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A novel mechanochemical synthesis of cyclopentadienyl-type Ni/NHC complexes

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S1. General information and materials

General Procedures. All manipulations were performed under open air. LAG solvents were purified and dried according to standard methods and stored over activated 3Å molecular sieves prior to use. The column chromatography was executed on silica gel 60 (0.04 – 0.063 mm, Macherey-Nagel).

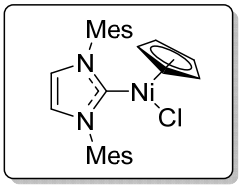
Instrumentation. ^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded on a Bruker Avance NEO 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent signals as internal standards: δ 7.26 for ^{1}H, δ 77.2 for ^{13}C. The milling treatments were carried out using a planetary ball mill Fritsch Pulverisette 7 *Classic Line* operated at room temperature with a zirconium oxide jar (12 and 45 mL) and zirconium oxide balls (Ø 5 mm and Ø 10 mm). Elemental analyses were performed using a Perkin Elmer 2400 elemental analyzer.

Materials. 1,3-Bis(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium chloride (**1a**),[S1] 1,3-bis(2,6-dimethylphenyl)-1*H*-imidazol-3-ium chloride (**1b**),[S1] 1,3-bis(2,4-dimethylphenyl)-1*H*-imidazol-3-ium chloride (**1c**),[S2] 1,3-bis[2,6-bis(propan-2-yl)phenyl]-1*H*-imidazol-3-ium chloride (**1d**),[S1] 1,3-bis(2,4,6-trimethylphenyl)-4-(phenylsulfanyl)-1*H*-imidazol-3-ium chloride (**1e**),[S3] 1,3-bis(2,4,6-trimethylphenyl)-4-[(4-methylphenyl)sulfanyl]-1*H*-imidazol-3-ium chloride (**1f**),[S3] 4-(butylsulfanyl)-1,3-bis(2,6-dimethylphenyl)-1*H*-imidazol-3-ium chloride (**1g**),[S3] 1,3-bis[2,6-di(propan-2-yl)phenyl]-4-(phenylsulfanyl)-1*H*-imidazol-3-ium chloride (**1h**),[S3] 1,3-bis[2,6-di(propan-2-yl)phenyl]-4-[(4-methylphenyl)sulfanyl]-1*H*-imidazol-3-ium chloride (**1i**),[S3] 4-(butylsulfanyl)-1,3-bis[2,6-di(propan-2-yl)phenyl]-1*H*-imidazol-3-ium chloride (**1j**),[S3] 1,3-bis(2,4,6-trimethylphenyl)-1*H*-benzimidazol-3-ium chloride (**1k**),[S4] 1,3-bis(4-methylphenyl)-1*H*-benzimidazol-3-ium chloride (**1l**),[S5] 7,9-bis(2,4,6-trimethylphenyl)-7*H*-acenaphtho[1,2-*d*]imidazol-9-ium chloride (**1m**),[S6] 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**1n**),[S7] 1,3-bis[2,6-di(propan-2-yl)phenyl]-4,5-dihydro-1*H*-imidazol-3-ium chloride (**1o**)[S7] were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

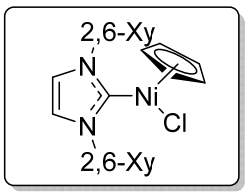
S2. Experimental procedures and characterization of synthesized compounds

Synthesis of Ni/NHC complexes 2a-o.

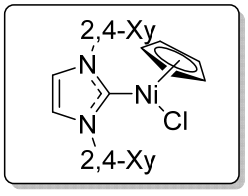
The azolium salts **1a-o** (0.5 mmol), $NiCp_2$ (103 mg, 0.55 mmol), and K_2CO_3 (138 mg, 1 mmol, 2 equiv.) were added to a 12 mL zirconium oxide vessel equipped with a 5 mm zirconium oxide balls (4 g). The jar was closed and mounted on the planetary ball-mill machine. The mixture of solids was ground for 60 min (for **2a-c,e-n**) or 90 min (for **2d,o**) at 650 rpm. Afterwards, the balls and the jar were washed with 2 × 2 mL CH_2Cl_2 and filtered through Celite. The combined filtrates were concentrated in vacuo and the crude residue was subjected to flash column chromatography to obtain the corresponding pure products.



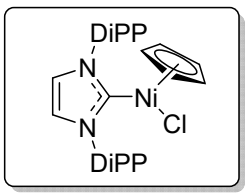
[1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](chloro) (η^5-cyclopentadienyl)nickel (2a). Yield 216 mg (93%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.17 (s, 12H), 2.44 (s, 6H), 4.56 (s, 5H), 7.08 (s, 2H), 7.11 (br s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.6, 21.4, 92.2, 124.6, 129.3, 136.0, 136.8, 139.2, 167.1. The spectral characteristics of the product obtained are similar to those described in the literature.[S8]



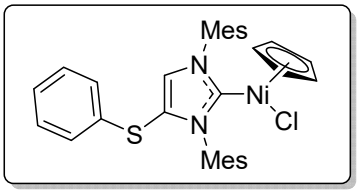
[1,3-Bis(2,6-dimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](chloro) (η^5-cyclopentadienyl)nickel (2b). Yield 191 mg (88%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2,22 (s, 12H), 4.54 (s, 5H), 7.13 (s, 2H), 7.30-7.32 (m, 4H), 7.39-7.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.7, 92.2, 124.4, 128.7, 129.5, 136.4, 139.2, 167.2. Anal. calcd. for $C_{24}H_{25}ClN_2Ni$ (%): C, 66.11; H, 5.78; N, 6.43. Found (%): C, 66.05; H, 5.74; N, 6.51.



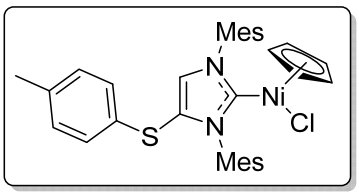
[1,3-Bis(2,4-dimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](chloro) (η^5-cyclopentadienyl)nickel (2c). Yield 200 mg (92%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.15 (s, 6H), 2.48 (s, 6H), 4.54 (s, 5H), 7.13 (s, 2H), 7.24-7.30 (m, 4H), 7.73-7.74 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.0, 21.4, 91.6, 124.3, 127.4, 129.4, 131.6, 134.5, 137.5, 139.5, 166.3. Anal. calcd. for $C_{24}H_{25}ClN_2Ni$ (%): C, 66.11; H, 5.78; N, 6.43. Found (%): C, 66.19; H, 5.75; N, 6.51.



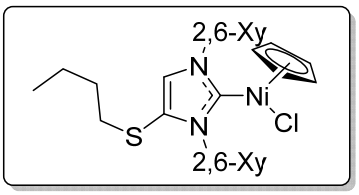
{1,3-Bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η⁵-cyclopentadienyl)nickel (2d). Yield 214 mg (78%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.09 (d, *J* = 6.8 Hz, 12H), 1.42 (d, *J* = 6.8 Hz, 12H), 2.85 (sept, *J* = 6.8 Hz, 4H), 4.51 (s, 5H), 7.13 (s, 2H), 7.40-7.42 (m, 4H), 7.54-7.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.7, 26.3, 28.8, 92.2, 124.1, 125.7, 130.3, 136.9, 146.5, 169.5. The spectral characteristics of the product obtained are similar to those described in the literature.[S9]



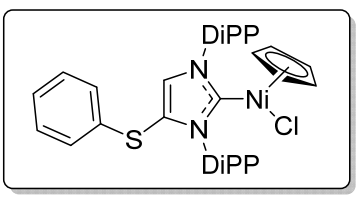
Chloro(η⁵-cyclopentadienyl)[4-(phenylsulfanyl)-1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene]nickel (2e). Yield 208 mg (73%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.79 (s, 6H), 2.14 (s, 6H), 2.38 (s, 6H), 4.45 (s, 5H), 6.96 (s, 2H), 6.99-7.02 (m, 2H), 7.06 (s, 2H), 7.11-7.20 (m, 3H), 7.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.1, 18.3, 21.05, 21.10, 92.0, 127.4, 127.9, 128.7, 128.8, 129.0, 129.4, 131.3, 132.1, 134.1, 135.4, 136.1, 136.5, 138.8, 139.0, 171.4. The spectral characteristics of the product obtained are similar to those described in the literature.[S3]



Chloro(η⁵-cyclopentadienyl){4-[(4-methylphenyl)sulfanyl]-1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene}nickel (2f). Yield 231 mg (79%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (s, 6H), 2.18 (s, 6H), 2.30 (s, 3H), 2.43 (s, 3H), 2.44 (s, 3H), 4.51 (s, 5H), 6.94-7.02 (m, 6H), 7.10 (br s, 2H), 7.24 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.5, 18.7, 21.2, 21.4, 21.5, 92.4, 128.7, 128.8, 129.1, 129.2, 129.4, 130.0, 131.4, 132.2, 134.7, 136.6, 137.0, 138.7, 139.2, 139.4, 171.2. Anal. calcd. for $C_{33}H_{35}ClN_2NiS$ (%): C, 67.65; H, 6.02; N, 4.78. Found (%): C, 67.73; H, 6.05; N, 4.74.

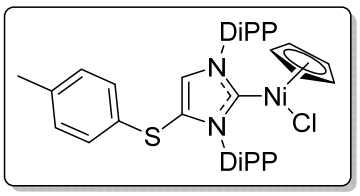


[4-(Butylsulfanyl)-1,3-bis(2,6-dimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene](chloro)(η⁵-cyclopentadienyl)nickel (2g). Yield 175 mg (67%), red crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, *J* = 7.3 Hz, 3H), 1.22-1.38 (m, 2H), 1.42-1.51 (m, 2H), 2.24 (s, 6H), 2.25 (s, 6H), 2.48 (t, *J* = 7.2 Hz, 2H), 4.51 (s, 5H), 7.15 (s, 1H), 7.31-7.37 (m, 4H), 7.40-7.49 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 18.8, 19.0, 21.5, 31.0, 34.7, 92.4, 128.2, 128.3, 128.7, 128.7, 129.6, 129.7, 136.3, 137.2, 137.4, 139.0, 170.5. Anal. calcd. for $C_{28}H_{33}ClN_2NiS$ (%): C, 64.21; H, 6.35; N, 5.35. Found (%): C, 64.14; H, 6.31; N, 5.31.

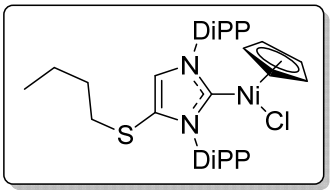


{1,3-Bis[2,6-di(propan-2-yl)phenyl]-4-(phenylsulfanyl)-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η⁵-cyclopentadienyl)nickel (2h). Yield 194 mg (59%), red crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (d, *J* =

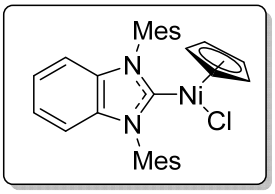
7.0 Hz, 6H), 1.11 (d, *J* = 7.0 Hz, 6H), 1.47-1.49 (m, 12H), 2.74 (sept, *J* = 7.0 Hz, 2H), 2.95 (sept, *J* = 7.0 Hz, 2H), 4.57 (s, 5H), 7.11-7.28 (m, 6H), 7.39-7.45 (m, 4H), 7.52-7.66 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7, 21.3, 22.4, 23.4, 25.3, 25.6, 89.2, 121.0, 121.5, 124.5, 124.8, 125.1, 126.7, 127.4, 127.7, 128.2, 131.2, 133.3, 142.6, 144.3, 170.7. The spectral characteristics of the product obtained are similar to those described in the literature.[S3]



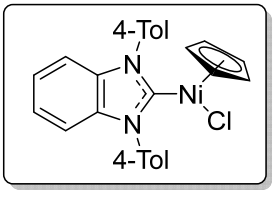
{1,3-Bis[2,6-di(propan-2-yl)phenyl]-4-[(4-methylphenyl)sulfanyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (2i). Yield 188 mg (56%), red crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (d, *J* = 6.8 Hz, 6H), 1.18 (d, *J* = 6.8 Hz, 6H), 1.47-1.51 (m, 12H), 2.33 (s, 3H), 2.78 (sept, *J* = 7.0 Hz, 2H), 2.94 (sept, *J* = 7.0 Hz, 2H), 4.57 (s, 5H), 6.99 (s, 1H), 7.10-7.17 (m, 4H), 7.41-7.49 (m, 4H), 7.57-7.59 (m, 1H), 7.64-7.69 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4, 21.7, 23.4, 24.5, 25.4, 27.6, 28.0, 91.4, 123.2, 123.6, 128.1, 128.9, 129.0, 129.3, 129.4, 129.5, 129.8, 133.6, 135.7, 136.9, 145.0, 146.7, 172.1. Anal. calcd. for $C_{39}H_{47}ClN_2NiS$ (%): C, 69.91; H, 7.07; N, 4.18. Found (%): C, 69.98; H, 7.11; N, 4.25.



{4-(Butylsulfanyl)-1,3-bis[2,6-di(propan-2-yl)phenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (2j). Yield 213 mg (67%), red crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.08 (d, J = 7.1 Hz, 6H), 1.25 (d, J = 7.0 Hz, 6H), 1.30-1.40 (m, 2H), 1.42-1.46 (m, 12H), 1.57-1.62 (m, 2H), 2.68-2.77 (m, 4H), 2.87 (sept, J = 7.0 Hz, 2H), 4.51 (s, 5H), 7.04 (s, 1H), 7.39-7.45 (m, 4H), 7.52-7.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 22.0, 22.6, 24.3, 25.5, 26.4, 28.6, 29.0, 31.1, 36.1, 92.3, 124.1, 124.5, 126.6, 130.2, 130.6, 131.6, 134.8, 136.9, 146.1, 147.6, 171.7. Anal. calcd. for $C_{36}H_{49}ClN_2NiS$ (%): C, 67.99; H, 7.77; N, 4.40. Found (%): C, 67.89; H, 7.74; N, 4.29.

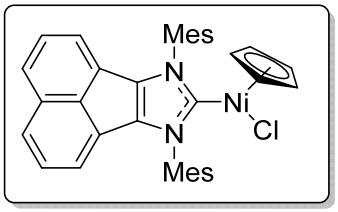


[1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-benzimidazol-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (2k). Yield 207 mg (81%), red crystals. ^{1}H NMR (300 MHz, CDCl3): δ 2.08 (s, 12H), 2.48 (s, 6H), 4.67 (s, 5H), 6.92-6.95 (m, 2H), 7.17-7.20 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.5, 21.5, 92.7, 110.5, 123.4, 129.6, 133.8, 135.7, 136.8, 139.5, 181.7. The spectral characteristics of the product obtained are similar to those described in the literature.[S10]

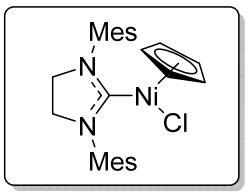


[1,3-Bis(4-methylphenyl)-1,3-dihydro-2*H*-benzimidazol-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (2l). Yield 189 mg (83%), red crystals. ^{1}H NMR (300 MHz, CDCl3) δ 2.59 (s, 6H), 4.63 (s, 5H), 7.25-7.28 (m, 4H), 7.53-

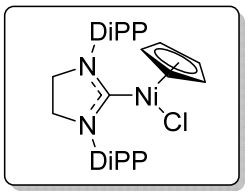
7.55 (m, 4H), 7.97-7.99 (m, 4H). ^{13}C NMR (75 MHz, CDCl3) δ 21.6, 92.3, 110.8, 123.4, 127.9, 130.2, 136.0, 136.4, 139.3, 180.4. The spectral characteristics of the product obtained are similar to those described in the literature.[10]



[7,9-Bis(2,4,6-trimethylphenyl)-7,9-dihydro-8*H*-acenaphtho[1,2-*d*]imidazol-8-ylidene](chloro)(η^5-cyclopentadienyl)nickel (2m). Yield 208 mg (71%), red crystals. ^{1}H NMR (300 MHz, CDCl3) δ 2.28 (s, 12H), 2.50 (s, 6H), 4.67 (s, 5H), 6.93-6.95 (m, 2H), 7.20 (br s, 4H), 7.34-7.39 (m, 2H), 7.69-7.72 (m, 2H). 13C NMR (75 MHz, CDCl3) δ ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7, 21.5, 92.5, 120.5, 125.9, 127.7, 127.9, 129.5, 129.7, 129.7, 135.3, 135.9, 139.4, 139.9, 173.1. Anal. calcd. for $C_{36}H_{33}ClN_2Ni$ (%): C, 73.56; H, 5.66; N, 4.77. Found (%): C, 73.64; H, 5.69; N, 4.83.



[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene](chloro)(η^5-cyclopentadienyl)nickel (2n). Yield 181 mg (78%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.39 (s, 18H), 3.90 (s, 4H), 4.54 (s, 5H), 7.07 (s, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.7, 21.3, 51.1, 92.6, 129.6, 136.9, 137.0, 138.4, 200.9. The spectral characteristics of the product obtained are similar to those described in the literature.[S11]



{1,3-Bis[2,6-di(propan-2-yl)phenyl]imidazolidin-2-ylidene}(chloro)(η^5-cyclopentadienyl)nickel (2o). Yield 146 mg (53%), red crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.29 (d, *J* = 7.3 Hz, 12H), 1.53 (d, *J* = 7.3 Hz, 12H), 3.36 (sept, *J* = 7.3 Hz, 4H), 4.04 (s, 4H), 4.54 (s, 5H), 7.40-7.42 (m, 4H), 7.50-7.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.0, 26.4, 28.2, 53.1, 92.1, 124.0, 128.9, 136.9, 147.1, 202.5. The spectral characteristics of the product obtained are similar to those described in the literature.[S11]

Procedure for scaled-up preparation of Ni/NHC complex 2a.

Azolium salt **1a** (682 mg, 2 mmol), $NiCp_2$ (395 mg, 2.1 mmol) and K_2CO_3 (552 mg, 4 mmol, 2 equiv.) were added to a 45 mL zirconium oxide vessel fitted with a 10 mm zirconium oxide balls (21 g). The jar was sealed and mounted on the planetary ball mill, then ground at 650 rpm for 90 minutes. The balls and jar were then washed with 2 × 5 mL of CH_2Cl_2 and filtered through a short pad of Celite. The combined filtrates were concentrated in vacuo to a small volume and the solution obtained was chromatographed on silica gel using CH_2Cl_2 as eluent to give 826 mg (89% yield) of **2a**.

S3. ^{1}H and ^{13}C NMR spectra

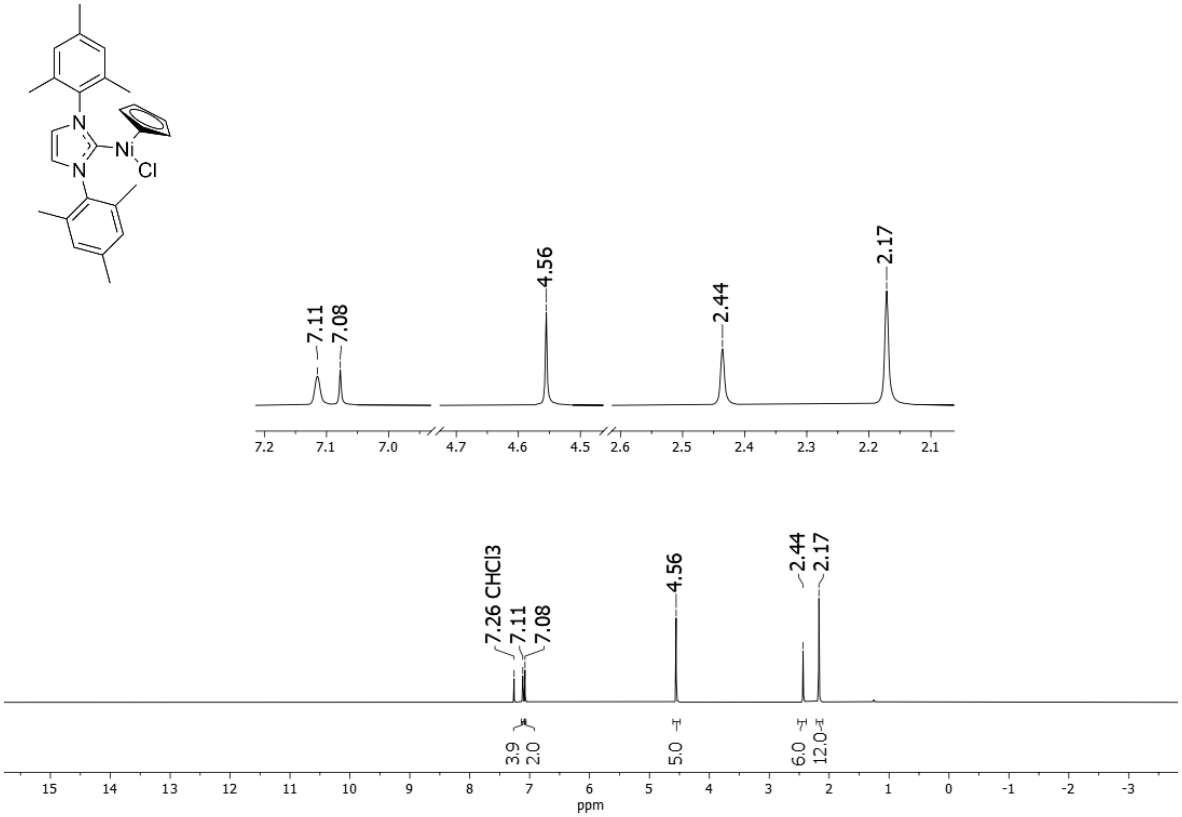


Figure S1. ^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 300 MHz)

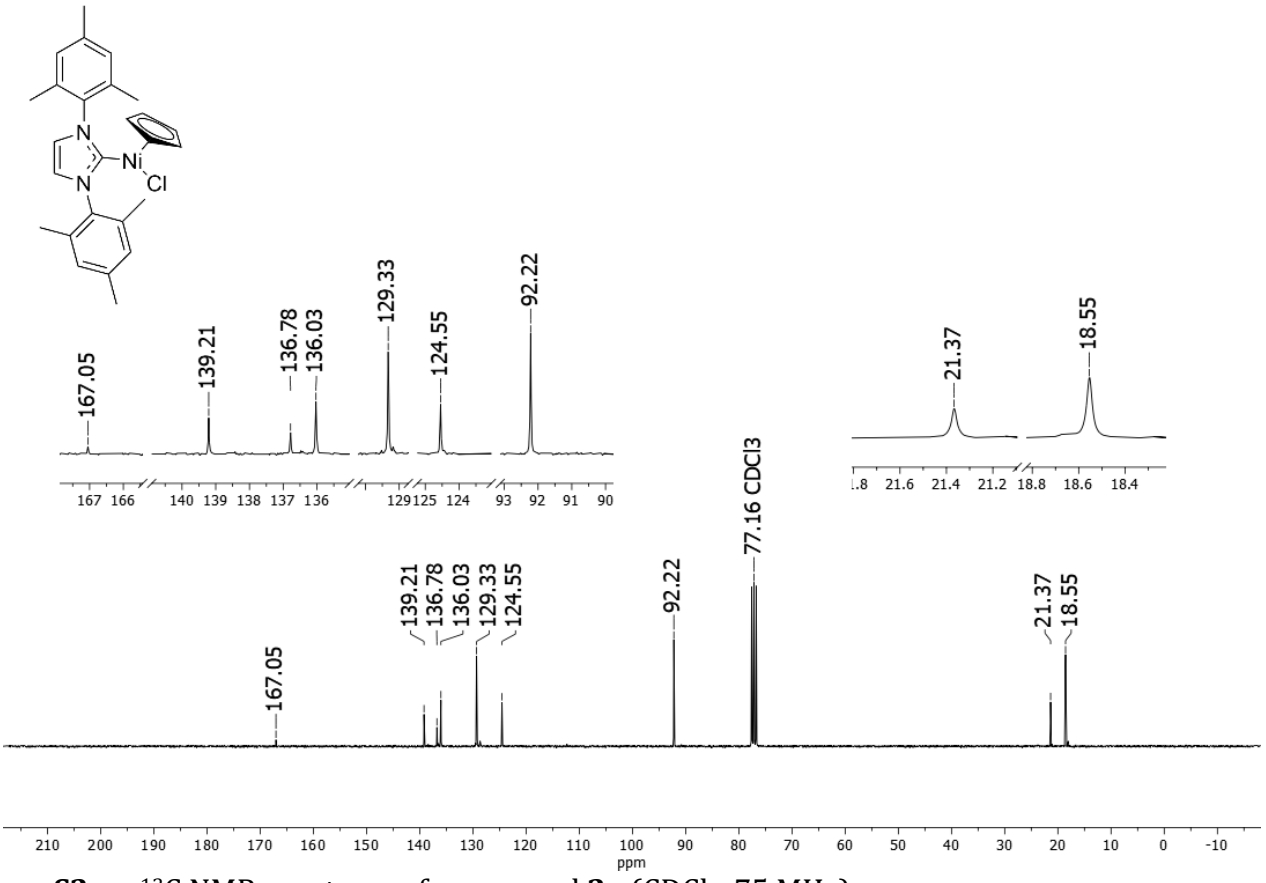


Figure S2. ^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 75 MHz)

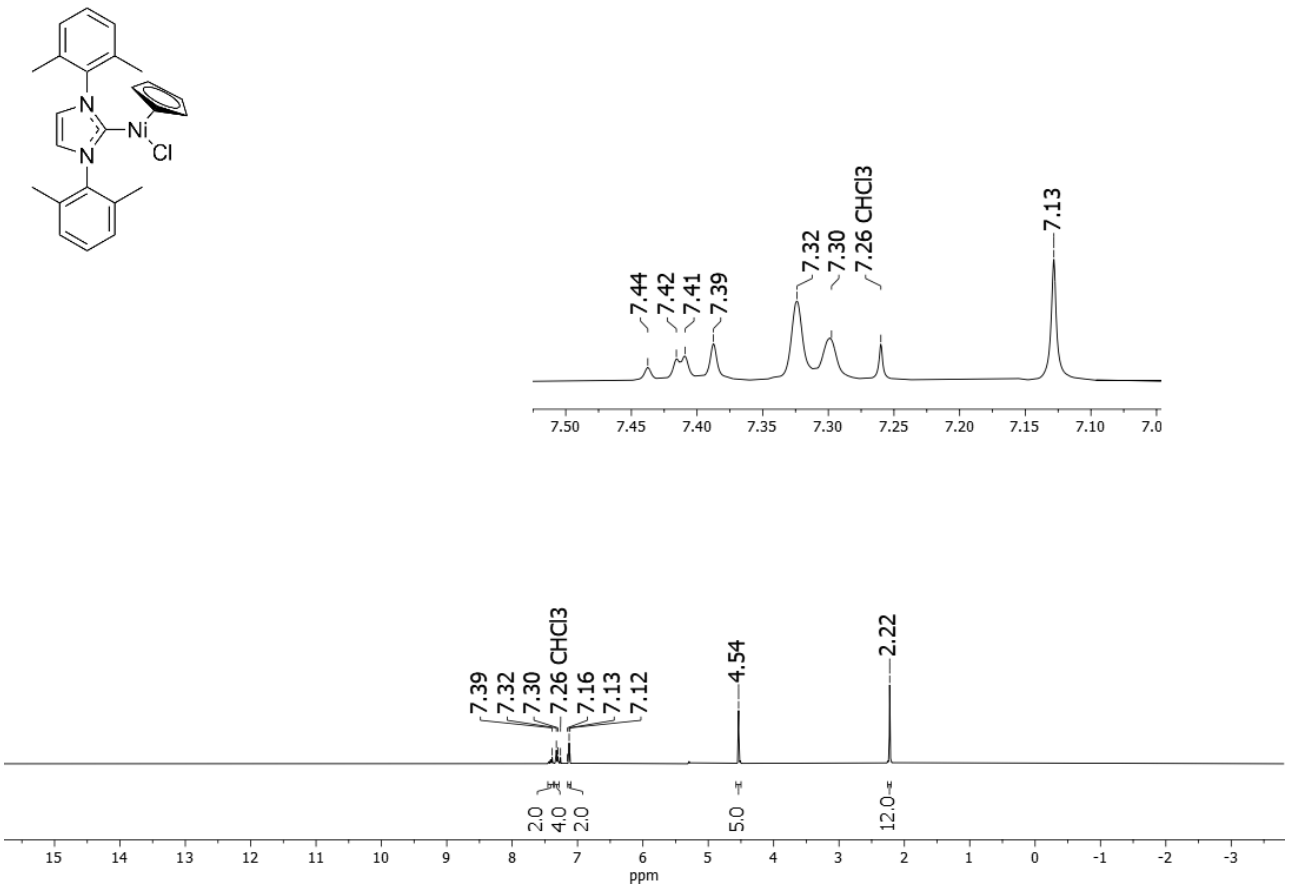


Figure S3. ^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 300 MHz)

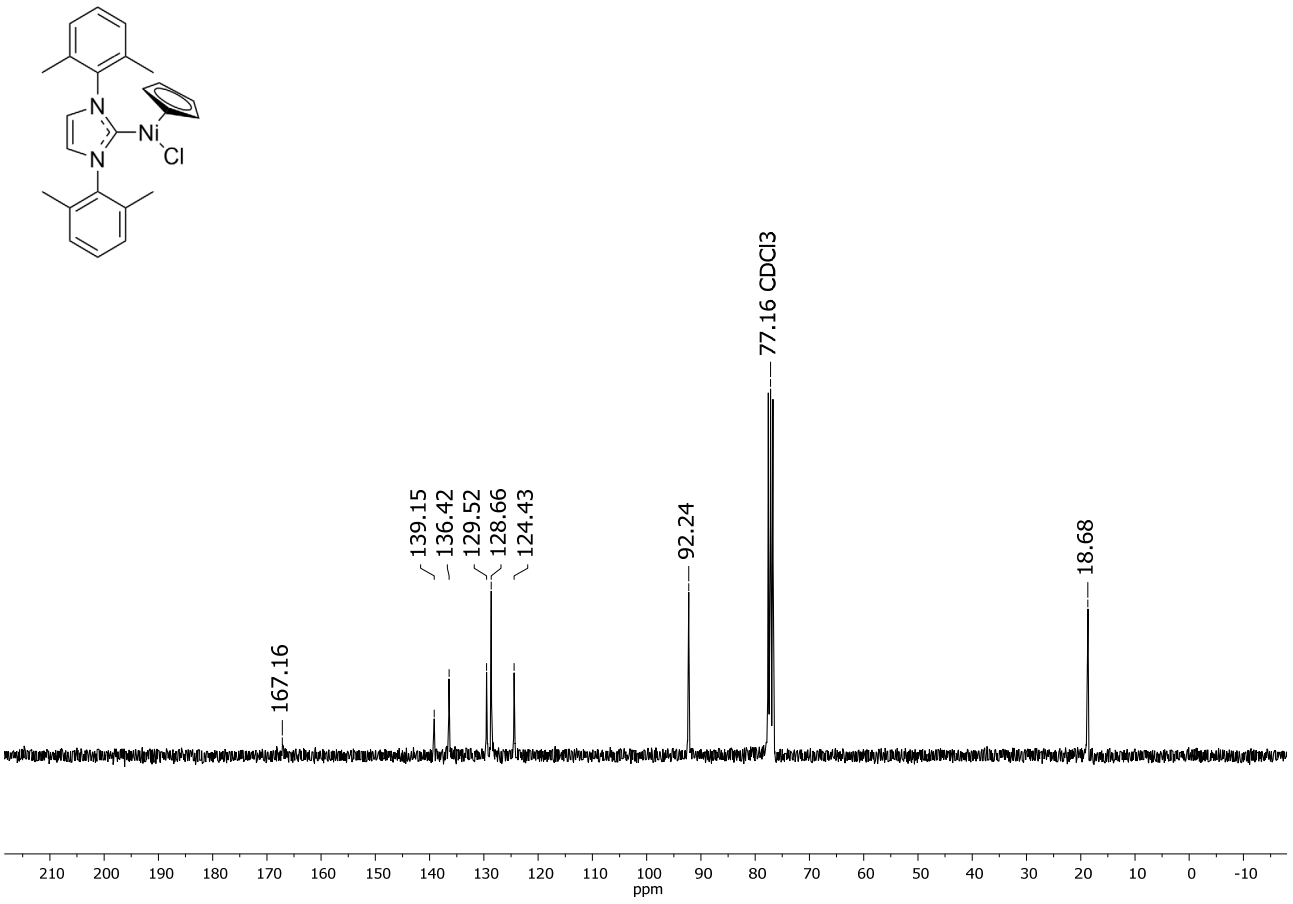


Figure S4. ^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 75 MHz)

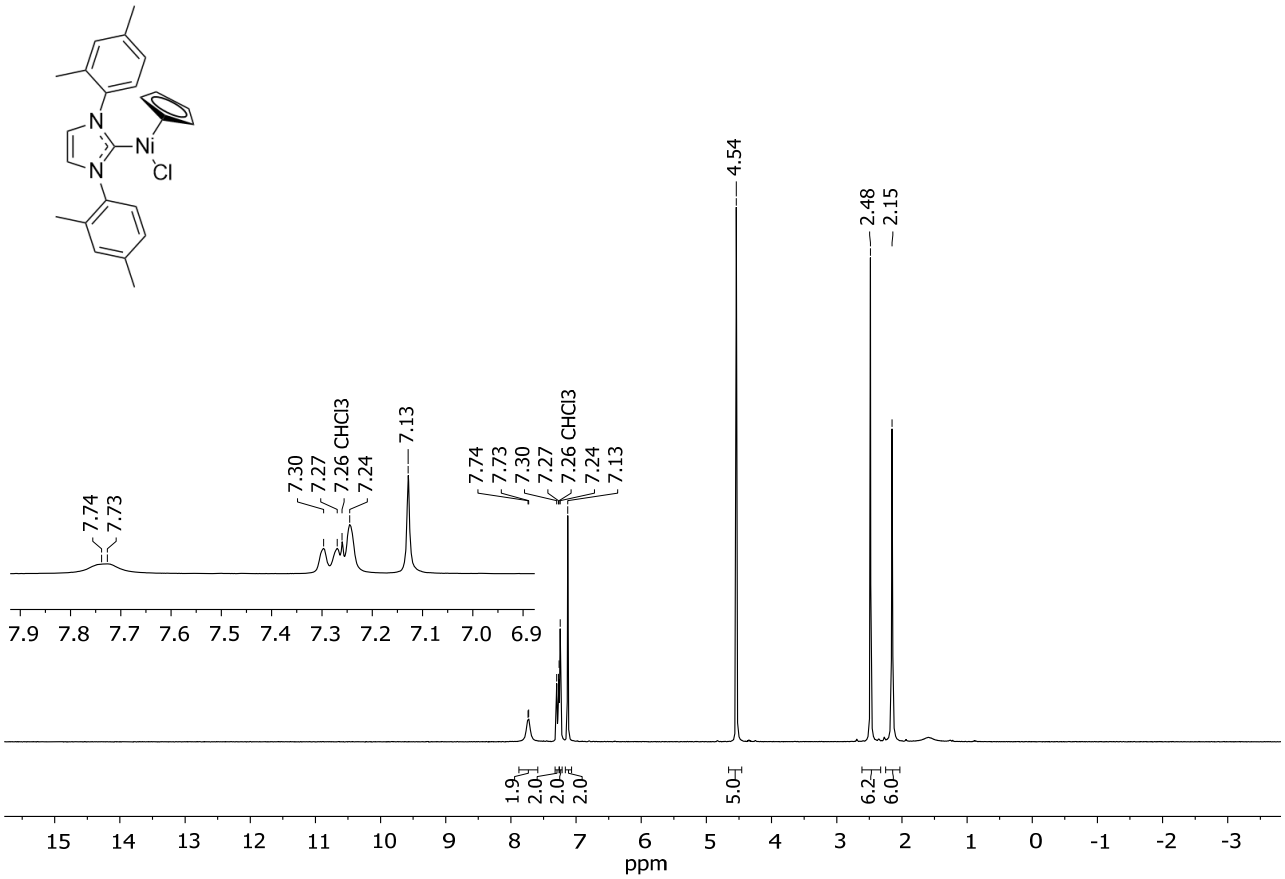


Figure S5. ^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 300 MHz)

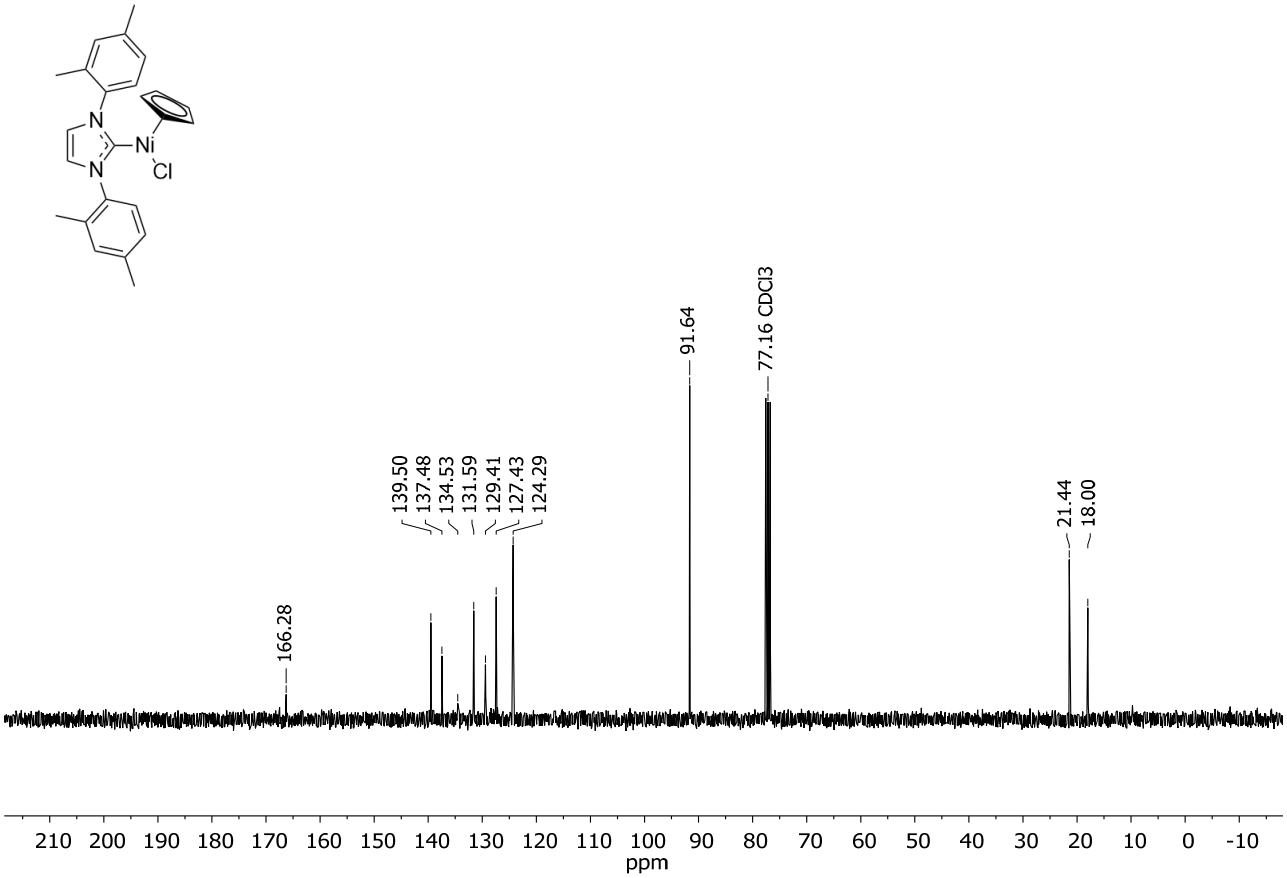


Figure S6. ^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 75 MHz)

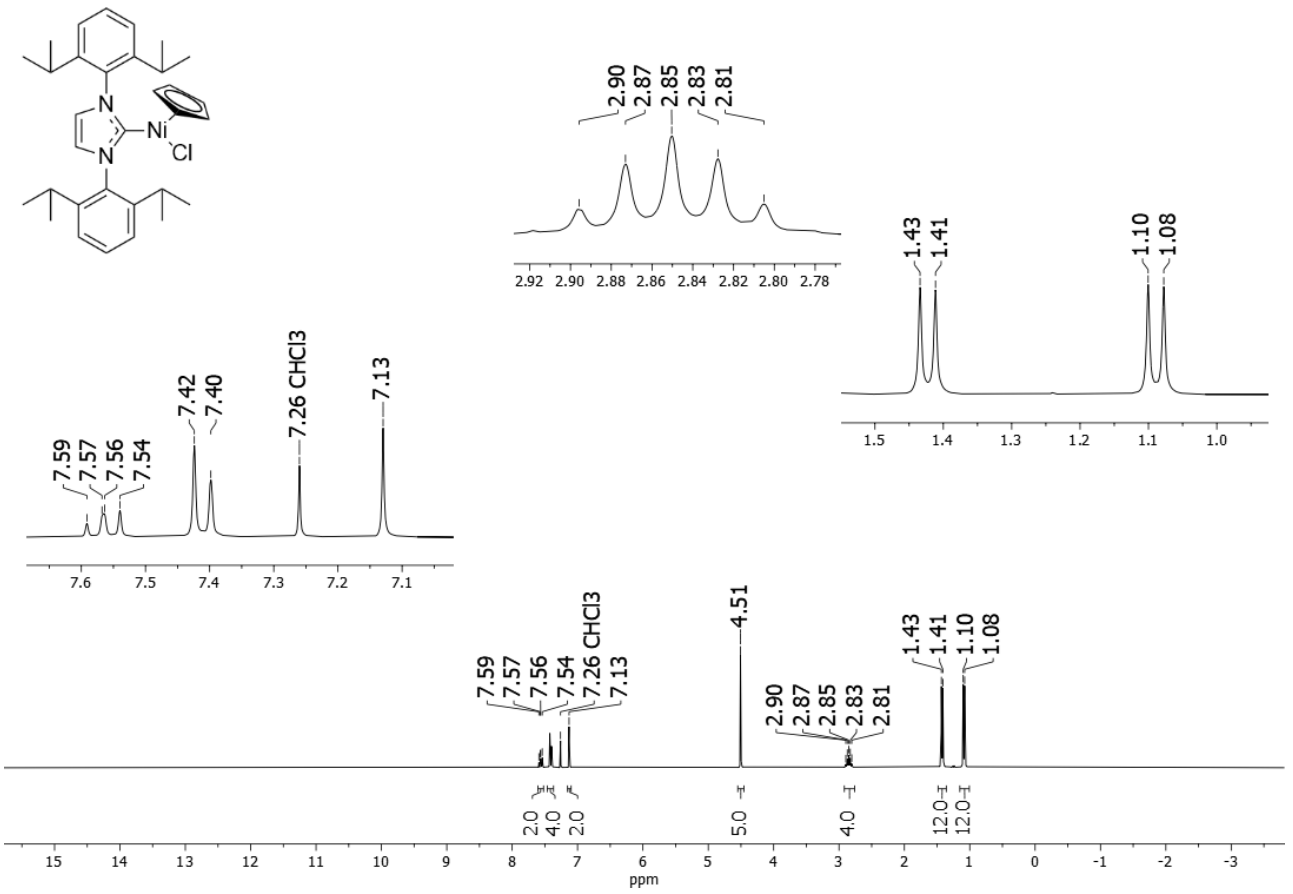


Figure S7. ^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 300 MHz)

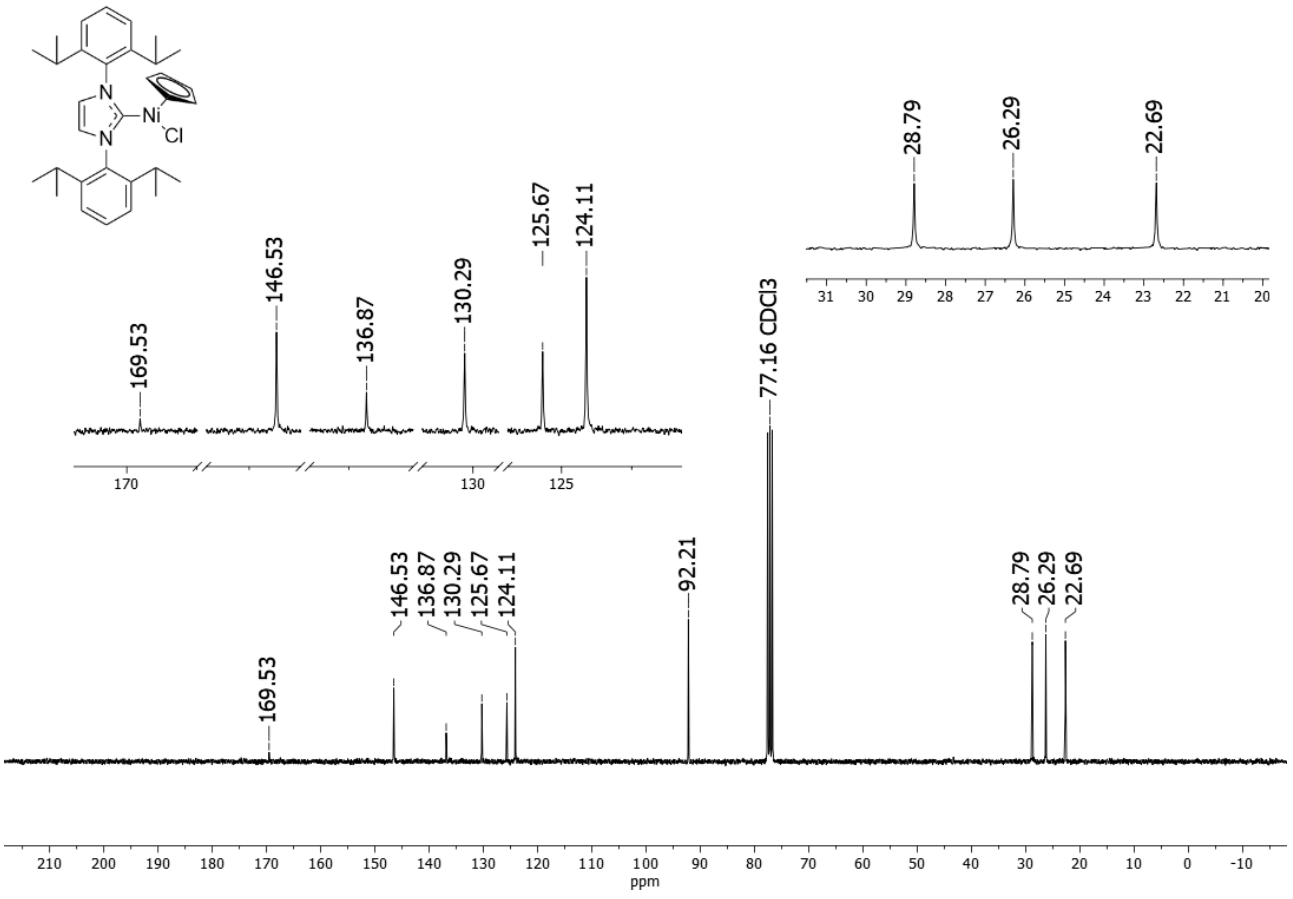


Figure S8. ^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 75 MHz)

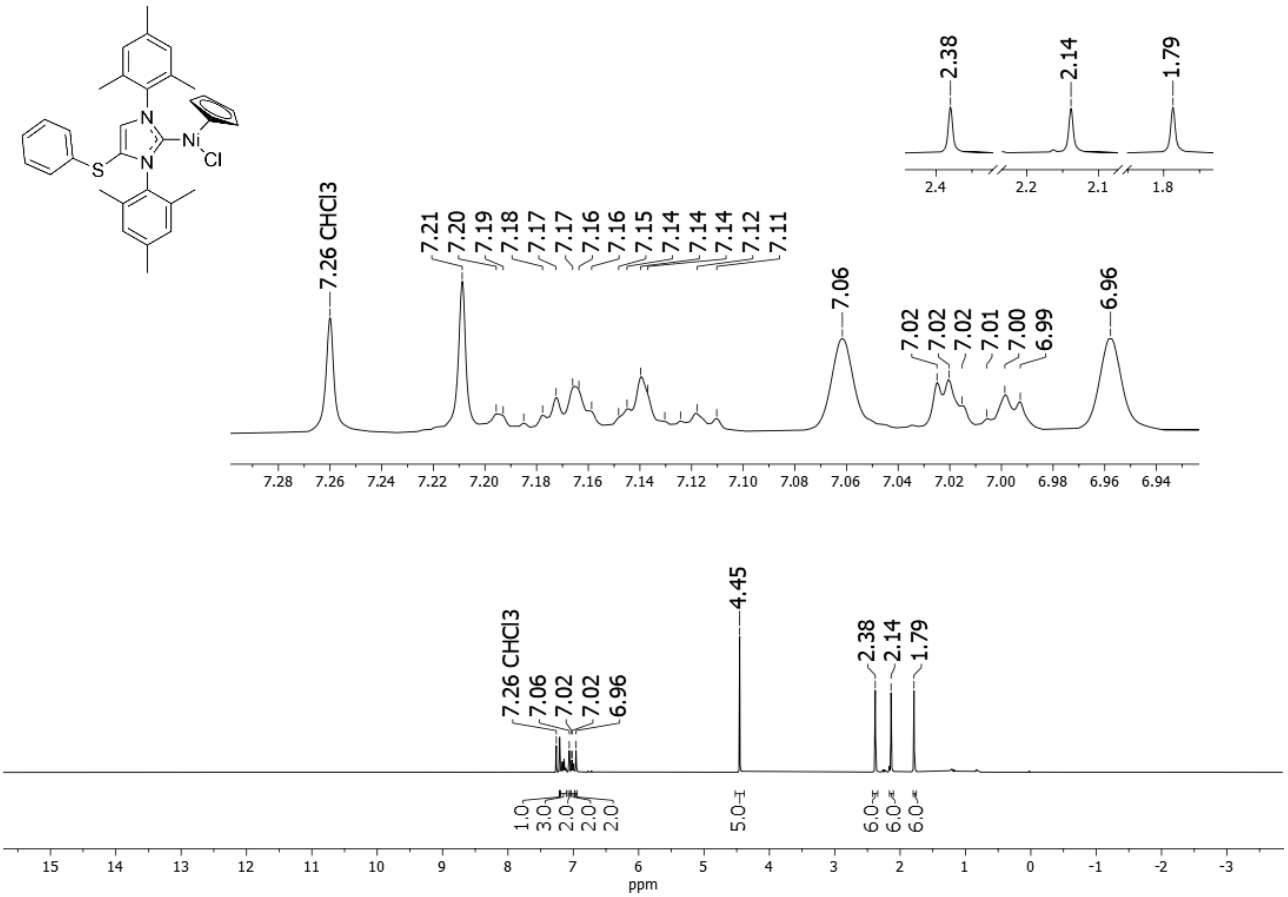


Figure S9. ^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 300 MHz)

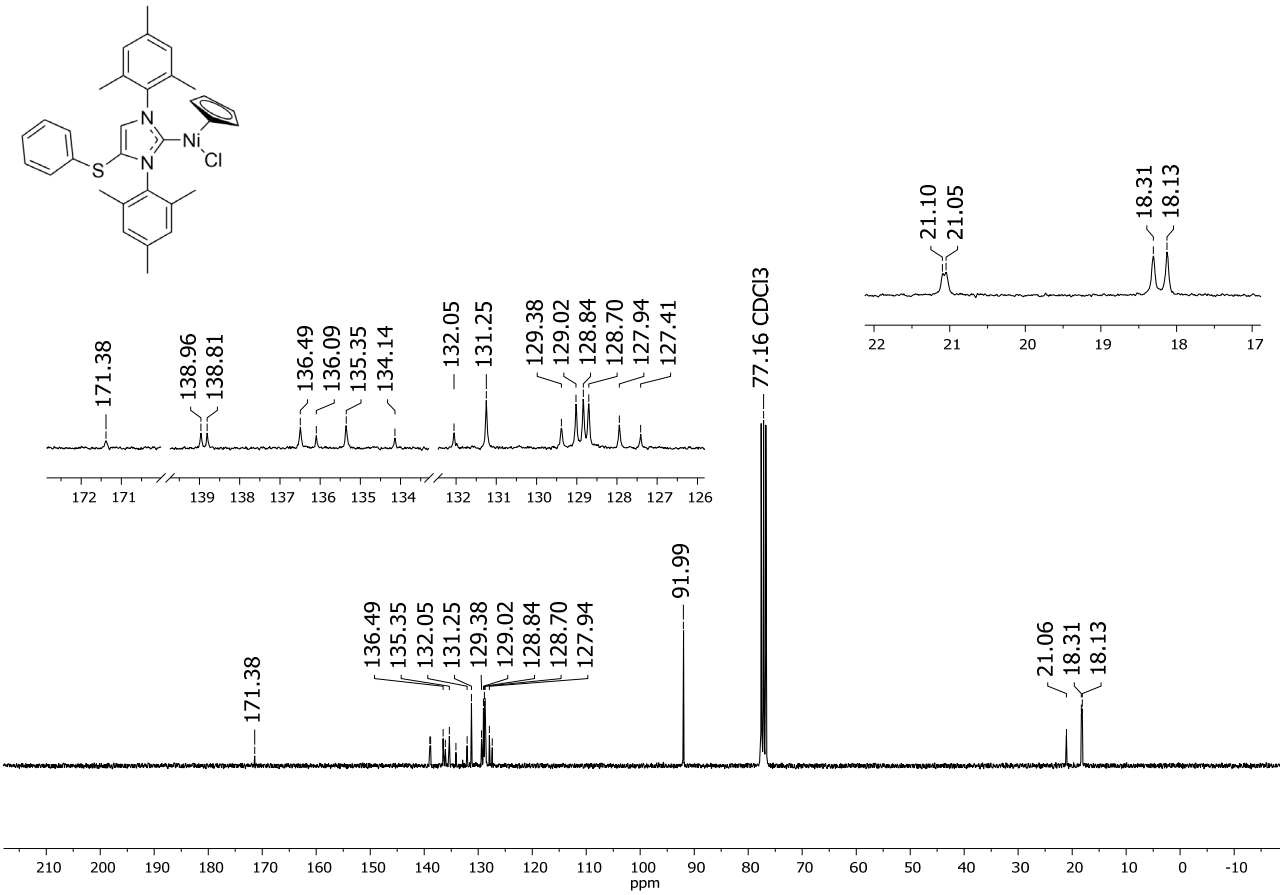


Figure S10. ^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 75 MHz)

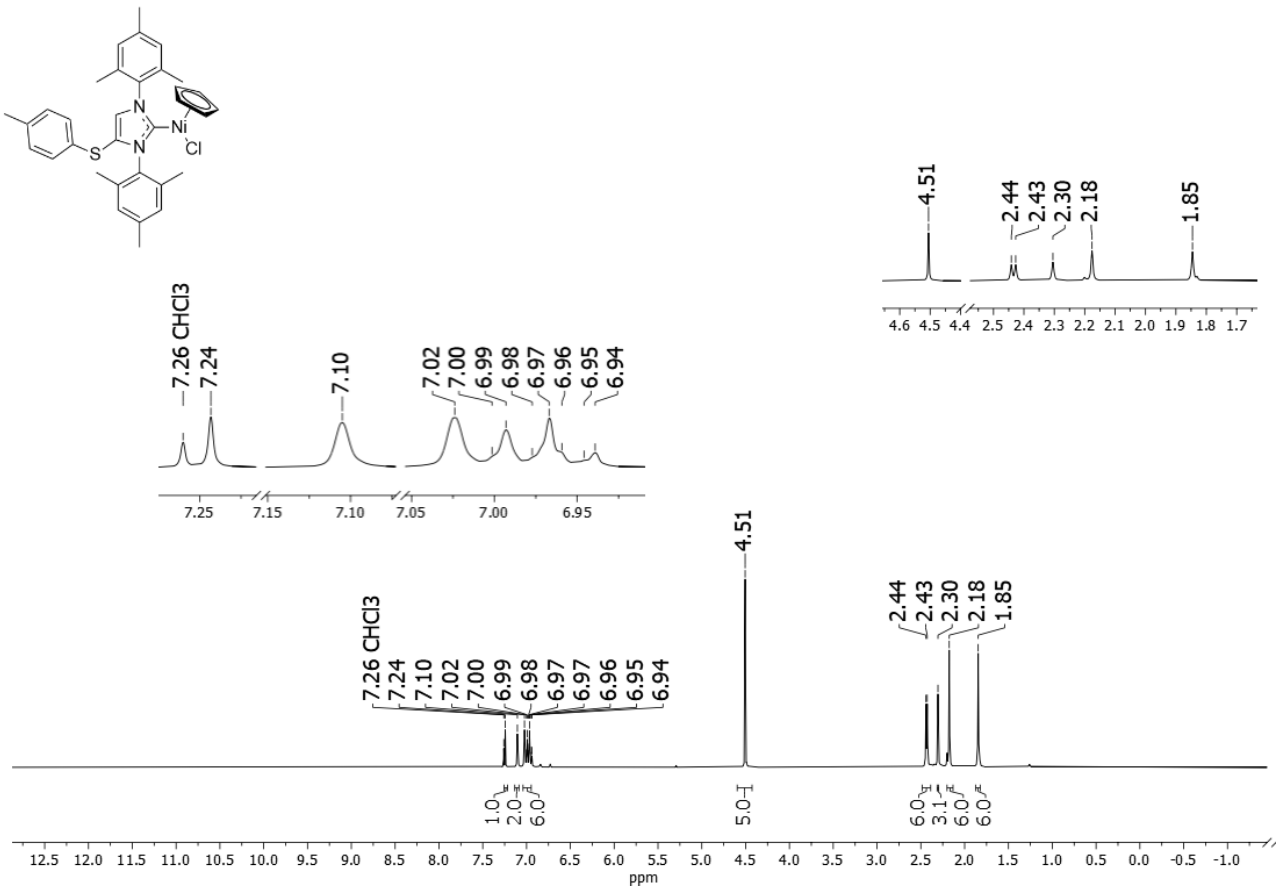


Figure S11. ^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 300 MHz)

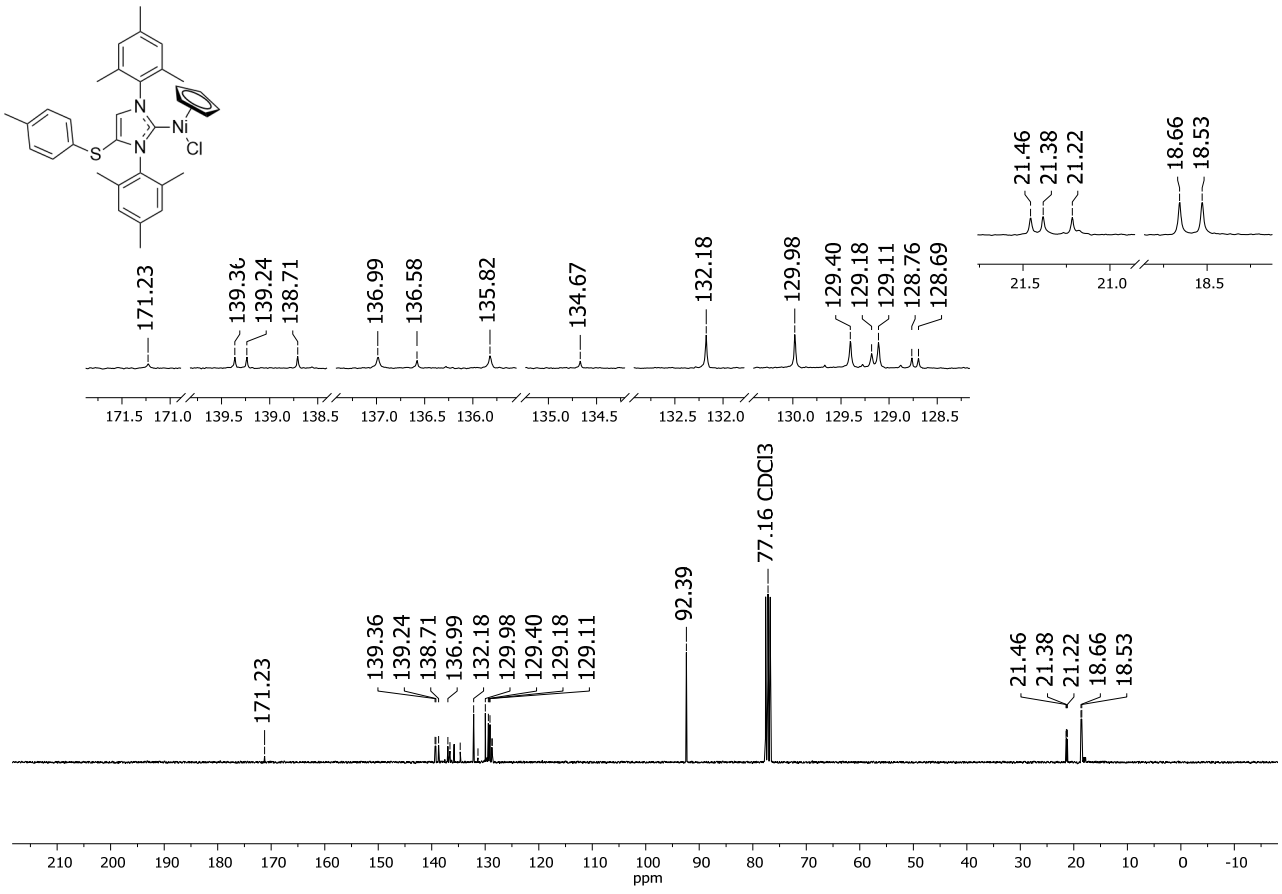


Figure S12. ^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 75 MHz)

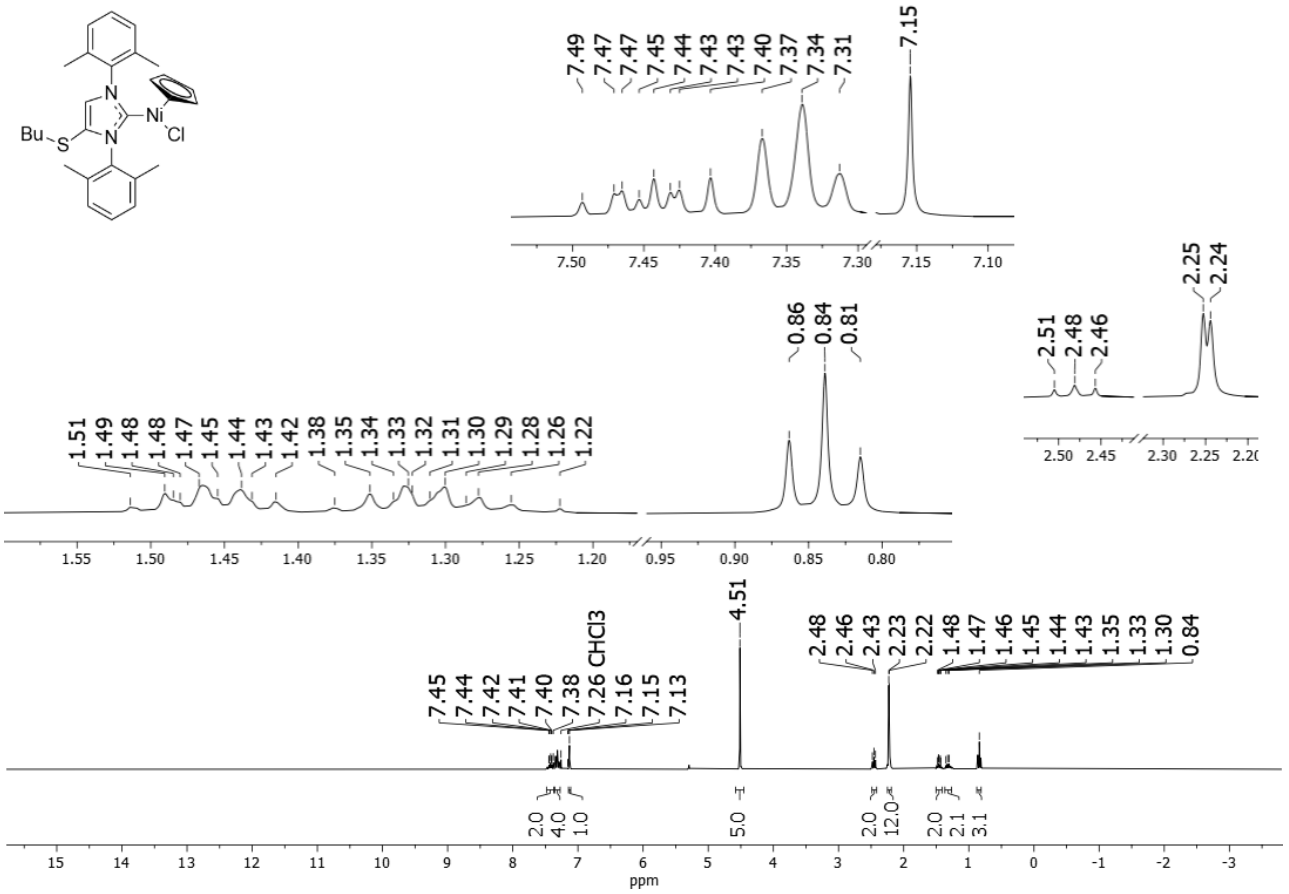


Figure S13. ^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 300 MHz)

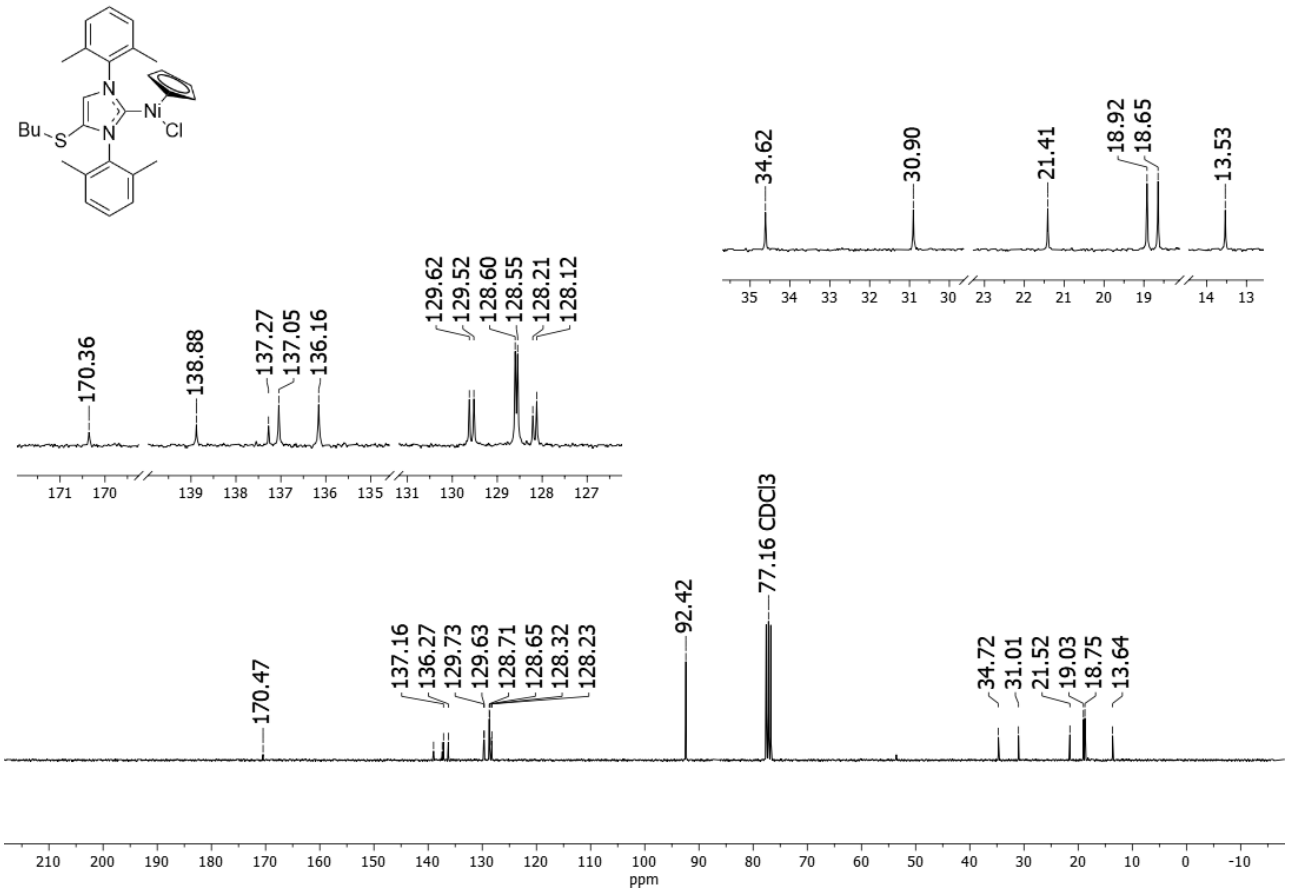


Figure S14. ^{13}C NMR spectrum of compound **2g** ($CDCl_3$, 75 MHz)

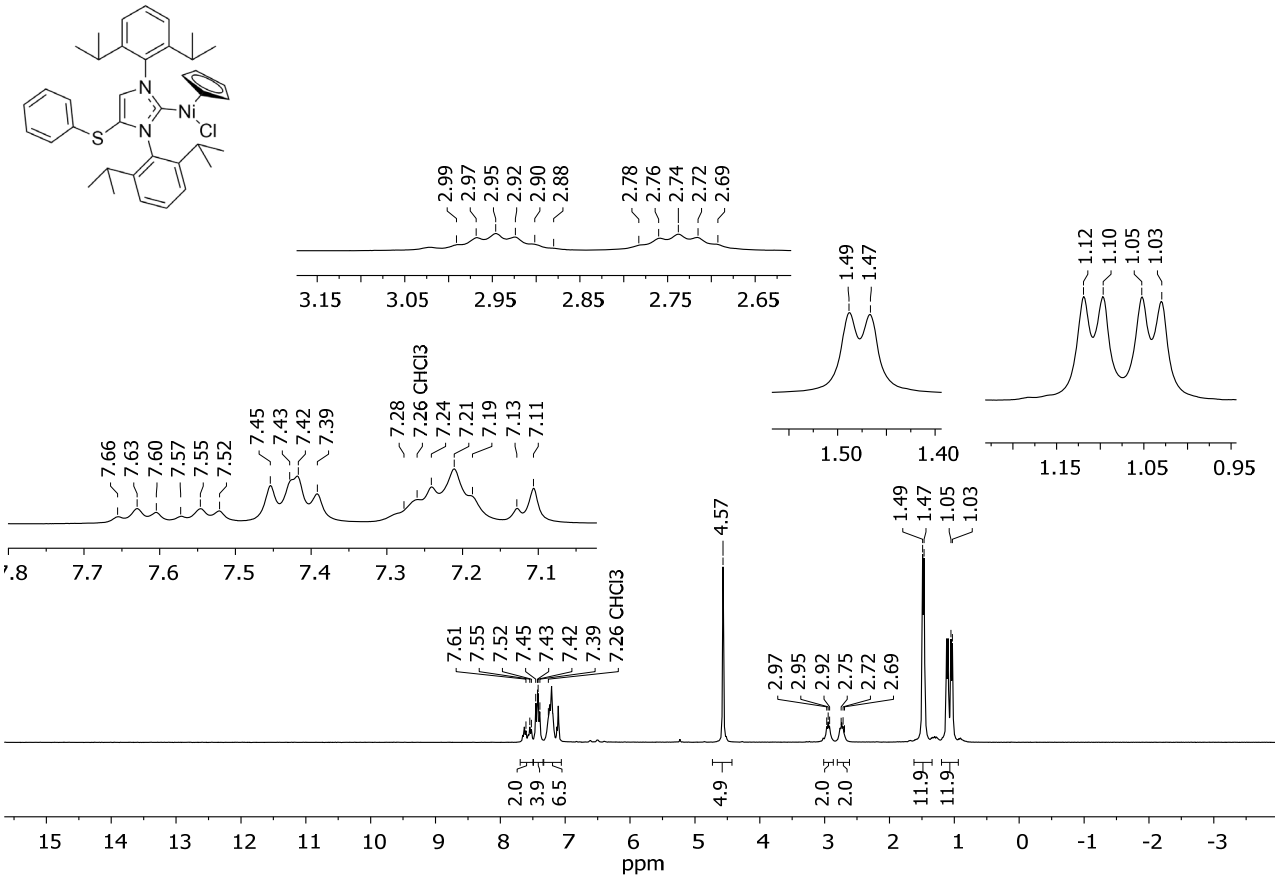


Figure S15. ^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 300 MHz)

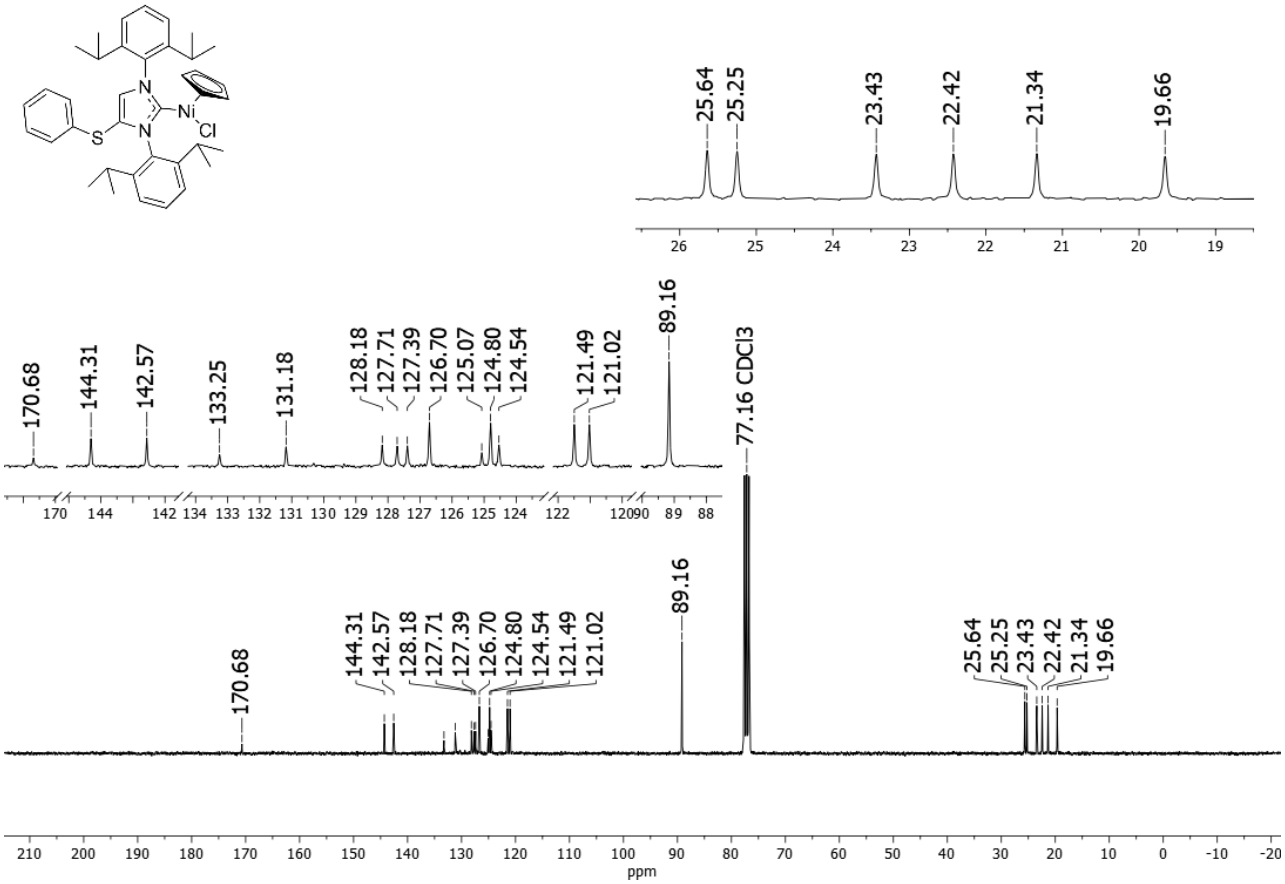


Figure S16. ^{13}C NMR spectrum of compound **2h** ($CDCl_3$, 75 MHz)

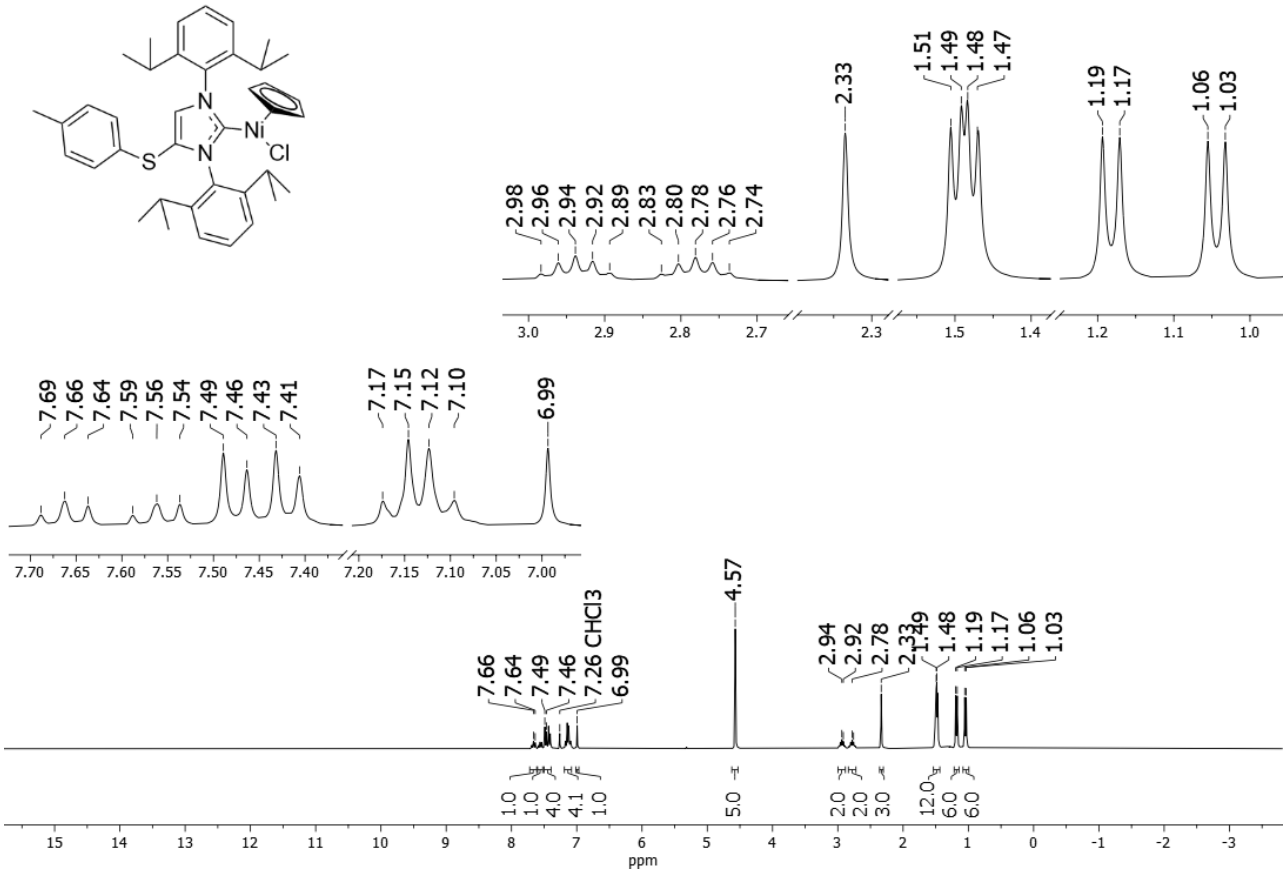


Figure S17. ^{1}H NMR spectrum of compound **2i** ($CDCl_3$, 300 MHz)

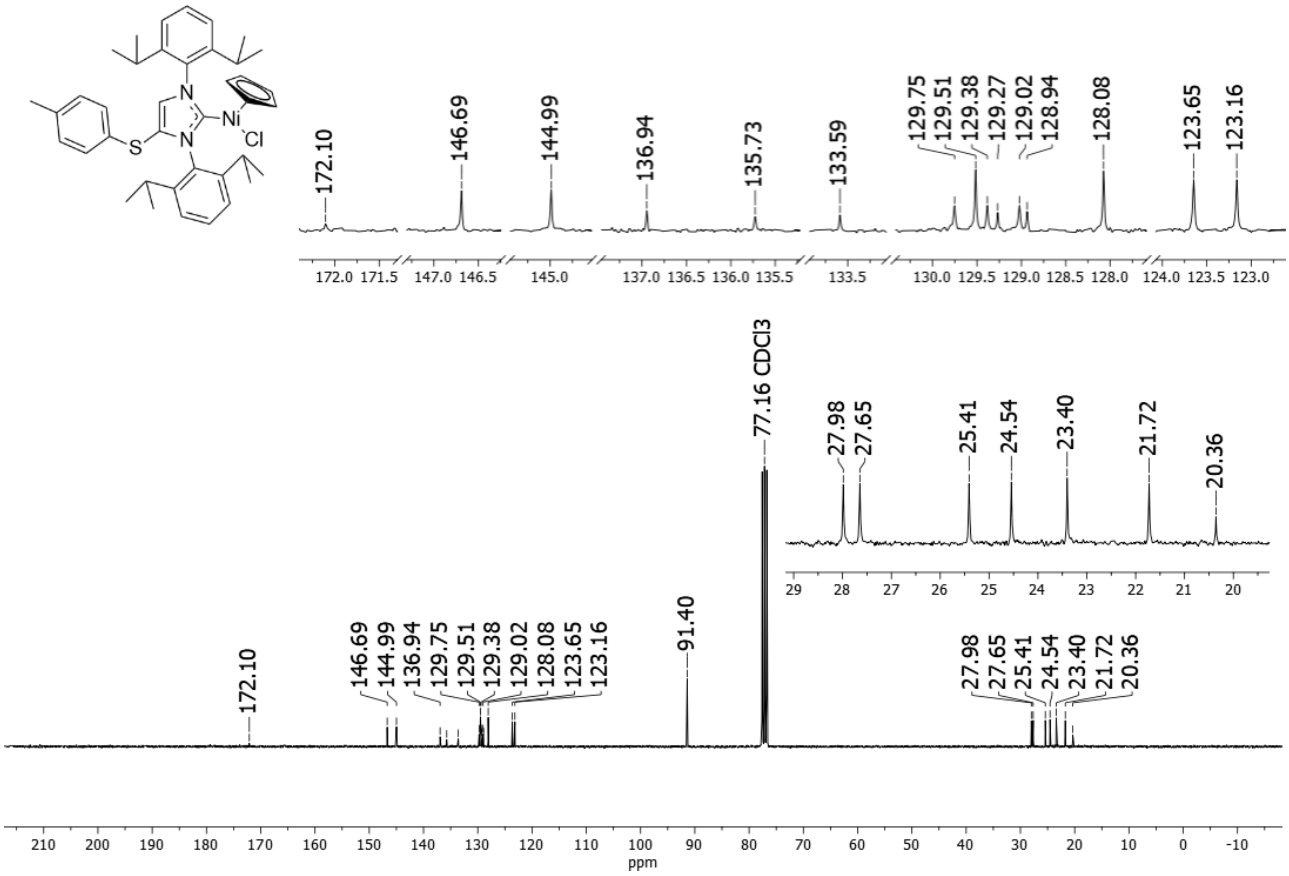


Figure S18. ^{13}C NMR spectrum of compound **2i** ($CDCl_3$, 75 MHz)

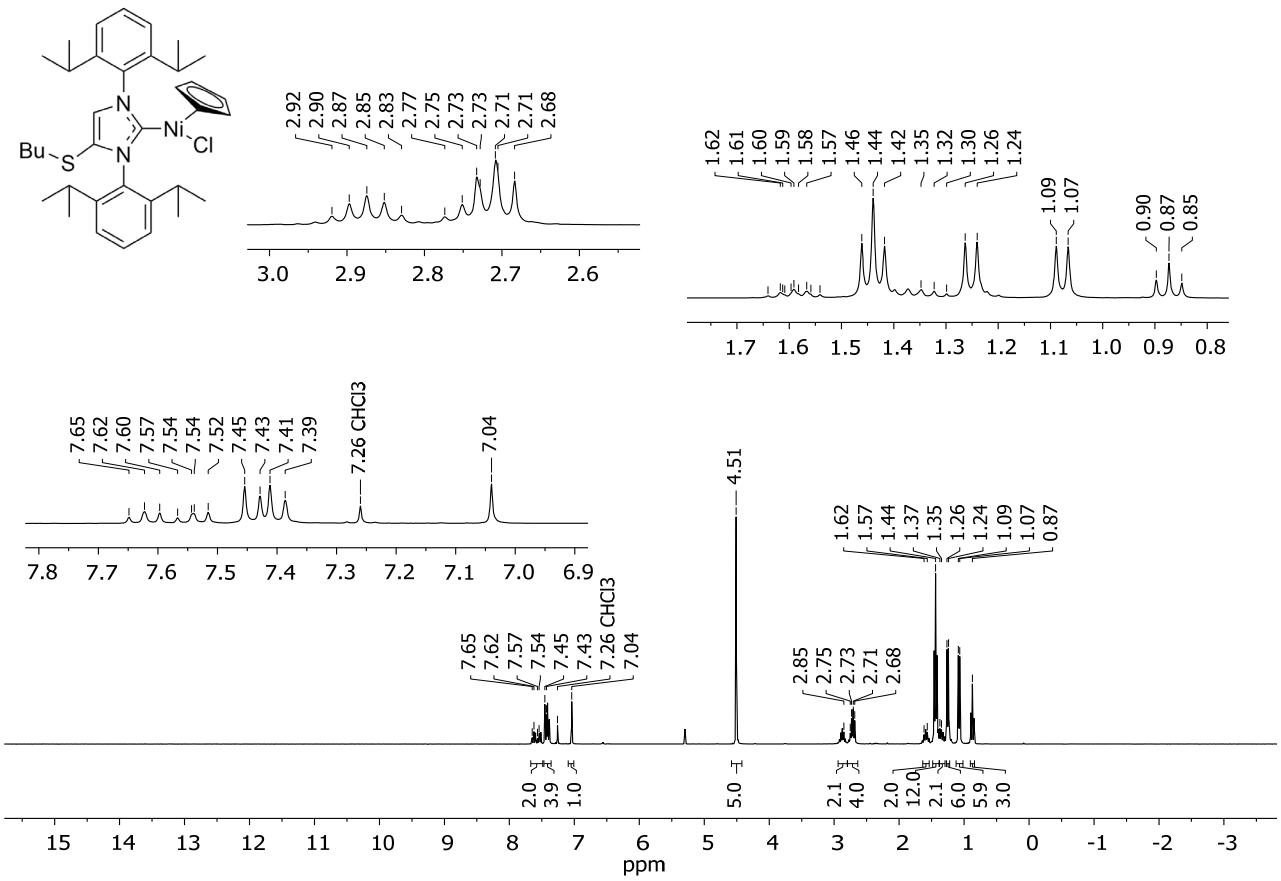


Figure S19. ^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 300 MHz)

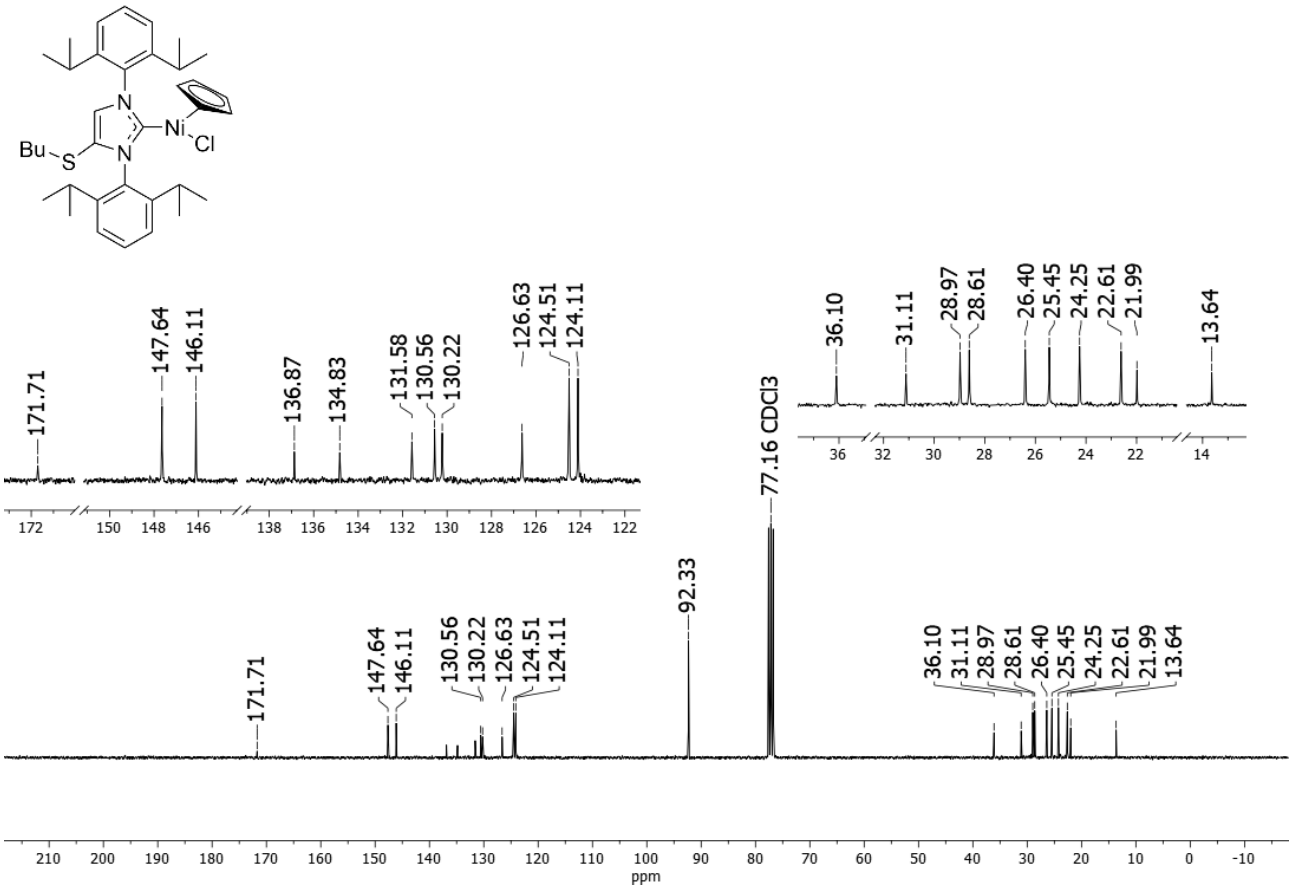


Figure S20. ^{13}C NMR spectrum of compound **2j** ($CDCl_3$, 75 MHz)

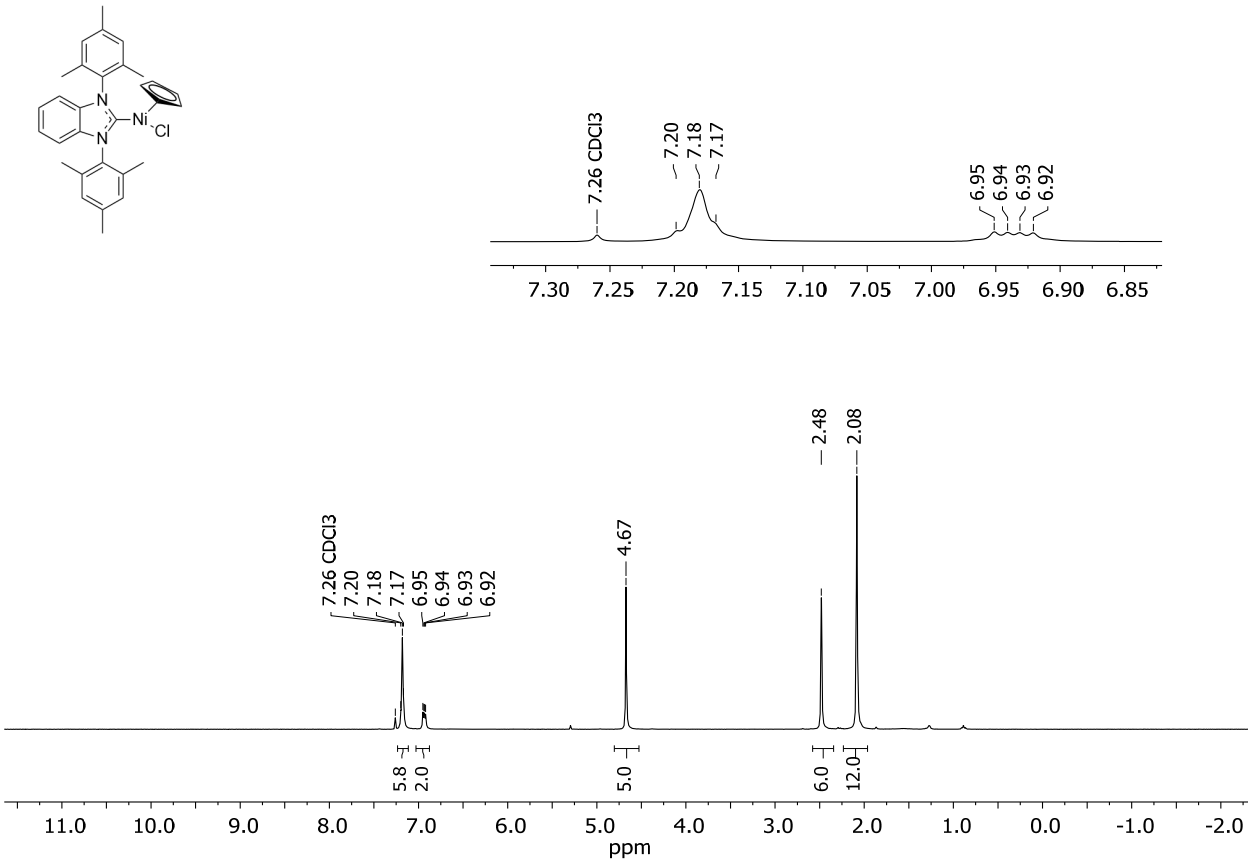


Figure S21. ^{1}H NMR spectrum of compound **2k** ($CDCl_3$, 300 MHz)

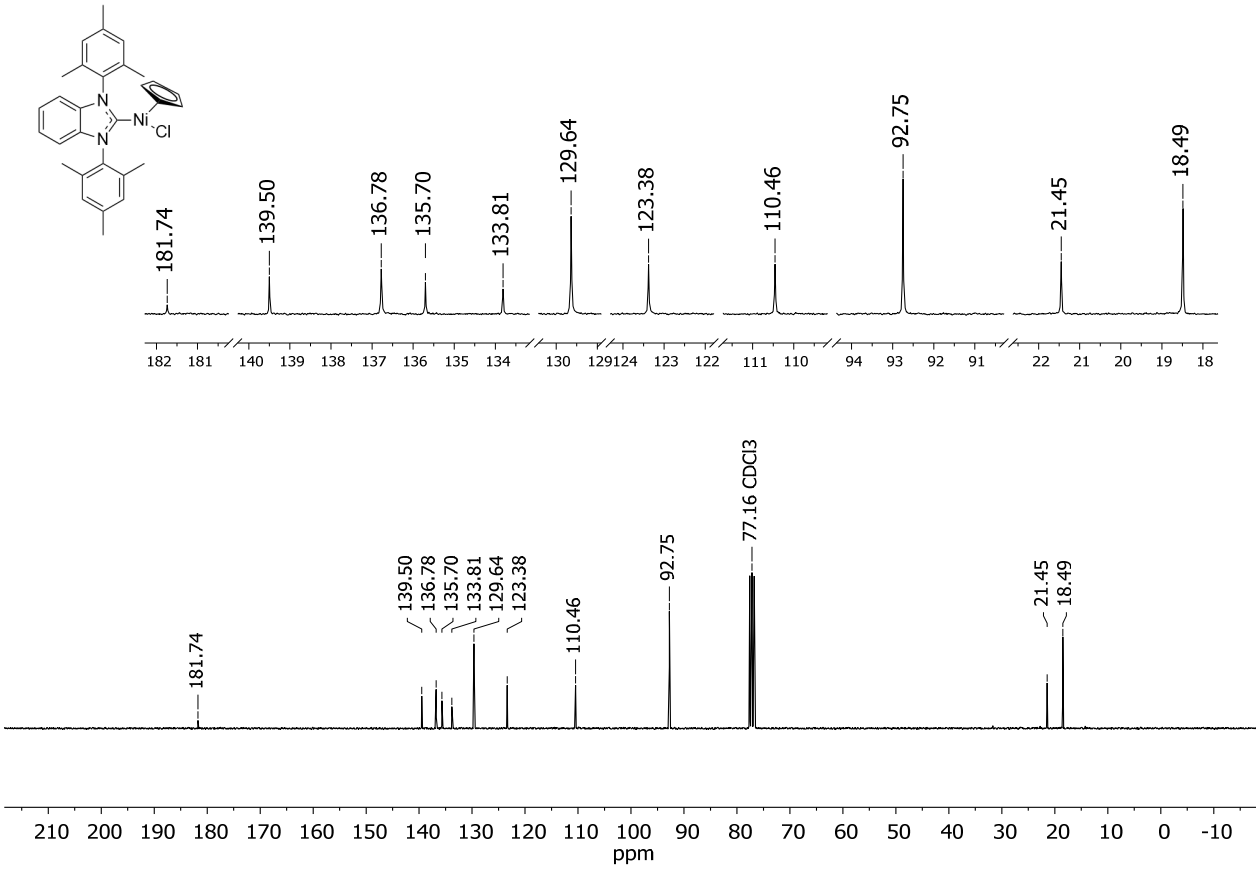


Figure S22. ^{13}C NMR spectrum of compound **2k** ($CDCl_3$, 75 MHz)

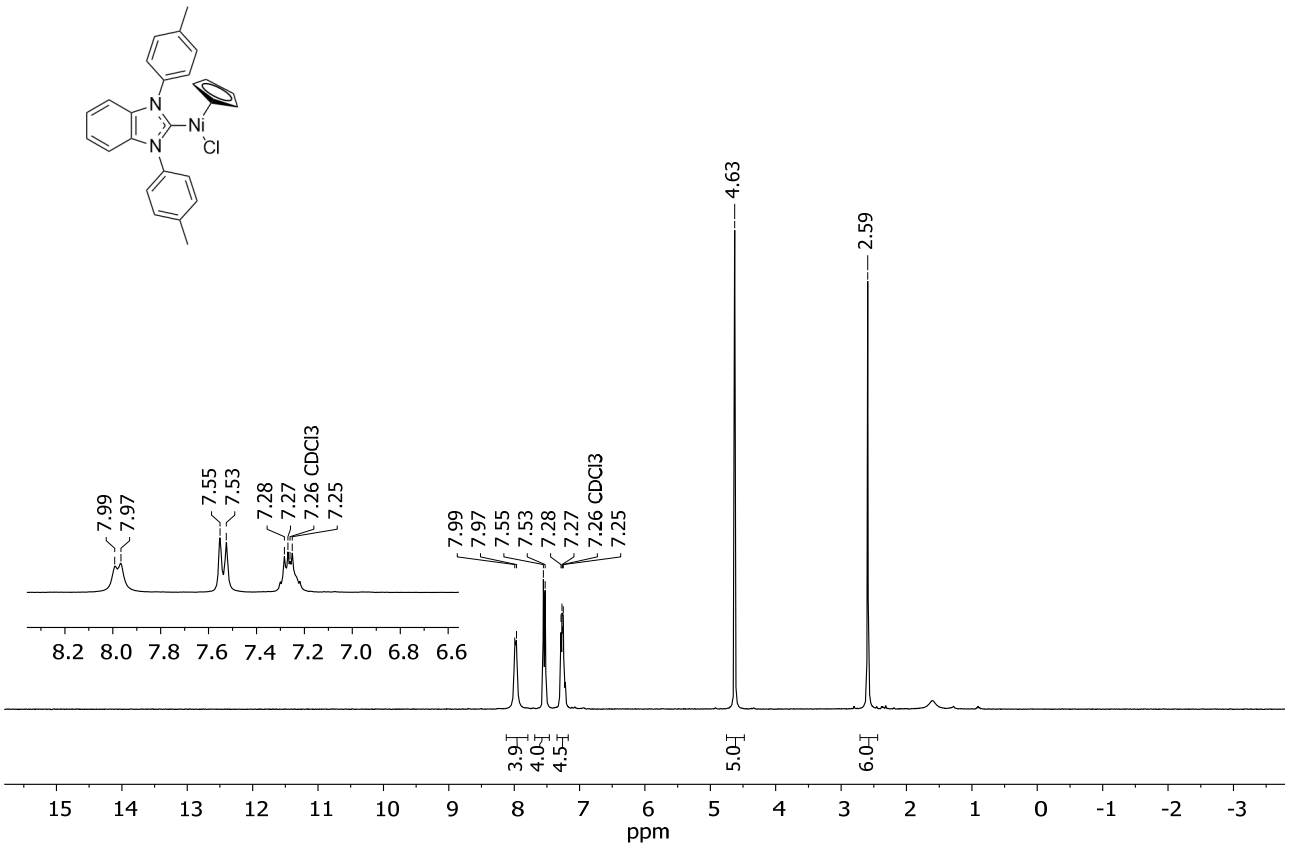


Figure S23. ^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 300 MHz)

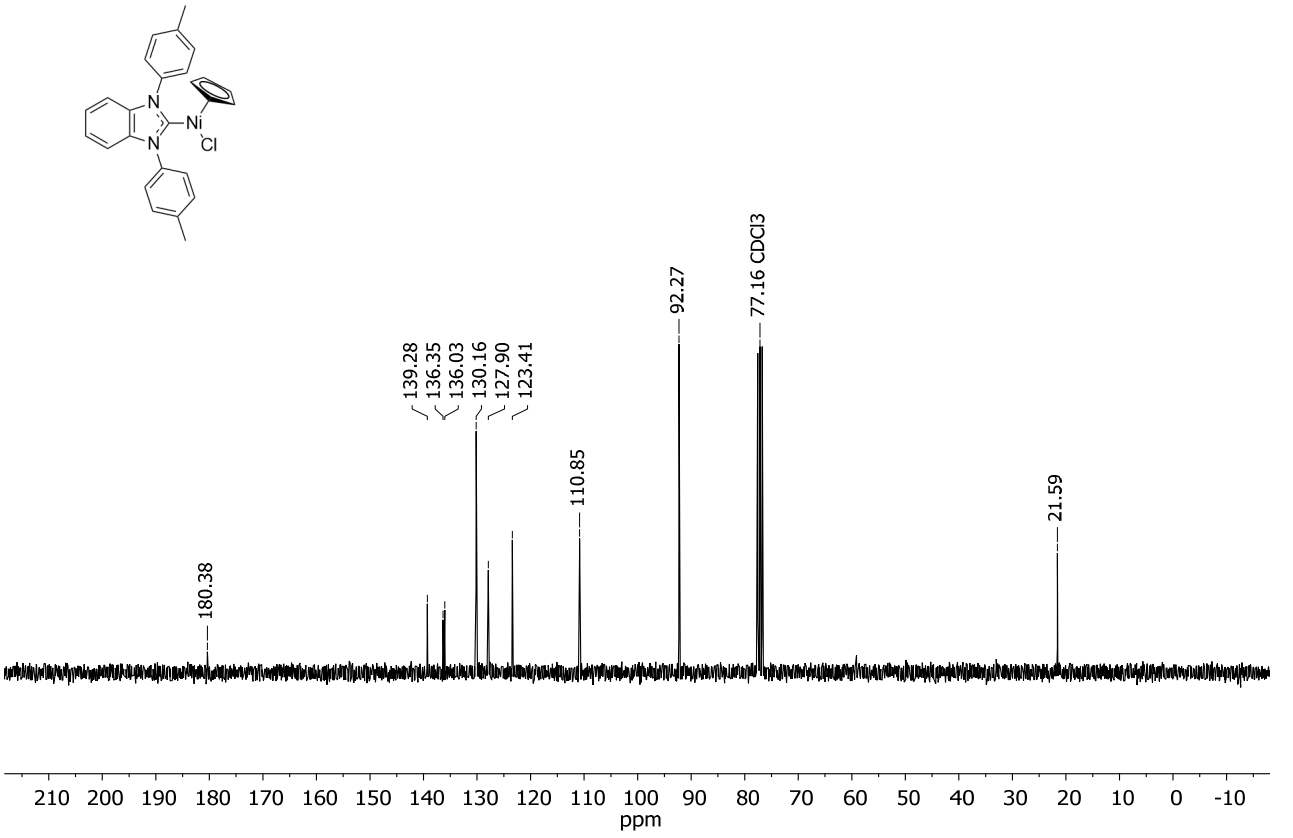


Figure S24. ^{13}C NMR spectrum of compound **2l** ($CDCl_3$, 75 MHz)

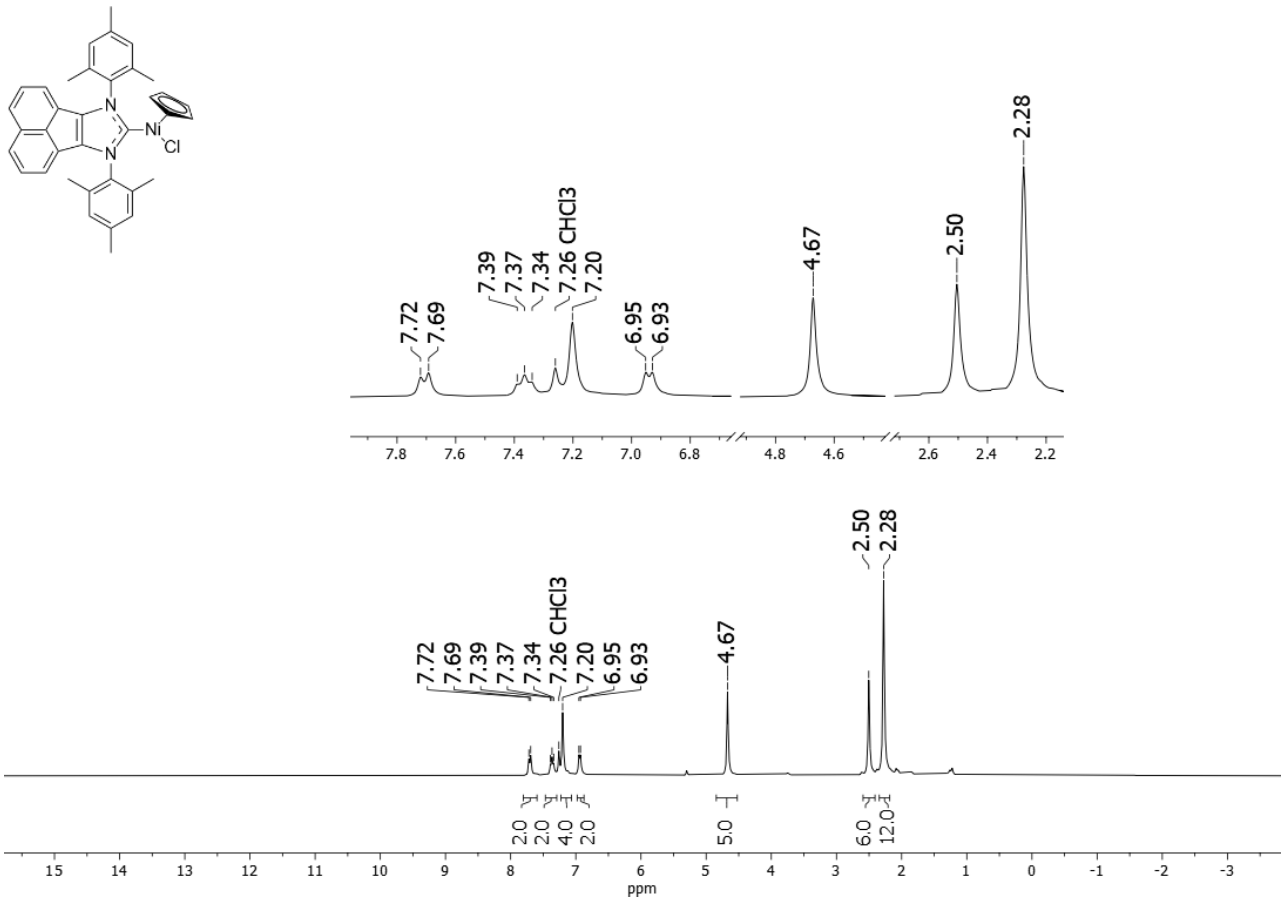


Figure S25. ^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 300 MHz)

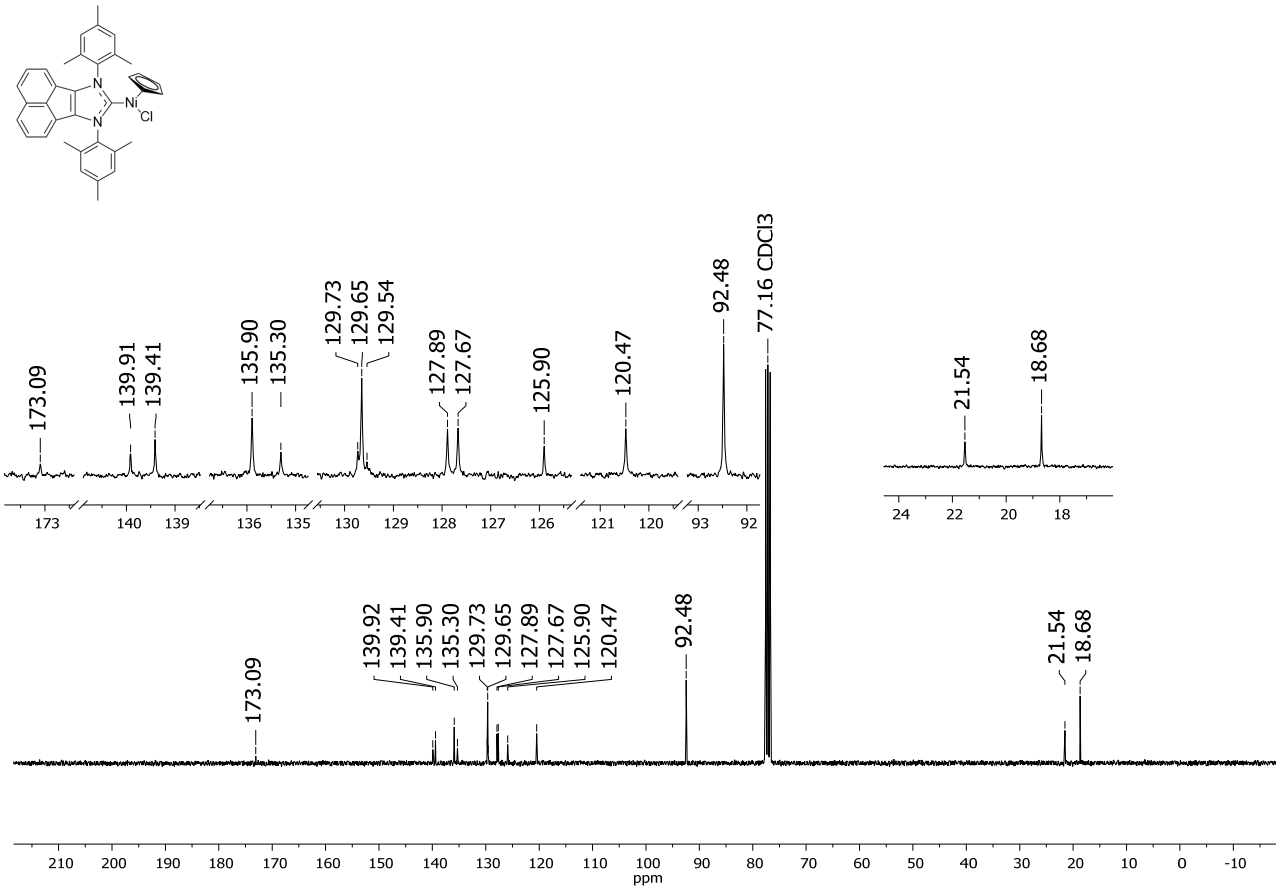


Figure S26. ^{13}C NMR spectrum of compound **2m** ($CDCl_3$, 75 MHz)

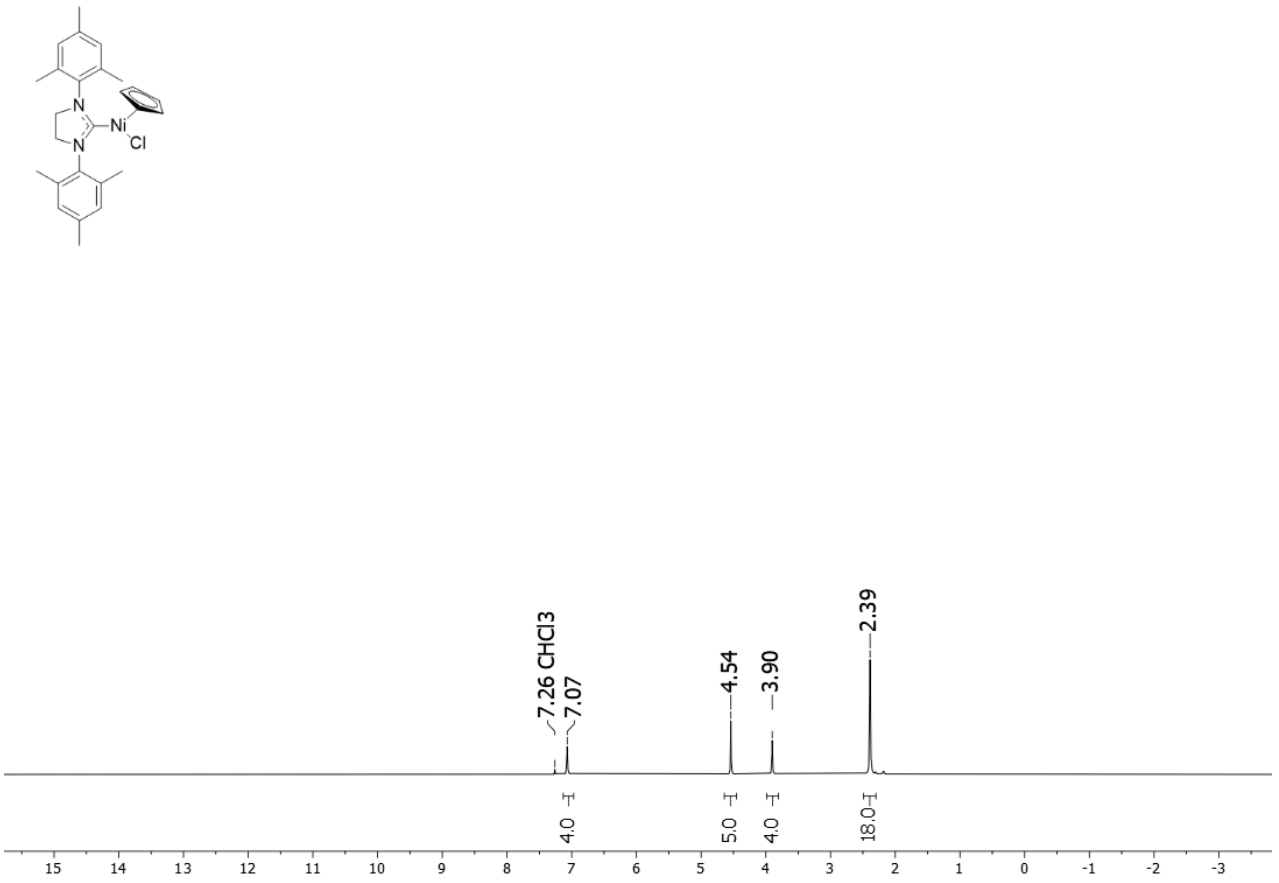


Figure S27. ^{1}H NMR spectrum of compound **2n** ($CDCl_3$, 300 MHz)

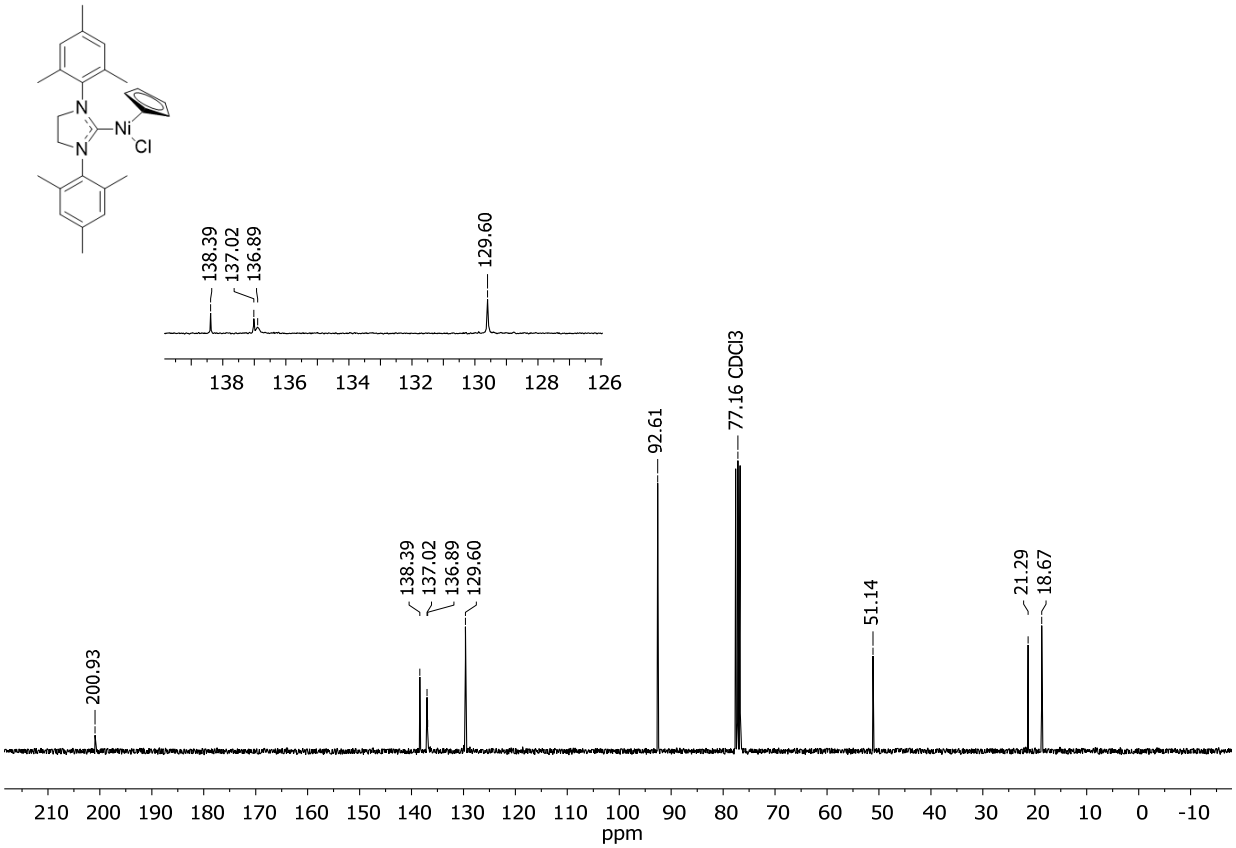


Figure S28. ^{13}C NMR spectrum of compound **2n** ($CDCl_3$, 75 MHz)

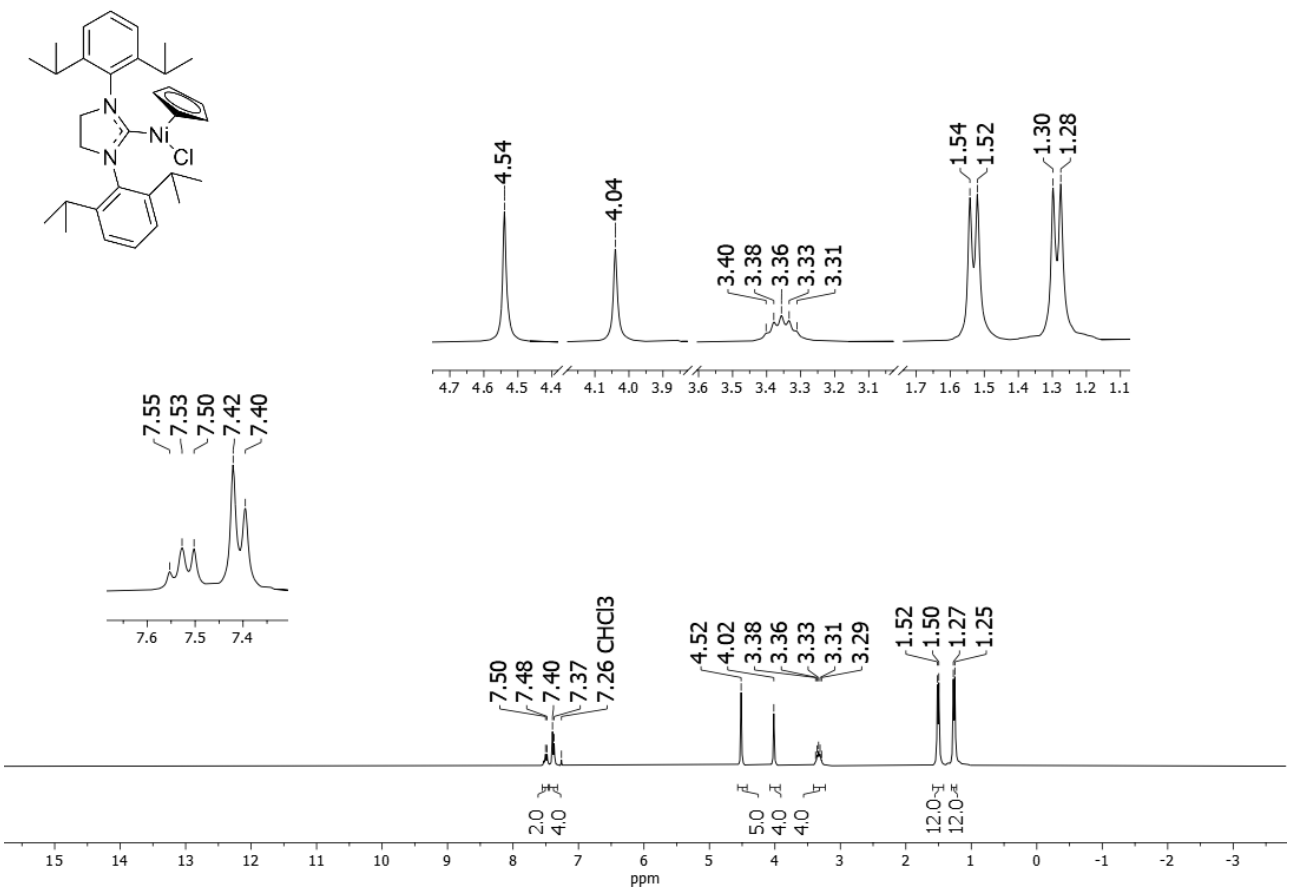


Figure S29. ^{1}H NMR spectrum of compound **2o** ($CDCl_3$, 300 MHz)

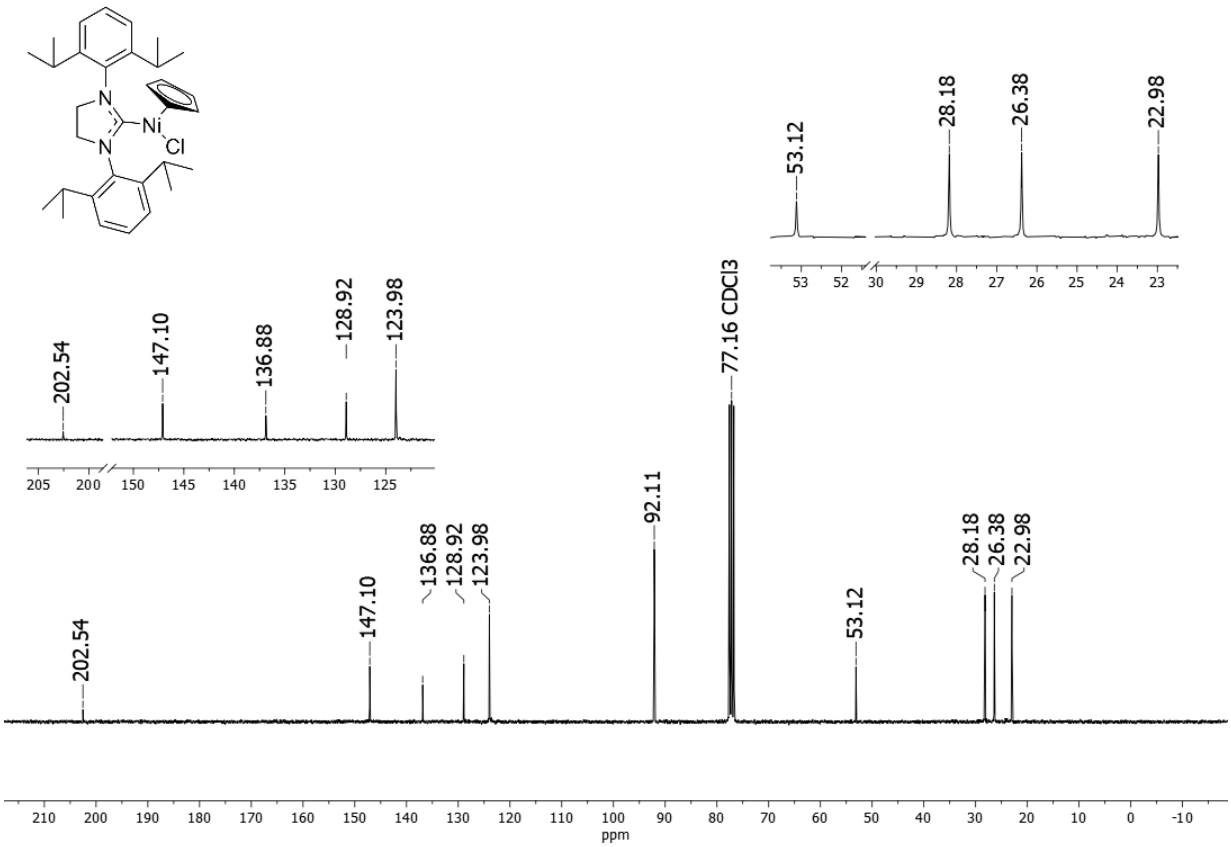


Figure S30. ^{13}C NMR spectrum of compound **2o** ($CDCl_3$, 75 MHz)

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