Supplementary Information for:

Targeting an Achilles Heel in Olefin Metathesis: A Strategy for High-Yield Synthesis of Second-Generation Grubbs Methylidene Catalysts

Justin A.M. Lummiss,[a] Nicholas J. Beach,[a] Jeffrey C. Smith[b] and Deryn E. Fogg*[a]

[a] *Department of Chemistry and Centre for Catalysis Research & Innovation, University of Ottawa, Ottawa, Ontario, Canada. Tel: 613-562-5800 ext. 6057; E-mail: dfogg@uottawa.ca*

[b] *Department of Chemistry, Carleton University, Ottawa, Ontario, Canada.*

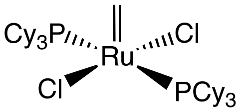
Contents:

1. Experimental Details

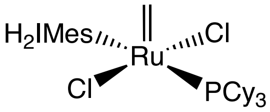
General Procedures. Reactions were carried out under N_2 using standard Schlenk and glove-box techniques. Dry, oxygen-free C_6H_6, CH_2Cl_2 and hexanes were obtained using a Glass Contour solvent purification system. Pentane was distilled over sodium benzophenone, acetone over calcium sulphate. All solvents were stored under N_2 over Linde 4 Å molecular sieves. C_6D_6 was purchased in 1-gram ampoules packed under N_2 (Cambridge Isotopes). Given the documented reactivity of free carbenes with even traces of water,[1,2] NMR spectra of free carbenes were measured in C_6D_6 that had been dried over 4 Å molecular sieves in an N_2-filled glove box for at least 4 h. Ethylene (BOC Ultra-High Purity Grade 3.0; 99.9%) was used as received. Free IMes,[3] H_2IMes•HBF_4,[4] and **GI**[5] were prepared by literature methods. Free H_2IMes was obtained from Strem or prepared by literature methods.[6] As a precautionary measure, all samples of free NHCs were dissolved in benzene and filtered through Celite to remove any potential contaminants (such as unconverted imidazolinium salt or residual base remaining from the deprotection procedure), prior to storage at -35 °C under N_2.

NMR spectra were recorded on a Bruker Avance 300 or 500 MHz spectrometer at 298 K, and referenced to the residual proton or carbon signals of the deuterated solvent (^{1}H, ^{13}C NMR). Signals are reported in ppm, relative to TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P) at 0 ppm. The kinetics of ligand exchange between **GI=CH$_2$** and free H_2IMes or IMes were monitored in the NMR probe at 60 °C. ^{1}H NMR data (and ^{31}P{^{1}H} NMR data, where applicable) for known compounds are provided for convenience; in some cases the NMR solvent differs from that in the literature report.

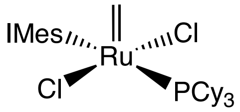
A) Identification of H_2IMes•H^+. Traces of the unconverted imidazolinium salt were observed in one batch of free H_2IMes. Any such contaminant is readily removed by the protocol described in the General Procedures above. A sample of the salt was isolated for the purposes of identification by filtering a benzene solution of (predominantly) H_2IMes through a fine-frit filter. The identity of the cation was established by electrospray mass spectrometric (ESI-MS) analysis using a QSTAR XL hybrid quadrupole time-of-flight mass spectrometer (AB Sciex, Framingham, MA) equipped with a nanoelectrospray ionization source, operating in positive ion mode. ESI-MS (aq. 33% MeCN + aq. 0.1% formic acid), *m/z*: Calcd $[C_{21}H_{27}N_2]^+$ (H_2IMes•H^+), 307.2169; Found, 307.2177.



B) Synthesis of GI=CH$_2$. In a modified version of the reported procedure,[5] a 100 mL Schlenk tube was charged with solid **GI** (1.00 g, 1.22 mmol) and 25 mL C_6H_6 in a glovebox, and equipped with a fritted gas-dispersion tube. (Benzene was chosen as reaction solvent, in preference to the CH_2Cl_2 used in the literature report, as we found that it afforded higher yields). To maintain saturation, a very slow flow of ethylene was passed through the stirred solution via the gas-dispersion frit, and vented to the box atmosphere through the open stopcock. A colour change from purple to brown was observed within 15 min. After 45 min, the solvent was stripped off under vacuum to afford a pink solid, which was washed with cold pentane (2 × 2 mL; –35 °C), cold acetone (2 × 1 mL), and again with cold pentane (2 × 2 mL). NMR analysis of the light pink powder revealed ca. 5% residual **GI**. The crude product was re-subjected to reaction with ethylene and isolated as before to afford clean **GI=CH$_2$** as a light pink powder. Yield: 769 mg (85%). NMR spectra were measured in C_6D_6: signals are shifted slightly relative to the reported[5] values in CD_2Cl_2, but are otherwise in good agreement. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 43.5 ppm (s, *P*Cy$_3$). ^1H NMR (300.1 MHz, C_6D_6): δ 19.42 (s, 2H, Ru=C*H*$_2$), 2.77-2.61 (m, 6H, Cy), 2.08-1.88 (m, 12H, Cy), 1.85-1.49 (m, 30H, Cy), 1.38-1.13 (m, 18H, Cy).



C) Synthesis of GII=CH$_2$. In the glovebox, light pink **GI=CH$_2$** (150 mg, 0.200 mmol) was dissolved in 10 mL C_6H_6 in a 50 mL Schlenk tube. Free H_2IMes (75 mg, 0.245 mmol) was added as a white crystalline powder. The Schlenk tube was removed to a vacuum line and heated to 60 °C for 45 min under Ar. The solution changed colour from pink to yellow-brown within 15 min. The solvent was removed under vacuum to yield a yellow solid, which was washed with cold pentane (3 × 2 mL; glovebox) to yield **GII=CH$_2$** as a fine yellow powder. Yield: 125 mg (81%). NMR spectra are in good agreement with the reported[7] values. $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): δ 38.2 ppm (s, *P*Cy$_3$). ^1H NMR (500.1 MHz, C_6D_6): δ 18.42 (s, 2H, Ru=C*H*$_2$), 6.93 (s, 2H, Mes *m*-C*H*), 6.75 (s, 2H, Mes *m*-C*H*), 3.30-3.18 (m, 4H, NC*H*$_2$C*H*$_2$), 2.78 (s, 6H, *o*-C*H*$_3$), 2.56 (s, 6H *o*-C*H*$_3$), 2.42-2.29 (m, 3H, Cy), 2.18 (s, 3H, *p*-C*H*$_3$), 2.11 (s, 3H, *p*-C*H*$_3$), 1.70-1.49 (m, 15H, Cy), 1.37-0.95 (m, 15H, Cy).



D) Synthesis of GII'=CH$_2$. Prepared as in (C) above, but using free IMes (as a white crystalline powder). Yield 150 mg (78%) of **GII'=CH$_2$**, a fine yellow powder. $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): δ 40.9 ppm (s, *P*Cy$_3$). ^1H NMR (500.1 MHz, C_6D_6): δ 18.77 (s, 2H, Ru=C*H*$_2$), 6.90 (s, 2H, Mes *m*-C*H*), 6.72 (s, 2H, Mes *m*-C*H*), 6.22 (d, $^3J_{HH}$ = 2 Hz, 1H, NC*H*=), 6.13 (dd, $^3J_{HH}$ = 2 Hz, $^5J_{PH}$ = 1 Hz, 1H, NC*H*=), 2.60 (s, 6H, *o*-C*H*$_3$), 2.37 (s, 6H *o*-C*H*$_3$), 2.44-2.30 (m, 3H, Cy), 2.19 (s, 3H, *p*-C*H*$_3$), 2.12 (s, 3H, *p*-C*H*$_3$), 1.77-1.47 (m, 15H, Cy), 1.30-1.01 (m, 15H, Cy). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 294.5 (d, $^2J_{PC}$ = 12 Hz, Ru=*C*H$_2$), 191.6 (d, $^2J_{PC}$ = 79 Hz, N*C*N), 139.4, 139.0, 138.4, 137.4, 137.0, 135.6, 129.8, 129.4, 124.1 (d, $^4J_{PC}$ = 3 Hz, N*C*H=), 123.6 (s, N*C*H=), 30.9 (d, J_{PC} = 19 Hz, Cy), 29.4 (Cy), 28.2 (d, J_{PC} = 10 Hz, Cy), 26.8 (Cy), 21.34 (*p*-*C*H$_3$), 21.32 (*p*-*C*H$_3$), 19.8 (*o*-*C*H$_3$), 18.9 (*o*-*C*H$_3$). Anal. Calcd. for $C_{40}H_{61}Cl_2N_2PRu$: C, 62.16%; H, 7.96%; N, 3.62%. Found: C, 62.46%; H, 7.59%; N, 3.62%.

2. NMR Spectra

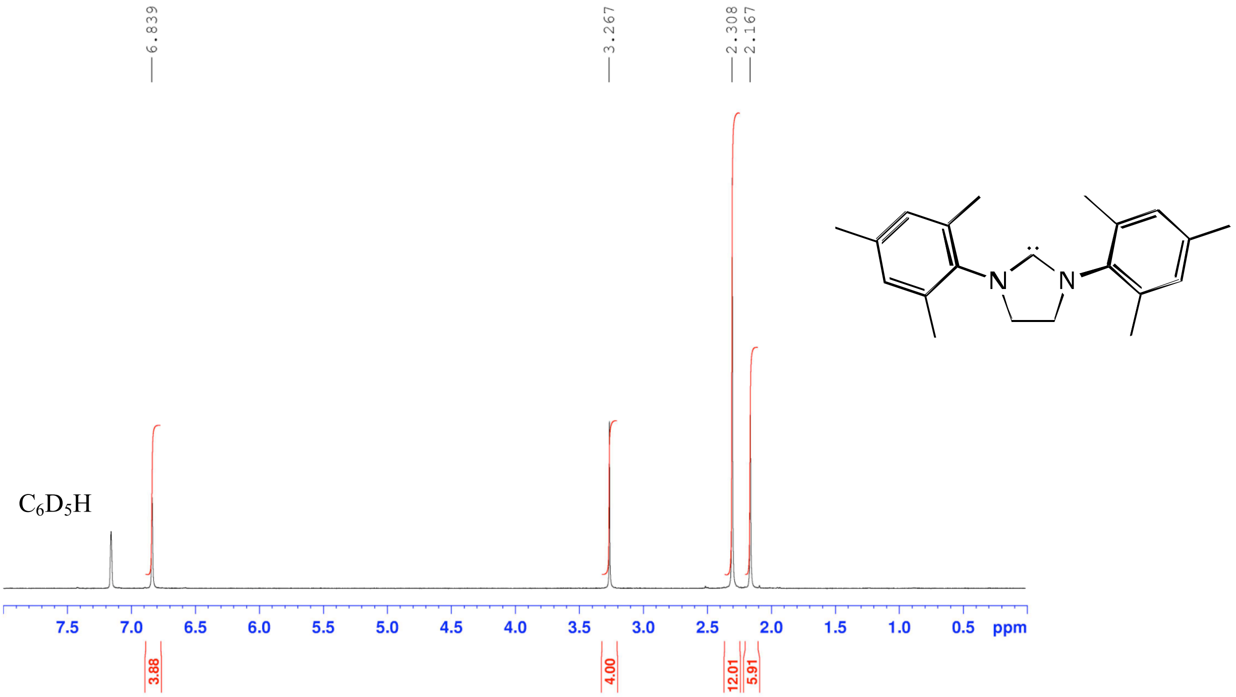


Figure S1a. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of free H_2IMes.

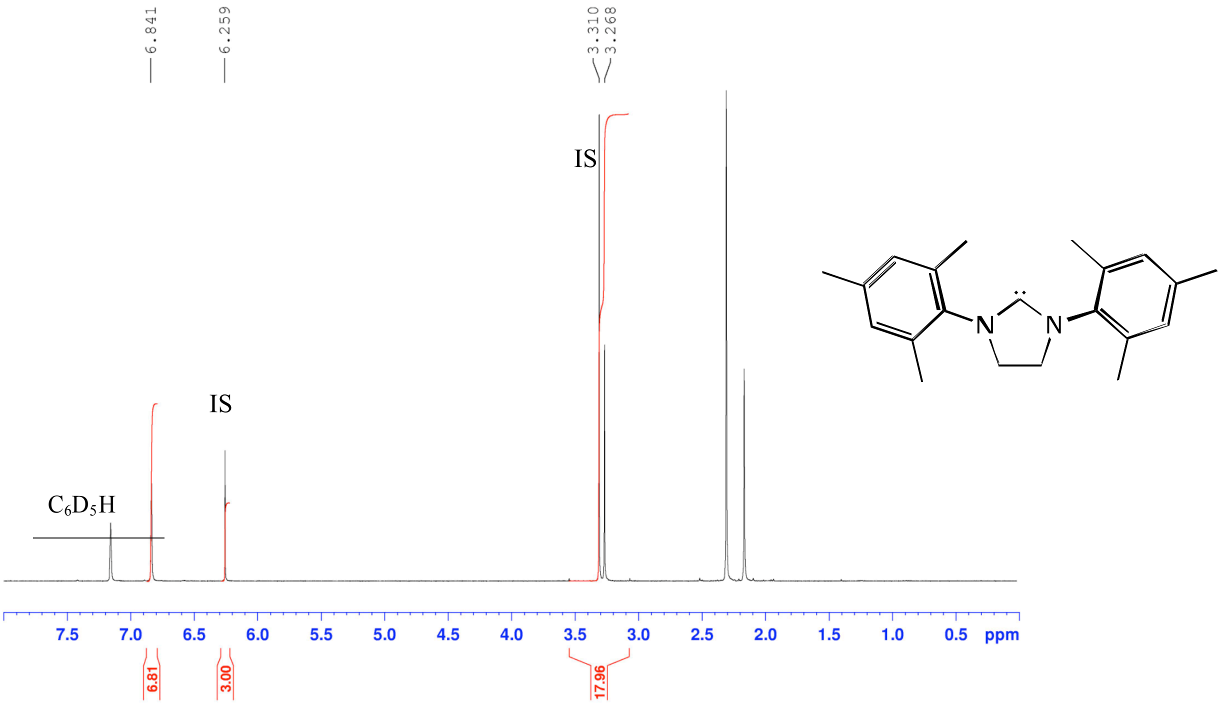


Figure S1b. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of free H_2IMes prior to thermolysis, with TMB present as internal standard (IS).

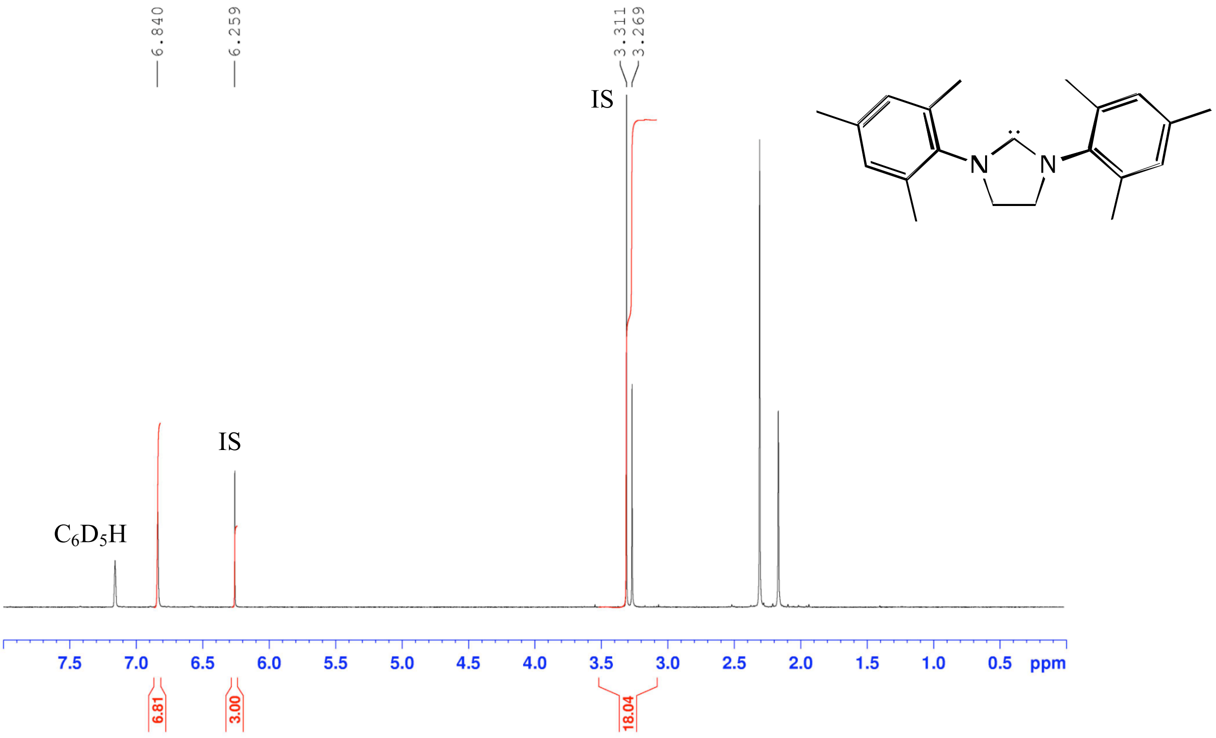


Figure S1c. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of free H_2IMes after thermolysis at 60 °C for 10 h, integrated relative to TMB as internal standard (IS). No detectable decomposition of the free H_2IMes.

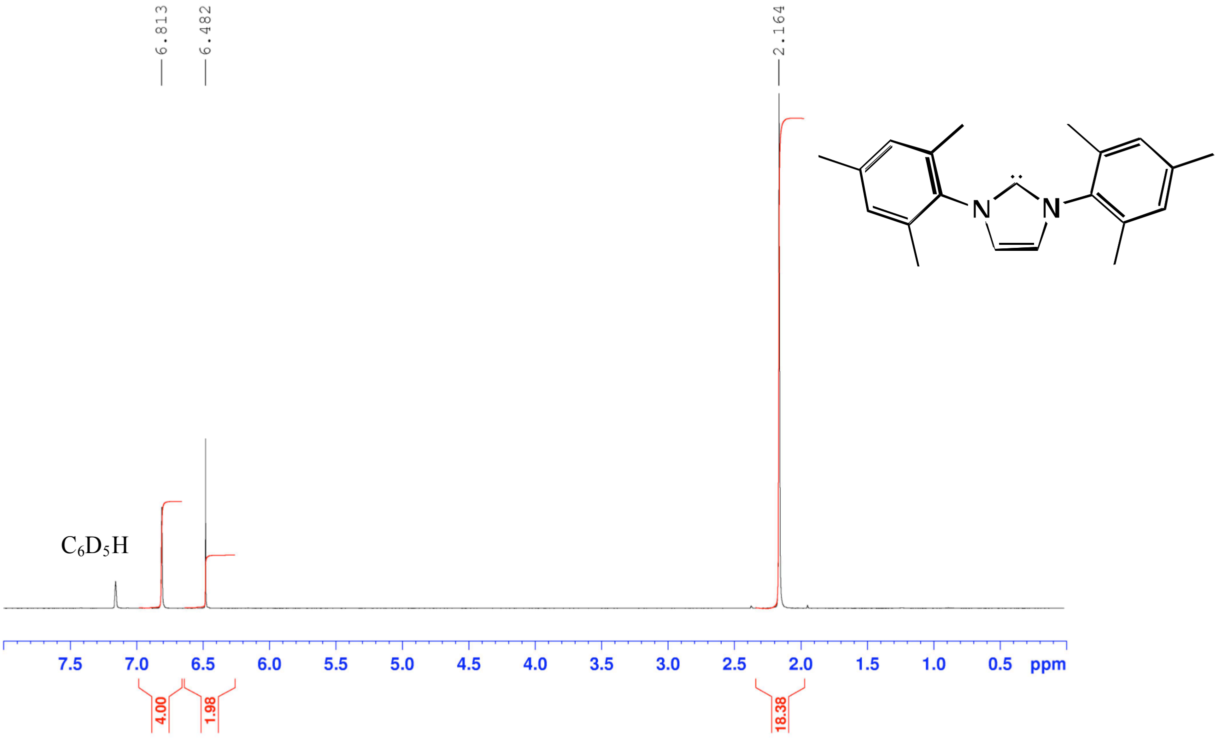


Figure S2a. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of free IMes.

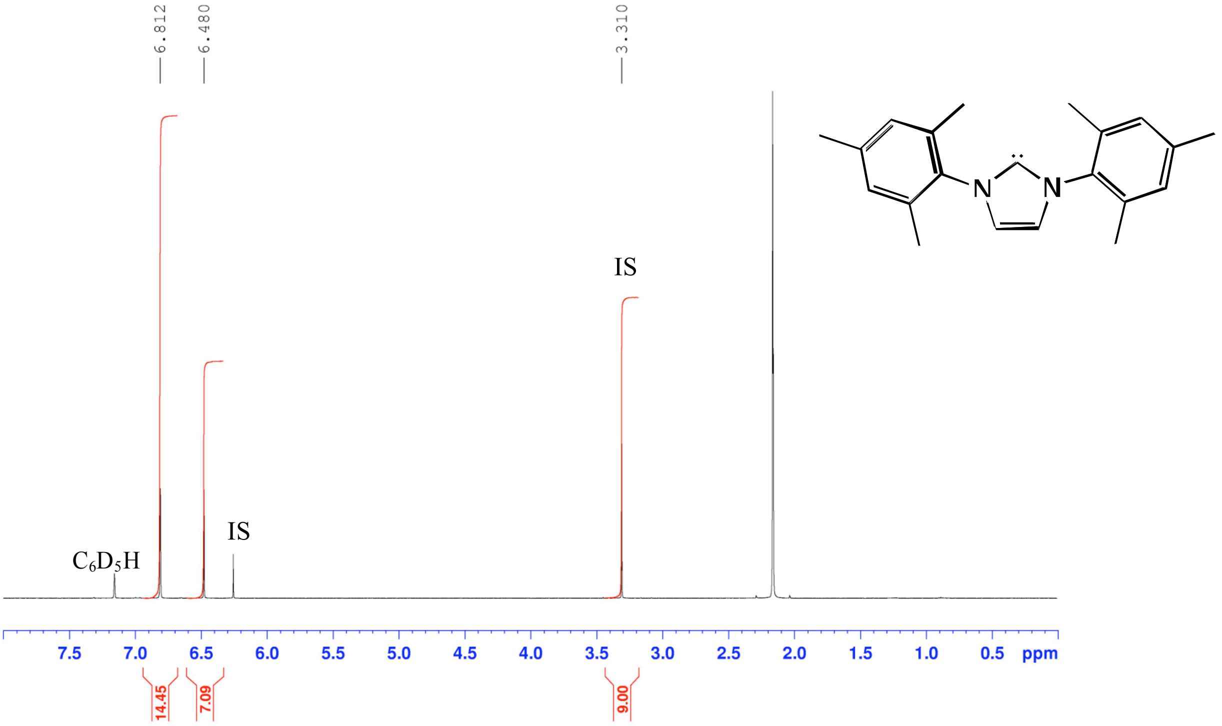


Figure S2b. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of free IMes prior to thermolysis, with TMB present as internal standard (IS).

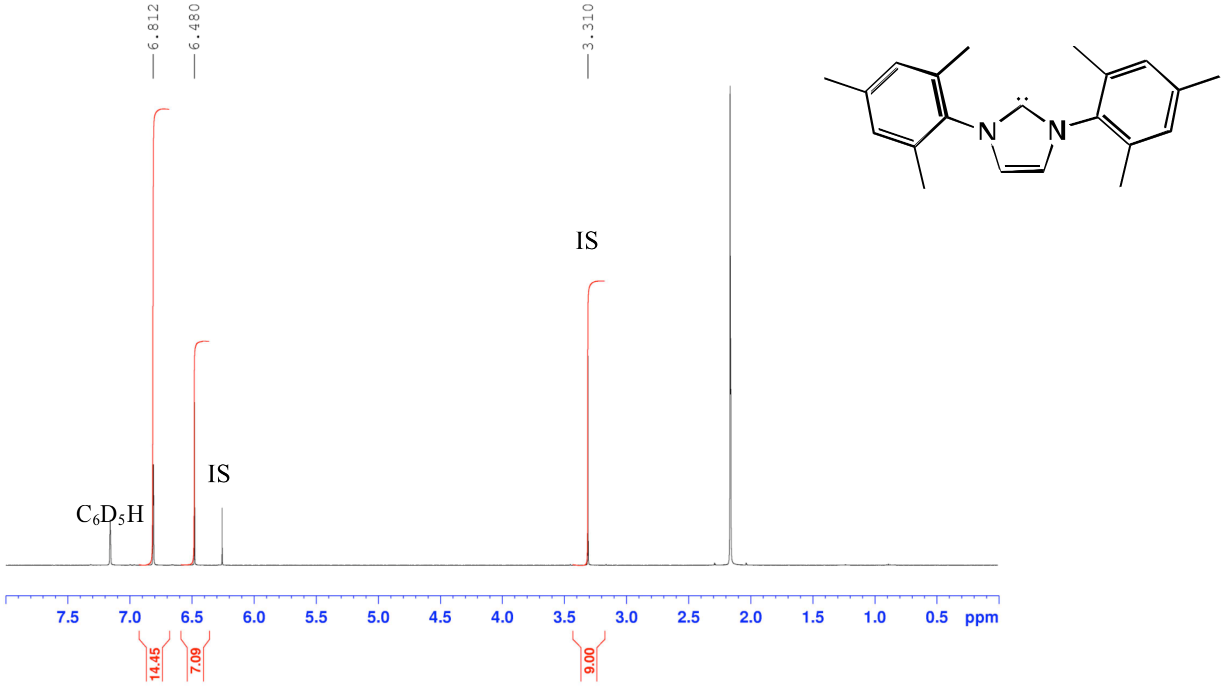


Figure S2c. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of free IMes after thermolysis at 60 °C for 10 h. Integration vs TMB as internal standard (IS) demonstrates no detectable decomposition of the free IMes.

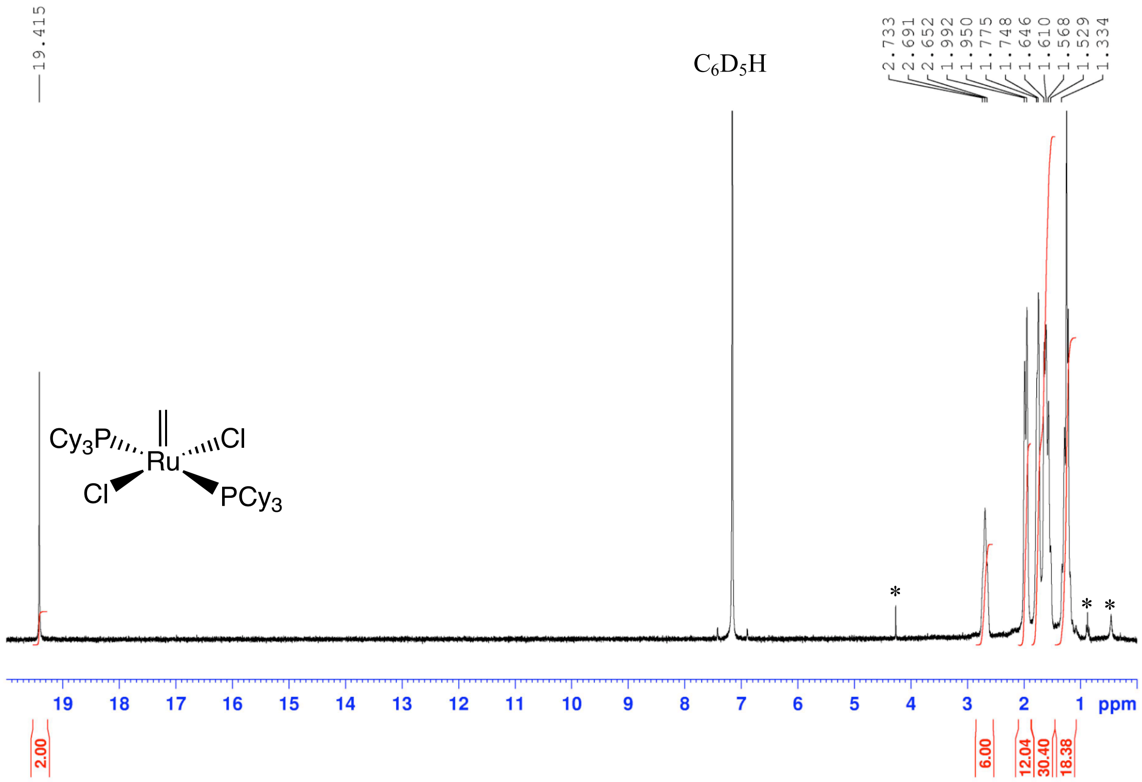


Figure S3a. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of **GI=CH$_2$**. Residual solvent is designated by (*).

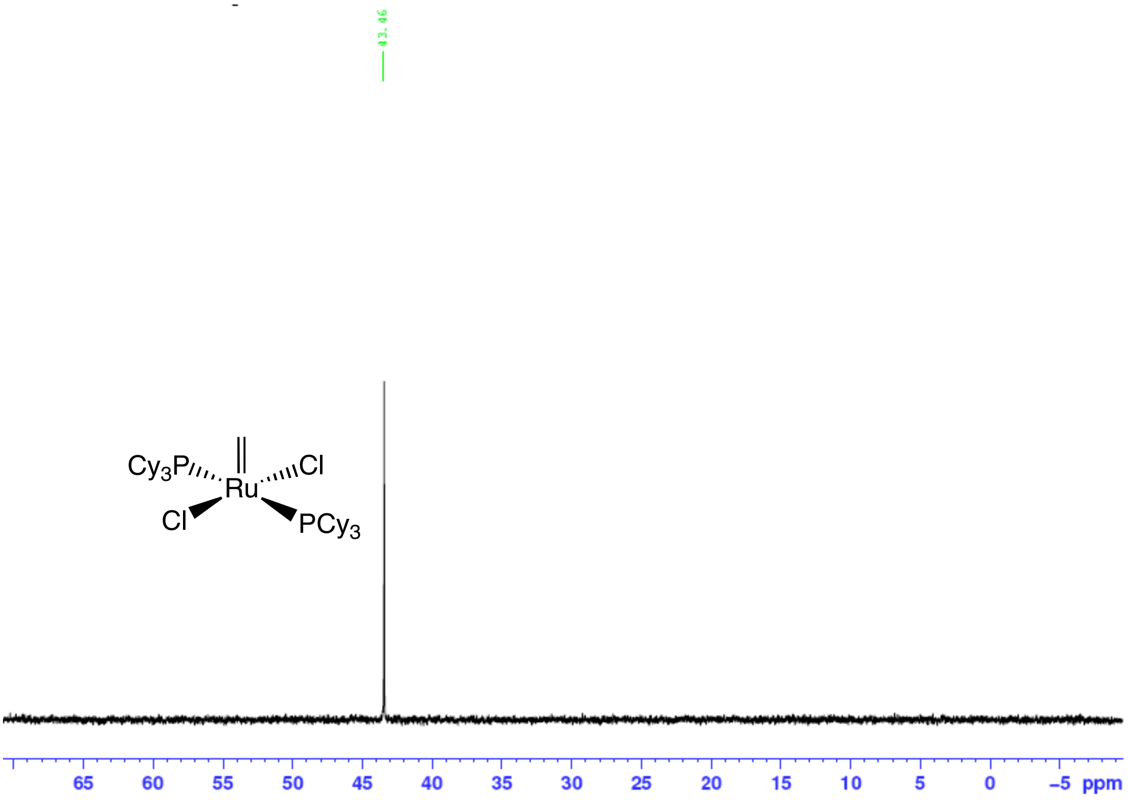


Figure S3b. ^{31}P{^{1}H} NMR spectrum (121.5 MHz, C_6D_6) of **GI=CH$_2$**.

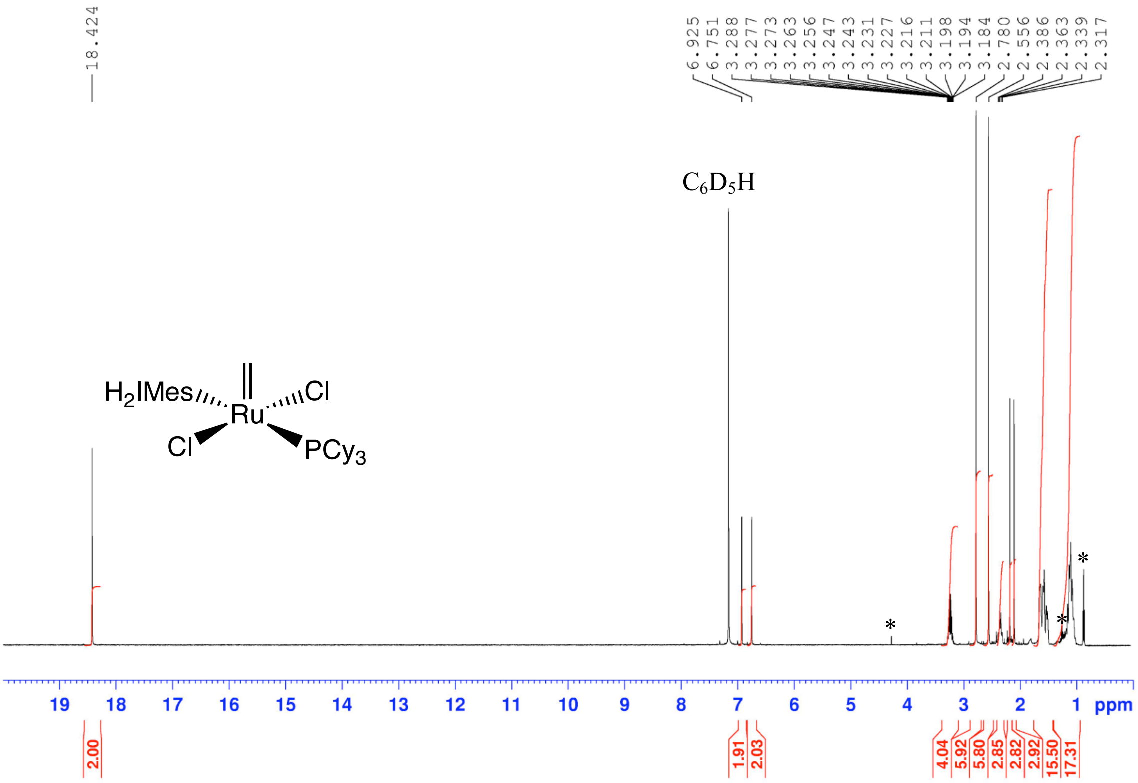


Figure S4a. ^{1}H NMR spectrum (500.1 MHz, C_6D_6) of **GII=CH$_2$**. Residual solvent is designated by (*).

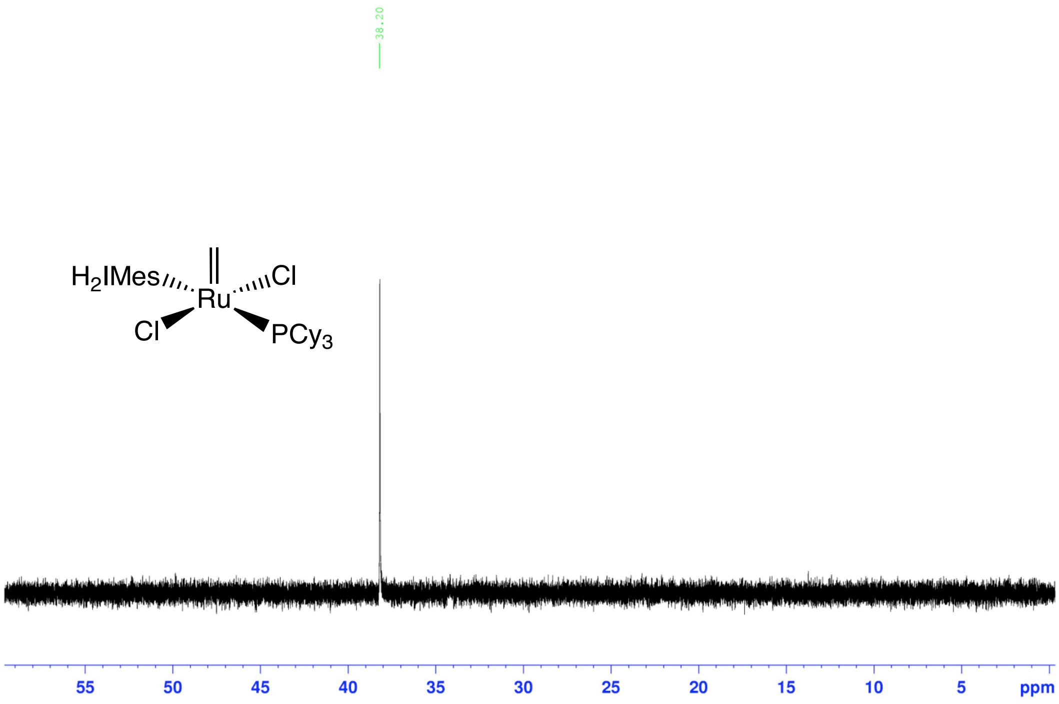


Figure S4b. $^{31}P\{^1H\}$ NMR spectrum (202.5 MHz, C_6D_6) of **GII=CH$_2$**.

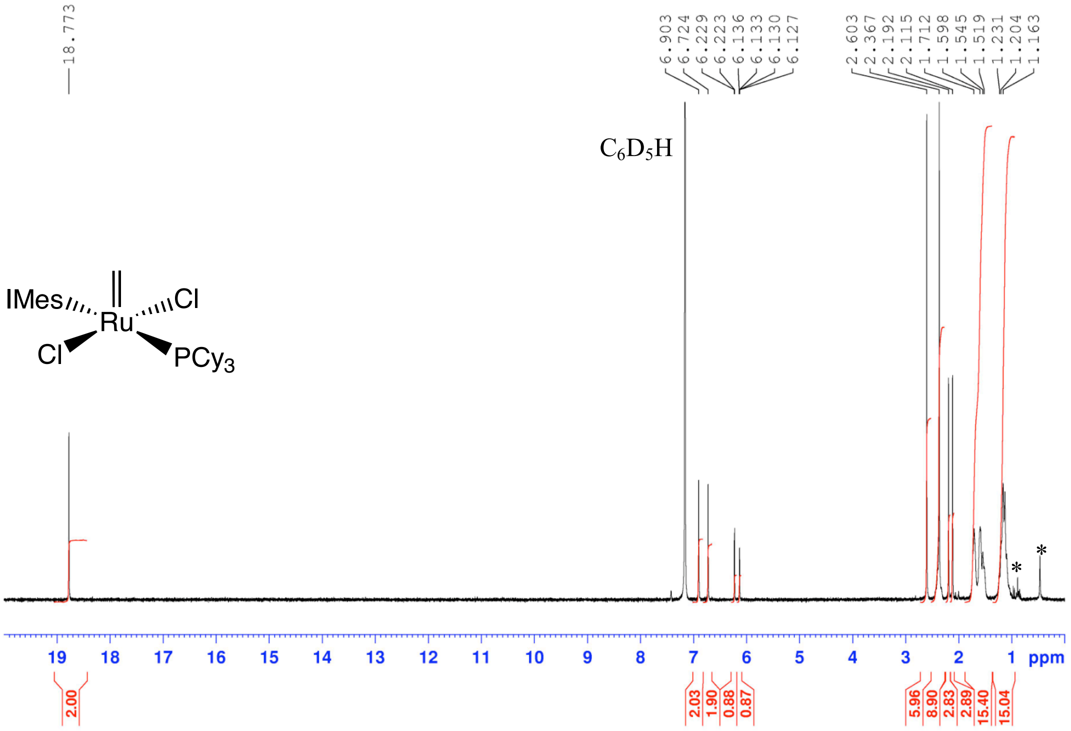


Figure S5a. ^{1}H NMR spectrum (500.1 MHz, C_6D_6) of **GII'=CH$_2$**. Residual solvent is designated by (*).

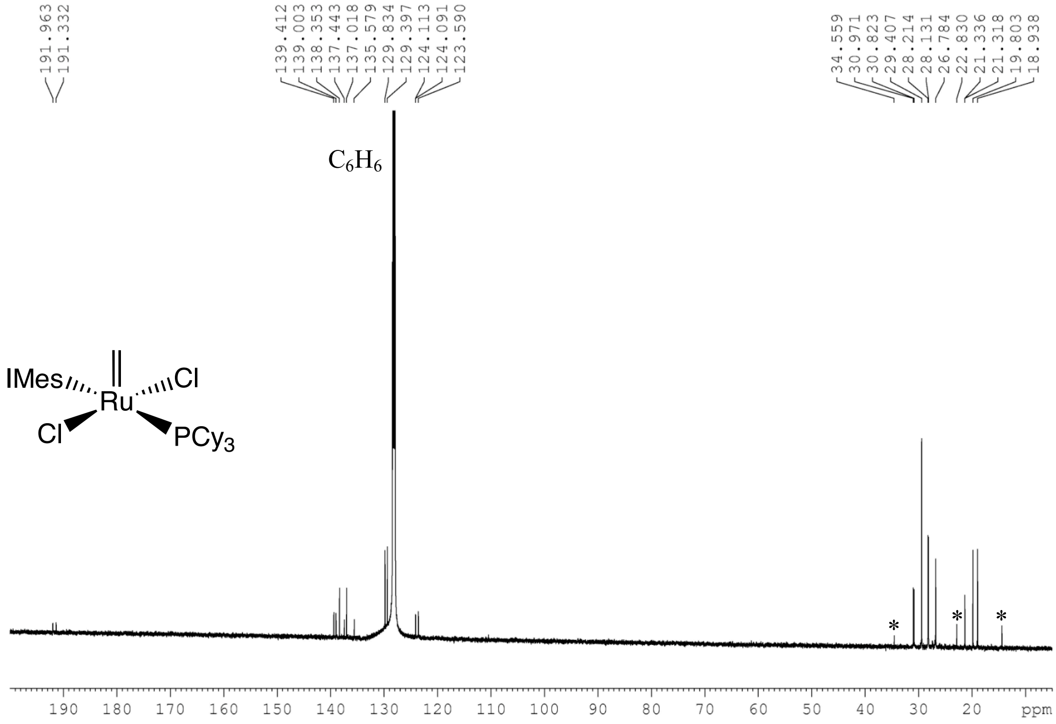


Figure S5b. $^{13}C\{^1H\}$ NMR spectrum (125.8 MHz, C_6D_6) of **GII'=CH$_2$**. Residual solvent is designated by (*).

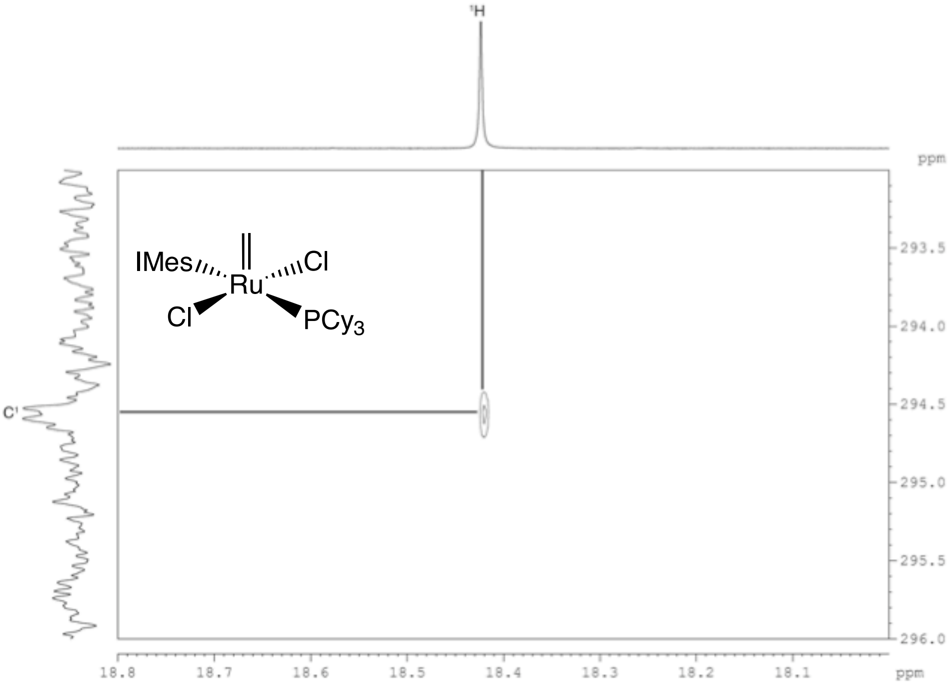


Figure S5c. ^{1}H-^{13}C HMBC correlation spectrum of **GII'=CH$_2$** (500.1 MHz, C_6D_6), showing location of Ru=*C*H$_2$ carbon signal.

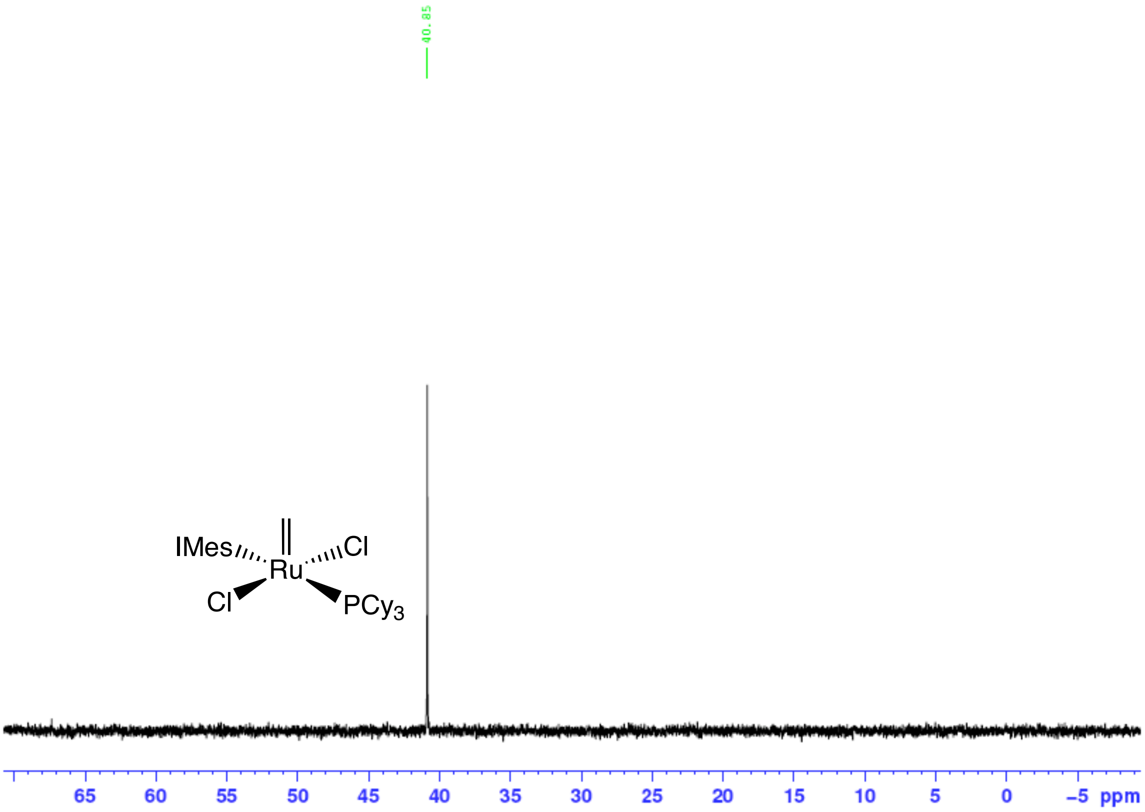


Figure S5d. ^{31}P{^{1}H} NMR spectrum (202.5 MHz, C_6D_6) of **GII'=CH$_2$**.

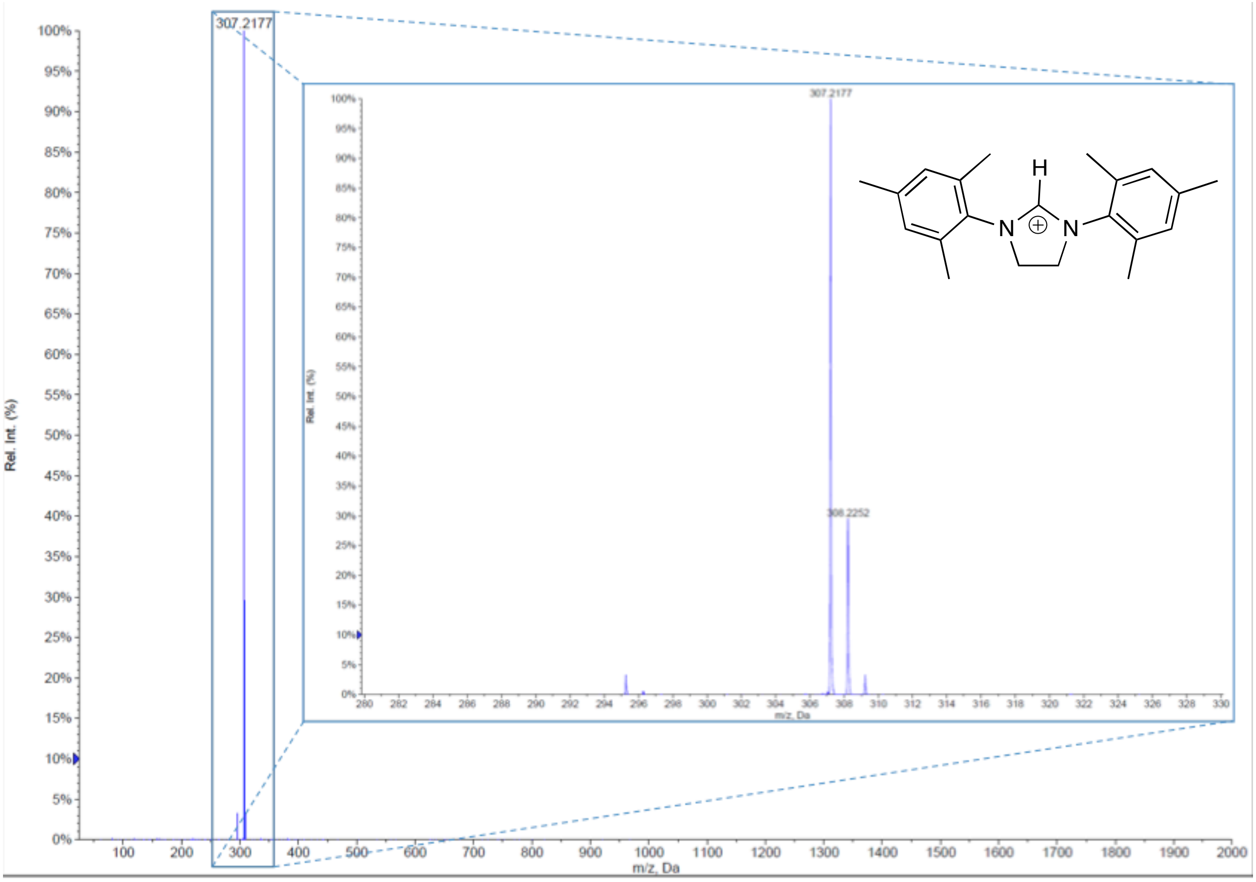


Figure 6. ESI mass spectrum of imidazolinium cation present in one batch of free H_2IMes. Sample measured in aqueous MeCN (33% v/v) with 0.1% v/v formic acid.

3. References

1. M. K. Denk, J. M. Rodezno, S. Gupta and A. J. Lough, *J. Organomet. Chem.*, 2001, **617-618**, 242-253.
2. A. J. Arduengo, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall and T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12742-12749.
3. A. J. Arduengo, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530-5534.
4. L. Jafarpour, A. C. Hillier and S. P. Nolan, *Organometallics*, 2002, **21**, 442-444.
5. P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100-110.
6. A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523-14534.
7. M. S. Sanford, J. A. Love and R. H. Grubbs, *J. Am. Chem. Soc.*, 2001, **123**, 6543-6554.