

Supplementary Materials

Rhodium-catalyzed *trans*-bis-silylation reactions of 2-ethynyl-3-pentamethyldisilanylpyridines

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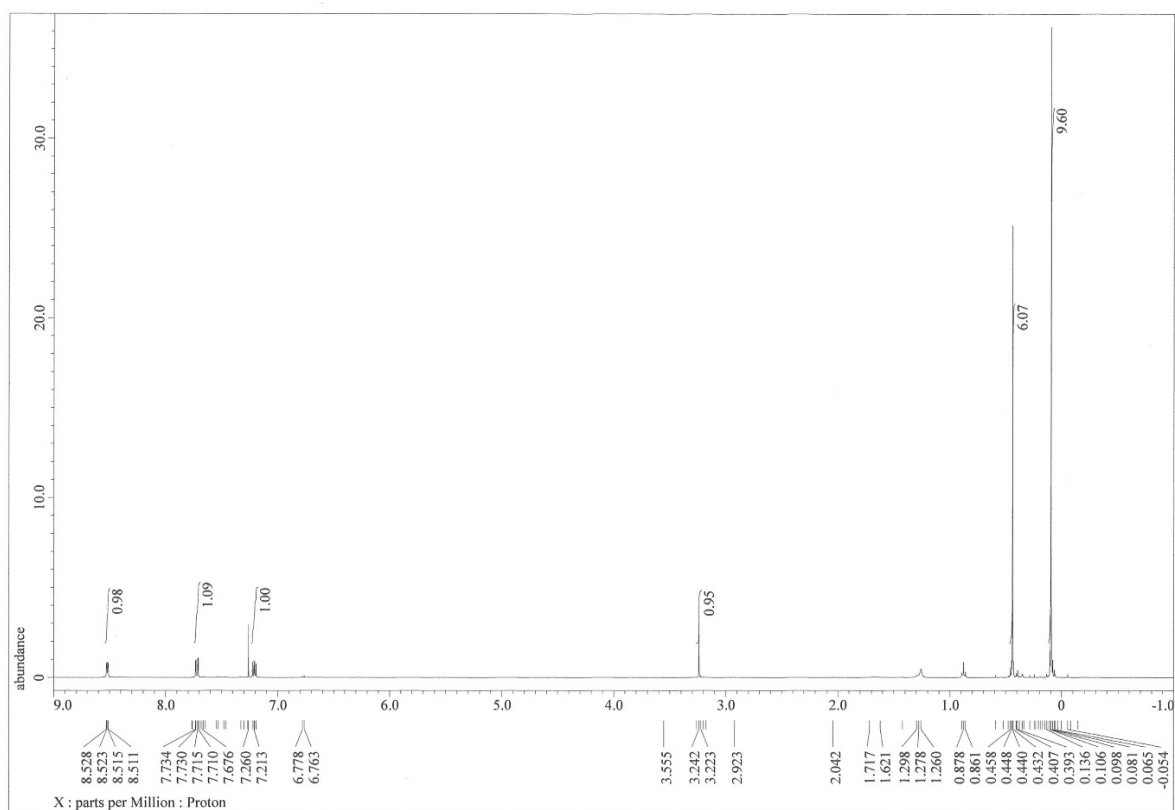


Figure S1. ^1H NMR spectrum of **2** in CDCl_3 .

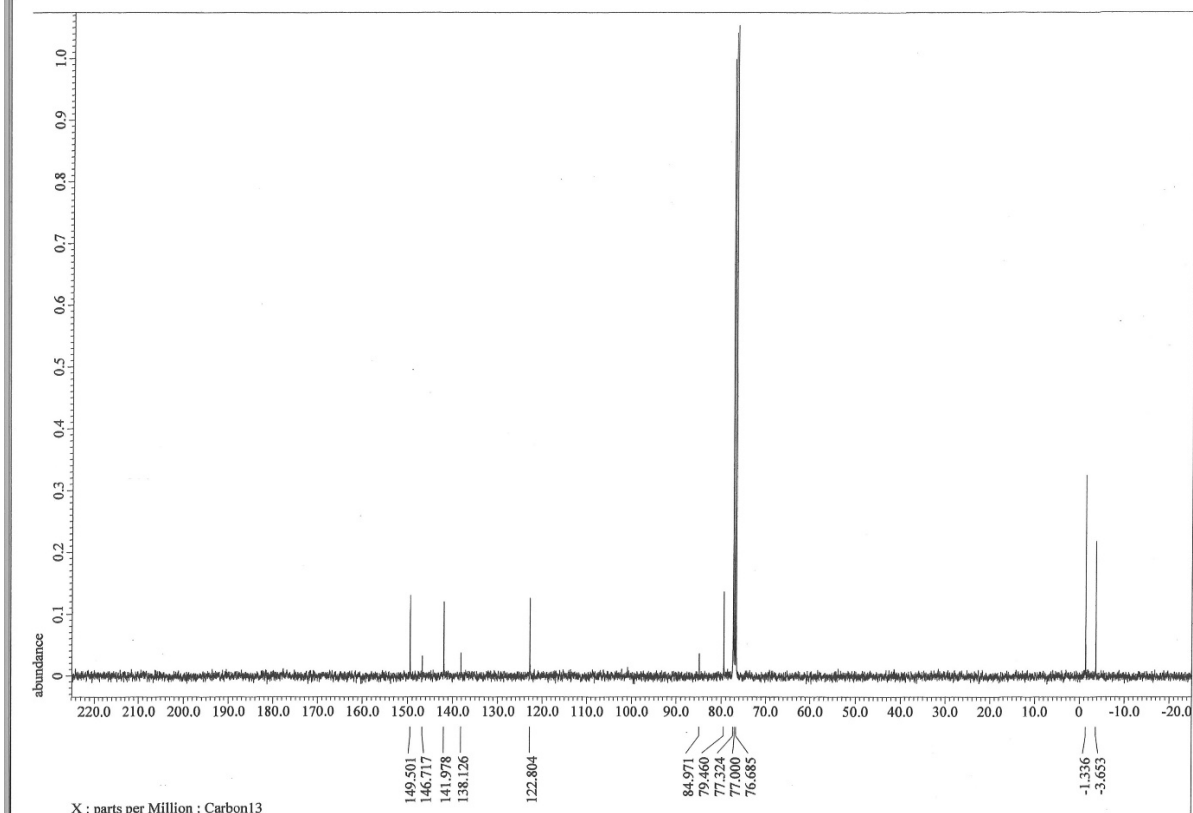


Figure S2. ^{13}C NMR spectrum of **2** in CDCl_3 .

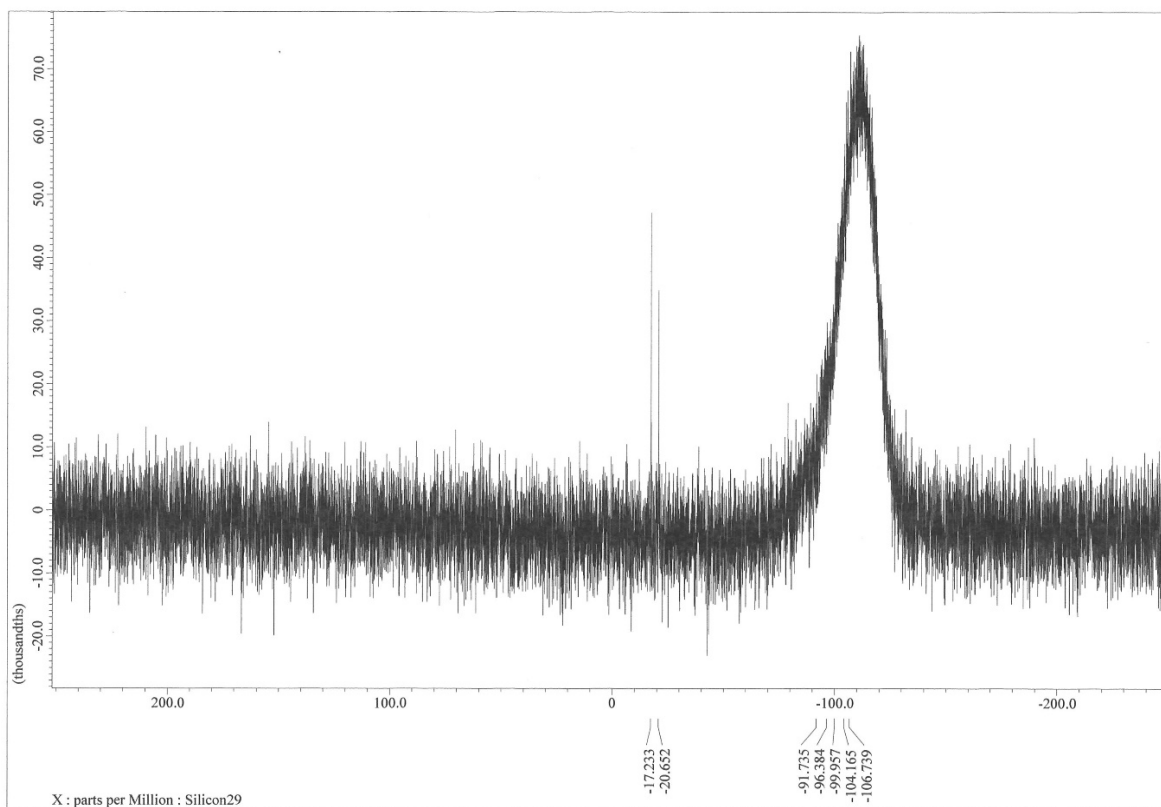


Figure S3. ^{29}Si NMR spectrum of **2** in CDCl_3 .

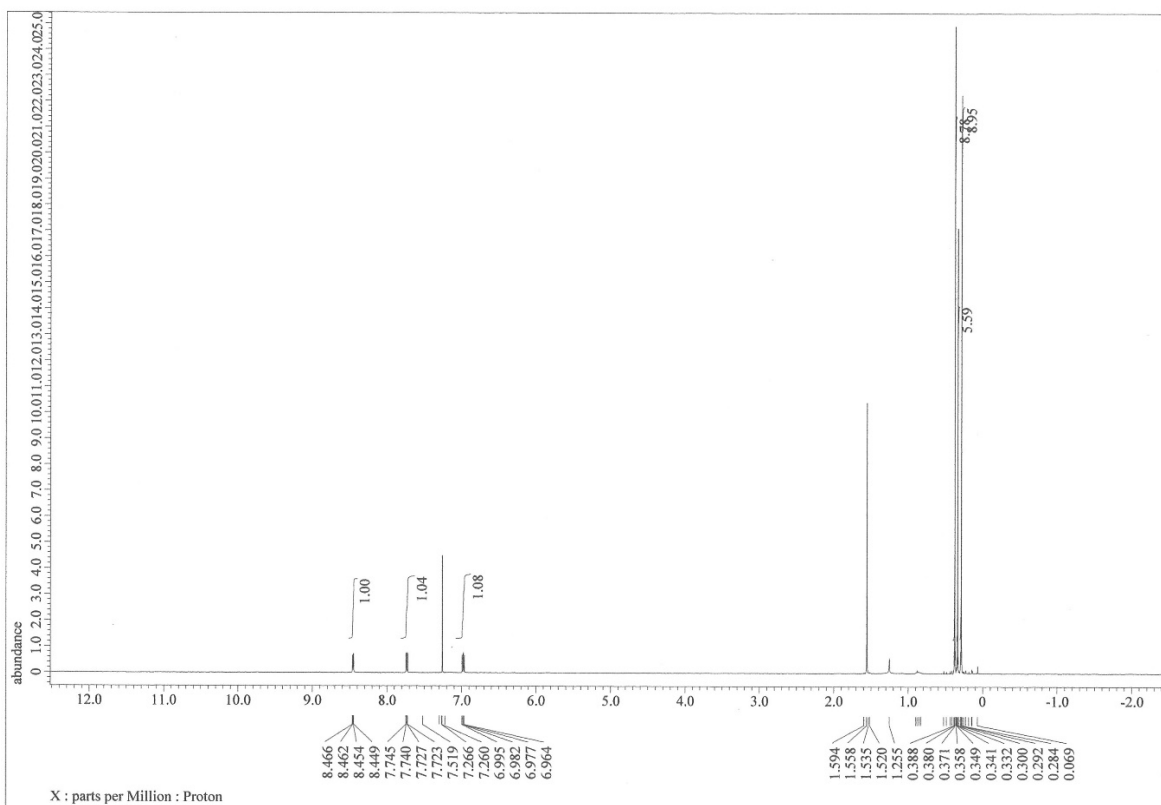


Figure S4. ^1H NMR spectrum of **3** in CDCl_3 .

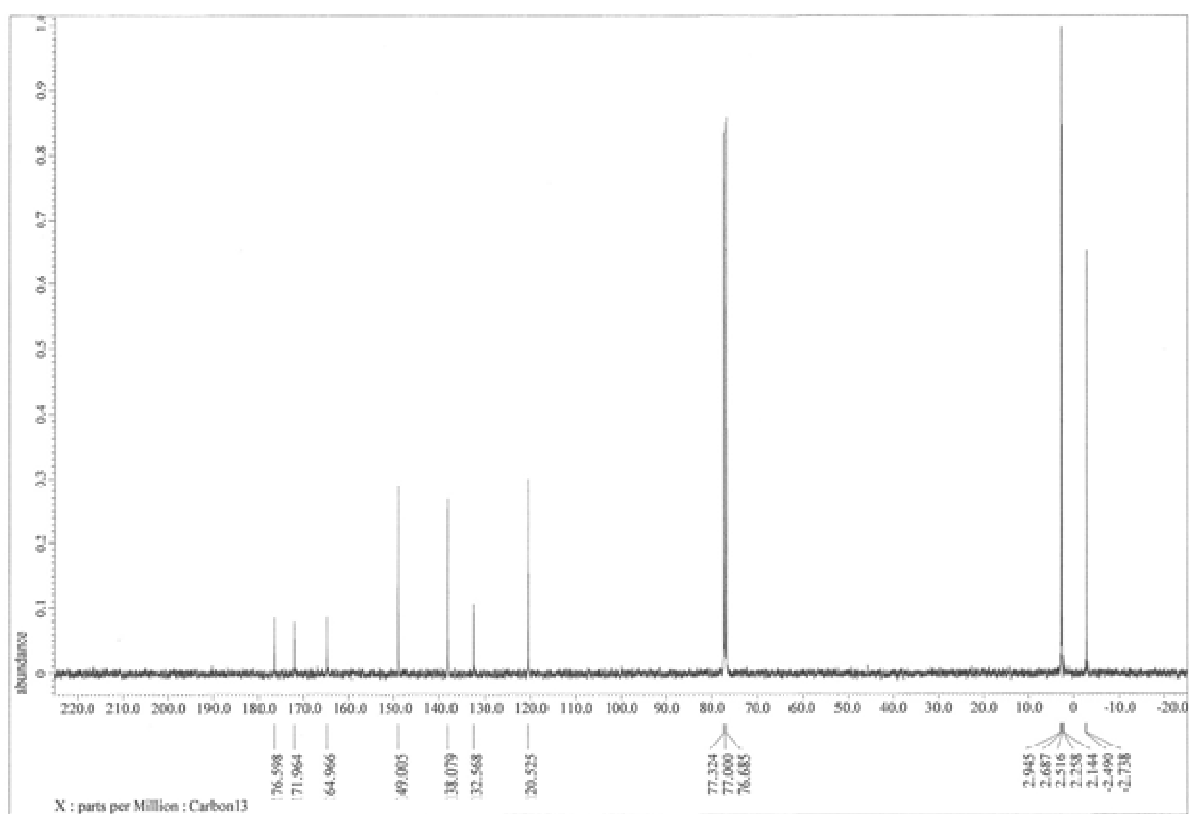


Figure S5. ¹³C NMR spectrum of **3** in CDCl₃.

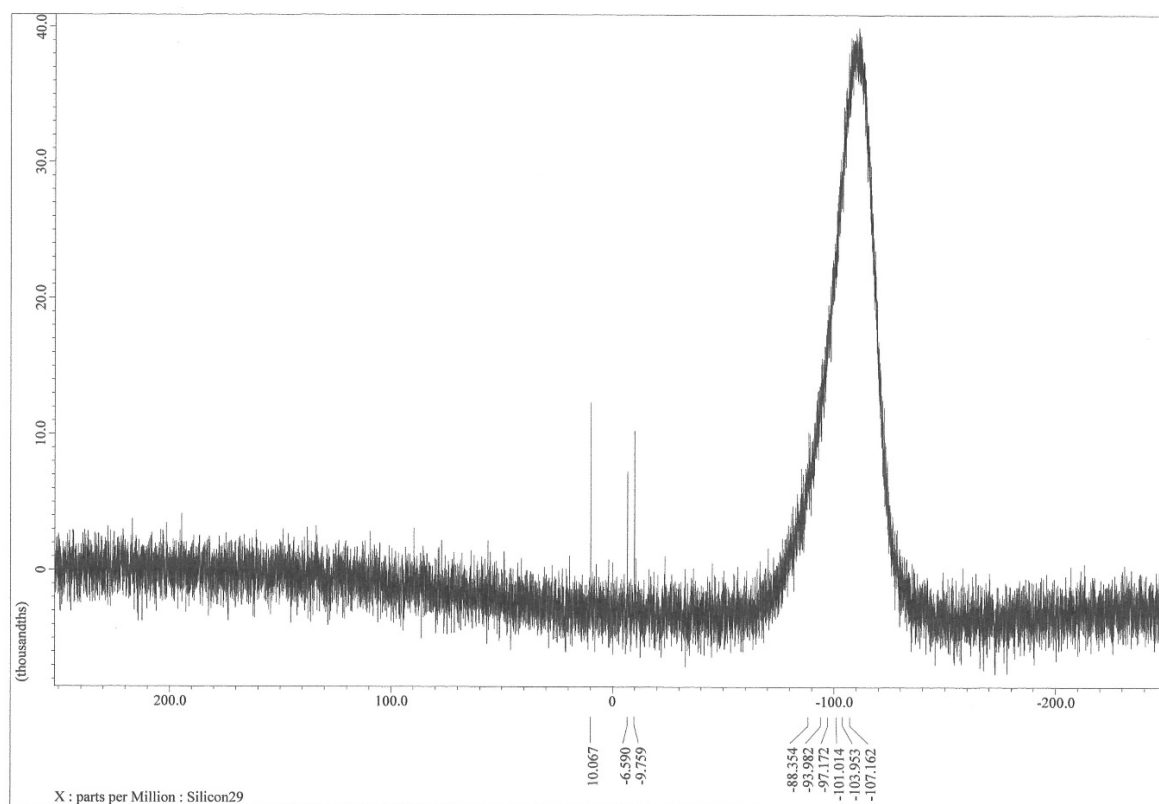


Figure S6. ²⁹Si NMR spectrum of **3** in CDCl₃.

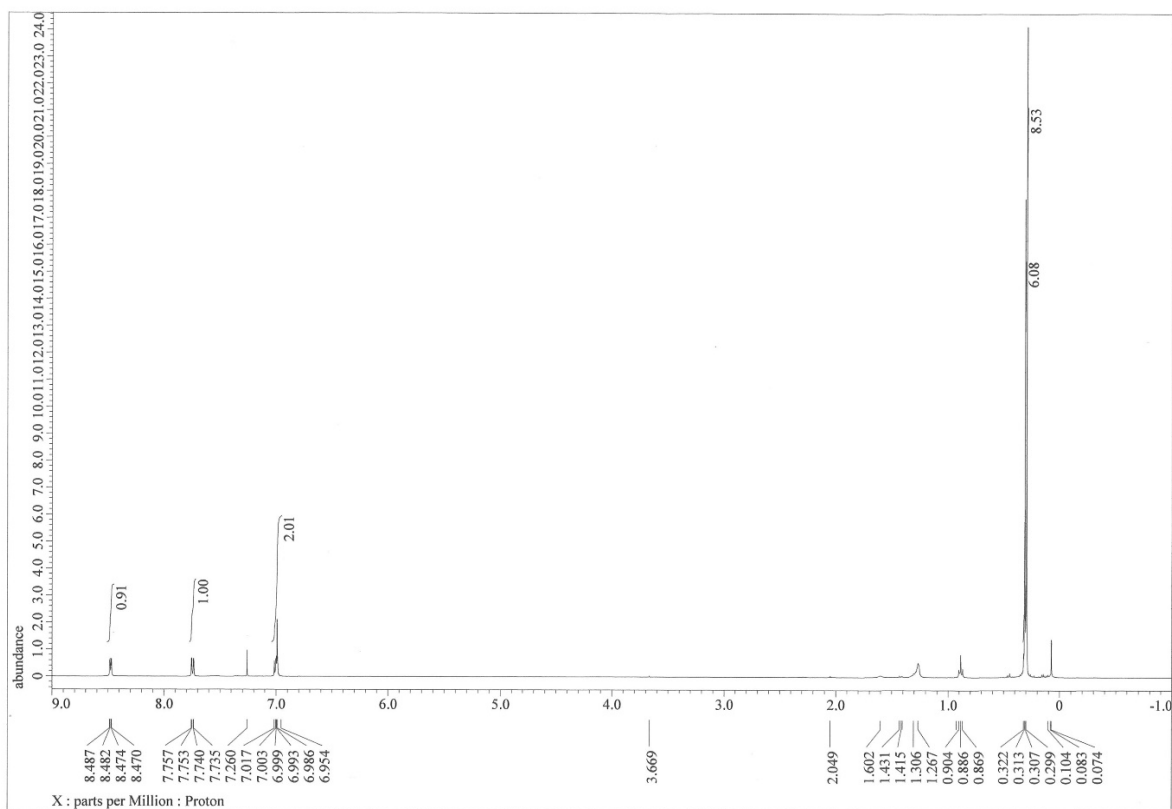


Figure S7. ^1H NMR spectrum of **4** in CDCl_3 .

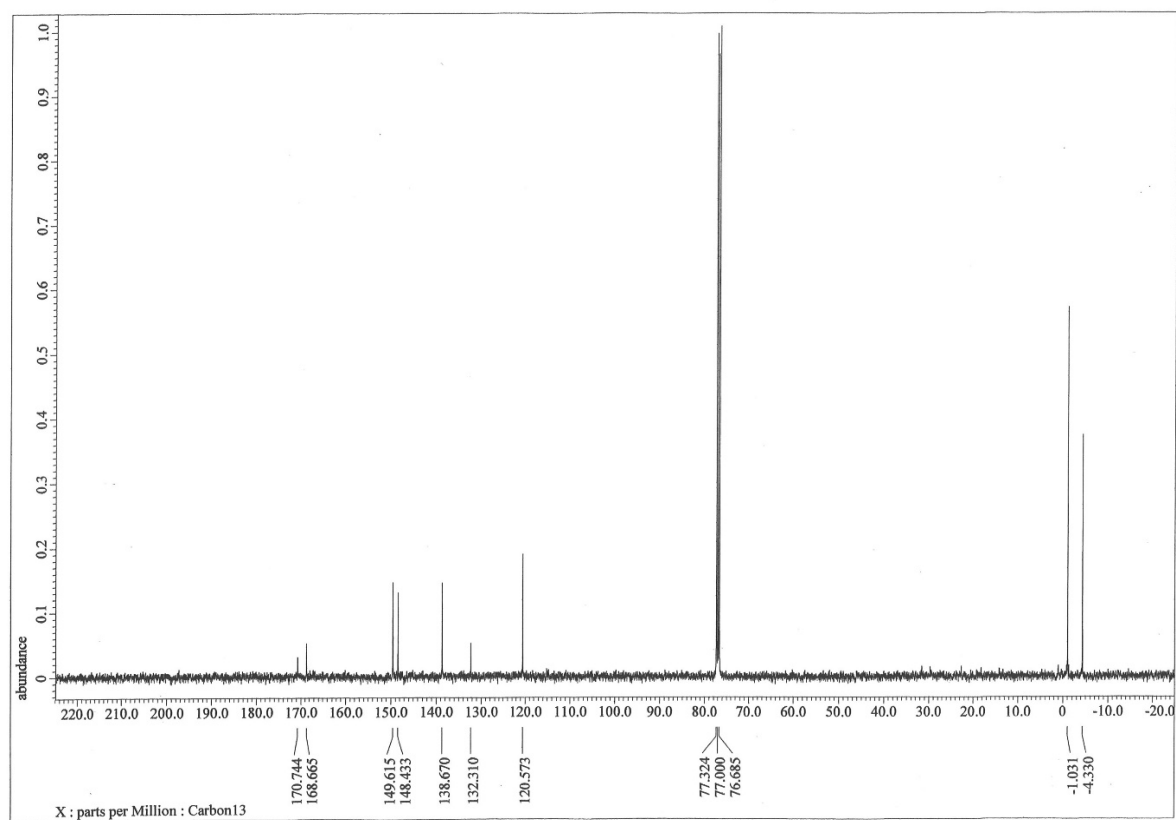


Figure S8. ^{13}C NMR spectrum of **4** in CDCl_3 .

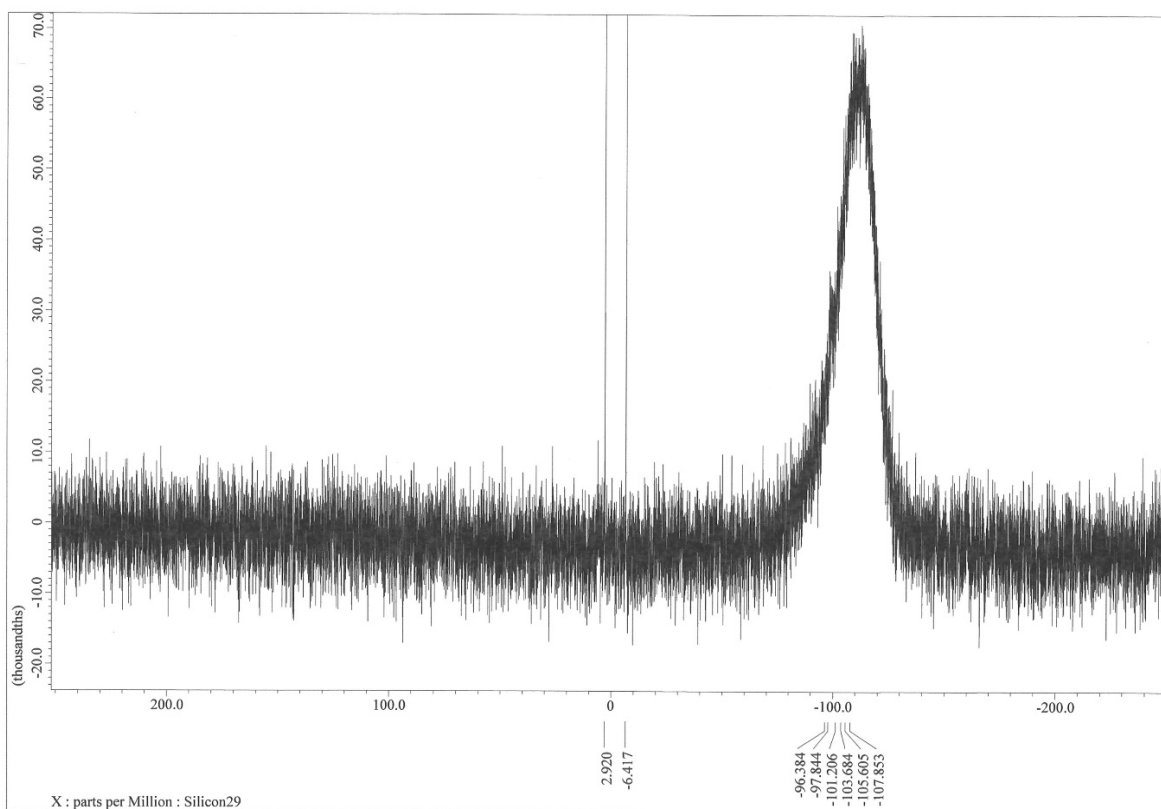


Figure S9. ^{29}Si NMR spectrum of **4** in CDCl_3 .

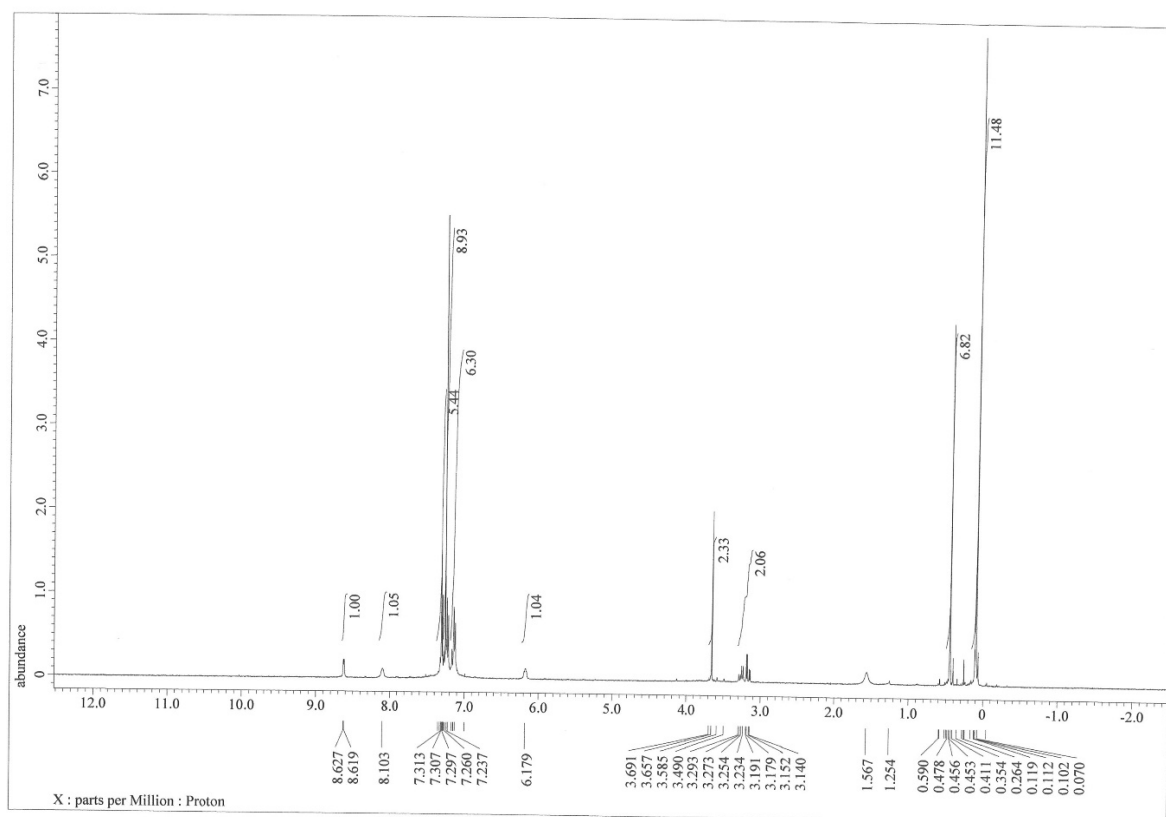


Figure S10. ^1H NMR spectrum of **6** in CDCl_3 .

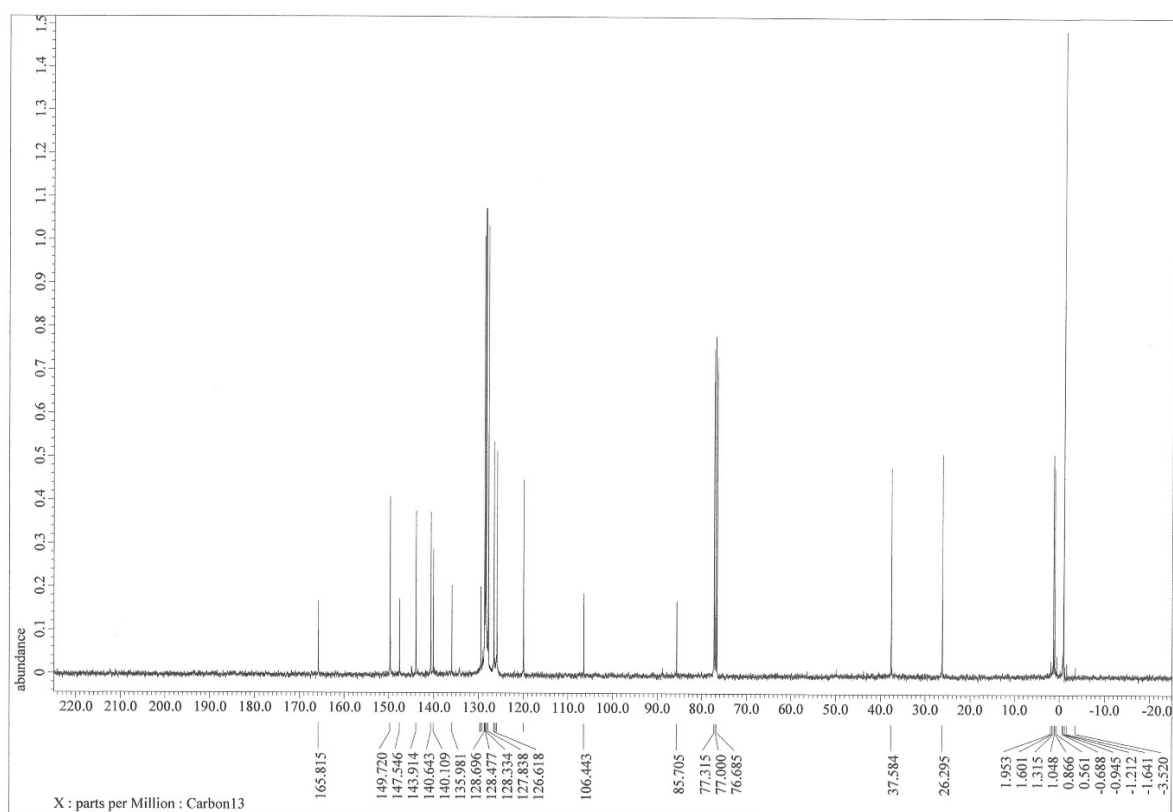


Figure S11. ¹³C NMR spectrum of **6** in CDCl₃.

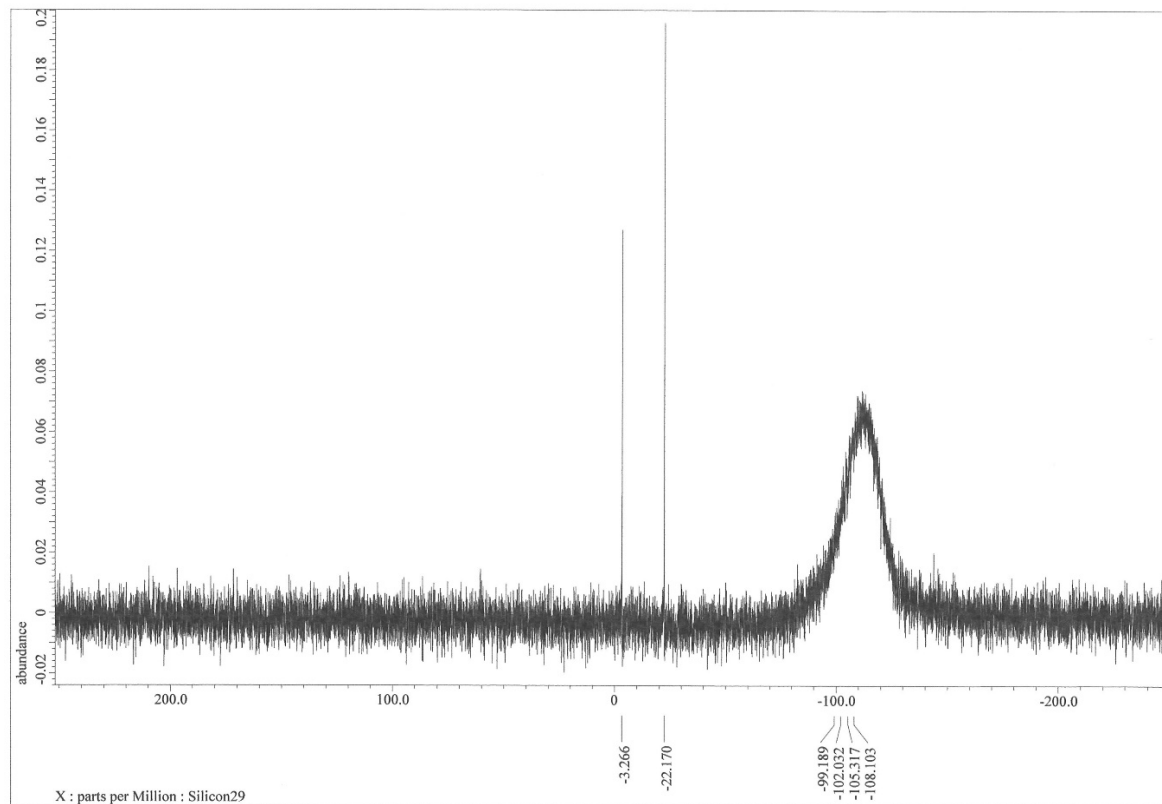


Figure S12. ²⁹Si NMR spectrum of **6** in CDCl₃.

Optimized structures for all LM's and TS's on the trans route with RhCl(CO) model.

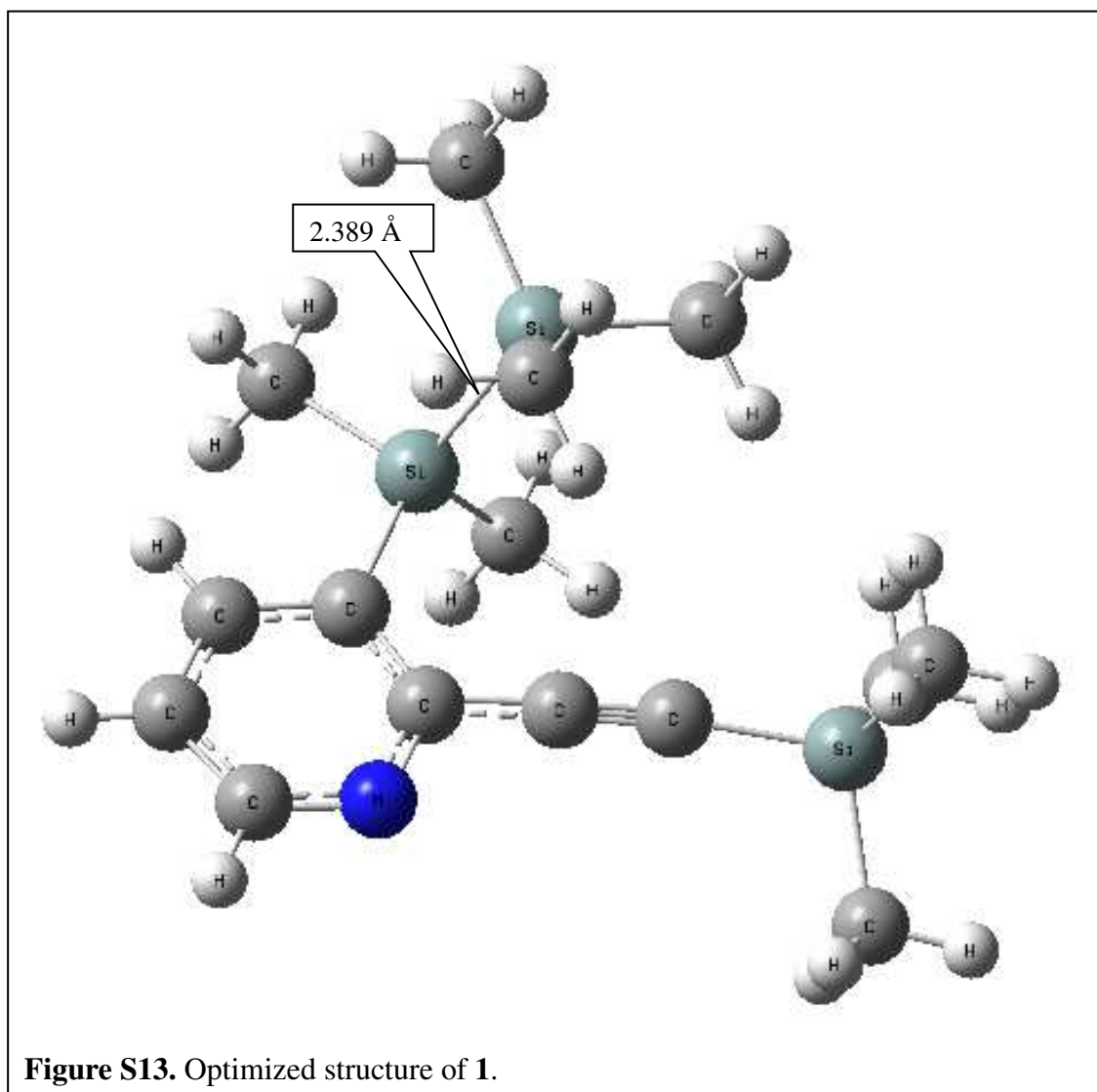
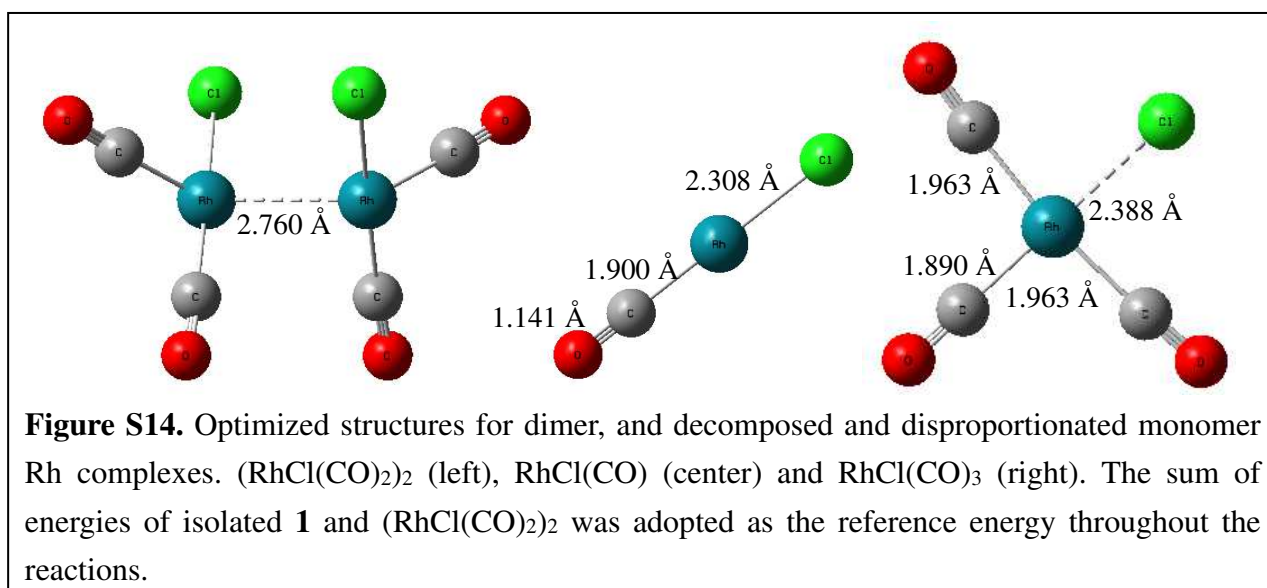


Figure S13. Optimized structure of **1**.



From **Figures S15** to **S21**, LM and TS structures on trans route with RhCl(CO) model are drawn.

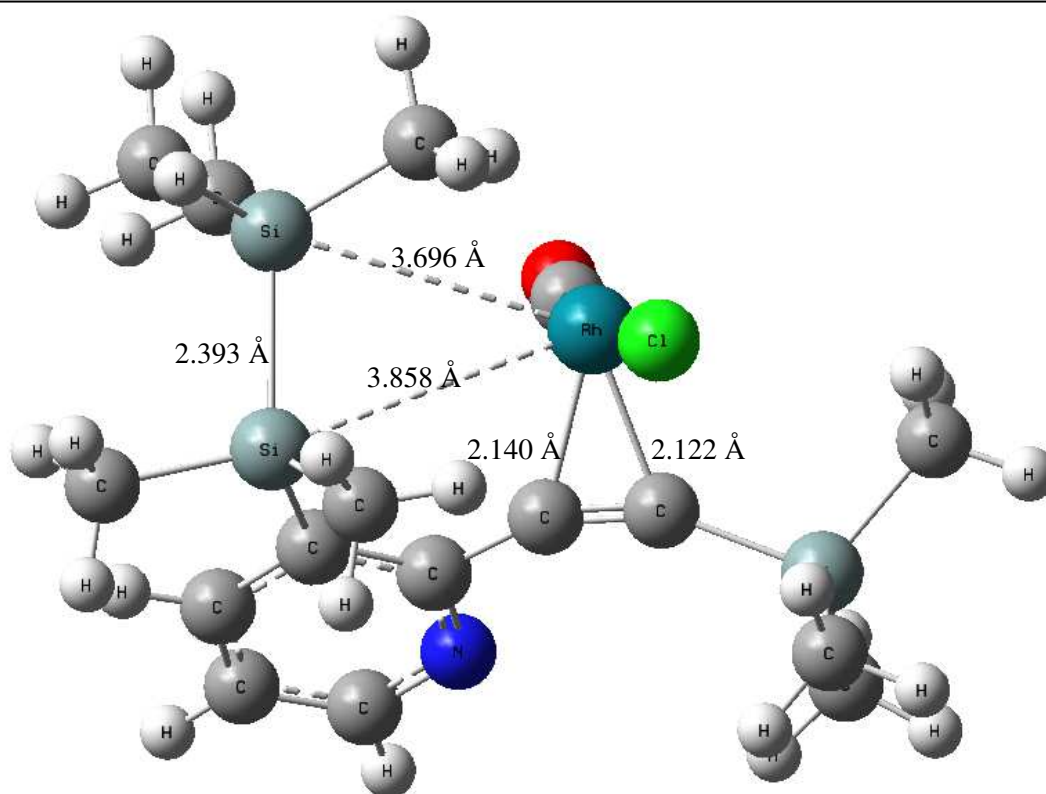


Figure S15. Optimized structure of **model 0(1)**. **Model 0** is a combined structure of **1** and RhCl(CO).

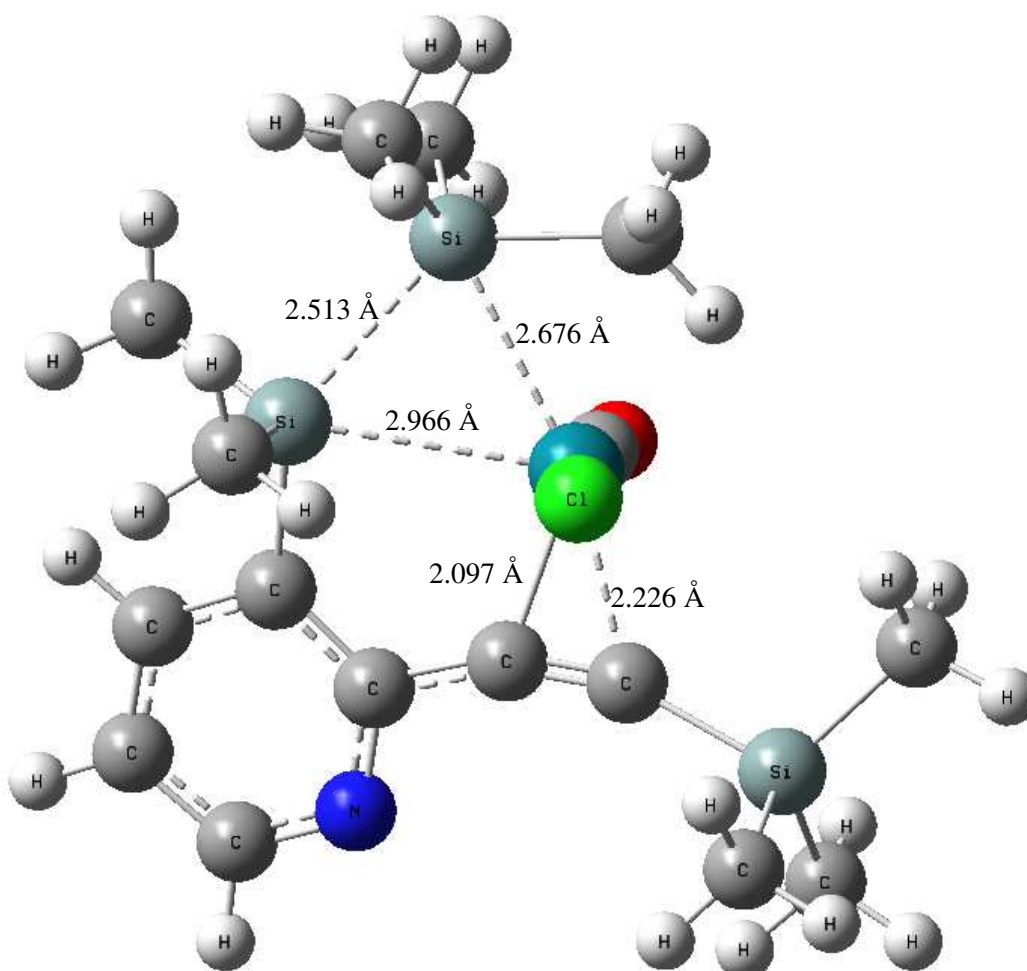


Figure S16. Optimized structure of TS 0-1(1). TS 0-1(1) is the TS between **model 0(1)** and **model 1(1)** with RhCl(CO) model.

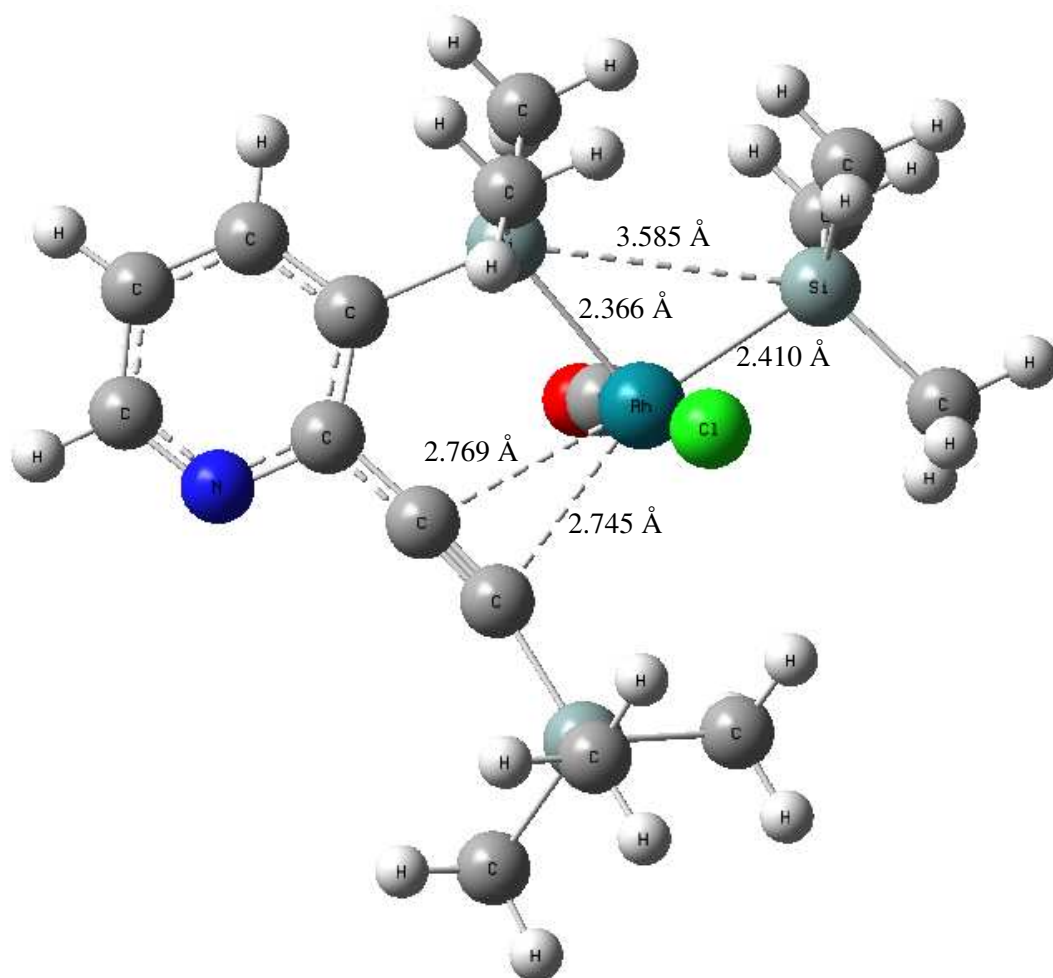


Figure S17. Optimized structure of **model 1(1)** with RhCl(CO) model.

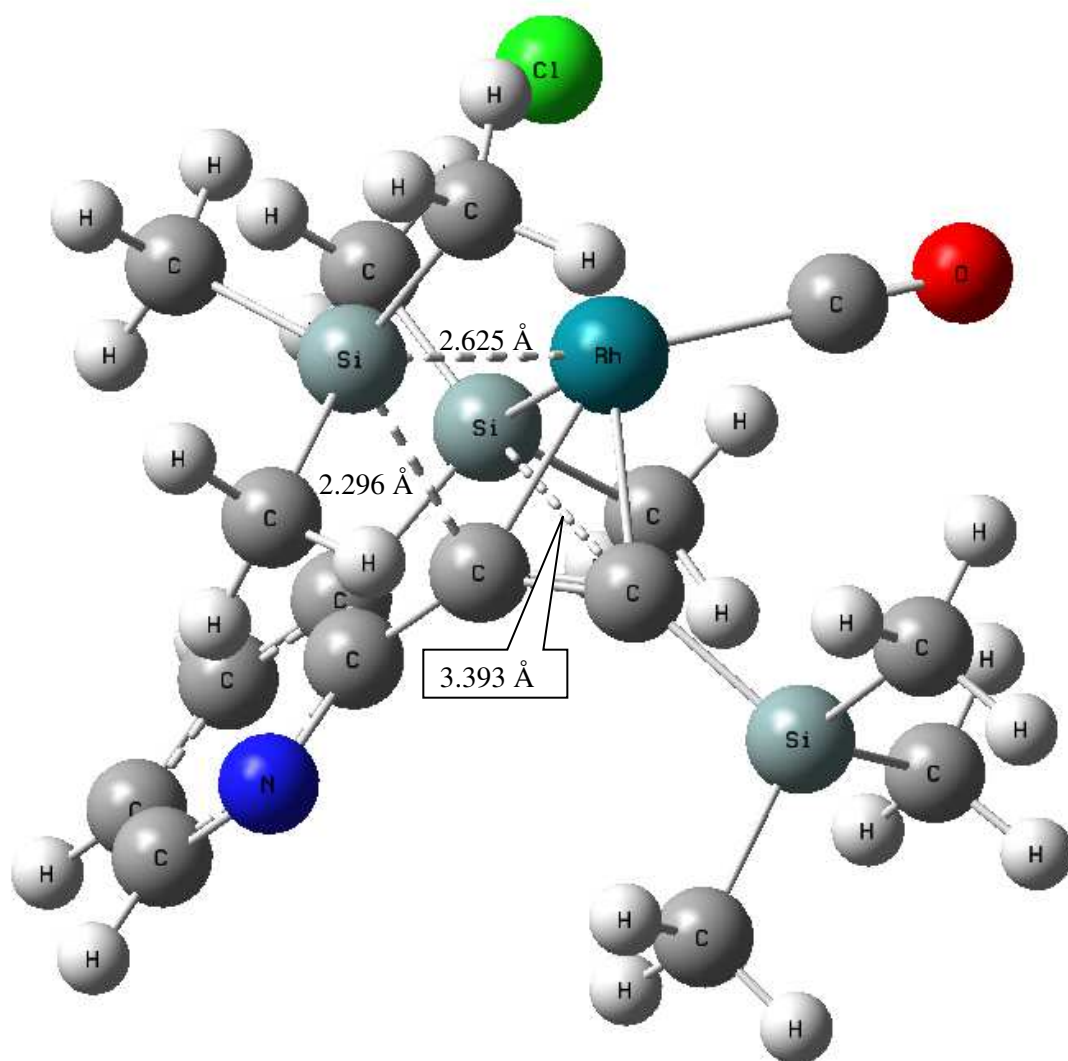


Figure S18. Optimized structure of **TS 1-2(1)** with RhCl(CO) model. **TS 1-2(1)** is the TS between **model 1(1)** and **model 2(1)**.

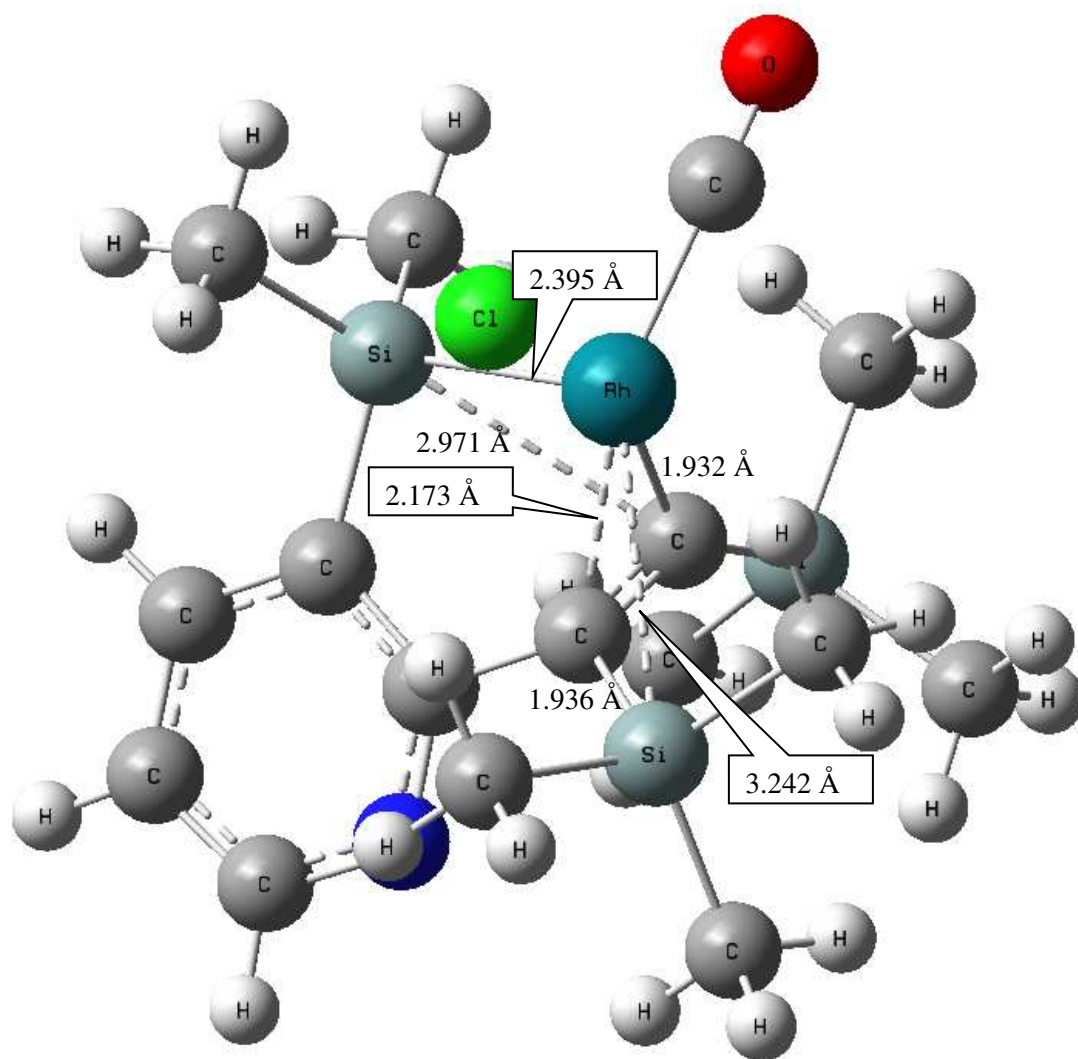


Figure S19. Optimized structure of **model 2(1)** with RhCl(CO) model.

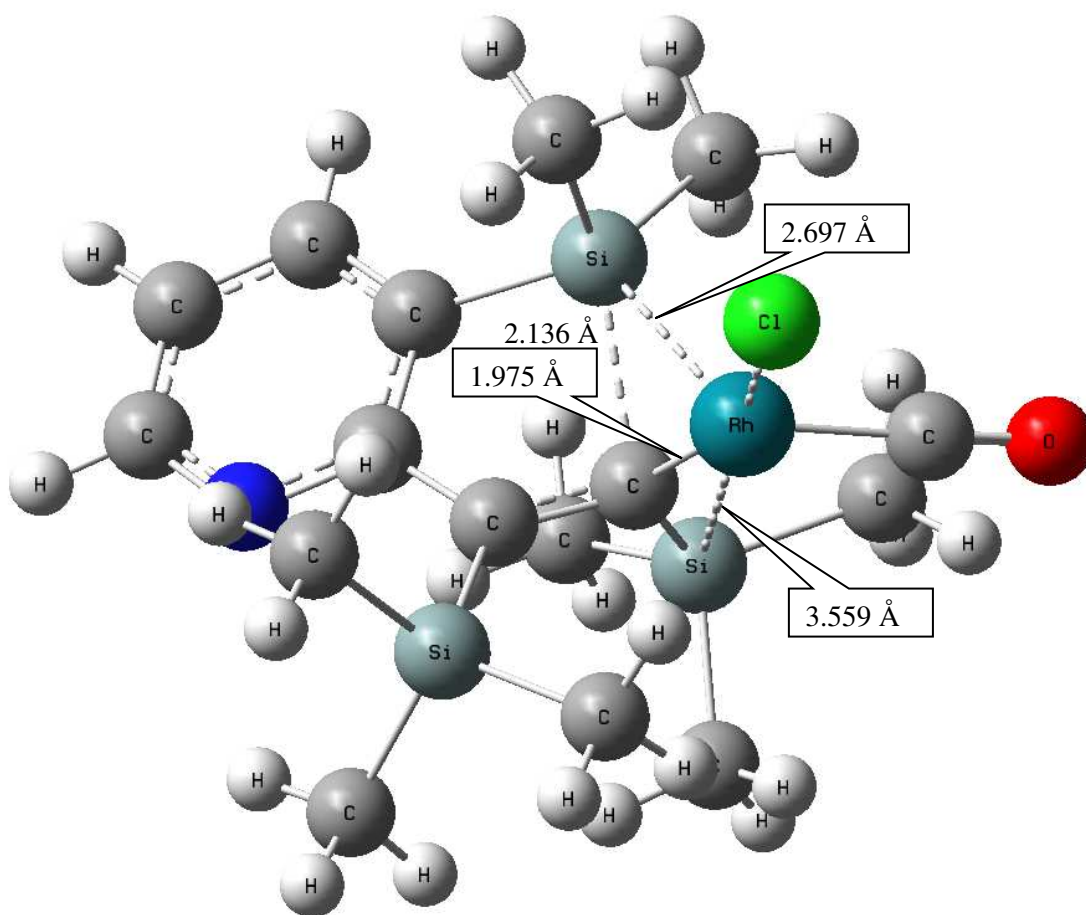


Figure S20. Optimized structure of **TS 2-3(1)** with RhCl(CO) model. **TS 2-3(1)** is the TS between **model 2(1)** and **model 3(1)**.

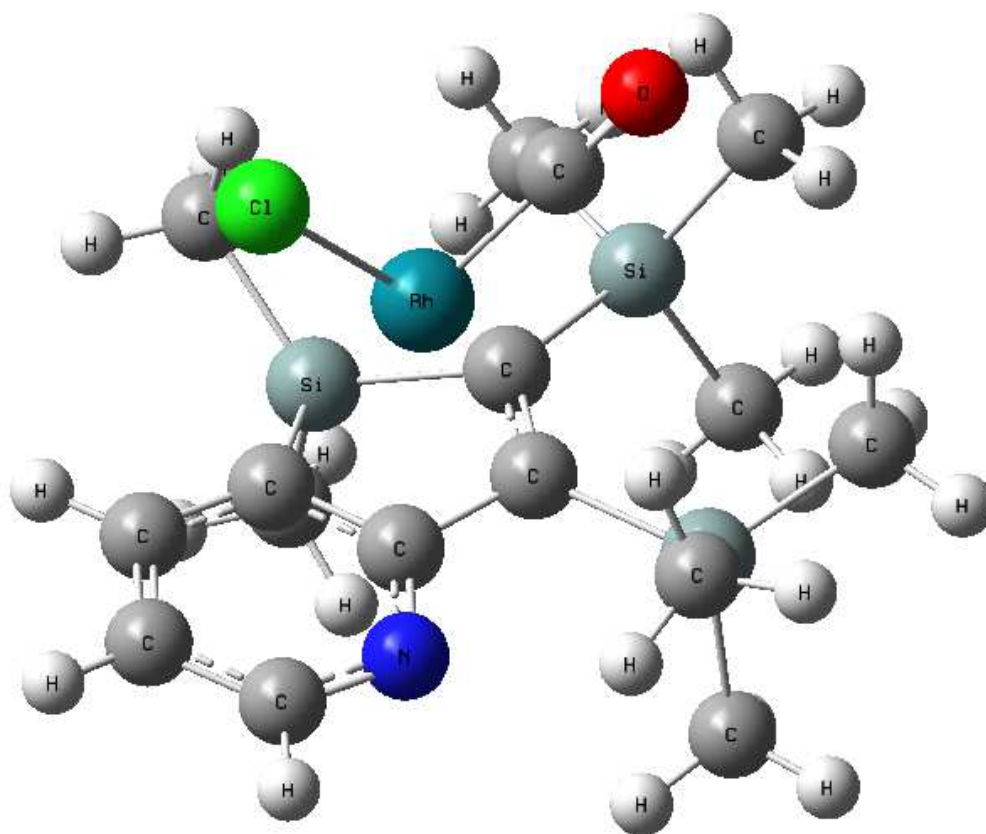


Figure S21. Optimized structure of **model 3(1)** corresponding to combined structure of compound **3** and RhCl(CO).

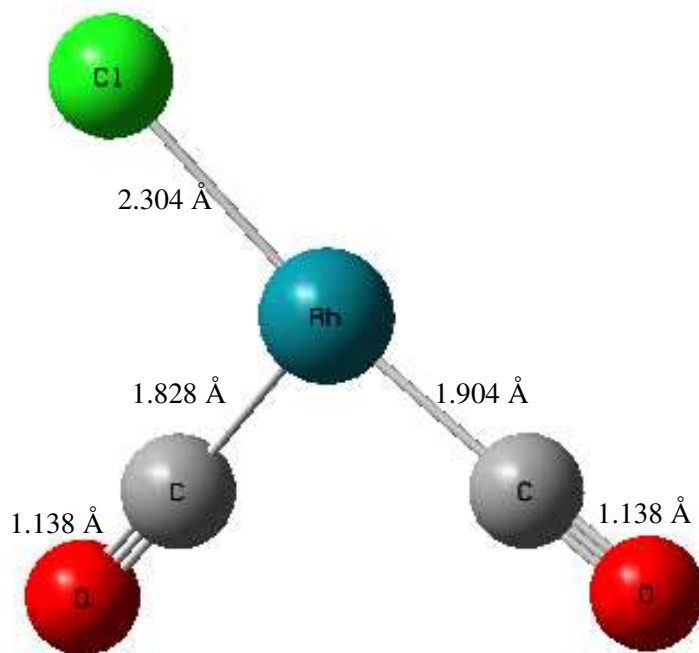


Figure S22. Optimized structure of RhCl(CO)₂.

From **Figures S23** to **S29**, LM and TS structures on trans route with $\text{RhCl}(\text{CO})_2$ model are drawn. For clarity of figures, H atoms are omitted in the drawing.

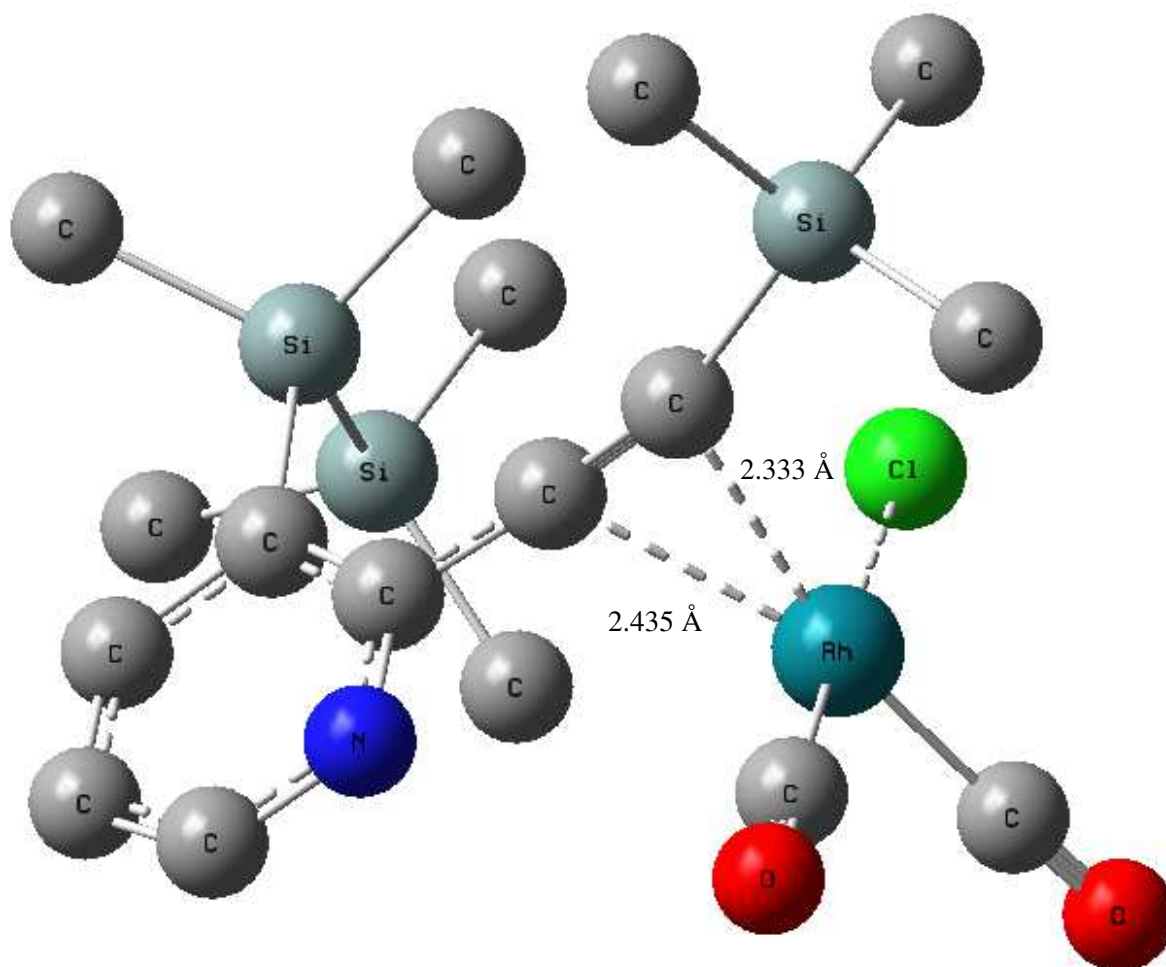


Figure S23. Optimized structure of **model 0(2)**. **Model 0(2)** is a combined structure of **1** and $\text{RhCl}(\text{CO})_2$.

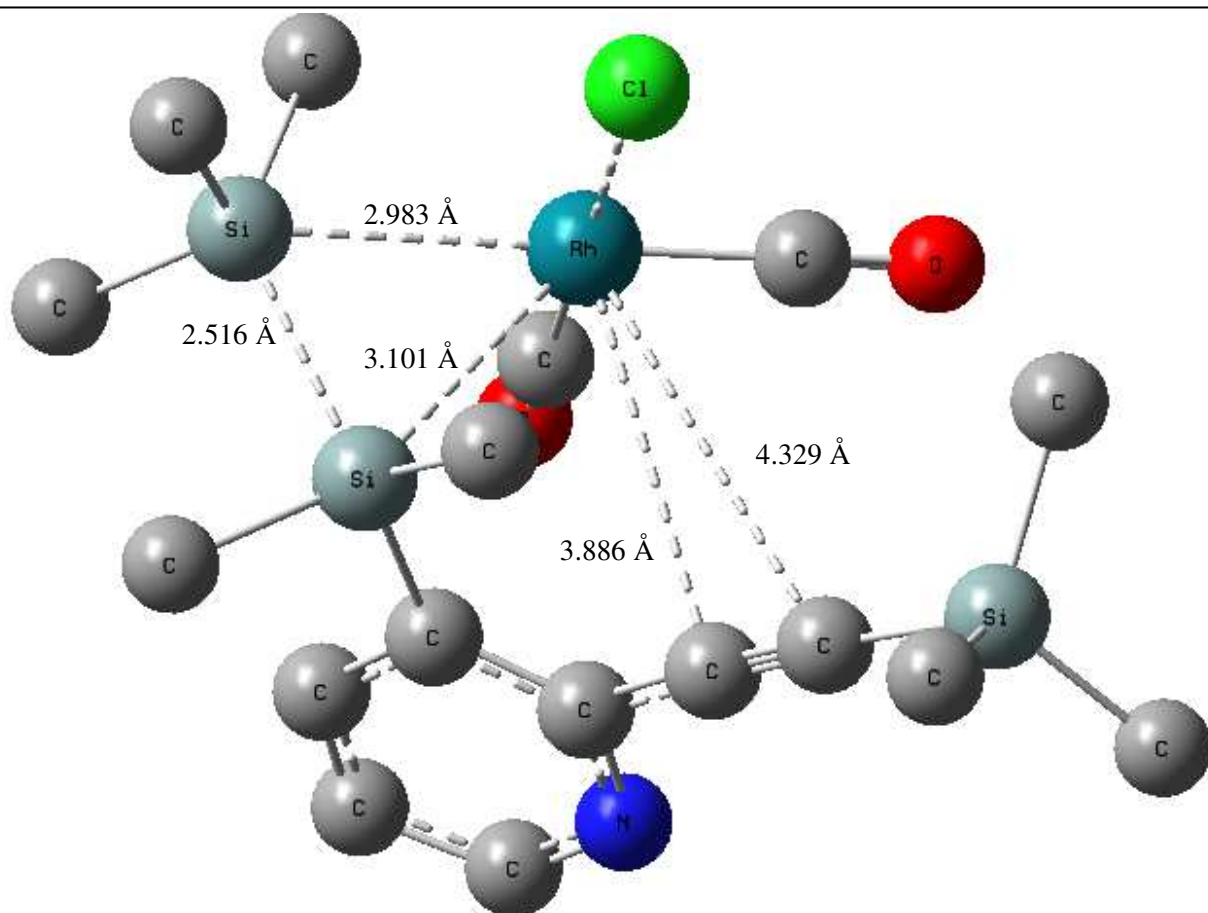


Figure S24. Optimized structure of TS 0-1(2). TS 0-1(2) is the TS between **model 0(2)** and **model 1(2)** with RhCl(CO)₂ model.

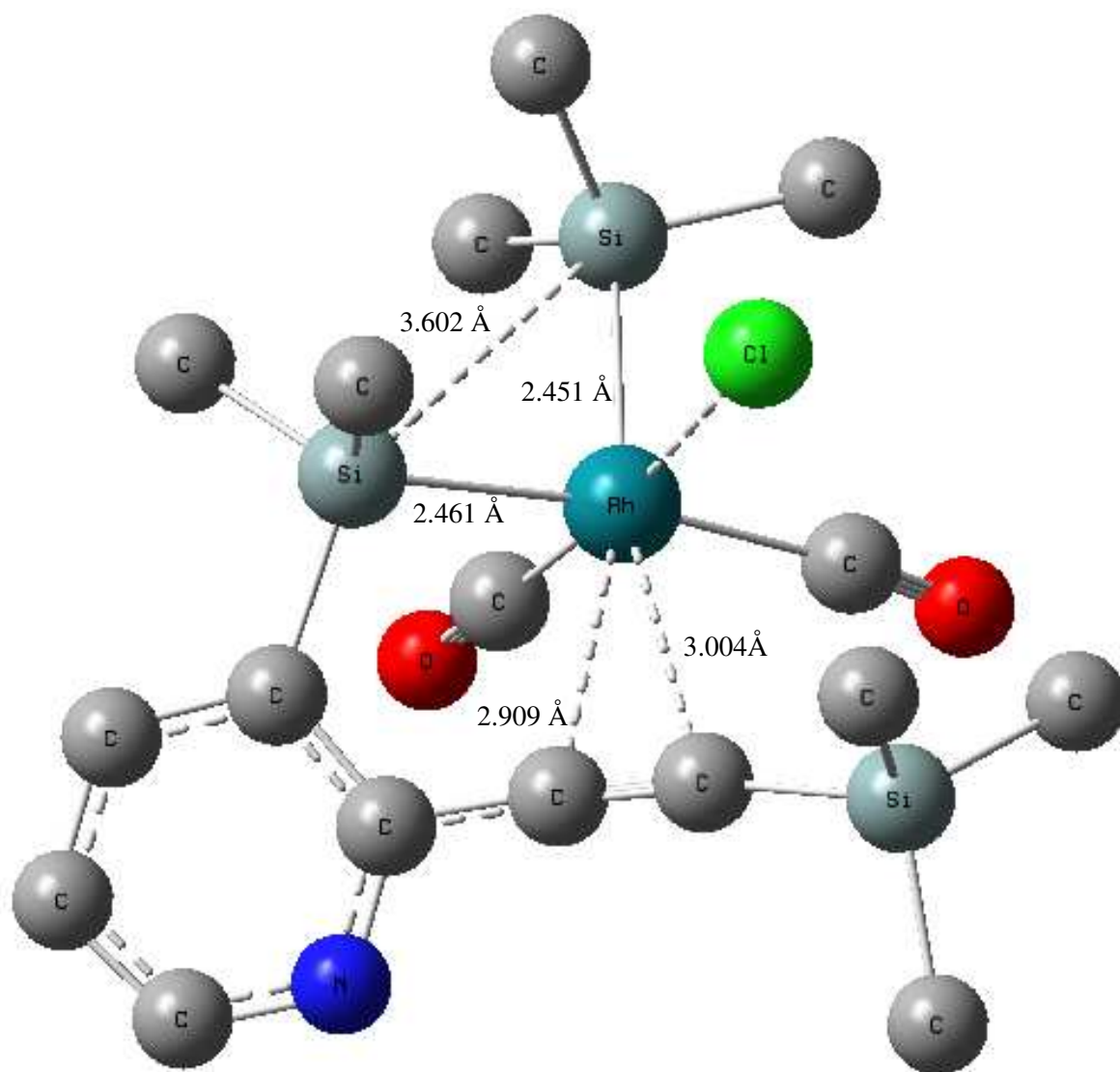


Figure S25. Optimized structure of **model 1(2)** with RhCl(CO)₂ model.

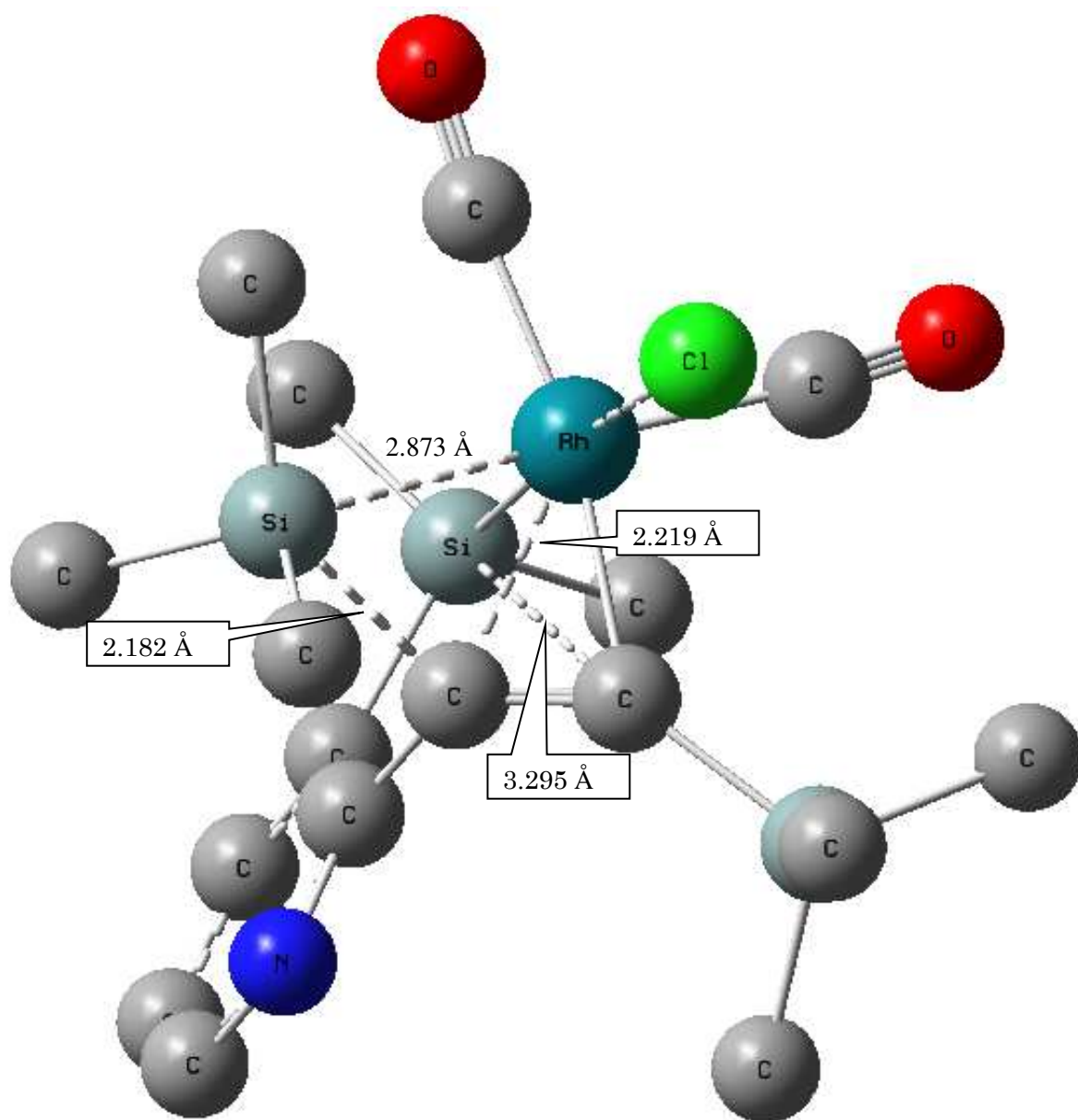


Figure S26. Optimized structure of **TS 1-2(2)**. **TS 1-2(2)** is the TS between **model 1(2)** and **model 2(2)** with RhCl(CO)₂ model.

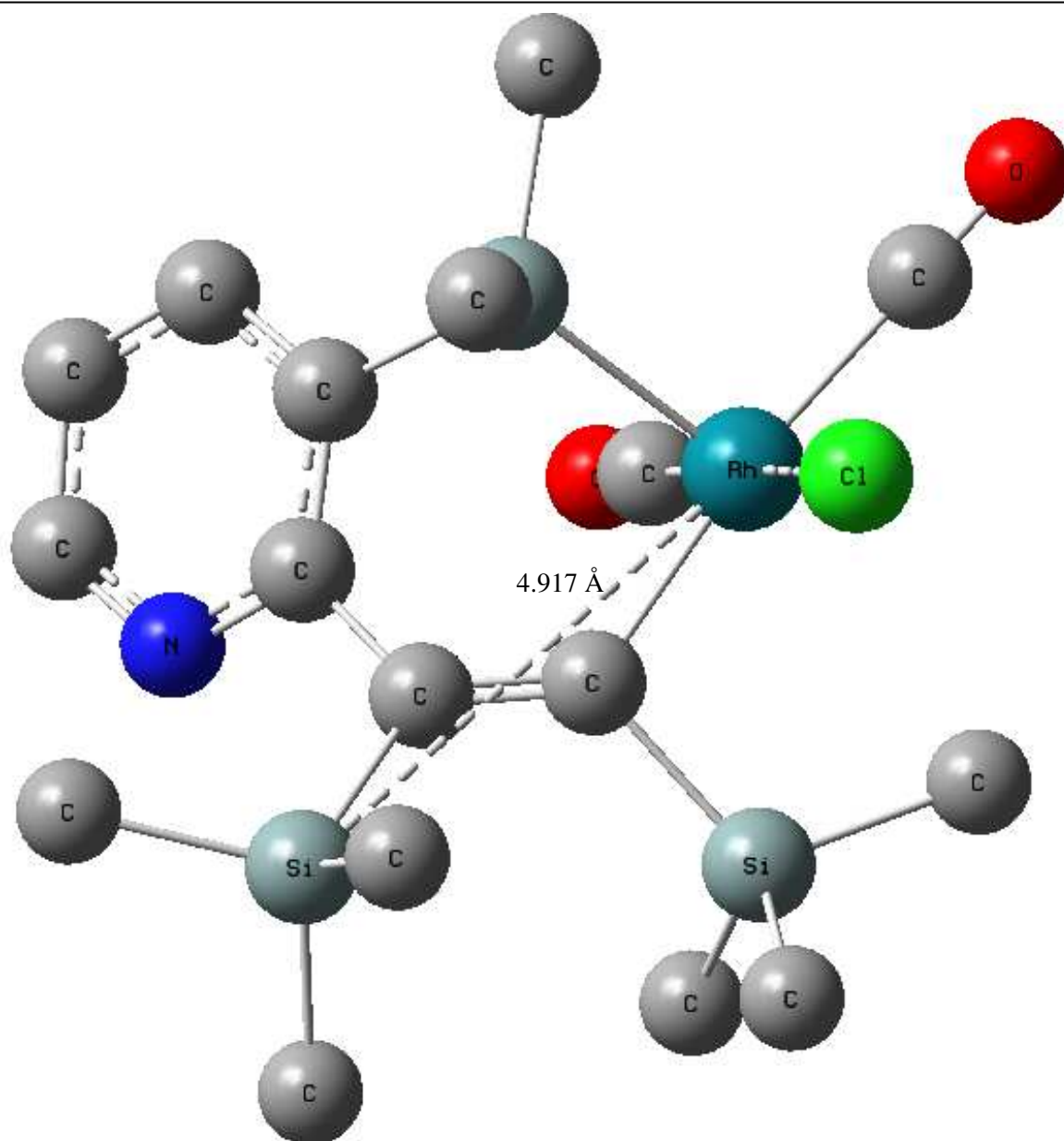


Figure S27. Optimized structure of **model 2(2)** with RhCl(CO)₂ model.

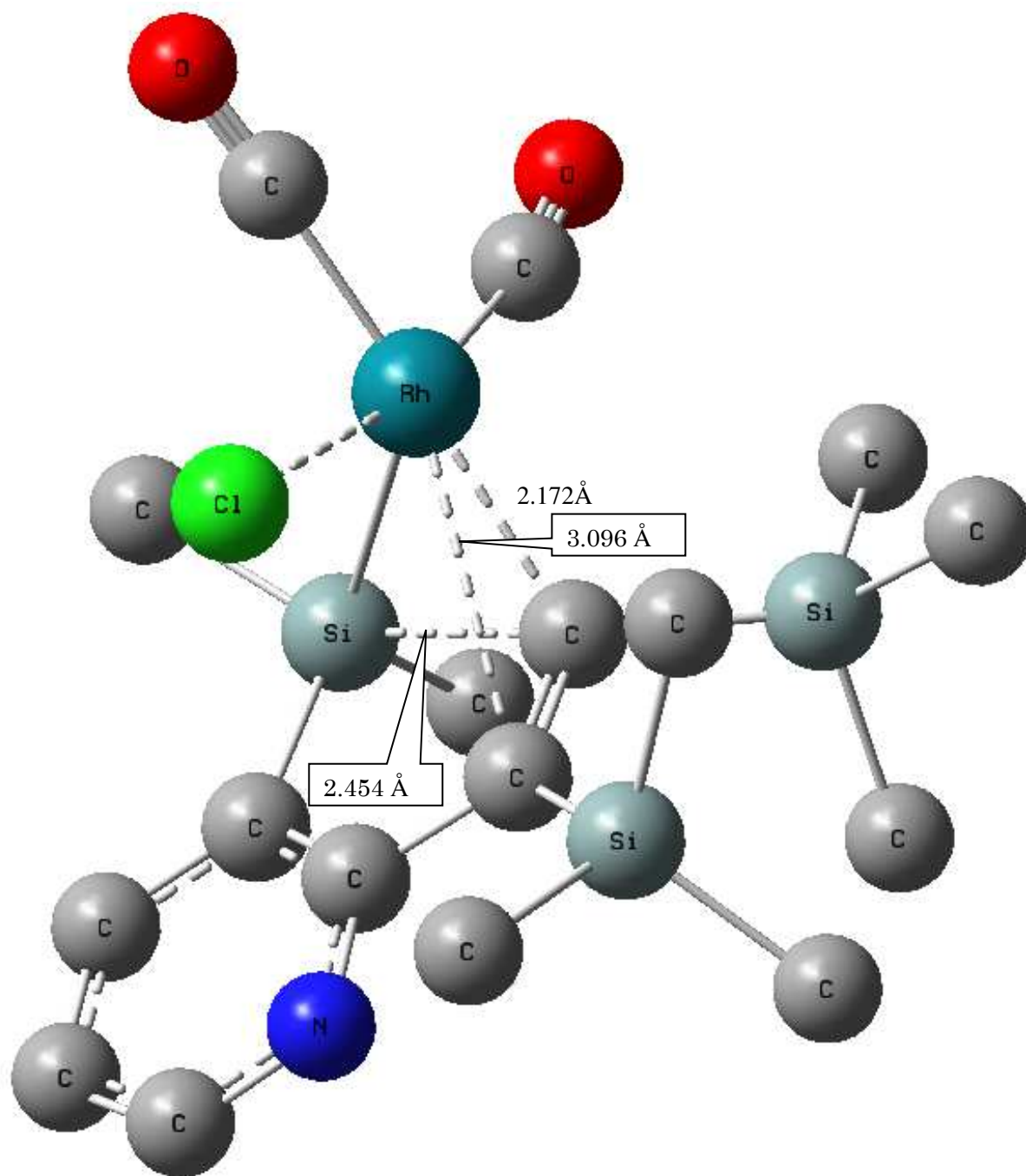


Figure S28. Optimized structure of **TS 2-3(2)**. **TS 2-3(2)** is the TS between **model 2(2)** and **model 3(2)** with $\text{RhCl}(\text{CO})_2$ model.

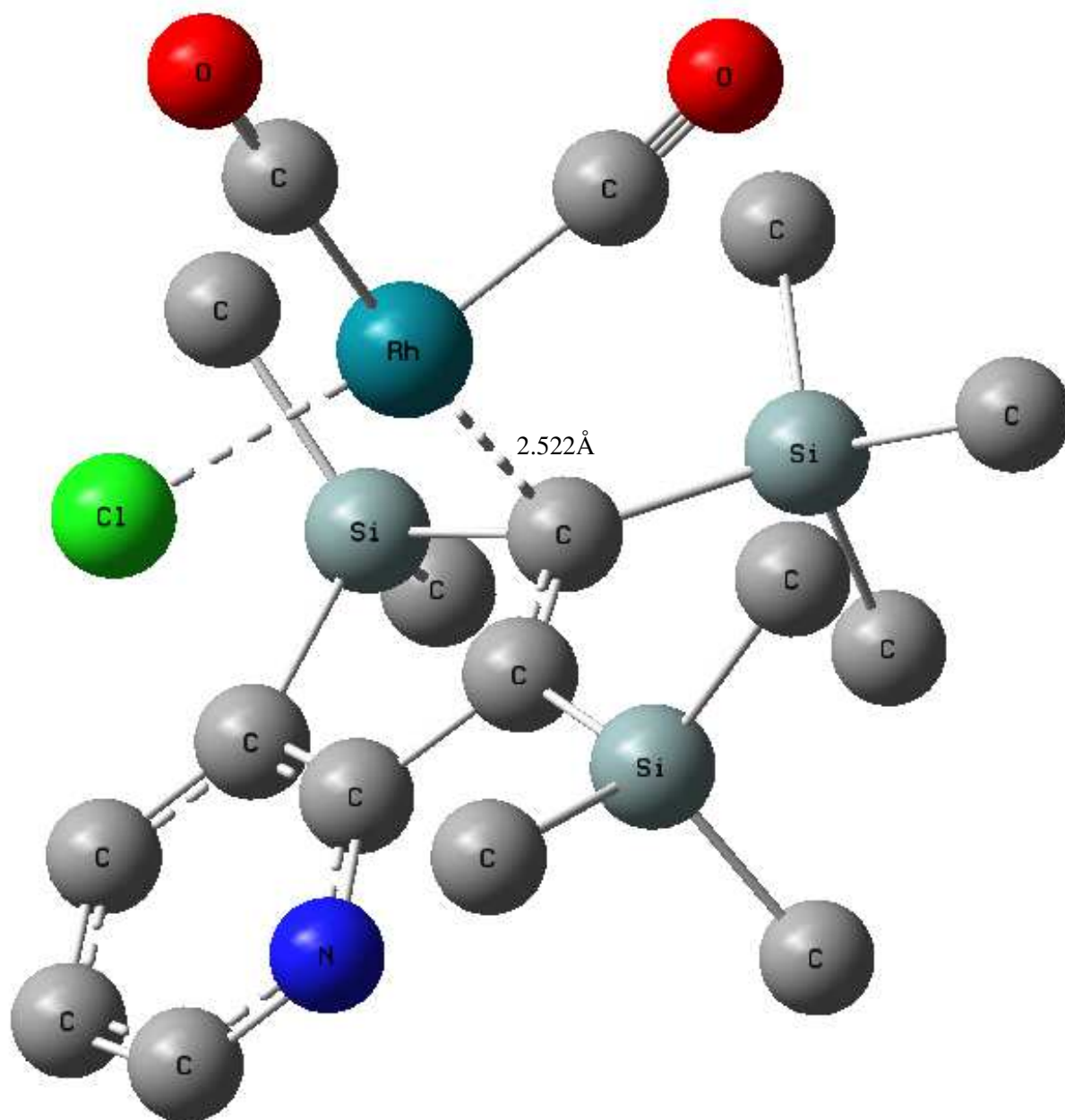
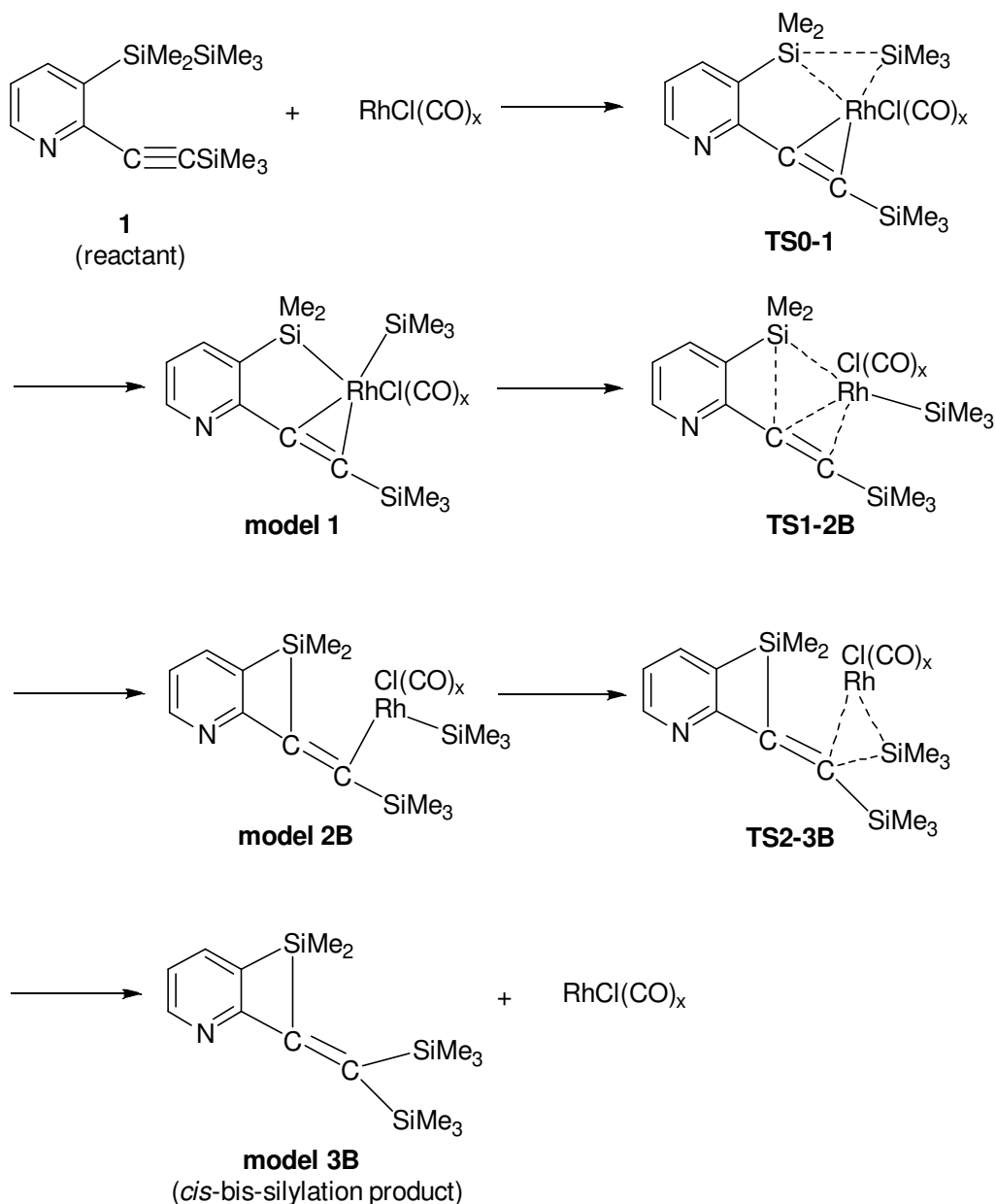
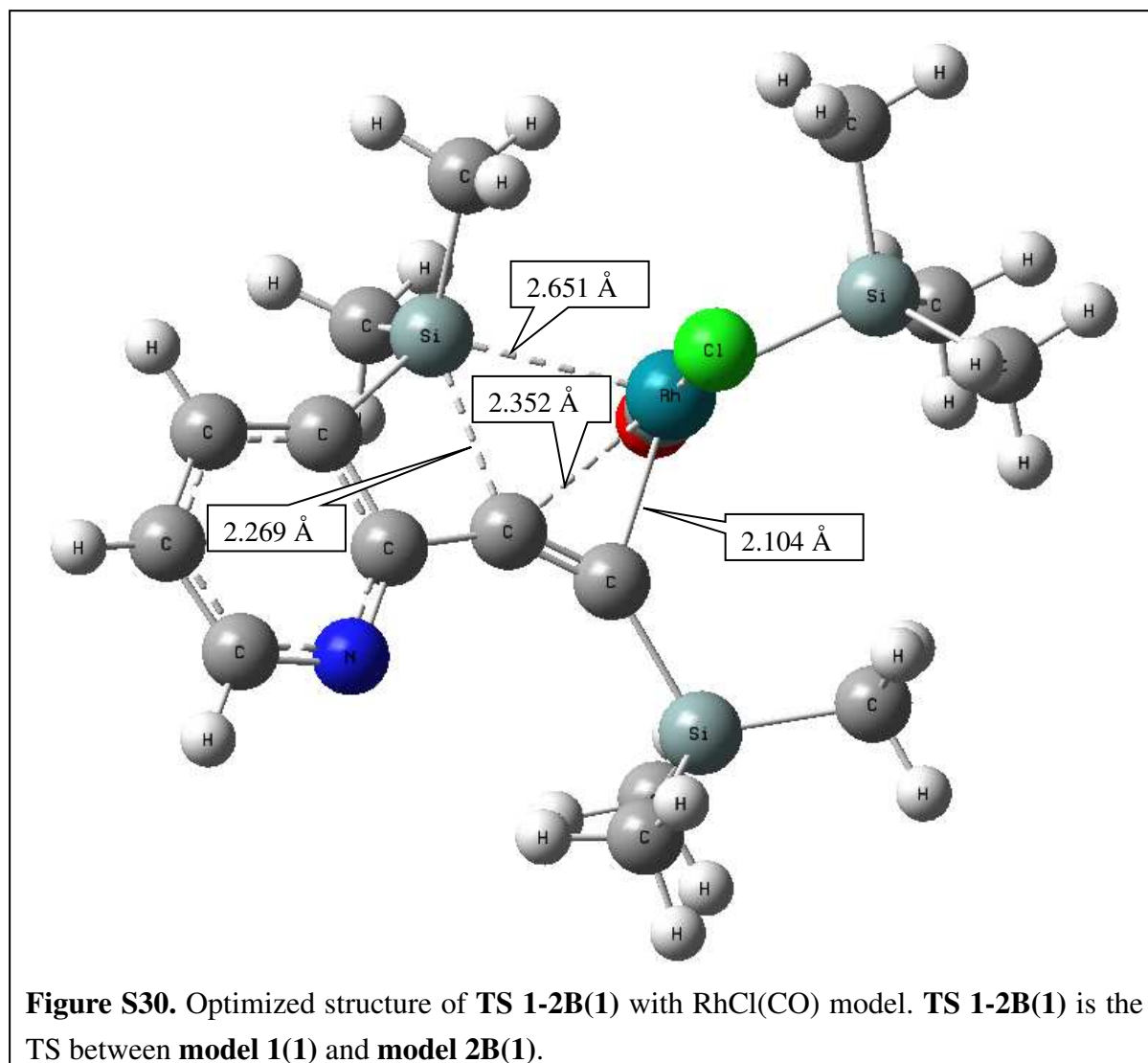


Figure S29. Optimized structure of **model 3(2)** with $\text{RhCl}(\text{CO})_2$ model.



Scheme S1. Proposed Mechanism for Production of *cis*-bis-silylation product. The structures from **model 0** to **model 1** are common to *trans*-bis-silylation product formation route. Each LM and TS names are discriminated by adding suffix “B” from those on *trans*-bis-silylation product formation route.

From **Figures S30 to S33**, LM and TS structures on cis route with RhCl(CO) model are drawn.



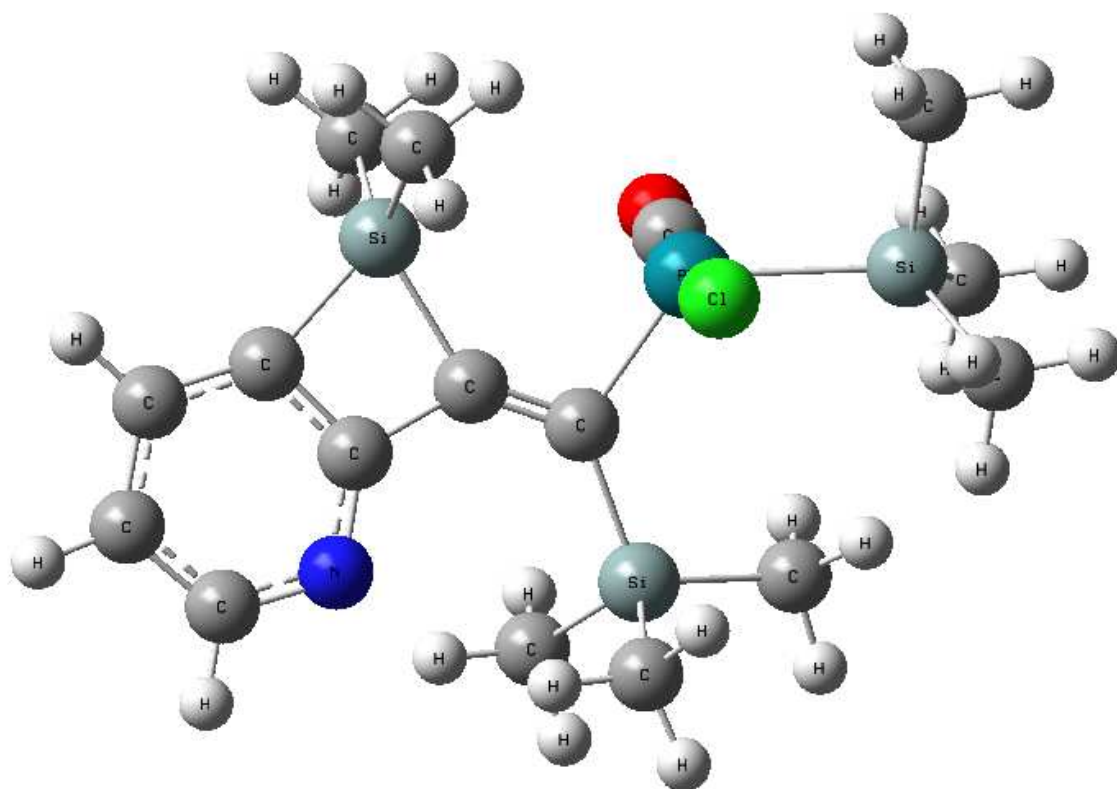


Figure S31. Optimized structure of **model 2B(1)** with RhCl(CO) model.

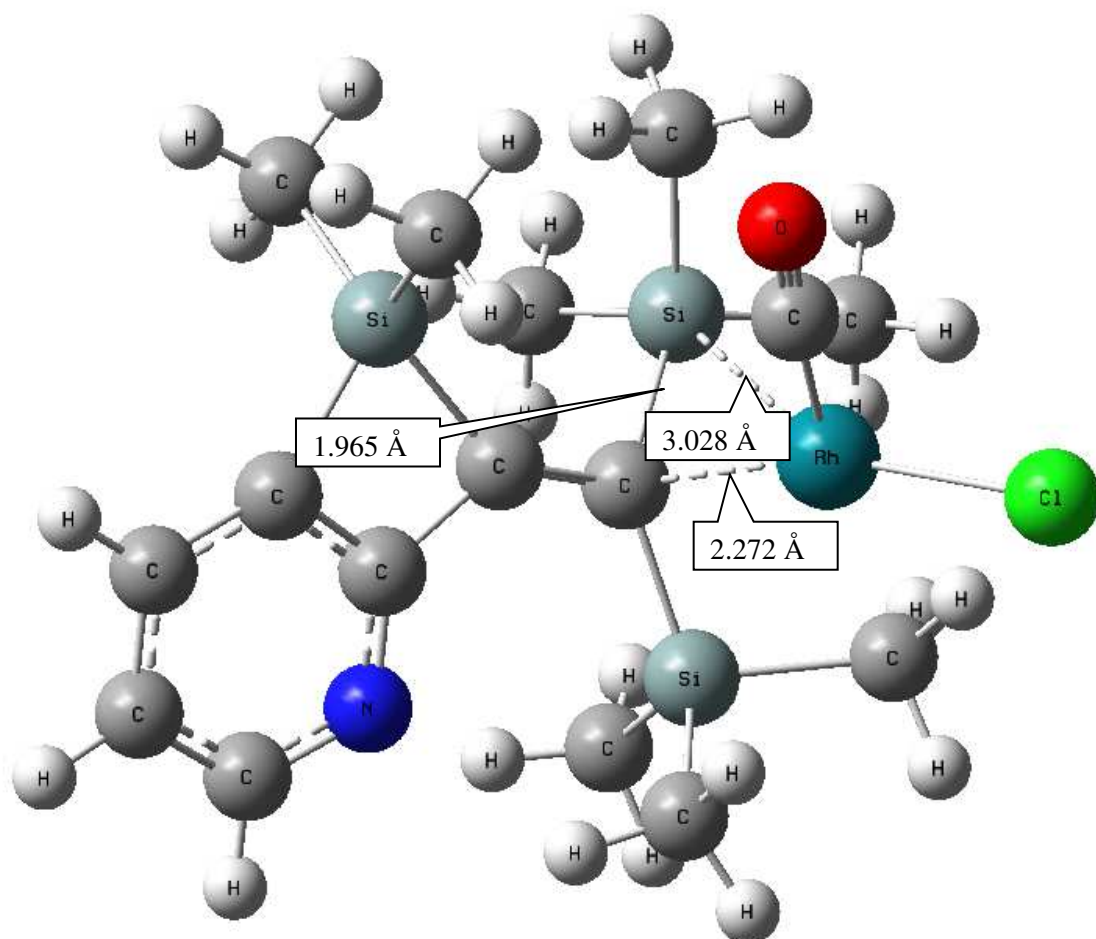


Figure S32. Optimized structure of TS 2-3B(1) with RhCl(CO) model. TS 2-3B(1) is the TS between **model 2B(1)** and **model 3B(1)**.

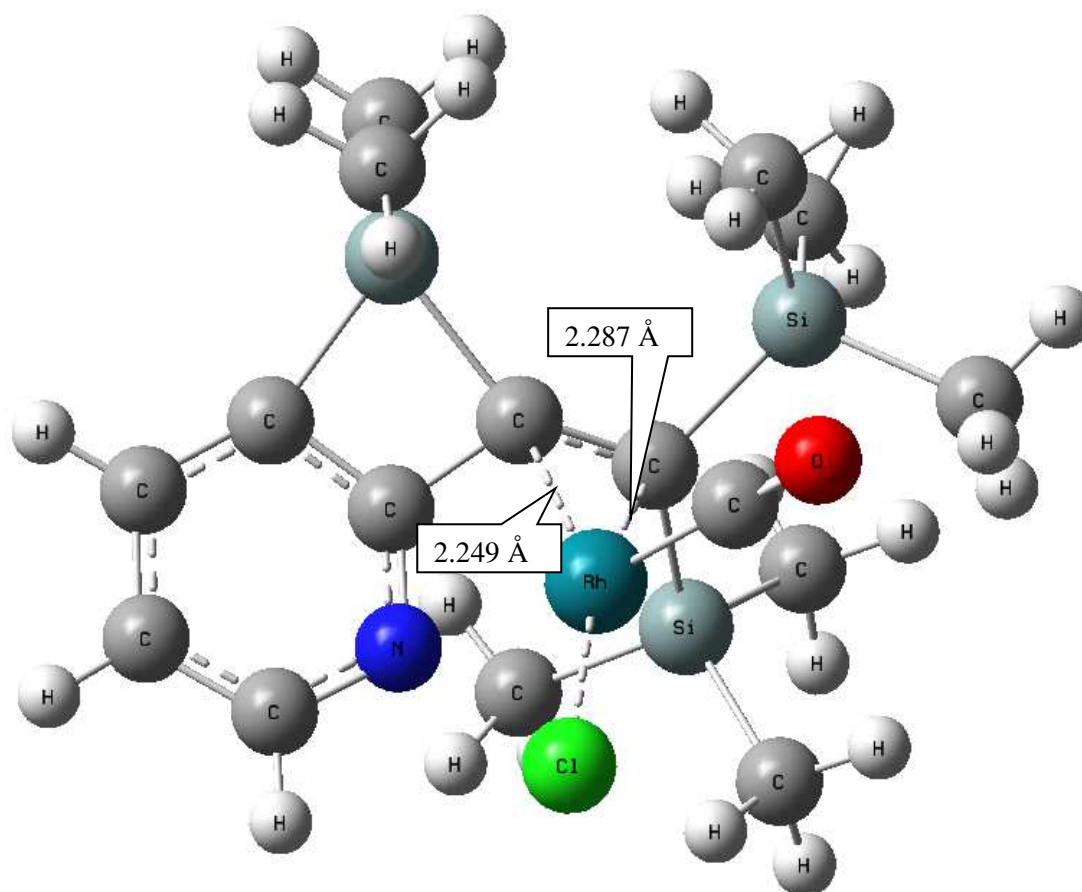
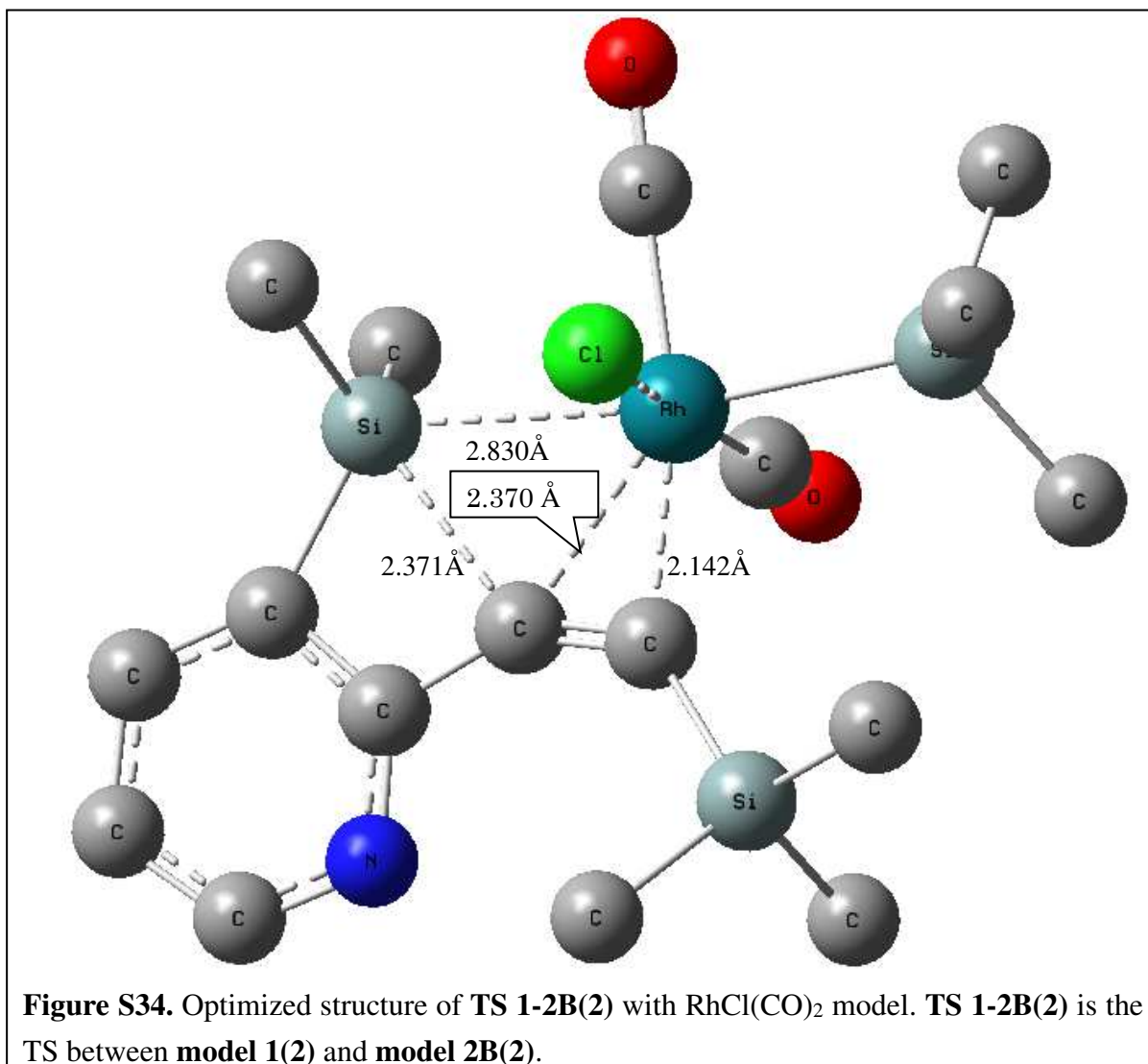


Figure S33. Optimized structure of **model 3B(1)** corresponding to combined structure of *cis*-bis-silylation product and RhCl(CO).

From **Figures S34** to **S37**, LM and TS structures on cis route with $\text{RhCl}(\text{CO})_2$ model are drawn. For clarity of figures, H atoms are omitted in the drawing.



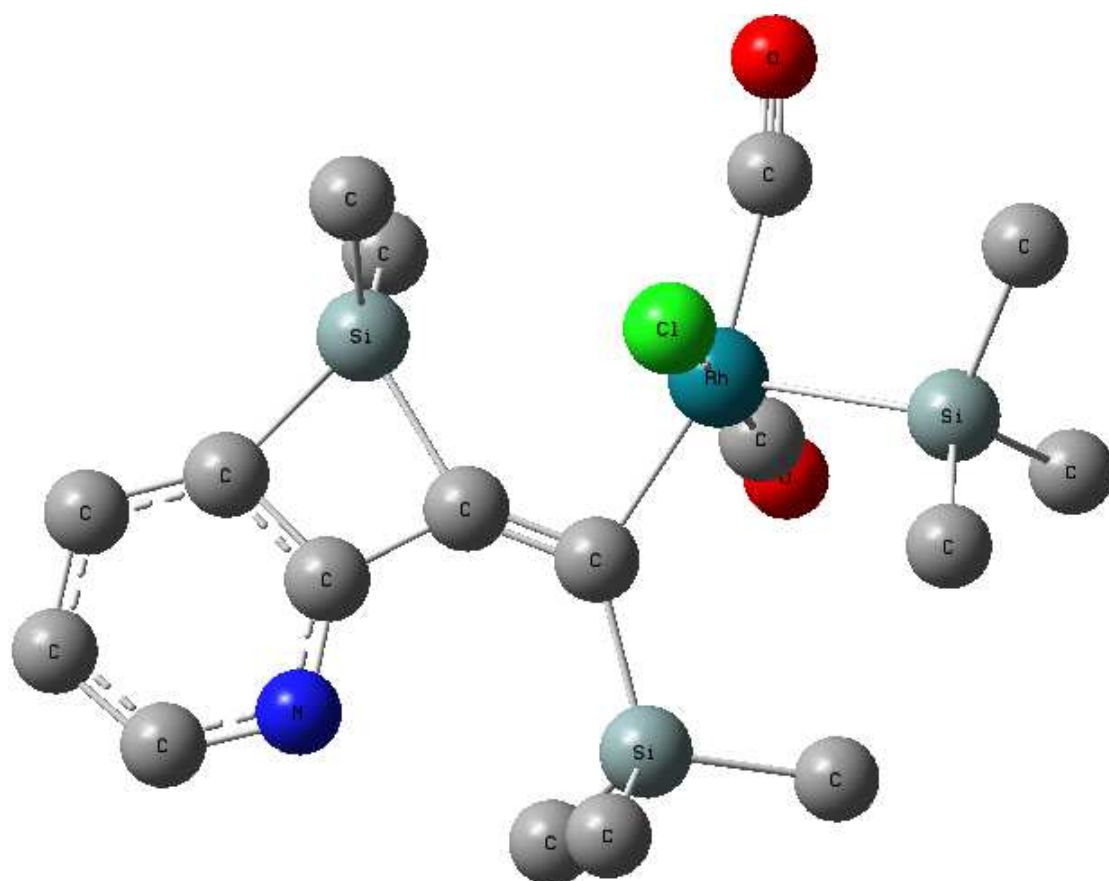


Figure S35. Optimized structure of **model 2B(2)** with RhCl(CO)₂ model.

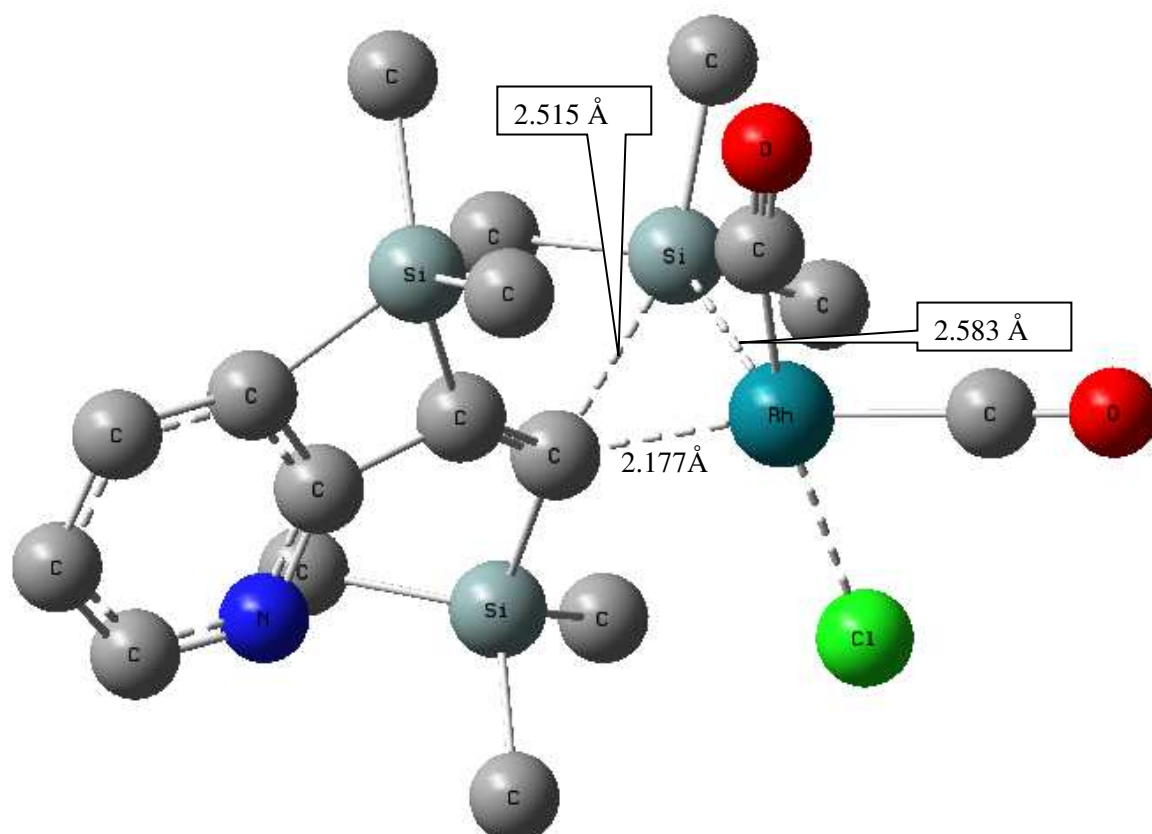


Figure S36. Optimized structure of **TS 2-3B(2)** with RhCl(CO)_2 model. **TS 2-3B(2)** is the TS between **model 2B(2)** and **model 3B(2)**.

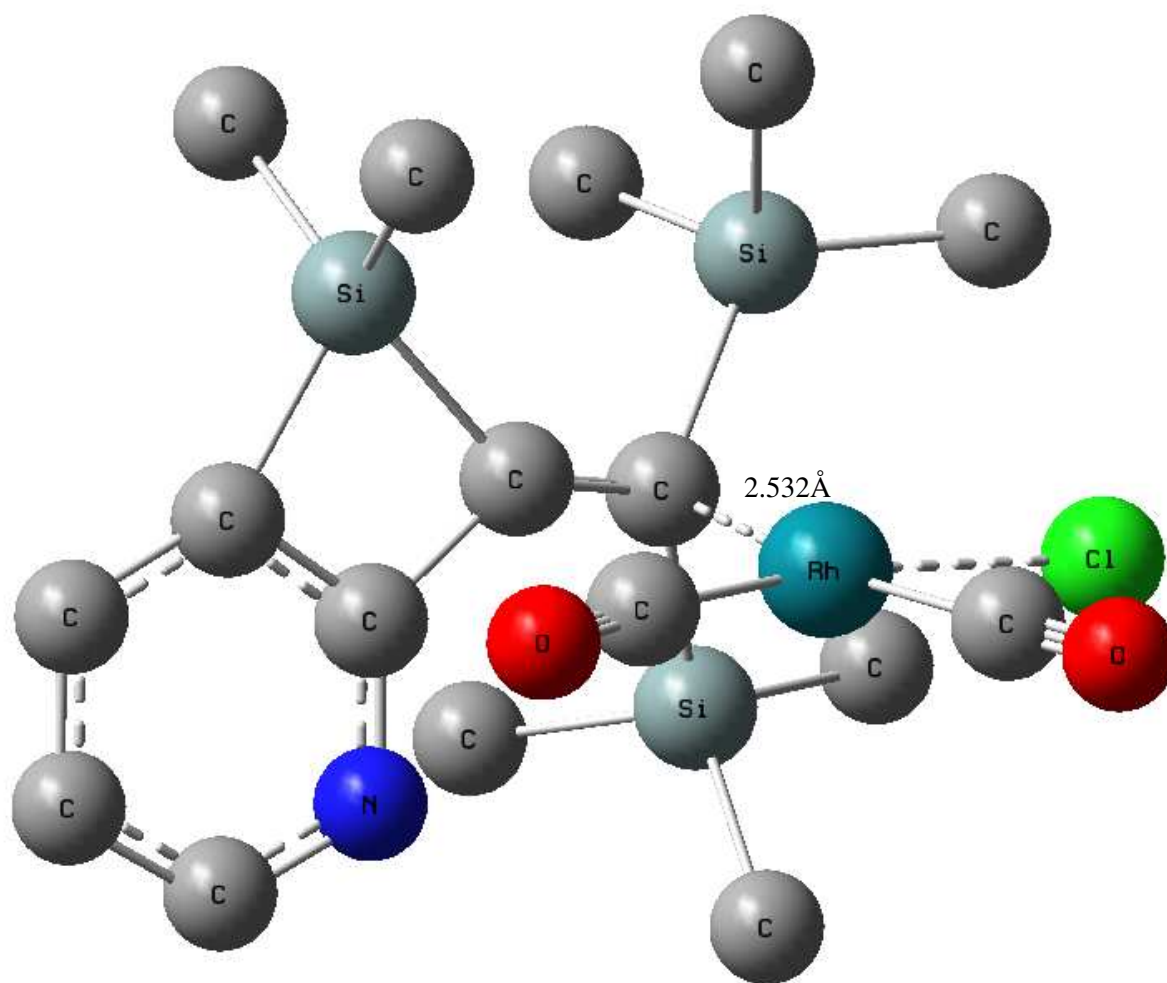


Figure S37. Optimized structure of **model 3B(2)** corresponding to combined structure of *cis*-bis-silylation product and $\text{RhCl}(\text{CO})_2$.