Supporting Information for:

Activation of CS_2 by a “Masked” Terminal Nickel Sulfide

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, toluene, and tetrahydrofuran (THF) were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3Å sieves for 24 h prior to use. Benzene-*d*$_6$, tetrahydrofuran-*d*$_8$, and C_8H_{18} (isooctane) were dried over 3Å molecular sieves for 24 h prior to use, and CS_2 was dried using CaH_2. [K(18-crown-6)][L^{tBu}Ni(S)] and [K(2,2,2-cryptand)][L^{tBu}Ni(S)] were synthesized according to the previously reported procedures.[1] All other reagents were purchased from commercial suppliers and used as received.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Agilent Technologies 400-MR DD2 400 MHz spectrometer or a Varian UNITY INOVA 500 MHz spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Synthesis of [K(18-crown-6)][(L^{tBu})Ni(*S*,*S*:κ_2-CS_3)] (1). To a brown, stirring solution of [K(18-crown-6)][L^{tBu}Ni(S)] (44.5 mg, 0.0497 mmol) in toluene (2 mL) was added CS_2 (3.0 μL, 0.0497 mmol). After addition, the color of the solution turned from brown to orange. This solution was allowed to stir for 10 min, whereupon the volatiles were removed *in vacuo*. The resulting orange residue was rinsed with hexanes (1 mL × 2), extracted into toluene (2 mL), and filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). This yielded a yellow-orange filtrate. The volume of this solution was reduced *in vacuo* to 0.5 mL and the solution was layered with isooctane (2 mL).

Storage of the solution at -25 °C for 24 h resulted in the deposition of yellow-orange plates of [K(18-crown-6)][(L^{tBu})Ni(*S,S*:κ$_2$-CS$_3$)] (**1**), which were isolated by decanting off the superntant (36.7 mg, 76%). Anal. Calcd for: $C_{48}H_{77}KN_2NiO_6S_3$: C, 59.30; H, 7.98; N, 2.88. Found: C, 59.60; H, 8.14; N, 2.69. ^{1}H NMR (400 MHz, 25 °C, benzene-*d$_6$*): δ = 6.99 (m, 6H, Ar-**H**), 5.56 (s, 1H, γ-**H**), 4.37 (sept, $^3J_{HH}$, = 6.7 Hz, 4H, C**H**(CH$_3$)$_2$), 3.09 (s, 24H, 18-crown-6), 2.09 (d, $^3J_{HH}$, = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$), 1.48 (d, $^3J_{HH}$, = 6.9 Hz, 12H, CH(C**H**$_3$)$_2$), 1.26 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, benzene-*d$_6$*): δ = 166.55 (Ar-C), 150.50 (Ar-C), 142.85 (Ar-C), 124.26 (Ar C), 122.35 (Ar-C), 98.18 (γ-C), 70.20 (18-crown-6), 42.71 (**C**(CH$_3$)$_3$), 33.89 (C(**C**H$_3$)$_3$), 28.70 (CH(**C**H$_3$)$_2$), 25.66 (CH(**C**H$_3$)$_2$), 24.62 (**C**H(CH$_3$)$_2$). Note: a resonanace assignable to [CS$_3$]$^{2-}$ was not observed; it should appear around ca. 250 ppm.[2] IR (KBr Pellet, cm^{-1}): 1633 (w, br), 1541 (m), 1508 (s), 1464 (m), 1458 (m), 1435 (m), 1403 (s), 1379 (w), 1363 (m), 1348 (m), 1317 (s), 1280 (w), 1248 (m), 1215 (w), 1186 (w), 1178 (w), 1159 (w), 1105 (s), 1032 (s), 960 (m), 930 (w), 881 (w), 862 (w), 829 (w), 800 (w), 779 (w), 709 (w, br), 528 (w), 472 (w), 451 (w).

Synthesis of [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS$_3$)Ni{*S,S*:κ$_2$-CS$_2$(L^{tBu})}] (2). To a brown, stirring solution of [K(2,2,2-cryptand)][L^{tBu}Ni(S)] (48.0 mg, 0.0414 mmol) in THF (2 mL) was added CS$_2$ (5.0 µL, 0.0827 mmol). After addition, the color of the solution quickly changed from brown to red. This solution was allowed to stir for 1 hr, slowly becoming deep purple. The volatiles were removed *in vacuo* and the resulting purple residue was rinsed with hexanes (1 mL), extracted into THF (2 mL), and filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). This yielded a purple filtrate. The volume of this solution was reduced *in vacuo* to 0.5 mL and the solution was layered with C_8H_{18} (2 mL). Storage of the solution at -25 °C for 24 h resulted in the deposition of purple needles of [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS_3)Ni{*S,S*:κ$_2$-CS_2(L^{tBu})}] (**2**), which were isolated by decanting off the supernatant (31.6 mg, 55%). Anal. Calcd for: $C_{55}H_{89}KN_4NiO_6S_5$: C, 56.93; H, 7.73; N, 4.38. Found: C, 57.02; H, 7.92; N, 4.42. ^{1}H NMR (400 MHz, 25 °C, benzene-*d$_6$*): δ = 6.97 - 6.79 (m, 6H, Ar-**H**, dipp), 5.53 (br s, 1H, γ-**H**), 3.62-3.57 (24H, 2,2,2-cryptand), 3.44 (br m, 2H, C**H**(CH_3)$_2$), 2.89 (br m, 2H, C**H**(CH_3)$_2$), 2.58 (12 H, 2,2,2-cryptand), 1.23 (br m, 42H, CH(C**H**$_3$)$_2$ & C(C**H**$_3$)$_3$). IR (KBr Pellet, cm^{-1}): 1658 (m, br), 1587 (w), 1537 (w), 1506 (w), 1473 (m), 1456 (m), 1440 (m), 1429 (m), 1400 (w), 1398 (w), 1376 (w), 1359 (m), 1319 (m), 1301 (m), 1257 (m), 1234 (w), 1205 (w), 1170 (w), 1128 (w), 1101 (s), 1076 (w), 1035 (s), 1008 (w, br), 995 (w), 964 (w), 946 (m), 931 (w), 887 (w), 858 (w), 825 (m), 792 (m), 755 (m), 748 (m), 619 (w, br), 520 (w), 476 (w), 416 (w).

Reaction of [K(2,2,2-cryptand)][L^{tBu}Ni(S)] with one equiv CS_2. To a J-Young NMR tube containing [K(2,2,2-cryptand)][L^{tBu}Ni(S)] (15 mg, 0.0155 mmol) in C_6D_6 (0.5 mL) was added CS_2 (0.9 μL, 0.0155 mmol). After addition, the color of the solution quickly changed from brown to red. This solution was allowed to stir for 1 hr, slowly becoming deep purple. The reaction mixture was then transferred to a 20 mL scintillation vial and volatiles were removed *in vacuo*. The resulting purple residue was extracted into THF (1 mL), filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), concentrated *in vacuo* to 0.25 mL, and layered with Et_2O (1 mL). Storage of this solution at -25 °C for 12 h resulted in the deposition of purple plates of [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS_3)Ni{*S,S*:κ$_2$-CS_2(L^{tBu})}] (**2**), which were isolated by decanting off the supernatnat (6.9 mg, 36%). ^{1}H NMR (400 MHz, 25 °C, thf-*d$_8$*): δ = 6.97-6.75 (br m, 6H, Ar-**H**), 5.53 (br s, 1H, γ-**H**), 3.57-3.53 (br m, 24H, 2,2,2-cryptand), 2.90 (br s, 2H, C**H**(CH$_3$)$_2$), 2.55 (br s, 12H, 2,2,2-cryptand), 1.23 (br m, 42H, C(C**H**$_3$)$_3$ & CH(C**H**$_3$)$_2$).

Variable temperature ^{1}H NMR spectra of [K(2,2,2-cryptand)][(*S*,*S*:κ$_2$-CS$_3$)Ni{*S*,*S*:κ$_2$-CS$_2$(L^{tBu})}] (2). To an NMR tube was added a thf-*d$_8$* (0.5 mL) solution of **2** (12.6 mg, 0.0109 mmol). ^{1}H NMR spectra were collected at ca. 20 °C intervals. ^{1}H NMR (500 MHz, 25 °C, thf-*d$_8$*): δ = 6.97-6.78 (m, 6H, Ar-**H**), 5.53 (br s, 1H, γ-**H**), 3.62-3.57 (24H, 2,2,2-cryptand), 3.48 (br m, 2H, C**H**(CH$_3$)$_2$), 2.89 (br m, 2H, C**H**(CH$_3$)$_2$), 2.59 (m, 12H, 2,2,2-cryptand), 1.23 (br, 42H, C(C**H**$_3$)$_3$ & CH(C**H**$_3$)$_2$). ^{1}H NMR (500 MHz, 0 °C, thf-*d$_8$*): δ = 6.97-6.79 (m, 6H, Ar-**H**), 5.54 (br s, 1H, γ-**H**), 3.61-3.57 (24H, 2,2,2-cryptand), 3.45 (br m, 1H, C**H**(CH$_3$)$_2$), 2.89 (br m, 2H, C**H**(CH$_3$)$_2$), 2.58 (m, 12H, 2,2,2-cryptand), 1.21 (br, 42H, C(C**H**$_3$)$_3$ & CH(C**H**$_3$)$_2$) . ^{1}H NMR (500 MHz, -20 °C, thf-*d$_8$*): δ = 6.97-6.76 (m, 6H, Ar-**H**), 5.52 (s, 1H, γ-**H**), 3.60-3.57 (24H, 2,2,2-cryptand), 3.46 (br m, 1H, C**H**(CH$_3$)$_2$), 3.40 (br m, 1H, C**H**(CH$_3$)$_2$), 2.91 (br m, 1H, C**H**(CH$_3$)$_2$), 2.83 (br m, 1H, C**H**(CH$_3$)$_2$), 2.57 (m, 12H, 2,2,2-cryptand), 2.09 (br d, 3H, CH(C**H**$_3$)$_2$), 1.28 (br s, 9H, C(C**H**$_3$)$_3$), 1.14 (br s, 9H, C(C**H**$_3$)$_3$), 0.63 (br d, 3H, $^3J_{HH}$, = 5.1 Hz, CH(C**H**$_3$)$_2$). ^{1}H NMR (500 MHz, -40 °C, thf-*d$_8$*): δ = 6.99-6.74 (m, 6H, Ar-**H**), 5.51 (s, 1H, γ-**H**), 3.60-3.56 (24H, 2,2,2-cryptand), 3.48 (br m, 1H, C**H**(CH$_3$)$_2$), 3.39 (br m, 1H, C**H**(CH$_3$)$_2$), 2.90 (br m, 1H, C**H**(CH$_3$)$_2$), 2.82 (br m, 1H, C**H**(CH$_3$)$_2$), 2.56 (br m, 12H, 2,2,2-cryptand), 2.11 (br d, 3H, $^3J_{HH}$, = 6.0 Hz, CH(C**H**$_3$)$_2$), 1.31 (br d, 3H, CH(C**H**$_3$)$_2$), 1.28 (s, 9H, C(C**H**$_3$)$_3$), 1.24 (br d, 3H, $^3J_{HH}$, = 6.6 Hz, CH(C**H**$_3$)$_2$), 1.14 (s, 9H, C(C**H**$_3$)$_3$), 1.11 (br d, 3H, $^3J_{HH}$, = 6.5 Hz, CH(C**H**$_3$)$_2$), 1.06 (br d, 3H, $^3J_{HH}$, = 6.5 Hz, CH(C**H**$_3$)$_2$), 1.00 (br d, 3H, $^3J_{HH}$, = 6.9 Hz, CH(C**H**$_3$)$_2$), 0.93 (br d, 3H, $^3J_{HH}$, = 6.6 Hz, CH(C**H**$_3$)$_2$), 0.63 (br d, 3H, $^3J_{HH}$, = 6.0 Hz, CH(C**H**$_3$)$_2$). ^{1}H NMR (500 MHz, -75 °C, thf-*d$_8$*): δ = 7.01-

6.74 (m, 6H, Ar-**H**), 5.50 (s, 1H, γ-**H**), 3.58-3.56 (24H, 2,2,2-cryptand), 3.47 (br m, 1H, C**H**(CH_3)$_2$), 3.38 (br m, 1H, C**H**(CH_3)$_2$), 2.88 (br m, 1H, C**H**(CH_3)$_2$), 2.82 (br m, 1H, C**H**(CH_3)$_2$), 2.53 (br, 12H, 2,2,2-cryptand), 2.14 (d, 3H, $^3J_{HH}$, = 7.1 Hz, CH(C**H**$_3$)$_2$), 1.30 (br d, 3H, $^3J_{HH}$, = 6.0 Hz CH(C**H**$_3$)$_2$), 1.27 (s, 9H, C(C**H**$_3$)$_3$), 1.24 (br d, 3H, $^3J_{HH}$, = 6.0 Hz CH(C**H**$_3$)$_2$), 1.13 (s, 9H, C(C**H**$_3$)$_3$), 1.10 (d, 3H, $^3J_{HH}$, = 6.6 Hz, CH(C**H**$_3$)$_2$), 1.05 (d, 3H, $^3J_{HH}$, = 6.6 Hz, CH(C**H**$_3$)$_2$), 0.99 (d, 3H, $^3J_{HH}$, = 7.1Hz, CH(C**H**$_3$)$_2$), 0.94 (d, 3H, $^3J_{HH}$, = 6.6 Hz, CH(C**H**$_3$)$_2$), 0.61 (d, 3H, $^3J_{HH}$, = 6.0 Hz, CH(C**H**$_3$)$_2$).

Reaction of [K(18-crown-6)][L^{tBu}Ni(S)] with two equiv CS_2. To a J-Young NMR tube containing [K(18-crown-6)][L^{tBu}Ni(S)] (20.0 mg, 0.0223 mmol) in thf-*d*$_8$ (0.6 mL) was added CS_2 (2.7 µL, 0.0446 mmol). After addition, the color of the solution quickly changed from brown to red. This solution was allowed to stand for 1 hr, slowly becoming deep purple. An *in situ* ^{1}H NMR spectrum taken after 1 h reveals the formation of a new product which we have tentatively identified as [K(18-crown-6)][(*S,S*:κ$_2$-CS_3)Ni{*S,S*:κ$_2$-CS_2(L^{tBu})}] (**3**) (i.e., the product of double CS_2 insertion) on the basis of the similarity of its ^{1}H NMR spectrum with that of complex **2** (Figure S7). ^{1}H NMR (400 MHz, 25 °C, thf-*d*$_8$): δ = 6.98-6.78 (br m, 6H, Ar-**H**), 5.54 (br s, 1H, γ-**H**), 3.63 (br s, 24H, 18-crown-6), 3.46 (br m, 2H, C**H**(CH_3)$_2$), 2.90 (br m, 2H, C**H**(CH_3)$_2$), 1.23 (br m, 42H, CH(C**H**$_3$)$_2$ & C(C**H**$_3$)$_3$).

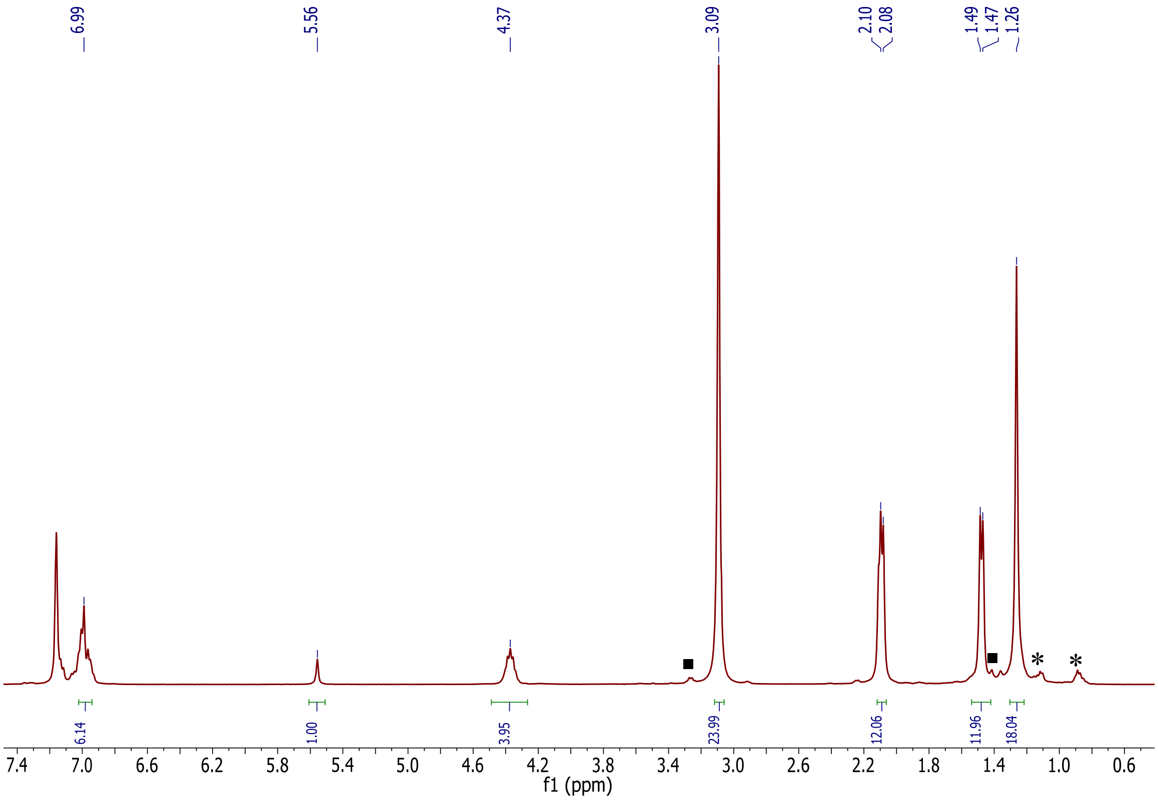

Figure S1. ^{1}H NMR spectrum of [K(18-crown-6)][(L^{tBu})Ni(*S*,*S*:κ_2-CS_3)] (**1**) in benzene-*d*$_6$. (*) indicates the presence of isooctane and (■) indicates the presence of Et_2O.

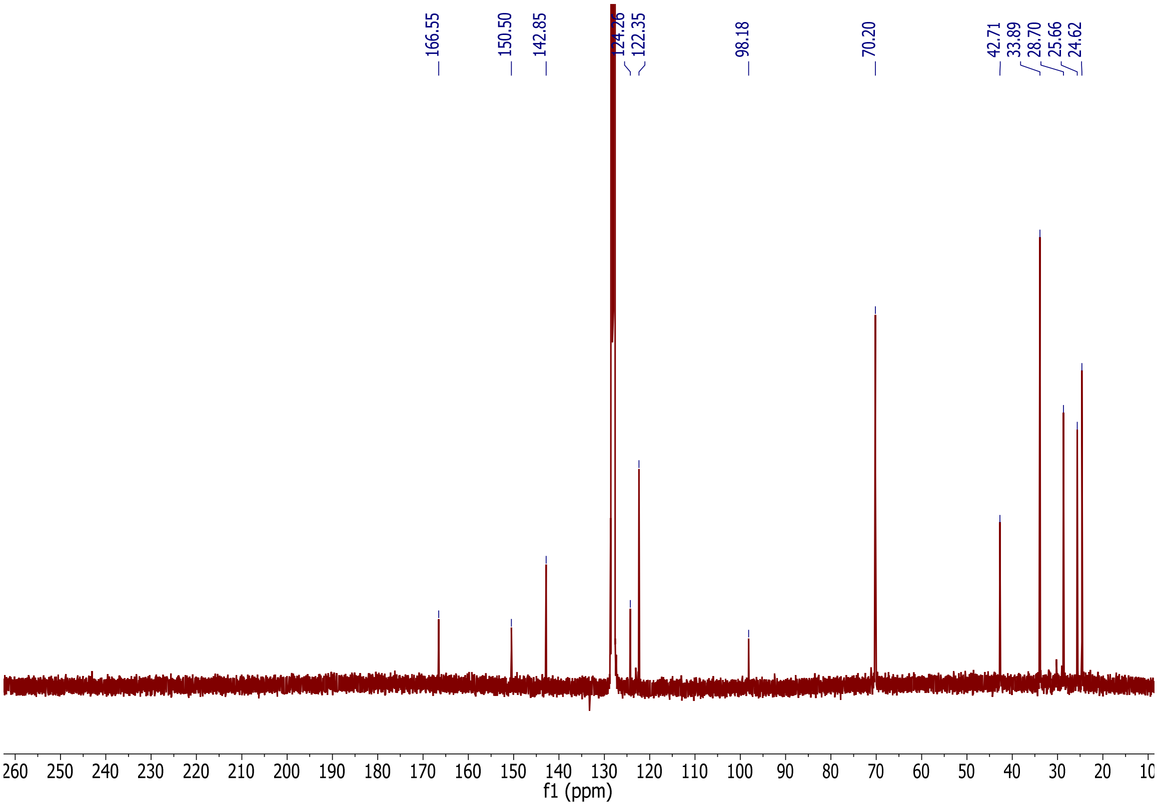

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-crown-6)][(L^{tBu})Ni(*S,S*:κ$_2$-CS$_3$)] (**1**) in benzene-*d*$_6$.

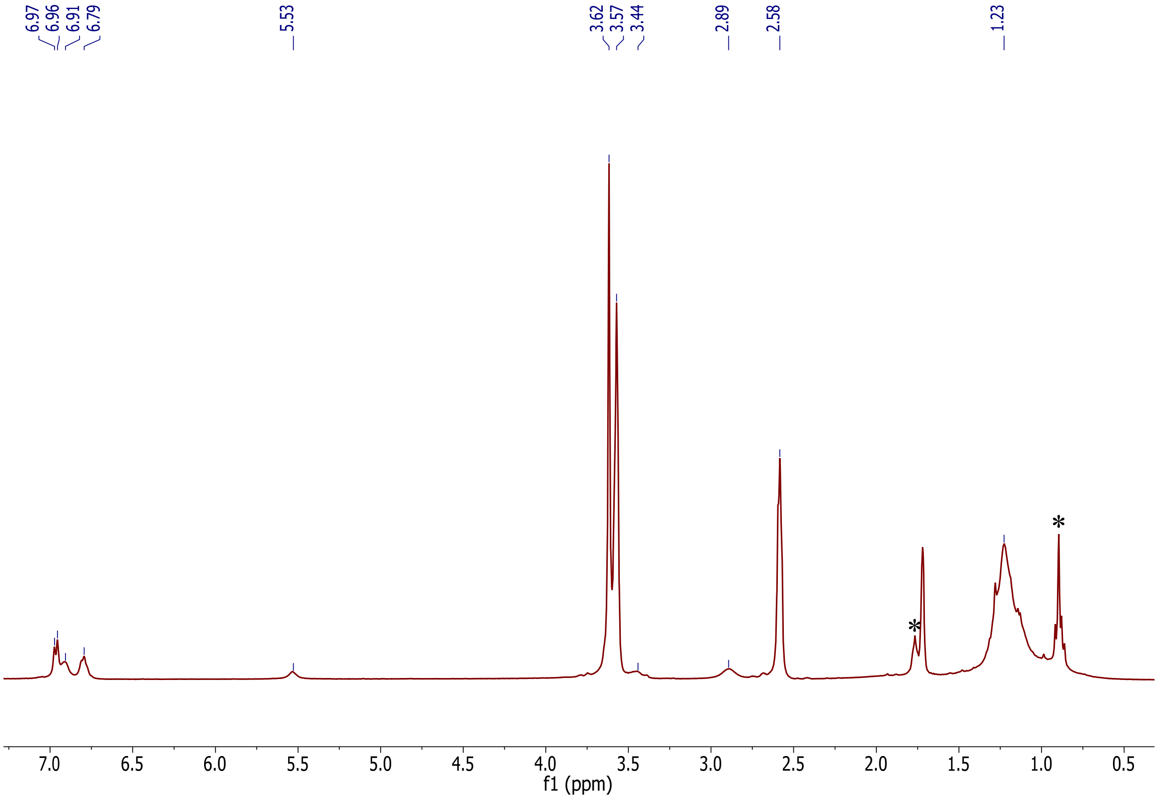

Figure S3. ^{1}H NMR spectrum of [K(2,2,2-cryptand)][(S,S:κ_2-CS_3)Ni{S,S:κ_2-CS_2(L^{tBu})}] (**2**) in THF-d_8. (*) indicates the presence of isooctane.

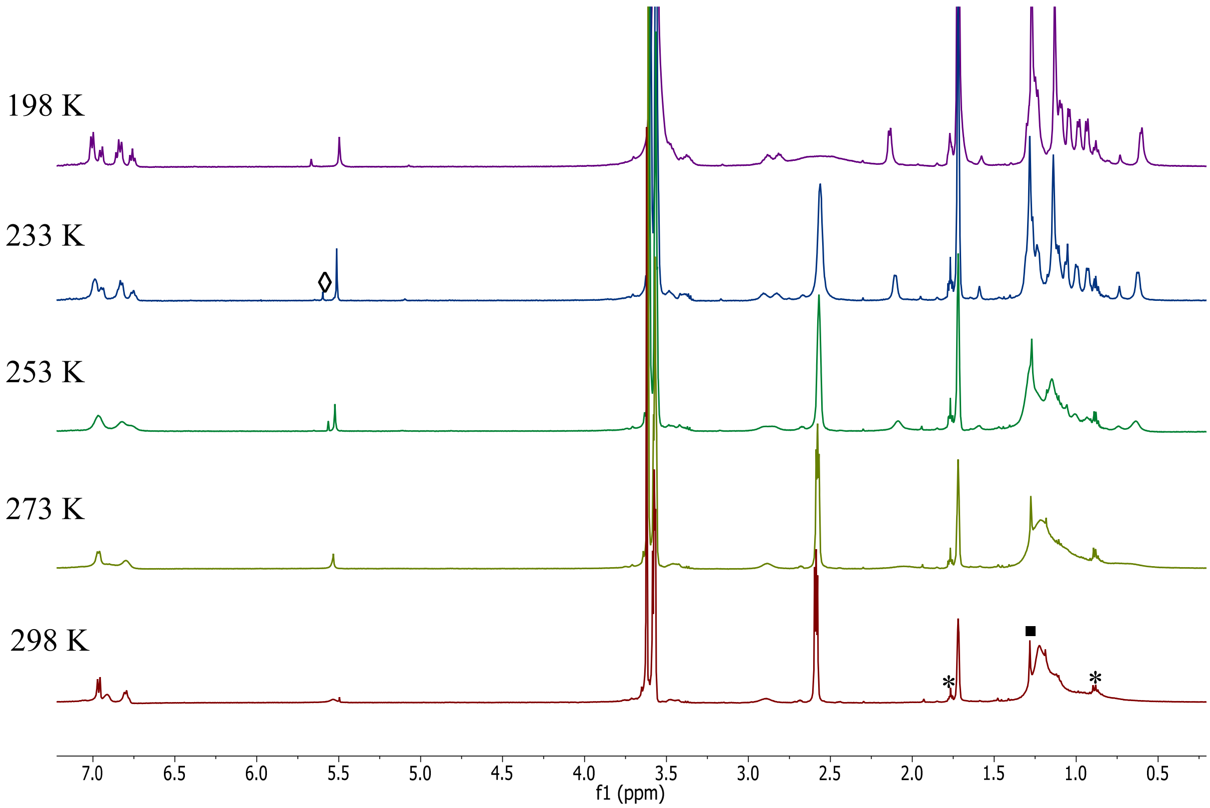

Figure S4. Variable temperature ^{1}H NMR spectra of [K(2,2,2-cryptand)][(*S,S*:κ_2-CS_3)Ni{*S,S*:κ_2-CS_2(L^{tBu})}] (**2**) in THF-d_8. (*) indicates the presence of isooctane and (◊) indicates the presence of dichloromethane, and (■) indicates the presence of an unidentified impurity.

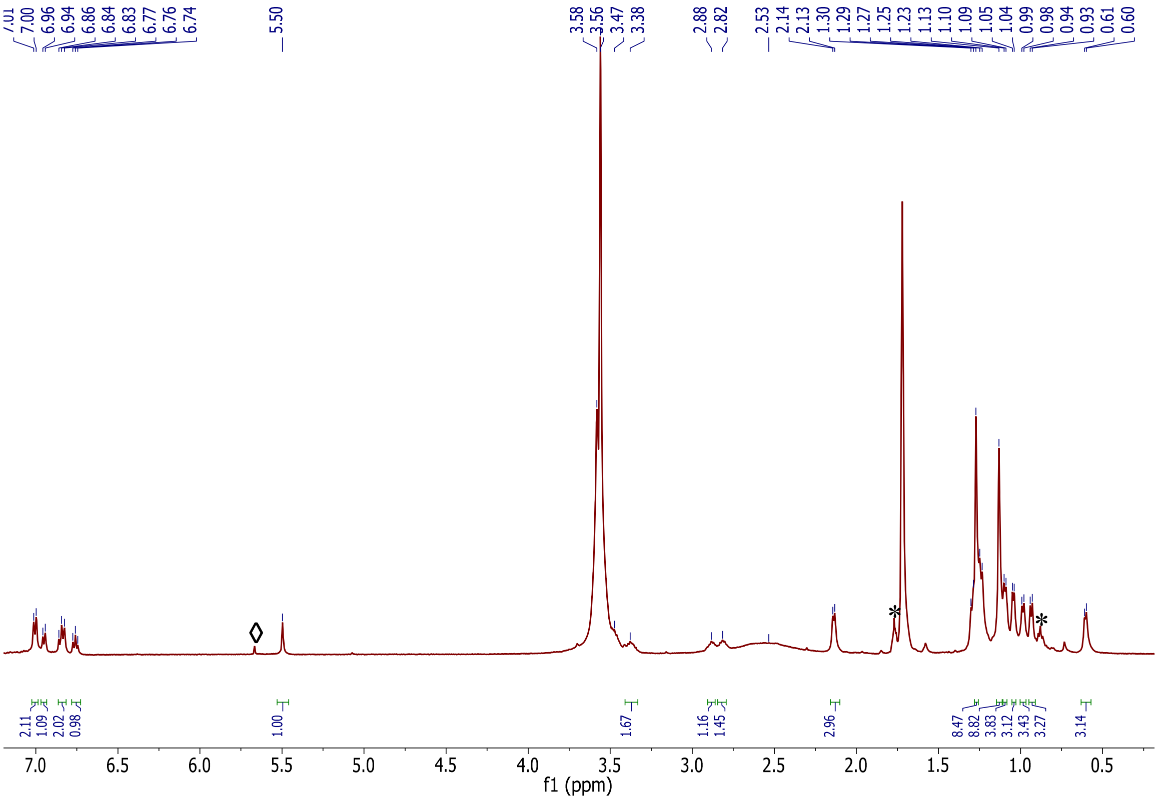

Figure S5. ^{1}H NMR spectrum of [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS$_3$)Ni{*S,S*:κ$_2$-CS$_2$(L^{tBu})}] (**2**) at -75 °C in THF-*d*$_8$. (*) indicates the presence of isooctane and (◊) indicates the presence of dichloromethane.

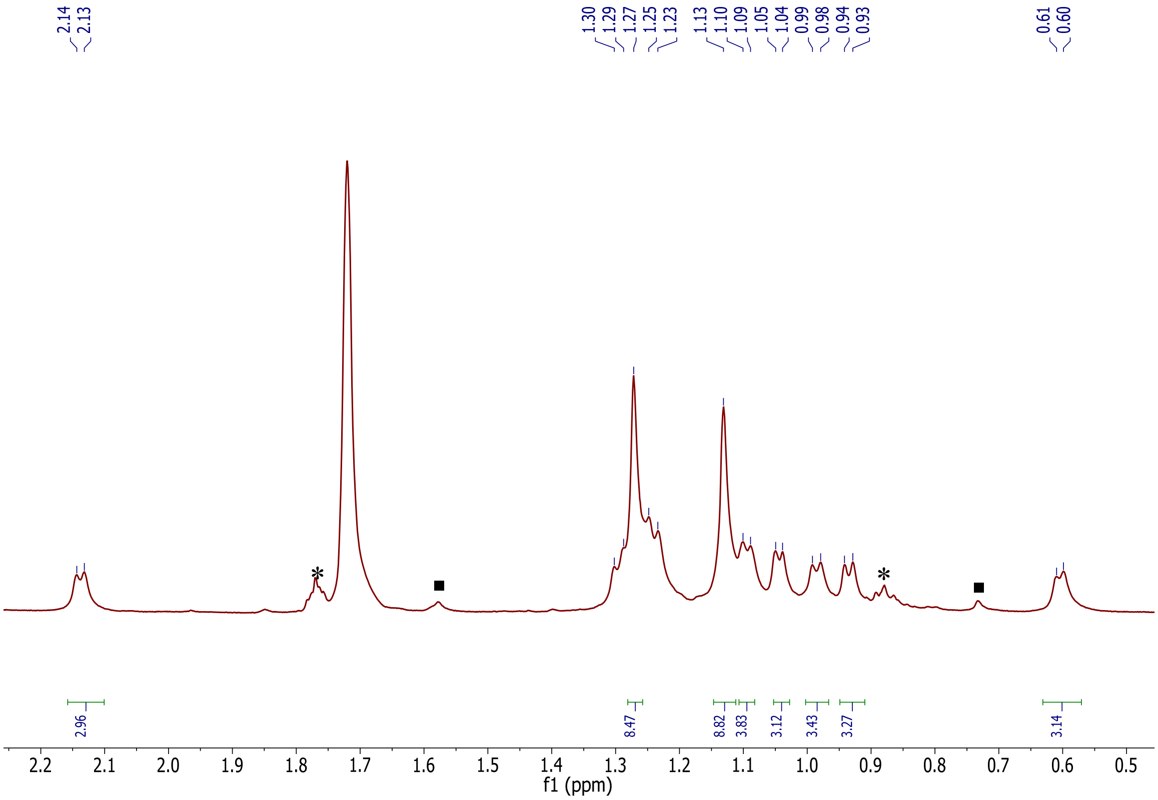

Figure S6. Partial ^{1}H NMR spectrum of [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS$_3$)Ni{*S,S*:κ$_2$-CS$_2$(L^{tBu})}] (**2**) at -75 °C in THF-*d*$_8$. (*) indicates the presence of isooctane and (■) indicates the presence of unknown impurities.

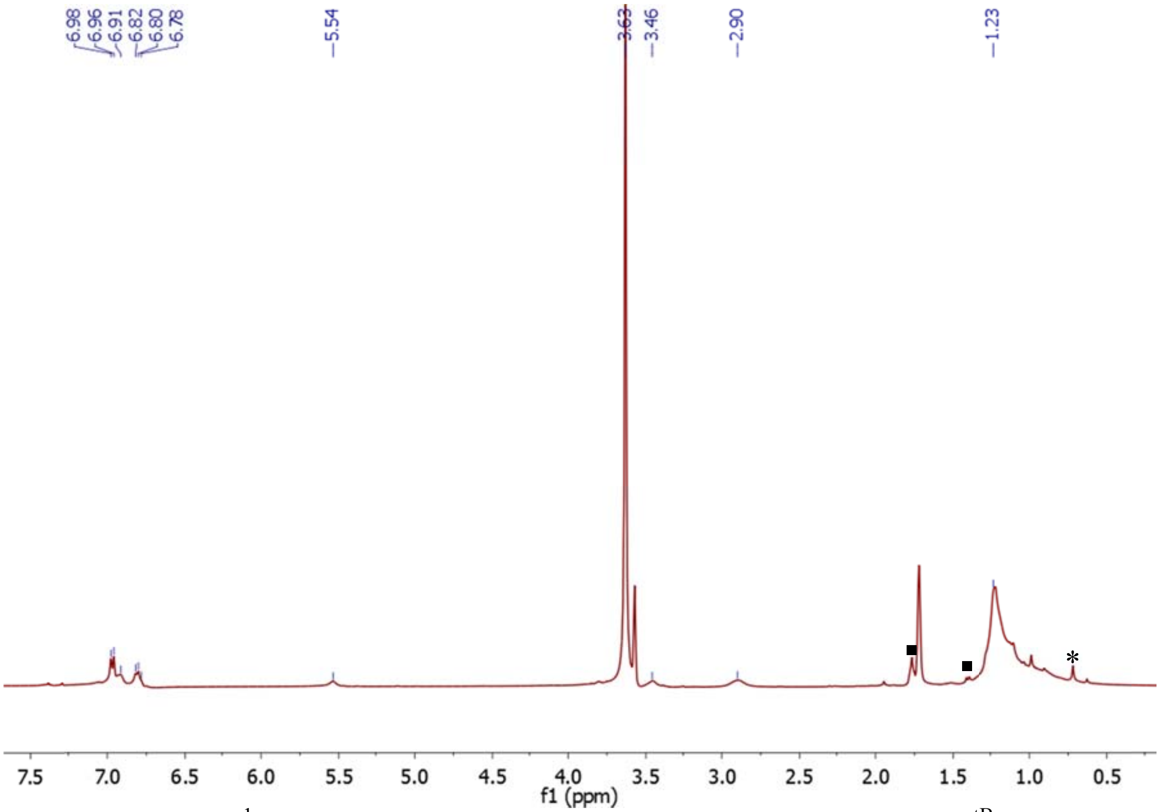

Figure S7. In situ ^{1}H NMR spectrum of the reaction of [K(18-crown-6)][L^{tBu}Ni(S)] with two equiv CS_2 in THF-d_8. (▪) indicate the presence of unidentified impurities and (*) indicates the presence of isooctane.

X-ray Crystallography. Data for **1** and **2** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.71073 Å). The crystals were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream. Data were collected using ω scans with 0.5° frame widths. Frame exposures of 20 seconds were used for both **1** and **2**. Data collection and cell parameter determination were conducted using the SMART program.[3] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[4] Absorption correction of the data was carried out using the multi-scan method SADABS.[5] Subsequent calculations were carried out using SHELXTL.[6] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[6]

In complex **1**, the 18-crown-6 molecule is disordered over two positions. These two orientations were modelled in a 60:40 ratio using the FVAR, EADP, and PART commands in SHELXL. The C-C and C-O bonds in the 18-crown-6 molecule in complex **1** were constrained using the SADI command. Additionally, the positions of the C and O atoms in the 18-crown-6 molecule were restrained using the RIGU ADP command. In complex **2**, both the 2,2,2-cryptand moiety and the $C_4H_{10}O$ solvate are disordered. The $C_4H_{10}O$ molecule was found to be disordered over two positions. These two orientations each were modelled in a 56:44 ratio, using the FVAR and EADP commands in SHELXL. The C–C, C-N, C-O, and O-K bonds of 2,2,2-cryptand and $C_4H_{10}O$ were constrained using the SADI command. The disordered 2,2,2-cryptand molecule was further refined using the DELU and SIMU commands for the O atoms. Further crystallographic details for complexes **1**-**2** can be found in Table S1. Complexes **1**-**2** have been deposited in the Cambridge Structural Database (**1**: CCDC 1454634; **2**: CCDC 1454635).

Table S1. X-ray Crystallographic Data for complexes **1** and **2**.

	1·C_7H_8	**2**·$C_4H_{10}O$
empirical formula	$C_{36}H_{53}N_2NiS_3$, $C_{12}H_{24}O_6K$, C_7H_8	$C_{37}H_{53}N_2NiS_5$,$C_{18}H_{36}KN_2O_6$, $C_4H_{10}O$
crystal habit, color	Plate, Yellow	Needle, Purple
crystal size (mm)	0.3 × 0.25 × 0.1	0.3 × 0.1 × 0.05
crystal system	Monoclinic	Monoclinic
space group	*P2(1)/c*	*P2(1)/c*
volume (Å^3)	5709.8(1)	6521.8(8)
a (Å)	17.647(2)	20.301(1)
b (Å)	17.840(2)	18.450(1)
c (Å)	18.241(2)	17.415(1)
α (deg)	90	90
β (deg)	96.149(6)	90.816(4)
γ (deg)	90	90
Z	4	4
formula weight (g/mol)	1064.23	1232.53
density (calculated) (Mg/m^3)	1.238	1.257
absorption coefficient (mm^{-1})	0.570	0.572
F_{000}	2288	2656
total no. reflections	35379	27276
unique reflections	11684	13438
R_{int}	0.1186	0.1144
final R indices (I >2σ(I)]	$R_1 = 0.0629$ $wR_2 = 0.1118$	$R_1 = 0.1404$ $wR_2 = 0.3083$
largest diff. peak and hole (e$^-$ A^{-3})	0.630 and -0.485	2.299 and -1.076
GOF	1.007	1.391

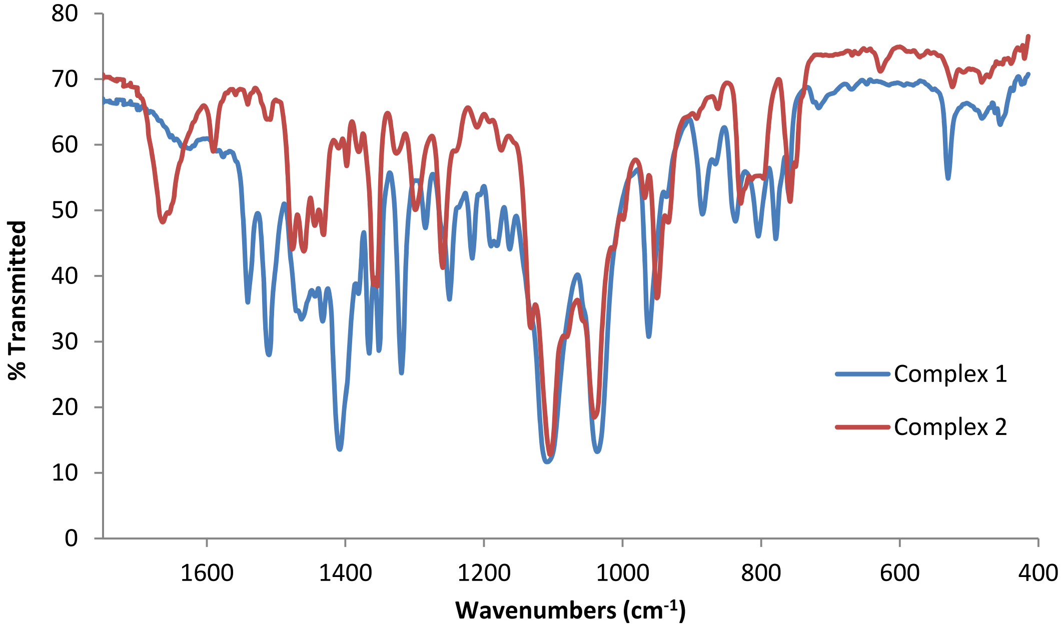

Figure S8. Partial IR spectra of complexes **1-2** (KBr pellets).

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