Supporting Information

Half-sandwich Ni(II) complexes bearing enantiopure bidentate NHC-carboxylate ligands: efficient catalysts for the hydrosilylative reduction of acetophenones.

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General procedures and characterization techniques

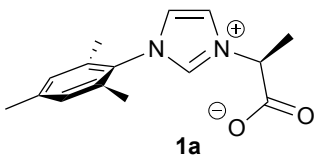
All operations were carried out under argon atmosphere using standard Schlenk and dry-box techniques. Solvents were dried using an MBraun-Solvent Purification System and deoxygenated prior to use. Alternatively, solvents and other chemicals were dried and purified as described elsewhere.[1] Unless otherwise stated, chemicals were used as received from commercial sources. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV water purification system. Argon N-50 and other gases were purchased from Abelló-Linde. Microwave reactions were conducted in a Biotage Initiator+ Microwave System with Robot Eight. NMR spectra were recorded at room temperature (25 ºC) using Varian Mercury Plus-300, Bruker AVANCE Neo 400 Nanobay. Bruker 400 Ultrashield or Varian NMR System 500 spectrometers. When required, monodimensional ^{1}H selective excitation and two-dimensional ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, ^{1}H-^{1}H COSY, or ^{1}H-^{1}H NOESY experiments were performed for unequivocal assignment of resonances for the new complexes. Chemical shifts (δ, parts per million) are quoted relative to $SiMe_4$, and were measured by internal referencing to residual signals of the deuterated solvents. Coupling constants (*J*) are given in Hertz. The abbreviations Mes and Imz used here refer to mesityl group and imidazolic heterocycle, respectively. IR spectra were recorded on an Agilent Cary 630 FTIR spectrophotometer equipped with an ATR unit. High-resolution mass spectra were conducted in an Agilent LC/MS-TOF 6210 mass spectrometer at the Chemical Research Support Center of the University of Alcalá. Polarimetry was carried out using a Perkin-Elmer 341 polarimeter and the measurements were made at 20 ºC temperature in ethanol or dichloromethane (concentration of ca. 0.100 g/100mL). The progress of the catalytic reactions was determined using an Agilent GC-MS turbo system (5975-7820A model) equipped with an autoinjector, and using an Agilent 19091S-433 HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm df) under the following conditions injector and detector temperatures: 250 °C and 230 °C, respectively, oven temperature program: 2.5 min initial isotherm at 50 ºC, ramp up to 120 °C at 4 °C/min, and ramp up to 220 °C at 25 °C/min, solvent delay of 2.5 min. The enantiomeric ratio of the products from the catalysis was determined using an Agilent HPLC Serie 1200 system with UV-Vis spectrophotometer detector and using an Chiralcel OD-H column (25 cm × 4.5 mm i.d) under the following conditions solvent and flow: hexane:^{i}PrOH (90:10), 1 mL/min for 1-PhEtOH and 0.5 ml/min for 1-Ph(pCl)EtOH and 1-Ph(*p*O Me)EtOH. Samples for Transmission Electron Microscopy (TEM) were prepared by deposition after evaporation on a covered holey copper grid of a drop of the crude catalytic solution. TEM analyses were performed at the “Service Commun de Microscopie Electronique de l’Université Paul Sabatier” (TEMSCAN-UPS) by using a JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 Å.

Synthesis of zwitterinonic imidazolium salts **1a-h**

The chiral carboxylate imidazolium salts were prepared adapting the procedure reported by Mauduit and Baslé for the synthesis of **1b**.[2] Thus, a mixture of the corresponding (*S*)-enantiopure amino acid (20 mmol, 1 equiv) of alanine for **1a**, valine for **1b**, leucine for **1c**, isoleucine for **1d**, phenylglycine for **1e**, phenylalanine for **1f**, methylcysteine for **1g**, or methionine for **1h**), 2,4,6-trimethylaniline (20-23 mmol, 1 equiv) and acetic acid (6.9 mL) was heated at 60 ºC until an homogeneous solution resulted. In a second

flask glyoxal (21 mmol, 1.05 equiv, 40%$_{wt}$ in water), formaldehyde (21 mmol, 1.05 equiv, 37%$_{wt}$ in water) and acetic acid (1.6 mL) were combined and warmed also at 60 ºC, and the mixture added over the first one. After 15 min of stirring, the volatiles were removed under vacuum. The selectivity of the reaction was calculated at this point by integrating in the ^{1}H NMR spectrum of the crude, signals corresponding to the different compounds. The residue was then dissolved in H_2O (40 mL) and ethyl acetate (40 mL) and the mixture neutralized by adding solid Na_2CO_3 in small portions. The aqueous layer was separated, concentrated under reduced pressure up to half of the initial volume, and the imidazolium compound extracted by washings with CH_2Cl_2 (6 × 10 mL). After evaporation of the chlorinated solvent, the resulting solid was purified by column chromatography using EtOH/CH_2Cl_2 1:9 as eluent. Alternatively, series of reprecipitations from CH_2Cl_2 solutions by addition of dry diethyl ether, can be used to purify these compounds.

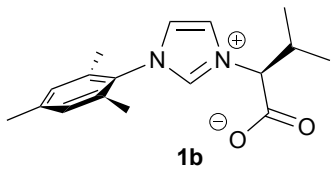
(*S*)-2-(3-mesityl-1*H*-imidazol-3-ium-1-yl)propanoate (**1a**)



1a

White solid. Yield: 47%.**^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.37 (t, *J* = 2, 1H, Imz-H^2), 7.95 (t, *J* = 2, 1H, Imz-H^5), 7.76 (t, *J* = 2, 1H, Imz-H^4), 7.13 (s, 2H, Mes-*m*-H), 4.68 (q, *J* = 7, 1H, NC*H*COO), 2.33 (s, 3H, Mes-*p*-Me), 2.02 and 2.01 (2 × s, 3+3H, Mes-*o*-Me), 1.65 (d, *J* = 7, 3H, NCHC*H*$_3$). $[\alpha]^{20}_D$ = +35 (C = 0.104 in EtOH).

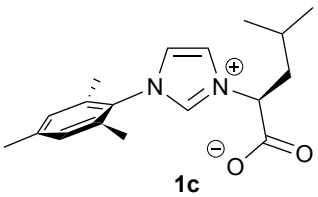
(*S*)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-3-methylbutanoate (**1b**)



1b

White solid. Yield: 36%. **^{1}H NMR (500 MHz, dmso-d$_6$):** δ 9.44 (t, *J* = 2, 1H, Imz-H^2), 8.02 (t, *J* = 2, 1H, Imz-H^4), 7.81 (t, *J* = 2, 1H, Imz-H^5), 7.14 (s, 2H, Mes-*m*-H), 4.38 (d, *J* = 7, 1H, NC*H*COO), 2.5 – 2.4 (m, 1H, C*H*Me$_2$), 2.33 (s, 3H, Mes-*p*-Me), 2.01 (s, 6H, Mes-*o*-Me), 0.94 (d, *J* = 7, 3H, CH*Me*$_2$), 0.78 (d, *J* = 7, 3H, CH*Me*$_2$). $[\alpha]^{20}_D$ = –16 (C = 0.0988 in EtOH).

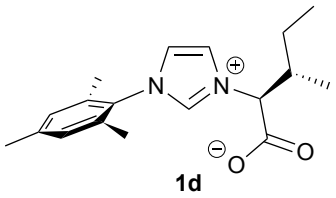
(*S*)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-4-methylpentanoate (**1c**)



1c

White solid. Yield: 61 %.**^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.43 (t, *J* = 2, 1H, Imz-H^2), 8.02 (t, *J* = 2, 1H, Imz-H^4), 7.78 (t, *J* = 2, 1H, Imz-H^5), 7.14 (s, 2H, Mes-*m*-H), 4.65 (dd, *J* = 10 and 6, 1H, NC*H*COO), 2.33 (s, 3H, Mes-*p*-Me), 2.01 (s, 3H, Mes-*o*-Me), 2.00 (s, 3H, Mes-*o*-Me), 2.0 – 1.9 (m, 2H, NCHC*H*$_2$), 1.4 – 1.2 (m, 1H, C*H*Me$_2$), 0.90 (d, *J* = 7, 3H, CH*Me*$_2$), 0.86 (d, *J* = 7, 3H, CH*Me*$_2$). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 167.8 (COO), 140.0 (Mes-*p*-C), 137.2 (Imz-C^2), 134.3 (Mes-*o*-C), 134.2 (Mes-*o*-C), 131.5 (Mes-*ipso*-C), 129.2 (Mes-*m*-C), 123.3 (Imz-C^4), 122.2 (Imz-C^5), 64.6 (N*C*HCOO), 41.4 (NCH*C*H$_2$), 25.1 (*C*HMe$_2$), 22.8 (CH*Me*$_2$), 21.2 (CH*Me*$_2$), 20.6 (Mes-*p*-Me), 16.8 (Mes-*o*-Me), 16.8 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 301.1912 [**1c** + H]$^+$ (301.1911 calcd for $C_{18}H_{25}N_2O_2$). $[\alpha]^{20}_D$ = +43 (C = 0.085 in EtOH).

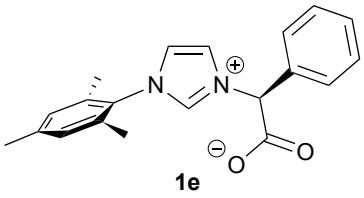
(2*S*,3*S*)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-3-methylpentanoate (**1d**)



1d

White solid. Yield: 61 %. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.46 (t, *J* = 2, 1H, Imz-H^2), 8.03 (t, *J* = 2, 1H, Imz-H^4), 7.81 (t, *J* = 2, 1H, Imz-H^5), 7.14 (s, 2H, Mes-*m*-H), 4.44 (d, *J* = 8, 1H, NC*H*COO), 2.33 (s, 3H, Mes-*p*-Me), 2.3 – 2.1 and 1.34 (m and dtq, *J* = 14, 7 and 3, 1+1H, C*H*$_2$CH$_3$), 2.00 (s, 6H, Mes-*o*-Me), 0.93 (d, 3H, *J* = 7, CH(Et)*Me*), 0.83 (t, *J* = 7, 3H, CH$_2$C*H*$_3$).**^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 166.9 (COO), 140.0 (Mes-*p*-C), 137.3 (Imz-C^2), 134.2 (Mes-*o*-C), 134.2 (Mes-*o*-C), 131.5 (Mes-*ipso*-C), 129.2 (Mes-*m*-C), 129.1 (Mes-*m*-C), 123.7 (Imz-C^4), 122.1 (Imz-C^5), 71.2 (N*C*HCOO), 37.3 (NCH*C*H), 24.8 (*C*H$_2$CH$_3$), 20.6 (Mes-*p*-Me), 16.8 (Mes-*o*-Me), 16.8 (Mes-*o*-Me), 16.0 (CH(Et)*Me*), 10.9 (CH$_2$*C*H$_3$). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 301.1907 [**1d** + H]$^+$ (301.1911 calcd for $C_{18}H_{25}N_2O_2$), and 323.1724 [**1d** + Na]$^+$ (323.1735 calcd for $C_{18}H_{24}N_2O_2Na$). $[\alpha]^{20}_D$ = +61 (C = 0.1056 in EtOH)

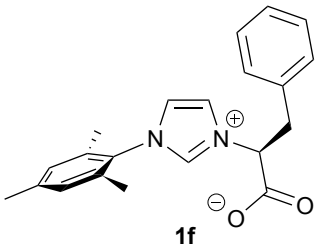
(*S*)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-2-phenylacetate (**1e**)



1e

Light yellowish white solid. Yield: 36%. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.59 (t, *J* = 2, 1H, Imz-H^2), 7.94 (t, *J* = 2, 1H, Imz-H^5), 7.77 (t, *J* = 2, 1H, Imz-H^4), 7.5 (m, 2H, Ph-*o*-H), 7.40 (m, 2H, Ph-*m*-H), 7.3 (m, 1H, Ph-*p*-H), 7.12 and 7.11(2 × s, 1+1H, Mes-*m*-H), 5.87 (s, 1H, NC*H*COO), 2.32 (s, 3H, Mes-*p*-Me), 2.01 and 1.95 (s, 3+3H, Mes-*o*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 165.4 (COO), 139.9 (Mes-*p*-C), 138.2 (Ph-*ipso*-C), 137.7 (Imz-C^2), 134.3 (Mes-*o*-C), 134.2 (Mes-*o*-C), 131.5 (Mes-*ipso*-C), 129.1 (Mes-*m*-C), 128.5 (Ph-*m*-C), 128.1 (Ph-*o*-C), 127.9 (Ph-*p*-C), 123.2 (Imz-C^5), 122.2 (Imz-C^4), 68.7 (N*C*HCOO), 20.6 (Mes-*p*-Me), 16.9 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 321.1598 [**1e** + H]$^+$ (321.1603 calcd for $C_{20}H_{21}N_2O_2$), $[\alpha]^{20}_D$ = +1 (C = 0.076 in EtOH).

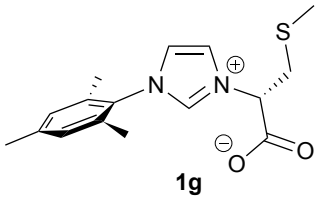
(S)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-3-phenylpropanoate (**1f**)



1f

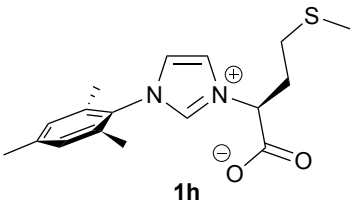
White solid. Yield: 49%. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.27 (t, *J* = 2, 1H, Imz-H^2), 7.86 (t, *J* = 2, 1H, Imz-H^5), 7.64 (t, *J* = 2, 1H, Imz-H^4), 7.2 (m, 2H, Ph-*m*-H), 7.2 (m, 2H, Ph-*o*-H), 7.1 (m, 1H, Ph-*p*-H), 7.09 (s, 1H, Mes-*m*-H), 7.08 (s, 1H, Mes-*m*-H), 4.94 (dd, *J* = 12 and 4, 1H, NC*H*COO), 3.60 (dd, *J* = 14 and 4, 1H, NCHC*H*$_2$-*anti*), 3.23 (dd, *J* = 15 and 12, 1H, NCHC*H*$_2$-*sin*), 2.30 (s, 3H, Mes-*p*-Me), 1.86 (s, 3H, Mes-*o*-Me), 1.75 (s, 3H, Mes-*o*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ = 167.0 (COO), 140.0 (Mes-*p*-C), 137.9 (Ph-*ipso*-C), 137.0 (Imz-C^2), 134.2 (Mes-*o*-C), 134.2 (Mes-*o*-C), 131.2 (Mes-*ipso*-C), 129.1 (Mes-*m*-C), 129.0 (Mes-*m*-C), 128.6 (Ph-*o*-C), 128.3 (Ph-*m*-C), 126.4 (Ph-*p*-C), 123.4 (Imz-C^5), 122.1 (Imz-C^4), 67.2 (N*C*HCOO), 38.7 (NCH*C*H$_2$), 20.6 (Mes-*p*-Me), 16.7 (Mes-*o*-Me), 16.5 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 335.1756 [**1f** + H]$^+$ (335.1760 calcd for $C_{21}H_{23}N_2O_2$), $[\alpha]^{20}_D$ = –60 (C = 0.086 in EtOH).

(S)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-3-(methylthio)propanoate (**1g**)


1g

Light yellowish white solid. Yield: 39%. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.45 (d, *J* = 2, 1H, Imz-H^2), 8.04 (t, *J* = 2, 1H, Imz-H^5), 7.82 (t, *J* = 2, 1H, Imz-H^4), 7.14 (s, 2H, Mes-*m*-H), 4.80 (dd, *J* = 12 and 3, 1H, NC*H*COO), 3.33 (dd, *J* = 15 and 3, 1H, CHC*H*$_2$-*sin*), 3.14 (dd, *J* = 15 and 12, 1H, CHC*H*$_2$-*anti*)), 2.33 (s, 3H, Mes-*p*-Me), 2.06 (s, 3H, SMe), 2.03 (s, 3H, Mes-*o*-Me), 2.02 (s, 3H, Mes-*o*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 166.0 (*C*OO), 140.1 (Mes-*p*-C), 137.4 (Imz-C^2), 134.4 (Mes-*o*-C), 134.3 (Mes-*o*-C), 131.4 (Mes-*ipso*-C), 129.2 (Mes-*m*-C), 123.5 (Imz-C^5), 122.3 (Imz-C^4), 64.2 (N*C*HCOO), 37.1 (NCH*C*H$_2$), 20.6 (Mes-*p*-Me), 16.8 (Mes-*o*-Me), 16.8 (Mes-*o*-Me), 14.2 (SMe). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 305.1320 [**1g** + H]$^+$ (305.1324 calcd for $C_{16}H_{21}N_2O_2S$). $[\alpha]^{20}_D$ = -10 (C = 0.078 in EtOH).

(*S*)-2-(1-mesityl-1*H*-imidazol-3-ium-3-yl)-4-(methylthio)butanoate (**1h**)

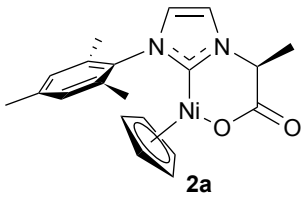

1h

Light yellowish white solid. Yield: 70%. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 9.42 (t, *J* = 2, 1H, Imz-H^2), 7.98 (t, *J* = 2, 1H, Imz-H^4), 7.79 (t, *J* = 2, 1H, Imz-H^5), 7.14 (s, 2H, Mes-*m*-H), 4.69 (dd, *J* = 10 and 4, 1H, NC*H*COO), 2.5 – 2.4 (m, 2H, C*H*$_2$S), 2.33 (s, 3H, Mes-*p*-Me), 2.3 – 2.2 (m, 2H, CHC*H*$_2$), 2.03 (s, 3H, SMe), 2.02 (s, 6H, Mes-*o*-Me). **^{1}H NMR (500 MHz, D$_2$O)**: δ 7.84 and 7.61 (2 x d, *J* = 2.0, 1+1H, Imz-H^{4,5}), 7.18 (s, 2H, Mes-*m*-C), 5.22 (dd, *J* = 10 and 4, 1H, NC*H*COO), 2.7 – 2.6 (m, 2H, C*H*$_2$S), 2.5 – 2.4 (m, 2H, CHC*H*$_2$), 2.36 (s, 3H, Mes-*p*-Me), 2.13 (s, 3H, SMe), 2.08 (s, 3H, Mes-*o*-Me), 2.07 (s, 3H, Mes-*o*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 167.0 (COO), 140.0 (Mes-*p*-C), 137.4 (Imz-C^2), 134.4 (Mes-*ipso*-C), 131.3 (Mes-*o*-C), 129.1 (Mes-*m*-C), 123.3 (Imz-C^4), 122.3 (Imz-C^5), 65.0 (N*C*HCOO), 32.0 (CH*C*H$_2$), 30.5 (*C*H$_2$S), 20.6 (Mes-*p*-Me), 16.8 (Mes-*o*-Me), 14.5 (SMe). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 319.1481 [**1h** + H]$^+$ (319.1480 calcd for $C_{17}H_{23}N_2O_2S$). $[\alpha]^{20}_D$ = +20 (C = 0.087 in EtOH).

Synthesis of nickel complexes **2a-h** and **3b-d,f**

The nickel compounds were prepared by conventional heating using the procedure reported by Cowley and coworkers (Method A),[3] or alternatively by microwave heating as has been described by Navarro's group (Method B).[4] Complexes **2b** and **3b** were both previously isolated in our group by using Method A (*vide infra*).[5] *Method A:* The corresponding imidazolium salt **1** (1 mmol) and $NiCp_2$ (1 mmol, 190.8 mg), were combined in a Schlenk tube under inert atmosphere with 40 mL of dry solvent (MeCN or THF, 0.025 M). The mixture was stirred 3 days at 60 ºC, then the solvent was removed under vacuum, the residue extracted with portions of toluene at 60 ºC (6 × 15 mL), which were finally removed at reduced pressure. *Method B:* A microwave vial containing the corresponding imidazolium salt **1** (0.8 mmol), $NiCp_2$ (0.8 mmol, 153.0 mg) and 4 mL of dry solvent (MeCN or THF, 0.2 M) was sealed into a dry box. The vial was heated at 110 ºC into a MW oven (70 W) during 0.5 h. The mixture was poured into a flask, the solvent was removed under vacuum, the residue extracted with portions of toluene at 60 ºC (6 × 15 mL), which were finally removed at reduced pressure.

[Cyclopentadienyl{1-[(*S*)-2-propanoate]-3-(mesityl)-1*H*-imidazol-2-ylidene}nickel(II)] (**2a**)

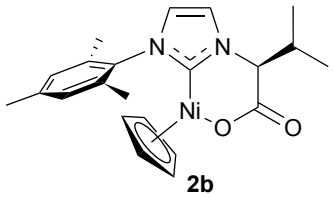


2a

Prepared by method A in MeCN. Purification: washings with cold diethyl ether. Brown solid. Yield: 43%. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.76 (d, *J* = 2, 1H, Imz-H^5), 7.24 (d, *J* = 2, 1H, Imz-H^4), 7.15 and 7.02 (2 × s, 1+1H, Mes-*m*-H), 4.77 (q, *J* = 7, 1H, NCHCOO), 4.72 (s, 4H, C_5H_5), 2.31 (s, 3H, Mes-*p*-Me), 2.27 and 1.85 (2 × s, 3+3H, Mes-*o*-H), 2.00 (d, *J* = 7, 3H, NCHC*H*$_3$). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 172.7 (COO), 156.0 (Imz-C^2), 138.8 (Mes-*p*-C), 136.0 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.6 (Mes-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes-*m*-C), 123.3 (Imz-C^5), 123.0 (Imz-C^4), 90.6 (C_5H_5), 60.4 (N*C*HCOO), 21.1 (NCH*C*H$_3$), 20.6 (Mes-*p*-Me), 17.7 (Mes-*o*-Me), 17.0 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 381.1102 [**2a** + H]$^+$ (381.1113 calcd for $C_{20}H_{23}N_2O_2Ni$). $[\alpha]^{20}_D$ = -169 (C = 0.122 in EtOH).

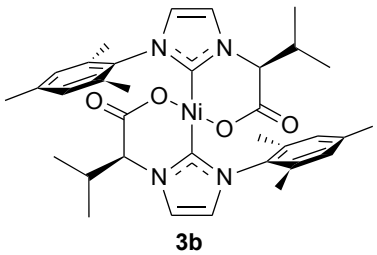
[Cyclopentadienyl{1-[(*S*)-2-(3-methylbutanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**2b**) and [bis{1-[(*S*)-2-(3-methylbutanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**3b**)

Method A in MeCN results in a mixture 68:32 of **2b** and **3b**. Method A in THF results in only **3b**. Method B in MeCN results in a mixture 85:15 of **2b** and **3b**. Purification: Column chromatography using neat ethyl acetate for the separation of **3b** and then with 20% EtOH for **2b**.



2b

Brown Solid. Yield: 37% by Method A in MeCN, 40% by Method B in MeCN. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.76 (d, *J* = 2, 1H, Imz-H^5), 7.23 (d, *J* = 2, 1H, Imz-H^4), 7.16 and 7.00 (2 × s, 1+1H, Mes-*m*-H), 4.69 (s, 5H, C_5H_5), 4.21 (d, *J* = 9, 1H, NCHCOO), 3.64 (dp, *J* = 9 and 7, 1H, C*H*Me$_2$), 2.33 and 1.79 (2 × s, 3+3H, Mes-*o*-Me), 2.31 (s, 3H, Mes-*p*-Me), 1.08 (d, *J* = 7, 3H, CH*Me*$_2$), 0.96 (d, *J* = 7, 3H, CH*Me*$_2$). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 171.4 (COO), 155.9 (Imz-C^2), 138.9 (Mes-*p*-C), 136.0 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.5 (Mes-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes-*m*-C), 125.3 (Imz-C^5), 122.4 (Imz-C^4), 90.7 (C_5H_5), 71.7 (N*C*HCOO), 32.9 (*C*HMe$_2$), 20.6 (Mes-*p*-Me), 19.9 (Mes-*o*-Me), 19.1 (Mes-*o*-Me), 17.7 (CH*Me*$_2$), 16.7 (CH*Me*$_2$). **IR:** ν_{MAX} (cm^{-1}) = 3147.7, 3110.5, 3078.8 (C*sp*^{2}-H), 2961.4, 2920.4, 2871.9 (C*sp*^{3}-H), 1636.3 (CO). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 409.1415 [**2b** + H]$^+$ (409.1426 calcd for $C_{22}H_{27}N_2O_2Ni$). Anal. Calcd for $C_{22}H_{26}N_2O_2Ni$ (**2b**): C, 64.58; H, 6.41; N, 6.85%. Found: C, 64.50; H, 6.399; N, 6.892%. $[\alpha]^{20}_D$ = -553 (C = 0.1101 in EtOH). $[\alpha]^{20}_D$ = -531 (C = 0.0372 in MeCN).



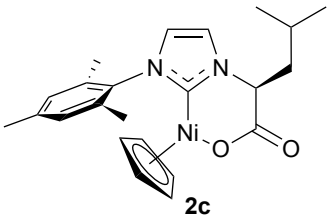
3b

Yellow solid. Yield: 25% by Method A in MeCN, 44% by Method A in THF, 19% by Method B in MeCN. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.46 (d, *J* = 2, 2H, Imz-H^5), 7.06 (2 × s, 2H, Mes-*m*-H), 6.83 (s, 2H, Imz-H^4), 4.25 (broad s, 2H, C*H*Me$_2$), 3.91 (d, *J* = 10, 2H, NC*H*COO), 2.37 and 1.81 (2 × s, 6+6H, Mes-*o*-Me), 2.26 (s, 6H, Mes-*p*-Me), 1.12 (d, *J* = 7, 6H, CH*Me*$_2$), 1.06 (d, *J* = 7 Hz, 6H, CH*Me*$_2$).**^{13}C NMR (125 MHz, dmso-d$_6$):** δ 170.5 (*C*OO), 159.1 (Imz-C^2), 137.1 (Mes-*p*-C), 135.6 (Mes-*o*-C), 135.3 (Mes-*o*-C), 133.7 (Mes-*ipso*-C), 128.4 (Mes-*m*-C), 127.9 (Mes-*m*-C), 122.7 (Imz-C^4), 122.3 (Imz-C^5), 70.5 (N*C*HCOO), 36.1 (*C*HMe$_2$), 20.7 (Mes-*p*-Me), 19.5 (CH*Me*$_2$), 18.9 (CH*Me*$_2$), 17.8 (Mes-*o*-Me), 17.1 (Mes-*o*-Me). **IR:** ν_{MAX} (cm^{-1}) = 3112.3, 3157.1,

3080.6 (Csp^2-H), 2959.5, 2918.5, 2871.9 (Csp^3-H), 1632.6 (CO). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 629.2619 [**3b** + H]$^+$ (629.2638 calcd for $C_{34}H_{43}N_4O_4Ni$). Anal. Calcd for $C_{34}H_{44}N_4O_5Ni$ (**3b**·H_2O): C, 63.07; H, 6.85; N, 8.65%. Found: C, 62.91; H, 6.429; N, 8.209%. $[\alpha]^{20}_D$ = -220 (C = 0.125 in EtOH). $[\alpha]^{20}_D$ = -264 (C = 0.0386 in CH_2Cl_2).

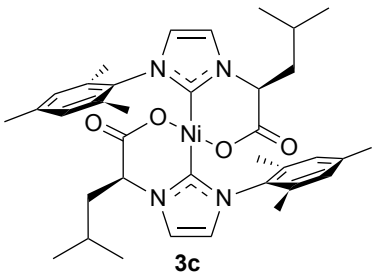
[Cyclopentadienyl{1-[(*S*)-2-(4-methylpentanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**2c**) and [bis{1-[(*S*)-2-(4-methylpentanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**3c**)

Method A in MeCN results in a mixture 72:28 of **2c** and **3c**. Method A in THF results in a mixture 67:33 of **2c** and **3c**. Method B in MeCN results in only **2c**. Purification: Column chromatography using neat ethyl acetate for the separation of **3c** and then with 20% EtOH for **2c**.



2c

Brown Solid. Yield: 56% by Method A in MeCN, 29% by Method A in THF, 86% by Method B in MeCN. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.81 (d, *J* = 2, 1H, Imz-H^5), 7.23 (d, *J* = 2, 1H, Imz-H^4), 7.16 and 7.00 (2 × s, 1+1H, Mes-*m*-C), 4.71 (s, 5H, C_5H_5), 4.65 (dd, *J* = 10 and 6, 1H, NC*H*COO), 3.02 (ddd, *J* = 13, 10 and 7 Hz, 1H, NCHCH_2-sin), 2.33 and 1.78 (2 × s, 3+3H, Mes-*o*-Me), 2.31 (s, 3H, Mes-*p*-Me), 2.32 – 2.25 (m, 1H, NCHCH_2-anti), , 1.59 – 1.45 (m, 1H, C*H*Me$_2$), 1.04 (d, *J* = 7, 3H, CH*Me*$_2$), 0.99 (d, *J* = 7, 3H, C*H*Me$_2$). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 172.3 (*C*OO), 156.1 (Imz-C^2), 138.9 (Mes-*p*-C), 135.9 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.5 (Mes-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes-*m*-C), 124.5 (Imz-H^4), 122.7 (Imz-H^5), 90.6 (C_5H_5), 64.0 (N*C*HCOO), 43.9 (NCH*C*H$_2$), 24.5 (*C*HMe$_2$), 22.9 (CH*Me*$_2$), 22.1 (CH*Me*$_2$), 20.6 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 16.6 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 423.1575 [**2c** + H]$^+$ (423.1582 calcd for $C_{23}H_{29}N_2O_2Ni$). $[\alpha]^{20}_D$ = -450 (C = 0.086 in EtOH).

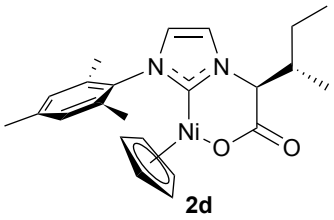


3c

Yellow Solid. Yield: 20% by Method A in THF. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.50 (s, 2H, Imz-H^5), 7.09 (s, 2H, Imz-H^4), 7.04 (s, 2H, Mes-*m*-H), 6.85 (s, 2H, Mes-*m*-H), 4.40 (t, *J* = 8, 2H, NC*H*COO), 3.2 (m, 2H, NCHCH_2), 2.46 (m, 2H, CHCH_2), 2.34 and 1.85 (2 × s, 6+6H, Mes-*o*-Me), 2.26 (s, 6H Mes-*p*-Me), 1.59 (broad s, 2H, C*H*Me$_2$), 1.04 (d, *J* = 6, 6H, CH*Me*$_2$), 1.01 (d, *J* = 6, 6H, CH*Me*$_2$). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 171.4 (*C*OO), 160.1 (Imz-C^2), 137.2 (Mes-*p*-C), 135.6 (Mes-*ipso*-C), 135.3 (Mes-*o*-C), 134.0 (Mes-*o*-C), 128.4 (Mes-*m*-C), 128.0 (Mes-*m*-C), 122.8 (Imz-C^4), 121.3 (Imz-C^5), 62.5 (N*C*HCOO), 45.9 (NCH*C*H$_2$), 24.8 (*C*HMe$_2$), 22.8 (CH*Me*$_2$), 22.3 (CH*Me*$_2$), 20.7 (Mes-*p*-Me), 17.9 (Mes-*o*-Me), 17.3 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 657.2950 [**3c** + H]$^+$ (657.2951 calcd for $C_{36}H_{47}N_4O_4Ni$), and 679.2768 [**3c** + Na]$^+$ (679.2765 calcd for $C_{36}H_{46}N_4O_4NaNi$). $[\alpha]^{20}_D$ = -106 (C = 0.088 in EtOH).

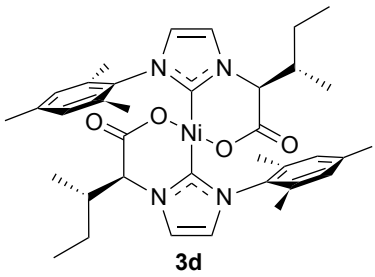
[Cyclopentadienyl{1-[(2*S*,3*S*)-2-(4-methylpentanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**2d**) and [bis{1-[(2*S*,3*S*)-2-(4-methylpentanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**3d**)

Method A in MeCN results in a mixture 90:10 of **2d** and **3d**. Method B in MeCN results in a mixture 81:19 of **2d** and **3d** only **2d**. Purification: Column chromatography using neat ethyl acetate for the separation of **3d** and then with 20% EtOH for **2d**.



2d

Brown Solid. Yield: 41% by Method A in MeCN, 54% by Method B in MeCN **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ = 7.78 (s, 1H, Imz-H^5), 7.23 (s, 1H, Imz-H^4), 7.16 and 7.00 (2 × s, 1+1H, Mes-*m*-H), 4.69 (s, 5H, C_5H_5), 4.28 (d, *J* = 10, 1H, NC*H*COO), 3.6 (m, 1H, C*H*(Et)Me), 2.33 and 1.78 (2 × s, 3+3H, Mes-*o*-Me), 2.31 (s, 3H, Mes-*p*-Me), 1.5-1.3 (m, 1H, CH_2CH$_3$), 1.16 (m, 1H, CH_2CH$_3$), 1.06 (d, *J* = 7 Hz, 3H, CH(Et)*Me*), 0.94 (t, *J* = 7, 3H, CH$_2$CH_3). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 171.4 (*C*OO), 156.2 (Imz-C^2), 138.9 (Mes-*p*-C), 135.9 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.5 (Mes-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes-*m*-C), 125.3 (Imz-C^5), 122.5 (Imz-C^4), 90.7 (C_5H_5), 70.4 (N*C*HCOO), 39.0 (*C*H(Et)Me)), 24.9 (*C*H$_2$CH$_3$), 20.6 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 16.6 (Mes-*o*-Me), 16.1 (CH$_2$*C*H$_3$), 10.9 (CH(Et)*Me*). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 423.1566 [**2d** + H]$^+$ (423.1582 calcd for $C_{23}H_{29}N_2O_2Ni$), and 445.1384 [**2d** + Na]$^+$ (445.1402 calcd for $C_{23}H_{28}N_2O_2NaNi$). $[\alpha]^{20}_D$ = -598 (C = 0.0988 in EtOH).

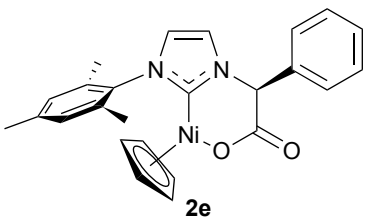


3d

Brownish yellow solid. Yield: 5% by Method A in MeCN, 15% by Method B in MeCN. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.48 (d, *J* = 2, 2H, Imz-H^5), 7.1-7.0 (m, 4H, Imz-H^4, Mes-*m*-H), 6.82 (s, 2H, Mes-*m*-H), 4.21 (s, 2H, C*H*(Et)Me), 3.94 (d, *J* = 10, 2H, NC*H*COO), 2.39 and 1.79(2 × s, 6+6H, Mes-*o*-Me), 2.26 (s, 6H, Mes-*p*-Me), 1.6-1.5 (m, 2H, CH_2CH$_3$), 1.25 (m, *J* 2H, CH_2CH$_3$), 1.09 (d, *J* = 7, 6H, CH(Et)*Me*), 0.98 (t, *J* = 7, 6H, CH$_2$CH_3). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 170.6 (*C*OO), 159.3 (Imz-C^2), 137.0 (Mes-*p*-C), 135.7 (Mes-*ipso*-C), 135.5 (Mes-*o*-C), 133.6 (Mes-*o*-C), 128.3 (Mes-*m*-C), 127.8 (Mes-*m*-C), 122.6 (Imz-C^5), 122.3 (Imz-C^4), 69.3 (N*C*HCOO), 42.4 (*C*H(Et)Me), 25.0 (*C*H$_2$CH$_3$), 20.7 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 17.0 (Mes-*o*-Me), 15.9 (CH(Et)*Me*), 10.9 (CH$_2$*C*H$_3$). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 657.2959 [**3d** + H]$^+$ 657.2951 calcd for $C_{36}H_{47}N_4O_4Ni$), and 679.2772 [**3d** + Na]$^+$ (679.2765 calcd for $C_{36}H_{46}N_4O_4NaNi$). $[\alpha]^{20}_D$ = -284 (C = 0.0944 in EtOH).

[Cyclopentadienyl{1-[(*S*)-2-(2-phenylacetate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**2e**)

Method A in MeCN results in **2e**. Purification: Percolation in silica gel with ethyl acetate.

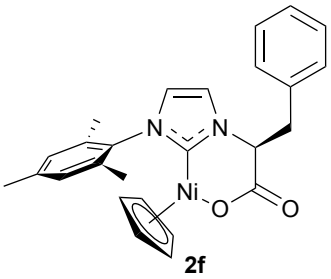


2e

Brown solid. Yield: 30%. **^{1}H NMR (500 MHz, dmso-d$_6$):** δ 7.87 (s, 1H, Imz-H^5), 7.74 (d, *J* = 8, 2H, Ph-*o*-H), 7.50 (t, *J* = 7, 2H, Ph-*m*-H), 7.41 (t, *J* = 8, 1H, Ph-*p*-H), 7.32 (s, 1H, Imz-H^4), 7.17 (s, 1H, Mes-*m*-H), 7.03 (s, 1H, Mes-*m*-H), 5.95 (s, 1H, NC*H*COO), 4.60 (s, 5H, C_5H_5), 2.35 (s, 3H, Mes-*o*-H), 2.31 (s, 3H, Mes-*p*-H), 1.85 (s, 3H, Mes-*o*-H). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 169.9 (*C*OO), 157.5 (Imz-C^2), 139.0 (Mes-*p*-C), 138.1 (Ph-*ipso*-C), 135.9 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.5 (Mes-*o*-C), 128.9 (Mes-*m*-C)), 128.7 (Mes-*m*-C), 128.5 (Ph-*m*-C), 127.9 (Ph-*p*-C), 126.3 (Ph-*o*-C), 124.6 (Imz-C^5), 123.6 (Imz-C^4), 90.9 (C_5H_5), 67.7 (N*C*HCOO), 20.6 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 17.0 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeCN): *m/z* found 441.1266 [**2e** + H]$^+$ (441.1269 calcd for $C_{24}H_{25}N_2O_2Ni$). $[\alpha]^{20}_D$ = -7 (C = 0.085 in EtOH).

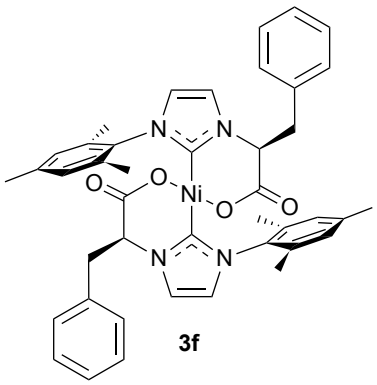
[Cyclopentadienyl{1-[(*S*)-2-(3-phenylpropanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**2f**) and [bis{1-[(*S*)-2-(3-phenylpropanoate)]-3-(mesityl)imidazol-2-ylidene}nickel(II)] (**3f**)

Method B in MeCN during 1 h results in a mixture 87:13 of **2f** and **3f**. Method B in THF results in a mixture 25:75 of **2f** and **3f**. Purification: Column chromatography using neat ethyl acetate for the separation of **3f** and then with 20% EtOH for **2f**.



2f

Brown solid. Yield: 46% by Method B in MeCN, 25% by Method B in THF. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.3-7.2 (m, 5H, Ph), 7.14 (s, 1H, Mes-*m*-H), 7.09 (d, *J* = 2, 1H, Imz-H^5), 7.00 (s, 1H, Mes-*m*-H), 6.97 (d, *J* = 2, 1H, Imz-H^4), 4.85 (dd, *J* = 11 and 5, 1H, NC*H*CH$_2$), 4.76 (s, 5H, C$_5$H$_5$), 4.45 (dd, *J* = 13 and 11, 1H, NCHC*H*$_2$), 3.52 (dd, *J* = 13 and, 5, 1H, NCHC*H*$_2$), 2.30 (s, 3H, Mes-*p*-Me, 2.30 (s, 3H, Mes-*o*-Me), 1.80 (s, 3H, Mes-*o*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 171.7 (*C*OO),155.5 (Ph-*ipso*-C)), 138.8 (Mes-*p*-C), 136.6 (Imz-C^2), 135.9 (Mes-*ipso*-C)), 135.5 (Mes-*o*-C), 134.6 (Mes-*o*-C), 129.5 (Ph-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes-*m*-C), 128.3 (Ph-*m*-C), 126.8 (Ph-*p*-C), 124.6 (Imz-C^5), 122.2 (Imz-C^4), 90.7 (C$_5$H$_5$), 66.3 (N*C*HCH$_2$), 40.2 (^{1}H^{13}C-HMBC, (NCH*C*H$_2$), 20.6 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 16.8 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 457.1420 [**2f** + H]$^+$ (457.1426 calcd for C$_{26}$H$_{27}$N$_2$O$_2$Ni), and 479.1241 [**2f** + Na]$^+$ (479.1245 calcd for C$_{26}$H$_{26}$N$_2$O$_2$NaNi). [α]$^{20}_D$ = -574 (C = 0.092 in EtOH).

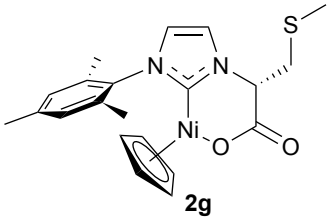


3f

Brown solid. Yield: 12% by Method B in MeCN, 30% by Method B in THF. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.24 (m, 10H, Ph), 7.04 (s, 2H , Mes-*m*-H), 6.91 (s, 2H, Imz-H^4), 6.87 (s, 2H, Mes-*m*-H) 6.81 (broad s, 2H, Imz-H^5), 4.84 (broad s, 2H, NCHC*H*$_2$), 4.58 (dd, *J* = 10 and 5, 2H, NC*H*CH$_2$), 3.94 (d, *J* = 10, 2H, NCHC*H*$_2$), 2.36 (broad s, 6H, Mes-*o*-Me), 2.24 (s, 6H Mes-*p*-Me), 1.94 (s, 6H, Mes-*o*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 170.9 (*C*OO), 159.1 (Imz-C^2), 137.3 (Mes-*p*-C), 136.4 (Ph-*ipso*-C), 135.5 (Mes-*o*-C), 135.4 (Mes-*ipso*-C), 134.0 (Mes-*o*-C), 129.1 (Ph-*o*-C and Ph-*m*-C), 128.4 (Mes-*m*-C), 128.3 (Ph-*o*-C and Ph-*m*-C), 127.9 (Mes-*m*-C), 126.8 (Ph-*p*-C, 122.6 (Imz-C^4), 121.7 (Imz-C^5), 65.1 (N*C*HCH), 42.8 (NCH*C*H$_2$), 20.6 (Mes-*p*-Me), 17.7 (Mes-*o*-Me), 17.3 (Mes-*o*-Me). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 725.2644 [**3f** + H]$^+$ (725.2638 calcd for C$_{42}$H$_{43}$N$_4$O$_4$Ni), and 747.2460 [**3f** + Na]$^+$ (747.2457 calcd for C$_{42}$H$_{42}$N$_4$O$_4$NaNi). [α]$^{20}_D$ = -278 (C = 0.171 in EtOH).

[Cyclopentadienyl[1-{(*S*)-2-[3-(methylthio)propanoate]}-3-(mesityl)imidazol-2-ylidene]nickel(II)] (**2g**)

Method A or B in MeCN results in **2g**. Purification: washings with cold diethyl ether.



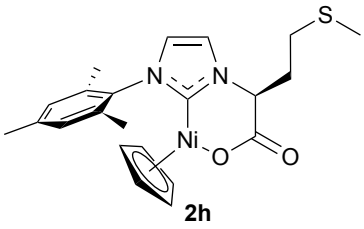
2g

Brown solid. Yield: 72-68%.**^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.83 (d, *J* = 2, 1H, Imz-H^5), 7.28 (d, *J* = 2, 1H, Imz-H^4), 7.17 (d, *J* = 2, 1H, Mes-*m*-H), 7.01 (d, *J* = 2, 1H, Mes-*m*-H), 4.72 (dd, *J* = 10 and 4, 1H, NC*H*COO), 4.57 (s, 5H, C$_5$H$_5$), 4.34 (dd, *J* = 14 and 10, 1H, C*H*$_2$S-anti), 3.39 (dd, *J* = 14 and 4, 1H, C*H*$_2$S-sin), 2.33 (s, 3H, Mes-*o*-Me), 2.31 (s, 3H, Mes-*p*-Me), 2.20 (s, 3H, Mes-*o*-Me), 1.81 (s, 3H, SC*H*$_3$). **^{1}H NMR (500 MHz, acetone-d$_6$, T = -50 ºC)**: δ 7.89 (d, *J* = 2, 1H, Imz-H^5), 7.25 (d, *J* = 2, 1H, Imz-H^4), 7.19 (s, 1H, Mes-*m*-H), 7.03 (s, 1H, Mes-*m*-H), 4.78 (dd, *J* = 11 and 3, 1H,

NC*H*COO), 4.74 (s, 5H, C_5H_5), 4.52 (dd, *J* = 14 and 12, 1H, CH_2S-anti), 3.26 (dd, *J* = 14 and 3, 1H, CH_2S-sin), 2.38 (s, 3H, Mes-*o*-Me), 2.33 (s, 3H, Mes-*p*-Me), 2.13 (s, 3H, Mes-*o*-Me), 1.85 (s, 3H, SCH_3). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 170.9 (*C*OO), 138.9 (Mes-*p*-C), 136.0 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.5 (Mes-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes*mp*-C), 125.9 (Imz-C^5), 123.0 (Imz-C^4), 91.7 (C_5H_5), 64.6 (N*C*HCOO), 38.2 (*C*H_2S), 20.6 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 16.8 (Mes-*o*-Me), 15.0 (S*C*H_3). **^{13}C NMR (125 MHz, acetone-d$_6$. T = -50 ºC)**: δ = 171.8 (*C*OO), 158.5 (Imz-C^2), 140.0 (Mes-*p*-C), 136.8 (Mes-*ipso*-C), 136.5 (Mes-*o*-C), 135.3 (Mes-*o*-C), 129.6 (Mes-*m*-C), 129.4 (Mes-*m*-C), 126.3 (Imz-C^5), 122.7 (Imz-C^4), 91.4 (C_5H_5), 65.7 (N*C*HCOO), 39.3 (*C*H_2S), 20.9 (Mes-*p*-Me), 18.4 (Mes-*o*-Me), 17.4 (Mes-*o*-Me), 15.2 (S*C*H_3). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 427.0982 [**2g** + H]$^+$ (427.0990 calcd for $C_{21}H_{25}N_2O_2SNi$). $[\alpha]^{20}_D$ = -8 (C = 0.091 in EtOH).

[Cyclopentadienyl[1-{(*S*)-2-[4-(methylthio)butanoate]}-3-(mesityl)imidazol-2-ylidene]nickel(II)] (**2h**)

Method A or B in MeCN results in **2h**. Purification: washings with cold diethyl ether.



2h

Brown solid. Yield: 69-51%. **^{1}H NMR (500 MHz, dmso-d$_6$)**: δ 7.75 (d, *J* = 2, 1H, Imz-H^5), 7.26 (d, *J* = 2, 1H, , Imz-H^4), 7.16 (s, 1H, Mes-*m*-H), 7.01 (s, 1H, Mes-*m*-H), 4.8-4.7 (s+m, 5+1H, C_5H_5 and NC*H*COO, Cp), 3.2-3.1 (m, 1H, CH_2S), 2.7-2.5 (m, 1H, CHCH_2), 2.32 (s, 3H, Mes-*o*-Me), 2.31 (s, 3H, Mes-*p*-Me), 2.13 (s, 3H, SCH_3), 1.81 (s, 2H, Mes-*p*-Me). **^{13}C NMR (125 MHz, dmso-d$_6$)**: δ 171.7 (*C*OO), 156.4 (Imz-C^2), 138.9 (Mes-*p*-C), 135.9 (Mes-*ipso*-C), 135.4 (Mes-*o*-C), 134.5 (Mes-*o*-C), 128.8 (Mes-*m*-C), 128.6 (Mes-*m*-C), 124.5 (Imz-C^5), 123.0 (Imz-C^4), 90.7 (C_5H_5), 64.2 (N*C*HCOO), 34.4 (*C*H_2S), 29.5 (CHCH$_2$), 20.6 (Mes-*p*-Me), 17.8 (Mes-*o*-Me), 16.8 (Mes-*o*-Me), 14.7 (S*C*H_3). HR-MS (ESI/TOF, positive mode, MeOH): *m/z* found 441.1132 [**2h** + H]$^+$ (441.1147 calcd for $C_{22}H_{27}N_2O_2SNi$). $[\alpha]^{20}_D$ = -423 (C = 0.090 in EtOH).

X-Ray molecular structure determinations

Crystals of **2a-h** suitable for X-ray diffraction studies were obtained from saturated toluene:pentane mixtures (1:1) while those of **3b-d** were obtained from chloroform:pentane (1:1). Single crystals were coated with mineral oil, mounted on Mitegen MicroMounts with the aid of a microscope, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets for all complexes were collected at 200 K on a Bruker D8 Venture diffractometer equipped with multilayer optics for monochromatization and collimator, Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryostream 800 unit. Crystallographic data for all complexes is presented in Table S1 in this Supporting Information, while the ORTEP drawings of the complexes **2a-h** and **3b-d** are shown in Figures S1-S11 together with a selection of bond lengths and angles.

The structures of all compounds were solved by applying intrinsic phasing (SHELXT)[6] using the Olex2 package.[7] All were refined by least-squares against F^2 (SHELXL).[8] All non-hydrogen atoms were anisotropically refined, while hydrogen atoms were placed at idealized positions and refined using a riding model.

In complexes **2d**, **2e**, and **2h**, there was some dynamic disorder within the cyclopentadienyl carbon atoms. We were able to use SIMU and ISOR restraints to refine the C21-C25 carbon atoms in **2e** and **2h**, but we

needed to apply EADP constraints to the C1-C5 atoms in **2d**. In addition, the C32, C33, C35, and C36 phenyl carbon atoms in **2e** showed disorder, with two sites being found for each carbon atom and optimized occupancies of 34.5% and 65.5% respectively. Finally, it is worth noting that each molecule of **3b** crystallized with two chloroform solvent molecules.

CCDC 2302830-2302837 (for **2a-2h**), and 2302838-2302840 (for **3b-3d**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Experimental data for the X-ray diffraction studies on complexes **2a-h**, and **3b-d**.

	2a	**2b**	**2c**	**2d**
Formula	$C_{20}H_{22}N_2NiO_2$	$C_{22}H_{26}N_2NiO_2$	$C_{23}H_{28}N_2NiO_2$	$C_{23}H_{28}N_2NiO_2$
M	381.10	409.16	423.18	423.18
T [K]	200(2)	200(2)	200(2)	200(2)
λ[Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a [Å]; α [º]	10.0587(6)	9.0157(3)	9.1875(7)	9.4289(5)
b [Å]; β [º]	11.4836(6)	14.8412(5)	13.481(1)	13.1499(6)
c [Å]; γ [º]	15.7711(8)	15.2205(5)	17.073(2)	17.0940(9)
V [Å^3]	1821.7(2)	2036.6(1)	2114.5(3)	2119.5(2)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.390	1.334	1.329	1.326
μ [mm^{-1}]	1.080	0.971	0.938	0.935
F(000)	800	864	896	896
Crystal size [mm^3]	0.35 x 0.28 x 0.13	0.22 x 0.18 x 0.12	0.30 x 0.23 x 0.16	0.27 x 0.17 x 0.14
θ range [deg]	3.732 to 27.648	3.835 to 27.493	3.249 to 27.553	1.954 to 27.490
Index ranges	13 to -13, 14 to -14, 20 to -20	11 to -11, 18 to -19, 17 to -19	11 to -11, 16 to -17, 22 to -22	12 to -12, 17 to -16, 22 to -22
Reflections collected	85563	17642	27641	30035
Unique data	4215 (R_{int} = 0.077)	4624 (R_{int} = 0.044)	4818 (R_{int} = 0.070)	4837 (R_{int} = 0.070)
Reflections [I>2σ(I)]	4064	4176	3994	4077
Goodness-of-fit on F^2	1.085	1.030	1.057	1.035
Final R indices [I>2σ(I)]	R1 = 0.029, wR2 = 0.071	R1 = 0.032; wR2 = 0.067	R1 = 0.042; wR2 = 0.075	R1 = 0.042; wR2 = 0.100
R indices (all data)	R1 = 0.031 wR2 = 0.072	R1 = 0.038; wR2 = 0.070	R1 = 0.058, wR2 = 0.079	R1 = 0.058, wR2 = 0.110
Largest diff. peak/hole [e·Å^{-3}]	0.571 / -0.219	0.236 / -0.257	0.291 / -0.451	0.698 / -0.414

[a] $R1=\Sigma||F_0|-|F_c||/[\Sigma|F_0|]$ $\quad wR2=\{[\Sigma w(F_0^2-F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$

Table S1 (Cont.). Experimental data for the X-ray diffraction studies on complexes **2a-h**, and **3b-d**.

	2e	**2f**	**2g**	**2h**
Formula	$C_{25}H_{24}N_2NiO_2$	$C_{26}H_{26}N_2NiO_2$	$C_{21}H_{24}N_2NiO_2S$	$C_{22}H_{26}N_2NiO_2S$
M	443.17	457.20	427.19	441.22
T [K]	200(2)	200(2)	200(2)	200(2)
λ[Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*P2₁*/c	*P2₁2₁2₁*	*P2₁*/c	*P2₁2₁2₁*
a [Å]; α [º]	12.3904(10)	9.5852(3)	11.3923(7)	9.5632(3)
b [Å]; β [º]	11.4363(9); 105.807(2)	15.2321(6)	11.6720(6); 90.693(2)	14.2948(5)
c [Å]; γ [º]	16.023(1)	15.8061(5)	15.6603(7)	16.1641(6)
V [Å^3]	2184.6(3)	2307.7(1)	2082.2(2)	2209.7(1)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.347	1.316	1.363	1.326
μ [mm^{-1}]	0.911	0.865	1.049	0.991
F(000)	928	960	896	928
Crystal size [mm^3]	0.21 x 0.13 x 0.04	0.32 x 0.25 x 0.08	0.20 x 0.18 x 0.11	0.46 x 0.07 x 0.05
θ range [deg]	3.258 to 25.03	3.341 to 27.503	3.726 to 27.505	2.475 to 27.495
Index ranges	14 to -14, 13 to -13, 19 to -17	11 to -12, 19 to -19, 20 to -20	14 to -14, 15 to -15, 20 to -19	11 to -12, 18 to -18, 20 to -20
Reflections collected	48749	36082	17587	35090
Unique data	3855 (R_{int} = 0.133)	5273 (R_{int} = 0.064)	4624 (R_{int} = 0.076)	5070 (R_{int} = 0.060)
Reflections [I>2σ(I)]	3231	4452	3565	4245
Goodness-of-fit on F^2	1.174	1.028	1.064	1.045
Final R indices [I>2σ(I)]	R1 = 0.079, wR2 = 0.167	R1 = 0.033; wR2 = 0.069	R1 = 0.048; wR2 = 0.104	R1 = 0.034; wR2 = 0.075
R indices (all data)	R1 = 0.0944 wR2 = 0.174	R1 = 0.046; wR2 = 0.074	R1 = 0.071, wR2 = 0.113	R1 = 0.048, wR2 = 0.083
Largest diff. peak/hole [e·Å^{-3}]	1.692 / -0.943	0.304 / -0.239	0.616 / -0.473	0.293 / -0.272

[a] $R1=\Sigma||F_0|-|F_c||/[\Sigma|F_0|]$ $\quad wR2=\{[\Sigma w(F_0^2-F_c^2)^2]/[\Sigma w(F_0^2)^2]\}^{1/2}$

Table S1 (Cont.). Experimental data for the X-ray diffraction studies on complexes **2a-h**, and **3b-d**.

	3b	**3c**	**3d**
Formula	$C_{34}H_{42}N_4NiO_4 \cdot 2\ CHCl_3$	$C_{36}H_{46}N_4NiO_4$	$C_{36}H_{46}N_4NiO_4$
M	868.16	657.48	657.48
T [K]	200(2)	200(2)	200(2)
λ[Å]	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*P2₁*	*P2₁*	*P* 1
a [Å]; α [º]	10.7822(4)	13.4002(6)	7.9269(4); 71.267(2)
b [Å]; β [º]	17.9182(5); 107.076(1)	7.5080(3); 109.185(1)	10.0993(5); 81.256(2)
c [Å]; γ [º]	11.2267(4)	17.3761(7)	11.2121(5); 77.531(2)
V [Å^3]	2073.4(1)	1651.1(1)	826.67(7)
Z	2	2	1
ρ_{calcd} [g cm^{-3}]	1.391	1.322	1.321
μ [mm^{-1}]	0.896	0.632	0.632
F(000)	900	700	350
Crystal size [mm^3]	0.23 x 0.17 x 0.06	0.33 x 0.21 x 0.09	0.24 x 0.21 x 0.08
θ range [deg]	1.976 to 27.487	3.374 to 27.510	3.30 to 27.511
Index ranges	11 to -13, 23 to -23, 14 to -14	17 to -17, 9 to -9, 22 to -22	10 to -10, 13 to -13, 14 to -14
Reflections collected	56426	41111	42919
Unique data	9405 (R_{int} = 0.046)	7366 (R_{int} = 0.033)	7558 (R_{int} = 0.047)
Reflections [I>2σ(I)]	8896	7139	7168
Goodness-of-fit on F^2	1.031	1.043	1.030
Final R indices [I>2σ(I)]	R1 = 0.031, wR2 = 0.068	R1 = 0.026; wR2 = 0.070	R1 = 0.030; wR2 = 0.066
R indices (all data)	R1 = 0.034 wR2 = 0.070	R1 = 0.027; wR2 = 0.071	R1 = 0.033, wR2 = 0.068
Largest diff. peak/hole [e·Å^{-3}]	0.326 / -0.361	0.354 / -0.269	0.252 / -0.214

[a] $R1 = \Sigma||F_0|-|F_c||/[\Sigma|F_0|]$ $\quad wR2 = \{[\Sigma w(F_0^2 - F_c^2)^2] / [\Sigma w(F_0^2)^2]\}^{1/2}$

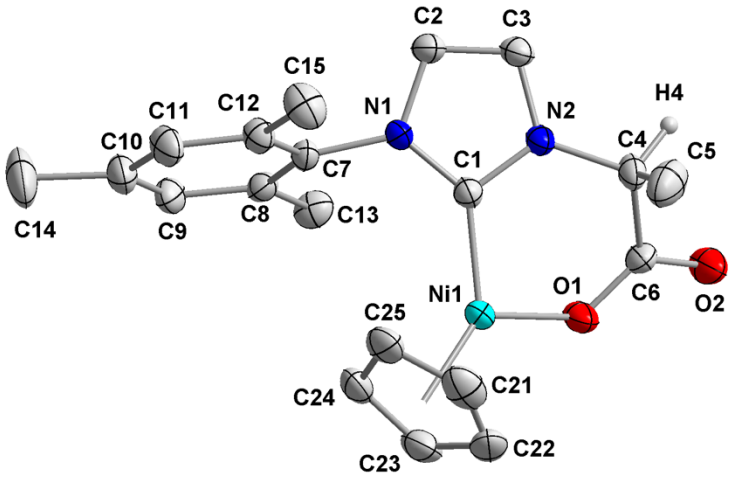


Figure S1. Molecular structure of **2a**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.887(2), Ni1-C1 1.851(3), O1-C6 1.269(4), O2-C6 1.226(4), N1-C1 1.349(4), N1-C2 1.388(4), N1-C7 1.444(4), N2-C1 1.352(4), N2-C3 1.382(4), N2-C4 1.461(4), C1-Ni1-O1 92.6(1), C6-O1-Ni1 126.9(2), C1-N1-C2 110.8(2), C1-N1-C7 127.9(2), C2-N1-C7 121.1(2), C1-N2-C3 111.8(2), C1-N2-C4 124.8(3), C3-N2-C4 123.4(2), N1-C1-Ni1 135.2(2), N1-C1-N2 104.0(2), N2-C1-Ni1 120.7(2), C3-C2-N1 107.3(3), C2-C3-N2 106.1(3), N2-C4-C5 110.5(3), N2-C4-C6 111.6(2), O1-C6-C4 119.2(3), O2-C6-O1 124.0(3), O2-C6-C4 116.8(3).

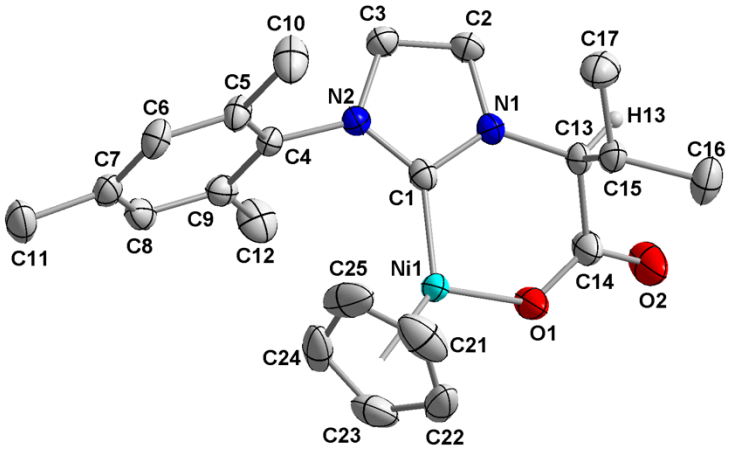


Figure S2. Molecular structure of **2b**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.882(2), Ni1-C1 1.860(3), O1-C14 1.284(4), O2-C14 1.226(4), N1-C1 1.349(3), N1-C2 1.385(4), N1-C13 1.469(4), N2-C1 1.357(3), N2-C3 1.389(4), N2-C4 1.440(3), C2-C3 1.345(4), C13-C14 1.530(4), C1-Ni1-O1 92.8(1), C14-O1-Ni1 128.1(2), C1-N1-C2 111.2(2), C1-N1-C13 124.3(2), C2-N1-C13 124.2(2), C1-N2-C3 111.3(2), C1-N2-C4 124.5(2), C3-N2-C4 124.1(2), N1-C1-Ni1 120.8(2), N1-C1-N2 104.3(2), N2-C1-Ni1 134.9(2), C3-C2-N1 107.0(2), C2-C3-N2 106.1(3), N1-C13-C14 110.8(2), N1-C13-C15 111.5(2), O1-C14-C13 117.6(3), O2-C14-O1 123.9(3), O2-C14-C13 118.4(3).

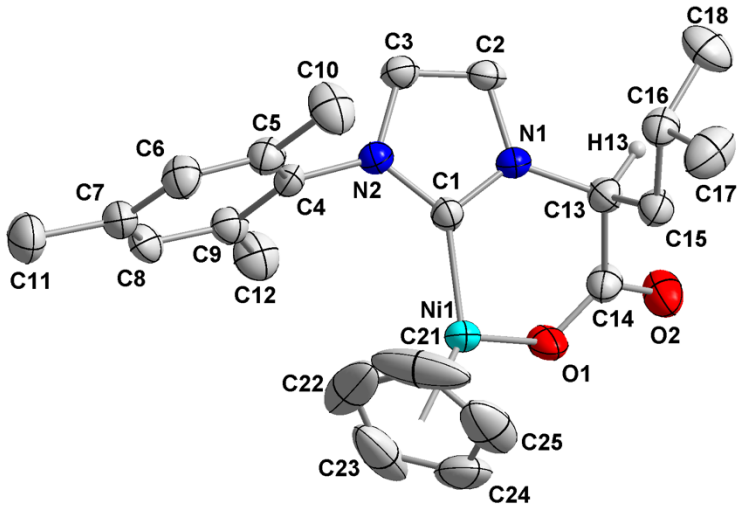


Figure S3. Molecular structure of **2c**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.882(3), Ni1-C1 1.858(4), O1-C14 1.278(5), O2-C14 1.227(5), N1-C1 1.339(5), N1-C2 1.384(4), N1-C13 1.468(5), N2-C1 1.364(4), N2-C3 1.382(5), N2-C4 1.426(5), C13-C14 1.528(5), C13-C15 1.529(5), C1-Ni1-O1 92.1(1), C14-O1-Ni1 126.9(2), C1-N1-C2 111.7(3), C1-N1-C13 123.7(3), C2-N1-C13 124.6(3), C1-N2-C3 110.2(3), C1-N2-C4 126.3(3), C3-N2-C4 123.5(3), N1-C1-Ni1 121.3(3), N1-C1-N2 104.5(3), N2-C1-Ni1 134.1(3), C3-C2-N1 106.2(3), C2-C3-N2 107.5(3), N1-C13-C14 111.4(3), N1-C13-C15 111.9(3), O1-C14-C13 118.5(4), O2-C14-O1 124.1(4), O2-C14-C13 117.4(4).

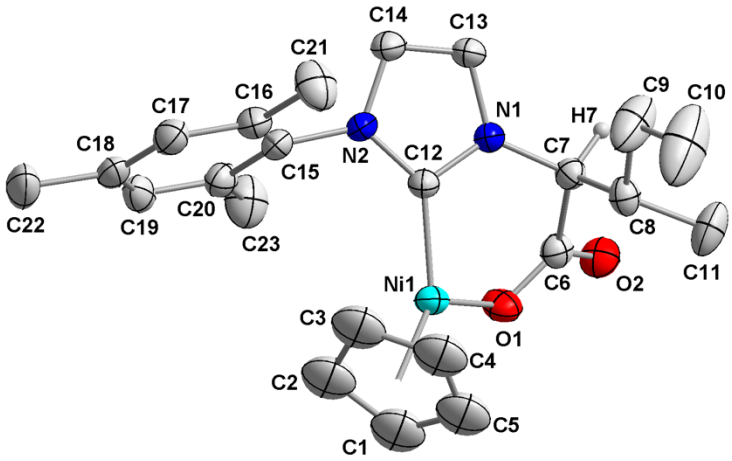


Figure S4. Molecular structure of **2d**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.876(3), C12-Ni1 1.860(4), C6-O1 1.286(5), C6-O2 1.220(5), C6-C7 1.537(6), C7-C8 1.542(6), C7-N1 1.461(5), C12-N1 1.355(5), C12-N2 1.350(5), C13-C14 1.340(7), C13-N1 1.384(5), C14-N2 1.387(6), C15-N2 1.445(5), C12-Ni1-O1 91.6(2), C6-O1-Ni1 127.5(3), N1-C12-Ni1 120.5(3), N2-C12-N1 104.6(3), N2-C12-Ni1 134.8(3), C14-C13-N1 107.2(4), C13-C14-N2 106.4(4), C12-N1-C7 123.6(4), C12-N1-C13 110.7(3), C13-N1-C7 125.7(4), C12-N2-C14 111.2(4), C12-N2-C15 126.5(3), C14-N2-C15 122.3(3), C6-O1-Ni1 127.5(3).

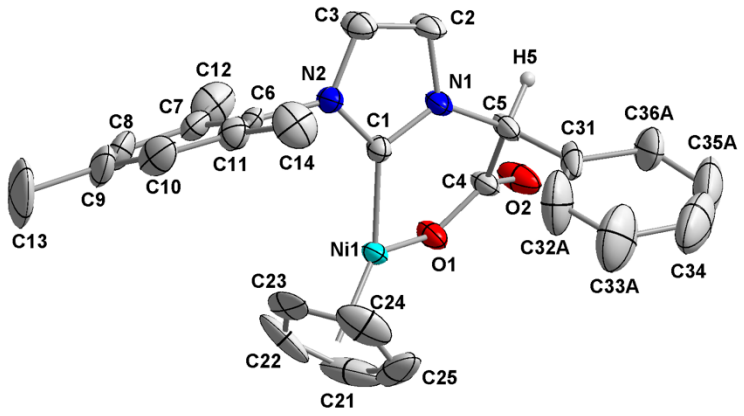


Figure S5. Molecular structure of **2e**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.873(4), Ni1-C1 1.858(5), O1-C4 1.287(6), O2-C4 1.216(6), N1-C1 1.343(6), N1-C2 1.396(6), N1-C5 1.463(7), N2-C1 1.362(6), N2-C3 1.375(7), N2-C6 1.438(6), C2-C3 1.346(8), C4-C5 1.530(7), C5-C31 1.528(9), C1-Ni1-O1 92.1(2), C4-O1-Ni1 128.9(3), C1-N1-C2 111.9(4), C1-N1-C5 125.8(4), C2-N1-C5 122.3(4), C1-N2-C3 111.5(4), C1-N2-C6 123.7(4), C3-N2-C6 124.0(4), N1-C1-Ni1 121.7(4), N1-C1-N2 103.8(4), N2-C1-Ni1 134.4(4), C3-C2-N1 105.7(5), C2-C3-N2 107.1(5), O1-C4-C5 118.6(5), O2-C4-O1 122.9(5), O2-C4-C5 118.5(5), N1-C5-C4 112.6(4), N1-C5-C31 112.7(5).

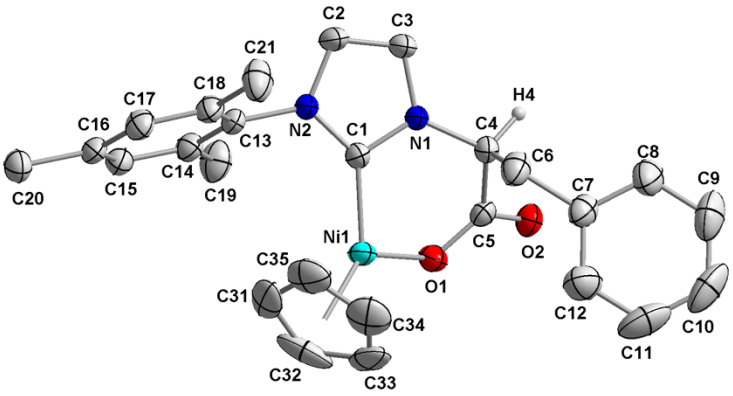


Figure S6. Molecular structure of **2f**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.888(2), Ni1-C1 1.860(3), O1-C5 1.281(3), O2-C5 1.230(3), N1-C1 1.359(4), N1-C3 1.383(4), N1-C4 1.465(4), N2-C1 1.346(4), N2-C2 1.388(4), N2-C13 1.451(4), C2-C3 1.341(4), C4-C5 1.533(4), C4-C6 1.531(5), C1-Ni1-O1 92.6(1), C5-O1-Ni1 125.7(2), C1-N1-C3 110.9(2), C1-N1-C4 123.6(2), C3-N1-C4 125.2(2), C1-N2-C2 110.8(3), C1-N2-C13 125.4(2), C2-N2-C13 123.9(2), N1-C1-Ni1 119.8(2), N2-C1-Ni1 135.5(2), N2-C1-N1 104.7(2), C3-C2-N2 107.1(3), C2-C3-N1 106.5(3), N1-C4-C5 110.8(2), N1-C4-C6 108.5(3), O1-C5-C4 118.6(3), O2-C5-O1 123.2(3), O2-C5-C4 118.2(3).

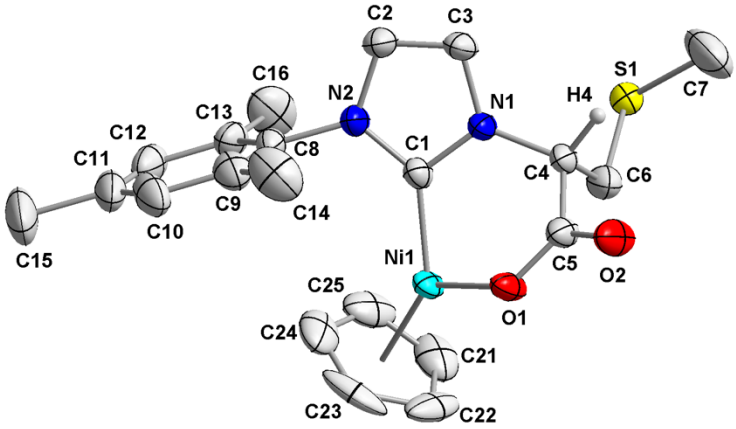


Figure S7. Molecular structure of **2g**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.889(2), Ni1-C1 1.851(3), S1-C6 1.803(3), S1-C7 1.784(5), O1-C5 1.283(3), O2-C5 1.224(3), N1-C1 1.348(3), N1-C3 1.381(3), N1-C4 1.462(3), N2-C1 1.358(3), N2-C2 1.389(3), N2-C8 1.445(3), C2-C3 1.345(4), C4-C5 1.530(4), C4-C6 1.537(4), C1-Ni1-O1 91.9(1), C7-S1-C6 99.8(2), C5-O1-Ni1 125.9(2), C1-N1-C3 111.9(2), C1-N1-C4 122.9(2), C3-N1-C4 125.1(2), C1-N2-C2 110.8(2), C1-N2-C8 124.6(2), C2-N2-C8 123.6(2), N1-C1-Ni1 121.1(2), N1-C1-N2 104.2(2), N2-C1-Ni1 134.6(2), C3-C2-N2 106.8(2), C2-C3-N1 106.3(2), N1-C4-C5 111.0(2), N1-C4-C6 112.1(2), O1-C5-C4 118.2(2), O2-C5-O1 123.3(3), O2-C5-C4 118.4(2), C4-C6-S1 115.2(2).

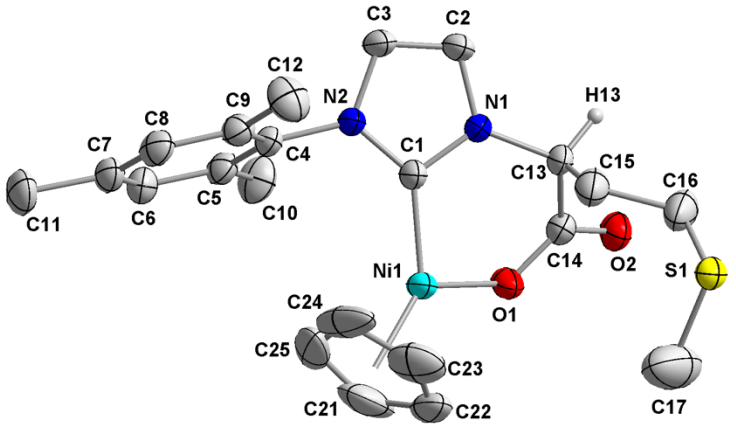


Figure S8. Molecular structure of **2h**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except that at the stereogenic center. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.889(2), Ni1-C1 1.857(3), S1-C16 1.801(5), S1-C17 1.801(6), O1-C14 1.281(4), O2-C14 1.226(4), N1-C1 1.351(4), N1-C2 1.385(4), N1-C13 1.475(4), N2-C1 1.357(4), N2-C3 1.392(4), N2-C4 1.444(4), C2-C3 1.335(5), C13-C14 1.527(4), C13-C15 1.515(6), C15-C16 1.529(5), C1-Ni1-O1 92.6(1), C17-S1-C16 98.3(3), C14-O1-Ni1 126.7(2), C1-N1-C2 111.5(3), C1-N1-C13 123.7(3), C2-N1-C13 124.7(3), C1-N2-C3 110.7(3), C1-N2-C4 126.2(3), C3-N2-C4 123.1(3), N1-C1-Ni1 120.6(2), N1-C1-N2 104.2(3), N2-C1-Ni1 135.2(2), C3-C2-N1 106.6(3), C2-C3-N2 107.0(3), N1-C13-C14 110.4(3), N1-C13-C15 110.3(3), O1-C14-C13 118.2(3), O2-C14-O1 123.3(3), O2-C14-C13 118.4(3), C13-C15-C16 113.2(3), C15-C16-S1 113.2(3).

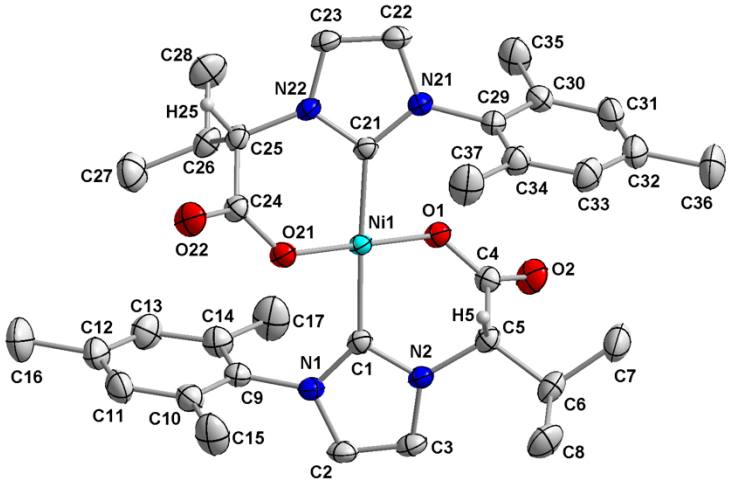


Figure S9. Molecular structure of **3b**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except those at the stereogenic centers. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.874(2), Ni1-O21 1.860(2), Ni1-C1 1.911(3), Ni1-C21 1.893(3), O1-C4 1.284(4), O2-C4 1.227(4), O21-C24 1.292(3), O22-C24 1.222(4), N1-C1 1.348(4), N1-C2 1.389(4), N1-C9 1.445(4), N2-C1 1.349(4), N2-C3 1.386(4), N2-C5 1.490(4), N21-C21 1.358(4), N21-C22 1.388(4), N21-C29 1.442(4), N22-C21 1.350(3), N22-C23 1.383(4), N22-C25 1.463(4) C2-C3 1.335(5), C4-C5 1.542(4), C5-C6 1.522(4), C22-C23 1.341(4), C24-C25 1.534(4), C25-C26 1.534(4), O1-Ni1-C1 87.8(1), O1-Ni1-C21 90.8(1), O21-Ni1-O1 178.8(1), O21-Ni1-C1 91.7(1), O21-Ni1-C21 89.8(1), C21-Ni1-C1 177.3(1), C4-O1-Ni1 124.8(2), C24-O21-Ni1 128.4(2), C1-N1-C2 110.5(2), C1-N1-C9 126.3(2), C2-N1-C9 122.9(3), C1-N2-C3 111.5(3), C1-N2-C5 119.2(2), C3-N2-C5 128.9(2), C21-N21-C22 110.7(2), C21-N21-C29 126.3(2), C22-N21-C29 122.2(3), C21-N22-C23 111.5(2), C21-N22-C25 122.9(2), C23-N22-C25 125.4(2), N1-C1-Ni1 135.9(2), N1-C1-N2 104.6(2), N2-C1-Ni1 119.2(2), C3-C2-N1 107.5(3), C2-C3-N2 106.0(3), O1-C4-C5 115.6(2), O2-C4-O1 123.0(3), O2-C4-C5 121.3(3), N2-C5-C4 103.5(2), N2-C5-C6 113.3(2), N21-C21-Ni1 133.0(2), N22-C21-Ni1 122.7(2), N22-C21-N21 104.3(2), C23-C22-N21 107.0(3), C22-C23-N22 106.5(3), O21-C24-C25 118.7(2), O22-C24-O21 122.7(3), O22-C24-C25 118.6(3), N22-C25-C24 109.7(2), N22-C25-C26 112.3(2), C24-C25-C26 112.5(2).

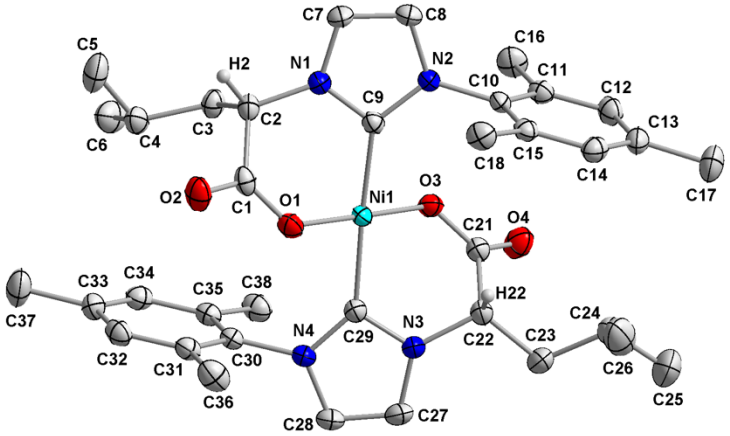


Figure S10. Molecular structure of **3c**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except those at the stereogenic centers. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.852(2), Ni1-O3 1.858(2), Ni1-C9 1.900(2), Ni1-C29 1.915(2), O1-C1 1.291(3), O2-C1 1.215(3), O3-C21 1.290(3), O4-C21 1.215(3), N1-C2 1.462(3), N1-C7 1.379(3), N1-C9 1.350(3), N2-C8 1.385(3), N2-C9 1.362(3), N2-C10 1.447(3), N3-C22 1.484(3), N3-C27 1.386(3), N3-C29 1.351(3), N4-C28 1.387(3), N4-C29 1.354(3), N4-C30 1.444(3), C1-C2 1.541(3), C2-C3 1.533(3), C7-C8 1.341(3), C21-C22 1.554(3), C22-C23 1.509(3), C27-C28 1.336(4), O1-Ni1-O3 177.3(1), O1-Ni1-C9 90.0(1), O1-Ni1-C29 91.3(1), O3-Ni1-C9 90.5(1), O3-Ni1-C29 88.3(1), C9-Ni1-C29 176.9(1), C1-O1-Ni1 129.0(1), C21-O3-Ni1 126.3(1), C7-N1-C2 124.6(2), C9-N1-C2 124.0(2), C9-N1-C7 111.4(2), C8-N2-C10 122.5(2), C9-N2-C8 110.3(2), C9-N2-C10 125.8(2), C27-N3-C22 128.8(2), C29-N3-C22 119.8(2), C29-N3-C27 111.3(2), C28-N4-C30 123.1(2), C29-N4-C28 110.6(2), C29-N4-C30 125.4(2), O1-C1-C2 119.0(2), O2-C1-O1 123.7(2), O2-C1-C2 117.3(2), N1-C2-C1 112.0(2), N1-C2-C3 109.9(2), C8-C7-N1 106.6(2), C7-C8-N2 107.3(2), N1-C9-Ni1 122.1(2), N1-C9-N2 104.5(2), N2-C9-Ni1 133.4(2), O3-C21-C22 114.9(2), O4-C21-O3 123.8(2), O4-C21-C22 121.3(2), N3-C22-C21 106.0(2), N3-C22-C23 112.4(2), C28-C27-N3 106.4(2), C27-C28-N4 107.2(2), N3-C29-Ni1 119.4(2), N3-C29-N4 104.5(2), N4-C29-Ni1 136.2(2).

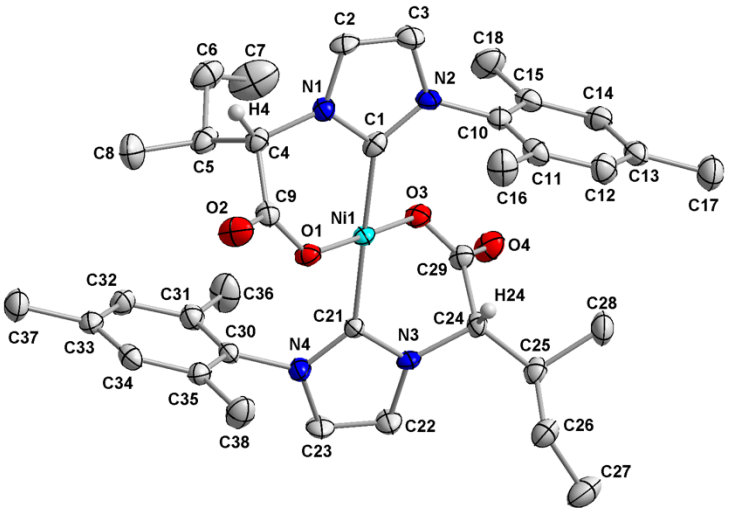
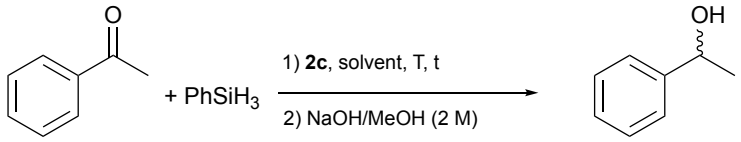


Figure S11. Molecular structure of **3d**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity except those at the stereogenic centers. Selected bond lengths (Å) and angles (deg): Ni1-O1 1.865(3), Ni1-O3 1.873(3), C1-N1 1.352(5), C1-N2 1.354(5), C1-Ni1 1.890(4), C2-C3 1.335(6), C2-N1 1.370(5), C3-N2 1.386(5), C9-C4 1.533(6), C9-O1 1.284(5), C9-O2 1.228(5), C4-C5 1.551(5), C4-N1 1.459(5), C10-N2 1.451(5), C29-C24 1.557(5), C29-O3 1.294(5), C29-O4 1.212(5), C21-N3 1.346(5), C21-N4 1.347(5), C21-Ni1 1.915(4), C22-C23 1.343(6), C22-N3 1.401(5), C23-N4 1.383(5), C24-C25 1.523(4), C24-N3 1.483(5), C30-N4 1.442(5), N1-C1-N2 104.3(3), N1-C1-Ni1 122.9(3), N2-C1-Ni1 132.8(3), C3-C2-N1 106.9(4), C2-C3-N2 106.9(4), O1-C9-C4 118.8(3), O2-C9-C4 118.5(4), O2-C9-O1 122.6(4), C9-C4-C5 110.4(3), N1-C4-C9 109.8(3), O3-C29-C24 114.5(3), O4-C29-C24 121.2(4), O4-C29-O3 124.3(4), N3-C21-N4 105.1(3), N3-C21-Ni1 120.0(3), N4-C21-Ni1 134.2(3), C23-C22-N3 105.7(4), C22-C23-N4 107.4(4), C25-C24-C29 117.5(3), N3-C24-C29 103.4(3), N3-C24-C25 113.4(3), C1-N1-C2 111.4(3), C1-N1-C4 122.8(3), C2-N1-C4 125.7(3), C1-N2-C3 110.5(3), C1-N2-C10 124.5(3), C3-N2-C10 123.2(3), C21-N3-C22 111.0(3), C21-N3-C24 119.4(3), C22-N3-C24 129.1(3), C21-N4-C23 110.8(3), C21-N4-C30 125.1(3), C23-N4-C30 123.6(3), C1-Ni1-C21 178.8(2), O1-Ni1-C1 89.1(1), O1-Ni1-C21 92.1(1), O1-Ni1-O3 178.5(2), O3-Ni1-C1 91.1(1), O3-Ni1-C21 87.7(1), C9-O1-Ni1 128.5(3), C29-O3-Ni1 126.1(3).

Catalysis: hydrosilylative reduction of acetophenones

Based on the results reported by Royo's and Ritleg's groups with related half-sandwich-NHC nickel complexes,[9,10] we tested complex **2c** in toluene and THF under different conditions summarized in Table S2 without additives. Due to the high conversion in short reaction time, resulting in a good kinetic rate under mild conditions and without the addition of any activator, the conditions of entry 5 were selected for the rest of the study.

Table S2. Preliminary testing in the hydrosilylative reduction of acetophenore with **2c**.[a]



Entry	[Ni] (mol%)	solvent	T (ºC)	t (h)	Conv (%)[b]	TOF_{av} (h^{-1})
1	2	toluene	100	1	96	48
2	2	toluene	50	2	96	24
3	2	THF	50	6	96	8
4	5	THF	50	2.5	96	8
5	10	THF	50	0.5	99	20

[a] Acetophenone: 1.5 mmol; $PhSiH_3$: 1.8 mmol; dry solvent: 7.5 mL. [b] Conversion determined by GC-MS after methanolysis

In a typical catalytic reaction, the nickel catalyst (10 mol%, 0.15 mmol), the ketone (1.5 mmol), THF (or H_2O MilliQ) . (7.5 mL), and $PhSiH_3$ (226 µL, 1.8 mmol,) were combined and sealed into a Schlenk tube. The solution was warmed at 50 ºC and aliquots were taken periodically for monitoring the evolution of the reaction by GC-MS. The reaction was quenched by addition of NaOH in MeOH (7.5 mL, 2 M), and final conversion determined by GC-MS. The secondary alcohol can be isolated by elimination of the solvent under vacuum, washings with H_2O dissolved in diethyl ether, and further purification by column chromatography using ethyl acetate/hexane 1:9 as eluent.

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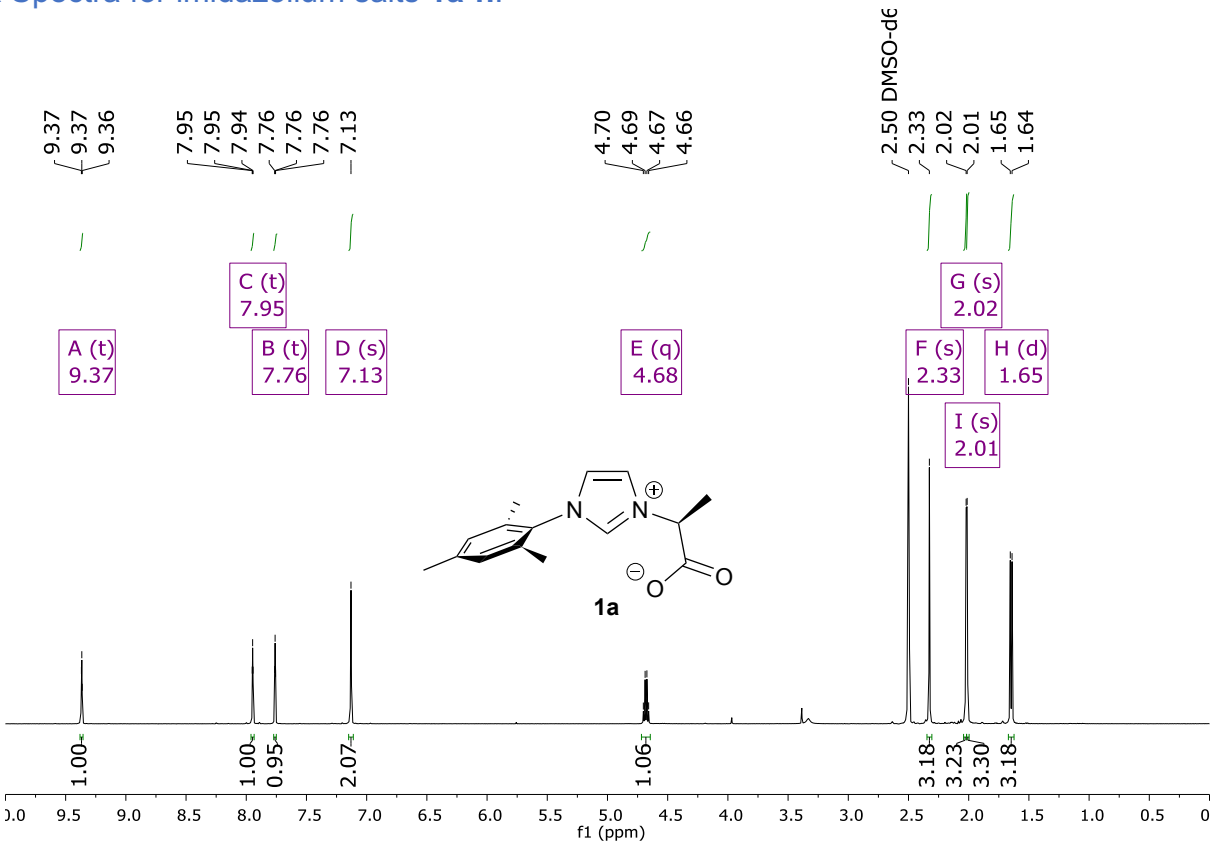
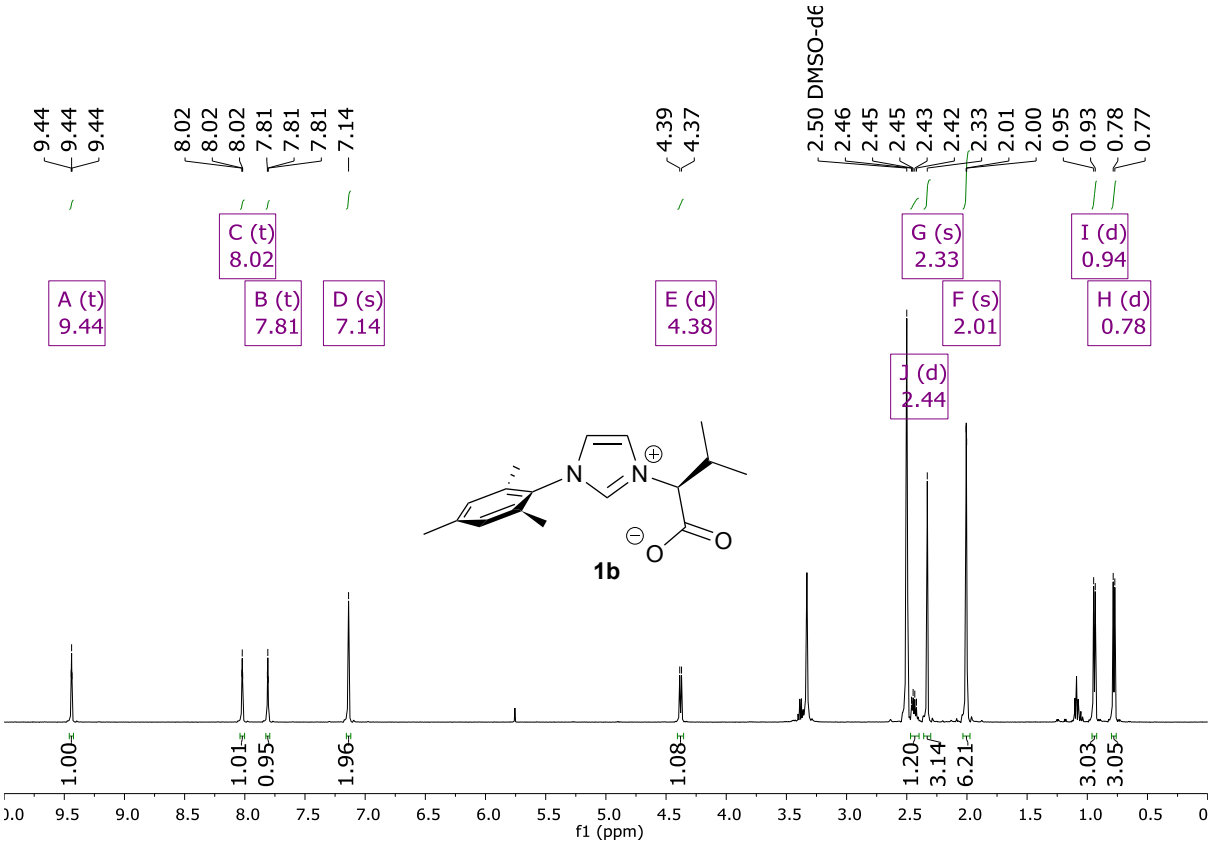
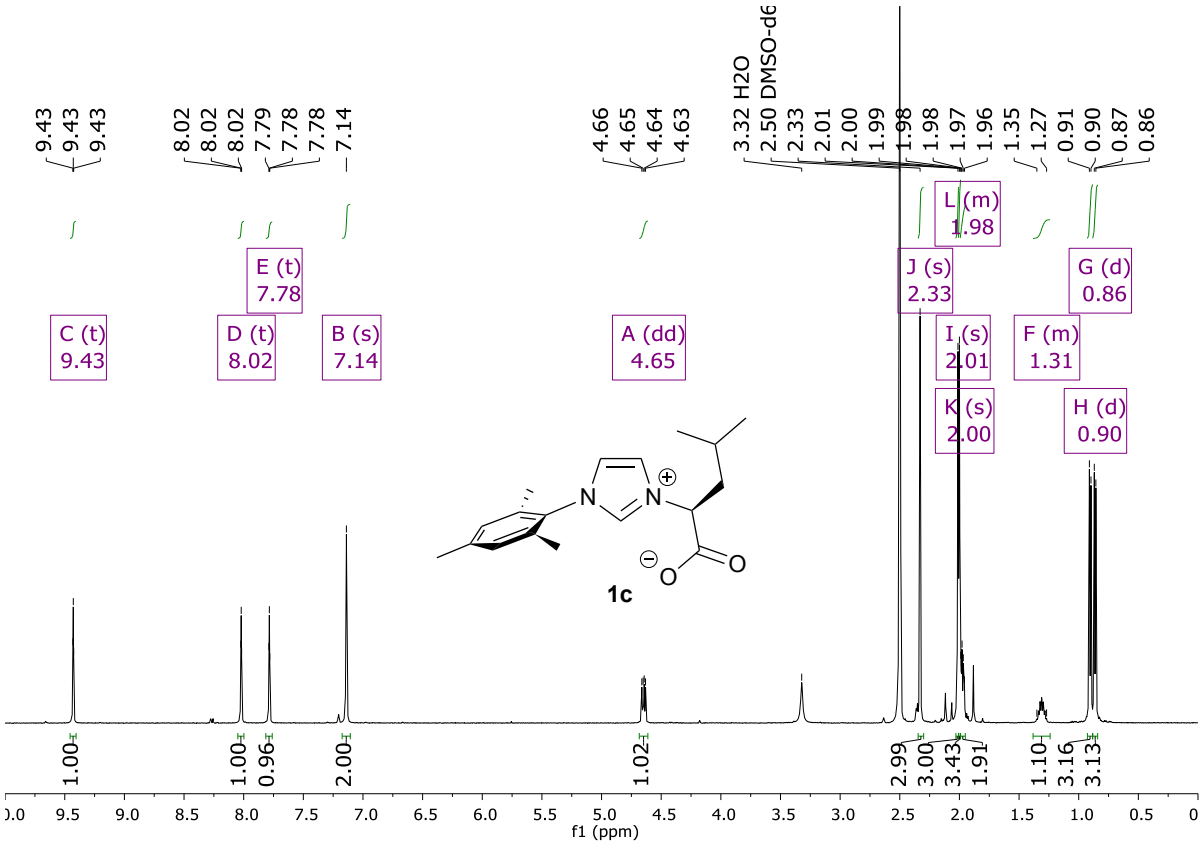
NMR Spectra for imidazolium salts **1a-h**.



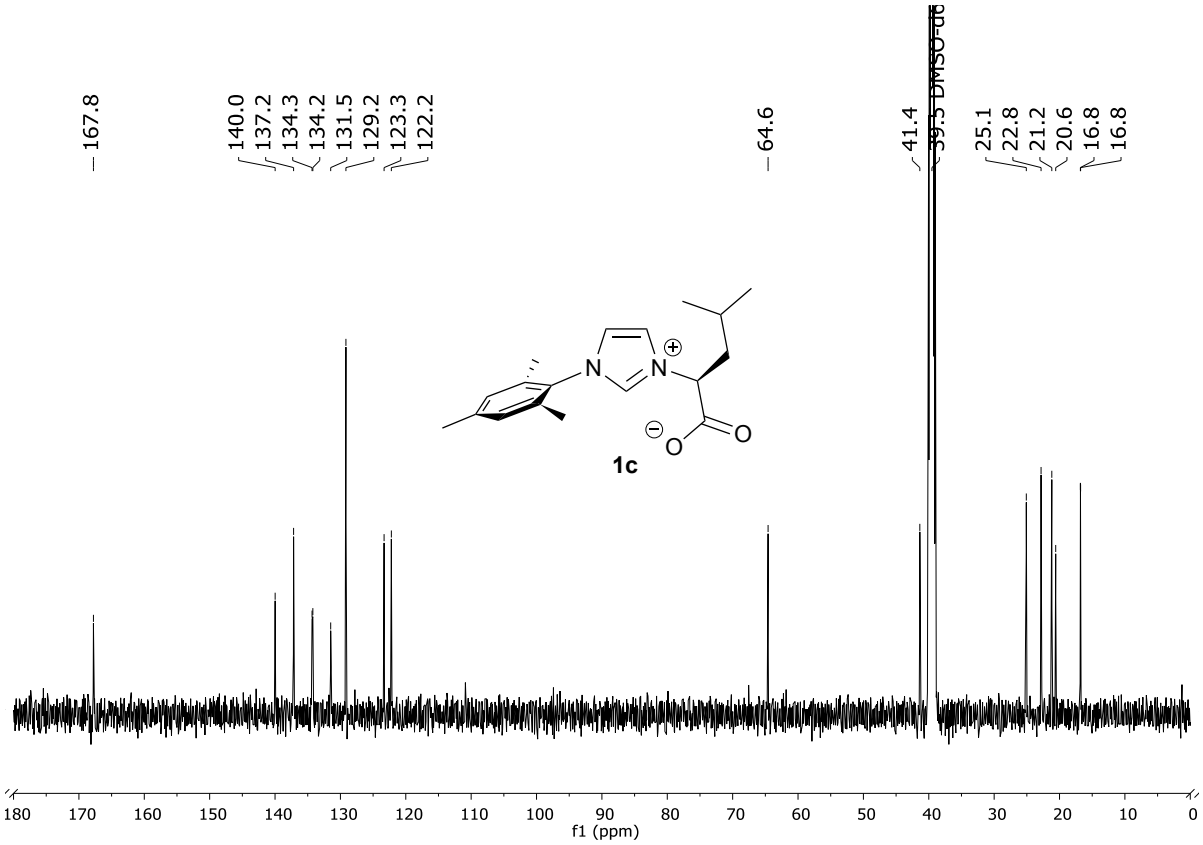
Spectrum S1. ^{1}H NMR (500 MHz, dmso-d$_6$) spectrum of **1a**.



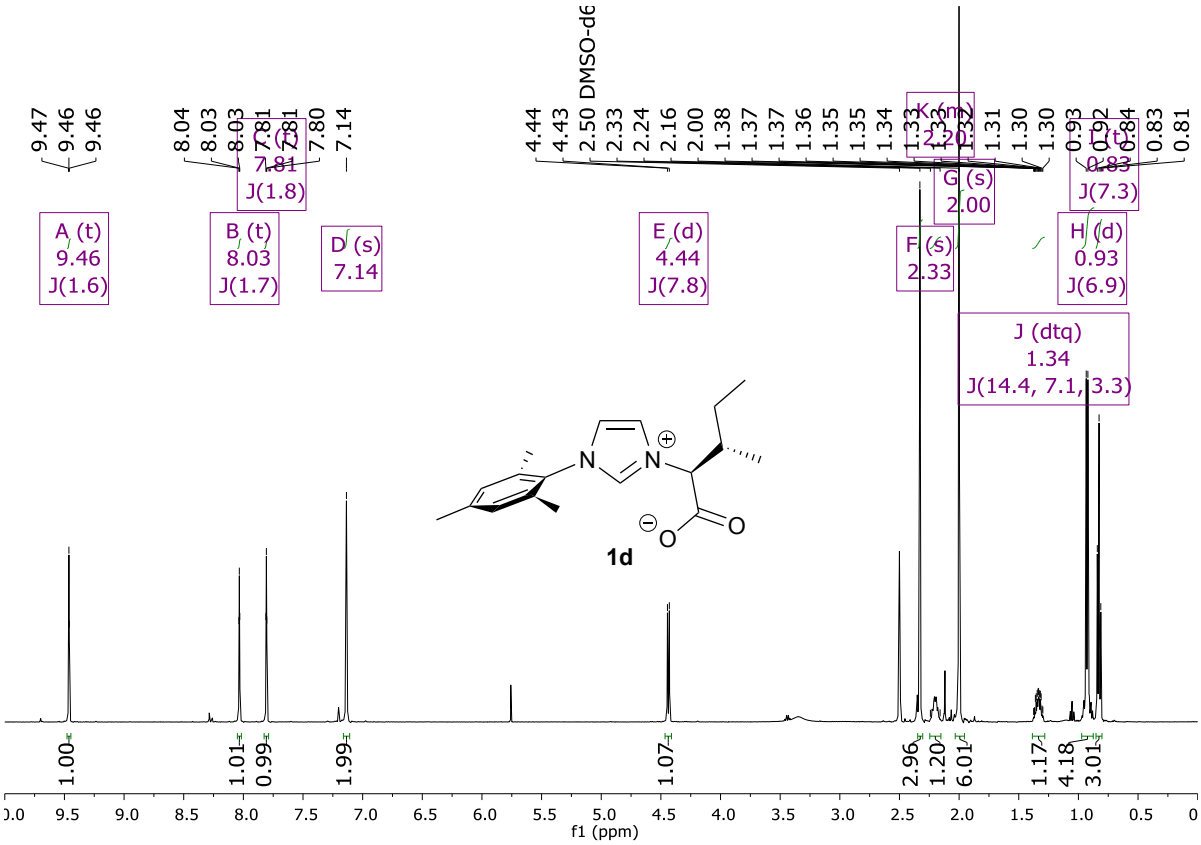
Spectrum S2. ^{1}H NMR (500 MHz, dmso-d$_6$) spectrum of **1b**.



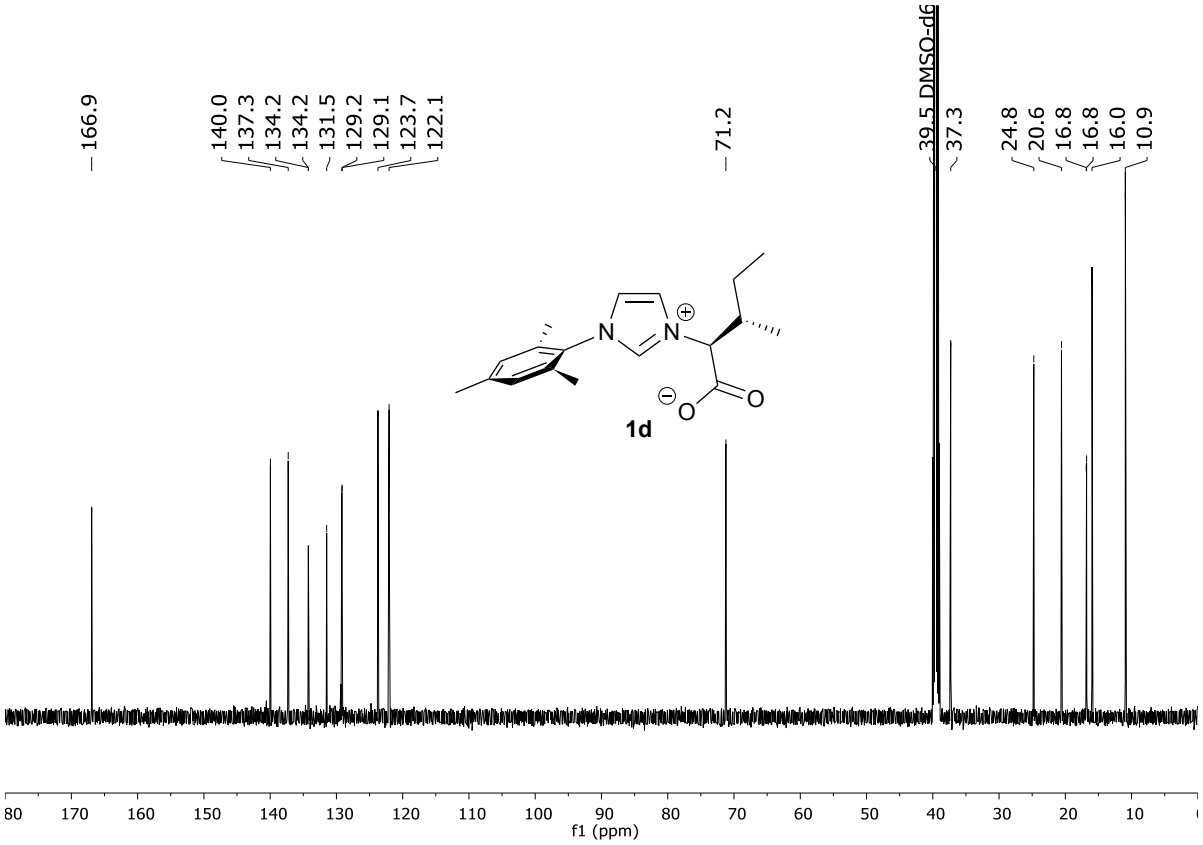
Spectrum S3. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **1c**.



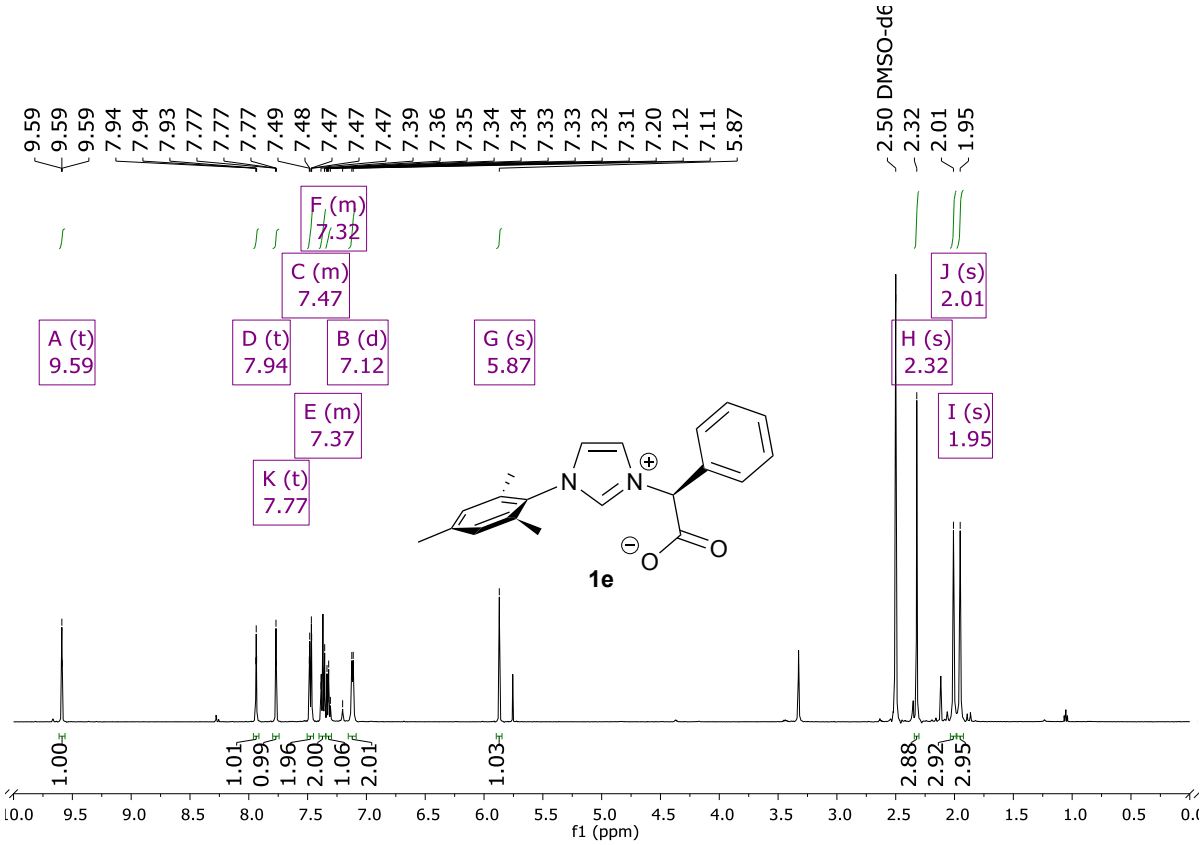
Spectrum S4. ^{13}C{^{1}H} NMR (125 MHz, dmso-d_6) spectrum of **1c**



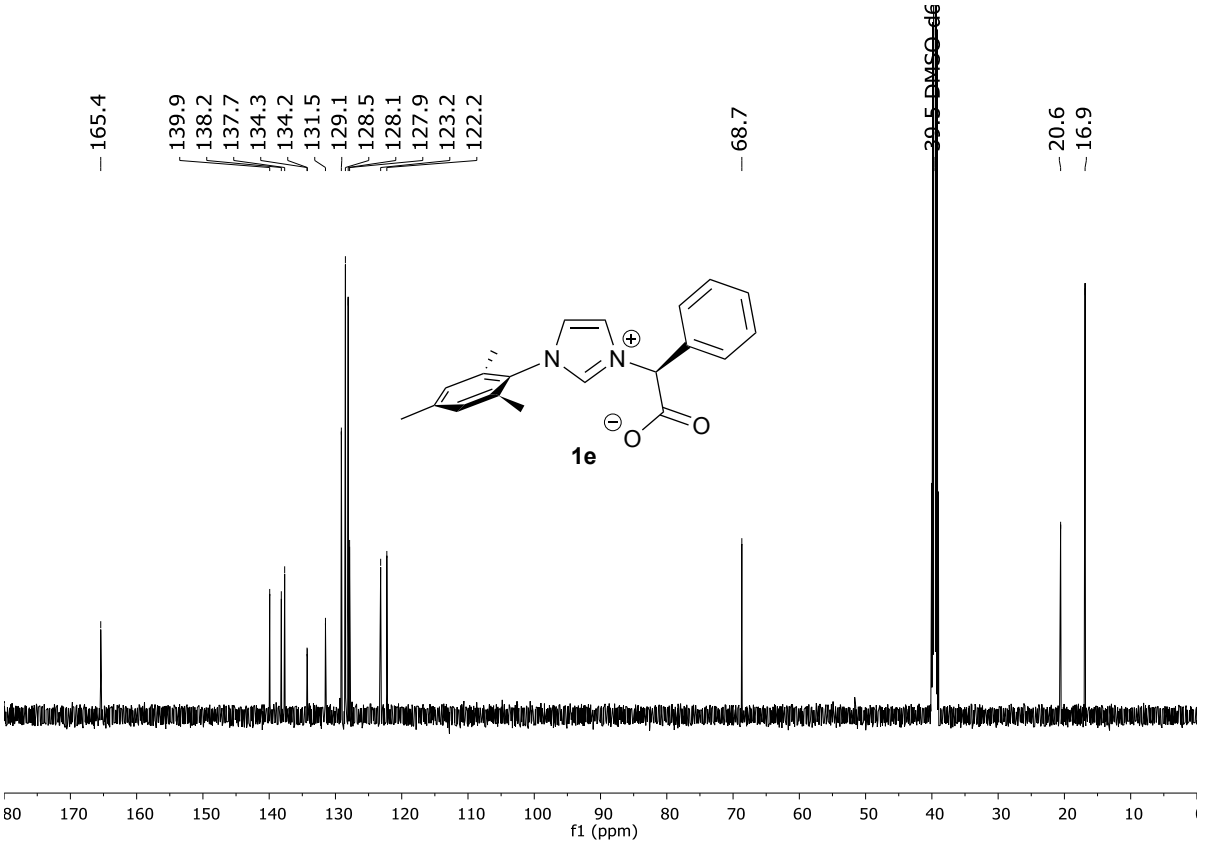
Spectrum S5. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **1d**.



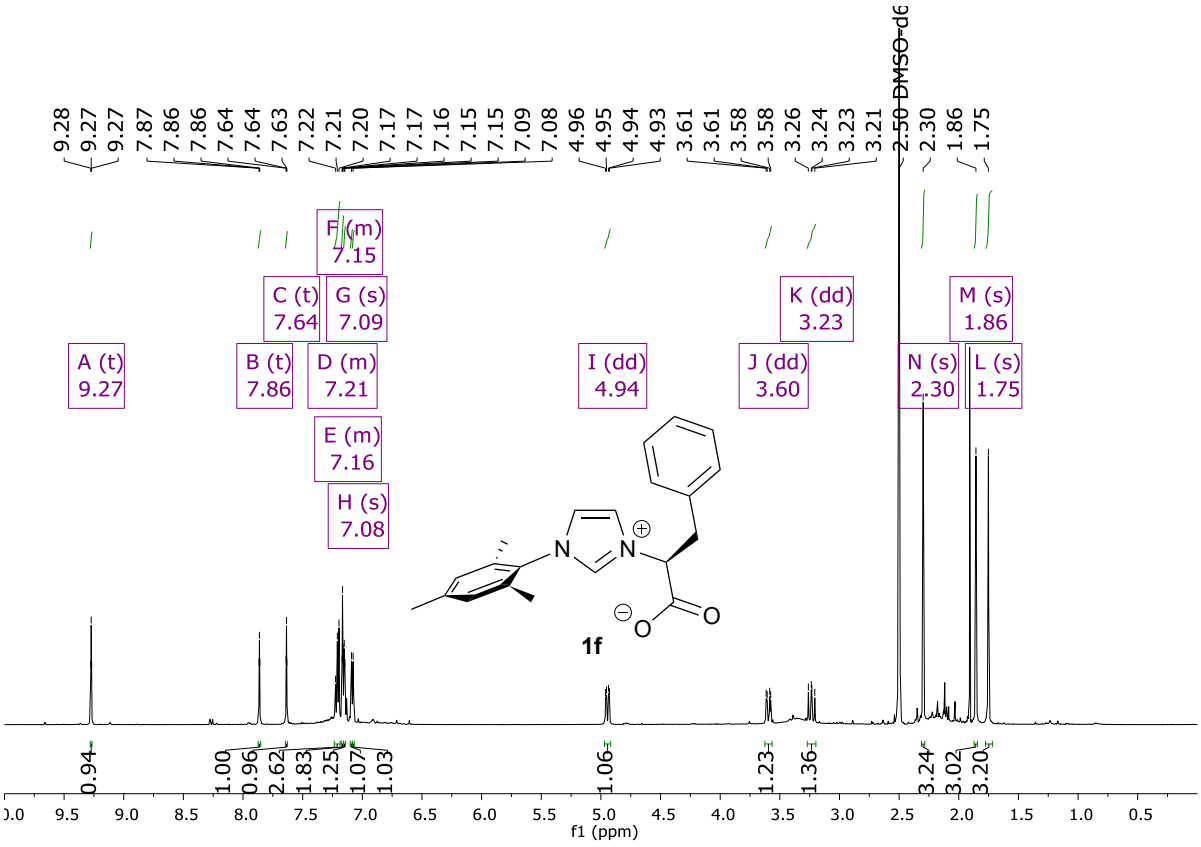
Spectrum S6. ^{13}C{^{1}H} NMR (125 MHz, dmso-d_6) spectrum of **1d**



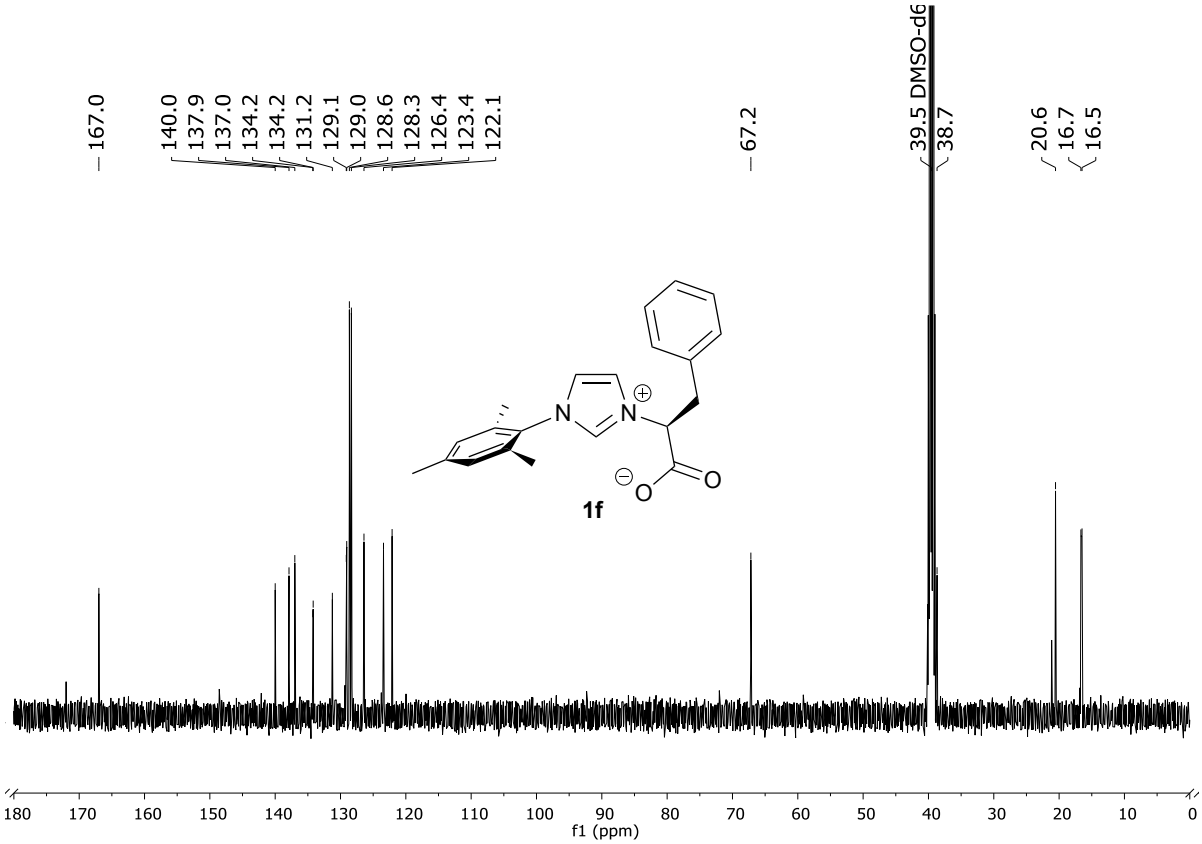
Spectrum S7. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **1e**.



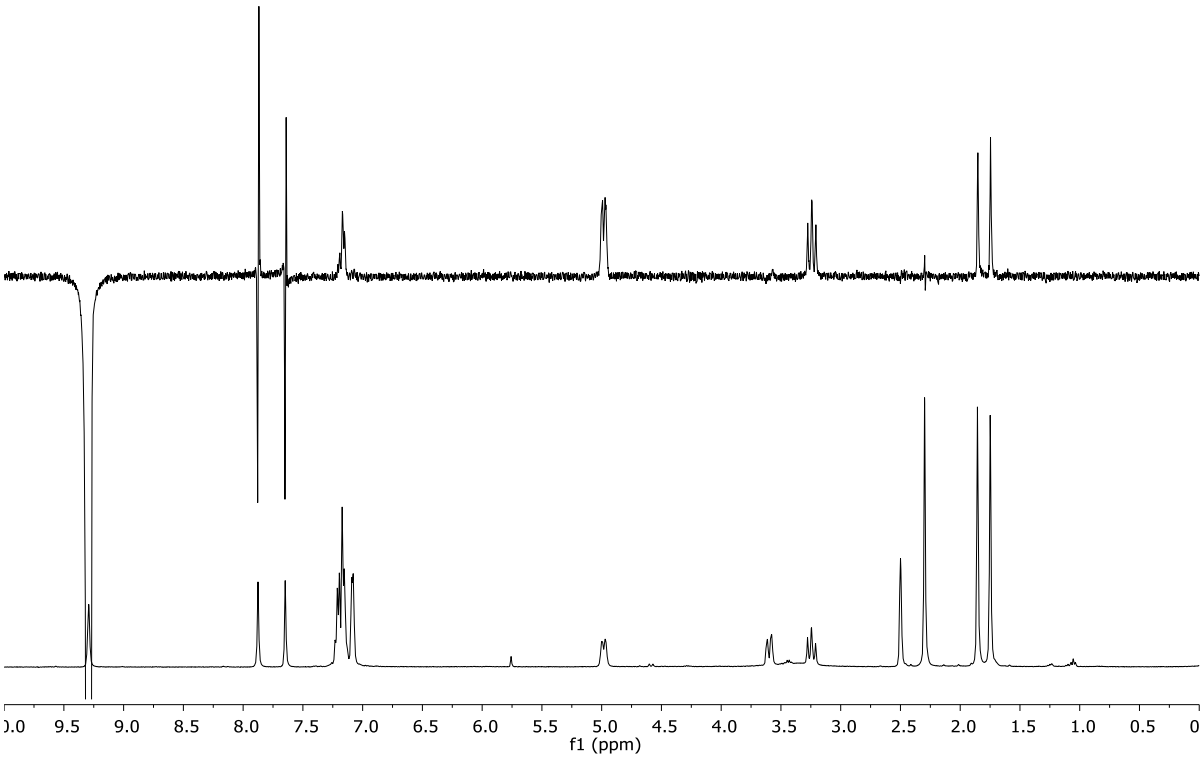
Spectrum S8. ^{13}C{^{1}H} NMR (125 MHz, dmso-d_6) spectrum of **1e**



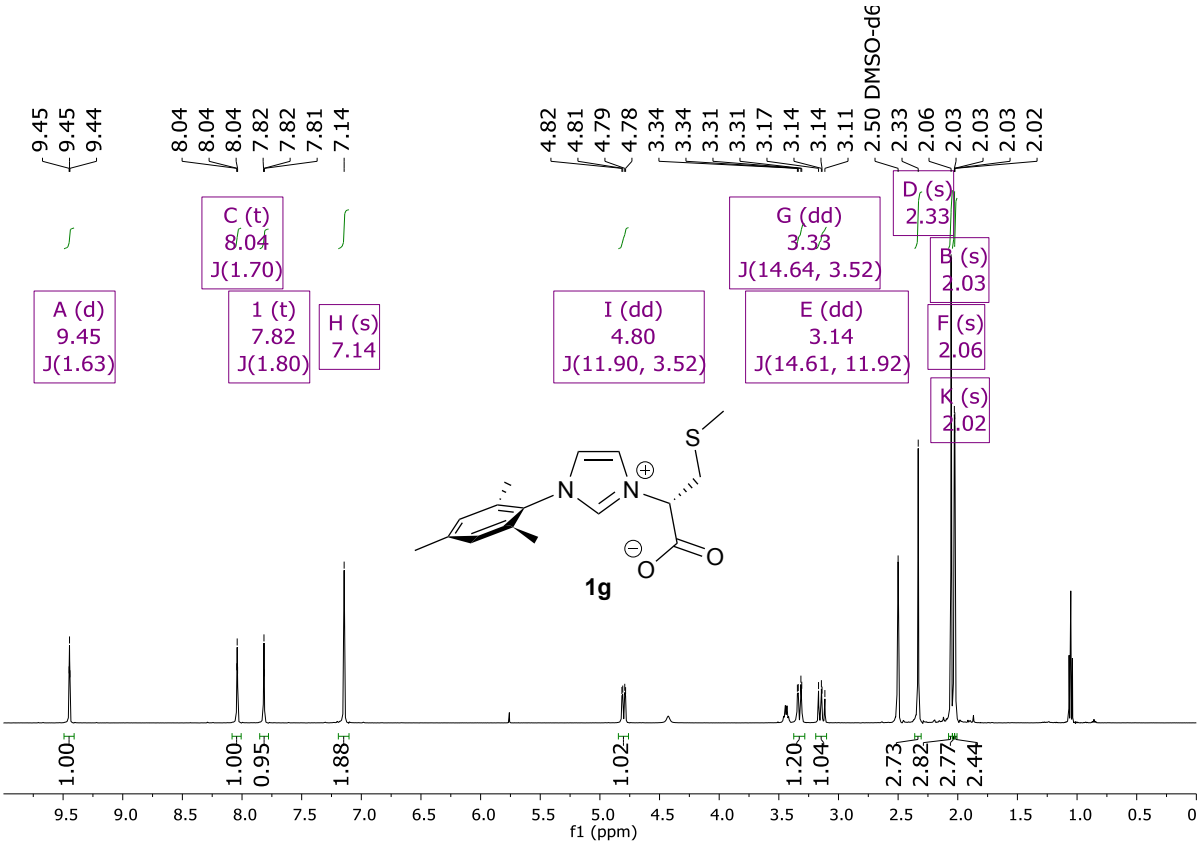
Spectrum S9. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **1f**.



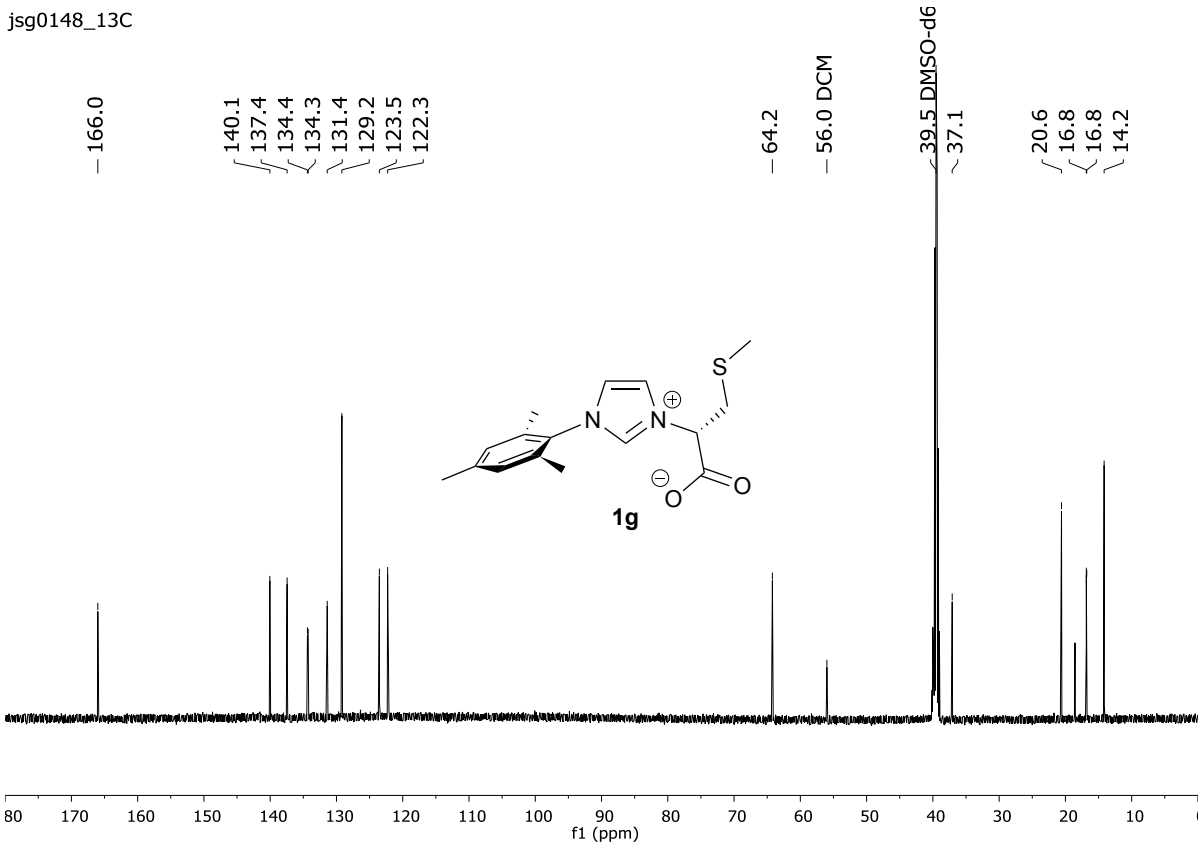
Spectrum S10. ^{13}C{^{1}H} NMR (125 MHz, dmso-d_6) spectrum of **1f.**



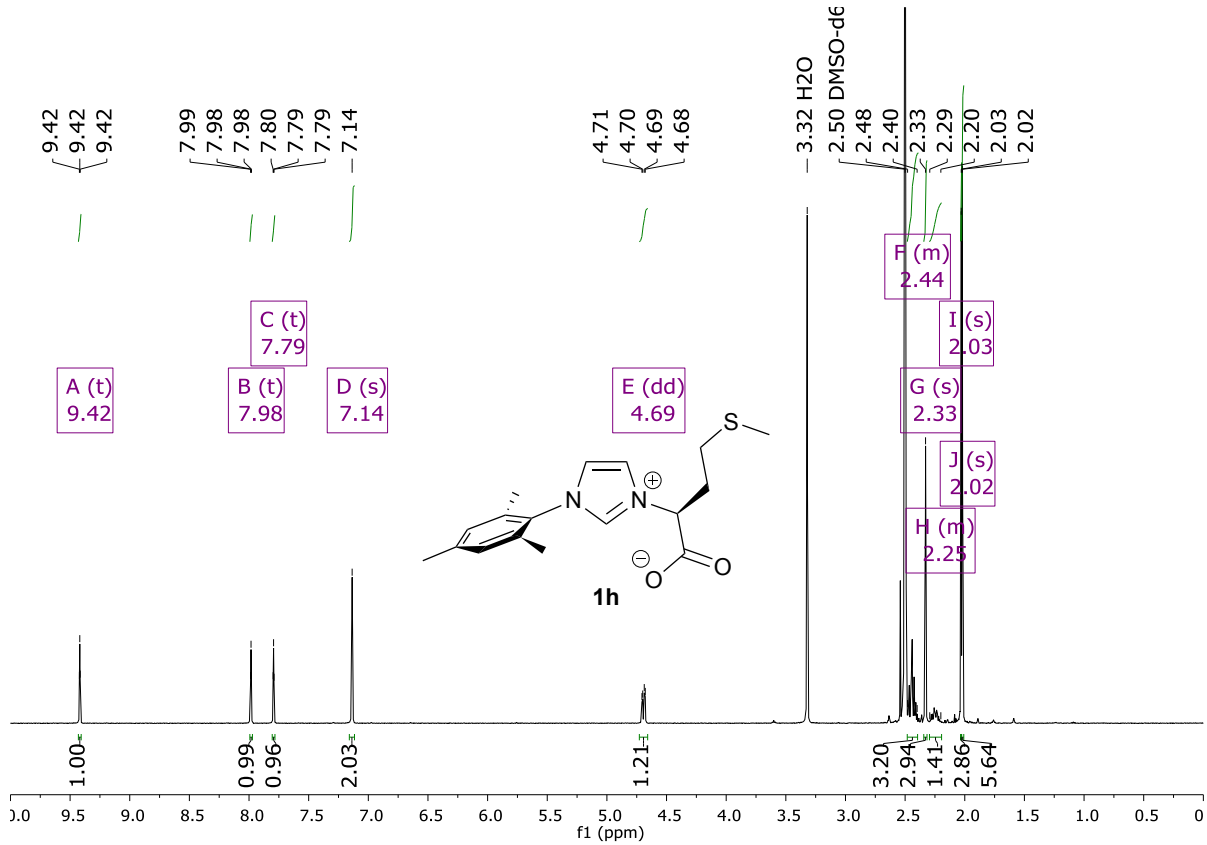
Spectrum S11. 1D NOE (400 MHz, dmso-d_6) spectrum of **1f** with selective inversion of the peak for Imd-H^2 showing the spatial correlation with *o*-Ph and CH_2 protons.



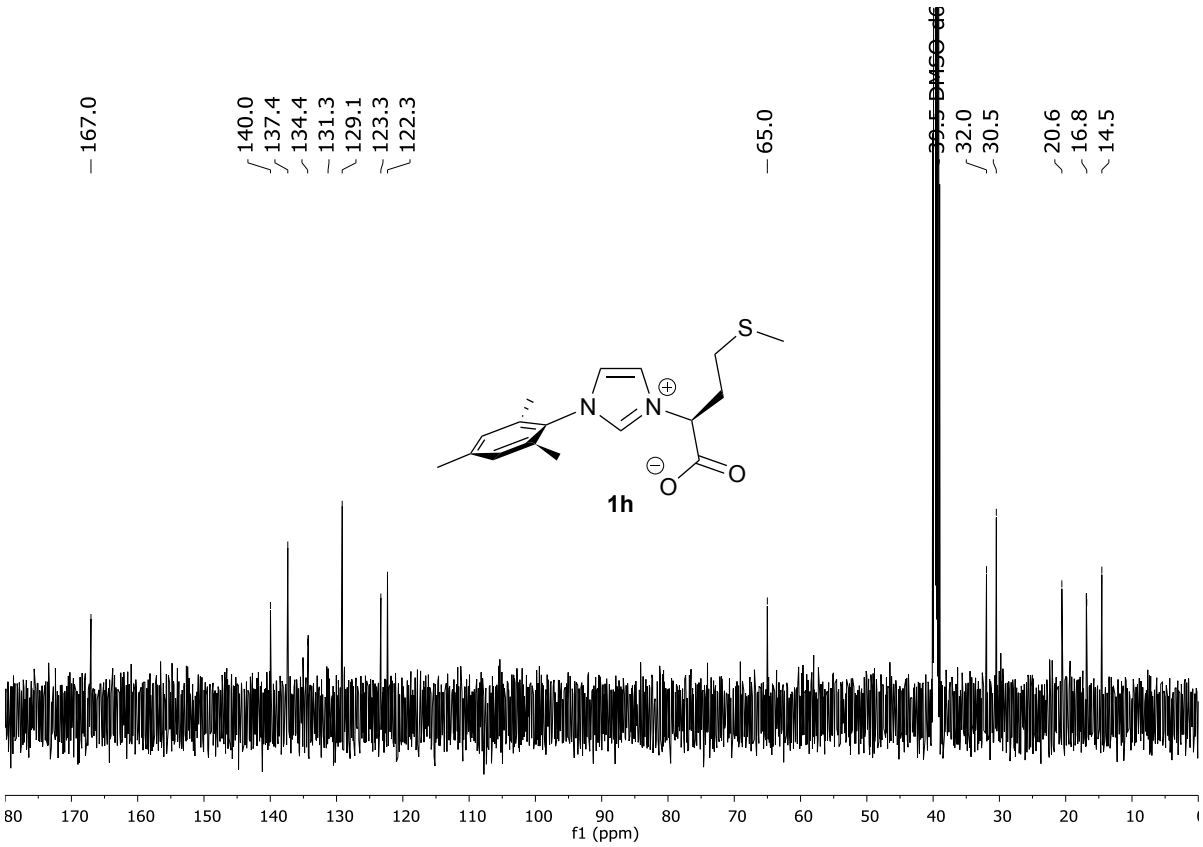
Spectrum S12. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **1g**.



Spectrum S13. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **1g**.

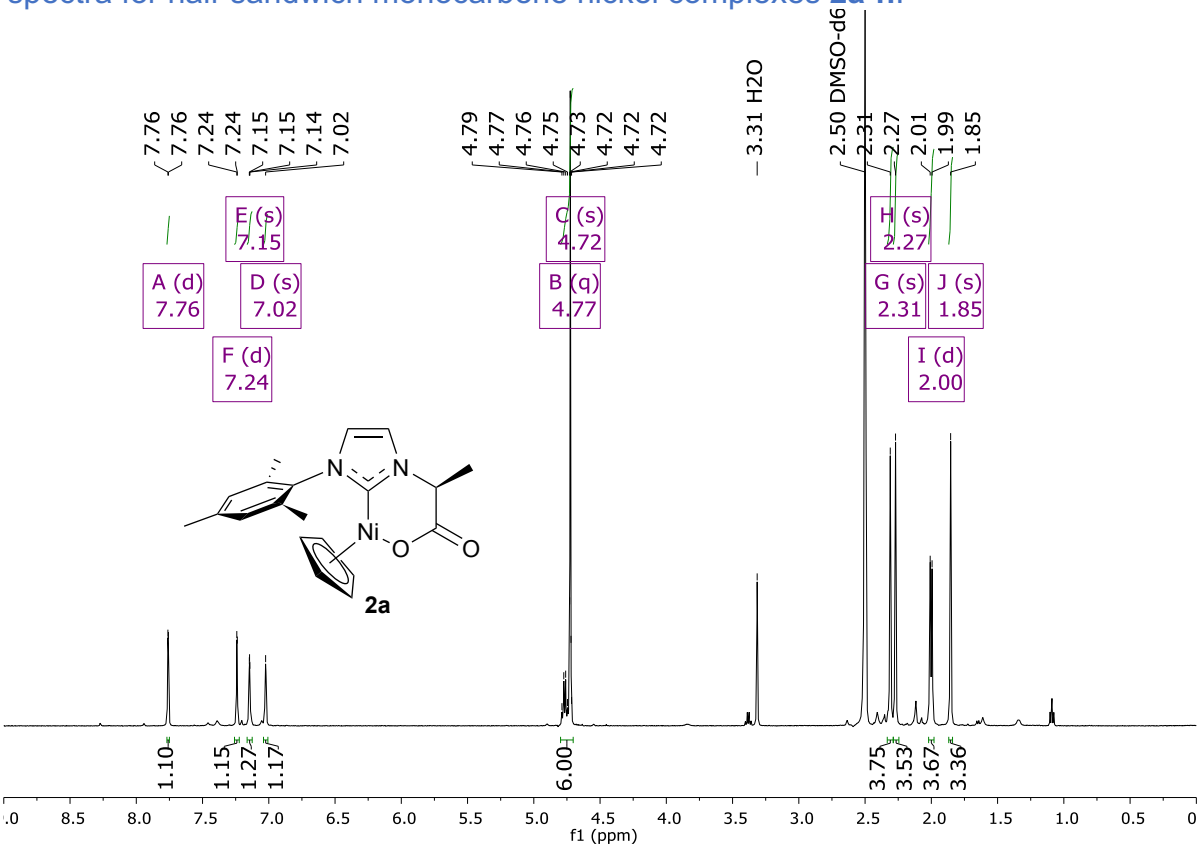


Spectrum S14. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **1h**.

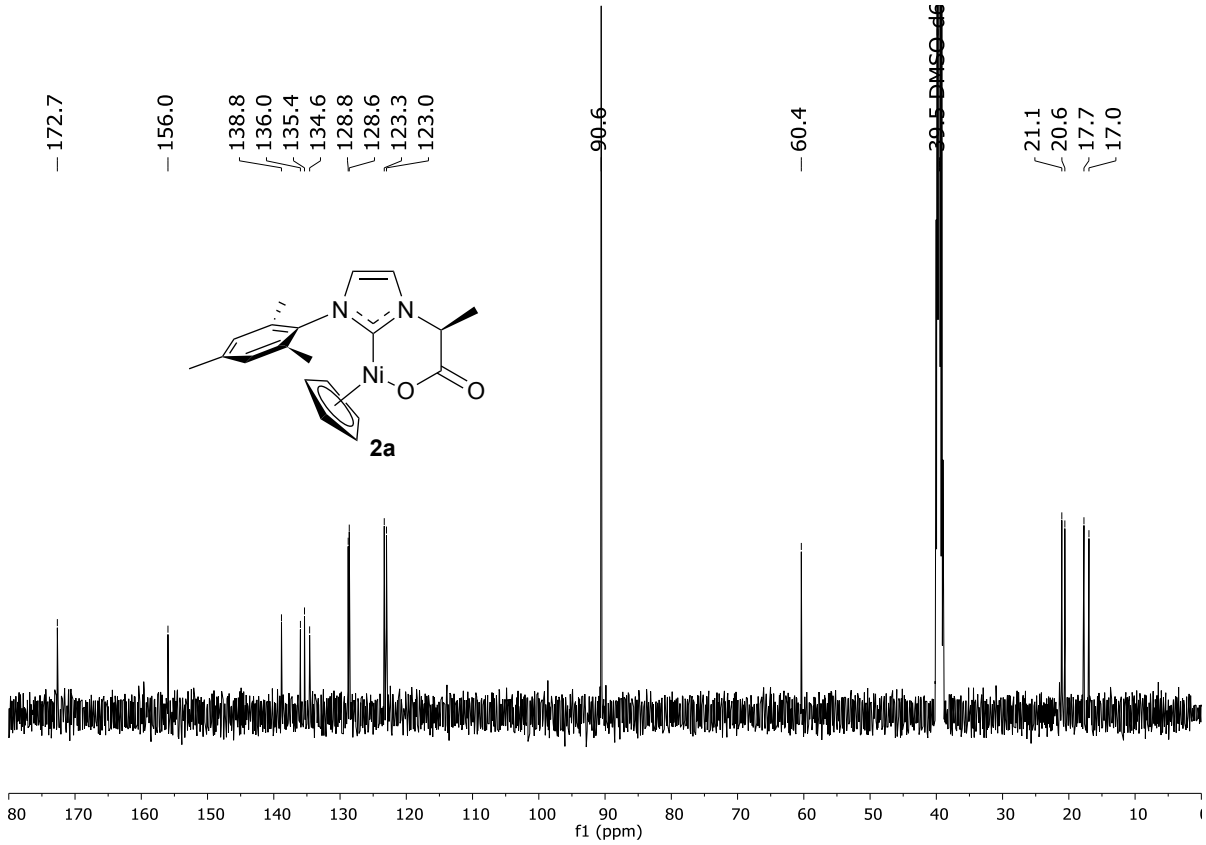


Spectrum S15. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **1h**.

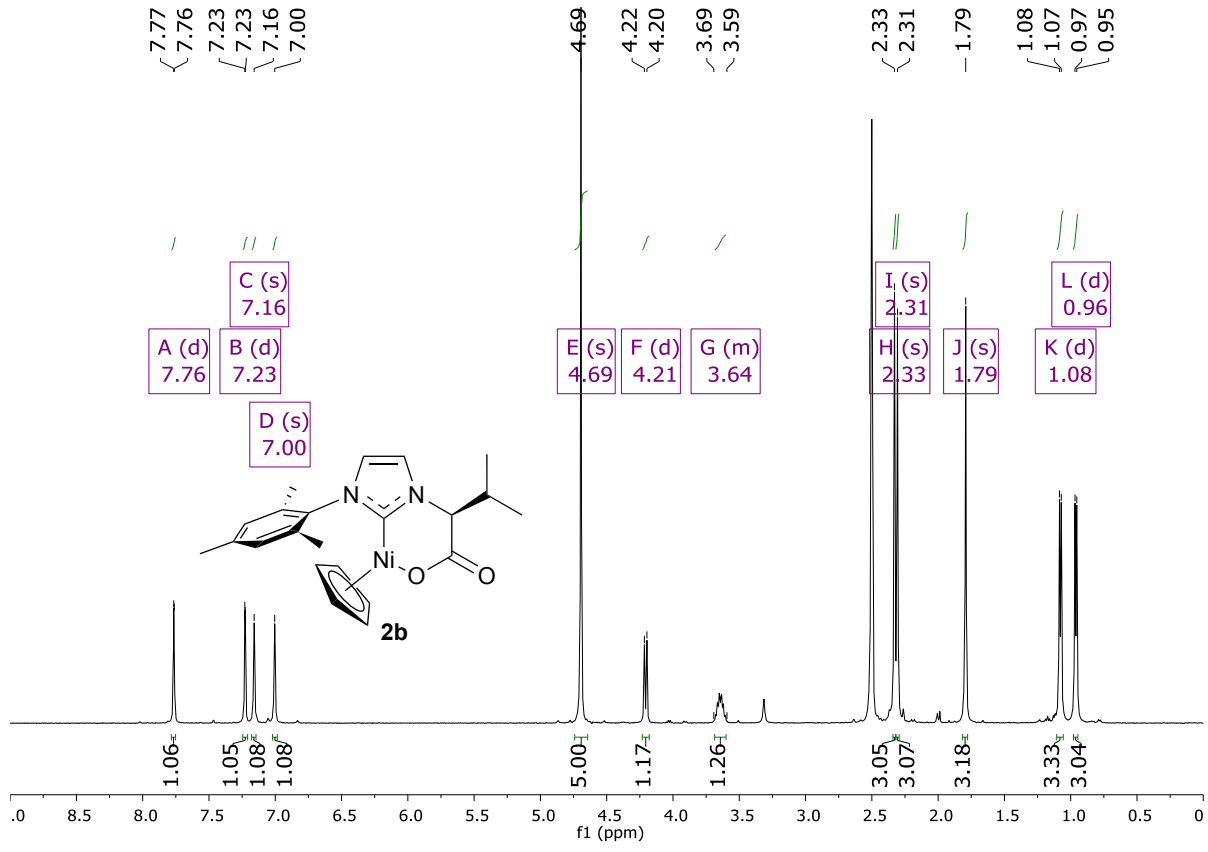
NMR spectra for half-sandwich monocarbene nickel complexes **2a-h**.



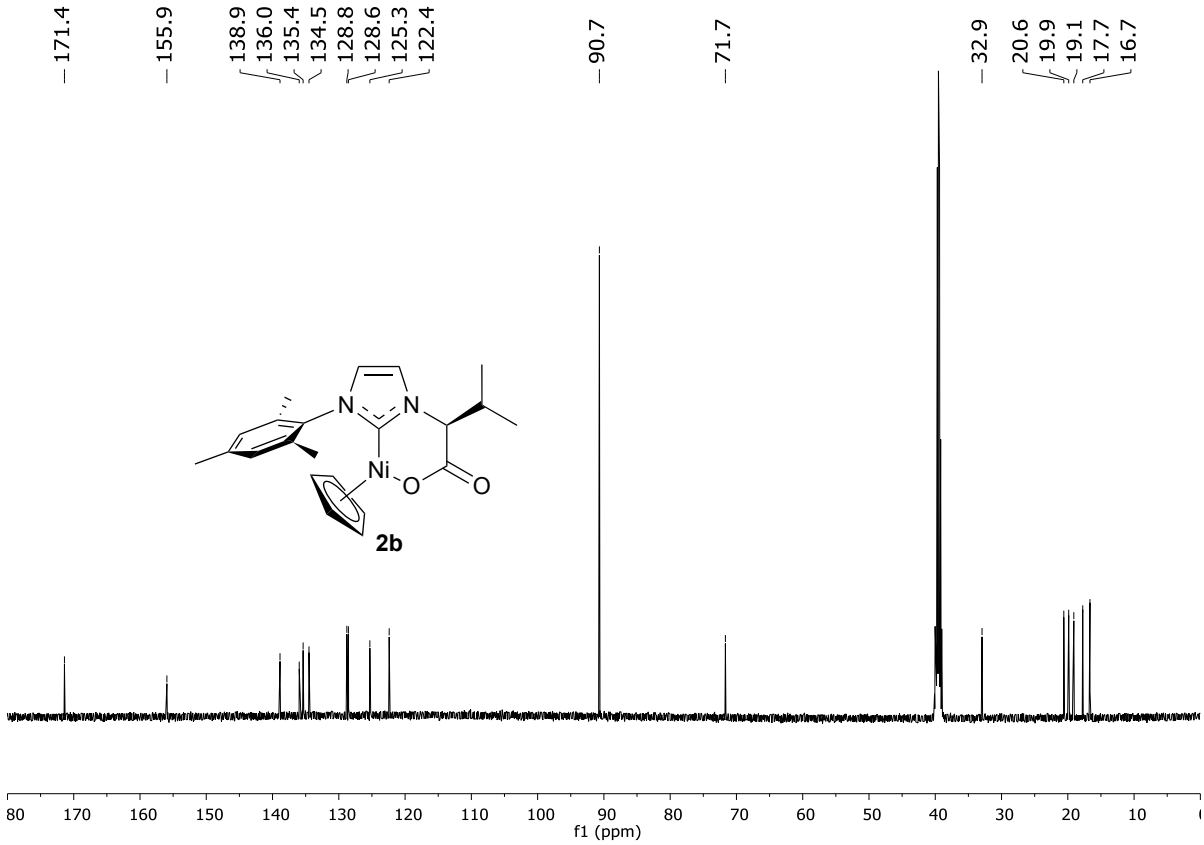
Spectrum S16. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2a**.



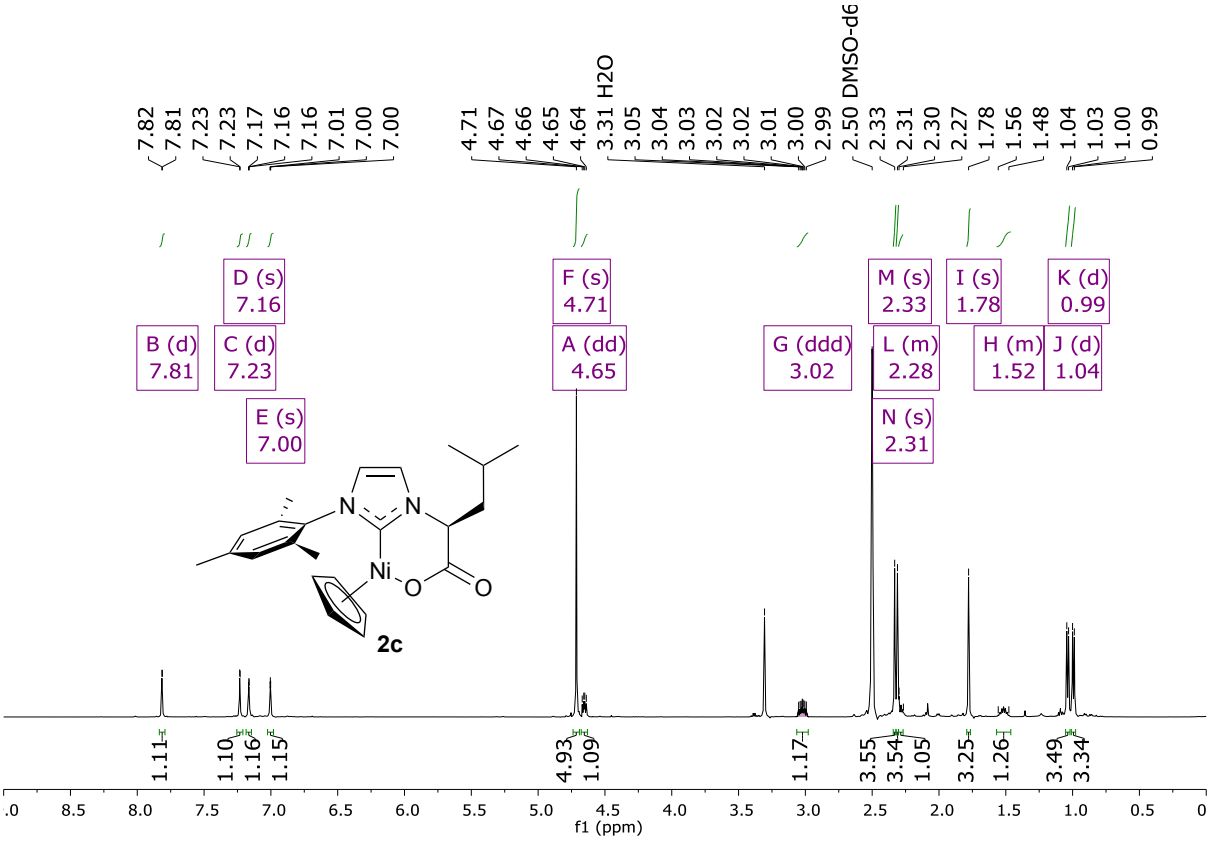
Spectrum S17. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **1h**.



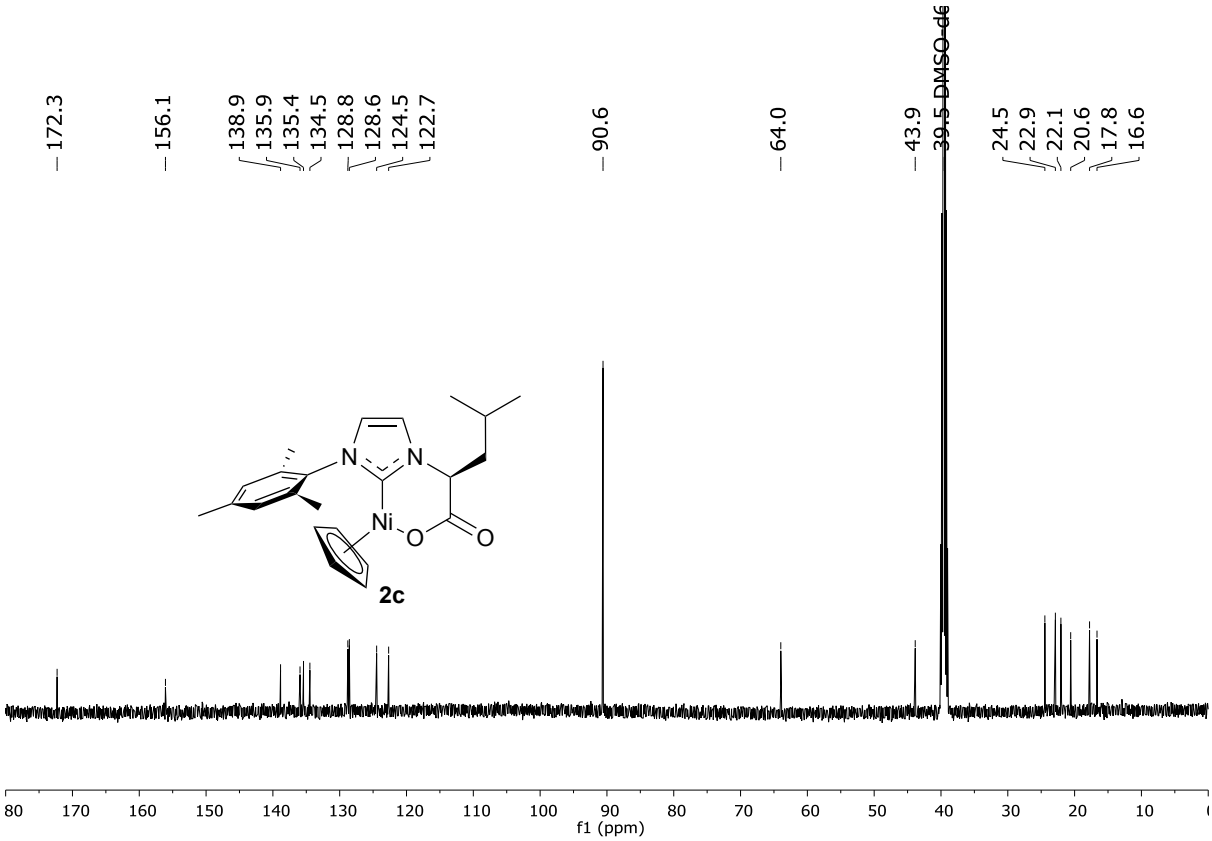
Spectrum S18. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2b**.



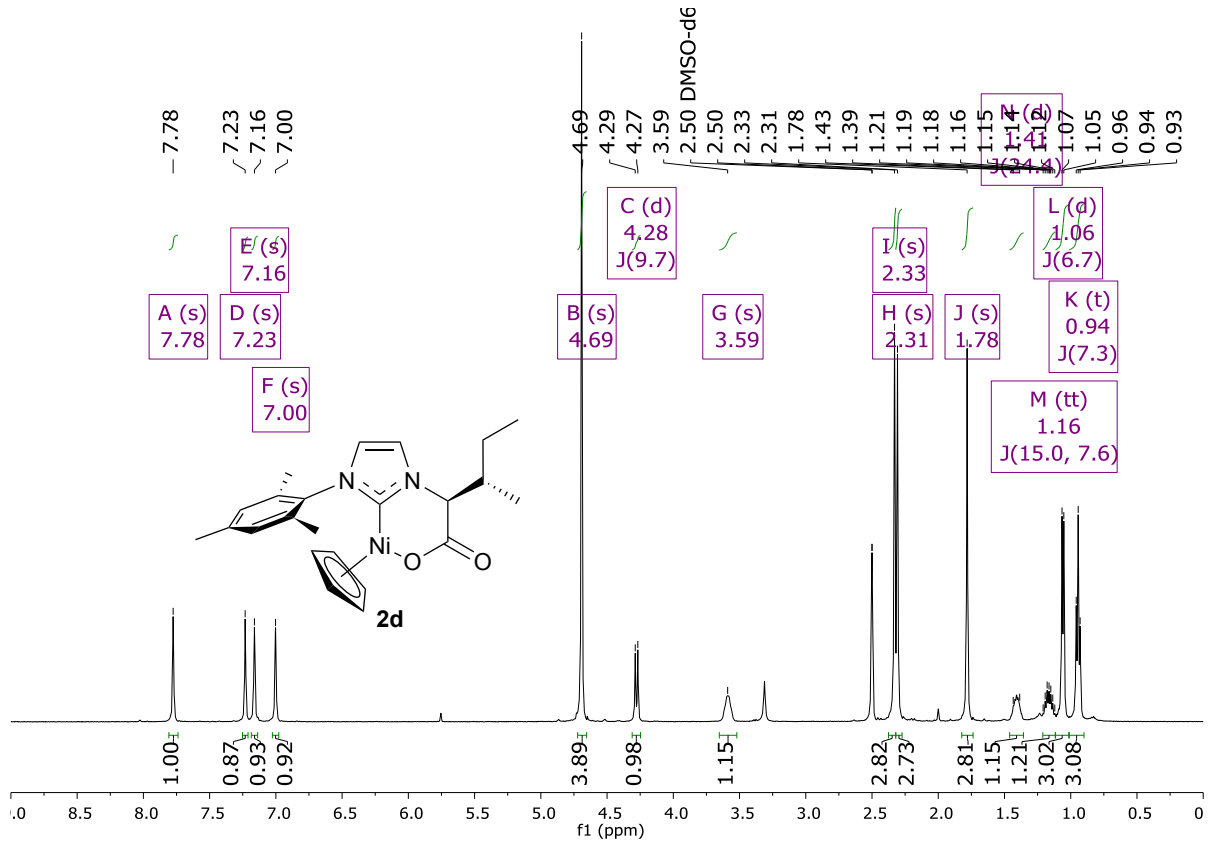
Spectrum S19. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2b**.



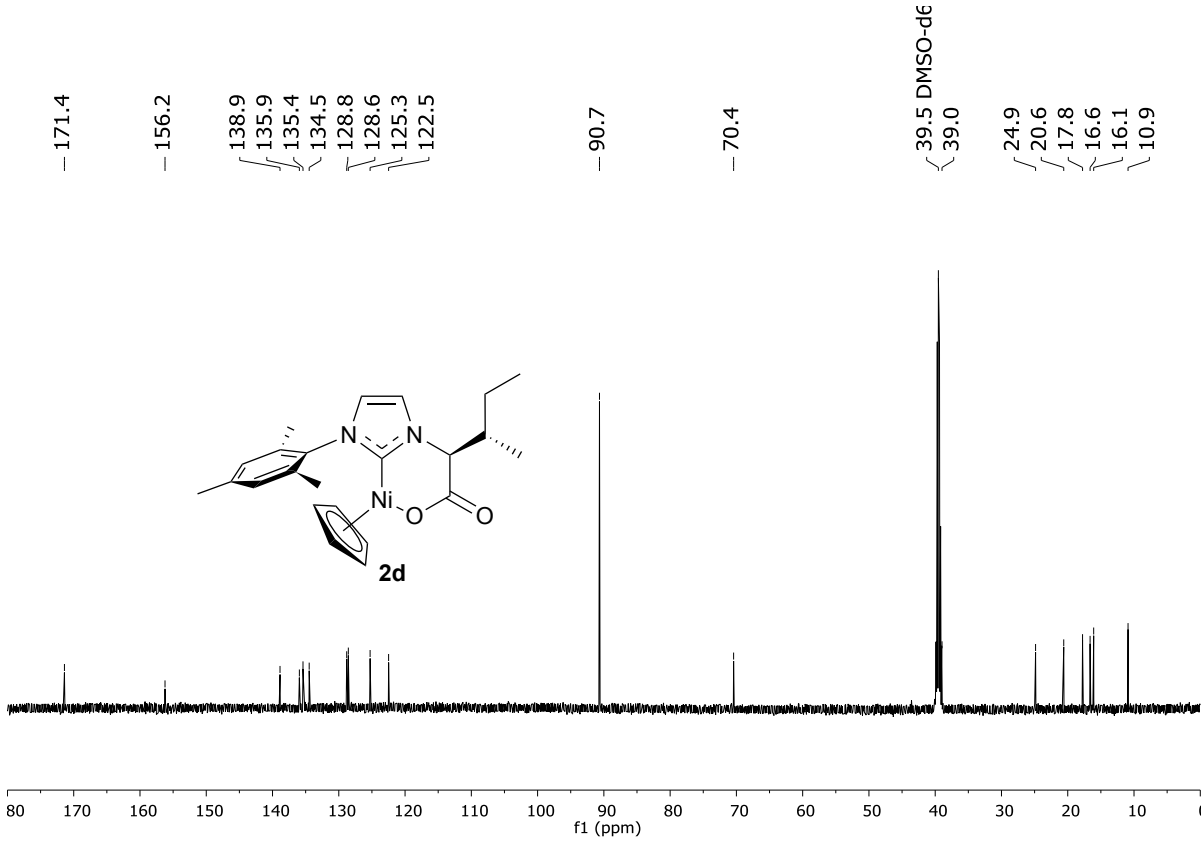
Spectrum S20 ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2c**.



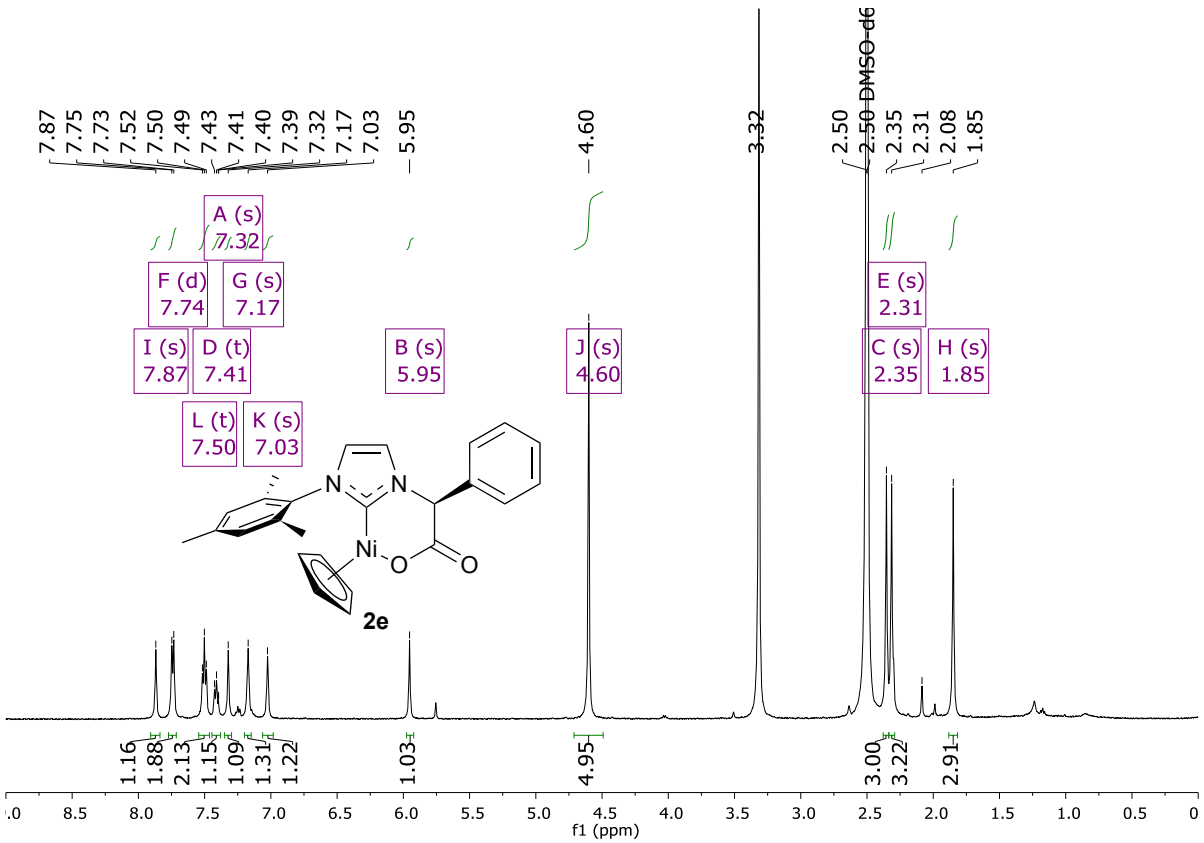
Spectrum S21. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2c**.



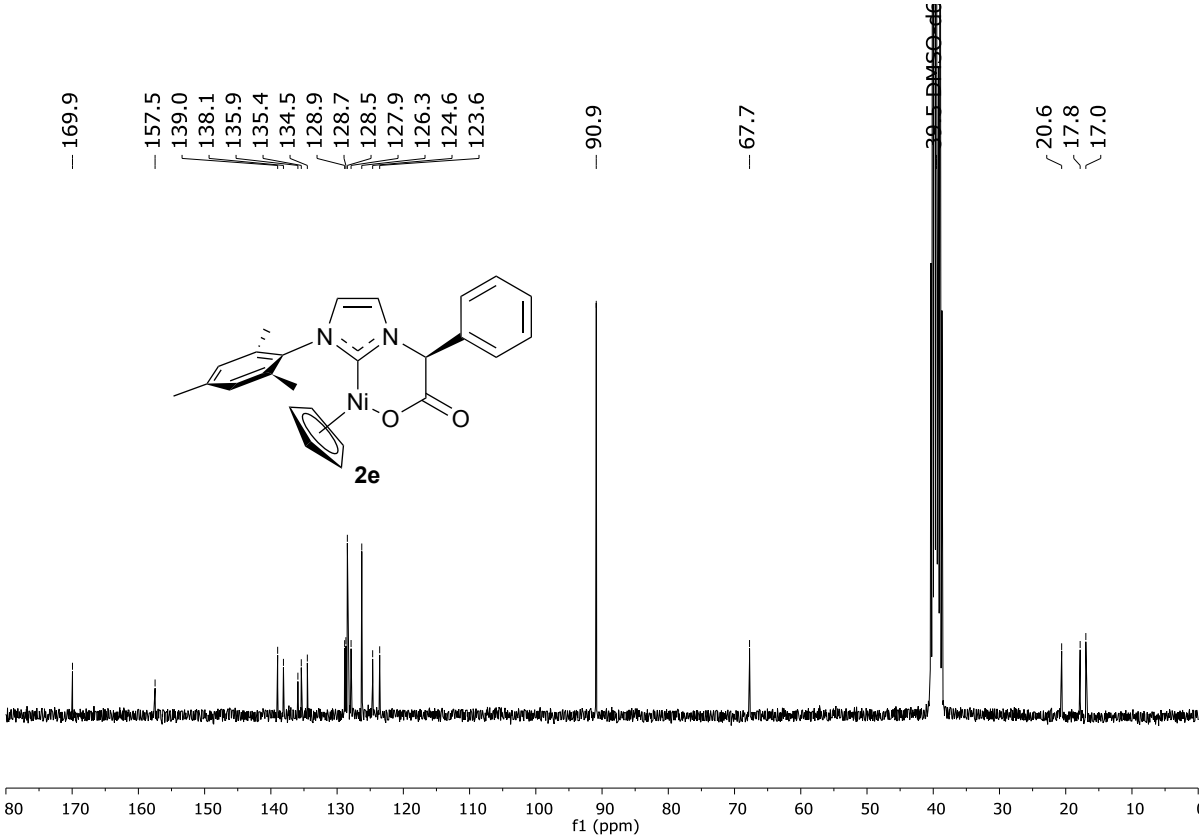
Spectrum S22. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2d**.



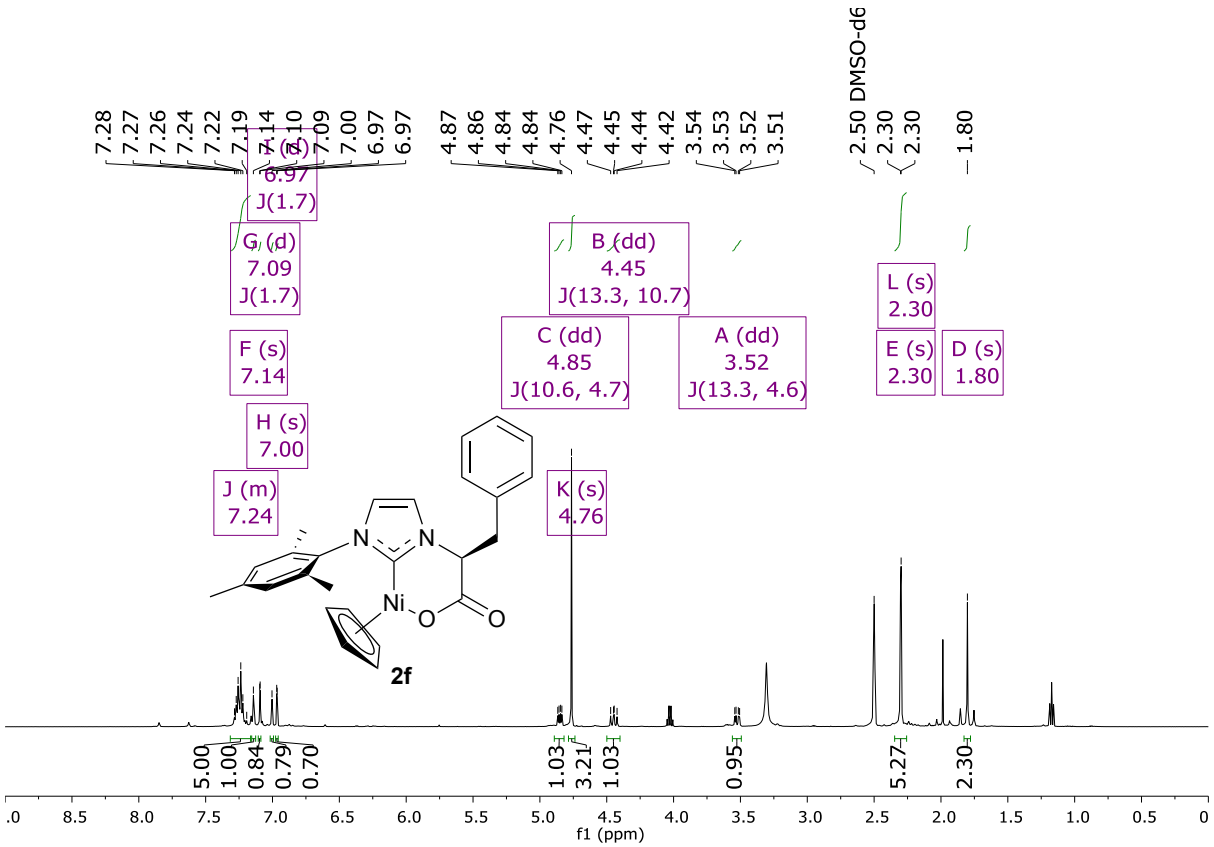
Spectrum S23. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2d**.



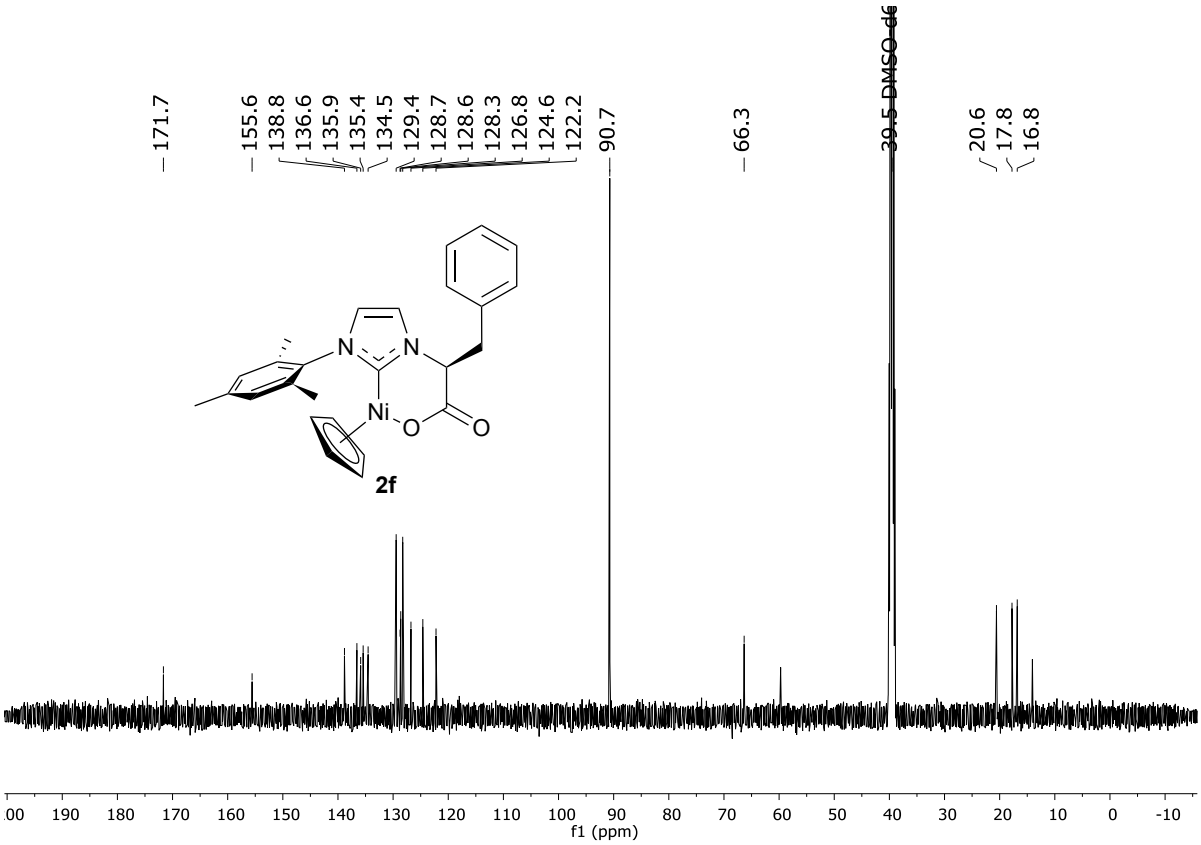
Spectrum S24. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2e**.



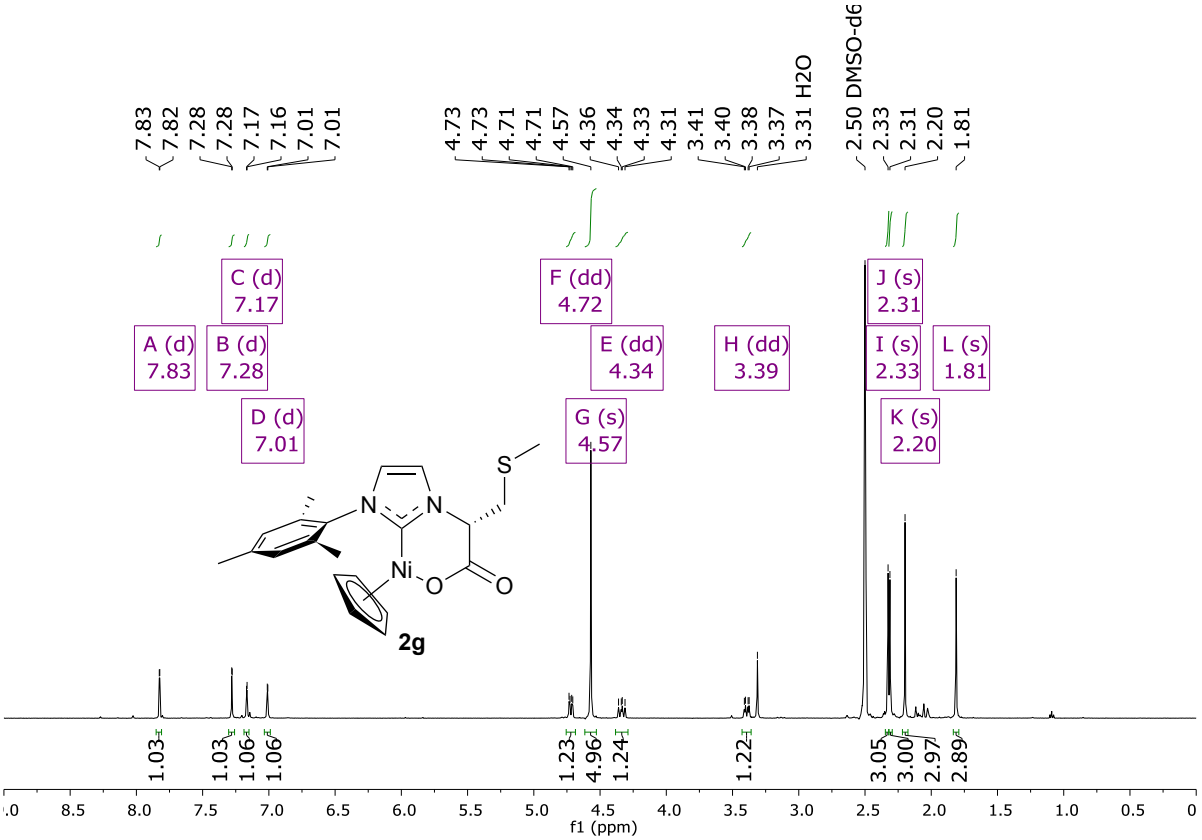
Spectrum S25. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2e**.



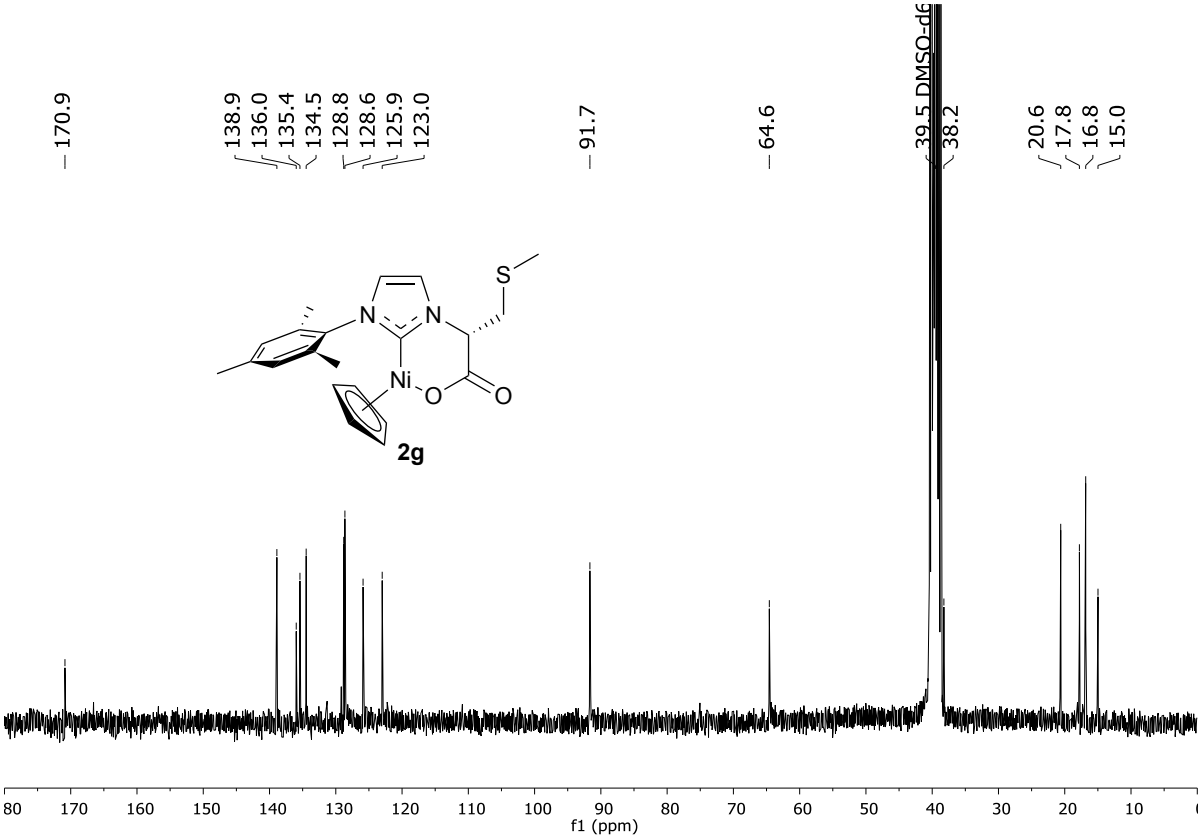
Spectrum S26. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2f**.



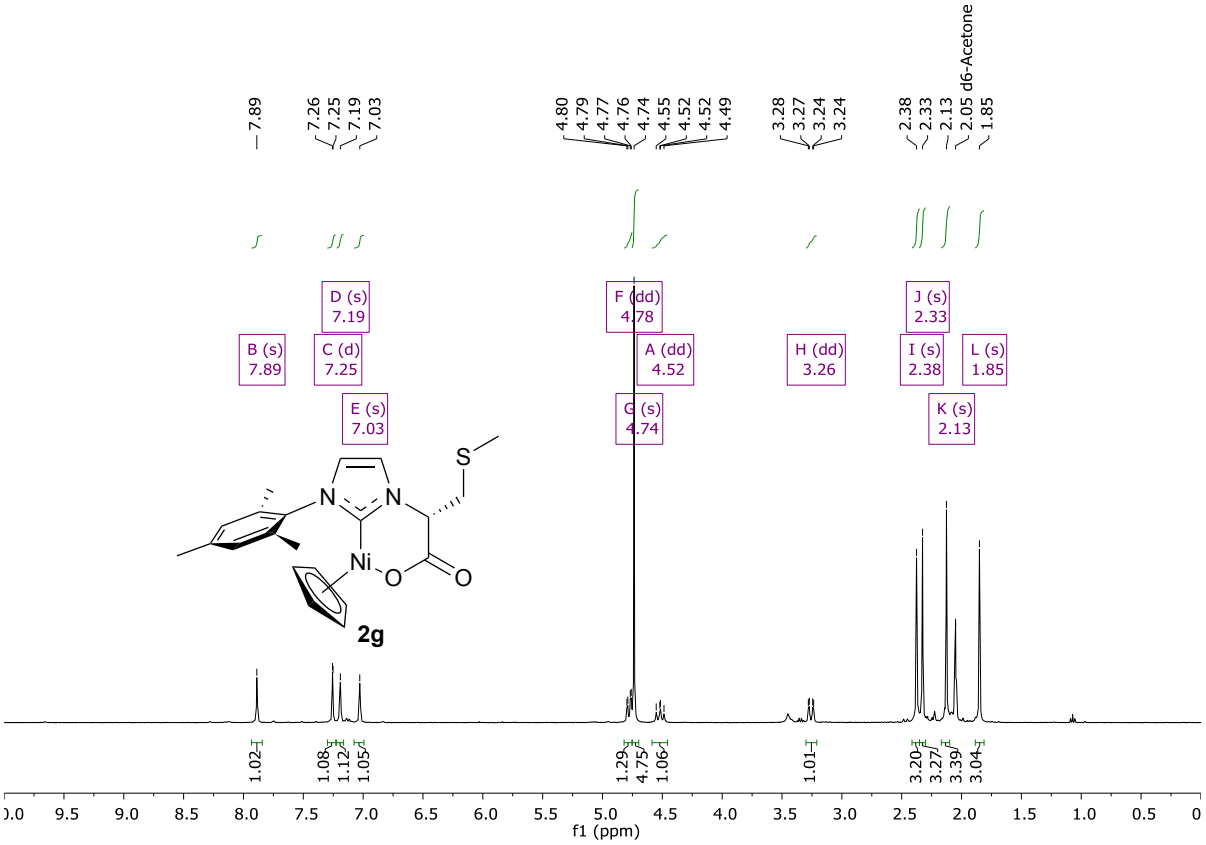
Spectrum S27. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2f**.



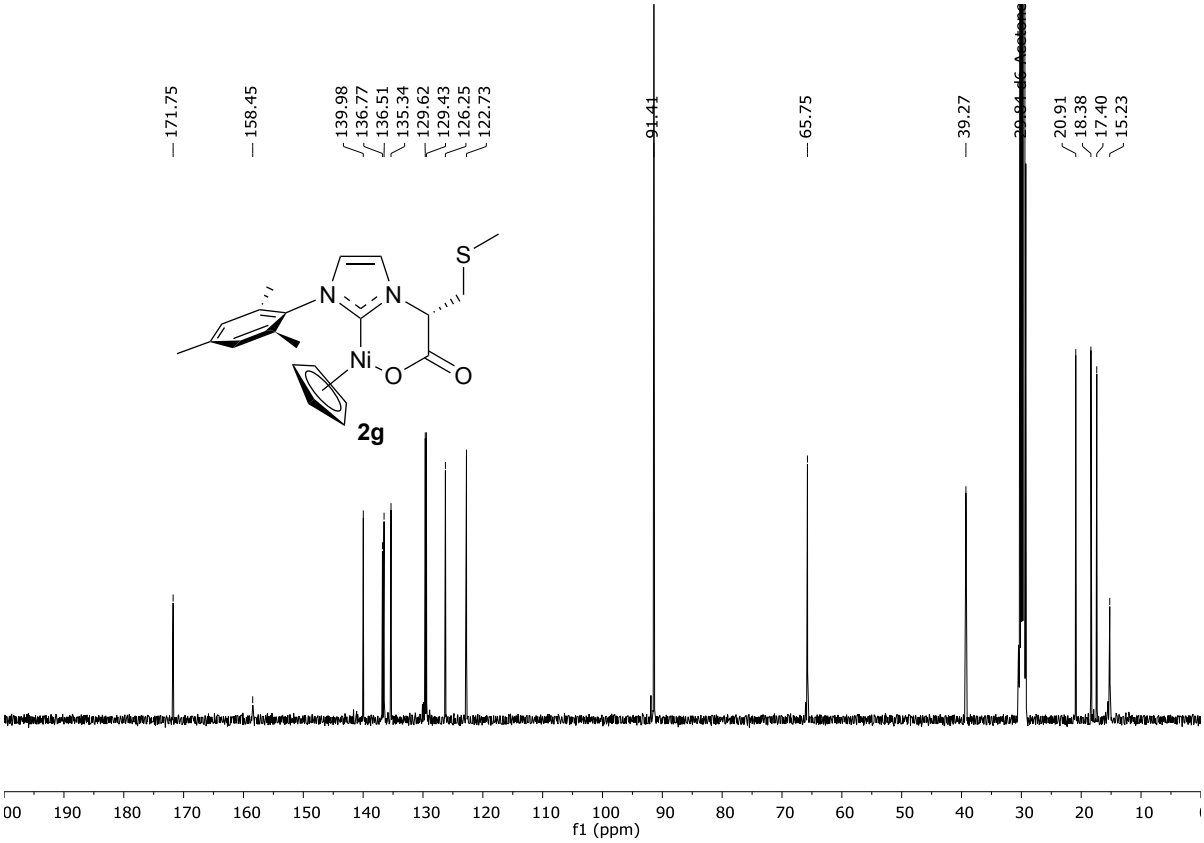
Spectrum S28. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2g**.



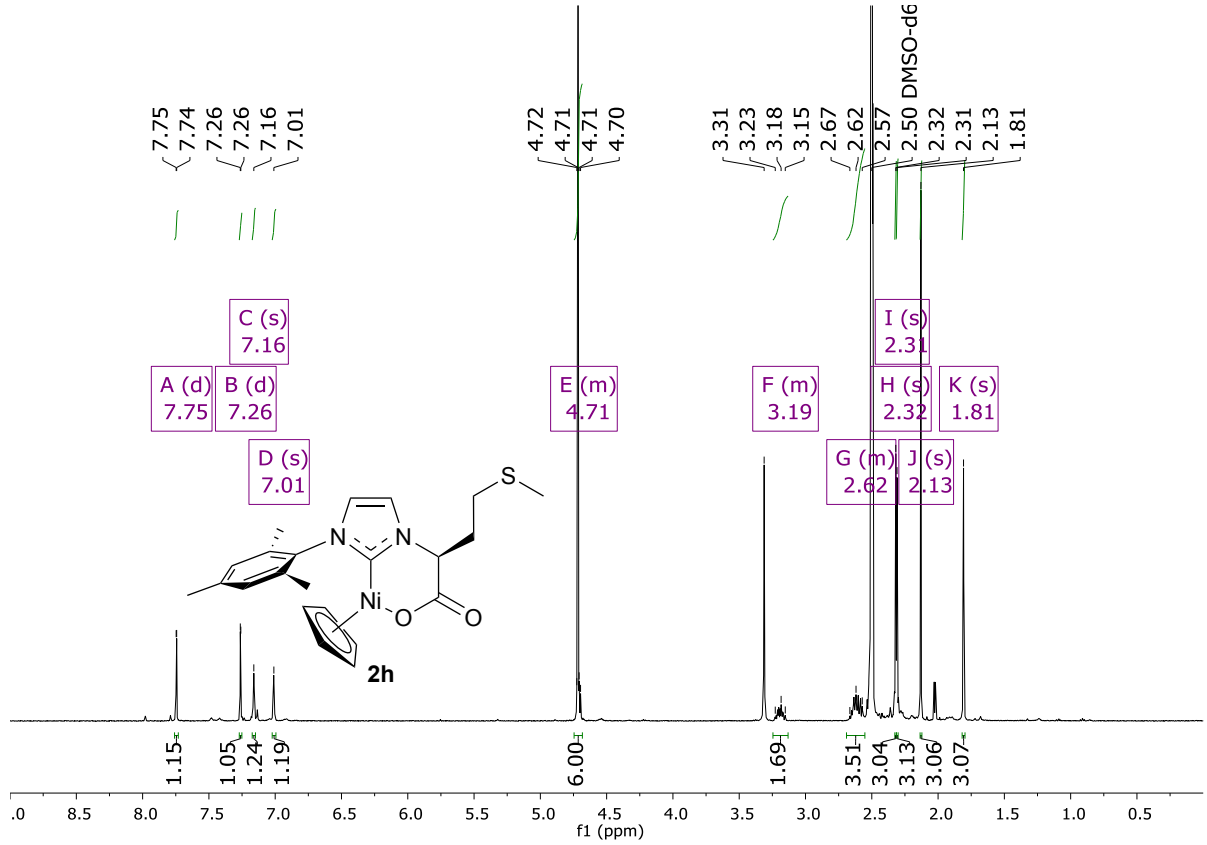
Spectrum S29. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2g**.



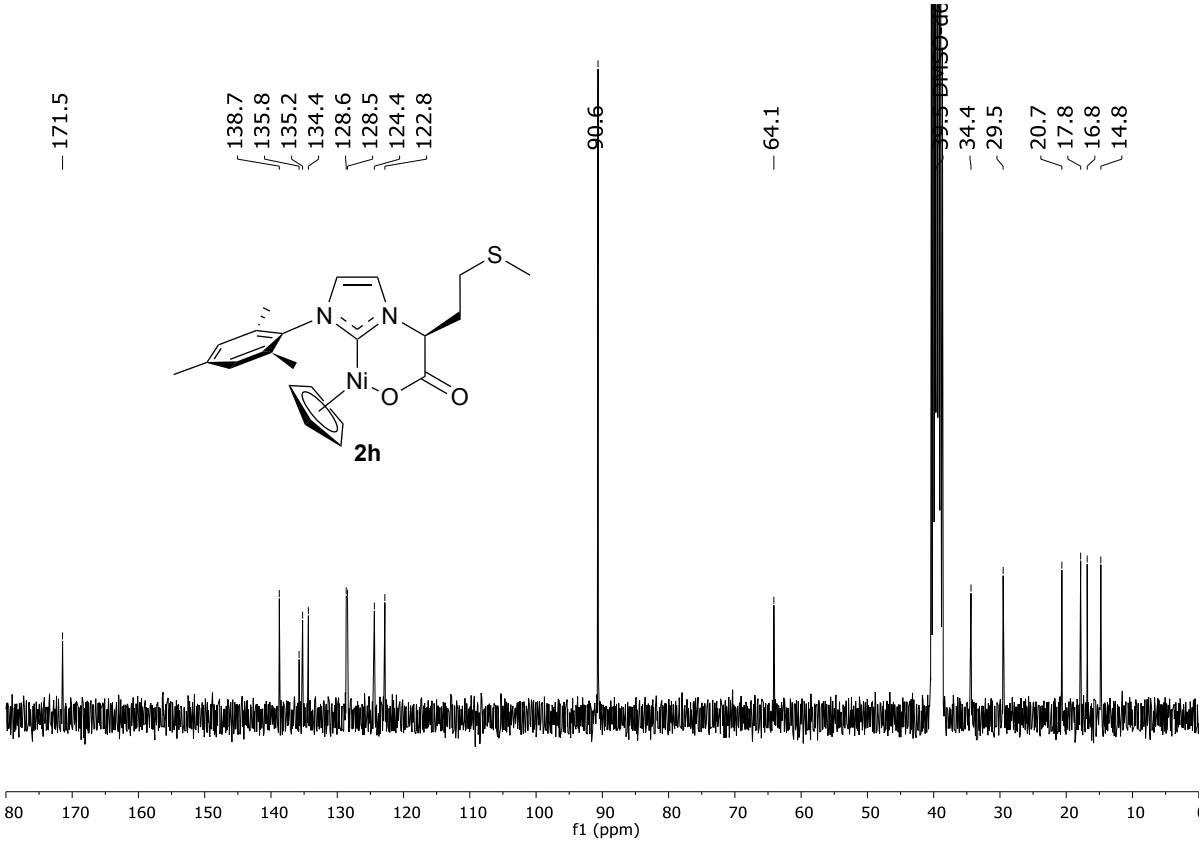
Spectrum S30. ^{1}H NMR (500 MHz, acetone-d_6, T = –50 ºC) spectrum of **2g**.



Spectrum S31. $^{13}C\{^{1}H\}$ NMR (125 MHz, acetone-d_6, T = –50 ºC) spectrum of **2g**.

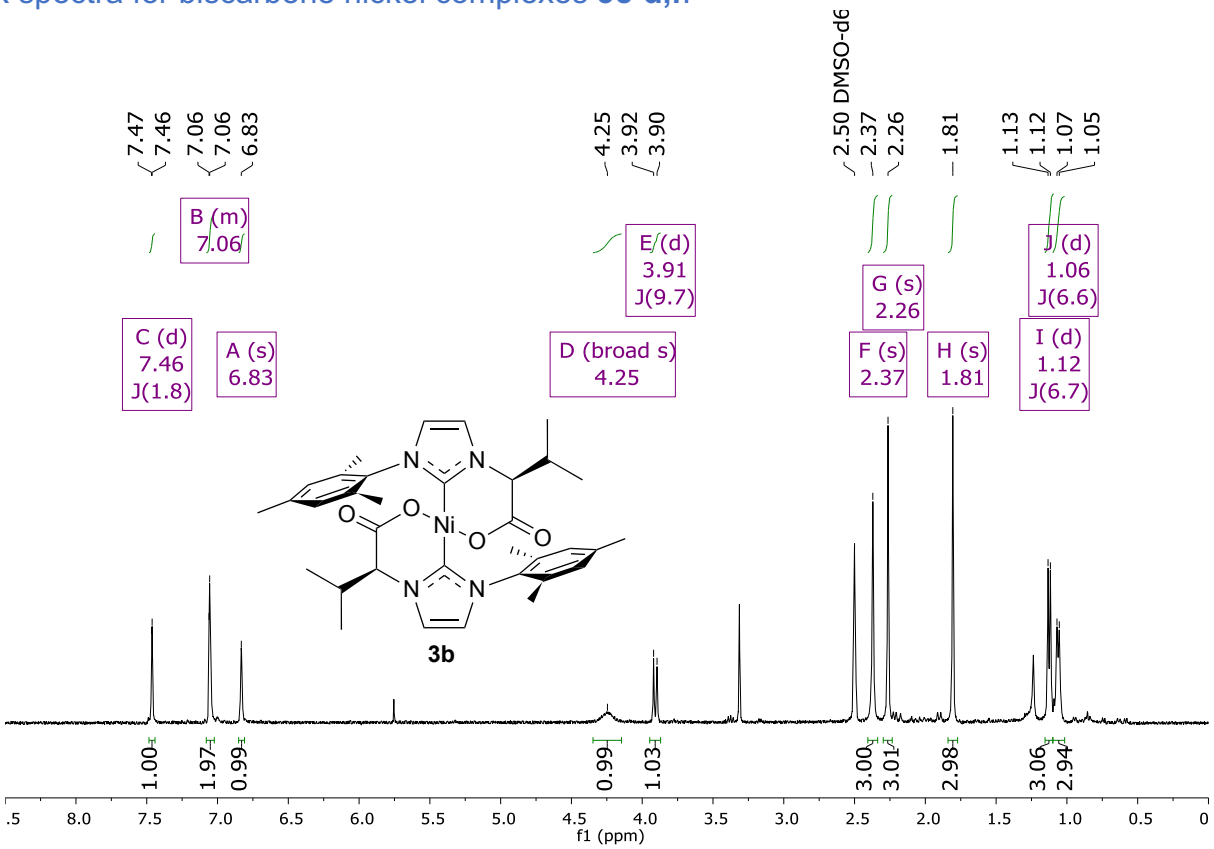


Spectrum S32. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **2h**.

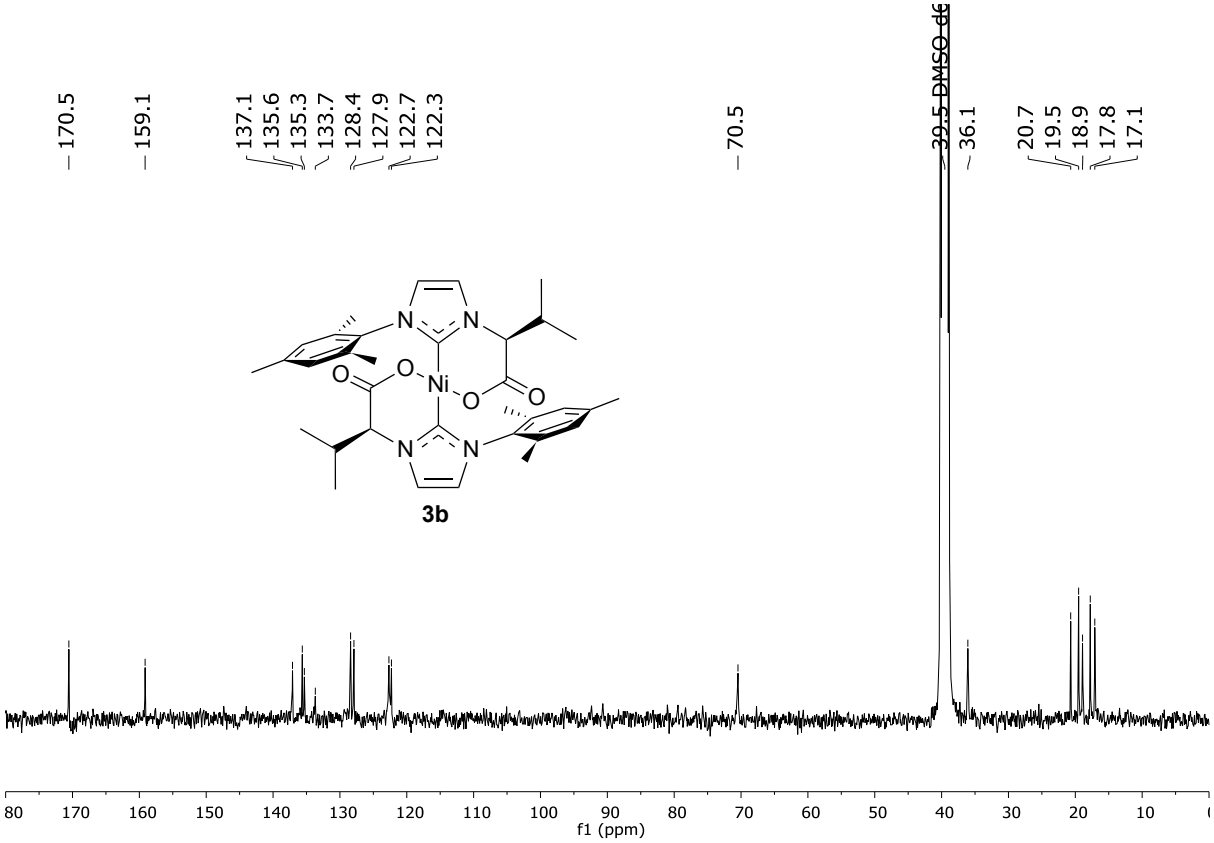


Spectrum S33. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **2h**.

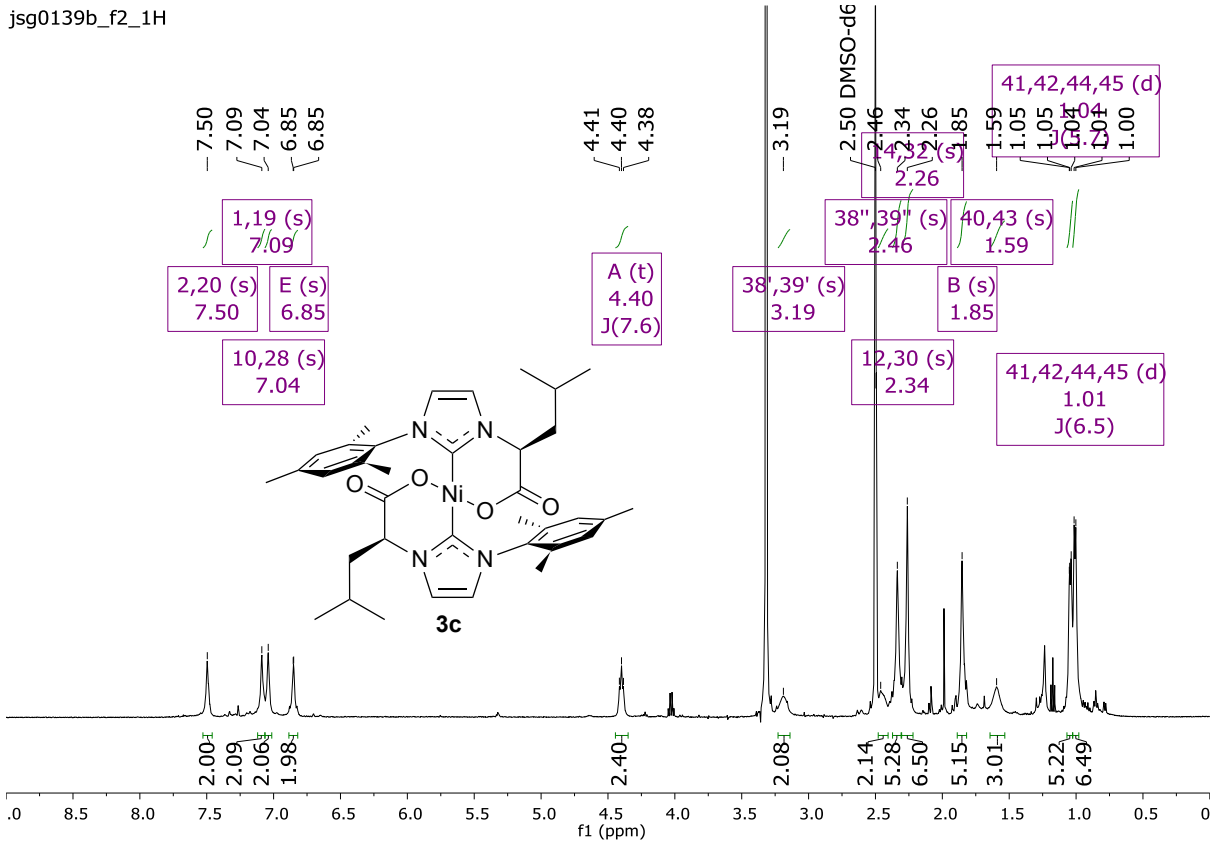
NMR spectra for biscarbene nickel complexes **3c-d,f**.



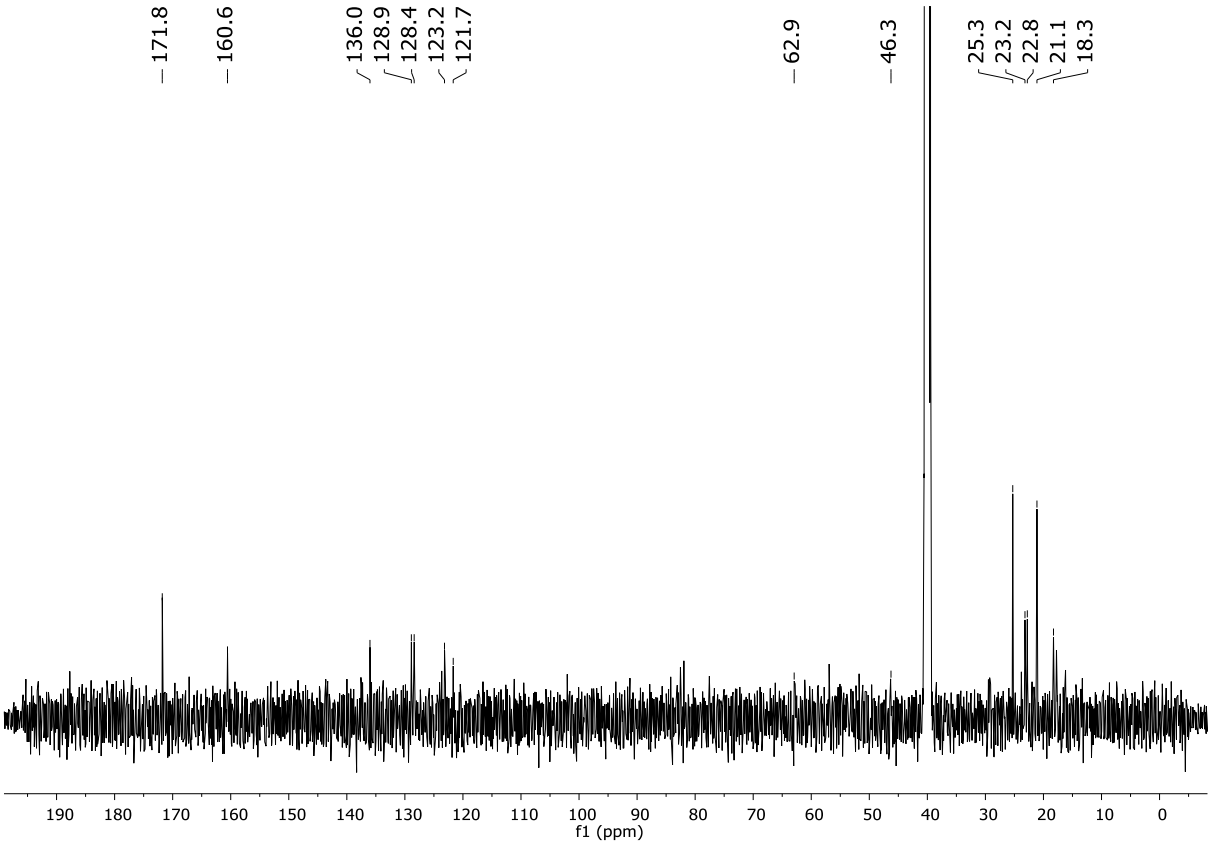
Spectrum S34. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **3b**.



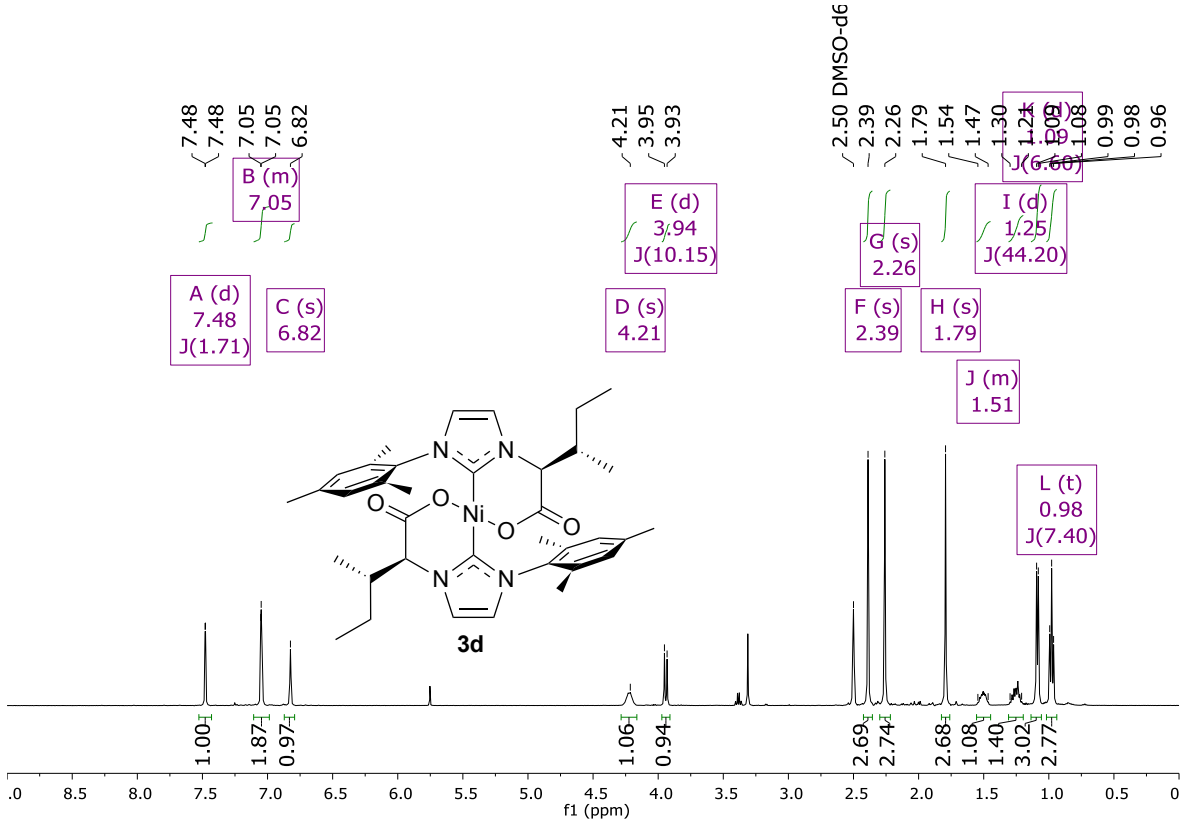
Spectrum S35. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **3b**.



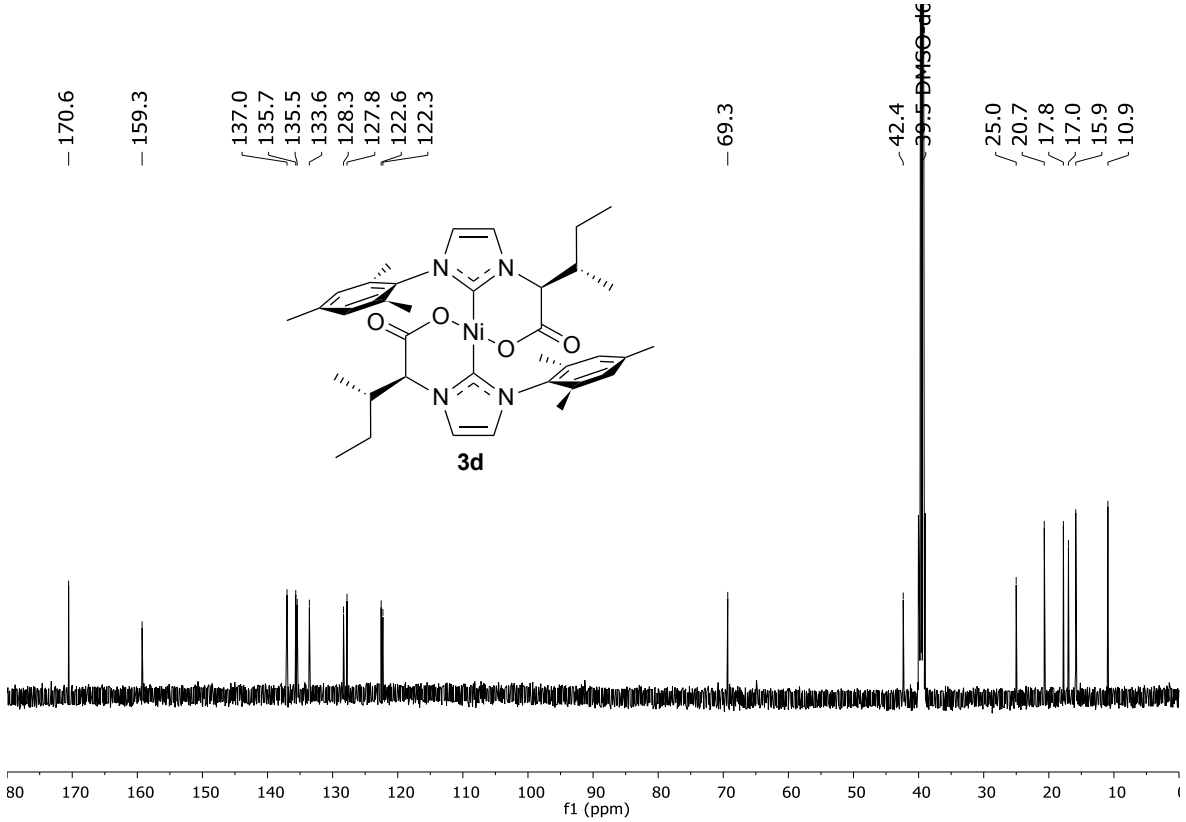
Spectrum S36. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **3c**.



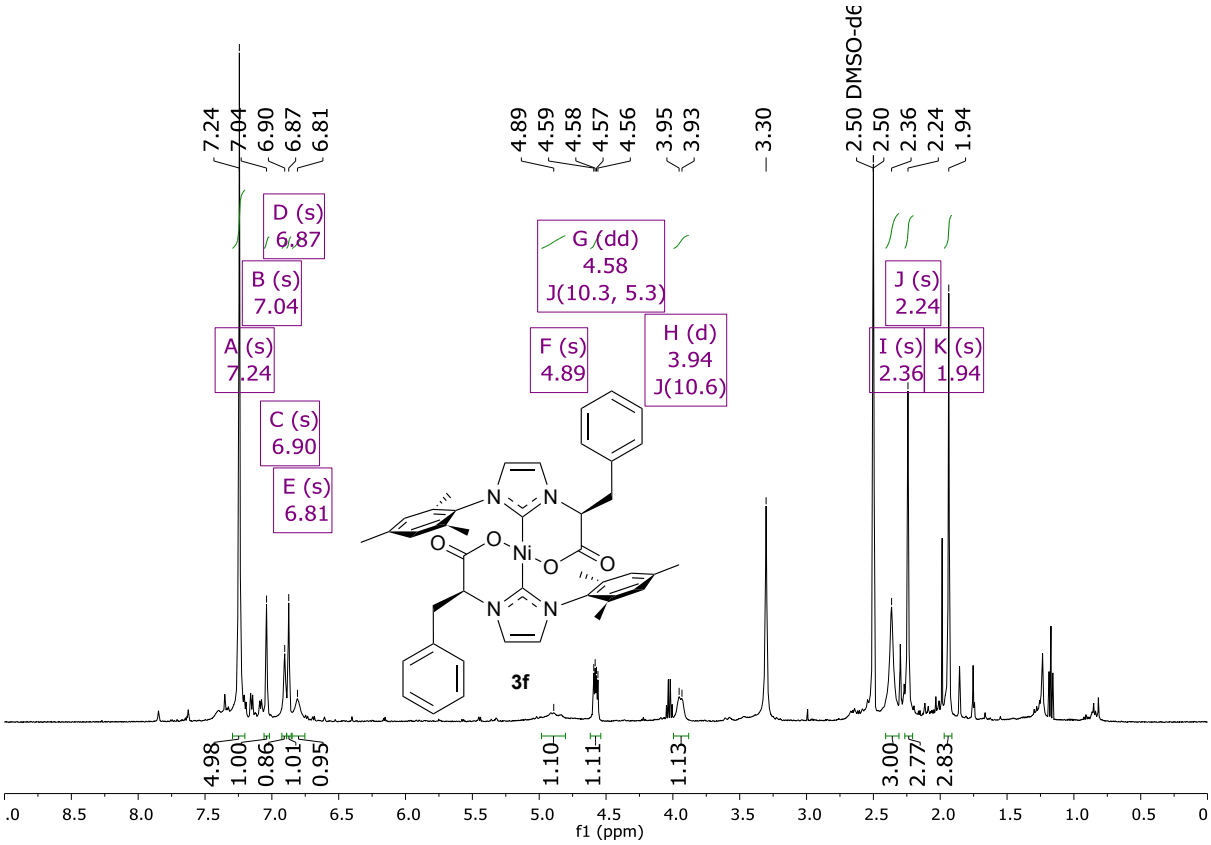
Spectrum S37. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **3c**.



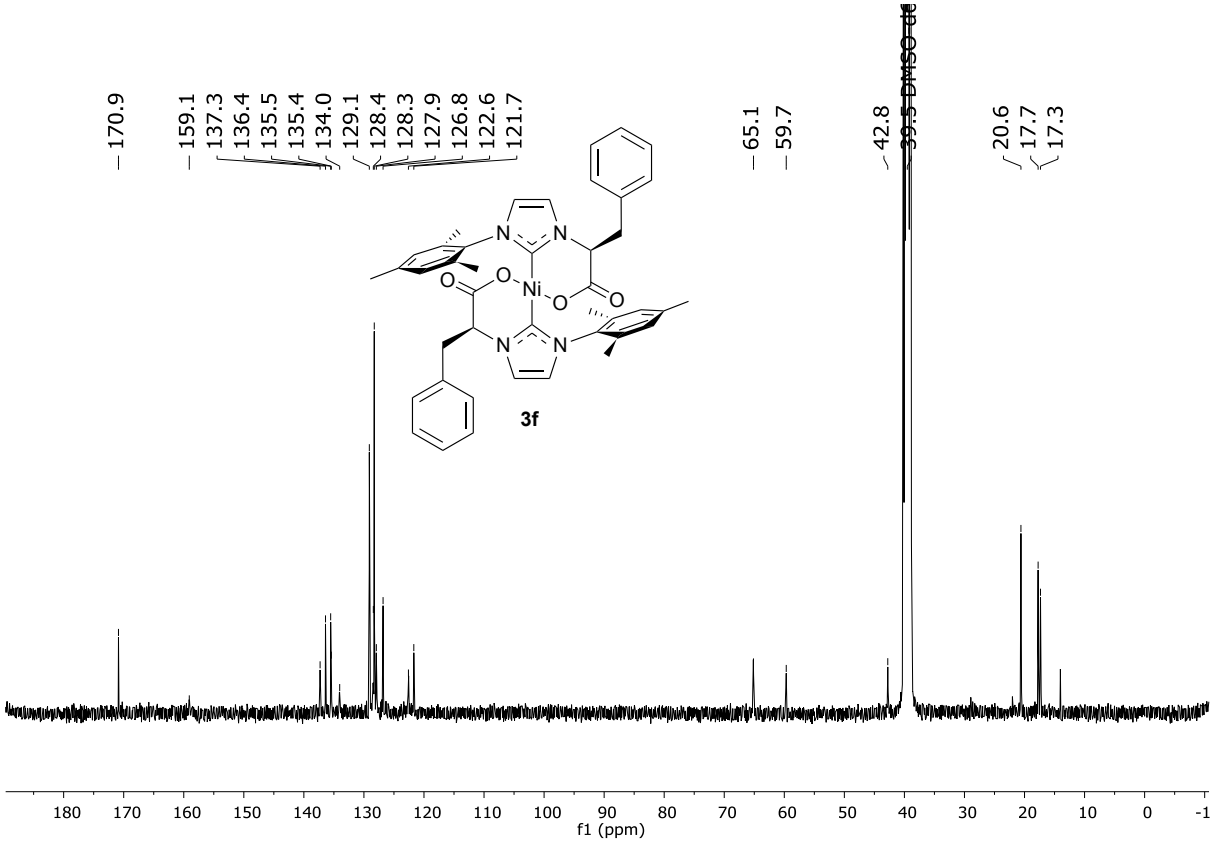
Spectrum S38. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **3d**.



Spectrum S39. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **3d**.



Spectrum S40. ^{1}H NMR (500 MHz, dmso-d_6) spectrum of **3f**.



Spectrum S41. $^{13}C\{^{1}H\}$ NMR (125 MHz, dmso-d_6) spectrum of **3f**.