SUPPORTING INFORMATION

Heterobimetallic Ruthenium-Zinc Complexes with Bulky N-Heterocyclic Carbenes: Syntheses, Structures and Reactivity

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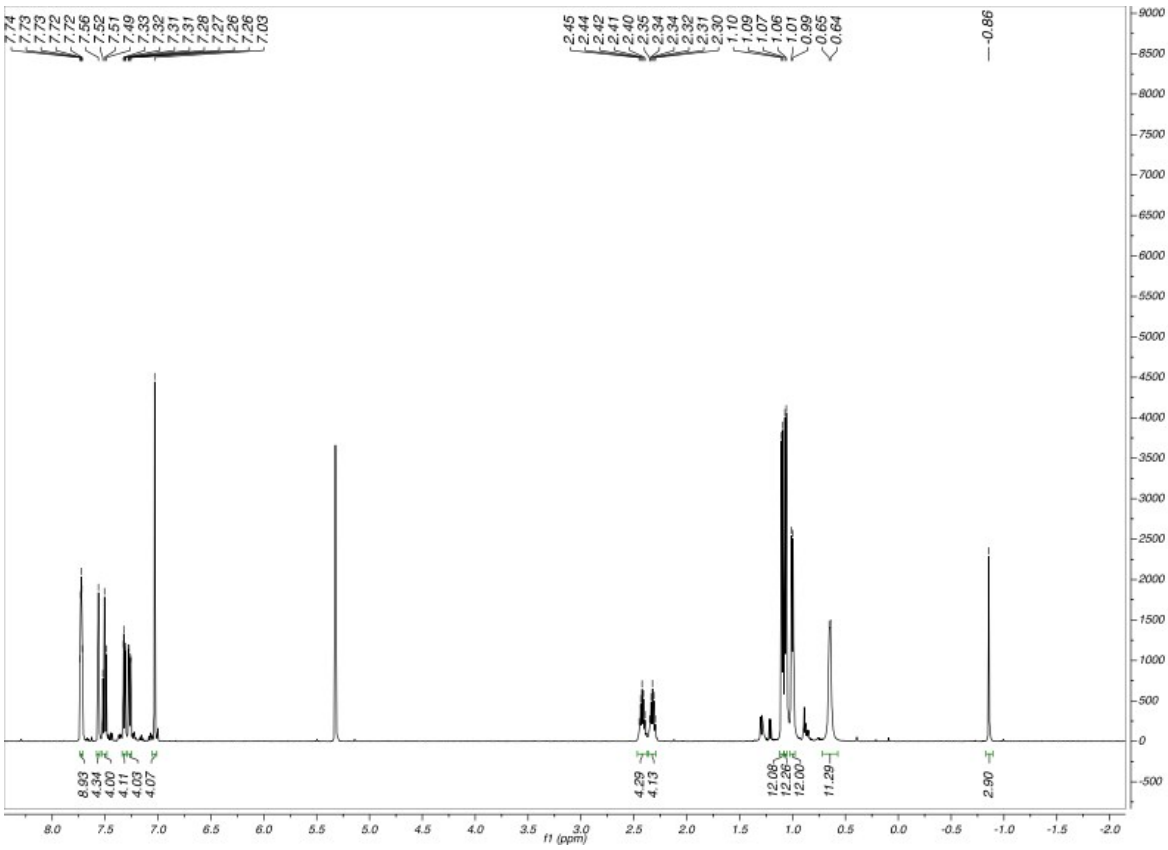


Figure S1. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of $[Ru(IPr)_2(CO)ZnMe][BAr^F{}_4]$ (**7**).

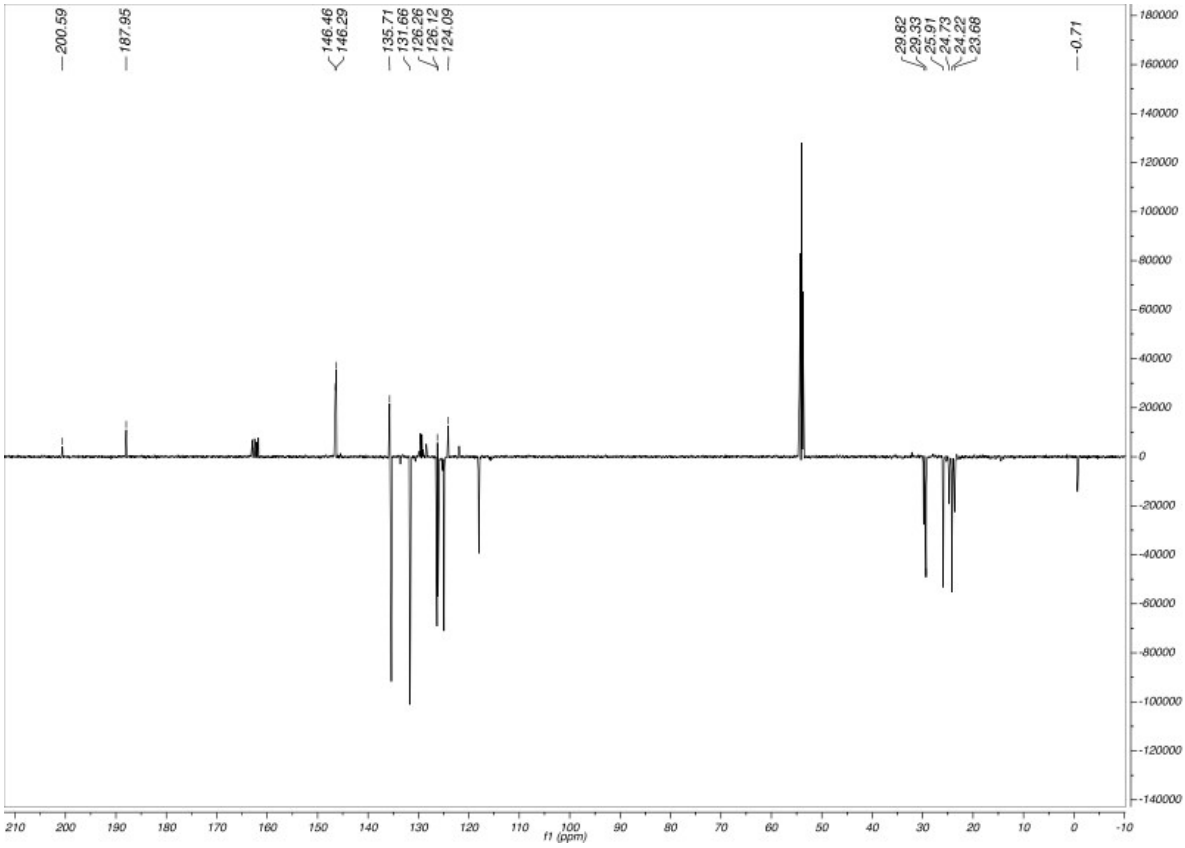


Figure S2. ^{13}C{^{1}H} PENDANT NMR spectrum (101 MHz, CD_2Cl_2, 298 K) of $[Ru(IPr)_2(CO)ZnMe][BAr^F{}_4]$ (**7**).

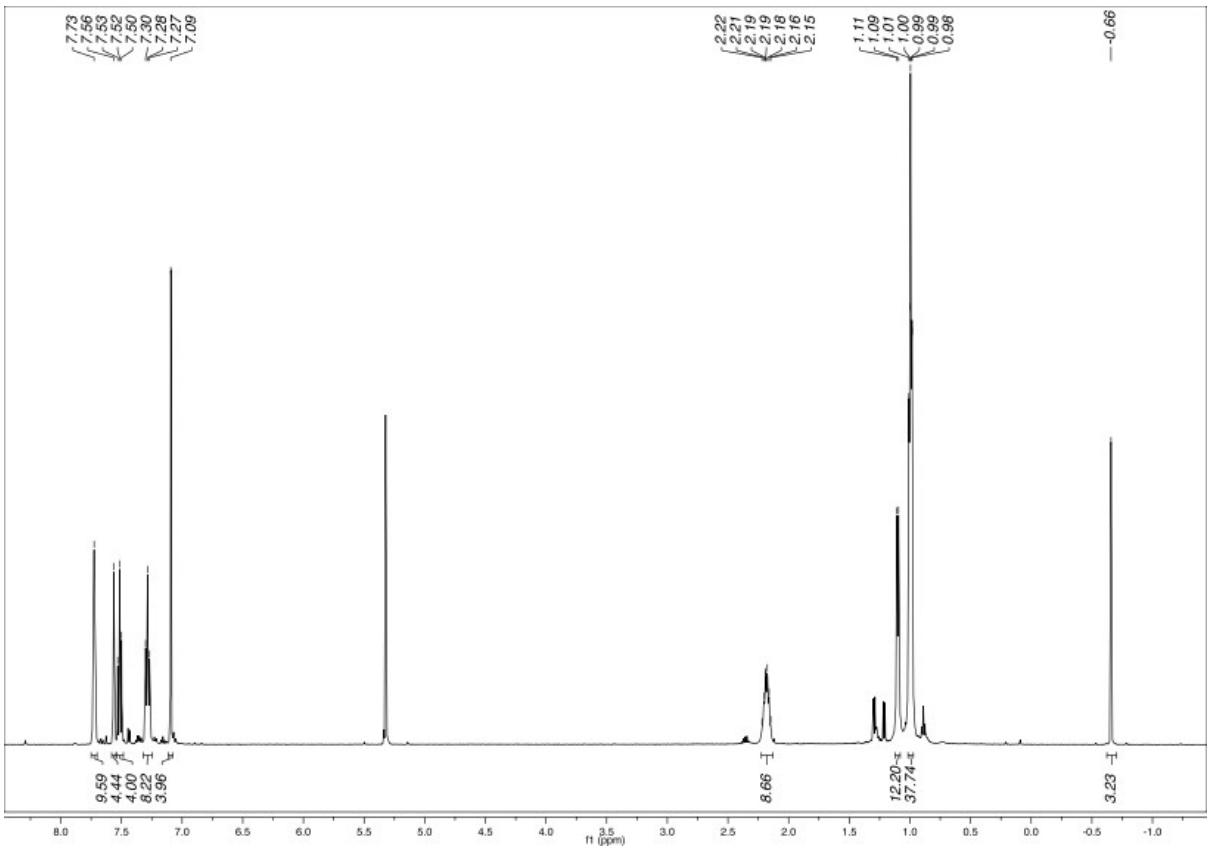


Figure S3. High frequency region of the ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of $[Ru(IPr)_2(CO)(\eta^2\text{-}H_2)(H)_2ZnMe][BAr^F{}_4]$ (**8**).

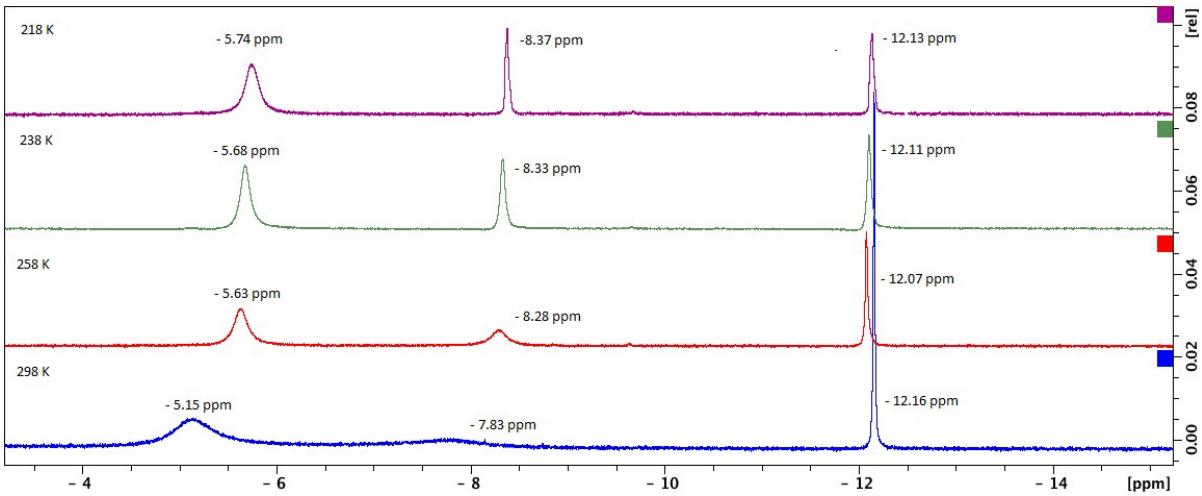


Figure S4. Variable temperature proton NMR spectra of the low frequency region of the ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of $[Ru(IPr)_2(CO)(\eta^2\text{-}H_2)(H)_2ZnMe][BAr^F{}_4]$ (**8**).

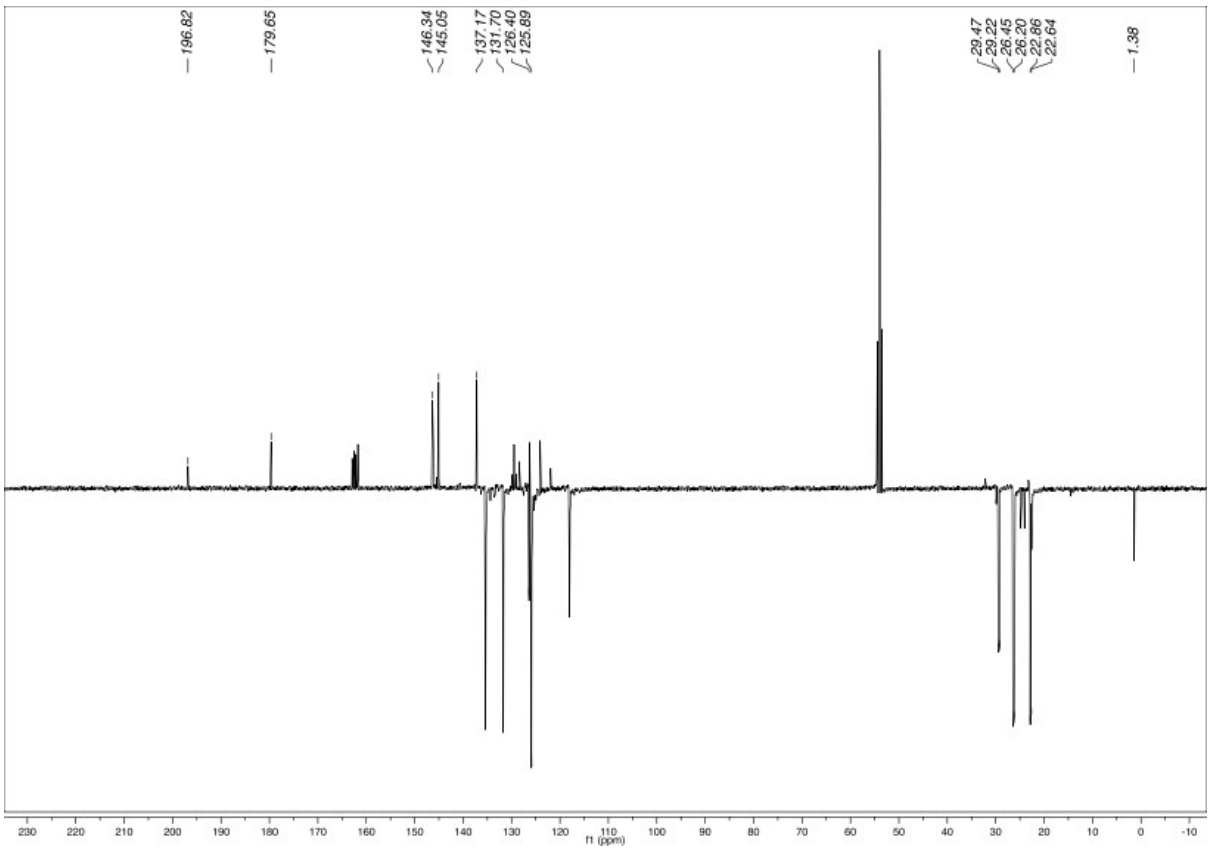


Figure S5. $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (101 MHz, CD_2Cl_2, 298 K) of $[Ru(IPr)_2(CO)(\eta^2\text{-}H_2)(H)_2ZnMe][BAr^F{}_4]$ (**8**).

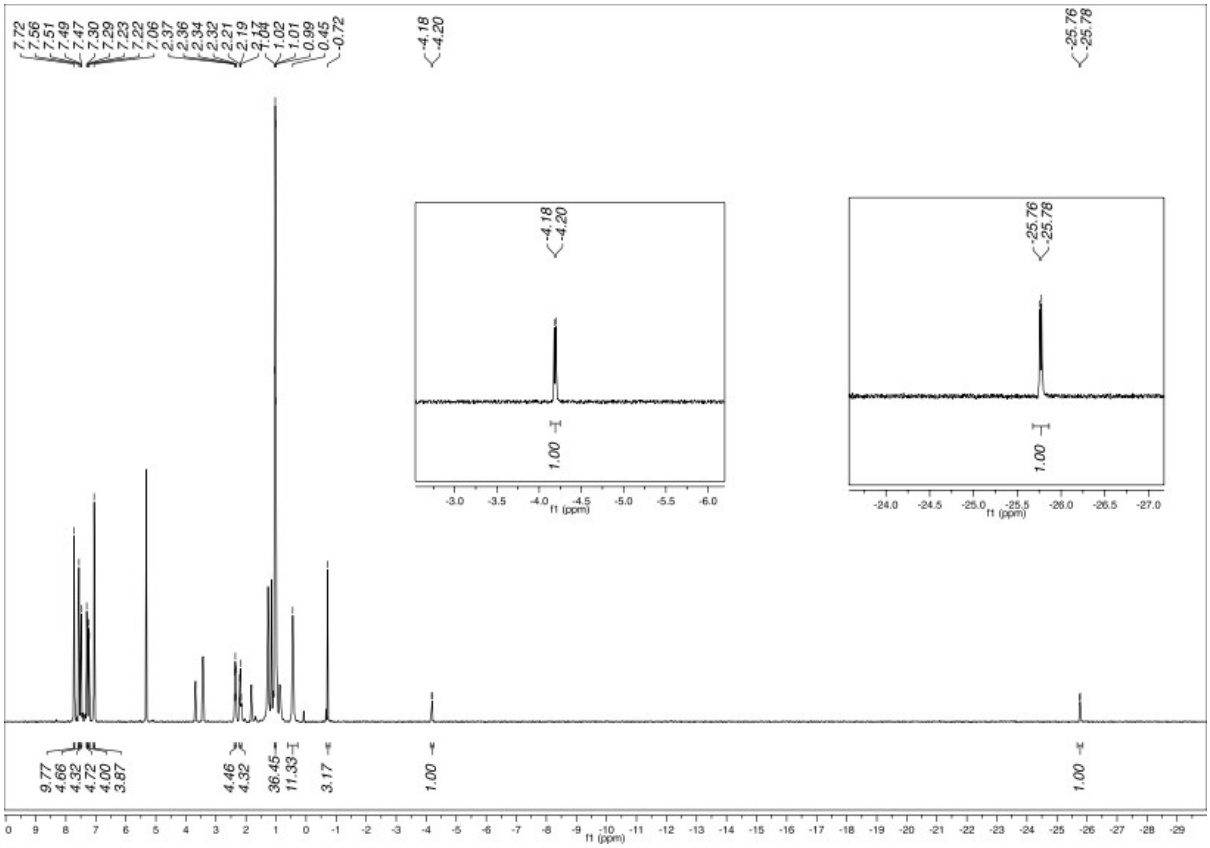


Figure S6. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of $[Ru(IPr)_2(CO)(H)_2ZnMe][BAr^F{}_4]$ (**9**).

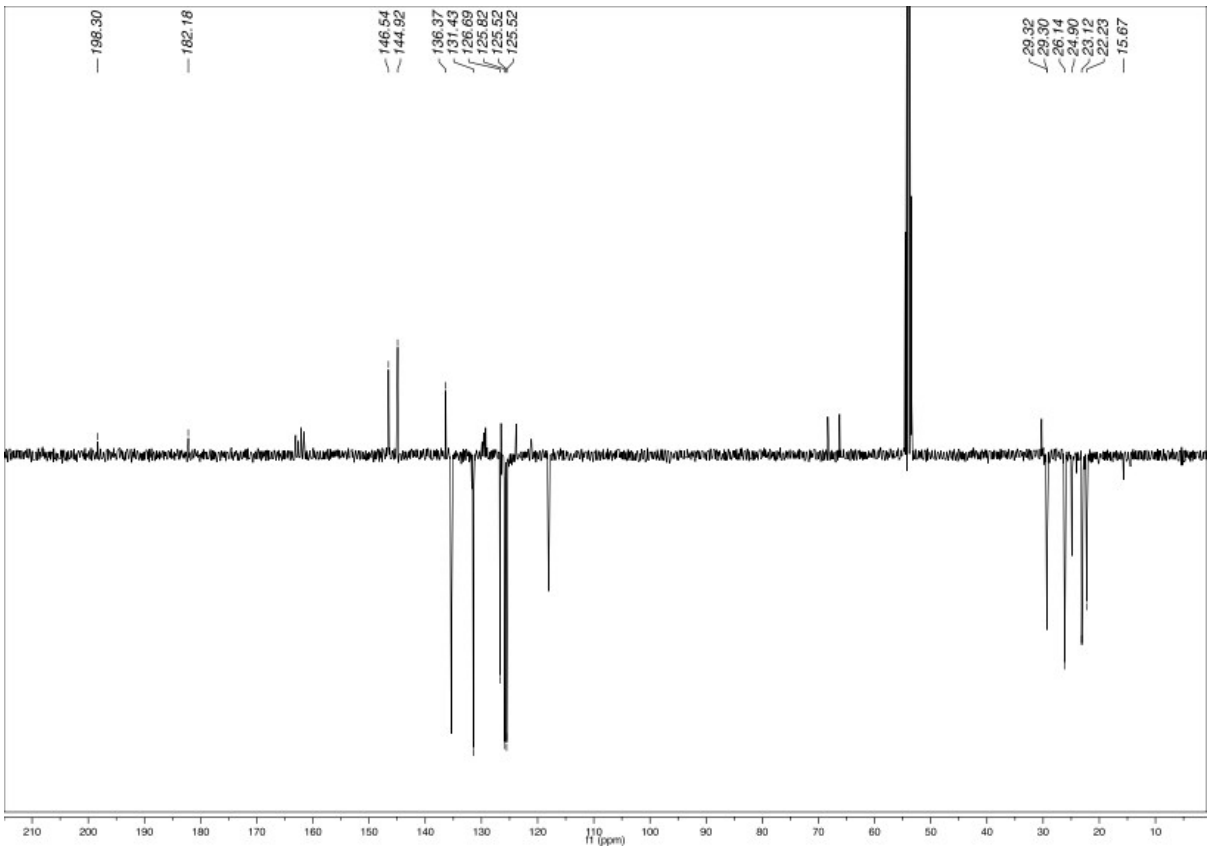


Figure S7. $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (101 MHz, CD_2Cl_2, 298 K) of $[Ru(IPr)_2(CO)(H)_2ZnMe][BAr^F{}_4]$ (**9**).

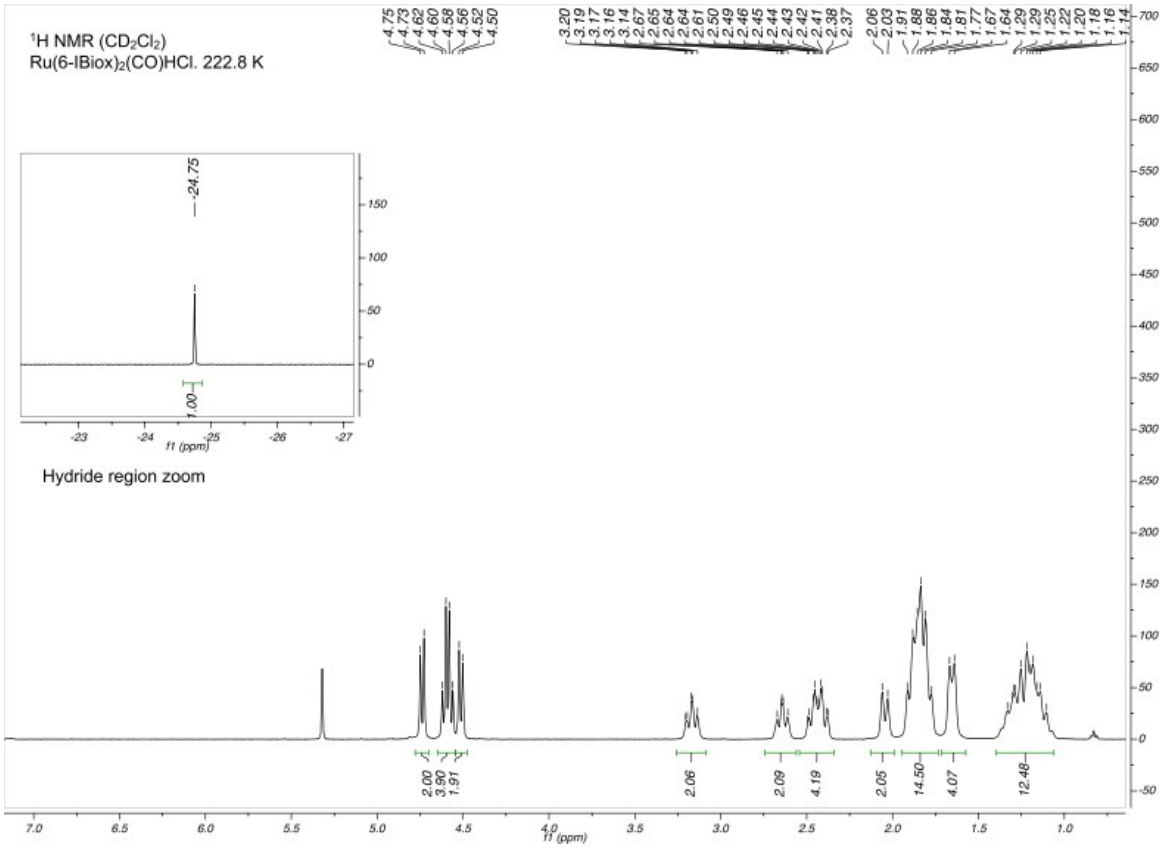


Figure S8. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 223 K) of $[Ru(IBiox6)_2(CO)HCl]$ (**10**).

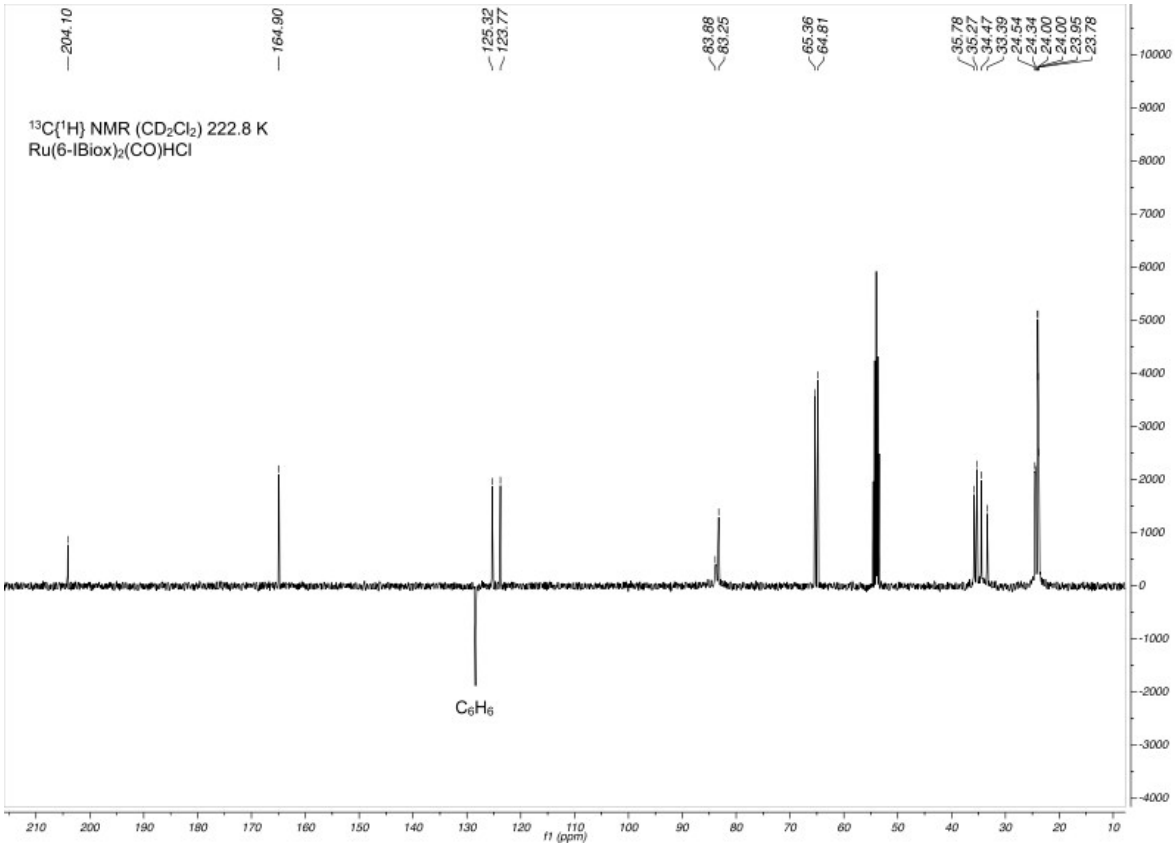


Figure S9. $^{13}C\{^1H\}$ PENDANT NMR spectrum (126 MHz, CD_2Cl_2, 223 K) of $[Ru(IBiox6)_2(CO)HCl]$ (**10**).

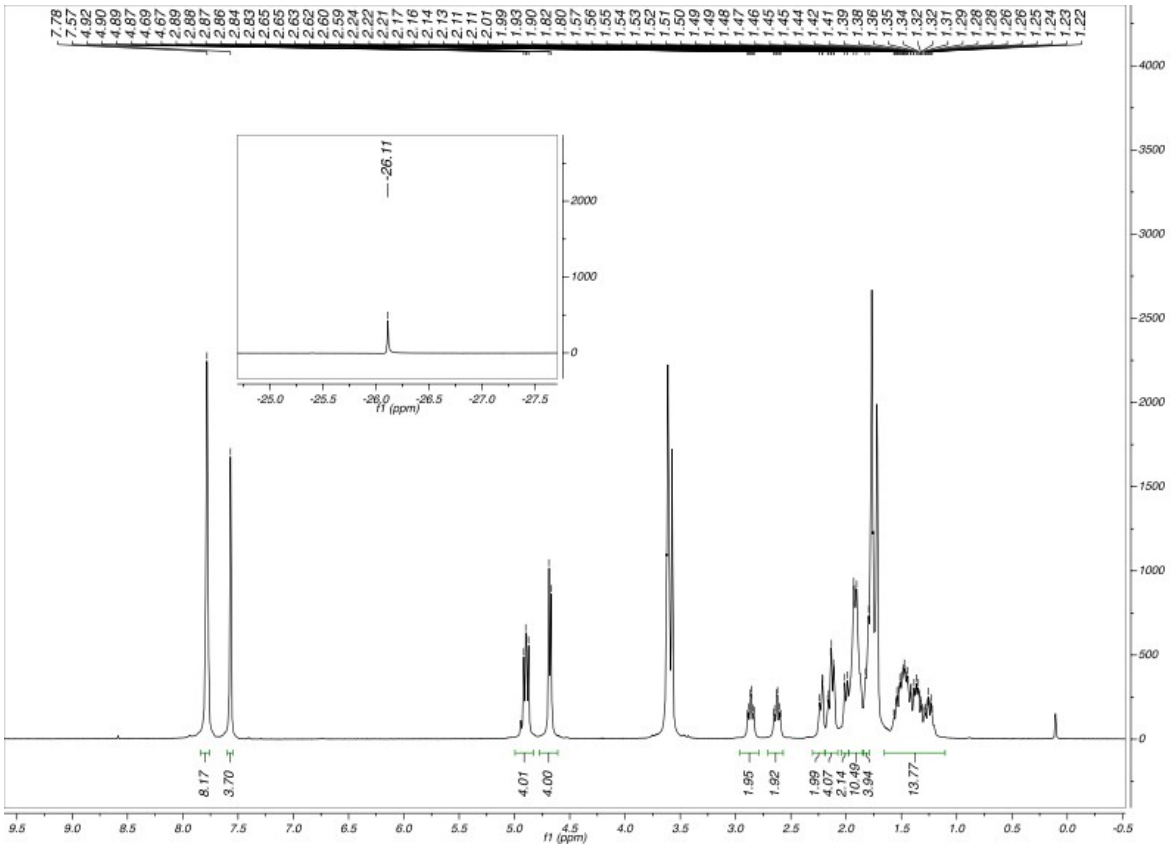


Figure S10. ^1H NMR spectrum (500 MHz, THF-d_8, 298 K) of $[Ru(IBiox6)_2(CO)(THF)H][BAr^F{}_4]$ (**11**).

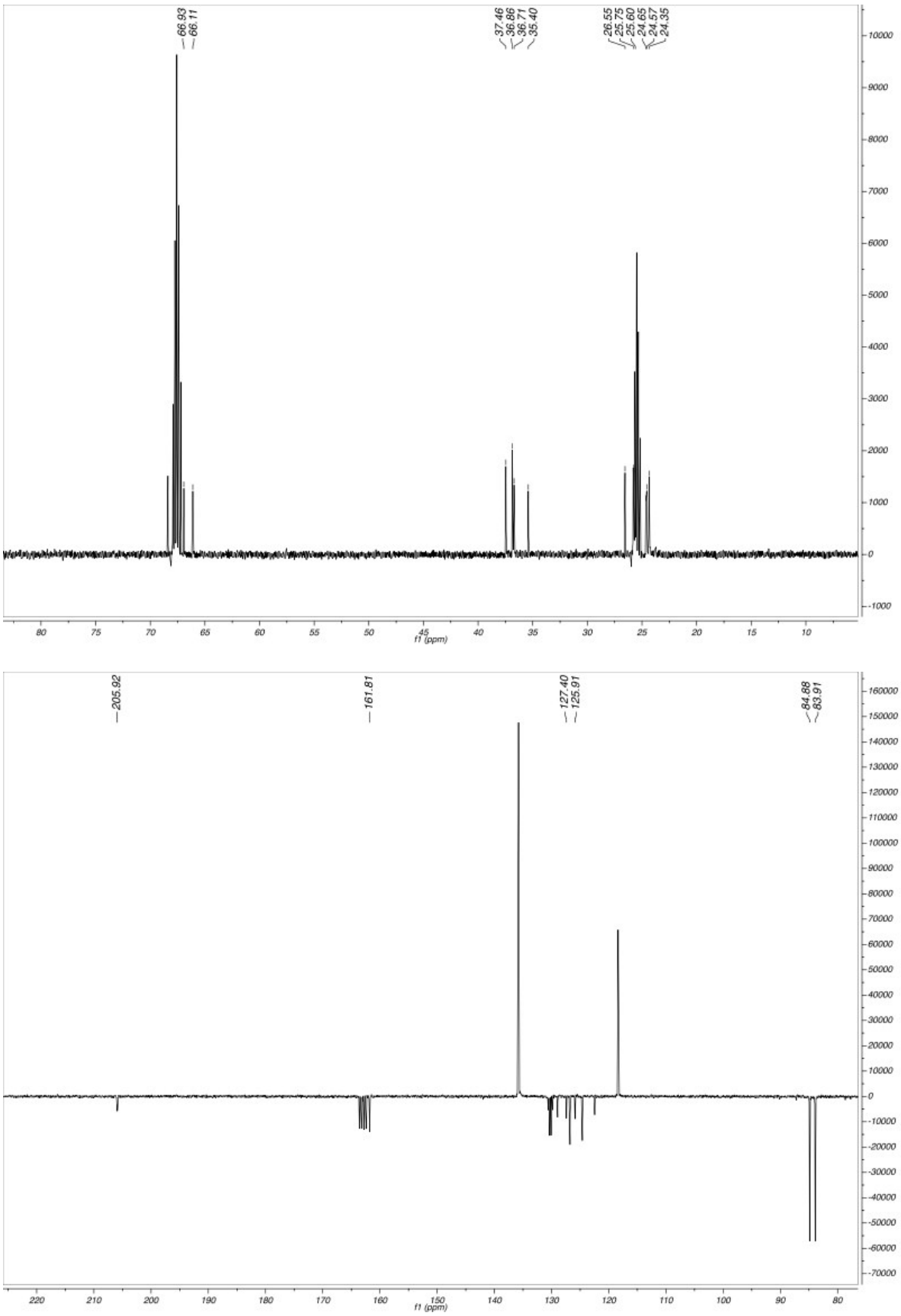


Figure S11. High (top) and lower (bottom) frequency regions of the $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (126 MHz, THF-d_8, 298 K) of $[Ru(IBiox6)_2(CO)(THF)H][BAr^F{}_4]$ (**11**).

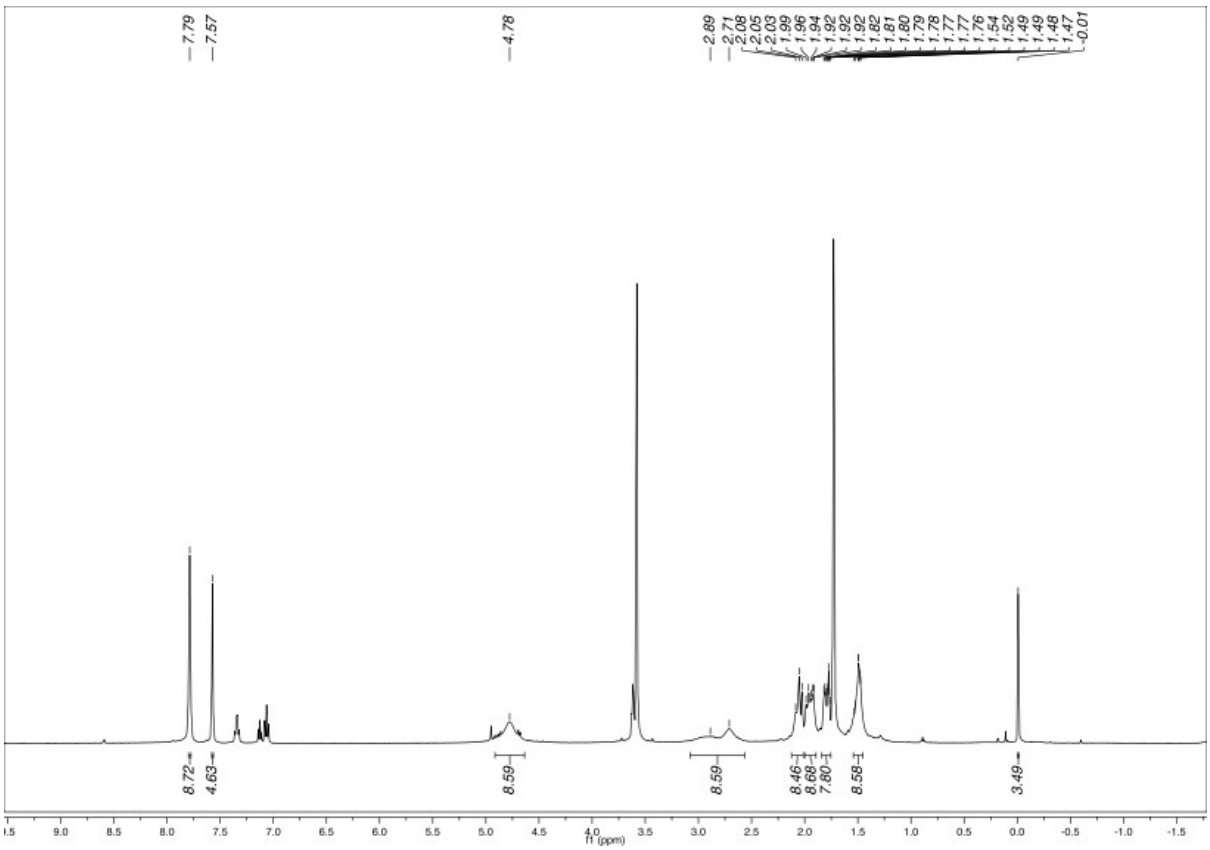


Figure S12. ^{1}H NMR spectrum (500 MHz, THF-d_8, 298 K) of [Ru(IBiox6)$_2$(CO)(THF)ZnMe][BAr$^F{}_4$] (**12**).

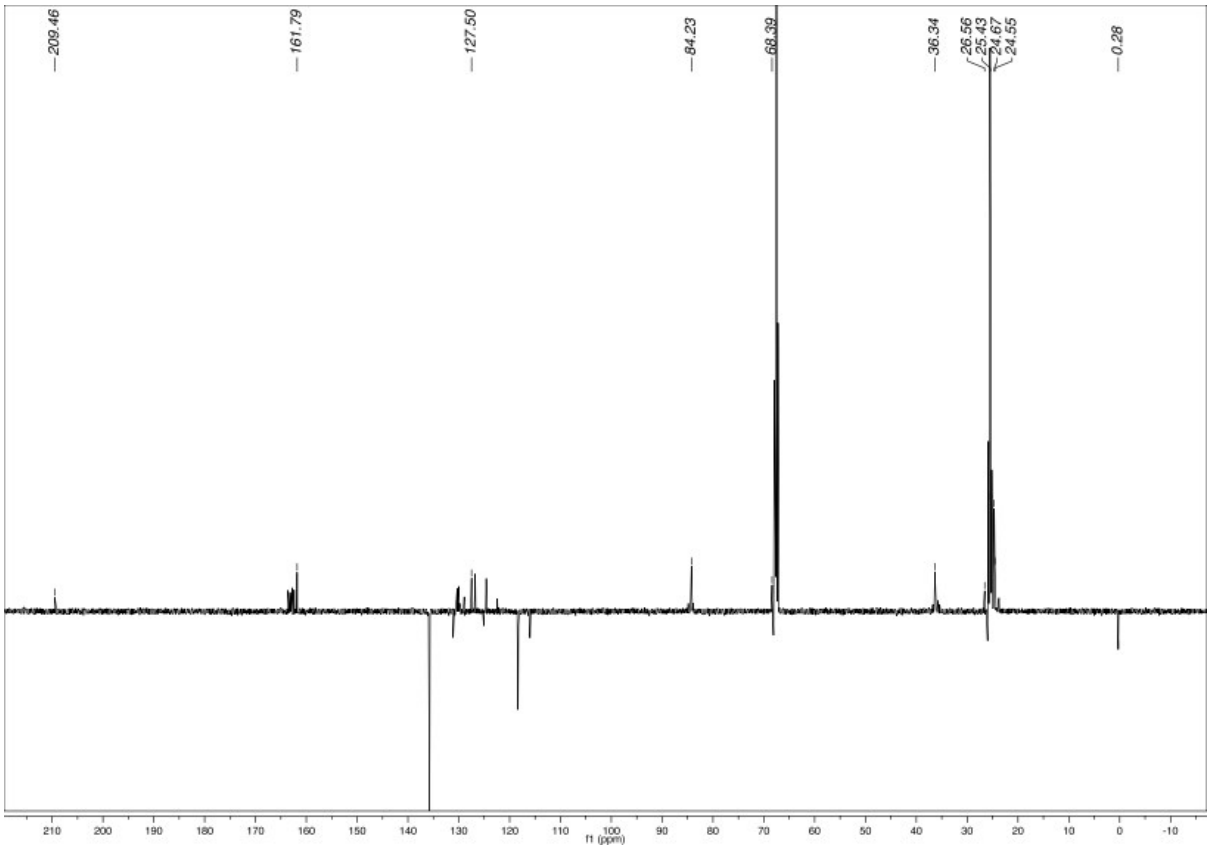


Figure S13. ^{13}C{^{1}H} PENDANT NMR spectrum (126 MHz, THF-d_8, 298 K) of [Ru(IBiox6)$_2$(CO)(THF)ZnMe][BAr$^F{}_4$] (**12**).

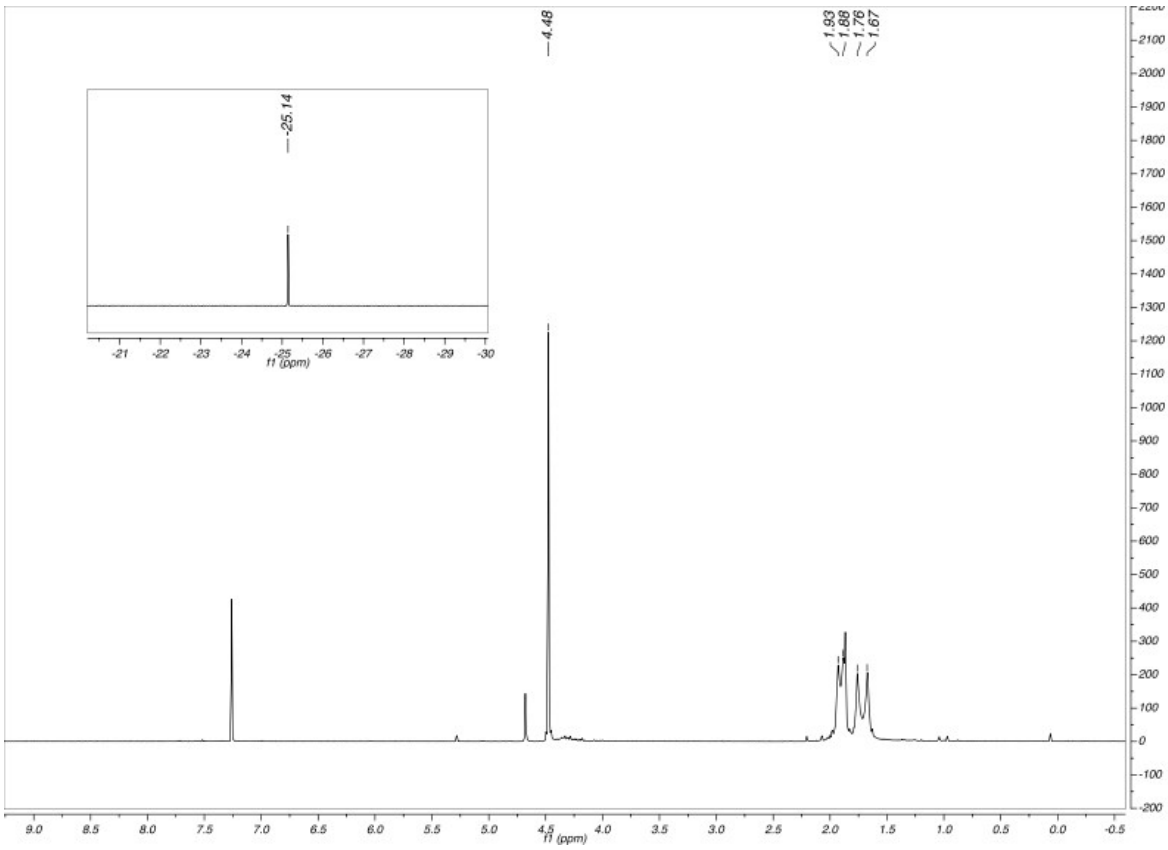


Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of $[Ru(IBioxMe_4)_2(CO)HCl]$ (**13**).

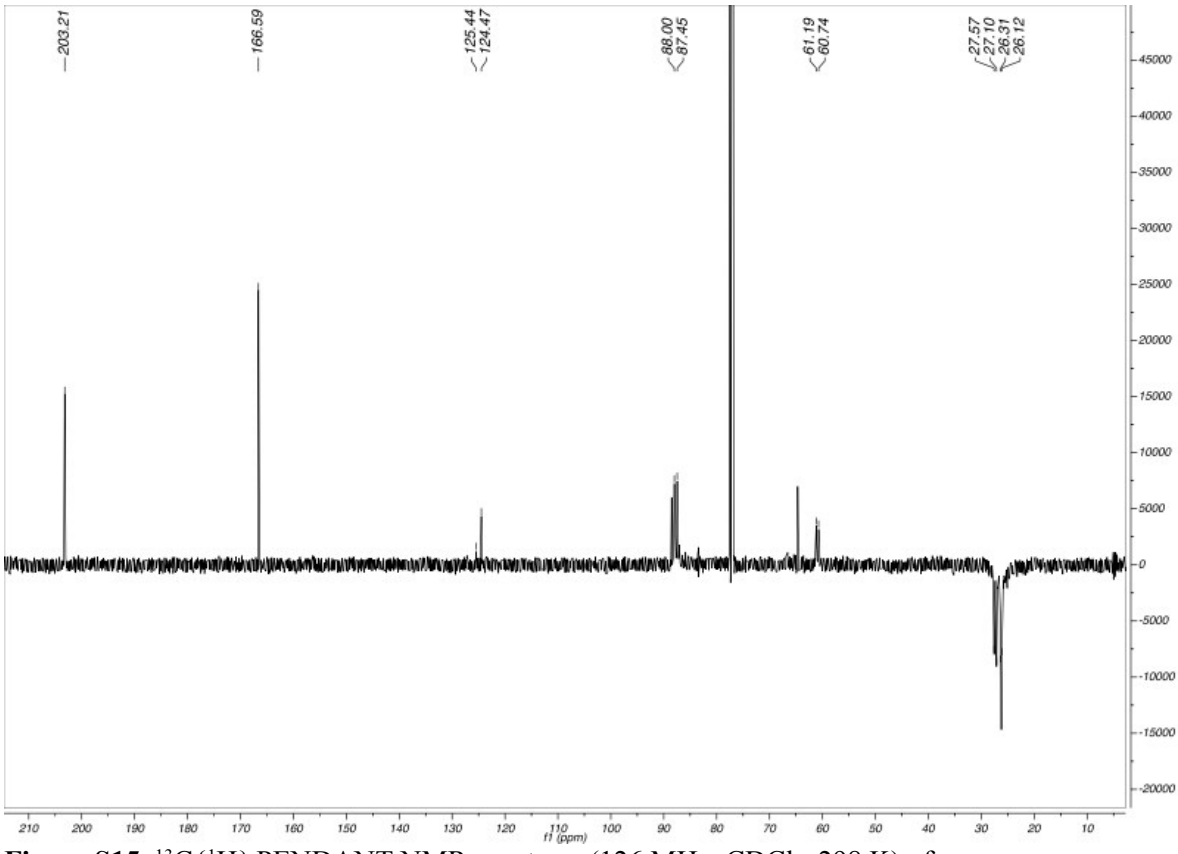


Figure S15. ^{13}C{^{1}H} PENDANT NMR spectrum (126 MHz, $CDCl_3$, 298 K) of $[Ru(IBioxMe_4)_2(CO)HCl]$ (**13**).

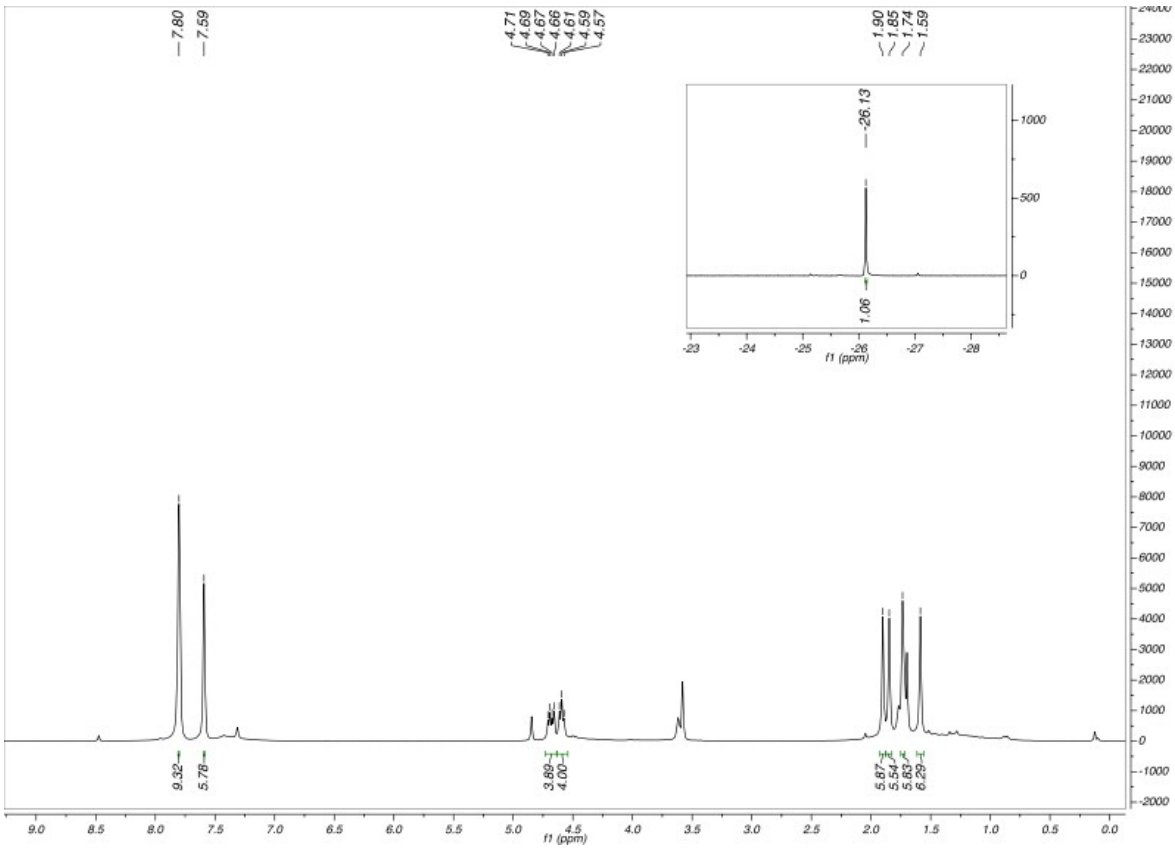


Figure S16. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of $[Ru(IBioxMe_4)_2(CO)(THF)H][BAr^F{}_4]$ (**14**).

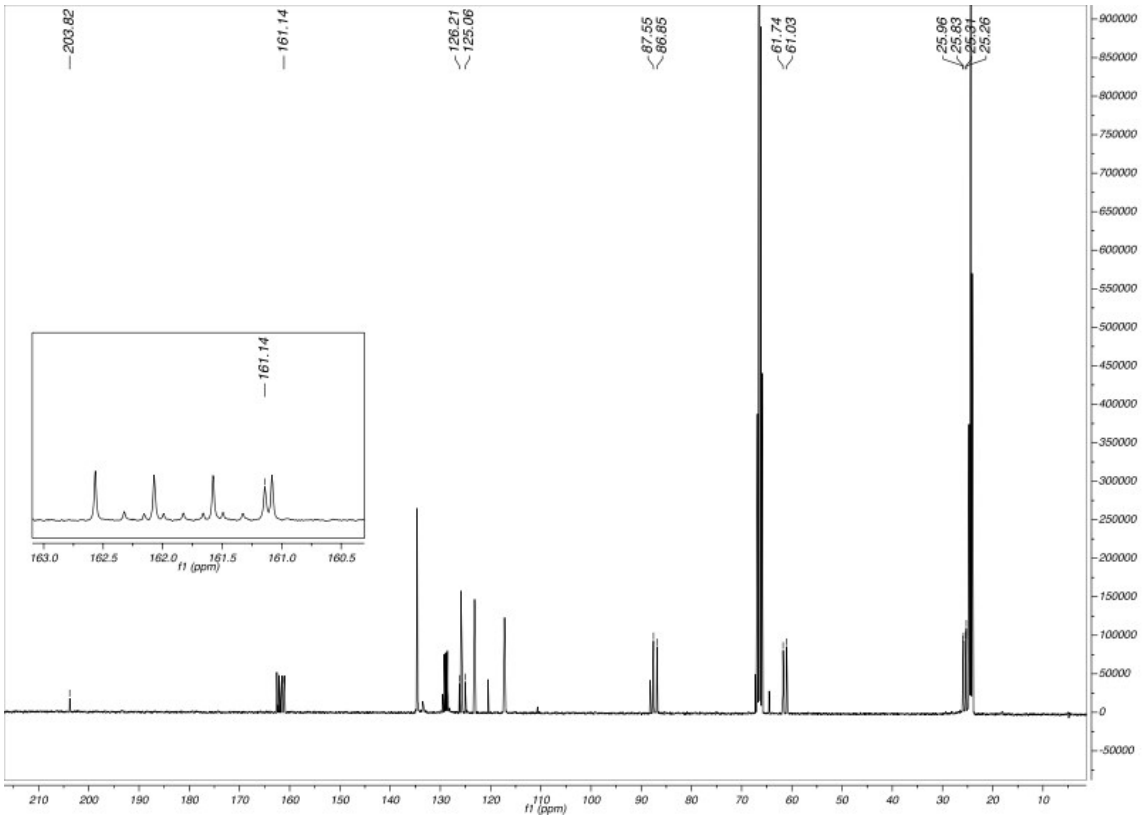


Figure S17. ^{13}C{^{1}H} NMR spectrum (101 MHz, THF-d_8, 298 K) of $[Ru(IBioxMe_4)_2(CO)(THF)H][BAr^F{}_4]$ (**14**).

[Ru(IMes)(PPh$_3$)(CO)HCl]. The compound was synthesised by a minor modification of the literature procedure.[1] IMes (200 mg, 0.655 mmol) was added to the suspension of finely powdered [Ru(PPh$_3$)$_3$(CO)HCl]·CH$_2$Cl$_2$ (426 mg, 0.410 mmol) in toluene (5 mL). The solution was stirred overnight, after which time reaction was complete by ^{31}P{^{1}H} NMR spectroscopy. The solvent was concentrated under vacuum to ca. 0.5 mL and treated with hexane (8 mL) at room temperature. A yellow-orange microcrystalline precipitate was filtered off, washed with hexane (3 x 5 mL) and dried under vacuum. Yield 256 mg (85%).

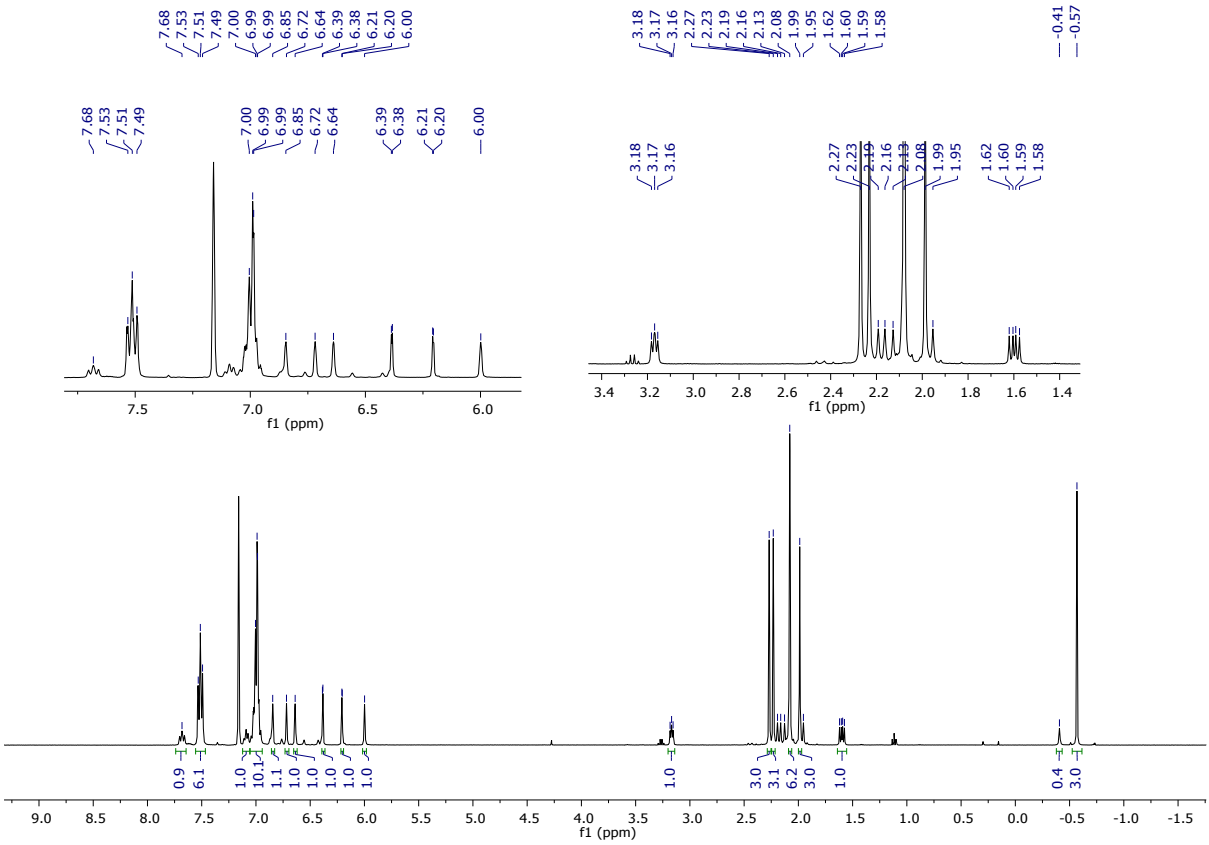


Figure S18. ^{1}H NMR spectrum (500 MHz, C$_6$D$_6$, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).

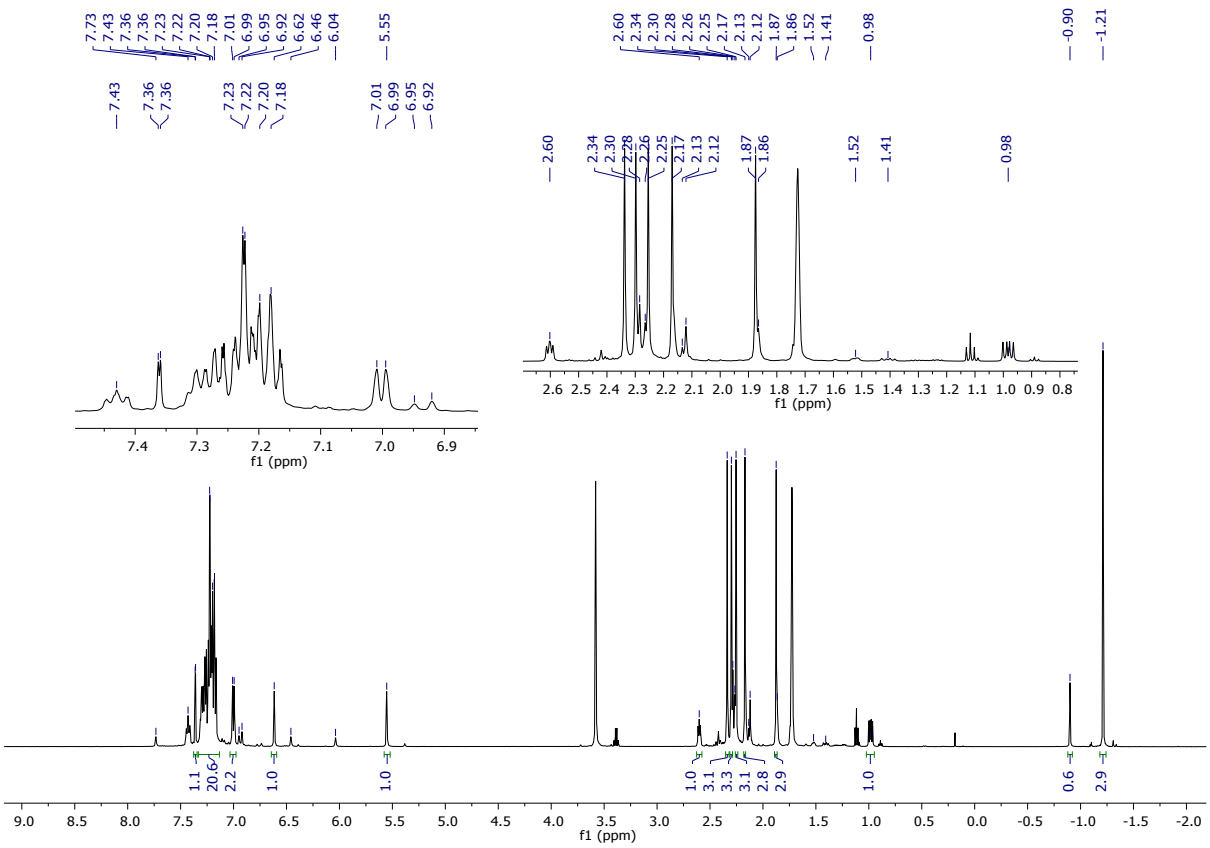


Figure S19. ^{1}H NMR spectrum (500 MHz, THF-d_8, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).

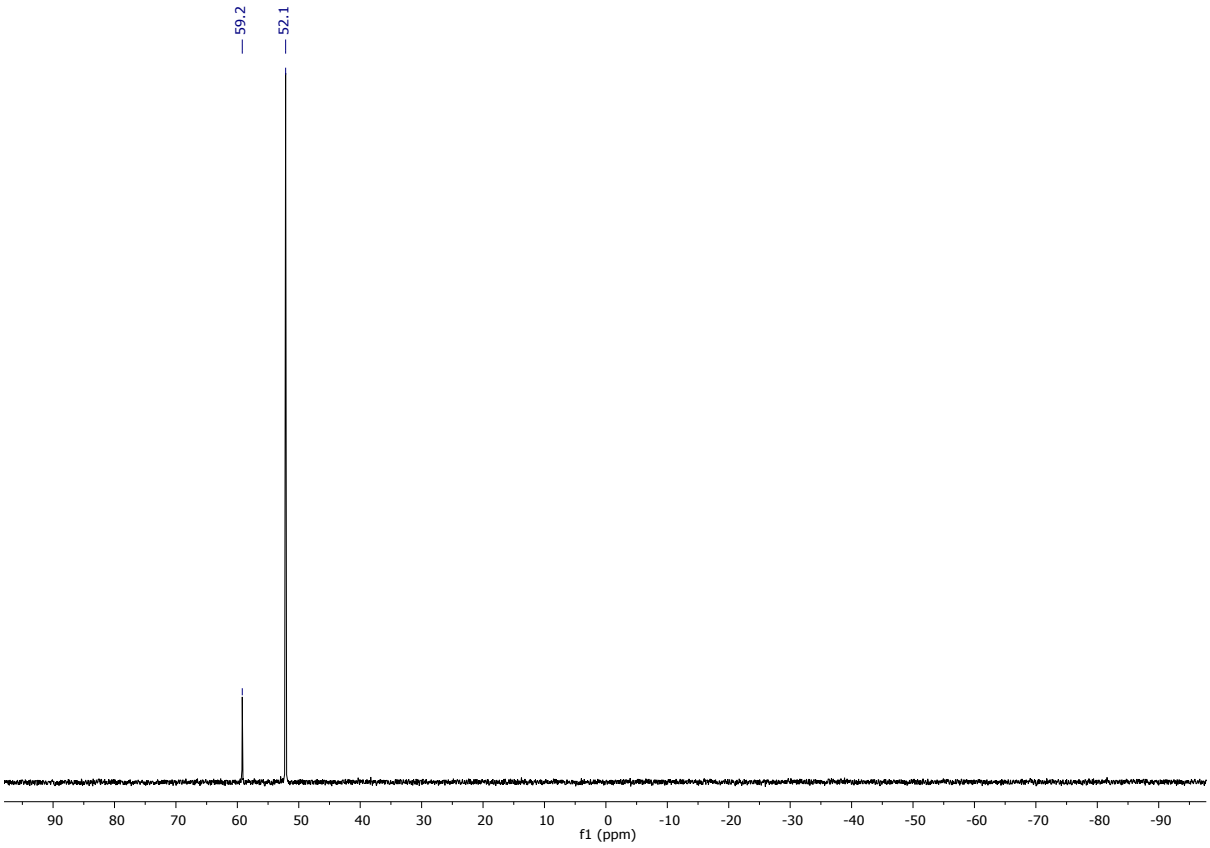


Figure S20. ^{31}P{^{1}H} NMR spectrum (162 MHz, C_6D_6, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).

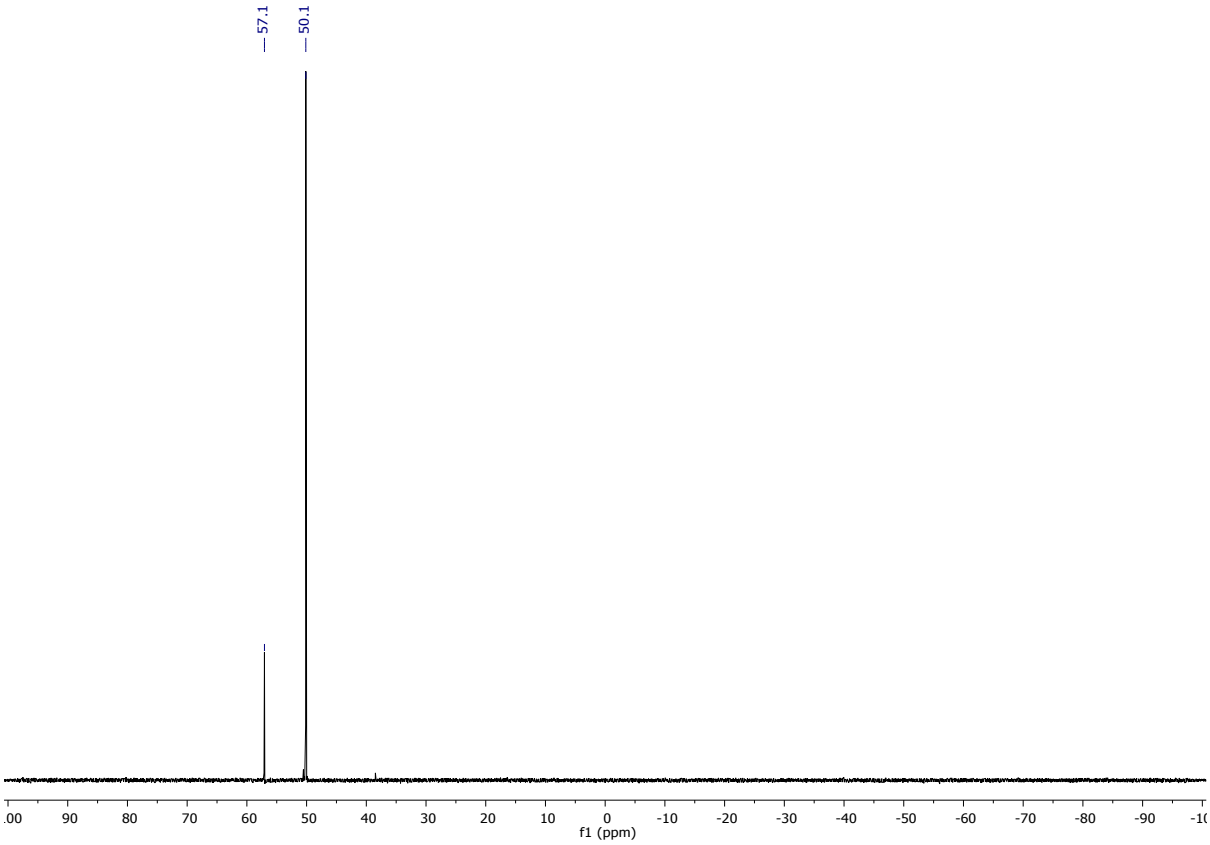


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).

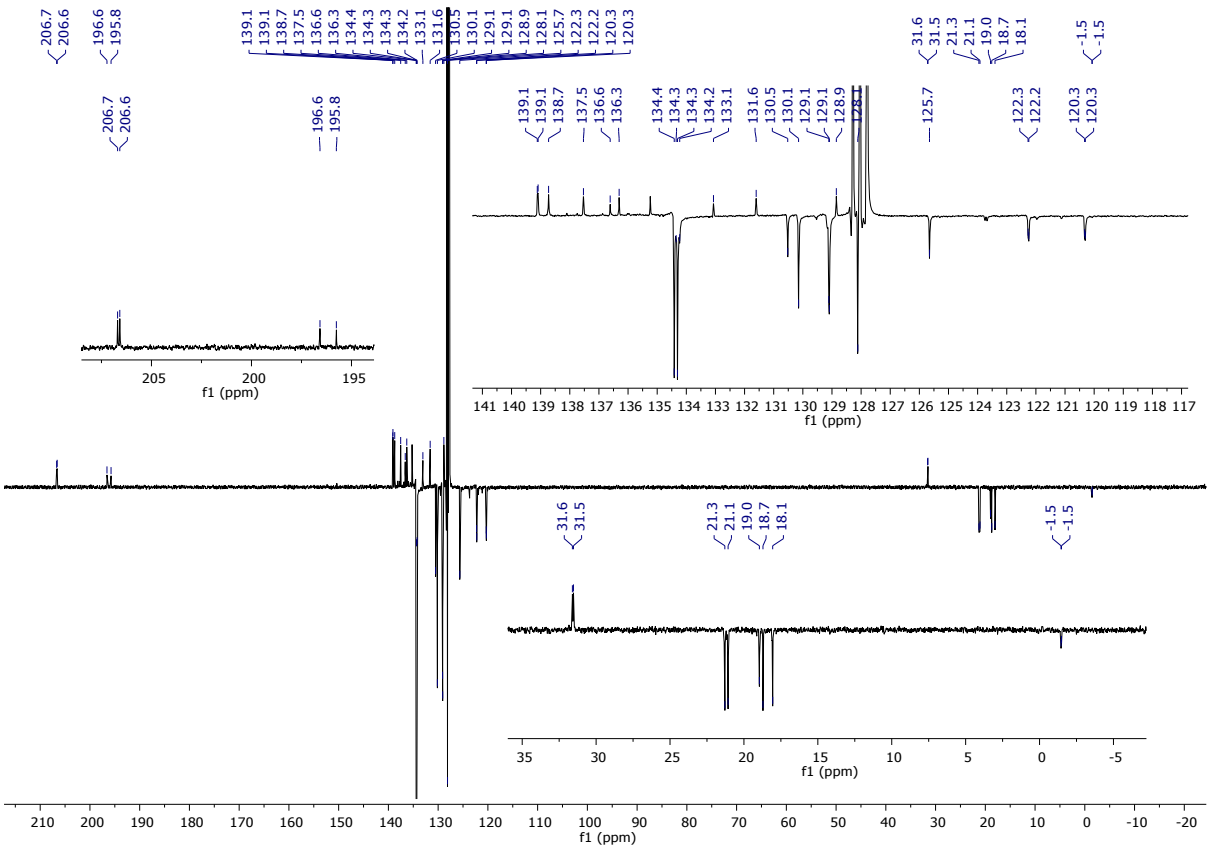


Figure S22. $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (101 MHz, C_6D_6, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).

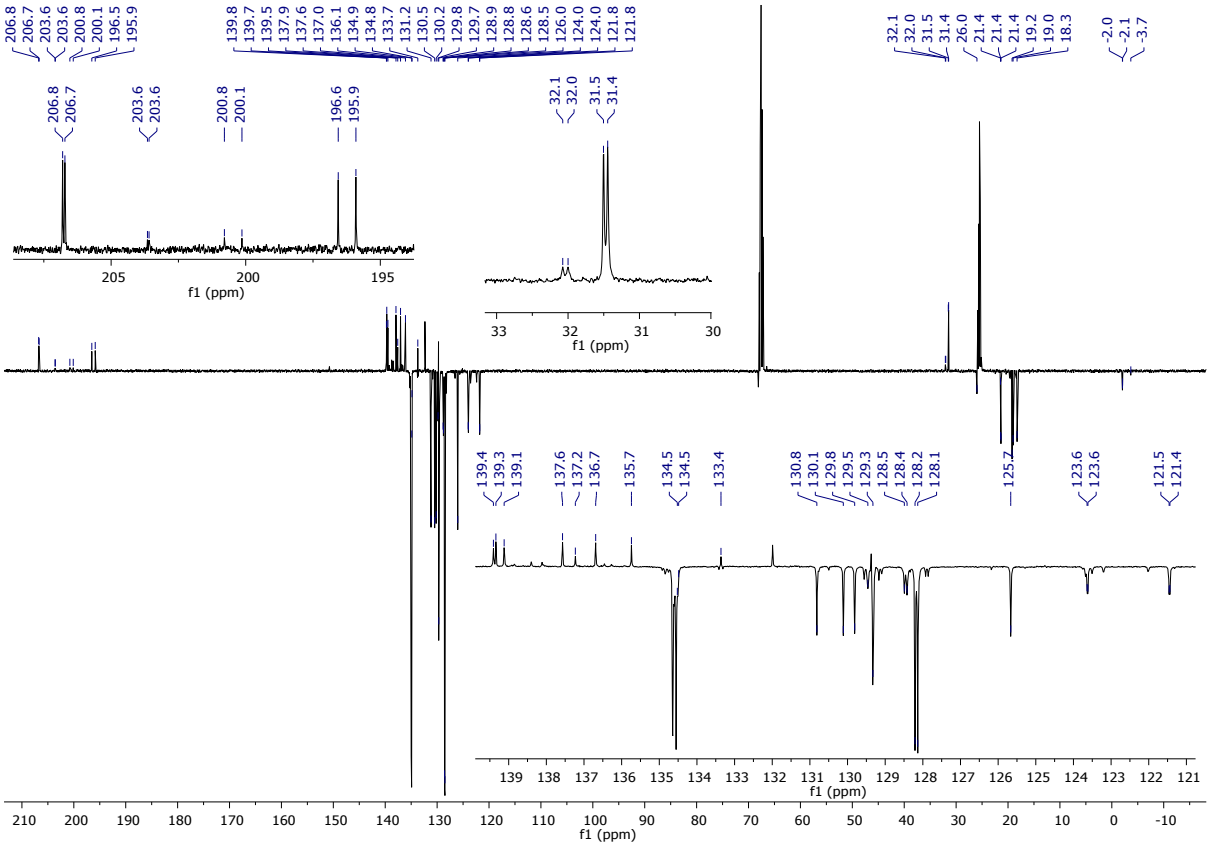
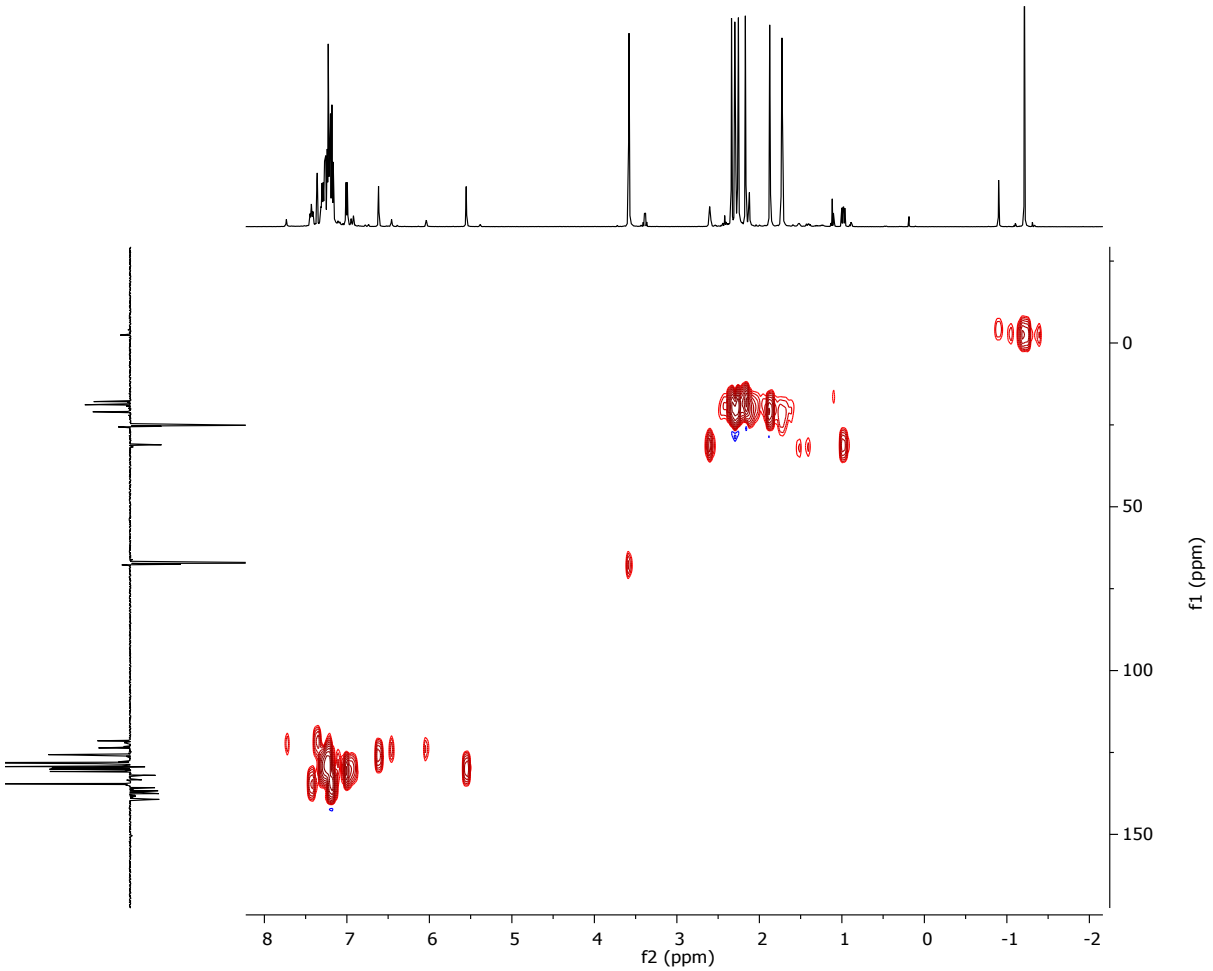


Figure S23. $^{13}C\{^{1}H\}$ DEPTQ NMR spectrum (126 MHz, THF-d_8, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).



IMes cyclometallated region (Ru-CH_2):

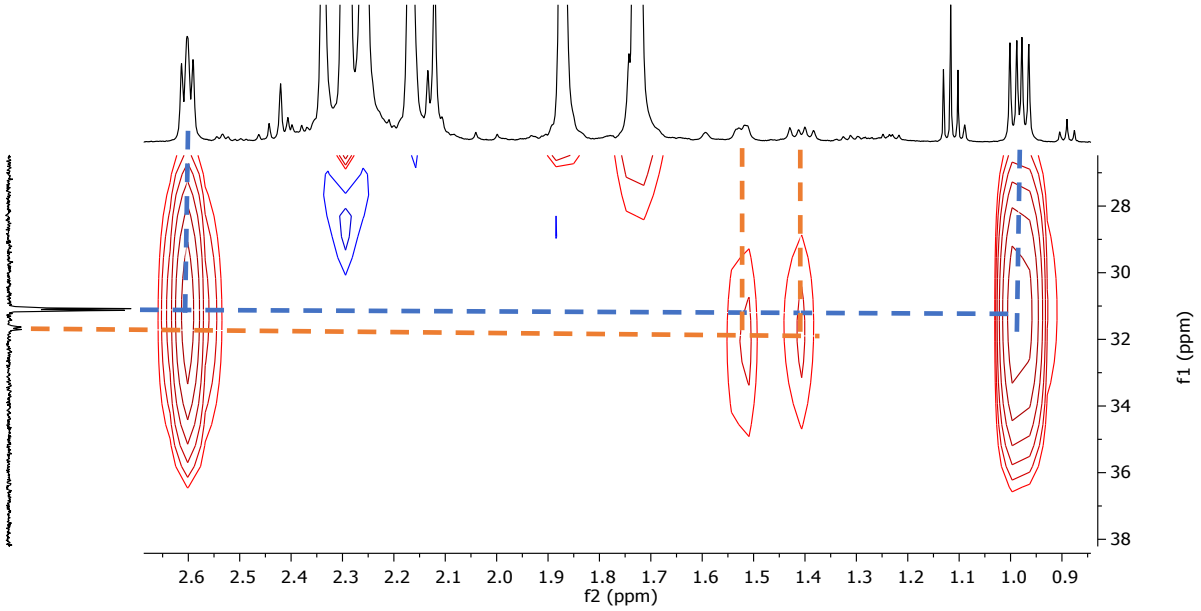
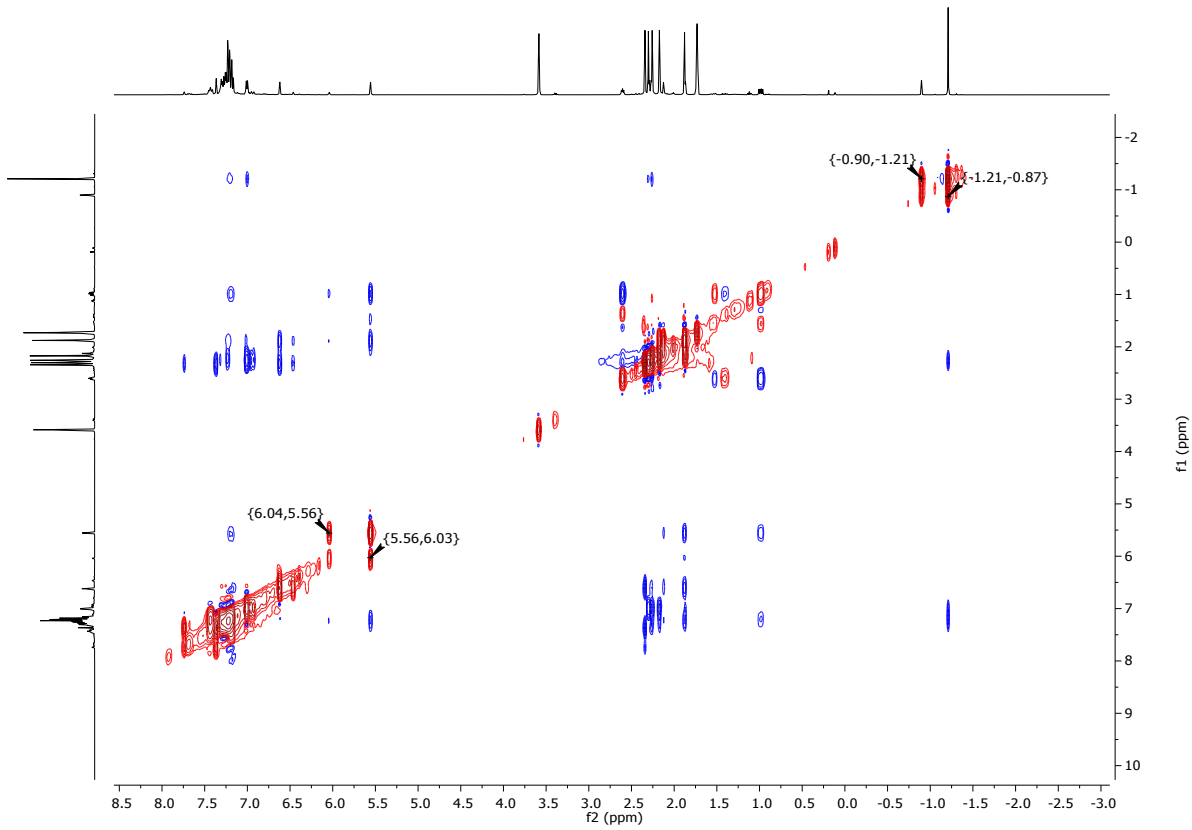


Figure S24. ^{1}H-^{13}C HSQC spectra (THF-d_8, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**).



IMes cyclometallated region (Ru-CH_2):

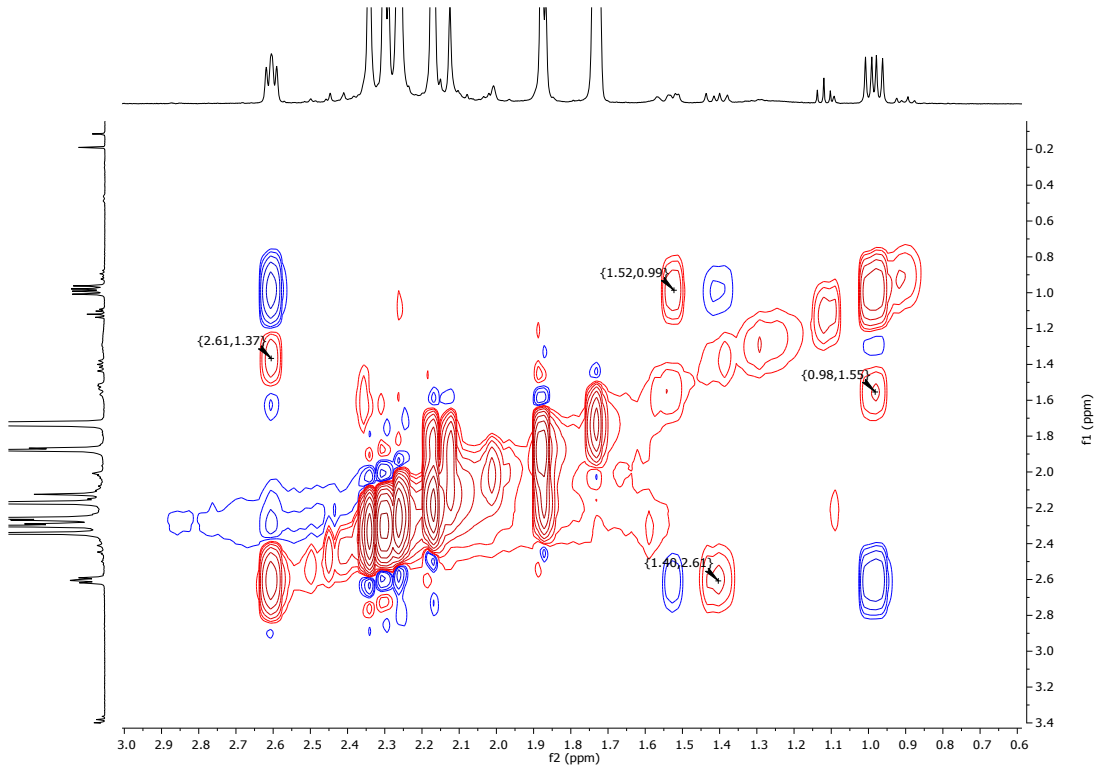


Figure S25. NOESY NMR spectra (400 MHz, THF-d_8, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)ZnMe] (**15**). The exchange peaks are labelled.

[Ru(IMes)(PPh$_3$)(CO)(ZnMe)Cl] (16). The slow, dropwise addition of $ZnMe_2$ (0.60 mL of 1.2 M in toluene, 0.72 mmol) to a THF (4 mL) solution of [Ru(IMes)(PPh$_3$)(CO)HCl] (105 mg, 0.143 mmol) brought about a colour change from yellow to dark orange. After stirring for 1 h, the volatiles were removed under vacuum and the residue treated with Et_2O (15 mL). This afforded a yellow precipitate of **16**, which was separated and dried in vacuum. Yield 20 mg (17 % yield). ^{1}H NMR: δ_H (400 MHz, C_6D_6, 298 K) 7.66-7.55 (m, 6H, PPh$_3$), 6.99 (br s, 9H, PPh$_3$), 6.79 (s, 2H, Ar), 6.76 (s, 2H, Ar), 6.18 (s, 2H, NC*H*=NC*H*), 2.43 (s, 6H, C*H*$_3$), 2.31 (br s, 6H, C*H*$_3$), 2.19 (s, 6H, C*H*$_3$), -0.51 (s, 3H, ZnC*H*$_3$). ^{31}P{^{1}H} NMR: δ_P (162 MHz, C_6D_6, 298 K) 40.3 (s). Selected ^{13}C{^{1}H}NMR: δ_C (101 MHz, C_6D_6, 298 K) 200.8 (d, $^2J_{CP}$ = 13 Hz, Ru-*C*O), 192.2 (d, $^2J_{CP}$ = 95 Hz, Ru-C_{NHC}), 134.7 (d, J_{CP} = 11 Hz, PPh$_3$), 129.3 (d, J_{CP} = 2 Hz, PPh$_3$), 21.3 (s, *C*H$_3$), 19.0 (br s, *C*H$_3$), -2.7 (d, $^3J_{CP}$ = 3 Hz, Zn*C*H$_3$). IR (KBr, cm^{-1}): 1878 (ν_{CO}).

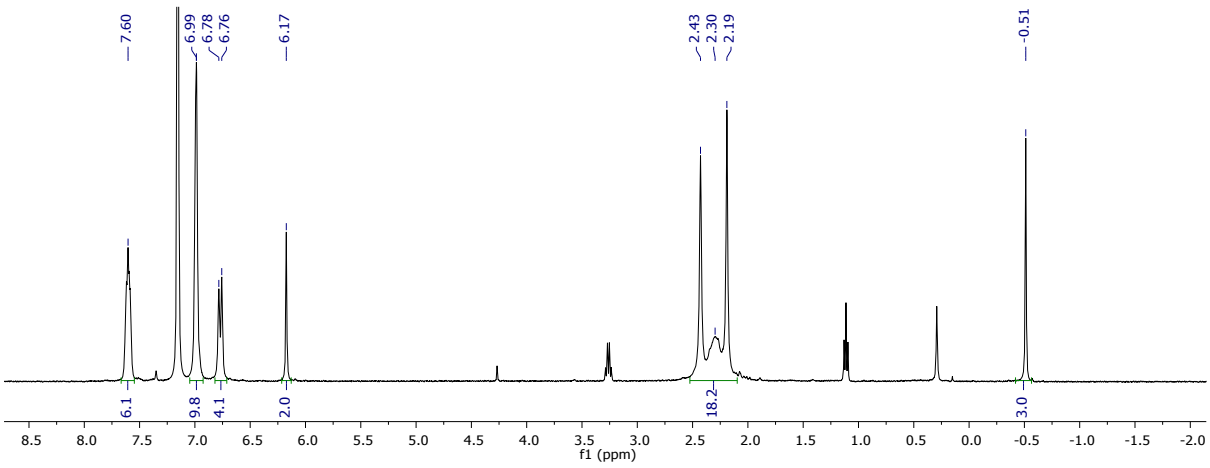


Figure S26. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of [Ru(IMes)(PPh$_3$)(CO)(ZnMe)Cl] (**16**).

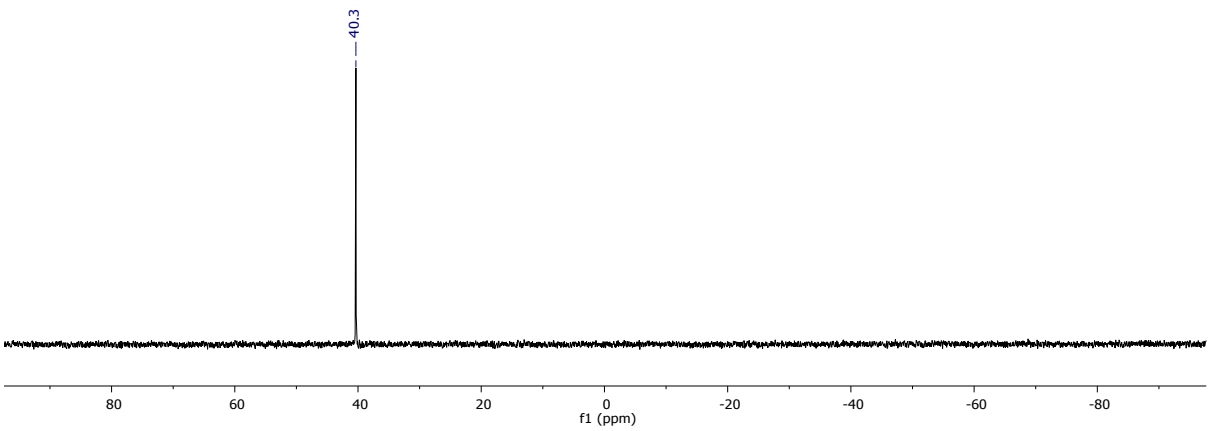


Figure S27. ^{31}P{^{1}H} NMR spectrum (162 MHz, C_6D_6, 298 K) of [Ru(IMes)(PPh$_3$)(CO)(ZnMe)Cl] (**16**).

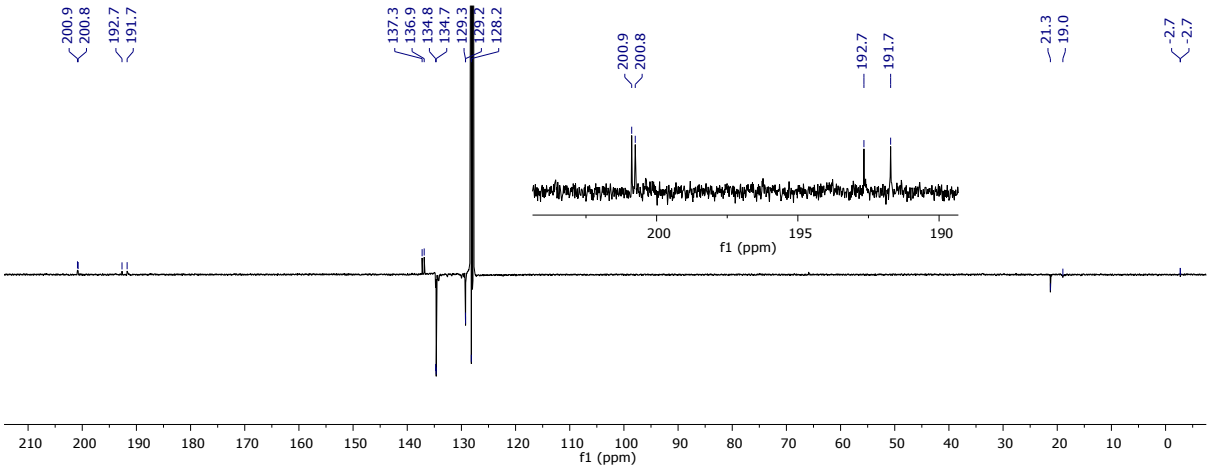


Figure S28. $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (101 MHz, C_6D_6, 298 K) of [Ru(IMes)(PPh_3)(CO)(ZnMe)Cl] (**16**).

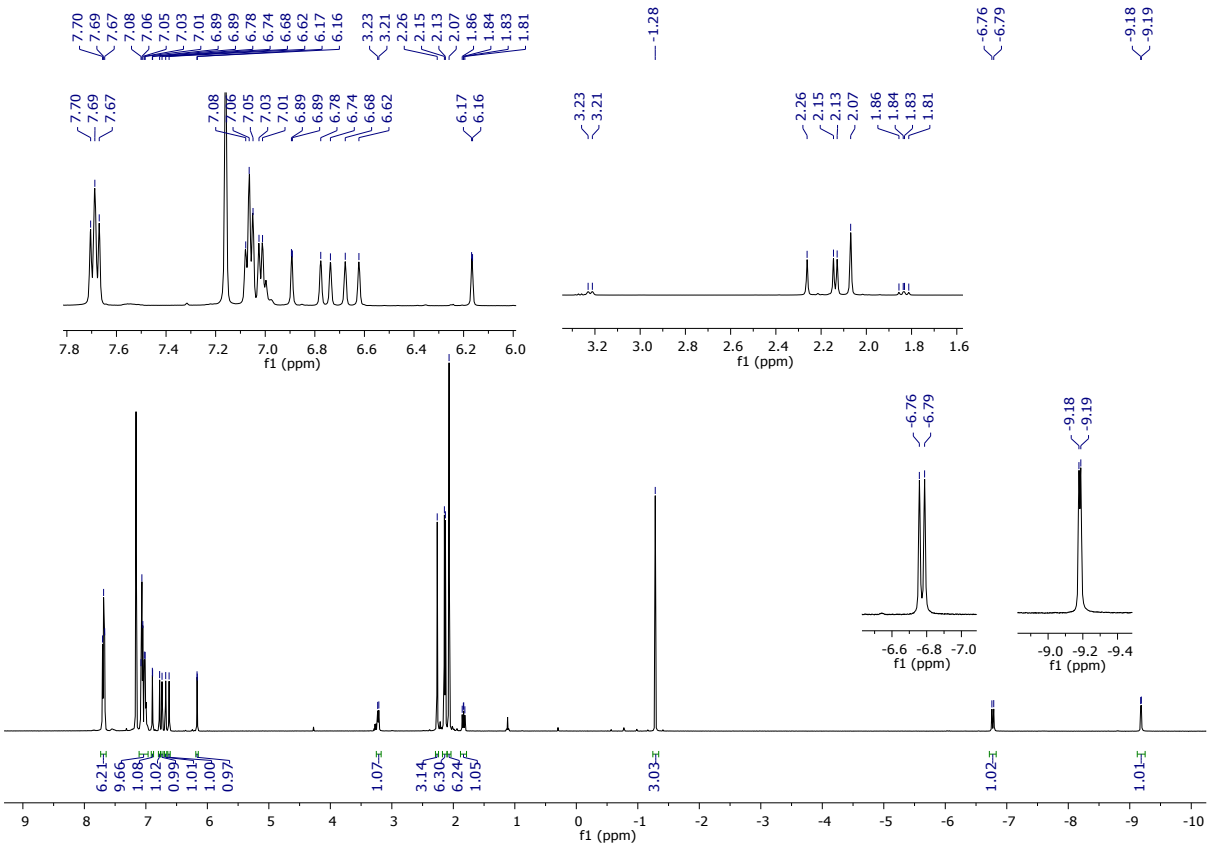


Figure S29. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of [Ru(IMes)′(PPh_3)(CO)$(H)_2$ZnMe] (**17**).

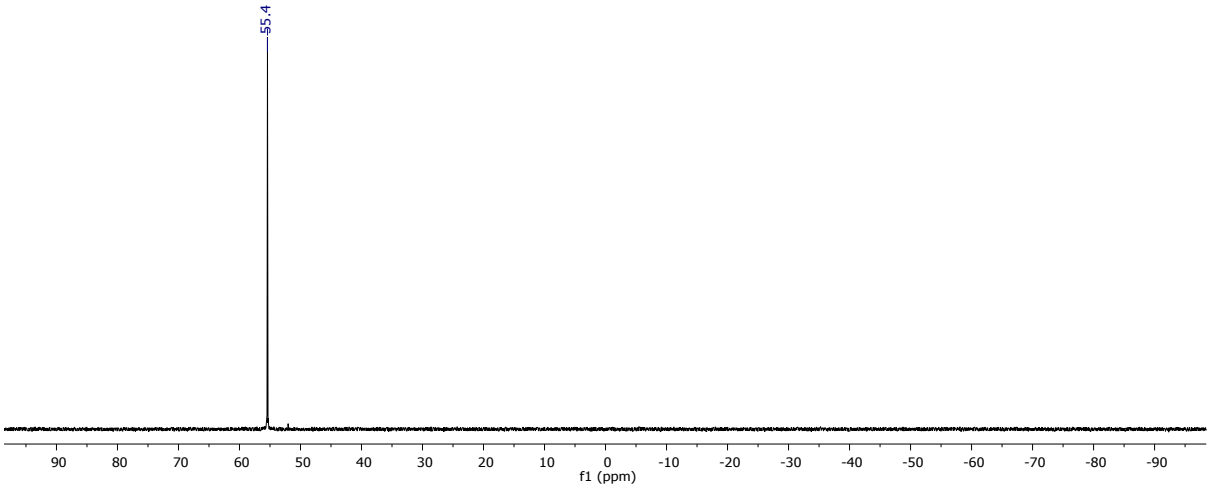


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, C_6D_6, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)(H)$_2$ZnMe] (**17**).

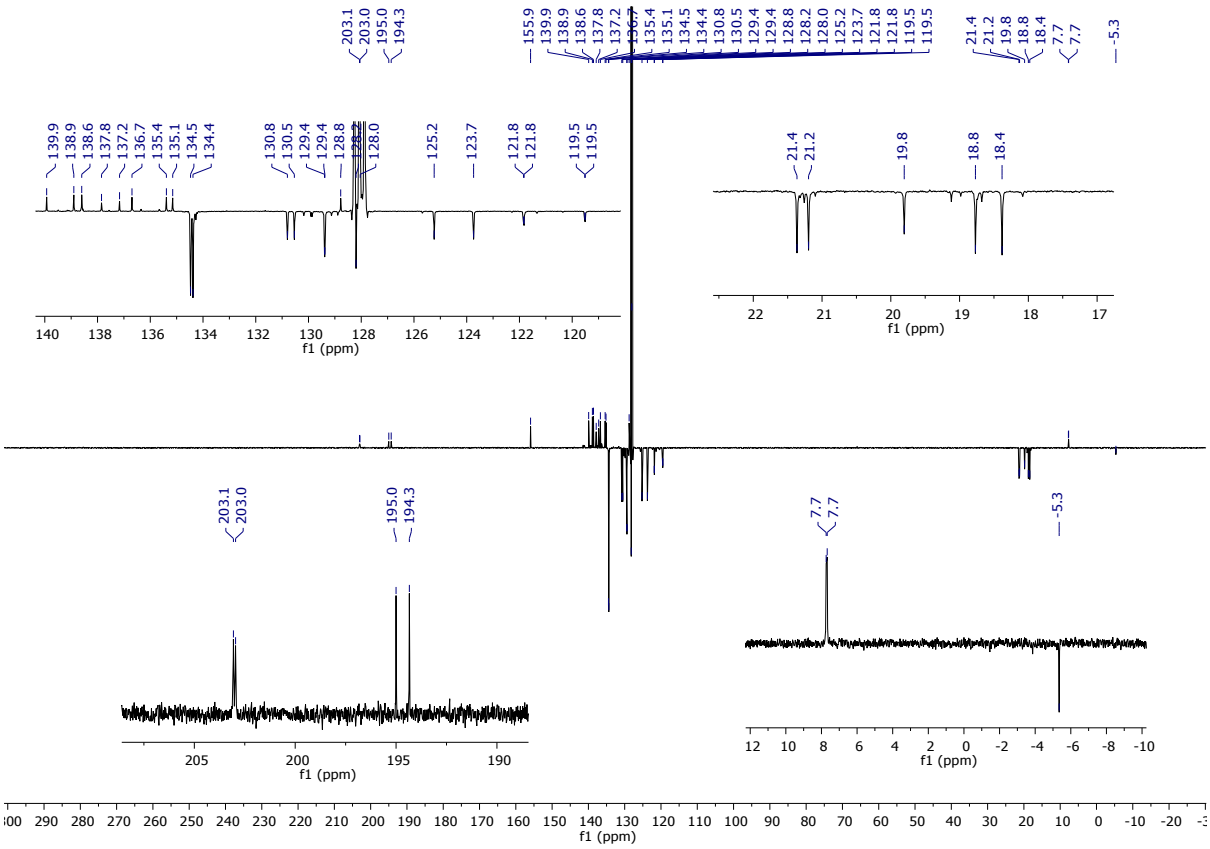


Figure S31. $^{13}C\{^{1}H\}$ PENDANT NMR spectrum (126 MHz, C_6D_6, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)(H)$_2$ZnMe] (**17**).

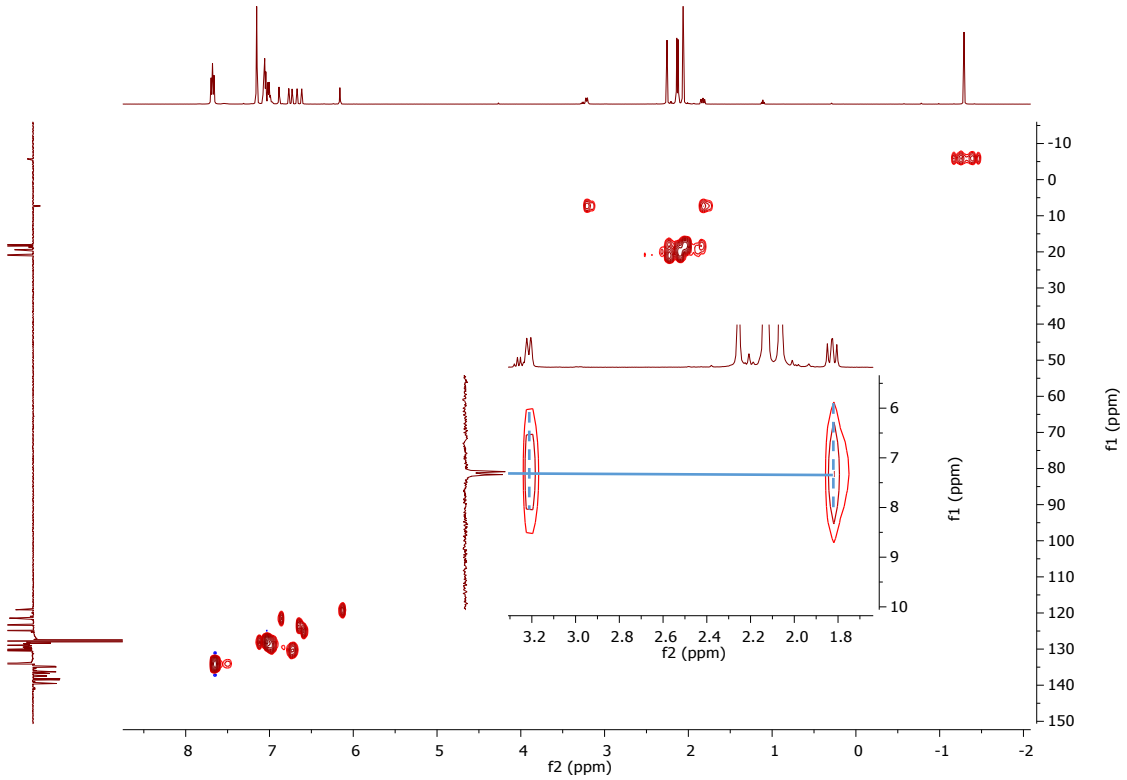


Figure S32. ^{1}H-^{13}C HSQC spectrum (THF-d_8, 298 K) of [Ru(IMes)′(PPh$_3$)(CO)(H)$_2$ZnMe] (**17**), with expansion of the cyclometallated (Ru-CH$_2$) region.

1. U. L. Dharmasena, H. M. Foucault, E. N. dos Santos, D. E. Fogg and S. P. Nolan, *Organometallics*, 2005, **24**, 1056-1058.