(62) – C(65)	111.7(2)	C(66) – C(62) – P(22)	110.1(2)
C(65) – C(62) – P(22)	111.79(19)	C(66) – C(62) – H(62)	107.7
C(65) – C(62) – H(62)	107.7	P(22) – C(62) – H(62)	107.7
C(61) – C(63) – H(63A)	109.5	C(61) – C(63) – H(63B)	109.5
H(63A) – C(63) – H(63B)	109.5	C(61) – C(63) – H(63C)	109.5
H(63A) – C(63) – H(63C)	109.5	H(63B) – C(63) – H(63C)	109.5
C(61) – C(64) – H(64A)	109.5	C(61) – C(64) – H(64B)	109.5
H(64A) – C(64) – H(64B)	109.5	C(61) – C(64) – H(64C)	109.5
H(64A) – C(64) – H(64C)	109.5	H(64B) – C(64) – H(64C)	109.5
C(62) – C(65) – H(65A)	109.5	C(62) – C(65) – H(65B)	109.5
H(65A) – C(65) – H(65B)	109.5	C(62) – C(65) – H(65C)	109.5
H(65A) – C(65) – H(65C)	109.5	H(65B) – C(65) – H(65C)	109.5
C(62) – C(66) – H(66A)	109.5	C(62) – C(66) – H(66B)	109.5
H(66A) – C(66) – H(66B)	109.5	C(62) – C(66) – H(66C)	109.5
H(66A) – C(66) – H(66C)	109.5	H(66B) – C(66) – H(66C)	109.5
C(24) – C(23) – N(2)	109.0(2)	C(24) – C(23) – C(21)	134.4(3)
N(2) – C(23) – C(21)	116.5(2)	C(29) – O(23) – P(23)	124.64(17)

3.4 Crystal data for [(PN^{pyr}P)Ni(PPh$_2$)] (5)

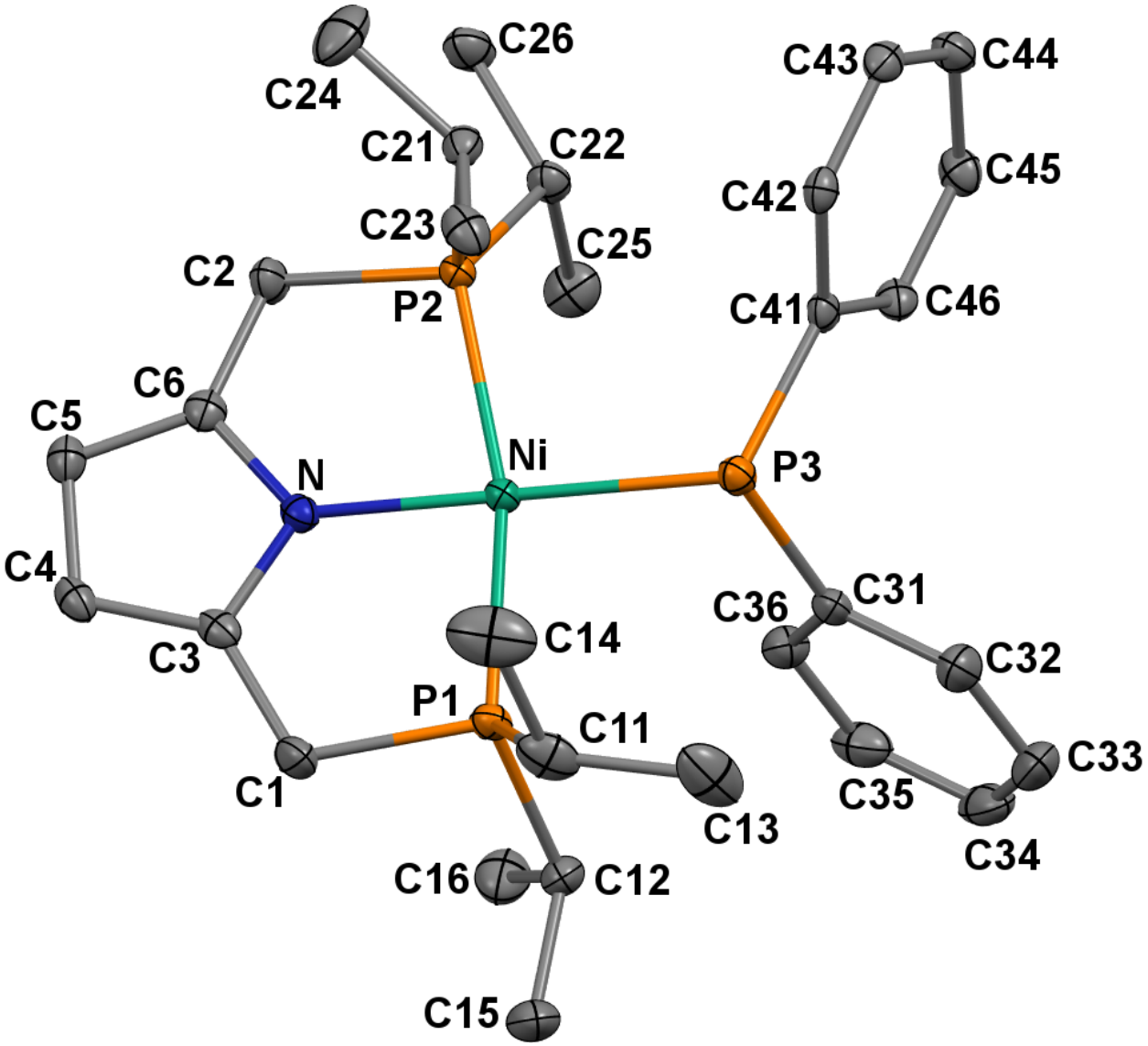

Figure S27. Thermal-ellipsoid representation of [(PN^{pyr}P)Ni(PPh$_2$)] (**5**) at 50% probability. Hydrogen atoms were omitted for clarity.

Table S16. Crystal data and structure refinement for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

Identification code:	jk2_74	
Empirical formula:	$C_{30}H_{44}NNiP_3$	
Formula weight:	570.28	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 9.2144(8) Å	α = 86.080(3)°
	b = 9.2591(8) Å	β = 84.872(3)°
	c = 19.2579(16) Å	γ = 63.320(2)°
Volume:	1461.5(2) Å^3	
Z:	2	
Density (calculated):	1.296 g·cm^{-3}	
Absorption coefficient (μ):	0.847 mm^{-1}	
F(000):	608	
Crystal size:	0.12 × 0.10 × 0.09 mm^3	
θ range for data collection:	2.12 to 25.00°	
Index ranges:	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-22 \leq l \leq 22$	
Reflections collected:	34813	
Independent reflections:	5134 [R_{int} = 0.0275]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.745 and 0.6697	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	5134 / 0 / 318	
Goodness-of-fit on F^2:	1.050	
Final R indices [I>2σ(I)]:	R_1 = 0.0234, wR_2 = 0.0588	
R indices (all data):	R_1 = 0.0258, wR_2 = 0.0598	
Largest diff. peak and hole:	0.421 and −0.629 e$^-$·Å^{-3}	

Table S17. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Ni	0.66013(2)	0.10843(2)	0.76453(1)	0.012(1)
P(1)	0.72515(5)	−0.03177(5)	0.66704(2)	0.015(1)
C(1)	0.8458(2)	−0.24361(19)	0.69782(9)	0.022(1)
P(3)	0.56659(5)	0.34801(5)	0.70736(2)	0.014(1)
C(3)	0.84885(18)	−0.24530(18)	0.77487(8)	0.016(1)
C(2)	0.6925(2)	0.00453(18)	0.92502(8)	0.019(1)
P(2)	0.64291(5)	0.19104(4)	0.87099(2)	0.012(1)
N	0.76824(15)	−0.10009(15)	0.80777(7)	0.014(1)
C(5)	0.87464(18)	−0.29763(18)	0.88993(8)	0.018(1)
C(4)	0.91537(18)	−0.36868(18)	0.82375(8)	0.017(1)
C(6)	0.78430(18)	−0.13369(18)	0.87817(8)	0.016(1)
C(11)	0.8704(2)	−0.0032(2)	0.60183(9)	0.025(1)
C(12)	0.5723(2)	−0.04213(19)	0.61450(8)	0.019(1)
C(13)	0.7906(3)	0.1441(2)	0.55318(10)	0.035(1)
C(14)	1.0070(2)	0.0028(3)	0.63902(12)	0.042(1)
C(15)	0.6482(2)	−0.1545(2)	0.55277(9)	0.030(1)
C(16)	0.4589(2)	−0.0940(2)	0.66034(10)	0.029(1)
C(21)	0.80085(19)	0.25868(19)	0.88386(8)	0.017(1)
C(22)	0.45079(19)	0.33762(19)	0.91425(8)	0.017(1)
C(23)	0.92898(19)	0.20841(19)	0.82236(9)	0.021(1)
C(24)	0.8863(2)	0.2001(3)	0.95210(10)	0.034(1)
C(25)	0.3101(2)	0.3070(2)	0.89456(9)	0.025(1)
C(26)	0.4538(2)	0.3356(2)	0.99359(8)	0.023(1)
C(31)	0.38992(19)	0.37381(18)	0.66041(8)	0.017(1)
C(32)	0.3599(2)	0.4625(2)	0.59708(9)	0.025(1)
C(33)	0.2274(2)	0.4868(2)	0.56026(10)	0.033(1)
C(34)	0.1226(2)	0.4239(2)	0.58562(10)	0.031(1)
C(35)	0.1487(2)	0.3373(2)	0.64827(10)	0.027(1)
C(36)	0.2815(2)	0.31238(19)	0.68503(9)	0.021(1)
C(41)	0.46415(18)	0.52693(17)	0.76186(8)	0.014(1)
C(42)	0.56191(18)	0.58732(18)	0.78847(8)	0.015(1)
C(43)	0.49578(19)	0.72188(18)	0.82972(8)	0.017(1)
C(44)	0.32834(19)	0.80176(19)	0.84435(8)	0.019(1)
C(45)	0.22897(19)	0.74647(19)	0.81724(8)	0.019(1)
C(46)	0.29576(18)	0.61118(18)	0.77627(8)	0.016(1)
H(1A)	0.7957	−0.3120	0.6848	0.026
H(1B)	0.9580	−0.2869	0.6760	0.026
H(2A)	0.7596	−0.0003	0.9633	0.022
H(2B)	0.5915	0.0014	0.9456	0.022
H(5)	0.9038	−0.3522	0.9338	0.021

Continued on next page

Table S17. – continued from previous page

atom	x	y	x	U(eq)
H(4)	0.9770	−0.4805	0.8148	0.021
H(11)	0.9205	−0.1008	0.5724	0.030
H(12)	0.5049	0.0692	0.5952	0.023
H(13A)	0.8723	0.1480	0.5178	0.053
H(13B)	0.7446	0.2426	0.5802	0.053
H(13C)	0.7037	0.1365	0.5302	0.053
H(14A)	1.0875	0.0117	0.6044	0.062
H(14B)	1.0595	−0.0961	0.6678	0.062
H(14C)	0.9618	0.0969	0.6688	0.062
H(15A)	0.5620	−0.1621	0.5292	0.045
H(15B)	0.7238	−0.2623	0.5698	0.045
H(15C)	0.7072	−0.1110	0.5199	0.045
H(16A)	0.3652	−0.0764	0.6345	0.043
H(16B)	0.4211	−0.0300	0.7025	0.043
H(16C)	0.5177	−0.2090	0.6735	0.043
H(21)	0.7455	0.3796	0.8836	0.020
H(22)	0.4310	0.4482	0.8960	0.021
H(23A)	0.8766	0.2583	0.7791	0.032
H(23B)	0.9808	0.0904	0.8191	0.032
H(23C)	1.0116	0.2443	0.8295	0.032
H(24A)	0.9552	0.0831	0.9511	0.050
H(24B)	0.8046	0.2247	0.9914	0.050
H(24C)	0.9539	0.2551	0.9574	0.050
H(25A)	0.3094	0.3087	0.8437	0.038
H(25B)	0.2069	0.3916	0.9136	0.038
H(25C)	0.3238	0.2012	0.9138	0.038
H(26A)	0.5444	0.3554	1.0055	0.034
H(26B)	0.4680	0.2299	1.0131	0.034
H(26C)	0.3511	0.4202	1.0130	0.034
H(32)	0.4311	0.5069	0.5790	0.030
H(33)	0.2091	0.5472	0.5173	0.039
H(34)	0.0326	0.4401	0.5601	0.038
H(35)	0.0759	0.2946	0.6663	0.033
H(36)	0.2987	0.2520	0.7280	0.025
H(42)	0.6763	0.5348	0.7780	0.018
H(43)	0.5647	0.7594	0.8480	0.020
H(44)	0.2824	0.8937	0.8728	0.023
H(45)	0.1144	0.8014	0.8267	0.022
H(46)	0.2260	0.5752	0.7577	0.019

Table S18. Anisotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.0130(1)	0.0108(1)	0.0118(1)	−0.0011(1)	−0.0009(1)	−0.0046(1)
P(1)	0.0159(2)	0.0144(2)	0.0137(2)	−0.0034(2)	−0.0001(2)	−0.0056(2)
C(1)	0.0235(8)	0.0141(8)	0.0224(9)	−0.0049(6)	−0.0052(7)	−0.0025(7)
P(3)	0.0154(2)	0.0130(2)	0.0139(2)	−0.0010(2)	0.0003(2)	−0.0059(2)
C(3)	0.0112(7)	0.0138(7)	0.0223(8)	−0.0037(6)	−0.0015(6)	−0.0055(6)
C(2)	0.0247(8)	0.0143(7)	0.0159(8)	0.0020(6)	−0.0002(6)	−0.0088(7)
P(2)	0.0130(1)	0.0108(1)	0.0118(1)	−0.0011(1)	−0.0009(1)	−0.0046(1)
N	0.0133(6)	0.0125(6)	0.0167(7)	−0.0015(5)	−0.0021(5)	−0.0057(5)
C(5)	0.0159(8)	0.0157(8)	0.0209(8)	0.0041(6)	−0.0039(6)	−0.0072(6)
C(4)	0.0132(7)	0.0116(7)	0.0266(9)	−0.0016(6)	−0.0023(6)	−0.0045(6)
C(6)	0.0151(7)	0.0169(8)	0.0175(8)	0.0009(6)	−0.0021(6)	−0.0093(6)
C(11)	0.0244(9)	0.0269(9)	0.0251(9)	−0.0107(7)	0.0108(7)	−0.0127(7)
C(12)	0.0232(8)	0.0183(8)	0.0155(8)	0.0000(6)	−0.0061(6)	−0.0087(7)
C(13)	0.0486(12)	0.0285(10)	0.0288(10)	−0.0068(8)	0.0211(9)	−0.0203(9)
C(14)	0.0296(10)	0.0579(14)	0.0468(13)	−0.0222(11)	0.0150(9)	−0.0281(10)
C(15)	0.0401(11)	0.0246(9)	0.0222(9)	−0.0050(7)	−0.0105(8)	−0.0105(8)
C(16)	0.0300(10)	0.0300(10)	0.0335(10)	0.0034(8)	−0.0091(8)	−0.0188(8)
C(21)	0.0185(8)	0.0155(7)	0.0186(8)	0.0017(6)	−0.0062(6)	−0.0083(6)
C(22)	0.0191(8)	0.0153(7)	0.0147(8)	−0.0022(6)	0.0020(6)	−0.0059(6)
C(23)	0.0165(8)	0.0175(8)	0.0312(9)	−0.0012(7)	−0.0017(7)	−0.0082(7)
C(24)	0.0348(10)	0.0450(11)	0.0285(10)	0.0103(9)	−0.0164(8)	−0.0238(9)
C(25)	0.0190(8)	0.0306(9)	0.0246(9)	−0.0024(7)	0.0015(7)	−0.0099(7)
C(26)	0.0310(9)	0.0206(8)	0.0166(8)	−0.0043(7)	0.0040(7)	−0.0116(7)
C(31)	0.0208(8)	0.0124(7)	0.0156(8)	−0.0034(6)	−0.0032(6)	−0.0037(6)
C(32)	0.0349(10)	0.0205(8)	0.0193(9)	0.0012(7)	−0.0053(7)	−0.0112(8)
C(33)	0.0448(11)	0.0256(9)	0.0213(9)	0.0012(7)	−0.0154(8)	−0.0074(9)
C(34)	0.0288(10)	0.0282(9)	0.0299(10)	−0.0105(8)	−0.0145(8)	−0.0027(8)
C(35)	0.0232(9)	0.0276(9)	0.0311(10)	−0.0113(8)	−0.0028(7)	−0.0101(8)
C(36)	0.0238(9)	0.0201(8)	0.0182(8)	−0.0023(7)	−0.0037(7)	−0.0085(7)
C(41)	0.0168(7)	0.0111(7)	0.0124(7)	0.0028(6)	−0.0011(6)	−0.0059(6)
C(42)	0.0133(7)	0.0146(7)	0.0154(8)	0.0035(6)	−0.0015(6)	−0.0061(6)
C(43)	0.0198(8)	0.0180(8)	0.0165(8)	0.0024(6)	−0.0040(6)	−0.0116(7)
C(44)	0.0219(8)	0.0151(8)	0.0180(8)	−0.0035(6)	0.0007(6)	−0.0067(7)
C(45)	0.0142(8)	0.0168(8)	0.0227(8)	−0.0011(6)	−0.0006(6)	−0.0049(6)
C(46)	0.0151(7)	0.0155(7)	0.0191(8)	0.0003(6)	−0.0034(6)	−0.0082(6)

Table S19. Distances [Å] for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

atom – atom	distance	atom – atom	distance
Ni – N	1.9012(12)	Ni – P(2)	2.2047(5)
Ni – P(3)	2.2349(5)	Ni – P(1)	2.2367(4)
P(1) – C(12)	1.8456(16)	P(1) – C(11)	1.8466(17)
P(1) – C(1)	1.8534(16)	C(1) – C(3)	1.486(2)
C(1) – H(1A)	0.9900	C(1) – H(1B)	0.9900
P(3) – C(41)	1.8422(15)	P(3) – C(31)	1.8462(16)
C(3) – C(4)	1.376(2)	C(3) – N	1.3771(19)
C(2) – C(6)	1.489(2)	C(2) – P(2)	1.8452(15)
C(2) – H(2A)	0.9900	C(2) – H(2B)	0.9900
P(2) – C(22)	1.8448(15)	P(2) – C(21)	1.8644(16)
N – C(6)	1.376(2)	C(5) – C(6)	1.379(2)
C(5) – C(4)	1.416(2)	C(5) – H(5)	0.9500
C(4) – H(4)	0.9500	C(11) – C(13)	1.526(3)
C(11) – C(14)	1.527(3)	C(11) – H(11)	1.0000
C(12) – C(16)	1.526(2)	C(12) – C(15)	1.534(2)
C(12) – H(12)	1.0000	C(13) – H(13A)	0.9800
C(13) – H(13B)	0.9800	C(13) – H(13C)	0.9800
C(14) – H(14A)	0.9800	C(14) – H(14B)	0.9800
C(14) – H(14C)	0.9800	C(15) – H(15A)	0.9800
C(15) – H(15B)	0.9800	C(15) – H(15C)	0.9800
C(16) – H(16A)	0.9800	C(16) – H(16B)	0.9800
C(16) – H(16C)	0.9800	C(21) – C(24)	1.531(2)
C(21) – C(23)	1.532(2)	C(21) – H(21)	1.0000
C(22) – C(25)	1.529(2)	C(22) – C(26)	1.529(2)
C(22) – H(22)	1.0000	C(23) – H(23A)	0.9800
C(23) – H(23B)	0.9800	C(23) – H(23C)	0.9800
C(24) – H(24A)	0.9800	C(24) – H(24B)	0.9800
C(24) – H(24C)	0.9800	C(25) – H(25A)	0.9800
C(25) – H(25B)	0.9800	C(25) – H(25C)	0.9800
C(26) – H(26A)	0.9800	C(26) – H(26B)	0.9800
C(26) – H(26C)	0.9800	C(31) – C(36)	1.391(2)
C(31) – C(32)	1.399(2)	C(32) – C(33)	1.389(3)
C(32) – H(32)	0.9500	C(33) – C(34)	1.376(3)
C(33) – H(33)	0.9500	C(34) – C(35)	1.380(3)
C(34) – H(34)	0.9500	C(35) – C(36)	1.390(2)
C(35) – H(35)	0.9500	C(36) – H(36)	0.9500
C(41) – C(46)	1.400(2)	C(41) – C(42)	1.400(2)
C(42) – C(43)	1.386(2)	C(42) – H(42)	0.9500
C(43) – C(44)	1.390(2)	C(43) – H(43)	0.9500
C(44) – C(45)	1.384(2)	C(44) – H(44)	0.9500
C(45) – C(46)	1.388(2)	C(45) – H(45)	0.9500

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Table S19. – continued from previous page

atom – atom	distance	atom – atom	distance
C(46) – H(46)	0.9500		

Table S20. Angles [°] for [(PN^{pyr}P)Ni(PPh$_2$)] (**5**).

atom – atom – atom	angle	atom – atom – atom	angle
N – Ni – P(2)	83.21(4)	N – Ni – P(3)	172.18(4)
P(2) – Ni – P(3)	98.952(17)	N – Ni – P(1)	83.37(4)
P(2) – Ni – P(1)	165.900(17)	P(3) – Ni – P(1)	93.796(17)
C(12) – P(1) – C(11)	104.24(8)	C(12) – P(1) – C(1)	104.00(7)
C(11) – P(1) – C(1)	101.75(8)	C(12) – P(1) – Ni	123.19(5)
C(11) – P(1) – Ni	117.28(6)	C(1) – P(1) – Ni	103.50(5)
C(3) – C(1) – P(1)	108.17(11)	C(3) – C(1) – H(1A)	110.1
P(1) – C(1) – H(1A)	110.1	C(3) – C(1) – H(1B)	110.1
P(1) – C(1) – H(1B)	110.1	H(1A) – C(1) – H(1B)	108.4
C(41) – P(3) – C(31)	98.29(7)	C(41) – P(3) – Ni	115.89(5)
C(31) – P(3) – Ni	108.21(5)	C(4) – C(3) – N	109.56(14)
C(4) – C(3) – C(1)	132.45(14)	N – C(3) – C(1)	117.96(13)
C(6) – C(2) – P(2)	106.85(10)	C(6) – C(2) – H(2A)	110.4
P(2) – C(2) – H(2A)	110.4	C(6) – C(2) – H(2B)	110.4
P(2) – C(2) – H(2B)	110.4	H(2A) – C(2) – H(2B)	108.6
C(22) – P(2) – C(2)	103.01(7)	C(22) – P(2) – C(21)	106.95(7)
C(2) – P(2) – C(21)	106.87(7)	C(22) – P(2) – Ni	123.08(5)
C(2) – P(2) – Ni	102.79(5)	C(21) – P(2) – Ni	112.54(5)
C(6) – N – C(3)	106.97(12)	C(6) – N – Ni	126.19(10)
C(3) – N – Ni	126.82(11)	C(6) – C(5) – C(4)	106.53(14)
C(6) – C(5) – H(5)	126.7	C(4) – C(5) – H(5)	126.7
C(3) – C(4) – C(5)	107.09(13)	C(3) – C(4) – H(4)	126.5
C(5) – C(4) – H(4)	126.5	N – C(6) – C(5)	109.84(14)
N – C(6) – C(2)	116.42(13)	C(5) – C(6) – C(2)	133.45(15)
C(13) – C(11) – C(14)	111.58(16)	C(13) – C(11) – P(1)	113.47(12)
C(14) – C(11) – P(1)	109.39(13)	C(13) – C(11) – H(11)	107.4
C(14) – C(11) – H(11)	107.4	P(1) – C(11) – H(11)	107.4
C(16) – C(12) – C(15)	110.00(14)	C(16) – C(12) – P(1)	110.45(11)
C(15) – C(12) – P(1)	113.12(12)	C(16) – C(12) – H(12)	107.7
C(15) – C(12) – H(12)	107.7	P(1) – C(12) – H(12)	107.7
C(11) – C(13) – H(13A)	109.5	C(11) – C(13) – H(13B)	109.5
H(13A) – C(13) – H(13B)	109.5	C(11) – C(13) – H(13C)	109.5
H(13A) – C(13) – H(13C)	109.5	H(13B) – C(13) – H(13C)	109.5
C(11) – C(14) – H(14A)	109.5	C(11) – C(14) – H(14B)	109.5
H(14A) – C(14) – H(14B)	109.5	C(11) – C(14) – H(14C)	109.5
H(14A) – C(14) – H(14C)	109.5	H(14B) – C(14) – H(14C)	109.5
C(12) – C(15) – H(15A)	109.5	C(12) – C(15) – H(15B)	109.5
H(15A) – C(15) – H(15B)	109.5	C(12) – C(15) – H(15C)	109.5
H(15A) – C(15) – H(15C)	109.5	H(15B) – C(15) – H(15C)	109.5
C(12) – C(16) – H(16A)	109.5	C(12) – C(16) – H(16B)	109.5
H(16A) – C(16) – H(16B)	109.5	C(12) – C(16) – H(16C)	109.5

Continued on next page

Table S20. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(16A) – C(16) – H(16C)	109.5	H(16B) – C(16) – H(16C)	109.5
C(24) – C(21) – C(23)	109.14(14)	C(24) – C(21) – P(2)	115.63(12)
C(23) – C(21) – P(2)	109.95(11)	C(24) – C(21) – H(21)	107.3
C(23) – C(21) – H(21)	107.3	P(2) – C(21) – H(21)	107.3
C(25) – C(22) – C(26)	110.28(13)	C(25) – C(22) – P(2)	109.52(11)
C(26) – C(22) – P(2)	113.63(11)	C(25) – C(22) – H(22)	107.7
C(26) – C(22) – H(22)	107.7	P(2) – C(22) – H(22)	107.7
C(21) – C(23) – H(23A)	109.5	C(21) – C(23) – H(23B)	109.5
H(23A) – C(23) – H(23B)	109.5	C(21) – C(23) – H(23C)	109.5
H(23A) – C(23) – H(23C)	109.5	H(23B) – C(23) – H(23C)	109.5
C(21) – C(24) – H(24A)	109.5	C(21) – C(24) – H(24B)	109.5
H(24A) – C(24) – H(24B)	109.5	C(21) – C(24) – H(24C)	109.5
H(24A) – C(24) – H(24C)	109.5	H(24B) – C(24) – H(24C)	109.5
C(22) – C(25) – H(25A)	109.5	C(22) – C(25) – H(25B)	109.5
H(25A) – C(25) – H(25B)	109.5	C(22) – C(25) – H(25C)	109.5
H(25A) – C(25) – H(25C)	109.5	H(25B) – C(25) – H(25C)	109.5
C(22) – C(26) – H(26A)	109.5	C(22) – C(26) – H(26B)	109.5
H(26A) – C(26) – H(26B)	109.5	C(22) – C(26) – H(26C)	109.5
H(26A) – C(26) – H(26C)	109.5	H(26B) – C(26) – H(26C)	109.5
C(36) – C(31) – C(32)	117.38(15)	C(36) – C(31) – P(3)	123.71(12)
C(32) – C(31) – P(3)	118.90(13)	C(33) – C(32) – C(31)	121.01(17)
C(33) – C(32) – H(32)	119.5	C(31) – C(32) – H(32)	119.5
C(34) – C(33) – C(32)	120.39(17)	C(34) – C(33) – H(33)	119.8
C(32) – C(33) – H(33)	119.8	C(33) – C(34) – C(35)	119.74(17)
C(33) – C(34) – H(34)	120.1	C(35) – C(34) – H(34)	120.1
C(34) – C(35) – C(36)	119.91(18)	C(34) – C(35) – H(35)	120.0
C(36) – C(35) – H(35)	120.0	C(35) – C(36) – C(31)	121.56(16)
C(35) – C(36) – H(36)	119.2	C(31) – C(36) – H(36)	119.2
C(46) – C(41) – C(42)	117.48(14)	C(46) – C(41) – P(3)	125.08(12)
C(42) – C(41) – P(3)	117.38(11)	C(43) – C(42) – C(41)	121.56(14)
C(43) – C(42) – H(42)	119.2	C(41) – C(42) – H(42)	119.2
C(42) – C(43) – C(44)	119.85(15)	C(42) – C(43) – H(43)	120.1
C(44) – C(43) – H(43)	120.1	C(45) – C(44) – C(43)	119.59(15)
C(45) – C(44) – H(44)	120.2	C(43) – C(44) – H(44)	120.2
C(44) – C(45) – C(46)	120.37(14)	C(44) – C(45) – H(45)	119.8
C(46) – C(45) – H(45)	119.8	C(45) – C(46) – C(41)	121.12(14)
C(45) – C(46) – H(46)	119.4	C(41) – C(46) – H(46)	119.4

3.5 Crystal data for [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (6)

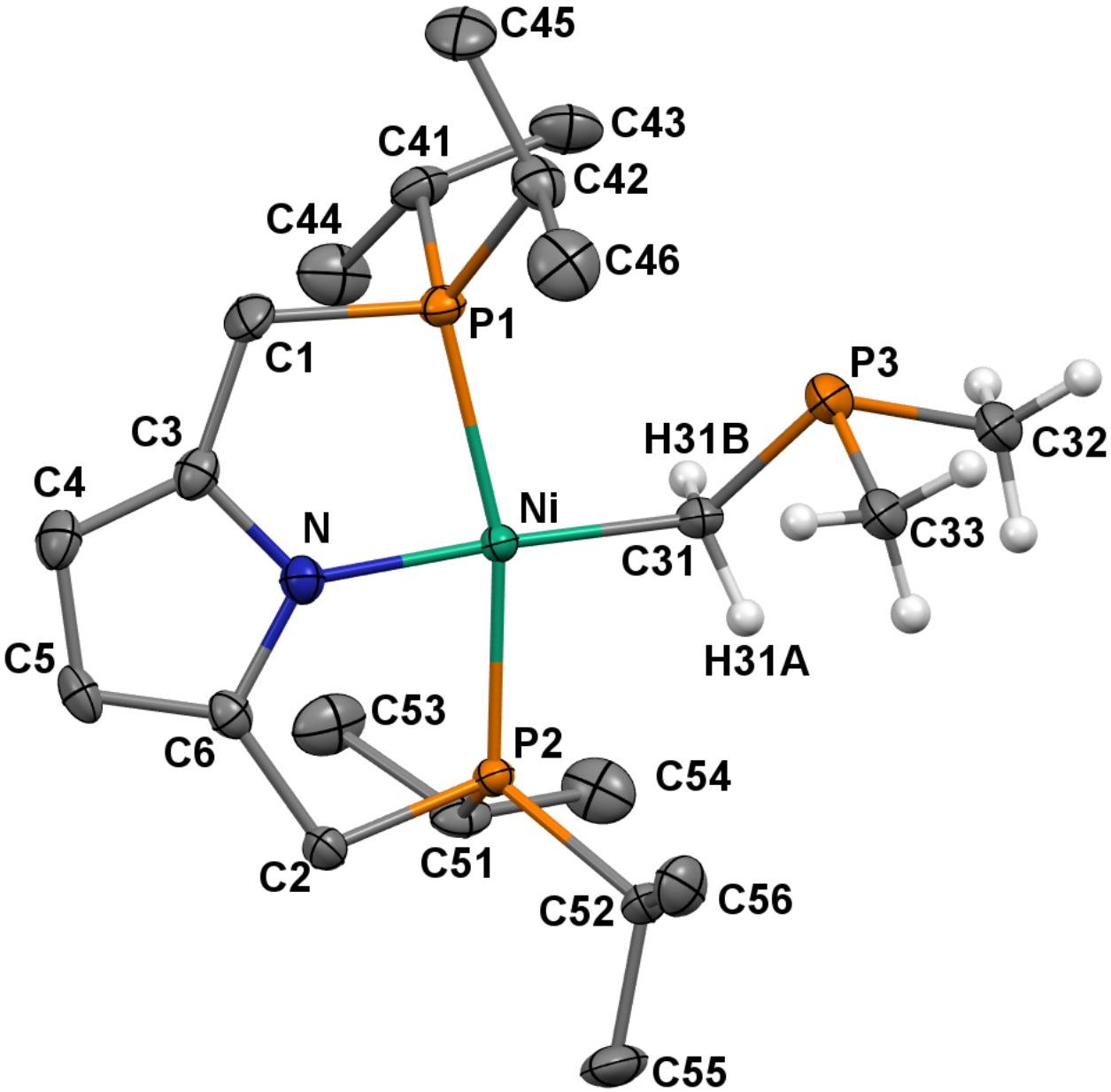

Figure S28. Thermal-ellipsoid representation of [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (**6**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S21. Crystal data and structure refinement for [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (**6**).

Identification code:	jk2_62	
Empirical formula:	$C_{21}H_{42}NNiP_3$	
Formula weight:	460.18	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 7.6605(16) Å	α = 90°
	b = 11.777(2) Å	β = 92.670(3)°
	c = 27.694(6) Å	γ = 90°
Volume:	2495.8(9) Å^3	
Z:	4	
Density (calculated):	1.225 g·cm^{-3}	
Absorption coefficient (μ):	0.976 mm^{-1}	
F(000):	992	
Crystal size:	0.08 × 0.08 × 0.08 mm^3	
θ range for data collection:	1.47 to 25.00°	
Index ranges:	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-32 \leq l \leq 32$	
Reflections collected:	44437	
Independent reflections:	4387 [R_{int} = 0.0923]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6501	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	4387 / 0 / 233	
Goodness-of-fit on F^2:	1.023	
Final R indices [I>2σ(I)]:	R_1 = 0.0417, wR_2 = 0.0878	
R indices (all data):	R_1 = 0.0651, wR_2 = 0.0940	
Largest diff. peak and hole:	0.733 and −1.365 e$^-$·Å^{-3}	

Table S22. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (**6**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Ni	0.28050(5)	0.27971(3)	0.13454(1)	0.014(1)
C(1)	0.0660(4)	0.0747(3)	0.17945(12)	0.025(1)
P(1)	0.17746(10)	0.10391(7)	0.12292(3)	0.018(1)
P(2)	0.39253(10)	0.43493(7)	0.16538(3)	0.015(1)
C(2)	0.2728(4)	0.4562(3)	0.22072(11)	0.019(1)
C(5)	0.1485(4)	0.2934(3)	0.27491(11)	0.021(1)
C(3)	0.1118(4)	0.1684(3)	0.21408(11)	0.020(1)
P(3)	0.29373(14)	0.26121(8)	0.01802(3)	0.033(1)
C(6)	0.2010(4)	0.3422(3)	0.23288(11)	0.018(1)
C(4)	0.0929(4)	0.1821(3)	0.26291(12)	0.024(1)
N	0.1801(3)	0.2659(2)	0.19546(9)	0.018(1)
C(42)	0.0175(4)	0.0598(3)	0.07457(12)	0.025(1)
C(41)	0.3448(4)	−0.0083(3)	0.12279(12)	0.024(1)
C(46)	−0.1334(4)	0.1448(3)	0.07046(14)	0.037(1)
C(45)	−0.0496(5)	−0.0615(3)	0.07988(14)	0.035(1)
C(43)	0.4271(5)	−0.0220(3)	0.07419(13)	0.031(1)
C(51)	0.6234(4)	0.4261(3)	0.18759(12)	0.022(1)
C(53)	0.6510(5)	0.3209(3)	0.21911(14)	0.034(1)
C(54)	0.7516(4)	0.4291(3)	0.14692(14)	0.034(1)
C(52)	0.3750(4)	0.5698(3)	0.13217(11)	0.020(1)
C(55)	0.4419(5)	0.6717(3)	0.16131(14)	0.035(1)
C(56)	0.1876(4)	0.5895(3)	0.11279(12)	0.029(1)
C(44)	0.4840(5)	0.0147(3)	0.16318(13)	0.034(1)
C(31)	0.4049(4)	0.2997(3)	0.07459(11)	0.020(1)
C(33)	0.1401(5)	0.3786(3)	0.00879(12)	0.033(1)
C(32)	0.4552(5)	0.3077(3)	−0.02517(12)	0.033(1)
H(1A)	−0.0621	0.0716	0.1729	0.030
H(1B)	0.1051	0.0008	0.1932	0.030
H(2A)	0.3522	0.4843	0.2473	0.023
H(2B)	0.1772	0.5118	0.2151	0.023
H(5)	0.1494	0.3278	0.3059	0.026
H(4)	0.0505	0.1270	0.2845	0.029
H(42)	0.0786	0.0631	0.0435	0.030
H(41)	0.2864	−0.0817	0.1304	0.029
H(46A)	−0.0870	0.2210	0.0651	0.055
H(46B)	−0.1966	0.1441	0.1004	0.055
H(46C)	−0.2132	0.1236	0.0433	0.055
H(45A)	−0.1320	−0.0792	0.0528	0.053
H(45B)	−0.1088	−0.0685	0.1104	0.053

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Table S22. – continued from previous page

atom	x	y	x	U(eq)
H(45C)	0.0490	−0.1145	0.0799	0.053
H(43A)	0.3380	−0.0471	0.0500	0.047
H(43B)	0.5207	−0.0787	0.0770	0.047
H(43C)	0.4757	0.0509	0.0643	0.047
H(51)	0.6480	0.4939	0.2085	0.027
H(53A)	0.6289	0.2527	0.1995	0.051
H(53B)	0.5702	0.3229	0.2455	0.051
H(53C)	0.7716	0.3197	0.2326	0.051
H(54A)	0.7263	0.3661	0.1245	0.051
H(54B)	0.8713	0.4217	0.1607	0.051
H(54C)	0.7395	0.5013	0.1295	0.051
H(52)	0.4493	0.5628	0.1036	0.024
H(55A)	0.4374	0.7395	0.1408	0.053
H(55B)	0.5628	0.6579	0.1730	0.053
H(55C)	0.3686	0.6833	0.1890	0.053
H(56A)	0.1859	0.6508	0.0888	0.043
H(56B)	0.1147	0.6107	0.1395	0.043
H(56C)	0.1421	0.5198	0.0976	0.043
H(44A)	0.5630	−0.0506	0.1664	0.052
H(44B)	0.4270	0.0267	0.1937	0.052
H(44C)	0.5508	0.0826	0.1553	0.052
H(31A)	0.4388	0.3806	0.0725	0.024
H(31B)	0.5142	0.2550	0.0777	0.024
H(33A)	0.0870	0.3749	−0.0240	0.050
H(33B)	0.2024	0.4509	0.0132	0.050
H(33C)	0.0486	0.3731	0.0323	0.050
H(32A)	0.4050	0.3004	−0.0582	0.050
H(32B)	0.5601	0.2603	−0.0214	0.050
H(32C)	0.4864	0.3872	−0.0188	0.050

Table S23. Anisotropic displacement parameters (Å^2) for [(PN^{pyr}P)Ni(CH$_2$PMe$_2$)] (**6**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ni	0.0172(2)	0.0115(2)	0.0128(2)	0.0001(2)	−0.0007(2)	−0.0008(2)
C(1)	0.0309(19)	0.0215(18)	0.0237(18)	0.0023(15)	0.0024(15)	−0.0112(15)
P(1)	0.0195(4)	0.0141(4)	0.0191(4)	−0.0003(3)	−0.0021(3)	−0.0024(3)
P(2)	0.0184(4)	0.0118(4)	0.0150(4)	0.0002(3)	−0.0013(3)	−0.0003(3)
C(2)	0.0257(17)	0.0169(17)	0.0157(16)	−0.0009(13)	0.0016(13)	0.0022(14)
C(5)	0.0192(16)	0.032(2)	0.0131(16)	−0.0028(14)	0.0035(13)	0.0008(15)
C(3)	0.0167(16)	0.0212(18)	0.0214(18)	0.0041(14)	0.0005(13)	−0.0021(14)
P(3)	0.0583(6)	0.0237(5)	0.0171(4)	−0.0012(4)	−0.0013(4)	−0.0069(4)
C(6)	0.0168(16)	0.0206(18)	0.0159(16)	−0.0008(14)	−0.0013(13)	0.0017(14)
C(4)	0.0218(17)	0.0281(19)	0.0220(18)	0.0057(15)	0.0036(14)	−0.0045(15)
N	0.0172(13)	0.0192(14)	0.0171(14)	0.0006(12)	0.0004(11)	0.0001(12)
C(42)	0.0231(17)	0.030(2)	0.0220(18)	−0.0026(15)	−0.0035(14)	−0.0028(15)
C(41)	0.0267(18)	0.0143(17)	0.0305(19)	0.0025(15)	−0.0037(15)	−0.0001(15)
C(46)	0.0233(18)	0.045(2)	0.041(2)	0.0005(19)	−0.0079(17)	0.0006(18)
C(45)	0.034(2)	0.032(2)	0.038(2)	−0.0056(18)	−0.0062(17)	−0.0152(18)
C(43)	0.0307(19)	0.0213(19)	0.041(2)	−0.0072(17)	−0.0008(17)	0.0063(16)
C(51)	0.0197(16)	0.0186(17)	0.0278(18)	−0.0032(14)	−0.0086(14)	−0.0022(14)
C(53)	0.0296(19)	0.027(2)	0.044(2)	0.0046(17)	−0.0166(17)	0.0042(16)
C(54)	0.0198(18)	0.041(2)	0.041(2)	−0.0070(18)	0.0003(16)	−0.0002(17)
C(52)	0.0286(18)	0.0126(16)	0.0184(17)	0.0006(13)	0.0009(14)	0.0015(14)
C(55)	0.054(2)	0.0133(18)	0.037(2)	−0.0004(16)	−0.0096(19)	−0.0034(17)
C(56)	0.034(2)	0.027(2)	0.0252(19)	0.0053(15)	−0.0043(16)	0.0064(16)
C(44)	0.030(2)	0.032(2)	0.040(2)	−0.0024(18)	−0.0136(17)	0.0063(17)
C(31)	0.0278(18)	0.0136(17)	0.0191(17)	−0.0016(13)	0.0032(14)	−0.0022(14)
C(33)	0.0583(6)	0.0237(5)	0.0171(4)	−0.0012(4)	−0.0013(4)	−0.0069(4)
C(32)	0.0583(6)	0.0237(5)	0.0171(4)	−0.0012(4)	−0.0013(4)	−0.0069(4)

Table S24. Distances [Å] for [(PN^{pyr}P)Ni(CH_2PMe_2)] (**6**).

atom – atom	distance	atom – atom	distance
Ni – N	1.894(3)	Ni – C(31)	1.966(3)
Ni – P(2)	2.1769(9)	Ni – P(1)	2.2337(10)
C(1) – C(3)	1.493(4)	C(1) – P(1)	1.850(3)
C(1) – H(1A)	0.9900	C(1) – H(1B)	0.9900
P(1) – C(41)	1.841(3)	P(1) – C(42)	1.847(3)
P(2) – C(52)	1.837(3)	P(2) – C(2)	1.840(3)
P(2) – C(51)	1.848(3)	C(2) – C(6)	1.495(4)
C(2) – H(2A)	0.9900	C(2) – H(2B)	0.9900
C(5) – C(6)	1.375(4)	C(5) – C(4)	1.414(5)
C(5) – H(5)	0.9500	C(3) – N	1.372(4)
C(3) – C(4)	1.376(4)	P(3) – C(31)	1.806(3)
P(3) – C(33)	1.826(4)	P(3) – C(32)	1.843(4)
C(6) – N	1.376(4)	C(4) – H(4)	0.9500
C(42) – C(45)	1.527(5)	C(42) – C(46)	1.529(5)
C(42) – H(42)	1.0000	C(41) – C(43)	1.521(5)
C(41) – C(44)	1.533(4)	C(41) – H(41)	1.0000
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(51) – C(53)	1.524(5)
C(51) – C(54)	1.529(5)	C(51) – H(51)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(52) – C(55)	1.522(4)	C(52) – C(56)	1.527(4)
C(52) – H(52)	1.0000	C(55) – H(55A)	0.9800
C(55) – H(55B)	0.9800	C(55) – H(55C)	0.9800
C(56) – H(56A)	0.9800	C(56) – H(56B)	0.9800
C(56) – H(56C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(31) – H(31A)	0.9900	C(31) – H(31B)	0.9900
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800

Table S25. Angles [°] for [(PN^{pyr}P)Ni(CH_2PMe_2)] (**6**).

atom – atom – atom	angle	atom – atom – atom	angle
N – Ni – C(31)	174.53(12)	N – Ni – P(2)	83.78(8)
C(31) – Ni – P(2)	91.89(9)	N – Ni – P(1)	83.87(8)
C(31) – Ni – P(1)	99.87(9)	P(2) – Ni – P(1)	164.80(4)
C(3) – C(1) – P(1)	107.6(2)	C(3) – C(1) – H(1A)	110.2
P(1) – C(1) – H(1A)	110.2	C(3) – C(1) – H(1B)	110.2
P(1) – C(1) – H(1B)	110.2	H(1A) – C(1) – H(1B)	108.5
C(41) – P(1) – C(42)	103.59(15)	C(41) – P(1) – C(1)	102.53(16)
C(42) – P(1) – C(1)	104.15(15)	C(41) – P(1) – Ni	115.09(11)
C(42) – P(1) – Ni	125.68(12)	C(1) – P(1) – Ni	102.97(11)
C(52) – P(2) – C(2)	105.77(15)	C(52) – P(2) – C(51)	105.18(15)
C(2) – P(2) – C(51)	103.70(15)	C(52) – P(2) – Ni	120.75(10)
C(2) – P(2) – Ni	103.79(10)	C(51) – P(2) – Ni	115.90(11)
C(6) – C(2) – P(2)	105.6(2)	C(6) – C(2) – H(2A)	110.6
P(2) – C(2) – H(2A)	110.6	C(6) – C(2) – H(2B)	110.6
P(2) – C(2) – H(2B)	110.6	H(2A) – C(2) – H(2B)	108.8
C(6) – C(5) – C(4)	106.6(3)	C(6) – C(5) – H(5)	126.7
C(4) – C(5) – H(5)	126.7	N – C(3) – C(4)	109.3(3)
N – C(3) – C(1)	117.4(3)	C(4) – C(3) – C(1)	133.3(3)
C(31) – P(3) – C(33)	101.88(15)	C(31) – P(3) – C(32)	100.65(16)
C(33) – P(3) – C(32)	97.56(17)	C(5) – C(6) – N	109.6(3)
C(5) – C(6) – C(2)	133.7(3)	N – C(6) – C(2)	116.6(3)
C(3) – C(4) – C(5)	107.2(3)	C(3) – C(4) – H(4)	126.4
C(5) – C(4) – H(4)	126.4	C(3) – N – C(6)	107.3(3)
C(3) – N – Ni	125.8(2)	C(6) – N – Ni	125.2(2)
C(45) – C(42) – C(46)	111.3(3)	C(45) – C(42) – P(1)	114.1(2)
C(46) – C(42) – P(1)	110.1(2)	C(45) – C(42) – H(42)	107.0
C(46) – C(42) – H(42)	107.0	P(1) – C(42) – H(42)	107.0
C(43) – C(41) – C(44)	111.2(3)	C(43) – C(41) – P(1)	113.3(2)
C(44) – C(41) – P(1)	109.4(2)	C(43) – C(41) – H(41)	107.6
C(44) – C(41) – H(41)	107.6	P(1) – C(41) – H(41)	107.6
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(53) – C(51) – C(54)	111.4(3)	C(53) – C(51) – P(2)	110.0(2)
C(54) – C(51) – P(2)	113.0(2)	C(53) – C(51) – H(51)	107.4

Continued on next page

Table S25. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(54) – C(51) – H(51)	107.4	P(2) – C(51) – H(51)	107.4
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(55) – C(52) – C(56)	110.7(3)	C(55) – C(52) – P(2)	113.7(2)
C(56) – C(52) – P(2)	110.7(2)	C(55) – C(52) – H(52)	107.1
C(56) – C(52) – H(52)	107.1	P(2) – C(52) – H(52)	107.1
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
P(3) – C(31) – Ni	118.36(17)	P(3) – C(31) – H(31A)	107.7
Ni – C(31) – H(31A)	107.7	P(3) – C(31) – H(31B)	107.7
Ni – C(31) – H(31B)	107.7	H(31A) – C(31) – H(31B)	107.1
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5