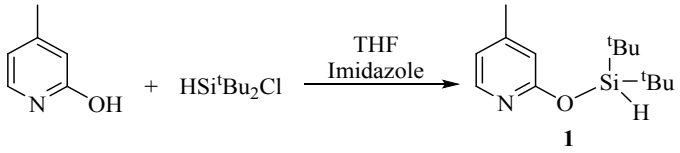
Supporting Information

1. Characterization of the ligand precursor **1**



1

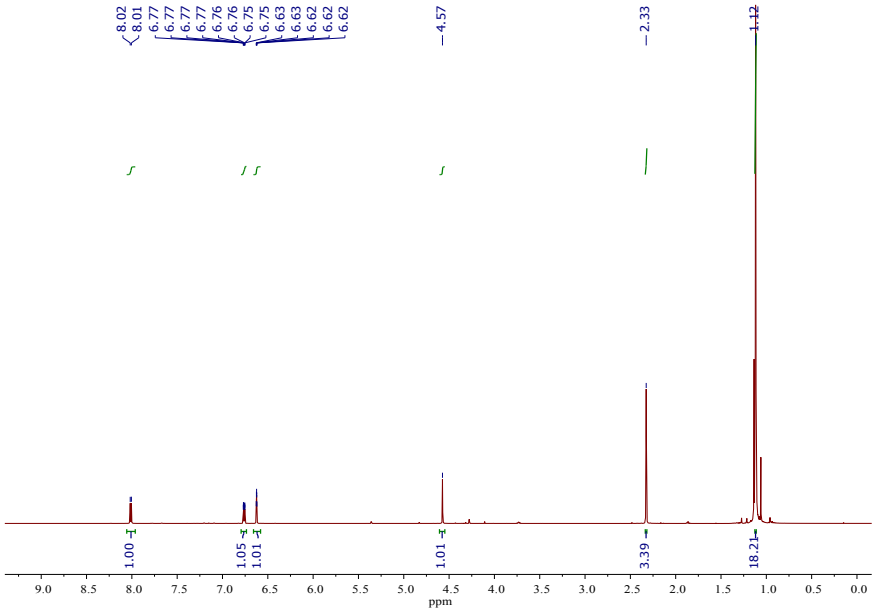


Figure 1. ^{1}H-NMR spectrum of **1**

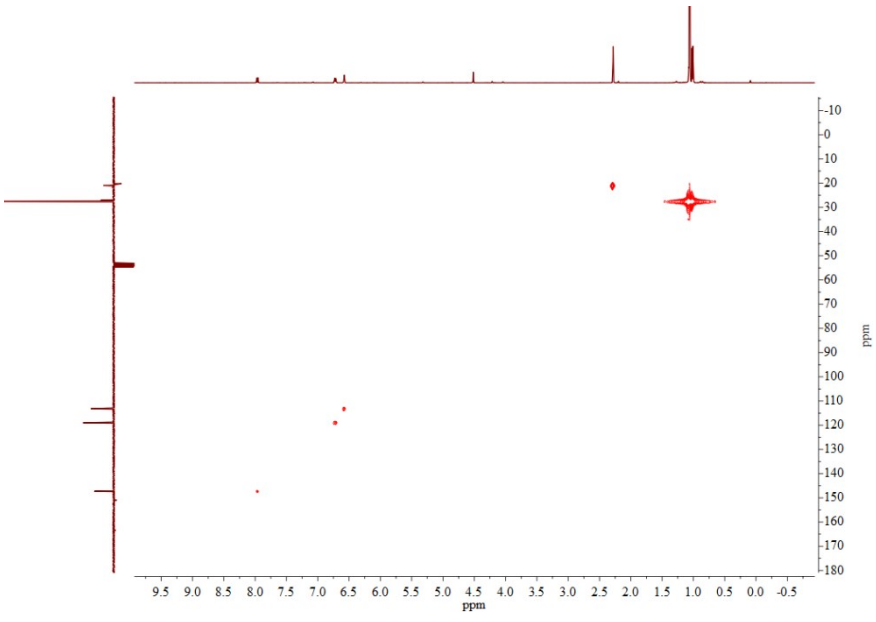


Figure 2. ^{1}H-^{13}C HSQC NMR spectrum of **1**

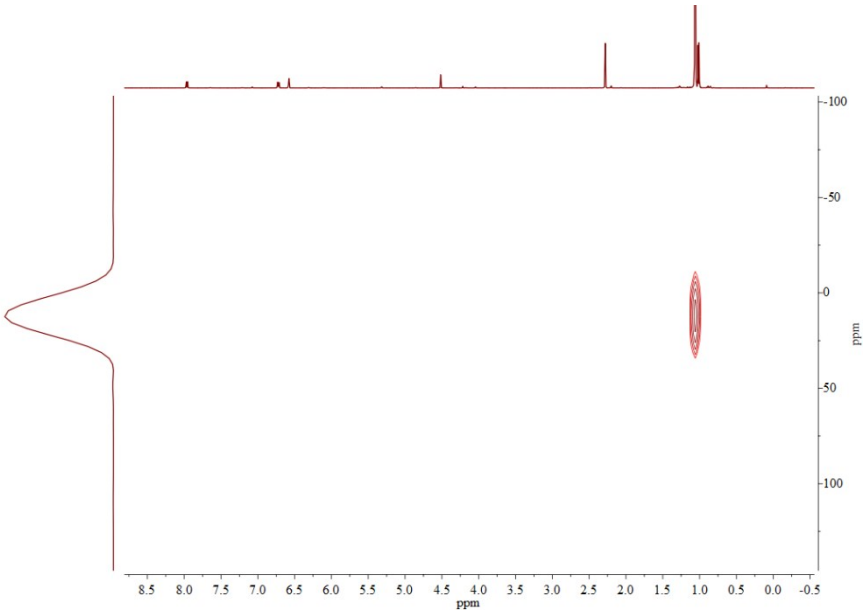


Figure 3. ^{1}H-^{29}Si HMBC NMR spectrum of **1**

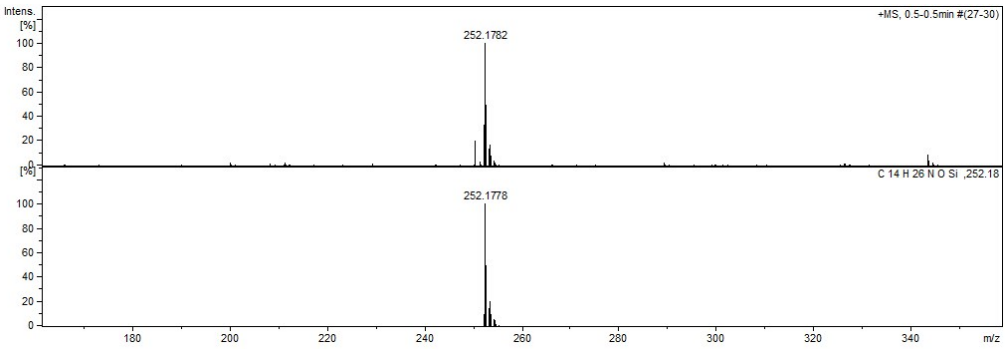
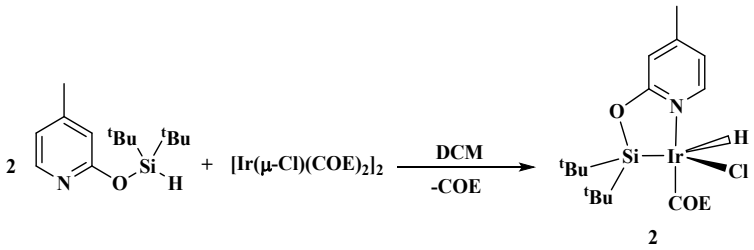


Figure 4. High Resolution Mass Spectrometry (ESI^{+}) of compound **1** (found and calculated)

2. Characterization of complex **2**



2

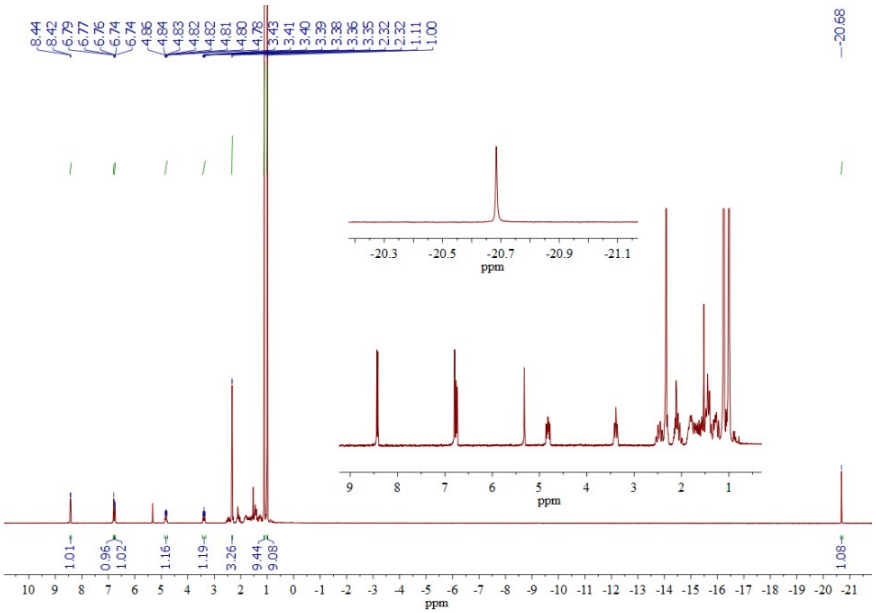


Figure 5. ^{1}H-NMR spectrum of complex **2**

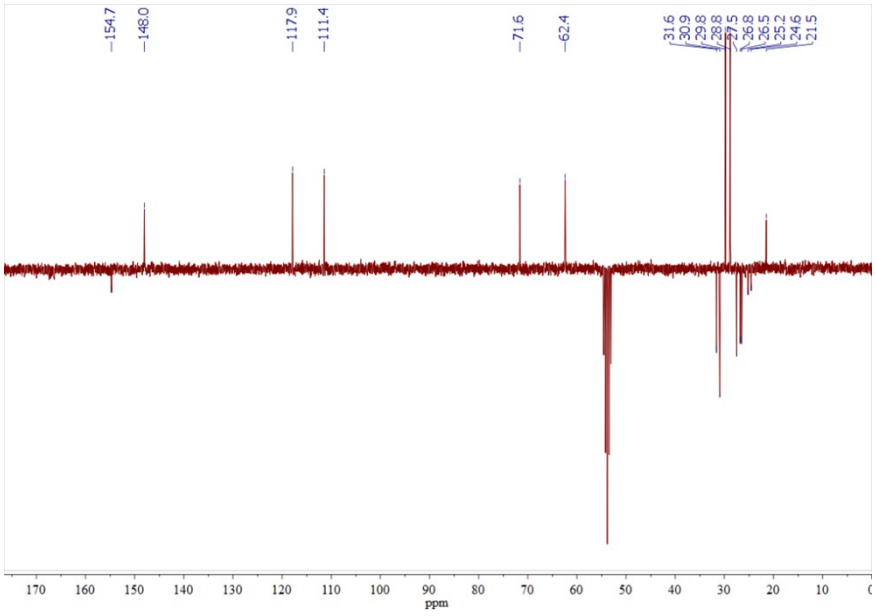


Figure 6. ^{13}C-APT NMR spectrum of complex **2**

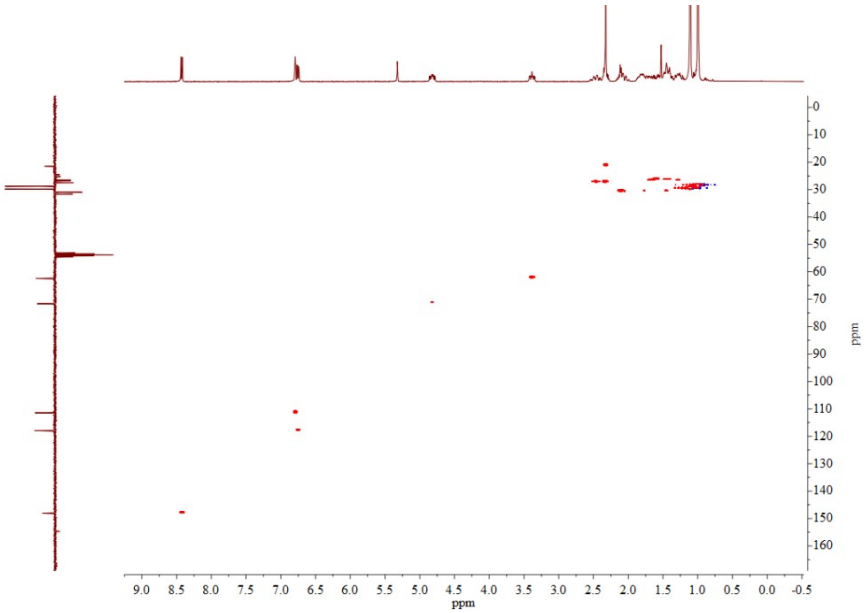


Figure 7. ^{1}H-^{13}C HSQC NMR spectrum of complex **2**

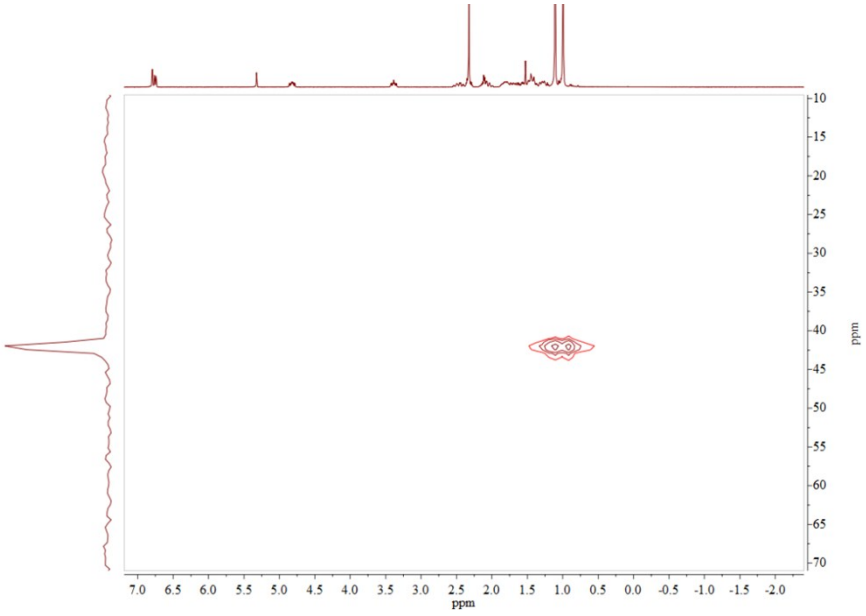
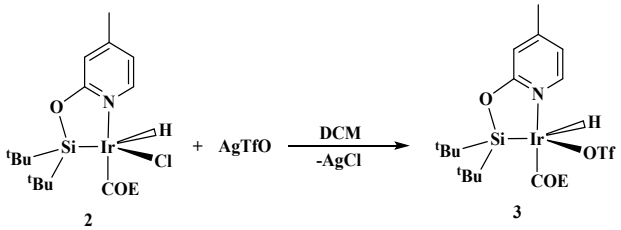


Figure 8. ^{1}H-^{29}Si HMBC NMR spectrum of complex **2**

3. Characterization of complex **3**



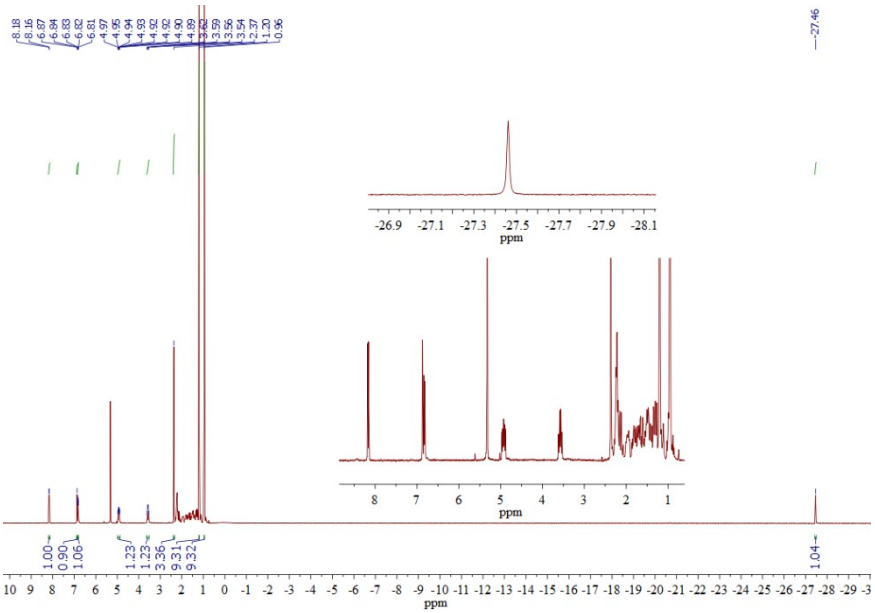


Figure 9. ^{1}H-NMR spectrum of complex **3**

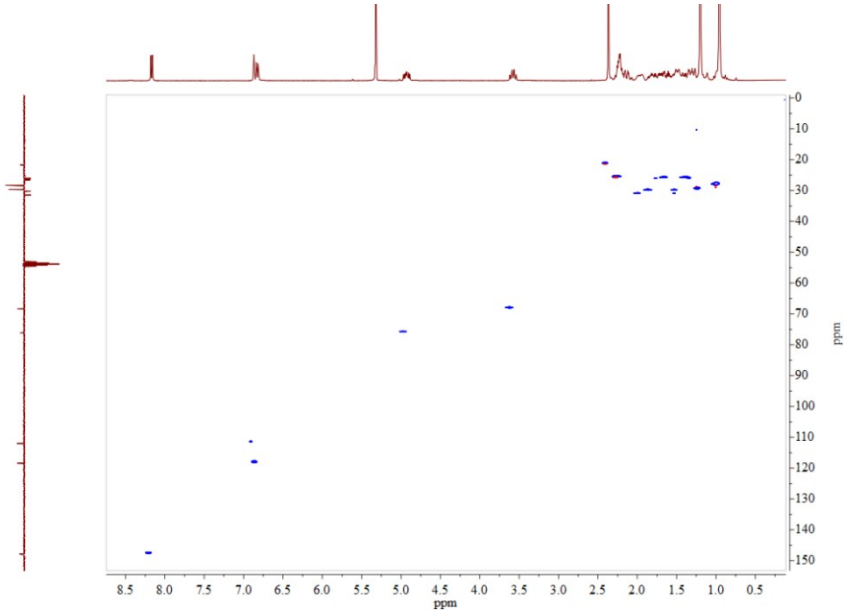


Figure 10. ^{1}H-^{13}C HSQC NMR spectrum of complex **3**

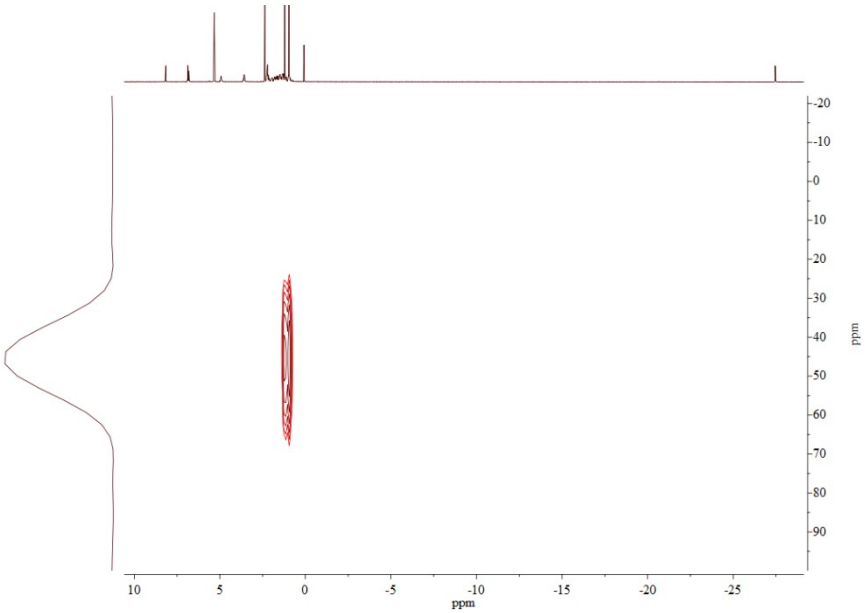


Figure 11. ^{1}H-^{29}Si HMBC NMR spectrum of complex **3**

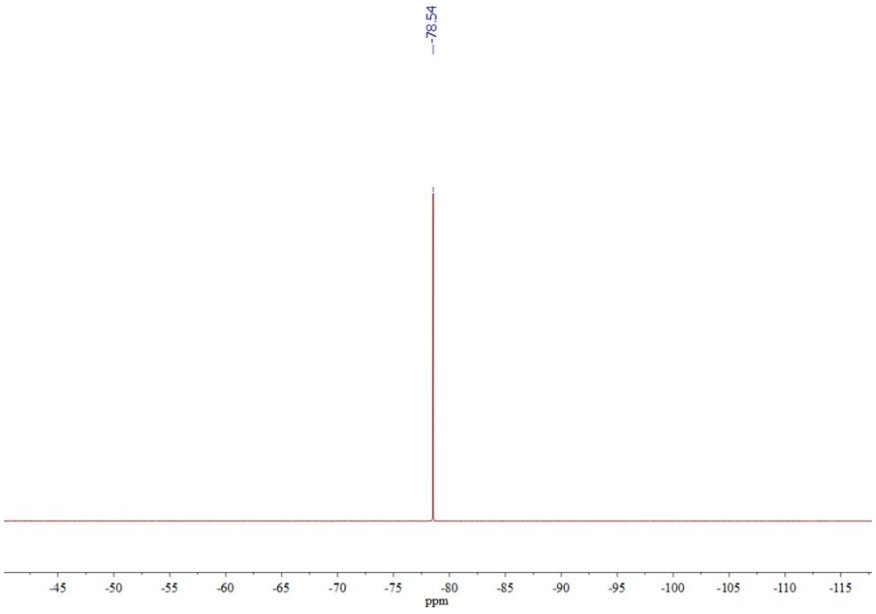


Figure 12. ^{19}F NMR spectrum of complex **3**

4. Characterization of the reaction products

a) $(CH_2)_4NCH_2OSiMe_2Ph$ (**4a**)

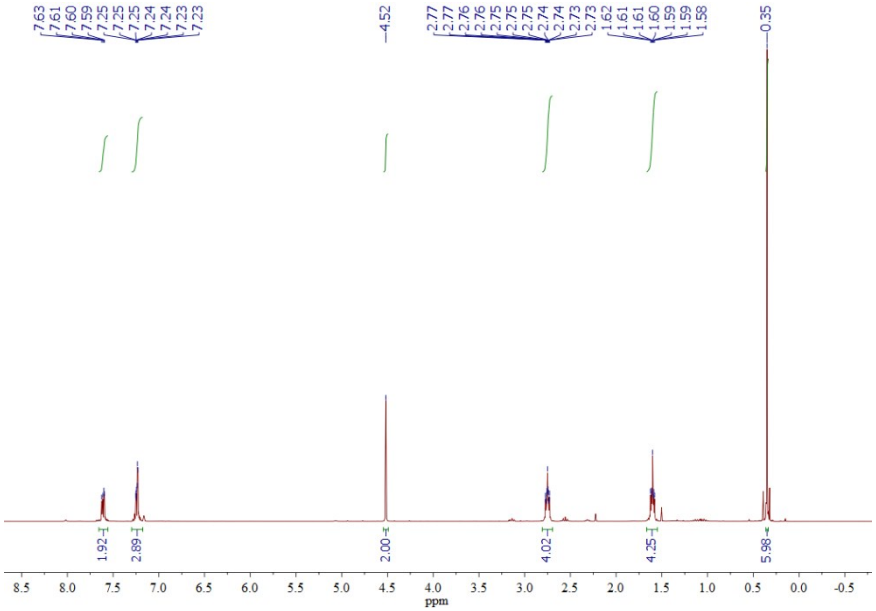


Figure 13. ^{1}H-NMR spectrum from the **2**-catalyzed reaction of *N*-formylpyrrolidine with 1 eq. of $HSiMe_2Ph$

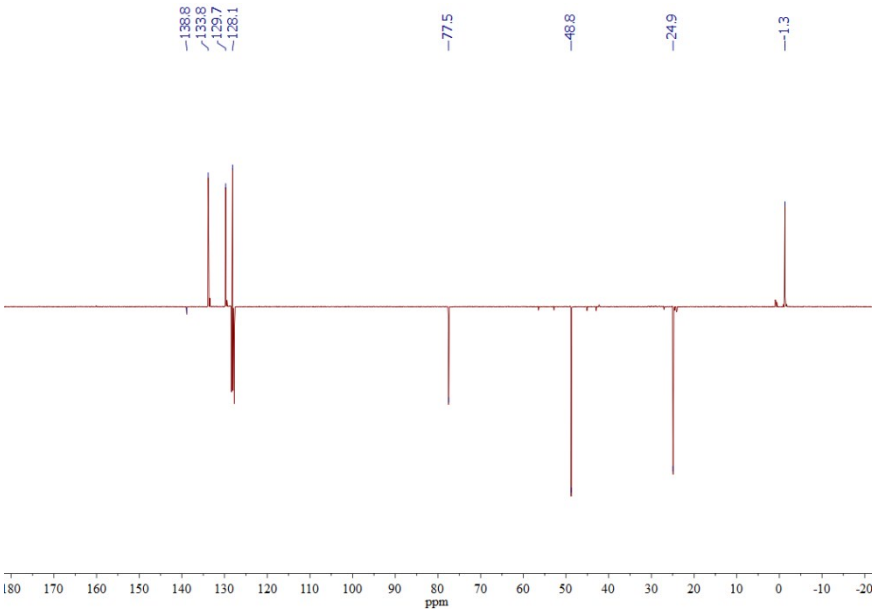


Figure 14. ^{13}C-APT NMR spectrum from the **2**-catalyzed reaction of *N*-formylpyrrolidine with 1 eq. of $HSiMe_2Ph$

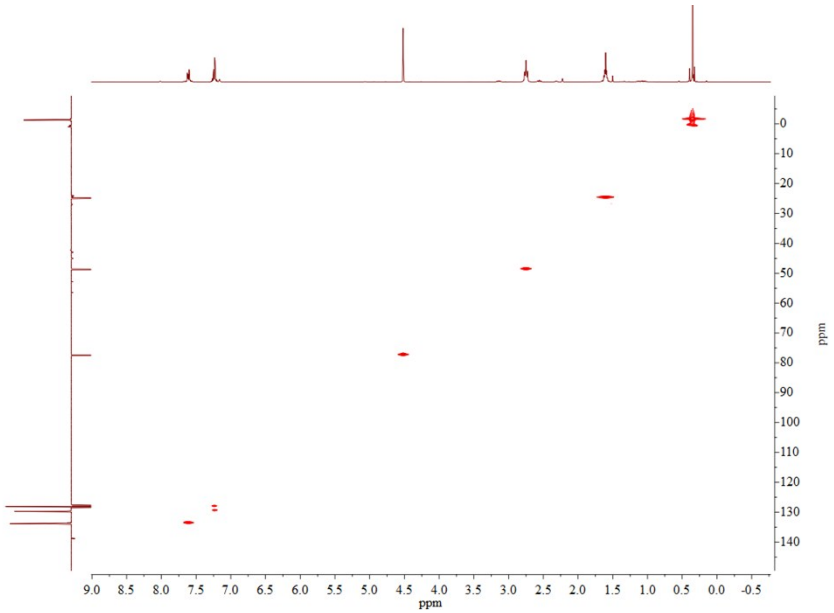


Figure 15. ^{1}H-^{13}C-HSQC NMR spectrum from the **2**-catalyzed reaction of *N*-formylpyrrolidine with 1 eq. of $HSiMe_2Ph$

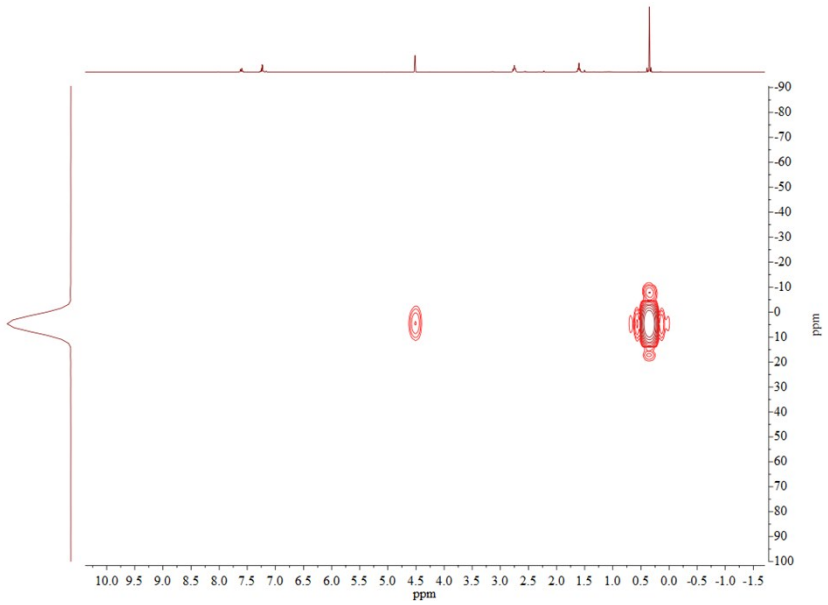


Figure 16. ^{1}H-^{29}Si-HMBC NMR spectrum from the **2**-catalyzed reaction of *N*-formylpyrrolidine with 1 eq. of $HSiMe_2Ph$

b) $(CH_2)_4NMe$ (**5a**)

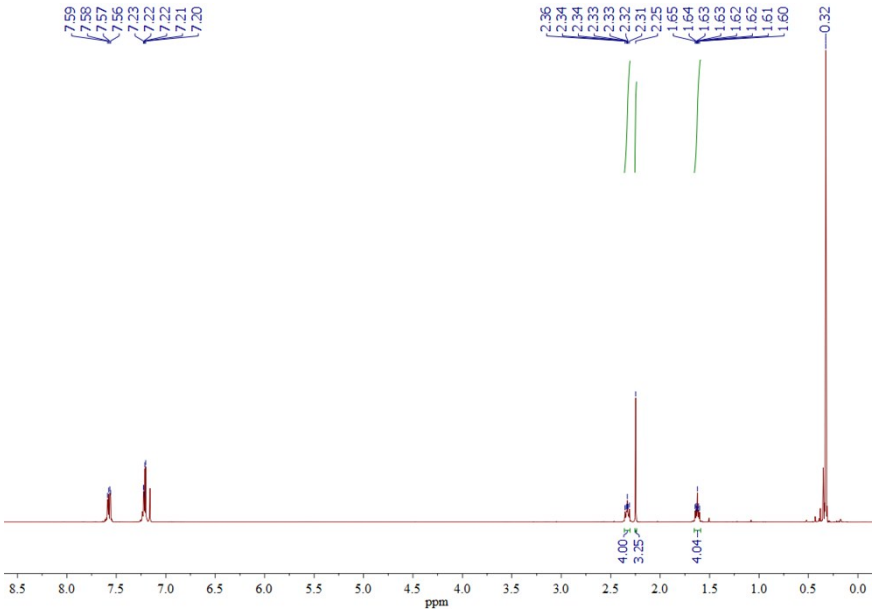


Figure 17. ^{1}H-NMR spectrum from the **3**-catalyzed reaction of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$

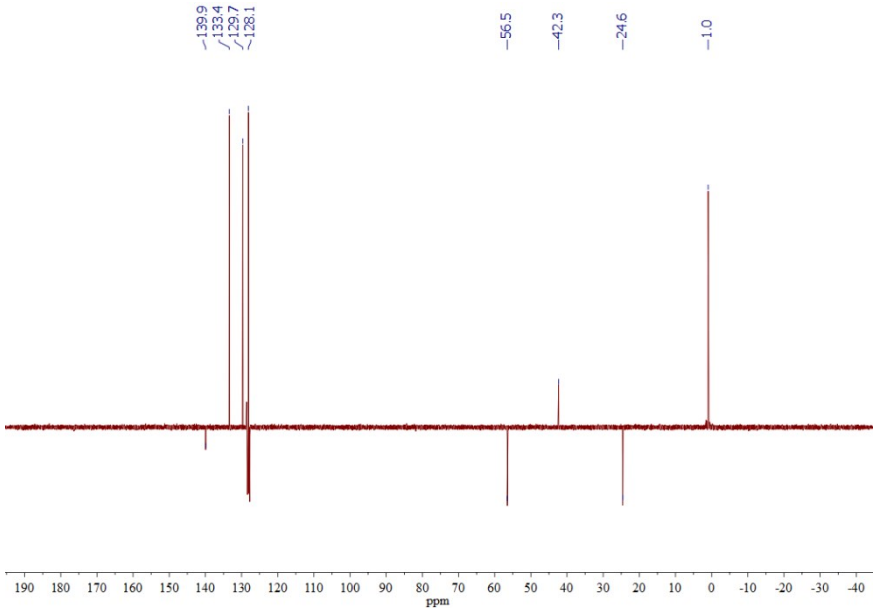


Figure 18. ^{13}C-APT NMR spectrum from the **3**-catalyzed reaction of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$

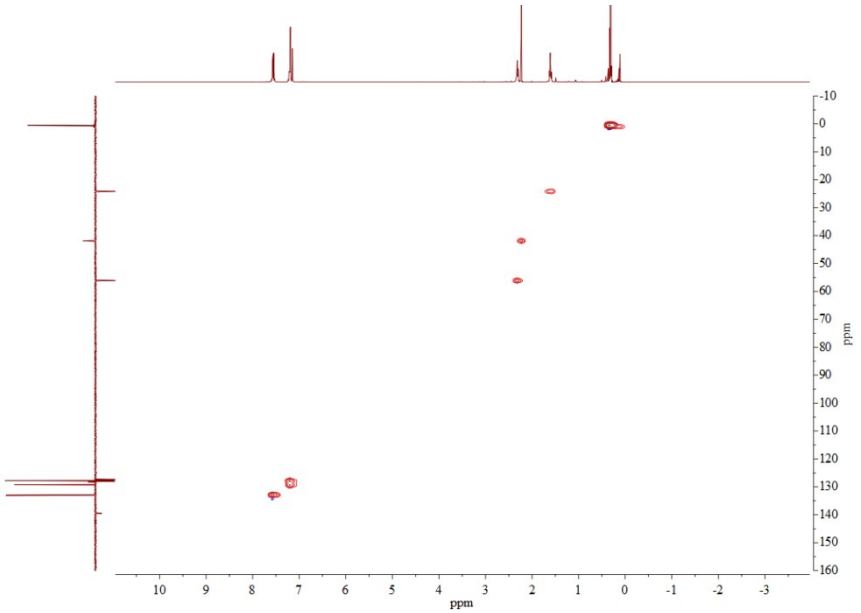


Figure 19. ^{1}H-^{13}C HSQC NMR spectrum from the **3**-catalyzed reaction of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$

c) $Me_2NCH_2OSiMe_2Ph$ (**4b**)

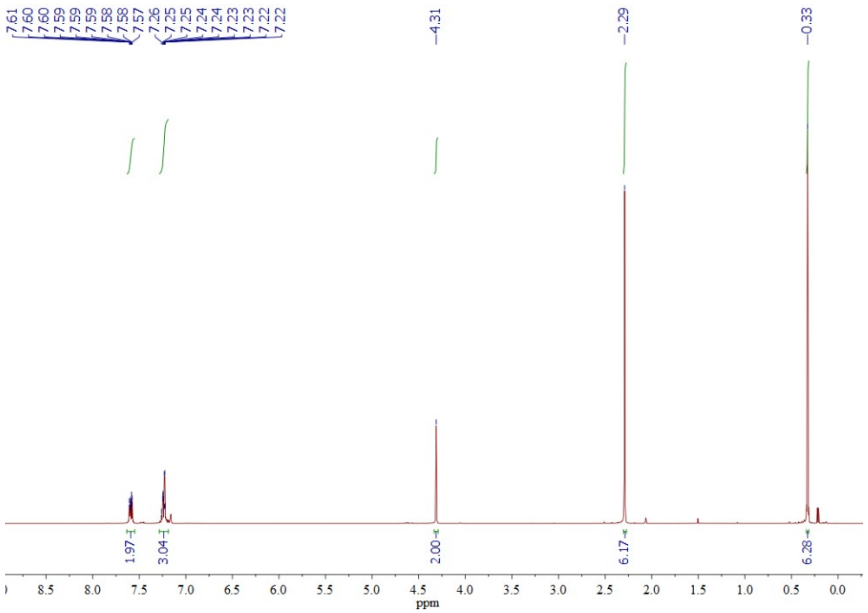


Figure 20. ^{1}H-NMR spectrum from the **2**-catalyzed reaction of DMF with 1 eq. of $HSiMe_2Ph$

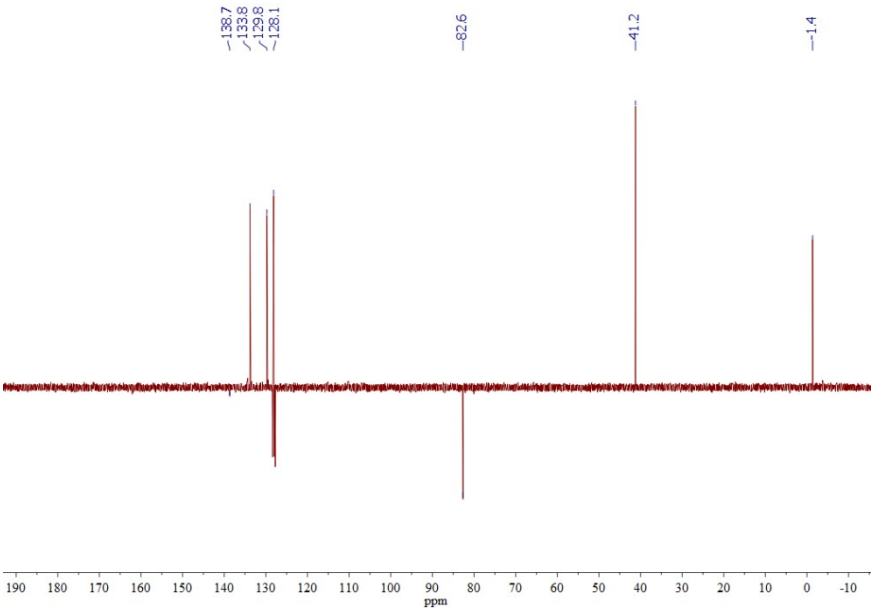


Figure 21. ^{13}C-APT NMR spectrum from the **2**-catalyzed reaction of DMF with 1 eq. of $HSiMe_2Ph$

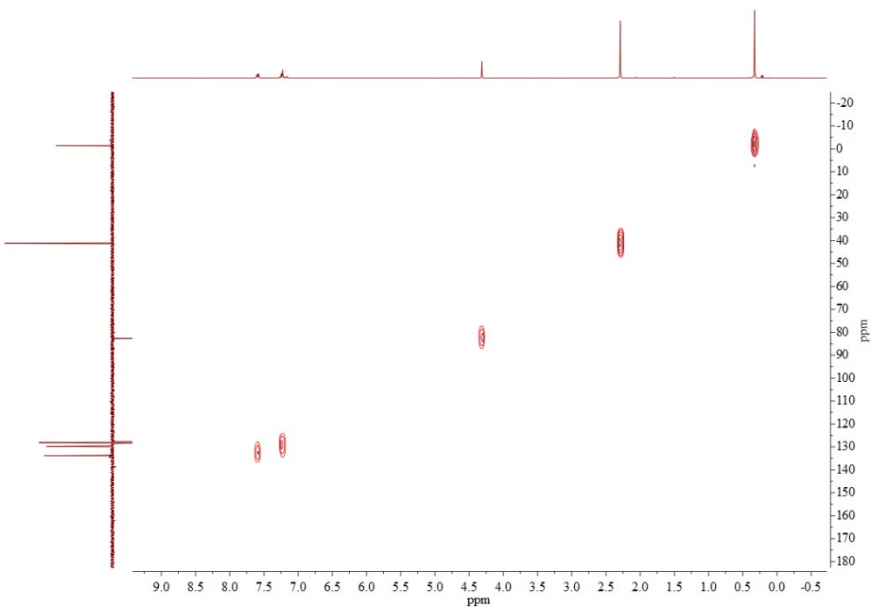


Figure 22. ^{1}H-^{13}C-HSQC NMR spectrum from the **2**-catalyzed reaction of DMF with 1 eq. of $HSiMe_2Ph$

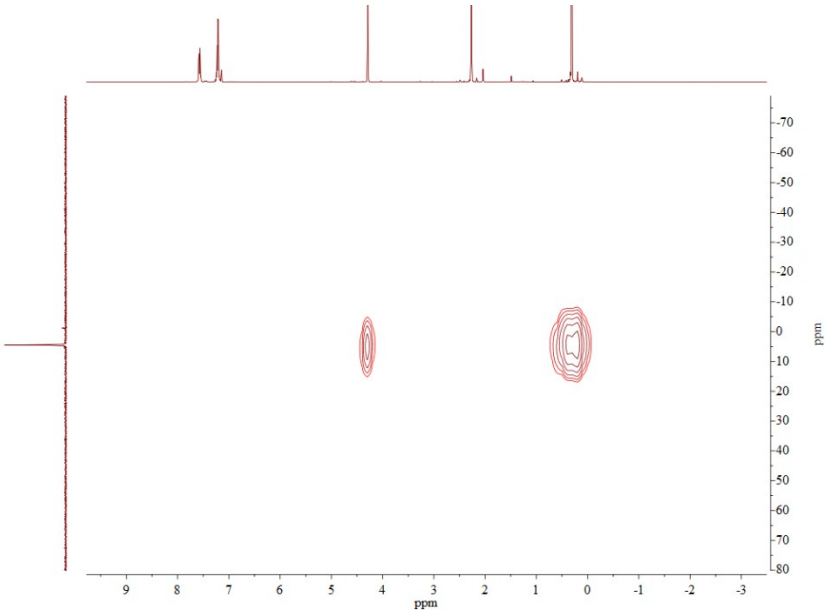


Figure 23. ^{1}H-^{29}Si-HMBC NMR spectrum from the **2**-catalyzed reaction of DMF with 1 eq. of $HSiMe_2Ph$

d) Me_3N (**5b**)

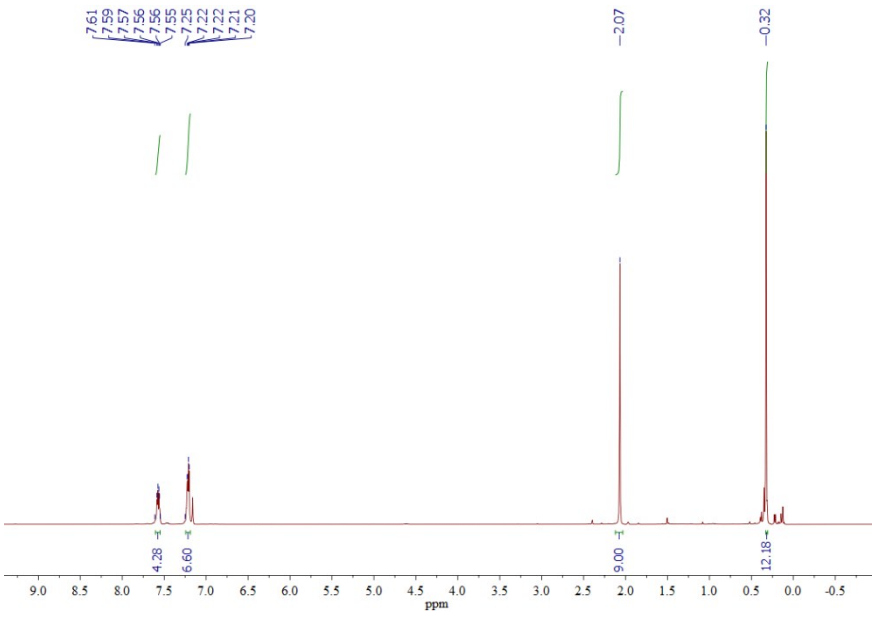


Figure 24. ^{1}H-NMR spectrum from the **3**-catalyzed reaction of DMF with 2 eq. of $HSiMe_2Ph$

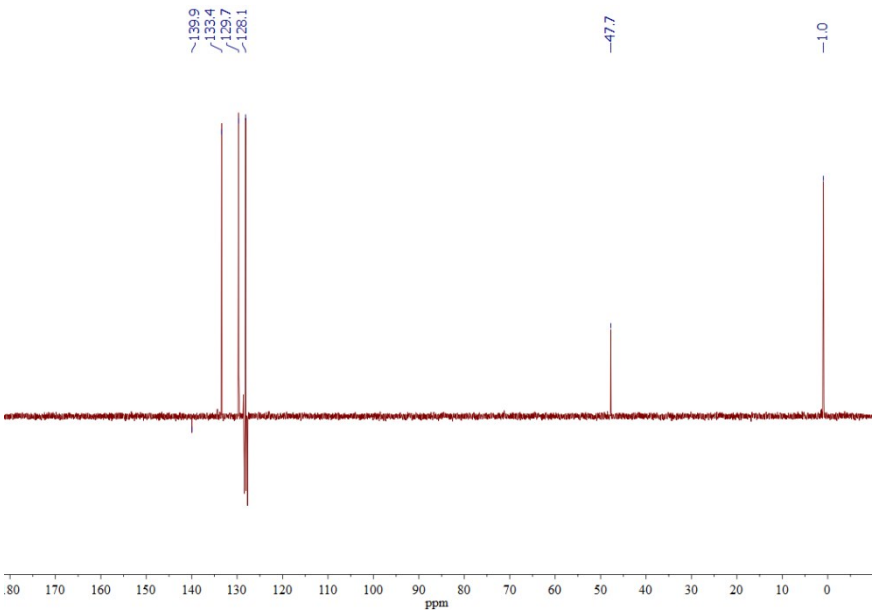


Figure 25. ^{13}C-APT NMR spectrum from the **3**-catalyzed reaction of DMF with 2 eq. of $HSiMe_2Ph$

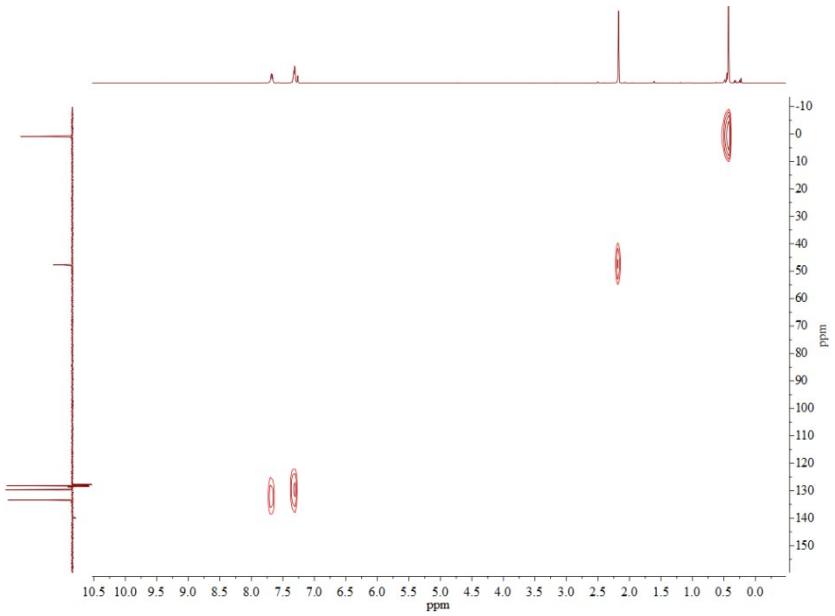


Figure 26. ^{1}H-^{13}C HSQC NMR spectrum from the **3**-catalyzed reaction of DMF with 2 eq. of $HSiMe_2Ph$

e) $PhMeNCH_2OSiMe_2Ph$ (**4c**)

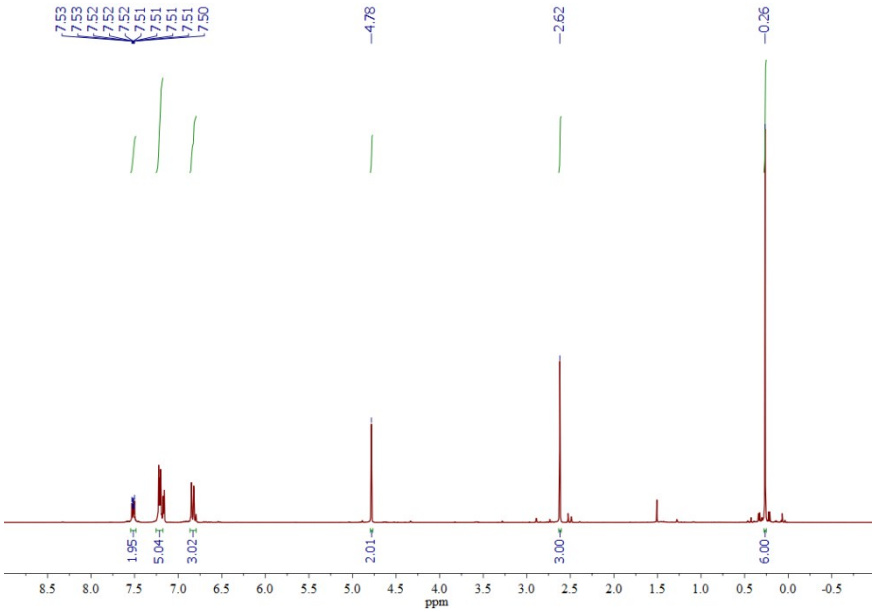


Figure 27. ^{1}H-NMR spectrum from the **2**-catalyzed reaction of *N*-methyl-*N*-phenylformamide with 1 eq. of $HSiMe_2Ph$

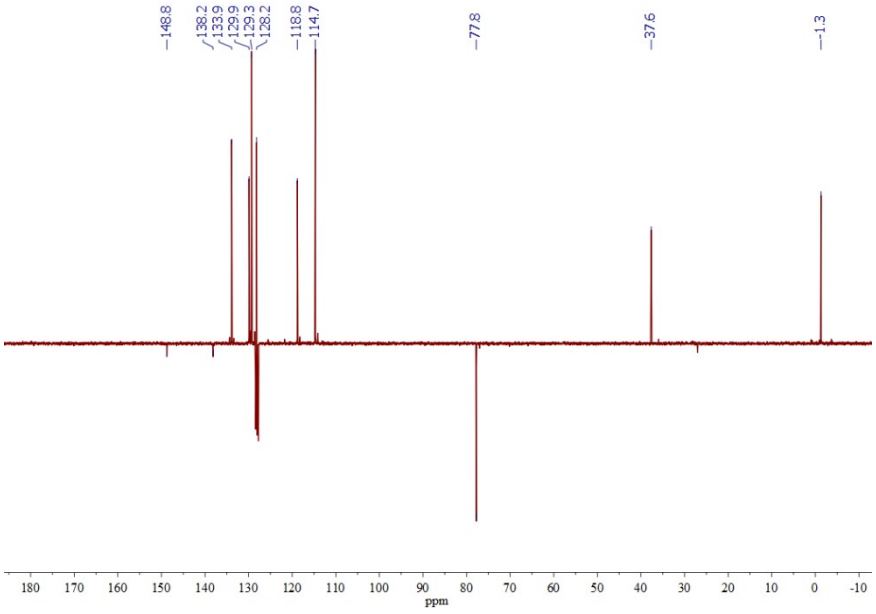


Figure 28. ^{13}C-APT spectrum from the **2**-catalyzed reaction of *N*-methyl-*N*-phenylformamide with 1 eq. of $HSiMe_2Ph$

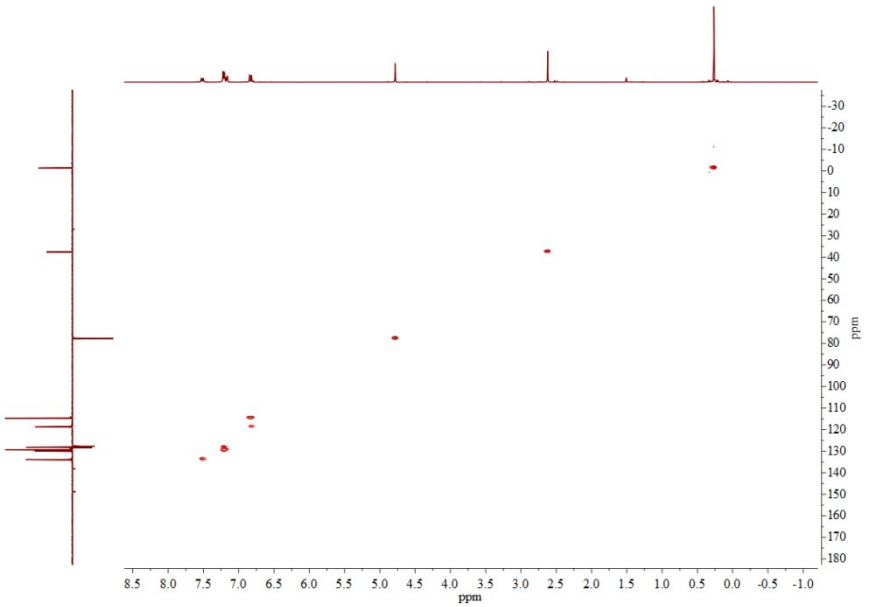


Figure 29. ^{1}H-^{13}C-HSQC spectrum from the **2**-catalyzed reaction of *N*-methyl-*N*-phenylformamide with 1 eq. of $HSiMe_2Ph$

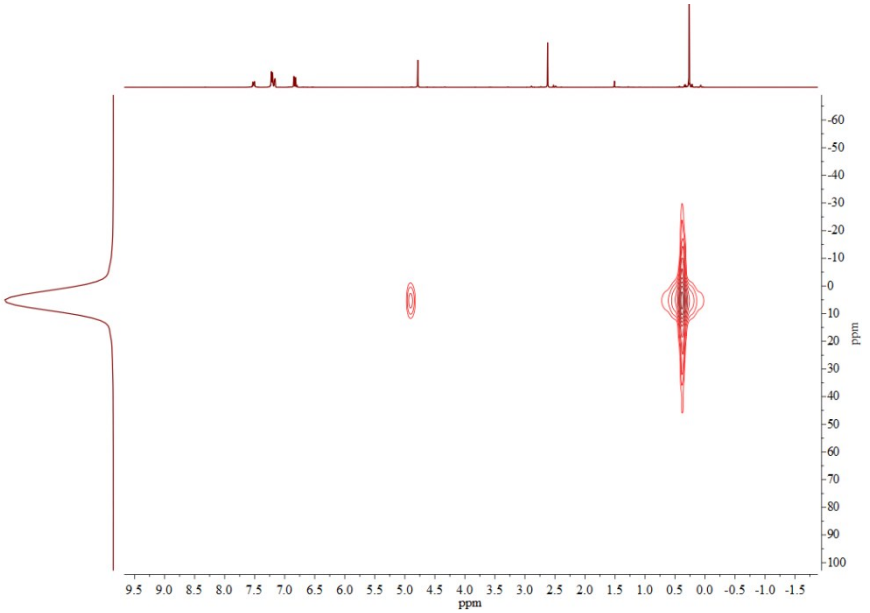


Figure 30. ^{1}H-^{29}Si-HMBC spectrum from the **2**-catalyzed reaction of *N*-methyl-*N*-phenylformamide with 1 eq. of $HSiMe_2Ph$

f) $PhNMe_2$ (**5c**)

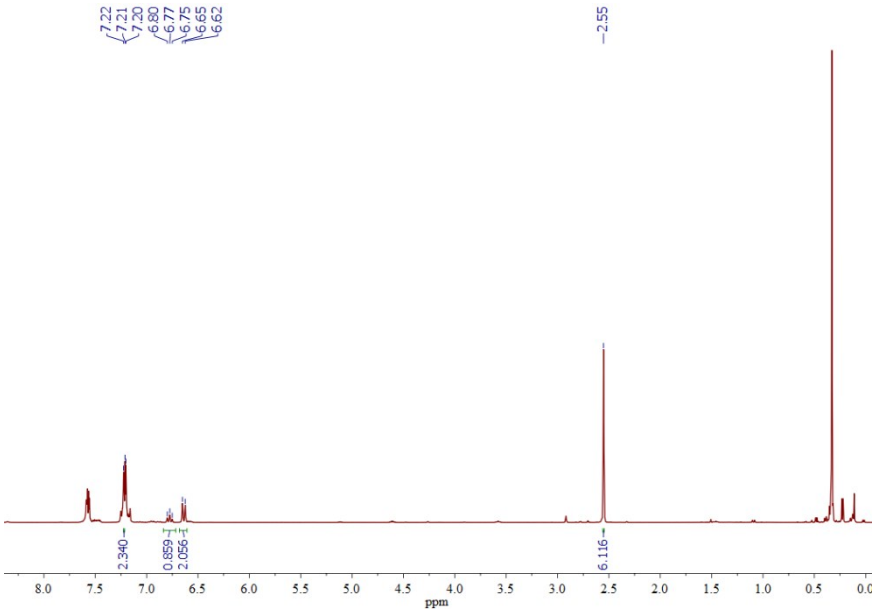


Figure 31. ^{1}H-NMR spectrum from the **3**-catalyzed reaction of *N*-methyl-*N*-phenylformamide with 2 eq. of $HSiMe_2Ph$

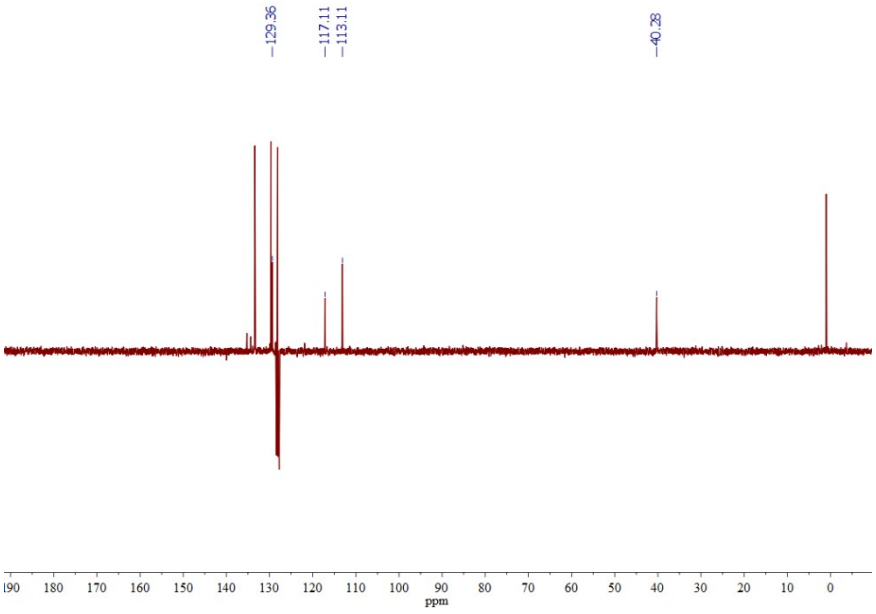


Figure 32. ^{13}C-APT NMR spectrum from the **3**-catalyzed reaction of *N*-methyl-*N*-phenylformamide with 2 eq. of $HSiMe_2Ph$

g) $Ph_2NCH_2OSiMe_2Ph$ (**4d**)

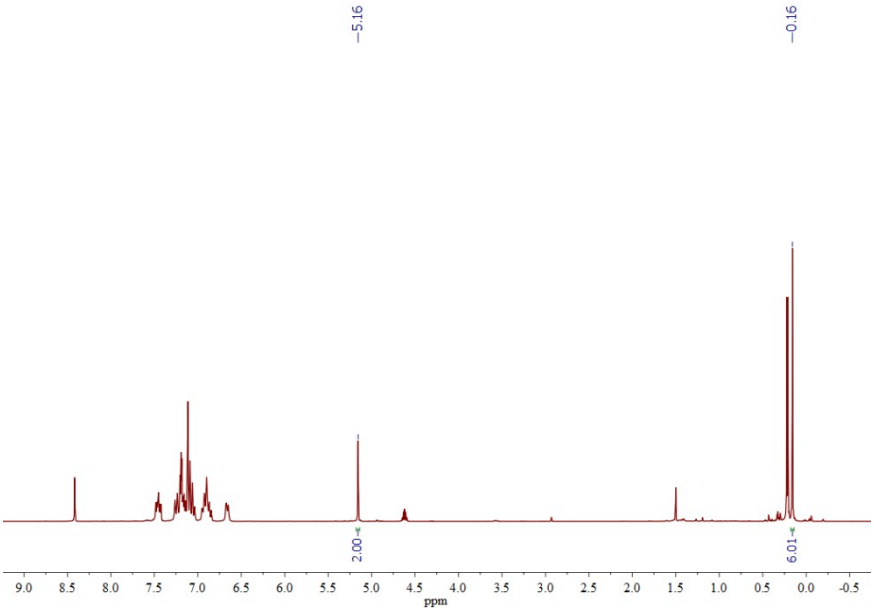


Figure 33. ^{1}H-NMR spectrum from the **2**-catalyzed reaction of *N,N*-diphenylformamide with 1 eq. of $HSiMe_2Ph$

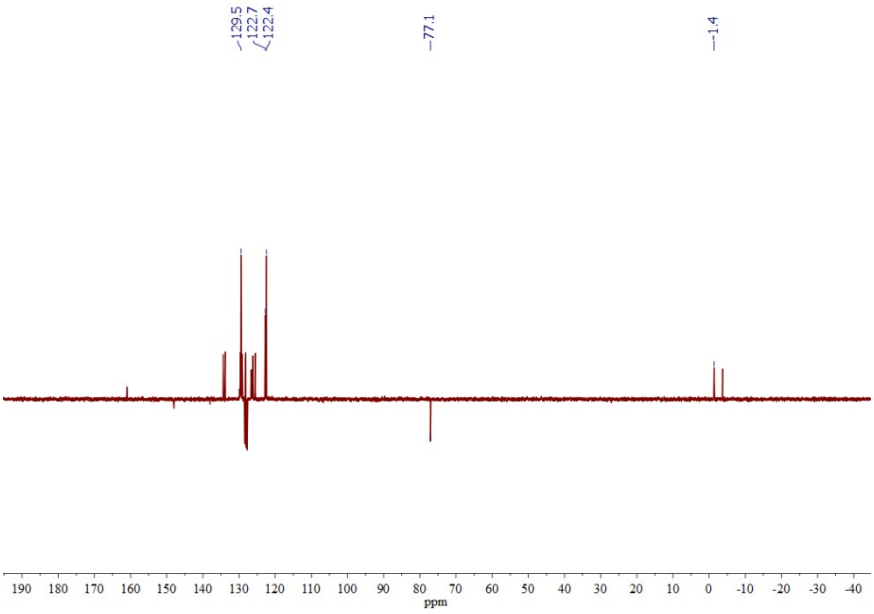


Figure 34. ^{13}C-APT NMR spectrum from the **2**-catalyzed reaction of *N,N*-diphenylformamide with 1 eq. of $HSiMe_2Ph$

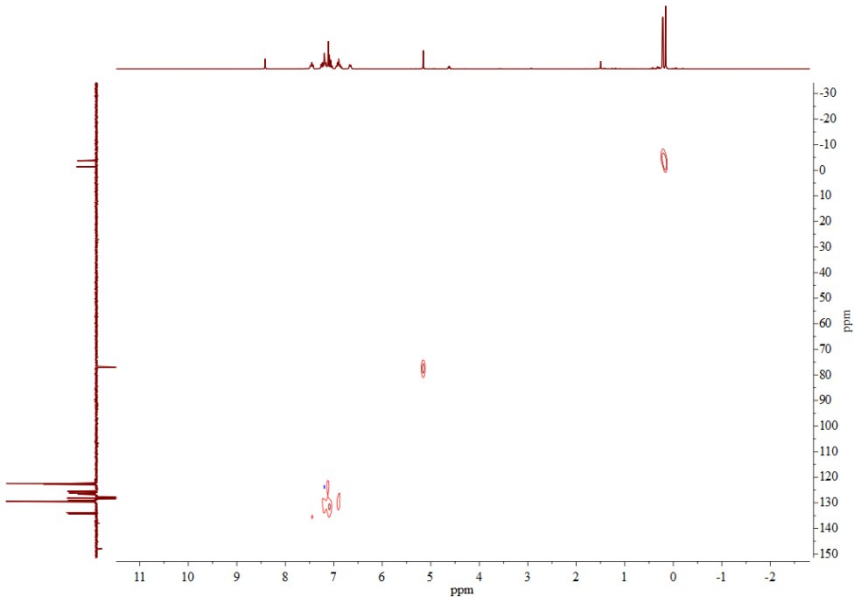


Figure 35. ^{1}H-^{13}C-HSQC spectrum from the **2**-catalyzed reaction of *N,N*-diphenylformamide with 1 eq. of $HSiMe_2Ph$

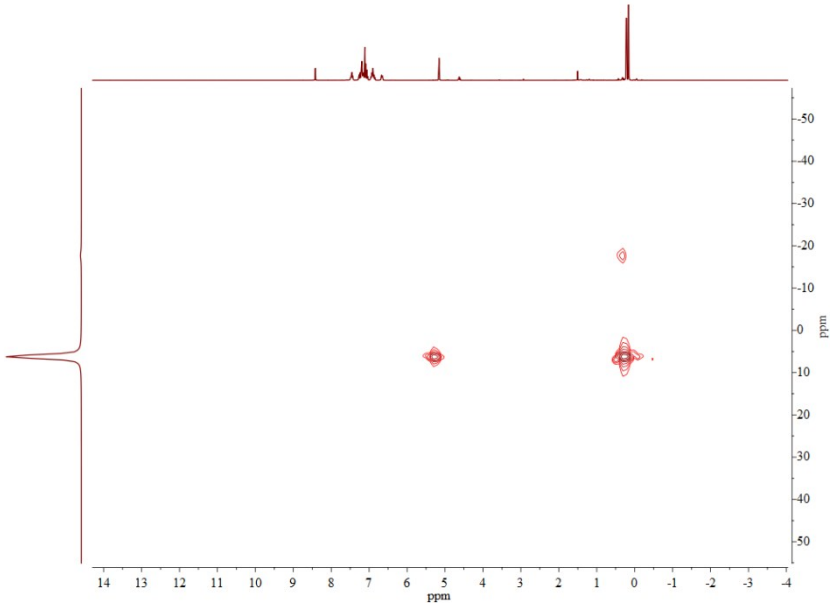


Figure 36. ^{1}H-^{29}Si-HMBC spectrum from the **2**-catalyzed reaction of *N,N*-diphenylformamide with 1 eq. of $HSiMe_2Ph$

h) Ph_2NMe (**5d**)

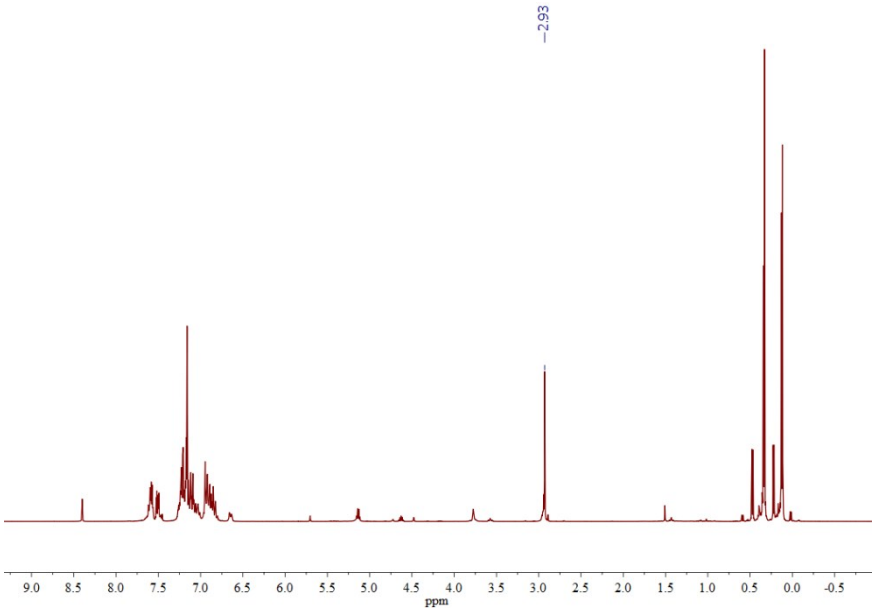


Figure 37. ^{1}H-NMR spectrum from the **3**-catalyzed reaction of *N,N*-diphenylformamide with 2 eq. of $HSiMe_2Ph$

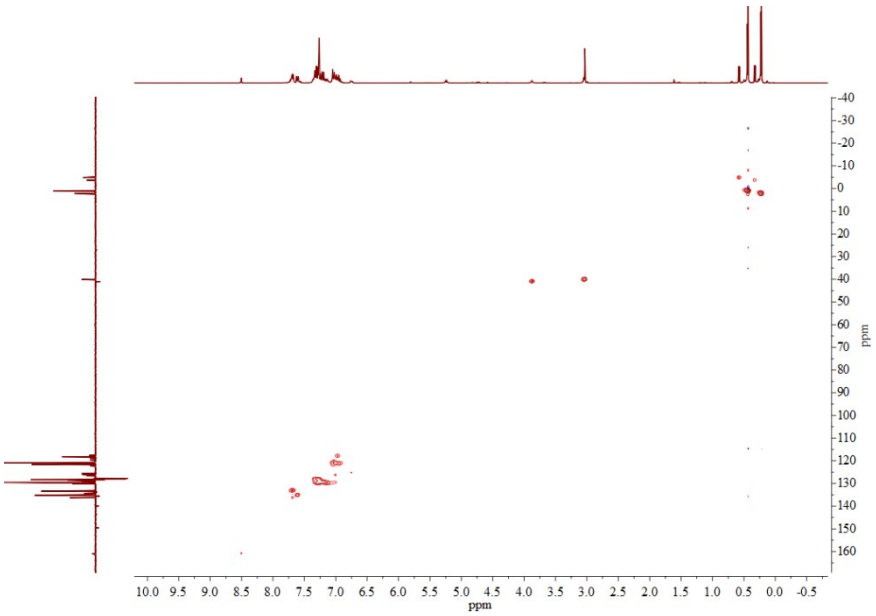


Figure 38. ^{1}H-^{13}C HSQC NMR spectrum from the **3**-catalyzed reaction of *N,N*-diphenylformamide with 2 eq. of $HSiMe_2Ph$

i) $^{i}Pr_2NCH_2OSiMe_2Ph$ (**4e**)

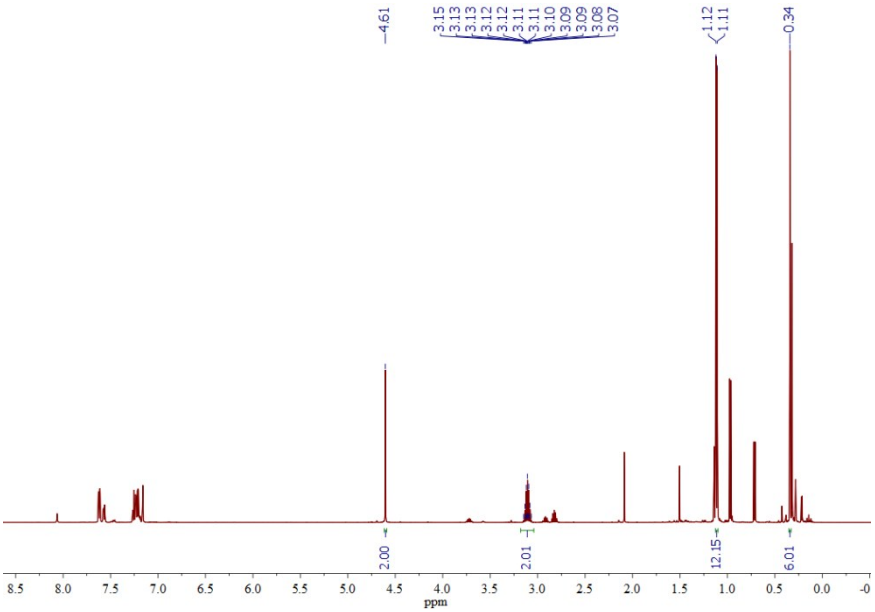


Figure 39. ^{1}H-NMR spectrum from the **2-**catalyzed reaction of *N,N*-diisopropylformamide with 1 eq. of $HSiMe_2Ph$

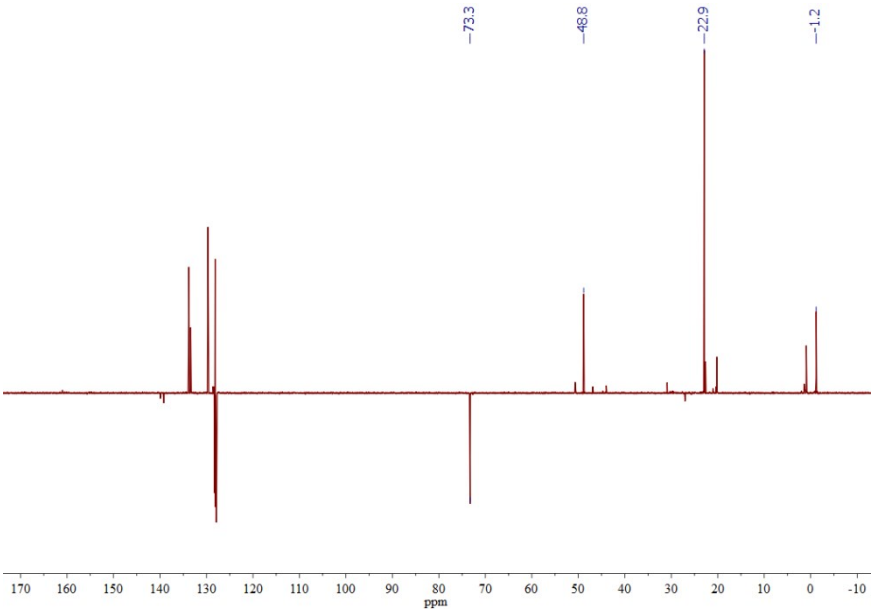


Figure 40. ^{13}C-APT NMR spectrum from the **2-**catalyzed reaction of *N,N*-diisopropylformamide with 1 eq. of $HSiMe_2Ph$

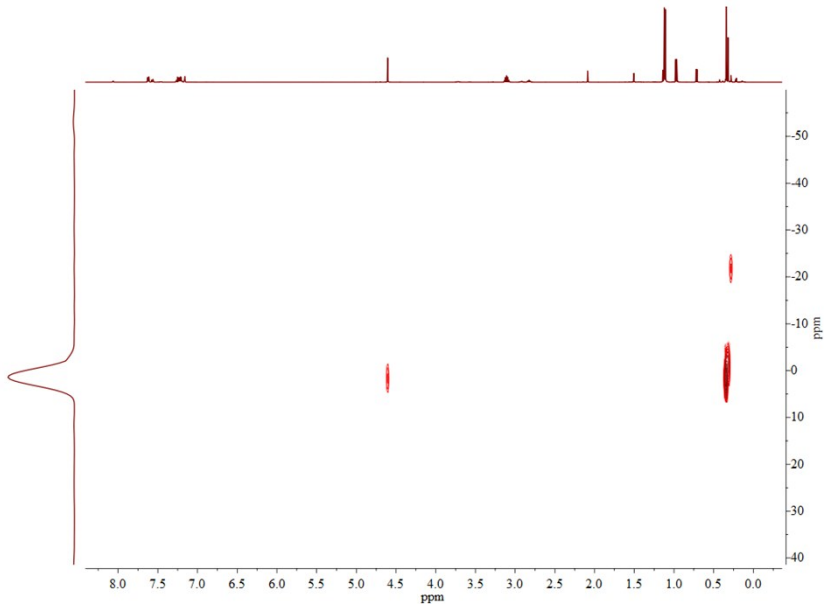


Figure 41. ^{1}H-^{29}Si-HMBC spectrum from the **2**-catalyzed reaction of *N,N*-diisopropylformamide with 1 eq. of $HSiMe_2Ph$

j) $^{i}Pr_2NMe$ (**5e**)

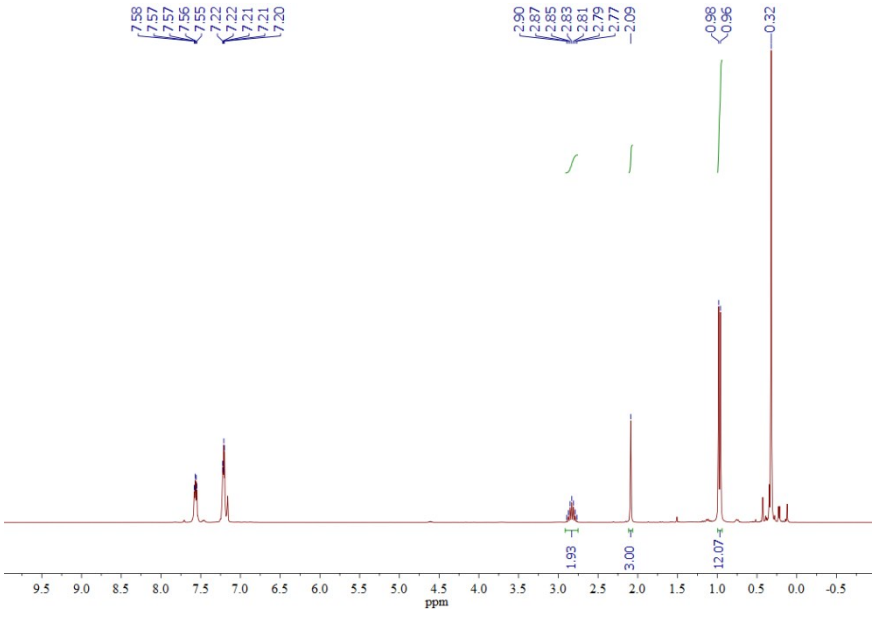


Figure 42. ^{1}H-NMR spectrum from the **3**-catalyzed reaction of *N,N*-diisopropylformamide with 2 eq. of $HSiMe_2Ph$

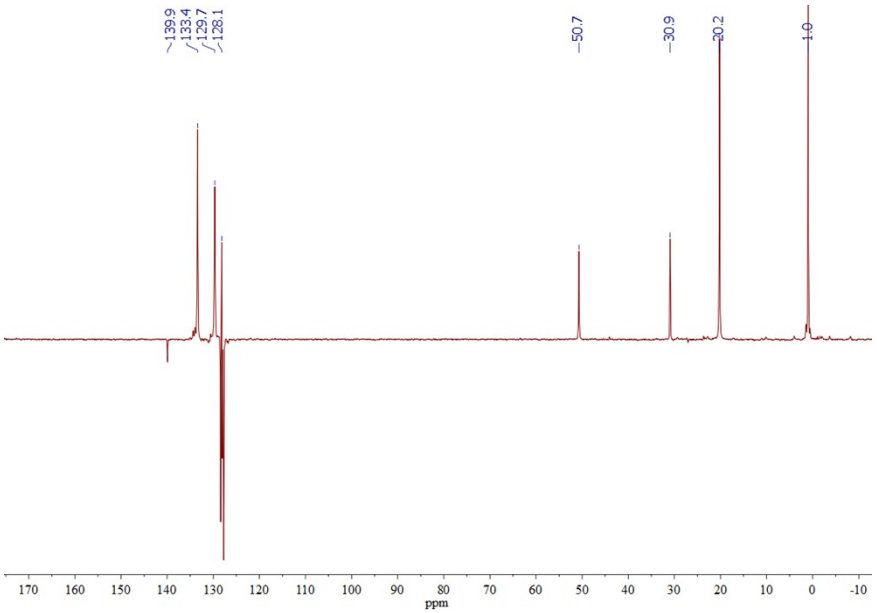


Figure 43. ^{13}C APT NMR spectrum from the **3**-catalyzed reaction of *N,N*-diisopropylformamide with 2 eq. of $HSiMe_2Ph$

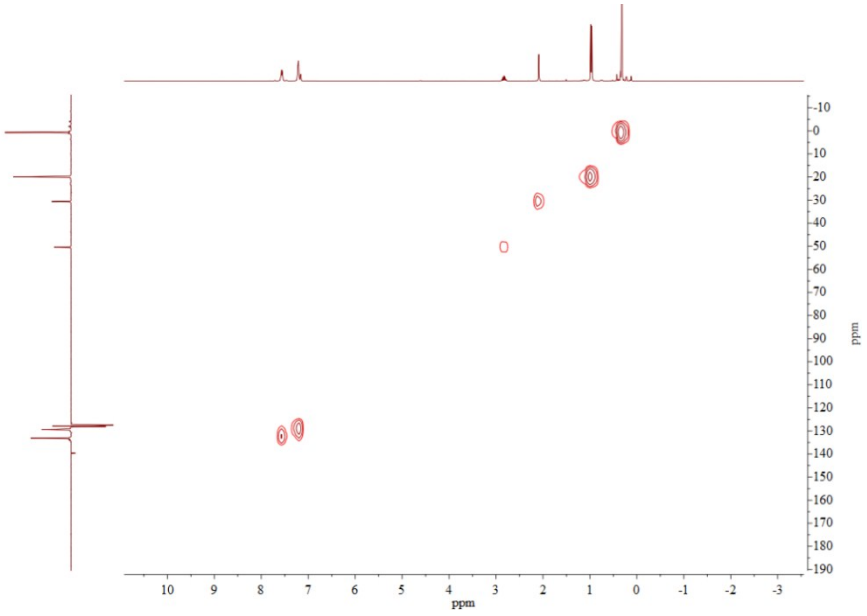


Figure 44. ^{1}H-^{13}C HSQC NMR spectrum from the **3**-catalyzed reaction of *N,N*-diisopropylformamide with 2 eq. of $HSiMe_2Ph$

5. NMR studies of the **2** or **3**-catalyzed reactions (5 mol%) of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$ at RT

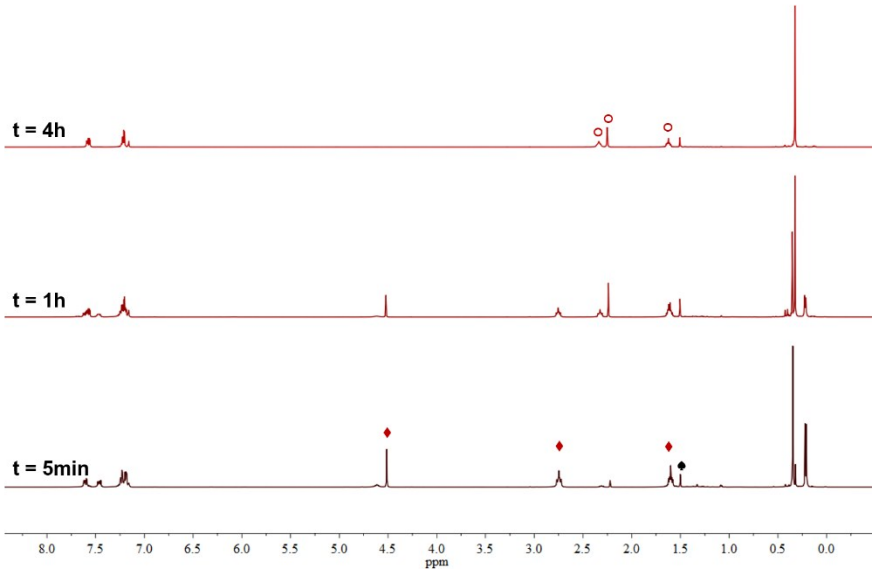


Figure 45. ^{1}H-NMR spectra of the **2**-catalyzed reaction (5 mol%) of N-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$ at RT. (♦, **4a**; ○: **5a**; ♠: cyclooctane)

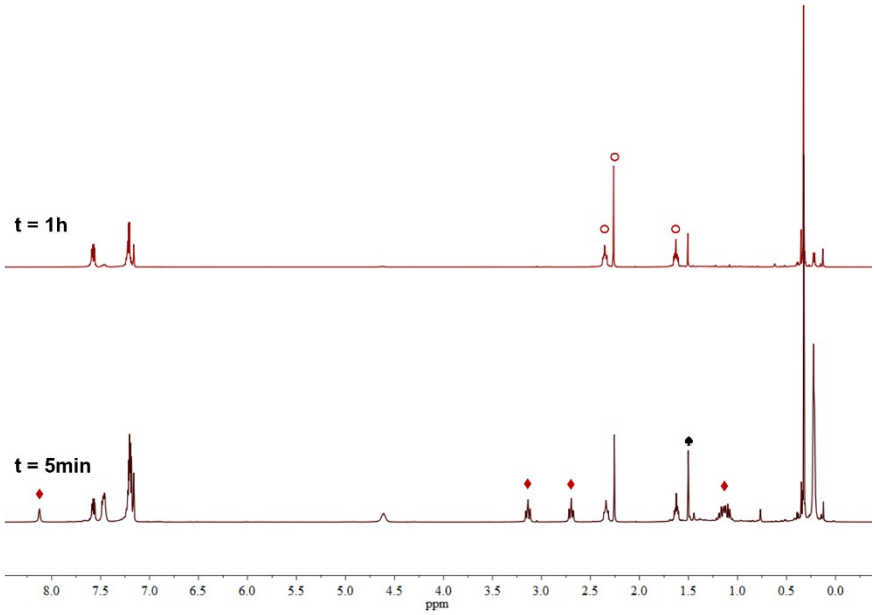


Figure 46. ^{1}H-NMR spectra of the **3**-catalyzed reaction (5 mol%) of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$ at RT. (♦, *N*-formylpyrrolidine; ○: **5a**; ♠: cyclooctane)

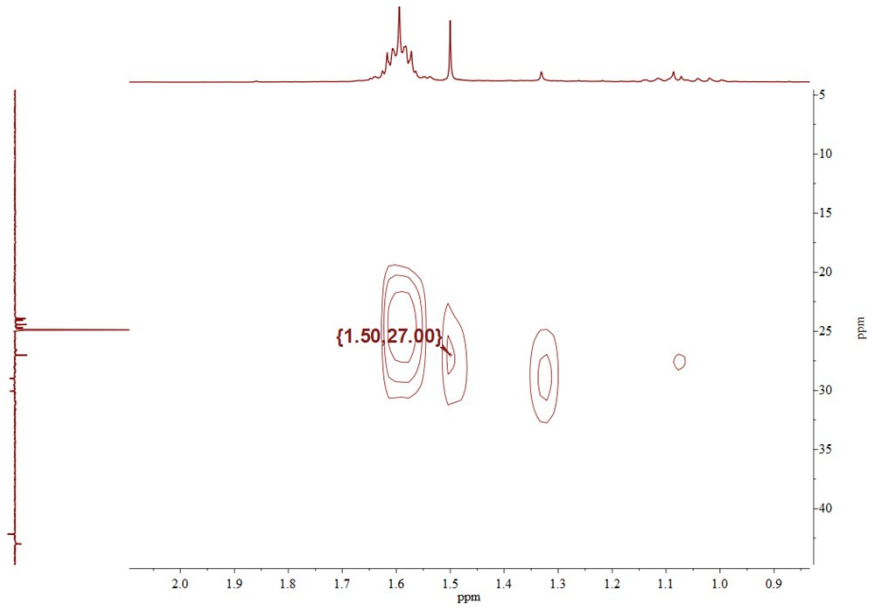


Figure 47. ^{1}H-^{13}C HSQC NMR spectrum showing the formation of cyclooctane

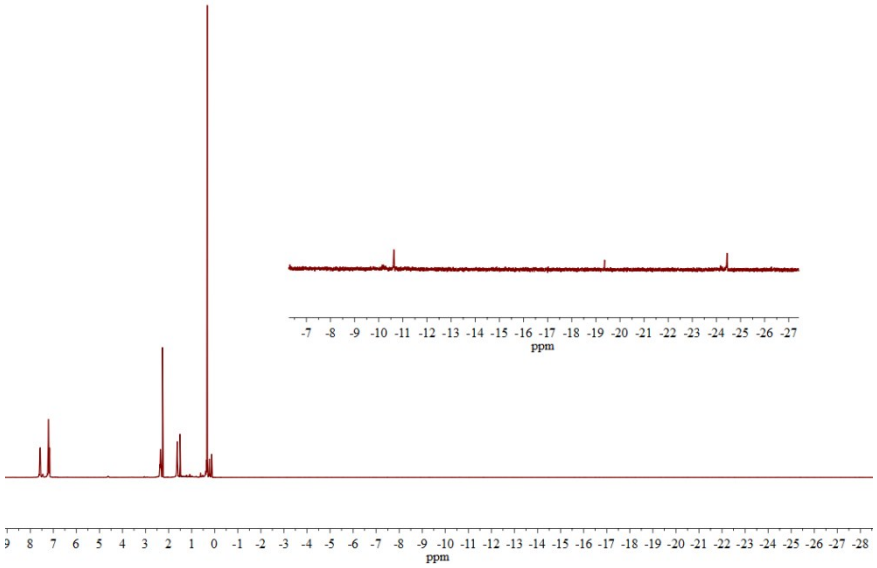


Figure 48. ^{1}H-NMR spectrum from reaction (5 mol%) of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$ showing the formation of unidentified [Ir]-Hydride species

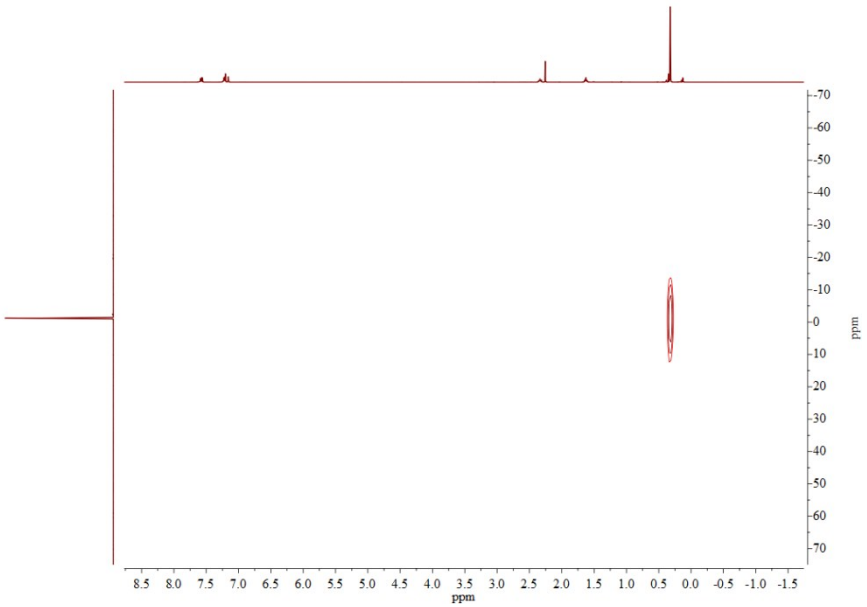


Figure 49. ^{1}H-^{29}Si-HMBC spectrum showing the formation of the siloxane $O(SiMe_2Ph)_2$

6. NMR monitoring of the **2** or **3**-catalyzed reactions (0.5 mol%) of *N*-formylpyrrolidine with $HSiMe_2Ph$ at RT

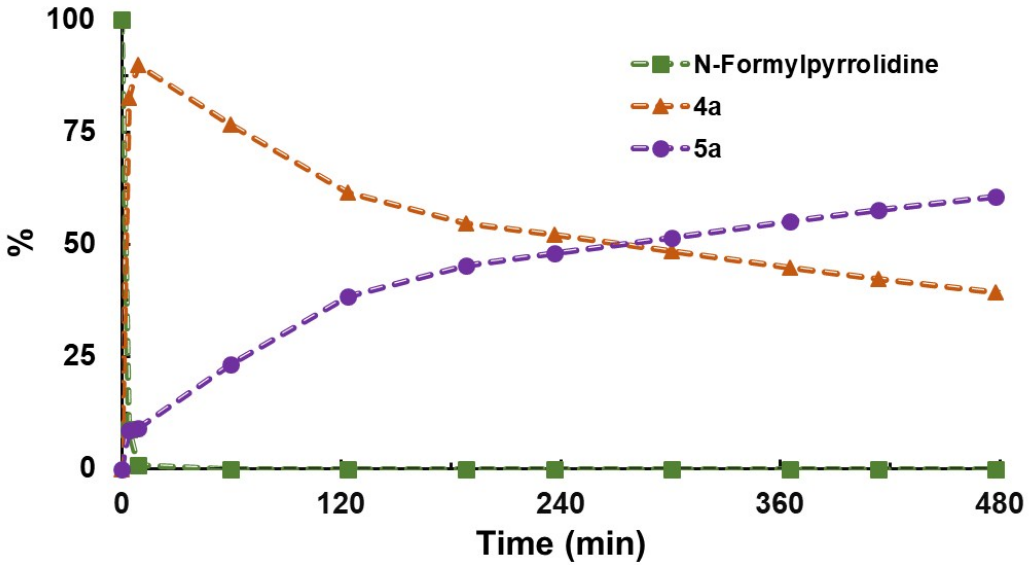


Figure 50. Reaction profile of the **2**-catalyzed reaction of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$. The discontinuous lines only represent a connection between the data points.

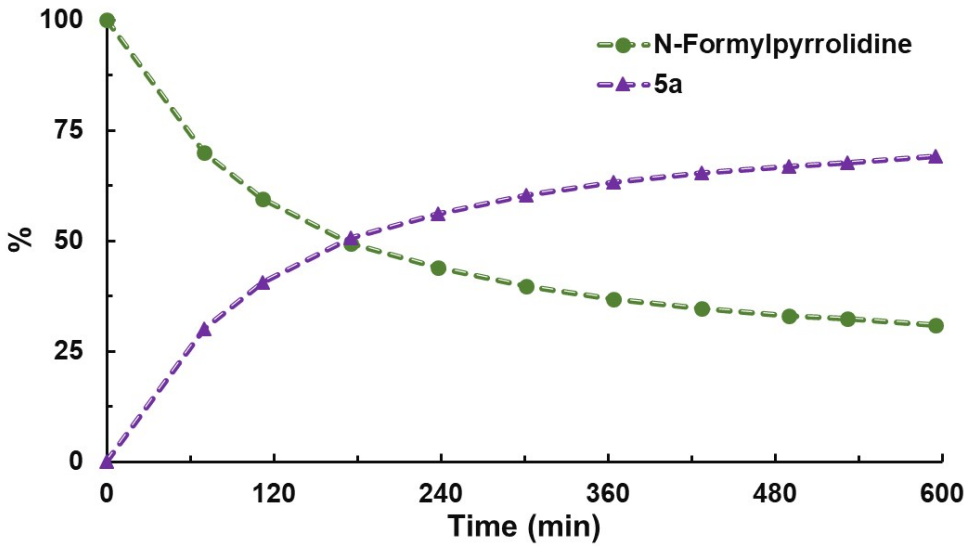


Figure 51. Reaction profile of the **3**-catalyzed reaction of *N*-formylpyrrolidine with 2 eq. of $HSiMe_2Ph$ (**4a** was not observed). The discontinuous lines only represent a connection between the data points.

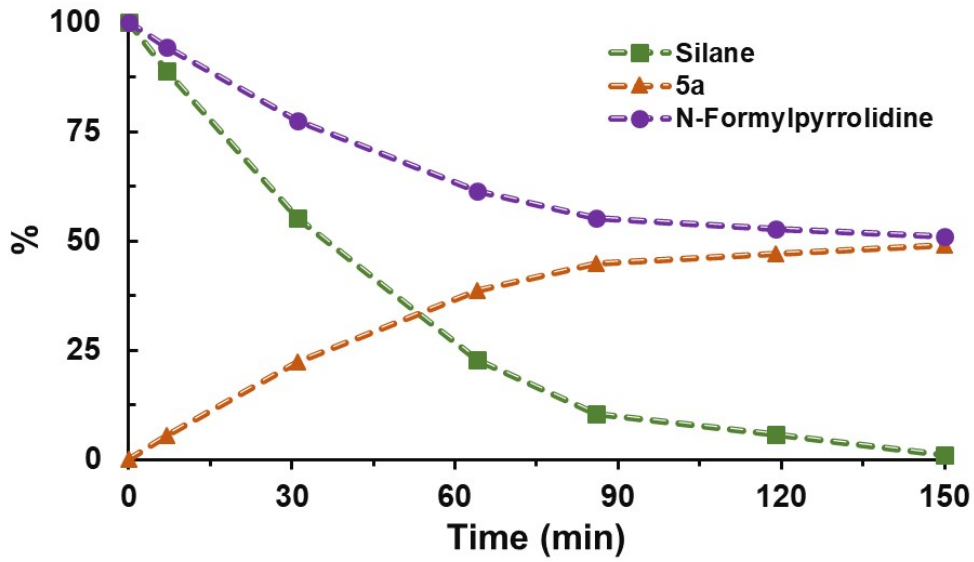


Figure 52. Reaction profile of the **3**-catalyzed reaction of N-formylpyrrolidine with 1 eq. of $HSiMe_2Ph$ (**4a** was not observed). The discontinuous lines only represent a connection between the data points.

7. NMR monitoring of the **2**-catalyzed reactions (0.5 mol%) of *N*-formylpyrrolidine with $HSiMe_2Ph$ at 323 K

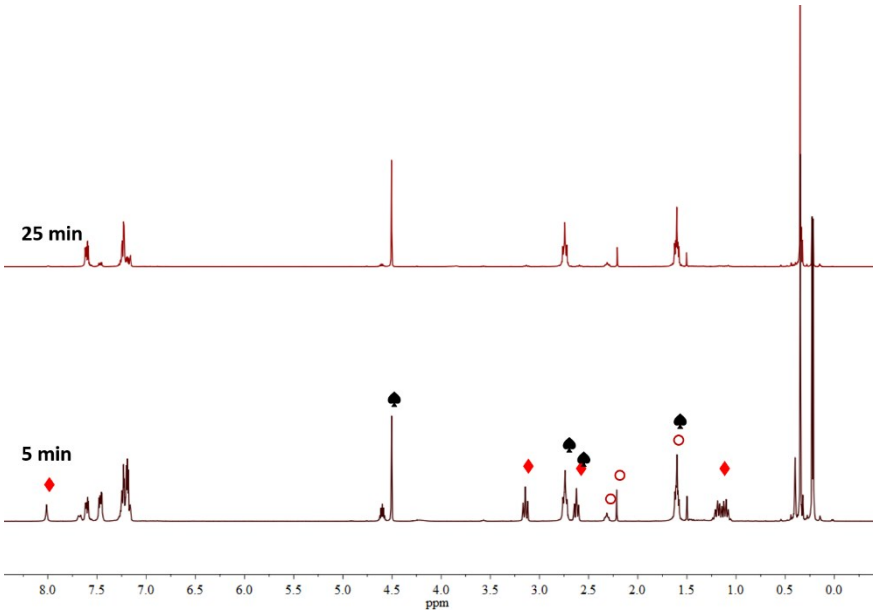


Figure 53. ^{1}H-NMR spectra of the **2**-catalyzed reaction (0.5 mol%) of *N*-formylpyrrolidine with 1 eq. of $HSiMe_2Ph$ at 323 K. (♦, *N*-formylpyrrolidine; ♠: **4a**; ○: **5a**)

8. NMR studies

a) 2-catalyzed reaction of amides and 1 eq. of $HSiMe_2Ph$

I. *N*-Formylpyrrolidine

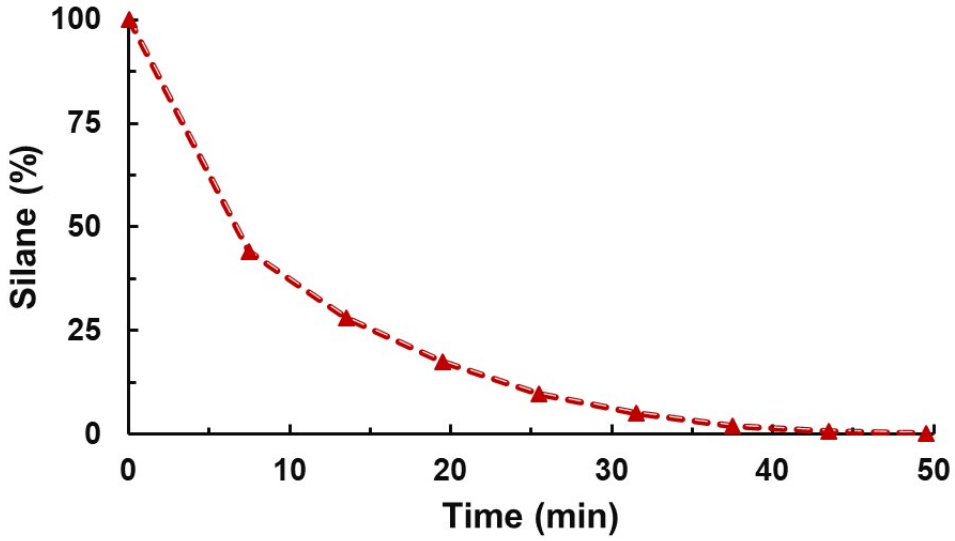


Figure 54. Silane consumption in the formation of **4a** The discontinuous lines only represent a connection between the data points.

II. DMF

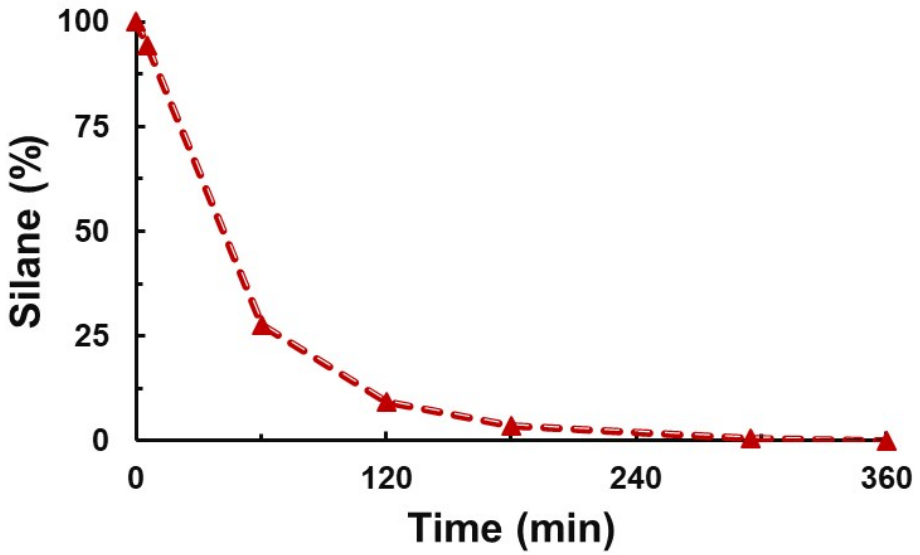


Figure 55. Silane consumption in the formation of **4b**. The discontinuous lines only represent a connection between the data points.

III. *N*-Methyl-*N*-phenylformamide

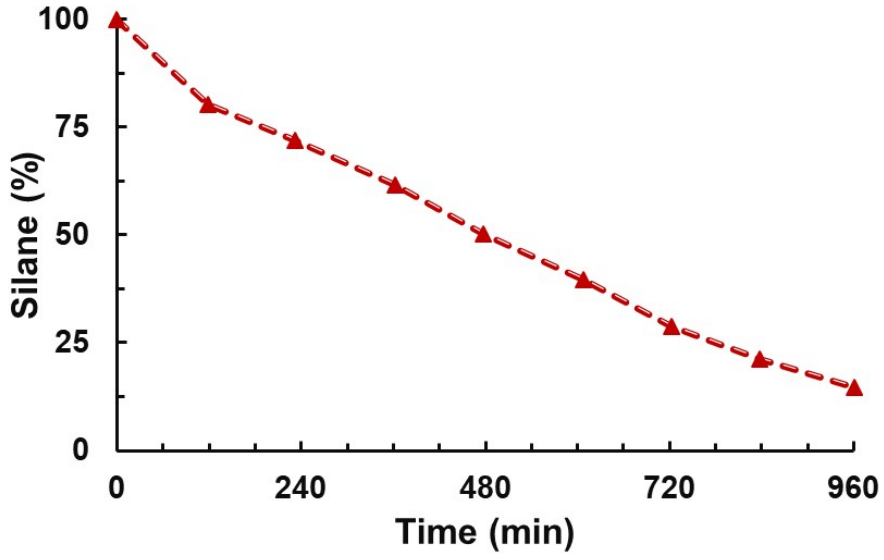


Figure 56. Silane consumption in the formation of **4c.** The discontinuous lines only represent a connection between the data points.

IV. *N*,*N*-diphenylformamide

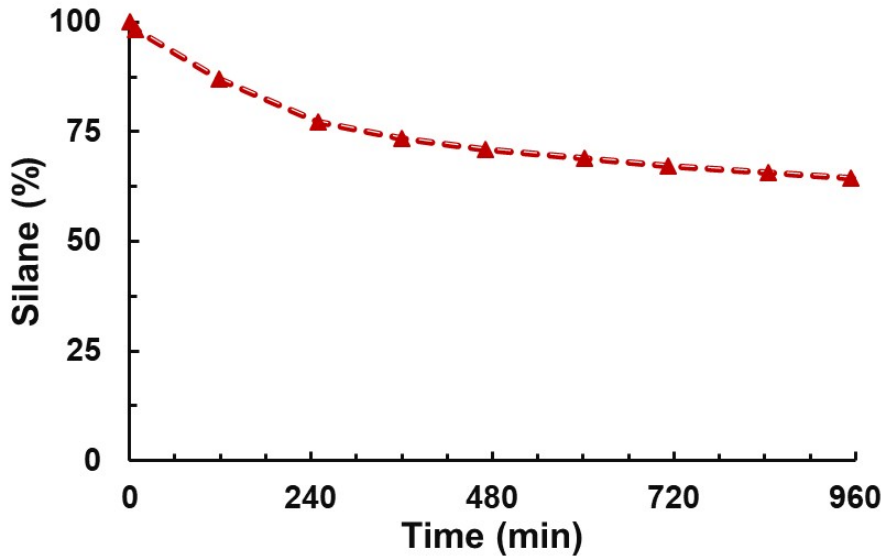


Figure 57. . Silane consumption in the formation of **4d.** The discontinuous lines only represent a connection between the data points.

V. Diisopropylformamide

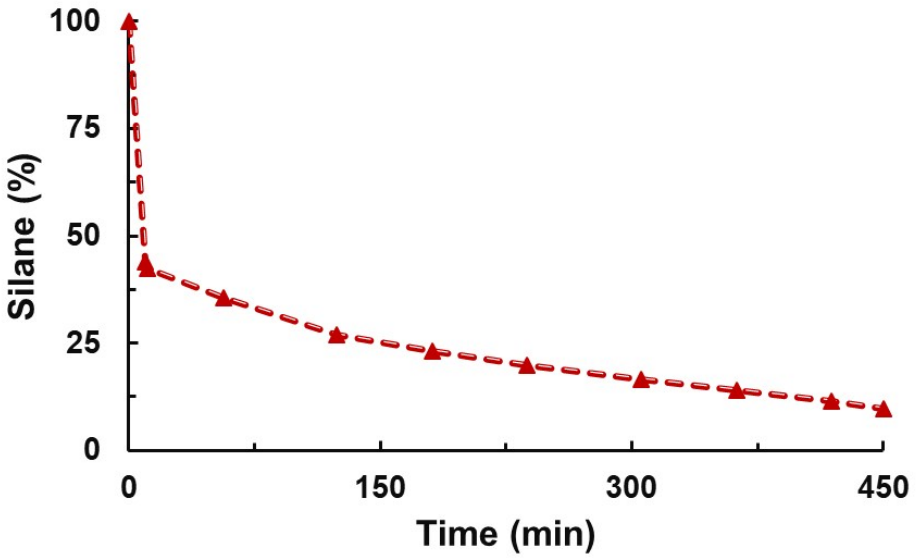


Figure 58. Silane consumption in the formation of **4e.** The discontinuous lines only represent a connection between the data points.

b) 3-catalyzed reaction of amides and 2 eq. of $HSiMe_2Ph$

I. *N*-Formylpyrrolidine

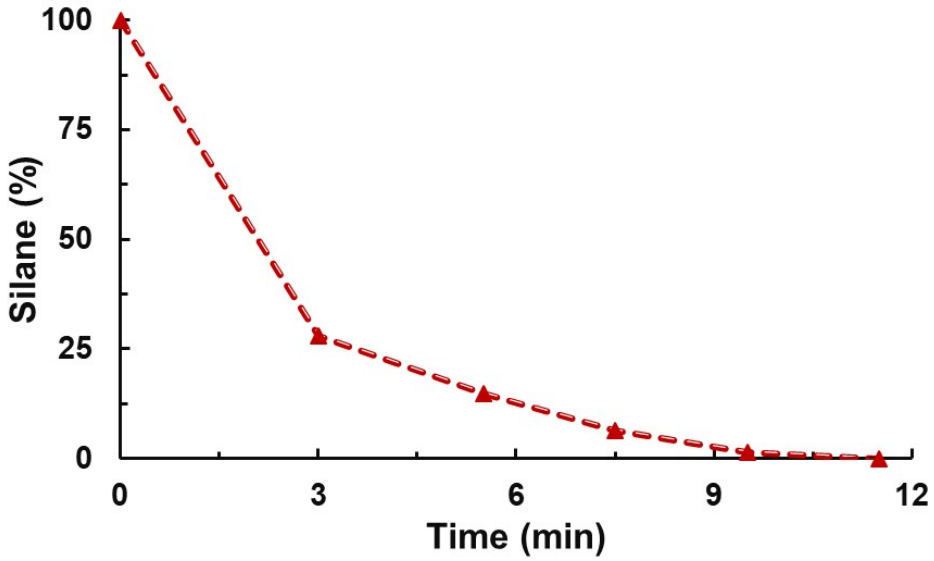


Figure 59. Silane consumption in the formation of **5a**. The discontinuous lines only represent a connection between the data points.

II. DMF

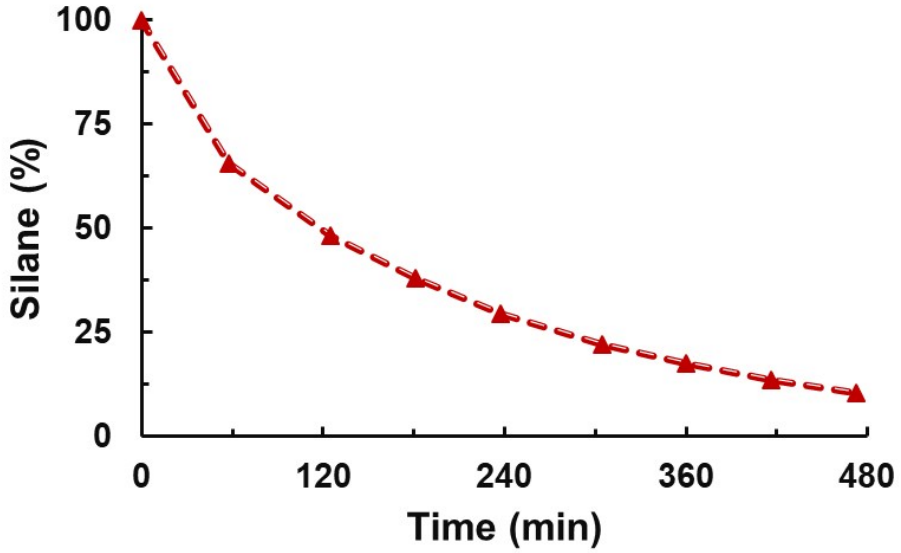


Figure 60. Silane consumption in the formation of **5b.** The discontinuous lines only represent a connection between the data points.

III. *N*-Methyl-*N*-phenylformamide

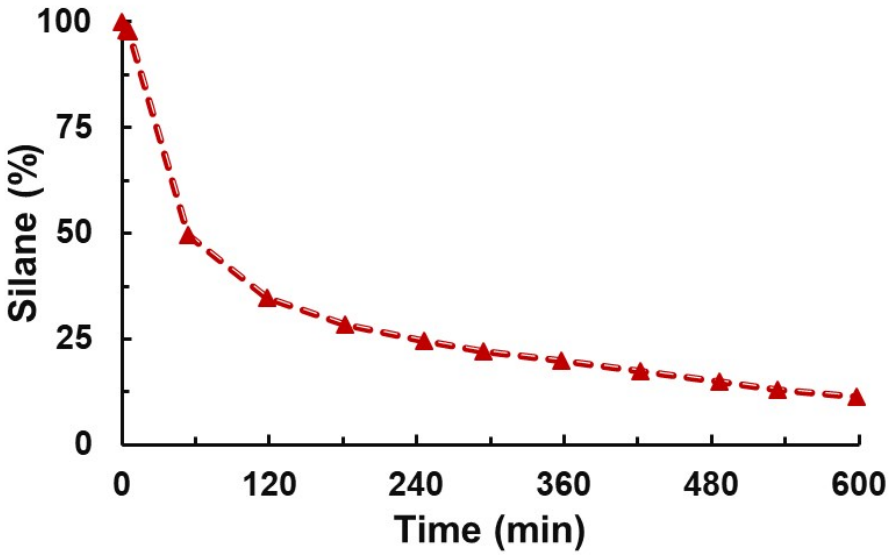


Figure 61. Silane consumption in the formation of **5c.** The discontinuous lines only represent a connection between the data points.

IV. *N,N*-Diphenylformamide

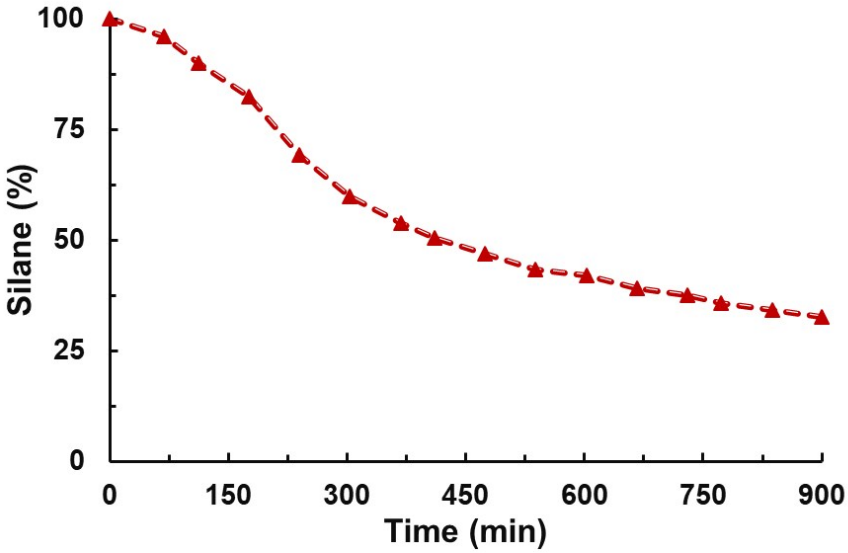


Figure 62. Silane consumption in the formation of **5d.** The discontinuous lines only represent a connection between the data points.

V. Diisopropylformamide

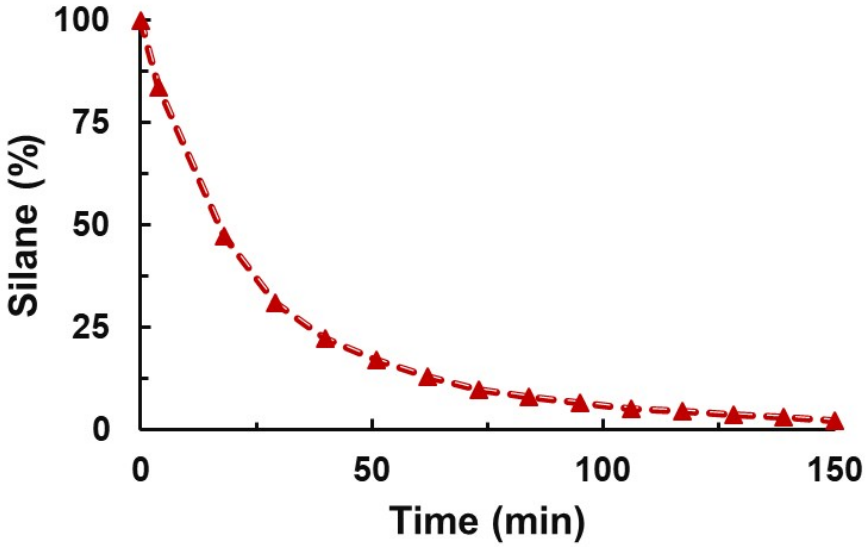


Figure 63. Silane consumption in the formation of **5e.** The discontinuous lines only represent a connection between the data points.