Supporting Information

Reactivity of a NHC-Stabilized Silylene towards Ketones. Formation of Silicon Bis-enolates vs. Bis-silylation of C=O Bond

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^{1}H NMR and ^{13}C NMR Spectra of Products 2a-o and 3

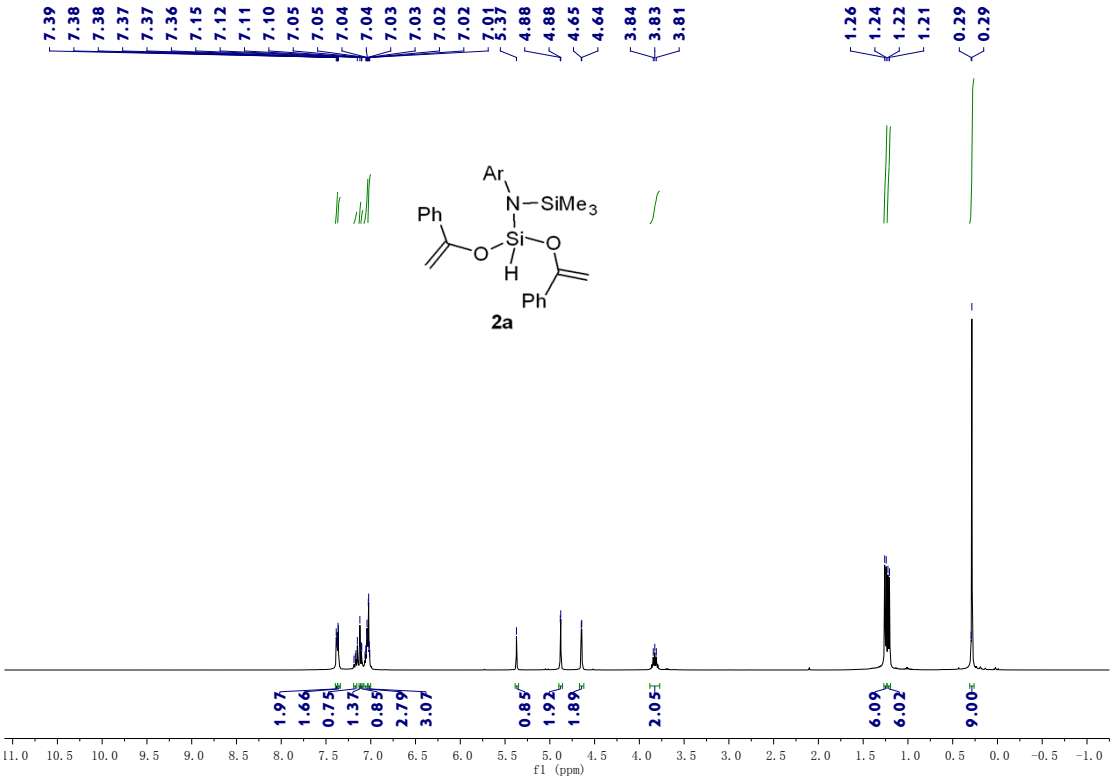


Figure 1. ^{1}H NMR spectra of 2a.

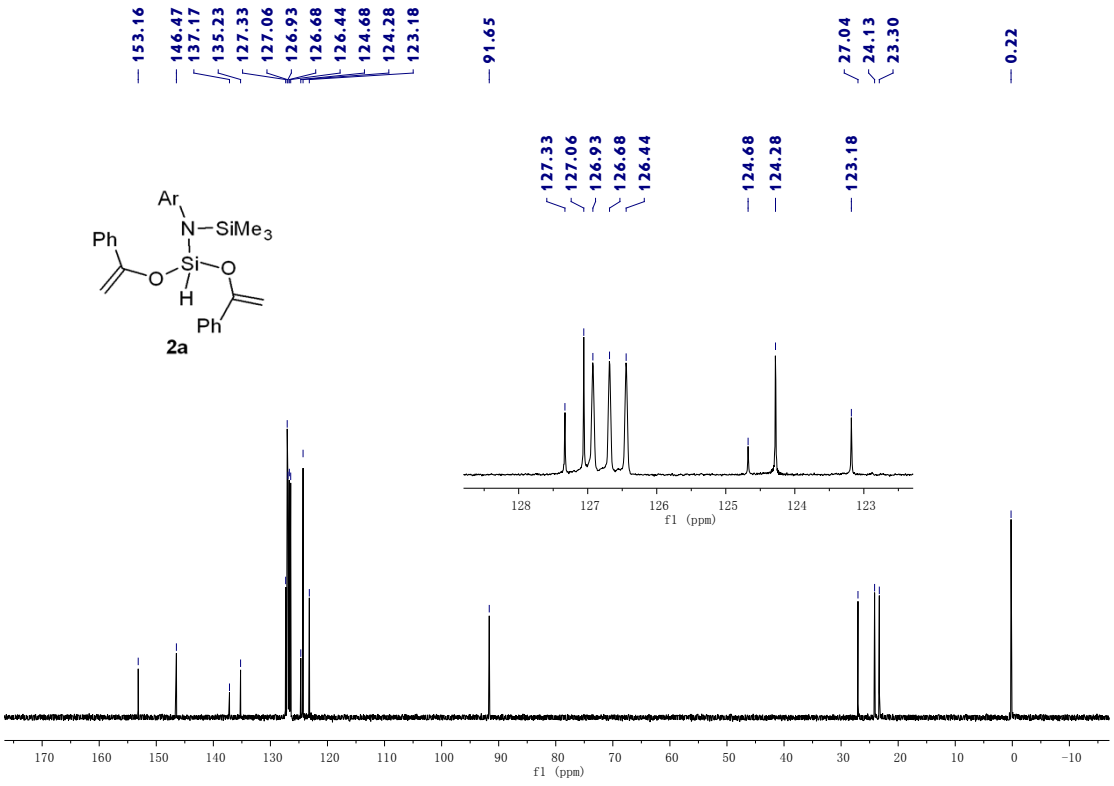


Figure 2. ^{13}C NMR spectra of 2a.

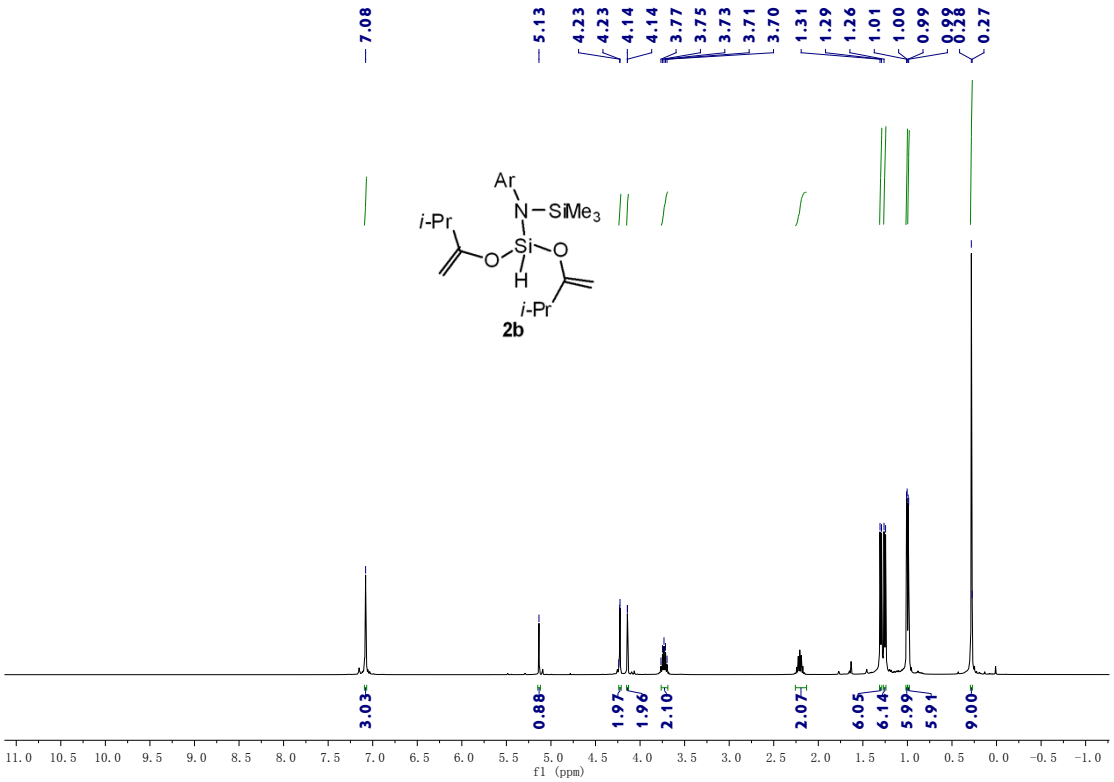


Figure 3. ^{1}H NMR spectra of 2b.

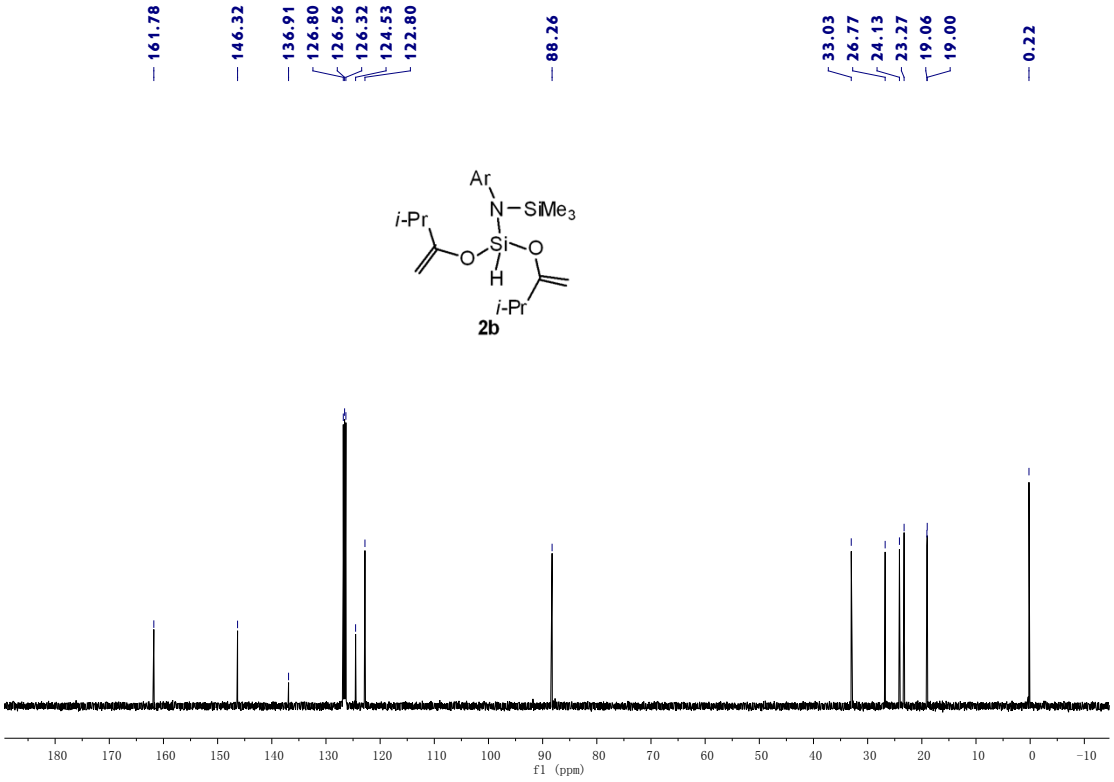


Figure 4. ^{13}C NMR spectra of 2b.

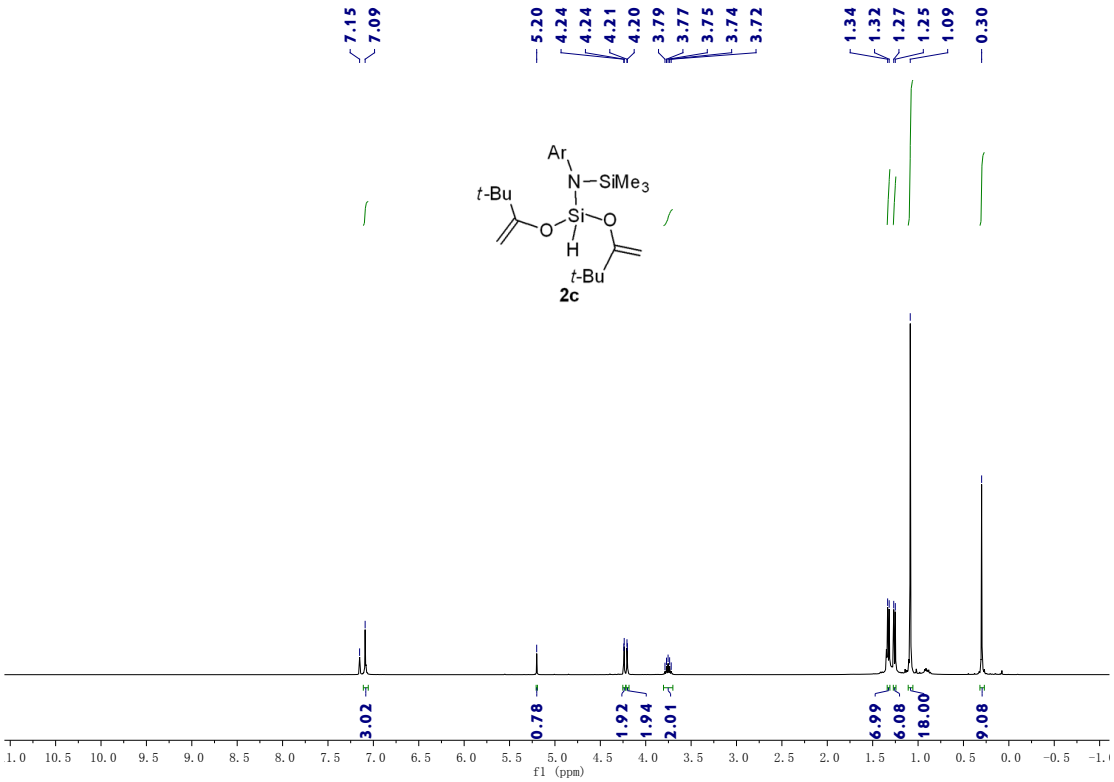


Figure 5. ^{1}H NMR spectra of 2c.

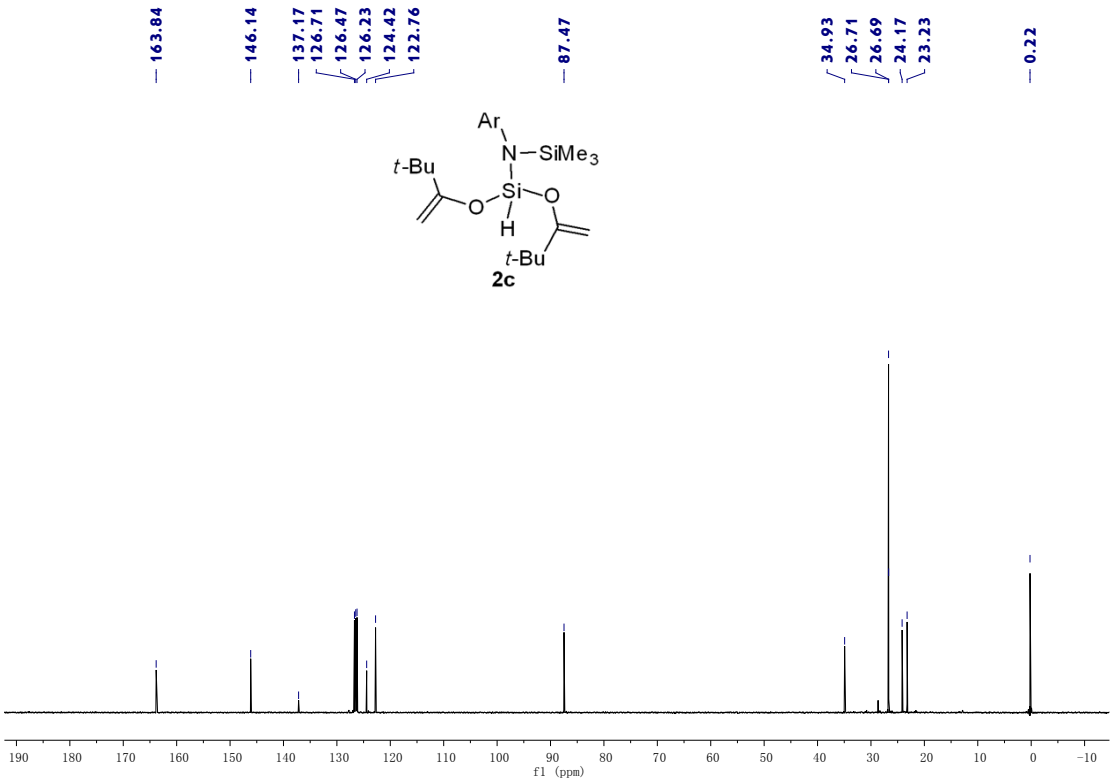


Figure 6. ^{13}C NMR spectra of 2c.

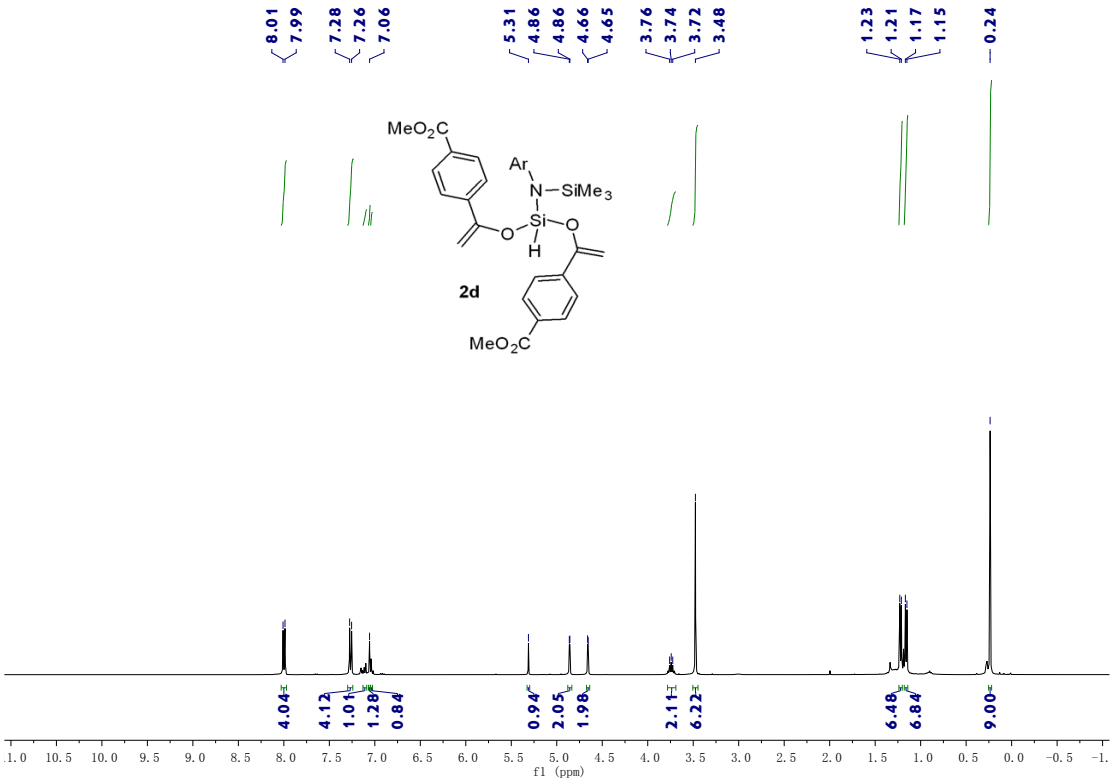


Figure 7. ^{1}H NMR spectra of 2d.

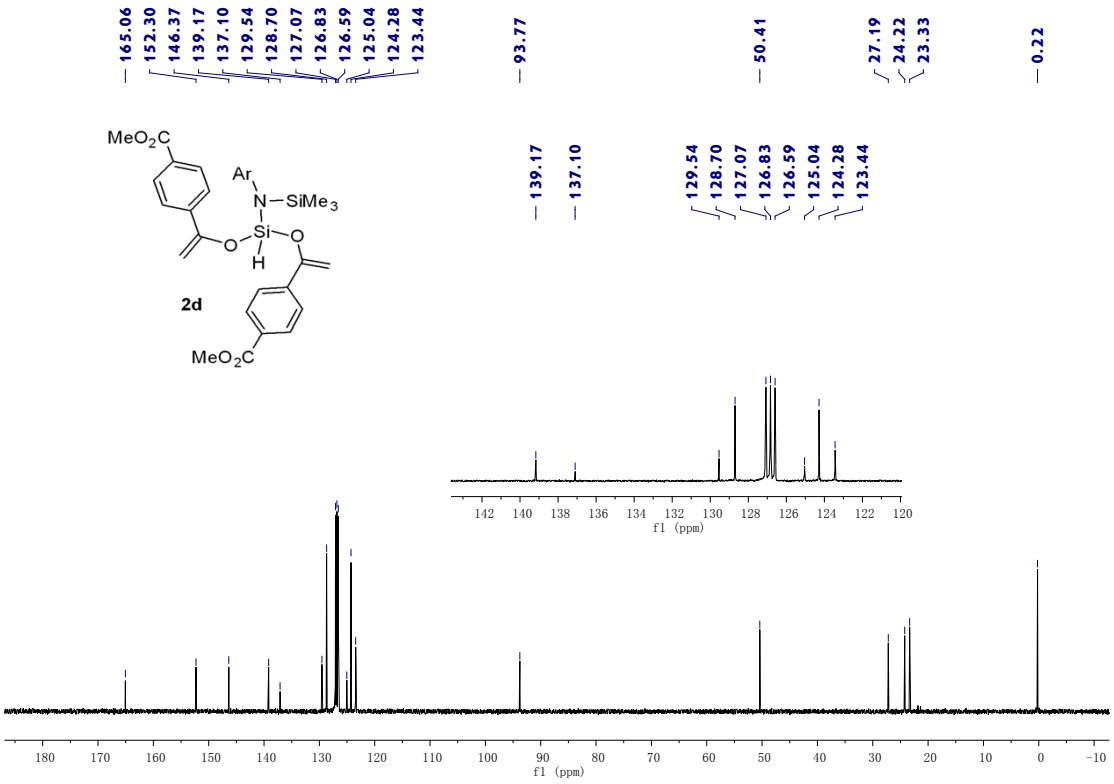


Figure 8. ^{13}C NMR spectra of 2d.

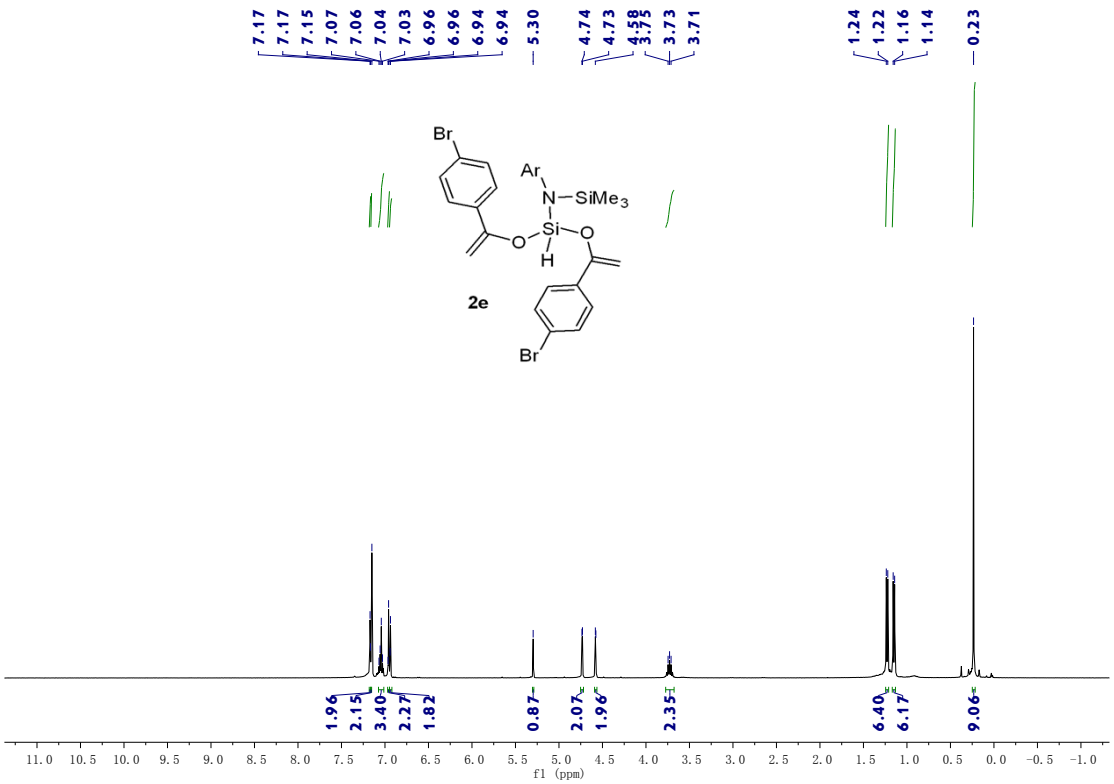


Figure 9. ^{1}H NMR spectra of 2e.

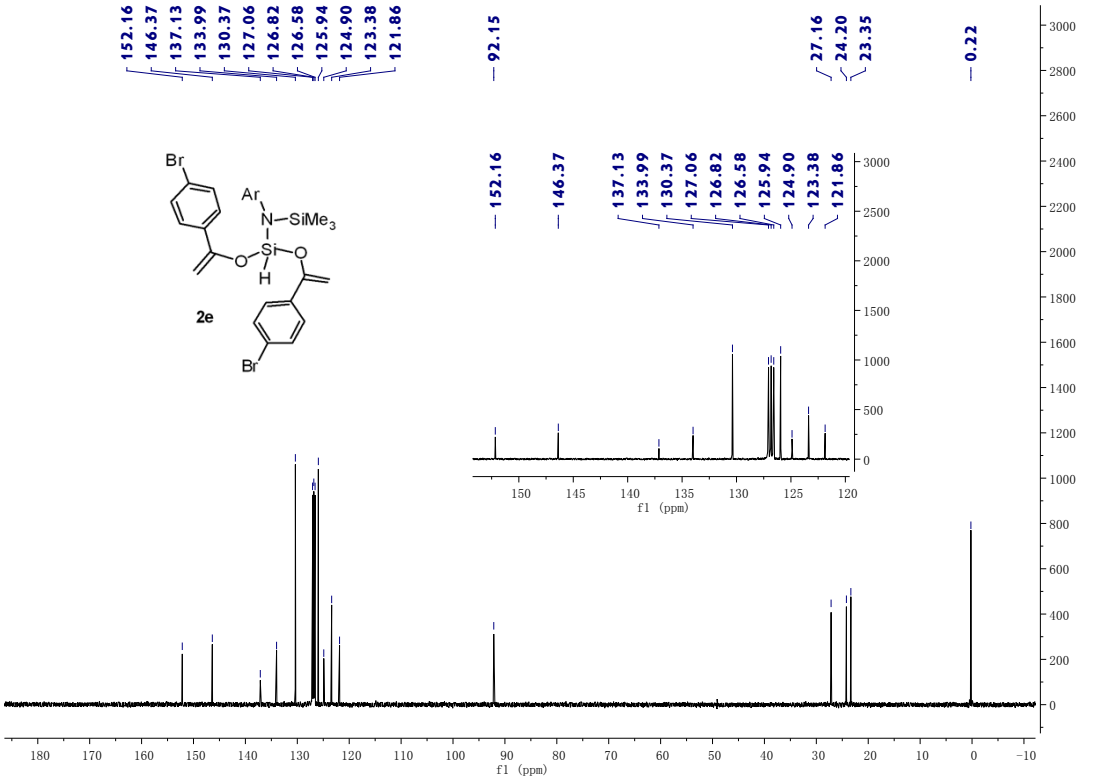


Figure 10. ^{13}C NMR spectra of 2e.

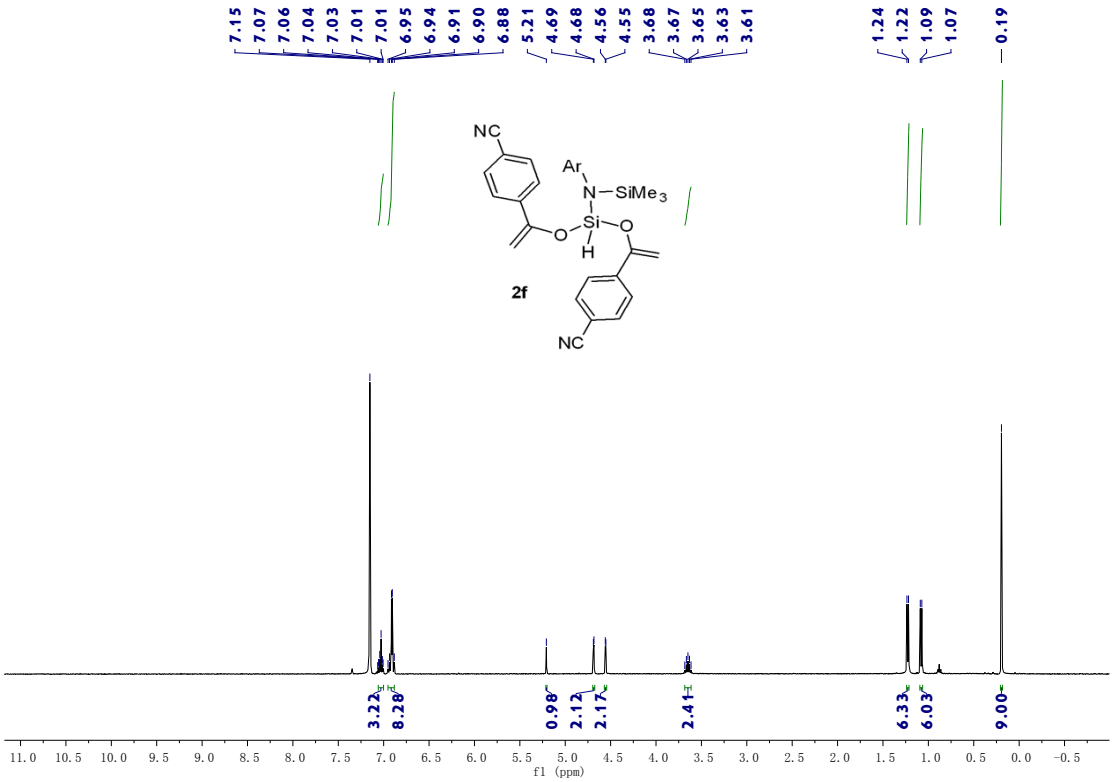


Figure 11. ^{1}H NMR spectra of 2f.

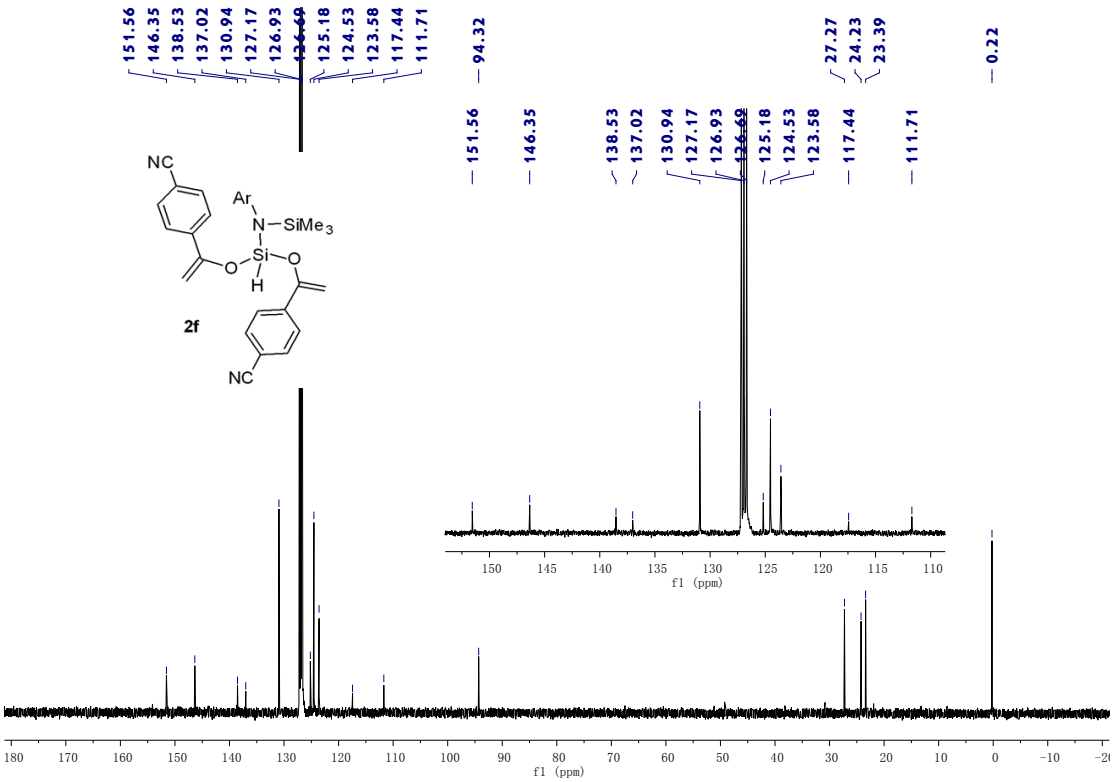


Figure 12. ^{13}C NMR spectra of 2f.

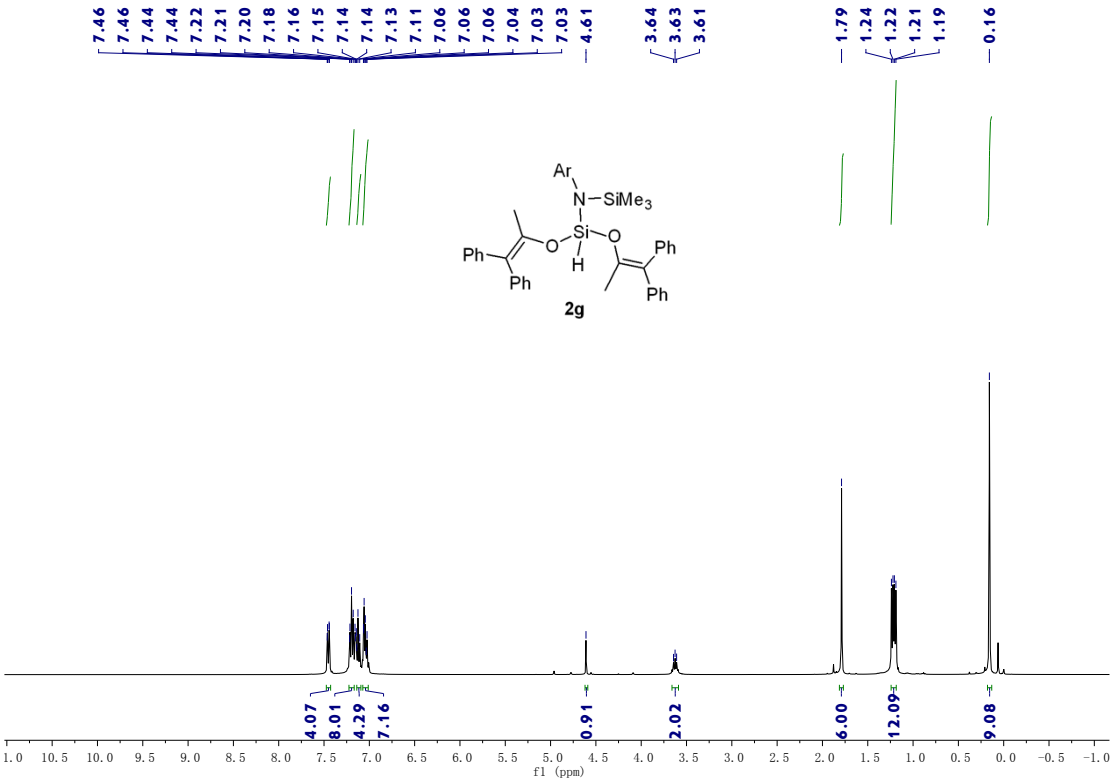


Figure 13. ^{1}H NMR spectra of 2g.

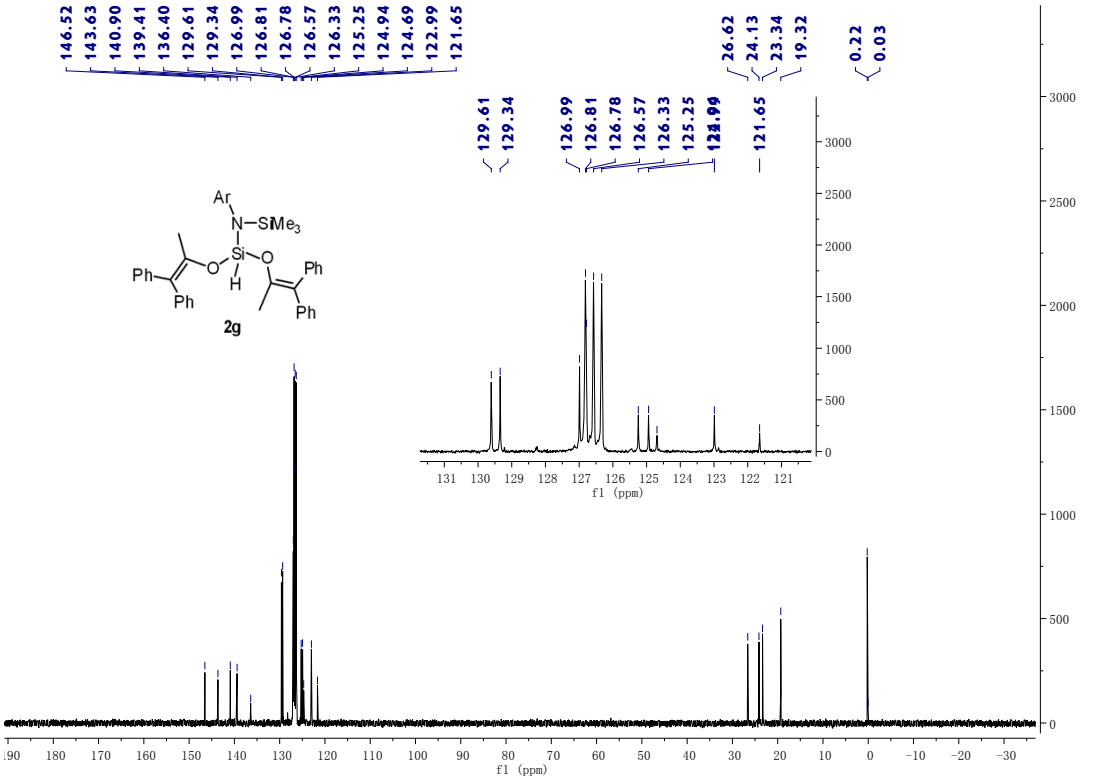


Figure 14. ^{13}C NMR spectra of 2g.

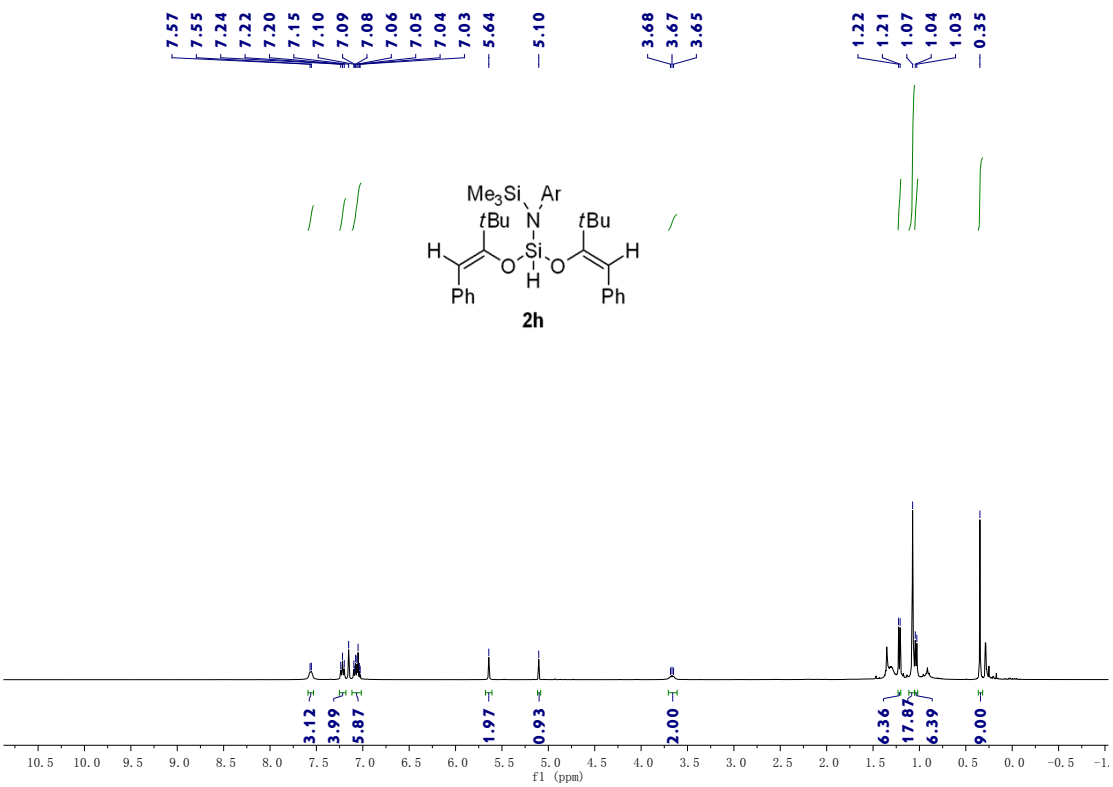


Figure 15. ^{1}H NMR spectra of 2h.

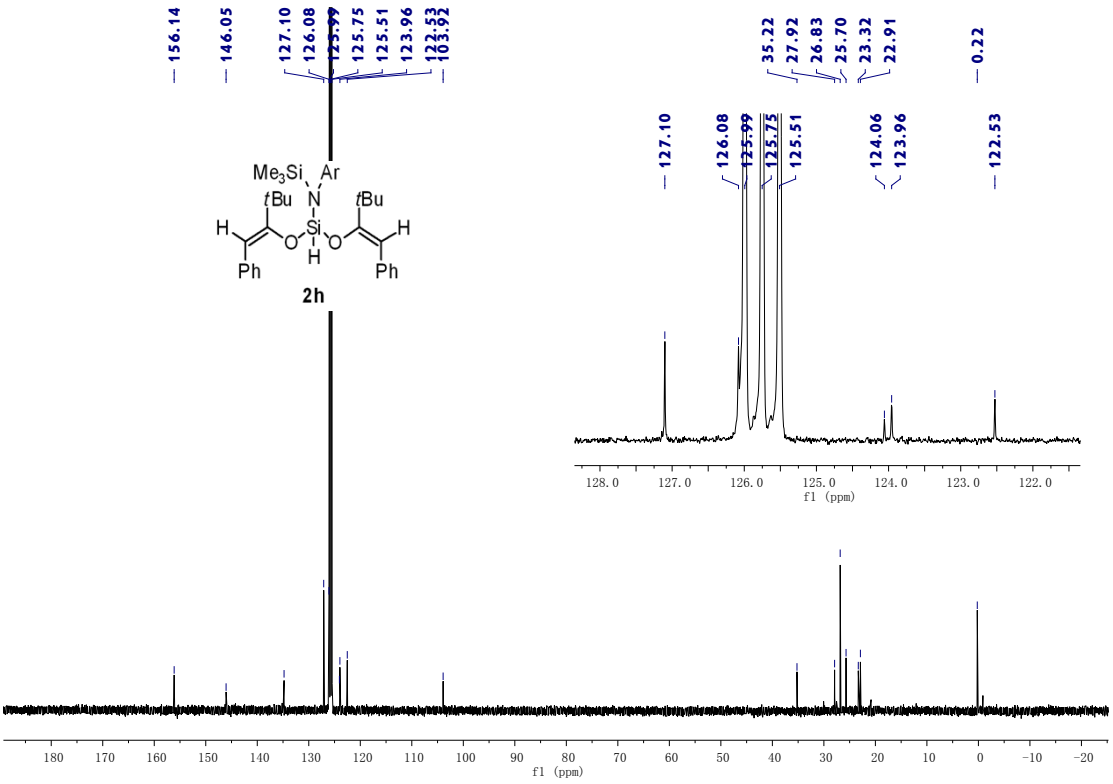


Figure 16. ^{13}C NMR spectra of 2h.

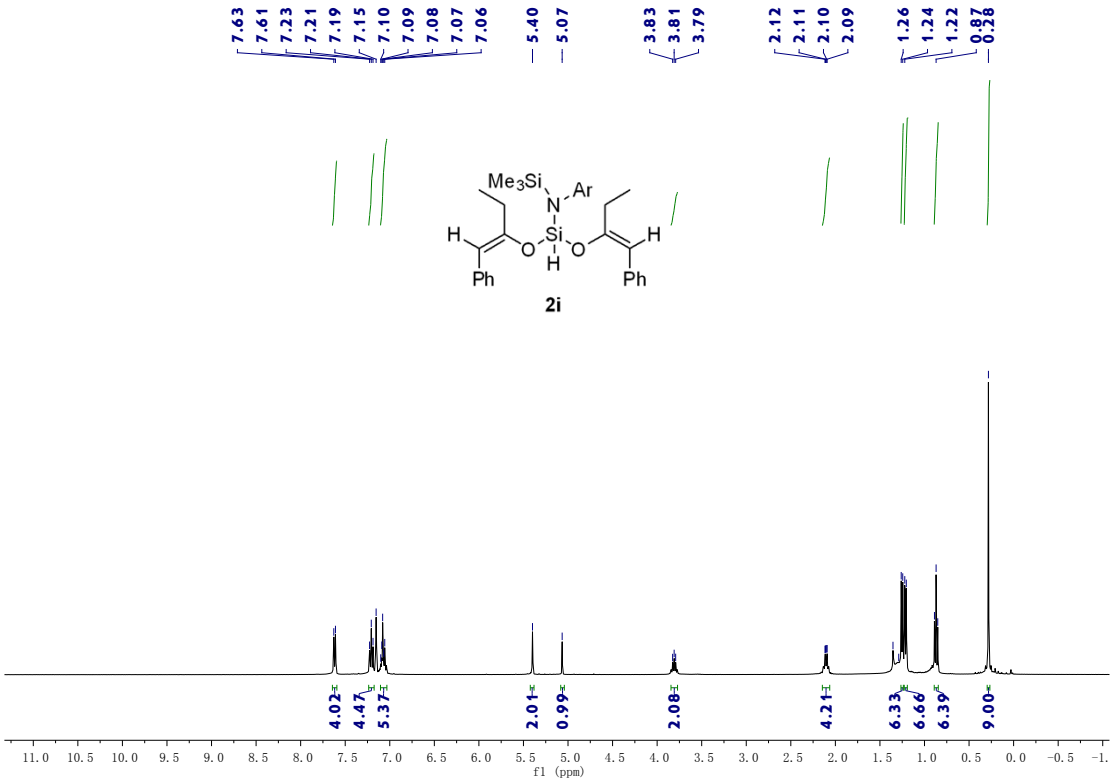


Figure 17. ^{1}H NMR spectra of 2i.

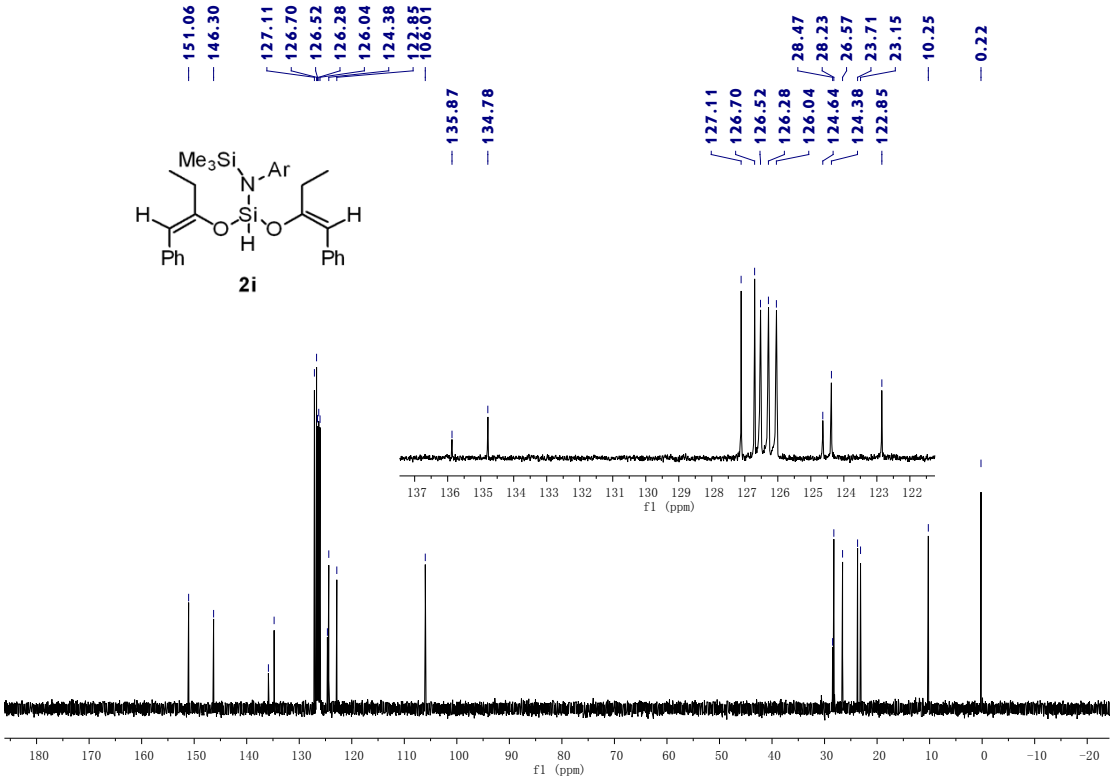


Figure 18. ^{13}C NMR spectra of 2i.

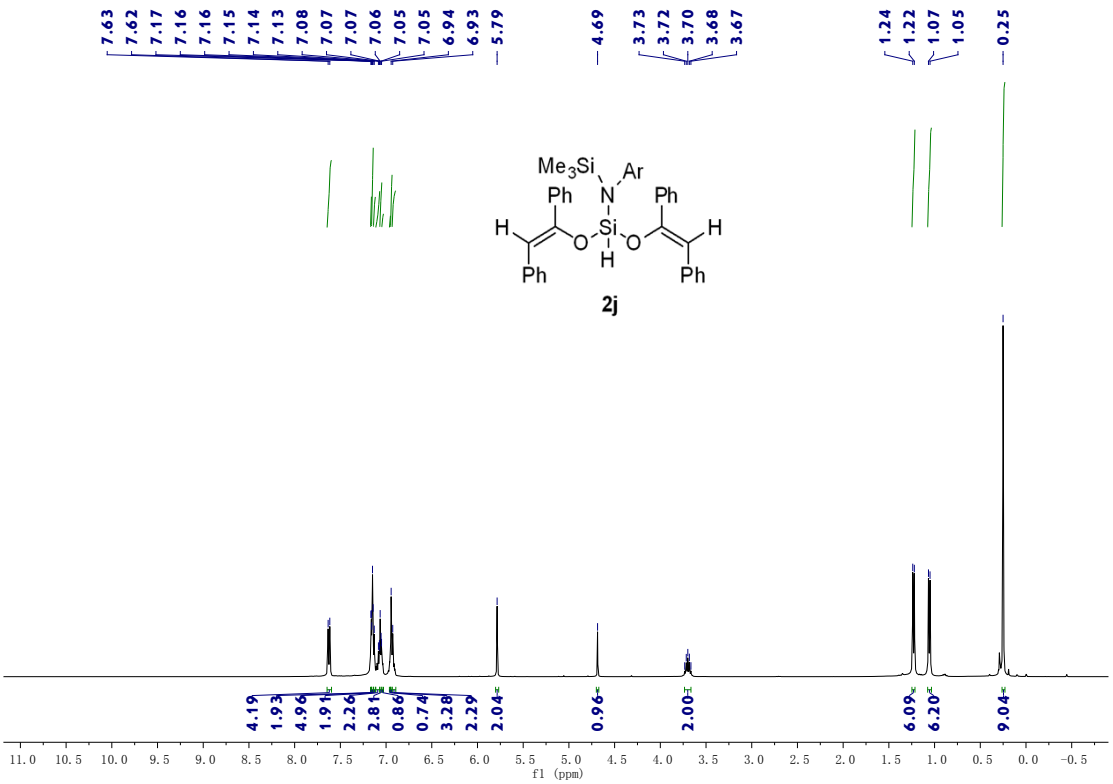
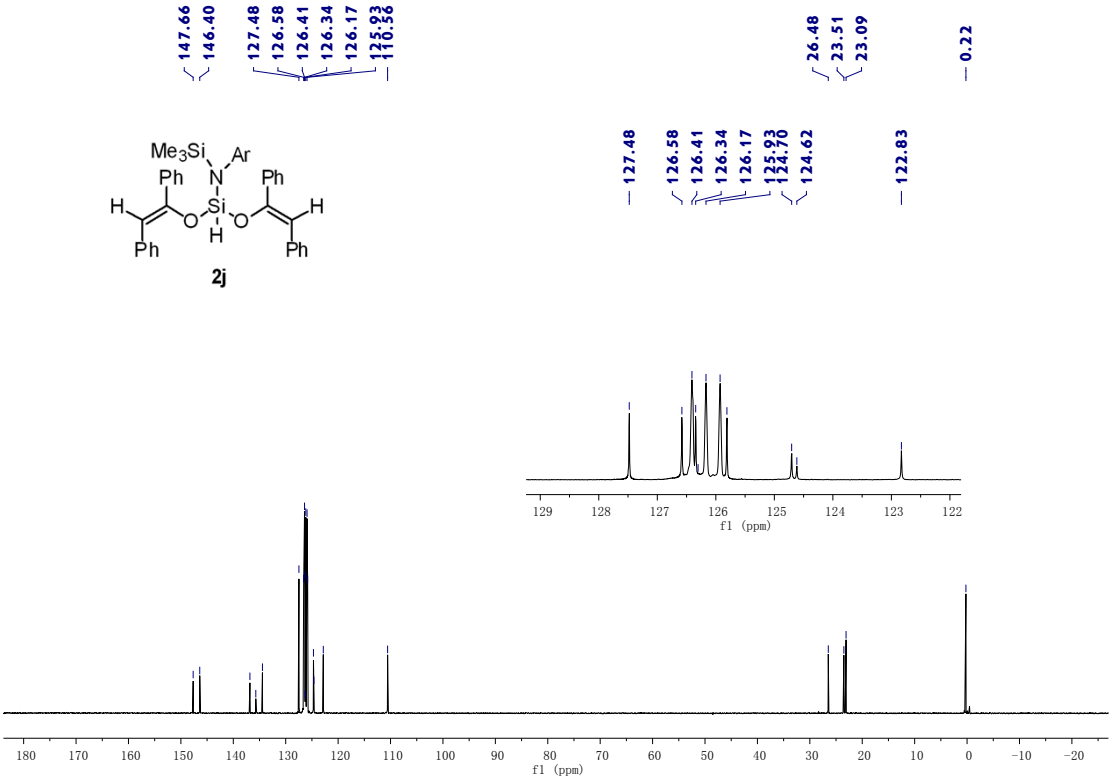


Figure 19. ^{1}H NMR spectra of 2j.



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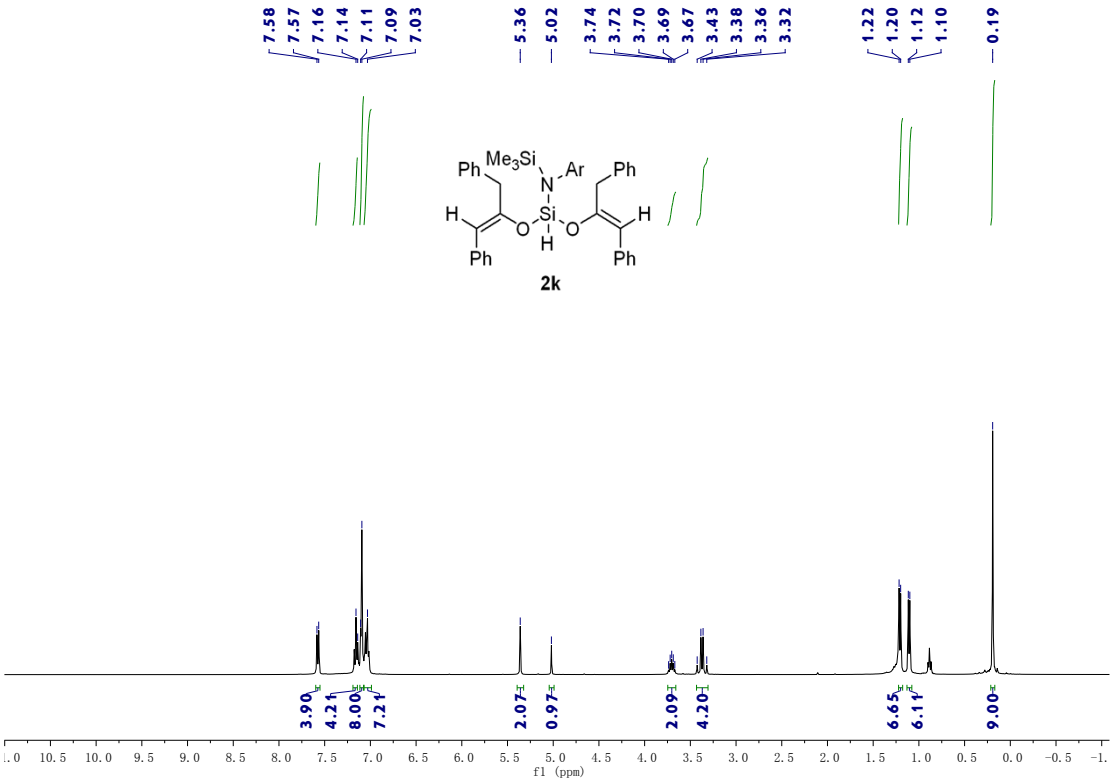

Figure 21. ^{1}H NMR spectra of 2k.

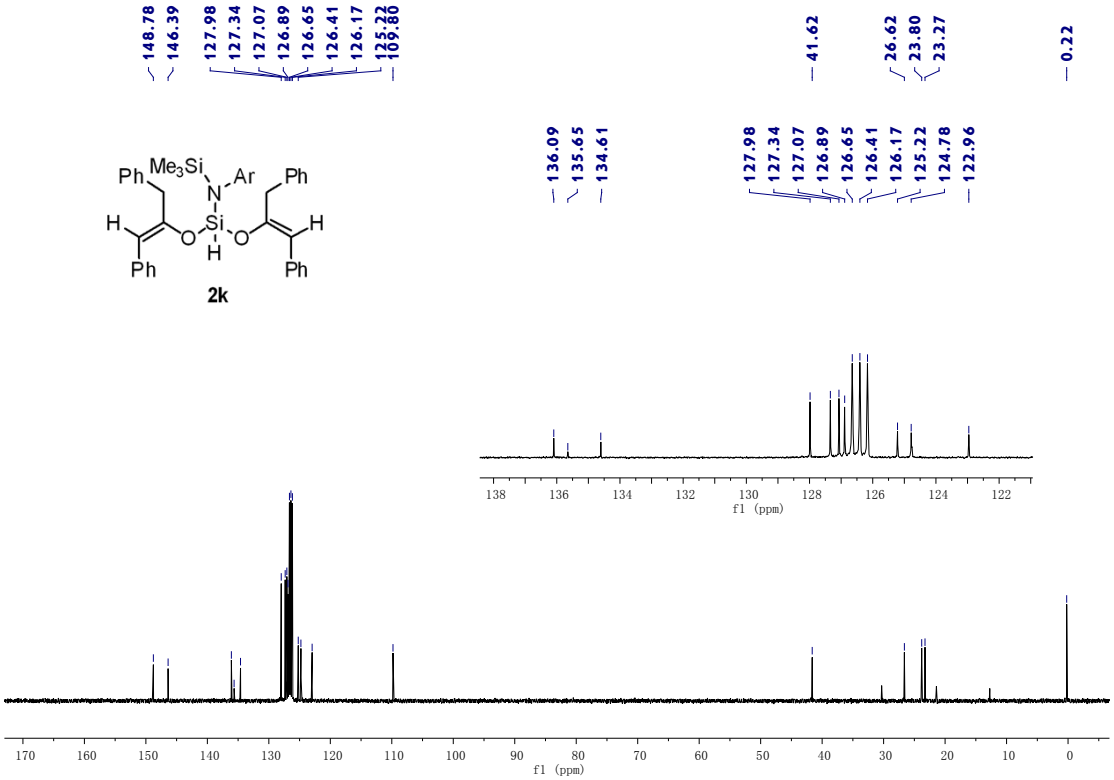

Figure 22. ^{13}C NMR spectra of 2k.

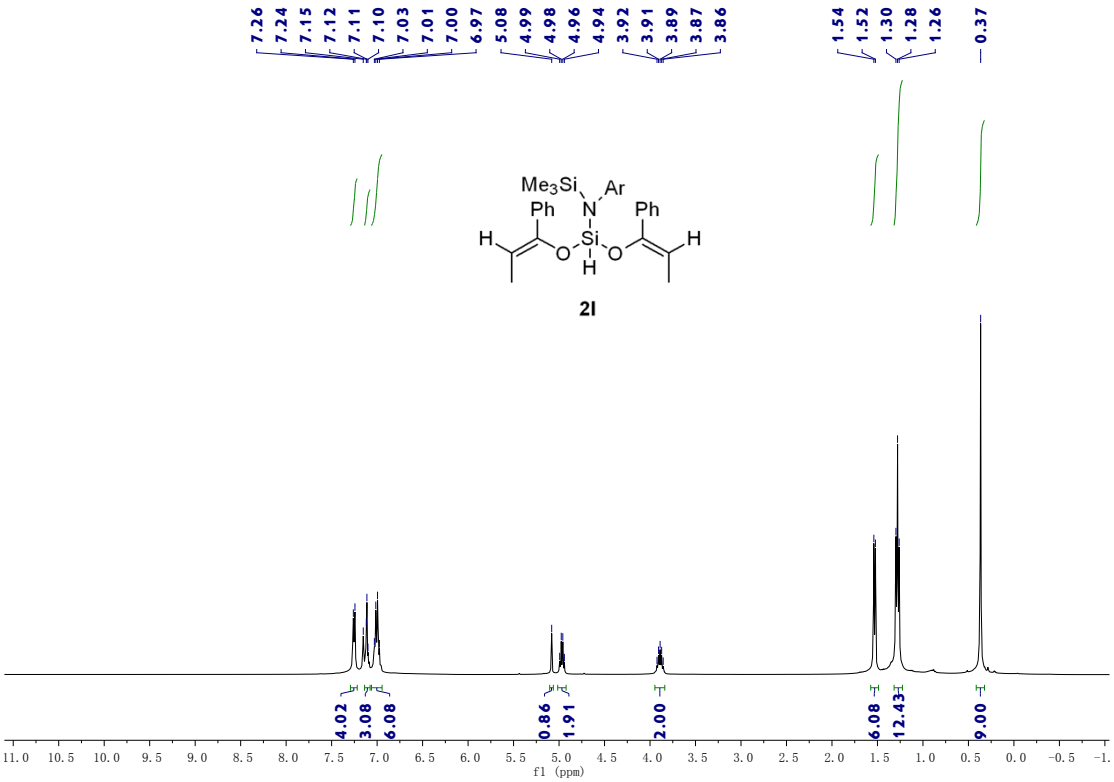

Figure 23. ^{1}H NMR spectra of 2l.

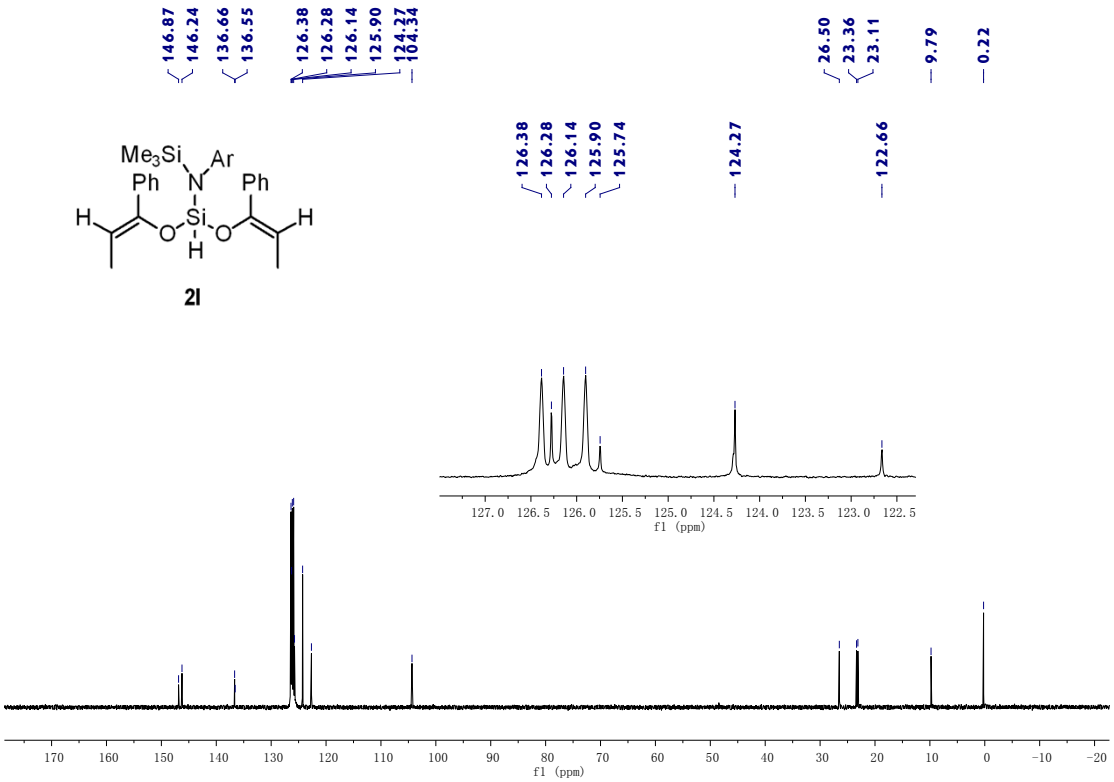

Figure 24. ^{13}C NMR spectra of 2l.

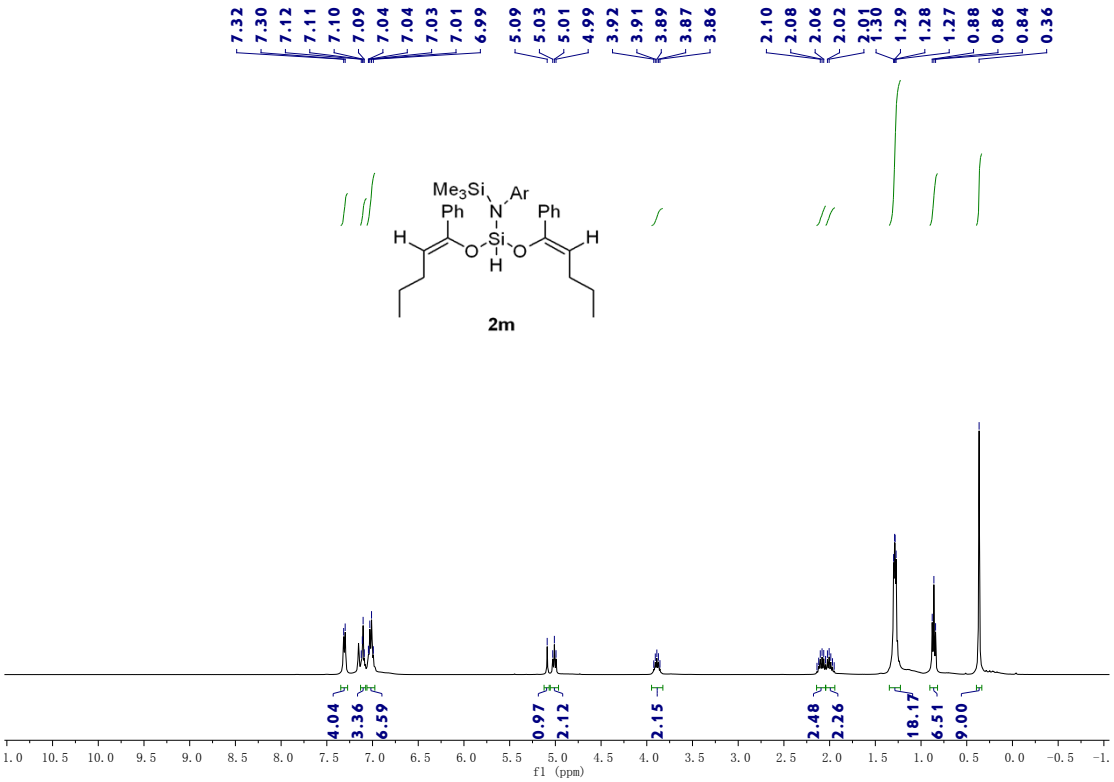

Figure 25. ^{1}H NMR spectra of 2m.

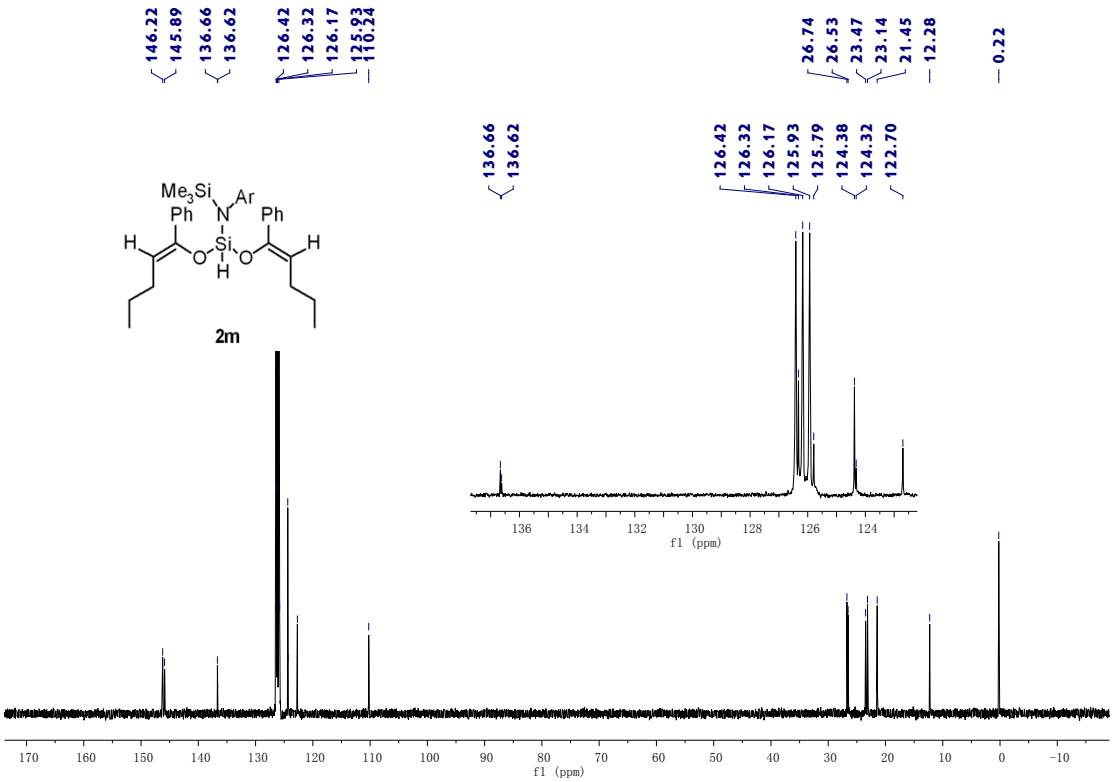

Figure 26. ^{13}C NMR spectra of 2m.

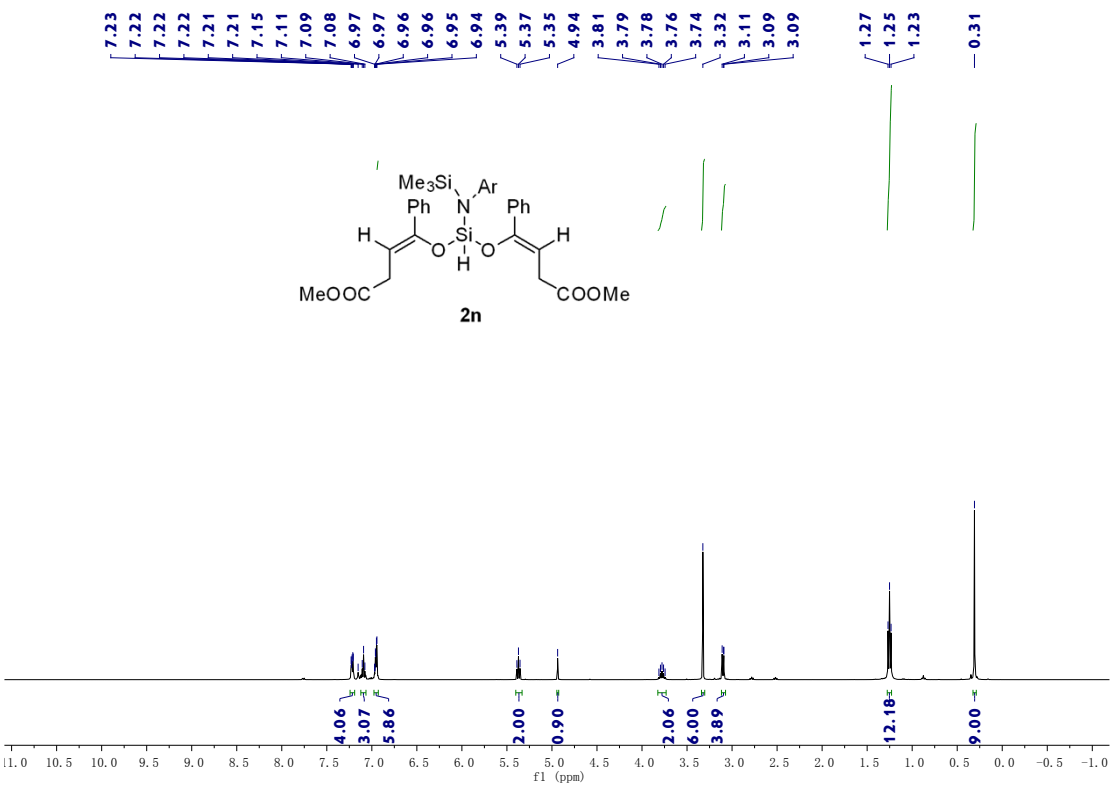

Figure 27. ^{1}H NMR spectra of 2n.

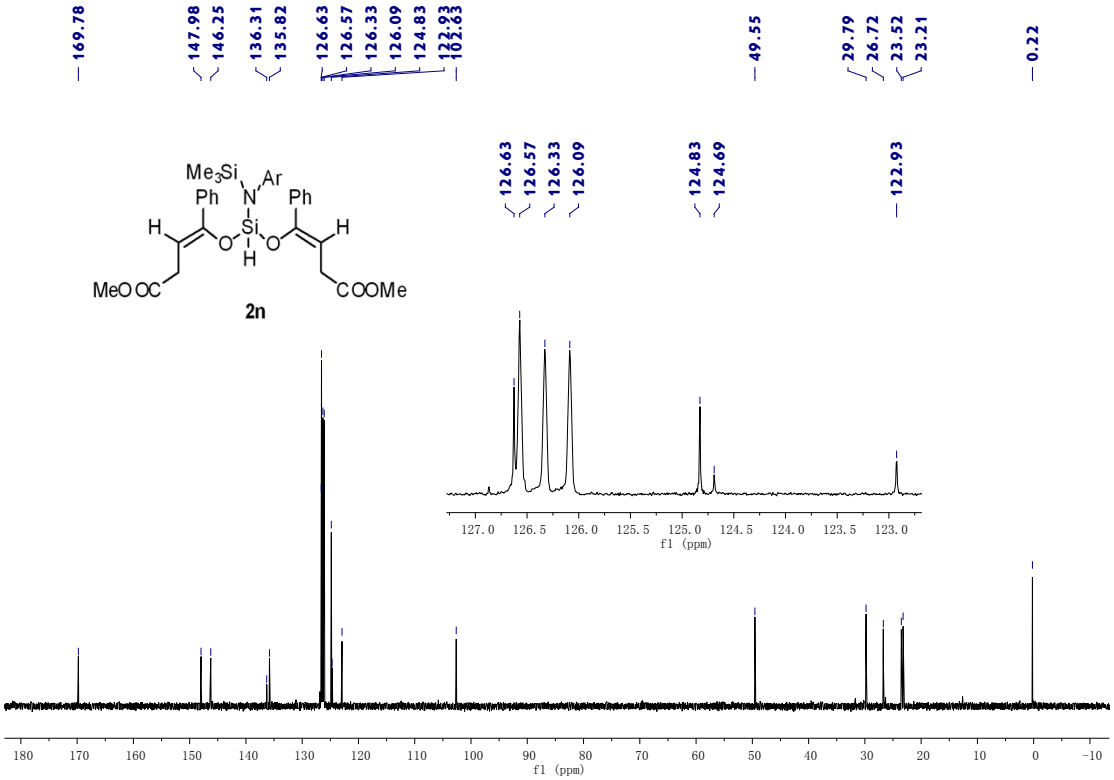

Figure 28. ^{13}C NMR spectra of 2n.

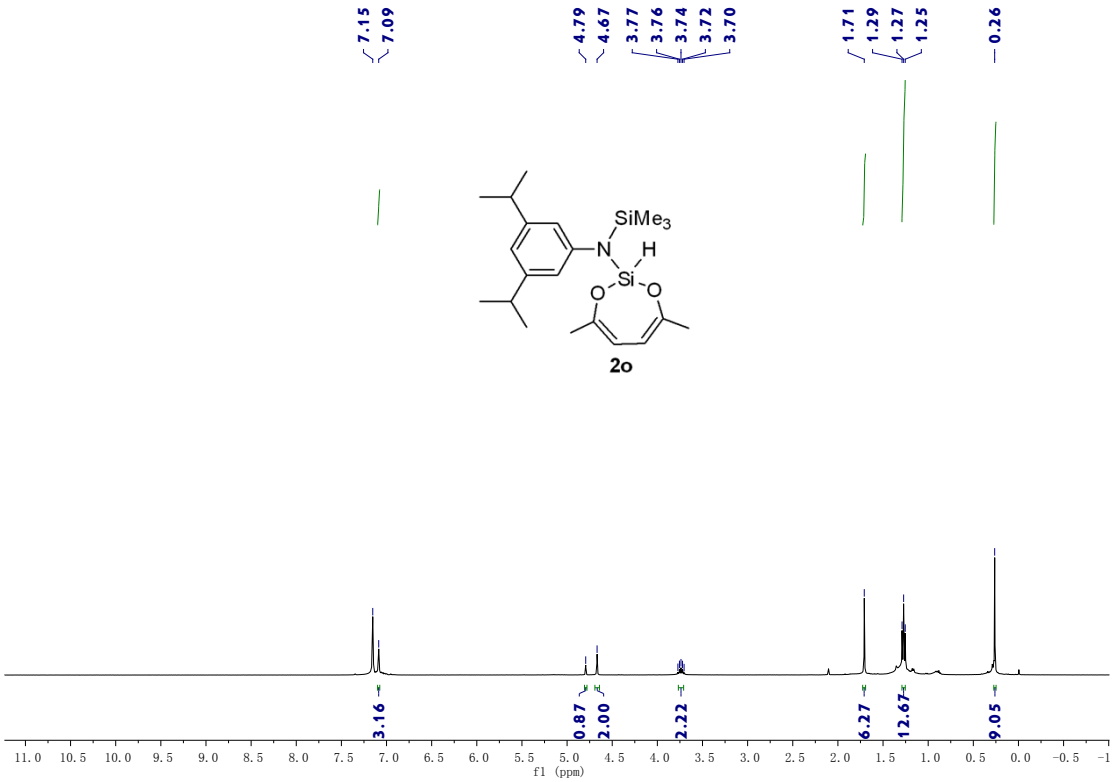

Figure 29. ^{1}H NMR spectra of 2o.

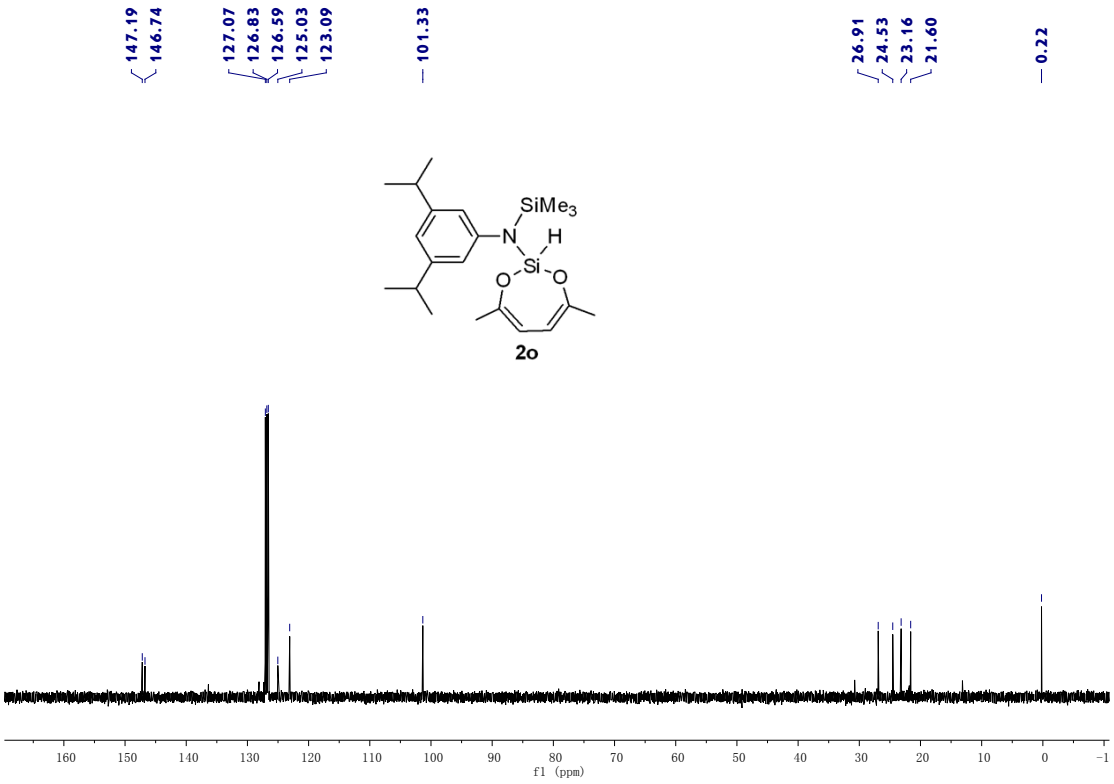

Figure 30. ^{13}C NMR spectra of 2o.

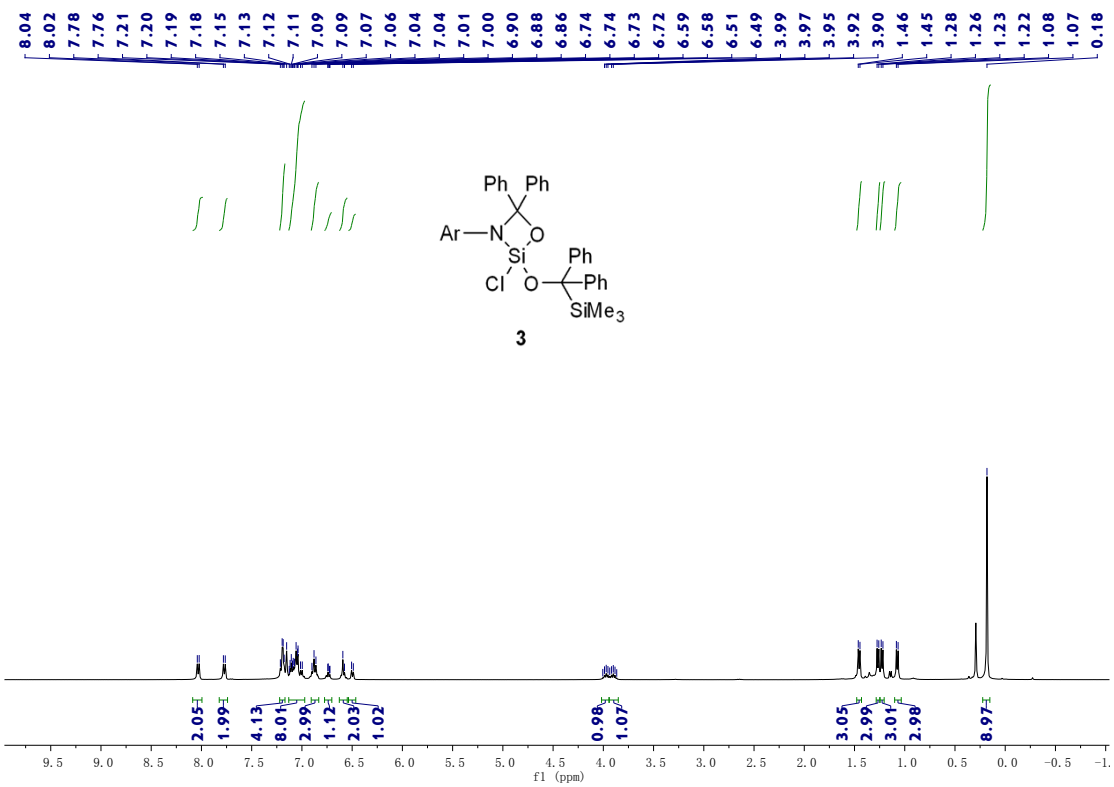

Figure 31. ^{1}H NMR spectra of 3.

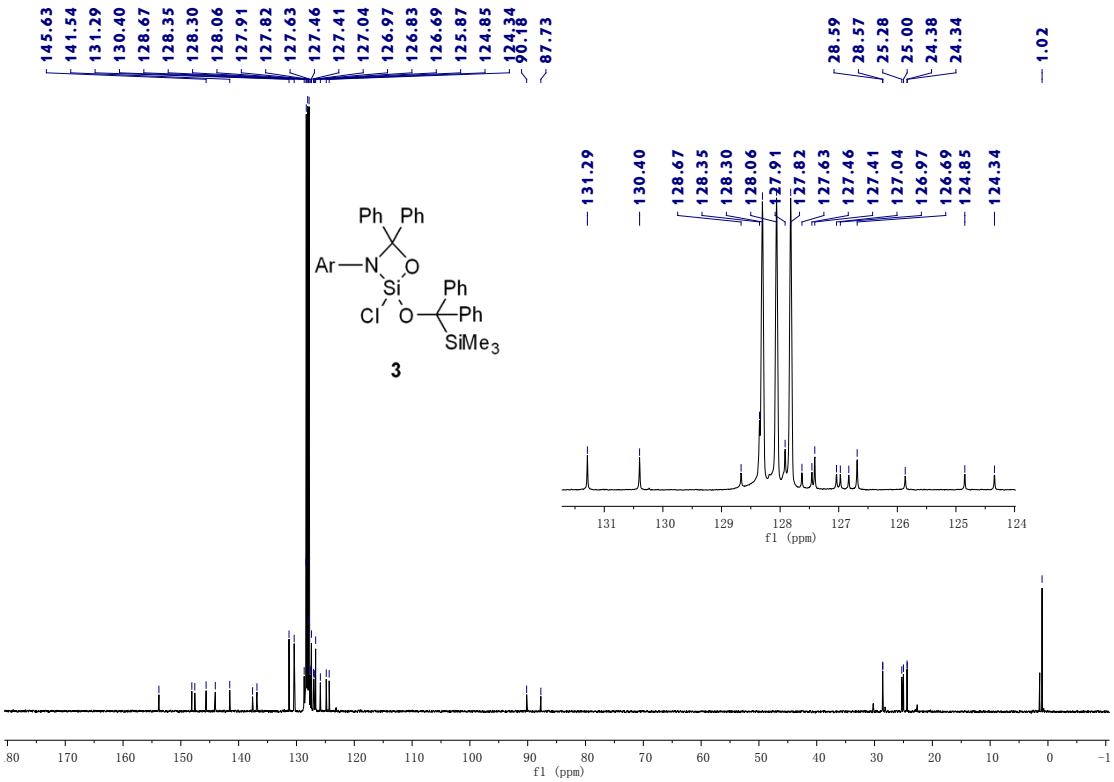

Figure 32. ^{13}C NMR spectra of 3.

NOESY Spectra of Selected Products 2h-n (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$):

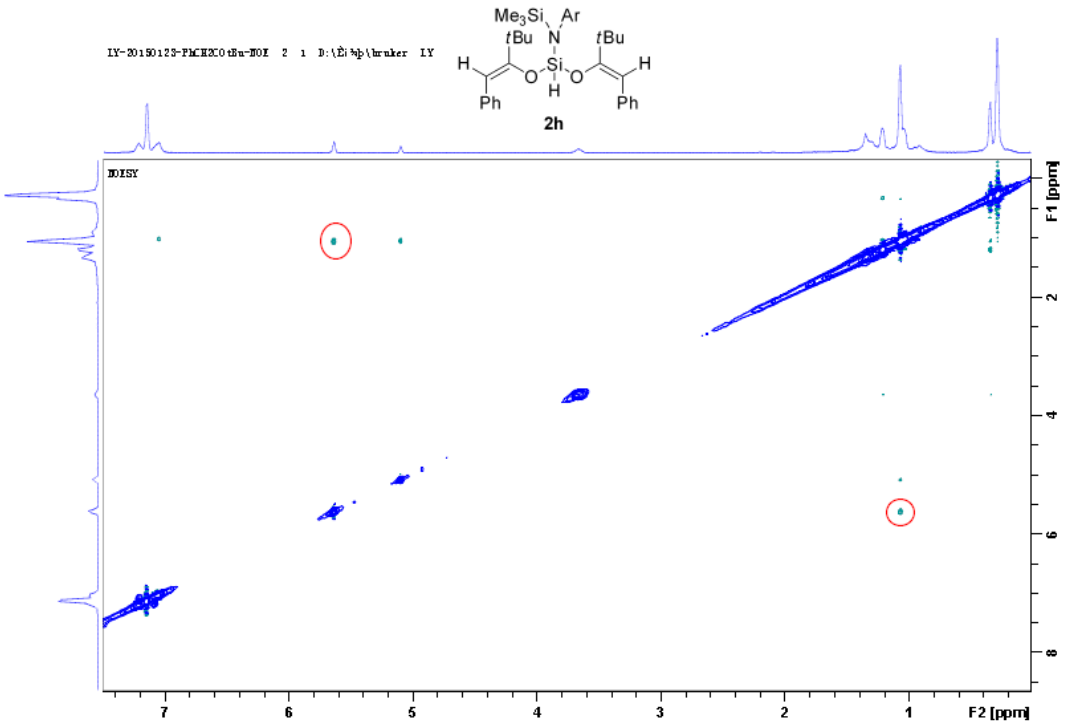

Figure 33. **NOESY spectrum of compound 2h.** The hydrogen atom of the tertiary butyl (δ = 1.08 ppm) couple strongly only with the hydrogen atom of C*H*= (δ = 5.64 ppm) and do not couple with the hydrogen atom of phenyl, indicating that the tertiary butyl and the hydrogen atom of C*H*= on the same side of the C=C double bond. The configuration of product **2h** is *cis* isomer.

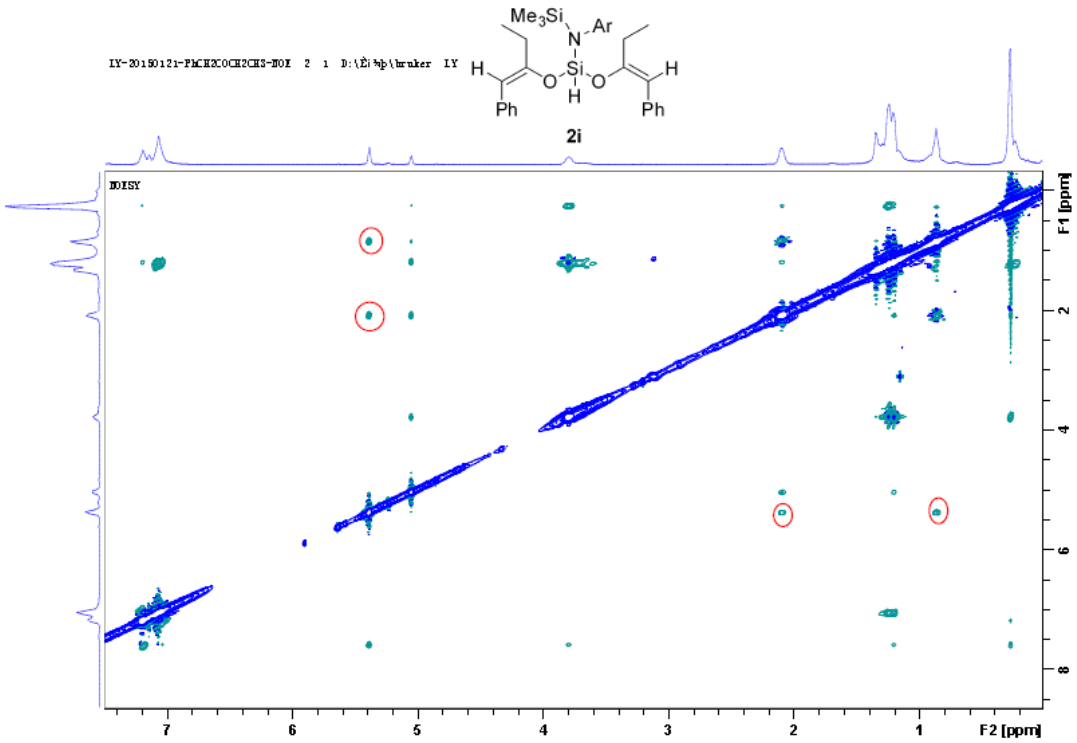

Figure 34. NOESY spectrum of compound 2i. The hydrogen atom of the ethyl (δ = 0.87, 2.09 ppm) couple strongly only with the hydrogen atom of C*H*= (δ = 5.40 ppm) and do not couple with the hydrogen atom of phenyl, indicating that the ethyl and the hydrogen atom of C*H*= on the same side of the C=C double bond. The configuration of product **2i** is *cis* isomer.

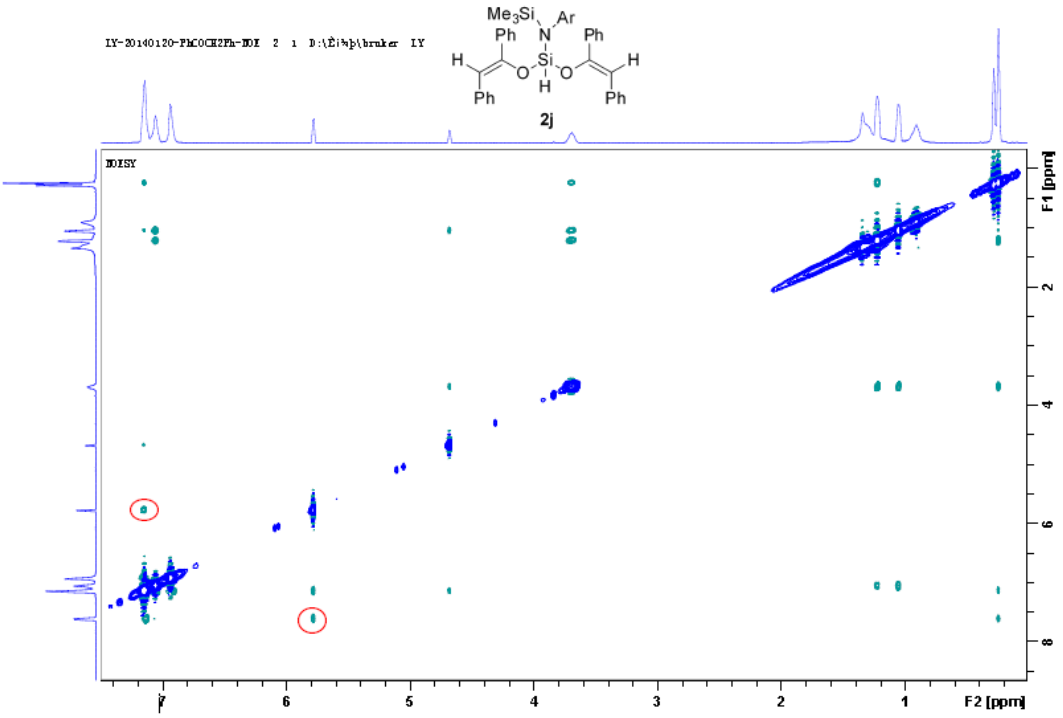

Figure 35. NOESY spectrum of compound 2j. The hydrogen atom of the phenyl (δ = 7.63 ppm, *Ph*OC=) couple strongly with the hydrogen atom of C*H*= (δ = 5.79 ppm), indicating that the phenyl (*Ph*OC=) and the hydrogen atom of C*H*= on the same side of the C=C double bond. The configuration of product **2j** is *cis* isomer.

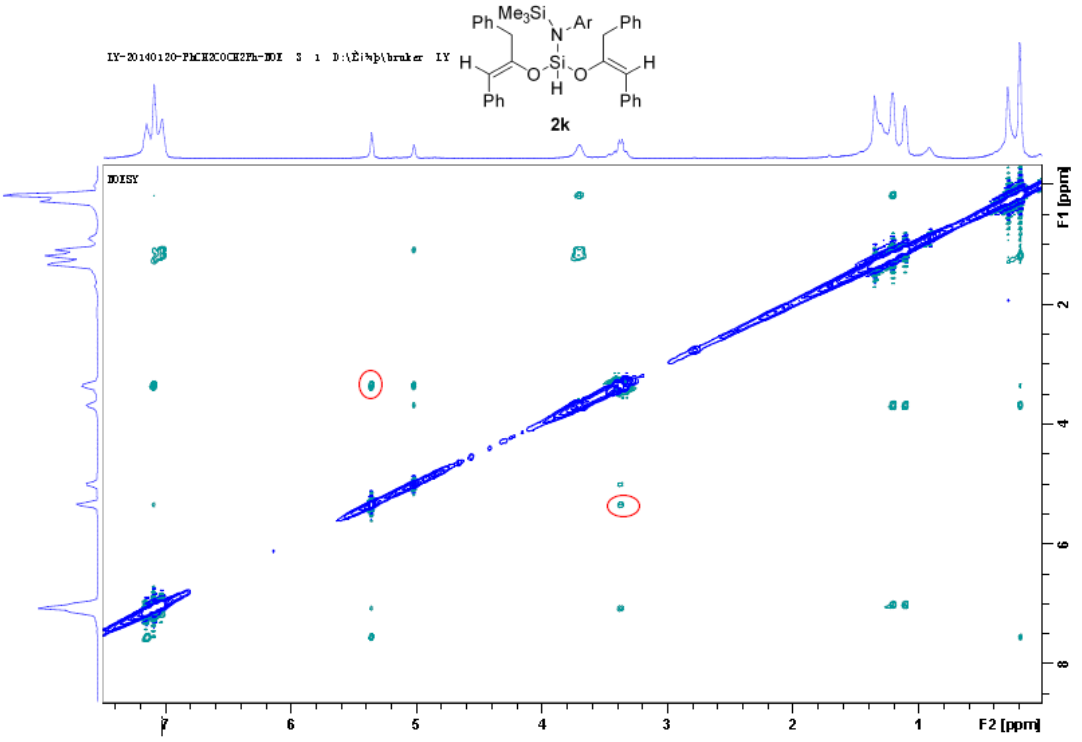

Figure 36. NOESY spectrum of compound 2k. The hydrogen atom of the benzyl (δ = 3.36 ppm, PhCH_2) couple strongly with the hydrogen atom of C*H*= (δ = 5.36 ppm), indicating that the benzyl(PhCH_2) and the hydrogen atom of C*H*= on the same side of the C=C double bond. The configuration of product **2k** is *cis* isomer.

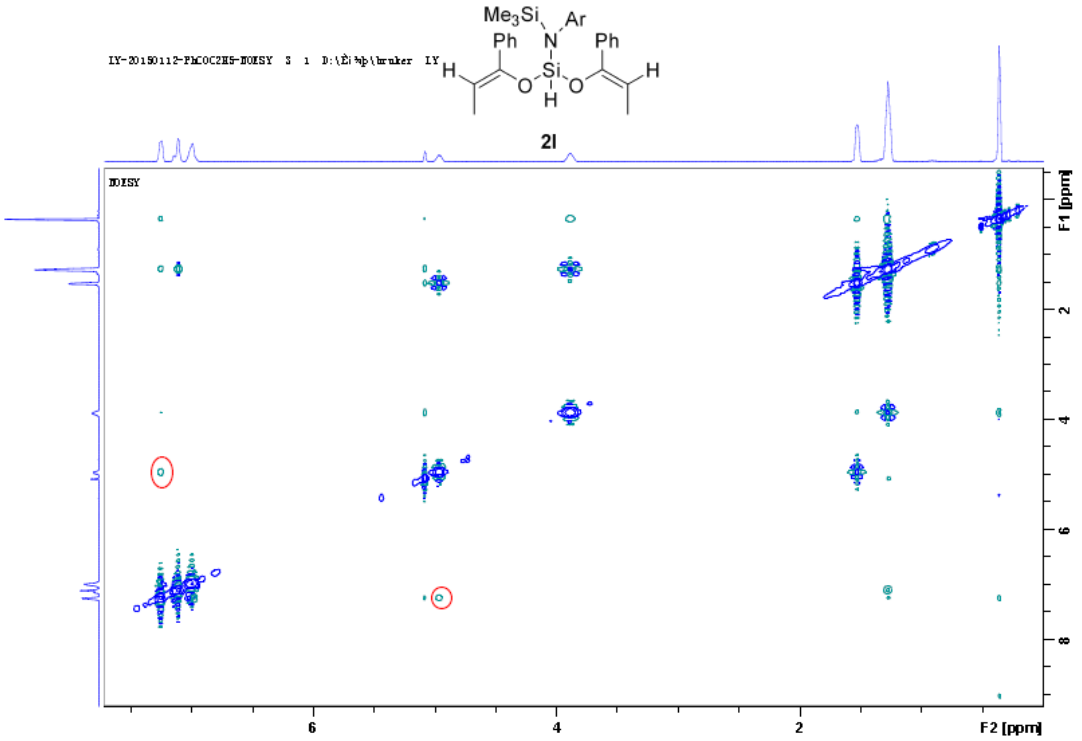

Figure 37. NOESY spectrum of compound 2l. The hydrogen atom of the phenyl (δ = 7.25 ppm) couple strongly only with the hydrogen atom of =C*H* (δ = 4.97 ppm) and do not couple with the hydrogen atom of =CCH_3 (δ = 1.53 ppm), indicating that the hydrogen atom of =C*H* and the phenyl group on the same side of the C=C double bond. The configuration of product **2l** is *cis* isomer.

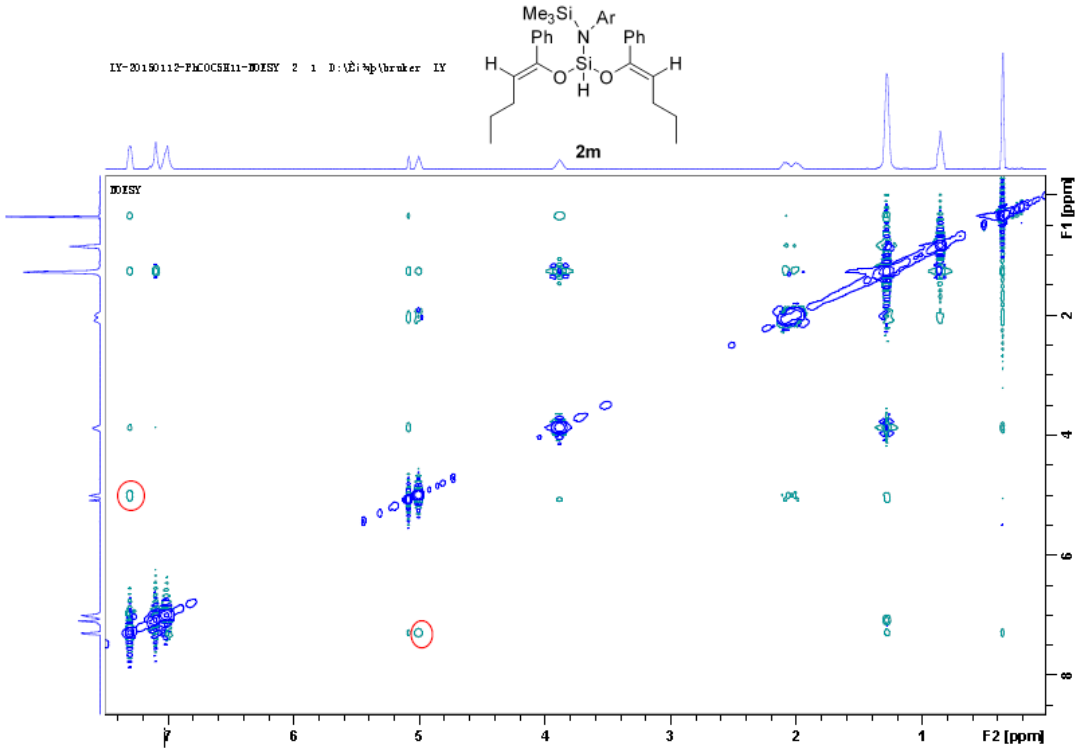

Figure 38. NOESY spectrum of compound 2m. The hydrogen atom of the phenyl (δ = 7.31 ppm) couple strongly only with the hydrogen atom of =C*H* (δ = 5.01 ppm) and do not couple with the hydrogen atom of the propyl, indicating that the hydrogen atom of =C*H* and the phenyl group on the same side of the C=C double bond. The configuration of product **2m** is *cis* isomer.

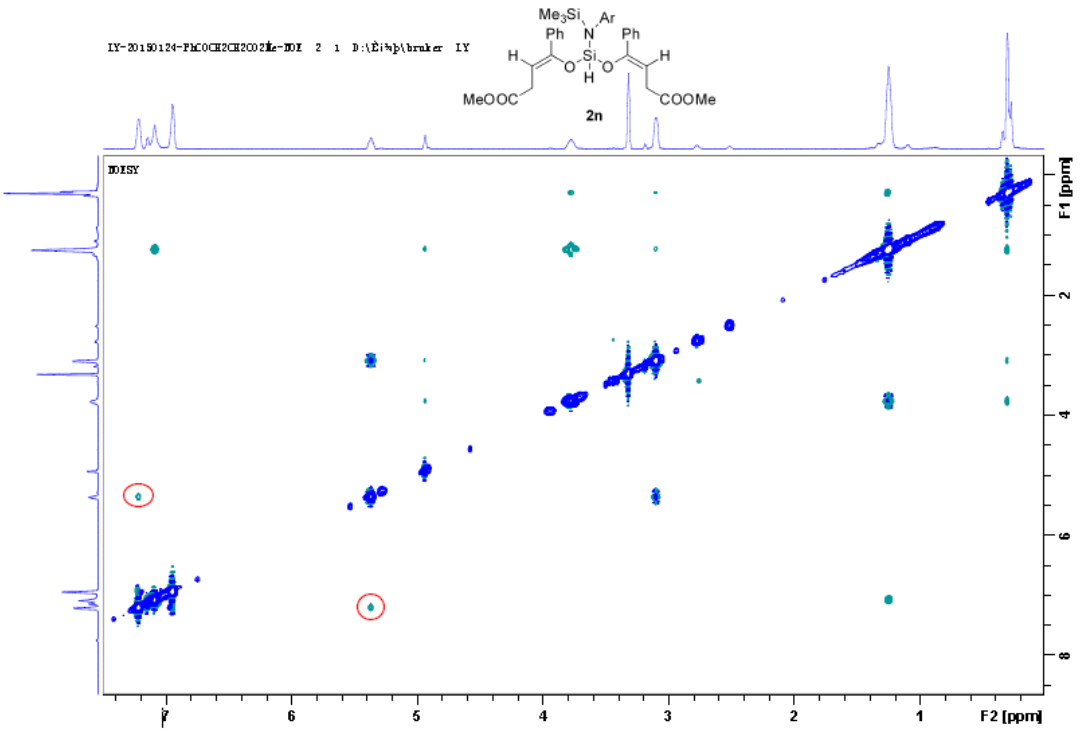

Figure 39. NOESY spectrum of compound 2n. The hydrogen atom of the phenyl (δ = 7.01 ppm) couple strongly only with the hydrogen atom of C*H*= (δ = 5.15 ppm) and do not couple with the hydrogen atom of $CH_2CO_2CH_3$ (δ = 3.12, 3.32 ppm), indicating that the hydrogen atom of C*H*= (δ = 5.15 ppm) and the phenyl group on the same side of the C=C double bond. The configuration of product **2n** is *cis* isomer.