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Supplementary Information

Imidazolium-benzimidazolates as convenient sources of donor-functionalised normal and abnormal *N*-heterocyclic carbenes

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1. Experimental Section

General

All reactions were carried out in an inert atmosphere (argon or dinitrogen) by applying standard Schlenk or glove-box techniques, unless indicated otherwise. Starting materials were procured from standard commercial sources and used as received. **3a**H,[S1] 1-*tert*-butylimidazole[S2] and nickelocene[S3] were prepared by following adapted versions of the published procedures. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature with Varian NMRS-500 and MR-400 spectrometers operating at 500 and 400 MHZ, respectively, for ^{1}H. ^{77}Se NMR spectra were recorded with a Varian NRMS-500 spectrometer with neat dimethylselenide as external standard (δ = 4 ppm).[S4] High-resolution (HR) ESI mass spectra were obtained with a micrOTOF time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany) using an Apollo^{TM} "ion funnel" ESI source. Mass calibration was performed immediately prior to the measurement with ESI Tune Mix Standard (Agilent, Waldbronn, Germany). Elemental analyses were carried out with a HEKAtech Euro EA-CHNS elemental analyser at the Institute of Chemistry, University of Kassel, Germany.

Synthesis of 3bH_2Cl

A mixture of 2-chlorobenzimidazole (1.53 g, 10.0 mmol) and 1-isopropylimidazole (1.65 g, 15.0 mmol) was stirred at a bath temperature of 135 °C for 1 h. The mixture was allowed to cool to room temperature. Diethyl ether (50 mL) was added and the solid filtered off.

Recrystallization from chloroform afforded the product as colourless crystals. Yield: 1.77 g (67%).

^{1}H NMR (DMSO-d_6): δ = 14.19 (br. s, 1H, NH), 10.21 (s, 1H, NCHN), 8.52, 8.22 (2 s, 2 × 1H, NCHCHN), 7.68, 7.33 (2 m, 2 × 2H, C_6H_4), 4.81 (sept, 1H, *J* = 6.7 Hz, C*H*Me$_2$), 1.58 (d, 6H, *J* = 6.7 Hz, CH*Me*$_2$).

^{13}C NMR (DMSO-d_6): δ = 141.4 (N_3C), 137.2 (br., C_6H_4), 134.7 (NCHN), 123.2 (C_6H_4), 121.9, 120.2 (2 × NCHCHN), 115.5 (br., C_6H_4), 53.4 (*C*HMe$_2$), 22.1 (CH*Me*$_2$).

HRMS/ESI(+): *m*/*z* = 227.1269 $[M - Cl]^+$, calcd. for $[C_{13}H_{15}N_4]^+$ 227.1297.

Anal. calcd. for $C_{13}H_{15}N_4Cl$ (%): C, 59.43; H, 5.75; N, 21.32. Found: C, 59.44; H, 5.81; N, 21.24.

Synthesis of 3cH_2Cl

A mixture of 2-chlorobenzimidazole (1.53 g, 10.0 mmol) and 1-*tert*-butylimidazole (1.86 g, 15.0 mmol) was stirred at a bath temperature of 135 °C for 1 h. The mixture was allowed to cool to room temperature. Diethyl ether (50 mL) was added and the solid filtered off. Recrystallization from chloroform afforded the product as colourless crystals. Yield: 2.34 g (85%).

^{1}H NMR (DMSO-d_6): δ = 14.78 (br. s, 1H, NH), 10.42 (s, 1H, NCHN), 8.65, 8.35 (2 s, 2 × 1H, NCHCHN), 7.66, 7.32 (2 m, 2 × 2H, C_6H_4), 1.70 (s, 9H, CMe$_3$).

^{13}C NMR (DMSO-d_6): δ = 141.3 (N_3C), 136.5 (br., C_6H_4), 134.5 (NCHN), 123.3 (br., C_6H_4), 121.5, 120.2 (2 × NCHCHN), 115.3 (br., C_6H_4), 61.0 (*C*Me$_3$), 28.8 (C*Me*$_3$).

HRMS/ESI(+): *m*/*z* = 241.1505 $[M - Cl]^+$, calcd. for $[C_{14}H_{17}N_4]^+$ 241.1453.

Anal. calcd. for $C_{14}H_{17}N_4Cl$ (%): C, 60.76; H, 6.19; N, 20.24. Found: C, 60.23; H, 6.12; N, 19.98.

Synthesis of 3cH_2[BPh_4]

The reaction was carried out under aerobic conditions. **3c**H_2Cl (2.30 g, 8.3 mmol) was dissolved in water (10 mL). A saturated aqueous solution of Na[BPh_4] (7.10 g, 20.7 mmol) was added. The colourless precipitate was filtered off, washed with water (2 × 5 mL) and dried under vacuum. The crude product was recrystallized from dichloromethane. Yield 2.47 g (53%).

^{1}H NMR (DMSO-d_6): δ = 13.68 (br. s, 1H, NH), 9.93 (s, 1H, NCHN), 8.48, 8.32 (2 s, 2 × 1H, NCHCHN),), 7.72, 7.35 (2 m, 2 × 2H, C_6H_4), 7.19, 6.93 (2 m, 2 × 8H, Ph), 6.79 (m, 4H, Ph), 1.69 (s, 9H, CMe$_3$).

^{13}C NMR (DMSO-d_6): δ = 163.5 (q, J = 49.3 Hz, phenyl C_{ipso}), 141.1 (N_3C), 135.7 (m, phenyl CH), 134.1 (NCHN), 125.4 (m, phenyl CH), 123.6 (C_6H_4), 121.6 (phenyl CH), 121.5, 120.4 (2 × NCHCHN), 115.7 (br., C_6H_4), 61.1 (CMe$_3$), 28.8 (CMe_3).
Anal. calcd. for $C_{38}H_{37}N_4B$ (%): C, 81.42; H, 6.65; N, 10.00. Found: C, 81.69; H, 6.78; N, 10.09.

Synthesis of 3bH

The reaction was carried out under aerobic conditions. An aqueous sodium hydroxide solution (14 M, 0.20 mL, 2.8 mmol) was added dropwise to a stirred solution of **3b**H_2Cl (526 mg, 2.00 mmol) in water (5 mL). The colourless solid was filtered off, washed with water (4 × 5 mL) and dried under vacuum. The crude product was recrystallized from toluene. Similar to **3a**H,[S1] the compound forms a dihydrate according to the result of an X-ray diffraction analysis. Yield 346 mg (66%).
^{1}H NMR (CD_2Cl_2): δ = 9.37 (s, 1H, NCHN), 8.29 (s, 1H, NCHCHN), 7.51 (m, 2H, C_6H_4), 7.21 (s, 1H, NCHCHN), 7.01 (m, 2H, C_6H_4), 4.46 (sept, J = 6.7 Hz, 1H, CHMe$_2$), 1.58 (d, J = 6.7 Hz, 6H, CHMe_2).
^{13}C NMR (CD_2Cl_2): δ = 146.5 (N_3C), 130.6 (NCHN), 120.8, 120.0 (2 × NCHCHN), 119.9, 117.2 (2 × C_6H_4), 54.1 (CHMe$_2$), 23.3 (CHMe_2).
Anal. calcd. for $C_{13}H_{14}N_4$·1.7 H_2O (%): C, 60.78; H, 6.83; N, 21.81. Found: C, 61.05; H, 6.64; N, 21.36. The dihydrate obviously loses part of its water upon prolongued drying under vacuum.

Synthesis of 3cH

The product was obtained as a colourless solid by a procedure analogous to that described for **3b**H from **3c**H_2Cl (554 mg, 2.00 mmol) and aqueous sodium hydroxide solution (14 M, 0.20 mL, 2.8 mmol). Yield 322 mg (67%).
Alternative procedure: A solution of KO*t*Bu (269 mg, 2.40 mmol) in THF (50 mL) was cooled to −40 °C and added dropwise to a stirred suspension of **3c**H_2[BPh_4] (1.121 g, 2.00 mmol) in THF (50 mL) kept at the same temperature. After 1 h the cooling bath was removed. Stirring was continued for 2 h. Volatile components were removed under vacuum. Dichloromethane (50 mL) was added to the residue and the suspension filtered through a Celite pad. The filtrate was reduced to dryness under vacuum. Yield 413 mg (86%).
^{1}H NMR (CD_2Cl_2): δ = 9.30 (s, 1H, NCHN), 8.33 (s, 1H, NCHCHN), 7.51 (m, 2H, C_6H_4), 7.33 (s, 1H, NCHCHN), 7.01 (m, 2H, C_6H_4), 1.71 (s, 9H, CMe$_3$).
^{13}C NMR (CD_2Cl_2): δ = 146.6 (N_3C), 129.9 (NCHN), 120.8 (NCHCHN), 119.7 (C_6H_4), 119.4 (NCHCHN), 117.2 (C_6H_4), 60.7 (CMe$_3$), 30.3 (CMe_3).
Anal. calcd. for $C_{14}H_{16}N_4$ (%): C, 69.97; H, 6.71; N, 23.32. Found: C, 69.23; H, 7.19; N, 22.62.

Synthesis of thiourea and selenourea derivatives of the type 3HE (E = S, Se)

General procedure: Toluene (20 mL) was added to a mixture of the betaine **3**H (1.00 mmol) and elemental sulfur (64 mg, 2.00 mmol S) or grey selenium (160 mg, 2.00 mmol). The reaction vessel was sealed and subsequently heated with stirring for 3 h at a bath temperature of 150 °C in the case of **3a**H and **3b**H·2 H_2O or 135 °C in the case of **3c**H. The mixture was allowed to cool to room temperature. Volatile components were removed under reduced pressure. The residue was subjected to purification by column chromatography (silica gel, ethyl acetate), which afforded the product as off-white crystals.

3aHS: Yield 150 mg (65%).

^{1}H NMR ($CDCl_3$): δ = 13.08 (br. s, 1H, NH), 7.92 (d, 1H, *J* = 2.6 Hz, NCHCHN), 7.69, 7.52 (2 br. m, 2 × 1H, C_6H_4), 7.30 (m, 2H, C_6H_4), 6.86 (d, 1H, *J* = 2.6 Hz, NCHCHN), 3.68 (s, 3H, Me).

^{13}C NMR ($CDCl_3$): δ = 161.5 (CS), 140.2, 131.7, 123.2, 123.0, 119.7, 118.8 (6 × C_6H_4), 114.9, 111.7 (2 × NCHCHN), 35.1 (Me).

HRMS/ESI(+): *m*/*z* = 231.1209 $[M + H]^+$, calcd. for $[C_{11}H_{11}N_4S]^+$ 231.0704.

Anal. calcd. for $C_{11}H_{10}N_4S$ (%): C, 57.37; H, 4.38; N, 24.33. Found: C, 57.29; H, 4.55; N, 24.25.

3bHS: Yield 150 mg (68%).

^{1}H NMR ($CDCl_3$): δ = 13.25 (br. s, 1H, NH), 8.07 (d, 1H, *J* = 2.7 Hz, NCHCHN), 7.81, 7.63 (2 m, 2 × 1H, C_6H_4), 7.40 (m, 2H, C_6H_4), 5.27 (sept, 1H, *J* = 6.7 Hz, C*H*Me_2), 1.56 (d, 6H, *J* = 6.6 Hz, CH*Me*$_2$).

^{13}C NMR ($CDCl_3$): δ = 160.2 (CS), 144.9 (N_3C), 140.2, 131.7, 123.2, 123.0 (4 × C_6H_4), 118. 7 (NCHCHN), 115.6, 114.8 (2 × C_6H_4), 111.7 (NCHCHN), 48.8 (*C*HMe_2), 21.7 (CH*Me*$_2$).

HRMS/ESI(+): *m*/*z* = 259.1002 $[M + H]^+$, calcd. for $[C_{13}H_{15}N_4S]^+$ 259.1017.

Anal. calcd. for $C_{13}H_{14}N_4S$ (%): C, 60.44; H, 5.46; N, 21.69. Found: C, 60.44; H, 5.41; N, 21.70.

3cHS: Yield 215 mg (79%).

^{1}H NMR ($CDCl_3$): δ = 13.45 (br. s, 1H, NH), 7.98 (d, 1H, *J* = 2.7 Hz, NCHCHN), 7.61 (br. s, 2H, C_6H_4), 7.28 (m, 2H, C_6H_4), 7.04 (d, 1H, *J* = 2.7 Hz, NCHCHN), 1.86 (s, 9H, CMe_3).

^{13}C NMR ($CDCl_3$): δ = 160.4 (CS), 145.1 (N_3C), 122.9 (C_6H_4), 116.5, 114.3 (2 × NCHCHN), 60.4 (*C*Me_3), 28.0 (C*Me*$_3$).

HRMS/ESI(+): *m*/*z* = 273.1335 $[M + H]^+$, calcd. for $[C_{14}H_{17}N_4S]^+$ 273.1174.

Anal. calcd. for $C_{14}H_{16}N_4S$ (%): C, 61.74; H, 5.92; N, 20.57. Found: C, 61.77; H, 5.92; N, 20.08.

3aHSe: Yield 144 mg (52%).

^{1}H NMR ($CDCl_3$): δ = 13.38 (br. s, 1H, NH), 8.13 (d, 1H, *J* = 2.4 Hz, NCHCHN), 7.70, 7.55 (2 m, 2 × 1H, C_6H_4), 7.30 (m, 2H, C_6H_4), 7.01 (d, 1H, *J* = 2.4 Hz, NCHCHN), 3.77 (s, 3H, Me).

^{13}C NMR ($CDCl_3$): δ = 154.5 (CSe), 140.2 (N_3C), 131.5, 127.4, 123.5, 123.1 (4 × C_6H_4), 121.4 (NCHCHN), 118.9 (C_6H_4), 117.6 (NCHCHN), 111.9 (C_6H_4), 37.2 (Me).

^{77}Se NMR ($CDCl_3$): δ = 116.

HRMS/ESI(+): *m*/*z* = 279.0149 $[M + H]^+$, calcd. for $[C_{11}H_{11}N_4Se]^+$ 279.0149.

Anal. calcd. for $C_{11}H_{10}N_4Se$ (%): C, 47.66; H, 3.64; N, 20.21. Found: C, 47.77; H, 3.70; N, 20.15.

3bHSe: Yield 204 mg (67%).

^{1}H NMR ($CDCl_3$): δ = 13.48 (br. s, 1H, NH), 8.17 (d, 1H, *J* = 2.3 Hz, NCHCHN), 7.62 (br. m, 2H, C_6H_4), 7.29 (m, 2H, C_6H_4), 7.06 (d, 1H, *J* = 2.4 Hz, NCHCHN), 5.27 (sept, 1H, *J* = 6.7 Hz, C*H*Me_2), 1.46 (d, 6H, *J* = 6.7 Hz, CH*Me*$_2$).

^{13}C NMR ($CDCl_3$): δ = 153.0 (CSe), 144.7 (N_3C), 123.4, 123.1 (2 × C_6H_4), 118. 8 (NCHCHN), 118.3, 116.5 (2 × C_6H_4), 111.9 (NCHCHN), 50.9 (*C*HMe_2), 21.8 (CH*Me*$_2$).

^{77}Se NMR ($CDCl_3$): δ = 101.

HRMS/ESI(+): *m*/*z* = 307.0444 $[M + H]^+$, calcd. for $[C_{13}H_{15}N_4Se]^+$ 307.0462.

Anal. calcd. for $C_{13}H_{14}N_4Se$ (%): C, 51.15; H, 4.62; N, 18.36. Found: C, 50.45; H, 4.52; N, 18.02.

3cHSe: Yield 223 mg (70%).

^{1}H NMR (acetone-d_6): δ = 13.65 (br. s, 1H, NH), 8.11 (d, 1H, *J* = 2.6 Hz, NCHCHN), 7.74, 7.64 (2 br. s, 2 × 1H, C_6H_4), 7.58 (d, 1H, *J* = 2.5 Hz, NCHCHN), 7.27 (m, 2H, C_6H_4), 1.96 (s, 9H, CMe_3).

^{13}C NMR (acetone-d_6): δ = 153.1 (CSe), 146.1 (N_3C), 141.4, 132.9, 123.6, (3 × C_6H_4), 120.3 (NCHCHN), 119.5 (C_6H_4), 118.2 (NCHCHN), 113.2 (C_6H_4), 62.3 (*C*Me_3), 28.7 (C*Me*$_3$).

^{77}Se NMR ($CDCl_3$): δ = 195.

HRMS/ESI(+): *m*/*z* = 321.0590 $[M + H]^+$, calcd. for $[C_{14}H_{17}N_4Se]^+$ 321.0618.

Anal. calcd. for $C_{14}H_{16}N_4Se$ (%): C, 52.67; H, 5.05; N, 17.55. Found: C, 53.03; H, 5.06; N, 17.38.

Synthesis of [RuCl(3'aH)(MeCN)(PPh_3)$_2$]Cl

A solution of [$RuCl_2(PPh_3)_3$] (163 mg, 0.17 mmol) in acetonitrile (10 mL) was added dropwise to a stirred solution of **1a**H (40 mg, 0.17 mmol) in acetonitrile (15 mL) cooled in an ice bath. The ice bath was removed and stirring was continued for 2 h. Volatile components were removed under vacuum. The solid residue was washed with diethyl ether (10 mL) and

subsequently taken up in dichloromethane (5 mL). Traces of insoluble material were removed by filtration. The volume of the filtrate was reduced to *ca.* 1 mL. The crude product was precipitated as a yellow solid by slow addition of diethyl ether (10 mL), isolated by filtration and dried under vacuum. Numerous attempts to obtain the product in analytically pure form by crystallisation and/or column chromatography did not furnish satisfactory results. Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a chloroform solution. Yield 109 mg (68%).

^{1}H NMR ($CDCl_3$): δ = 9.36, 8.10 (2 s, 2 × 1H, NCHCHN), 8.10 (m, 1H, C_6H_4), 7.58 – 7.01 (m, 34H, NH, C_6H_4 and Ph), 3.72 (s, 3H, NMe), 1.78 (s, 3H, MeCN).

^{31}P NMR ($CDCl_3$): δ = 46.5.

HRMS/ESI(+): *m*/*z* = 900.1726 $[M - Cl]^+$, calcd. for $[C_{49}H_{43}ClN_5P_2Ru]^+$ 900.1726.

Synthesis of [RuCl(3''bH)(MeCN)(PPh_3)$_2$]Cl

The crude product was obtained as a yellow solid by a procedure analogous to that described for [RuCl(**3'a**H)(MeCN)(PPh_3)$_2$]Cl from [$RuCl_2(PPh_3)_3$] (163 mg, 0.17 mmol) and **3b**H·2 H_2O (45 mg, 0.17 mmol). Numerous attempts to obtain the product in analytically pure form by crystallisation and/or column chromatography did not furnish satisfactory results. Single crystals suitable for an X-ray diffraction study were obtained by slow evaporation of a benzene solution. Yield 124 mg (76%).

^{1}H NMR (CD_2Cl_2): δ = 10.58 (br. s, 1H, NCHN), 8.39 (m, 1H, NCHCRu), 8.00 (m, 1H, C_6H_4), 7.61 – 7.01 (m, 34H, NH, C_6H_4, Ph; the integral is compromised by substantial amounts of free PPh_3), 4.65 (sept, 1H, *J* = 6.7 Hz, $CHMe_2$), 1.89 (s, 3H, MeCN), 1.70 (d, 6H, *J* = 6.7 Hz, $CH\mathit{Me}_2$).

^{31}P NMR (CD_2Cl_2): δ = 45.6; the spectrum reveals the presence of substantial amounts of free PPh_3 (δ = –6.4).

Synthesis of [Ru(3''cH)$_2$(PPh_3)$_2$]Cl_2

Benzene (20 mL) was added to [$RuCl_2(PPh_3)_3$] (201 mg, 0.21 mmol) and **1c**H (101 mg, 0.42 mmol). The reaction vessel was sealed and the stirred mixture heated at a bath temperature of 50 °C for 17 h. The mixture was allowed to cool to room temperature. The solid was filtered off by using a Celite pad and washed with benzene (2 × 5 mL). The crude product was dissolved by addition of dichloromethane (5 mL) and the solution passed through the Celite pad. The volume of the solution was reduced under vacuum until first signs of incipient crystallisation were observed. The solution was layered with diethyl ether and stored at –20 °C. The product was obtained as a yellow crystalline solid, which was filtered off and dried under vacuum. Yield 215 mg (87%).

^{1}H NMR (CD_2Cl_2): δ = 15.08 (br. s, 2H, NH), 10.80 (s, 2H, NCHN), 7.82 (m, 2H, NCHCRu), 7.48 – 6.78 (m, 38H, C_6H_4, Ph; the integral is compromised by residual free PPh_3), 1.61 (s, 18H, C*Me*$_3$).
^{13}C NMR (CD_2Cl_2): δ = 147.1, 140.3, 134.1, 133.5, 133.3, 133.2, 132.9, 129.4, 128.8, 128.7, 127.6, 125.0, 123.8, 122.2, 119.0, 113.5, 58.8 (*C*Me$_3$), 30.0 (C*Me*$_3$).
^{31}P NMR (CD_2Cl_2): δ = 34.2; the spectrum reveals the presence of residual free PPh_3 (δ = −6.4).
HRMS/ESI(+): *m*/*z* = 422.1243 $[M - Cl - PPh_3]^{2+}$, calcd. for $[C_{46}H_{47}N_8PRu]^{2+}$ 422.1352.
Anal. calcd. for $C_{64}H_{62}Cl_2N_8P_2Ru \cdot CH_2Cl_2$ (%): C, 61.86; H, 5.11; N, 8.88. Found: C, 61.43; H, 5.35; N, 8.55.

Synthesis of nickel complexes of the type [NiCp(3')]

General procedure: THF (20 mL) was added to the betaine **3**H (1.00 mmol) and nickelocene (283 mg, 1.50 mmol). The reaction vessel was sealed and the stirred mixture heated at a bath temperature of 80 °C for 16 h. The mixture was allowed to cool to room temperature. Volatile components were removed under vacuum. The remaining solid was washed with hexane (2 × 20 mL) and the residue taken up in dichloromethane (5 mL). Traces of insoluble material were removed by filtration. The volume of the filtrate was reduced to *ca.* 1 mL under vacuum. The crude product was precipitated by slow addition of hexane (20 mL), isolated by filtration, dried under vacuum and subjected to purification by column chromatography (silica gel). The products were obtained as yellow-green crystalline solids.

[NiCp(**3'a**)]: Ethyl acetate was used as eluent for column chromatography. Yield 247 mg (77%).
^{1}H NMR ($CDCl_3$): δ = 7.83 (m, 1H, NCHCHN), 7.61 (m, 1H, C_6H_4), 7.06 (m, 2H, C_6H_4), 6.91 (m, 1H, C_6H_4), 6.75 (m, 1H, NCHCHN), 5.70 (s, 5H, Cp), 3.56 (s, 3H, Me).
^{13}C NMR ($CDCl_3$): δ = 168.4 ($NiCN_2$), 154.4 (N_3C), 146.2, 146.0 (2 × C_6H_4), 123. 1 (NCHCHN), 120.1, 119.7, 118.8 (3 × C_6H_4), 116.3 (NCHCHN), 112.5 (C_6H_4), 90.2 (Cp), 37.5 (Me).
HRMS/ESI(+): *m*/*z* = 321.0633 $[M + H]^+$, calcd. for $[C_{16}H_{15}N_4Ni]^+$ 321.0650.
Anal. calcd. for $C_{16}H_{14}N_4Ni$ (%): C, 59.87; H, 4.40; N, 17.45. Found: C, 60.38; H, 4.31; N, 17.63.

[NiCp(**3'b**)]: Ethyl acetate was used as eluent for column chromatography. Yield 304 mg (87%).

^{1}H NMR ($CDCl_3$): δ = 7.87 (br. s, 1H, NCHCHN), 7.61 (br. s, 1H, C_6H_4), 7.05 (br. m, 2H, C_6H_4), 6.93 (br. s, 1H, C_6H_4), 6.87 (br. s, 1H, NCHCHN), 5.67 (s, 5H, Cp), 4.04 (sept, 1H, *J* = 6.8 Hz, C*H*Me$_2$) 1.46 (d, 6H, *J* = 6.7 Hz, CH*Me*$_2$).
^{13}C NMR ($CDCl_3$): δ = 166.1 ($NiCN_2$), 154.5 (N_3C), 146.1, 120.0 (2 × C_6H_4), 119.6 (NCHCHN), 118.8, 117.1 (2 × C_6H_4), 116.7 (NCHCHN), 112.4 (C_6H_4), 90.4 (Cp), 51.9 (*C*HMe$_2$), 23.2 (CH*Me*$_2$).
HRMS/ESI(+): *m*/*z* = 349.0929 $[M + H]^+$, calcd. for $[C_{18}H_{19}N_4Ni]^+$ 349.0963.
Anal. calcd. for $C_{18}H_{18}N_4Ni$ (%): C, 61.94; H, 5.20; N, 16.05. Found: C, 61.10; H, 5.25; N, 16.06.

[NiCp(**3'c**)]: Acetone was used as eluent for column chromatography. Yield 196 mg (54%).
^{1}H NMR (CD_2Cl_2): δ = 7.80 (d, 1H, *J* = 2.0 Hz, NCHCHN), 7.48 (m, 1H, C_6H_4), 7.07 (d, 1H, *J* = 2.1 Hz, NCHCHN), 7.00 (m, 2H, C_6H_4), 6.92 (m, 1H, C_6H_4), 5.69 (s, 5H, Cp), 1.58 (s, 9H, CMe_3).
^{13}C NMR (CD_2Cl_2): δ = 162.6 ($NiCN_2$), 147.3, 147.1, 120.2, 119.8 (4 × C_6H_4), 119.7 (NCHCHN), 118.9 (C_6H_4), 115.0 (NCHCHN), 112.8 (C_6H_4), 92.7 (Cp), 57.9 (*C*Me$_3$), 30.8 (C*Me*$_3$).
HRMS/ESI(+): *m*/*z* = 363.1116 $[M + H]^+$, calcd. for $[C_{19}H_{21}N_4Ni]^+$ 363.1120.
Anal. calcd. for $C_{19}H_{20}N_4Ni$ (%): C, 62.85; H, 5.55; N, 15.43. Found: C, 62.86; H, 5.51; N, 15.46.

Synthesis of heterodinuclear complexes of the type [RhCl(COD){NiCp(μ-3')}]
General procedure: THF (10 mL) was added to the nickel complex [NiCp(**3'**)] (0.30 mmol) and [{Rh(μ-Cl)(COD)}$_2$] (74 mg, 0.15 mmol). The mixture was stirred for 16 h. Volatile components were removed under vacuum. The residue was taken up in dichloromethane (0.5 mL). Slow addition of hexane (10 mL) afforded a precipitate, which was filtered off by using a Celite pad and washed with hexane (10 mL). It was subsequently dissolved by addition of dichloromethane (3 mL) and the solution passed through the Celite pad. The solvent was removed under vacuum, leaving the product as a yellow-green solid.

[RhCl(COD){NiCp(μ-**3'a**)}]: Yield 153 mg (90%).
^{1}H NMR ($CDCl_3$): δ = 10.28 (s, 1H, NCHCHN), 8.26 (d, *J* = 8.0 Hz, 1H, C_6H_4), 7.18, 7.09 (2 "t", apparent *J* = 7.6 Hz, 2 × 1H, C_6H_4), 6.97 (s, 1H, NCHCHN), 6.84 (d, *J* = 8.0 Hz, 1H, C_6H_4) 5.68 (s, 5H, Cp), 4.82, 4.73, 3.76 (3 m, 3 × 1H, CH_{COD}), 3.62 (s, 3H, Me) 3.49 (m, 1H, CH_{COD}), 2.70 (m, 1H, CH_2), 2.46 (m, 3H, CH_2), 1.96 (m, 1H, CH_2), 1.82 (m, 2H, CH_2), 1.71 (m, 1H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 169.9 ($NiCN_2$), 151.3 (N_3C), 144.9, 143.1 (2 × C_6H_4), 123.0 (NCHCHN), 121.3, 121.0, 119.3 (3 × C_6H_4), 119.2 (NCHCHN), 113.3 (C_6H_4), 90.5 (Cp), 85.3, 83.8 (2 d, J_{CRh} = 11.7 Hz, CH_{COD}), 76.0 (d, J_{CRh} = 14.0 Hz, CH_{COD}), 75.4 (d, J_{CRh} = 13.7 Hz, CH_{COD}), 37.8 (Me), 32.5, 31.1, 30.9, 30.5 (4 × CH_2).
HRMS/ESI(+): *m*/*z* = 530.9498 [M – Cl]$^+$, calcd. for [$C_{24}H_{26}N_4NiRh$]$^+$ 531.0566.
Anal. calcd. for $C_{24}H_{26}N_4ClNiRh$ (%): C, 50.79; H, 4.62; N, 9.87. Found: C, 49.90; H, 4.61; N, 9.45.

[RhCl(COD){NiCp(μ-**3'b**)}]: Yield 105 mg (59%).
^{1}H NMR (CD_2Cl_2): δ = 10.30 (s, 1H, NCHCHN), 8.22 (d, *J* = 8.1 Hz, 1H, C_6H_4), 7.18 (m, 2H, NCHCHN and C_6H_4), 7.10 ("t", apparent *J* = 7.5 Hz, 1H, C_6H_4), 6.90 (d, *J* = 7.9 Hz, 1H, C_6H_4) 5.69 (s, 5H, Cp), 4.70 (m, 2H, CH_{COD}), 4.11 (sept, *J* = 6.7 Hz, 1H, C*H*Me$_2$) 3.75, 3.53 (2 m, 2 × 1H, CH_{COD}), 2.67 (m, 1H, CH_2), 2.50 (m, 3H, CH_2), 1.97 (m, 1H, CH_2), 1.80 (m, 3H, CH_2), 1.52 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$).
^{13}C NMR (CD_2Cl_2): δ = 168.2 ($NiCN_2$), 152.0 (N_3C), 145.3, 143.6 (2 × C_6H_4), 121.6 (NCHCHN), 121.2, 119.9, 119.2 (3 × C_6H_4), 117.7 (NCHCHN), 114.0 (C_6H_4), 91.9 (Cp), 85.3 (d, J_{CRh} = 11.8 Hz, CH_{COD}), 84.2 (d, J_{CRh} = 11.9 Hz, CH_{COD}), 76.3 (d, J_{CRh} = 13.8 Hz, CH_{COD}), 75.8 (d, J_{CRh} = 13.6 Hz, CH_{COD}), 52.8 (*C*HMe$_2$), 32.7, 31.4, 30.9 (3 × CH_2), 23.4 (CH*Me*$_2$).
HRMS/ESI(+): *m*/*z* = 559.0872 [M – Cl]$^+$, calcd. for [$C_{26}H_{30}N_4NiRh$]$^+$ 559.0879.
Anal. calcd. for $C_{26}H_{30}N_4ClNiRh$ (%): C, 52.43; H, 5.08; N, 9.41. Found: C, 52.39; H, 5.11; N, 8.71.

[RhCl(COD){NiCp(μ-**3'c**)}]: Yield 143 mg (78%).
^{1}H NMR (CD_2Cl_2): δ = 10.46 (s, 1H, NCHCHN), 8.28 (d, *J* = 8.0 Hz, 1H, C_6H_4), 7.28 (s, 1H, NCHCHN), 7.20, 7.11 (2 "t", apparent *J* = 7.6 Hz, 2 × 1H, C_6H_4), 6.92 (d, *J* = 8.0 Hz, 1H, C_6H_4) 5.69 (s, 5H, Cp), 4.70 (br. s, 2H, CH_{COD}), 3.73, 3.52 (2 br. s, 2 × 1H, CH_{COD}), 2.68 (m, 1H, CH_2), 2.52 (m, 3H, CH_2), 1.97 (m, 1H, CH_2), 1.80 (m, 3H, CH_2), 1.63 (s, 9H, CMe_3).
^{13}C NMR (CD_2Cl_2): δ = 164.7 ($NiCN_2$), 152.0 (N_3C), 145.8, 143.9 (2 × C_6H_4), 121.6 (NCHCHN), 121.3, 119.6, 119.5 (3 × C_6H_4), 117.9 (NCHCHN), 113.9 (C_6H_4), 93.2 (Cp), 85.3 (d, J_{CRh} = 11.1 Hz, CH_{COD}), 84.2 (d, J_{CRh} = 11.7 Hz, CH_{COD}), 76.3, 76.0 (2 d, J_{CRh} = 13.4 Hz, CH_{COD}), 58.4 (*C*Me$_3$), 32.7, 31.4 (two closely spaced signals), 30.9 (4 × CH_2), 30.8 (C*Me*$_3$).
HRMS/ESI(+): *m*/*z* = 573.0824 [M – Cl]$^+$, calcd. for [$C_{27}H_{32}N_4NiRh$]$^+$ 573.1035.

Synthesis of heterodinuclear complexes of the type [CuBr{NiCp(μ-3')}]
General procedure: Dichloromethane (1 mL) was added to the nickel complex [NiCp(**3'**)] (0.30 mmol) and CuBr (50 mg, 0.35 mmol) and the mixture stirred for 1 h. Hexane (15 mL)

was added. The solid was isolated by filtration and taken up in dichloromethane (3 mL). Traces of insoluble material were removed by filtration. The product was precipitated as a green solid by slow addition of hexane (30 mL), isolated by filtration and dried under vacuum.

[CuBr{NiCp(μ-**3a'**)}]: Yield 96 mg (69%).
^{1}H NMR ($CDCl_3$): δ = 8.51 (s, 1H, NCHCHN), 7.63 (m, 1H, C_6H_4), 7.13 (m, 2H, C_6H_4), 6.93 (m, 1H, C_6H_4), 6.86 (s, 1H, NCHCHN), 5.73 (s, 5H, Cp), 3.65 (s, 3H, Me).
^{13}C NMR ($CDCl_3$): δ = 123.7 (NCHCHN), 121.9, 121.6, 118.2 (3 × C_6H_4), 117.1 (NCHCHN), 113.6 (C_6H_4), 90.7 (Cp), 37.9 (Me); signals due to quaternary C atoms could not be detected.
Anal. calcd. for $C_{16}H_{14}N_4BrCuNi{\cdot}CH_2Cl_2$ (%): C, 37.17; H, 2.98; N, 11.57. Found: C, 37.13; H, 2.98; N, 11.08.

[CuBr{NiCp(μ-**3b'**)}]: Yield 103 mg (70%).
^{1}H NMR (CD_2Cl_2): δ = 8.56 (d, 1H, *J* = 2.2 Hz, NCHCHN), 7.62 (m, 1H, C_6H_4), 7.15 (m, 2H, C_6H_4), 7.04 (d, 1H, *J* = 2.2 Hz, NCHCHN), 6.99 (m, 1H, C_6H_4), 5.74 (s, 5H, Cp), 4.11 (sept, 1H, *J* = 6.8 Hz, C*H*Me_2), 1.50 (d, 6H, *J* = 6.8 Hz, CHMe_2).
^{13}C NMR (CD_2Cl_2): δ = 169.2 ($NiCN_2$), 144.5, 143.0, 122.4 (3 × C_6H_4), 122.1 (NCHCHN), 118.6, 118.2 (2 × C_6H_4), 117.7 (NCHCHN), 114.3 (C_6H_4), 91.5 (Cp), 53.0 (*C*HMe_2), 23.3 (CH*Me*$_2$).
Anal. calcd. for $C_{18}H_{18}N_4BrCuNi{\cdot}0.5\ CH_2Cl_2$ (%): C, 41.54; H, 3.58; N, 10.47. Found: C, 41.88; H, 3.51; N, 10.85.

[CuBr{NiCp(μ-**3c'**)}]: Yield 52 mg (34%).
^{1}H NMR (CD_2Cl_2): δ = 8.58 (s, 1H, NCHCHN), 7.63 (m, 1H, C_6H_4), 7.16 (m, 3H, NCHCHN and C_6H_4), 7.01 (m, 1H, C_6H_4), 5.73 (s, 5H, Cp), 1.61 (s, 9H, CMe_3).
^{13}C NMR (CD_2Cl_2): δ = 138.1, 122.4, 122.1 (3 × C_6H_4), 120.5 (NCHCHN), 118.4 (C_6H_4), 115.5 (NCHCHN), 114.2 (C_6H_4), 93.5 (Cp), 54.5 (*C*Me_3), 30.8 (C*Me*$_3$).
Anal. calcd. for $C_{19}H_{20}N_4BrCuNi$ (%): C, 45.05; H, 3.98; N, 11.06. Found: C, 44.15; H, 4.12; N, 10.74.

Synthesis of heterodinuclear complexes of the type [ZnI_2{NiCp(μ-3')}$_2$]
General procedure: The nickel complex [NiCp(**3'**)] (0.30 mmol) and ZnI_2 (64 mg, 0.20 mmol) were dissolved in a minimal amount of dichloromethane–diethyl ether (8 mL, 3:5). The mixture was stirred for 16 h. The solvent was removed under vacuum. The solid residue was taken up in dichloromethane (1 mL). The product was precipitated as a green solid by slow addition of diethyl ether (15 mL), filtered off, washed with diethyl ether (5 mL) and dried under vacuum.

[ZnI_2{NiCp(μ-**3'a**)}$_2$]: Yield 123 mg (85%).

^{1}H NMR (DMSO-d_6): δ = 8.02 (m, 2H, NCHCHN), 7.40 (m, 4H, NCHCHN and C_6H_4), 6.91 (m, 6H, C_6H_4), 5.80 (s, 10H, Cp), 3.63 (s, 6H, Me).

^{13}C NMR (DMSO-d_6): δ = 167.4 ($NiCN_2$), 153.9 (N_3C), 145.6, 145.4 (2 × C_6H_4), 125.1 (NCHCHN), 119.6, 119.0, 117.7 (3× CH), 115.9 (NCHCHN), 112.8 (C_6H_4), 90.2 (Cp), 37.1 (Me).

Anal. calcd. for $C_{32}H_{28}N_8I_2Ni_2Zn$ (%): C, 39.99; H, 2.94; N, 11.66. Found: C, 39.95; H, 2.96; N, 11.69.

[ZnI_2{NiCp(μ-**3'b**)}$_2$]: Yield 122 mg (80%).

^{1}H NMR ($CDCl_3$): δ = 8.81 (s, 2H, NCHCHN), 7.99 (d, 2H, *J* = 8.2 Hz, C_6H_4), 7.07, 6.96 (2 "t", 2 × 2H, apparent *J* = 7.8 Hz, C_6H_4), 6.90 (d, 2H, *J* = 8.1 Hz, C_6H_4), 6.65 (s, 2H, NCHCHN), 5.70 (s, 10H, Cp), 4.02 (sept, 2H, *J* = 6.9 Hz, C*H*Me_2), 1.41 (d, 12H, *J* = 6.8 Hz, CH*Me*$_2$).

^{13}C NMR ($CDCl_3$): δ = 168.1 ($NiCN_2$), 144.2, 142.0, 122.4 (3 × C_6H_4), 121.8 (NCHCHN), 121.6, 118.9 (2 × C_6H_4), 116.3 (NCHCHN), 113.3 (C_6H_4), 91.0 (Cp), 52.1 (*C*HMe_2), 23.1 (CH*Me*$_2$).

Anal. calcd. for $C_{36}H_{36}N_8I_2Ni_2Zn$ (%): C, 42.50; H, 3.57; N, 11.01. Found: C, 42.92; H, 3.71; N, 10.77.

[ZnI_2{NiCp(μ-**3'c**)}$_2$]: Yield 124 mg (79%).

^{1}H NMR (CD_2Cl_2): δ = 8.65 (br. s, 2H, NCHCHN), 7.92 (br. s, 2H, C_6H_4), 7.12 (m, 2H, C_6H_4), 7.00 (m, 4H, C_6H_4), 6.86 (br. s, 2H, NCHCHN), 5.72 (s, 10H, Cp), 1.56 (s, 12H, CMe_3).

^{13}C NMR (CD_2Cl_2): δ = 144.9, 142.1, 122.0 (3 × C_6H_4), 121.5 (NCHCHN), 119.3, 118.8 (2 × C_6H_4), 113.6 (NCHCHN), 110.3 (C_6H_4), 93.1 (Cp), 58.1 (*C*Me_3), 30.5 (C*Me*$_3$).

X-ray Crystallography

For each data collection a single crystal was mounted on a micro-mount and transferred in the cold nitrogen gas stream [T = 100(2) K]. All geometric and intensity data were taken from this sample by ω-scans with steps of 1°. Data collections were carried out either on a Stoe IPDS2 diffractometer equipped with a 2-circle goniometer and an area detector or on a Stoe StadiVari diffractometer equipped with a 4-circle goniometer and a DECTRIS Pilatus 200K detector. For the diffraction experiments CuK_α or MoK_α radiation (λ = 1. 54186 Å or 0.71073 Å, respectively) was used, monochromatised by graded multilayer mirrors. The data sets were corrected for absorption (by integration), Lorentz and polarisation effects. The structures were solved by direct methods (SHELXT-2014/7) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL-2014/7).[S5] H atoms were included to the models in calculated positions, except for N-bonded H atoms, which were found in the difference Fourier maps and freely refined. All H atoms have the 1.2 fold isotropic displacement parameter of their bonding partner. Experimental details for each diffraction experiment are given below. CCDC 1939115 – 1939140 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystal structure determination of **3b**H_2Cl:

Crystal data: $C_{13}H_{15}ClN_4$, M = 262.74, monoclinic, a = 13.8200(7), b = 11.3092(4), c = 16.8646(8) Å, β = 104.920(4)°, U = 2547.0(2) Å^3, space group $P2_1/n$ (no. 14), Z = 8, 10079 reflections measured, 4743 unique (R_{int} = 0.0504), which were used in all calculations. The final $R1$ value was 0.0575 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1759 (all data). CCDC 1939115.

Crystal structure determination of **3c**H_2Cl:

Crystal data: $C_{14}H_{17}ClN_4$, M = 276.76, orthorhombic, a = 6.4586(5), b = 24.9625(12), c = 17.2461(7) Å, U = 2780.5(3) Å^3, space group $Cmca$ (no. 64), Z = 8, 6154 reflections measured, 1493 unique (R_{int} = 0.0519), which were used in all calculations. The final $R1$ value was 0.0512 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1231 (all data). CCDC 1939116.

Crystal structure determination of **3c**$H_2[BPh_4]$:

Crystal data: $C_{38}H_{37}BN_4$, M = 560.52, monoclinic, a = 10.9377(4), b = 16.6444(7), c = 16.3724(6) Å, β = 92.771(3)°, U = 2977.1(2) Å^3, space group $P2_1/n$ (no. 14), Z = 4, 13311 reflections measured, 5594 unique (R_{int} = 0.0143), which were used in all calculations. The final $R1$ value was 0.0335 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.0817 (all data). CCDC 1939117.

Crystal structure determination of **3b**$H\cdot 2\ H_2O$:

Crystal data: $C_{13}H_{18}N_4O_2$, M = 262.31, monoclinic, a = 12.1903(7), b = 13.3007(8), c = 8.4206(5) Å, β = 102.568(5)°, U = 1332.60(14) Å^3, space group $P2_1/c$ (no. 14), Z = 4, 5603 reflections measured, 2433 unique (R_{int} = 0.0602), which were used in all calculations. The final $R1$ value was 0.1028 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2665 (all data). CCDC 1939118.

Crystal structure determination of **3c**H:

Crystal data: $C_{14}H_{16}N_4$, M = 240.31, monoclinic, a = 10.2454(12), b = 17.3799(19), c = 14.473(2) Å, β = 98.817(11)°, U = 2546.7(6) Å^3, space group $P2_1/n$ (no. 14), Z = 8, 15234 reflections measured, 6086 unique (R_{int} = 0.0495), which were used in all calculations. The final $R1$ value was 0.0472 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1264 (all data). CCDC 1939119.

Crystal structure determination of **3a**HS:

Crystal data: $C_{11}H_{10}N_4S$, M = 230.29, monoclinic, a = 5.7440(4), b = 14.7496(13), c = 12.5630(8) Å, β = 99.892(5)°, U = 1048.54(14) Å^3, space group $P2_1/c$ (no. 14), Z = 4, 4849 reflections measured, 1966 unique (R_{int} = 0.0275), which were used in all calculations. The final $R1$ value was 0.0344 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.0919 (all data). CCDC 1939120.

Crystal structure determination of **3b**HS:

Crystal data: $C_{13}H_{14}N_4S$, M = 258.34, triclinic, a = 6.9905(8), b = 7.0369(8), c = 14.5190(14) Å, α = 78.264(8), β = 78.151(8), γ = 64.286(8)°, U = 624.46(13) Å^3, space group P-1 (no. 2), Z = 2, 4516 reflections measured, 2314 unique (R_{int} = 0.0405), which were used in all calculations. The final $R1$ value was 0.0411 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1070 (all data). CCDC 1939121.

Crystal structure determination of **3c**HS:

Crystal data: $C_{14}H_{16}N_4S$, M = 272.34, orthorhombic, a = 17.423(2), b = 11.8598(10), c = 6.6646(5) Å, U = 1377.1(2) Å^3, space group $Pna2_1$ (no. 64), Z = 4, 4606 reflections measured, 2449 unique (R_{int} = 0.0662), which were used in all calculations. Flack parameter 0.3(5) inversion twin. The final $R1$ value was 0.1166 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2720 (all data). CCDC 1939122.

Crystal structure determination of **3a**HSe:

Crystal data: $C_{11}H_{10}N_4Se$, M = 277.19, monoclinic, a = 7.8616(6), b = 12.1269(7), c = 11.1928(9) Å, β = 97.003(6)°, U = 1059.13(13) Å^3, space group $P2_1/c$ (no. 14), Z = 4, 4504 reflections measured, 1971 unique (R_{int} = 0.0607), which were used in all calculations. The final $R1$ value was 0.0712 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2056 (all data). CCDC 1939123.

Crystal structure determination of **3b**HSe:

Crystal data: $C_{13}H_{14}N_4Se$, M = 305.24, triclinic, a = 7.1160(5), b = 7.0723(4), c = 14.8576(10) Å, α = 77.256(5), β = 77.551(5), γ = 63.341(5)°, U = 645.92(8) Å^3, space group P-1 (no. 2), Z = 2, 8538 reflections measured, 2398 unique (R_{int} = 0.0278), which were used in all calculations. The final $R1$ value was 0.0293 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.0753 (all data). CCDC 1939124.

Crystal structure determination of **3c**HSe:

Crystal data: $C_{14}H_{16}N_4Se$, M = 319.27, monoclinic, a = 6.8554(3), b = 13.1808(9), c = 15.3404(7) Å, β = 96.866(3)°, U = 1376.21(13) Å^3, space group $P2_1/n$ (no. 14), Z = 4, 8517 reflections measured, 3854 unique (R_{int} = 0.0434), which were used in all calculations. The final $R1$ value was 0.0395 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1011 (all data). CCDC 1939125.

Crystal structure determination of [Ru(**3''c**H)$_2$(PPh$_3$)$_2$]Cl$_2$:

Crystal data: $C_{64}H_{62}Cl_2N_8P_2Ru$, M = 1177.12, orthorhombic, a = 23.5797(4), b = 35.6568(9), c = 29.9355(7) Å, U = 25169.1(10) Å^3, space group $Pbca$ (no. 61), Z = 16, 62293 reflections measured, 23439 unique (R_{int} = 0.1041), which were used in all calculations. The final $R1$ value was 0.0792 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2021 (all data). CCDC 1939126.

Crystal structure determination of [RuCl(**3'a**H)(MeCN)(PPh_3)$_2$]Cl·2 $CHCl_3$:

Crystal data: $C_{51}H_{45}Cl_8N_5P_2Ru$, M = 1174.53, monoclinic, a = 9.5141(5), b = 22.5212(9), c = 12.1912(7) Å), β = 98.997(4)°, U = 2580.1(2) Å^3, space group $P2_1$ (no. 4), Z = 2, 14862 reflections measured, 9591 unique (R_{int} = 0.0573), which were used in all calculations, Flack parameter -0.08(5).The final R1 value was 0.0499 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1238 (all data). CCDC 1939127.

Crystal structure determination of [RuCl(**3''b**H)(MeCN)(PPh_3)$_2$]Cl·C_6H_6:

Crystal data: $C_{57}H_{53}Cl_2N_5P_2Ru$, M = 1041.95, monoclinic, a = 14.1205(4), b = 15.7166(6), c = 22.8944(6) Å, β = 98.417(2)°, U = 5026.1(3) Å^3, space group $P2_1/c$ (no. 14), Z = 4, 20014 reflections measured, 8843 unique (R_{int} = 0.0692), which were used in all calculations. The final R1 value was 0.0872 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2553 (all data). CCDC 1939128.

Crystal structure determination of [NiCp(**3'a**)]:

Crystal data: $C_{16}H_{14}N_4Ni$, M = 321.02, monoclinic, a = 8.3030(6), b = 12.2487(9), c = 13.1031(12) Å, β = 98.019(7)°, U = 1319.57(18) Å^3, space group $P2_1/n$ (no. 14), Z = 4, 6403 reflections measured, 3342 unique (R_{int} = 0.0391), which were used in all calculations. The final R1 value was 0.0381 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1074 (all data). CCDC 1939129.

Crystal structure determination of [NiCp(**3'b**)]:

Crystal data: $C_{18}H_{18}N_4Ni$, M = 349.07, monoclinic, a = 15.4397(4), b = 13.0180(2), c = 15.7193(4) Å, β = 100.060(2)°, U = 3110.91(12) Å^3, space group $P2_1/c$ (no. 14), Z = 8, 14051 reflections measured, 5650 unique (R_{int} = 0.0188), which were used in all calculations. The final R1 value was 0.0281 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.0653 (all data). CCDC 1939130.

Crystal structure determination of [NiCp(**3'c**)]:

Crystal data: $C_{19}H_{20}N_4Ni$, M = 363.10, orthorhombic, a = 9.5555(2), b = 24.2364(7), c = 21.3888(6) Å, U = 4953.5(2) Å^3, space group *Pnma* (no. 62), Z = 12, 20251 reflections measured, 4733 unique (R_{int} = 0.0593), which were used in all calculations. The final R1 value was 0.0403 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.1201 (all data). CCDC 1939131.

Crystal structure determination of [RhCl(COD){NiCp(μ-**3'a**)}]:

Crystal data: $C_{24}H_{26}ClN_4NiRh$, M = 567.56, triclinic, a = 7.1632(7), b = 13.0691(12), c = 13.5288(14) Å, α = 117.501(7), β = 95.030(8), γ = 100.470(8)°, U = 1083.1(2) Å^3, space group P-1 (no. 2), Z = 2, 7900 reflections measured, 4024 unique (R_{int} = 0.0723), which were used in all calculations. The final R1 value was 0.0779 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2236 (all data). CCDC 1939132.

Crystal structure determination of [RhCl(COD){NiCp(μ-**3'b**)}]·CH_2Cl_2:

Crystal data: $C_{27}H_{32}Cl_3N_4NiRh$, M = 680.53, monoclinic, a = 11.3628(4), b = 21.1456(7), c = 12.1342(5) Å, β = 109.851(3)°, U = 2742.3(2) Å^3, space group $P2_1/n$ (no. 14), Z = 4, 13276 reflections measured, 4981 unique (R_{int} = 0.0720), which were used in all calculations. The final R1 value was 0.0935 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.2686 (all data). CCDC 1939133.

Crystal structure determination of [RhCl(COD){NiCp(μ-**3'c**)}]:

Crystal data: $C_{27}H_{32}ClN_4NiRh$, M = 609.63, tetragonal, a = 34.3321(4), b = 34.3321(4), c = 10.30900(10) Å, U = 12151.1(3) Å^3, space group $P4/n$ (no. 85), Z = 16, 47405 reflections measured, 11145 unique (R_{int} = 0.0291), which were used in all calculations. The final R1 value was 0.0375 ($I > 2\sigma(I)$) and the final w$R(F^2)$ was 0.0916 (all data). CCDC 1939134.

Crystal structure determination of [CuBr{NiCp(μ-**3a'**)}]:

Crystal data: $C_{16}H_{14}BrCuN_4Ni$, M = 464.47, triclinic, a = 8.8137(6), b = 9.8816(7), c = 10.4045(7) Å, α = 116.637(5), β = 102.468(6), γ = 93.764(6)°, U = 777.07(10) Å^3, space group P-1 (no. 2), Z = 2, 9092 reflections measured, 3044 unique (R_{int} = 0.0723), which were used in all calculations. The final R1 value was 0.0229 ($I > 2\sigma(I)$) and the final wR(F^2) was 0.0514 (all data). CCDC 1939135.

Crystal structure determination of [CuBr{NiCp(μ-**3b'**)}]:

Crystal data: $C_{36}H_{36}Br_2Cu_2N_8Ni_2$, M = 985.05, monoclinic, a = 9.5888(12), b = 20.771(2), c = 9.4041(12) Å, β = 112.364(9)°, U = 1732.1(4) Å^3, space group $P2_1/c$ (no. 14), Z = 2, 6735 reflections measured, 3164 unique (R_{int} = 0.0643), which were used in all calculations. The final R1 value was 0.1025 ($I > 2\sigma(I)$) and the final wR(F^2) was 0.3287 (all data). CCDC 1939136.

Crystal structure determination of [CuBr{NiCp(μ-**3c'**)}]:

Crystal data: $C_{38}H_{40}Br_2Cu_2N_8Ni_2$, M = 1013.10, monoclinic, a = 9.6279(5), b = 21.6105(13), c = 9.4506(5) Å, β = 112.988(4)°, U = 1810.2(2) Å^3, space group $P2_1/c$ (no. 14), Z = 2, 7273 reflections measured, 3381 unique (R_{int} = 0.0431), which were used in all calculations. The final R1 value was 0.0586 ($I > 2\sigma(I)$) and the final wR(F^2) was 0.1729 (all data). CCDC 1939137.

Crystal structure determination of [ZnI_2{NiCp(μ-**3'a**)}$_2$]:

Crystal data: $C_{32}H_{28}I_2N_8Ni_2Zn$, M = 961.21, orthorhombic, a = 17.7226(7), b = 16.5686(5), c = 21.4449(7) Å, U = 6297.1(4) Å^3, space group $Pbca$ (no. 61), Z = 8, 15493 reflections measured, 6010 unique (R_{int} = 0.0384), which were used in all calculations. The final R1 value was 0.0497 ($I > 2\sigma(I)$) and the final wR(F^2) was 0.1328 (all data). CCDC 1939138.

Crystal structure determination of [ZnI_2{NiCp(μ-**3'b**)}$_2$]·CH_2Cl_2:

Crystal data: $C_{37}H_{38}Cl_2I_2N_8Ni_2Zn$, M = 1102.24, orthorhombic, a = 20.5758(7), b = 17.6627(8), c = 11.0017(4) Å, U = 3998.3(3) Å^3, space group $Pna2_1$ (no. 64), Z = 4, 27223 reflections measured, 4797 unique (R_{int} = 0.0352), which were used in all calculations. Flack parameter 0.009(16) inversion twin. The final R1 value was 0.0883 ($I > 2\sigma(I)$) and the final wR(F^2) was 0.2592 (all data). CCDC 1939139.

Crystal structure determination of [ZnI_2{NiCp(μ-**3'c**)}$_2$]·CH_2Cl_2:

Crystal data: $C_{39}H_{42}Cl_2I_2N_8Ni_2Zn$, M = 1130.29, monoclinic, a = 9 13.0554(7), b = 13.5100(5), c = 23.7059(11) Å, β = 101.001(4)°, U = 4104.4(3) Å^3, space group $P2_1/c$ (no. 14), Z = 4, 18157 reflections measured, 8820 unique (R_{int} = 0.0714), which were used in all calculations. The final R1 value was 0.0603 ($I > 2\sigma(I)$) and the final wR(F^2) was 0.1656 (all data). CCDC 1939140.

2. Additional Molecular Structures in the Crystal (ORTEP Plots, 30% probability ellipsoids)

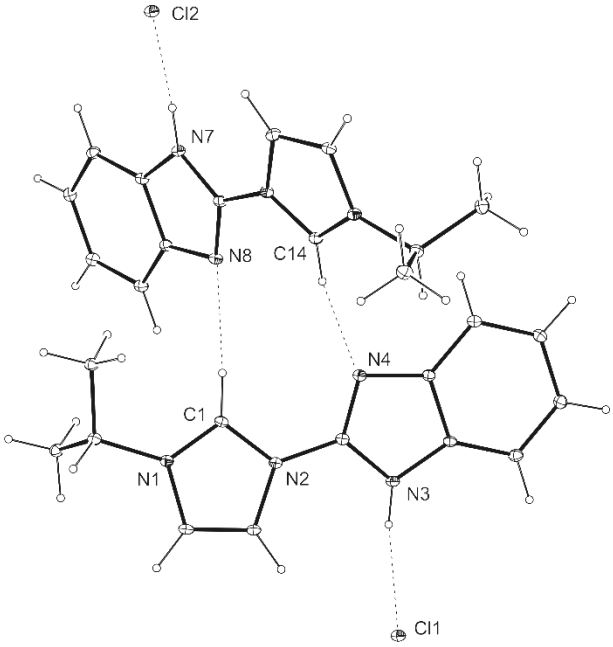

Fig. S1 Molecular structure of **3b**H_2Cl in the crystal.

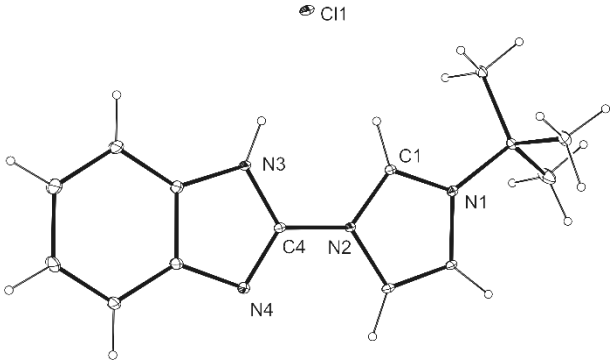

Fig. S2 Molecular structure of **3c**H_2Cl in the crystal.

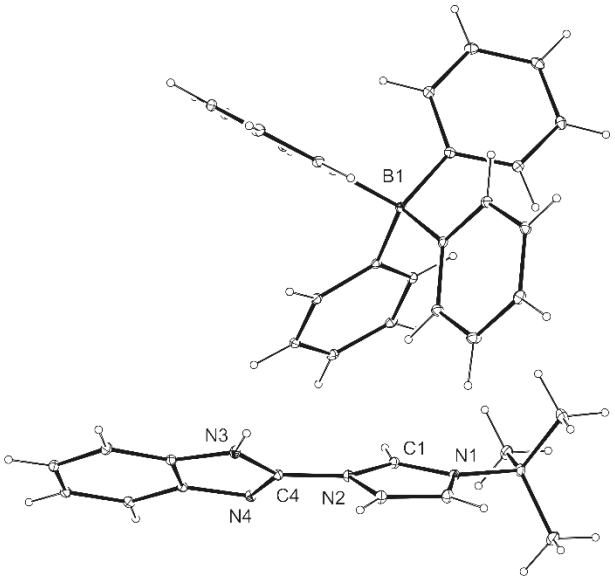

Fig. S3 Molecular structure of **3c**H_2[BPh_4] in the crystal.

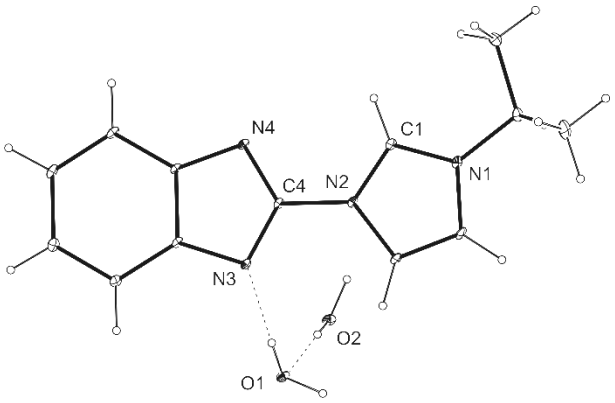

Fig. S4 Molecular structure of **3b**H·2 H_2O in the crystal.

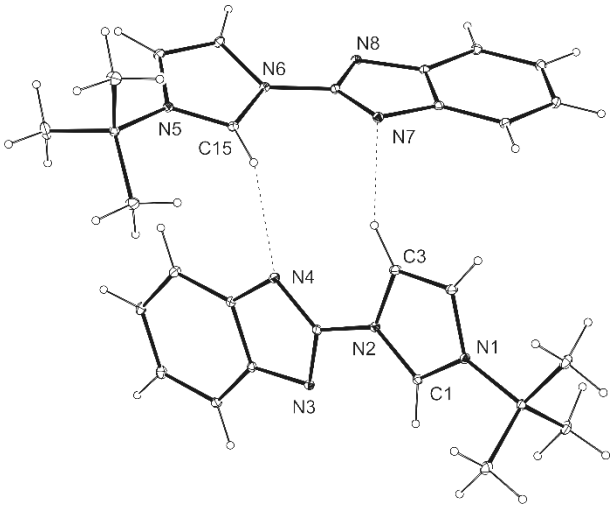

Fig. S5 Molecular structure of **3c**H in the crystal.

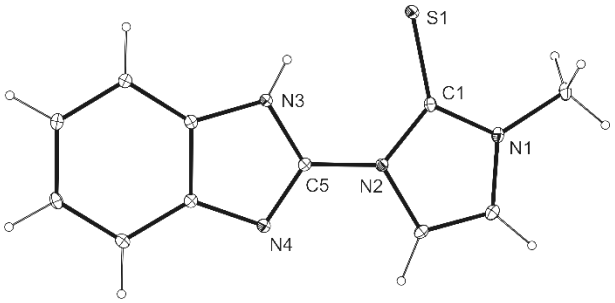

Fig. S6 Molecular structure of **3a**HS in the crystal.

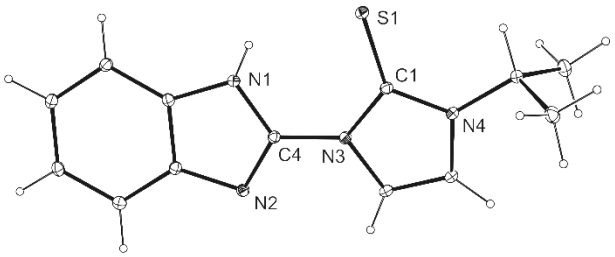

Fig. S7 Molecular structure of **3b**HS in the crystal.

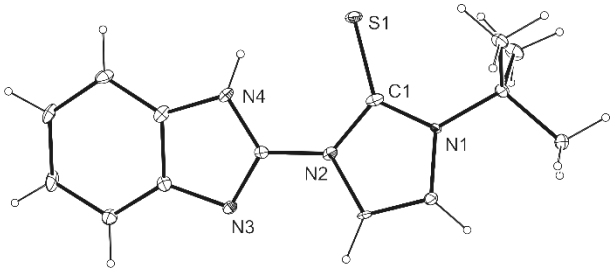

Fig. S8 Molecular structure of **3c**HS in the crystal.

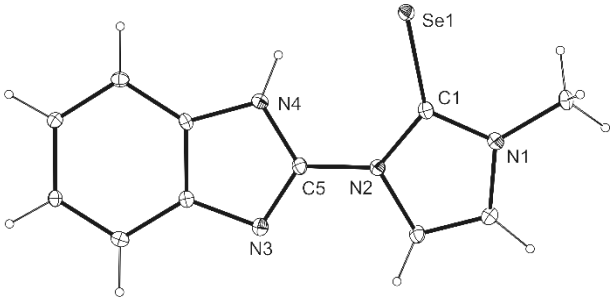

Fig. S9 Molecular structure of **3a**HSe in the crystal.

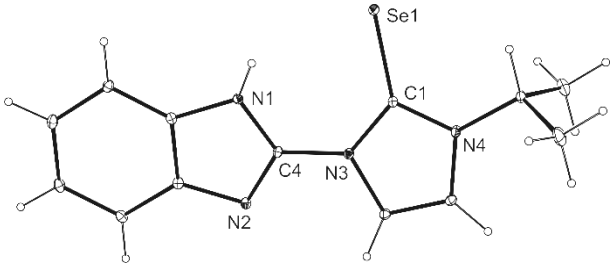

Fig. S10 Molecular structure of **3b**HSe in the crystal.

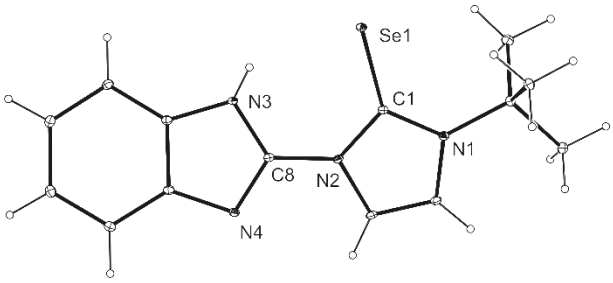

Fig. S11 Molecular structure of **3c**HSe in the crystal.

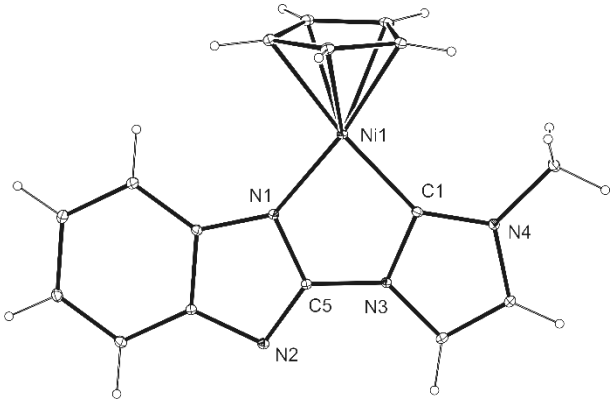

Fig. S12 Molecular structure of [NiCp(**3'a**)] in the crystal.

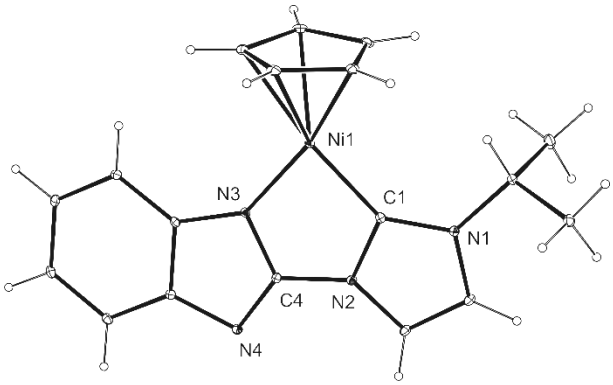

Fig. S13 Molecular structure of [NiCp(**3'b**)] in the crystal.

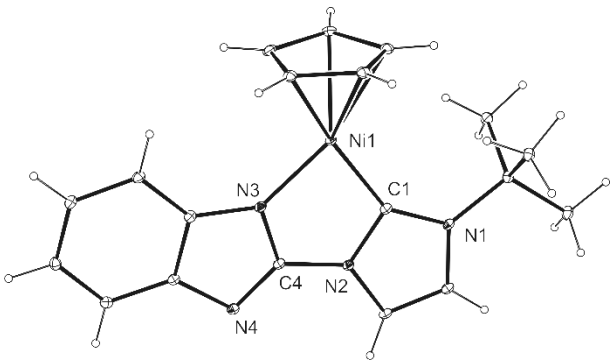

Fig. S14 Molecular structure of [NiCp(**3'c**)] in the crystal.

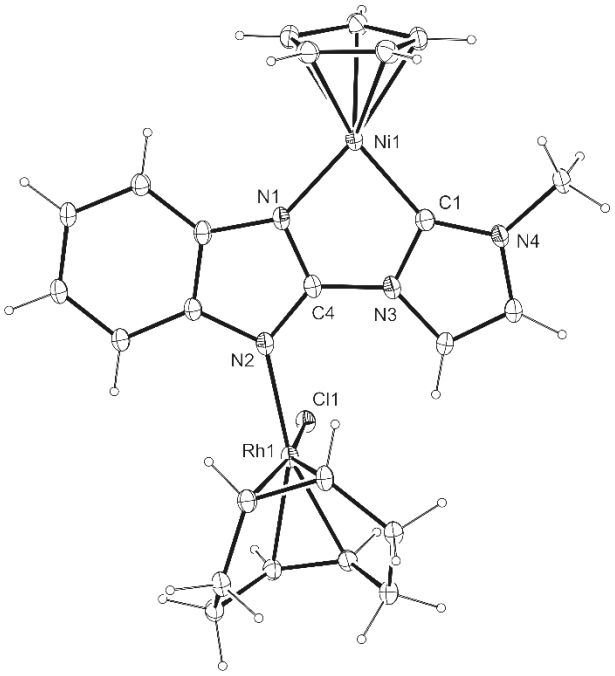

Fig. S15 Molecular structure of [RhCl(COD){NiCp(μ-**3'a**)}] in the crystal.

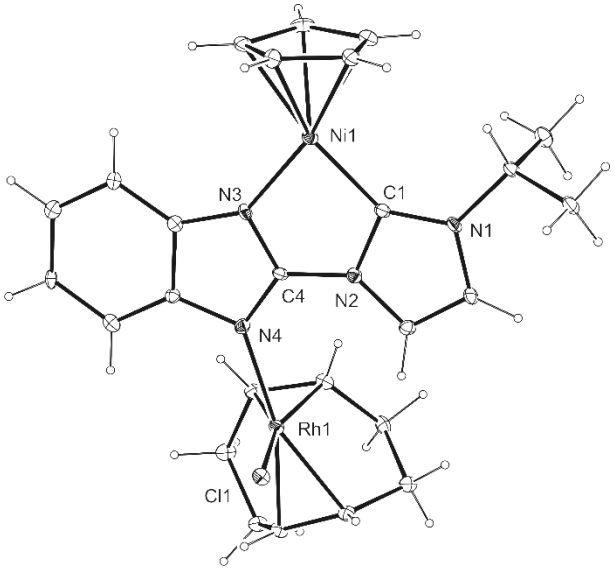

Fig. S16 Molecular structure of [RhCl(COD){NiCp(μ-**3'b**)}] in the crystal.

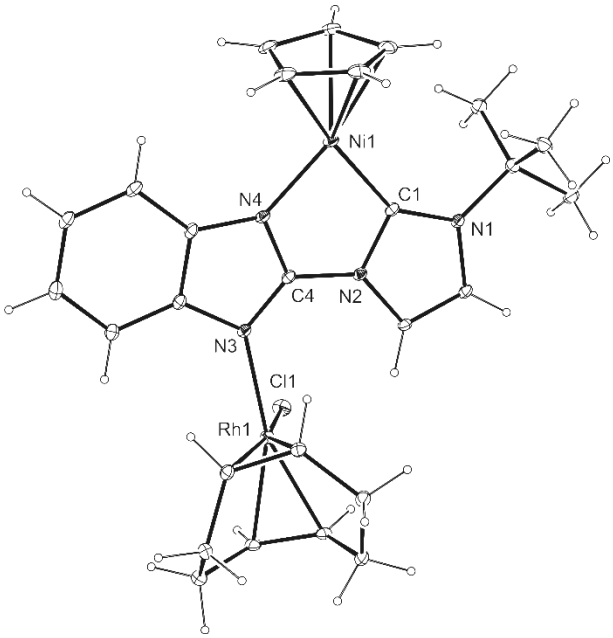

Fig. S17 Molecular structure of [RhCl(COD){NiCp(μ-**3'c**)}] in the crystal.

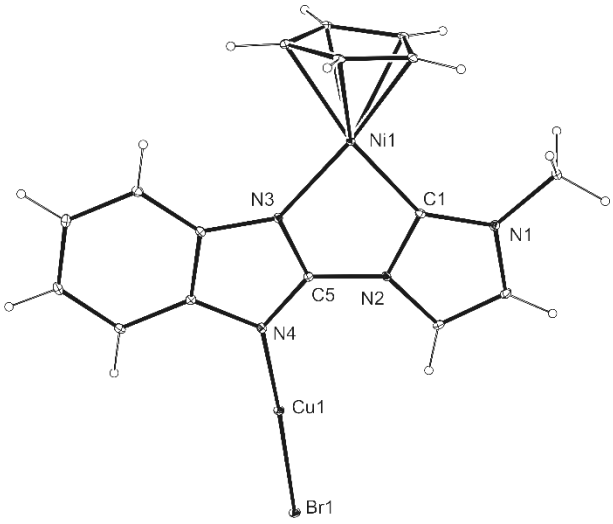

Fig. S18 Molecular structure of [CuBr{NiCp(μ-**3a'**)}] in the crystal.

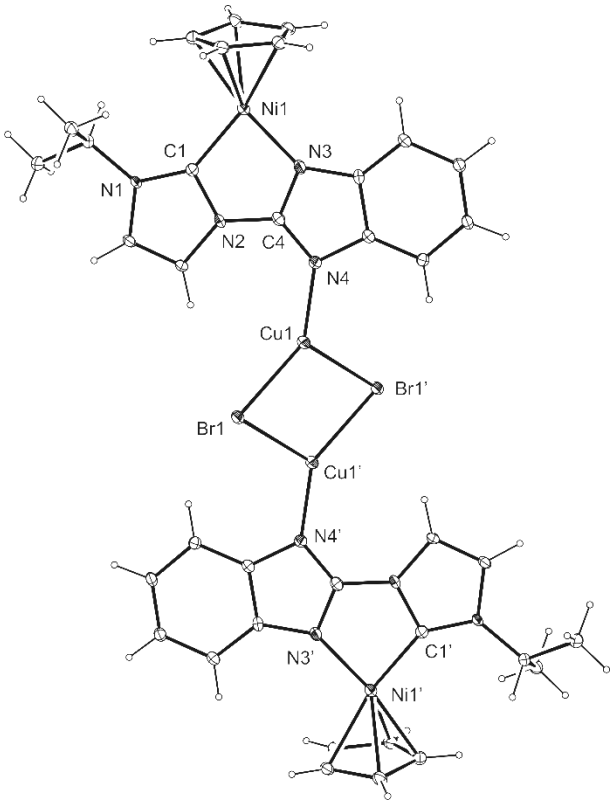

Fig. S19 Molecular structure of [Cu(μ-Br){NiCp(μ-**3b'**)}]$_2$ in the crystal.

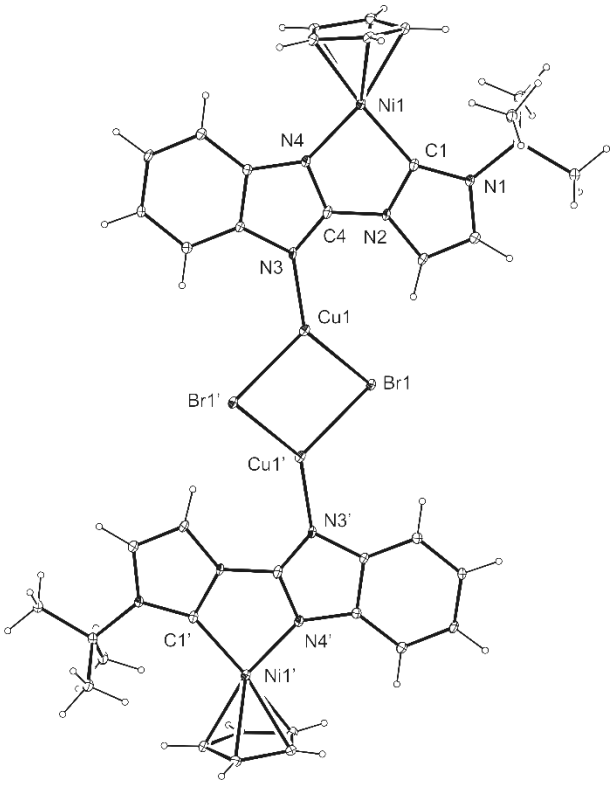

Fig. S20 Molecular structure of [Cu(μ-Br){NiCp(μ-**3c'**)}]$_2$ in the crystal.

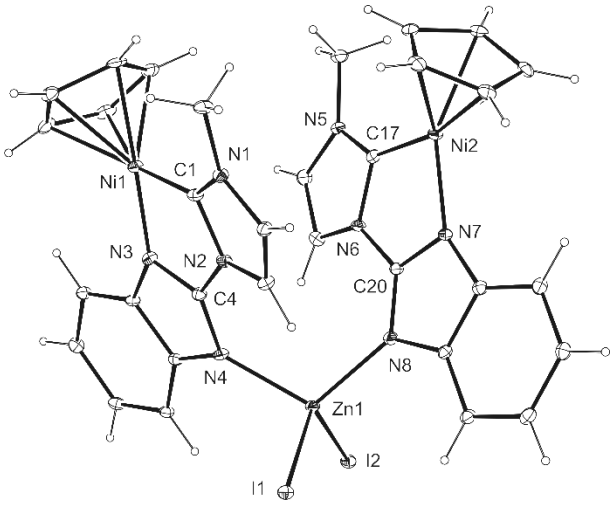

Fig. S21 Molecular structure of $[ZnI_2\{NiCp(\mu\text{-}\mathbf{3'a})\}_2]$ in the crystal.

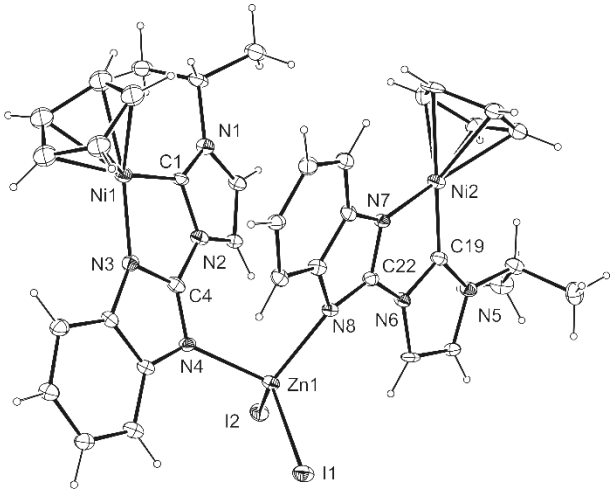

Fig. S22 Molecular structure of $[ZnI_2\{NiCp(\mu\text{-}\mathbf{3'b})\}_2]$ in the crystal.

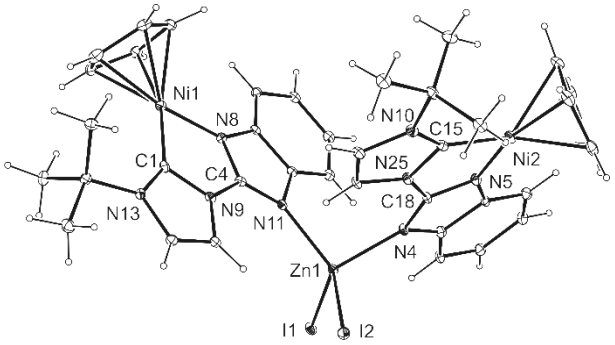

Fig. S23 Molecular structure of $[ZnI_2\{NiCp(\mu\text{-}\mathbf{3'c})\}_2]$ in the crystal.

3. Plots of NMR Spectra

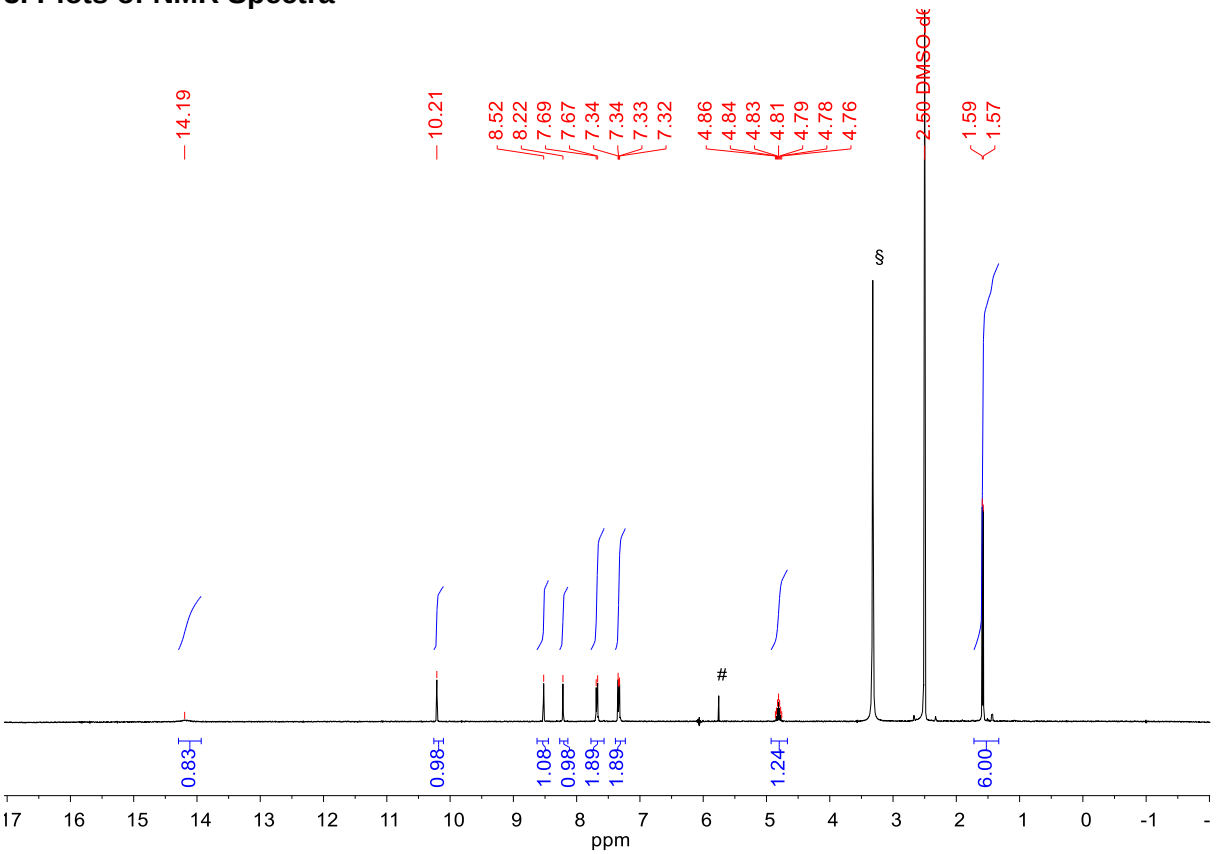

Fig. S24 ^{1}H NMR spectrum of **3b**H_2Cl (DMSO-d_6, 400 MHz). Signals marked belong to dichloromethane (#) and water (§).

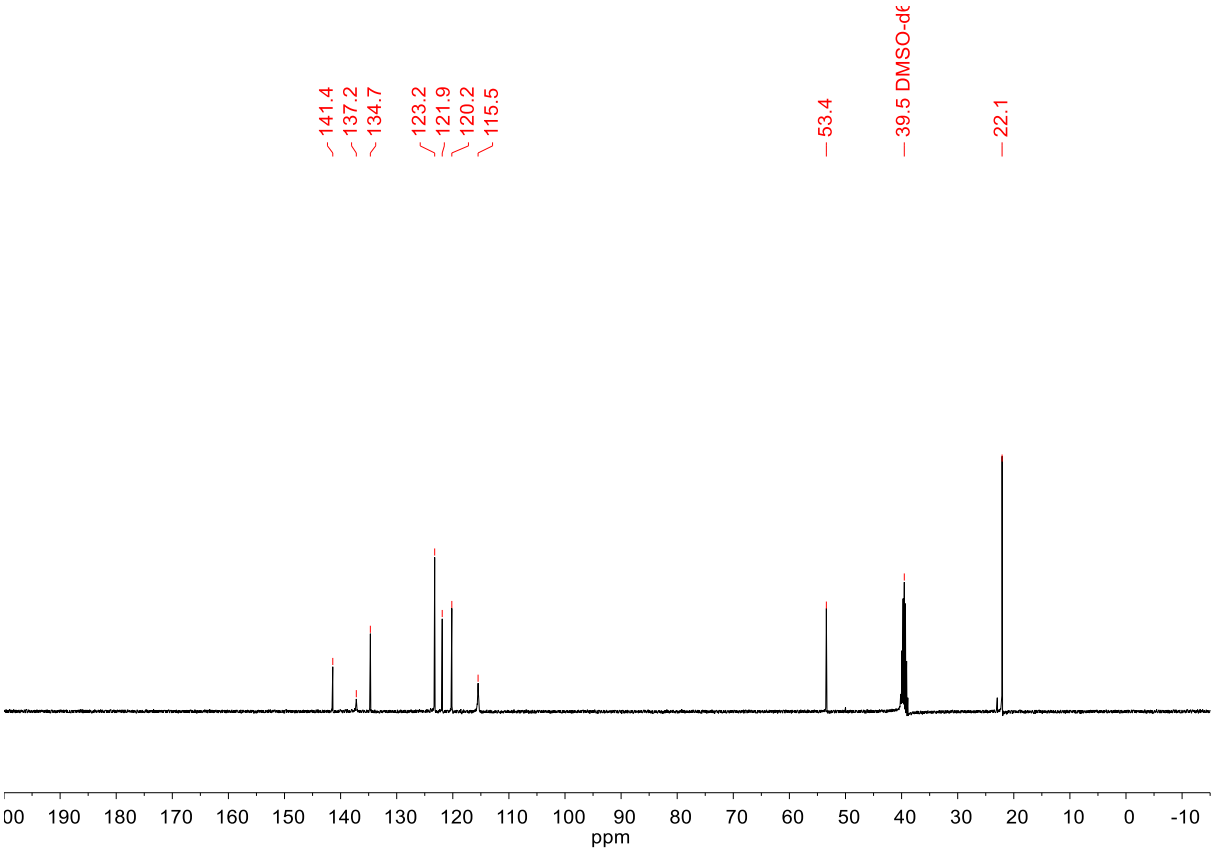

Fig. S25 ^{13}C NMR spectrum of **3b**H_2Cl. (DMSO-d_6, 101 MHz).

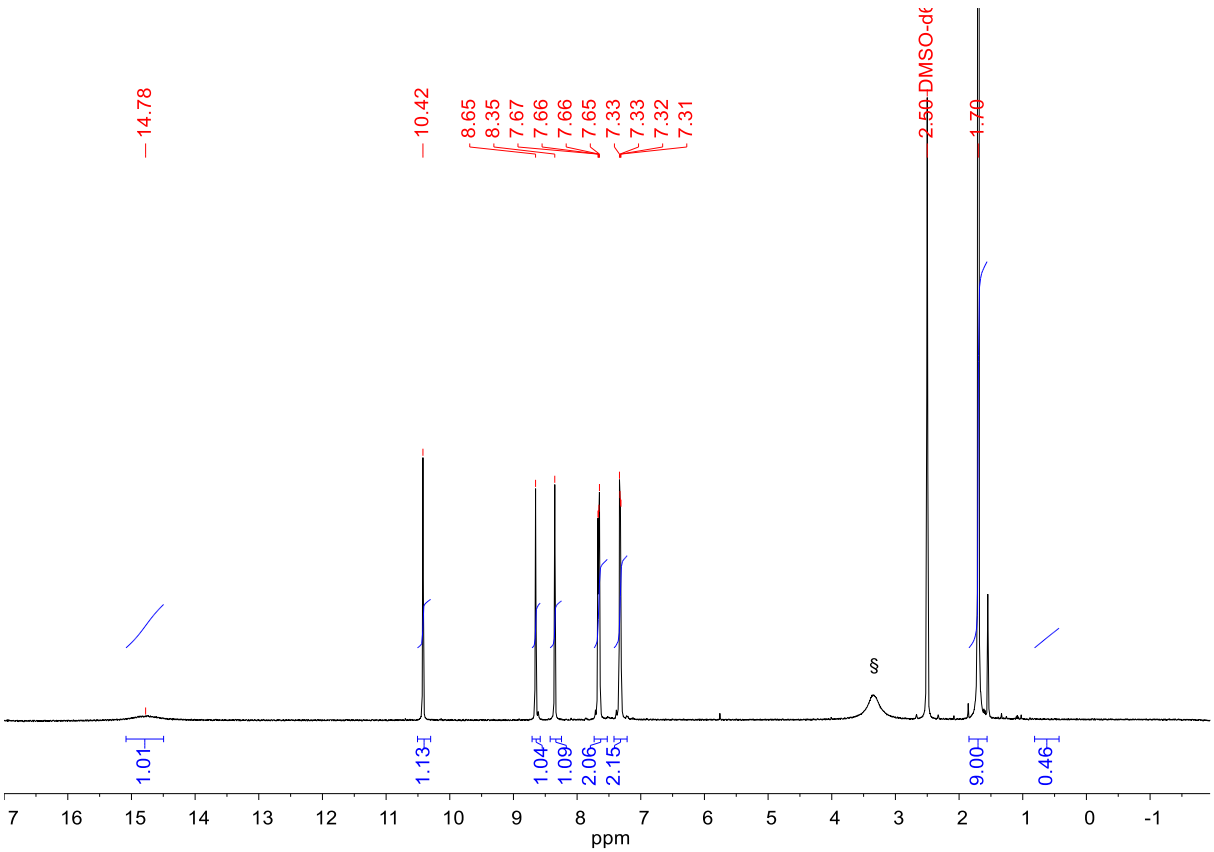

Fig. S26 ^{1}H NMR spectrum of **3c**H_2Cl (DMSO-d_6, 400 MHz). The Signal marked belongs to water (§).

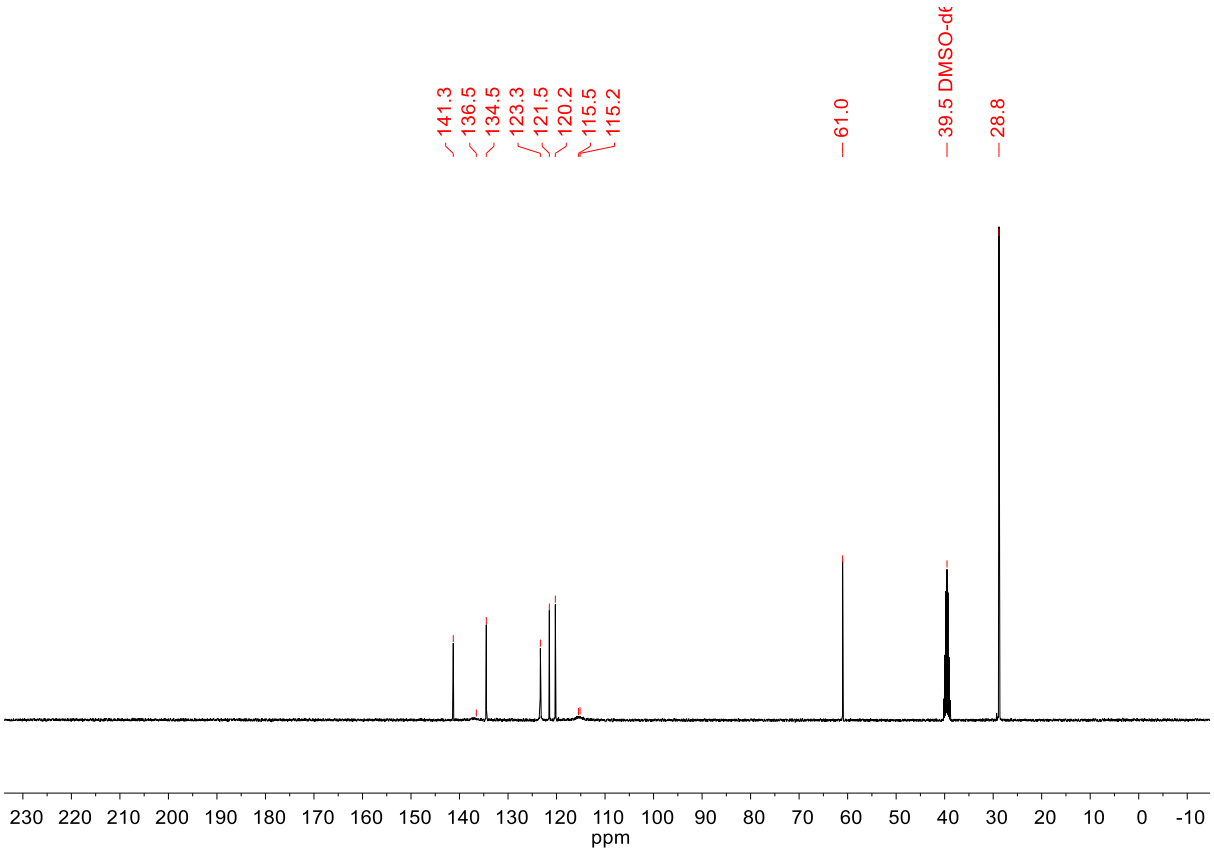

Fig. S27 ^{13}C NMR spectrum of **3c**H_2Cl. (DMSO-d_6, 101 MHz).

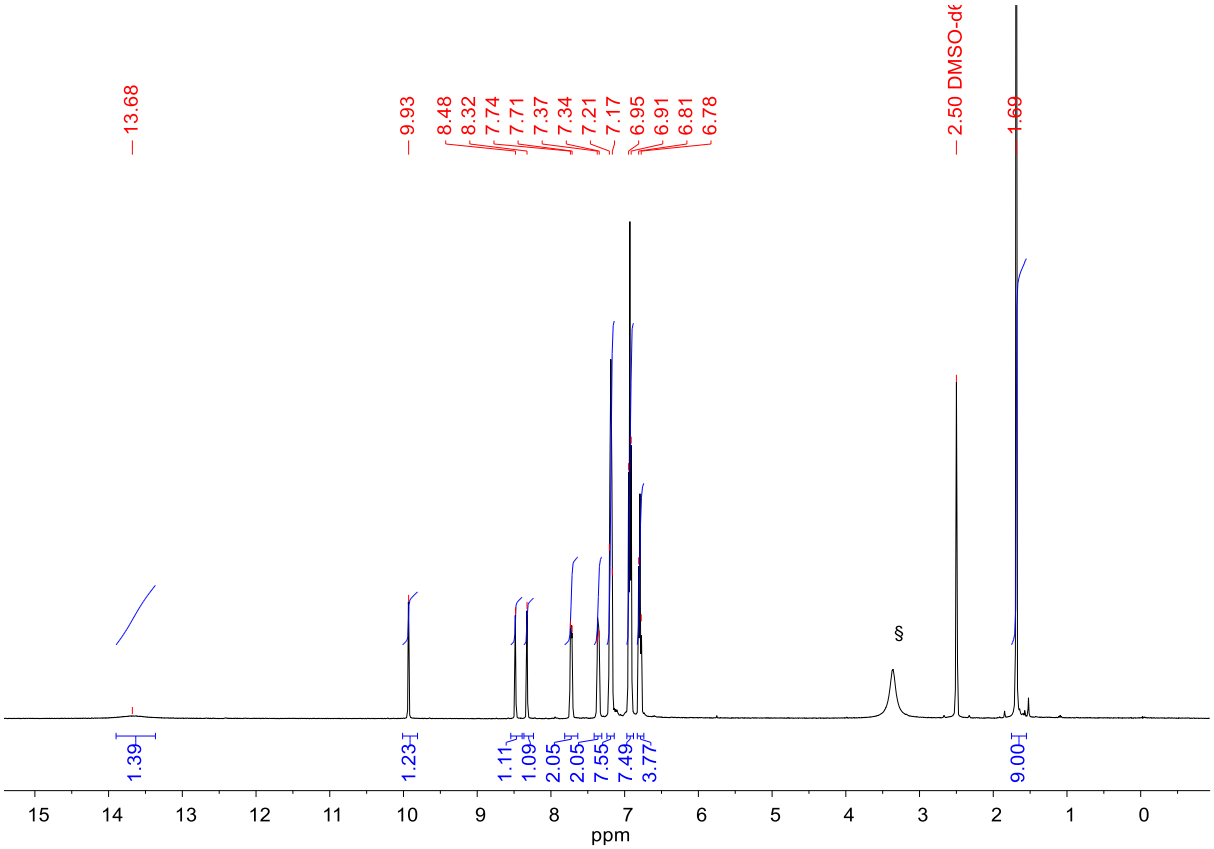

Fig. S28 ^{1}H NMR spectrum of **3c**H_2[BPh_4] (DMSO-d_6, 400 MHz). The signal marked belongs to water (§).

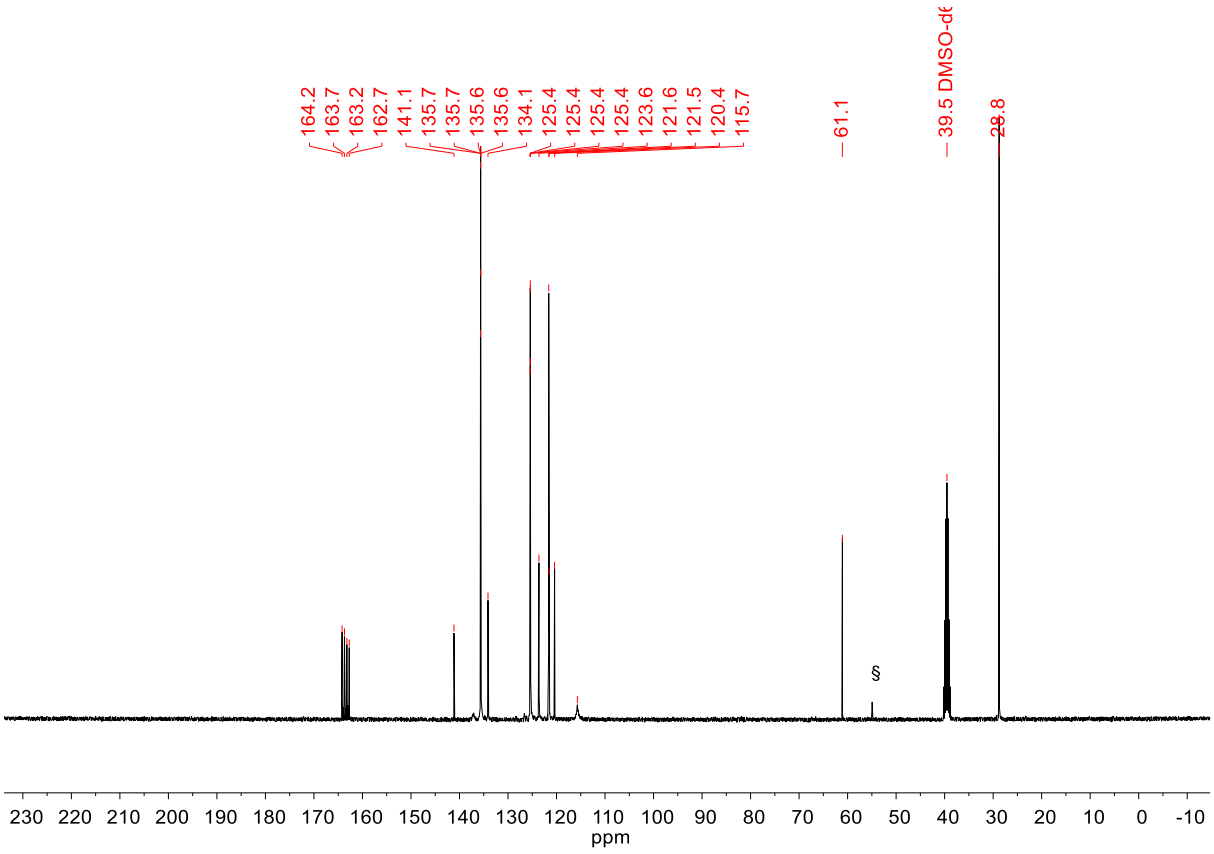

Fig. S29 ^{13}C NMR spectrum of **3c**H_2[BPh_4] (DMSO-d_6, 101 MHz). The signal marked belongs to Et_2O (§).

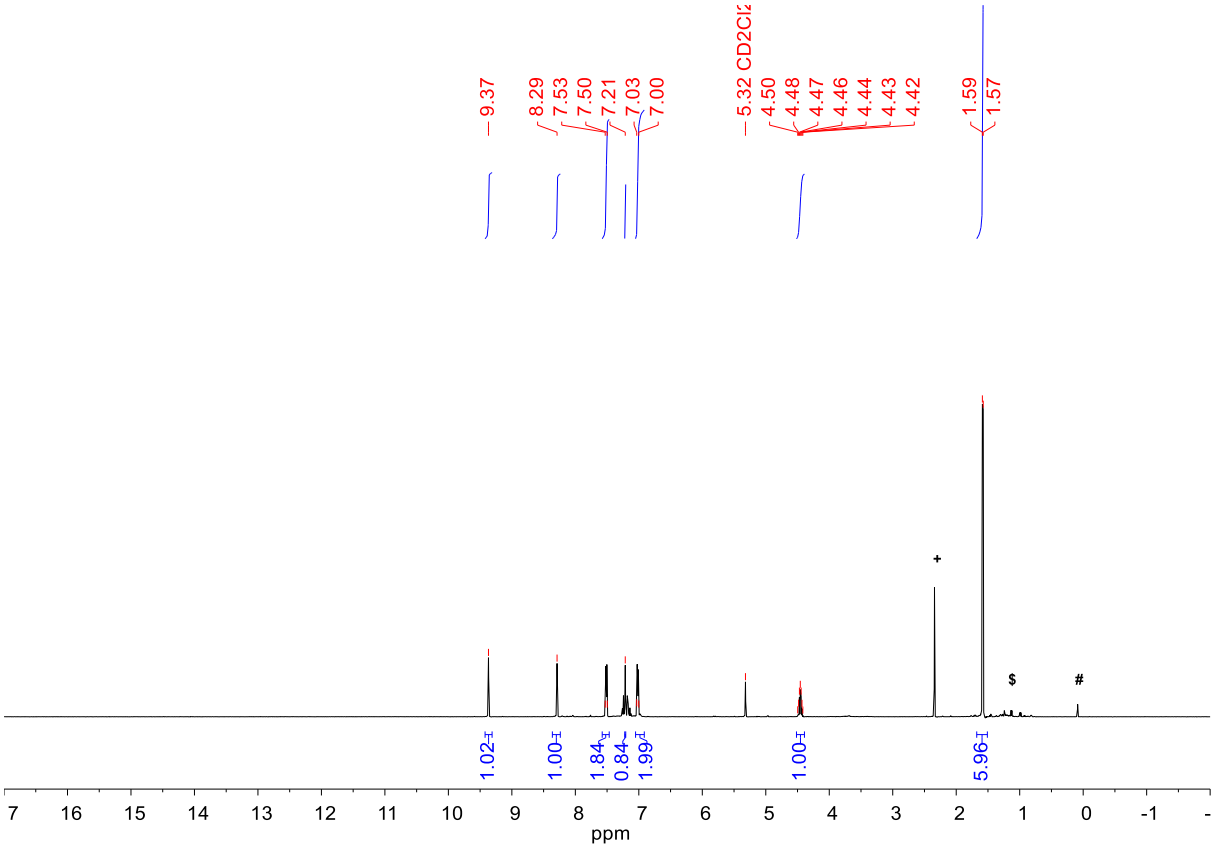

Fig. S30 ^{1}H NMR spectrum of **3b**H (CD_2Cl_2, 400 MHz). Signals marked belong to toluene (+), an unknown impurity ($) and silicone grease (#).

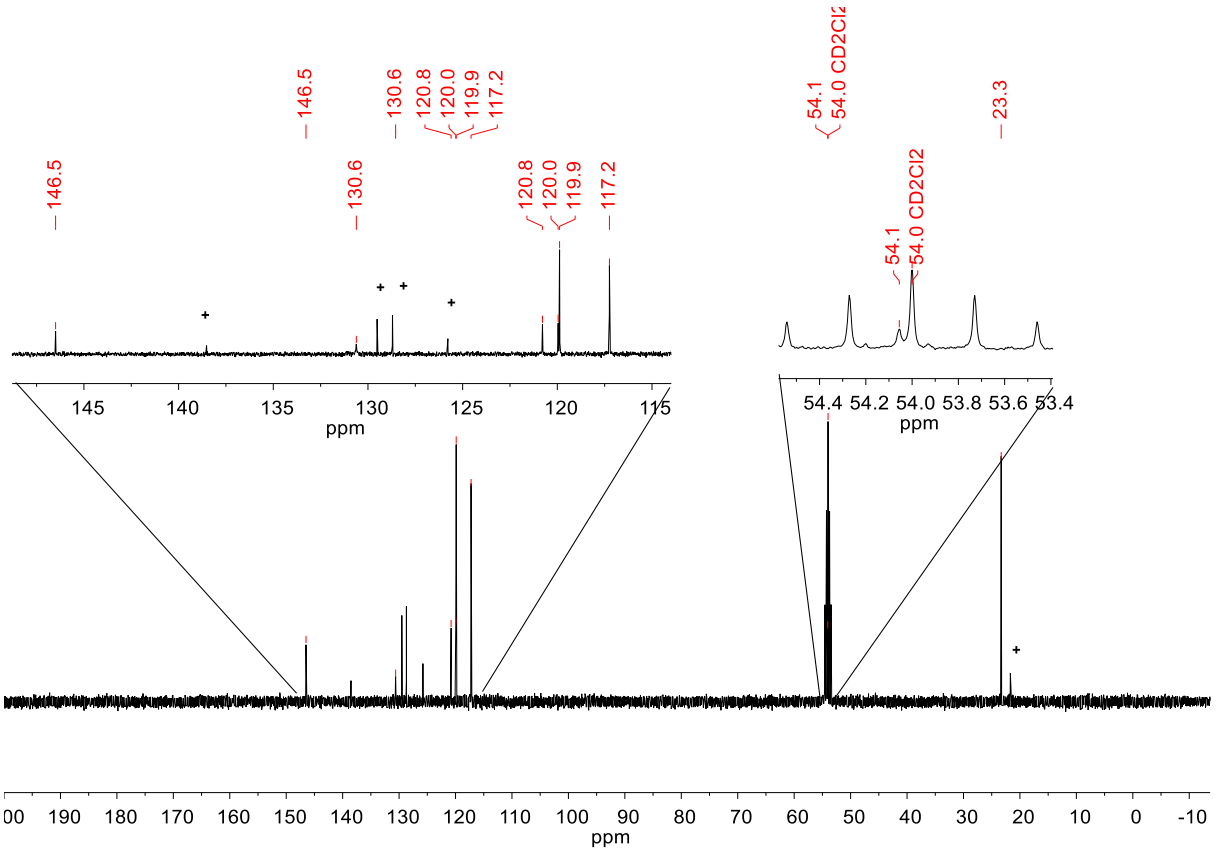

Fig. S31 ^{13}C NMR spectrum of **3b**H (CD_2Cl_2, 101 MHz). Signals marked belong to toluene (+).

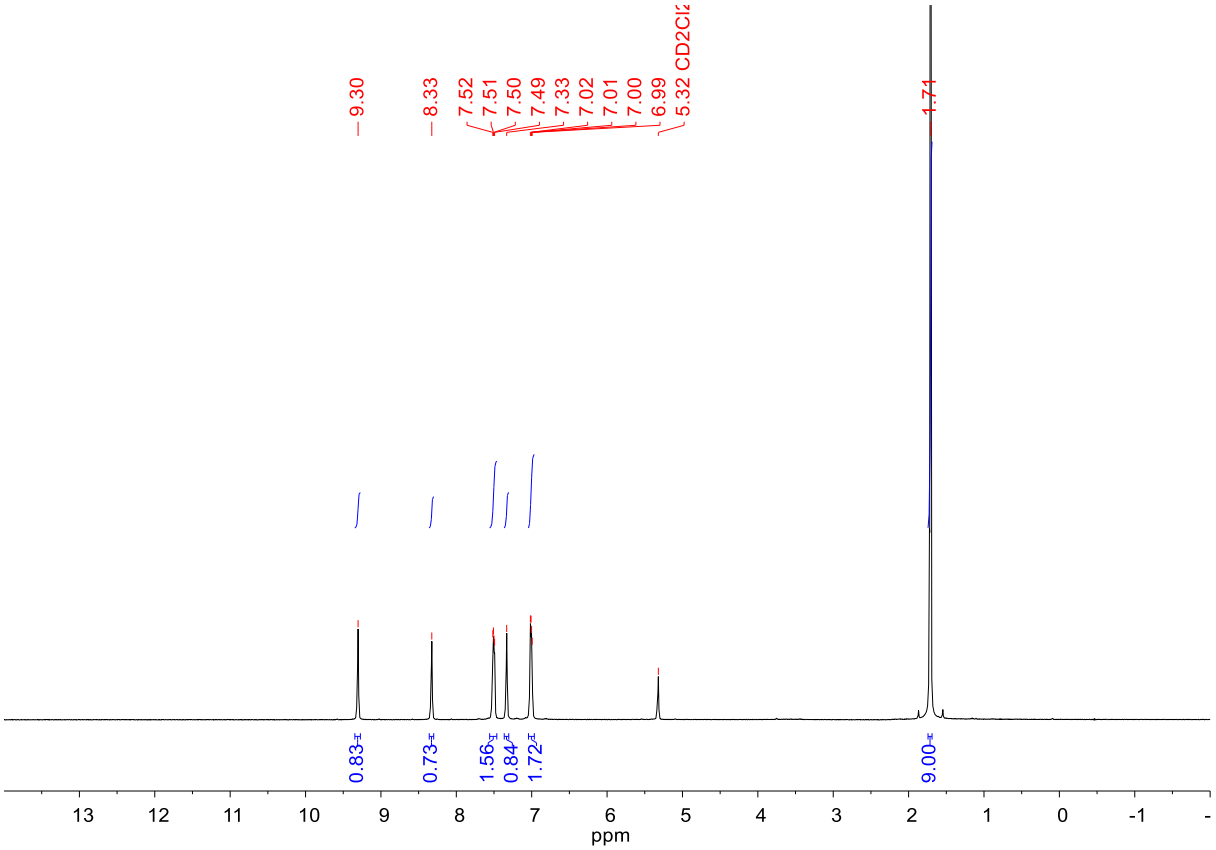

Fig. S32 ^{1}H NMR spectrum of **3c**H (CD_2Cl_2, 400 MHz).

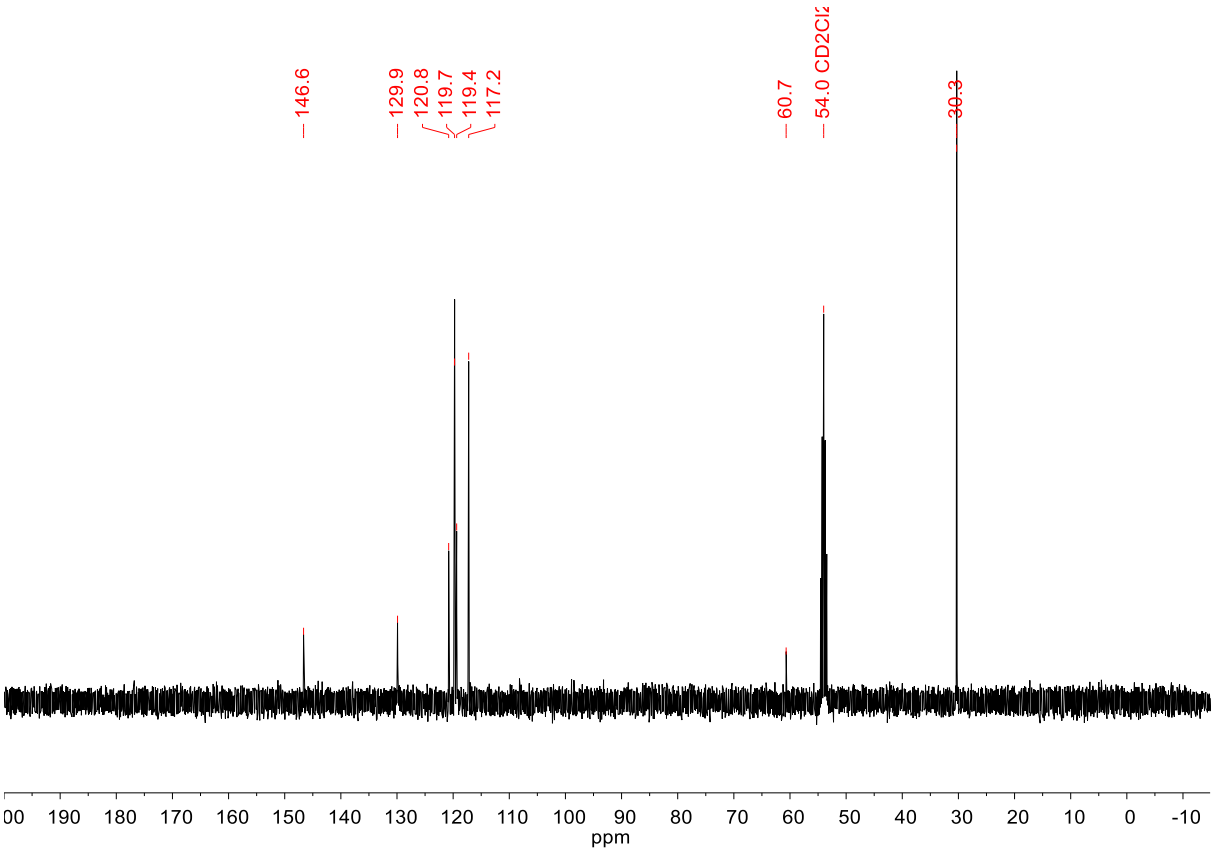

Fig. S33 ^{13}C NMR spectrum of **3c**H (CD_2Cl_2, 101 MHz).

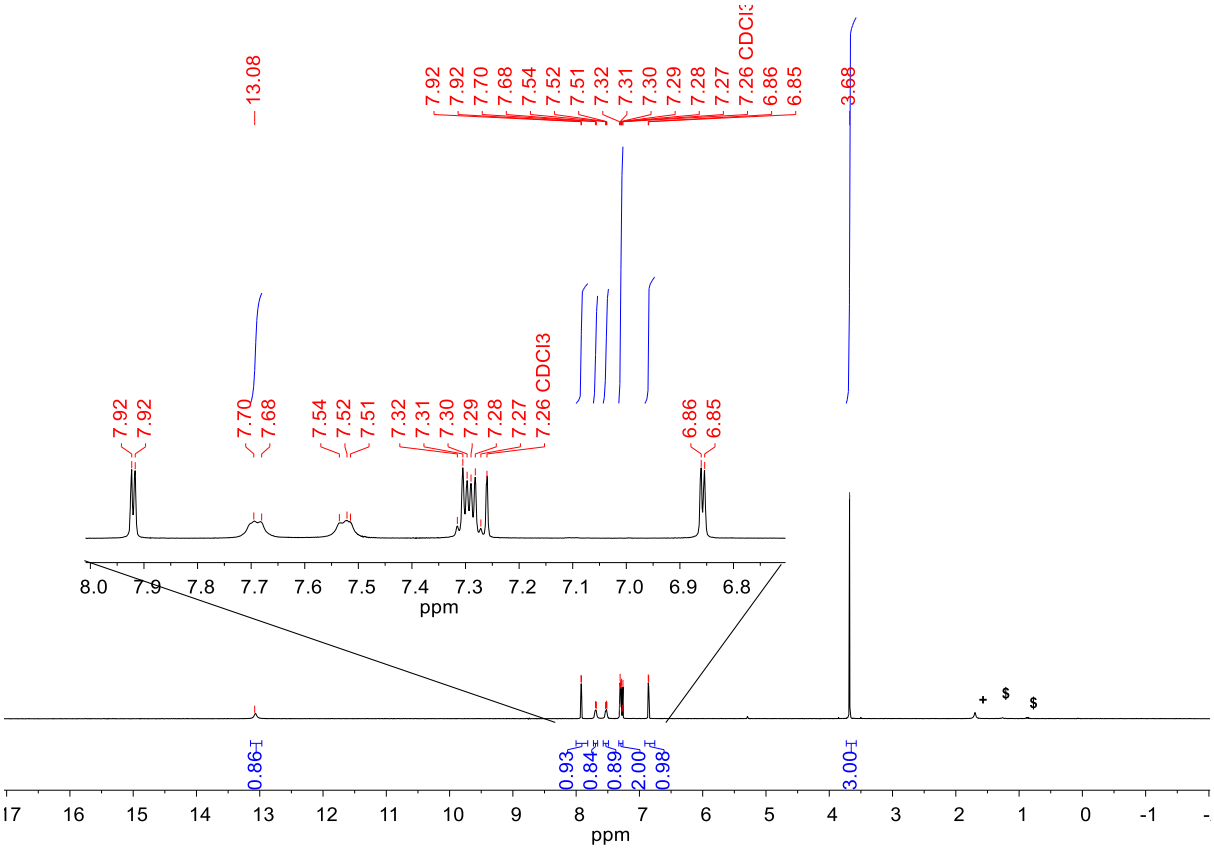

Fig. S34 ^{1}H NMR spectrum of **3a**HS ($CDCl_3$, 400 MHz). Signals marked belong to an unknown impurity (+) and H grease ($).

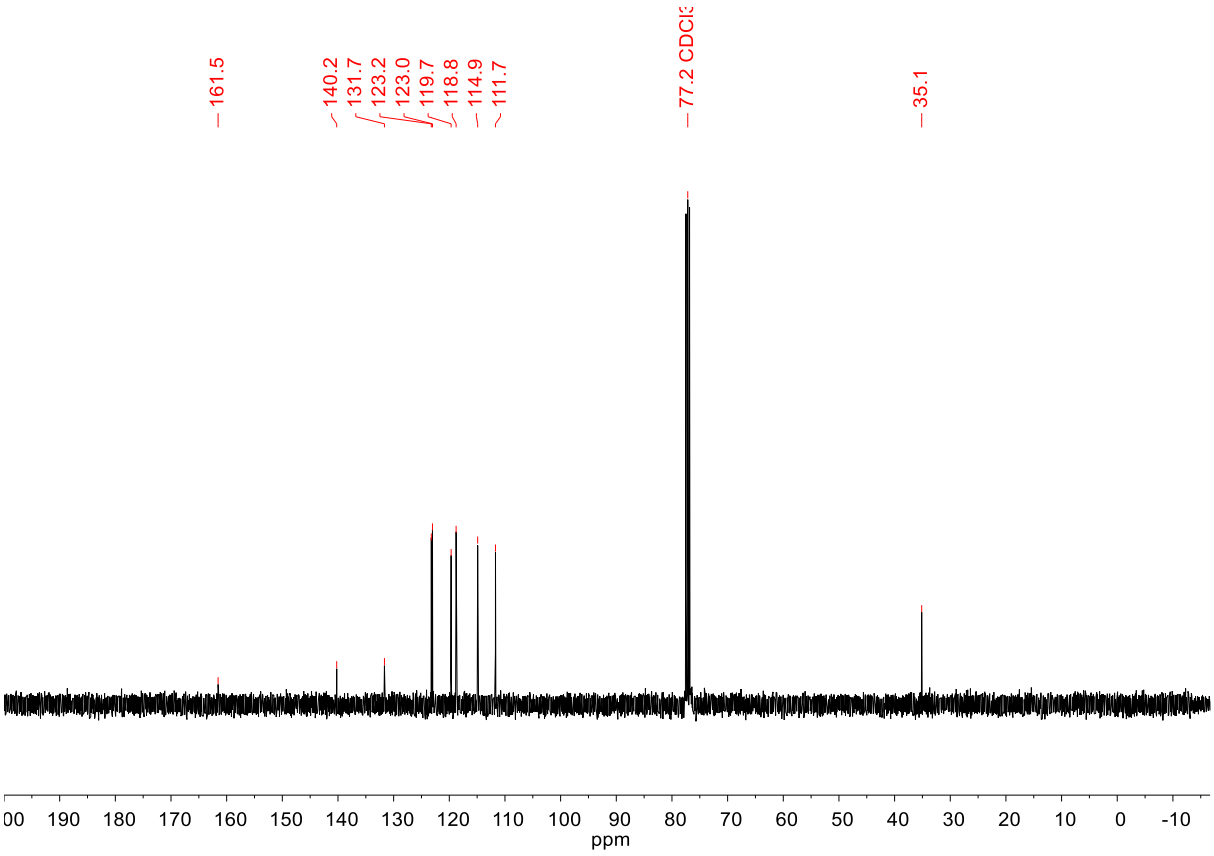

Fig. S35 ^{13}C NMR spectrum of **3a**HS ($CDCl_3$, 101 MHz).

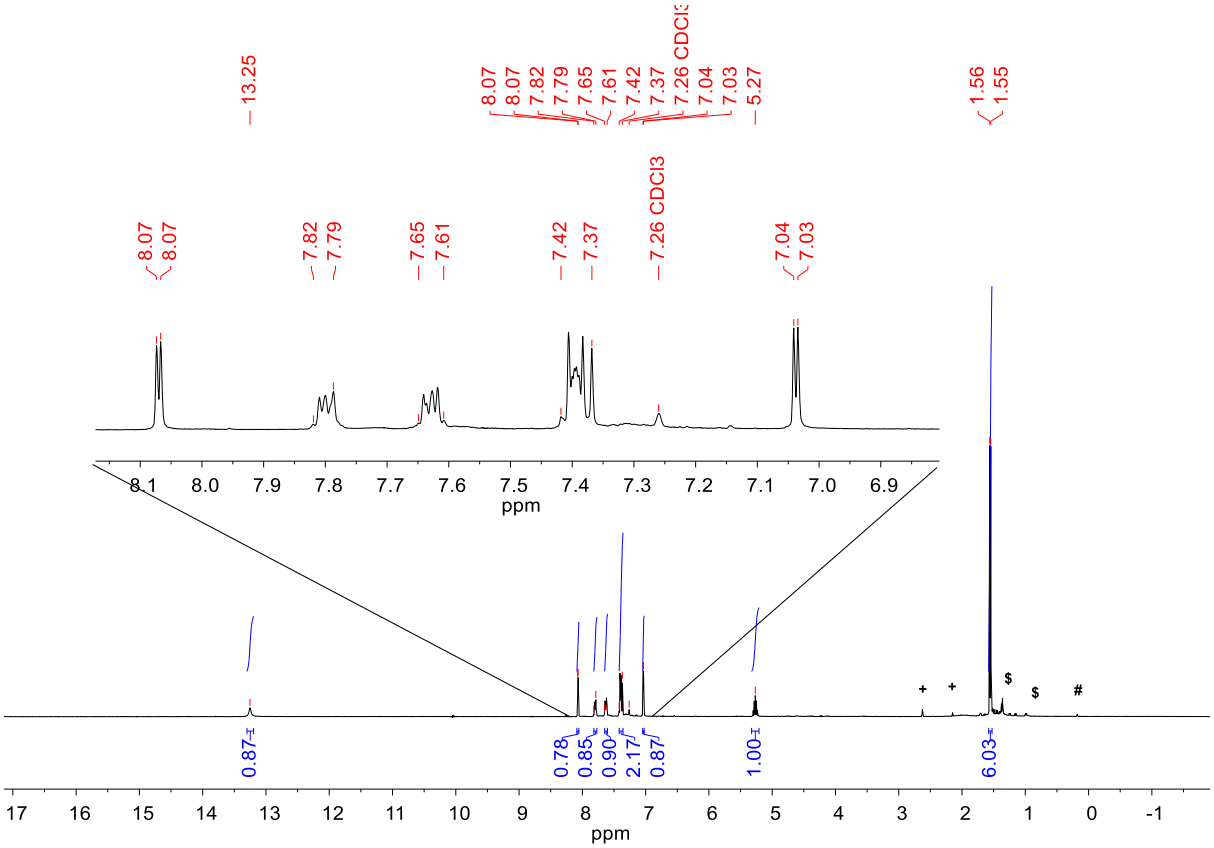

Fig. S36 ^{1}H NMR spectrum of **3b**HS ($CDCl_3$, 400 MHz). Signals marked belong to an unknown impurity (+), H grease ($) and silicone grease (#).

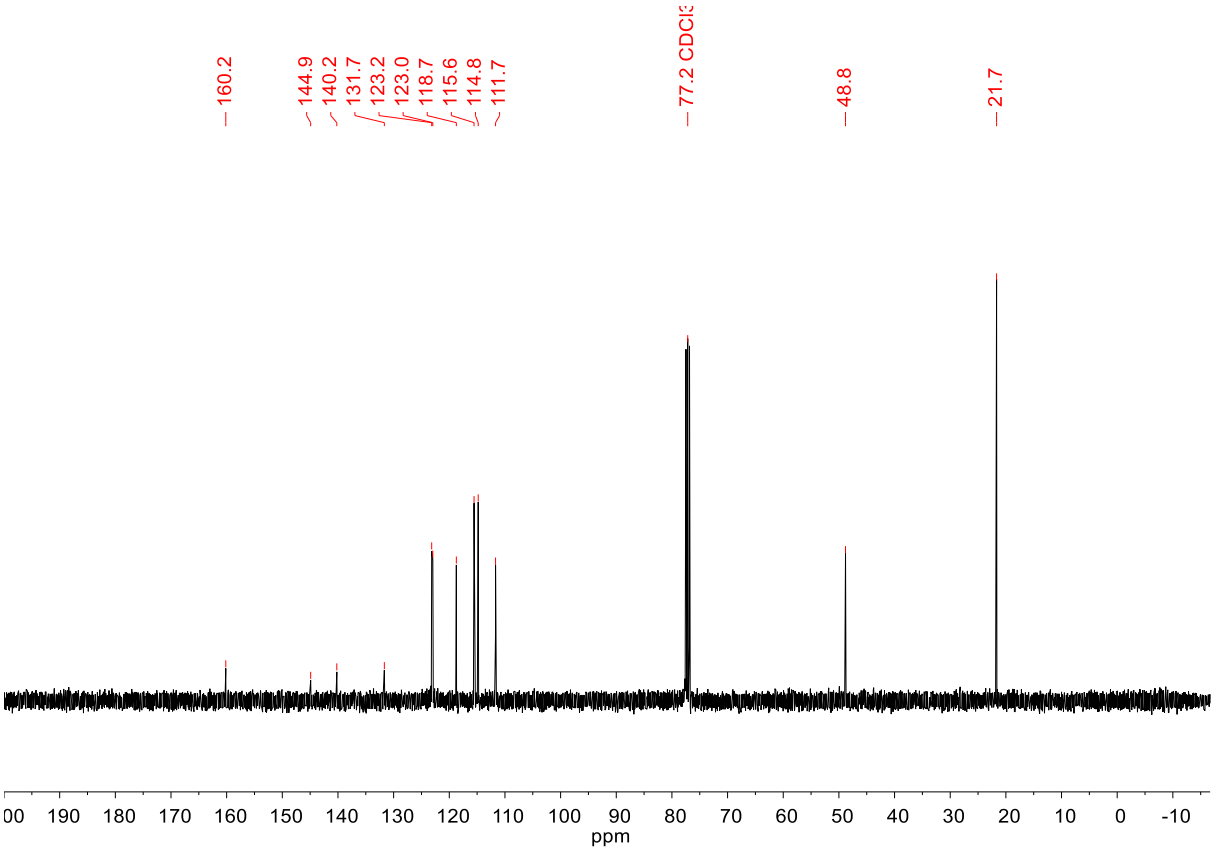

Fig. S37 ^{13}C NMR spectrum of **3b**HS ($CDCl_3$, 101 MHz).

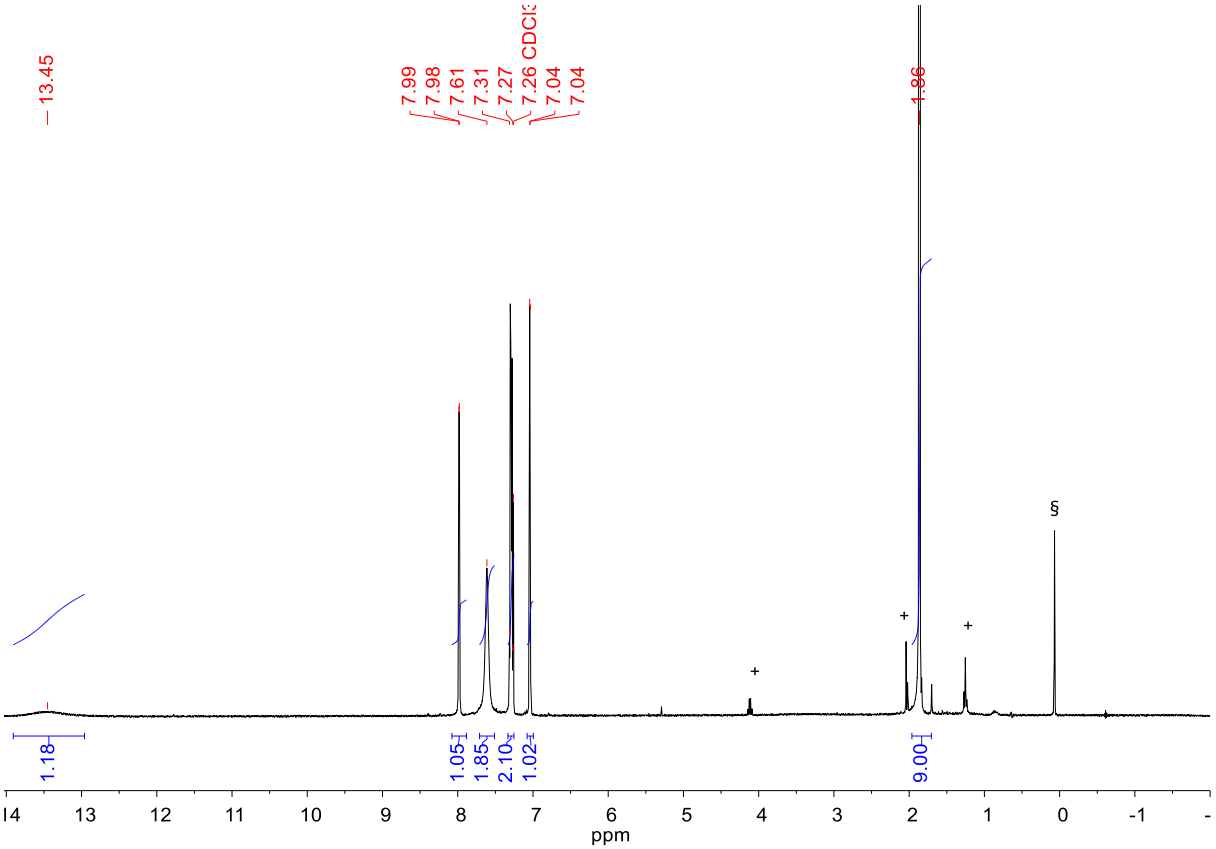

Fig. S38 ^{1}H NMR spectrum of **3c**HS ($CDCl_3$, 400 MHz). Signals marked belong to ethyl acetate (+) and silicone grease (§).

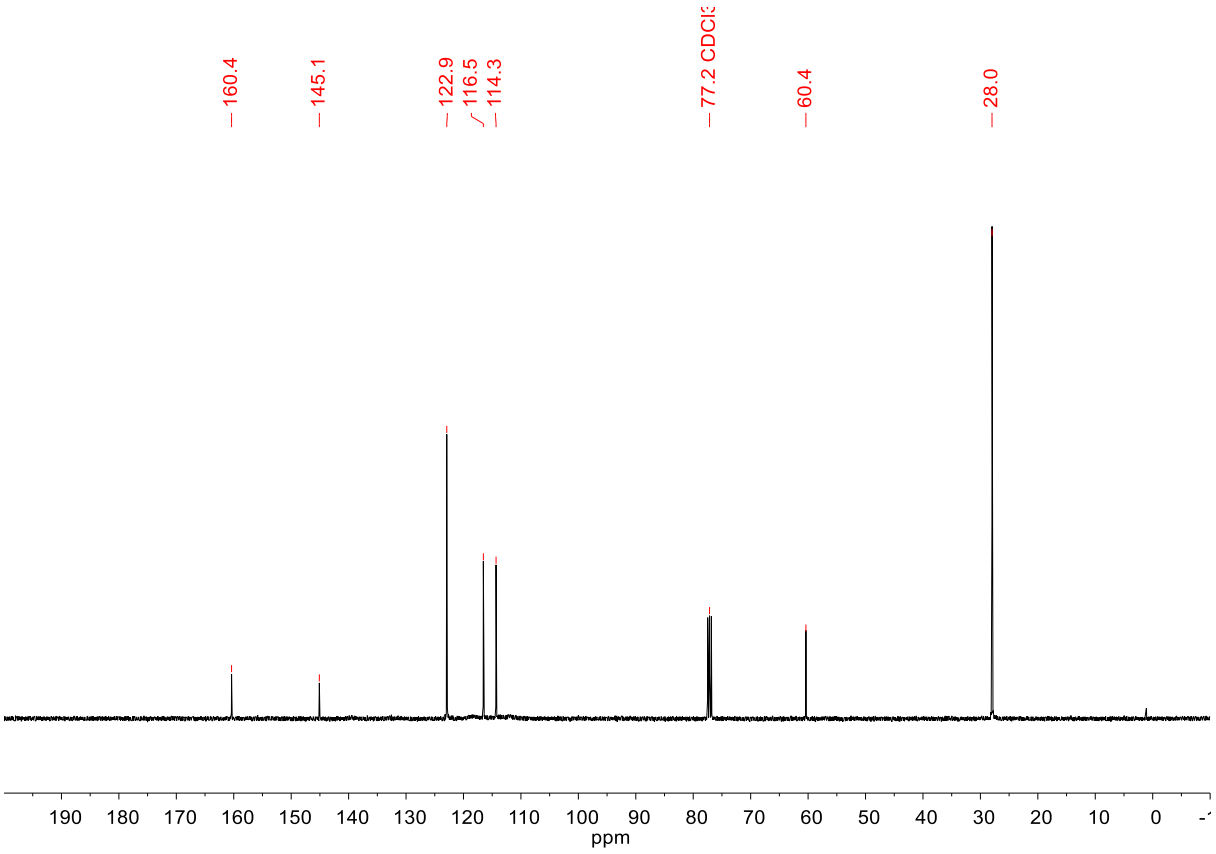

Fig. S39 ^{13}C NMR spectrum of **3c**HS ($CDCl_3$, 101 MHz).

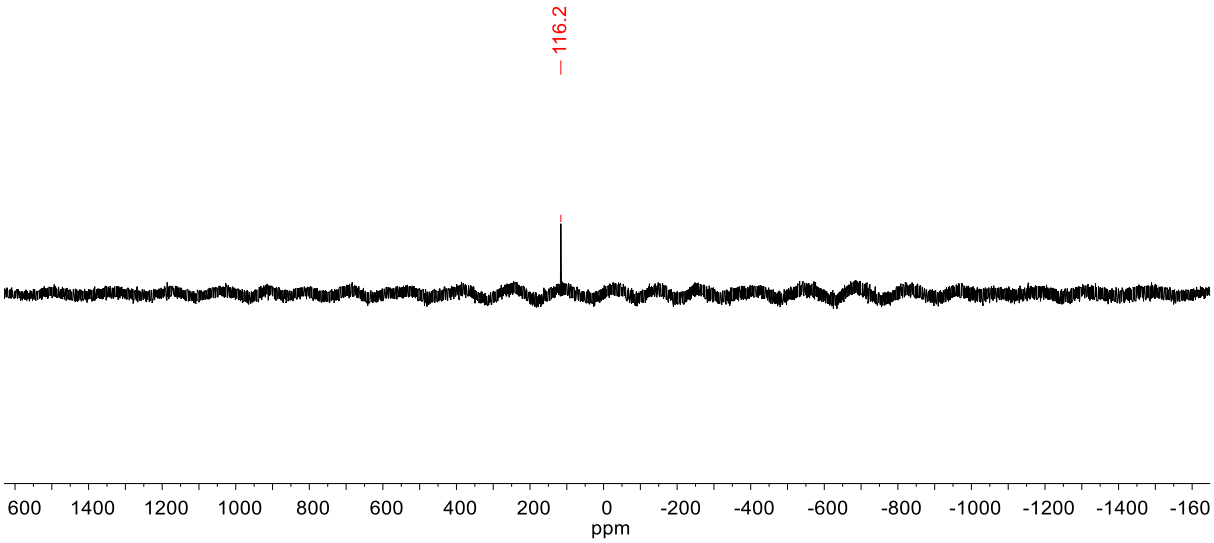

Fig. S40 ^{77}Se NMR spectrum of **3a**HSe ($CDCl_3$, 95 MHz).

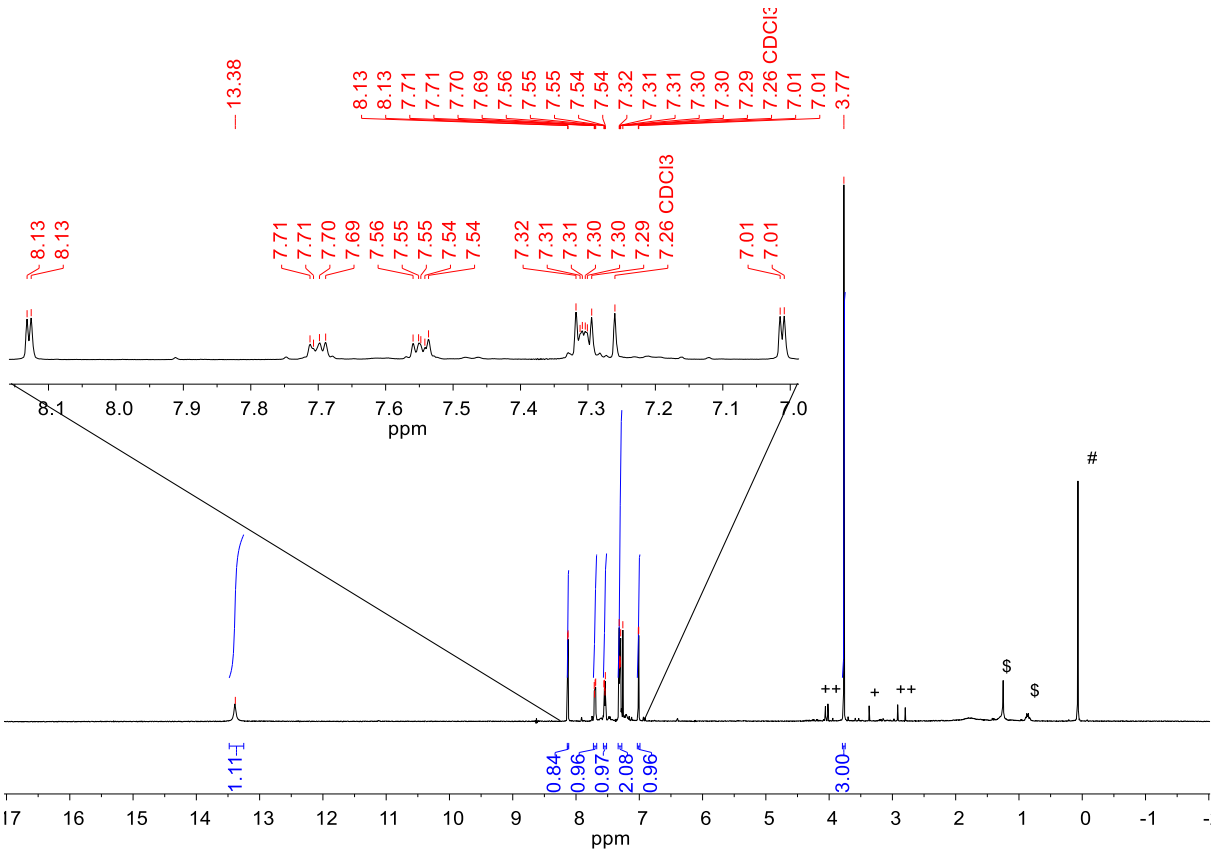

Fig. S41 ^{1}H NMR spectrum of **3a**HSe ($CDCl_3$, 400 MHz). Signals marked belong to an unknown impurity (+), H grease ($) and silicone grease (#).

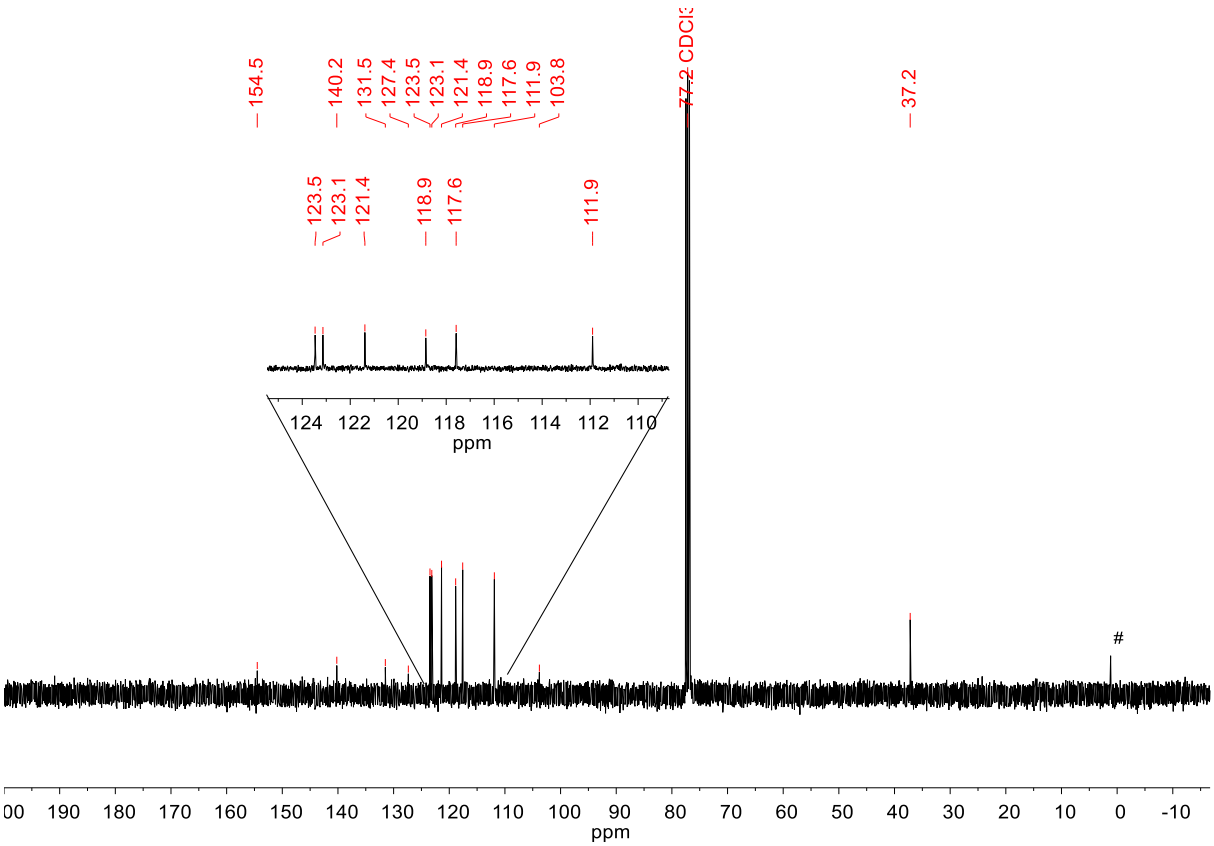

Fig. S42 ^{13}C NMR spectrum of **3a**HSe ($CDCl_3$, 101 MHz). The signal marked belongs to silicone grease (#).

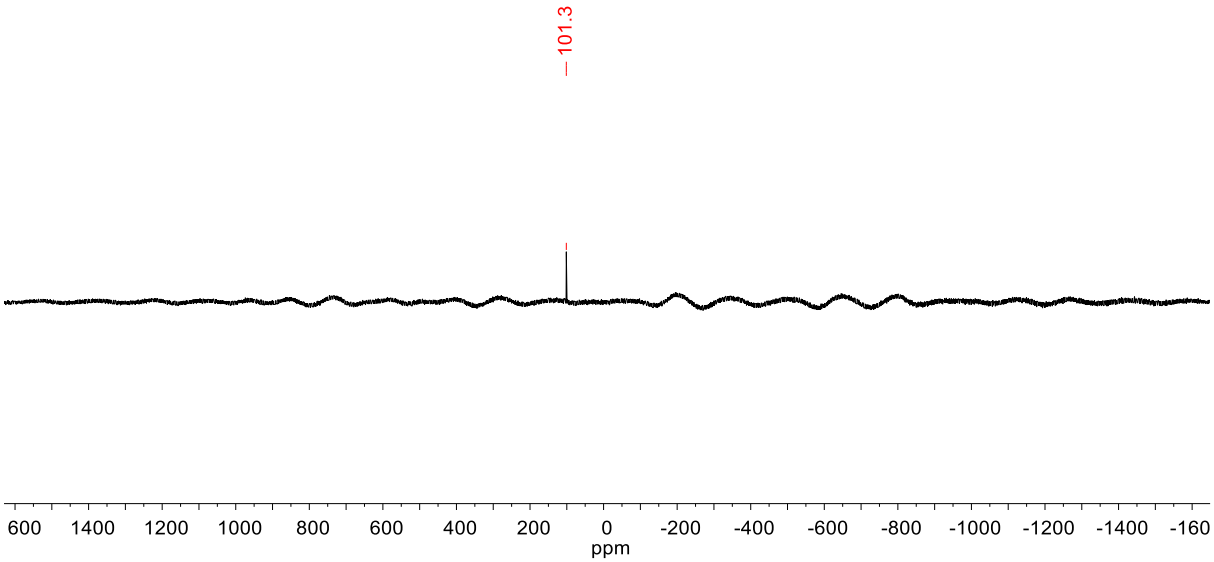

Fig. S43 ^{77}Se NMR spectrum of **3b**HSe ($CDCl_3$, 95 MHz).

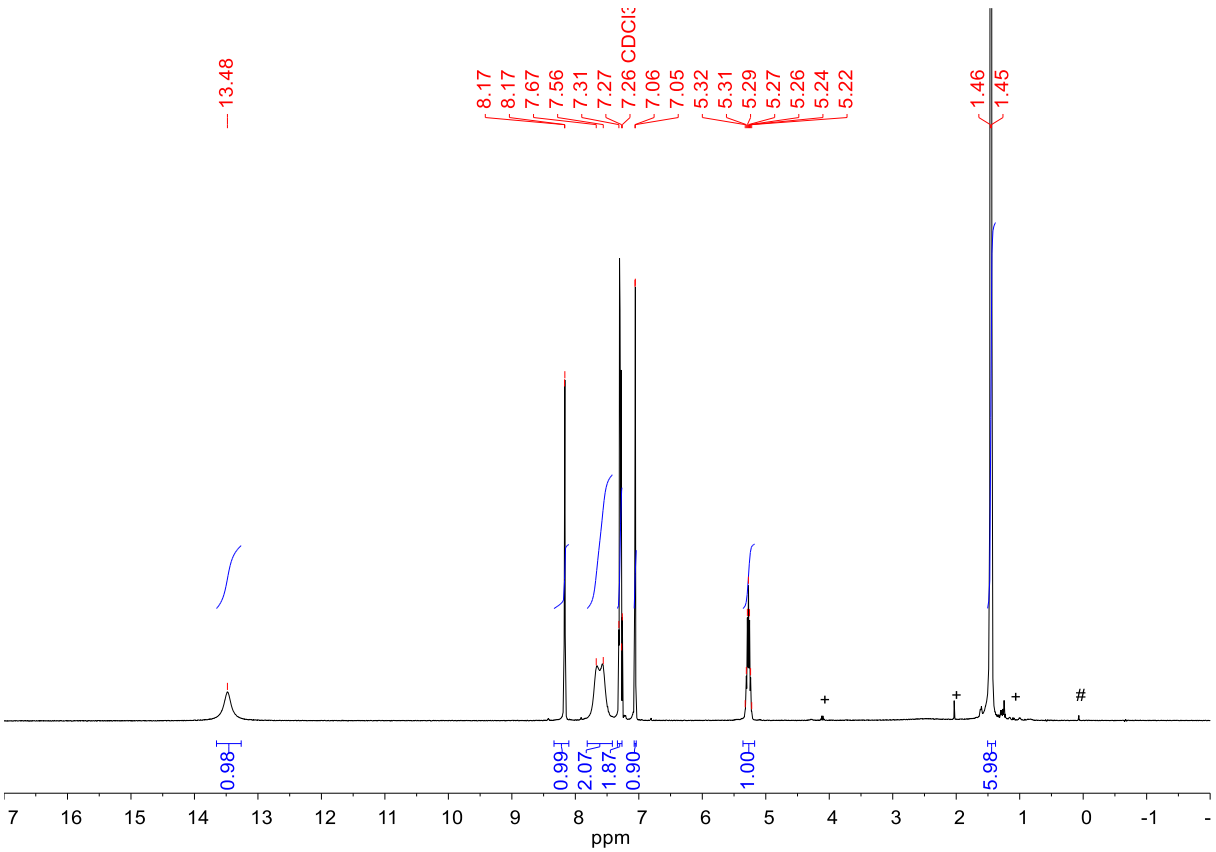

Fig. S44 ^{1}H NMR spectrum of **3b**HSe ($CDCl_3$, 400 MHz). Signals marked belong to ethyl acetate (+) and silicone grease (#).

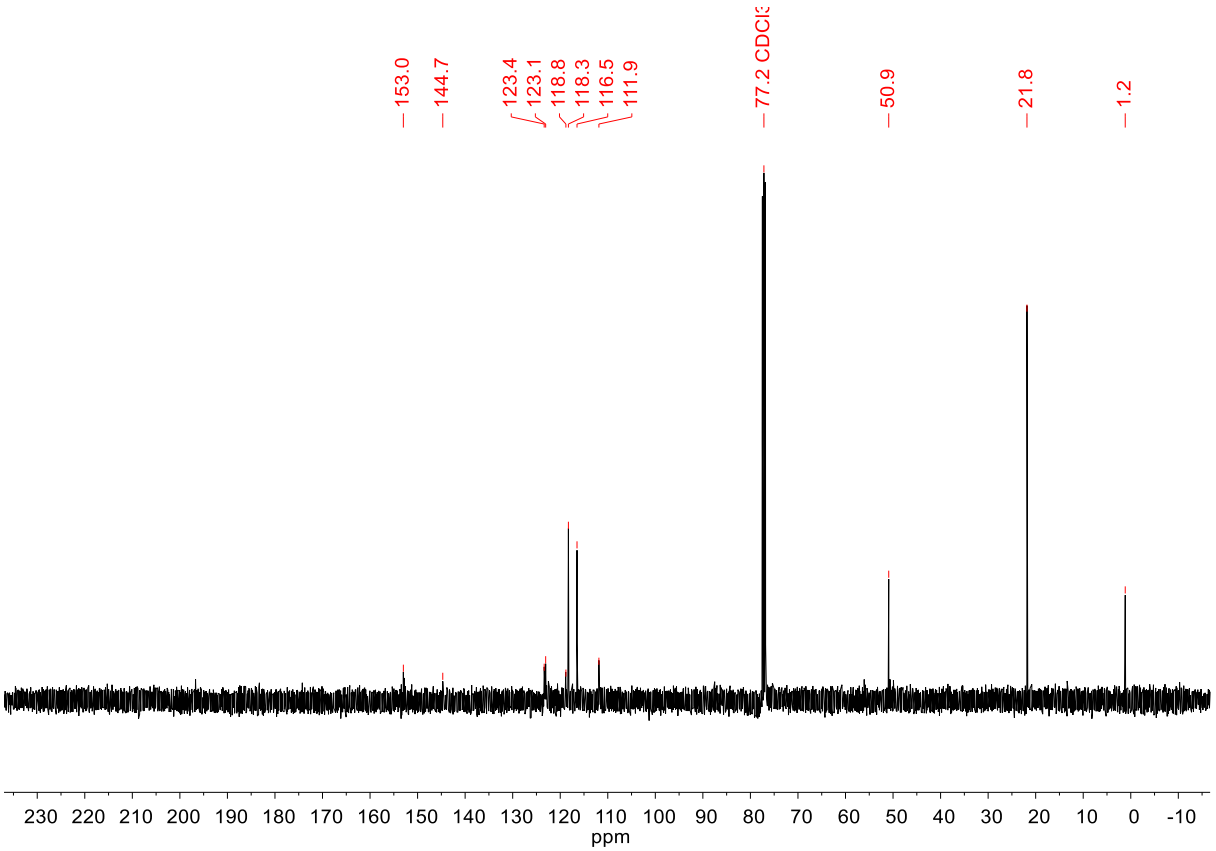

Fig. S45 ^{13}C NMR spectrum of **3b**HSe ($CDCl_3$, 101 MHz). The signal at 1.2 ppm is due to silicone grease.

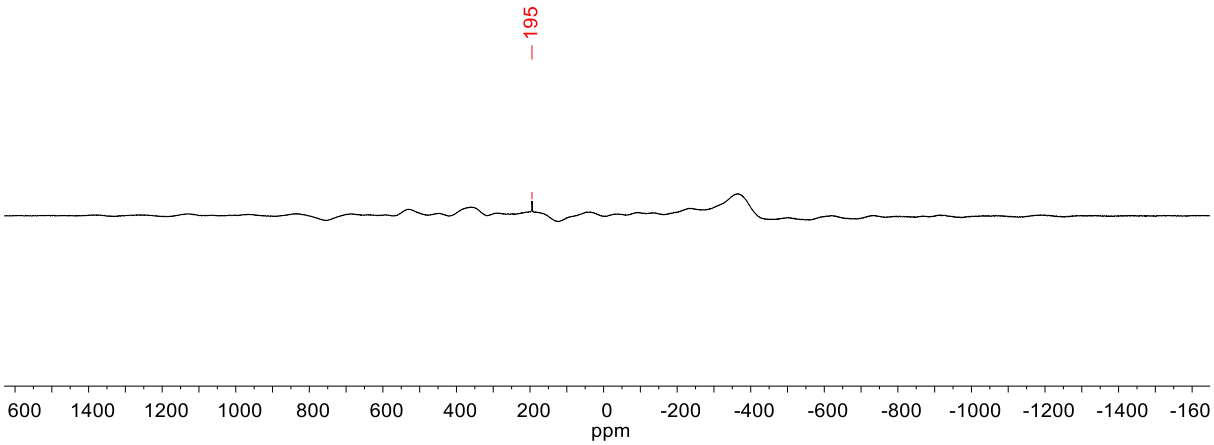

Fig. S46 ^{77}Se NMR spectrum of **3c**HSe ($CDCl_3$, 95 MHz).

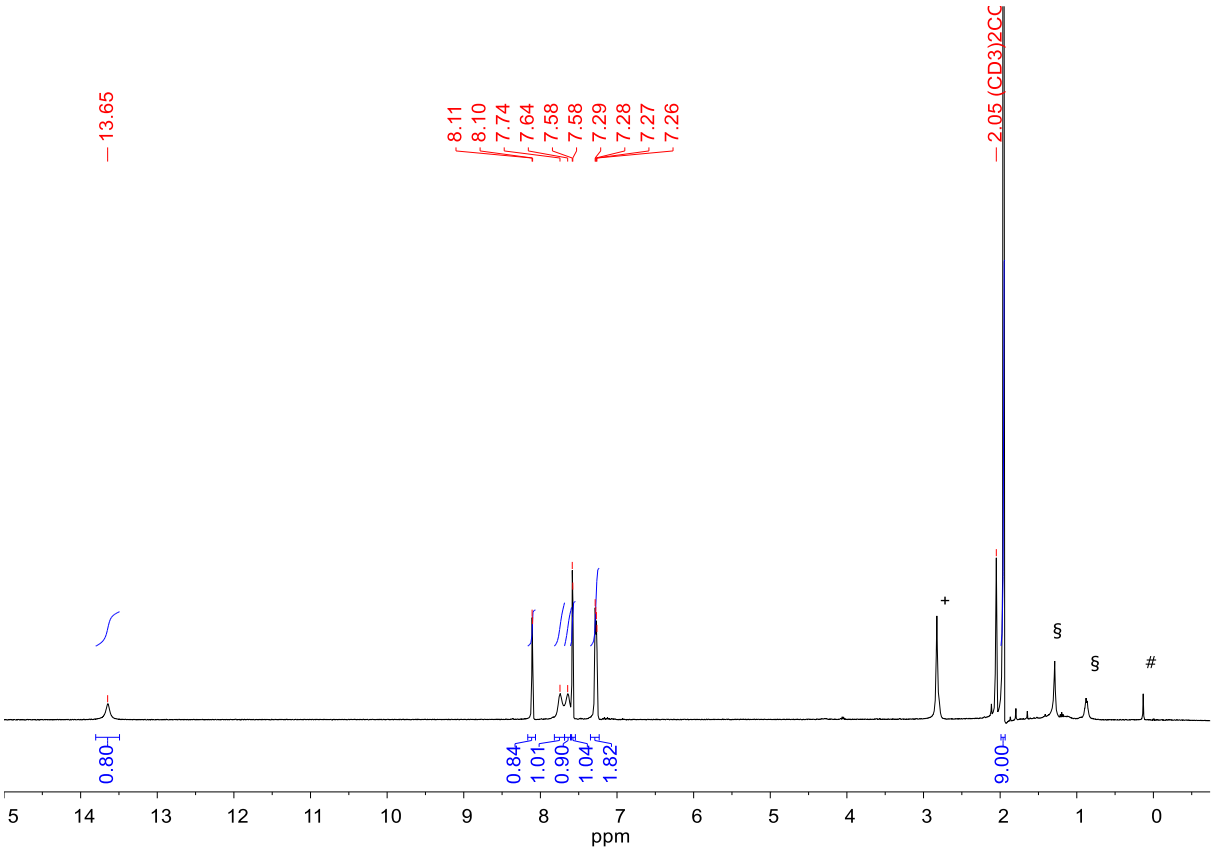

Fig. S47 ^{1}H NMR spectrum of **3c**HSe (acetone-d_6, 400 MHz). Signals marked belong to water (+), H grease (§) and silicone grease (#).

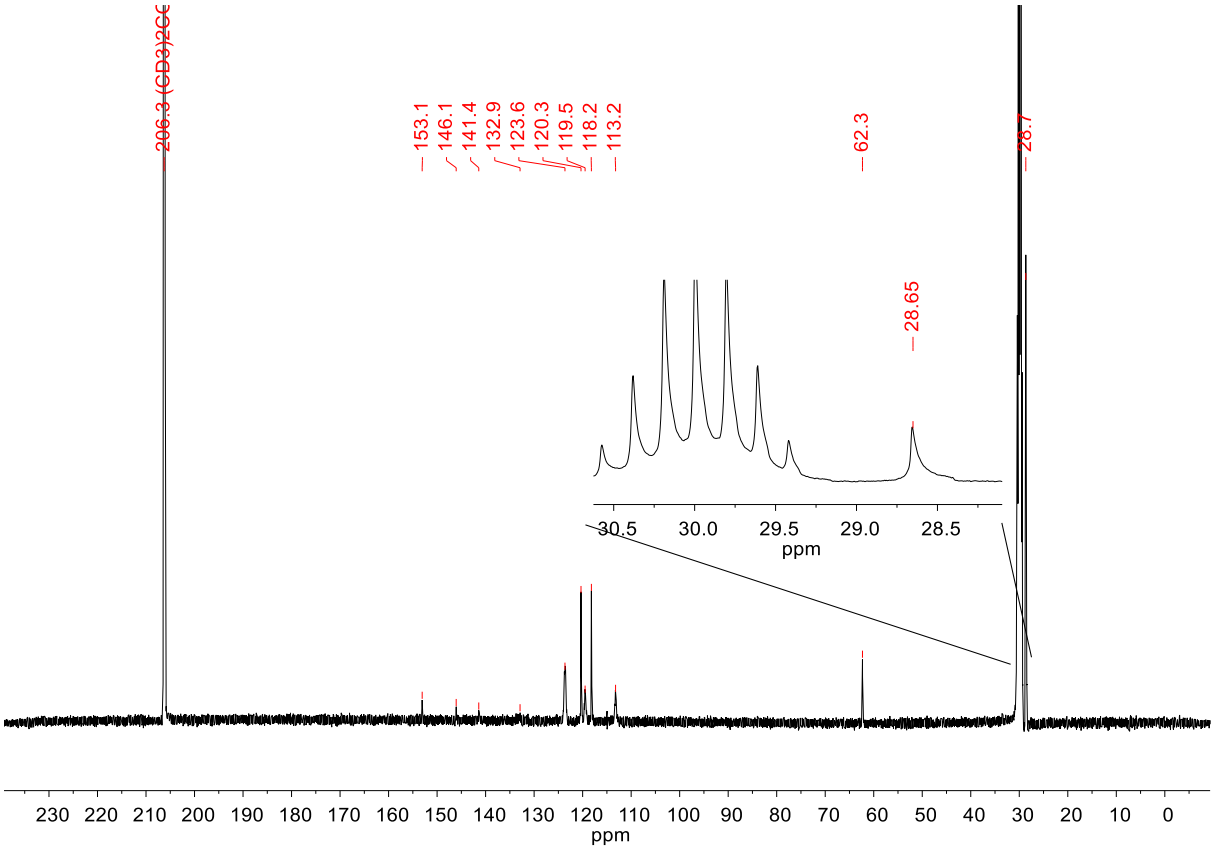

Fig. S48 ^{13}C NMR spectrum of **3c**HSe (acetone-d_6, 101 MHz).

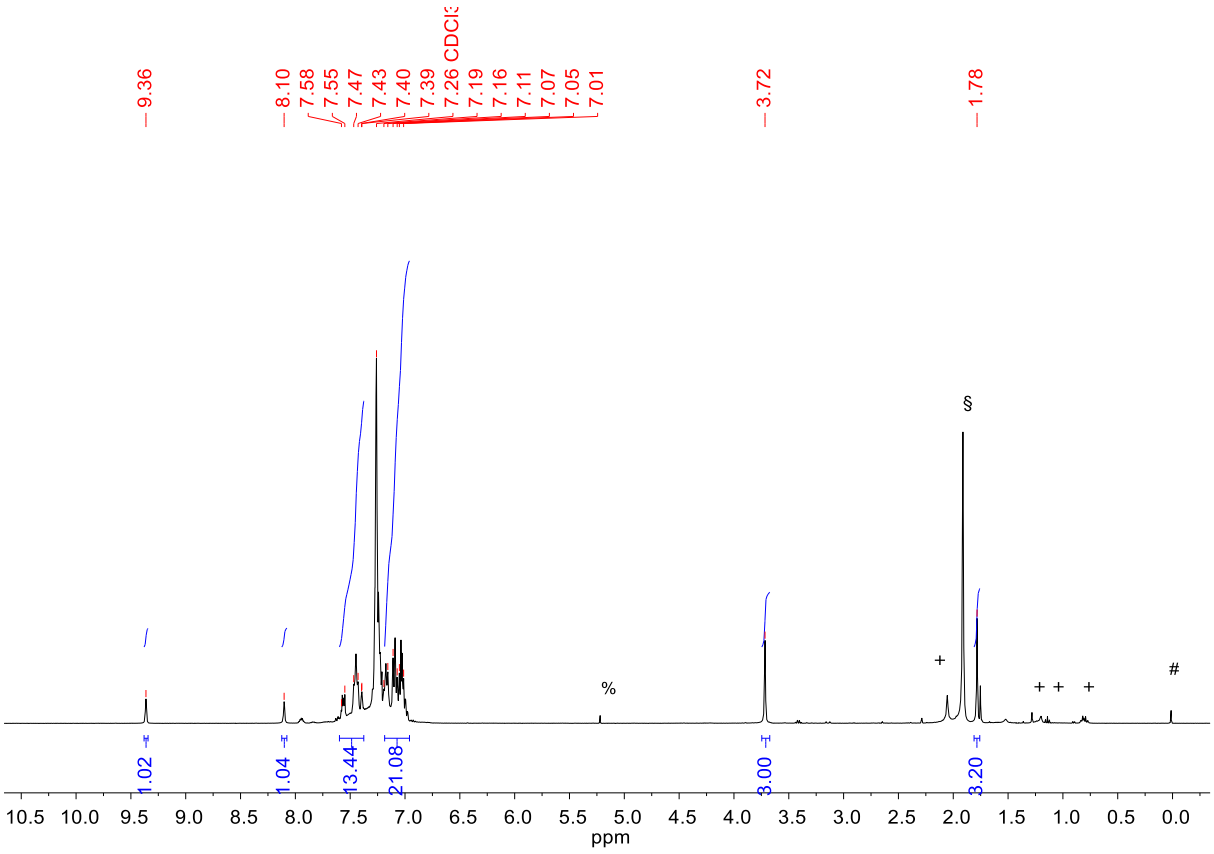

Fig. S49 ^{1}H NMR spectrum of [RuCl(**3'a**H)(MeCN)(PPh_3)$_2$]Cl ($CDCl_3$, 500 MHz). Signals marked belong to CH_2Cl_2 (%), MeCN (§), an unknown impurity (+) and silicone grease (#).

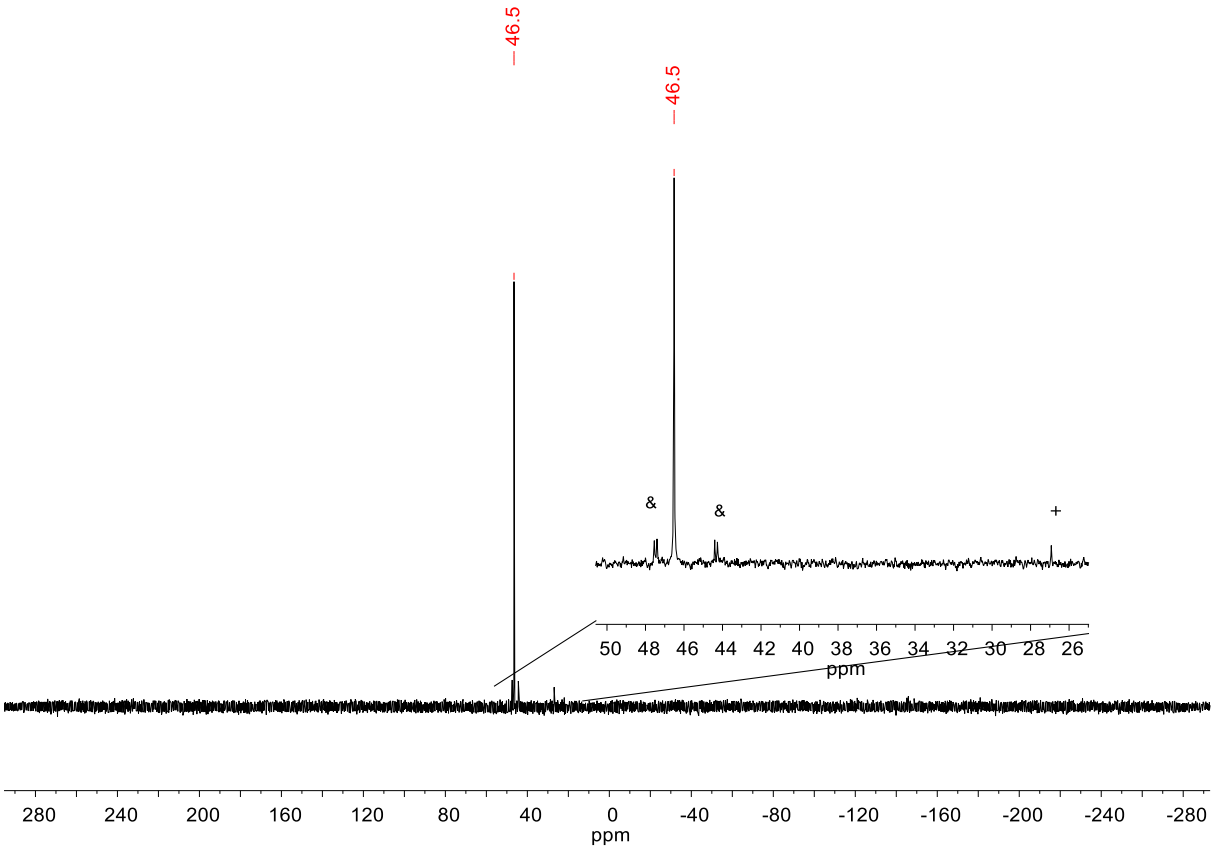

Fig. S50 ^{31}P NMR spectrum of [RuCl(**3'a**H)(MeCN)(PPh_3)$_2$]Cl ($CDCl_3$, 202 MHz). The highest intensity signal is due to the *trans*-isomer. Signals marked belong to an unknown impurity (+) and the *cis*-isomer (&).

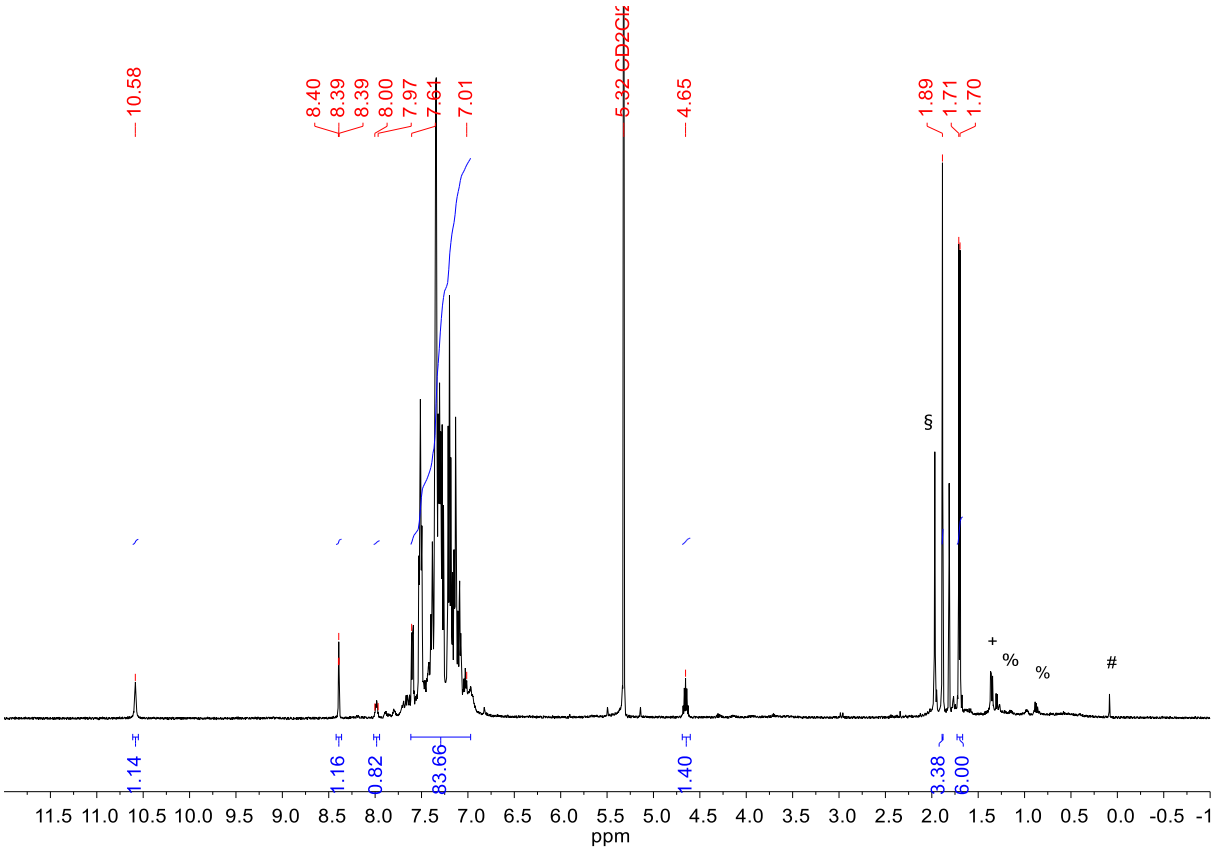

Fig. S51 ^{1}H NMR spectrum of [RuCl(**3''b**H)(MeCN)(PPh_3)$_2$]Cl (CD_2Cl_2, 500 MHz). Signals marked belong to MeCN (§), an unknown impurity (+), H grease (%) and silicone grease (#).

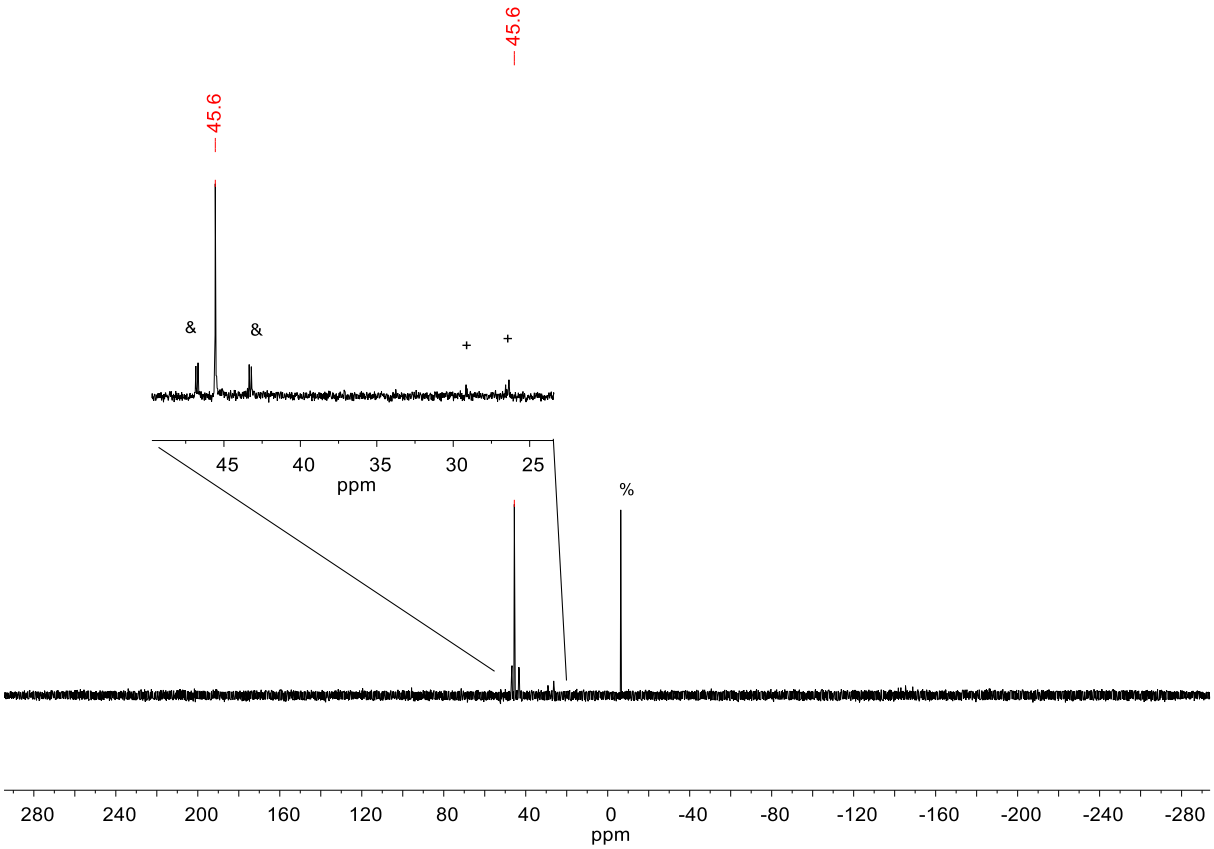

Fig. S52 ^{31}P NMR spectrum of [RuCl(**3''b**H)(MeCN)$(PPh_3)_2$]Cl (CD_2Cl_2, 202 MHz). The highest intensity signal is due to the *trans*-isomer. Signals marked belong to an unknown impurity (+), triphenylphosphine (%) and the *cis*-isomer (&).

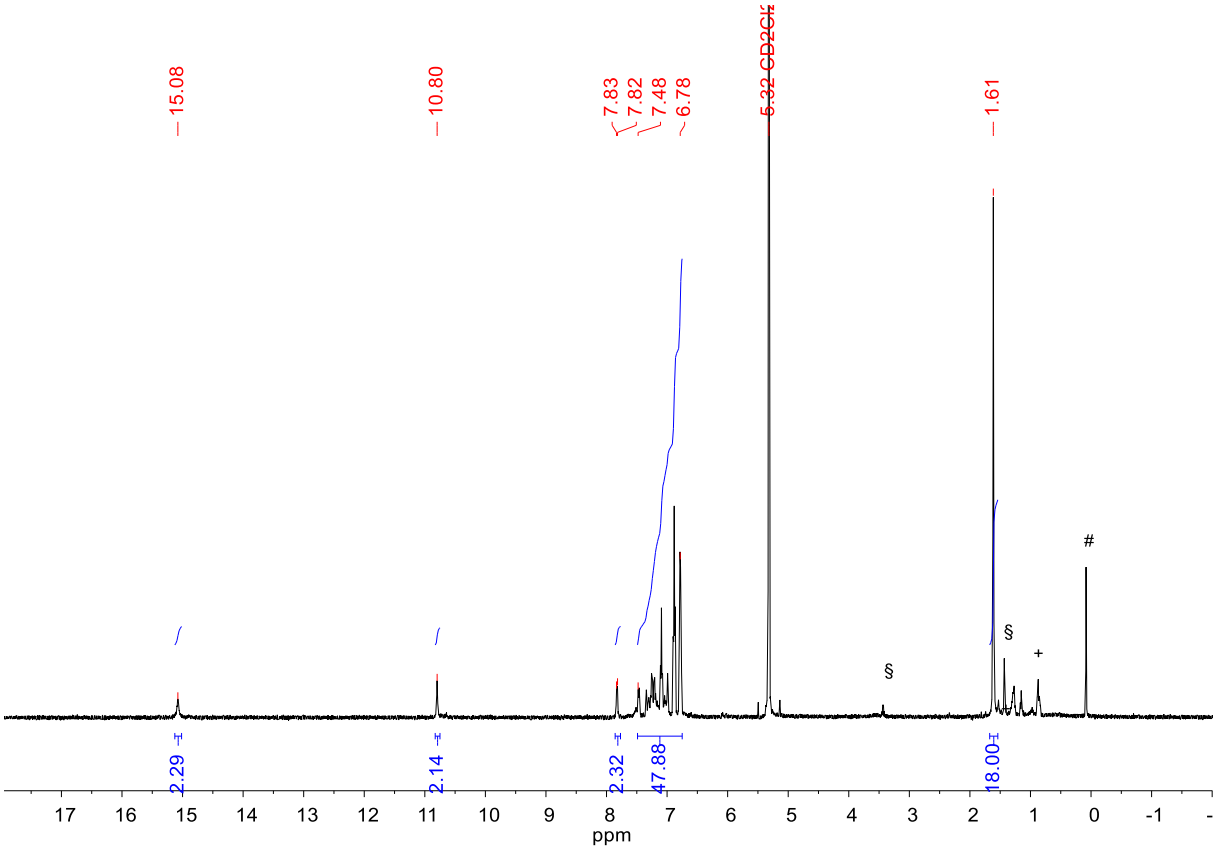

Fig. S53 ^{1}H NMR spectrum of [Ru(**3''c**H)$_2(PPh_3)_2]Cl_2$ (CD_2Cl_2, 500 MHz). Signals marked belong to Et_2O (§), an unknown impurity (+) and silicone grease (#).

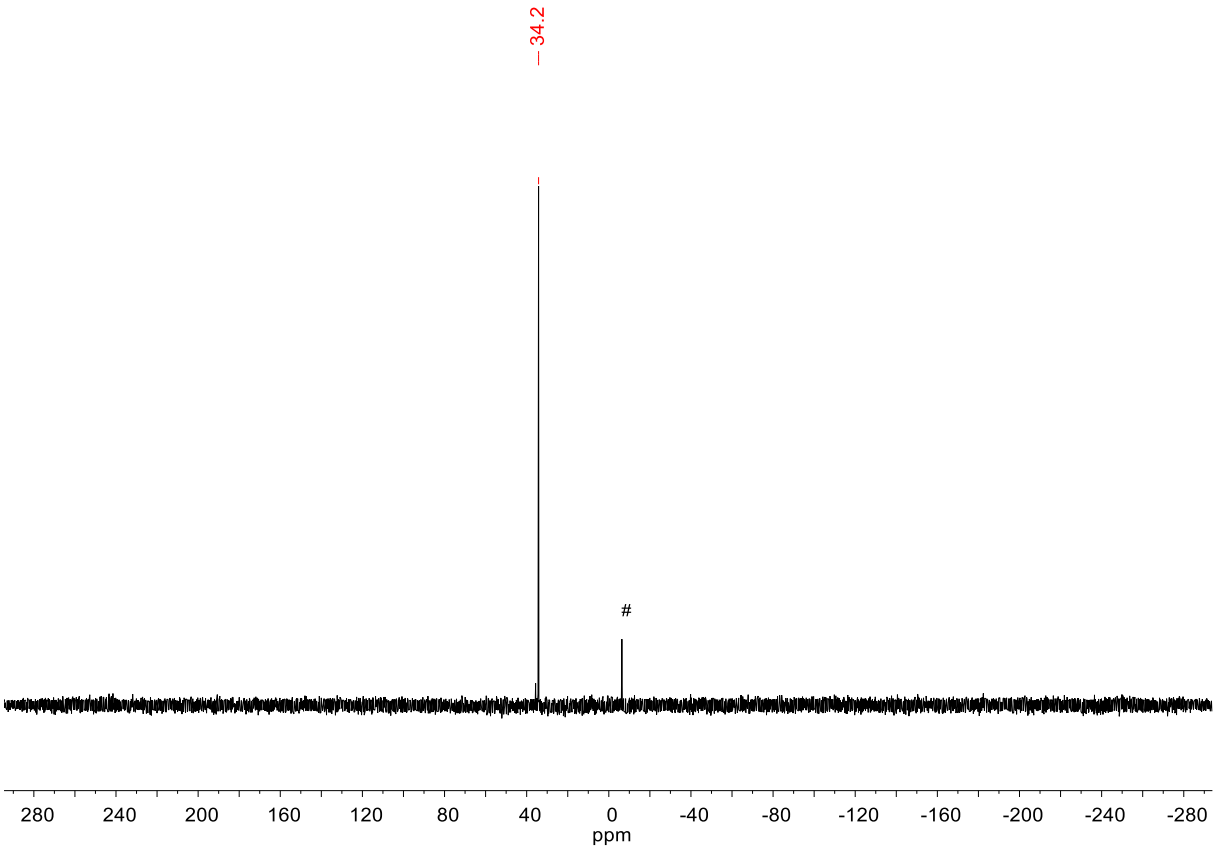

Fig. S54 ^{31}P NMR spectrum of [Ru(**3''c**H)$_2$(PPh$_3$)$_2$]Cl$_2$ (CD$_2$Cl$_2$, 202 MHz). The signal marked belongs to triphenylphosphine (#)

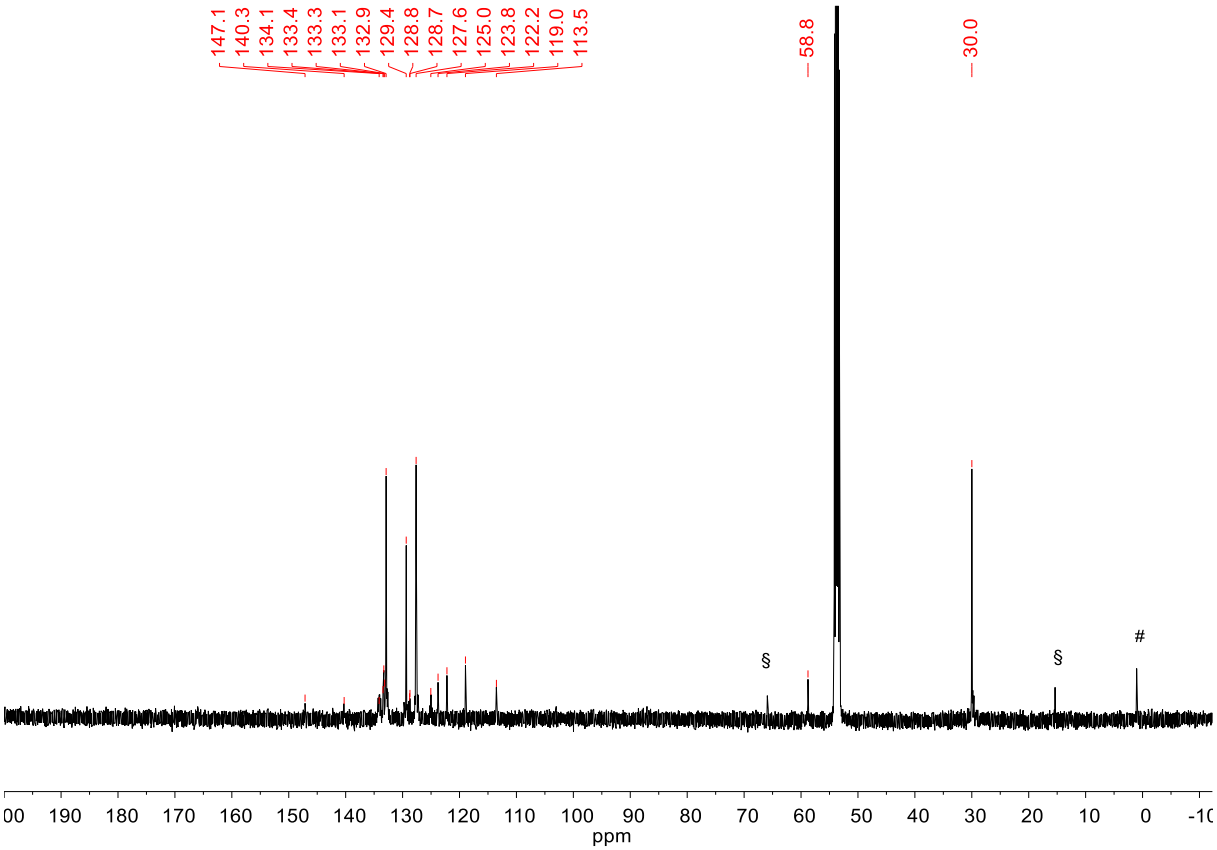

Fig. S55 ^{13}C NMR spectrum of [Ru(**3''c**H)$_2$(PPh$_3$)$_2$]Cl$_2$ (CD$_2$Cl$_2$, 126 MHz). Signals marked belong to Et$_2$O (§) and silicone grease (#).

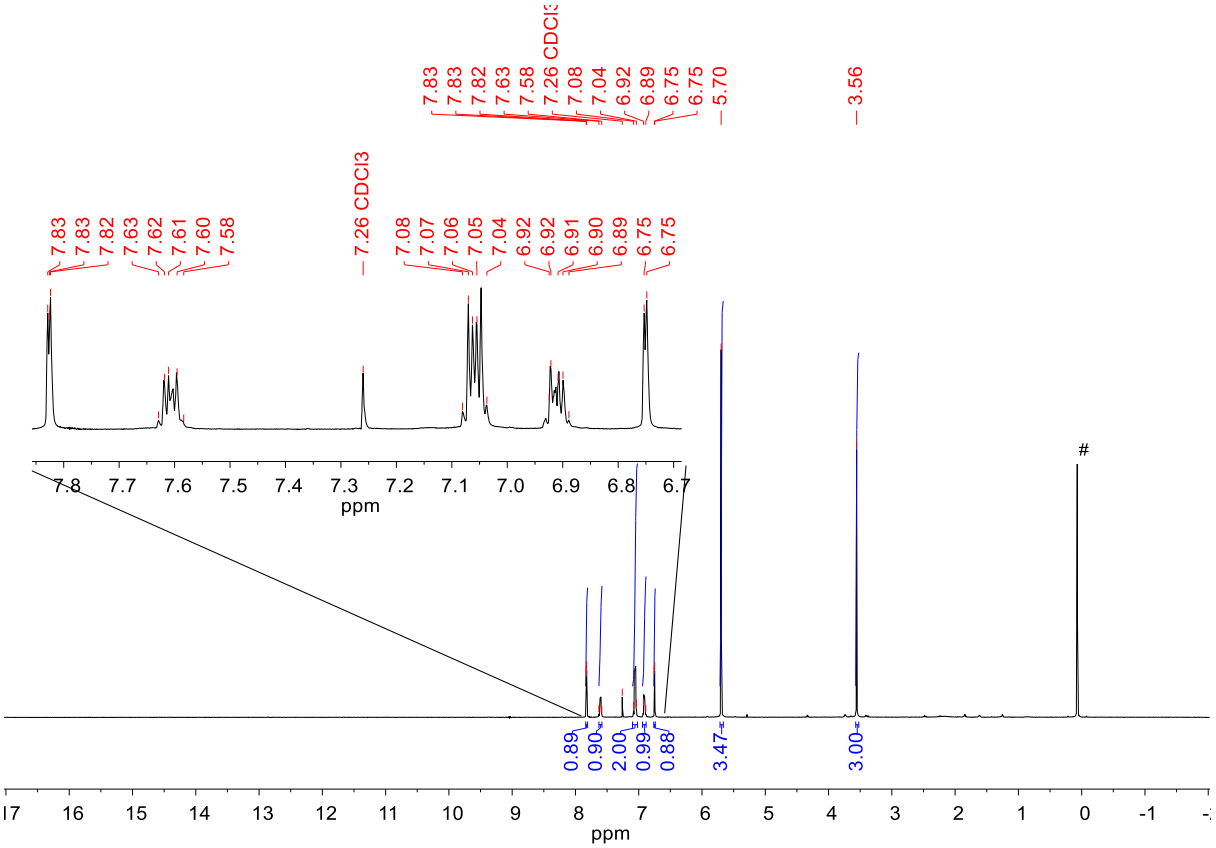

Fig. S56 ^{1}H NMR spectrum of [NiCp(**3'a**)] ($CDCl_3$, 400 MHz). The signal marked belongs to silicone grease (#).

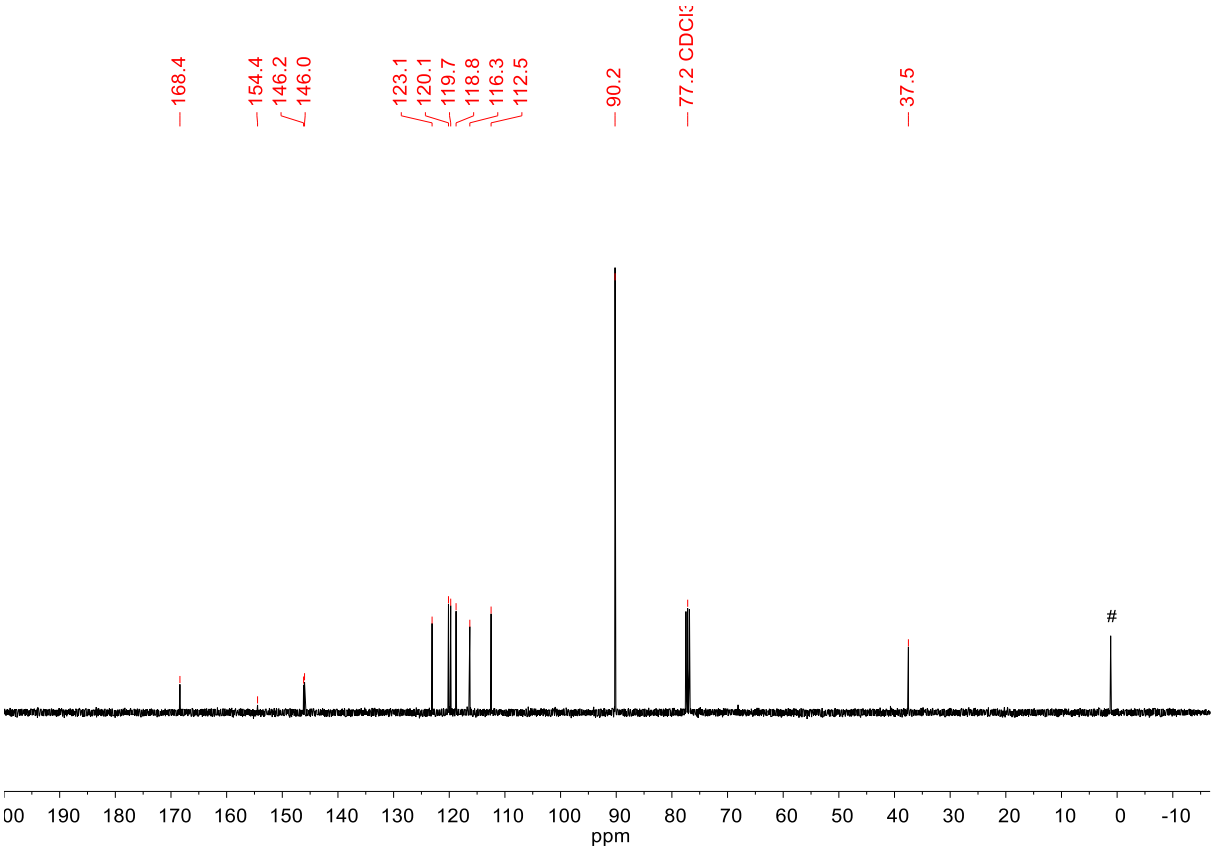

Fig. S57 ^{13}C NMR spectrum of [NiCp(**3'a**)] ($CDCl_3$, 101 MHz). Signal marked belongs silicone grease (#).

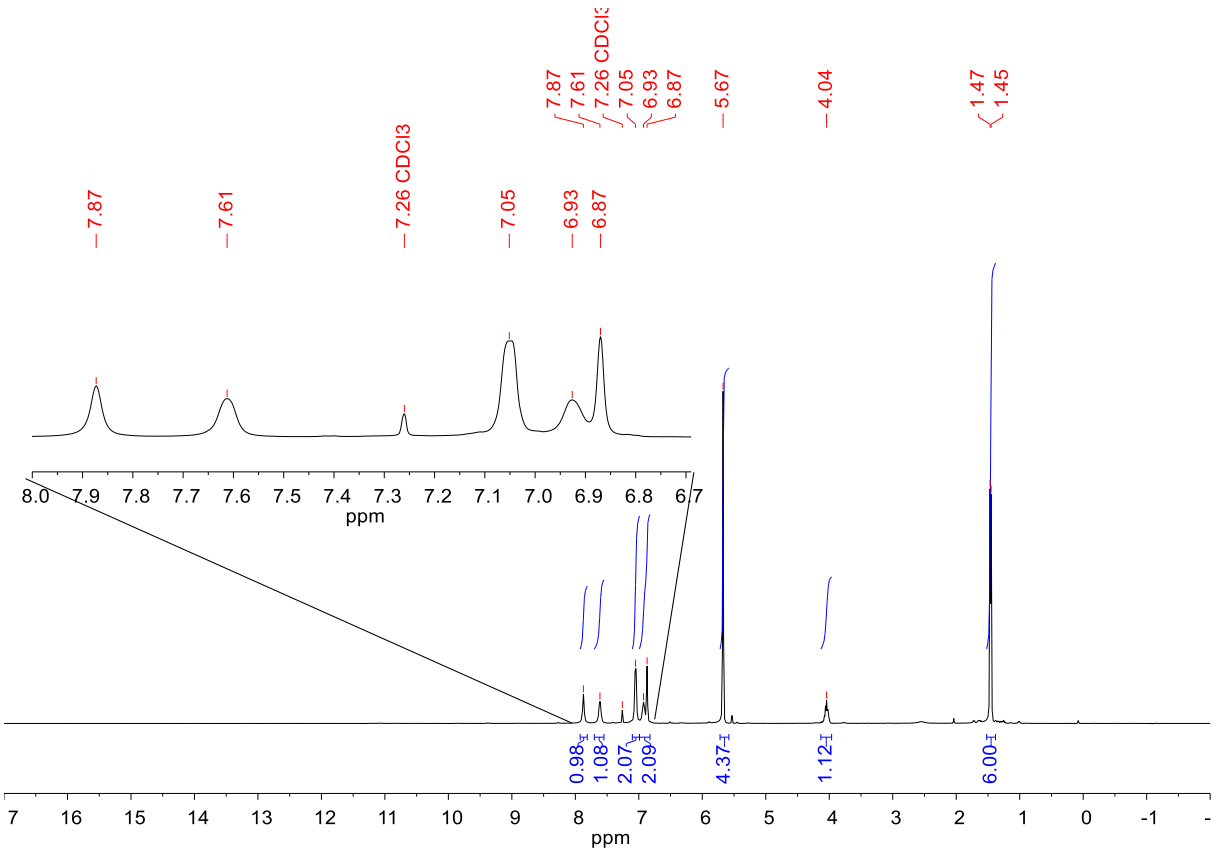

Fig. S58 ^{1}H NMR spectrum of [NiCp(**3'b**)] ($CDCl_3$, 400 MHz).

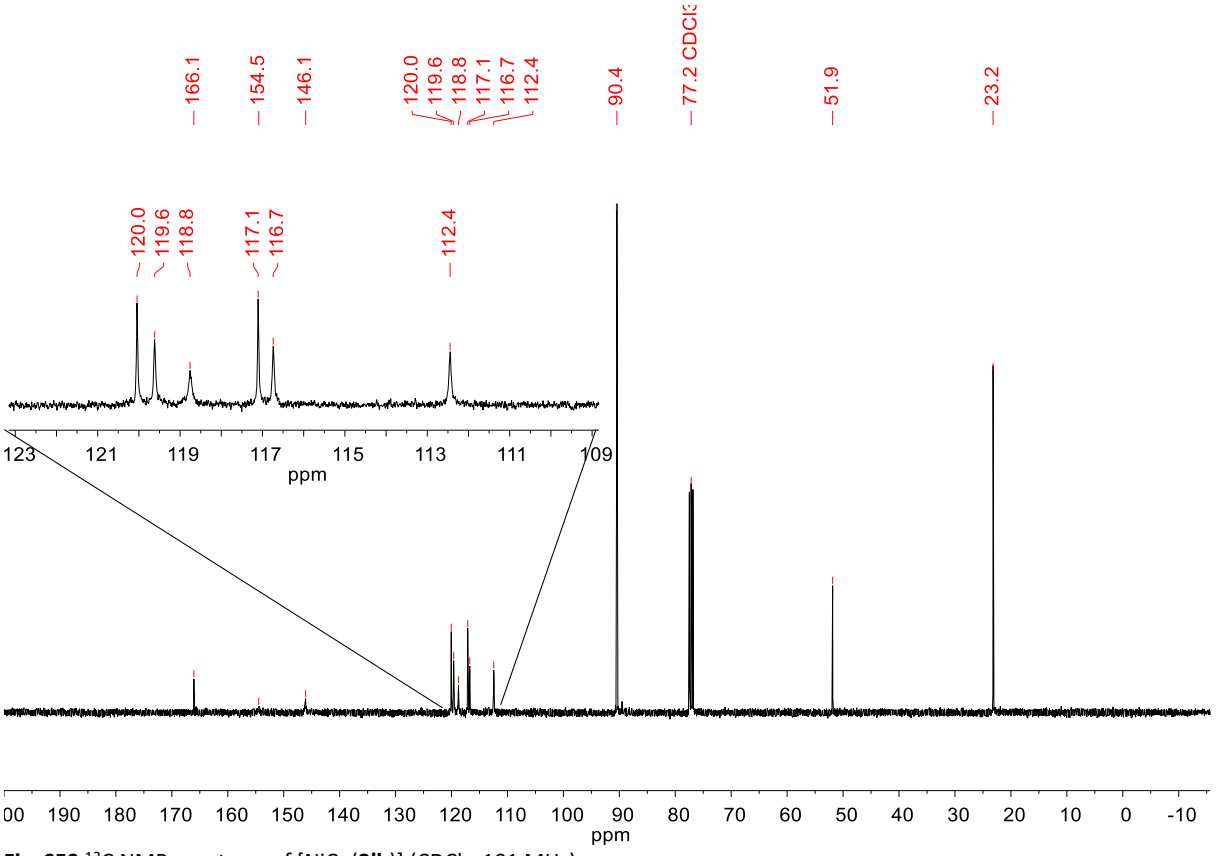

Fig. S59 ^{13}C NMR spectrum of [NiCp(**3'b**)] ($CDCl_3$, 101 MHz).

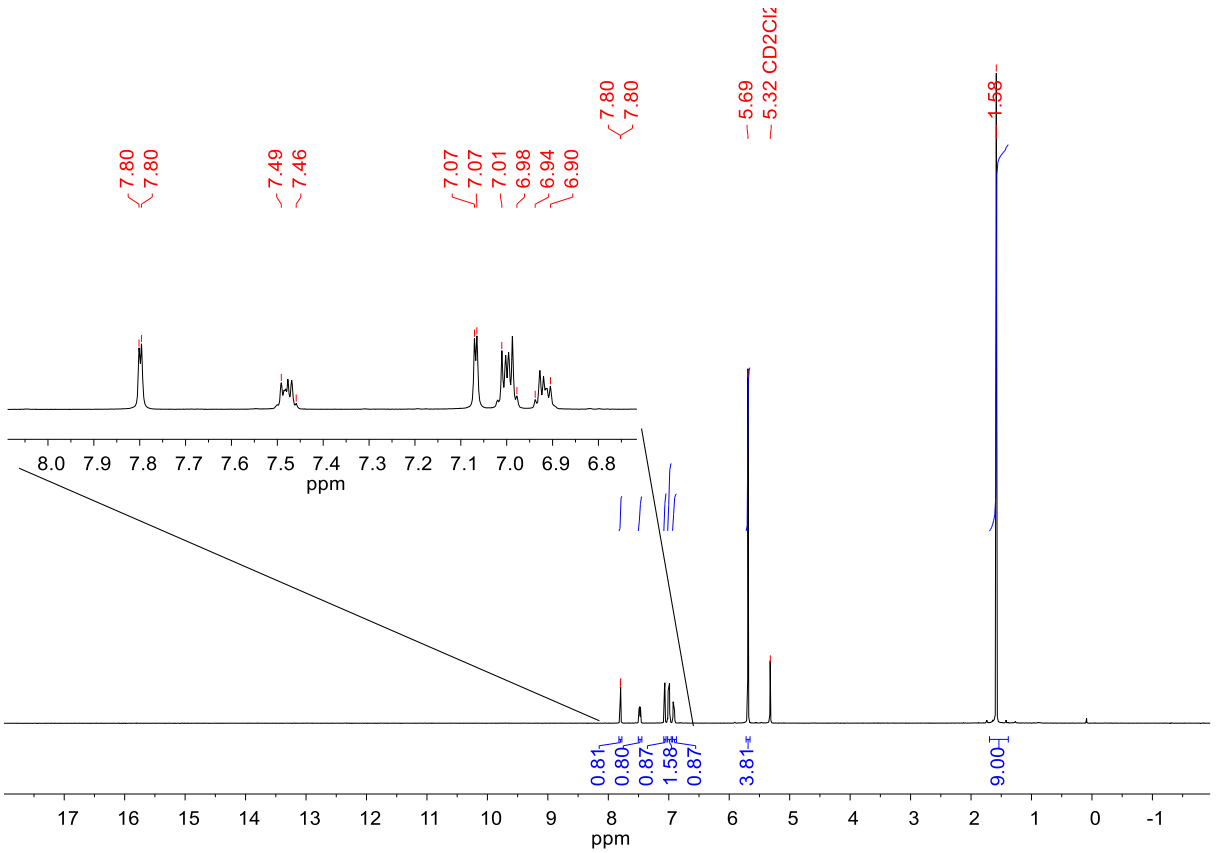

Fig. S60 ^{1}H NMR spectrum of [NiCp(**3'c**)] (CD_2Cl_2, 400 MHz).

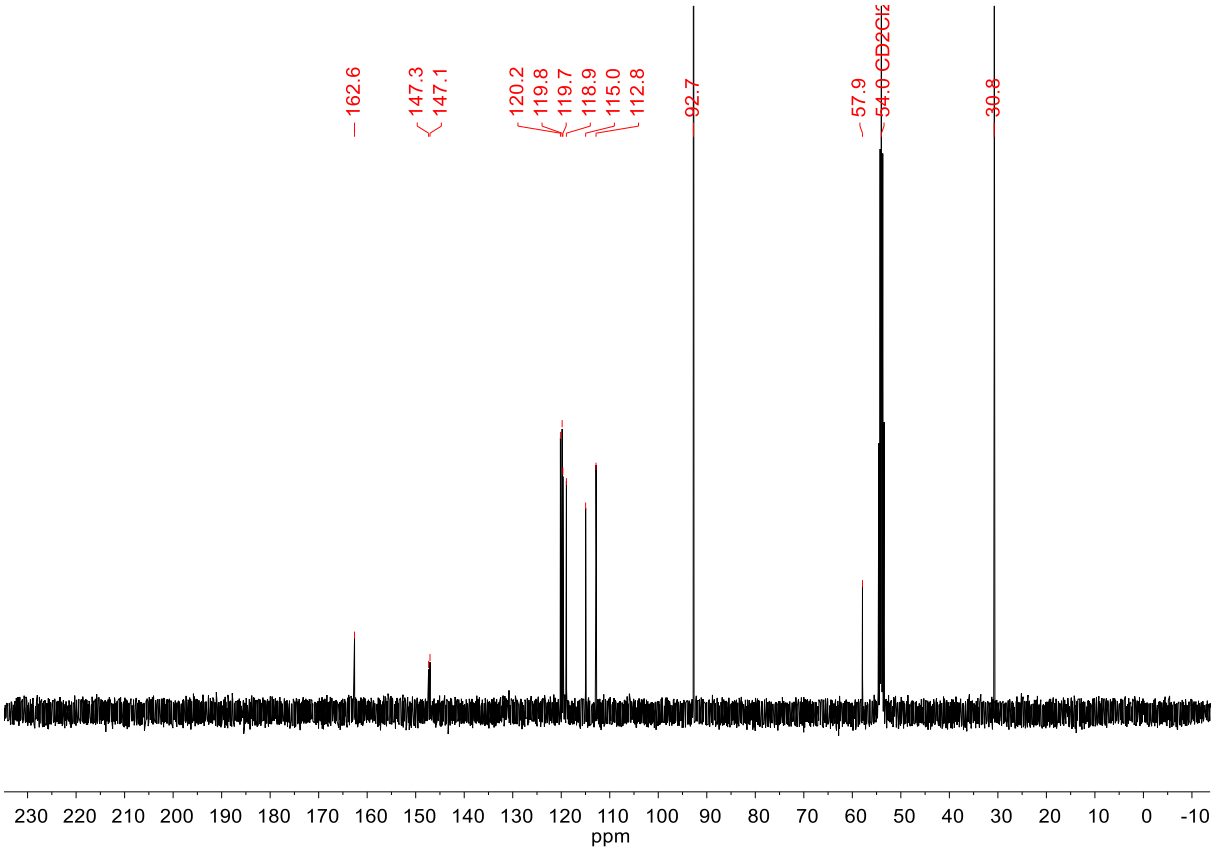

Fig. S61 ^{13}C NMR spectrum of [NiCp(**3'c**)] (CD_2Cl_2, 101 MHz).

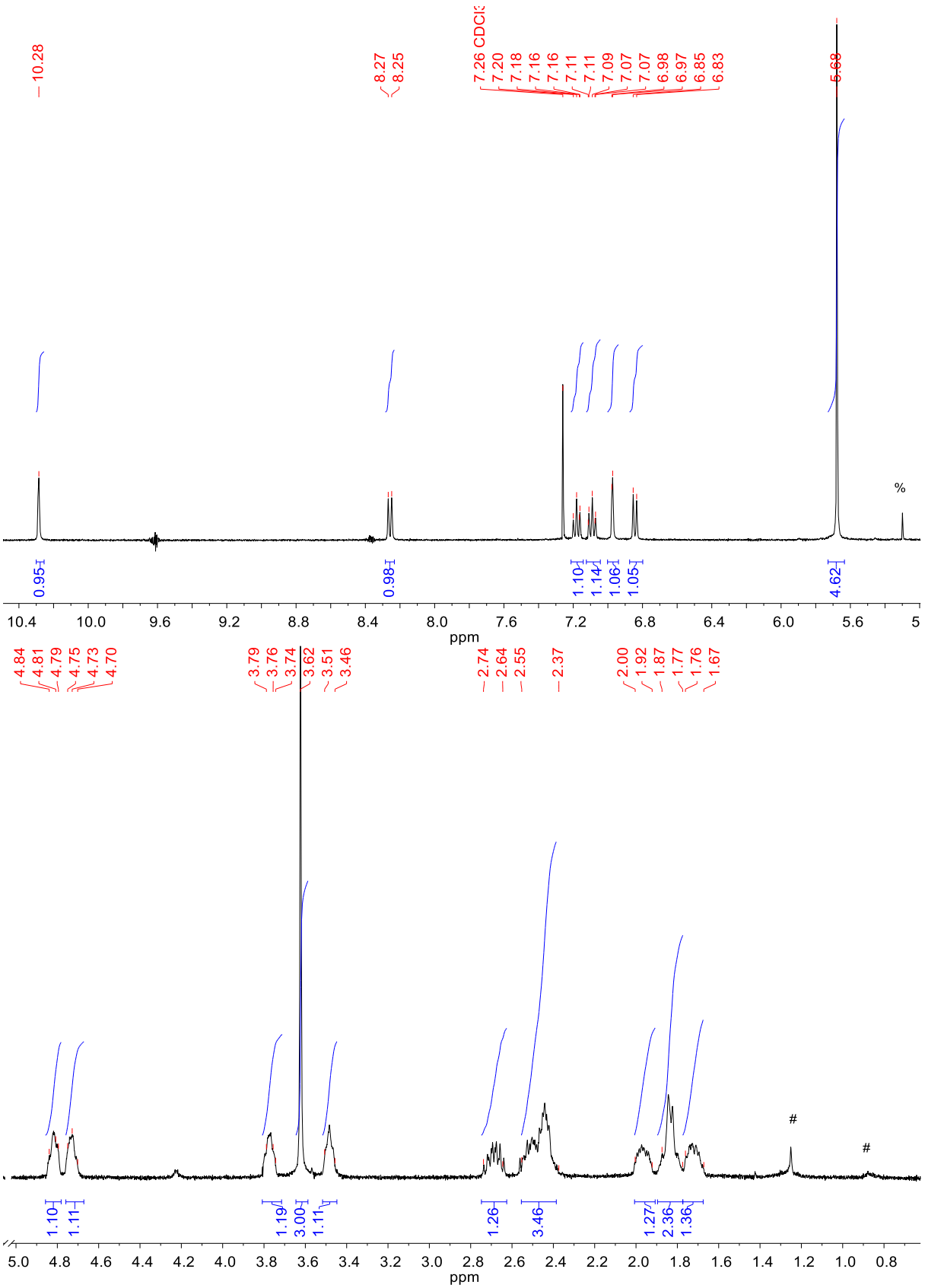

Fig. S62 ^{1}H NMR spectrum of [RhCl(COD){NiCp(μ-**3'a**)}] ($CDCl_3$, 400 MHz). Signals marked belong to CH_2Cl_2 (%) and H grease (#).

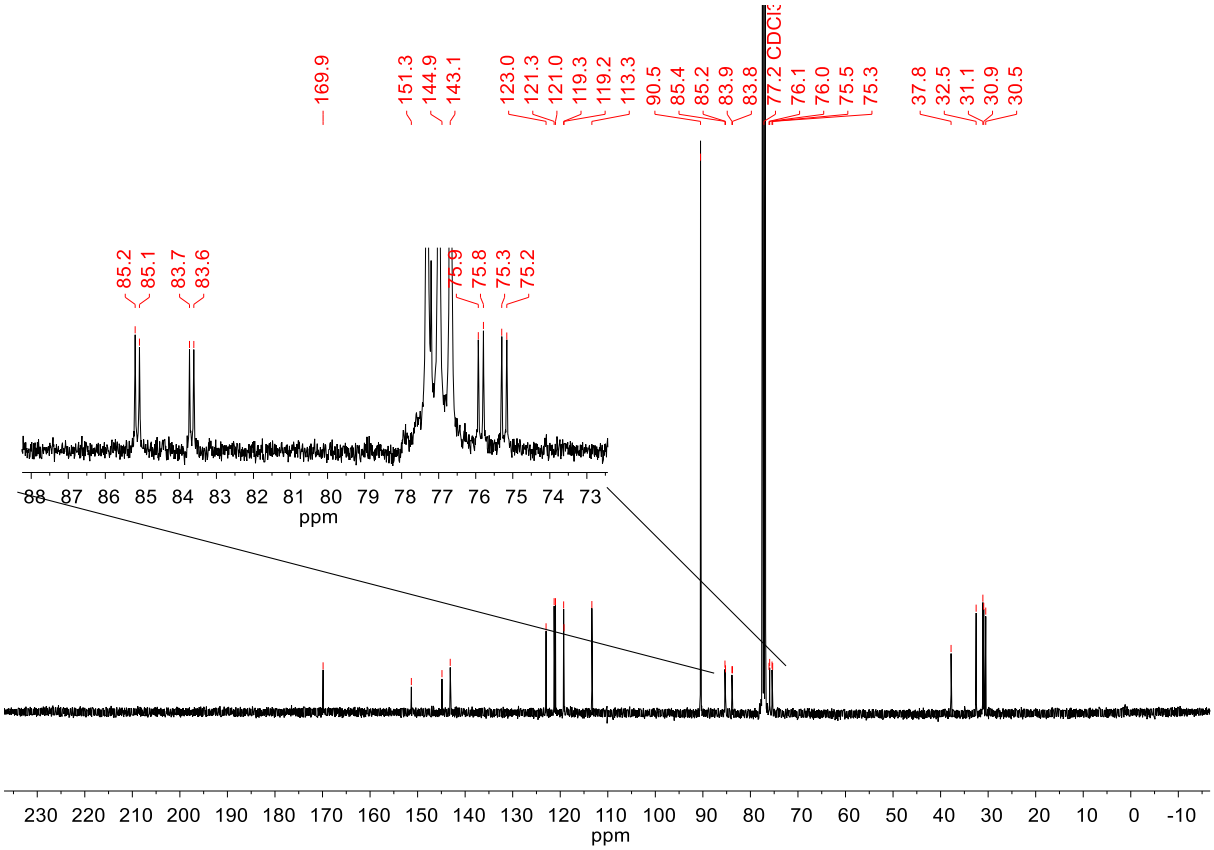

Fig. S63 ^{13}C NMR spectrum of [RhCl(COD){NiCp(μ-**3'a**)}] ($CDCl_3$, 101 MHz).

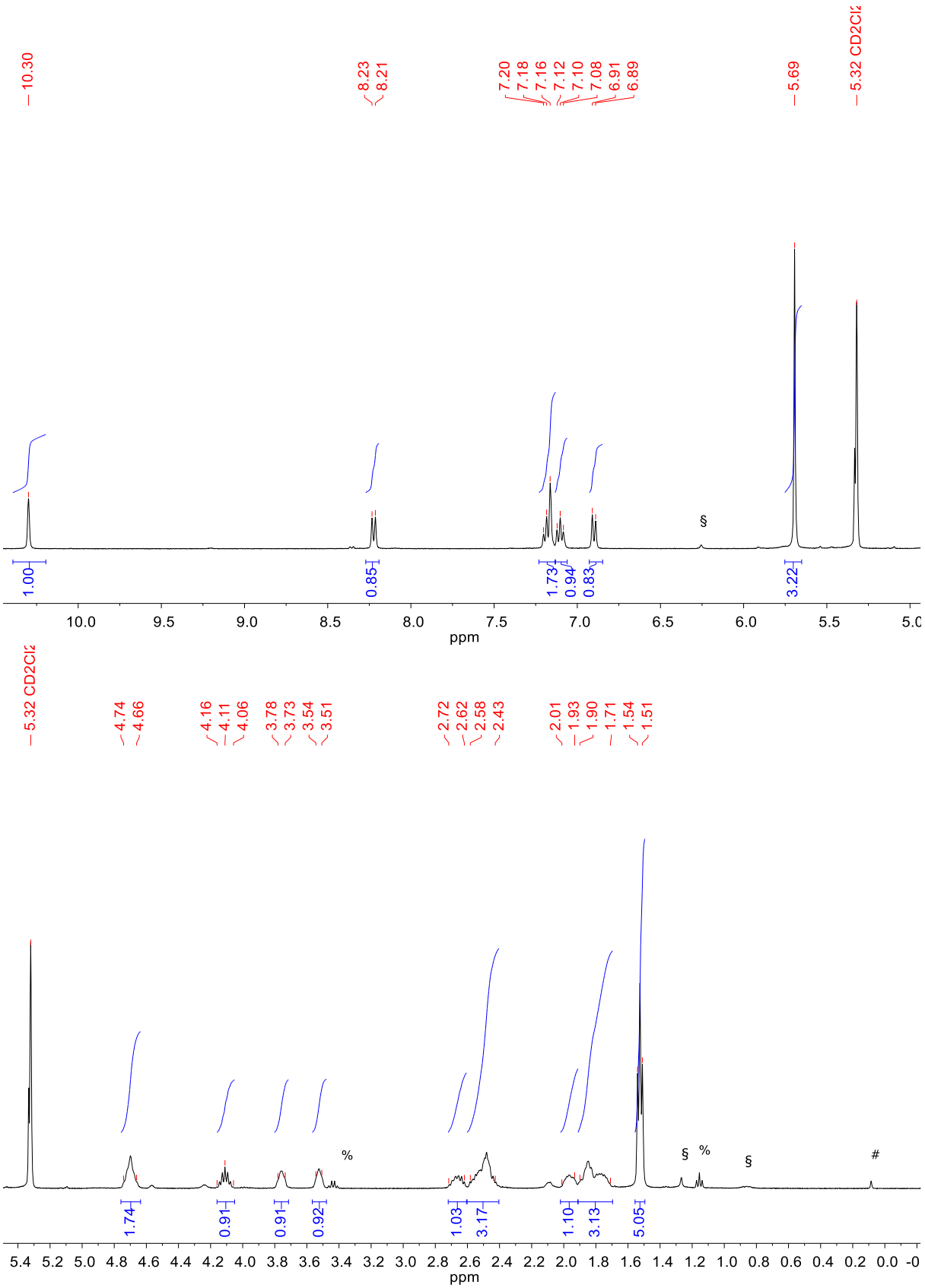

Fig. S64 ^{1}H NMR spectrum of [RhCl(COD){NiCp(μ-**3'b**)}] (CD_2Cl_2, 400 MHz). Signals marked belong to Et_2O (%), an unknown impurity (§) and silicone grease (#).

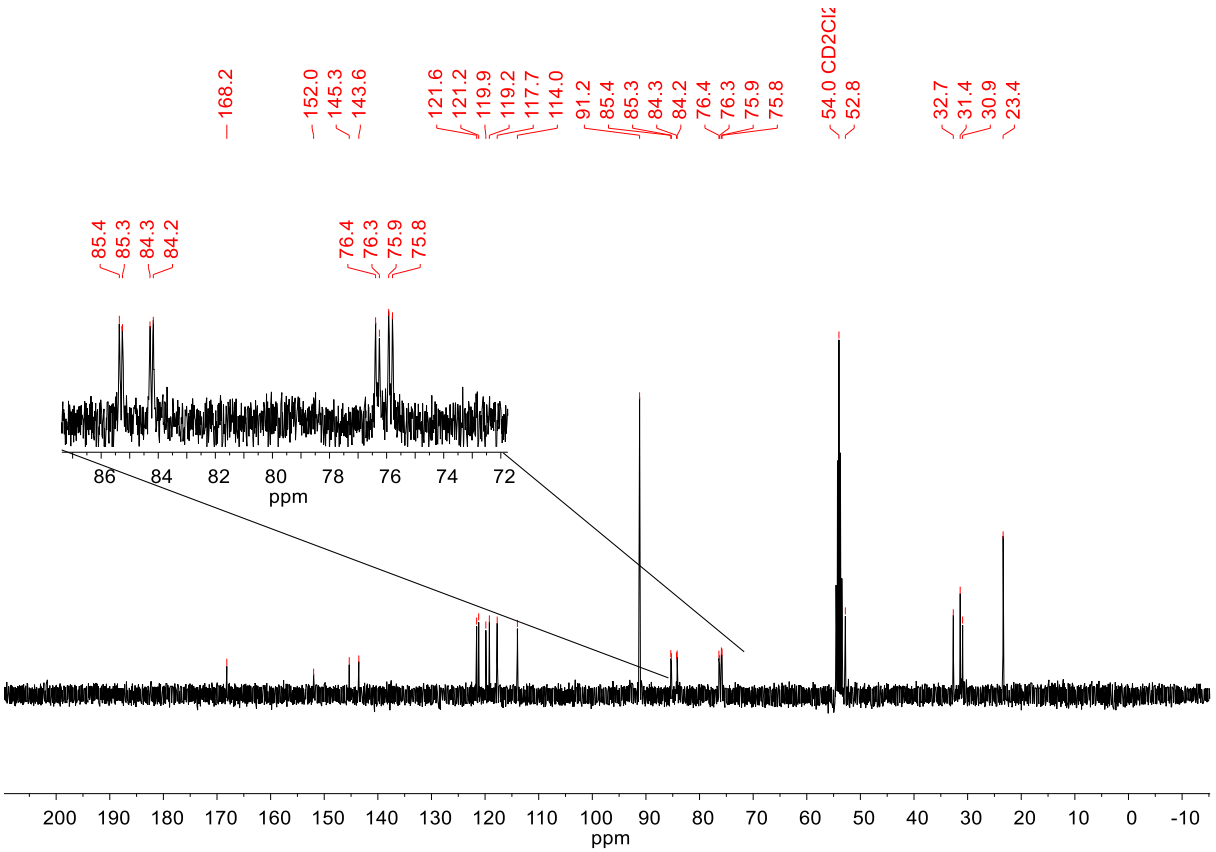

Fig. S65 ^{13}C NMR spectrum of [RhCl(COD){NiCp(μ-**3'b**)}] (CD_2Cl_2, 101 MHz).

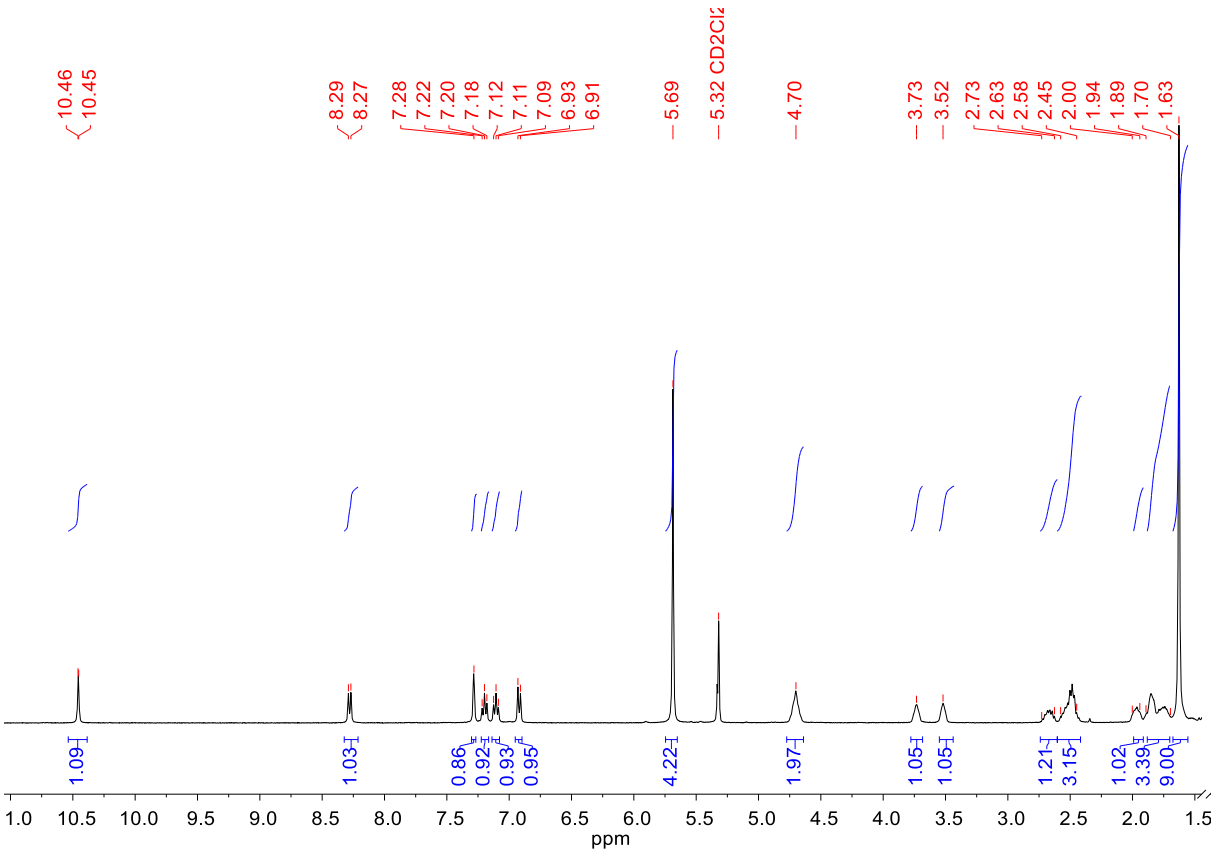

Fig. S66 ^{1}H NMR spectrum of [RhCl(COD){NiCp(μ-**3'c**)}] (CD_2Cl_2, 400 MHz).

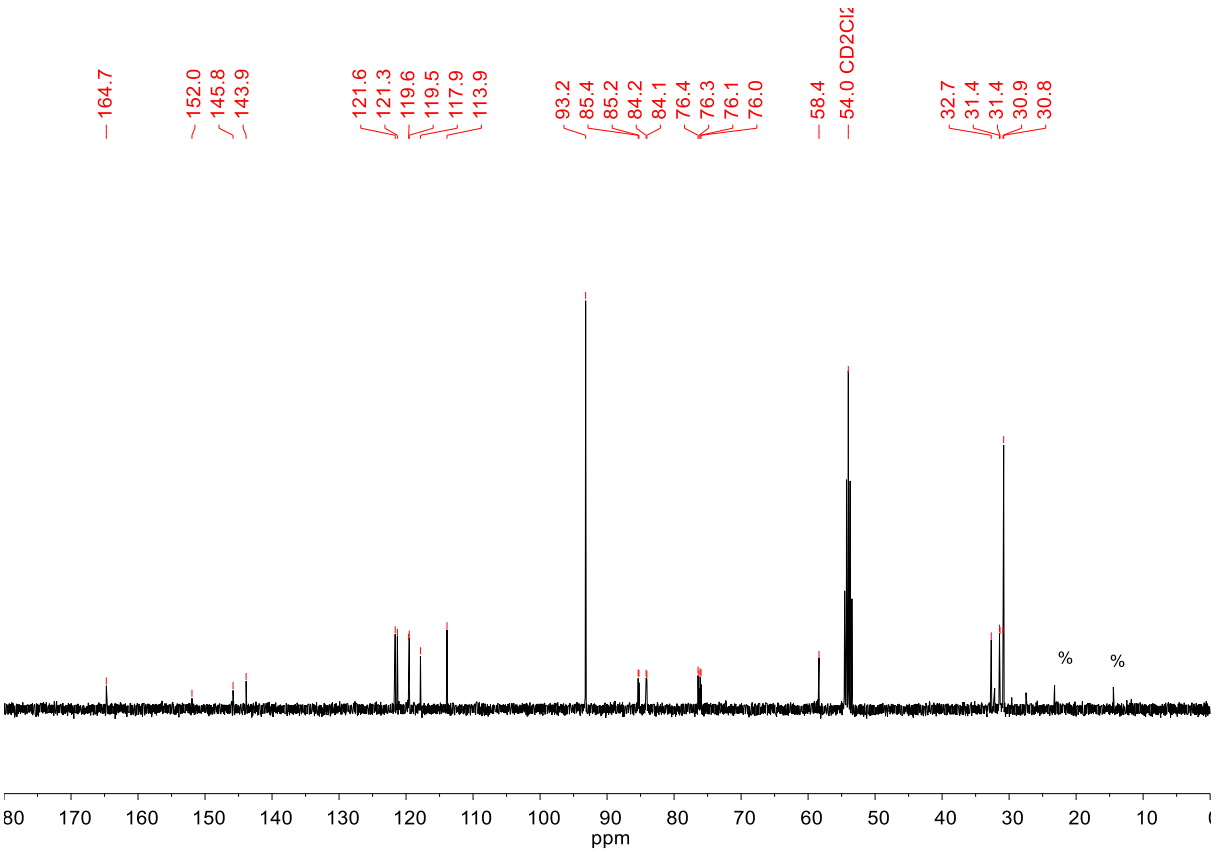

Fig. S67 ^{13}C NMR spectrum of [RhCl(COD){NiCp(μ-**3'c**)}] (CD_2Cl_2, 101 MHz). Signals marked belong to hexane (%).

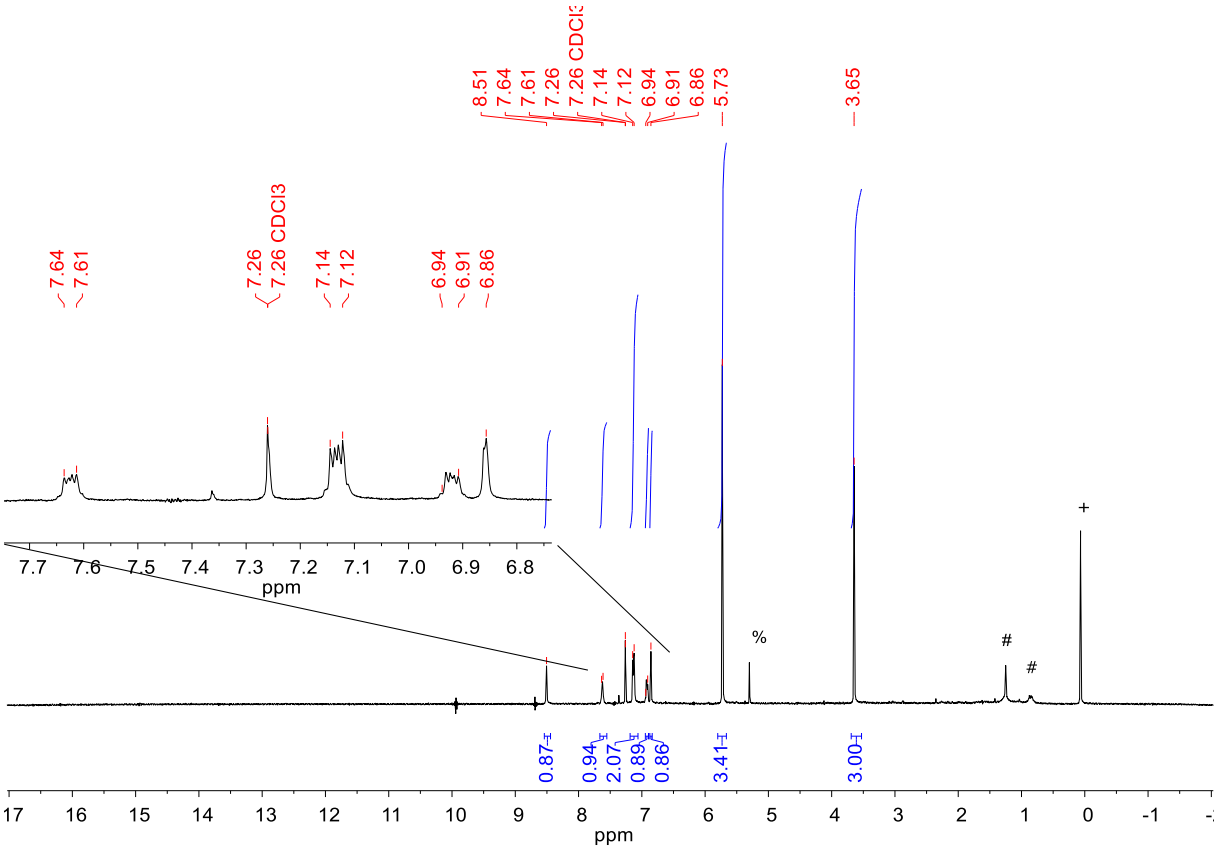

Fig. S68 ^{1}H NMR spectrum of [CuBr{NiCp(μ-**3'a**)}] ($CDCl_3$, 400 MHz). Signals marked belong to CH_2Cl_2 (%), H grease (#) and silicone grease (+).

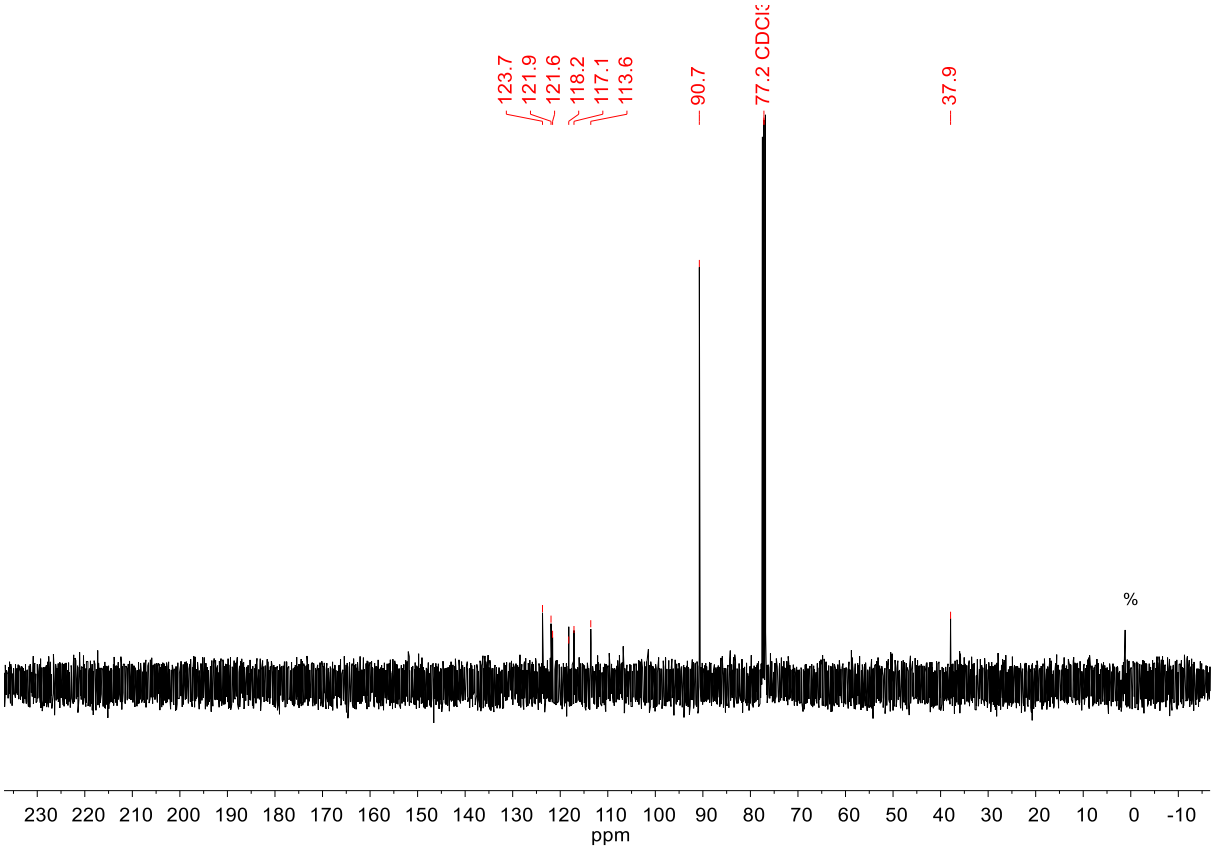

Fig. S69 ^{13}C NMR spectrum of [CuBr{NiCp(μ-**3'a**)}] ($CDCl_3$, 101 MHz). The signal marked belongs to silicone grease (%).

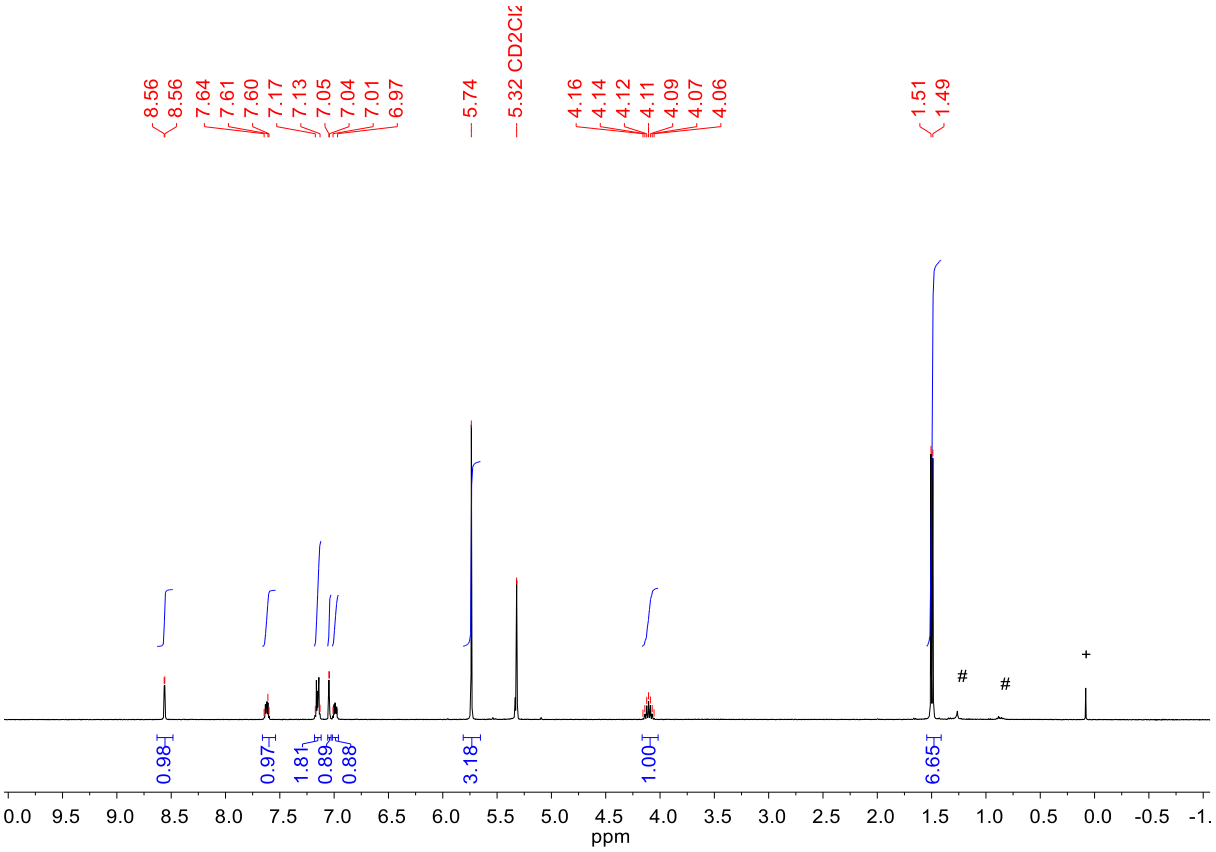

Fig. S70 ^{1}H NMR spectrum of [CuBr{NiCp(μ-**3'b**)}] (CD_2Cl_2, 400 MHz). Signals marked belong to H grease (#) and silicone grease (+).

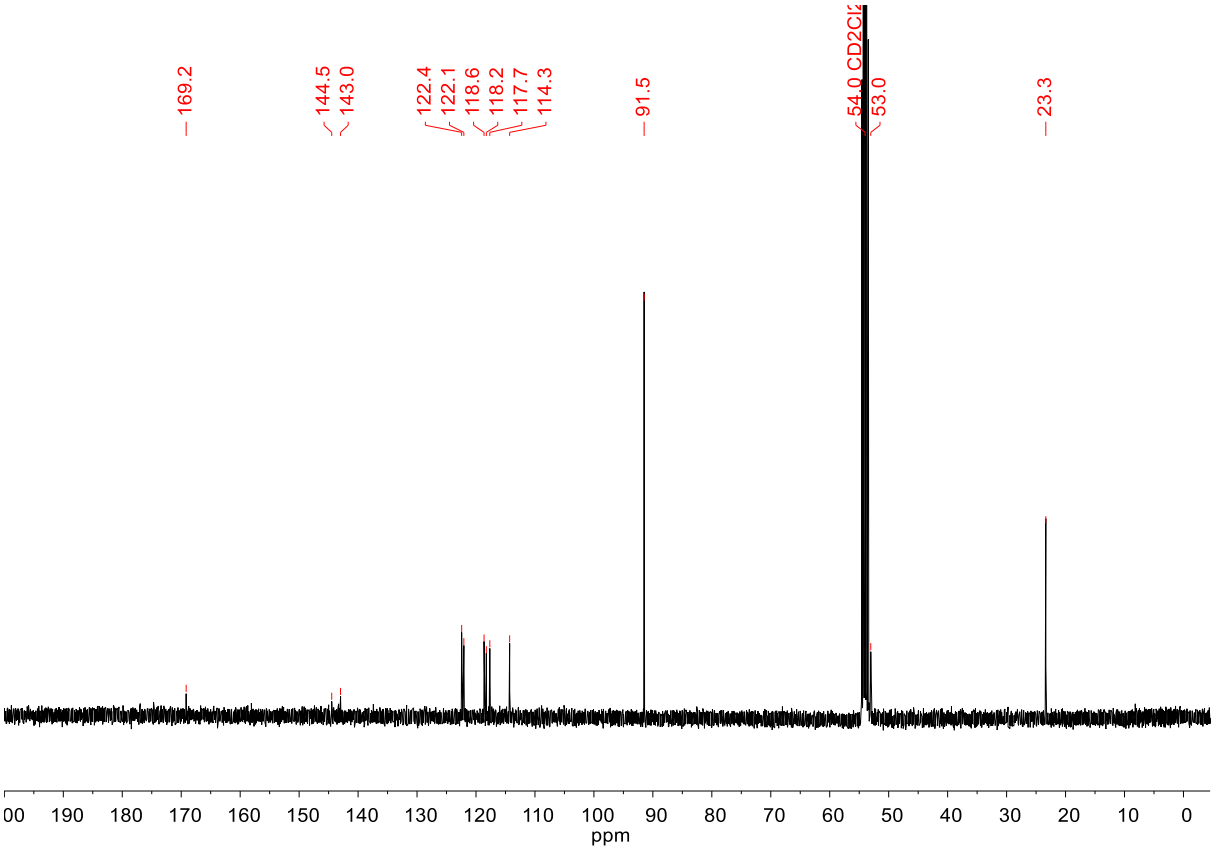

Fig. S71 ^{13}C NMR spectrum of [CuBr{NiCp(μ-**3'b**)}] (CD_2Cl_2, 101 MHz).

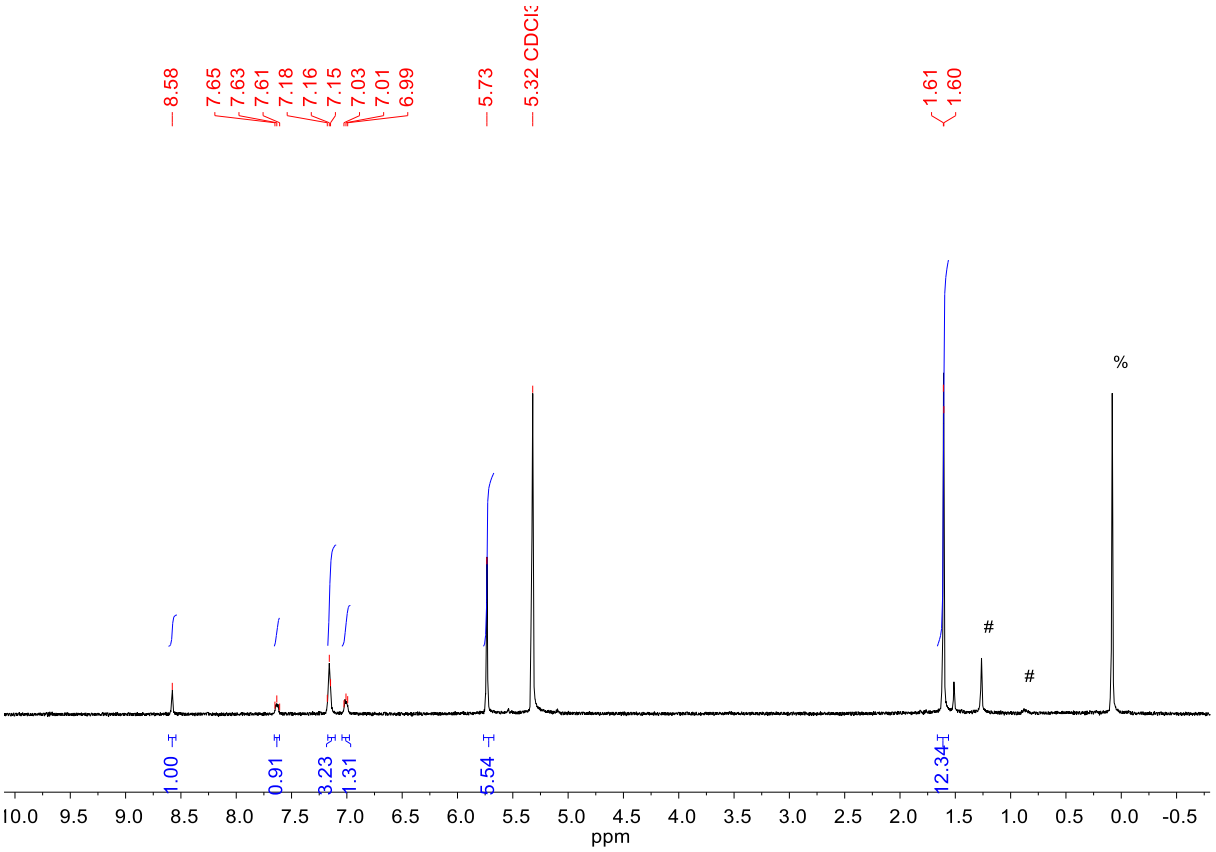

Fig. S72 ^{1}H NMR spectrum of [CuBr{NiCp(μ-**3'b**)}] (CD_2Cl_2, 400 MHz). Signals marked belong to H grease (#) and silicone grease (+).

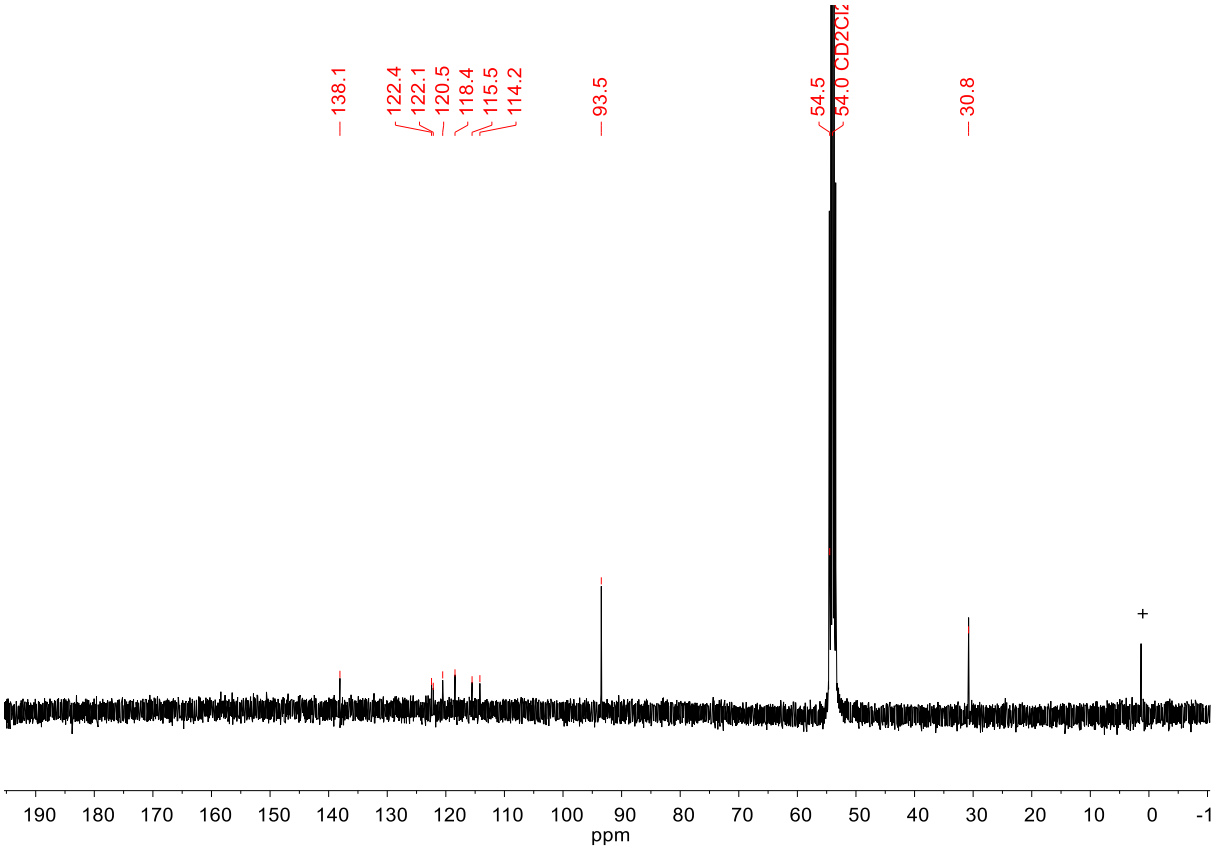

Fig. S73 ^{13}C NMR spectrum of [CuBr{NiCp(μ-**3'c**)}] (CD_2Cl_2, 101 MHz). The signal marked belongs silicone grease (+).

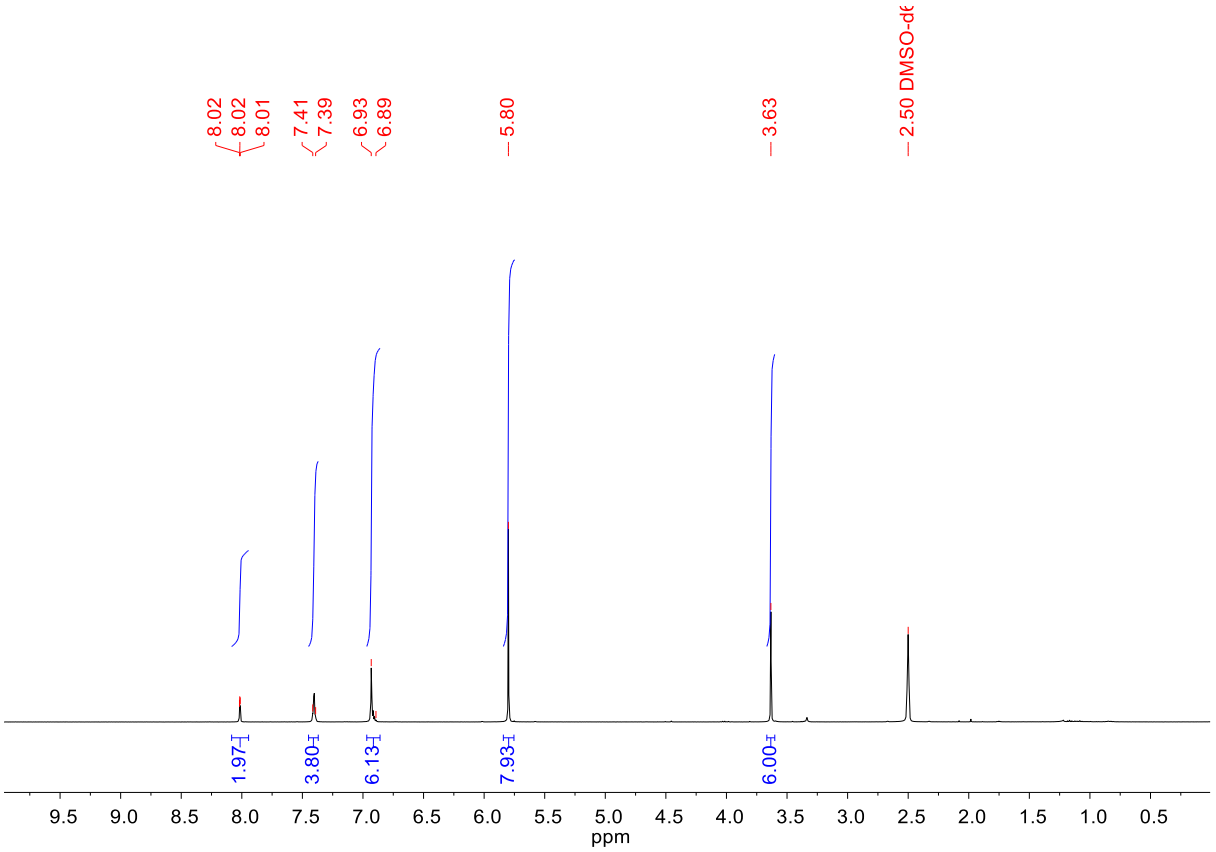

Fig. S74 ^{1}H NMR spectrum of [ZnI_2{NiCp(μ-**3'a**)}$_2$] (DMSO-d_6, 400 MHz).

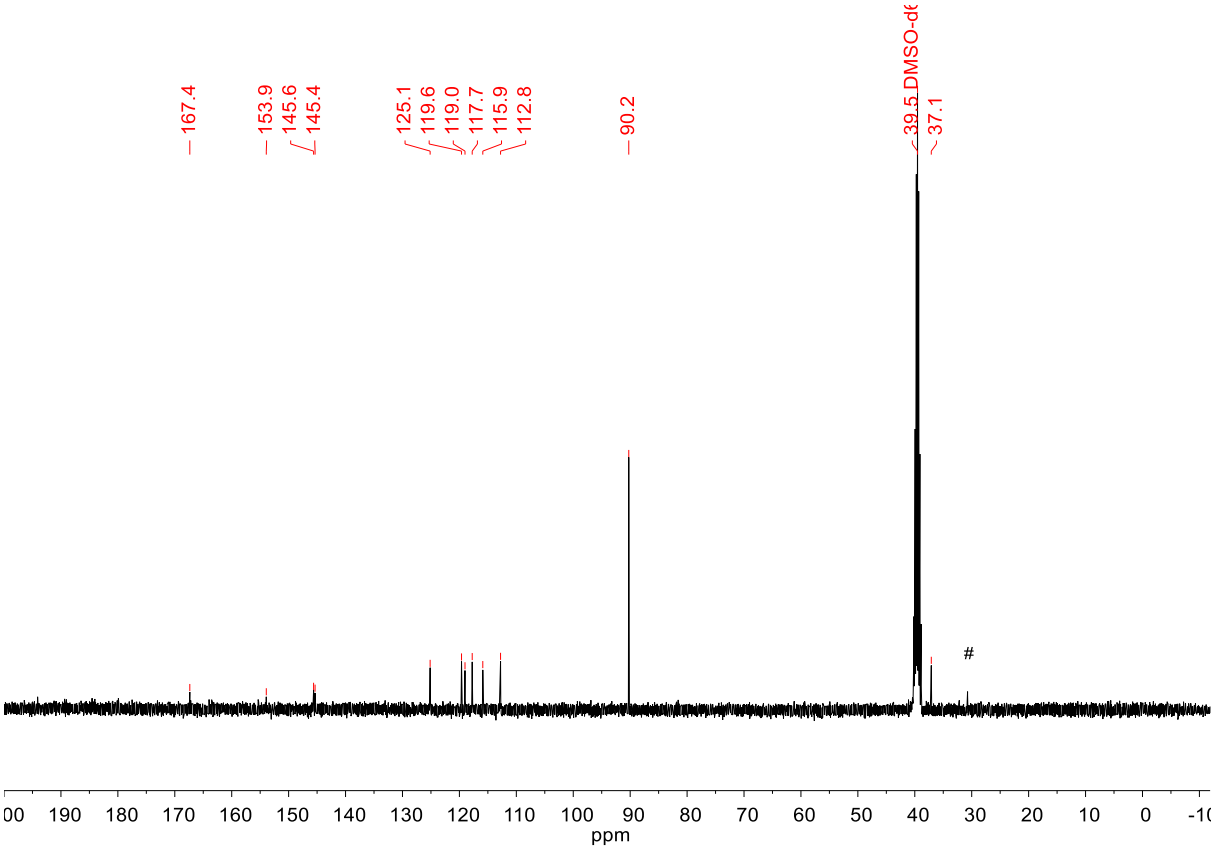

Fig. S75 ^{13}C NMR spectrum of [ZnI_2{NiCp(μ-**3'a**)}$_2$] (DMSO-d_6, 101 MHz). The signal marked belongs to an unknown impurity (#).

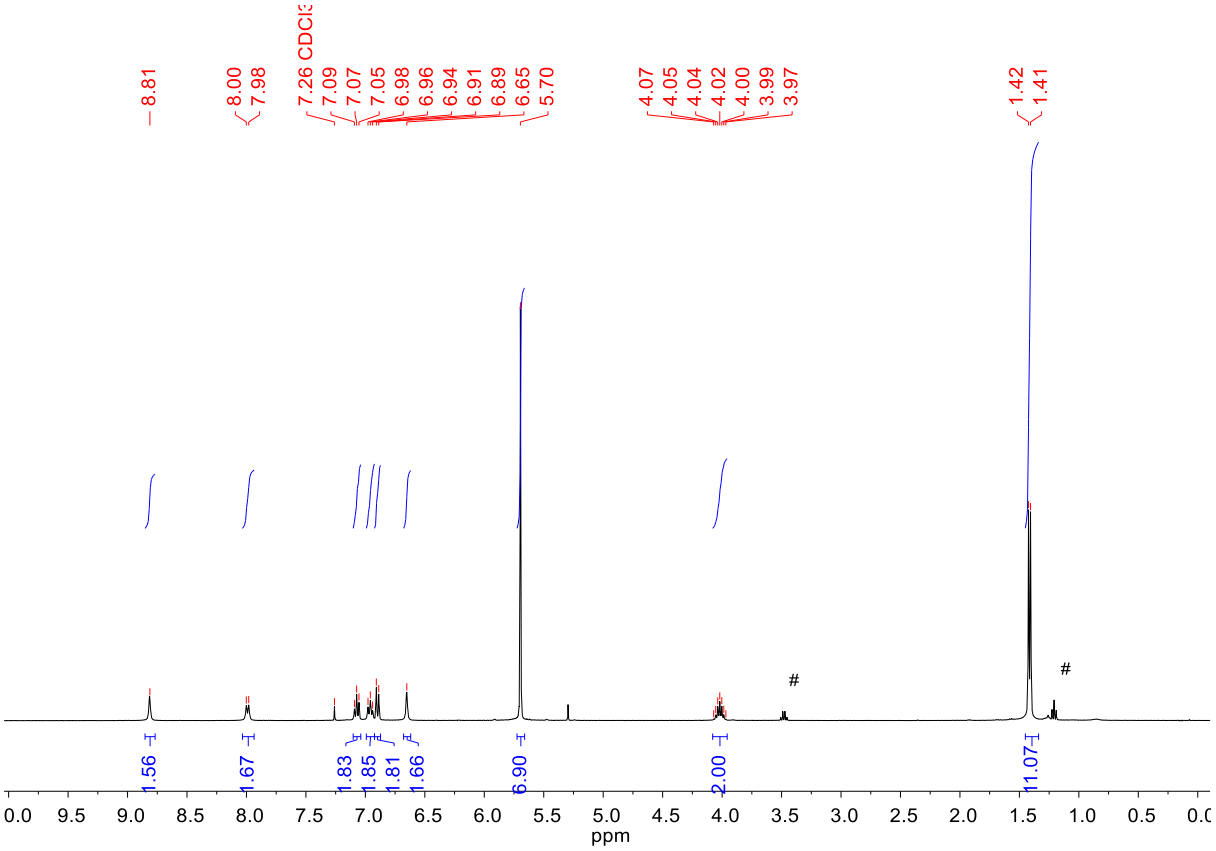

Fig. S76 ^{1}H NMR spectrum of [ZnI_2{NiCp(μ-**3'b**)}$_2$] ($CDCl_3$, 400 MHz). Signals marked belong to Et_2O (#).

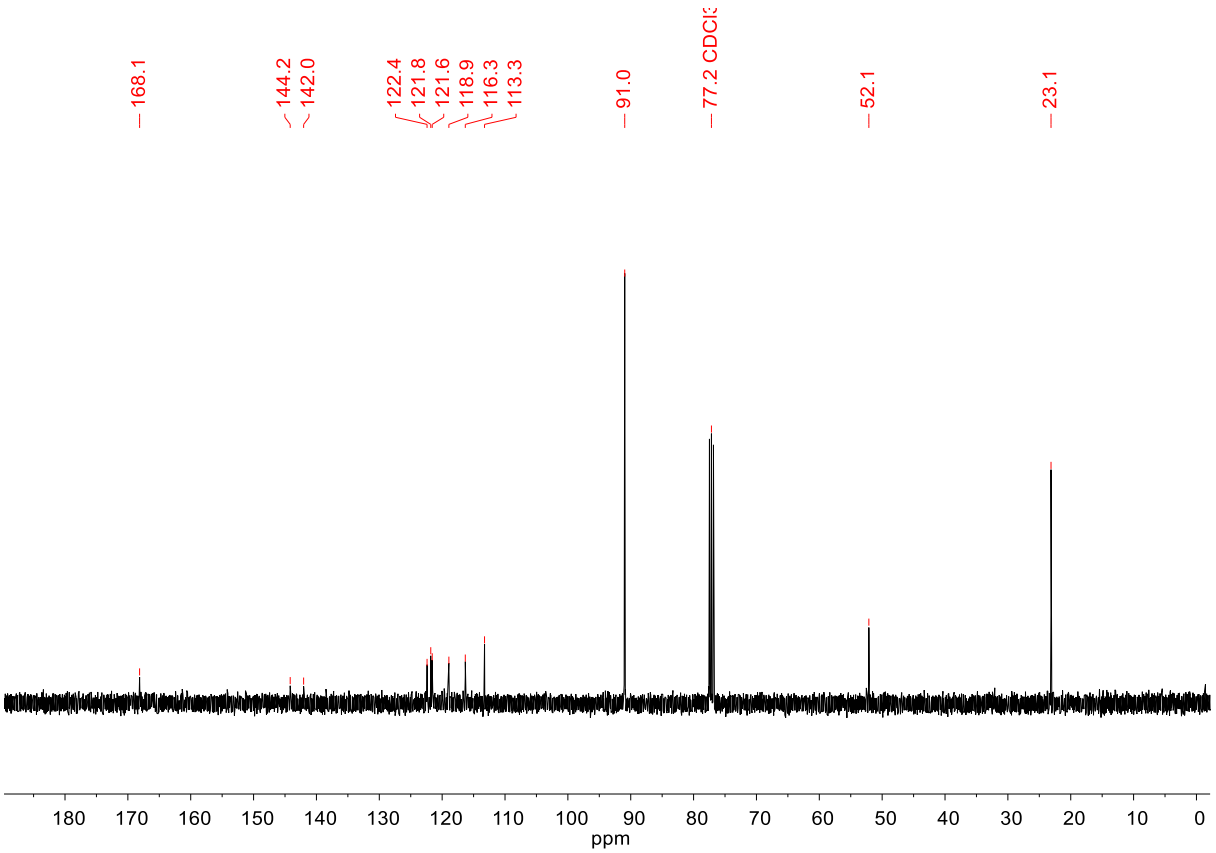

Fig. S77 ^{13}C NMR spectrum of $[ZnI_2\{NiCp(\mu\text{-}\mathbf{3'b})\}_2]$ ($CDCl_3$, 101 MHz).

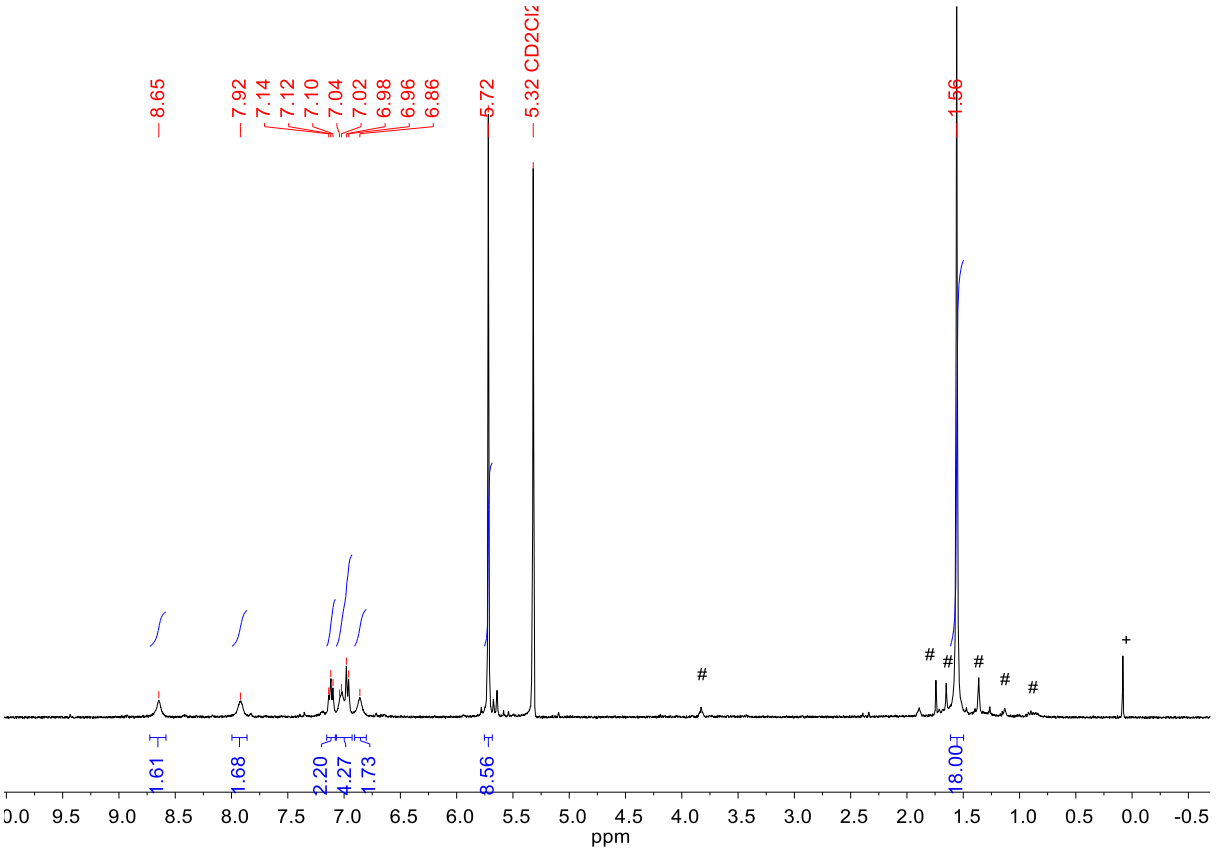

Fig. S78 ^{1}H NMR spectrum of $[ZnI_2\{NiCp(\mu\text{-}\mathbf{3'c})\}_2]$ (CD_2Cl_2, 400 MHz). Signals marked belong toan unknown impurity (#) and silicone grease (+).

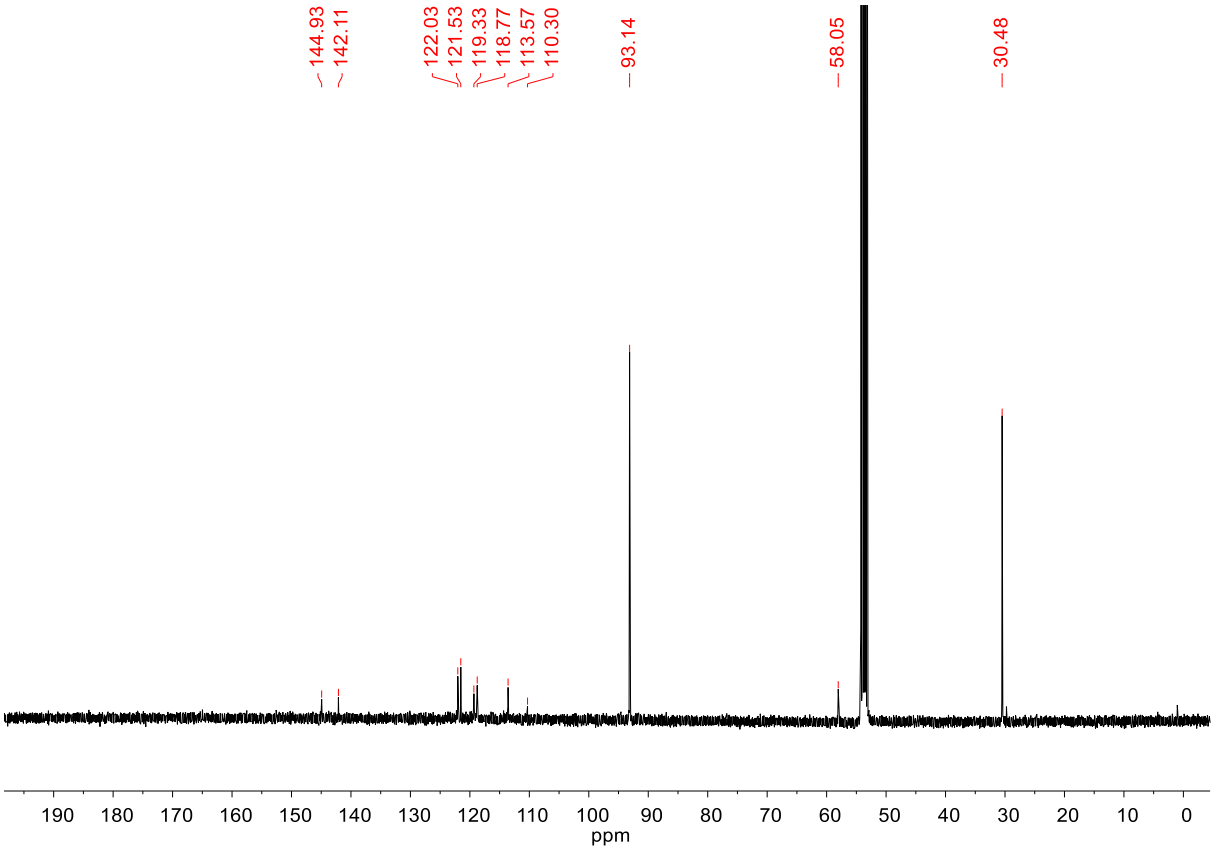

Fig. S79 ^{13}C NMR spectrum of $[ZnI_2\{NiCp(\mu\text{-}\mathbf{3'c})\}_2]$ (CD_2Cl_2, 101 MHz).

4. References

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