Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supporting Information For :

Aerobic Oxidation-Functionalization of the aryl moiety in van Koten's Pincer Complex (NCN)$Ni^{II}Br$: Relevance to Carbon-HeBrteroatom Coupling Reactions Promoted by High-Valent Nickel Species

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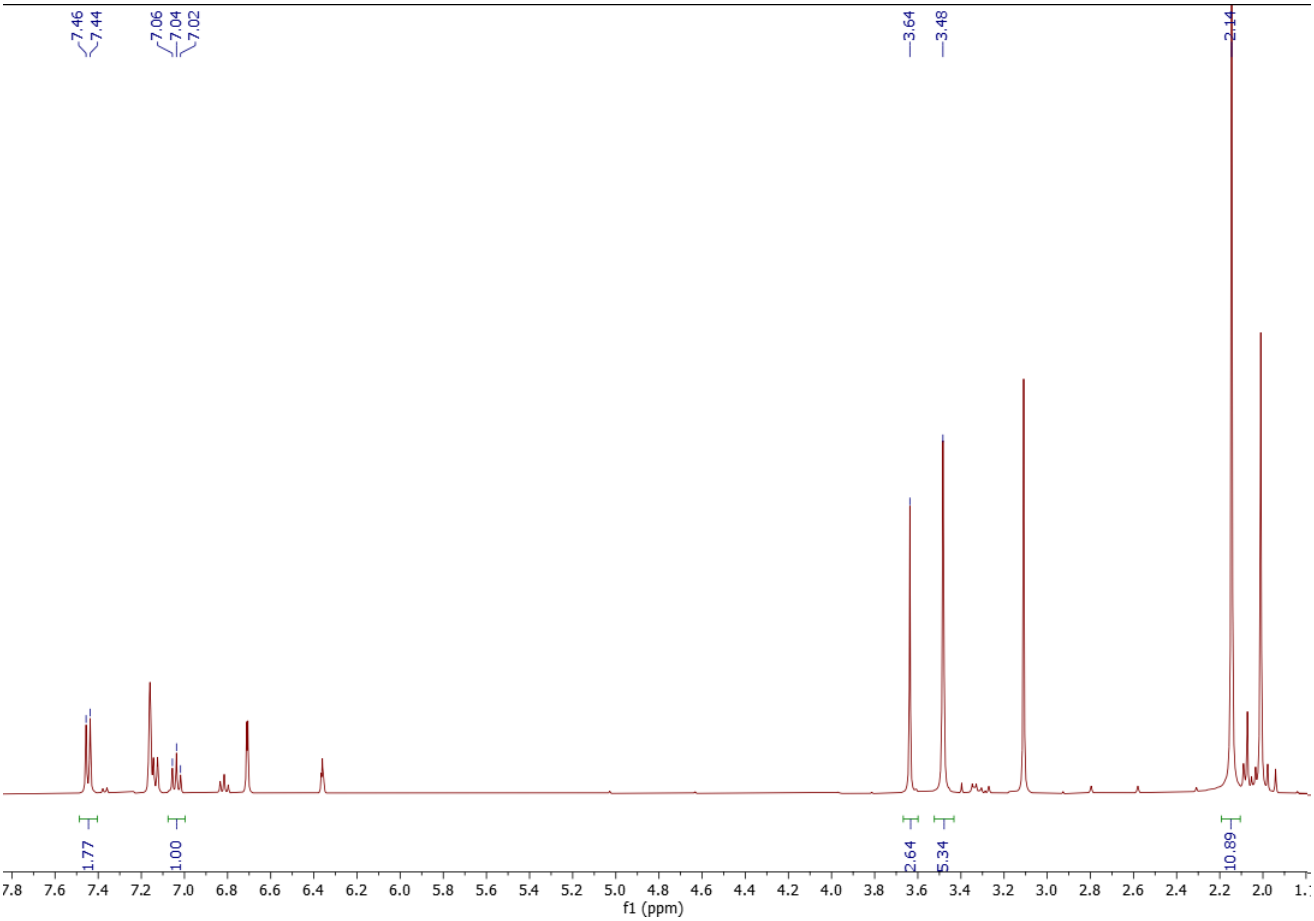

Figure S1. Reaction of (NCN)Ni^{II}Br with MeOH in air at reflux. ^{1}H NMR C_6D_6, δ 7.45 (2H, d, J_{HH} = *7.6*), δ 7.04 (1H, t, J_{HH} = *7.6*), δ 3.64 (3H, s), δ 3.49 (4H, s), δ 2.16 (12H, s).

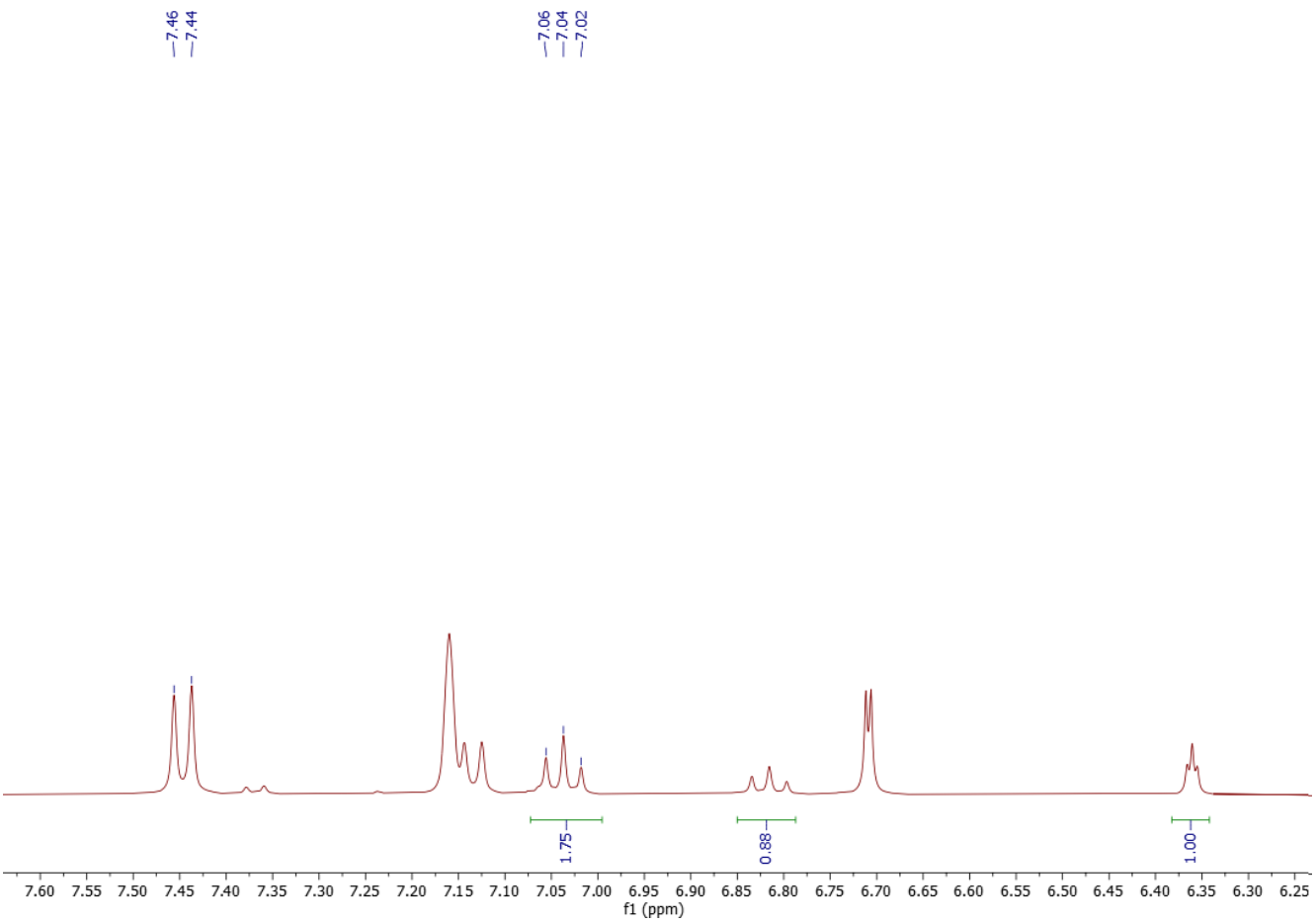

Figure S2. ^{1}H NMR spectrum for the reaction of (NCN)Ni^{II}Br with MeOH in air at reflux with internal standard integrated to 1.00 (C_6D_6,). NC(OMe)N major product.

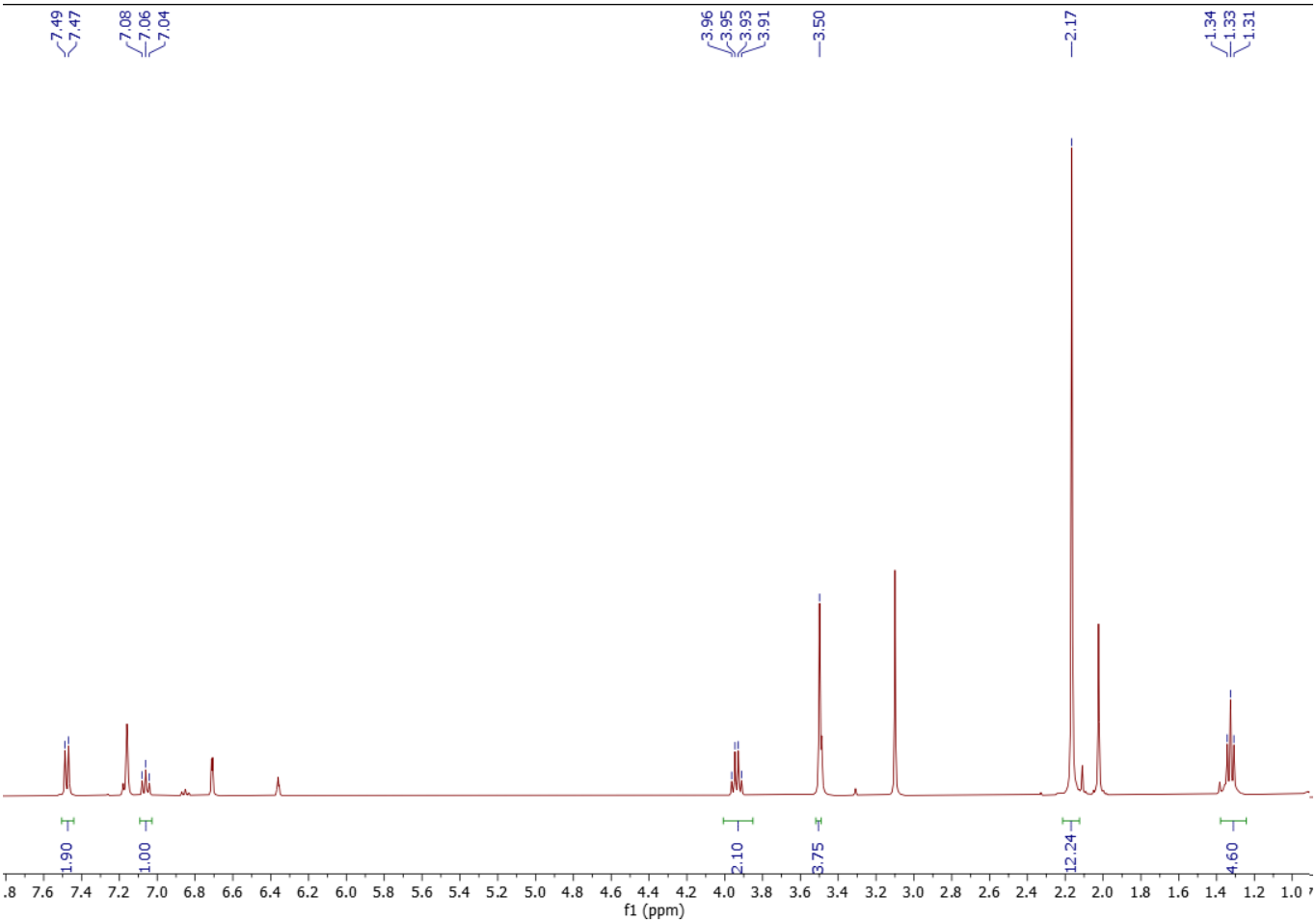

Figure S3. Reaction of (NCN)Ni^{II}Br with refluxing EtOH in air. ^{1}H NMR C_6D_6, δ 7.48 (2H, d, J_{HH} = *7.6*), δ 7.06 (1H, t, J_{HH} = *7.6*), δ 3.94 (2H, q, J_{HH} = *7.0*), δ 3.50 (4H, s), δ 2.17 (12H, s) δ 1.33 (3H, t, J_{HH} = *7.0*).

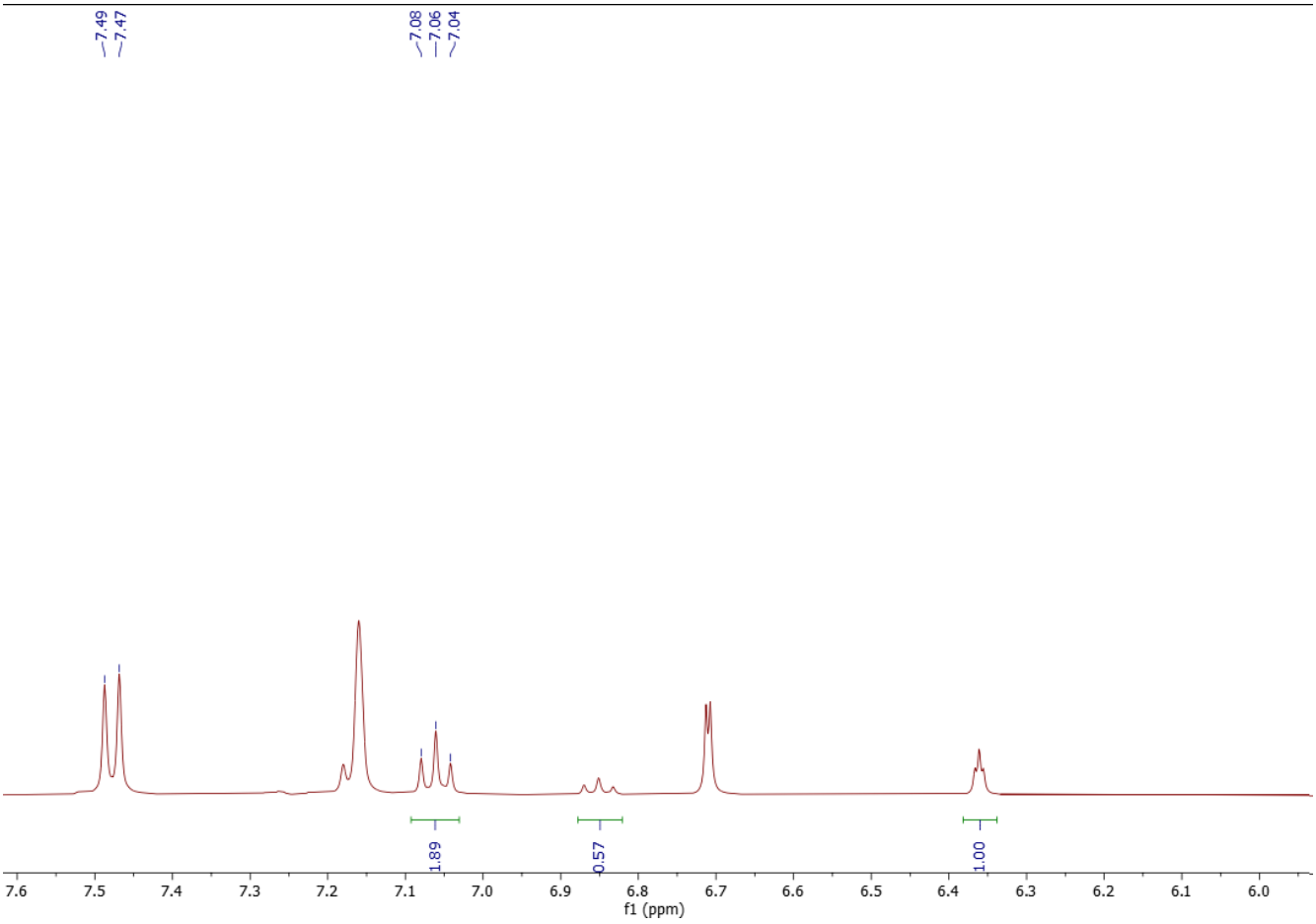

Figure S4. ^{1}H NMR spectrum of reaction of (NCN)Ni^{II}Br with EtOH in air with internal standard in C_6D_6 (integrated to 1.00). NC(OEt)N major product and NC(OH)N minor product.

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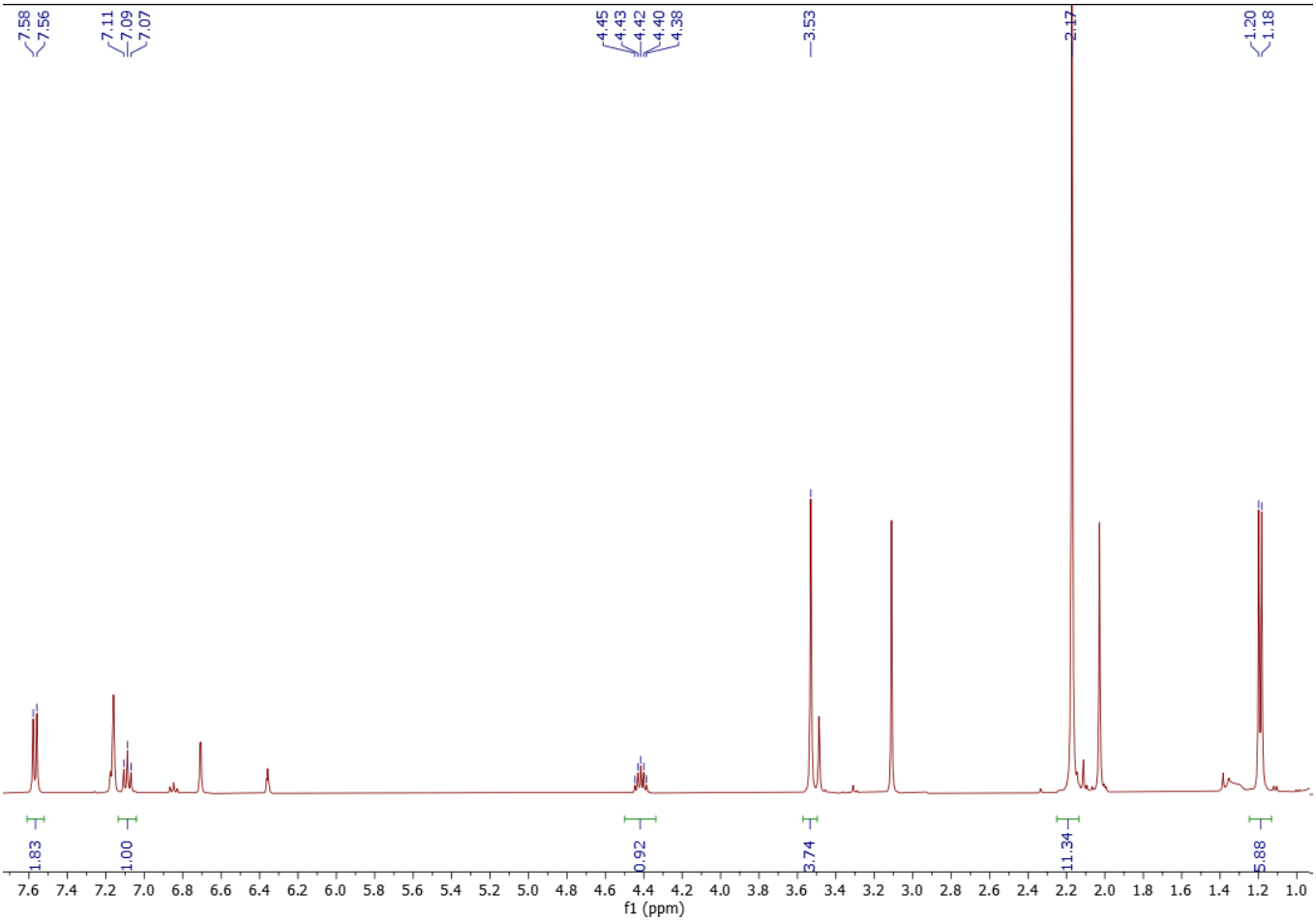

Figure S5. Reaction of (NCN)Ni^{II}Br with *i*-PrOH in air at reflux. ^{1}H NMR C_6D_6, δ 7.57 (2H, d, J_{HH} = *7.6*), δ 7.09 (1H, t, J_{HH} = *7.6*), δ 4.42 (1H, sept, J_{HH} = *6.1*), δ 3.53 (4H, s), δ 2.17 (12H, s), δ 1.9 (6H, d, J_{HH} = *6.1*).

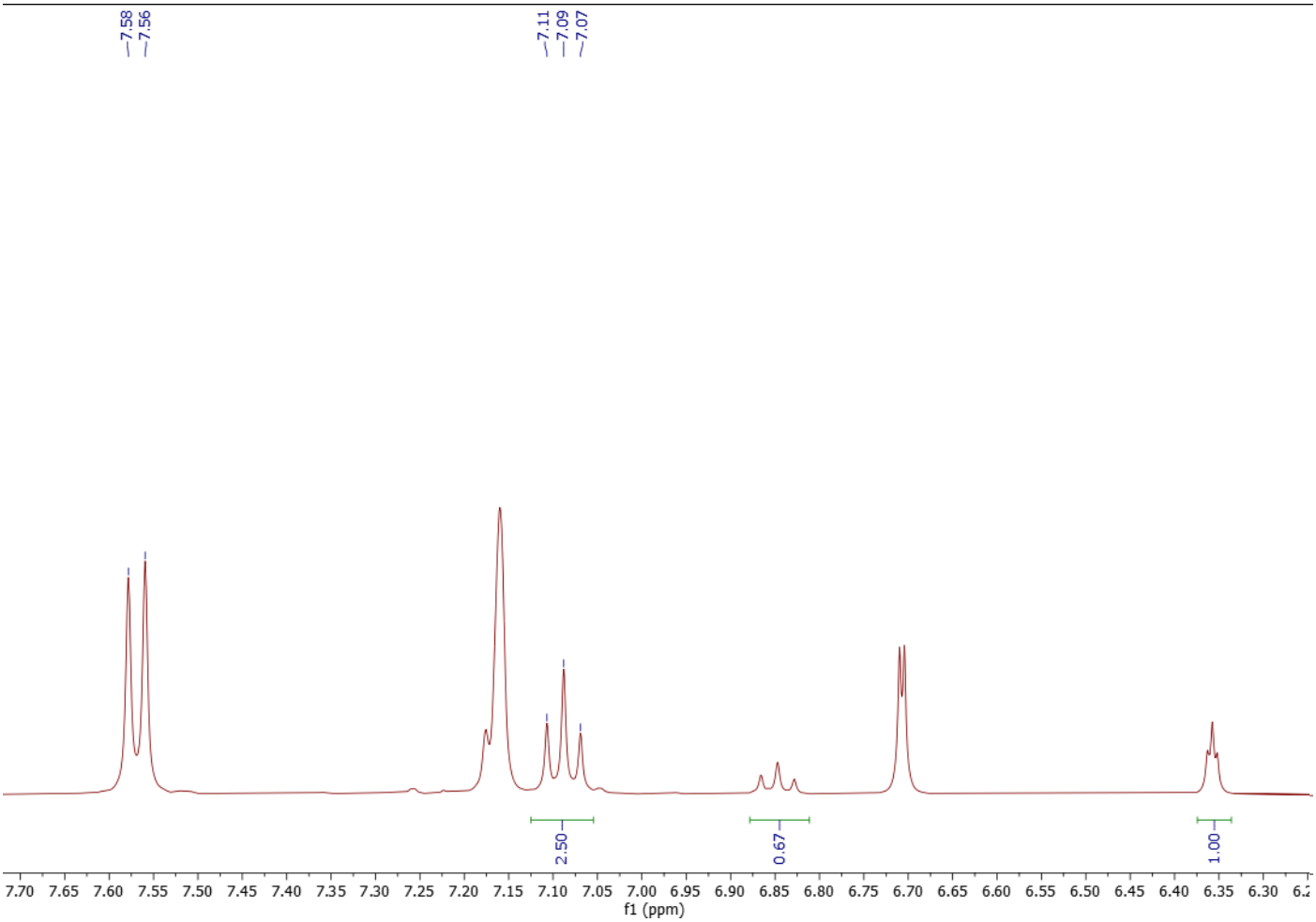

Figure S6. ^{1}H NMR spectrum of reaction of (NCN)Ni^{II}Br with *i*-PrOH in air with internal standard in C_6D_6 (integrated to 1.00). NC(O-i-Pr)N major product and NC(OH)N minor product.

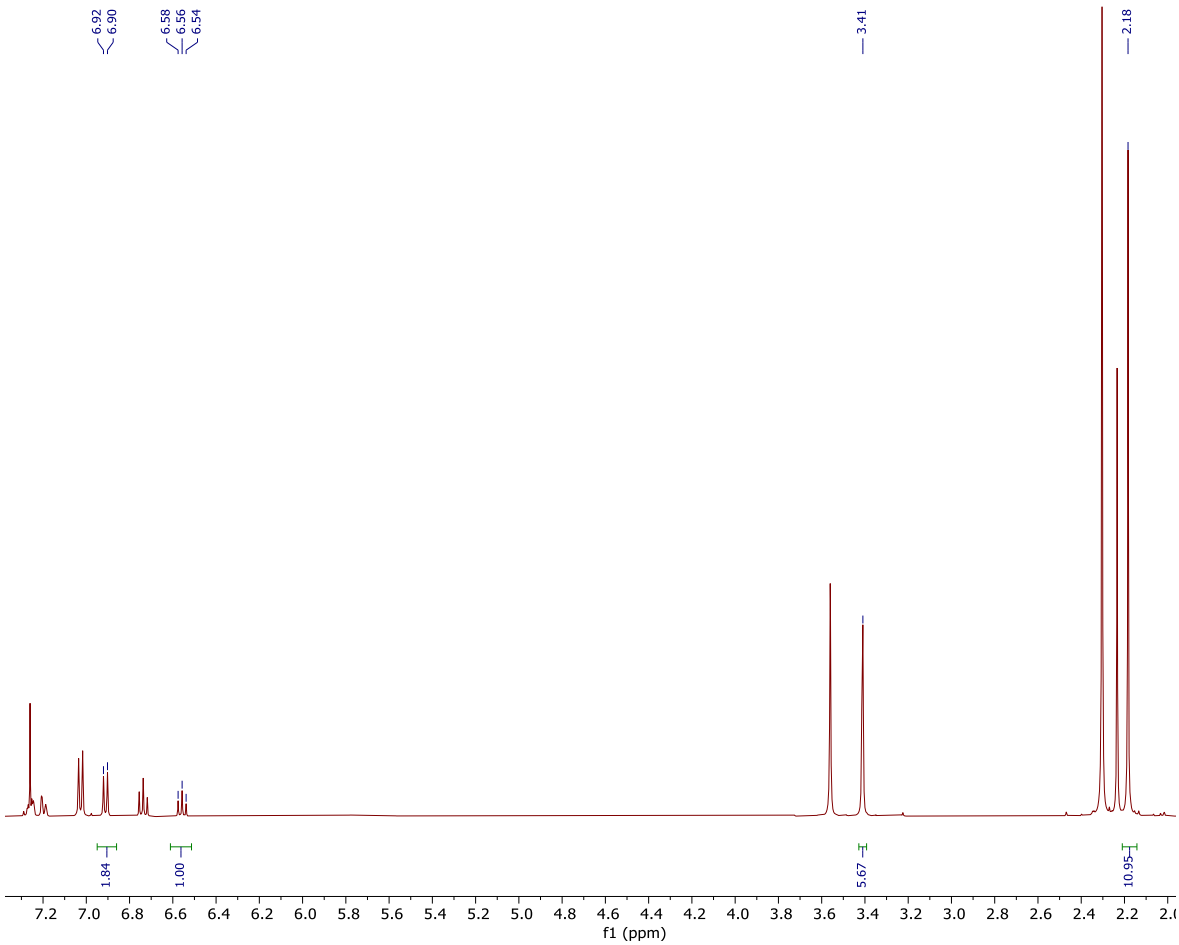

Figure S7. Reaction of (NCN)$Ni^{II}Br$ with NH_4OH in air. ^1H NMR C_6D_6, δ 6.91 (2H, d, J_{HH} = *7.4*), δ 6.56 (1H, t, J_{HH} = *7.4*), δ 3.41 (4H, s), δ 3.53 (4H, s), δ 2.18 (12H, s).

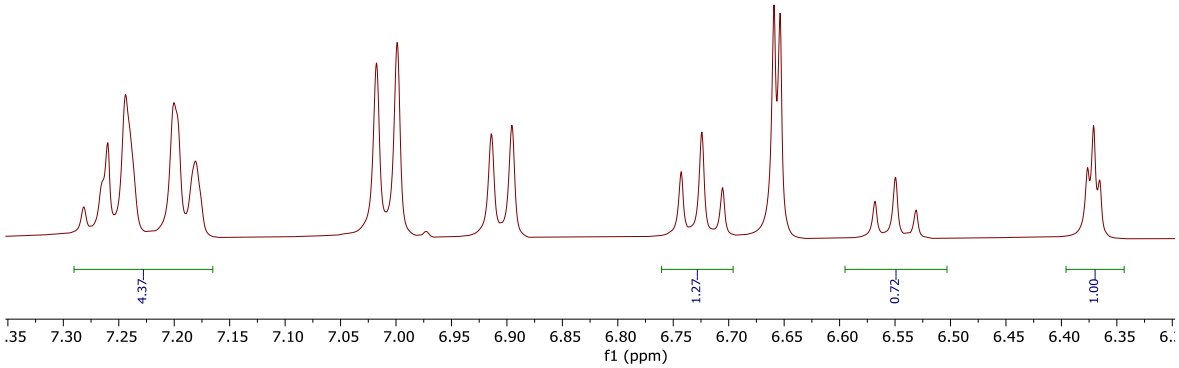

Figure S8. ^{1}H NMR spectrum of reaction of (NCN)$Ni^{II}Br$ with aqueous NH_4OH in air with internal standard in C_6D_6 (integrated to 1.00). $NC(NH_2)N$ minor product, NC(OH)N and proligand major products.

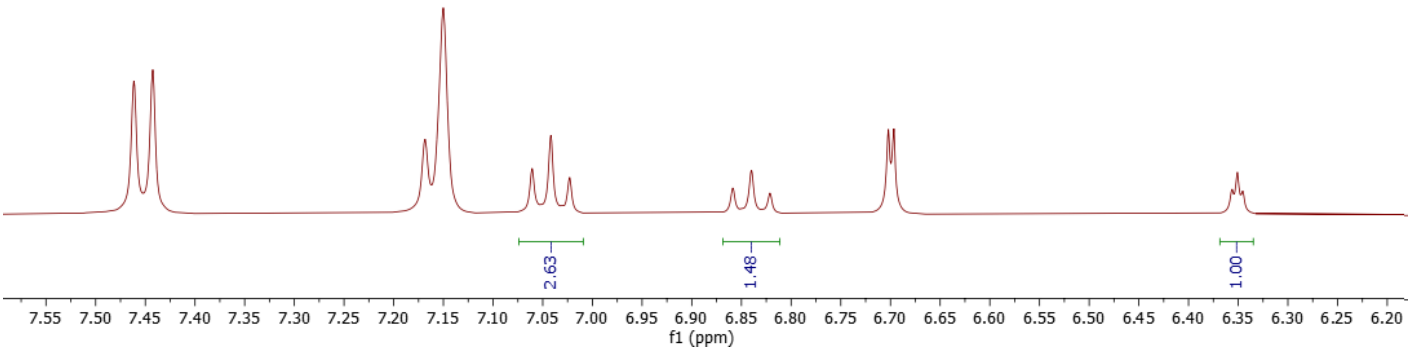

Figure S9. ^{1}H NMR spectrum of reaction of (NCN)$Ni^{II}Br$ with MeOH under O_2 with internal standard in C_6D_6 (integrated to 1.00). NC(OMe)N major product and NC(OH)N minor product.

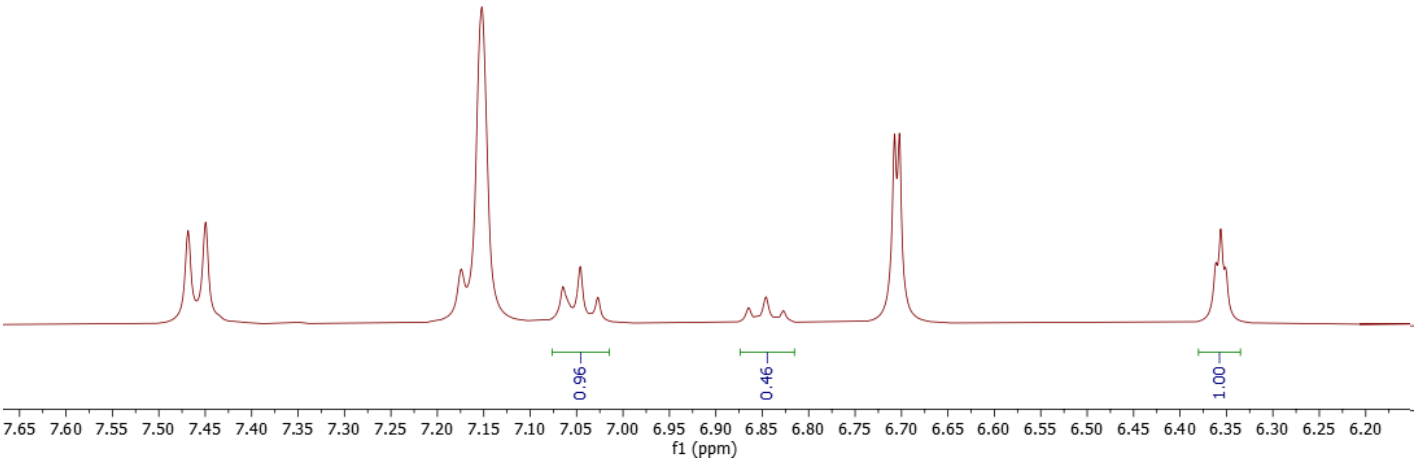

Figure S10. ^{1}H NMR spectrum of reaction of (NCN)$Ni^{II}Br$ with MeOH under O_2 with internal standard in C_6D_6 (integrated to 1.00). NC(OMe)N major product and NC(OH)N minor product.

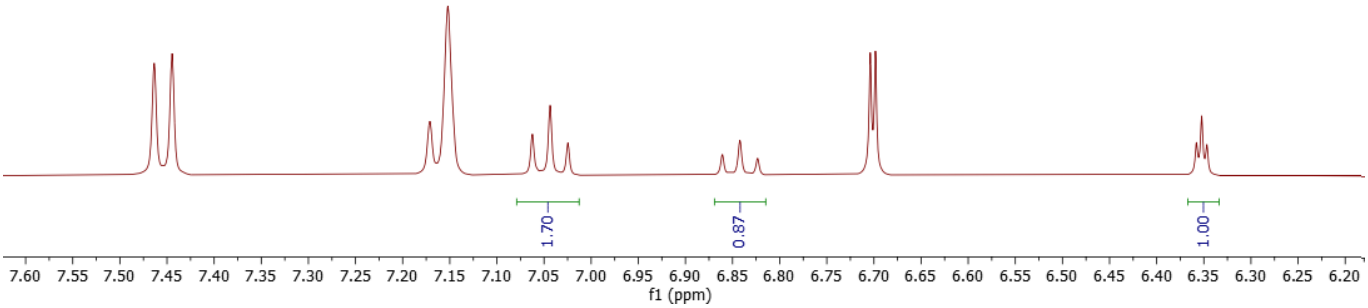

Figure S11. ^{1}H NMR spectrum of reaction of (NCN)$Ni^{II}Br$ with MeOH in air with NEt_3 with internal standard in C_6D_6 (integrated to 1.00). NC(OMe)N major product and NC(OH)N minor product.

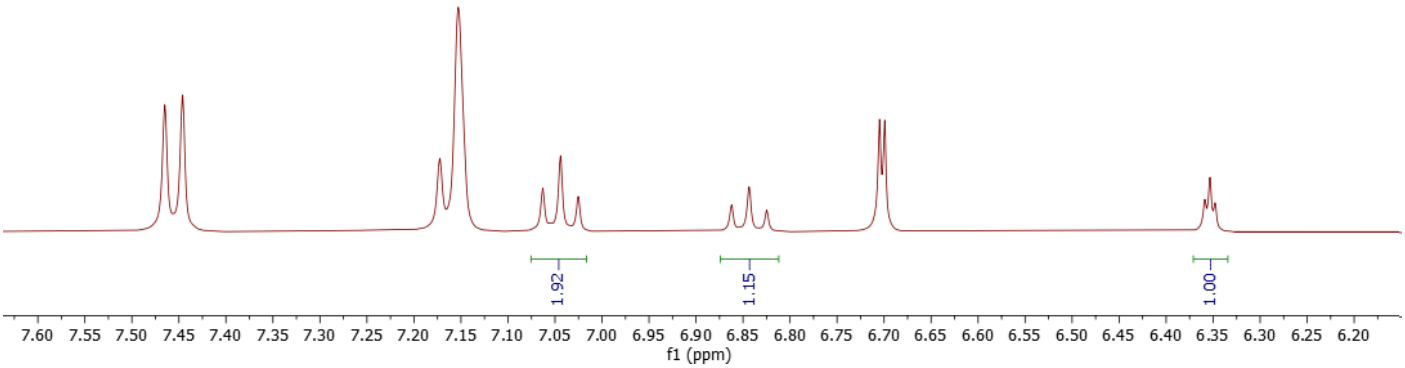

Figure S12. ^{1}H NMR spectrum of reaction of $(NCN)Ni^{II}Br$ with MeOH under O_2 with NEt_3 with internal standard in C_6D_6 (integrated to 1.00). NC(OMe)N major product and NC(OH)N minor product.

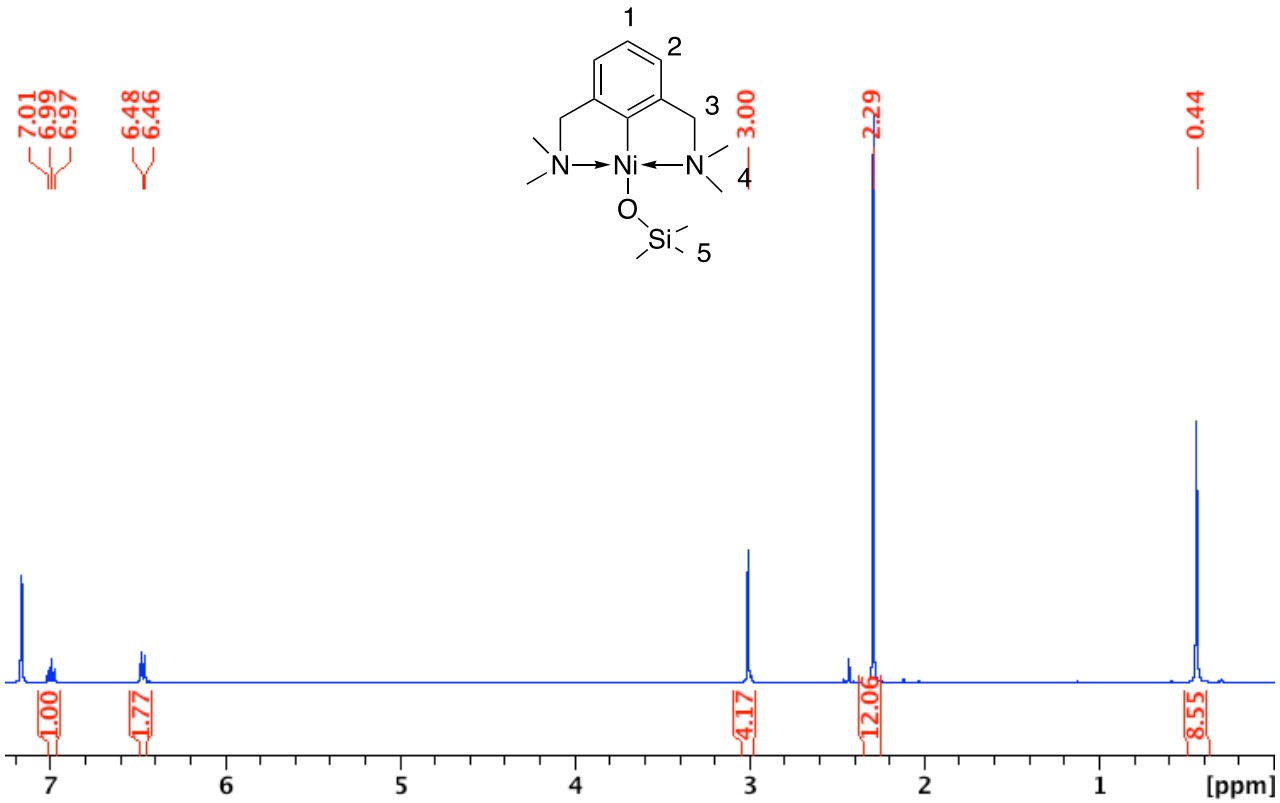

Figure S13. ^{1}H NMR C_6D_6, δ 6.99 (1H, t, J_{HH} = *7.4,* H_1), δ 6.47 (2H, d, J_{HH} = *7.4,* H_2), δ 3.00 (4H, s, H_3), δ 2.29 (12H, s, H_4), δ 0.440 (9H, s, H_5)

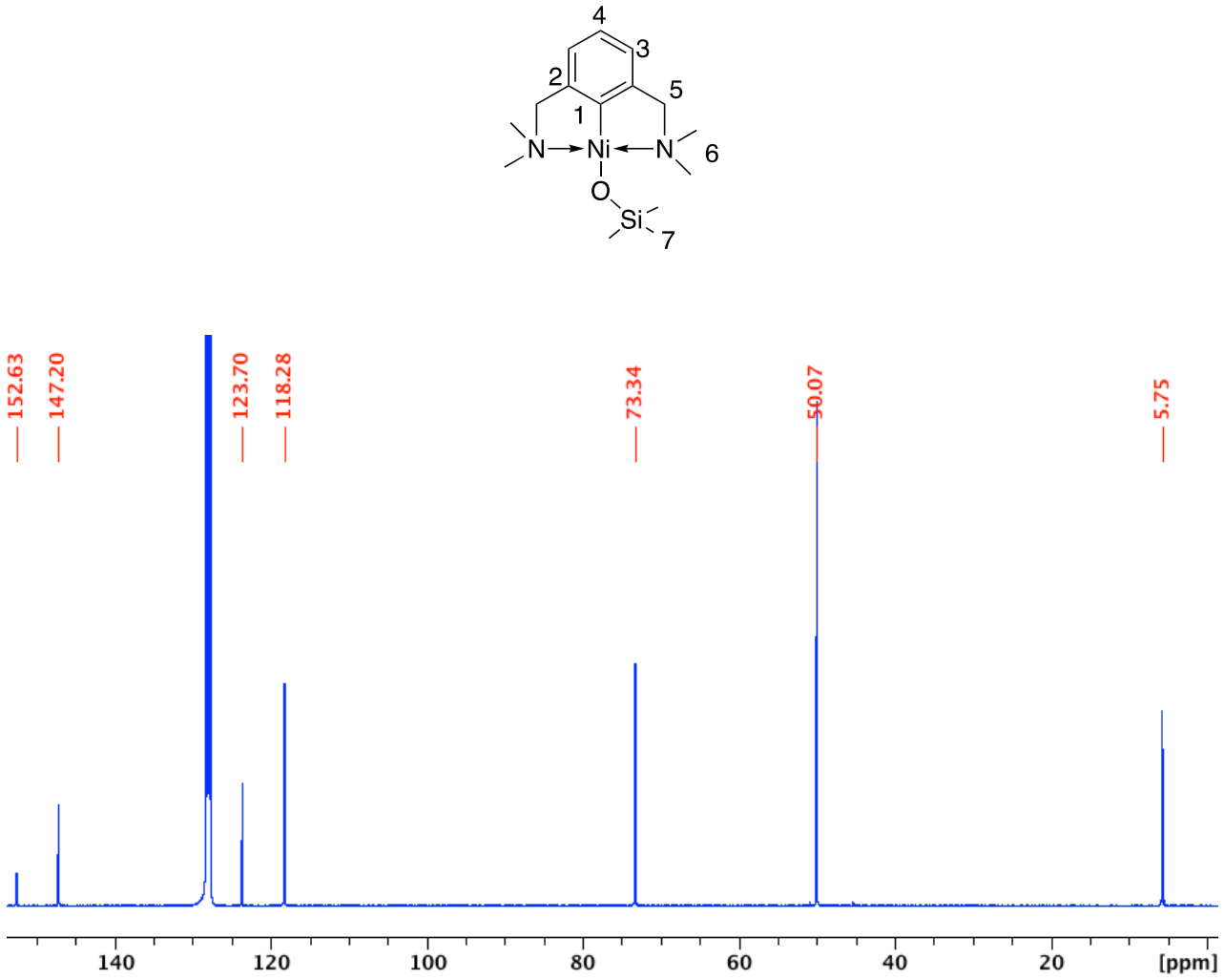

Figure S14. ^{13}C NMR C_6D_6, δ 152.63 (1C, s, C_1), δ 147.20 (2C, s, C_2), δ 123.70 (1C, s C_4), δ 118.28 (2C, s, C_3), δ 73.34 (2C, s, C_5), δ 50.07 (4C, s, C_6), δ 5.75 (3C, s, C_7)

XRD data.

The crystallographic data for all structures were collected a Bruker Venture Metaljet (Ga radiation) via the Bruker APEX III [1] software packages. Cell refinement and data reduction were performed using SAINT.[2] An empirical absorption correction, based on multiple measurements of equivalent reflections, was applied using the program SADABS or TWINABS.[3] Space group was confirmed by the XPREP[4] APEX routine. The structure solved in OLEX[5] using the SHELX[6] suite and refined by full-matrix least squares with SHEXL.[7] Non-hydrogen atoms were refined with S2 anisotropic displacement parameters, whereas hydrogen atoms were set in calculated positions and refined via the riding model, with thermal parameters being 1.5 times that of the carbon bearing the H in question. All Thermal ellipsoid plots were drawn using OLEX.

Table S1. Crystal Data Collection and Refinement Parameters for Complex (NCN)Ni($OSiMe_3$)

Empirical formula	$C_{15}H_{28}N_2NiOSi$	**Crystal size/mm³**	0.24 × 0.2 × 0.12
Formula weight	339.19	**2Θ range for data collection/°**	7.536 to 134.264
***T* (K)**	100	**Index ranges**	-15 ≤ h ≤ 16,
Rad. wavelength (Å)	GaKα (λ = 1.34139)		-19 ≤ k ≤ 19,
Crystal system	monoclinic		-16 ≤ l ≤ 16
space group	Cc	**Reflections collected**	21692
***a* (Å)**	12.3810(7)	**Independent reflections**	3926 [R_{int} = 0.0459, R_{sigma} = 0.0326]
***b* (Å)**	13.9962(8)		
***c* (Å)**	11.9361(7)	**Data/restraints/parameters**	3926/2/191
α (deg)	90	**Goodness-of-fit on F^2**	1.063
β (deg)	121.2275(19)	**Final R indexes [I>=2σ (I)]**	R_1 = 0.0343, wR_2 = 0.0865
γ (deg)	90	**Final R indexes [all data]**	R_1 = 0.0348, wR_2 = 0.0875
Z	4	**Largest diff. peak/hole / e Å⁻³**	0.47/-0.30
***V* (Å³)**	1768.69(18)		
ρ_{calcd} (g cm⁻³)	1.274		
μ (mm⁻¹)	6.394		
θ range (deg)	3.768 – 67.132		
wR2[b] [I > 2σ(I)]	0.1633		

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

Footnotes

[1] Bruker (2012). APEX2 / Bruker (2016) APEX3, Bruker AXS Inc., Madison, WI, USA.
[2] Bruker (2012). "SAINT Integration Software for Single Crystal Data", Bruker AXS Inc., Madison, WI, USA.
[3] (a) Sheldrick, G. M. (1996). SADABS/TWINABS. University of Göttingen, Germany. (b) Bruker (2001). SADABS/TWINABS. Bruker AXS Inc., Madison, Wisconsin, USA.
[4] Bruker (2012). Data Preparation and Reciprocal Space Exploration Program, Bruker AXS Inc., Madison, WI, USA.
[5] A: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. "OLEX2: a complete structure solution, refinement and analysis program". J. Appl. Cryst.2009, 42, 339-341.
[6] Sheldrick, G. M., "SHELXT - Integrated space-group and crystal structure determination", Acta Cryst., 2015, A71, 3-8.
[7] Sheldrick, G. M., Crystal structure refinement with SHELXL, Acta Cryst., 2015, C71, 3-8