Supporting Information

Exploring the Bimodal Nature of a Nickel-Based Catalytic System for the Hydrogenation of Alkenes and Polycyclic Aromatic Hydrocarbons

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1 General Considerations

If not stated otherwise, all manipulations with the metal complexes were carried out either in a sealed glovebox system (MBraun, Ar 5.0, O_2 and H_2O <1 ppm) or using standard Schlenk techniques (Ar 5.0); the workup of the hydrogenation products was performed under ambient conditions without any protection from air. The hydrogenation reactions were performed in glass vials (4 mL) that were closed with screw caps equipped with cannula-pierced, PTFE-coated rubber septa. The thus-prepared vessels were then placed in a drilled Al inlet which was put in a 300 mL stainless steel autoclave (Parr Instruments). GC-MS analysis was performed on a Shimadzu GC-MS QP 2020 device using He 5.0 (Linde Gas GmbH) as carrier gas. The NMR data were collected on a Bruker AVANCE 300 MHz or 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) on the delta (δ) scale and are referenced to residual solvent signals according to the literature[1] or to TMS in case of spectra that were recorded in $CDCl_3$; the HRMS measurements were carried out on an Agilent QTOF 6520 with ESI+ ionization mode with reference masses at m/z = 121.052873 and m/z = 922.009798.

Safety Statement Concerning the Pressure Hydrogenation with Gaseous H_2

The H_2 pressure tank (200 bar, 50 l) was placed in a safety storage cabinet with an installed tapping unit and the gas container was connected to a control panel that allowed for fine adjustment of the H_2 pressure. Autoclave charging was performed in a fume hood that was equipped with a sensor which was wired to a magnetic valve. The latter instantaneously stops the gas supply in case of any H_2 leakage that might occur during the filling procedure. Furthermore, both optical and acoustic alarm signals are triggered whenever free flammable gas is detected inside the hood.

2 Materials

The solvents which were used in the syntheses of the metal complexes and hydrogenation reactions (THF, 1,4-dioxane, toluene, diethyl ether) were distilled from sodium/benzophenone, degassed with three freeze-pump-thaw cycles, and stored inside the glovebox. *n*-Hexane was purified by way of an MBraun solvent purification system, degassed, transferred to a glovebox, and stored over 3 Å molecular sieves. *n*-Heptane, *n*-pentane, ethyl acetate, dichloromethane, and triethylamine used for the workup and purification of the hydrogenation products were distilled prior to use. Benzene-d_6 and toluene-d_8 were degassed with three freeze-pump-thaw cycles, transferred to a glovebox, and stored over 3 Å molecular sieves. THF-d_8 was dried over sodium/benzophenone, vacuum transferred, and stored inside a glovebox.

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

The 3 Å molecular sieves were dried in a drying cabinet for 2 days (200 °C) followed by 300 °C under vacuum overnight before being transferred into the glovebox.

[Ni(acac)$_2$] was prepared according to a published procedure,[2] dried under vacuum overnight (100 °C), sublimed (170 °C, <0.01 mbar), and stored inside the glovebox. Commercial Cp*H was passed through a plug of activated, neutral alumina prior to use. LiCl and LiBr were dried under vacuum overnight (120 °C) and put in the glovebox. Common NHC-precursors (IMes·HCl, SIMes·HCl, IPr·HCl, SIPr·HCl) were prepared according to the literature,[3] dried under vacuum (100 °C), and transferred to the glovebox. KH was purchased as a 30 wt% dispersion in mineral oil which was filtered under Ar, washed three times with *n*-hexane, dried in vacuo, and stored in the glovebox. KO*t*Bu was purified by sublimation (140 °C, <0.01 mbar) and put in the glovebox. Acenaphthenequinone was purchased and purified according to the literature[4] and NH_4Br was dried under high vacuum (100 °C) prior to use. The syntheses of nickelocene, [Ni(acac)Cp*], IPr, SIPr, acenaphthene-fused NHC precursors, [Ni(SIPr)(η^6-toluene)], and complexes **[Ni] 1–5** are described below.

The alkene substrates **1b**, **1c**, and **1s** were prepared according to the literature.[5] Liquid alkene substrates obtained from commercial sources were passed through a plug of activated neutral alumina and transferred to a glovebox. Compounds **1e**, **1f**, **1h**, **1i**, **1m**, **1u**, **1v**, **1w**, and **1aj** were used as received. Substrates **1d**, **1l**, **1t**, and **1ai** were purified by way of Kugelrohr distillation prior to use; **1ac** and **3a** were purified by Kugelrohr distillation and then passed through a plug of activated, neutral alumina. Compounds **3b**, **3e**, **3g**, and **3h** were used as received; **3c** and **3d** were passed through a plug of activated neutral alumina. Substrates **1aa**, **1ab**, and **3d** were dissolved in *n*-pentane, filtered through a plug of activated neutral alumina, and eluted with *n*-pentane. Compounds **3f**, **3i**, and **3j** were purified by the same procedure using a mixture of *n*-pentane/toluene (1:1 by volume) instead. Phenyl-(1-phenylethylidene)amine was prepared according to a published procedure.[6] Benzaldehyde was purified through washing a DCM solution with 1 M, aqueous NaOH solution, removal of the solvent and passing the residue through a plug of activated, neutral alumina. After purification, the substrates were stored in the glovebox.

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[2] K. A. Rufanov, A. V. Shevelyuhina, K. P. Kayrite, D. B. Shpakovsky, E. R. Milaeva, *Inorg. Chim. Acta*, 2024, **567**, 122051.

[3] M. Hans, J. Lorkowski, A. Demonceau, L. Delaude, *Beilstein J. Org. Chem.*, 2015, **11**, 2318–2325.

[4] S. Redl, D. Timelthaler, P. Sunzenauer, K. Faust, C. Topf, *Organometallics*, 2023, **42**, 1639–1648.

[5] S. Redl, C. Topf, *Tetrahedron Chem*, 2024, **12**, 100089.

[6] F. H. Westheimer, K. Taguchi, *J. Org. Chem*., 1971, **36**, 1570–1572.

3 Synthetic Procedures

The preparation of starting materials and Ni-NHC complexes is described below.

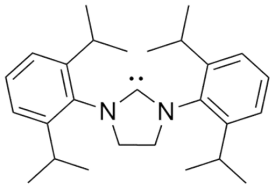
3.1 Syntheses of the Starting Materials

Synthesis of IPr

In the glovebox, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (425 mg, 1.00 mmol, 1 equiv.) and KO*t*Bu (112 mg, 1.00 mmol, 1 equiv.) were suspended in THF (5 mL) and stirred for 1 h at RT. The volatiles were removed in vacuo and the residue was extracted with toluene (8 mL). The mixture was filtered through a 0.2 µm syringe filter and the solvent removed in vacuo which yielded a white solid. Yield: 373 mg (96%).

The purity was checked by ^{1}H NMR spectroscopy (see spectral data).

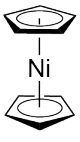
Synthesis of SIPr



In a glovebox, 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (427 mg, 1.00 mmol, 1 equiv.), KH (52 mg, 1.30 mmol, 1.3 equiv.) and KO*t*Bu (2 mg, 2 mol%) were suspended in THF (5 mL) and stirred for 16 h at RT. The volatiles were removed in vacuo and the residue was extracted with toluene (8 mL). The mixture was filtered through a 0.2 µm syringe filter and the solvent removed in vacuo which yielded a white solid. Yield: 364 mg (93%).

The purity was checked by ^{1}H NMR spectroscopy (see spectral data).

Synthesis of Nickelocene, [$NiCp_2$]



In a dry, Ar-flushed, three-neck-round bottom flask equipped with a reflux condenser, $[Ni(NH_3)_6]Cl_2$ [7] (11.59 g, 50 mmol, 1 equiv.) was suspended in THF (20 mL). NaCp[8] (8.81 g, 100 mmol, 2 equiv.) was dissolved in THF (40 mL) and added. The mixture was heated under reflux (2 h) whereupon the green suspension was filtered and the solvent removed. The product was isolated by sublimation from the thoroughly dried residue at 0.5 mbar and 90 °C. Yield: 7.5 g (79%).

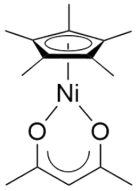
Synthesis of (acetylacetonato)(η^5-pentamethylcyclopentadienyl)nickel(II), [Ni(acac)Cp*]

[7] V. Ritleng, E. Brenner, M. J. Chetcuti, *J. Chem. Educ.*, 2008, **85**, 1646.

[8] T. K. Panda, M. T. Gamer, P. W. Roesky, *Organometallics*, 2003, **22**, 877–878.

[9] E. E. Bunel, L. Valle, J. M. Manriquez, *Organometallics*, 1985, **4**, 1680–1682.

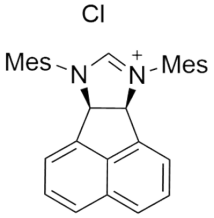
[Ni(acac)Cp*] was prepared according to a modified literature procedure.[9] Pentamethylcyclopentadiene (545 mg, 650 µL, 4 mmol) was dissolved in THF (10 mL) and 2.5 M *n*-BuLi in *n*-hexane (1.6 mL, 4.0 mmol, 1 equiv.) was added at 0 °C. The mixture was stirred at RT overnight. The white suspension was cooled to -70 °C and a solution of $Ni(acac)_2$ (1.13 g, 4.4 mmol, 1.1 equiv.) in THF (2 mL) added dropwise upon which a pale blue suspension was obtained. On reaching RT (3 h) a color change to red was observed. After stirring for another hour at RT, the volatiles were removed in vacuo and the residue was thoroughly dried at RT under vacuum. The product was isolated by sublimation from the residue (75 °C, <0.01 mbar) and isolated as a red solid. Yield: 935 mg (80%).



The purity was checked by ^{1}H NMR spectroscopy (see spectral data).

Synthesis of (6b*R*,9a*S*)-7,9-bis(2,4,6-trimethylphenyl)-6b,9a-dihydroacenaphtho[1,2-d] imidazolium chloride, SBIAN-Mes·HCl

Mes-BIANH_4 [4] (1.00 g, 2.38 mmol, 1 equiv.) and finely grinded NH_4Cl (191 mg, 3.57 mmol, 1.5 equiv.) were suspended in triethyl orthoformate (TEOF, 6 mL) and heated at 150 °C for 16 h in an Ar-flushed distillation apparatus. On cooling to RT, the precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo. The title compound was obtained as an off-white solid. Yield: 0.98 g (88%). The NMR data are in accordance with the literature.[10]



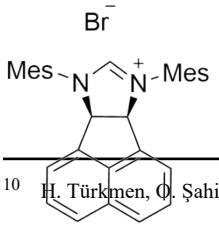
Note: An excess of NH_4Cl is used due to its slow decomposition when heated in TEOF.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.48 (dd, J = 8.2 Hz, J = 7.1 Hz, 2H), 7.09 (s, 2H), 6.89 (s, 2H), 6.87 (d, J = 7.0 Hz, 2H), 6.61 (s, 2H), 2.69 (s, 6H), 2.34 (s, 6H), 1.57 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 159.0, 140.5, 137.3, 136.2, 136.1, 135.2, 131.7, 130.5, 130.2, 129.0, 128.5, 126.7, 122.1, 70.3, 21.2, 18.9, 18.3.

Synthesis of (6b*R*,9a*S*)-7,9-bis(2,4,6-trimethylphenyl)-6b,9a-dihydroacenaphtho[1,2-d] imidazolium bromide, SBIAN-Mes·HBr

Mes-BIANH_4 (421 mg, 1.00 mmol, 1 equiv.) and NH_4Br (147 mg, 1.50 mmol, 1.5 equiv.) were suspended in triethyl orthoformate (3 mL) and heated at 115 °C for 16 h in an Ar-flushed distillation apparatus.



[10] H. Türkmen, O. Şahin, O. Büyükgüngör, B. Çetinkaya, *Eur. J. Inorg. Chem.*, 2006, **2006**, 4915–4921.

Method A: Heating was continued at 150 °C for 6 h. On cooling to RT, the precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo. The product was obtained as an off-white solid. Yield: 403 mg (79%).

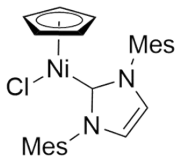
Method B: The precipitate was collected by filtration, dissolved in DCM (350 mL), filtered again, and evaporated to dryness. Yield: 471 mg (97%).

Note: Heating at 150 °C from the beginning of the reaction leads to significantly faster decomposition of NH_4Br resulting in lower yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.48 (dd, J = 8.3 Hz, J = 7.0 Hz, 2H), 7.10 (s, 2H), 6.89 (s, 2H), 6.86 (d, J = 7.0 Hz, 2H), 6.75 (s, 2H), 2.71 (s, 6H), 2.35 (s, 6H), 1.53 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 157.7, 140.7, 137.3, 136.1, 135.9, 135.5, 131.7, 130.7, 130.1, 128.8, 128.5, 126.7, 122.2, 70.6, 21.2, 19.2, 18.3.

3.2 Syntheses of the Ni-NHC Complexes



(1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene)chlorido(η^5-cyclopentadienyl) nickel(II), [Ni] 1

Similar to a literature report,[11] in a glovebox, a microwave vial (5 mL) equipped with a stirring bar was charged with 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (682 mg, 2.0 mmol, 1 equiv.), nickelocene (378 mg, 2.0 mmol, 1 equiv.) and THF (4 mL). In the microwave reactor, the mixture was kept at 110 °C for 5 min. whilst stirring (900 rpm). After that, the solvent was removed under ambient conditions and reduced pressure. The residue was dissolved in toluene (40 mL) and filtered through a plug of celite. The solution was concentrated to 3 ml and *n*-hexane was added to initiate the crystallization of the product. The solid was collected by filtration and washed with *n*-hexane. The product was obtained as a purple, crystalline solid. Yield: 836 mg (90%). The NMR data are in accordance with the literature.[12]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (s, 4H), 7.08 (s, 2H), 4.56 (s, 5H), 2.44 (s, 6H), 2.17 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 166.9, 139.1, 136.7, 135.9, 129.2, 124.4, 92.1, 21.2, 18.4.

Chlorido(η^5-cyclopentadienyl)[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]nickel(II), [Ni] 2

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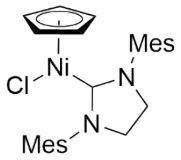
11 B. Landers, O. Navarro, *Inorg. Chim. Acta*, 2012, **380**, 350–353.

12 C. D. Abernethy, A. H. Cowley, R. A. Jones, *J. Organomet. Chem.*, 2000, **596**, 3–5.

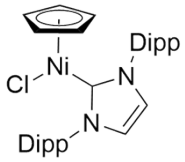


On a 2 mmol scale, **[Ni] 2** was prepared by the same procedure as for **[Ni] 1** but the reaction mixture was heated for 30 min. The product was obtained as a purple, crystalline solid. Yield: 818 mg (88%). The NMR data are in accordance with the literature.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (s, 4H), 4.54 (s, 5H), 3.90 (s, 4H), 2.38 (s, 18H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.8, 138.3, 136.9, 136.8, 129.5, 92.5, 51.0, 21.2, 18.5.

Chlorido(η^5-cyclopentadienyl)[1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene]nickel(II), [Ni] 3



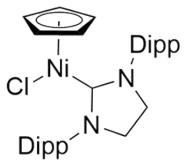
[Ni] 3 was prepared by the same procedure as for **[Ni] 1** using 1,3-is(2,6-diisopropylphenyl)imidazolium chloride (213 mg, 0.5 mmol, 1 equiv.), nickelocene (95 mg, 0.5 mmol, 1 equiv.), and dry THF (1 mL) whereby a 2 mL microwave vial was used. The product was obtained as a red, crystalline solid. Yield: 183 mg (66%). The NMR data are in accordance with the literature.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.2 Hz, J = 7.3 Hz, 2H), 7.41 (d, J = 7.7 Hz, 4H), 7.13 (s, 2H), 4.51 (s, 5H), 2.85 (sept, J = 6.8 Hz, 4H), 1.42 (d, J = 6.8 Hz, 12H), 1.09 (d, J = 6.9 Hz, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4, 146.4, 136.7, 130.2, 125.5, 124.0, 92.1, 28.6, 26.2, 22.5.

[13] R. A. Kelly, N. M. Scott, S. Díez-González, E. D. Stevens, S. P. Nolan, *Organometallics*, 2005, **24**, 3442–3447.

(1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene)chlorido(η^5-cyclopentadienyl) nickel(II), [Ni] 4



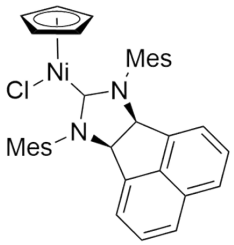
A pressure tube was charged with 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (854 mg, 2.0 mmol, 1 equiv.), nickelocene (378 mg, 2.0 mmol, 1 equiv.), and dry THF (4 mL). The mixture was stirred at 80 °C for 20 h. Under aerobic conditions, the volatiles were removed, the residue dissolved in toluene (25 mL), and filtered through a plug of celite. The solution was concentrated to 2 mL and *n*-hexane was added to initiate crystallization of the product. The solid was collected by filtration and washed with *n*-hexane. The product was obtained as a purple, crystalline solid. Yield: 859 mg (78%). The NMR data are in accordance with the literature.[13]

Note: In this case, using standard oil-bath heating at lower temperature overnight gave a higher yield and a product of higher purity compared to the synthesis performed under microwave conditions as used for the preparation of **[Ni] 2**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.4 Hz, J = 7.0 Hz, 2H), 7.37–7.34 (m, 4H), 4.48 (s, 5H), 3.99 (s, 4H), 3.30 (sept, J = 6.7 Hz, 4H), 1.47 (d, J = 6.7 Hz, 12H), 1.23 (d, J = 6.9 Hz, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 203.0, 147.5, 137.3, 129.3, 124.4, 92.5, 53.4, 28.6, 26.7, 23.3.

Chlorido((6b*R*,9a*S*)-7,9-dimesityl-6b,9a-dihydro-acenaphtho[1,2-d]imidazol-8-ylidene) (η^5-cyclopentadienyl) nickel(II), [Ni] 5



On a 0.5 mmol scale and using THF (2 mL) as the solvent, **[Ni] 5** was prepared in the same fashion as **[Ni] 4**. The reaction mixture was stirred for 48 h at 120 °C and the product obtained as a purple, crystalline solid. Yield: 236 mg (80%).

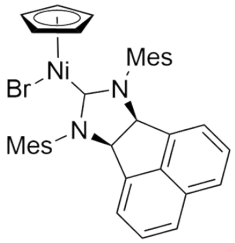
Crystals suitable for SC-XRD analysis were grown by slow diffusion of Et_2O into as solution of **[Ni] 5** in THF.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, J = 8.2 Hz, 2H), 7.41 (dd, J = 8.2 Hz, J = 7.1 Hz, 2H), 7.18 (s, 2H), 7.00 (s, 2H), 6.85 (d, J = 6.9 Hz, 2H), 6.00 (s, 2H), 4.47 (s, 5H), 2.66 (s, 6H), 2.44 (s, 6H), 1.47 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 201.3, 139.2, 138.3, 138.0, 137.0, 136.9, 135.7, 131.5, 130.1, 129.4, 128.0, 125.5, 121.9, 92.7, 70.9, 21.3, 19.3, 19.2.

HRMS (ESI+): m/z calculated for $C_{36}H_{35}N_2Ni^+$ $[M–Cl]^+$: 553.2149; found 553.2151.

Bromido((6b*R*,9a*S*)-7,9-dimesityl-6b,9a-dihydro-acenaphtho[1,2-d]imidazol-8-ylidene) (η^5-cyclopentadienyl) nickel(II), [Ni] 5-Br



On a 0.5 mmol scale and using THF (2 mL) as the solvent, **[Ni] 5-Br** was prepared in the same fashion as **[Ni] 4**. The reaction mixture was stirred for 16 h at 140 °C and the product was obtained as a purple, crystalline solid. Yield: 140 mg (44%).

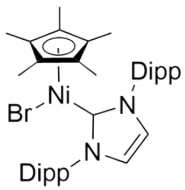
Crystals suitable for SC-XRD analysis were obtained by slow diffusion of *n*-hexane into as solution of **[Ni] 5-Br** in toluene.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.39 (dd, J = 8.2 Hz, J = 6.9 Hz, 2H), 7.17 (br, 2H), 6.98 (br, 2H), 6.80 (d, J = 6.9 Hz, 2H), 6.00 (s, 2H), 4.54 (s, 5H), 2.71 (s, 6H), 2.43 (s, 6H), 1.42 (br, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 201.2, 139.2, 138.2, 137.8, 137.1, 137.1, 135.6, 131.5, 130.2, 129.3, 128.0, 125.5, 121.9, 92.9, 70.9, 21.3, 19.9, 19.3.

HRMS (ESI+): m/z calculated for $C_{36}H_{35}N_2Ni^+$ $[M–Br]^+$: 553.2149; found 553.2146.

(1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene)bromido(η^5-pentamethylcyclopentadienyl) nickel(II), [Ni] 3-Br-Cp*



The following procedure was inspired by the one used to prepare the analogous PPh_3 complex.[14] In a glovebox, [Ni(acac)Cp*] (146 mg, 0.50 mmol, 1 equiv.) and IPr (195 mg, 0.50 mmol, 1 equiv.) were dissolved in THF (3 mL) to obtain a red solution. Anhydrous LiBr (174 mg, 2.0 mmol, 4 equiv.) was dissolved in THF (1 mL) and then added whereupon an immediate color change to deep purple occurred. After the mixture had been stirred for a period of 15 min, the solvent was removed in vacuo, and the residue thoroughly dried in vacuo. The solid was extracted with a mixture of toluene/*n*-hexane (1:1 by volume, 8 mL), filtered over celite, and hereafter the volatiles were removed, leaving behind the target complex as deep purple, needle-like crystals. Yield: 290 mg (88%).

Crystals suitable for SC-XRD analysis were grown by slow evaporation of a solution of **[Ni] 3-Br-Cp*** in toluene.

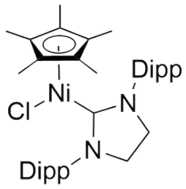
^{1}H NMR (300 MHz, C_6D_6): δ 7.39 (dd, J = 7.8 Hz, J = 1.4 Hz, 2H), 7.30 (app t, J = 7.7 Hz, 2H), 7.11 (dd, J = 7.6 Hz, J = 1.5 Hz, 2H), 6.67 (s, 2H), 4.35 (sept, J = 6.7 Hz, 2H), 2.33 (sept, J = 6.7 Hz, 2H), 1.67 (d, J = 6.5 Hz, 6H), 1.24 (d, J = 6.8 Hz, 6H), 1.18 (s, 15H), 1.08 (d, J = 6.9 Hz, 6H), 0.85 (d, J = 6.7 Hz, 6H).

[14] J. Liu, J.-Y. Chen, M. Jia, B. Ming, J. Jia, R.-Z. Liao, C.-H. Tung, W. Wang, *ACS Catal.*, 2019, **9**, 3849–3857.

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 179.5, 149.0, 145.4, 137.6, 129.7, 125.8, 125.4, 122.7, 102.1, 28.7, 28.3, 26.8, 26.5, 23.8, 22.3, 10.1.

HRMS (ESI+): m/z calculated for $C_{37}H_{51}N_2Ni^+$ [M–Br]$^+$: 581.3401; found 581.3403.

(1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene)chlorido(η^5-pentamethyl cyclopentadienyl)nickel(II), [Ni] 4-Cp*



[Ni] 4-Cp* was prepared by the same procedure as **[Ni] 3-Br-Cp*** using [Ni(acac)Cp*] (146 mg, 0.50 mmol, 1 equiv.), SIPr (195 mg, 0.50 mmol, 1 equiv.), and anhydrous LiCl (43 mg, 1.0 mmol, 2 equiv.) in THF (2 mL). The product was obtained as a deep purple, crystalline solid. Heating at 55 °C under vacuum removed intercalated toluene whereupon the crystals lost their shiny, deep purple color and changed to a dull, lighter purple. Yield: 260 mg (84%).

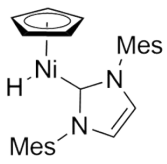
Crystals suitable for SC-XRD analysis were obtained by slow evaporation of a solution of **[Ni] 4-Cp*** in toluene.

^1H NMR (300 MHz, C_6D_6): δ 7.39 (dd, J = 7.7 Hz, J = 1.2 Hz, 2H), 7.28 (app t, J = 7.7 Hz, 2H), 7.10 (dd, J = 7.6 Hz, J = 1.2 Hz, 2H), 4.55 (sept, J = 6.7 Hz, 2H), 3.76–3.44 (m, 4H), 2.90 (sept, J = 6.7 Hz, 2H), 1.71 (d, J = 6.4 Hz, 6H), 1.29 (d, J = 6.7 Hz, 6H), 1.17 (d, J = 6.9 Hz, 6H), 1.12 (s, 15H), 1.01 (d, J = 6.7 Hz, 6H).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 212.0, 151.2, 146.5, 138.6, 129.2, 126.1, 123.5, 102.5, 53.8, 28.7, 28.5, 27.2, 27.0, 24.8, 23.3, 10.1.

HRMS (ESI+): m/z calculated for $C_{37}H_{53}N_2Ni^+$ [M–Cl]$^+$: 583.3557; found 583.3553.

(1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene)(η^5-cyclopentadienyl)hydridonickel(II), [Ni] 1-H

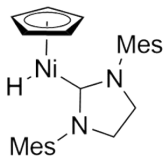


To a solution of **[Ni] 1** (930 mg, 2.0 mmol, 1 equiv.) in THF (10 mL) was added dropwise a 1 M solution of $LiHBEt_3$ in THF (2.1 mL, 2.1 mmol, 1.05 equiv.) at -50 °C. After that, cooling was discontinued and the mixture stirred for 1 h. Solvents were removed in vacuo and the residue was triturated with *n*-hexane (5 mL). The supernatant was discarded, the residue extracted with toluene (7 mL), and filtered through a 0.2 µm syringe filter. Upon removal of the solvent, the product was obtained as an orange solid. If necessary, the title compound can be recrystallized by concentrating a pertinent toluene solution and overlayering it with *n*-hexane to obtain dark orange crystals. Crude yield: 762 mg (89%); Recrystallized product: (586 mg; 68%). The NMR data are in accordance with the literature.[15]

^{1}H NMR (300 MHz, C_6D_6): δ 6.80 (s, 4H), 6.14 (s, 2H), 5.00 (s, 5H), 2.12 (s, 6H), 2.11 (s, 12H), -23.25 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 185.3 (d, J = 10.2 Hz), 138.6, 138.3, 135.8, 129.2, 121.0, 86.8, 21.1, 18.3.

(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene)(η^5-cyclopentadienyl)hydrido nickel(II), [Ni] 2-H



To a solution of **[Ni] 2** (699 mg, 1.5 mmol) in toluene (12 mL) was added dropwise a 1 M solution of $NaHBEt_3$ in THF (1.5 mL, 1.5 mmol, 1 equiv.) at 0 °C. After that, cooling was discontinued and the mixture stirred for 1 h. The volatiles were removed in vacuo, the residue was extracted with toluene (10 mL), and then filtered through a 0.2 μm syringe filter. The filtrate was reduced to a small volume (1.5 ml), overlayered with *n*-hexane (5 mL), and then stored in a glovebox freezer (-40 °C) overnight. The product was obtained as dark orange crystals. Yield: 538 mg (83%).

Note: Application of the conditions used for **[Ni] 1-H** produced the 17e complex **[Ni(η^5-Cp)(SIMes)]** as the major side product.

Crystals suitable for single SC-XRD analysis were obtained by slow evaporation of a solution of **[Ni] 2-H** toluene.

^{1}H NMR (300 MHz, C_6D_6): δ 6.83 (br s, 4H), 4.92 (s, 5H), 3.09 (s, 4H), 2.27 (s, 12H), 2.13 (s, 6H), -22.55 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 212.9 (d, J = 13.9 Hz), 139.0, 137.4, 136.7, 129.5, 87.1, 49.8, 21.1, 18.3.

HRMS (ESI+): m/z calculated for $C_{26}H_{31}N_2Ni^+$ $[M–H]^+$: 429.1836; found 429.1850.

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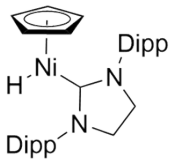
15 L. P. Bheeter, M. Henrion, L. Brelot, C. Darcel, M. J. Chetcuti, J. Sortais, V. Ritleng, *Adv. Synth. Catal.*, 2012, **354**, 2619–2624.

(1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene)(η^5-cyclopentadienyl)hydrido nickel(II), [Ni] 4-H



To a solution of **[Ni] 4** (825 mg, 1.50 mmol) in toluene (12 mL) was added dropwise a 1 M solution of $NaHBEt_3$ in THF (1.5 mL, 1.5 mmol, 1 equiv.) at RT whereupon a color change from deep red-purple to orange occurred. The reaction mixture was stirred for 1 h and the solvents were then removed in vacuo. Hereafter, the residue was extracted with toluene (10 mL) and filtered through a 0.2 µm syringe filter. The filtrate was reduced to a small volume (3 mL), overlayered with *n*-hexane (5 mL), and stored overnight inside the glove freezer (-40 °C). The supernatant was decanted, the residue washed with *n*-hexane (2 mL), and dried in vacuo. The product was obtained as an orange crystalline solid. Yield: 633 mg (82%).

Note: Application of the conditions used for **[Ni] 1-H** furnished the 17e complex **[Ni(η^5-Cp)(SIPr)]** as the main product.

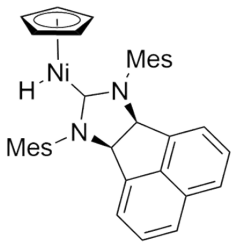
Crystals suitable for SC-XRD analysis were grown by overlayering a solution of **[Ni] 4-H** in toluene with *n*-hexane and storing it in the glovebox freezer (-40 °C).

^{1}H NMR (300 MHz, C_6D_6): δ 7.23 (dd, J = 8.5 Hz, J = 6.7 Hz, 2H), 7.14–7.11 (m, 4H), 4.86 (s, 5H), 3.39 (s, 4H), 3.23 (sept, J = 6.8 Hz, 4H), 1.52 (d, J = 6.8 Hz, 12H), 1.18 (d, J = 6.9 Hz, 12H), -23.02 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 147.3, 139.3, 129.0, 124.4, 87.4, 53.0, 28.9, 25.7, 24.0.

HRMS (ESI+): m/z calculated for $C_{32}H_{43}N_2Ni^+$ $[M–H]^+$: 513.2775; found 513.2777.

((6bR,9aS)-7,9-dimesityl-6b,9a-dihydro-acenaphtho[1,2-d]imidazol-8-ylidene) (η^5-cyclopenta dienyl)hydrido nickel(II), [Ni] 5-H



On a 1.0 mmol scale, **[Ni] 5-H** was prepared in the same fashion as **[Ni] 2-H**. The product was obtained as an orange, crystalline solid. Yield: 426 mg (76%).

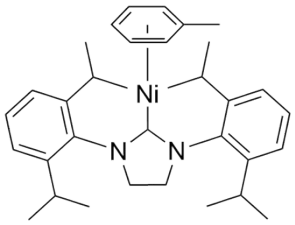
Crystals suitable for single SC-XRD analysis were obtained by slow diffusion of *n*-hexane into a solution of **[Ni] 5-H** in toluene.

^{1}H NMR (300 MHz, C_6D_6): δ 7.47 (d, J = 8.2 Hz, 2H), 7.09 (dd, J = 8.2 Hz, J = 7.0 Hz, 2H), 6.98 (br, 2H), 6.82 (br, 2H), 6.72 (d, J = 6.9 Hz, 2H), 5.43 (s, 2H), 4.89 (s, 5H), 2.44 (s, 6H), 2.20 (s, 6H), 1.78 (s, 6H), -22.55 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 147.3, 139.3, 129.0, 124.4, 87.4, 53.0, 28.9, 25.7, 24.0.

HRMS (ESI+): m/z calculated for $C_{36}H_{35}N_2Ni^+$ $[M–H]^+$: 553.2149; found 553.2173.

[NiSIPr(η^6-toluene)]



Under an Ar atmosphere, a glass vial (4 mL) equipped with a stirring bar was charged with **[Ni] 4-H** (103 mg, 0.20 mmol) and toluene (2 mL). The vial was closed with a septum screw cap and taken out from the glovebox. The septum was pierced with a cannula and the vial transferred to an Ar-flushed autoclave. The latter was tightly sealed, purged with H_2 (3x10 bar, 2x20 bar), and then pressurized with 20 bar H_2. The mixture was stirred for 16 h at RT. On completion of the reaction, the pressure was released from the vessel, the autoclave disassembled, and the cannula quickly removed. The deep red solution was transferred to a dry Schlenk flask with a syringe whereupon the volatiles were removed in vacuo. Upon drying under vacuum, the title compound was obtained as a red solid. Yield: 106 mg (98%). The NMR data are well in accord with the literature.[16]

Notes: This is an alternative method for the preparation of this literature-known compound.[17] The established procedure employs [Ni(COD)$_2$] and an equimolar amount of the free carbene SIPr. It is described that, in spite of all lab-technical precautions (including the assemblage of the autoclave in the glovebox), formation of a small amount of nickel black was observed.[16] Since the high solubility of the title compound renders its recrystallization from hexamethyldisiloxane (HMDSO) uneconomical, the quality of the highly sensitive starting materials will strongly impact the purity of the product. Employing the 18e starting complex **[Ni] 4-H** instead effectively remedies issues associated with the instability of the starting materials, i.e., SIPr and [Ni(COD)$_2$].

The NMR data correspond to in-situ formed complex [**Ni(SIPr)(η^6-benzene-d$_6$)**].

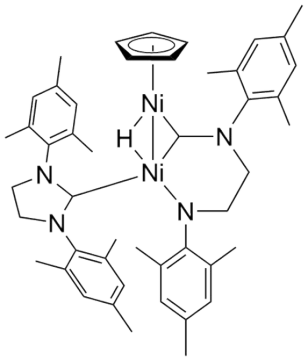
^{1}H NMR (300 MHz, C_6D_6): 7.28 (dd, J = 8.4 Hz, J = 6.8 Hz, 2H), 7.18 (overlapping with C_6D_5H, 4H), 3.35 (s, 4H), 3.14 (sept, J = 6.9 Hz, 4H), 1.46 (d, J = 6.8 Hz, 12H), 1.21 (d, J = 7.0 Hz, 12H).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6): 213.8, 147.9, 140.0, 128.0, 123.8, 52.1, 28.8, 25.2, 24.3.

16 N. I. Saper, J. F. Hartwig, *J. Am. Chem. Soc*., 2017, **139**, 17667–17676.

17 Y. Hoshimoto, Y. Hayashi, H. Suzuki, M. Ohashi, S. Ogoshi, *Organometallics*, 2014, **33**, 1276–1282.

[Ni$_2$]H-SIMes



A microwave vial (20 mL) equipped with a stirring bar was charged with **[Ni] 2-H** (216 mg, 0.5 mmol) and diethyl ether (5 mL). Then, the vial was closed and taken out from the glovebox. The septum was pierced with a cannula and placed in an Ar-flushed autoclave which was closed, purged with H_2 (3x10 bar, 2x20 bar), and pressurized with 20 bar H_2. The steel vessel was then placed in a preheated water bath and the reaction mixture stirred for 7 h at 45 °C. On completion of the reaction, the autoclave was cooled to RT, the over pressure released, and the vessel disassembled. The cannula was quickly removed and the reaction mixture transferred to a dry filtration apparatus via a syringe. The precipitated, crystalline orange-brown solid was collected by filtration, washed with *n*-hexane, and eventually dried in vacuo. Yield: 160 mg (81%).

Crystals suitable for SC-XRD analysis were grown by slow evaporation of a solution of **[Ni$_2$]H-SIMes** in THF.

Note: The compound is thermally stable in the solid state but unstable (in equilibrium) in solution.

^{1}H NMR (300 MHz, THF-d_8): δ 6.85 (s, 2H), 6.71 (br, 4H), 6.25 (s, 2H), 4.57 (s, 5H), 3.80 (s, 4H), 3.07–3.04 (m, 2H), 2.89–2.86 (m, 2H), 2.31 (br, 12H), 2.26 (s, 6H), 2.24 (s, 3H), 2.10 (s, 3H), 2.06 (s, 6H), 1.91 (s, 6H), -20.50 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, THF-d_8): δ 287.5, 219.5, 158.8, 154.4, 137.2, 137.1, 136.9, 134.1, 129.7, 129.2, 129.1, 124.2, 88.2, 63.3, 56.9, 51.1, 22.5, 21.2, 21.0, 20.8, 18.0.

HRMS (ESI+): m/z calculated for $C_{47}H_{59}N_4Ni_2^+$ $[M+H]^+$: 795.3442; found 795.3446.

4 Optimization of the Alkene Hydrogenation

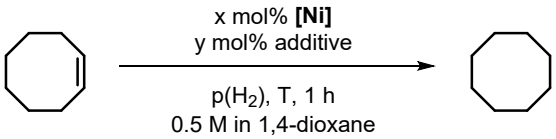


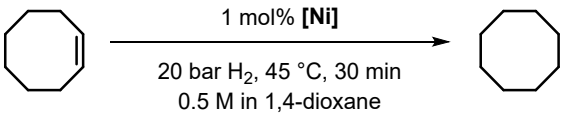
Table S1. Combined Screening Results for the Hydrogenation of Cyclooctene Under in-situ Conditions

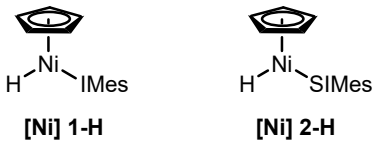
Entry	[Ni]	[Ni] loading / mol%	Additive	Additive loading / mol%	$p(H_2)$ / bar	T / °C	Conversion[a] / %
1	**[Ni] 2**	2	$LiHBEt_3$	4	20	60	>99
2	**[Ni] 2**	2	LiHMDS	30	20	60	<5
3[b]	**[Ni] 2**	2	LiHMDS	30	20	60	>99
4	**[Ni] 1**	1	$LiHBEt_3$	2	20	45	15
5	**[Ni] 2**	1	$LiHBEt_3$	2	20	45	25
6	**[Ni] 3**	1	$LiHBEt_3$	2	20	45	>99
7	**[Ni] 4**	1	$LiHBEt_3$	2	20	45	>99
8	**[Ni] 5-Cl**	1	$LiHBEt_3$	2	20	45	88
9	**[Ni] 5-Br**	1	$LiHBEt_3$	2	20	45	61
10	**[Ni] 4-Cp***	1	$LiHBEt_3$	2	20	45	>99
11	**[Ni] 3**	1	$LiHBEt_3$	2	5	45	22
12	**[Ni] 4**	1	$LiHBEt_3$	2	5	45	34
13	**[Ni] 5-Cl**	1	$LiHBEt_3$	2	5	45	29

All reactions were performed on a 0.5 mmol scale using 1.0 mL of solvent.

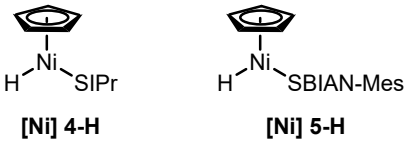
[a]Determined by way of GC-MS analysis using *n*-hexadecane as standard

[b]16 h reaction time





[Ni] 1-H **[Ni] 2-H**



[Ni] 4-H **[Ni] 5-H**

Table S2. Testing of Different Defined Hydride Complexes Without Preactivation

Entry	[Ni]	Conversion[a] / %
1	**[Ni] 1-H**	4
2	**[Ni] 2-H**	6
3	**[Ni] 4-H**	30
4	**[Ni] 5-H**	6

[a]Determined by way of GC-MS analysis using *n*-hexadecane as standard

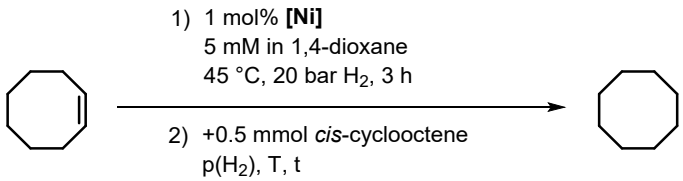


Table S3. Testing of Different Defined Hydride Complexes With Preactivation

Entry	[Ni]	p(H_2) / bar	T / °C	t / min	Conversion[a] / %
1	**[Ni] 1-H**	20	45	5	2
2	**[Ni] 2-H**	20	45	5	26
3	**[Ni] 4-H**	20	45	5	>99
4	**[Ni] 5-H**	20	45	5	95
5	**[Ni] 1-H**	5	RT	30	12
6	**[Ni] 2-H**	5	RT	30	39
7	**[Ni] 4-H**	5	RT	30	>99
8	**[Ni] 5-H**	5	RT	30	>99

[a]Determined by way of GC-MS analysis using *n*-hexadecane as standard

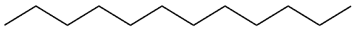
5 Catalytic Reactions

The catalytic hydrogenation reactions were performed in two ways. **Mode I** refers to reactions in which the substrate is present from the start while **Mode II** involves reaction of the precatalyst with H_2 prior substrate addition. General procedures can be found in the experimental part of the manuscript.

5.1 Catalytic Hydrogenation Without Preactivation (Mode I)

In a glovebox, glass vials (4 mL) equipped with a stirring bar were charged with the substrate (0.50 mmol). The respective amount of precatalyst (**[Ni] 4-H**, 1 mol% or as stated) was added as a stock solution. Then, solvent was added until the total volume amounted to 1.0 mL. The vials were closed with a screw cap equipped with a PTFE-coated rubber septum, placed inside an Al inlet, and taken out from the glovebox. Each septum was pierced with a cannula and the vials together with the inlet were placed inside the autoclave which was then flushed with Ar for 15 s, tightly sealed, purged with H2 (3x10 bar, 2x20 bar) and pressurized with 20 bar H_2. The thus-prepared steel vessel was then placed into a preheated (45 °C) water bath and the reaction mixture stirred for 3 h. After cooling to room temperature, the overpressure was released and the autoclave was disassembled. The reaction mixtures were analyzed via GC-MS. If conversions or yields were determined via GC-MS analysis, stock solution of *n*-hexadecane was added after the reaction. Standard conditions: 1 mol% **[Ni] 4-H**, 1,4-dioxane, 45 °C, 20 bar H_2, 3 h. Deviating reaction conditions and workup methods are described below for each substrate.

Dodecane, 2b



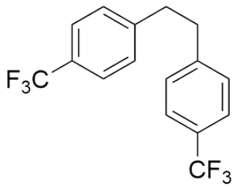
cis-6-Dodecene was hydrogenated using the standard procedure with diethyl ether as the solvent. On completion of the reaction the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2b** was obtained as a colorless liquid (78 mg, 90%).

^{1}H NMR (300 MHz, $CDCl_3$): 1.26 (br, 20H), 0.88 (t, J = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 32.2, 29.9, 29.9, 29.6, 22.9, 14.3.

MS (EI, 70eV) m/z (%): 171.2 (13.2), 170.2 (100.0) M^+.

4,4'-trifluoromethyl-1,2-diphenylethane, 2c



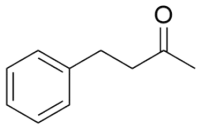
cis-4,4'-Trifluoromethylstilbene was hydrogenated using the standard procedure. On completion of the reaction the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2c** was obtained as a white solid. Minor amounts of over-hydrogenated products were detected in the GC-MS analysis. The yield of **2c** (94%) was therefore determined by way of ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.

^{1}H NMR (300 MHz, $CDCl_3$): 7.51 (d, J = 8.0 Hz, 4H), 7.22 (d, J = 8.1 Hz, 4H), 2.96 (s, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 145.3 (app d, $J_{C\text{-}F}$ = 1.3 Hz), 128.9, 128.7 (q, $J_{C\text{-}F}$ = 32.5 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.5 (q, $J_{C\text{-}F}$ = 271.4 Hz), 37.3.

MS (EI, 70eV) m/z (%): 319.1 (17.7), 318.1 (100.0) M^+.

4-Phenylbutan-2-one, 2e



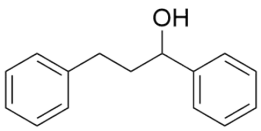
Benzylideneacetone was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by column chromatography over silica with *n*-heptane/ethyl acetate (10:1 by volume) as eluent; **2e** was obtained as a colorless liquid (65 mg, 88%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.29–7.24 (m, 2H), 7.19–7.15 (m, 3H), 2.91–2.84 (m, 2H), 2.78–2.71 (m, 2H), 2.11 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 207.9, 141.0, 128.5, 128.3, 126.1, 45.2, 30.1, 29.8.

MS (EI, 70eV) m/z (%): 149.2 (11.3), 148.2 (100.0) M^+.

1,3-Diphenyl-1-propanol, 2f



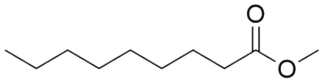
trans-Chalcone was hydrogenated using the standard procedure. On completion of the reaction the solvent was removed and the product purified by column chromatography over silica with *n*-heptane/ethyl acetate (3:1 by volume) as eluent; **2f** was obtained as a white solid (103 mg, 97%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.32–7.19 (m, 7H), 7.16–7.12 (m, 3H), 4.57 (dd, J = 7.7 Hz, J = 5.6 Hz, 1H), 2.73–2.54 (m, 2H), 2.34 (br, 1H), 2.12–1.89 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 144.6, 141.9, 128.5, 128.5, 128.4, 127.6, 126.0, 125.9, 73.8, 40.5, 32.1.

MS (EI, 70eV) m/z (%): 213.1 (16.7), 212.1 (100.0) M^+.

Methyl nonanoate, 2g



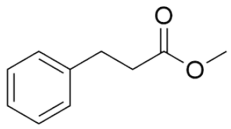
Methylnon-2-enoate was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2g** was obtained as a colorless liquid (66 mg, 77%).

^{1}H NMR (300 MHz, $CDCl_3$): 3.66 (s, 3H), 2.30 (t, J = 7.5 Hz, 2H), 1.67–1.57 (m, 2H), 1.28 (br, 10H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 174.4, 51.5, 34.2, 31.9, 29.3, 29.3, 29.2, 25.1, 22.7, 14.2.

MS (EI, 70eV) m/z (%): 173.2 (49.1), 172.2 (100.0) M^+. The M^+ signal is very low, resulting in a large deviation from the theoretical signal ratio $[M+1]^+/M^+$.

Methyl 3-phenylpropanoate, 2h



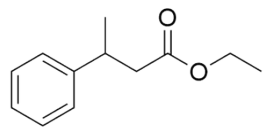
Methyl cinnamate was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by column chromatography over silica with *n*-heptane/ethyl acetate (10:1 by volume) as eluent; **2h** was obtained as a colorless liquid (73 mg, 90%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.30–7.25 (m, 2H), 7.22–7.16 (m, 3H), 3.65 (s, 3H), 2.94 (t, J = 7.8 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 173.3, 140.6, 128.6, 128.3, 126.3, 51.6, 35.7, 31.0.

MS (EI, 70eV) m/z (%): 165.1 (11.3), 164.1 (100.0) M^+.

Ethyl 3-phenylbutanoate, 2i



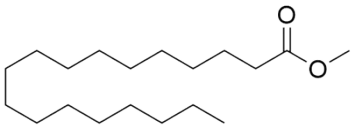
Methyl (*E*)-3-phenylbut-2-enoate was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation, **2i** was obtained as a colorless liquid (95 mg, 99%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.31–7.26 (m, 2H), 7.23–7.15 (m, 3H), 4.06 (t, J = 7.1 Hz, 2H), 3.26 (app sext, J = 7.3 Hz, 1H), 2.60 (dd, J = 15.0 Hz, J = 7.0 Hz, 1H), 2.52 (dd, J = 15.0 Hz, J = 8.1 Hz, 1H), 1.29 (d, J = 7.0 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 172.4, 145.8, 128.5, 126.8, 126.4, 60.3, 43.1, 36.6, 21.9, 14.2.

MS (EI, 70eV) m/z (%): 193.1 (13.9), 192.1 (100.0) M^+.

Methyl stearate, 2k



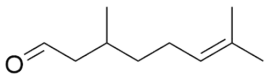
Methyl (*E*)-octadec-9-enoate was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2k** was obtained as a white solid (139 mg, 93%).

^{1}H NMR (300 MHz, $CDCl_3$): 3.66 (s, 3H), 2.30 (t, J = 7.5 Hz, 2H), 1.67–1.57 (m, 2H), 1.26 (br, 28H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 174.3, 51.5, 34.2, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 25.1, 22.8, 14.2.

MS (EI, 70eV) m/z (%): 299.3 (24.5), 298.3 (100.0) M^+.

3,7-dimethyloct-6-enal (2l)



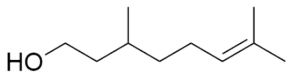
(*E*)-3,7-Dimethylocta-2,6-dienal (citral) was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2l** was obtained as a colorless liquid (55 mg, 71%).

^{1}H NMR (300 MHz, $CDCl_3$): 9.75 (t, J = 2.3 Hz, 1H), 5.09 (m, J = 10.6 Hz, J = 1.4 Hz, 1H), 2.41 (ddd, J = 16.0 Hz, J = 5.6 Hz, J = 2.0 Hz, 1H), 2.23 (ddd, J = 16.0 Hz, J = 7.9 Hz, J = 2.6 Hz, 1H), 2.15–1.93 (m, 3H), 1.68 (d, J = 0.9 Hz, 3H), 1.60 (br, 3H), 1.43–1.21 (m, 2H), 0.97 (d, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 203.1, 131.8, 124.1, 51.1, 37.0, 27.9, 25.8, 25.5, 20.0, 17.7.

MS (EI, 70eV) m/z (%): 155.2 (11.4), 154.2 (100.0) M^+.

3,7-dimethyloct-6-en-1-ol, 2m



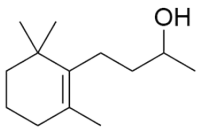
(*E*)-3,7-Dimethylocta-2,6-dien-1-ol (geraniol) was hydrogenated employing the standard procedure. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2m** was obtained as a colorless liquid (69 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$): 5.09 (m, J = 10.7 Hz, J = 1.4 Hz, 1H), 3.73–360 (m, 2H), 2.08–1.89 (m, 2H), 1.68 (d, J = 0.9 Hz, 3H), 1.71–1.52 (m, 3H), 1.60 (br, 3H), 1.44–1.29 (m, 2H), 1.24–1.11 (m, 1H), 0.91 (d, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 131.3, 124.8, 61.2, 40.0, 37.3, 29.3, 25.8, 25.6, 19.6, 17.7.

MS (EI, 70eV) m/z (%): 157.2 (11.4), 156.2 (100.0) M^+.

4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-ol, 2n



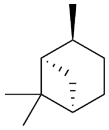
(*E*)-4-(2,6,6-Trimethylcyclohex-1-en-1-yl)but-3-en-2-one (*β*-ionone) was hydrogenated using the standard procedure with 16 h reaction time. On completion of the reaction, the solvent was removed, and the product purified by Kugelrohr distillation; **2n** was obtained as a colorless liquid (95 mg, 98%).

^{1}H NMR (300 MHz, $CDCl_3$): 3.79 (app sept, J = 5.8 Hz, 1H), 2.19–2.08 (m, 1H), 2.01–1.88 (m, 3H), 1.65 (d, J = 4.7 Hz, 1H), 1.59 (s, 3H), 1.61–1.47 (m, 4H), 1.43–1.39 (m, 2H), 1.21 (d, J = 6.2 Hz, 3H), 0.99 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 137.0, 127.1, 68.9, 40.0, 39.9, 35.1, 32.9, 29.3, 28.7, 24.9, 23.4, 19.9, 19.6.

MS (EI, 70eV) m/z (%): 197.2 (14.6), 196.2 (100.0) M^+.

(1*R*,2*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]heptane, *cis*-pinane, 2o



(1*R*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene ((+)-*α*-pinene) was hydrogenated using the standard procedure but using diethyl ether as the solvent instead and 16 h reaction time. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2o** was obtained as a colorless liquid (39 mg, 56%).

The NMR data are identical to those reported in the literature.[18]

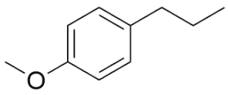
[18] A. Stolle, B. Ondruschka, W. Bonrath, T. Netscher, M. Findeisen, M. M. Hoffmann, *Chem. Eur. J.*, 2008, **14**, 6805–6814.

^{1}H NMR (300 MHz, $CDCl_3$): 2.34–2.27 (m, 1H), 2.17–2.06 (m, 1H), 2.01–1.73 (m, 5H), 1.47–1.35 (m, 1H), 1.18 (s, 3H), 1.02 (s, 3H), 1.00 (d, J = 7.3 Hz, 3H), 0.86 (d, J = 9.4 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 48.3, 41.5, 39.0, 36.1, 34.1, 28.5, 26.7, 24.0, 23.4, 23.0.

MS (EI, 70eV) m/z (%): 139.2 (10.5), 138.2 (100.0) M^+.

1-methoxy-4-propylbenzene, 2p



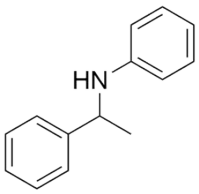
(*E*)-1-Methoxy-4-(prop-1-en-1-yl)benzene (*trans*-anethol) was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2p** was obtained as a colorless liquid (65 mg, 86%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.10–7.06 (m, 2H), 6.84–6.79 (m, 2H), 3.77 (s, 3H), 2.52 (t, J = 7.6 Hz, 2H), 1.60 (app sext, J = 7.5 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 157.8, 134.9, 129.4, 113.7, 55.3, 37.3, 24.9, 13.9.

MS (EI, 70eV) m/z (%): 151.2 (11.0), 150.2 (100.0) M^+.

***N*-(1-phenylethyl)aniline, 6b**



Phenyl-(1-phenylethyliden)amine was hydrogenated using the standard procedure. On completion of the reaction the solvent was removed and the product purified by column chromatography over silica with *n*-heptane/ethyl acetate/triethylamine (20:2:1 by volume as eluent); **6b** was obtained as a colorless liquid (96 mg, 95%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.35–7.25 (m, 4H), 7.21–7.15 (m, 1H), 7.10–7.03 (m, 2H), 6.64–6.59 (m, 1H), 6.49–6.46 (m, 2H), 4.44 (q, J = 6.7 Hz, 1H), 3.96 (s, 1H), 1.46 (d, J = 6.7 Hz, 3H).

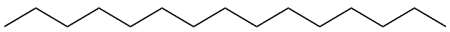
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 147.4, 145.3, 129.2, 128.7, 126.9, 125.9, 117.3, 113.4, 53.5, 25.1.

MS (EI, 70eV) m/z (%): 198.1 (15.6), 197.1 (100.0) M^+.

5.2 Catalytic Hydrogenation with Preactivation (Mode II)

The same procedure as was followed for Mode I was applied but no substrate was added at first. After preactivation for 3 h at 45 °C under 20 bar H_2, the autoclave was disassembled and the cannulas were quickly removed. Liquid substrates were added through a Hamilton syringe whereas solid substrates were weighed into a separate glass vial in the glovebox. The vials were tightly sealed and then removed from the box. The preactivated catalyst solution was transferred to the substrate-containing vial with a syringe. The septa were then pierced again with cannulas and the autoclave (preheated bottom part at 45 °C) assembled and charged with H_2 according to the standard procedure. The remaining steps were performed as described for **Mode I**. Standard conditions: 1 mol% **[Ni] 4-H**, 1,4-dioxane, 45 °C, 20 bar H_2, and 30 min. Deviating reaction conditions and workup methods are described below for each substrate.

Pentadecane, 2r



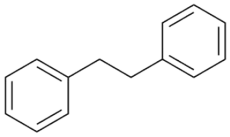
1-Pentadecene was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2r** was obtained as a colorless liquid (105 mg, 99%).

^{1}H NMR (300 MHz, $CDCl_3$): 1.26 (br, 26H), 0.88 (t, J = 6.7 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 32.2, 30.0, 29.9, 29.6, 22.9, 14.3.

MS (EI, 70eV) m/z (%): 213.2 (16.7), 212.2 (100.0) M^+.

1,2-Diphenylethane, 2s



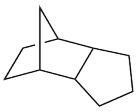
cis-Stilbene was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the residue was suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2s** was obtained as a white solid (91 mg, 96%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.28–7.22 (m, 4H), 7.18–7.14 (m, 6H), 2.89 (s, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 141.9, 128.6, 128.4, 126.0, 38.1.

MS (EI, 70eV) m/z (%): 183.2 (15.2), 182.1 (100.0) M^+.

***endo*-Tetrahydrodicyclopentadiene, 2t**



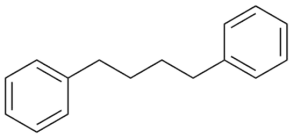
Dicyclopentadiene was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2t** was obtained as a colorless solid (50 mg, 72%). The NMR data are identical to those reported in the literature.[19]

^{1}H NMR (300 MHz, $CDCl_3$): 2.39–2.28 (m, 2H), 2.08 (br, 2H), 1.65–1.35 (m, 10H), 1.31–1.22 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 45.6, 43.4, 41.7, 28.9, 27.1, 23.2.

MS (EI, 70eV) m/z (%): 137.2 (11.3), 136.2 (100.0) M^+.

1,4-Diphenylbutane, 2v



(*E*,*E*)-1,4-Diphenyl-1,3-butadiene was hydrogenated using the standard procedure with 3 h reaction time. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2v** was obtained as a white solid. Minor amounts of over-hydrogenated products were detected in the GC-MS analysis. The yield of **2v** (98%) was therefore determined by way of ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

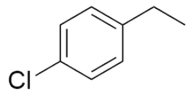
^{1}H NMR (300 MHz, $CDCl_3$): 7.26–7.21 (m, 4H), 7.15–7.11 (m, 6H), 2.63–2.56 (m, 4H), 1.70–1.57 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 142.6, 128.5, 128.3, 125.7, 35.9, 31.2.

MS (EI, 70eV) m/z (%): 211.1 (17.6), 210.2 (100.0) M^+.

[19] B. Nguyen, J. M. Brown, *Adv. Synth. Catal.*, 2009, **351**, 1333–1343.

1-Chloro-4-ethylbenzene, 2x



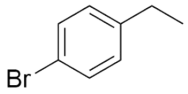
1-Chloro-4-vinylbenzene was hydrogenated using the standard procedure with 2 mol% of **[Ni] 4-H** and THF as the solvent. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2x** was obtained as a colorless liquid (50 mg, 72%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.25–7.21 (m, 2H), 7.13–7.09 (m, 2H), 2.60 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 142.8, 131.4, 129.3, 128.5, 28.4, 15.7.

MS (EI, 70eV) m/z (%): 142.1 (32.1), 141.1 (9.9), 140.1 (100.0) M^+.

1-Bromo-4-ethylbenzene, 2y



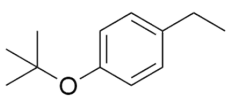
1-Bromo-4-vinylbenzene was hydrogenated using the standard procedure with 2 mol% of **[Ni] 4-H** and THF as the solvent. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2y** was obtained as a colorless liquid (69 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.40–7.36 (m, 2H), 7.07–7.03 (m, 2H), 2.59 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 142.8, 131.4, 129.3, 128.5, 28.4, 15.7.

MS (EI, 70eV) m/z (%): 186.0 (93.9), 185.0 (10.4), 184.0 (100.0) M^+.

1-(*tert*-Butoxy)-4-ethylbenzene, 2z



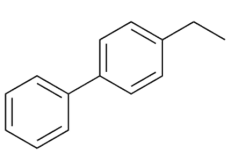
1-(*tert*-Butoxy)-4-vinylbenzene was hydrogenated using the standard procedure with THF as the solvent. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2z** was obtained as a colorless liquid (80 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.09–7.05 (m, 2H), 6.92–6.87 (m, 2H), 2.60 (q, J = 7.6 Hz, 2H), 1.32 (s, 9H), 1.21 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 153.2, 139.2, 128.2, 124.2, 78.1, 29.0, 28.3, 15.7.

MS (EI, 70eV) m/z (%): 179.1 (13.4), 178.1 (100.0) M^+.

4-Ethyl-1,1'-biphenyl, 2aa



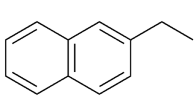
4-Vinyl-1,1'-biphenyl was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2aa** was obtained as a white solid (86 mg, 94%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.57–7.53 (m, 2H), 7.51–7.47 (m, 2H), 7.41–7.36 (m, 2H), 7.31–7.22 (m, 3H), 2.66 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 143.5, 141.3, 138.7, 128.8, 128.4, 127.2, 127.1, 127.1, 28.6, 15.7.

MS (EI, 70eV) m/z (%): 183.1 (15.1), 182.1 (100.0) M^+.

2-Ethylnaphthalin, 2ab



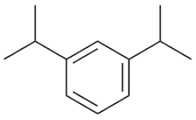
4-Vinylnaphthalin was hydrogenated using the standard procedure. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica and eluted with *n*-pentane; **2aa** was obtained as a white solid. Minor amounts of over-hydrogenated products were detected in the GC-MS analysis. The yield of **2aa** (96%) was therefore determined by way of ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

^{1}H NMR (300 MHz, $CDCl_3$): 7.78–7.71 (m, 3H), 7.59 (br, 1H), 7.44–7.34 (m, 2H), 7.31 (dd, J = 8.4 Hz, J = 1.7 Hz, 1H), 2.78 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 141.8, 133.8, 132.1, 127.9, 127.7, 127.5, 127.2, 125.9, 125.6, 125.1, 29.2, 15.6.

MS (EI, 70eV) m/z (%): 157.2 (13.1), 156.2 (100.0) M^+.

1,3-Diisopropylbenzene, 2ag



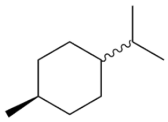
1,3-Di(prop-1-en-2-yl)benzene was hydrogenated using the standard procedure with 2 mol% of **[Ni] 4-H** and THF as solvent. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane; **2ag** was obtained as a colorless liquid. Minor amounts of over-hydrogenated products were detected in the GC-MS analysis. The yield of **2ag** (85%) was therefore determined by way of ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

^{1}H NMR (300 MHz, $CDCl_3$): 7.21 (t, J = 7.5 Hz, 1H), 7.07 (br, 1H), 7.04 (dd, J = 7.5 Hz, J = 1.6 Hz, 2H), 2.88 (sept, J = 6.9 Hz, 2H), 1.25 (d, J = 7.0 Hz, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 148.9, 128.4, 124.9, 123.9, 34.3, 24.2.

MS (EI, 70eV) m/z (%): 163.2 (13.0), 162.2 (100.0) M^+.

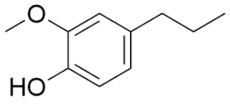
1-Isopropyl-4-methylcyclohexane, 2ah



(+)-Limonene was hydrogenated using the standard procedure with 2 mol% of **[Ni]-4-H**, THF as solvent and 3 h reaction time. On completion of the reaction, the solvent was removed, the residue suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane. A *cis*/*trans*-mixture (45:55)[20] of **2ah** was obtained as a colorless liquid (63 mg, 91%).

^{1}H NMR (300 MHz, $CDCl_3$): 1.71–1.21 (m, 8H), 1.07–0.84 (m, 12H).

2-Methoxy-4-propylphenol, 2ai



4-Allyl-2-methoxyphenol (eugenol) was hydrogenated using the standard procedure with 2 mol% of **[Ni] 4-H** and THF as solvent. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **2ai** was obtained as a colorless liquid (77 mg, 95%).

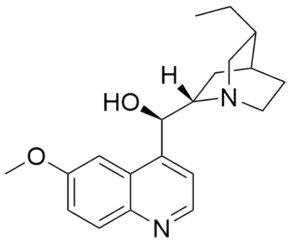
^{1}H NMR (300 MHz, $CDCl_3$): 6.84–6.81 (m, 1H), 6.67 (s, 1H) 6.67–6.64 (m, 1H), 5.54 (br, 1H), 3.84 (s, 3H), 2.50 (t, J = 7.6 Hz, 2H), 2.88 (app sext, J = 7.5 Hz, 2H), 0.93 (t, J = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 146.4, 143.6, 134.8, 121.0, 114.2, 111.1, 55.9, 37.8, 25.0, 13.9.

MS (EI, 70eV) m/z (%): 167.1 (11.0), 166.2 (100.0) M^+.

[20] E. Bogel-Łukasik, R. Bogel-Łukasik, M. N. da Ponte, *Monatsh. Chem.*, 2009, **140**, 1361–1369.

Dihydroquinine, 2aj



Quinine was hydrogenated using the standard procedure with 3 h reaction time. On completion of the reaction, the solvent was removed and the product purified by column chromatography over silica with dichloromethane/methanol/triethylamine (20:1:1 by volume) as eluent; **2aj** was obtained as a white solid (151 mg, 93%).

^{1}H NMR (300 MHz, $CDCl_3$): 8.34 (d, J = 4.5 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.46 (d, J = 4.6 Hz, 1H), 7.28 (d, J = 2.5 Hz, 1H), 7.21 (dd, J = 9.2 Hz, J = 2.6 Hz, 1H), 6.68 (br, 1H), 5.58 (br, 1H), 3.87 (s, 3H), 3.54 (br, 1H), 3.02–2.95 (m, 2H), 2.62–2.53 (m, 1H), 2.32 (dd, J = 13.4 Hz, J = 1.7 Hz, 1H), 1.79–1.74 (m, 3H), 1.42–1.30 (m, 3H), 1.24–1.10 (m, 2H), 0.76 (t, J = 7.3 Hz, 3H).

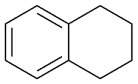
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 157.6, 148.8, 147.1, 143.7, 130.9, 126.5, 121.2, 118.6, 101.6, 71.1, 59.8, 58.4, 55.8, 43.3, 37.3, 28.0, 27.5, 25.3, 20.8, 12.0.

MS (EI, 70eV) m/z (%): 327.3 (22.8), 326.3 (100.0) M^+.

5.3 Catalytic Hydrogenation of Polycyclic Aromatic Hydrocarbons

The same procedure as delineated for **Mode I** was used. Exact reaction conditions and purification methods are described below for each substrate. In most cases, hydrogenation gave at least two products which were not separated during the course of the purification step. Instead, the respective yields were determined by way of ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

1,2,3,4-Tetrahydronaphthalene, 4b



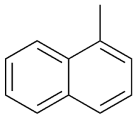
Naphthalene was hydrogenated employing the standard procedure with 2 mol% of **Ni [4]-H** and 16 h reaction time. On completion of the reaction, the solvent was removed and the product purified by Kugelrohr distillation; **4b** was obtained as a colorless liquid (50 mg, 73%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.09–7.02 (m, 4H), 2.78–2.74 (m, 4H), 1.81–1.76 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 137.2, 129.2, 125.5, 29.5, 23.4.

MS (EI, 70eV) m/z (%): 133.2 (11.0), 132.2 (100.0) M^+.

Hydrogenation of 1-Methylnaphthalene, 3c



1-Methylnaphthalene (0.25 mmol) was hydrogenated employing the standard procedure with 5 mol% of **Ni [4]-H** and 16 h reaction time. The residue was suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane. A mixture of hydrogenation products was obtained as a colorless liquid; 1,3,5-trimethoxybenzene (0.100 mmol, 16.9 mg) was added to determine each yield of 5-methyl-1,2,3,4-tetrahydronaphthalene (**4c$_A$**, 72%) and 1-methyl-1,2,3,4-tetrahydronaphthalene (**4c$_B$**, 12%).

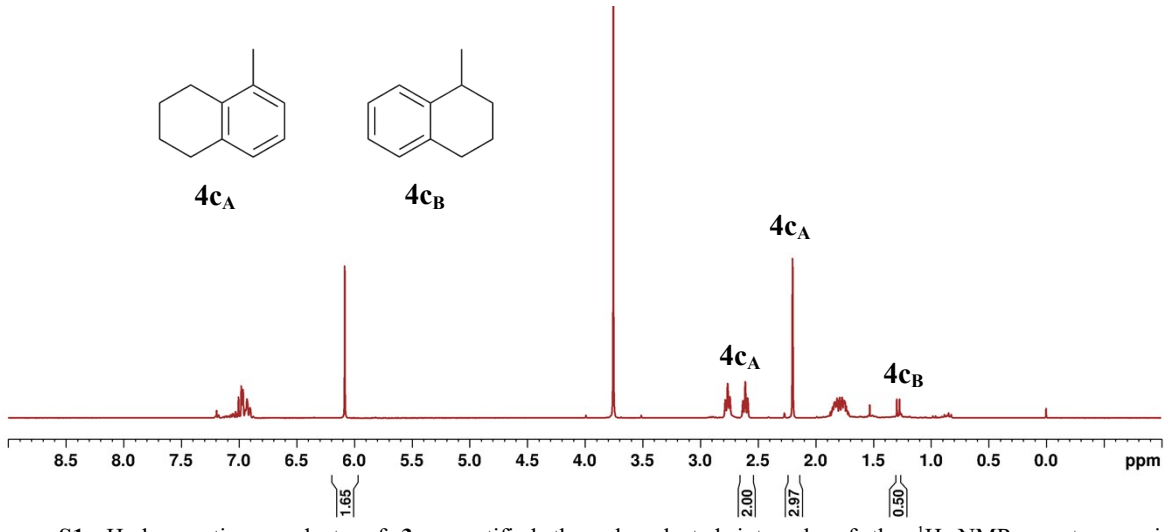
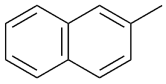


Figure S1. Hydrogenation products of **3c** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of 2-Methylnaphthalene, 3d



2-Methylnaphthalene (0.25 mmol) was hydrogenated employing the standard procedure (45 °C, 40 bar H_2, 16 h) with 5 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane. A mixture of hydrogenation products was obtained as a colorless liquid; 1,3,5-trimethoxybenzene (0.099 mmol, 16.7 mg) was added to determine each yield of 6-methyl-1,2,3,4-tetrahydronaphthalene (**4d$_A$**, 68%) and 2-methyl-1,2,3,4-tetrahydronaphthalene (**4d$_B$**, 15%).

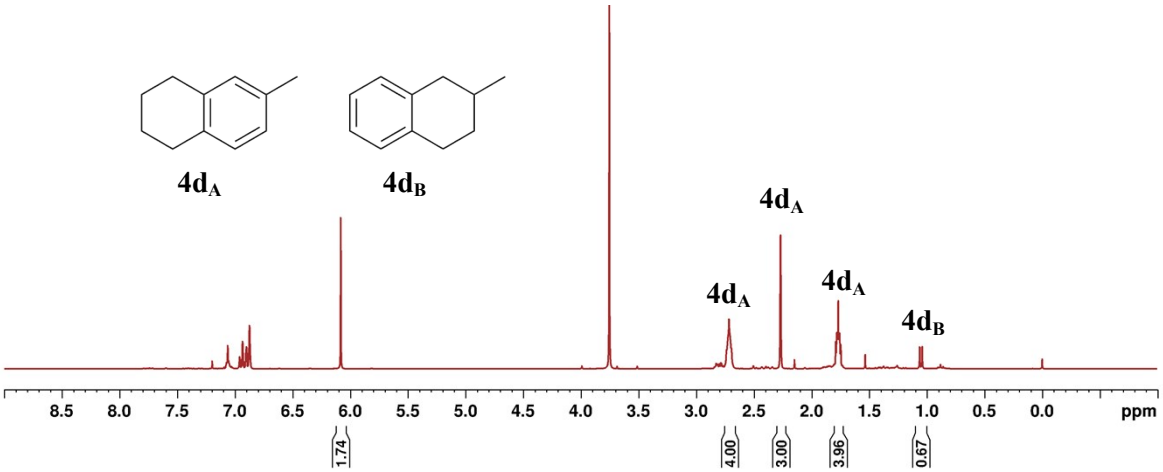
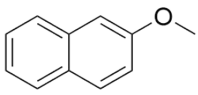


Figure S2. Hydrogenation products of **3d** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of 2-Methoxynaphthalene, 3e



2-Methoxynaphthalene (0.25 mmol) was hydrogenated employing the standard procedure (45 °C, 40 bar H_2, 16 h) with 5 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane. A mixture of hydrogenation products was obtained as a colorless liquid; 1,3,5-trimethoxybenzene (0.102 mmol, 17.2 mg) was added to determine the yield of 6-methoxy-1,2,3,4-tetrahydronaphthalene (**4e$_A$**, 87%) and 2-methoxy-1,2,3,4-tetrahydronaphthalene (**4e$_B$**, 7%).

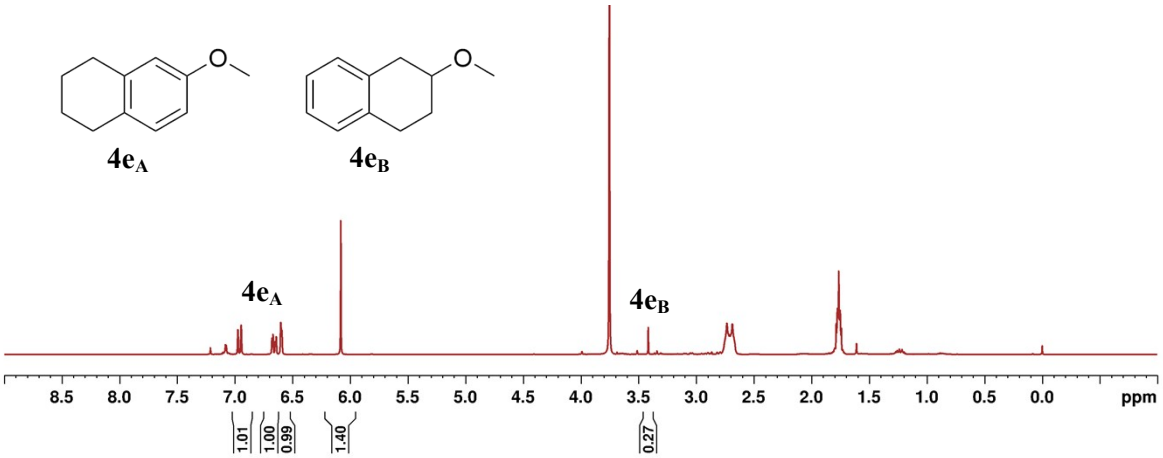
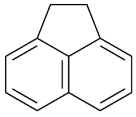


Figure S3. Hydrogenation products of **3e** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of Acenaphthene, 3f



Acenaphthene (0.25 mmol) was hydrogenated employing the standard procedure (45 °C, 40 bar H_2, 16 h) with 5 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane, passed through a plug of silica and eluted with *n*-pentane. A mixture of hydrogenation products was obtained as a colorless liquid. 1,3,5-trimethoxybenzene (0.099 mmol, 16.7 mg) was added to determine the yield of 2a,3,4,5-tetrahydroacenaphthene (**4f**, 79%).

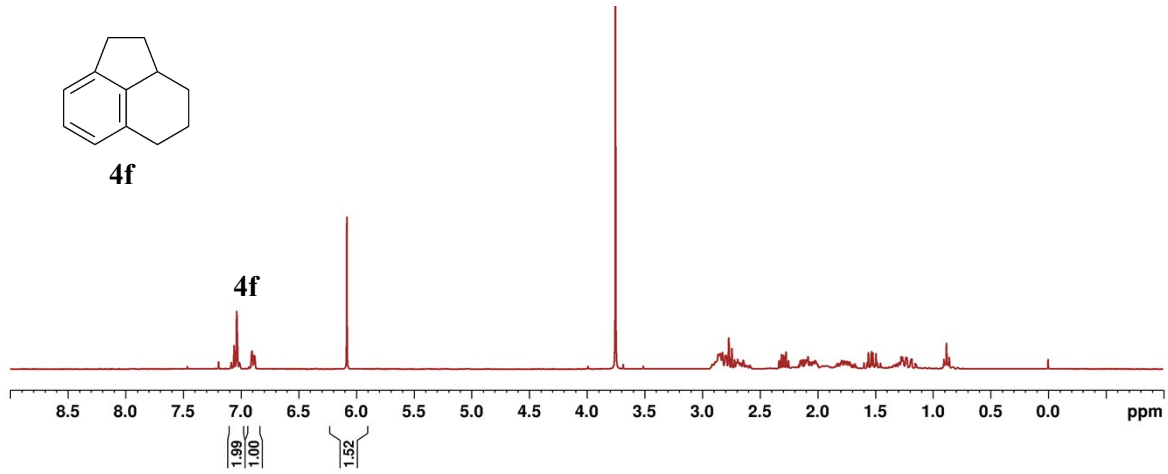
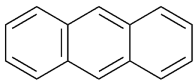


Figure S4. Hydrogenation products of **3f** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of Anthracene, 3g



Anthracene (0.25 mmol) was hydrogenated using the standard procedure (45 °C, 40 bar H_2, 16 h) with 5 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane. A mixture of hydrogenation products was obtained as a colorless solid; 1,3,5-trimethoxybenzene (0.099 mmol, 16.6 mg) was added to determine the yield of 1,2,3,4,5,6,7,8-octahydroanthracene (**4g$_{AC}$**, 92%), 1,2,3,4-tetrahydroanthracene (**4g$_{C}$**, 7%) and 9,10-dihydroanthracene (**4g$_{B}$**, 1%).

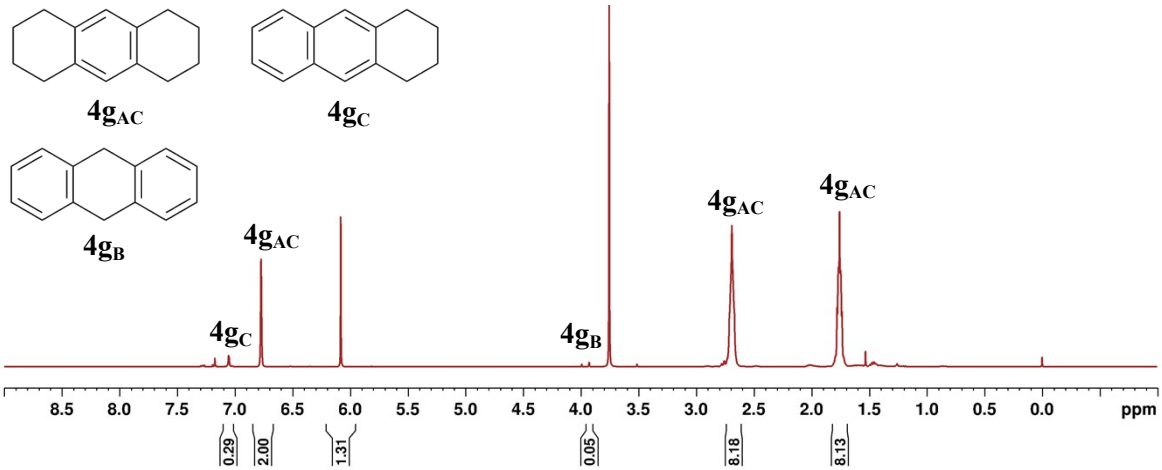
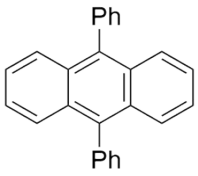


Figure S5. Hydrogenation products of **3g** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of 9,10-Diphenylanthracene, 3h



9,10-Diphenylanthracene (0.25 mmol) was hydrogenated using the standard procedure (45 °C, 40 bar H_2, 16 h) with 5 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane/toluene 1:1, passed through a plug of silica, and eluted with *n*-pentane/toluene 1:1. A mixture of hydrogenation products was obtained as a colorless solid; 1,3,5-trimethoxybenzene (0.098 mmol, 16.4 mg) was added to determine the yield of 9,10-diphenyl-1,2,3,4,5,6,7,8-octahydroanthracene (**4h$_{AC}$,** 77%) and 9,10-diphenyl-1,2,3,4-tetrahydroanthracene (**4h$_A$**, 23%).

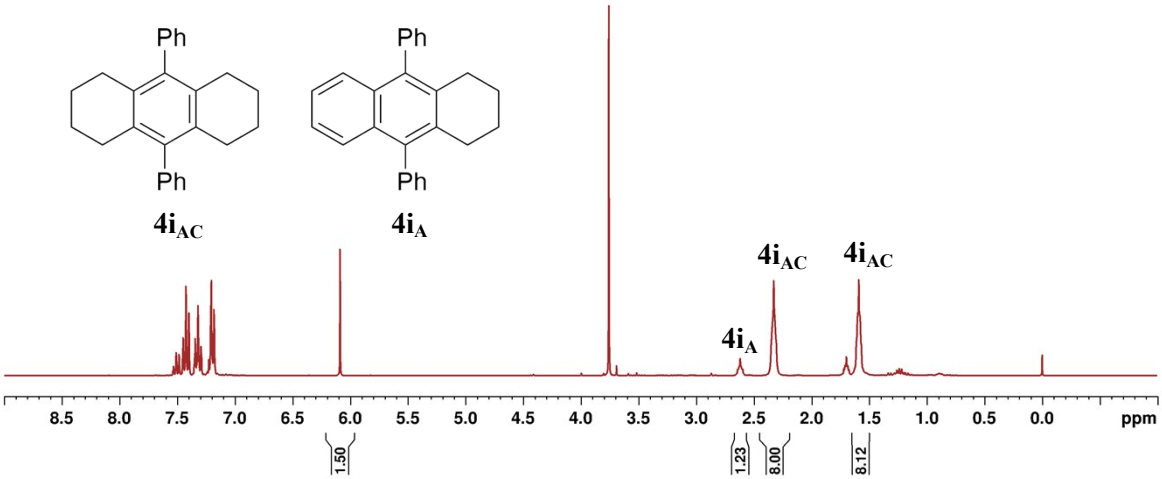
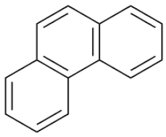


Figure S6. Hydrogenation products of **3i** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of Phenanthrene, 3i



Phenanthrene (0.25 mmol) was hydrogenated using the standard procedure (60 °C, 40 bar H_2, 16 h) with 10 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane, passed through a plug of silica, and eluted with *n*-pentane. A mixture of hydrogenation products was obtained as a colorless liquid. 1,3,5-trimethoxybenzene (0.103 mmol, 17.3 mg) was added to determine the yield of 1,2,3,4,5,6,7,8-octahydrophenanthrene (**4i$_{AC}$,** 43%), 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**4i$_{BC}$**, 24%), and 9,10-dihydrophenanthrene (**4i$_B$**, 32%).

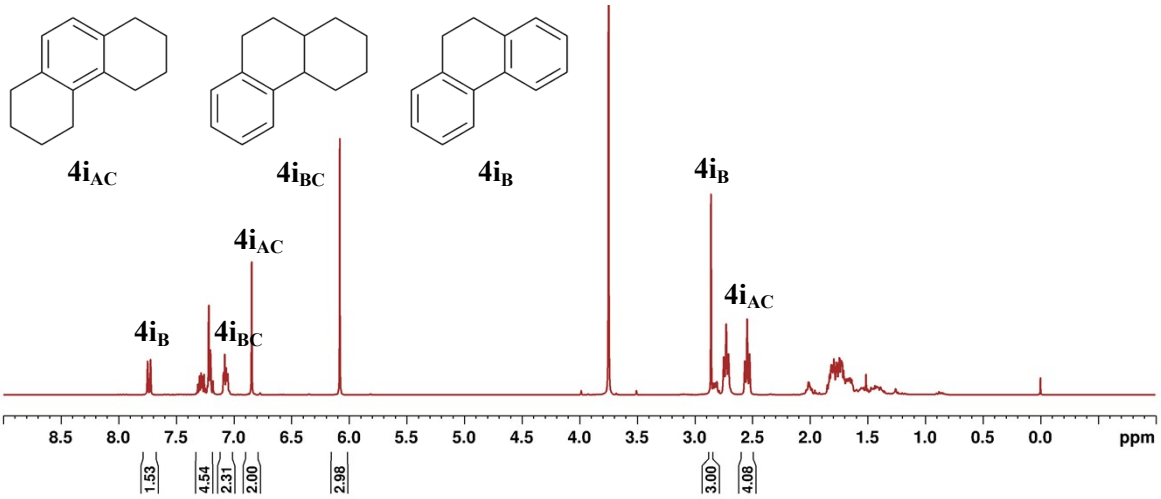
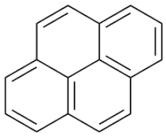


Figure S7. Hydrogenation products of **3i** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

Hydrogenation of Pyrene, 3j



Pyrene (0.25 mmol) was hydrogenated employing the standard procedure (60 °C, 40 bar H_2, 16 h) with 5 mol% of **Ni [4]-H**. The residue was suspended in *n*-pentane/toluene 1:1, passed through a plug of silica, and eluted with *n*-pentane/toluene 1:1. A mixture of hydrogenation products (95% conversion) was obtained as a white solid; 1,3,5-trimethoxybenzene (0.102 mmol, 17.2 mg) was added to determine the yield of 4,5-dihydropyrene (**4j$_A$,** 60%) and 4,5,9,10-tetrahydropyrene (**4j$_{AB}$,** 24%). Minor amounts (3-4% each) of 1,2,3,6,7,8-hexahydropyrene and 1,2,3,3a,4,5-hexahydropyrene were also detected in the GC-MS analysis.

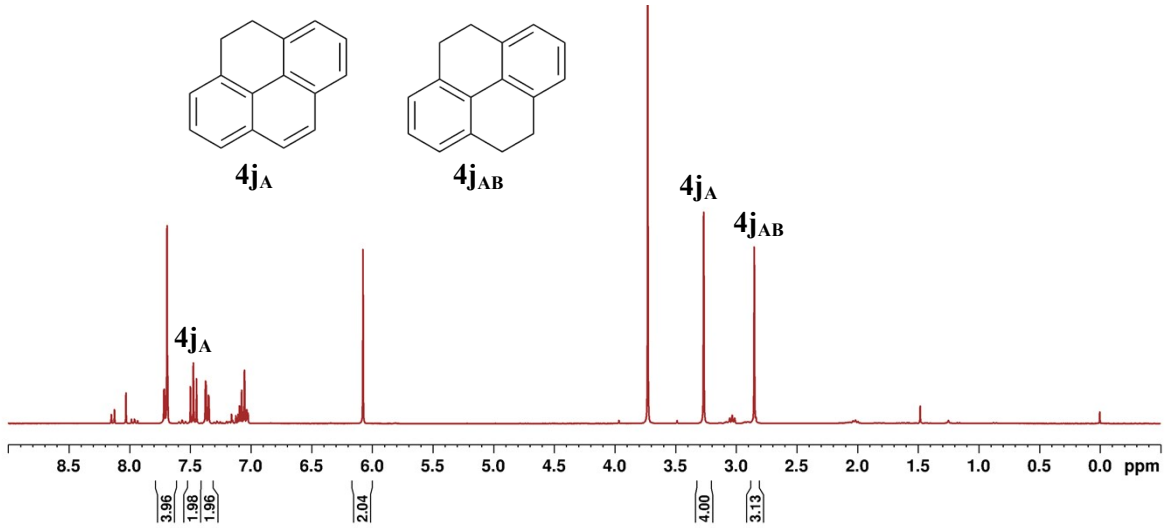
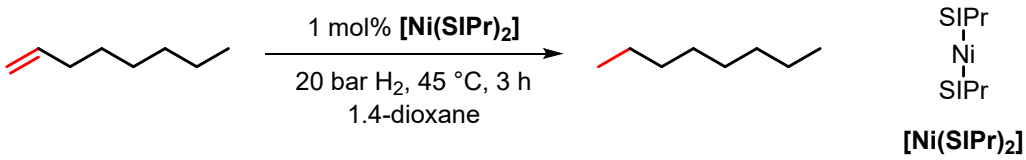


Figure S8. Hydrogenation products of **3j** quantified through selected integrals of the ^{1}H NMR spectrum using 1,3,5-trimethoxybenzene as internal standard.

6 Additional Experiments Under Modified Catalytic Conditions

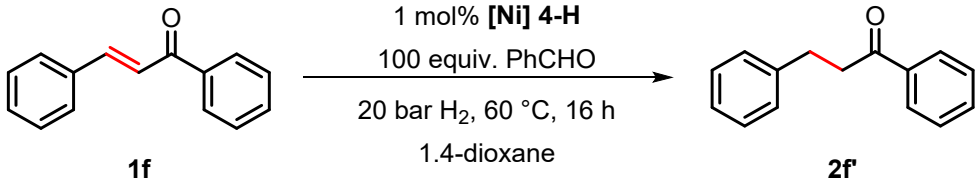
Procedural details and reaction conditions used for catalytic reactions deviating from the standard procedures are outlined below.

6.1 Hydrogenation of 1-Octene With [Ni(SIPr)$_2$]



In a glovebox, a glass vial (4 mL) was charged with **[Ni(SIPr)(η^6-toluene)]** (10.8 mg, 0.02 mmol, 1 equiv.) and SIPr (7.8 mg, 0.02 mmol, 1 equiv.). The solids were dissolved in dioxane (0.8 mL) and stirred at RT overnight. A volume of 0.2 mL of the deep purple solution was transferred to another vial loaded with a stirring bar whereupon dioxane (0.8 mL) and 1-octene (0.50 mmol, 56.1 mg, 79 µL) were added in that order. The mixture was subjected to hydrogenation according to the standard procedure (20 bar H_2, 45 °C, 3 h); 1-octene was fully converted whereas 20% were converted under the same conditions using **[Ni] 4-H** or **[Ni(SIPr)(η^6-toluene)]** instead.

6.2 Hydrogenation of *trans*-Chalcone in the Presence of Benzaldehyde



A glass vial (4 mL) equipped with a stirring bar was charged with *trans*-chalcone (0.50 mmol, 104.1 mg) and benzaldehyde (0.50 mmol, 53.1 mg, 51 µL). The **[Ni] 4-H** stock solution (0.005 mmol, 1.0 mL dioxane) was added and the mixture subjected to hydrogenation according to the standard procedure (20 bar H_2, 60 °C, 16 h). The substrate was selectively reduced at the C=C double bond in contrast to the standard conditions at which the ketone motif is also reduced. Upon removal of the solvent, the raw mixture was purified by way of column chromatography. The product **2f'** still contained 3.5% of benzyl benzoate. Corrected yield: 103 mg, 98%.

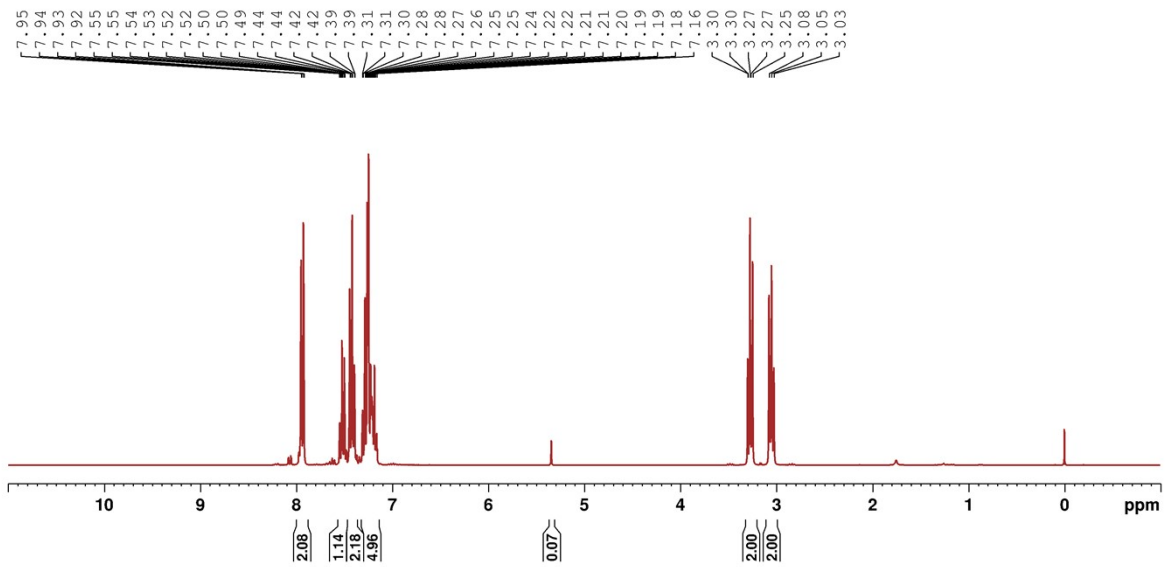
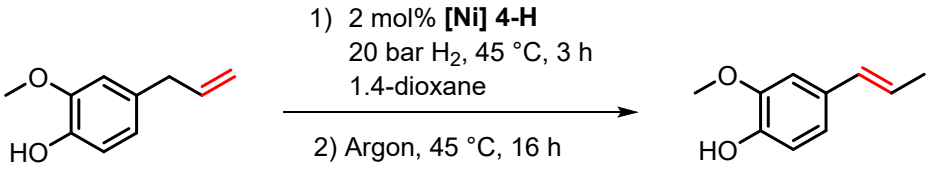


Figure S9. [1]H NMR spectrum of **2f'** still containing benzyl benzoate (3.5%).

6.3 Isomerization of Eugenol to Isoeugenol



1ai **1ai'**

A glass vial (4 mL) equipped with a stirring bar was charged with **[Ni] 4-H** (5.2 mg, 0.01 mmol) and dioxane (1.0 mL). The solution was activated under standard conditions (**Mode II**) and then transferred to a Schlenk tube containing eugenol (0.50 mmol, 82.1 mg, 79 µL) and a stirring bar. After that, the mixture was agitated for 16 h at 45 °C. On completion of the reaction, the solvent was removed and the product separated from the residue through Kugelrohr distillation. Yield: 74 mg, 90% (*E*/*Z* 20:1).

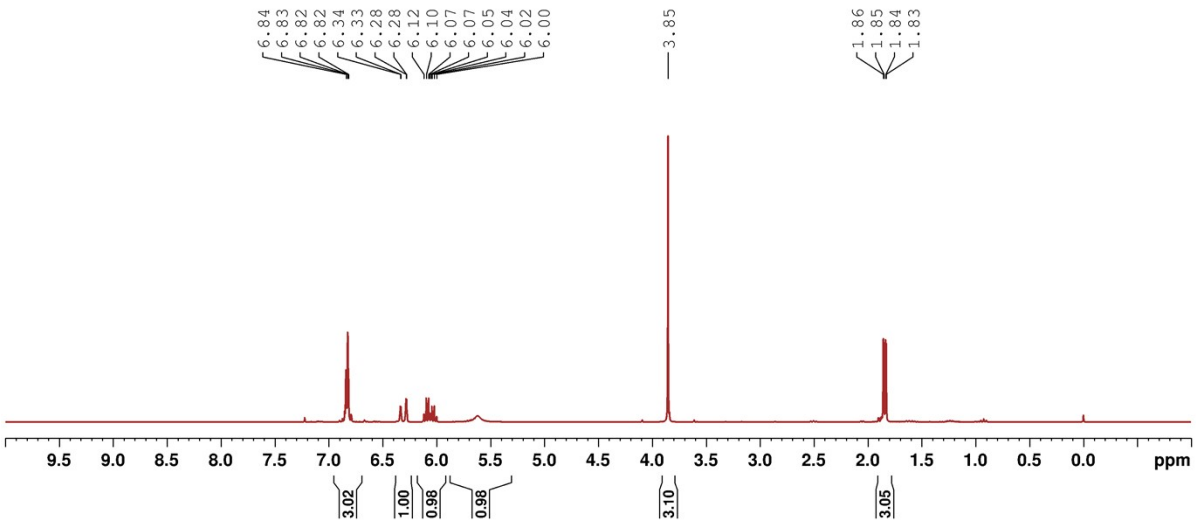


Figure S10. [1]H NMR spectrum of isoeugenol **1ai'**.

7 Mechanistic Investigation

The NMR experiments outlined in the following section were performed to gain insights into the activation process under H_2 in different solvents, interactions between the mononuclear catalyst and alkene substrates, and the reaction of cyclooctene with preactivated catalysts. Furthermore, the established deactivation pathway of Mes-NHC-coordinated (pre)catalysts as well as the relationship between the catalyst structure and its reactivity is discussed.

7.1 Activation of [Ni] 4-H Under H_2 in Benzene-d_6 and THF-d_8

A GC vial (1.5 mL) loaded with a stirring bar was charged with **[Ni] 4-H** (10.8 mg, 0.02 mmol) and either benzene-d_6 (0.60 mL) or THF-d_8 (0.60 mL). The vial was closed with a septum screw cap and taken out from the glovebox. The septum was pierced with a cannula and the vial transferred to an Ar-flushed autoclave. The autoclave was closed, purged with H_2 (3x10 bar, 2x20 bar), and pressurized with 20 bar H_2. Hereafter, the mixture was stirred at RT for 16 h. On completion of the reaction, the overpressure was released, the autoclave disassembled, and the cannula quickly removed. Under a stream of Ar, the reaction mixture was transferred to an NMR tube which was then closed and sealed with Parafilm.

Activation in Benzene-d_6

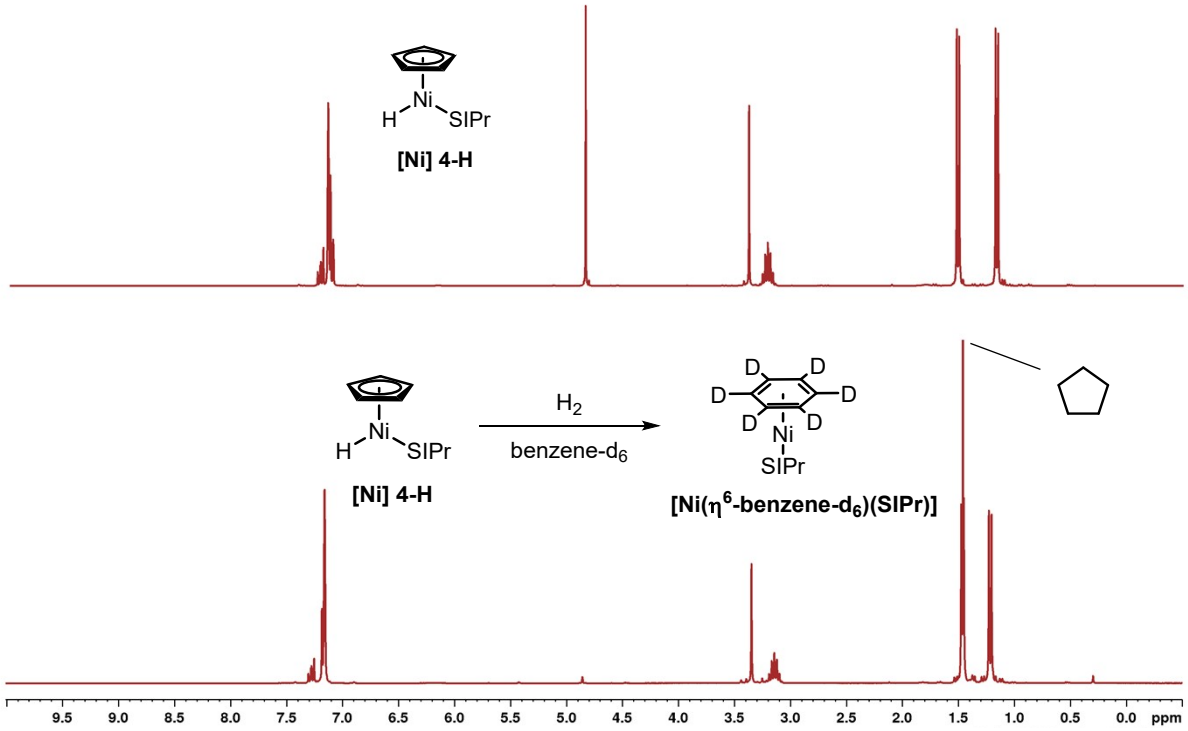


Figure S11. ^{1}H NMR spectrum of **[Ni] 4-H** (top) juxtaposed with the hydrogenated sample (bottom).

Hydrogenation of **[Ni] 4-H** in benzene-d_6 led to formation of **[Ni(η^6-benzene-d_6)(SIPr)]** and cyclopentane (**Figure S11**). **[Ni] 4-H** is thermally stable in benzene-d_6 even at elevated temperatures (60 °C) from which it follows that reductive elimination to form cyclopentadiene as the initial activation step can be excluded. The activation mechanism must therefore involve the reaction between **[Ni] 4-H** and H_2.

Activation in THF-d_8

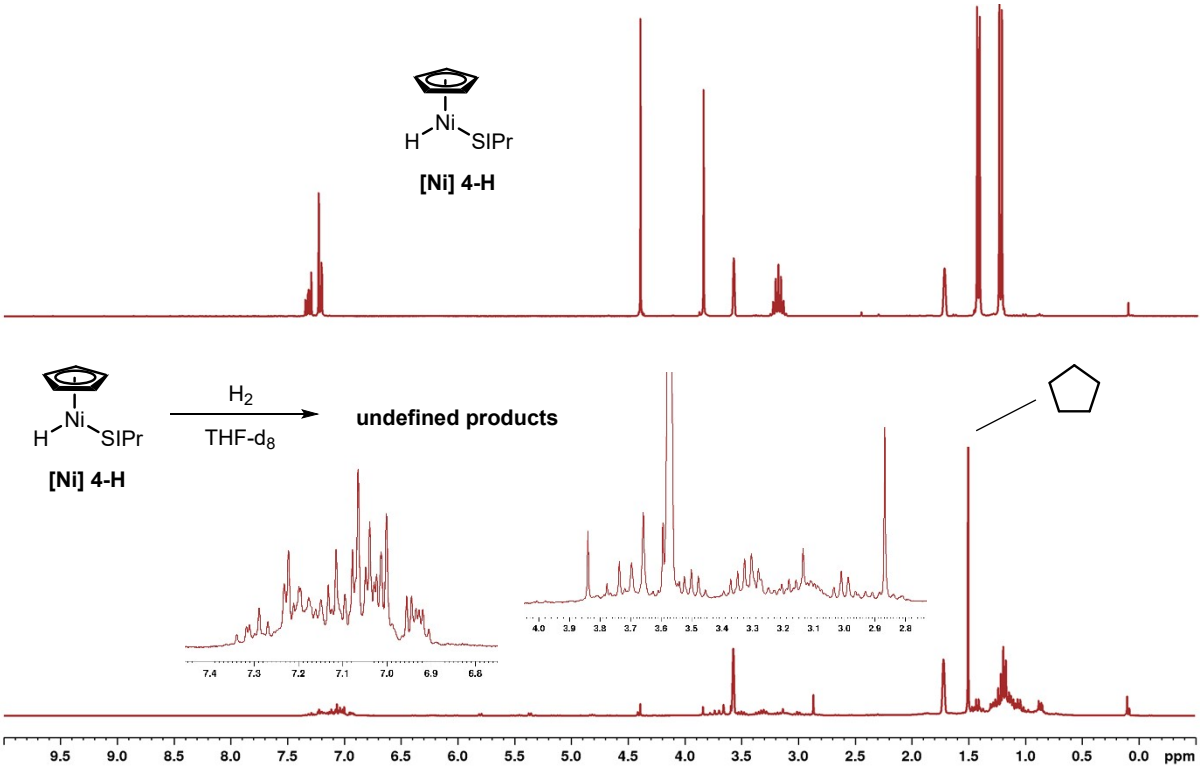


Figure S12. ^{1}H NMR spectrum of **[Ni] 4-H** (top) compared to the hydrogenated sample (bottom).

Reaction of **[Ni] 4-H** with H_2 in a non-aromatic solvent (THF-d_8) gave a complex spectrum due to the presence of several species (**Figure S12**). Interpretation was therefore limited to the hydride region (**Figure S13**). Besides multiple singlets including the one at -23.62 ppm of the remaining precursor **[Ni] 4-H**, a prominent set of multiplets in a 1:1:1 ratio was observed: δ = -16.19 (dd, J = 10.8 Hz, J = 6.9 Hz), -16.78 (dd, J = 10.8 Hz, J = 7.0 Hz), and -23.16 (app t, J = 7.0 Hz). We hypothesize that the pattern stems from a Ni-hydride cluster most likely supported by SIPr. A phosphine-tagged Ni-H-clusters was reported to show a single signal in the hydridic region due to fluxional behavior.[21] A similar cluster tagged by much more sterically demanding SIPr could lead to a structure rigid enough to cause splitting of the distinct η-hydrido-ligands observed in our case.

[21] R. Beck, M. Shoshani, S. A. Johnson, *Angew. Chem. Int. Ed.*, 2012, **51**, 11753–11756.

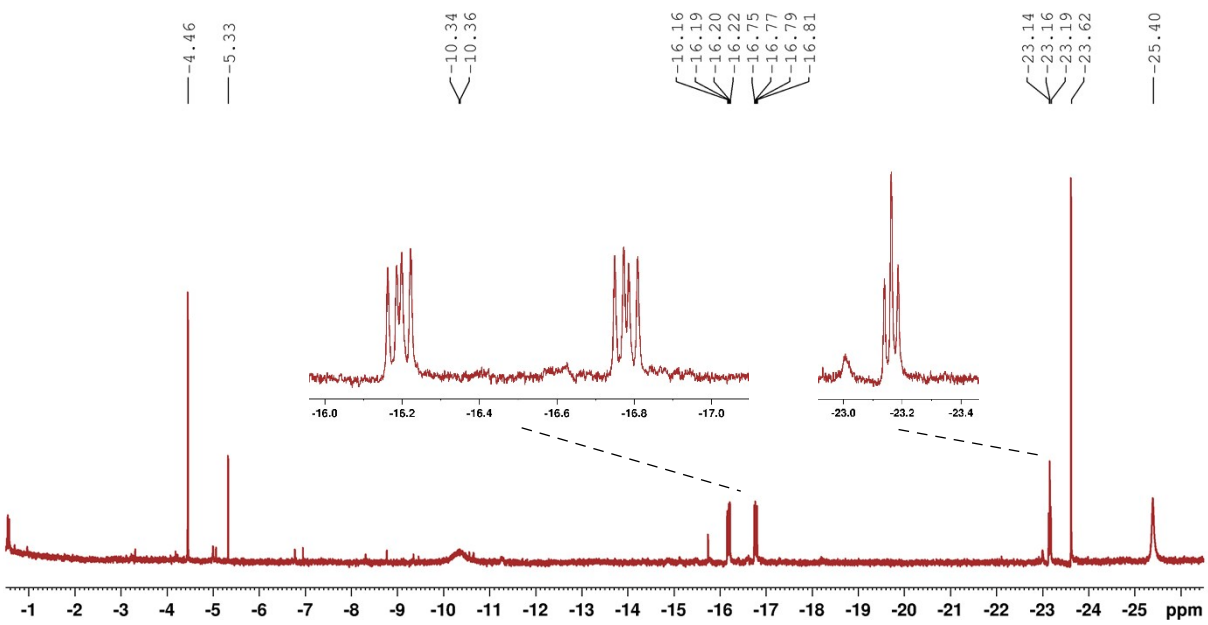


Figure S13. Hydride region of the ^{1}H NMR spectrum after hydrogenation of **[Ni] 4-H** in THF-d_8; the signal at -23.62 stems from unreacted precursor **[Ni] 4-H**.

7.2 Reaction of the Preactivated Catalyst with Cyclooctene

To the NMR sample of the preactivated catalyst in THF-d_8 prepared as described above was added cyclooctene (4.4 mg, 5 µL, 0.04 mmol, 2 equiv.) via a Hamilton syringe under a stream of Ar. The NMR tube was closed, sealed with Parafilm and mixed whereupon an ^{1}H NMR spectrum was immediately recorded (**Figure S14**).

Addition of cyclooctene caused several changes in the hydride region of the preactivated catalyst solution. A singlet at -4.46 ppm and the three doublets of doublets attributed to a Ni-hydrido-cluster at -16.19 ppm, -16.78 ppm, and -23.16 ppm disappeared whereas new singlets at -8.78 ppm, -24.80 ppm, and -55.01 emerged. Presumably, these new signals belong to products formed during the reaction between the active catalytic species and the alkene, i.e, various insertion products. Other signals (-5.33 ppm, -25.40 ppm) as well as the one of the starting complex at -23.62 ppm where not affected by the alkene addition and were therefore deemed unreactive in the hydrogenation of cyclooctene.

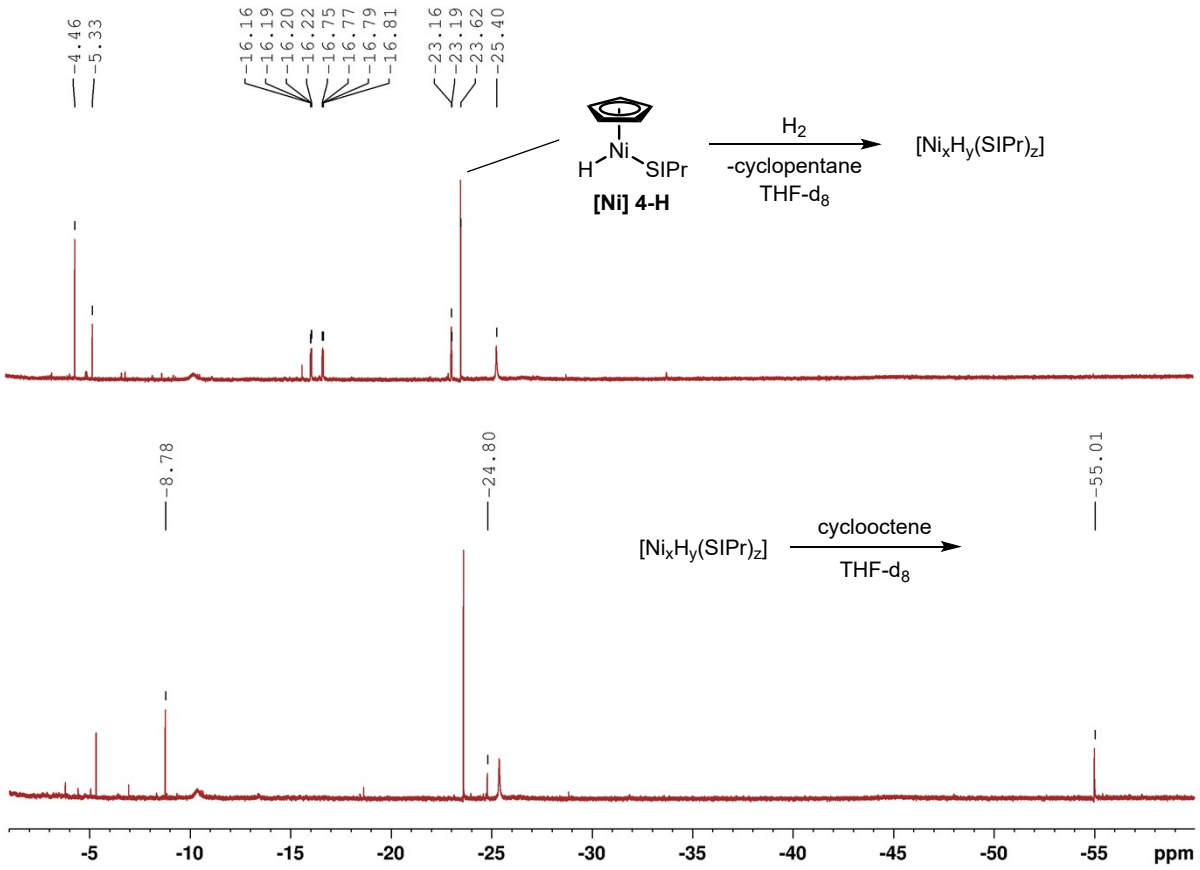


Figure S14. Hydride region of the ^{1}H NMR spectrum on hydrogenation of **[Ni] 4-H** in THF-d_8 before (top) and after (bottom) the addition of cyclooctene.

7.3 Reaction of [Ni(SIPr)(η^6-toluene)] with Cyclooctene and 1-Octene

Reaction With Cyclooctene

In a glovebox, **[Ni(SIPr)(η^6-toluene)]** (27.1 mg, 0.05 mmol, 1 equiv.) and cyclooctene (22.0 mg, 26 µL, 0.2 mmol, 4 equiv.) were dissolved in THF-d_8 (0.6 mL) to produce a dark yellow-brownish solution. The latter was transferred into an NMR tube which was closed and sealed with Parafilm before taking it out from the glovebox.

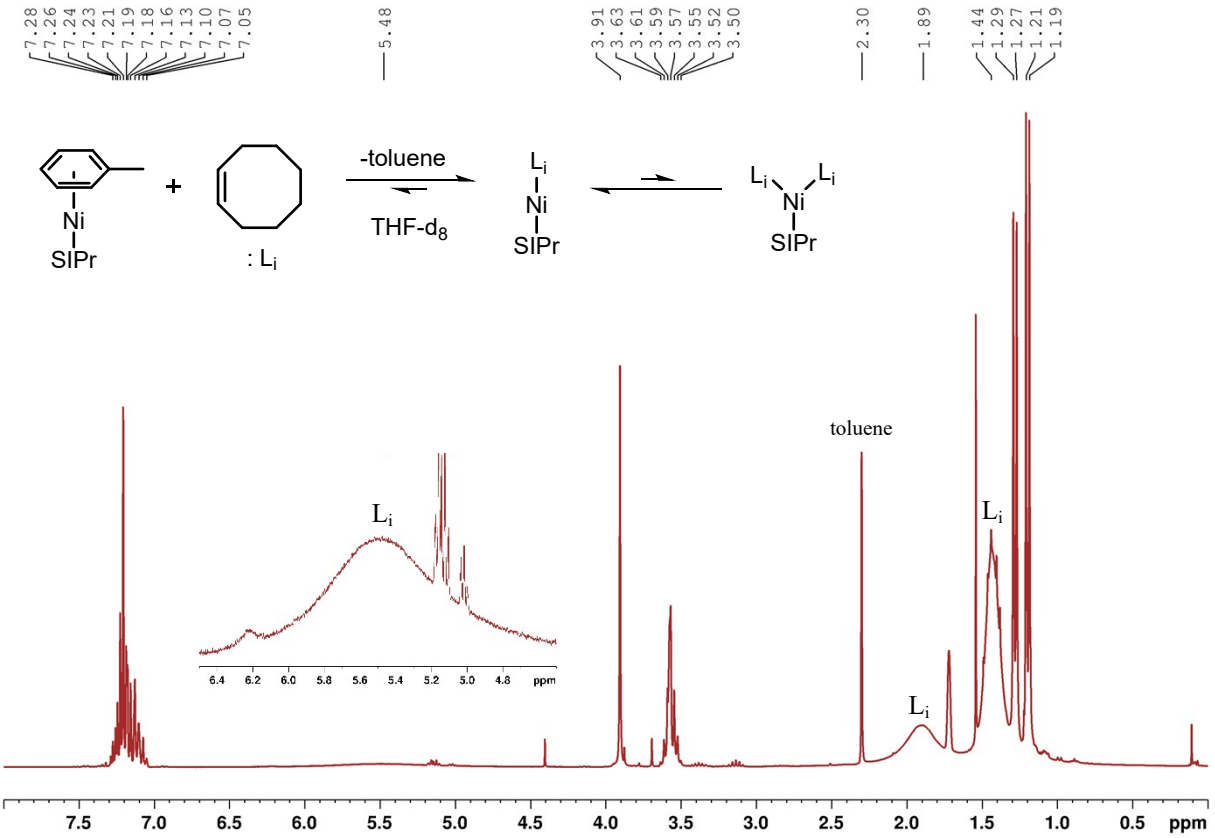


Figure S15. ^{1}H NMR spectrum of in-situ formed [Ni(cyclooctene)(SIPr)] showing dynamic alkene association/dissociation.

Signals pertaining to cyclooctene were significantly broadened whereat the magnitude of broadening decreases as the distance from the Ni-coordinated C=C bond gets larger (**Figure S15**). This result of fluxional behaviour of complexes is used extensively as an analytical tool in macromolecular chemistry, e. g. in studying the binding of a ligand to a protein.[22,23] Occasionally, the same is observed and utilized in the characterization of metal olefin complexes.[24,25,26] As discrimination between Ni-bound and free alkene is impossible due to coalescence, it is obvious that, in our case, excess cyclooctene is involved

[22] M. P. Williamson, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2013, **73**, 1–16.

[23] I. R. Kleckner, M. P. Foster, *Biochim. Biophys. Acta*, 2011, 1814, 942–968.

[24] R. van Asselt, C. J. Elsevier, W. J. Smeets, A. L. Spek, *Inorg. Chem.*, 1994, **33**, 1521–1531.

[25] M. Navarro, D. Bourissou, *Adv. Organomet. Chem.*, 2021, **76**, 101–144.

[26] K. Thum, A. Friedrich, J. Pahl, H. Elsen, J. Langer, S. Harder, *Chem. Eur. J.*, 2020, **27**, 2513–2522.

in the exchange process. Since toluene is readily displaced and no significant formation of dimeric **[Ni$_2$(SIPr)$_2$]** is observed, at least 1 equiv. of cyclooctene must be coordinated to otherwise unstable [Ni(SIPr)].[27] The 14e species **[Ni(cyclooctene)(SIPr)]** is still coordinatively unsaturated and likely undergoes further dynamic alkene-association/dissociation which causes the observed broadening.

Reaction With 1-Octene

In a glovebox, **[Ni(SIPr)(η^6-toluene)]** (27.1 mg, 0.05 mmol, 1 equiv.) and 1-octene (22.4 mg, 32 µL, 0.20 mmol, 4 equiv.) were dissolved in THF-d_8 (0.6 mL) to produce a yellow solution. The latter was transferred into an NMR tube which was closed and sealed with Parafilm before taking it out from the glovebox.

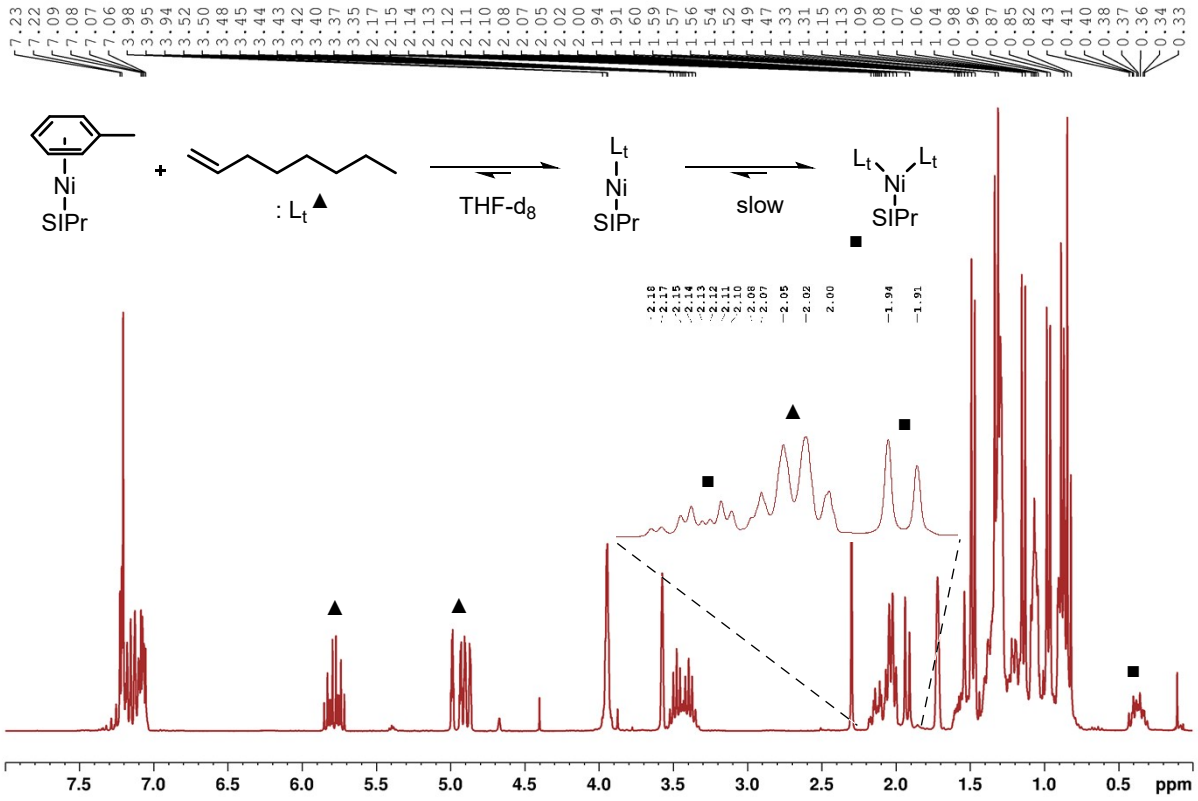


Figure S16. ^{1}H NMR spectrum of in-situ formed **[Ni(1-octene)$_2$(SIPr)]**.

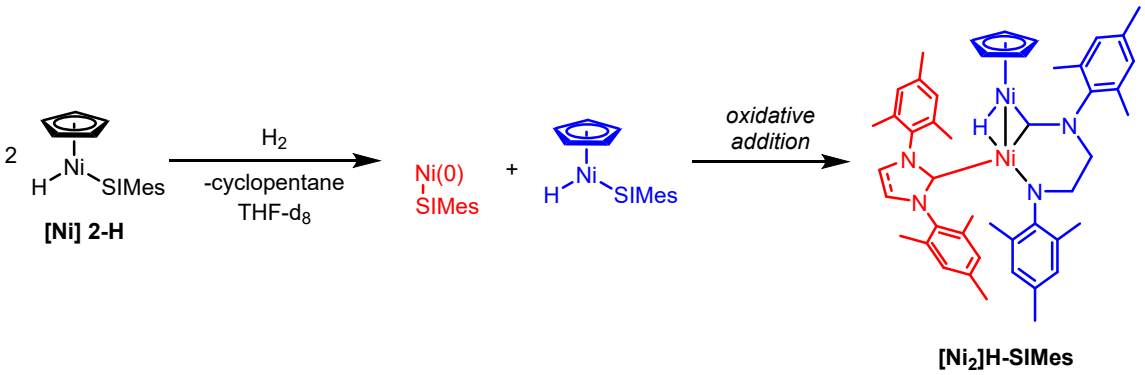
The NMR spectrum shows the quantitative formation of **[Ni(η^2-1-octene)$_2$SIPr]** (**Figure S16**); signals of free 1-octene can be clearly distinguished from the ones of Ni-coordinated 1-octene. No signal broadening is observed, indicating a slow exchange process. The stability of [Ni(η^2-alkene)$_2$(SIPr)] is likely the reason for the slow conversion of terminal and/or unhindered alkene substrates in the pertinent catalytic hydrogenation.

[27] B. Sawatlon, T. Wititsuwannakul, Y. Tantirungrotechai, P. Surawatanawong, *Dalton Trans*., 2014, **43**, 18123–18133.

7.4 Deactivation Through Oxidative Addition of Mes-NHC Ligands

With the intention to simplify the interpretation of NMR spectra of activated catalyst solutions, Mes-NHC-tagged precatalysts **[Ni] 1-H** and **[Ni] 2-H** were deployed. In each case, one major hydride-species accumulated regardless of the type of deuterated solvent used, i.e., benzene-d_6, toluene-d_8, or THF-d_8. The hydride signal was shifted low-field compared to the starting complex and was used to monitor its formation. It was found that after 7 h under 20 bar H_2 at 45 °C, the starting complex was almost fully converted. The exceptionally high solubility of the formed complex when using **[Ni] 1-H** obstructed its isolation; only a small amount was obtained by crystallization from hexamethyldisiloxane (HMDSO). Surprisingly, on switching to **[Ni] 2-H**, the analogues product complex has a much lower solubility, especially in diethyl ether, from which it readily precipitates during the hydrogenation process.

Upon determination of its molecular structure by way of SC-XRD, it became obvious that **[Ni$_2$]H-SIMes** was formed through oxidative addition of SIMes (bound as **[Ni] 2-H**) to highly reactive in-situ generated **[Ni(0)(SIMes)]** (**Scheme S1**).



Scheme S1. Catalyst deactivation through formation of metallacycle **[Ni$_2$]H-SIMes**.

The metallacycle was tested in the hydrogenation of cyclooctene. No activity was observed after the first 30 min under standard conditions whereas **[Ni] 4-H** and **[NiSIPr(η^6-toluene)]** convert 30-60% within the same period of time. This clearly indicates that **[Ni$_2$]H-SIMes** is rather stable under hydrogenation conditions and the product of a deactivation pathway. To check whether deactivation through formation of **[Ni$_2$]H-SIMes** is definite, the metallacycle was subjected to hydrogenation for several hours (20 bar H_2, 45 °C, 3 h) in the absence of any substrate. Cyclooctene was then added and the mixture pressurized again (20 bar H_2, 45 °C, 5 min) which led to substantial substrate conversion. The deactivation is therefore only temporary but still likely to corrupt the overall conversion rate.

It was also found that **[Ni$_2$]H-SIMes** is not stable in solution at RT (**Figure S17**) whereby a minor decomposition product is the starting complex **[Ni] 2-H**. The major species, also containing a Cp-ligand, could not be identified. Since single crystals of **[Ni$_2$]H-SIMes** were obtained by slow evaporation from a THF solution during the course of 1 week, it is likely that the observed species exist in an equilibrium.

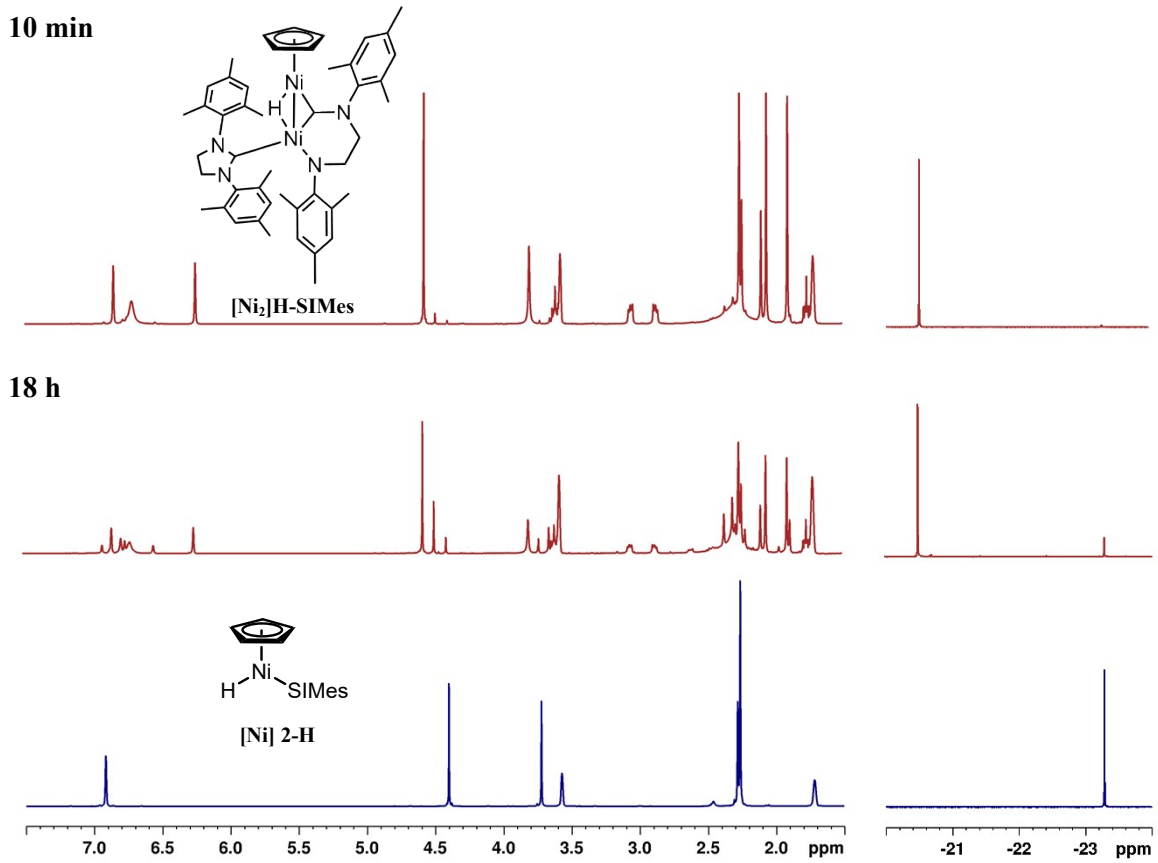
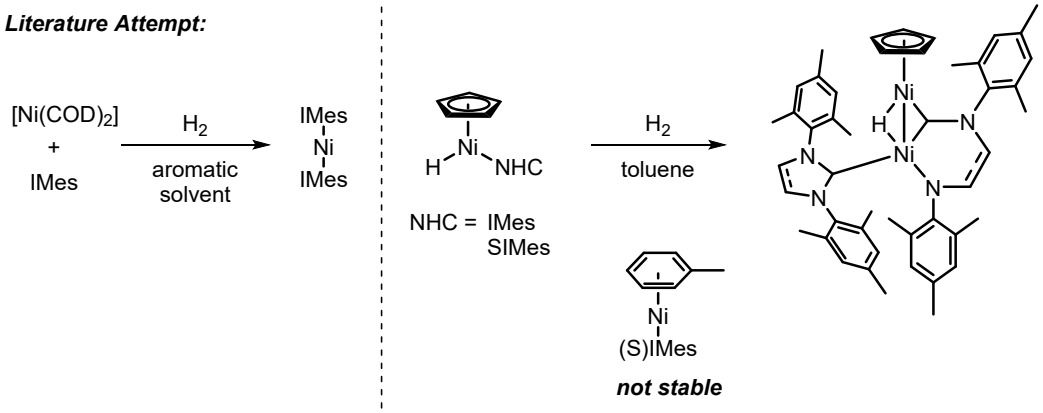


Figure S17. Time-resolved ^{1}H NMR spectra of **[Ni$_2$]H-SIMes** in THF-d$_8$ and **[Ni] 2-H** for comparison. The magnified hydride region is shown on the right.

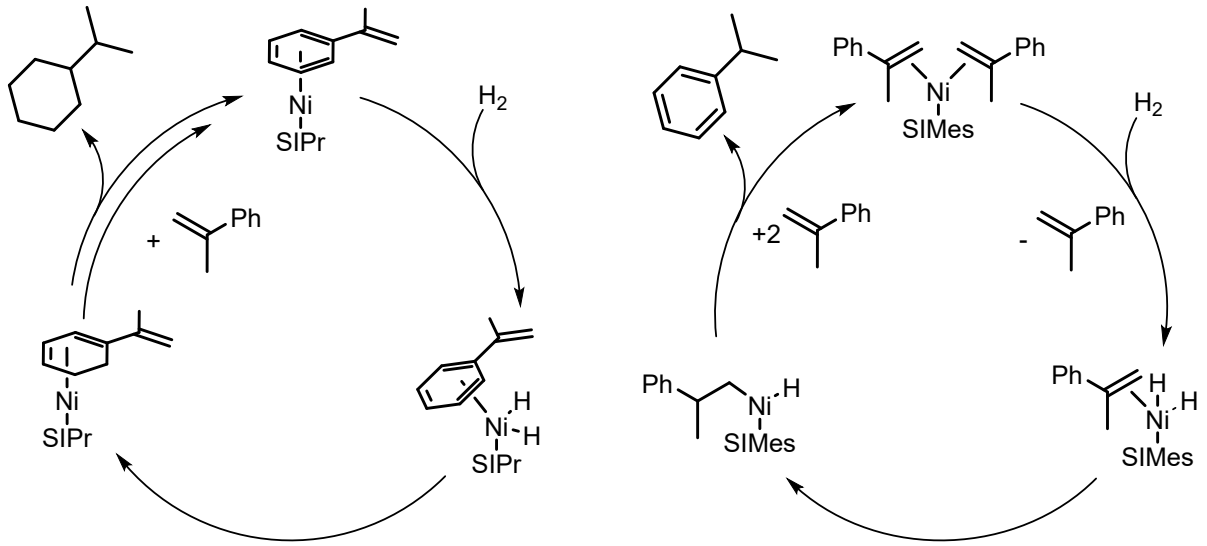
Up to now, attempts to synthesize **[Ni(0)(η^6-arene)(IMes)]** failed. Using [Ni(COD)$_2$] and IMes led to formation of [Ni(SIMes)$_2$] as the major product.[17] With our approach of using **[Ni] 2-H** as starting material, **[Ni$_2$]H-SIMes** formed instead (**Scheme S2**). These are strong indications that [Ni(0)(NHC)] (NHC = IMes, SIMes) is not sufficiently stabilized by η^6-coordination of arenes which also reflects in the reactivity towards certain substrates in this study.



Scheme S2. Unsuccessful approaches towards the preparation of complexes of the type [Ni(0)(NHC)(η^6-arene)] (NHC = IMes, SIMes).

7.5 Influence of the NHC-Ligand on Reaction Rates and Selectivity

During the hydrogenation of α-methylstyrene with **[Ni] 4-H** as precatalyst we observed that isopropylcyclohexane was obtained as the major product (>90%) when applying **Mode I**. Yet, selectivity was reversed by way of preactivation through **Mode II** and mostly isopropylbenzene was formed. Application of **[Ni] 2-H** and **Mode I** led to exclusive hydrogenation of the alkene portion. It was recently established, for a Mo-based catalytic system, that η^6-coordination is a pivotal mechanistic step in arene hydrogenation.[28] Hence, we reason that this also applies to our Ni(0)-NHC system: [Ni(0)(SIPr)] with its aptitude to form η^6-arene complexes facilitates the reduction of the aromatic core and, subsequently, the exhaustive hydrogenation of the substrate whereas double-alkene-stabilized [Ni(0)(SIMes)] gives rise to sole hydrogenation of the olefinic C=C bond (**Scheme S3**).



Scheme S3. Proposed catalytic cycles for the exhaustive hydrogenation of α-methylstyrene (left) and the alkene-only hydrogenation (right).

A similar selectivity pattern was observed for the hydrogenation of *cis*-stilbene where **[Ni] 4-H** produced a mixture of partially hydrogenated products. Yet, **[Ni] 2-H** gave a mixture of 1,2-diphenylethane and *trans*-stilbene; β-hydride elimination apparently competes with reductive elimination which enables the formation of the *trans* isomer.

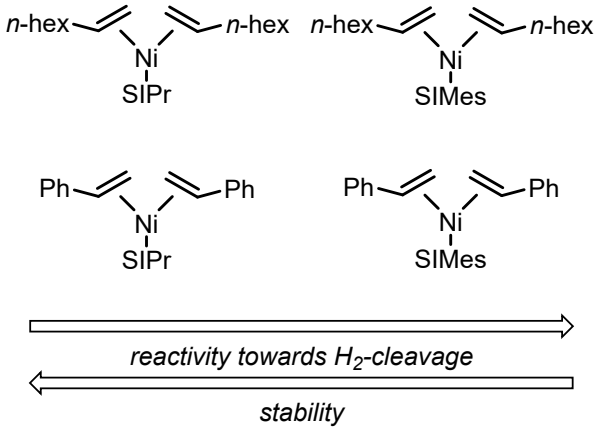
It was also observed that **[Ni] 2-H** (SIMes) was more efficient in catalyzing the hydrogenation of terminal alkenes compared to **[Ni] 4-H** (SIPr). A reason for this might be the lower buried volume of

[28] J. C. Greenbaum, A. J. King, M. V. Pecoraro, P. Tosatti, K. Puentener, P. J. Chirik, *J. Am. Chem. Soc.*, 2025, **147**, 30423–30435.

[NiL$_{t2}$SIMes] (L_t = terminal alkene) which explains the increased reactivity towards H_2 cleavage (**Scheme S4**).

Table S4. Conditions: Substrate (0.5 mmol), 1 mol% [Ni], 20 bar H_2, 45 °C, 3 h, 1,4-dioxane (1 mL)

Entry	[Ni]	Substrate	Conv. / %
1	**[Ni] 2-H**	1-octene	>99
2	**[Ni] 4-H**	1-octene	20
3	**[Ni] 2-H**	styrene	>99
4	**[Ni] 4-H**	styrene	91



Scheme S4. Proposed rationale for the observed activities in the hydrogenation of terminal alkenes.

8 Spectral Data

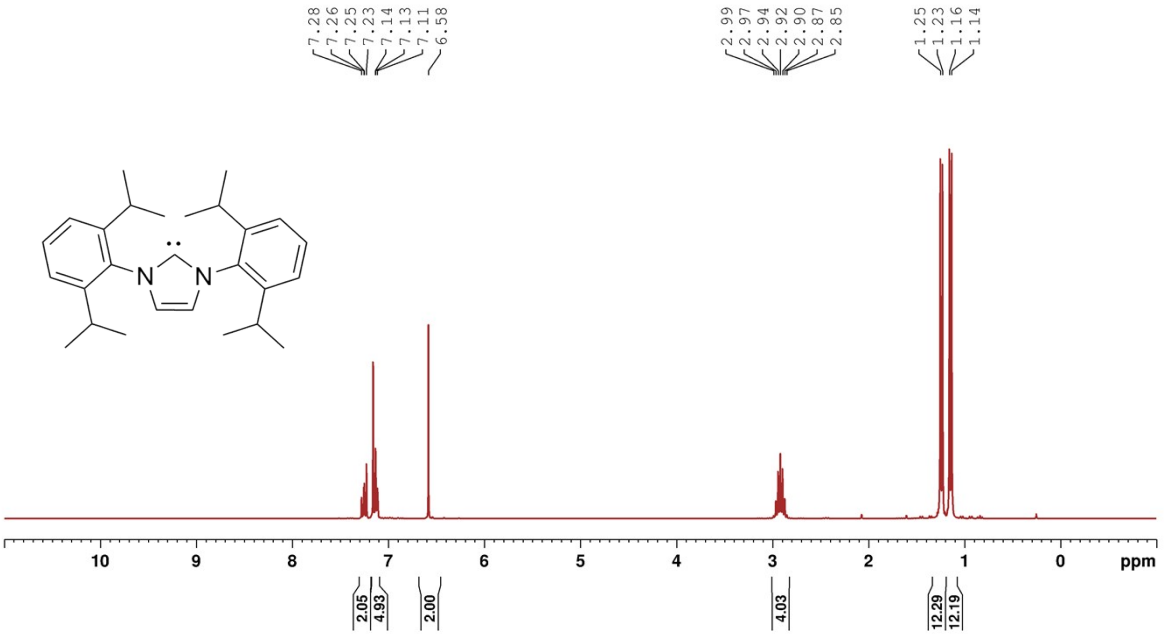


Figure S18. ^{1}H NMR spectrum of **IPr** in C_6D_6.

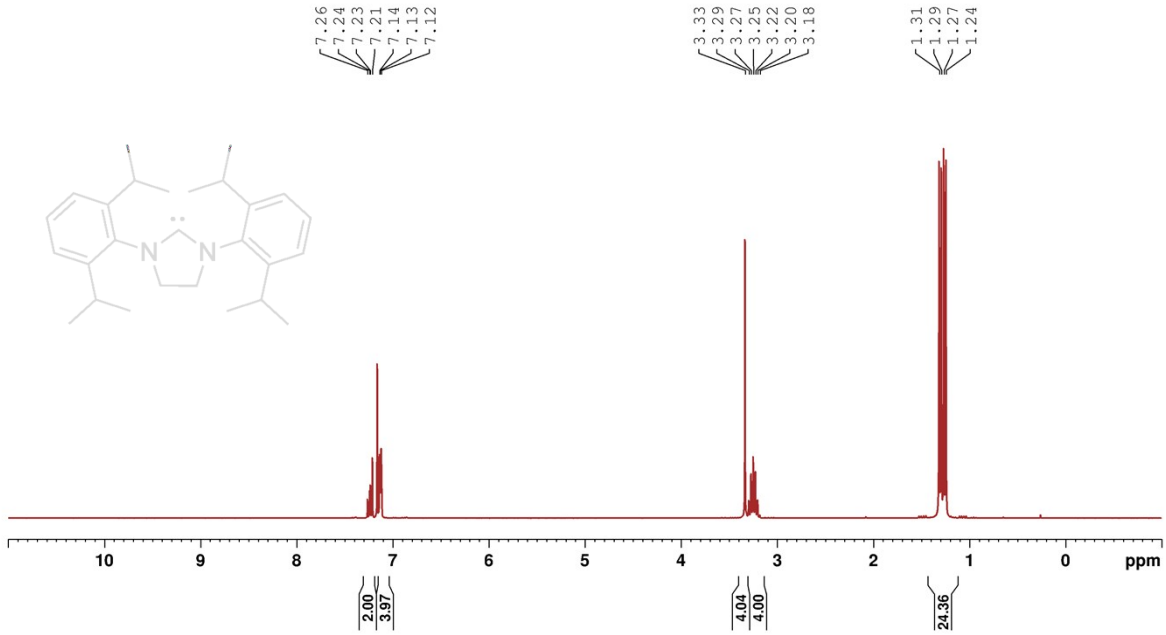


Figure S19. ^{1}H NMR spectrum of **SIPr** in C_6D_6.

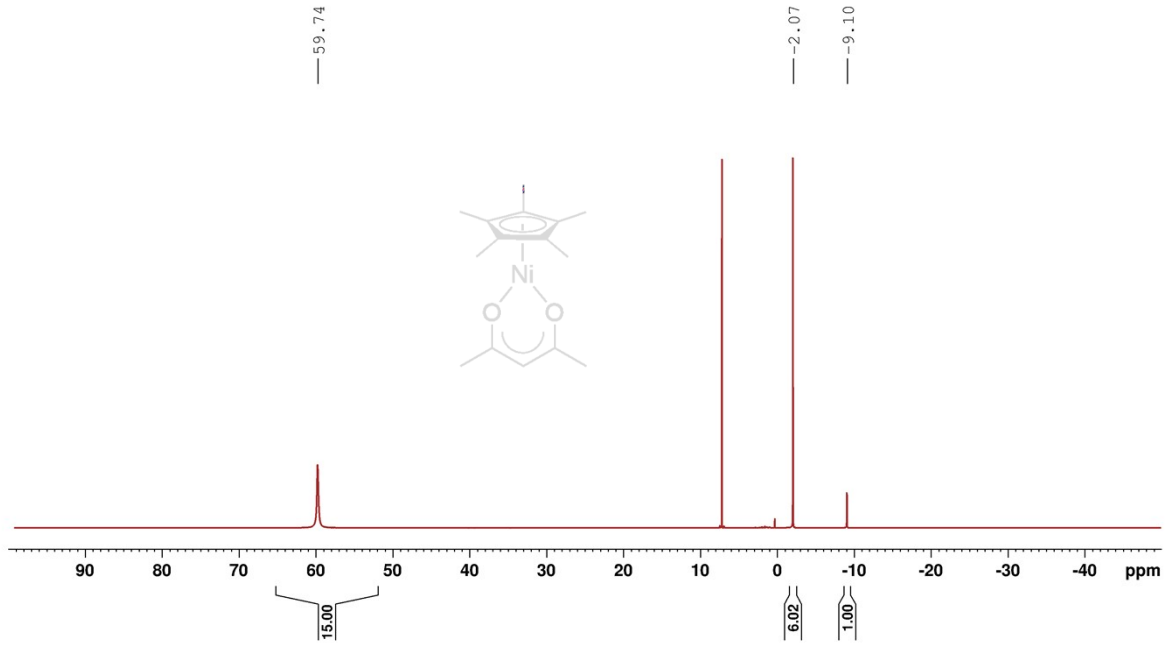


Figure S20. ^{1}H NMR spectrum of **[Ni(acac)Cp*]** in C_6D_6.

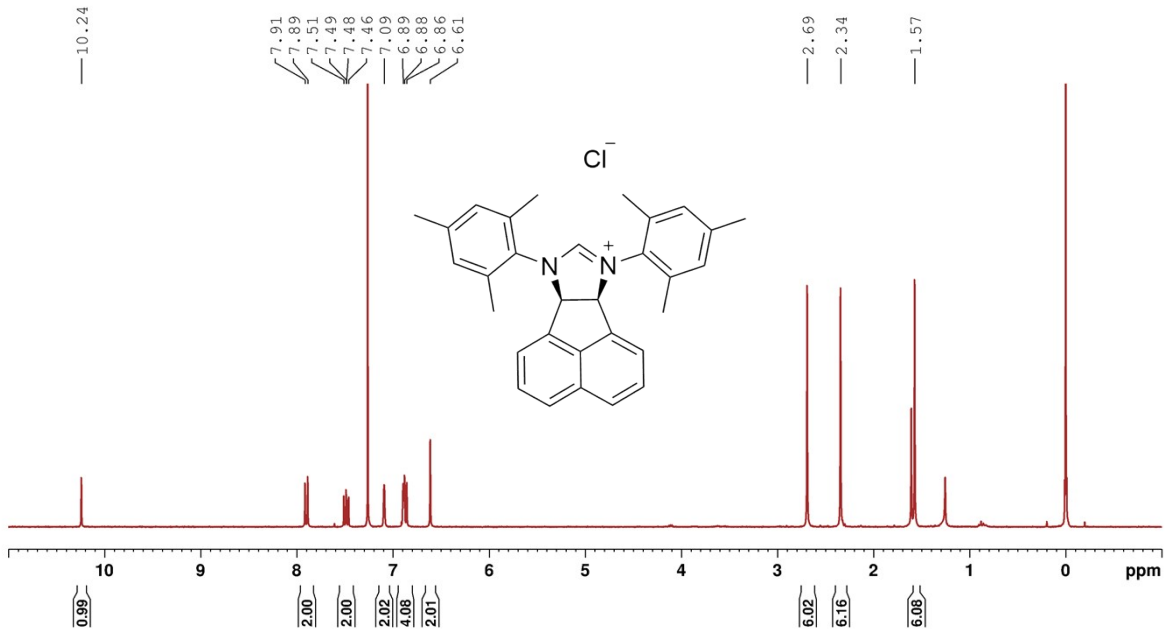


Figure S21. ^{1}H NMR spectrum of **SBIAN-Mes·HCl** in $CDCl_3$.

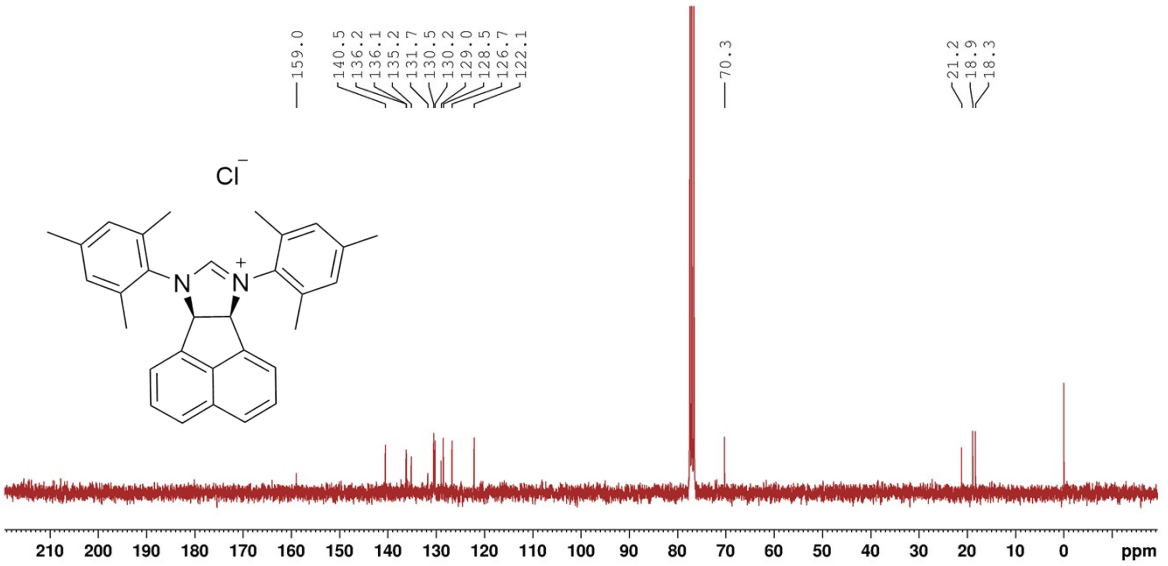


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **SBIAN-Mes·HCl** in $CDCl_3$.

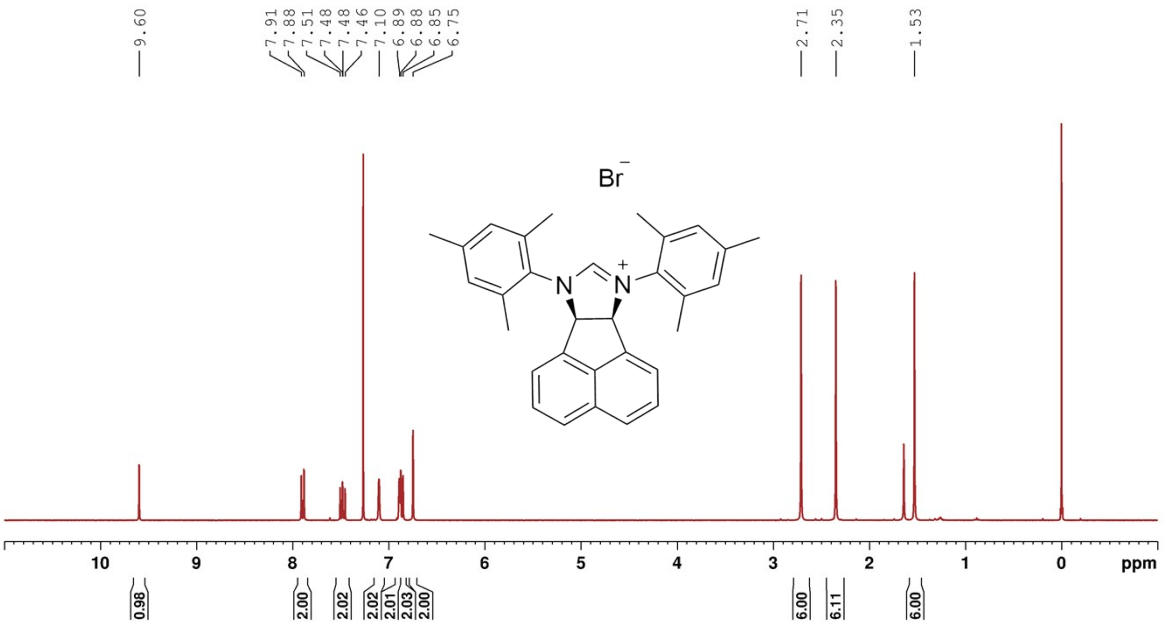


Figure S23. ^{1}H NMR spectrum of **SBIAN-Mes·HBr** in $CDCl_3$.

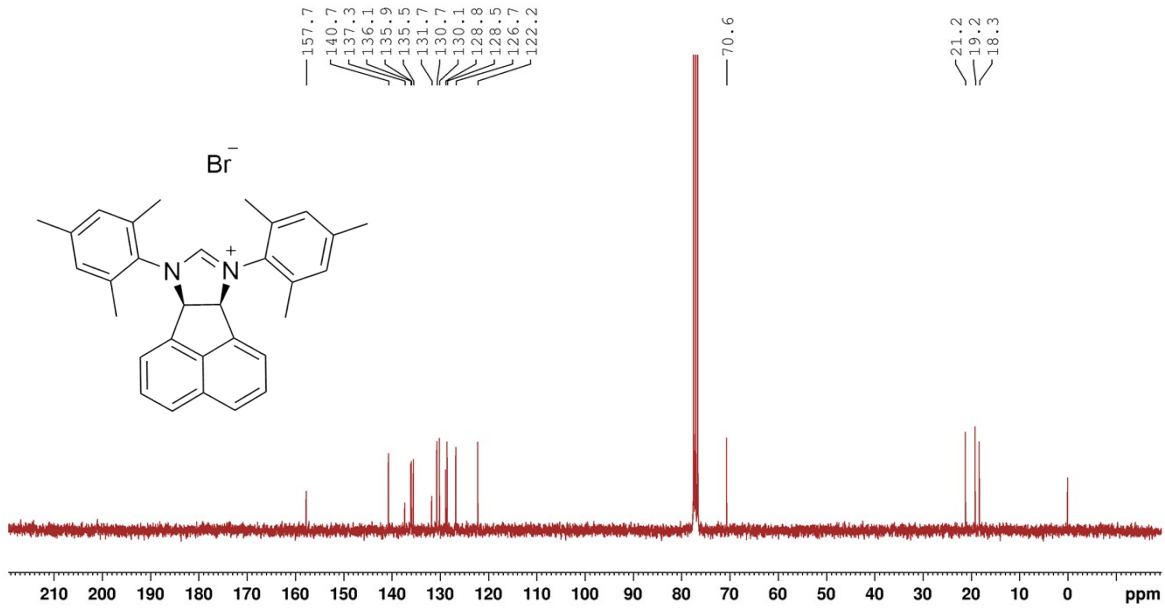


Figure S24. ^{13}C{^{1}H} NMR spectrum of **SBIAN-Mes·HBr** in $CDCl_3$.

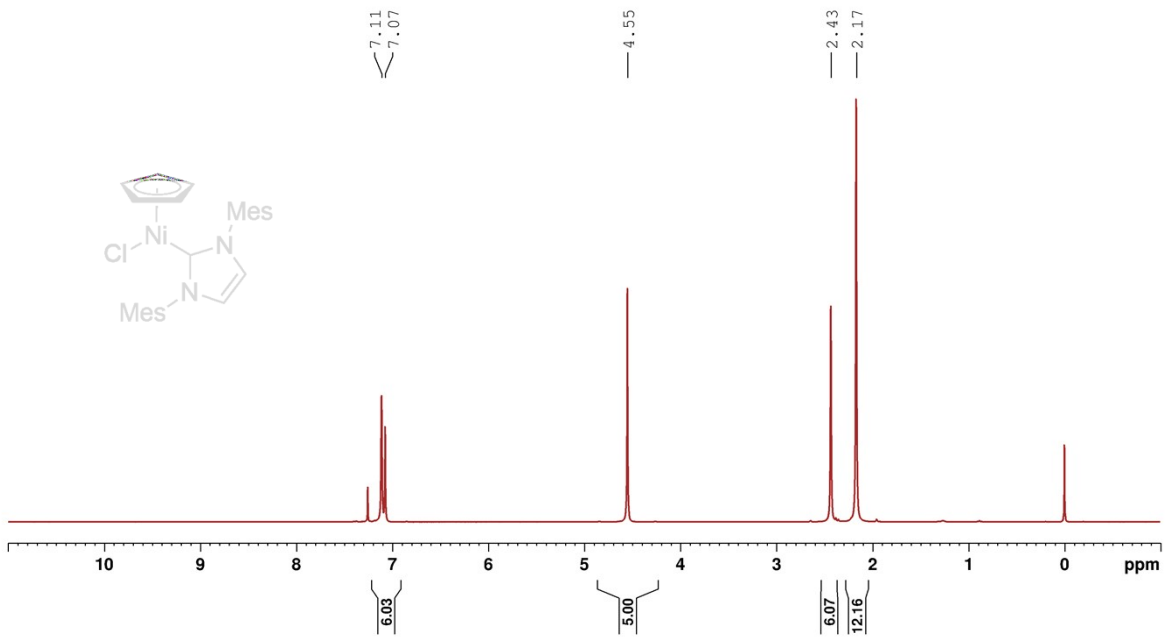


Figure S25. ^{1}H NMR spectrum of **[Ni] 1** in $CDCl_3$.

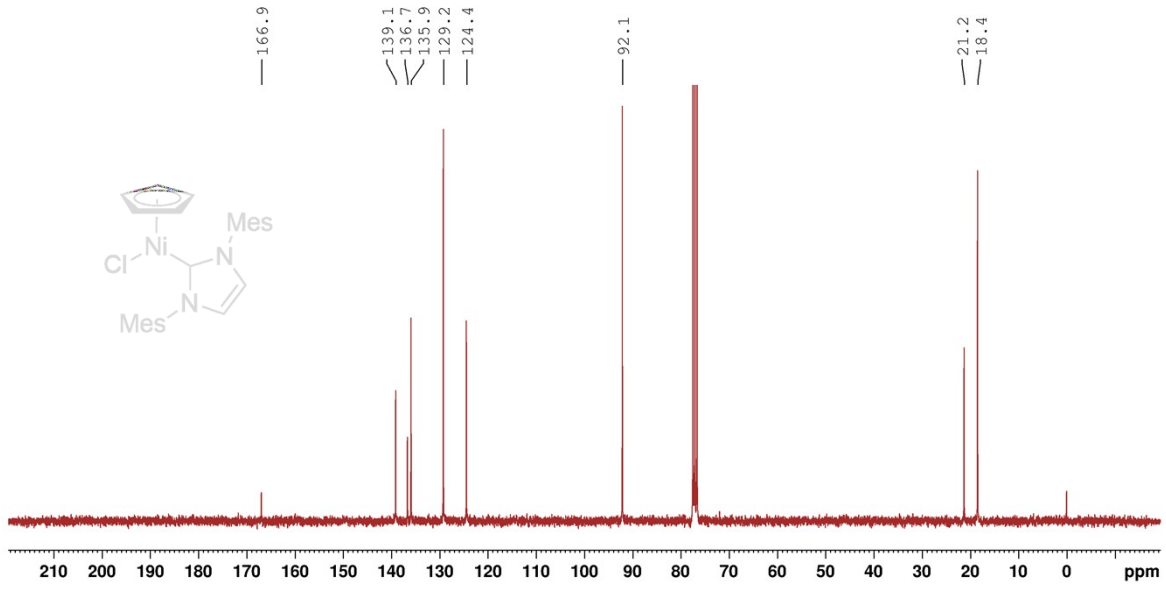


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 1** in $CDCl_3$.

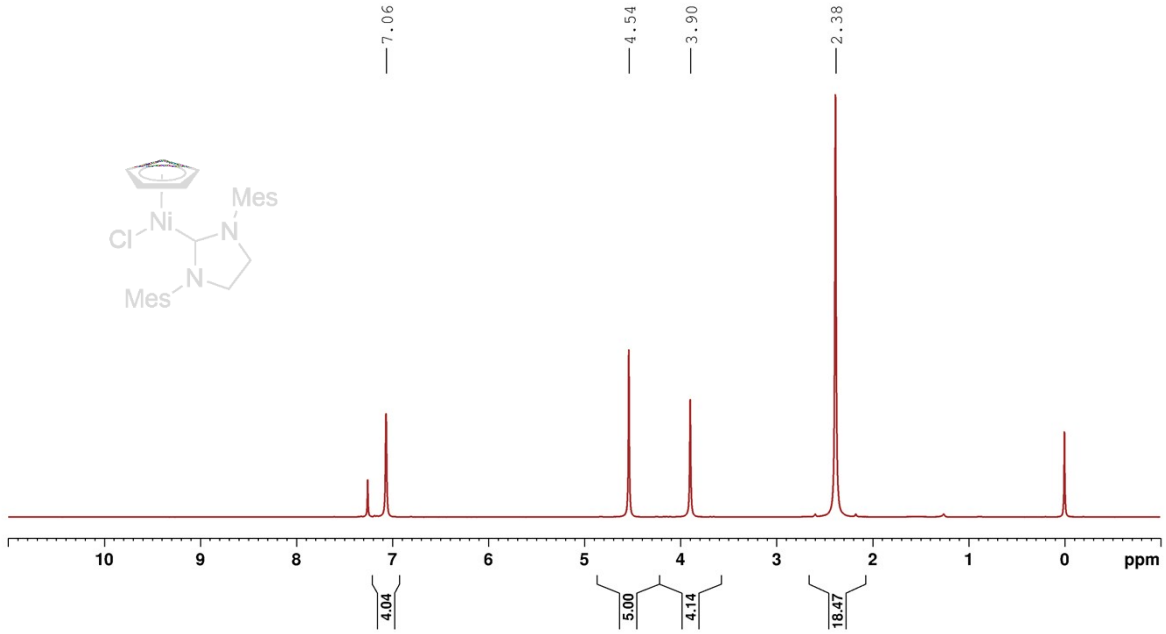


Figure S27. ^{1}H NMR spectrum of **[Ni] 2** in $CDCl_3$.

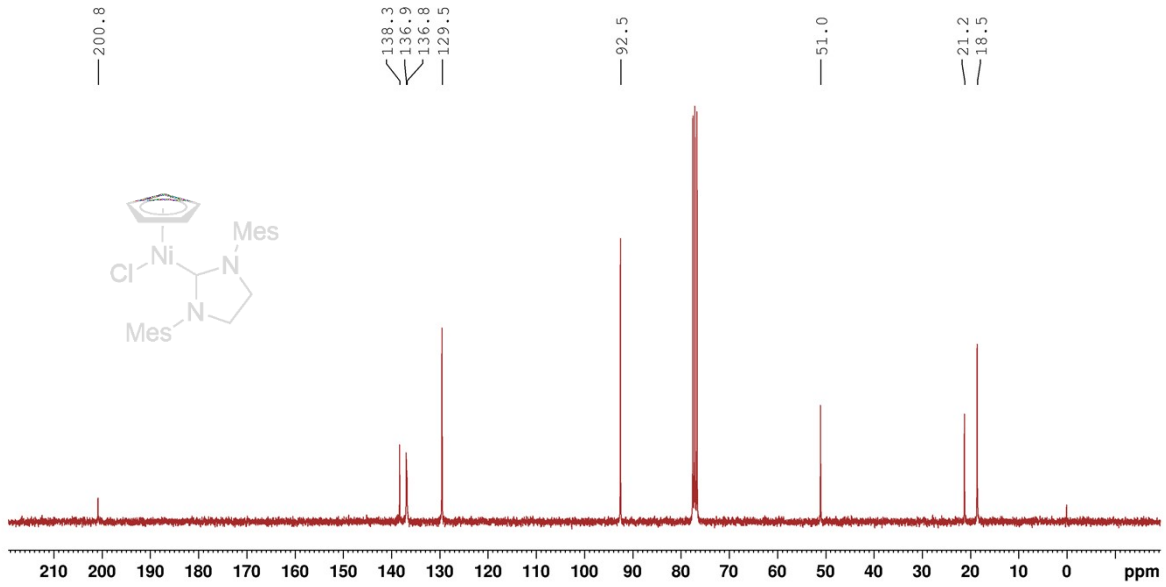


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 2** in $CDCl_3$.

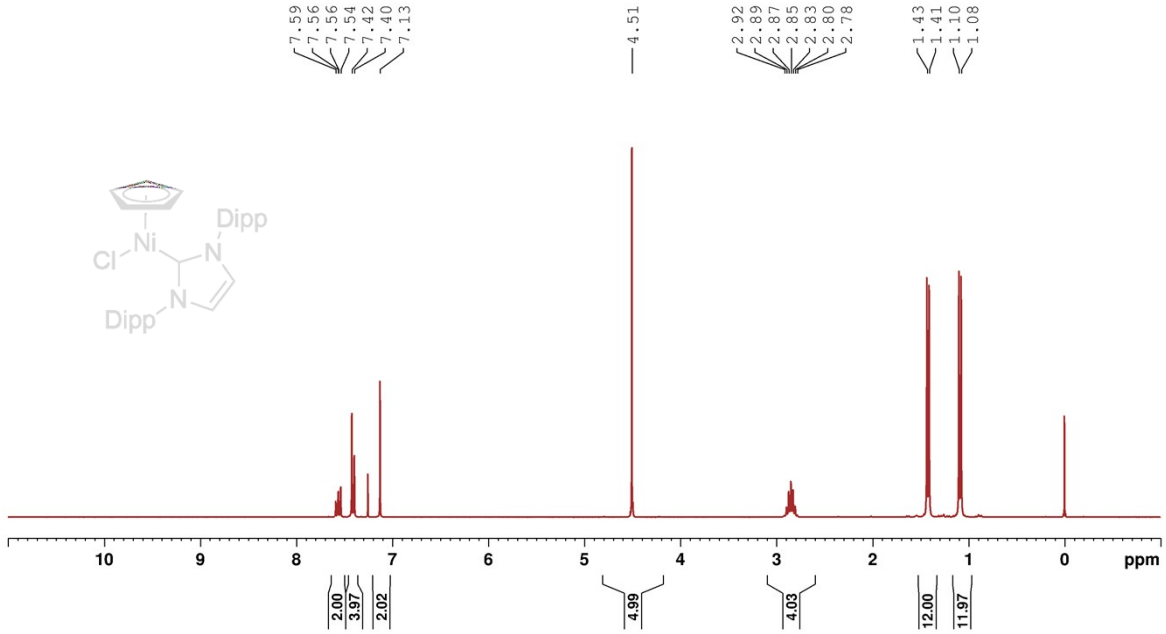


Figure S29. ^{1}H NMR spectrum of **[Ni] 3** in $CDCl_3$.

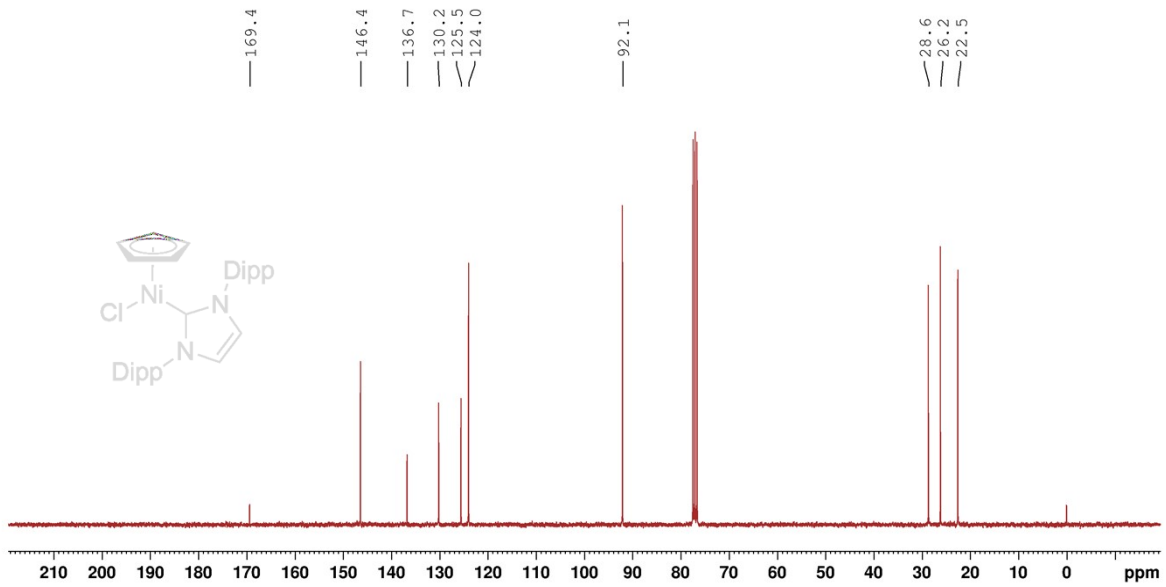


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 3** in $CDCl_3$.

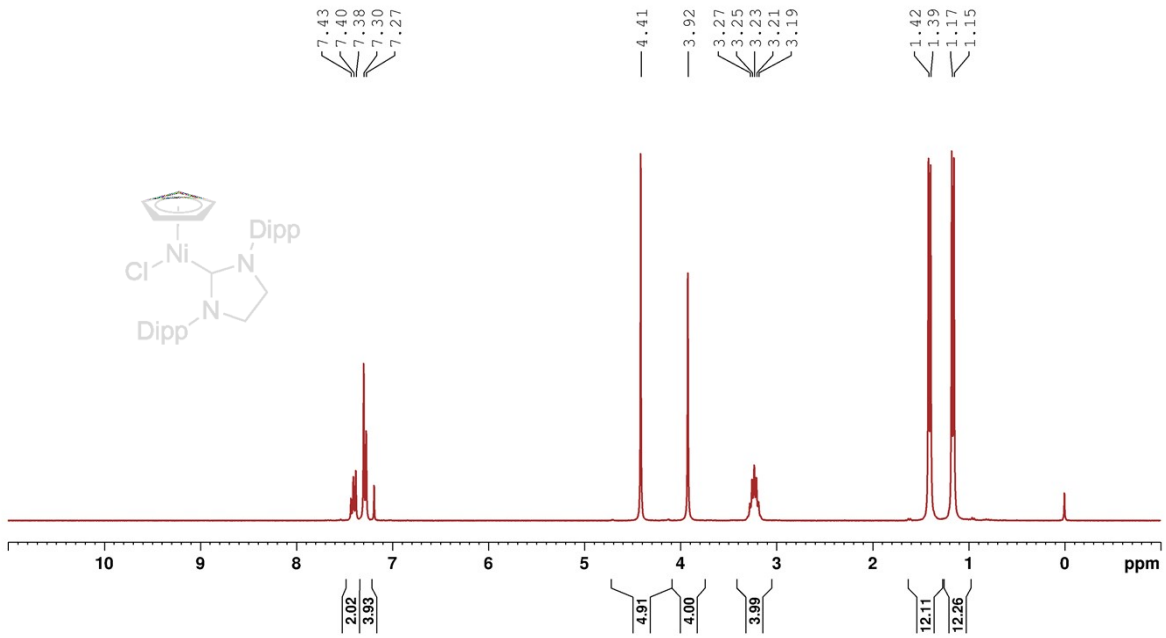


Figure S31. ^{1}H NMR spectrum of **[Ni] 4** in $CDCl_3$.

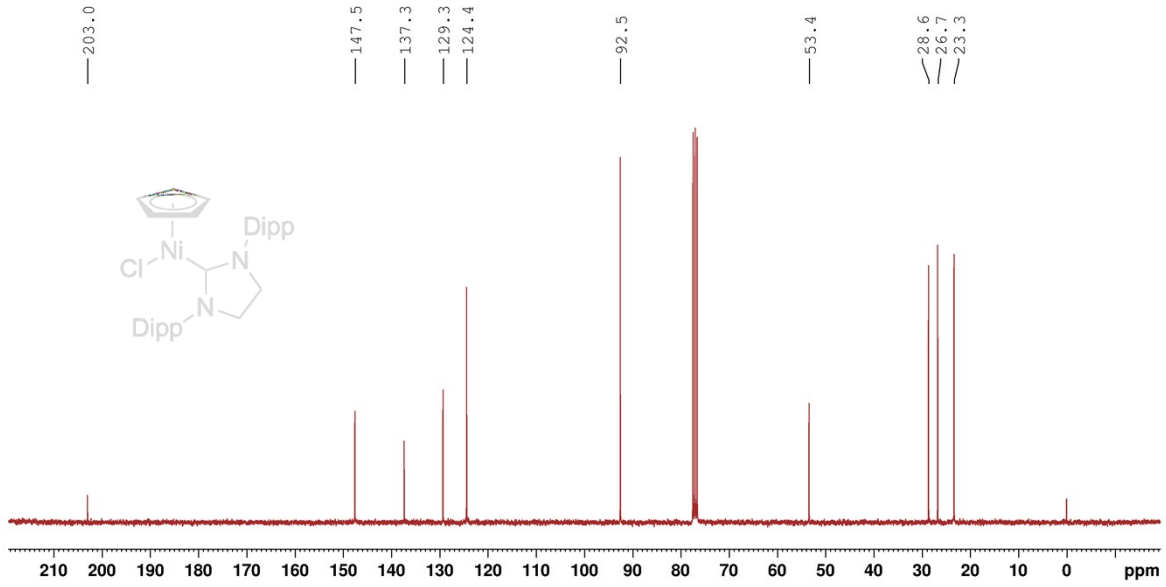


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 4** in $CDCl_3$.

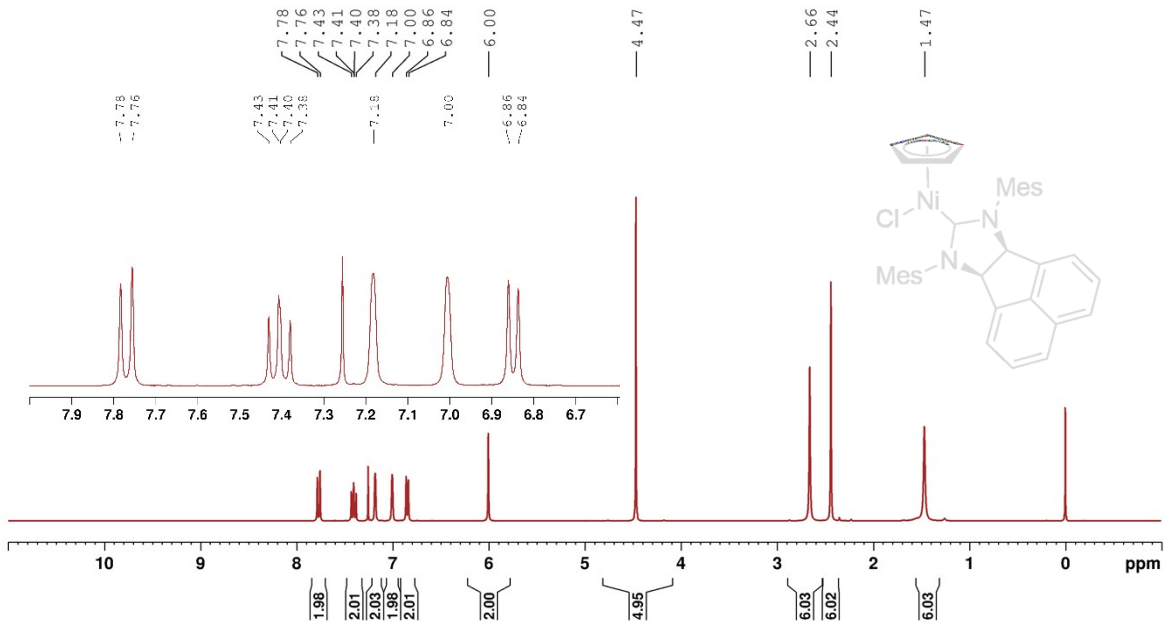


Figure S33. ^{1}H NMR spectrum of **[Ni] 5** in $CDCl_3$.

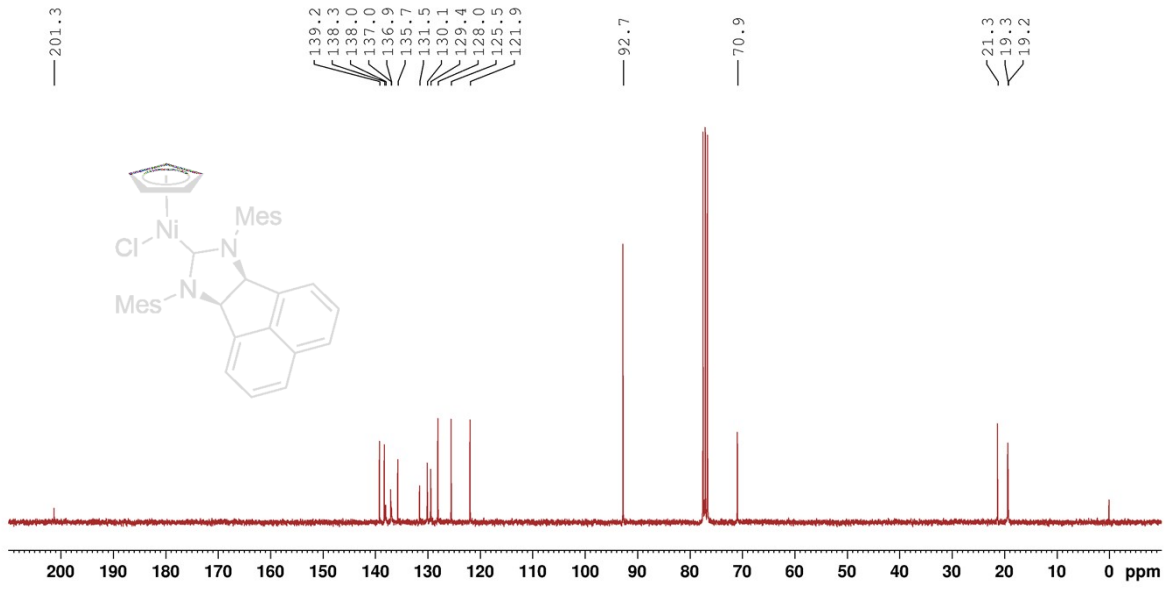


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 5** in $CDCl_3$.

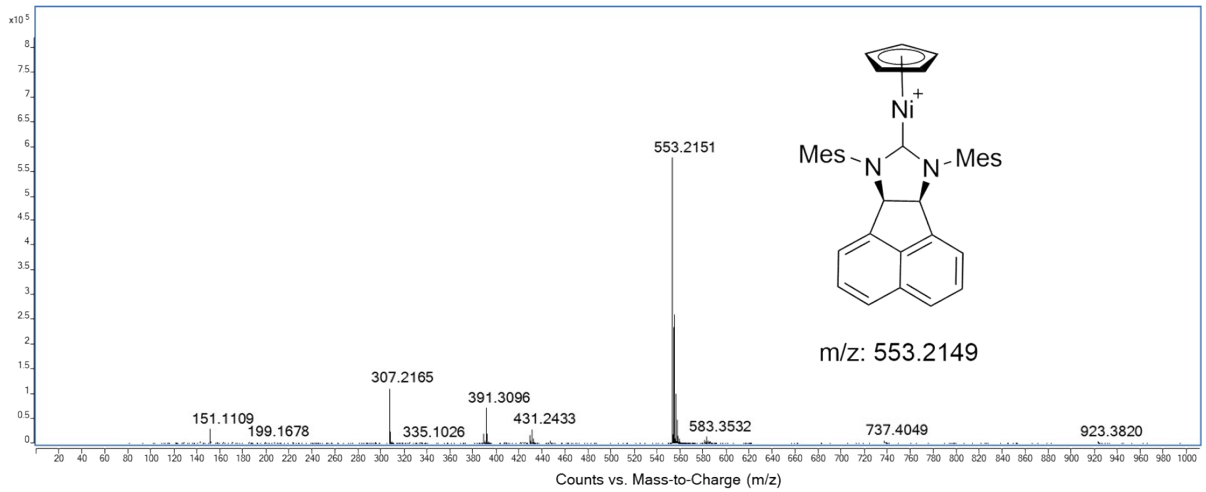


Figure S35. HRMS (ESI+) spectrum of **[Ni] 5**.

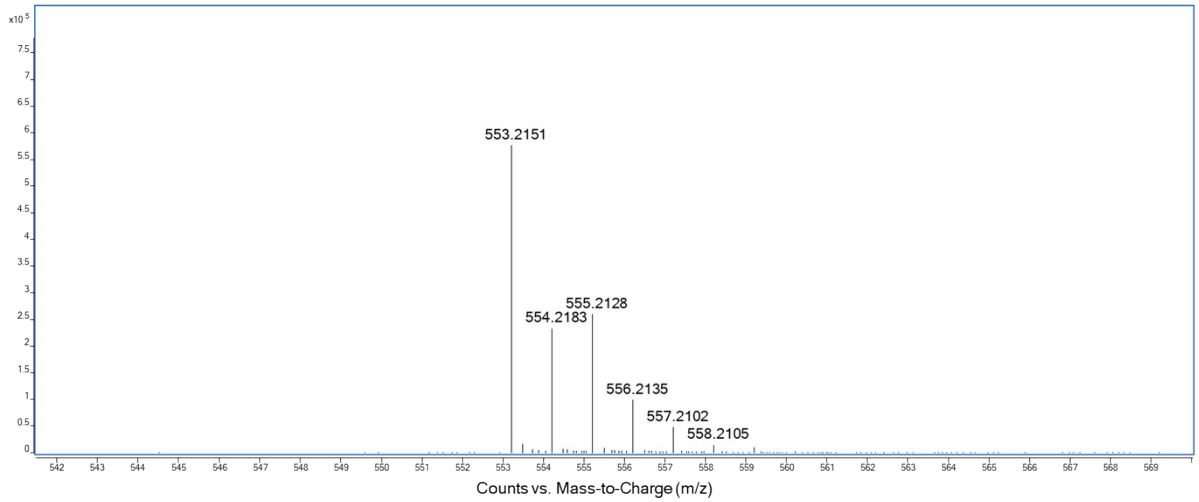


Figure S36. HRMS (ESI+) isotope pattern of **[Ni] 5** $[M–Cl]^+$.

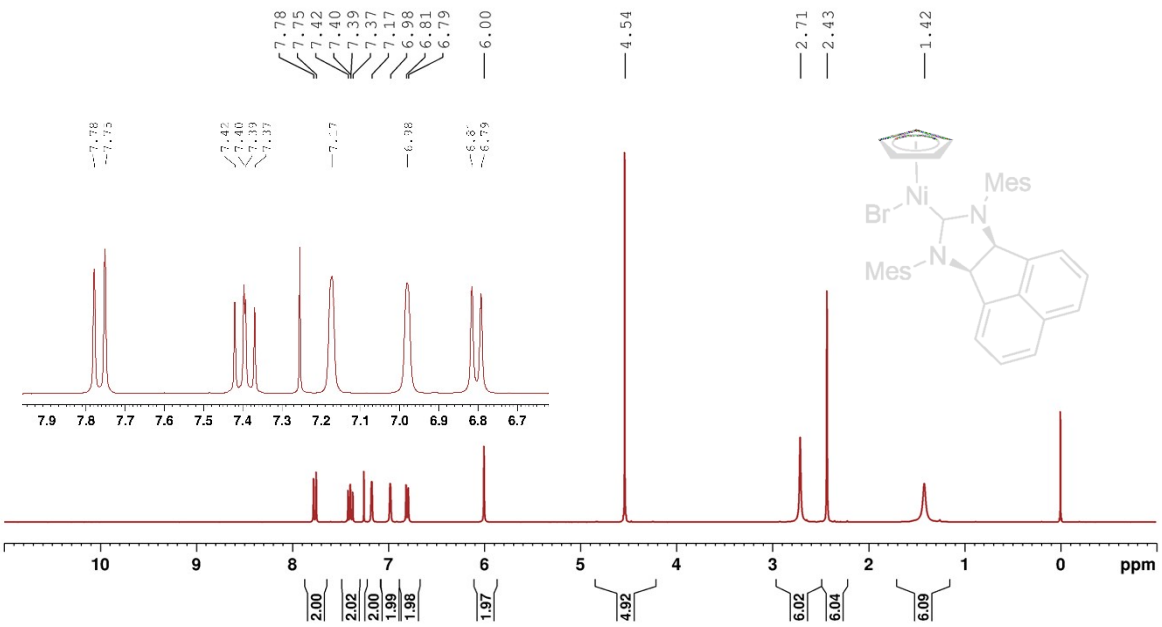


Figure S37. ^{1}H NMR spectrum of **[Ni] 5-Br** in $CDCl_3$.

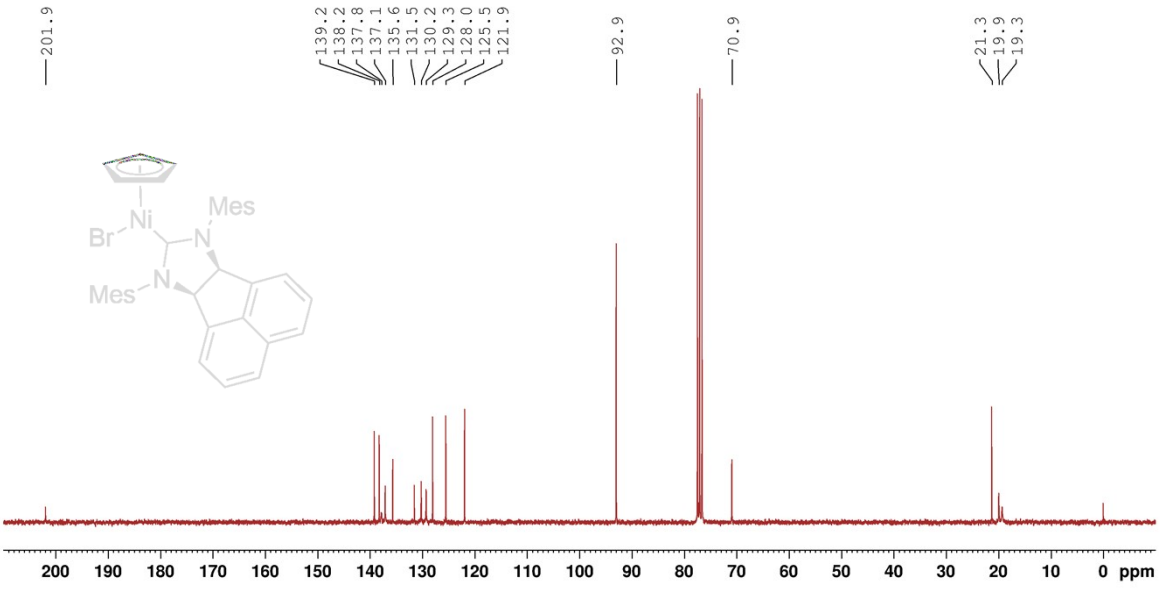


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 5-Br** in $CDCl_3$.

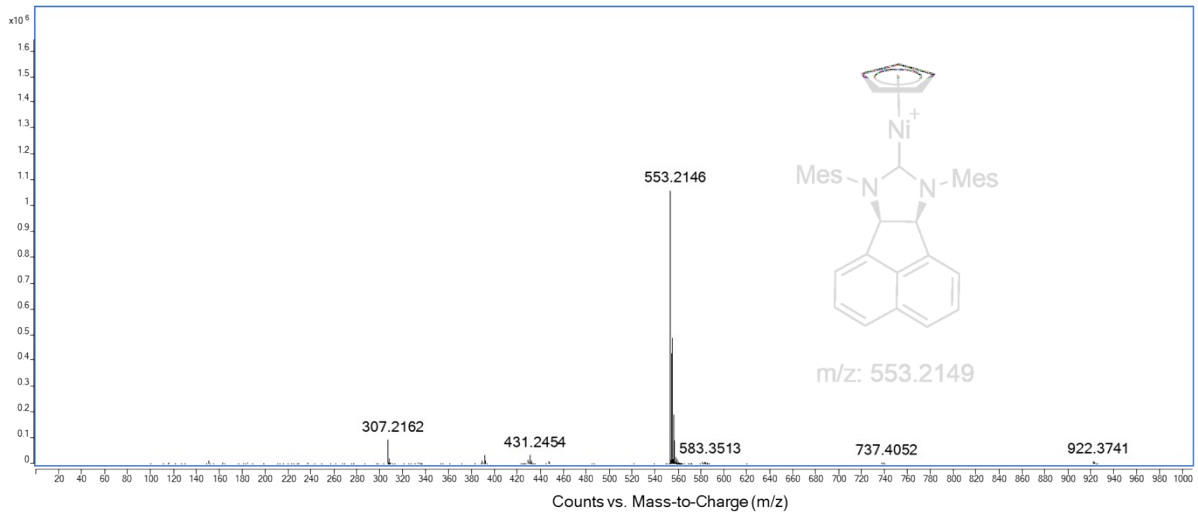


Figure S39. HRMS (ESI+) spectrum of **[Ni] 5-Br**.

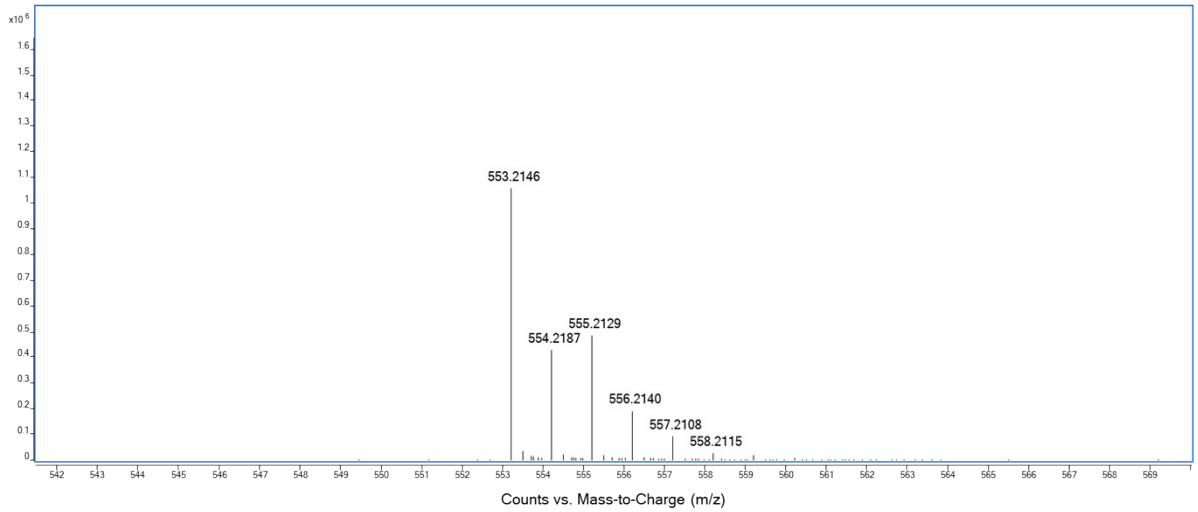


Figure S40. HRMS (ESI+) isotope pattern of **[Ni] 5-Br** $[M–Br]^+$.

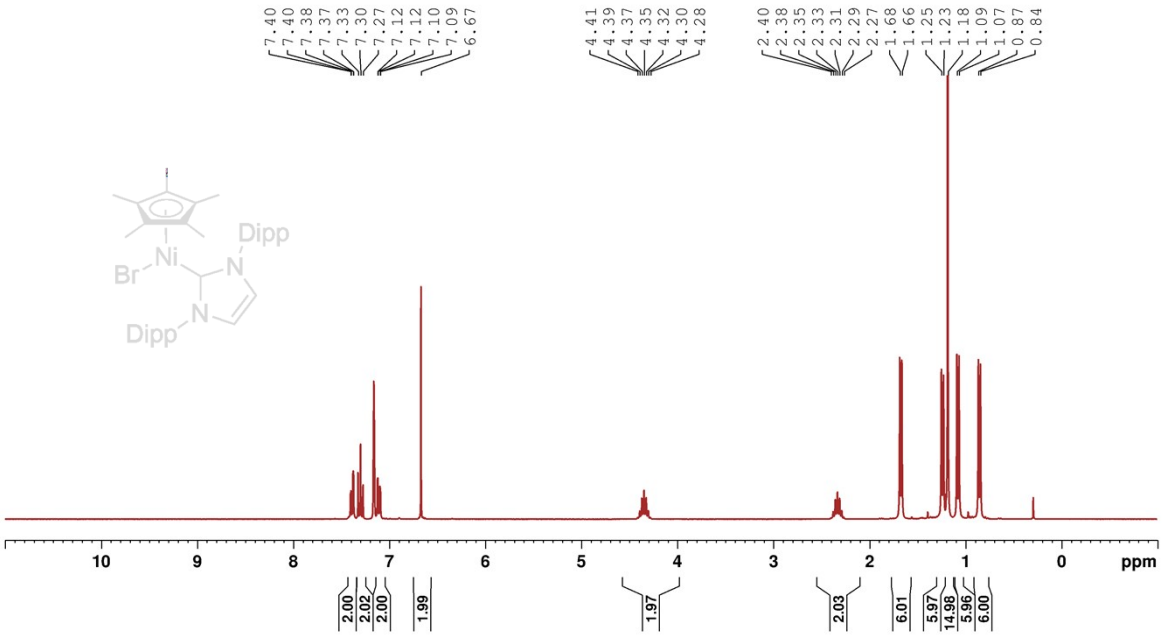


Figure S41. ^{1}H NMR spectrum of **[Ni] 3-Br-Cp*** in C_6D_6.

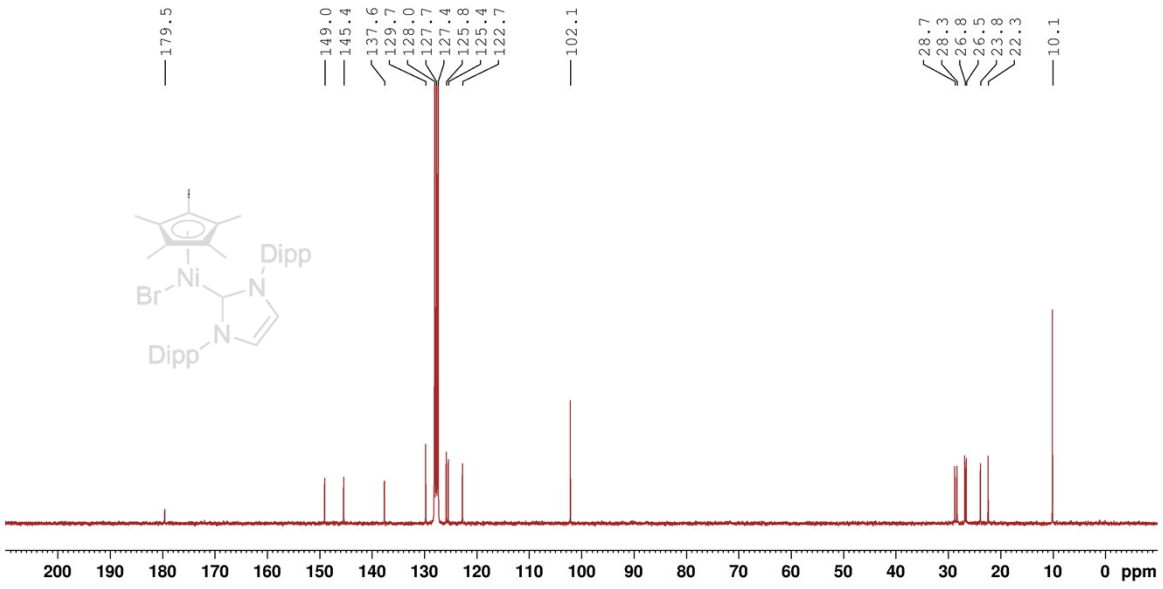


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 3-Br-Cp*** in C_6D_6.

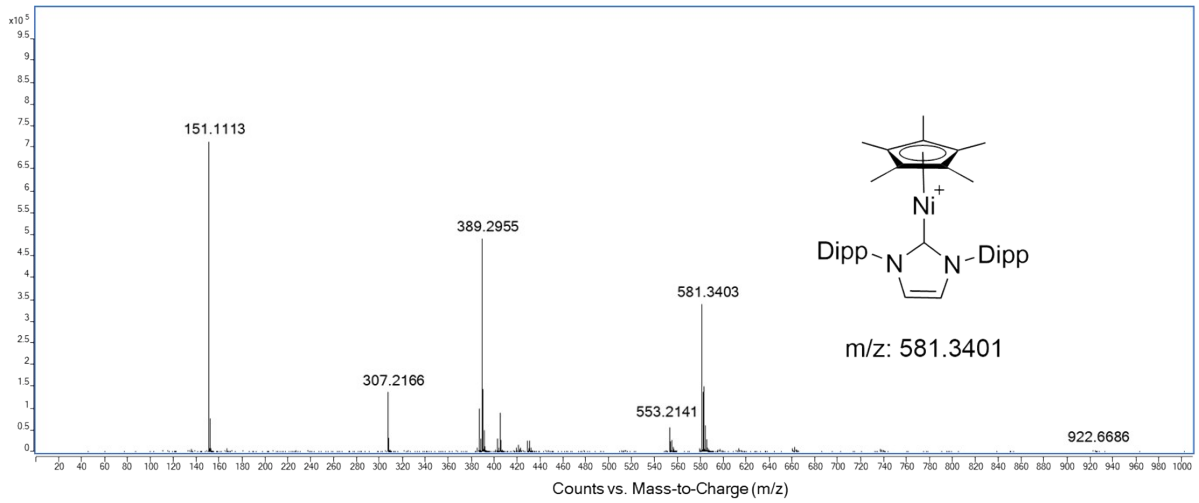


Figure S43. HRMS (ESI+) spectrum of **[Ni] 3-Br-Cp***.

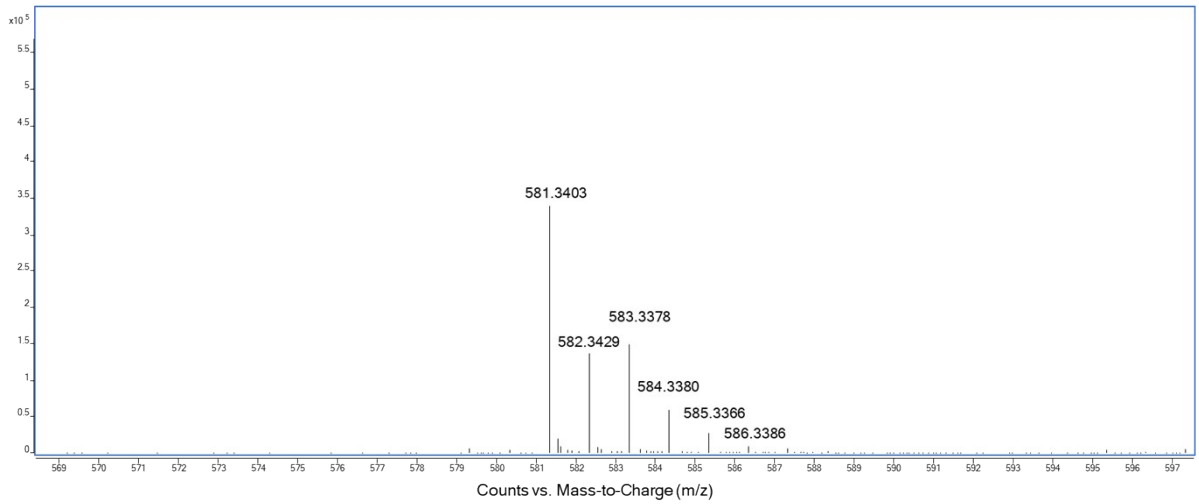


Figure S44. HRMS (ESI+) isotope pattern of **[Ni] 5-Br-Cp*** $[M–Br]^+$.

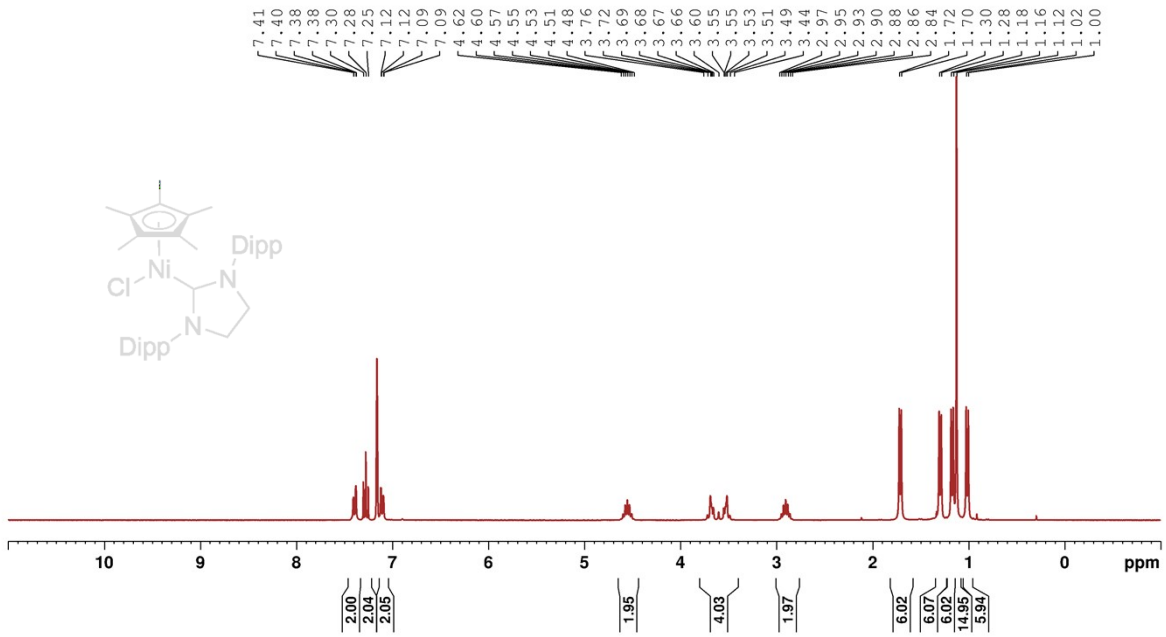


Figure S45. ^{1}H NMR spectrum of **[Ni] 4-Cp*** in C_6D_6.

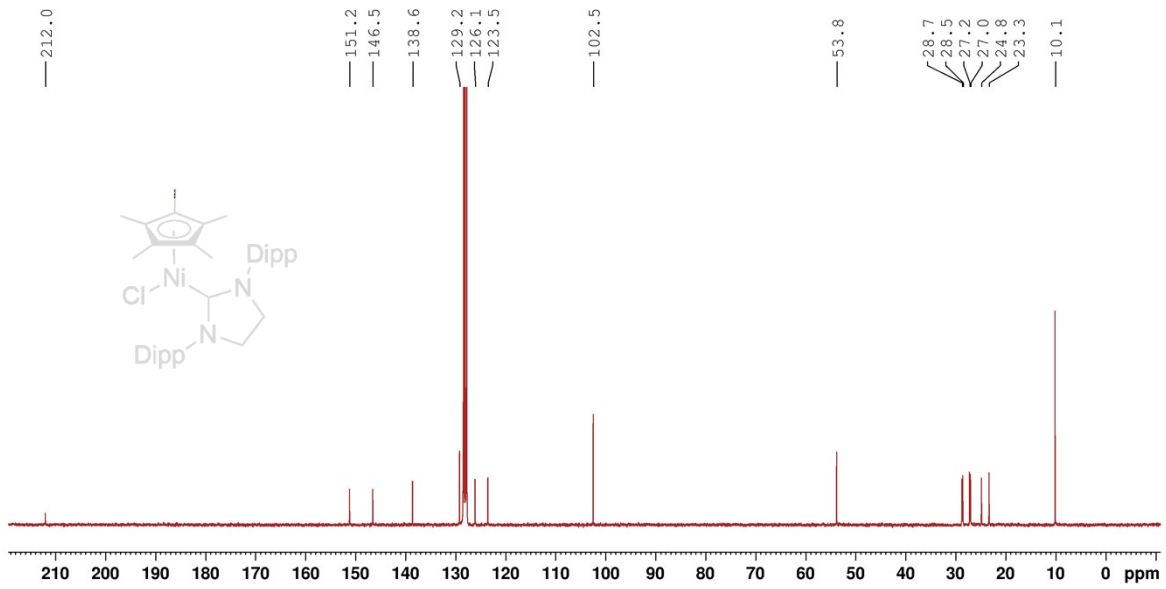


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 4-Cp*** in C_6D_6.

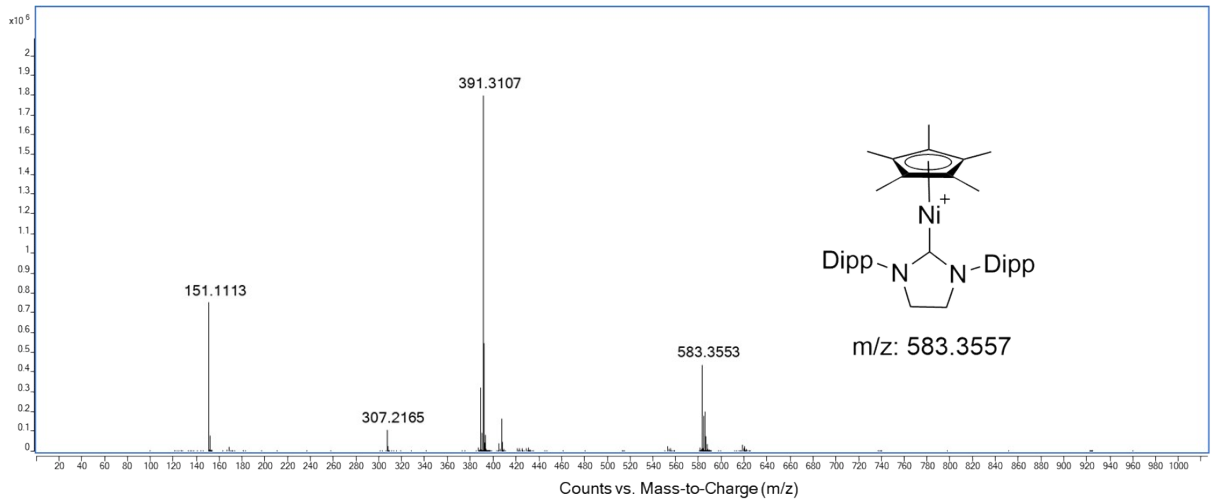


Figure S47. HRMS (ESI+) spectrum of **[Ni] 4-Cp***.

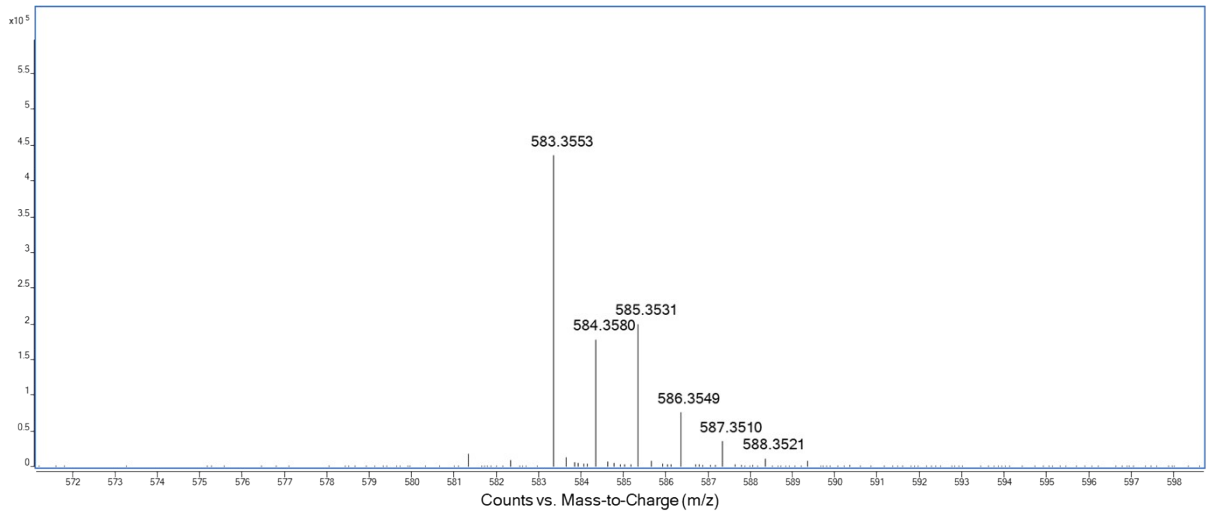


Figure S48. HRMS (ESI+) isotope pattern of **[Ni] 4-Cp*** $[M–Cl]^+$.

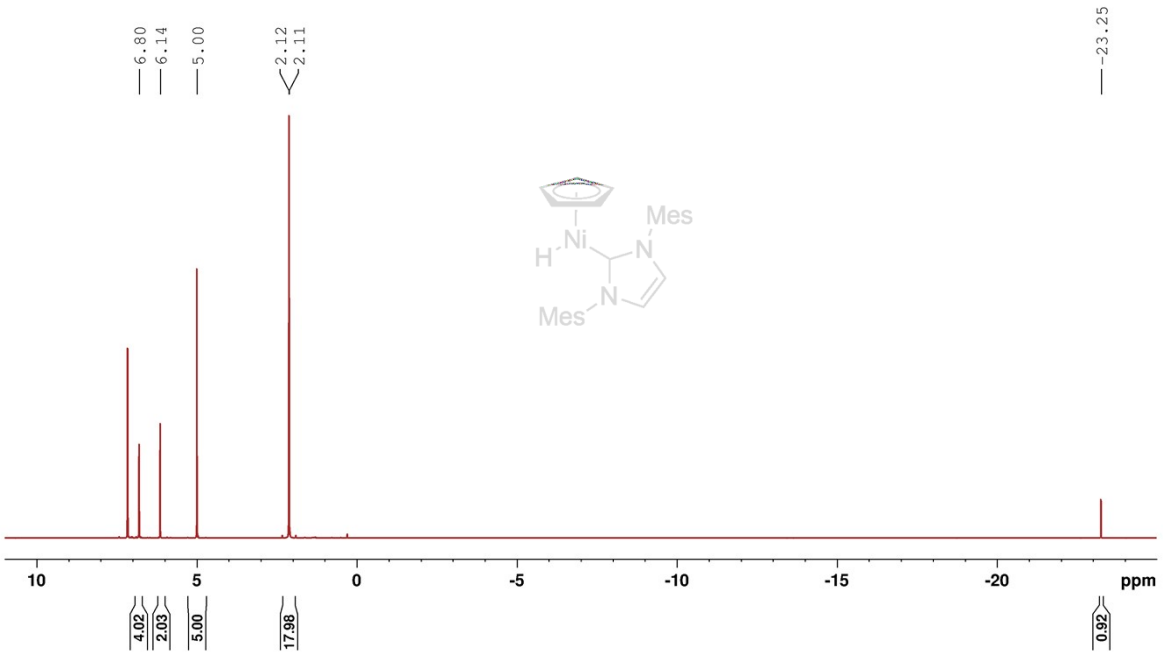


Figure S49. ^{1}H NMR spectrum of **[Ni] 1-H** in C_6D_6.

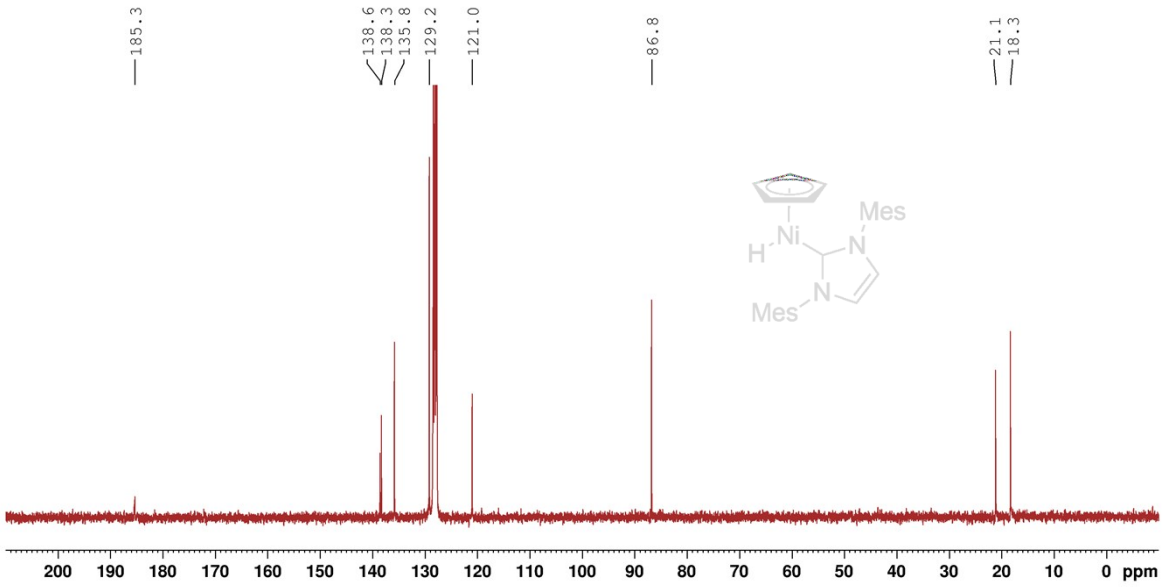


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 1-H** in C_6D_6.

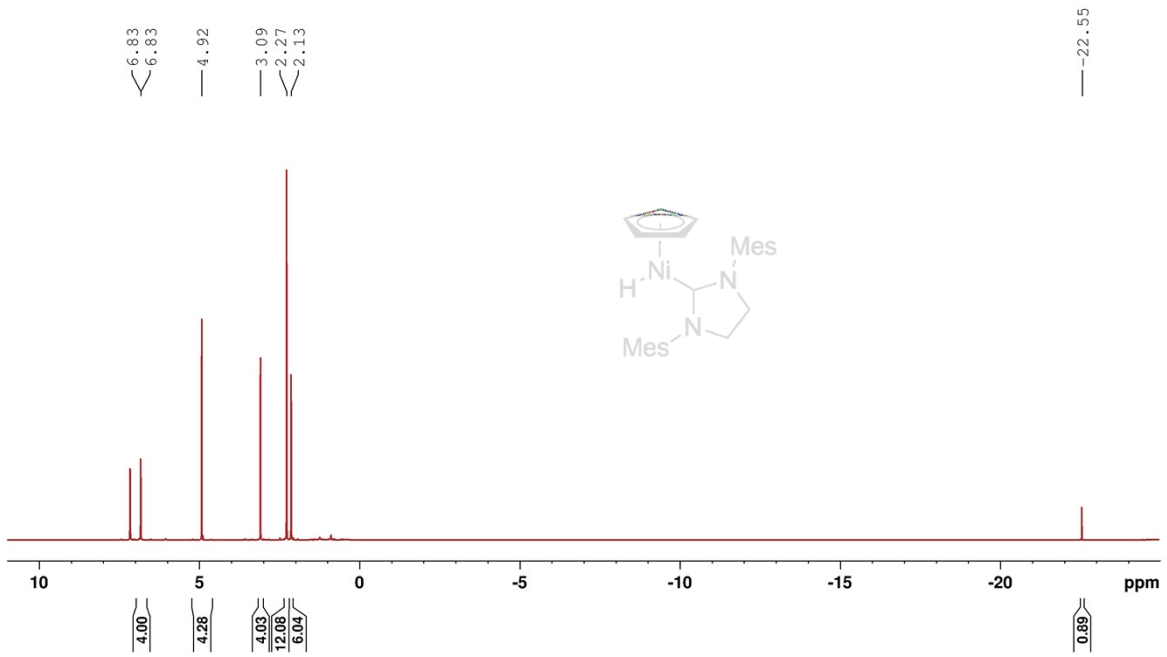


Figure S51. ^{1}H NMR spectrum of **[Ni] 2-H** in C_6D_6.

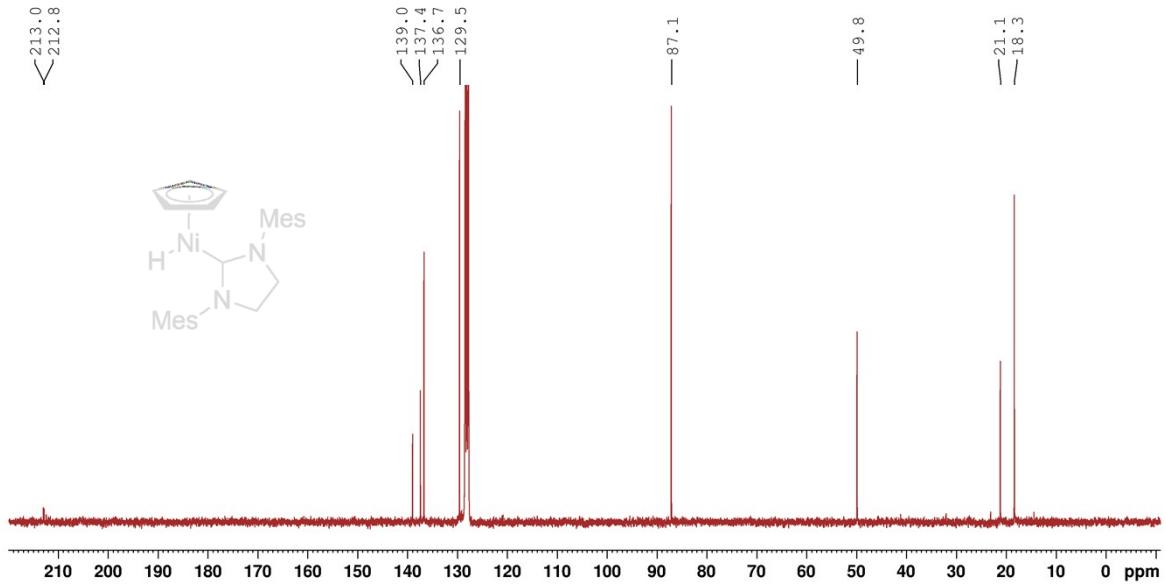


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 2-H** in C_6D_6.

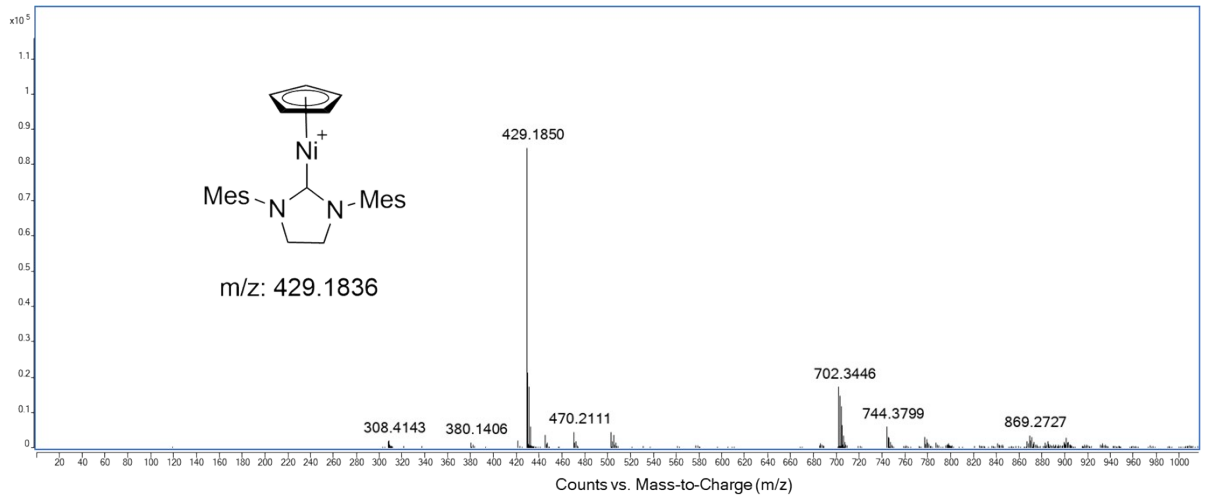


Figure S53. HRMS (ESI+) spectrum of **[Ni] 2-H**.

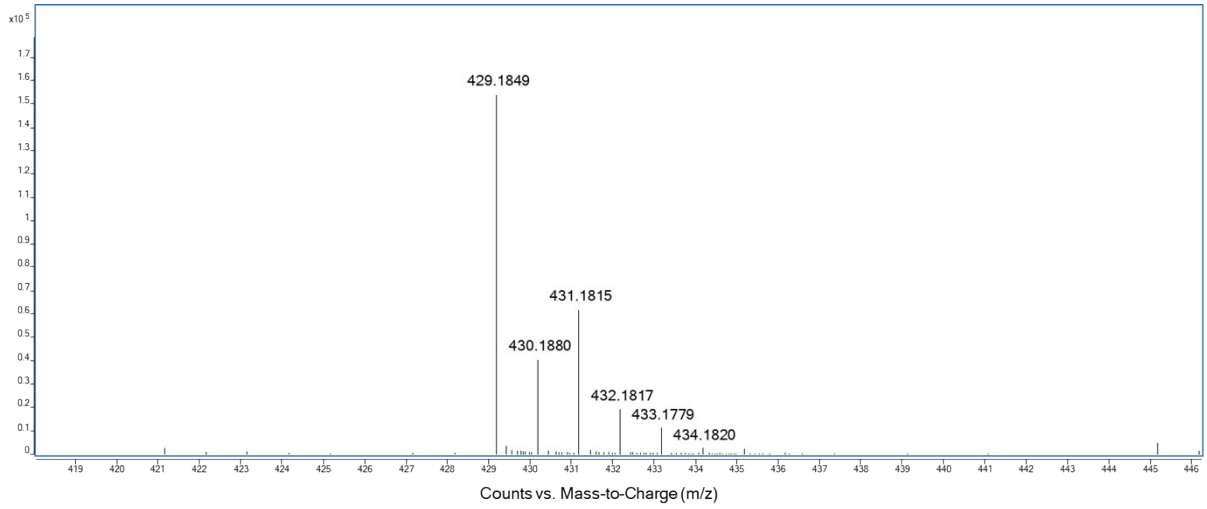


Figure S54. HRMS (ESI+) isotope pattern of **[Ni] 2-H** $[M–H]^+$.

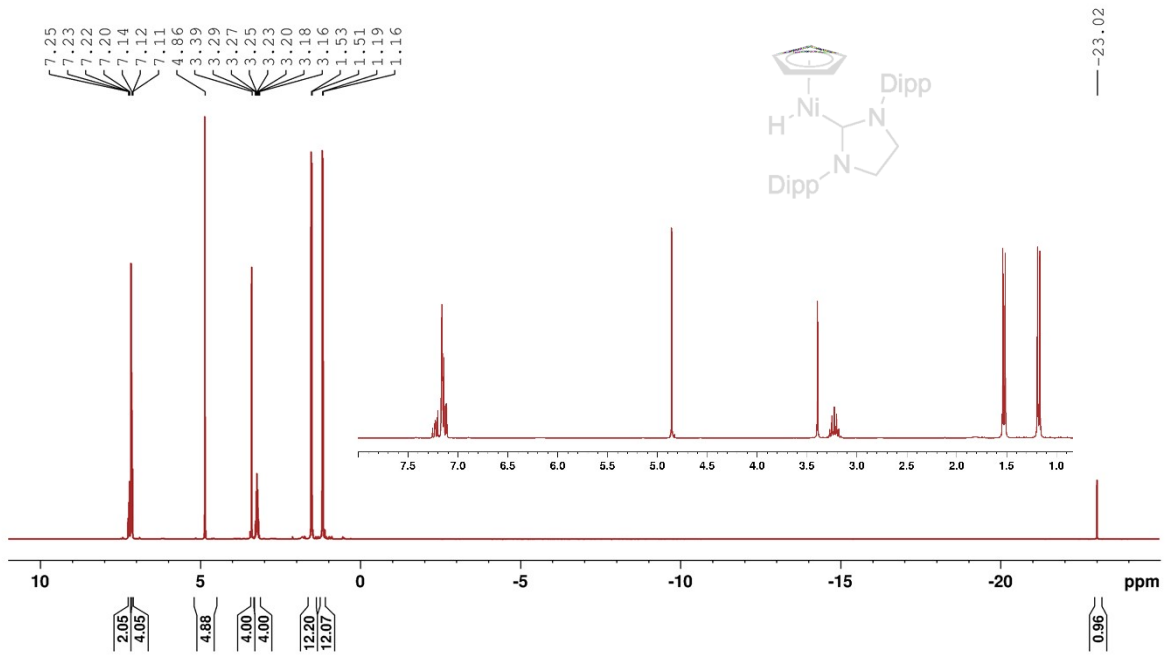


Figure S55. ^{1}H NMR spectrum of **[Ni] 4-H** in C_6D_6.

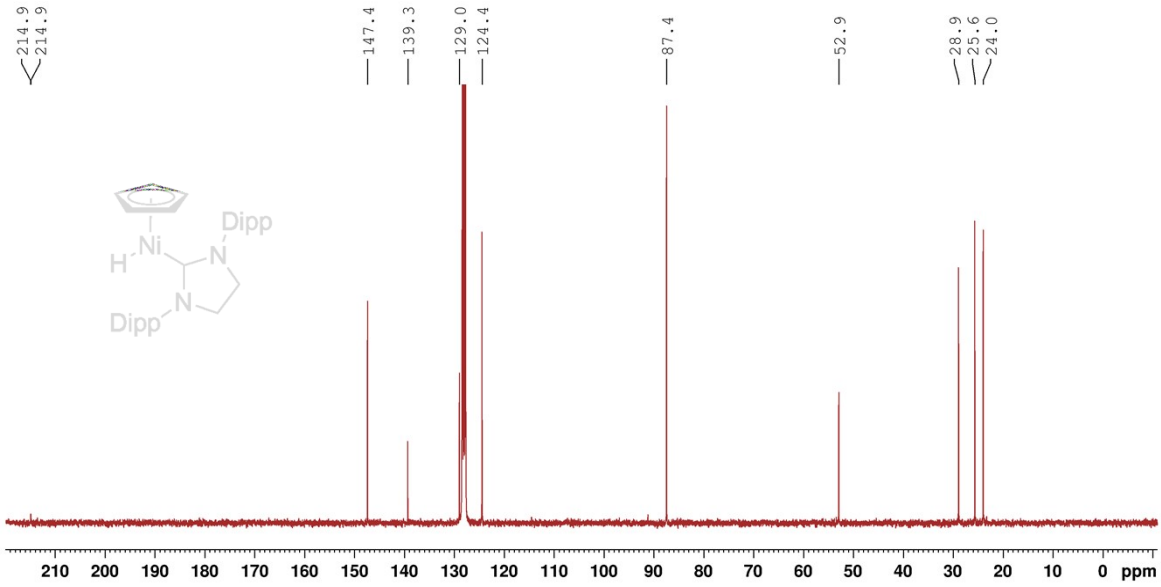


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 4-H** in C_6D_6.

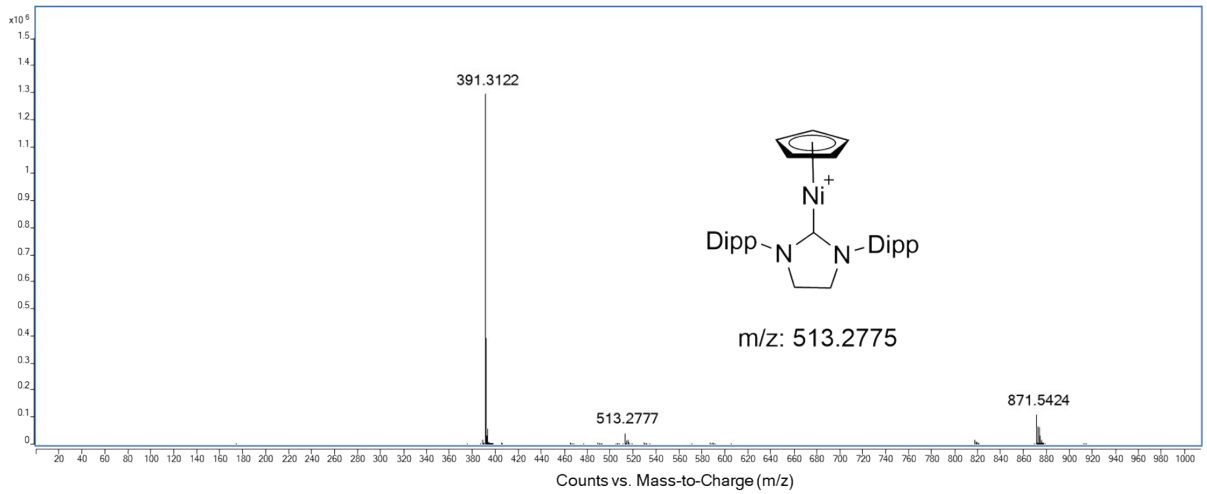


Figure S57. HRMS (ESI+) spectrum of **[Ni] 4-H**.

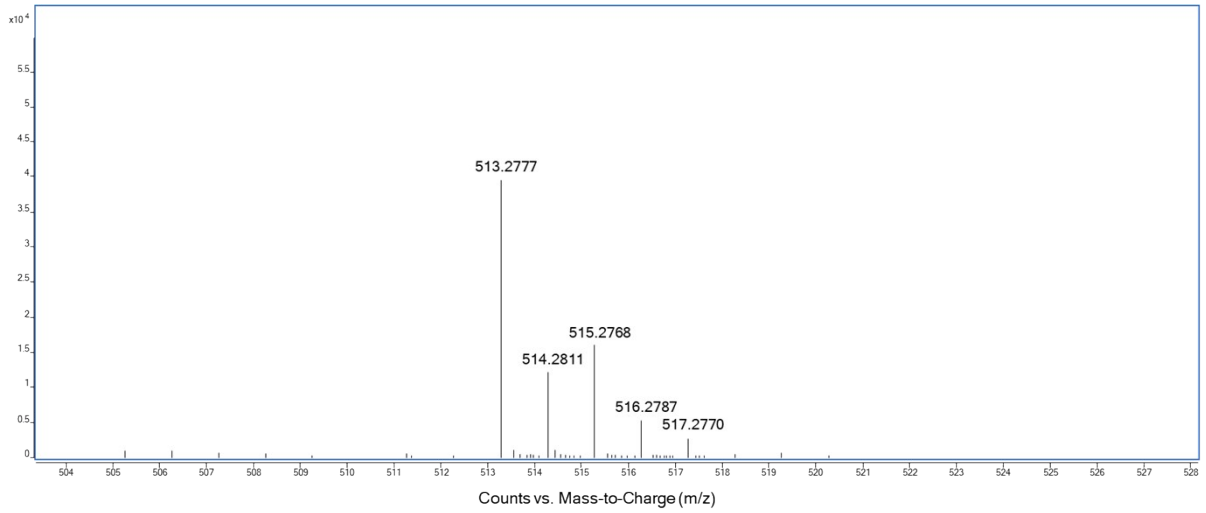


Figure S58. HRMS (ESI+) isotope pattern of **[Ni] 4-H** $[M–H]^+$.

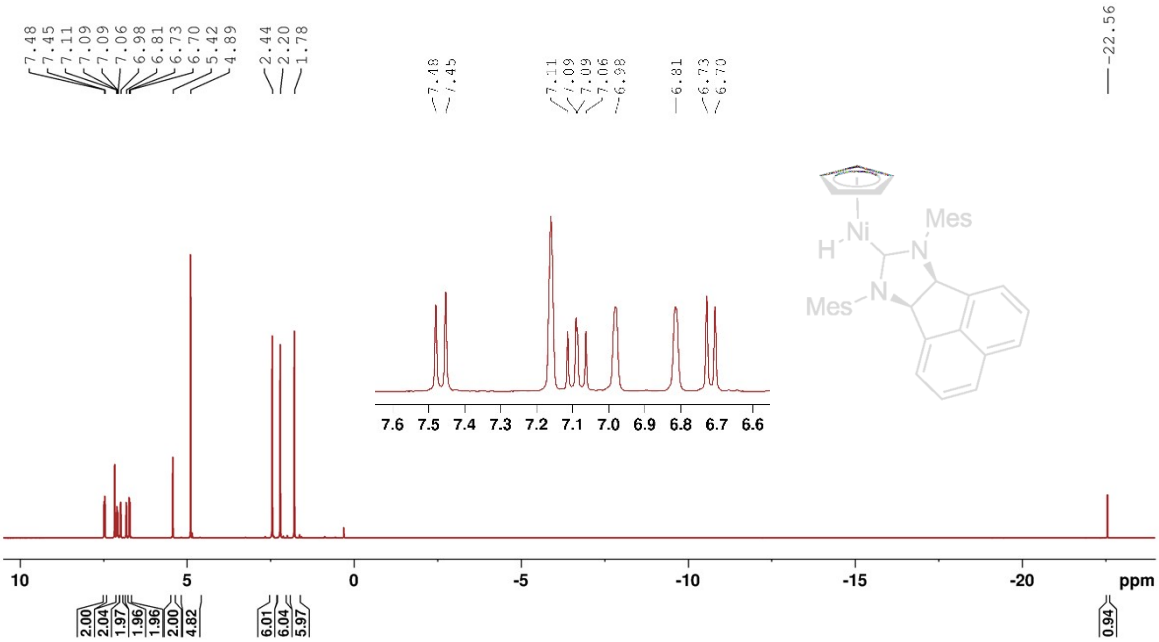


Figure S59. ^{1}H NMR spectrum of **[Ni] 5-H** in C_6D_6.

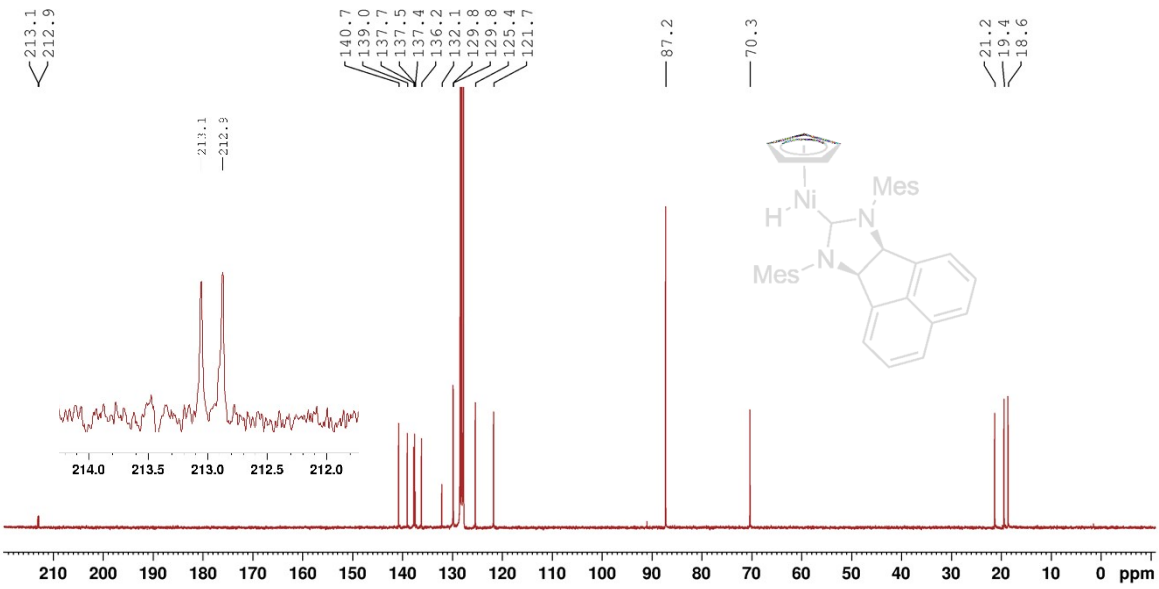


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni] 5-H** in C_6D_6.

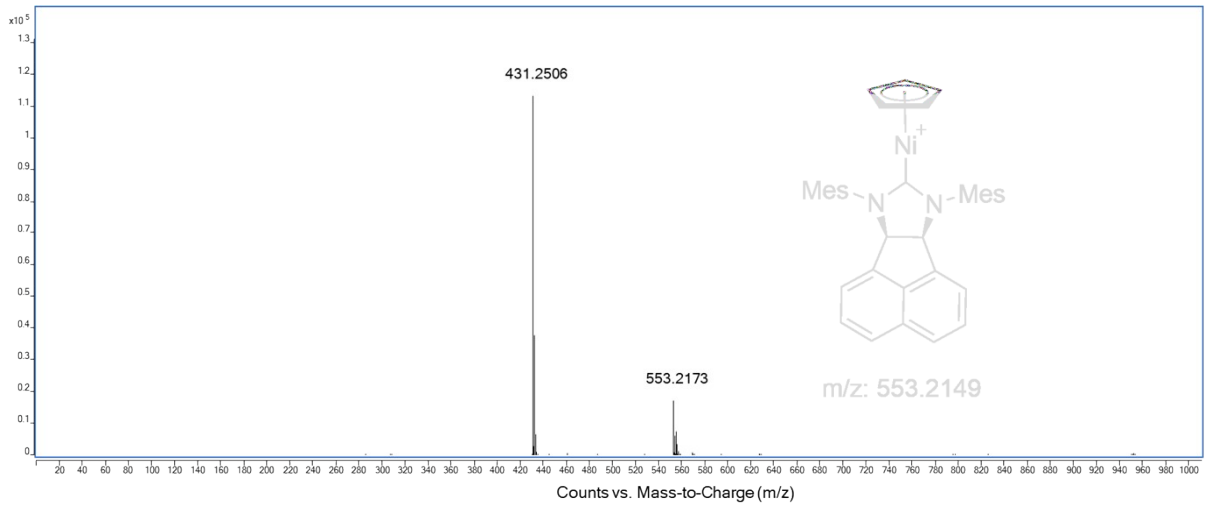


Figure S61. HRMS (ESI+) spectrum of **[Ni] 5-H**.

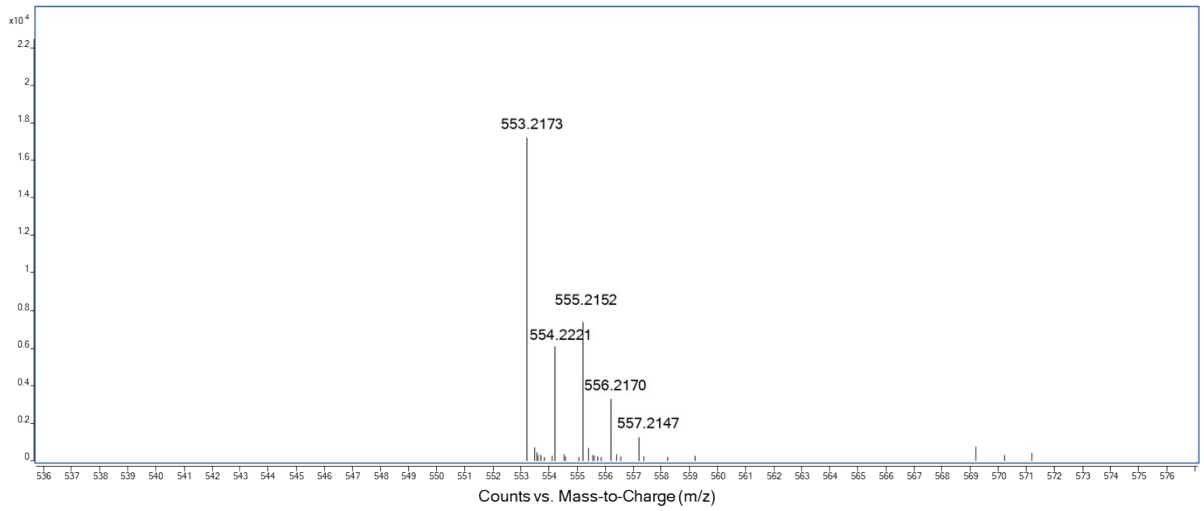


Figure S62. HRMS (ESI+) isotope pattern of **[Ni] 5-H** $[M–H]^+$.

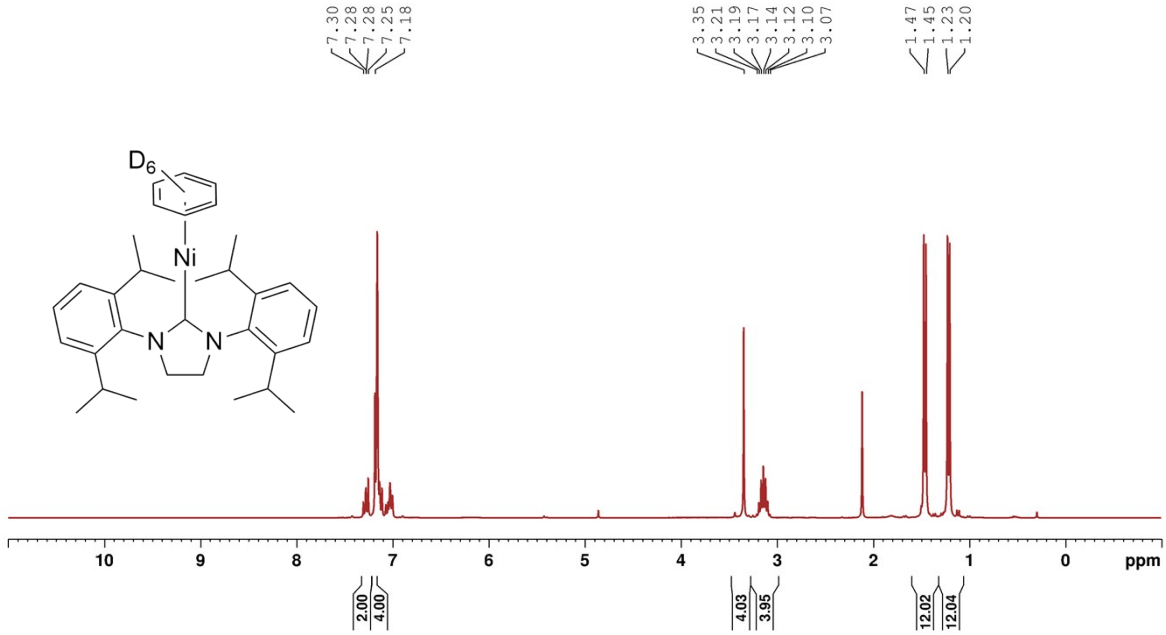


Figure S63. ^{1}H NMR spectrum of **[Ni(η^{6}-toluene)(SIPr)]** in C_6D_6. Unlabeled peaks originate from displaced toluene.

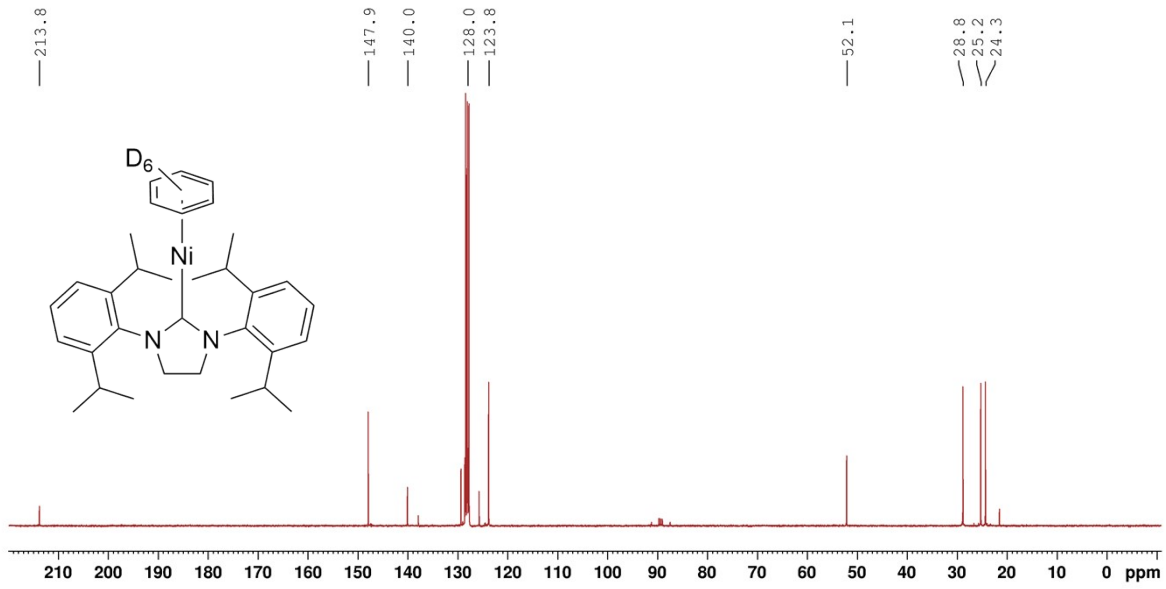


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni(η^{6}-toluene)(SIPr)]** in C_6D_6. Unlabeled peaks originate from displaced toluene.

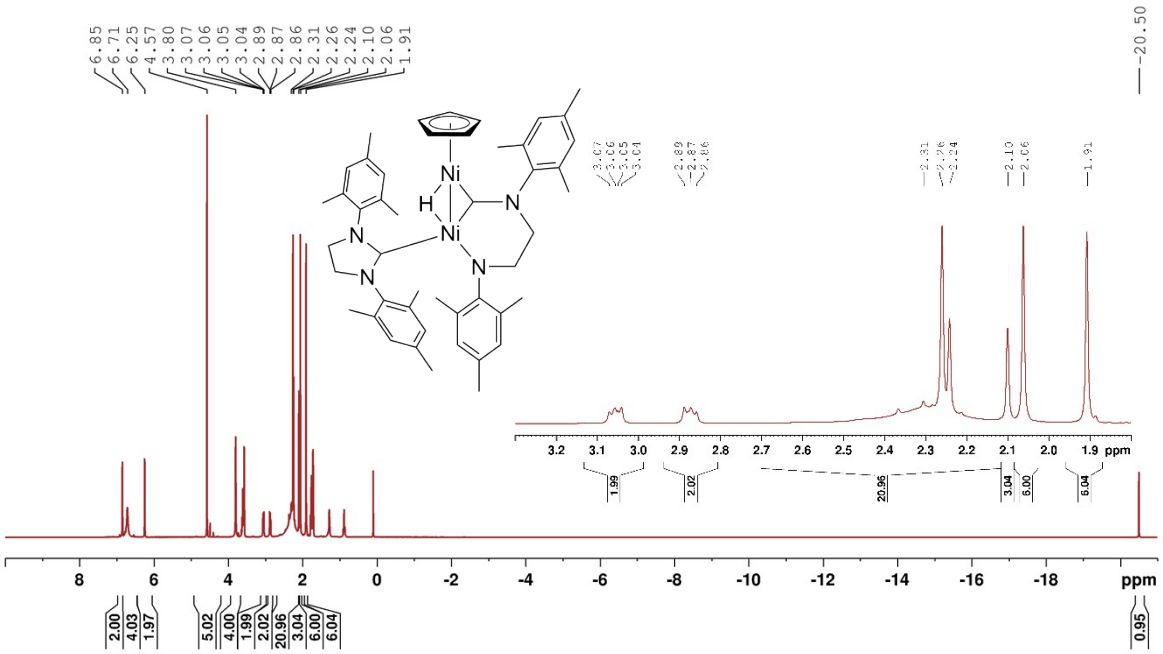


Figure S65. ^{1}H NMR spectrum of **[Ni$_2$]H-SIMes** in THF-d$_8$.

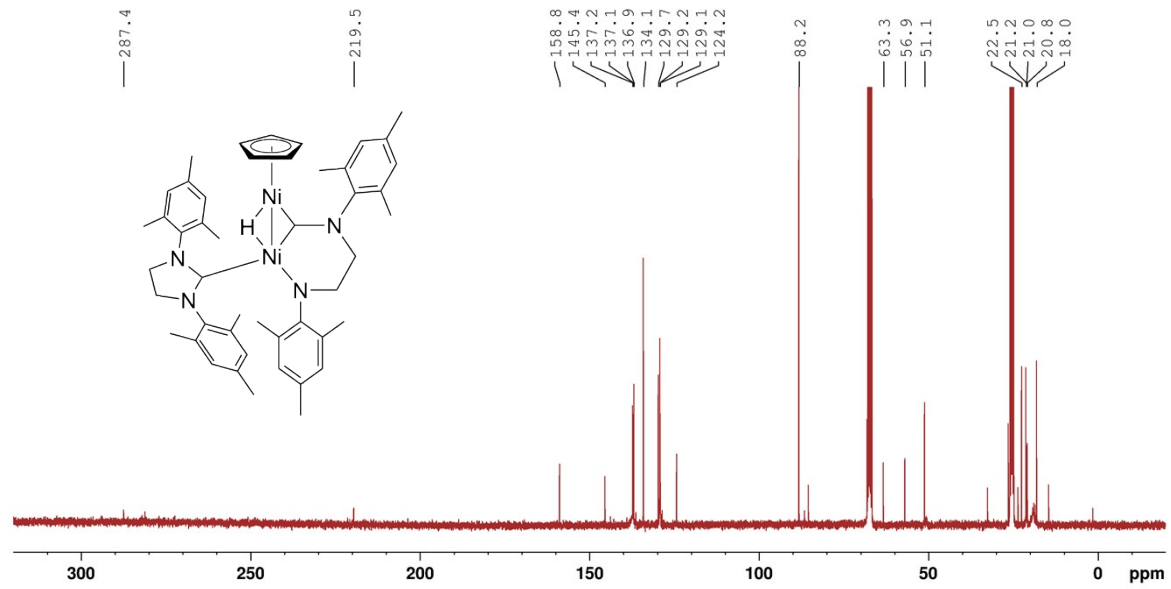


Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **[Ni$_2$]H-SIMes** in THF-d$_8$.

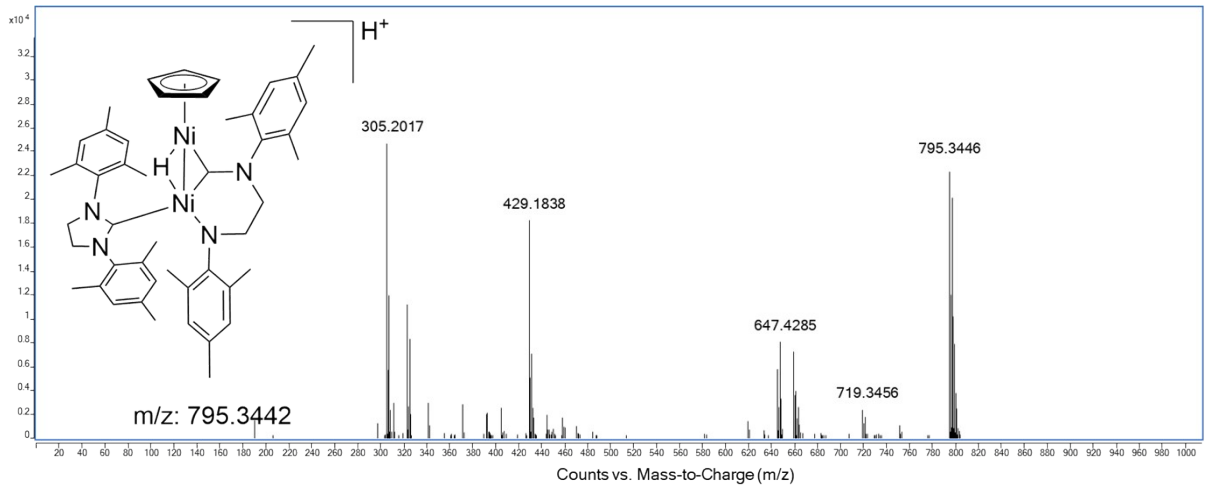


Figure S67. HRMS (ESI+) spectrum of **[Ni$_2$]H-SIMes**.

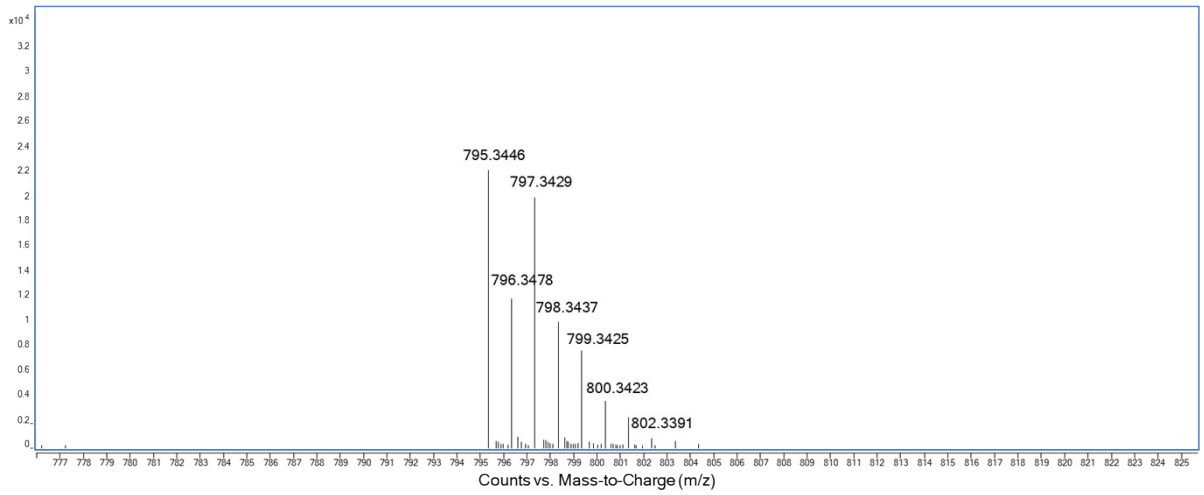


Figure S68. HRMS (ESI+) isotope pattern of **[Ni$_2$]H-SIMes** $[M+H]^+$.

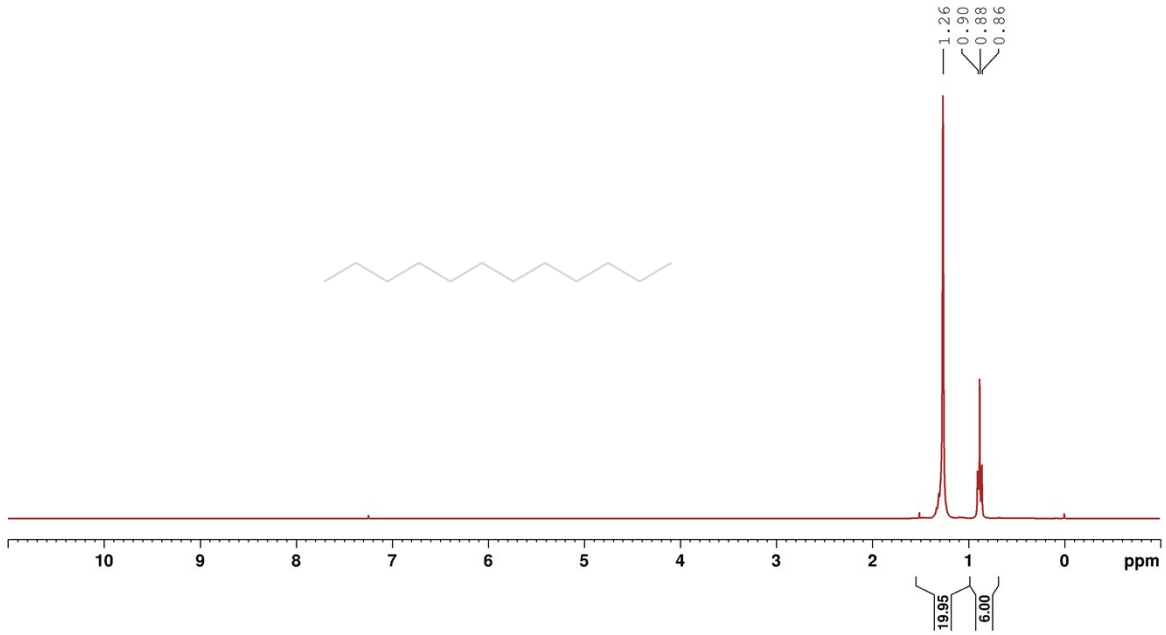


Figure S69. ^{1}H NMR spectrum of **2b** in $CDCl_3$.

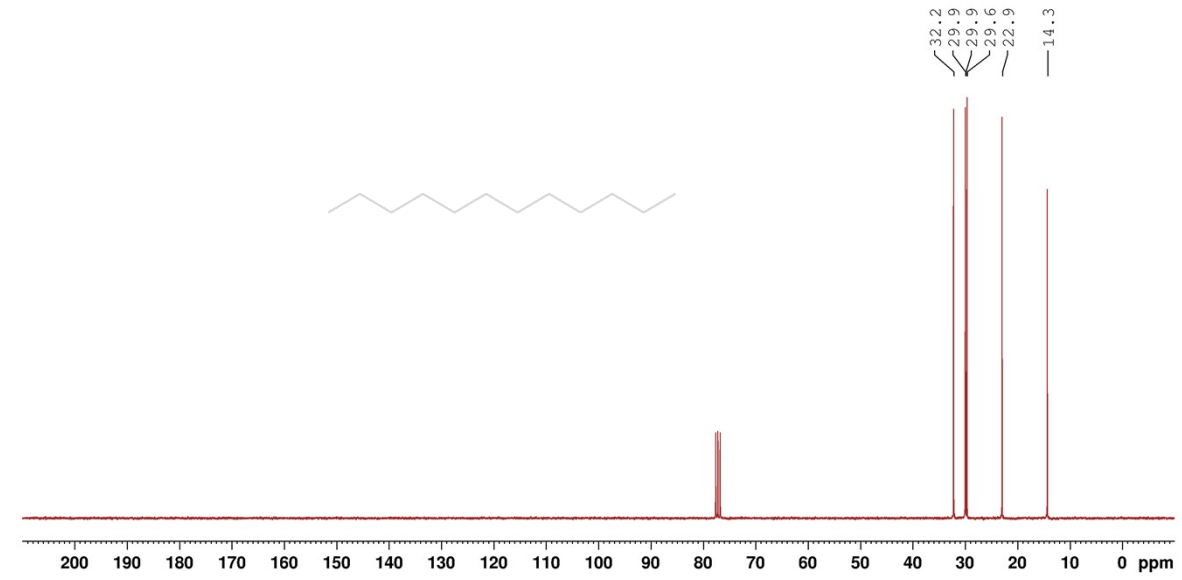


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in $CDCl_3$.

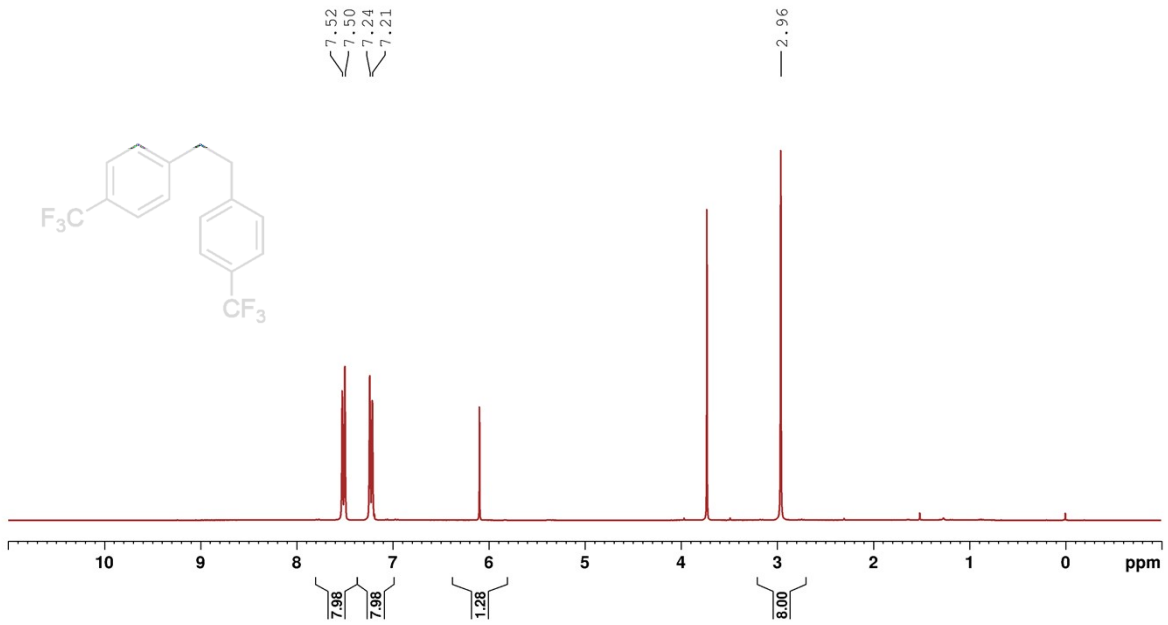


Figure S71. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

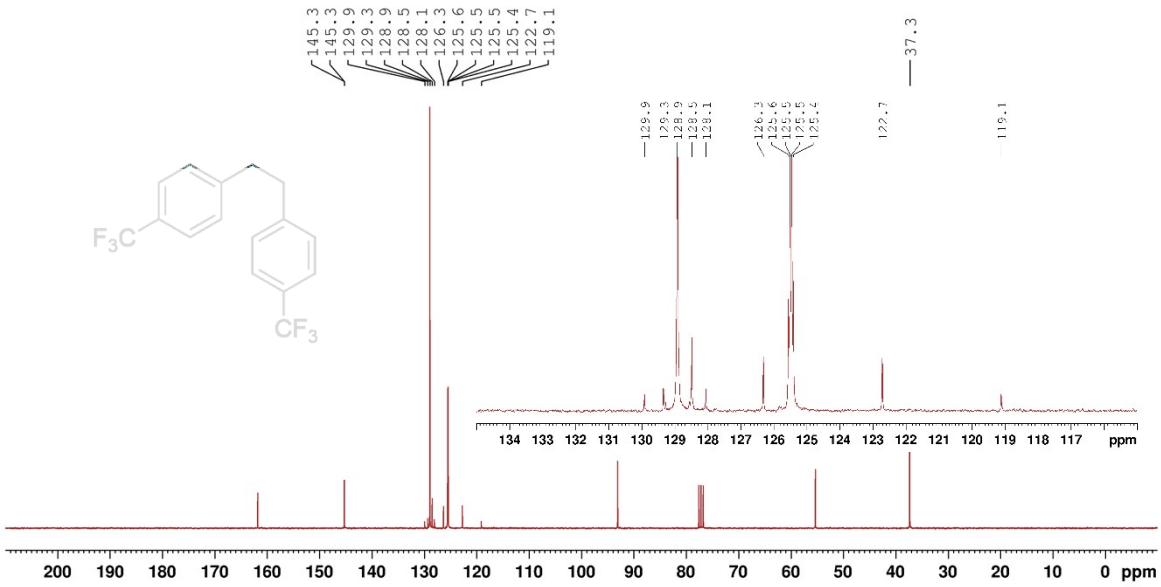


Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in $CDCl_3$.

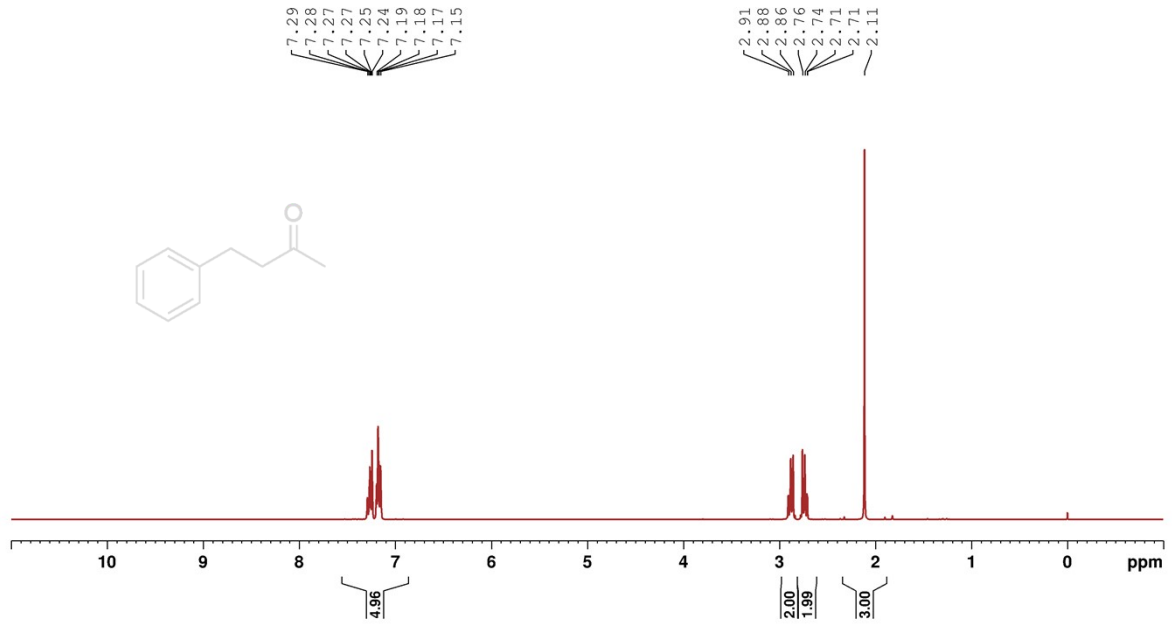


Figure S73. ^{1}H NMR spectrum of **2e** in $CDCl_3$.

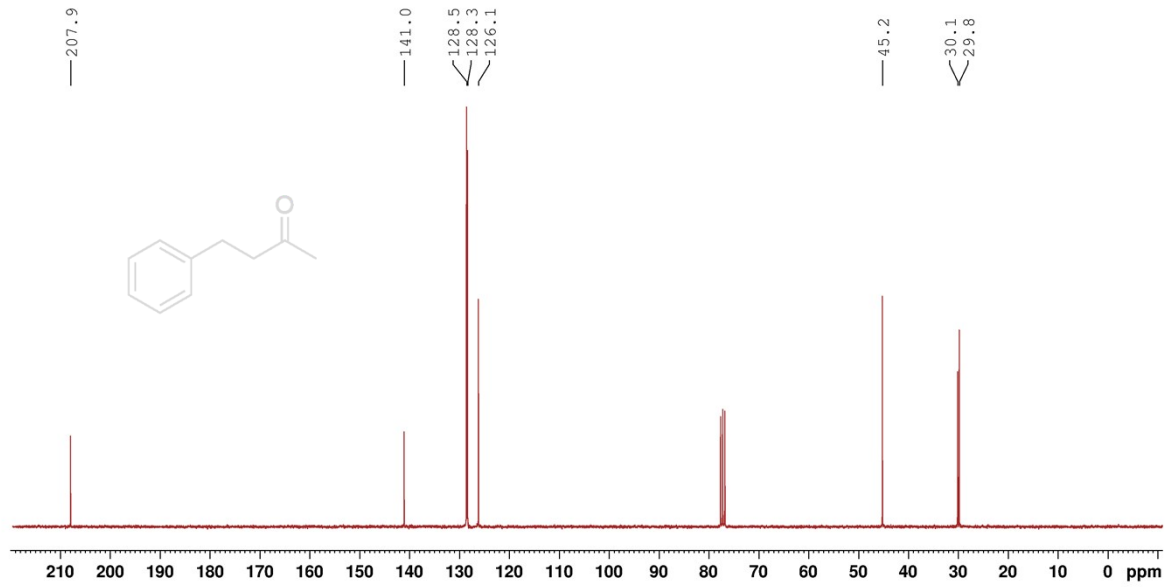


Figure S74. $^{13}C\{^{1}H\}$ NMR spectrum of **2e** in $CDCl_3$.

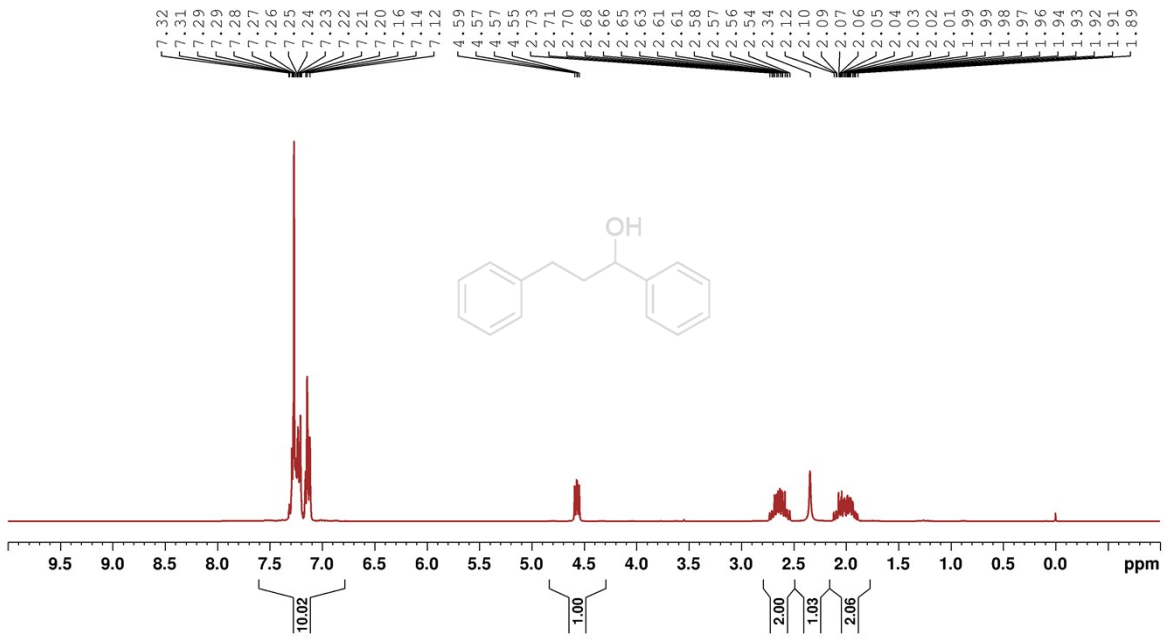


Figure S75. ^{1}H NMR spectrum of **2f** in $CDCl_3$.

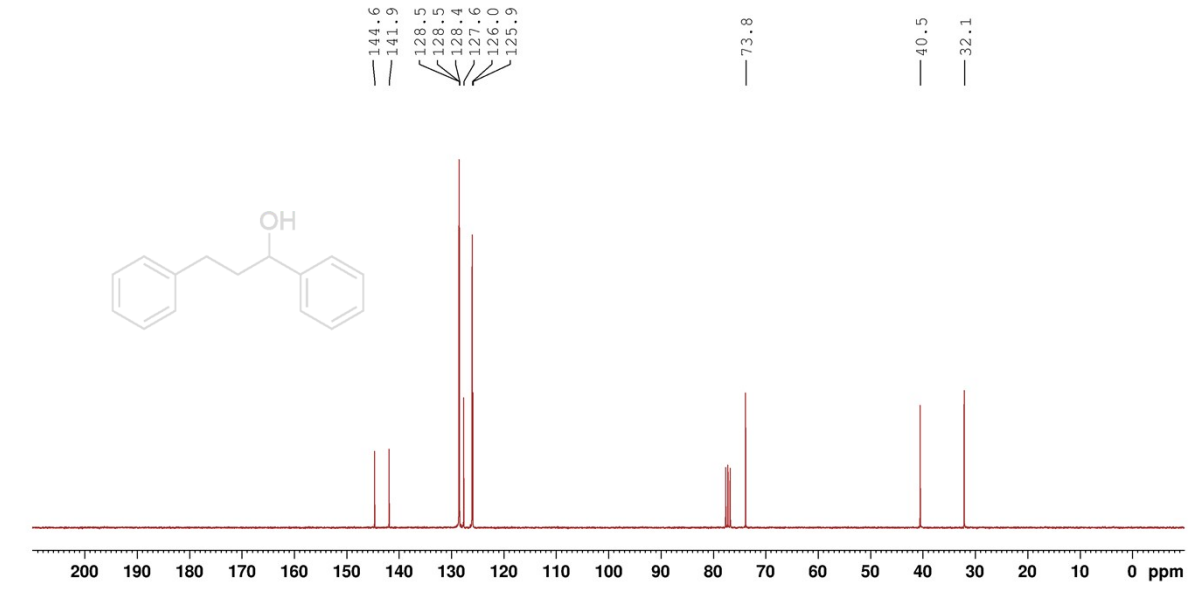


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **2f** in $CDCl_3$.

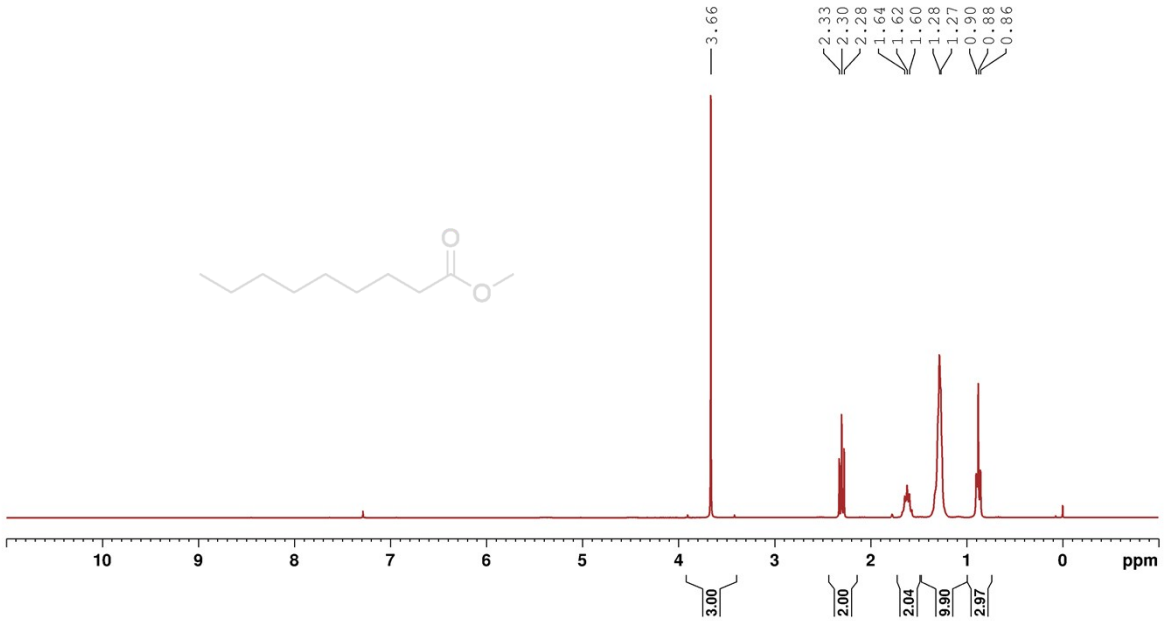


Figure S77. ^{1}H NMR spectrum of **2g** in $CDCl_3$.

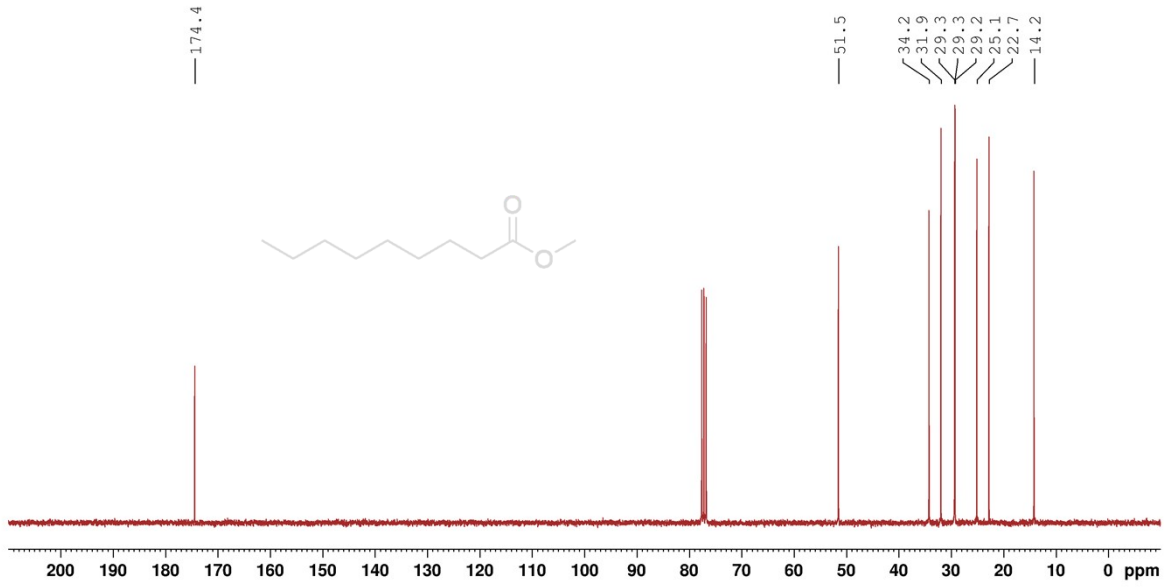


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum of **2g** in $CDCl_3$.

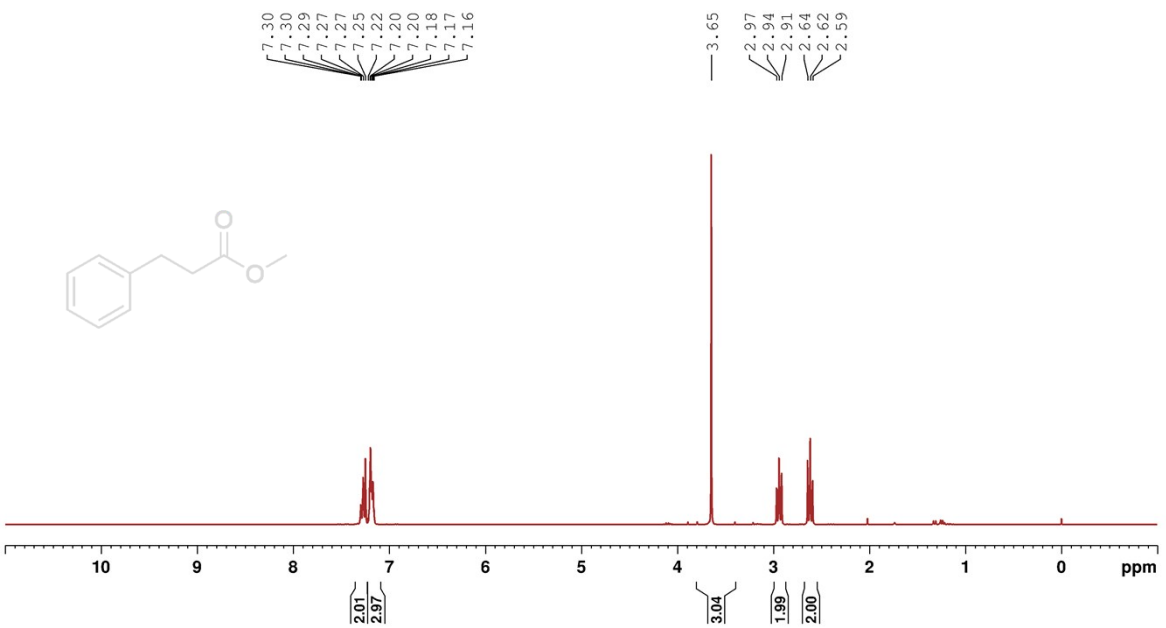


Figure S79. ^{1}H NMR spectrum of **2h** in $CDCl_3$.

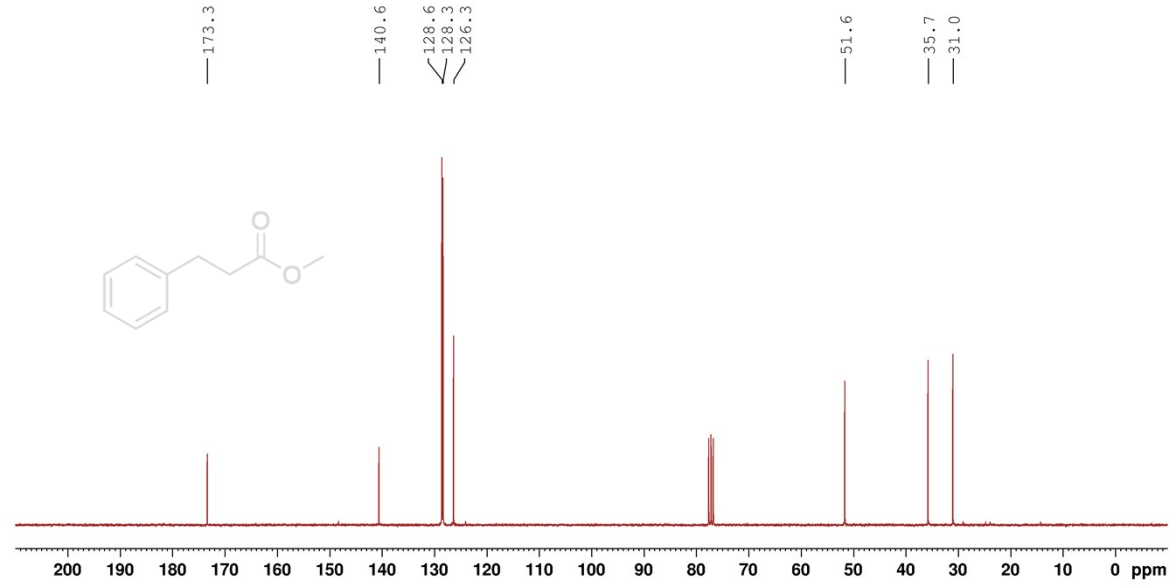


Figure S80. $^{13}C\{^{1}H\}$ NMR spectrum of **2h** in $CDCl_3$.

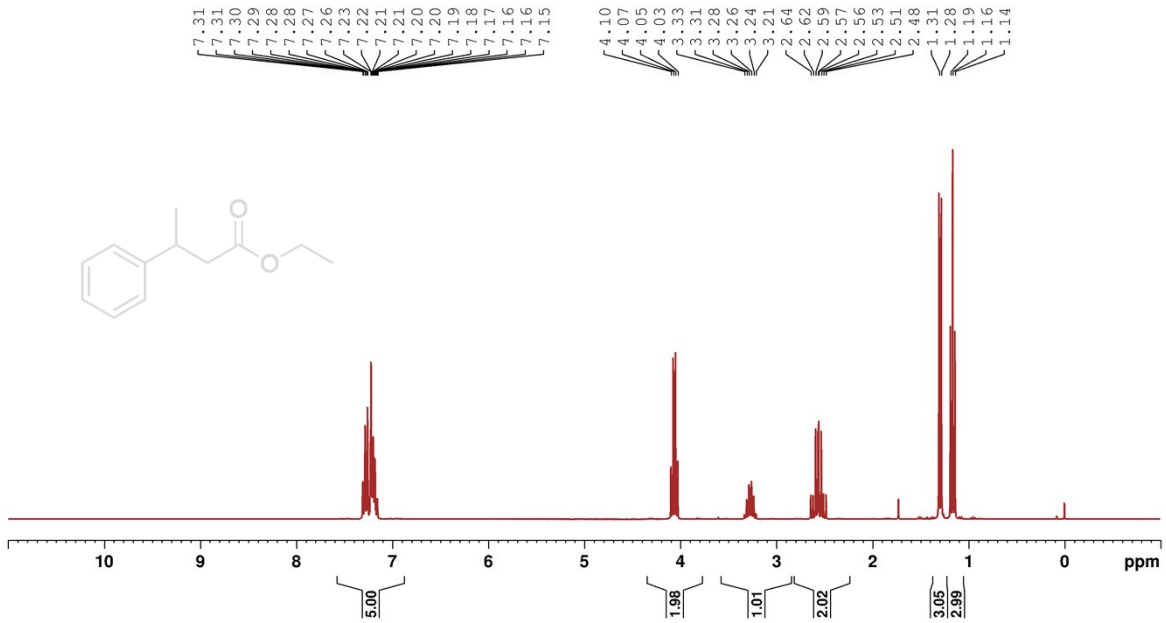


Figure S81. ^{1}H NMR spectrum of **2i** in $CDCl_3$.

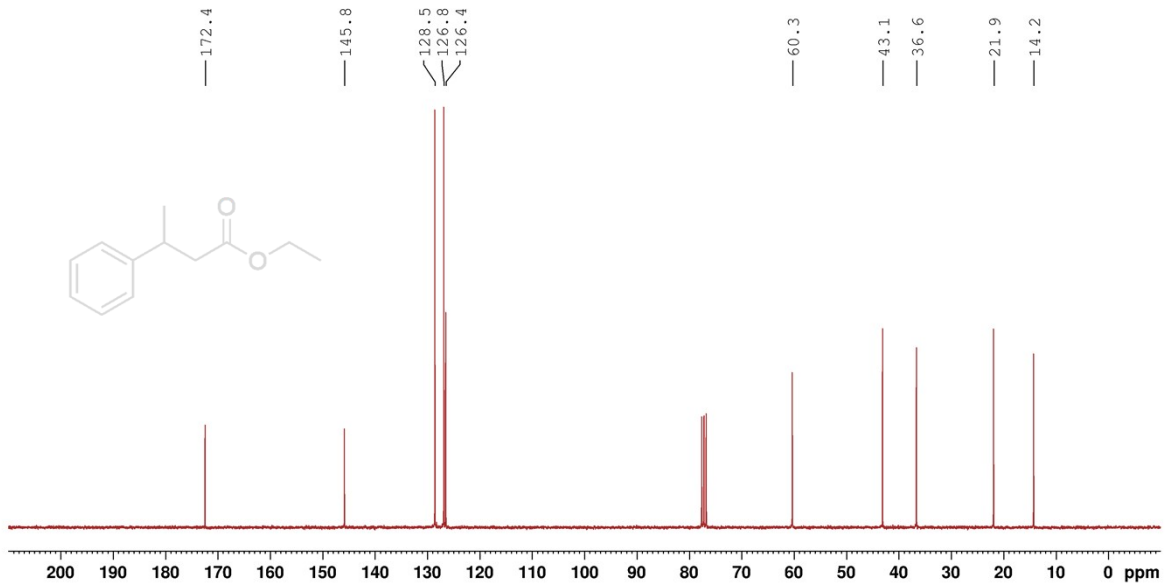


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of **2i** in $CDCl_3$.

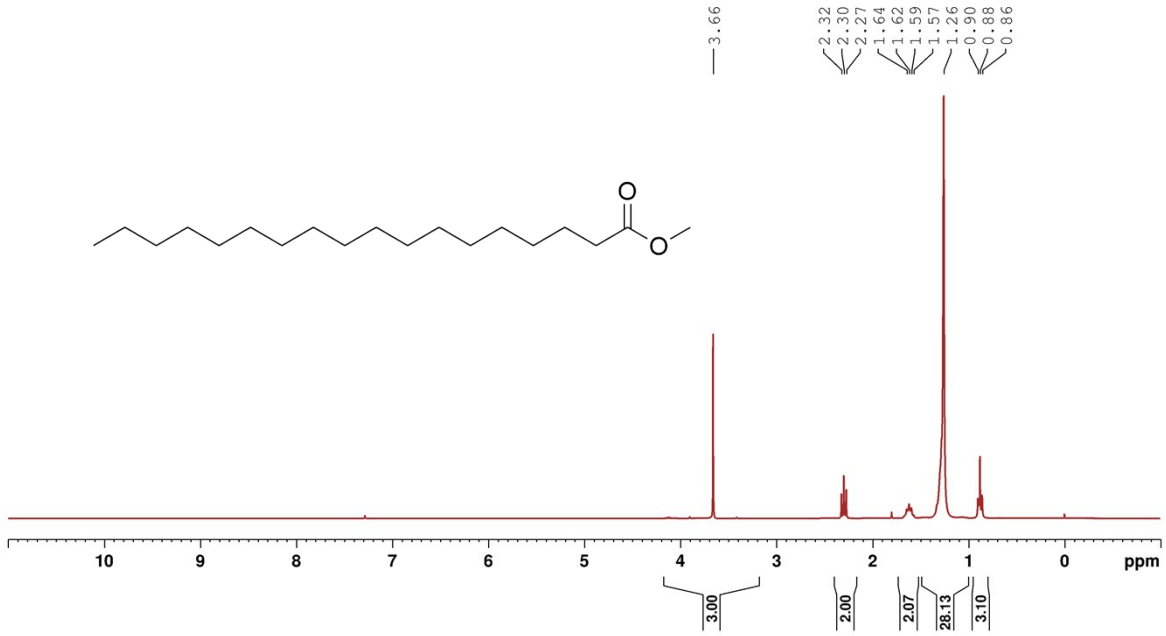


Figure S83. ^{1}H NMR spectrum of **2k** in $CDCl_3$.

Figure S84. $^{13}C\{^{1}H\}$ NMR spectrum of **2k** in $CDCl_3$.

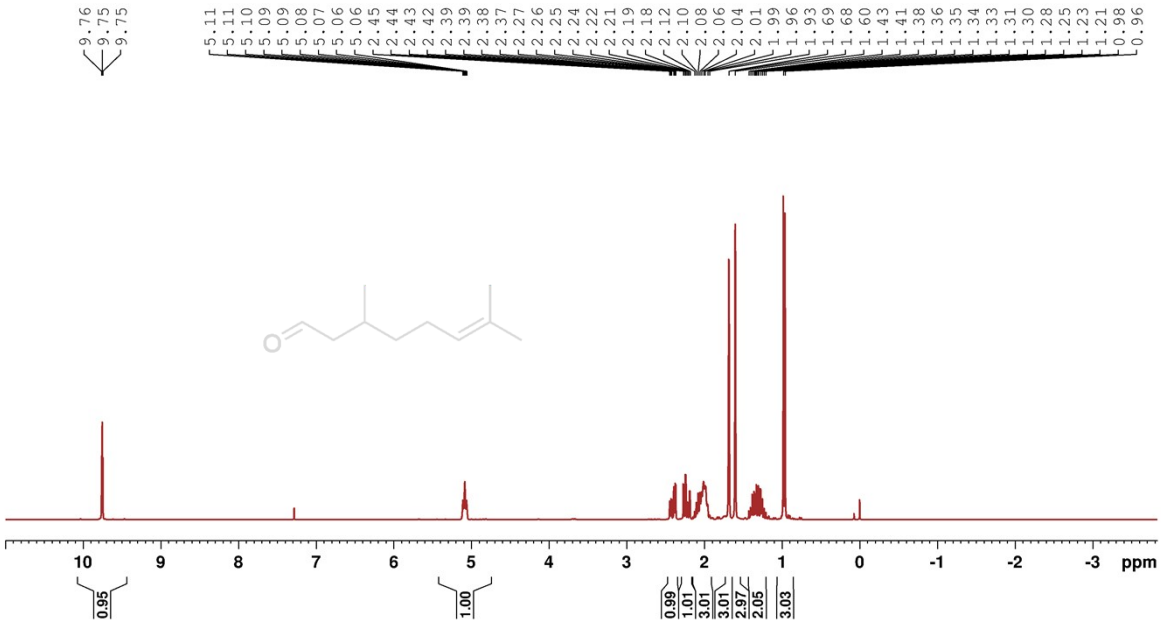


Figure S85. ^{1}H NMR spectrum of **2l** in $CDCl_3$.

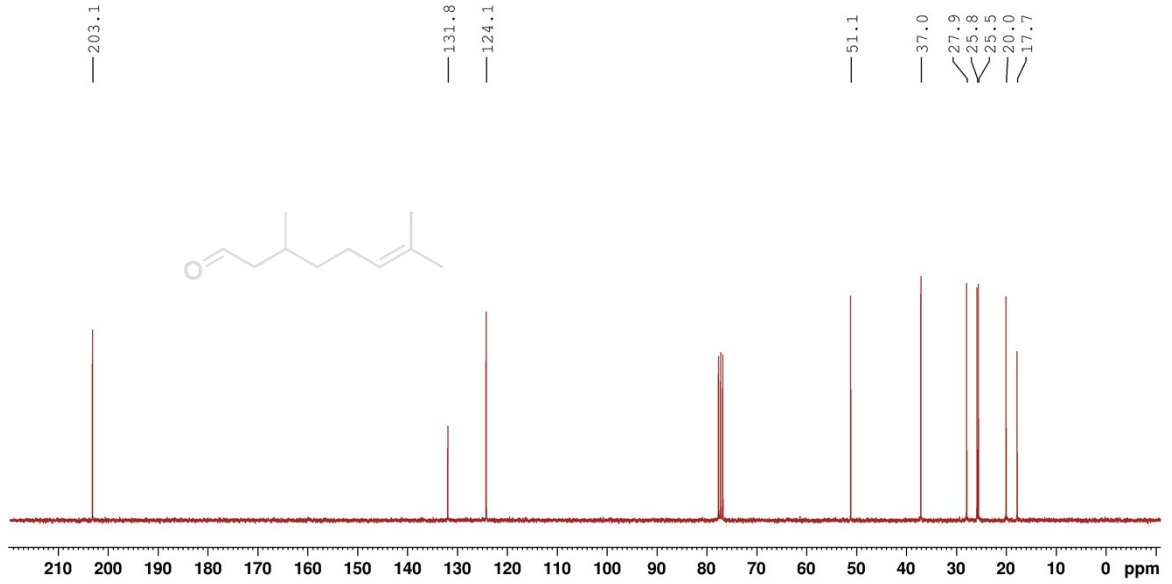


Figure S86. $^{13}C\{^{1}H\}$ NMR spectrum of **2l** in $CDCl_3$.

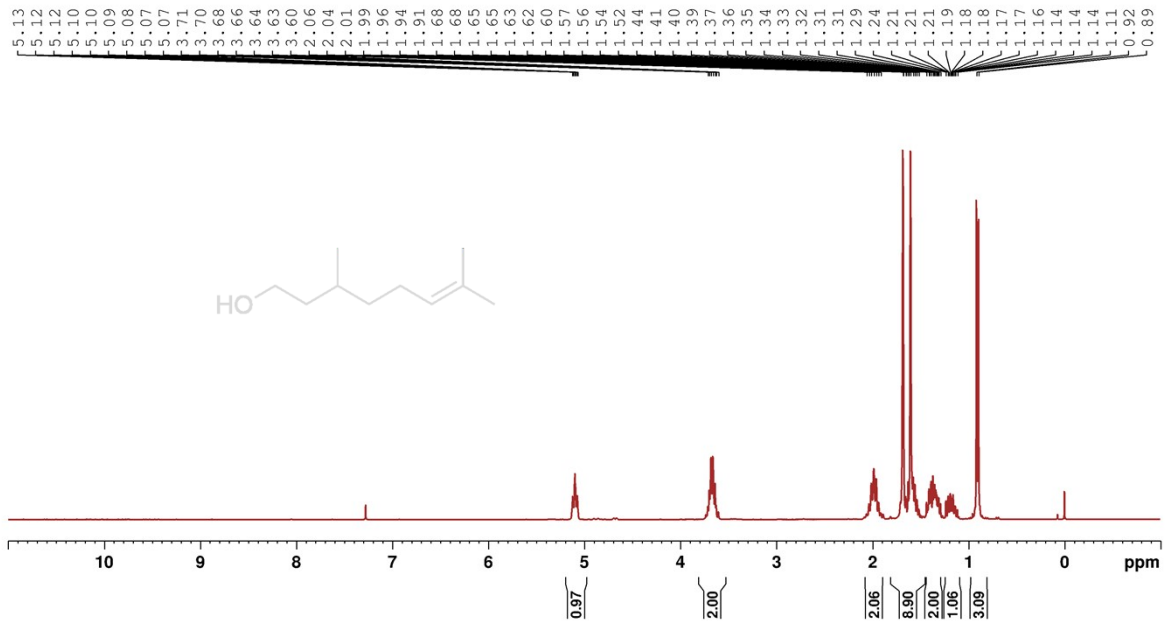


Figure S87. ^{1}H NMR spectrum of **2m** in $CDCl_3$.

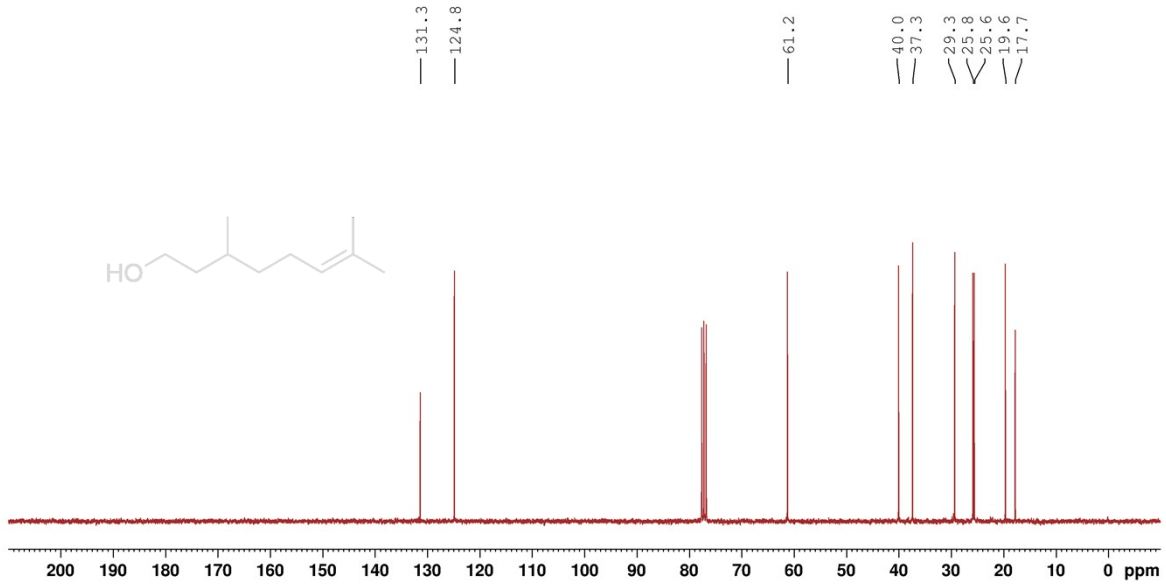


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of **2m** in $CDCl_3$.

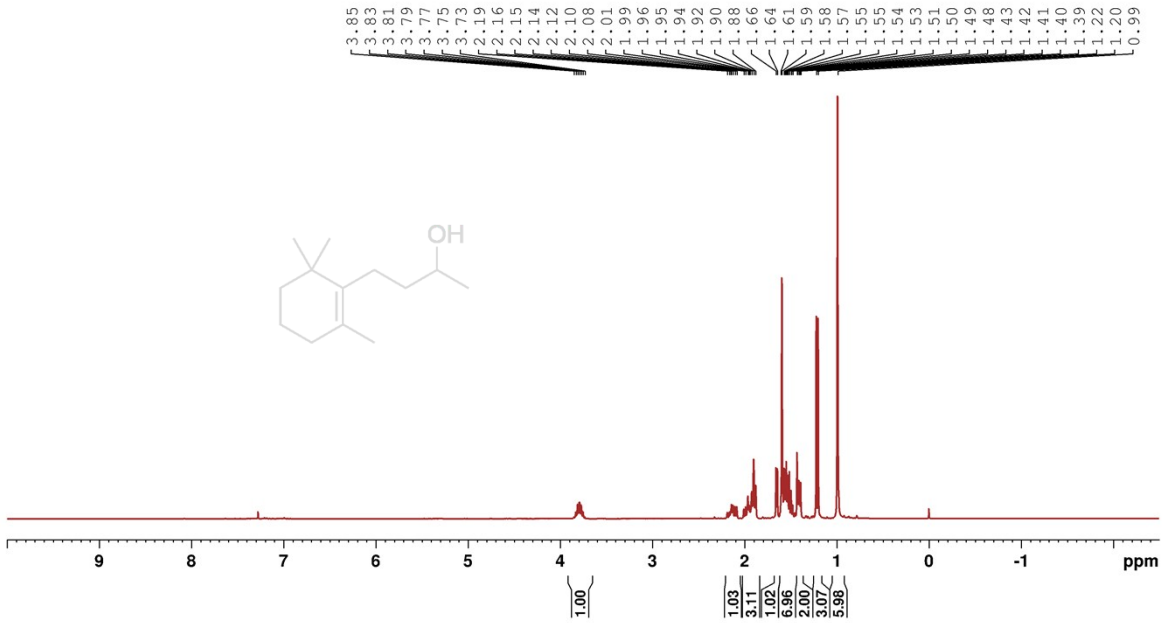


Figure S89. ^{1}H NMR spectrum of **2n** in $CDCl_3$.

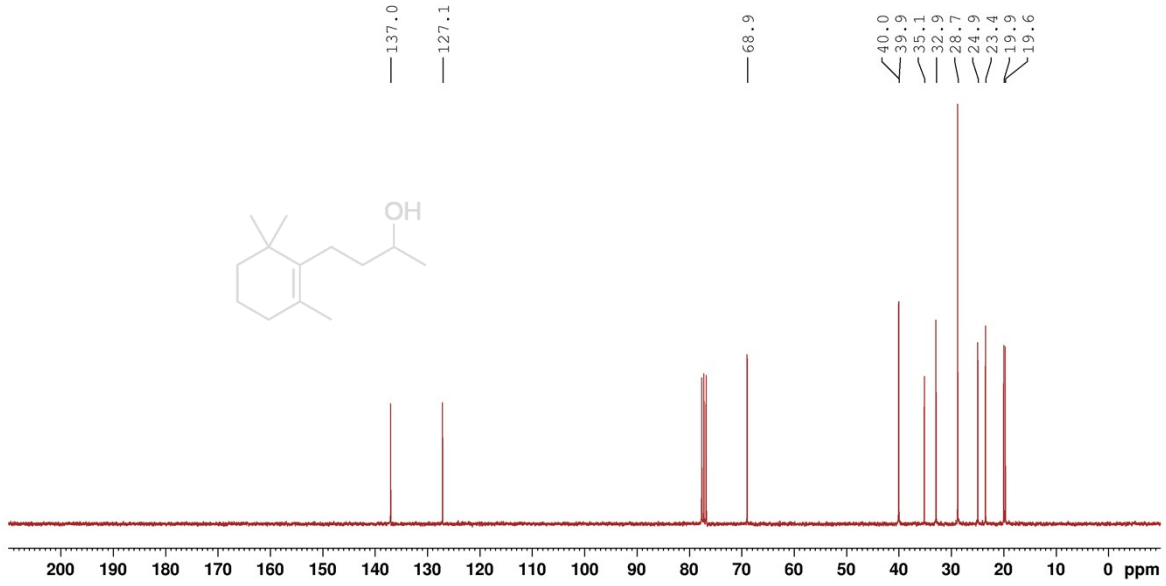


Figure S90. $^{13}C\{^{1}H\}$ NMR spectrum of **2n** in $CDCl_3$.

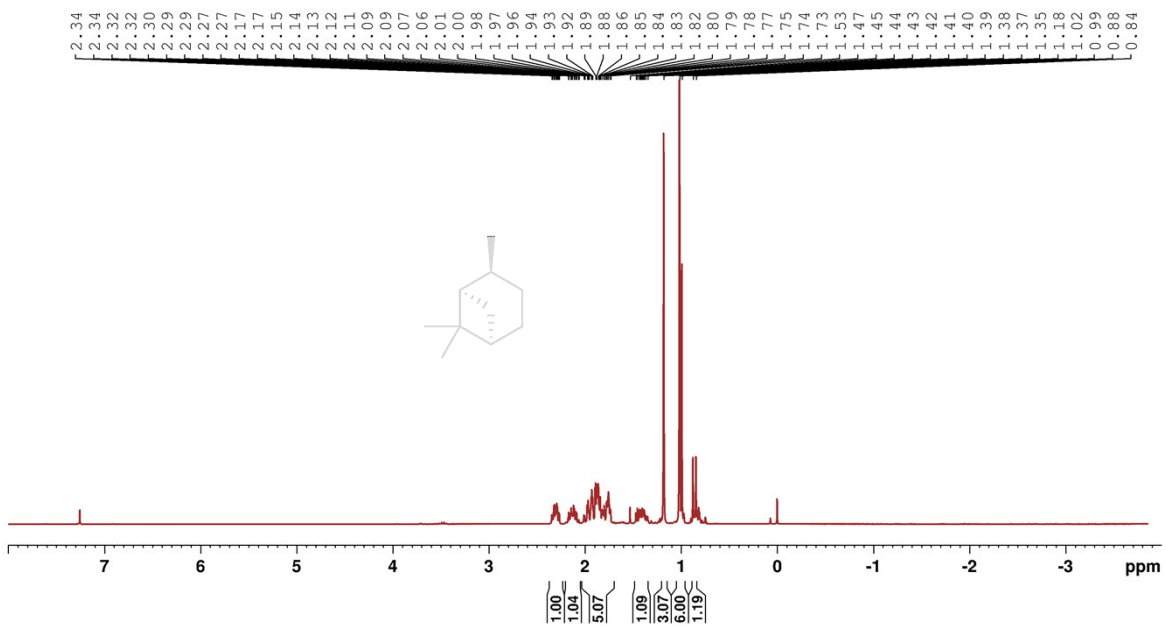


Figure S91. ^{1}H NMR spectrum of **2o** in $CDCl_3$.

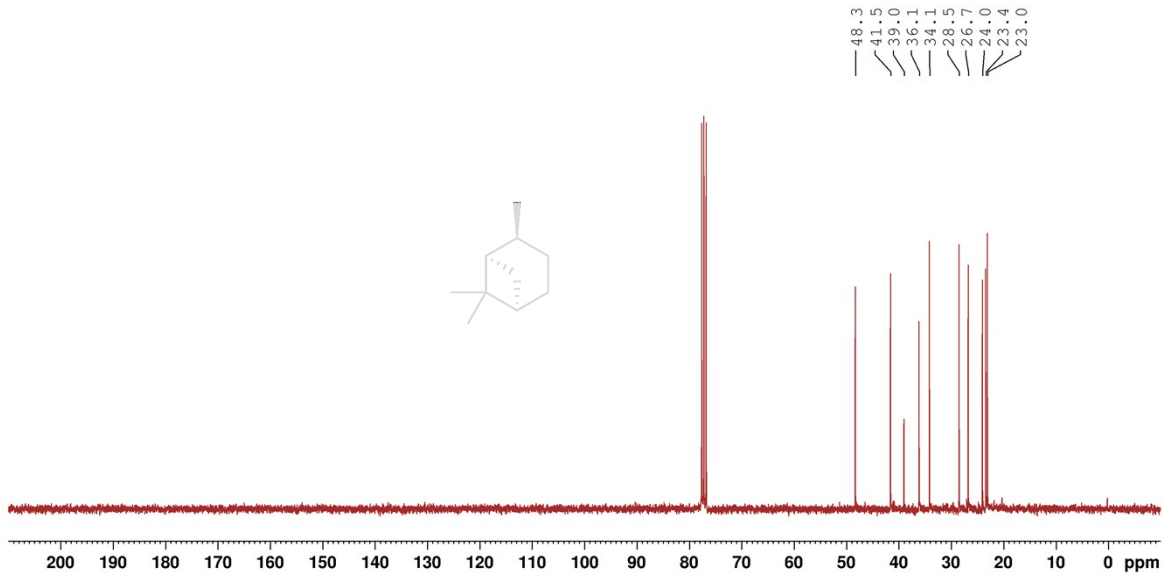


Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum of **2o** in $CDCl_3$.

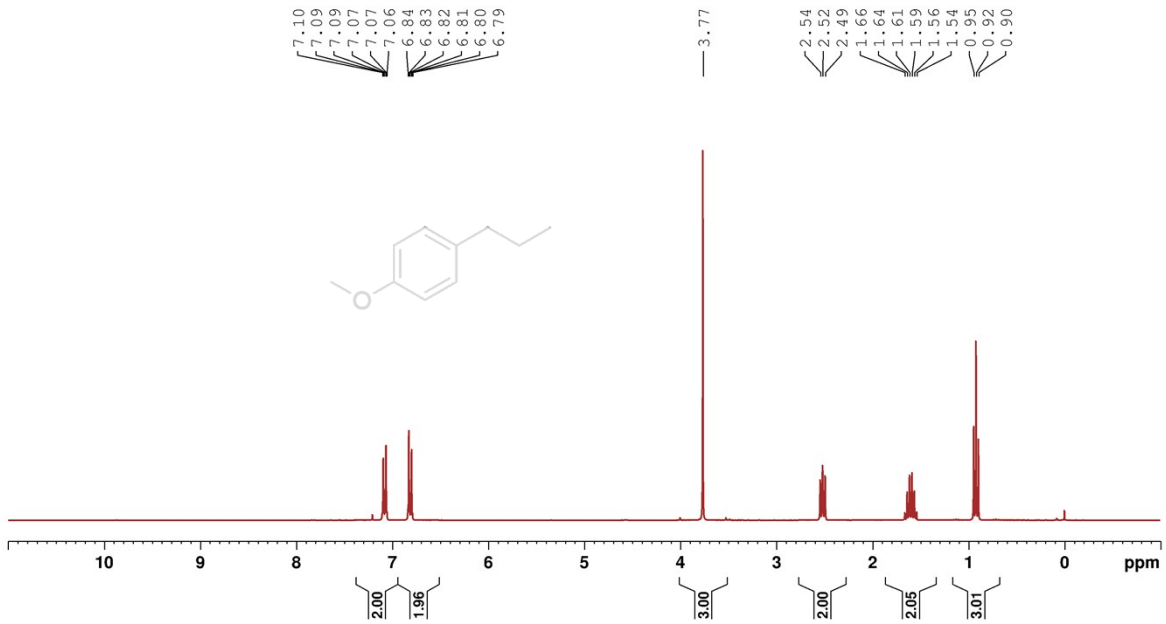


Figure S93. ^{1}H NMR spectrum of **2p** in $CDCl_3$.

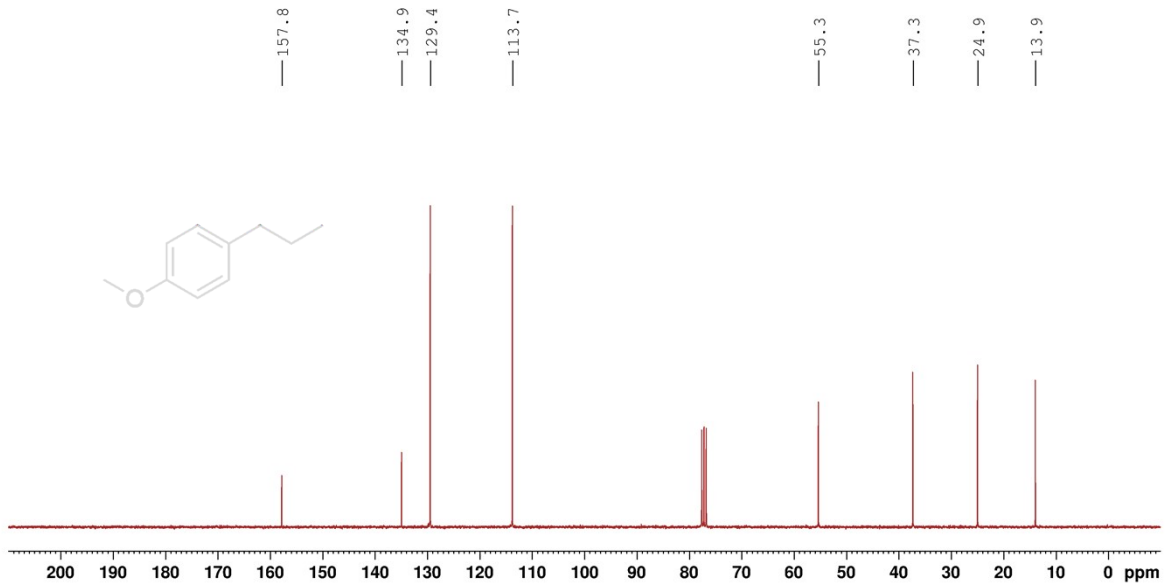


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of **2p** in $CDCl_3$.

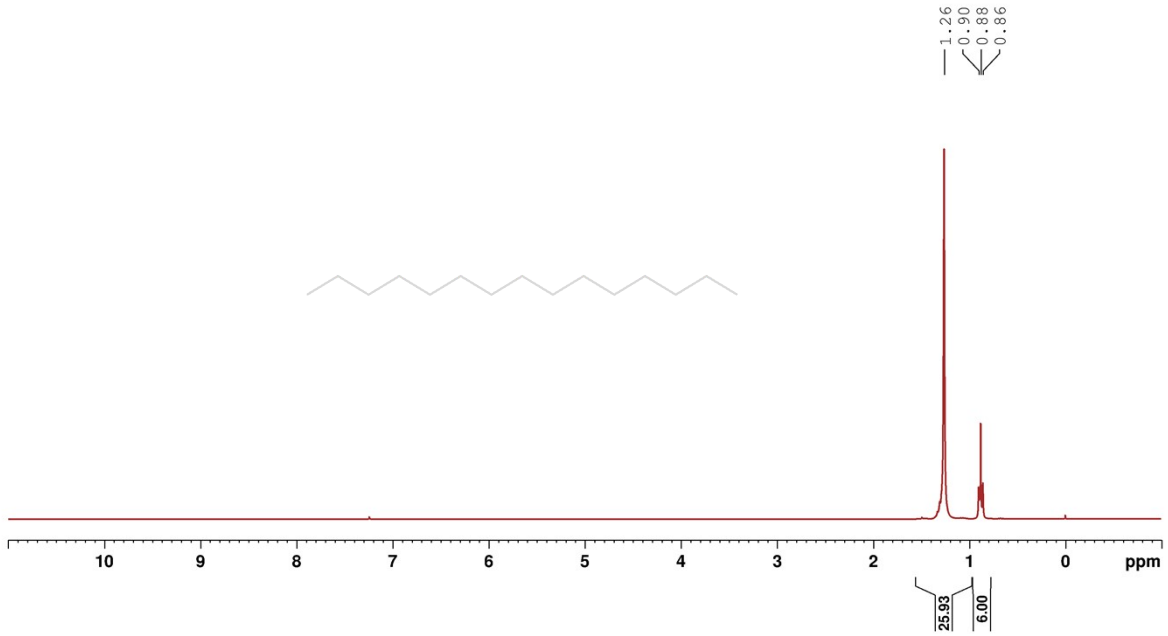


Figure S95. ^{1}H NMR spectrum of **2r** in $CDCl_3$.

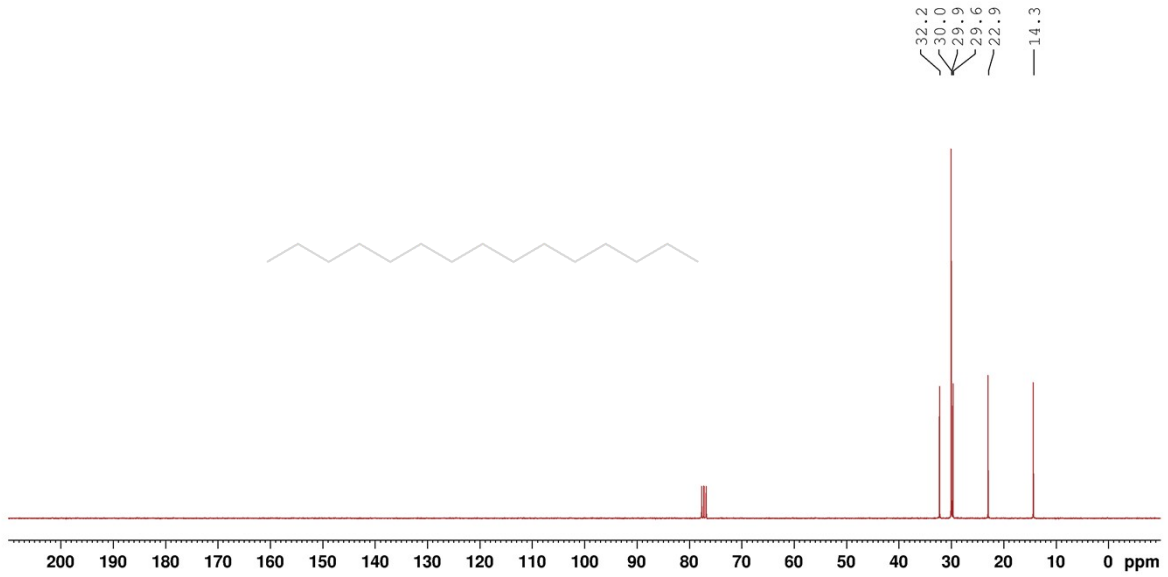


Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum of **2r** in $CDCl_3$.

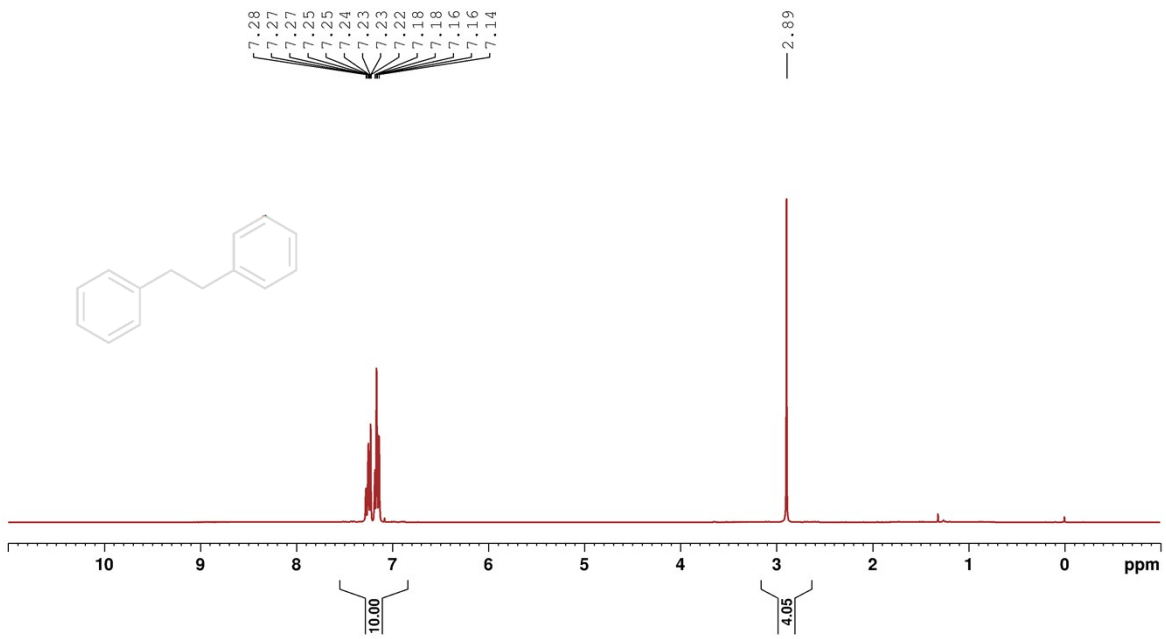


Figure S97. ^{1}H NMR spectrum of **2s** in $CDCl_3$.

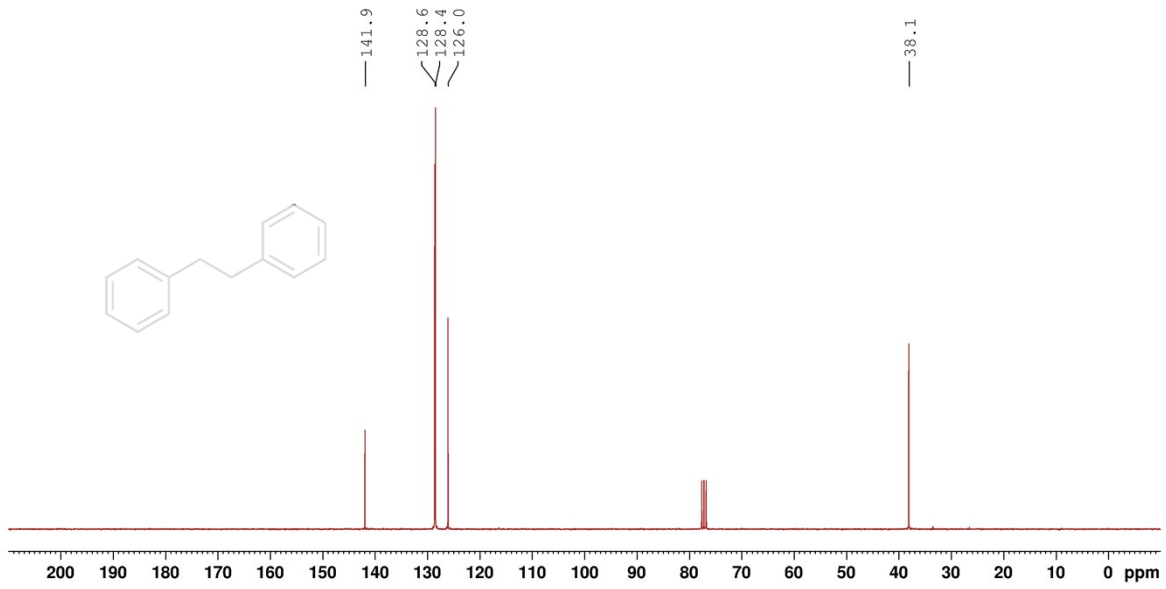


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of **2s** in $CDCl_3$.

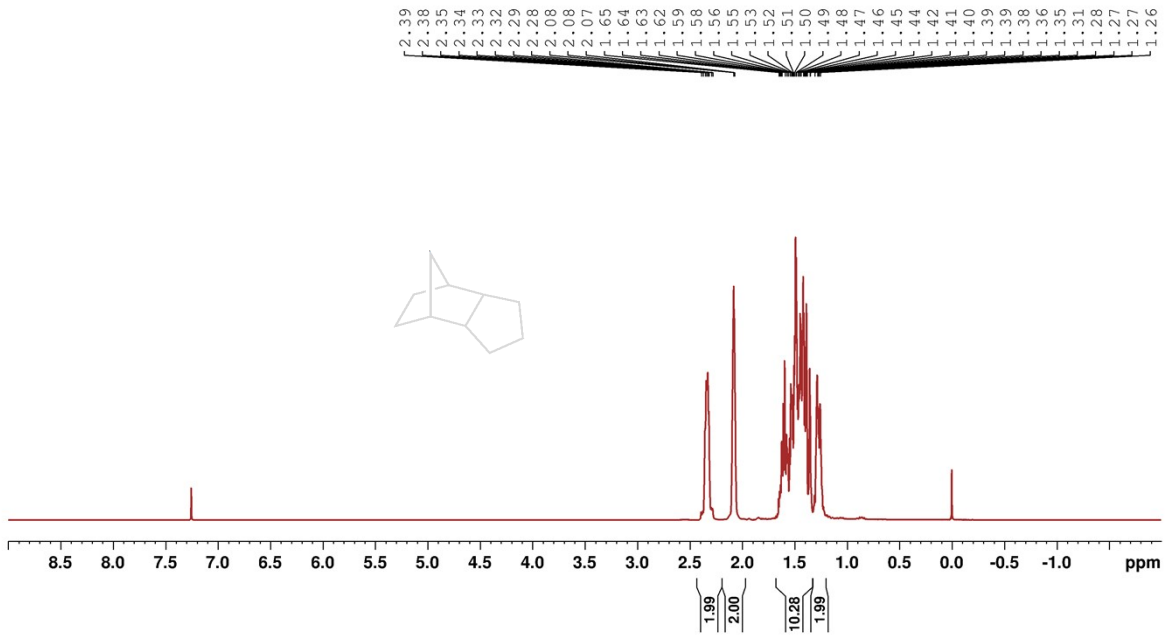


Figure S99. ^{1}H NMR spectrum of **2t** in $CDCl_3$.

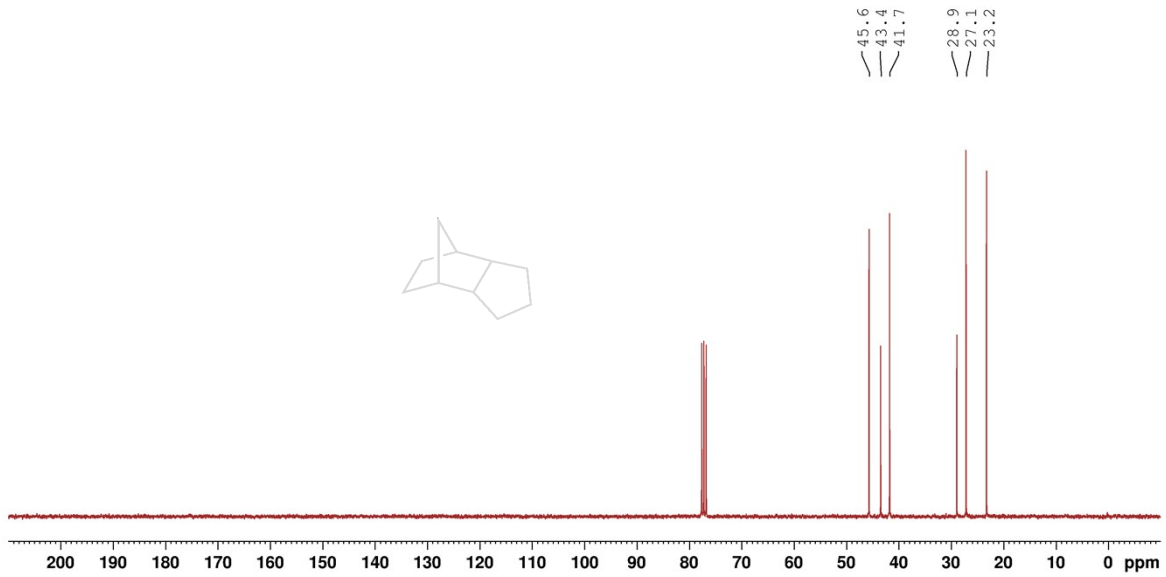


Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum of **2t** in $CDCl_3$.

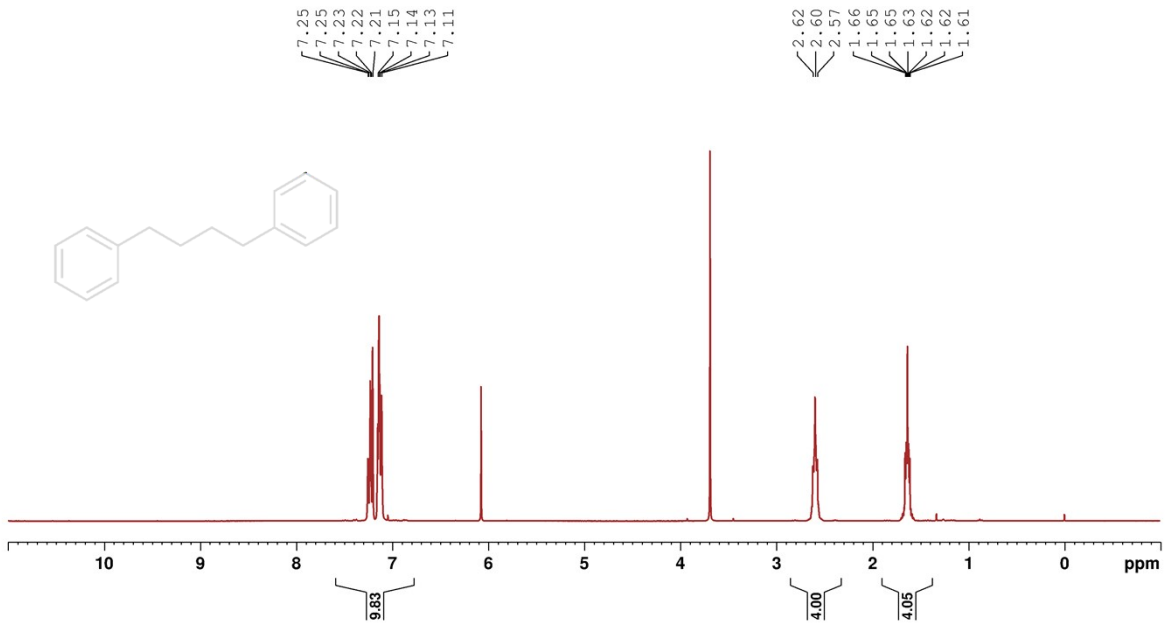


Figure S101. ^{1}H NMR spectrum of **2v** in $CDCl_3$.

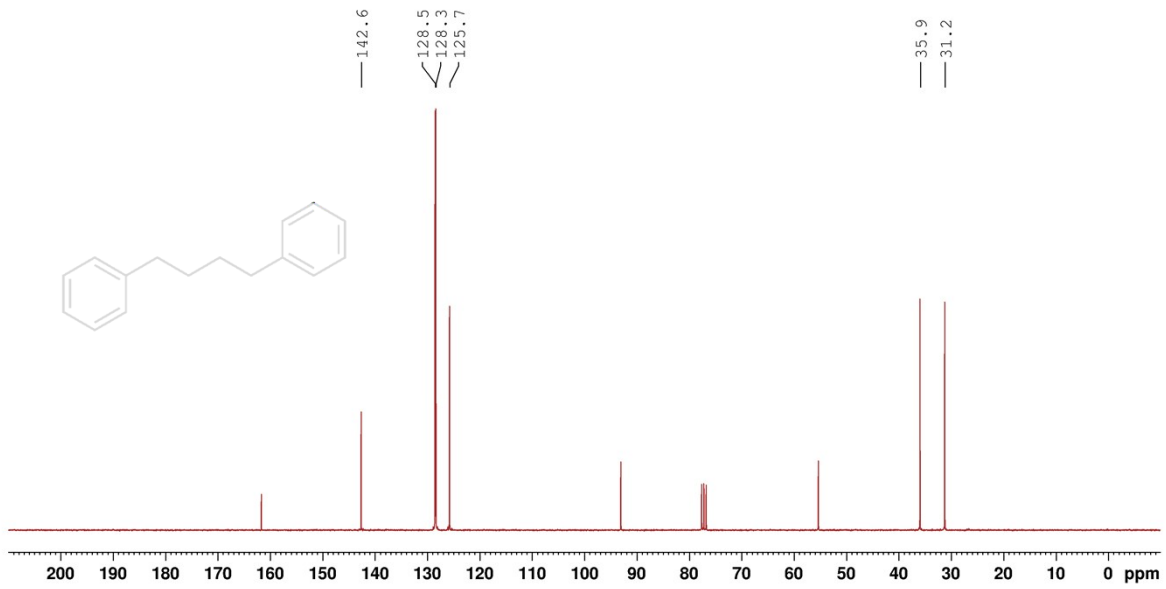


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum of **2v** in $CDCl_3$.

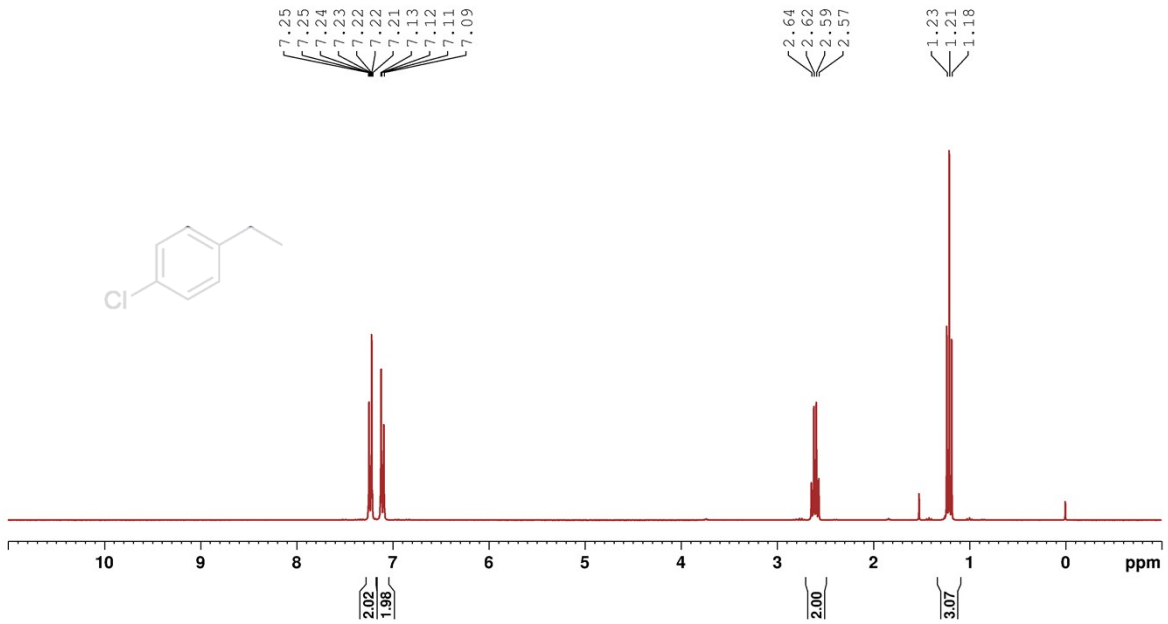


Figure S103. ^{1}H NMR spectrum of **2x** in $CDCl_3$.

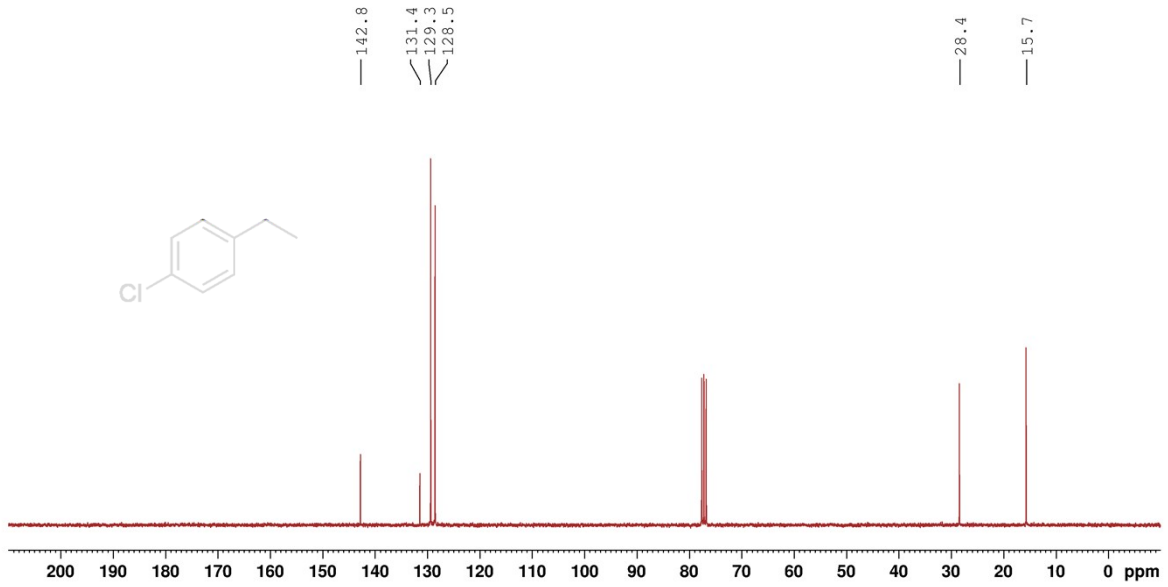


Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of **2x** in $CDCl_3$.

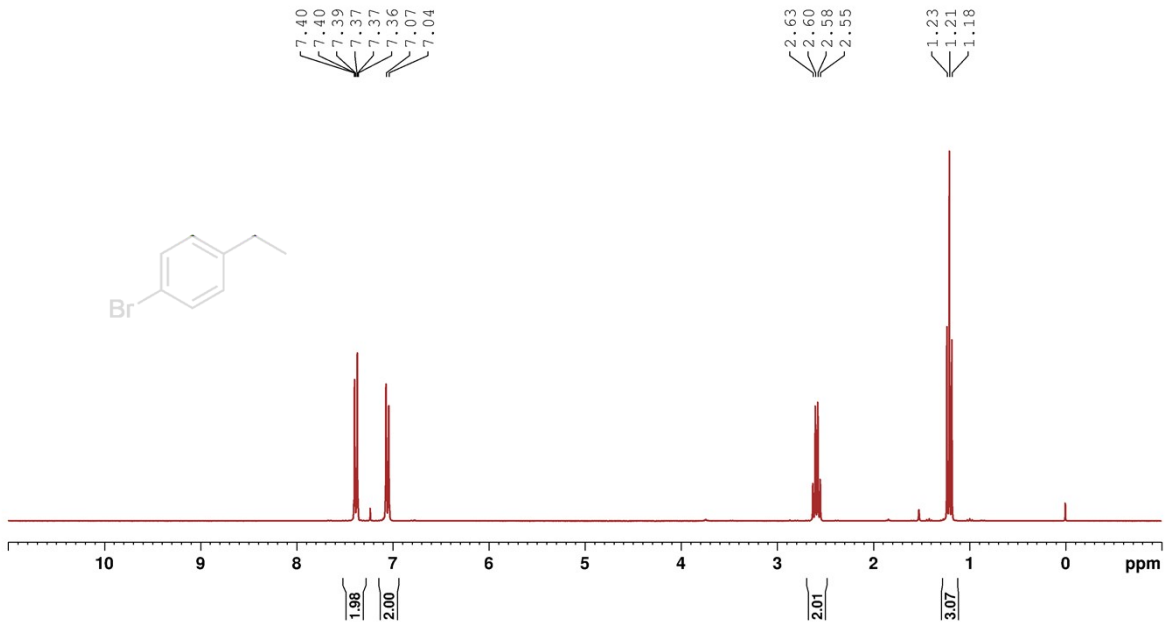


Figure S105. ^{1}H NMR spectrum of **2y** in $CDCl_3$.

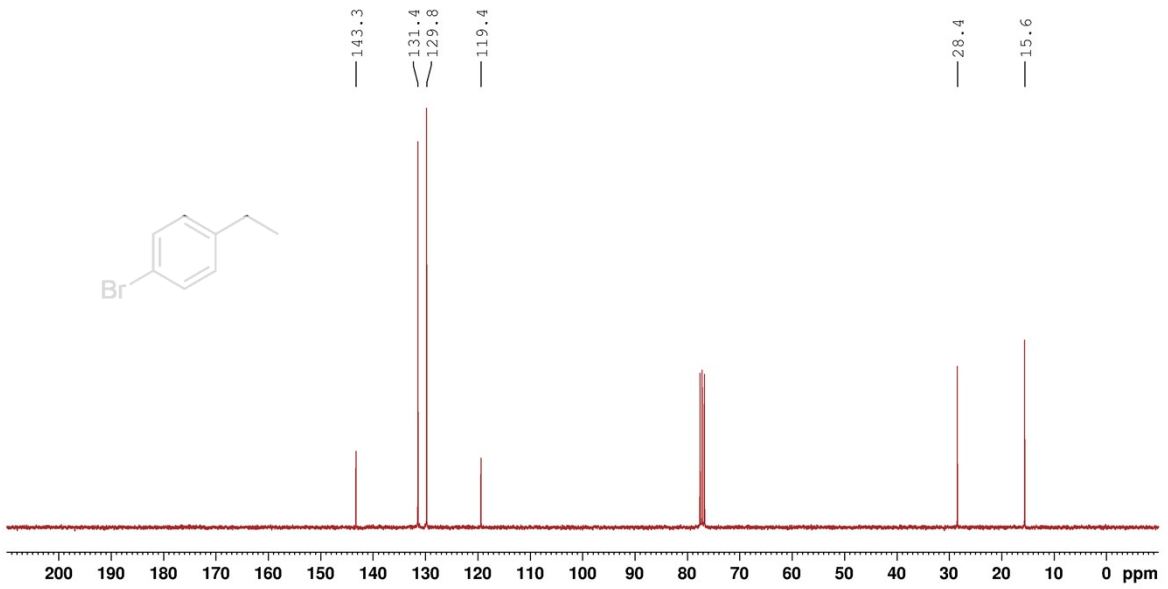


Figure S106. $^{13}C\{^{1}H\}$ NMR spectrum of **2y** in $CDCl_3$.

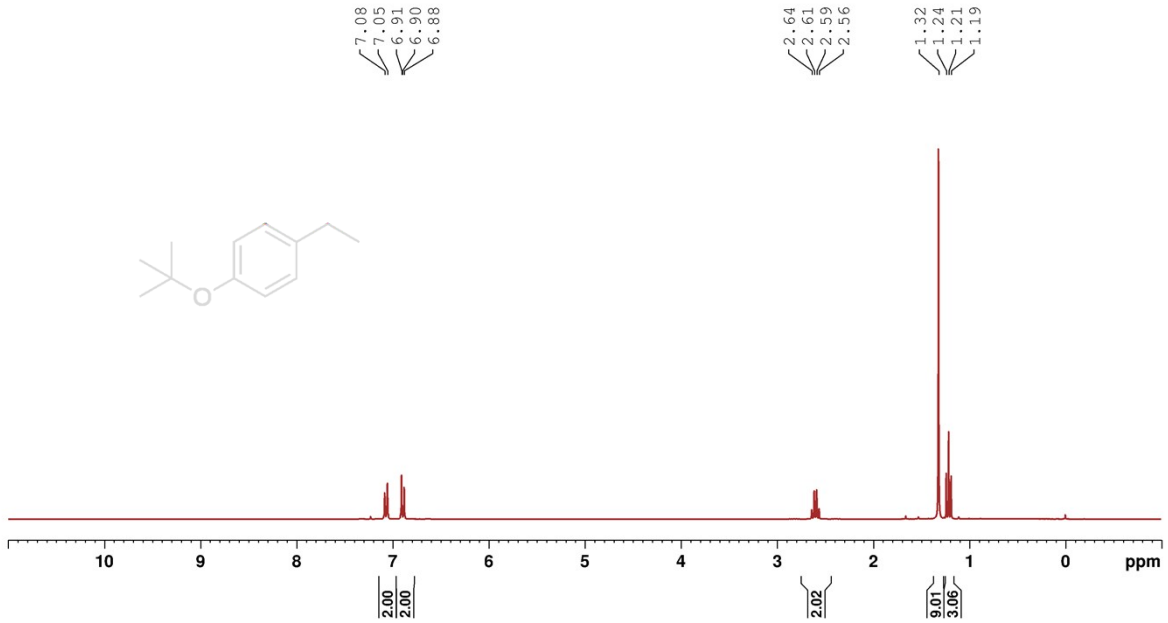


Figure S107. ^{1}H NMR spectrum of **2z** in $CDCl_3$.

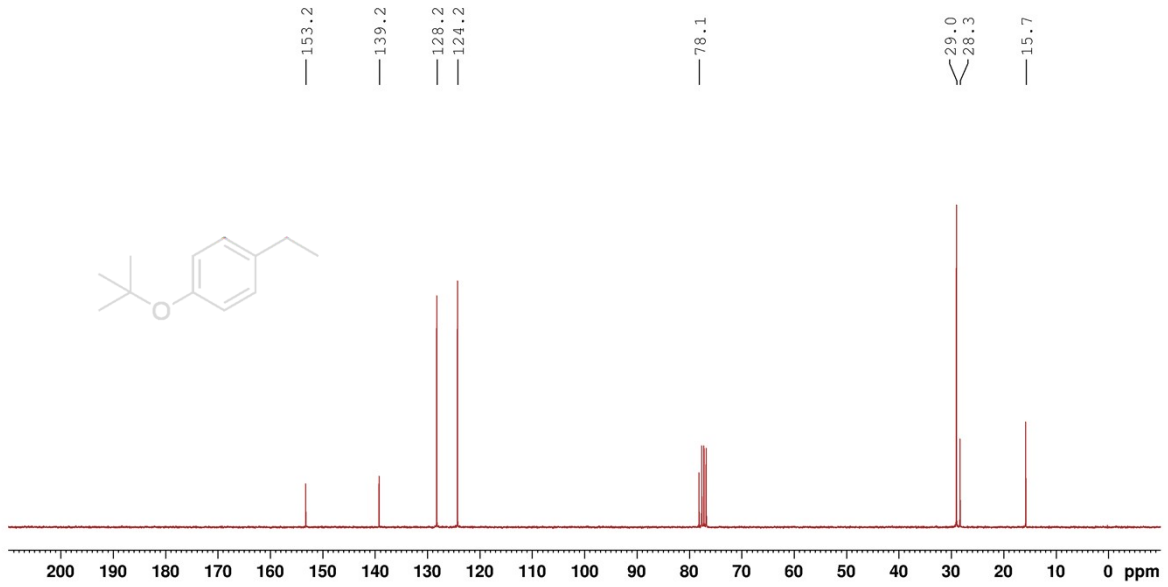


Figure S108. $^{13}C\{^{1}H\}$ NMR spectrum of **2z** in $CDCl_3$.

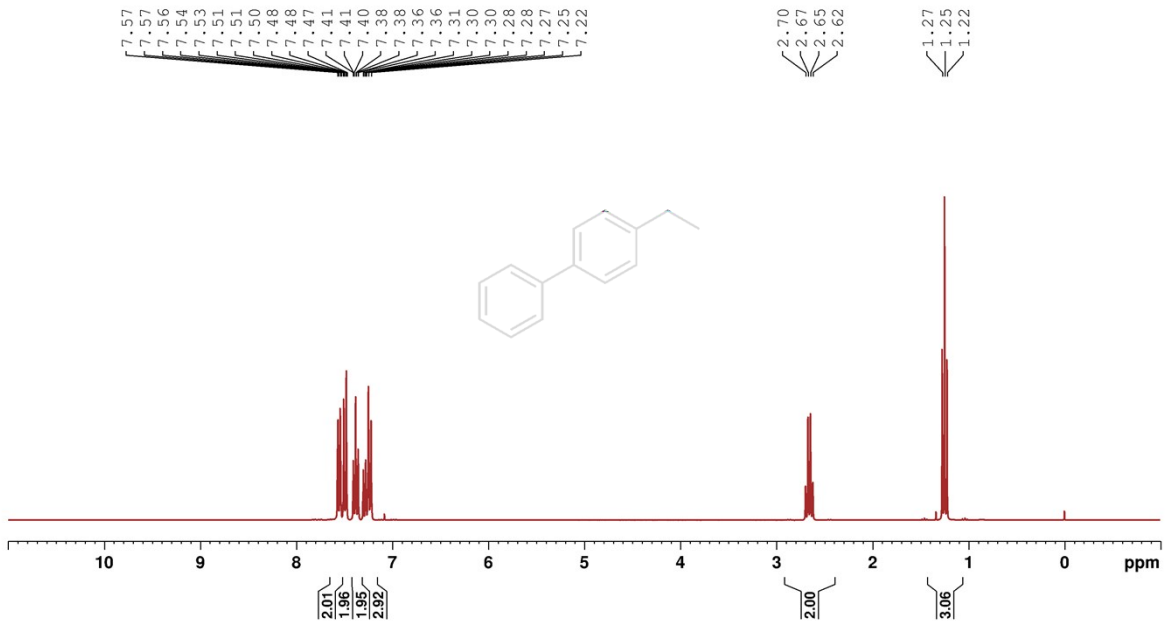


Figure S109. ^{1}H NMR spectrum of **2aa** in $CDCl_3$.

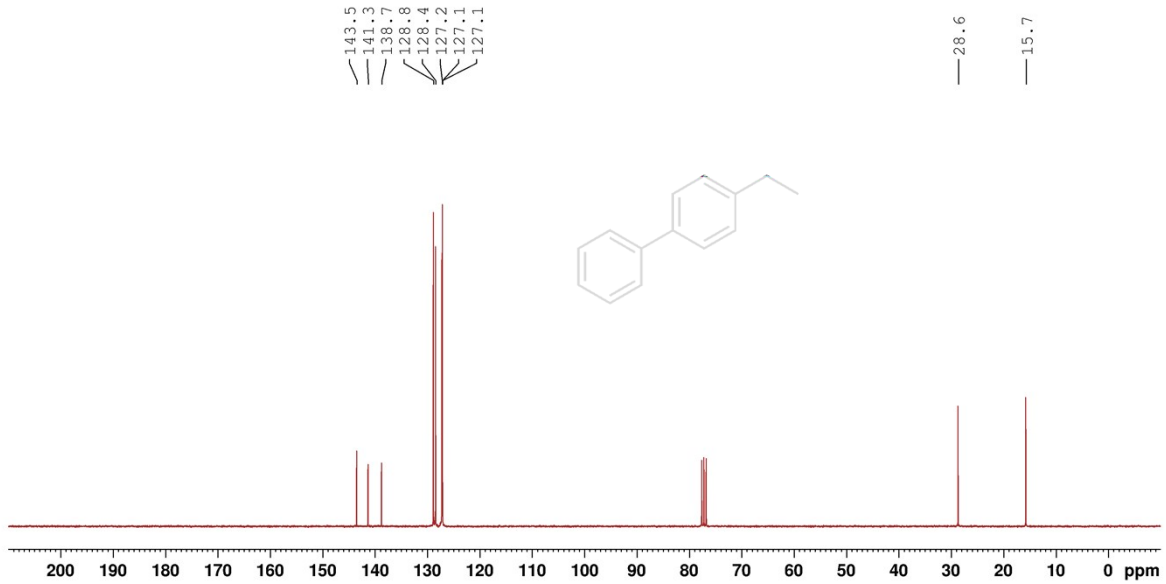


Figure S110. $^{13}C\{^{1}H\}$ NMR spectrum of **2aa** in $CDCl_3$.

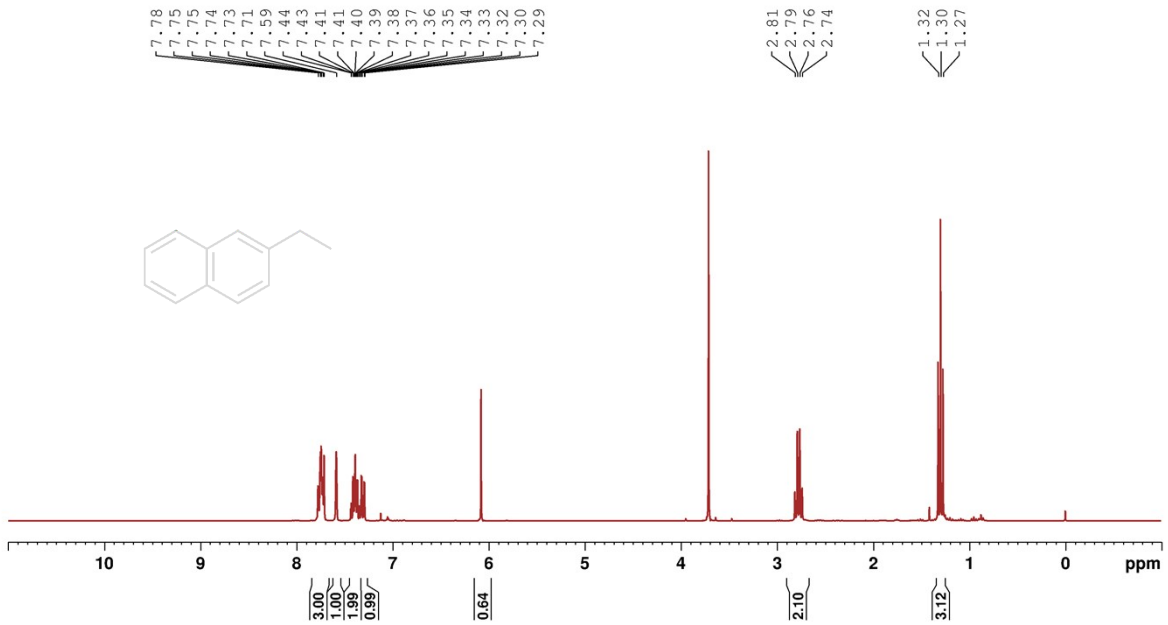


Figure S111. ^{1}H NMR spectrum of **2ab** in $CDCl_3$.

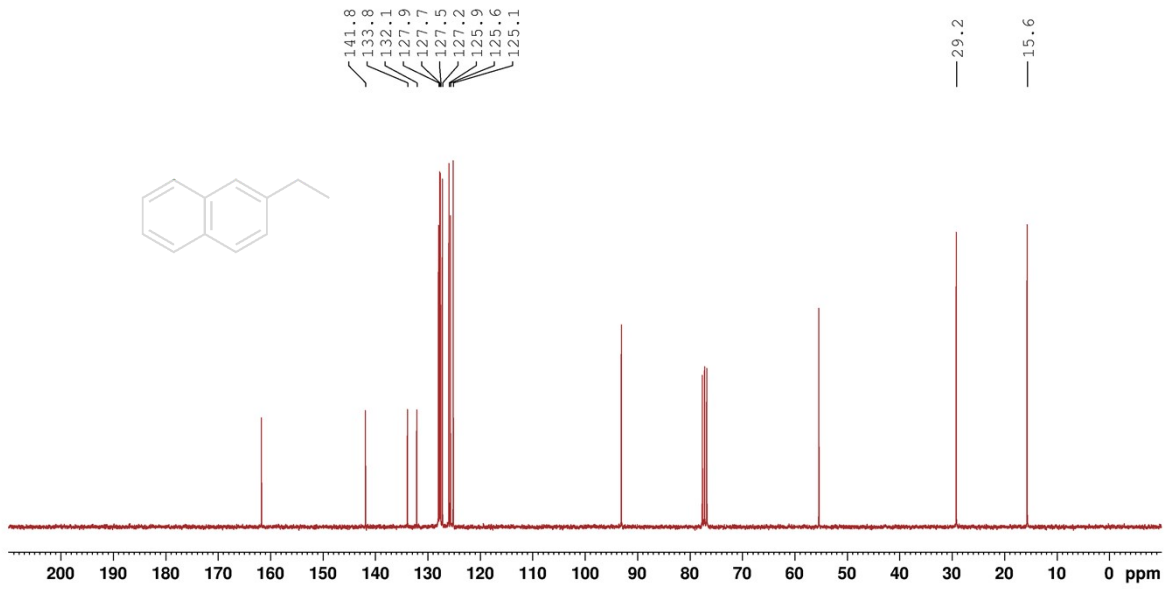


Figure S112. $^{13}C\{^{1}H\}$ NMR spectrum of **2ab** in $CDCl_3$.

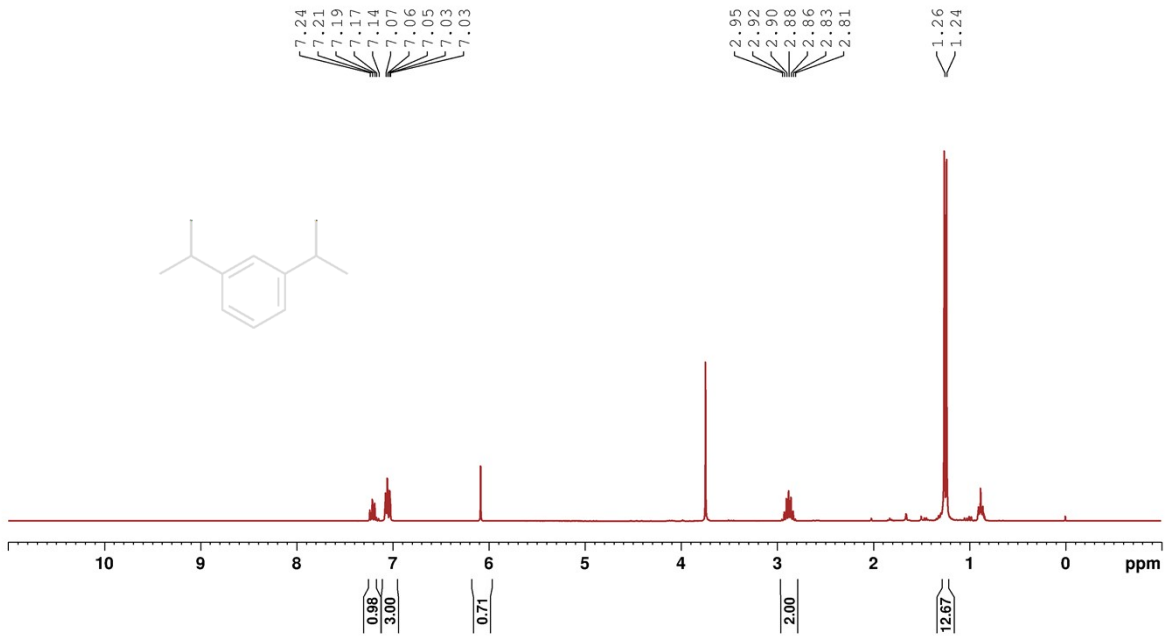


Figure S113. ^{1}H NMR spectrum of **2ag** in $CDCl_3$.

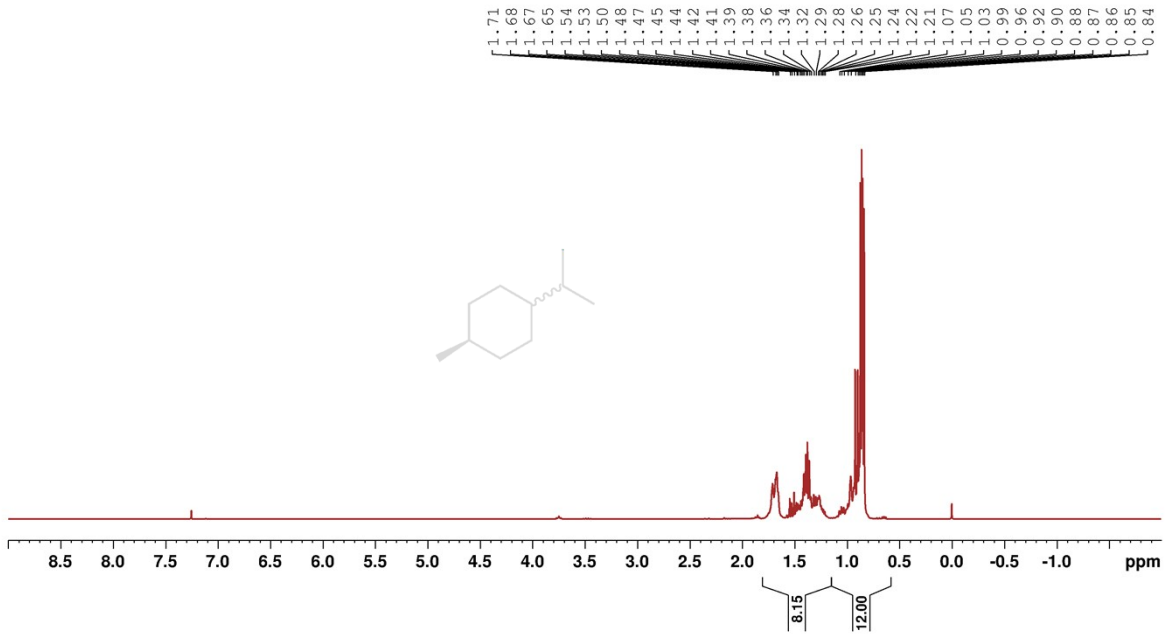


Figure S114. ^{1}H NMR spectrum of **2ah** in $CDCl_3$.

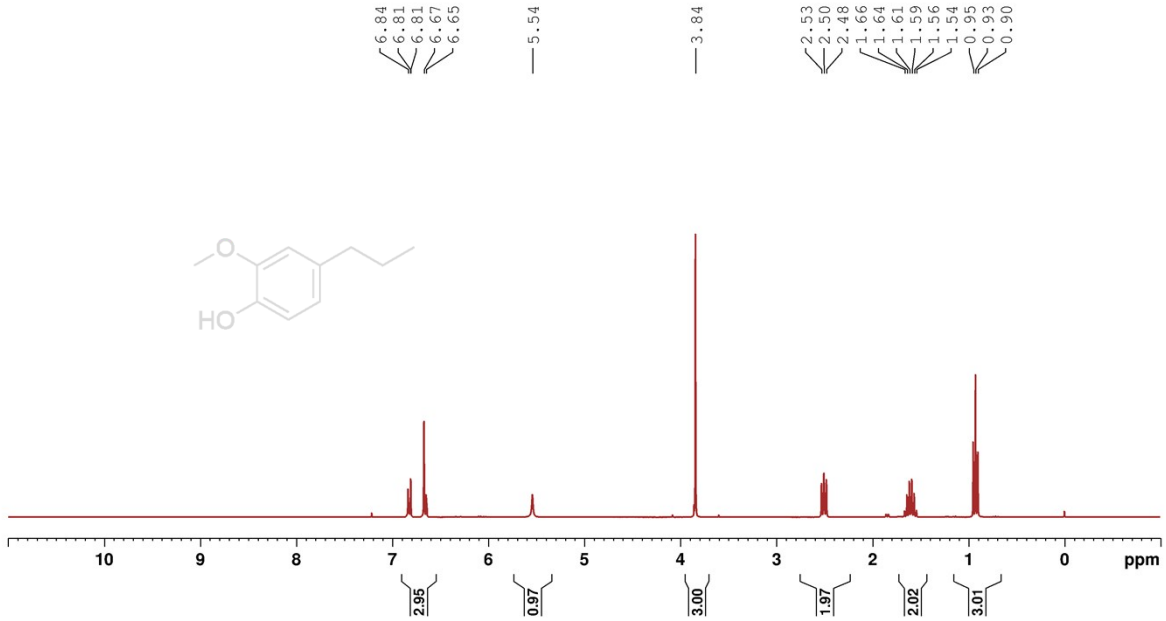


Figure S115. ^{1}H NMR spectrum of **2ai** in $CDCl_3$.

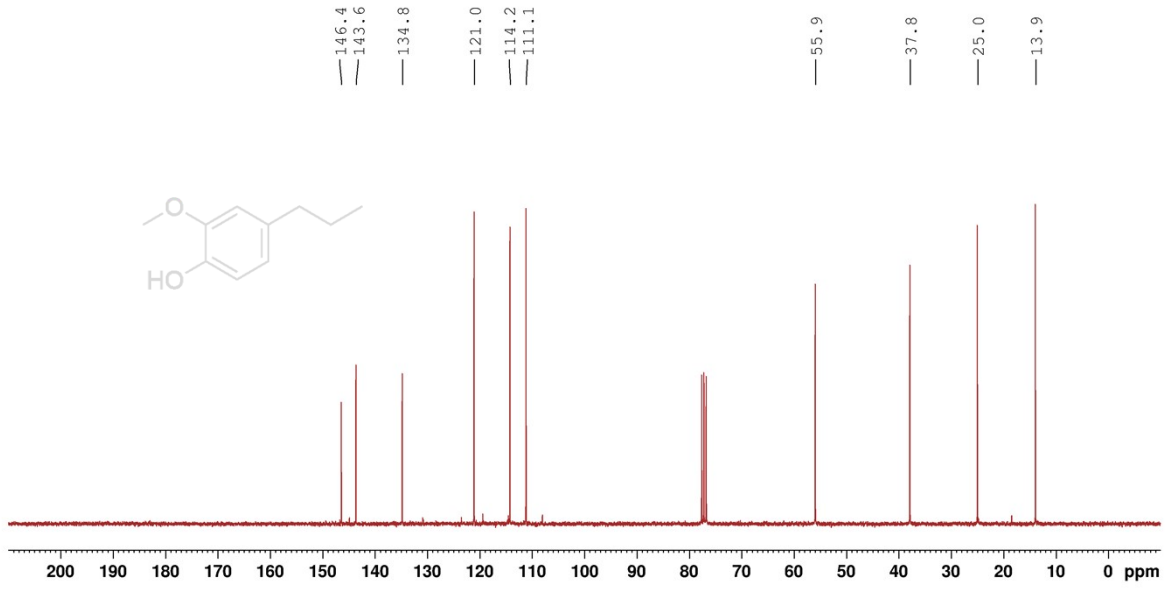


Figure S116. $^{13}C\{^{1}H\}$ NMR spectrum of **2ai** in $CDCl_3$.

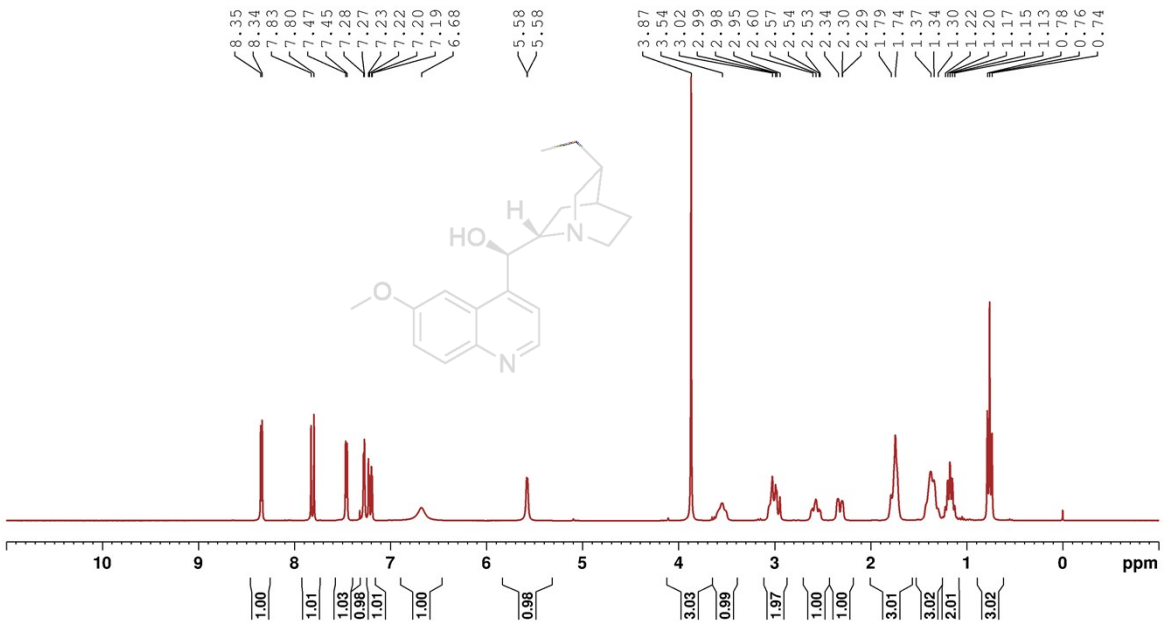


Figure S117. ^{1}H NMR spectrum of **2aj** in $CDCl_3$.

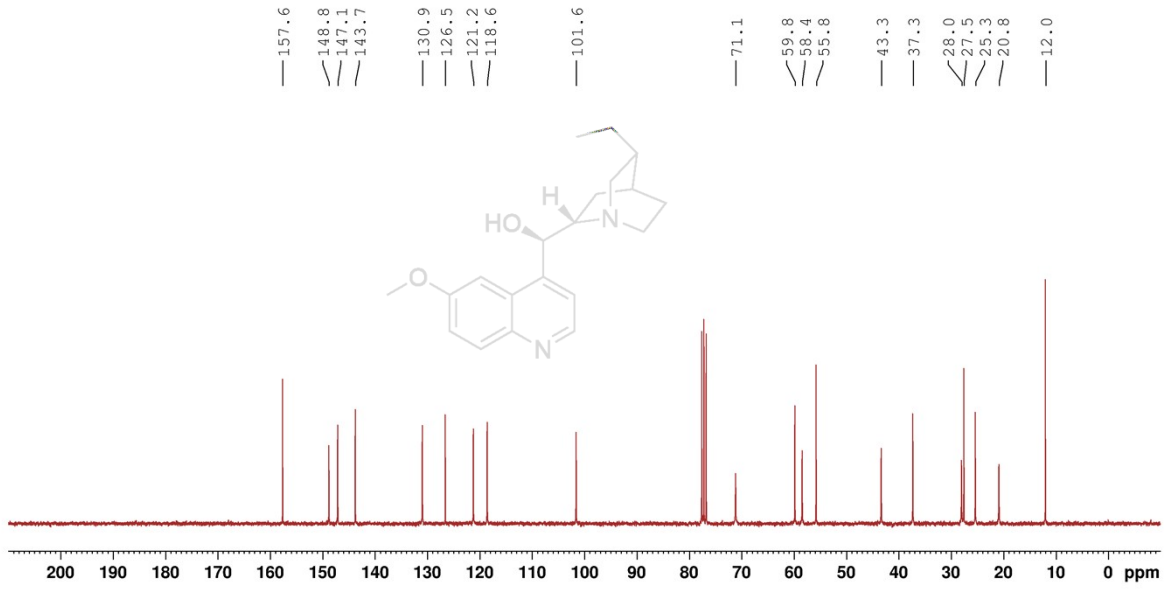


Figure S118. $^{13}C\{^{1}H\}$ NMR spectrum of **2aj** in $CDCl_3$.

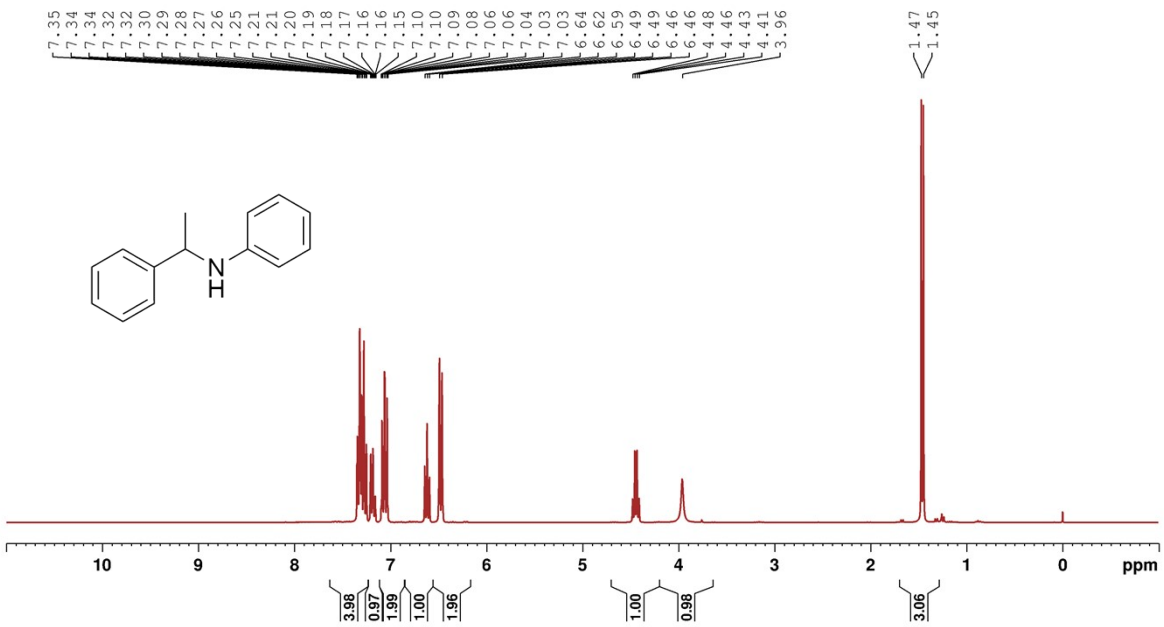


Figure S119. ^{1}H NMR spectrum of **6b** in $CDCl_3$.

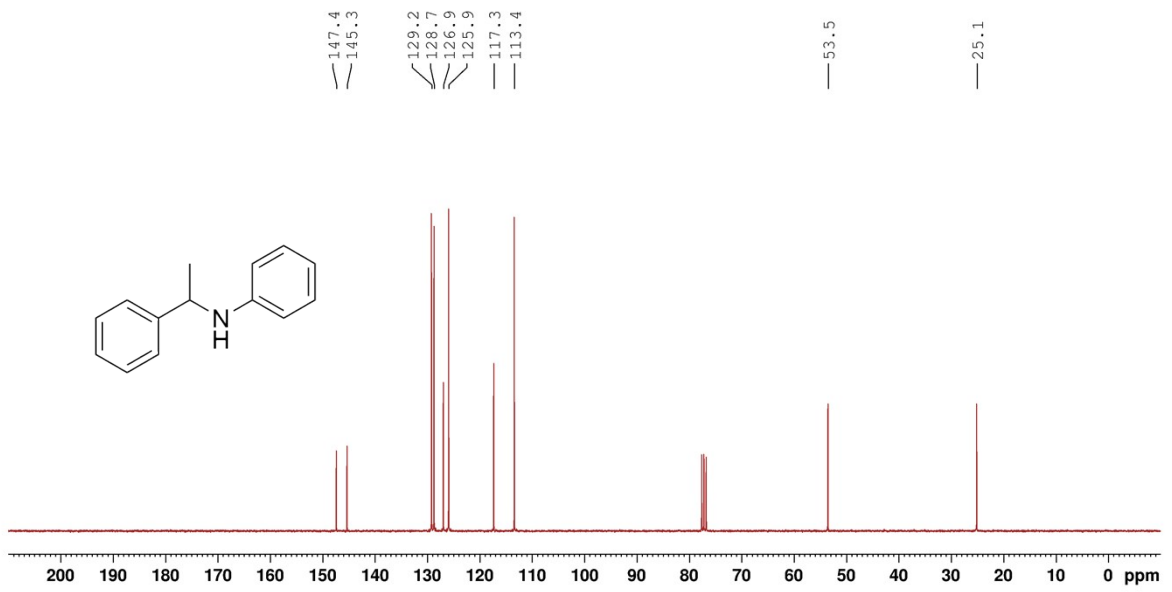


Figure S120. $^{13}C\{^{1}H\}$ NMR spectrum of **6b** in $CDCl_3$.

9 Crystallographic Data

SC-XRD quality crystals were coated with Fomblin® Y H-VAC 140/13 perfluoropolyether in a glovebox and selected under ambient conditions. The data was collected at 296(2) K on a *Bruker **D8 Quest Eco*** diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). The data was processed using APEX4 and 6,[29] the structures were solved by intrinsic phasing (XT, Version 2018/2),[30] and refined by full matrix least squares procedures on F^2 (SHELXL, Version 2018/3)[31] using the graphical interface Shelxle[32] within the SHELXTL suite of programs by Bruker. All non-hydrogen atoms were refined anisotropically. All H atoms (except for Ni–H) were calculated geometrically and a riding model was applied in the refinement process. All Ni–H hydrogen atoms were located directly from the Fourier difference maps. **[Ni] 3-Br-Cp*** and **[Ni] 4-Cp*** were refined as a 2-component inversion twin. For **[Ni] 5**, electron densities were detected which could not be assigned to a reasonable model; their contribution was then removed from the final refinement using the SQUEEZE procedure in PLATON.[33] Crystallographic details can be found in Tables S5–S12. CCDC **2493263**, **2493261**, **2493264**, **2493262**, **2493267**, **2493265**, **2493266**, and **2493739** contain the supplementary crystallographic data. This information can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/

[29] Bruker (2019), *APEX4 v2021.10-0*, *SAINT V8.40B*, *SHELXTL-2018*, Bruker Nano, Inc.: Madison (WI), USA, 2021.

[30] a) G. M. Sheldrick, *SHELXT-2018: Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 2014. b) G. M Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, **64**, 112−122. c) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.* 2015, **71**, 3−8.

[31] a) G. M. Sheldrick, *SHELXL-2018: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 2018. b) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 3−8.

[32] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *Shelxle: a Qt graphical user interface for SHELXL*, *J. Appl. Crystallogr.* 2011, **44**, 1281−1284.

[33] a) A. L. Spek, *Acta Crystallogr., Sect. C: Struct. Chem.* 2015, **71**, 9−18; b) A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.* 2009, **65**, 148−155; c) A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7−13.

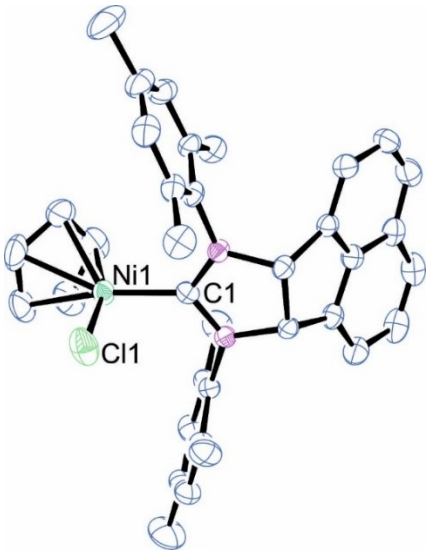


Figure S121. Solid-state molecular structure of **[Ni] 5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S5. Crystallographic Data for [Ni] 5

Compound	**[Ni] 5**
Empirical formula	$C_{72}H_{68}Cl_2N_4Ni_2$
Formula weight	1177.62
Temperature [K]	296(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	11.3520(7)
b [Å]	16.5221(11)
c [Å]	20.3395(14)
α [°]	85.126(2)
β [°]	78.915(2)
γ [°]	76.110(2)
Volume [Å^3]	3631.2(4)
Z	2
ρ_{calc} [g·cm^{-3}]	1.077
μ [mm^{-1}]	0.630
Reflections collected	142515
Independent reflections	12916 R_{int} = 0.0688 R_{sigma} = 0.0565
Data / Restraints / Parameters	12916 / 0 / 733
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0668 wR_2 = 0.1570
Final *R* indexes [all data]	R_1 = 0.1082 wR_2 = 0.1741
Largest peak/hole [e·Å^{-3}]	0.50/−0.27
CCDC number	**2493263**

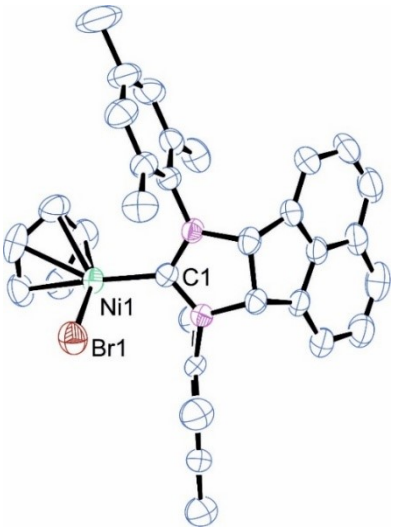


Figure S122. Solid-state molecular structure of **[Ni] 5-Br**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S 6. Crystallographic Data for [Ni] 5-Br

Compound	**[Ni] 5-Br**
Empirical formula	$C_{36}H_{35}BrN_2Ni$
Formula weight	634.28
Temperature [K]	296(2)
Crystal system	triclinic
Space group	$P\overline{1}$
a [Å]	10.977(2)
b [Å]	11.712(3)
c [Å]	12.949(3)
α [°]	95.407(5)
β [°]	103.657(5)
γ [°]	103.770(5)
Volume [Å^3]	1551.1(6)
Z	2
ρ_{calc} [g·cm^{-3}]	1.358
μ [mm^{-1}]	1.940
Reflections collected	49171
Independent reflections	6400 R_{int} = 0.0628 R_{sigma} = 0.0561
Data / Restraints / Parameters	6400 / 0 / 355
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0447 wR_2 = 0.1075
Final *R* indexes [all data]	R_1 = 0.0845 wR_2 = 0.1176
Largest peak/hole [e·Å^{-3}]	0.54/−0.68
CCDC number	**2493261**

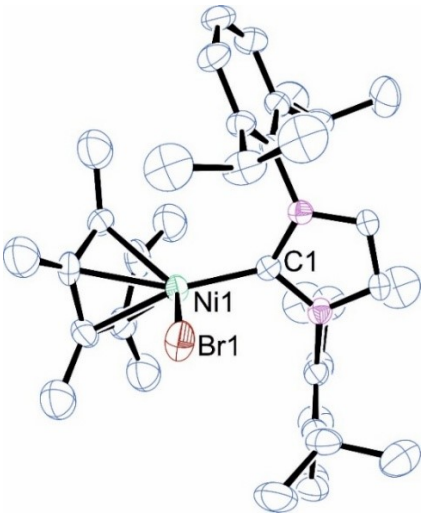


Figure S123. Solid-state molecular structure of **[Ni] 3-Br-Cp***. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S7. Crystallographic Data for [Ni] 3-Br-Cp*

Compound	**[Ni] 3-Br-Cp***
Empirical formula	$C_{37}H_{50}BrN_2Ni$
Formula weight	661.41
Temperature [K]	296(2)
Crystal system	monoclinic
Space group	*Cc*
a [Å]	12.2007(4)
b [Å]	31.6600(9)
c [Å]	10.5824(3)
α [°]	90
β [°]	93.3980(10)
γ [°]	90
Volume [Å^3]	4080.5(2)
Z	4
ρ_{calc} [g·cm^{-3}]	1.077
μ [mm^{-1}]	1.477
Reflections collected	90997
Independent reflections	8384 R_{int} = 0.0539 R_{sigma} = 0.0455
Data / Restraints / Parameters	8384 / 2 / 342
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0492 wR_2 = 0.1301
Final *R* indexes [all data]	R_1 = 0.0754 wR_2 = 0.1413
Largest peak/hole [e·Å^{-3}]	0.47/−0.45
Flack parameter	0.111(15)
CCDC number	**2493264**

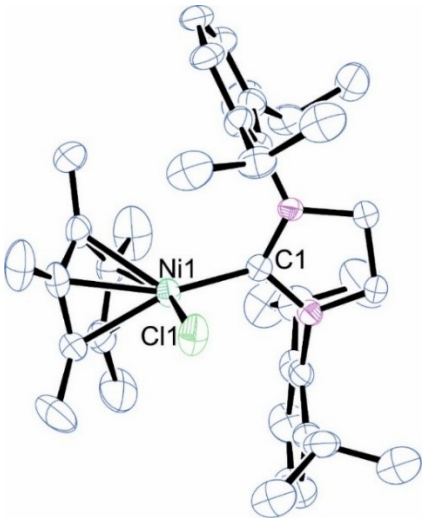


Figure S124. Solid-state molecular structure of **[Ni] 4-Cp***. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S8. Crystallographic Data for [Ni] 4-Cp*

Compound	**[Ni] 4-Cp***
Empirical formula	$C_{37}H_{53}ClN_2Ni$
Formula weight	619.97
Temperature [K]	296(2)
Crystal system	monoclinic
Space group	*Cc*
a [Å]	12.0486(4)
b [Å]	31.6028(10)
c [Å]	10.6772(3)
α [°]	90
β [°]	92.9820(10)
γ [°]	90
Volume [Å^3]	4060.0(2)
Z	4
ρ_{calc} [g·cm^{-3}]	1.014
μ [mm^{-1}]	0.566
Reflections collected	89288
Independent reflections	7161 R_{int} = 0.0675 R_{sigma} = 0.0586
Data / Restraints / Parameters	7161 / 2 / 366
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0528 wR_2 = 0.1373
Final *R* indexes [all data]	R_1 = 0.0825 wR_2 = 0.1479
Largest peak/hole [e·Å^{-3}]	0.39/−0.33
Flack parameter	0.07(3)
CCDC number	**2493262**

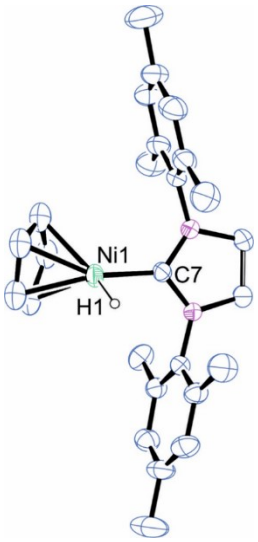


Figure S125. Solid-state molecular structure of **[Ni] 2-H**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms in the periphery are omitted for clarity.

Table S9. Crystallographic Data for [Ni] 2-H

Compound	**[Ni] 2-H**
Empirical formula	$C_{26}H_{32}N_2Ni$
Formula weight	431.24
Temperature [K]	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	16.2483(15)
b [Å]	16.9672(16)
c [Å]	8.7426(8)
α [°]	90
β [°]	100.492(2)
γ [°]	90
Volume [Å^3]	2369.9(4)
Z	4
ρ_{calc} [g·cm^{-3}]	1.209
μ [mm^{-1}]	0.832
Reflections collected	122685
Independent reflections	4853 R_{int} = 0.1078 R_{sigma} = 0.0561
Data / Restraints / Parameters	4853 / 0 / 248
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0599 wR_2 = 0.1554
Final R indexes [all data]	R_1 = 0.1134 wR_2 = 0.1753
Largest peak/hole [e·Å^{-3}]	0.82/−0.57
CCDC number	**2493267**

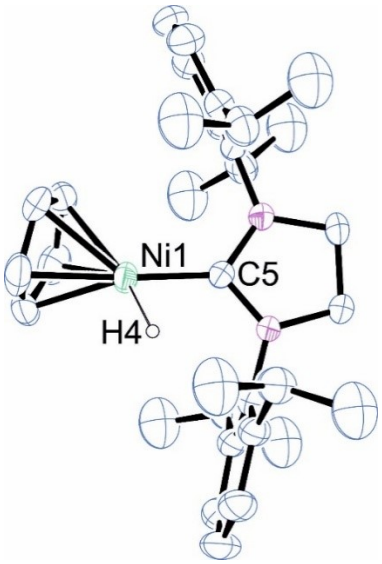


Figure S126. Solid-state molecular structure of **[Ni] 4-H**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms in the periphery are omitted for clarity. The asymmetric unit contains two complexes, only one is shown.

Table S10. Crystallographic Data for [Ni] 4-H

Compound	**[Ni] 4-H**
Empirical formula	$C_{32}H_{44}N_2Ni$
Formula weight	515.40
Temperature [K]	296(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	12.6985(3)
b [Å]	36.7921(10)
c [Å]	12.8730(4)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	6014.3(3)
Z	8
ρ_{calc} [g·cm^{-3}]	1.138
μ [mm^{-1}]	0.666
Reflections collected	250413
Independent reflections	14215 R_{int} = 0.1713 R_{sigma} = 0.1618
Data / Restraints / Parameters	14215 / 0 / 613
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0715 wR_2 = 0.1692
Final R indexes [all data]	R_1 = 0.2046 wR_2 = 0.2064
Largest peak/hole [e·Å^{-3}]	0.53/−0.53
CCDC number	**2493265**

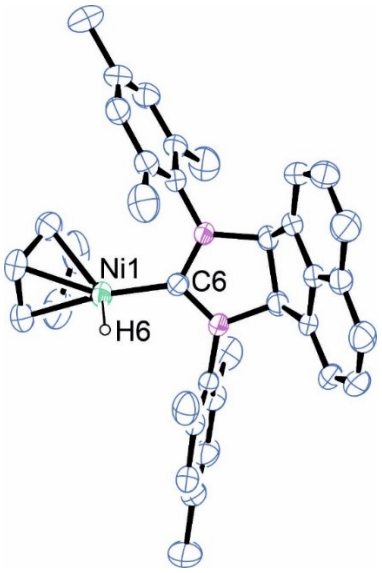


Figure S127. Solid-state molecular structure of **[Ni] 5-H**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms in the periphery are omitted for clarity. The asymmetric unit contains two complexes, only one is shown.

Table S11. Crystallographic Data for [Ni] 5-H

Compound	**[Ni] 5-H**
Empirical formula	$C_{79}H_{80}N_4Ni_2$
Formula weight	1202.89
Temperature [K]	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	21.2448(12)
b [Å]	18.7524(8)
c [Å]	18.5759(8)
α [°]	90
β [°]	115.8890(10)
γ [°]	90
Volume [Å^3]	6657.8(6)
Z	4
ρ_{calc} [g·cm^{-3}]	1.2
μ [mm^{-1}]	0.611
Reflections collected	349632
Independent reflections	13728 R_{int} = 0.1063 R_{sigma} = 0.0617
Data / Restraints / Parameters	13728 / 26 / 750
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0581 wR_2 = 0.1310
Final *R* indexes [all data]	R_1 = 0.1286 wR_2 = 0.1536
Largest peak/hole [e·Å^{-3}]	0.29/-0.45
CCDC number	**2493266**

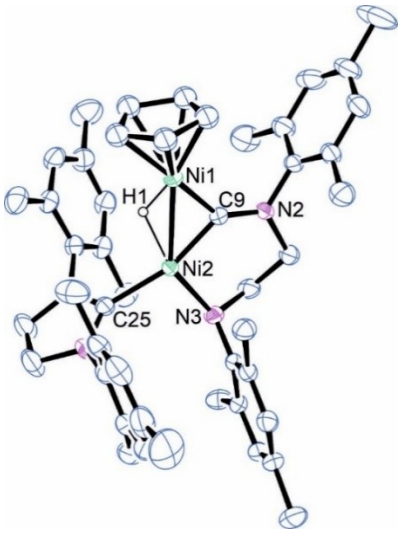


Figure S128. Solid-state molecular structure of **[Ni$_2$]H-SIMes**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms in the periphery are omitted for clarity.

Table S12. Crystallographic Data for [Ni$_2$]H-SIMes

Compound	**[Ni$_2$]H-SIMes**
Empirical formula	$C_{47}H_{58}N_4Ni_2$
Formula weight	796.39
Temperature [K]	296(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	11.702(3)
b [Å]	14.611(3)
c [Å]	15.051(3)
α [°]	104.655(9)
β [°]	103.443(9)
γ [°]	95.282(9)
Volume [Å^3]	2390.1(9)
Z	2
ρ_{calc} [g·cm^{-3}]	1.107
μ [mm^{-1}]	0.822
Reflections collected	197418
Independent reflections	9814 R_{int} = 0.0618 R_{sigma} = 0.0361
Data / Restraints / Parameters	9814 / 21 / 486
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0647 wR_2 = 0.2086
Final *R* indexes [all data]	R_1 = 0.0938 wR_2 = 0.2266
Largest peak/hole [e·Å^{-3}]	1.30/−0.46
CCDC number	**2493739**