Electronic Supplementary Information for

Azolium-2-dithiocarboxylates as redox active ligands in nickel chemistry

Martin S. Luff,[a] Tin M. Filipovic,[a] Celine S. Corsei,[a] Kai Oppel,[a] Ivo Krummenacher,[a,b] Rüdiger Bertermann[a,b], Maik Finze[a,b], Holger Braunschweig[a,b], Udo Radius*[a]

[a] Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

[b] Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

*Corresponding author Email address: u.radius@uni-wuerzburg.de

Table of Content

1 Additional Figures and Tables

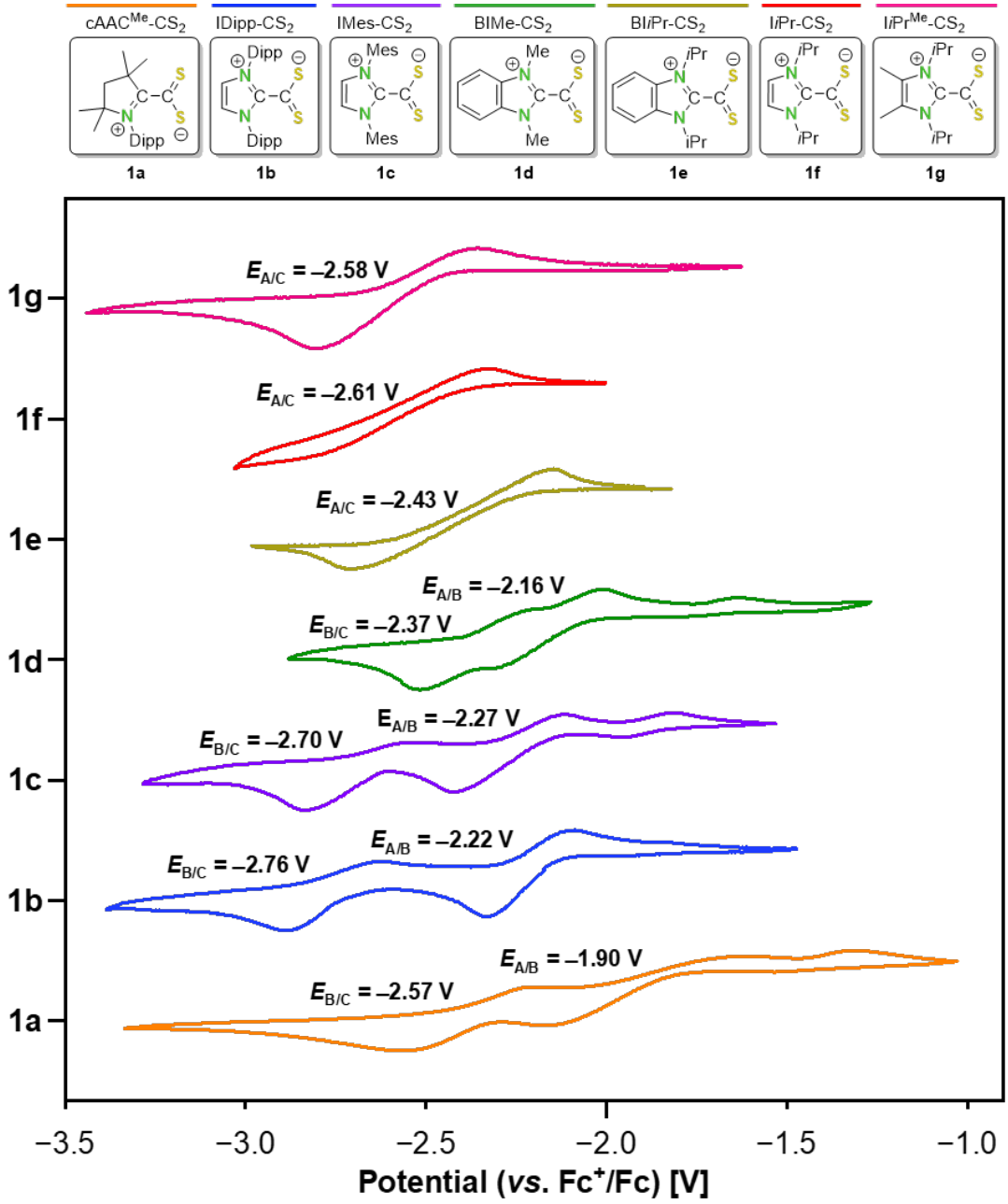


Figure S1. Cyclic voltammograms of the **A**/**B**, **B**/**C** redox-couples (neutral/monoanion, monoanion/dianion, see Scheme 2 of the main text) of the carbene-CS_2 adducts **1a**–**g** in THF (concentrations *ca.* 1 mM) with added [TBA][PF_6] (TBA = tetra(*n*-butyl) ammonium; 0.1 M). Potentials are internally referenced relative to the ferrocenium/ferrocene (Fc^+/Fc) couple with negative sweep directions. For clarity, due to varying resolution of the redox-events at different scan velocities (*v*), the curves containing the best separation of the occurring redox-events are shown in the area of –0.8 to –3.5 V at different values of *v* (IMes-CS_2 (**1c**), BI*i*Pr-CS_2 (**1e**), I*i*Pr-CS_2 (**1f**): 10 mV/s; cAAC^{Me}-CS_2 (**1a**), BIMe-CS_2 (**1d**): 25 mV/s; I*i*Pr^{Me}-CS_2 (**1g**), IDipp-CS_2 (**1b**): 50 mV/s).

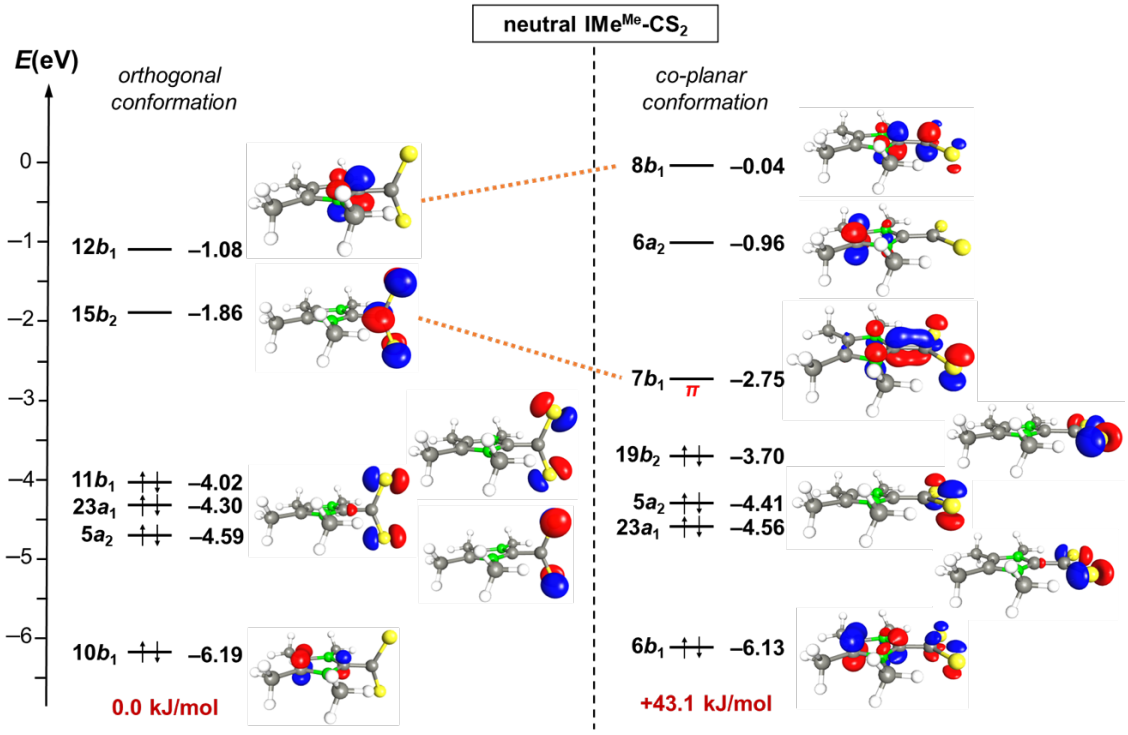


Figure S2. Quantum-chemical DFT calculations (B3LYP/def2-TZVP) of IMe^{Me}-CS$_2$ in an ideal orthogonal- (left) and a co-planar (right) conformation of the CS$_2$-moiety relative to the plane of the carbene ring (C_{2V} restricted symmetry).

To evaluate the important frontier molecular orbitals (FMOs) of NHC-substituted dithiocarboxylates on an easy-to-analyze system and to save computational effort these calculations have been performed on the model system IMe^{Me}-CS$_2$ (Figure S2). The neutral molecule IMe^{Me}-CS$_2$ was optimized in symmetry-restricted orthogonal and co-planar conformations. The orthogonal alignment of the CS$_2$ moiety relative to the plane of the carbene ring is favored by 43.1 kJ/mol for neutral IMe^{Me}-CS$_2$ with respect to a co-planar alignment. Rotation of the CS$_2$ moiety of the orthogonal structure along the central C–C axis by 90 ° into the carbene plane does essentially not affect the occupied orbitals too much but switches on π-interaction between the carbene and the CS$_2$-moiety. Upon planarization the MOs 15b_2 (CS$_2$-centered) and 12b_1 (carbene-centered) mix to give the π-bonding orbital 7b_1 and the π^*-anti-bonding orbital 8b_1, highlighted in orange dashes in Figure S2. These orbitals are unoccupied for the neutral dithiocarboxylates, and the π-bonding orbital 7b_1 is the LUMO of neutral, co-planar IMe^{Me}-CS$_2$. This orbital becomes occupied upon reduction of the neutral carbene-CS$_2$ adducts to yield the mono- and dianionic forms **B** and **C** (Figure 2 of the main text), which is in line with the observed changes in the C–C distances for complexes **2** (and **3**).

Calculations on the orthogonal and in-plane structure of the anionic [IMe^{Me}-CS$_2$]$^{\cdot-}$ radical show that the orthogonal conformer, in which the additional electron is either located at the carbene (SOMO: 15b_2) or at the CS$_2$ group (SOMO: 12b_1) are 133.3 kJ/mol and 75.2 kJ/mol,

respectively, higher in energy compared to the in-plane π-radical (SOMO: $7b_1$), in which the additional electron is delocalized. The calculated energy minimum structure of the non-constrained radical mono-anion $[IMe^{Me}\text{-}CS_2]^{\bullet-}$ confirms a slightly twisted conformation with a ∡NCCS dihedral angle of 29.7 °, which is favored by 10.3 kJ/mol over the symmetry-restricted co-planar form.

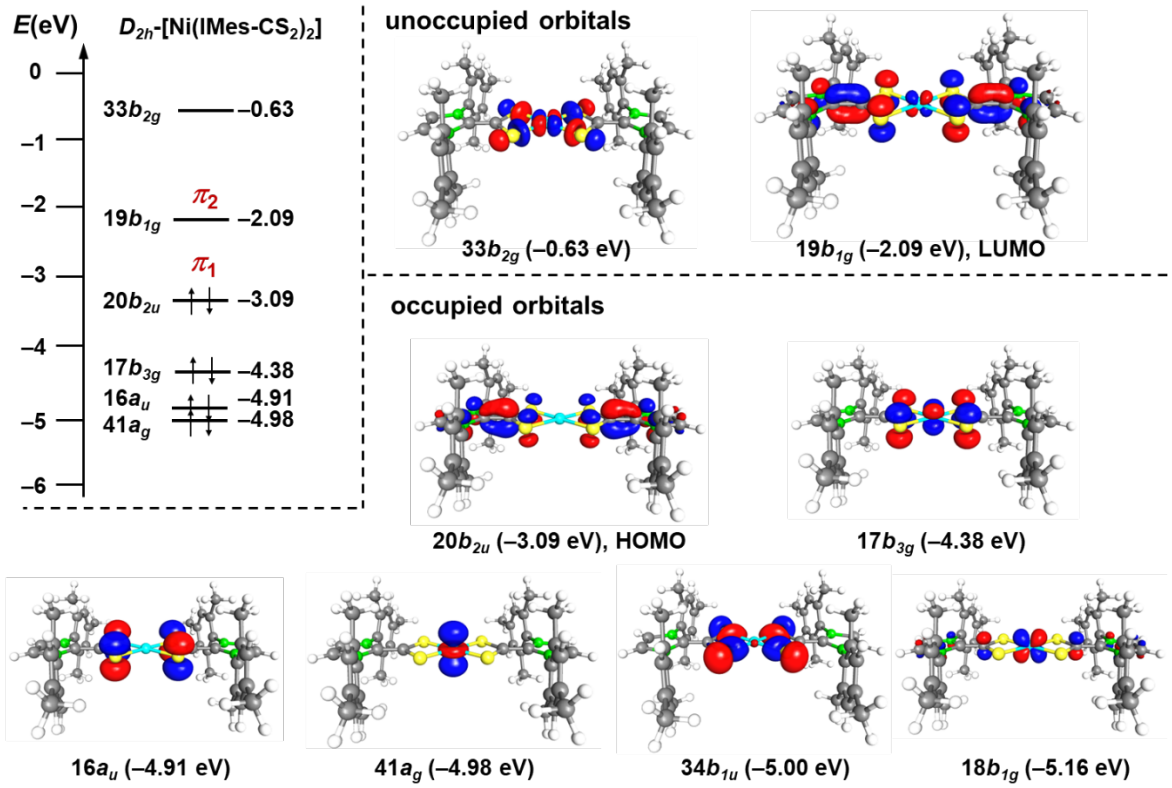
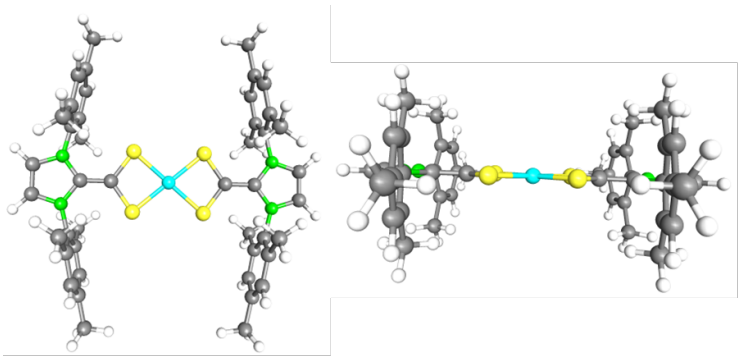


Figure S3. Molecular orbital diagram obtained from DFT calculations at the B3-LYP//def2-TZVP(Ni)/def2-SVP(C,H,N,S) level of theory for geometry-optimized D_{2h}-symmetric $[Ni(IMes\text{-}CS_2)_2]$ (**3c**) and relevant molecular orbitals of this complex.



D_{2h}-[Ni(IMes-CS_2)$_2$]
= [Ni(IMes-CS_2)$_2$]
closed shell singlet

d(Ni–S) = 2.2202 Å

d(C–S) = 1.7483 Å

d(C–C) = 1.4019 Å

∡(S–Ni–S) = 79.34°, 100.66°

∡(S–C–S) = 108.32°

[Ni(IMes-CS_2)$_2$]
singlet diradical

d(Ni–S) = 2.2477 Å

d(C–S) = 1.7470 Å

d(C–C) = 1.4050 Å

∡(S–Ni–S) = 78.80°, 101.20°

∡(S–C–S) = 109.48°

[Ni(IMes-CS_2)$_2$]
triplet

d(Ni–S) = 2.2607–2.2608 Å

d(C–S) = 1.7469–1.7470 Å

d(C–C) = 1.4058 Å

∡(S–Ni–S) = 78.53°, 101.47°

∡(S–C–S) = 109.98°

[Ni(IMes-CS_2)$_2$]
quintet

d(Ni–S) = 2.3956 Å

d(C–S) = 1.7493 Å

d(C–C) = 1.4113 Å

∡(S–Ni–S) = 75.57°, 104.43°

∡(S–C–S) = 114.08°

Figure S4. Changes in the most important metric parameter for geometry-optimized [Ni(IMes-CS_2)$_2$] (**3c**) for the closed shell singlet, open shell diradical singlet, triplet, and quintet state calculated at the B3-LYP//def2-TZVP(Ni)/def2-SVP(C,H,N,S) level of theory).

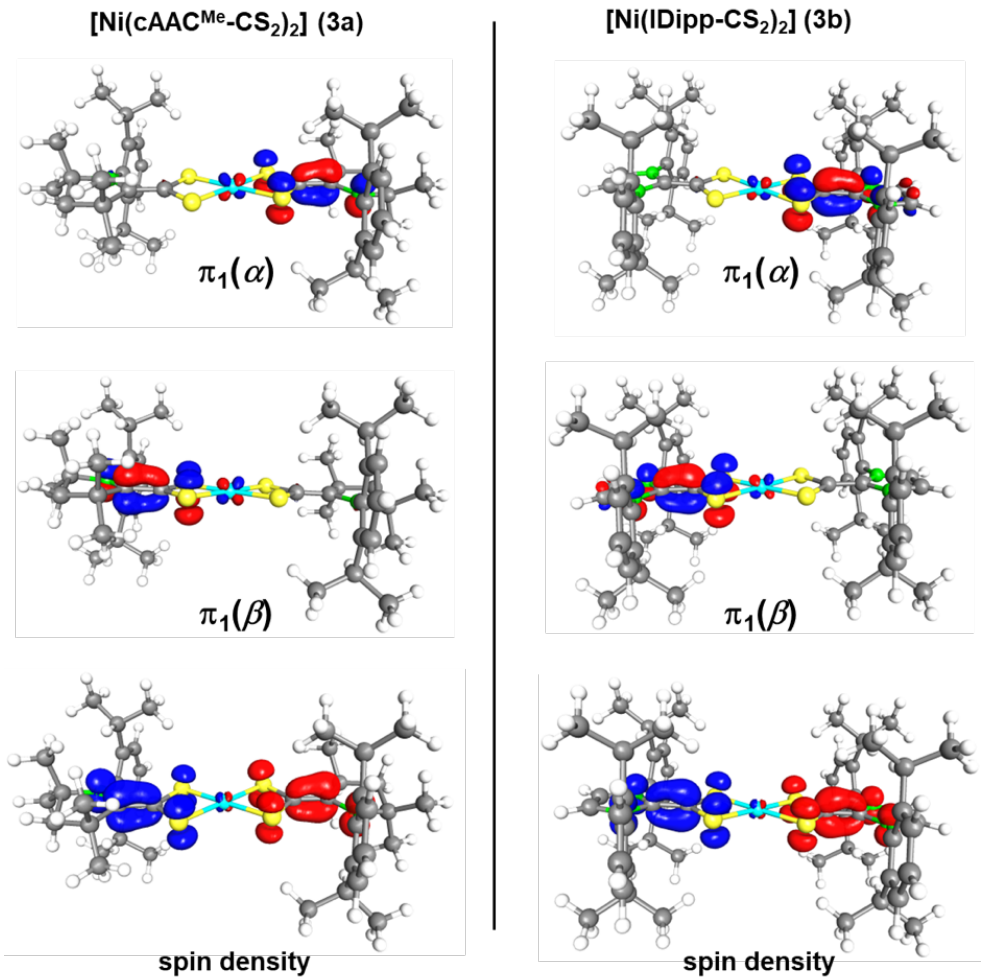


Figure S5. The π_1 spin orbitals $\pi_1(\alpha)$ and $\pi_1(\beta)$ as well as the spin densities (blue: spin up; red: spin down) of the singlet diradical ground states of [Ni(cAAC^{Me}-CS$_2$)$_2$] (**3a**) and [Ni(IDipp-CS$_2$)$_2$] (**3b**) calculated at the B3-LYP//def2-TZVP(Ni)/def2-SVP(C,H,N,S) level of theory.

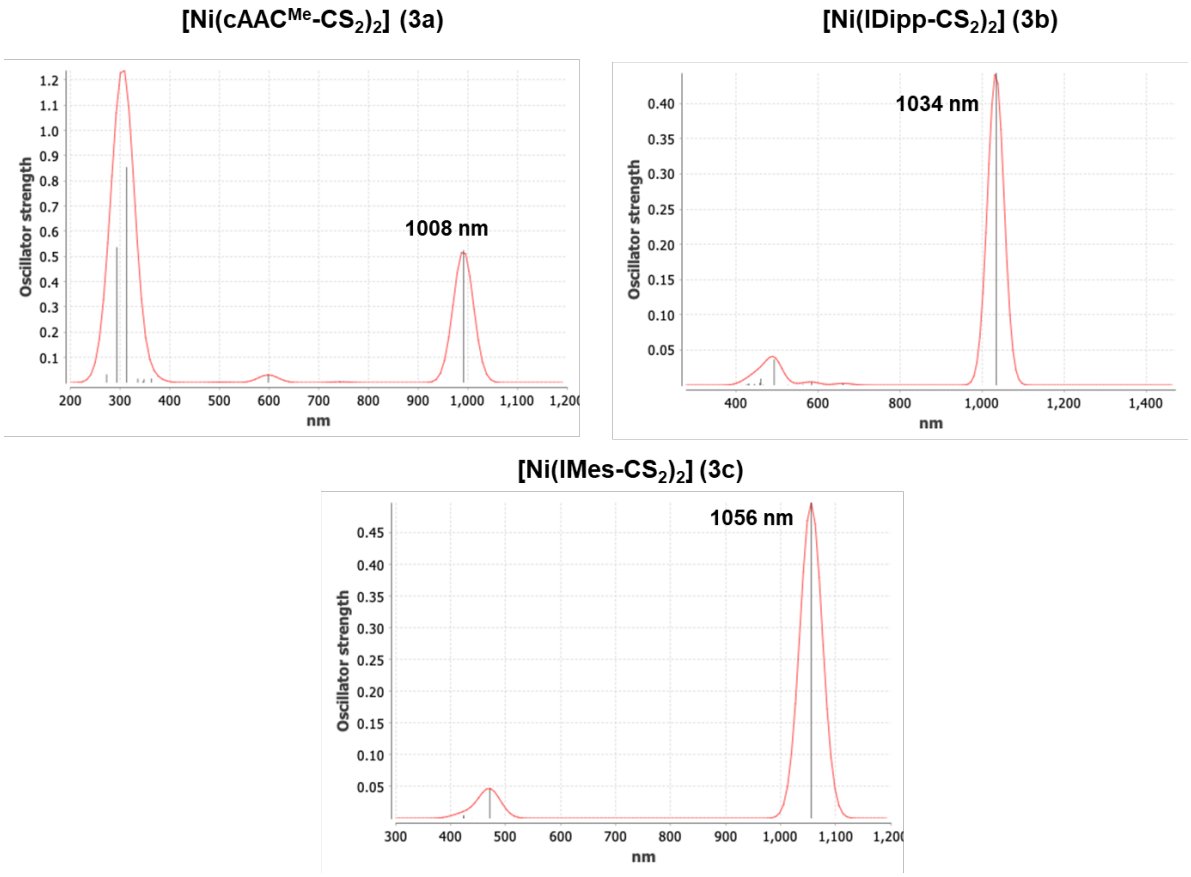


Figure S6. TD-DFT (PBE0-D3BJ//def2-TZVPP(Ni)/def2-TZVP(C,H,N,S)/COSMO(benzene)) calculated UV/VIS/NIR spectra of [Ni(cAAC^{Me}-CS_2)$_2$] (**3a**), [Ni(IDipp-CS_2)$_2$] (**3b**), and [Ni(IMes-CS_2)$_2$] (**3c**), which predict characteristic intense absorptions for the complexes **3a–c** in the NIR region at 1008 nm (**3a**), 1034 nm (**3b**) and 1056 nm (**3c**).

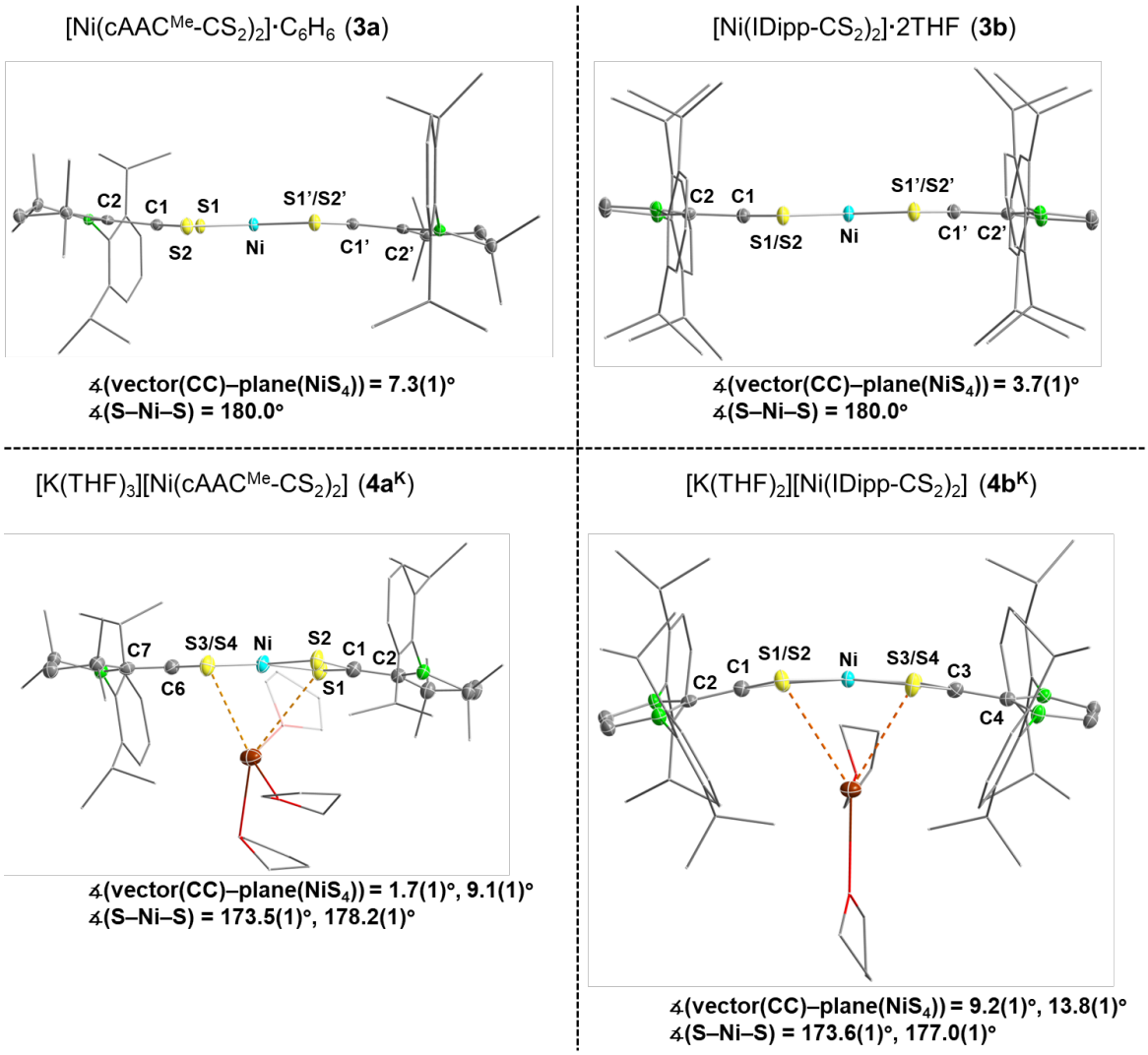


Figure S7. Side-on perspectives on the molecular structures of neutral and monoanionic *bis*-carbene-CS_2 complexes **3a**–**b** *vs.* **4a**–**b**^{K} and differences in the structural distortion as indicated by the angle ∡(vector(CC)–plane(NiS_4)) between the vector given by the bond between the carbene and the CS_2 carbon atoms and the central NiS_4 plane as well as the angles ∡(S–Ni–S) between *trans*-aligned nickel-sulfur bonds.

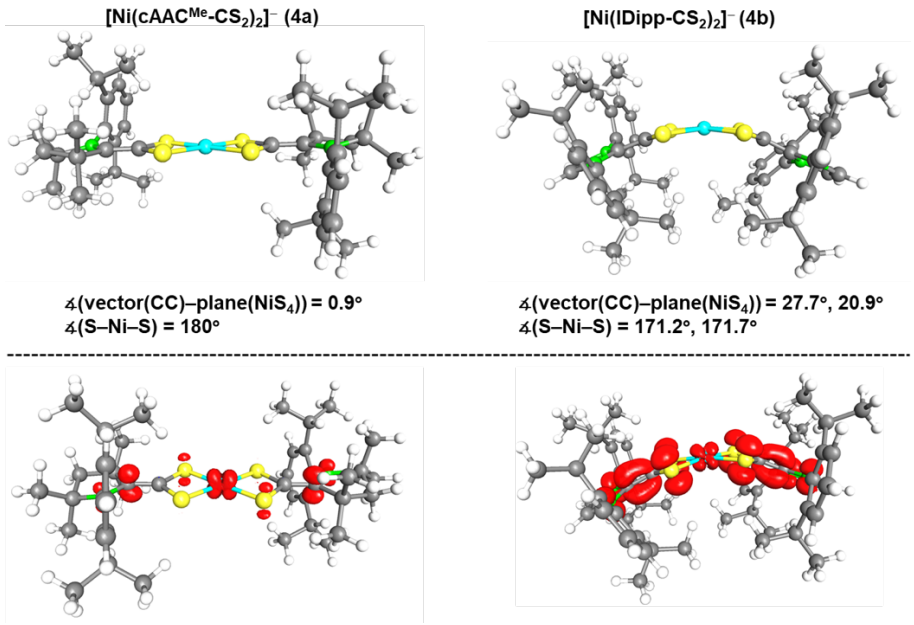


Figure S8. Geometry-optimized (PBE(0)-D3(BJ)//def2-TZVP(Ni)/def2-SVP(C,H,N,S); top) nickelates $[Ni(cAAC^{Me}\text{-}CS_2)_2]^-$ (**4a**) and $[Ni(IDipp\text{-}CS_2)_2]^-$ (**4b**) and structural distortion parameters (∡(vector(CC)–plane(NiS_4) and ∡(S–Ni–S)) and their DFT calculated spin densities (bottom).

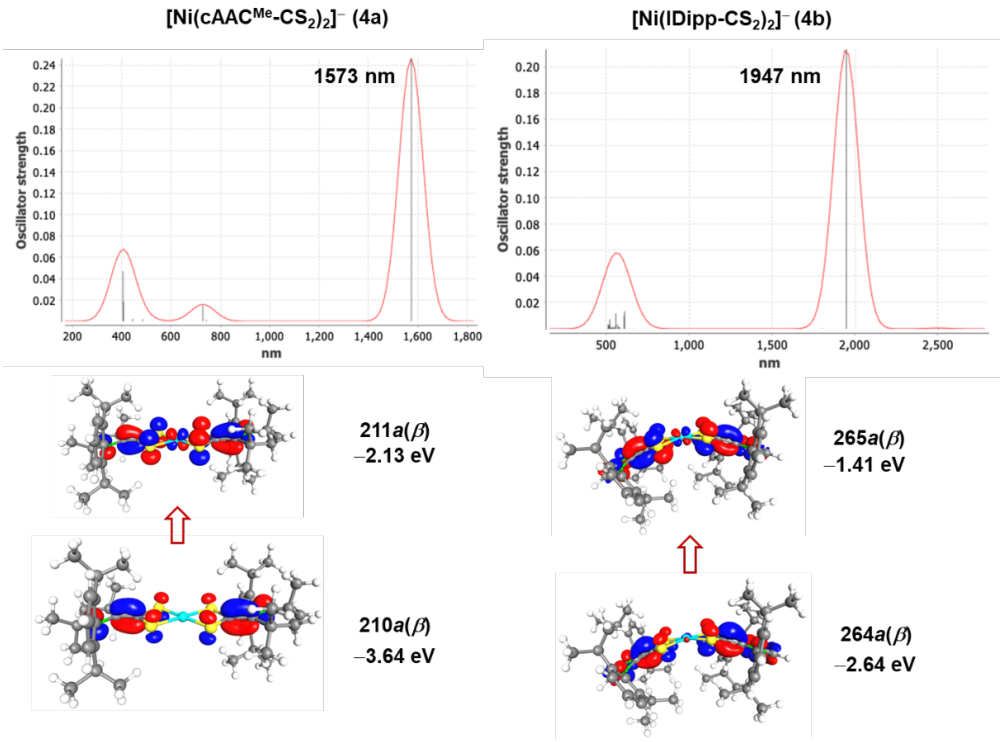


Figure S9. Top: TD-DFT (PBE0-D3BJ//def2-TZVPP(Ni)/def2-TZVP(C,H,N,S)/COSMO(THF)) calculated UV/VIS/NIR spectra of $[Ni(cAAC^{Me}\text{-}CS_2)_2]^-$ (**4a**) and $[Ni(IDipp\text{-}CS_2)_2]^-$ (**4b**), which predict characteristic intense absorptions of the complexes **4a** and **4b** in the NIR region at 1573 nm (**4a**), 1947 nm (**4b**). These absorptions are shifted to higher energies compared to the neutral nickel complexes at 1008 nm (**3a**) and 1034 nm (**3b**). Bottom: Transitions from the π_1 to the π_2 orbital associated with these NIR absorptions.

Table S1. Relative energies (ΔE in kJ/mol) and S^2 statistics of geometry-optimized complexes [Ni(NHC-$CS_2)_2$] NHC = $cAAC^{Me}$ (**3a**), IDipp (**3b**), IMes (**3c**) in their singlet diradical (oss = open shell singlet), closed shell (cs), triplett and quintet state at the PBE0-D3BJ//def2-TZVP(Ni)/def2-SVP(C,H,N,S) and B3-LYP//def2-TZVP(Ni)/def2-SVP(C,H,N,S) level of theory.

		PBE0-D3(BJ)		**B3-LYP**	
Cmpd.	**Spin**	**ΔE**	**S^2**	**ΔE**	**S^2**
3a	oss	0.00	0.882	0.00	0.844
	cs	26.87		19.82	
	t	7.80	2.008	8.61	2.006
	q	47.57	6.014	59.76	6.013
3b	oss	0.00	0.866	0.00	0.866
	cs	21.24		20.95	
	t	15.18	2.076	7.28	2.076
	q	27.50	6.017	55.47	6.012
3c	oss	0.00	0.752	0.00	0.867
	cs	27.54		21.21	
	t	7.16	2.092	7.22	2.007
	q	39.20	6.014	54.03	6.011

Table S2. Relative energies (ΔE in kJ/mol) and S^2 statistics of geometry-optimized complexes [Ni(NHC-$CS_2)_2$] NHC = $cAAC^{Me}$ (**3a**), IDipp (**3b**), IMes (**3c**) in their singlet diradical (oss = open shell singlet), closed shell (cs), triplett and quintet state at the PBE0-D3BJ//def2-TZVPP(Ni)/def2-TZVP(C,H,N,S) and B3-LYP//def2-TZVPP(Ni)/def2-TZVP(C,H,N,S) level of theory.

		PBE0-D3(BJ)		**B3-LYP**	
Cmpd.	**Spin**	ΔE	S^2	ΔE	S^2
3a	oss	0.00	0.848	0.00	0.797
	cs	15.75		15.75	
	t	10.12	2.001	11.28	2.010
	q	61.30	6.016	73.17	6.015
3b	oss	0.00	0.822	0.00	0.806
	cs	18.59		16.71	
	t	23.26	2.879	44.13	2.838
	q	58.36	6.018	63.92	6.015
3c	oss	0.00	0.845	0.00	0.813
	cs	22.04		16.44	
	t	50.96	2.960	64.55	2.94
	q	52.28	6.017	66.26	6.014

In the case that spin-contamination of the singlet state comes exclusively from the triplet state a value of $S^2 = 0.80$ would mean that the admixture is 40% of the triplet state into the singlet state ($S^2 = (1–x)0 + 2x = 2x$; for $S^2 = 0.8$: $x = 0.40$; 40% admixture).

In the case that spin-contamination of the triplet state comes exclusively from the quintet state a value of $S^2 = 2.90$ would mean that the admixture is 45% of the quintet state into the triplet state ($S^2 = (1–x)2 + 6x = 4x + 2$; for $S^2 = 2.90$: $x = 0.45$; 45% admixture).

Table S3. Wiberg bond indices (WBI) of the $C_{carbene}$–C_{CS2} (C–C), C–N, and C–S bond calculated at the PBE0-D3BJ//def2-TZVP(Ni)/def2-SVP(C,H,N,S) level of theory for the compounds cAAC^{Me}-CS_2 (**1a**), IDipp-CS_2 (**1b**), and IMes-CS_2 (**1c**), complexes [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS_2)] (**2a**), [Ni(I*i*Pr)$_2$(IDipp-CS_2)] (**2b**), [Ni(I*i*Pr)$_2$(IMes-CS_2)] (**2c**), [Ni(I*i*Pr)$_2$(IPr-CS_2)] (**2f**), [Ni(cAAC^{Me}-CS_2)$_2$] (**3a**), [Ni(IDipp-CS_2)$_2$] (**3b**), and [Ni(IMes-CS_2)$_2$] (**3c**), and of the nickelates [Ni(cAAC^{Me}-CS_2)$_2$]$^-$ (**4a**), and [Ni(IDipp-CS_2)$_2$]$^-$ (**4b**)

Compound	WBI(C–C)	WBI (C–N)	WBI (C–S)
1a	0.95	1.44	1.48 (avg.)
1b	0.95	1.25	1.48 (avg.)
1c	0.95	1.26	1.49 (avg.)
2a	1.83	1.04	1.02–1.03
2b	1.73	1.02	1.02
2c	1.76	1.03	1.01
2f	1.73	1.07	1.00
3a	1.45	1.28	1.20–1.22
3b	1.40	1.13	1.18–1.20
3c	1.44	1.13	1.18
4a	1.70	1.07	1.09
4b	1.59	1.04	1.09

2 Experimental Section

2.1 General Information

All reactions and subsequent manipulations involving organometallic reagents were performed under argon atmosphere by using standard Schlenk techniques or in a Glovebox (Innovative Technology Inc. and MBraun Uni Lab) as reported previously.[1] All reactions were carried out in oven-dried glassware. Toluene, *n*-hexane and THF were obtained from a solvent purification station (Innovative Technology) by purification through alumina columns. The deuterated solvents were purchased from Sigma-Aldrich and dried over molecular sieves. Benzene was dried over sodium and freshly distilled before use. The starting materials were prepared according to published procedures (*N*-alkyl and *N*-aryl substituted imidazole-based NHCs[2], cAAC^{Me}[3], [Ni(COD)$_2$][4], [Ni(I*i*Pr)$_2$(η^2-C$_2$H$_4$)][5]). BI*i*Pr[6] and BIMe[7] were prepared in modified literature procedures. The azolium-2-dithiocarboxylates were prepared according to the earlier reported modified general method.[8] Elemental analyses were performed in the microanalytical laboratory of the University of Würzburg with an Elementar Vario Micro Cube. Further information on analytical methods (NMR, EPR, IR, CV, UV/VIS/NIR, HRMS, SC-XRD and quantum chemical calculations) is found in the general information sub-sections of the respective analytical sections.

2.2 Experimental details

Literature known compounds and starting materials:

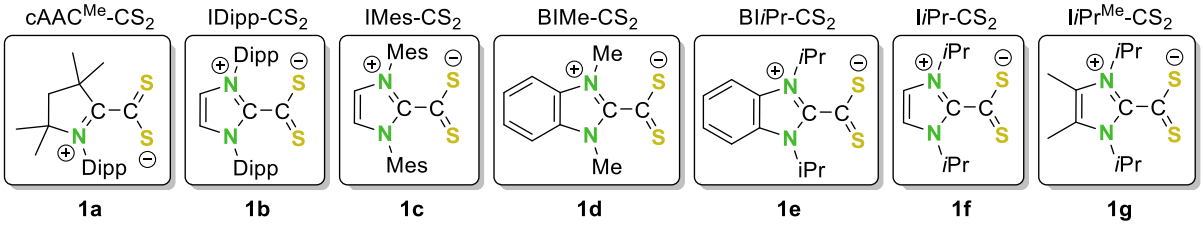
Modified literature procedure for the synthesis of BI*i*Pr[6]

$[H^+BI\textit{i}Pr]I^-$ (2.00 g, 6.06 mmol, 1.0 eq.) was dissolved in THF (10 mL) and slowly added to a suspension of NaH (159.9 mg, 6.66 mmol, 1.1 eq.) and KO*t*Bu (34.0 mg, 302.8 *µ*mol, 0.05 eq.) in THF (10 mL) and stirred for 18 hours at room temperature. After removal of all volatiles *in vacuo* the residue was sublimed at 90 °C and 10^{-3} hPa at a sublimation finger cooled to –10 °C to afford 1,3-di-*iso*-propylbenzimidazolin-2-ylidene (BI*i*Pr) as a colorless microcrystalline powder. **Yield**: 56% (694.0 mg, 3.39 mmol), colorless microcrystalline powder. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 7.06 (br., 4H, CH_{aryl}), 4.42 (sept, $^3J_{H\text{-}H}$ = 6.5 Hz, 2H, C$H_{methine}$), 1.53 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, $C_{methine}$-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 222.4 (N*C*N), 135.2 ($C_{backbone}$), 121.1 ($C_{4,aryl}$), 110.3 ($C_{5,aryl}$), 49.6 ($C_{methine}$), 23.4 ($C_{methine}$-*C*H$_3$) ppm. The obtained spectroscopical data match those previously reported.[6]

Modified literature procedure for the synthesis of {BIMe}$_2$[7]

$[H^+BIMe]I^-$ (5.00 g, 18.2 mmol, 1.0 eq.) was dissolved in THF (30 mL) and slowly added to a suspension of NaH (481.5 mg, 20.1 mmol, 1.1 eq.) and KO*t*Bu (102.4 mg, 912.1 *µ*mol, 0.05 eq.) in THF (30 mL) and stirred for 18 hours at room temperature. After removal of all volatiles *in vacuo* the residue was sublimed at 145 °C and 10^{-3} hPa at a sublimation finger to afford the *N*, *N*, *N*, *N*-tetramethyltetraazafulvalene {BIMe}$_2$ as an orange microcrystalline powder. **Yield**: 55% (1.46 g, 2.49 mmol), orange microcrystalline powder. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 6.83–6.79 (m, 4H, CH_{aryl}), 6.46–6.42 (m, 4H, CH_{aryl}), 2.68 (s, 12H, N-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 143.6 (N_2C=*C*N_2), 124.5 ($C_{backbone}$), 121.1 ($C_{4,aryl}$), 108.6 ($C_{5,aryl}$), 36.0 (N-*C*H$_3$) ppm. The obtained spectroscopical data match those previously reported.[7]

General synthesis for azolium-2-dithiocarboxylates[8]



CS_2 (2.0 eq.) was added to a solution of the carbene (1.0 eq., batch sizes *ca*. 0.5–4.0 g) in THF (20 mL). After stirring for 1 h at room temperature, all volatiles were evaporated *in vacuo.* The residue was suspended in *n*-hexane. After filtration the residue was washed with *n*-hexane (3 x 10 mL) and dried *in vacuo* to afford the azolium-2-dithiocarboxylates (**1a**–**g**) as orange to red solids in yields between 72% and 94%. The spectroscopical data obtained for **1a**–**d** and **1f**–**g** match the values reported in literature.[8,9]

cAAC^{Me}-CS_2 (1a)[8c]

cAAC^{Me}-CS_2 (**1a**) was synthesized according to the general route using 1.0 eq. of cAAC^{Me} (3.90 g, 13.7 mmol) in THF (25 mL) and 2.0 eq. of CS_2 (2.08 g, 1.65 mL, 27.3 mmol). Single crystals of the product suitable for X-ray diffraction were grown by evaporation of a saturated solution of the product in dichloromethane. **Yield**: 79% (3.91 g, 10.81 mmol), orange microcrystalline powder. **Elemental analysis**: $C_{21}H_{31}NS_2$ [361.61 g/mol] found (calc.): C 69.69 (69.75), H 8.80 (8.64), N 3.89 (3.87), S 17.89 (17.73) %. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 7.04–7.00 (m, 1H, CH_{aryl}), 6.94–6.92 (m, 2H, CH_{aryl}), 3.01 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, C$H_{methine}$), 1.55 (s, 2H, CH_2), 1.54 (s, 6H, N-C(CH_3)$_2$), 1.45 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, C$_{methine}$-CH_3), 1.09 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, C$_{methine}$-CH_3), 0.93 (s, 6H, C-C(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 226.6 (*C*S_2), 187.5 (C*C*N), 147.1 (*C*$_{aryl}$), 138.3 (*C*$_{aryl}$), 130.5 (*C*$_{aryl}$), 130.0 (*C*$_{aryl}$), 126.3 (*C*$_{aryl}$), 125.0 (*C*$_{aryl}$), 75.6 (N-*C*(CH$_3$)$_2$), 50.9 (N-C(*C*H$_3$)$_2$), 47.8 (*C*-(CH$_3$)$_2$), 33.0 (N-C(*C*H$_3$)$_2$), 29.8 (*C*$_{methine}$), 28.5 (*C*H_2), 28.4 (C$_{methine}$-*C*H$_3$), 25.7 (C$_{methine}$-*C*H$_3$) ppm. **IR** (ATR): $\tilde{\nu}$ = 2963 (m), 2923 (w), 2865 (w), 1584 (w), 1527 (s), 1472 (m), 1457 (m), 1388 (m), 1374 (m), 1366 (m), 1345 (m), 1326 (m), 1281 (w), 1210 (w), 1193 (w), 1178 (m), 1148 (m), 1124 (m), 1094 (m), 1075 (m), 1035 (vs), 1019 (s), 979 (m), 960 (m), 948 (m), 809 (m), 772 (s), 731 (m), 715 (w), 698 (s), 602 (m), 564 (m), 542 (m), 485 (m), 436 (m) cm^{-1}. **UV/VIS/NIR** (C_6H_6): λ_{abs} = 306, 381 (br.) nm. **CV** (*v* = 25 mV/s, THF): *U* = –2.30 (q. rev., 1e$^-$), –1.90 (q. rev., 1e$^-$) V.

IDipp-CS_2 (1b)[8a]

IDipp-CS_2 (**1b**) was synthesized according to the general route using 1.0 eq. of IDipp (2.00 g, 5.15 mmol) and 2.0 eq. of CS_2 (783.7 mg, 621.9 µL, 10.3 mmol). **Yield**: 91% (2.19 g, 4.70 mmol), red solid. **^{1}H NMR** (400.1 MHz, $CDCl_3$): δ = 7.43 (m, 2H, *para*-C*H*), 7.23 (m, 4H, *meta*-C*H*), 7.01 (s, 2H, C$H_{backbone}$), 3.00 (sept, 4H, $^3J_{H\text{-}H}$ = 8.0 Hz, C$H_{methine}$), 1.33 (d, 12H, $^3J_{H\text{-}H}$ = 8.0 Hz, C$H_{3,methine}$), 1.15 (d, 12H, $^3J_{H\text{-}H}$ = 8.0 Hz, $C_{methine}$-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ = 219.7 (CS_2), 149.1 (N*C*N), 146.5 (*ortho*-*C*H$_{aryl}$), 131.4 (*para*-*C*H$_{aryl}$),130.8 (*ipso*-C_{aryl}), 124.6 (*meta*-C_{aryl}), 120.6 (*C*H$_{backbone}$), 29.5 (*C*H$_{methine}$), 26.0 (*C*H$_{3,Dipp}$), 22.8 (*C*H$_{3,Dipp}$) ppm. **CV** (v = 50 mV/s, THF): U = –2.76 (q. rev., 1e$^-$), –2.22 (q. rev., 1e$^-$) V.

IMes-CS_2 (1c)[8a]

IMes-CS_2 (**1c**) was synthesized according to the general route using 1.0 eq. of IMes (622.8 mg, 2.05 mmol) and 2.0 eq. of CS_2 (311.5 mg, 247.2 µL, 4.09 mmol). **Yield**: 81% (633.0 mg, 1.66 mmol), red solid. **^{1}H NMR** (400.1 MHz, d_6-DMSO): δ = 7.84 (s, 2H, C$H_{backbone}$), 7.03 (s, 4H, *meta*-C*H*), 2.28 (s, 6H, *para*-CH_3), 2.23 (s, 12H, *ortho*-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, d_6-DMSO): δ = 221.6 (CS_2), 146.7 (N*C*N), 139.8 (C_{aryl}), 135.3 (C_{aryl}),131.1 (C_{aryl}), 129.0 (*meta*-*C*H$_{aryl}$), 121.2 (*C*H$_{backbone}$), 20.5 (*para*-*C*H$_3$), 18.1 (*ortho*-*C*H$_3$) ppm. **CV** (v = 10 mV/s, THF): U = –2.70 (q. rev., 1e$^-$), –2.27 (q. rev., 1e$^-$) V.

BIMe-CS_2 (1d)[9b]

BIMe-CS_2 (**1d**) was synthesized according to the general procedure using 1.0 eq. of {BIMe}$_2$ (545.0 mg, 1.87 mmol) and 4.0 eq. of CS_2 (567.6 mg, 450.5 µL, 7.46 mmol). **Yield**: 94% (775.4 mg, 3.49 mmol), red solid. Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution of the product in dichloromethane. **^{1}H NMR** (400.1 MHz, $CDCl_3$): δ = 7.57 (m, 2H, C$H_{aryl\text{-}backbone}$), 7.56 (m, 2H, C$H_{aryl\text{-}backbone}$), 3.94 (s, 6H, N-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ = 223.8 (*C*S$_2$), 153.0 (N*C*N), 130.8 ($C_{backbone}$), 126.5 ($C_{4,aryl}$), 112.2 ($C_{5,aryl}$), 31.5 (N-*C*H$_3$) ppm. **CV** (v = 25 mV/s, THF): U = –2.37 (q. rev., 1e$^-$), –2.16 (q. rev., 1e$^-$) V.

I*i*Pr-CS_2 (1f)[9c]

I*i*Pr-CS_2 (**1f**) was synthesized according to the general route using 1.0 eq. of I*i*Pr (1.00 g, 1.00 mL, 6.57 mmol) and 2.0 eq. of CS_2 (1.00 g, 793.8 µL, 13.1 mmol). **Yield**: 75% (1.12 g, 4.92 mmol), red solid. **^{1}H NMR** (400.1 MHz, $CDCl_3$): δ = 6.98 (s, 2H, C$H_{backbone}$), 4.94 (sept,

2H, $^{3}J_{H\text{-}H}$ = 6.6 Hz, C$H_{methine}$), 1.49 (d, 12H, $^{3}J_{H\text{-}H}$ = 6.6 Hz, $C_{methine}$-CH_3) ppm. **CV** (v = 10 mV/s, THF): U = –2.61 (q. rev., 2e$^-$) V.

I*i*Pr^{Me}-CS$_2$ (1g)[9a]

I*i*Pr^{Me}-CS$_2$ (**1g**) was synthesized according to the general route using 1.0 eq. of I*i*Pr^{Me} (695.0 mg, 3.85 mmol) and 2.0 eq. of CS_2 (586.9 mg, 465.8 µL, 7.71 mmol). **Yield**: 85% (837.1 mg, 3.26 mmol), red solid. **^{1}H NMR** (400.1 MHz, $CDCl_3$): δ = 5.01 (sept, 2H, $^{3}J_{H\text{-}H}$ = 7.1 Hz, C$H_{methine}$), 2.29 (s, 6H, $C_{backbone}$-CH_3), 1.55 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.1 Hz, $C_{methine}$-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ = 229.2 (CS_2), 156.7 (N*C*N), 122.9 ($C_{backbone}$), 51.1 (*C*H$_{methine}$), 21.1 ($C_{methine}$-CH_3), 10.2 (*C*H$_3$) ppm. **CV** (v = 50 mV/s, THF): U = –2.58 (q. rev., 2e$^-$) V.

New Compounds:

Synthesis of BI*i*Pr-CS$_2$ (1e)

BI*i*Pr-CS$_2$ was prepared according to the general synthesis of carbene-CS$_2$ adducts published previously[8] using 1.0 eq. of BI*i*Pr (160.0 mg, 790.9 µmol) and 2.0 eq. of CS_2 (120.4 mg, 95.6 µL, 1.58 mmol). Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution of the product in dichloromethane, which confirms the structure reported in the CCDC.[10] **Yield**: 72% (158.0 mg, 567.5 µmol), red microcrystalline powder. **Elemental analysis**: $C_{14}H_{18}N_2S_2$ [278.43 g/mol] found (calc.): C 60.70 (60.39), H 6.58 (6.52), N 9.95 (10.06), S 22.71 (23.03). **^{1}H NMR** (400.1 MHz, $CDCl_3$): δ = 7.78–7.71 (m, 2H, C$H_{aryl\text{-}backbone}$), 7.53–7.42 (m, 2H, C$H_{aryl\text{-}backbone}$), 5.15 (sept, 2H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, C$H_{methine}$), 1.69 (d, 12H, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $C_{methine}$-CH_3) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ = 226.3 (CS_2), 152.2 (N*C*N),129.4 ($C_{backbone}$), 125.3 ($C_{4,aryl}$), 115.0 ($C_{5,aryl}$), 51.5 ($C_{methine}$), 20.6 ($C_{methine}$-*C*H$_3$) ppm. **IR** (ATR): $\tilde{\nu}$ = 2979 (vw), 2930 (vw), 2873 (vw), 1494 (m), 1451 (s), 1386 (m), 1367 (m), 1312 (m), 1294 (w), 1247 (vw), 1194 (vw), 1172 (w), 1139 (s), 1114 (w), 1094 (s), 1055 (vs), 959 (s), 921 (m), 890 (w), 833 (vw), 741 (vs), 715 (m), 680 (m), 647 (m), 571 (w), 503 (m), 475 (w), 420 (s) cm^{-1}. **UV/VIS/NIR** (THF): λ_{abs} = 313, 362, 446, 520 nm. **CV** (v = 10 mV/s, THF): U = –2.43 (q. rev., 2e$^-$) V.

Synthesis of [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (2a)

A mixture of cAAC^{Me}-CS$_2$ (110.0 mg, 304.2 µmol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C_2H_4)] (125.0 mg, 319.4 µmol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for 4 hours at room

temperature. All volatiles were removed *in vacuo* and the residue was suspended in *n*-hexane. After filtration the residue was washed with *n*-hexane (3 x 10 mL) and dried *in vacuo* to produce [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (**2a**) as a pale yellow solid. Single crystals of **2a** suitable for X-ray diffraction were grown by diffusion of *n*-hexane into a saturated solution of the product in THF. **Yield**: 72% (158.0 mg, 218.0 *µ*mol), pale yellow solid. **Elemental analysis**: $C_{39}H_{63}N_5NiS_2$ [724.78 g/mol] found (calc.): C 64.68 (64.63), H 8.89 (8.76), N 9.69 (9.66), S 8.71 (8.85)%. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 7.18 (m, 3H, C$H_{aryl,Dipp}$), 6.18 (s, 2H, C$H_{backbone,IiPr}$), 6.12 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, C$H_{methine,IiPr}$), 6.10 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, C$H_{methine,IiPr}$), 6.09 (s, 2H, C$H_{backbone,IiPr}$), 3.80 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 2H, C$H_{methine,cAAC}$), 2.13 (s, 6H, N-C-C$H_{3,cAAC}$), 2.00 (s, 2H, C$H_{2,cAAC}$), 1.75 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, C$_{methine}$-C$H_{3,cAAC}$), 1.39 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, C$_{methine}$-C$H_{3,cAAC}$), 1.35 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, C$_{methine}$-C$H_{3,IiPr}$), 1.28 (s, 6H, C-C$H_{3,cAAC}$), 1.20 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, C$_{methine}$-C$H_{3,IiPr}$), 0.83 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, C$_{methine}$-C$H_{3,IiPr}$), 0.75 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 6H, C$_{methine}$-C$H_{3,IiPr}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 183.9 (N*C*N$_{IiPr}$) 183.4 (N*C*N$_{IiPr}$),149.5 (*ortho*-C$_{aryl,cAAC}$), 141.6 (*ipso*-C$_{aryl,cAAC}$), 139.7 (*C*=CS$_2$), 125.4 (*para*-C$_{aryl,cAAC}$), 123.6 (*meta*-C$_{aryl,cAAC}$), 116.4 (C$_{backbone,IiPr}$), 113.4 (*C*S$_2$), 61.9 (C-*C*-CH$_{3,cAAC}$), 60.5 (*C*H$_{2,cAAC}$), 51.7 (*C*H$_{methine,IiPr}$), 43.0 (N-*C*-CH$_{3,cAAC}$), 30.3 (N-C-*C*H$_{3,cAAC}$), 30.0 (C-C-*C*H$_{3,cAAC}$), 28.7 (C$_{methine,cAAC}$), 25.6 (C$_{methine}$-*C*H$_{3,cAAC}$), 24.8 (C$_{methine}$-*C*H$_{3,cAAC}$), 24.8 (C$_{methine}$-*C*H$_{3,IiPr}$), 24.4 (C$_{methine}$-*C*H$_{3,IiPr}$), 22.3 (2 x C$_{methine}$-*C*H$_{3,IiPr}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3073 (vw), 2968 (m), 2929 (m), 2863 (w), 1678 (w, br.), 1585 (vw), 1465 (m), 1442 (w), 1415 (m), 1391 (m), 1369 (m), 1323 (w), 1289 (m), 1211 (vs), 1131 (s), 1105 (w), 1022 (m), 993 (w), 955 (vw), 878 (w), 798 (w), 766 (w), 692 (s), 629 (w), 606 (vw), 572 (m), 470 (vw), 427 (w) cm^{-1}. **UV/VIS/NIR** (C_6H_6): λ_{abs} = 575, 359, 292 nm.

Synthesis of [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)] (2b)

A mixture of IDipp-CS$_2$ (100.0 mg, 215.2 *µ*mol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C$_2$H$_4$)] (88.4 mg, 225.9 *µ*mol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for 18 hours at room temperature. All volatiles were removed *in vacuo* and the residue was dispersed in Et$_2$O (30 mL) and filtrated. *n*-Hexane (15 mL) was added and the solution was stored for crystallization at –30 °C affording [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)] (**2b**) as brown needles that were collected by filtration and dried *in vacuo*. Single crystals suitable for X-ray diffraction were grown from a saturated solution of the product in benzene. NMR data were collected from a crystalline sample (**2b**·**tol**) that was obtained from recrystallization with toluene containing one equivalent of co-crystallized toluene. **Yield**: 65% (116.1 mg, 140.2 *µ*mol), brown needles. **Elemental analysis**: $C_{46}H_{68}N_6NiS_2$ [827.91 g/mol] found (calc.): C 66.08 (66.74), H 7.59 (8.28), N 10.98 (10.15), S 7.75 (7.74)%. **HRMS** (LIFDI): m/z found (calc.): [M]$^+$: 826.4257 (826.43); "[M]$^+$–I*i*Pr": 674.2956 (674.30); "[M]$^+$–IDipp-CS$_2$": 362.1960 (363.18). **^{1}H NMR**

(400.1 MHz, C_6D_6): δ = 7.22–7.09 (m, 6H, C$H_{aryl,\ IDipp\text{-}CS2}$), 6.05 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, C$H_{methine,liPr}$), 6.03 (s, 4H, C$H_{backbone,liPr}$), 5.77 (s, 2H, C$H_{backbone,IDipp\text{-}CS2}$), 3.98 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, C$H_{methine,IDipp\text{-}CS2}$), 1.73 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, $CH_{methine}$-C$H_{3,IDipp\text{-}CS2}$), 1.40 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, $CH_{methine}$-C$H_{3,IDipp\text{-}CS2}$), 1.15 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, $CH_{methine}$-C$H_{3,liPr}$), 0.74 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, $CH_{methine}$-C$H_{3,liPr}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 183.9 (N*C*N$_{liPr}$), 149.4 (N*C*N$_{IDipp\text{-}CS2}$), 138.5 (*C*$_{aryl,IDipp\text{-}CS2}$), 127.4 (*C*$_{aryl,IDipp\text{-}CS2}$), 123.2 (*C*$_{aryl,IDipp\text{-}CS2}$), 117.3 (*C*$_{backbone,IDipp\text{-}CS2}$), 116.2 (*C*$_{backbone,liPr}$), 79.8 (*C*S$_2$), 51.4 (*C*$_{methine,liPr}$), 29.0 (*C*$_{methine,IDipp\text{-}CS2}$), 25.1 ($C_{methine}$-*C*H$_{3,IDipp\text{-}CS2}$), 24.0 ($C_{methine}$-*C*H$_{3,IDipp\text{-}CS2}$), 22.3 ($C_{methine}$-*C*H$_{3,liPr}$), 21.4 ($C_{methine}$-*C*H$_{3,liPr}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3159(vw), 3130 (vw), 2970 (m), 2913 (m), 2864 (m), 2278 (w), 1673 (w) 1629 (s), 1588 (w), 1566 (w), 1480 (m), 1462 (m), 1405 (s), 1368 (s), 1291 (m), 1266 (w), 1208 (vs), 1155 (m), 1127 (m), 1092 (m), 1019 (m), 992 (m), 884 (m), 846 (m), 811 (w), 728 (m), 699 (m), 686 (s), 638 (m), 574 (m), 498 (s), 438 (w) cm^{-1}.

Synthesis of [Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (2c)

A mixture of IMes-CS$_2$ (100.0 mg, 262.8 *µ*mol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C$_2$H$_4$)] (107.9 mg, 275.9 *µ*mol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for 18 hours at room temperature. All volatiles were removed *in vacuo* and the residue was dispersed in Et$_2$O (30 mL) and filtrated. *n*-Hexane (15 mL) was added and the solution was stored for crystallization at –30 °C affording [Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (**2c**) as a brown crystalline solid that was collected by filtration and dried *in vacuo*. The single crystals obtained this way were suitable for X-ray diffraction. **Yield**: 51% (195.4 mg, 134.5 *µ*mol), brown crystalline solid. **Elemental analysis**: $C_{40}H_{56}N_6NiS_2$ [743.74 g/mol] found (calc.): C 64.61 (64.60), H 8.06 (7.59), N 9.99 (11.30), S 7.56 (8.62)%. **HRMS** (LIFDI): m/z found (calc.): [M]$^+$: 742.3328 (742.34); "[M]$^+$–I*i*Pr": 590.2023 (590.20); "[M]$^+$–IMes-CS$_2$": 362.1962 (363.18). **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 6.80 (s, 4H, *meta*-C$H_{aryl,IMes}$), 6.06 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, C$H_{methine,liPr}$), 6.04 (s, 4H, C$H_{backbone,liPr}$), 5.66 (s, 2H, C$H_{backbone,IMes}$), 2.72 (s, 12H, *ortho*-C$H_{3,aryl}$), 2.05 (s, 6H, *para*-C$H_{3,aryl}$), 1.08 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, $C_{methine}$-C$H_{3,liPr}$), 0.56 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, $C_{methine}$-C$H_{3,liPr}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 183.4 (N*C*N$_{liPr}$), 138.8 (*ipso*-*C*$_{aryl,IMes}$), 137.9 (*ortho*-*C*$_{aryl,IMes}$), 135.2 (*para*-*C*$_{aryl,IMes}$), 130.0 (N*C*N$_{IMes}$), 128.5 (*meta*-*C*$_{aryl,IMes}$), 116.2 (*C*$_{backbone,liPr}$), 115.5 (*C*$_{backbone,IMes}$), 78.5 (*C*S$_2$), 51.5 (*C*$_{methine}$), 24.3 ($C_{methine}$-*C*H$_3$), 22.3 ($C_{methine}$-*C*H$_3$), 21.2 ppm. **IR** (ATR): $\tilde{\nu}$ = 3062 (vw), 2960 (m), 2928 (m), 2864 (m), 1677 (w), 1623 (m), 1582 (w), 1464 (m), 1419 (m), 1408 (m), 1388 (m), 1369 (m), 1292 (m), 1255 (m), 1208 (vs), 1173 (m), 1129 (m), 1111 (m), 1059 (m), 1022 (w), 992 (m), 880 (m), 799 (m), 757 (m), 718 (m), 699 (m), 684 (s), 640 (m), 572 (w), 552 (w), 501 (w), 420 (m) cm^{-1}.

Synthesis of [Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (2d)

A mixture of BIMe-CS$_2$ (150.0 mg, 674.7 *µ*mol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C$_2$H$_4$)] (277.2 mg, 708.4 *µ*mol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for 4 hours at room temperature. All volatiles were removed *in vacuo* and the residue was suspended in *n*-hexane (10 mL). After filtration the residue was washed with *n*-hexane (3 x 10 mL) and diethyl ether (3 x 10 mL) and dried *in vacuo* to produce [Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (**2d**) as a green solid. Single crystals of **2d** suitable for X-ray structure determination were grown by diffusion of *n*-hexane into a saturated solution of the product in THF. **Yield**: 76% (301.9 mg, 515.6 *µ*mol), green solid. **Elemental analysis**: $C_{28}H_{42}N_6NiS_2$ [584.50 g/mol] found (calc.): C 57.40 (57.44), H 7.45 (7.23), N 13.78 (14.35), S 10.17 (10.95)%. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 6.71 (m, 2H, C$H_{aryl,BIMe}$), 6.27 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, C$H_{methine,IiPr}$), 6.24 (s, 4H, C$H_{backbone,IiPr}$), 6.17 (m, 2H, C$H_{aryl,BIMe}$), 3.73 (s, 4H, N-C$H_{3,BIMe}$), 1.37 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, C$_{methine}$-C$H_{3,IiPr}$), 0.77 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, C$_{methine}$-C$H_{3,IiPr}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 181.2 (N*C*N$_{IiPr}$), 140.5 (*C*$_{backbone,BIMe}$), 136.1 (N*C*N$_{BIMe}$), 118.3 (*C*$_{4,aryl,BIMe}$), 116.4 (*C*$_{backbone,IiPr}$), 102.4 (*C*$_{5,aryl,BIMe}$), 86.0 (*C*S$_2$), 51.5 (*C*$_{methine,IiPr}$), 33.6 (N-CH$_{3,BIMe}$), 24.2 (C$_{methine}$-*C*H$_{3,IiPr}$), 21.9 (C$_{methine}$-*C*H$_{3,IiPr}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3163 (vw), 3119 (vw), 3090 (w), 3051 (vw), 2968 (m), 2928 (w), 2871 (w), 2109 (vw), 1699 (vw), 1623 (s), 1610 (s), 1563 (w), 1501 (s), 1465 (m), 1408 (s), 1391 (s), 1369 (m), 1297 (s), 1263 (w), 1237 (m), 1212 (vs), 1157 (m), 1129 (s), 1080 (w), 1015 (s), 994 (w), 957 (s), 906 (vw), 878 (w), 811 (vw), 728 (s), 720 (s), 702 (m), 688 (s), 676 (m), 631 (vw), 575 (w), 437 (w), 411 (w) cm^{-1}. **UV/VIS/NIR** (C_6H_6): λ_{abs} = 682, 409, 286 nm.

Synthesis of [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (2e)

A mixture of BI*i*Pr-CS$_2$ (150.0 mg, 538.7 *µ*mol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C$_2$H$_4$)] (221.3 mg, 565.7 *µ*mol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for 4 hours at room temperature. All volatiles were removed *in vacuo* and the residue was suspended in *n*-hexane (10 mL). After filtration the residue was washed with *n*-hexane (3 x 10 mL) and diethyl ether (3 x 10 mL) to produce [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (**2e**) as a green solid. **Yield**: 76% (264.0 mg, 411.5 *µ*mol), green solid. **Elemental analysis**: $C_{32}H_{50}N_6NiS_2$ [641.61 g/mol] found (calc.): C 59.24 (59.90), H 7.81 (7.86), N 12.79 (13.10), S 9.59 (9.99)%. **HRMS** (LIFDI): m/z found (calc.): [M]$^+$: 640.2867 (640.29); "[M]$^+$–I*i*Pr": 488.1560 (488.16); "[M]$^+$–IB*i*Pr-CS$_2$": 362.1963 (363.18). **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 6.69 (m, 2H, C$H_{aryl,BIiPr}$), 6.66 (m, 2H, C$H_{aryl,BIiPr}$), 6.24 (sept, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H, C$H_{methine,IiPr}$), 6.24 (s, 4H, C$H_{backbone,IiPr}$), 6.22 (sept, $^3J_{H\text{-}H}$ = 6.9 Hz, 2H, C$H_{methine,BIiPrBim}$), 1.47 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, C$_{methine}$-C$H_{3,BIiPr}$), 1.33 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, C$_{methine}$-C$H_{3,BIiPr}$), 0.73 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, C$_{methine}$-C$H_{3,BIiPr}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 181.8 (N*C*N$_{IiPr}$), 138.9 (*C*$_{backbone,BIiPr}$), 136.9 (N*C*N$_{BIiPr}$), 118.2 (*C*$_{4,aryl,BIiPr}$), 116.8 (*C*$_{backbone,BIiPr}$), 107.8 (*C*$_{5,aryl,BIiPr}$), 89.7 (*C*S$_2$), 51.8 (*C*$_{methine,IiPr}$), 48.5 (C$_{methine,BIiPr}$), 24.6 (C$_{methine}$-

$CH_{3,IiPr}$), 22.3 ($C_{methine}$-$CH_{3,IiPr}$), 20.8 ($C_{methine}$-$CH_{3,BIiPr}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3085 (w), 2967 (m), 2927 (w), 2869 (w), 2112 (vw), 1613 (m), 1593 (s), 1484 (s), 1465 (m), 1416 (s), 1391 (s), 1370 (m), 1318 (m), 1298 (m), 1262 (s), 1211 (vs), 1183 (s), 1160 (m), 1127 (s), 1091 (s), 1026 (m), 993 (m), 971 (m), 925 (w), 882 (m), 768 (vw), 723 (vs), 701 (m), 687 (s), 675 (m), 631 (w), 596 (w), 573 (m), 549 (vw), 529 (vw), 476 (vw), 431 (m), 413 (m) cm^{-1}. **UV/VIS/NIR** (C_6H_6): λ_{abs} = 670, 405, 290 nm.

Synthesis of [Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (2f)

A mixture of I*i*Pr-CS$_2$ (116.8 mg, 511.2 μmol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C_2H_4)] (200.0 mg, 511.2 μmol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for 18 hours at room temperature. All volatiles were removed *in vacuo* and the residue was suspended in Et_2O. After filtration the residue was washed with Et_2O (3 x 5 mL) and *n*-hexane (3 x 5 mL) to yield [Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (**2f**) as a green solid. **Yield**: 94% (199.9 mg, 336.4 μmol), green solid. **Elemental analysis**: $C_{28}H_{48}N_6NiS_2$ [591.55 g/mol] found (calc.): C 56.78 (56.85), H 8.02 (8.18), N 14.01 (14.12), S 10.45 (10.84)%. **HRMS** (LIFDI): m/z found (calc.): $[M–H]^+$: 591.2793 (591.27); "$[M]^+$–I*i*Pr": 439.1485 (438.14); "$[M]^+$–I*i*Pr-CS$_2$": 362.1964 (363.18). **^{13}C CP/MAS NMR** (100.6 MHz, ν_{rot} = 14.5 kHz): δ = 174.9 (N*C*N$_{IiPr}$), 137.3 (N*C*N$_{IiPr\text{-}CS2}$), 120.1 (C_{aryl}), 111.2 ($C_{backbone}$), 95.2 (*C*S$_2$), 52.0 ($C_{methine}$), 51.7 ($C_{methine}$), 46.9 ($C_{methine}$), 27.6 ($C_{methine}$-*C*H$_3$), 24.4 ($C_{methine}$-*C*H$_3$), 21.8 ($C_{methine}$-*C*H$_3$), 20.8 ($C_{methine}$-*C*H$_3$), 20.3 ($C_{methine}$-*C*H$_3$) ppm. **^{15}N CP/MAS NMR** (40.6 MHz, ν_{rot} = 9.0 kHz): δ = –173.5 (*NC*N$_{IiPr}$), –175.2 (*NC*N$_{IiPr}$), –267.0 (*NC*N$_{IDipp\text{-}CS2}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3159 (vw), 3119 (vw), 3092 (vw), 3079 (vw), 2962 (m), 2930 (m), 2868 (w), 1672 (m, br.), 1599 (m), 1570 (m), 1463 (m), 1441 (m), 1415 (m), 1392 (m), 1369 (m), 1323 (w), 1296 (m), 1212 (vs), 1187 (m), 1129 (m), 1036 (m), 1025 (m), 992 (m), 950 (vw), 930 (vw), 879 (m), 847 (w), 798 (w), 756 (w), 732 (m), 703 (m), 688 (s), 676 (m), 573 (w), 551 (w), 473 (w), 435 (w) cm^{-1}.

Synthesis of [Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (2g)

A mixture of I*i*Pr^{Me}-CS$_2$ (62.4 mg, 243.4 μmol, 1.0 eq.) and [Ni(I*i*Pr)$_2$(η^2-C_2H_4)] (100.0 mg, 255.6 μmol, 1.05 eq.) was dissolved in toluene (10 mL) and stirred for three hours at room temperature. All volatiles were removed *in vacuo* and the residue was suspended in Et_2O (10 mL). After filtration the residue was washed with Et_2O (3 x 10 mL) and *n*-hexane (3 x 5 mL) and dried *in vacuo* to yield [Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (**2g**) as a green solid. **Yield**: 76% (115.0 mg, 185.6 μmol), green solid. *Note*: Due to very low solubility and instability of **2g** no NMR and UV/VIS/NIR data in solution were obtained. **Elemental analysis**: $C_{30}H_{52}N_6NiS_2$ [619.60 g/mol] found (calc.): C 58.00 (58.16), H 8.30 (8.46), N 12.67 (13.56), S 9.57 (10.35)%. **HRMS**

(LIFDI): m/z found (calc.): $[M–H]^+$: 619.3104 (619.31); "$[M]^+$–I*i*Pr": 467.1798 (466.17); "$[M]^+$–I*i*Pr-CS_2": 362.1965 (363.18). **^{13}C CP/MAS NMR** (100.6 MHz, ν_{rot} = 14.5 kHz): δ = 175.8 (N*C*N$_{IiPr}$), 141.5 (N*C*N$_{IDipp\text{-}CS2}$), 119.7 (C_{aryl} + $C_{backbone}$), 99.6 (CS_2), 52.0 ($C_{methine}$), 47.8 ($C_{methine}$), 26.8 ($C_{methine}$-*C*H$_3$), 24.2 ($C_{methine}$-*C*H$_3$), 22.6 ($C_{methine}$-*C*H$_3$), 21.8 ($C_{methine}$-*C*H$_3$), 13.2 ($C_{backbone}$-*C*H$_{3,IiPrMe\text{-}CS2}$) ppm. **^{15}N CP/MAS NMR** (40.6 MHz, ν_{rot} = 9.0 kHz): δ = −173.3 (*N*C*N*$_{IiPr}$), −175.4 (*N*C*N*$_{IiPr}$), −268.6 (*N*C*N*$_{IDipp\text{-}CS2}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3162 (vw), 3117 (vw), 3080 (vw), 2972 (m), 2929 (m), 2868 (w), 1678 (m), 1600 (m), 1570 (w), 1563 (w), 1525 (vw), 1464 (m), 1415 (m), 1407 (m), 1392 (m), 1370 (m), 1321 (vw), 1297 (m), 1276 (m), 1212 (vs), 1183 (m), 1159 (m), 1128 (m), 1075 (m), 1025 (m), 993 (m), 930 (w), 923 (w), 882 (w), 861 (w), 793 (w), 730 (m), 702 (m), 689 (m), 676 (m), 573 (w), 494 (vw), 446 (vw), 436 (vw), 420 (vw) cm^{-1}.

Synthesis of [Ni(cAAC^{Me}-CS_2)$_2$] (3a)

A solution of [Ni(COD)$_2$] (190.7 mg, 691 *µ*mol, 1.0 eq.) in toluene (10 mL) was added to a solution of cAAC^{Me}-CS_2 (500.0 mg, 1.38 mmol, 2.0 eq.) in toluene (10 mL) and stirred for 18 hours at room temperature. All volatiles were removed *in vacuo* and the residue was suspended in Et_2O (10 mL). After filtration the residue was washed with Et_2O (3 x 10 mL) and *n*-hexane (3 x 10 mL) and dried *in vacuo* to afford [Ni(cAAC^{Me}-CS_2)$_2$] (**3a**) as a green-purple solid. Single crystals suitable for X-ray structure determination were obtained by evaporation of a saturated solution of the product in benzene. **Yield**: 78% (421.0 mg, 538 *µ*mol), green-purple solid. **Elemental analysis**: $C_{42}H_{62}N_2NiS_4$ [781.91 g/mol] found (calc.): C 63.92 (64.52), H 7.95 (7.99), N 3.57 (3.58), S 16.41 (16.40)%. **HRMS** (LIFDI): m/z found (calc.): $[M]^+$: 780.3161 (780.31). **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 7.11 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 2H, *para*-C*H*$_{aryl}$), 6.96 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, *meta*-C*H*$_{aryl}$), 2.82 (sept, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H, C*H*$_{methine}$), 1.67 (s, 12H, C-C-C*H*$_3$), 1.54 (s, 4H, C*H*$_2$), 1.32 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, $C_{methine}$-C*H*$_3$), 1.08 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, $C_{methine}$-C*H*$_3$), 0.89 (s, 12H, N-C-C*H*$_3$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ = 146.7 (C_{aryl}), 134.8 (C_{aryl}), 129.3 (C_{aryl}), 125.2 (C_{aryl}), 116.5 (C_{aryl}), 116.5 (C_{aryl}), 105.7 (C_{aryl}), 55.9 (*C*H$_2$), 46.4 (N-*C*-CH$_3$), 31.1 (N-C-*C*H$_3$), 29.3 ($C_{methine}$), 28.7 (C-C-*C*H$_3$), 25.6 ($C_{methine}$-*C*H$_3$), 25.2 (C-*C*-CH$_3$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3058 (vw), 2968 (m), 2926 (w), 2862 (w), 1583 (w), 1453 (m), 1373 (vs), 1335 (vs), 1311 (s), 1219 (m), 1185 (s), 1154 (s), 1131 (s), 1100 (s), 1041 (s), 918 (m), 890 (m), 842 (m), 811 (m), 800 (m), 766 (m), 730 (m), 694 (m), 610 (w), 595 (w), 575 (m), 512 (m), 495 (m), 429 (m), 408 (m) cm^{-1}. **UV/VIS/NIR** (C_6H_6): $\lambda_{abs}(\varepsilon)$ = 1076 (60378), 716 (2700), 453 (7644), 367 (70973), 293 (23401) nm (Lmol^{-1}cm^{-1}). **CV** (v = 25 mV/s, THF): U = −1.71 (rev., 1e$^-$), –1.19 (rev., 1e$^-$), –0.29 (q. rev., 1e$^-$) V.

Synthesis of [Ni(IDipp-CS_2)] (3b)

A mixture of IDipp-CS_2 (500.0 mg, 1.08 mmol, 1.0 eq.) and [Ni(COD)$_2$] (31.0 mg, 24.6 *µ*L, 407 *µ*mol, 1.1 eq.) was dissolved in toluene (15 mL) and stirred for 12 hours at room temperature. The mixture was filtrated through a pad of celite and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in *n*-hexane (10 mL), filtrated, and washed with *n*-hexane (3 x 10 mL) and consequently dried *in vacuo* to afford [Ni(IDipp-CS_2)] (**3b**) as a yellow-green solid. Single crystals of **3b** suitable for X-ray structure determination were obtained by diffusion of *n*-hexane into a saturated solution of the product in THF. **Yield**: 80% (423.1 mg, 428 *µ*mol), yellow-green solid. **Elemental analysis**: $C_{56}H_{72}N_4NiS_4$ [988.15 g/mol] found (calc.): C 67.95 (68.07), H 7.48 (7.34), N 5.65 (5.67), S 13.13 (12.98)%. **^{1}H NMR** (400.1 MHz, C_6D_6): δ = 7.03 (m, 4H, *para*-CH_{aryl}), 6.91 (m, 8H, *meta*-CH_{aryl}), 5.75 (s, 4H, C$H_{backbone}$), 2.86 (sept, 8H, $^3J_{H\text{-}H}$ = 6.7 Hz, C$H_{methine}$), 1.27 (d, 24H, $^3J_{H\text{-}H}$ = 6.7 Hz, C$H_{3,\ Dipp}$), 1.04 (d, 24H, $^3J_{H\text{-}H}$ = 6.7 Hz, C$H_{3,\ Dipp}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, C_6D_6): δ = 146.5 (*ipso*-C_{aryl}), 133.9 (*meta*-C_{aryl}), 130.3 (*para*-CH_{aryl}), 124.3 (*ortho*-CH_{aryl}), 120.1 (C$H_{backbone}$), 29.3 (C$H_{methine}$), 24.6 (C$H_{3,\ Dipp}$), 23.5 (C$H_{3,\ Dipp}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3068 (vw), 2957 (m), 2921 (w), 2863 (w), 1841 (w), 1627 (w), 1567 (m), 1457 (s), 1424 (vs), 1410 (vs), 1359 (m), 1327 (vs), 1291 (vs), 1234 (s), 1216 (s), 1198 (s), 1145 (s), 1077 (s), 922 (s), 896 (m), 795 (m), 750 (m), 700 (s), 656 (m), 428 (m) cm^{-1}. **UV/VIS/NIR** (C_6H_6): $\lambda_{abs}(\varepsilon)$ = 1077 (32415), 718 (1560), 470 (4031), 368 (50260), 291 (23018) nm (Lmol^{-1}cm^{-1}). **CV** (v = 50 mV/s, THF): U = –2.52 V (rev., 1e$^-$), –2.14 V (rev., 1e$^-$), –1.09 V (rev., 1e$^-$).

Synthesis of [Ni(IMes-CS_2)$_2$] (3c)

A mixture of IMes-CS_2 (200.0 mg, 526 *µ*mol, 2.0 eq.) and [Ni(COD)$_2$] (72.3 mg, 263 *µ*mol, 1.0 eq.) was dissolved in toluene (10 mL) and stirred for 18 hours at room temperature. The mixture was filtrated through a pad of celite and the filter pad was thoroughly extracted with THF (5 x 20 mL). All volatiles of the filtrate were removed *in vacuo* and the resulting residue was suspended in *n*-hexane (10 mL). After filtration the residue was washed with Et_2O (3 x 10 mL) and *n*-hexane (4 x 10 mL) and dried *in vacuo* to afford [Ni(IMes-CS_2)$_2$] (**3c**) as a dark-green solid. Single crystals of **3c** suitable for X-ray structure determination were grown by evaporation of a saturated solution of the product in benzene. **Yield**: 79% (170.6 mg, 208.1 *µ*mol), dark-green solid. **Elemental analysis**: $C_{44}H_{48}N_4NiS_4$ [819.83 g/mol] found (calc.): C 64.04 (64.46), H 6.08 (5.90), N 6.00 (6.83), S 14.09 (15.64)%. **^{1}H NMR** (400.1 MHz, d_8-THF): δ = 6.84 (s, 8H, *meta*-CH_{aryl}), 6.60 (s, 4H, C$H_{backbone}$), 2.25 (s, 12H, *para*-C$H_{3,aryl}$), 2.09 (*ortho*-C$H_{3,aryl}$) ppm. **^{13}C{^{1}H} NMR** (100.6 MHz, d_8-THF): δ = 139.2 (C_{aryl}), 136.6 (C_{aryl}), 129.5 (*meta*-CH_{aryl}), 120.3 ($C_{backbone}$), 21.1 (*para*-C$H_{3,aryl}$), 17.9 (*ortho*-C$H_{3,aryl}$) ppm. **IR** (ATR): $\tilde{\nu}$ = 3142 (vw), 3076 (vw), 2912 (w), 2854 (w), 1772 (vw), 1676 (vw), 1608 (w), 1552 (m), 1484

(m), 1414 (vs), 1375 (s), 1328 (vs), 1286 (s), 1223 (m), 1204 (s), 1165 (m), 1105 (w), 1052 (s), 1032 (m), 1014 (m), 930 (w), 916 (s), 873 (w), 846 (s), 726 (m), 673 (w), 628 (w) , 593 (w), 574 (w), 495(vw), 466 (w), 410 (w) cm^{-1}. **UV/VIS/NIR** (C_6H_6): $\lambda_{abs}(\varepsilon)$ = 1064 (19932), 702 (1633), 462 (3935), 367 (33014), 293 (14728) nm ($Lmol^{-1}cm^{-1}$). **CV** (v = 25 mV/s, THF): U = –2.31 (rev., $1e^-$), –1.96 (rev., $1e^-$), –1.05 (irrev., $1e^-$) V.

Synthesis of K[Ni(cAAC^{Me}-CS$_2$)$_2$] (4a^K)

A mixture of [Ni(cAAC^{Me}-CS$_2$)$_2$] (200.0 mg, 255.8 μmol, 1.0 eq.) and KC_8 (121.0 mg, 895.3 μmol, 3.5 eq.) was suspended in THF (10 mL) and stirred for 36 hours at room temperature. The mixture was filtrated through a pad of celite and the filter pad was extracted with THF (3 x 10 mL). After removing all volatiles by evaporation *in vacuo* the residue was suspended in *n*-hexane (10 mL) and collected *via* filtration. The product was washed with benzene (2 x 5 mL) and *n*-hexane (3 x 10 mL) and consequently dried *in vacuo* to afford K[Ni(cAAC^{Me}-CS$_2$)$_2$] (**4a^K**) as a yellow-green solid. Single crystals of **4a^K** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a saturated solution of the product in THF. **Yield**: 71% (149.3 mg, 181.9 μmol), yellow-green solid. **Elemental analysis**: $C_{42}H_{62}KN_2NiS_4$ [821.00 g/mol] found (calc.): C 59.23 (61.44), H 7.55 (7.61), N 3.18 (3.41), S 14.47 (15.62)%. **HRMS** (ESI$^-$): m/z found (calc.): [M]$^-$: 780.3161 (780.31). **IR** (ATR): $\tilde{\nu}$ = 2960 (m), 2928 (m), 2864 (m), 2050 (vw), 2008 (vw), 1571 (w), 1439 (m), 1380 (s), 1362 (m), 1322 (m), 1288 (m), 1253 (s), 1200 (s), 1128 (vs), 1105 (m), 1077 (w), 1051 (m), 1017 (m), 955 (w), 933 (w), 903 (m), 867 (m), 809 (s), 800 (s), 766 (m), 737 (w), 690 (m), 633 (w), 607 (m), 572 (s), 540 (w), 476 (m), 446 (w), 427 (m) cm^{-1}. **UV/VIS/NIR** (THF): λ_{abs} = 1499, 1196, 693, 356, 330 nm. **EPR** (THF, 70 K): g_1 = 2.0357, g_2 = 2.0413 and g_3 = 2.1274.

Synthesis of [CoCp$_2$][Ni(cAAC^{Me}-CS$_2$)$_2$] (4a^{Co})

A mixture of [Ni(cAAC^{Me}-CS$_2$)$_2$] (40.0 mg, 51.2 μmol, 1.0 eq.) and [CoCp$_2$] (9.7 mg, 51.2 μmol, 1.0 eq.) was dissolved in THF (10 mL) and stirred for 36 hours at room temperature. The formed precipitate was collected by filtration and washed with THF (3 x 5 mL) and *n*-hexane (3 x 5 mL) to yield [CoCp$_2$][Ni(cAAC^{Me}-CS$_2$)$_2$] (**4a^{Co}**) as an insoluble green solid. **Yield**: 70% (34.8 mg, 35.8 μmol), green solid. **Elemental analysis**: $C_{52}H_{72}CoN_2NiS_4$ [971.03 g/mol] found (calc.): C 63.57 (64.32), H 7.58 (7.47), N 2.52 (2.88), S 12.00 (13.21)%. **IR** (ATR): $\tilde{\nu}$ = 2960 (m), 2928 (m), 2864 (m), 1580 (vw), 1469 (m), 1455 (m), 1410 (vs), 1376 (s), 1307 (m), 1288 (s), 1179 (s), 1130 (s), 1101 (s), 1059 (m), 1010 (m), 937 (m), 905 (m), 882 (m), 809 (m), 797 (m), 766 (m), 730 (m), 686 (m), 638 (m), 590 (w), 569 (m), 540 (m), 462 (m), 421 (m) cm^{-1}.

Synthesis of K[Ni(IDipp-CS_2)] ($\mathbf{4b^K}$)

A mixture of [Ni(IDipp-CS_2)] (300.0 mg, 303.6 *µ*mol, 1.0 eq.) and KC_8 (143.7 mg, 1.06 mmol, 3.5 eq.) was suspended in THF (10 mL) and stirred for 36 hours at room temperature. The mixture was filtrated through a pad of celite and the filter pad was extracted with THF (3 x 10 mL). After removing all volatiles by evaporation *in vacuo* the residue was suspended in *n*-hexane (10 mL) and collected *via* filtration. The product was washed with benzene (2 x 5 mL) and *n*-hexane (3 x 10 mL) and consequently dried *in vacuo* to afford K[Ni(IDipp-CS_2)] (**$\mathbf{4b^K}$**) as a red solid. Single crystals of **$\mathbf{4b^K}$** suitable for X-ray structure determination were obtained by diffusion of *n*-hexane into a saturated solution of the product in THF. **Yield**: 41% (128.1 mg, 124.7 *µ*mol), red solid. **Elemental analysis**: $C_{56}H_{72}KN_4NiS_4$ [1027.25 g/mol] found (calc.): C 67.83 (65.48), H 7.67 (7.07), N 5.01 (5.45), S 11.81 (12.48)%. **HRMS** (ESI$^-$): m/z found (calc.): $[M]^-$: 986.4016 (986.40); "$[M]^-$–IDipp-CS_2": 664.2254 (664.23). **IR** (ATR): $\tilde{\nu}$ = 3137 (vw), 3067 (w), 3026 (w), 2958 (vs), 2926 (s), 2865 (s), 2099 (vw), 1623 (s), 1580 (m), 1562 (m), 1461 (vs), 1425 (vs), 1380 (s), 1361 (s), 1328 (s), 1271 (s), 1232 (s), 1204 (vs), 1162 (m), 1146 (m), 1111 (m), 1077 (s), 1060 (s), 1013 (m), 986 (s), 935 (m), 917 (s), 866 (m), 800 (vs), 756 (vs), 707 (m), 660 (m), 645 (m), 565 (w), 551 (vw), 462 (vw), 417 (w) cm^{-1}. **UV/VIS/NIR** (THF): λ_{abs} = 1909 nm. **EPR** (THF, 70 K): g_1 = 2.0069, g_2 = 2.0271, g_3 = 2.0469.

3 NMR Section

3.1 General Information

NMR spectra in solution were recorded at 298 K using a Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz) spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are listed in parts per million (ppm) relative to TMS and were referenced either to the residual proton resonances of the deuterated solvents (C_6D_6: 7.16 ppm; $CDCl_3$: 7.26 ppm; d_8-THF: 1.72 ppm, 3.58 ppm; d_6-DMSO: 2.50 ppm) or to the natural-abundance carbon resonances (C_6D_6: 128.06 ppm; $CDCl_3$: 77.16 ppm; d_8-THF: 67.21 ppm, 25.31 ppm; d_6-DMSO: 39.52 ppm).[11]

Solid-state CP/MAS (CP = cross polarization; MAS = magic angle spinning) NMR spectra were recorded at 293 K with a Bruker Avance NEO 400 NMR spectrometer with bottom layer rotors of ZrO_2 (outer diameter 4 mm with KelF rotor cap) containing approximately 100 μL of sample (*ca.* 60–130 mg) spinning the rotor at different speeds between 9.0 and 14.8 kHz (^{13}C: 100.6 MHz, ^{15}N: 40.6 MHz) . All chemical shifts were calibrated externally by setting the ^{13}C low-field signal of adamantane to δ = 38.48 ppm by adjusting the field value of the spectrometer according to the IUPAC recommendations.[12]

Spectra were plotted using the Mestre Nova software package.[13]

3.2 NMR Spectra

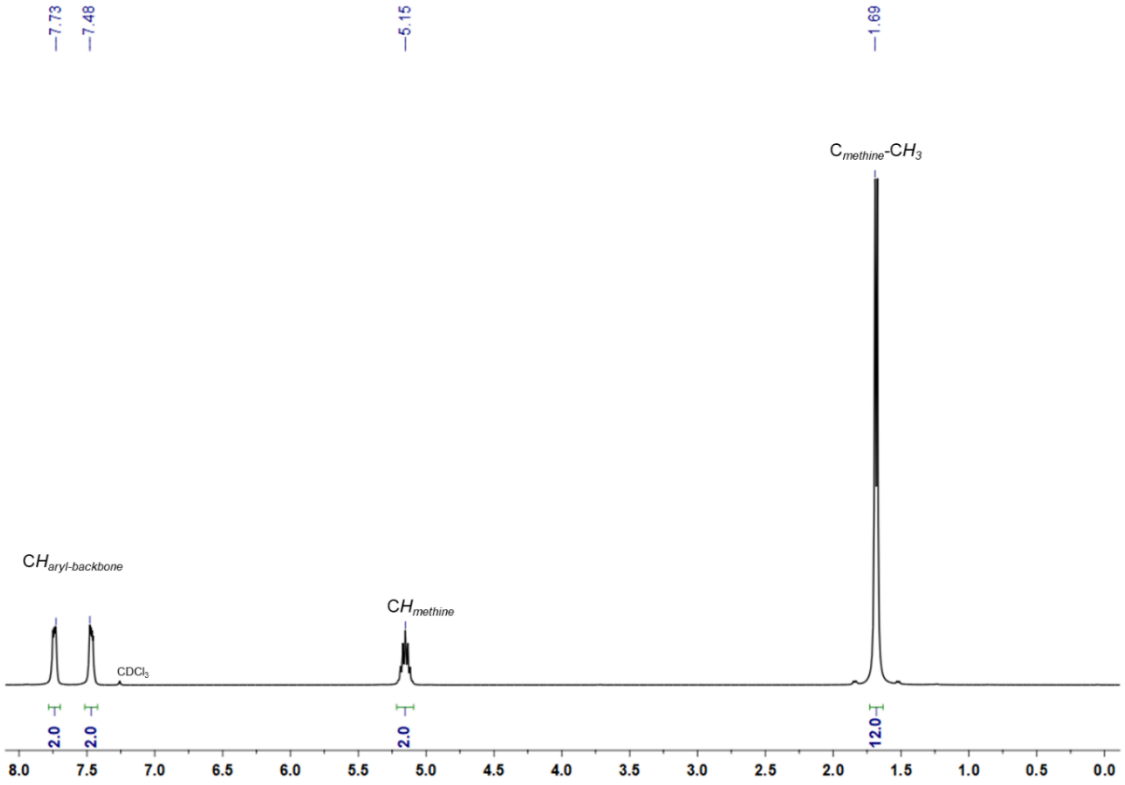


Figure S10. ^{1}H NMR spectrum of BI*i*Pr-CS_2 (**1e**) in $CDCl_3$.

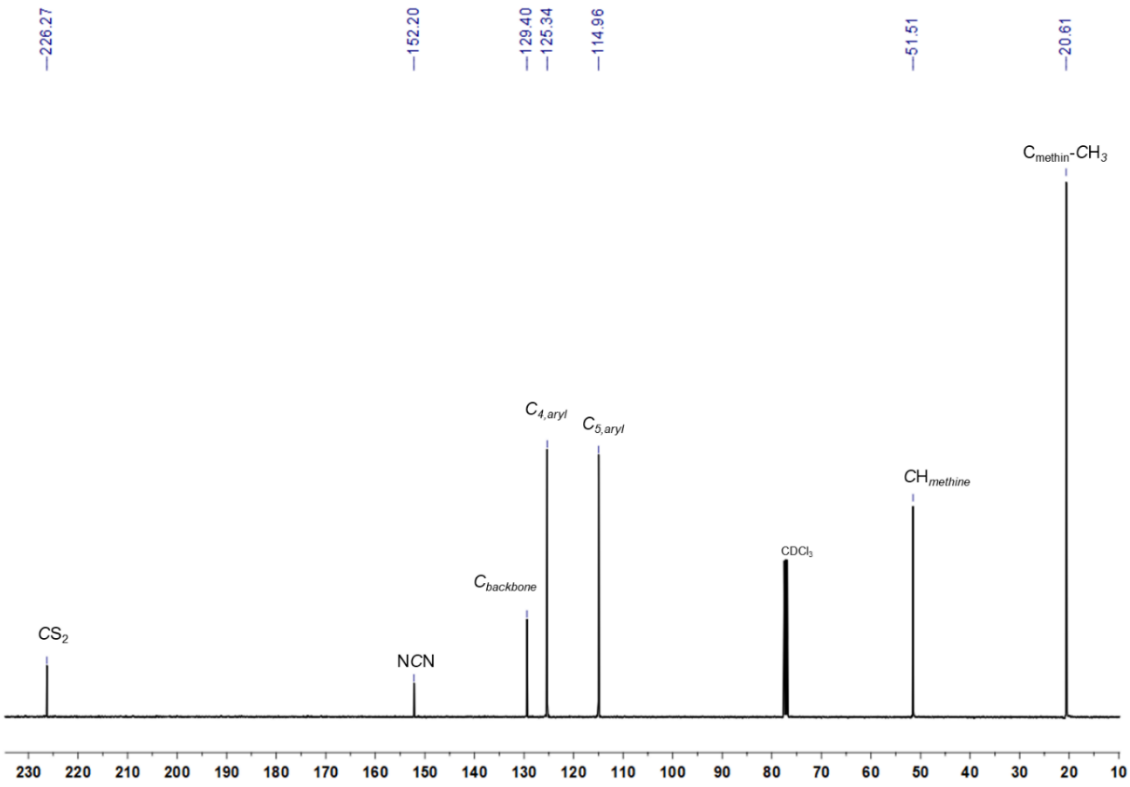


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of BI*i*Pr-CS_2 (**1e**) in $CDCl_3$.

[Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (2a)

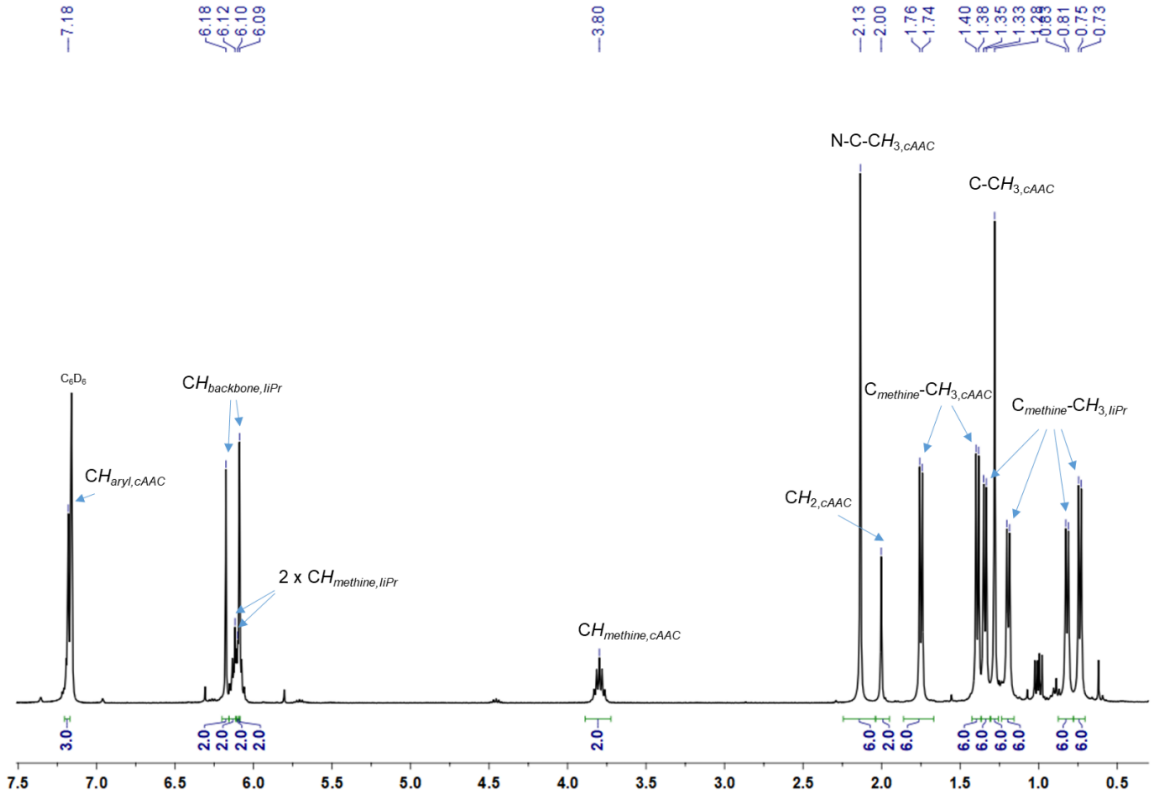


Figure S12. ^{1}H NMR spectrum of [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (**2a**) in C_6D_6.

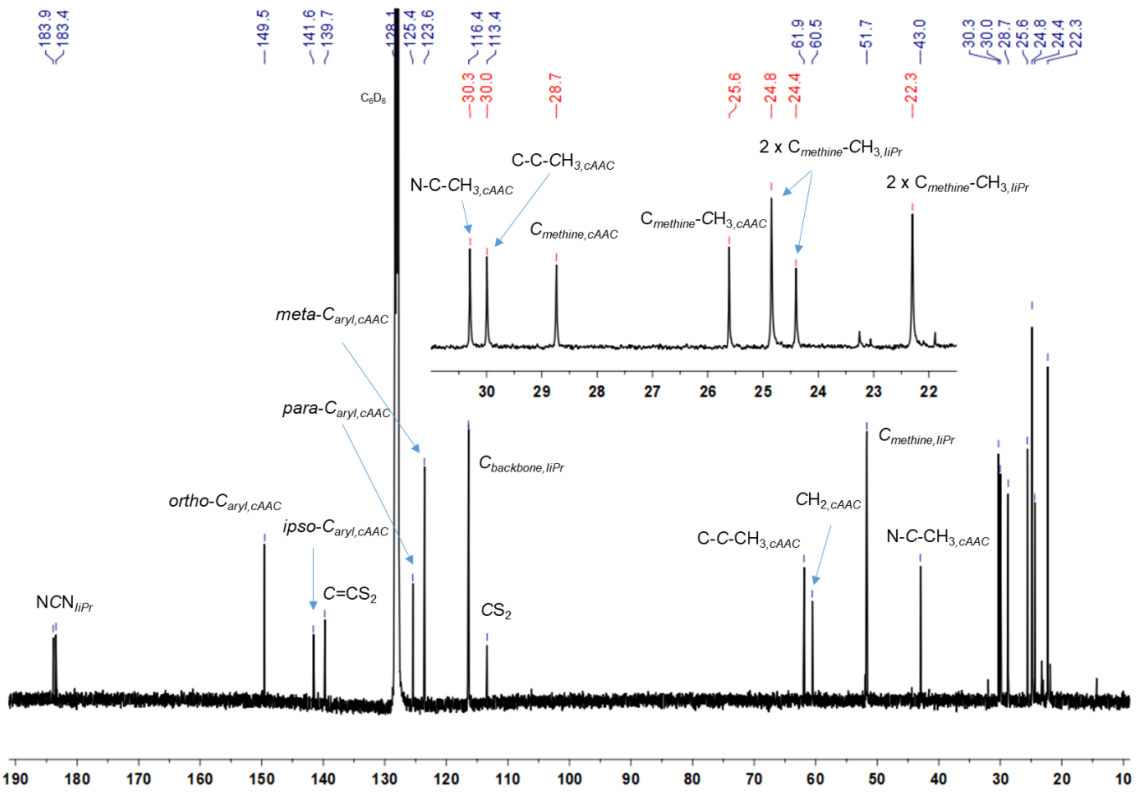


Figure S13. ^{13}C{^{1}H} NMR spectrum of [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (**2a**) in C_6D_6.

[Ni(I*i*Pr)$_2$(IDipp-CS$_2$)] (2b)

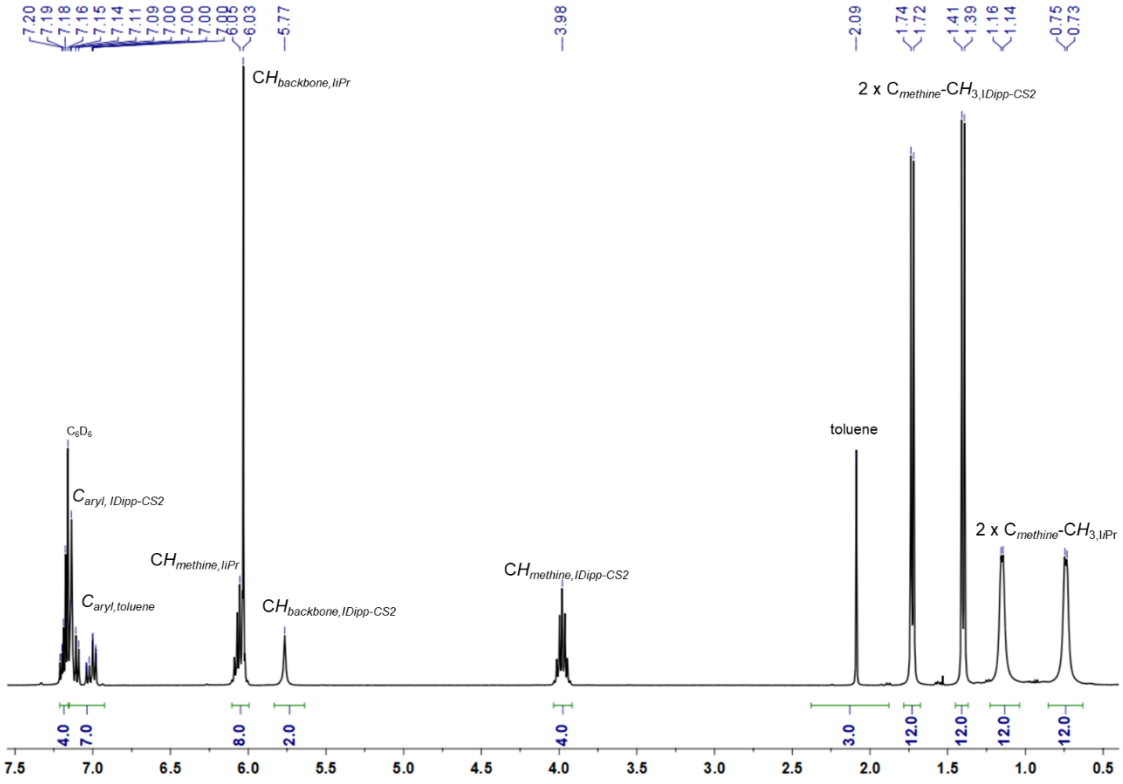


Figure S14. ^{1}H NMR spectrum of a co-crystal [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)]·(toluene) (**2b·tol**) with toluene.

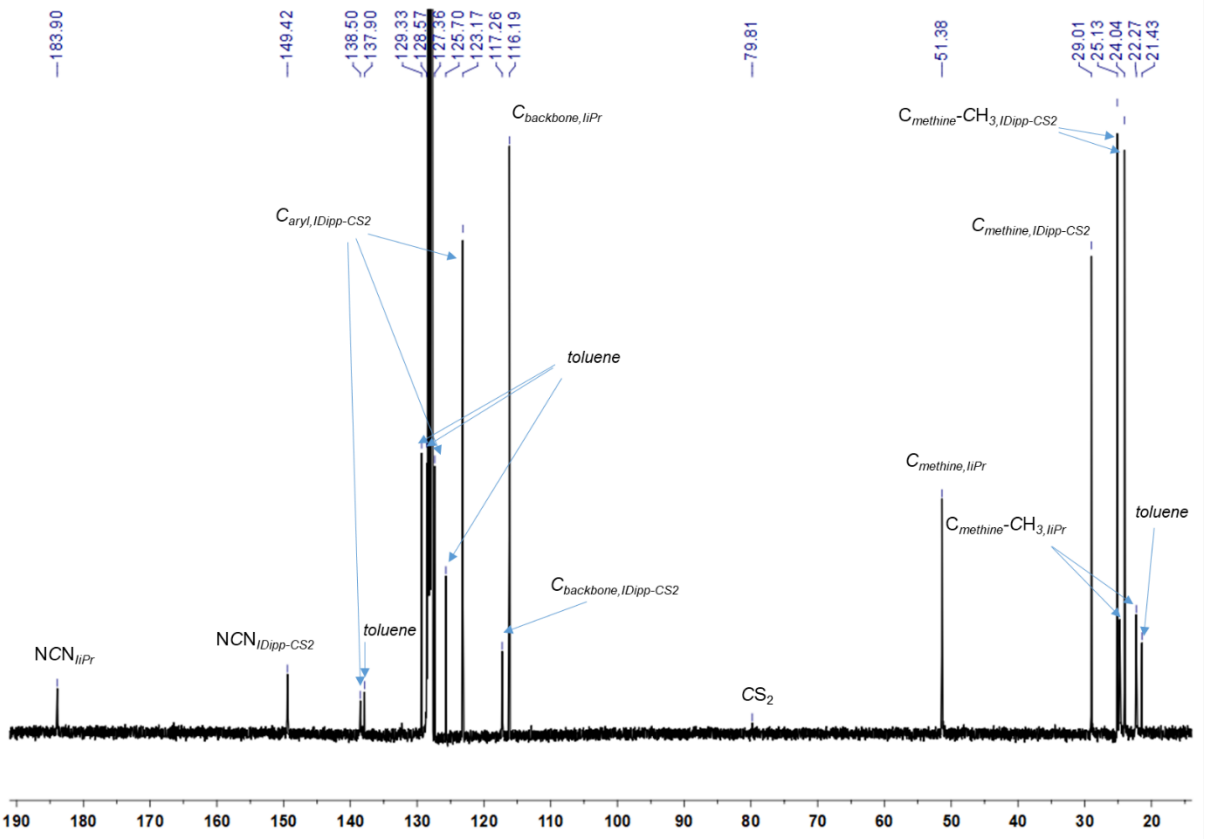


Figure S15. ^{13}C{^{1}H} NMR spectrum of a co-crystal [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)]·(toluene) (**2b·tol**) with toluene.

[Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (2c)

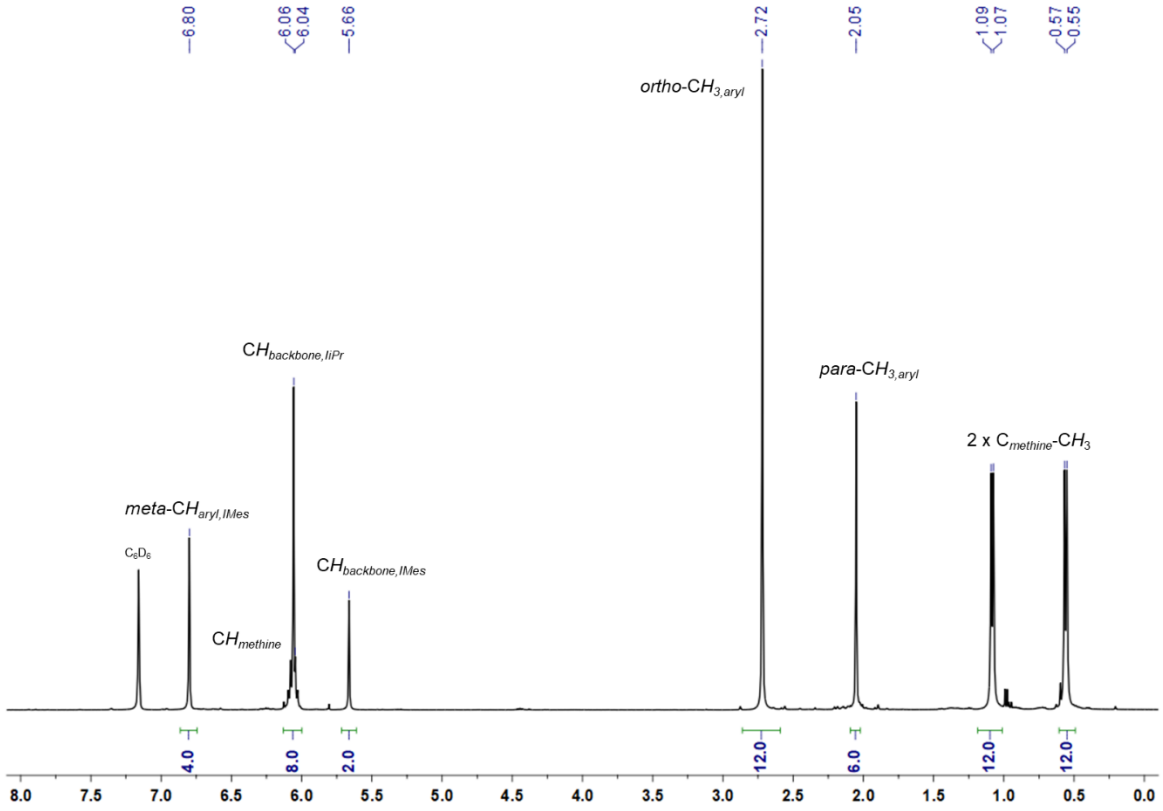


Figure S16. ^{1}H NMR spectrum of [Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (**2c**) in C$_6$D$_6$.

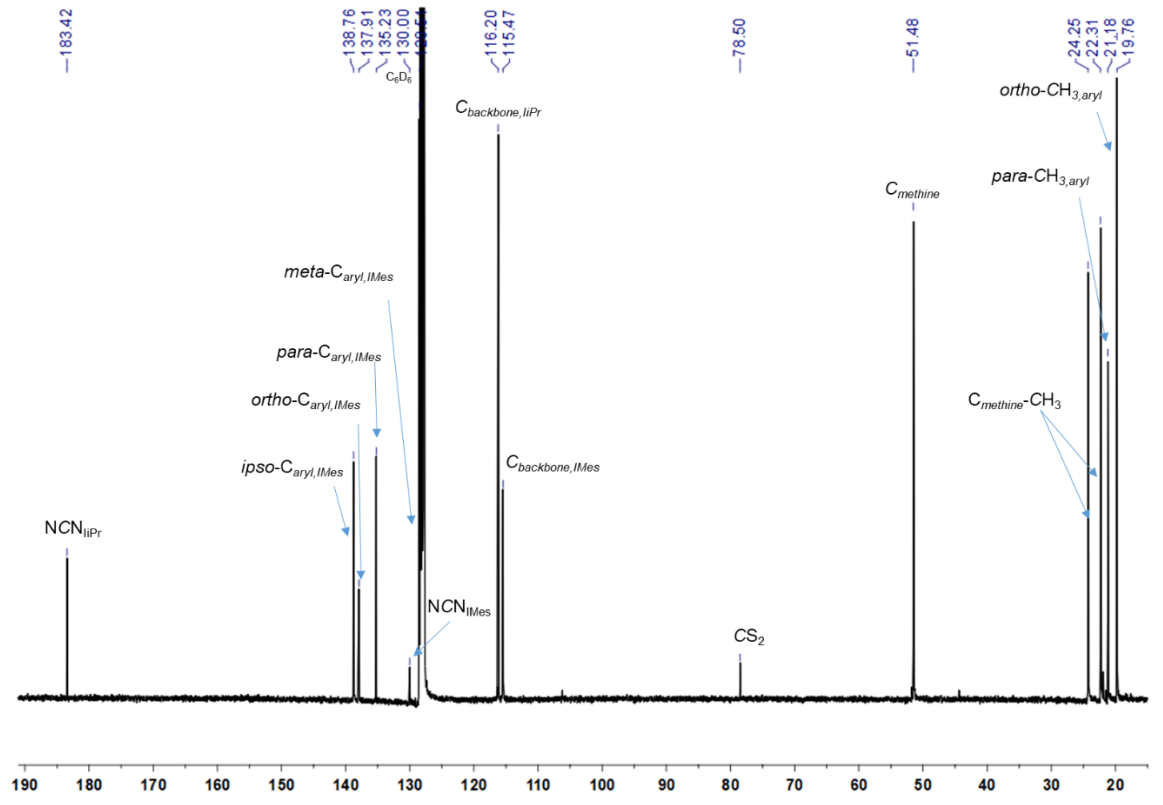


Figure S17. ^{13}C{^{1}H} NMR spectrum of [Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (**2c**) in C$_6$D$_6$.

[Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (2d)

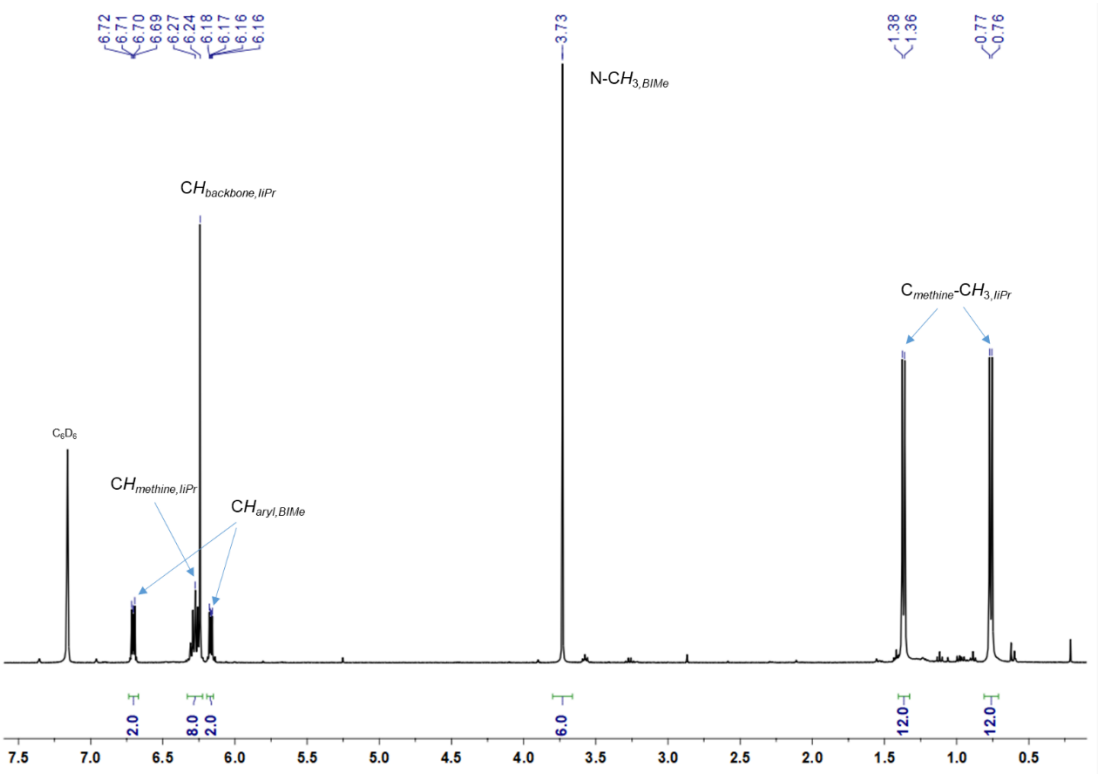


Figure S18. ^{1}H NMR spectrum of [Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (**2d**) in C$_6$D$_6$.

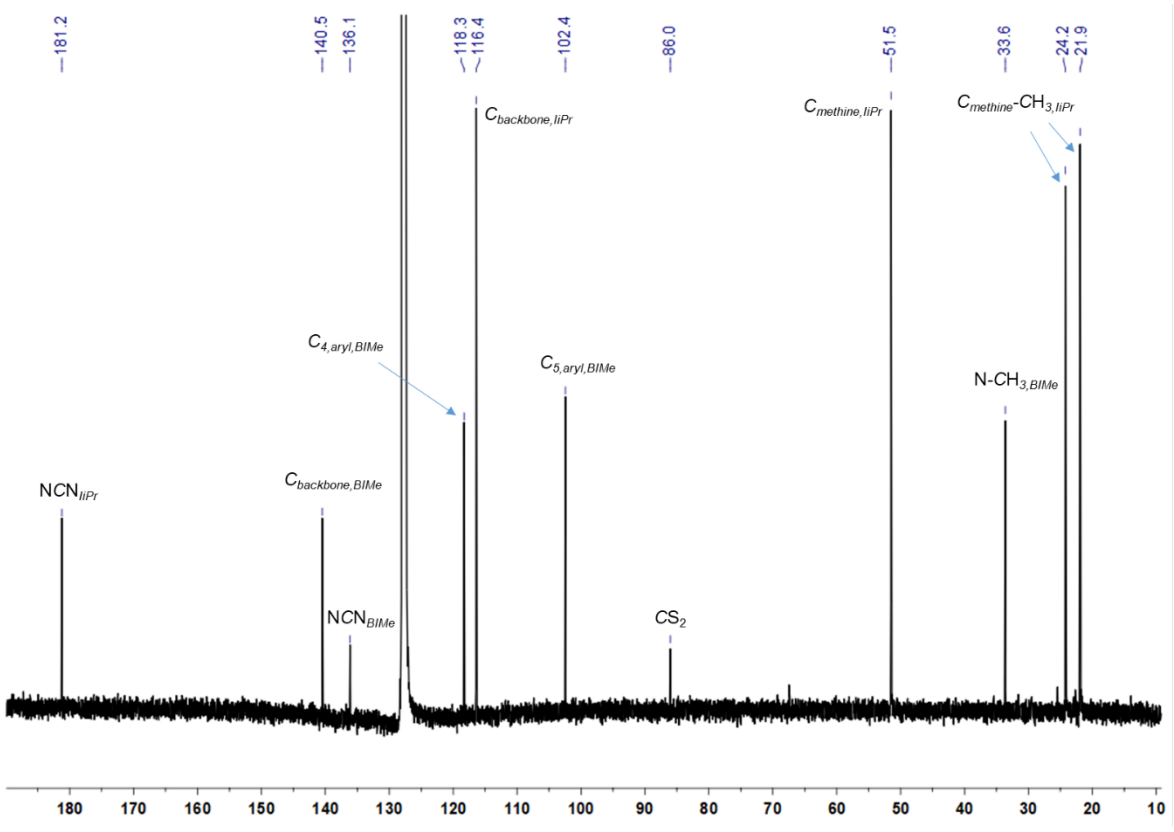


Figure S19. ^{13}C{^{1}H} NMR spectrum of [Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (**2d**) in C$_6$D$_6$.

[Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (2e)

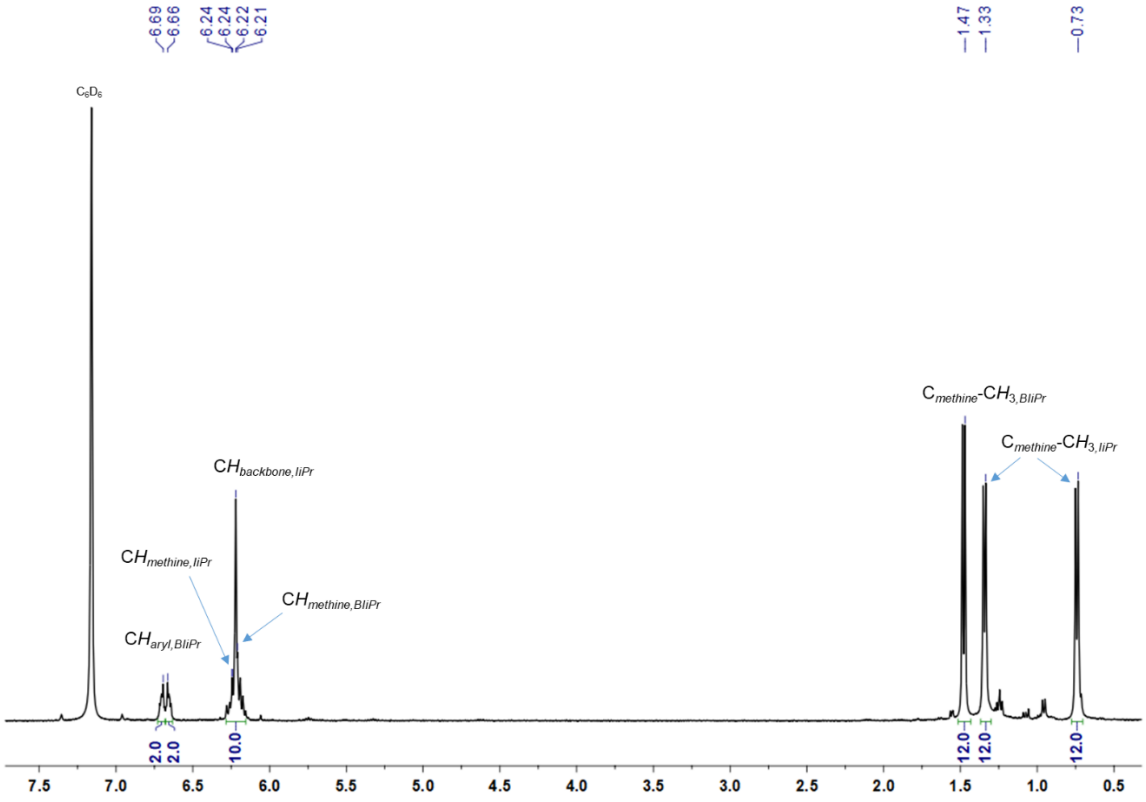


Figure S20. ^{1}H NMR spectrum of [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (**2e**) in C$_6$D$_6$.

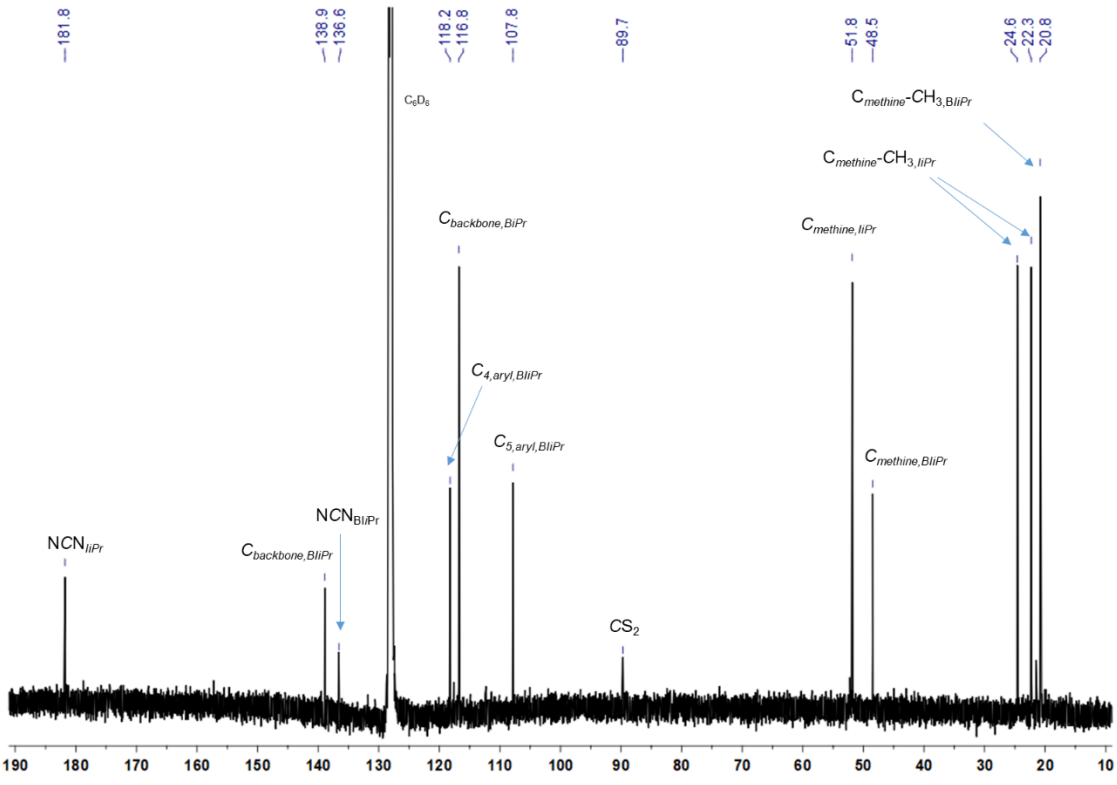


Figure S21. ^{13}C{^{1}H} NMR spectrum of [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (**2e**) in C$_6$D$_6$.

[Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (2f)

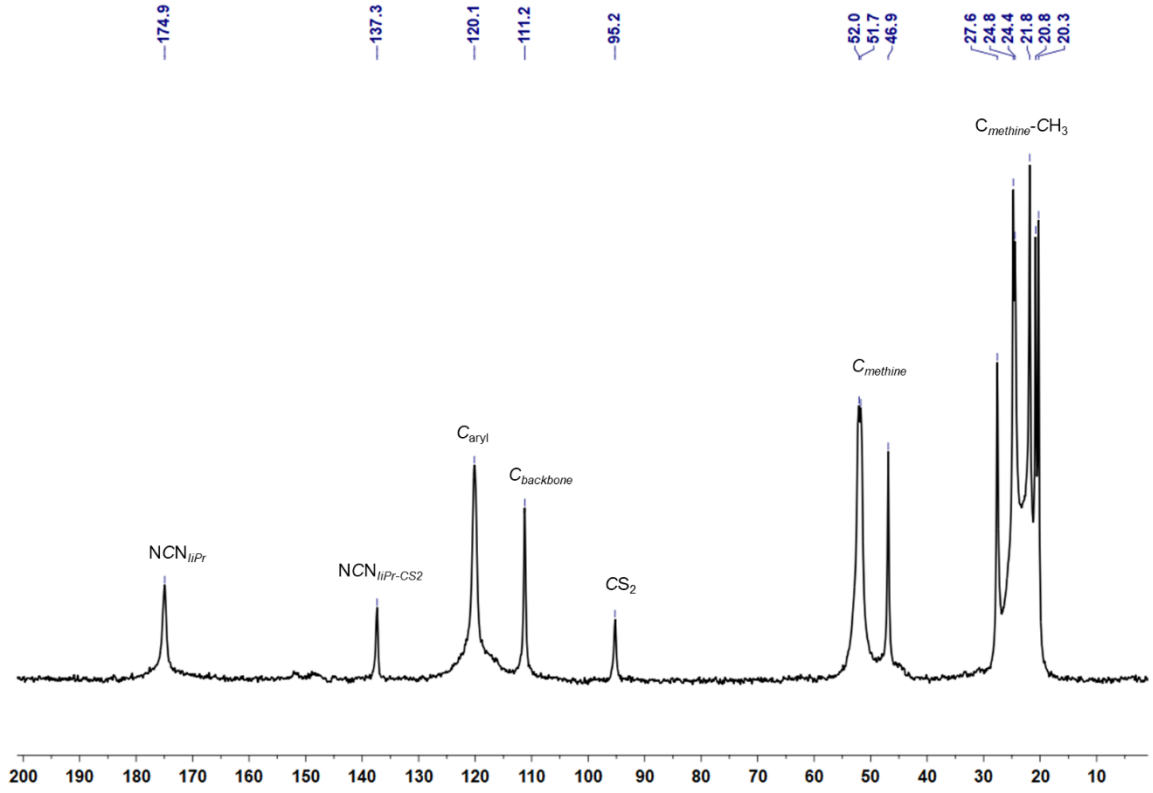


Figure S22. ^{13}C CP/MAS NMR spectrum of [Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (**2f**) (ν_{rot} = 14.5 kHz).

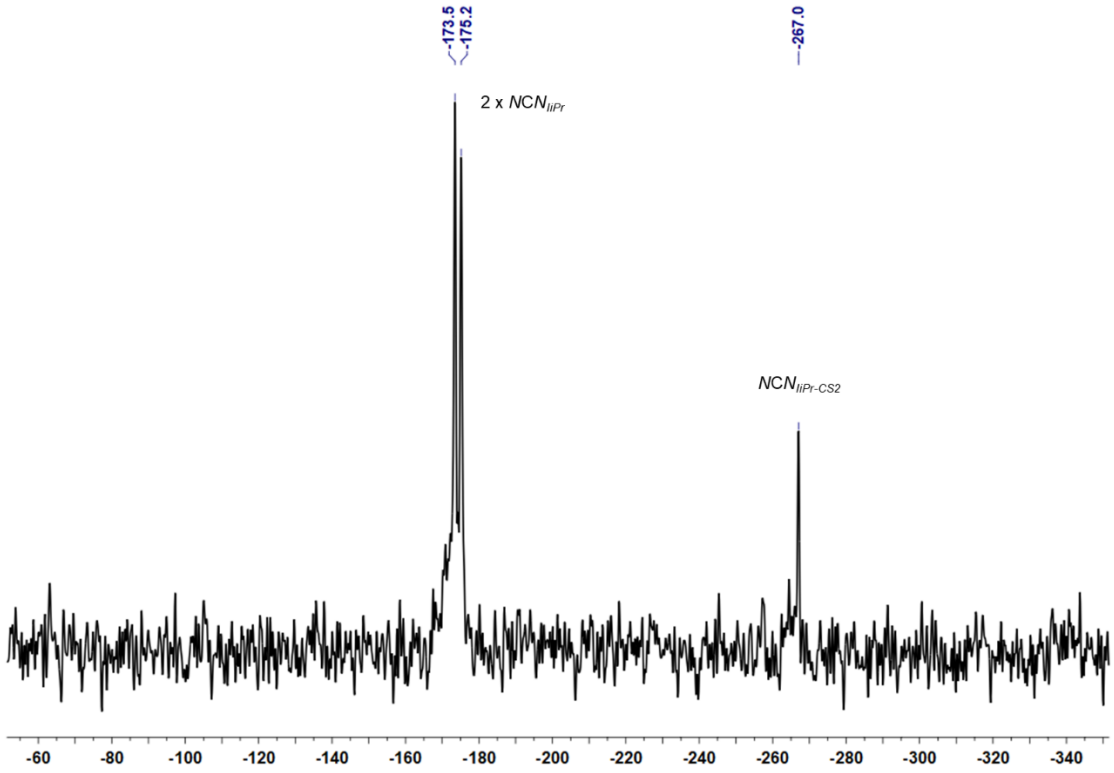


Figure S23. ^{15}N CP/MAS NMR spectrum of [Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (**2f**) (ν_{rot} = 9.0 kHz).

[Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (2g)

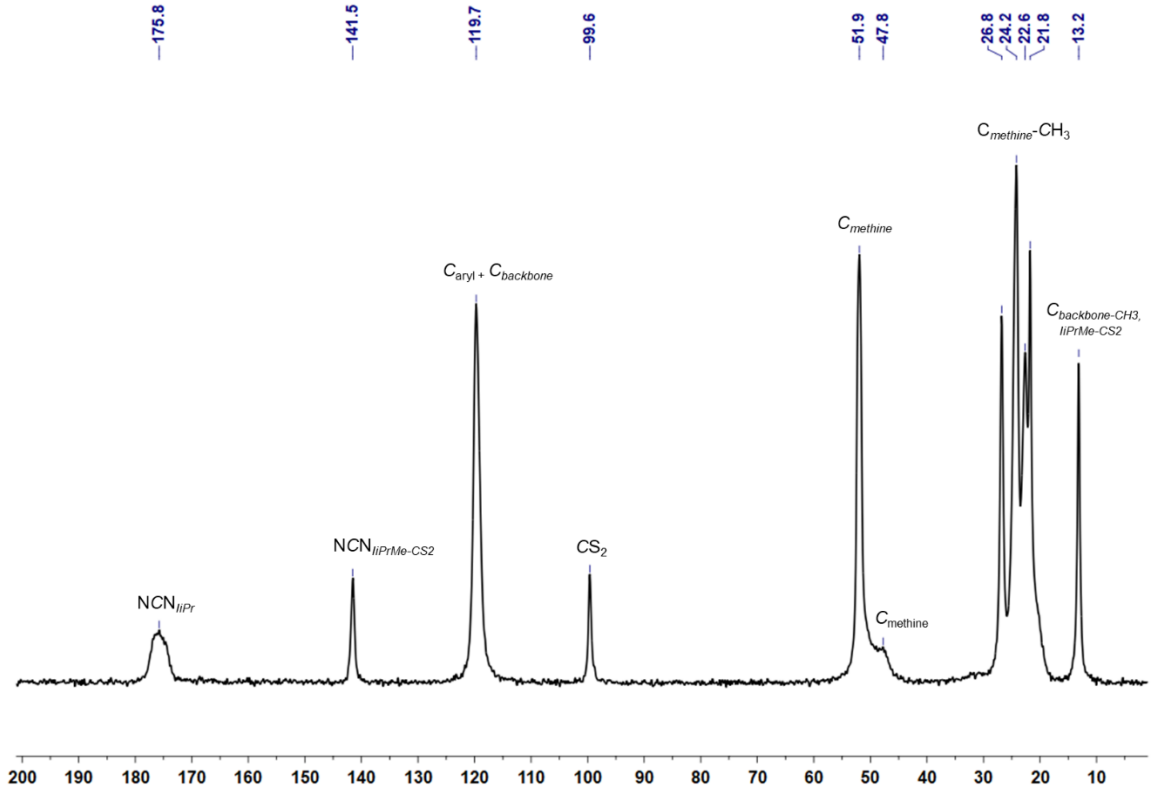


Figure S24. ^{13}C CP/MAS NMR spectrum of [Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (**2g**) (ν_{rot} = 14.5 kHz).

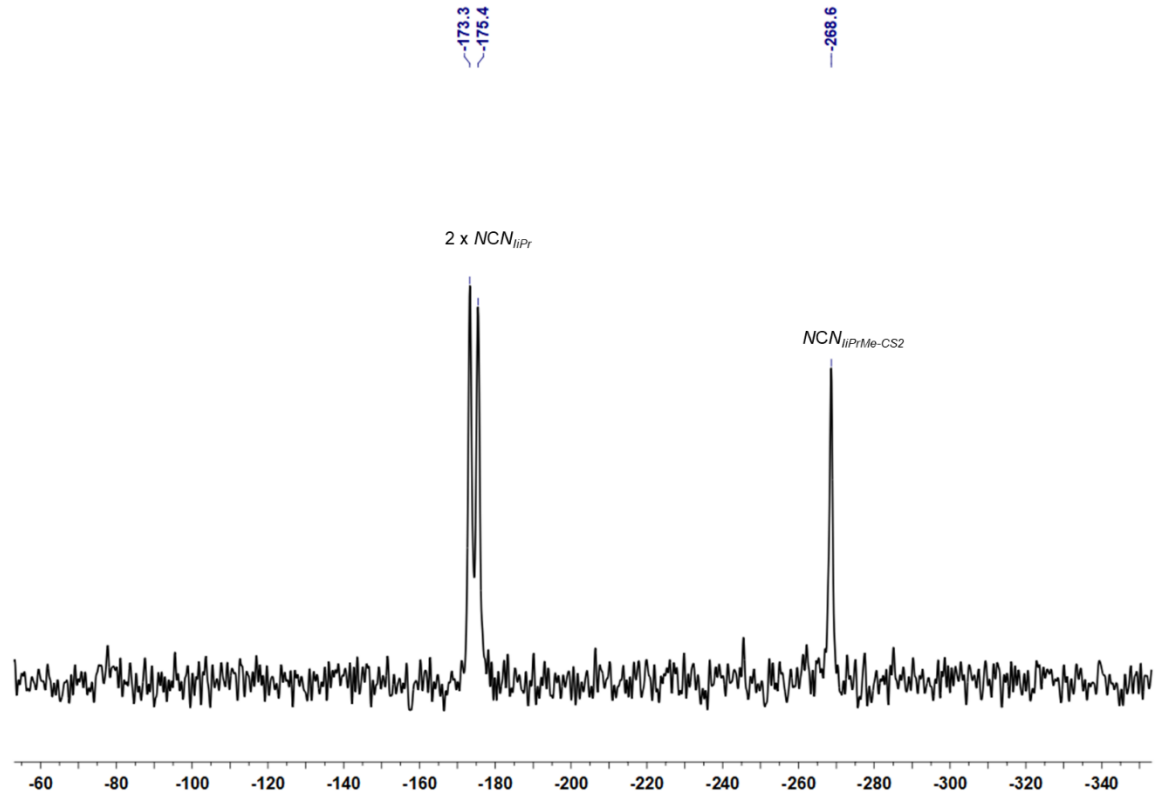


Figure S25. ^{15}N CP/MAS NMR spectrum of [Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (**2g**) (ν_{rot} = 9.0 kHz).

[Ni(cAAC^{Me}-CS$_2$)$_2$] (3a)

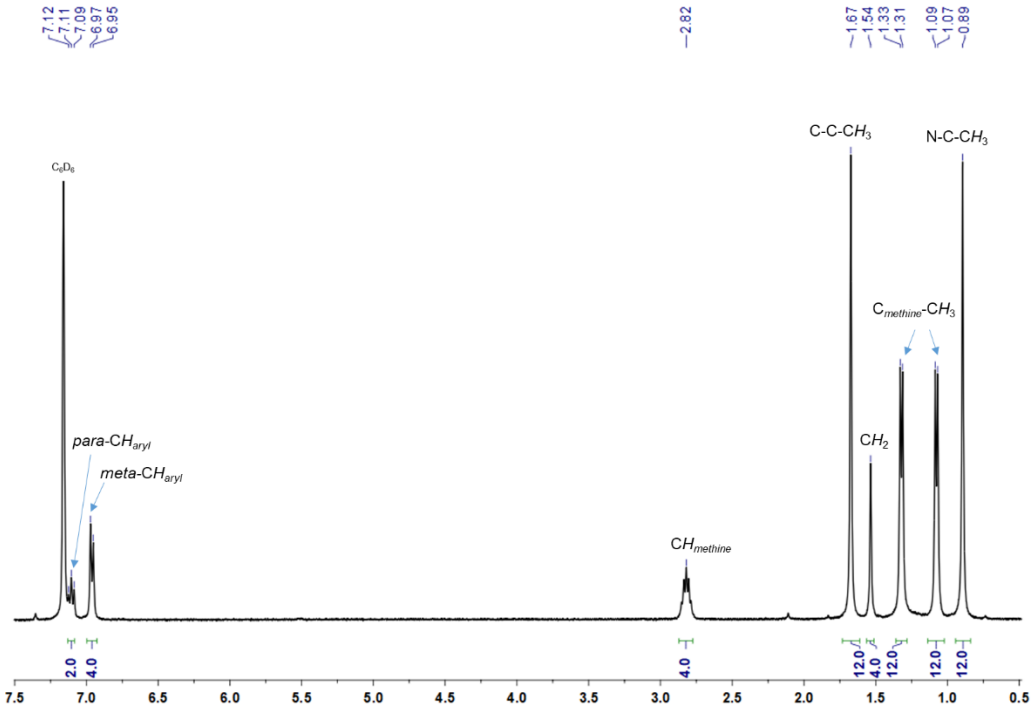


Figure S26. ^{1}H NMR spectrum of [Ni(cAAC^{Me}-CS$_2$)$_2$] (**3a**) in C$_6$D$_6$.

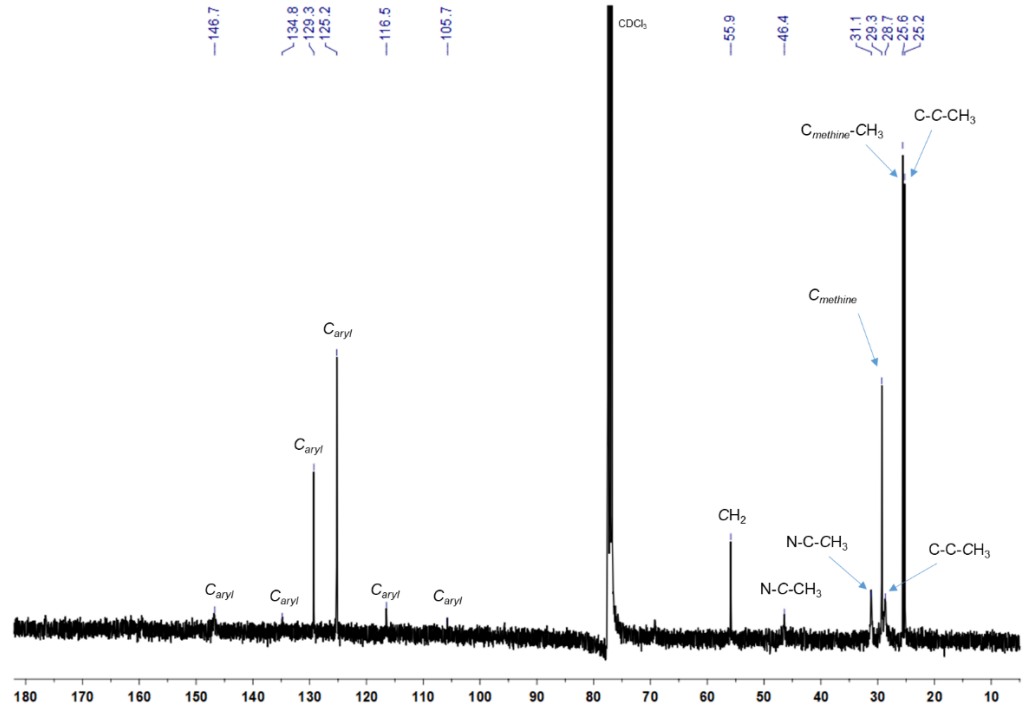


Figure S27. ^{13}C{^{1}H} NMR spectrum of [Ni(cAAC^{Me}-CS$_2$)$_2$] (**3a**) in CDCl$_3$. Resonances of the former carbene carbon atom as well as of the CS$_2$ group were not detected.

[Ni(IDipp-CS_2)$_2$] (3b)

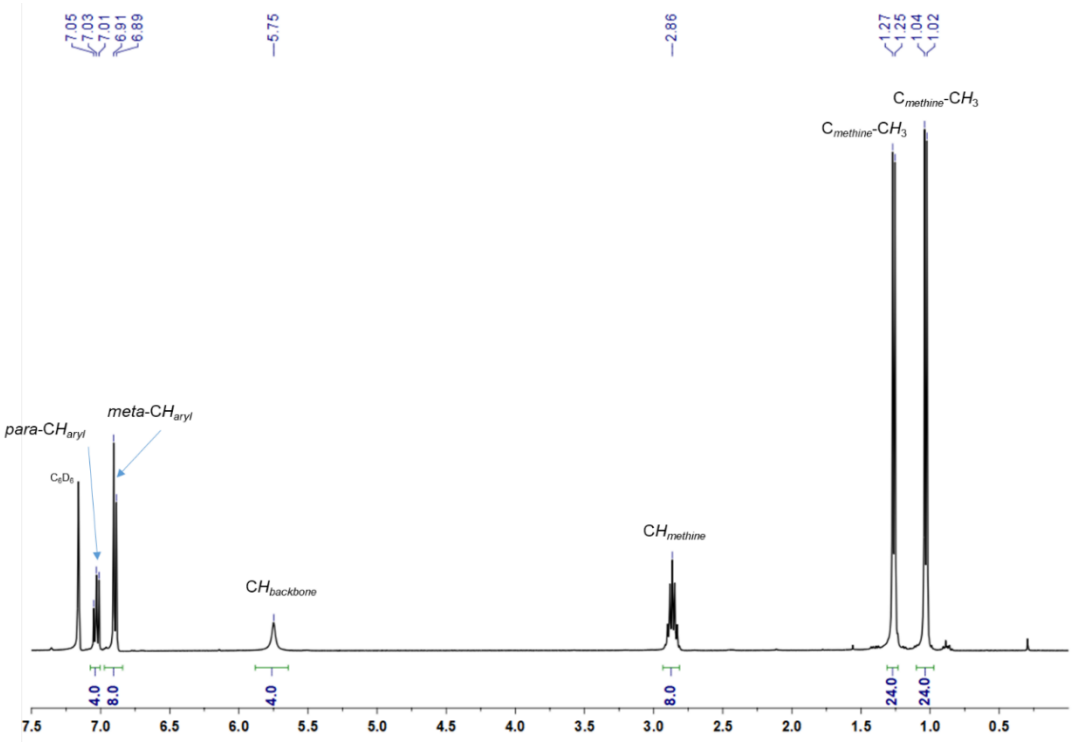


Figure S28. ^{1}H NMR spectrum of [Ni(IDipp-CS_2)$_2$] (**3b**) in C_6D_6.

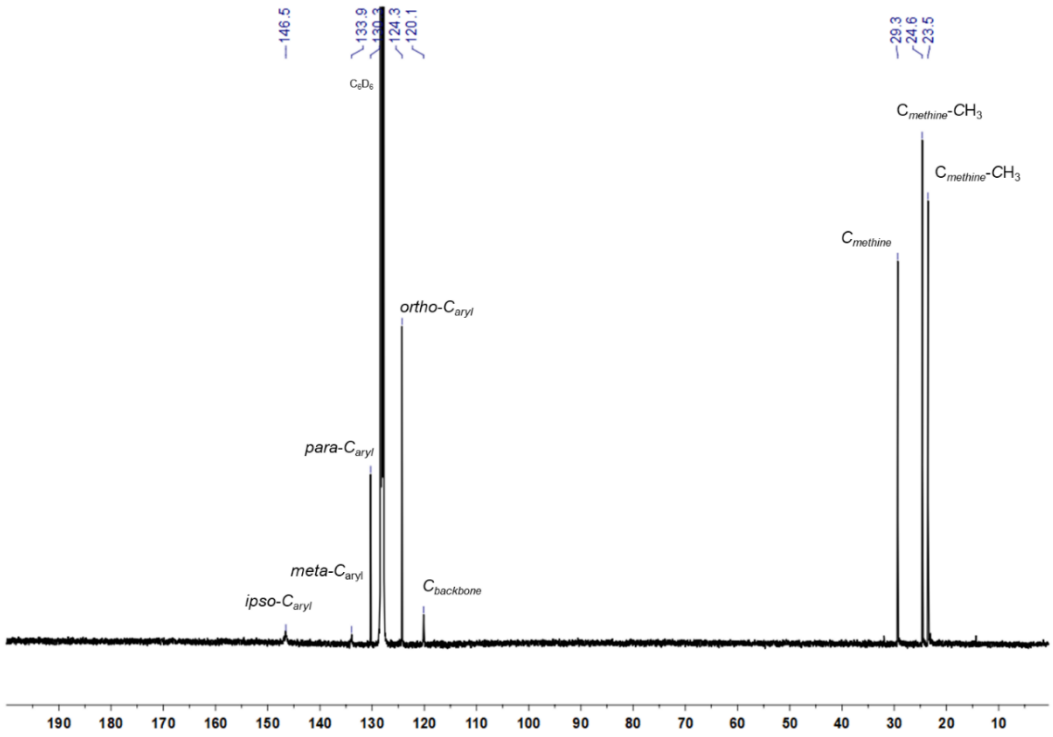


Figure S29. ^{13}C{^{1}H} NMR spectrum of [Ni(IDipp-CS_2)$_2$] (**3b**) in C_6D_6. The resonances of the CS_2 and NCN carbon atoms were not detected.

[Ni(IMes-CS_2)$_2$] (3c)

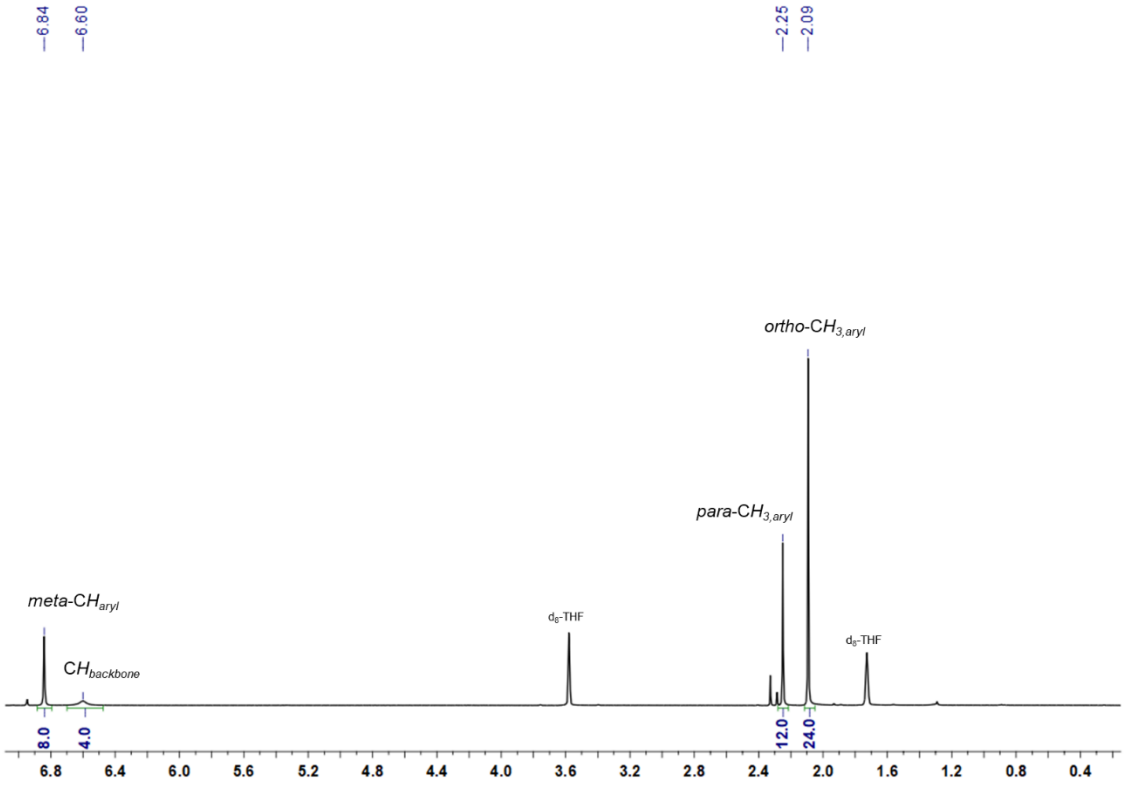


Figure S30. ^{1}H NMR spectrum of [Ni(IMes-CS_2)$_2$] (**3c**) in d_8-THF.

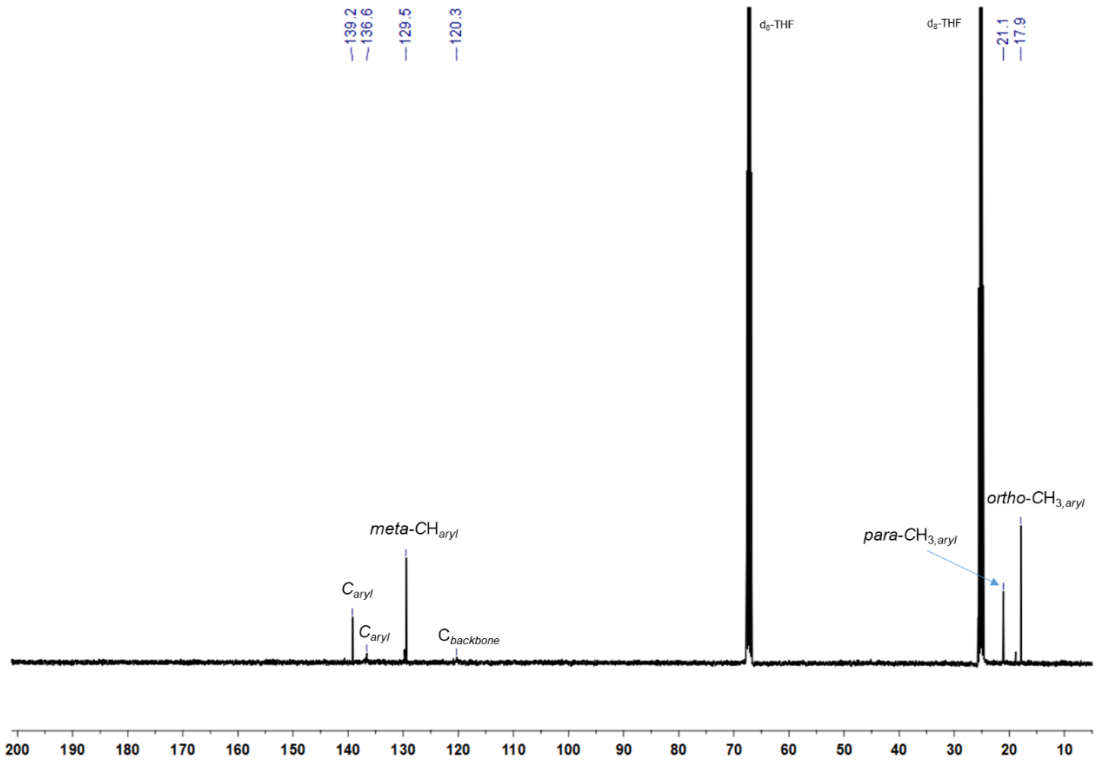


Figure S31. $^{13}C\{^1H\}$ NMR spectrum of [Ni(IMes-CS_2)$_2$] (**3c**) in d_8-THF. The resonances of the CS_2 and NCN carbon atoms were not detected.

4 EPR Section

4.1 General Information

EPR measurements at *X*-band (9.38 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. The spectral simulations were performed using MATLAB 9.14.0.2206163 (R2023a) and the EasySpin 5.2.35 toolbox.[11] Data plotting was performed with Origin 2023.[15]

4.2 EPR Spectra

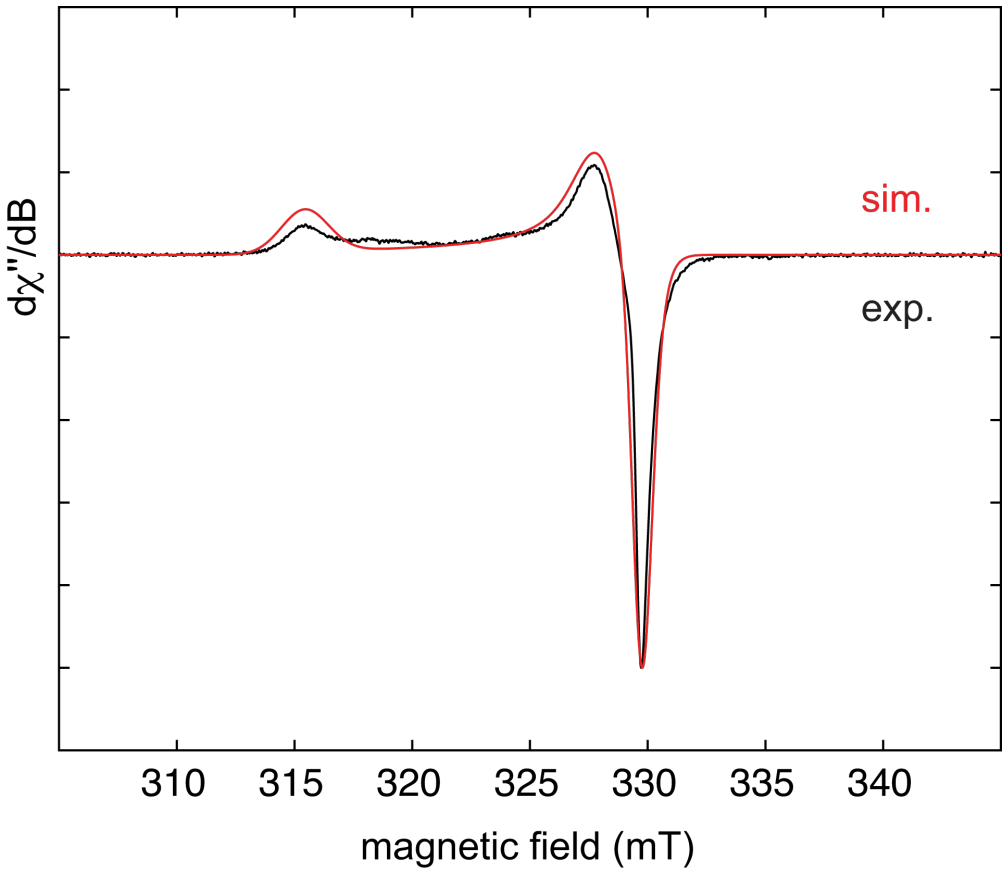


Figure S32. Experimental (black) and simulated (red) *X*-band EPR spectra of K[Ni(cAAC^{Me}-CS$_2$)$_2$] (**4a^K**) in frozen THF solution at 70 K. The best-fit simulation parameters are: g_1 = 2.0357, g_2 = 2.0413 and g_3 = 2.1274.

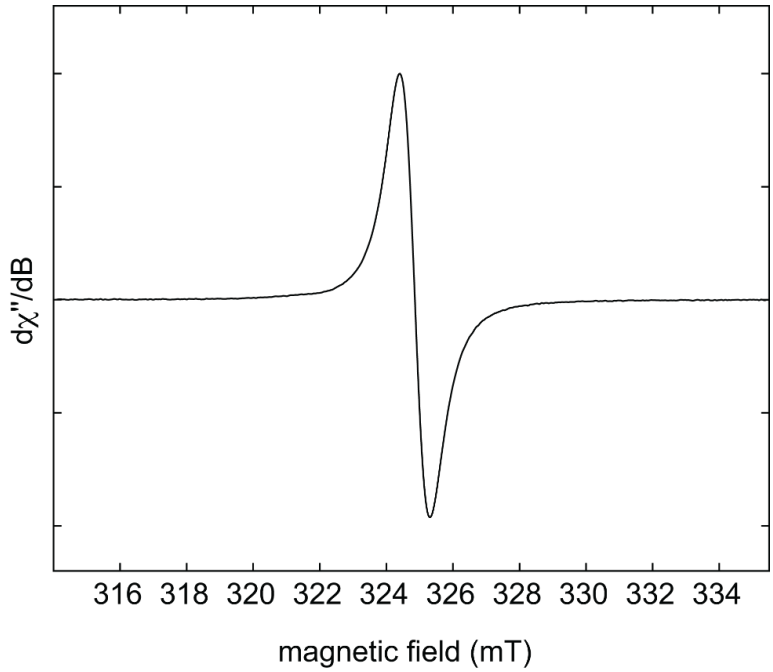


Figure S33. *X*-band EPR spectrum of K[Ni(cAAC^{Me}-CS_2)$_2$] (**4a^K**) in THF solution at room temperature. The signal is centered around a *g* factor of 2.064 with a peak-to-peak linewidth of 1 mT.

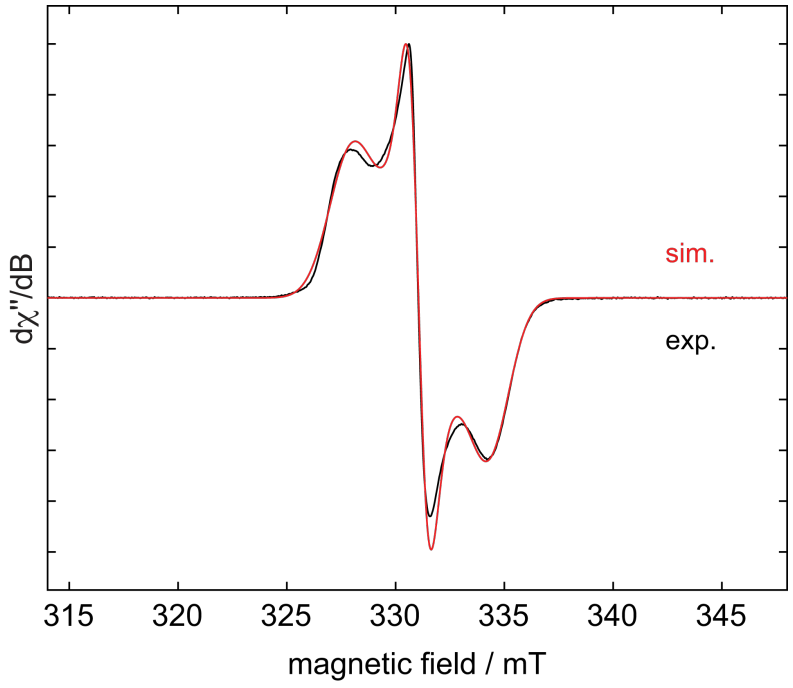


Figure S34. Experimental (black) and simulated (red) *X*-band EPR spectra of K[Ni(IDipp-CS_2)$_2$] (**4b^K**) in frozen THF solution at 70 K. The best-fit simulation parameters are: g_1 = 2.0469, g_2 = 2.0271, and g_3 = 2.0069.

5 IR Section

5.1 General Information

Infrared spectra were recorded on a Bruker Alpha II spectrometer in an argon filled glovebox as solids by using an ATR unit and plotted using the OPUS software package.[16]

5.2 IR Spectra

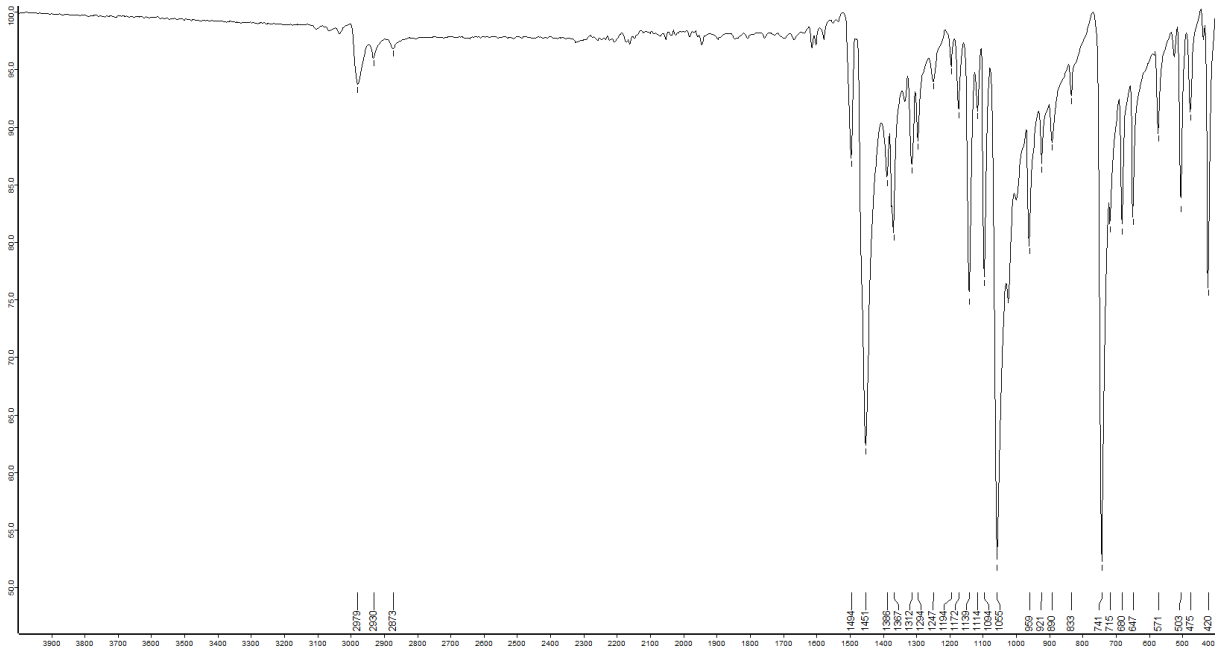


Figure S35. FT-IR spectrum (ATR) of BI*i*Pr-CS_2 (**1e**).

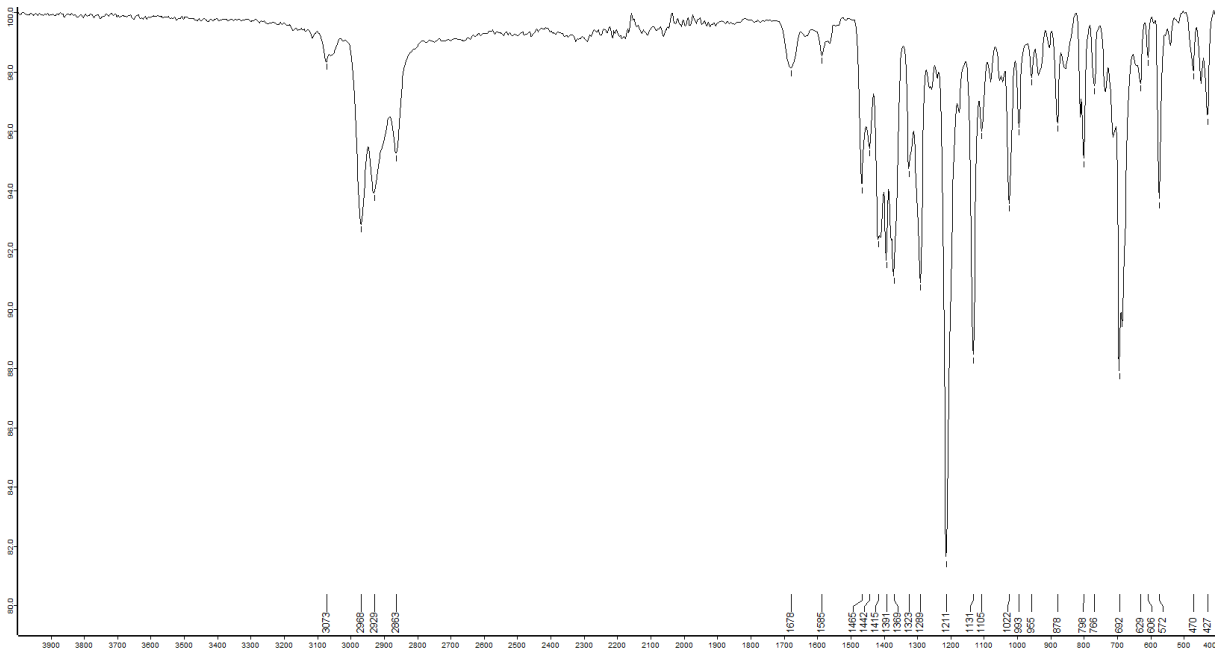


Figure S36. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS_2)] (**2a**).

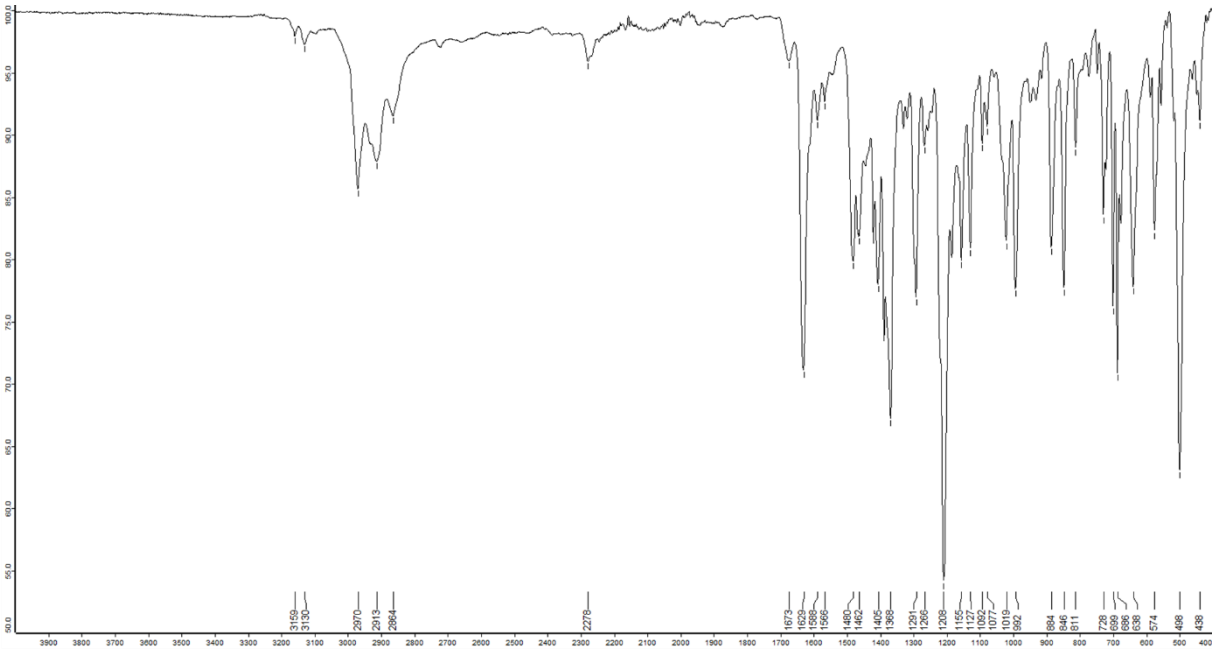


Figure S37. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)] (**2b**).

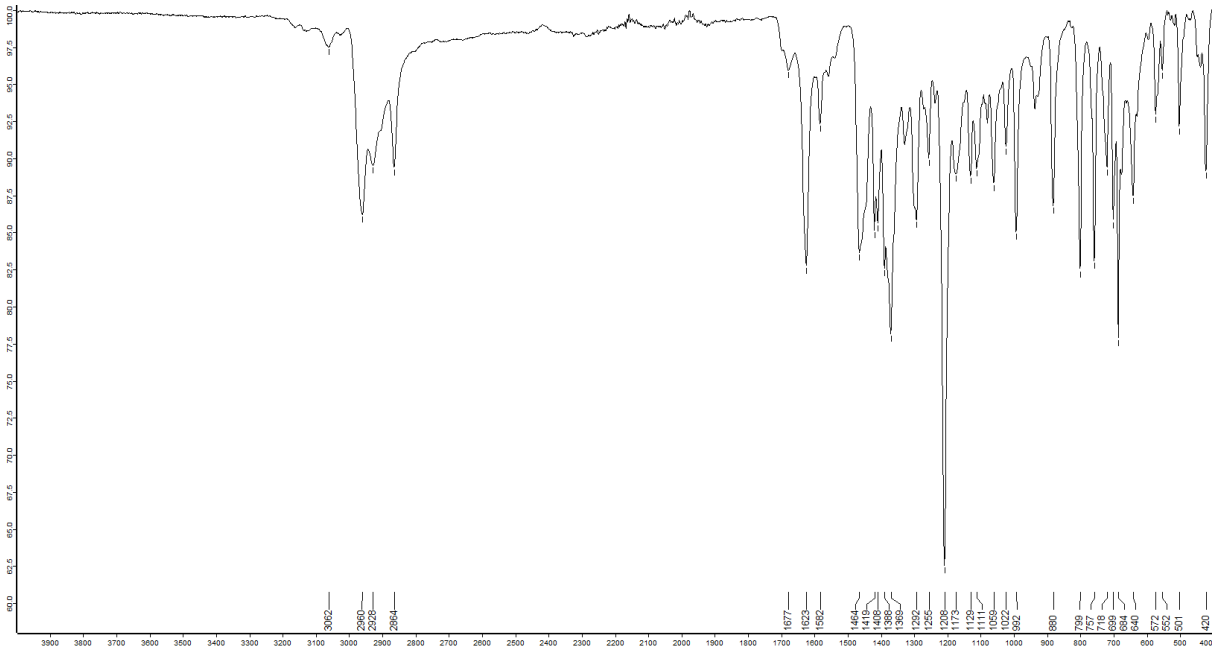


Figure S38. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (**2c**).

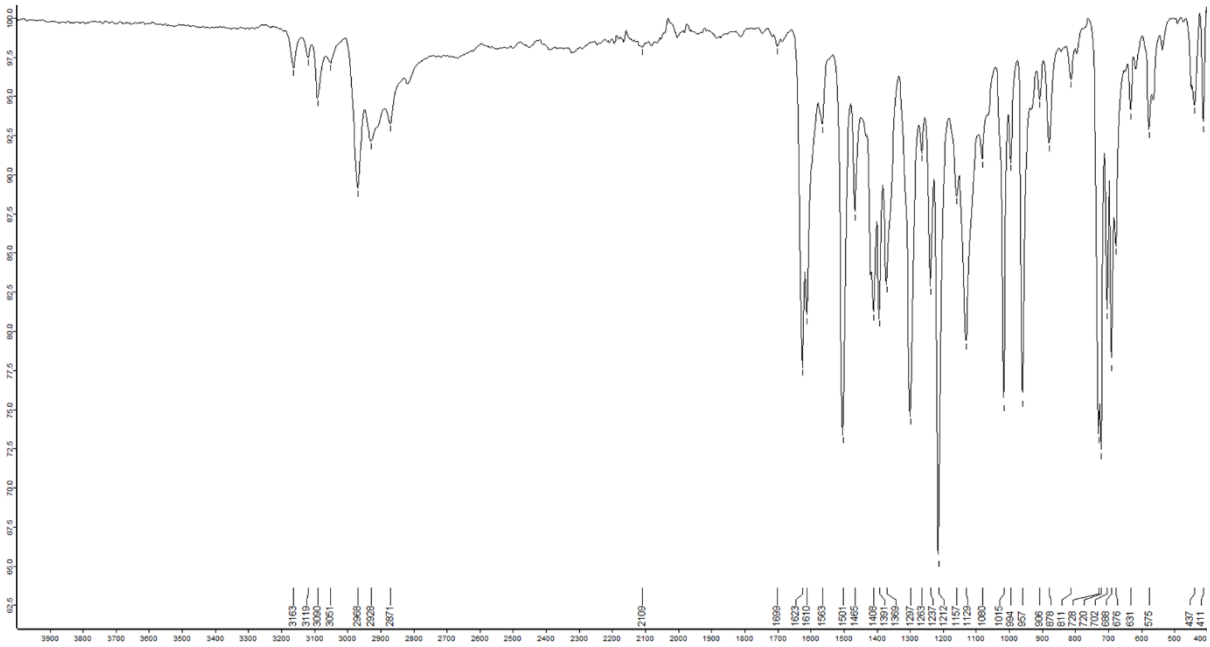


Figure S39. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (**2d**).

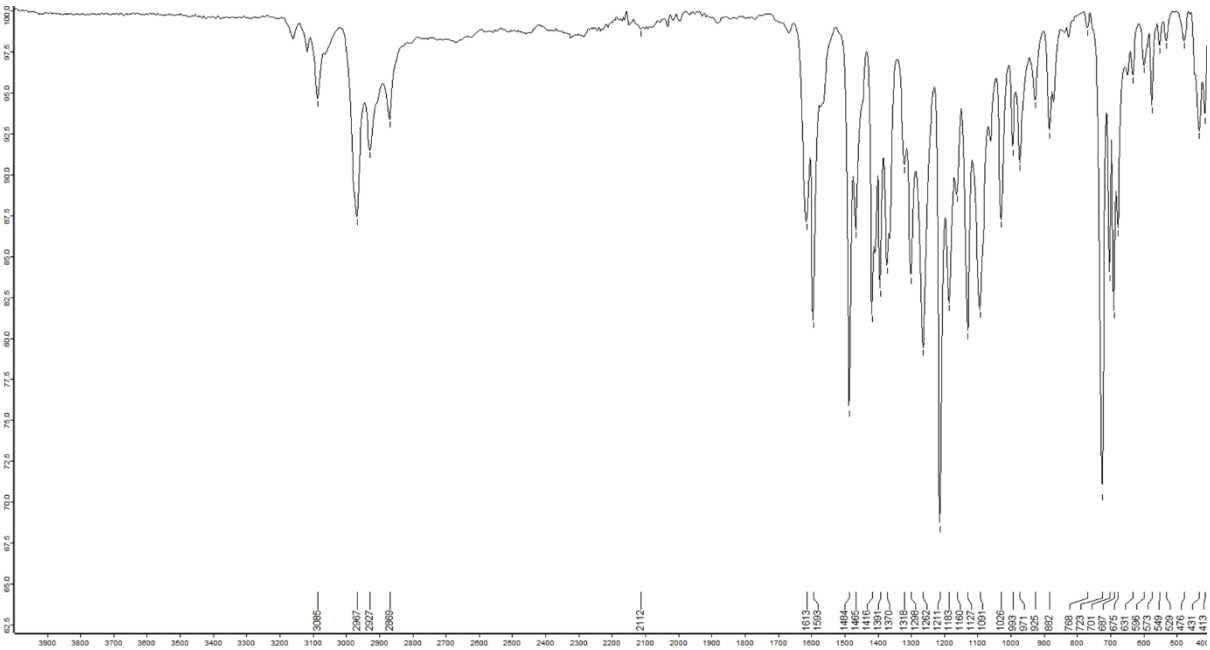


Figure S40. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (**2e**).

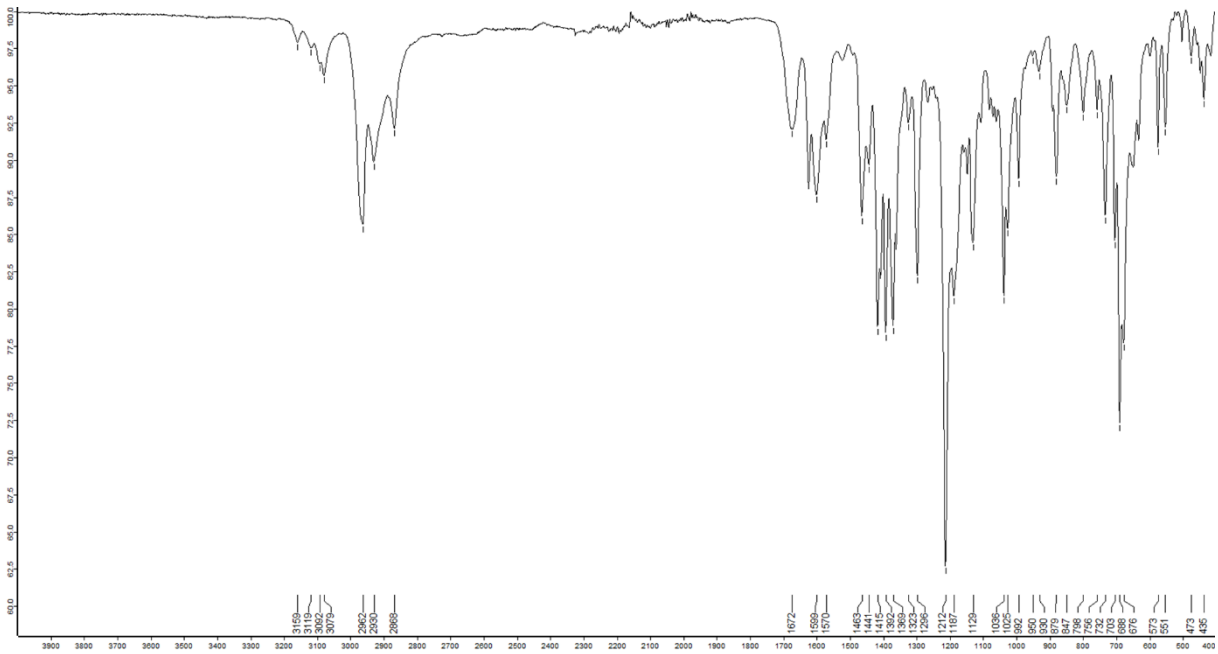


Figure S41. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (**2f**).

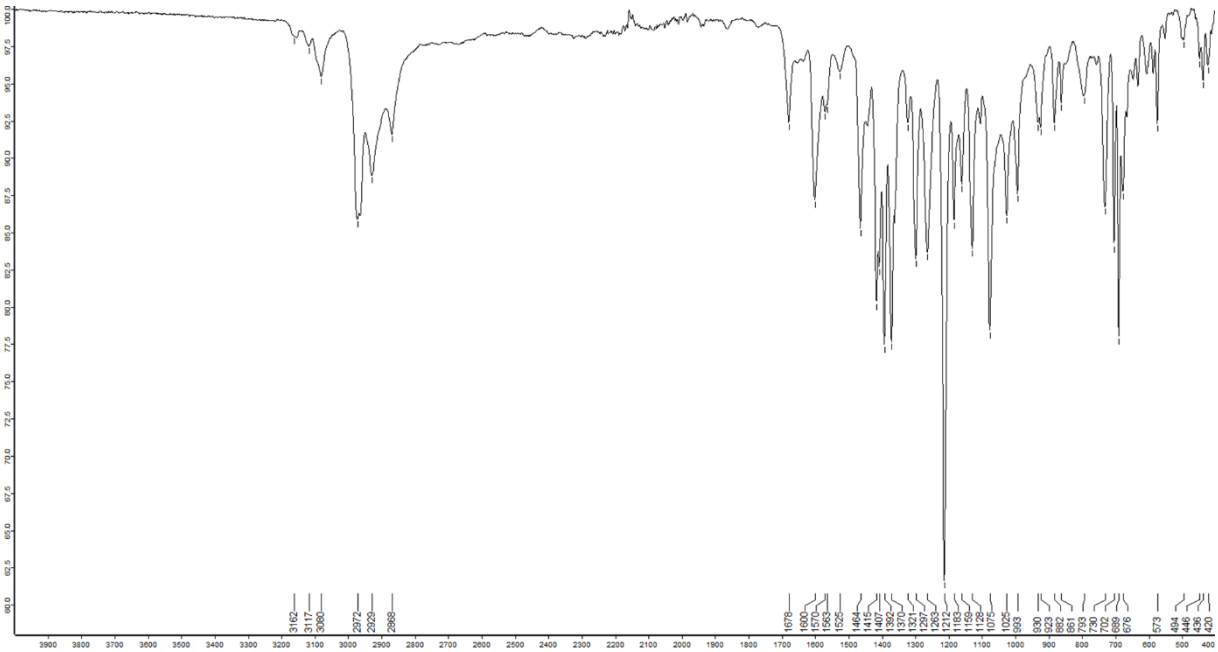


Figure S42. FT-IR spectrum (ATR) of [Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (**2g**).

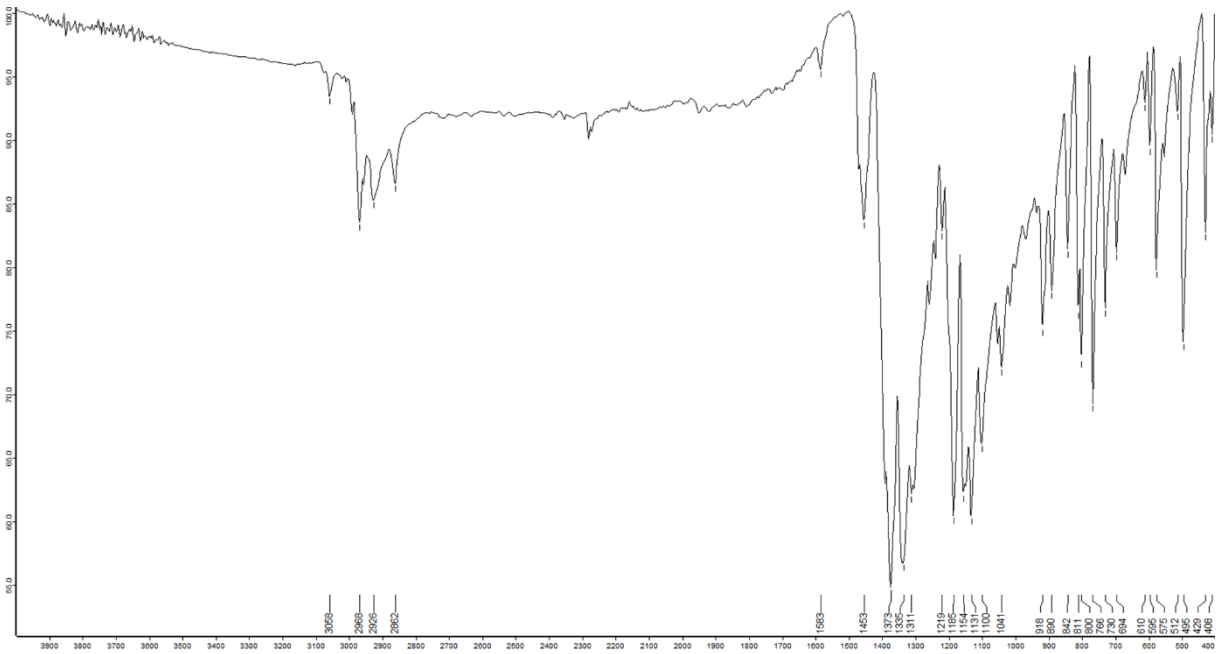


Figure S43. FT-IR spectrum (ATR) of [Ni(cAAC^{Me}-CS_2)$_2$)] (**3a**).

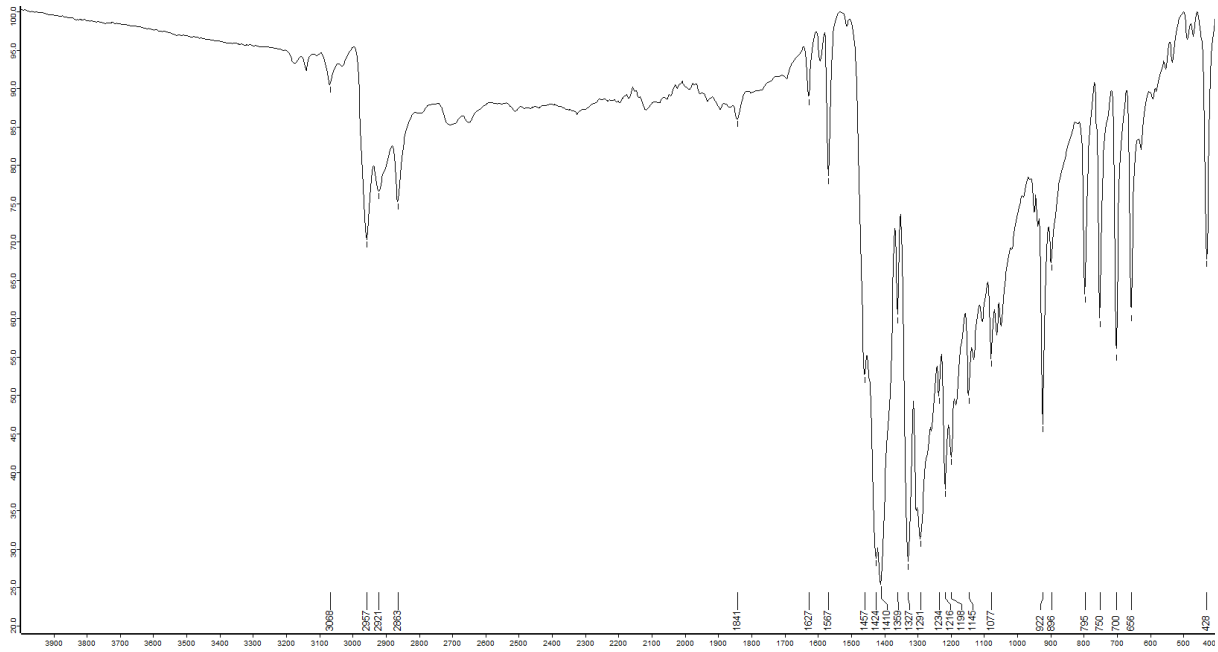


Figure S44. FT-IR spectrum (ATR) of [Ni(IDipp-CS_2)$_2$] (**3b**).

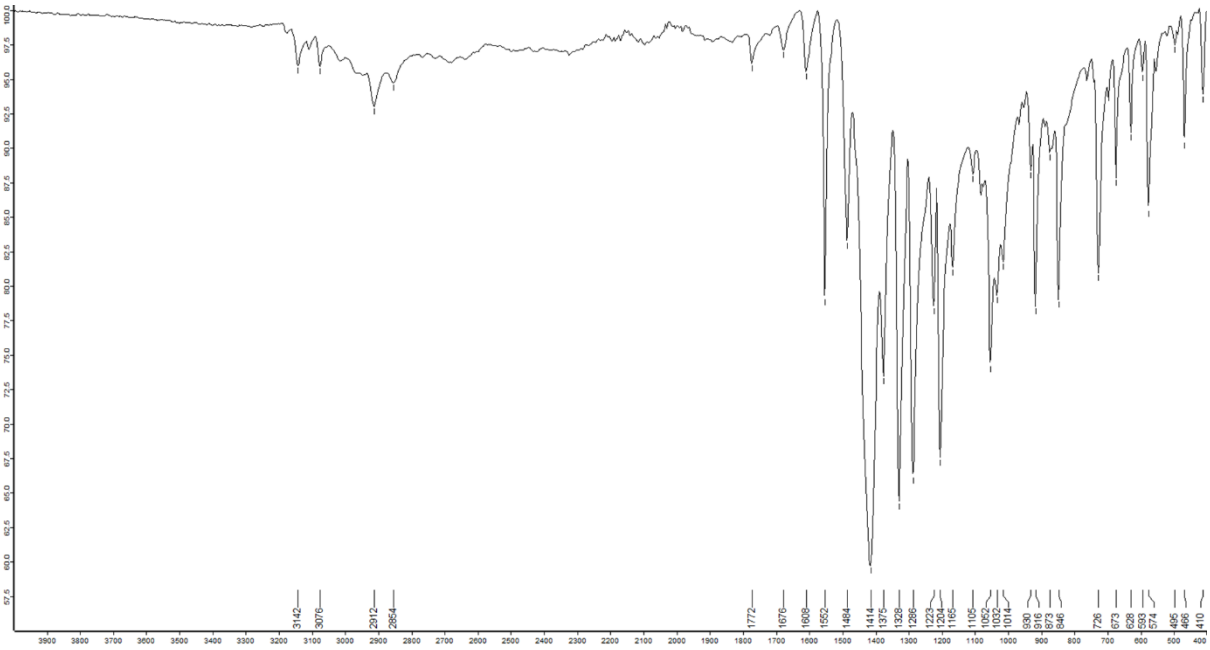


Figure S45. FT-IR spectrum (ATR) of [Ni(IMes-CS_2)$_2$] (**3c**).

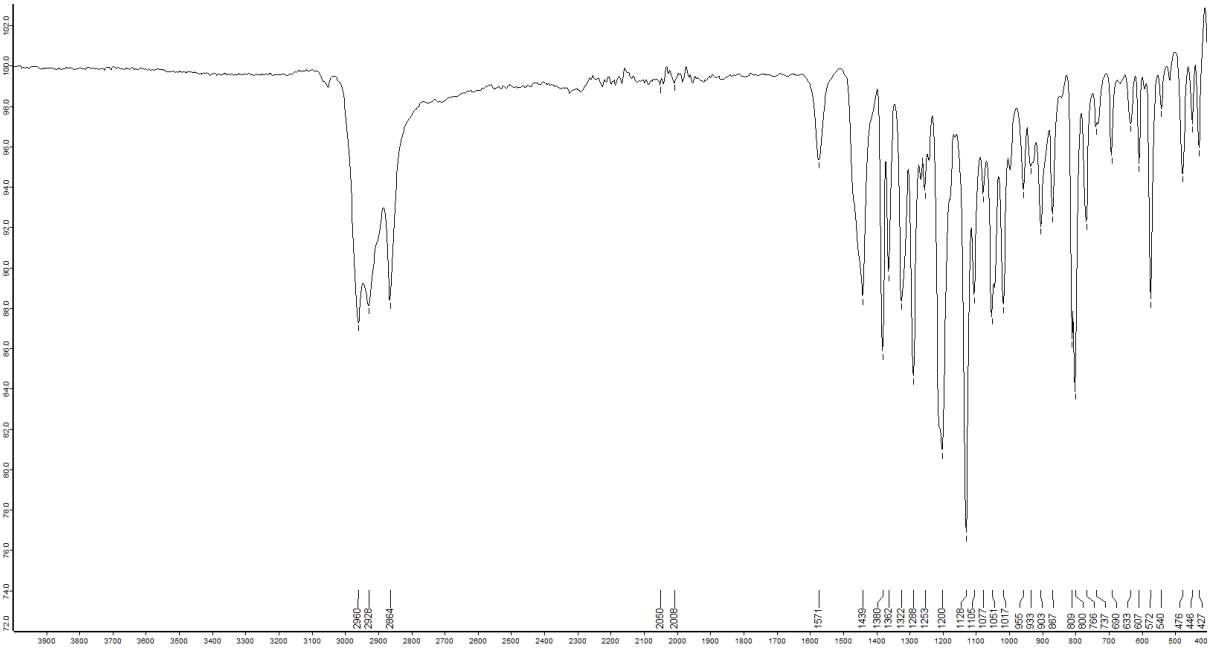


Figure S46. FT-IR spectrum (ATR) of K[Ni(cAAC^{Me}-CS_2)$_2$] (**4a^{K}**).

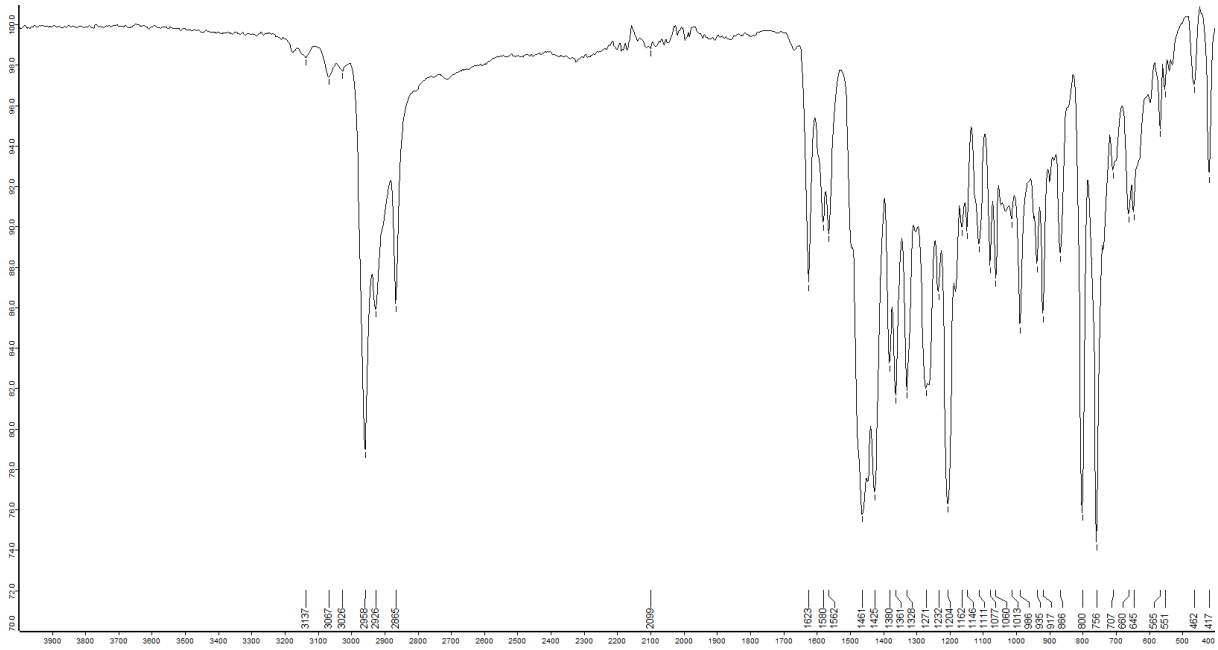


Figure S47. FT-IR spectrum (ATR) of K[Ni(IDipp-CS_2)$_2$] (**4b^{K}**).

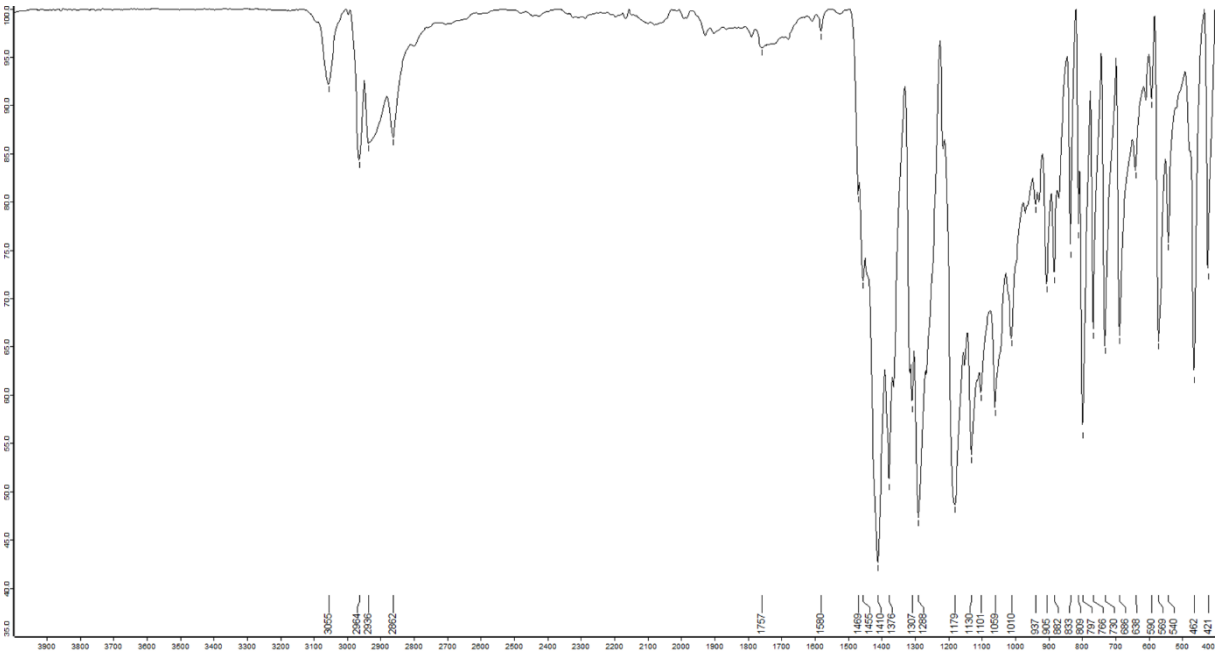


Figure S48. FT-IR spectrum (ATR) of [$CoCp_2$][Ni(cAAC^{Me}-CS_2)$_2$] (**4a^{Co}**).

6 Electrochemical Section

6.1 General Information

Cyclic voltammetry (CV) experiments were performed using a PINE Instruments AFCBP1 bipotentiostat with a commercially available cell (ALS Co. Ltd., VC-4) in an argon filled glovebox. The cell was used with a glassy carbon disc working electrode (2 mm diameter, BaSi) and a commercial platinum wire counter electrode (0.4 mm x 5.7 mm, ALS Co. Ltd.), as well as commercial silver wire reference electrodes separated from the main compartment by ion permeable porous glass (RE-7, ALS Co. Ltd.) and filled with a 0.01 M $AgNO_3$ stock solution in acetonitrile. Cyclovoltammetric measurements were performed with argon purged solvents. [TBA][PF_6] was bought from Fluka (98%+) and used without further purification. All measurements were referenced against Ag^+/Ag as well as Fc^+/Fc as an internal standard by addition of [$FeCp_2$] (Fc) at the end of the CV-experiment. The experiment control and recording were performed using the software packages AfterMath[17] or Nova[18], and data processing and plots were done with Origin 2023.[15]

6.2 Cyclovoltammetric Data

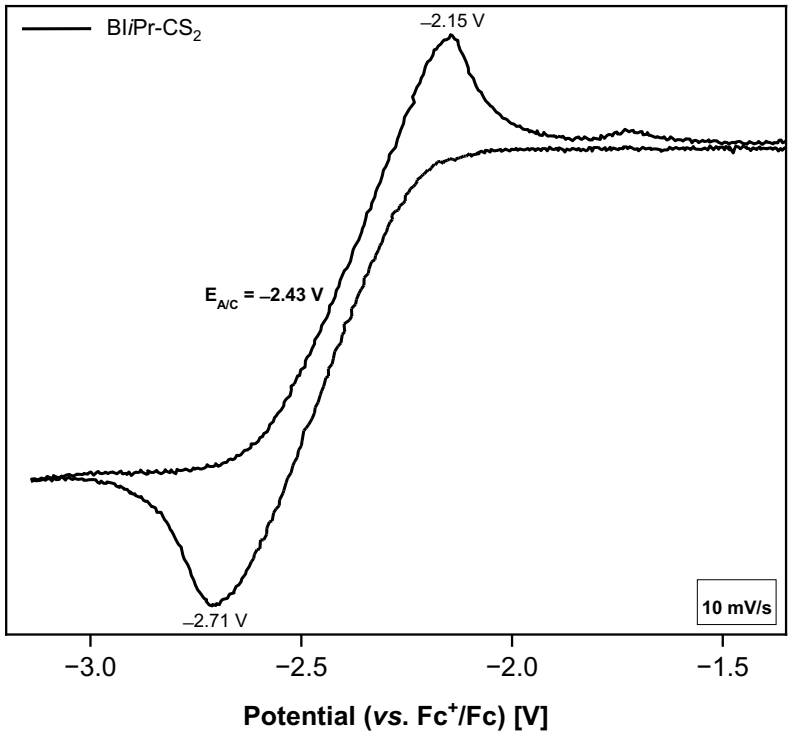


Figure S49. Cyclic voltammogram of BI*i*Pr-CS_2 (**1e**) in THF using 0.1 M [TBA][PF_6] as supporting electrolyte at a scan rate of 10 mV/s. Potentials are referenced to the ferrocene/ferrocenium redox couple and the current is normalized to a value of 1.

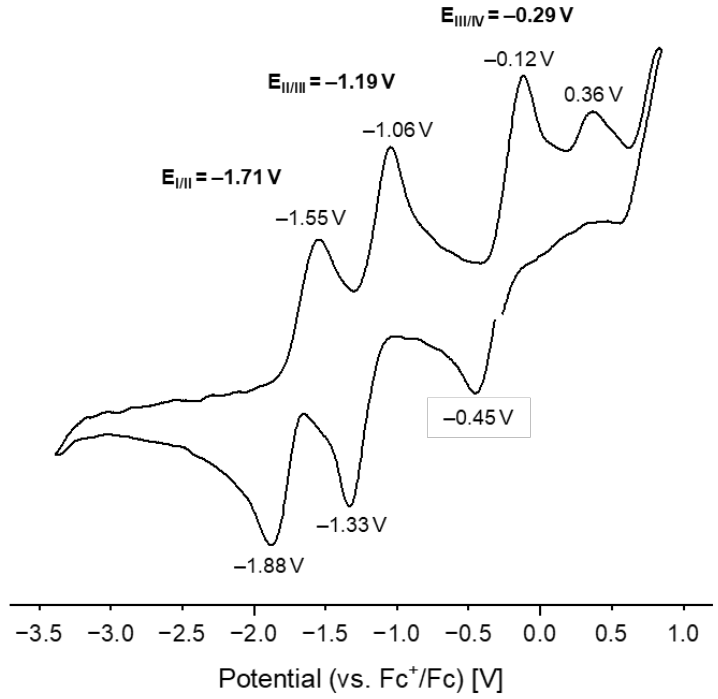


Figure S50. Cyclic voltammogram of [Ni(cAAC^{Me}-CS_2)$_2$] (**3a**) in THF using 0.1 M [TBA][PF_6] as supporting electrolyte at a scan rate of 25 mV/s. Potentials are referenced to the ferrocene/ferrocenium couple and the current is normalized to a value of 1.

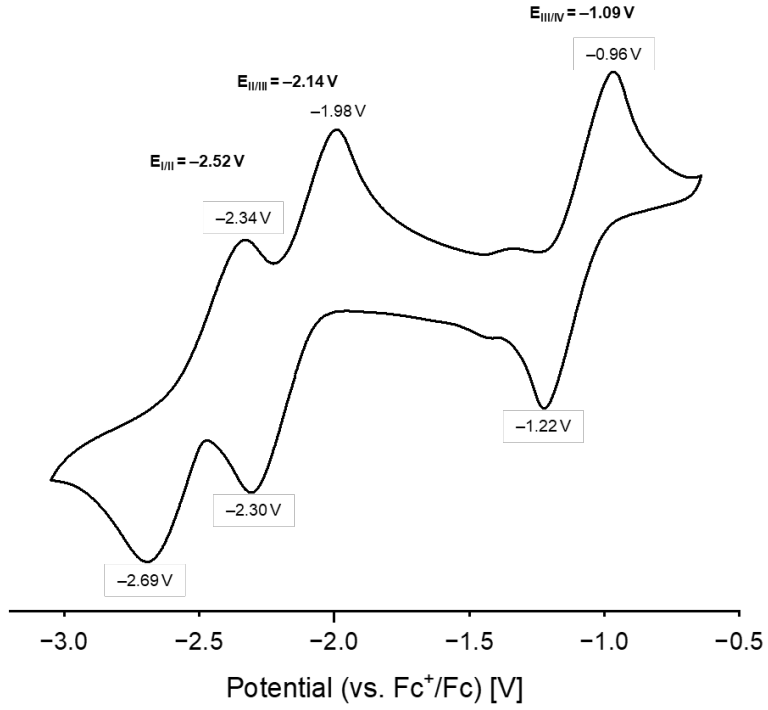


Figure S51. Cyclic voltammogram of [Ni(IDipp-CS_2)$_2$] (**3b**) in THF using 0.1 M [TBA][PF_6] as supporting electrolyte at a scan rate of 50 mV/s. Potentials are referenced to the ferrocene/ferrocenium couple and the current is normalized to a value of 1.

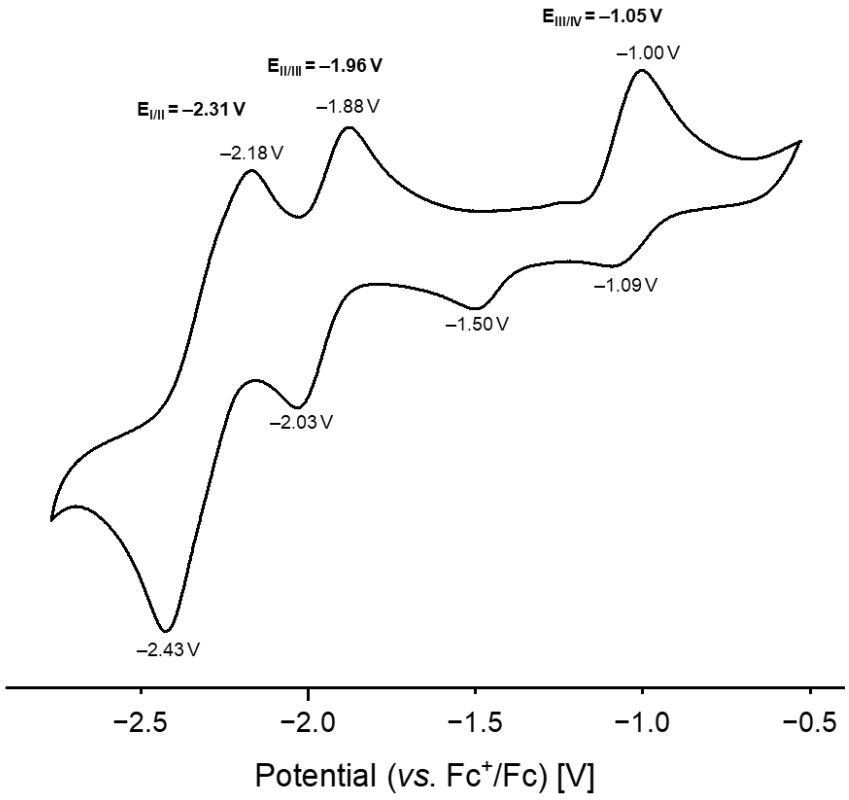


Figure S52. Cyclic voltammogram of [Ni(IMes-CS_2)$_2$] (**3c**) in THF using 0.1 M [TBA][PF_6] as supporting electrolyte at a scan rate of 25 mV/s. Potentials are referenced to the ferrocene/ferrocenium redox couple and the current is normalized to a value of 1.

7 UV/VIS/NIR Section

7.1 General Information

All measurements were performed in standard quartz cuvettes (1 cm x 1 cm cross-section). UV/VIS/NIR absorption spectra were recorded using a Perkin Elmer Lambda 1050+ or a Perkin Elmber Lambda 465 spectrophotometer. In the case of **4b^{K}**, rapid decomposition leading to formation of the respective neutral complex **3b** prevented measurements at low concentrations, thus higher concentrations were necessary with the downside of too high optical densities at wavelengths in the UV/VIS range, prohibiting effective experimental measurement of this area of the spectrum with the used setup. Spectra were plotted using the Origin software package.[15]

7.2 UV/VIS/NIR Spectra

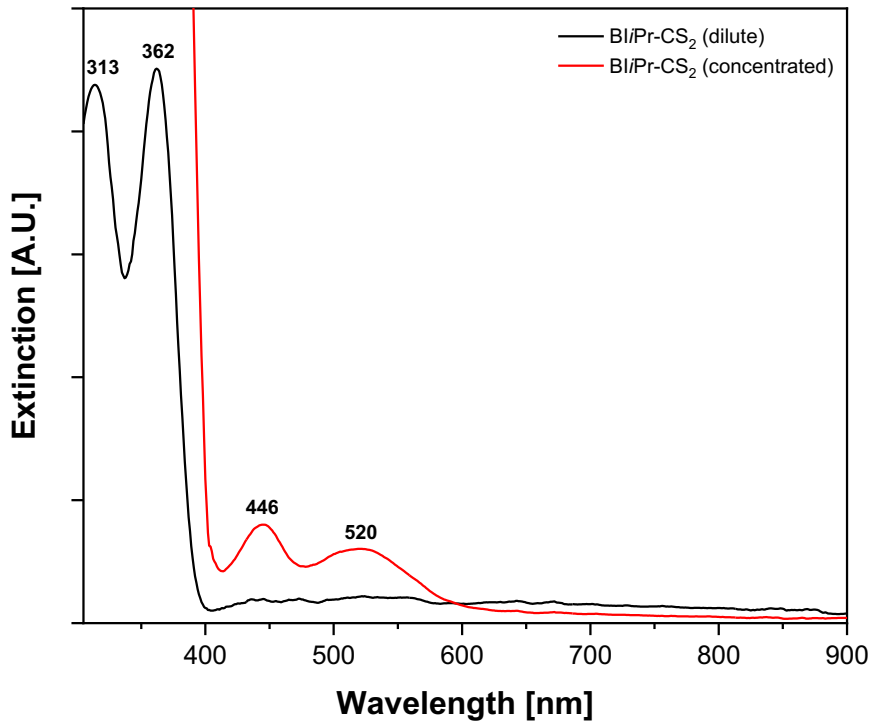


Figure S53. Absorption spectrum of BI*i*Pr-CS$_2$ (**1e**) in THF at different concentrations.

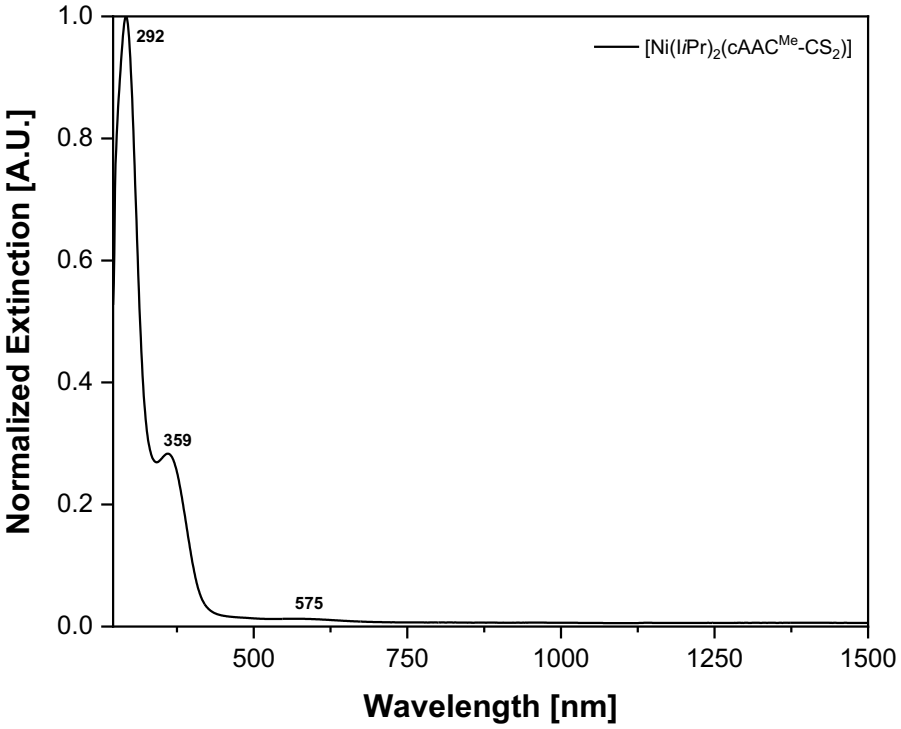


Figure S54. Absorption spectrum of [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (**2a**) in benzene.

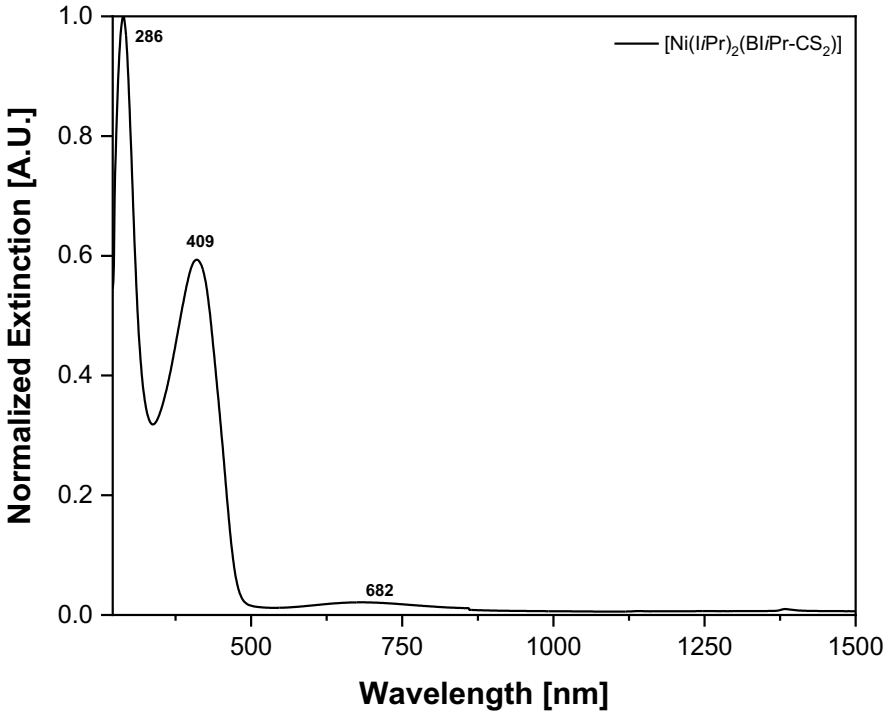


Figure S55. Absorption spectrum of [Ni(I*i*Pr)$_2$(BIMe-CS$_2$)] (**2d**) in benzene.

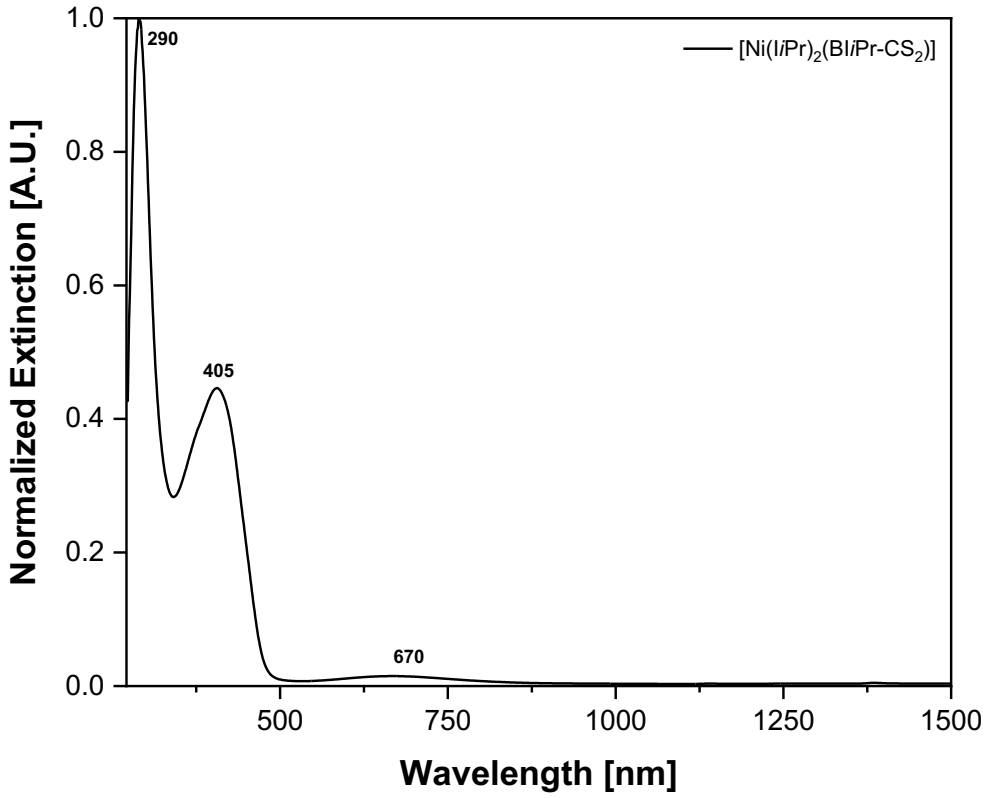


Figure S56. Absorption spectrum of [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (**2e**) in benzene.

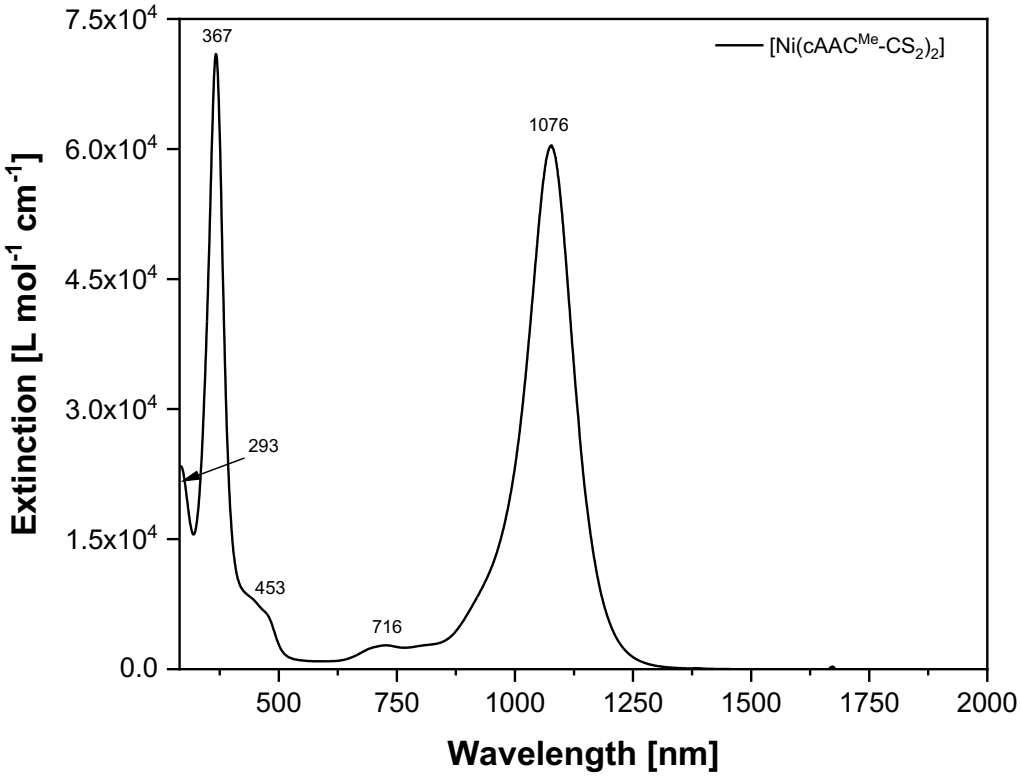


Figure S57. Absorption spectrum of [Ni(cAAC^{Me}-CS$_2$)$_2$] (**3a**) in benzene.

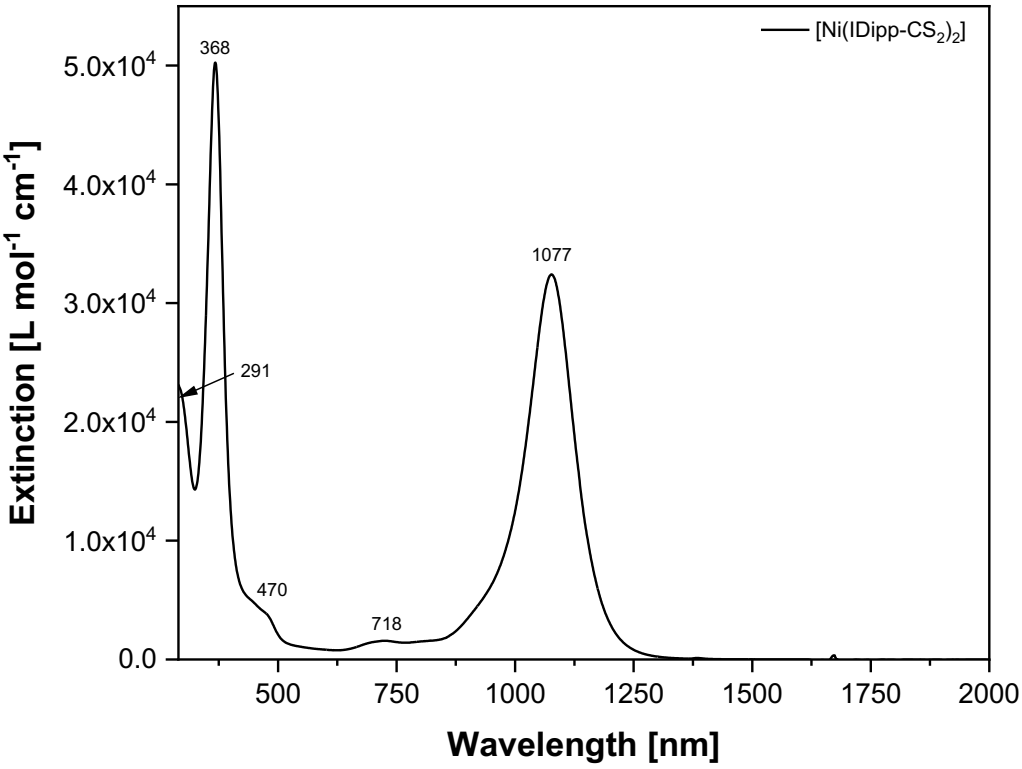


Figure S58. Absorption spectrum of [Ni(IDipp-CS_2)$_2$] (**3b**) in benzene.

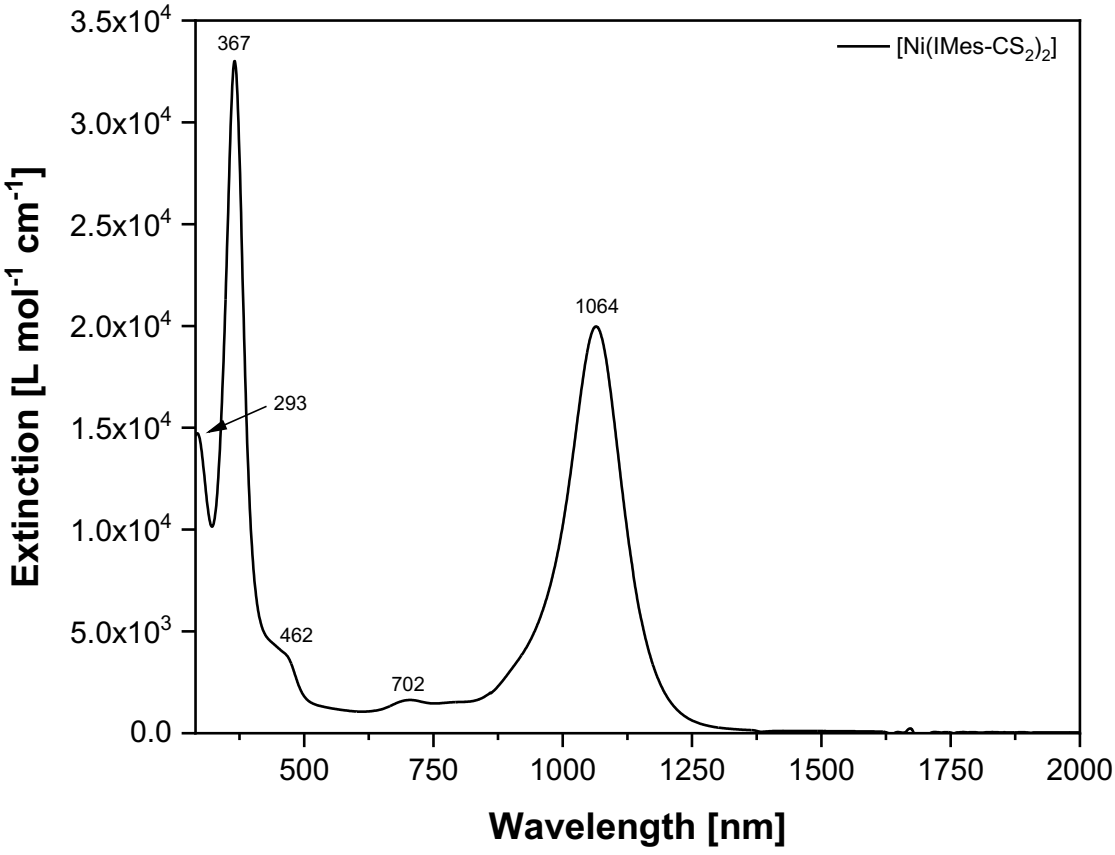


Figure S59. Absorption spectrum of [Ni(IMes-CS_2)$_2$] (**3c**) in benzene.

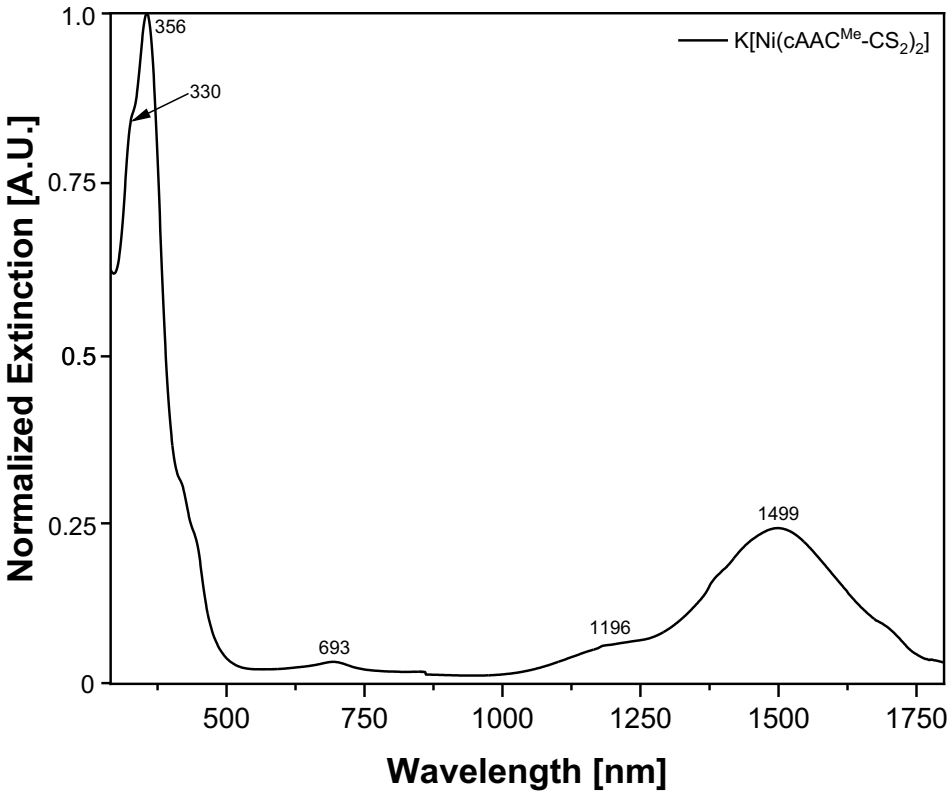


Figure S60. Absorption spectrum of K[Ni(cAAC^{Me}-CS_2)$_2$] (**4a^{K}**) in THF.

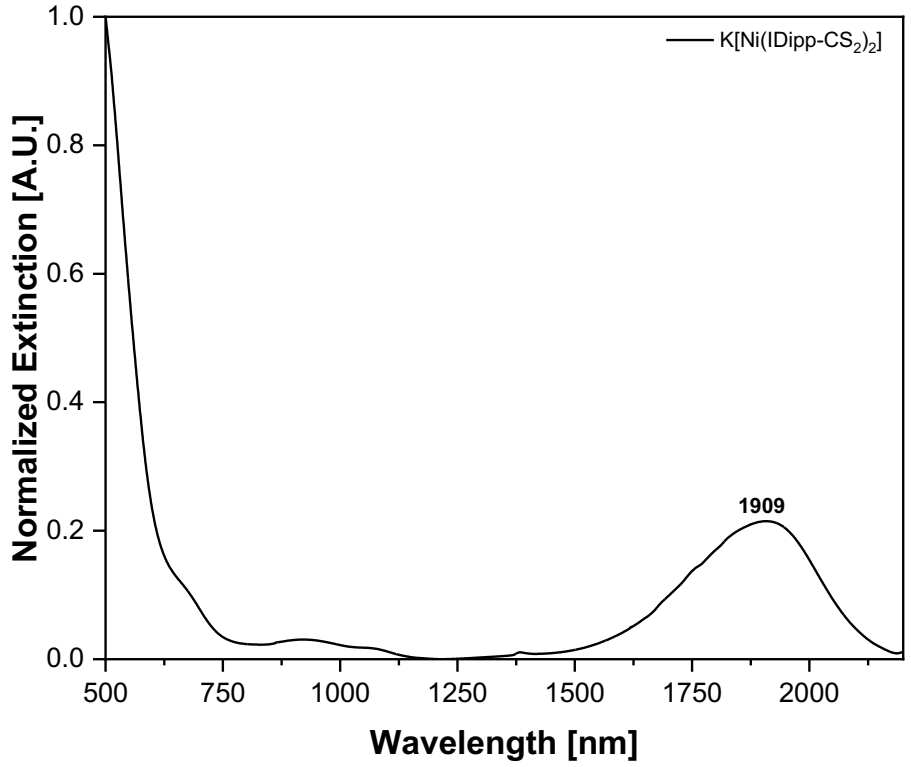


Figure S61. Absorption spectrum of K[Ni(IDipp-CS_2)$_2$] (**4b^{K}**) in THF.

8 High Resolution Mass Spectrometry Section

8.1 General Information

High resolution mass spectrometry was performed on a Thermo Scientific Exactive Plus mass spectrometer with an Orbitrap mass analyser. The measurement was performed using the LIFDI (Liquid Injection Field Desorption/Ionization) and ESI (Electron Spray Ionization) methods with nitrogen as a carrier gas.

8.2 HRMS Spectra

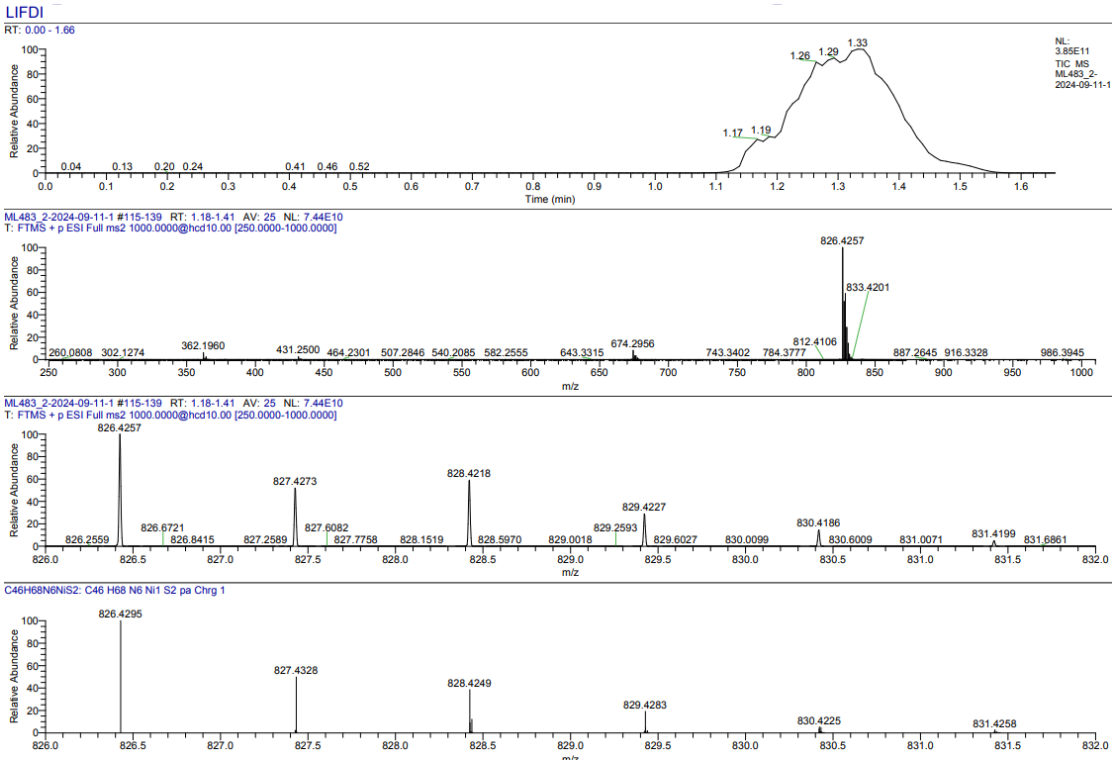


Figure S62. Results of the LIFDI mass spectrometric investigations of [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)] (**2b**) in toluene.

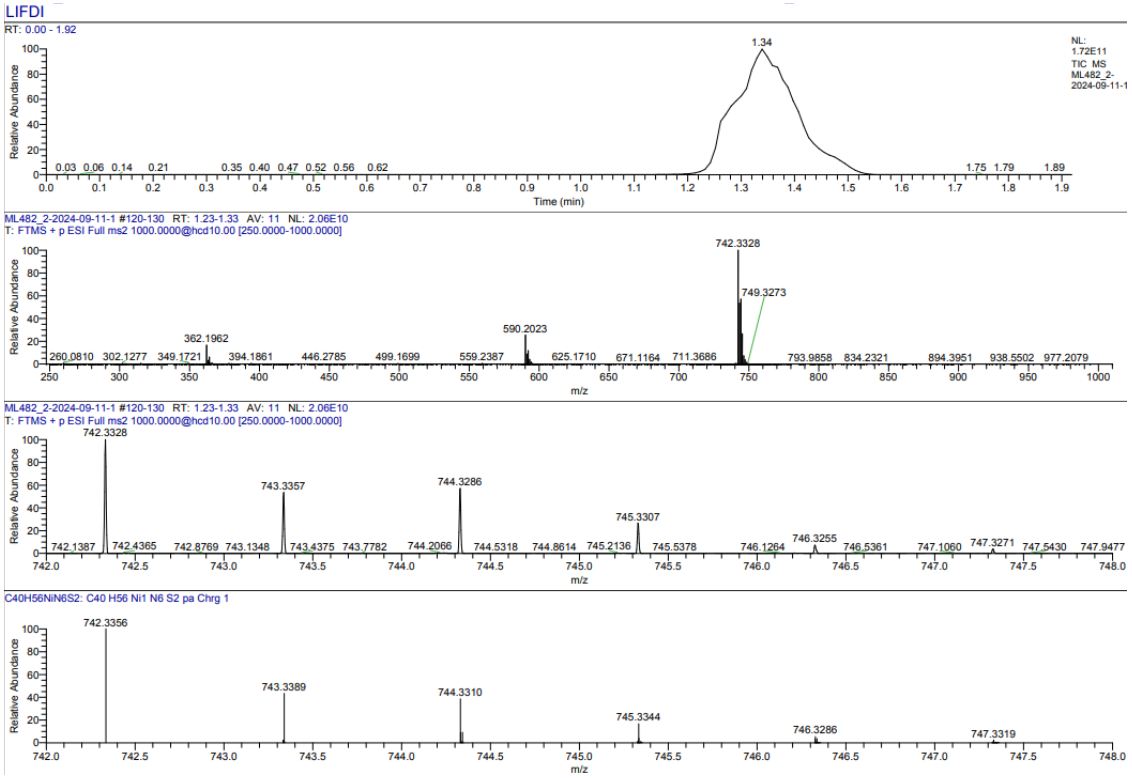


Figure S63. Results of the LIFDI mass spectrometric investigations of [Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (**2c**) in toluene.

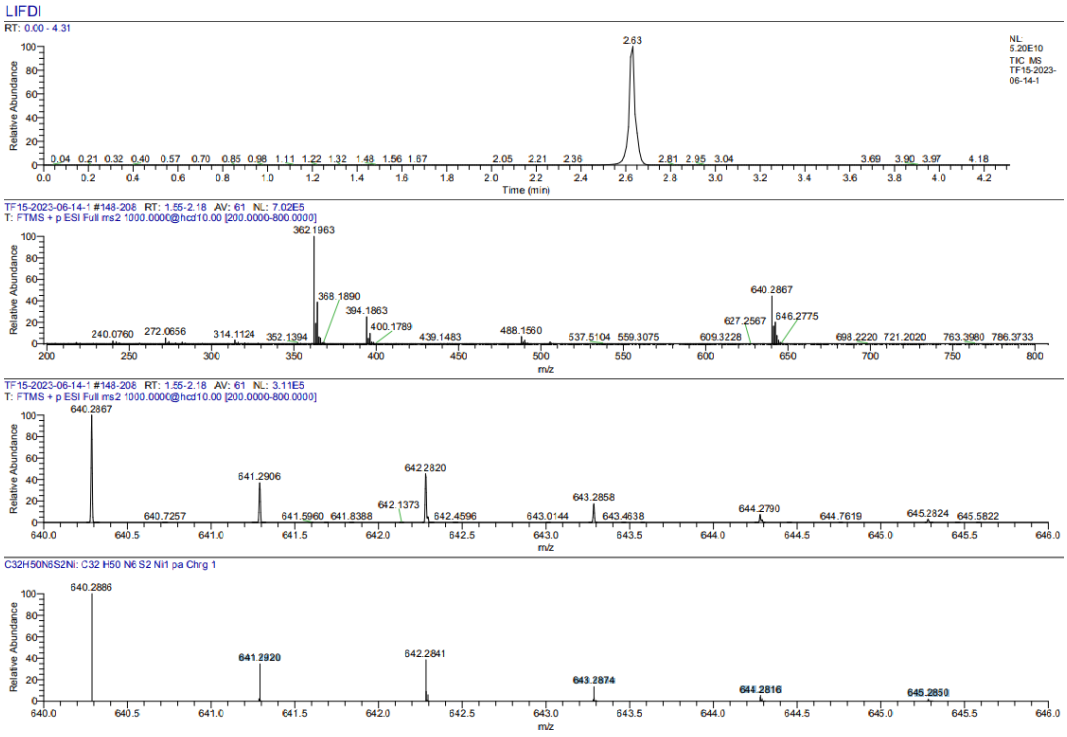


Figure S64. Results of the LIFDI mass spectrometric investigations of [Ni(I*i*Pr)$_2$(BI*i*Pr-CS$_2$)] (**2e**) in THF.

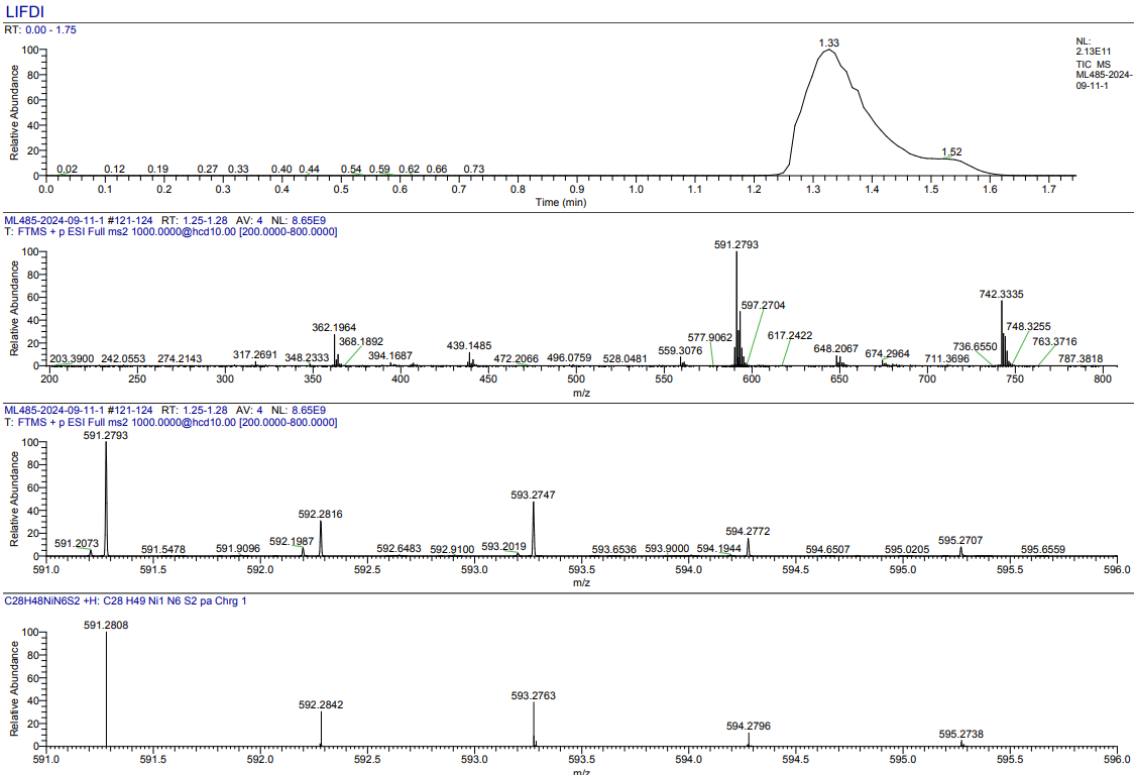


Figure S65. Results of the LIFDI mass spectrometric investigations of [Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (**2f**) in THF.

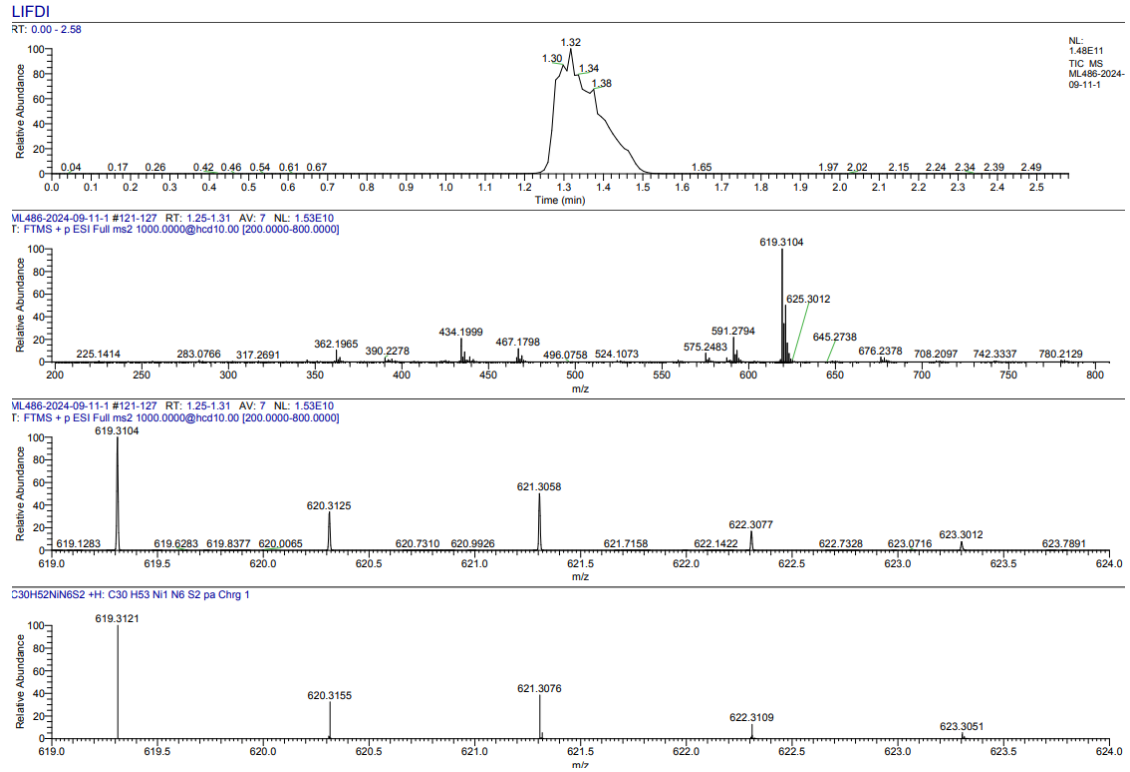


Figure S66. Results of the LIFDI mass spectrometric investigations of [Ni(I*i*Pr)$_2$(I*i*Pr^{Me}-CS$_2$)] (**2g**) in THF.

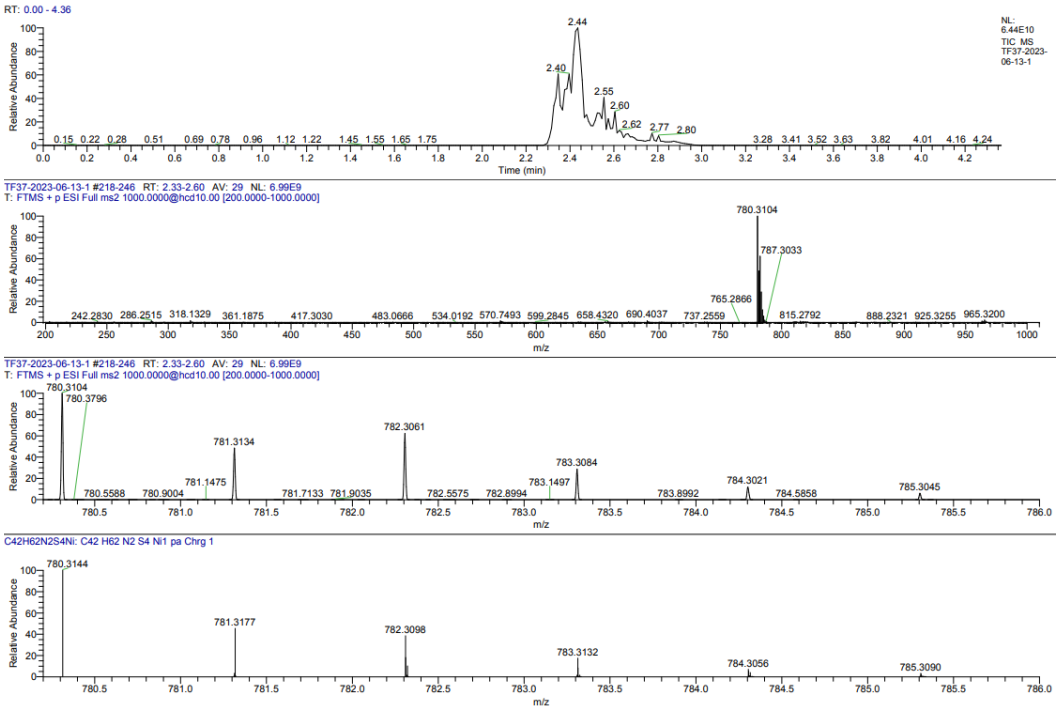


Figure S67. Results of the LIFDI mass spectrometric investigations of [Ni(cAAC^{Me}-CS$_2$)$_2$] (**3a**) dissolved in THF.

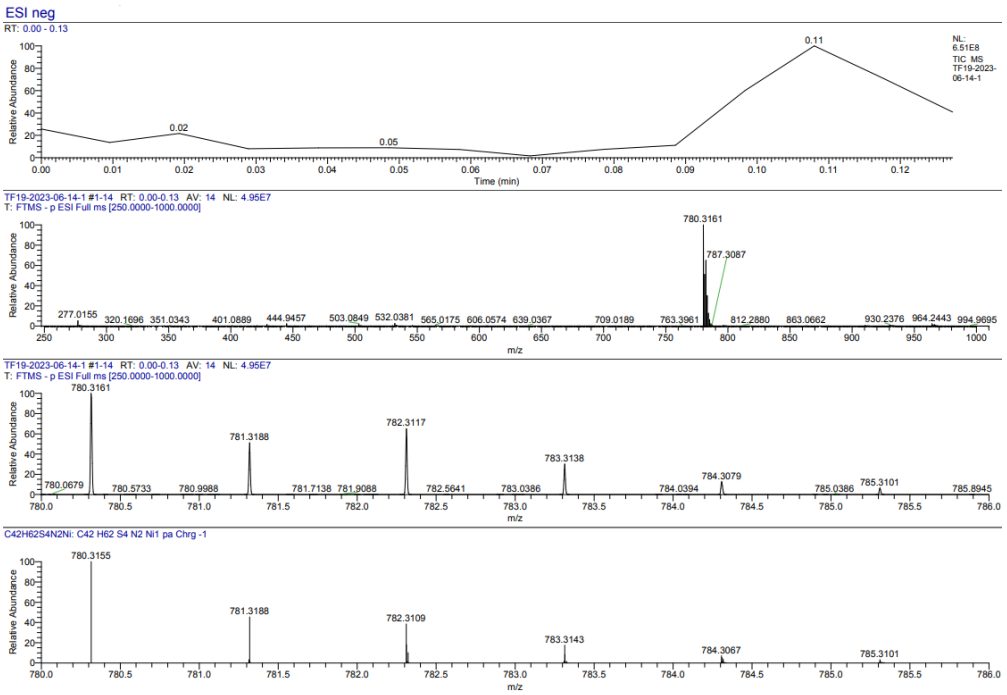


Figure S68. Results of the ESI mass spectrometric investigations of K[Ni(cAAC^{Me}-CS$_2$)$_2$] (**4a^{K}**) dissolved in THF.

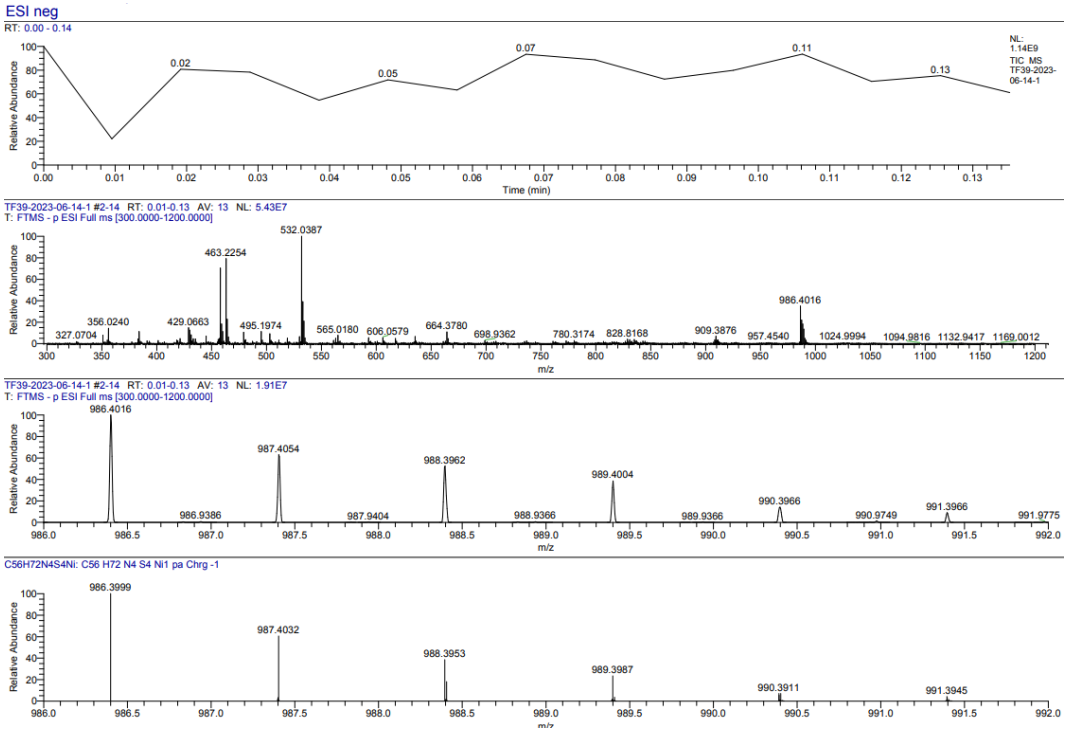


Figure S69. Results of the ESI mass spectrometric investigations of K[Ni(IDipp-CS_2)$_2$] (**4b^K**) dissolved in THF.

9 Crystallographic Section

9.1 General Information

Crystal data were either collected on a Rigaku XtaLAB Synergy-DW diffractometer with an HyPix-6000HE detector and monochromated CuKα or MoKα radiation equipped with an Oxford Cryo 800 cooling unit or on a XtaLAB Synergy Dualflex HyPix diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated CuKa radiation. The Crystals were immersed in a film of perfluoropolyether oil on a glass fiber MicroMount™ (MiTeGen) and data were collected at 100 K. The images were processed with the Bruker or Crysalis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations. Figures were created using Diamond Crystal and Molecular Structure Visualisation and Mercury software packages.[20]

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-2409879 (**1d**), CCDC-2409878 (**1e**),CCDC-2409886 (**2a**), CCDC-2409881 (**2b**), CCDC-2409883 (**2c**), CCDC-2409882 (**2d**), CCDC-2409880 (**3a**), CCDC-2409884 (**3b**), CCDC-2409885 (**3c**), CCDC-2409888 (**4a^{K}**), CCDC-2409887 (**4b^{K}**).

9.2 Crystal Data

Crystal Data for BIMe-CS_2·CH_2Cl_2 (1d): $C_{11}H_{12}Cl_2N_2S_2$, M_r = 307.25 g/mol, T = 100.00(10) K, λ = 1.54184 Å, red block, 0.280 × 0.170 × 0.090 mm^3, orthorhombic, space group *P*nma, a = 14.5441(2) Å, b = 6.83480(10) Å, c = 13.3132(2) Å, α = 90 °, β = 90 °, γ = 90 °, V = 1323.41(3) $Å^3$, Z = 4, ρ_{calc} = 1.542 Mg/m^3, μ = 7.182 mm^{-1}, $F(000)$ = 632, 26111 reflections, $-18 \le h \le 18$, $-8 \le k \le 8$, $-16 \le l \le 14$, 4.503° < θ < 77.650 °, completeness 100%, 1525 independent reflections, 1476 reflections observed with [$I > 2\sigma(I)$], 102 parameters, 0 restraints, R indices (all data): R_1 = 0.0572, wR_2 = 0.1798, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0564, wR_2 = 0.1787, largest difference peak and hole 0.943 and –0.744 e $Å^{-3}$, Goof = 1.165.

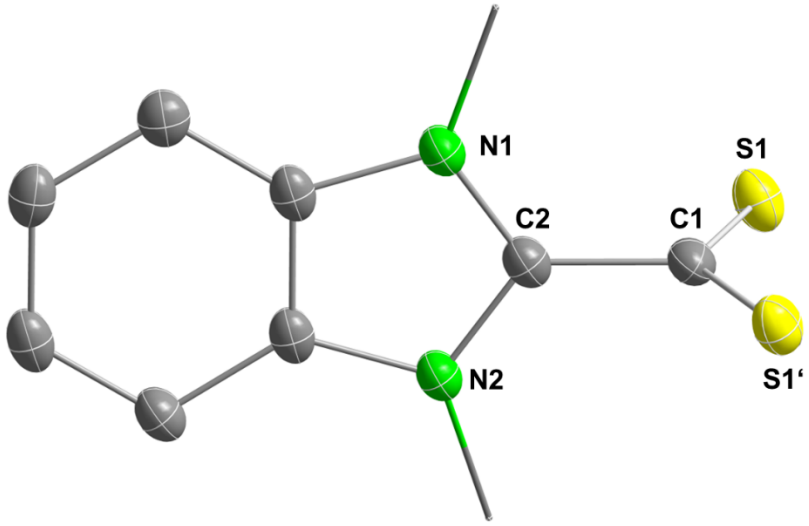


Figure S70. Molecular structure of BIMe-CS_2·CH_2Cl_2 (**1d**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and one molecule of co-crystallized CH_2Cl_2 were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.669(2), C1–C2 1.488(5), C2–N1 1.338(5), C2–N2 1.344(5), ∡S1C1S1’ 131.3(2), ∡N1C2C1S1 90.3(4).

Crystal Data for B*i*Pr-CS_2 (1e): $C_{14}H_{18}N_2S_2$, M_r = 278.42 g/mol, T = 100.00(10) K, λ = 1.54184 Å, red block, 0.260 × 0.130 × 0.090 mm^3, monoclinic, space group $P2_1/n$, a = 11.83520(10) Å, b = 8.48740(10) Å, c = 15.0477(2) Å, α = 90 °, β = 107.1900(10) °, γ = 90 °, V = 1444.02(3) $Å^3$, Z = 4, ρ_{calc} = 1.281 Mg/m^3, μ = 3.201 mm^{-1}, $F(000)$ = 592, 25991 reflections, $-14 \le h \le 14$, $-10 \le k \le 10$, $-16 \le l \le 18$, 4.200 ° < θ < 76.722 , completeness 99.6%, 2991 independent reflections, 2823 reflections observed with [$I > 2\sigma(I)$], 167 parameters, 0 restraints, R indices (all data): R_1 = 0.0364, wR_2 = 0.0950, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0350, wR_2 = 0.0943, largest difference peak and hole 0.402 and −0.235 e $Å^{-3}$, Goof = 1.139.

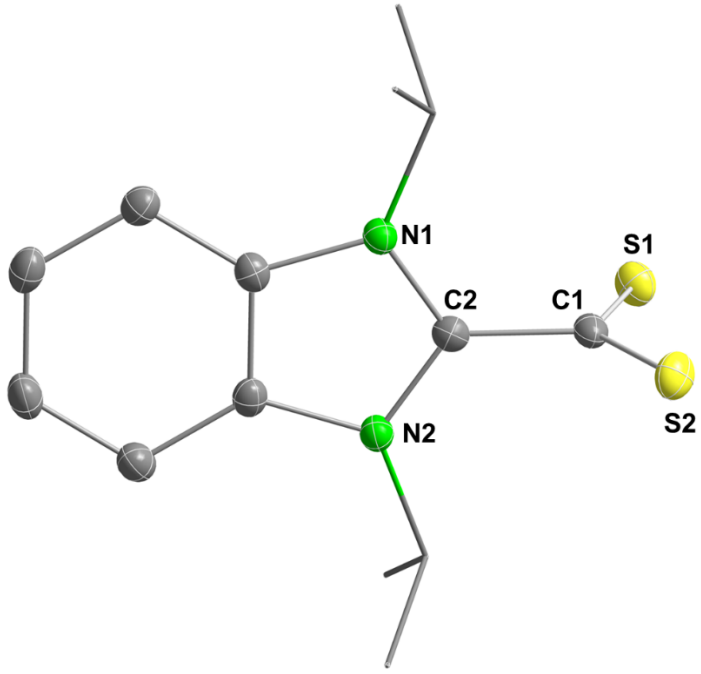


Figure S71. Molecular structure of BI*i*Pr-CS_2 (**1e**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.668(2), S2–C1 1.670(2), C1–C2 1.485(2), N1–C2 1.337(2), N2–C2 1.341(2), ∡S1C1S2 131.8(1), ∡N1C2C1S1 89.0(1).

Crystal Data for [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (2a):

$C_{39}H_{63}N_5NiS_2$, M_r = 724.77 g/mol, T = 100.00(10) K, λ = 1.54184 Å, yellow block, 0.180 × 0.140 × 0.080 mm^3, monoclinic, space group $P2_1/c$, a = 14.47860(10) Å, b = 13.86640(10) Å, c = 19.82980(10) Å, α = 90 °, β = 94.8560(10) °, γ = 90 °, V = 3966.86(4) Å^3, Z = 4, ρ_{calc} = 1.214 Mg/m^3, μ = 1.927 mm^{-1}, F(000) = 1568, 83291 reflections, –18 ≤ h ≤ 14, –17 ≤ k ≤ 17, –25 ≤ l ≤ 24, 3.063 ° < θ < 77.715 °, completeness 100%, 8420 independent reflections, 7815 reflections observed with [$I > 2\sigma(I)$], 440 parameters, 0 restraints, R indices (all data) R_1 = 0.0346, wR_2 = 0.0833, final R indices [$I > 2\sigma(I)$] R_1 = 0.0321, wR_2 = 0.0818, largest difference peak and hole 0.484 and –0.425 e Å^{-3}, Goof = 1.054.

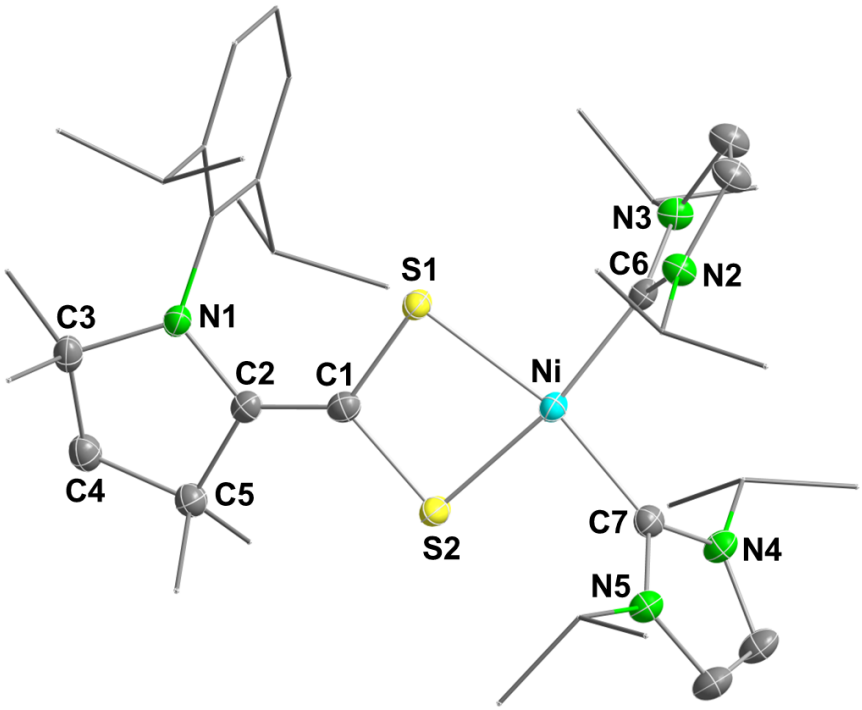


Figure S72. Molecular structure of [Ni(I*i*Pr)$_2$(cAAC^{Me}-CS$_2$)] (**2a**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–S1 2.188(1), Ni–S2 2.186(1), Ni–C6 1.918(1), Ni–C7 1.910(1), S1–C1 1.776(1), S2–C1 1.775(1), C1–C2 1.343(2), C2–N1 1.415(2), ∡C6NiC7 101.3(1), ∡S1NiS2 78.7(1), ∡S1C1S2 102.7(1), ∡C6NiC7 101.3(1), ∡S1NiC6 91.7(1), ∡S1NiC7 166.7(4), ∡S2NiC6 168.3(1), ∡N1C2C1S1 3.5(2).

Crystal Data for [Ni(I*i*Pr)$_2$(IDipp-CS$_2$)]·C$_6$H$_6$ (2b):

$C_{52}H_{74}N_6NiS_2$, M_r = 906.0 g/mol, T = 100.00(10) K, λ = 1.54184 Å, yellow block, 0.294 × 0.271 × 0.200 mm^3, triclinic, space group $P\bar{1}$, a = 12.2463(2) Å, b = 13.0402(2) Å, c = 18.3208(3) Å, α = 84.3840(10) °, β = 76.1050(10) °, γ = 64.1840(10) °, V = 2556.59(7) Å^3, Z = 2, ρ_{calc} = 1.177 Mg/m^3, μ = 1.601 mm^{-1}, F(000) = 976, 48749 reflections, –13 ≤ h ≤ 15, –16 ≤ k ≤ 16, –19 ≤ l ≤ 23, 2.484 ° < θ < 77.312 °, completeness 99.2%, 10489 independent reflections, 9871 reflections observed with [$I > 2\sigma(I)$], 566 parameters, 0 restraints, R indices (all data) R_1 = 0.0344, wR_2 = 0.0867, final R indices [$I > 2\sigma(I)$] R_1 = 0.0328, wR_2 = 0.0857, largest difference peak and hole 0.292 and –0.449 e Å^{-3}, Goof = 1.085.

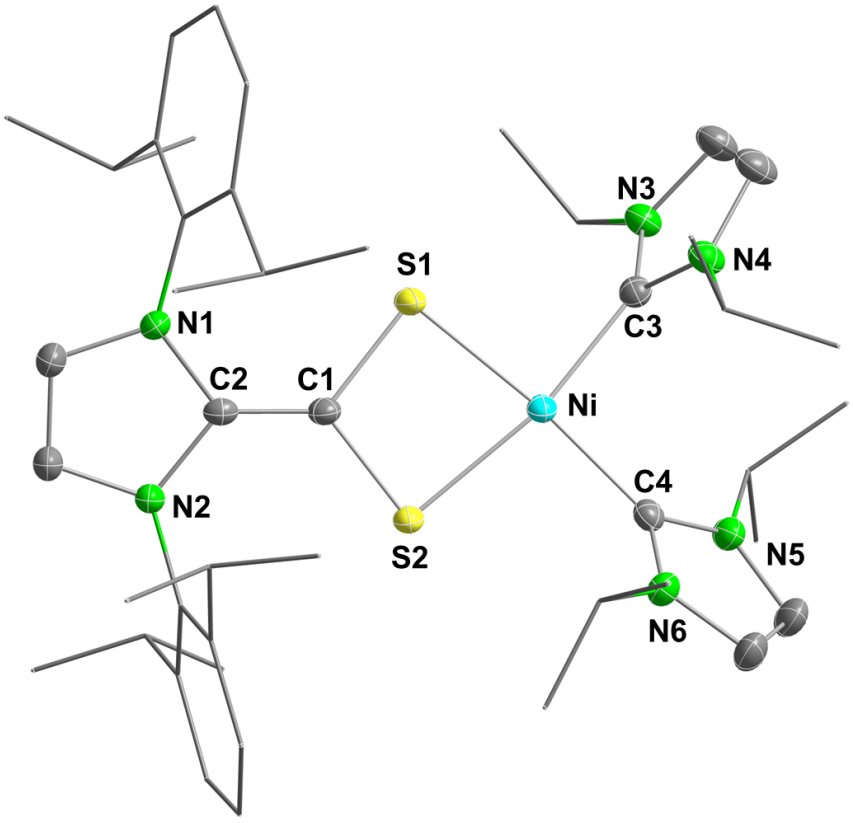


Figure S73. Molecular structure of [Ni(IiPr)$_2$(IDipp-CS$_2$)] (**2b**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and one molecule of co-crystallized C$_6$H$_6$ were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–S1 2.179(1), Ni–S2 2.199(1), Ni–C3 1.903(1), Ni–C4 1.917(1), S1–C1 1.768(1), S2–C1 1.777(1), C1–C2 1.343(2), C2–N1 1.417(2), C2–N2 1.422(2), ∡S1NiS2 79.2(1), ∡S1C1S2 103.8(1), ∡C3NiC4 96.3(1), ∡N1C2C1S1 0.6(2), ∡N2C2C1S2 5.4(2).

Crystal Data for [Ni(IMes-CS_2)(I*i*Pr)$_2$]·THF (2c):

$C_{44}H_{66}N_6NiOS_2$, M_r = 817.85 g/mol, T = 100.00(10) K, λ = 1.54184 Å, yellow block, 0.310 × 0.160 × 0.140 mm^3, orthorhombic, space group $P2_12_12_1$, a = 12.6464(2) Å, b = 14.4357(2) Å, c = 24.9817(3) Å, α = 90 °, β = 90 °, γ = 90 °, V = 4560.65(11) Å^3, Z = 4, ρ_{calc} = 1.191 Mg/m^3, μ = 1.753 mm^{-1}, F(000) = 1760, 23671 reflections, –15 ≤ h ≤ 15, –18 ≤ k ≤ 17, –19 ≤ l ≤ 30, 3.536 ° < θ < 76.962 °, completeness 99.1%, 8444 independent reflections, 7764 reflections observed with [$I > 2\sigma(I)$], 503 parameters, 0 restraints, R indices (all data) R_1 = 0.0351, wR_2 = 0.0742, final R indices [$I > 2\sigma(I)$] R_1 = 0.0304, wR_2 = 0.0723, largest difference peak and hole 0.456 and –0.237 e Å^{-3}, Goof = 1.048.

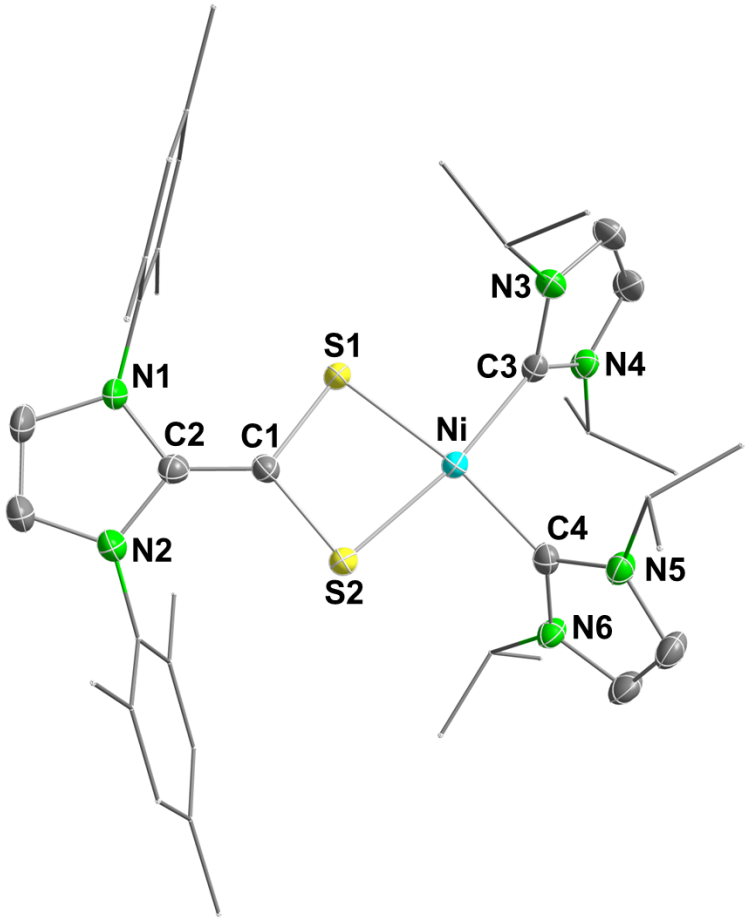


Figure S74. Molecular structure of [Ni(IMes-CS_2)(I*i*Pr)$_2$] (**2c**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–S1 2.180(1), Ni–S2 2.192(1), Ni–C3 1.914(3), Ni–C4 1.918(2), S1–C1 1.776(3), S2–C1 1.769(3), C1–C2 1.336(4), C2–N1 1.421(3), C2–N2 1.418(3), ∡S1NiS2 79.1(1), ∡S1C1S2 103.6(1), ∡C3NiC4 97.4(1), ∡N1C2C1S1 1.6(4), ∡N2C2C1S2 0.4(4).

Crystal Data for [Ni(BIMe-CS_2)(I*i*Pr)$_2$] (2d):

$C_{116}H_{176}N_{24}Ni_4OS_8$, M_r = 2414.05 g/mol, T = 100.00(10) K, λ = 1.54184 Å, green block, 0.470 × 0.350 × 0.240 mm^3, trigonal, space group $P2_12_12_1$, a = 41.9148(2) Å, b = 41.9148(2) Å, c = 19.73740(10) Å, α = 90 °, β = 90 °, γ = 120 °, V = 30030.0(3) Å^3, Z = 9, ρ_{calc} = 1.201 Mg/m^3, μ = 2.192 mm^{-1}, F(000) = 11592, 67581 reflections, –40 ≤ h ≤ 53, –51 ≤ k ≤ 53, –23 ≤ l ≤ 24, 3.308 ° < θ < 77.486 °, completeness 99.7%, 13943 independent reflections, 13223 reflections observed with [$I > 2\sigma(I)$], 720 parameters, 15 restraints, R indices (all data) R_1 = 0.0507, wR_2 = 0.1432, final R indices [$I > 2\sigma(I)$] R_1 = 0.0490, wR_2 = 0.1418, largest difference peak and hole 1.162 and –0.468 e Å^{-3}, Goof = 1.038.

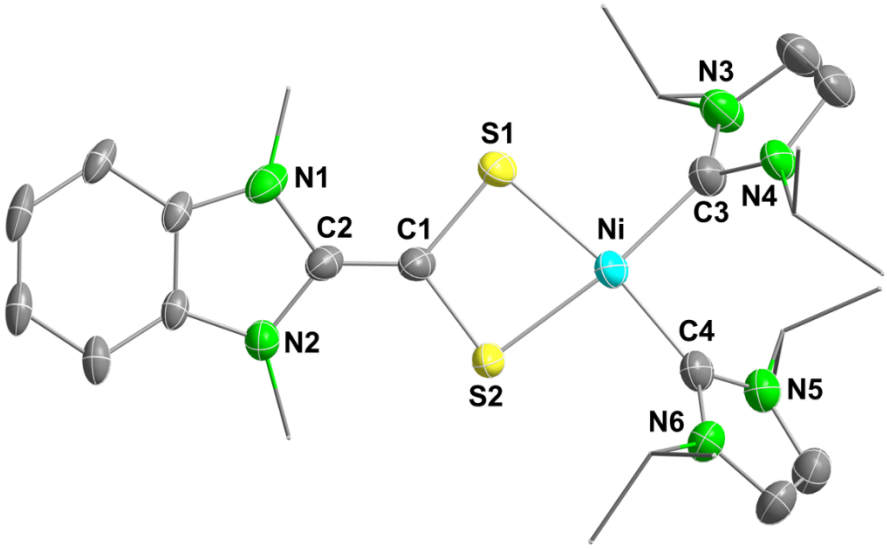


Figure S75. Molecular structure of [Ni(BIMe-CS_2)(I*i*Pr)$_2$] (**2d**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–S1 2.198(6), Ni–S2 2.185(1), Ni–C3 1.910(2), Ni–C4 1.899(2), S1–C1 1.780(2), S2–C1 1.769(2), C1–C2 1.341(3), C2–N1 1.421(3), C2–N2 1.417(3), ∡S1NiS2 78.8(1), ∡S1C1S2 103.3(1), ∡C3NiC4 93.9(1), ∡N1C2C1S1 8.2(4), ∡N2C2C1S2 9.8 (4).

Crystal Data for [Ni(cAAC^{Me}-CS$_2$)$_2$]·C$_6$H$_6$ (3a):

$C_{48}H_{68}N_2NiS_2$, M_r = 859.99 g/mol, T = 100.00(10) K, λ = 1.54184 Å, red block, 0.280 × 0.140 × 0.110 mm^3, triclinic, space group $P\bar{1}$, a = 8.83580(10) Å, b = 9.0954(2) Å, c = 14.2686(2) Å, α = 94.4900(10) °, β = 97.7310(10) °, γ = 97.2310(10) °, V = 1121.94(3) Å^3, Z = 1, ρ_{calc} = 1.273 Mg/m^3, μ = 2.616 mm^{-1}, F(000) = 462, 20196 reflections, −11 ≤ h ≤ 11, –11 ≤ k ≤ 11, –15 ≤ l ≤ 17, 4.924 ° < θ < 77.339 °, completeness 99.0%, 4581 independent reflections, 4462 reflections observed with [$I > 2\sigma(I)$], 258 parameters, 0 restraints, R indices (all data) R_1 = 0.0304, wR_2 = 0.0808, final R indices [$I > 2\sigma(I)$] R_1 = 0.0299, wR_2 = 0.0804, largest difference peak and hole 0.363 and –0.422 e Å^{-3}, Goof = 1.037.

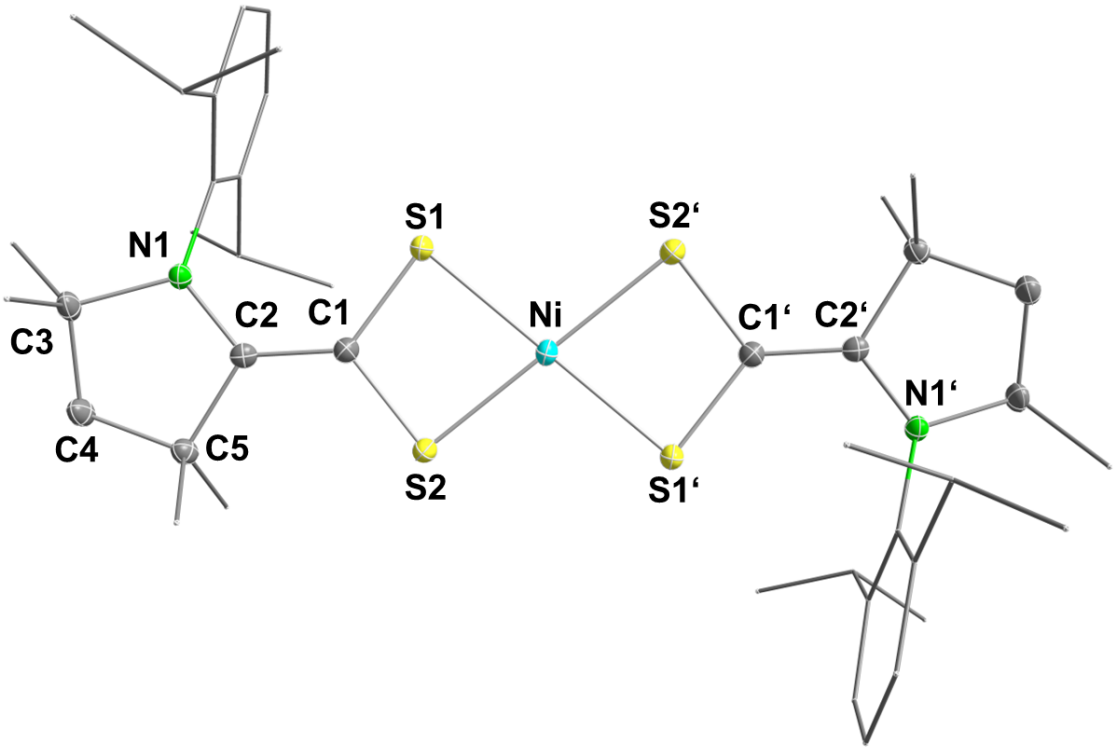


Figure S76. Molecular structure of [Ni(cAAC^{Me}-CS$_2$)$_2$]·C$_6$H$_6$ (**3a**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and one molecule of co-crystallized benzene were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–S1 2.190(1), Ni1–S2 2.161(1), S1–C1 1.740(1), S2–C1 1.732(1), C1–C2 1.391(2), C2–N1 1.361(2), C2–C5 1.536(2), N1–C3 1.508(2), C3–C4 1.532(2), ∡S1NiS2’ 101.2(1), ∡S1NiS2 78.8(1), ∡N1C2C1S1 5.9(2), ∡S1C1S2 105.4(1).

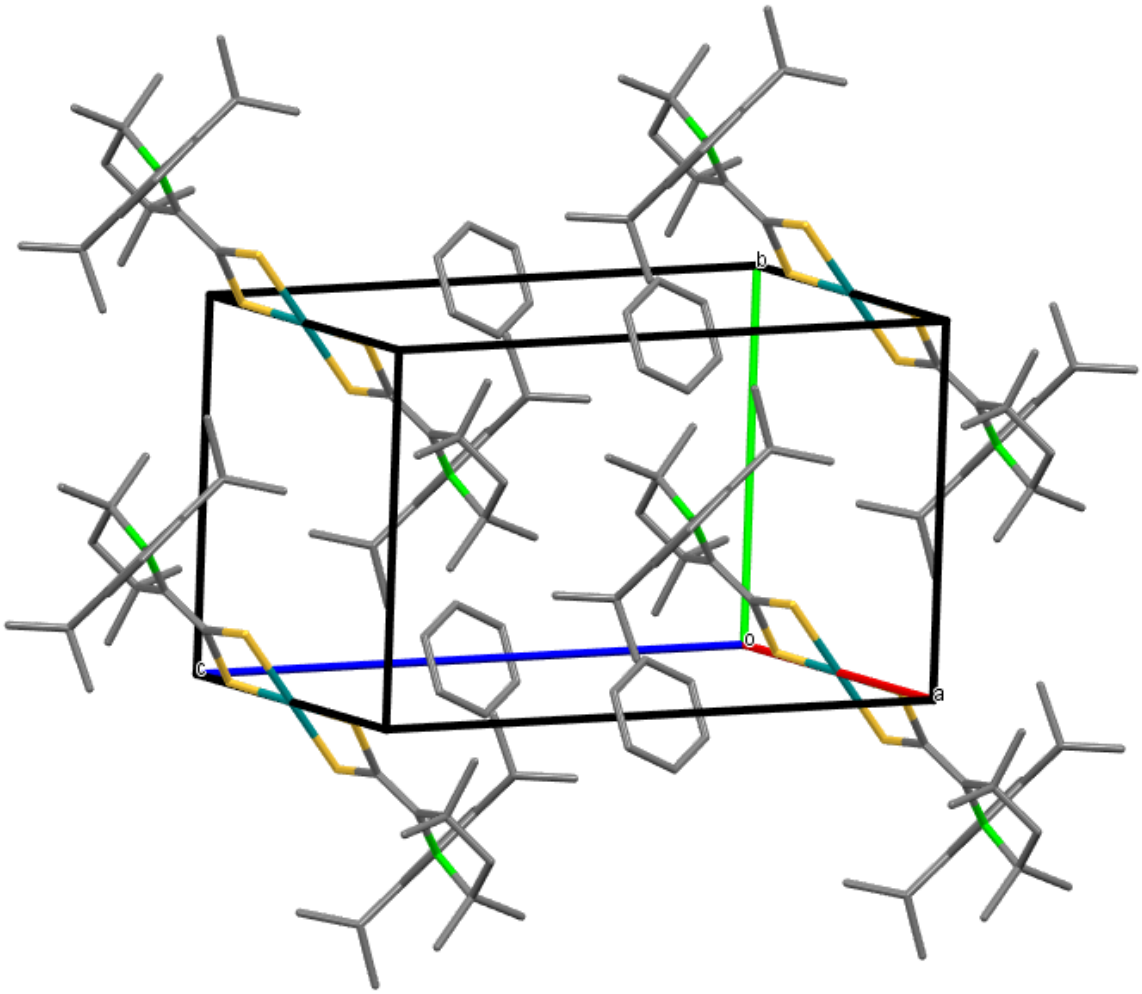


Figure S77. Molecular structure of the unit cell packing of [Ni(cAAC^{Me}-CS_2)$_2$]·C_6H_6 (**3a**) in the solid-state. The hydrogen atoms were omitted for clarity. Distance from one nickel atom to the plane NiS_4 of the next parallel molecule **3a**: *d*(Ni–plane(NiS4)) = 6.258(1) Å.

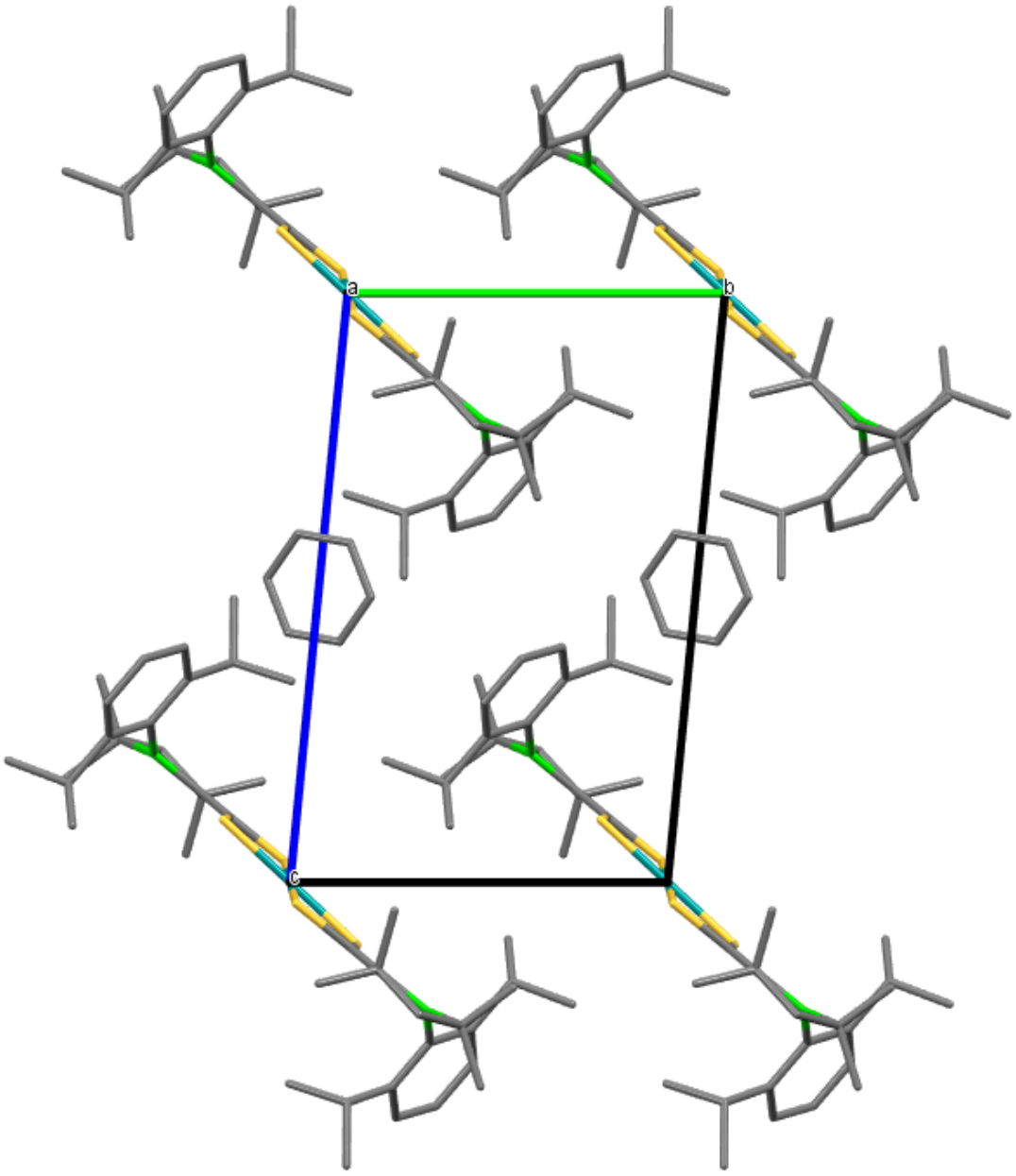


Figure S78. Molecular structure of the unit cell packing of [Ni(cAAC^{Me}-CS_2)$_2$]·C_6H_6 (**3a**) in the solid-state with perspective along the *a*-axis. The hydrogen atoms were omitted for clarity. Distance from one nickel atom to the plane NiS_4 of the next parallel molecule **3a**: *d*(Ni–plane(NiS4)) = 6.258(1) Å.

Crystal Data for [Ni(IDipp-CS_2)$_2$]·2THF (3b):

$C_{64}H_{88}N_4NiO_2S_4$, M_r = 1132.33 g/mol, T = 100.00(10) K, λ = 1.54184 Å, yellow block, 0.180 × 0.100 × 0.080 mm^3, monoclinic, space group $P2_1/n$, a = 10.36020(10) Å, b = 22.0224(2) Å, c = 13.63690(10) Å, α = 90 °, β = 91.7210(10) °, γ = 90 °, V = 3109.94(5) Å^3, Z = 2, ρ_{calc} = 1.209 Mg/m^3, μ = 2.037 mm^{-1}, $F(000)$ = 1216, 30670 reflections, –13 ≤ h ≤ 12, –25 ≤ k ≤ 27, –16 ≤ l ≤ 16, 3.814 ° < θ < 76.918 °, completeness 99.4%, 6379 independent reflections, 5793 reflections observed with [$I > 2\sigma(I)$], 348 parameters, 0 restraints, R indices (all data) R_1 = 0.0333, wR_2 = 0.0785, final R indices [$I > 2\sigma(I)$] R_1 = 0.0304, wR_2 = 0.0768, largest difference peak and hole 0.272 and –0.350 e Å^{-3}, Goof = 1.072.

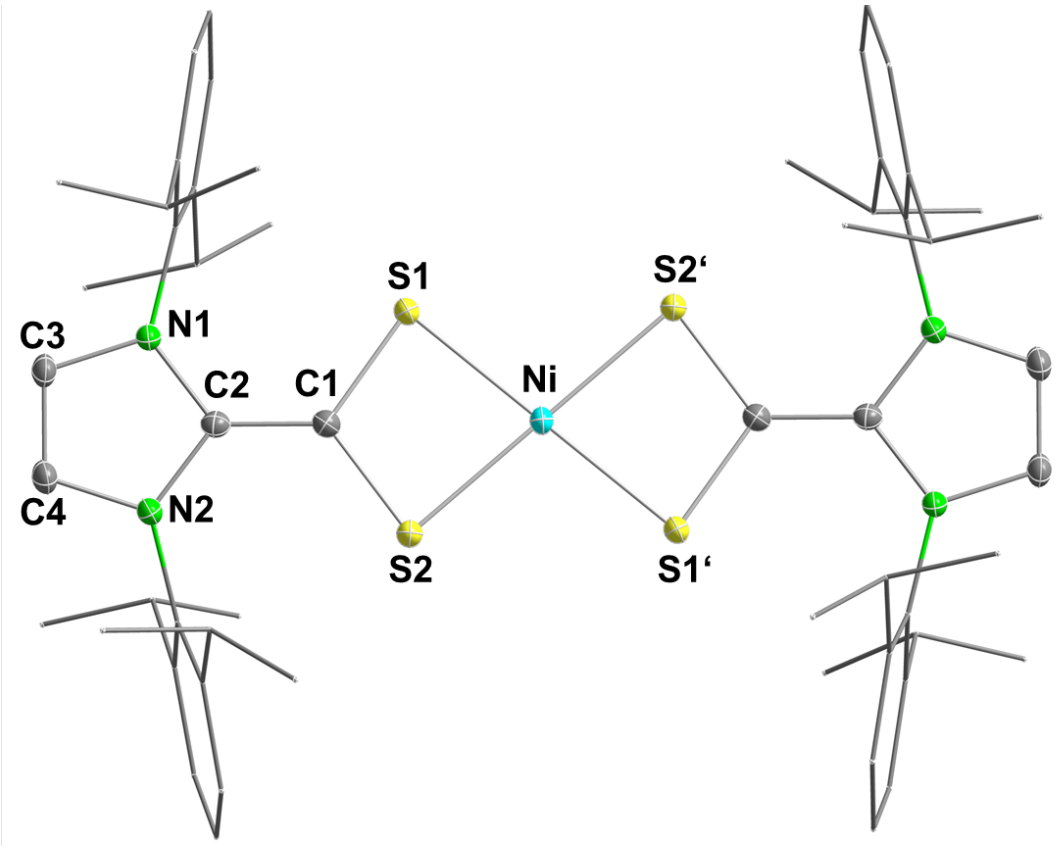


Figure S79. Molecular structure of [Ni(IDipp-CS_2)$_2$]·2THF (**3b**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and two molecules of co-crystallized THF were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–S1 2.177(1), Ni1–S2 2.181(1), S1–C1 1.732(1), S2–C1 1.730(1), C1–C2 1.395(2), C2–N2 1.380(2), C2–N1 1.378(2), ∡S1C1S2 107.3(1), ∡S1NiS2 79.6(1), ∡S1NiS2’ 100.4(1), ∡N1C2C1S1 4.7(2), ∡N2C2C1S2 3.6(2).

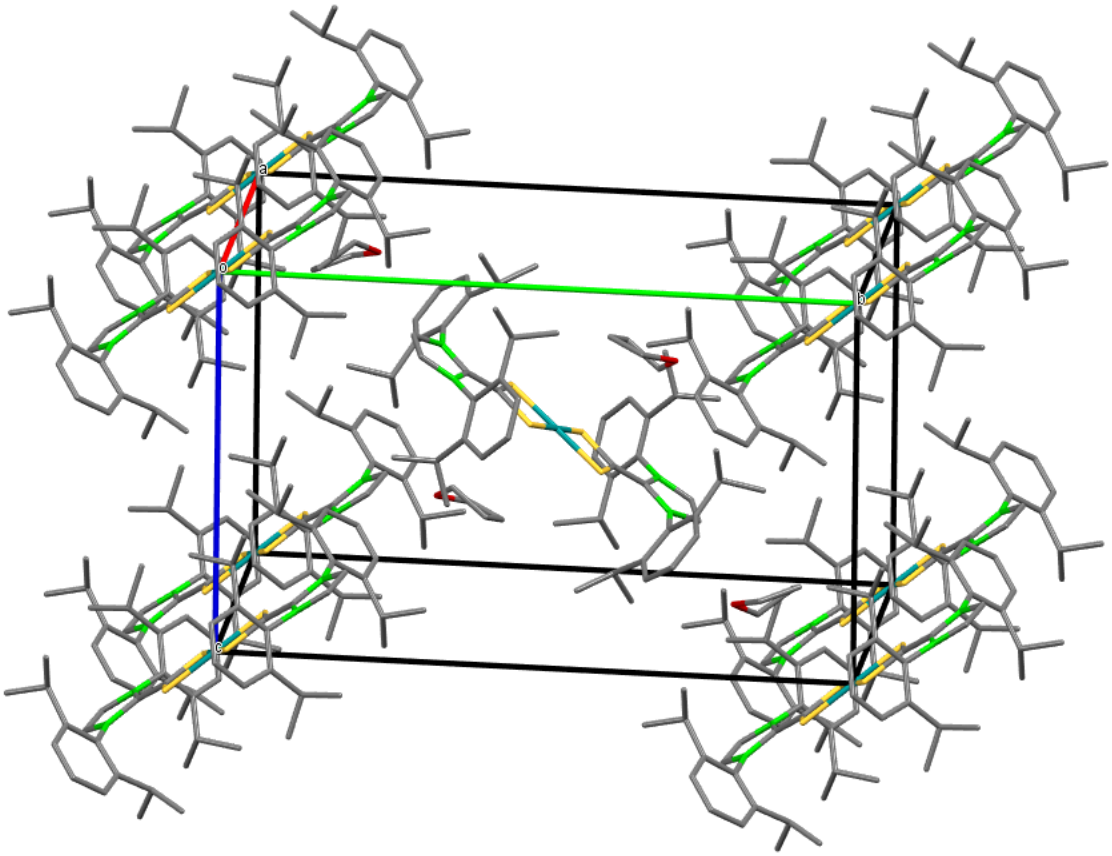


Figure S80. Molecular structure of the unit cell packing of [Ni(IDipp-CS_2)$_2$]·2THF (**3b**) in the solid-state. The hydrogen atoms were omitted for clarity. Distance from one nickel atom to the plane NiS_4 of the next parallel molecule **3b**: *d*(Ni–plane(NiS4)) = 10.473(1) Å.

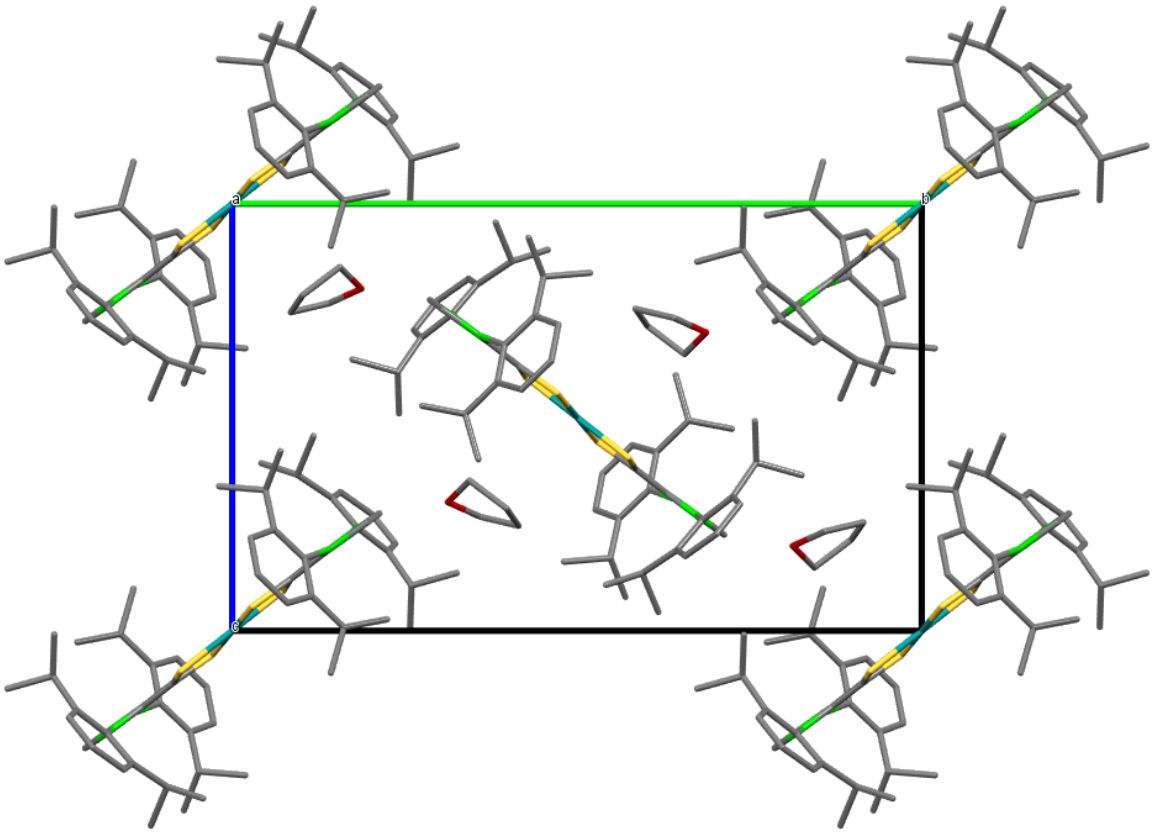


Figure S81. Molecular structure of the unit cell packing of [Ni(IDipp-CS_2)$_2$]·2THF (**3b**) in the solid-state with perspective along the *a*-axis. The hydrogen atoms were omitted for clarity. Distance from one nickel atom to the plane NiS_4 of the next parallel molecule **3b**: *d*(Ni–plane(NiS4)) = 10.473(1) Å.

Crystal Data for [Ni(IMes-CS_2)$_2$]·3C_6H_6 (3c):

$C_{62}H_{66}N_4NiS_4$, M_r = 1054.13 g/mol, T = 100.00(10) K, λ = 1.54184 Å, black block, 0.330 × 0.240 × 0.210 mm^3, monoclinic, space group $P2_1/c$, a = 16.39960(10) Å, b = 12.50180(10) Å, c = 14.17110(10) Å, α = 90 °, β = 101.8330(10) °, γ = 90 °, V = 2843.68(4) Å^3, Z = 2, ρ_{calc} = 1.231 Mg/m^3, μ = 2.177 mm^{-1}, $F(000)$ = 1116, 30979 reflections, −20 ≤ h ≤ 17, −15 ≤ k ≤ 15, −17 ≤ l ≤ 17, 2.753 ° < θ < 77.398 °, completeness 100%, 5962 independent reflections, 5778 reflections observed with [$I > 2\sigma(I)$], 328 parameters, 0 restraints, R indices (all data) R_1 = 0.0295, wR_2 = 0.0768, final R indices [$I > 2\sigma(I)$] R_1 = 0.0288, wR_2 = 0.0764, largest difference peak and hole 0.311 and −0.297 e Å^{-3}, Goof = 1.041.

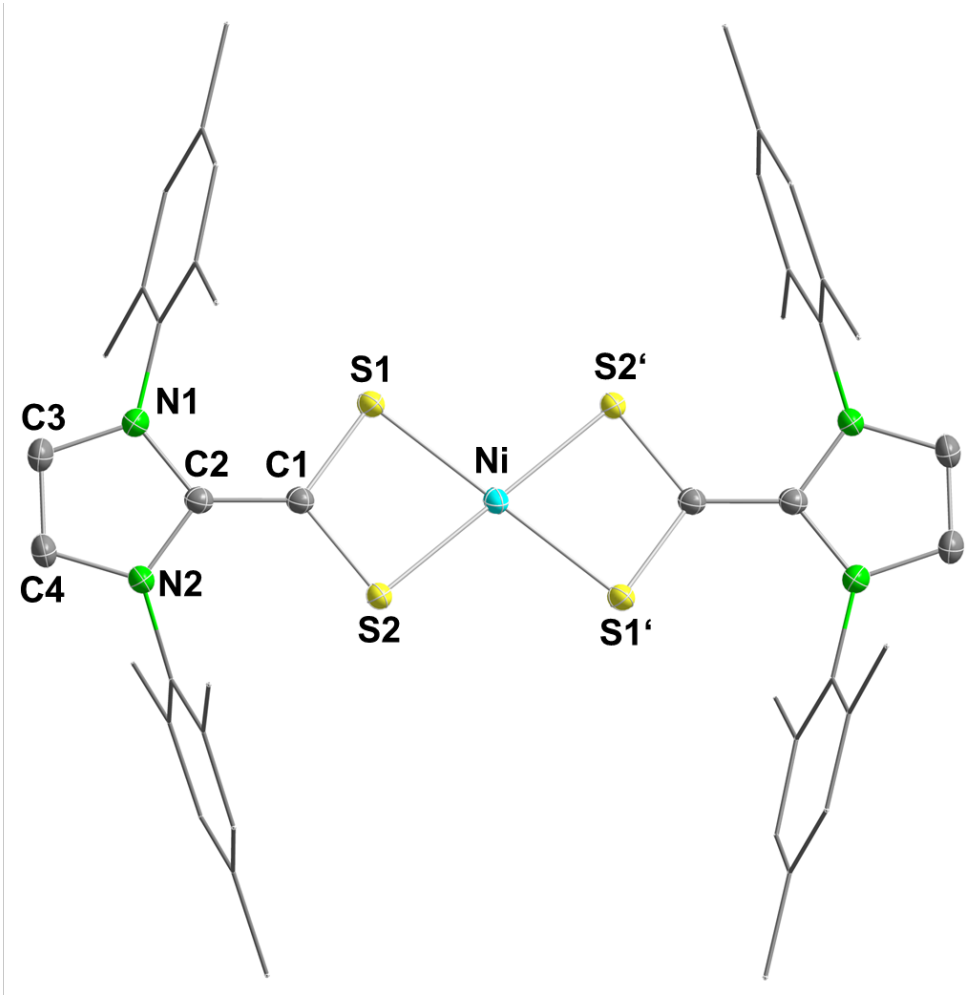


Figure S82. Molecular structure of [Ni(IMes-CS_2)$_2$]·3C_6H_6 (**3c**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and two molecules of co-crystallized benzene were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1−S1 2.181(1), Ni1−S2 2.174(1), S1−C1 1.734(1), S2−C1 1.734(1), C1−C2 1.399(2), C2−N1 1.377(2), C2–N2 1.379(2), ∡S1NiS2 79.5(1), ∡S1Ni1S2’ 100.5(1), ∡N1C2C1S1 6.5(2), ∡N2C2C1S2 8.7(2), ∡S1C1S2 106.8(1).

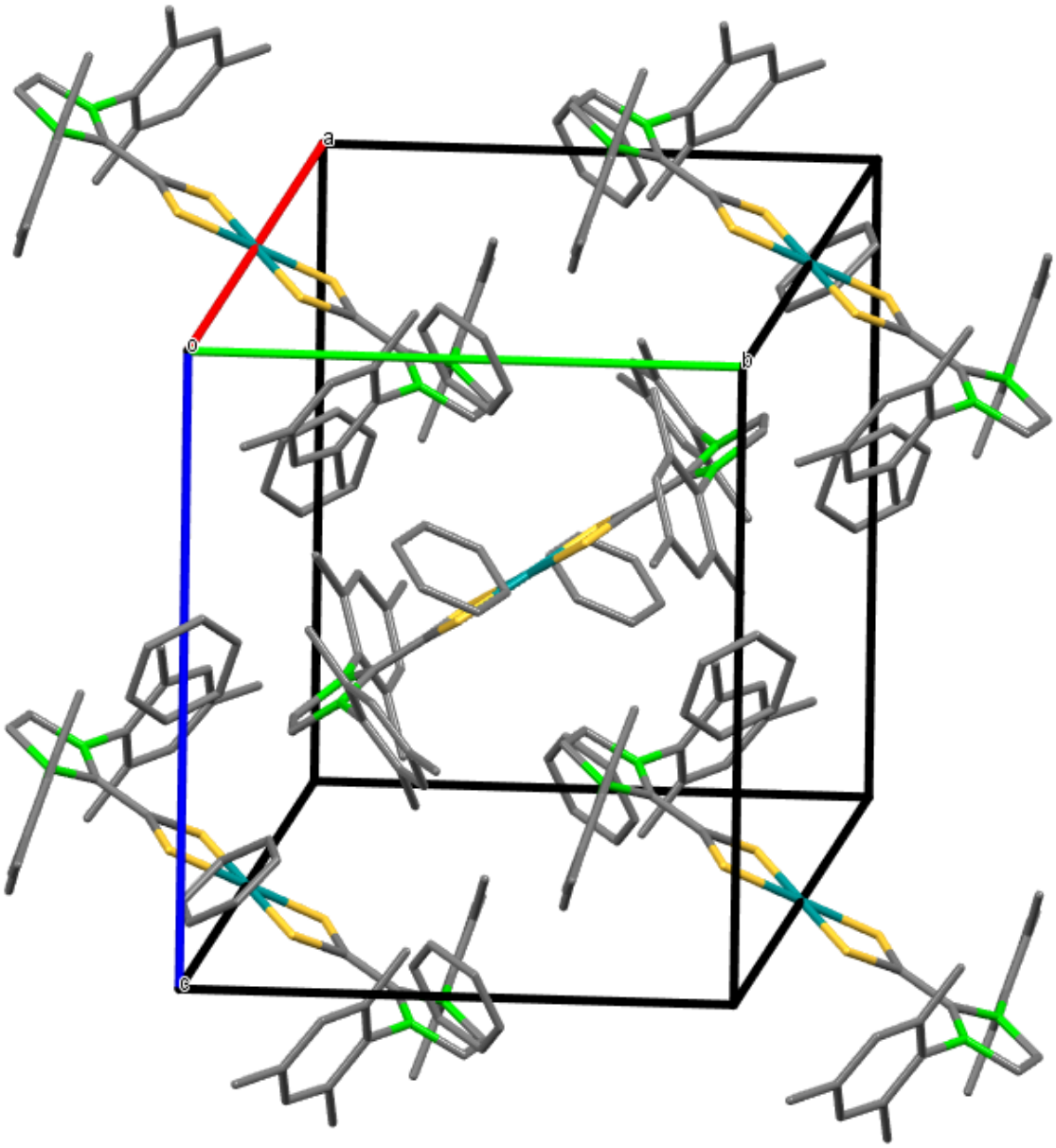


Figure S83. Molecular structure of the unit cell packing of [Ni(IMes-CS_2)$_2$]·3C_6H_6 (**3c**) in the solid-state. The hydrogen atoms were omitted for clarity. Distance from one nickel atom to the plane NiS_4 of the next parallel molecule **3c**: *d*(Ni–plane(NiS4)) = 6.680(1) Å.

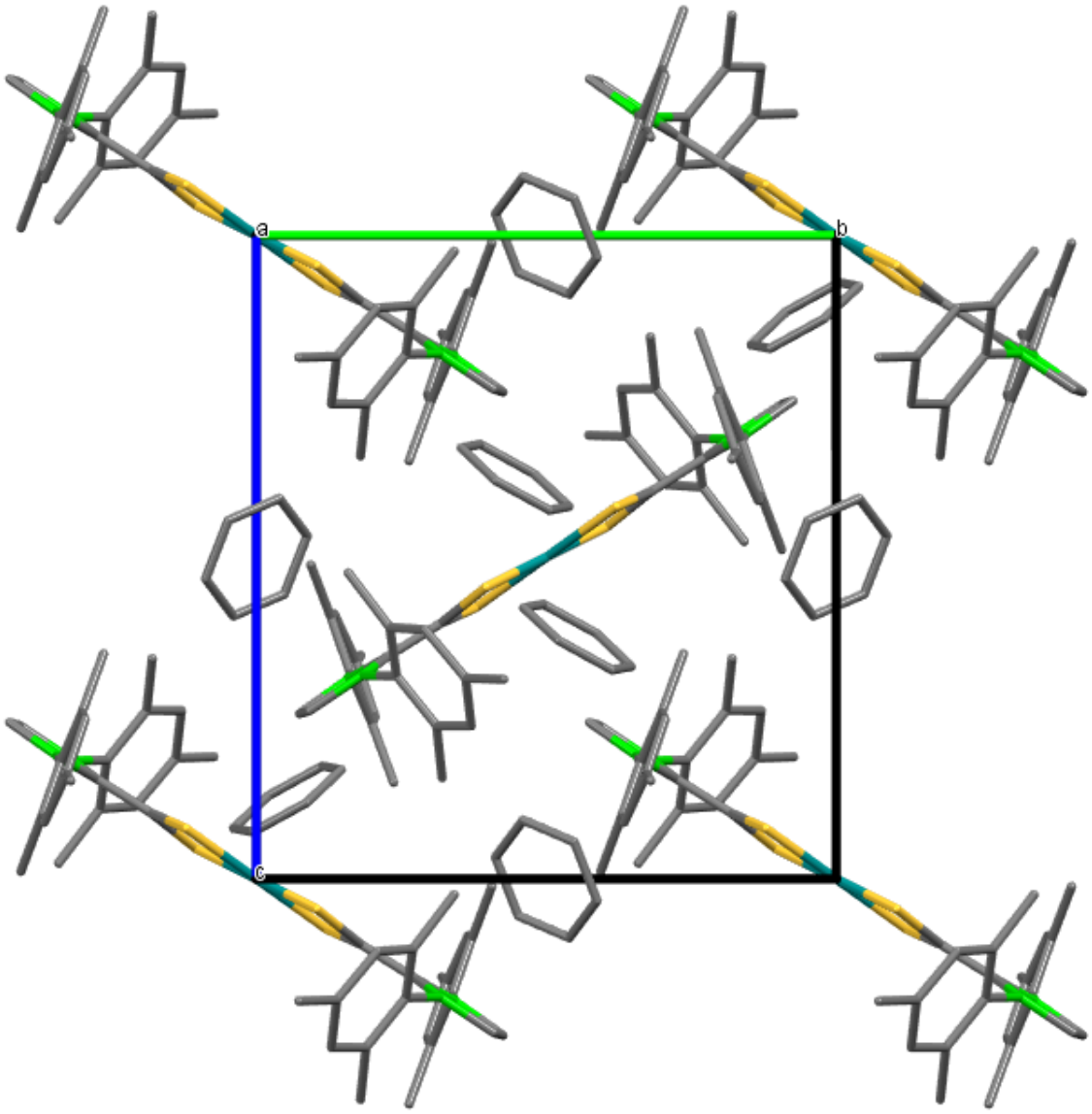


Figure S84. Molecular structure of the unit cell packing of [Ni(IMes-CS_2)$_2$]·3C_6H_6 (**3c**) in the solid-state with perspective along the *a*-axis. The hydrogen atoms were omitted for clarity. Distance from one nickel atom to the plane NiS_4 of the next parallel molecule **3c**: *d*(Ni–plane(NiS4)) = 6.680(1) Å.

Crystal Data for [K(THF)$_3$][Ni(cAAC^{Me}-CS$_2$)$_2$] (4a^K):

$C_{54}H_{86}N_2NiO_3S_4$, M_r = 1037.29 g/mol, T = 100.00(10) K, λ = 1.54184 Å, green block, 0.540 × 0.140 × 0.100 mm^3, monoclinic, space group $P2_1/n$, a = 11.042(10) Å, b = 30.09600(10) Å, c = 34.28230(10) Å, α = 90 °, β = 96.44 °, γ = 90 °, V = 11320.81(5) Å^3, Z = 8, ρ_{calc} = 1.217 Mg/m^3, μ = 2.845 mm^{-1}, $F(000)$ = 4472, 237467 reflections, –13 ≤ h ≤ 13, –38 ≤ k ≤ 37, –41 ≤ l ≤ 43, 2.594 ° < θ < 77.555 °, completeness 100%, 23923 independent reflections, 22708 reflections observed with [$I > 2\sigma(I)$], 1399 parameters, 1509 restraints, R indices (all data) R_1 = 0.0480, wR_2 = 0.1202, final R indices [$I > 2\sigma(I)$] R_1 = 0.0462, wR_2 = 0.1188, largest difference peak and hole 1.014 and –0.602 e Å^{-3}, Goof = 1.048.

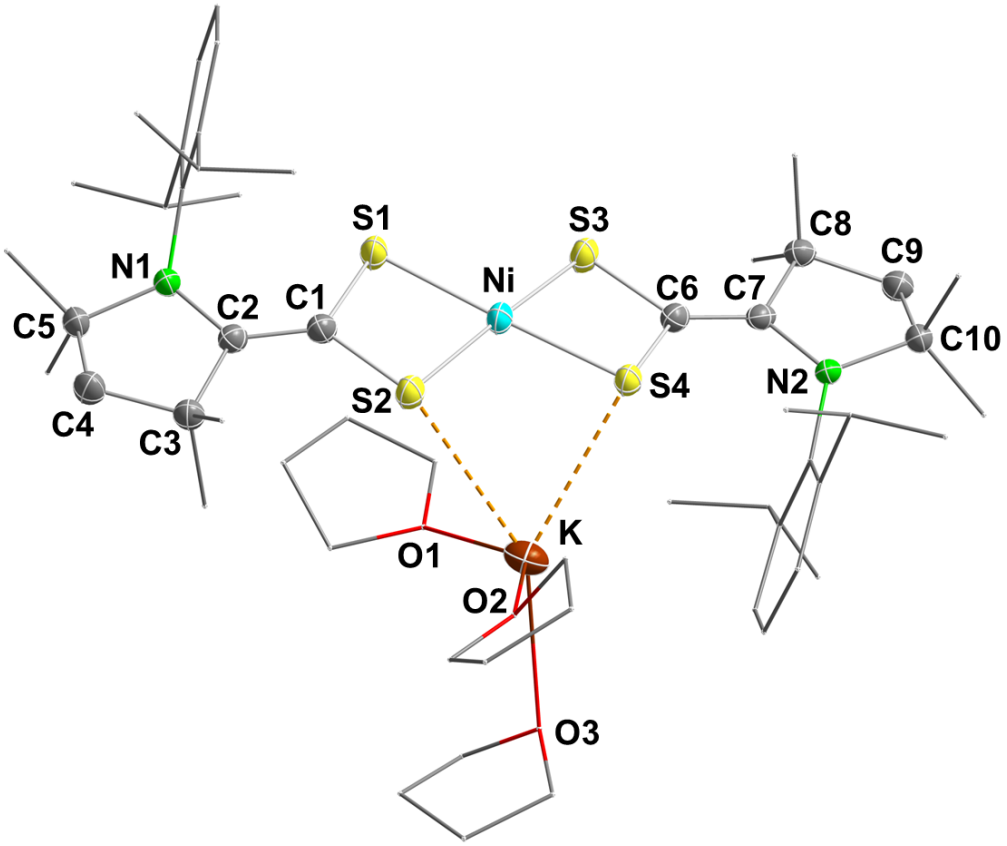


Figure S85. Molecular structure of [K(THF)$_3$][Ni(cAAC^{Me}-CS$_2$)$_2$] (**4a^K**) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and disordered THF-moieties were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–S1 2.163(1), Ni–S2 2.187(1), Ni–S3 2.170(1), Ni–S4 2.180(1), C1–S1 1.749(2), C1–S2 1.763(2), C6–S3 1.759(2), C6–S4 1.763(2), C1–C2 1.360(3), C6–C7 1.353(3), C2–N1 1.396(2), C7–N2 1.399(2), Ni–K 3.615(1), S2–K 3.459(1), S4–K 3.163(6), O1–K 2.620(5), O2–K 2.677(2), O3–K 2.699(2), ∡S1NiS3 100.0(1), ∡S2NiS4 101.3(1), ∡S1NiS2 79.4(2), ∡S3NiS4 79.5(1), ∡S1C1S2 104.7(1), ∡S3C6S4 104.2(1), ∡plane(S1C1S2)–plane(S3C6S4) 11.9(1), ∡N1C2C1S1 5.1(3), ∡N2C7C6S3 3.9(3).

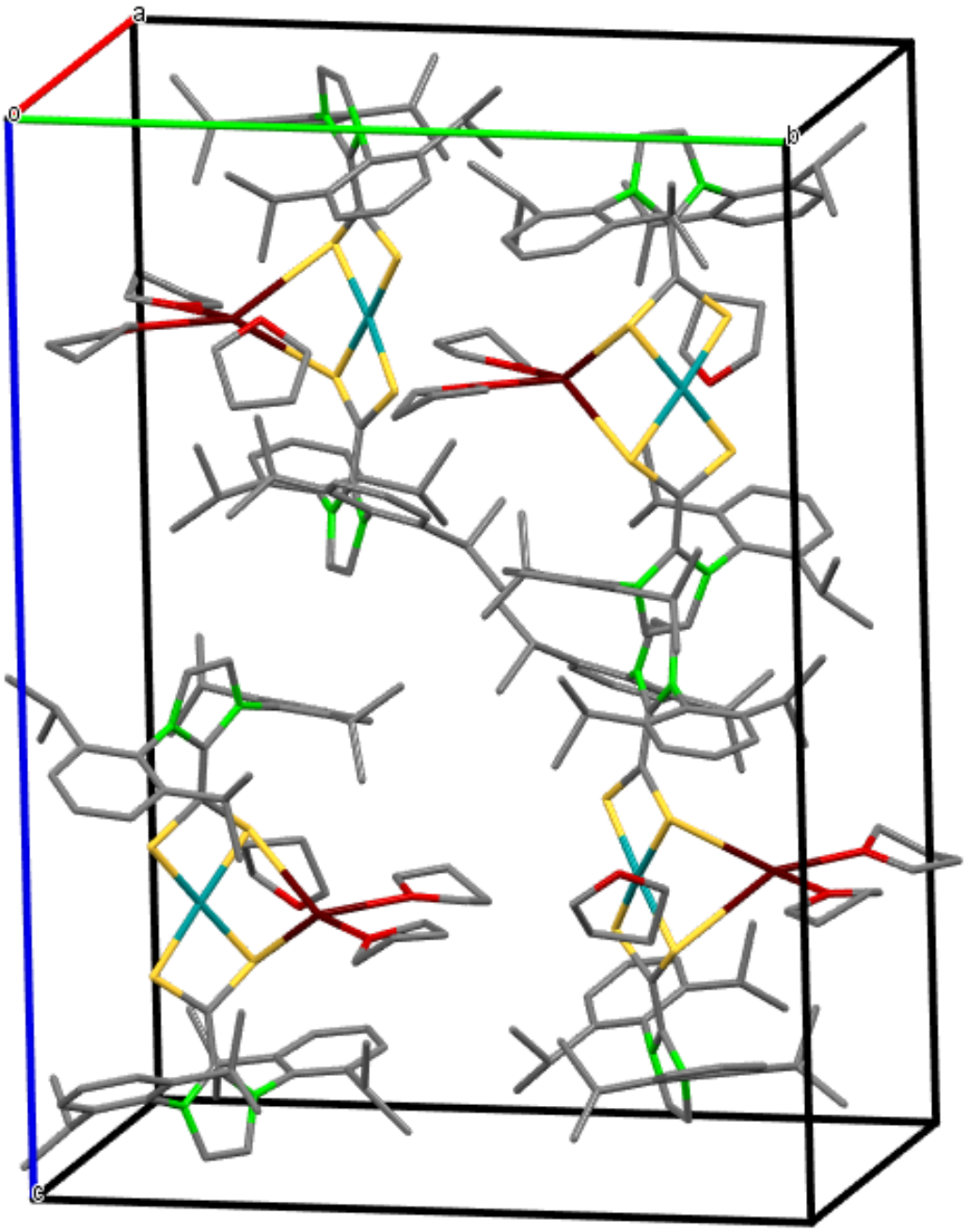


Figure S86. Molecular structure of the unit cell packing of $[K(THF)_3][Ni(cAAC^{Me}\text{-}CS_2)_2]$ (**4a^{K}**) in the solid-state. The hydrogen atoms were omitted for clarity.

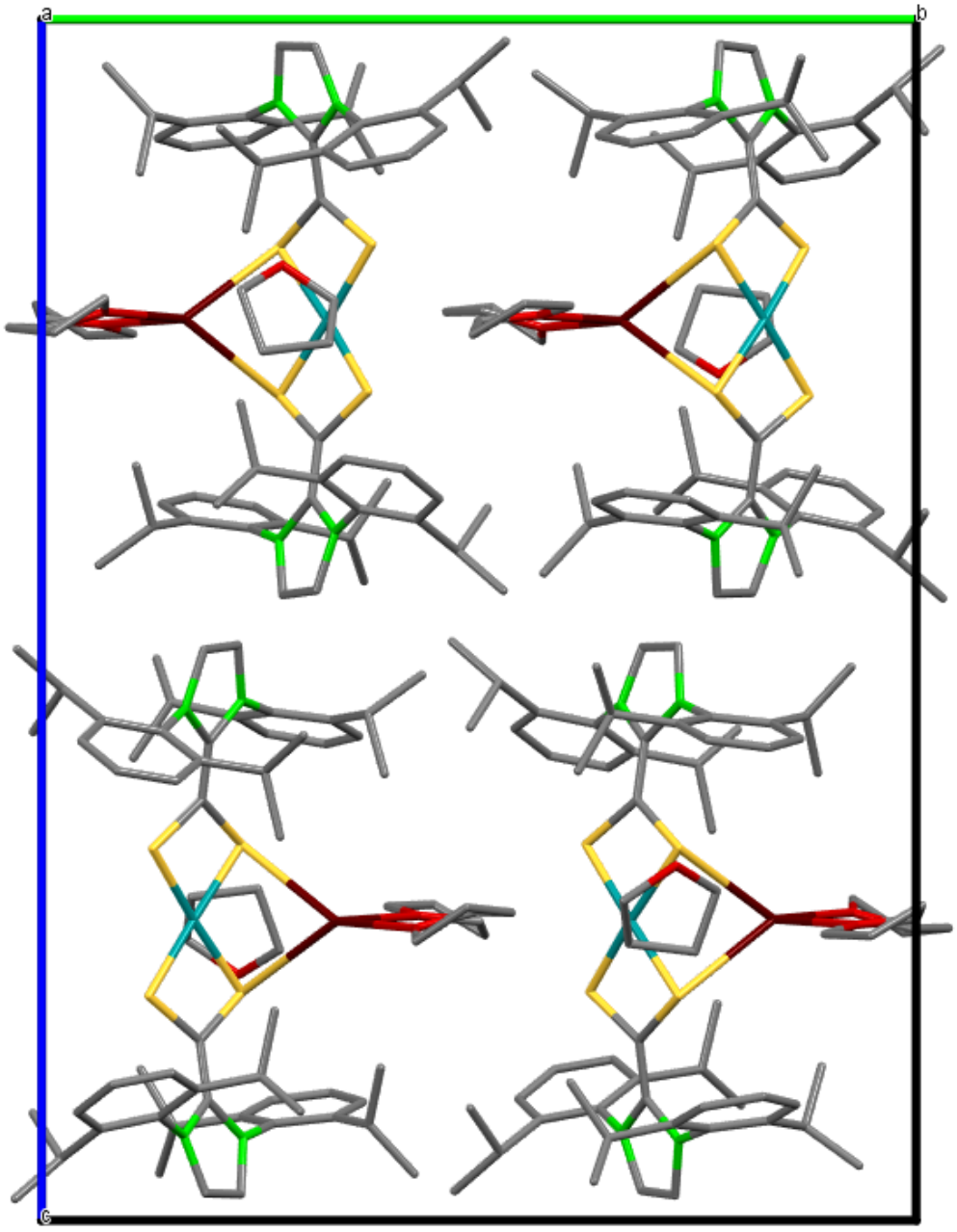


Figure S87. Molecular structure of the unit cell packing of $[K(THF)_3][Ni(cAAC^{Me}\text{-}CS_2)_2]$ (**4a^{K}**) in the solid-state with perspective along the *a*-axis. The hydrogen atoms were omitted for clarity.

Crystal Data for $[K(THF)_2][Ni(IDipp\text{-}CS_2)_2]\cdot THF$ ($\mathbf{4b^K}$):

$C_{64}H_{96}KN_4NiO_3S_4$, M_r = 1243.53 g/mol, T = 100.00(10) K, λ = 1.54184 Å, red block, 0.360 × 0.270 × 0.210 mm^3, orthorhombic space group $P2_12_12_1$, a = 12.25160(10) Å, b = 19.85030(10) Å, c = 27.24960(10) Å, α = 90 °, β = 90 °, γ = 90 °, V = 6627.05(7) Å^3, Z = 4, ρ_{calc} = 1.246 Mg/m^3, μ = 2.524 mm^{-1}, $F(000)$ = 2668, 119594 reflections, –14 ≤ h ≤ 14, –23 ≤ k ≤ 23, –32 ≤ l ≤ 32, 2.754 ° < θ < 67.069 °, completeness 100%, 11832 independent reflections, 11513 reflections observed with [$I > 2\sigma(I)$], 823 parameters, 296 restraints, R indices (all data) R_1 = 0.0336, wR_2 = 0.0914, final R indices [$I > 2\sigma(I)$] R_1 = 0.0327, wR_2 = 0.0908, largest difference peak and hole 1.192 and –0.704 e Å^{-3}, Goof = 1.088.

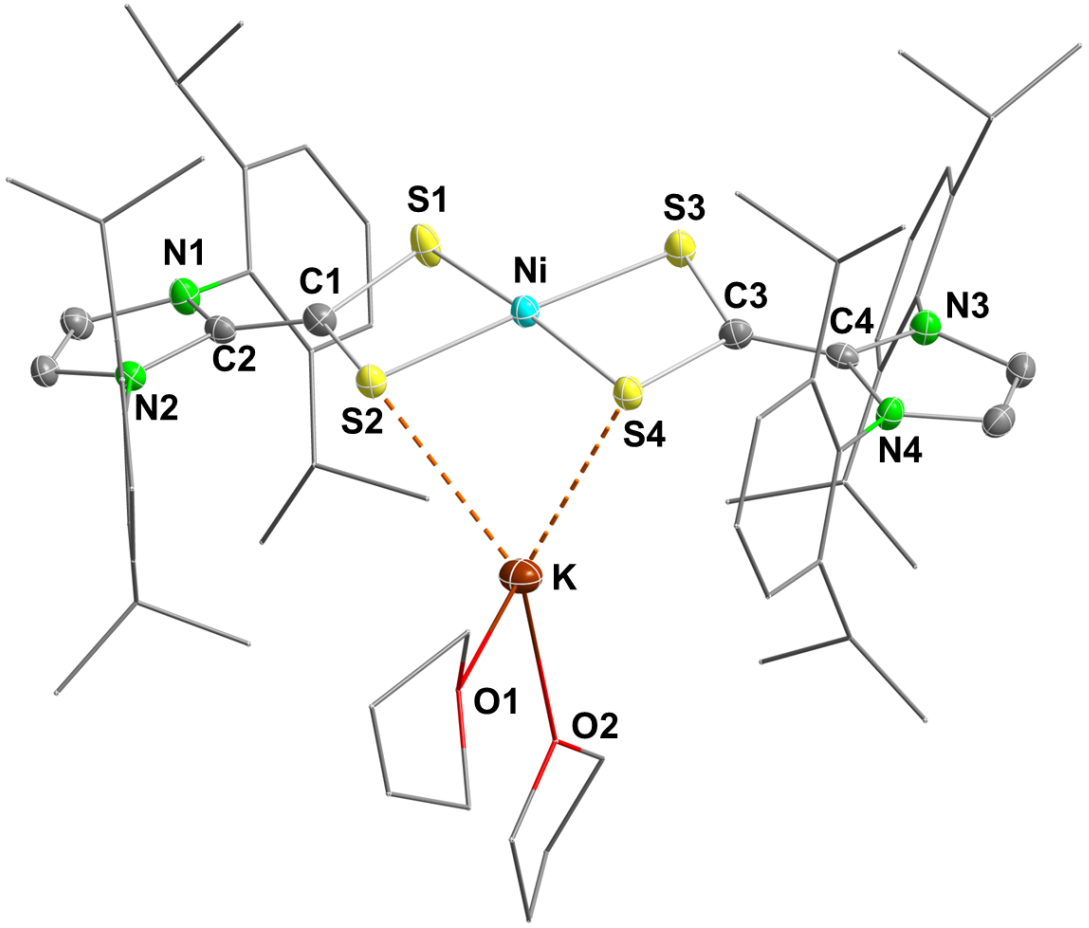


Figure S88. Molecular structure of $[K(THF)_2][Ni(IDipp\text{-}CS_2)_2]\cdot THF$ ($\mathbf{4b^K}$) in the solid-state (ellipsoids set at 50% probability level). The hydrogen atoms and one molecule of co-crystallized THF were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–S1 2.178(1), Ni–S2 2.184(1), Ni–S3 2.180(1), Ni–S4 2.199(1), C1–S1 1.751(3), C1–S2 1.766(3), C3–S3 1.746(3), C3–S4 1.757(3), C1–C2 1.362(5), C3–C4 1.378(5), N1–C2 1.402(4), N2–C2 1.401(4), N3–C4 1.389(4), N4–C4 1.389(4), Ni–K 3.358(1), S2–K 3.221(1), S4–K 3.242(1), O1–K 2.75(5), O2–K 2.668(3), ∡S1NiS3 100.6(1), ∡S2NiS4 100.4(3), ∡S1NiS2 79.4(3), ∡S3NiS4 79.3(3), ∡S1C1S2 104.8(2), ∡S3C3S4 105.8(2), ∡N1C2C1S1 10.3(5), ∡N2C2C1S2 11.9(5), ∡N3C4C3S3 10.1(5), ∡N4C4C3S4 13.4(5).

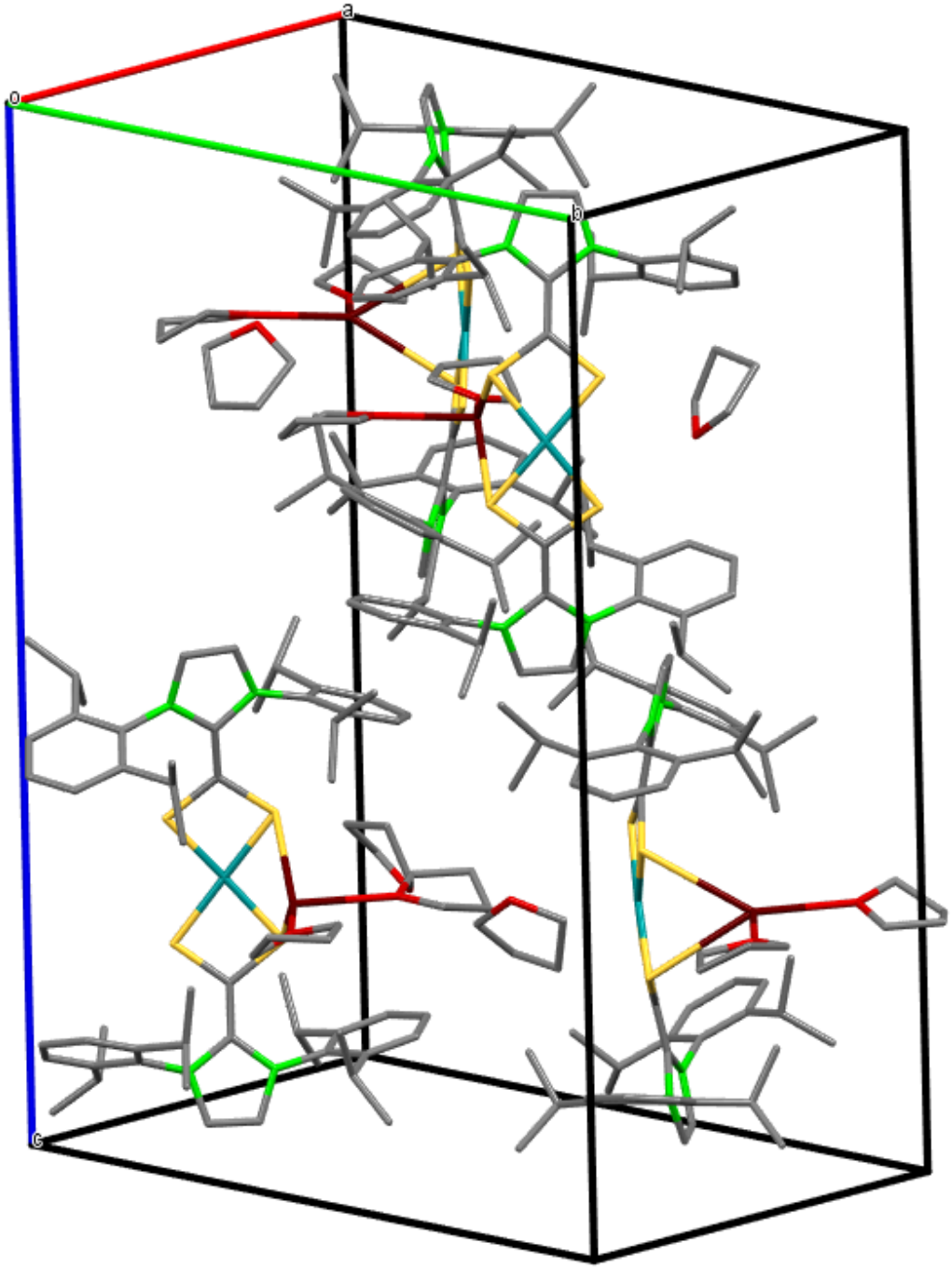


Figure S89. Molecular structure of the unit cell packing of $[K(THF)_2][Ni(IDipp\text{-}CS_2)_2]\cdot THF$ (**4b^K**) in the solid-state. The hydrogen atoms were omitted for clarity.

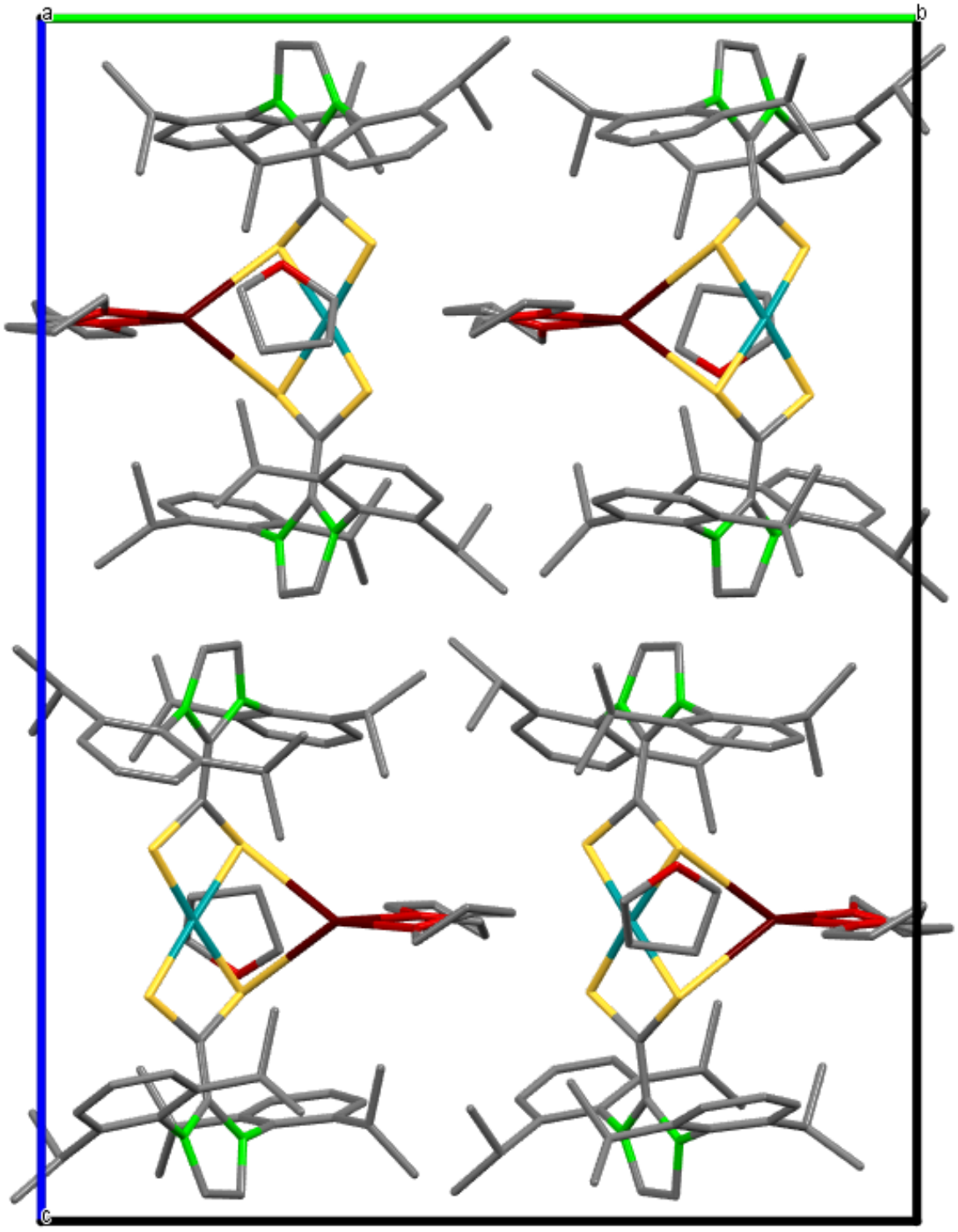


Figure S90. Molecular structure of the unit cell packing of $[K(THF)_2][Ni(IDipp\text{-}CS_2)_2]\cdot THF$ (**4b^K**) in the solid-state with perspective along the *a*-axis. The hydrogen atoms were omitted for clarity.

10 Quantumchemical Calculations Section

10.1 General Information

Calculations were carried out using the TURBOMOLE V7.8.1 program suite, a development of the University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from https://www.turbomole.org.[21] Geometry optimizations were performed using (RI-)DFT calculations[22] on a m4 grid employing the PBE0[23] or B3-LYP[24] functional and a def2-TZVP basis set for Ni, a def2-SVP basis set for all other atoms.[25] Dispersion corrections were considered in the PBE0 geometry optimizations by using Grimme's D3[26] correction together with the Becke-Johnson (BJ) damping function (levels denoted as PBE0-D3(BJ)//def2-TZVP(Ni)/def2-SVP(rest) or B3-LYP/def2-TZVP(Ni)/def2-SVP(rest)).[27] Vibrational frequencies were calculated at the same levels with the AOFORCE[28] module and all structures represented true minima without imaginary frequencies. For the evaluation of ground state energies, single point calculations have been performed on the optimized geometries using a def2-TZVPP basis set for Ni and a def2-TZVP basis set for all other atoms either at the PBE0-D3(BJ) level (denoted as PBE0-D3(BJ)/def2-TZVPP(Ni)/def2-TZVP(rest)) or with the B3-LYP functional (denoted as B3-LYP/def2-TZVPP(Ni)/def2-TZVP(rest)) or the structures were geometry-optimized at the def2-TZVPP(Ni)/def2-TZVP(rest) level of theory. Vertical excitation energies were computed with TD-DFT[29] at the PBE0-D3(BJ)//def2-TZVPP(Ni)/def2-TZVP(rest) or B3-LYP/def2-TZVPP(Ni)/def2-TZVP(rest) level. Solvent effects were considered by using the implicit solvent model COSMO.[30, 31] Natural population analysis,[32] NBO charges[33] and Wiberg bond indices[34] have been evaluated from the DFT ground state electron density.

10.2 Cartesian Coordinates of DFT-optimized compounds (here: PBE0-D3(BJ)//def2-TZVP(Ni)/def2-SVP(rest))

cAAC^{Me}-CS$_2$ (1a)

Energy = –1667.920595975

C	0.7837347	–0.3763069	0.9292061
C	0.4586703	0.3992543	2.2230311
C	0.4253847	1.8703853	1.7055522
C	1.1627868	1.8843880	0.3479050
H	–0.6253316	2.1927962	1.5544003
H	0.8860023	2.5746221	2.4250488
C	–0.9421071	–0.0520203	2.7119649
H	–1.7058028	0.0348102	1.9143613
H	–0.9271068	–1.1069730	3.0468451
H	–1.2532842	0.5863764	3.5649147
C	1.4633809	0.2058197	3.3771523
H	1.5223324	–0.8570673	3.6782588
H	2.4846075	0.5282923	3.1006861
H	1.1284647	0.8034515	4.2506062
C	0.6295351	2.9395961	–0.6212487
H	0.8851958	3.9439450	–0.2286661
H	1.0909388	2.8420864	–1.6238143
H	–0.4682804	2.8921295	–0.7334142
C	2.6812338	2.0779599	0.5354350
H	3.2084671	2.1079051	–0.4360916
H	2.8664876	3.0431804	1.0482801
H	3.1252949	1.2671774	1.1450856
N	0.8888101	0.4530362	–0.1197950
C	0.7435181	0.0675853	–1.5191490
C	–0.5634351	0.1426429	–2.0961754
C	1.8650654	–0.3552219	–2.2877338
C	–0.7075453	–0.2109076	–3.4520852
C	1.6516564	–0.6879681	–3.6421682
C	0.3839568	–0.6194718	–4.2249485
H	–1.7071835	–0.1677558	–3.9100267
H	2.5078655	–1.0191934	–4.2488771
H	0.2438569	–0.8905161	–5.2826482
C	–1.8248646	0.5754456	–1.3408366
H	–1.5156968	0.9137973	–0.3311457
C	–2.5429936	1.7534587	–2.0359007
H	–3.3734719	2.1257764	–1.4012161
H	–1.8647325	2.6038542	–2.2489345
H	–2.9891786	1.4404393	–3.0020643
C	–2.8070029	–0.5991096	–1.1456077
H	–3.6930724	–0.2661793	–0.5653754
H	–3.1720746	–0.9795911	–2.1224981
H	–2.3201040	–1.4351553	–0.6050384
C	3.2875821	–0.4776273	–1.7419170
H	3.2532714	–0.2730702	–0.6533628
C	4.2366254	0.5399253	–2.4112860
H	3.8578833	1.5804123	–2.3437109
H	5.2388862	0.5089514	–1.9361762
H	4.3737007	0.3149686	–3.4895653
C	3.8392393	–1.9096427	–1.9027659
H	4.8418161	–1.9854677	–1.4339595
H	3.1821552	–2.6510949	–1.4090966
H	3.9492199	–2.1907237	–2.9709883
C	0.8786684	–1.8510201	0.8637746
S	–0.3775617	–2.8739111	0.4728522
S	2.4897357	–2.1284742	1.3405273

lDipp-CS$_2$ (1b)

Energy = –1991.860450326

S	0.0000000	1.5431791	2.5881071
S	0.0000000	–1.5431791	2.5881071
C	0.0000000	0.0000000	1.9046386
C	0.0000000	0.0000000	0.4181267
N	–1.0993344	0.0000000	–0.3988756
N	1.0993344	0.0000000	–0.3988756
C	–0.6841106	0.0000000	–1.7305910
C	–2.4895455	0.0000000	0.0188784
C	0.6841106	0.0000000	–1.7305910
C	2.4895455	0.0000000	0.0188784
H	–1.4051681	0.0000000	–2.5516975
C	–3.1444638	–1.2478154	0.1894419
C	–3.1444638	1.2478154	0.1894419
H	1.4051681	0.0000000	–2.5516975
C	3.1444638	1.2478154	0.1894419
C	3.1444638	–1.2478154	0.1894419
C	–4.5085594	–1.2141299	0.5420071
C	–2.4423387	–2.5847769	–0.0448392
C	–4.5085594	1.2141299	0.5420071
C	–2.4423387	2.5847769	–0.0448392
C	4.5085594	1.2141299	0.5420071
C	2.4423387	2.5847769	–0.0448392
C	4.5085594	–1.2141299	0.5420071
C	2.4423387	–2.5847769	–0.0448392
C	–5.1841723	0.0000000	0.7165995
H	–5.0492317	–2.1611422	0.6860037
H	–1.3495655	–2.4005352	0.0082417
H	–5.0492317	2.1611422	0.6860037
H	–1.3495655	2.4005352	0.0082417
C	5.1841723	0.0000000	0.7165995
H	5.0492317	2.1611422	0.6860037
H	1.3495655	2.4005352	0.0082417
H	5.0492317	–2.1611422	0.6860037
H	1.3495655	–2.4005352	0.0082417
H	–6.2492362	0.0000000	0.9953862
H	6.2492362	0.0000000	0.9953862
C	2.7763487	–3.1380564	–1.4476129
H	2.4964344	–2.4282783	–2.2524197
H	3.8628120	–3.3433812	–1.5486136
H	2.2344326	–4.0887075	–1.6318591
C	2.7559320	–3.6200734	1.0501594
H	2.1490966	–4.5346319	0.8911973
H	3.8218009	–3.9298337	1.0442179
H	2.5077373	–3.2196703	2.0525298
C	–2.7763487	–3.1380564	–1.4476129
H	–2.2344326	–4.0887075	–1.6318591
H	–3.8628120	–3.3433812	–1.5486136
H	–2.4964344	–2.4282783	–2.2524197
C	–2.7559320	–3.6200734	1.0501594
H	–2.5077373	–3.2196703	2.0525298

H	–3.8218009	–3.9298337	1.0442179
H	–2.1490966	–4.5346319	0.8911973
C	–2.7559320	3.6200734	1.0501594
H	–3.8218009	3.9298337	1.0442179
H	–2.5077373	3.2196703	2.0525298
H	–2.1490966	4.5346319	0.8911973
C	–2.7763487	3.1380564	–1.4476129
H	–2.2344326	4.0887075	–1.6318591
H	–2.4964344	2.4282783	–2.2524197
H	–3.8628120	3.3433812	–1.5486136
C	2.7559320	3.6200734	1.0501594
H	3.8218009	3.9298337	1.0442179
H	2.1490966	4.5346319	0.8911973
H	2.5077373	3.2196703	2.0525298
C	2.7763487	3.1380564	–1.4476129
H	2.2344326	4.0887075	–1.6318591
H	3.8628120	3.3433812	–1.5486136
H	2.4964344	2.4282783	–2.2524197

IMes-CS_2 (1c)

Energy = –1756.428483419

S	0.0000000	1.5371955	2.3173836
S	0.0000000	–1.5371955	2.3173836
C	0.0000000	0.0000000	1.6159215
C	0.0000000	0.0000000	0.1253361
N	–1.0982592	0.0000000	–0.6913922
N	1.0982592	0.0000000	–0.6913922
C	–0.6843015	0.0000000	–2.0233200
C	–2.4865187	0.0000000	–0.2764029
C	0.6843015	0.0000000	–2.0233200
C	2.4865187	0.0000000	–0.2764029
H	–1.4080393	0.0000000	–2.8428757
C	–3.1442127	–1.2414936	–0.1098026
C	–3.1442127	1.2414936	–0.1098026
H	1.4080393	0.0000000	–2.8428757
C	3.1442127	1.2414936	–0.1098026
C	3.1442127	–1.2414936	–0.1098026
C	–4.5002659	–1.2090827	0.2665511
C	–2.4207045	–2.5484697	–0.3155158
C	–4.5002659	1.2090827	0.2665511
C	–2.4207045	2.5484697	–0.3155158
C	4.5002659	1.2090827	0.2665511
C	2.4207045	2.5484697	–0.3155158
C	4.5002659	–1.2090827	0.2665511
C	2.4207045	–2.5484697	–0.3155158
C	–5.1936918	0.0000000	0.4684481
H	–5.0283402	–2.1658617	0.4081412
H	–3.1035473	–3.4064574	–0.1681962
H	–1.9885847	–2.6270256	–1.3354417
H	–1.5784613	–2.6384600	0.4074432
H	–5.0283402	2.1658617	0.4081412
H	–3.1035473	3.4064574	–0.1681962
H	–1.5784613	2.6384600	0.4074432
H	–1.9885847	2.6270256	–1.3354417
C	5.1936918	0.0000000	0.4684481
H	5.0283402	2.1658617	0.4081412
H	1.5784613	–2.6384600	0.4074432
H	1.9885847	–2.6270256	–1.3354417
H	3.1035473	–3.4064574	–0.1681962
C	–6.6366134	0.0000000	0.9169700
C	6.6366134	0.0000000	0.9169700
H	–6.7037675	0.0000000	2.0265837
H	–7.1778736	0.8978721	0.5583626
H	–7.1778736	–0.8978721	0.5583626
H	7.1778736	–0.8978721	0.5583626
H	7.1778736	0.8978721	0.5583626
H	6.7037675	0.0000000	2.0265837

[Ni(I*i*Pr)$_2$(cAAC^{Me}-CS_2)] (2a)

Energy = –4098.670562911

Ni	0.1338970	0.0260143	–0.2396601
S	–2.0404413	0.3039516	0.0002198
S	0.0908661	1.6568319	1.2347599
N	–2.2165028	3.1992376	2.9338870
C	–0.0273504	3.9968004	3.7185696
C	1.1597367	2.7707930	5.4467747
H	2.0223935	2.6690671	6.1102765
C	–1.0701108	3.0430760	3.7584649
C	–4.0858662	2.2184591	1.7845165
C	–2.5621501	2.2699950	1.9369884
C	0.1526748	1.8127810	5.4529339
H	0.2316657	0.9543651	6.1253345
C	–4.5539241	3.1218074	2.9408494
H	–5.4587469	3.6932776	2.6839564
H	–4.8027666	2.4944595	3.8117488
C	–3.3745076	4.0340339	3.3193656
C	–0.0284048	5.1476194	2.7339079
H	–0.9213369	5.0169731	2.1075303
C	–3.4333086	5.3484877	2.5286508
H	–3.2908428	5.1706028	1.4541030
H	–2.6600182	6.0525867	2.8607236
H	–4.4110384	5.8352234	2.6701410
C	–4.5109803	2.7563229	0.4121480
H	–4.1586698	3.7835878	0.2468754
H	–5.6095887	2.7499514	0.3187783
H	–4.0874041	2.1261729	–0.3839416
C	1.0650568	3.8500061	4.5785348
H	1.8677957	4.5917574	4.5514035
C	–1.6776406	1.5710637	1.1910780
C	–0.9662997	1.9274669	4.6257167
C	–2.0205139	0.8414506	4.6732433
H	–2.8769375	1.2035005	4.0914229
C	–4.6686035	0.8114145	1.9591084
H	–5.7702298	0.8582512	1.9376606
H	–4.3665245	0.3692254	2.9201114
H	–4.3311561	0.1358686	1.1609888
C	–3.3756889	4.3476769	4.8100957
H	–2.5024564	4.9519927	5.0960651
H	–3.3585066	3.4282854	5.4120878
H	–4.2836162	4.9139182	5.0671268
C	–0.1130160	6.4993378	3.4425959
H	–0.2119271	7.3200390	2.7138414
H	0.7944656	6.6922900	4.0375537
H	–0.9695871	6.5504101	4.1317324
C	1.1836089	5.0962089	1.8034999
H	1.2166054	4.1318047	1.2757227

H	2.1279827	5.2239135	2.3572841
H	1.1261009	5.9039233	1.0558450
C	–2.5176501	0.5640101	6.0909070
H	–2.8729499	1.4821767	6.5836759
H	–1.7291839	0.1310794	6.7269297
H	–3.3512490	–0.1559607	6.0701388
C	–1.5227761	–0.4381892	3.9979928
H	–1.1818374	–0.2322936	2.9731278
H	–2.3259079	–1.1913477	3.9509589
H	–0.6834660	–0.8763747	4.5643566
C	2.0359104	–0.0474457	–0.1010919
N	2.7753785	–0.4450870	0.9654679
N	2.9434559	0.4566577	–0.9734201
C	4.1156771	–0.1838134	0.7653344
C	2.2199771	–0.9943823	2.2046080
C	4.2227411	0.3928792	–0.4585751
C	2.5524928	1.1484737	–2.1989912
H	4.8791642	–0.4270218	1.4983172
H	1.1353323	–1.0350031	2.0159827
C	2.4495126	–0.0430705	3.3667907
C	2.7638021	–2.3911756	2.4660290
H	5.0960803	0.7524647	–0.9934782
H	1.5788954	0.7037616	–2.4480118
C	3.5281472	0.8718371	–3.3294722
C	2.3449214	2.6307785	–1.9252970
H	1.9909822	–0.4532372	4.2777507
H	3.5231477	0.1059089	3.5650153
H	1.9725449	0.9260492	3.1644910
H	3.8381411	–2.3683716	2.7087170
H	2.2415712	–2.8401522	3.3234330
H	2.6282186	–3.0481423	1.5949850
H	3.1421225	1.3042620	–4.2637207
H	4.5123314	1.3308572	–3.1462570
H	3.6699014	–0.2085625	–3.4813235
H	1.6051716	2.7642617	–1.1202799
H	3.2884711	3.1124904	–1.6228804
H	1.9763164	3.1376302	–2.8298813
C	–0.1713578	–1.3105632	–1.5669615
N	–0.1530942	–2.6536887	–1.3874110
N	–0.6422963	–1.1428696	–2.8288522
C	–0.6175832	–3.3151861	–2.5064218
C	0.1346768	–3.2659592	–0.0920291
C	–0.9214824	–2.3588465	–3.4206383
C	–0.9155974	0.1595675	–3.4379762
H	–0.6912042	–4.3964973	–2.5680668
H	0.7406576	–2.5065383	0.4223174
C	0.9524066	–4.5360655	–0.2483724
C	–1.1512265	–3.4616553	0.6974401
H	–1.3053782	–2.4489268	–4.4325614
H	–0.5713278	0.8828527	–2.6810795
C	–2.4104920	0.3640489	–3.6255973
C	–0.1274593	0.3299372	–4.7282965
H	1.2453729	–4.9110821	0.7427359
H	0.3783425	–5.3381294	–0.7384951
H	1.8664303	–4.3541120	–0.8331083
H	–1.8144252	–4.1878202	0.2004212
H	–0.9238885	–3.8393448	1.7057349
H	–1.6813840	–2.5007167	0.7942222
H	–2.5997268	1.3652467	–4.0399487
H	–2.8368697	–0.3769427	–4.3205668
H	–2.9197284	0.2936469	–2.6537087
H	0.9435767	0.1338933	–4.5753754
H	–0.4872173	–0.3519060	–5.5151096
H	–0.2415989	1.3568265	–5.1049456

[Ni(I*i*Pr)$_2$(IDipp-CS$_2$)] (2b)

Energy = –4422.582343411

Ni	–0.3555875	–0.7743367	0.1716590
S	1.3808145	–1.1973634	1.4583183
S	1.2767132	–0.1049670	–1.1463925
C	2.3930118	–0.5754643	0.1450280
C	3.7461973	–0.4851269	0.1279138
N	4.6293918	–0.6549869	1.2073715
N	4.5702655	–0.2008080	–0.9745462
C	5.9415730	–0.4641219	0.7602671
C	4.2432037	–0.5175022	2.5661678
C	5.9073856	–0.2067172	–0.5595361
C	4.1797785	–0.4271614	–2.3208784
H	6.7780455	–0.5183275	1.4506917
C	3.8524693	0.7465914	3.0494283
C	4.2566997	–1.6553436	3.3917224
H	6.7112804	–0.0369039	–1.2696406
C	3.9645810	–1.7459547	–2.7670628
C	4.0173329	0.6791604	–3.1728899
C	3.4793031	0.8465573	4.3915106
C	3.8114242	1.9682726	2.1527773
C	3.8849700	–1.5050743	4.7303568
C	4.6216561	–3.0181528	2.8409328
C	3.5890392	–1.9322721	–4.0992614
C	4.1097717	–2.9384365	–1.8421524
C	3.6509152	0.4432587	–4.5006370
C	4.1950326	2.0935595	–2.6616476
C	3.4984765	–0.2655503	5.2278627
H	3.1681155	1.8157046	4.7903365
H	4.2307457	1.6788409	1.1788051
H	3.8855176	–2.3769736	5.3897662
H	4.8302077	–2.8774527	1.7697191
C	3.4379544	–0.8508910	–4.9620668
H	3.4132991	–2.9457901	–4.4695063
H	4.5060304	–2.5702534	–0.8853280
H	3.5178348	1.2892139	–5.1800971
H	4.4193922	2.0116349	–1.5874803
H	3.1466002	–1.0192765	–6.0020983
H	3.2046977	–0.1650029	6.2759533
C	2.3721311	2.4217023	1.9025038
H	1.8999251	2.7716864	2.8361155
H	2.3510340	3.2545466	1.1816103
H	1.7730525	1.5945537	1.4937925
C	4.6781726	3.1012655	2.6997034
H	4.3017869	3.4745143	3.6657293
H	5.7180839	2.7731580	2.8496058
H	4.6862378	3.9509206	1.9987674
C	5.3750867	2.7911211	–3.3360265
H	6.3090985	2.2248686	–3.1975493
H	5.2116379	2.9011467	–4.4205769
H	5.5233544	3.7994790	–2.9178642
C	2.9025104	2.8975156	–2.7943152
H	3.0241074	3.8984672	–2.3497062
H	2.6162609	3.0348096	–3.8499219
H	2.0796532	2.3800615	–2.2774418
C	2.7508109	–3.5760848	–1.5473622

H	2.3102244	–4.0078502	–2.4619375
H	2.8583410	–4.3869943	–0.8093247
H	2.0541339	–2.8283636	–1.1403968
C	5.1114509	–3.9574295	–2.3828177
H	4.7695906	–4.4056402	–3.3296740
H	6.0931693	–3.4947888	–2.5661898
H	5.2503258	–4.7782235	–1.6615170
C	5.8857074	–3.5713768	3.4962994
H	6.7351339	–2.8812179	3.3768054
H	5.7409855	–3.7356655	4.5765877
H	6.1664601	–4.5376709	3.0479737
C	3.4475958	–3.9903007	2.9489467
H	3.6991130	–4.9526576	2.4745288
H	3.1865697	–4.1950709	4.0002254
H	2.5608967	–3.5708880	2.4489346
C	–1.6149184	–0.3870746	–1.2052863
N	–1.7730394	–1.0189376	–2.3964962
N	–2.4127550	0.7057155	–1.2926652
C	–2.6441482	–0.3267038	–3.2135603
C	–1.0488982	–2.2273398	–2.7960505
C	–3.0445354	0.7682684	–2.5183410
C	–2.4120765	1.7568775	–0.2780138
H	–2.9105405	–0.6634369	–4.2110808
H	–0.4436063	–2.4784958	–1.9103464
C	–0.0906896	–1.9323254	–3.9380904
C	–2.0183017	–3.3568956	–3.1118081
H	–3.7211709	1.5701836	–2.7965600
H	–2.0965880	1.2325911	0.6351388
C	–3.8032496	2.3289234	–0.0694297
C	–1.3636763	2.8090681	–0.6078188
H	0.4662198	–2.8439691	–4.1987471
H	–0.6246130	–1.5915523	–4.8397678
H	0.6403765	–1.1714796	–3.6301402
H	–2.5991091	–3.1490078	–4.0245179
H	–1.4620289	–4.2904888	–3.2802447
H	–2.7293194	–3.5209876	–2.2892903
H	–3.7901230	3.0312477	0.7763313
H	–4.1537523	2.8918998	–0.9488042
H	–4.5335397	1.5360086	0.1508849
H	–0.3770310	2.3311468	–0.7174022
H	–1.6110780	3.3348457	–1.5439008
H	–1.3053178	3.5545994	0.1996204
C	–1.5183813	–1.3412588	1.5712679
N	–2.1456129	–2.5391988	1.6708727
N	–1.7447103	–0.7390845	2.7668518
C	–2.7380775	–2.6933058	2.9080566
C	–2.0098041	–3.5792778	0.6538509
C	–2.4894103	–1.5512456	3.5983821
C	–1.1980637	0.5625332	3.1556086
H	–3.2844868	–3.5856490	3.1969858
H	–1.7916840	–3.0148675	–0.2637062
C	–3.3057925	–4.3491538	0.4698523
C	–0.8124265	–4.4661961	0.9615243
H	–2.7832370	–1.2568907	4.6015879
H	–0.6518906	0.8989383	2.2596936
C	–0.1869016	0.4113769	4.2800757
C	–2.3165281	1.5384477	3.4903561
H	–3.2058454	–5.0423658	–0.3776315
H	–3.5536096	–4.9569525	1.3542970
H	–4.1483469	–3.6718761	0.2650177
H	–0.9627101	–5.0231507	1.9001938
H	–0.6595487	–5.1946478	0.1508239
H	0.0949809	–3.8483921	1.0550145
H	0.2343945	1.3949870	4.5334399
H	–0.6491715	–0.0039198	5.1900059
H	0.6422058	–0.2345004	3.9578263
H	–3.0576410	1.5962464	2.6801808
H	–2.8451631	1.2483234	4.4123225
H	–1.9000090	2.5435238	3.6512612

[Ni(I*i*Pr)$_2$(IMes-CS$_2$)] (2c)

Energy = –4187.137952636

Ni	–0.1741370	0.0504445	–0.0014639
S	1.4392866	–0.5656756	1.3728914
S	1.5530108	0.1500517	–1.3718033
C	2.5403418	–0.3695981	0.0016134
C	3.8793206	–0.5765290	0.0029961
N	4.7095235	–0.7615934	1.1215502
N	4.7285368	–0.6512591	–1.1142000
C	6.0270638	–0.9351742	0.6769804
C	4.3976863	–0.2559879	2.4108444
C	6.0362380	–0.8836225	–0.6672456
C	4.2802372	–1.0433566	–2.4029348
H	6.8426426	–1.0546833	1.3845967
C	4.2400407	1.1273190	2.6013748
C	4.2473365	–1.1590922	3.4723851
H	6.8511635	–1.0158039	–1.3733528
C	3.7158572	–2.3164810	–2.5906113
C	4.4075553	–0.1391244	–3.4665705
C	3.9433668	1.5853072	3.8855233
C	4.3526763	2.0776503	1.4494739
C	3.9524438	–0.6550819	4.7405778
C	4.3309842	–2.6333735	3.2166662
C	3.2962309	–2.6677872	–3.8741415
C	3.5387482	–3.2543548	–1.4365599
C	3.9758134	–0.5347456	–4.7339341
C	4.9286496	1.2430505	–3.2137903
C	3.7933196	0.7136984	4.9671886
H	3.8261179	2.6620992	4.0446001
H	4.4411958	3.1154380	1.8006875
H	5.2217567	1.8445630	0.8157505
H	3.4629274	1.9914040	0.8029068
H	3.8273833	–1.3556689	5.5717783
H	4.1709172	–3.2060998	4.1407367
H	3.5604451	–2.9229326	2.4839276
H	5.3022134	–2.9286601	2.7908099
C	3.4143970	–1.7938141	–4.9577935
H	2.8622517	–3.6605388	–4.0310347
H	2.7154745	–2.9042363	–0.7910658
H	3.3126623	–4.2718542	–1.7854940
H	4.4377404	–3.2907288	–0.8027166
H	4.0664113	0.1691764	–5.5667699
H	4.2787396	1.7522446	–2.4837634
H	5.9428340	1.2347525	–2.7858679
H	4.9493578	1.8349003	–4.1394675
C	3.4240413	1.2366955	6.3255605
C	2.9056443	–2.1849042	–6.3154520
H	3.6953081	0.5276303	7.1209861
H	3.9198229	2.1958579	6.5383402
H	2.3366212	1.4108197	6.3968686
H	1.8185259	–2.0111034	–6.3921924

H	3.3876631	–1.6013602	–7.1131136
H	3.0781130	–3.2522774	–6.5201135
C	–1.3379640	0.4847419	–1.4472272
N	–1.6464761	–0.2747056	–2.5300505
N	–1.8921478	1.6934677	–1.7134526
C	–2.3688692	0.4507478	–3.4561079
C	–1.1947703	–1.6527711	–2.7318489
C	–2.5191941	1.6983735	–2.9431658
C	–1.6482022	2.8659658	–0.8774579
H	–2.7180485	0.0283591	–4.3936776
H	–0.6406698	–1.8871439	–1.8083556
C	–0.2137613	–1.7361891	–3.8901993
C	–2.3820688	–2.5910254	–2.8922587
H	–3.0184879	2.5717851	–3.3509084
H	–1.4172271	2.4359967	0.1075453
C	–2.8876813	3.7361795	–0.7646959
C	–0.4185542	3.6151721	–1.3690776
H	0.1358455	–2.7724883	–4.0058468
H	–0.6802413	–1.4273173	–4.8397168
H	0.6653506	–1.1088147	–3.6841712
H	–2.9195735	–2.4061410	–3.8359450
H	–2.0351114	–3.6344763	–2.9099304
H	–3.1003115	–2.4786738	–2.0674456
H	–2.7062615	4.5460065	–0.0434665
H	–3.1460833	4.2123323	–1.7236290
H	–3.7551142	3.1538910	–0.4197082
H	0.4451380	2.9316480	–1.4031918
H	–0.5848814	4.0306559	–2.3759845
H	–0.1833636	4.4483015	–0.6895045
C	–1.4187121	–0.0114725	1.4408736
N	–2.3144392	–0.9950439	1.7042114
N	–1.4857244	0.8058026	2.5234372
C	–2.9174656	–0.8093120	2.9319451
C	–2.4348108	–2.1864438	0.8679799
C	–2.3972524	0.3338802	3.4464831
C	–0.6378911	1.9818647	2.7279947
H	–3.6596866	–1.4898917	3.3373366
H	–2.0825520	–1.8467795	–0.1163192
C	–3.8792153	–2.6408931	0.7520374
C	–1.4907144	–3.2726055	1.3618981
H	–2.6048975	0.8423343	4.3833962
H	–0.0348733	2.0363685	1.8070995
C	0.3170777	1.7642357	3.8905455
C	–1.4852140	3.2362132	2.8839132
H	–3.9498890	–3.4667757	0.0296215
H	–4.2714272	–3.0179026	1.7097385
H	–4.5293317	–1.8230788	0.4069938
H	–1.7776958	–3.6185275	2.3679476
H	–1.5164216	–4.1377282	0.6820318
H	–0.4608276	–2.8824223	1.3990065
H	0.9640279	2.6457431	4.0085404
H	–0.2251309	1.6119043	4.8377999
H	0.9653865	0.8996349	3.6877688
H	–2.1980980	3.3475682	2.0543182
H	–2.0597507	3.2230048	3.8238845
H	–0.8379427	4.1250446	2.9061329

[Ni(I*i*Pr)$_2$(I*i*Pr-CS$_2$)] (2f)

Energy = –3725.840567886

Ni	–0.2009162	0.0550599	0.0035198
S	1.4949586	–0.0497816	1.4012255
S	1.4511267	–0.3303314	–1.3971142
C	2.5486592	–0.3491312	0.0011228
C	3.8988679	–0.5489601	0.0004031
N	4.7132746	–0.8354532	1.1120075
N	4.7602259	–0.5100844	–1.1119028
C	6.0270942	–0.9781828	0.6616628
C	4.2060032	–1.5449660	2.2807686
C	6.0597218	–0.7524997	–0.6628329
C	4.4772636	0.3131049	–2.2818732
H	6.8392157	–1.2297891	1.3354802
H	6.9092855	–0.7459151	–1.3374683
C	–1.4601470	–0.1199136	–1.4148667
N	–1.8214477	–1.2679315	–2.0433800
N	–2.0559383	0.8620944	–2.1346946
C	–2.6156344	–1.0046269	–3.1413665
C	–1.3517687	–2.5996532	–1.6574690
C	–2.7598478	0.3437910	–3.2033182
C	–1.7959072	2.2785562	–1.8911234
H	–3.0146251	–1.7853366	–3.7822937
H	–0.7663757	–2.4167726	–0.7412809
C	–0.4033037	–3.1625925	–2.7035309
C	–2.5257210	–3.5206434	–1.3594349
H	–3.3040158	0.9617426	–3.9107206
H	–1.5001916	2.3074263	–0.8330378
C	–3.0497151	3.1145049	–2.0801909
C	–0.6158767	2.7497443	–2.7279146
H	–0.0428150	–4.1516676	–2.3842218
H	–0.9000248	–3.2809141	–3.6799474
H	0.4656637	–2.4955291	–2.8051992
H	–3.0975804	–3.7574129	–2.2707760
H	–2.1597391	–4.4711551	–0.9446998
H	–3.2181637	–3.0699434	–0.6336623
H	–2.8511263	4.1520160	–1.7750422
H	–3.3703268	3.1450953	–3.1334645
H	–3.8828149	2.7292612	–1.4734670
H	0.2652323	2.1225454	–2.5156469
H	–0.8463843	2.6915997	–3.8038458
H	–0.3713599	3.7952959	–2.4863949
C	–1.3539184	0.5806416	1.4256750
N	–2.1987719	–0.1936930	2.1495122
N	–1.3735544	1.7837532	2.0545876
C	–2.7225779	0.5017665	3.2209758
C	–2.3494289	–1.6260427	1.9068289
C	–2.2040688	1.7547357	3.1569018
C	–0.5476043	2.9282913	1.6660007
H	–3.4152063	0.0620648	3.9318968
H	–2.0668003	–1.7386864	0.8507622
C	–3.7900438	–2.0718170	2.0867483
C	–1.3566192	–2.4112152	2.7510098
H	–2.3630248	2.6159856	3.7991103
H	–0.0447858	2.5892507	0.7452217
C	0.5289757	3.1956512	2.7052441
C	–1.4136570	4.1455446	1.3773899
H	–3.8909421	–3.1248456	1.7868599
H	–4.1149988	–2.0044041	3.1370404
H	–4.4749195	–1.4698563	1.4710345
H	–1.5670266	–2.2881125	3.8255895
H	–1.4174352	–3.4835931	2.5110797
H	–0.3325827	–2.0604440	2.5434144
H	1.1533015	4.0424888	2.3839847

H	0.0930148	3.4474105	3.6854066
H	1.1732793	2.3089256	2.7999264
H	–2.2111794	3.9115822	0.6572760
H	–1.8875412	4.5329219	2.2933338
H	–0.7959366	4.9539038	0.9597353
H	3.4706009	0.0298406	–2.6249391
H	3.3229999	–0.9853864	2.6249222
C	5.2211114	–1.5386358	3.4117653
H	4.7520080	–1.9247051	4.3284829
H	6.0911062	–2.1796756	3.1971358
H	5.5804314	–0.5183446	3.6138576
C	3.7422100	–2.9506841	1.9156089
H	4.5870671	–3.5631793	1.5599053
H	3.2901395	–3.4493280	2.7871034
H	2.9848790	–2.8955175	1.1193797
C	5.4471816	0.0138069	–3.4129089
H	5.1081300	0.5167430	–4.3302887
H	6.4646556	0.3786420	–3.1993871
H	5.4985383	–1.0670041	–3.6132664
C	4.4365183	1.7933965	–1.9192475
H	5.4218689	2.1382167	–1.5650305
H	4.1458165	2.3992320	–2.7915939
H	3.6957644	1.9592238	–1.1227537

[Ni(cAAC^{Me}-CS$_2$)$_2$] (3a), singlet restricted

Energy = –4844.093484712

Ni	0.0004491	–0.0011396	0.0015980
S	–2.1417288	0.3190793	0.2027551
S	–0.0198784	1.4919451	1.5876339
N	–2.3871795	3.2140686	3.0457154
C	–0.1734742	4.2651762	3.3573863
C	1.3038681	3.3902776	5.0741411
H	2.2595992	3.4262613	5.6024076
C	–1.1291304	3.2953306	3.7220200
C	–4.1962305	2.1738570	1.9307465
C	–2.6823258	2.2653073	2.1186181
C	0.3623929	2.4230534	5.4032123
H	0.5884883	1.6974526	6.1878157
C	–4.7129566	3.0685537	3.0740541
H	–5.6252005	3.6136867	2.7927400
H	–4.9633046	2.4367943	3.9405323
C	–3.5739762	4.0136988	3.4644806
C	–0.3662640	5.2216089	2.1977799
H	–1.3492372	5.0065803	1.7579828
C	–3.6690926	5.3382063	2.7017955
H	–3.6097810	5.1907991	1.6153027
H	–2.8759372	6.0335512	3.0006302
H	–4.6343483	5.8152450	2.9286341
C	–4.6173630	2.6816695	0.5456067
H	–4.2846720	3.7130474	0.3642601
H	–5.7147599	2.6549771	0.4572748
H	–4.1866979	2.0462590	–0.2409122
C	1.0333548	4.2995667	4.0609957
H	1.7875071	5.0413177	3.7877295
C	–1.7518464	1.4861464	1.4318705
C	–0.8655006	2.3530850	4.7432831
C	–1.8333352	1.2447400	5.1164266
H	–2.7828212	1.4418415	4.5978839
C	–4.7231399	0.7483676	2.1382015
H	–5.8239247	0.7754376	2.1809100
H	–4.3534229	0.3245859	3.0844058
H	–4.4205350	0.0755637	1.3260278
C	–3.5526060	4.3085733	4.9575124
H	–2.6820718	4.9217250	5.2324889
H	–3.5273885	3.3875216	5.5534253
H	–4.4621674	4.8651968	5.2269338
C	–0.3472224	6.6779071	2.6646323
H	–0.6046812	7.3564870	1.8363129
H	0.6536454	6.9631703	3.0252403
H	–1.0516312	6.8606778	3.4905082
C	0.6716627	4.9967453	1.0964730
H	0.6538397	3.9548453	0.7460697
H	1.6902107	5.2188468	1.4525328
H	0.4667193	5.6596292	0.2410666
C	–2.1270103	1.2143197	6.6167631
H	–2.4673416	2.1911043	6.9924766
H	–1.2349715	0.9316911	7.1968022
H	–2.9076843	0.4700657	6.8383835
C	–1.3294213	–0.1197133	4.6390715
H	–1.1173177	–0.1206326	3.5613903
H	–2.0778794	–0.8996623	4.8508579
H	–0.3991459	–0.3964966	5.1604961
S	2.1424865	–0.3215655	–0.2001956
S	0.0202461	–1.4937104	–1.5849971
N	2.3871523	–3.2139767	–3.0460860
C	0.1727474	–4.2632546	–3.3611745
C	–1.3015688	–3.3857921	–5.0792355
H	–2.2562759	–3.4211436	–5.6093874
C	1.1293865	–3.2932541	–3.7231924
C	4.1960336	–2.1771369	–1.9276399
C	2.6823842	–2.2664220	–2.1177487
C	–0.3592852	–2.4185090	–5.4056770
H	–0.5839036	–1.6918752	–6.1897419
C	4.7131769	–3.0720096	–3.0706699
H	5.6241268	–3.6187074	–2.7882374
H	4.9658800	–2.4401657	–3.9363836
C	3.5733406	–4.0152274	–3.4634101
C	0.3635895	–5.2218778	–2.2030389
H	1.3456592	–5.0076413	–1.7609645
C	3.6655995	–5.3403321	–2.7013656
H	3.6048102	–5.1934194	–1.6148947
H	2.8720228	–6.0344710	–3.0018025
H	4.6305713	–5.8185177	–2.9269667
C	4.6143226	–2.6864181	–0.5421894
H	4.2799368	–3.7174516	–0.3620502
H	5.7116025	–2.6612800	–0.4520935
H	4.1832773	–2.0509396	0.2440418
C	–1.0330548	–4.2962057	–4.0665816
H	–1.7881911	–5.0375323	–3.7948965
C	1.7522279	–1.4879359	–1.4299234
C	0.8675440	–2.3496978	–4.7436702
C	1.8358604	–1.2405799	–5.1131780
H	2.7843932	–1.4382954	–4.5931636
C	4.7250750	–0.7521865	–2.1332948
H	5.8258737	–0.7806682	–2.1743534
H	4.3573464	–0.3272595	–3.0797406
H	4.4221179	–0.0795589	–1.3211071
C	3.5536873	–4.3091469	–4.9566458
H	2.6826690	–4.9208658	–5.2332298
H	3.5306625	–3.3877189	–5.5520902
H	4.4628218	–4.8669325	–5.2250732

C	0.3454294	–6.6771147	–2.6731455
H	0.6013338	–7.3575376	–1.8458579
H	–0.6547296	–6.9615838	–3.0363385
H	1.0514557	–6.8579684	–3.4980625
C	–0.6764975	–4.9995969	–1.1032665
H	–0.6595017	–3.9584656	–0.7506162
H	–1.6943332	–5.2210865	–1.4617426
H	–0.4731081	–5.6642852	–0.2488920
C	2.1322748	–1.2078982	–6.6128879
H	2.4734493	–2.1840954	–6.9893601
H	1.2412557	–0.9245941	–7.1941657
H	2.9132417	–0.4632143	–6.8319863
C	1.3307545	0.1230239	–4.6346196
H	1.1167154	0.1221783	–3.5573429
H	2.0794022	0.9034945	–4.8437595
H	0.4013734	0.4004276	–5.1572900

[Ni(cAAC^{Me}-CS$_2$)$_2$] (3a), singlet diradical unrestricted

Energy = –4844.103720249

Ni	–0.0000167	–0.0000032	–0.0000227
S	–2.1725833	0.3621990	0.2009906
S	–0.0407445	1.4808935	1.6439684
N	–2.4016955	3.2172015	3.0768924
C	–0.1881265	4.2709524	3.3819610
C	1.2823150	3.4174734	5.1155734
H	2.2368409	3.4590806	5.6455538
C	–1.1439104	3.3047760	3.7556046
C	–4.2142001	2.1914652	1.9492035
C	–2.7011002	2.2745009	2.1441019
C	0.3388043	2.4561757	5.4554128
H	0.5619628	1.7409896	6.2503048
C	–4.7296162	3.0825421	3.0956490
H	–5.6389856	3.6328315	2.8153184
H	–4.9844339	2.4476323	3.9584936
C	–3.5884428	4.0211626	3.4938686
C	–0.3745259	5.2130543	2.2093661
H	–1.3584679	4.9994511	1.7711516
C	–3.6699222	5.3480910	2.7347070
H	–3.6013354	5.2044015	1.6483464
H	–2.8761657	6.0383960	3.0439252
H	–4.6350949	5.8284948	2.9542805
C	–4.6312549	2.7097346	0.5666942
H	–4.2989447	3.7428531	0.3948002
H	–5.7283462	2.6832560	0.4747572
H	–4.1980201	2.0809258	–0.2236245
C	1.0160182	4.3134210	4.0894016
H	1.7718653	5.0506013	3.8087724
C	–1.7637727	1.4923291	1.4499879
C	–0.8866033	2.3778397	4.7914591
C	–1.8557874	1.2732427	5.1731054
H	–2.8055088	1.4666613	4.6534039
C	–4.7489370	0.7676774	2.1483669
H	–5.8494525	0.8005731	2.1937020
H	–4.3796460	0.3358253	3.0912440
H	–4.4511154	0.0988099	1.3312002
C	–3.5751656	4.3118217	4.9876954
H	–2.7015370	4.9159787	5.2722054
H	–3.5654760	3.3894206	5.5817302
H	–4.4819792	4.8764136	5.2496995
C	–0.3451405	6.6754049	2.6563714
H	–0.5993793	7.3437957	1.8189064
H	0.6584517	6.9589888	3.0106549
H	–1.0464602	6.8747102	3.4810082
C	0.6635275	4.9670708	1.1125368
H	0.6379816	3.9210271	0.7758201
H	1.6829080	5.1856737	1.4684267
H	0.4651180	5.6211817	0.2489022
C	–2.1487616	1.2531199	6.6737288
H	–2.4811933	2.2346174	7.0442194
H	–1.2589167	0.9667748	7.2553757
H	–2.9350437	0.5161151	6.8995735
C	–1.3528923	–0.0942277	4.7035253
H	–1.1480699	–0.1021647	3.6244809
H	–2.0975874	–0.8743971	4.9275186
H	–0.4171700	–0.3637255	5.2189614
S	2.1725810	–0.3622164	–0.2010098
S	0.0407461	–1.4808605	–1.6439586
N	2.4016882	–3.2172115	–3.0768940
C	0.1881158	–4.2709545	–3.3819620
C	–1.2823059	–3.4174560	–5.1155712
H	–2.2368185	–3.4590989	–5.6455591
C	1.1438863	–3.3047773	–3.7555858
C	4.2141960	–2.1914668	–1.9492126
C	2.7011182	–2.2744913	–2.1441146
C	–0.3387734	–2.4561762	–5.4554058
H	–0.5619766	–1.7410103	–6.2503131
C	4.7296079	–3.0825453	–3.0956333
H	5.6390087	–3.6328218	–2.8153193
H	4.9844339	–2.4476490	–3.9584913
C	3.5884533	–4.0211501	–3.4938628
C	0.3744935	–5.2130630	–2.2093753
H	1.3584741	–4.9994361	–1.7711367
C	3.6699095	–5.3480702	–2.7347119
H	3.6013333	–5.2044212	–1.6483739
H	2.8761811	–6.0383914	–3.0439039
H	4.6350806	–5.8285066	–2.9542540
C	4.6312645	–2.7097375	–0.5667139
H	4.2989384	–3.7428274	–0.3948146
H	5.7283327	–2.6832691	–0.4747369
H	4.1980227	–2.0809350	0.2236266
C	–1.0160111	–4.3134125	–4.0894163
H	–1.7718638	–5.0506096	–3.8087838
C	1.7637719	–1.4923451	–1.4499726
C	0.8866185	–2.3778371	–4.7914471
C	1.8557730	–1.2732272	–5.1731239
H	2.8054988	–1.4666401	–4.6534002
C	4.7489476	–0.7677057	–2.1483464
H	5.8494396	–0.8005667	–2.1936934
H	4.3796585	–0.3358358	–3.0912126
H	4.4511323	–0.0988206	–1.3311965
C	3.5751522	–4.3118115	–4.9876592
H	2.7015525	–4.9159508	–5.2722206
H	3.5654780	–3.3894518	–5.5817238
H	4.4819612	–4.8764036	–5.2497095
C	0.3451480	–6.6753880	–2.6563682
H	0.5993810	–7.3438100	–1.8189221
H	–0.6584431	–6.9590046	–3.0106493
H	1.0464499	–6.8747138	–3.4809952
C	–0.6635214	–4.9670754	–1.1125445

H	–0.6379789	–3.9210358	–0.7758274
H	–1.6829197	–5.1856640	–1.4684019
H	–0.4651411	–5.6211713	–0.2488910
C	2.1487657	–1.2531342	–6.6737362
H	2.4812057	–2.2346148	–7.0442271
H	1.2589352	–0.9667793	–7.2554014
H	2.9350636	–0.5161207	–6.8996002
C	1.3528838	0.0942312	–4.7035394
H	1.1480694	0.1021635	–3.6244903
H	2.0975749	0.8744262	–4.9275147
H	0.4171628	0.3637412	–5.2189598

[Ni(cAAC^{Me}-CS$_2$)$_2$] (3a), triplet

Energy = –4844.100747676

Ni	0.0001635	0.0034856	–0.0030831
S	–2.1865422	0.3302138	0.2480951
S	–0.0404155	1.5227275	1.6231793
N	–2.3918474	3.2380434	3.0701915
C	–0.1799699	4.2839027	3.4162310
C	1.2638641	3.4117186	5.1627490
H	2.2095306	3.4482631	5.7087933
C	–1.1415888	3.3144561	3.7645335
C	–4.2166715	2.1813024	1.9867885
C	–2.7013262	2.2790748	2.1560840
C	0.3135524	2.4493165	5.4797266
H	0.5225300	1.7277947	6.2726878
C	–4.7200301	3.0982547	3.1185106
H	–5.6351018	3.6385427	2.8371446
H	–4.9605982	2.4846598	4.0007288
C	–3.5768314	4.0511798	3.4761456
C	–0.3530292	5.2422529	2.2552190
H	–1.3246892	5.0226325	1.7929353
C	–3.6713822	5.3520155	2.6739656
H	–3.6032838	5.1720997	1.5929060
H	–2.8837370	6.0598502	2.9572407
H	–4.6404546	5.8307366	2.8795455
C	–4.6634602	2.6590981	0.5989293
H	–4.3491538	3.6921868	0.3960518
H	–5.7614074	2.6149213	0.5260067
H	–4.2346504	2.0164939	–0.1826843
C	1.0136216	4.3181368	4.1416088
H	1.7737612	5.0579964	3.8801324
C	–1.7644673	1.4944373	1.4580828
C	–0.9025002	2.3799637	4.7978649
C	–1.8845007	1.2813259	5.1627187
H	–2.8292195	1.4907296	4.6405530
C	–4.7361905	0.7584898	2.2311649
H	–5.8364325	0.7824517	2.2870143
H	–4.3535122	0.3558205	3.1814615
H	–4.4404072	0.0703562	1.4292929
C	–3.5457307	4.3879520	4.9597174
H	–2.6755519	5.0110664	5.2119830
H	–3.5141340	3.4845948	5.5819679
H	–4.4555557	4.9493504	5.2181221
C	–0.3540979	6.6965464	2.7290760
H	–0.6008470	7.3772518	1.8992156
H	0.6375513	6.9873849	3.1102111
H	–1.0754185	6.8699727	3.5423557
C	0.7097551	5.0288083	1.1759507
H	0.7008296	3.9890793	0.8194421
H	1.7195401	5.2519599	1.5554496
H	0.5210634	5.6966336	0.3206577
C	–2.1885476	1.2491846	6.6607364
H	–2.5193363	2.2290634	7.0372589
H	–1.3050208	0.9526267	7.2467351
H	–2.9806028	0.5145185	6.8737037
C	–1.3931418	–0.0863705	4.6822432
H	–1.1758170	–0.0846954	3.6057210
H	–2.1496830	–0.8600899	4.8880867
H	–0.4670451	–0.3734180	5.2054719
S	2.1869221	–0.3222478	–0.2552524
S	0.0406332	–1.5174909	–1.6276400
N	2.3932649	–3.2353013	–3.0716020
C	0.1831413	–4.2892994	–3.4036138
C	–1.2698467	–3.4304417	–5.1491445
H	–2.2177087	–3.4721962	–5.6909848
C	1.1407555	–3.3191946	–3.7610182
C	4.2174955	–2.1698948	–1.9960308
C	2.7021230	–2.2717734	–2.1620639
C	–0.3230867	–2.4676785	–5.4755723
H	–0.5369666	–1.7512553	–6.2718388
C	4.7203370	–3.0862086	–3.1283176
H	5.6396090	–3.6211524	–2.8504111
H	4.9533797	–2.4728025	–4.0126922
C	3.5800859	–4.0448090	–3.4796444
C	0.3639480	–5.2414708	–2.2386405
H	1.3371977	–5.0170970	–1.7820066
C	3.6820178	–5.3436983	–2.6753514
H	3.6174723	–5.1623202	–1.5943319
H	2.8954667	–6.0543998	–2.9544101
H	4.6517889	–5.8197296	–2.8838995
C	4.6677860	–2.6463526	–0.6087764
H	4.3552049	–3.6796341	–0.4043098
H	5.7658223	–2.6006790	–0.5381500
H	4.2397692	–2.0036769	0.1732390
C	–1.0134209	–4.3303022	–4.1237365
H	–1.7707525	–5.0704192	–3.8549663
C	1.7648998	–1.4874259	–1.4643266
C	0.8952420	–2.3911112	–4.7985624
C	1.8726820	–1.2916711	–5.1729289
H	2.8201721	–1.4957393	–4.6536711
C	4.7335556	–0.7461318	–2.2416382
H	5.8338143	–0.7675643	–2.2981036
H	4.3493600	–0.3450783	–3.1920264
H	4.4366210	–0.0581174	–1.4400941
C	3.5456287	–4.3851658	–4.9623909
H	2.6768355	–5.0118948	–5.2105000
H	3.5092701	–3.4835582	–5.5868584
H	4.4565571	–4.9441775	–5.2220772
C	0.3662932	–6.6980988	–2.7051216
H	0.6137920	–7.3743004	–1.8718092
H	–0.6250987	–6.9917818	–3.0846342
H	1.0876672	–6.8750285	–3.5175731
C	–0.6944528	–5.0249631	–1.1556016
H	–0.6863702	–3.9833766	–0.8044893
H	–1.7054263	–5.2521951	–1.5294116
H	–0.5004838	–5.6880170	–0.2977787
C	2.1702377	–1.2659951	–6.6724114
H	2.4971648	–2.2480331	–7.0466794
H	1.2847153	–0.9696745	–7.2555421
H	2.9628690	–0.5338378	–6.8917736

C	1.3796203	0.0770957	–4.6972452
H	1.1608452	0.0784904	–3.6210079
H	2.1357580	0.8508114	–4.9045693
H	0.4539600	0.3617143	–5.2226286

[Ni(cAAC^{Me}-CS$_2$)$_2$] (3a), quintet

Energy = –4844.085598637

Ni	–0.0002916	–0.0062103	0.0053585
S	–2.2990703	0.3206564	0.3714428
S	–0.0771144	1.6481543	1.6539768
N	–2.4067563	3.3026014	3.1081120
C	–0.2110827	4.3666592	3.5124475
C	1.1969109	3.5025532	5.2921413
H	2.1273078	3.5472610	5.8631630
C	–1.1685329	3.3817715	3.8260102
C	–4.2533362	2.2164997	2.0900063
C	–2.7309519	2.3201378	2.2215907
C	0.2491714	2.5286966	5.5788856
H	0.4434292	1.8072238	6.3756771
C	–4.7330463	3.1647729	3.2047830
H	–5.6584177	3.6909675	2.9306747
H	–4.9470082	2.5782427	4.1119488
C	–3.5869438	4.1317560	3.5023042
C	–0.3653067	5.3327609	2.3554770
H	–1.3153551	5.0960341	1.8578088
C	–3.6990700	5.3974173	2.6470803
H	–3.6237403	5.1738117	1.5747687
H	–2.9249992	6.1299989	2.9022806
H	–4.6767067	5.8679883	2.8294485
C	–4.7383474	2.6536534	0.7013705
H	–4.4277500	3.6786767	0.4569262
H	–5.8381444	2.6117463	0.6635911
H	–4.3359181	1.9832155	–0.0704527
C	0.9613873	4.4121026	4.2700925
H	1.7181667	5.1638521	4.0338899
C	–1.8006439	1.5257568	1.5115699
C	–0.9481375	2.4498915	4.8653524
C	–1.9300085	1.3443609	5.2072478
H	–2.8659393	1.5501082	4.6688946
C	–4.7768356	0.8052639	2.3907760
H	–5.8738348	0.8467471	2.4871666
H	–4.3653097	0.4225961	3.3371675
H	–4.5191598	0.0946513	1.5960853
C	–3.5334500	4.5272621	4.9704754
H	–2.6682895	5.1710595	5.1841624
H	–3.4774834	3.6490585	5.6264657
H	–4.4472893	5.0853041	5.2222672
C	–0.4135270	6.7814958	2.8439604
H	–0.6466241	7.4666780	2.0137682
H	0.5583675	7.0882035	3.2617661
H	–1.1649592	6.9306288	3.6343844
C	0.7377509	5.1547833	1.3110150
H	0.7585088	4.1207095	0.9395760
H	1.7298460	5.3904504	1.7275469
H	0.5660926	5.8315405	0.4590966
C	–2.2652383	1.3033806	6.6982187
H	–2.6113735	2.2794902	7.0709010
H	–1.3930733	1.0103974	7.3027498
H	–3.0571619	0.5629635	6.8908074
C	–1.4202085	–0.0173126	4.7294537
H	–1.1860610	–0.0075686	3.6565299
H	–2.1736747	–0.7984972	4.9175222
H	–0.5006688	–0.2991710	5.2669047
S	2.2983649	–0.3286928	–0.3640327
S	0.0771211	–1.6603914	–1.6434070
N	2.4086477	–3.3018254	–3.1101757
C	0.2162479	–4.3742691	–3.5098660
C	–1.2021248	–3.5107939	–5.2815823
H	–2.1343855	–3.5578832	–5.8493617
C	1.1680588	–3.3840217	–3.8236746
C	4.2541363	–2.2127608	–2.0933771
C	2.7317537	–2.3212058	–2.2212598
C	–0.2599190	–2.5316249	–5.5684980
H	–0.4604393	–1.8083787	–6.3621282
C	4.7341696	–3.1548201	–3.2132256
H	5.6621336	–3.6788197	–2.9436959
H	4.9436468	–2.5638089	–4.1185184
C	3.5907821	–4.1246627	–3.5117292
C	0.3788296	–5.3431071	–2.3563306
H	1.3302891	–5.1047002	–1.8622048
C	3.7103312	–5.3939921	–2.6629997
H	3.6376960	–5.1759892	–1.5893506
H	2.9381750	–6.1281779	–2.9193730
H	4.6891158	–5.8600055	–2.8508687
C	4.7438993	–2.6540540	–0.7077198
H	4.4371556	–3.6810885	–0.4668391
H	5.8436429	–2.6087375	–0.6722742
H	4.3410892	–1.9881325	0.0678125
C	–0.9587687	–4.4225759	–4.2633791
H	–1.7112854	–5.1784798	–4.0268405
C	1.8006955	–1.5324983	–1.5058877
C	0.9395932	–2.4496165	–4.8590280
C	1.9149133	–1.3381924	–5.2006447
H	2.8533756	–1.5404223	–4.6653376
C	4.7724451	–0.7987118	–2.3898359
H	5.8692797	–0.8365478	–2.4895783
H	4.3570317	–0.4134889	–3.3334990
H	4.5149716	–0.0920586	–1.5915759
C	3.5343942	–4.5134957	–4.9815924
H	2.6709487	–5.1594195	–5.1957758
H	3.4734272	–3.6324267	–5.6332637
H	4.4495113	–5.0670396	–5.2386425
C	0.4295380	–6.7903411	–2.8489620
H	0.6691056	–7.4769199	–2.0217734
H	–0.5433815	–7.0992945	–3.2627000
H	1.1775092	–6.9348040	–3.6435180
C	–0.7201771	–5.1715540	–1.3065237
H	–0.7425579	–4.1386124	–0.9320616
H	–1.7133385	–5.4090617	–1.7194470
H	–0.5427098	–5.8502260	–0.4573234
C	2.2456486	–1.2914468	–6.6924501
H	2.5964898	–2.2645074	–7.0686784
H	1.3700103	–1.0021498	–7.2937272
H	3.0326036	–0.5458391	–6.8853869
C	1.3992694	0.0195539	–4.7179297
H	1.1678202	0.0056822	–3.6444640
H	2.1481908	0.8051400	–4.9057958
H	0.4769312	0.2980644	–5.2523335

[Ni(IDipp-CS_2)$_2$] (3b), singlet restricted

Energy = –5491.954309725

Ni	–0.1579336	–1.3781960	0.2009536
S	–1.7163180	–1.1359248	–1.3022740
S	–1.7813625	–0.6648633	1.4761150
C	–2.6162926	–0.3880802	–0.0209835
S	1.4925652	–1.2115763	1.6288035
S	1.5279444	–1.5511096	–1.1735710
C	2.4945647	–1.1653611	0.2106765
C	3.8252172	–0.7343016	0.1773559
N	4.6883714	–0.6056083	1.2427804
N	4.5541042	–0.3541256	–0.9294293
C	5.9224196	–0.1675646	0.7956147
C	4.4115404	–0.9396044	2.6020865
C	5.8395183	–0.0095038	–0.5463262
C	3.9989939	–0.0403717	–2.2072587
H	6.7483621	–0.0229653	1.4850656
C	4.0328149	0.0893898	3.4803703
C	4.5328338	–2.2794367	3.0037951
H	6.5697633	0.3296824	–1.2743997
C	4.1422808	–0.9623886	–3.2544482
C	3.3139339	1.1790914	–2.3494394
C	3.8023738	–0.2541032	4.8135873
C	3.8480890	1.5161481	3.0052441
C	4.2789624	–2.5733510	4.3458118
C	4.8793854	–3.3831168	2.0259067
C	3.5668060	–0.6350539	–4.4842621
C	4.8622444	–2.2808672	–3.0609555
C	2.7420762	1.4514899	–3.5934524
C	3.1633259	2.1558337	–1.2003111
C	3.9240636	–1.5718232	5.2426163
H	3.5037019	0.5204082	5.5238719
H	3.9422142	1.5103451	1.9087307
H	4.3536052	–3.6070561	4.6917281
H	5.0753659	–2.9145709	1.0494787
C	2.8651619	0.5540650	–4.6493642
H	3.6512277	–1.3337458	–5.3199521
H	5.1317293	–2.3516164	–1.9958246
H	2.1833116	2.3791593	–3.7361152
H	3.7887021	1.7933427	–0.3704007
C	–3.7303721	0.4380731	–0.1989114
N	–4.3979472	1.1707497	0.7594333
N	–4.3838541	0.7156094	–1.3821994
C	–5.4305617	1.8816223	0.1747149
C	–4.1279406	1.1910710	2.1601711
C	–5.4224451	1.5996114	–1.1489994
C	–4.1633769	0.0908214	–2.6469098
H	–6.0735370	2.5239481	0.7681791
C	–4.7738403	0.2506182	2.9786852
C	–3.2363318	2.1535924	2.6599869
H	–6.0631943	1.9356608	–1.9580810
C	–3.2973335	0.7073245	–3.5646849
C	–4.8341915	–1.1121072	–2.9205044
C	–4.5100515	0.3021380	4.3494886
C	–5.6858060	–0.8162019	2.4079275
C	–3.0107458	2.1679474	4.0374199
C	–2.5156986	3.1240300	1.7475081
C	–3.1371743	0.0960263	–4.8088835
C	–2.5492525	1.9776078	–3.2171264
C	–4.6299623	–1.6918381	–4.1753825
C	–5.7005805	–1.8002318	–1.8852778
C	–3.6401857	1.2518330	4.8739288
H	–4.9865905	–0.4211256	5.0155504
H	–5.7710198	–0.6356931	1.3255448
H	–2.3168897	2.8983300	4.4601803
H	–2.7682569	2.8521575	0.7112218
C	–3.7964027	–1.0912755	–5.1118689
H	–2.4694025	0.5460583	–5.5466611
H	–2.6461973	2.1248206	–2.1301935
H	–5.1264037	–2.6341650	–4.4187661
H	–5.7931726	–1.1218471	–1.0234662
H	–3.4431533	1.2729335	5.9485010
H	–3.6489570	–1.5604965	–6.0876008
H	2.4046930	0.7841544	–5.6132388
H	3.7288275	–1.8230717	6.2879330
C	–2.9963956	4.5565967	1.9774069
H	–4.0835062	4.6468004	1.8280831
H	–2.7723770	4.8926961	3.0025106
H	–2.4978660	5.2497984	1.2818555
C	–0.9992535	2.9999683	1.8846619
H	–0.4963772	3.6520960	1.1539310
H	–0.6563574	3.2997250	2.8878678
H	–0.6765259	1.9629917	1.7074467
C	–1.0561652	1.8667357	–3.5180027
H	–0.8607298	1.7481463	–4.5956035
H	–0.5400578	2.7834832	–3.1924718
H	–0.6112573	1.0120029	–2.9868055
C	–3.1812726	3.1859075	–3.9092223
H	–3.1214979	3.0895323	–5.0052837
H	–4.2439477	3.2946328	–3.6429608
H	–2.6629571	4.1147621	–3.6234235
C	–5.0768845	–2.2075277	2.5854641
H	–4.9952498	–2.4737099	3.6514925
H	–5.7058491	–2.9682621	2.0969818
H	–4.0683019	–2.2520009	2.1483186
C	–7.0938968	–0.7296042	2.9938575
H	–7.0929173	–0.9232482	4.0782424
H	–7.5370028	0.2651598	2.8328909
H	–7.7529351	–1.4772671	2.5256061
C	–7.1128446	–2.0643595	–2.4030502
H	–7.5989053	–1.1361063	–2.7404931
H	–7.1099051	–2.7678890	–3.2505366
H	–7.7354125	–2.5078737	–1.6105240
C	–5.0274367	–3.0789517	–1.3835494
H	–5.6159418	–3.5312202	–0.5699842
H	–4.9408500	–3.8232135	–2.1913812
H	–4.0144456	–2.8698586	–1.0093357
C	2.4495549	2.0406179	3.3265956
H	2.2853287	2.1251898	4.4126639
H	2.3085918	3.0429701	2.8923693
H	1.6827690	1.3702806	2.9110303
C	4.9423257	2.4291342	3.5575036
H	4.9030489	2.4767937	4.6575957
H	5.9457419	2.0736677	3.2765235
H	4.8245272	3.4544466	3.1729680
C	3.6821193	3.5447371	–1.5699940
H	4.7269470	3.5080246	–1.9143499
H	3.0807108	4.0018544	–2.3715633
H	3.6316101	4.2159020	–0.6984467
C	1.7234016	2.2110706	–0.6892677

H	1.6613628	2.8541608	0.2017023
H	1.0480681	2.6250807	–1.4537713
H	1.3463903	1.2140378	–0.4198702
C	3.9548258	–3.4695974	–3.3740505
H	3.6649722	–3.4895708	–4.4366086
H	4.4737590	–4.4157299	–3.1541667
H	3.0366258	–3.4257695	–2.7696787
C	6.1583381	–2.3245123	–3.8702134
H	5.9560859	–2.2574781	–4.9512598
H	6.8275698	–1.4908105	–3.6067410
H	6.6991799	–3.2665721	–3.6892525
C	6.1512105	–4.1230620	2.4374264
H	7.0040658	–3.4342636	2.5381905
H	6.0236970	–4.6404789	3.4014461
H	6.4134258	–4.8845678	1.6866057
C	3.6979990	–4.3366610	1.8407399
H	3.9209616	–5.0780143	1.0576389
H	3.4817536	–4.8855775	2.7713580
H	2.7899962	–3.7864001	1.5536433

[Ni(IDipp-CS_2)$_2$] (3b), singlet diradical unrestricted

Energy = –5491.962398072

Ni	–0.1517920	–1.3240089	0.1845192
S	–1.7647987	–1.1251125	–1.3152978
S	–1.8246510	–0.6725482	1.4844473
C	–2.6529693	–0.3907619	–0.0161256
S	1.5356824	–1.1951188	1.6253638
S	1.5674083	–1.5323891	–1.1949666
C	2.5260405	–1.1529307	0.1977646
C	3.8663909	–0.7448985	0.1631408
N	4.7334351	–0.6276068	1.2272650
N	4.5958148	–0.3699397	–0.9459045
C	5.9693224	–0.2018081	0.7771442
C	4.4565324	–0.9429930	2.5918454
C	5.8839294	–0.0386998	–0.5646535
C	4.0471698	–0.0492721	–2.2259814
H	6.7988531	–0.0664862	1.4642271
C	4.1015038	0.1028257	3.4599668
C	4.5596097	–2.2795237	3.0080620
H	6.6157821	0.2957467	–1.2933544
C	4.2014461	–0.9644546	–3.2774047
C	3.3635784	1.1708946	–2.3670615
C	3.8708748	–0.2220075	4.7977651
C	3.9388129	1.5279046	2.9715133
C	4.3081054	–2.5538216	4.3546383
C	4.8849710	–3.3995717	2.0415468
C	3.6376841	–0.6293770	–4.5105189
C	4.9145889	–2.2869860	–3.0858581
C	2.8042079	1.4512836	–3.6149737
C	3.2007389	2.1429235	–1.2155827
C	3.9727274	–1.5366268	5.2412170
H	3.5882769	0.5653846	5.5004946
H	4.0553484	1.5151357	1.8772791
H	4.3682668	–3.5844910	4.7121758
H	5.0783262	–2.9458046	1.0575931
C	2.9378012	0.5608104	–4.6753771
H	3.7299382	–1.3232126	–5.3494454
H	5.1991647	–2.3542804	–2.0245004
H	2.2461903	2.3797557	–3.7566675
H	3.7873921	1.7589756	–0.3675120
C	–3.7807226	0.4232612	–0.1820032
N	–4.4412425	1.1535982	0.7838961
N	–4.4417892	0.7036240	–1.3608784
C	–5.4750592	1.8665841	0.2072735
C	–4.1604945	1.1826247	2.1834974
C	–5.4763245	1.5874444	–1.1178550
C	–4.2282581	0.0926859	–2.6346068
H	–6.1141831	2.5079238	0.8060218
C	–4.8193751	0.2632832	3.0147221
C	–3.2505324	2.1360732	2.6673604
H	–6.1233954	1.9256378	–1.9210330
C	–3.3694583	0.7220994	–3.5504121
C	–4.9033491	–1.1048339	–2.9185508
C	–4.5487268	0.3262734	4.3838579
C	–5.7448561	–0.7994829	2.4580841
C	–3.0199552	2.1633147	4.0435663
C	–2.5200627	3.0852343	1.7400645
C	–3.2218358	0.1287701	–4.8046320
C	–2.6163589	1.9860404	–3.1898674
C	–4.7113420	–1.6666003	–4.1836302
C	–5.7569074	–1.8083337	–1.8829354
C	–3.6613577	1.2677311	4.8933514
H	–5.0335346	–0.3815938	5.0603182
H	–5.8609888	–0.6075886	1.3803579
H	–2.3121996	2.8866942	4.4549779
H	–2.7580055	2.7866865	0.7076326
C	–3.8858646	–1.0531510	–5.1187851
H	–2.5598162	0.5881131	–5.5417676
H	–2.6913131	2.1086750	–2.0981293
H	–5.2105427	–2.6050522	–4.4359347
H	–5.8524271	–1.1360749	–1.0164959
H	–3.4596408	1.2983522	5.9668210
H	–3.7479616	–1.5081896	–6.1025951
H	2.4869901	0.7968804	–5.6423434
H	3.7779376	–1.7727851	6.2901203
C	–3.0104029	4.5207773	1.9286785
H	–4.0957302	4.6020290	1.7621914
H	–2.8024398	4.8814641	2.9488199
H	–2.5055063	5.1997496	1.2237354
C	–1.0045565	2.9728225	1.8970887
H	–0.4977487	3.6086427	1.1547758
H	–0.6725555	3.3004525	2.8951749
H	–0.6759572	1.9333687	1.7481642
C	–1.1290935	1.8859225	–3.5220252
H	–0.9539046	1.7967927	–4.6059216
H	–0.6075471	2.7940300	–3.1813336
H	–0.6748257	1.0181010	–3.0211844
C	–3.2638712	3.2081145	–3.8424418
H	–3.2259108	3.1354708	–4.9412842
H	–4.3211282	3.3094155	–3.5527529
H	–2.7411883	4.1314262	–3.5468197
C	–5.1234254	–2.1894024	2.6037469
H	–5.0140340	–2.4655739	3.6647649
H	–5.7596556	–2.9486911	2.1223166
H	–4.1245388	–2.2227254	2.1436975
C	–7.1368178	–0.7280043	3.0826561
H	–7.1072336	–0.9394737	4.1632247
H	–7.5883187	0.2670760	2.9493887
H	–7.8046959	–1.4713418	2.6202148

C	–7.1690138	–2.0869192	–2.3931194
H	–7.6685058	–1.1631657	–2.7232542
H	–7.1633041	–2.7868062	–3.2435582
H	–7.7809927	–2.5415928	–1.5987150
C	–5.0646165	–3.0816714	–1.3931089
H	–5.6381863	–3.5425787	–0.5737249
H	–4.9807128	–3.8219202	–2.2049413
H	–4.0483851	–2.8641169	–1.0324256
C	2.5374979	2.0642509	3.2608752
H	2.3508961	2.1517914	4.3430895
H	2.4135998	3.0667040	2.8215238
H	1.7755646	1.3974267	2.8309405
C	5.0284084	2.4364664	3.5396708
H	4.9663017	2.4945569	4.6381657
H	6.0346476	2.0704410	3.2833050
H	4.9271034	3.4592998	3.1440770
C	3.7688079	3.5191942	–1.5596204
H	4.8245823	3.4559943	–1.8646068
H	3.2102434	3.9930670	–2.3821998
H	3.7031516	4.1891883	–0.6881119
C	1.7465046	2.2327273	–0.7525148
H	1.6708113	2.8702818	0.1414080
H	1.1076925	2.6697342	–1.5356349
H	1.3373022	1.2427701	–0.5046714
C	3.9902556	–3.4683675	–3.3777707
H	3.6821028	–3.4887528	–4.4351823
H	4.5034322	–4.4188208	–3.1628338
H	3.0827864	–3.4117106	–2.7583312
C	6.1981176	–2.3484672	–3.9134280
H	5.9815160	–2.2893595	–4.9921029
H	6.8784144	–1.5185317	–3.6667871
H	6.7330661	–3.2937873	–3.7321609
C	6.1516836	–4.1486894	2.4523281
H	7.0134386	–3.4687417	2.5363645
H	6.0262810	–4.6510317	3.4245637
H	6.3984500	–4.9235733	1.7100081
C	3.6910921	–4.3414688	1.8782642
H	3.8973940	–5.0932322	1.1005728
H	3.4785682	–4.8784286	2.8166764
H	2.7863382	–3.7832311	1.5960442

[Ni(IDipp-CS_2)$_2$] (3b), triplet

Energy = –5491.956615043

Ni	–0.0283110	–0.2092451	–0.0033784
S	–1.7340348	0.0590672	–1.4258946
S	–1.7337430	0.0596548	1.4193067
C	–2.7068607	0.2762779	–0.0032441
S	1.6836227	–0.4271692	1.4201319
S	1.6866523	–0.4152956	–1.4249839
C	2.6772497	–0.5184241	–0.0017477
C	4.0728514	–0.6530340	–0.0009759
N	4.9064961	–0.7579626	1.0946651
N	4.9106362	–0.7193987	–1.0964323
C	6.2159339	–0.8909509	0.6762705
C	4.5396633	–0.6739772	2.4721466
C	6.2184764	–0.8675055	–0.6780213
C	4.5512238	–0.5650128	–2.4697976
H	7.0249763	–0.9870610	1.3936100
C	4.5038165	0.5930994	3.0764710
C	4.2546389	–1.8606097	3.1649098
H	7.0301501	–0.9391267	–1.3952384
C	4.2885603	–1.7155170	–3.2289993
C	4.5004909	0.7329172	–3.0036126
C	4.1749897	0.6484499	4.4322133
C	4.7679162	1.8626575	2.2927597
C	3.9336344	–1.7520962	4.5197012
C	4.2520975	–3.2088314	2.4744422
C	3.9744356	–1.5371436	–4.5779134
C	4.3007654	–3.0993436	–2.6131927
C	4.1790457	0.8581727	–4.3565344
C	4.7434709	1.9612831	–2.1502978
C	3.8946535	–0.5114059	5.1471724
H	4.1250974	1.6181903	4.9331389
H	4.9869186	1.5721448	1.2540489
H	3.6956286	–2.6538985	5.0888463
H	4.4860963	–3.0370880	1.4125187
C	3.9195646	–0.2643253	–5.1360193
H	3.7538382	–2.4095694	–5.1975656
H	4.5192434	–2.9814621	–1.5406283
H	4.1208838	1.8530689	–4.8044389
H	4.9712894	1.6177098	–1.1299011
C	–4.0710166	0.6003276	–0.0032144
N	–4.8816999	0.8230992	1.0919316
N	–4.8898303	0.7877176	–1.0990015
C	–6.1583043	1.1426018	0.6731678
C	–4.5292586	0.6931208	2.4694247
C	–6.1633600	1.1209916	–0.6811461
C	–4.5536634	0.5905762	–2.4727061
H	–6.9457140	1.3529053	1.3901699
C	–4.6844922	–0.5612355	3.0806857
C	–4.0644839	1.8265102	3.1543261
H	–6.9563176	1.3079057	–1.3985975
C	–4.1206848	1.6942318	–3.2236534
C	–4.6959064	–0.6967336	–3.0150172
C	–4.3601333	–0.6595576	4.4353135
C	–5.1373014	–1.7802514	2.3029440
C	–3.7580706	1.6774397	4.5083876
C	–3.8613923	3.1552448	2.4558159
C	–3.8353793	1.4802420	–4.5736206
C	–3.9297829	3.0607970	–2.5986182
C	–4.3920754	–0.8600034	–4.3681495
C	–5.1159080	–1.8812943	–2.1685265
C	–3.9032019	0.4477539	5.1423121
H	–4.4562622	–1.6229037	4.9417796
H	–5.3477543	–1.4569856	1.2721244
H	–3.3837735	2.5355502	5.0717133
H	–4.0992691	3.0085624	1.3910564
C	–3.9683775	0.2167580	–5.1400002
H	–3.4886250	2.3146221	–5.1879243
H	–4.1455501	2.9646772	–1.5233408
H	–4.4776206	–1.8502745	–4.8217589
H	–5.3146787	–1.5096938	–1.1518204
H	–3.6490993	0.3492202	6.2004499
H	–3.7314005	0.0675840	–6.1961536
H	3.6631580	–0.1449082	–6.1914189
H	3.6349771	–0.4468448	6.2065530
C	–4.8169096	4.2180710	2.9970279
H	–5.8676614	3.9050549	2.8963256
H	–4.6300553	4.4177127	4.0642737
H	–4.6897996	5.1670949	2.4532148
C	–2.4022451	3.6045918	2.5308183

H	–2.2531467	4.5215317	1.9395468
H	–2.1016056	3.8244822	3.5676950
H	–1.7368444	2.8203982	2.1397219
C	–2.4805929	3.5307194	–2.7236263
H	–2.2016579	3.7004647	–3.7758581
H	–2.3380135	4.4801631	–2.1842774
H	–1.7947695	2.7797913	–2.3035901
C	–4.9142494	4.0777168	–3.1748974
H	–4.7521481	4.2239946	–4.2547501
H	–5.9571862	3.7531663	–3.0363248
H	–4.7932589	5.0560525	–2.6842072
C	–4.0261784	–2.8277637	2.2252403
H	–3.7975041	–3.2414916	3.2204531
H	–4.3311785	–3.6640473	1.5766178
H	–3.1029051	–2.3857724	1.8216604
C	–6.4328935	–2.3598882	2.8683250
H	–6.2955147	–2.7239700	3.8988320
H	–7.2374913	–1.6086515	2.8846030
H	–6.7728695	–3.2116800	2.2588804
C	–6.4113098	–2.5081630	–2.6816372
H	–7.2278455	–1.7708199	–2.7218799
H	–6.2850696	–2.9217419	–3.6947594
H	–6.7277252	–3.3330493	–2.0243521
C	–3.9871662	–2.9066756	–2.0572857
H	–4.2669811	–3.7119433	–1.3599388
H	–3.7702159	–3.3690050	–3.0335317
H	–3.0638877	–2.4304040	–1.6948903
C	3.5286907	2.7574499	2.2545051
H	3.2794906	3.1392353	3.2575218
H	3.7031603	3.6259347	1.6000731
H	2.6587260	2.1994477	1.8769318
C	5.9936530	2.6040576	2.8241662
H	5.8415750	2.9398719	3.8622067
H	6.8898149	1.9647466	2.8085644
H	6.2001764	3.4966520	2.2132630
C	5.9537858	2.7538589	–2.6416730
H	6.8612925	2.1310015	–2.6648479
H	5.7922610	3.1457034	–3.6584578
H	6.1462592	3.6138844	–1.9814675
C	3.4877690	2.8290238	–2.0600449
H	3.6471188	3.6622016	–1.3576292
H	3.2296516	3.2617781	–3.0398280
H	2.6288842	2.2345254	–1.7141905
C	2.9282207	–3.7635897	–2.7205659
H	2.6586047	–3.9619582	–3.7701806
H	2.9255647	–4.7273736	–2.1878002
H	2.1522951	–3.1168807	–2.2841648
C	5.4061338	–3.9668945	–3.2138169
H	5.2464265	–4.1297128	–4.2916032
H	6.3962921	–3.5013455	–3.0910481
H	5.4307353	–4.9547691	–2.7280266
C	5.3352569	–4.1265334	3.0398478
H	6.3344494	–3.6720970	2.9541241
H	5.1594984	–4.3453230	4.1051839
H	5.3494428	–5.0868168	2.5011773
C	2.8674036	–3.8540856	2.5303708
H	2.8544344	–4.7868490	1.9451611
H	2.5830585	–4.1049170	3.5648012
H	2.1069485	–3.1709582	2.1231941

[Ni(IDipp-CS_2)$_2$] (3b), quintet

Energy = –5491.951924830

Ni	–0.2868966	–1.6357405	0.5301632
S	–2.2806579	–1.8674350	–0.6478468
S	–1.4917949	0.2601932	1.2204732
C	–2.6657479	–0.3422212	0.0924548
S	1.6630488	–1.7575724	1.7983972
S	1.3587776	–1.1184507	–1.0448587
C	2.4156428	–1.1983529	0.3273000
C	3.7653925	–0.8047829	0.2638693
N	4.7365586	–0.9398165	1.2373203
N	4.4082826	–0.1968657	–0.7995996
C	5.9377155	–0.4406876	0.7744228
C	4.5942964	–1.4630320	2.5595298
C	5.7346949	0.0207432	–0.4821359
C	3.8086021	0.3720255	–1.9666226
H	6.8288110	–0.4667252	1.3937811
C	4.2943314	–0.5683900	3.5998148
C	4.8035603	–2.8343191	2.7671931
H	6.4072320	0.4986745	–1.1875032
C	3.8771846	–0.3373589	–3.1747728
C	3.2069007	1.6365178	–1.8558876
C	4.2127028	–1.0901971	4.8918808
C	4.0323029	0.9016196	3.3423454
C	4.7085352	–3.3077809	4.0778166
C	5.0761229	–3.7847487	1.6199576
C	3.3146136	0.2595577	–4.3049267
C	4.4961305	–1.7172588	–3.2555668
C	2.6510734	2.1863350	–3.0124234
C	3.1211809	2.3753672	–0.5362135
C	4.4174667	–2.4456266	5.1294209
H	3.9716005	–0.4253961	5.7247715
H	4.0908806	1.0620972	2.2554750
H	4.8547020	–4.3723352	4.2758010
H	5.0952840	–3.1898015	0.6940556
C	2.7032966	1.5063396	–4.2247490
H	3.3413648	–0.2693210	–5.2606214
H	4.7859587	–2.0064582	–2.2336054
H	2.1608291	3.1613861	–2.9599663
H	3.6250271	1.7612961	0.2246695
C	–3.8348300	0.3720643	–0.2342565
N	–4.4533932	1.3519204	0.5121937
N	–4.6035084	0.2413436	–1.3713086
C	–5.5781757	1.8039040	–0.1518757
C	–4.1304977	1.7459799	1.8462360
C	–5.6676765	1.1218868	–1.3182566
C	–4.2470255	–0.4717388	–2.5573780
H	–6.2173284	2.5656492	0.2836410
C	–4.4890251	0.8972898	2.9062025
C	–3.4943151	2.9823170	2.0405368
H	–6.3824866	1.1866739	–2.1326453
C	–3.2550823	0.0700110	–3.3918500
C	–4.9170073	–1.6706593	–2.8454374
C	–4.1871391	1.3257758	4.2008874
C	–5.1511172	–0.4468398	2.6801797
C	–3.2256090	3.3699418	3.3545971
C	–3.0681138	3.8553973	0.8778094
C	–2.9298924	–0.6459349	–4.5461832

C	–2.5338486	1.3633636	–3.0678959
C	–4.5676933	–2.3377472	–4.0210010
C	–5.9567024	–2.2511334	–1.9084051
C	–3.5657096	2.5494256	4.4248083
H	–4.4410226	0.6855685	5.0490494
H	–5.3098374	–0.5676015	1.5981295
H	–2.7252689	4.3231687	3.5413289
H	–3.3235319	3.3193386	–0.0488679
C	–3.5789506	–1.8349174	–4.8599896
H	–2.1497454	–0.2646659	–5.2092368
H	–2.9813567	1.7802858	–2.1527861
H	–5.0644890	–3.2777028	–4.2731412
H	–5.9974881	–1.6023264	–1.0199382
H	–3.3380103	2.8646708	5.4459301
H	–3.3076425	–2.3790783	–5.7678444
H	2.2582174	1.9524839	–5.1174817
H	4.3428562	–2.8361234	6.1472445
C	–3.8241216	5.1831216	0.8671286
H	–4.9137116	5.0290894	0.8286599
H	–3.6055778	5.7754795	1.7699729
H	–3.5345582	5.7881194	–0.0062820
C	–1.5539165	4.0572365	0.8682480
H	–1.2465076	4.6213193	–0.0265772
H	–1.2143248	4.6225252	1.7508503
H	–1.0411156	3.0846781	0.8624914
C	–1.0543219	1.1191390	–2.7741020
H	–0.5235046	0.7327577	–3.6586369
H	–0.5606641	2.0560599	–2.4740305
H	–0.9184453	0.3933048	–1.9611485
C	–2.7288446	2.4011678	–4.1730137
H	–2.2748157	2.0717131	–5.1209868
H	–3.7957100	2.5957447	–4.3627579
H	–2.2515352	3.3530644	–3.8920796
C	–4.2409008	–1.5902566	3.1300715
H	–4.0962205	–1.5769678	4.2223521
H	–4.6820881	–2.5620493	2.8599468
H	–3.2525926	–1.5111642	2.6546080
C	–6.5240171	–0.5135293	3.3480469
H	–6.4450879	–0.4223080	4.4429161
H	–7.1844764	0.2920774	2.9922208
H	–7.0111407	–1.4767930	3.1304748
C	–7.3445150	–2.2468832	–2.5488077
H	–7.6457376	–1.2334885	–2.8565040
H	–7.3722517	–2.8861658	–3.4457063
H	–8.1000764	–2.6277604	–1.8439446
C	–5.5572272	–3.6438773	–1.4232232
H	–6.2899133	–4.0191419	–0.6914260
H	–5.5172879	–4.3665056	–2.2536545
H	–4.5672867	–3.6128135	–0.9445489
C	2.6223873	1.3034797	3.7743330
H	2.4927003	1.2121790	4.8645425
H	2.4235266	2.3520682	3.5023513
H	1.8722293	0.6657090	3.2835585
C	5.1026716	1.7790663	3.9899467
H	5.0962828	1.6752480	5.0867617
H	6.1108678	1.5130025	3.6364853
H	4.9277754	2.8406083	3.7544279
C	3.8601737	3.7115191	–0.5942820
H	4.9142283	3.5778508	–0.8826045
H	3.3981363	4.3960274	–1.3234334
H	3.8345166	4.2078711	0.3884813
C	1.6710553	2.5450933	–0.0859169
H	1.6305209	2.9963889	0.9175918
H	1.1168912	3.2079776	–0.7694928
H	1.1438314	1.5803167	–0.0521283
C	3.4842756	–2.7533017	–3.7435061
H	3.1694785	–2.5541450	–4.7802764
H	3.9259254	–3.7618554	–3.7185268
H	2.5889233	–2.7456741	–3.1042070
C	5.7627142	–1.7079831	–4.1108107
H	5.5395477	–1.4253094	–5.1520909
H	6.5056805	–0.9925154	–3.7254914
H	6.2278824	–2.7060033	–4.1284094
C	6.4408937	–4.4573804	1.7594835
H	7.2517064	–3.7152363	1.8219118
H	6.4906436	–5.0822452	2.6654121
H	6.6409393	–5.1097884	0.8952437
C	3.9462075	–4.8045436	1.4759840
H	4.1001660	–5.4266665	0.5804414
H	3.9020846	–5.4773795	2.3474514
H	2.9750726	–4.2945417	1.3898022

[Ni(IMes-CS_2)$_2$] (3c), singlet restricted

Energy = –5021.068792375

Ni	–0.0000443	–0.0011644	–0.0000283
S	–1.6578221	0.2431925	–1.4088914
S	–1.6577687	0.2432152	1.4088548
C	–2.6613254	0.3906272	0.0000003
S	1.6577407	–0.2452247	1.4088182
S	1.6577499	–0.2452663	–1.4088985
C	2.6613674	–0.3920456	–0.0000340
C	4.0425017	–0.5983654	–0.0000552
N	4.8725829	–0.7244516	1.0961874
N	4.8724964	–0.7244916	–1.0963504
C	6.1760645	–0.9253296	0.6765759
C	4.4961736	–0.6457820	2.4687728
C	6.1760066	–0.9253886	–0.6768416
C	4.4959840	–0.6458440	–2.4689089
H	6.9821067	–1.0476267	1.3936497
C	4.4886178	0.6069310	3.0946527
C	4.1471154	–1.8230440	3.1414092
H	6.9819723	–1.0478176	–1.3939775
C	4.1467551	–1.8231003	–3.1414676
C	4.4883965	0.6068572	–3.0948127
C	4.1357761	0.6567543	4.4428478
C	4.7703300	1.8489585	2.3063346
C	3.8020043	–1.7227633	4.4889571
C	4.0695595	–3.1231305	2.4015804
C	3.8013907	–1.7228205	–4.4889517
C	4.0692110	–3.1231622	–2.4015934
C	4.1353201	0.6566767	–4.4429473
C	4.7702220	1.8488916	–2.3065446
C	3.7882156	–0.4943392	5.1551083
H	4.1167438	1.6271112	4.9471211
H	4.8450889	2.7272080	2.9612127
H	5.7002706	1.7681553	1.7229158
H	3.9489262	2.0227487	1.5906495
H	3.5189993	–2.6304628	5.0295836
H	3.8887236	–3.9609745	3.0880092
H	3.2365687	–3.0844615	1.6794648
H	4.9871709	–3.3318479	1.8305988

C	3.7874699	–0.4943961	–5.1551013
H	3.5183132	–2.6305260	–5.0295321
H	3.2363267	–3.0844087	–1.6793582
H	3.8882147	–3.9610121	–3.0879731
H	4.9868883	–3.3319307	–1.8307374
H	4.1163698	1.6270130	–4.9472655
H	3.9489178	2.0226864	–1.5907455
H	5.7002435	1.7680907	–1.7232552
H	4.8448915	2.7271357	–2.9614404
C	3.3631998	–0.4064128	6.5919228
C	3.3619640	–0.4064381	–6.5917689
H	3.5871078	–1.3341073	7.1380574
H	3.8583324	0.4274620	7.1102915
H	2.2756893	–0.2375308	6.6636806
H	2.2744390	–0.2374881	–6.6631527
H	3.8569708	0.4274079	–7.1103057
H	3.5856261	–1.3341457	–7.1379838
C	–4.0421582	0.5990261	–0.0000055
N	–4.8720267	0.7264791	1.0962526
N	–4.8719707	0.7264577	–1.0963006
C	–6.1751913	0.9294738	0.6766455
C	–4.4958087	0.6466661	2.4688256
C	–6.1751629	0.9294258	–0.6767728
C	–4.4956588	0.6466965	–2.4688505
H	–6.9810169	1.0531876	1.3937291
C	–4.4902535	–0.6063406	3.0941486
C	–4.1450543	1.8230959	3.1420471
H	–6.9809628	1.0530281	–1.3939031
C	–4.1448078	1.8231458	–3.1419882
C	–4.4899319	–0.6063040	–3.0941848
C	–4.1380090	–0.6572686	4.4424611
C	–4.7733891	–1.8476161	2.3051455
C	–3.8005744	1.7217124	4.4896744
C	–4.0649413	3.1233050	2.4027044
C	–3.7998554	1.7217612	–4.4894954
C	–4.0651022	3.1233890	–2.4026601
C	–4.1372431	–0.6572286	–4.4423819
C	–4.7733346	–1.8475824	–2.3052810
C	–3.7889997	0.4930015	5.1553436
H	–4.1206403	–1.6278681	4.9463309
H	–4.8496856	–2.7260588	2.9595899
H	–5.7029604	–1.7652181	1.7213562
H	–3.9519328	–2.0222562	1.5897204
H	–3.5162781	2.6287383	5.0307574
H	–3.8828339	3.9605841	3.0894922
H	–3.2317670	3.0833780	1.6808579
H	–4.9819964	3.3338626	1.8314921
C	–3.7879758	0.4930400	–5.1551421
H	–3.5153996	2.6287926	–5.0304873
H	–3.2321643	3.0835833	–1.6805331
H	–3.8828680	3.9606696	–3.0894129
H	–4.9823733	3.3338516	–1.8317605
H	–4.1197198	–1.6278267	–4.9462512
H	–3.9521115	–2.0222309	–1.5895894
H	–5.7030947	–1.7651791	–1.7217939
H	–4.8494259	–2.7260208	–2.9597552
C	–3.3649637	0.4038601	6.5923719
C	–3.3633608	0.4038893	–6.5919987
H	–3.5876083	1.3317468	7.1386976
H	–3.8618174	–0.4293491	7.1101661
H	–2.2777841	0.2330992	6.6646986
H	–2.2761469	0.2331590	–6.6638862
H	–3.8599828	–0.4293425	–7.1099806
H	–3.5858125	1.3317625	–7.1384278

[Ni(IMes-CS_2)$_2$] (3c), singlet diradical unrestricted

Energy = –5021.079280352

Ni	0.0000500	–0.0000127	0.0000033
S	–1.6964201	0.2527463	–1.4204811
S	–1.6964164	0.2527482	1.4204658
C	–2.6834161	0.3962059	0.0000040
S	1.6964537	–0.2527489	1.4203464
S	1.6964541	–0.2527513	–1.4203531
C	2.6835232	–0.3962263	–0.0000081
C	4.0679738	–0.6004848	0.0000608
N	4.8974190	–0.7250452	1.0970564
N	4.8973885	–0.7250417	–1.0971973
C	6.1998193	–0.9239802	0.6769008
C	4.5341886	–0.6500286	2.4748245
C	6.1998457	–0.9239835	–0.6768572
C	4.5342199	–0.6500017	–2.4747240
H	7.0061943	–1.0454526	1.3937387
C	4.5423915	0.5998124	3.1060682
C	4.2031534	–1.8307175	3.1501709
H	7.0061968	–1.0454513	–1.3937437
C	4.2031436	–1.8307952	–3.1501520
C	4.5423881	0.5998505	–3.1060975
C	4.2285258	0.6423716	4.4640977
C	4.7959166	1.8467694	2.3161114
C	3.8970583	–1.7373378	4.5076263
C	4.0983364	–3.1268469	2.4069086
C	3.8970528	–1.7372949	–4.5076869
C	4.0983396	–3.1268125	–2.4069088
C	4.2285167	0.6423047	–4.4641068
C	4.7959179	1.8467508	–2.3160943
C	3.9043600	–0.5127517	5.1809324
H	4.2239955	1.6099709	4.9739081
H	4.9175013	2.7174981	2.9740491
H	5.6902524	1.7616394	1.6802478
H	3.9367221	2.0356458	1.6501837
H	3.6305869	–2.6482131	5.0512668
H	3.9753274	–3.9722517	3.0968907
H	3.2182371	–3.0939034	1.7423347
H	4.9785296	–3.3176388	1.7743997
C	3.9043726	–0.5127404	–5.1808807
H	3.6305894	–2.6482113	–5.0512656
H	3.2182342	–3.0939075	–1.7423331
H	3.9753261	–3.9722682	–3.0968996
H	4.9785354	–3.3176444	–1.7743976
H	4.2239949	1.6099928	–4.9739209
H	3.9367232	2.0356451	–1.6501835
H	5.6902527	1.7616380	–1.6802509
H	4.9175029	2.7175077	–2.9740539
C	3.5273687	–0.4326207	6.6315383
C	3.5273622	–0.4326293	–6.6315602
H	3.7734079	–1.3614947	7.1661075
H	4.0366742	0.4011319	7.1362209
H	2.4423200	–0.2684044	6.7409572
H	2.4423237	–0.2684089	–6.7409565
H	4.0366677	0.4011236	–7.1362251

H	3.7734036	–1.3614923	–7.1660964
C	–4.0679293	0.6004773	–0.0000163
N	–4.8974018	0.7250305	1.0971117
N	–4.8974510	0.7250353	–1.0970642
C	–6.1999489	0.9239912	0.6768914
C	–4.5341436	0.6500030	2.4746932
C	–6.1998554	0.9239760	–0.6768708
C	–4.5341324	0.6500326	–2.4747088
H	–7.0062857	1.0454644	1.3937434
C	–4.5423186	–0.5998048	3.1060345
C	–4.2030854	1.8307086	3.1501148
H	–7.0063262	1.0454704	–1.3937786
C	–4.2030857	1.8306988	–3.1501392
C	–4.5423300	–0.5998394	–3.1060179
C	–4.2285109	–0.6423353	4.4640727
C	–4.7959091	–1.8467205	2.3161162
C	–3.8970515	1.7373080	4.5076176
C	–4.0983413	3.1267931	2.4069332
C	–3.8970568	1.7372939	–4.5075862
C	–4.0983445	3.1267882	–2.4069233
C	–4.2285033	–0.6423327	–4.4640906
C	–4.7959062	–1.8467001	–2.3161261
C	–3.9043979	0.5127575	5.1808919
H	–4.2240603	–1.6099766	4.9738558
H	–4.9175029	–2.7174300	2.9740431
H	–5.6902195	–1.7616110	1.6802622
H	–3.9367572	–2.0356704	1.6501616
H	–3.6306427	2.6482390	5.0512008
H	–3.9753470	3.9721909	3.0969020
H	–3.2182591	3.0939390	1.7423329
H	–4.9785107	3.3176118	1.7744229
C	–3.9044023	0.5127665	–5.1808912
H	–3.6306419	2.6482529	–5.0512067
H	–3.2182605	3.0939370	–1.7423327
H	–3.9753461	3.9721969	–3.0969010
H	–4.9785105	3.3176095	–1.7744237
H	–4.2240629	–1.6099655	–4.9738479
H	–3.9367606	–2.0356746	–1.6501647
H	–5.6902259	–1.7616151	–1.6802646
H	–4.9175064	–2.7174410	–2.9740488
C	–3.5273858	0.4326264	6.6315310
C	–3.5273801	0.4326228	–6.6315284
H	–3.7733729	1.3614573	7.1661603
H	–4.0366393	–0.4010947	7.1362849
H	–2.4423399	0.2684043	6.7408707
H	–2.4423324	0.2684056	–6.7408657
H	–4.0366360	–0.4010949	–7.1362722
H	–3.7733684	1.3614593	–7.1661653

[Ni(IMes-CS_2)$_2$] (3c), triplet

Energy = –5021.076552276

Ni	0.0000027	–0.0000007	0.0000000
S	–1.7101989	0.2622463	–1.4270787
S	–1.7101988	0.2622466	1.4270791
C	–2.6871993	0.4027186	–0.0000008
S	1.7101978	–0.2622455	1.4270571
S	1.7101978	–0.2622458	–1.4270573
C	2.6872351	–0.4027242	0.0000003
C	4.0728369	–0.6038102	–0.0000003
N	4.9024955	–0.7281377	1.0978781
N	4.9024925	–0.7281367	–1.0978820
C	6.2042375	–0.9259972	0.6768585
C	4.5495526	–0.6537833	2.4789009
C	6.2042380	–0.9259974	–0.6768571
C	4.5495572	–0.6537666	–2.4788906
H	7.0111138	–1.0465674	1.3931196
C	4.5676572	0.5947850	3.1122899
C	4.2337598	–1.8363421	3.1582391
H	7.0111137	–1.0465681	–1.3931196
C	4.2337529	–1.8363593	–3.1582554
C	4.5676554	0.5947734	–3.1122959
C	4.2848385	0.6335404	4.4773402
C	4.8027761	1.8431291	2.3190340
C	3.9584537	–1.7468377	4.5226093
C	4.1188128	–3.1300001	2.4122815
C	3.9584593	–1.7468243	–4.5225907
C	4.1188147	–3.1299942	–2.4122822
C	4.2848409	0.6335579	–4.4773403
C	4.8027767	1.8431338	–2.3190292
C	3.9821075	–0.5242327	5.1993282
H	4.2907749	1.6001811	4.9891751
H	4.9031121	2.7184005	2.9743829
H	5.7034384	1.7730764	1.6899219
H	3.9445936	2.0130553	1.6469202
H	3.7063811	–2.6594827	5.0702667
H	3.9631288	–3.9729821	3.0985383
H	3.2550912	–3.0793304	1.7280061
H	5.0098595	–3.3387258	1.8005036
C	3.9821053	–0.5242424	–5.1993321
H	3.7063785	–2.6594910	–5.0702711
H	3.2550893	–3.0793311	–1.7280047
H	3.9631284	–3.9729825	–3.0985405
H	5.0098592	–3.3387277	–1.8005024
H	4.2907747	1.6001727	–4.9891718
H	3.9445957	2.0130541	–1.6469215
H	5.7034379	1.7730752	–1.6899236
H	4.9031122	2.7184005	–2.9743819
C	3.6466020	–0.4501601	6.6605664
C	3.6466022	–0.4501586	–6.6605675
H	3.9076198	–1.3818817	7.1830102
H	4.1716870	0.3804371	7.1542471
H	2.5654425	–0.2855840	6.8030716
H	2.5654424	–0.2855830	–6.8030717
H	4.1716861	0.3804372	–7.1542490
H	3.9076207	–1.3818816	–7.1830086
C	–4.0728342	0.6038107	0.0000015
N	–4.9025222	0.7281403	1.0978481
N	–4.9025269	0.7281410	–1.0978409
C	–6.2042109	0.9259933	0.6768867
C	–4.5495533	0.6537838	2.4788817
C	–6.2042135	0.9259937	–0.6768895
C	–4.5495473	0.6537757	–2.4789114
H	–7.0111288	1.0465715	1.3931317
C	–4.5676556	–0.5948007	3.1123082
C	–4.2337467	1.8363522	3.1582791
H	–7.0111277	1.0465716	–1.3931313
C	–4.2337563	1.8363502	–3.1582340
C	–4.5676639	–0.5947831	–3.1122604
C	–4.2848403	–0.6335491	4.4773411
C	–4.8027759	–1.8431187	2.3190205
C	–3.9584590	1.7468562	4.5225758

C	–4.1188158	3.1299985	2.4122716
C	–3.9584516	1.7468436	–4.5226176
C	–4.1188142	3.1299970	–2.4122802
C	–4.2848308	–0.6335531	–4.4773883
C	–4.8027743	–1.8431221	–2.3190272
C	–3.9821068	0.5242190	5.1993431
H	–4.2907753	–1.6001759	4.9891730
H	–4.9031148	–2.7184105	2.9743898
H	–5.7034418	–1.7730745	1.6899227
H	–3.9445950	–2.0130544	1.6469207
H	–3.7063788	2.6594829	5.0702690
H	–3.9631269	3.9729866	3.0985440
H	–3.2550890	3.0793295	1.7280052
H	–5.0098599	3.3387270	1.8005029
C	–3.9821114	0.5242248	–5.1993196
H	–3.7063797	2.6594824	–5.0702665
H	–3.2550875	3.0793294	–1.7280042
H	–3.9631271	3.9729863	–3.0985428
H	–5.0098618	3.3387269	–1.8005018
H	–4.2907759	–1.6001693	–4.9891680
H	–3.9445948	–2.0130537	–1.6469205
H	–5.7034434	–1.7730729	–1.6899225
H	–4.9031147	–2.7184099	–2.9743874
C	–3.6466049	0.4501633	6.6605652
C	–3.6466041	0.4501624	–6.6605678
H	–3.9076218	1.3818820	7.1830107
H	–4.1716904	–0.3804418	7.1542484
H	–2.5654380	0.2855814	6.8030722
H	–2.5654388	0.2855812	–6.8030721
H	–4.1716895	–0.3804415	–7.1542484
H	–3.9076218	1.3818815	–7.1830096

[Ni(IMes-CS_2)$_2$] (3c), quintet

Energy = –5021.064347435

Ni	0.0000443	0.0008743	0.0000500
S	–1.8350561	0.2720047	–1.4621181
S	–1.8350776	0.2720359	1.4621902
C	–2.7638530	0.4066622	0.0000270
S	1.8351209	–0.2706413	1.4621816
S	1.8350914	–0.2705527	–1.4621315
C	2.7638008	–0.4058258	0.0000105
C	4.1544285	–0.6135089	–0.0000230
N	4.9875217	–0.7413719	1.0970693
N	4.9874953	–0.7410400	–1.0971727
C	6.2879816	–0.9438224	0.6766059
C	4.6502777	–0.6664278	2.4827535
C	6.2879742	–0.9435628	–0.6768055
C	4.6502122	–0.6655559	–2.4828170
H	7.0938690	–1.0675878	1.3936147
C	4.6864089	0.5808926	3.1172059
C	4.3398514	–1.8480544	3.1655932
H	7.0938707	–1.0669370	–1.3938712
C	4.3398992	–1.8469252	–3.1661533
C	4.6861808	0.5820399	–3.1167347
C	4.4088618	0.6219422	4.4830587
C	4.9279424	1.8275529	2.3234281
C	4.0704285	–1.7564120	4.5307558
C	4.2160223	–3.1421165	2.4221439
C	4.0705659	–1.7547465	–4.5312971
C	4.2159581	–3.1412689	–2.4232133
C	4.4087368	0.6236252	–4.4825916
C	4.9272870	1.8284155	–2.3223781
C	4.0976806	–0.5330524	5.2058224
H	4.4229258	1.5885737	4.9946652
H	5.0433864	2.7008972	2.9790124
H	5.8225369	1.7487994	1.6867404
H	4.0666235	2.0075393	1.6579178
H	3.8168373	–2.6676406	5.0800570
H	4.0752841	–3.9853543	3.1114126
H	3.3403598	–3.0939991	1.7528241
H	5.0965725	–3.3483498	1.7945813
C	4.0977479	–0.5311061	–5.2058581
H	3.8170819	–2.6657703	–5.0809874
H	3.3402275	–3.0933865	–1.7539654
H	4.0752692	–3.9842378	–3.1128211
H	5.0964385	–3.3477662	–1.7956400
H	4.4227165	1.5904722	–4.9937929
H	4.0658385	2.0078946	–1.6568982
H	5.8218194	1.7496113	–1.6856102
H	5.0425932	2.7020762	–2.9775647
C	3.7572905	–0.4549717	6.6656100
C	3.7575517	–0.4524701	–6.6656605
H	4.0115352	–1.3868184	7.1910890
H	4.2833496	0.3744529	7.1601549
H	2.6762002	–0.2854883	6.8028628
H	2.6764611	–0.2830491	–6.8029877
H	4.2835857	0.3772140	–7.1597972
H	4.0119684	–1.3840752	–7.1914848
C	–4.1547701	0.6124117	0.0000074
N	–4.9880534	0.7388965	1.0971117
N	–4.9880593	0.7386147	–1.0971267
C	–6.2888919	0.9389617	0.6766761
C	–4.6504818	0.6653988	2.4827918
C	–6.2888968	0.9387800	–0.6767365
C	–4.6505196	0.6645631	–2.4827852
H	–7.0950031	1.0611640	1.3937008
C	–4.6842093	–0.5815761	3.1180627
C	–4.3421145	1.8480351	3.1648066
H	–7.0950167	1.0607646	–1.3937885
C	–4.3421964	1.8469228	–3.1653005
C	–4.6841881	–0.5826832	–3.1175254
C	–4.4066599	–0.6211733	4.4839578
C	–4.9228164	–1.8292696	2.3250291
C	–4.0724445	1.7578103	4.5300143
C	–4.2206169	3.1418040	2.4204554
C	–4.0724412	1.7561168	–4.5304528
C	–4.2208340	3.1410272	–2.4215120
C	–4.4065584	–0.6228609	–4.4833869
C	–4.9228458	–1.8300391	–2.3239747
C	–4.0975356	0.5348731	5.2059256
H	–4.4190977	–1.5874616	4.9962539
H	–5.0364673	–2.7024483	2.9811486
H	–5.8174485	–1.7528989	1.6881013
H	–4.0609484	–2.0077665	1.6598247
H	–3.8203161	2.6698456	5.0786507
H	–4.0813142	3.9857621	3.1091313
H	–3.3449325	3.0947928	1.7510886
H	–5.1015793	3.3460538	1.7928255
C	–4.0974278	0.5328841	–5.2058337
H	–3.8203124	2.6679238	–5.0794685
H	–3.3451889	3.0943657	–1.7520691

H	–4.0815412	3.9846908	–3.1105511
H	–5.1018507	3.3454960	–1.7940295
H	–4.4189313	–1.5893707	–4.9952666
H	–4.0610294	–2.0082467	–1.6586260
H	–5.8175279	–1.7534021	–1.6871494
H	–5.0364398	–2.7035000	–2.9797283
C	–3.7571200	0.4584273	6.6657934
C	–3.7568754	0.4558127	–6.6656365
H	–4.0131374	1.3901608	7.1906136
H	–4.2816701	–0.3716356	7.1608700
H	–2.6757261	0.2910524	6.8032392
H	–2.6754619	0.2884225	–6.8029093
H	–4.2813451	–0.3744895	–7.1603970
H	–4.0128833	1.3873050	–7.1908892

$[Ni(cAAC^{Me}\text{-}CS_2)_2]^-$ (4a)

Energy = –4844.177827447

Ni	0.0000038	0.0000169	–0.0000113
S	–2.1557194	0.2093040	0.3592968
S	–0.0177338	1.6596131	1.4515888
N	–2.3426920	3.3310264	3.0279619
C	–0.1623323	4.3658563	3.5040409
C	1.2483403	3.4433574	5.2508745
H	2.1761014	3.4707211	5.8283704
C	–1.1265696	3.3673941	3.7638431
C	–4.1912137	2.1445567	2.0760550
C	–2.6696218	2.2893537	2.1515662
C	0.3125913	2.4414616	5.4764199
H	0.5130670	1.6776859	6.2323216
C	–4.6641195	3.1274330	3.1638629
H	–5.6113952	3.6212107	2.8975134
H	–4.8371556	2.5734816	4.1004411
C	–3.5267080	4.1335668	3.3969235
C	–0.3190297	5.3617010	2.3740203
H	–1.2619738	5.1134133	1.8690174
C	–3.7056835	5.3655091	2.4973477
H	–3.6140071	5.0971596	1.4362294
H	–2.9591378	6.1385337	2.7192128
H	–4.7027287	5.8066404	2.6557862
C	–4.7125746	2.5161074	0.6818043
H	–4.4356397	3.5414616	0.4000612
H	–5.8121423	2.4340413	0.6482894
H	–4.2827636	1.8357242	–0.0681002
C	1.0056212	4.3956161	4.2700996
H	1.7560082	5.1645844	4.0672917
C	–1.7711701	1.5372821	1.4480730
C	–0.8811304	2.3867570	4.7545530
C	–1.8528821	1.2591414	5.0354490
H	–2.7708374	1.4787829	4.4749392
C	–4.6715754	0.7298603	2.4220759
H	–5.7742599	0.7079300	2.4571944
H	–4.2905722	0.4120946	3.4043235
H	–4.3248787	–0.0010282	1.6785980
C	–3.4706309	4.5879660	4.8501044
H	–2.6187030	5.2611039	5.0267958
H	–3.3695283	3.7327793	5.5324288
H	–4.3957616	5.1281043	5.1034640
C	–0.3993381	6.7971459	2.8935175
H	–0.6139807	7.5011972	2.0729787
H	0.5544245	7.1054033	3.3525447
H	–1.1814034	6.9160383	3.6597457
C	0.7919126	5.2145808	1.3341916
H	0.8166902	4.1843840	0.9484474
H	1.7811765	5.4498957	1.7599692
H	0.6188868	5.9029722	0.4907481
C	–2.2297483	1.1704527	6.5142041
H	–2.6171144	2.1278978	6.8970765
H	–1.3660194	0.8901030	7.1380495
H	–3.0050930	0.4022827	6.6666952
C	–1.3131712	–0.0771825	4.5224123
H	–1.0302187	–0.0126182	3.4622314
H	–2.0708639	–0.8695102	4.6348679
H	–0.4189997	–0.3815733	5.0911222
S	2.1556568	–0.2092996	–0.3593356
S	0.0177181	–1.6595683	–1.4515858
N	2.3427224	–3.3309956	–3.0279174
C	0.1623702	–4.3658493	–3.5040428
C	–1.2483415	–3.4433897	–5.2509062
H	–2.1761237	–3.4707422	–5.8284194
C	1.1266301	–3.3674076	–3.7638022
C	4.1912095	–2.1445103	–2.0760418
C	2.6696303	–2.2893035	–2.1515486
C	–0.3125638	–2.4414697	–5.4764474
H	–0.5130714	–1.6776884	–6.2323924
C	4.6641491	–3.1274066	–3.1638591
H	5.6113561	–3.6211951	–2.8974908
H	4.8371678	–2.5734774	–4.1004336
C	3.5267256	–4.1335567	–3.3968748
C	0.3190537	–5.3616883	–2.3740056
H	1.2619307	–5.1134029	–1.8690180
C	3.7056763	–5.3655276	–2.4973359
H	3.6139942	–5.0971328	–1.4361973
H	2.9591392	–6.1385349	–2.7191623
H	4.7027053	–5.8066453	–2.6557180
C	4.7125496	–2.5160825	–0.6818316
H	4.4356408	–3.5414218	–0.4000298
H	5.8120625	–2.4340250	–0.6482533
H	4.2827596	–1.8357056	0.0680847
C	–1.0056434	–4.3956365	–4.2701088
H	–1.7560420	–5.1646000	–4.0673146
C	1.7711657	–1.5372821	–1.4481100
C	0.8811462	–2.3867931	–4.7545631
C	1.8528762	–1.2591647	–5.0354742
H	2.7708561	–1.4787805	–4.4749517
C	4.6715821	–0.7298632	–2.4221099
H	5.7742307	–0.7079334	–2.4571840
H	4.2905736	–0.4121046	–3.4043207
H	4.3248693	0.0010403	–1.6786082
C	3.4706465	–4.5879987	–4.8500577
H	2.6187312	–5.2611220	–5.0267898
H	3.3695441	–3.7328275	–5.5324146
H	4.3957588	–5.1281219	–5.1034502
C	0.3993049	–6.7971604	–2.8935016
H	0.6139880	–7.5011836	–2.0729261
H	–0.5544146	–7.1054108	–3.3525221
H	1.1814193	–6.9160146	–3.6597214
C	–0.7919347	–5.2145865	–1.3342069
H	–0.8167414	–4.1843589	–0.9484606
H	–1.7811461	–5.4498733	–1.7599558
H	–0.6189167	–5.9029506	–0.4907309

C	2.2297759	–1.1704787	–6.5142140
H	2.6171441	–2.1279016	–6.8970676
H	1.3660366	–0.8901480	–7.1380880
H	3.0051339	–0.4023223	–6.6667192
C	1.3131984	0.0771550	–4.5224568
H	1.0302315	0.0126333	–3.4622969
H	2.0708620	0.8694977	–4.6348916
H	0.4190147	0.3815437	–5.0911475

$[Ni(IDipp\text{-}CS_2)_2]^-$ (4b)

Energy = –5492.009613934

Ni	–0.1378040	–1.2210247	0.0436568
S	–1.8322595	–0.7491988	–1.3081519
S	–1.6912320	–0.6729157	1.5263273
C	–2.6649795	–0.2097343	0.1399154
S	1.5994174	–1.3571525	1.3983226
S	1.4998195	–1.4576024	–1.4355130
C	2.5761330	–1.2584079	–0.0553733
C	3.8973604	–0.8829450	–0.1072760
N	4.7199861	–0.4749844	0.9557116
N	4.7295549	–0.8141057	–1.2336801
C	6.0008585	–0.2105004	0.4778012
C	4.3083846	–0.1248822	2.2692690
C	6.0038488	–0.4168508	–0.8551612
C	4.3488340	–1.0088925	–2.5869747
H	6.7876394	0.1258948	1.1461957
C	3.4749529	0.9937850	2.4644183
C	4.7624874	–0.9177647	3.3395993
H	6.7977375	–0.3185974	–1.5893042
C	4.3717503	–2.3081096	–3.1200703
C	3.9835081	0.1102909	–3.3557168
C	3.1151385	1.3127832	3.7754882
C	3.0142938	1.8403525	1.2945920
C	4.3887698	–0.5483364	4.6338553
C	5.5334283	–2.1960202	3.0655988
C	4.0381854	–2.4682591	–4.4669184
C	4.7092546	–3.5043925	–2.2555208
C	3.6586467	–0.0969468	–4.6977931
C	3.8682977	1.4867105	–2.7342186
C	3.5715595	0.5573419	4.8497548
H	2.4540649	2.1623111	3.9559390
H	2.9513597	1.1749207	0.4213056
H	4.7194186	–1.1464885	5.4850054
H	6.2047404	–2.0058068	2.2126931
C	3.6883850	–1.3735256	–5.2503263
H	4.0368738	–3.4700371	–4.9044375
H	4.8656815	–3.1284025	–1.2337607
H	3.3553846	0.7530970	–5.3146514
H	4.2285739	1.4059088	–1.6983379
C	–3.8186800	0.5330254	0.1894360
N	–4.5331015	0.9222718	1.3322313
N	–4.5353118	1.0970829	–0.8746286
C	–5.6302189	1.6922858	0.9596932
C	–4.4034229	0.3523207	2.6269820
C	–5.6259532	1.8050588	–0.3846345
C	–4.1612338	1.0928734	–2.2438350
H	–6.3181481	2.0797871	1.7048822
C	–4.9160228	–0.9362726	2.8617740
C	–3.7876641	1.1064662	3.6403942
H	–6.2914111	2.3375903	–1.0573421
C	–3.1883520	2.0047135	–2.6888135
C	–4.7867341	0.1817867	–3.1118435
C	–4.8118398	–1.4544902	4.1546765
C	–5.5255680	–1.7648812	1.7496690
C	–3.7217390	0.5545115	4.9213918
C	–3.1589117	2.4518929	3.3446904
C	–2.8611405	1.9985643	–4.0459293
C	–2.5023435	2.9571615	–1.7316921
C	–4.4277696	0.2118752	–4.4616655
C	–5.7470708	–0.8652233	–2.5858373
C	–4.2291196	–0.7148017	5.1783216
H	–5.1881272	–2.4600387	4.3605483
H	–5.5450117	–1.1393704	0.8456679
H	–3.2396144	1.1178984	5.7246000
H	–3.2589694	2.6156693	2.2611509
C	–3.4754258	1.1132050	–4.9255436
H	–2.0977381	2.6873952	–4.4160885
H	–2.8153216	2.6796074	–0.7148676
H	–4.8855410	–0.4967261	–5.1566836
H	–5.9957547	–0.5851332	–1.5511330
H	–4.1551664	–1.1386998	6.1832565
H	–3.1977252	1.1157291	–5.9828910
H	3.4208167	–1.5185803	–6.3003642
H	3.2748692	0.8239875	5.8676182
C	–3.8920835	3.5855628	4.0597254
H	–4.9577293	3.6147175	3.7825731
H	–3.8362975	3.4705902	5.1548707
H	–3.4467318	4.5604307	3.8037090
C	–1.6641814	2.4412889	3.6611959
H	–1.1958317	3.3874306	3.3454594
H	–1.4773831	2.3187533	4.7407397
H	–1.1744051	1.6134495	3.1260690
C	–0.9828899	2.8153112	–1.7812964
H	–0.5739553	3.1254207	–2.7568769
H	–0.5163238	3.4484660	–1.0102854
H	–0.6913393	1.7697594	–1.5980513
C	–2.9552524	4.3962291	–1.9793582
H	–2.6742422	4.7344891	–2.9904399
H	–4.0480831	4.4957768	–1.8846116
H	–2.4859664	5.0805808	–1.2543507
C	–4.6532714	–2.9807925	1.4357363
H	–4.6392411	–3.6874425	2.2821552
H	–5.0403072	–3.5155436	0.5539649
H	–3.6169296	–2.6706348	1.2323859
C	–6.9690235	–2.1576338	2.0595859
H	–7.0318922	–2.8076359	2.9475982
H	–7.5947040	–1.2711589	2.2476432
H	–7.4062958	–2.7114417	1.2132558
C	–7.0535446	–0.9141109	–3.3734313
H	–7.5495679	0.0689980	–3.3943995
H	–6.8898040	–1.2283044	–4.4170162
H	–7.7489166	–1.6384393	–2.9200737
C	–5.0601592	–2.2310926	–2.5308493
H	–5.7171870	–2.9773988	–2.0549957
H	–4.8164068	–2.5890663	–3.5447190
H	–4.1168286	–2.1715636	–1.9650852
C	1.6159465	2.4172965	1.4769650
H	1.5658366	3.1630409	2.2879597
H	1.2992112	2.9195205	0.5501260
H	0.8958903	1.6101235	1.6786823
C	4.0478178	2.9248743	0.9834454

H	4.1544316	3.6246413	1.8291184
H	5.0382725	2.4902938	0.7770444
H	3.7433388	3.5058260	0.0975707
C	4.7473620	2.5153377	–3.4414281
H	5.8040929	2.2049527	–3.4497424
H	4.4341256	2.6667297	–4.4874410
H	4.6821639	3.4905579	–2.9329096
C	2.4052828	1.9254207	–2.6693611
H	2.3077544	2.8721131	–2.1141127
H	1.9900677	2.0830430	–3.6785855
H	1.7939513	1.1558523	–2.1721482
C	3.5439978	–4.4910584	–2.1966659
H	3.3574556	–4.9548672	–3.1796261
H	3.7612567	–5.2996313	–1.4805150
H	2.6255949	–3.9736421	–1.8779359
C	6.0072223	–4.1710477	–2.7092447
H	5.9181539	–4.5678910	–3.7340825
H	6.8483988	–3.4602235	–2.6984341
H	6.2636454	–5.0132736	–2.0465815
C	6.4071572	–2.6481225	4.2300901
H	7.0822964	–1.8476457	4.5714702
H	5.8032736	–2.9717147	5.0930977
H	7.0228617	–3.5098560	3.9285318
C	4.5677994	–3.3054219	2.6385543
H	5.1215089	–4.2166413	2.3584888
H	3.8815224	–3.5558321	3.4629528
H	3.9414959	–2.9976041	1.7886352

11 References

[1] J. Attner, U. Radius, *Chem. Eur. J.* **2001**, *7*, 783–790.

[2] a) A. J. Arduengo III., *Preparation of 1,3-Disubstituted Imidazolium Salts,* **1991**, US-Patent US5077414A; b) A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534; c) T. Schaub, U. Radius, A. Brucks, M. P. Choules, M. T. Olsen, T. B. Rauchfuss*, Inorg. Synth.* **2010***, 35*, 78–91.

[3] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; *Angew. Chem.* **2005**, *117*, 5851–5855.

[4] a) R. A. Schunn, S. D. Ittel, M. A. Cushing, R. Baker, R. J. Gilbert, D. P. Madden, *Inorg. Synth.*, **1990**, *28*, 94–98; b) J. Wielandt, D. Ruckerbauer, T. Zell, U. Radius, *Inorg. Synth.* **2010**, *35*, 120.

[5] T. Schaub, U. Radius, *Chem. Eur. J.* **2005**, *11*, 5024–5030.

[6] C. M. Crudden, J. H. Horton, I. I. Ebralidze, O. V. Zenkina, A. B. McLean, B. Drevniok, Z. She, H.-B. Kraatz, N. J. Mosey, T. Seki, E. C. Keske, J. D. Leake, A. Rousina-Webb, G. Wu, *Nature Chem.* **2014**, *6*, 409–414.

[7] E. Çetinkaya, P. B. Hitchcock, H. Küçükbay, M. F. Lappert, S. Al-Juaid, *J. Organomet. Chem.* **1994**, *481*, 89–95.

[8] a) L. Delaude, A. Demonceau, J. Wouters, *Eur. J. Inorg. Chem.* **2009**, 1882–1891; b) L. Delaude, *Eur. J. Inorg. Chem.* **2009**, 1681–1699; c) M. S. Luff, K. Oppel, I. Krummenacher, H. Braunschweig, U. Radius, *Chem. Commun.* **2024**, *60*, 14447–14450.

[9] a) N. Kuhn, H. Bohnen, G. Henkel, *Z. Naturforsch. B* **1994**, *49*, 1473–1480, b) A. R. Katritzky, D. Jishkariani, R. Sakhuja, C. D. Hall, P. J. Steel, *J. Org. Chem.* **2011**, *76*, 4082–4087; c) U. Siemeling, H. Memczak, C. Bruhn, F. Vogel, F. Träger, J. E. Baio, T. Weidner, *Dalton Trans.* **2012**, *41*, 2986–2994.

[10] P. G. Jones, I. Dix, *CSD Commun.* **2004**, CCDC: 238439.

[11] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

[12] R. K. Harris, E. D. Becker, S. M. C. d. Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, **2001**, *73*, 1795–1818.

[13] M. R. Willcott, *J. Am. Chem. Soc.* **2009**, *131*, 13180–13180.

[14] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42–55.

[15] Origin(Pro), **2020**, OriginLab Corporation, Northampton, MA, USA.

[16] Opus 8.1, **2017**, Bruker Optik GmbH.

[17] AfterMath Data Organizer 1.6.10515, **2021**, Pine Research Instrumentation,

[18] NOVA 2.1.2, **2017**, Metrohm Autolab B.V., Utrecht.

[19] a) G. M. Sheldrick, *Acta Cryst. Sect. A: Found. Adv.* **2015**, *71*, 3–8; b) G. M. Sheldrick, *Acta Cryst. Sect. C* **2015**, *71*, 3–8.

[20] a) M. B. Günter Bergerhoff, Klaus Brandenburg, *J. Res. Natl. Inst. Stan. Technol.* **1996**, *101*, 221–225; b) W. T. Pennington, *J. Appl. Cryst.* **1999**, *32*, 1028–1029; c) Diamond 4.6.6, **2021**, Bonn.

[21] a) S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Voora, F. Weigend, A. Wodyński, J. M. Yu., *J. Chem. Phys.* **2020**, *152*, 184107; b) Y. J. Franzke, C. Holzer, J. H. Andersen, T. Begusĭc, F. Bruder, S. Coriani, F. D. Sala, E. Fabiano, D. A. Fedotov, S. Fürst, S. Gillhuber, R. Grotjahn, M. Kaupp, M. Kehry, M. Krstic, F. Mack, S. Majumdar, B. D. Nguyen, S. M. Parker, F. Pauly, A. Pausch, E. Perlt, G. S. Phun, A. Rajabi, D. Rappoport, B. Samal, T. Schrader, M. Sharma, E. Tapavicza, R. S. Treß, V. Voora, A. Wodyński, J. M. Yu, B. Zerulla, F. Furche, C. Hättig, M. Sierka, D. P. Tew, F. Weigend, *J. Chem. Theory Comput.* **2023**, *19*, 6859−6890.

[22] a) M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, *10*, 104–111; b) O. Treutler R. Ahlrichs, *J. Chem. Phys. C.* **1995**, *102*, 346–354; c) M. Sierka, A. Hogekamp R. Ahlrichs, *J. Chem. Phys.* **2003**, *118*, 9136–9148.

[23] a) M. Ernzerhof, G. E. Scuseria, *J. Chem. Phys.* **1999**, *110*, 5029–5036; b) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170.

[24] a) A. D. Becke, *J. Chem. Phys.* **1986**, *84*, 4524–4529; b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824; *erratum*: J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406; c) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[25] a) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835; b) K. Eichkorn, O. Treutler, H. Öhm, M. Häser R. Ahlrichs, *Chem. Phys. Letters* **1995**, *242*, 652–660; c) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124; d) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[26] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[27] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[28] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Let.* **2004**, *384*, 103–107.

[29] a) F. Furche, R. Ahlrichs, *J. Chem. Phys.* **2002**, *117*, 7433–7477; *erratum*: *J. Chem. Phys.* **2004**, *121*, 12772–12773; b) D. Rappoport, F. Furche, *J. Chem. Phys.* **2005**, *122*, 64105; c) F. Furche, D. Rappoport, M. Olivucci (ed.), *Computational Photochemistry*, Elsevier, Amsterdam, **2005**, Vol. 16, Ch. 3.

[30] J. Tomasi, B. Mennucci, V. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3094.

[31] a) A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2,* **1993**, 799–805; b) A. Klamt, *WIREs Comput. Mol. Sci.* **2011**, *1*, 699–709; c) A. Klamt, *WIREs Comput. Mol. Sci.,* **2018**, *8*, 1–11.

[32] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[33] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold., *NBO 6.0*; http://nbo6.chem.wisc.edu/.

[34] K. A. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.