

Supplementary Information for:

Merrifield Resin-Assisted Routes to Second-Generation Catalysts for Olefin

Metathesis

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S1. NMR Spectra for Second-Generation Catalysts Synthesized with Merrifield-Iodide Resin

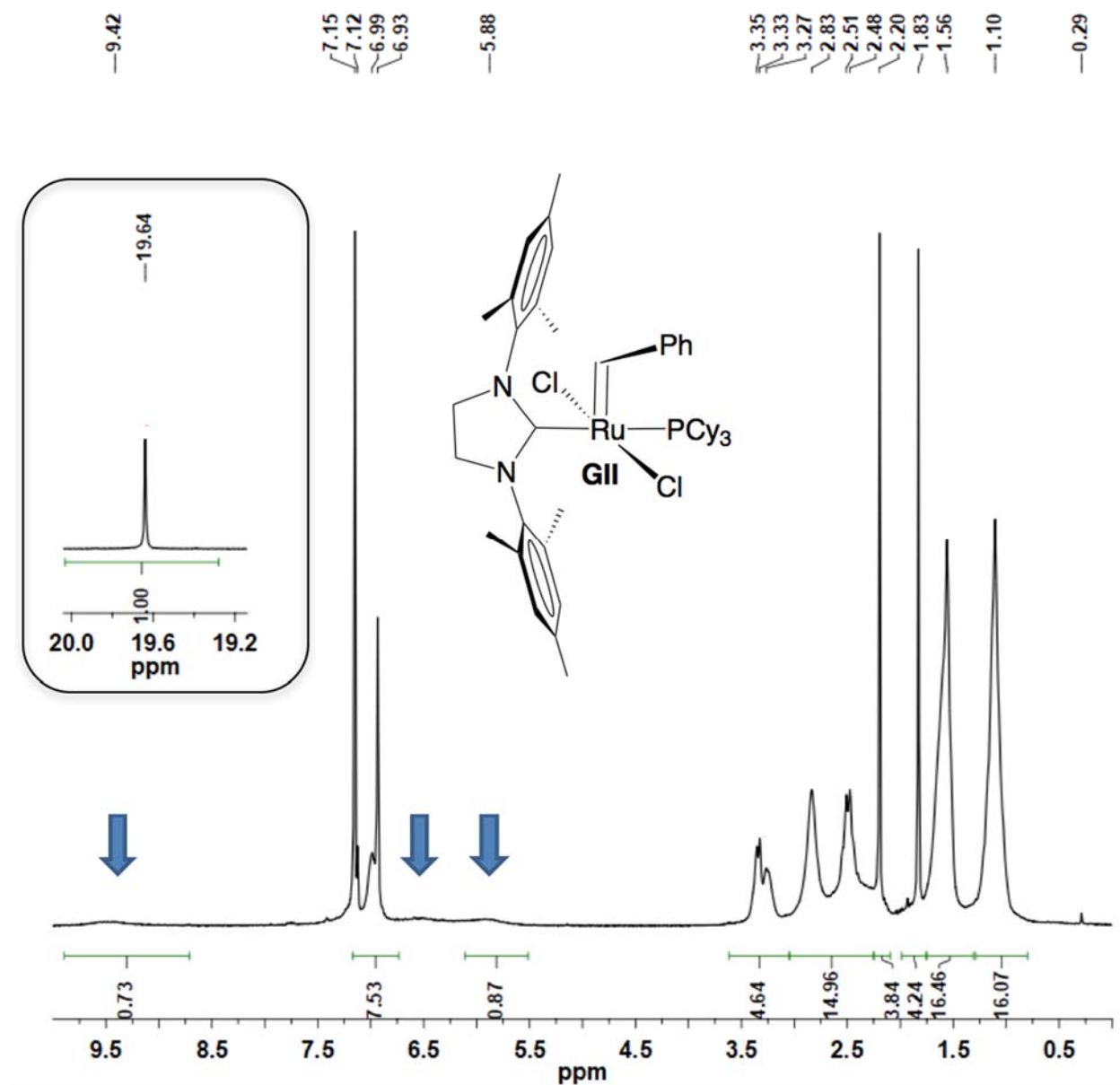


Figure S1a. ^1H NMR spectrum (C₆D₆, 300 MHz) of **GII**, prepared from **GI** by ligand exchange and worked up using **MF-I** to scavenge free PCy_3 . Arrows denote the broad signals arising from rotation of the aromatic rings.

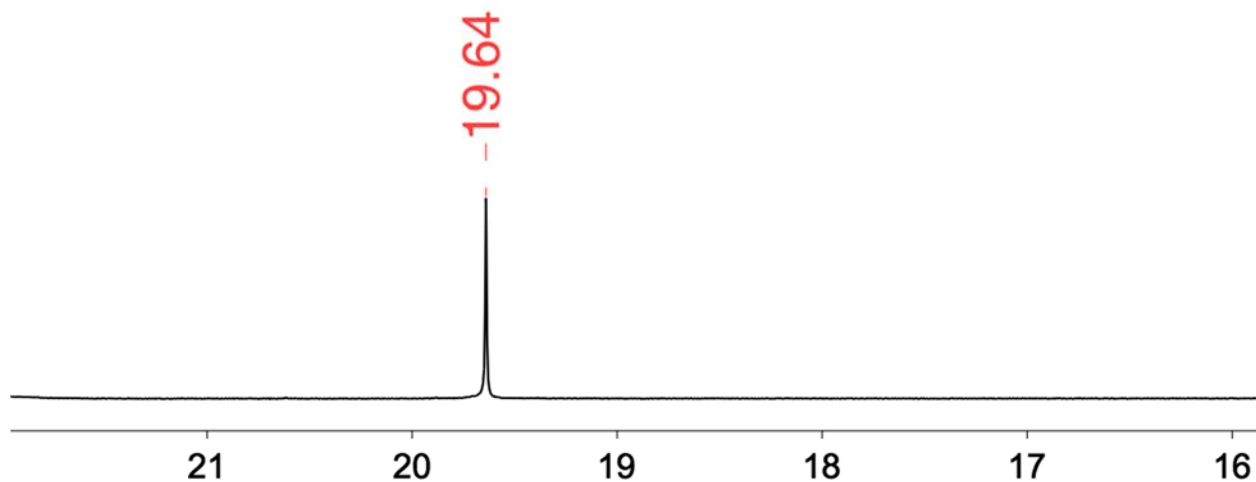


Figure S1b. Expanded alkydine region for the spectrum of Fig. S1a, showing the absence of additional signals.

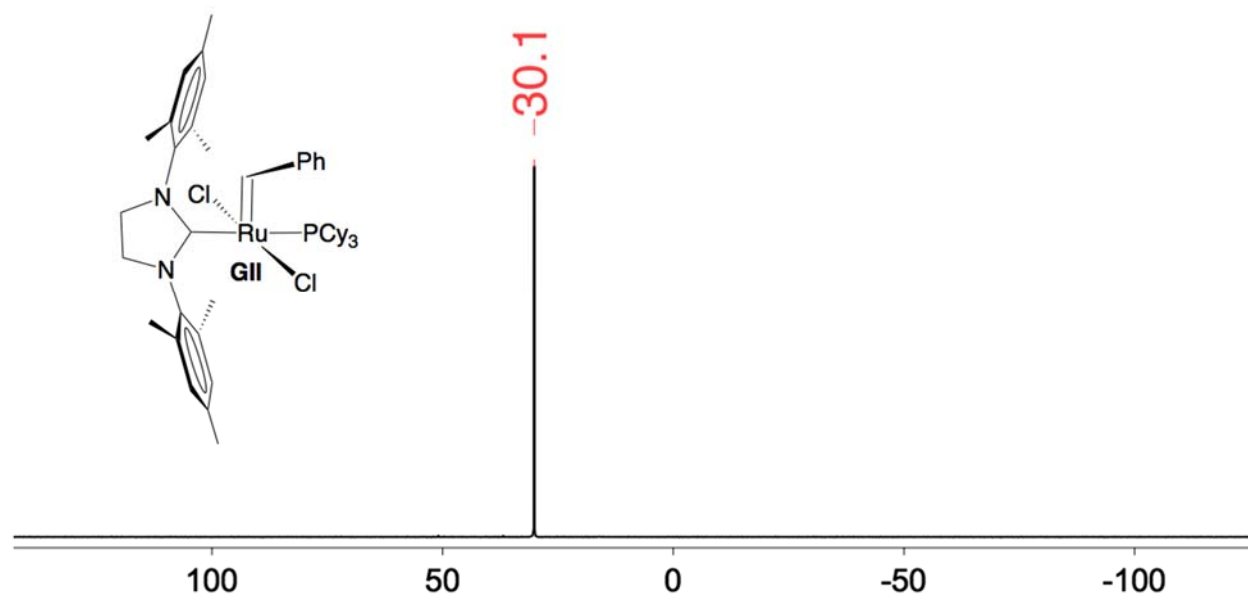


Figure S1c. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 121.2 MHz) of **GI**, prepared from **GI** by ligand exchange and worked up using **MF-I** to scavenge free PCy_3 .

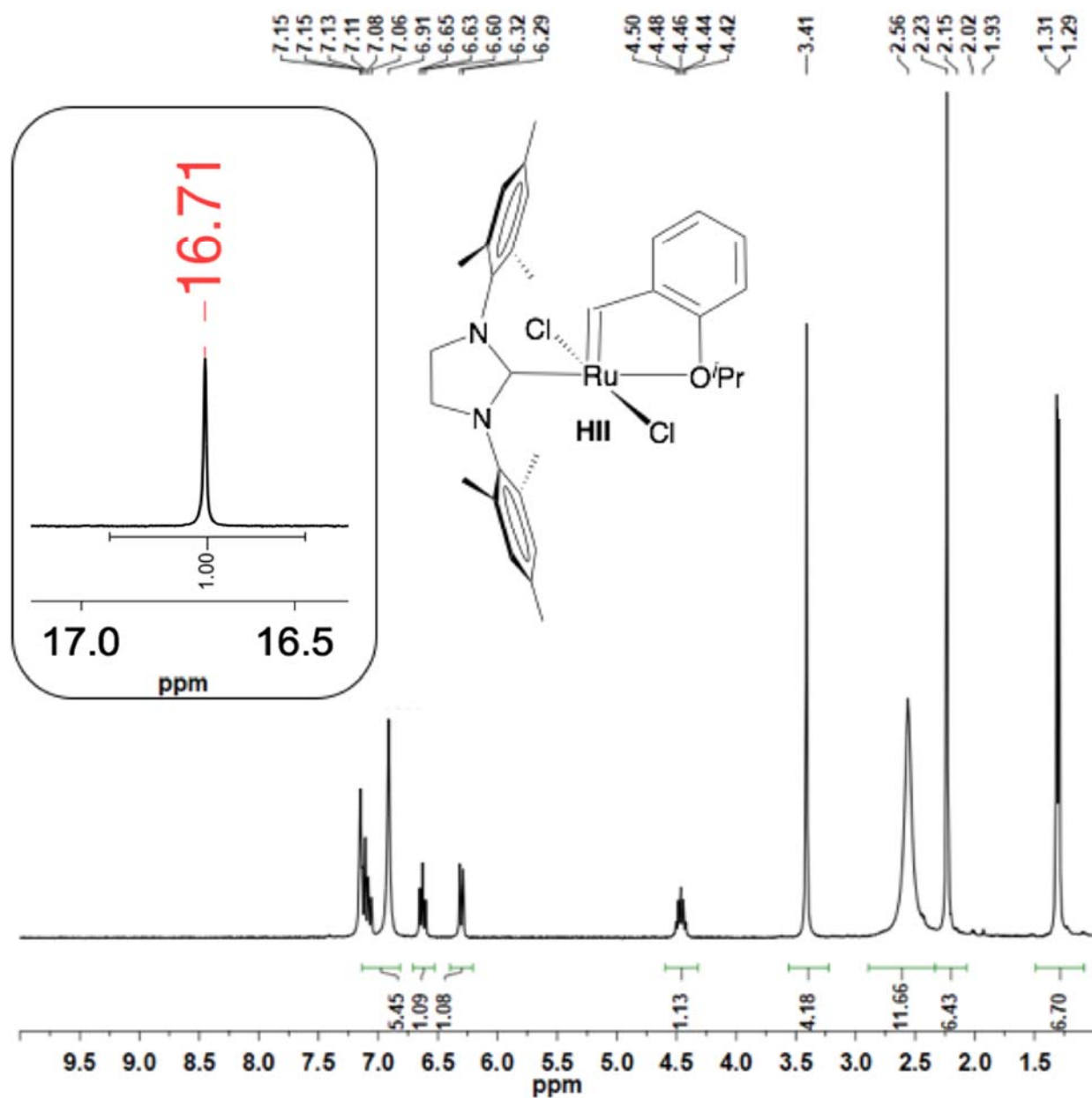


Figure S2a. ^1H NMR spectrum (C_6D_6 , 300 MHz) of **HII**, prepared from **HI** by ligand exchange and worked up using **MF-I** to scavenge free PCy_3 .

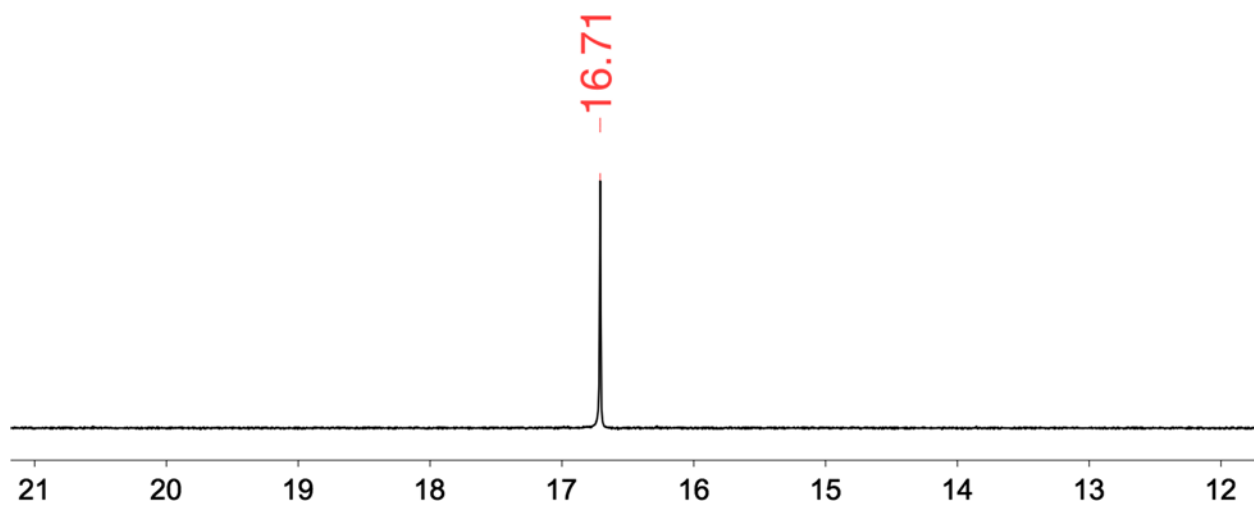


Figure S2b. Full alkydene region for the spectrum of Fig. S2a, showing the absence of additional signals.

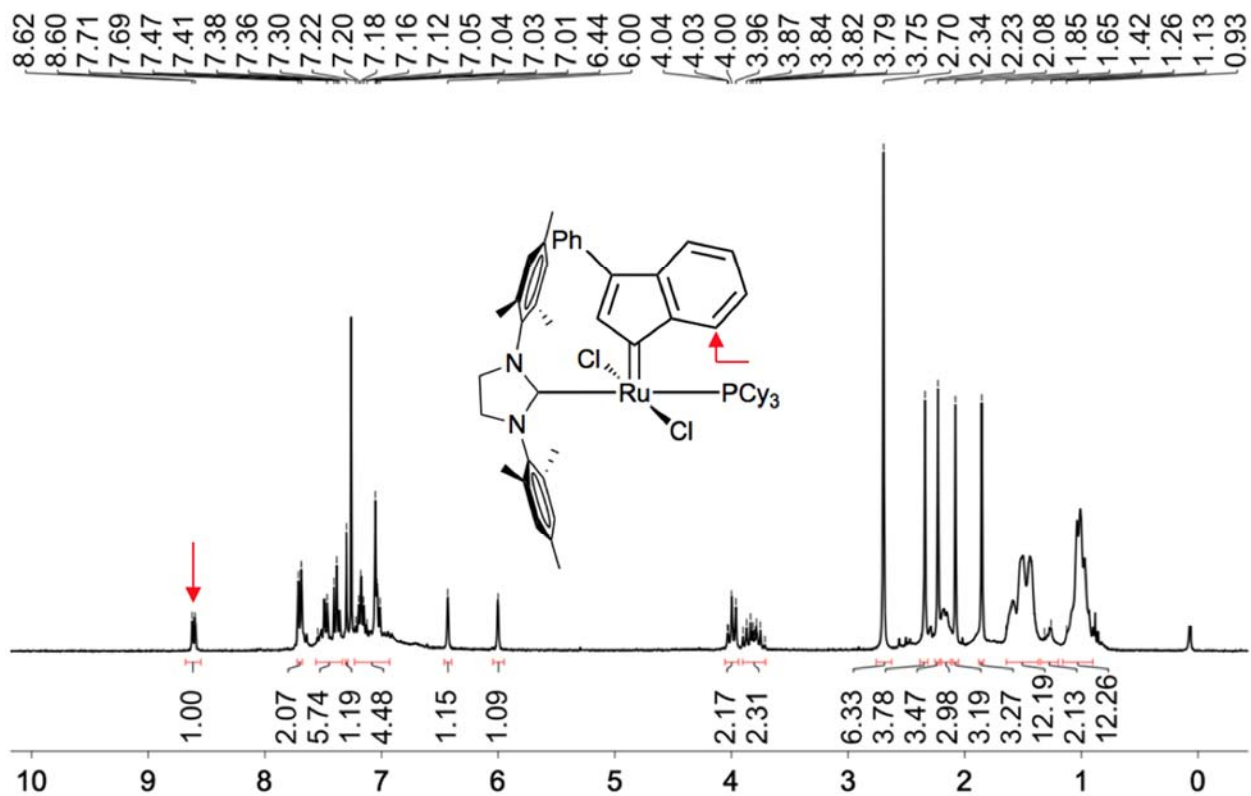


Figure S3a. ¹H NMR spectrum (CDCl₃, 300 MHz) of **InII**, prepared from **InI** by ligand exchange and worked up using **MF-I** to scavenge free PCy₃. Arrow indicates the location of the proton used to confirm the stability of **InII** in decomposition experiments.

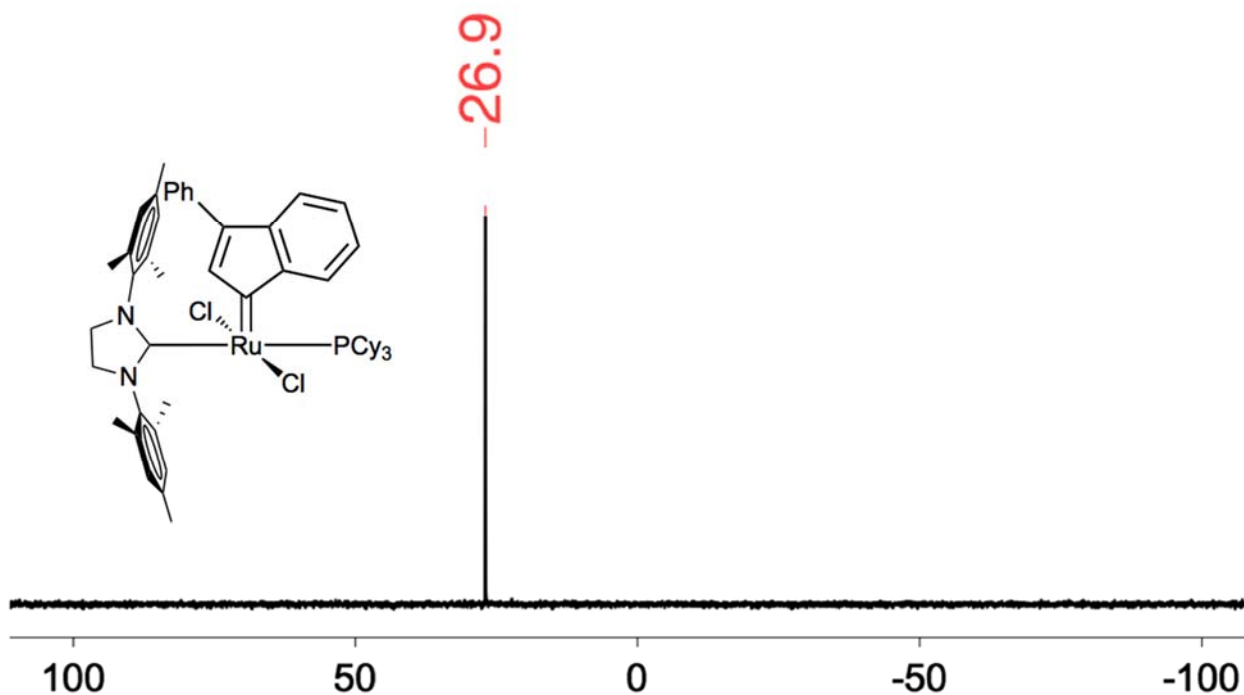


Figure S3b. ³¹P{¹H} NMR spectrum (CDCl₃, 121.2 MHz) of **InII**, prepared from **InI** by ligand exchange and worked up using **MF-I** to scavenge free PCy₃.

S2. NMR Spectra of Isotopically-Labelled Imidazolium Salts.

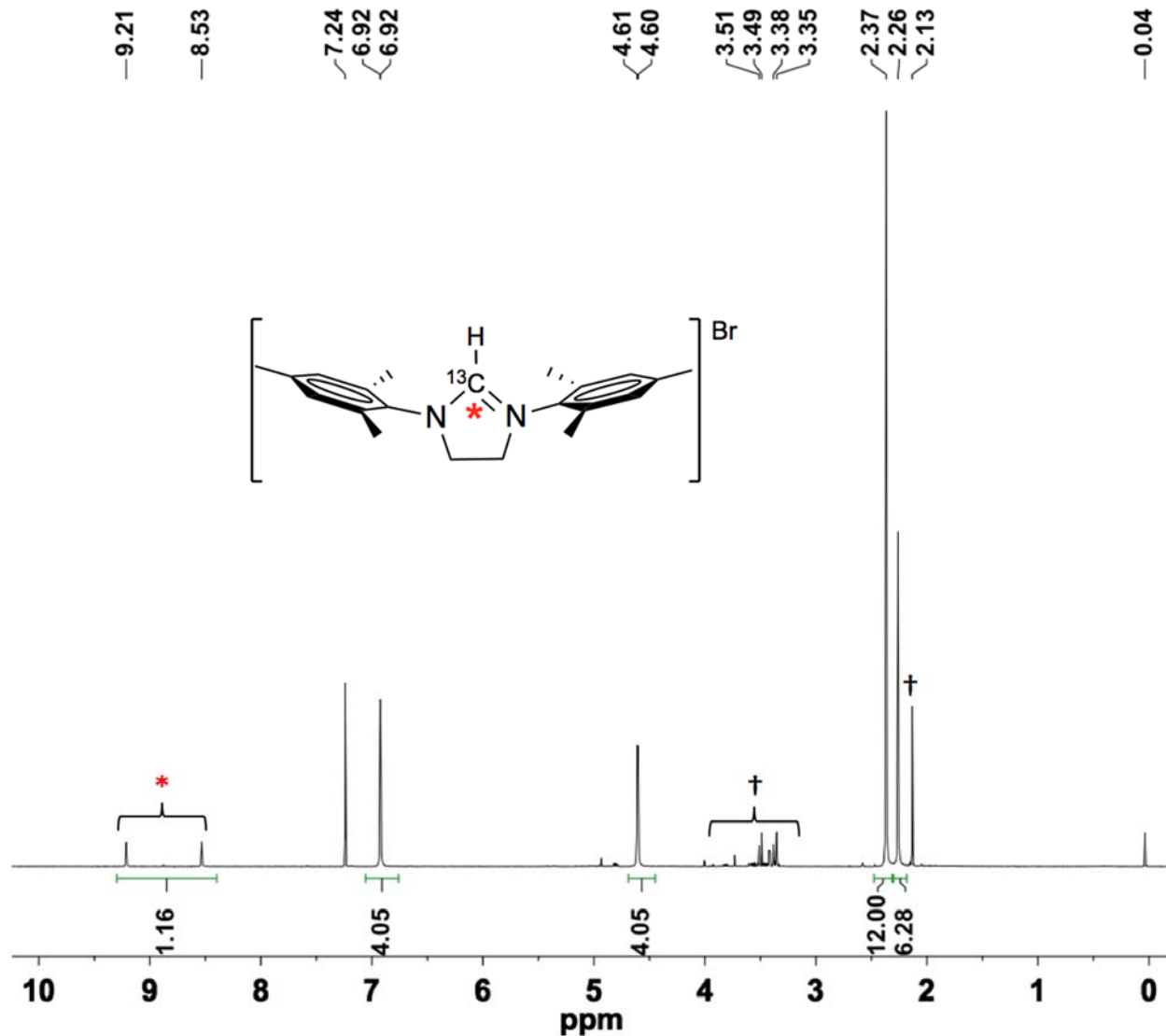


Figure S4a. ¹H NMR spectrum (300 MHz, CDCl₃) of ¹³C-H₂IMes·HBr (* = ¹³CH doublet showing ¹J_{CH} coupling of 204 Hz; †) = solvent and *N*-bromosuccinimide impurities removed in the next step).

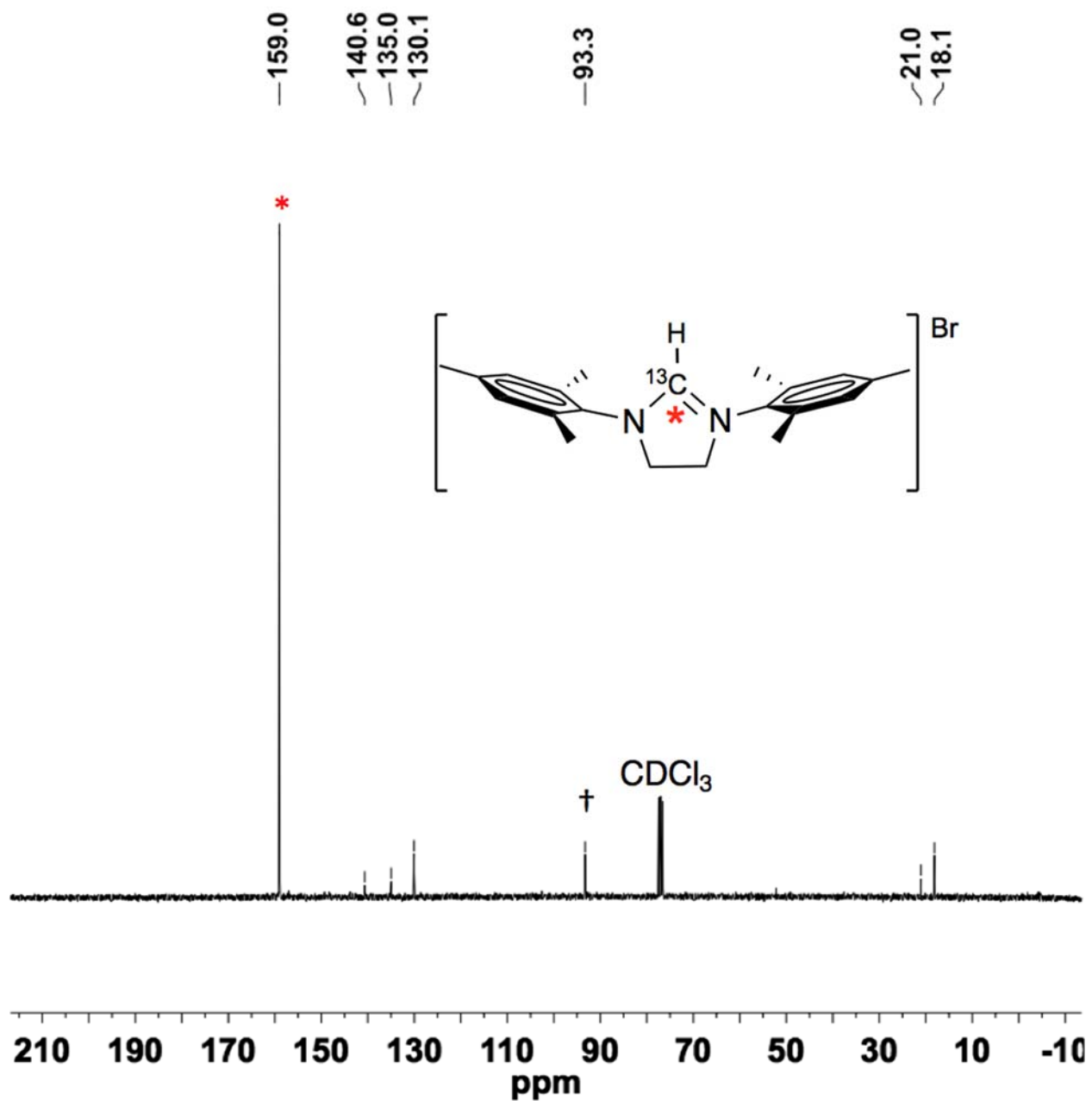


Figure S4b. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 75.5 MHz) of $^{13}\text{C}\text{-H}_2\text{IMes}\cdot\text{HBr}$ (* = ^{13}C -labelled carbon). (†) designates unidentified impurity.

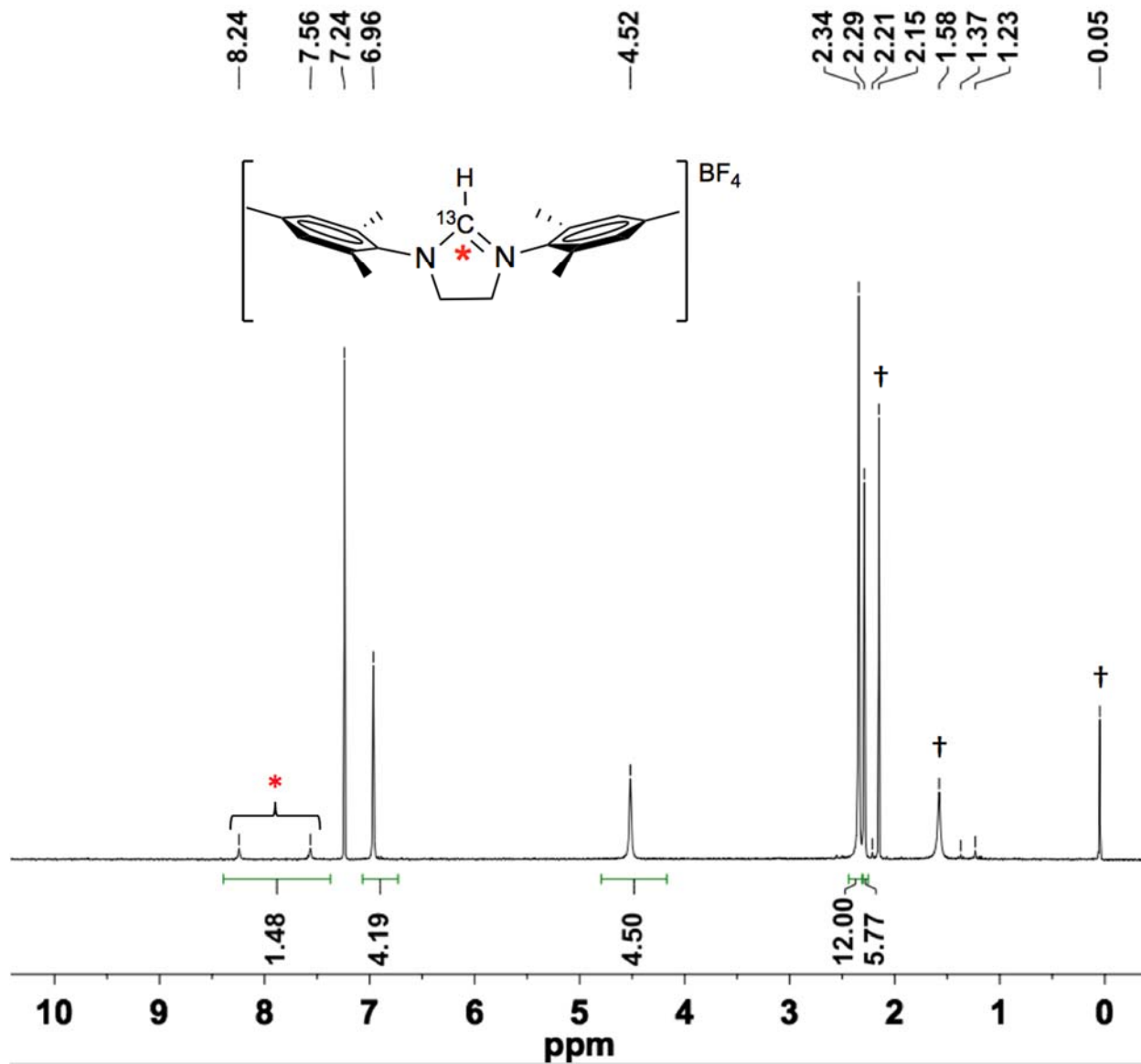


Figure S5a. ^1H NMR spectrum (300 MHz, CDCl_3) of $^{13}\text{C}\text{-H}_2\text{IMes}\cdot\text{HBF}_4$ (* = ^{13}CH doublet showing $^1J_{\text{CH}}$ coupling of 205 Hz; (†) = acetone, water, and silicon grease impurities).

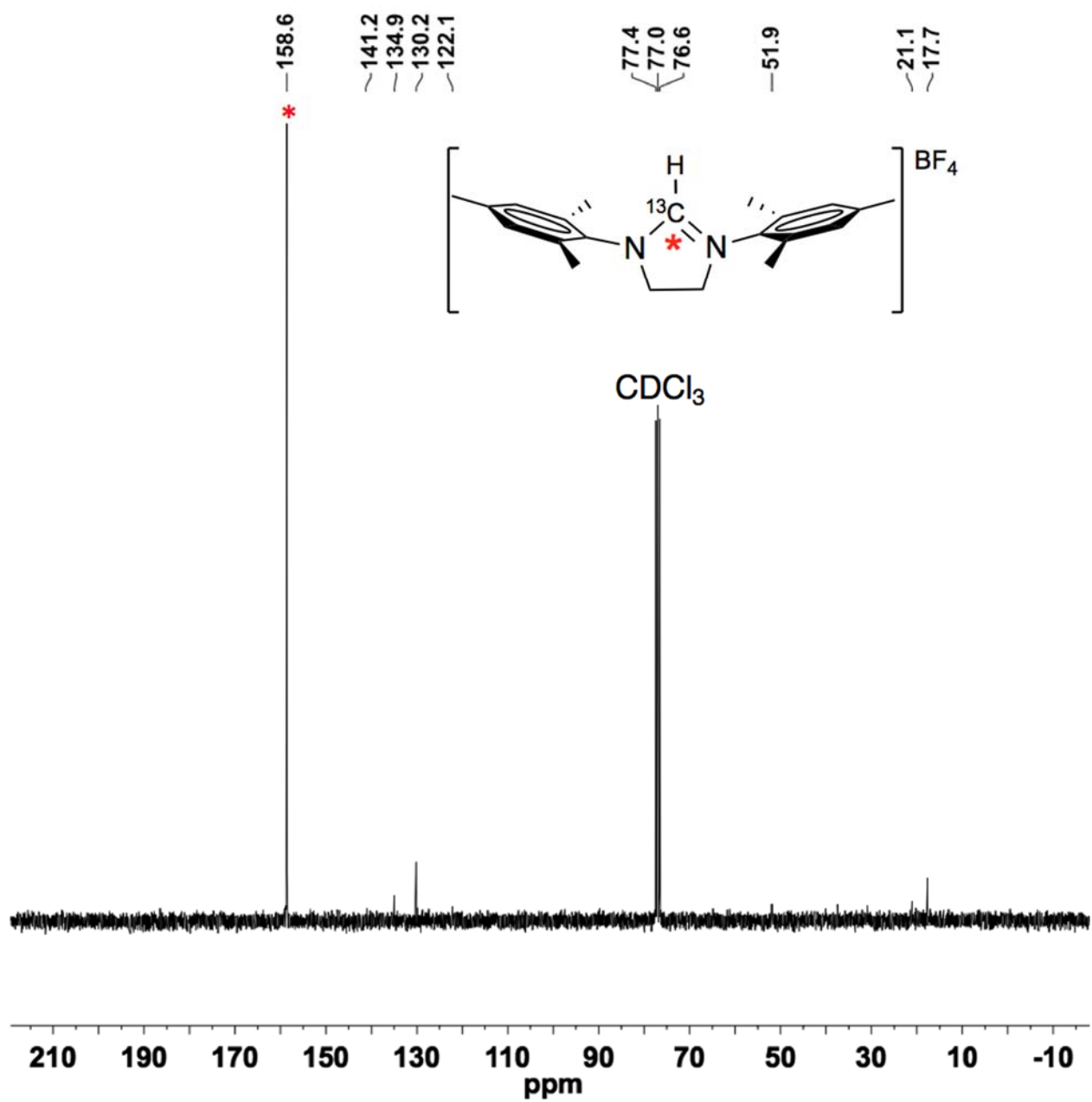


Figure S5b. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 75.5 MHz) of $^{13}\text{C}\text{-H}_2\text{IMes}\cdot\text{HBF}_4$ (* = ^{13}C -labelled carbon).

S3. NMR Spectra of New Labelled Ligands and Complexes

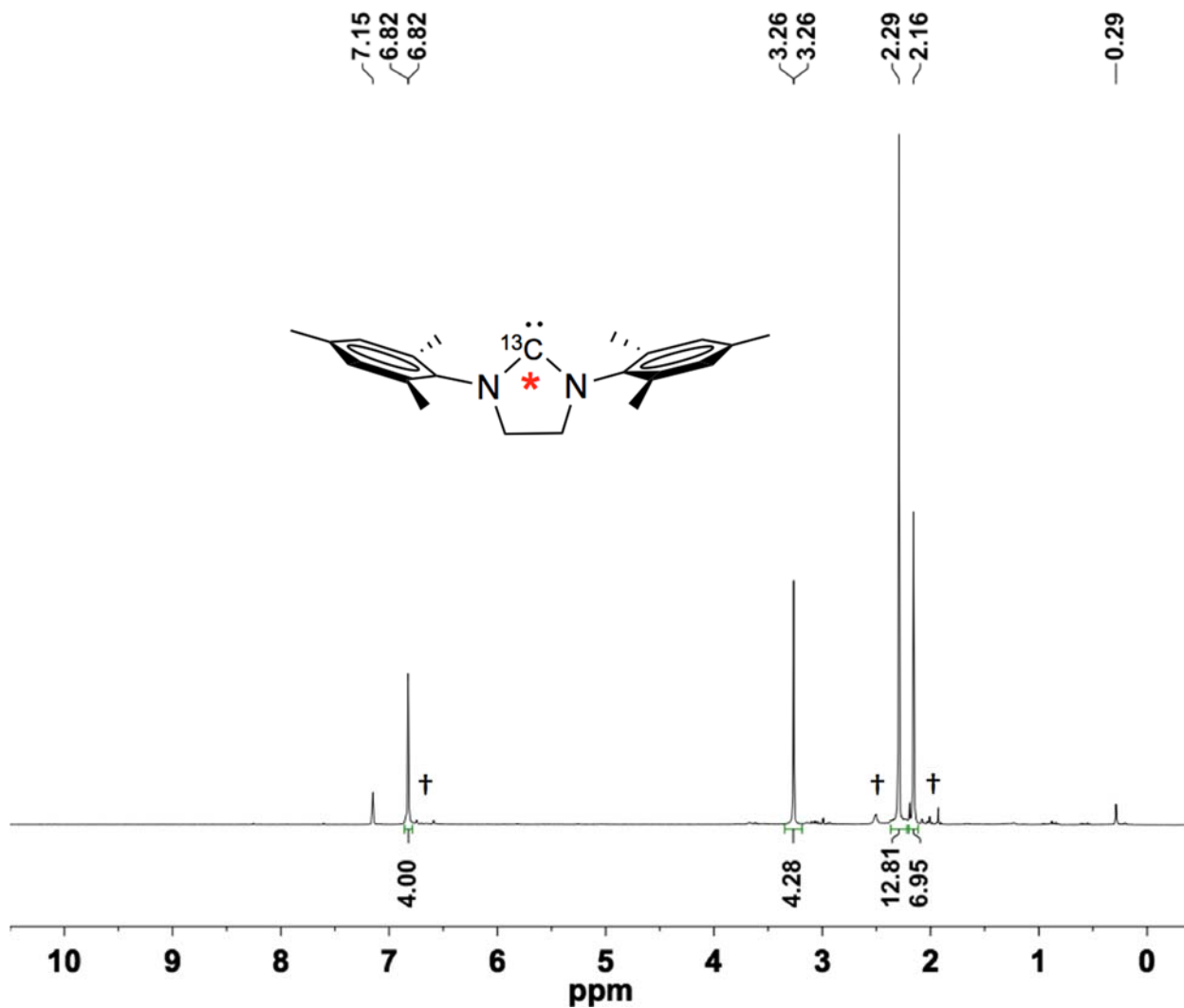


Figure S6a. ¹H NMR spectrum (C₆D₆, 300 MHz) of free ¹³C-H₂IMes; (†) = impurity generated by hydrolysis from residual water in deuterated solvent: see text and Scheme 2e.

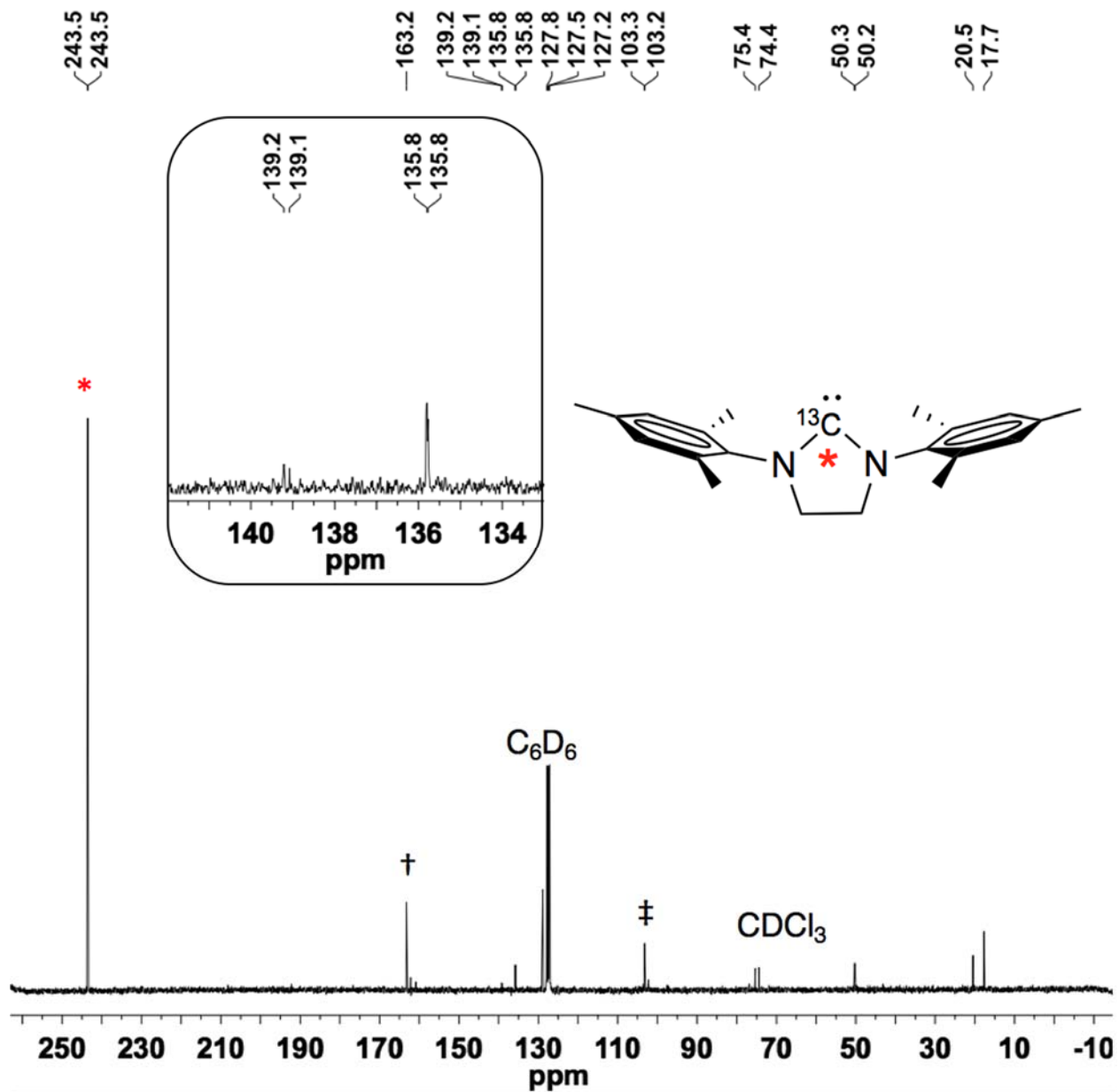


Figure S6b. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 75.5 MHz) of $^{13}\text{C}\text{-H}_2\text{IMes}$ (* = ^{13}C -labelled carbon; (†) = impurity generated by hydrolysis from residual water in deuterated solvent: see text and Scheme 2e. (‡) = unidentified impurity).

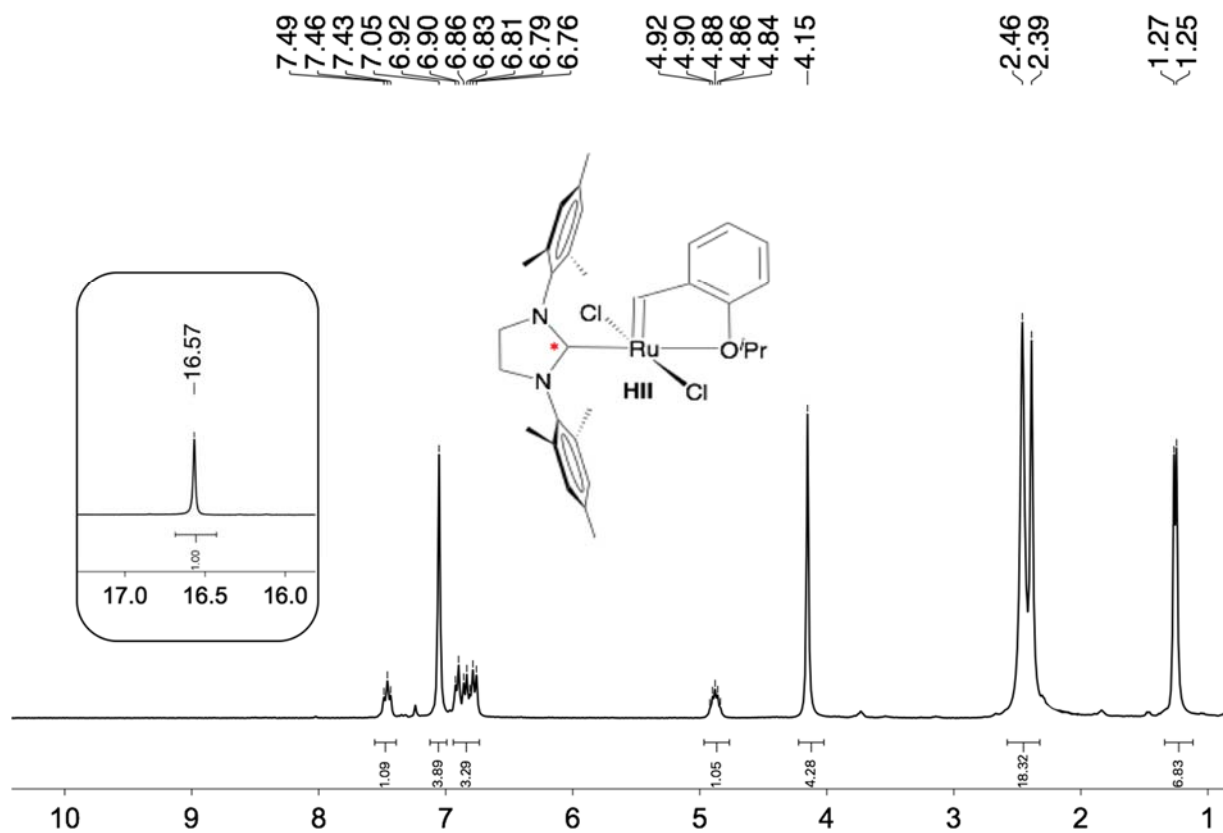


Figure S7a. ^1H NMR spectrum (CDCl₃, 300 MHz) of ^{13}C -HII (* = ^{13}C -labelled carbon).

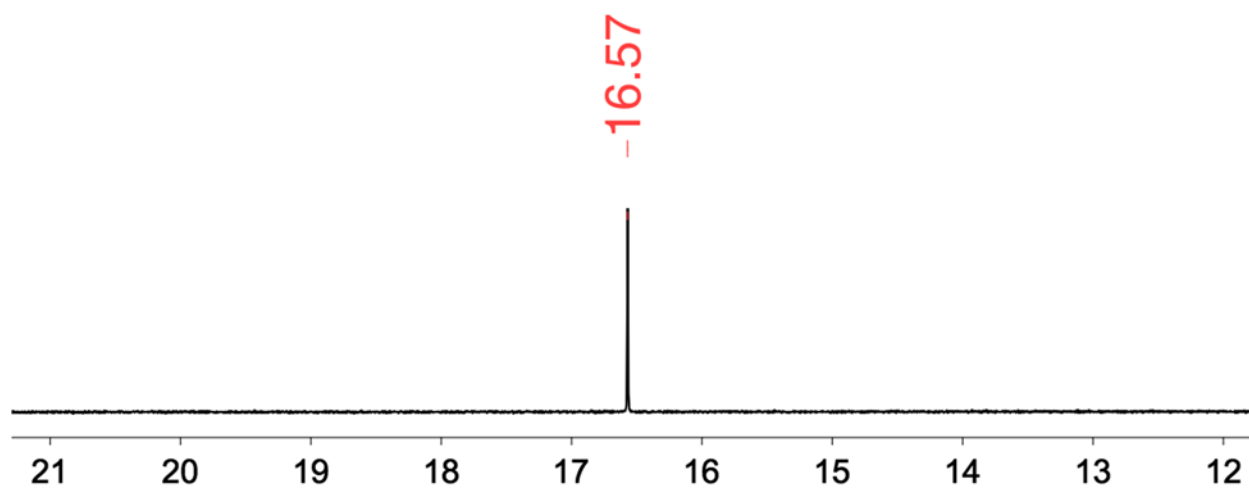


Figure S7b. Full alkylidene region for the spectrum of Fig. S7a, showing the absence of additional signals.

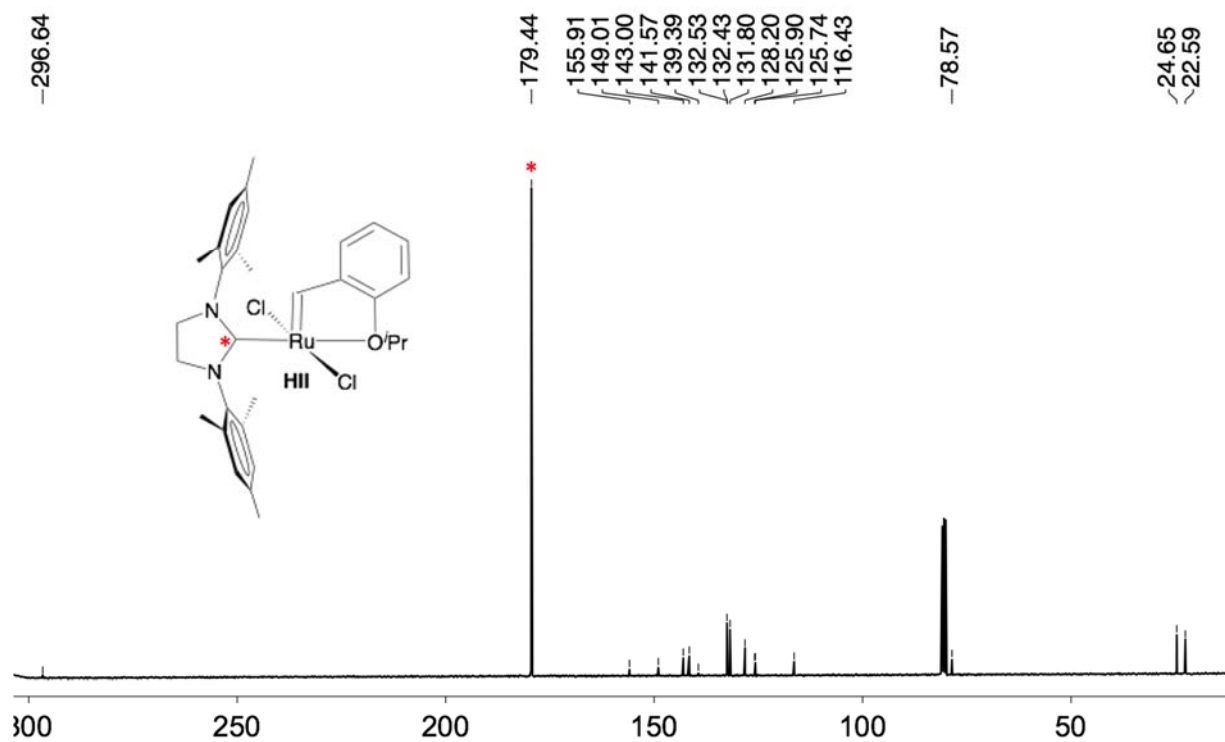


Figure S7c. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 75.5 MHz) of ^{13}C -HII (* = ^{13}C -labelled carbon).

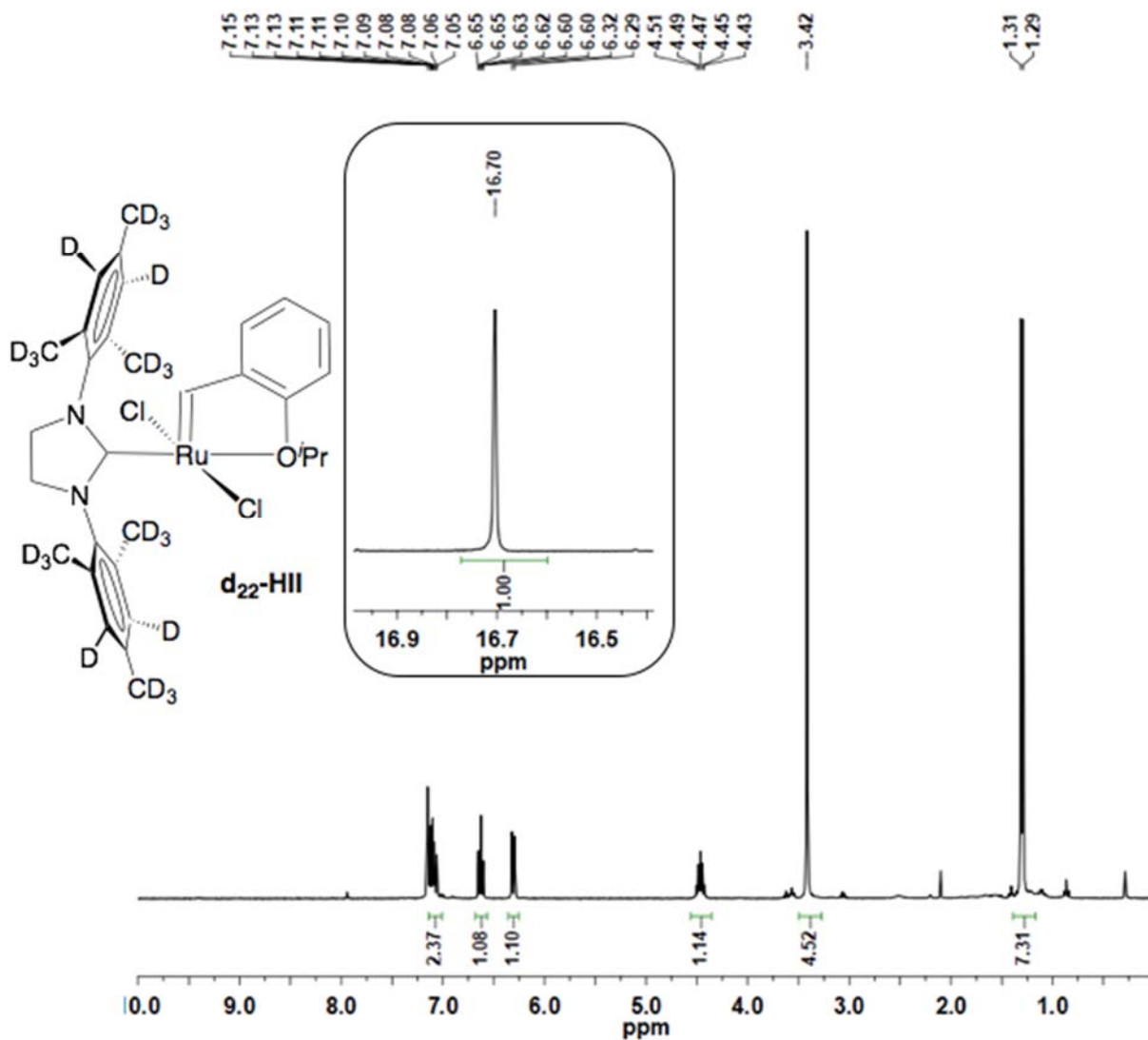


Figure S8a. ^1H NMR spectrum (C_6D_6 , 300 MHz) of $\text{d}_{22}\text{-HII}$.

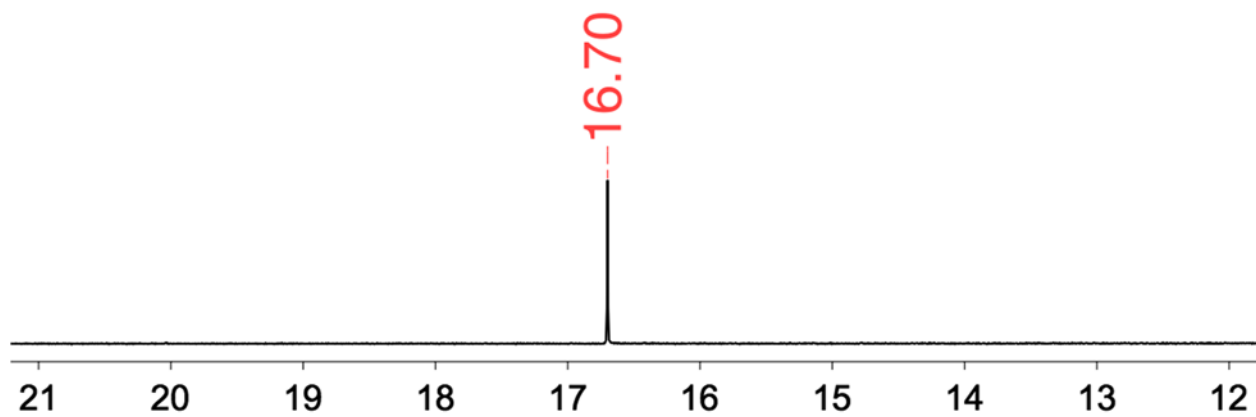


Figure S8b. Full alkylidene region for the spectrum of Fig. S8a, showing the absence of additional signals.

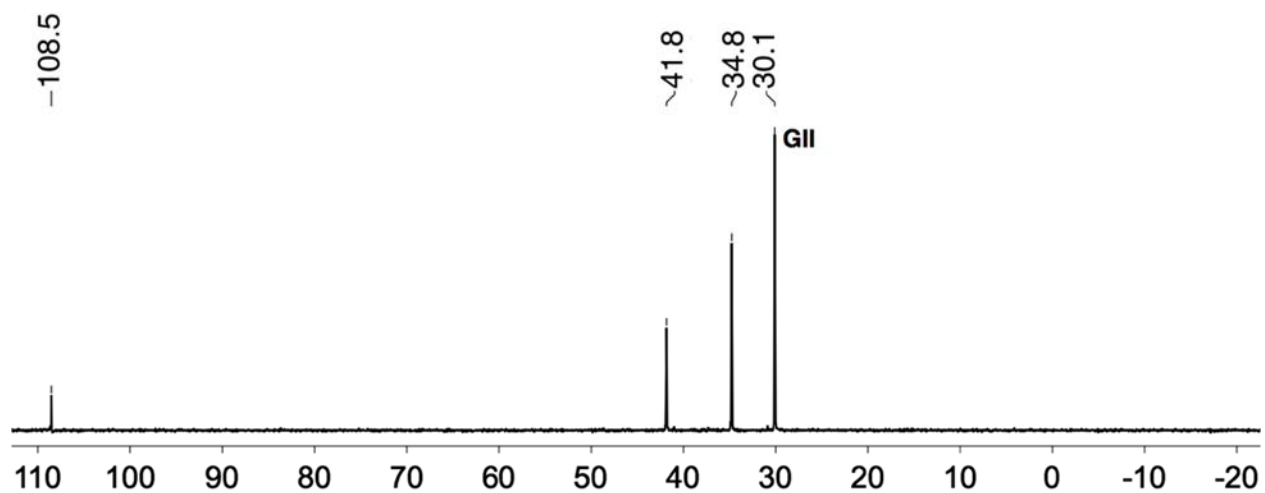


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 121.2 MHz) showing impurities present in a sample of **GII** prepared via Amberlyst-15 workup, using resin stored in the glovebox.