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Supporting Information for

Synthesis and Reactivity of Transition Metal Methoxysilanoates

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Part I. Synthetic Procedures

($^{Me,Me}N_2N$)NiCl.[1] $^{Me,Me}N_2NH$ was prepared from NH_3 (0.5 M in dioxane) and 2-bromo-N,N-dimethylanilnine through successive palladium-catalyzed cross coupling reactions.[2] $^{Me,Me}N_2NLi$ (1.14 g, 4.36 x 10^{-3} mol, 56 % yield) was prepared by the addition of ^{n}BuLi (1.6 M in hexanes, 4.8 mL, 7.77 x 10^{-3} mol, 1 equiv) to a pentane solution of $^{Me,Me}N_2NH$ (1.98 g, 7.77 x 10^{-3} mol, 1 equiv) at room temperature, and ($^{Me,Me}N_2N$)NiCl (0.96 g, 2.76 x 10^{-3} mol, 63 % yield) was prepared by the addition of $^{Me,Me}N_2NLi$ (1.14 g, 4.36 x 10^{-3} mol, 1 equiv) to a THF solution of (DME)$NiCl_2$ (0.96 g 4.36 x 10^{-3} mol, 1 equiv) at room temperature.[1] ^{1}H NMR (500 MHz, C_6D_6): δ 7.46 (dd, *J* = 8.6, 1.3 Hz, 2H), 6.92 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 2H), 6.42 (dt, *J* = 8.0, 1.3 Hz, 2H), 6.35 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 2.56 (s, 12H).

(IPr)CuCl. (IPr)CuCl was prepared according to the method of Nolan.[3] An anhydrous THF solution of CuCl (88 mg, 8.85 x 10^{-4} mol, 1 equiv), NaOBu^t (85 mg, 8.85 x 10^{-4} mol, 1 equiv) and 1,3-bis(2,6-di- isopropylphenyl)imidazolium chloride (302 mg, 8.85 x 10^{-4} mol, 1 equiv) was stirred under nitrogen at room temperature for 24 hours. The solution was filtered through Celite, and the solvent removed under vacuum. The white residual solid was used as obtained. Yield: 174 mg (46 %). ^{1}H NMR (500 MHz, THF-d_8) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.43 (s, 2H) 7.33 (d, *J* = 7.8 Hz, 4H), 2.65 (p, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H).

(triphos)CoCl.[4] Anhydrous $CoCl_2$ (309 mg, 2.40 x 10^{-3} mol, 1 equiv) was added to a THF (20 mL) solution of triphos ($CH_3C(CH_2PPh_2)_3$, 1.5 g, 2.40 x 10^{-3} mol, 1 equiv). The resulting blue-green solution was stirred at room temperature for 1 h. Activated zinc, freshly prepared from $ZnCl_2$ (327 mg, 2.40 x 10^{-3} mol, 1 equiv) and potassium (188 mg, 4.80 x 10^{-3} mol, 2 equiv), was then added to the reaction. The solution was stirred for another 3 hours, becoming tan in the process. The solvent was removed under vacuum and the residual solid extracted into CH_2Cl_2. The CH_2Cl_2 solution was filtered through Celite. The filtrate was collected and the solvent removed under vacuum. A tan solid remained. Yield: 1.3 g (75 %).

CpRu(DPPE)(OTf). Solutions of THF Cp*Ru(DPPE)(OTf) were prepared in situ by the reaction of $CpRu(PPh_3)_2Cl$ with AgOTf. The solutions were filtered through Celite, before treatment with $NaOSi(OMe)_2Me$. $CpRu(PPh_3)_2Cl$ (3.6 g, 4.96 x 10^{-3} mol, 78 % yield)was prepared by refluxing an ethanol solution of PPh_3 (7 g, 2.67 x 10^{-2} mol, 4 equiv), cyclopentadiene (3.3 mL, 2.6 g, 3.96 x 10^{-2} mol, 6.2 equiv), and $RuCl_3$•$3H_2O$ (1.67 g, 6.37 x 10^{-3} mol, 1 equiv),[5] and CpRu(DPPE)Cl[6] (562 mg, 9.37 x 10^{-4} mol, 68 % yield) was prepared by refluxing a solution of $CpRu(PPh_3)_2Cl$ (1 g, 1.38 x 10^{-3} mol, 1 equiv) and DPPE (549 mg, 1.38 x 10^{-3} mol, 1 equiv) in toluene overnight.

CpRu(DPPE)Cl: ^{1}H NMR (500 MHz, C_6D_6): δ 8.07 – 7.98 (m, 4H), 7.22 (m, 4H), 7.14-7.05 (overlapping signals, 6H), 6.96 – 6.89 (m, 6H), 4.49 (s, 5H), 2.53 (m, 2H), 2.07 (m, 2H). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 81.58.

Cp*$_2$Zr(OH)$_2$. To a solution of Cp*$_2$ZrCl$_2$ (500 mg, 1.16 x 10^{-3} mol, 1 equiv.) in 50 mL of THF was added 1.6 mL of a 1.7 M solution of *tert*-butyllithium in pentane (2.54 x 10^{-3} mol, 2.2 equiv.) at -78 °C. The reaction was stirred at -78 °C for 1 h. Deionized water (41.6 µL, 41.6 mg, 2.31 x 10^{-3} mol, 1 equiv.) was then added to the reaction, and the solution was stirred for another 18 h while the flask slowly warmed to room temperature. The solvent and all volatiles were then removed under vacuum. The residual solid was extracted into toluene and filtered through Celite. The filtrate was collected and the toluene was removed under vacuum yielding a white solid. Yield: 396 mg (78 %). The NMR data matched that previously reported.[7] ^{1}H NMR (500 MHz, C_6D_6): δ 5.07 (s, 2H), 1.82 (s, 30H).

Cp*$_2$Ti(OH)$_2$.[8] Cp*$_2$Ti(OH)$_2$ was prepared by the addition of water to either Cp*$_2$Ti(Me$_3$SiCCSiMe$_3$), Cp*$_2$Ti(C$_2$H$_4$), of Cp*$_2$TiMe$_2$. In the case of Cp*$_2$Ti(Me$_3$SiCCSiMe$_3$), a THF solution of Cp*$_2$Ti(Me$_3$SiCCSiMe$_3$) (744 mg, 1.52 x 10^{-3} mol, 1 equiv) was treated with H_2O (55 µL, 55 mg, 3.05 x 10^{-3} mol, 2 equiv) at room temperature. The reaction was stirred at room temperature for 24 h. The solvent was then removed under vacuum. The residual solid extracted into pentane. The pentane solution was filtered through Celite. The filtrate was collected and the solvent was removed under vacuum. A yellow solid was obtained. Yield: 551 mg (99 %). ^{1}H NMR (500 MHz, C_6D_6): δ 5.45 (s, 2H), 1.81 (s, 30H).

Cp*$_2$Zr(OH)Cl.[7] To a solution of Cp*$_2$ZrCl$_2$ (1.00 g, 2.31 x 10^{-3} mol, 1 equiv.) in 50 mL of THF was added 1.36 mL of a 1.7 M solution of *tert*-butyllithium in pentane (1.36 mL, 2.31 x 10^{-3} mol, 1 equiv.) at -78 °C. The reaction was stirred at -78 °C for 3 h. Deionized water (41.6 µL, 41.6 mg, 2.31 x 10^{-3} mol, 1 equiv.) was then added to the reaction, and the reaction was stirred for another 18 h while the flask slowly warmed to room temperature. The solvent and all volatiles were then removed under vacuum. The residual solid was extracted into toluene and filtered through Celite. The filtrate was collected and the toluene was removed under vacuum yielding a white solid (854 mg, 2.06 x 10^{-3} mol). Yield: 89 %. The NMR data matched that previously reported.[7] ^{1}H NMR (500 MHz, C_6D_6): δ 5.07 (s, 1H), 1.82 (s, 30H). ^{13}C{^{1}H} NMR (C_6D_6): δ 120.90, 11.75.

(IPr)CuOH. (IPr)CuOH was prepared according to the method of Nolan and co-workers.[9] A THF solution of (IPr)CuCl (100 mg, 2.06 x 10^{-4} mol, 1 equiv) and anhydrous CsOH (62 mg, 4.12 x 10^{-4} mol, 2 equiv) was stirred at room temperature for 12 h. The solution was filtered through Celite, and the solvent removed under vacuum leaving a white solid. Yield: 62 mg (64 %). The 1H NMR spectrum matched that

of (IPr)CuCl. ^{1}H NMR (500 MHz, THF-d_8) δ 7.46 (t, J = 7.8 Hz, 2H), 7.43 (s, 2H) 7.33 (d, J = 7.8 Hz, 4H), 2.65 (p, J = 6.9 Hz, 4H), 1.32 (d, J = 6.9 Hz, 12H), 1.21 (d, J = 6.9 Hz, 12H).

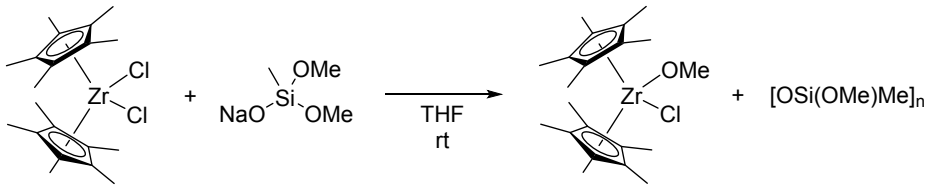
$Cp^*_2Ti(C_2H_4)$.[10] In a nitrogen-filled glovebox, a 300-mL Schlenk flask, equipped with a magnetic stir bar, was charged with $Cp^*_2TiCl_2$ (1.0 g, 2.6 x 10^{-3} mol, 1 equiv.) and 100 mL of dry THF. The flask was stoppered with a rubber septum, removed from the glovebox, and attached to a Schlenk manifold via Tygon tubing. The tubing was purged of ambient atmosphere by applying vacuum and nitrogen successively three times, and the flask was opened to a nitrogen atmosphere. The flask was then placed in a dry ice / acetone bath, and a solution of n-butyllithium (1.6 M; 3.4 mL, 5.4 x 10^{-3} mol, 2.1 equiv.) in hexanes was added to the flask by syringe. The reaction was stirred rapidly at -78 °C for 3 h. A red solution developed. Following the reaction, the flask was removed from the dry ice / acetone bath and placed in a liquid nitrogen bath. With the solution frozen, the flask was then opened to active vacuum and evacuated. After 10 min. of evacuating the flask, the flask was closed to active vacuum, removed from the liquid nitrogen bath, and charged with 1.5 atm of C_2H_4. The solution was allowed to warm to room temperature and then stirred at room temperature for 48 h. A yellow-brown solution developed. Volatile materials were removed under vacuum, and the residual solid was extracted into pentane. The pentane solution was filtered through Celite and collected. The Celite was then washed with additional pentane until it was colorless. The pentane solutions were combined and the pentane removed under vacuum. A green solid was obtained and used as collected. Yield: 0.56 g, 1.6 x 10^{-3} mol, 63 %. ^{1}H NMR (500 MHz, C_6D_6): δ 2.05 (s, 4H), 1.68 (s, 30H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 119.80 (s), 105.20 (s), 12.42 (s).

$Cp^*_2Ti(O)(py)$.[11] To a solution of $Cp^*_2Ti(C_2H_4)$ (562 mg, 1.62 x 10^{-3} mol, 1 equiv.) in THF (5 mL) was added excess dry pyridine (2 mL) and solid pyridine N-oxide (154 mg, 1.62 x10^{-3} mol, 1 equiv.). The green solution immediately turned red with the evolution of gas. The reaction was stirred for 12 h at room temperature, and the volatiles were then removed from the reaction under vacuum. The resulting yellow-orange solid was washed with pentane and dried under vacuum. Yield: ^{1}H NMR (500 MHz, C_6D_6): δ 8.90 (s, broad, 1H), 7.50 (s, broad, 1H), 6.76 (s, broad, 1H), 6.46 (s, broad, 2H), 1.86 (s, 30H).

$Cp^*_2Zr(OH)(OTf)$.[12] To a solution of $Cp^*_2Zr(OH)Cl$ (319 mg, 7.68 x 10^{-4} mol, 1 equiv.) in 5 mL of toluene was added AgOTf (197 mg, 7.68 x 10^{-4} mol, 1 equiv.). The reaction was stirred at room temperature for 30 minutes. A white precipitate formed. The solution was filtered through a glass frit to remove the precipitated solid. The filtrate was collected and the solvent from the filtrate removed under vacuum. A yellow solid was obtained (403 mg, 7.64 x 10^{-4} mol). Yield: 99 %. The NMR data matched that previously reported.[12] ^{1}H NMR (500 MHz, C_6D_6): δ 6.23 (s, 1H), 1.77 (s, 30H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 123.39, 11.32. $^{19}F\{^1H\}$ NMR (C_6D_6): δ -76.51.

Cp*2Zr(O)(py). $Cp^*_2Zr(O)(py)$ was prepared according to the method of Kortman, et al.[13]

Part II. Spectra



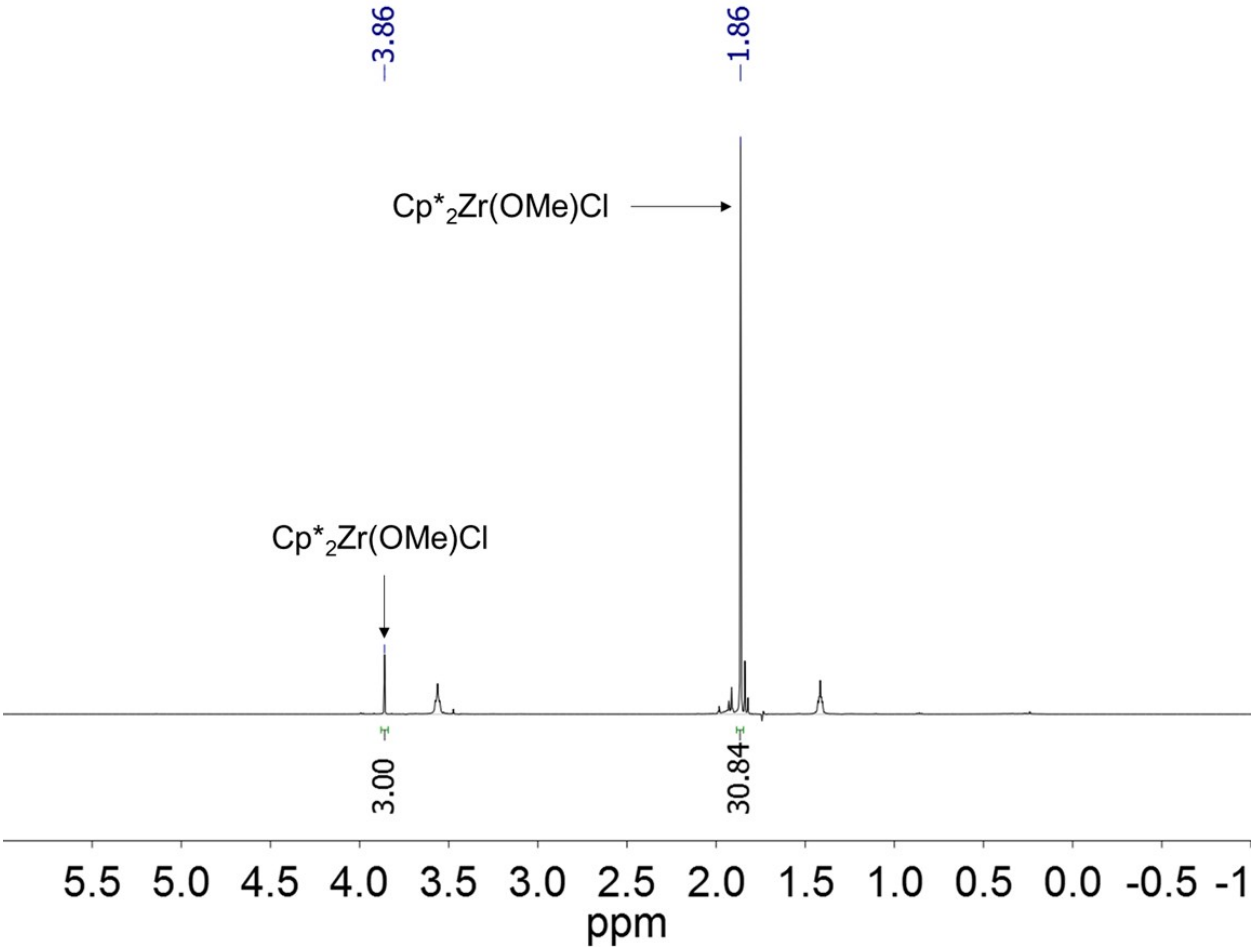
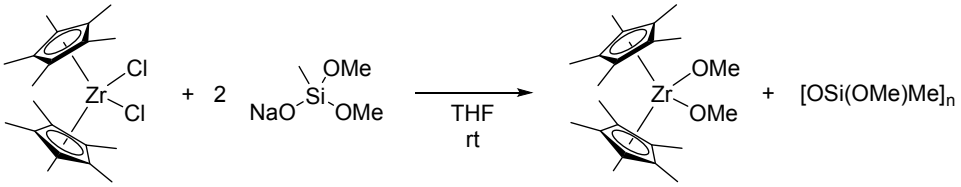


Figure 1. ^{1}H NMR spectrum of the crude material obtained from the addition of 1 equiv of $NaOSi(OMe)_2Me$ to a THF solution of $Cp^*_2ZrCl_2$. The reaction was kept at room temperature for 18 h. The solvent was then removed under vacuum and the residue extracted into C_6D_6.



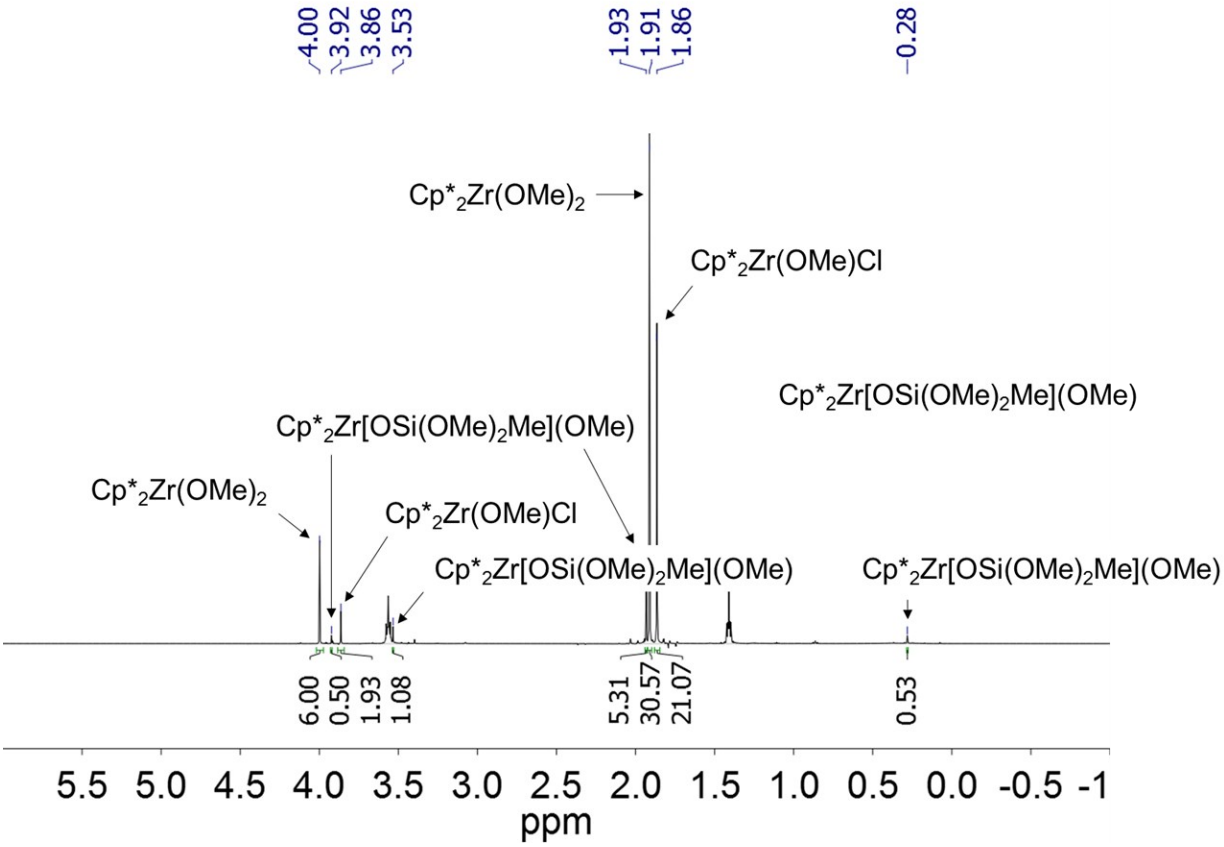
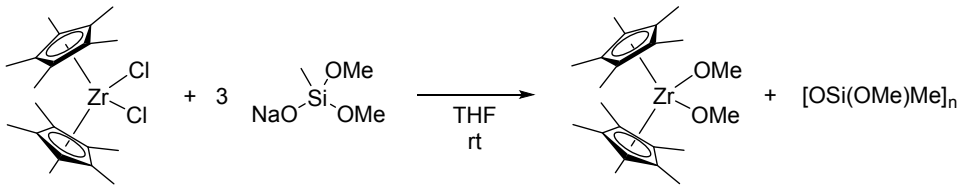


Figure 2. ^{1}H NMR spectrum of the crude material obtained from the addition of 2 equiv of $NaOSi(OMe)_2Me$ to a THF solution of $Cp^*_2ZrCl_2$. The reaction was kept at room temperature for 18 h. The solvent was then removed under vacuum and the residue extracted into C_6D_6.



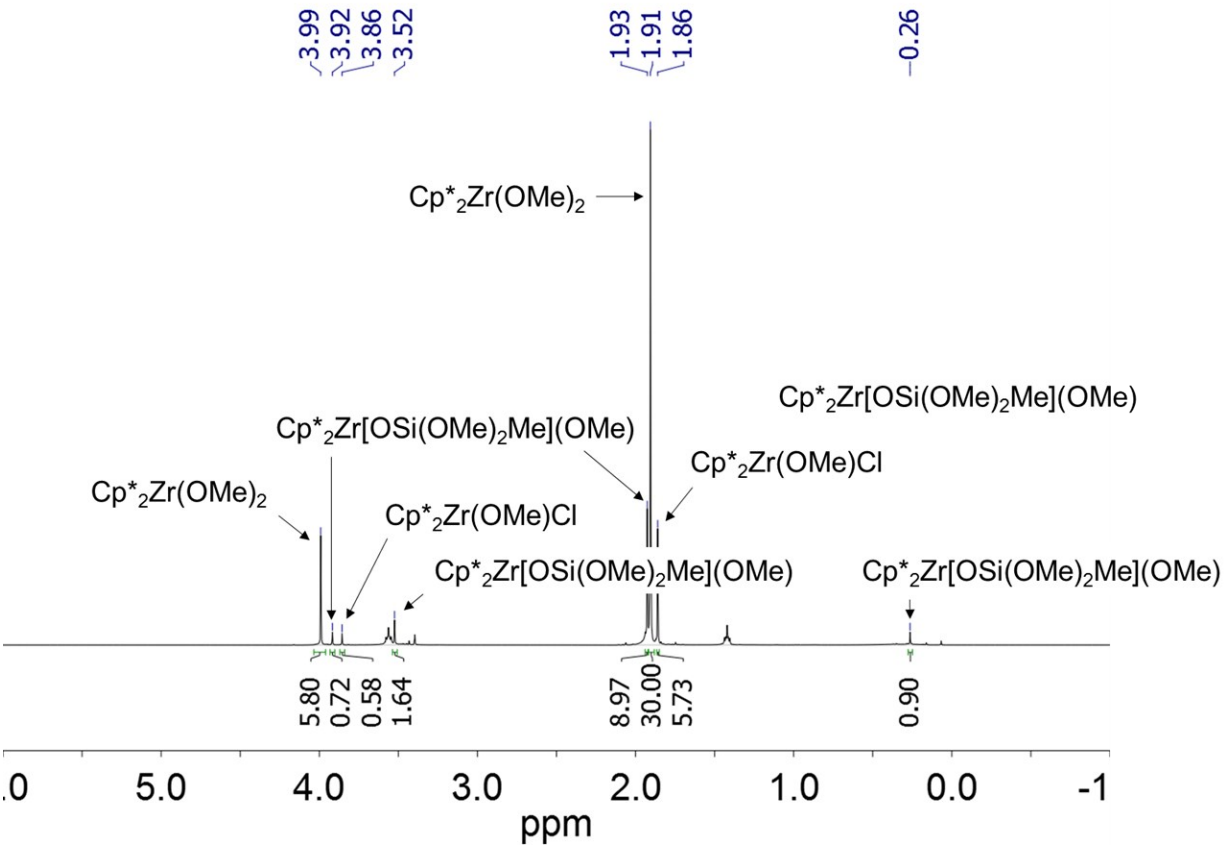


Figure 3. ^{1}H NMR spectrum of the crude material obtained from the addition of 3 equiv of $NaOSi(OMe)_2Me$ to a THF solution of $Cp^*_2ZrCl_2$. The reaction was kept at room temperature for 18 h. The solvent was then removed under vacuum and the residue extracted into C_6D_6.

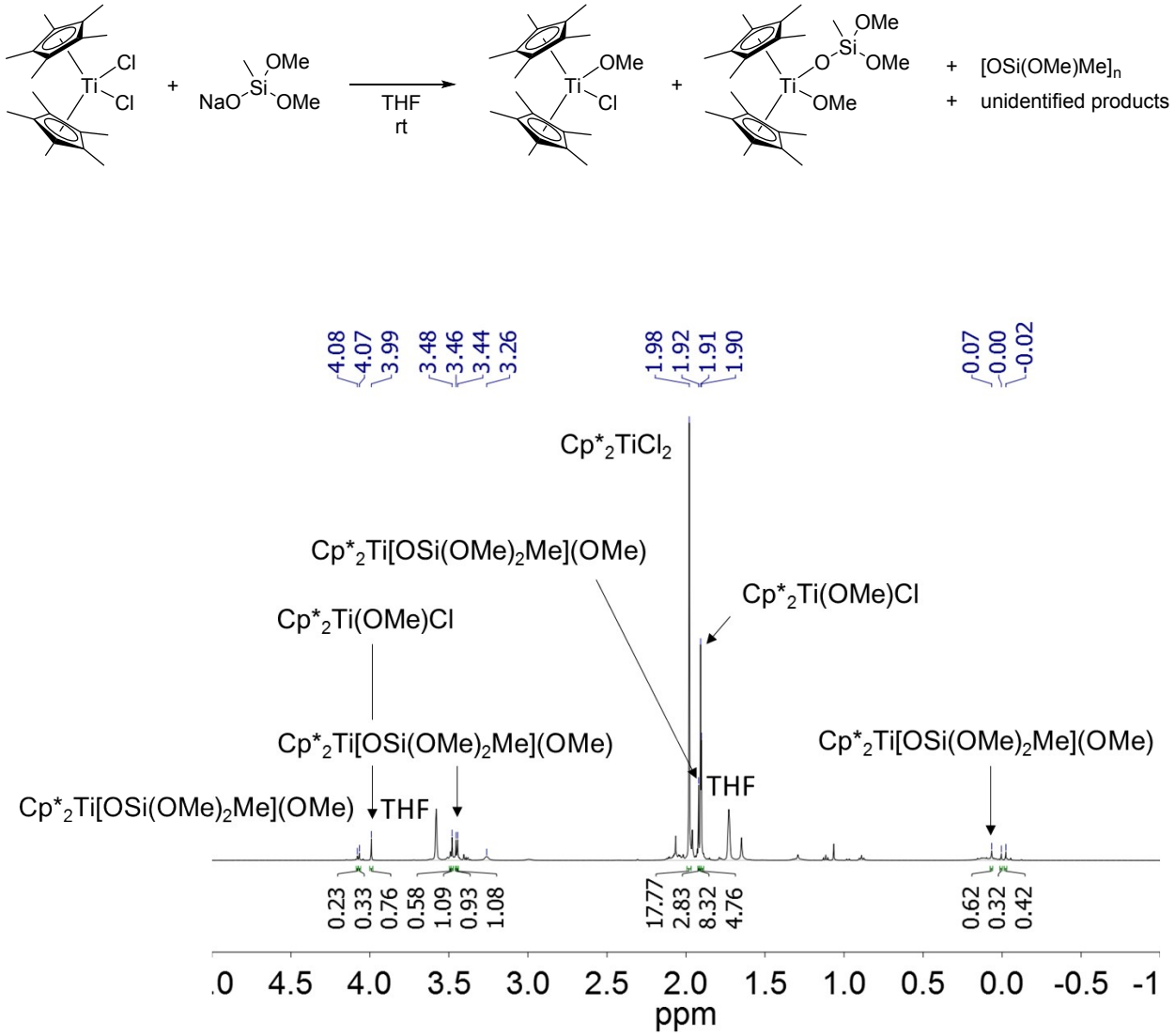


Figure 4. ^{1}H NMR spectrum obtained from the addition of 2 equiv of $NaOSi(OMe)_2Me$ to a THF-d_8 solution of $Cp^*_2TiCl_2$. The reaction was kept at room temperature for 18 h before collecting this spectrum. The signals at 3.48, 3.46, 1.90, 0.00, and 0.02 were not identified.

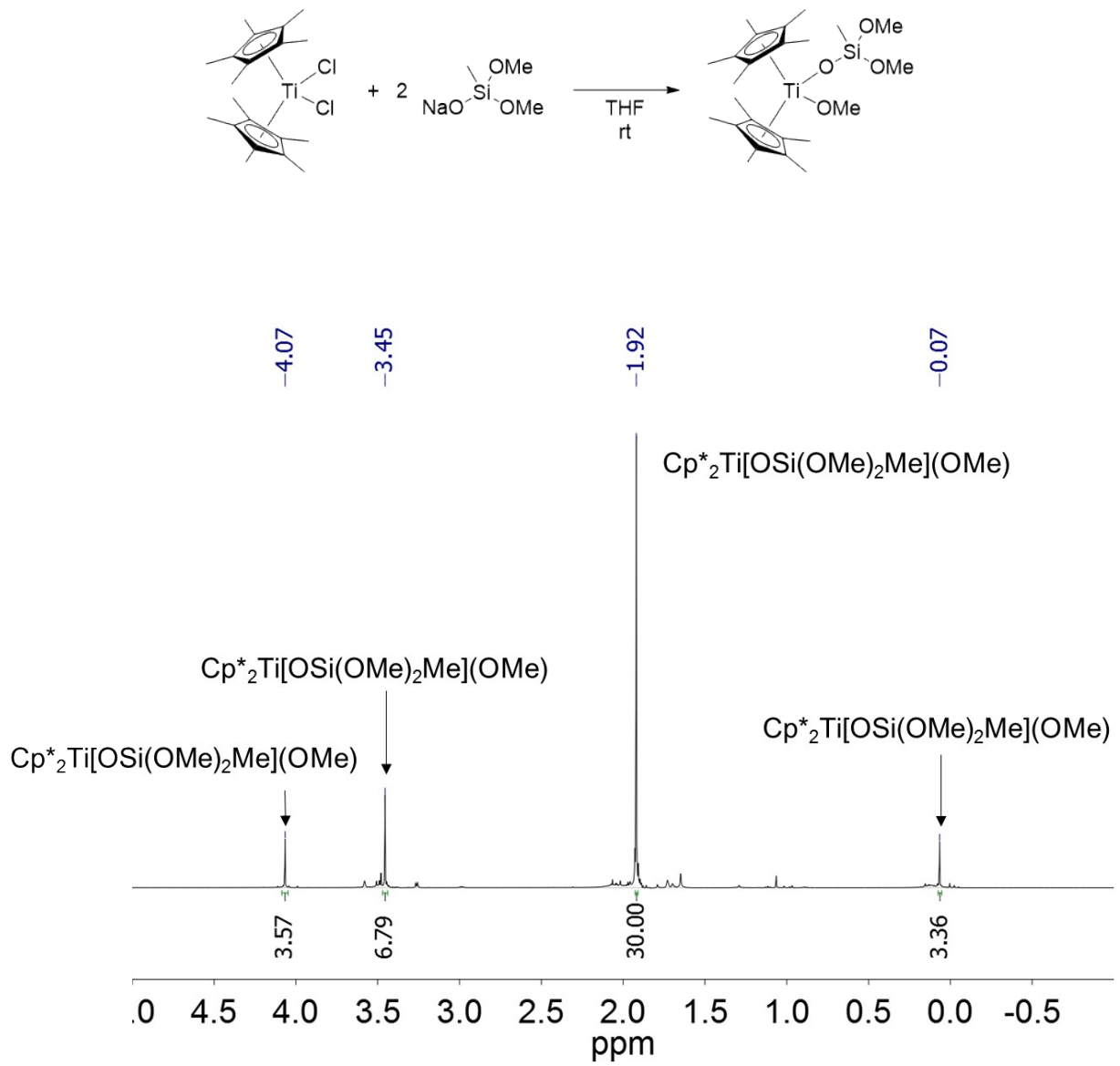


Figure 5. ^{1}H NMR spectrum obtained from the addition of 2 equiv of $NaOSi(OMe)_2Me$ to a THF-d_8 solution of $Cp^*_2TiCl_2$. The reaction was kept at room temperature for 18 h before collecting this spectrum.

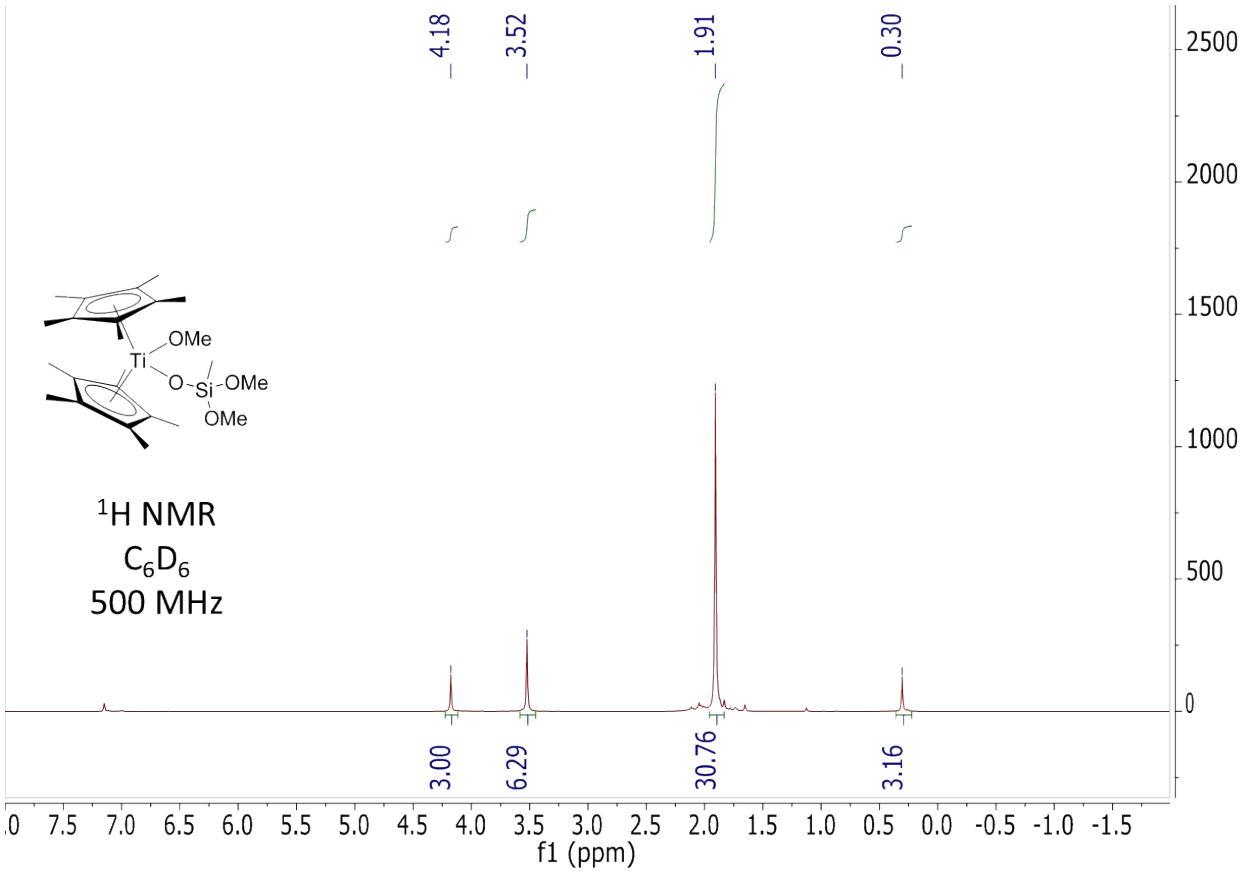


Figure 6. ^{1}H NMR spectrum of isolated Cp*$_2$Ti[OSi(OMe)$_2$Me](OMe) in C_6D_6 at room temperature.

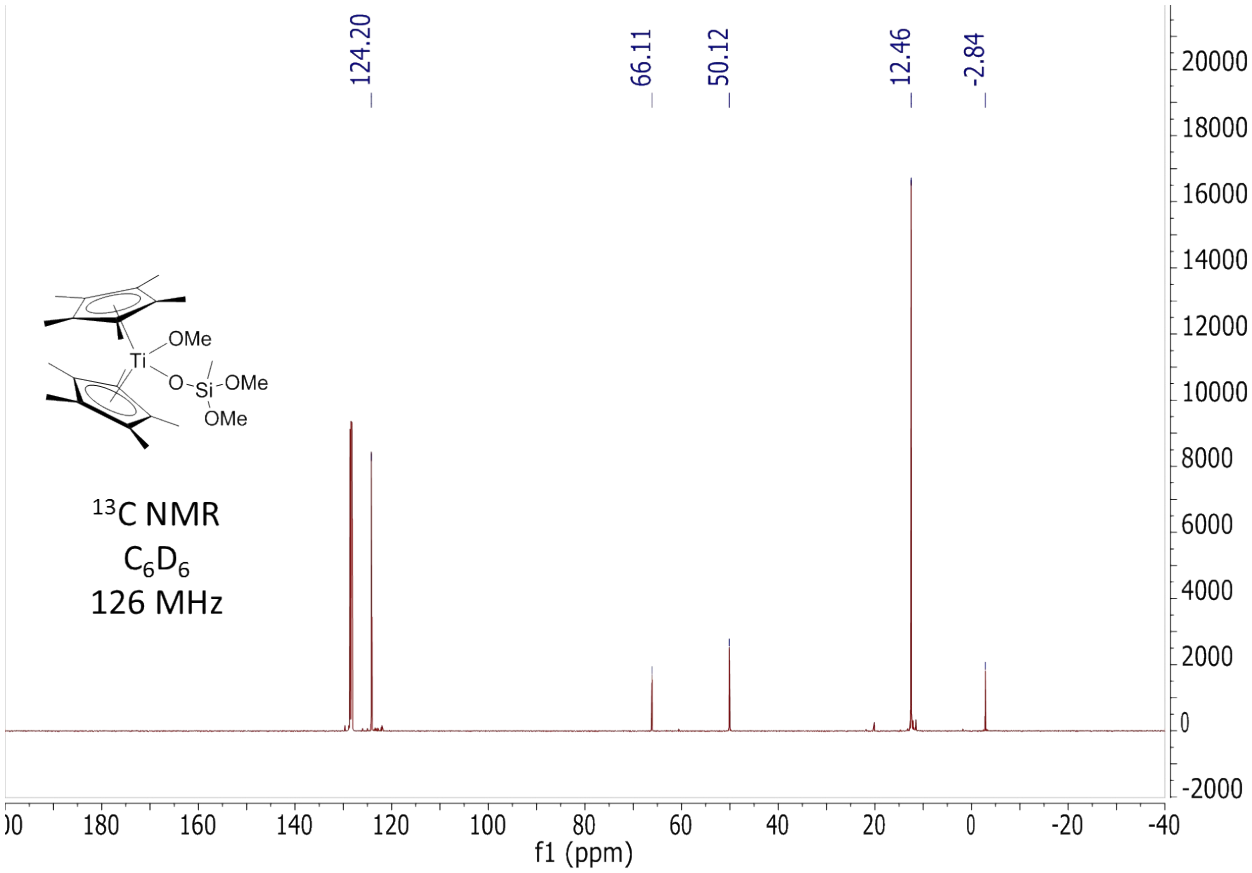
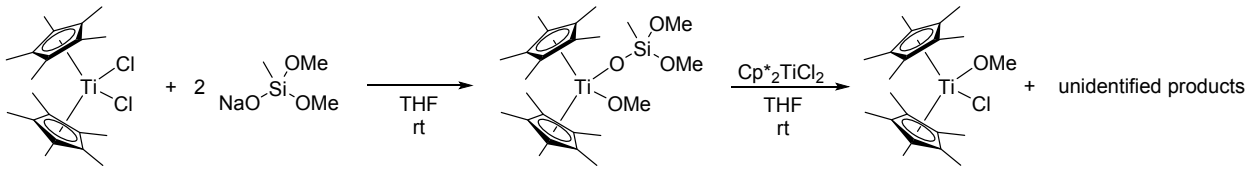


Figure 7. ^{13}C NMR spectrum of $Cp^*_2Ti[OSi(OMe)_2Me](OMe)$ in C_6D_6 at room temperature.



Initial ^{1}H NMR spectrum:

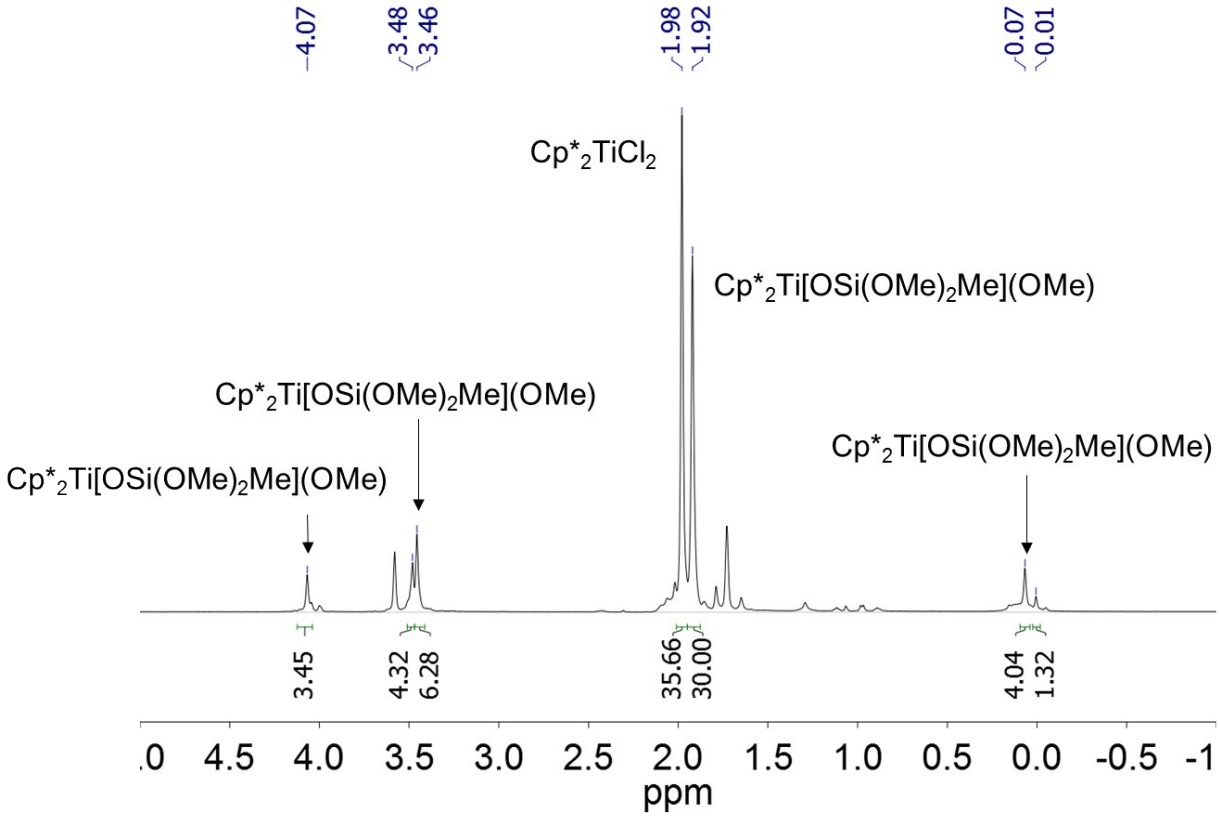
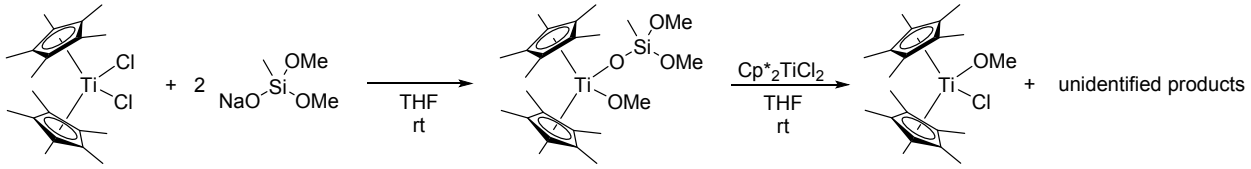


Figure 8. Initial ^{1}H NMR spectrum obtained for the reaction between $Cp^*_2TiCl_2$ and $Cp^*_2Ti[OSi(OMe)_2Me](OMe)$. $Cp^*_2Ti[OSi(OMe)_2Me](OMe)$ was obtained by the addition of 2 equiv of $NaOSi(OMe)_2Me$ to a THF-d_8 solution of $Cp^*_2TiCl_2$. Additional $Cp^*_2TiCl_2$ was then added to this crude product.



^{1}H NMR spectrum after 24 hours:

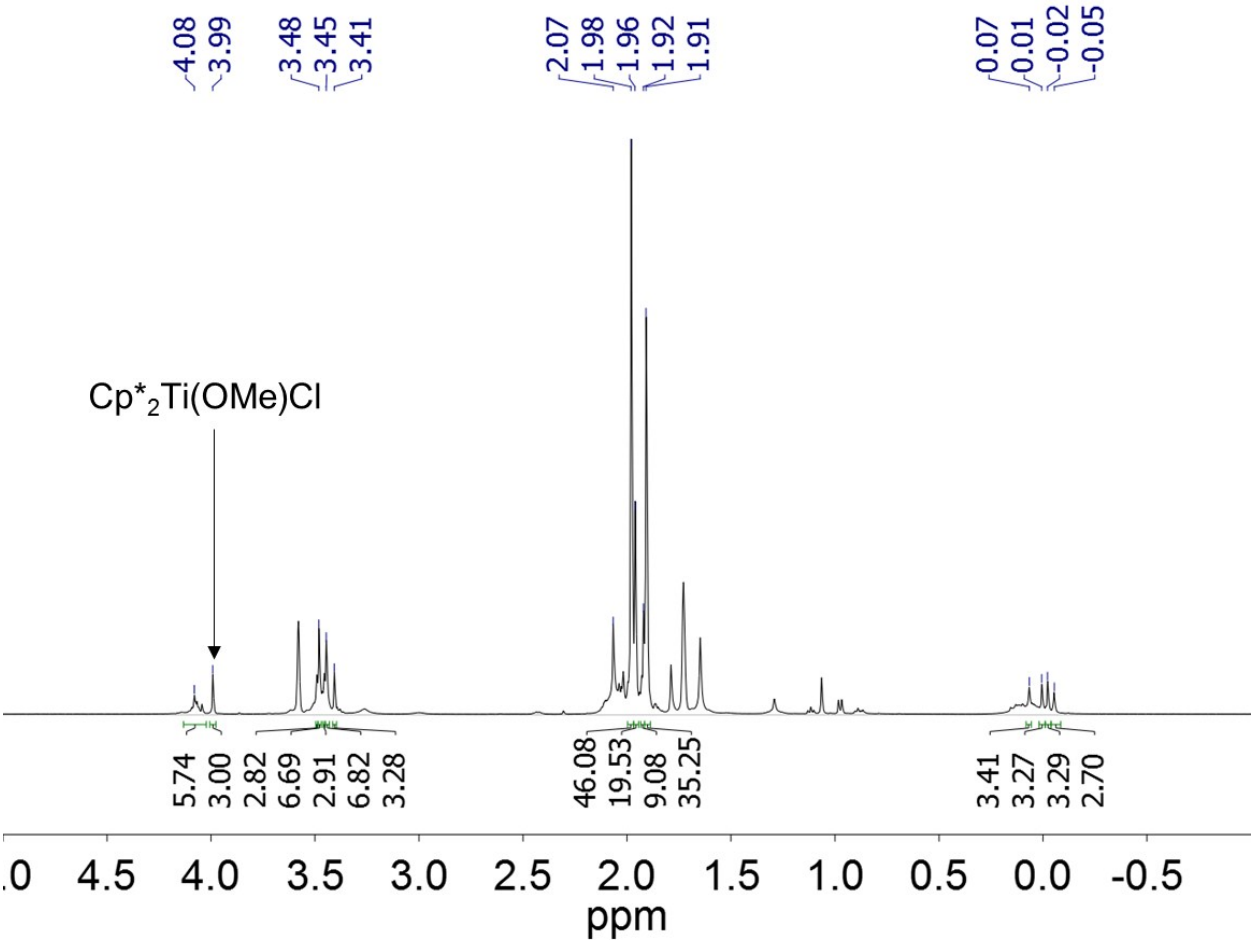


Figure 9. ^{1}H NMR spectrum of the crude reaction between $Cp^*_2TiCl_2$ and $Cp^*_2Ti[OSi(OMe)_2Me](OMe)$. This spectrum was collected 24 h after the addition of $Cp^*_2TiCl_2$ to a crude mixture of $Cp^*_2Ti[OSi(OMe)_2Me](OMe)$ obtained by the addition of 2 equiv of $NaOSi(OMe)_2Me$ to a THF-d_8 solution of $Cp^*_2TiCl_2$.

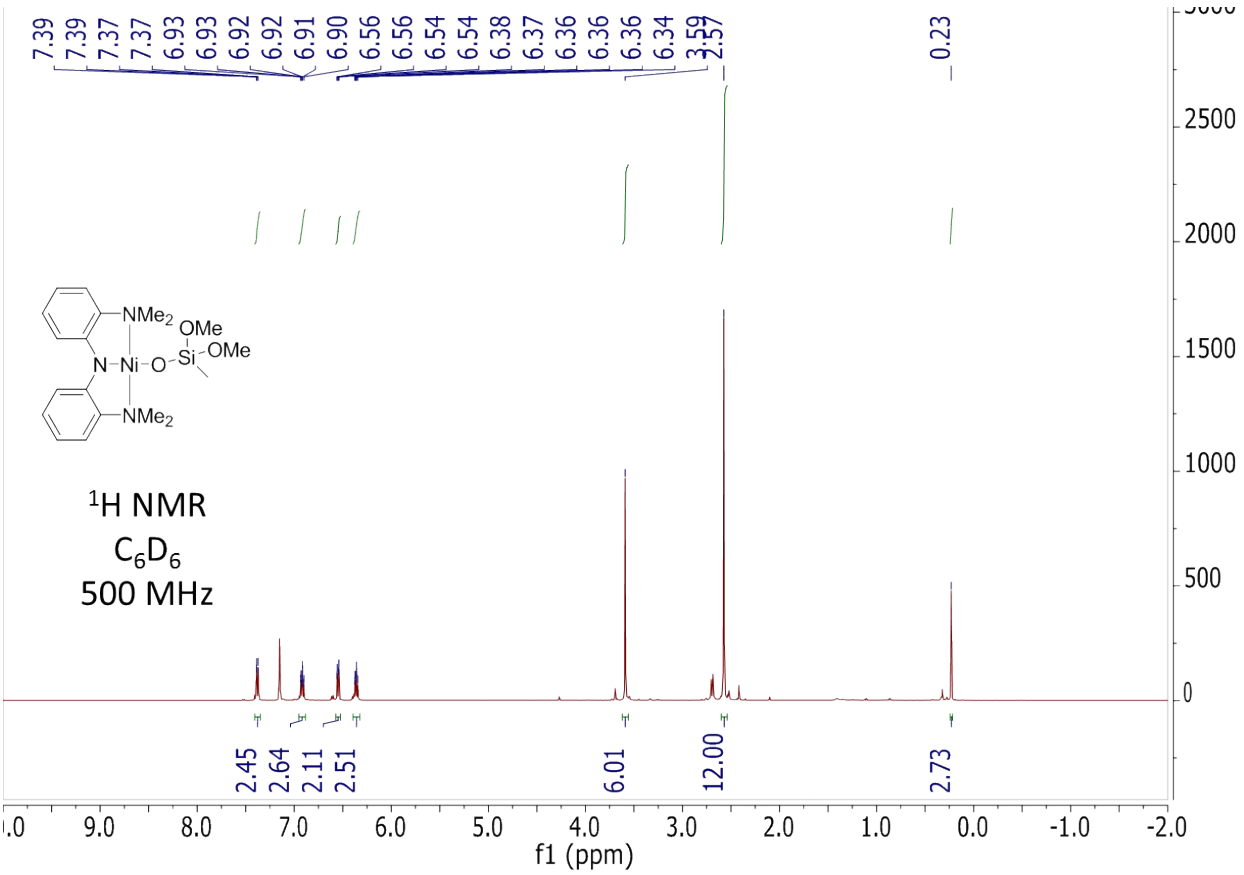


Figure 10. ^{1}H NMR spectrum of ($^{Me,Me}N_2N$)NiOSi(OMe)$_2$Me in C_6D_6 at room temperature. The nickel complex was obtained via the reaction of ($^{Me,Me}N_2N$)NiCl with NaOSi(OMe)$_2$Me in THF.

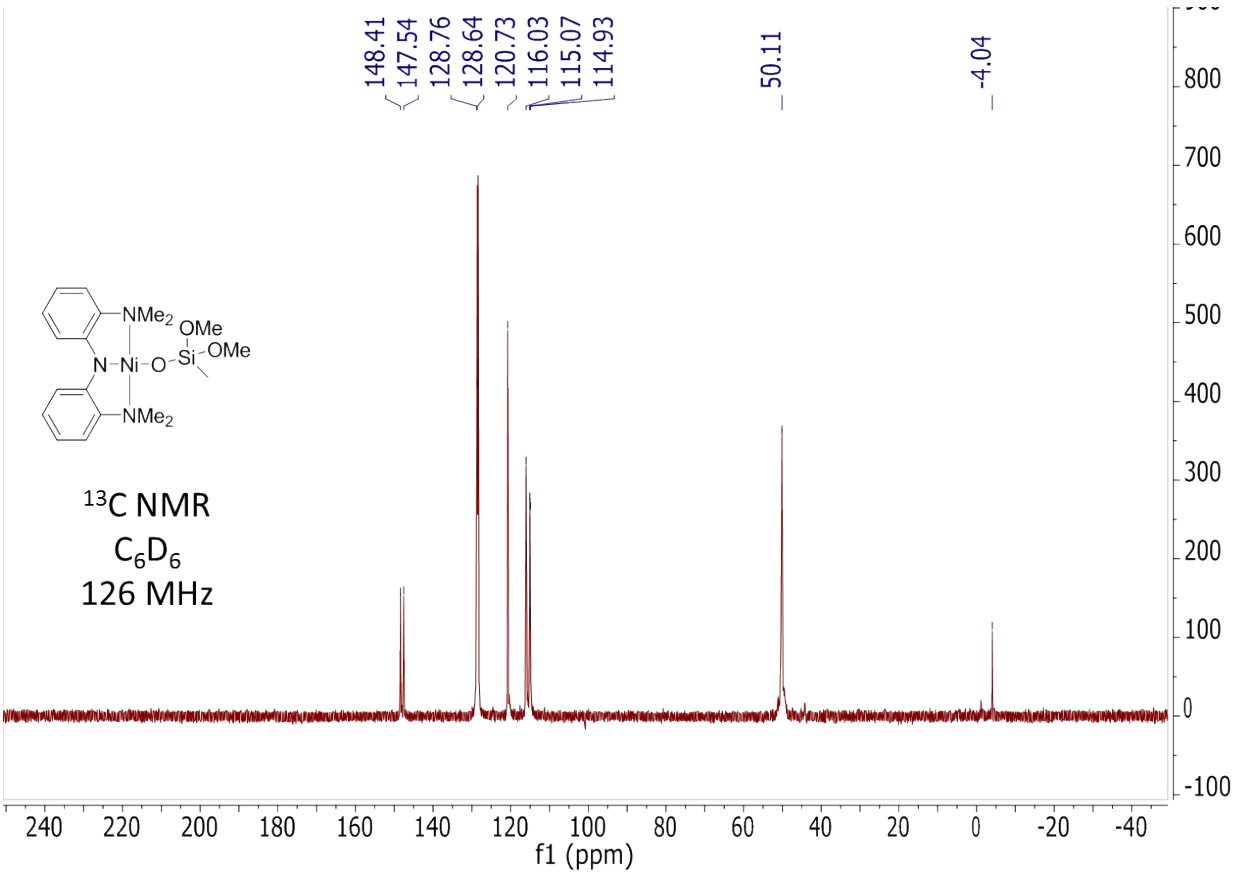


Figure 11. $^{13}C\{^{1}H\}$ NMR spectrum of ($^{Me,Me}N_2N$)NiOSi(OMe)$_2$Me in C_6D_6 at room temperature. The nickel complex was obtained via the reaction of ($^{Me,Me}N_2N$)NiCl with NaOSi(OMe)$_2$Me in THF.

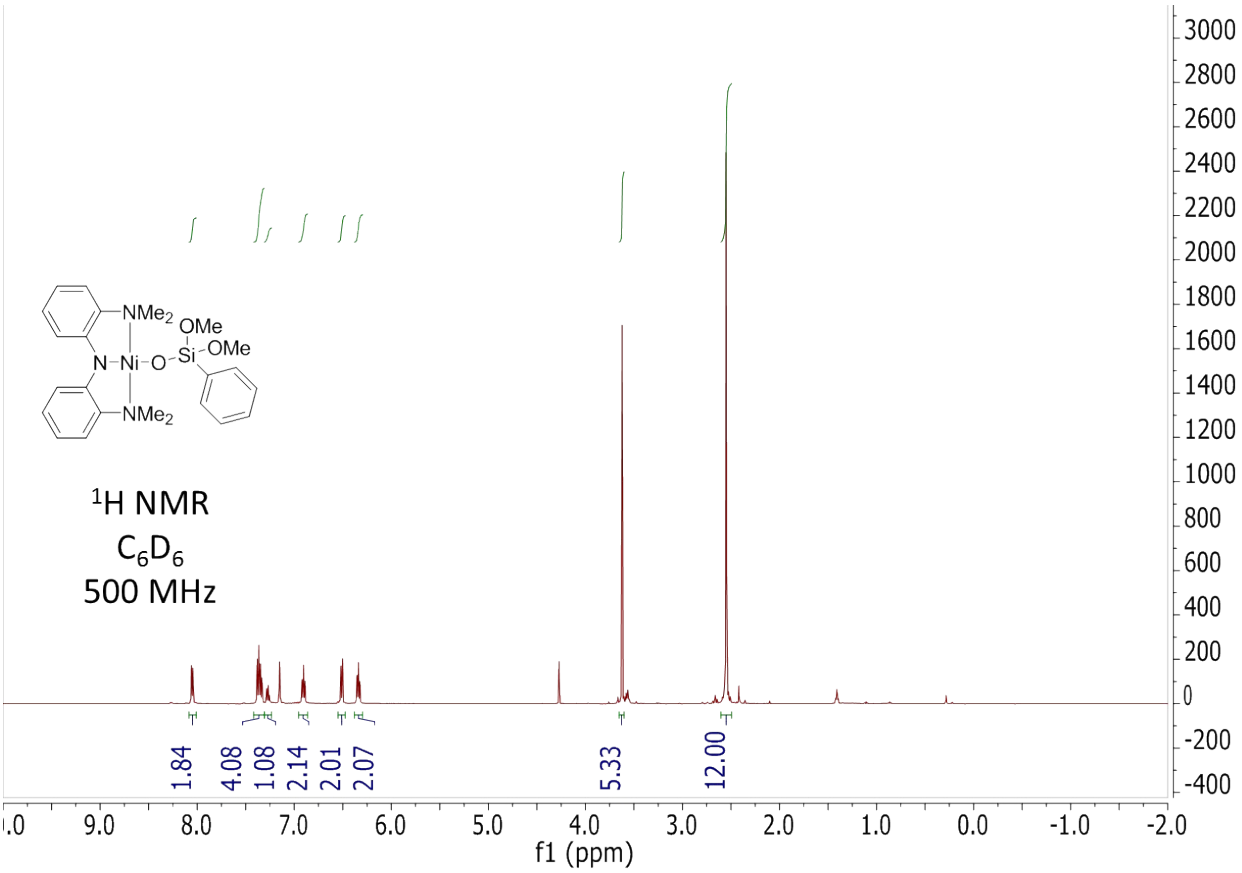


Figure 12. ^{1}H NMR spectrum of ($^{Me,Me}N_2N$)NiOSi(OMe)$_2$Ph in C_6D_6 at room temperature. The nickel complex was obtained via the reaction of ($^{Me,Me}N_2N$)NiCl with NaOSi(OMe)$_2$Ph in THF.

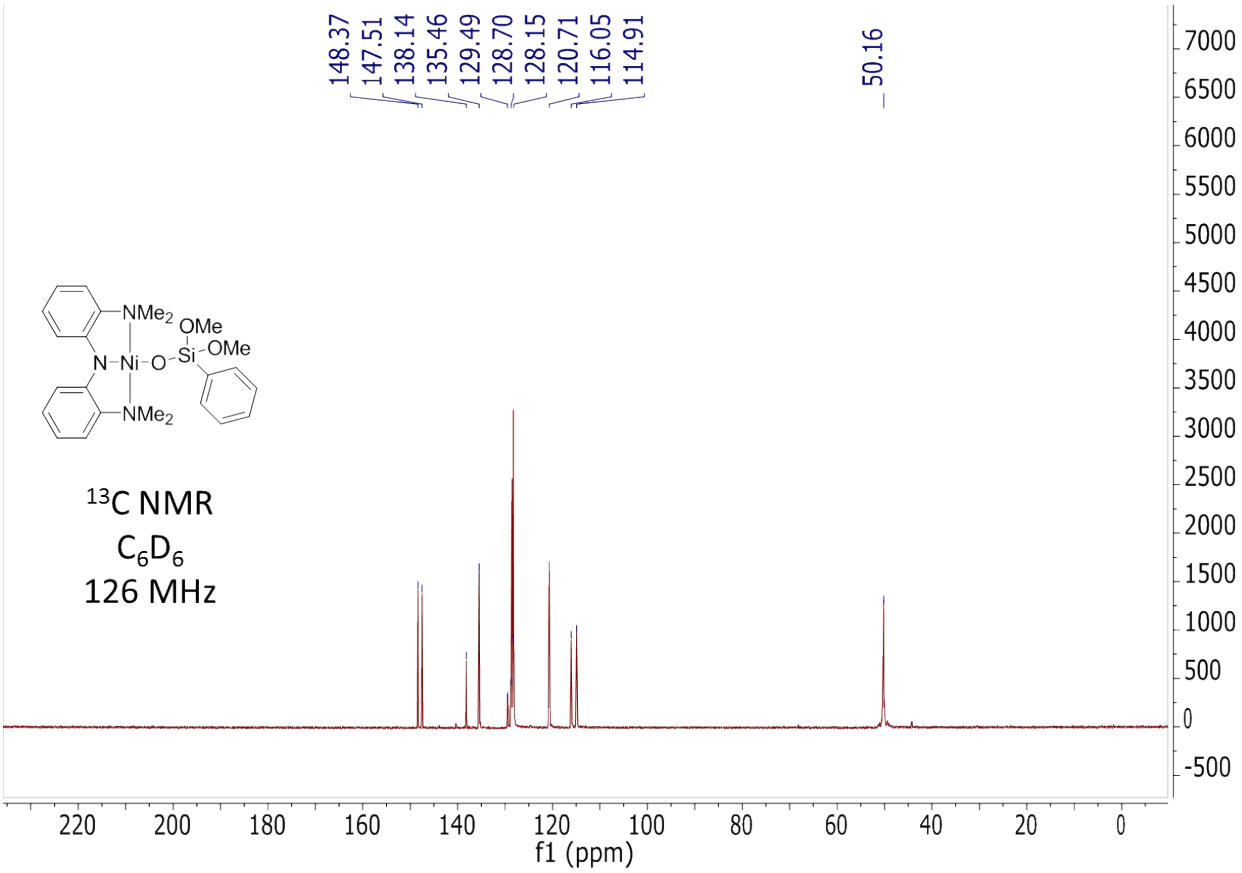


Figure 13. $^{13}C\{^{1}H\}$ NMR spectrum of ($^{Me,Me}N_2N$)NiOSi(OMe)$_2$Ph in C_6D_6 at room temperature. The nickel complex was obtained via the reaction of ($^{Me,Me}N_2N$)NiCl with NaOSi(OMe)$_2$Ph in THF.

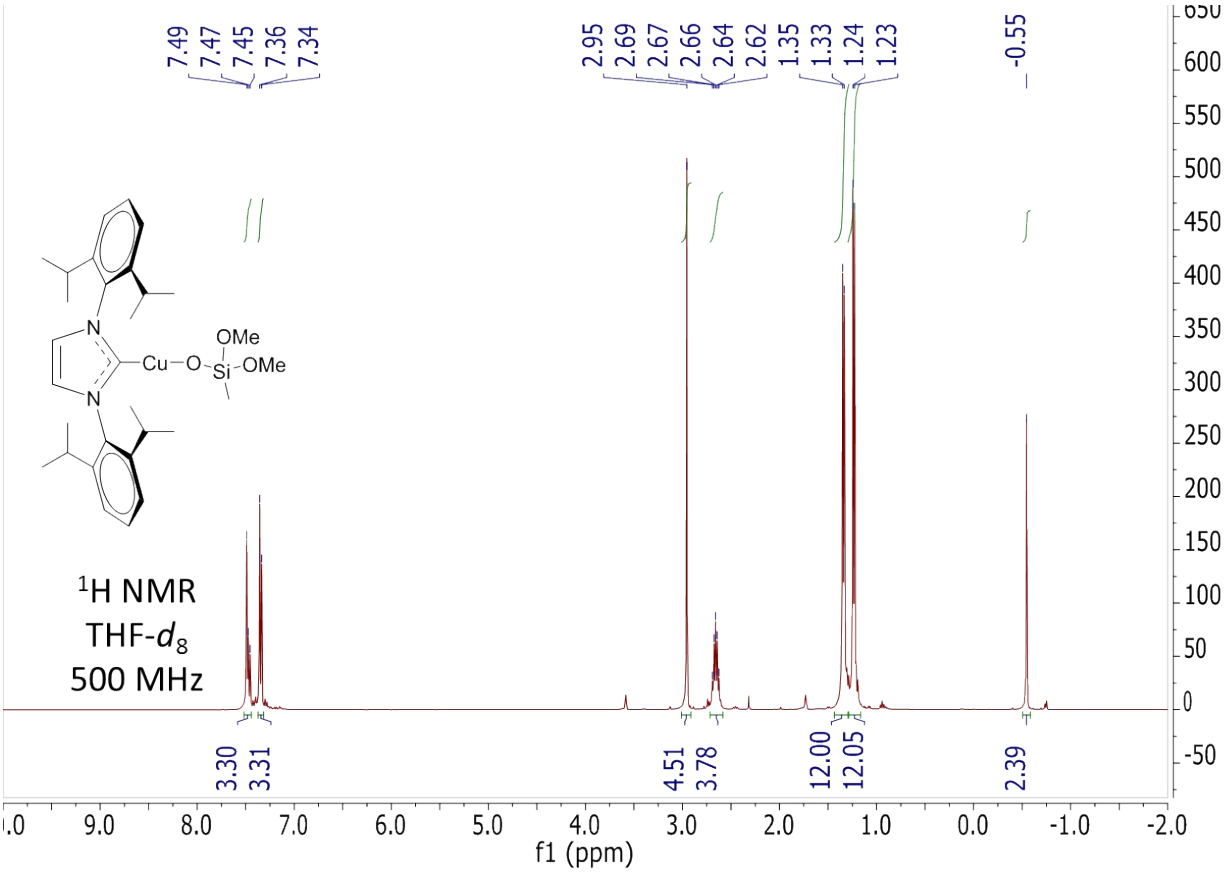


Figure 14. ^{1}H NMR spectrum of (IPr)CuOSi(OMe)$_2$Me in THF-d_8 at room temperature. The copper complex could be obtained by the addition of NaOSi(OMe)$_2$Me to a THF solution of (IPr)CuCl or by the addition of (MeO)$_3$SiMe to a THF solution of (IPr)CuOH.

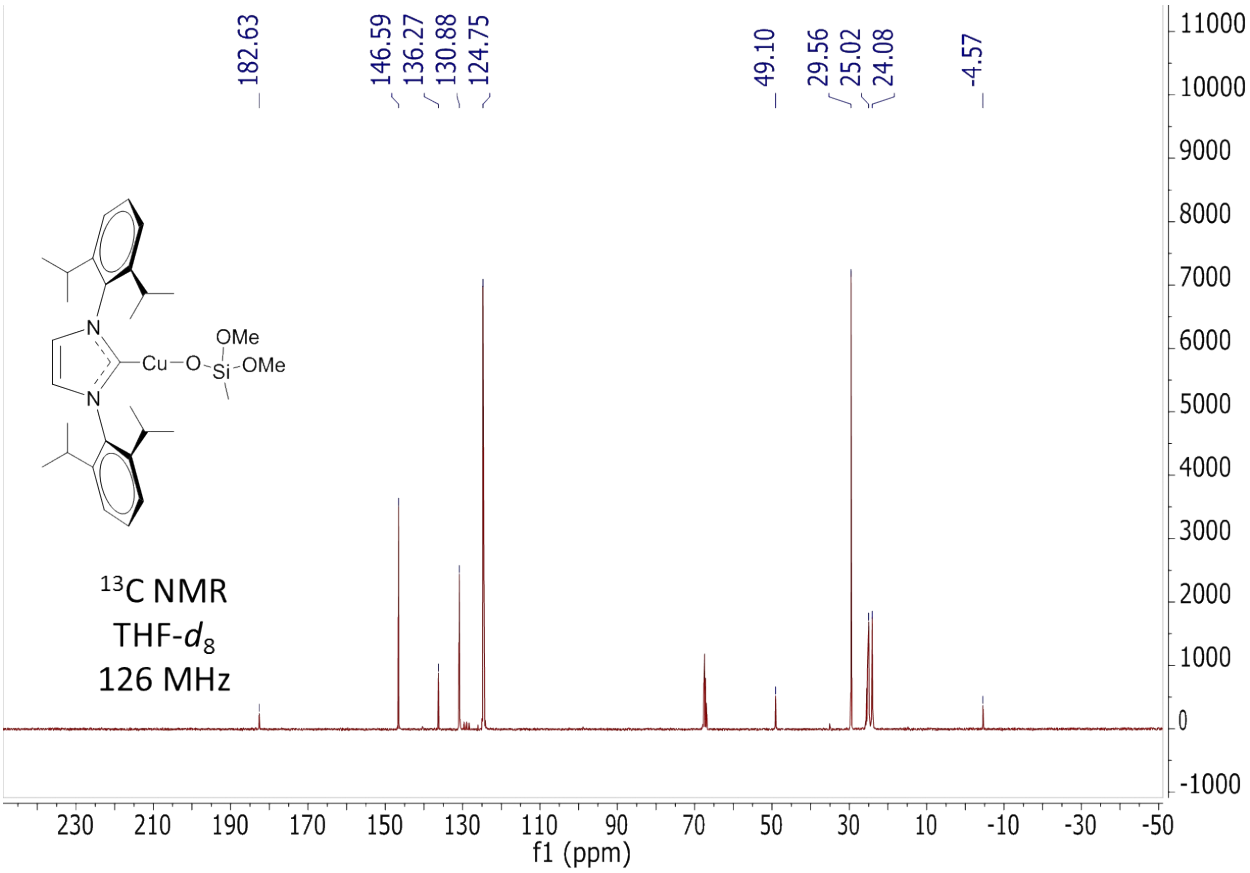


Figure 15. $^{13}C\{^1H\}$ NMR spectrum of (IPr)CuOSi(OMe)$_2$Me in THF-d_8 at room temperature. The copper complex could be obtained by the addition of NaOSi(OMe)$_2$Me to a THF solution of (IPr)CuCl or by the addition of (MeO)$_3$SiMe to a THF solution of (IPr)CuOH.

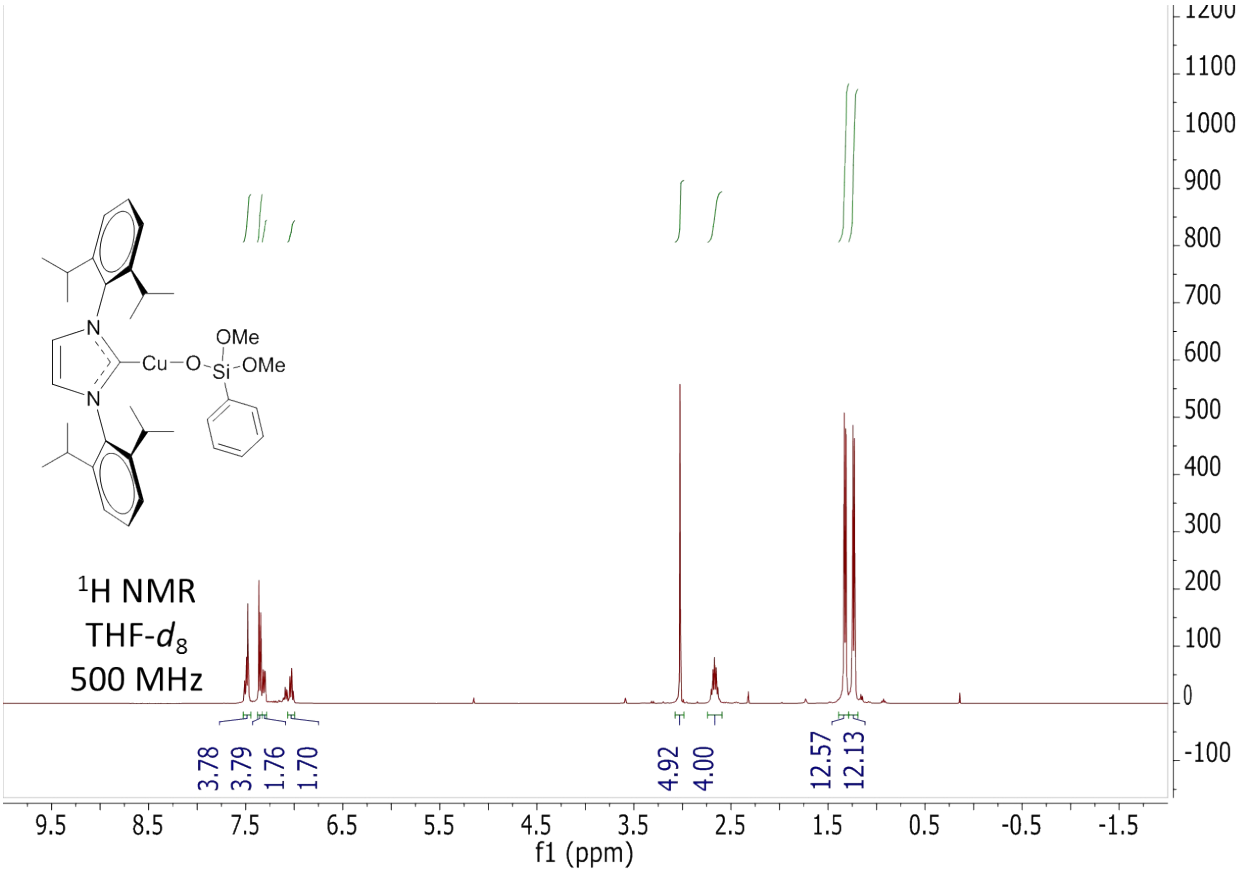


Figure 16. ^{1}H NMR spectrum of (IPr)CuOSi(OMe)$_2$Me in THF-d_8 at room temperature. The copper complex could be obtained by the addition of NaOSi(OMe)$_2$Ph to a THF solution of (IPr)CuCl or by the addition of (MeO)$_3$SiPh to a THF solution of (IPr)CuOH.

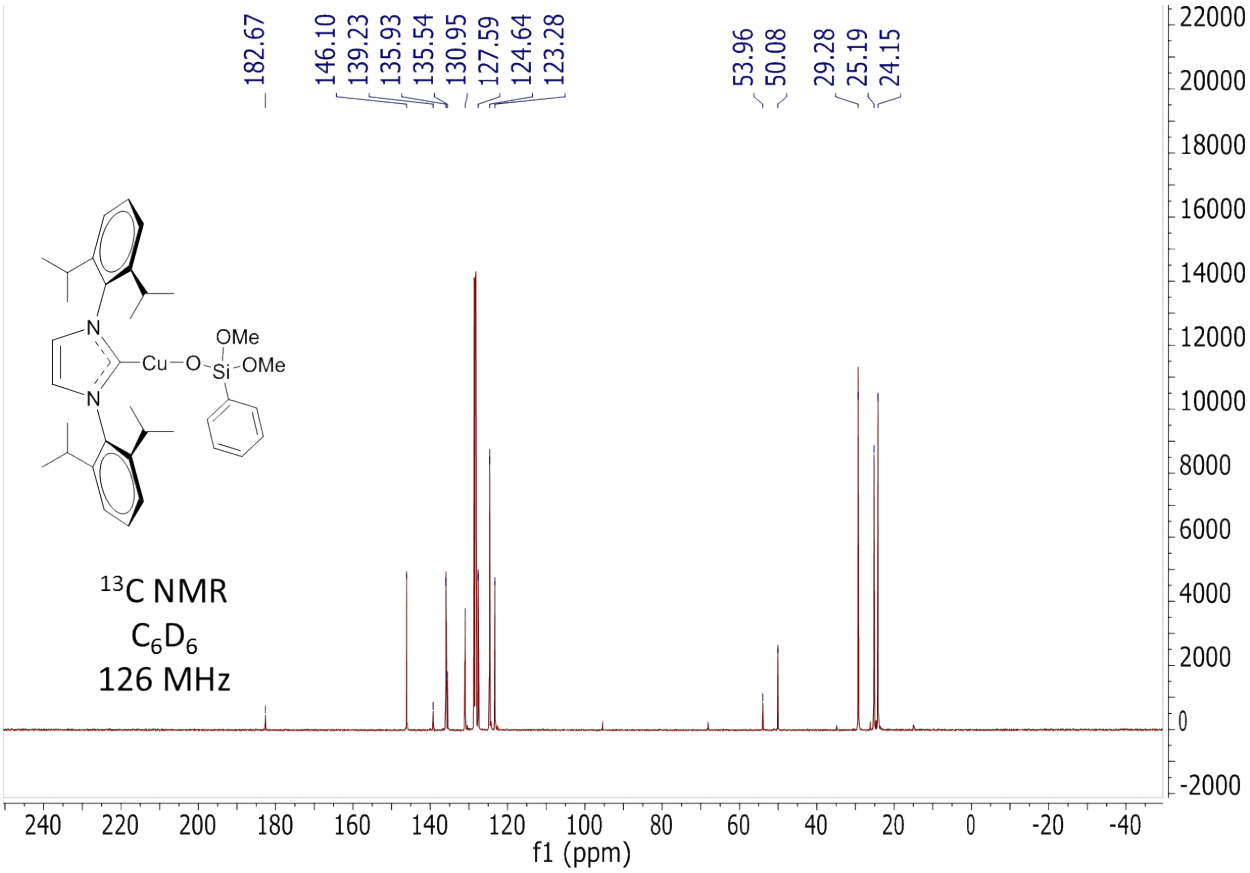


Figure 17. $^{13}C\{^1H\}$ NMR spectrum of (IPr)CuOSi(OMe)$_2$Me in THF-d_8 at room temperature. The copper complex could be obtained by the addition of NaOSi(OMe)$_2$Ph to a THF solution of (IPr)CuCl or by the addition of (MeO)$_3$SiPh to a THF solution of (IPr)CuOH.

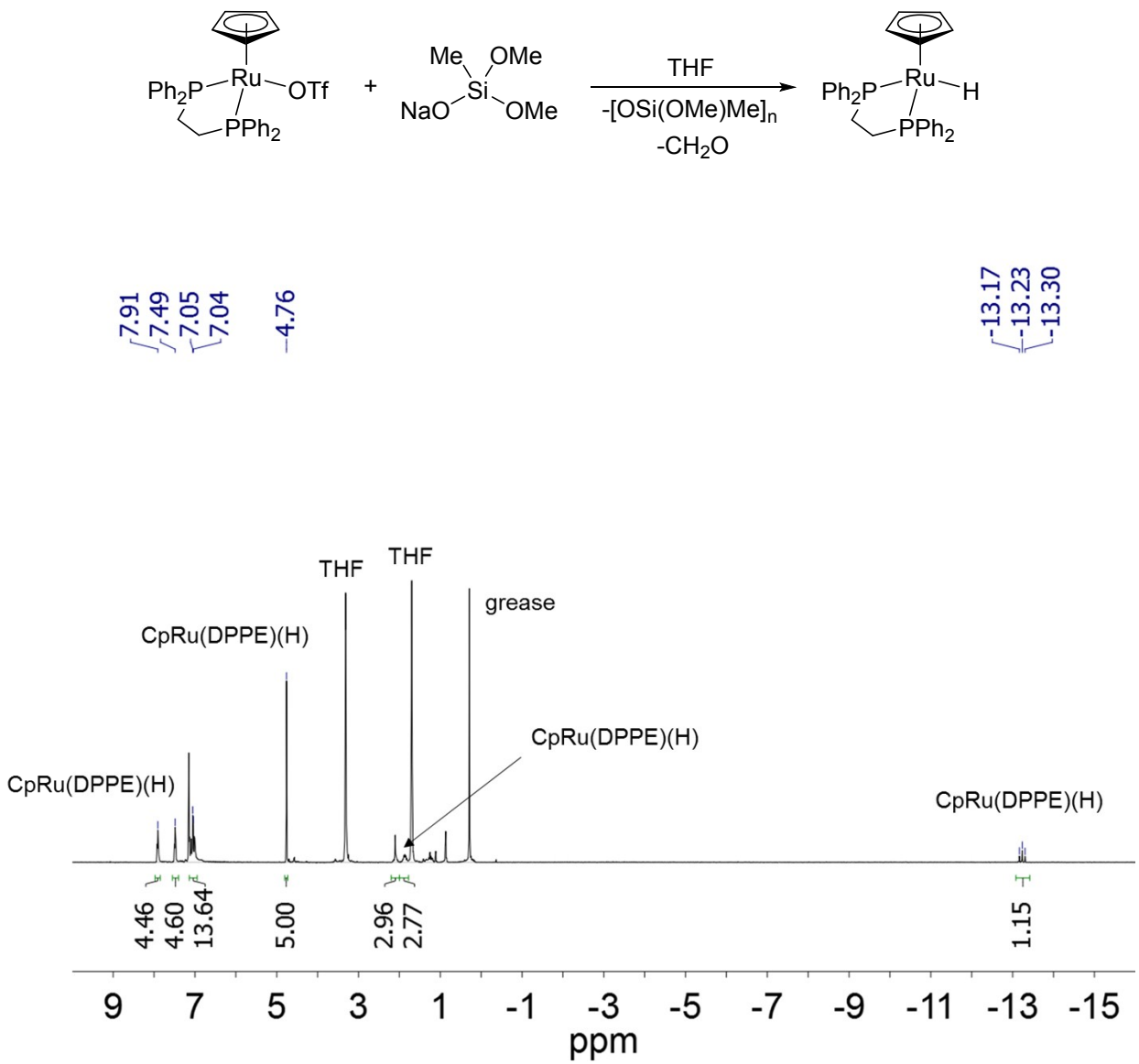
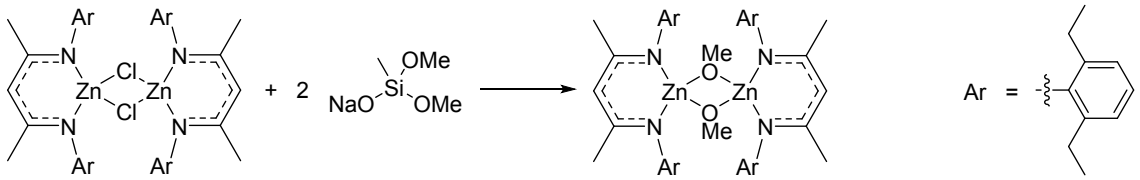


Figure 18. ^{1}H NMR spectrum of the solid obtained from the reaction of CpRu(DPPE)(OTf) with $NaOSi(OMe)_2Me$. The major product is CpRu(DPPE)(H), which is thought to arise through the intermediacy of CpRu(DPPE)(OMe).



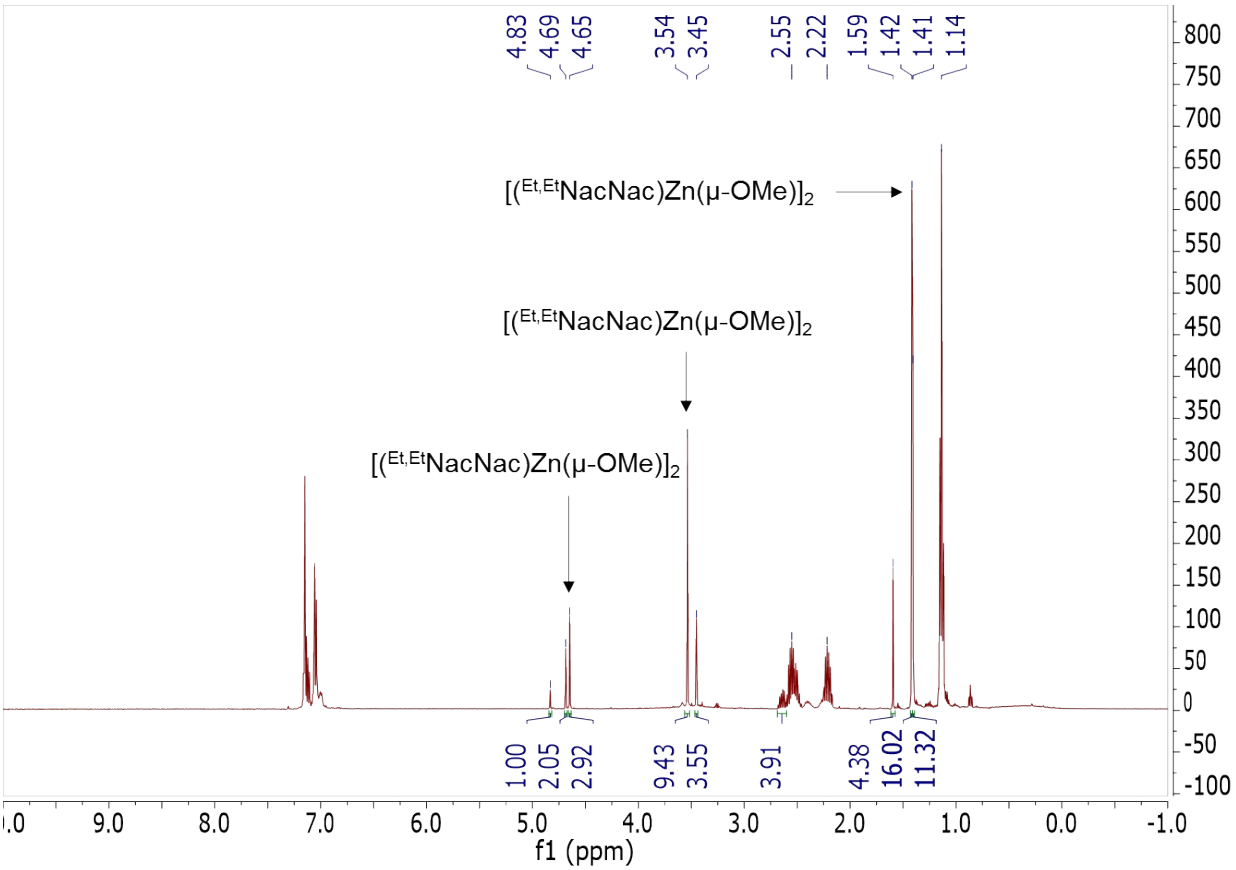


Figure 19. ^{1}H NMR spectrum of the residual solid from the reaction of $[(^{Et,Et}NacNac)Zn(\mu\text{-}OH)]_2$ and $(MeO)_3SiMe$. The major product is $[(^{Et,Et}NacNac)Zn(\mu\text{-}OMe)]_2$. The same product is obtained from the reaction of $[(^{Et,Et}NacNac)Zn(\mu\text{-}OH)]_2$ and $(MeO)_3SiMe$.

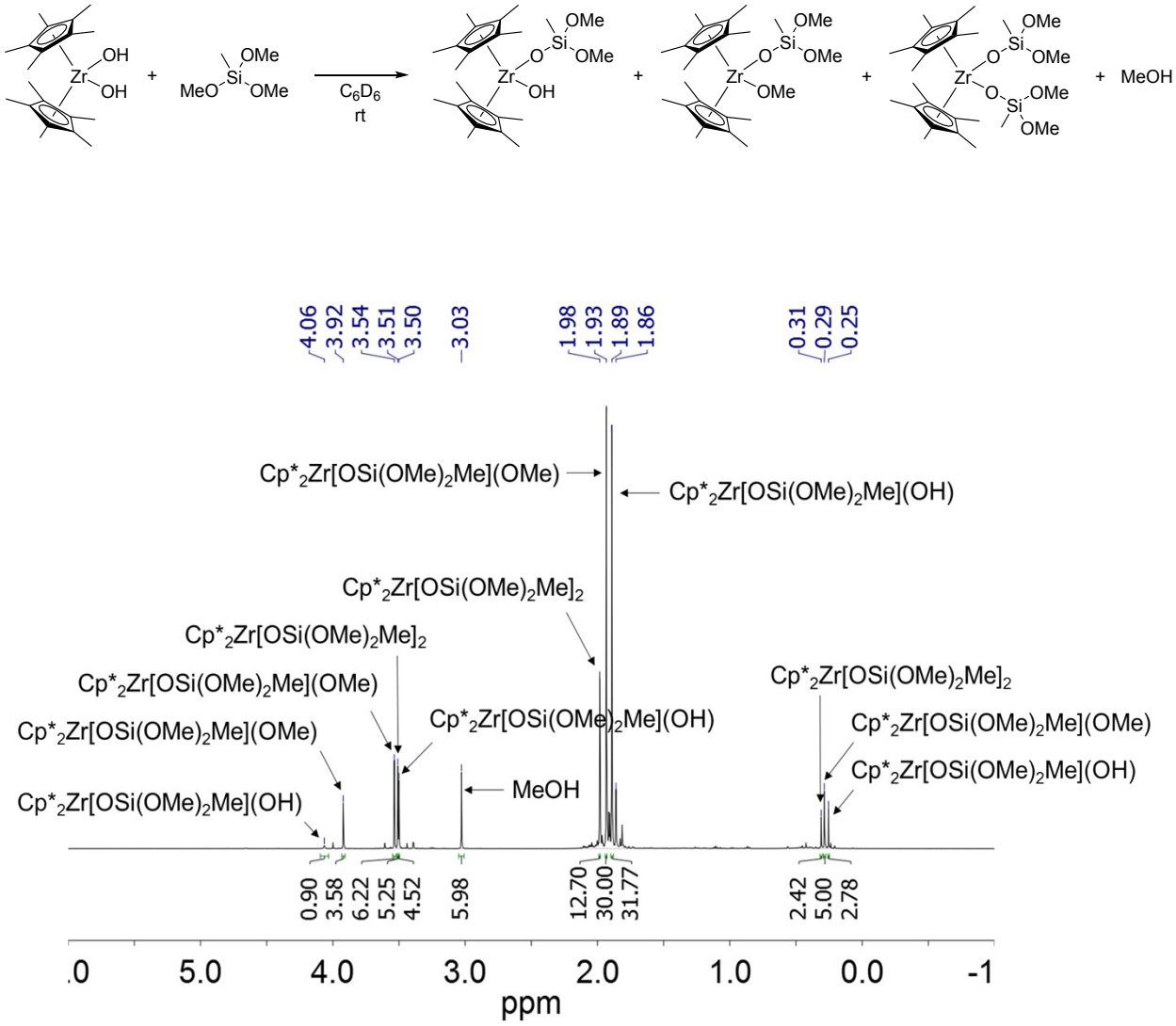
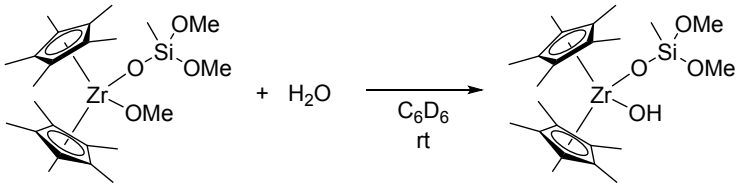


Figure 20. ^{1}H NMR spectrum of the crude reaction between $Cp^*_2Zr(OH)_2$ and $(MeO)_3SiMe$ in C_6D_6. The major products are assigned to $Cp^*_2Zr[OSi(OMe)_2Me](OH)$, $Cp^*_2Zr[OSi(OMe)_2Me]_2$, and $Cp^*_2Zr[OSi(OMe)_2Me](OMe)$.



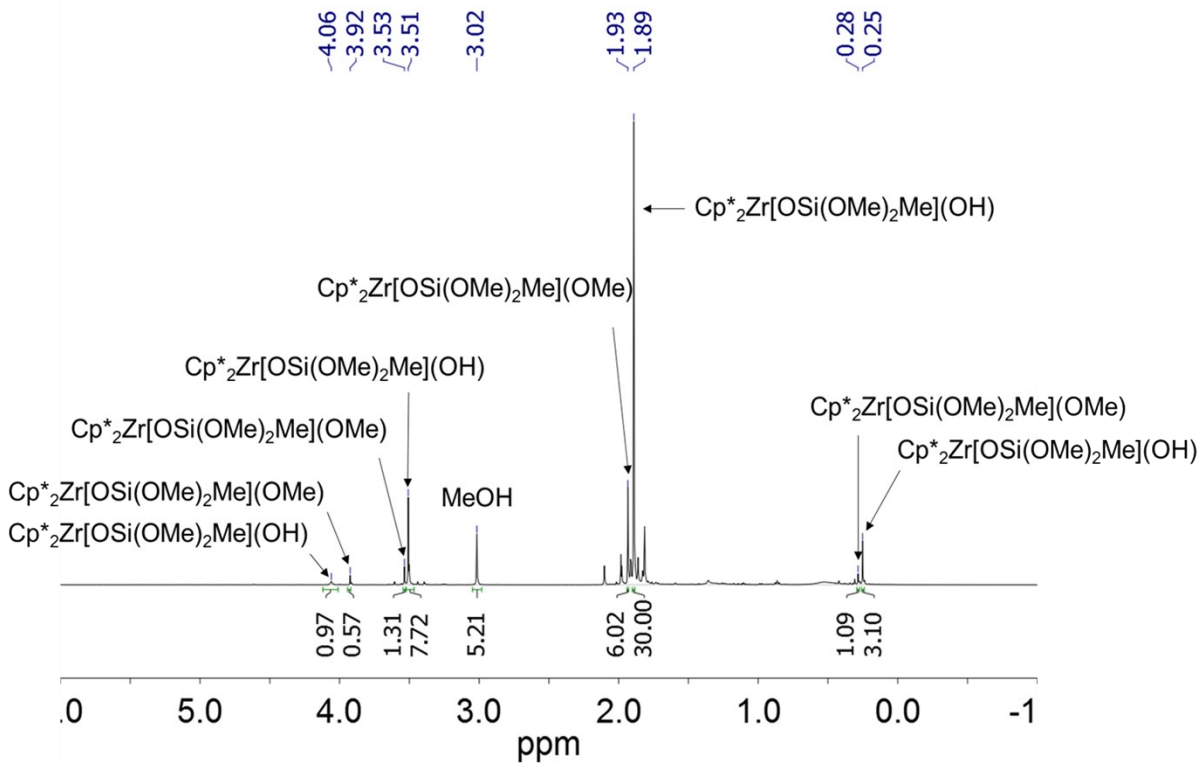


Figure 21. ^{1}H NMR spectrum of the crude reaction between Cp*$_2$Zr[OSi(OMe)$_2$Me](OMe) and H_2O in C_6D_6. The major product is Cp*$_2$Zr[OSi(OMe)$_2$Me](OH), which is observed above in the reaction between Cp*$_2$Zr(OH)$_2$ with (MeO)$_3$SiMe.

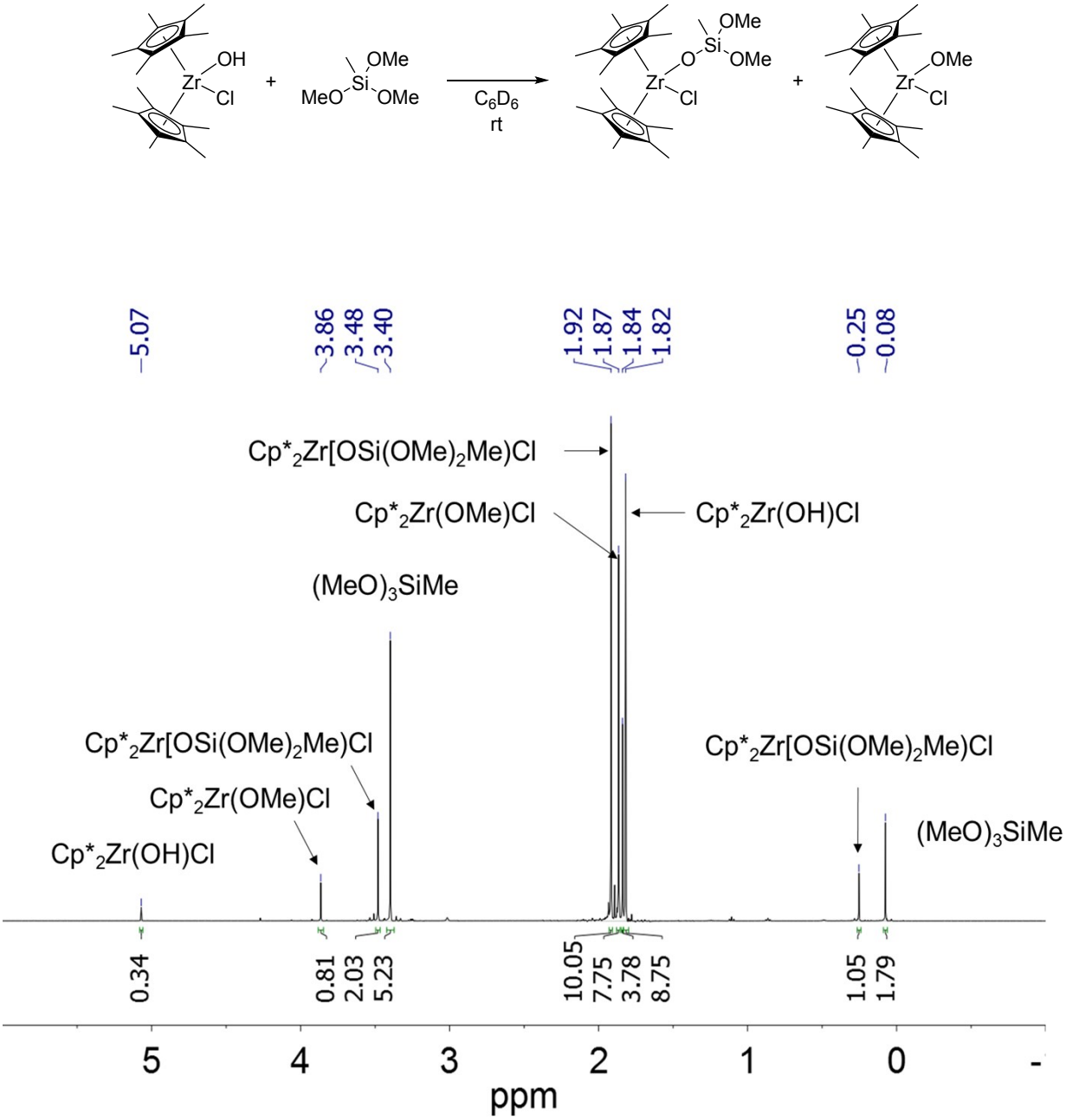
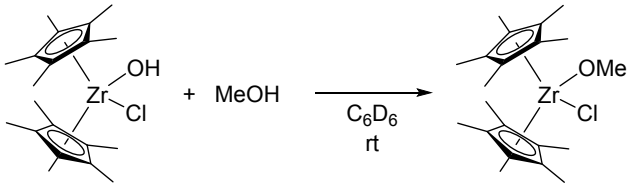


Figure 22. ^{1}H NMR spectrum of the crude reaction between Cp*$_2$Zr(OH)Cl and (MeO)$_3$SiMe in C_6D_6. The major products are Cp*$_2$Zr[OSi(OMe)$_2$Me](Cl) and Cp*$_2$Zr(OMe)Cl. The spectrum was collected after 11 h at room temperature.



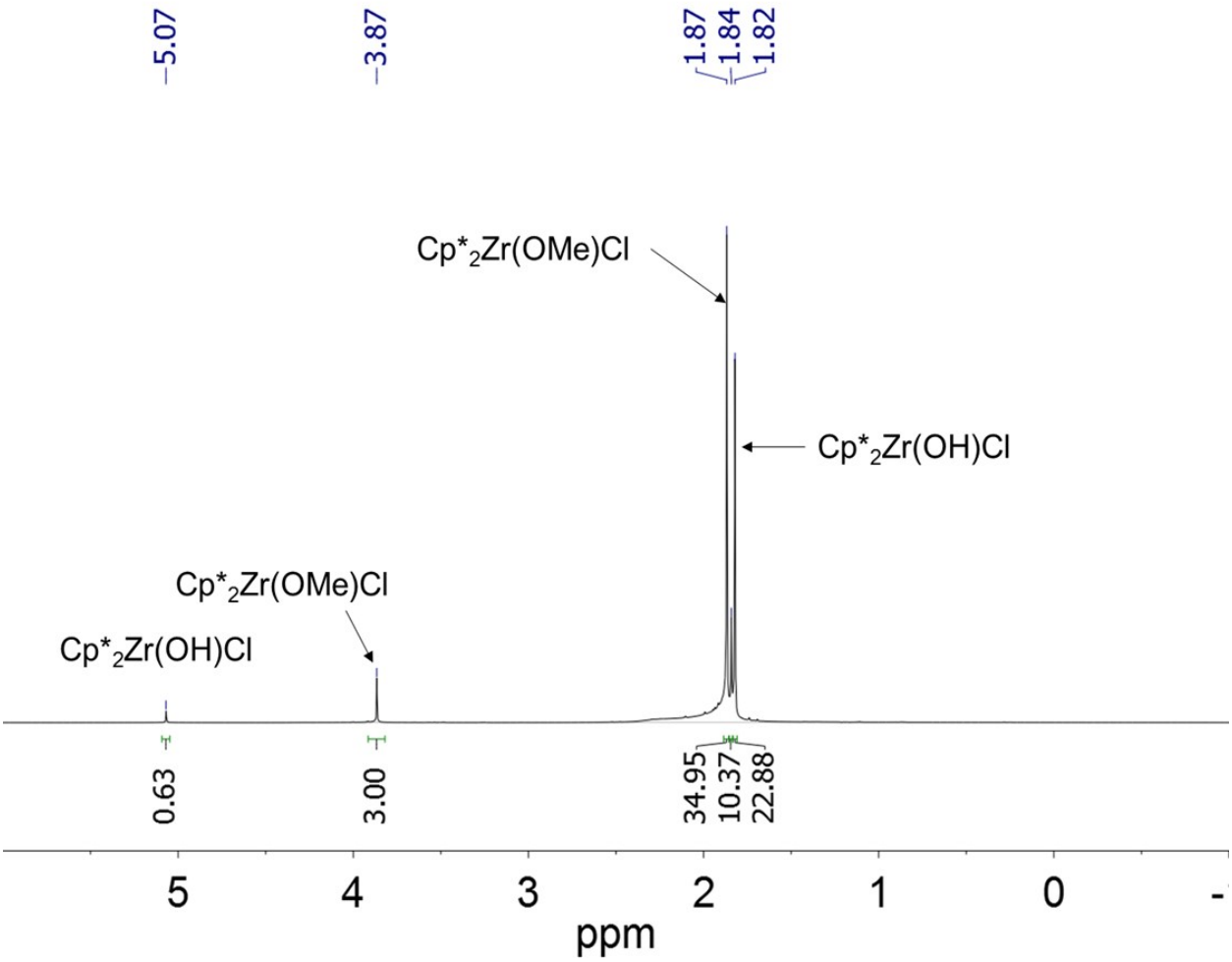


Figure 23. ^{1}H NMR spectrum of the crude reaction between Cp*$_2$Zr(OH)Cl and MeOH in C_6D_6. The spectrum reveals the formation of Cp*$_2$Zr(OMe)Cl, which is also observed in the reaction between Cp*$_2$Zr(OH)Cl and $(MeO)_3SiMe$.

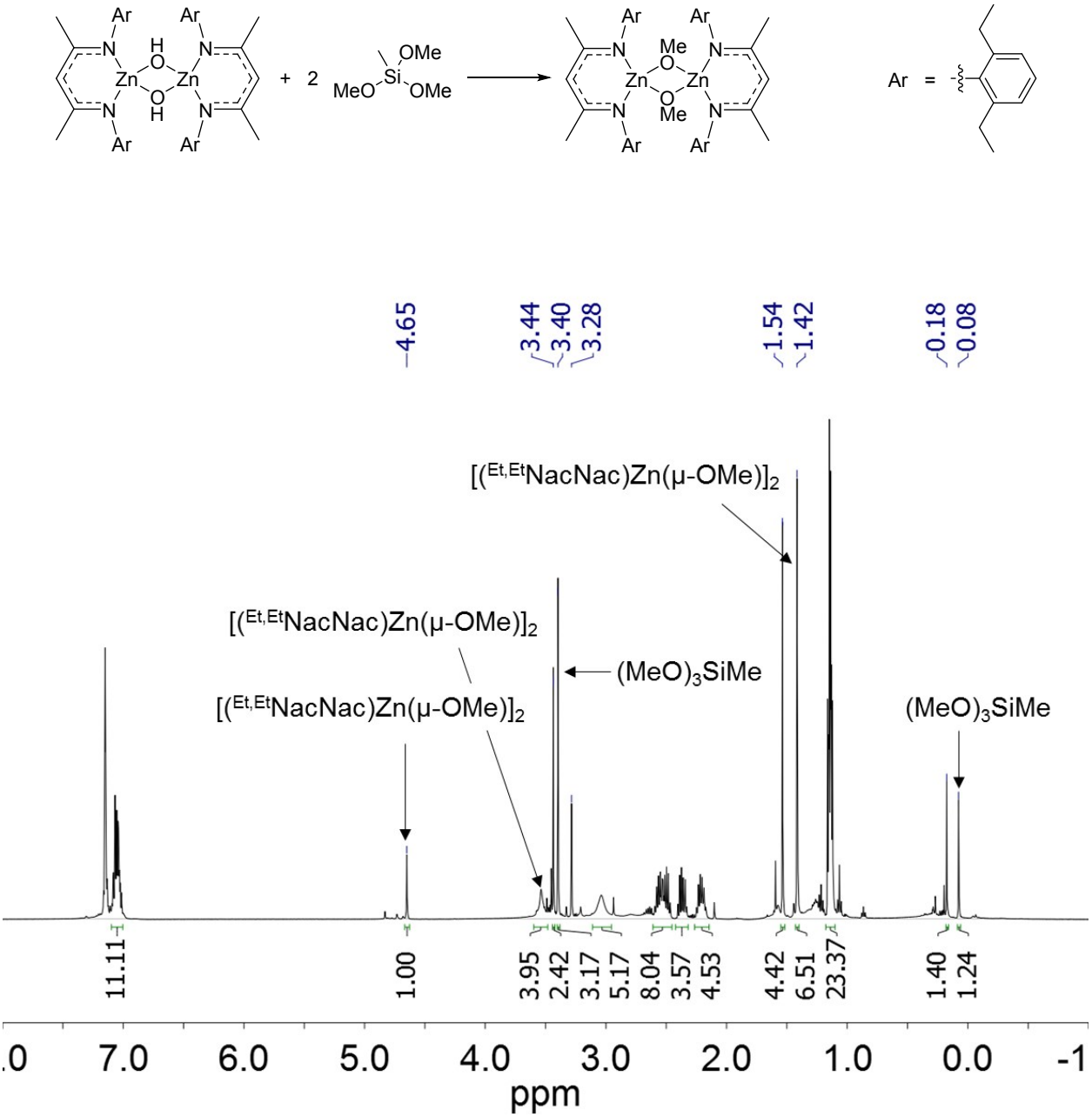


Figure 24. ^{1}H NMR spectrum of the crude reaction between [(^{Et,Et}NacNac)Zn(μ-OH)]$_2$ and (MeO)$_3$SiMe in C_6D_6 at room temperature. The spectrum was collected approximately 10 min after the addition of (MeO)$_3$SiMe, however, the signals persist for several hours. The identity(ies) of the compound(s) giving signals at δ 3.44, 1.54, and 0.18 is uncertain.

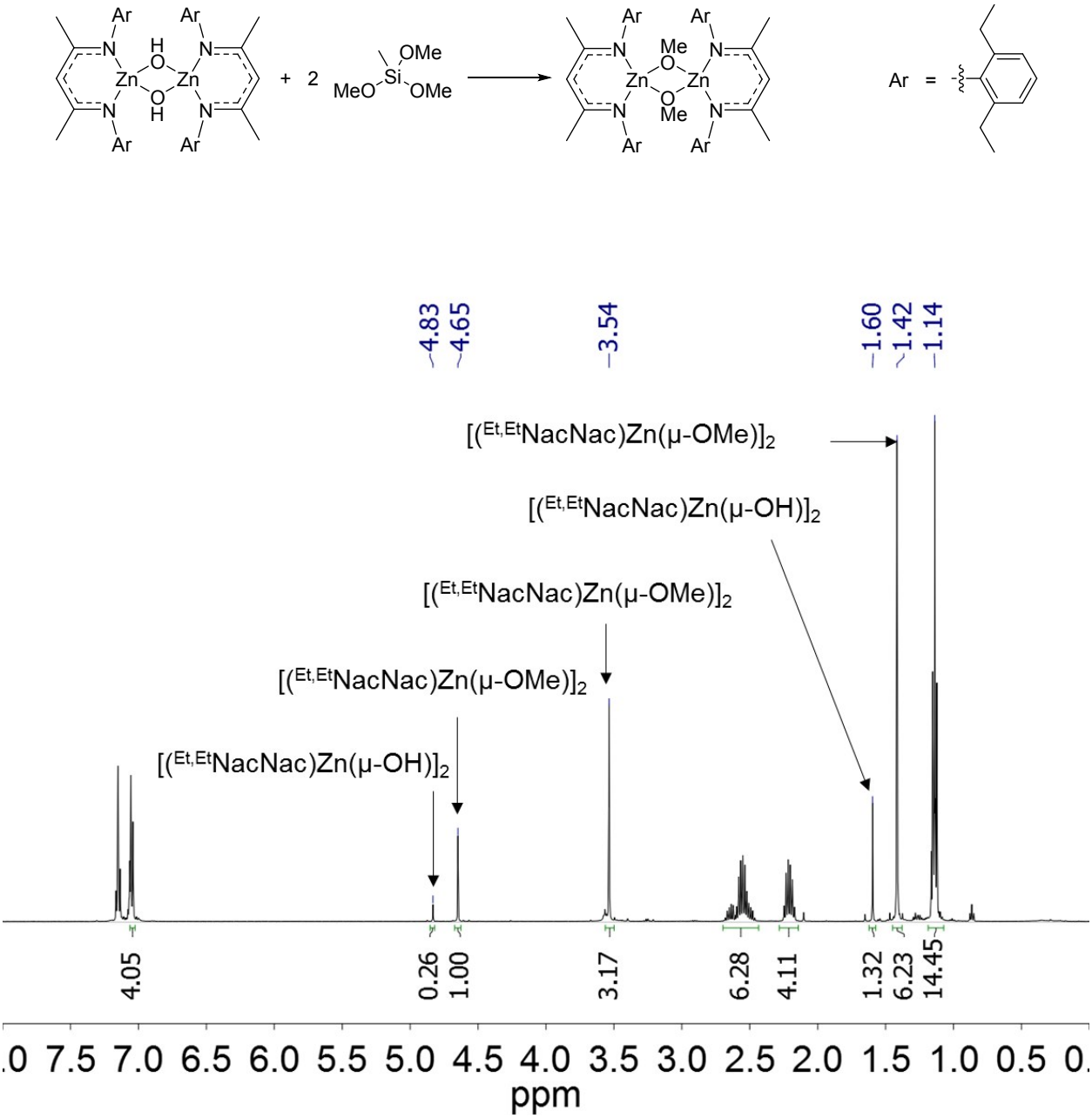


Figure 25. ^{1}H NMR spectrum of the residual solid from the reaction of $[(^{Et,Et}NacNac)Zn(\mu\text{-}OH)]_2$ and $(MeO)_3SiMe$. The major product is $[(^{Et,Et}NacNac)Zn(\mu\text{-}OMe)]_2$. The same product is obtained from the reaction of $[(^{Et,Et}NacNac)Zn(\mu\text{-}Cl)]_2$ and $NaOSi(OMe)_2Me$.

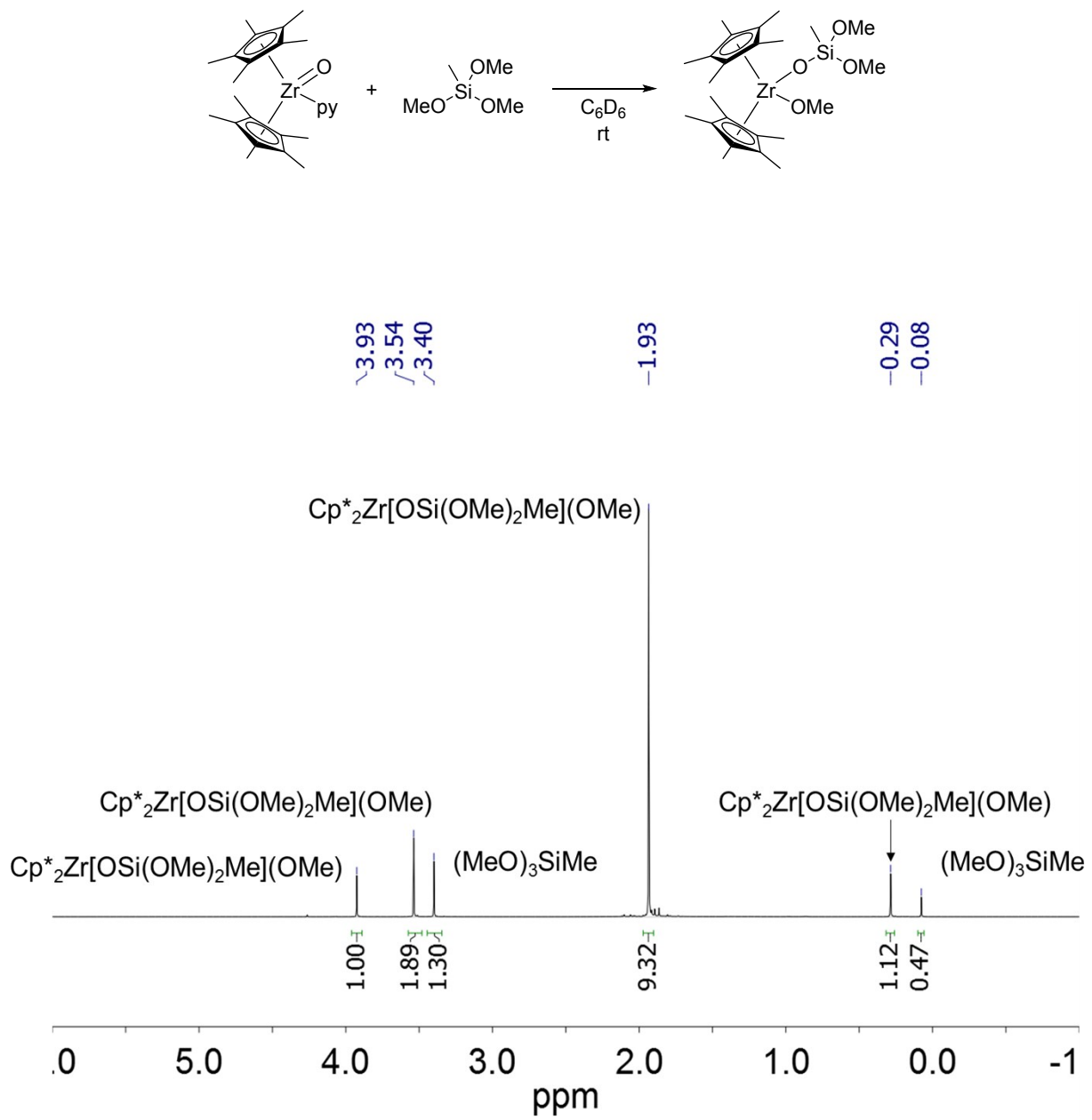


Figure 26. ^{1}H NMR spectrum of the crude reaction between Cp*$_2$Zr(O)(py) and $(MeO)_3SiMe$ in C_6D_6. The spectrum reveals the formation of Cp*$_2$Zr[OSi(OMe)2Me](OMe) in near quantitative yield.

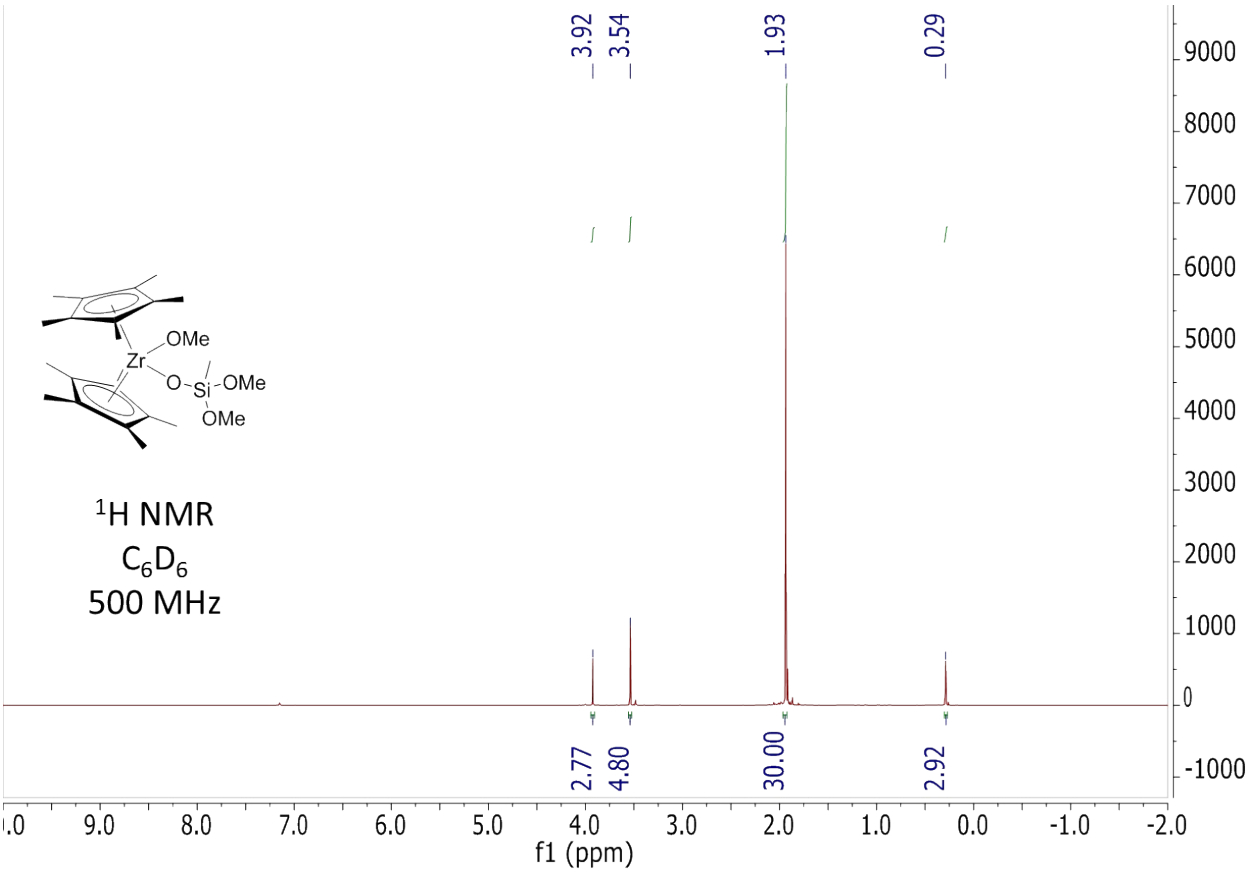


Figure 27. ^{1}H NMR spectrum of $Cp^*_2Zr[OSi(OMe)_2Me](OMe)$ in C_6D_6 at room temperature.

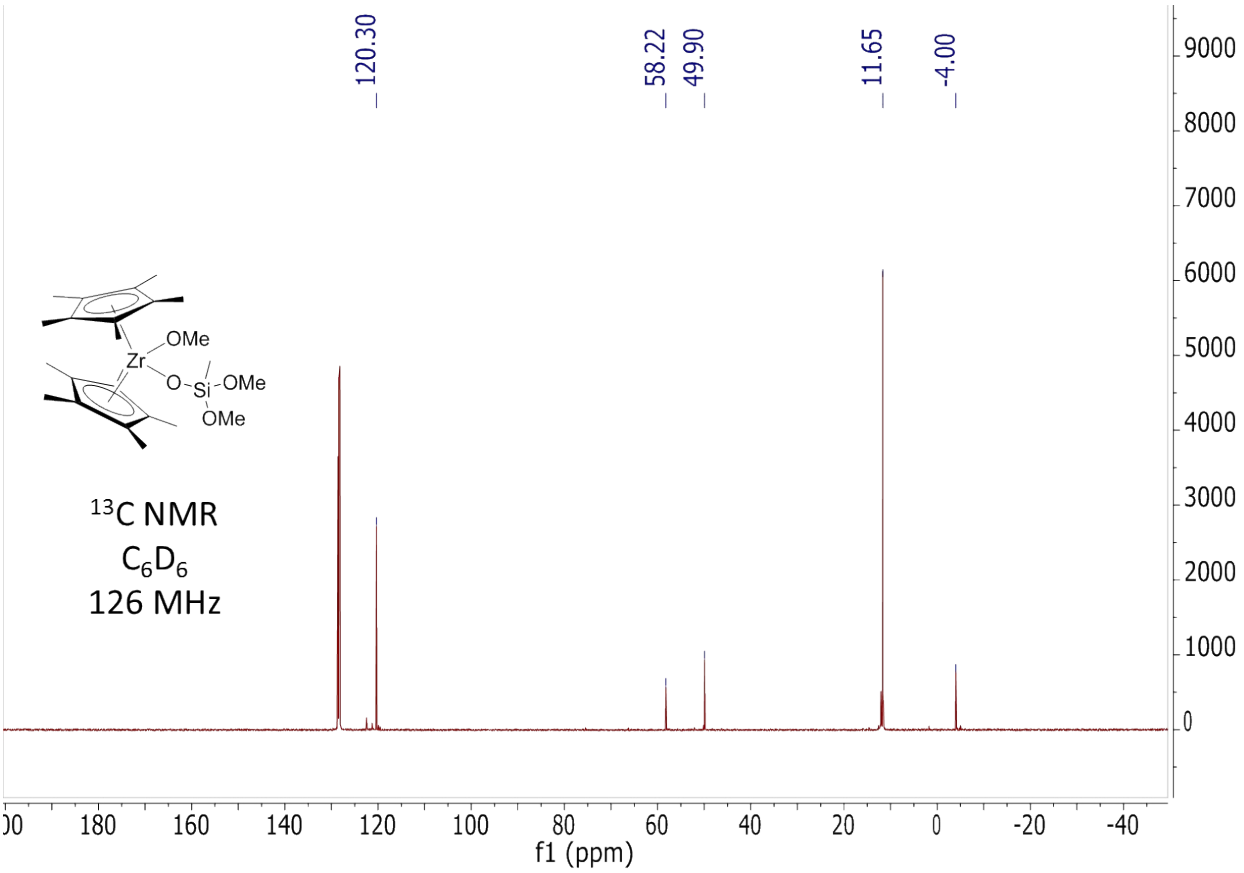


Figure 28. $^{13}C\{^{1}H\}$ NMR spectrum of $Cp^*_2Zr[OSi(OMe)_2Me](OMe)$ in C_6D_6 at room temperature.

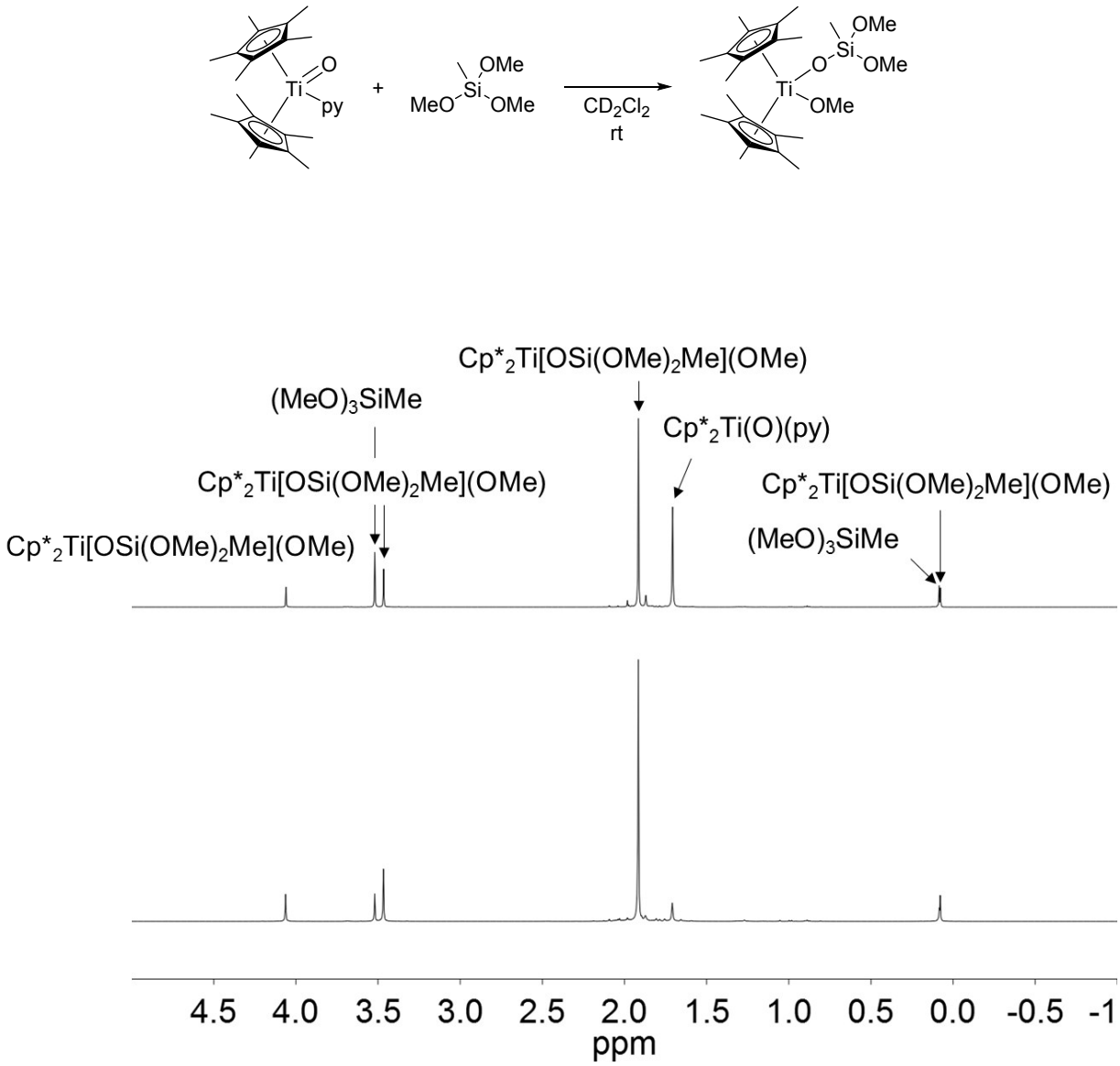


Figure 29. ^{1}H NMR spectrum of the crude reaction between $Cp^*_2Ti(O)(py)$ and $(MeO)_3SiMe$ in CD_2Cl_2 at room temperature. The top spectrum was collected 10 minutes after mixing. The bottom spectrum was collected 6 h after mixing.

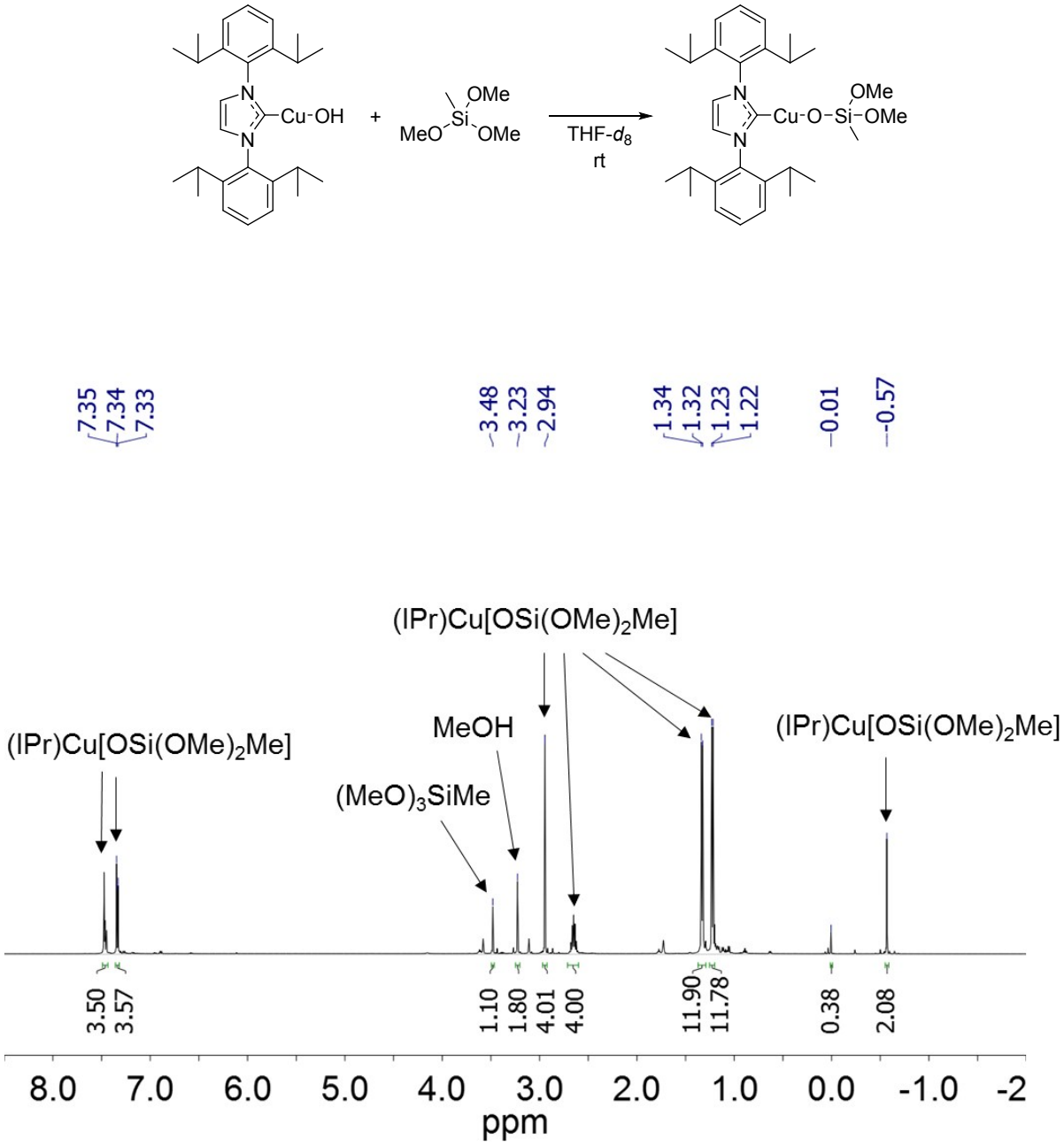
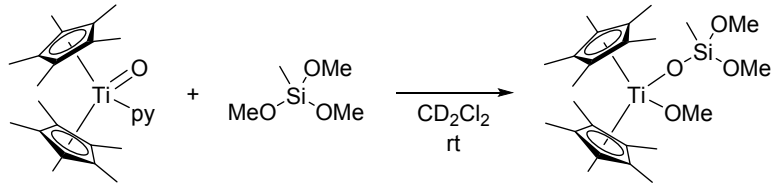


Figure 30. ^{1}H NMR spectrum (THF-d_8, rt) of the crude reaction between (IPr)CuOH and $(MeO)_3SiMe$. The major products are (IPr)Cu[OSi(OMe)2Me] and MeOH.



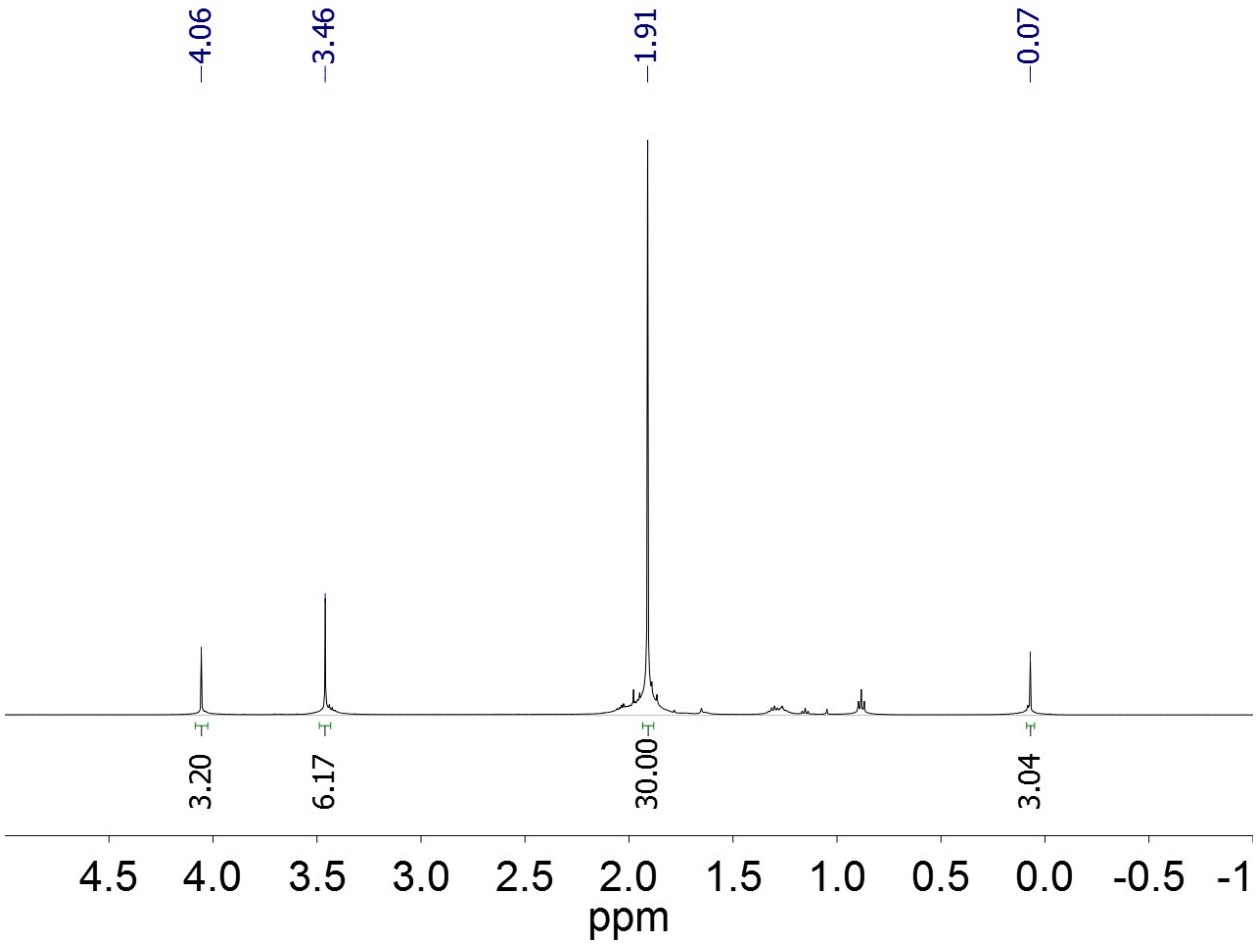


Figure 31. ^{1}H NMR spectrum of the crude reaction between $Cp^*_2Ti[OSi(OMe)2Me](OMe)$ in CD_2Cl_2 at room temperature.

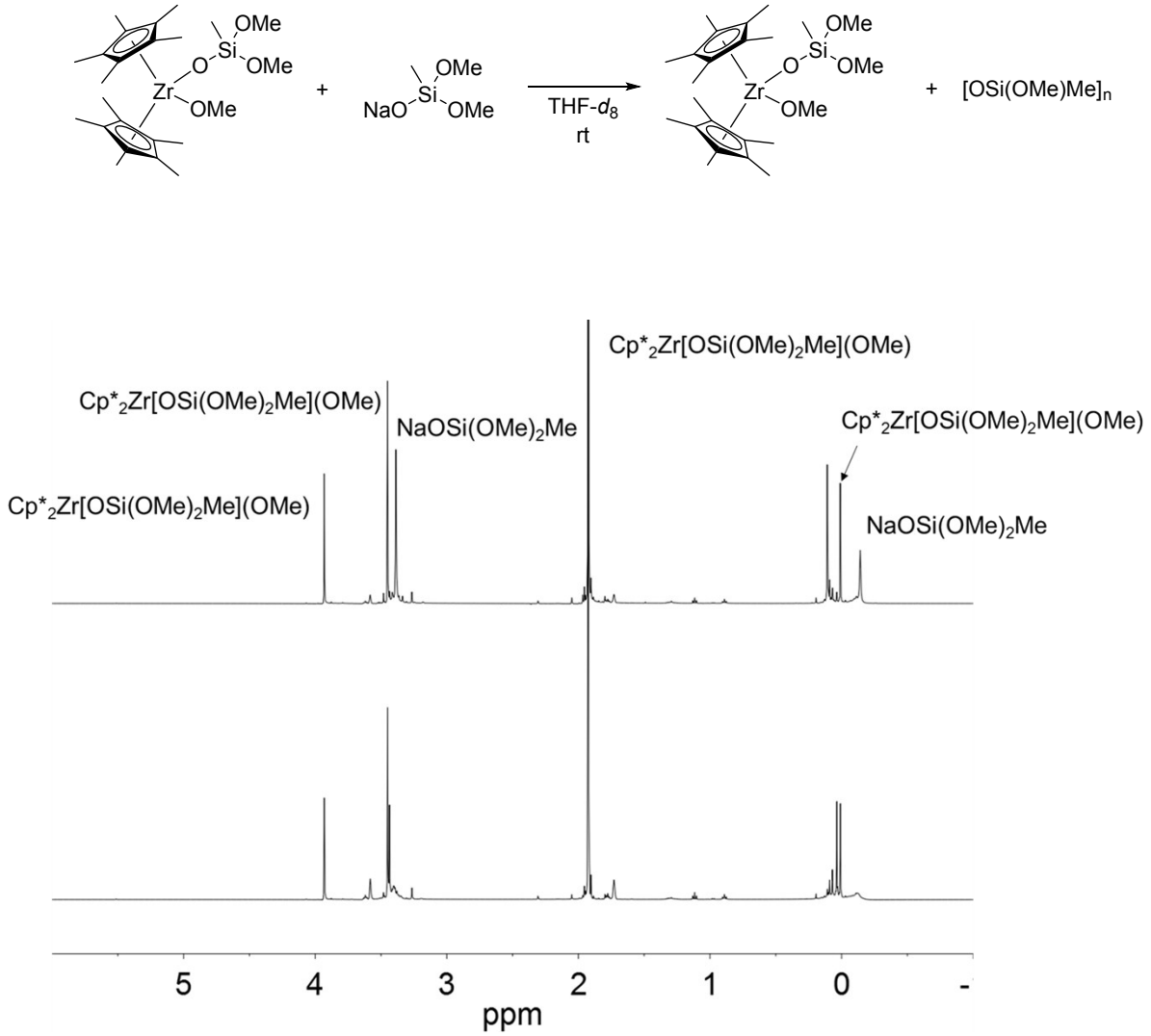


Figure 32. ^{1}H NMR spectra of the crude reaction between Cp*$_2$Zr[OSi(OMe)$_2$Me](OMe) and NaOSi(OMe)$_2$Me in THF-d_8 at room temperature. The top spectrum was collected 10 min after the addition of NaOSi(OMe)$_2$Me to Cp* Zr[OSi(OMe)$_2$Me](OMe). The bottom spectrum was collected 4 h after the addition of NaOSi(OMe)$_2$Me to Cp* Zr[OSi(OMe)$_2$Me](OMe).

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