Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Steric and electronic effects on arylthiolate coordination in the pseudotetrahedral complexes [($Tp^{Ph,Me}$)Ni–SAr] ($Tp^{Ph,Me}$ = hydrotris{3-phenyl-5-methyl-1-pyrazolyl}borate)

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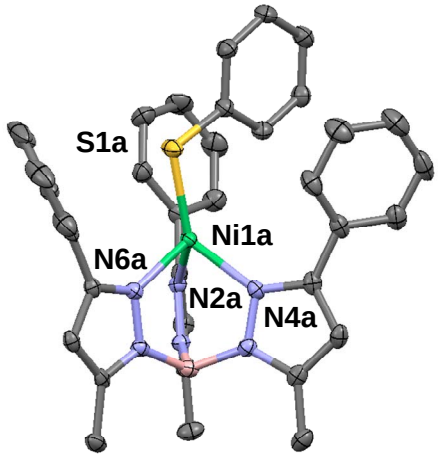

Figure S1. Thermal ellipsoid plot (50% probability) of [(Tp^{Ph,Me})Ni–SPh]. Hydrogen atoms are omitted for clarity. Relevant bond lengths for [(Tp^{Ph,Me})Ni–SPh] (Å): Ni1a–N2a, 2.005(2); Ni1a–N4a, 2.019(2); Ni1a–N6a, 2.013(2); Ni1a–S1a, 2.2224(7). Relevant bond angles for [(Tp^{Ph,Me})Ni–SPh] (°): N2a–Ni1a–N4a, 90.61(8); N2a–Ni1a–N6a, 91.66(8); N4a–Ni1a–N6a, 92.86(8); N2a–Ni1a–S1a, 129.21(6); N4a–Ni1a–S1a, 131.42(6); N6a–Ni1a–S1a, 109.85(6); Ni1a–S1a–C31a, 106.63(8).

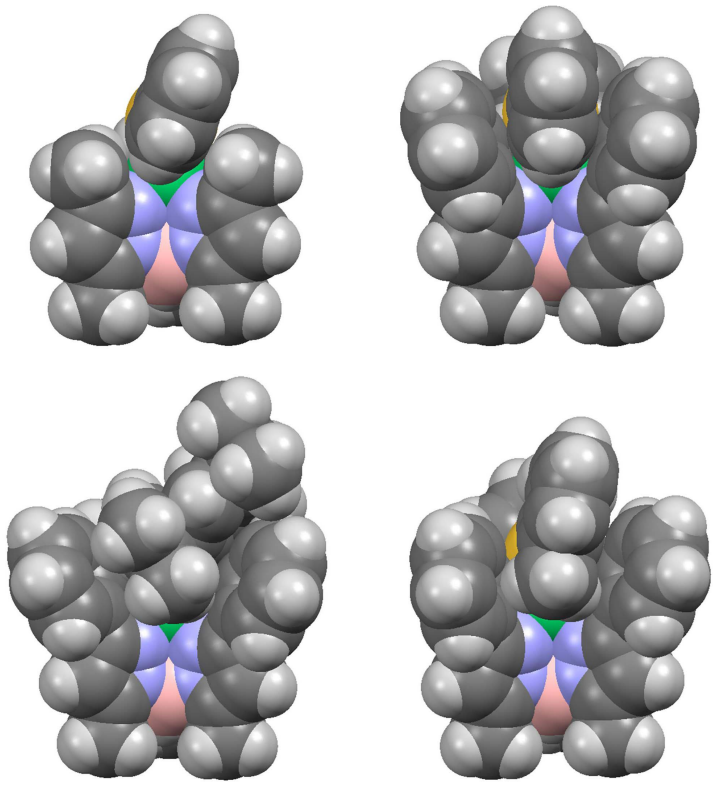

Figure S2. Space-filling diagrams (clockwise from top left) of [(Tp^{Me,Me})Ni–SPh], [(Tp^{Ph,Me})Ni–SPh], [(Tp^{Ph,Me})Ni–S–2,6-$Me_2C_6H_3$] and [(Tp^{Ph,Me})Ni–S–2,4,6-$^{i}Pr_3C_6H_2$].

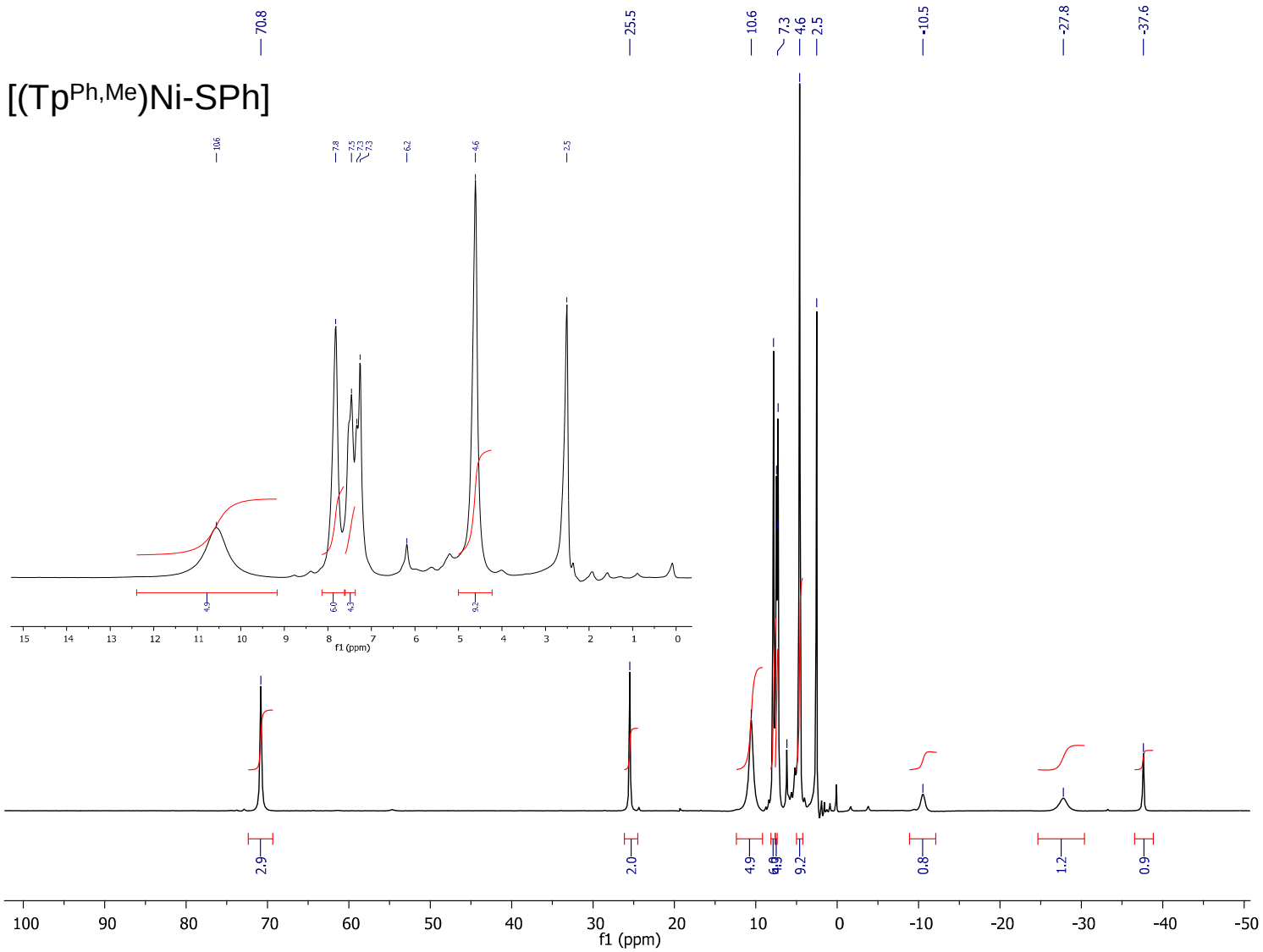

Figure S3. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–SPh] in $CDCl_3$.

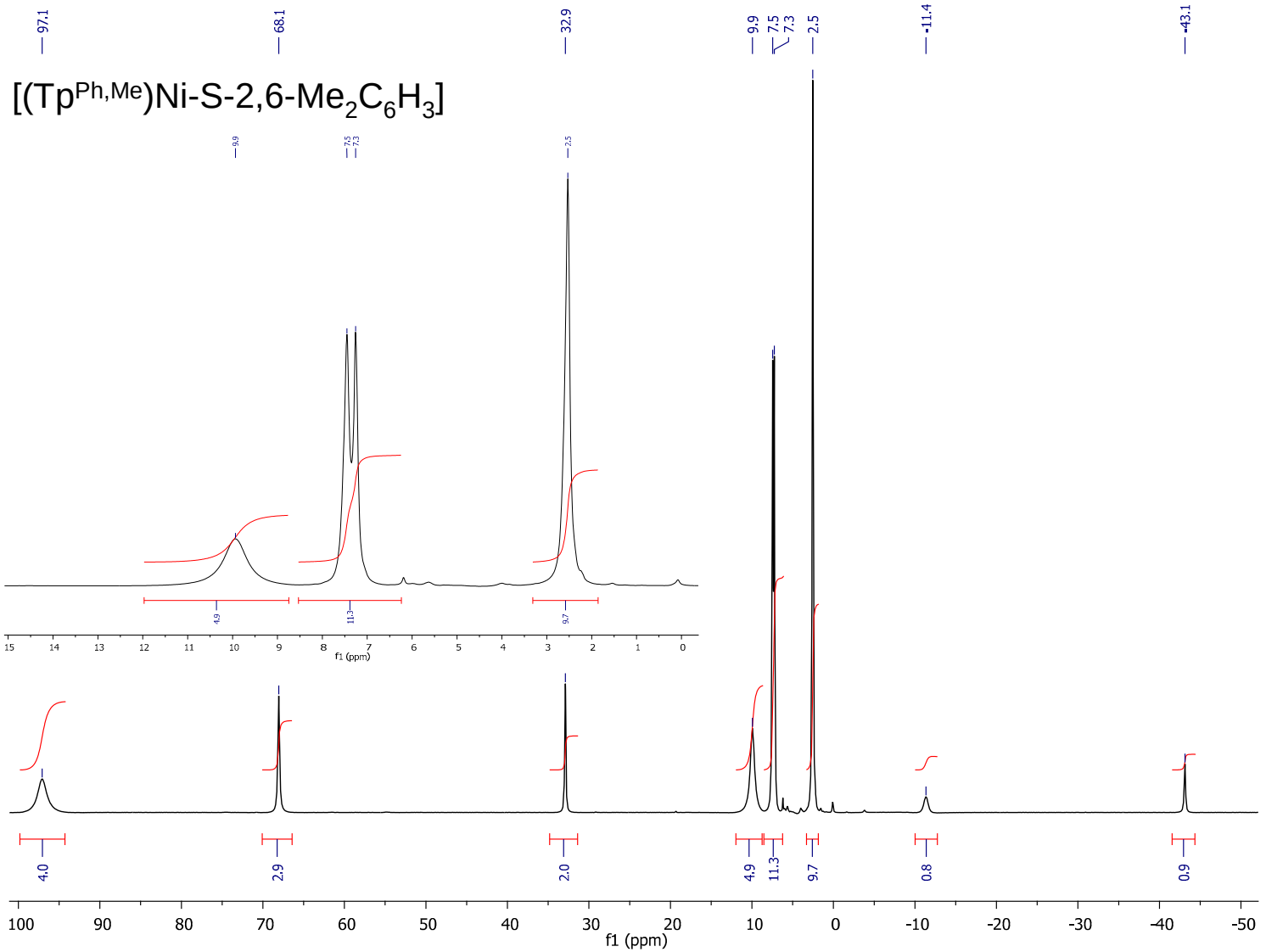

Figure S4. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–S–2,6-$Me_2C_6H_3$] in $CDCl_3$.

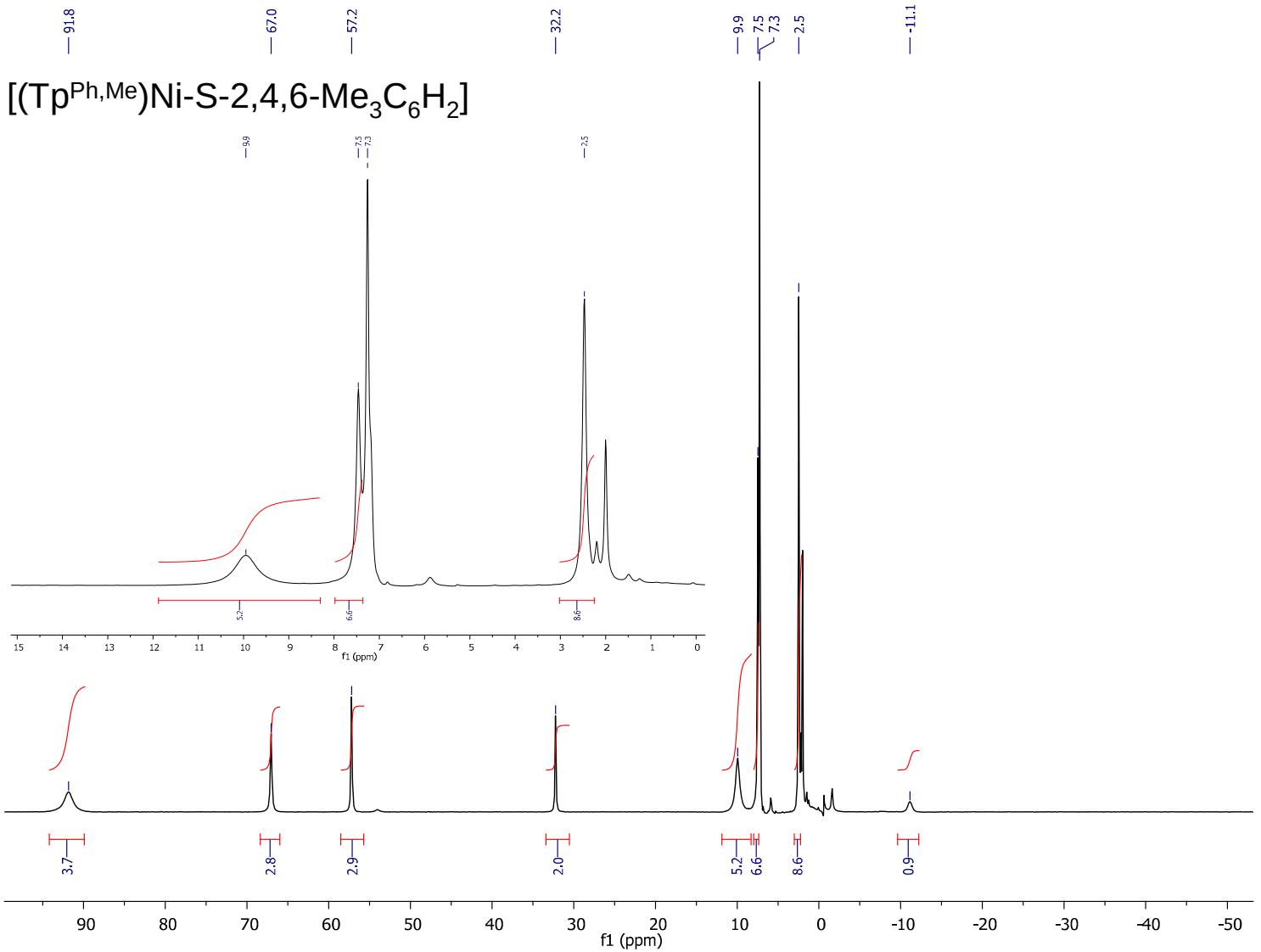

Figure S5. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–S–2,4,6-$Me_3C_6H_2$] in $CDCl_3$.

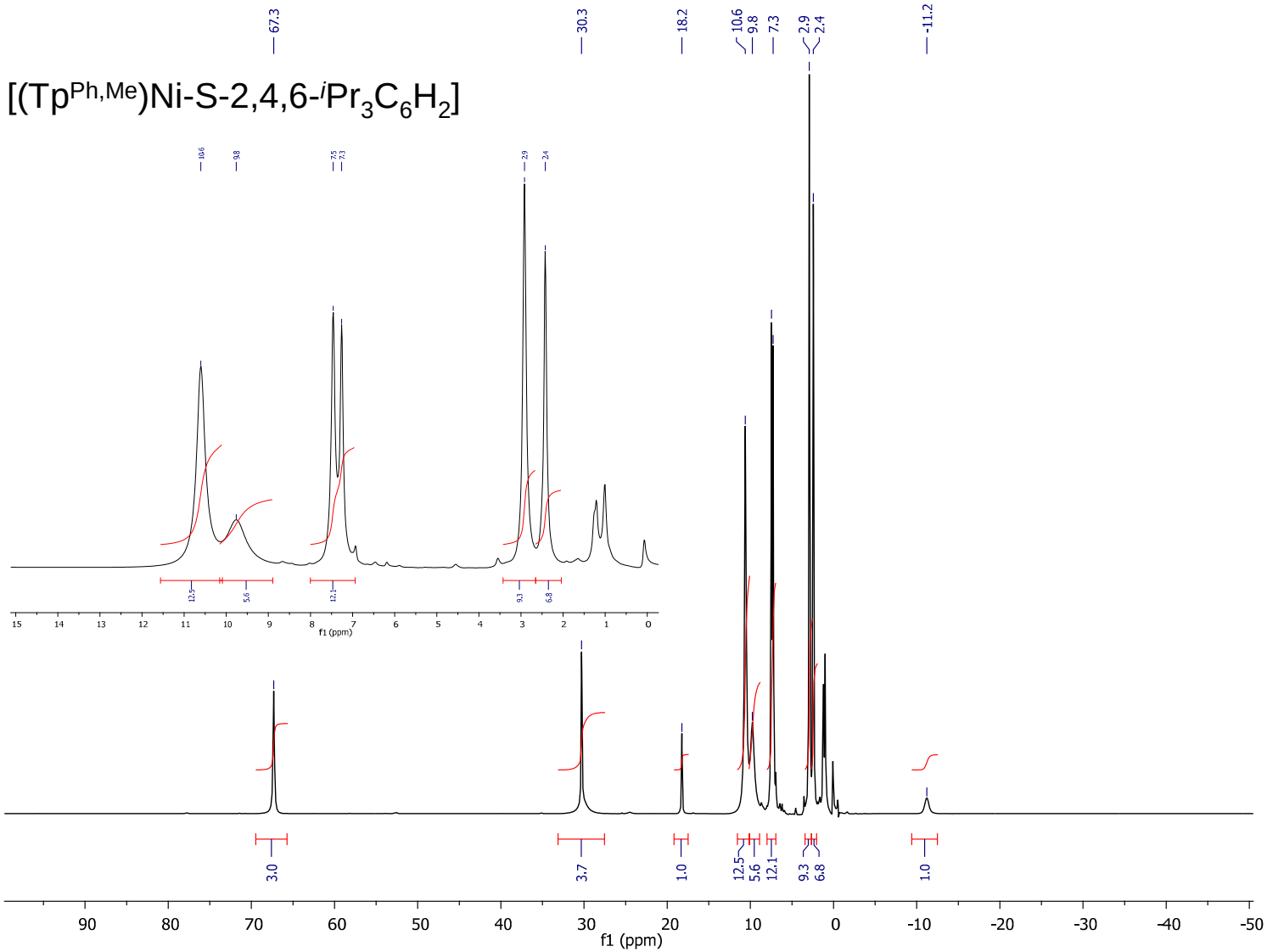

Figure S6. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–S–2,4,6-^{i}Pr$_3$C$_6$H$_2$] in CDCl$_3$.

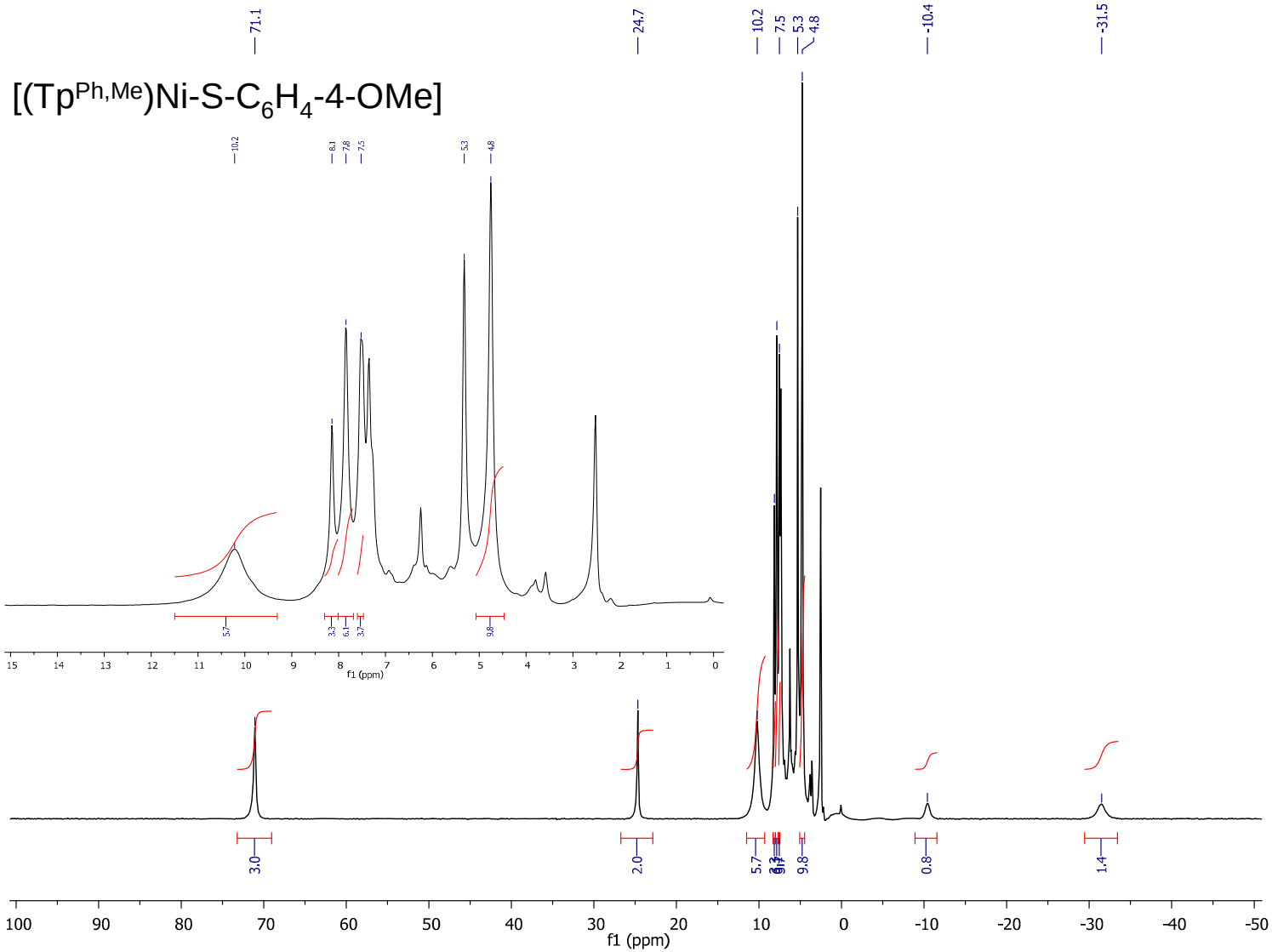

Figure S7. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–S–C_6H_4-4–OMe] in CD_2Cl_2.

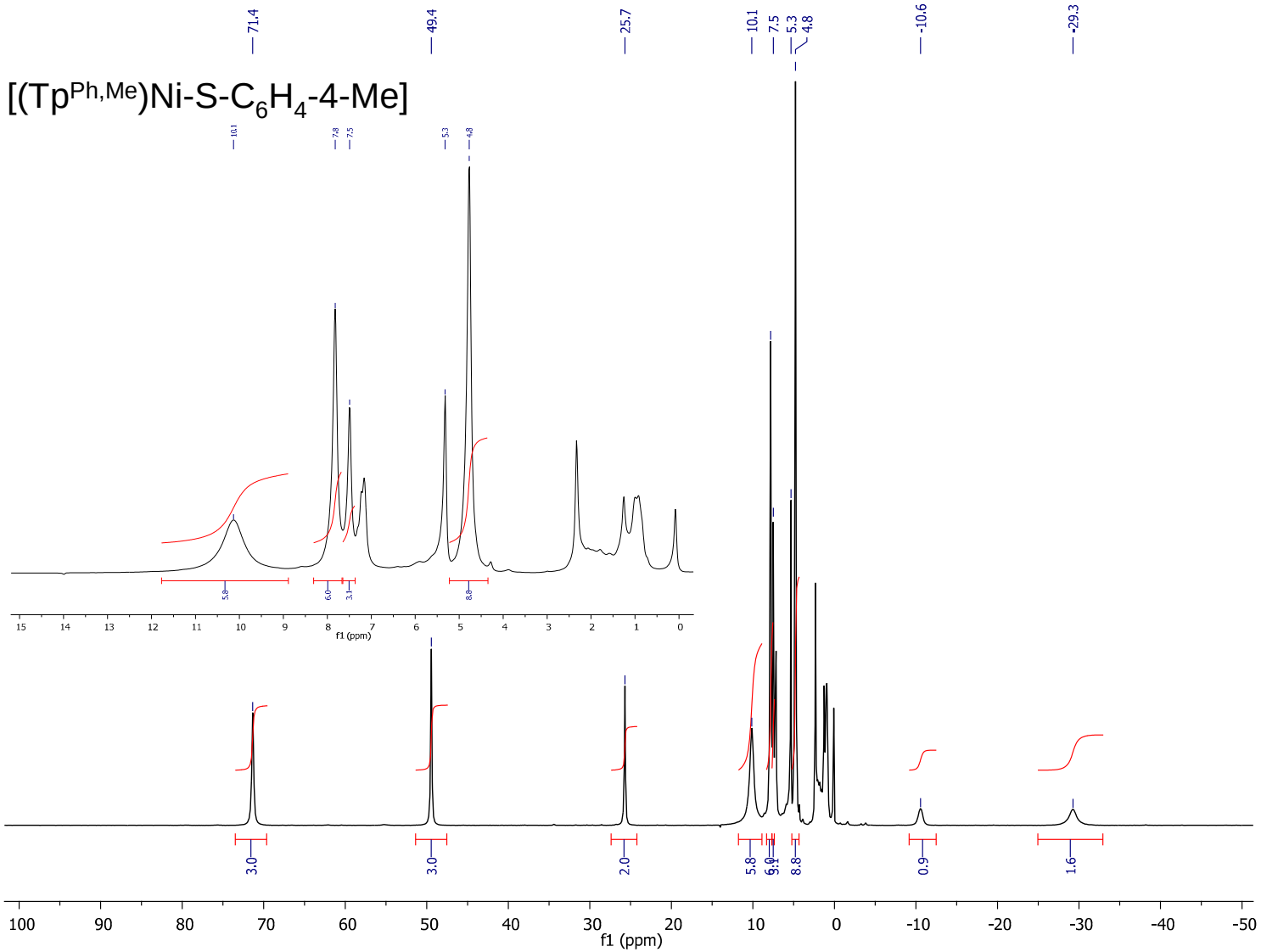

Figure S8. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–S–C_6H_4-4–Me] in CD_2Cl_2.

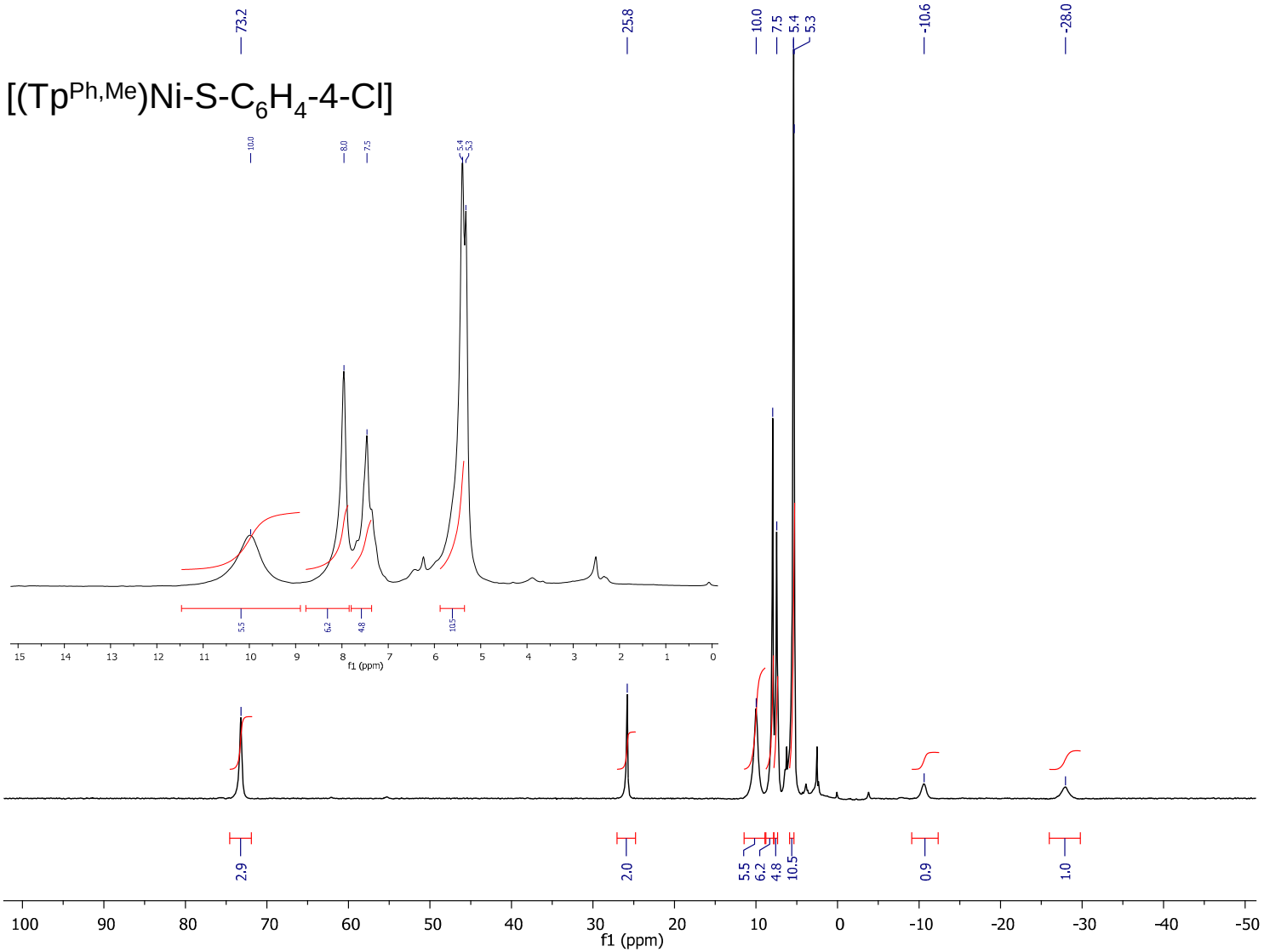

Figure S9. ^{1}H NMR spectrum (500 MHz, 295 K) of [(Tp^{Ph,Me})Ni–S–C_6H_4-4–Cl] in CD_2Cl_2.

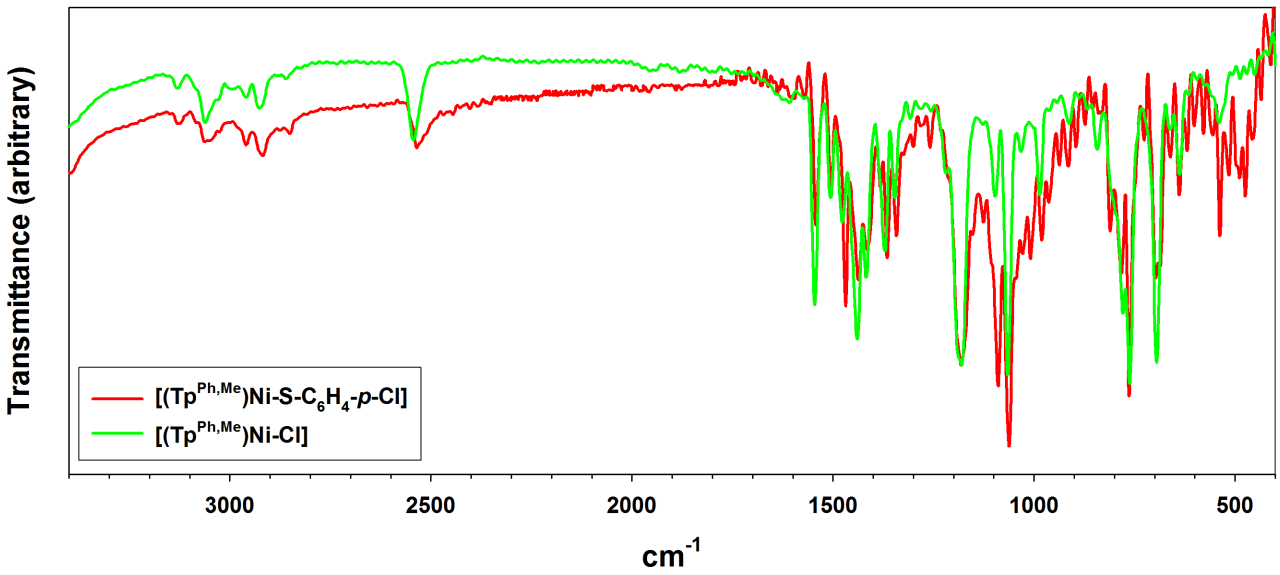

Figure S10. FTIR spectra (KBr pellets) of [(Tp^{Ph,Me})Ni–S–C_6H_4-4-Cl] (red) and [(Tp^{Ph,Me})Ni–Cl] (green).

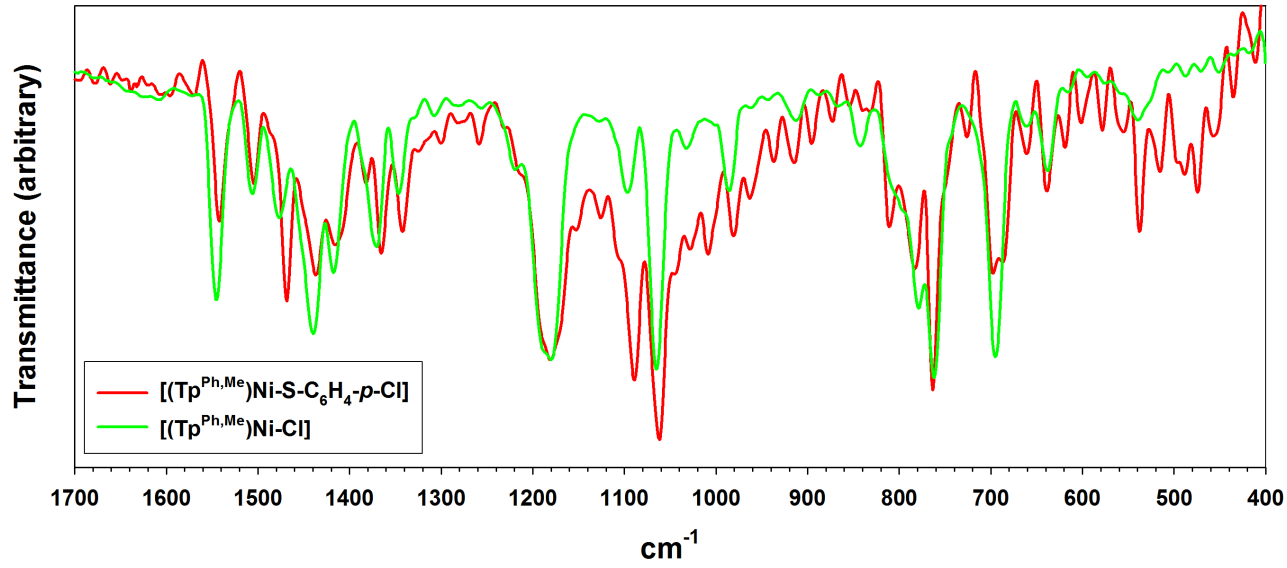

Figure S11. Detail of the FTIR spectra of [(Tp^{Ph,Me})Ni–S–C_6H_4-4-Cl] (red) and [(Tp^{Ph,Me})Ni–Cl] (green).

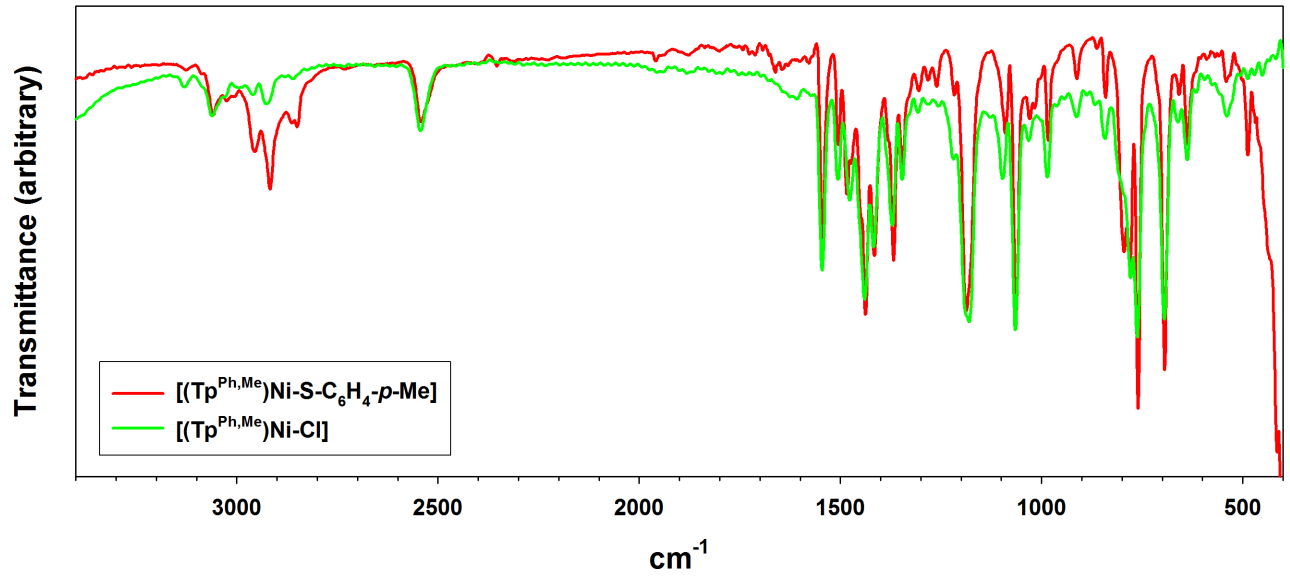

Figure S12. FTIR spectra (KBr pellets) of [(Tp^{Ph,Me})Ni–S–C_6H_4-4-Me] (red) and [(Tp^{Ph,Me})Ni–Cl] (green).

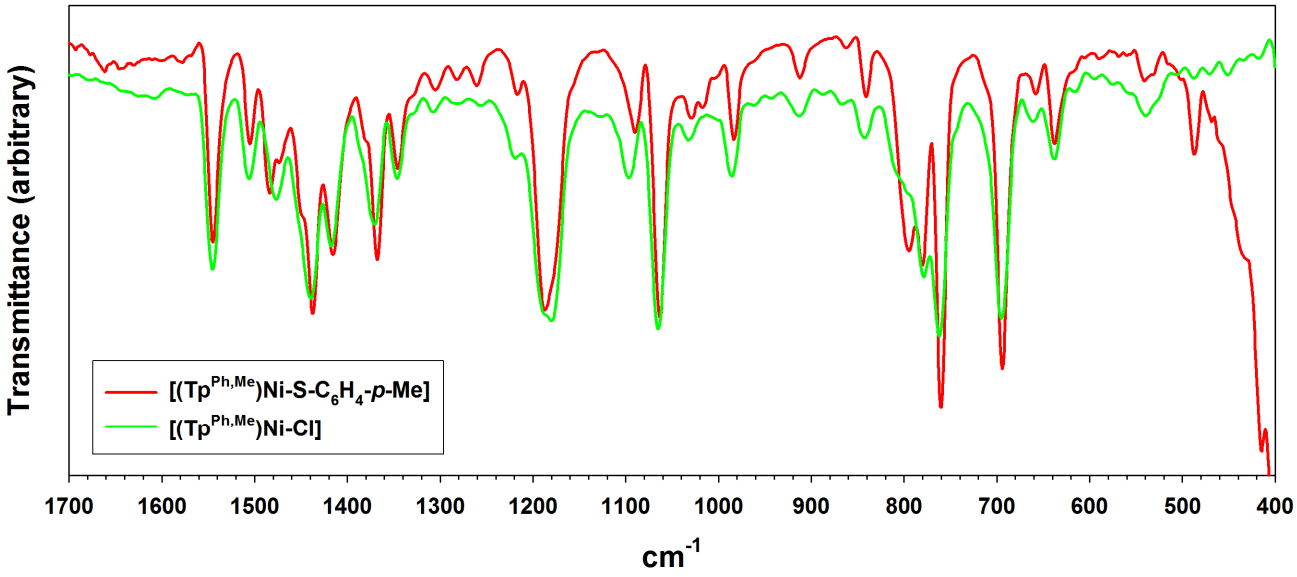

Figure S13. Detail of the FTIR spectra of [(Tp^{Ph,Me})Ni–S–C_6H_4-4-Me] (red) and [(Tp^{Ph,Me})Ni–Cl] (green).

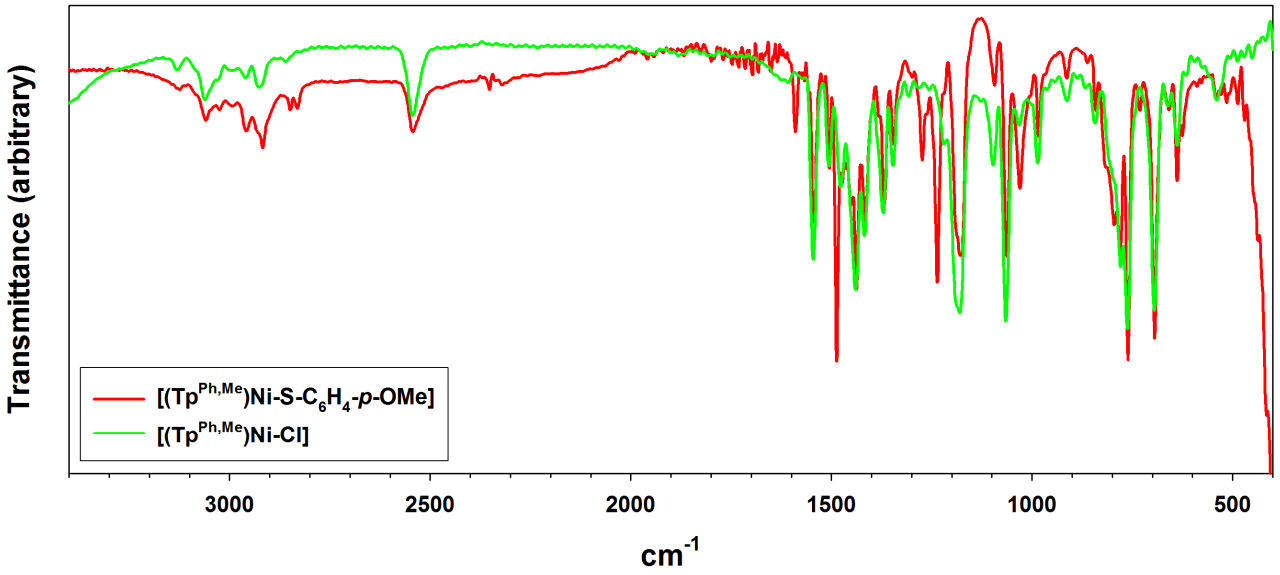

Figure S14. FTIR spectra (KBr pellets) of [(Tp^{Ph,Me})Ni–S–C_6H_4-4-OMe] (red) and [(Tp^{Ph,Me})Ni–Cl] (green).

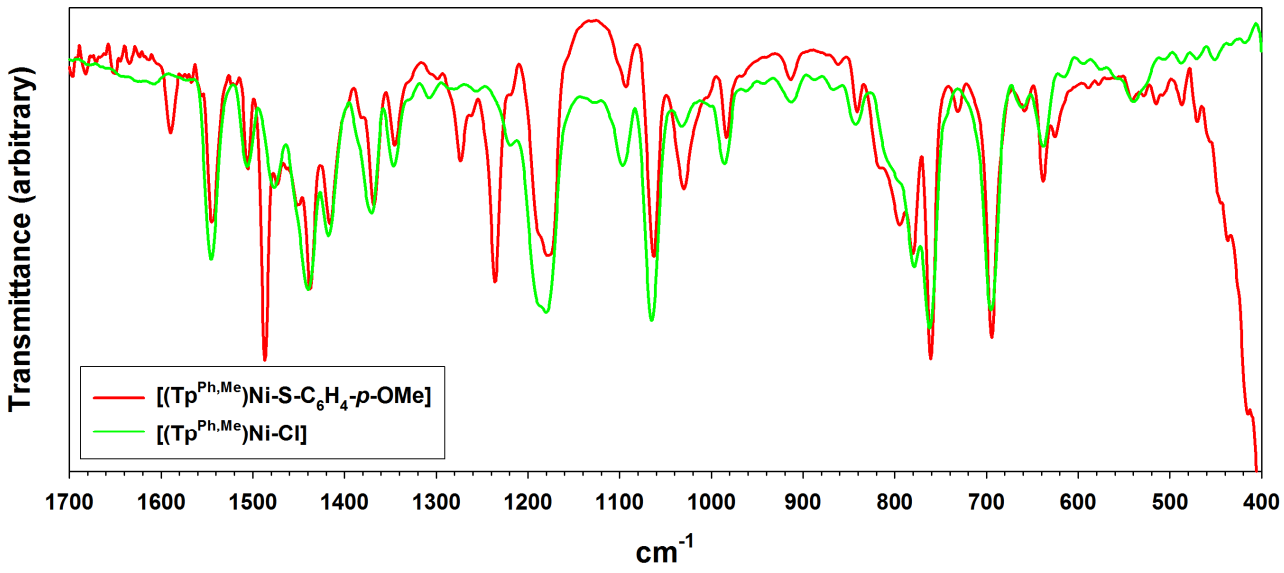

Figure S15. Detail of the FTIR spectra of [(Tp^{Ph,Me})Ni–S–C_6H_4-4-OMe] (red) and [(Tp^{Ph,Me})Ni–Cl] (green).

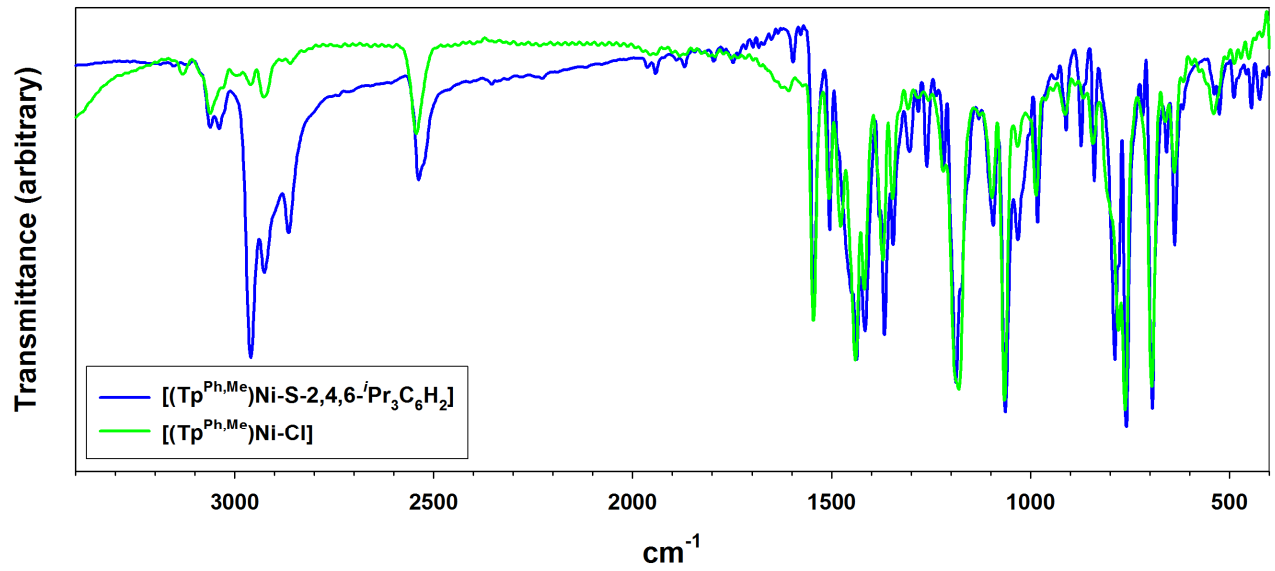

Figure S16. FTIR spectra (KBr pellets) of [(Tp^{Ph,Me})Ni–S–2,4,6-^{i}Pr$_3$C$_6$H$_2$] (blue) and [(Tp^{Ph,Me})Ni–Cl] (green).

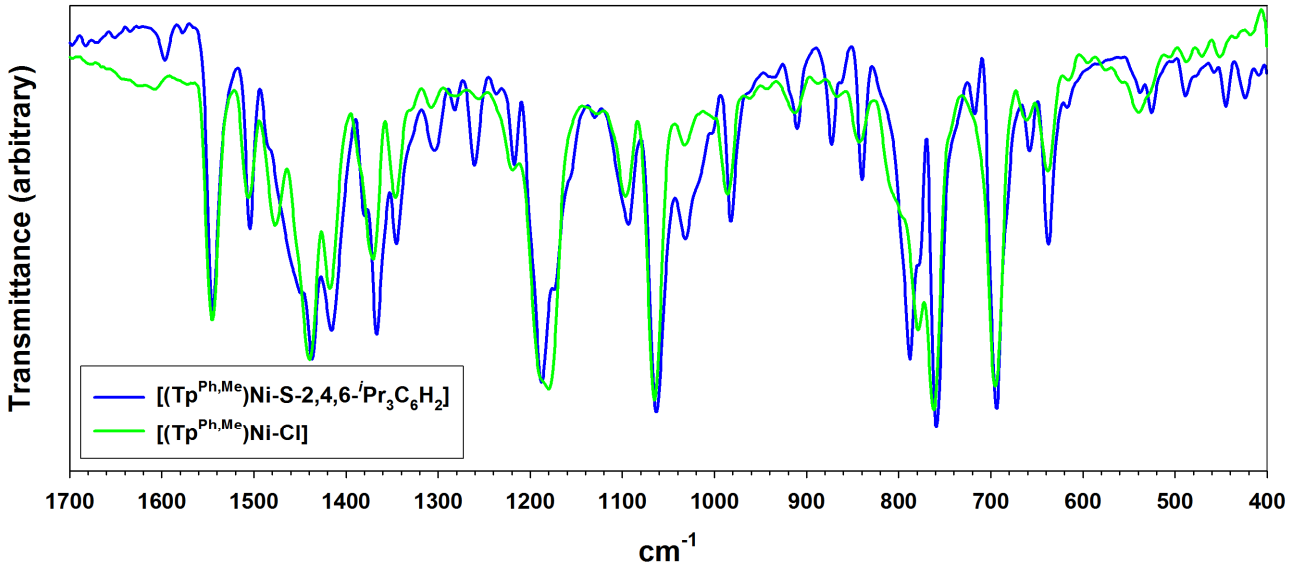

Figure S17. Detail of the FTIR spectra of [(Tp^{Ph,Me})Ni–S–2,4,6-^{i}Pr$_3$C$_6$H$_2$] (blue) and [(Tp^{Ph,Me})Ni–Cl] (green).

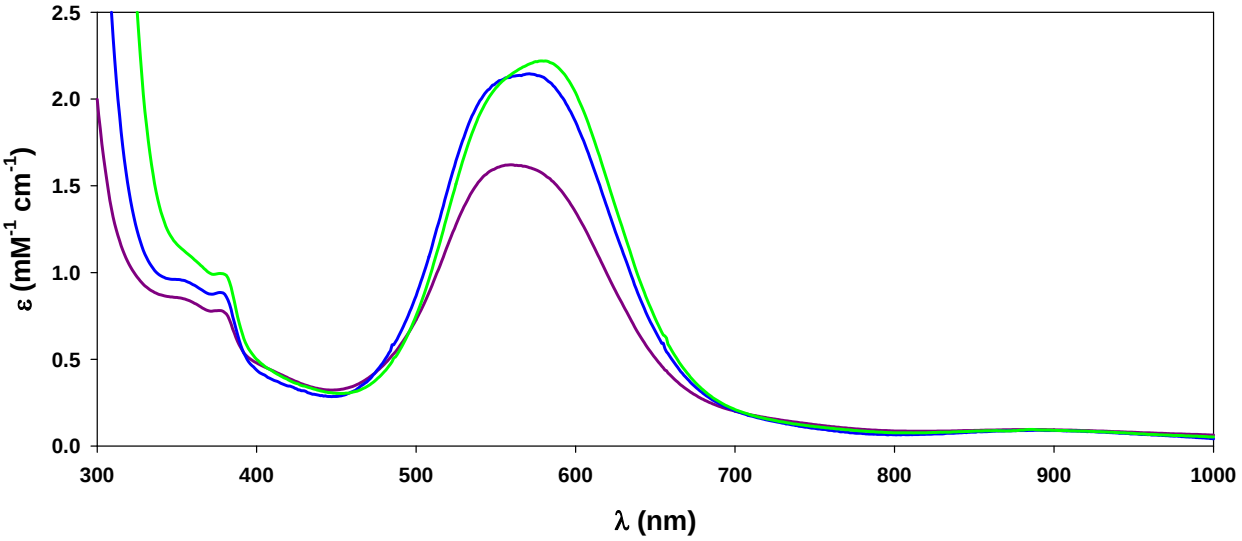

Figure S18. UV-Vis-NIR spectra of [(Tp^{Ph,Me})Ni–S–2,4,6-$Me_3C_6H_2$] at room temperature (295 K) in toluene (green), CH_2Cl_2 (blue) and CH_3CN (violet) solutions.

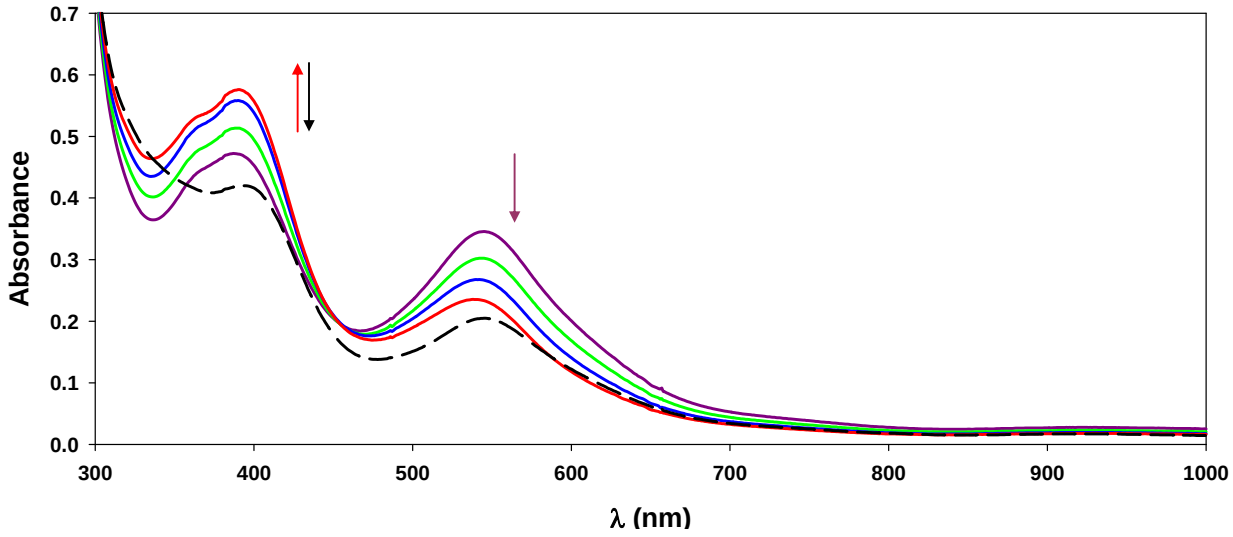

Figure S19. Variable temperature UV-Vis-NIR spectra of [(Tp^{Ph,Me})Ni–S–2,4,6-$^{i}Pr_3C_6H_2$] obtained with increased cooling from room temperature in CH_3CN: purple, 298 K; green, 294 K; blue, 286 K; red 278 K. The dashed black spectrum was recorded on subsequent warming to 316 K. Raw data are shown, not corrected for changes in solvent density.

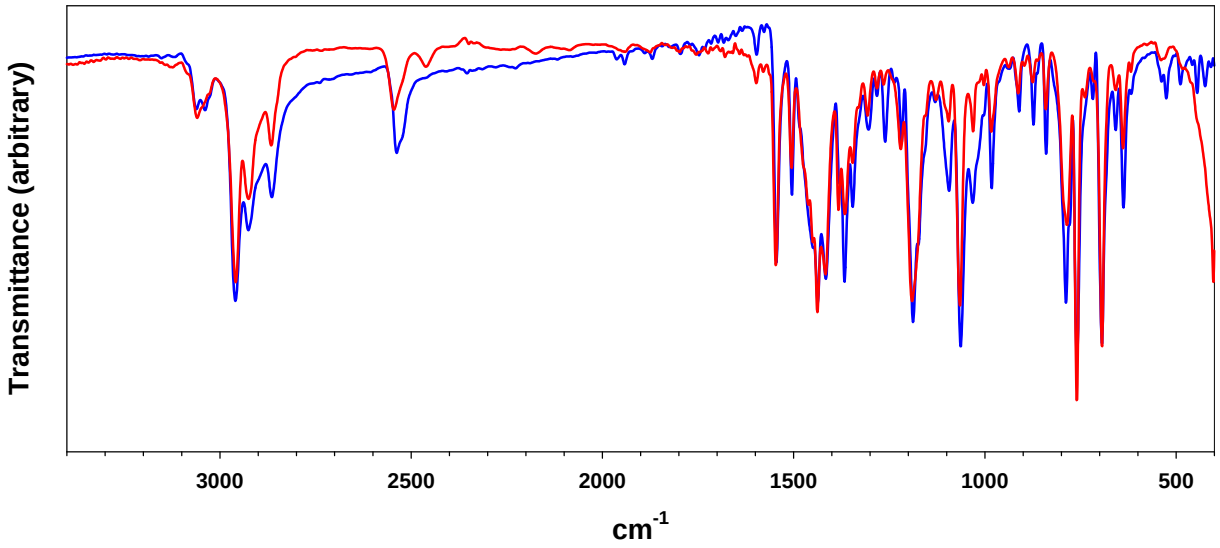

Figure S20. FTIR spectra (KBr pellets) of [(κ^3-Tp^{Ph,Me})Ni–S–2,4,6-^{i}Pr$_3$C$_6$H$_2$] recrystallized from CH_2Cl_2/hexane (blue) and a mixture of [(κ^3-Tp^{Ph,Me})Ni–S–2,4,6-^{i}Pr$_3$C$_6$H$_2$] and [(κ^2-Tp^{Ph,Me})Ni(NCMe)(S–2,4,6-^{i}Pr$_3$C$_6$H$_2$)]•MeCN recrystallized from CH_3CN (red).

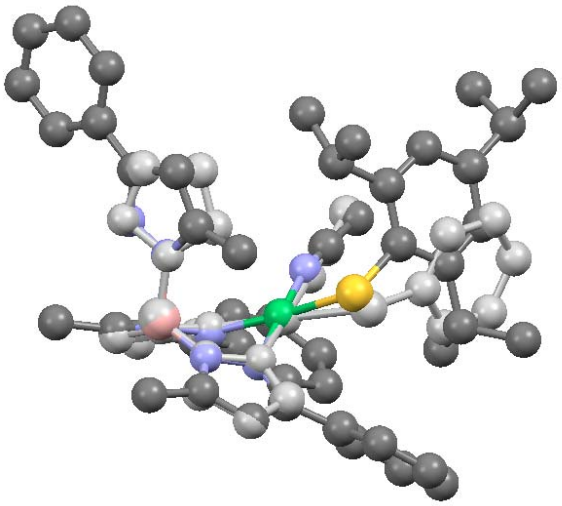

Figure S21. Least-squares overlay of the theoretical [(k^2-Tp)Ni(NCMe)(SPh)] model (gray) with the experimental [(k^2-Tp^{Ph,Me})Ni(NCMe)(S–2,4,6-^{i}Pr$_3$C$_6$H$_2$)] X-ray structure (color), aligned on a common basal BN_3 moiety. Hydrogen atoms are omitted for clarity.

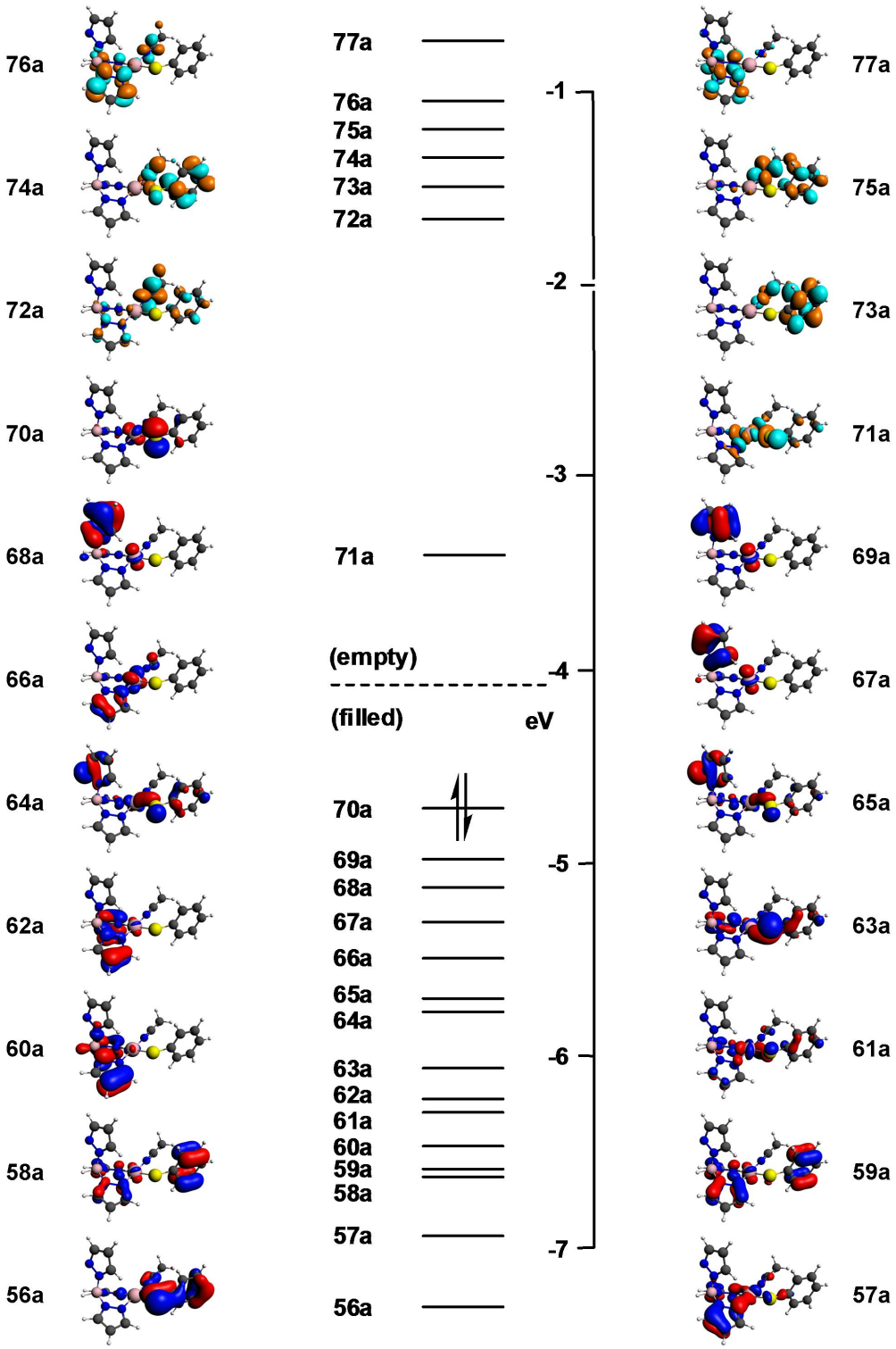

Figure S22. Frontier molecular orbitals for the [(k^2-Tp)Ni(NCMe)(SPh)] model (see Figure S21).

Table S1. Coordinates for minimized structure of [(k^2-Tp)Ni(NCMe)(SPh)].

	x	y	z (Å)
Ni	0.06122635	0.04588338	0.06487979
B	2.76893645	-1.69213365	-0.59747702
H	3.52403892	-2.44873163	-1.14658764
N	2.31456025	-0.62377946	-1.62548276
N	1.21127953	0.17404010	-1.47020882
H	3.76893866	-0.90216655	-3.13220990
C	2.87850946	-0.36329143	-2.82805367
C	2.13623094	0.62060750	-3.47252421
H	2.31617368	1.05168599	-4.45090106
C	1.09709760	0.92516206	-2.58526906
H	0.28443444	1.63740359	-2.66979758
N	1.49726875	-2.50453775	-0.20100405
N	0.31948775	-1.90542667	0.12228405
H	2.21371777	-4.49162811	-0.27847548
C	1.36655715	-3.84523973	-0.07990942
C	0.06511799	-4.13324240	0.32477086
H	-0.37106661	-5.10904084	0.50889256
C	-0.55510133	-2.88180951	0.43725324
H	-1.57479765	-2.63504401	0.71013001
N	3.44224546	-1.05359403	0.62430722
N	4.17202553	-1.86764312	1.44850798
H	2.85869438	1.01164224	0.59467469
C	3.39284550	0.22143098	1.11293293
C	4.11833184	0.24931573	2.29608536
H	4.29724467	1.10857592	2.93538287
C	4.57500207	-1.07861296	2.45415920
H	5.18855439	-1.49640284	3.24889738
S	-0.16676413	2.28509939	-0.05928102
C	-1.58692984	2.84671014	0.86315136
C	-2.90060205	2.60654640	0.41383875
C	-3.99688094	3.12351713	1.10791706
H	-5.00750628	2.93219474	0.74198667
C	-3.80207119	3.90351747	2.25522698
C	-2.50071039	4.15760893	2.70369931
H	-2.33814960	4.77323522	3.59030093
C	-1.40171835	3.62727810	2.02011241
H	-3.04940414	2.01621284	-0.49163641
H	-4.65866522	4.32006755	2.78832554
H	-0.38615106	3.81879875	2.37016982
N	-1.03416248	-0.02492269	1.54791722
C	-1.66694177	-0.03268866	2.52076903
C	-2.47240232	-0.02626339	3.72736872
H	-3.21881832	-0.83171690	3.69286275
H	-2.98808148	0.94102782	3.81367854
H	-1.83086994	-0.17298850	4.60724466

Table S2. Calculated excitations (TD-DFT) for [(k^2-Tp)Ni(NCMe)(SPh)] model.

no.	E/eV	f/AU	Occupied to virtual orbitals	Contribution(%)
1	1.5326	0.002044	70a → 71a	0.7373
			69a → 71a	0.1657
2	1.5990	0.001799	69a → 71a	0.4660
			68a → 71a	0.2741
			70a → 71a	0.2378
3	1.7486	0.000967	67a → 71a	0.4627
			68a → 71a	0.4199
			69a → 71a	0.1092
4	2.2887	0.000217	65a → 71a	0.6882
			64a → 71a	0.3088
5	2.2916	0.001272	67a → 71a	0.4997
			69a → 71a	0.2470
			68a → 71a	0.2321
6	2.3956	0.003823	66a → 71a	0.9103
7	2.6000	0.009209	64a → 71a	0.4185
			63a → 71a	0.2780
			65a → 71a	0.1995
8	2.8195	0.003812	62a → 71a	0.9041
9	2.8966	0.021493	63a → 71a	0.3659
			61a → 71a	0.2989
			64a → 71a	0.1321
10	3.0156	0.003505	60a → 71a	0.8859
11	3.0934	0.001358	70a → 72a	0.6793
			61a → 71a	0.2309
12	3.1665	0.002089	58a → 71a	0.5308
			59a → 71a	0.3388
13	3.2226	0.079702	59a → 71a	0.3153
			70a → 73a	0.2193
			61a → 71a	0.1337
			70a → 72a	0.1121
14	3.2574	0.066696	70a → 73a	0.6512
			61a → 71a	0.0976
15	3.3159	0.065843	58a → 71a	0.3048
			59a → 71a	0.2278
			61a → 71a	0.1223
			63a → 71a	0.1043

no.	E/eV	f/AU	Occupied to virtual orbitals	Contribution(%)
16	3.3275	0.011992	69a → 72a	0.8759
17	3.4247	0.002000	70a → 74a	0.8698
18	3.4642	0.000664	69a → 73a	0.5509
			68a → 72a	0.4261
19	3.4716	0.002927	68a → 72a	0.5135
			69a → 73a	0.4386
20	3.5074	0.018594	70a → 75a	0.8693
21	3.6030	0.009664	57a → 71a	0.9112
22	3.6136	0.000331	68a → 73a	0.9678
23	3.6254	0.000411	69a → 74a	0.9217
24	3.6519	0.000115	67a → 72a	0.9285
25	3.6599	0.004569	70a → 76a	0.9269
26	3.7189	0.000773	69a → 75a	0.9615
27	3.7683	0.001302	68a → 74a	0.9649
28	3.7905	0.000161	67a → 73a	0.9798
29	3.8612	0.000946	68a → 75a	0.9598
30	3.8764	0.000395	69a → 76a	0.9481
31	3.9258	0.016394	66a → 73a	0.4733
			66a → 72a	0.4638
32	3.9456	0.000247	67a → 74a	0.9708
33	4.0111	0.030450	70a → 77a	0.3775
			66a → 73a	0.2924
			66a → 72a	0.1323
34	4.0279	0.000719	68a → 76a	0.8520
35	4.0384	0.008686	67a → 75a	0.6159
			70a → 77a	0.1640
36	4.0428	0.014569	67a → 75a	0.3491
			70a → 77a	0.2655
37	4.0727	0.000424	65a → 72a	0.7958
			64a → 72a	0.1546
38	4.1105	0.001950	70a → 78a	0.9061

no.	E/eV	f/AU	Occupied to virtual orbitals	Contribution(%)
39	4.1370	0.057805	56a → 71a	0.4440
			66a → 74a	0.2087
			64a → 72a	0.1008
40	4.1631	0.007740	64a → 72a	0.6069
			66a → 74a	0.1786
41	4.2007	0.011276	67a → 76a	0.8362
42	4.2248	0.015310	66a → 75a	0.7896
43	4.2369	0.000715	65a → 73a	0.8258
			64a → 73a	0.1490
44	4.2480	0.059177	69a → 77a	0.2270
			66a → 74a	0.2034
			56a → 71a	0.1014
45	4.2501	0.012447	69a → 77a	0.7291
			66a → 75a	0.0994
46	4.3424	0.008714	64a → 73a	0.6736
			63a → 72a	0.1222
47	4.3567	0.000314	69a → 78a	0.9666
48	4.3811	0.003717	55a → 71a	0.6180
			65a → 74a	0.2906
49	4.3841	0.001351	65a → 74a	0.4484
			55a → 71a	0.3363
			64a → 74a	0.1628
50	4.4055	0.009455	68a → 77a	0.9341