

Supporting Information

Analysis of Autoinduction, Inhibition and Autoinhibition in a Rh-Catalyzed C-C Cleavage: Mechanism of Decyanative Aryl-Silylation

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General Comments

All procedures were performed using degassed and anhydrous solvents (vide infra) and standard Schlenk techniques, under an atmosphere of anhydrous nitrogen or in a N₂ filled mBraun glovebox with O₂ and H₂O kept < 0.1 ppm. All glassware used was oven dried (200 °C) or flame-dried and allowed to cool under vacuum (ca 0.5 Torr) before use.

Solvents and Chemicals:

Dry solvents (Toluene, THF, hexane) were obtained by passing solvent through a column of anhydrous alumina using an Anhydrous Engineering Grubbs-type system. Mesitylene was distilled at reduced pressure from CaH₂. All solvents were degassed by three freeze-pump-thaw cycles and stored over 4Å molecular sieves under nitrogen. Anhydrous NMP was purchased from Acros Organics and was degassed prior to use. K¹³CN and KC¹⁵N were purchased from Goss Scientific and used as received without further purification. Unless stated otherwise, reagents were purchased from commercial sources (Sigma Aldrich, Alfa Aesar, Acros Organics, or Fluorochem), and were used without purification. 1-Fluoronaphthalene was used as an internal standard for all ¹⁹F NMR spectroscopy, which was purchased from Fluorochem, and distilled from CaH₂ at reduced pressure prior to use and stored under N₂.

A genuine sample of 1-fluoro-4-(trimethylsilyl)benzene was synthesised by literature procedure,^{S1} which was used for product determination and comparison.

NMR Spectroscopy:

NMR spectra were recorded at 27 °C unless stated otherwise; ¹H, ¹³C{¹H}, ¹⁹F, ²⁹Si and ¹⁵N NMR spectra were recorded at 400 MHz, 100 MHz, 376 MHz, 79 MHz and 40 MHz respectively, using Bruker Avance I 400 and Bruker Avance III+ 400 spectrometers. ¹H and ¹³C{¹H} NMR spectra were referenced to residual solvent peaks (CHCl₃, δ_H 7.26 ppm; CDCl₃, δ_C 77.16 ppm); chemical shifts are reported in ppm

relative to tetramethylsilane standard. ^{19}F NMR spectra are reported in ppm relative to a $\text{BF}_3\cdot\text{OEt}_2$ external standard. Coupling constants, J , were calculated using MestReNova x64, and are reported to the nearest 0.1 Hz. Coupling constants that did not match as a result of digitization are reported as rounded averages. The following abbreviations (and their combinations) are used to label the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet) and br (broad).

For quantitative ^{19}F NMR spectra, a 30° pulse angle was employed with an acquisition time of 1.468 s and a relaxation delay of 6 s, with 1-fluoronaphthalene as an internal standard ($\delta_{\text{F}} -123.98$ (ddd, $J = 10.6, 5.3, 1.7$ Hz) in h_{12} -mesitylene).

Chromatography:

Analytical thin-layer chromatography was performed on precoated aluminium-backed plates (Silica gel 60 F254; Merck), and visualised using a combination of UV light (254 nm) and/or aqueous basic potassium permanganate (KMnO_4) solution. Flash column chromatography was performed using Merck Geduran[®] Si 60 (40-63 μm) silica gel.

Infrared Spectroscopy:

Infrared (IR) spectra of neat compounds were recorded over the range $4000\text{--}400\text{ cm}^{-1}$ using a Bruker APLHA[™] ATR-FTIR spectrometer, peaks are reported in cm^{-1} .

Mass Spectrometry:

Electron impact (EI^+) spectra were recorded on a ThermoElectron MAT 900 mass spectrometer using a double focusing sector field mass analyser. Electrospray ionisation (ESI^+) spectra were recorded on a Bruker ESI Micro-Tof mass spectrometer using a time-of-flight mass analyser. Data are reported in the form of m/z .

Melting Points:

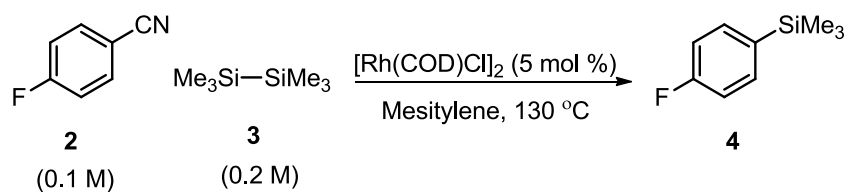
Melting points (mp) were determined on a Griffin capillary apparatus in capillary melting point tubes and are uncorrected.

Kinetic Modelling:

Kinetic modelling of experimental data was performed using Dynochem 2011.

Experiments Monitoring Reaction Progress

Monitoring Reaction Progress Under Standard Conditions



Adapted from the original procedure reported by Chatani and Tobisu.^{S2} To a Youngs' tap NMR tube was added, 400 μL from a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.75 mg, 0.032 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (130 μL , 0.64 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene in the glovebox. 100 μL of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.89 mg, 0.63 mmol) in mesitylene and 100 μL of mesitylene was added to the NMR tube. The NMR tube was sealed and removed from the glovebox and heated at 130 °C (oil bath temperature). At the designated time points, the samples were removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy (Fig. S1).

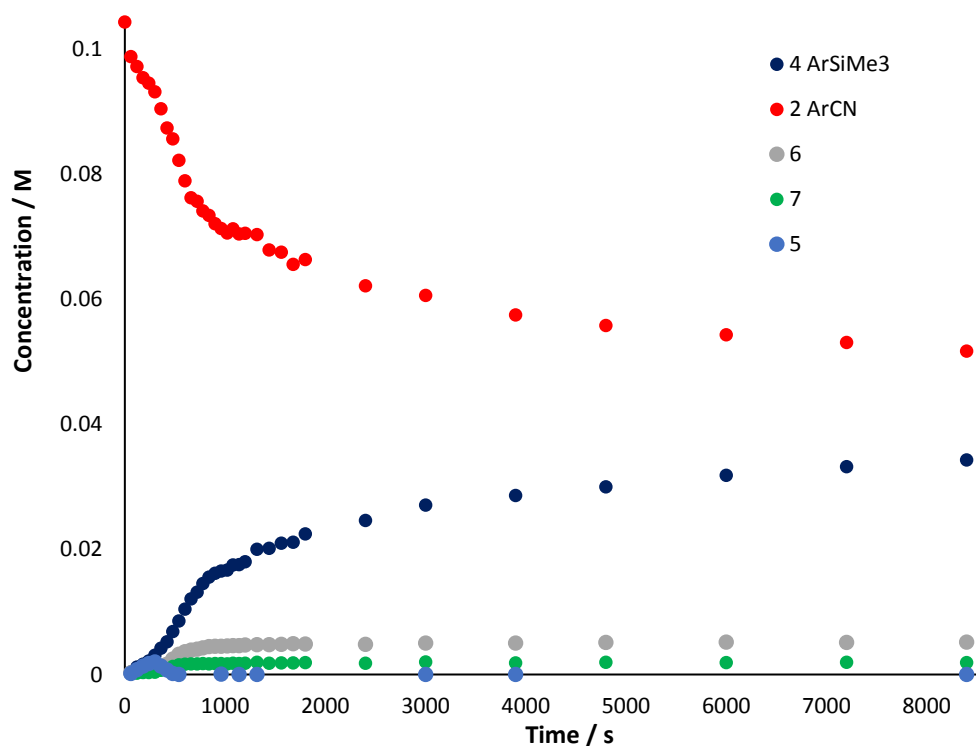


Figure S1: Typical temporal reaction profile

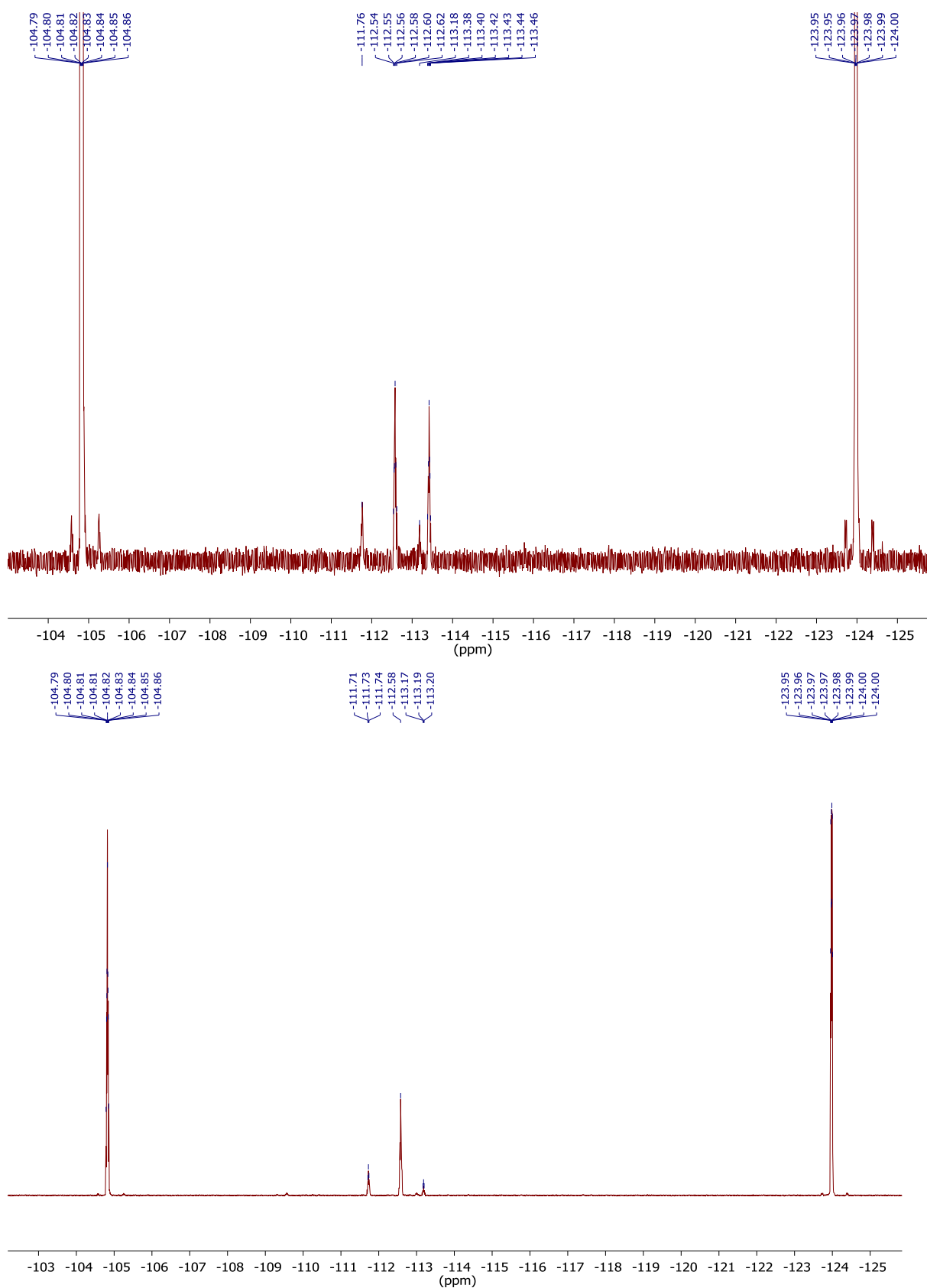
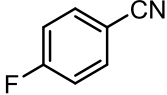
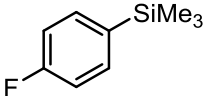
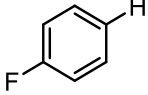
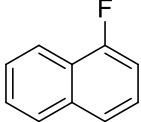


Figure S2: Typical ^{19}F NMR spectra (376 MHz, h_{12} -mesitylene), 300 K in the ArF region. Upper spectrum: after 4 mins of heating at 130 °C. Lower spectrum: after 30 mins of heating at 130 °C, **2** (0.1 M), **3** (0.2 M), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mol %)

Table S1: Reaction components monitored by ^{19}F NMR (377 MHz, h_{12} -mesitylene).

Reaction component	δ_{F} (h_{12} -mesitylene)
 2	-104.82 ppm
6	-111.74 ppm
 4	-112.58 ppm
5	-113.42 ppm
 7	-113.19 ppm
 1-Fluoronaphthalene	-123.98 ppm

In-Situ observation of 5, 6 and 7

Monitoring of the reaction by ^{19}F NMR spectroscopy using the standard procedure shows the presence of two un-identified species **5** ($\delta_{\text{F}} = -113.4$ ppm) and **6** ($\delta_{\text{F}} = -111.7$ ppm) (Fig. S2 A). Additionally, compounds **5** and **6** can be observed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy when **2**- ^{13}C is employed as a substrate (Figure S2, B).

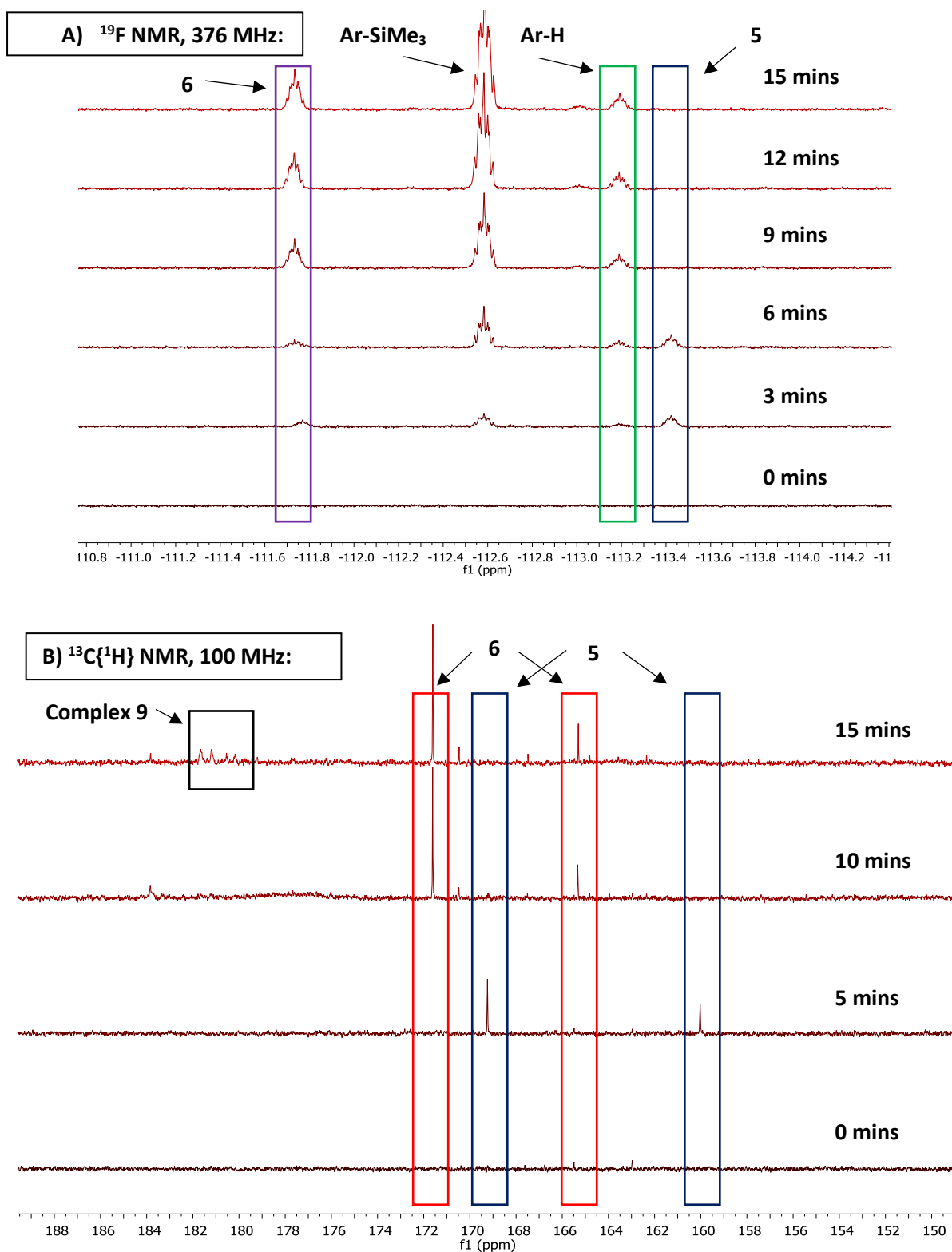
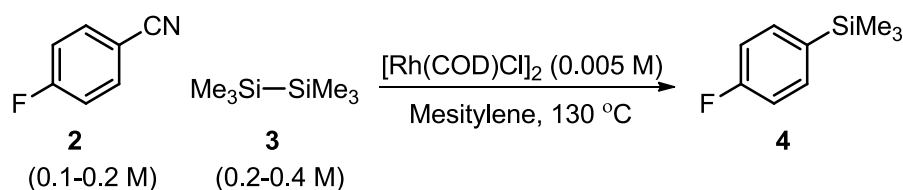


Figure S3: A) Partial ^{19}F NMR spectra (376 MHz, h_{12} -mesitylene) 300 K in the ArF region at 0 -15 mins, **2** (0.1 M), **3** (0.2 M), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.005 M). B) Partial $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (100 MHz, h_{12} -mesitylene) 300 K in the 155 – 188 ppm region at 0- 15 mins, ^{13}C -**2** (0.25 M), **3** (0.5 M), $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0125 M).

Reaction Progress with Varying [Si-Si] and [RCN]:



To three separate Youngs' tap NMR tubes was added, 400 μL from a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.75 mg, 0.016 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (130 μL , 0.64 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene in the glovebox. To each of these NMR tubes, a variable amount (100-200 μL) of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.89 mg, 0.63 mmol) in mesitylene (1.0 mL total volume). The NMR tubes were further diluted with additional mesitylene (0 to 100 μL) and $\text{Me}_3\text{Si-SiMe}_3$ (0-26 μL) such that each NMR tube contained a total volume of 600 μL (see table below). The NMR tubes were sealed and removed from the glovebox and heated in parallel at 130 °C (oil bath temperature). At the designated time points, the samples were removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy.

Initial Concentration: $[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0026 M

Entry	RCN (μL)	[RCN] (M)	Additional Si-Si (μL)	Total [Si-Si] (M)	Additional Mesitylene (μL)
1	200	0.2	0	0.2	0
2	100	0.1	0	0.2	100
3	100	0.1	26	0.4	74

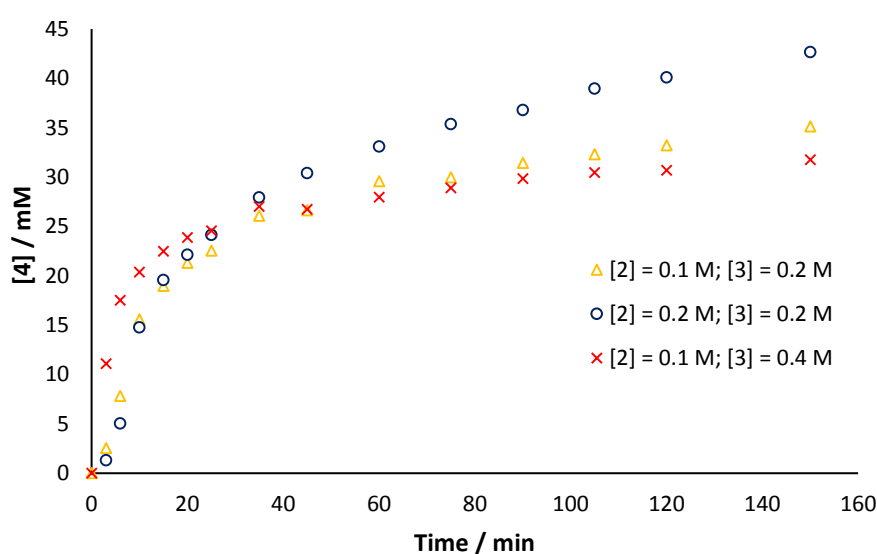
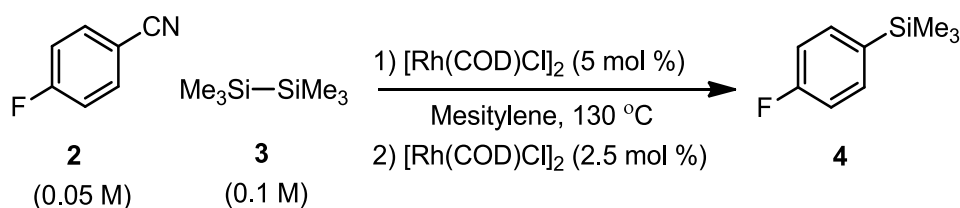


Figure S4: Temporal concentration profile of Ar-SiMe₃ (**4**) with at different concentrations of Ar-CN (**2**) and Me₃Si-SiMe₃ (**3**).

Addition of Second Batch of Precatalyst:



To a Youngs' tap NMR tube was added, 400 μL from a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.73 mg, 0.016 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (130 μL , 0.64 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene in the glovebox. 100 μL of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.83 mg, 0.63 mmol) in mesitylene was then added, followed by 100 μL of additional mesitylene (600 μL total volume). The NMR tube was sealed and removed from the glovebox and heated to 130 $^\circ\text{C}$ (oil bath temperature). At one-minute intervals, the samples were removed from the heat, crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy. This process was repeated for a duration of 24 minutes, at which time the NMR tube was brought back into the glovebox and 200 μL of a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ in mesitylene (7.53 mg, 0.015 mmol) was added to the NMR tube (0.8 mL total reaction volume). The heating process was continued at one-minute intervals, and the reaction progress was monitored by ^{19}F NMR spectroscopy.

Initial Concentrations:

$[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0026 M

4-Fluorobenzonitrile: 0.1044 M

Hexamethyldisilane: 0.2122 M

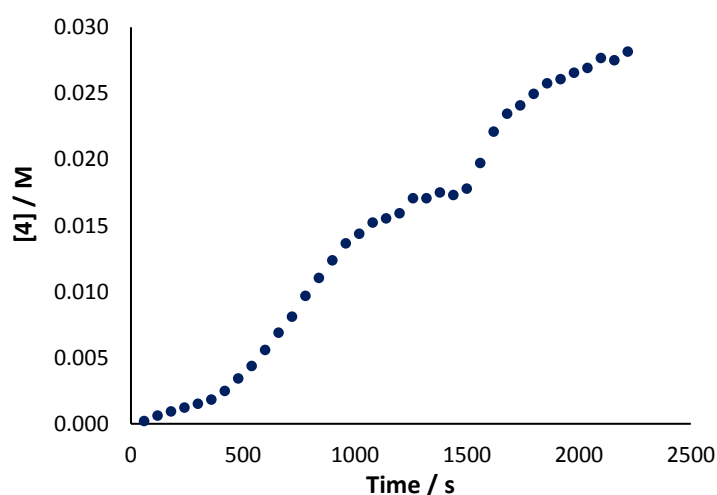
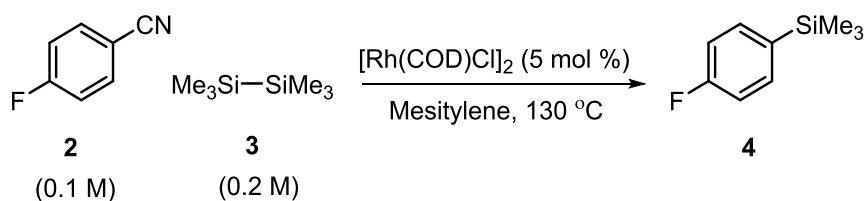


Figure S5. Temporal concentration of Ar-SiMe_3 (**4**) demonstrating the effect of additional $[\text{Rh}(\text{COD})\text{Cl}]_2$ after 1500 s.

Investigations on Inhibition by Product



at $t = 0$

Control [4] = 0 M

Addition of Product [4] = 0.05 M

To two separate Youngs' tap NMR tubes was added 400 μL of a 2 mL stock solution containing $[\text{Rh}(\text{cod})\text{Cl}]_2$ (7.73 mg, 0.031 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (130 μL , 0.64 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene in the glovebox. A 100 μL sample of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.83 mg, 0.63 mmol) in mesitylene was then added, followed by **A**) 100 μL of mesitylene (control) or **B**) a 100 μL sample of a 1 mL stock solution containing **4** (53 mg, 0.315 mmol) (Addition of Product) (600 μL total volume). The NMR tubes were sealed and removed from the glovebox and heated to 130 $^\circ\text{C}$ (oil bath temperature). At one-minute intervals, the samples were removed from the oil bath, crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy. This process was repeated for a duration of 30 minutes.

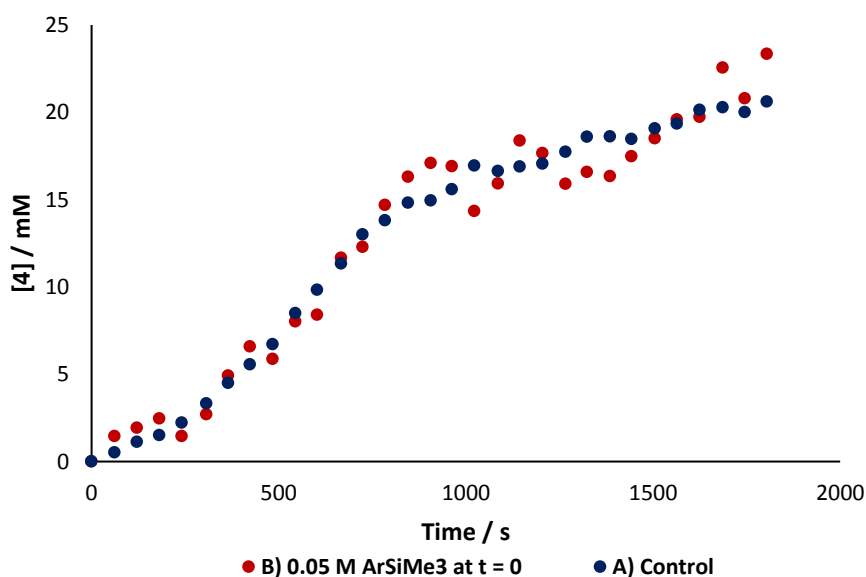
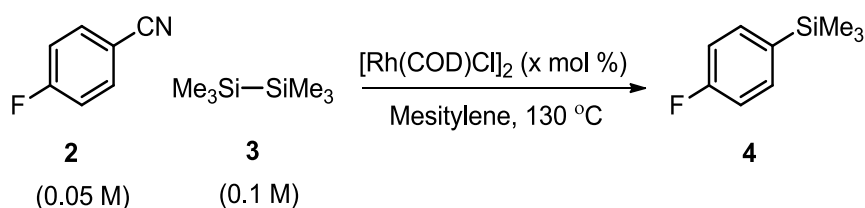


Figure S6: Effect of exogenous product **4** (added at $t = 0$) on the rate of generation of **4**. Data for (A) is control reaction (no additive). Data for (B) has been normalized by subtraction of the concentration of exogenous product **4**.

Investigations on the Induction Period

Induction period length dependence on catalyst



Representative procedure: To four separate Youngs' tap NMR tubes was added a variable amount (100 - 400 μL) from a stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.53 mg, 0.015 mmol) in mesitylene (2.0 mL total) in the glovebox. To each of these NMR tubes, 200 μL of a 2.0 mL stock solution containing 4-fluorobenzonitrile (37.94 mg, 0.31 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (150 μL , 0.735 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene. Each NMR tube was further diluted with additional (25 - 325 μL) of mesitylene, such that each NMR tube contained a total volume of 625 μL . The NMR tubes were sealed and removed from the glovebox and heated in parallel at 130 °C (oil bath temperature). At one-minute intervals, the samples were removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy.

A sixth order polynomial was fitted to the reaction profile, and the time at which the max rate was observed was determined from the derivative of this curve. A linear extrapolation from this point to the x-axis was used to determine the length of the induction period.

Initial Concentrations:

4-Fluorobenzonitrile: 0.0501 M

Hexamethyldisilane: 0.1172 M

Entry	[Rh] (mM)	Induction Period (s)
1	2.45	32
2	3.67	129
3	4.89	177
4	6.12	322
5	7.34	421
6	9.79	602

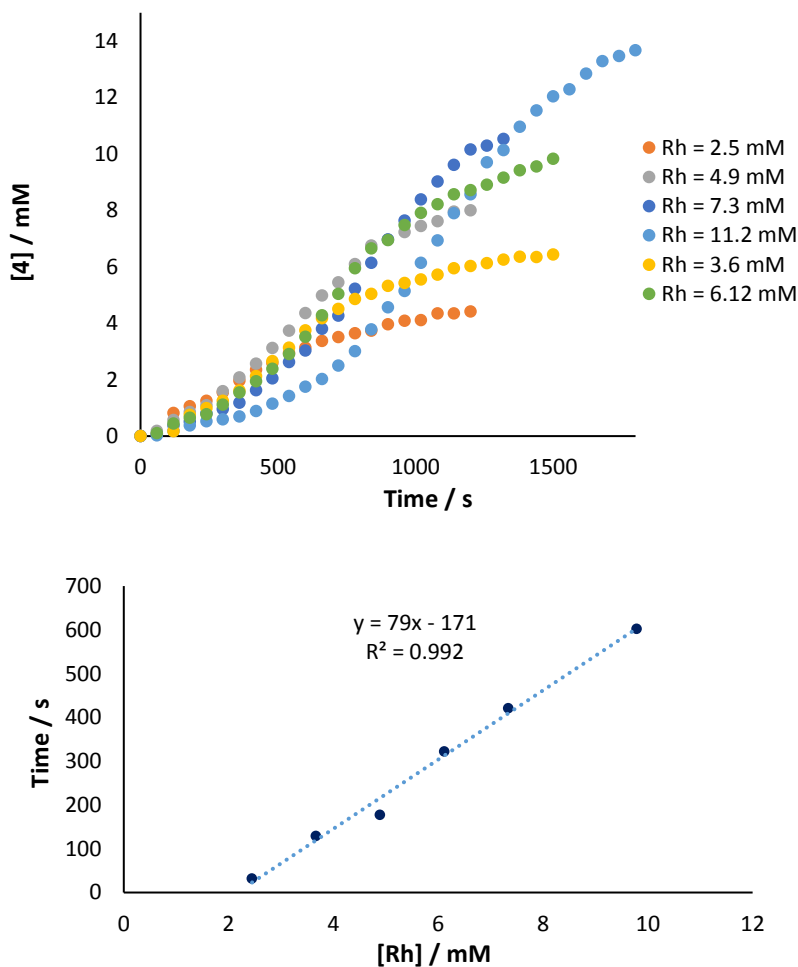
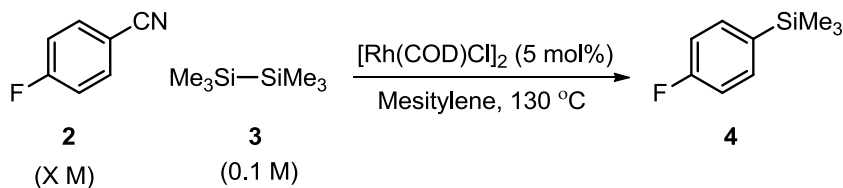


Figure S7. Upper: Temporal concentration profiles of Ar-SiMe₃ (**4**) at different loadings of [Rh(COD)Cl]₂. Lower: Induction period dependence on [Rh].

*Induction period length dependence on Ar-CN (**2**)*



Representative procedure: To four separate Youngs' tap NMR tubes in a N₂ filled glovebox was added, 400 μ L of a 2.0 mL stock solution containing [Rh(COD)Cl]₂ (7.75 mg, 0.016 mmol), Me₃Si-SiMe₃ (65 μ L, 0.32 mmol) and 1-fluoronaphthalene (internal standard, 40 μ L) in mesitylene. To each of these NMR tubes, a variable amount (50 to 200 μ L) of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.61 mg, 0.62 mmol) in mesitylene was added. Each NMR tube was further diluted with an extra (0 to 150 μ L) of mesitylene, such that each NMR tube contained a total volume of 600 μ L. The NMR tubes were sealed and removed from the glovebox and heated in parallel at 130 °C (oil bath temperature)

for one-minute intervals, removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy.

A sixth order polynomial was fitted to the reaction profile, and the time at which the max rate was observed was determined from the derivative of this curve. A linear extrapolation from this point to the x-axis was used to determine the length of the induction period.

Initial Concentrations:

$[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0026 M

Hexamethyldisilane: 0.1020 M

Entry	4-Fluorobenzonitrile (M)	Induction Period (s)
1	0.052	158
2	0.104	265
3	0.156	338
4	0.208	408

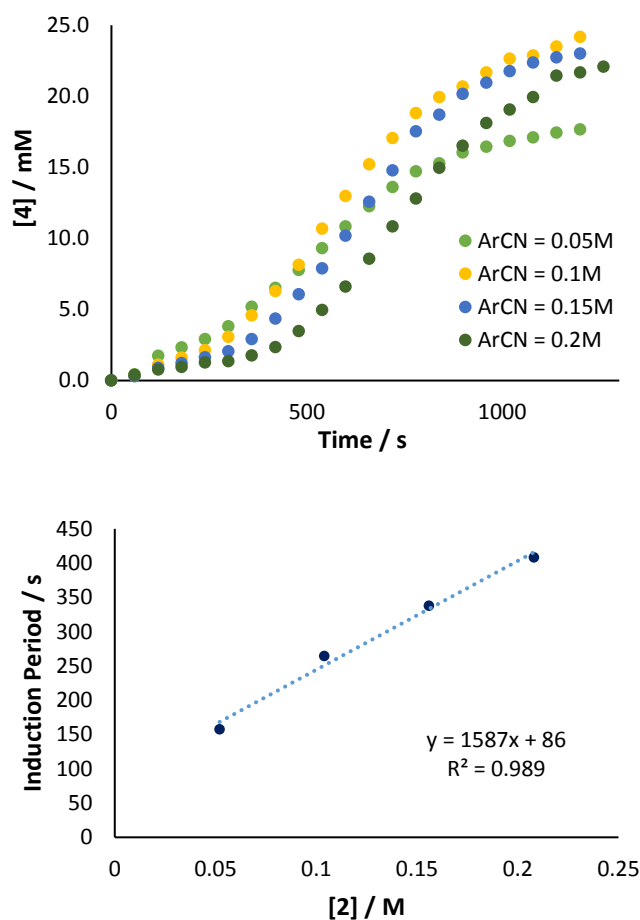
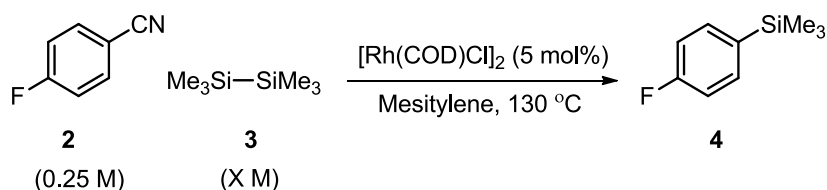


Figure S8. Upper: Temporal concentration profiles of Ar-SiMe₃ (**4**) at different loadings of **[2]**. Lower: Induction period dependence on **[2]**.

*Induction period length dependence on Me₃Si-SiMe₃ (**3**)*



Representative procedure: In the glove box, solutions of [Rh(COD)Cl]₂ (3.08 mg, 0.0062 mmol), 4-fluorobenzonitrile (15.14 mg, 0.125 mmol), and variable amounts of hexamethyldisilane (52 µL, 0.13 mmol) in mesitylene (0.5 mL) were added to NMR tubes. The NMR tubes were sealed and heated in parallel at 130 °C (oil bath temperature) for one-minute intervals, removed from the heat and crash cooled in a room temperature pentane bath and analysed by ¹⁹F NMR spectroscopy.

A sixth order polynomial was fitted to the reaction profile, and the time at which the max rate was observed was determined from the derivative of this curve. The induction period was estimated by extrapolation of the maximum rate of generation of **4** to the time point where [**4**] = 0.

Initial Concentrations:

[Rh(COD)Cl]₂: 0.0125 M

4-Fluorobenzonitrile: 0.250 M

Entry	Hexamethyldisilane (M)	Induction Period (s)
1	0.26	562
2	0.38	368
3	0.51	195
4	0.64	95
5	0.76	52
6	1.02	9

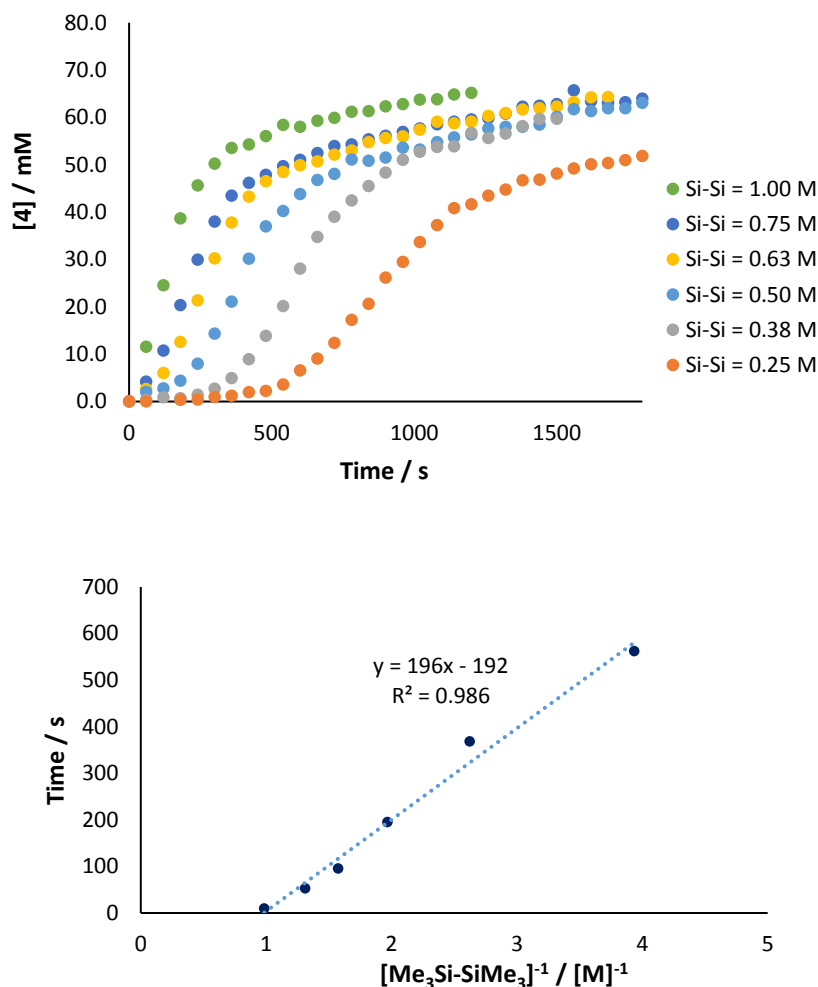
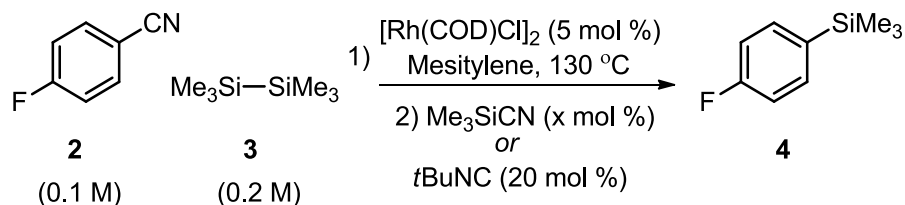


Figure S9. Upper: Temporal concentration profiles of Ar-SiMe₃ (**4**) at different loadings of [**3**]. Lower: Induction period dependence on [**3**]

Me₃SiCN Poisoning Tests

Addition of Me₃SiCN to reaction mixtures after the induction period:



In the glovebox, to four separate Youngs' tap NMR tubes was added, 400 μ L from a 2.0 mL stock solution containing [Rh(COD)Cl]₂ (7.79 mg, 0.016 mmol), Me₃Si-SiMe₃ (130 μ L, 0.64 mmol) and 1-fluoronaphthalene (internal standard, 40 μ L) in mesitylene. To each of these NMR tubes, 100 μ L of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.89 mg, 0.63 mmol) in mesitylene was added.

Each NMR tube was further diluted with an extra 100 μL of mesitylene, such that each NMR tube contained a total volume of 600 μL . The NMR tubes were sealed and removed from the glovebox and heated in parallel at 130 $^{\circ}\text{C}$ (oil bath temperature). At one-minute intervals, the samples were removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy. After eight minutes, the reactions were paused, and under N_2 , variable amounts of 1.0 mL stock solutions containing either Me_3SiCN (40 μL) or $t\text{BuNC}$ (35 μL) in toluene were injected to the NMR tubes, and additional toluene was injected (if necessary) such that the total volume of each NMR tube was now 640 μL (see table below). The NMR tubes were resubjected to heating at 130 $^{\circ}\text{C}$ for one-minute intervals, and the reaction progress was monitored by ^{19}F NMR spectroscopy.

Initial Concentrations:

4-Fluorobenzonitrile: 0.1044 M

Hexamethyldisilane: 0.2122 M

$[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0027 M

Entry	Me_3SiCN stock solution (μL)	Me_3SiCN (M)	$t\text{BuNC}$ stock solution (μL)	$t\text{BuNC}$ (M)	Toluene (μL)
1	0	0	0	0	40
2	20	0.011	0	0	20
3	40	0.021	0	0	0
4	0	0	40	0.021	0

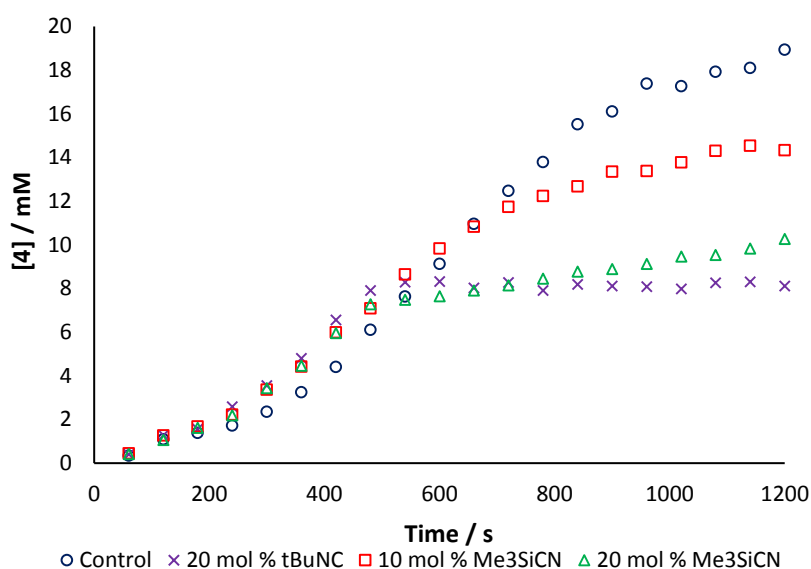
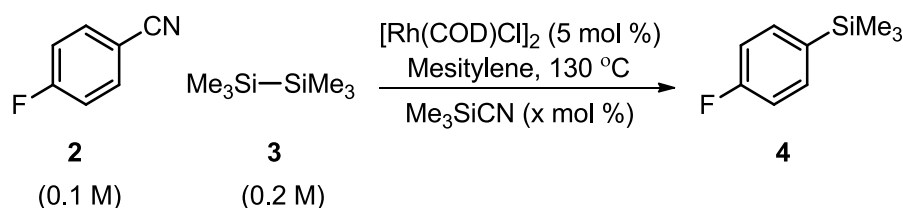


Figure S10. Effect of Me_3SiCN addition to the reaction mixture at 480 s, after the completion of the induction period

Addition of Me₃SiCN to reaction mixtures at T=0



To four separate Youngs' tap NMR tubes was added, 400 μL from a 5.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (18.85 mg, 0.038 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (325 μL , 1.60 mmol) and 1-Fluoronaphthalene (internal standard, 100 μL) in mesitylene in the glovebox. To each of these NMR tubes, 100 μL of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.83 mg, 0.63 mmol) such that the volume of each NMR tube was 500 μL . The NMR tubes were sealed and removed from the glovebox. Under N_2 , variable amounts of a 1.0 mL stock solution containing Me_3SiCN (40 μL) in toluene were injected to the NMR tubes, and additional toluene was injected (if necessary) such that the total volume of each NMR tube was now 600 μL (see table below). The NMR tubes were subjected to heating at 130 °C and the progress of the reactions were monitored by ^{19}F NMR spectroscopy at one-minute intervals.

Initial Concentrations:

4-Fluorobenzonitrile: 0.1044 M

Hexamethyldisilane: 0.2122 M

$[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0051 M

Entry	Me_3SiCN stock solution (μL)	Me_3SiCN (M)	Mesitylene (μL)
1	0	0	100
2	20	0.010	80
3	40	0.021	60
4	60	0.031	40
5	80	0.042	20
6	100	0.052	0

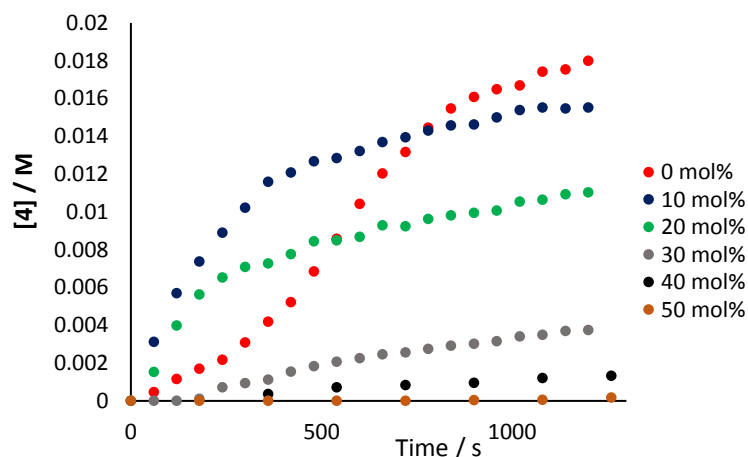
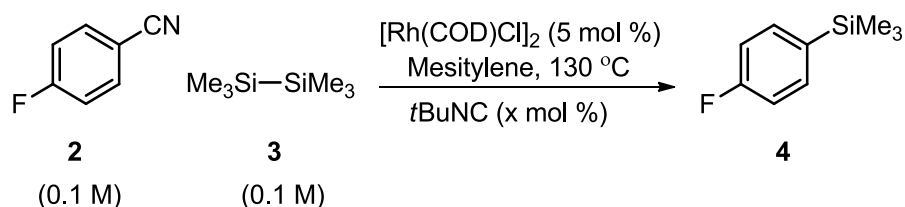


Figure S11. Temporal Concentration profiles of Ar-SiMe₃ (**4**) with varying [Me₃SiCN] added at T=0

*Addition of *t*BuNC to reaction mixtures at T=0*



To two separate Youngs' tap NMR tubes was added, 400 μ L from a 2.0 mL stock solution containing [Rh(COD)Cl]₂ (7.73 mg, 0.016 mmol), Me₃Si-SiMe₃ (65 μ L, 0.32 mmol) and 1-fluoronaphthalene (internal standard, 40 μ L) in mesitylene in the glovebox. 100 μ L of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.83 mg, 0.63 mmol) in mesitylene and 100 μ L of mesitylene was added to each NMR tube. The NMR tubes were sealed and removed from the glovebox. Under N₂, 20 μ L from a 1.0 mL stock solution containing *t*BuNC (39 μ L, 0.32 mmol) in toluene was injected to one NMR tube followed by 40 μ L of toluene. 60 μ L of toluene was injected into the second NMR tube, such that the total volume of each was 660 μ L. The two NMR tubes were sealed under N₂ and heated in parallel at 130 °C (oil bath temperature) at one-minute intervals, where they were removed from the heat and crash cooled in a room temperature pentane bath and analysed by ¹⁹F NMR spectroscopy at regular intervals.

Initial Concentrations:

4-Fluorobenzonitrile: 0.0949 M

Hexamethyldisilane: 0.0965 M

[Rh(COD)Cl]₂: 0.0047 M

Entry	tBuNC stock solution (μL)	[tBuNC] (M)	Toluene (μL)
1	20	0.0965	40
2	0	0	60

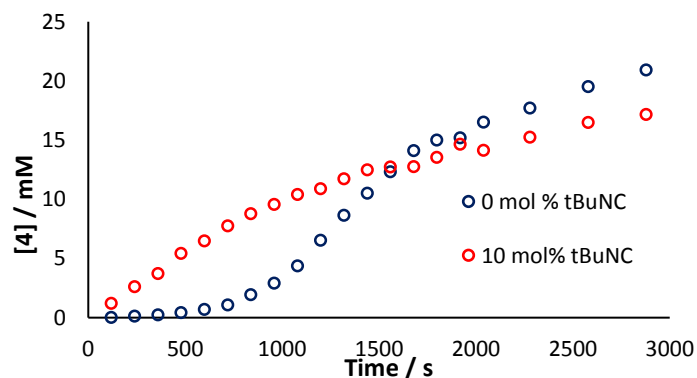
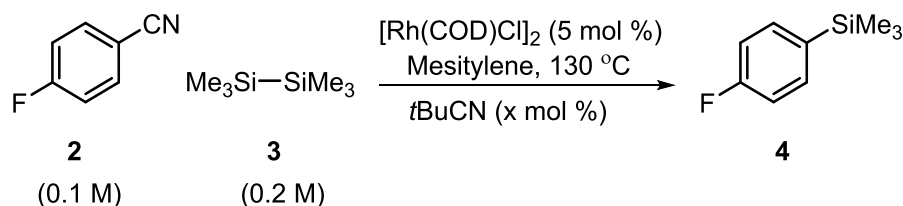


Figure S12. Temporal concentration profile of ArSiMe_3 (**4**) with the addition of tBuNC at $t = 0$

Addition of tBuCN to reaction mixtures at $T=0$



To two separate Youngs' tap NMR tubes was added, a 400 μL sample from a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.73 mg, 0.016 mmol), $\text{Me}_3\text{Si}-\text{SiMe}_3$ (130 μL , 0.64 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene in the glovebox. A 100 μL sample of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.83 mg, 0.63 mmol) in mesitylene a was added to each NMR tube. To the control tube 100 μL of mesitylene was added, to the other tube a 100 μL sample from a 5.0 mL stock solution containing tBuCN (34.8 μL , 0.315 mmol). The NMR tubes were sealed and removed from the glovebox. The NMR tubes were then heated in parallel at 130 $^\circ\text{C}$ (oil bath temperature) and at regular intervals (every one-minute for the first 13 mins, then at two minutes for the remainder of the analysis) they were removed from the oil bath, crash cooled in a room temperature pentane bath, and then analysed by ^{19}F NMR spectroscopy before being returned to the oil bath for the next time period.

Initial Concentrations:

4-Fluorobenzonitrile: 0.0949 M

Hexamethyldisilane: 0.0965 M

$[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0047 M

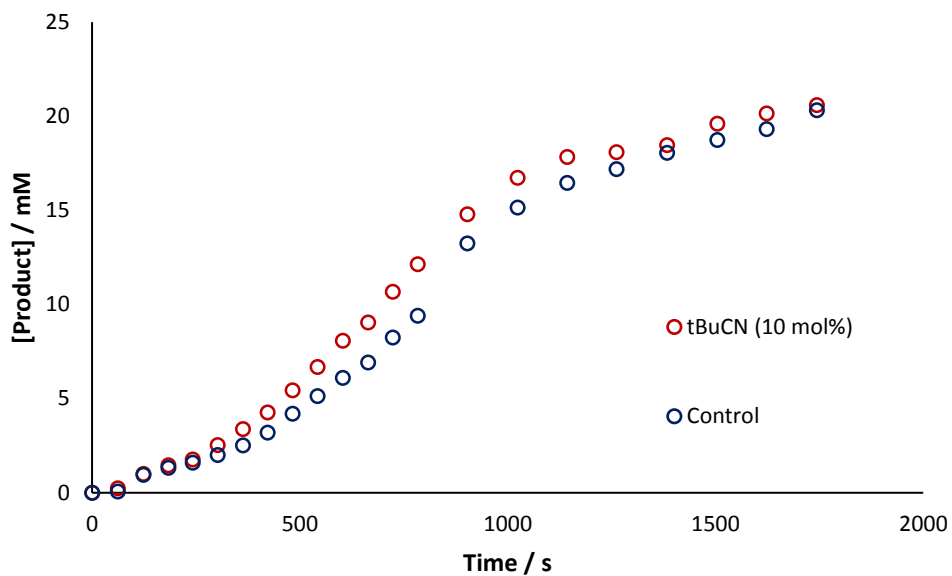
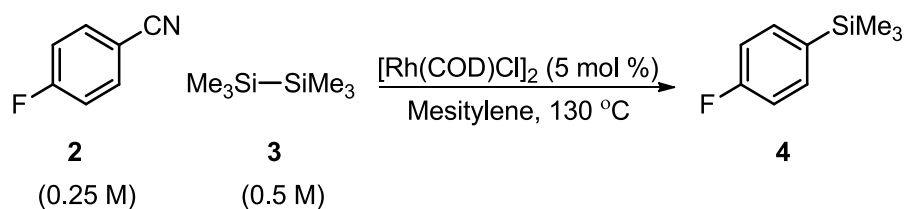


Figure S13. Temporal product concentration profile in the presence of added *t*BuCN.

In-Situ Investigation into Rhodium Resting States and Speciation



In the glove box, solutions of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (3.11 mg, 0.0063 mmol), 4-fluorobenzonitrile (15.10 mg, 0.125 mmol), and hexamethyldisilane (52 μL , 0.13 mmol) were dissolved in mesitylene (0.5 mL) was added to a Youngs tap NMR tube. The NMR tube was sealed and removed from the glovebox where it was then heated at 130 $^\circ\text{C}$ (oil bath temperature), removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{29}Si INEPT NMR spectroscopy. This process was repeated at regular intervals.

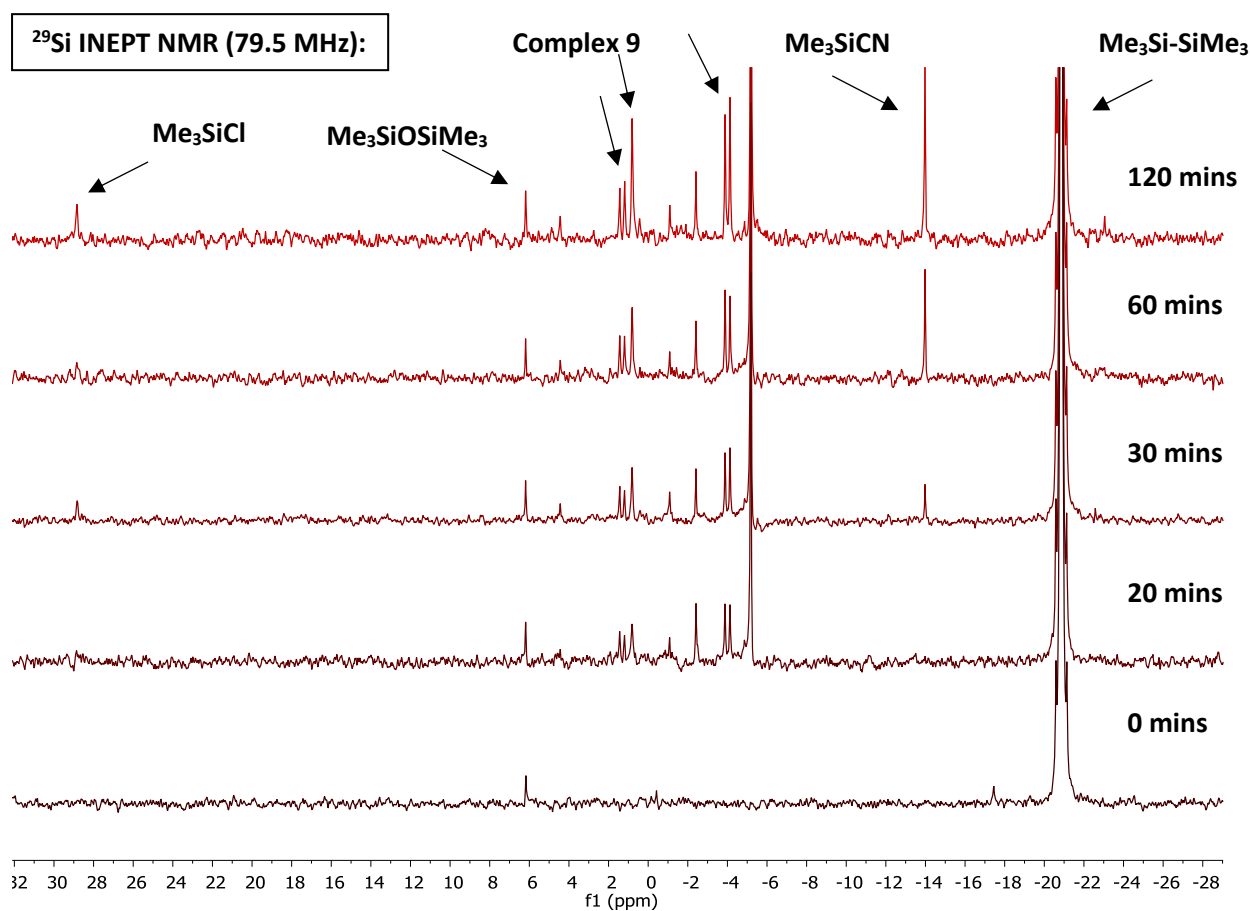
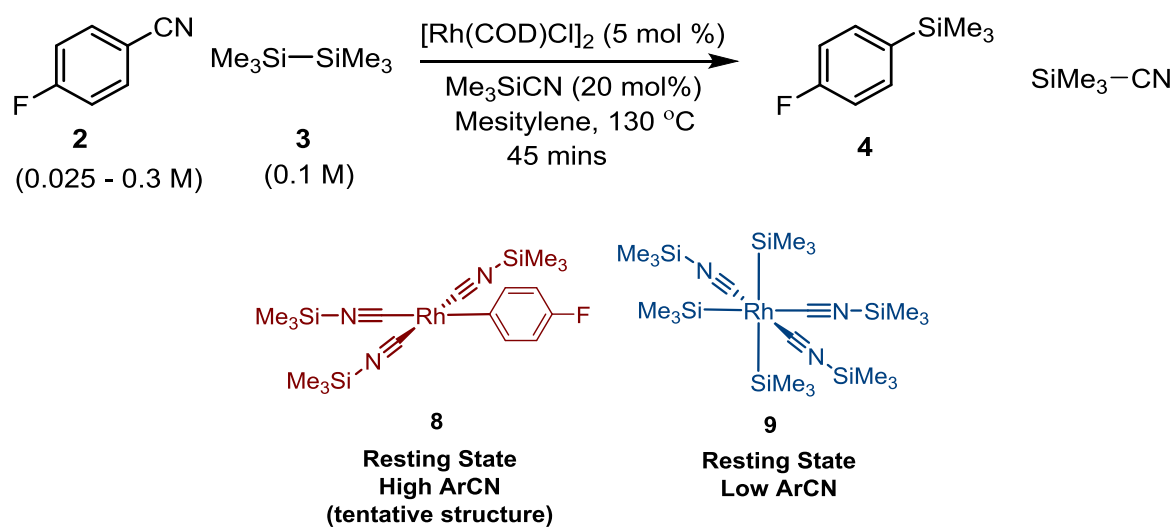


Figure S14. Partial ^{29}Si INEPT NMR spectra of a typical reaction mixture over time displaying the formation of complex **9** before the production of Me_3SiCN .

Observation of Catalyst Resting States at varying [2] by ^{29}Si NMR:



Representative procedure: To four separate Youngs' tap NMR tubes in a N₂ filled glovebox was added, 400 μ L of a 2.0 mL stock solution containing [Rh(COD)Cl]₂ (7.73 mg, 0.016 mmol), Me₃Si-SiMe₃ (65 μ L, 0.32 mmol) and 1-fluoronaphthalene (internal standard, 40 μ L) in mesitylene. To each of these NMR tubes, a variable amount (33 to 200 μ L) of a 1.0 mL stock solution containing 4-fluorobenzonitrile (113.4 mg, 0.94 mmol) in mesitylene was added. Each NMR tube was further diluted with an extra (0 to 167 μ L) of mesitylene, such that each NMR tube contained a total volume of 600 μ L. The NMR tubes were sealed and removed from the glovebox. Under N₂, 20 μ L of a 1.0 mL stock solution containing Me₃SiCN (80 μ L) was injected to each NMR tube. The sealed NMR tubes were heated in parallel at 130 °C (oil bath temperature) for 45 minutes, removed from the heat and crash cooled in a room temperature pentane bath and analysed by ²⁹Si NMR spectroscopy.

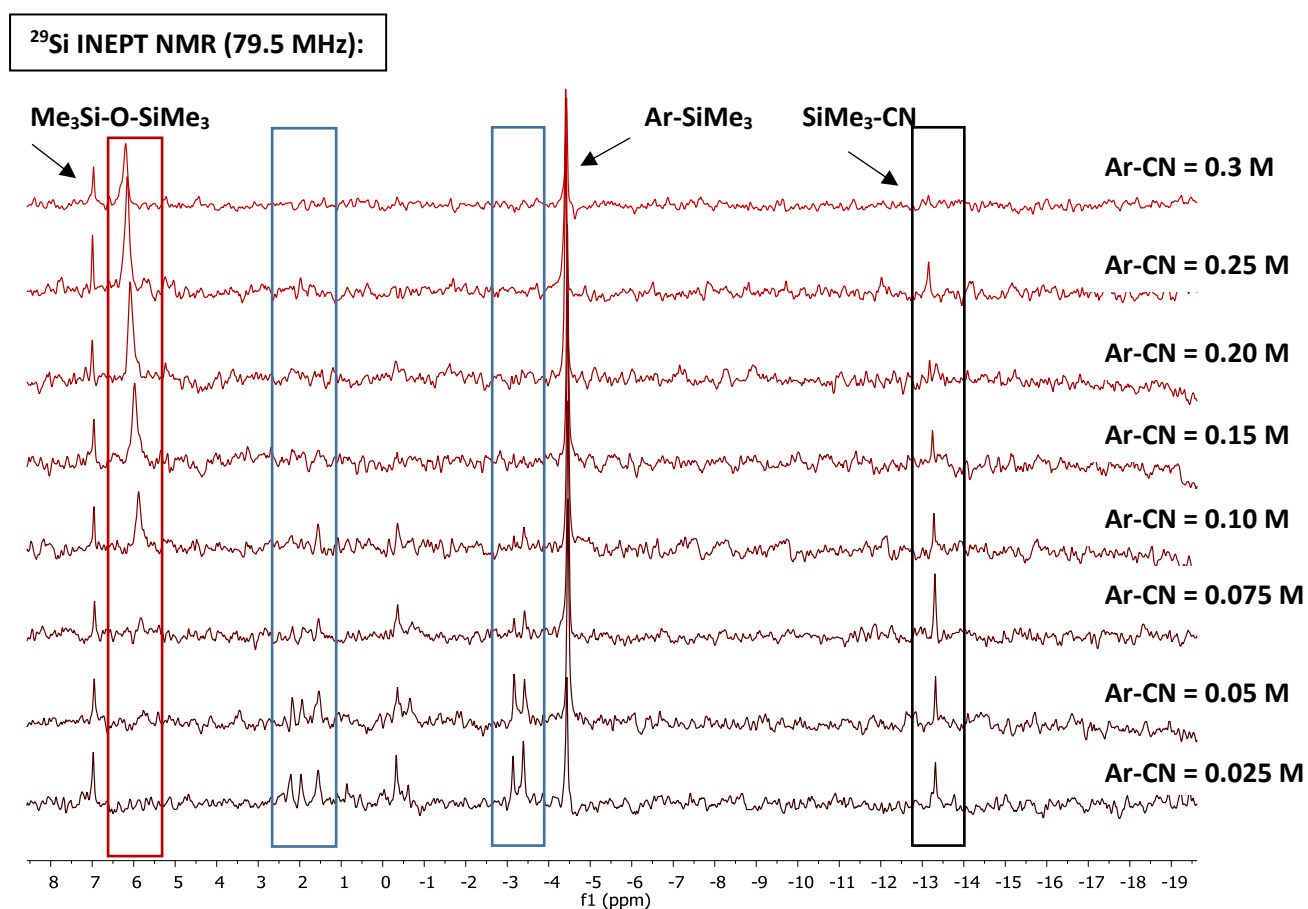
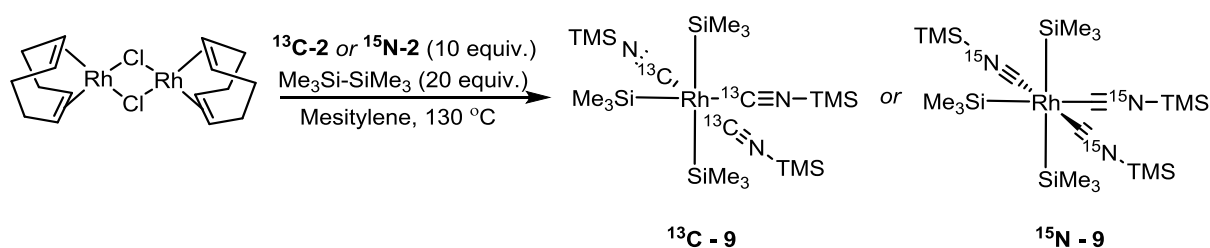


Figure S15. Partial ²⁹Si INEPT NMR experiments with varying the concentration of Ar-CN (**2**) displaying the presence and varying concentrations of complexes **8** (highlighted in the red box) and **9** (highlighted in the blue boxes).

Observation of ^{15}N -9 and ^{13}C -9 in-situ



Representative procedure: In the glove box, solutions of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (3.06 mg, 0.0062 mmol), hexamethyldisilane (52 μL , 0.26 mmol), and labelled 4-fluorobenzonitrile (^{13}C -2) (15.23 mg, 0.125 mmol), in mesitylene (0.5 mL) was mixed in a vial and the contents transferred to a Youngs' tap NMR tube. The NMR tube were sealed and heated to 130 °C (oil bath temperature) for 60 minutes, where it was then removed from the heat and crash cooled in a room temperature pentane bath and analysed by NMR spectroscopy (Figs. S14 A and S15). A similar procedure was performed using ^{15}N -2 to prepare ^{15}N -9 (Fig. S14 C).

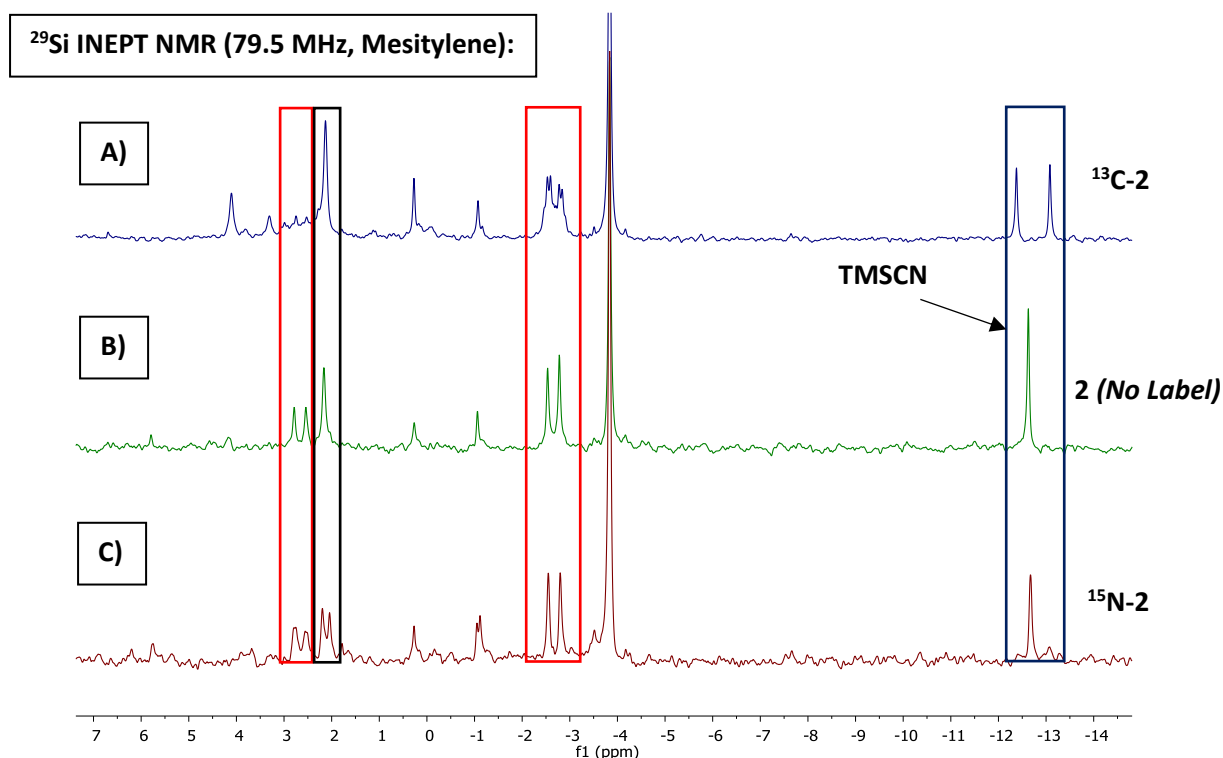


Figure S16: Partial ^{29}Si INEPT NMR spectra of reaction mixtures with A) ^{13}C -2 (0.25 M), B) 2 (0.25 M) and C) ^{15}N -2 (0.25 M) after the onset of inhibition

Table S2: Comparison of select ^{29}Si NMR signals, obtained by *in situ* analysis of reactions **A)** ^{13}C -**2** (0.25 M), **B)** **2** (0.25 M) and **C)** ^{15}N -**2** (0.25 M) after 30 mins. ^a -12.8 ppm (^{13}C -isotope shift -0.2 ppm).

Entry	$\delta = 2.7$ ppm	$\delta = 2.2$ ppm	$\delta = -2.7$ ppm	$\delta = -12.6$ ppm
A) $^{13}\text{C}_3$ - 9	ddt, $^2J_{\text{Si-C}} = 36.8$ Hz, $^1J_{\text{Si-Rh}} = 19.3$ Hz, $^2J_{\text{Si-C}} = 5.5$ Hz	s	dq, $^1J_{\text{Si-C}} = 5.1$ Hz	d, $^1J_{\text{Si-C}} = 55.8$ Hz ^a
B) 9	d, $^1J_{\text{Si-Rh}} = 19.2$ Hz	s	d, $^1J_{\text{Si-Rh}} = 19.7$ Hz	s
C) $^{15}\text{N}_3$ - 9	dd, $^1J_{\text{Si-N}} = 3.1$ Hz	d, $^1J_{\text{Si-N}} = 12.0$ Hz	d, $^1J_{\text{Si-Rh}} = 19.7$ Hz	s

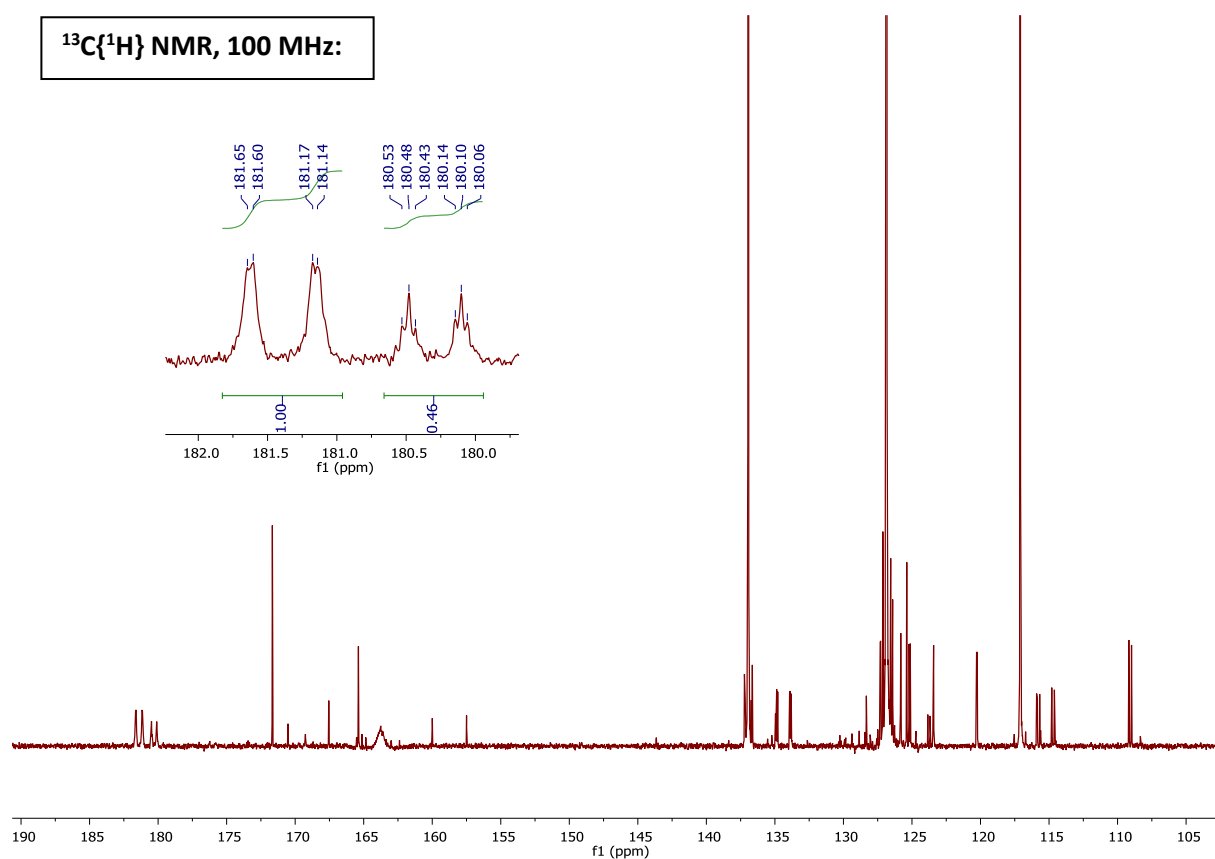


Figure S17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a typical reaction mixture using ^{13}C -**2** (0.25 M) in h_{12} -mesitylene at 45 min, displaying the formation of complex **9**

Observation of Higher Order Isocyanide complexes:

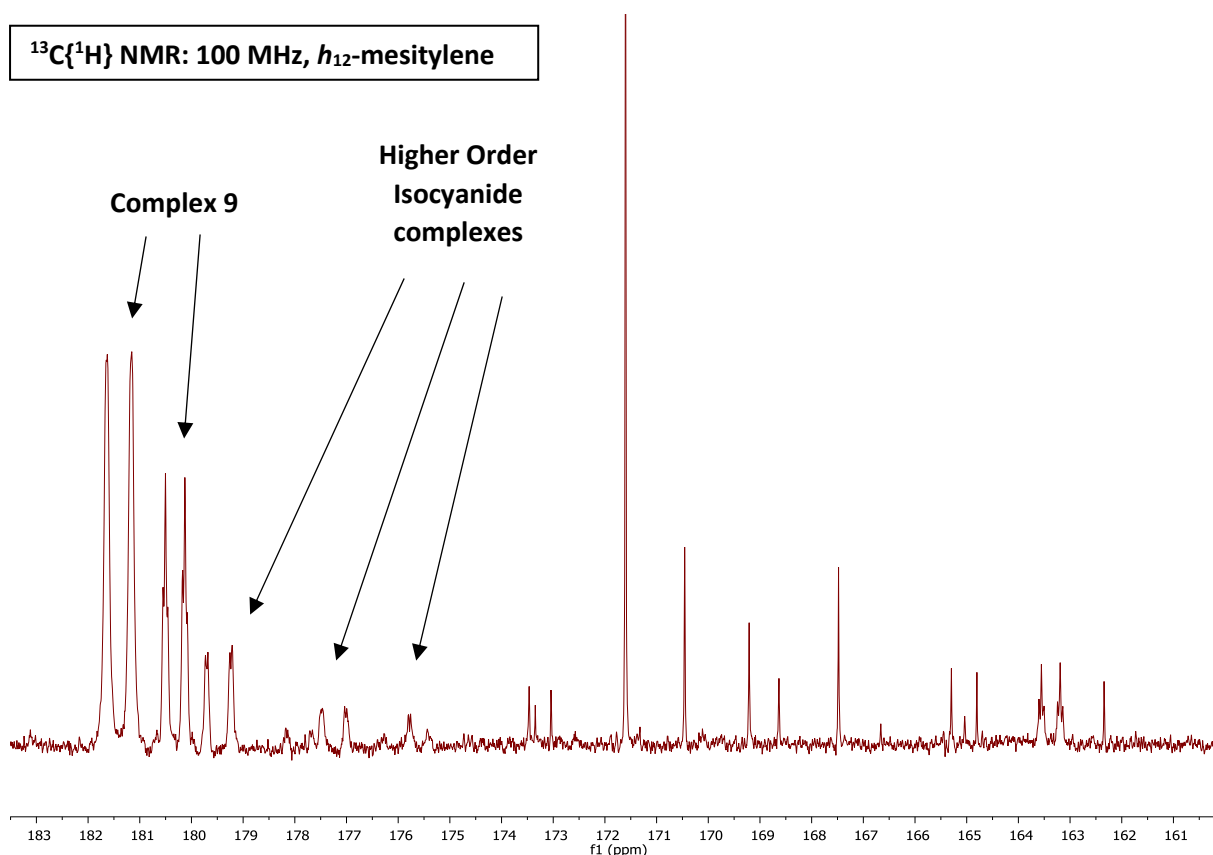
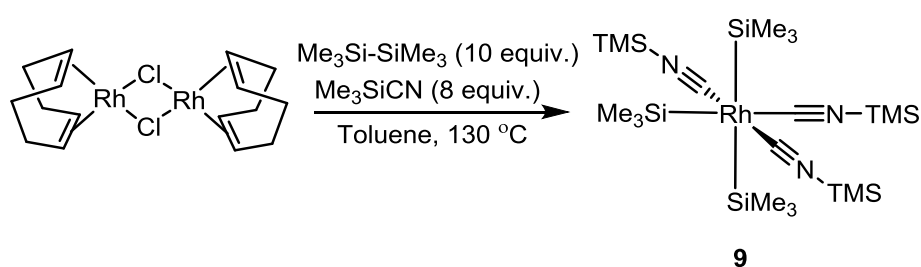


Figure S18: Partial $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a reaction mixture of **2** (0.25 M), **3** (0.5 M) and $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5 mol%) in mesitylene- H_{12} after 16 hours.

In-Situ Preparation of Compound 9:



In the glovebox, a solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (8 mg, 0.016 mmol) in $\text{tol-}D_8$ (2 mL) was added to a flame dried 5 mL ampoule. Me_3SiCN (16 μL , 0.128 mmol) and $\text{Me}_3\text{Si-SiMe}_3$ (33 μL , 0.16 mmol) were added via syringe resulting in an orange/red homogeneous solution. The ampoule was sealed with a Youngs tap, and heated to 130 $^\circ\text{C}$ for 30 minutes, during which time the solution turned a deep yellow. The ampoule was returned to room temperature, and brought inside a N_2 filled glovebox, whereupon the contents were transferred to a Youngs tap NMR tube and the formation of the complex was confirmed by in situ NMR analysis. Compound **9** decomposes rapidly upon exposure to air or moisture.

In situ NMR analysis: ^{29}Si NMR (79.5 MHz, Tol- D_8): 3.77, 2.26 (d, $^1J_{\text{Si-Rh}} = 19.4$ Hz), 1.86, -3.05 (d, $^1J_{\text{Si-Rh}} = 19.6$ Hz); $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, Tol- D_8): 181.13 (d, $^1J_{\text{C-Rh}} = 47.3$ Hz), 180.01 (d, $^1J_{\text{C-Rh}} = 37.8$ Hz)

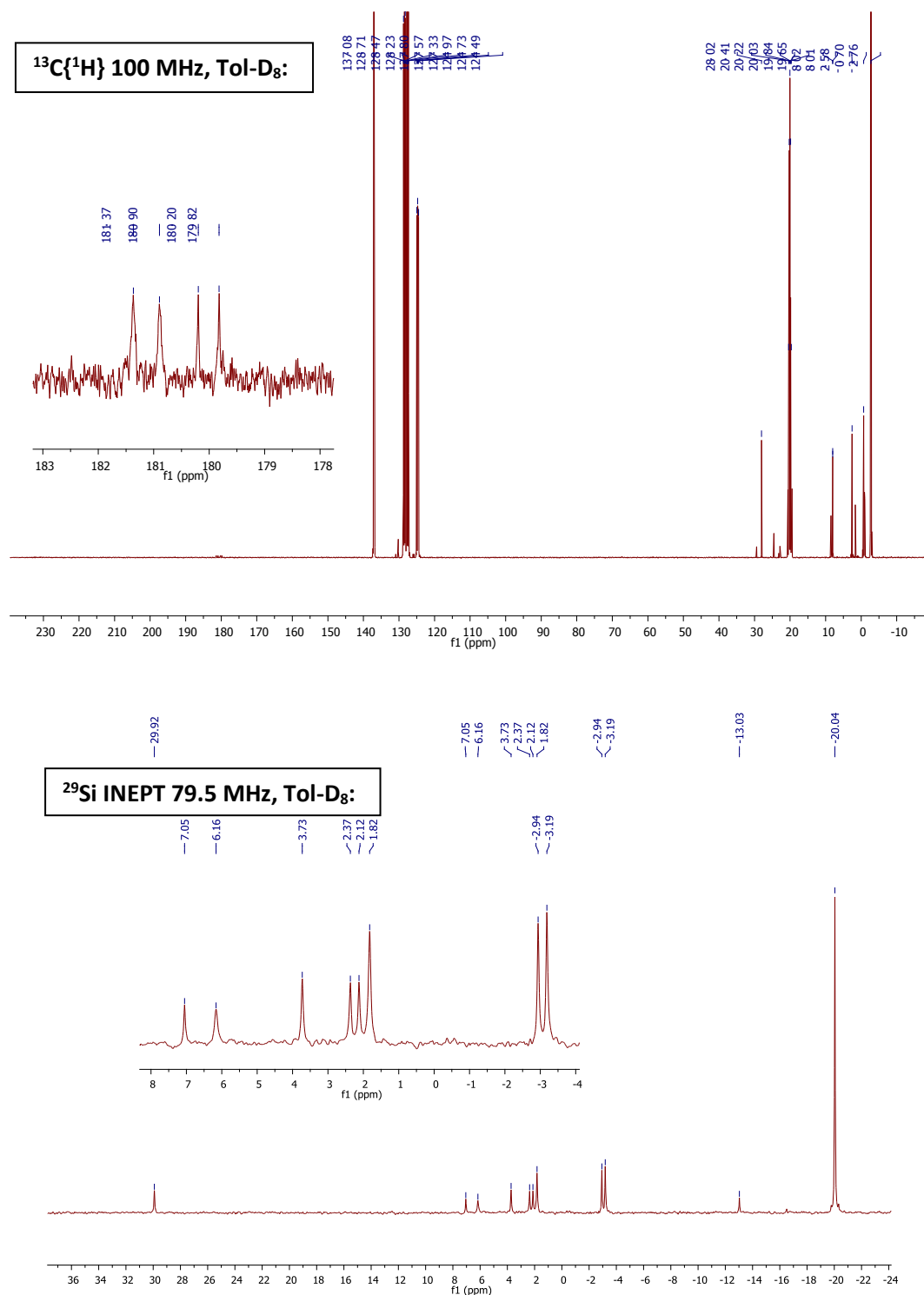
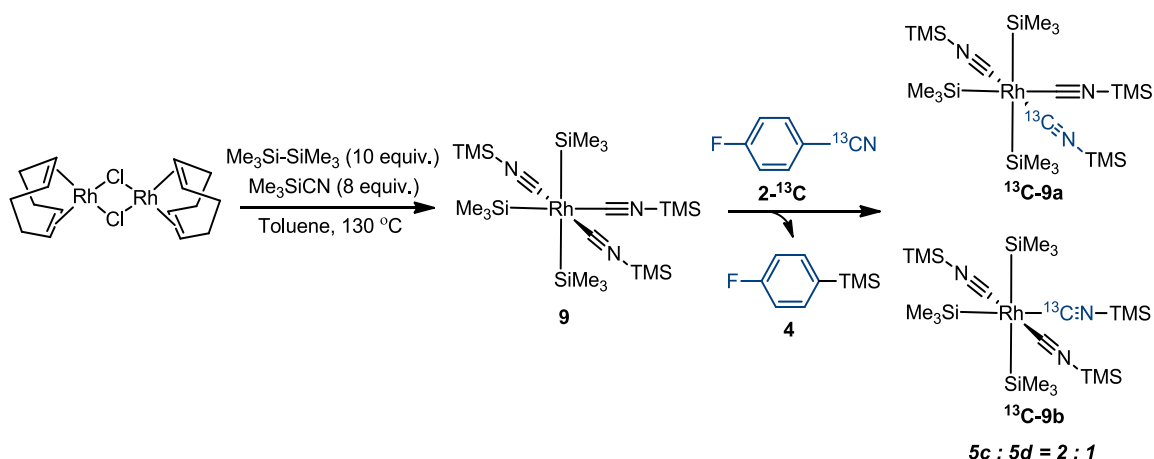
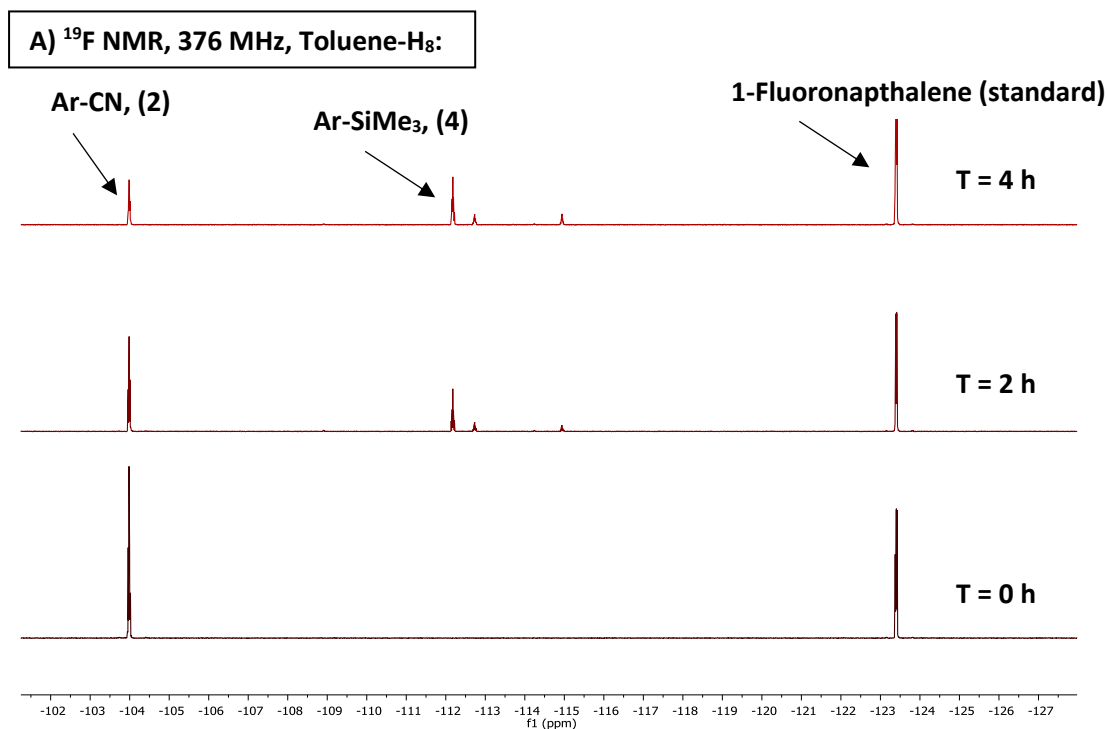


Figure S19: Upper: *In situ* $^{13}\text{C}\{^1\text{H}\}$ and Lower: *In situ* ^{29}Si INEPT NMR spectra of complex **9** synthesized in Tol- d_8

Treatment of complex 9 with ^{13}C labelled 4-Fluorobenzonitrile 2- ^{13}C :



A solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (5.0 mg, 0.01 mmol), $\text{Me}_3\text{Si-SiMe}_3$ (21 μL , 0.10 mmol) and $\text{Me}_3\text{Si-CN}$ (10 μL , 0.81 mmol) in toluene (1.0 mL) was heated to 130 °C in a Youngs tap NMR tube for 30 mins. At this time, ^{29}Si INEPT NMR confirmed the formation of complex 9. The sample was taken back into the glovebox, where 100 μL from a 1.0 mL stock solution containing ^{13}C labelled Fluorobenzonitrile 13C-2 (24.4 mg, 0.2 mmol) and 1-Fluoronaphthalene (20 μL , 0.15 mmol) was added to the NMR tube. The NMR tube was removed from the box, and heated to 130 °C, and periodically monitored by ^{19}F and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.



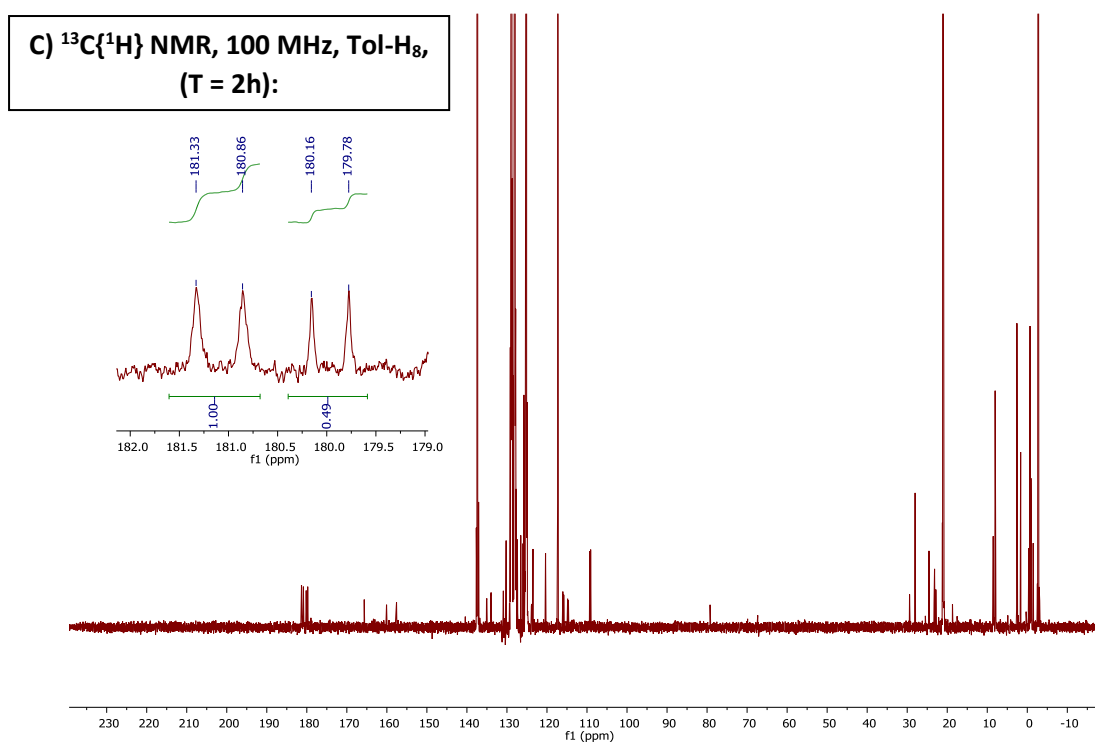
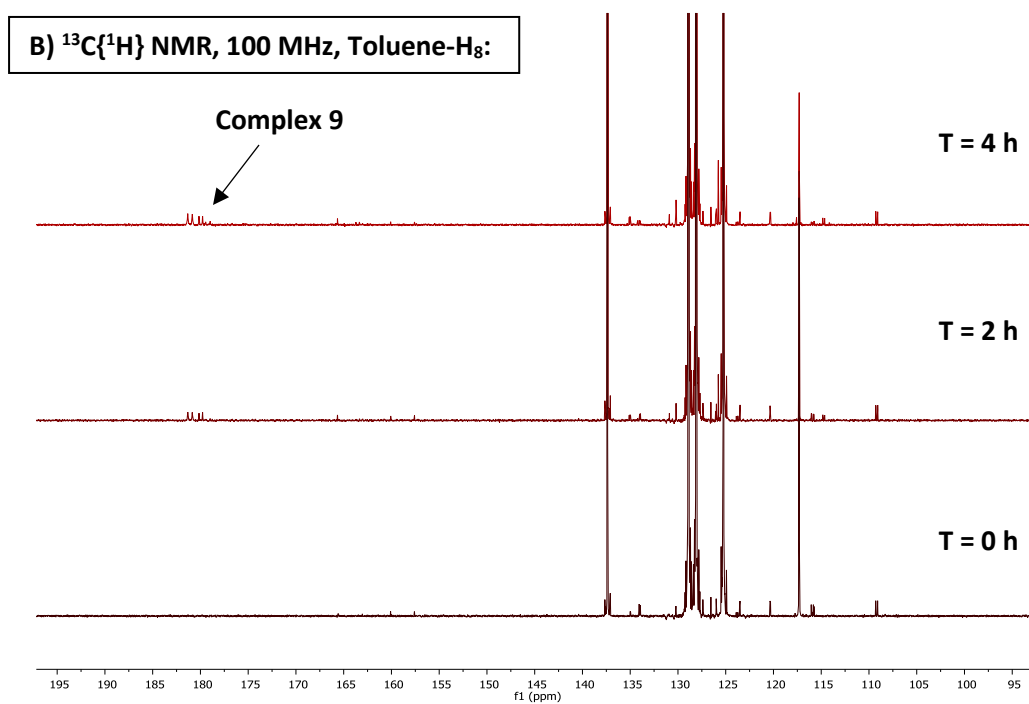
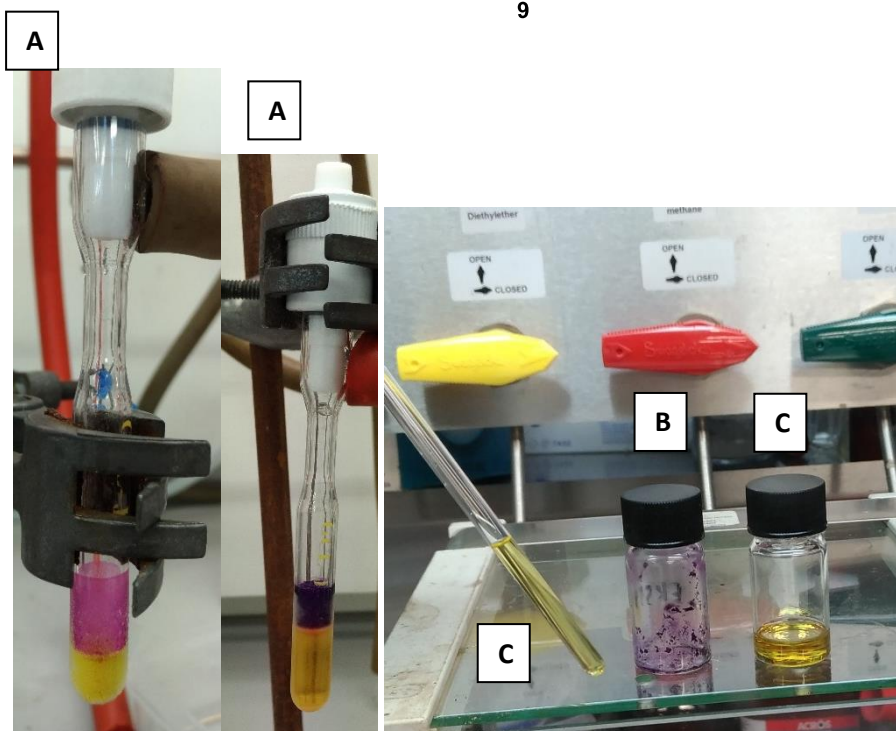
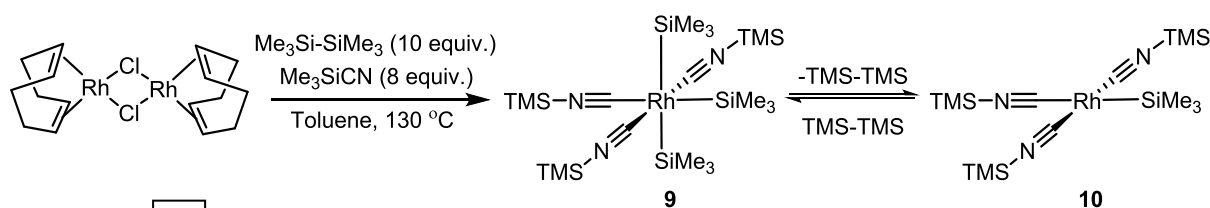


Figure S20: A) ^{19}F NMR spectra displaying the formation of product and consumption of starting material over time and B) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of reaction mixtures overtime displaying the formation of complex 9 C) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex 9 after 2 hours of reaction time.

Experiments on the reversibility of Me₃Si-SiMe₃ loss and addition to complex **9**

A solution of [Rh(COD)Cl]₂ (30.0 mg, 0.061 mmol) in toluene (5 mL) was added to a flame dried ampoule under N₂. Me₃SiCN (62 μL, 0.487 mmol) and Me₃Si-SiMe₃ (125 μL, 0.61 mmol) were added via syringe resulting in an orange/red homogeneous solution. The ampoule was sealed with a Youngs tap, and heated to 130 °C for 30 minutes, during which time the solution turned a deep yellow. The ampoule was returned to room temperature, and brought inside a N₂ filled glovebox, whereupon the contents were transferred to a Youngs tap NMR tube and the formation of complex **9** was confirmed by in situ NMR analysis. Exposure of this solution to either high vacuum or *n*-hexane (20 mL) resulted in the precipitation of a purple solid, which could be isolated by decanting off the solution.

Redissolution of the precipitate in toluene (5 mL) resulted in a homogeneous yellow solution, an aliquot of which was taken for NMR analysis, which confirmed the loss of **9**. Addition of **3** (10 μL, 0.049 mmol) and 100 μL of a stock solution of **2** (30 mg, 0.25 mmol in 1.0 mL) to the NMR tube, followed by heating at 130 °C returned the signals of complex **9**.



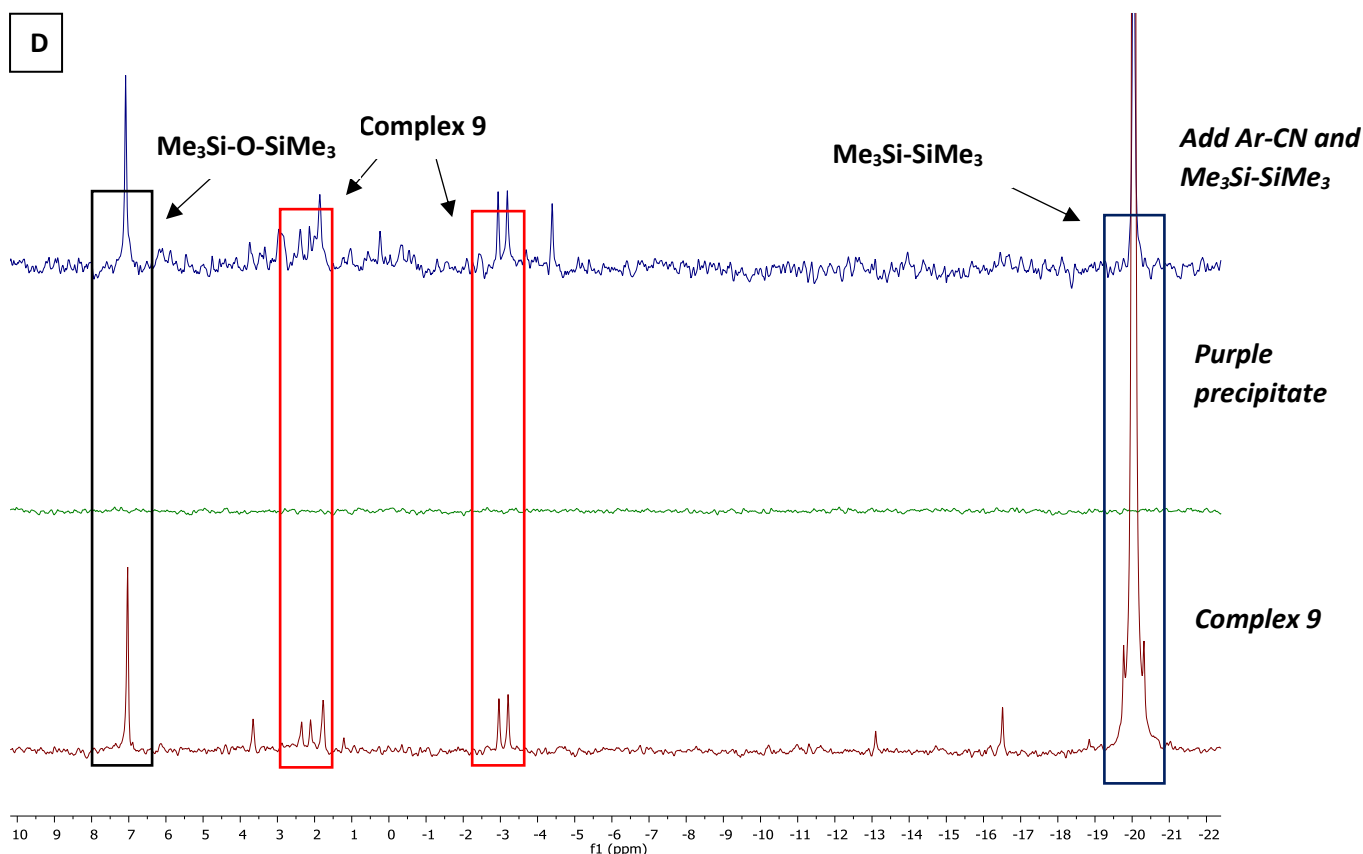
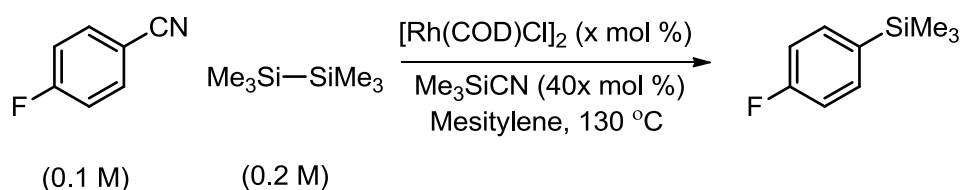


Figure S21: Treatment of a toluene solution of complex **9** to high vacuum resulted in the formation of a purple film (**A**; two examples) and to hexane resulted in the precipitation of a purple solid (**B**). Redissolution into toluene resulted in a yellow homogeneous solution (**C**). Partial ²⁹Si INEPT NMR spectra (**D**) displaying the formation and loss of complex **9**.

Kinetic analysis at inhibition

Determination of Reaction Order in Rhodium



Representative Procedure: To six separate Youngs' tap NMR tubes in a N₂ filled glovebox was added, a variable amount (100 to 400 μ L) of a 2.0 mL stock solution containing [Rh(COD)Cl]₂ (11.61 mg, 0.024 mmol), Me₃Si-SiMe₃ (260 μ L, 1.28 mmol) and 1-fluoronaphthalene (internal standard, 80 μ L) in mesitylene. To each of these NMR tubes was added, 100 μ L of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.84 mg, 0.63 mmol) in mesitylene. Each NMR tube was further diluted with mesitylene (0 to 300 μ L), such that each NMR tube contained a total volume of 500 μ L. The NMR tubes

were sealed and removed from the glovebox. A variable amount (25 to 100 μL) from a 1.0 mL stock solution of Me_3SiCN (22 μL) in toluene was injected to each NMR tube under N_2 . Each NMR tube was further diluted with toluene (0 to 75 μL) such that the total volume was 600 μL . The sealed NMR tubes were heated in parallel to 130 $^\circ\text{C}$ (oil bath temperature) for five-minute intervals, removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy. This process was continued for a duration of 45 mins. The rate of the reaction was measured after the onset of inhibition (10 mins).

Initial Concentrations:

4-Fluorobenzonitrile: 0.1043 M

Hexamethyldisilane: 0.2122 M

Entry	[Rh] (mM)	Me_3SiCN (mM)
1	3.93	8.1
2	5.22	10.7
3	7.85	16.2
4	10.5	21.7
5	13.1	26.9
6	15.7	32.4

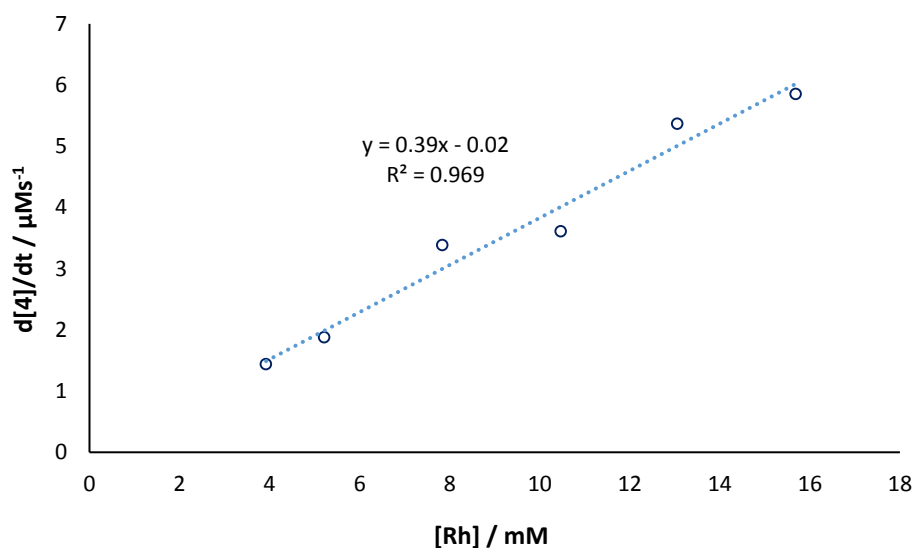
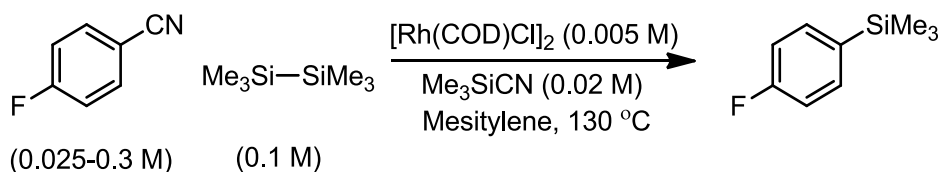


Figure S22: Rate dependence upon concentration of rhodium

Determination of Reaction Order in 4-fluorobenzonitrile (2)



Representative procedure: To four separate Youngs' tap NMR tubes in a N_2 filled glovebox was added, 400 μL of a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.73 mg, 0.016 mmol), $\text{Me}_3\text{Si}-\text{SiMe}_3$ (65 μL , 0.32 mmol) and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene. To each of these NMR tubes, a variable amount (50 to 200 μL) of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.5 mg, 0.62 mmol) in mesitylene was added. Each NMR tube was further diluted with an extra (0 to 150 μL) of mesitylene, such that each NMR tube contained a total volume of 600 μL . The NMR tubes were sealed and removed from the glovebox. Under N_2 , 20 μL of a 1.0 mL stock solution containing Me_3SiCN (80 μL) was injected to each NMR tube. The sealed NMR tubes were heated in parallel at 130 °C (oil bath temperature) for five-minute intervals, removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy. This process was continued for a duration of 45 mins. The rate of the reaction was measured after the onset of inhibition (10 mins).

Initial Concentrations:

$[\text{Rh}(\text{COD})\text{Cl}]_2$: 0.0025 M

Hexamethyldisilane: 0.1020 M

Trimethylsilylcyanide: 0.0196 M

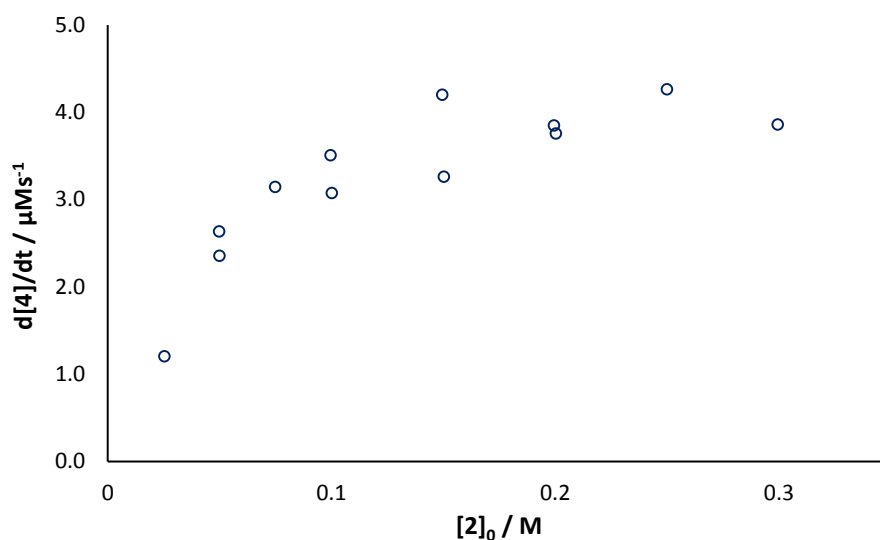
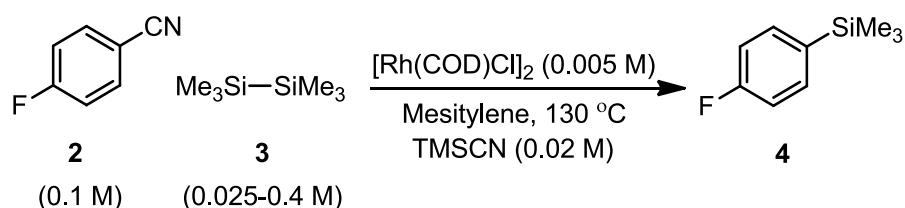


Figure S23: Rate dependence upon concentration of **2**

*Determination of Reaction Order in Hexamethyldisilane (**3**)*



Representative procedure: To four separate Youngs' tap NMR tubes in the glovebox was added, 400 μL of a 2.0 mL stock solution containing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (7.73 mg, 0.016 mmol), and 1-fluoronaphthalene (internal standard, 40 μL) in mesitylene. To each of these NMR tubes, 100 μL of a 1.0 mL stock solution containing 4-fluorobenzonitrile (75.84 mg, 0.63 mmol) in mesitylene was added, followed by a variable amount (25 to 100 μL) of a 1.0 mL stock solution containing $\text{Me}_3\text{Si-SiMe}_3$ (130 μL , 0.64 mmol or 510 μL , 2.51 mmol) in mesitylene. Each NMR tube was further diluted with mesitylene (0 to 75 μL), such that each NMR tube contained a total volume of 600 μL (see table below). The NMR tubes were sealed and removed from the glovebox. Under N_2 , 20 μL of a 1.0 mL stock solution containing Me_3SiCN (80 μL in toluene) was injected to each NMR tube. The sealed NMR tubes were heated in parallel at 130 $^\circ\text{C}$ (oil bath temperature) for five-minute intervals, removed from the heat and crash cooled in a room temperature pentane bath and analysed by ^{19}F NMR spectroscopy for a total duration of 45 mins. The rate of the reaction was measured after the onset of inhibition (10 mins).

Initial Concentrations:

$[Rh(COD)Cl]_2$: 0.0025 M

4-fluorobenzonitrile: 0.1010 M

Trimethylsilylcyanide: 0.0206 M

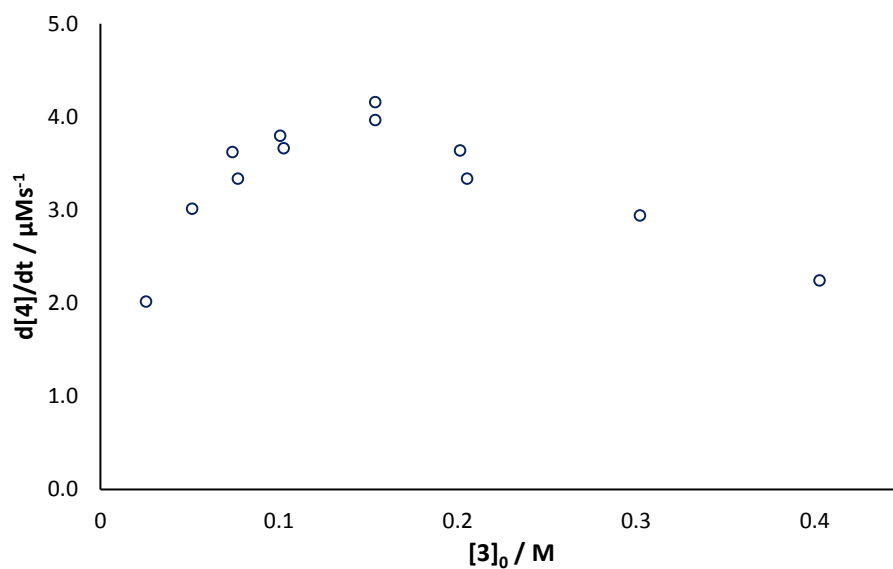


Figure S24: Rate dependence upon concentration of **3**

Kinetics at inhibition under synthetically relevant conditions

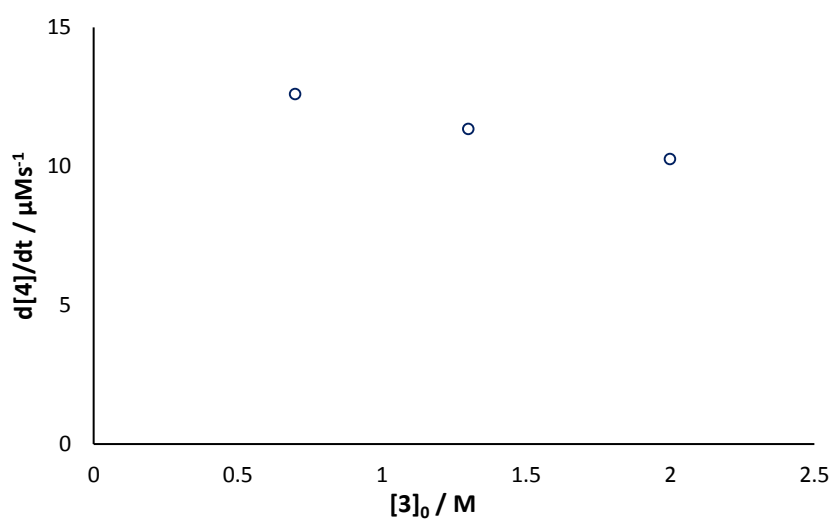
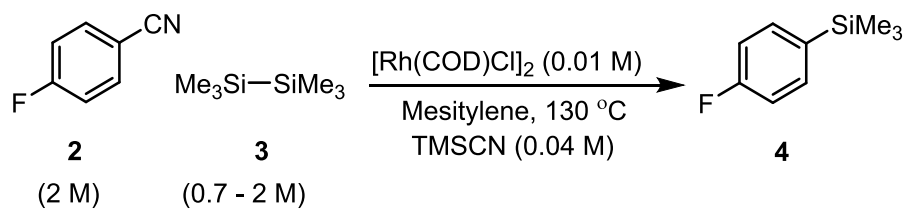
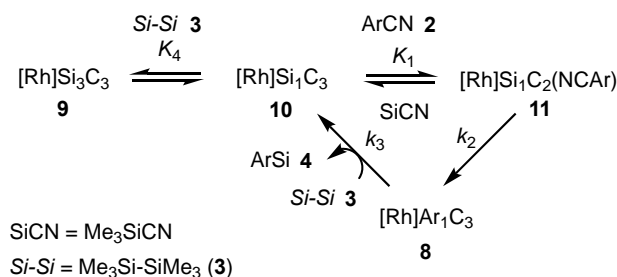


Figure S25: Rate dependence upon concentration of **3**, under synthetically utilised conditions

Derivation of steady-state rate equation

Equation S1 describes steady-state turnover frequency for reagent **3** liberating the reaction product (**4**) from aryl rhodium intermediate **8** that is present as x_8 mol fraction of the total rhodium concentration (**8**, **9**, **10**, **11**), equation S2. Application of the method of King and Altman for the terms in S2 gives equation S3, which can be rearranged to S4.



$$\text{TOF} = d[\mathbf{4}]/dt \approx k_3[\mathbf{3}] (x_8 [\text{Rh}]_{\text{tot}}) \quad (\text{eqn. S1})$$

$$x_8 = \frac{[\mathbf{8}]}{[\mathbf{8}] + [\mathbf{9}] + [\mathbf{10}] + [\mathbf{11}]} \quad (\text{eqn. S2})$$

$$x_8 = \frac{k_1 k_2 k_{-4} [\mathbf{2}]}{k_1 k_2 k_{-4} [\mathbf{2}] + [\mathbf{3}] (k_1 k_3 k_{-4} [\text{SiCN}] + k_2 k_3 k_{-4} + k_1 k_3 k_{-4} [\mathbf{2}] + k_{-1} k_3 k_4 [\mathbf{3}] [\text{SiCN}] + k_2 k_3 k_4 [\mathbf{3}])} \quad (\text{eqn. S3})$$

$$x_8 = \frac{[\mathbf{2}]}{[\mathbf{2}] + \frac{k_3}{k_2} [\mathbf{3}] (1 + [\mathbf{2}] + \frac{K_4}{K_1} [\mathbf{3}] [\text{SiCN}] + \frac{K_4 k_2}{k_1} [\mathbf{3}] + \frac{1}{K_1} [\text{SiCN}])} \quad (\text{eqn. S4})$$

By application of a limiting condition that K_4 is far greater than K_1 , equation S4 can be simplified to S5. Substituting S5 into S1 gives the approximate steady-state rate equation S6.

$$\text{when } K_4 \gg K_1 \quad x_8 \approx \frac{[\mathbf{2}]}{[\mathbf{2}] + K [\text{SiCN}] [\mathbf{3}]^2} \quad K = \frac{k_3 K_4}{k_2 K_1} \quad (\text{eqn. S5})$$

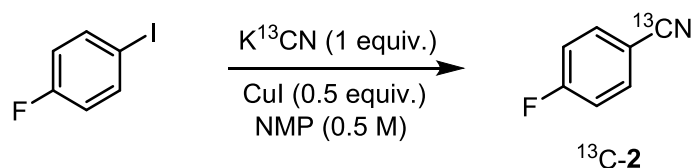
$$d[\mathbf{4}]/dt \approx \frac{k_3 [\mathbf{2}] [\mathbf{3}] [\text{Rh}]_{\text{tot}}}{[\mathbf{2}] + K [\text{SiCN}] [\mathbf{3}]^2} \quad (\text{eqn. S6})$$

$$x_8 + x_9 \approx \frac{[\mathbf{2}]}{[\mathbf{2}] + K [\text{SiCN}] [\mathbf{3}]^2} + \frac{K [\text{SiCN}] [\mathbf{3}]^2}{[\mathbf{2}] + K [\text{SiCN}] [\mathbf{3}]^2} = 1 \quad (\text{eqn. S7})$$

Equation S6 has been applied in the main paper to calculate the turnover rate in the inhibition phase, using $K[\text{Me}_3\text{SiCN}] = 4.3 \text{ M}^{-1}$ and $k_3 = 4.9 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$. Equation S7 shows how the simplification made in S5 results in **8** and **9** being the 'sole' rhodium species.

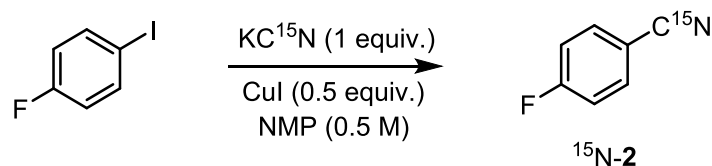
Preparation of Labelled Substrates

Synthesis of ^{13}C -2: ^{13}C -4-fluorobenzonitrile



General Procedure: Based on the literature procedure,⁵³ copper iodide (438.7 mg, 2.3 mmol), and K^{13}CN (304.1 mg, 4.6 mmol) were combined as solids in an ampoule under N_2 and dissolved into anhydrous NMP (8 mL) resulting in a dark yellow/brown heterogeneous suspension. 4-Fluoriodobenzene (531 μL , 4.6 mmol) was added via syringe, and the ampoule was sealed with a Youngs tap. The flask was heated to 150 $^\circ\text{C}$ for 18 hours at which time it was returned to room temperature and analysis by TLC indicated complete consumption of starting material. The contents of the ampoule were diluted with 50 mL of Et_2O and washed against aqueous saturated solution of Na_2CO_3 . The organic layers were combined and washed with brine then dried with MgSO_4 , filtered, and all volatiles were removed by rotary evaporation, keeping water bath temperature at 22 $^\circ\text{C}$, resulting in a lightly pink oil which crystallized upon standing at room temperature. Purified by column chromatography 10:1 pentane: Et_2O , resulting in ^{13}C -2 a white crystalline solid in 410 mg (3.35 mmol, 73 %) yield.

mp: 31 – 34 $^\circ\text{C}$; **ν_{max} (film, cm^{-1}):** 3072, 2181, 1912, 1604, 1507, 1407, 1292, 1239, 1193, 1165, 1097, 1022, 966, 947, 831; **^1H NMR (400 MHz, CDCl_3):** δ = 7.74 – 7.64 (m, 2H), 7.23 – 7.15 (m, 2H); **$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3):** δ = 165.20 (dd, $^1J_{\text{CF}}$ = 256.6, $^4J_{\text{CC}}$ = 2.0 Hz, ArC-F), 134.83 (dd, $^3J_{\text{CF}}$ = 9.3, $^2J_{\text{CC}}$ = 3.0 Hz, ArC), 118.16 (Ar-CN), 117.01 (dd, $^2J_{\text{CF}}$ = 22.7 $^3J_{\text{CC}}$ = 6.0 Hz, ArC), 108.73 (dd, $^1J_{\text{CC}}$ = 83.4 $^4J_{\text{CF}}$ = 3.6 Hz, ArC-CN); **^{19}F NMR (376.5 MHz, CDCl_3):** δ = -102.42 (tt, J = 8.3, 5.1 Hz); **HRMS** calcd. for $\text{C}_6^{13}\text{C}_1\text{H}_4\text{NF}$: 122.03558 $[\text{M}]^+$; found (EI+): 122.03453.

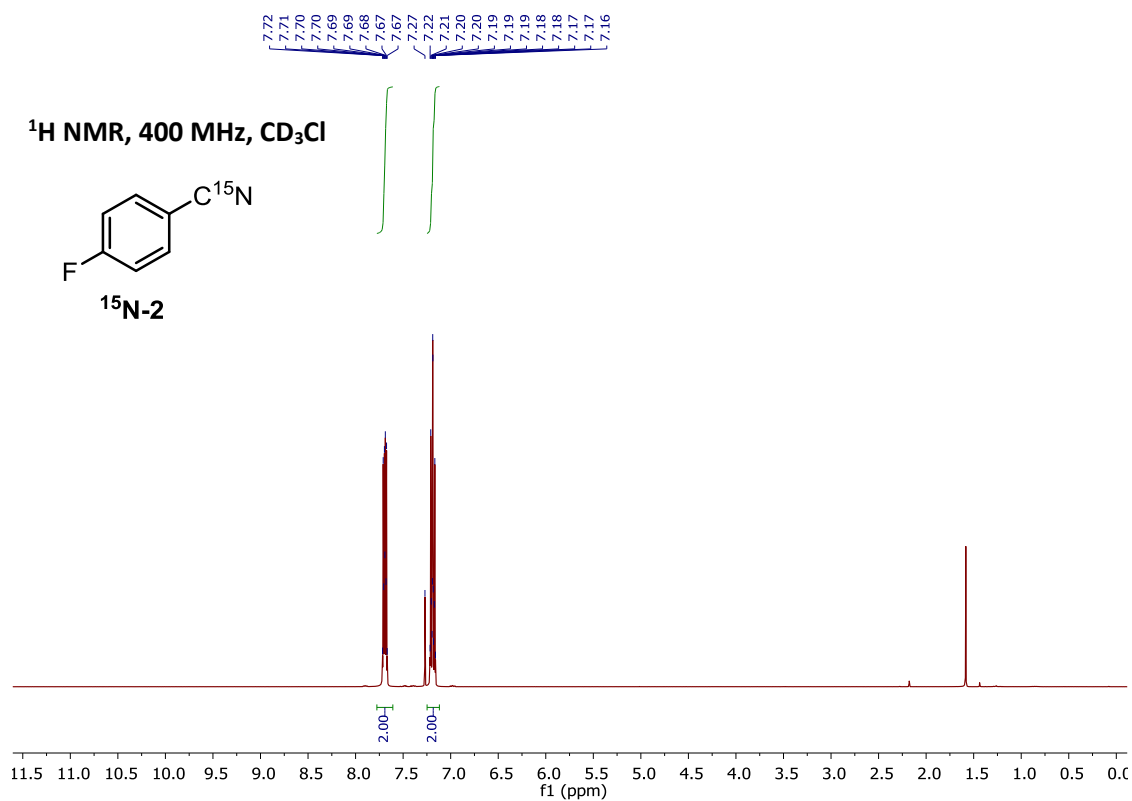
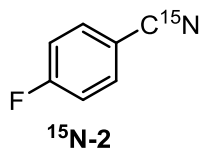
¹⁵N-4-fluorobenzonitrile ¹⁵N-2

General Procedure: Based on the literature procedure,⁵³ copper iodide (438.7 mg, 2.3 mmol), and KC¹⁵N (304.0 mg, 4.6 mmol) were combined as solids in an ampoule under N₂ and dissolved into anhydrous NMP (8 mL) resulting in a dark yellow/brown heterogeneous suspension. 4-Fluoriodobenzene (531 μL, 4.6 mmol) was added via syringe, and the ampoule was sealed with a Youngs tap. The flask was heated to 150 °C for 18 hours at which time it was returned to room temperature and analysis by TLC indicated complete consumption of starting material. The contents of the ampoule were diluted with 50 mL of Et₂O and washed against aqueous saturated solution of Na₂CO₃. The organic layers were combined and washed with brine then dried with MgSO₄, filtered, and all volatiles were removed by rotary evaporation, keeping water bath temperature at 22 °C, resulting in a lightly pink oil which crystallized upon standing at room temperature. Purified by column chromatography 10:1 pentane:Et₂O, resulting in ¹⁵N-2 a white crystalline solid in 325.7 mg (2.67 mmol, 58 %) yield.

mp: 31 – 34 °C; **u_{max} (film, cm⁻¹):** 3072, 2207, 1912, 1604, 1507, 1420, 1408, 1239, 1194, 1165, 1097, 1022, 966, 947, 831; **¹H NMR (400 MHz, CDCl₃):** δ = 7.70 (ddd, *J* = 9.0, 5.0, 2.5 Hz, 2H), 7.26 – 7.10 (m, 2H); **¹³C{¹H} (100 MHz, CDCl₃):** δ = 165.18 (d, ¹*J*_{CF} = 256.6 Hz, ArC-F), 134.82 (d, ³*J*_{CF} = 9.4 Hz, ArC), 118.14 (d, ¹*J*_{CN} = 17.9 Hz, Ar-CN), 117.00 (d, ²*J*_{CF} = 22.7 Hz, ArC), 109.24 – 108.18 (m, ArC-CN); **¹⁹F NMR (376.5 MHz, CDCl₃):** δ = -102.41 (tt, *J* = 8.3, 5.0 Hz); **¹⁵N NMR (40.56 MHz, CDCl₃):** δ = 255.48 (s, 1N); **HRMS** calcd. for C₇H₄¹⁵NF: 122.02928 [M]⁺; found (EI⁺): 122.02928.

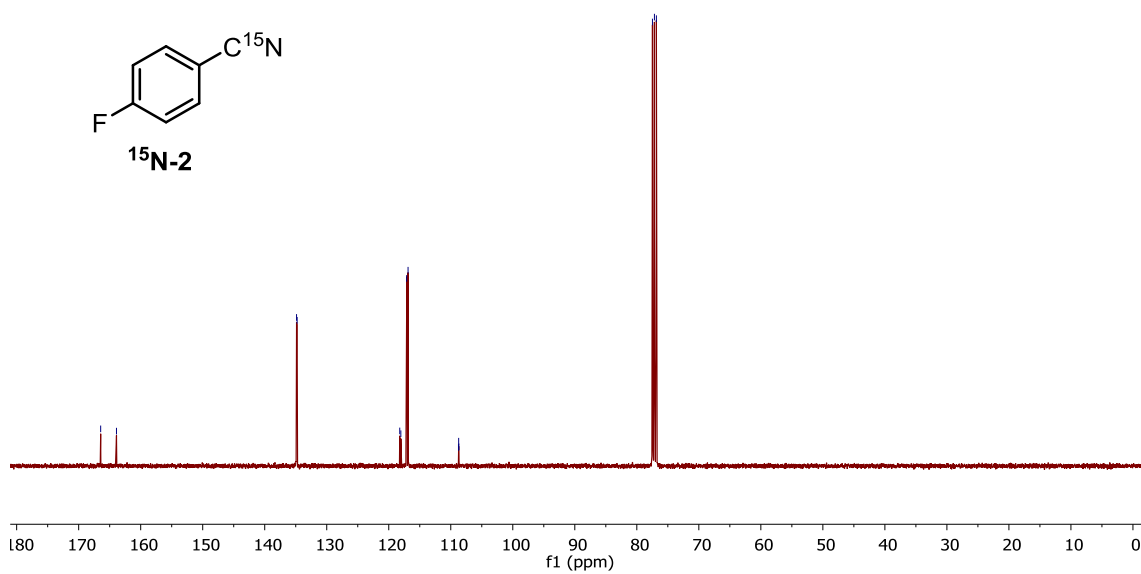
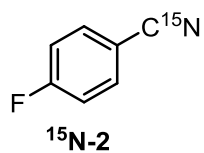
NMR Spectra

^1H NMR, 400 MHz, CD_3Cl

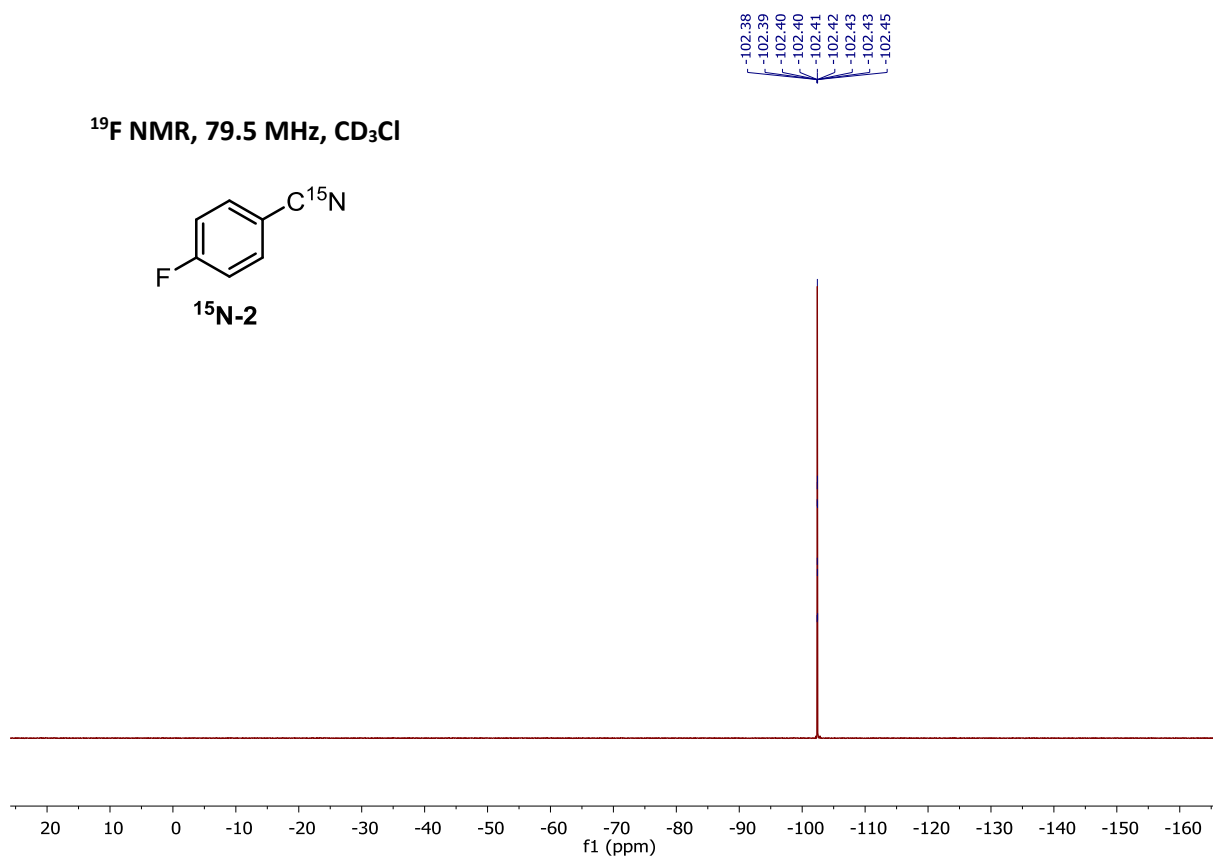
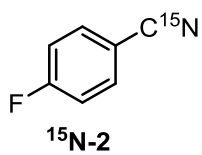


166.5
 163.9
 134.9
 134.8
 118.2
 118.0
 117.1
 116.9
 108.8
 108.7
 108.7
 77.5
 77.2
 76.8

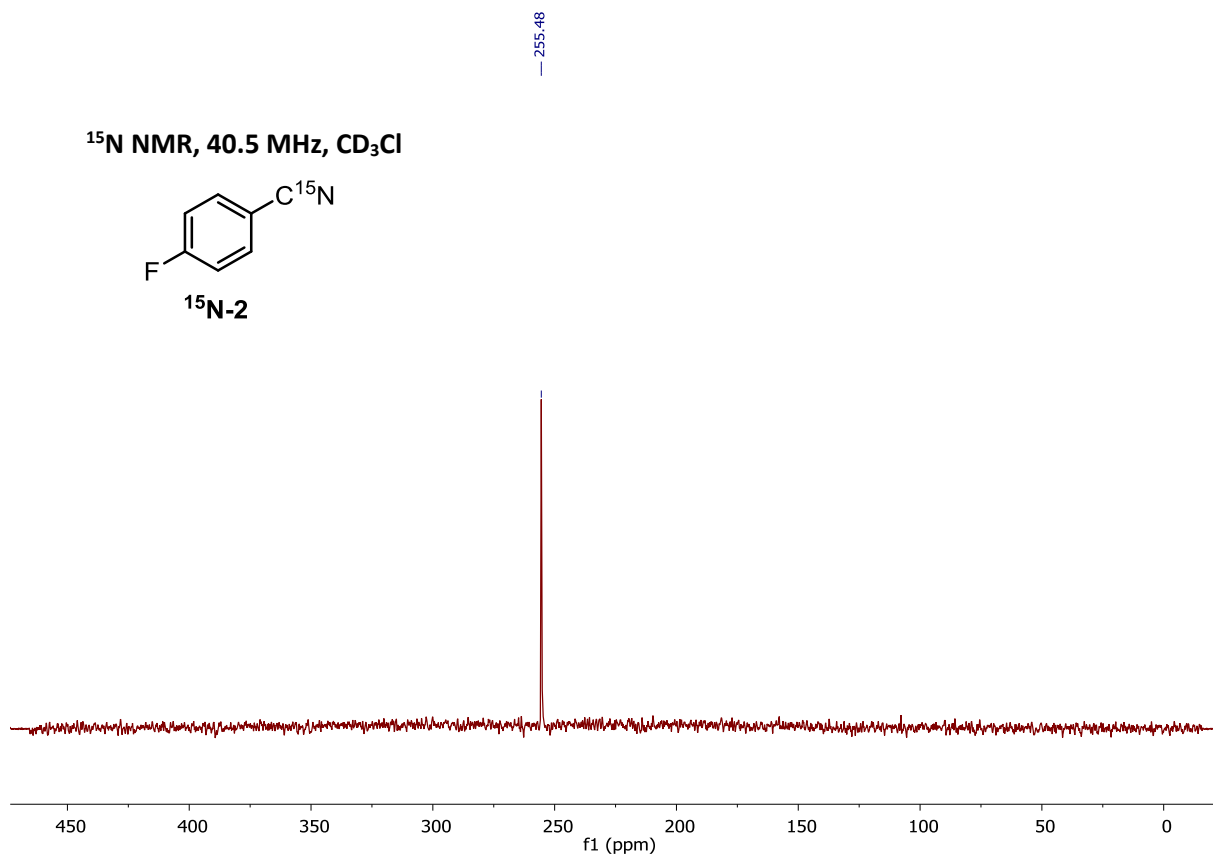
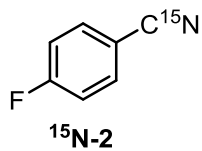
$^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CD_3Cl

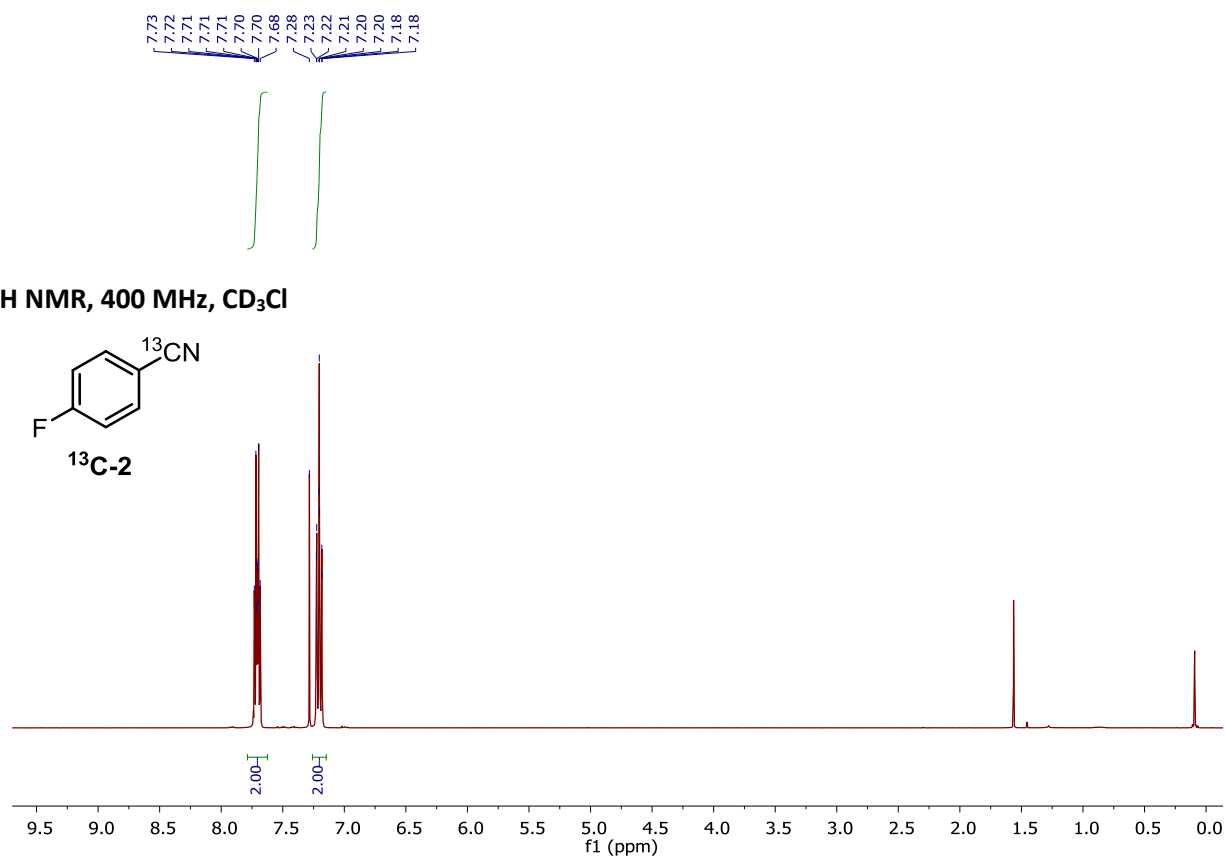


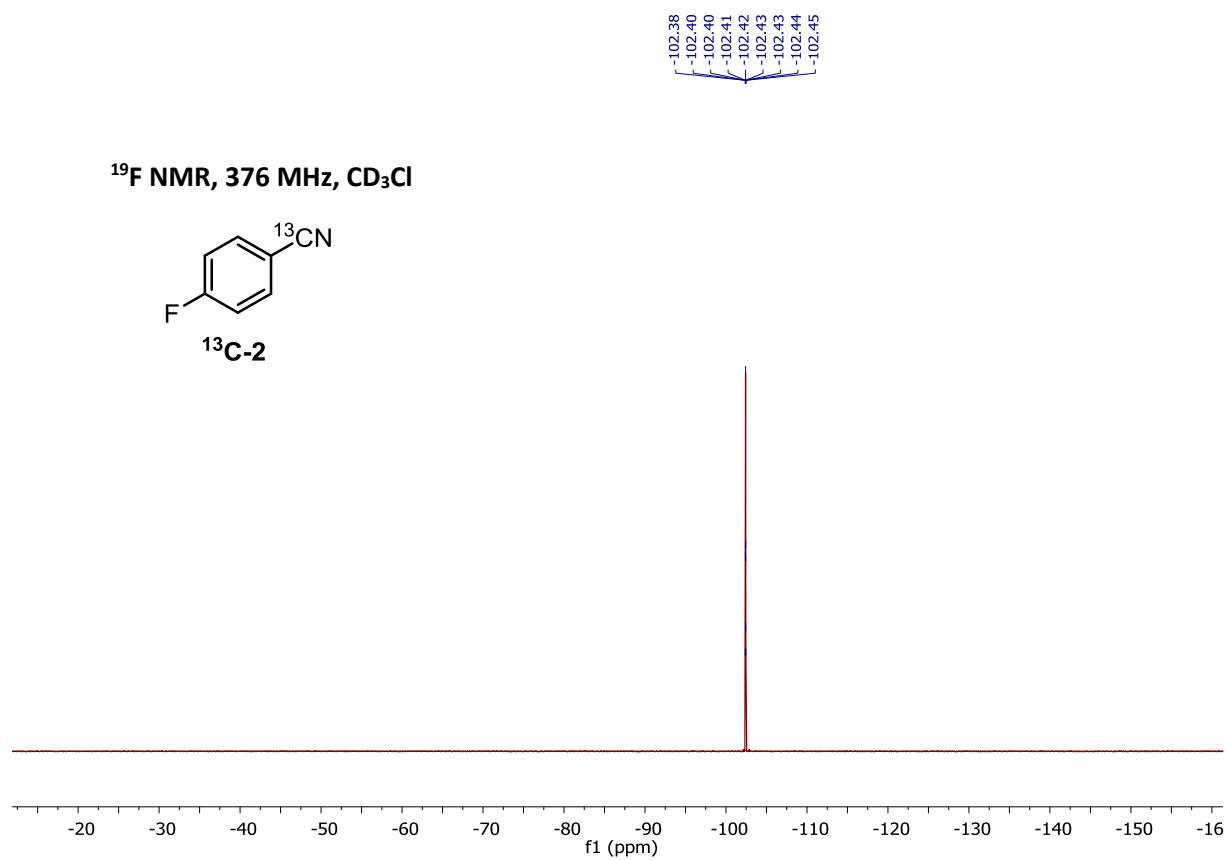
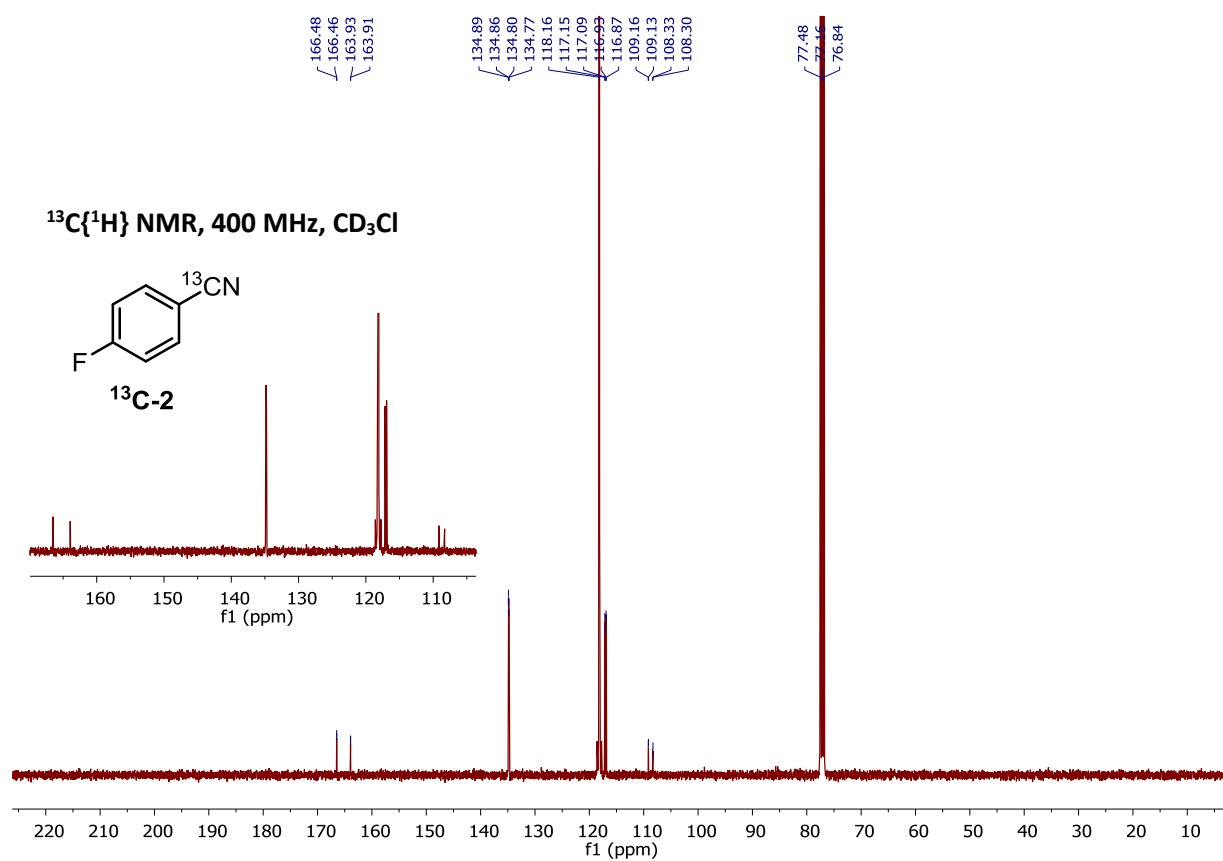
^{19}F NMR, 79.5 MHz, CD_3Cl



^{15}N NMR, 40.5 MHz, CD_3Cl







References

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