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Facile synthesis of half-sandwich (NHC)Ni(Cp)X complexes from labile NHC proligands

Oleg V. Khazipov, Anastasia S. Pyatachenko, Olga V. Khazipova, Ivan A. Chapurny, Dmitry V. Pasyukov, Mikhail E. Minyaev and Victor M. Chernyshev

Table of contents:

S1. General information and materials

General Procedures. Solvents were purified and dried according to standard methods and stored over activated 3Å molecular sieves prior to use. Column chromatography was conducted on silica gel 60 (230−400 mesh, Merck). Glassware was dried at 120 °C in an oven for at least 3 h before the use.

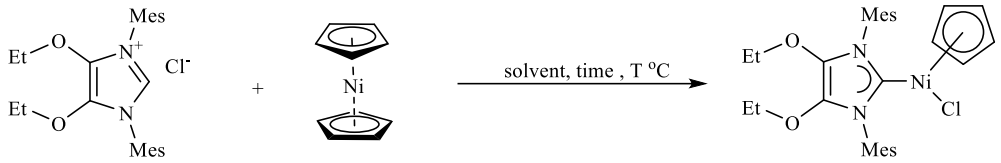
Instrumentation. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance NEO 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent signals as internal standards: δ 7.26 for ^{1}H, δ 77.2 for ^{13}C.

High-resolution mass spectra (HRMS) were made on a Bruker maXis QTOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The HRMS measurements were performed in a positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: −500 V) with a scan range of m/z 50 – 1500. External calibration of the mass spectrometer was performed with the use of a low-concentration tuning mix solution (Agilent). Direct syringe injection was applied for the analyzed solutions at a 3 μL min^{-1} flow rate. In HRMS measurements, nitrogen was applied as the nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}). The dry temperature was 250 °C. All the spectra were recorded with 1 Hz frequency and processed using the Bruker Data Analysis 4.0 software.

Materials 4,5-Diethoxy-1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**1a**),[S1] 4,5-diethoxy-1,3-bis(2,6-dimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride **(1b)**,[S1] 1,3-bis[2,6-di(propan-2-yl)phenyl]-4,5-diethoxy-4,5-dihydro-1*H*-imidazol-3-ium chloride **(1c)**,[S1] 4-(phenylsulfonyl)-1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium chloride **(3a)**,[S2] 4-[(4-methylphenyl)sulfonyl]-1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium chloride (**3b**),[S2] 1,3-bis(2,6-dimethylphenyl)-4-(phenylsulfonyl)-1*H*-imidazol-3-ium chloride (**3c**),[S2] 4-(butylsulfonyl)-1,3-bis(2,6-dimethylphenyl)-1*H*-imidazol-3-ium chloride (**3d**),[S2] 1,3-bis[2,6-di(propan-2-yl)phenyl]-4-[(4-methylphenyl)sulfonyl]-1*H*-imidazol-3-ium chloride (**3e**)[S2] were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

S2. Extended experimental data

Table S1. Effect of reaction conditions on the yield of **2a** complex.[a]



1a Ni(Cp)$_2$ **2a**

Entry	Solvent	T, °C	Time, h	Yield of **2a**, %
1	THF	25	16	0
2	THF	60	2	0
3	THF	60	16	0
4	Toluene	60	2	0
5	Toluene	60	16	0
6	Toluene	100	16	0
7	Dioxane	60	2	0
8	Dioxane	60	20	0
9	Dioxane	100	1	0
10	Dioxane	100	20	0
11	CH_2Cl_2	40	5	0
12	CH_3CN	60	5	0
13	Acetone	40	5	0
14	DMA	60	4	0
15	NMP	60	4	0
16	DME	60	4	0

[a] Reaction conditions: **1a** (0.105 mmol), $NiCp_2$ (0.1 mmol), solvent (1 mL), 25-100 °C, 1-20 h.

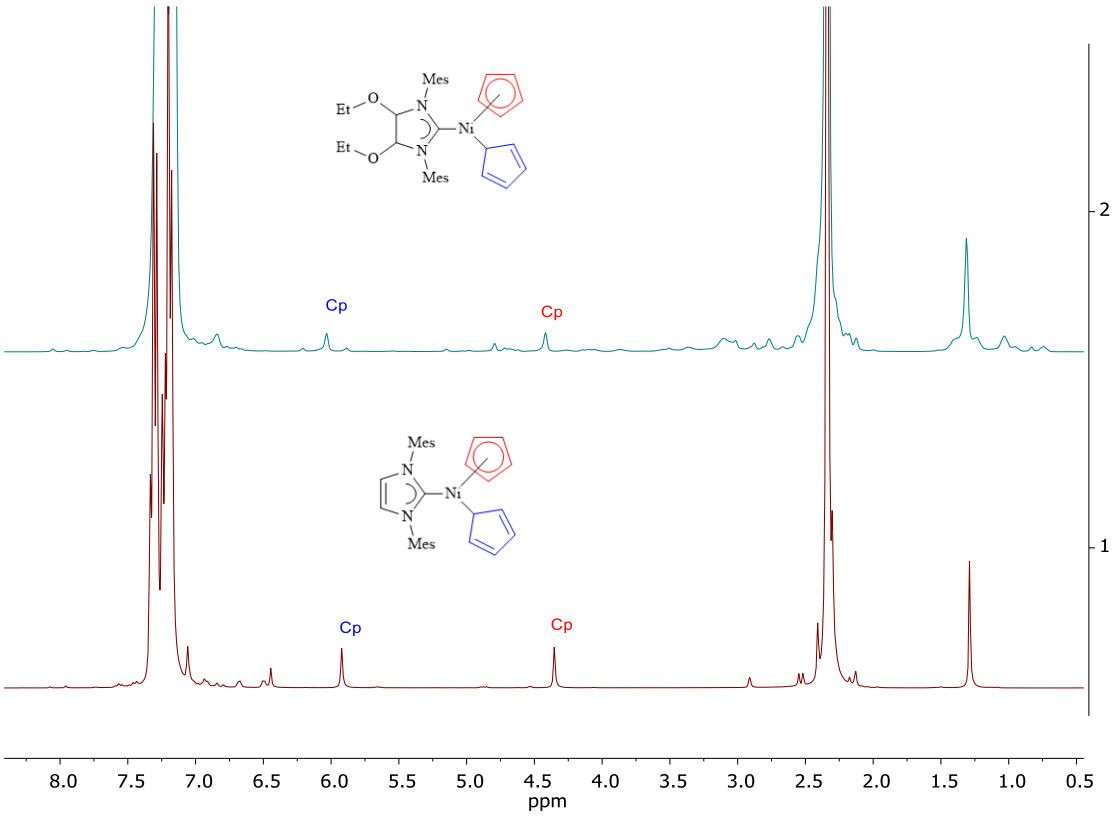
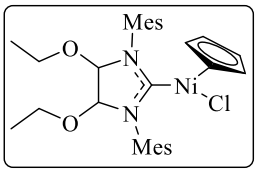


Figure S1. Observing the formation of (NHC)NiCp$_2$ complexes in toluene after 16 h at 25 ºC.

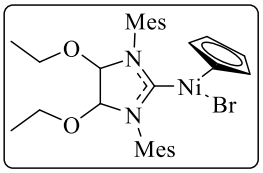
S3. Experimental procedures and characterization of synthesized compounds

Synthesis of (NHC)NiCpX complexes.

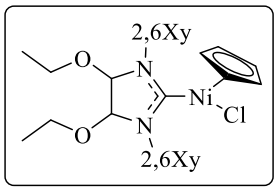
A mixture of azolium salt **1a-c** or **3a-e** (0.25 mmol), $NiCp_2$ (49 mg, 0.26 mmol) and *t*BuOK (29 mg, 0.26 mmol) in 1,4-dioxane (1 mL) was stirred at 25 °C for 8 h. Then 1M solution of HX (X = Cl or Br) in 1,4-dioxane (280 mkl, 0.28 mmol HCl or HBr) was added to the reaction mixture and the resulting solution was stirred for 5 min. The solvent was then evaporated to dryness by rotary evaporator in vacuo to give the crude product, which was dissolved in CH_2Cl_2 (1 mL) and purified by column chromatography using silica gel and CH_2Cl_2 as eluent.



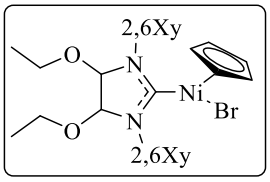
Chloro(η^5-cyclopentadienyl)[4,5-diethoxy-1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]nickel (2a) Yield 108, mg (78%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (t, *J* = 7.0 Hz, 6H), 2.19 (s, 6H), 2.37 (s, 6H), 2.65 (s, 6H), 3.33-3.42 (m, 4H), 4.52 (s, 5H), 4.85 (s, 2H), 6.95 (s, 2H), 7.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.5, 18.6, 19.8, 21.3, 66.5, 93.0, 97.6, 129.3, 129.7, 135.8, 138.3, 207.0. ESI-MS(TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd for $C_{30}H_{39}N_2NiO_2^+$ 517,2360 Found 517,2367.

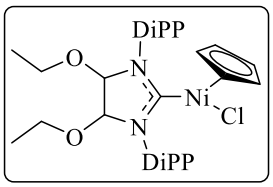


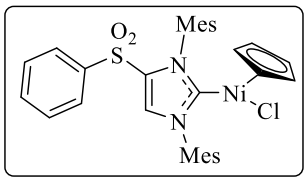
Bromo(η^5-cyclopentadienyl)[4,5-diethoxy-1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]nickel (2b). Yield 110 mg (74%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (t, *J* = 7.0 Hz, 6H), 2.20 (s, 6H), 2.37 (s, 6H), 2.66 (s, 6H), 3.29-3,45 (m, 4H), 4.58 (s, 5H), 4.83 (s, 2H), 6.94 (s, 2H), 7.10 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.5, 18.8, 20.2, 21.3, 66.4, 93.2, 97.5, 129.3, 129.7, 136.0, 138.3, 208.2. ESI-MS(TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd for $C_{30}H_{39}N_2NiO_2^+$ 517,2360 Found 517,2367.

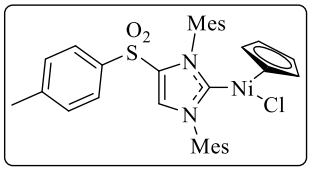


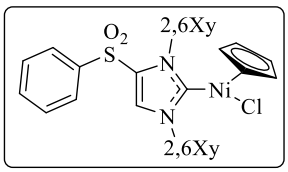
[1,3-Bis(2,6-dimethylphenyl)-4,5-diethoxyimidazolidin-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (2c) Yield 98 mg (75%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (t, *J* = 7.0 Hz, 6H), 2.25 (s, 6H), 2.72 (s, 6H), 3.32-3.44 (m, 4H), 4.50 (s, 5H), 4.91 (s, 2H), 7.13-7.16 (m, 2H), 7.27-7.32 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.5, 18.7, 20.0, 66.6, 93.0, 97.6, 128.6, 128.9, 129.0, 138.3, 207.1. ESI-MS(TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd for $C_{28}H_{35}N_2NiO_2^+$ 489,2047 Found 489,2059.

[1,3-Bis(2,6-dimethylphenyl)-4,5-diethoxyimidazolidin-2-ylidene](bromo)(η^5-cyclopentadienyl)nickel (2d)  Yield 99 mg (70%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (t, *J* = 7.0 Hz, 6H), 2.26 (s, 6H), 2.73 (s, 6H), 3.34-3.44 (m, 4H), 4.56 (s, 5H), 4.89 (s, 2H), 7.13-7.15 (m, 2H), 7.29-7.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.5, 18.8, 20.3, 66.5, 93.3, 97.6, 128.6, 128.8, 129.0, 138.4, 208.2. ESI-MS(TOF) *m/z*: [M-Cl]$^+$ Calcd for $C_{28}H_{35}N_2NiO_2^+$ 489,2047 Found 489,2041.

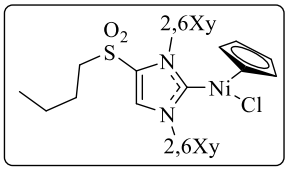
{1,3-Bis[2,6-di(propan-2-yl)phenyl]-4,5-diethoxyimidazolidin-2-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (2e)  Yield 121 mg (76%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13-1.22 (m, 12H), 1.29-1.35 (m, 12H), 1.73 (d, *J* = 7 Hz, 6H), 2.91 (hept, *J* = 6.7 Hz, 2H), 3.31-3.50 (m, 4H), 3.76 (hept, *J* = 6.7 Hz, 2H), 4.54 (s, 5H), 4.82 (s, 2H), 7.19-7.22 (m, 2H), 7.44-7.45 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 23.9, 25.1, 26.61, 26.64, 27.9, 28.8, 64.6, 93.8, 97.1, 124.4, 125.0, 129.4, 135.8, 146.9, 149.7, 209.1. ESI-MS(TOF) *m/z*: [M-Cl]$^+$ Calcd for $C_{36}H_{51}N_2NiO_2^+$ 601,3299 Found 601,3287.

Chloro(η^5-cyclopentadienyl)[4-(phenylsulfonyl)-1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene]nickel (4a)  Yield 108 mg (72%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.73 (s, 6H), 2.15 (s, 6H), 2.43 (s, 3H), 2.46 (s, 3H), 4.52 (s, 5H), 6.99 (br s, 2H), 7.11 (br s, 2H), 7.39-7.40 (m, 4H), 7.62-7.65 (m, 1H), 7.85 (br s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.3, 18.7, 21.4, 21.5, 92.8, 129.0, 129.3, 129.7, 131.2, 133.2, 134.5, 135.5, 135.8, 136.0, 137.6, 138.5, 140.0, 140.3, 179.6. ESI-MS(TOF) *m/z*: [M-Cl]$^+$ Calcd for $C_{32}H_{33}N_2NiO_2S^+$ 567,1611 Found 567,1620.

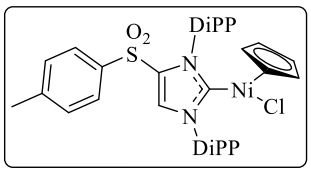
Chloro(η^5-cyclopentadienyl){4-[(4-methylphenyl)sulfonyl]-1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene}nickel (4e)  Yield 122 mg (79%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.74 (s, 6H), 2.15 (s, 6H), 2.43-2.46 (m, 9H), 4.52(s, 5H), 7.00 (m, 2H), 7.11 (m, 2H), 7.18-7.21 (m, 2H), 7.26-7.29 (m, 2H), 7.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.4, 18.7, 21.4, 21.5, 21.9, 92.8, 129.0, 129.2, 129.6, 129.8, 131.0, 133.3, 135.4, 135.5, 135.8, 136.3, 137.6, 140.0, 140.2, 145.8, 179.2. ESI-MS(TOF) *m/z*: [M-Cl]$^+$ Calcd for $C_{33}H_{35}N_2NiO_2S^+$ 581,1767 Found 581,1772.

[1,3-Bis(2,6-dimethylphenyl)-4-(phenylsulfonyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (4b)  Yield 93 mg (65%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.78 (s, 6H), 2.21 (s, 6H), 4.50 (s, 5H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.30-7.33 (m, 2H),

7.35-7.47 (m, 6H), 7.61-7.67 (m, 1H), 7.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.4, 18.8, 92.8, 128.6, 128.98, 129.02, 129.3, 130.2, 130.5, 131.1, 134.6, 135.6, 135.9, 136.0, 136.3, 138.1, 138.3, 138.6, 179.6. ESI-MS(TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd for $C_{30}H_{29}N_2NiO_2S^+$ 539,1298 Found 539,1288.



{4-(Butylsulfonyl)-1,3-bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (4c) Yield 94 mg (68%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, *J* = 7.3 Hz, 3H), 1.35-1.42 (m, 2H), 1.62-1.72 (m, 2H), 2.22(s, 6H), 2.28 (s, 6H), 2.84-2.90 (m, 2H), 4.56 (s, 5H), 7.31-7.37 (m, 4H), 7.42-7.52 (m, 2H), 7.77 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 13.6, 18.9, 19.2, 21.5, 24.5, 54.9, 92.9, 129.01, 129.05, 130.3, 130.7, 132.6, 133.8, 135.9, 137.4, 138.1, 180.4. ESI-MS(TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd for $C_{28}H_{33}N_2NiO_2S^+$ 519,1611 Found 519,1617.



{1,3-Bis[2,6-di(propan-2-yl)phenyl]-4-[(4-methylphenyl)sulfonyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (4d) Yield 133 mg (76%), pink crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.93 (d, *J* = 6.8 Hz, 6H), 1.18 (d, *J* = 6.7 Hz, 6H), 1.40-1.46 (m, 12H), 2.42(s, 3H), 2.66-2.80 (m, 4H), 4.52 (s, 5H), 7.28-7.31 (m, 2H), 7.36-7.38 (m, 2H), 7.42-7.47 (m, 3H), 7.51-7.56 (m, 1H), 7.61-7.66 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.7, 22.5, 24.8, 25.1, 26.1, 28.9, 29.1, 93.0, 124.3, 124.8, 127.4, 130.2, 130.8, 130.9, 133.5, 134.4, 135.5, 136.1, 138.3, 145.6, 145.7, 147.3, 182.1. ESI-MS(TOF) *m/z*: $[M\text{-}Cl]^+$ Calcd for $C_{39}H_{47}N_2NiO_2S^+$ 665,2706 Found 665,2715.

S4. X-Ray structure determination

X-ray crystallographic data and refinement details for 2a

X-ray diffraction data for **2a** were collected at 170K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (shutterless φ- and ω-scan technique), using graphite-monochromatized Mo K_α-radiation. The intensity data were integrated by the SAINT program[S3] and semi-empirically corrected for absorption and decay with SADABS.[S4] The structure was solved by direct methods using SHELXT[S5] and refined by full-matrix least-squares on F^2 using SHELXL-2018.[S6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.950 Å for aromatic, 0.980 Å for methyl, 0.990 Å for methylene and 1.000 Å for cyclopentadienyl and tertiary hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters (taken as U_{iso}(H)=1.5U_{eq}(C) for methyl groups and U_{iso}(H)=1.2U_{eq}(C) otherwise). A rotating group model was applied for methyl groups. The SHELXTL program suite[S3] was used for molecular graphics. The disordered mesityl fragment was modeled by applying similarity constraints on anisotropic displacement parameters on similar atoms and by constraining similar distances to be equal within the deviation of 0.003Å.

Crystal data, data collection and structure refinement details for **2a** are summarized in Table S2. The structure has been deposited at the Cambridge Crystallographic Data Center with the reference CCDC number 2402209; it also contains the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/data_request/cif

Table S2. Crystal data, data collection and structure refinement details for **2a**

Identification code	**2a**
Empirical formula	$C_{30}H_{39}ClN_2NiO_2$
Formula weight	553.79
Temperature, K	100(2)
Wavelength, Å	0.71073
Crystal system	Tetragonal
Space group	$P4_32_12$
Unit cell dimensions	
a, Å	12.9909(3)
b, Å	12.9909(3)
c, Å	33.7830(12)
Volume, $Å^3$	5701.3(3)
Z	8
Calculated density, g/cm^3	1.290
Absorption coefficient, mm^{-1}	0.803
F(000)	2352
Crystal size, mm	0.852 × 0.390 × 0.350
θ range for data collection, °	2.298 ÷ 34.348°.
Index ranges	$-20 \le h \le 20$,
	$-20 \le k \le 20$,
	$-53 \le l \le 53$
Reflections	
Collected	140494
Independent [R_{int}]	11954 [0.0522]
Observed (with I>2σ(I))	10761
Completeness to θ_{full} / θ_{max},°	0.999 / 0.999
Transmission max. / min.	0.4963 / 0.4229
Data / restraints / parameters	11954 / 45 / 361
Goodness-of-fit on F^2	1.066
Final R1 / wR2 indices with I>2σ(I)	0.0310 / 0.0732
Final R1 / wR2 indices (all data)	0.0390 / 0.0774
Absolute structure parameter	-0.006(3)
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, $\bar{e}\cdot Å^3$	0.762 and -0.396
CCDC number	2402209

The X-ray structure of 2a

Compound **2a** crystalizes in a chiral space group ($P4_32_12$). Ethoxy groups are in the *trans* position.

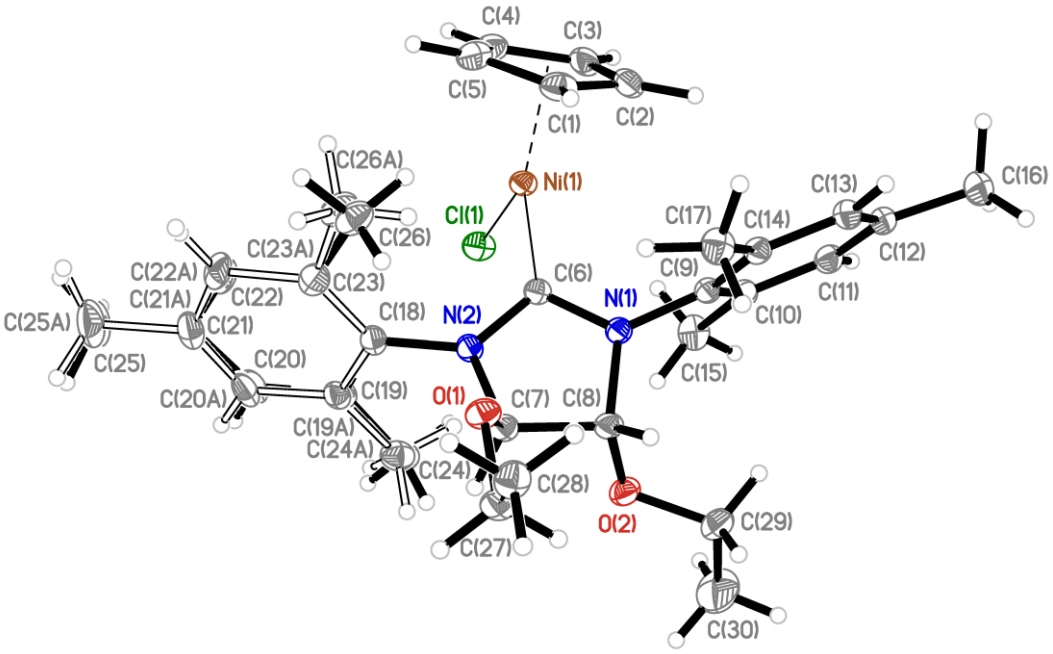


Figure S2. The crystal structure of **2a**. The thermal displacement ellipsoids for non-hydrogen atoms are set to a 50% probability level. One mesityl fragment (atoms C19...C26) is disordered over two positions with the disorder ratio of 0.70(2) : 0.30(2). The minor component of the disorder is shown with open solid lines.

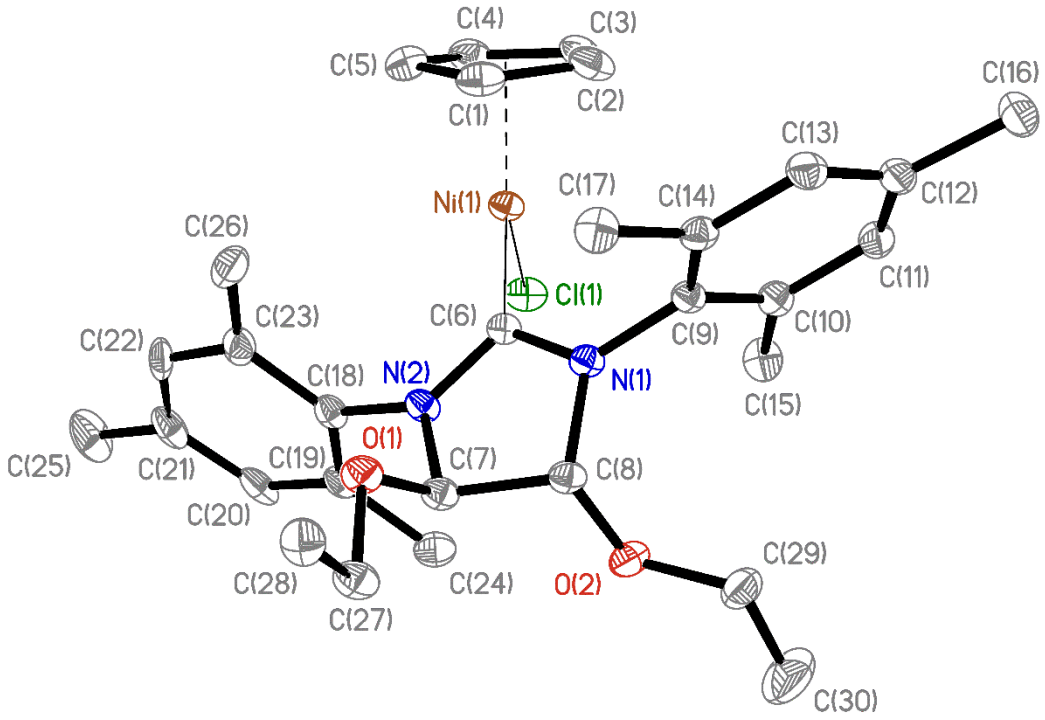


Figure S3. The crystal structure of **2a**. The disorder and hydrogen atoms are omitted for clarity (p=50%).

S5. ^{1}H and ^{13}C NMR spectra

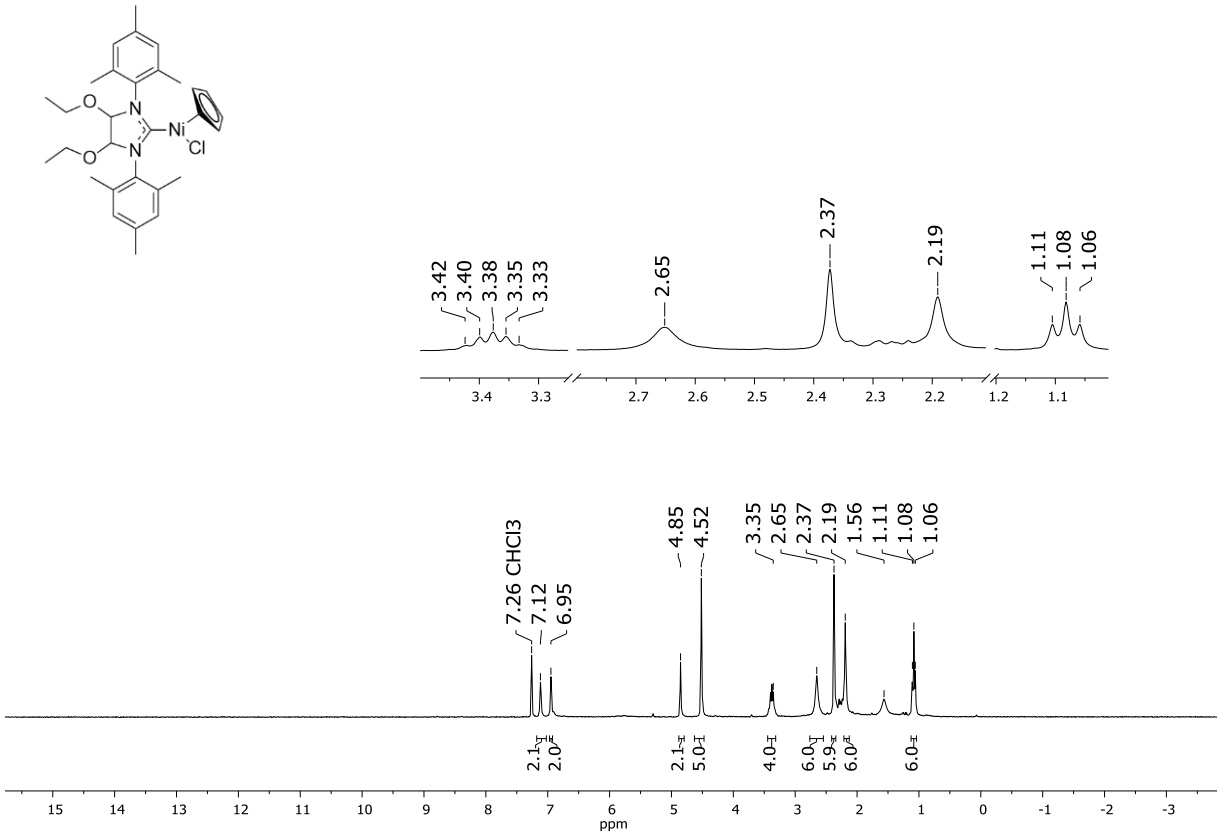


Figure S4. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 300 MHz).

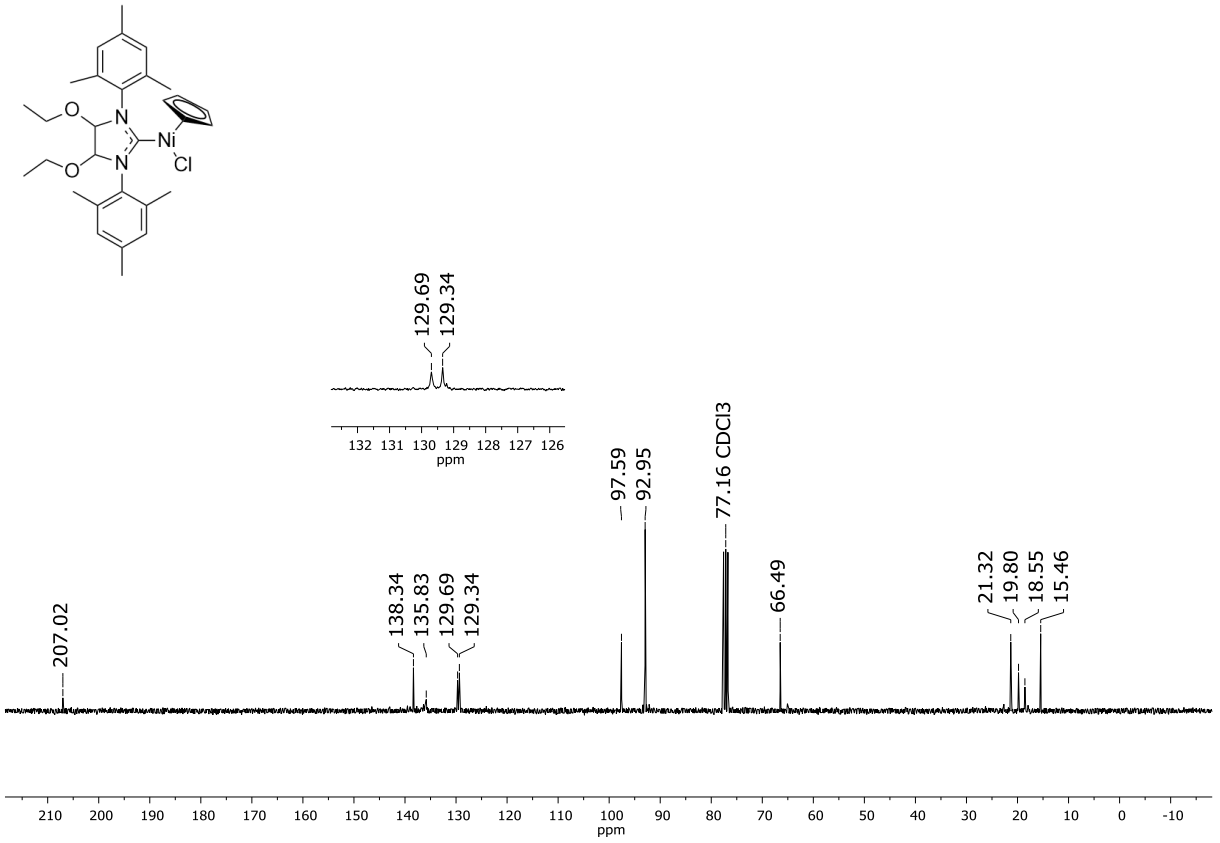


Figure S5. ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 75 MHz).

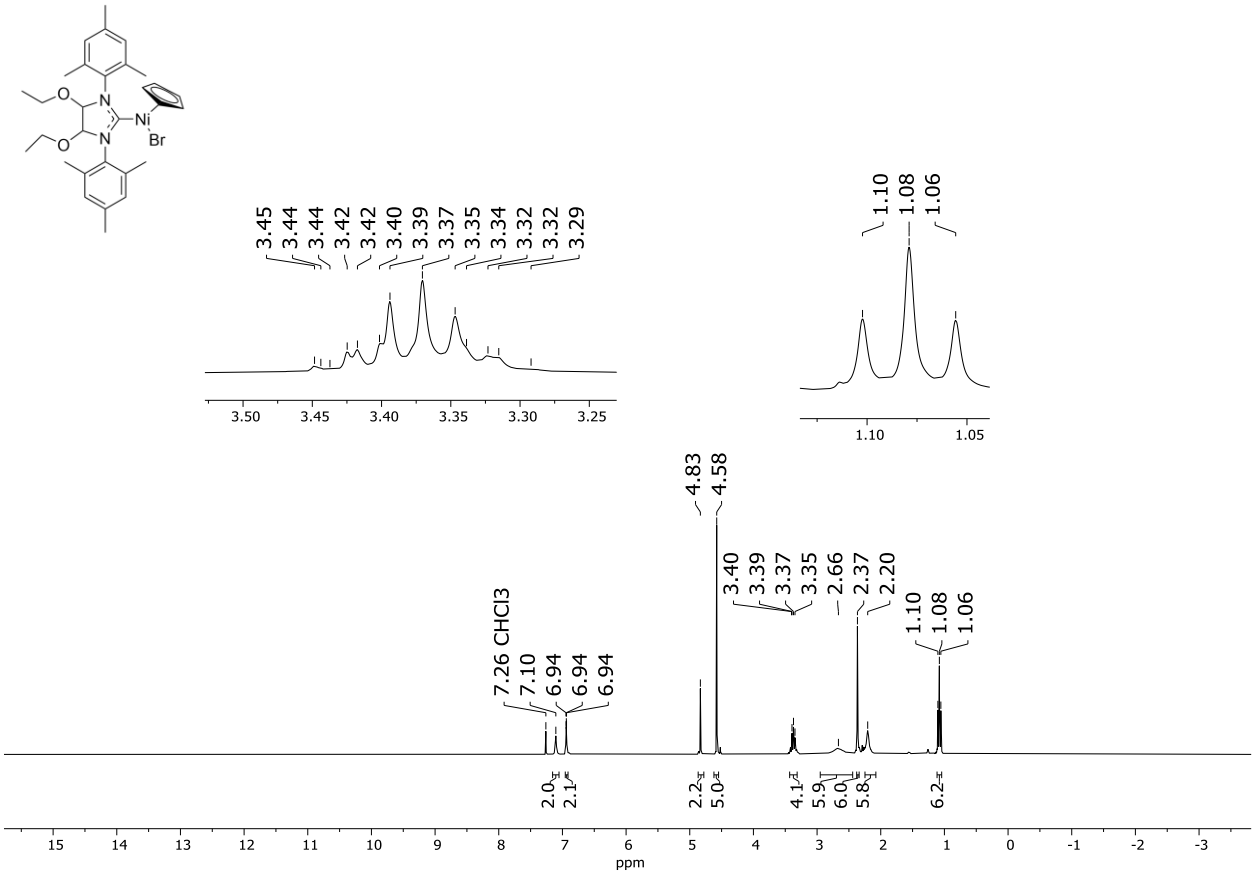


Figure S6. ^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 300 MHz).

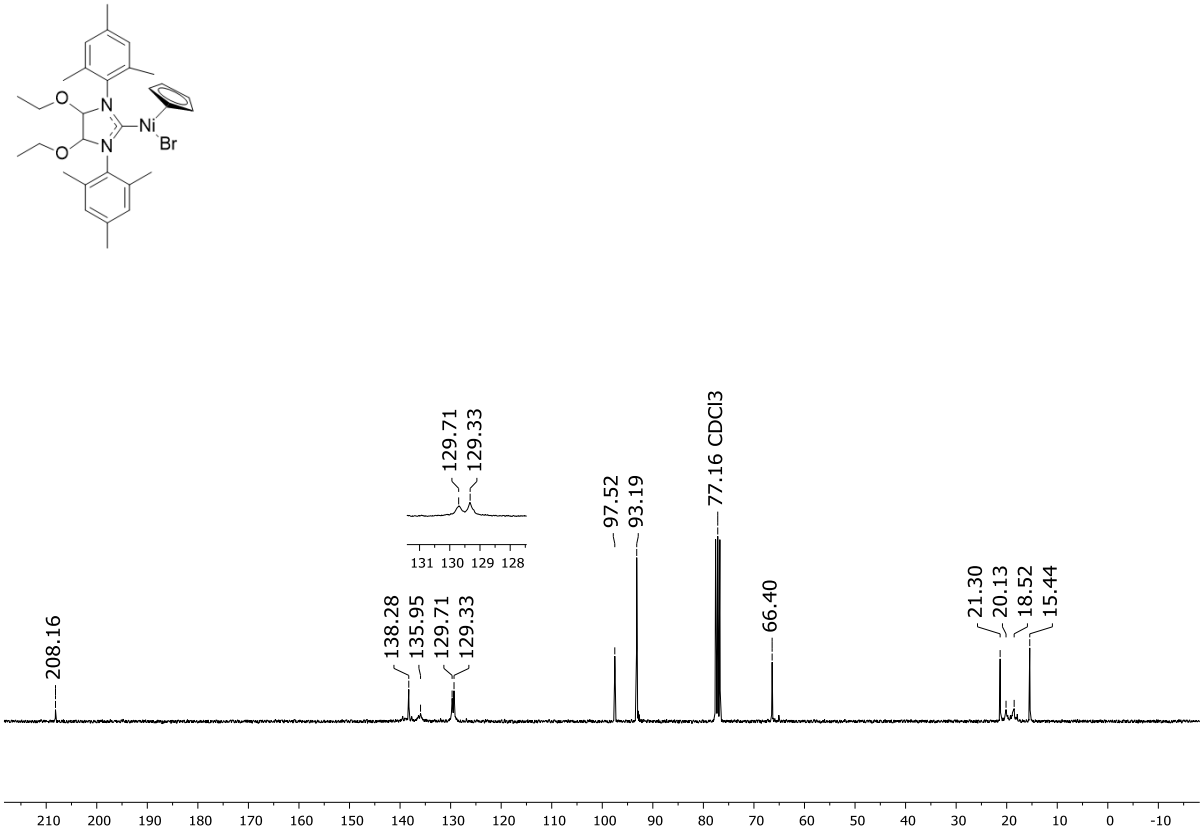


Figure S7. ^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 75 MHz).

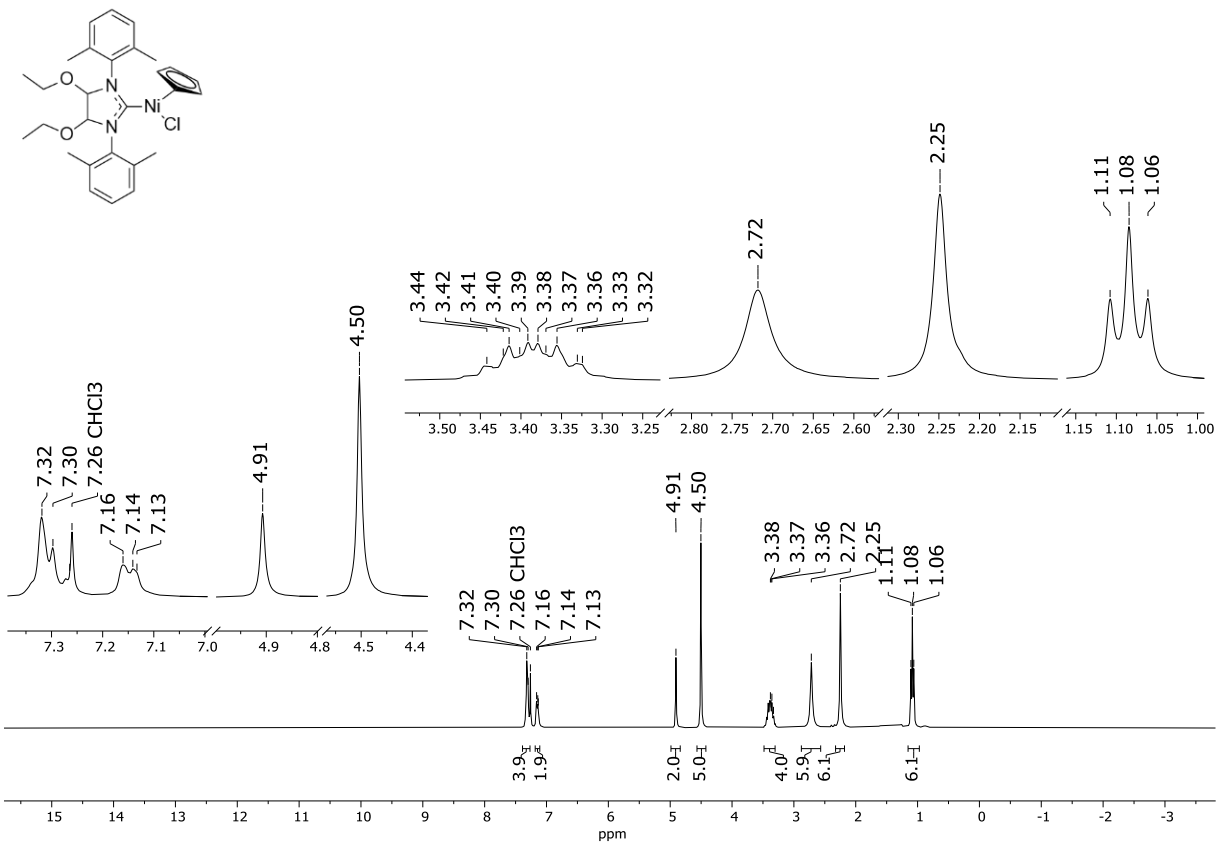


Figure S8. ^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 300 MHz).

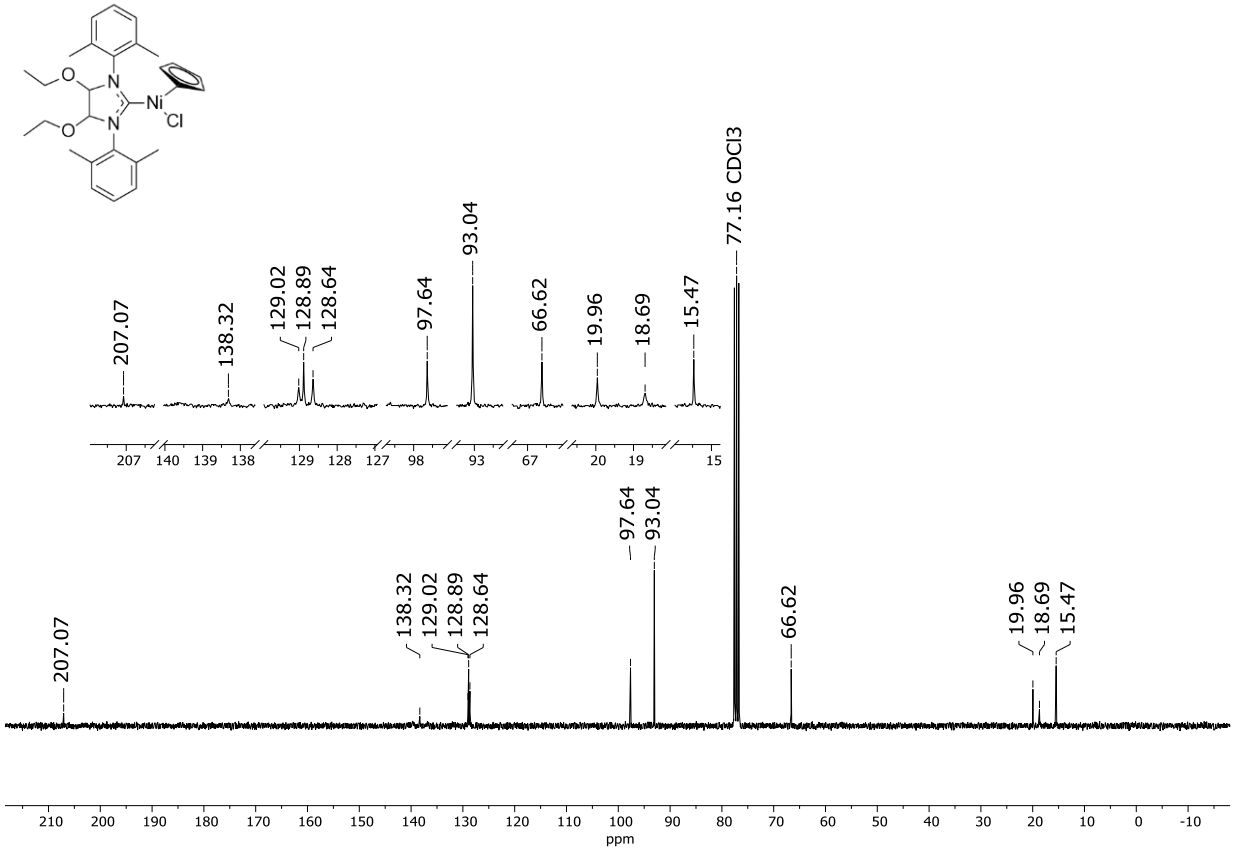


Figure S9. ^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 75 MHz).

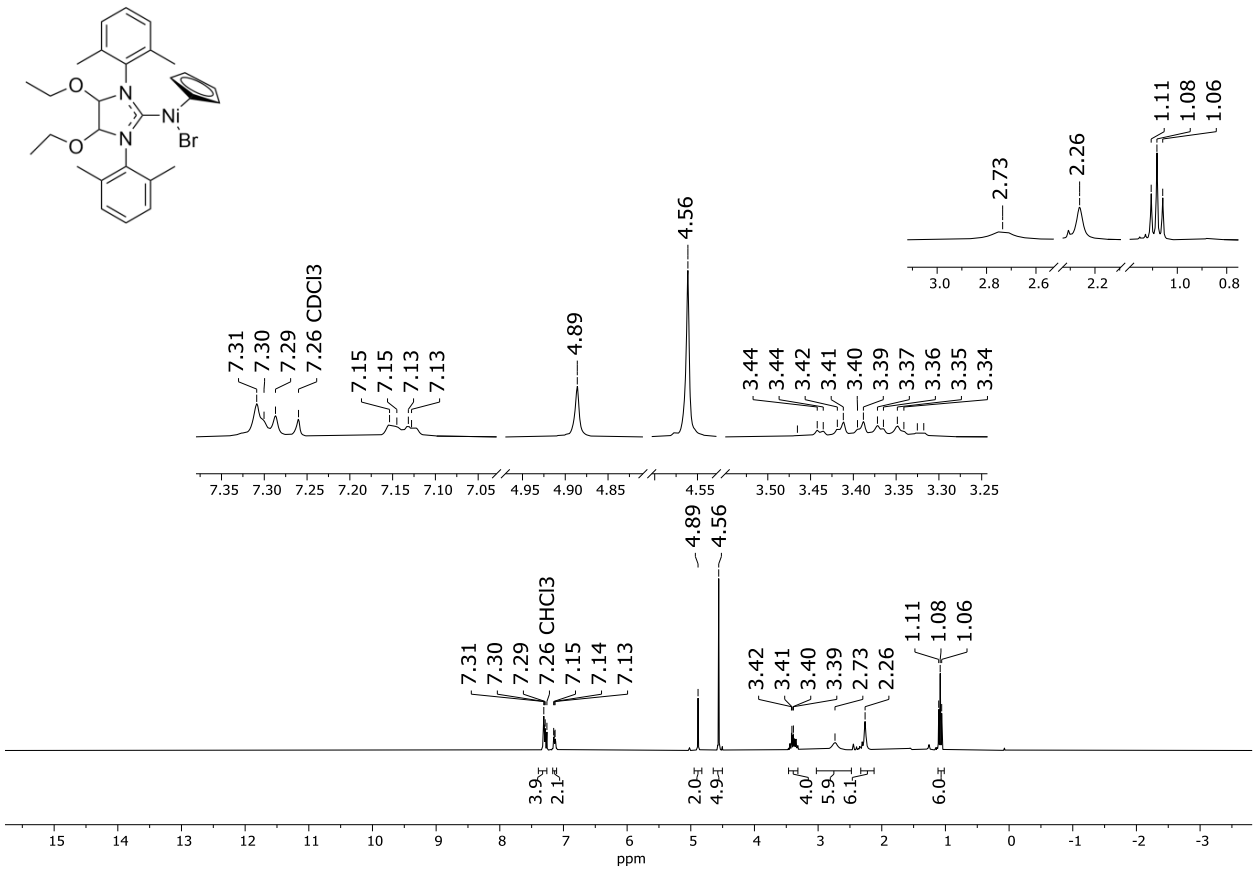


Figure S10. ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 300 MHz).

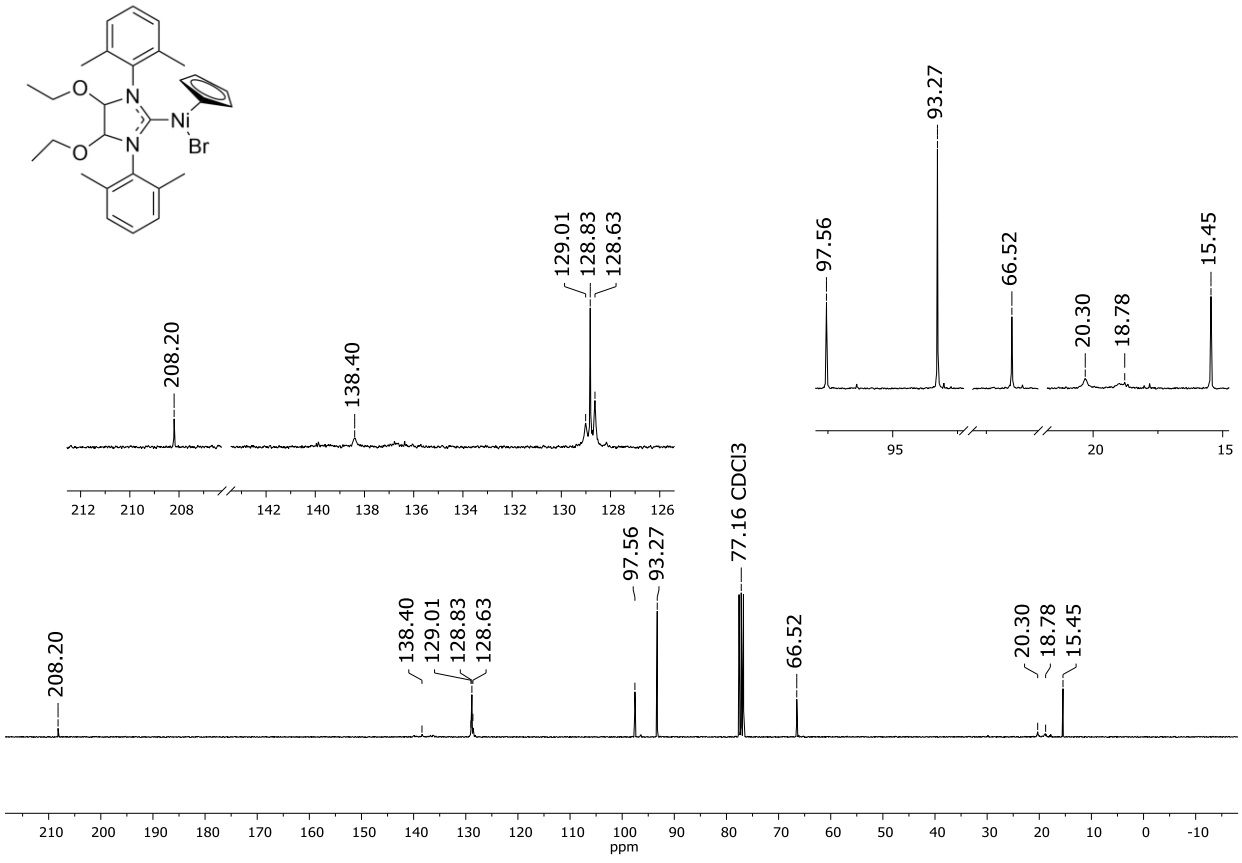


Figure S11. ^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 75 MHz).

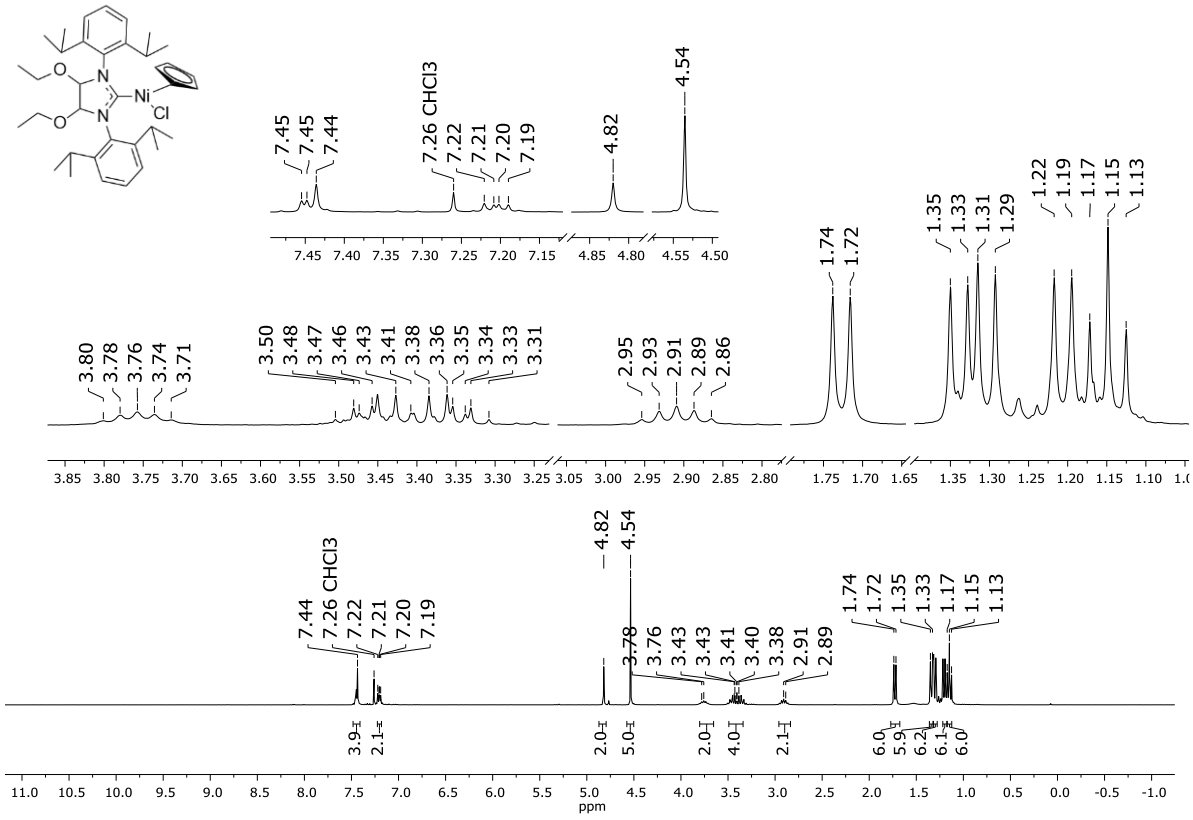


Figure S12. ^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 300 MHz).

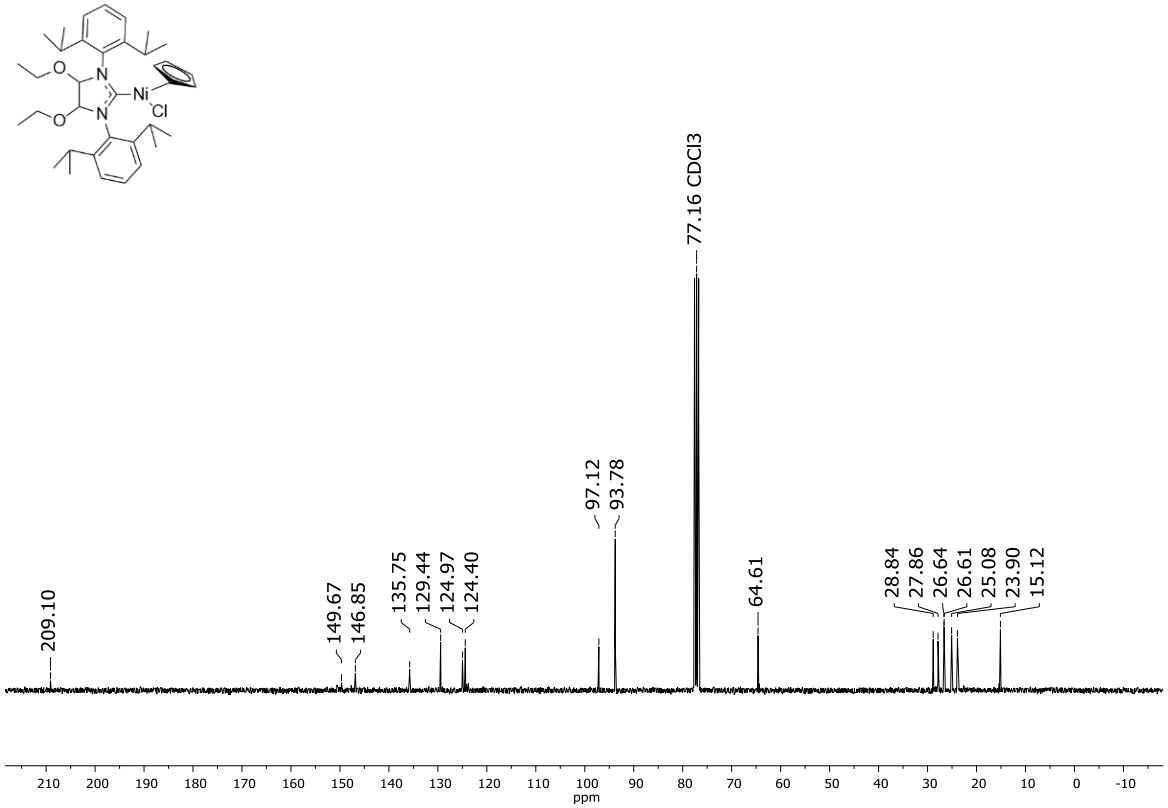


Figure S13. ^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 75 MHz).

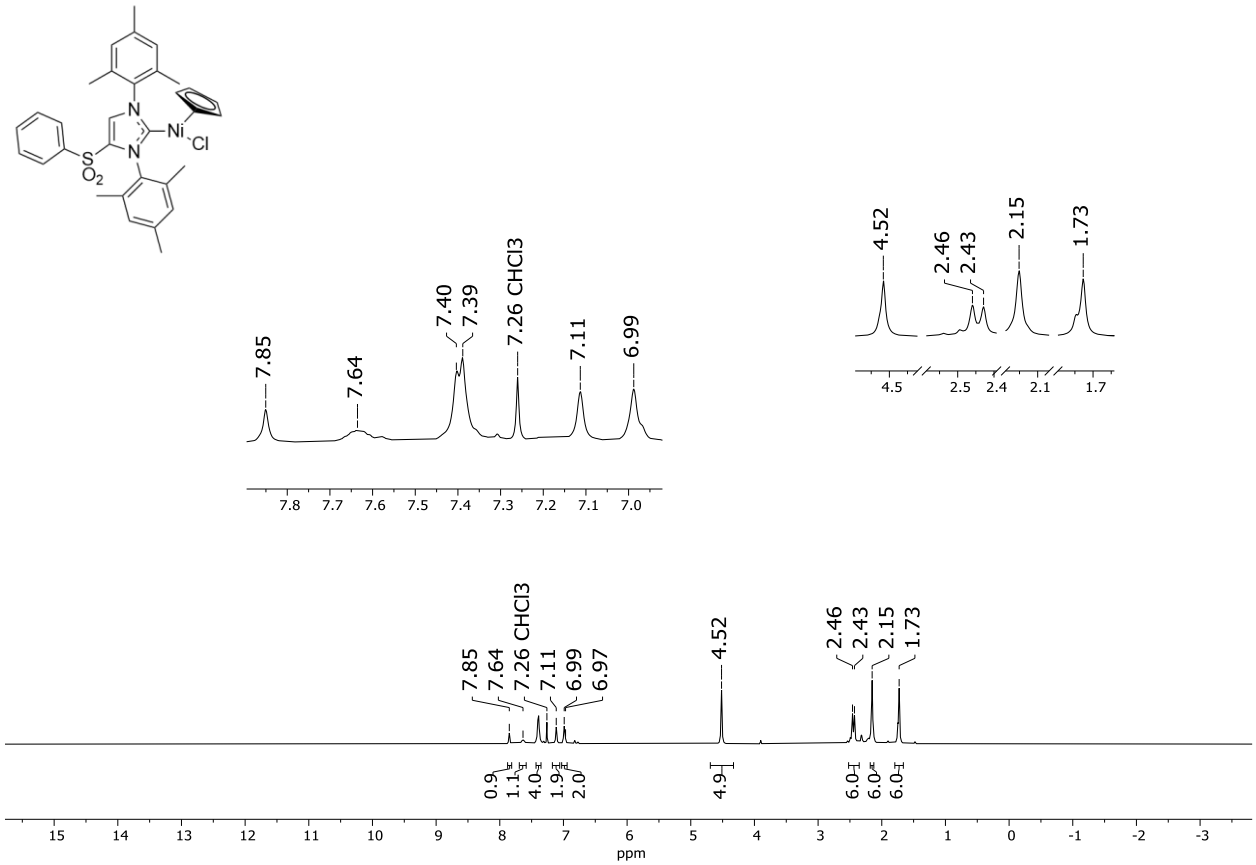


Figure S14. ^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 300 MHz).

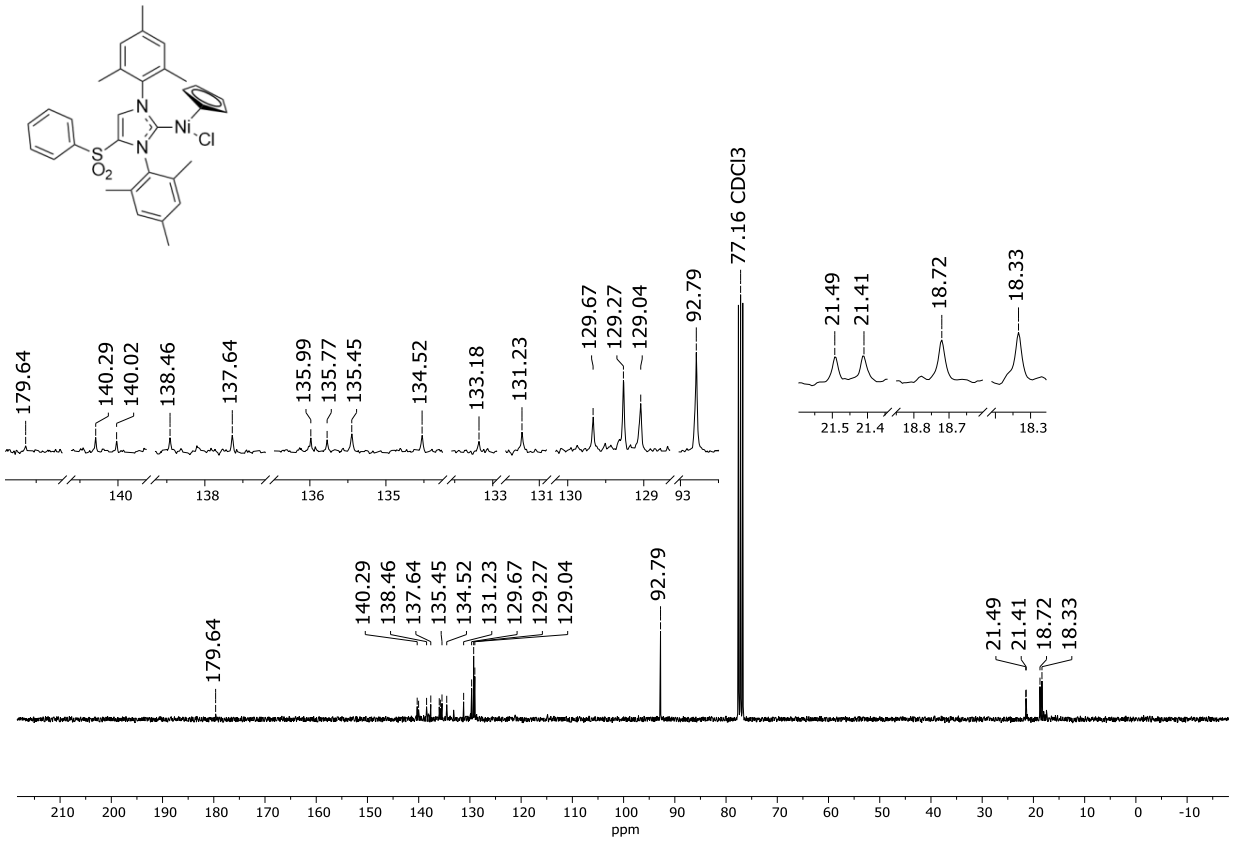


Figure S15. ^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 75 MHz).

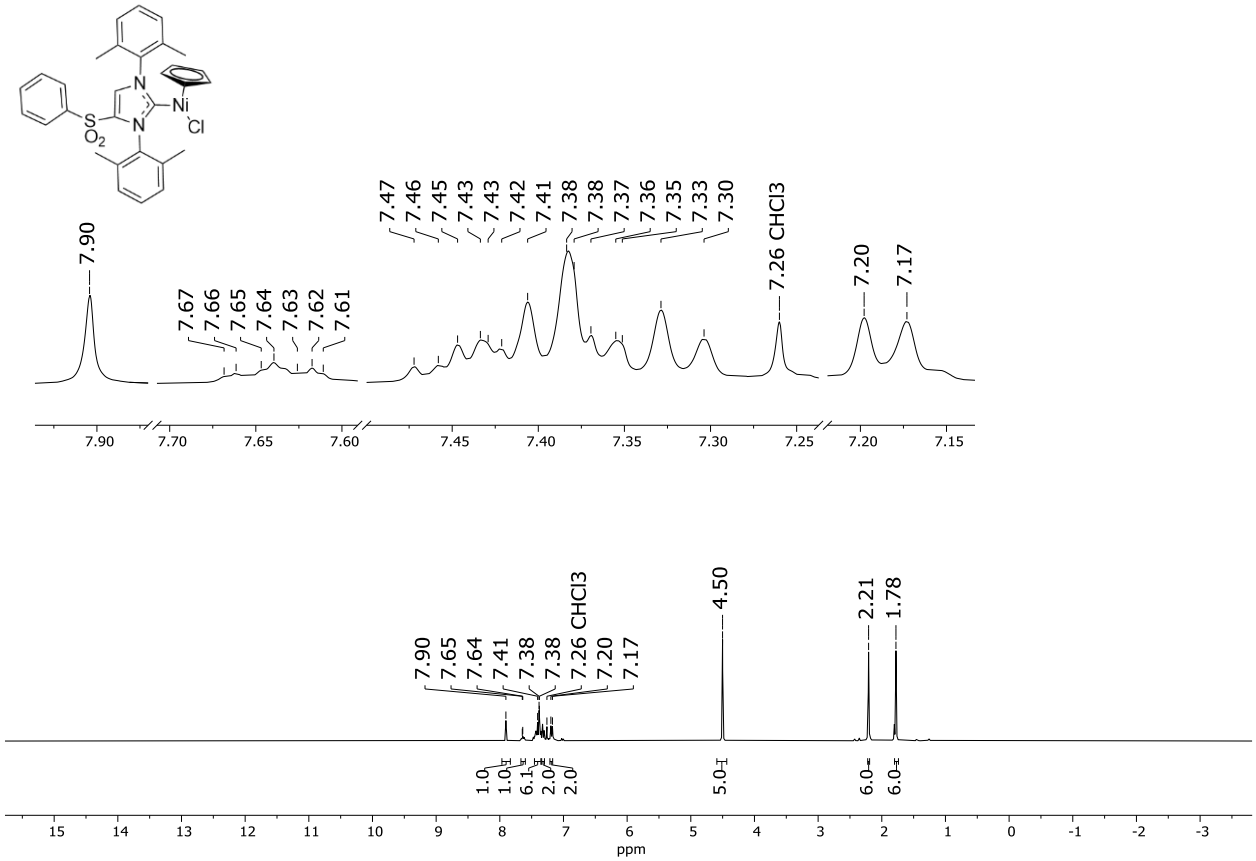


Figure S16. ^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 300 MHz).

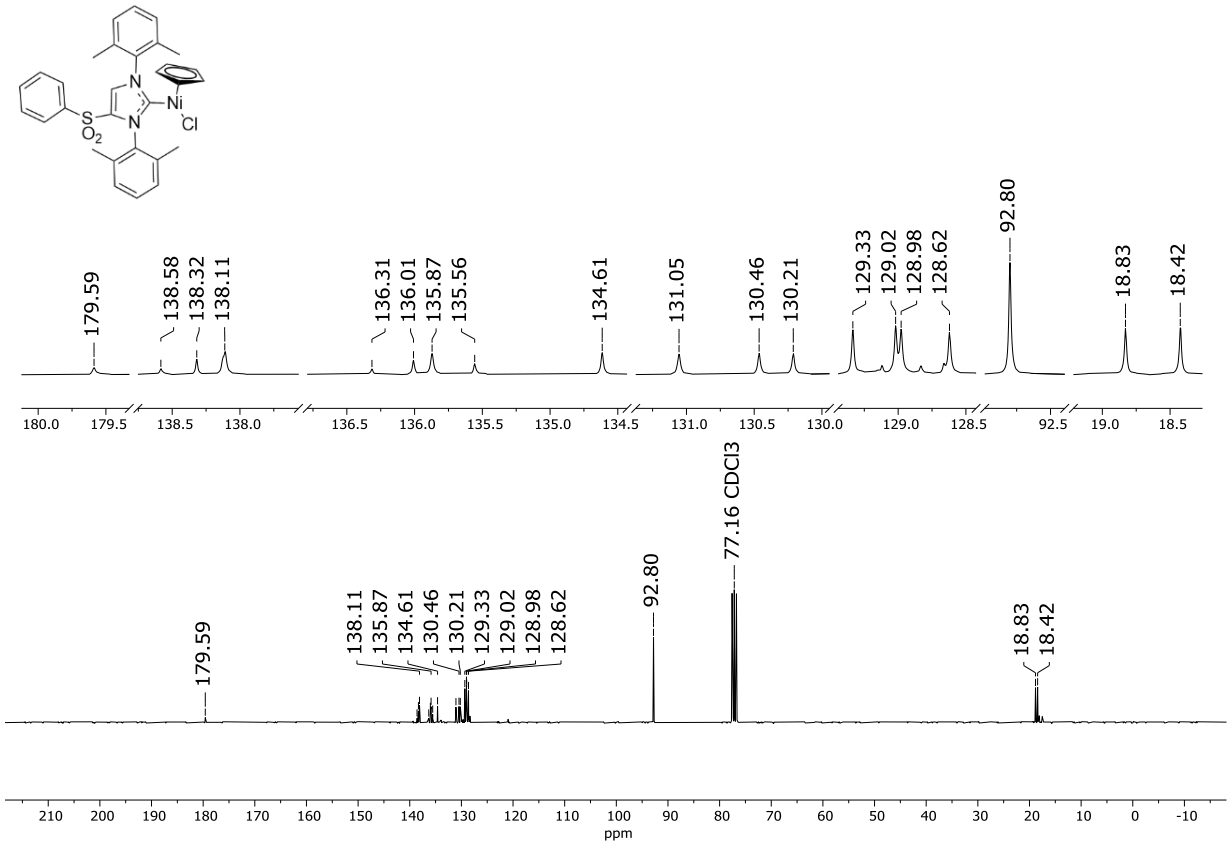


Figure S17. ^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 75 MHz).

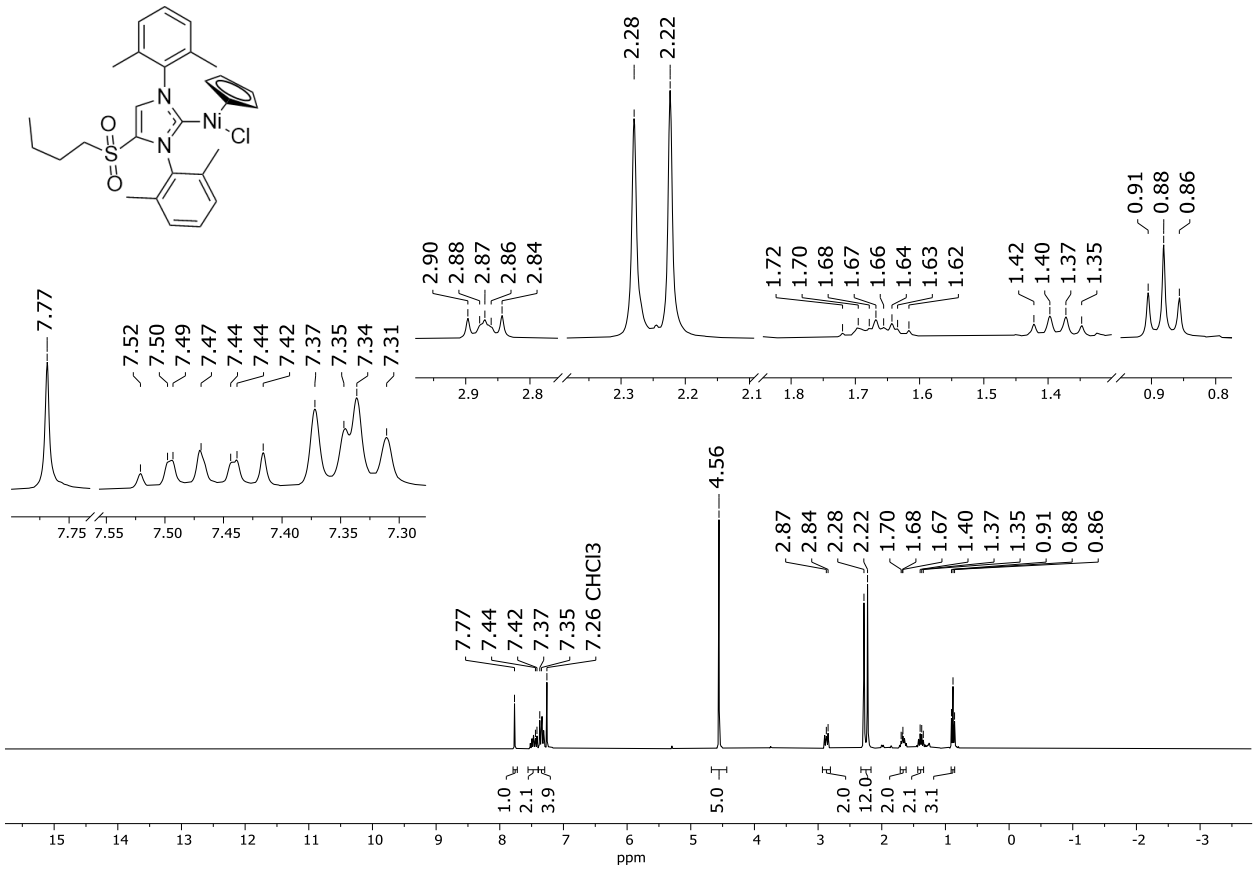


Figure S18. ^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 300 MHz).

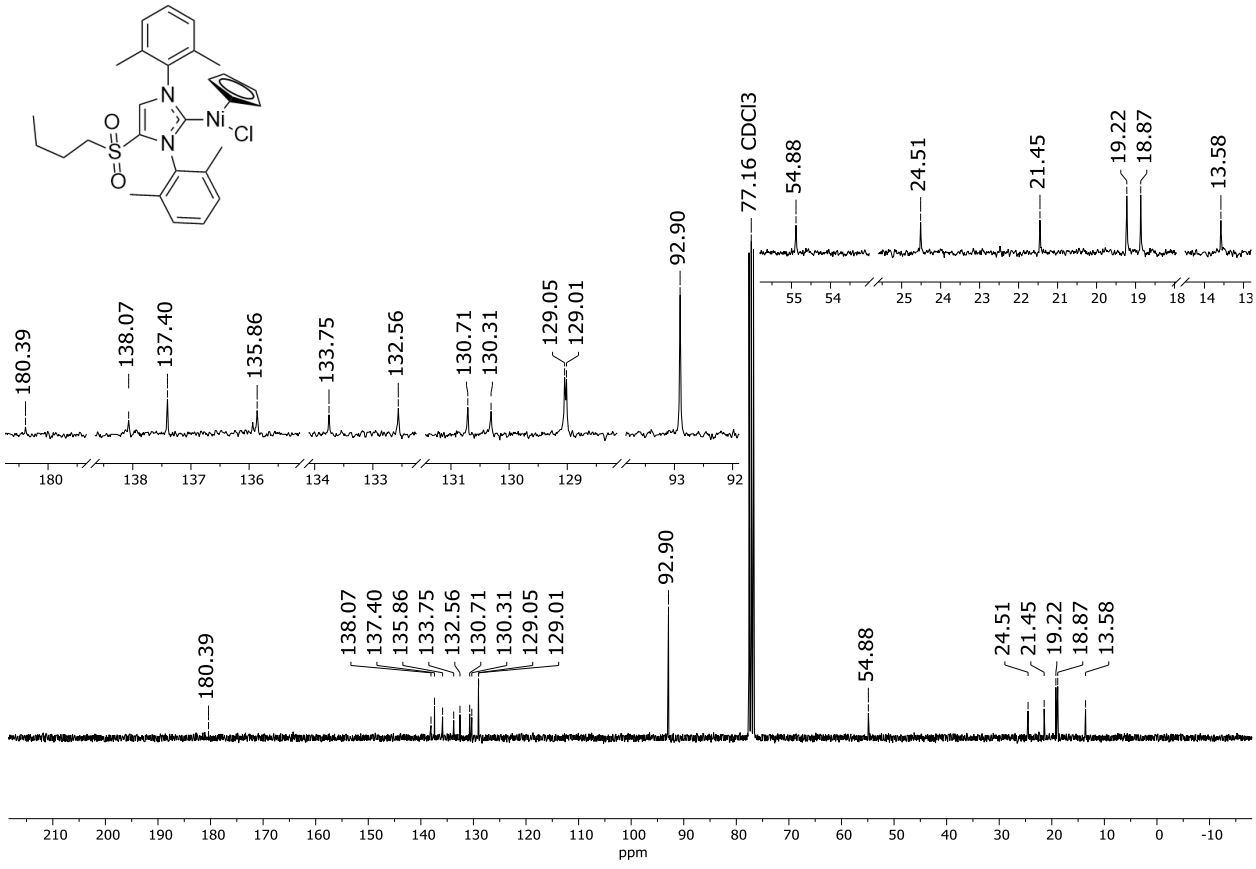


Figure S19. ^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 75 MHz).

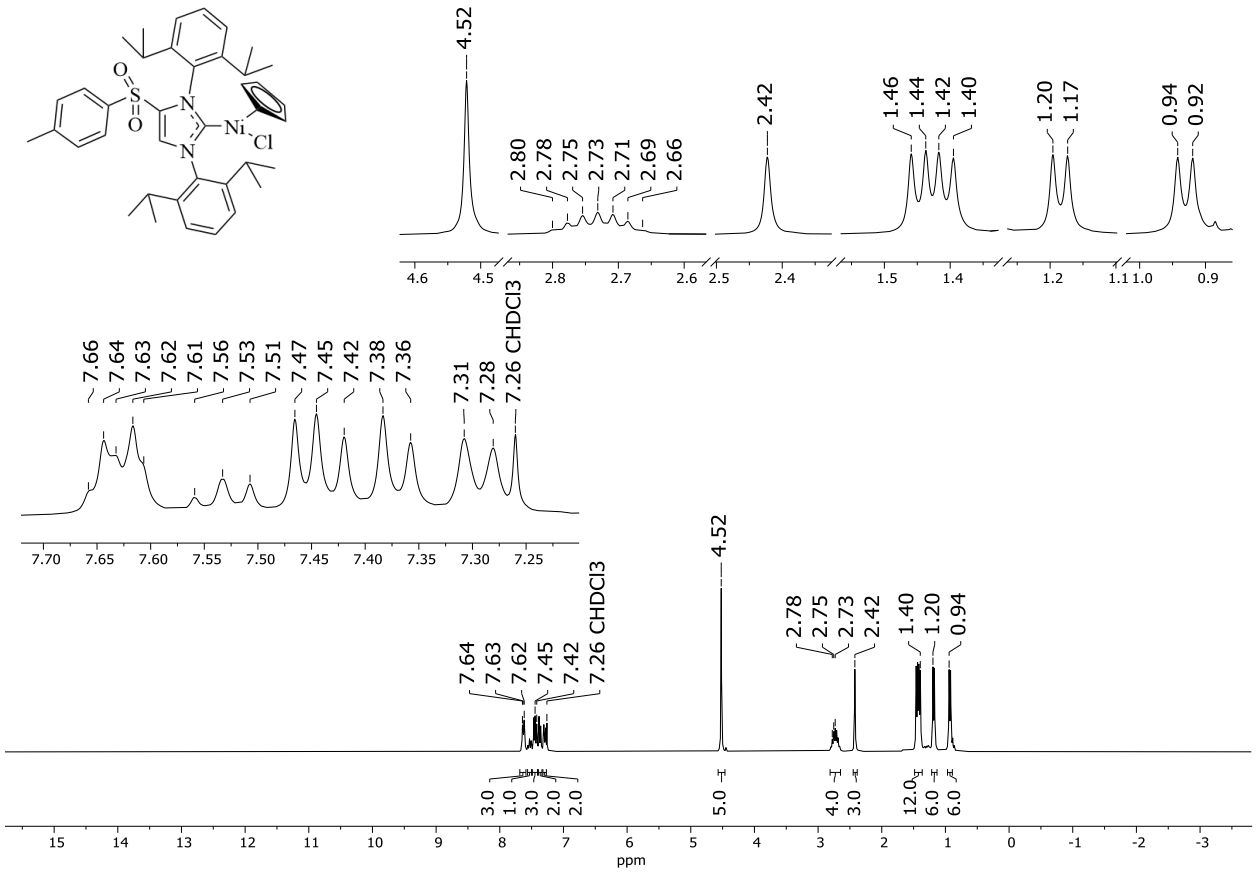


Figure S20. ^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 300 MHz).

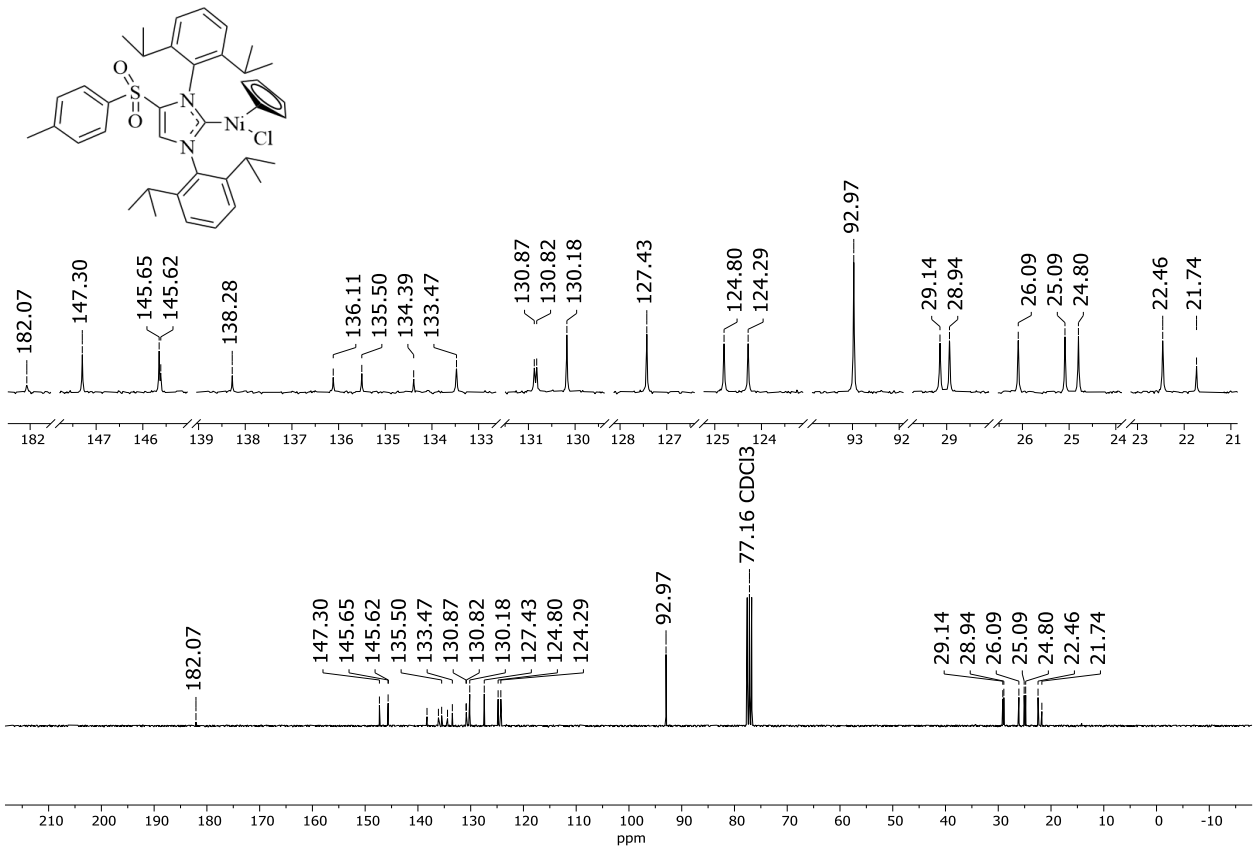


Figure S21. ^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 75 MHz).

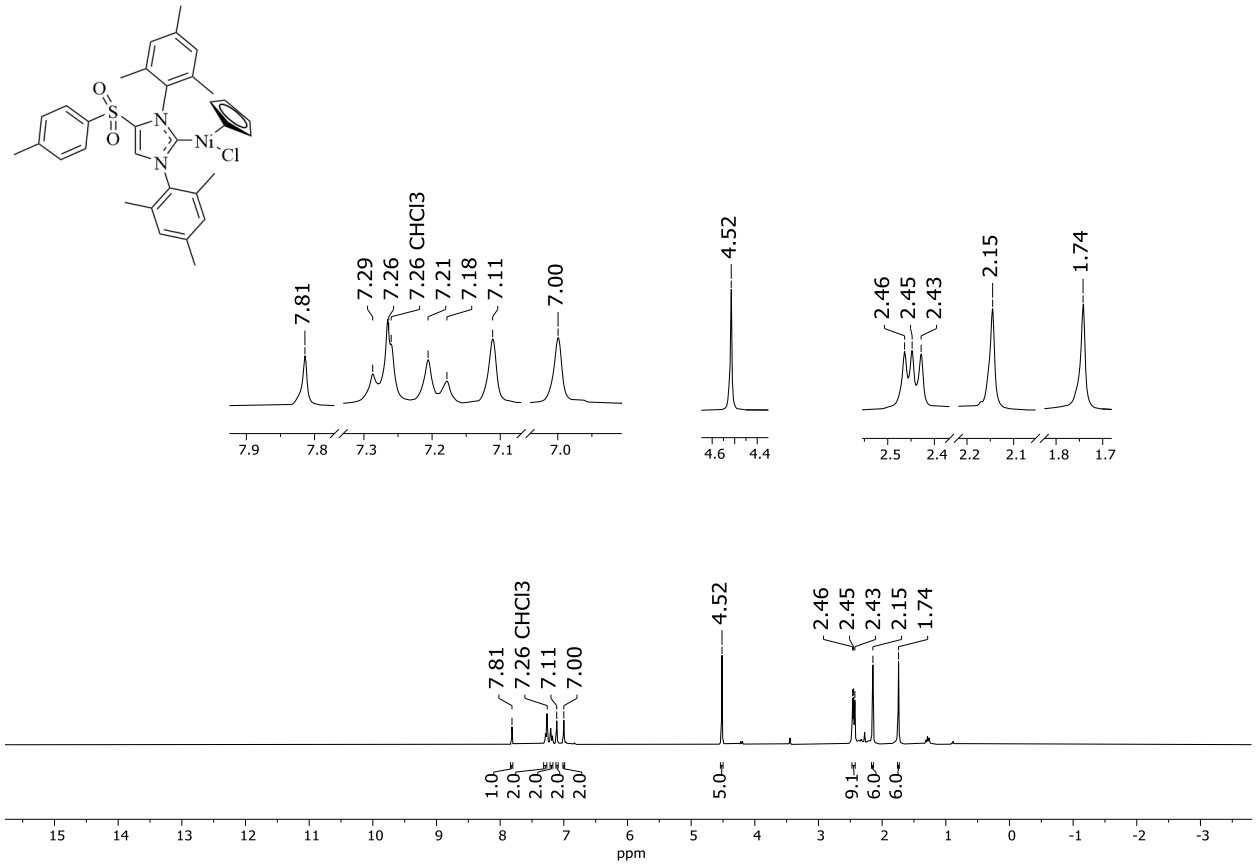


Figure S22. ^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 300 MHz).

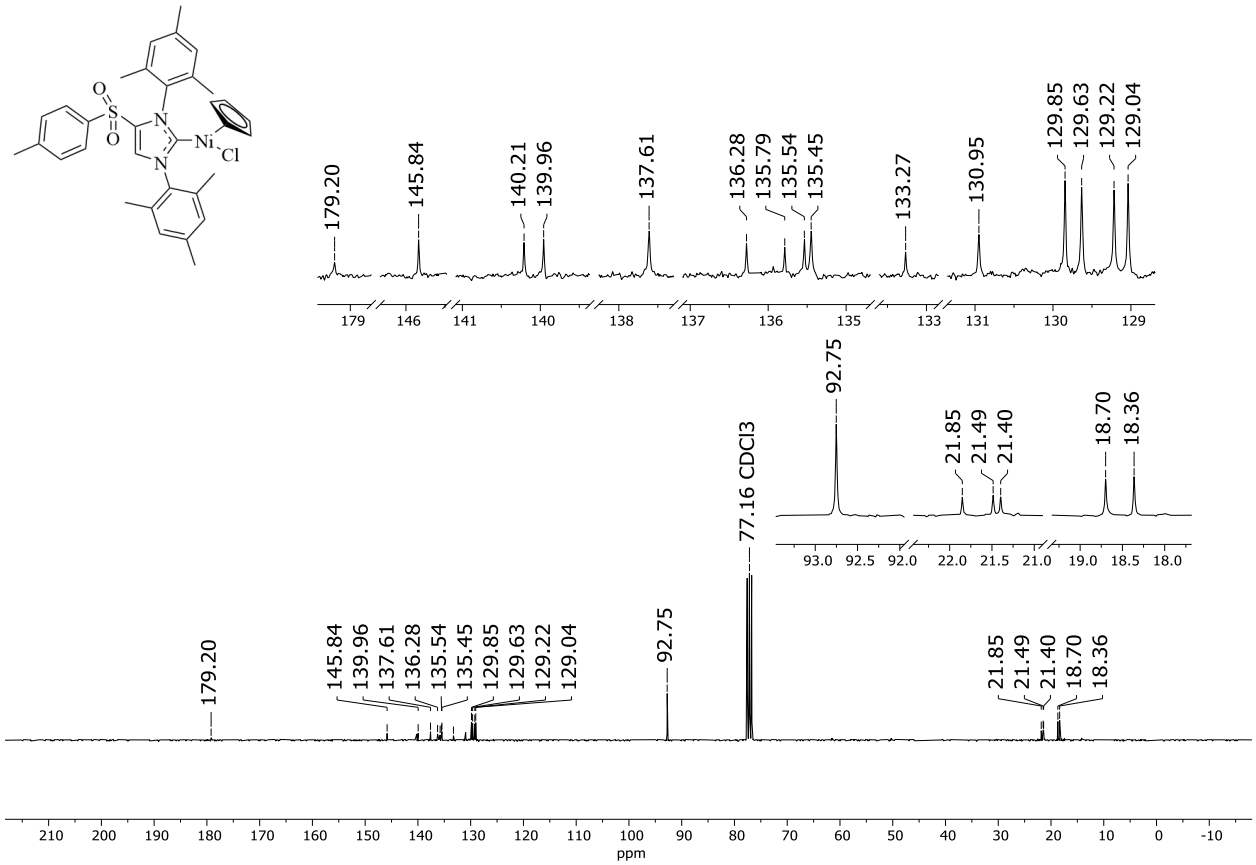


Figure S23. ^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 75 MHz).

S6. Literature references

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