Supporting Information

Revisiting the Iridacycle-Catalyzed Hydrosilylation of Enolizable Imines.

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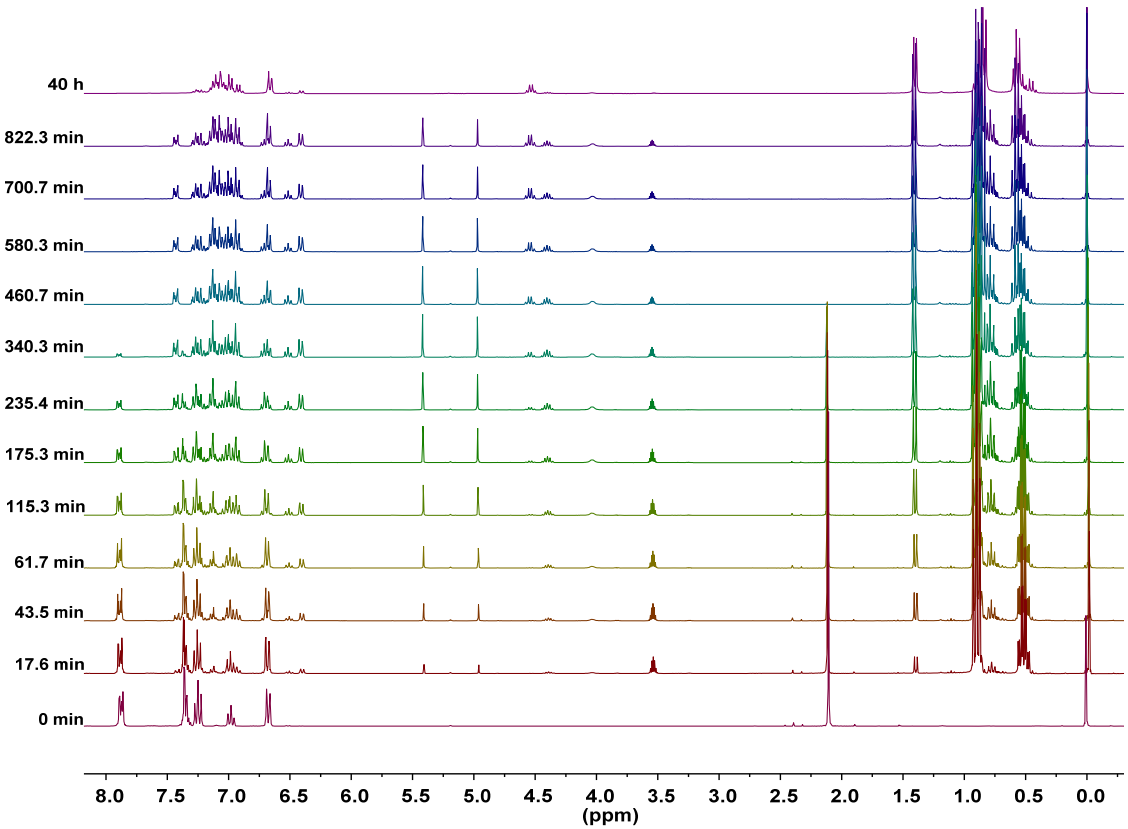


Fig S1. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** (300 MHz). Reaction conditions: **1** (0.13 mg, 0.00025 mmol), $NaBArF_{24}$ (0.46 mg, 0.0005 mmol), N-(1-phenylethylidene)aniline (50.9 mg, 0.2591 mmol), Et_3SiH (50.0 µL, 0.3110 mmol), 0.7 mL CD_2Cl_2, internal capillary TMS (10% v/v in $CDCl_3$).

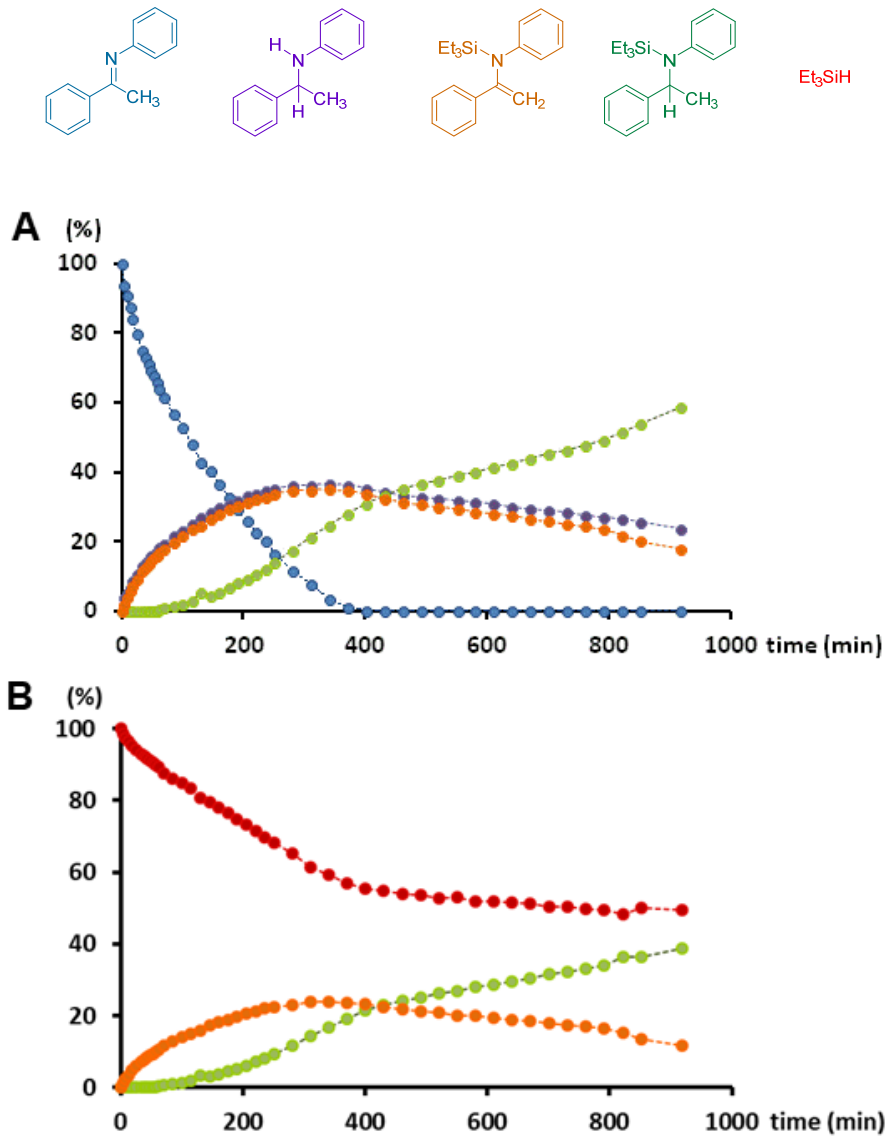


Fig S2. Reaction profile of **A**) imine-derived and **B**) silane-containing products, according to *in situ* ^{1}H NMR spectroscopy. Reaction conditions: **1** (0.13 mg, 0.00025 mmol), $NaBArF_{24}$ (0.46 mg, 0.0005 mmol), N-(1-phenylethylidene)aniline (50.9 mg, 0.2591 mmol), Et_3SiH (50.0 µL, 0.3110 mmol), 0.5 mL CD_2Cl_2, internal capillary TMS (10% v/v in $CDCl_3$).

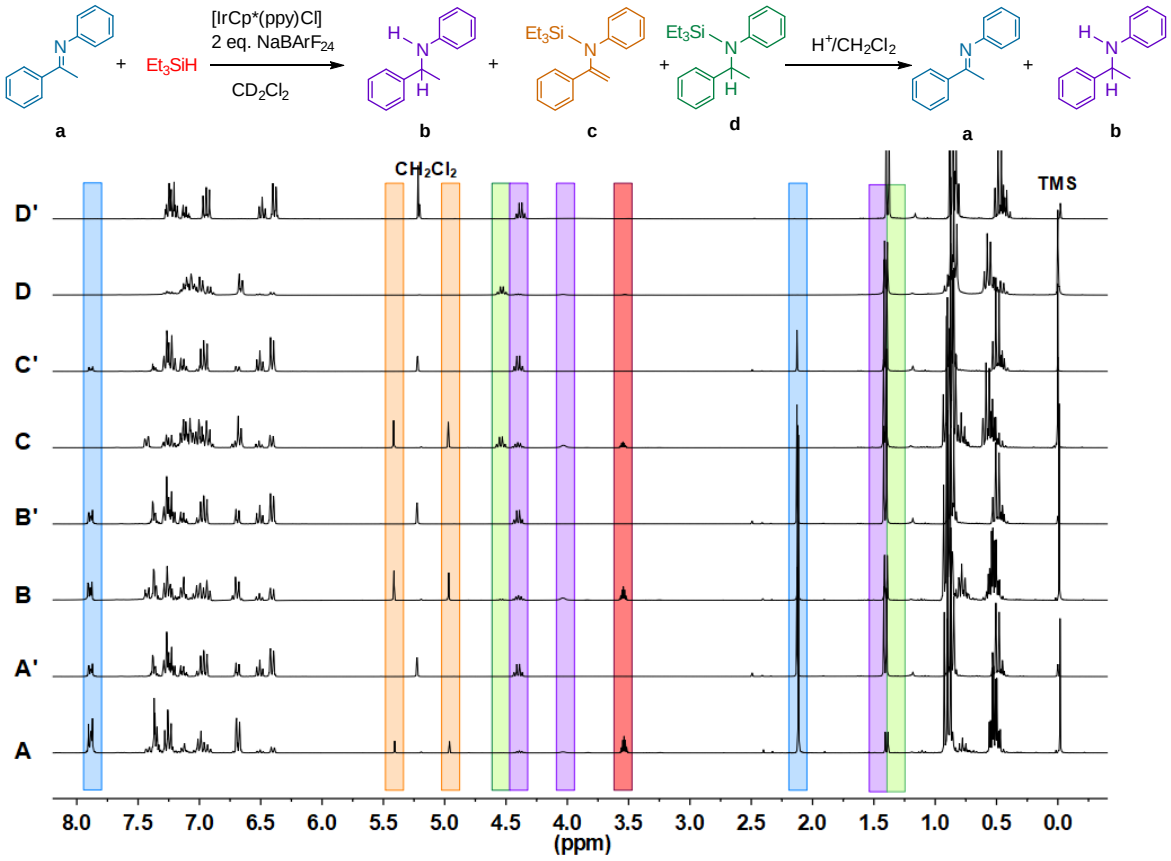


Fig S3. *In situ* ^{1}H NMR spectra (A, 25 min; B, 130 min; C, 791 min; D, 24 h) and after acidic work-up (A', B', C', D'). Reaction conditions: precatalyst **1** (0.13 mg, 0.00025 mmol), $NaBArF_{24}$ (0.46 mg, 0.0005 mmol), N-(1-phenylethylidene)aniline (50.9 mg, 0.2591 mmol), Et_3SiH (50.0 µL, 0.3110 mmol), 0.7 mL CD_2Cl_2, internal capillary TMS (10% v/v in $CDCl_3$).

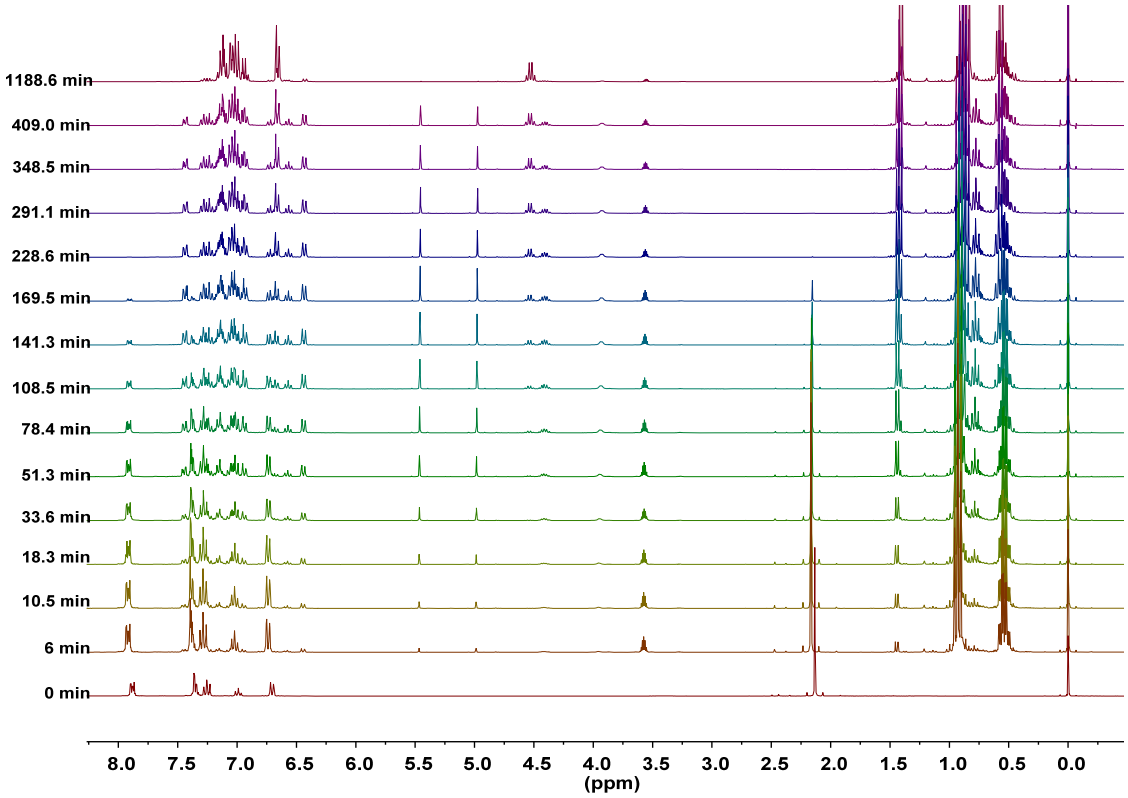


Fig S4. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** (300 MHz). Reaction conditions: **1** (0.10 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

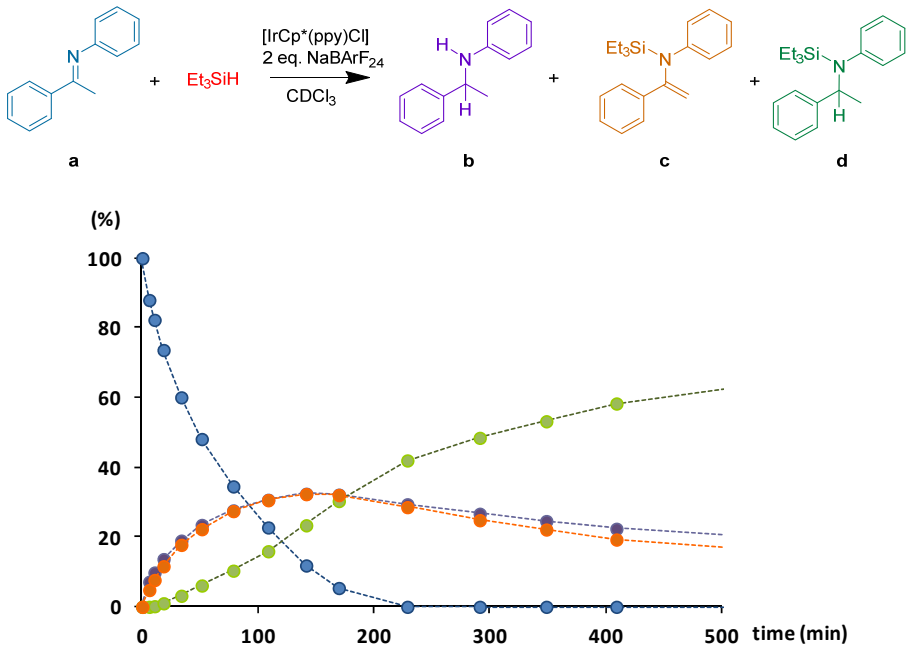


Fig S5. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: **1** (0.10 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

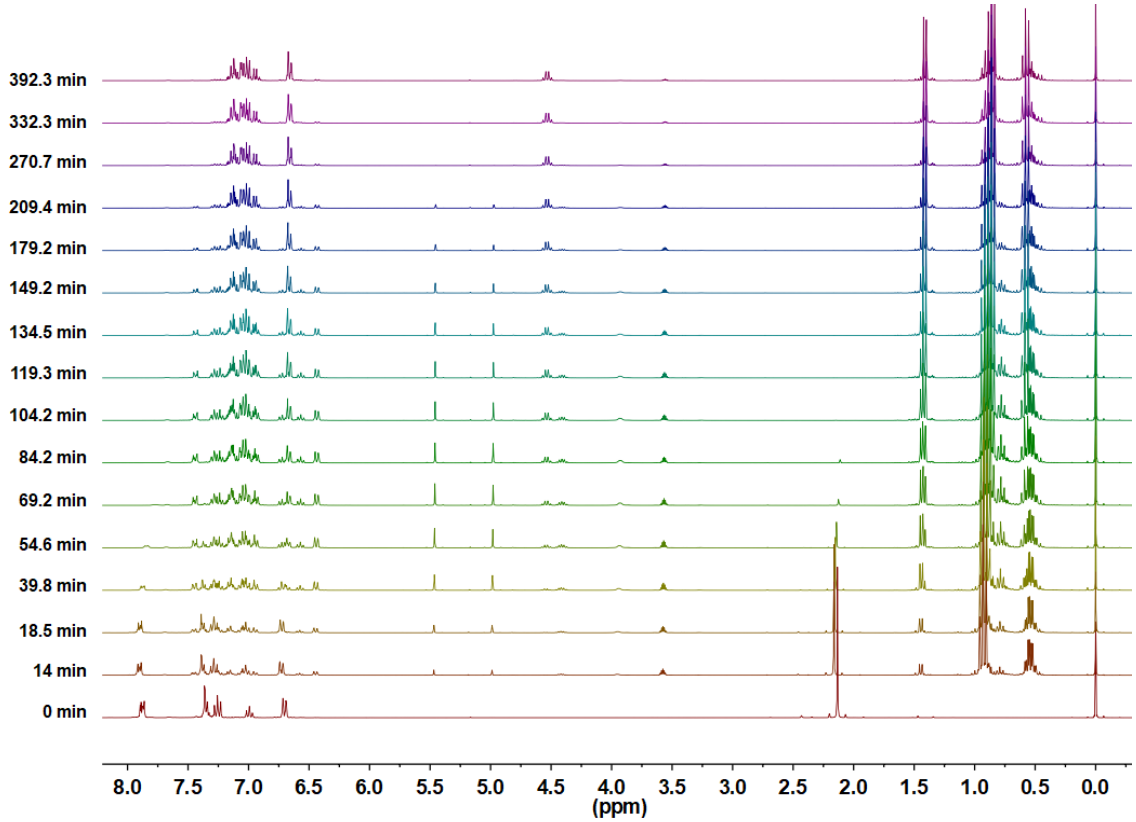


Fig S6. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, int ernal capillary TMS (10% v/v in $CDCl_3$).

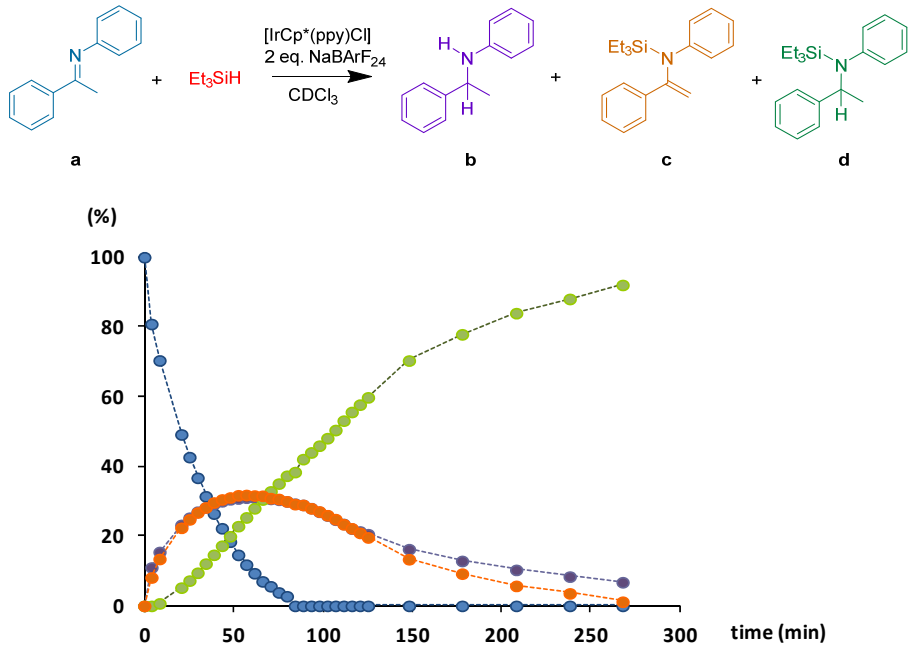


Fig S7. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

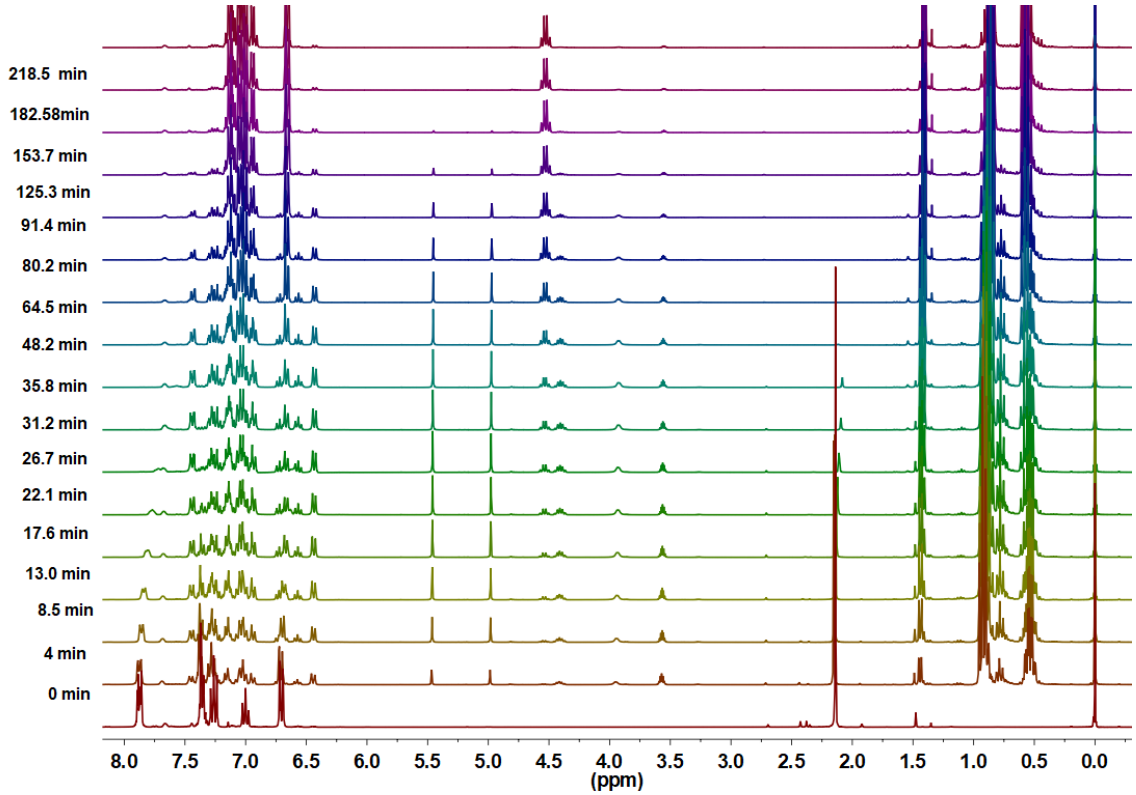


Fig S8. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** (300 MHz). Reaction conditions: precatalyst **1** (1.00 mg, 0.0019 mmol), $NaBArF_{24}$ (3.42 mg, 0.0039 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, int ernal capillary TMS (10% v/v in $CDCl_3$).

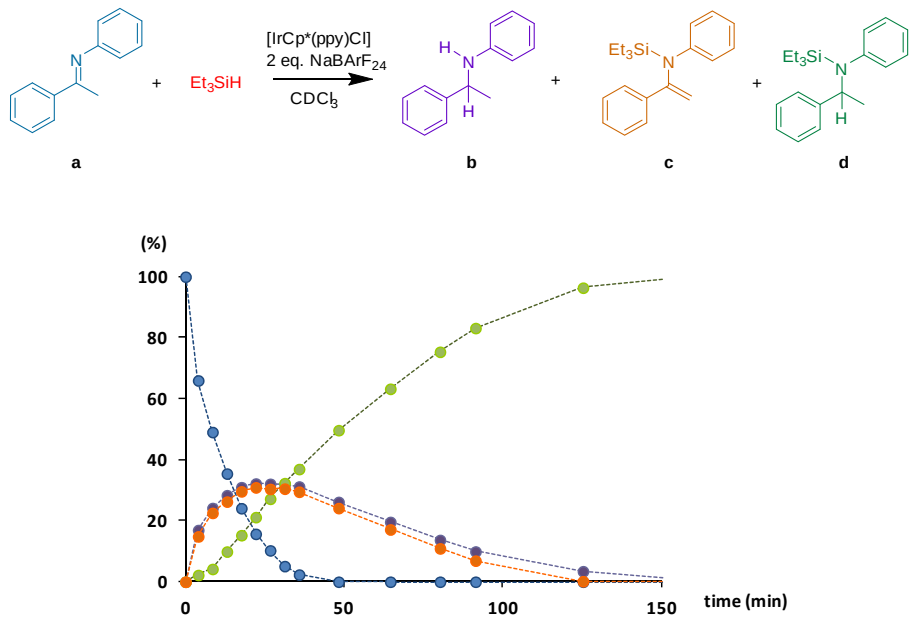


Fig S9. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (1.00 mg, 0.0019 mmol), $NaBArF_{24}$ (3.42 mg, 0.0039 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

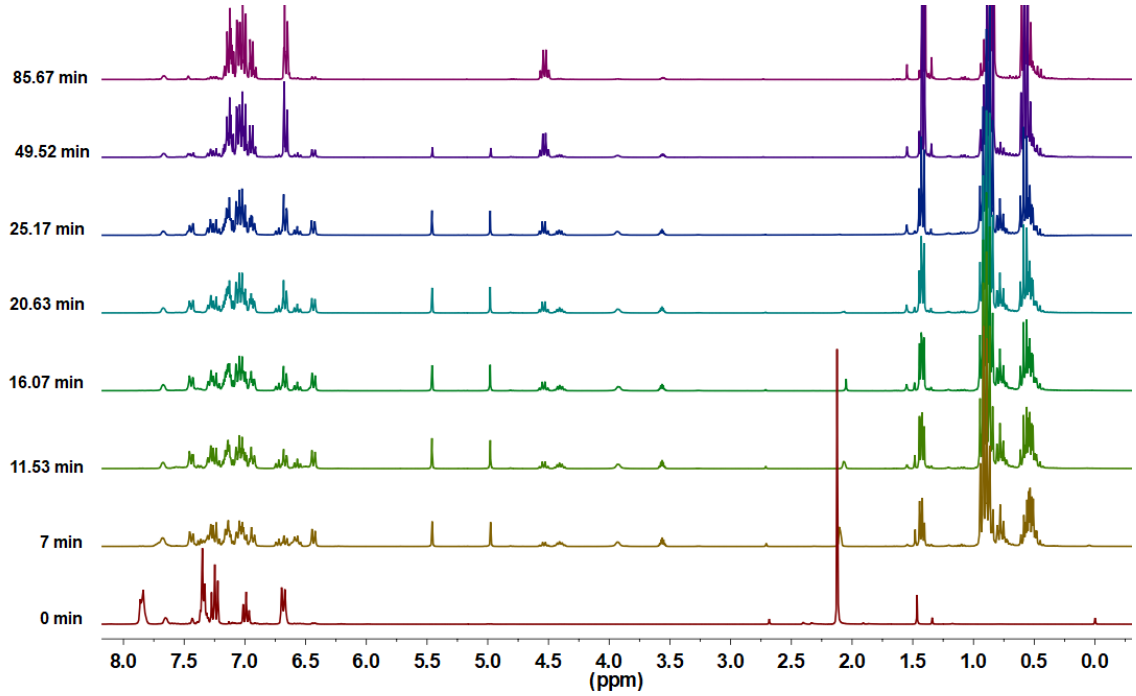


Fig S10. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** (300 MHz). Reaction conditions: precatalyst **1** (2.00 mg, 0.0039 mmol), $NaBArF_{24}$ (6.84 mg, 0.0077 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, int ernal capillary TMS (10% v/v in $CDCl_3$).

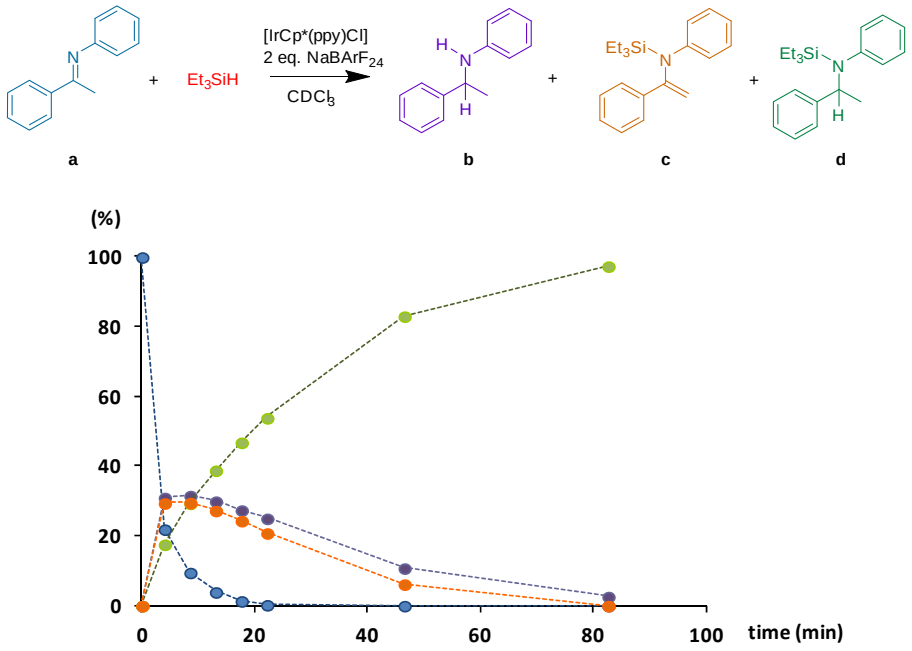


Fig S11. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (2.00 mg, 0.0039 mmol), $NaBArF_{24}$ (6.84 mg, 0.0077 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

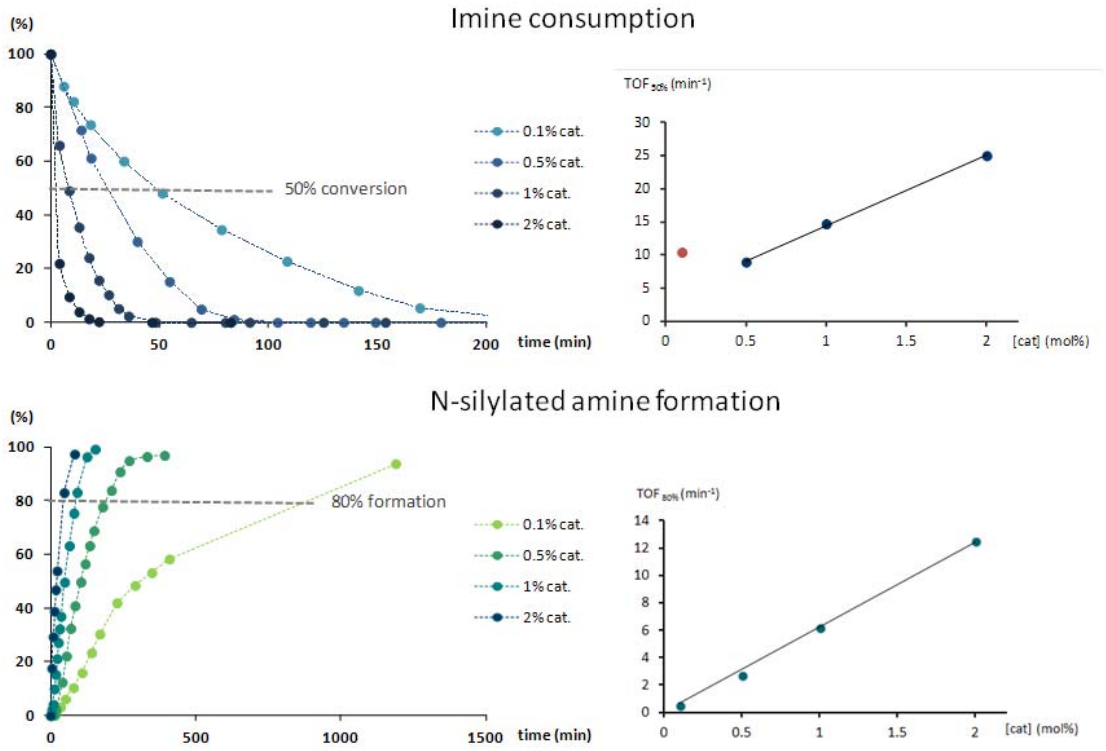


Fig S12. Reaction profiles of imine consumption and N-silylated amine formation using different catalyst loadings. Analysis of the dependence of the TOF on the catalyst concentration. The deviation from the linearity observed for the value at 50% consumption of imine when 0.1 mol% of catalyst was used could be due to the low catalyst loading, which can induce some experimental error in the exact catalyst amount.

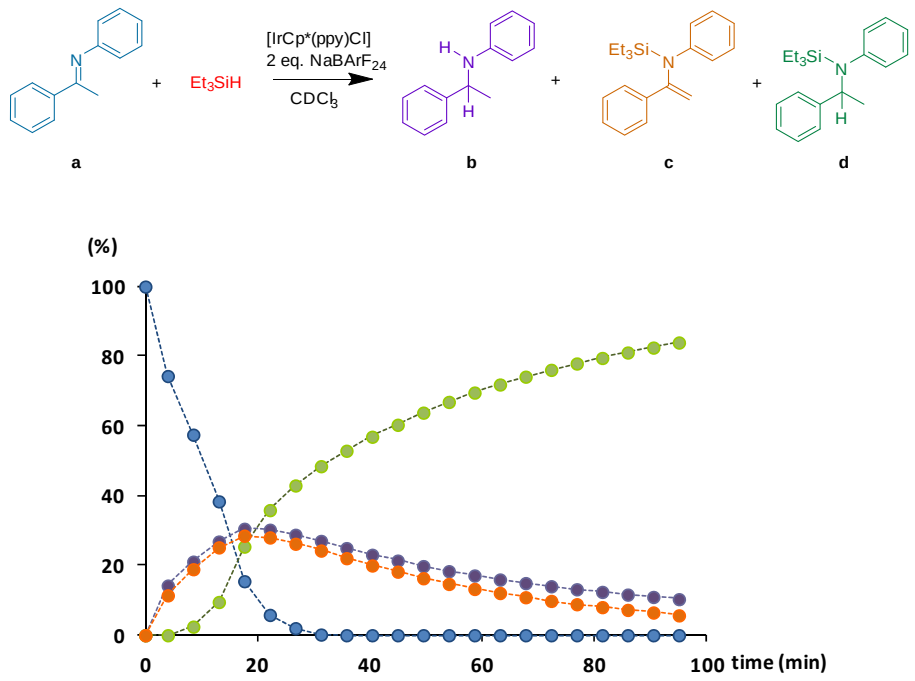


Fig S13. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$). Reaction run not strictly under nitrogen.

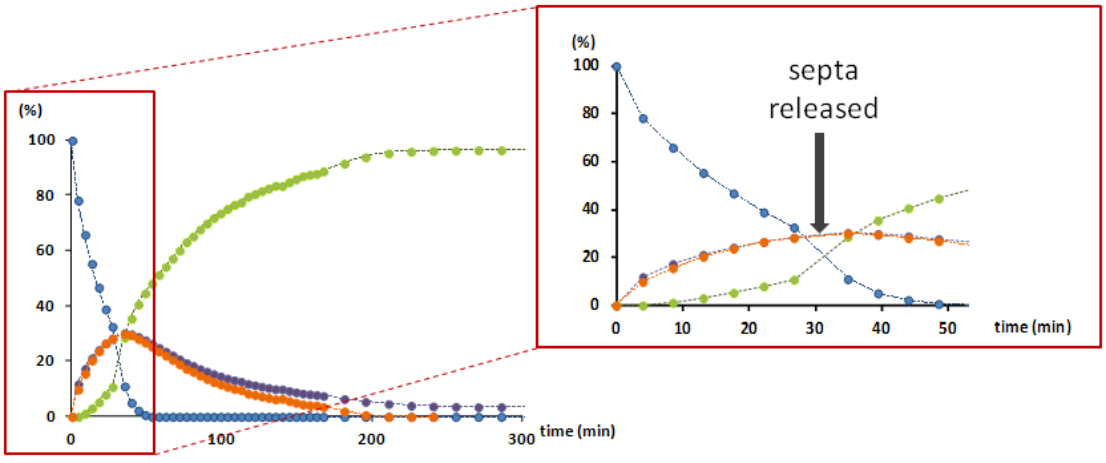


Fig S14. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS 10% v/v in $CDCl_3$. The NMR tube was open to the air and closed again at 30 min (black arrow).

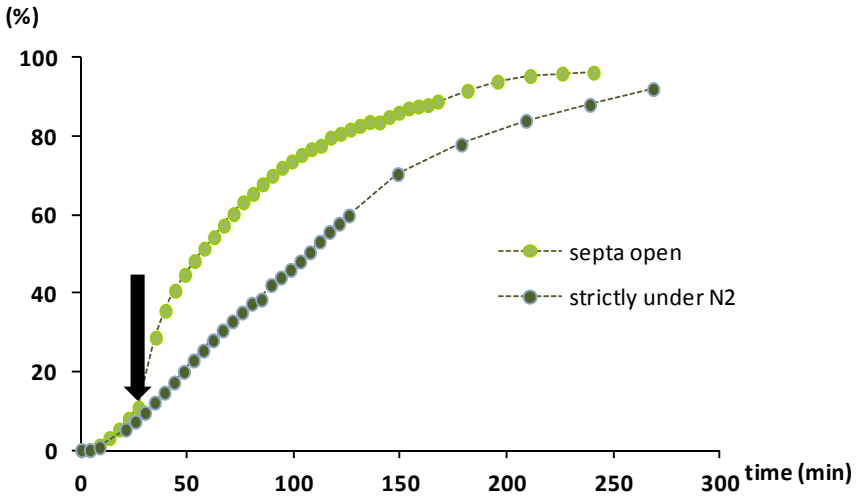


Fig S15. Comparative of the N-silylated amine formation of a reaction run strictly under N2 and exposing it to the air. Black arrow indicates when the septa was open. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

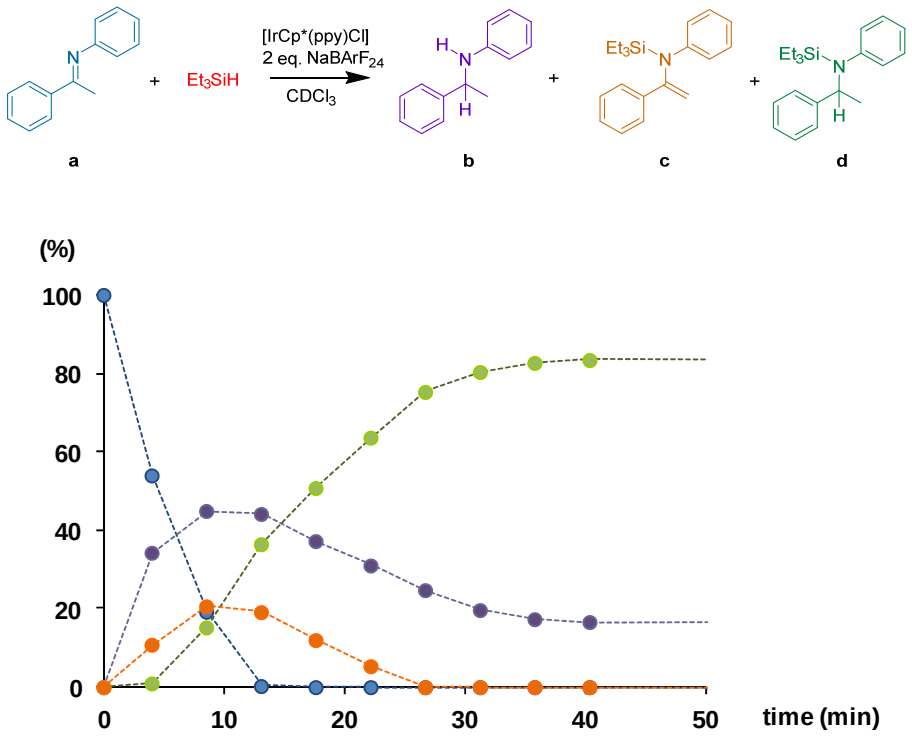


Fig S16. Reaction profile of imine-derived products according to *in situ* ^1H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), H_2O (0.35 µL, 0.01946 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

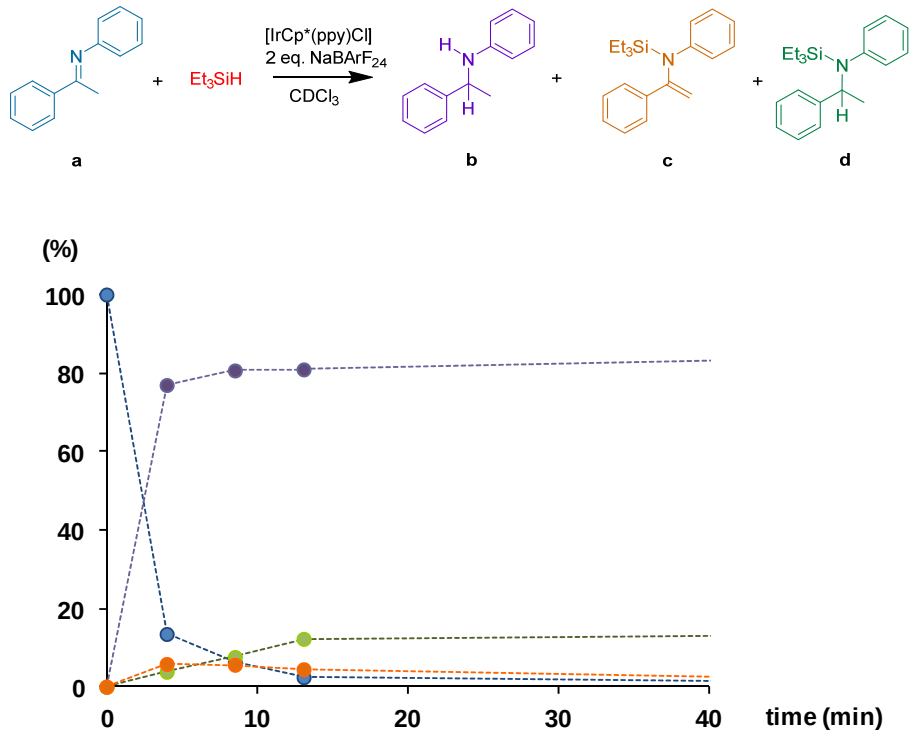


Fig S17. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), H_2O (3.50 µL, 0.1946 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

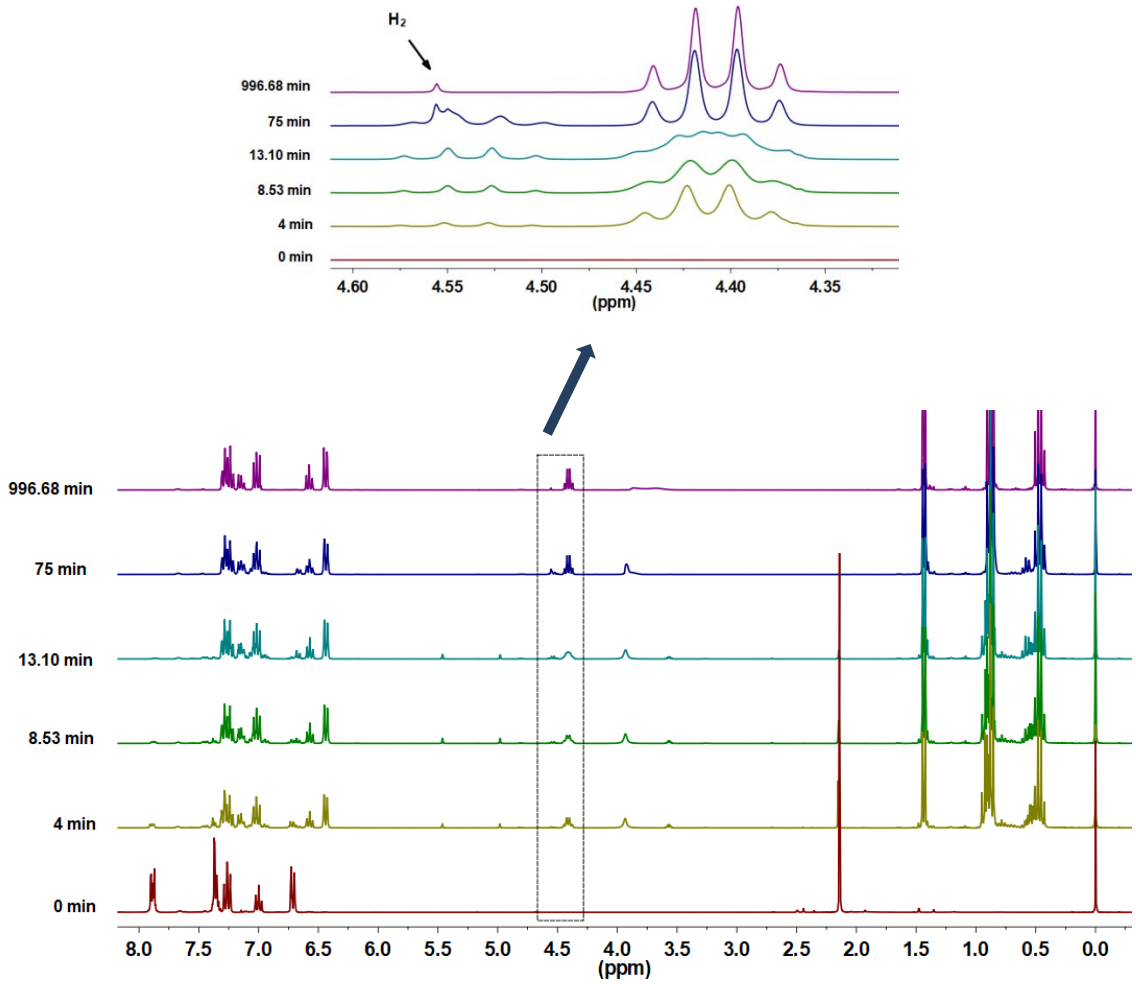


Fig S18. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** (300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), H_2O (3.50 µL, 0.1946 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

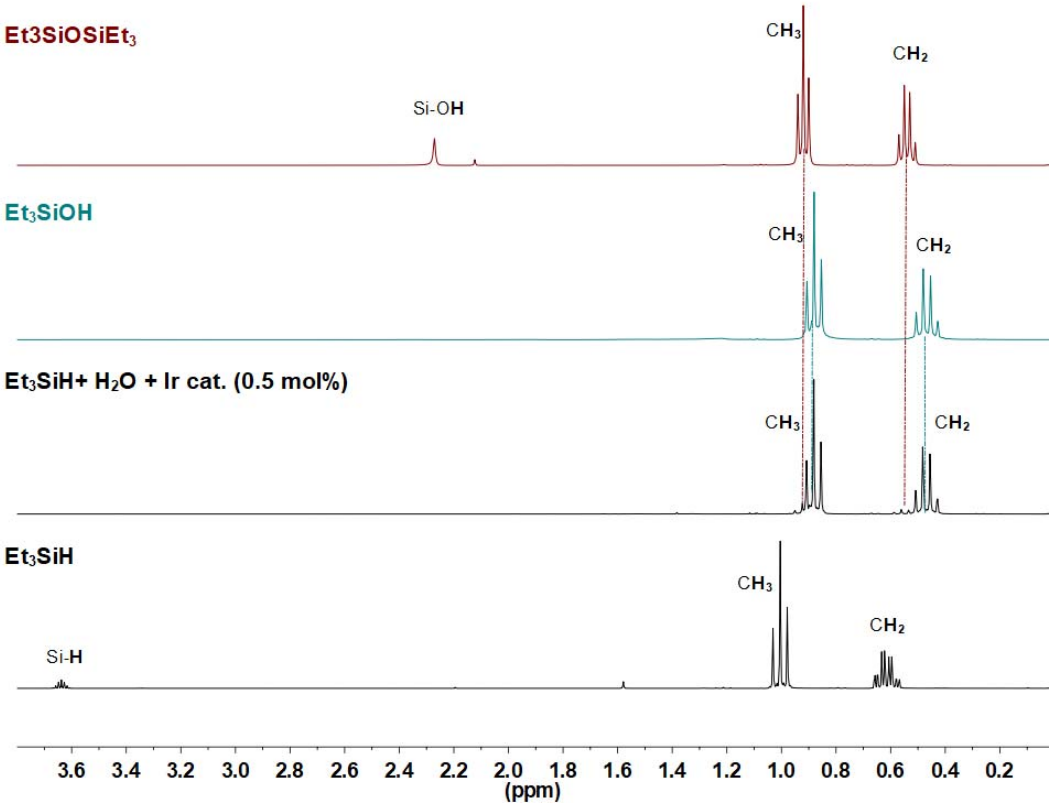


Fig S19. ^{1}H NMR spectra (300 MHz) of a solution of precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), in 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$) before and after addition of H_2O (10.0 µL, 0.5556 mmol). In green and red, respectively, spectra of $HOSiEt_3$ and $Et3SiOSiEt_3$ are shown for comparative purposes.

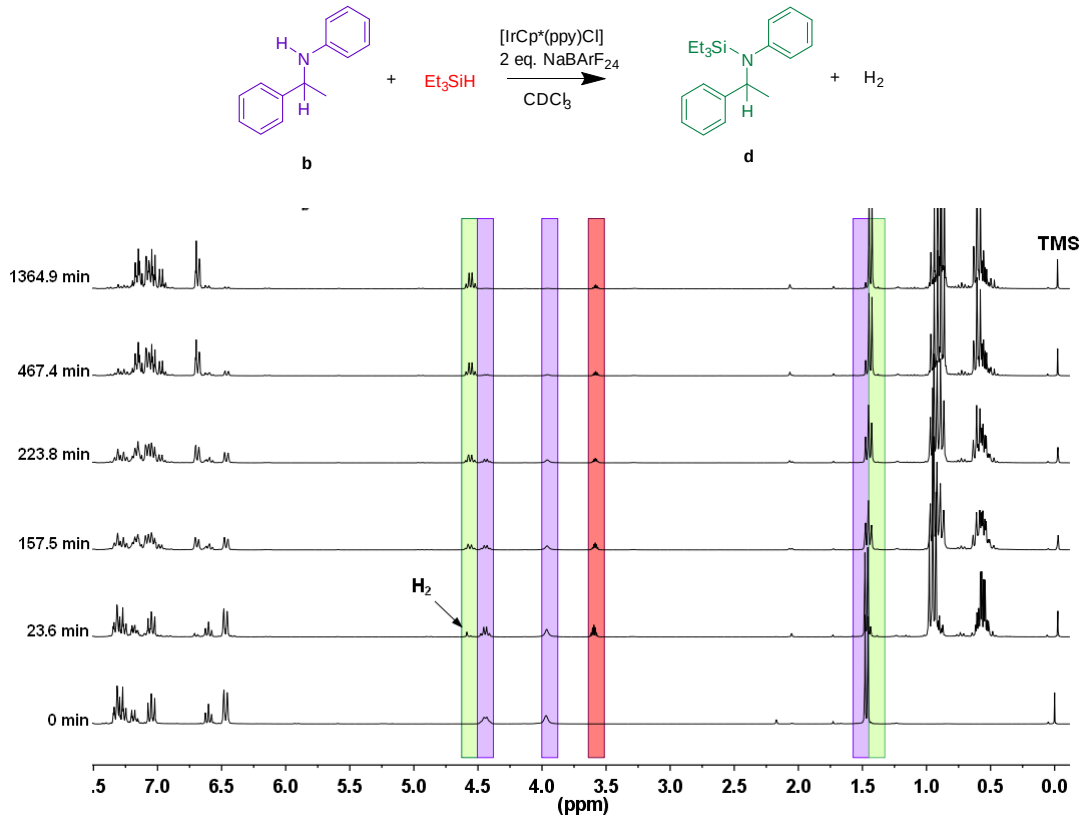


Fig S20. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethyl)aniline (**b**) using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethyl)aniline (**b**) (38.40 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

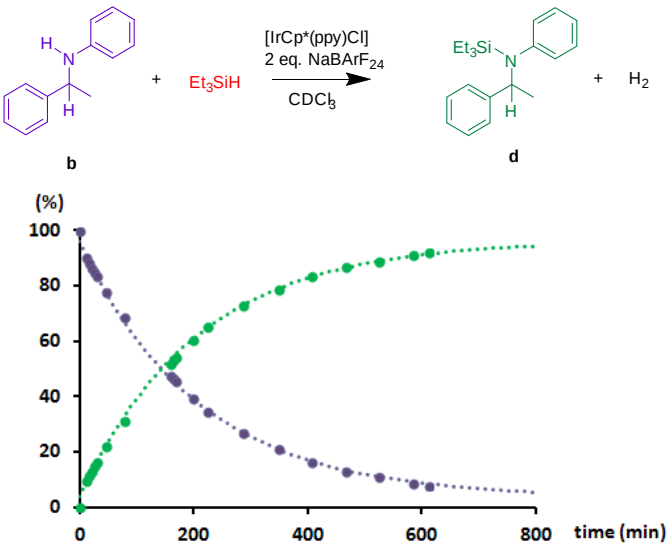


Fig S21. Reaction profile of amine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Solid circles represent experimental data and dotted lines calculated consumption and formation profiles using a first order kinetic equation (v = kobs·[amine], r^2= 0.9989, kobs= 0.0048 min^{-1}). Reaction conditions: precatalyst **1** (0.5 mg, 0.0010 mmol), $NaBArF_{24}$ (1.7 mg, 0.0019 mmol), N-(1-phenylethyl)aniline (**b**) (38.4 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

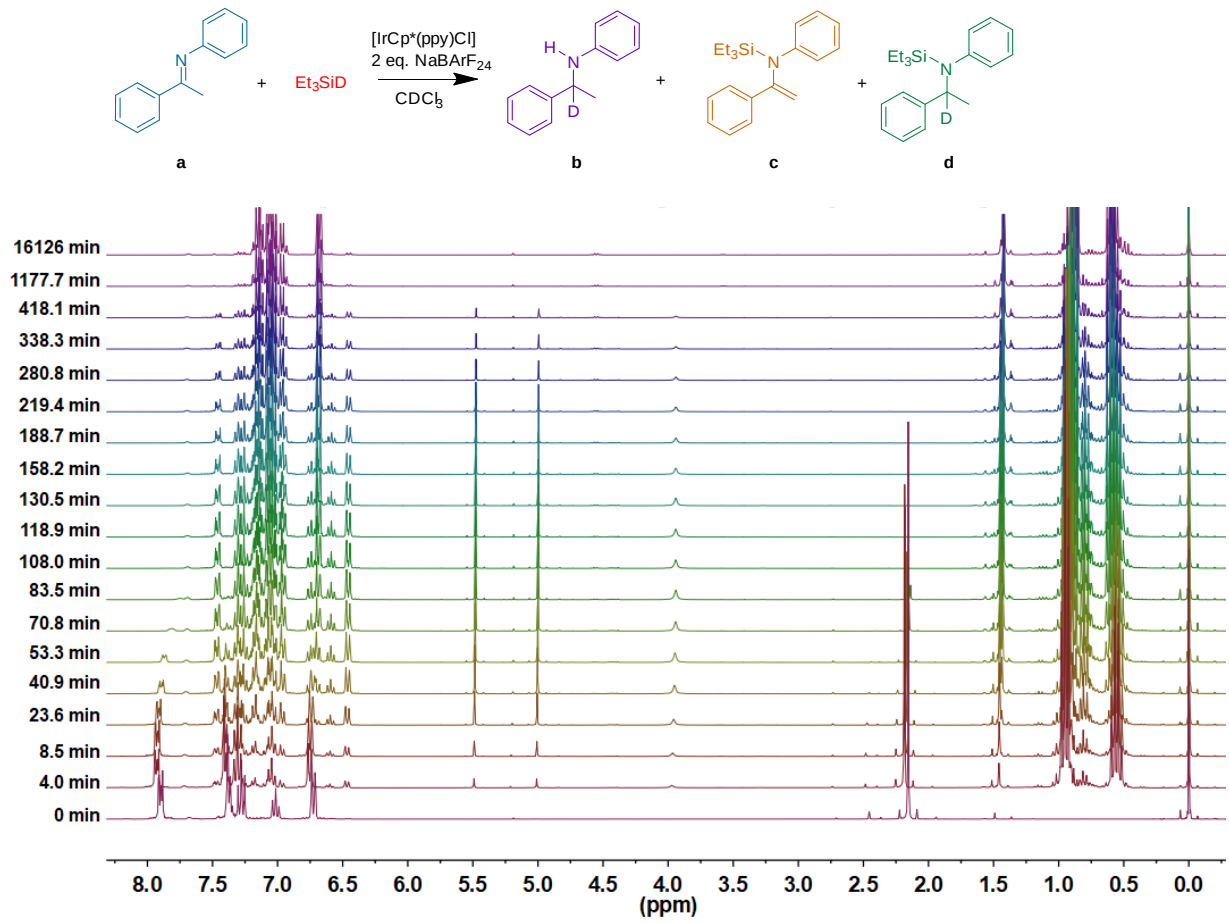


Fig S22. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiD (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

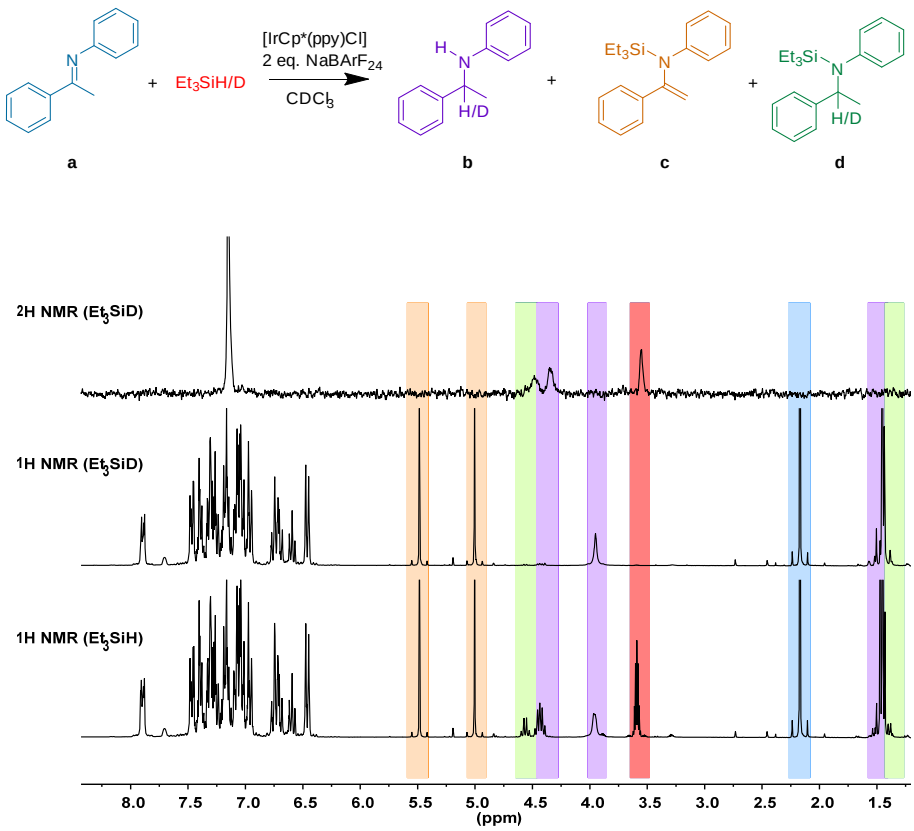


Fig S23. ^{1}H NMR spectra of hydrosilylation reactions at 40 min using Et_3SiH (bottom) and ^{1}H and ^{2}H NMR spectra using Et_3SiD (top). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), imine (38.00 mg, 0.1946 mmol), Et_3SiH or Et_3SiD (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$ or $CHCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

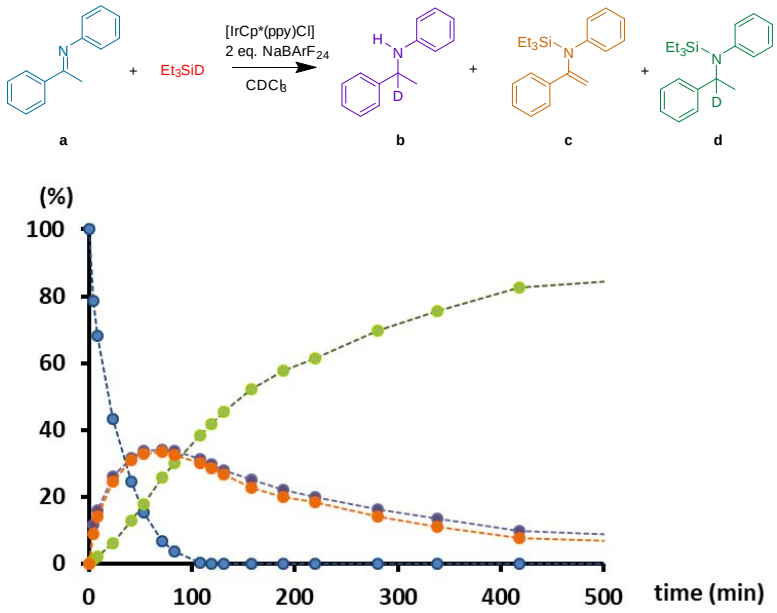


Fig S24. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Et_3SiD (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

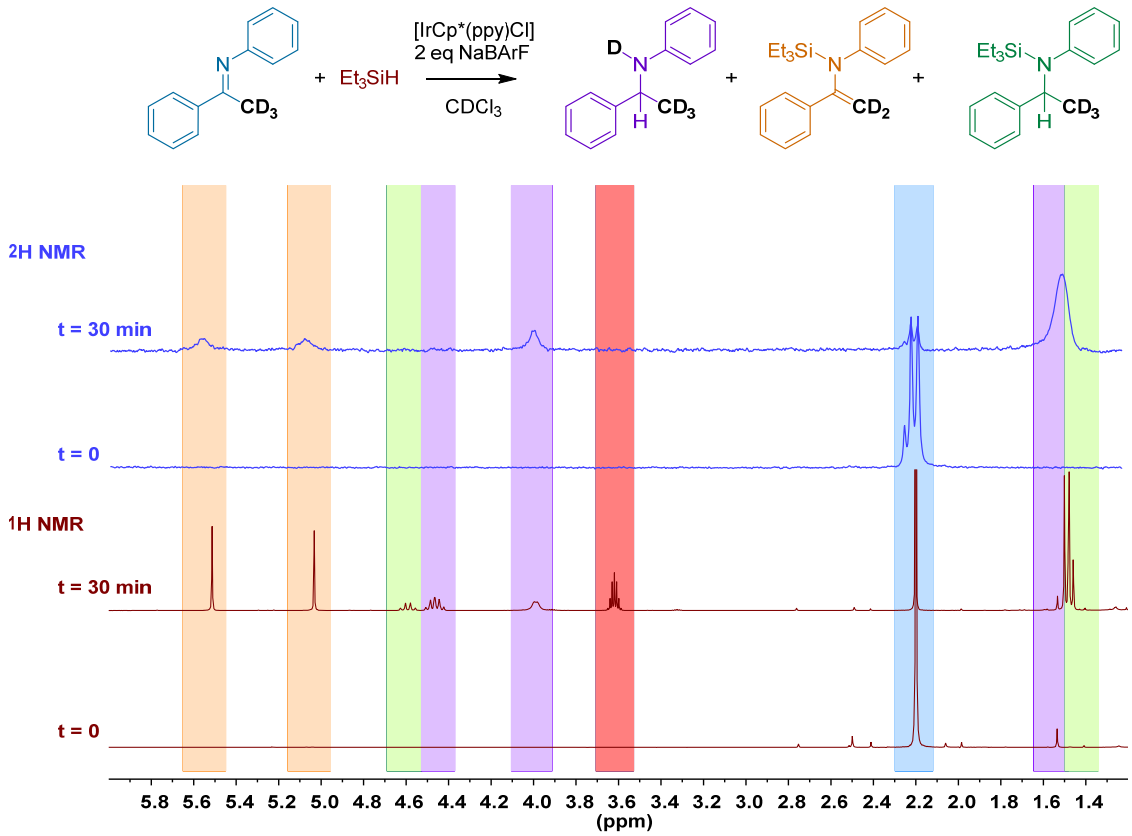


Fig S25. ^{2}H NMR study of the hydrosilylation of deuterium-labeled N-(1-phenylethylidene)aniline (**a**^{CD3}) using precatalyst **1** ($CDCl_3$, 500 MHz). Reaction conditions: precatalyst **1** (0.5 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), deuterium-labeled N-(1-phenylethylidene)aniline (38.6 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS 10% v/v in $CDCl_3$ (blue spectra). For comparison, ^{1}H NMR spectra of the same reaction using non-deuterated substrate **a** is shown (red spectra).

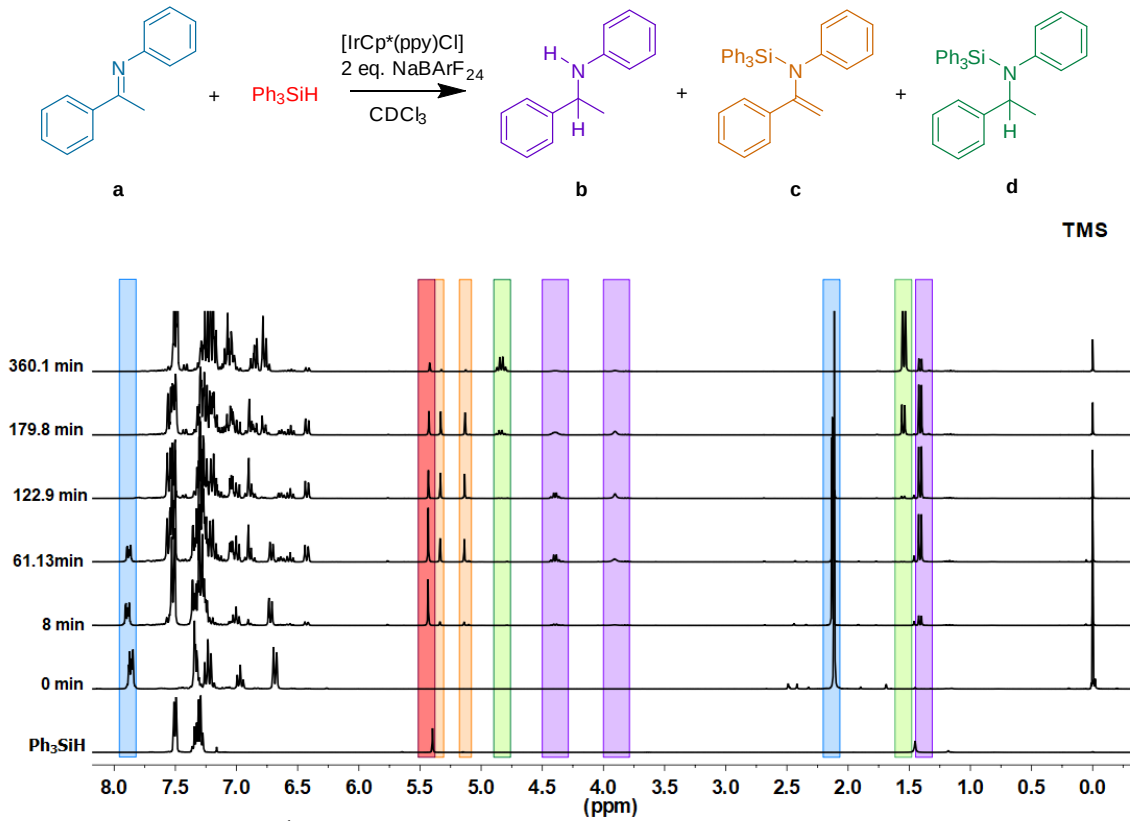


Fig S26. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.5 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Ph_3SiH (60.93 mg, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

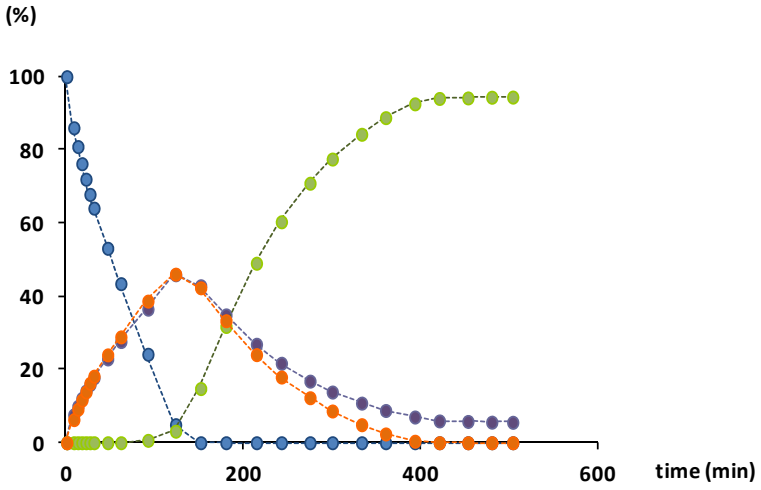


Fig S27. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Ph_3SiH (60.93 mg, 0.2335 mmol), 0.5 mL $CDCl_3$.

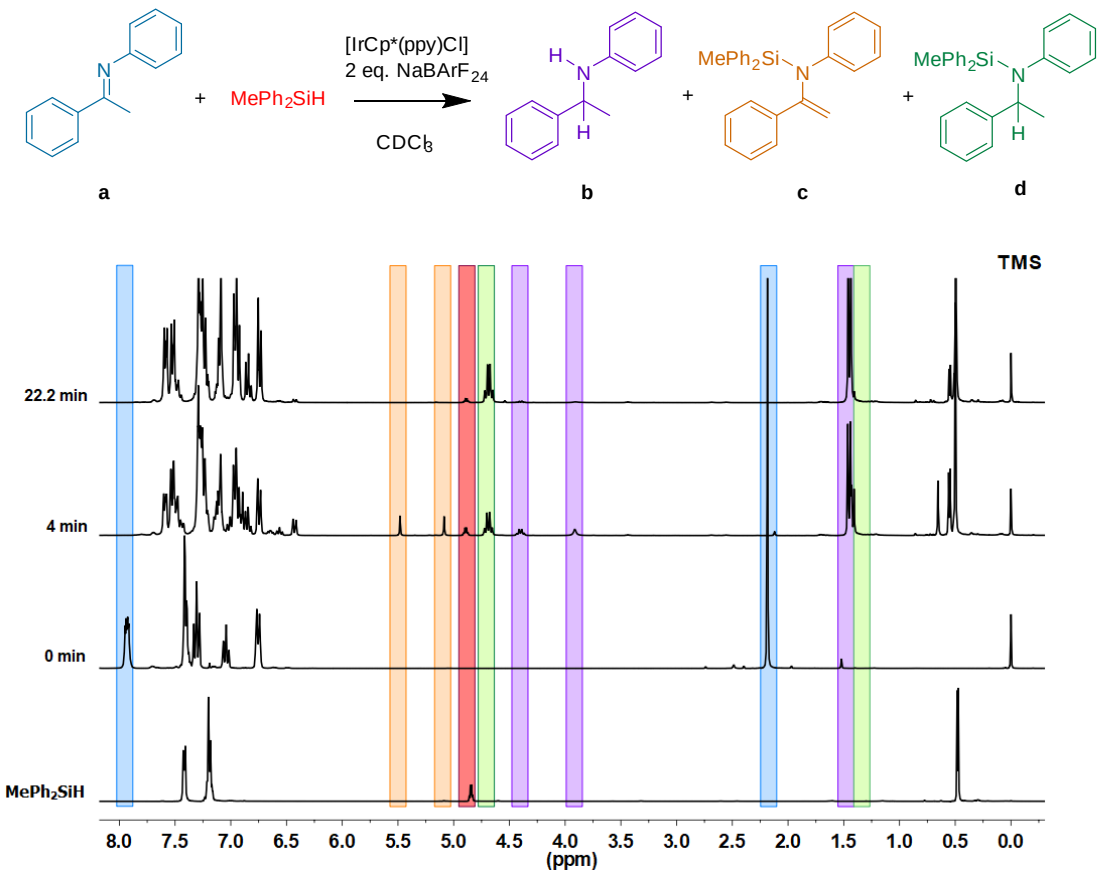


Fig S28. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), $MePh_2SiH$ (46.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

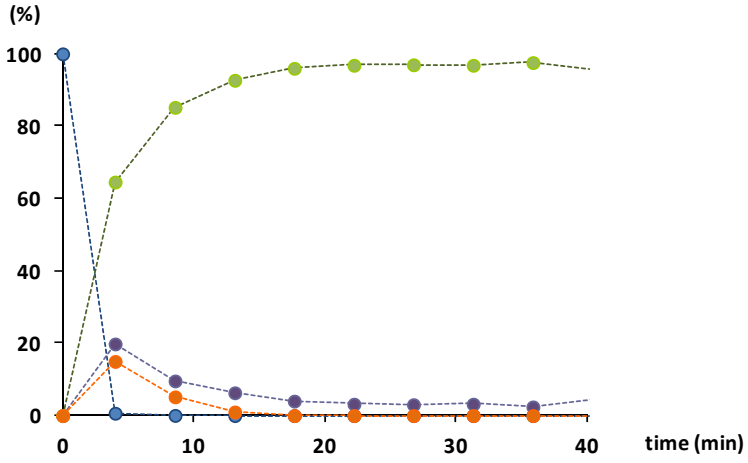


Fig S29. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), $MePh_2SiH$ (46.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

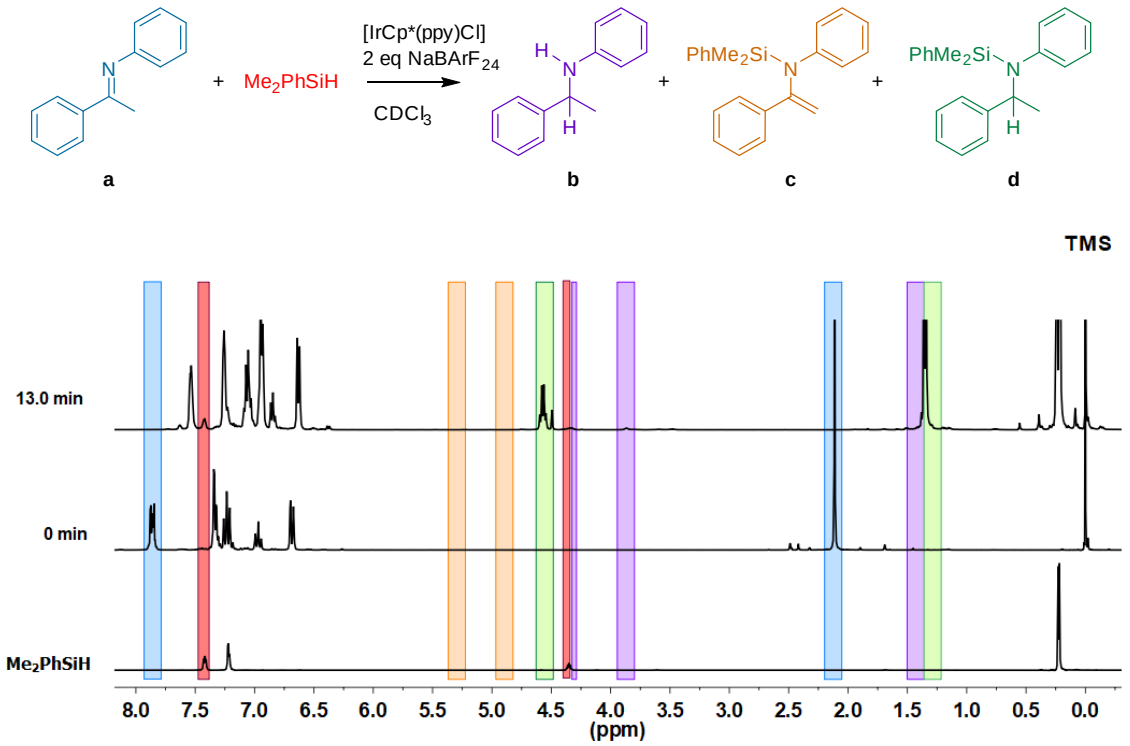


Fig S30. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Me_2PhSiH (36.2 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

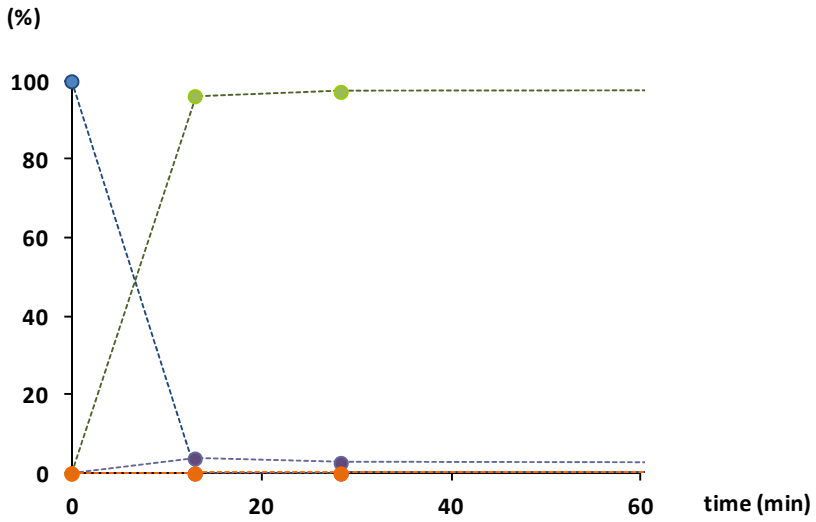


Fig S31. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Me_2PhSiH (36.2 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

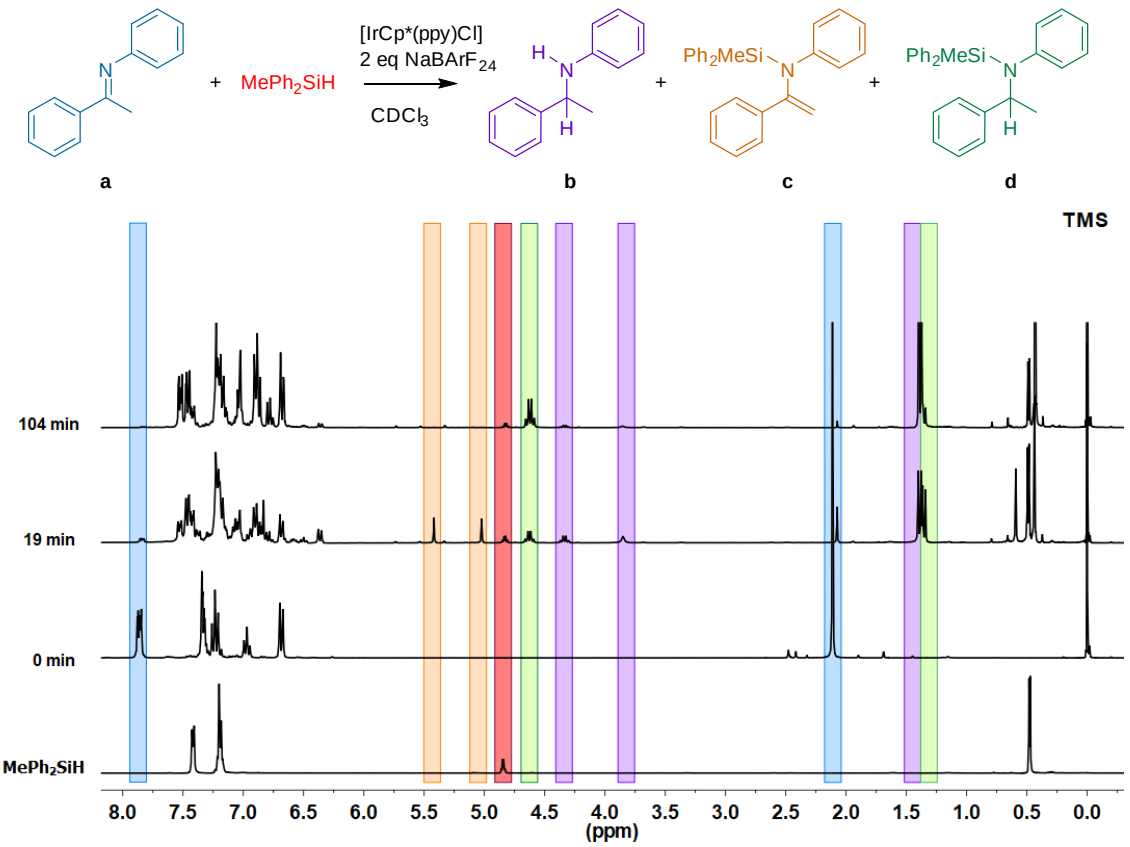


Fig S32. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.10 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), $MePh_2SiH$ (46.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

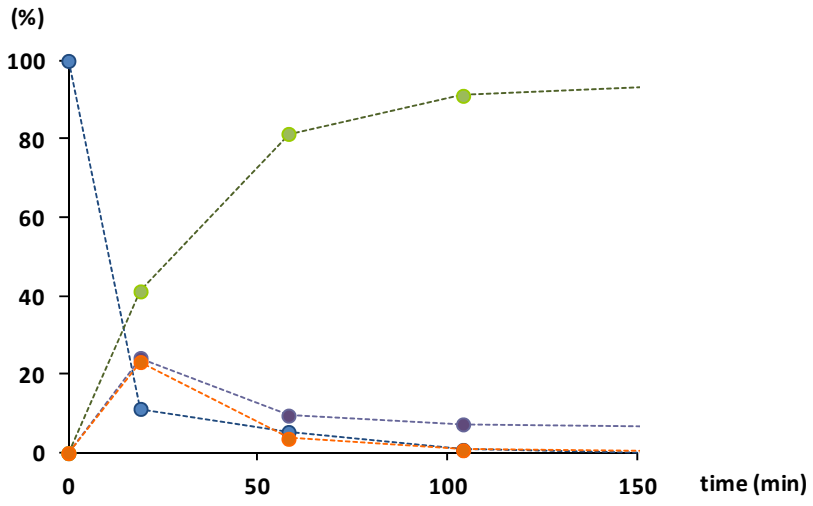


Fig S33. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.10 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), $MePh_2SiH$ (46.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

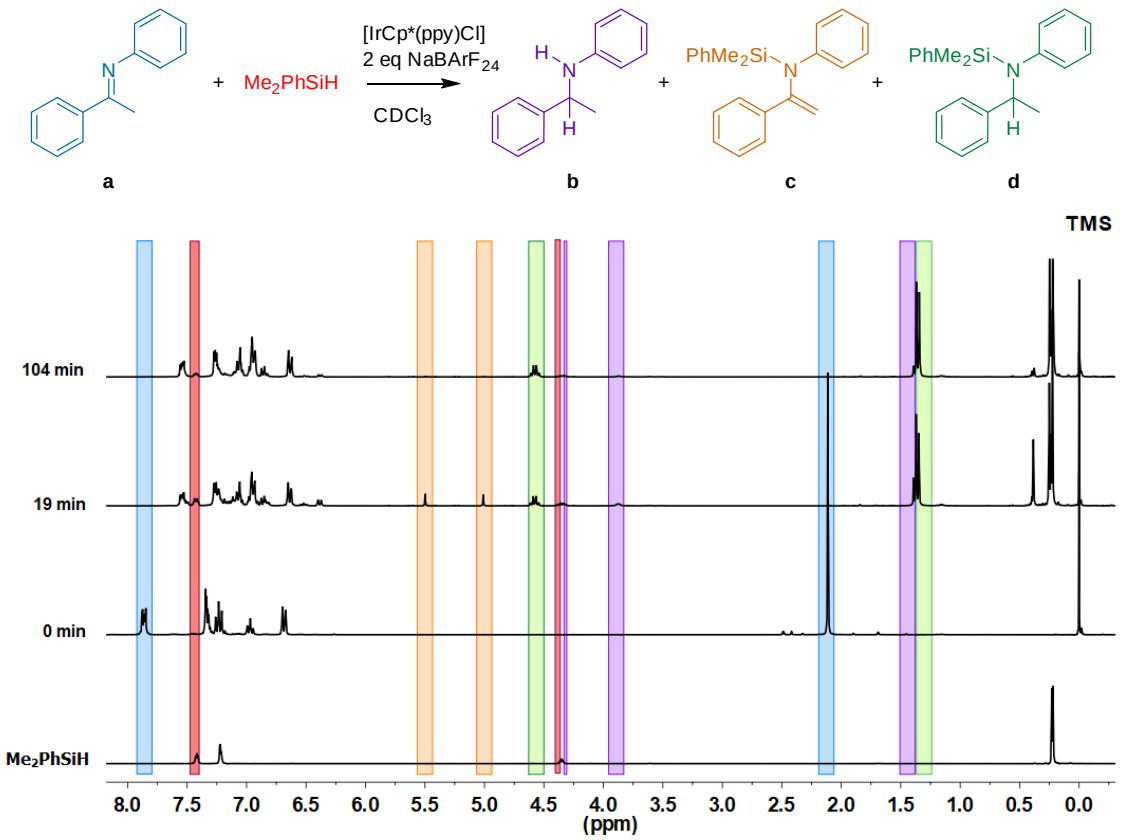


Fig S34. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.10 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Me_2PhSiH (36.2 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

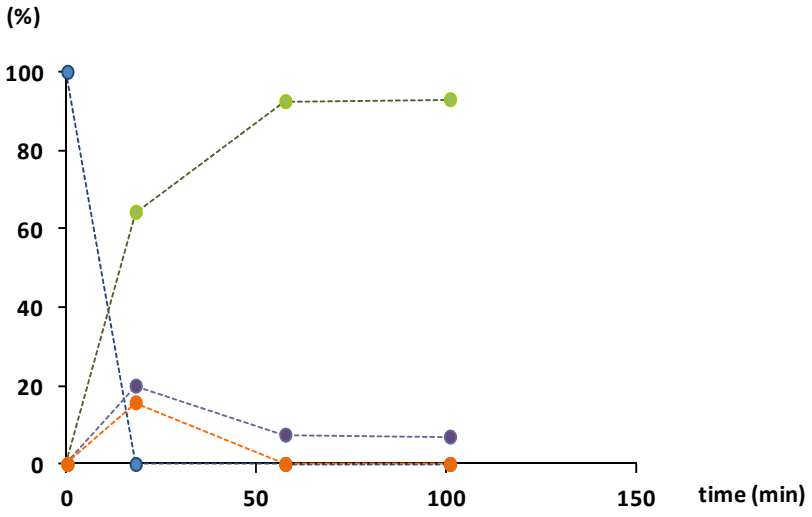


Fig S35. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.10 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Me_2PhSiH (36.2 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

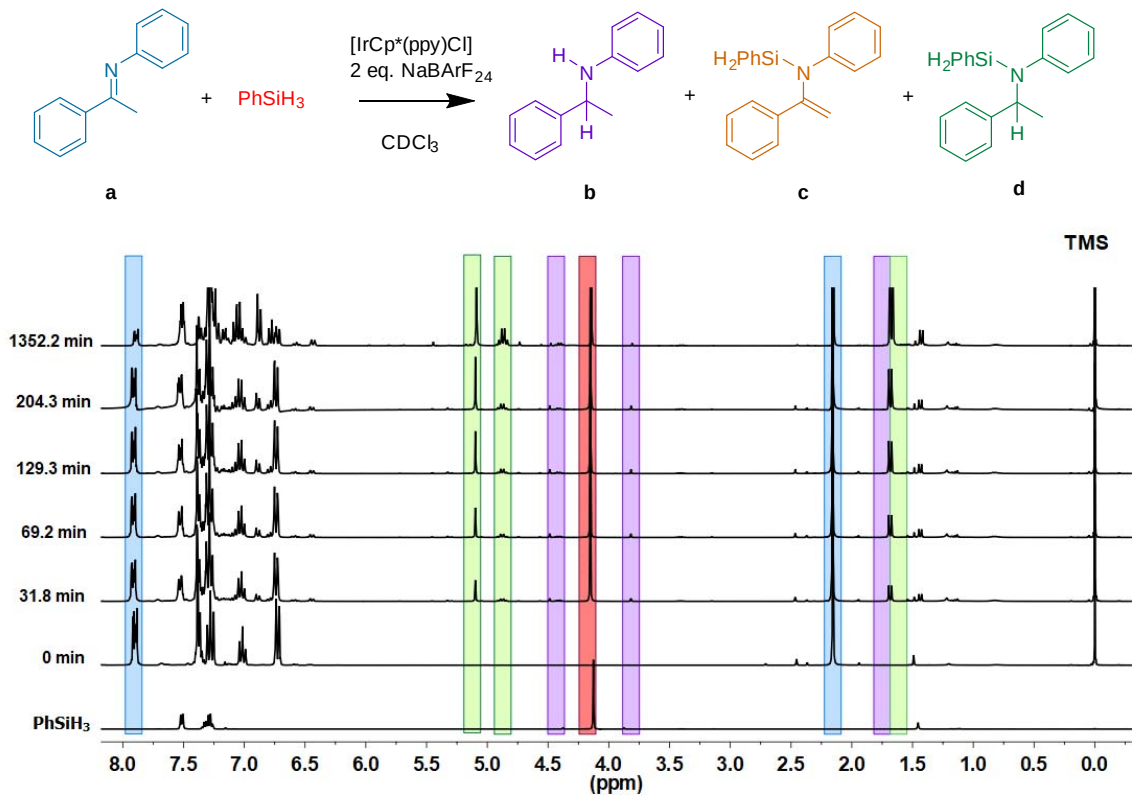


Fig S36. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), $PhSiH_3$ (28.8 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

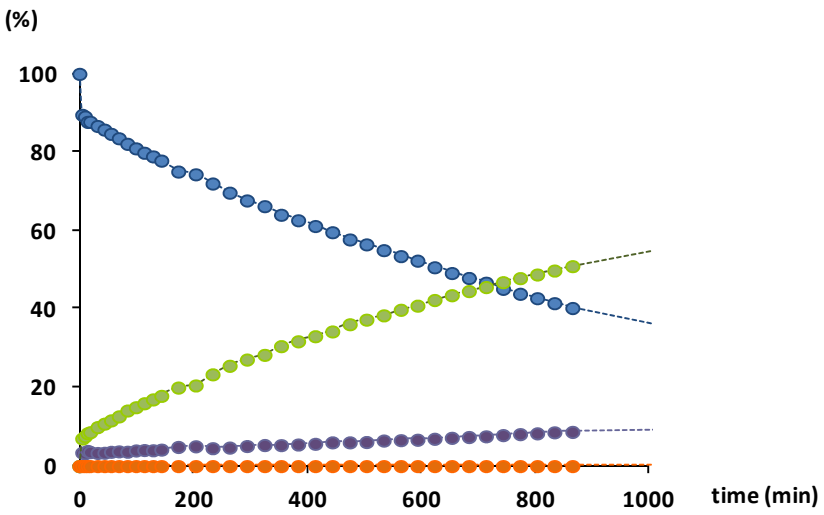


Fig S37. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), $PhSiH_3$ (28.8 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

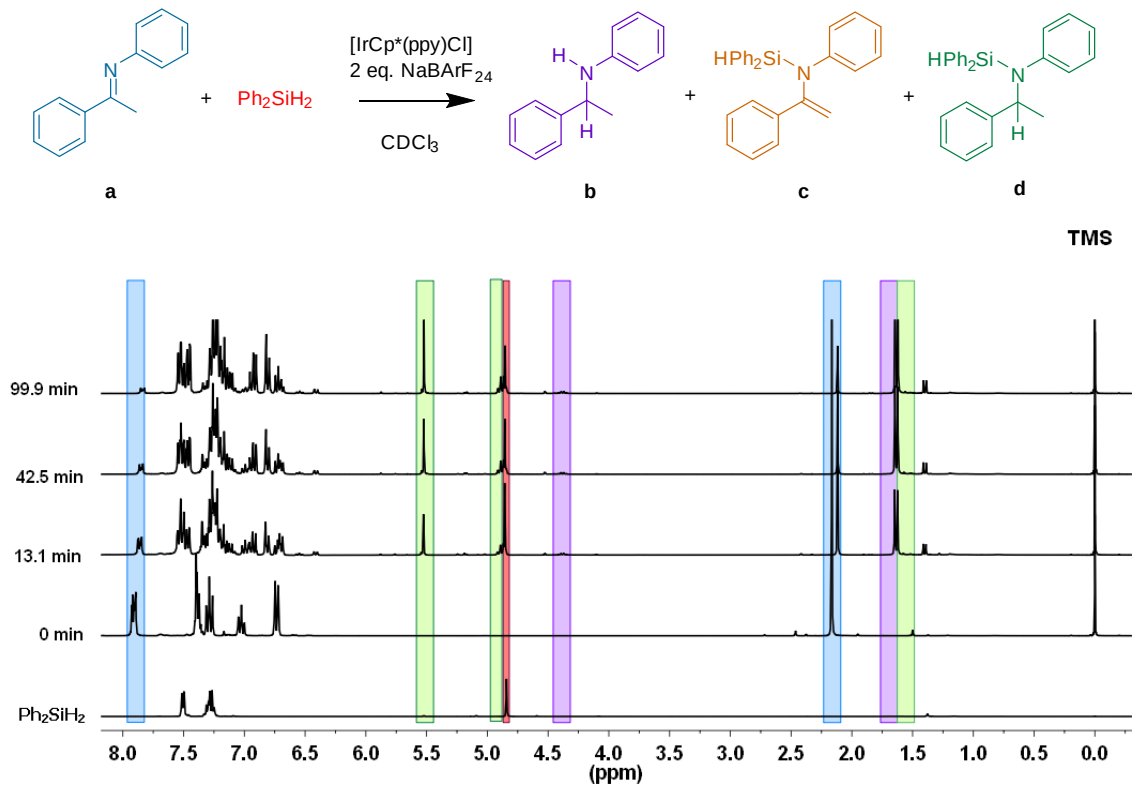


Fig. S38. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **1** ($CDCl_3$, 300 MHz). Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Ph_2SiH_2 (43.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

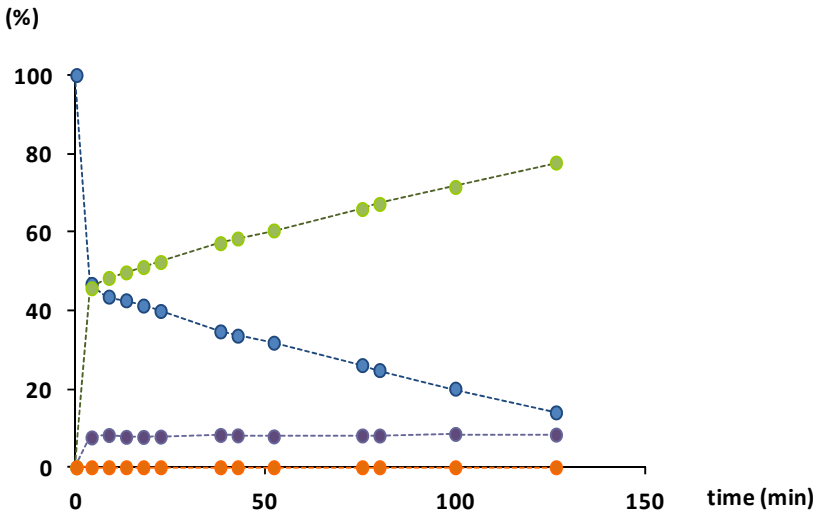
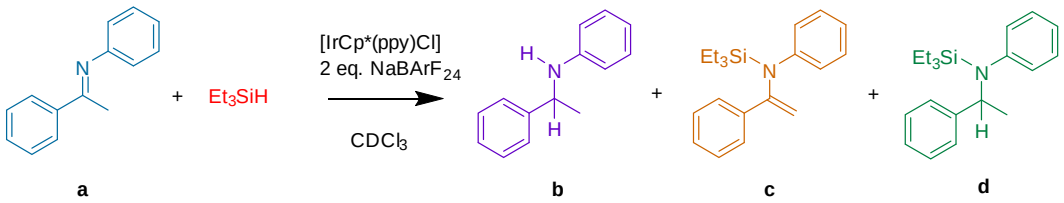


Fig S39. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst **1** (0.50 mg, 0.0010 mmol), $NaBArF_{24}$ (1.70 mg, 0.0019 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Ph_2SiH_2 (43.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.



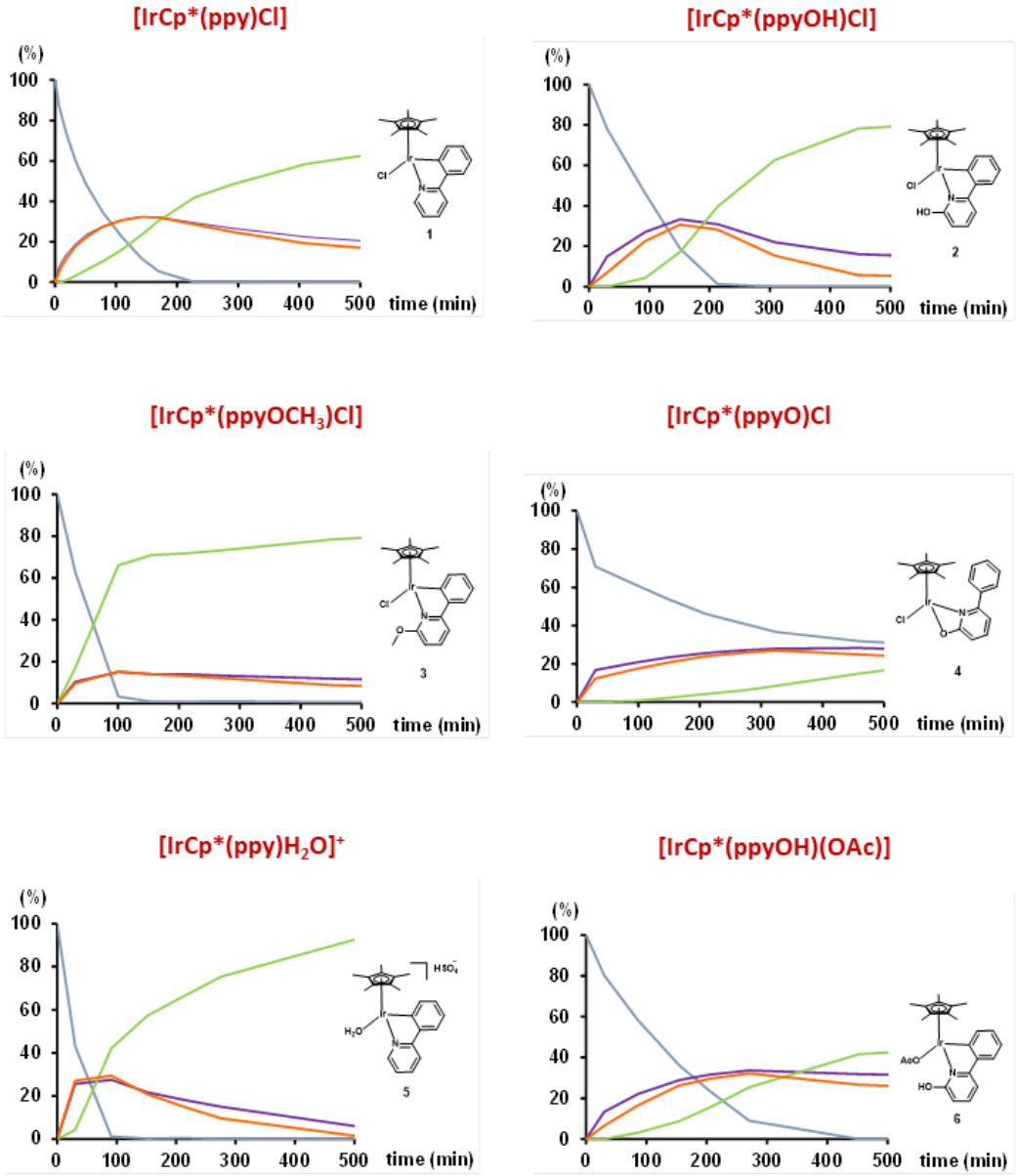


Fig S40. Screening of catalysts. Reaction profile of imine-derived products according to *in situ* ^{1}H NMR spectroscopy. $CDCl_3$, 300 MHz. Reaction conditions: precatalyst (0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.00 mg, 0.1946 mmol), Ph_2SiH_2 (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$.

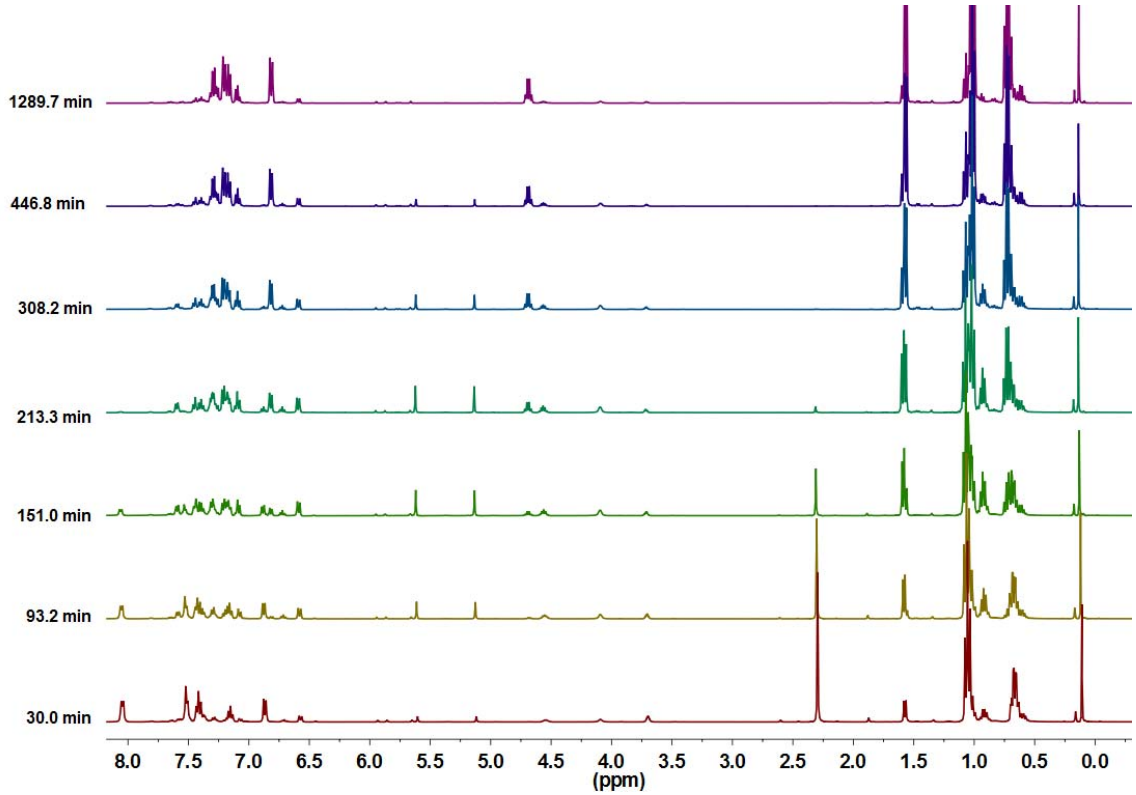


Fig S41. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **2** (300 MHz). Reaction conditions: precatalyst **2** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

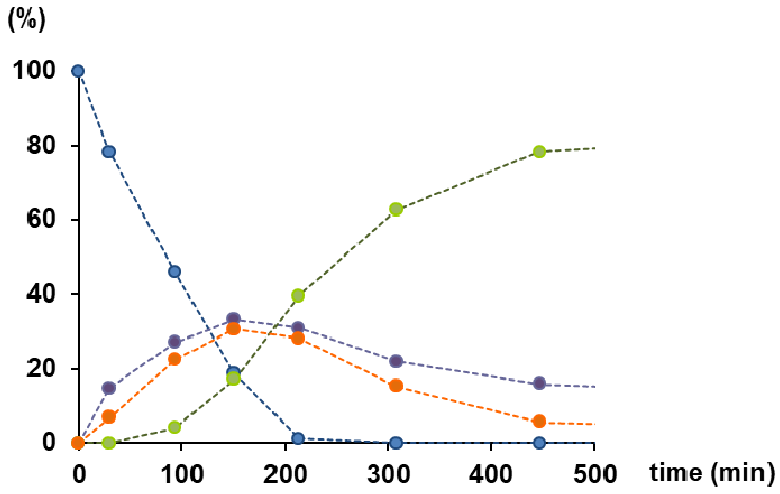


Fig S42. Reaction profile of **A**) imine-derived and **B**) silane-containing products, according to *in situ* ^{1}H NMR spectroscopy. Reaction conditions: precatalyst **2** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol),Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

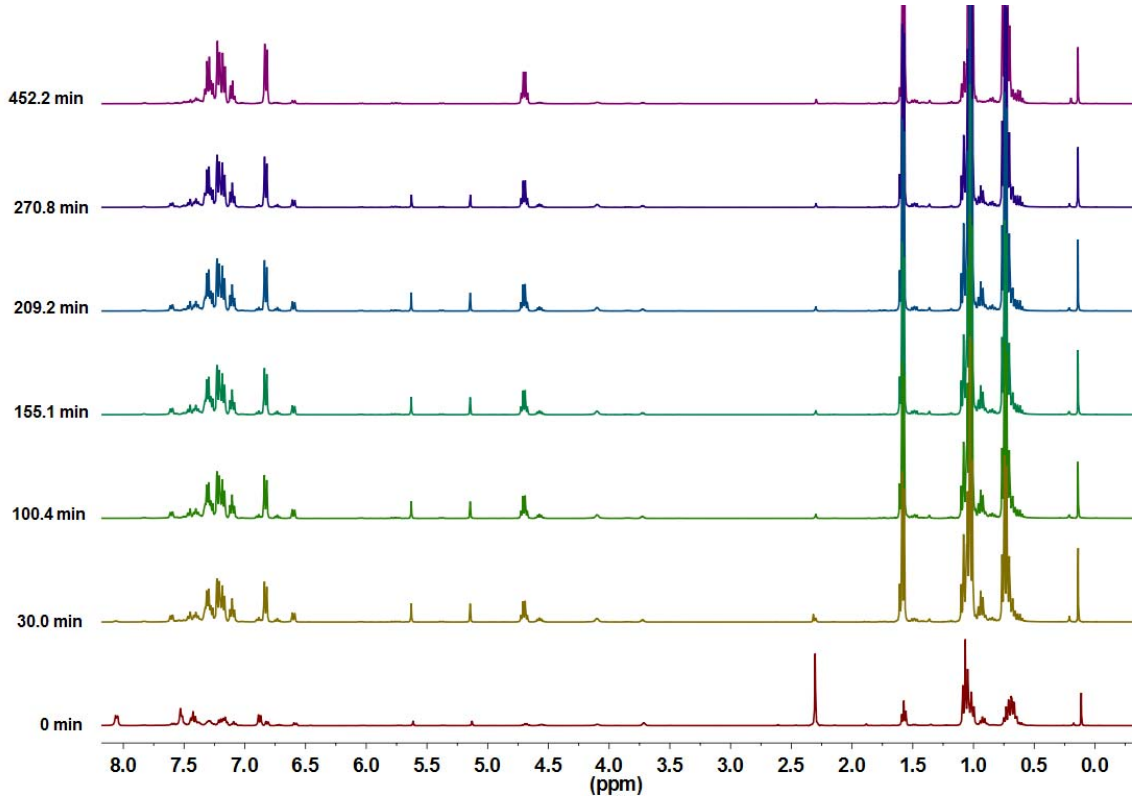


Fig S43. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **3** (300 MHz). Reaction conditions: precatalyst **3** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

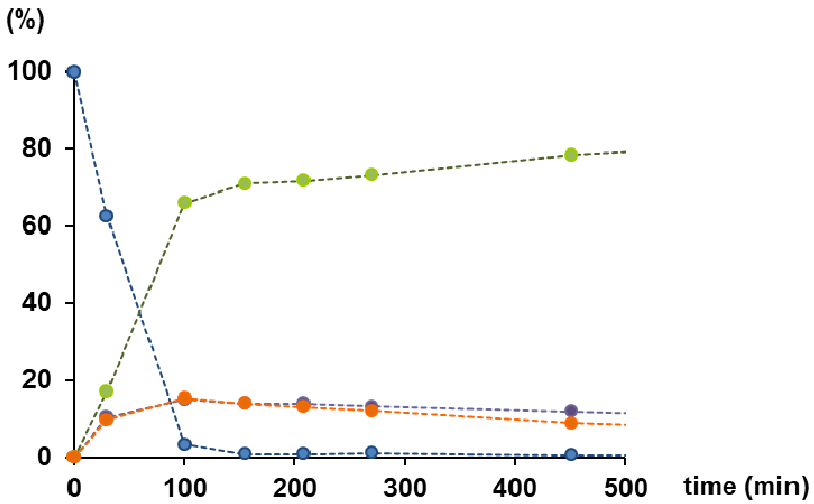


Fig S44. Reaction profile of **A**) imine-derived and **B**) silane-containing products, according to *in situ* ^{1}H NMR spectroscopy. Reaction conditions: precatalyst **3** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol),Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

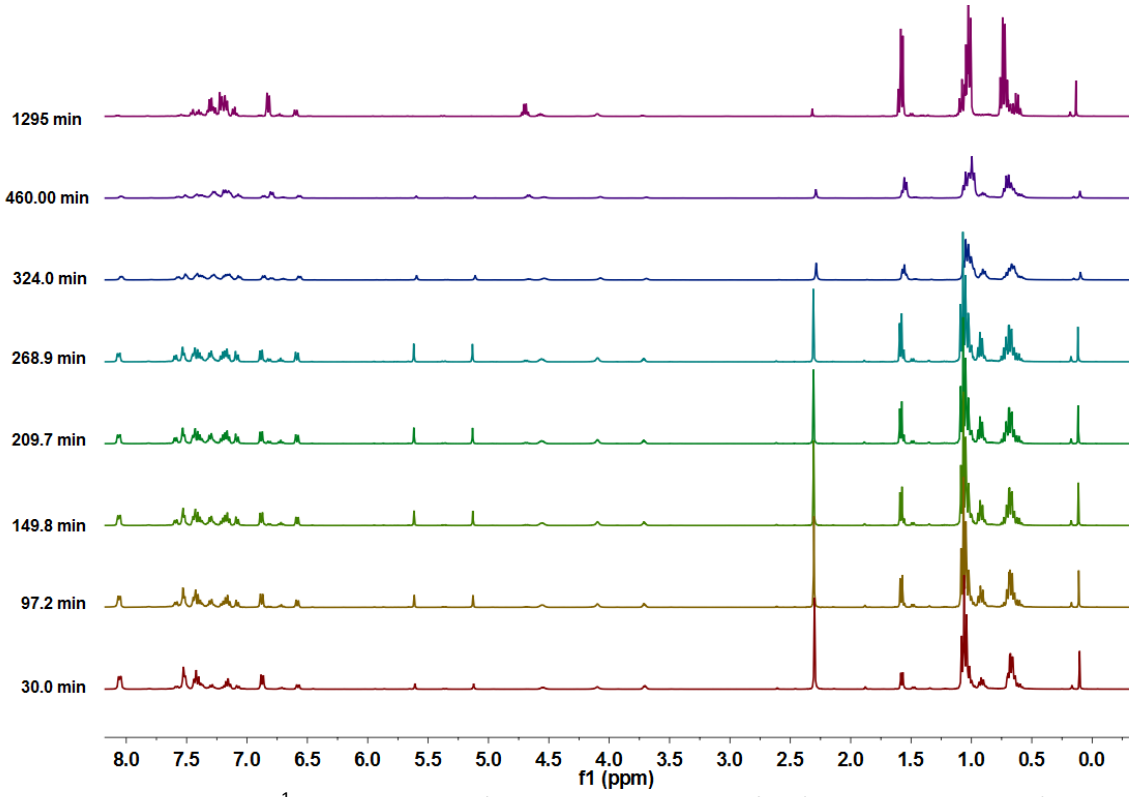


Fig S45. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **4** (300 MHz). Reaction conditions: precatalyst **4** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

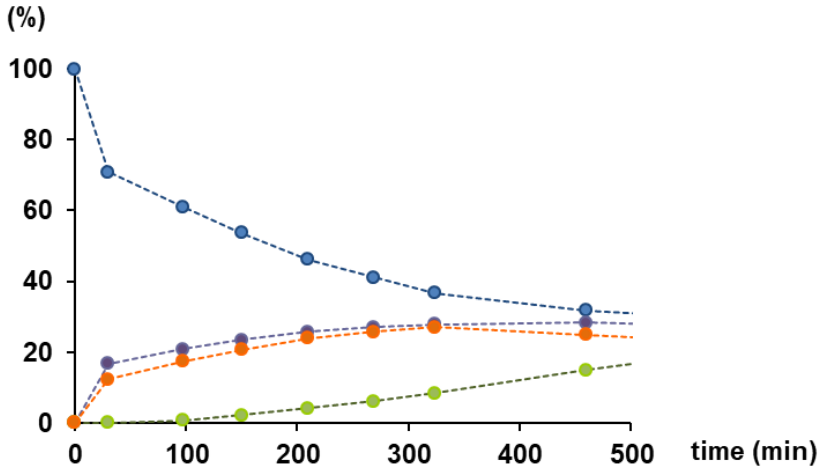


Fig S46. Reaction profile of **A**) imine-derived and **B**) silane-containing products, according to *in situ* ^{1}H NMR spectroscopy. Reaction conditions: precatalyst **4** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol),Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

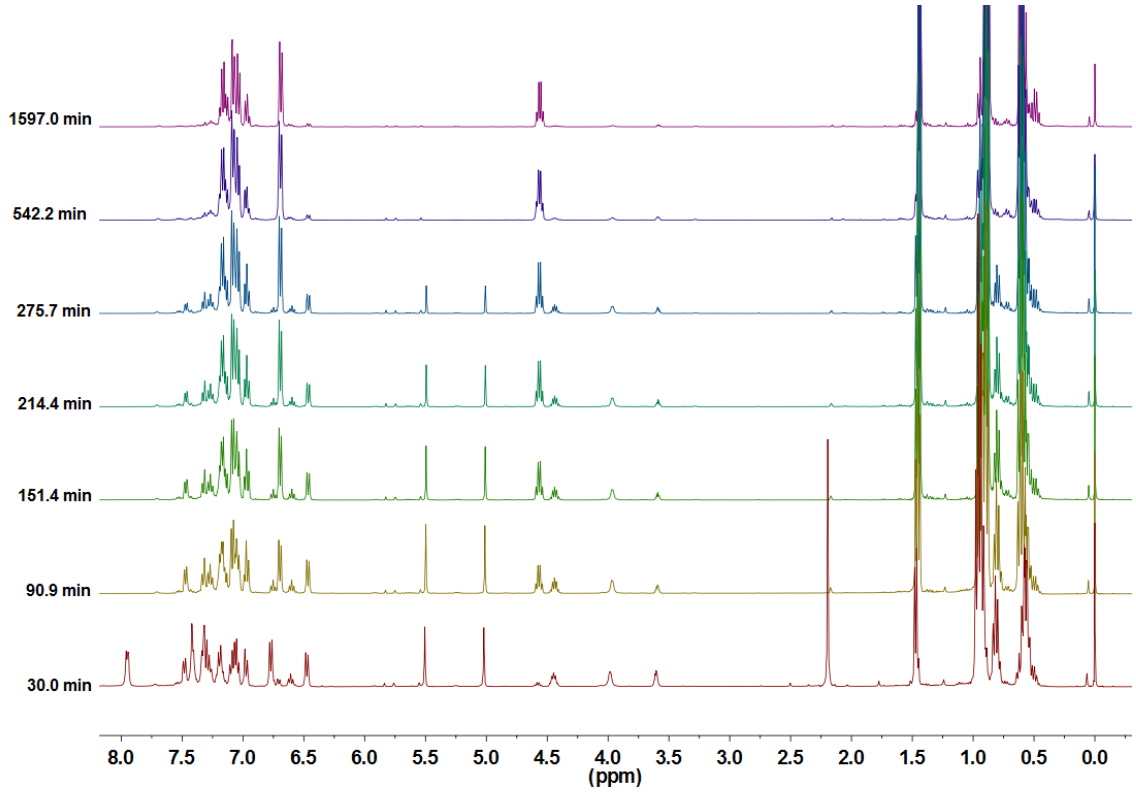


Fig S47. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **5** (300 MHz). Reaction conditions: precatalyst **5** (0.12 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

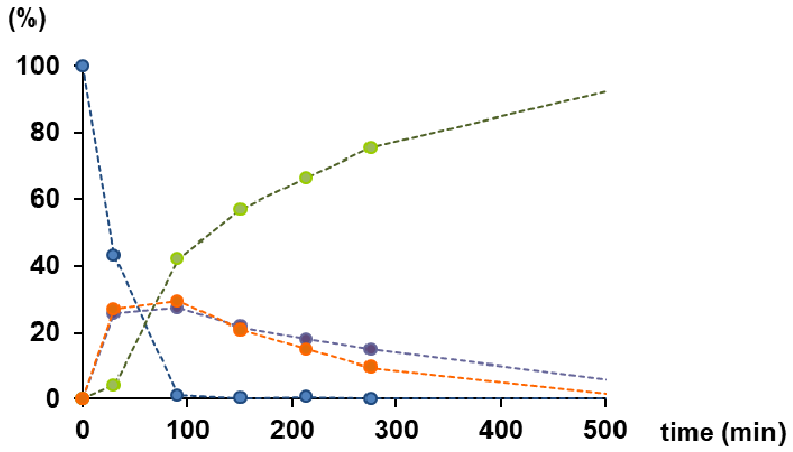


Fig S48. Reaction profile of **A**) imine-derived and **B**) silane-containing products, according to *in situ* ^{1}H NMR spectroscopy. Reaction conditions: precatalyst **5** (0.12 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol),Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

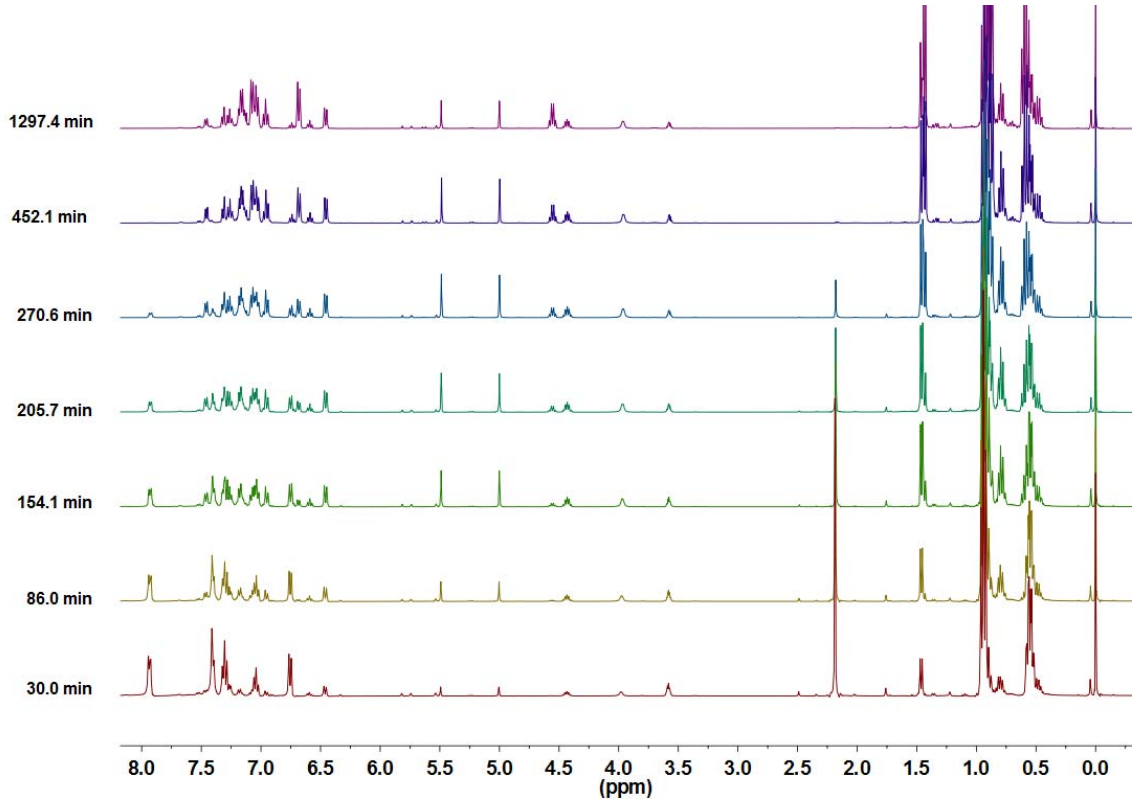


Fig S49. Time-resolved ^{1}H NMR study of the hydrosilylation of N-(1-phenylethylidene)aniline using precatalyst **6** (300 MHz). Reaction conditions: precatalyst **6** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol), Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

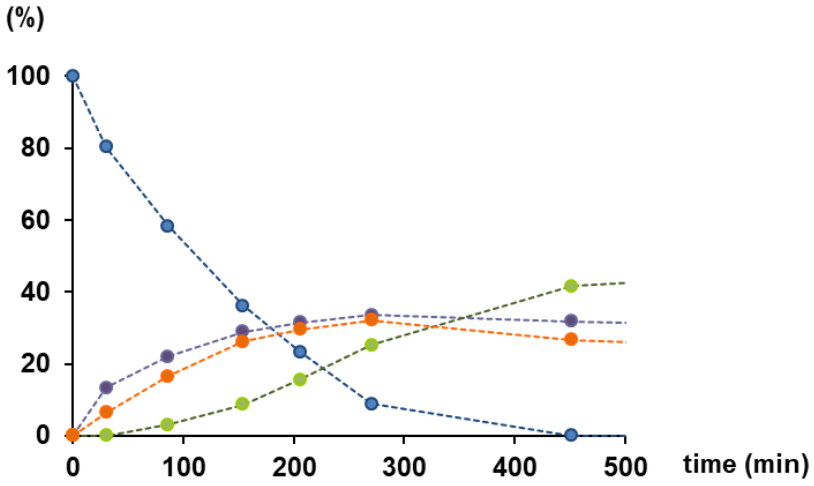


Fig S50. Reaction profile of **A**) imine-derived and **B**) silane-containing products, according to *in situ* ^{1}H NMR spectroscopy. Reaction conditions: precatalyst **6** (0.11 mg, 0.0002 mmol), $NaBArF_{24}$ (0.34 mg, 0.0004 mmol), N-(1-phenylethylidene)aniline (38.0 mg, 0.1946 mmol),Et_3SiH (37.3 µL, 0.2335 mmol), 0.5 mL $CDCl_3$, internal capillary TMS (10% v/v in $CDCl_3$).

Syntheses and characterizations:

6-methoxy-2-phenylpyridine. Under nitrogen, 6-methoxy-2-chloropyridine (1.1 mL, 9.42 mmol), tetrakis(triphenylphosphine)palladium (0.16 g, 0.13 mmol) and a degassed 2M aqueous sodium carbonate (10 mL) were added over a solution of phenylboronic acid pinacolester (2.20 g, 10.79 mmol) in 50 mL of ethanol. The reaction mixture was then stirred at 90 ℃ for 48 h. Water was added to the reaction mixture, which was extracted by ethyl acetate. The organic layer was dried with anhydrous sodium sulfate, and after filtration the solvent was evaporated in vacuum. The product was purified by circular chromatography (hexane/CH_2Cl_2 = 1/1) (yield 96%). The compound was identified by its ^{1}H NMR spectra, by comparison with the already published data.[1]

6-phenyl-2-pyridone This compound was synthesized following a procedure analogous to the one described for the synthesis of 6-hydroxy-2,2'-bipyridine.[2] A mixture of 2-methoxy-6-phenylpyridine (0.27 g, 1.48 mmol) and pyridine hydrochloride (3.92 g, 33.99 mmol) was heated under N_2 at 210 °C for 90 min. The reaction mixture was cooled to ambient temperature, and the white solid residue dissolved in H_2O (25 mL). The product was extracted from the aqueous solution with ethyl acetate. The ethyl acetate layer was further treated with saturated aqueous $NaHCO_3$ solution. The organic layer was dried with anhydrous sodium sulfate, and after filtration the solvent was evaporated to dryness. Recrystallization from CH_2Cl_2/hexane (1:1, v/v) gave 6-phenyl-2-pyridone as a white solid (0.25 g, 97% yield).

Elemental Analysis: calculated for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.18; H, 5.07; N, 8.15.

^{1}H NMR ($CDCl_3$ with 0.1% v/v TMS, 300 MHz,): δ 10.78 (1H, s, NH), 7.60 - 7.50 (2H, m, H8, H10), 7.42 (4H, m, H3, H97, H9, H11), 6.48 (1H, dd, *J* = 9.1, 0.9 Hz, H2), 6.40 (1H, dd, *J* = 7.0, 1.0 Hz, H2).^{13}C NMR ($CDCl_3$, 75 MHz,): δ 165.0 (C1), 146.8 (C5), 141.4 (C3), 133.5 (C9), 129.2 (2C, C8, C10), 126.5 (2C, C7, C11), 118.7 (C2), 104.8 (C4).

Compound 3. Under a N_2, atmosphere $[Cp^*IrCl_2]_2$ (100 mg, 0.125 mmol), 6-methoxy-2-phenyl-pyridine (44.0 mg, 0.259 mmol), NaOAc · $3H_2O$ (64.0 mg, 0.770 mmol) were placed in a schlenk flask. Methanol (6 mL) was added, and the mixture was stirred overnight at room temperature. The orange solid that precipitated from the reaction mixture, was filtered and dried under vacuum (90 mg, 66% yield).

Elemental Analysis: calculated for $C_{22}H_{25}ClIrNO$: C, 48.30; H, 4.61; N, 2.56. Found: C, 48.10; H, 4.38; N, 2.34.

^{1}H NMR ($CDCl_3$, 300 MHz,): δ 7.82 (1H, dd, *J* = 7.7, 1.2 Hz, H5), 7.62 (1H, dd, *J* = 7.8, 1.2 Hz, H2), 7.62 (1H, t, *J* = 8.0Hz, H9), 7.45 (1H, dd, *J* = 1.2, 7.9 Hz, H8 or H10), 7.16 (1H, td, *J* = 1.5, 7.4 Hz, H4), 6.99 (1H, td, *J* = 7.8, 1.2 Hz, H3), 6.56 (1H, dd, *J* = 8.2, 1.2 Hz, H8 or H10), 4.03 (3H, s, H14), 1.64 (15H, s, H13). ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 166.0, 164.4, 162.6, 144.5, 139.44 (C9), 135.6 (C5), 130.2 (C4), 123.8 (C2), 121.4 (C3), 111.0 (C8 or C10), 101.8 (C8 or C10), 88.3 (5C, C12), 57.2 (C14), 9.1 (5C, C13).

Compound 4. Under a N_2, atmosphere $[Cp^*IrCl_2]_2$ (103 mg, 0.129 mmol), 6-phenyl-2-pyridone (44.0 mg, 0.259 mmol), and sodium *tert*-butoxide (25.0 mg, 0.259 mmol) were placed in a schlenk flask. Dichloromethane (4 mL) was added, and the mixture was stirred for 2h at room temperature. The red solution was filtered through a celite pad to separate the insoluble salts. After solvent evaporation the product was obtained as a dark yellow powder (80 mg, 58% yield).

Elemental Analysis: calculated for $C_{21}H_{23}ClIrNO \cdot 0.2CH_2Cl_2$: C, 46.29; H, 4.29; N, 2.55. Found: C, 46.15; H, 4.35; N, 2.36.

^{1}H NMR ($CDCl_3$ with 0.1% v/v TMS, 300 MHz,): δ 7.92–7.88 (m, 2H, H1, H5), 7.52 (t, *J* = 7.4, 1H, H9), 7.48–7.45 (m, 3H, H2,H3,H4), 6.64 (d, *J* = 7.3, 1H, H10), 6.21 (d, *J* = 8.6, 1H, H8), 1.48 (s, 15H, H13). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.3 , 152.6 , 138.3 (C9), 137.6, 128.0–127.4 (5C, C1,C2, C3, C5), 110.6 (C8), 109.3 (C10), 82.6 (5C, C12), 8.1 (5C, C13).

Compound 6. Under a N_2, atmosphere $[Cp^*Ir(H_2O)_3]SO_4$ (109 mg, 0.228 mmol), 6-phenyl-2-pyridone (39.1 mg, 0.228 mmol) and sodium acetate (18.7 mg, 0228 mmol) were placed in a schlenk flask. Distilled water (5 mL) was added, and the mixture was stirred for 24h at room temperature. After this period of time, the product (which precipitated as a yellow solid) was separated from the reaction mixture by filtration and washed with water (20 mL) (70 mg, 55% yield).

Elemental Analysis: calculated for $C_{23}H_{26}ClIrNO_3 \cdot 0.3H_2O$: C, 49.09; H, 4.78; N, 2.49. Found: C, 48.78; H, 4.44; N, 2.53.

^{1}H NMR ($CDCl_3$ with 0.1% v/v TMS, 300 MHz,): δ 13.51 (1H, s, OH), 7.95 (1H, dd, *J* = 7.5, 0.9 Hz, H5), 7.50 (1H, dd, *J* = 7.9, 1.1 Hz, H2), 7.46 (1H, t, *J* = 7.8 Hz, H9), 7.17 (1H, dd, *J* = 1.3, 7.3 Hz, H8 or H10), 7.15 (1H, td, *J* = 1.3, 7.3 Hz, H4), 6.99 (1H, td, *J* = 7.6, 1.2 Hz, H3), 6.66 (1H, dd, *J* = 8.1, 1.1 Hz, H8 or H10), 1.93 (3H, s, H15), 1.46 (15H, s, H13). ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 181.6 (C14), 166.0, 165.2, 162.8, 146.2, 140.0 (C9), 135.0 (C5), 130.1 (C4), 124.0 (C2), 122.7 (C3), 109.8 (C8 or C10), 109.2 (C8 or C10), 87.2 (5C, C12), 23.3 (C15), 9.2 (5C, C13).

Compound 1.

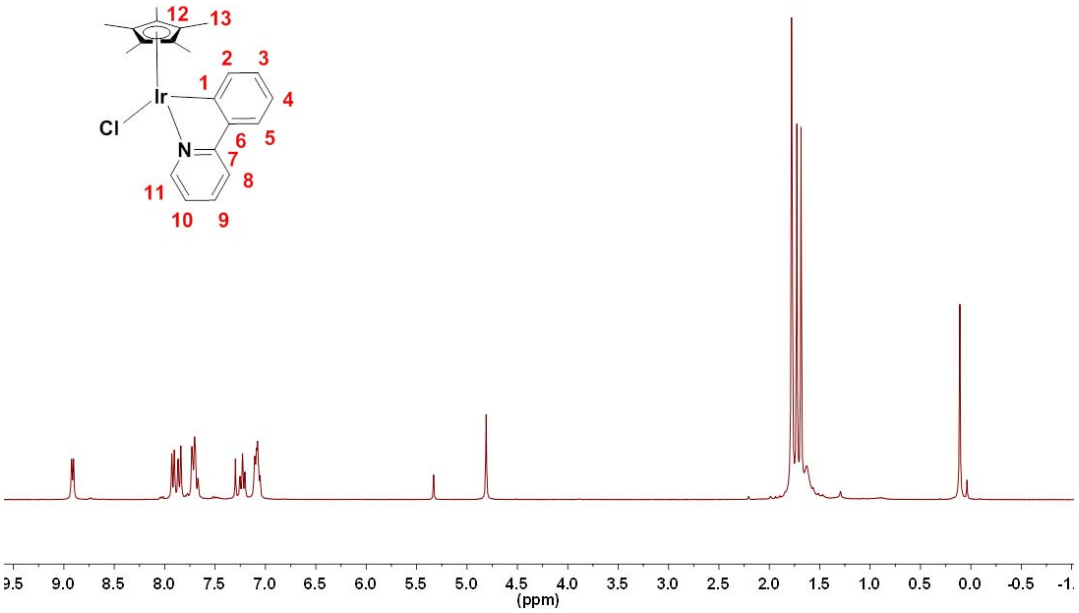


Fig S51. ^{1}H NMR spectra of compound **1** in $CDCl_3$ (300 MHz).

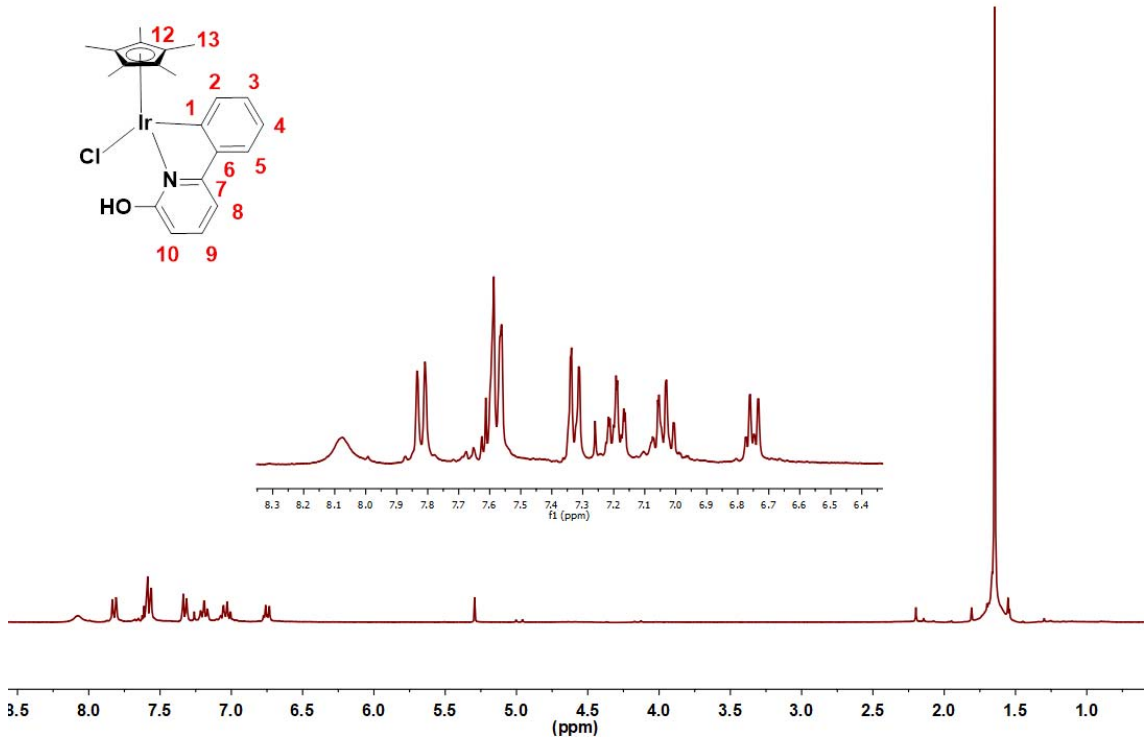


Fig S52. ^{1}H NMR spectra of compound **2** in $CDCl_3$ (300 MHz).

Compound 3.

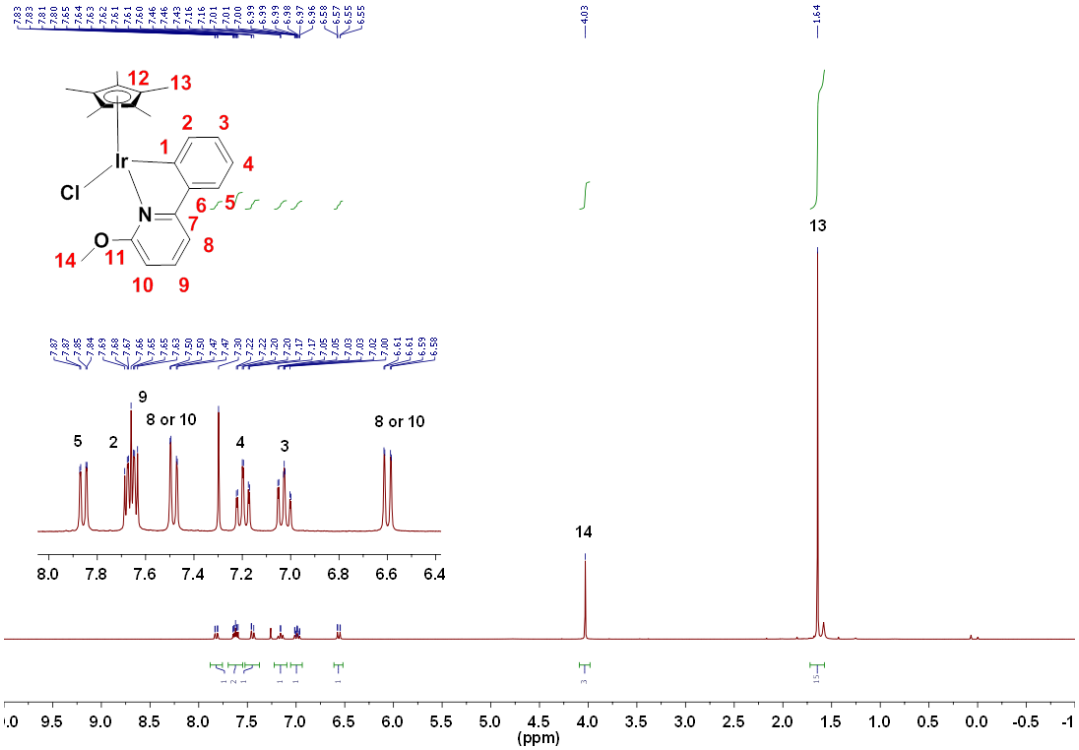


Fig S53. ^{1}H NMR spectra of compound **3** in $CDCl_3$ (300 MHz).

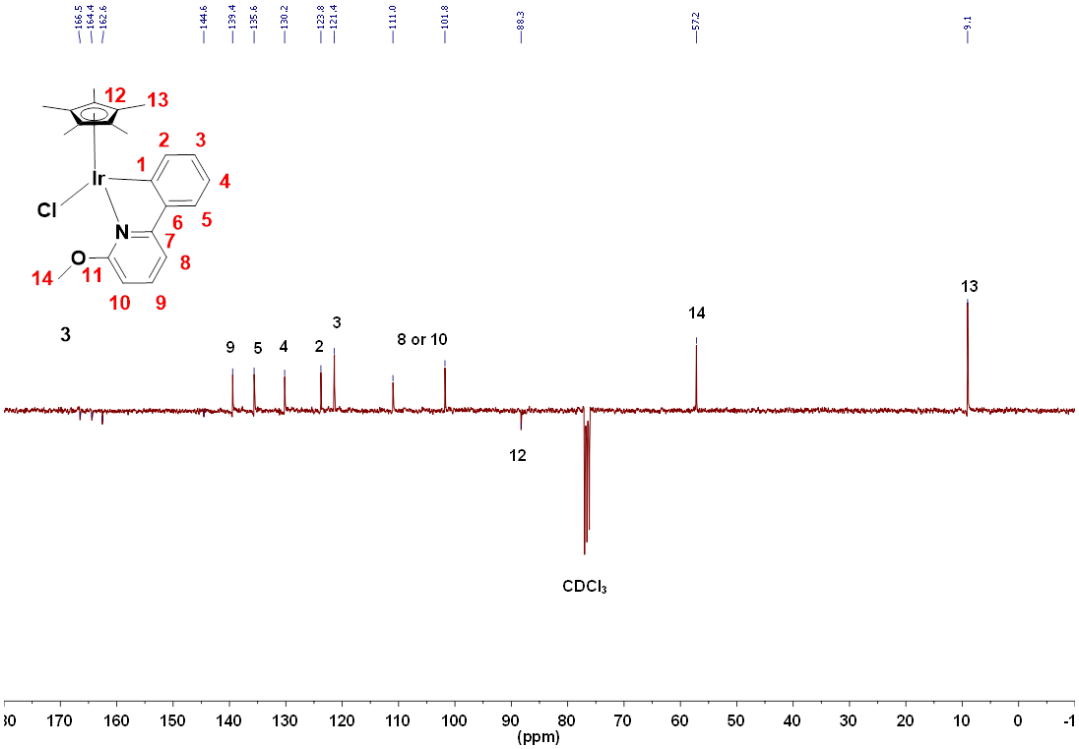


Fig S54. ^{13}C APT NMR spectra of compound **3** in $CDCl_3$ (75 MHz).

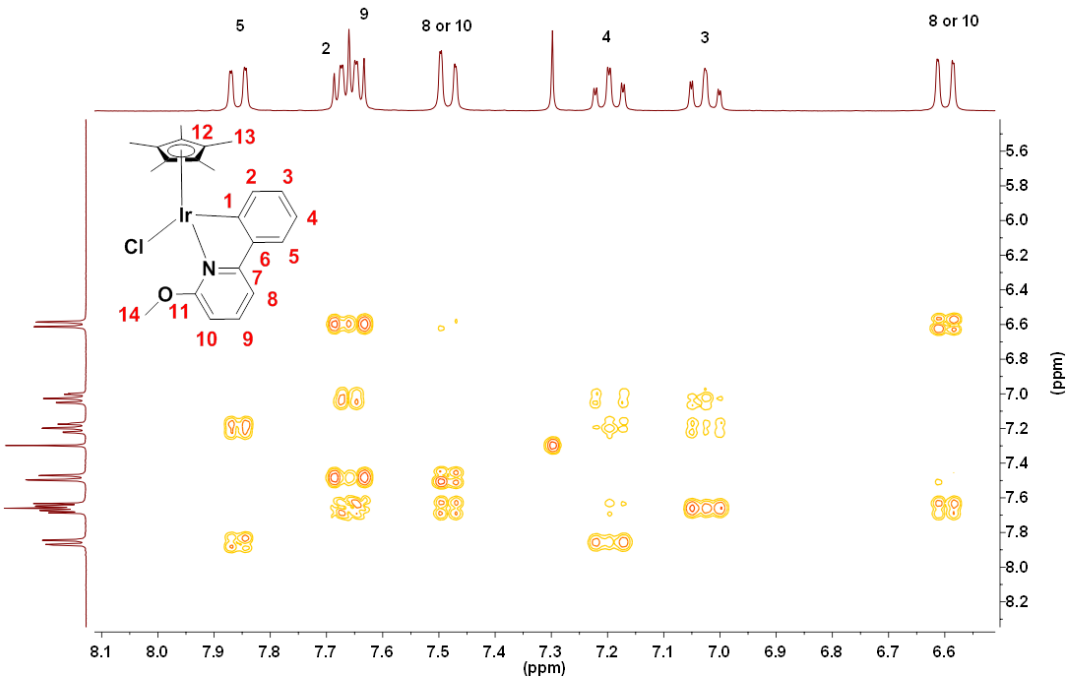


Fig S55. Aromatic region of the COSY NMR spectra of compound **3** in $CDCl_3$ (300 MHz).

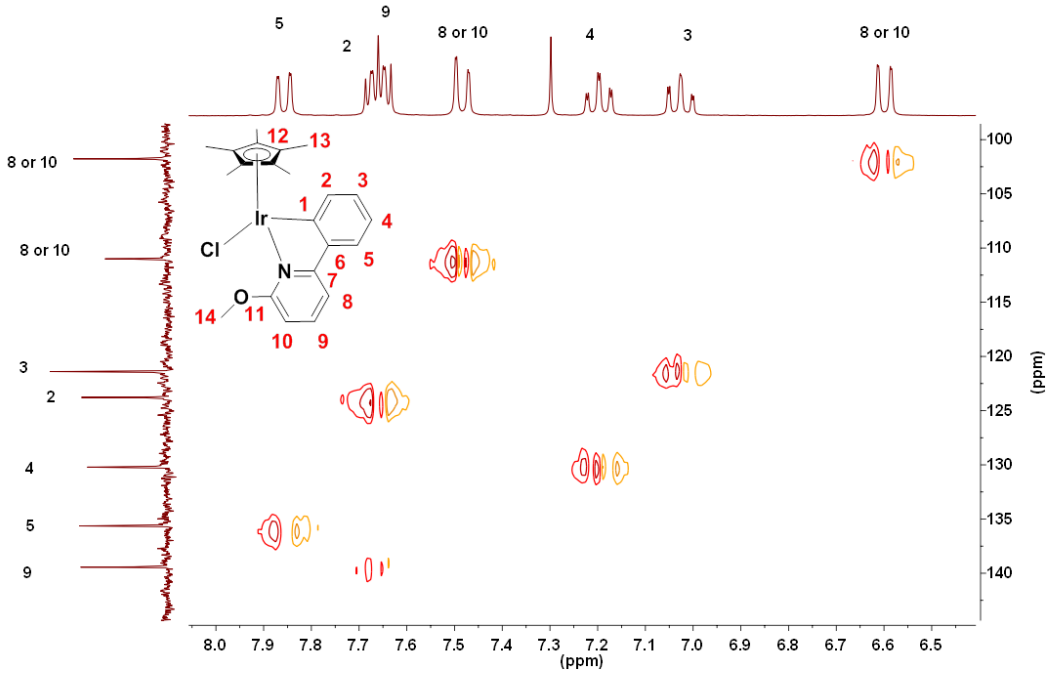


Fig S56. Aromatic region of the HSQC NMR spectra of compound **3** in $CDCl_3$.

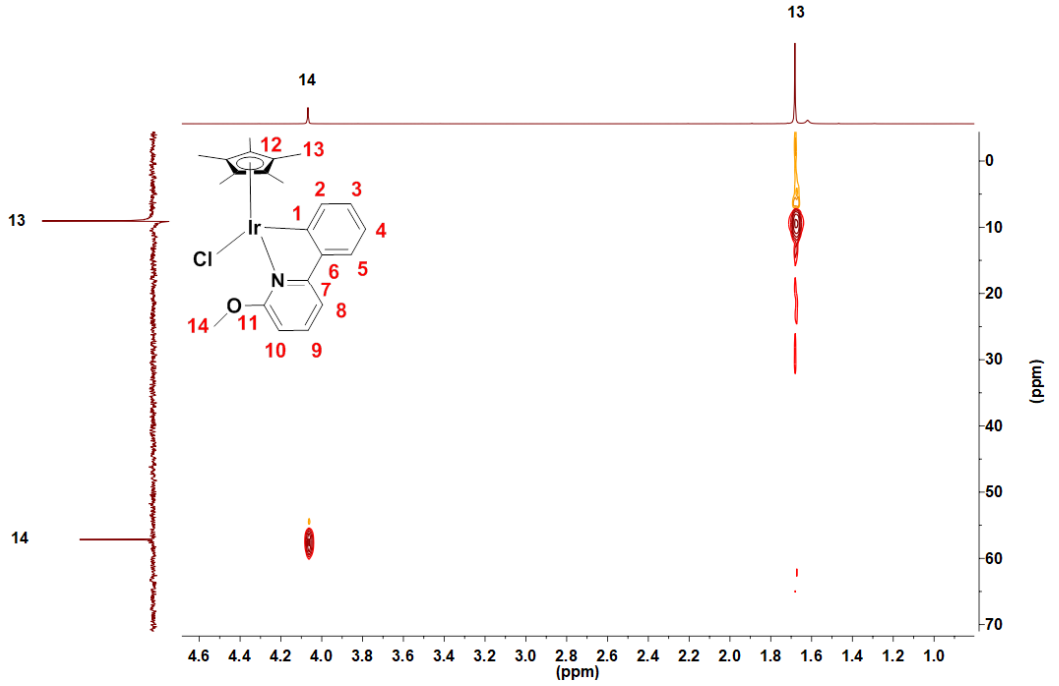


Fig S57. Aliphatic region of the HSQC NMR spectra of compound **3** in $CDCl_3$.

Compound 4.

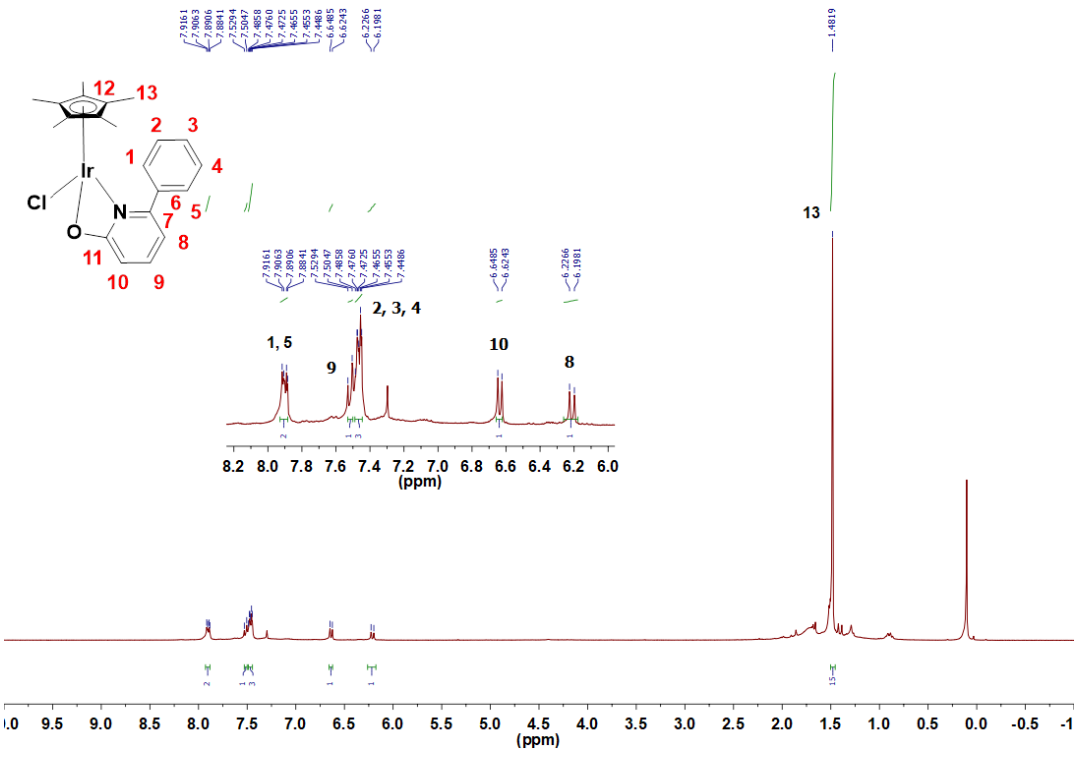


Fig S58. ^{1}H NMR spectra of compound **4** in $CDCl_3$ (300 MHz).

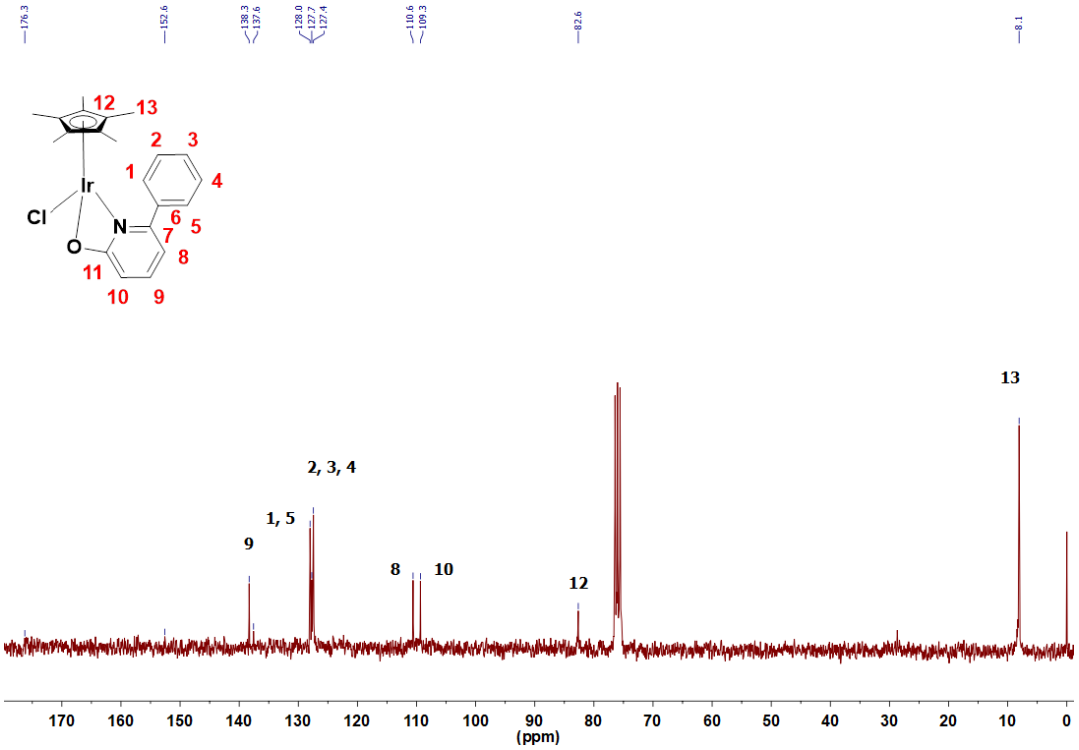


Fig S59. ^{13}C NMR spectra of compound **4** in $CDCl_3$ (300 MHz).

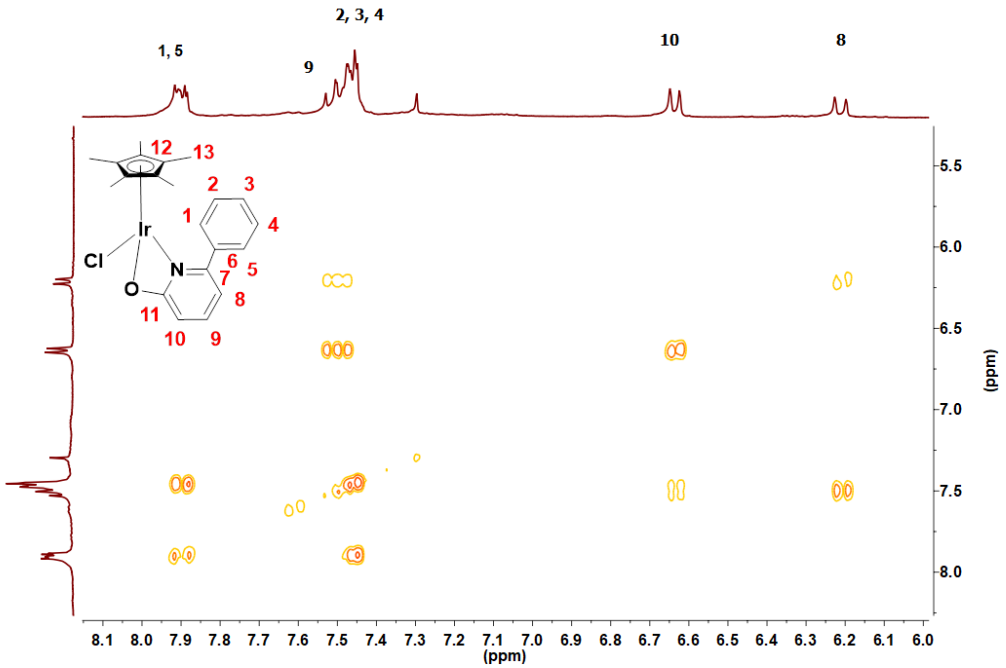


Fig S60. Aromatic region of the COSY NMR spectra of compound **4** in $CDCl_3$ (300 MHz).

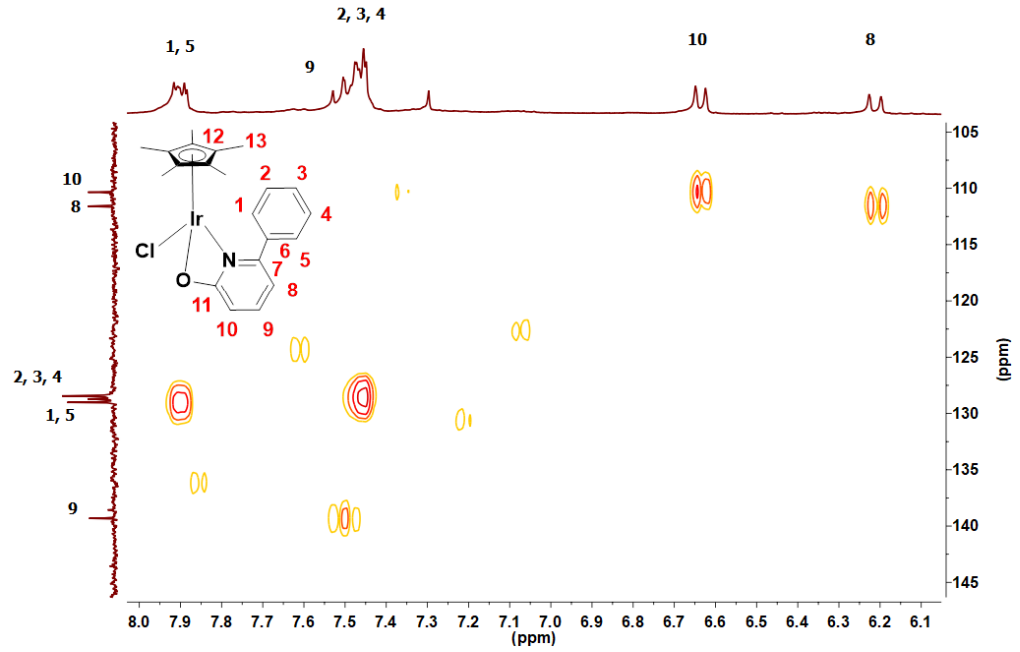


Fig S61. Aliphatic region of the HSQC NMR spectra of compound **4** in $CDCl_3$.

Compound 5.

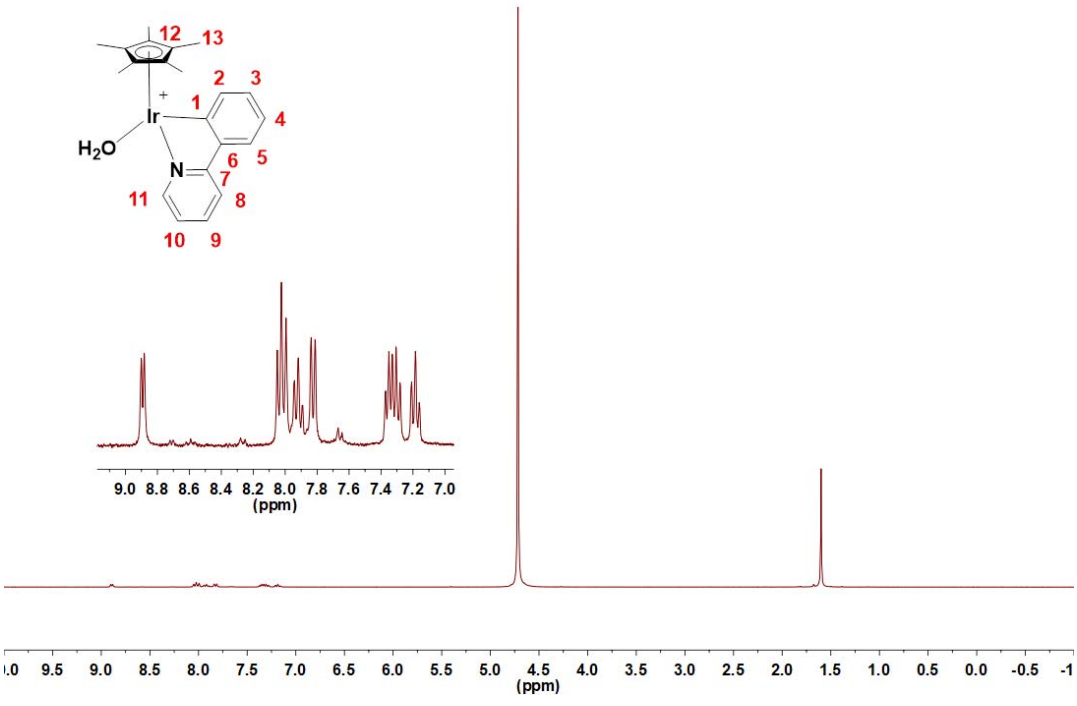


Fig S62. ^{1}H NMR spectra of compound **5** in D_2O (300 MHz).

Compound 6.

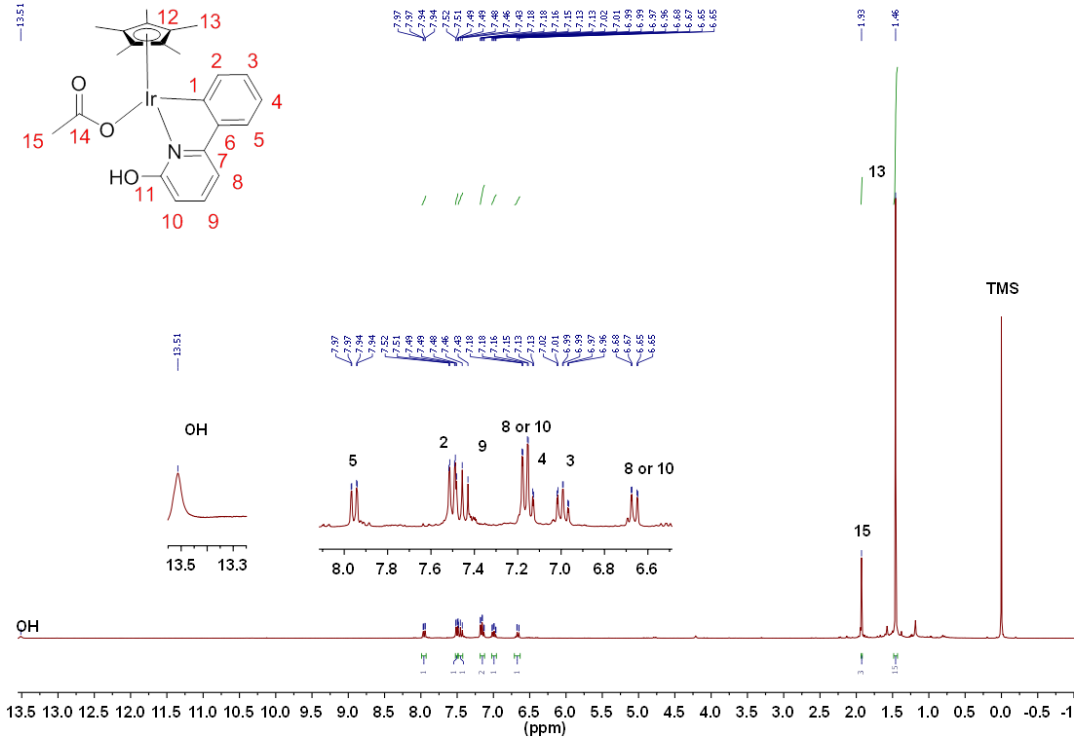


Fig S63. ^{1}H NMR spectra of compound **6** in $CDCl_3$ (300 MHz).

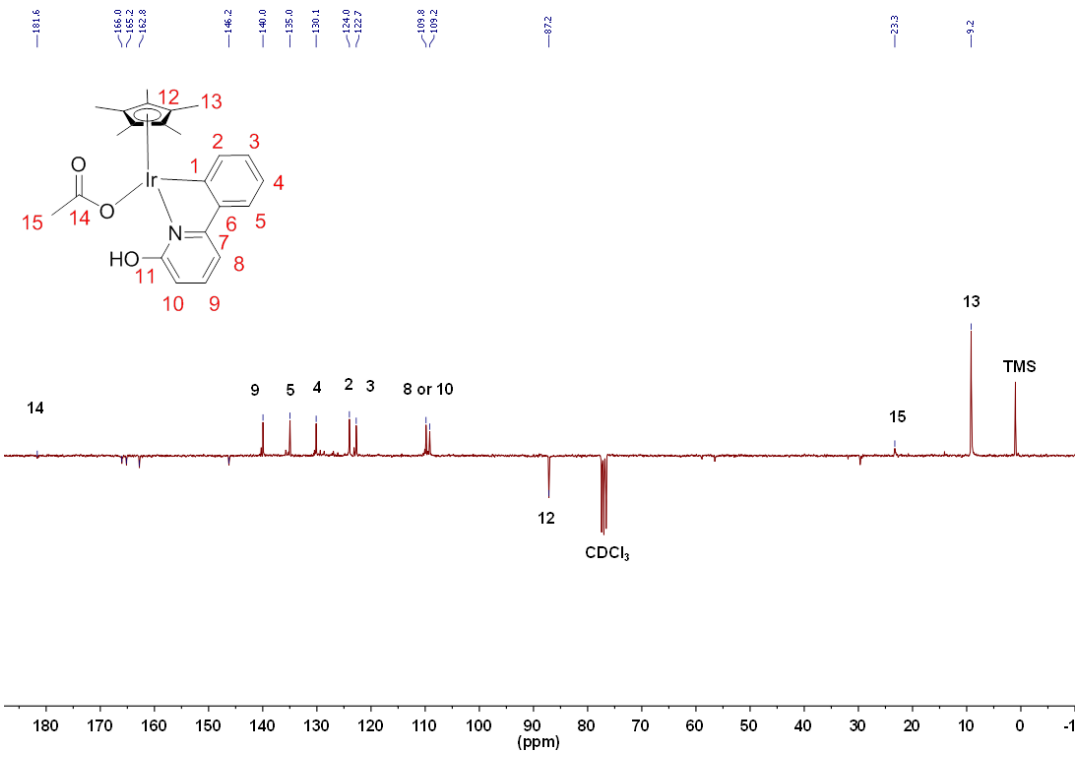


Fig S64. ^{13}C APT NMR spectra of compound **6** in $CDCl_3$ (75 MHz).

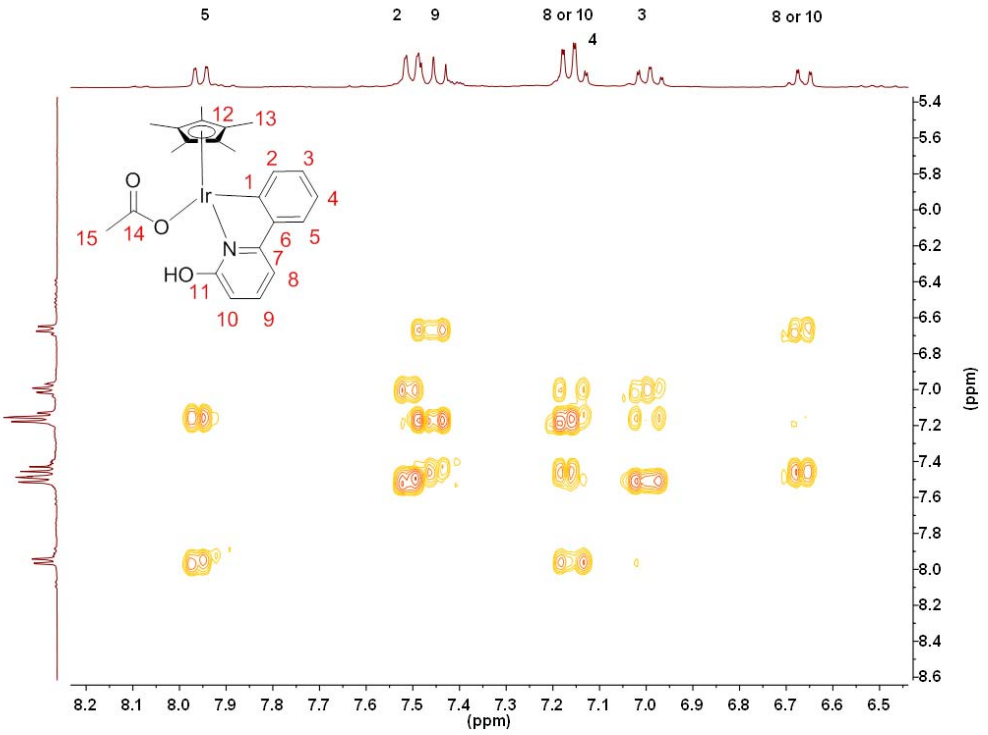


Fig S65. Aromatic region of the COSY NMR spectra of compound **6** in $CDCl_3$ (300 MHz).

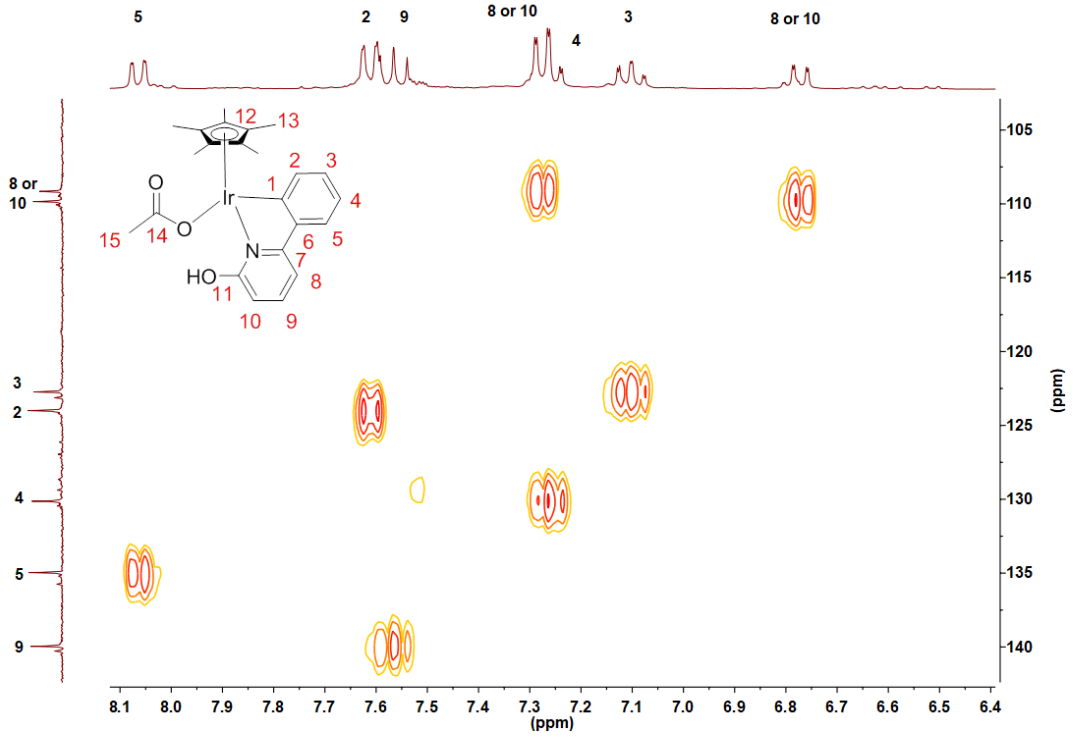


Fig S66. Aromatic region of the HSQC NMR spectra of compound **6** in $CDCl_3$.

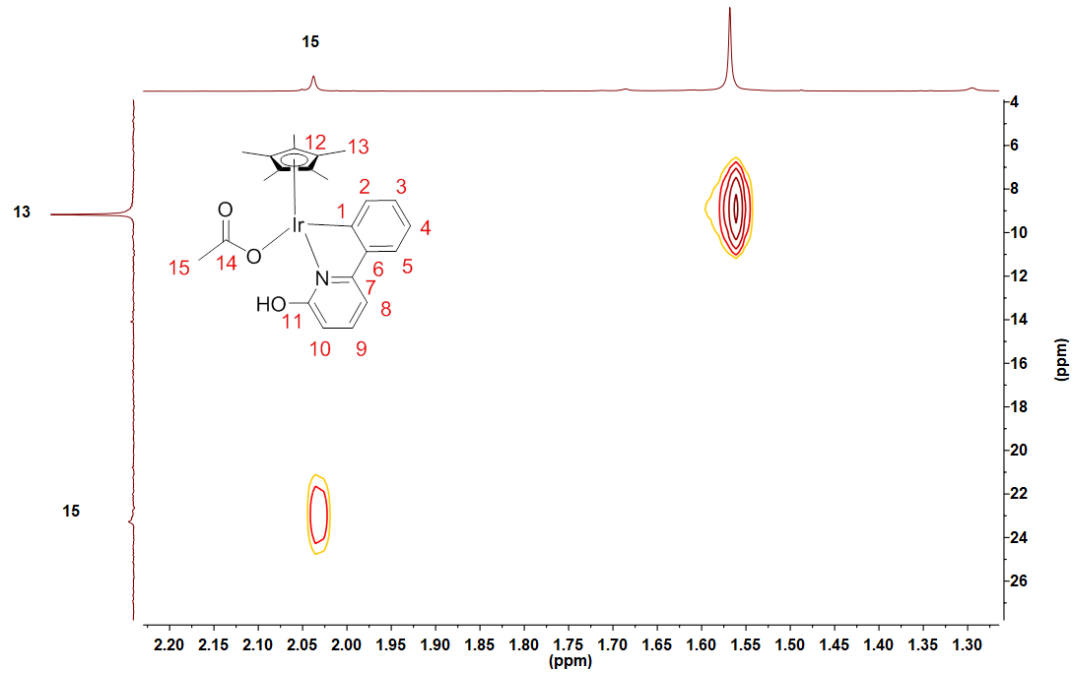


Fig S67. Aliphatic region of the HSQC NMR spectra of compound **6** in $CDCl_3$.

6-phenyl-2-pyridone

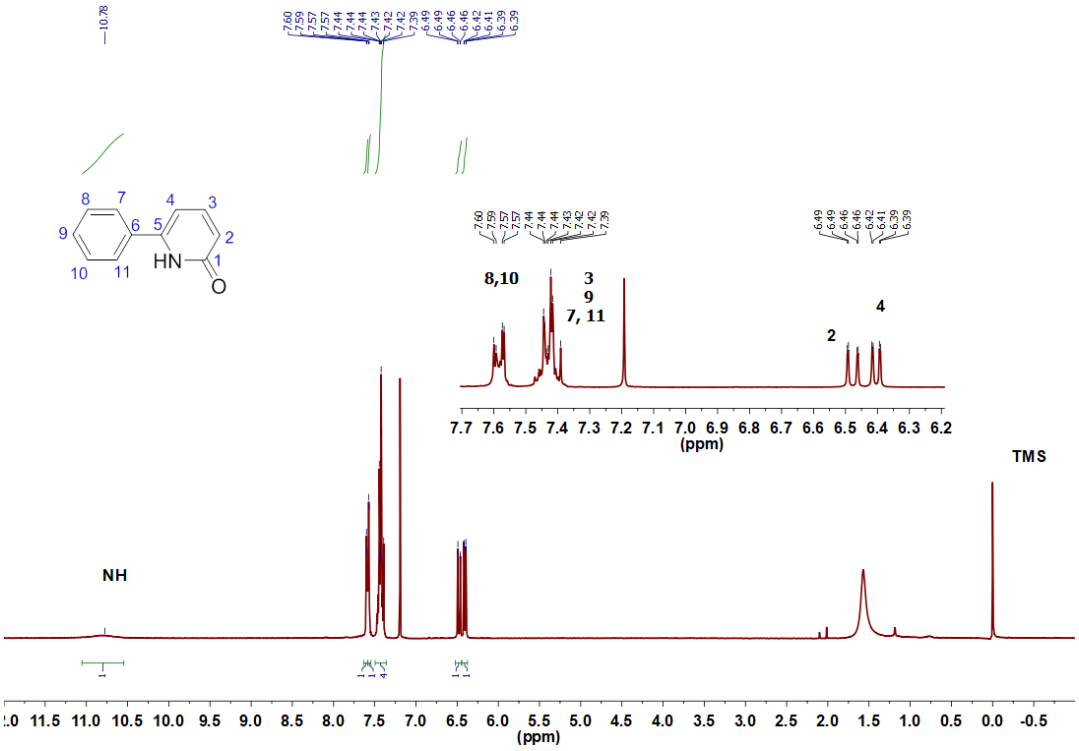


Fig S68. ^{1}H NMR spectra of 6-phenyl-2-pyridone in $CDCl_3$ (300 MHz).

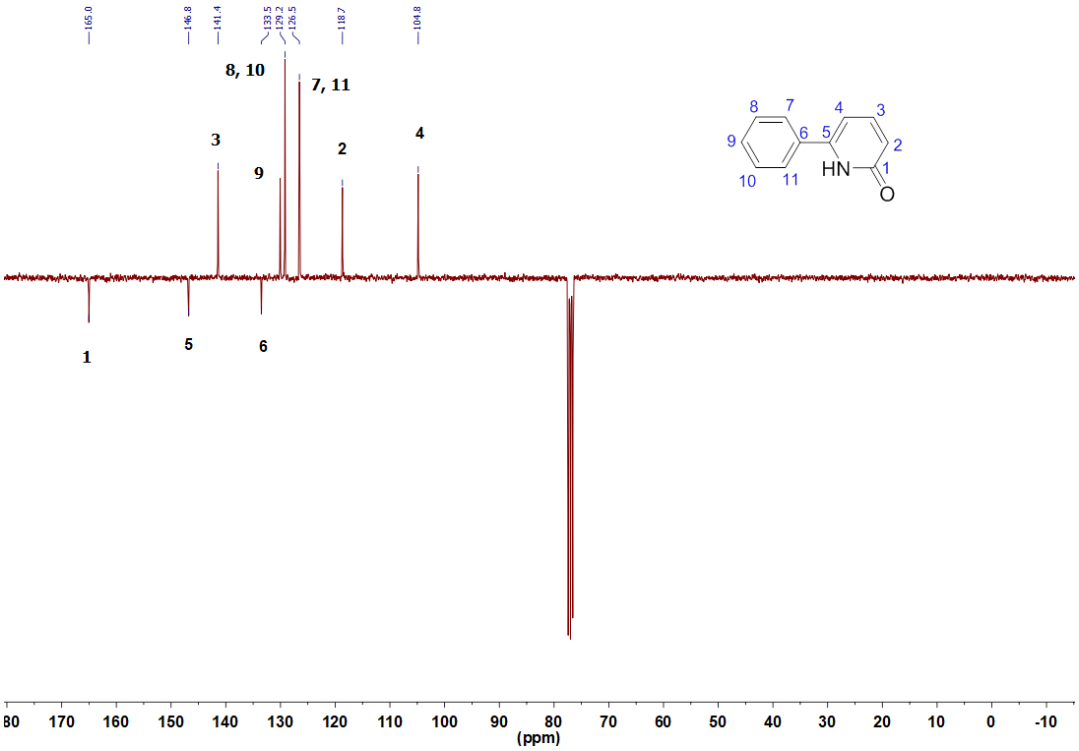


Fig S69. ^{13}C APT NMR spectra of 6-phenyl-2-pyridone in $CDCl_3$ (75 MHz).

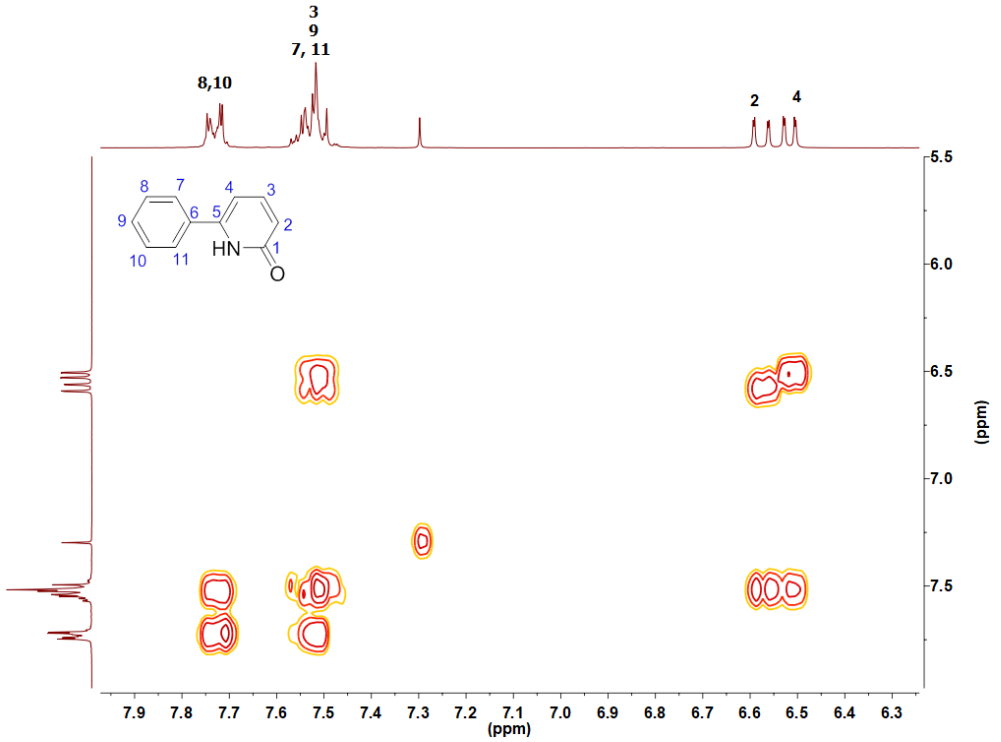


Fig S70. Aromatic region of the COSY NMR spectra of 6-phenyl-2-pyridone in $CDCl_3$ (300 MHz).

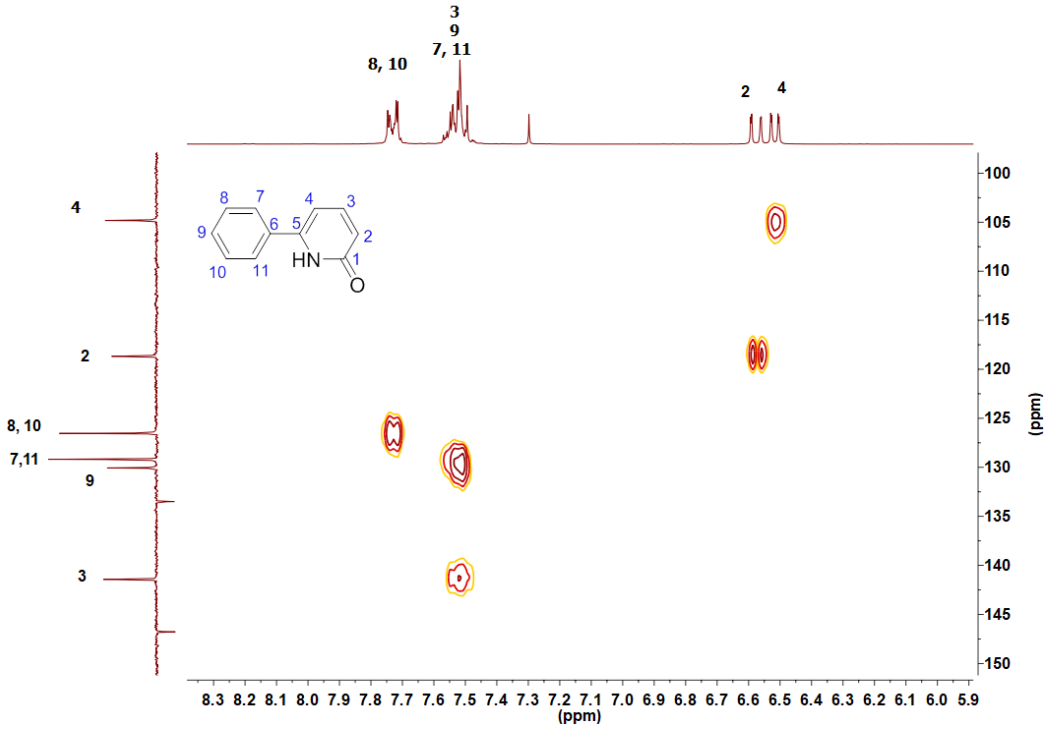


Fig S71. Aromatic region of the HSQC NMR spectra of 6-phenyl-2-pyridone in $CDCl_3$.

6-methoxy-2-phenylpyridine.

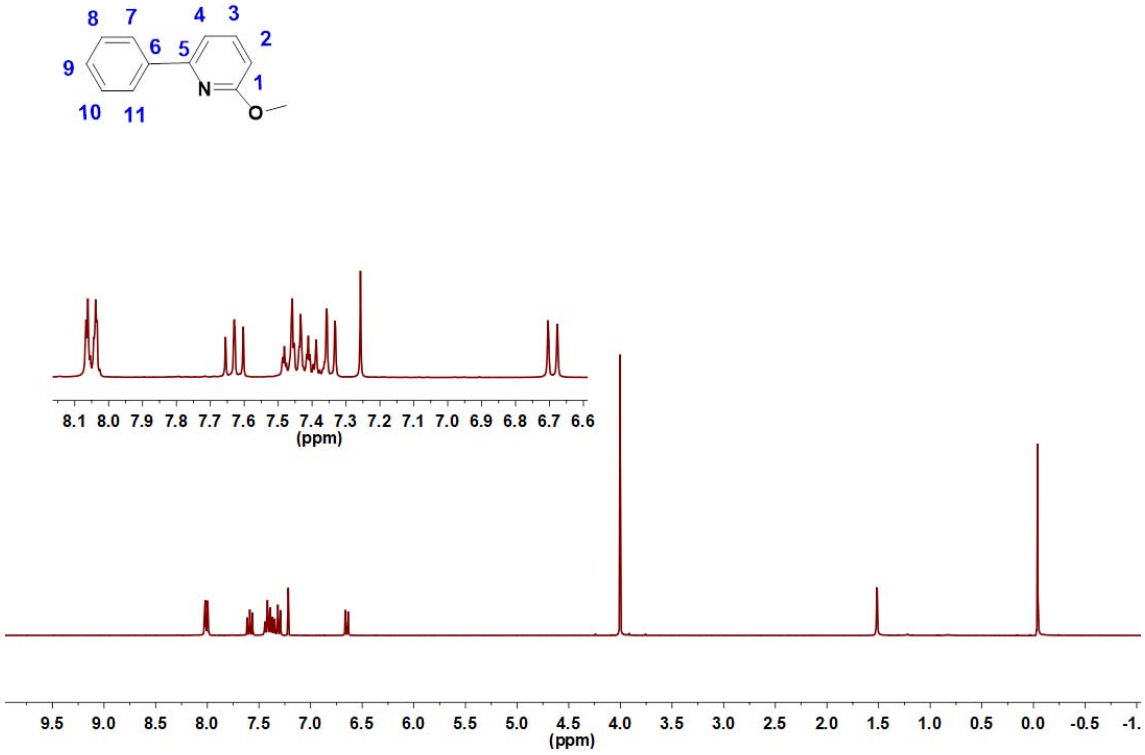


Fig S72. ^{1}H NMR spectra of 6-methoxy-2-phenylpyridine in $CDCl_3$ (300 MHz).

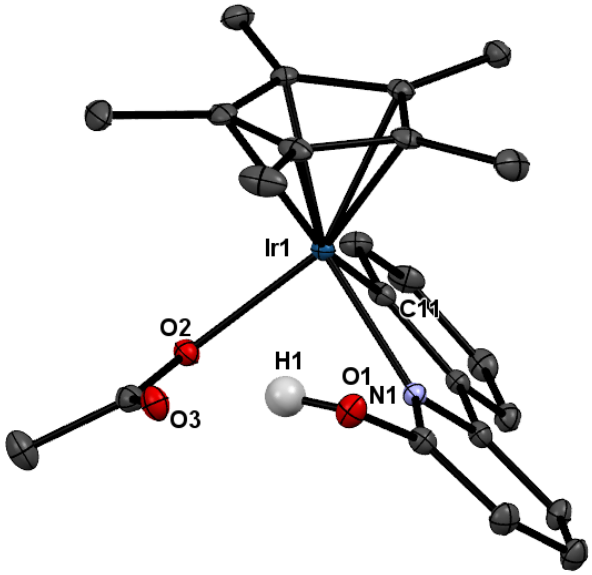


Fig S73. ORTEP-type drawings of the molecular structures of **6** drawn at the 30% probability level. Most of the hydrogen atoms are omitted for the sake of clarity.

Table 1 Crystal data and structure refinement for compound6.

Identification code	compound6
Empirical formula	$C_{23}H_{26}IrNO_3$
Formula weight	556.65
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.13031(15)
b/Å	14.54437(12)
c/Å	17.33703(17)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4067.35(6)
Z	8
ρ_{calc}g/cm^3	1.818
μ/mm^{-1}	12.917
F(000)	2176.0
Crystal size/mm^3	0.137 × 0.077 × 0.043
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.648 to 139.998
Index ranges	-19 ≤ h ≤ 19, -17 ≤ k ≤ 17, -21 ≤ l ≤ 19
Reflections collected	33175
Independent reflections	3856 [R_{int} = 0.0285, R_{sigma} = 0.0137]
Data/restraints/parameters	3856/1/262
Goodness-of-fit on F^2	1.042

Final R indexes [I>=2σ (I)]	R_1 = 0.0172, wR_2 = 0.0437
Final R indexes [all data]	R_1 = 0.0191, wR_2 = 0.0450
Largest diff. peak/hole / e Å^{-3}	0.76/-0.64

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound6. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ir(1)	1792.1(2)	1838.6(2)	5544.2(2)	13.10(5)
O(1)	2049.0(11)	1545.8(12)	7402.3(9)	23.0(3)
O(2)	1094.0(11)	605.0(11)	5600.9(9)	19.0(3)
O(3)	749.8(11)	786.5(12)	6847.8(10)	24.5(4)
N(1)	2694.6(11)	1197.8(12)	6249.9(11)	15.2(4)
C(1)	2716.0(14)	1251.7(15)	7025.6(13)	18.2(4)
C(2)	3425.3(16)	1014.2(17)	7445.6(14)	23.2(5)
C(3)	4098.6(15)	659.4(17)	7057.0(14)	23.8(5)
C(4)	4045.8(14)	522.5(16)	6265.9(13)	20.7(5)
C(5)	3348.5(14)	800.2(15)	5868.6(14)	16.7(4)
C(6)	3222.4(13)	728.1(15)	5035.5(13)	15.3(4)
C(7)	3774.7(15)	265.9(16)	4544.1(14)	20.1(5)
C(8)	3617.6(15)	217.8(16)	3761.3(14)	22.8(5)
C(9)	2897.2(17)	614.3(16)	3474.2(13)	23.7(5)
C(10)	2343.4(15)	1066.1(15)	3957.5(13)	20.5(5)
C(11)	2499.8(14)	1147.1(14)	4750.4(13)	16.2(4)
C(12)	2001.5(16)	3186.0(14)	5079.3(14)	17.0(4)
C(13)	1185.8(14)	2871.2(15)	4846.7(13)	17.2(4)
C(14)	703.3(15)	2769.1(16)	5541.4(14)	20.9(5)
C(15)	1186.0(16)	3017.8(15)	6190.3(15)	21.7(5)
C(16)	2005.5(17)	3246.4(14)	5903.6(15)	19.7(5)
C(17)	2696.2(15)	3452.9(17)	4553.4(14)	22.4(5)
C(18)	858.1(16)	2810.5(16)	4042.4(15)	25.0(5)
C(19)	-176.9(16)	2450.1(19)	5563.4(17)	30.8(6)
C(20)	873(2)	3115.5(18)	6999.4(17)	33.9(7)
C(21)	2723.4(18)	3552.9(17)	6385.3(16)	29.1(6)
C(22)	690.2(15)	394.3(16)	6203.8(14)	21.0(5)
C(23)	86.8(18)	-391.7(19)	6117.0(17)	32.2(6)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for compound6. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir(1)	14.37(7)	12.36(7)	12.57(7)	0.57(3)	1.38(3)	1.07(3)
O(1)	21.3(8)	31.5(9)	16.1(8)	-2.0(7)	2.9(7)	3.1(7)
O(2)	19.4(8)	15.9(7)	21.6(8)	0.2(6)	1.8(6)	-1.4(6)
O(3)	23.5(8)	27.8(8)	22.3(9)	-1.8(7)	6.7(7)	-4.3(7)
N(1)	15.2(8)	14.2(8)	16.1(9)	0.3(7)	0.5(7)	-0.7(7)

C(1)	20.8(11)	17(1)	16.9(11)	-0.5(8)	1.3(9)	-1.4(9)
C(2)	23.9(12)	28.5(12)	17.3(11)	-1.1(9)	-4.2(9)	-1.1(10)
C(3)	19.0(11)	30.4(12)	22.0(12)	0.8(10)	-5.8(9)	0.5(9)
C(4)	15(1)	25.4(11)	21.5(11)	-1.2(9)	1.4(9)	1.1(9)
C(5)	17.3(10)	14.5(10)	18.3(11)	-0.3(8)	1.1(9)	-2.9(8)
C(6)	16.8(10)	12.7(10)	16.4(11)	0.6(8)	1.5(8)	-2.3(8)
C(7)	17.2(11)	19.5(11)	23.6(12)	-1.6(9)	2.3(9)	0.5(9)
C(8)	24.2(12)	20.6(11)	23.8(12)	-4.0(9)	9.5(10)	0.1(9)
C(9)	34.6(13)	21.7(11)	14.7(11)	1.4(9)	3.1(10)	0.6(10)
C(10)	25.9(12)	18.2(10)	17.4(11)	1.5(8)	0.3(9)	3.4(9)
C(11)	20(1)	12.4(9)	16.2(10)	0.9(8)	3.6(8)	-0.8(8)
C(12)	20.6(11)	10.3(10)	20.2(12)	1.7(8)	0.6(10)	1.4(8)
C(13)	18.3(11)	11.1(9)	22.1(11)	2.6(8)	-0.7(9)	3.6(8)
C(14)	18.5(11)	14.1(11)	30.1(13)	3.5(8)	4.4(9)	7.2(9)
C(15)	27.9(13)	13.4(10)	23.7(12)	-0.2(9)	7.5(10)	5.5(9)
C(16)	28.3(12)	9.5(10)	21.4(12)	-0.1(8)	-0.8(10)	0.2(9)
C(17)	20.1(12)	20.4(11)	26.5(13)	5.2(9)	5.2(9)	0.6(10)
C(18)	29.2(13)	18.7(11)	27.2(13)	2.7(9)	-10.1(10)	2.2(10)
C(19)	17.7(12)	24.4(13)	50.4(17)	5.5(11)	7.5(11)	3.8(10)
C(20)	53.8(19)	24.1(13)	23.9(14)	1.5(10)	15.6(13)	10.6(12)
C(21)	37.6(14)	20.2(12)	29.6(14)	-3.6(10)	-11.4(11)	-4.3(10)
C(22)	20.1(11)	19.5(10)	23.4(12)	2.4(9)	2.9(9)	2.4(9)
C(23)	33.2(14)	30.2(13)	33.0(14)	-0.9(11)	4.7(11)	-12.0(11)

Table 4 Bond Lengths for compound6.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ir(1)	O(2)	2.1206(16)	C(6)	C(7)	1.404(3)
Ir(1)	N(1)	2.1177(18)	C(6)	C(11)	1.405(3)
Ir(1)	C(11)	2.051(2)	C(7)	C(8)	1.382(3)
Ir(1)	C(12)	2.146(2)	C(8)	C(9)	1.389(4)
Ir(1)	C(13)	2.162(2)	C(9)	C(10)	1.390(3)
Ir(1)	C(14)	2.217(2)	C(10)	C(11)	1.403(3)
Ir(1)	C(15)	2.270(2)	C(12)	C(13)	1.450(3)
Ir(1)	C(16)	2.168(2)	C(12)	C(16)	1.432(4)
O(1)	C(1)	1.329(3)	C(12)	C(17)	1.496(3)
O(2)	C(22)	1.269(3)	C(13)	C(14)	1.442(3)
O(3)	C(22)	1.258(3)	C(13)	C(18)	1.494(3)
N(1)	C(1)	1.348(3)	C(14)	C(15)	1.415(4)
N(1)	C(5)	1.373(3)	C(14)	C(19)	1.494(3)
C(1)	C(2)	1.400(3)	C(15)	C(16)	1.451(4)
C(2)	C(3)	1.378(4)	C(15)	C(20)	1.498(4)
C(3)	C(4)	1.388(3)	C(16)	C(21)	1.496(4)
C(4)	C(5)	1.379(3)	C(22)	C(23)	1.509(3)
C(5)	C(6)	1.462(3)			

Table 5 Bond Angles for compound68.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O(2)	Ir(1)	C(12)	150.90(8)	C(7)	C(6)	C(11)	121.4(2)
O(2)	Ir(1)	C(13)	111.93(8)	C(11)	C(6)	C(5)	115.58(19)
O(2)	Ir(1)	C(14)	95.50(8)	C(8)	C(7)	C(6)	120.2(2)
O(2)	Ir(1)	C(15)	112.81(8)	C(7)	C(8)	C(9)	118.9(2)
O(2)	Ir(1)	C(16)	150.48(8)	C(8)	C(9)	C(10)	121.2(2)
N(1)	Ir(1)	O(2)	88.04(7)	C(9)	C(10)	C(11)	121.0(2)
N(1)	Ir(1)	C(12)	120.71(8)	C(6)	C(11)	Ir(1)	115.98(16)
N(1)	Ir(1)	C(13)	160.02(8)	C(10)	C(11)	Ir(1)	126.77(17)
N(1)	Ir(1)	C(14)	144.53(8)	C(10)	C(11)	C(6)	117.2(2)
N(1)	Ir(1)	C(15)	110.09(8)	C(13)	C(12)	Ir(1)	70.93(12)
N(1)	Ir(1)	C(16)	98.08(8)	C(13)	C(12)	C(17)	126.3(2)
C(11)	Ir(1)	O(2)	84.94(7)	C(16)	C(12)	Ir(1)	71.45(12)
C(11)	Ir(1)	N(1)	77.84(8)	C(16)	C(12)	C(13)	107.5(2)
C(11)	Ir(1)	C(12)	96.21(9)	C(16)	C(12)	C(17)	126.1(2)
C(11)	Ir(1)	C(13)	102.53(9)	C(17)	C(12)	Ir(1)	125.73(16)
C(11)	Ir(1)	C(14)	137.60(9)	C(12)	C(13)	Ir(1)	69.72(12)
C(11)	Ir(1)	C(15)	160.25(9)	C(12)	C(13)	C(18)	126.8(2)
C(11)	Ir(1)	C(16)	124.58(9)	C(14)	C(13)	Ir(1)	72.86(13)
C(12)	Ir(1)	C(13)	39.35(9)	C(14)	C(13)	C(12)	106.9(2)
C(12)	Ir(1)	C(14)	64.30(9)	C(14)	C(13)	C(18)	125.6(2)
C(12)	Ir(1)	C(15)	64.09(9)	C(18)	C(13)	Ir(1)	129.88(16)
C(12)	Ir(1)	C(16)	38.77(10)	C(13)	C(14)	Ir(1)	68.72(12)
C(13)	Ir(1)	C(14)	38.41(9)	C(13)	C(14)	C(19)	124.5(2)
C(13)	Ir(1)	C(15)	63.66(9)	C(15)	C(14)	Ir(1)	73.65(13)
C(13)	Ir(1)	C(16)	64.94(9)	C(15)	C(14)	C(13)	109.9(2)
C(14)	Ir(1)	C(15)	36.74(9)	C(15)	C(14)	C(19)	125.6(2)
C(16)	Ir(1)	C(14)	63.25(10)	C(19)	C(14)	Ir(1)	124.27(17)
C(16)	Ir(1)	C(15)	38.08(9)	C(14)	C(15)	Ir(1)	69.60(13)
C(22)	O(2)	Ir(1)	120.99(15)	C(14)	C(15)	C(16)	106.7(2)
C(1)	N(1)	Ir(1)	124.65(15)	C(14)	C(15)	C(20)	125.7(3)
C(1)	N(1)	C(5)	119.0(2)	C(16)	C(15)	Ir(1)	67.15(12)
C(5)	N(1)	Ir(1)	115.81(15)	C(16)	C(15)	C(20)	127.3(3)
O(1)	C(1)	N(1)	119.2(2)	C(20)	C(15)	Ir(1)	132.77(17)
O(1)	C(1)	C(2)	119.0(2)	C(12)	C(16)	Ir(1)	69.78(12)
N(1)	C(1)	C(2)	121.7(2)	C(12)	C(16)	C(15)	108.9(2)
C(3)	C(2)	C(1)	118.8(2)	C(12)	C(16)	C(21)	125.4(2)
C(2)	C(3)	C(4)	119.2(2)	C(15)	C(16)	Ir(1)	74.77(13)
C(5)	C(4)	C(3)	120.1(2)	C(15)	C(16)	C(21)	125.6(2)
N(1)	C(5)	C(4)	120.6(2)	C(21)	C(16)	Ir(1)	124.40(17)
N(1)	C(5)	C(6)	113.51(19)	O(2)	C(22)	C(23)	115.6(2)
C(4)	C(5)	C(6)	125.8(2)	O(3)	C(22)	O(2)	125.6(2)
C(7)	C(6)	C(5)	123.0(2)	O(3)	C(22)	C(23)	118.8(2)

Table 6 Torsion Angles for compound 6.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Ir(1)	O(2)	C(22)	O(3)	-11.3(3)	C(7)	C(8)	C(9)	C(10)	0.9(4)
Ir(1)	O(2)	C(22)	C(23)	168.10(17)	C(8)	C(9)	C(10)	C(11)	0.9(4)
Ir(1)	N(1)	C(1)	O(1)	15.5(3)	C(9)	C(10)	C(11)	Ir(1)	176.74(17)
Ir(1)	N(1)	C(1)	C(2)	-163.88(17)	C(9)	C(10)	C(11)	C(6)	-2.0(3)
Ir(1)	N(1)	C(5)	C(4)	167.42(17)	C(11)	C(6)	C(7)	C(8)	0.3(3)
Ir(1)	N(1)	C(5)	C(6)	-11.7(2)	C(12)	C(13)	C(14)	Ir(1)	-61.81(14)
Ir(1)	C(12)	C(13)	C(14)	63.88(15)	C(12)	C(13)	C(14)	C(15)	0.6(2)
Ir(1)	C(12)	C(13)	C(18)	-125.3(2)	C(12)	C(13)	C(14)	C(19)	-179.6(2)
Ir(1)	C(12)	C(16)	C(15)	-65.05(15)	C(13)	C(12)	C(16)	Ir(1)	62.15(14)
Ir(1)	C(12)	C(16)	C(21)	118.5(2)	C(13)	C(12)	C(16)	C(15)	-2.9(2)
Ir(1)	C(13)	C(14)	C(15)	62.45(16)	C(13)	C(12)	C(16)	C(21)	-179.4(2)
Ir(1)	C(13)	C(14)	C(19)	-117.8(2)	C(13)	C(14)	C(15)	Ir(1)	-59.43(15)
Ir(1)	C(14)	C(15)	C(16)	57.03(15)	C(13)	C(14)	C(15)	C(16)	-2.4(3)
Ir(1)	C(14)	C(15)	C(20)	-128.7(2)	C(13)	C(14)	C(15)	C(20)	171.9(2)
Ir(1)	C(15)	C(16)	C(12)	61.85(14)	C(14)	C(15)	C(16)	Ir(1)	-58.58(15)
Ir(1)	C(15)	C(16)	C(21)	-121.7(2)	C(14)	C(15)	C(16)	C(12)	3.3(2)
O(1)	C(1)	C(2)	C(3)	176.3(2)	C(14)	C(15)	C(16)	C(21)	179.7(2)
N(1)	C(1)	C(2)	C(3)	-4.3(4)	C(16)	C(12)	C(13)	Ir(1)	-62.48(14)
N(1)	C(5)	C(6)	C(7)	-173.7(2)	C(16)	C(12)	C(13)	C(14)	1.4(2)
N(1)	C(5)	C(6)	C(11)	5.7(3)	C(16)	C(12)	C(13)	C(18)	172.3(2)
C(1)	N(1)	C(5)	C(4)	-4.9(3)	C(17)	C(12)	C(13)	Ir(1)	120.8(2)
C(1)	N(1)	C(5)	C(6)	176.02(19)	C(17)	C(12)	C(13)	C(14)	-175.3(2)
C(1)	C(2)	C(3)	C(4)	-1.9(4)	C(17)	C(12)	C(13)	C(18)	-4.4(4)
C(2)	C(3)	C(4)	C(5)	4.6(4)	C(17)	C(12)	C(16)	Ir(1)	-121.2(2)
C(3)	C(4)	C(5)	N(1)	-1.2(3)	C(17)	C(12)	C(16)	C(15)	173.8(2)
C(3)	C(4)	C(5)	C(6)	177.8(2)	C(17)	C(12)	C(16)	C(21)	-2.7(3)
C(4)	C(5)	C(6)	C(7)	7.3(3)	C(18)	C(13)	C(14)	Ir(1)	127.2(2)
C(4)	C(5)	C(6)	C(11)	-173.4(2)	C(18)	C(13)	C(14)	C(15)	-170.4(2)
C(5)	N(1)	C(1)	O(1)	-172.92(19)	C(18)	C(13)	C(14)	C(19)	9.4(4)
C(5)	N(1)	C(1)	C(2)	7.7(3)	C(19)	C(14)	C(15)	Ir(1)	120.8(2)
C(5)	C(6)	C(7)	C(8)	179.6(2)	C(19)	C(14)	C(15)	C(16)	177.8(2)
C(5)	C(6)	C(11)	Ir(1)	3.2(2)	C(19)	C(14)	C(15)	C(20)	-7.9(4)
C(5)	C(6)	C(11)	C(10)	-177.94(19)	C(20)	C(15)	C(16)	Ir(1)	127.3(2)
C(6)	C(7)	C(8)	C(9)	-1.5(4)	C(20)	C(15)	C(16)	C(12)	-170.9(2)
C(7)	C(6)	C(11)	Ir(1)	-177.44(17)	C(20)	C(15)	C(16)	C(21)	5.6(4)
C(7)	C(6)	C(11)	C(10)	1.5(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound6.

Atom	*x*	*y*	*z*	U(eq)
H(2)	3442.47	1096.09	7989.02	28
H(3)	4592.94	510.14	7327.19	29
H(4)	4490.53	237.28	5997.87	25
H(7)	4258.1	-14.77	4750.34	24
H(8)	3996.1	-81.65	3424.96	27
H(9)	2781.13	575.97	2938	28
H(10)	1851.46	1323.79	3747.6	25
H(17A)	3224.97	3391.57	4826.94	34
H(17B)	2622.45	4092.1	4388.28	34
H(17C)	2696.25	3049.89	4100.37	34
H(18A)	1318.27	2859.15	3675.59	38
H(18B)	464.85	3312.88	3952.54	38
H(18C)	576.06	2219.73	3971.33	38
H(19A)	-288.08	2059.98	5114.27	46
H(19B)	-547.57	2983.91	5553.57	46
H(19C)	-272.49	2097.37	6036.7	46
H(20A)	553.7	2567.56	7140.2	51
H(20B)	517.39	3659.99	7035.22	51
H(20C)	1343.91	3182.95	7352.33	51
H(21A)	2685.34	3271.66	6897.72	44
H(21B)	2712.78	4223.9	6435.95	44
H(21C)	3242.37	3364.01	6137.81	44
H(23A)	-475.87	-147.57	6057.61	48
H(23B)	111.26	-783.3	6576.47	48
H(23C)	233.07	-754.74	5660.7	48
H(1)	1592(13)	1360(20)	7155(18)	39

Crystal structure determination of compound6

Crystal Data for $C_{23}H_{26}IrNO_3$ (*M* =556.65 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 16.13031(15) Å, *b* = 14.54437(12) Å, *c* = 17.33703(17) Å, *V* = 4067.35(6) Å^3, *Z* = 8, *T* = 100.01(10) K, μ(CuKα) = 12.917 mm^{-1}, *Dcalc* = 1.818 g/cm^3, 33175 reflections measured (9.648° ≤ 2Θ ≤ 139.998), 3856 unique (R_{int} = 0.0285, R_{sigma} = 0.0137) which were used in all calculations. The final R_1 was 0.0172 (I > 2σ(I)) and wR_2 was 0.0450 (all data).

1. **A. Shen, Y.-C. Hua, T.-T. Liu, C. Ni, Y. Luo and Y.-C. Cao, *Tetrahedron Lett.*, 2016, 57, 2055-2058.**
2. **T. Tomon, T.-A. Koizumi and K. Tanaka, *Eur. J. Inorg. Chem.*, 2005, 285-293.**