Supporting Information for:

Synthesis and reactivity of a nickel(II) thioperoxide complex: Demonstration of sulfide-mediated N_2O reduction

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General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, Et_2O, and toluene 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, toluene-d_8, thf-d_8, pentane, and C_8H_{18} (isooctane) were dried over 3 Å molecular sieves for 24 h prior to use. [K(18-crown-6)][$L^{tBu}Ni^{II}$(S,O:κ^2-SNNO)] (**II**), [K(18-crown-6)][$L^{tBu}Ni^{II}$(S)] (**I**), [L^{tBu}NiCl], and $[K]_6[L^{tBu}Ni(\kappa^2\text{-}CO_3)]_6$ were synthesized according to previously reported procedures.[1-3] 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. The chemical shifts of $^{19}F\{^1H\}$ were referenced indirectly with the ^1H resonance of $SiMe_4$ at 0 ppm, according to IUPAC standard.[4,5] IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Synthesis of [L^{tBu}Ni(OTf)]. A 20 mL scintillation vial was charged with a dark green solution of [L^{tBu}NiCl] (41 mg, 0.0688 mmol) in THF (3 mL). To this stirring solution was added solid AgOTf (17.8 mg, 0.688 mmol). After addition, the solution gradually transformed from dark green to bright green in color, concomitant with the deposition of a white precipitate (presumably AgCl). This solution was allowed to stir for 12 h, whereupon the reaction mixture was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). The solution was concentrated to 0.5 mL *in vacuo*, layered with hexane (2 mL), and stored at -25 °C for 24 h, which resulted in the deposition of bright green needles that were isolated by decanting off the supernatant (40 mg, 82% yield). ^{1}H NMR (400 MHz, 25 °C, benzene-d$_6$): δ 7.20 (d, $^3J_{HH}$, = 7.5 Hz, 4H, m-Ar-**H**), 6.81 (t, $^3J_{HH}$, = 7.1 Hz, 2H, o-Ar-**H**), 4.58 (sept, $^3J_{HH}$, = 6.3 Hz, 4H, C**H**(CH$_3$)$_2$), 3.20 (s, 1H, γ-**H**), 2.55 (d, $^3J_{HH}$, = 6.2 Hz, 12H, CH(C**H**$_3$)$_2$), 1.33 (d, $^3J_{HH}$, = 6.1 Hz, 12H, CH(C**H**$_3$)$_2$), 0.83 (s, 18H, C(C**H**$_3$)$_3$) ppm. ^{19}F{^{1}H} NMR (376 MHz, 25 °C, benzene-d$_6$): δ -77.98 (s) ppm. Single crystals of [L^{tBu}Ni(OTf)] were analyzed by X-ray diffraction. This analysis unambiguously confirmed the proposed formulation of the complex, however the crystals were badly twinned, which greatly reduced the data quality. Crystallographic details: Monoclinic, P2$_1$/n, a = 25.044(3), b = 10.7335(15), c = 32.146(4), α = 90, β = 96.992(8), γ = 90, V = 8577(2) g/cm^3, Z = 4.

Synthesis of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (1). In a glovebox, a J-Young NMR tube was charged with a yellow orange solution of [K(18-crown-6)][L^{tBu}Ni(*S,O*:κ$_2$-SNNO)] (**II**) (74 mg, 0.0787 mmol) and toluene-*d$_8$* (1 mL). The NMR tube was then sealed, removed from the glovebox and heated at 45 °C for 6 d in an oil bath, which resulted in a gradual color change from yellow to orange. After 6 d, a ^{1}H NMR spectrum was recorded, which revealed the presence of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**), along with formation of trace amounts of [K(18-crown-6)][L^{tBu}Ni(η^2-OSSO)] (**2**) and [K(18-crown-6)][L^{tBu}Ni(η^2-S$_2$)] (**3**). ^{1}H NMR (400 MHz, 25 °C, toluene-*d$_8$*): δ 7.01-6.73 (**1**, m, 6H, Ar-**H**, dipp), 5.53 (**2**, s, γ-**H**), 5.47 (**3**, s, γ-**H**), 5.43 (**1**, s, 1H, γ-**H**), 4.50 (**1**, sept, $^3J_{HH}$, = 6.7 Hz, 2H, C**H**(CH$_3$)$_2$), 4.38 (**1**, sept, $^3J_{HH}$, = 6.7 Hz, 2H, C**H**(CH$_3$)$_2$), 3.04 (**1**, s, 24H, 18-crown-6), 2.21 (**1**, d, $^3J_{HH}$, = 6.7 Hz, 6H, CH(C**H**$_3$)$_2$), 2.05 (**1**, d, $^3J_{HH}$, = 6.7 Hz, 6H, CH(C**H**$_3$)$_2$), 1.57 (**1**, overlapping doublets, CH(C**H**$_3$)$_2$), 1.30 (**1**, s, 9H, C(C**H**$_3$)$_3$), 1.25 (**1**, s, 9H, C(C**H**$_3$)$_3$). We do not observe any other resonances for **2** and **3** in this spectrum, presumably because they are buried under those of complex **1**. The NMR tube was then transferred to a glovebox, and the reaction mixture was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). The volatiles were removed from the filtrate *in vacuo.* The resulting orange residue was extracted into toluene (1 mL), filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), and concentrated *in vacuo* to ca. 0.5 mL. This solution was then layered with pentane (2 mL) and subsequent storage at -25 °C for 48 h resulted in the deposition of orange plates of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**), which were isolated by decanting off the supernatant (62 mg, 82% yield). In one instance, a few orange plates of [K(18-crown-6)][L^{tBu}Ni(η^2-OSSO)] (**2**) were also isolated from the reaction mixture. These were analyzed by X-ray diffraction. Anal. Calcd for **1**: $C_{47}H_{77}KN_2NiO_7S\cdot C_7H_8$: C, 64.59; H, 8.53; N, 2.79. Found: C, 63.68; H, 8.38; N, 3.01. ^{1}H NMR (400 MHz, 25 °C, benzene-*d_6*): δ 7.01-6.73 (m, 6H, Ar-**H**, dipp), 5.54 (s, 1H, γ-**H**), 4.62 (sept, $^3J_{HH}$, = 6.7 Hz, 2H, C**H**(CH_3)$_2$), 4.48 (sept, $^3J_{HH}$, = 6.7 Hz, 2H, C**H**(CH_3)$_2$), 3.01 (s, 24H, 18-crown-6), 2.31 (d, $^3J_{HH}$, = 6.7 Hz, 6H, CH(C**H**$_3$)$_2$), 2.15 (d, $^3J_{HH}$, = 6.7 Hz, 6H, CH(C**H**$_3$)$_2$), 1.57 (overlapping doublets, 12H, CH(C**H**$_3$)$_2$), 1.37 (s, 9H, C(C**H**$_3$)$_3$), 1.32 (s, 9H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, benzene-*d_6*): δ 164.91 (Ar-C), 163.28 (Ar-C), 155.40 (Ar-C), 150.77 (Ar-C), 142.13 (Ar-C), 140.54 (Ar-C), 122.19 (Ar-C), 120.99 (Ar-C), 97.87 (γ-**C**), 69.78 (18-crown-6), 42.34 (**C**(CH_3)$_3$), 42.31 (**C**(CH_3)$_3$), 33.79 (C(**C**H$_3$)$_3$), 33.66 (C(**C**H$_3$)$_3$), 28.80 (CH(**C**H$_3$)$_2$), 28.64 (CH(**C**H$_3$)$_2$), 26.24 (CH(**C**H$_3$)$_2$), 25.94 (CH(**C**H$_3$)$_2$), 24.66 (**C**H(CH_3)$_2$), 23.70 (**C**H(CH_3)$_2$). IR (KBr Pellet, cm^{-1}): 1535 (m), 1519 (s), 1457 (m), 1429 (m), 1412 (m), 1409 (s), 1385 (m), 1365 (m), 1352 (s), 1321 (s), 1284 (w), 1250 (w), 1214 (w), 1192 (w), 1160 (w), 1110 (s), 1056 (w), 964 (s), 937 (w), 902 (s, ν_{SO}), 896 (w), 839 (m), 819 (w) 804 (w), 779 (m), 759 (m), 728 (w), 669(w), 636 (s), 561 (w), 528 (w).

Synthesis of [K(18-crown-6)][L^{tBu}Ni(η^2-S_2)] (3). A 20 mL scintillation vial was charged with a brown solution of [K(18-crown-6)][L^{tBu}Ni(S)] (**I**) (29.7 mg, 0.0312 mmol) in toluene (1 mL). S_8 (1.0 mg, 0.0038 mmol) was then added to the stirring brown solution, which resulted in a gradual color change from brown to dark orange. The reaction mixture was stirred for 30 min. The reaction mixture was then filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), concentrated *in vacuo* to ca. 0.25 mL, and layered with pentane (1.5 mL). Storage of this vial at -25 °C for 24 h resulted in the deposition of dark yellow plates of [K(18-crown-6)][L^{tBu}Ni(η^2-S_2)] (**3**), which were isolated by decanting off the supernantant (23 mg, 81 %). Anal. Calcd for $C_{47}H_{77}KN_2NiO_6S_2$: C, 60.83; H, 8.36; N, 3.02. Found: C, 60.61; H, 8.18; N, 2.70. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ 7.02-7.00 (m, 6H, Ar-**H**, dipp), 5.56 (s, 1H, γ-**H**), 4.42 (sept, $^3J_{HH}$, = 6.7 Hz, 4H, C**H**($CH_3)_2$), 3.03 (s, 24H, 18-crown-6), 2.25 (d, $^3J_{HH}$, = 6.8 Hz, 12H, CH(C**H**$_3)_2$), 1.54 (d, $^3J_{HH}$, = 6.8 Hz, 12H, CH(C**H**$_3)_2$), 1.36 (s, 18H, C(C**H**$_3)_3$). ^{1}H NMR (400 MHz, 25 °C, Toluene-d_8): δ 7.09-6.92 (m, 6H, Ar-**H**, dipp), 5.46 (s, 1H, γ-**H**), 4.32 (sept, $^3J_{HH}$, = 6.9 Hz, 4H, C**H**($CH_3)_2$), 3.05 (s, 24H, 18-crown-6), 2.17 (d, $^3J_{HH}$, = 6.7 Hz, 12H, CH(C**H**$_3)_2$), 1.51 (d, $^3J_{HH}$, = 6.7 Hz, 12H, CH(C**H**$_3)_2$), 1.30 (s, 18H, C(C**H**$_3)_3$). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, benzene-d_6): δ 140.05 (Ar-C), 137.47 (Ar-C), 128.91 (Ar-C), 125.28 (Ar-C), 98.08 (γ-**C**), 69.56 (18-crown-6), 34.03 (**C**($CH_3)_3$), 33.70 (C(**C**H$_3)_3$), 28.16 (CH(**C**H$_3)_2$), 22.33 (CH(**C**H$_3)_2$), 21.03 (**C**H($CH_3)_2$). IR (KBr Pellet, cm^{-1}): 1535 (m), 1519 (s), 1457 (m), 1429 (m), 1412 (m), 1409 (s), 1385 (m), 1365 (m), 1352 (s), 1321 (s), 1284 (w), 1250 (w), 1214 (w), 1192 (w), 1160 (w), 1110 (s), 1056 (w), 964 (s), 937 (w), 896 (w), 839 (m), 819 (w) 804 (w), 779 (m), 759 (m), 728 (w), 669(w), 541 (w), 528 (w).

Reaction of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (1) with ^{13}CO. In a glovebox, a J-Young NMR tube was charged with a yellow-orange solution of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (12.2 mg, 0.0134 mmol) in C_6D_6 (1 mL). The NMR tube was then sealed and removed from the glovebox. Its headspace was evacuated and replaced with 1 atm of ^{13}CO. Over the course of the reaction, the color gradually lightens from yellow-orange to yellow. After 1 h, a ^{1}H NMR spectrum was recorded, which revealed the presence of the nickel(II) sulfide **I**, ([L^{tBu}Ni(S)]$^-$), an unidentified diamagnetic intermediate, as well as [K(18-crown-6)][L^{tBu}Ni(η^2-SCO)] (**4**), [K(18-crown-6)][L^{tBu}Ni(κ^2-SCO_2)] (**5**), [K(18-crown-6)][L^{tBu}Ni(κ^2-CO_3)] (**6**), and [K(18-crown-6)][L^{tBu}Ni(κ^2-S_2CO)] (**8**). ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$, note: spectral data have only been tabulated for the [K(18-crown-6)][L^{tBu}Ni(S)] intermediate and the region from 5.00-5.75 ppm, which is diagnostic for the γ-H environment of the β-diketiminate ligand): 32.92 ([L^{tBu}Ni(S)]$^-$), 31.91 ([L^{tBu}Ni(S)]$^-$), 8.50 ([L^{tBu}Ni(S)]$^-$), 5.87 ([L^{tBu}Ni(S)]$^-$), 5.62 (s, 1H, γ-**H**, **2**), 5.57 (s, 1H, γ-**H**, **8**, tentative assignment), 5.56 (s, 1H, γ-**H**, **3**), 5.54 (s, 1H, γ-**H**, **1**), 5.48 (s, 1H, γ-**H**, overlapping **4** and **5**), 5.43 (s, 1H, γ-**H**, unidentified diamagnetic intermediate), 5.42 (s, 1H, γ-**H**, **6**), -0.63 ([L^{tBu}Ni(S)]$^-$), -23.24 ([L^{tBu}Ni(S)]$^-$), -130.25 ([L^{tBu}Ni(S)]$^-$). Note that the observation of **2** and **3** in the reaction mixture can be rationalized by their presence, in small amounts, in the starting material. After 6 h, ^{1}H and ^{13}C NMR spectra were recorded. These spectra revealed the absence of [K(18-crown-6)][L^{tBu}Ni(S)] (**I**) and the aforementioned unidentified diamagnetic intermediate. The spectrum also reveals the presence of [K(18-crown-6)][L^{tBu}Ni(η^2-SCO)] (**4**), [K(18-

crown-6)][L^{tBu}Ni(κ^2-SCO$_2$)] (**5**), [K(18-crown-6)][L^{tBu}Ni(κ^2-CO$_3$)] (**6**), COS (**7**), [K(18-crown-6)][L^{tBu}Ni(κ^2-S$_2$CO)] (**8**), as well as two unidentified products. ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$, note: spectral data have only been tabulated for the region from 5.00-5.75 ppm, which is diagnostic for the γ-H environment of the β-diketiminate ligand): 5.62 (s, 1H, γ-**H**, **2**), 5.57 (s, 1H, γ-**H**, **8**, tentative assignment), 5.56 (s, 1H, γ-**H**, **3**), 5.48 (s, 1H, γ-**H**, overlapping **4** and **5**), 5.42 (s, 1H, γ-**H**, **6**). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, benzene-*d*$_6$, note: spectral data have only been tabulated for the region from 140-220 ppm, which is diagnostic for the ^{13}C chemical shifts of $[CO_xS_y]^{2-}$–type species): δ 214.72 ([L^{tBu}Ni(η^2-S**C**O)]$^-$, **4**), 206.88 ([L^{tBu}Ni(S$_2$**C**O)]$^-$, **8**, tentative assignment), 191.38 (unassigned), 184.00 (**C**O), 178.47 (unassigned), 177.30 (([L^{tBu}Ni(κ^2-S**C**O$_2$)]$^-$, **5**, 165.27 ([L^{tBu}Ni(κ^2-**C**O$_3$)]$^-$, **6**), 152.93 (S**C**O, **7**).

Reaction of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (1) with CO, Monitored by IR Spectroscopy. In a glovebox, a J-Young NMR tube was charged with a yellow-orange solution of [K(18-crown-6)][L^{tBu}Ni(SO)] (10.0 mg, 0.0110 mmol) in C$_6$D$_6$ (1 mL). The NMR tube was then sealed and removed from the glovebox. The headspace of the NMR tube was then evacuated and replaced with 1 atm of CO. The reaction was monitored by ^{1}H NMR spectroscopy. During the course of the reaction, the color of the solution gradually lightened to yellow. After 6 h the J-Young tube was then transferred into a glove box, where the solution was transferred into a 20 mL scintillation vial. The volatiles were removed *in vacuo* to yield an orange residue, which was extracted into hexane (0.5 mL) and transferred into a solution IR cell. IR (hexanes solution, cm^{-1}): 2021 (m, L^{tBu}Ni^{I}(CO), **9**),[6] 1666 (m, [L^{tBu}Ni^{II}(η^2-SCO)]$^-$, **4**),[7] 1620 (m, [L^{tBu}Ni^{II}(κ^2-CO$_3$)]$^-$, **6**).

These assignments were confirmed by comparison with IR spectra of authentic samples in hexane.

Synthesis of [K(18-crown-6)][L^{tBu}Ni(κ$_2$-SCO$_2$)] (5). In a glovebox, a J-Young NMR tube was charged with a brown solution of [K(18-crown-6)][L^{tBu}Ni(S)] (**I**) (35.0 mg, 0.0391 mmol) dissolved in C_6D_6 (1 mL). The NMR tube was then sealed, removed from the glovebox, and the headspace of the NMR tube was evacuated and replaced with 1 atm of CO_2. Upon CO_2 addition, the solution quickly changed color to gold. A ^{1}H NMR spectrum was collected, which revealed the clean formation of a new diamagnetic Ni-containing complex. The NMR tube was then transferred to a glove box, and the reaction mixture was transferred into a 20 mL scintillation vial. The volatiles were then removed *in vacuo* to give a pale brown residue. The residue was extracted into toluene (1 mL), filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), and concentrated *in vacuo* to ca. 0.5 mL. This solution was then layered with hexanes (2 mL). Subsequent storage at -25 °C for 48 h resulted in the deposition of pale brown blocks of [K(18-crown-6)][L^{tBu}Ni(η^2-SCO$_2$)] (**5**), which were isolated by decanting off the supernatant (21 mg, 57 %). Anal. Calcd for: $C_{48}H_{77}KN_2NiO_8S\cdot 1.5C_7H_8$: C, 65.17; H, 8.32; N, 2.60. Found: C, 64.70; H, 8.17; N, 2.61. ^{1}H NMR (400 MHz, 25 °C, benzene-*d$_6$*): δ 6.95 (s, 6H, Ar-**H**, dipp), 5.48 (s, 1H, γ-**H**), 4.50 (sept, $^3J_{HH}$, = 6.7 Hz, 4H, C**H**(CH$_3$)$_2$), 3.03 (s, 24H, 18-crown-6), 2.20 (d, $^3J_{HH}$, = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$), 1.51 (d, $^3J_{HH}$, = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$), 1.22 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, benzene-*d$_6$*): δ 177.31 (S**C**O$_2$), 165.85 (Ar-C) , 142.76 (Ar-C), 123.60 (Ar-C), 121.55 (Ar-C), 98.02 (γ-**C**), 69.61 (18-crown-6), 41.68 (**C**(CH$_3$)$_3$), 33.32 (C(**C**H$_3$)$_3$), 28.34 (CH(**C**H$_3$)$_2$), 25.51 (CH(**C**H$_3$)$_2$), 23.94 (**C**H(CH$_3$)$_2$). IR (KBr Pellet, cm^{-1}): 1606 (s, ν_{CO}), 1535 (m), 1519 (s), 1457 (m), 1429 (m), 1412 (m), 1409 (s), 1385 (m), 1365 (m), 1352 (s), 1321 (s), 1284 (w), 1250 (w), 1214 (w), 1205(m), 1180 (w), 1161 (w), 1110 (s), 1056 (w), 964 (s), 937 (w), 896 (w), 839 (m), 819 (w) 804 (w), 779 (m), 759 (m), 728 (w), 669(w), 582 (w), 532 (w), 503 (m).

Synthesis of [K(18-crown-6)][L^{tBu}Ni(κ^2-CO_3)] (6). In a glovebox, a 20 mL scintillation vial was charged with a suspension of $[K]_6[L^{tBu}Ni(\kappa^2\text{-}CO_3)]_6$ (34 mg, 0.00859 mmol) in toluene (2 mL). To this stirring, pale brown suspension was added 18-crown-6 (14 mg, 0.0515 mmol). The solution was stirred for 2 h, whereupon the pale brown solid was completely consumed. The volatiles were then removed *in vacuo* from the pale yellow solution to give a yellow solid. The solid was extracted into pentane (1 mL), filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), and concentrated *in vacuo* to ca. 0.25 mL. Addition of hexamethyldisiloxane (0.5 mL) to this solution, followed by storage at -25 °C for 48 h, resulted in the deposition of colorless crystals of 18-crown-6, which were isolated by decanting off the supernatant. The volatiles were then removed from the supernatant *in vacuo* to give a yellow solid. This solid was extracted into pentane (0.5 mL), filtered through a Celite column supported on glass wool (0.5 cm × 2 cm), concentrated *in vacuo* to ca. 0.25 mL, and transferred to a 5 mL vial. This vial was placed inside a 20 mL scintillation vial. Toluene (2 mL) was then added to the outer vial, which was then sealed. Storage of this two vial system at -25 °C for 96 h resulted in the deposition of yellow plates of [K(18-crown-6)][L^{tBu}Ni(κ^2-CO_3)] (**6**), which were isolated by decanting off the supernatant (8.2 mg, 17% yield). The supernatant was then transferred to a 5 mL vial. This vial was placed inside a 20 mL scintillation vial. Toluene (2 mL) was then added to the outer vial, which was then sealed.

Storage of this two vial system at -25 °C for 10 d resulted in the deposition of a second crop of yellow plates of **6**, which were isolated by decanting off the supernatant (17 mg, overall yield: 52%). ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$): δ 6.96-6.88 (m, 6H, Ar-**H**, dipp), 5.42 (s, 1H, γ-**H**), 4.47 (br s, 4H, C**H**(CH$_3$)$_2$), 3.14 (s, 24H, 18-crown-6), 2.14 (br s, 12H, CH(C**H**$_3$)$_2$), 1.50 (d, $^3J_{HH}$, = 5.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.15 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, 25 °C, benzene-*d*$_6$): δ 165.74 (Ar-C), 165.29 (**C**O$_3^{2-}$), 146.21 (Ar-C), 142.27 (Ar-C), 123.76 (Ar-C), 121.30 (Ar-C), 97.76 (γ-**C**), 69.75 (18-crown-6), 41.09 (**C**(CH$_3$)$_3$), 32.99 (C(**C**H$_3$)$_3$), 28.41 (CH(**C**H$_3$)$_2$), 25.34 (CH(**C**H$_3$)$_2$), 23.40 (**C**H(CH$_3$)$_2$). IR (hexanes solution, cm^{-1}): 1620 (ν_{CO}).

Synthesis of [K(18-crown-6)][L^{tBu}Ni(η^2-CO$_2$)] (10). In a glovebox, a 20 mL scintillation vial was charged with a suspension of [L^{tBu}Ni(OTf)] (87 mg, 0.113 mmol) in hexane (5 mL). To this stirring bright green suspension was added KC$_8$ (45.7 mg, 0.338 mmol), which resulted in a rapid color change to deep red and then more slowly to deep purple, concomitant with dissolution of the solid. The deep purple color is indicative of the formation of K$_2$[{L^{tBu}Ni}$_2$(N$_2$)].[6] This solution was stirred for 48 h, whereupon it was then filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) into a 50 mL Schlenk flask equipped with a Teflon rotoflow valve, a ground glass joint with a rubber septum, and a magnetic stir bar. The Schlenk flask was then sealed, removed from the glovebox, and attached to a Schlenk line in a fume hood. Carbon dioxide (2.5 mL, 0.113 mmol) was injected into the stirring solution using an airtight syringe. Upon addition, the deep purple reaction mixture quickly changed to deep red and then to pale orange. After 5 min, the Schlenk flask was transferred to a glove box, where a solution of 18-crown-6 (29.8 mg, 0.113 mmol) in hexane (1 mL) was added to the reaction mixture.

This addition resulted in the deposition of a small amount of orange solid, but there was no obvious color change. The reaction mixture was then filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) and concentrated *in vacuo* to ca. 1 mL. Benzene (0.25 mL) was then added to this solution as a crystallization aid. Storage of this solution at -25 °C for 48 h resulted in the deposition of a pale orange plates of [K(18-crown-6)][$L^{tBu}Ni(\eta^2-CO_2)$] (**10**), which were isolated by decanting off the supernatant (33 mg, yield 41%). Anal. Calcd for: $C_{48}H_{77}KN_2NiO_8 \cdot C_6H_6$: C, 65.78; H, 8.48; N, 2.84. Found: C, 65.99; H, 8.68; N, 2.76. ^1H NMR (400 MHz, 25 °C, benzene-*d$_6$*): δ 7.11-6.81 (m, 6H, Ar-**H**, dipp), 5.42 (s, 1H, γ-**H**), 4.37 (sept, $^3J_{HH}$, = 6.7 Hz, 2H, C**H**(CH_3)$_2$), 4.26 (sept, $^3J_{HH}$, = 6.7 Hz, 2H, C**H**(CH_3)$_2$), 2.99 (s, 24H, 18-crown-6), 1.96 (d, $^3J_{HH}$, = 6.8 Hz, 6H, CH(C**H**$_3$)$_2$), 1.86 (d, $^3J_{HH}$, = 6.8 Hz, 6H, CH(C**H**$_3$)$_2$), 1.56 (overlapping doublets, 12H, CH(C**H**$_3$)$_2$), 1.42 (s, 9H, C(C**H**$_3$)$_3$), 1.34 (s, 9H, C(C**H**$_3$)$_3$). $^{13}C\{^1H\}$ NMR (125 MHz, 25 °C, benzene-*d$_6$*): δ 167.23 (**C**O$_2$) 165.74 (Ar-C), 163.83 (Ar-C), 153.43 (Ar-C), 149.49 (Ar-C), 141.42 (Ar-C), 139.56 (Ar-C), 121.99 (Ar-C), 121.67 (Ar-C), 121.63 (Ar-C), 121.29 (Ar-C), 95.22 (γ-**C**), 69.64 (18-crown-6), 42.47 (**C**(CH_3)$_3$), 42.21 (**C**(CH_3)$_3$), 33.58 (C(**C**H$_3$)$_3$), 33.08 (C(**C**H$_3$)$_3$), 28.04 (CH(**C**H$_3$)$_2$), 27.83 (CH(**C**H$_3$)$_2$), 26.01 (CH(**C**H$_3$)$_2$), 24.10 (CH(**C**H$_3$)$_2$), 23.82 (**C**H(CH_3)$_2$), 23.37 (**C**H(CH_3)$_2$). IR (KBr Pellet, cm^{-1}): 1664 (m, ν_{CO}), 1618 (m), 1514 (m), 1464 (m), 1446 (m), 1433 (m), 1414 (s), 1381 (m), 1365 (m), 1352 (m), 1321 (m), 1284 (w), 1252 (w), 1221 (w), 1196 (w), 1159 (w), 1113 (s), 1055 (w), 1032 (w), 962 (m), 937 (w), 896 (w), 983 (m), 831 (w) 804 (w), 779 (m), 766 (m), 758 (m), 728 (w), 681(w).

Reaction of [K(18-crown-6)][$L^{tBu}Ni(\eta^2-SO)$] (1) with CO_2, Monitored by ^1H NMR Spectroscopy. In a glovebox, a J-Young NMR tube was charged with a yellow-orange solution of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (10.0 mg, 0.0110 mmol) in C_6D_6 (0.6 mL). The NMR tube was then sealed and removed from the glovebox. The headspace of the NMR tube was evacuated and replaced with 1 atm of CO_2. Upon addition of CO_2, the color of the solution lightened slightly to pale yellow. A ^{1}H NMR spectrum was taken after 10 min, which revealed complete consumption of complex **1** and clean formation of a single new diamagnetic product, which we have tentatively assigned as the monothiopercarbonate complex [K(18-crown-6)][L^{tBu}Ni(κ^2-SOCO$_2$)] (**11**). (400 MHz, 25 °C, benzene-*d*$_6$): δ 7.20 (d, $^3J_{HH}$, = 7.6 Hz, 4H, meta-Ar-**H**, dipp), 6.89 (t, $^3J_{HH}$, = 7.5 Hz, 2H, para-Ar-**H**, dipp), 4.62 (sept, $^3J_{HH}$, = 6.6Hz, 4H, C**H**(CH$_3$)$_2$), 4.49 (s, 1H, γ-**H**), 2.99 (s, 24H, 18-crown-6), 2.37 (d, $^3J_{HH}$, = 6.3 Hz, 12H, CH(C**H**$_3$)$_2$), 1.52 (d, $^3J_{HH}$, = 6.6 Hz, 12H, CH(C**H**$_3$)$_2$), 1.20 (s, 18H, C(C**H**$_3$)$_3$).

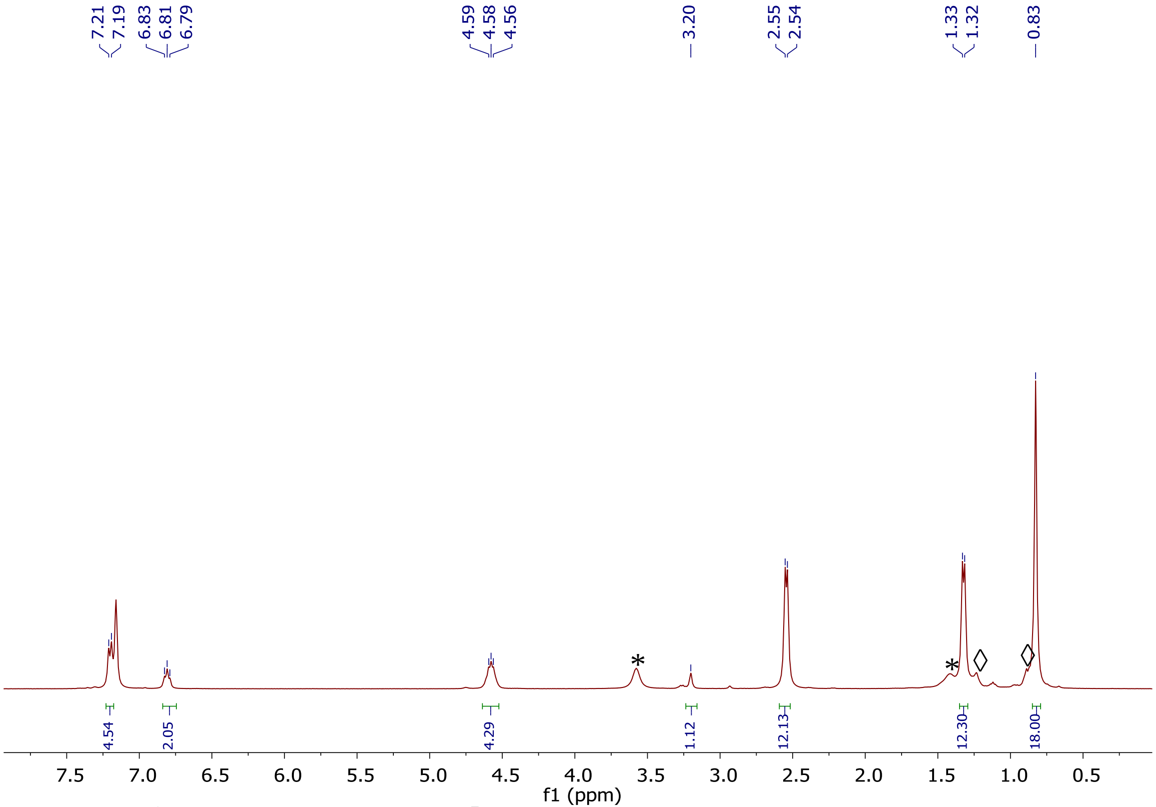

Figure S1. ^{1}H NMR spectrum of [L^{tBu}Ni(OTf)] in benzene-d_6. (*) indicates the presence of THF, (◊) indicates the presence of hexane.

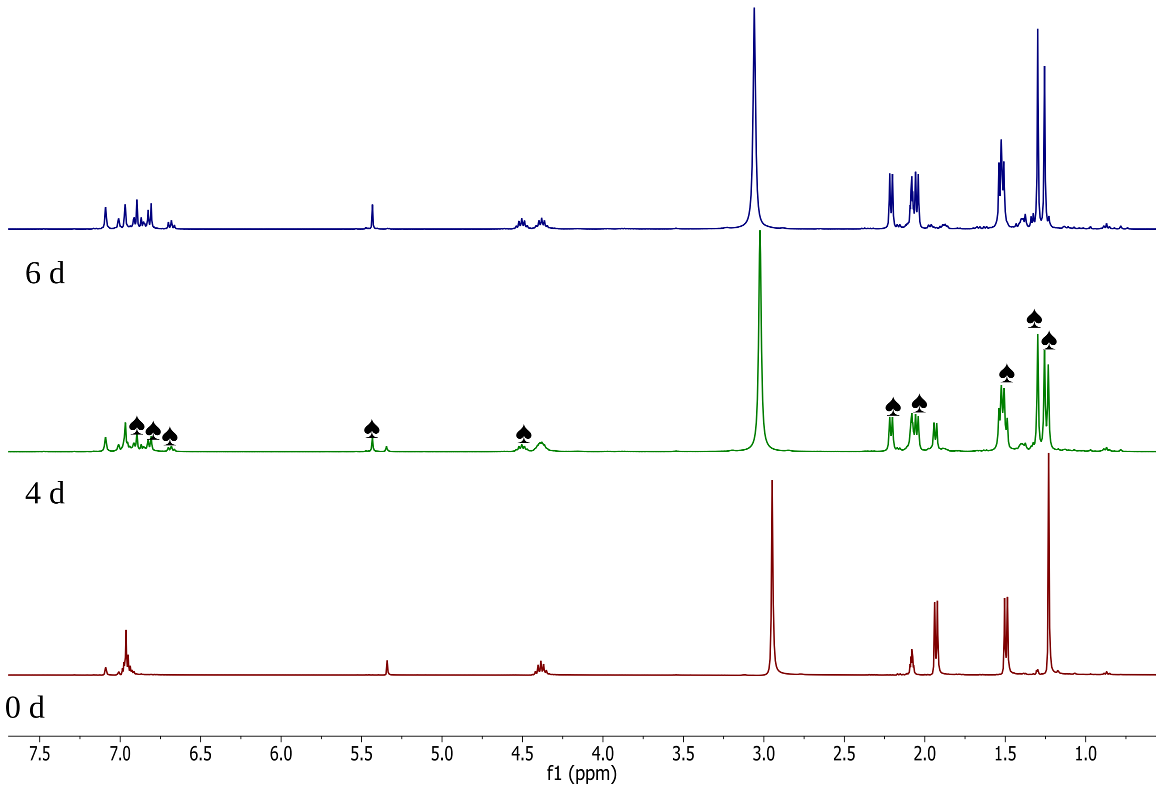

Figure S2. ^{1}H NMR spectra of the thermolysis of [K(18-crown-6)][L^{tBu}Ni(S,O:κ^2-SNNO)] (**II**) to form [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**) in toluene-d_8 at 45 °C. (♠) indicates the presence of **1**.

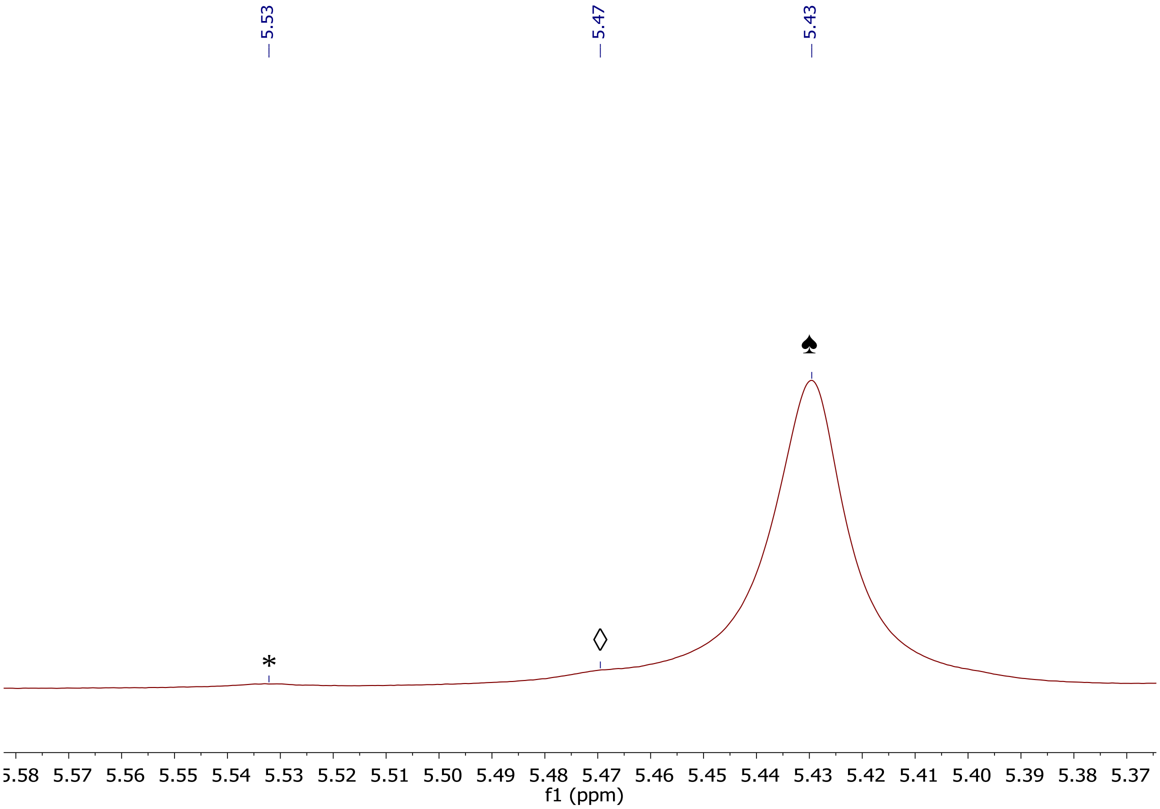

Figure S3. Partial ^{1}H NMR spectra of the thermolysis of [K(18-crown-6)][L^{tBu}Ni(*S*,*O*:κ^2-SNNO)] (**II**) to form [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**) after 6 days in toluene-d_8. (♠) indicates the presence of **1**, (*) indicates the presence of **2**, and (◊) indicates the presence of **3**.

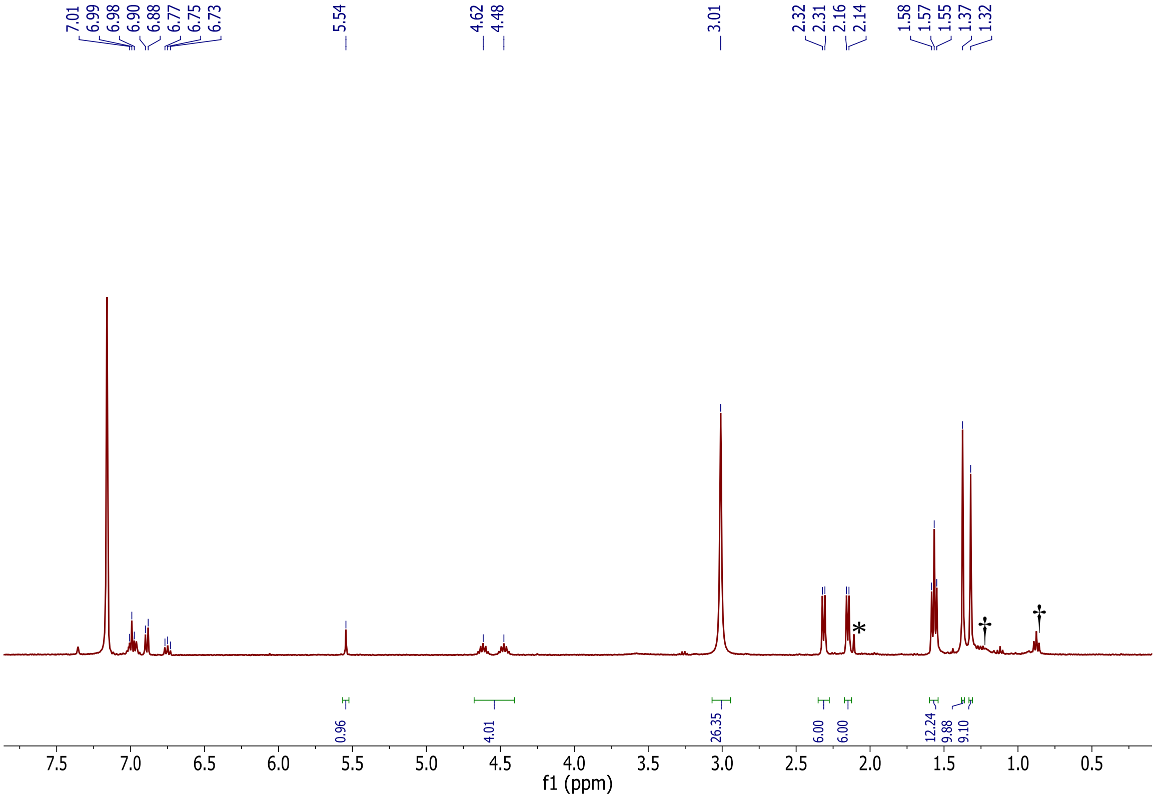

Figure S4. ^{1}H NMR spectrum of [K(18-crown-6)][L$^{\mathrm{tBu}}$Ni(SO)] (**1**) in benzene-d_6. (*) indicates the presence of toluene, and (†) indicates the presence of pentane.

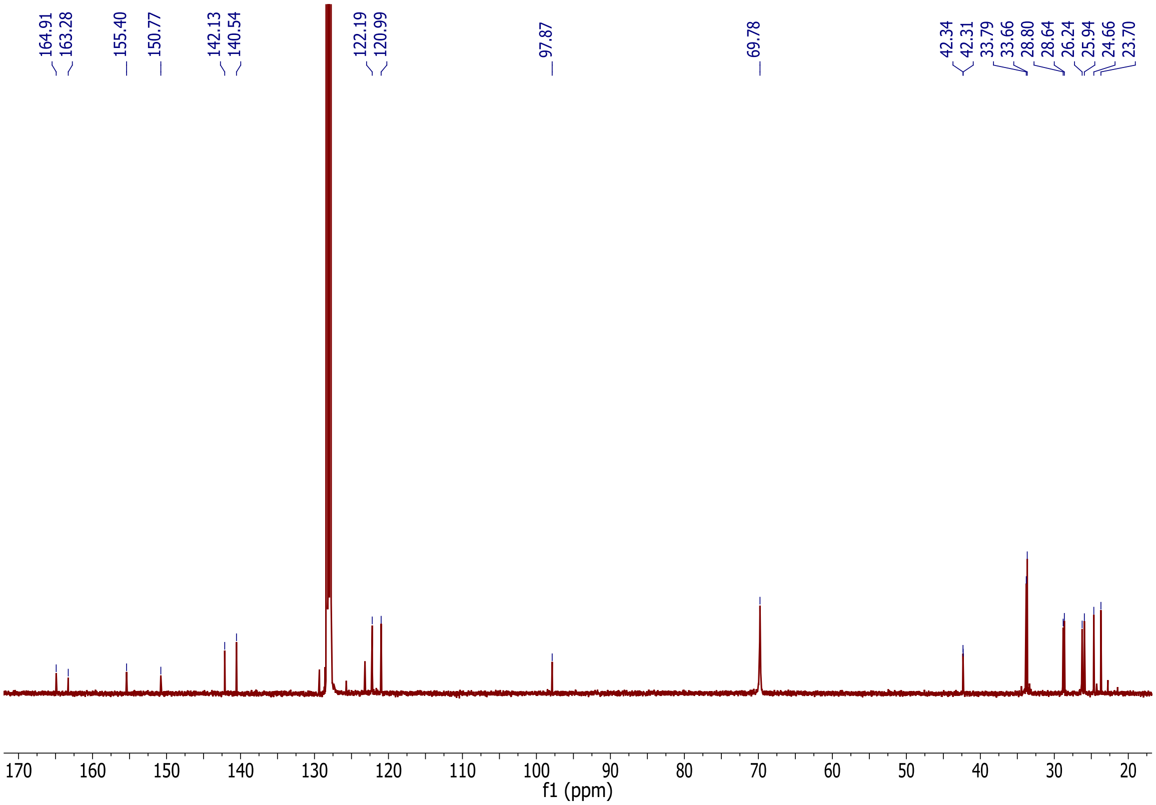

Figure S5. $^{13}C\{^1H\}$ NMR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\eta^2$-SO)] (**1**) in benzene-*d*$_6$.

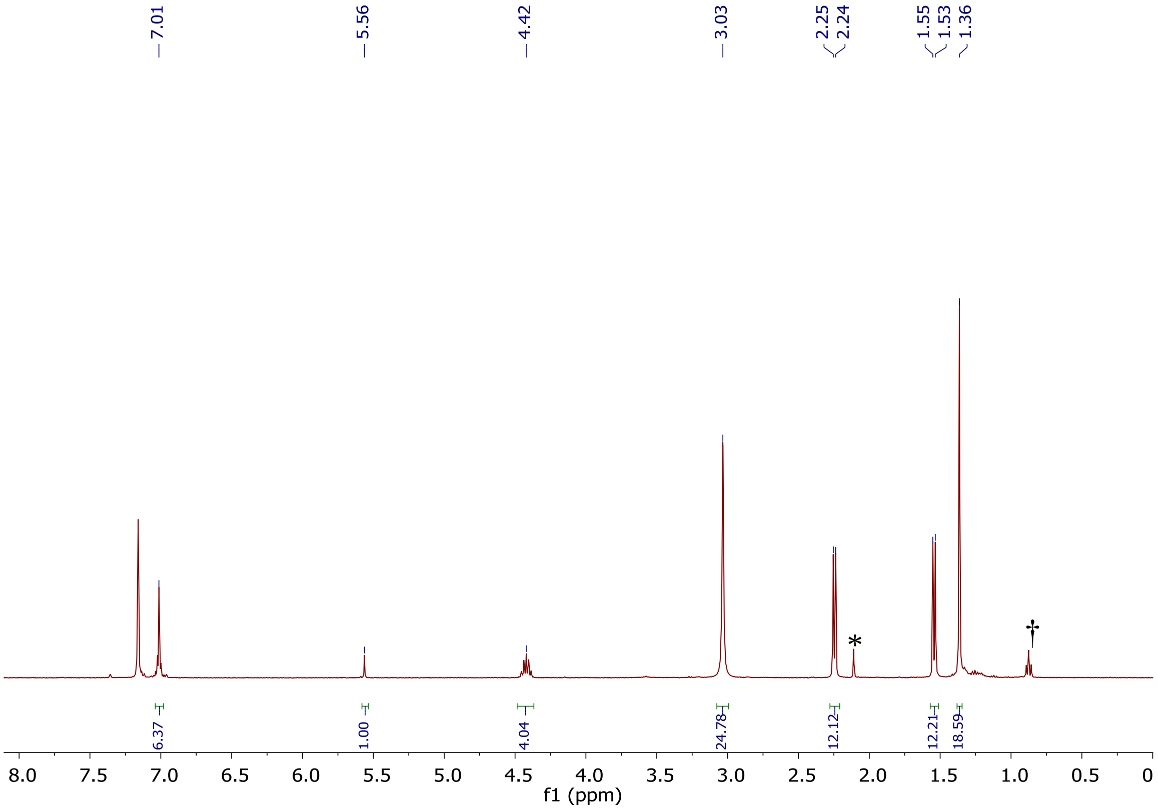

Figure S6. ^{1}H NMR spectrum of [K(18-crown-6)][L$^{\mathrm{tBu}}$Ni(η^2-S_2)] (**3**) in benzene-d_6. (*) indicates the presence of toluene, and (†) indicates the presence of pentane.

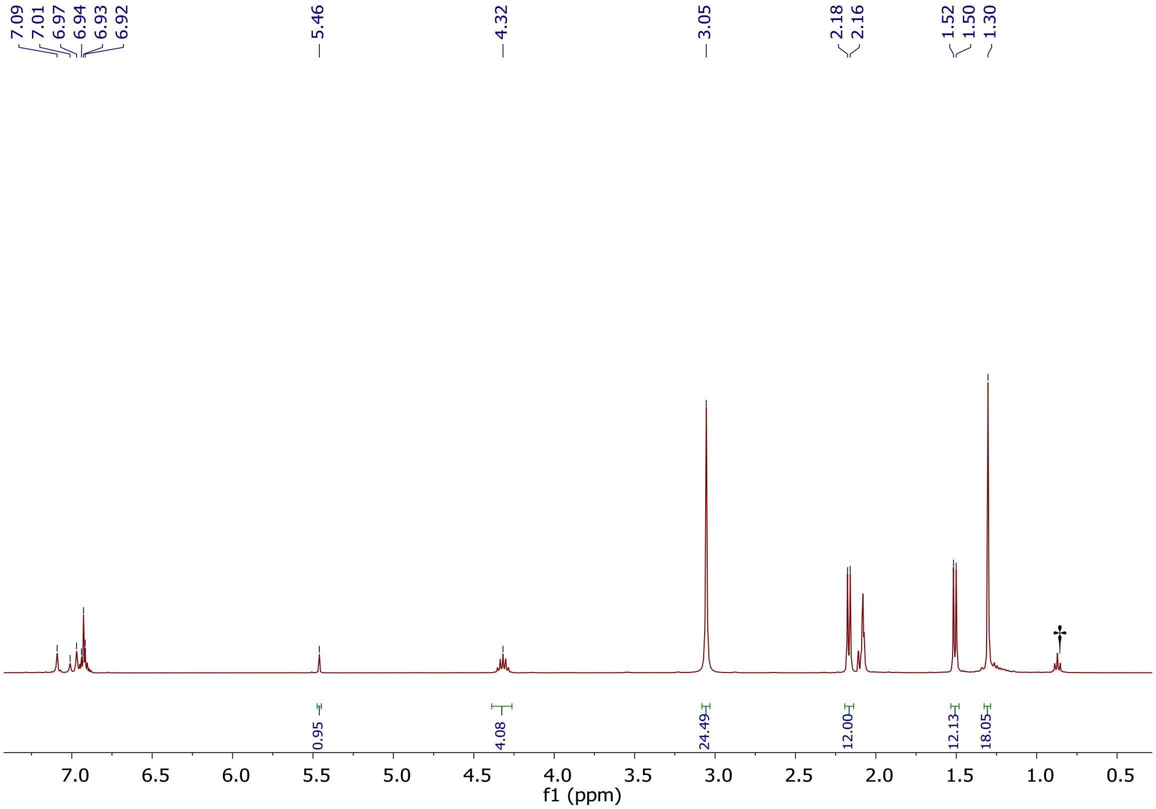

Figure S7. ^{1}H NMR spectrum of [K(18-crown-6)][L^{tBu}Ni(η^2-S$_2$)] (**3**) in toluene-*d*$_8$. (†) indicates the presence of pentane.

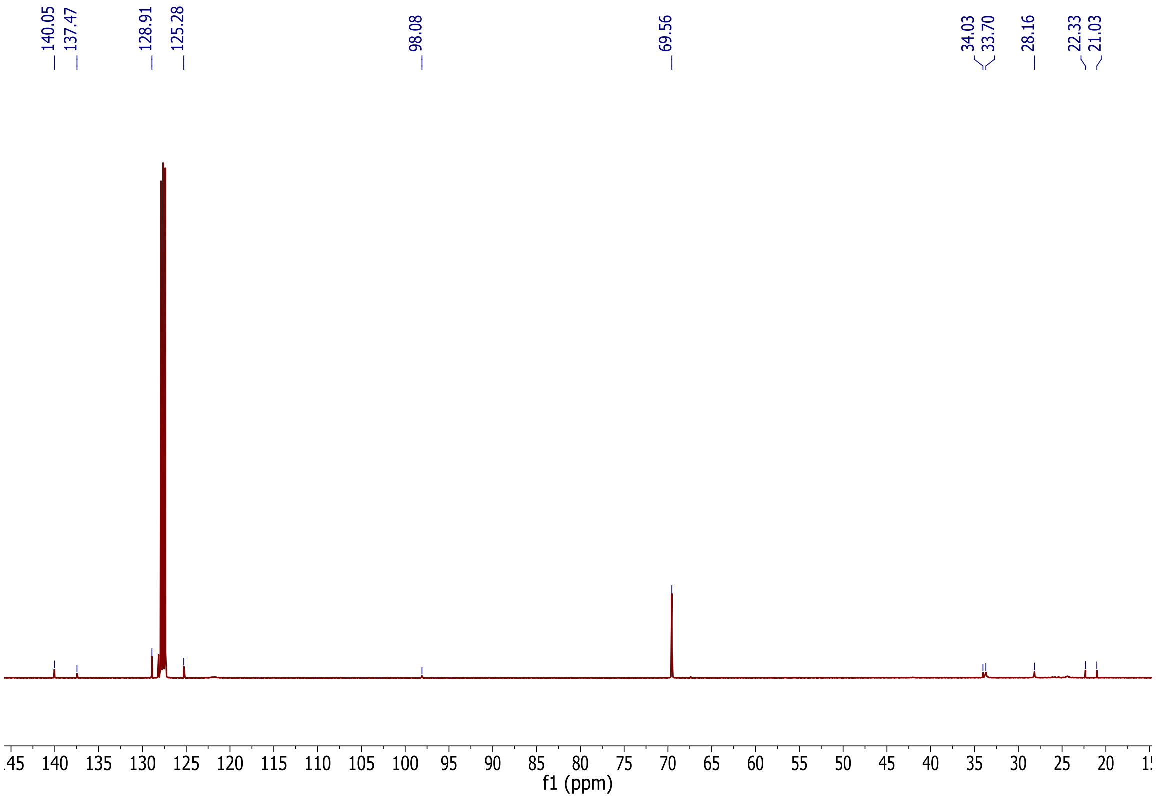

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\eta^2-S_2)$] (**3**) in benzene-d_6.

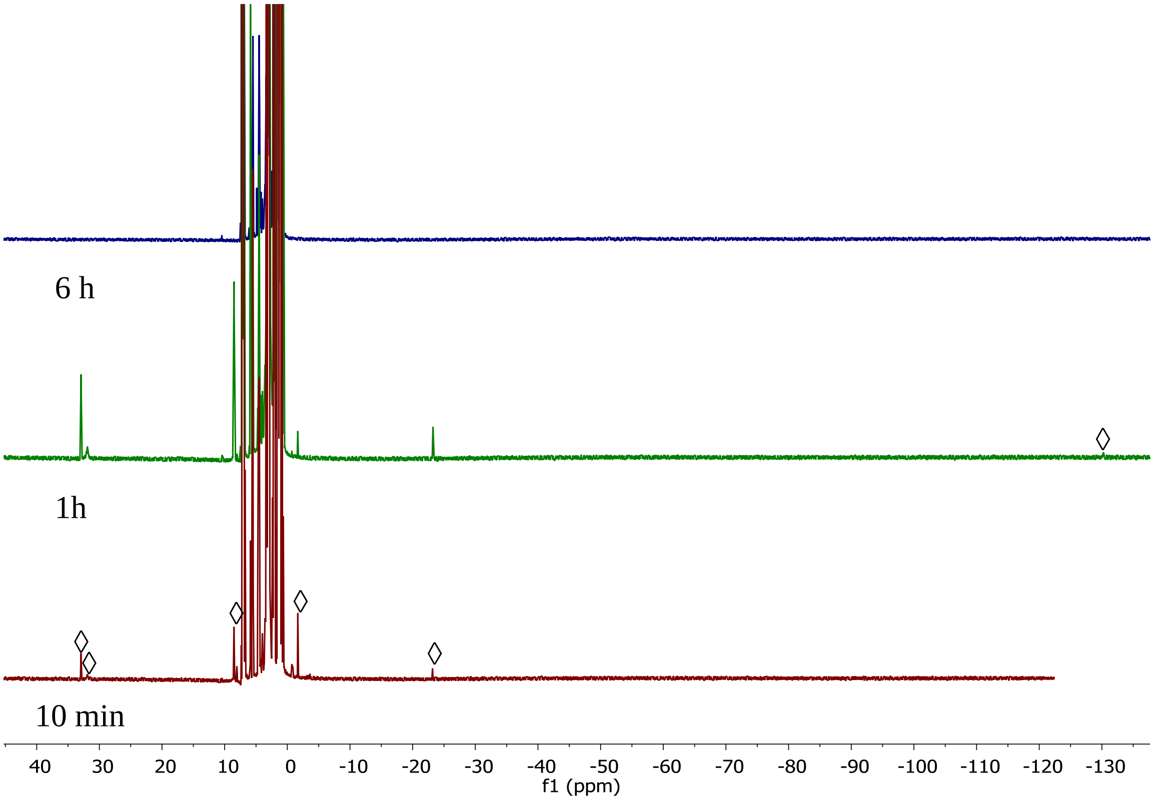

Figure S9. Partial ^{1}H NMR spectra of the reaction of [K(18-crown-6)][L^{tBu}Ni(η^{2}-SO)] (**1**) with ^{13}CO in C_6D_6. (◊) indicates the presence of a [K(18-crown-6)][L^{tBu}Ni(S)] (**I**).

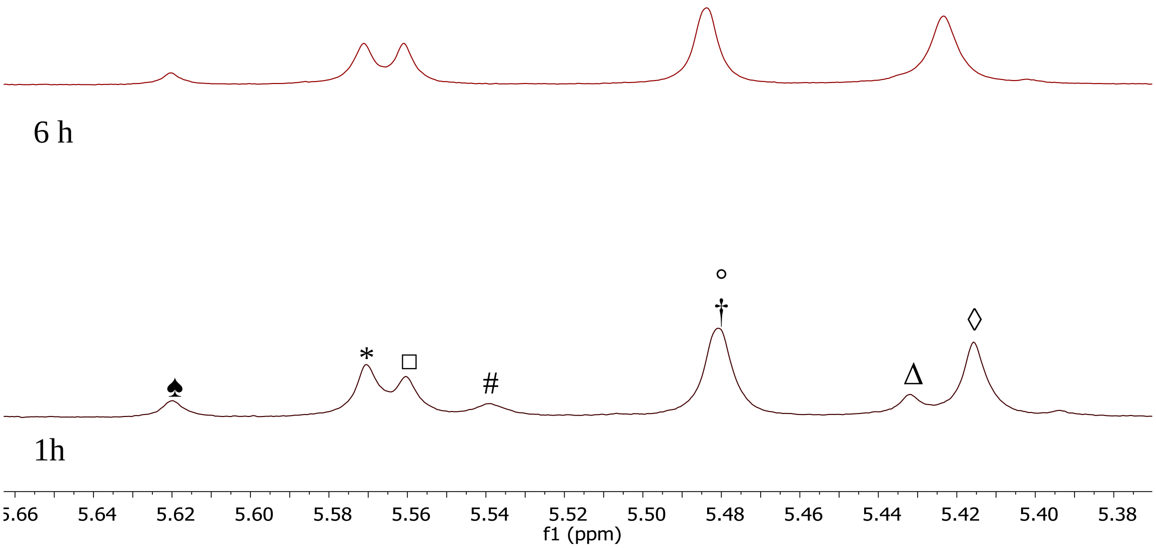

Figure S10. Partial ^{1}H NMR spectra of the reaction of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**) with ^{13}CO in C_6D_6. (#) indicates the presence of **1**, (♠) indicates the presence of **2**, (□) indicates the presence of **3**, (°) indicates the presence of [K(18-crown-6)][L^{tBu}Ni(η^2-SCO)] (**4**), (†) indicates the presence of [K(18-crown-6)][L^{tBu}Ni(κ^2-SCO$_2$)] (**5**), (◊) indicates the presence of [K(18-crown-6)][L^{tBu}Ni(κ^2-CO$_3$)] (**6**), (*) has been tentatively assigned to [K(18-crown-6)][L^{tBu}Ni(κ^2-S$_2$CO)] (**8**), and (Δ) indicates the presence of an unidentified diamagnetic intermediate.

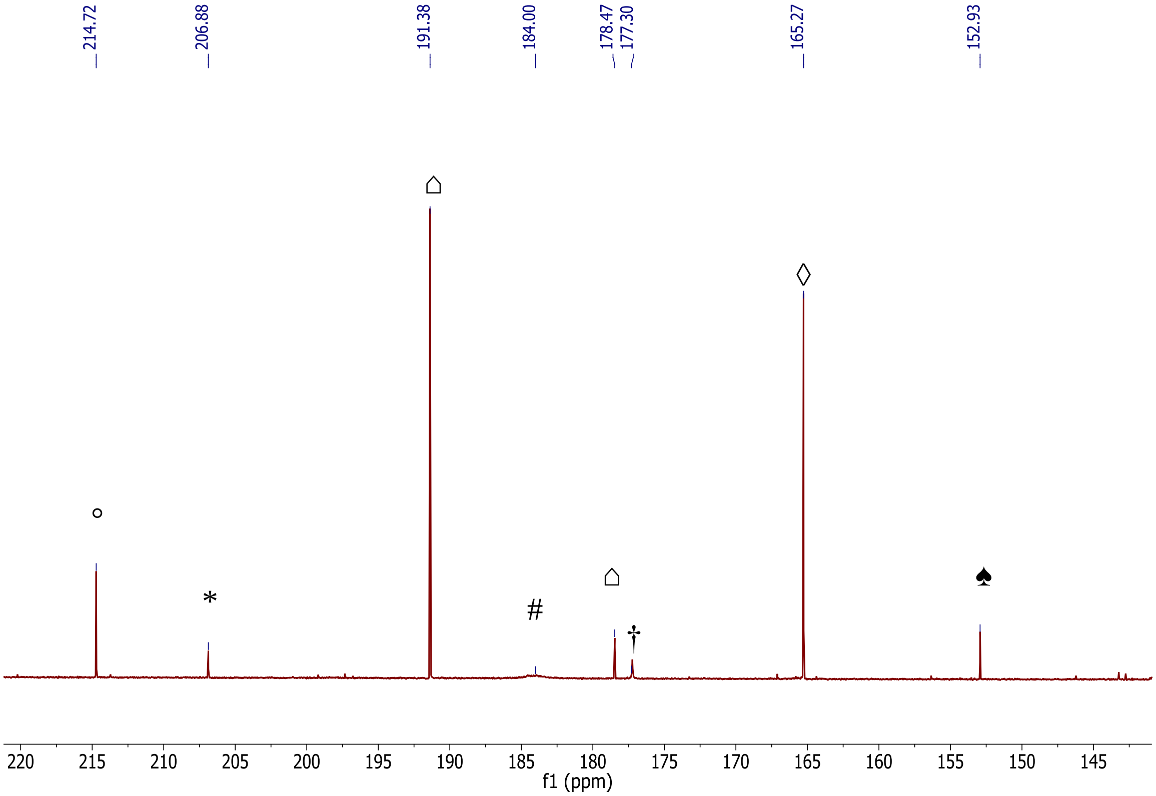

Figure S11. Partial $^{13}C\{^1H\}$ NMR spectrum of the reaction of [K(18-crown-6)][$L^{tBu}Ni(\eta^2\text{-}SO)$] (**1**) with ^{13}CO in C_6D_6 after 6 h. (†) indicates the presence of [K(18-crown-6)][$L^{tBu}Ni(\kappa^2\text{-}SCO_2)$] (**5**), (◊) indicates the presence of [K(18-crown-6)][$L^{tBu}Ni(\kappa^2\text{-}CO_3)$] (**6**), (°) indicates the presence of [K(18-crown-6)][$L^{tBu}Ni(\eta^2\text{-}SCO)$] (**4**), (♠) indicates the presence of SCO (**7**),[8] (#) indicates the presence of ^{13}CO, and (⌂) indicates the presence of unidentified products. (*) has been tentatively assigned to [K(18-crown-6)][$L^{tBu}Ni(\kappa^2\text{-}S_2CO)$] (**8**).

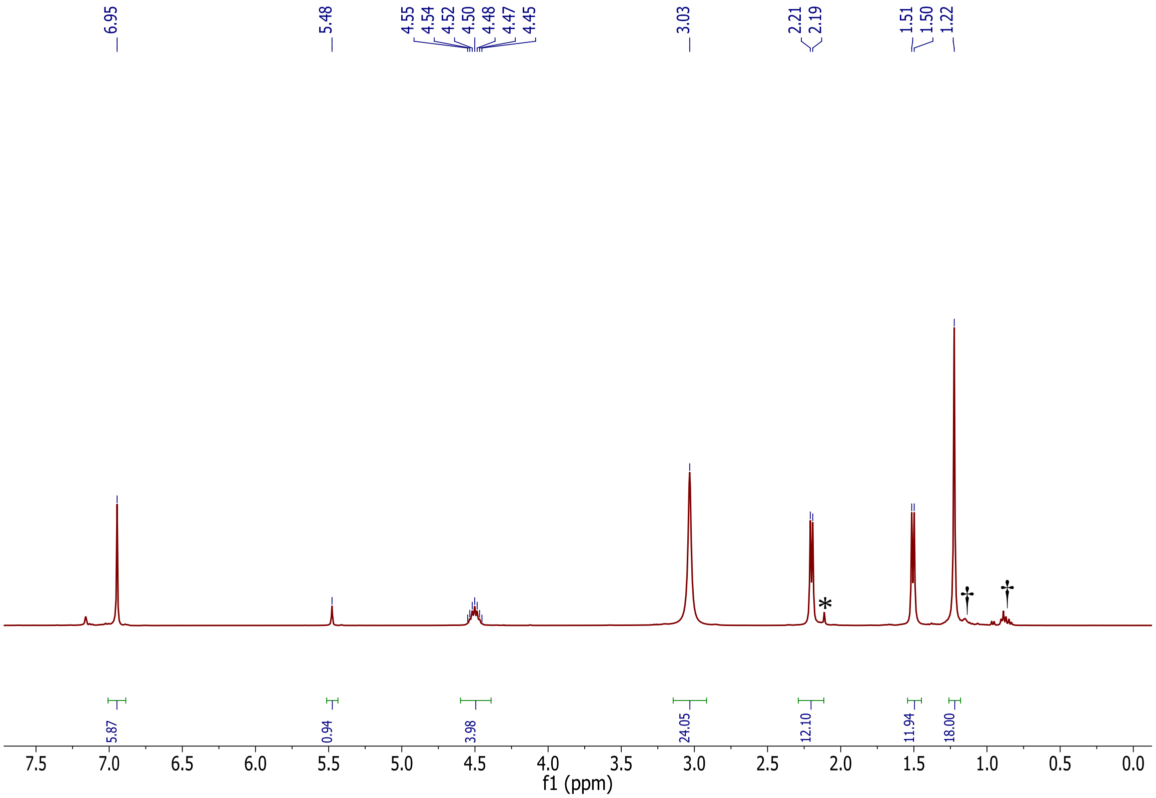

Figure S12. ^{1}H NMR spectrum of [K(18-crown-6)][L^{tBu}Ni(κ^2-SCO$_2$)] (**5**) in benzene-*d*$_6$. (*) indicates the presence of toluene, and (†) indicates the presence of pentane.

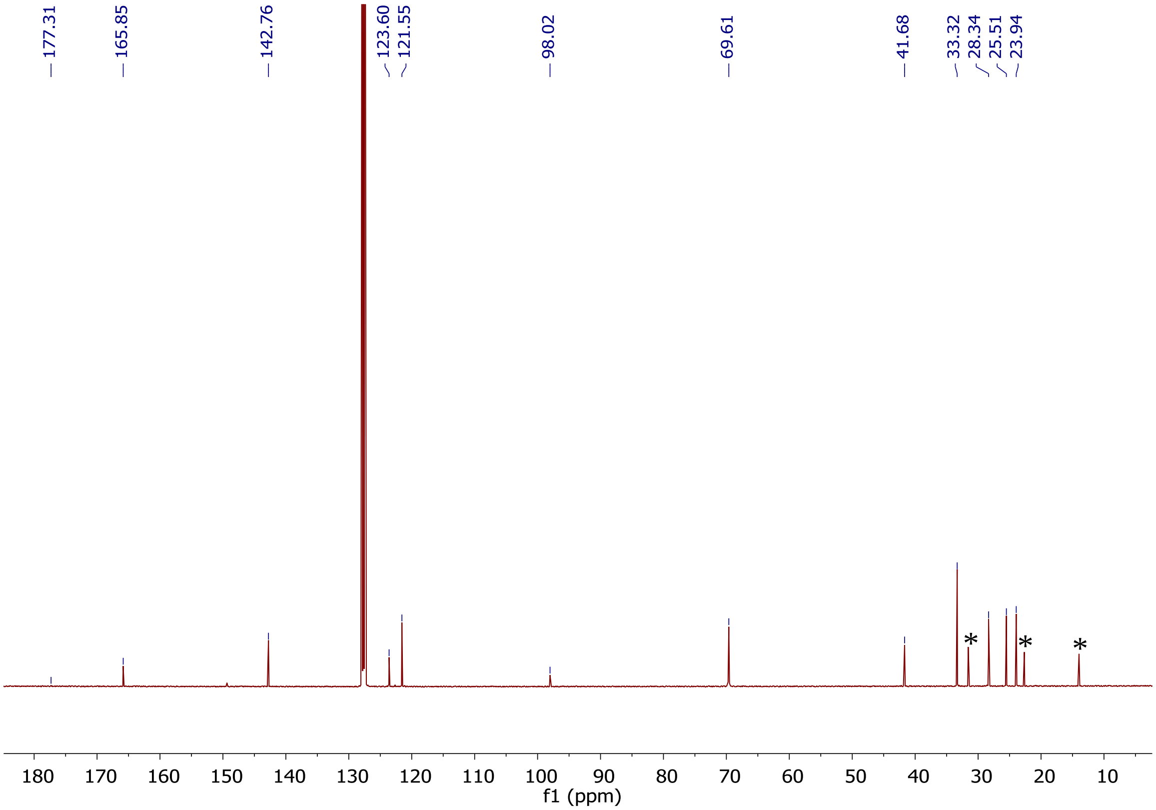

Figure S13. $^{13}C\{^1H\}$ NMR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\kappa^2-SCO_2)$] (**5**) in benzene-$d_6$. (*) indicates the presence of hexane.

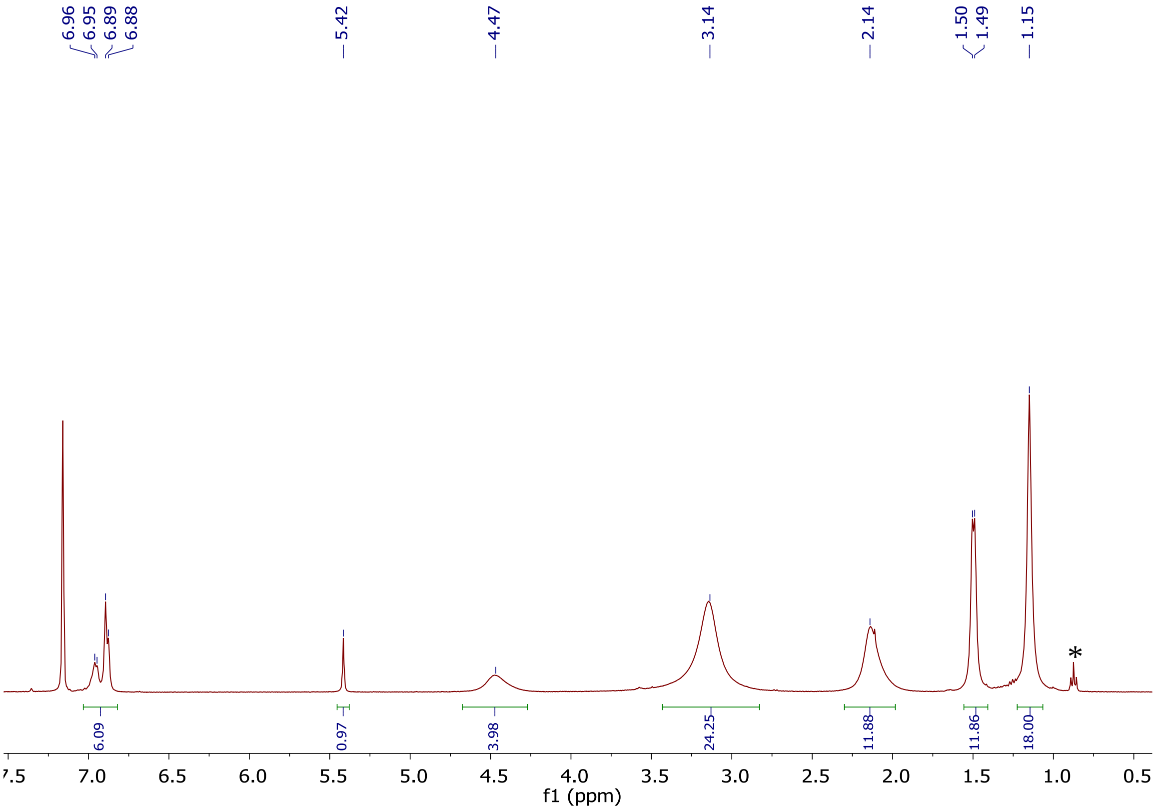

Figure S14. ^{1}H NMR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\kappa^2-CO_3)$] (**6**) in benzene-d_6. (*) indicates the presence of pentane.

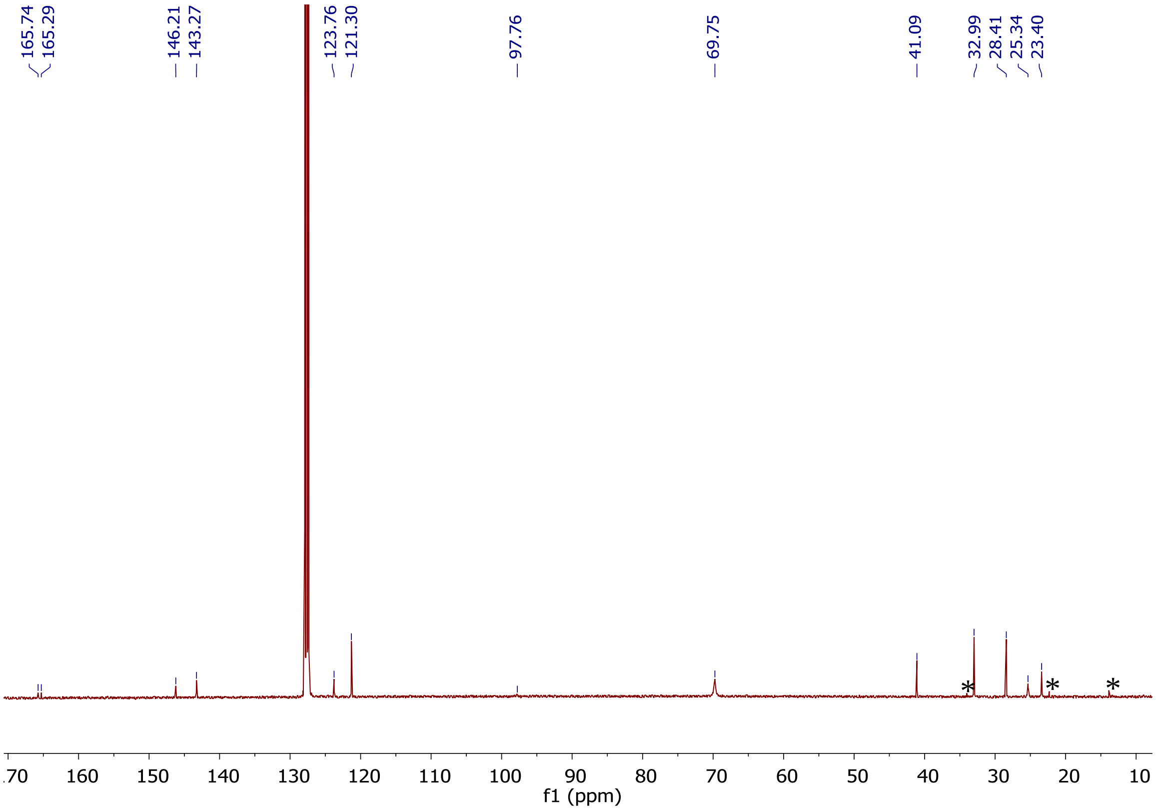

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of $[K(18\text{-crown-}6)][L^{tBu}Ni(\kappa^{2}\text{-}CO_3)]$ (**6**) in benzene-d_6. (*) indicates the presence of pentane.

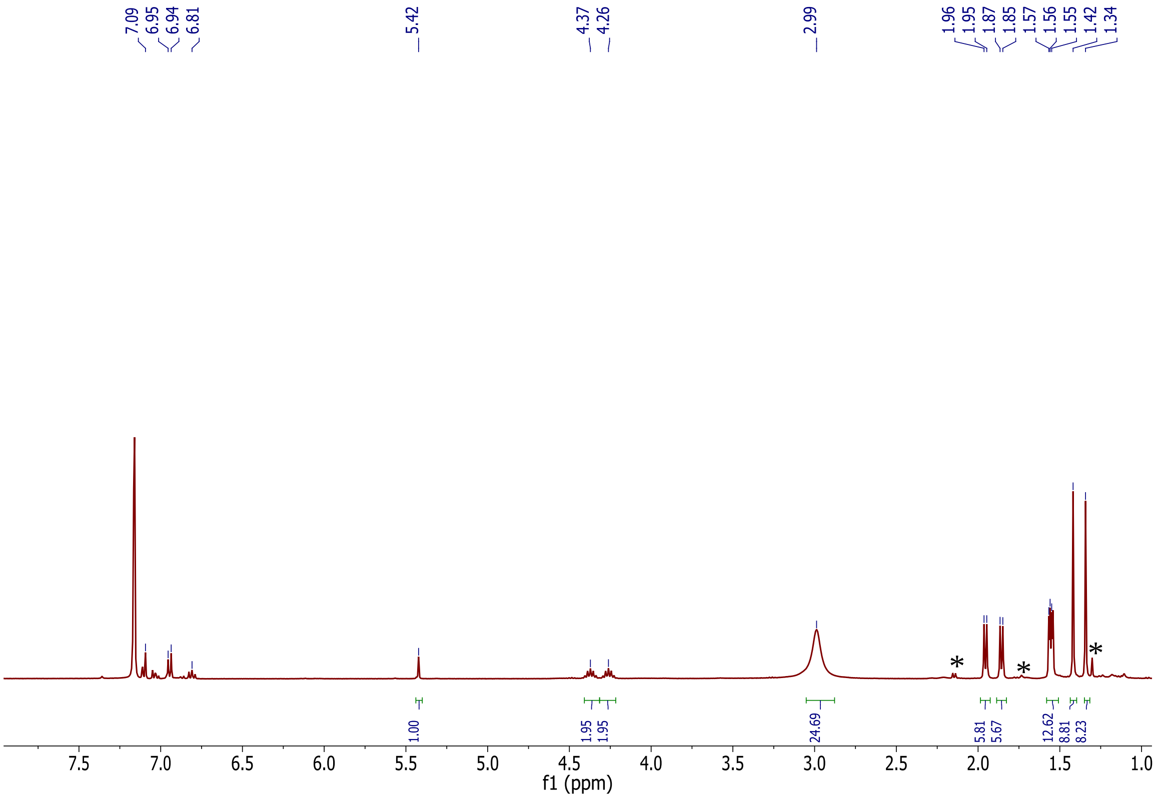

Figure S16. ^{1}H NMR spectrum of [K(18-crown-6)][L^{tBu}Ni(η^2-CO$_2$)] (**10**) in benzene-d_6. (*) indicates the presence of trace unidentified diamagnetic impurities.

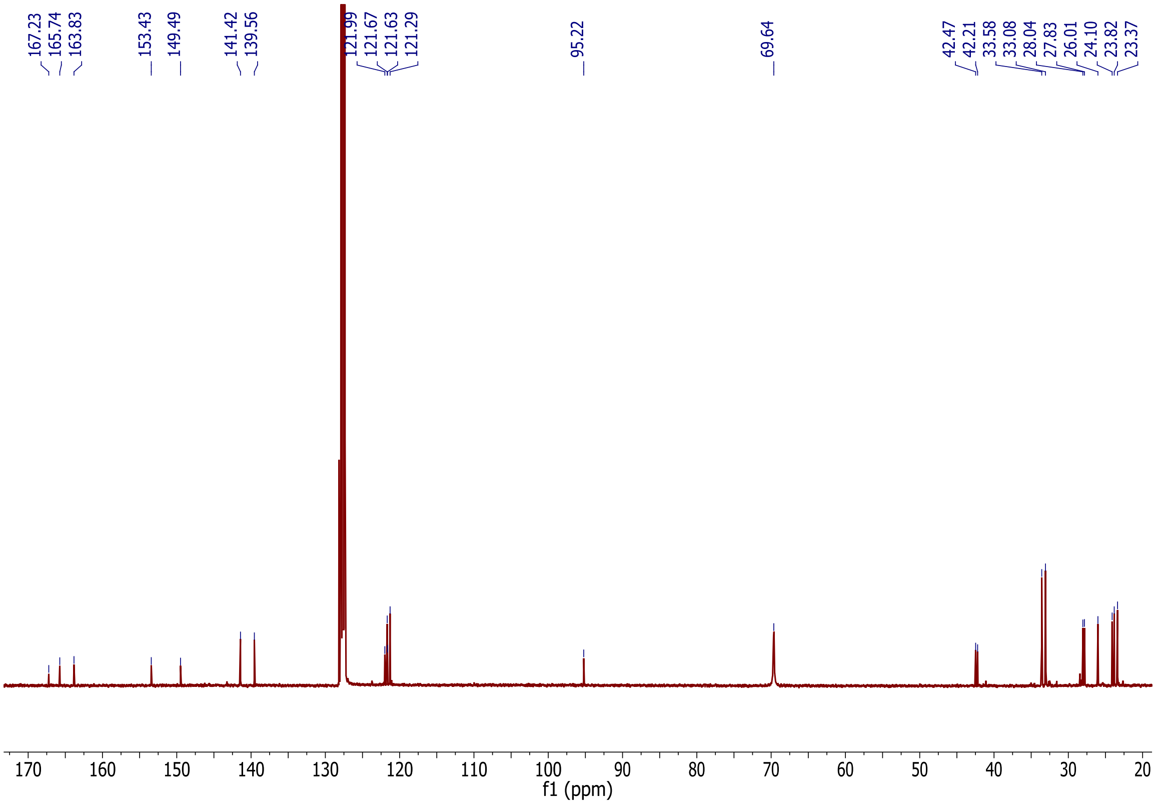

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\eta^{2}\text{-}CO_{2})$] (**10**) in benzene-$d_6$.

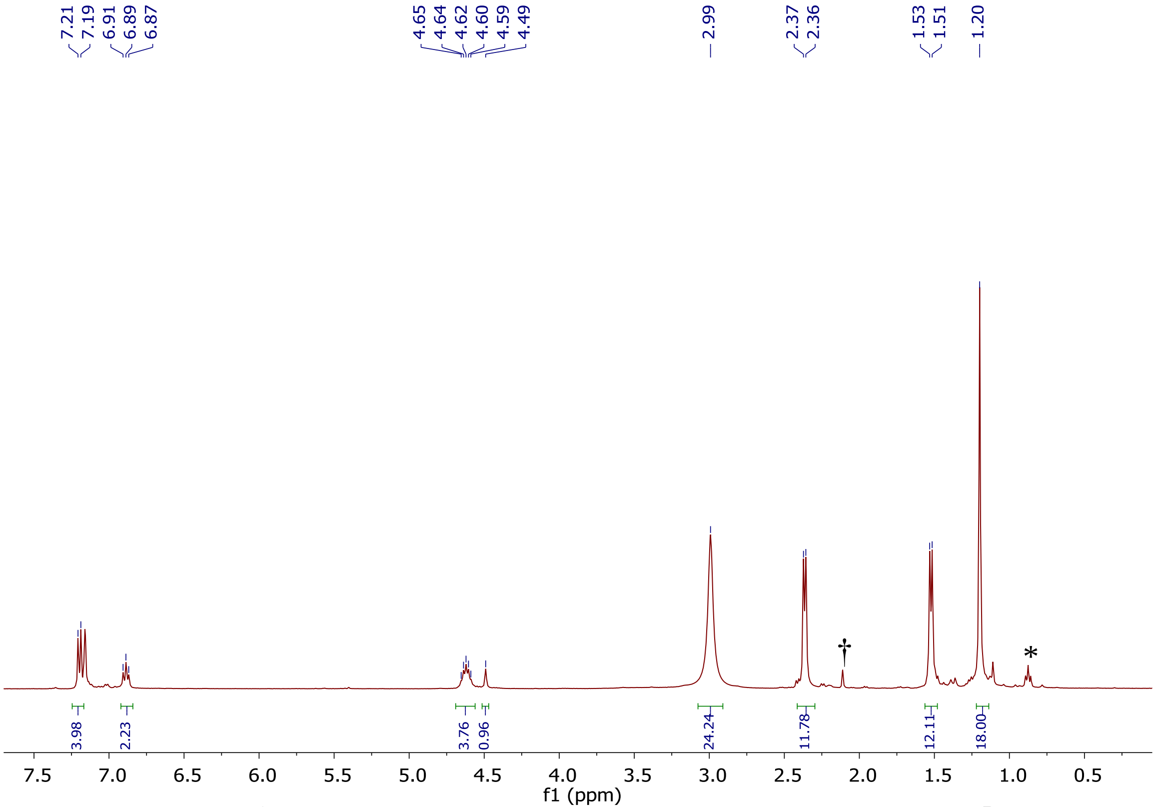

Figure S18. *In situ* ^{1}H NMR spectrum of the reaction of [K(18-crown-6)][L^{tBu}Ni(SO)] (**1**) with CO_2 in benzene-d_6. (*) indicates the presence of pentane, (†) indicates the presence of toluene.

X-ray Crystallography. Data for **1-3**, **5**, **6**, and **10** 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 15 seconds were used for all six crystals. Data collection and cell parameter determinations were conducted using the SMART program.[9] Integration of the data frames and final cell parameter refinements were performed using SAINT software.[10] Absorption correction of the data was carried out using the multi-scan method SADABS.[11] Subsequent calculations were carried out using SHELXTL.[12] 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. However, hydrogen atoms were not added to disordered carbon atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[12]

For complex **1**, the C_7H_8 solvate molecule is disordered over two positions, which were related by a 180° rotation. These two orientations were modeled in a 51:49 ratio using the FVAR command in SHELXL. The C-C bonds in the C_7H_8 molecules were constrained to 1.4 or 1.5 Å, for the double and single bonds, respectively, using the DFIX command. Additionally, one of the O atoms, and the two adjacent C atoms on the 18-crown-6 ring, were found to be disordered over two positions. These disordered atoms were modeled in a 50:50 ratio. Hydrogen atoms were not added to the carbon atoms that were adjacent to the disordered carbons. Additionally, the $[SO]^{2-}$ ligand in **1** was found to be disordered over two positions in a 97:3 ratio, which are related by a C_2 rotation about the Ni-K axis. The relative occupancy of these two orientations was determined with the FVAR command in SHELXL.

For complex **2**, one of the C_6H_{14} solvate molecules was found to be disordered over two positions, which were modeled in a 50:50 ratio. In addition, the C-C bonds within the disordered C_6H_{14} molecule were constrained using the SADI command in SHELXL.

For complex **3**, both C_7H_8 solvate molecules were all found to be disordered over two positions, which were each modeled in a 50:50 ratio. The C-C bond lengths in these molecules were constrained using the SADI command in SHELXL.

For complex **5**, one of the C_7H_8 solvate molecules was found to be disordered over two positions, which were modeled in a 50:50 ratio. The C-C bond lengths in this molecule were constrained using the SADI command in SHELXL. Additionally, the $[SCO_2]^{2-}$ ligand was found to be disordered over two orientations, which were related by a C_2 rotation about the Ni-K vector. These two orientations were modeled in a 87:13 ratio using the FVAR command in SHELXL. The S, C, and O atoms of the $[SCO_2]^{2-}$ ligand were refined isotropically.

For complex **6**, the ligand *tert*-butyl groups on the β-diketiminate ligand were found to be disordered over two positions. These disordered groups were modeled in a 50:50 ratio. In addition, the C-C bond lengths within the C_5H_{12} solvate molecule were constrained using the SADI and FLAT commands in SHELXL. The carbon atoms of the C_5H_{12} solvate were refined isotropically.

For complex **10**, the 18-crown-6 molecule was found to be disordered over two positions. These two orientations were modeled in a 76:24 ratio using the FVAR command in SHELXL. The C-C and C-O bond lengths in this molecule were constrained using the SADI command in SHELXL. These C and O atoms were refined isotropically. Additionally, the C-C bonds within the C_6H_6 solvate molecules were constrained using both the SADI and DFIX commands in SHELXL. Additionally, the $[CO_2]^{2-}$ ligand was found to be disordered over two orientations, which were related by a C_2 rotation about the Ni-K vector. These two orientations were modeled in a 53:47 ratio using the FVAR command in SHELXL.

Further crystallographic details for complexes **1-3**, **5**, **6**, and **10** can be found in Tables S1 and S2. Complexes **1-3**, **5**, **6**, and **10** have been deposited in the Cambridge Structural Database (**1**: CCDC 1847162; **2**: CCDC 1847163; **3**: CCDC 1847164; **5**: CCDC 1847165; **6**: CCDC 1847166; **10**: CCDC 1847167).

Table S1. X-ray Crystallographic Data for complexes **1**, **2**, and **3**.

	1·C_7H_8	**2**·$2C_6H_{14}$	**3**·$2C_7H_8$
empirical formula	$C_{47}H_{77}KN_2NiO_7S\cdot C_7H_8$	$C_{47}H_{77}KN_2NiO_8S_2\cdot 2C_6H_{14}$	$C_{47}H_{77}KN_2NiO_6S_2\cdot 2C_7H_8$
crystal habit, color	Plate, Orange	Plate, Orange	Plate, Yellow
crystal size (mm)	0.15 × 0.1 × 0.02	0.2 × 0.1 × 0.03	0.2 × 0.1 × 0.02
crystal system	Triclinic	Monoclinic	Triclinic
space group	*P-1*	*C2/c*	*P-1*
volume (Å^3)	2743.8(7)	12534.2(2)	3085.8(7)
a (Å)	12.564(2)	38.446(4)	12.814(2)
b (Å)	13.325(2)	18.600(2)	13.340 (2)
c (Å)	17.435(3)	18.970(2)	20.566(3)
α (deg)	83.702(5)	90	80.905(4)
β (deg)	82.251(5)	112.480(2)	87.457(4)
γ (deg)	72.027(5)	90	62.801(4)
Z	2	8	2
formula weight (g/mol)	1004.10	1132.37	1112.30
density (calculated) (Mg/m^3)	1.215	1.200	1.197
absorption coefficient (mm^{-1})	0.517	0.493	0.498
F_{000}	1084	4928	1200
total no. reflections	18945	27994	12552
unique reflections	11164	12832	8893
R_{int}	0.0442	0.0616	0.0684
final R indices (I >2σ(I)]	$R_1 = 0.0730$ $wR_2 = 0.1674$	$R_1 = 0.0865$ $wR_2 = 0.2195$	$R_1 = 0.0635$ $wR_2 = 0.1444$
largest diff. peak and hole (e$^-$ A^{-3})	1.585 and -0.961	1.285 and -1.141	2.496 and -0.787
GOF	1.004	1.029	1.012

Table S2. X-ray Crystallographic Data for complex **5, 6,** and **10**.

	5$\cdot 1.5C_7H_8$	**6**$\cdot 0.5C_5H_{12}$	**10**$\cdot 2C_6H_6$
empirical formula	$C_{48}H_{77}KN_2NiO_8S$ $\cdot 1.5C_7H_8$	$C_{48}H_{77}KN_2NiO_9$ $\cdot 0.5C_5H_{12}$	$C_{48}H_{77}KN_2NiO_8\cdot 2C_6H_6$
crystal habit, color	Block, Pale-Brown	Plate, Yellow	Plate, Orange
crystal size (mm)	0.15 × 0.1 × 0.1	0.2 × 0.2 × 0.05	0.2 × 0.1 × 0.05
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*P21/n*	*P21/n*	*P21/c*
volume (Å^3)	5851.6(9)	10592.8(1)	5909(3)
a (Å)	12.594 (1)	24.849(2)	20.875(6)
b (Å)	20.265(2)	17.449(1)	11.044(3)
c (Å)	22.942(2)	27.016(2)	26.136(8)
α (deg)	90	90	90
β (deg)	92.030(5)	115.268(3)	101.289(7)
γ (deg)	90	90	90
Z	2	4	4
formula weight (g/mol)	1078.20	1919.99	1064.14
density (calculated) (Mg/m^3)	1.219	1.204	1.196
absorption coefficient (mm^{-1})	0.491	0.497	0.451
F_{000}	2308	4152.0	2296
total no. reflections	35435	47795	24126
unique reflections	12142	21602	11782
R_{int}	0.0980	0.0894	0.0834
final R indices (I >2σ(I)]	$R_1 = 0.0582$ $wR_2 = 0.1176$	$R_1 = 0.0905$ $wR_2 = 0.2063$	$R_1 = 0.1112$ $wR_2 = 0.2693$
largest diff. peak and hole (e^- A^{-3})	0.878 and -0.754	1.776 and -0.986	1.995 and -0.744
GOF	1.009	1.032	1.070

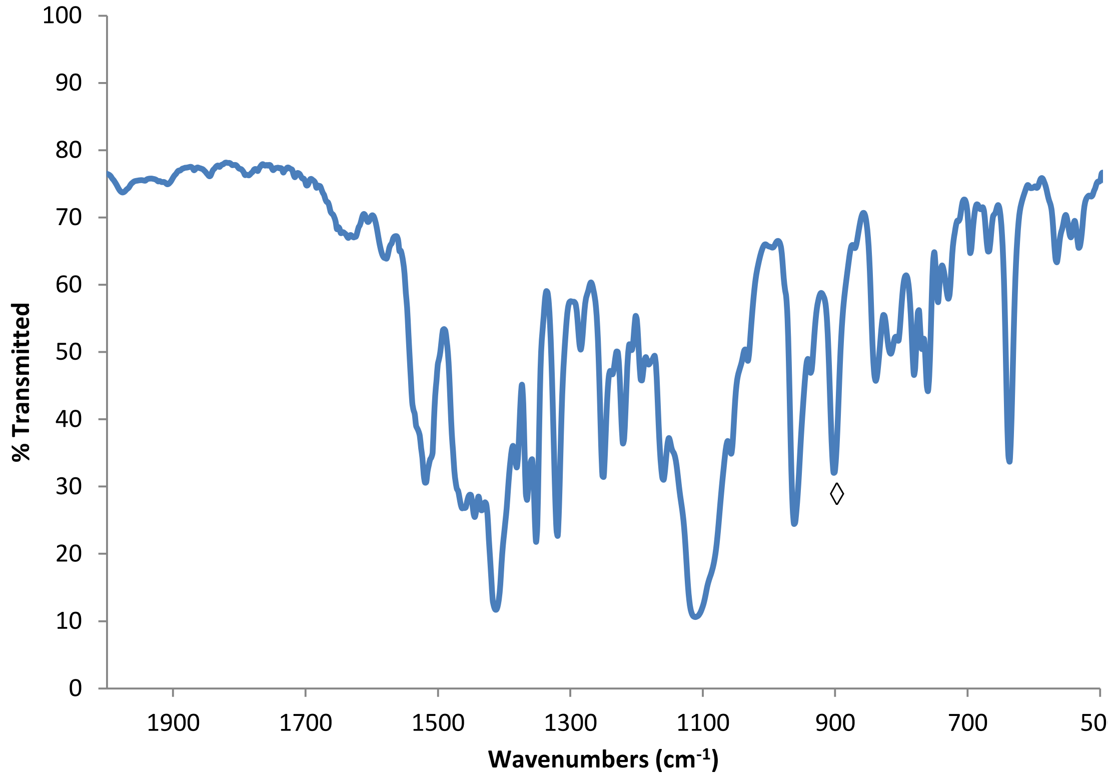

Figure S19. Partial IR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\eta^2$-SO)] (**1**) (KBr pellet), (◊) indicates the presence of the ν_{SO} mode.

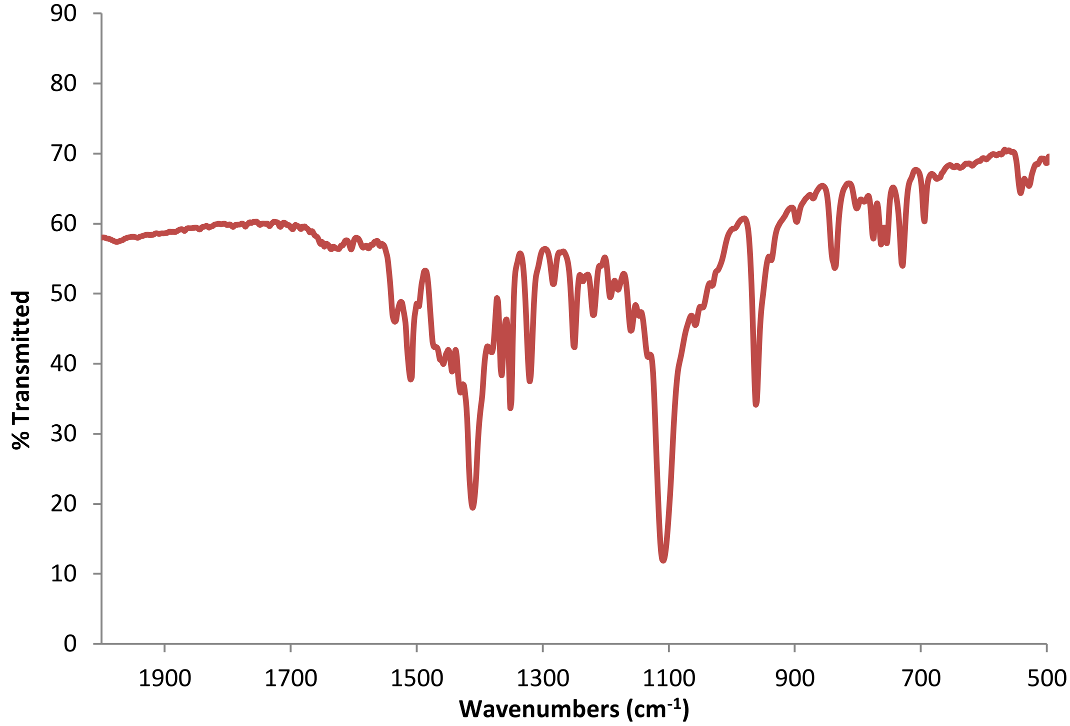

Figure S20. Partial IR spectrum of [K(18-crown-6)][$L^{tBu}Ni(\eta^2$-S_2)] (**3**) (KBr pellet).

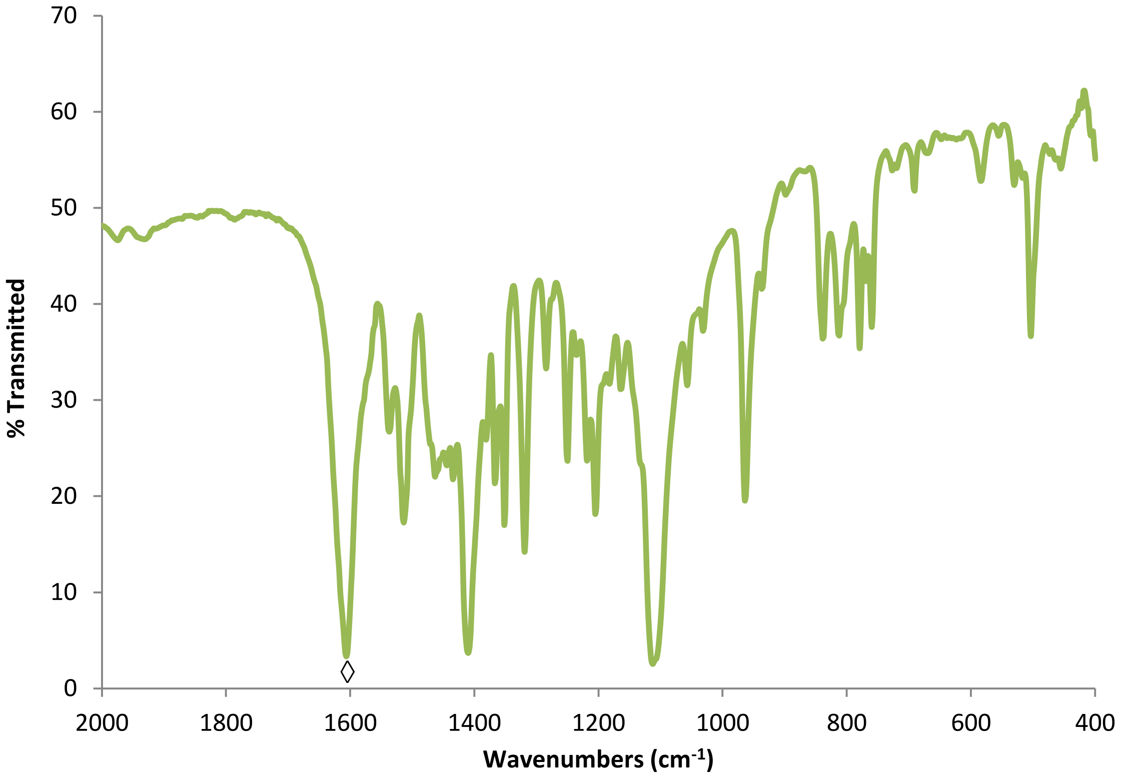

Figure S21. Partial IR spectrum of [K(18-crown-6)][L^{tBu}Ni(κ^2-SCO_2)] (**5**) (KBr pellet), (◊) indicates the presence of the ν_{CO} mode.

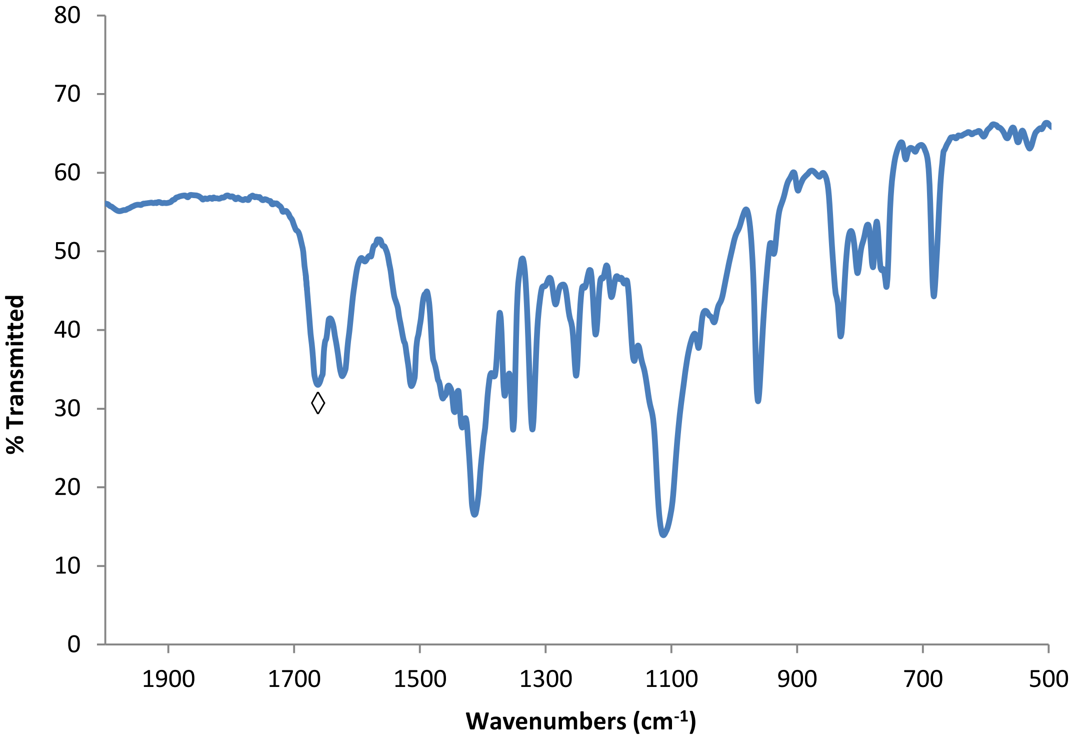

Figure S22. Partial IR spectrum of [K(18-crown-6)][L^{tBu}Ni(η^2-CO_2)] (**10**) (KBr pellet) , (◊) indicates the presence of the ν_{CO} mode.

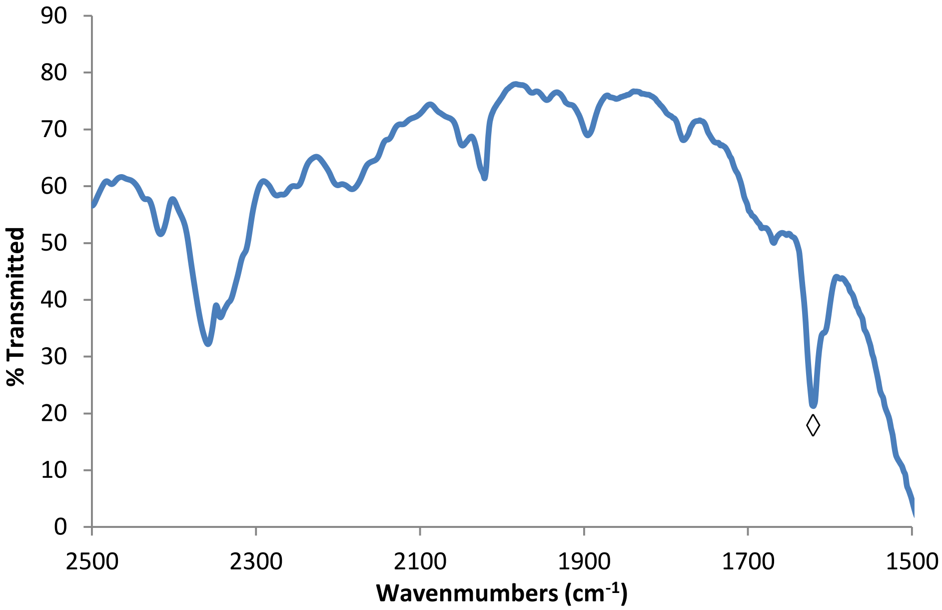

Figure S23. Partial solution IR (hexane) of [K(18-crown-6)][L^{tBu}Ni(κ^2-CO$_3$)] (**6**). (◊) indicates the presence of the ν_{CO} mode.

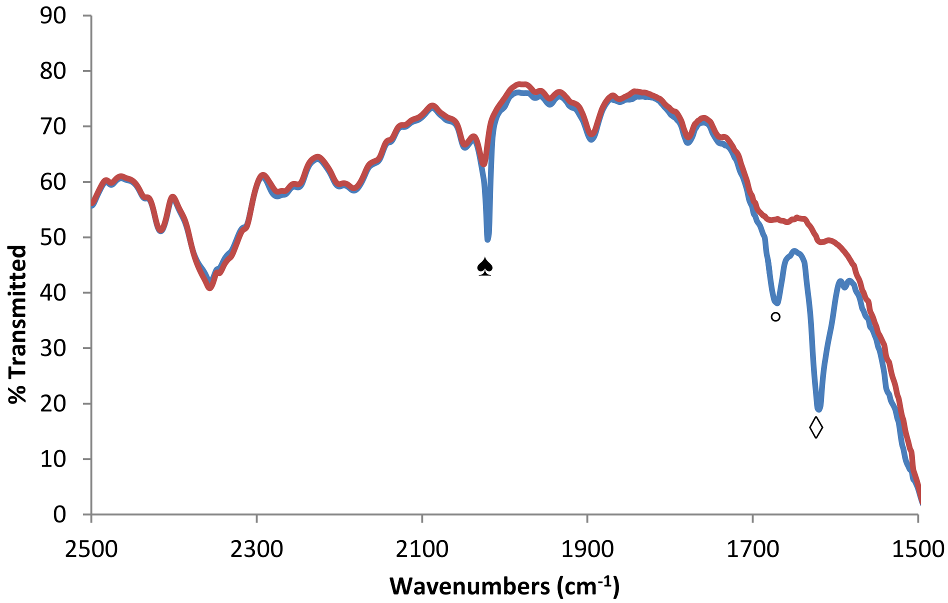

Figure S24. Partial solution IR (hexane) of the reaction of [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**) with CO (blue trace). Hexane background (red trace). (°) indicates the presence of [K(18-crown-6)][L^{tBu}Ni(η^2-SCO)] (**4**), (◊) indicates the presence of [K(18-crown-6)][L^{tBu}Ni(κ^2-CO$_3$)] (**6**), (♠) indicates the presence of [L^{tBu}Ni^{I}(CO)] (**9**).[6]

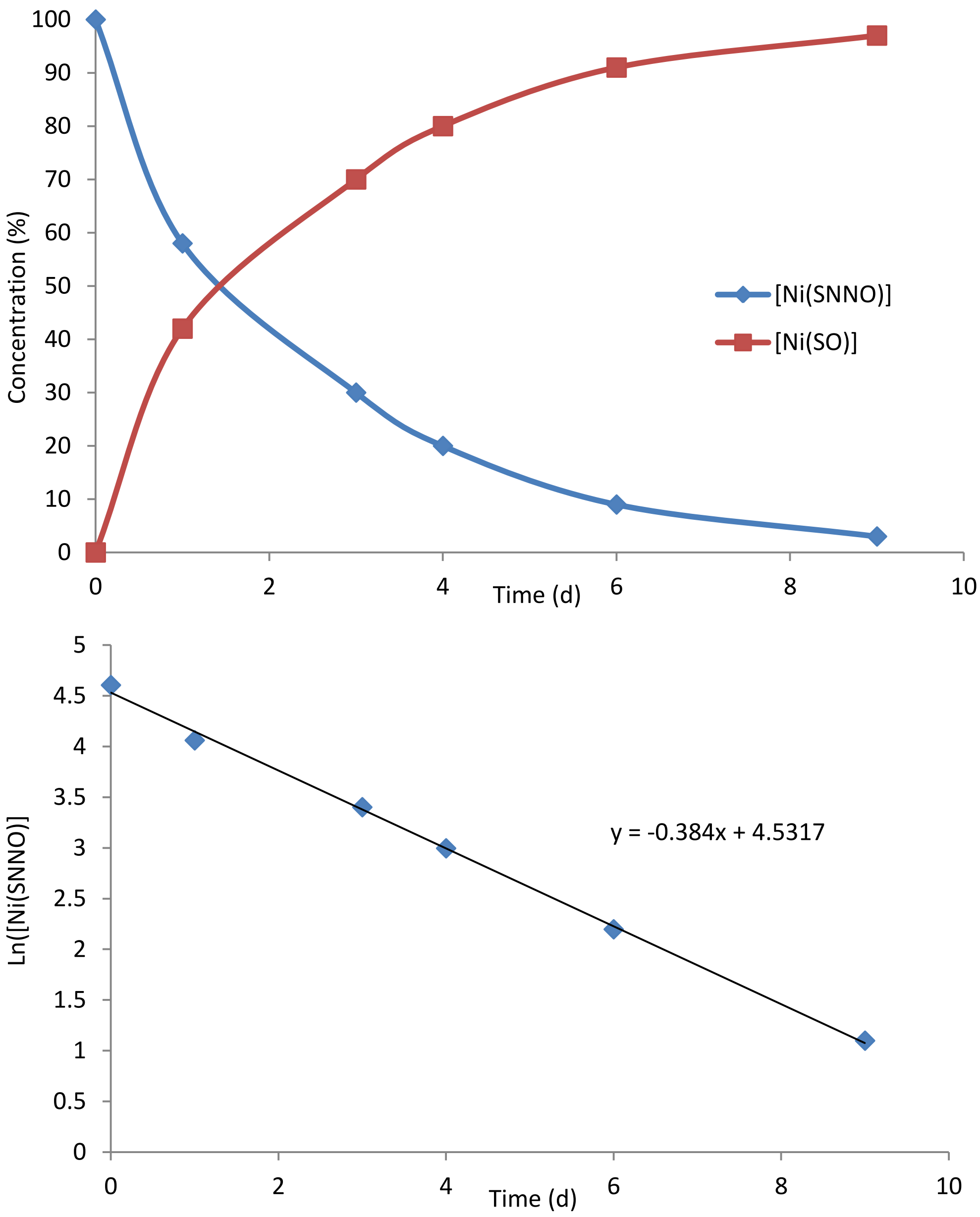

Figure S25. Kinetics analysis of the thermolysis of [K(18-crown-6)][L^{tBu}Ni(κ^2-SNNO)] (**II**) to form [K(18-crown-6)][L^{tBu}Ni(η^2-SO)] (**1**) in toluene-d_8. Relative concentrations of **II** and **1** derived from *in situ* ^{1}H NMR spectra collected over the course of the thermolysis reaction (top). Linear fit for the first-order decay of [K(18-crown-6)][L^{tBu}Ni(κ^2-SNNO)] (**II**) (bottom).

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