Electronic Supporting Information for

Hydrogen-Atom Non-Innocence of a Tridentate [SNS] Pincer Ligand

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Table S1. Data collection and refinement parameters for tricyclohexylphosphine derivatives **1a**, **2a**, and **3a**.

	[SNHS^{cat}]Ni(PPh$_3$) (**1a**)	[SNS^{cat}]Ni(PCy$_3$) [KCrypt] (**2a**)	[SNS$^{sq\bullet}$]Ni(PCy$_3$) (**3a**)
empirical formula	$C_{32}H_{46}NNiPS_2$	$C_{32}H_{45}NNiPS_2$ •K[$C_{18}N_2H_{36}O_6$][C_4H_8O]	$C_{32}H_{45}NNiPS_2$
formula weight [g/mol]	598.50	1085.18	597.49
crystal system	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
T [K]	128(2) K	133(2) K	88(2) K
a [Å]	13.402(2)	10.9764(9)	8.4569(18)
b [Å]	15.360(2)	12.9217(11)	25.523(5)
c [Å]	14.855(2)	22.0785(19)	14.038(3)
α [deg]	90	76.7086(11)	90
β [deg]	97.142(2)	86.4006(11)	99.178(3)
γ [deg]	90	67.6215(11)	90
V [Å^3]	34245	2817.0(4)	5968.9(9)
Z	4	2	4
refl collected	42087	32815	35168
data/restr/param	7375/0/375	13223/0/599	7483/0/336
R_1 [I > 2σ(I)][a]	0.0362	0.0497	0.0403
wR_2(all data)[a]	0.0813	0.1392	0.1031
GOF[a]	0.919	1.029	1.024

[a] $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\ ]^{1/2}$, GOF = S = $[\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$

Table S2. Data collection and refinement parameters for triphenylphosphine derivatives **1b**, **2b**, and **3b**.

	[SNHS^{cat}]Ni(PPh$_3$) (**1b**)	[SNS^{cat}]Ni(PPh$_3$) [KCrypt] (**2b**)	[[SNS$^{sq\bullet}$]Ni(PPh$_3$)]$_2$ (**3b**)
empirical formula	$C_{32}H_{28}NNiPS_2$ •2[C_4H_8O]	$C_{32}H_{27}NNiPS_2$ •K[$C_{18}N_2H_{36}O_6$][CH_3CN]	$C_{64}H_{54}N_2Ni_2P_2S_4$ •2[CH_3CN]
formula weight [g/mol]	724.56	1035.98	1240.80
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
T [K]	128(2) K	88(2) K	88(2) K
a [Å]	13.4137(10)	13.1895(16)	13.4463(12)
b [Å]	20.2277(15)	17.229(2)	22.515(2)
c [Å]	13.6316(10)	23.327(3)	19.8162(18)
α [deg]	90	90	90
β [deg]	104.8655(9)	104.0797(17)	95.7673(11)
γ [deg]	90	90	90
V [Å^3]	3574.8(5)	5141.5(11)	5968.9(9)
Z	4	4	4
refl collected	42087	62909	73363
data/restr/param	8686/0/430	12870/0/607	14980/0/727
R_1 [I > 2σ(I)][a]	0.0357	0.0377	0.0289
wR_2(all data)[a]	0.0980	0.0903	0.0727
GOF[a]	1.018	1.038	1.037

[a] $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\ ]^{1/2}$, GOF = S = $[\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$

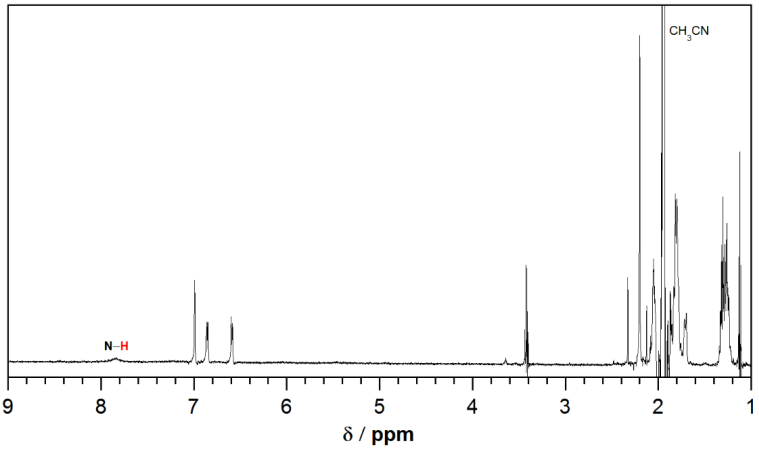


Figure S1. ^{1}H NMR spectra for [[SNHS^{cat}]Ni(PCy$_3$)]$_2$ (**1a**) dissolved in CD$_3$CN.

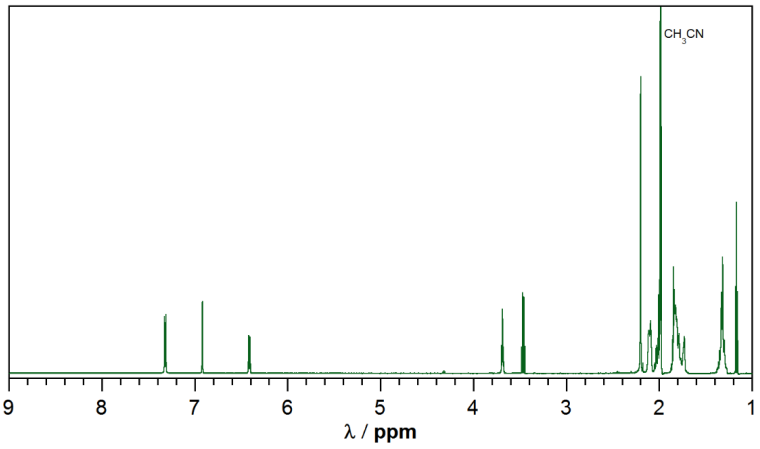


Figure S2. ^{1}H NMR spectra for [SNS^{cat}]Ni(PCy$_3$)][K] (**2a**) dissolved in CD$_3$CN.

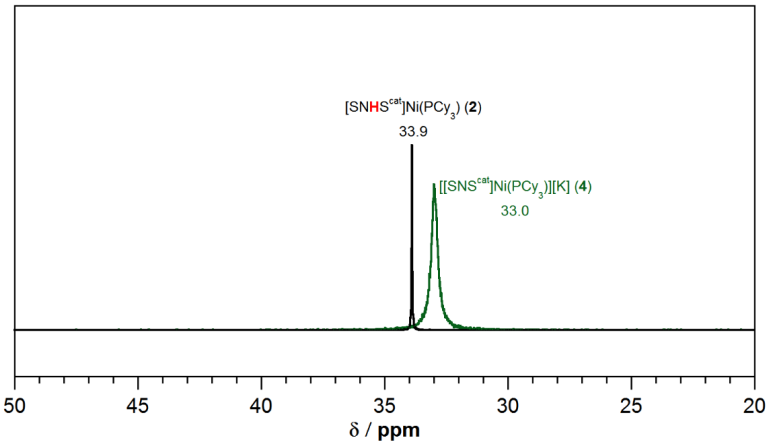


Figure S3. ^{31}P{^{1}H} NMR spectra for complexes **1a** and **2a** dissolved in CD$_3$CN. Signals are displayed as power spectra to eliminate signal-to-noise.

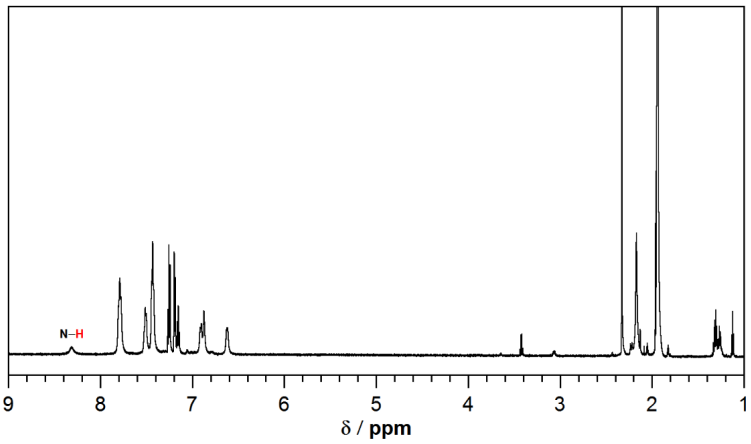


Figure S4. ^{1}H NMR spectra for [SNHS^{cat}]Ni(PPh$_3$) (**1b**) dissolved in CD_3CN.

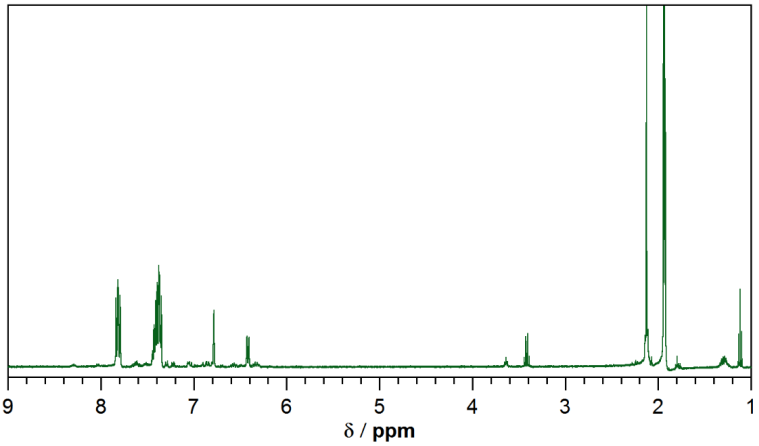


Figure S5. ^{1}H NMR spectra for [[SNS^{cat}]Ni(PPh$_3$)][K] (**2b**) dissolved in CD_3CN.

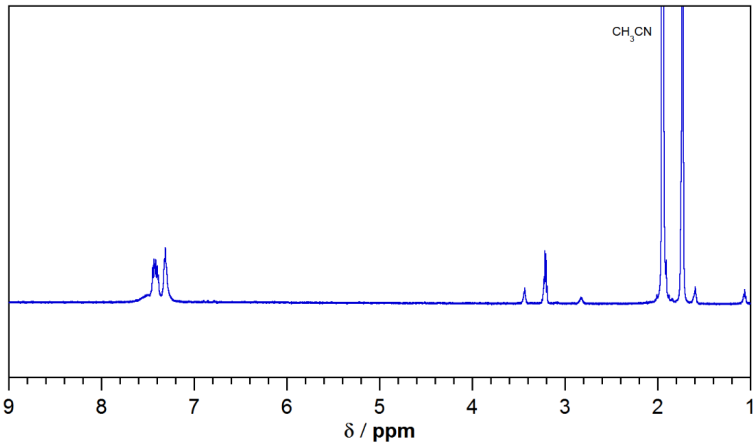


Figure S6. ^{1}H NMR spectra for [[SNS^{sq}]Ni(PPh$_3$)]$_2$ {**3b**}$_2$ dissolved in CD_3CN.

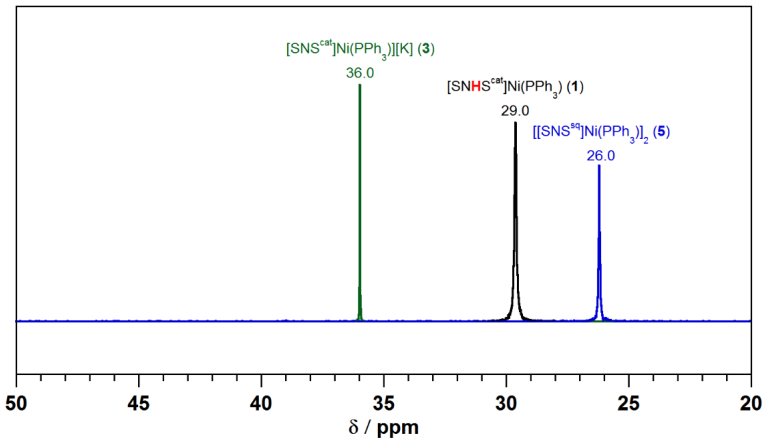


Figure S7. $^{31}P\{^{1}H\}$ NMR spectra for complexes **1b**, **2b**, and $\{\mathbf{3b}\}_2$ dissolved in CD_3CN. Signals are displayed as power spectra to eliminate signal-to-noise.

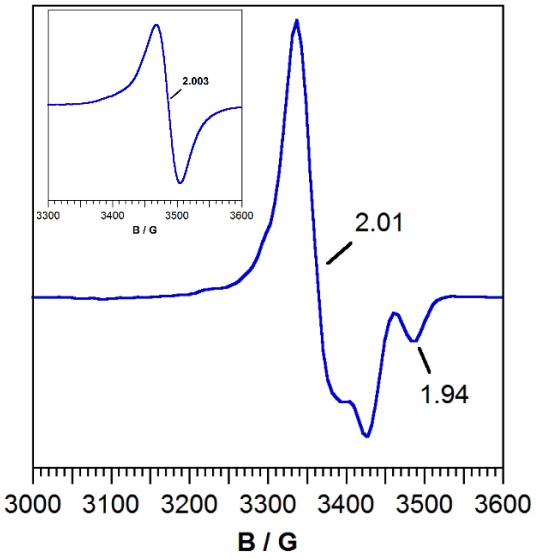
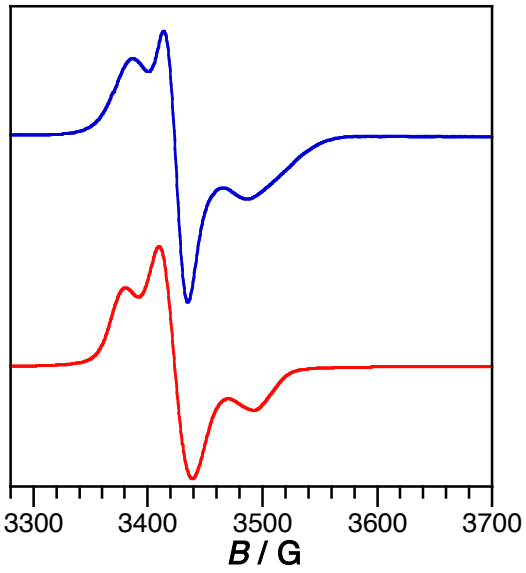


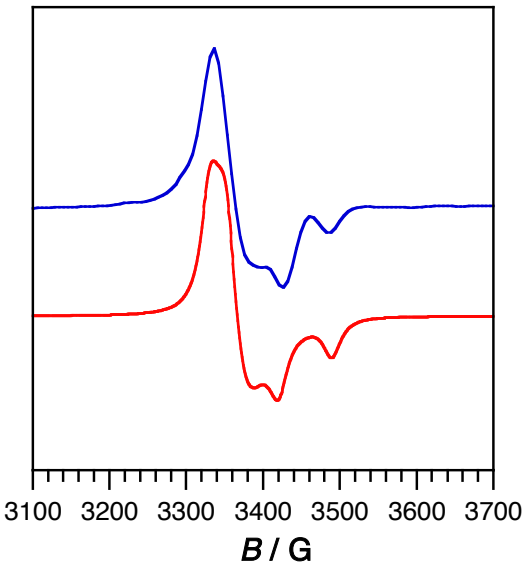
Figure S8. X-Band EPR spectra for $[[SNS^{sq\bullet}]Ni(PPh_3)]_2$,$\{\mathbf{3b}\}_2$, dissolved in benzene at 77 K and (*inset*) 298 K.



Parameters

	g_1	g_2	g_3	
	1.99	2.01	2.03	
^{31}P	177	38	35	MHz
^{1}H(1)	16	0	5	MHz
^{1}H(2)	105	26	0	MHz

Figure S9. X-band EPR spectrum (blue) and simulation (red) of [SNS$^{sq\bullet}$]Ni(PCy$_3$) (**3a**) dissolved in THF at 10 K.



Parameters

	g_1	g_2	g_3	
	1.95	2	2.02	
^{31}P	189	11.85	7.71	MHz
^{1}H	31.24	32.7	16.09	MHz
^{33}S	60.32	17.1	4.12	MHz

Figure S10. X-band EPR spectrum (blue) and simulation (red) of [[SNS$^{sq\bullet}$]Ni(PPh$_3$)]$_2$,{**3b**}$_2$, dissolved in benzene at 77 K.

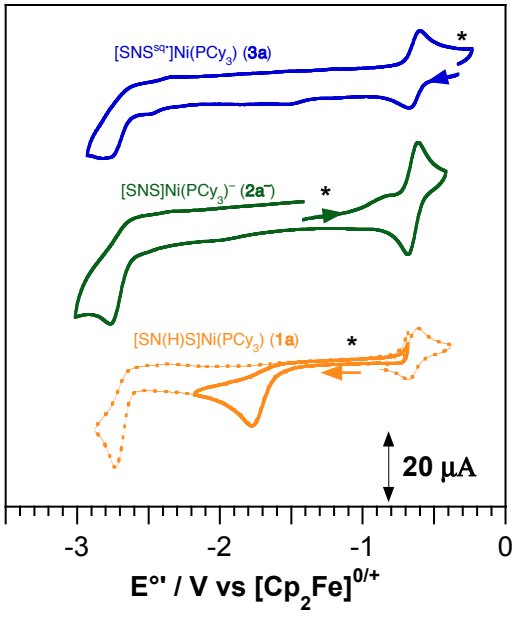


Figure S11. Cyclic voltammograms for [SNS]Ni(PCy$_3$) (**3a**, *top*), [SNS]Ni(PCy$_3$)$^{\ominus}$ ([**2a**]$^{\ominus}$, *middle*) and [SN(H)S]Ni(PCy$_3$) (**1a**, *bottom*) at 200 mV sec^{-1} in MeCN containing 0.1 M [Bu$_4$N][PF$_6$] using a glassy carbon working electrode. Potentials are referenced to the [Cp$_2$Fe]$^{+/0}$ couple.

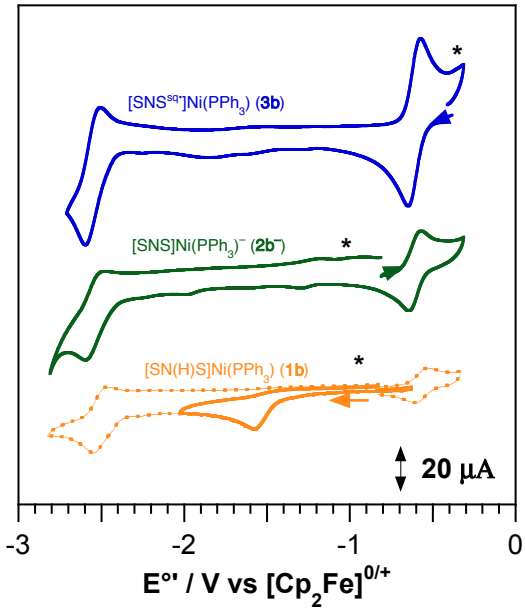


Figure S12. Cyclic voltammograms for [SNS]Ni(PPh$_3$) (**3b**, *top*), [SNS]Ni(PPh$_3$)$^{\ominus}$ ([**2b**]$^{\ominus}$, *middle*) and [SN(H)S]Ni(PPh$_3$) (**1b**, *bottom*) at 200 mV sec^{-1} in MeCN containing 0.1 M [Bu$_4$N][PF$_6$] using a glassy carbon working electrode. Potentials are referenced to the [Cp$_2$Fe]$^{+/0}$ couple.

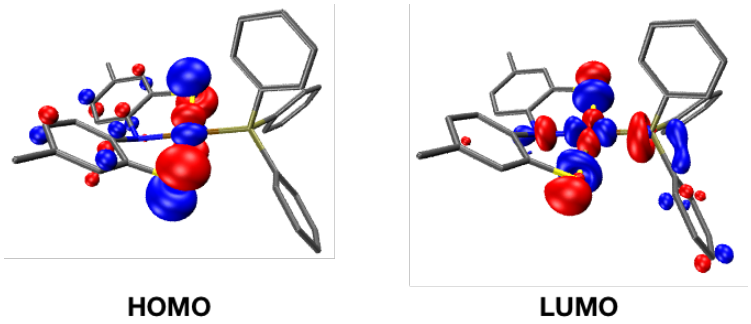


Figure S13. Kohn-Sham frontier molecular orbitals for [SN(H)S]Ni(PPh_3) (**1b**).

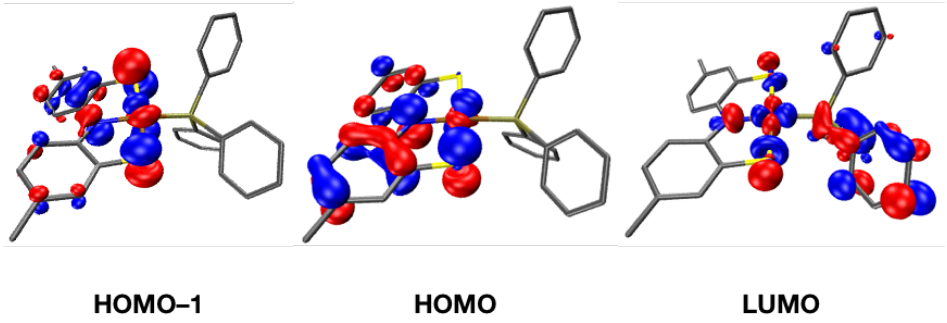


Figure S14. Kohn-Sham frontier molecular orbitals for [SNS]Ni$(PPh_3)^-$ ([**2b**]$^-$).

pK_a Determinations

The pK_a values for **1a** and **1b** were determined by spectrophotometric titration using 2,4,6-trimethylpyridine according to the method reported in reference 42 of the manuscript. Since the base and it's conjugate acid have negligible absorption at wavelengths above 350 nm, their contributions to the UV-vis spectra were neglected in all calculations. For the titration of **1a-b** (MH) with 2,4,6-trimethylpyridine (B), the following equilibrium holds,

$$MH + B \underset{}{\overset{K_{eq}}{\rightleftharpoons}} M^- + BH^+$$

Mass balance allows K_{eq} to be determined from a plot of $[M^-]_t[BH^+]_t/[MH]_t$ vs $[B]_t$. The pK_a of MH is then given by,

$$pK_a\left(MH\right) = pK_a\left(BH\right) - \log K_{eq}$$

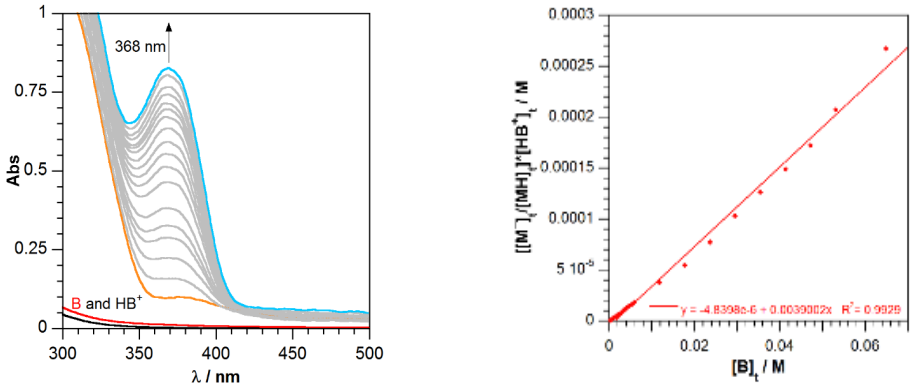


Figure S15. (*left*) Electronic absorption titration of [SNHS^{cat}]Ni(PCy$_3$) (**1a**) with 2,4,6-collidine (bottom two traces correspond to absorption data collected for 2,4,6-collidine (red) and 2,4,6-collidinium tetrafluoroborate (black)); (*right*) K_{eq} determination plot using mass balance formulas.

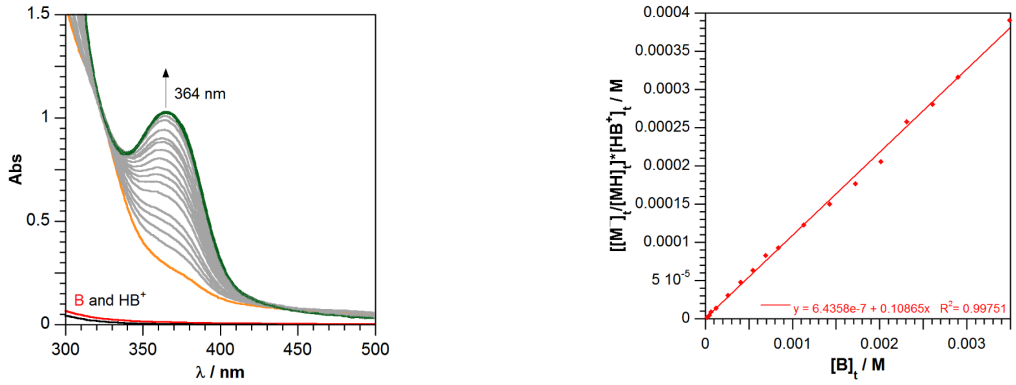


Figure S16. (*left*) Electronic absorption titration of [SNHS^{cat}]Ni(PPh$_3$) (**1b**) with 2,4,6-collidine (bottom two traces correspond to absorption data collected for 2,4,6-collidine (red) and 2,4,6-collidinium tetrafluoroborate (black)); (*right*) K_{eq} determination plot using mass balance formulas.