Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for:

Isotopic Probes for Ruthenium-Catalyzed Olefin Metathesis

Justin A.M. Lummiss, Adrian G.G. Botti, Deryn E. Fogg*

Center for Catalysis Research & Innovation, Chemistry Department, University of Ottawa,

Ottawa, ON, Canada, K1N 6N5

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S1. Handling of isotopically-labelled ethylene

A needle valve was installed on lecture bottles of labelled gases to permit controlled dispensing of small gas volumes. Once the bottle pressure dropped below 1 atm (14.7±1 psi local value), the lecture bottle was warmed in a hot-water bath to increase the pressure to the 1 atm level required for continued dispensing. Labelled gases were transferred to evacuated flasks via a delivery system of minimum volume (Figure S1).

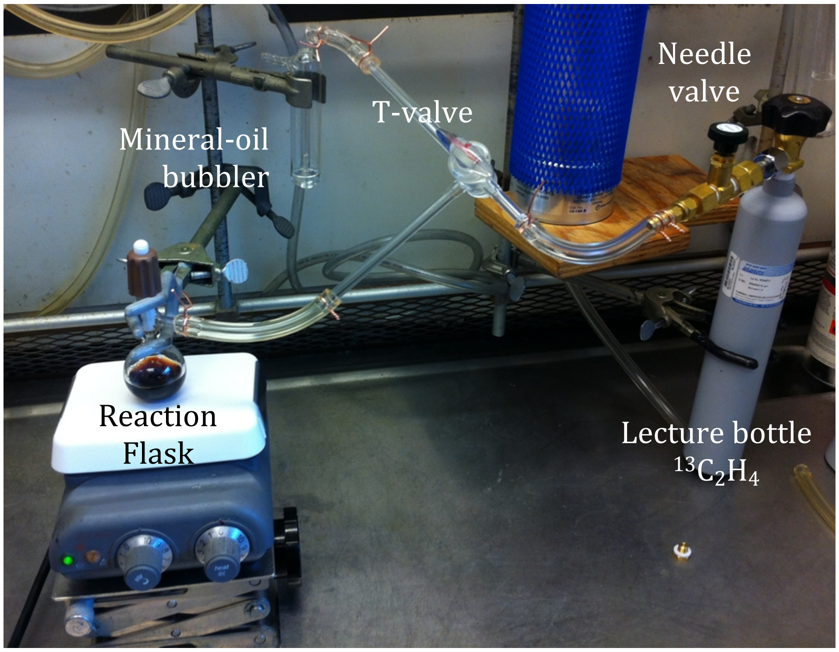

Figure S1. Transferring isotopically-labelled ethylene from lecture bottle to reaction flask using a T-valve connected to an oil bubbler. Load position: T-valve open to flask and lecture bottle; Pressure check position: T-valve open to oil bubbler.

S2. Improved gram-scale synthesis of $RuCl_2(H_2IMes)(PCy_3)(=CH_2)$, GIIm

Note: The original route[1] was carried out on 150 mg scale. The route below scales this up ca. fivefold, and improves purity by extracting the phosphonium chloride byproduct.

In the glovebox, **GIm** (697 mg, 0.933 mmol) of free H_2IMes (380 mg, 1.24 mmol, 1.3 equiv; slight excess used to compensate for trace water in the solvent), and 45 mL C_6H_6 was placed in a 100 mL Schlenk tube. 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 brown-yellow paste, which was washed with cold pentane (3 x 2 mL; glovebox) to yield yellow **GIm**. The yellow powder was washed with degassed H_2O (3 x 2 mL; aggressive stirring of the suspension), followed by acetone (3 x 2 mL; removes residual water and transforms the tacky solid to a fine yellow powder), the pentane (3 x 2 mL; removes residual PCy_3). Yield 578 mg (80 %).

S3. Representative NMR spectra

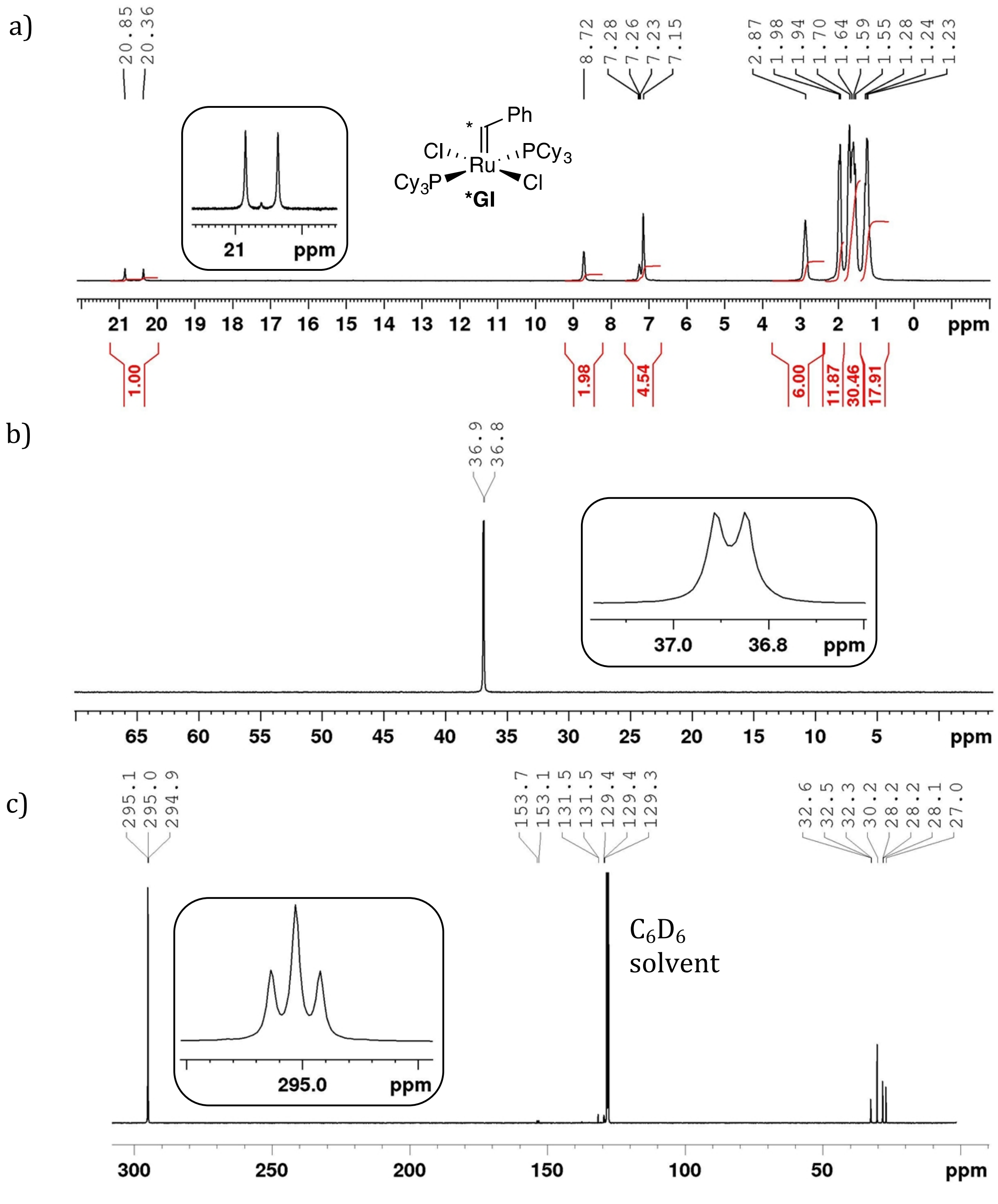

Figure S2. NMR spectra for $RuCl_2(PCy_3)_2(={}^{13}CHPh)$, ***GI**: (a) ^1H NMR spectrum (300.1 MHz, C_6D_6). (b) $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz, C_6D_6). (c) $^{13}C\{^1H\}$ NMR spectrum (75.5 MHz, C_6D_6).

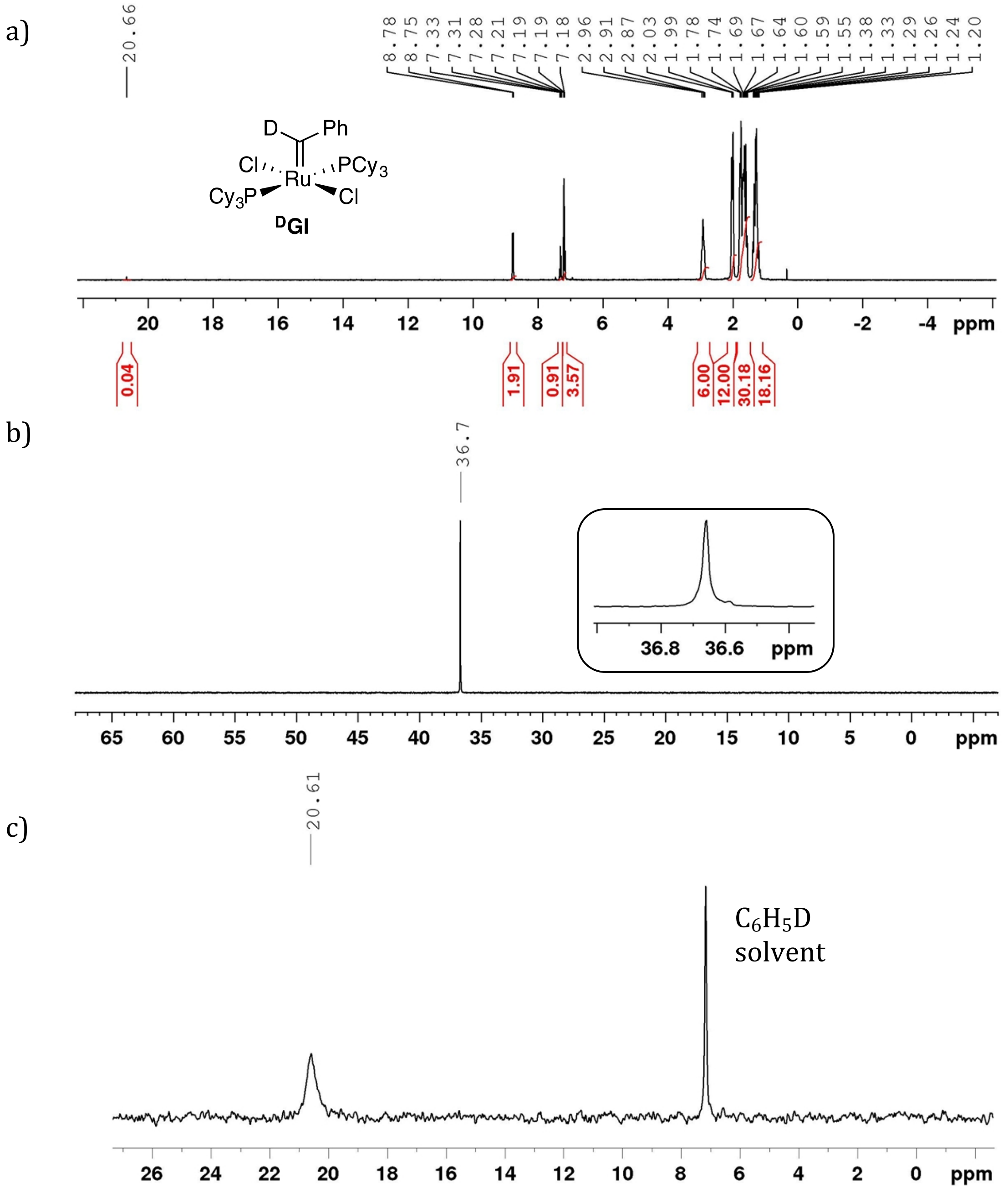

Figure S3. NMR spectra for $RuCl_2(PCy_3)_2(=CDPh)$, $^{\mathbf{D}}$**GI**: (a) ^1H NMR spectrum (300.1 MHz, C_6D_6); <5 min acquisition. (b) $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz, C_6D_6); ca. 10 min acquisition. (c) ^2H NMR spectrum (46.1 MHz, C_6H_6); >1 h acquisition. Note breadth of the downfield ^2H signal for $^{\mathbf{D}}$**GI**, relative to that for solvent (reflecting the fast relaxation discussed in the text). Both acquisition times and linewidths underscore the advantages associated with ^{13}C NMR analysis of appropriately enriched isotopologues.

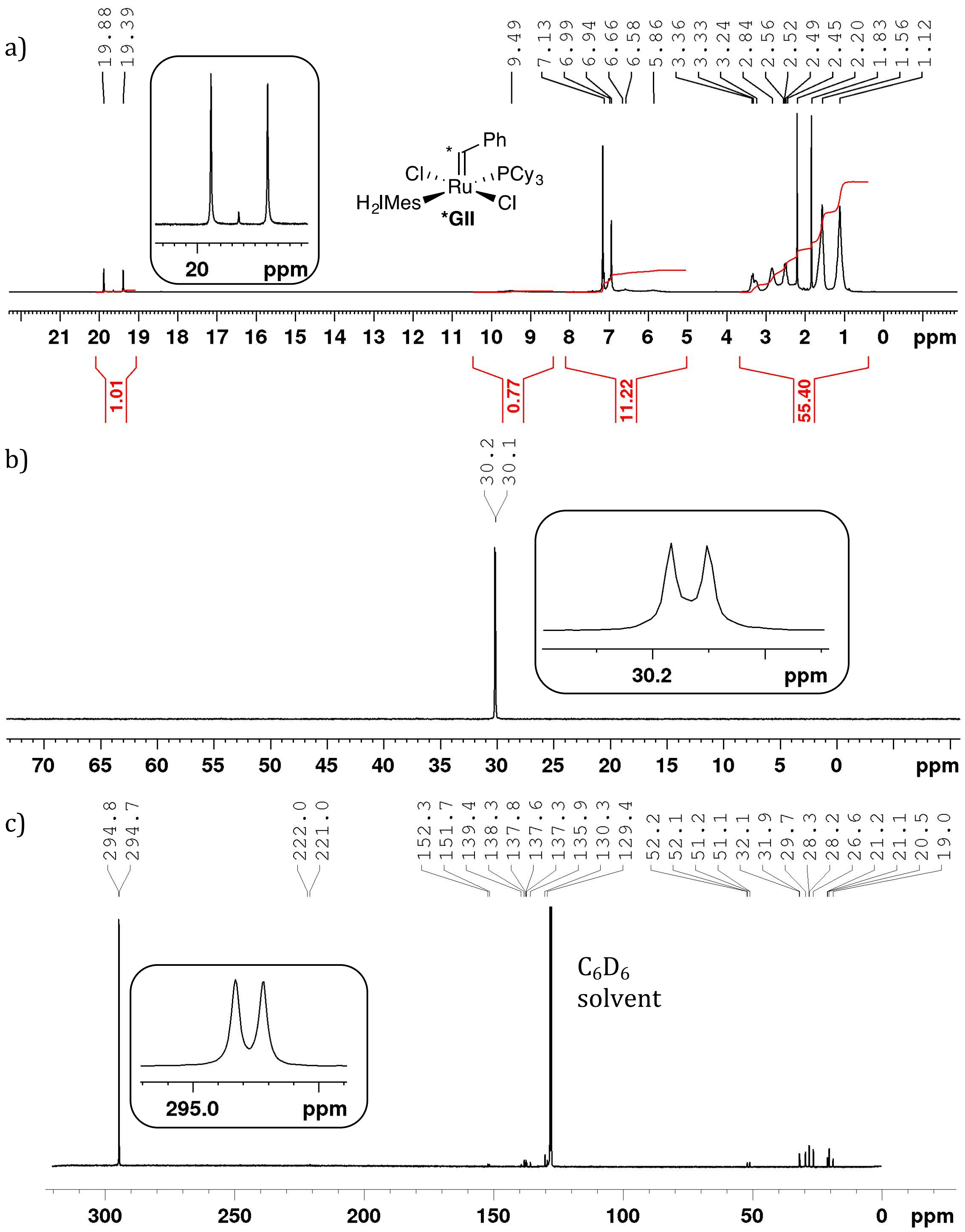

Figure S4. NMR spectra for $RuCl_2(PCy_3)(H_2IMes)(={}^{13}CHPh)$, ***GII**: (a) ^1H NMR spectrum (300.1 MHz, C_6D_6). (b) $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz, C_6D_6). (c) $^{13}C\{^1H\}$ NMR spectrum (75.5 MHz, C_6D_6). The poor resolution of the benzylidene phenyl signals is due to swiveling of this group.[2,3]

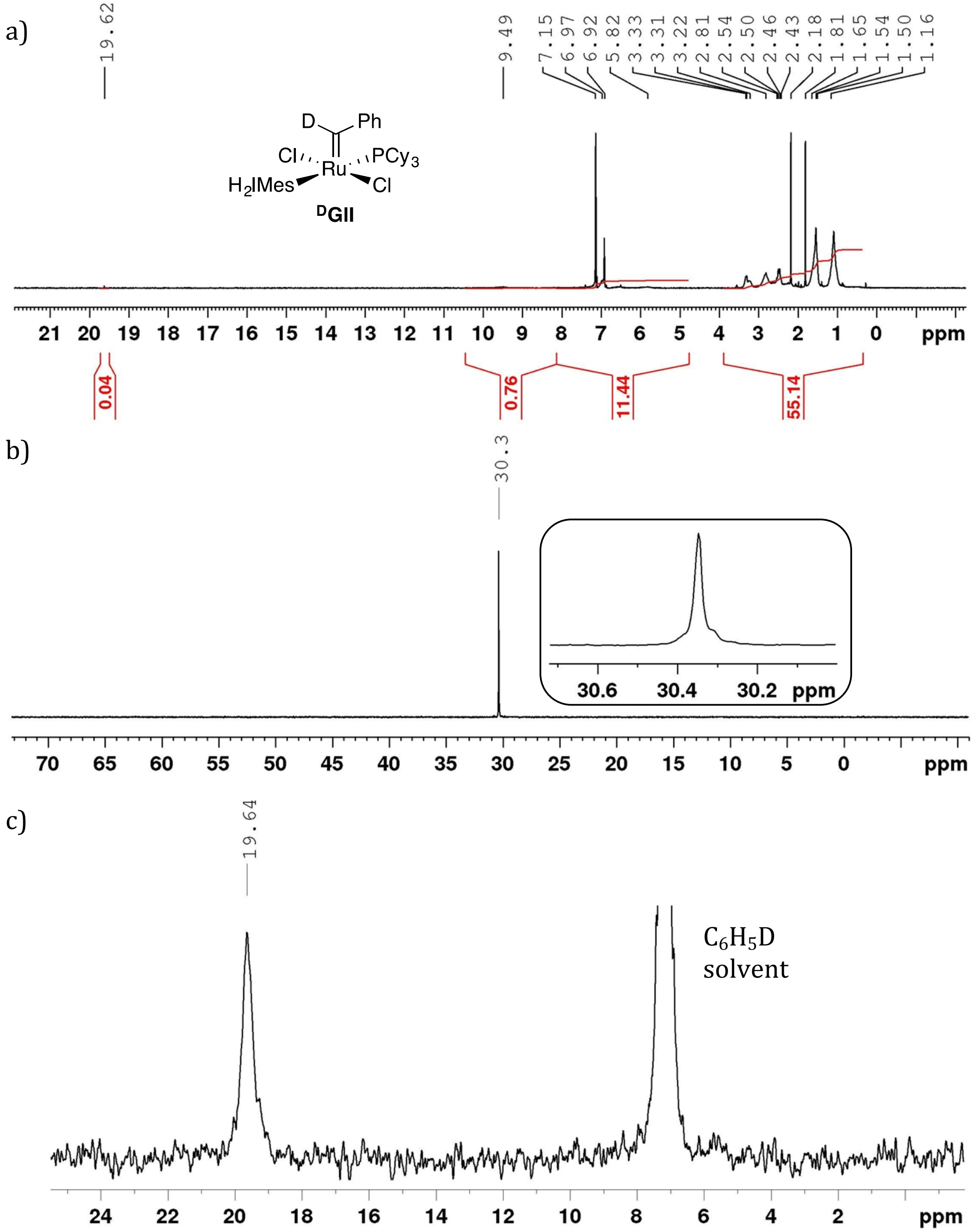

Figure S5. NMR spectra for $RuCl_2(PCy_3)(H_2IMes)(=CDPh)$, **^{D}GII**: (a) ^1H NMR spectrum (300.1 MHz, C_6D_6). (b) $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz, C_6D_6). (c) ^2H (46.1 MHz, C_6H_6).

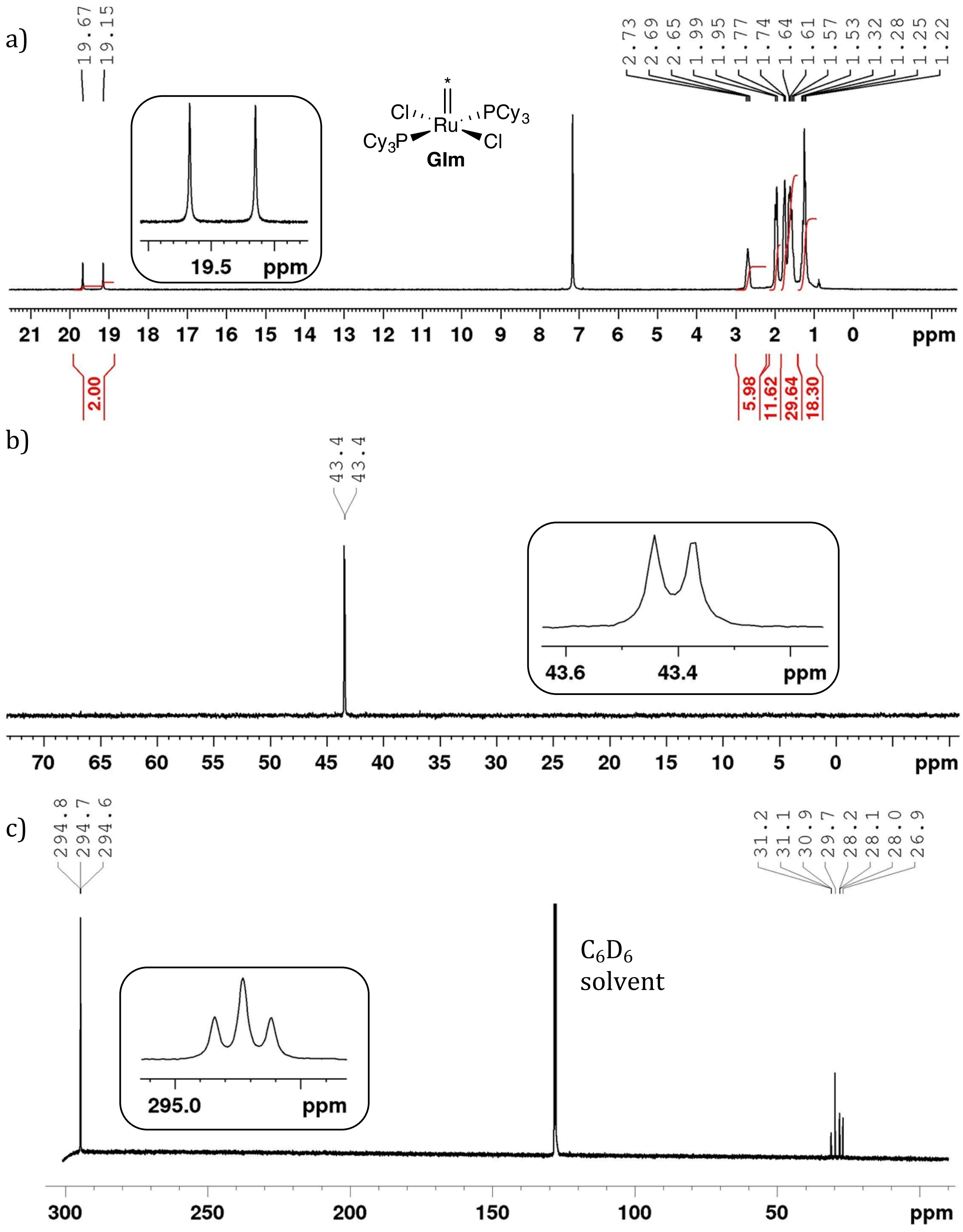

Figure S6. NMR spectra for $RuCl_2(PCy_3)_2(={}^{13}CH_2)$, ***GIm**: (a) ^1H NMR spectrum (300.1 MHz, C_6D_6). (b) $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz, C_6D_6). (c) $^{13}C\{^1H\}$ NMR spectrum (75.5 MHz, C_6D_6).

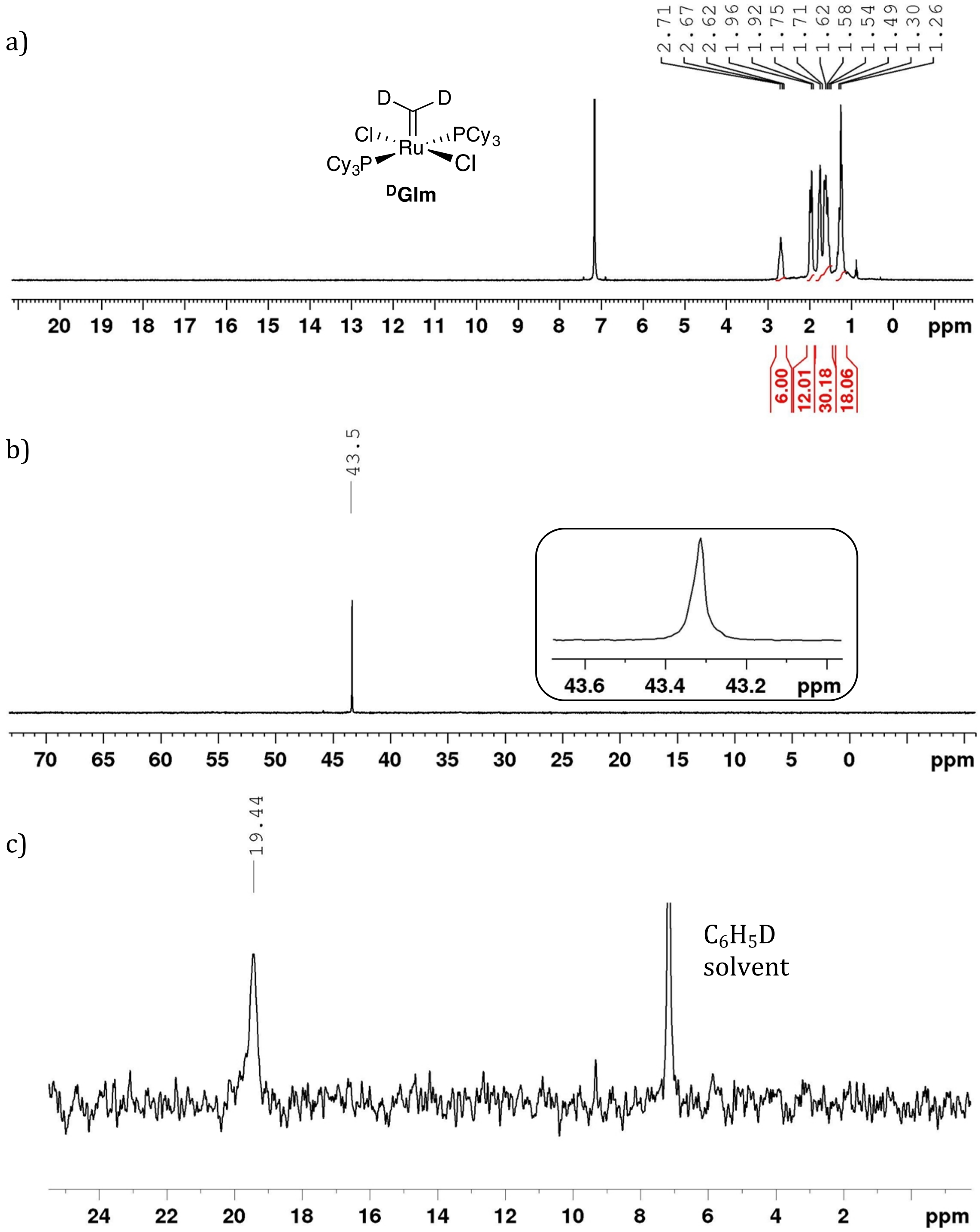

Figure S7. NMR spectra for $RuCl_2(PCy_3)_2(=CD_2)$, **^{D}GIm**: (a) ^{1}H NMR spectrum (300.1 MHz, C_6D_6). (b) $^{31}P\{^{1}H\}$ NMR spectrum (121.5 MHz, C_6D_6). (c) ^{2}H (46.1 MHz, C_6H_6).

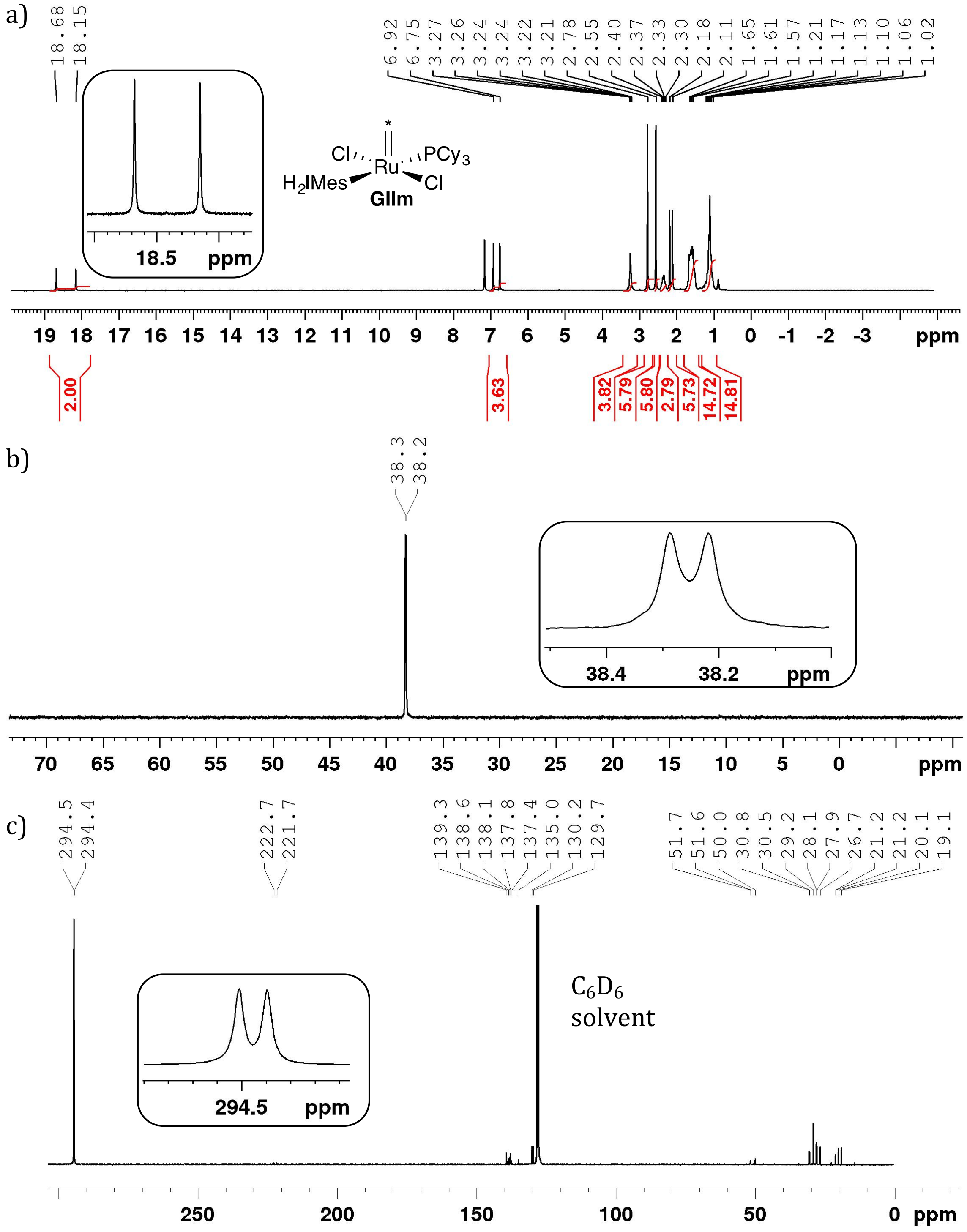

Figure S8. NMR spectra for $RuCl_2(PCy_3)(H_2IMes)(={}^{13}CH_2)$, ***GIIm**: (a) ^1H NMR spectrum (300.1 MHz, C_6D_6). (b) $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz, C_6D_6). (c) $^{13}C\{^1H\}$ NMR spectrum (75.5 MHz, C_6D_6).

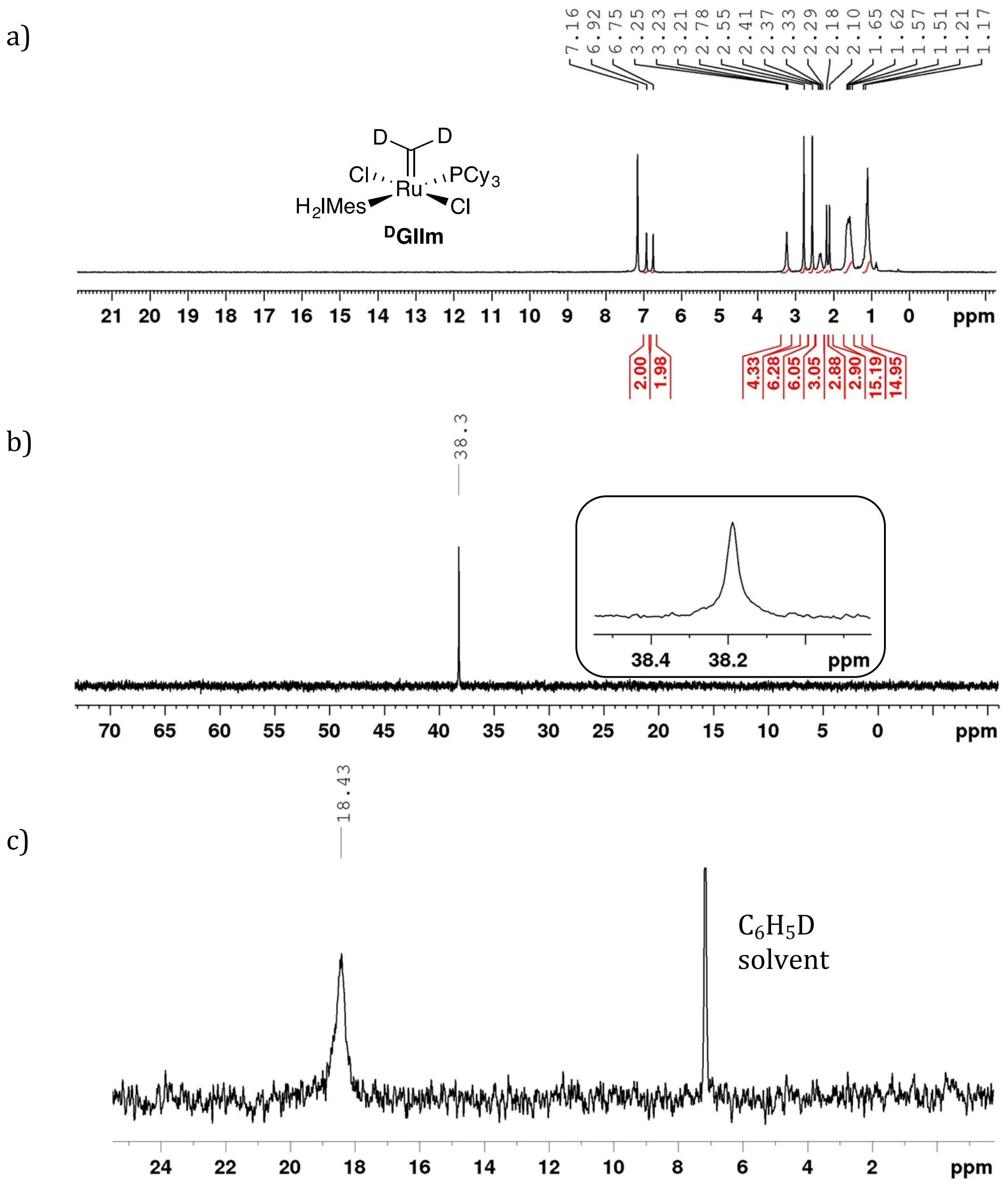

Figure S9. NMR spectra for RuCl$_2$(PCy$_3$)(H$_2$IMes)(=CD$_2$), **^{D}GIIm**: (a) ^{1}H NMR spectrum (300.1 MHz, C$_6$D$_6$). (b) ^{31}P{^{1}H} NMR spectrum (121.5 MHz, C$_6$D$_6$). (c) ^{2}H (46.1 MHz, C$_6$H$_6$).

S4. References.

1. J. A. M. Lummiss, N. J. Beach, J. C. Smith and D. E. Fogg, *Catal. Sci. Technol.*, 2012, 2, 1630–1632.
2. M. M. Gallagher, A. D. Rooney and J. J. Rooney, *J. Organomet. Chem.*, 2008, 693, 1252–1260.
3. M. W. Kotyk, S. I. Gorelsky, J. C. Conrad, C. Carra and D. E. Fogg, *Organometallics*, 2009, 28, 5424–5431.