Supporting Information

Accessing the $Cp^{Ar}Ni(I)$ Synthon: Reactions with N-heterocyclic Carbenes, TEMPO, Sulfur, and Selenium

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The Supporting Information contains

1 Synthesis and characterization of complexes 3 – 6

1.1 NMR and EPR spectra of the reaction mixture of 1 with KC_8:

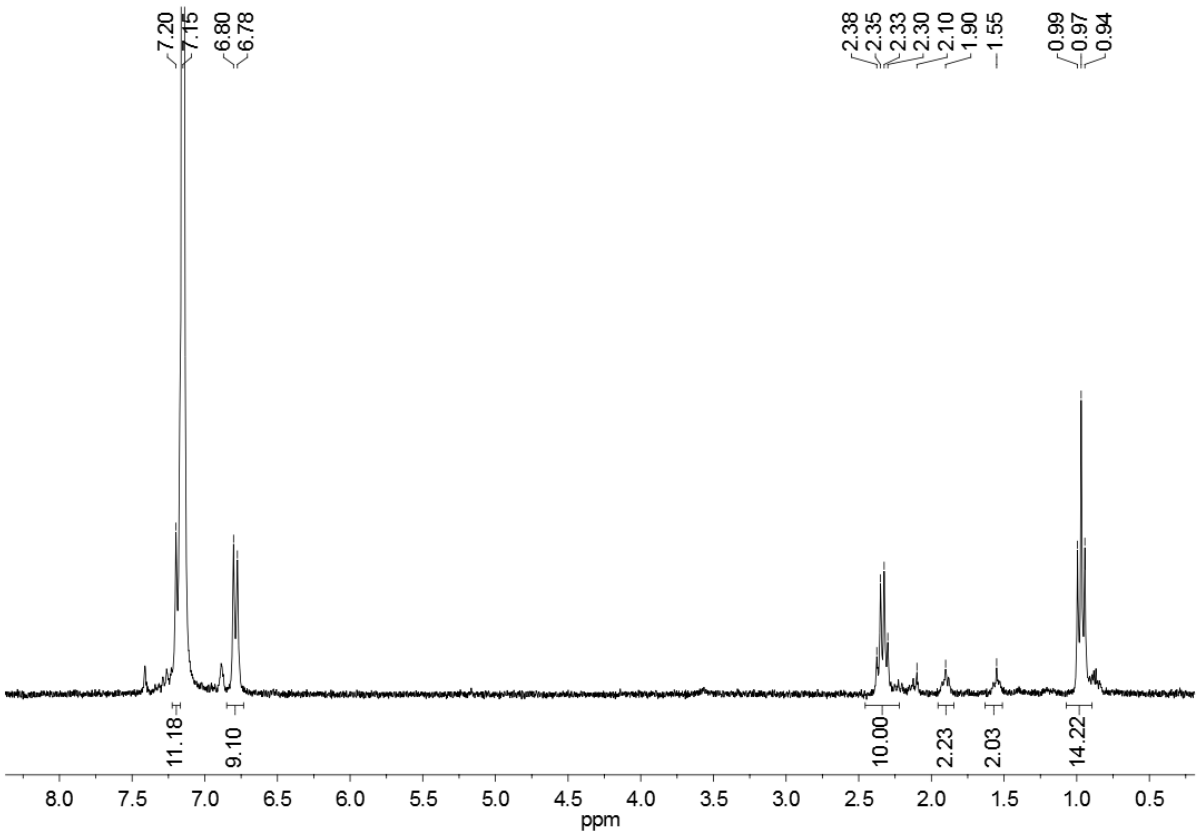

Figure S1. ^{1}H NMR spectrum of the "$Cp^{Ar}Ni$" solution (400.13 MHz, C_6D_6, 300 K) obtained upon reduction of $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (**1**) with KC_8 (two equiv.) in C_6D_6 after two days (after filtration), suggesting conversion of **1** to a diamagnetic product.

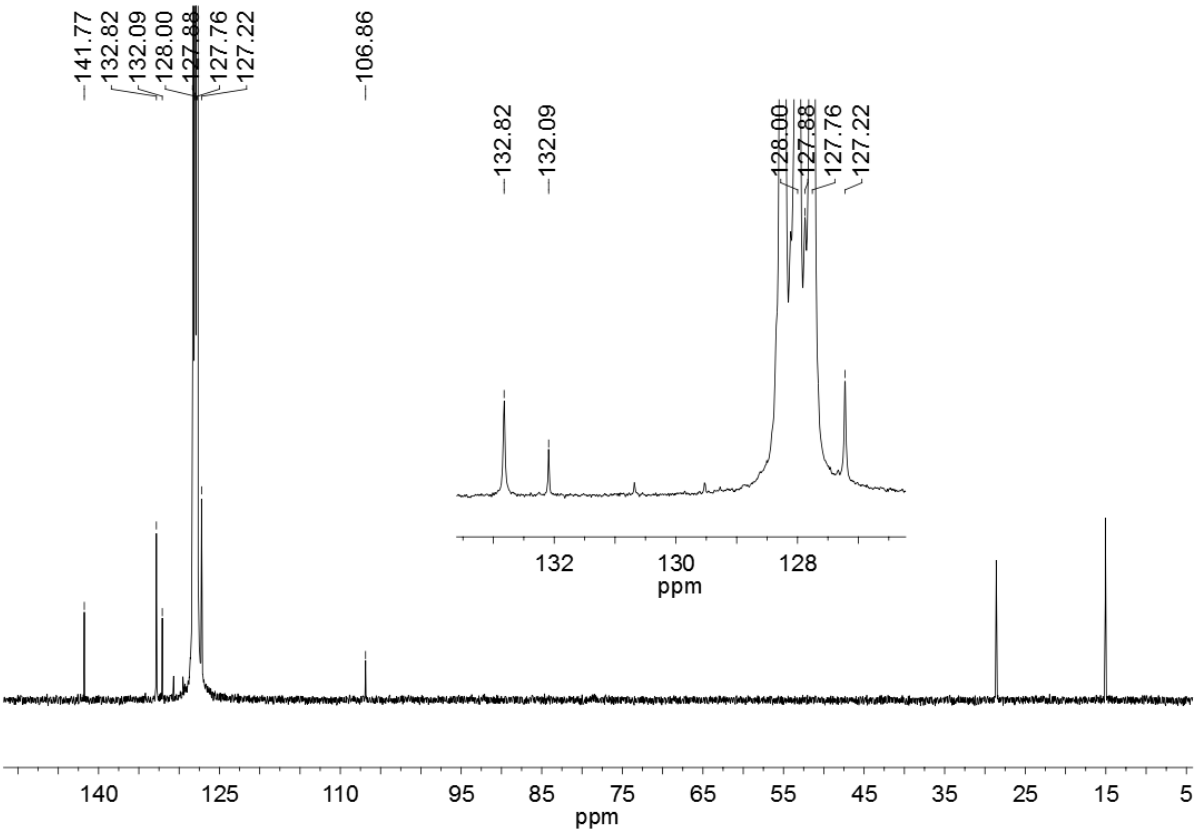

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of the "$Cp^{Ar}Ni$" solution (100.61 MHz, C_6D_6, 300 K) after filtration obtained upon reduction of $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (**1**) with KC_8 (two equiv.) in C_6D_6 after two days (after filtration).

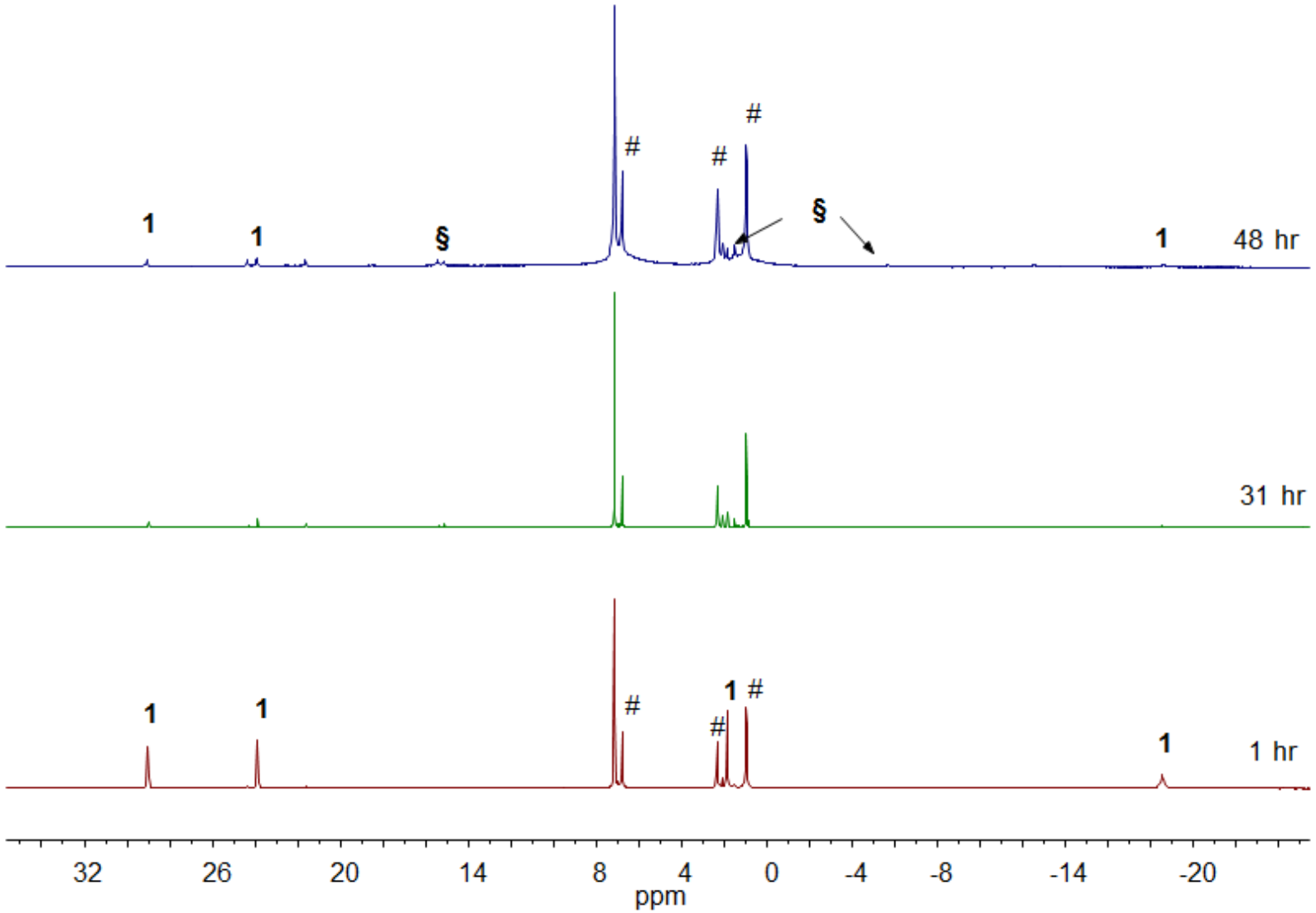

Figure S3. ^{1}H NMR monitoring (400.13 MHz, C_6D_6, 300 K) of the reduction of $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (**1**) with KC_8 (two equivalents) in C_6D_6 over two days, suggesting conversion of **1** to a diamagnetic main product (marked with #); signals marked with § are assigned to $[Cp^{Ar}Ni(\mu\text{-}H)]_2$.

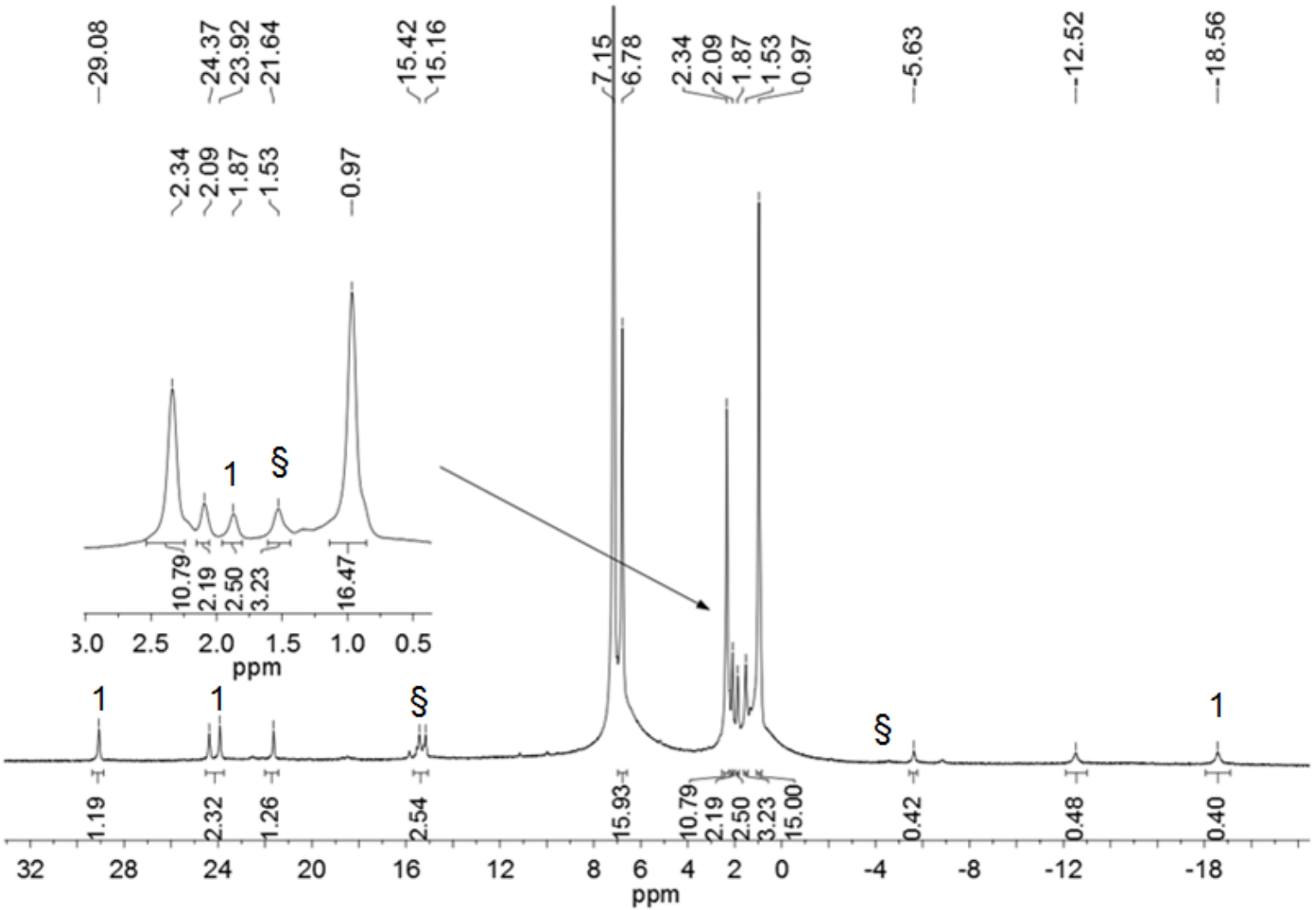

Figure S4. ^{1}H NMR spectrum of the "$Cp^{Ar}Ni$" solution (400.13 MHz, C_6D_6, 300 K) obtained upon reduction of $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (**1**) with KC_8 (two equivalents) in C_6D_6 after two days (without filtration of the NMR sample); broadening of the signals is presumably due to the presence of graphite; signals marked with § are assigned to $[Cp^{Ar}Ni(\mu\text{-}H)]_2$.

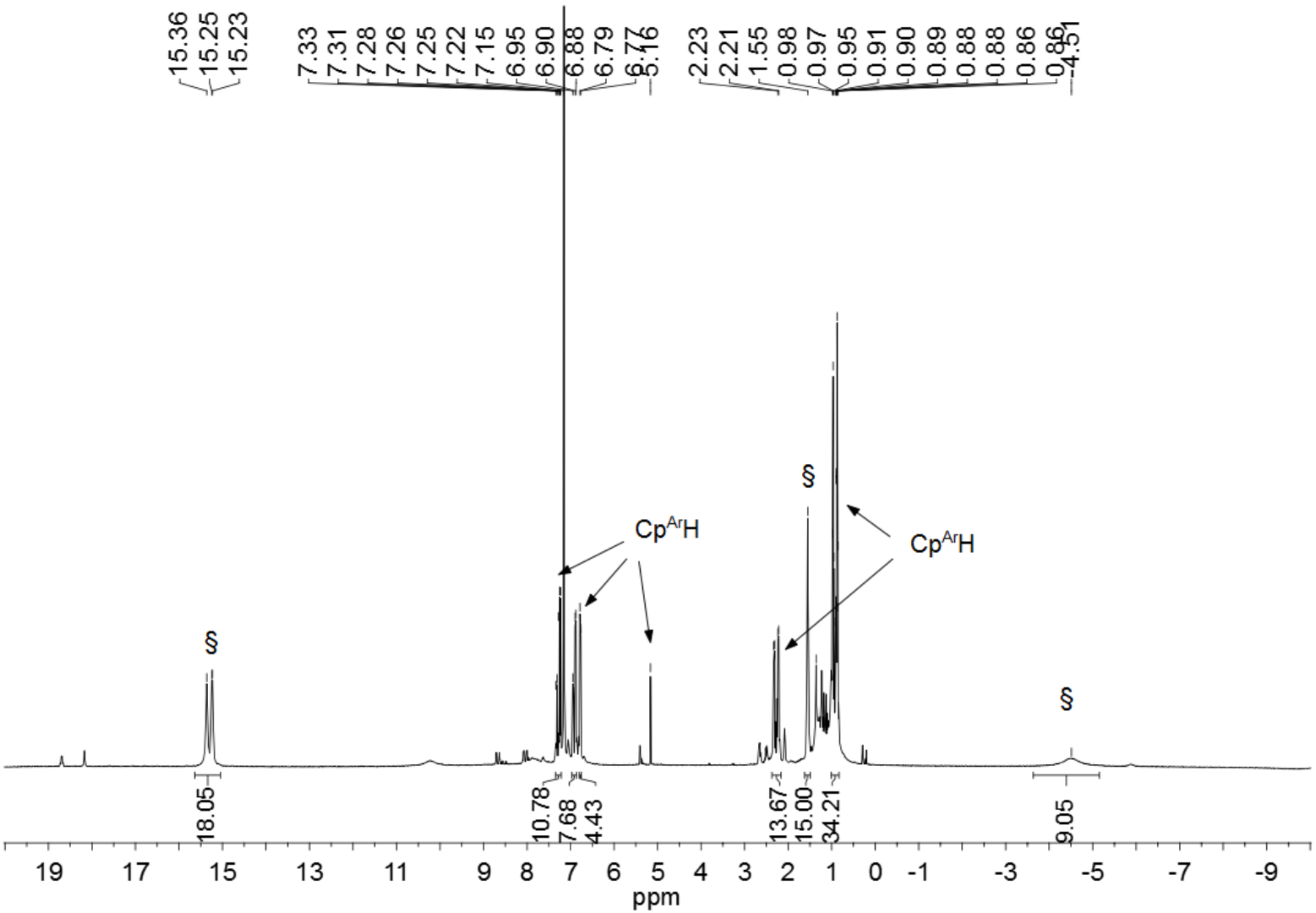

Figure S5. ^{1}H NMR spectrum (400.13 MHz, C_6D_6, 300 K) of the reduction of $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (**1**) with Na/Hg (two equivalents) in THF after three days. Signals marked with § are assigned to $[Cp^{Ar}Ni(\mu\text{-}H)]_2$ (see Figure S7); $Cp^{Ar}H$ represents $C_5(C_6H_4\text{-}4\text{-}Et)_5H$.

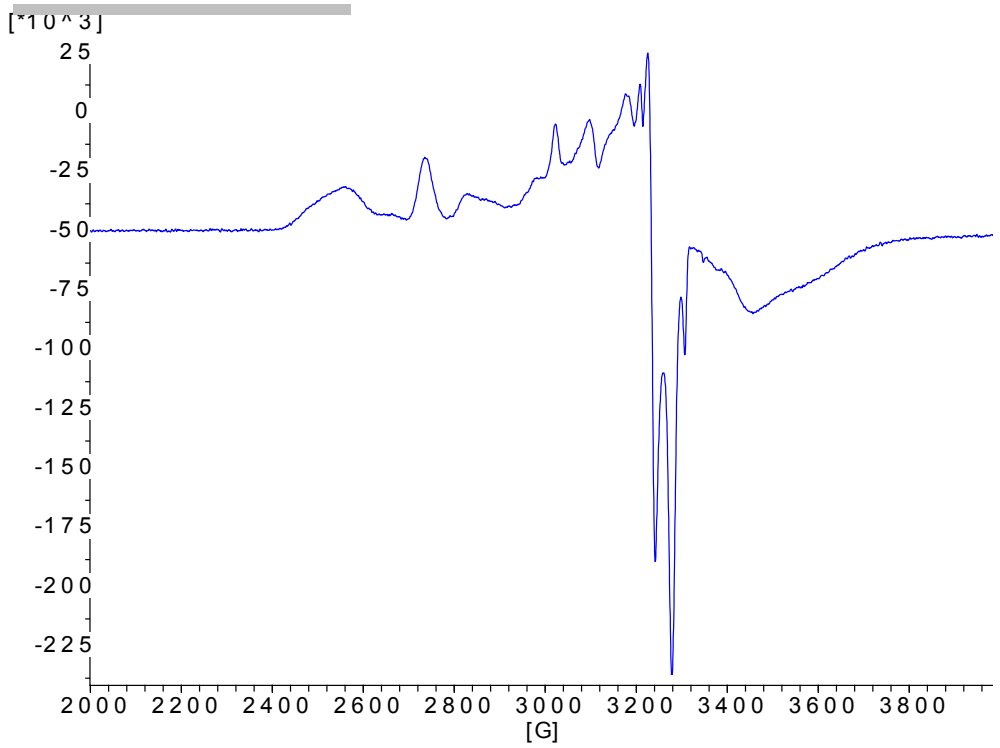

Figure S6. EPR spectrum of the reduction $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (**1**) with KC_8 (two equiv.) obtained after stirring the reaction mixture in toluene for two days; a mixture of paramagnetic species is observed.

1.2 Synthesis and ^{1}H NMR spectrum of $[Cp^{Ar}Ni(\mu\text{-}H)]_2$.

A solid mixture of $[Cp^{Ar}Ni(\mu\text{-}Br)]_2$ (100 mg, 0.069 mmol) and NaH (12 mg, 0.50 mmol) was suspended in THF (10 mL) and stirred for 24 hours. The color of the turbid solution turned from brown to brownish red. The turbid solution was filtered. The filtrate was evaporated completely to a red-brown residue, which was extracted with hot *n*-hexane (10 mL, 65 °C). The purple extract was stored at – 30 °C for crystallization. Red-purple crystals of $[Cp^{Ar}Ni(\mu\text{-}H)]_2$ suitable for X-ray crystallography were obtained after two days. Yield: 13 mg (0.010 mmol, 15%). ^{1}H NMR (400.13 MHz, C_6D_6, 300 K) −4.51 (s vbr, 20H, 10 × *o*/*m*-C*H*), 1.55 (vt, 30H, 10 × CH_3), 15.24 (m br, 20H, 10 × CH_2), 15.36 (s br, 20H, 10 × *o*/*m*-C*H*). The hydride signal was not observed in the range +100 to −100 ppm.

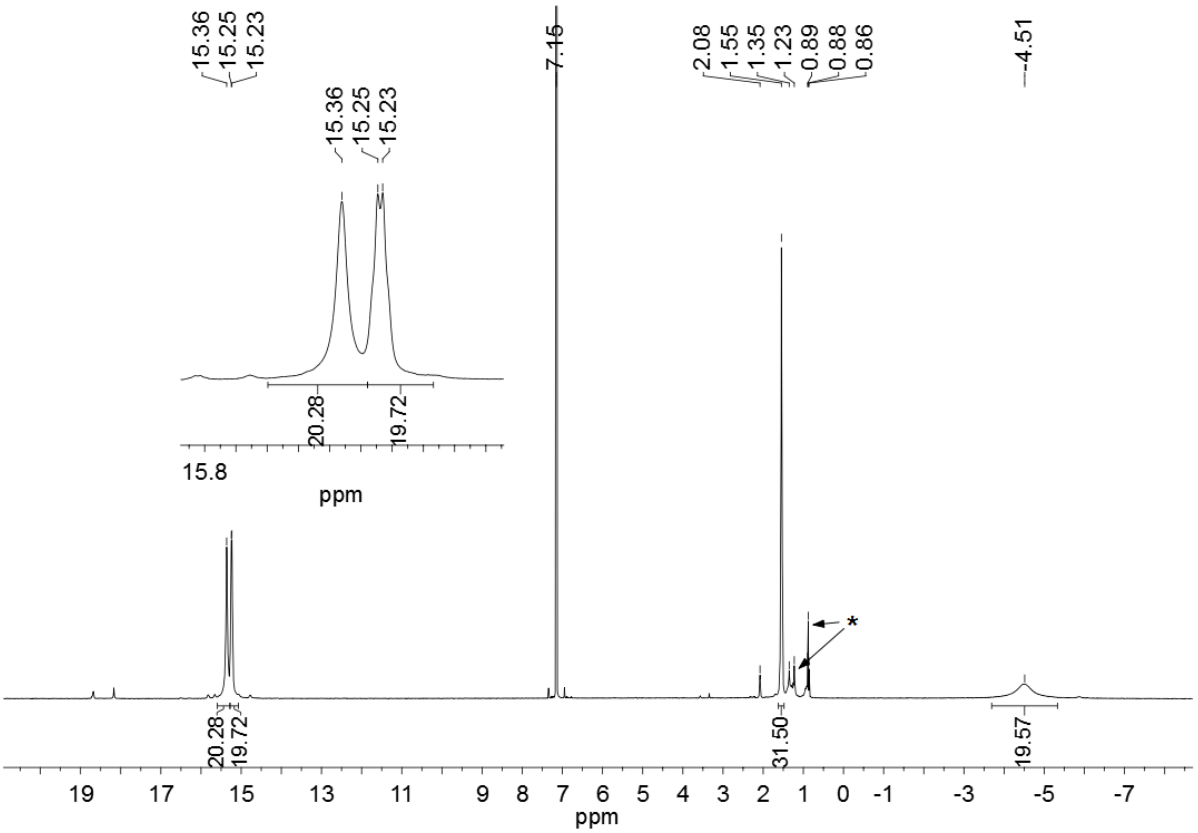

Figure S7. ^{1}H NMR spectrum of $[Cp^{Ar}Ni(\mu\text{-}H)]_2$ (400.13 MHz, C_6D_6, 300 K); * denotes signals of *n*-hexane.

1.3 NMR spectra of [Cp^{Ar}Ni(TEMPO)] (3).

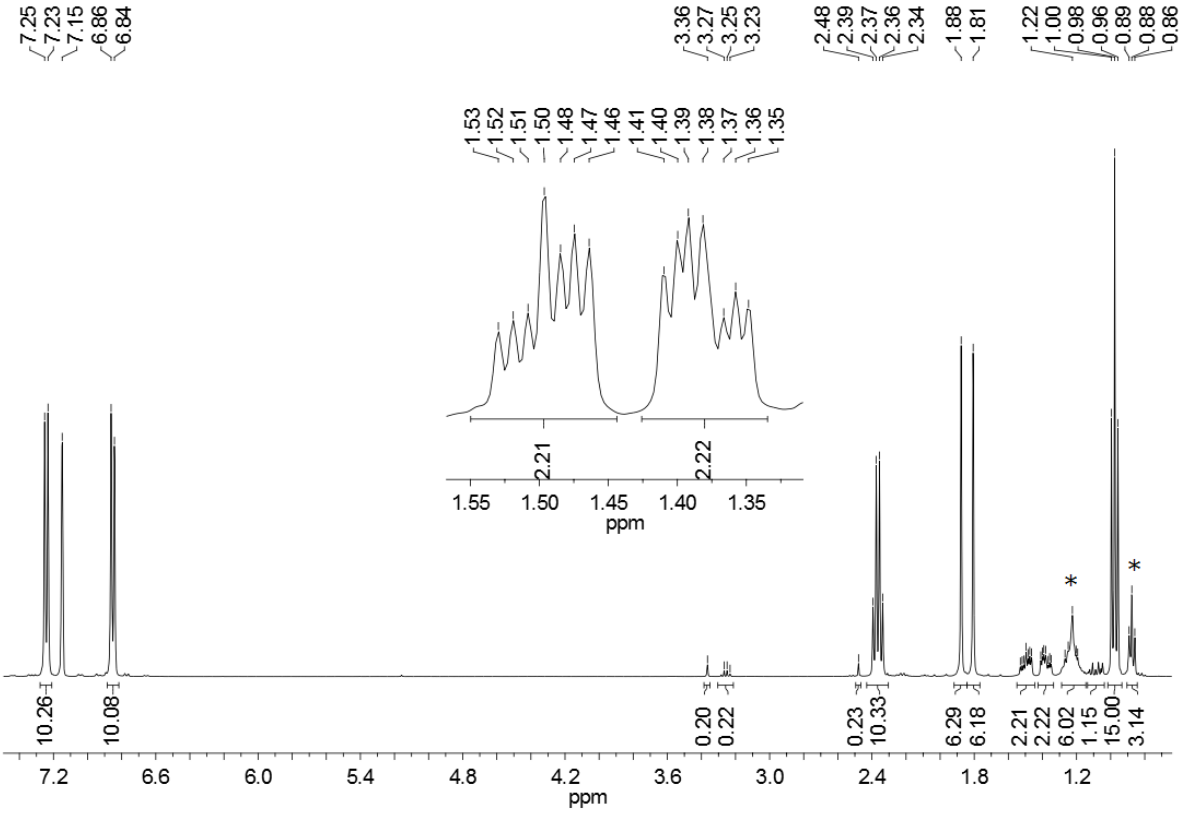

Figure S8. ^{1}H NMR spectrum of complex **3** (400.13 MHz, C_6D_6, 300 K); * denotes signals of *n*-hexane solvent.

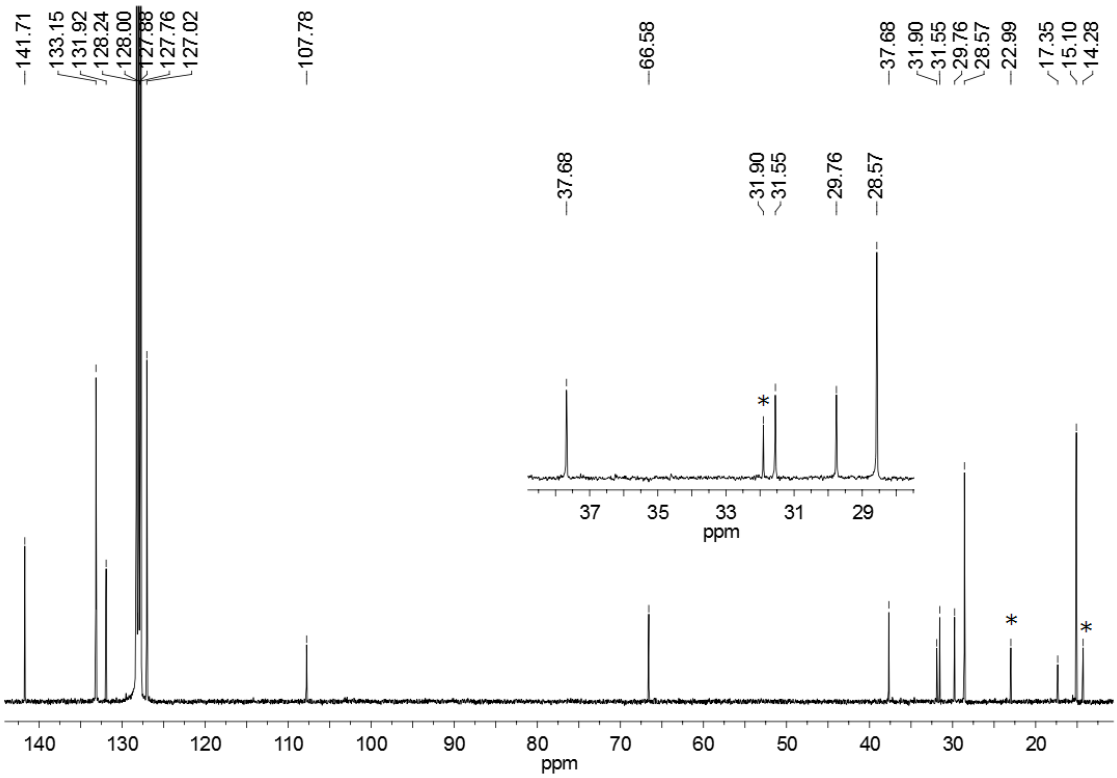

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3** (100.61 MHz, C_6D_6, 300 K). * denotes the signals of *n*-hexane.

1.4 ^{1}H NMR spectrum of [Cp^{Ar}Ni(IPr)] (4a).

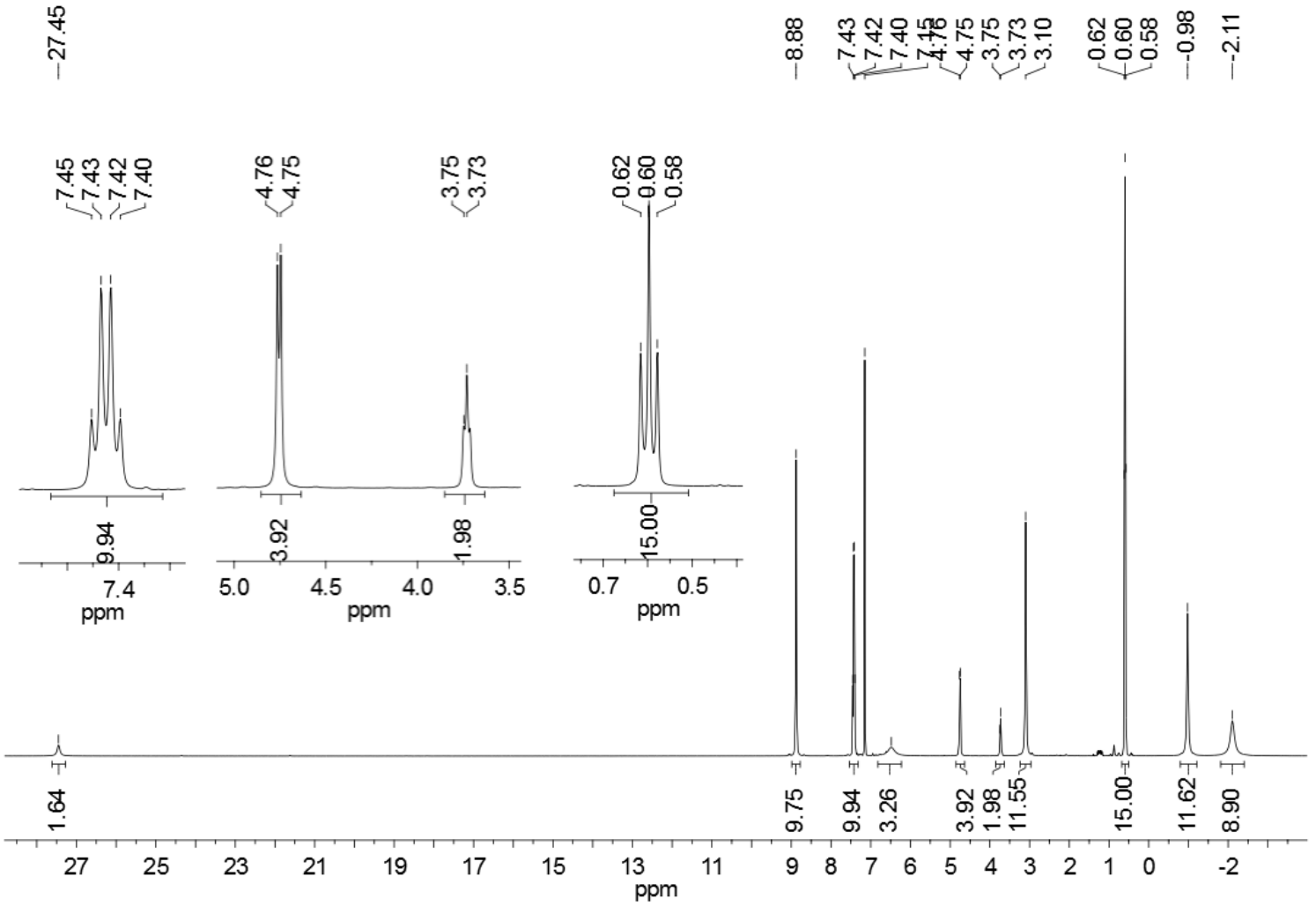

Figure S10. ^{1}H NMR spectrum of **4a** (400.13 MHz, C_6D_6, 300 K).

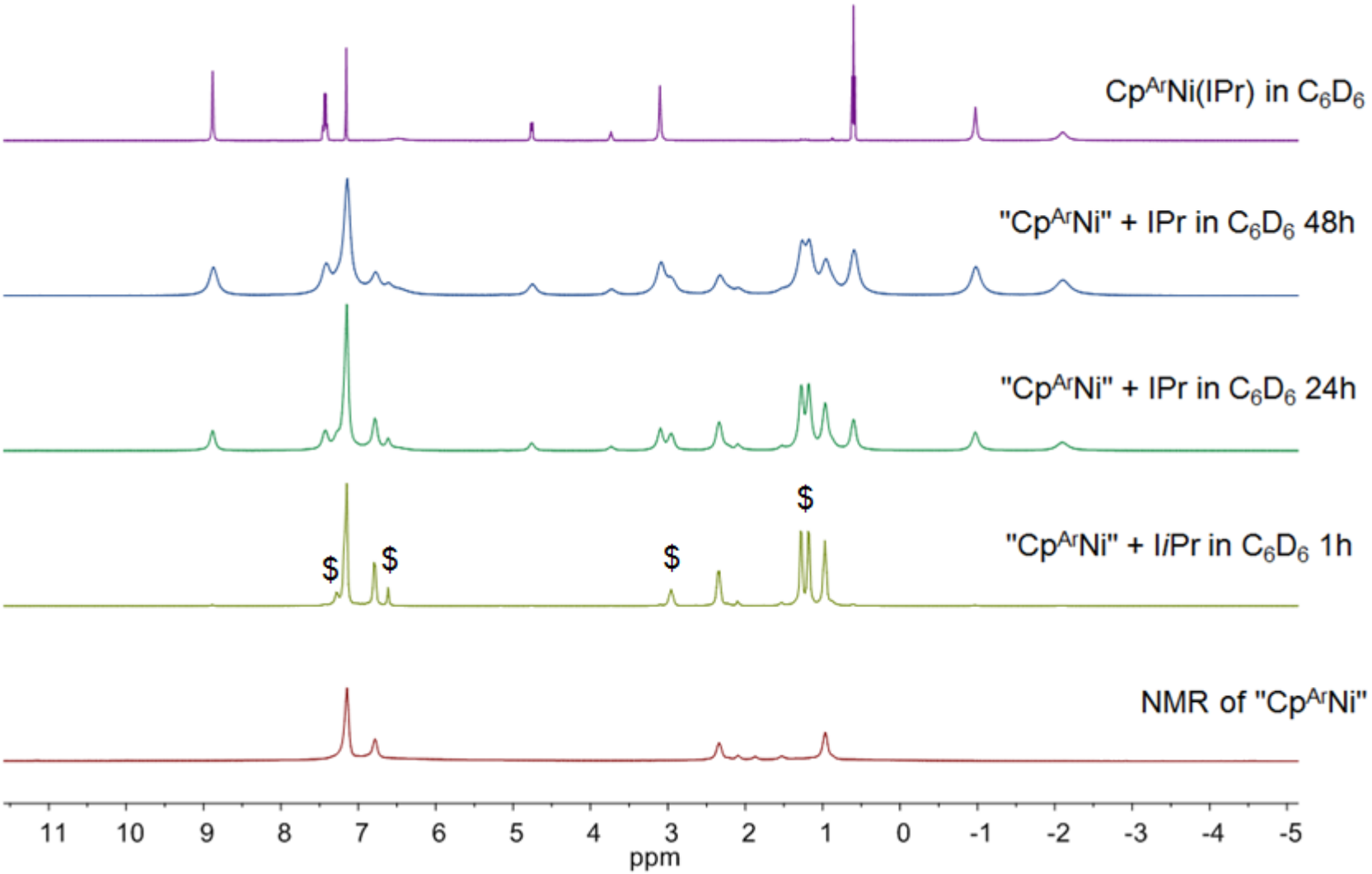

Figure S11. ^{1}H NMR monitoring (400.13 MHz, C_6D_6, 300 K) of the reaction of "$Cp^{Ar}Ni$" with one equivalent of IPr in C_6D_6 over two days. This experiment suggests the selective conversion of "$Cp^{Ar}Ni$" to [$Cp^{Ar}Ni$(IPr)] (**4a**). Signals marked with $ are from the free IPr carbene.

1.5 ^{1}H NMR spectrum of [Cp^{Ar}Ni(I*i*Pr$_2$Me$_2$)] (4b).

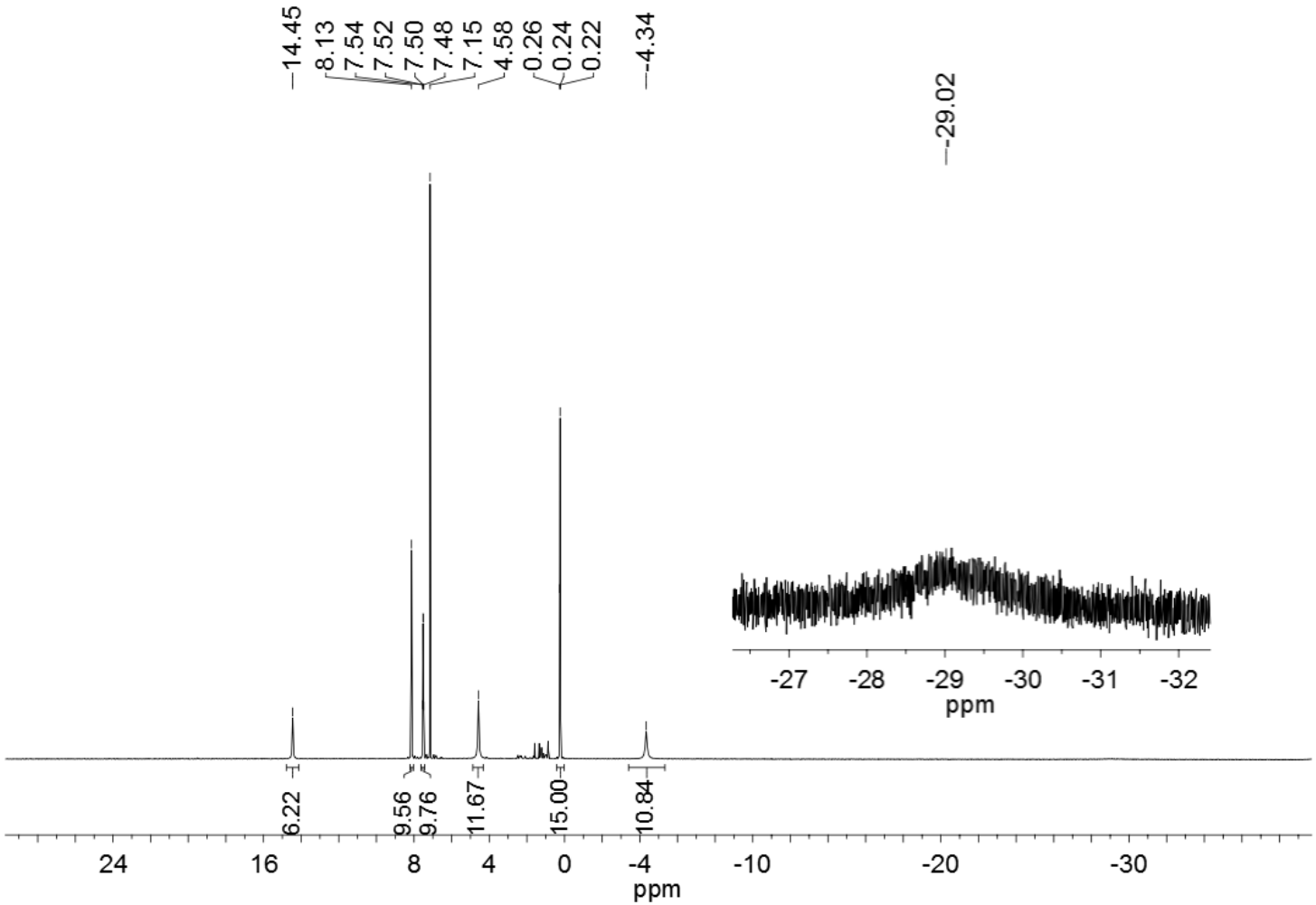

Figure S12. ^{1}H NMR spectrum of **4b** (400.13 MHz, C_6D_6, 300 K).

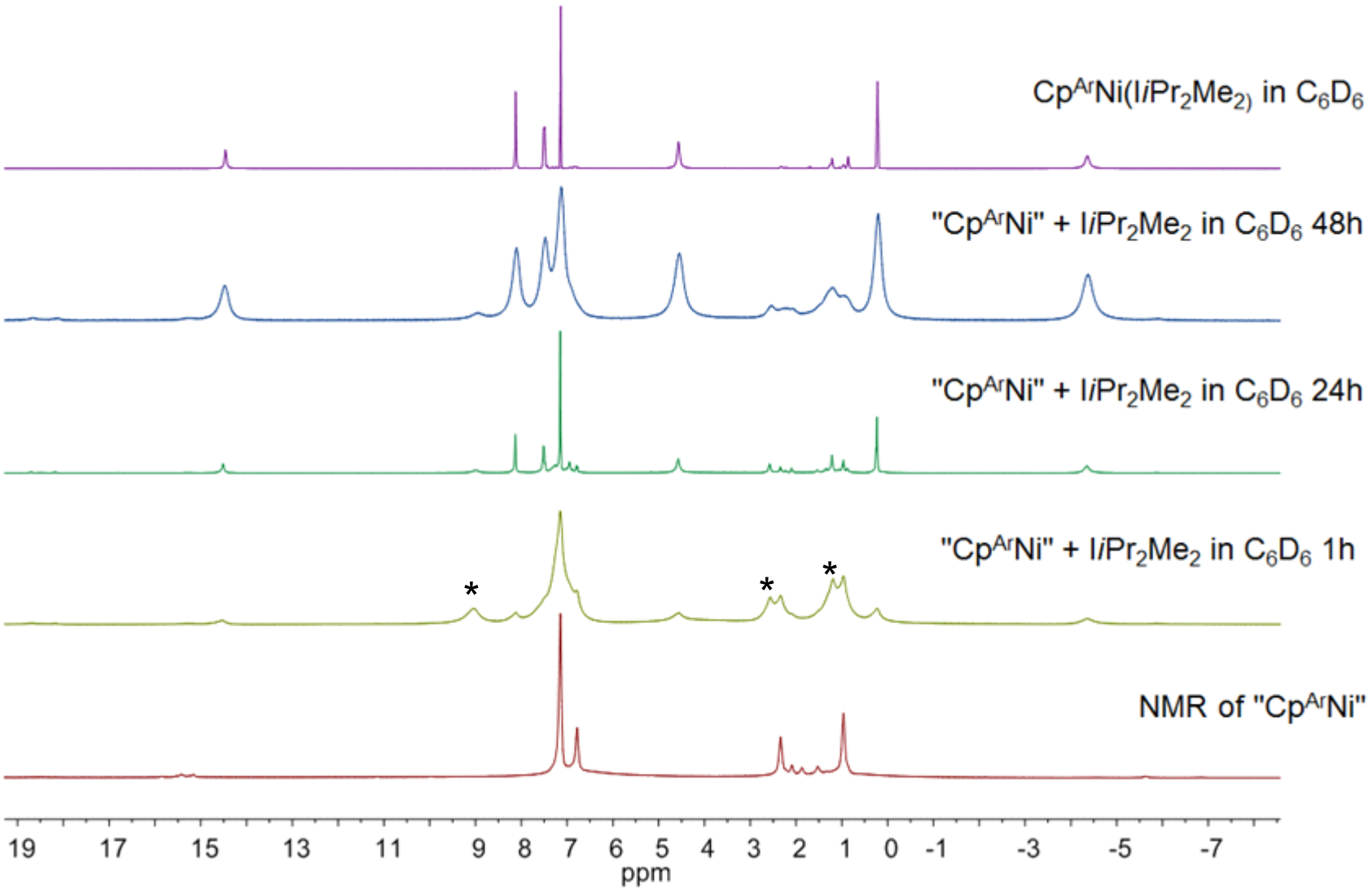

Figure S13. ^{1}H NMR monitoring (400.13 MHz, C_6D_6, 300 K) for the reaction of of "$Cp^{Ar}Ni$" synthon with one equivalent of I*i*Pr$_2$Me$_2$ carbene in C_6D_6 over two days, suggesting selective conversion of "$Cp^{Ar}Ni$" to [$Cp^{Ar}Ni$(I*i*Pr$_2$Me$_2$)] **(4b)** via an unknown intermediate (marked with *).

1.6 ^{1}H NMR spectrum of [(Cp^{Ar}Ni)$_2$(μ-S$_6$)] (5).

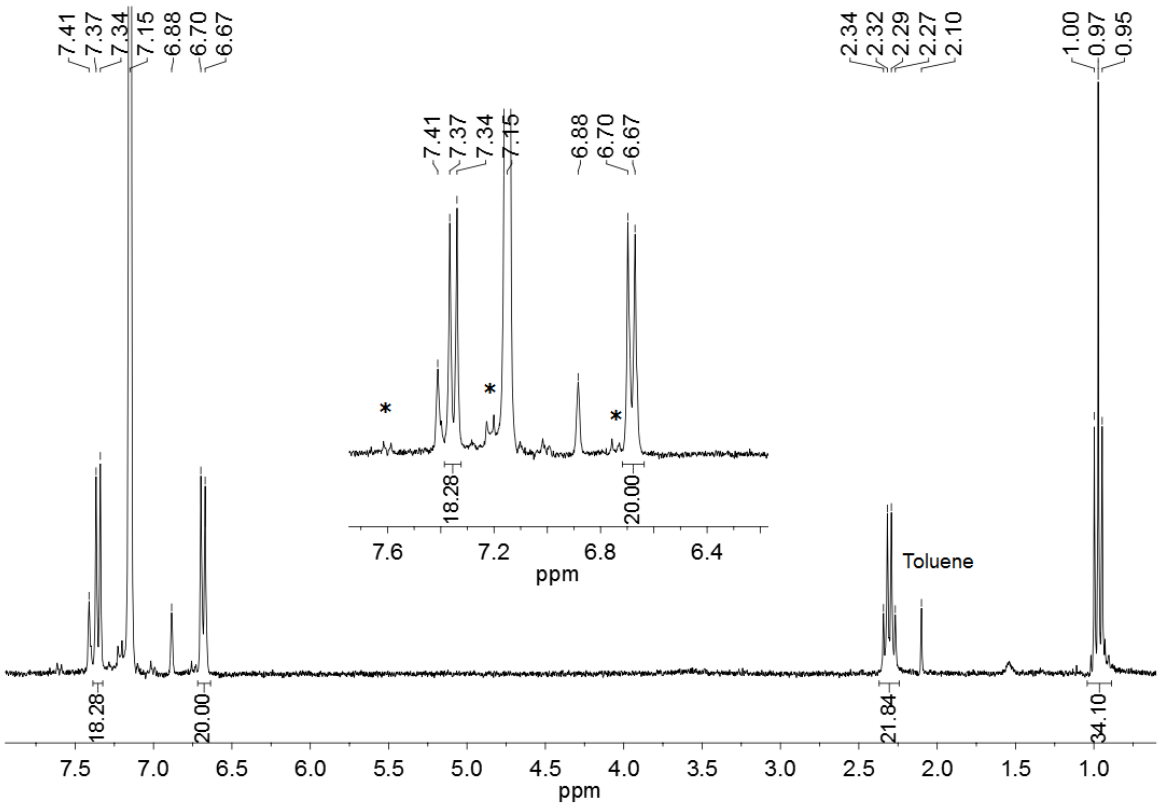

Figure S14. ^{1}H NMR spectrum of complex **5** (400.13 MHz, C_6D_6, 300 K); * denotes the signal corresponding to the unknown side products.

1.7 NMR spectra of [(Cp^{Ar}Ni)$_2$(μ-Se$_2$)] (6).

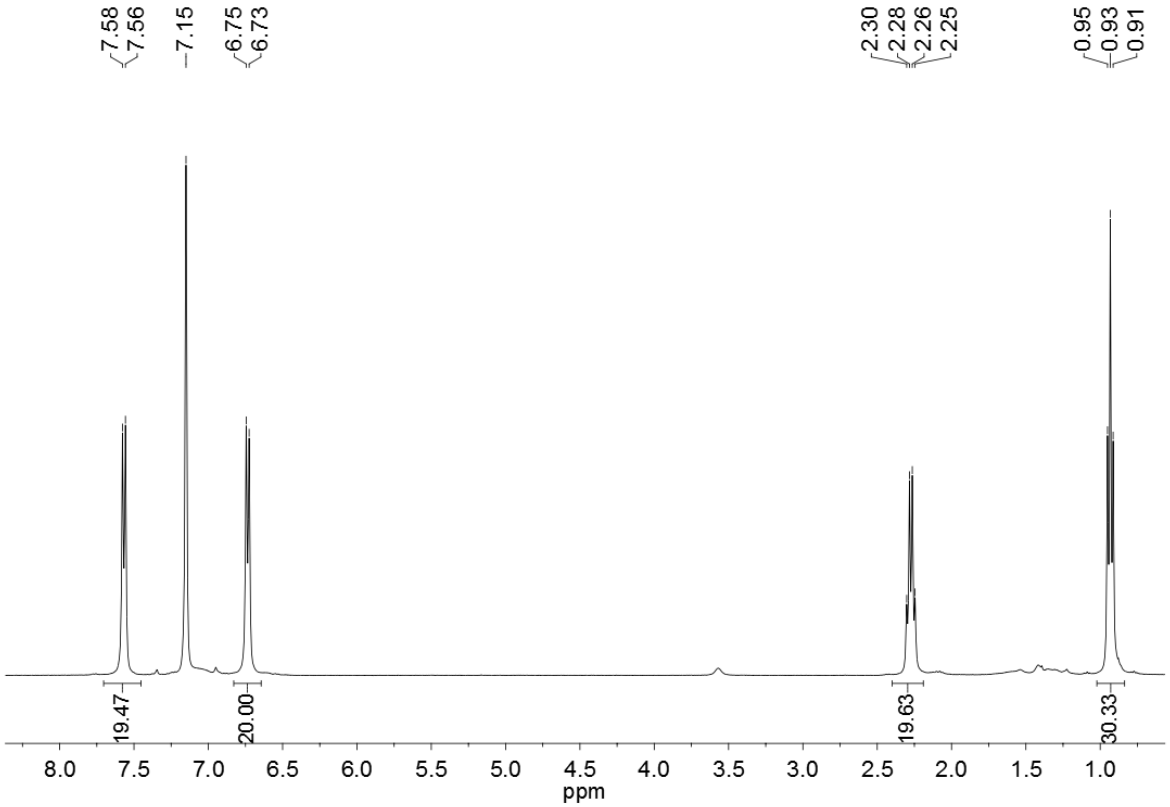

Figure S15. ^{1}H NMR spectrum of complex **6** (400.13 MHz, C_6D_6, 300 K); * denotes the signal corresponding to *n*-hexane.

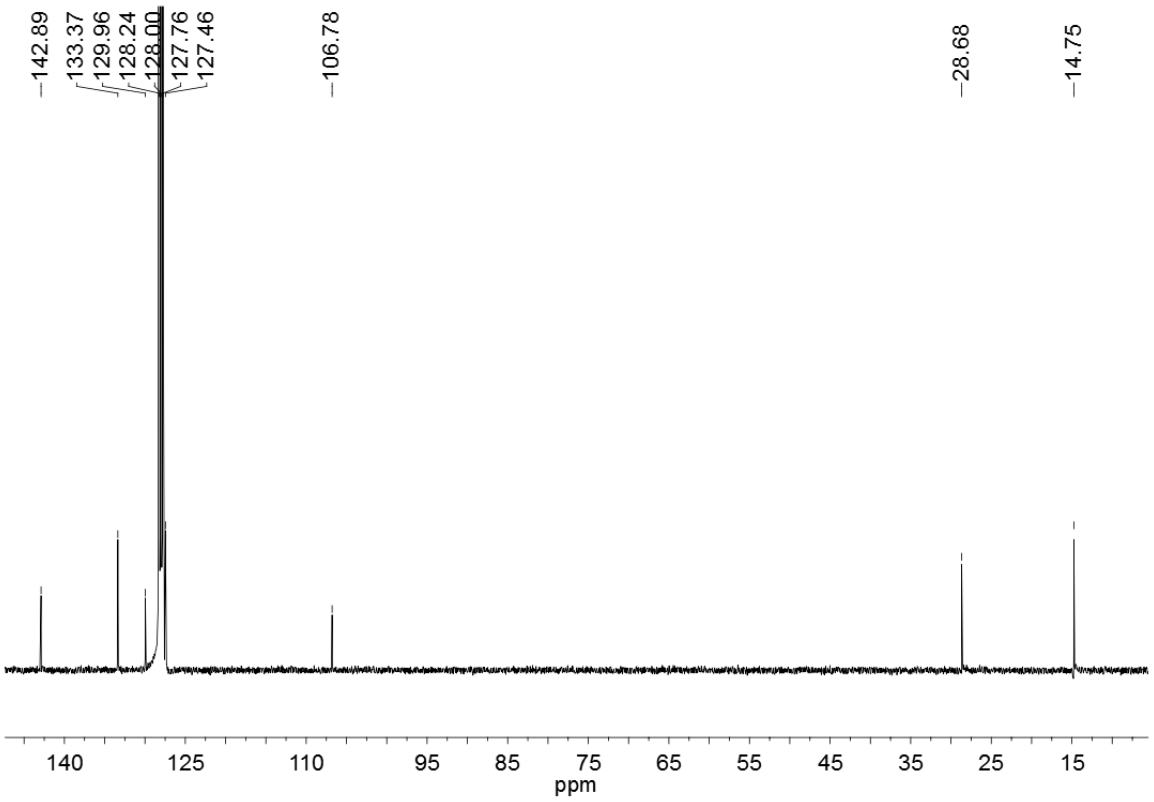

Figure S16. ^{13}C{^{1}H} NMR spectrum of complex **6** (100.61 MHz, C_6D_6, 300 K).

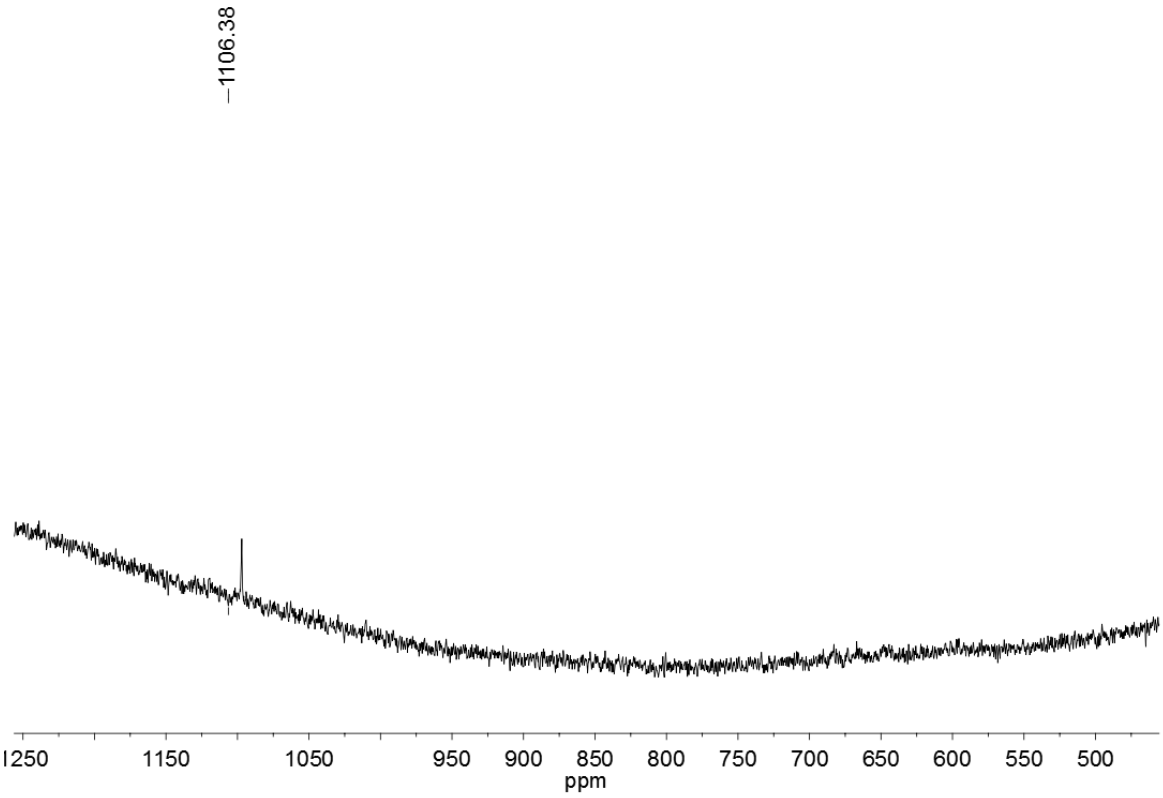

Figure S17. $^{77}Se\{^{1}H\}$ NMR spectrum of complex **6** (76.31 MHz, C_6D_6, 300 K).

2 Crystallographic data of 3 – 6 and molecular structure of $[Cp^{Ar}Ni(\mu\text{-}H)]_2$.

Table S1

	3·0.5(Et_2O)	**4a**	**4b**	**5**·0.5(C_6D_6)	**6**·(C_6H_6)
Empirical formula	$C_{56}H_{68}NNiO_{1.5}$	$C_{72}H_{81}N_2Ni$	$C_{56}H_{65}N_2Ni$	$C_{93}H_{93}D_{0.5}Ni_2S_6$	$C_{48}H_{48}NiSe$
Formula weight	837.82	1033.09	824.81	1521.46	762.53
Temperature/K	123(1)	123(1)	293(2)	125(2)	123(1)
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	*P*-1	$P2_1$	$P2_1/n$	*P*-1	*P*-1
a/Å	14.2539(5)	10.88422(10)	27.7545(3)	14.1755(6)	12.2418(2)
b/Å	14.7412(5)	20.99784(19)	11.82467(14)	14.3510(6)	13.8410(3)
c/Å	26.6743(9)	13.29748(12)	27.9694(3)	22.4716(8)	14.1751(3)
α/°	74.778(3)	90	90	75.613(3)	93.5632(19)
β/°	88.323(3)	107.9126(9)	95.0662(11)	87.361(3)	113.434(2)
γ/°	62.727(4)	90	90	63.023(4)	115.153(2)
Volume/$Å^3$	4779.8(3)	2891.76(5)	9143.37(19)	3934.5(3)	1915.91(8)
Z	4	2	8	2	2
ρ_{calc} mg/mm^3	1.164	1.186	1.198	1.284	1.322
μ/mm^{-1}	0.876	0.804	0.891	2.428	2.047
F(000)	1804	1110	3544	1607	796
Crystal size/mm^3	0.283× 0.248 × 0.112	0.3 × 0.3 × 0.2	0.205 × 0.183 ×0.129	0.206 × 0.149 × 0.108	0.244 × 0.161 × 0.137
2Θ range for data collection	3.454 to 67.043°	4.269 to 66.735°	4.066 to 73.575	3.634 to 66.651	3.538 to 74.454
Index ranges	$-16 \le h \le 15$, $-17 \le k \le 17$, $-31 \le l \le 31$	$-12 \le h \le 12$, $-21 \le k \le 24$, $-15 \le l \le 15$	$-34 \le h \le 33$, $-14 \le k \le 14$, $-34 \le l \le 34$	$-16 \le h \le 16$, $-15 \le k \le 17$, $-26 \le l \le 26$	$-15 \le h \le 15$, $-17 \le k \le 17$, $-17 \le l \le 17$
Reflections collected	74199	26054	69695	35656	58042
Independent reflections	16764 (R_{int} = 0.0295)	9535 (R_{int} = 0.0263)	18140 (R_{int} = 0.0267)	13733 (R_{int} = 0.0546)	7771 (R_{int} = 0.0413)
Data/restraints/parameters	16764/144/1159	9535/1/690	18140/0/1089	13733/65/1040	7771/0/465
Goodness-of-fit on F^2	1.043	1.048	1.017	1.020	1.042
R_1 ,wR_2 [I>=2σ (I)]	0.0446, 0.1203	0.0290, 0.0750	0.0515, 0.1423	0.0620, 0.1545	0.0471, 0.1243

R_1 ,wR_2 [all data]	0.0487, 0.1243	0.0293, 0.0753	0.0595, 0.1492	0.0909, 0.1743	0.0486, 0.1256
Largest diff. peak/ hole / e Å^{-3}	1.102/-0.738	0.478/-0.282	2.001/-0.546	0.674/-0.471	1.680/-0.802

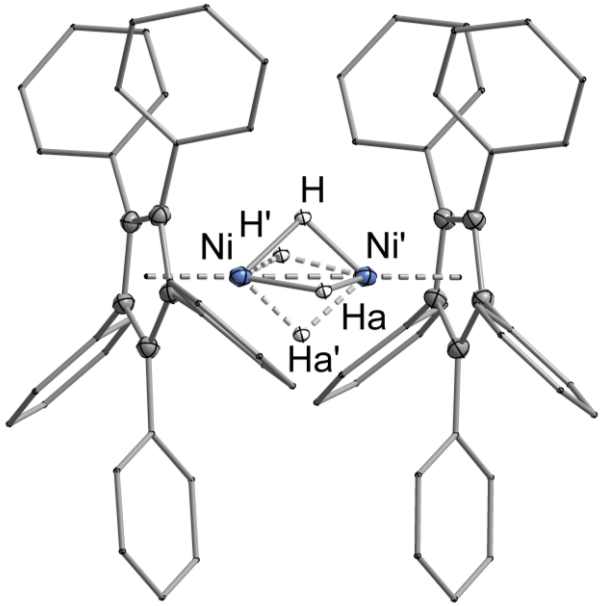

Figure S18. Solid-state molecular structure of [Cp^{Ar}Ni(μ-H)]$_2$. Thermal ellipsoids are drawn at the 35% probability level. The H atoms and ethyl group on the phenyl rings are omitted for clarity. The H atoms attached to Ni center are disordered over two sites with an occupancy of 0.5.

Crystal data for [Cp^{Ar}Ni(μ-H)]$_2$: $C_{45}H_{46}Ni$ (M =645.53 g/mol), monoclinic, space group C2/c (no. 15), a = 23.2006(3) Å, b = 15.05392(15) Å, c = 21.1694(2) Å, β = 110.0972(15)°, V = 6943.42(16) Å^3, Z = 8, T = 123(1) K, μ(CuKα) = 1.018 mm^{-1}, *Dcalc* = 1.235 g/cm^3, 34576 reflections measured (7.138° ≤ 2Θ ≤ 133.572°), 6123 unique (R_{int} = 0.0326, R_{sigma} = 0.0223) which were used in all calculations. The final R_1 was 0.0335 (I > 2σ(I)) and wR_2 was 0.1023 (all data).

3 EPR spectroscopy.

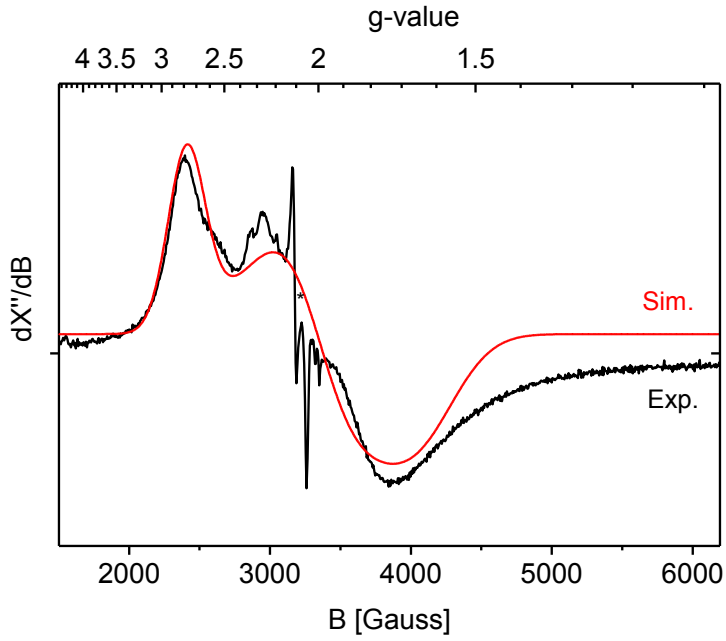

Figure S19. Experimental and simulated X-band EPR spectrum of **4b** in frozen toluene recorded at 20 K. Frequency = 9.362623 GHz, microwave power = 2.00 mW, T = 20 K, modulation amplitude = 4 Gauss. The sharp signals indicated with * is a minor impurity. The simulated spectrum was obtained using the parameters shown in Table S3.

Table S2. Experimental and DFT calculated isotropic EPR parameters of **4a**.

	g_x	g_y	g_z
Exp. [(a)]	1.980	2.180	2.585
DFT [(b)]	*2.148*	*2.266*	*2.326*
DFT [(c)]	*2.140*	*2.239*	*2.304*

(a) Values from spectral simulation.
(b) DFT, ADF, B3LYP, TZ2P, unrestricted, collinear.
(c) DFT, Orca, b3-lyp, def2-TZVP.

Table S3. Experimental and DFT calculated isotropic EPR parameters of **4b**.

	g_x	g_y	g_z
Exp. [(a)]	1.65	1.99	2.73
DFT [(b)]	*2.106*	*2.194*	*2.956*
DFT [(c)]	*2.116*	*2.281*	*2.403*

(a) Values from spectral simulation.
(b) DFT, ADF, B3LYP, TZ2P, unrestricted, collinear.
(c) DFT, Orca, b3-lyp, def2-TZVP.

4 SOMOs of 4a and 4b.

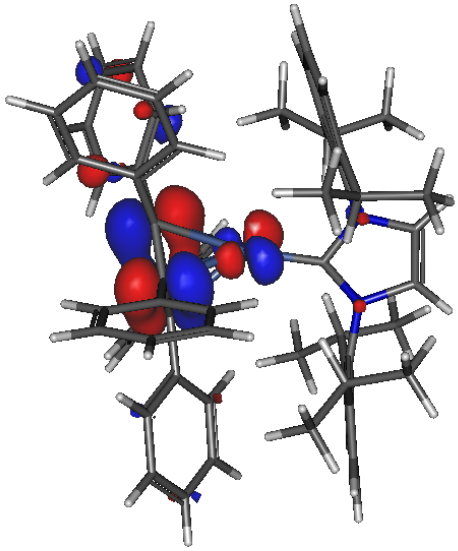

Figure S20. The SOMO spin up (no 237, occ 1, -4.507 eV) of **4a** calculated at the B3LYP / def2-TZVP level of theory.

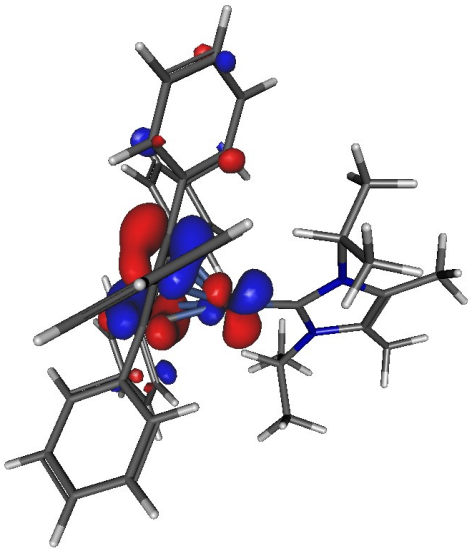

Figure S21. The SOMO spin up (no 181, occ 1, -4.3481 eV) of **4b** calculated at the B3LYP / def2-TZVP level of theory.

5 Cartesian Coordinates of 4a and 4b

5.1 Cartesian Coordinates of 4a (optimized at the B3LYP / def2-TZVP level of theory)

Electronic energy = -4016.765569328100 Hartree

Ni	0.692824	10.189037	10.187910
C	-0.930308	11.680892	9.445525
C	2.584782	10.123049	9.870396
C	-1.206764	11.413997	10.817178
C	-1.013605	10.439764	8.716813
C	-0.655397	13.030620	8.924496
N	3.396764	9.884642	10.945945
N	3.473137	10.261188	8.839163
C	-1.420536	10.005266	10.947180
C	-1.416828	12.372471	11.911614
C	-1.329302	9.409006	9.661257
C	-0.903956	10.270307	7.259441
C	-1.371889	13.563699	7.848495
C	0.281083	13.852036	9.562445
C	2.908645	9.692968	12.279673
C	4.738961	9.889974	10.604009
C	3.249093	10.379295	7.419991
C	4.788509	10.121133	9.280417
C	-1.948832	9.327462	12.149491
C	-2.052448	13.602154	11.692515
C	-1.057126	12.054081	13.228457
C	-1.638825	7.982773	9.419685
C	-0.002827	11.024646	6.499312
C	-1.741188	9.379144	6.574181
C	-1.167859	14.875107	7.436217
C	0.470544	15.166393	9.166083
C	2.617027	8.389661	12.711137
C	2.778733	10.820073	13.100559
C	3.476023	11.616210	6.804300
C	3.003654	9.208543	6.689832
C	-3.266348	9.573754	12.541919
C	-1.177094	8.463428	12.921081
C	-2.292954	14.481329	12.738719
C	-1.313739	12.925146	14.276452
C	-2.971079	7.570220	9.327345
C	-0.641297	7.014645	9.333146
C	0.052678	10.905271	5.119497
C	-1.670790	9.242842	5.194126
C	-0.251662	15.686347	8.097406
C	2.204588	8.237154	14.032737
C	2.774252	7.194435	11.783942

C	3.172966	12.198741	12.604729
C	2.344395	10.614061	14.408378
C	3.565915	11.634039	5.412286
C	3.620574	12.903112	7.597915
C	3.103369	9.280728	5.303512
C	2.641276	7.906386	7.380531
C	-3.799437	8.964701	13.669571
C	-1.706723	7.846853	14.048027
C	-1.925673	14.150423	14.038924
C	-3.293547	6.234302	9.133518
C	-0.958264	5.675619	9.140851
C	-0.776953	10.008658	4.455271
C	2.067976	9.335907	14.869209
C	1.768632	6.072385	12.053589
C	4.205096	6.638428	11.844163
C	4.634429	12.486517	12.987929
C	2.257926	13.318545	13.100542
C	3.413274	10.474382	4.671264
C	2.819994	14.049783	6.970325
C	5.089459	13.322315	7.751720
C	1.638500	7.084958	6.567140
C	3.889646	7.080188	7.724980
C	-3.020616	8.094816	14.426840
C	-2.285648	5.279818	9.038370
H	-2.099504	12.945498	7.340668
H	0.846701	13.447224	10.389920
H	5.515017	9.729766	11.328147
H	5.615471	10.176917	8.598168
H	-2.365901	13.869749	10.694031
H	-0.563935	11.115788	13.431838
H	0.663223	11.707280	7.001350
H	-2.459307	8.792095	7.124490
H	-1.736172	15.267565	6.602121
H	1.193489	15.784357	9.684357
H	-3.866918	10.259093	11.957067
H	-0.145374	8.302650	12.648718
H	-2.781620	15.426391	12.536759
H	-1.023571	12.644329	15.281754
H	-3.755467	8.312538	9.406505
H	0.389331	7.327496	9.428216
H	0.761541	11.503318	4.564457
H	-2.328366	8.542098	4.694670
H	-0.091510	16.707322	7.774397
H	1.969431	7.252425	14.410537
H	2.595689	7.551581	10.768415
H	3.103651	12.188264	11.516530
H	2.220617	11.460258	15.069582
H	3.761732	12.567879	4.903668

H	3.209601	12.721755	8.592770
H	2.926709	8.395813	4.709743
H	2.147567	8.175013	8.314691
H	-4.818392	9.180609	13.966538
H	-1.087180	7.183461	14.639161
H	-2.124851	14.832876	14.855432
H	-4.331724	5.934587	9.062048
H	-0.166844	4.938795	9.077569
H	-0.723375	9.902183	3.379076
H	1.730093	9.194699	15.887971
H	1.943840	5.596063	13.019882
H	1.874370	5.299376	11.290746
H	0.739599	6.426891	12.025464
H	4.314694	5.795940	11.158439
H	4.437091	6.287293	12.852305
H	4.943502	7.389451	11.567199
H	4.754166	12.478324	14.073880
H	4.940012	13.467219	12.616870
H	5.315210	11.743720	12.573057
H	2.343555	13.468735	14.178822
H	1.213877	13.115807	12.872997
H	2.538330	14.257000	12.618149
H	3.504711	10.505895	3.592761
H	1.770672	13.789981	6.839867
H	3.227983	14.336269	5.999429
H	2.863834	14.926119	7.615809
H	5.685029	12.550385	8.238320
H	5.164812	14.231435	8.352052
H	5.532395	13.528685	6.774739
H	2.094706	6.661562	5.669879
H	0.783944	7.691751	6.267537
H	1.265760	6.253597	7.165522
H	4.414252	6.778539	6.815256
H	3.609774	6.175294	8.269091
H	4.585375	7.642119	8.347862
H	-3.434488	7.618048	15.306529
H	-2.535025	4.236770	8.889776

5.2 Cartesian Coordinates of 4b (optimized at the B3LYP / def2-TZVP level of theory)

Electronic energy = -3397.519177499848 Hartree

C	7.513356	1.802271	10.703001
C	6.441228	2.442136	11.340144
C	5.527717	1.725854	12.099991
H	6.333356	3.513471	11.240567
H	6.839003	-1.372247	11.729710

H	4.710585	2.247054	12.583826
C	8.490984	2.556767	9.905709
C	7.624840	0.414271	10.849195
C	5.662083	0.349479	12.249148
C	6.719010	-0.301329	11.620735
C	9.914624	2.403133	9.927251
C	8.185369	3.589962	8.965516
H	8.436466	-0.103620	10.357338
Ni	9.516729	4.438684	10.589162
C	10.471480	3.323413	8.972857
C	10.694614	1.455522	10.747757
C	9.400733	4.036006	8.356892
C	6.841818	4.078742	8.610916
C	8.983411	5.879506	11.748957
H	9.560294	6.827017	9.598591
H	8.389491	3.786321	12.803192
C	11.893977	3.413014	8.598274
C	10.432659	1.294607	12.112955
C	11.728668	0.696912	10.187646
C	9.517844	5.024427	7.276154
C	5.839652	3.194593	8.201658
C	6.550864	5.446191	8.623091
N	9.035906	7.215413	11.506803
N	8.563905	5.779418	13.037016
C	9.567215	7.716472	10.226862
C	8.355059	4.460758	13.658861
C	12.887080	3.684762	9.542300
C	12.280799	3.192240	7.273734
H	9.634538	1.866402	12.563403
C	11.175659	0.419491	12.891341
C	12.484682	-0.169519	10.968458
C	8.628898	5.013061	6.194016
C	10.517565	6.007105	7.287783
H	6.049118	2.133456	8.177530
C	4.589359	3.663768	7.819766
C	5.306887	5.918316	8.231999
H	7.320416	6.138591	8.931456
C	8.667396	7.945464	12.633616
C	8.381188	7.035076	13.607654
C	8.686105	8.768260	9.564334
C	11.014957	8.170344	10.376054
C	9.508549	4.095562	14.585216
C	6.979260	4.322507	14.303746
H	12.600200	3.863256	10.570894
C	14.226593	3.715117	9.178444
C	13.618898	3.232257	6.905185
H	11.520428	2.984163	6.532678
H	10.943861	0.308058	13.943732

C	12.213912	-0.312647	12.323429
H	7.858475	4.256248	6.150662
C	8.718411	5.958648	5.181271
C	10.611202	6.949000	6.273183
H	11.225543	6.029046	8.104763
H	3.827047	2.962008	7.504904
C	4.316839	5.027315	7.830359
H	5.108374	6.983352	8.236923
C	8.545122	9.427602	12.688059
C	7.964351	7.280724	15.017076
H	7.631880	8.497866	9.634782
H	8.950665	8.825246	8.507791
H	8.824155	9.759164	9.995682
H	11.108057	9.023832	11.050524
H	11.406447	8.467631	9.402235
H	11.630434	7.356893	10.760942
H	10.453306	4.142209	14.042995
H	9.377628	3.077020	14.953449
H	9.572394	4.758773	15.449019
H	6.908431	4.836418	15.261464
H	6.772571	3.265783	14.472339
H	6.204629	4.709249	13.641305
H	14.982259	3.919002	9.927074
C	14.599083	3.487635	7.857982
H	13.897480	3.056350	5.873576
H	8.014635	5.927222	4.358813
C	9.707367	6.935637	5.215197
H	11.393632	7.697332	6.308595
H	9.473829	9.933446	12.418791
H	8.270584	9.738813	13.694459
H	7.767311	9.789418	12.014124
H	6.892008	7.138671	15.168848
H	8.212419	8.302548	15.300910
H	8.483288	6.618988	15.709276
H	9.778775	7.671871	4.424845
H	3.345083	5.393086	7.523771
H	13.285397	-0.737814	10.512109
H	11.950623	0.794221	9.134314
H	12.803330	-0.987594	12.930789
H	15.643420	3.510197	7.572946
H	4.952727	-0.208744	12.846654