Monomeric Lithium and Sodium Silylbenzyl Complexes: Syntheses, Structures, and C=O bond Olefination

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Materials and Methods

Section 1. Experimental methods and data

1.1 General procedures

All manipulations were carried out using Schlenk techniques, or in a Vigor™ glovebox equipped with a −35 ˚C freezer and a cold well, under an atmosphere of dry argon. Benzene, toluene and n-hexane was dried with sodium press, sodium-potassium alloy and distilled under reduced pressure, and kept in the glovebox. Chemicals were purchased from Merck, Fluorochem or Alfa Aesar, and dried under dynamic vacuum for several hours (for solids), or over activated 4Å molecular sieves, prior to use.

All glassware, including pipettes, vials and ampoules, must be silylated prior to use by treating with trimethylsilyl chloride (Me_3SiCl), rinsing with water, and dried in a 150 °C oven for 12 hours. Failing to silylate glassware will lead to significantly reduced yields, and in some cases, irreproducible results.

The organolithium and organosodium complexes in this work are highly reactive towards silicone grease. We would suggest excluding grease as much as possible for all chemicals used herein, including in the solvent distillation apparatus. Otherwise, irreproducible by-products or side products may appear. For this purpose, we used J. Young tap solvent flasks and vacuum transfer apparatus to dry our solvents.

[$NaCH_2SiMe_3$] was prepared as previously described.[1]

^1H, $^{13}C\{^1H\}$ and ^7Li NMR spectra were recorded on a Bruker 300 Avance III spectrometer operating at 300.13, 75.48 and 116.64 MHz respectively. Chemical shifts are quoted in ppm and are relative to $SiMe_4$ (^1H and ^{13}C) or external 0.1 M LiCl in D_2O (^7Li). ^1H NMR spectra with internal standard (cyclohexane) and integratable ^{19}F NMR spectra were ran with a 50 second and 120 second D1 relaxation delay respectively, to ensure accurate integration values.

1.2 Synthesis and characterization of [LiCH(Ph)($SiMe_{3)}$)(Me_6Tren)] (**2**-Li)

[$LiCH_2SiMe_3$] (0.0941 g, 1 mmol) was dissolved in n-hexane (0.5 mL), the solution was transferred to a separate solution of Me_6Tren (0.2303, 1 mmol) in n-hexane (0.5 mL). The resulting solution was transferred to a vial containing neat $PhCH_2SiMe_3$ (0.1642, 1 mmol). After standing at room temperature for 24 hours the mixture separated into two layers: the bottom layer is a bright yellow oil, while the top layer is slightly yellow and constitutes the majority of the volume. The vial with the two layer was placed in a -35 °C freezer. Yellow crystalline solid (clusters of crystals) were grown after standing at room temperature for 24 hours. The mother liquor was removed, and crystals dried *in vacuo*. A fine yellow crystalline solid (**2**-Li) was retrieved (0.3097g, 81% yield).

SXCRD Study: Single crystals of **2**-Li suitable was grown from highly diluted n-hexane + benzene solution. **2**-Li (0.030 g, 0.07 mmol) was added to n-hexane (3 mL), benzene was added drop wise to the suspension until all solid was fully dissolved. The resulting solution was then filtered through a pipette equipped with glass-wool plug and celite. The clear yellow solution was placed in a -35 ^{O}C freezer. Yellow needle shaped crystals of **2**-Li formed overnight which were suitable for SCXRD study.

NOTE: Toluene should be avoided as a crystallisation solvent: it reacts with **2**-Li to produce [Li(CH_2Ph)(Me_6Tren)].

^{1}H NMR (*d_6*-benzene, 25 ˚C, 300 MHz): δ (ppm) 7.13 (t, $^3J_{HH}$ = 7.5 ; 2H, Ar-*H*), 6.86 (broad s, 1H, Ar-*H*), 6.45 (t, $^3J_{HH}$ = 7.0, 2H, Ar-*H*), 2.32-2.28 (t, $^3J_{HH}$ = 5.7, 6H, NCH_2CH_2N), 2.00 (s, 18H, $N(CH_3)_2$) 1.92-1.88 (t, $^3J_{HH}$ = 5.7, 6H, NCH_2CH_2N), 0.88 (s, 1H, PhC*H*Si) 0.55 (s, 9H, $Si(CH_3)_3$).

^{13}C{^{1}H} NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 159.4 (ArC^{ipso}), 128.7 (Ar*C*H), 120.5 (Ar*C*H), 108.9 (Ar*C*H), 56.8(NCH_2CH_2N), 51.6 (NCH_2CH_2N), 45.6 ($N(CH_3)_2$), 40.6 (Ph*C*HSi), 3.4 ($Si(CH_3)_3$).

^{7}Li NMR (*d_6*-benzene, 25 ˚C, 117 MHz): δ (ppm) 0.59.

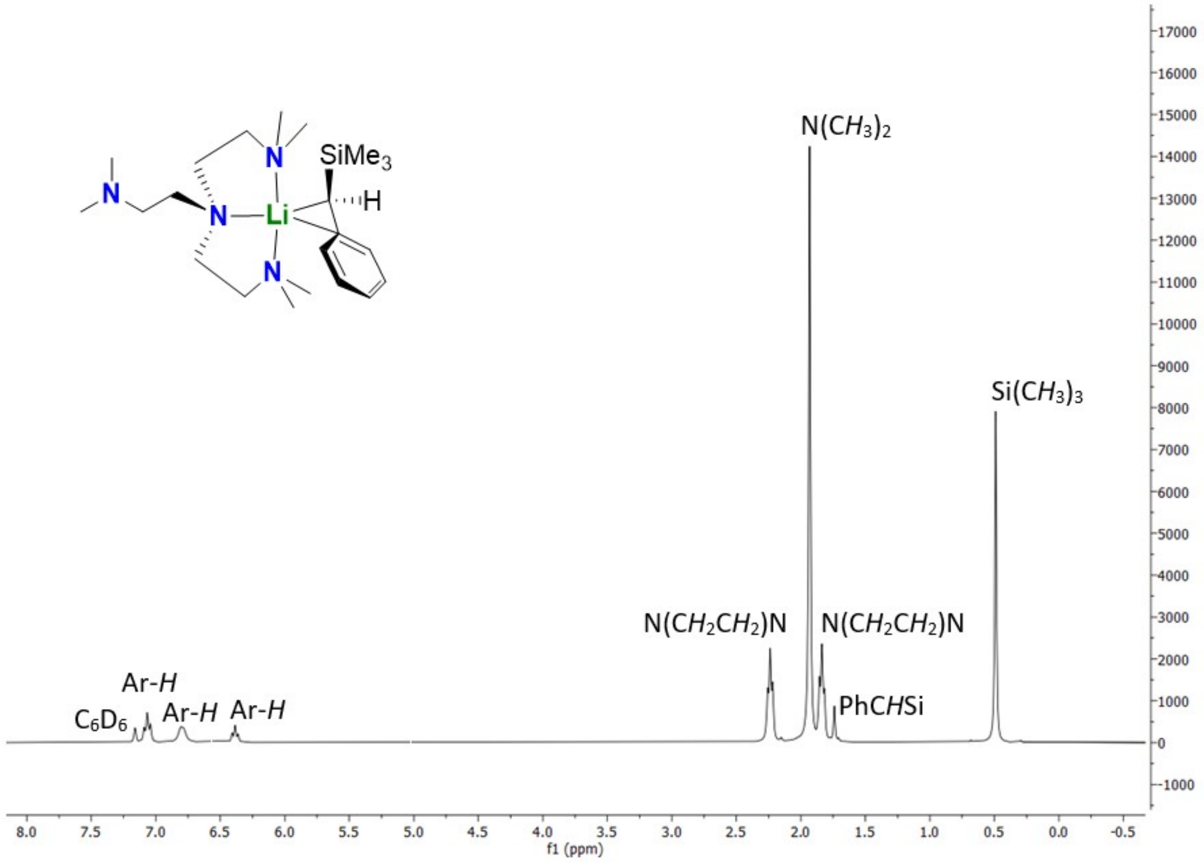

Figure S1: ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) of **2**-Li.

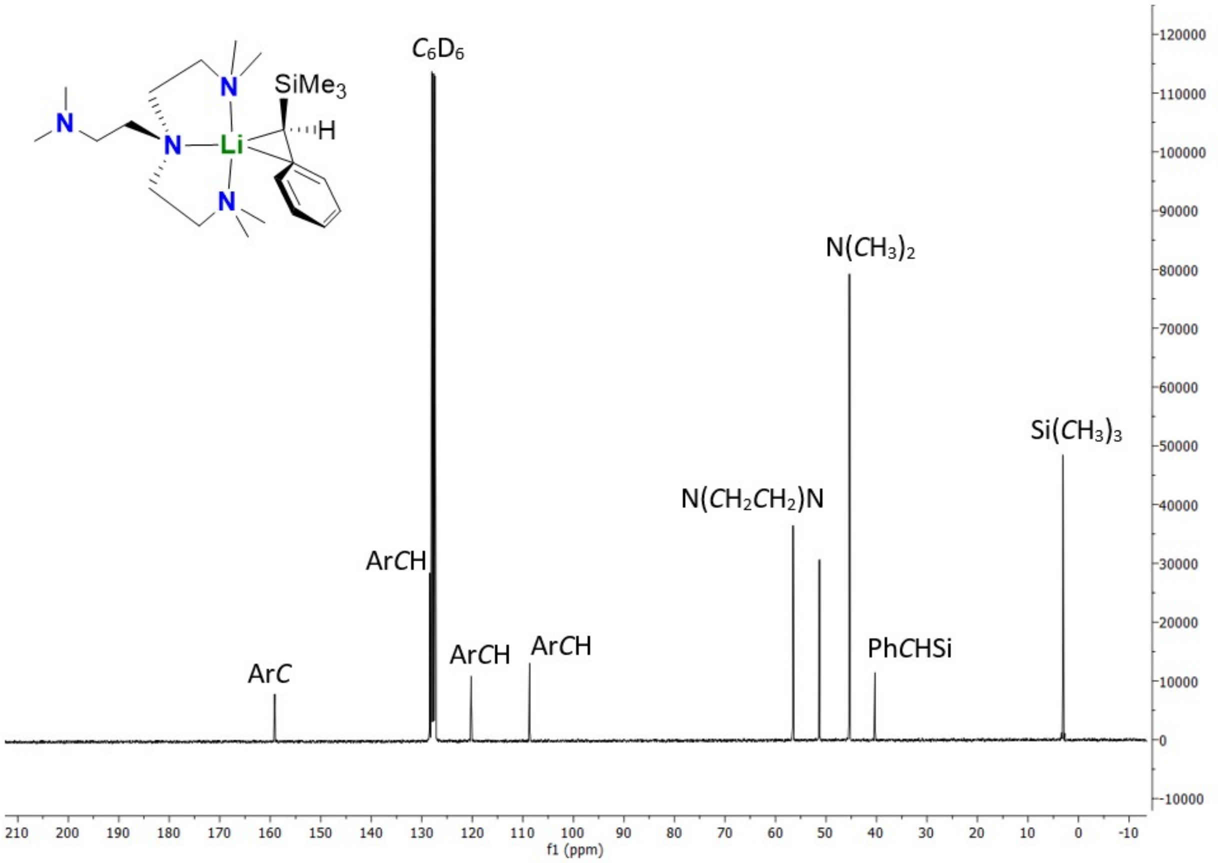

Figure S2: $^{13}C\{^1H\}$ NMR (*d₆*-benzene, 25 ˚C, 75 MHz) of **2**-Li.

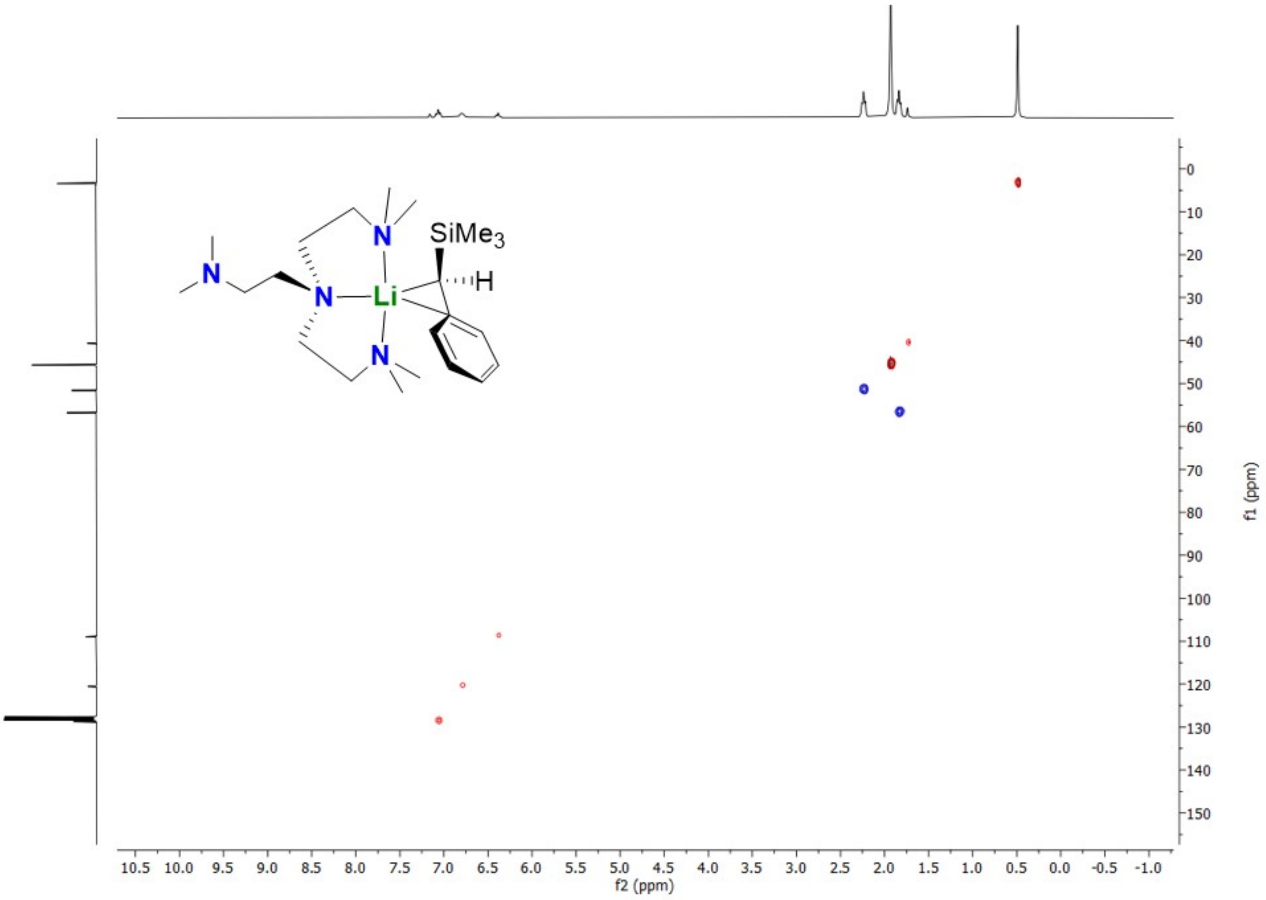

Figure S3: HSQC (*d₆*-benzene, 25 ˚C, 300 MHz) of **2**-Li. Red: (CH, CH_3); Blue: (CH_2)

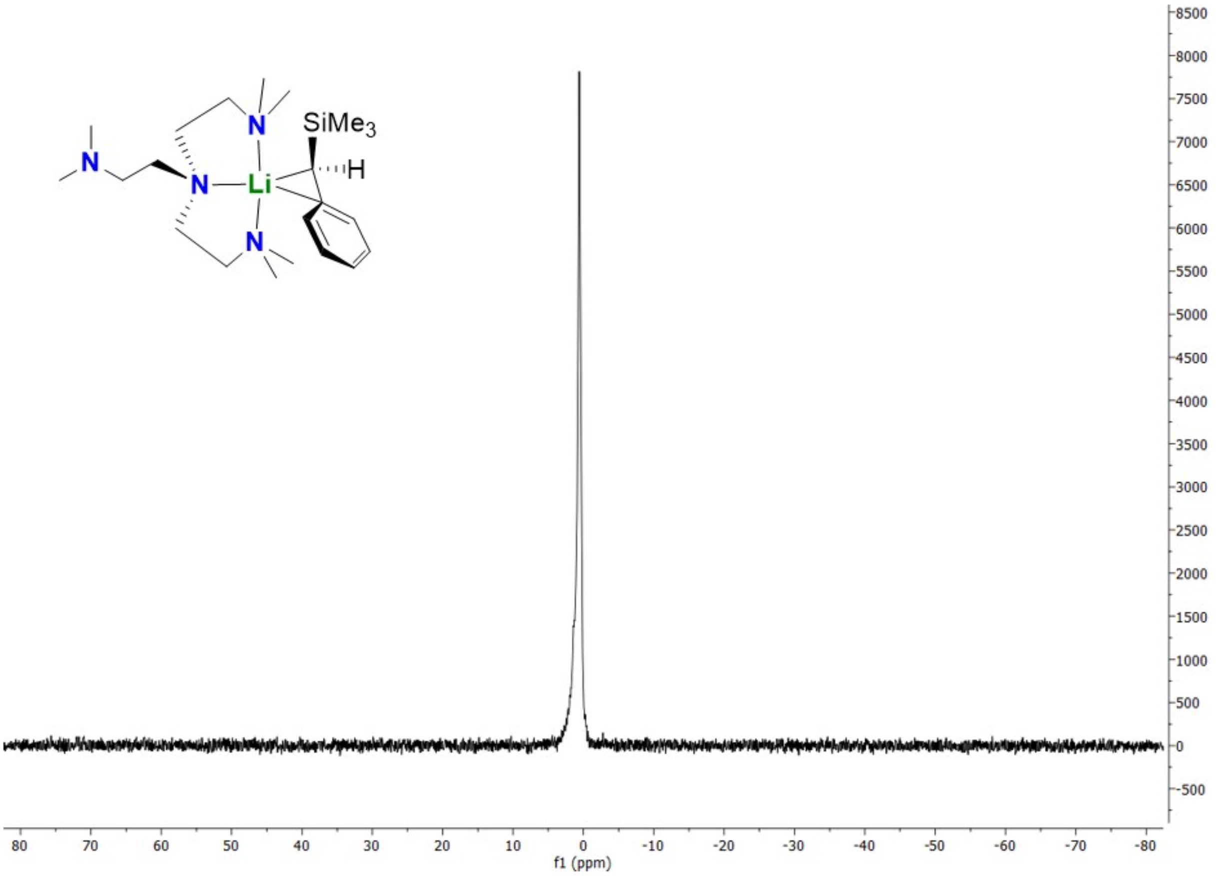

Figure S4: ^{7}Li NMR (d_6-benzene, 25 ˚C, 117 MHz) of **2**-Li.

1.3 Synthesis and characterization of [NaCH(Ph)(SiMe$_{3)}$)(Me$_6$Tren)] (**2**-Na)

Me$_6$Tren (0.2303 g, 1 mmol) was dissolved in n-hexane (2 mL). The solution was transferred in one portion to [NaCH$_2$SiMe$_3$] (0.1102 g, 1 mmol). A further 6 mL of n-hexane was added to the suspension. The resulting suspension was added to neat PhCH$_2$SiMe$_3$ (0.1643 g, 1 mmol) in n-hexane (0.5 mL). The resulting orange solution was then filtered through a pipette equipped with glass-wool plug and celite. After standing at room temperature for 2 hours, the solution was placed in a -35 ^{O}C freezer overnight. Orange crystalline solid formed after 20 hours. The mother liquor was removed, and the crystalline solid was dried *in vacuo*. An orange crystalline solid (**2**-Na) was retrieved (0.0.3302g, 79% yield)

SCXRD Study: Single crystals of **2**-Na suitable for SCXRD study were grown from highly diluted n-hexane + benzene solution at -35 °C. **2**-Na (0.030 g, 0.07 mmol) was added to n-hexane (6 mL), benzene was added drop wise to the suspension until all solid was fully dissolved. The resulting solution was filtered through a pipette equipped with glass-wool plug and celite. The resulting clear orange solution was placed in a -35 ^{O}C freezer. Orange needle shaped crystals of **2**-Na formed overnight, which were suitable for SCXRD study.

NOTE: Toluene should be avoided as a crystallisation solvent: it reacts with **2**-Na to produce [Na(CH$_2$Ph)(Me$_6$Tren)].

^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz): δ (ppm) 7.00 – 6.53 (m, 3H, Ar-*H*), 6.03 (m, 2H, Ar-*H*), 2.31 (s, 1H, PhC*H*Si), 1.95 (s, 18H, N(CH_3)$_2$) 1.74 (s, 12H, NCH_2CH_2N), 0.56 (s, 9H, Si(CH_3)$_3$).

^{13}C{^{1}H} NMR (75 MHz, d$_6$-benzene, 25 °C): δ (ppm) 159.5 (ArC^{ipso}), 128.9 (Ar*C*H), 113.7 (Ar*C*H), 104.3 (Ar*C*H), 57.2 (N*C*H$_2$CH$_2$N), 51.0 (N(CH$_3$)$_2$), 47.3 (Ph*C*HSi), 45.2 (NCH$_2$*C*H$_2$N), 3.4 (Si(CH$_3$)$_3$).

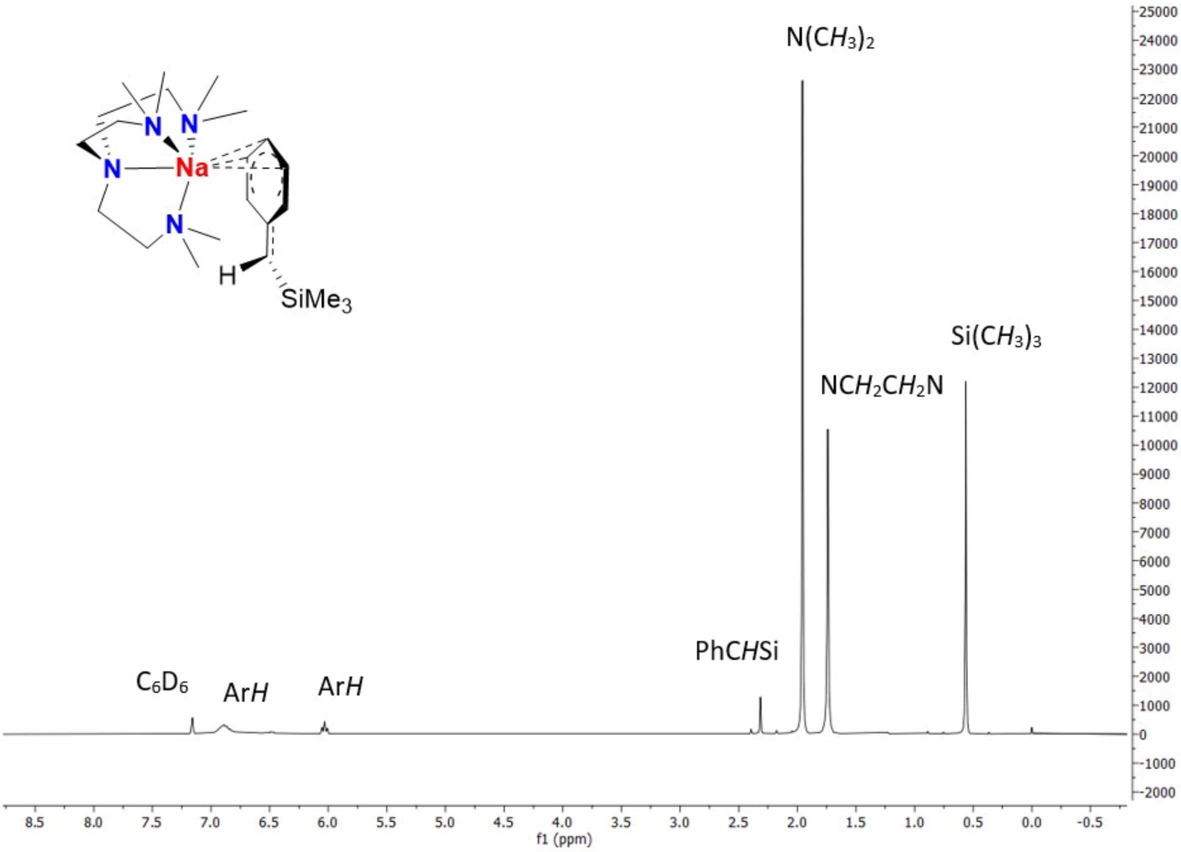

Figure S5: ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) of **2**-Na.

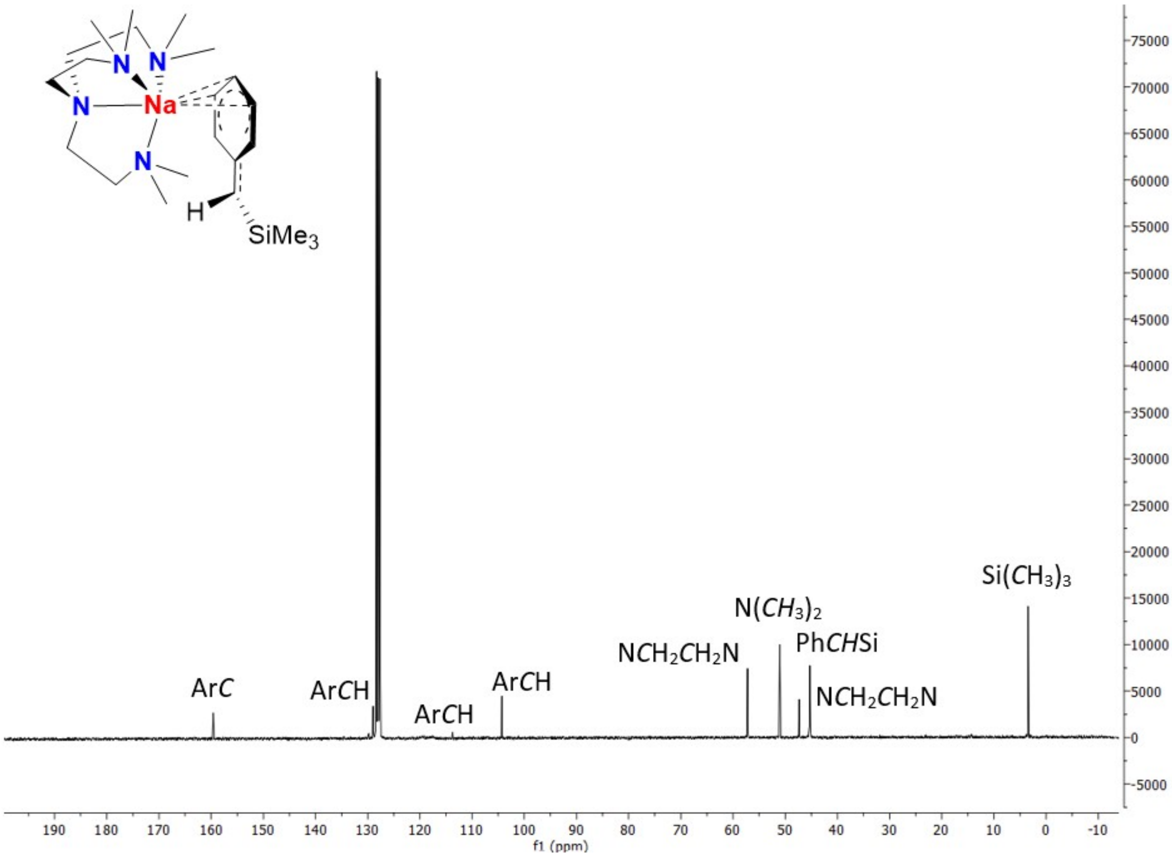

Figure S6: $^{13}C\{^{1}H\}$ NMR (d_6-benzene, 25 ˚C, 75 MHz) of **2**-Na.

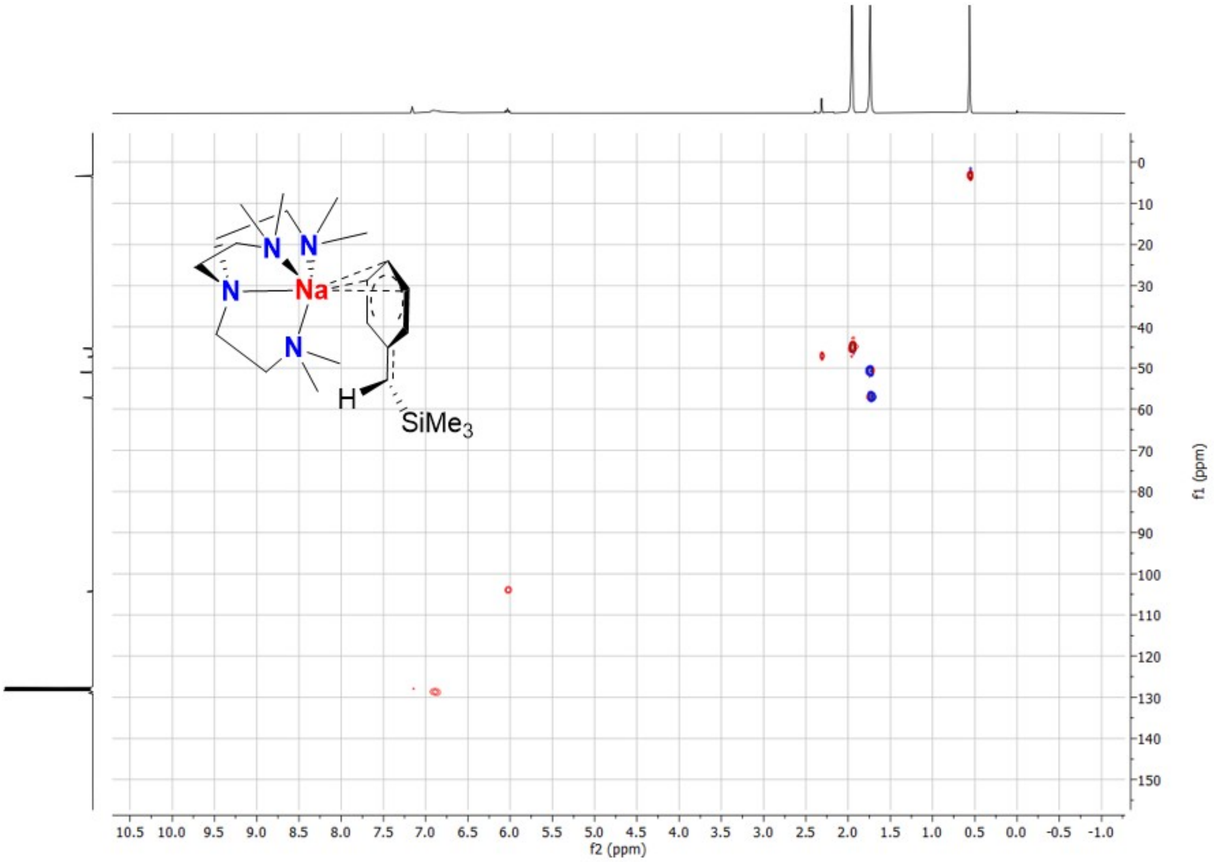

Figure S7. HSQC (*d_6*-benzene, 25 ˚C, 300 MHz) of **2**-Na. Red: (CH, CH_3) Blue: (CH_2)

1.4 Reactions between **2**-Li and organic carbonyl substrates

Reaction between 2-Li and Benzophenone (3a) to produce triphenylethylene (4a)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to benzophenone (**3a**) (0.0055g, 0.03 mmol). The resulting green solution was transferred to a J. Young NMR tube and heated to 60 ^{O}C for 2 hours. The resulting colourless solution was monitored by ^{1}H, which showed the benzophenone had a >95% conversion to the alkene.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Li (0.0120 g, 0.03 mmol). The solution was added to benzophenone (**3a**) (0.0055g, 0.03 mmol). The resulting green solution was transferred to a J. Young NMR tube and heated to 60 ^{O}C for 2 hours. The resulting colourless solution was monitored by ^{1}H NMR spectroscopy, which showed the **3a** had a >95% conversion to **4a**.

Data for triphenylethylene (**4a**):

^{1}H NMR (300 MHz, d_6-benzene, 25 °C): δ (ppm) 7.33 – 7.29 (2H, m, Ar*H*), 7.19 – 7.02 (10H, Ar*H*), 7.00 – 6.87 (4H, Ar*H*, *H*C=, overlapping signals).

^{13}C{^{1}H} NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 143.9 (quaternary carbon), 143.1 (quaternary carbon), 140.9 (quaternary carbon), 137.8 (quaternary carbon), 130.4 (Ar*C*H), 129.6 (Ar*C*H), 128.5 (Ar*C*H), 128.3 (Ar*C*H), 128.1 (Ar*C*H), 127.9 (Ar*C*H), 127.4 (Ar*C*H), 127.2 (Ar*C*H),126.7 (=*C*H).

NMR data are consistent with literature[2].

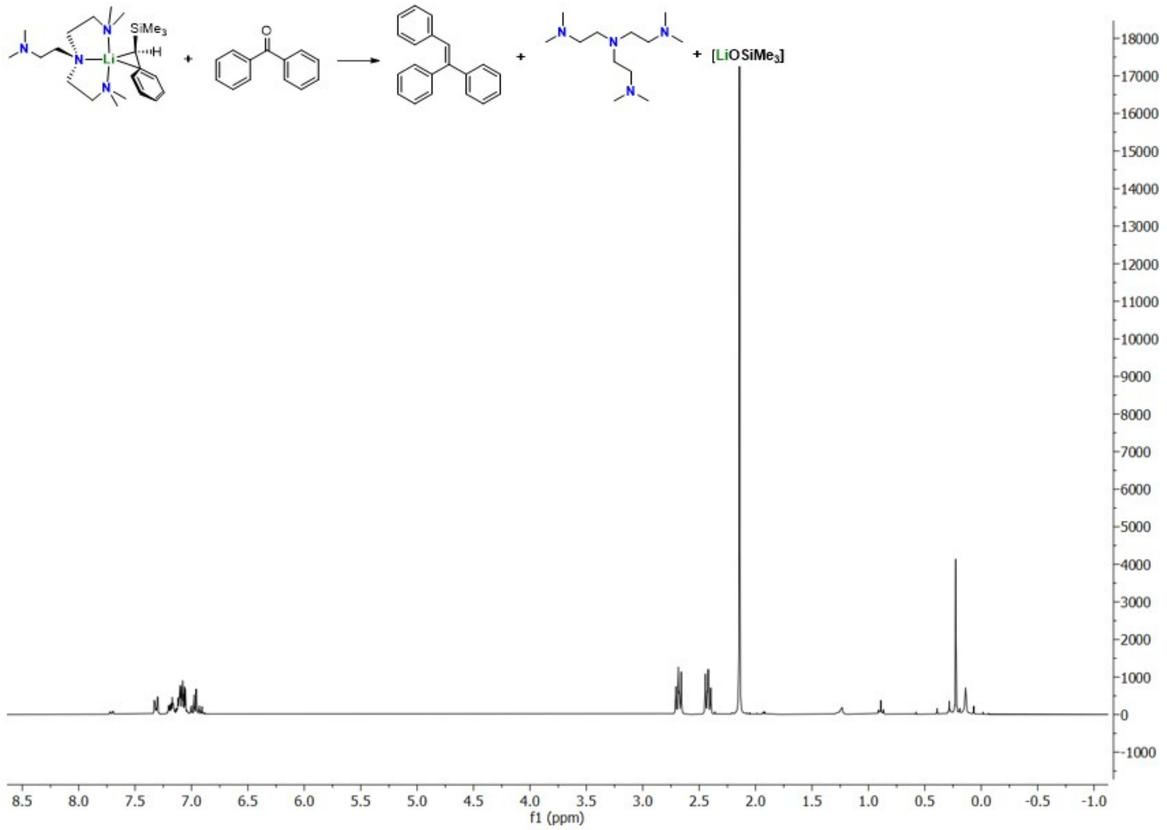

Figure S8. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and benzophenone (**3a**).

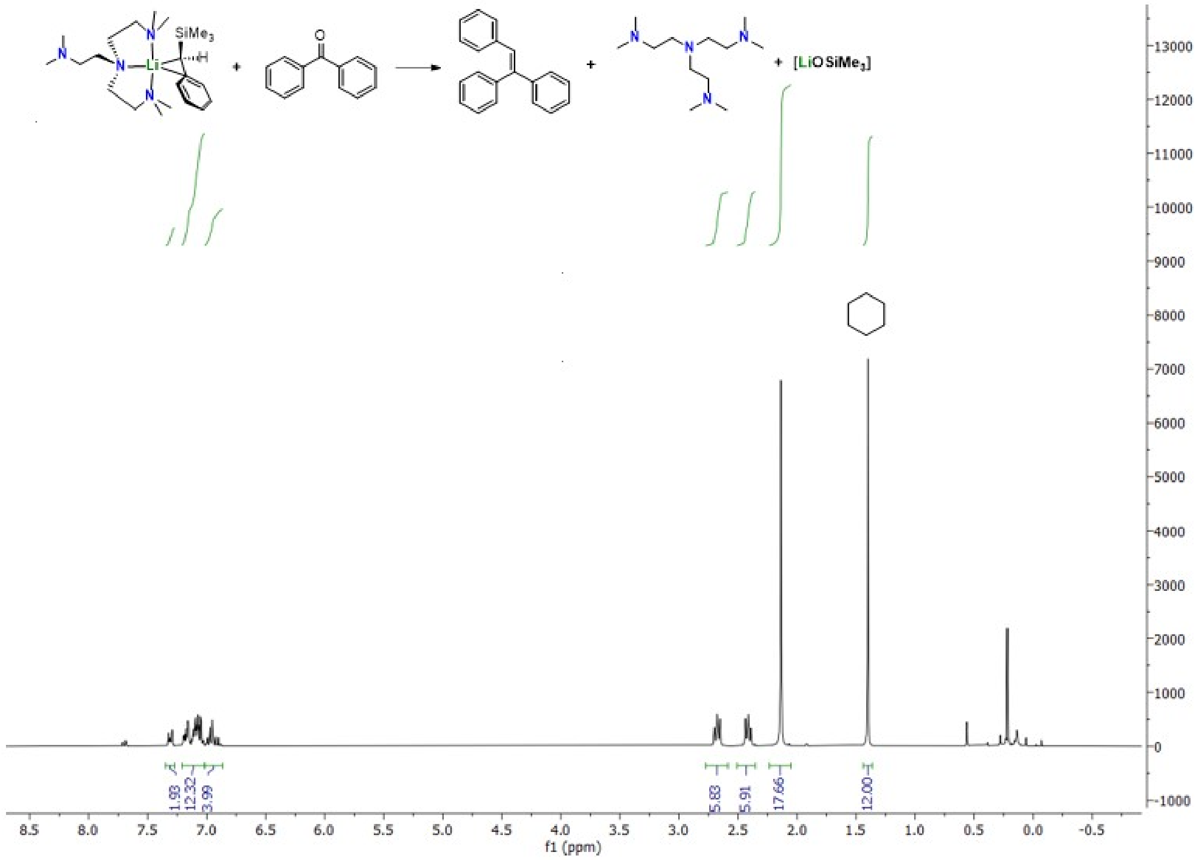

Figure S9. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and benzophenone (**3a**). Internal Standard (**I**) = Cyclohexane. [I] = 0.06M

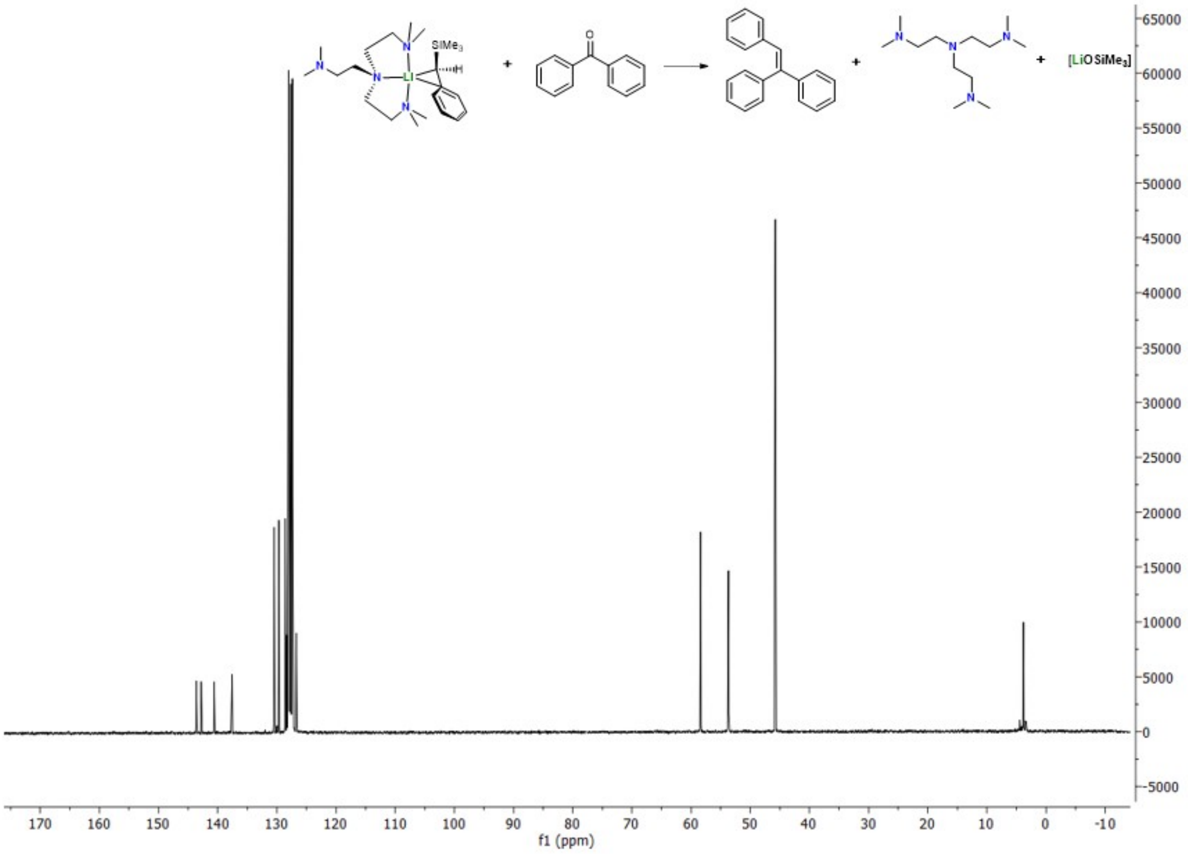

Figure S10. ^{13}C{^{1}H} NMR (75 MHz, d$_6$-benzene, 25 °C) for an NMR scale reaction between **2**-Li and benzophenone (**3a**).

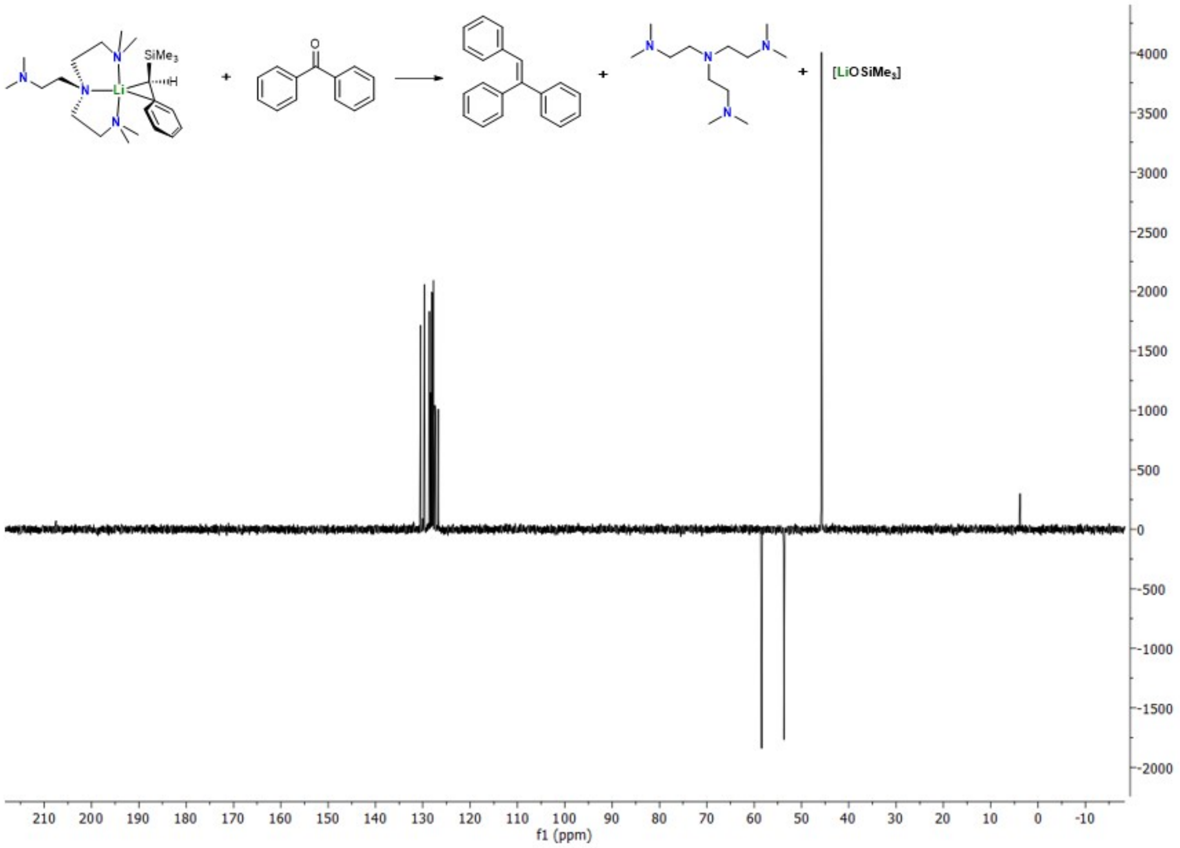

Figure S11. ^{13}C DEPT 135 NMR (d_6-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and benzophenone (**3a**).

Reaction between 2-Li and benzaldehyde (3b), to produce a mixture of E/Z-stilbene (4b)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to benzaldehyde (0.0031 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and was monitored by ^1H NMR after 30 minutes. The NMR showed >95% conversion of benzaldehyde to both E-Stilbene and Z-Stilbene at a 2:3 ratio respectively.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.4775g, 0.03 mmol) was added to **2**-Li (0.0120 g, 0.03 mmol). The solution was added to benzaldehyde (**3b**) (0.0031g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and was monitored by ^1H after 30 minutes, which showed a >95% conversion to the alkene.

Resolution of E/Z ratio: Reaction was repeated at 0.03 mmol, then dried in vacuo. The resulting solid was dissolved in $CDCl_3$ and the E/Z ratio was determined as 2:3 using ^1H NMR (**Figure S14**).

NOTE: It should be noted that, while E/Z-**4b** are inert with $CDCl_3$, upon dissolving in $CDCl_3$ some unidentifiable signals appeared on ^1H NMR spectrum within the region of 2.0-4.0 ppm (Figure S14). We rationalise the formation of these unidentifiable signals by reacting of Li- and Me_6Tren-containing species with $CDCl_3$ (such as the silyloxo cluster $[Na_9(OSiMe_3)_{10}]^-[Na(C_6H_6)(Me_6Tren)]^+$ reported in our previous work[1]). The formation of these unidentifiable signals does not interfere with the determining of the E/Z-ratio of **4b**.

Data for E/Z Stilbene (**4b**):

^{1}H NMR (300 MHz, d6-benzene, 25 °C): δ (ppm) 7.33 – 7.29 (m, 2H, Ar*H*), 7.24 – 7.18 (m, 3H, Ar*H*) 7.09 – 6.92 (m, 5.80H, Ar*H*, (E)*H*C=C*H*, overlapping signals), 6.46 (s, 1.20H, (Z)*H*C=C*H*).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.42 – 7.40 (m, 2H, Ar*H*), 7.25 – 7.0 (s, 8H, Ar*H*), 7.01 (s, 0.80H, (E)*H*C=C*H*), 6.49 (s, 1.20H, (Z)*H*C=C*H*).

^{13}C{1H} NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 137.7 (quaternary carbon), 137.6 (quaternary carbon) 130.1 ((E)=*C*H), 129.2 ((Z)=*C*H), 129.0 (Ar*C*H), 128.8 (Ar*C*H), 128.4 (Ar*C*H), 127.7 (Ar*C*H), 127.3 (Ar*C*H), 126.8 (Ar*C*H)

NMR data was consistent with literature.[3, 4]

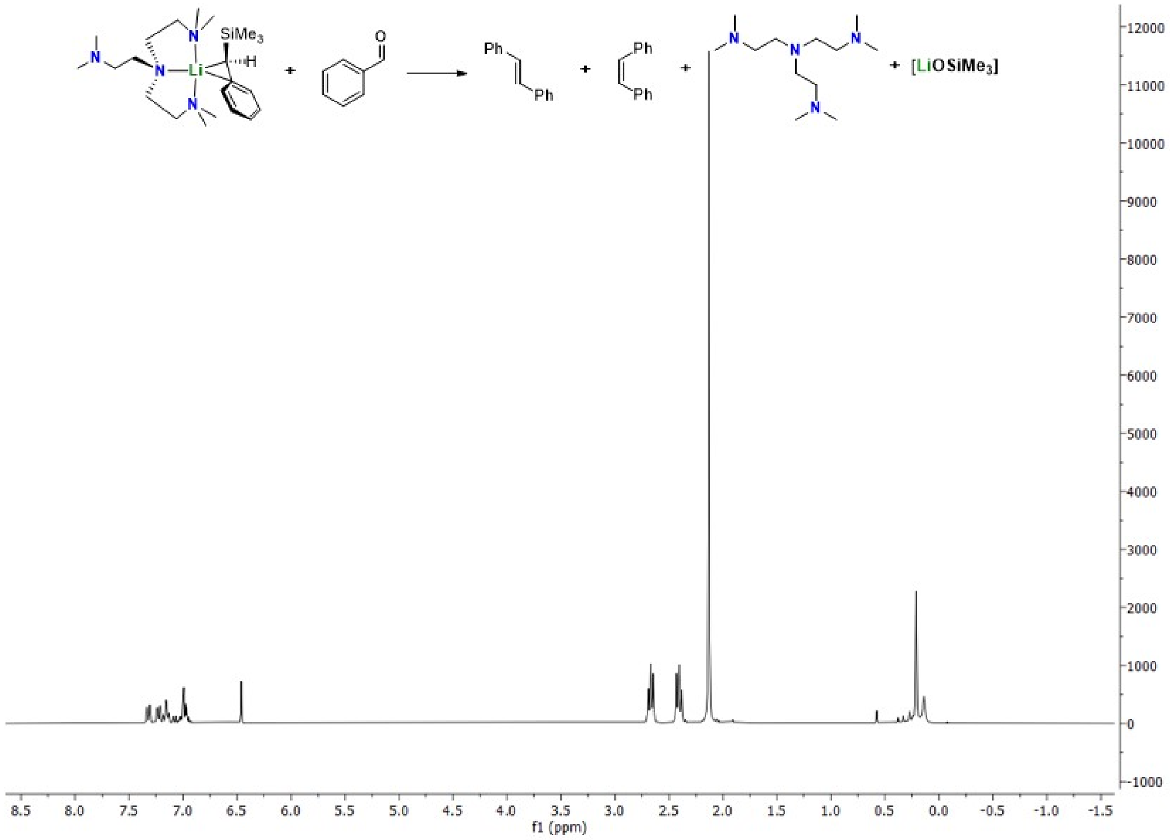

Figure S12. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and benzaldehyde (**3b**). The signals within the 0-0.5 ppm region are likely to be the $LiOSiMe_3$ species eliminated from the reaction.

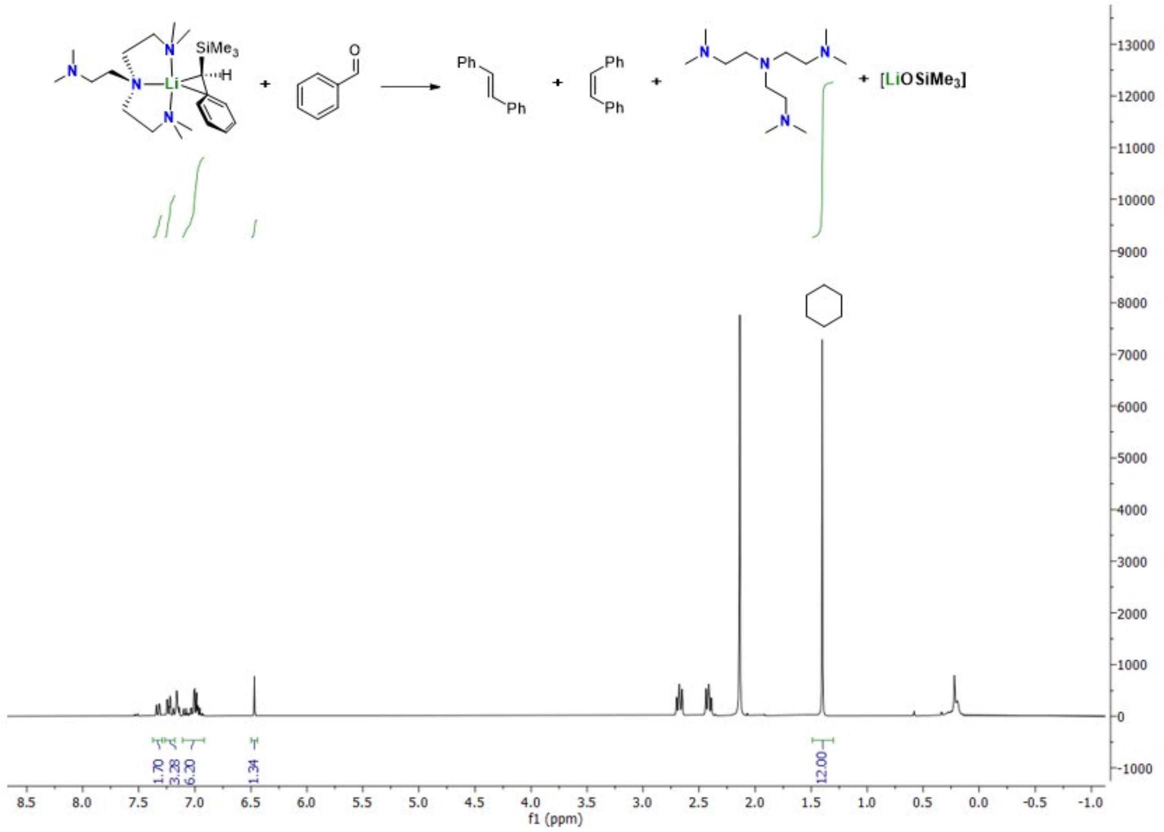

Figure S13. ^1H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and benzaldehyde (**3b**). Internal Standard (**I**) = Cyclohexane. [I] = 0.06M

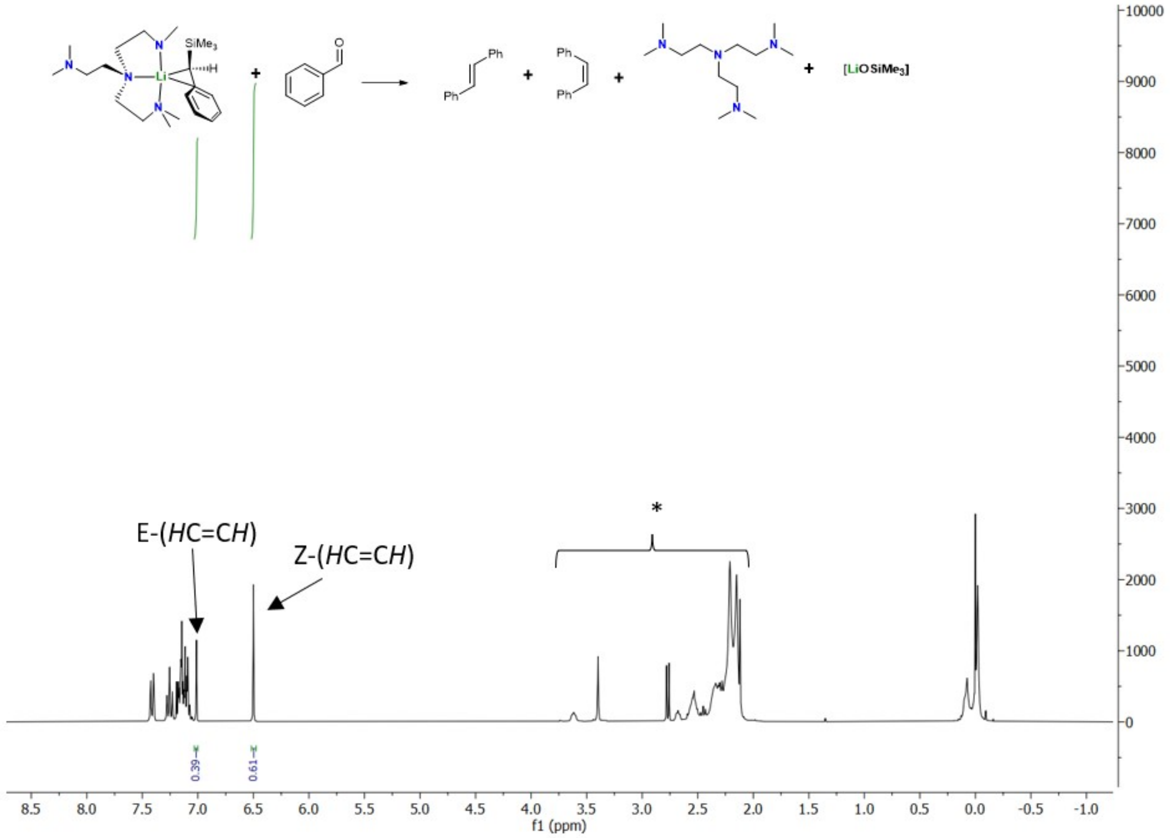

Figure S14. ^{1}H NMR (CDCl$_3$, 25 ˚C, 300 MHz) for the products from a reaction between **2**-Li and benzaldehyde (**3b**) carried out in benzene. *Unidentified signals. For details, see NOTE on page S11. The signals within the 0-0.5 ppm region are likely to be the LiOSiMe$_3$ species eliminated from the reaction.

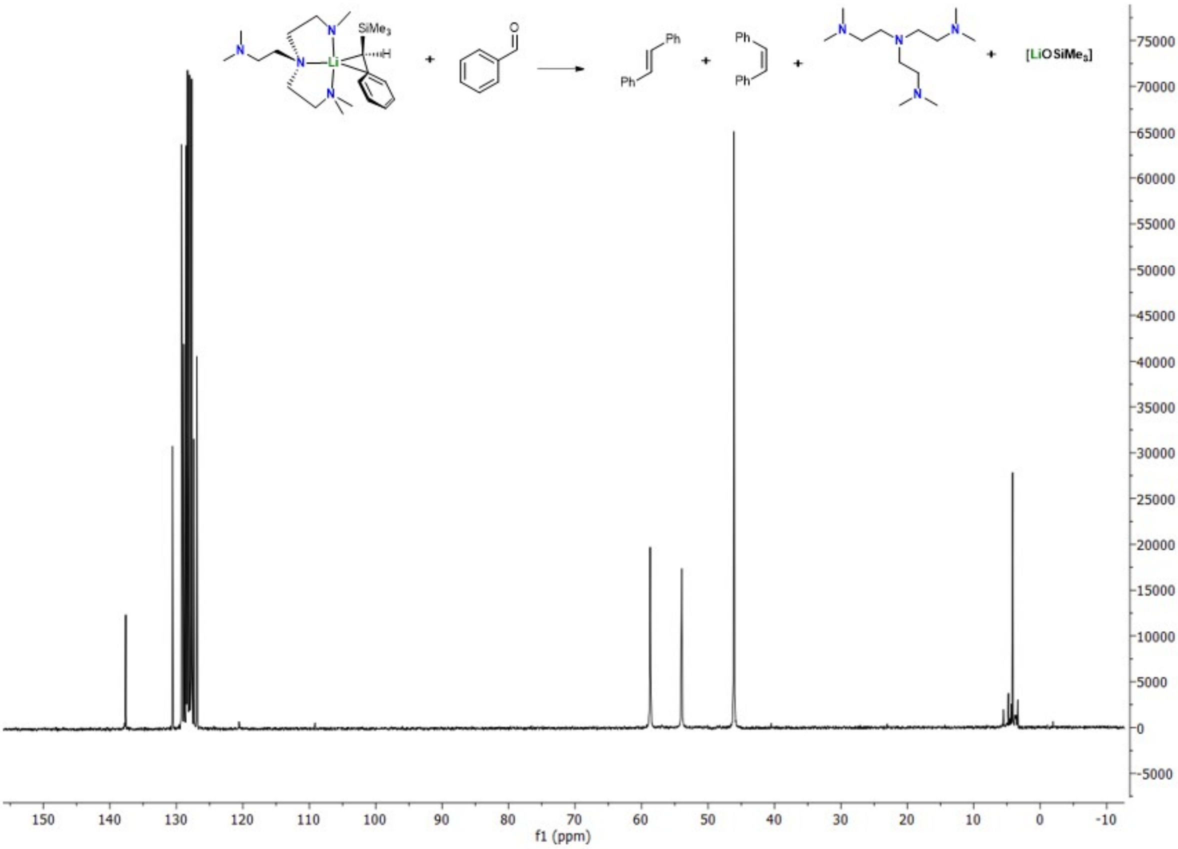

Figure S15. ^{13}C{^{1}H} NMR (75 MHz, d$_6$-benzene, 25 °C) for an NMR scale reaction between **2**-Li and benzaldehyde (**3b**).

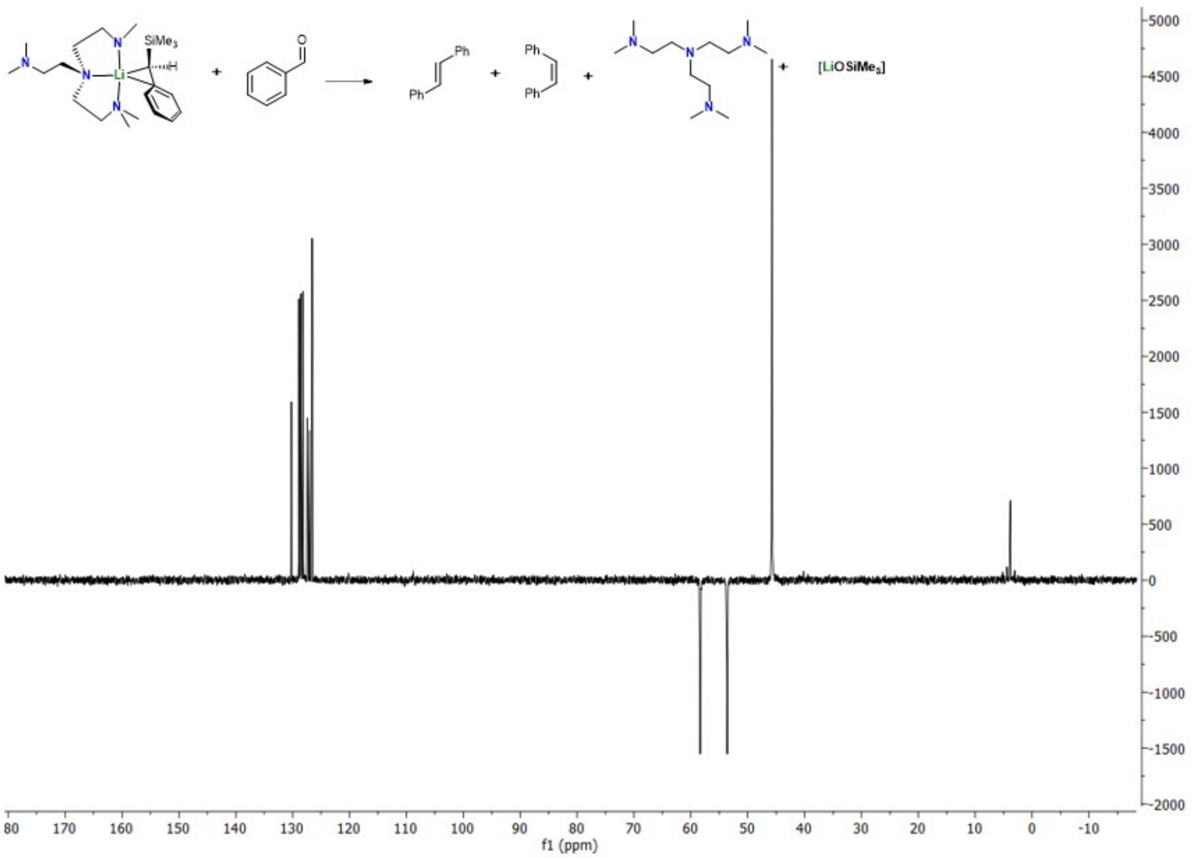

Figure S16. ^{13}C DEPT 135 NMR (d_6-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and benzaldehyde (**3b**).

Reaction between 2-Li and 2-Adamantanone (3c), to produce 2-benzylideneadamantane (4c)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to 2-adamantanone (0.0045 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^1H after 30 minutes, which showed >95% conversion to the alkene.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.4775g, 0.03 mmol) was added to **2**-Li (0.0120 g, 0.03 mmol). The solution was added to 2-Adamantanone (**3c**) (0.0045g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and was monitored by ^1H after 30 minutes, which showed a >95% conversion to the alkene.

Data for 2-benzylideneadamantane (**4c**):

^1H NMR (300 MHz, d_6-benzene, 25 °C): δ (ppm) 7.29 – 7.17 (m, 4H, Ar*H*), 7.09 – 7.03 (m, 1H, Ar*H*), 6.26 (s, 1H, *H*C=Ad), 3.26 (s, 1H, Ad*H*), 2.43 – 2.38 (m, 1H, Ad*H*, overlapping signals), 1.87 – 1.41 (m , 12H, Ad*H*).

$^{13}C\{^1H\}$ NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 151.1 (quaternary carbon), 138.7 (quaternary carbon), 129.1 (Ar*C*H), 128.4 (Ar*C*H), 120.1 (Ar*C*H), 117.9 (=*C*H), 41.2 (Ad*C*H) 40.1 (AdCH_2), 39.9 (AdCH_2), 37.3 (AdCH_2), 32.6 (Ad*C*H), 28.7 (Ad*C*H).

NMR data are consistent with literature.[5]

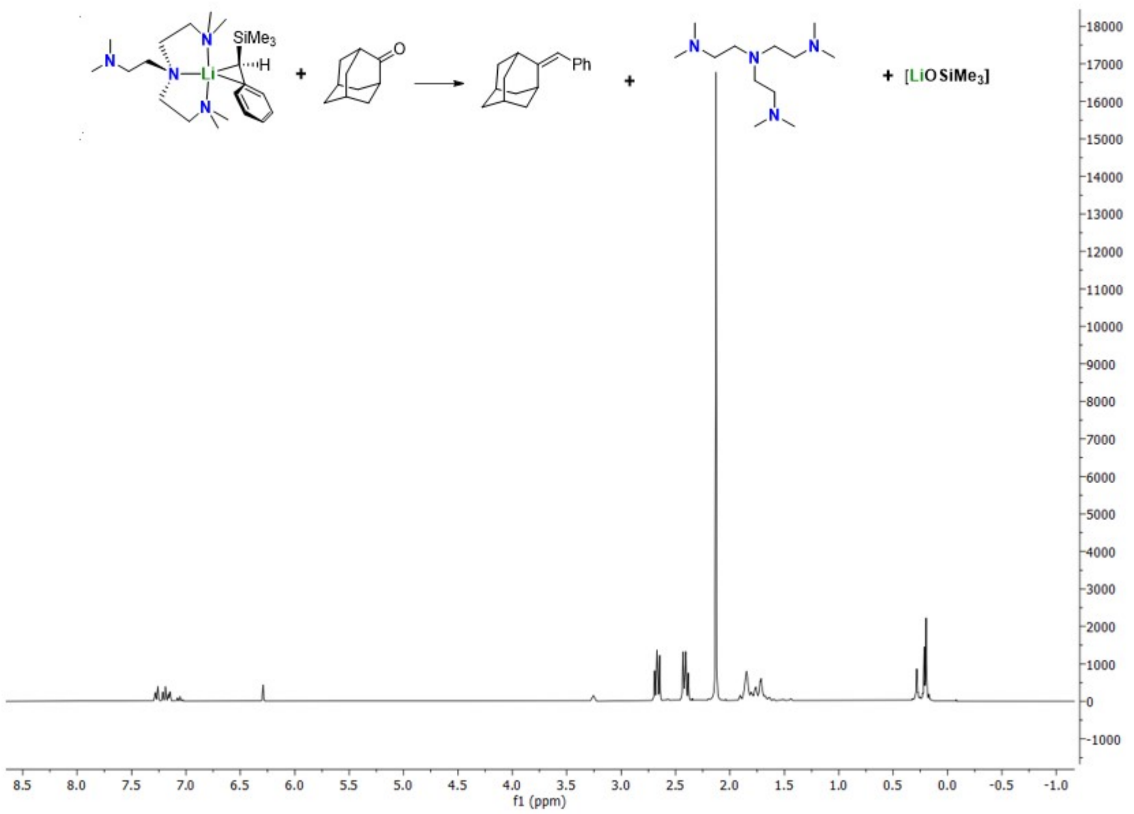

Figure S17. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and 2-adamantanone (**3c**).

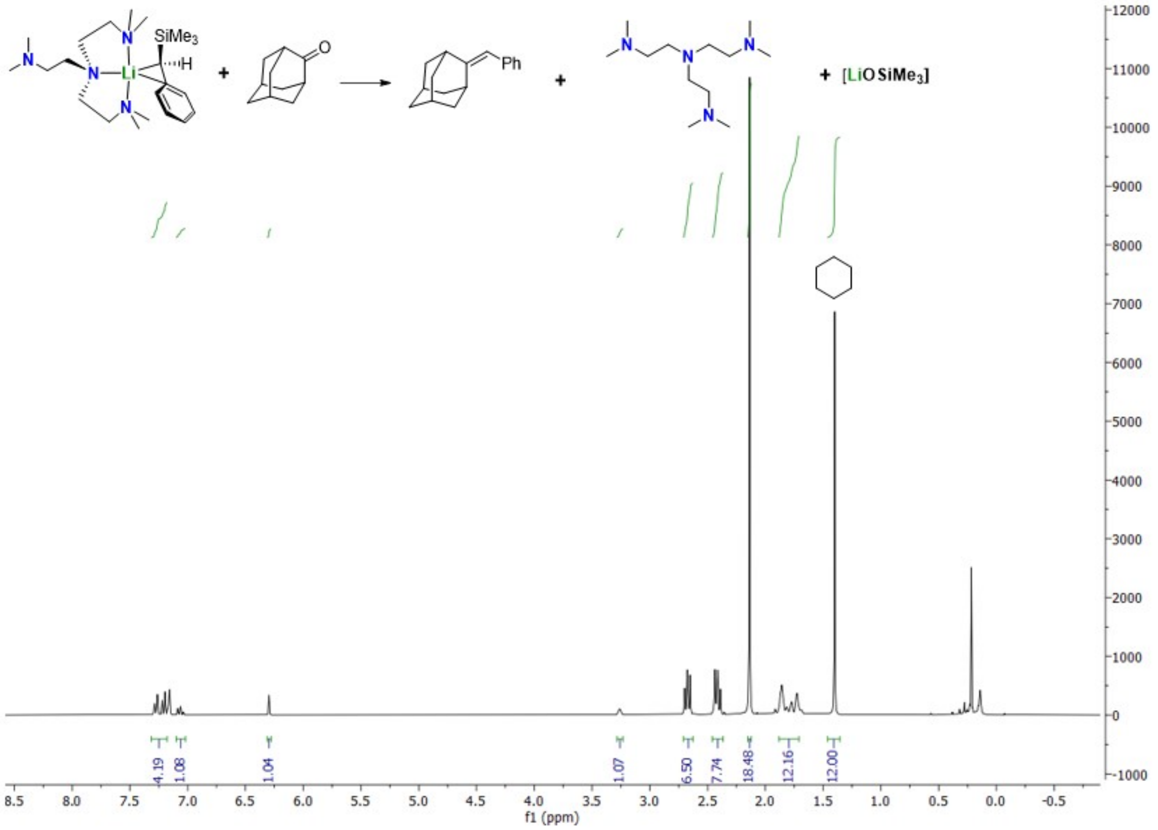

Figure S18. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and 2-adamantanone (**3c**). Internal Standard (**I**) = Cyclohexane. [I] = 0.06M

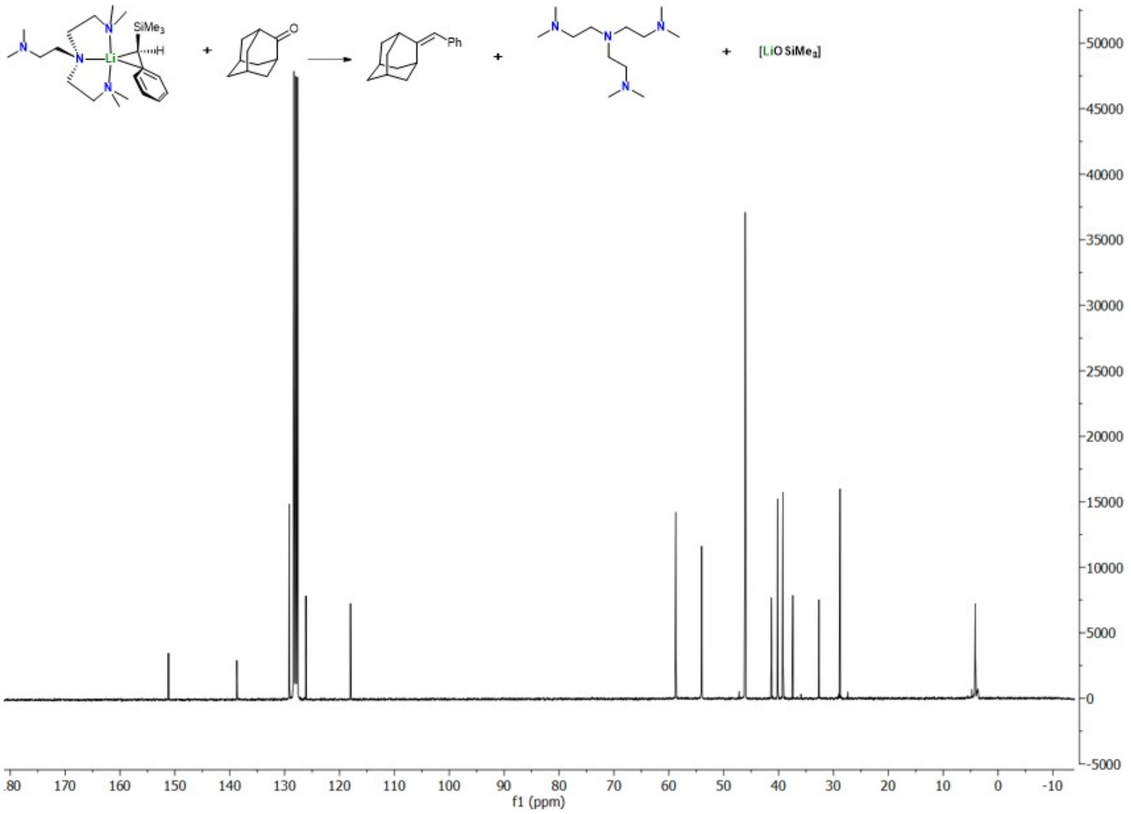

Figure S19. ^{13}C{^{1}H} NMR (75 MHz, d$_6$-benzene, 25 °C) for an NMR scale reaction between **2**-Li and 2-Adamantanone (**3c**).

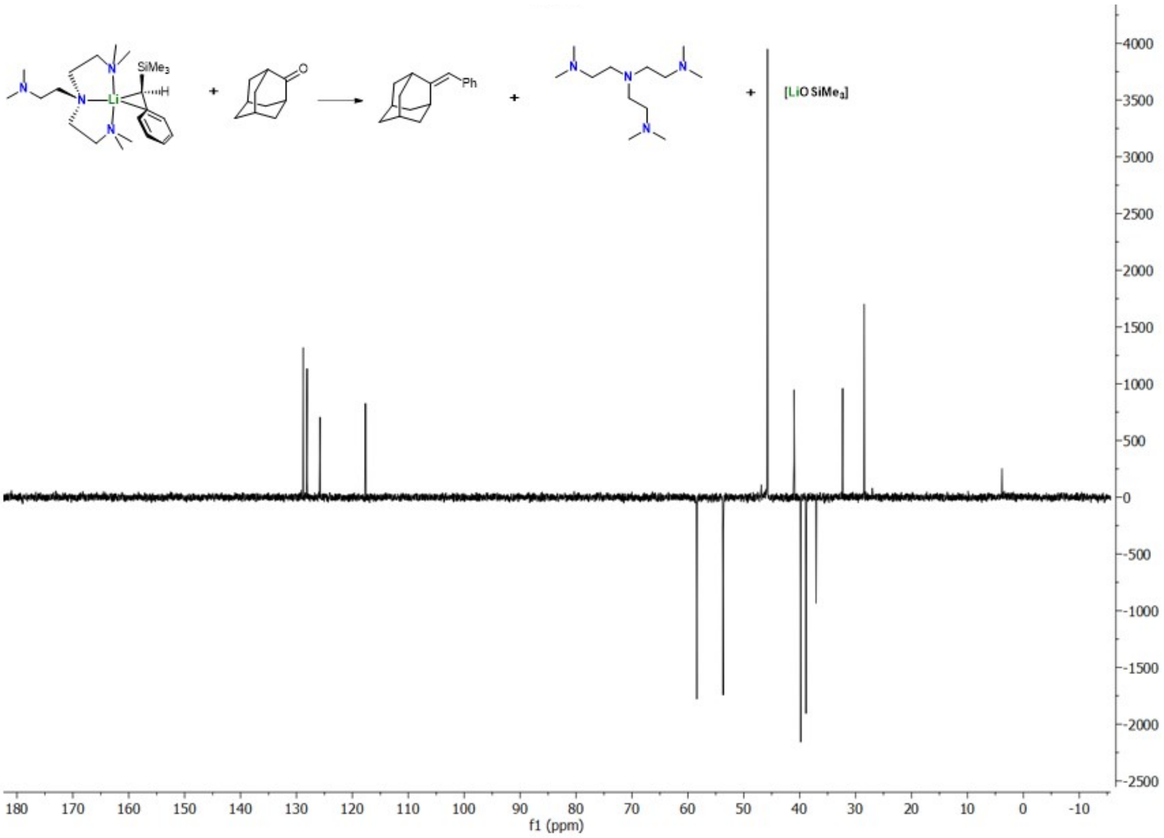

Figure S20. ^{13}C DEPT 135 NMR (d$_6$-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and 2-Adamantanone (**3c**).

Reaction between 2-Li and 2,2,2-trimethylacetophenone (3d), to produce E/Z (3,3-dimethylbut-1-ene-1,2-diyl)dibenzene (4d)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to 2,2,2-trimethylacetophenone (0.0049 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 30 minutes and 24 hours, which showed >95% conversion to both E/Z alkenes at a 2:3 ratio.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.4775g, 0.03 mmol) was added to **2**-Li (0.0120 g, 0.03 mmol). The solution was added to 2,2,2-trimethylacetophenone (**3d**) (0.0049g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and was monitored by ^{1}H after 30 minutes, which showed a >95% conversion to E/Z-**4d**.

Data for E/Z (3,3-dimethylbut-1-ene-1,2-diyl)dibenzene (**4d**):

^{1}H NMR (300 MHz, d$_6$-benzene, 25 °C): δ (ppm) 7.23 – 7.01 (m, 8H, ArC*H*), 6.97 – 6.85 (m, 2H, ArC*H*), 6.62 (s, 0.4H, ((E)=C*H*), 6.52 (s, 0.6H, ((Z)=C*H*), 1.13 (s, 3.6H, ((E)(($C\mathit{H}_3$))$_3$), 1.04 (s, 5.4H, ((Z)(($C\mathit{H}_3$))$_3$).

^{13}C{1H} NMR (75 MHz, d$_6$-benzene, 25 °C): δ (ppm) 152.6 (quaternary carbon), 151.9 (quaternary carbon), 146.1 (quaternary carbon) 140.8 (quaternary carbon), 140.6 (quaternary carbon), 138.0 (quaternary carbon), 130. 3 (Ar*C*H), 130.2 (Ar*C*H), 129.5 (Ar*C*H), 129.1 (Ar*C*H), 129.0 (Ar*C*H), 126.8 (=*C*H), 126.4 (Ar*C*H), 126.3 (Ar*C*H), 124.7 (=*C*H), 36.9 (quaternary carbon), 36.7 (quaternary carbon), 32.0 (($\mathit{C}H_3$)$_3$), 29.9 (($\mathit{C}H_3$)$_3$).

NMR data are consistent with literature[6].

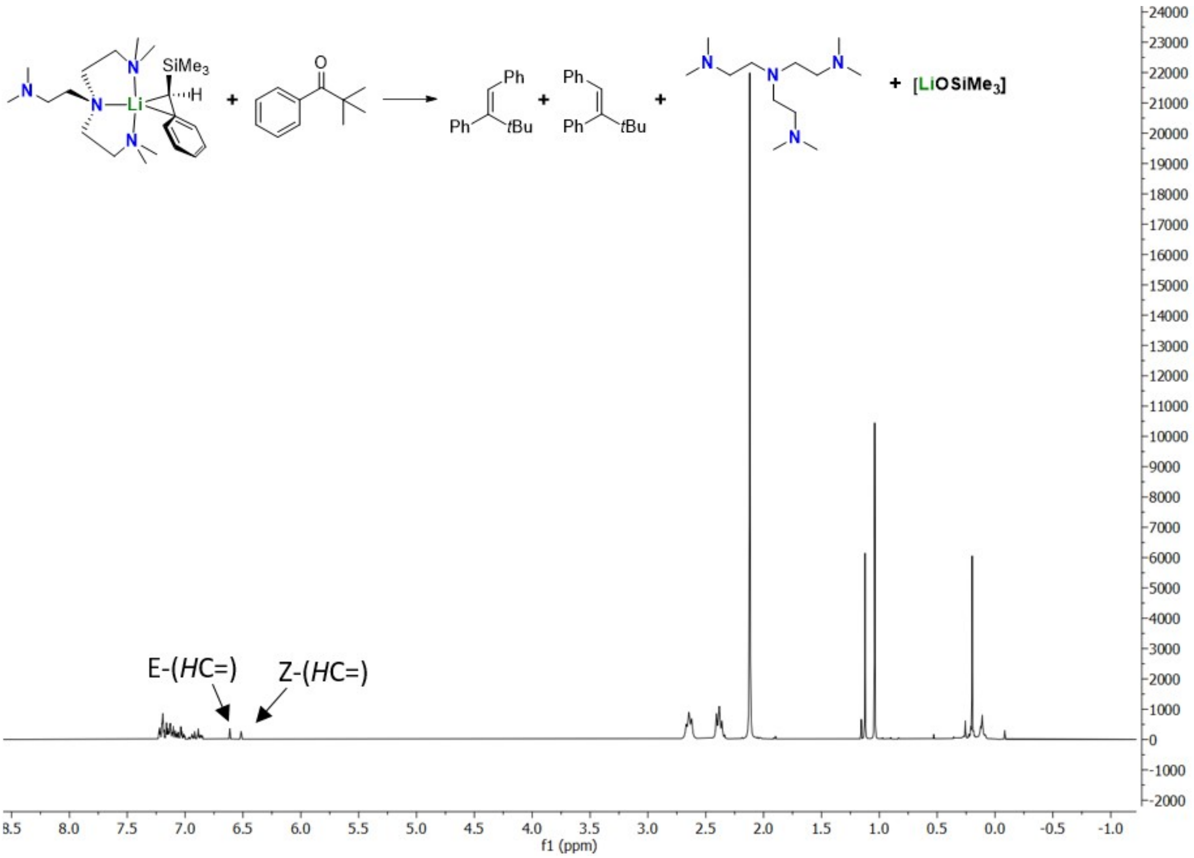

Figure S21. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and 2,2,2-trimethyl acetophenone (**3d**).

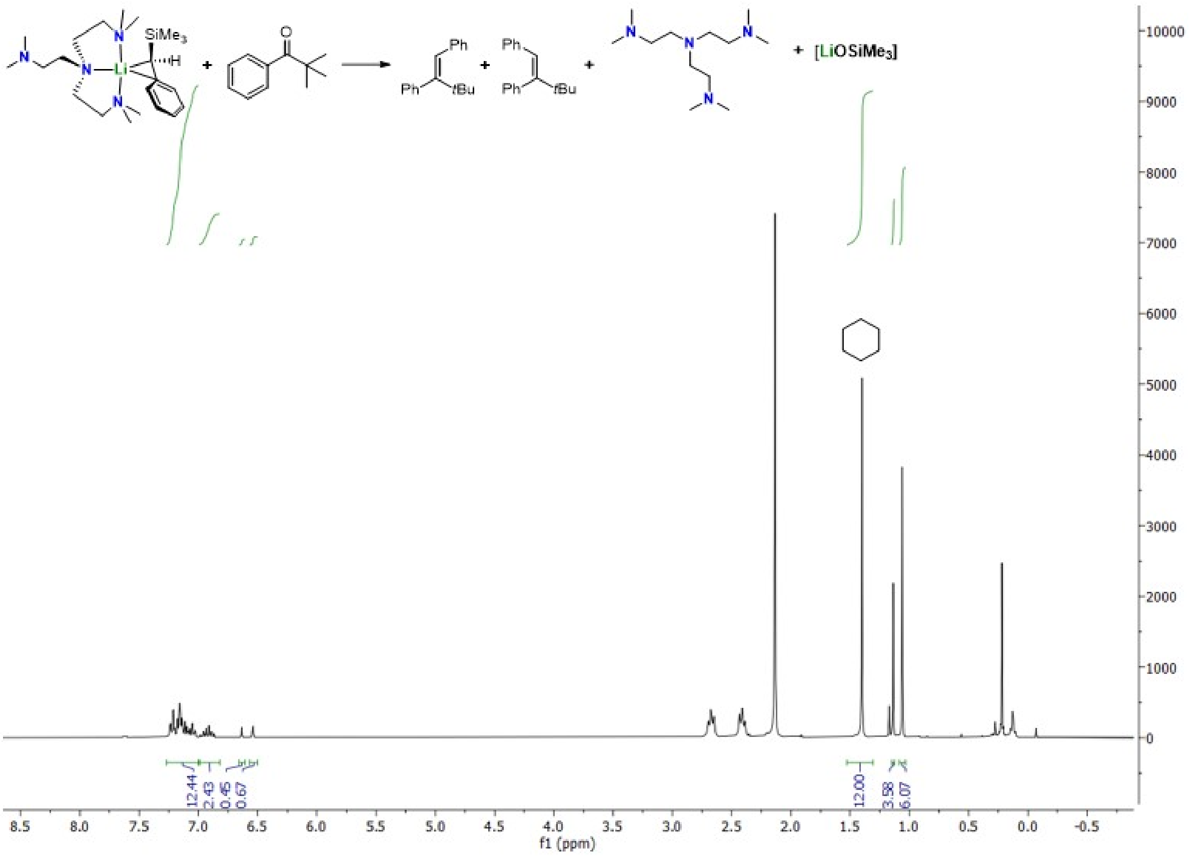

Figure S22. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and 2,2,2-trimethylacetophenone (**3d**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

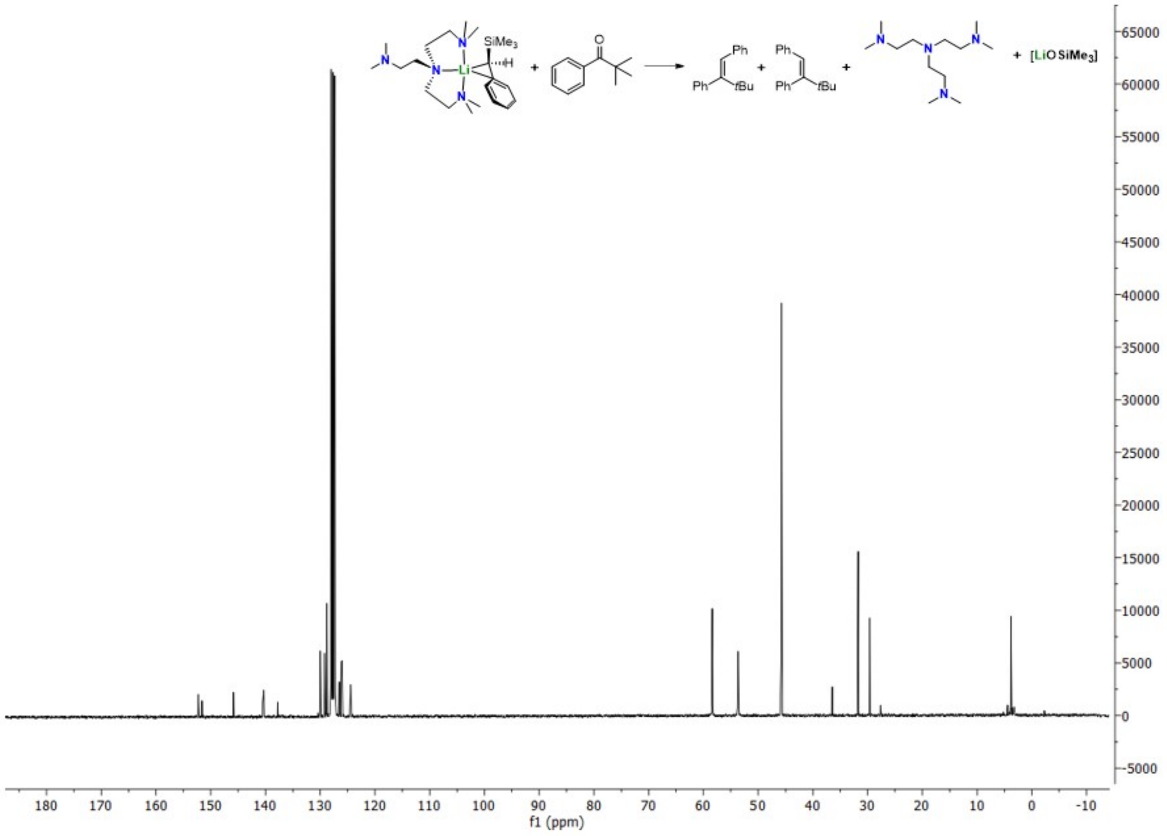

Figure S23. $^{13}C\{^1H\}$ NMR (75 MHz, d_6-benzene, 25 °C) for an NMR scale reaction between **2**-Li and 2,2,2-trimethyl acetophenone (**3d**).

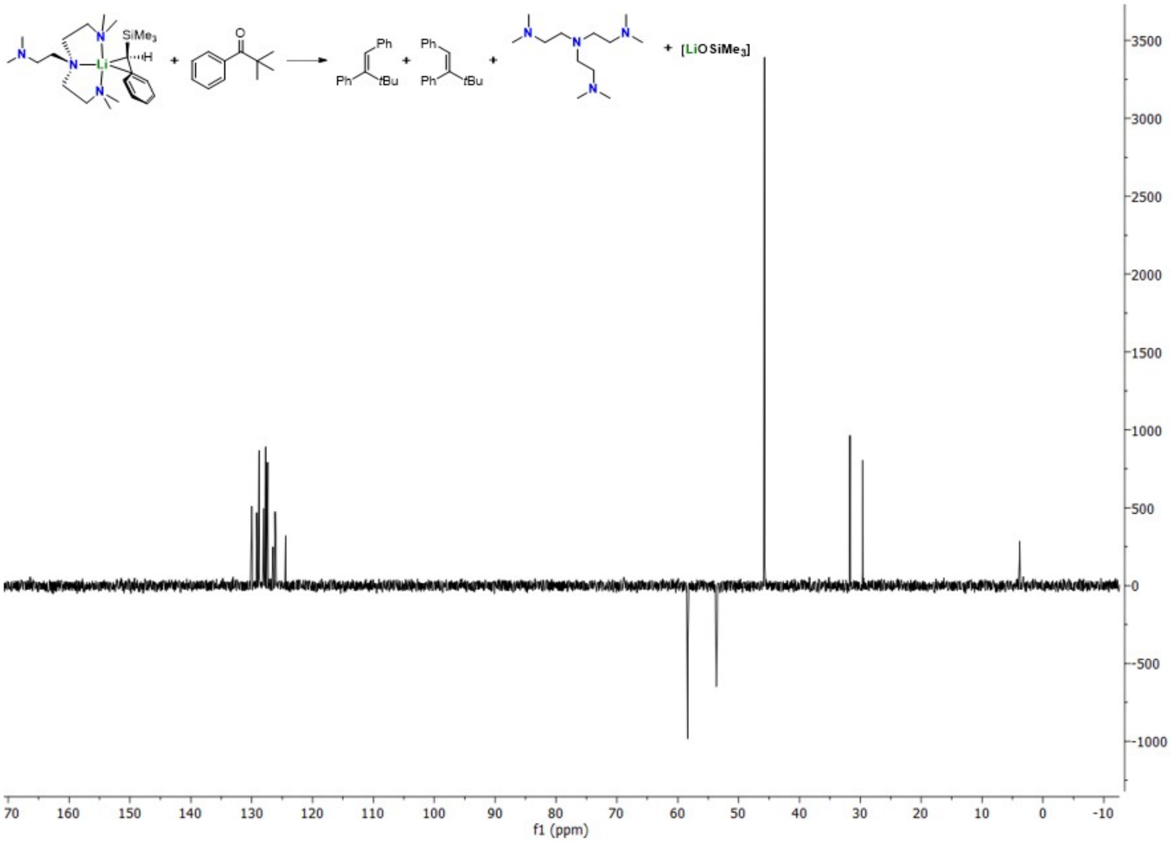

Figure S24. ^{13}C DEPT 135 NMR (d_6-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and 2,2,2-trimethyl acetophenone (**3d**).

Reaction between 1-Li and Michler's Ketone (3e), to produce 4,4'-(2-phenylethene-1,1-diyl)bis(N,N-dimethylaniline) (4e).

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to Michler's ketone (0.0080 g, 0.03 mmol). The resulting brown solution was transferred to a J. Young NMR tube and monitored by ^1H NMR after 30 minutes and 20 hours, which showed >95% conversion to the alkene.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Li (0.0120 g, 0.03 mmol). The solution was added to Michler's Ketone (**3e**) (0.0080g, 0.03 mmol). The resulting brown solution was transferred to a J. Young NMR tube and was monitored by ^1H after 20 hours, which showed a >95% conversion to the alkene.

Data for 4,4'-(2-phenylethene-1,1-diyl)bis(N,N-dimethylaniline) (**4e**).

^1H NMR (300 MHz, d6-benzene, 25 °C): δ (ppm) 7.54 – 7.51 (d, 2H, ArC*H*), 7.38-7.32 (m, 4H, ArC*H*), 7.06 – 7.00 (m, 3H, ArC*H*), 6.90 – 6.89 (s, 1H, =C*H*), 6.60 – 6.51 (m, 4H, ArC*H*) 2.5 (s, 6H, N(CH_3)$_2$), 2.46 (s, 6H, N(CH_3)$_2$).

$^{13}C\{1H\}$ NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 150.3 (quaternary carbon), 149.9 (quaternary carbon), 143.7 (quaternary carbon), 139.4 (quaternary carbon), 133.2 (quaternary carbon), 131.9

(Ar*C*H), 129.8 (Ar*C*H), 129.3 (Ar*C*H), 129.1 (quaternary carbon), 128.2 (=*C*H), 125.9 (Ar*C*H), 124.2 (Ar*C*H), 112.6 (Ar*C*H) 112.4 (Ar*C*H) 40.1 (N(CH_3)$_2$), 39.9 (N(CH_3)$_2$).

NMR data are consistent with literature[7].

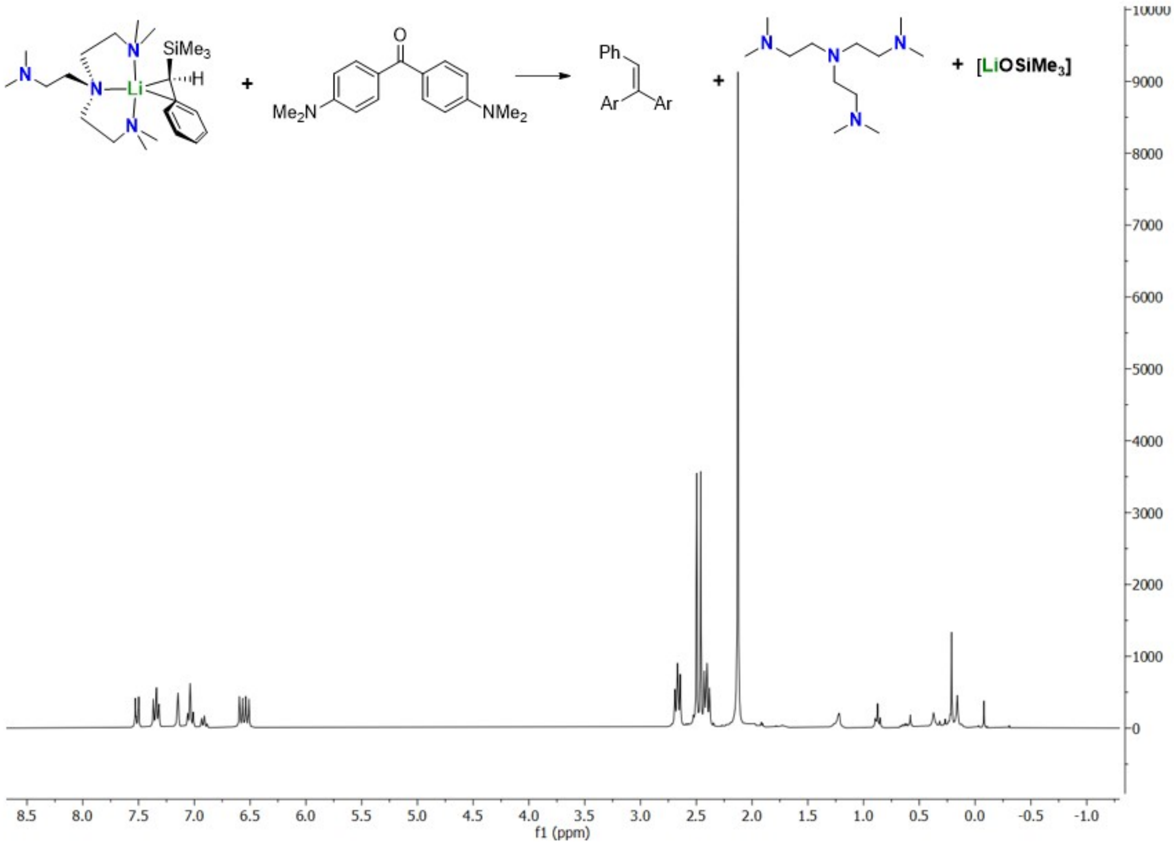

Figure S25. ^{1}H NMR (d$_6$-benzene, 25 ˚ C, 300 MHz) for an NMR scale reaction between **2**-Li and Michler's ketone (**3e**). The signals within the 0-0.5 ppm region are likely to be the LiOSiMe3 species eliminated from the reaction.

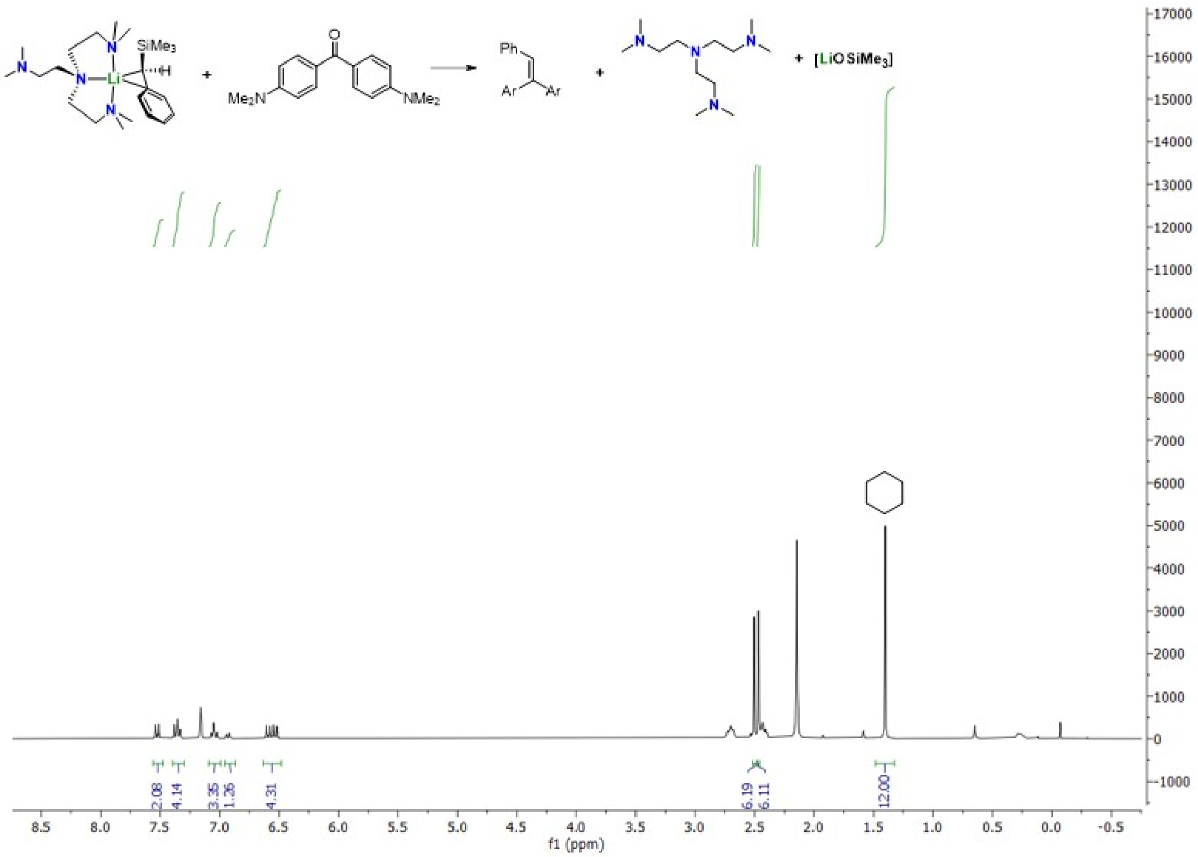

Figure S26. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and Michler's ketone (**3e**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

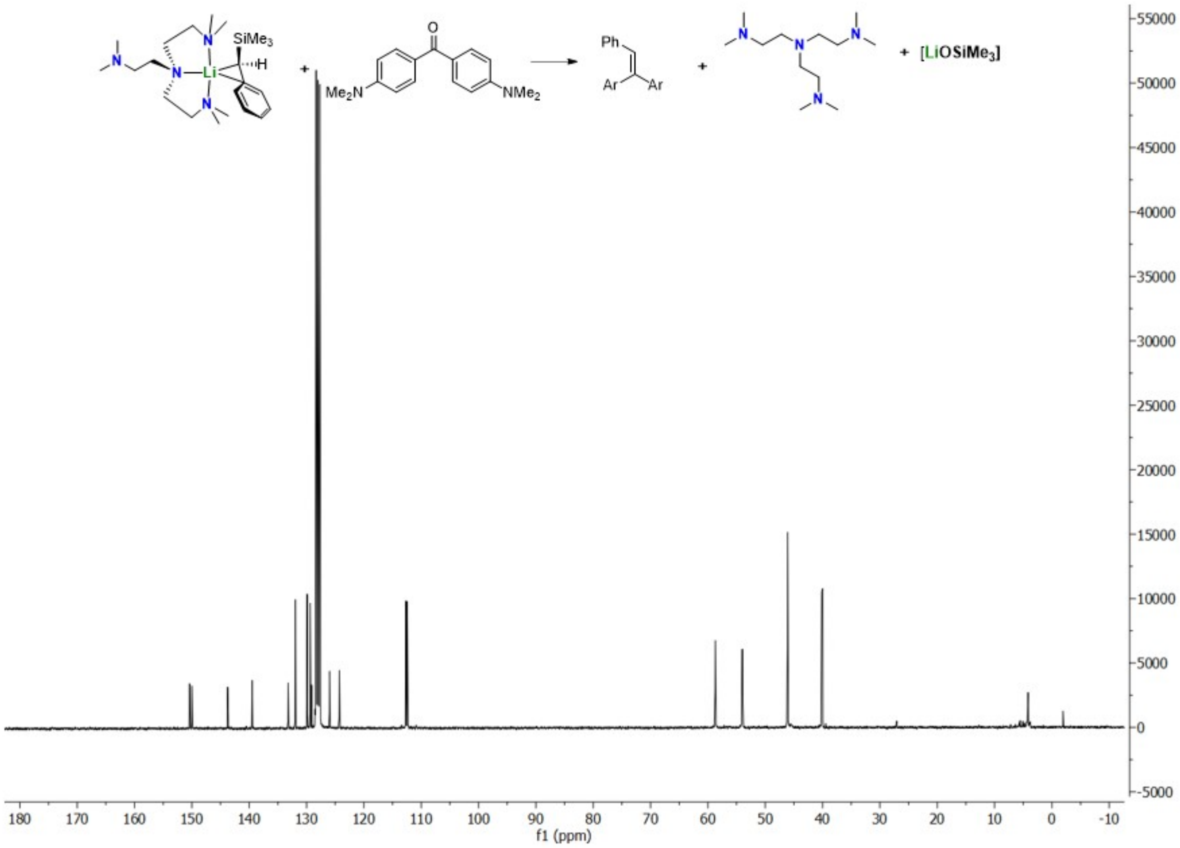

Figure S27. $^{13}C\{^1H\}$ NMR (75 MHz, d$_6$-benzene, 25 °C) for an NMR scale reaction between **2**-Li and Michler's Ketone (**3e**).

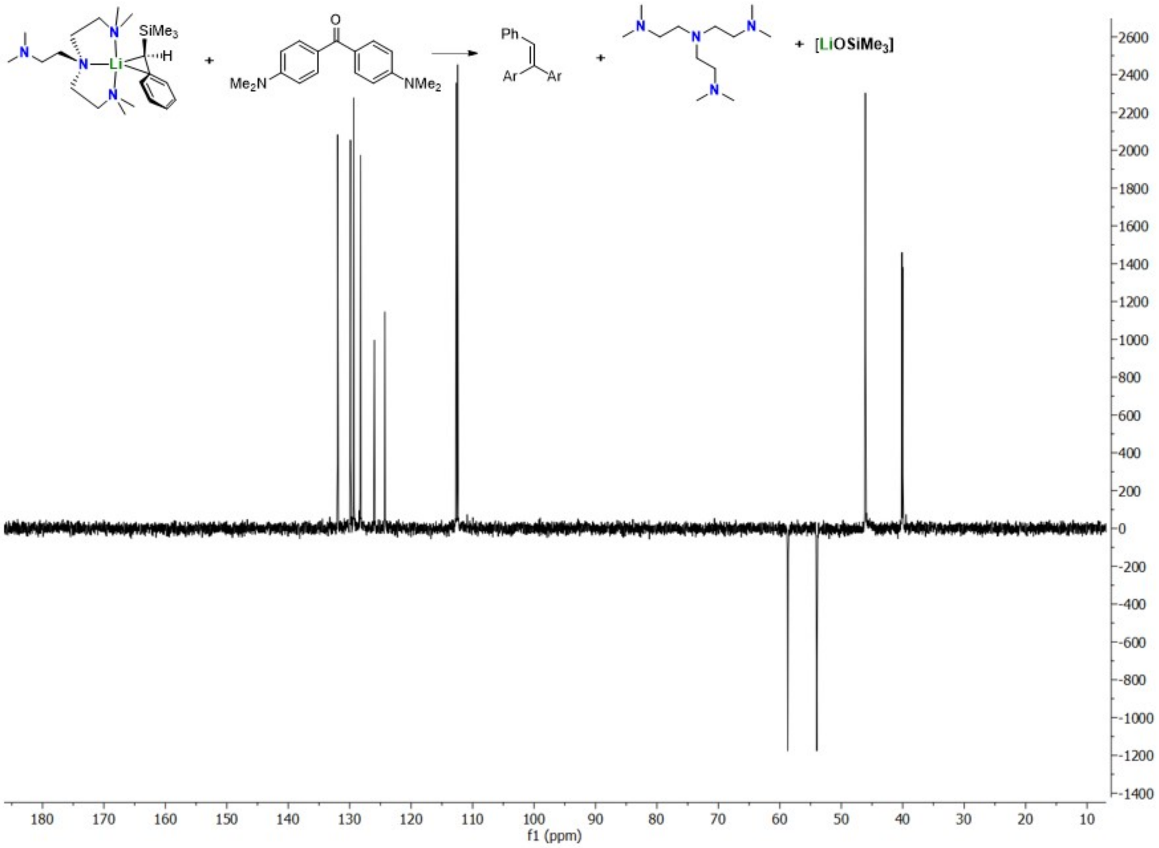

Figure S28. ^{13}C DEPT 135 NMR (d$_6$-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and Michler's Ketone (**3e**).

Reaction between 2-Li decafluorobenzophenone (3f)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to decafluorobenzophenone (0.0108 g, 0.03 mmol). The resulting black solution was transferred to a J. Young NMR tube and monitored by ^1H and ^{19}F NMR after 30 minutes, which turned out to be an intractable mixture and coordination-free Me$_6$Tren.

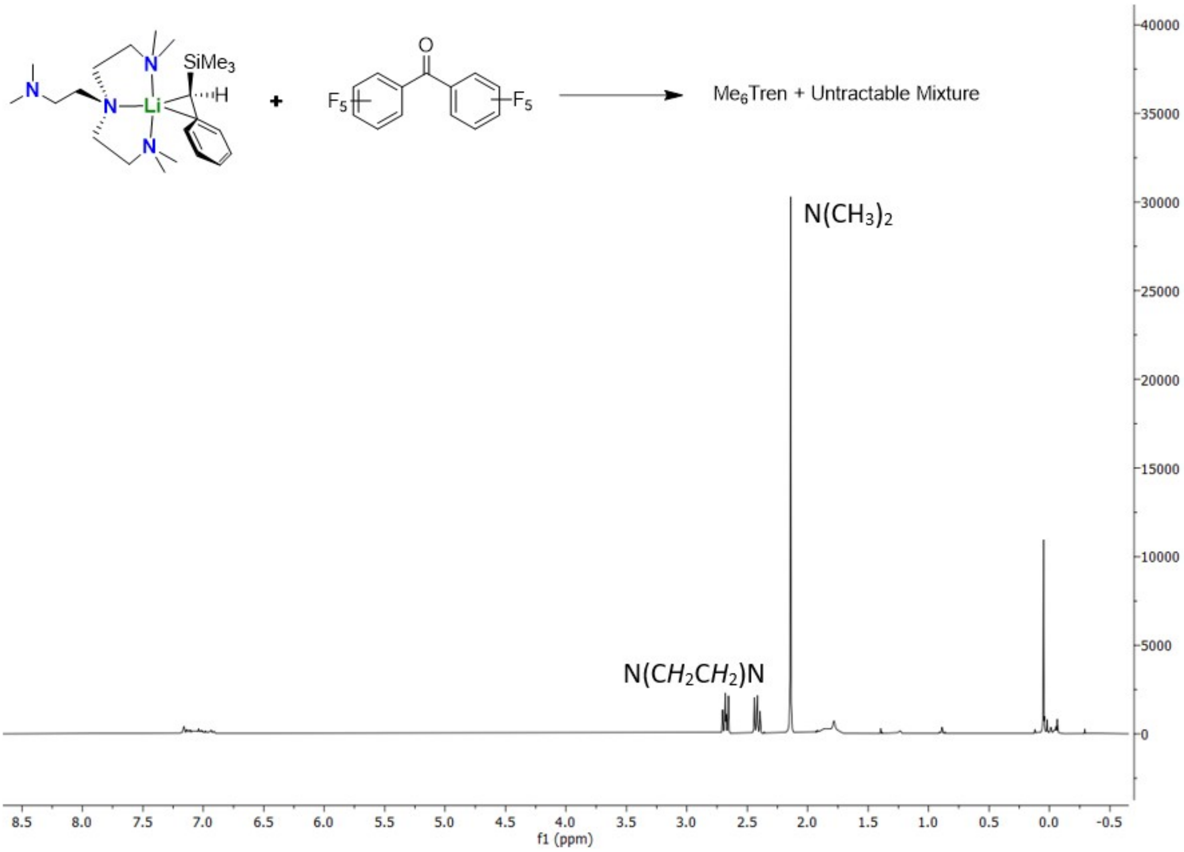

Figure S29. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and decafluorobenzophenone (**3f**).

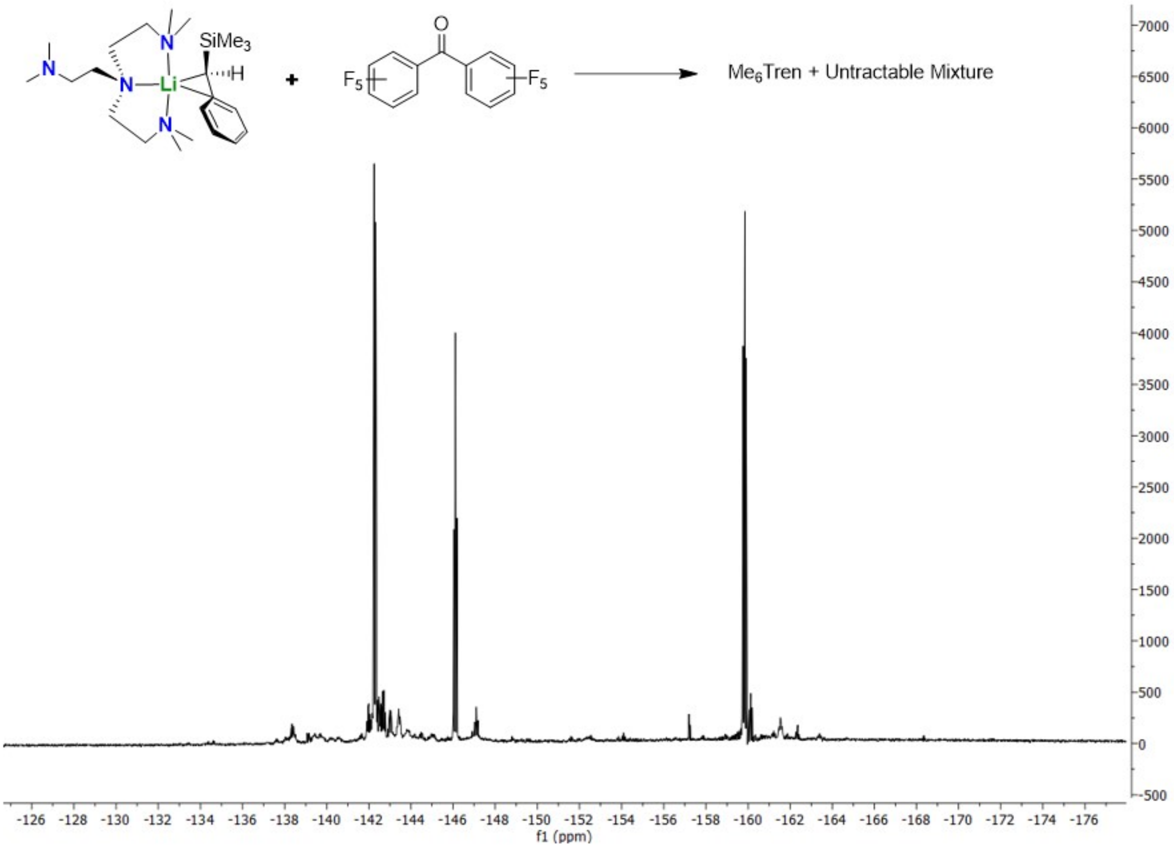

Figure S30. ^{19}F NMR (d_6-benzene, 25 ˚C, 282 MHz) for an NMR scale reaction between **2**-Li and decafluorobenzophenone (**3f**).

Reaction between 2-Li and 1-benzoylpiperidine (3g) to produce 1-(1,2-diphenylvinyl)piperidine (4g)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to 1-benzoylpiperidine (0.0056 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 30 minutes. The solution was then dried in vacuo and the solids were dissolved in *d*$_8$-THF, which showed >95% conversion to the both E/Z alkenes at a 3:2 ratio.

Data for 1-(1,2-diphenylvinyl)piperidine (**4g**):

^{1}H NMR (300 MHz, d_6-benzene, 25 °C): δ (ppm) 7.51 – 7.47 (m, 1H, Ar*H*), 7.35 – 7.32 (m, 1H, Ar*H*), 7.20 – 7.08 (m, 3H, Ar*H*), 7.02 – 6.76 (m, 5H, Ar*H*), 5.73 (s, 0.4H, (Z)-*H*C=C), 5.62 (s, 0.6H, (E)-*H*C=C), 2.65 – 2.63 (m, 4H, C*H*$_2$), 1.32 – 1.22 (m, 6H, C*H*$_2$).

^{13}C{^{1}H} NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 152.1 (HC=*C*), 151.0 (HC=*C*), 141.9 (quaternary carbon), 139.7 (quaternary carbon), 139.6 (quaternary carbon), 138.5 (quaternary carbon), 130.4 (Ar*C*), 128.8 (Ar*C*), 128.6 (Ar*C*), 128.3 (Ar*C*), 128.0 (Ar*C*), 127.9 (Ar*C*), 127.8 (Ar*C*), 127.7 (Ar*C*), 127.5 (Ar*C*), 125.0 (Ar*C*), 124.0 (Ar*C*), 110.2 (H*C*=C), 106.0 (H*C*=C), 51.7 (*C*H$_2$), 49.9 (*C*H$_2$), 26.5 (*C*H$_2$), 26.0 (*C*H$_2$), 24.4 (*C*H$_2$), 24.3 (*C*H$_2$).

^{1}H NMR (300 MHz, d_8-THF, 25 °C): 7.51 – 7.47 (m, 1H, Ar*H*), 7.34 – 7.15 (m, 6H, Ar*H*), 6.92 – 6.69 (m, 4H, Ar*H*), 5.63 (s, 1H, *H*C=C), 5.60 (s, 1H, *H*C=C), 2.86 – 2.77 (m, 4H, C*H*$_2$), 1.60 – 1.52 (m, 6H, C*H*$_2$).

^{13}C{^{1}H} NMR (75 MHz, d_8-THF, 25 °C): δ (ppm) 152.1 (HC=*C*), 151.1 (HC=*C*), 141.0 (quaternary carbon), 139.6 (quaternary carbon), 139.7 (quaternary carbon), 138.5 (quaternary carbon), 131.1 (Ar*C*), 129.4 (Ar*C*), 129.4 (Ar*C*), 129.2 (Ar*C*), 129.1 (Ar*C*), 129.0 (Ar*C*), 128.8 (Ar*C*), 128.7 (Ar*C*), 128.6 (Ar*C*), 128.2 (Ar*C*), 128.1 (Ar*C*), 110.8 (H*C*=C), 106.5 (H*C*=C), 52.6 (*C*H$_2$), 50.9 (*C*H$_2$), 27.5 (*C*H$_2$), 27.0 (*C*H$_2$), 25.4 (*C*H$_2$), 25.3 (*C*H$_2$).

NMR data are consistent with literature[8, 9]

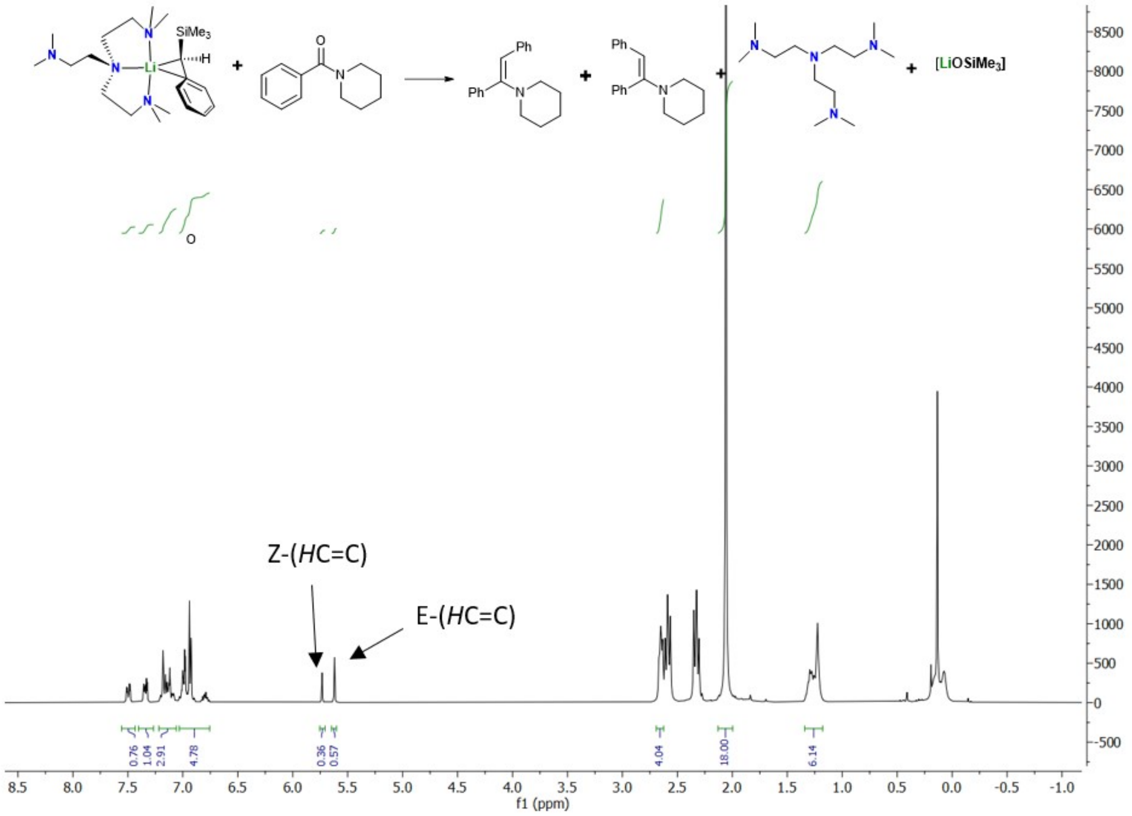

Figure S31. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and 1-benzoylpiperidine (**3g**).

Figure S32. ^{1}H NMR (d_8-THF, 25 ˚C, 300 MHz) of the products from an NMR scale reaction between **2**-Li and 1-benzoylpiperidine (**3g**) carried out in C_6D_6.

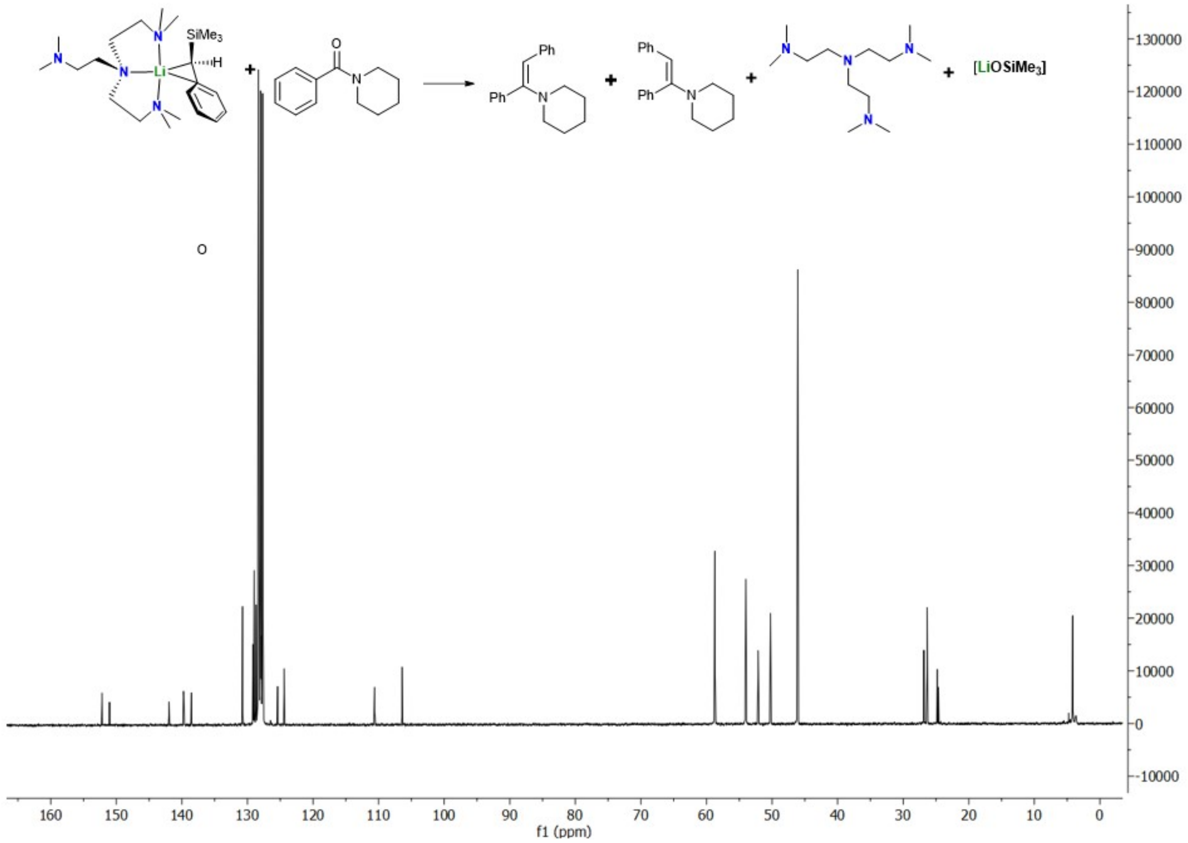

Figure S33. $^{13}C\{^1H\}$ NMR (d_6-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and 1-benzolypiperidine (**3g**).

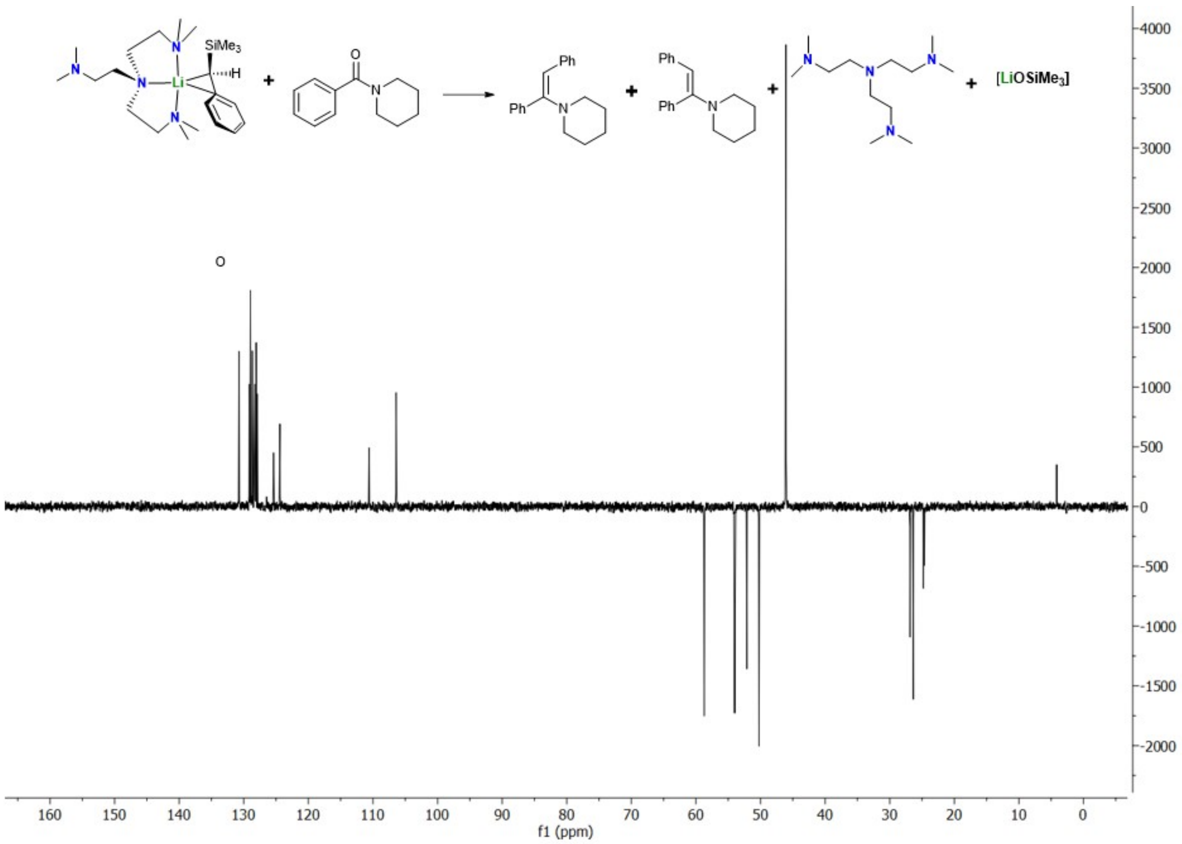

Figure S34. ^{13}C DEPT 135 NMR (d_6-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and 1-benzolypiperidine (**3g**).

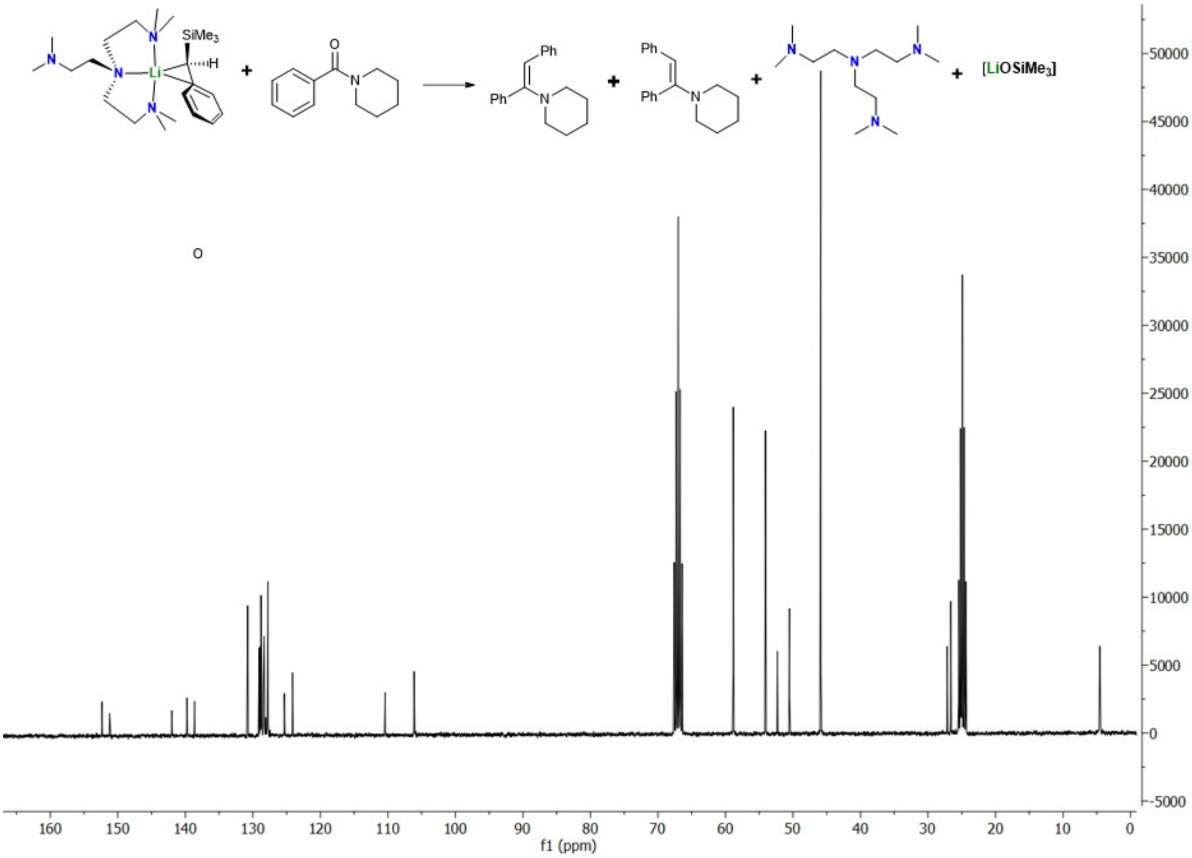

Figure S35. $^{13}C\{^{1}H\}$ NMR (d_8-THF, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and 1-benzolypiperidine (**3g**).

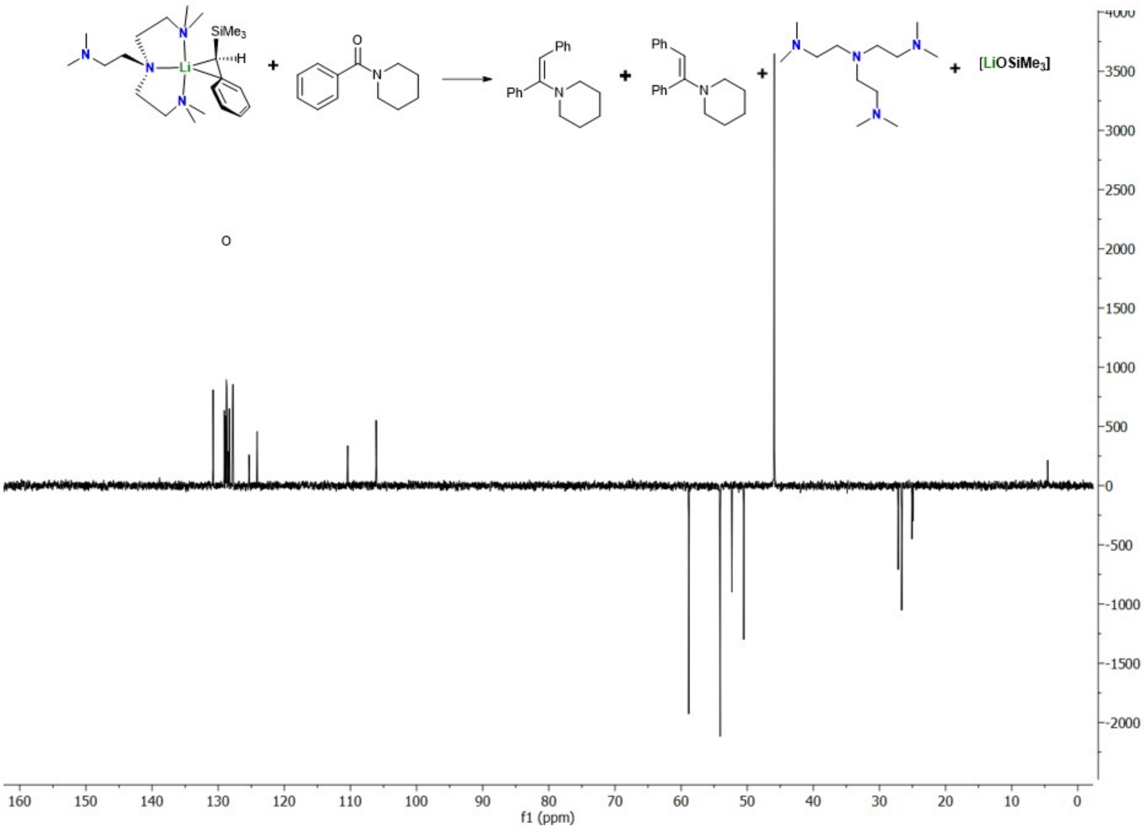

Figure S36. ^{13}C DEPT 135 NMR (d_8-THF, 25 ˚C, 75 MHz) for an NMR scale reaction between **2**-Li and 1-benzolypiperidine (**3g**).

Reaction between 2-Li and 2,2,2-trifluoroacetophenone (3h) to produce E/Z 1,2-Diphenyl-3,3,3-trifluoroprop-1-ene (4h)

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Li (0.0120 g, 0.03 mmol). The solution was added to 2,2,2-trifluoroacetophenone (**3h**) (0.0052g, 0.03 mmol). The colourless solution was transferred to a J. Young NMR tube and was heated to 60°C for 2 hours. The resulting brown solution was then monitored by ^{1}H after, which showed a >90% conversion to both E/Z alkenes. E/Z ratio determined as 1:2 from ^{19}F NMR integrals.

Resolution of E/Z ratio: Reaction was repeated at 0.03 mmol, then dried in vacuo. The resulting solid was dissolved in $CDCl_3$ and the E/Z ratio was determined using ^{1}H NMR

Data for E/Z 1,2-Diphenyl-3,3,3-trifluoroprop-1-ene (**4h**):

^{1}H NMR (300 MHz, d6-benzene, 25 °C): δ (ppm) 7.30 – 7.24 (m, 3H, Ar*H*), 7.12 – 6.91 (m, 6H, Ar*H, H*C=, overlapping signals), 6.81 – 6.76 (m, 2H, Ar*H, H*C=, overlapping signals).

^{19}F NMR (282 MHz, d6-benzene, 25 ˚C): δ (ppm) -65.50 (s, 1F, E – HC=), -55.99 (s, 2F, Z – HC=).

$^{19}F\{^{1}H\}$ NMR (282 MHz, d6-benzene, 25 ˚C): δ (ppm) -65.50 (s, 1F, E – HC=), -55.99 (s, 2F, Z – HC=).

NMR data are consistent with literature[10, 11]

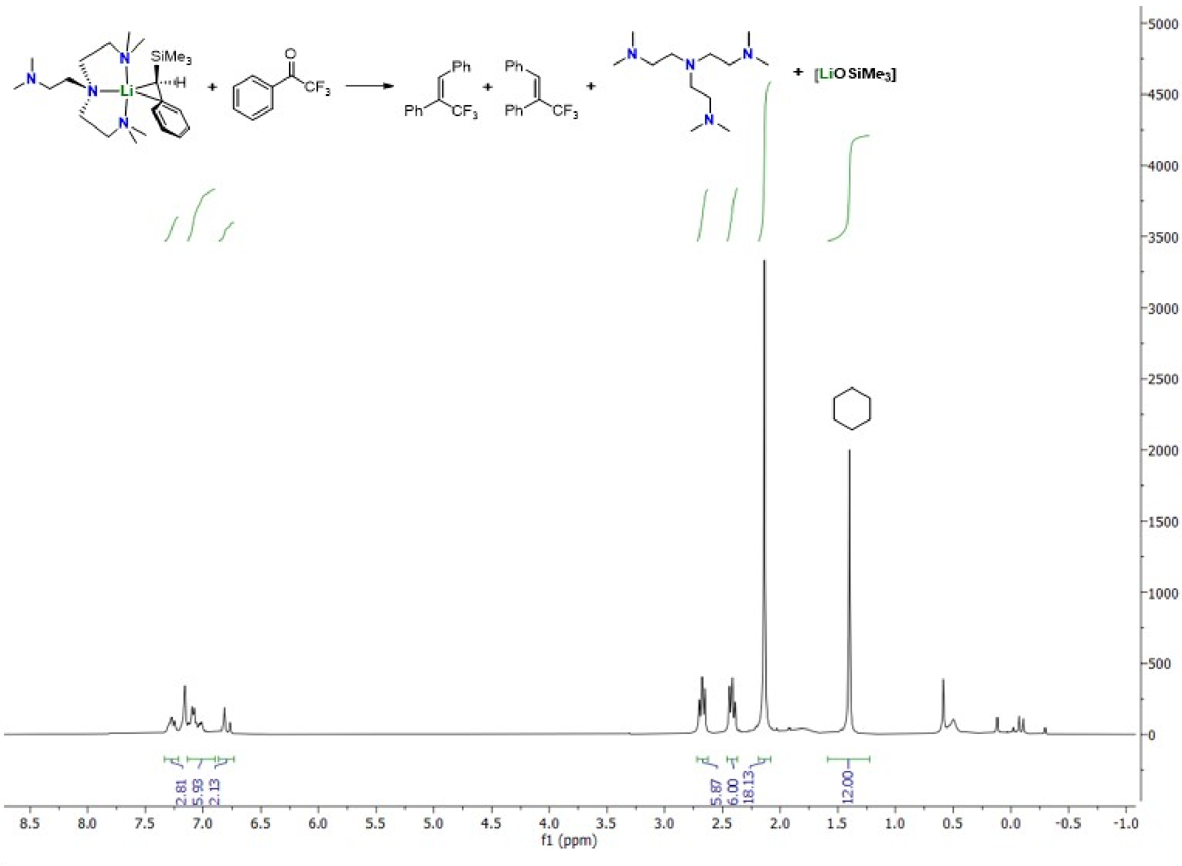

Figure S37. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and 2,2,2-trifluoroacetophenone (**3h**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

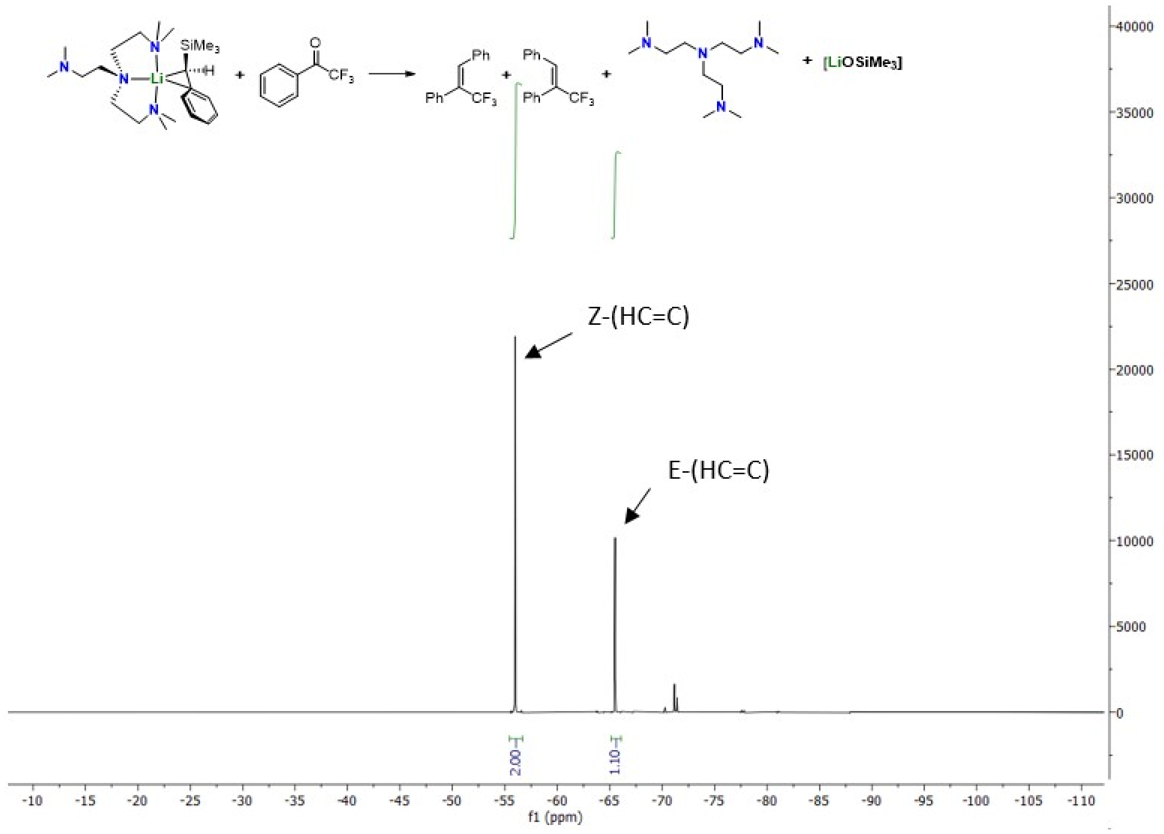

Figure S38. ^{19}F NMR (d_6-benzene, 25 ˚C, 282 MHz) for an NMR scale reaction between **2**-Li and 2,2,2-trifluoroacetophenone (**3h**).

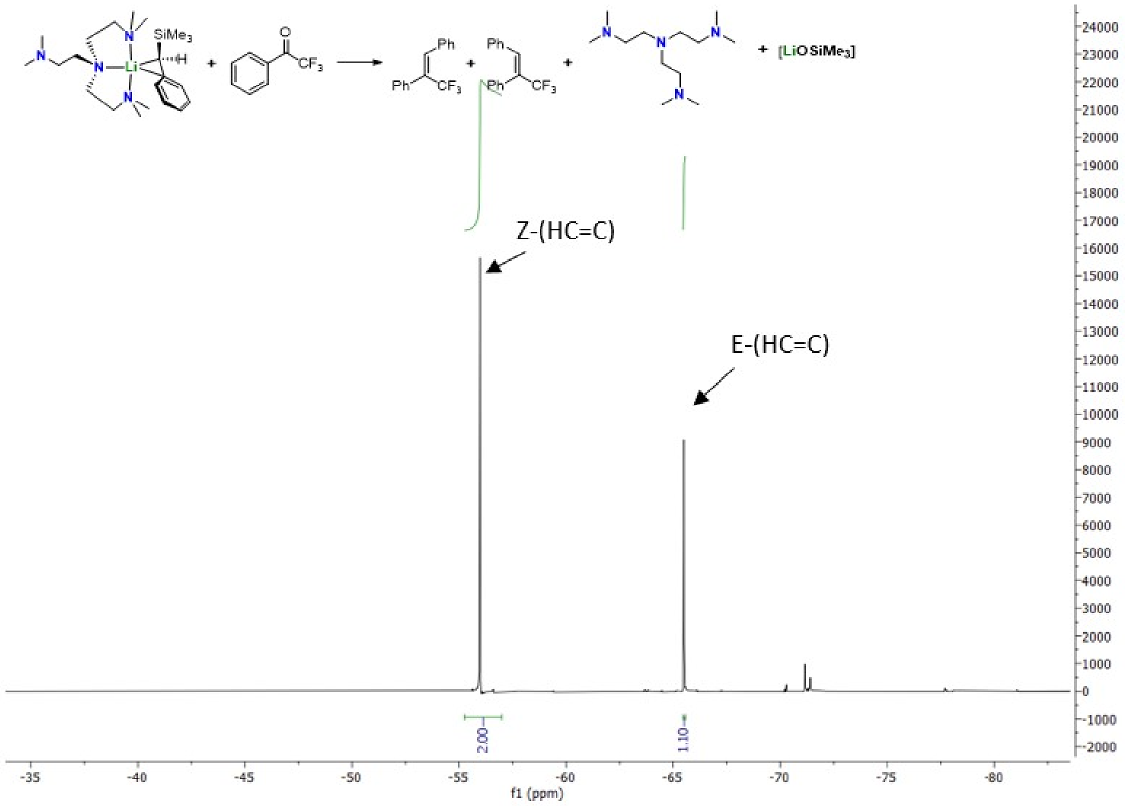

Figure S39. $^{19}F\{^1H\}$ NMR (d_6-benzene, 25 ˚C, 282 MHz) for an NMR scale reaction between **2**-Li and 2,2,2-trifluoroacetophenone (**3h**).

Reaction between 2-Li and phenylcyclohexylketone (3i) to produce 1-Cyclohexylethen-1,2-diyl)dibenzene (4i)

2-Li (0.0120 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to phenylcyclohexylketone (0.0056 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^1H NMR after 30 minutes, which showed >90% conversion to the both E/Z alkenes at a 2:3 ratio.

Resolution of E/Z-4i ratio: Reaction was repeated at 0.03 mmol, then dried in vacuo. The resulting solid was dissolved in $CDCl_3$ and the E/Z ratio was determined using ^1H NMR.

^1H NMR (300 MHz, d6-benzene, 25 °C): δ (ppm) 7.35 – 7.12 (m, 5H, Ar*H*), 7.11 – 6.84 (m, 5.4H, Ar*H* (E)*H*C=, overlapping signals), 6.43 (s, 0.6H, (Z)*H*C=), 1.84 – 1.51 (m, 6H, C*H*$_2$), 1.32 – 1.07 (m, 5H, C*H*$_2$).

^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.39 – 7.22 (m, 6H, Ar*H*), 7.11 – 7.00 (m, 3H, Ar*H*), 6.85 – 6.82 (m, 1H, Ar*H*), 6.37 (s, 0.6H, Z-*H*C=), 6.30 (s, 0.4H, E-*H*C=), 1.86 – 1.53 (m, 6H, C*H*$_2$), 1.35 – 1.10 (m, 6H, C*H*$_2$).

$^{13}C\{1H\}$ NMR (75 MHz, d_6-benzene, 25 °C): δ (ppm) 149.7 (quaternary carbon), 148.9 (quaternary carbon), 143.6 (quaternary carbon), 141.9 (quaternary carbon), 138.2 (quaternary carbon), 138.1 (quaternary carbon), 129.5 (Ar*C*H), 129.2 (Ar*C*H), 129.1 (Ar*C*H), 129.0 (Ar*C*H), 128.6 (Ar*C*H), 128.5 (Ar*C*H), 128.1 (Ar*C*H), 127.8 (Ar*C*H) 126.9 (Ar*C*H), 126.8 (Ar*C*H) 126.4 (=*C*H), 125.2 (=CH), 47.9 (*C*H), 40.8 (*C*H), 32.5 (*C*H$_2$), 32.4 (*C*H$_2$), 27.0 (*C*H$_2$),, 26.5 (*C*H$_2$), 26.1 (*C*H$_2$).

NMR data are consistent with literature.[12]

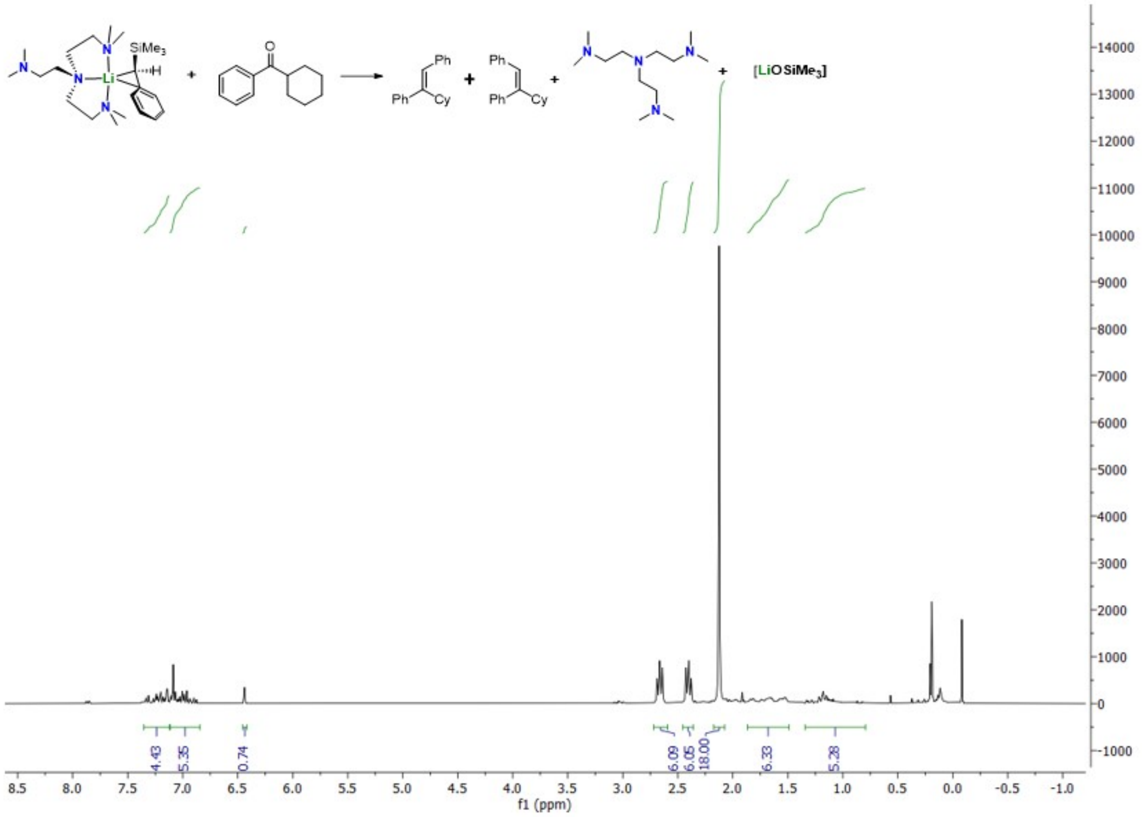

Figure S40. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Li and phenylcyclohexylketone (**3i**).

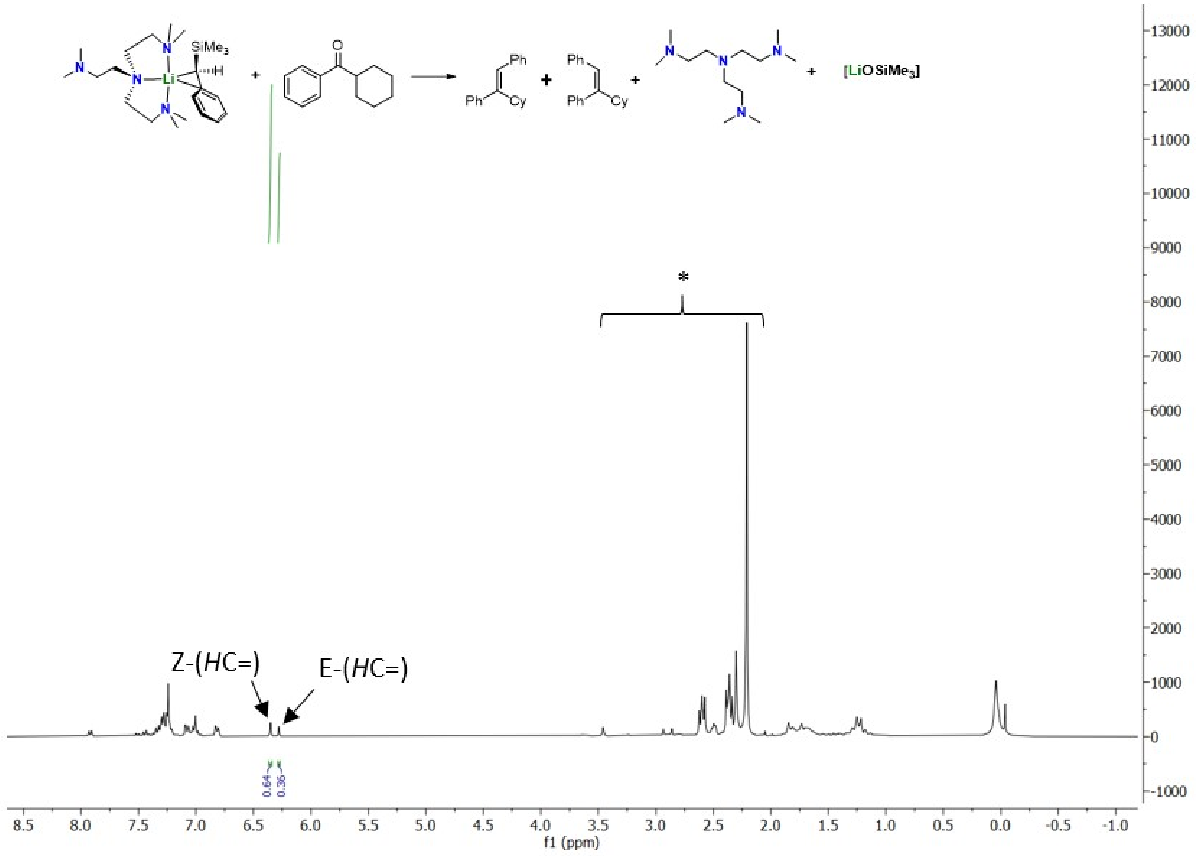

Figure S41. ^{1}H NMR (CDCl$_3$, 25 ˚C, 300 MHz) for the products from an NMR scale reaction between **2**-Li and phenylcyclohexylketone (**3i**) carried out in benzene. *Me$_6$Tren and unidentified products.

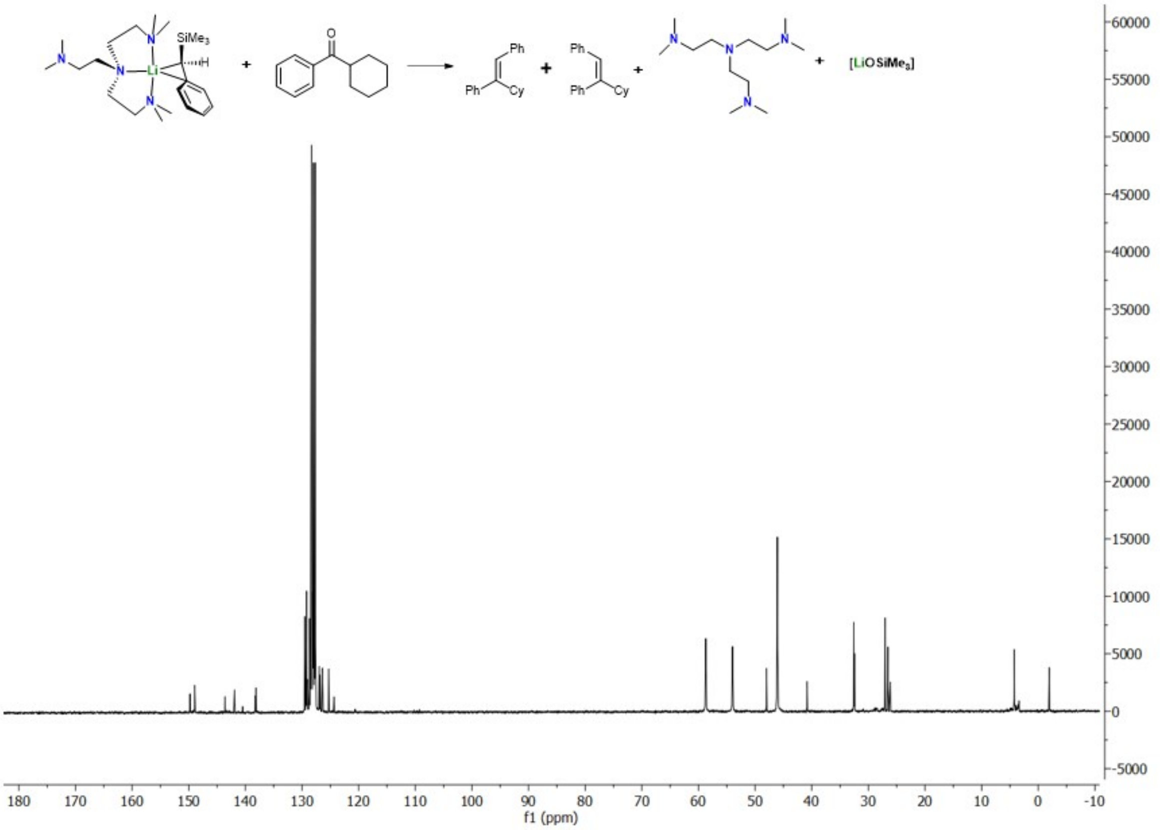

Figure S42. ^{13}C{^{1}H} NMR (75 MHz, d$_6$-benzene, 25 °C) for an NMR scale reaction between **2-Li** and cyclohexyl phenyl ketone (**3i**).

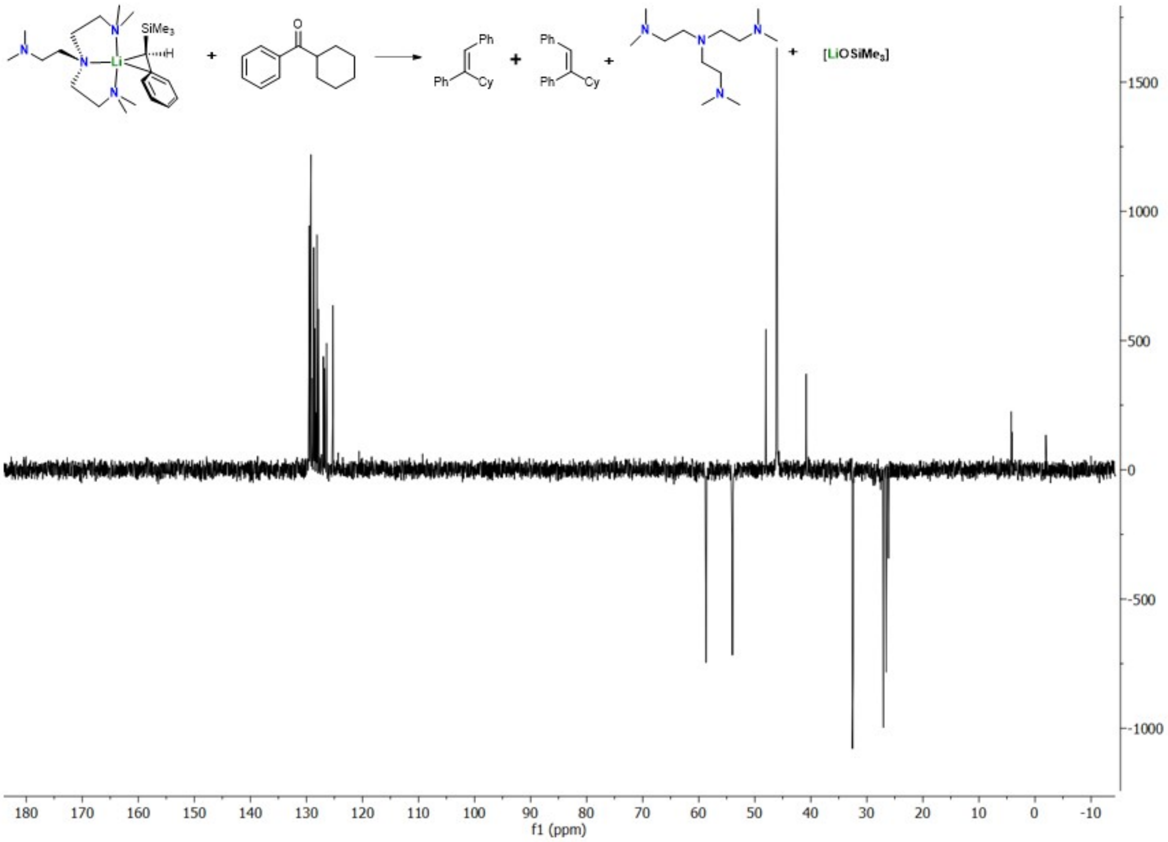

Figure S43. ^{13}C DEPT 135 NMR (d_6-benzene, 25 ˚C, 75 MHz) for an NMR scale reaction between **2-Li** and cyclohexyl phenyl ketone (**3i**).

1.5 Reactions between **2**-Na and organic carbonyl substrates

The reactions were carried out following the same protocols at the same concentrations with the **2**-Li-mediated reactions in Section 1.4.

Reaction between 2-Na and Benzophenone (3a), to produce triphenylethylene (4a)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was added to benzophenone (0.0055 g, 0.03 mmol). The resulting green solution was transferred to a J. Young NMR tube and heated to 60 ^{O}C for 2 hours. The resulting colourless solution was monitored by ^{1}H NMR which showed >95% conversion to the alkene.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Na (0.0125 g, 0.03 mmol). The solution was added to benzophenone (**3a**) (0.0055g, 0.03 mmol). The green solution was transferred to a J. Young NMR tube and heated to 60 ^{O}C for 2 hours. The resulting colourless solution was monitored by ^{1}H NMR.

NMR data of **4a** are consistent with literature[2].

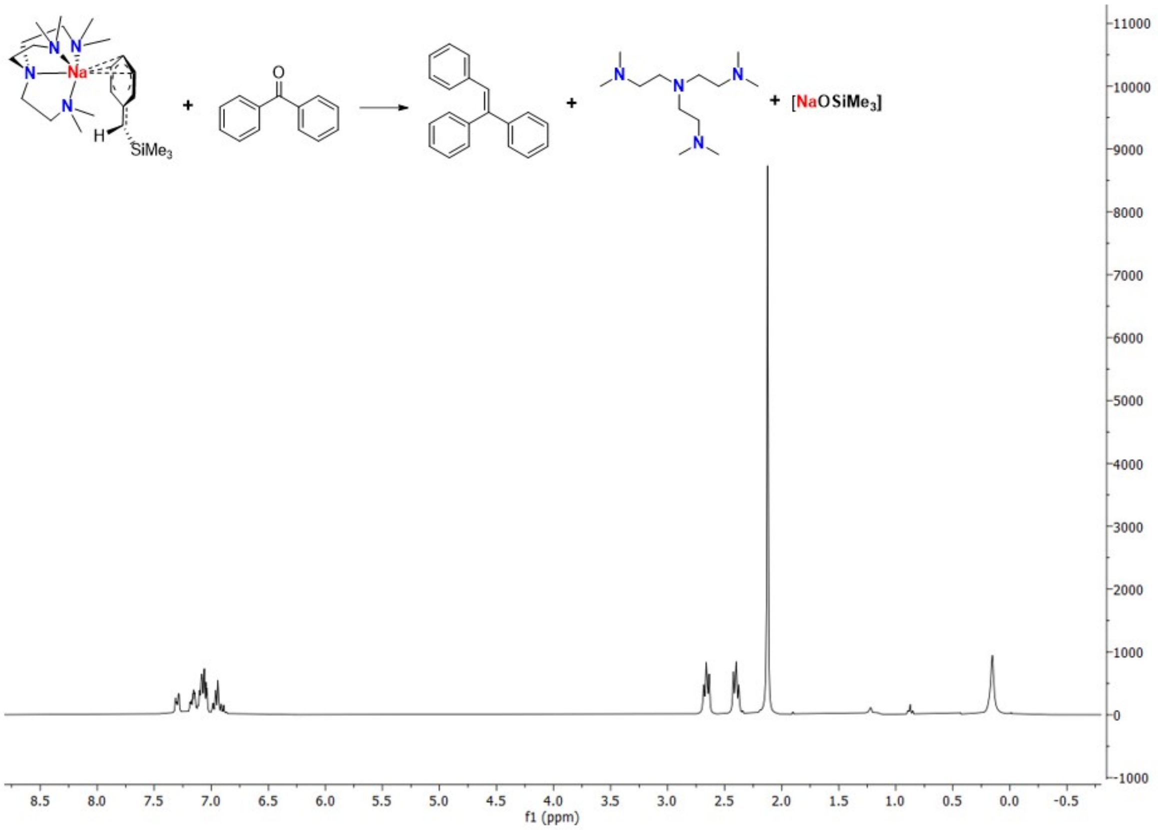

Figure S44. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and benzophenone (**3a**).

Figure S45. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and benzophenone (**3a**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

Reaction between 2-Na and benzaldehyde (3b), to produce a mixture of E/Z-stilbene (4b)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL).The solution was added to benzaldehyde (0.0031 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 30 minutes, which showed >95% conversion to both alkenes at a 1:1 ratio.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Na (0.0125 g, 0.03 mmol). The solution was added to benzaldehyde (**3b**) (0.0031g, 0.03 mmol). The resulting colourless was transferred to a J. Young NMR tube and was monitored by ^{1}H NMR after 30 mins.

Resolution of E/Z ratio: Reaction was repeated at 0.03 mmol, then dried in vacuo. The resulting solid was dissolved in $CDCl_3$, and the E/Z ratio was determined as 1:1 using ^{1}H NMR (**Figure S48**).

NMR data of **4b** was consistent with literature [3, 4].

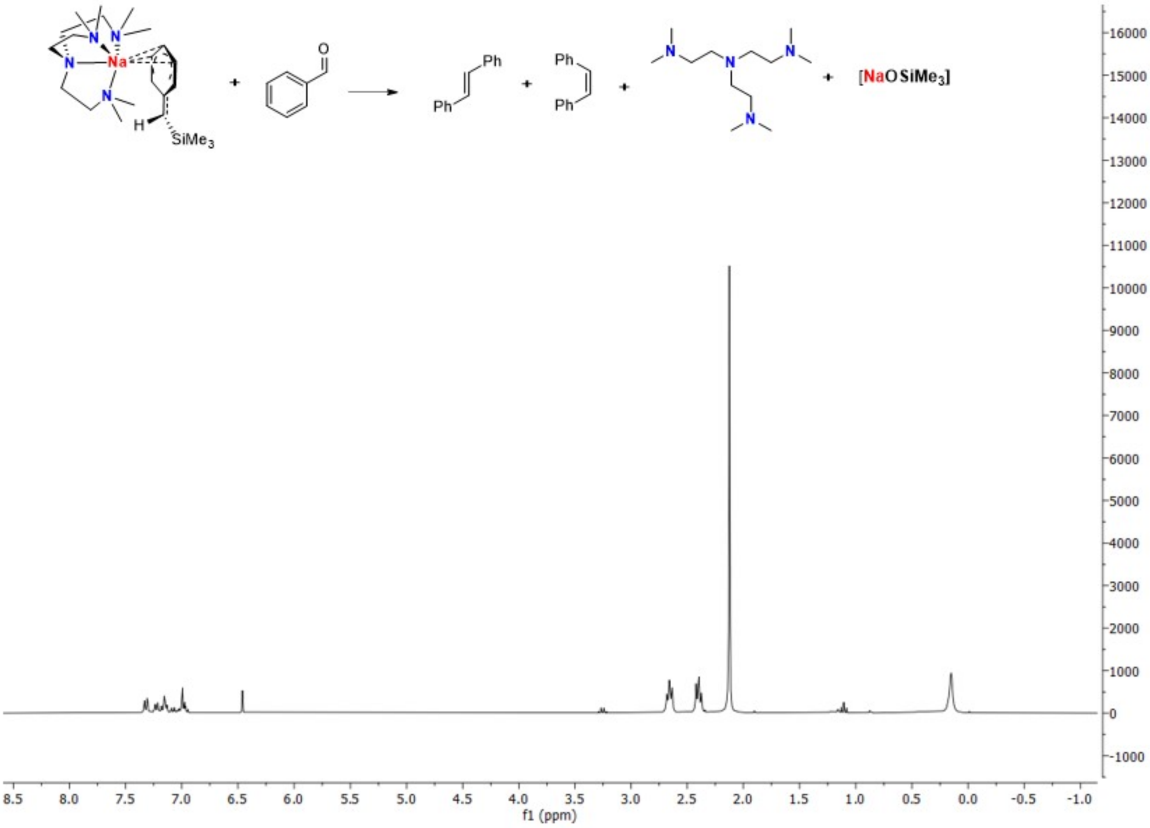

Figure S46. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and benzaldehyde (**3b**).

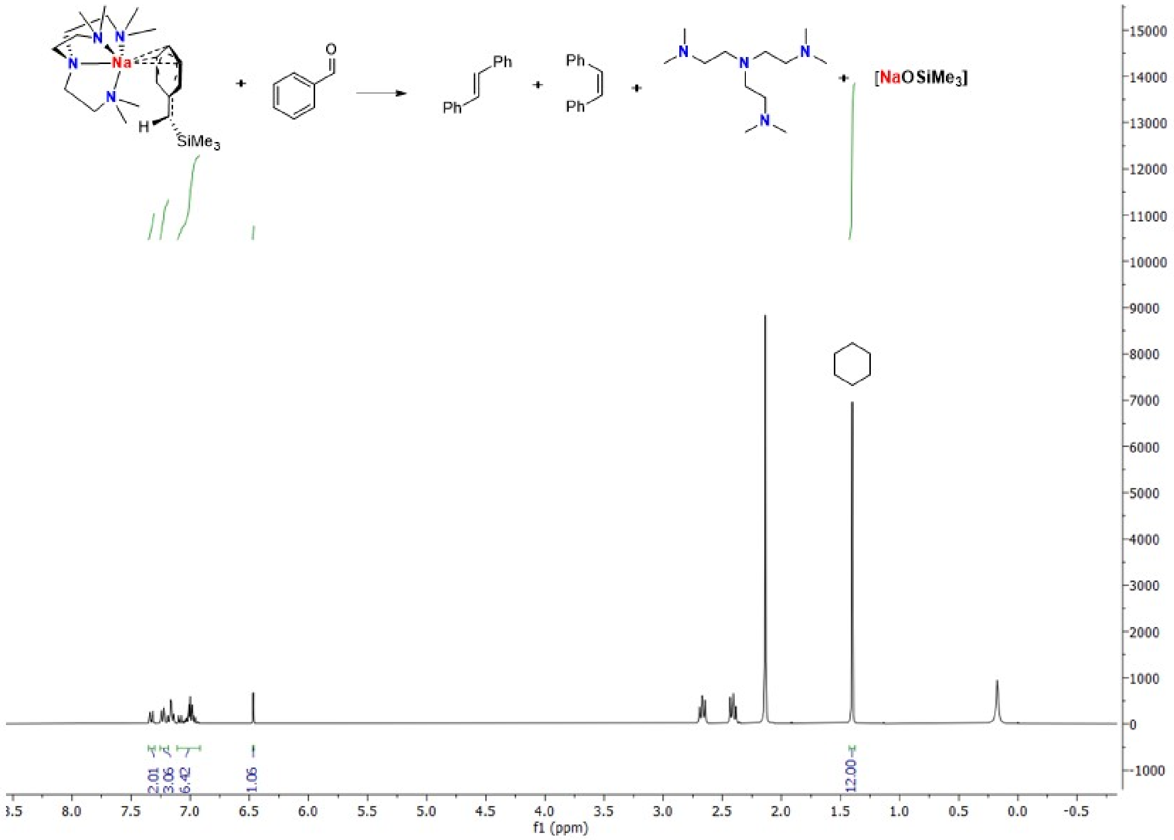

Figure S47. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and benzaldehyde (**3b**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

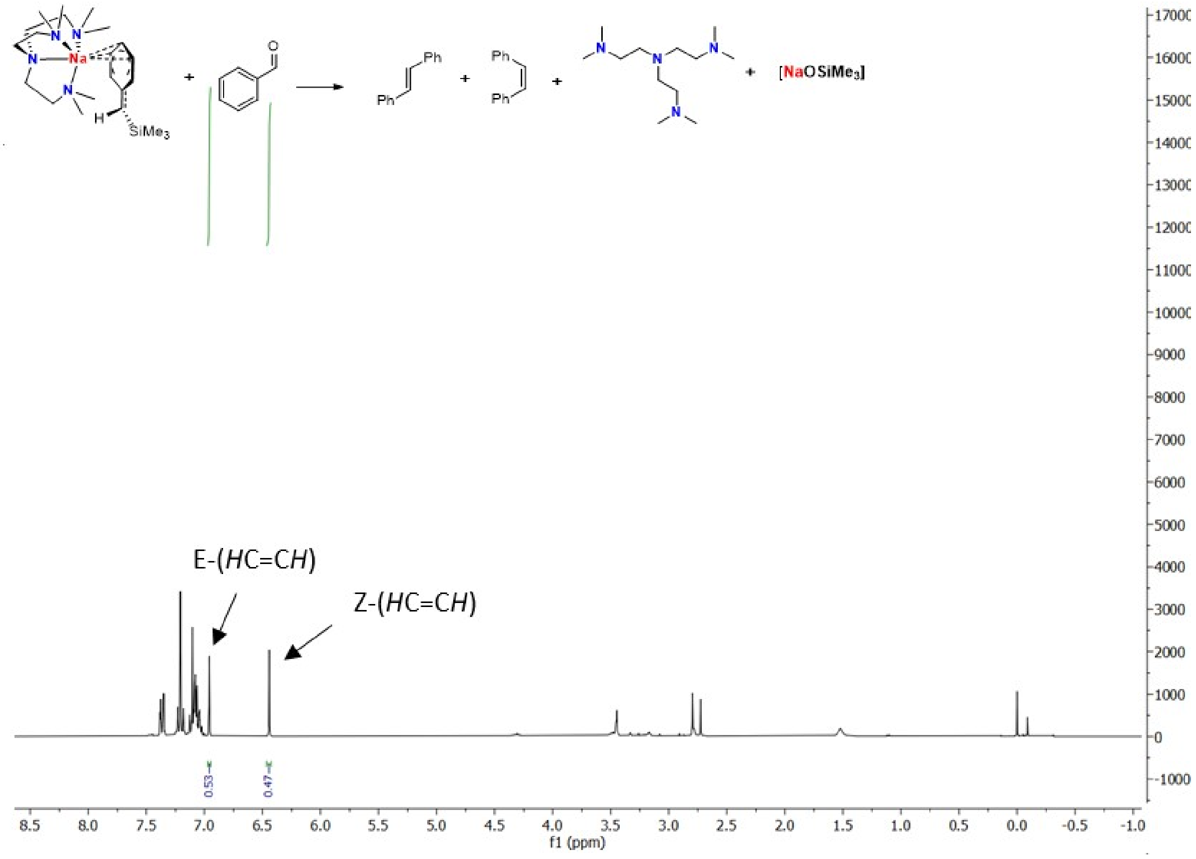

Figure S48. ^{1}H NMR ($CDCl_3$, 25 ˚C, 300 MHz) for the products from an NMR scale reaction between **2**-Na and benzaldehyde carried out in benzene (**3b**).

Reaction between 2-Na and Adamantanone (3c), to produce 2-benzylideneadamantane (4c)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was added to adamantanone (0.0045 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 30 minutes, which showed >95% conversion to the alkene.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Na (0.0125 g, 0.03 mmol). The solution was added to Adamantanone (**3c**) (0.0045g, 0.03 mmol). The resulting colourless was transferred to a J. Young NMR tube and was monitored by ^{1}H NMR after 30 mins.

NMR data of **4c** are consistent with literature.[5]

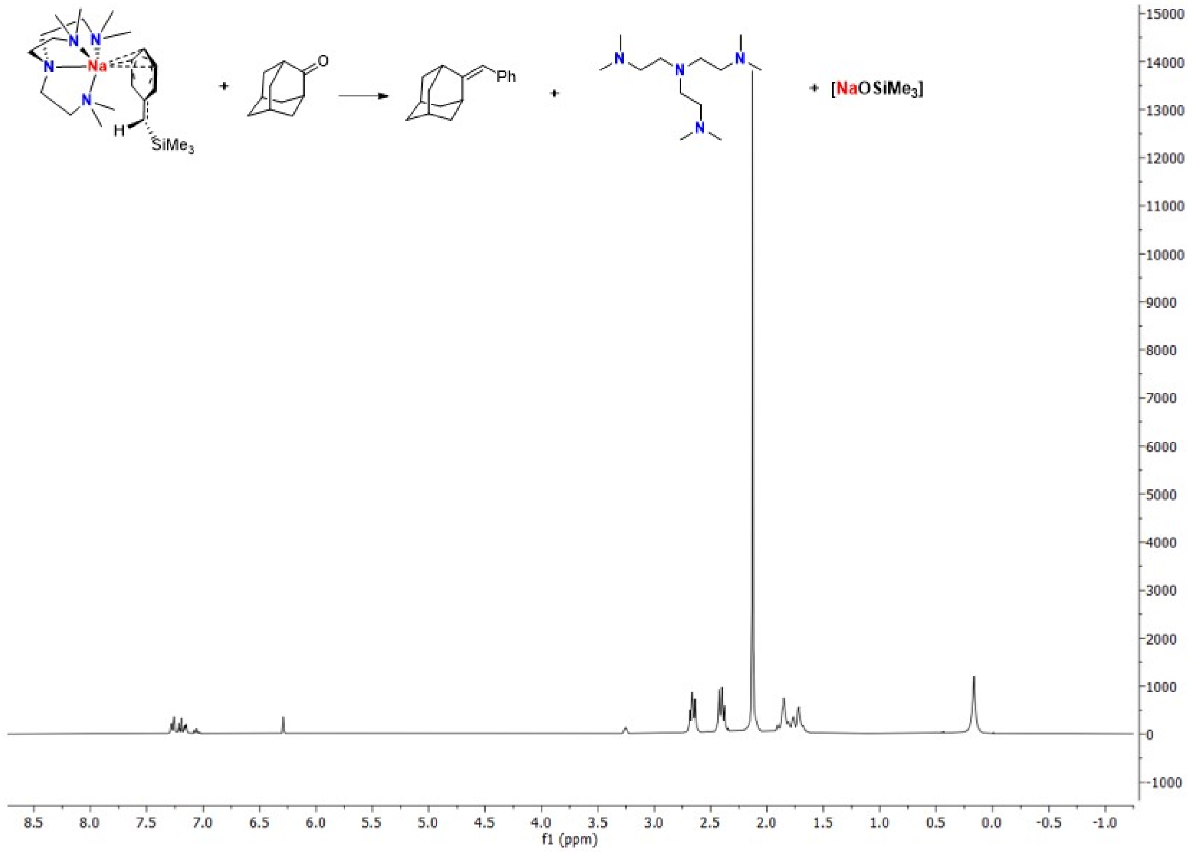

Figure S49. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and 2-adamantanone (**3c**).

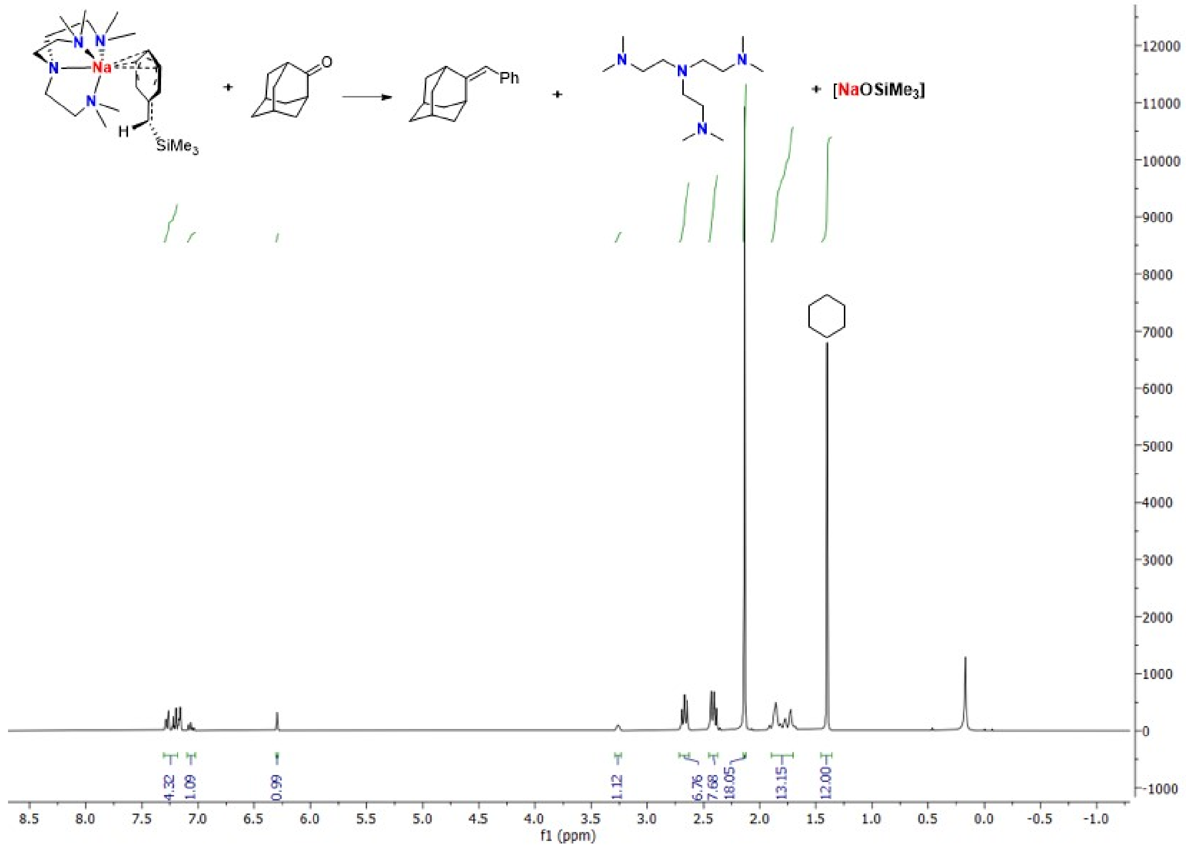

Figure S50. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and 2-adamantanone (**3c**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

Reaction between 2-Na and 2,2,2-trimethylacetophenone (3d), to produce (E/Z)-(3,3-dimethylbut-1-ene-1,2-diyl)dibenzene (4d)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to 2,2,2-trimethylacetophenone (0.0049 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H after 30 minutes, which showed >95% conversion to both alkenes at a 1:1 ratio.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Na (0.0125 g, 0.03 mmol). The solution was added to 2,2,2-trimethylacetophenone (**3d**) (0.0049g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 30 minutes.

NMR data of **4d** are consistent with literature[6].

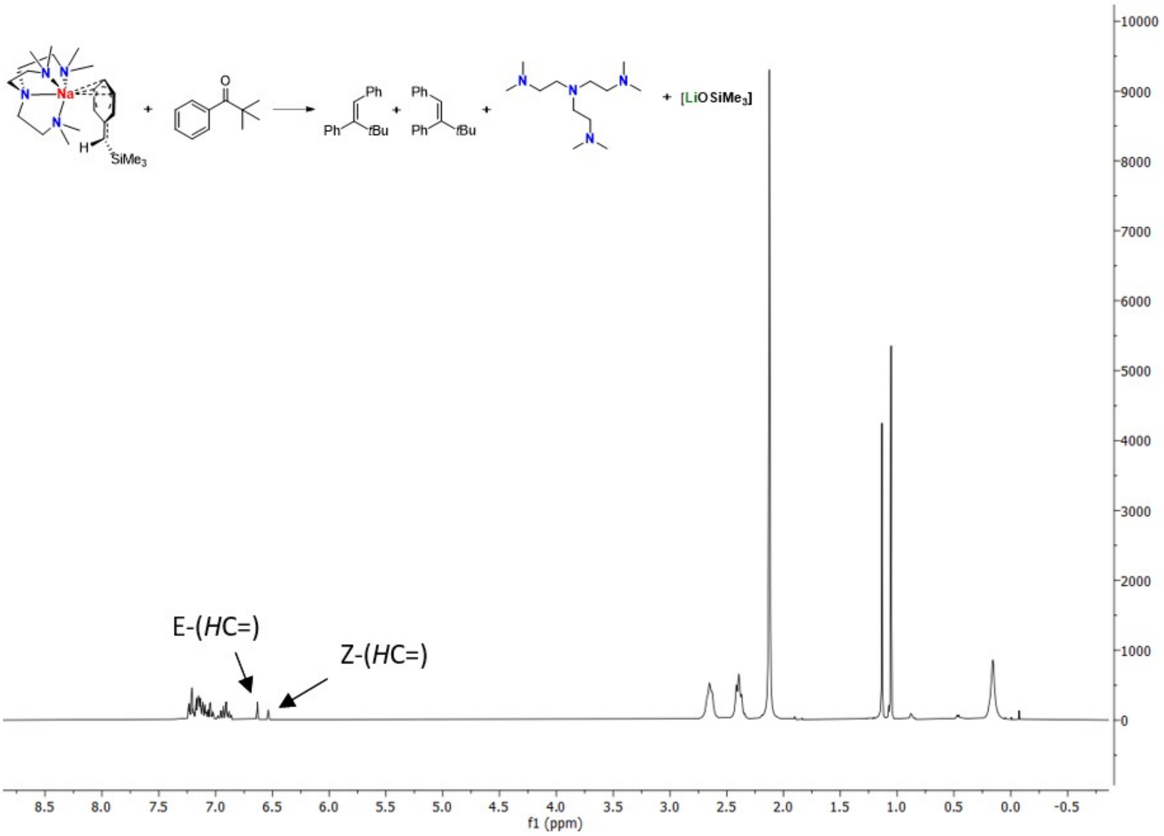

Figure S51. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and 2,2,2-trimethyl acetophenone (**3d**).

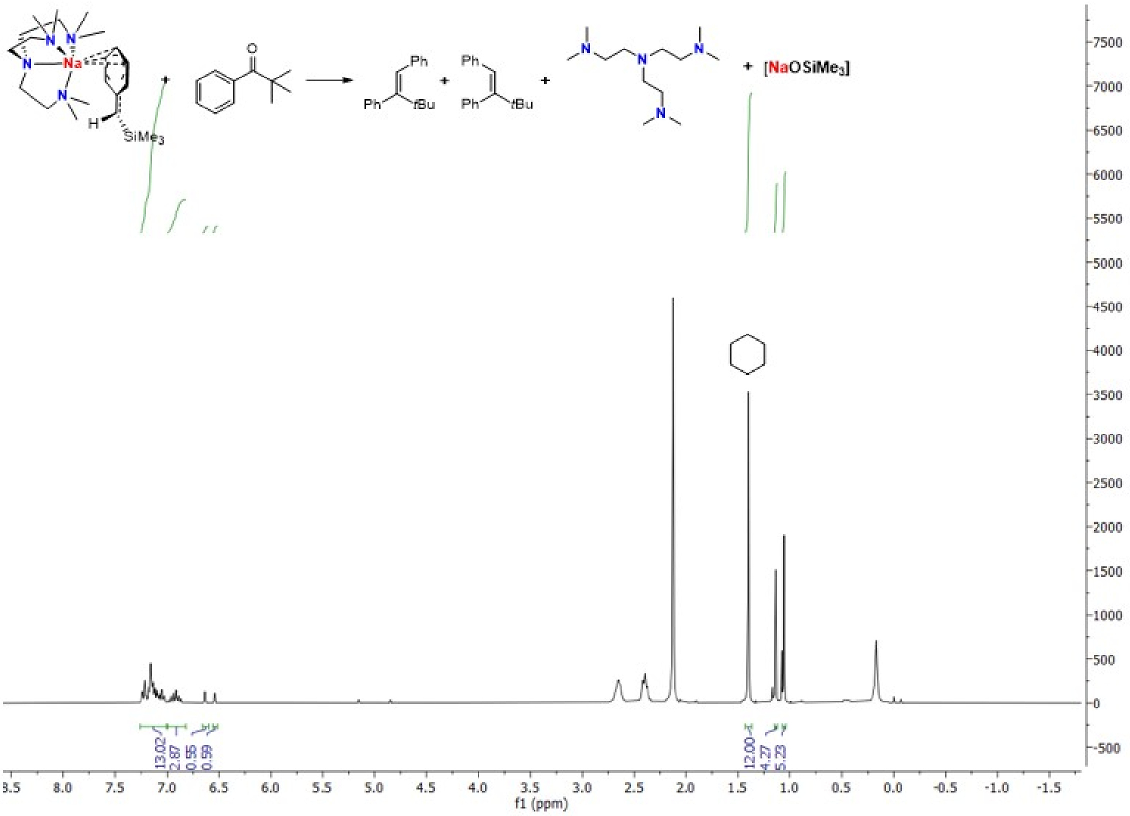

Figure S52. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and 2,2,2-trimethylacetophenone (**3d**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

Reaction between 2-Na and Michler's Ketone (3e), to produce 4,4'-(2-phenylethene-1,1-diyl)bis(N,N-dimethylaniline) (4e).

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to Michler's ketone (0.0080 g, 0.03 mmol). The resulting brown solution was transferred to a J. Young NMR tube and monitored by ^{1}H after 30 minutes and 24 hours, which showed >95% conversion to the alkene.

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Na (0.0125 g, 0.03 mmol). The solution was added to Michler's Ketone (**3e**) (0.0049g, 0.03 mmol). The resulting brown solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 24 hours.

NMR data of **4e** are consistent with literature[7].

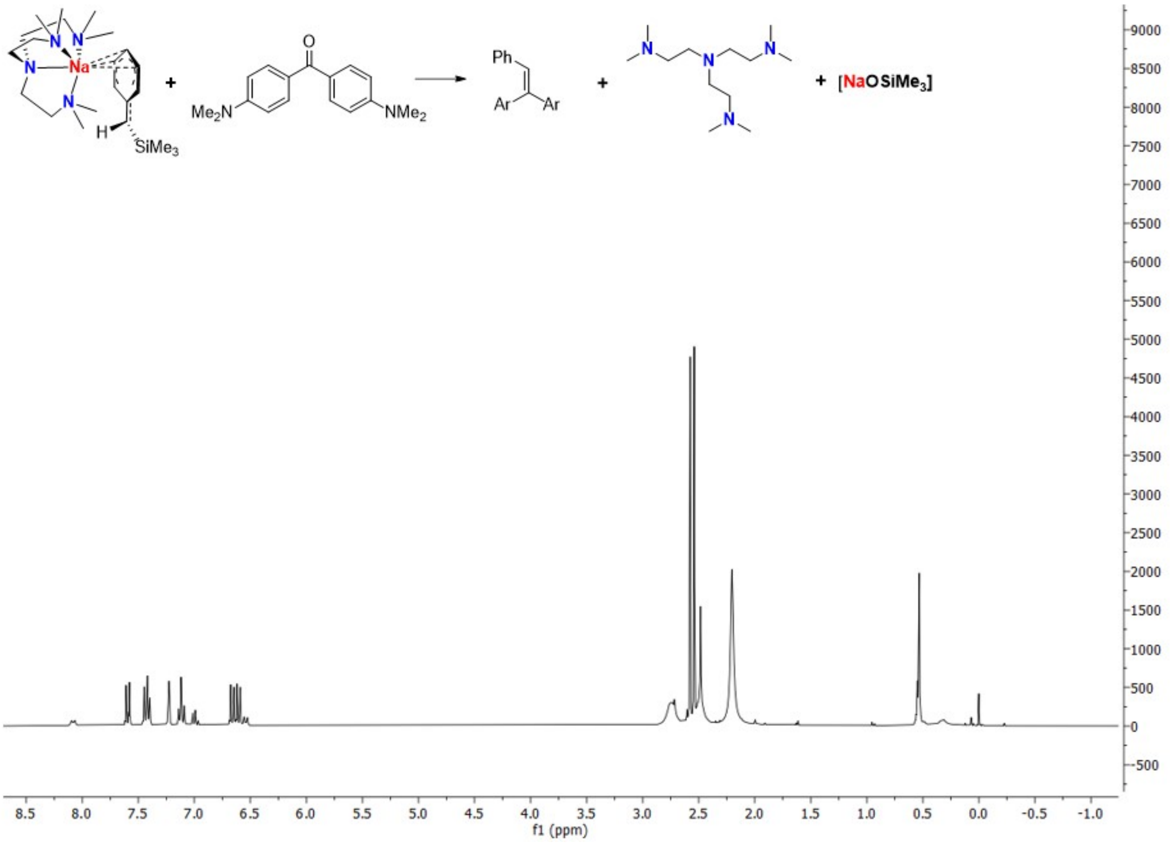

Figure S53. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and Michler's Ketone (**3e**).

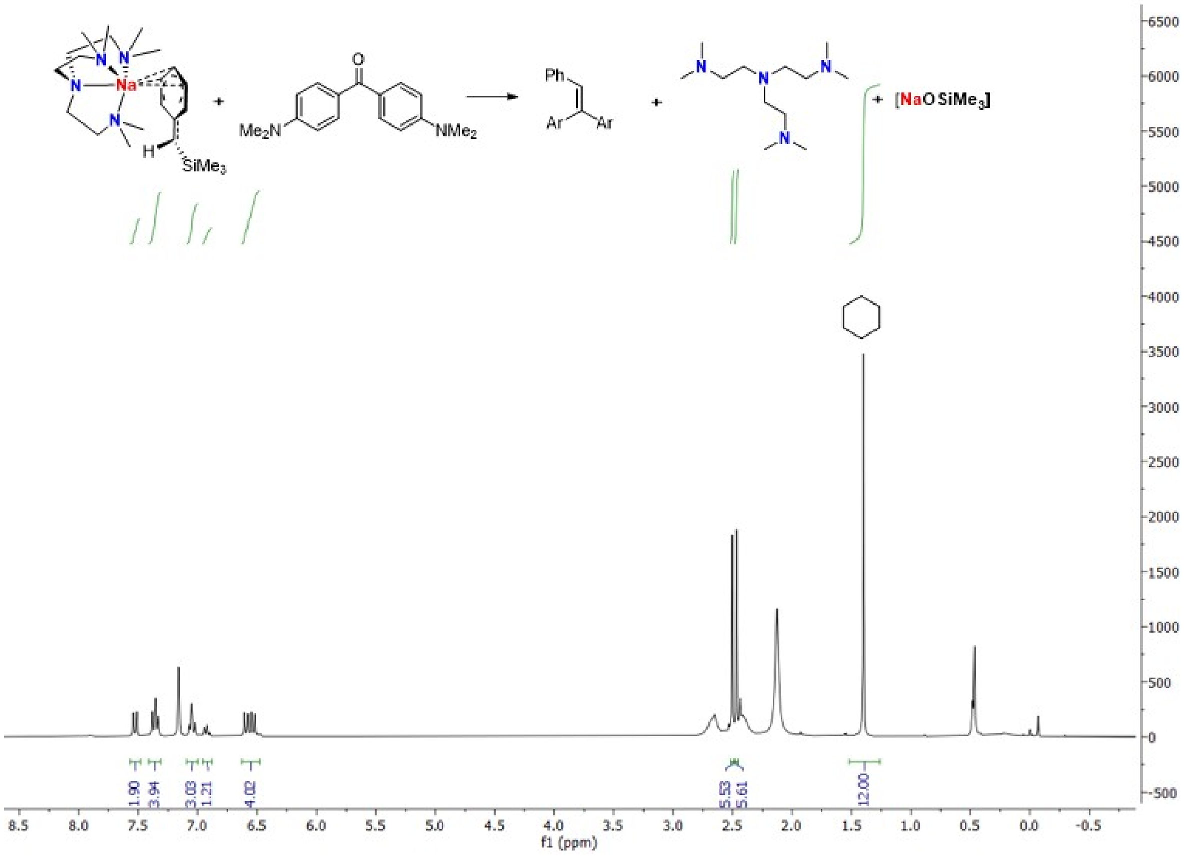

Figure S54. ^{1}H NMR (d$_6$-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and **3e**. Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

Reaction between 2-Na and decafluorobenzophenone (3f)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to decafluorobenzophenone (0.0108 g, 0.03 mmol). The resulting black solution was transferred to a J. Young NMR tube and monitored by ^{1}H and ^{19}F NMR after 30 minutes, which turned out to be an intractable mixture.

Reaction between 2-Na and 1-benzoylpiperidine (3g) to produce 1-(1,2-diphenylvinyl)piperidine (4g)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C_6D_6 (0.5 mL). The solution was transferred to 1-benzoylpiperidine (0.0056 g, 0.03 mmol). The resulting colourless solution was transferred to a J. Young NMR tube and monitored by ^{1}H NMR after 30 minutes. The solution was then dried in vacuo and the solids were dissolved in *d*$_8$-THF, which showed >90% conversion to the both E/Z alkenes at a 1:1 ratio.

Data for 1-(1,2-diphenylvinyl)piperidine (**4g**):

^{1}H NMR (300 MHz, d$_6$-benzene, 25 °C): δ (ppm) 7.51 – 7.47 (m, 1H, Ar*H*), 7.35 – 7.32 (m, 1H, Ar*H*), 7.20 – 7.08 (m, 3H, Ar*H*), 7.02 – 6.76 (m, 5H, Ar*H*), 5.73 (s, 0.5H, (Z)-*H*C=C), 5.62 (s, 0.5H, (E)-*H*C=C), 2.65 – 2.63 (m, 4H, C*H*$_2$), 1.32 – 1.22 (m, 6H, C*H*$_2$).

^{1}H NMR (300 MHz, d$_8$-THF, 25 °C): 7.51 – 7.47 (m, 1H, Ar*H*), 7.34 – 7.15 (m, 6H, Ar*H*), 6.92 – 6.69 (m, 4H, Ar*H*), 5.63 (s, 1H, *H*C=C), 5.60 (s, 1H, *H*C=C), 2.86 – 2.77 (m, 4H, C*H*$_2$), 1.60 – 1.52 (m, 6H, C*H*$_2$).

NMR data are consistent with literature[8, 9]

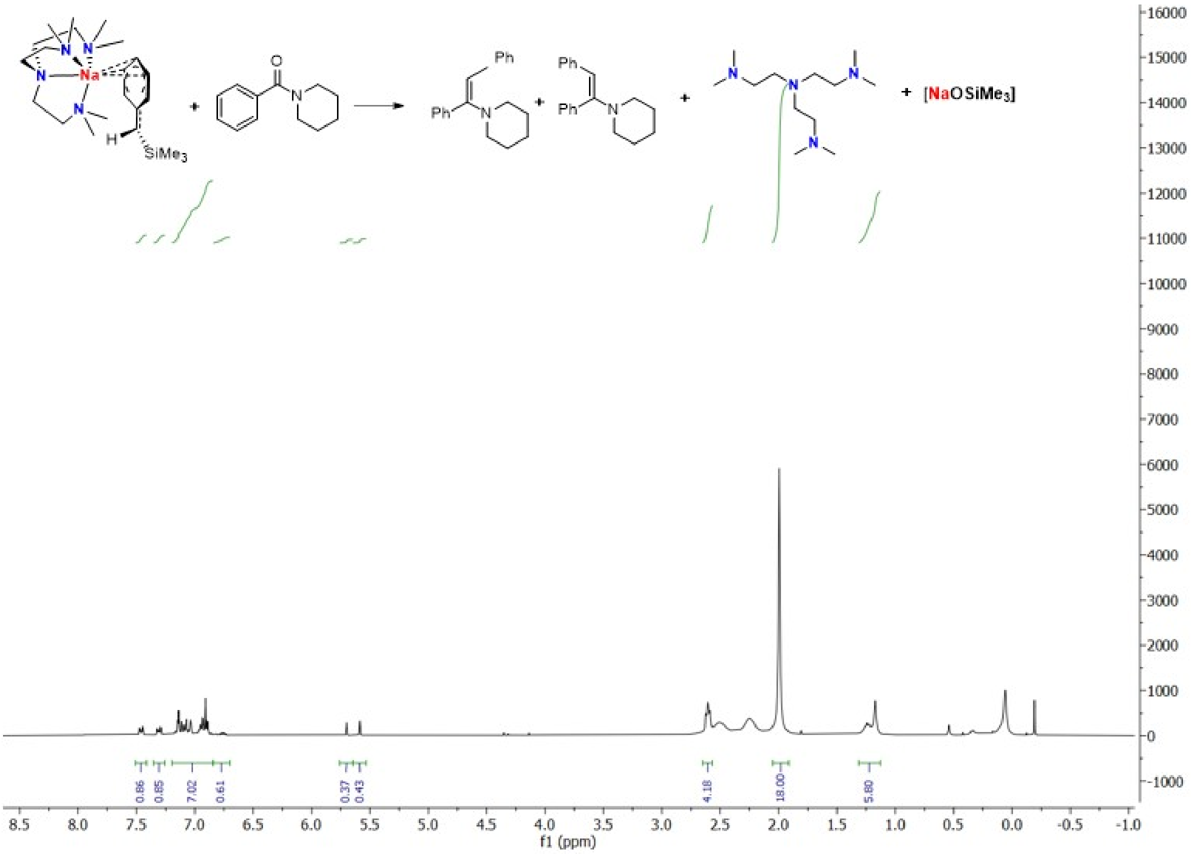

Figure S55. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and 1-benzoylpiperidine (**3g**).

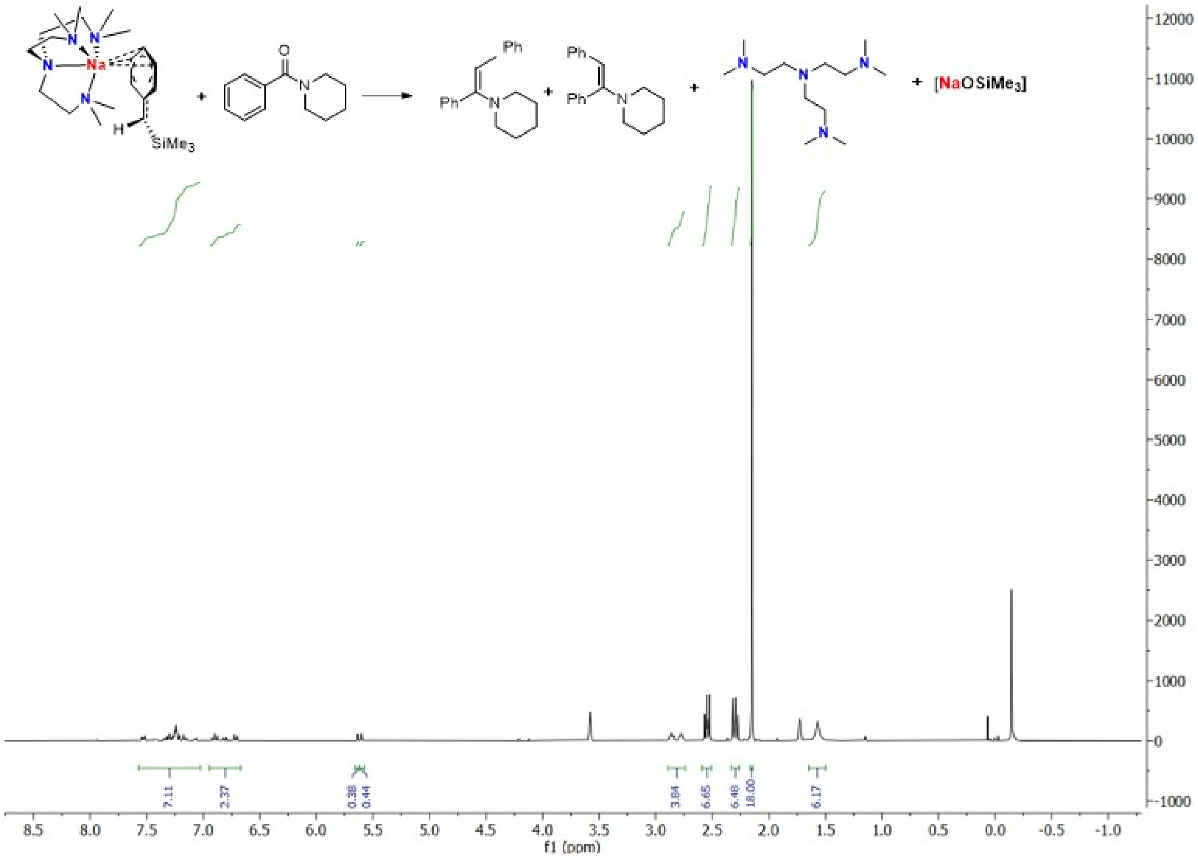

Figure S56. ^{1}H NMR (d_8-THF, 25 ˚C, 300 MHz) of the products from an NMR scale reaction between 2-Na and 1-benzoylpiperidine (**3g**) carried out in C_6D_6.

Reaction between 2-Na and 2,2,2-trifluoroacetophenone (3h) to produce E/Z 1,2-Diphenyl-3,3,3-trifluoroprop-1-ene (4h)

With Internal Standard: A solution of cyclohexane in C_6D_6 (0.5 mL, 0.4775g, 0.03 mmol) was added to **2**-Na (0.0125 g, 0.03 mmol). The solution was added to 2,2,2-trifluoroacetophenone (**3h**) (0.0052g, 0.03 mmol). The colourless solution was transferred to a J. Young NMR tube and was heated to 60 ^{O}C monitored by ^{1}H after 30 minutes, which showed a >95% conversion to both E/Z alkenes. E/Z ratio determined as 1:3 from ^{19}F NMR integrals.

Data for E/Z 1,2-Diphenyl-3,3,3-trifluoroprop-1-ene (**4h**):

^{1}H NMR (300 MHz, d6-benzene, 25 °C): δ (ppm) 7.30 – 7.24 (m, 3H, Ar*H*), 7.12 – 6.91 (m, 6H, Ar*H, H*C=, overlapping signals), 6.81 – 6.76 (m, 2H, Ar*H, H*C=, overlapping signals).

^{19}F NMR (282 MHz, d6-benzene, 25 ˚C): δ (ppm) -65.50 (s, 0.75, E – HC=), -55.99 (s, 2.25, Z – HC=).

^{19}F{^{1}H} NMR (282 MHz, d6-benzene, 25 ˚C): δ (ppm) -65.50 (s, 0.75, E – HC=), -55.99 (s, 2.25, Z – HC=).

NMR data are consistent with literature[10, 11]

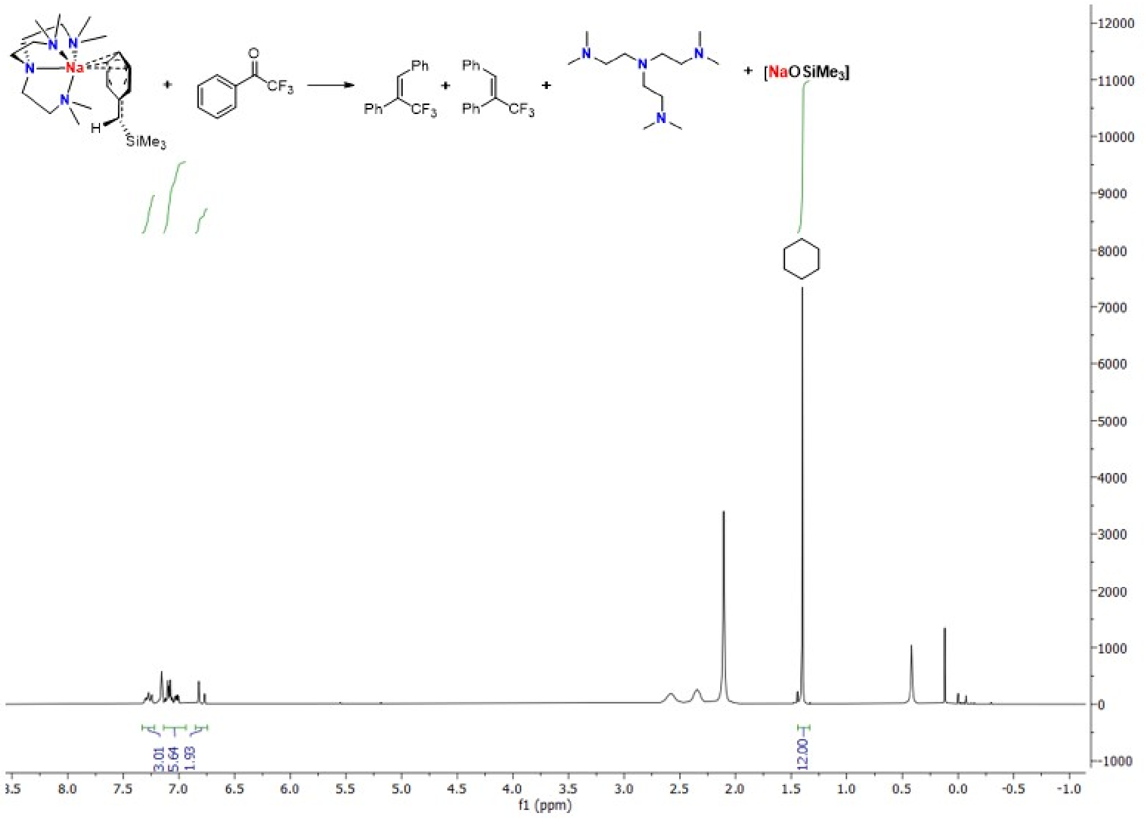

Figure S57. ^{1}H NMR (d6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and 2,2,2-trifluoroacetophenone (**3h**). Internal Standard (**I**) = Cyclohexane. [**I**] = 0.06M

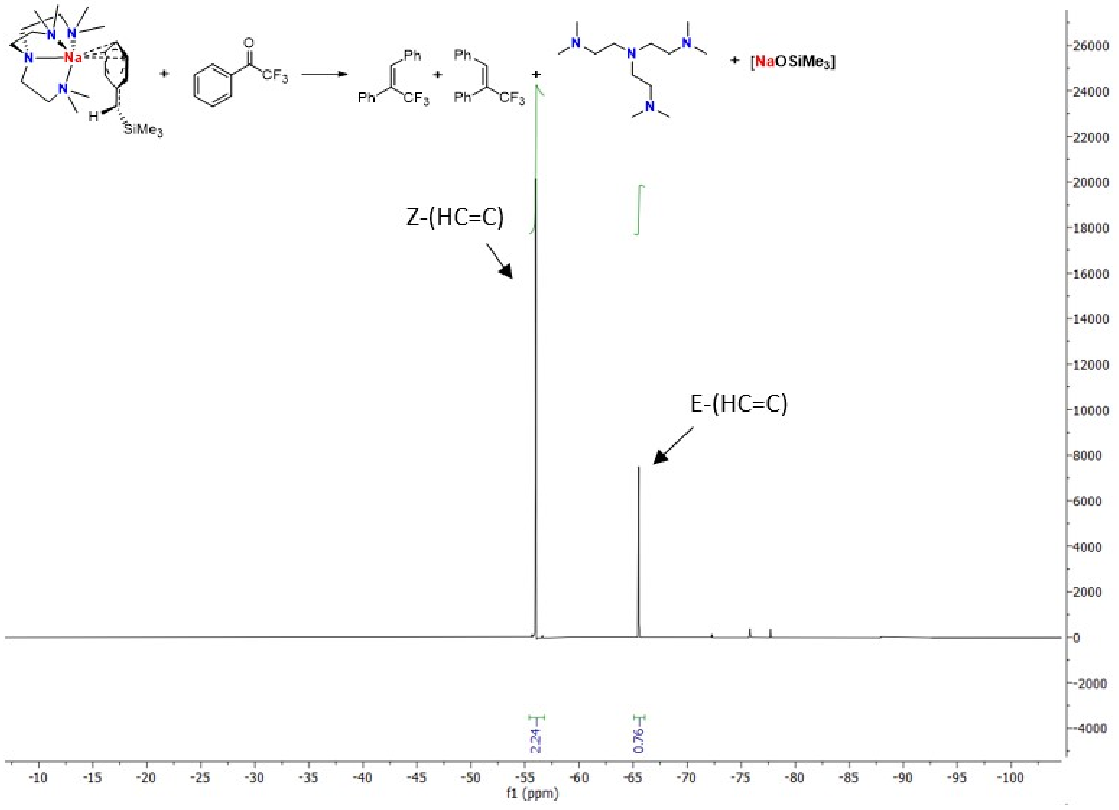

Figure S58. ^{19}F NMR (d_6-benzene, 25 ˚C, 282 MHz) for an NMR scale reaction between **2**-Na and 2,2,2-trifluoroacetophenone (**3h**).

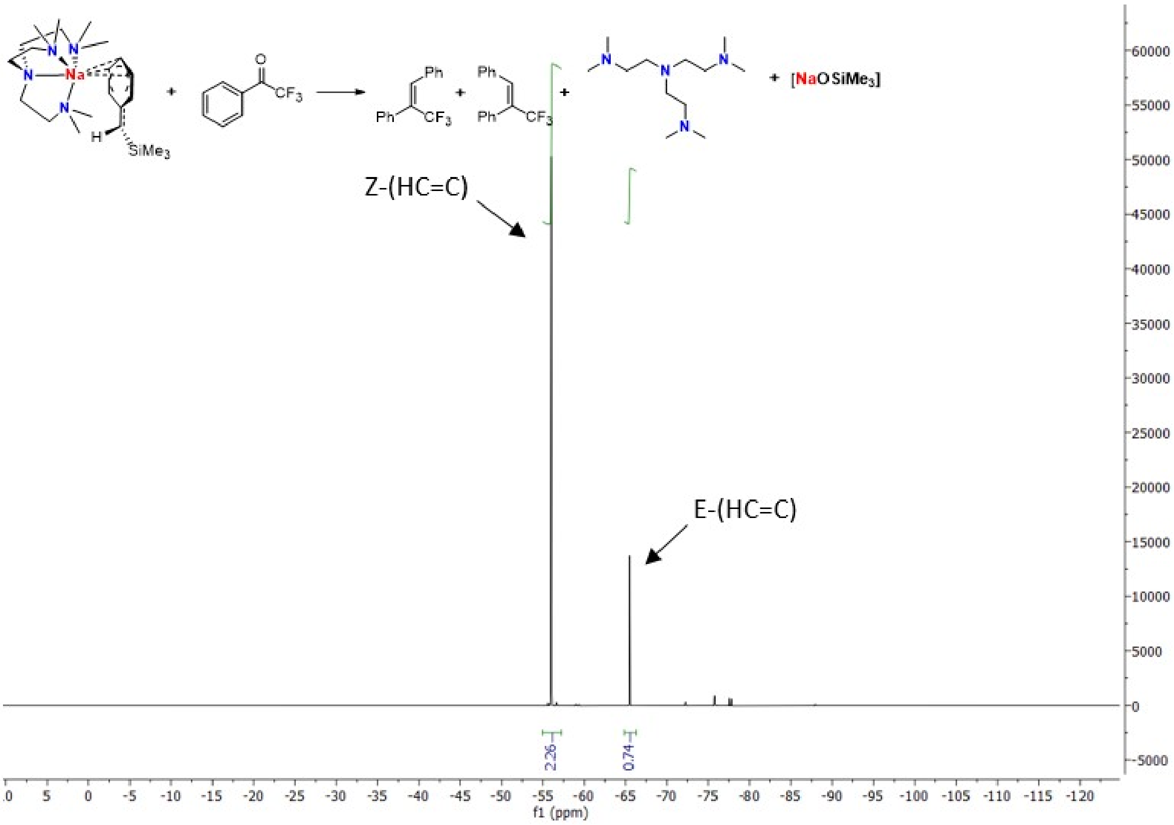

Figure S59. ^{19}F{^{1}H] NMR (d_6-benzene, 25 ˚C, 282 MHz) for an NMR scale reaction between **2**-Na and 2,2,2-trifluoroacetophenone (**3h**).

Reaction between 2-Na and phenylcyclohexylketone (3i) to produce 1-Cyclohexylethen-1,2-diyl)dibenzene (4i)

2-Na (0.0125 g, 0.03 mmol) was dissolved in C6D6 (0.5 mL). The solution was added to cyclohexyl phenyl ketone (0.0056 g, 0.03 mmol). The resulting clear solution was transferred to a J. Young NMR tube and monitored by 1H NMR after 30 minutes, which showed >95% conversion to both alkenes at a 2:3.

Resolution of E/Z ratio: Reaction was repeated at 0.03 mmol, then dried in vacuo. The resulting solid was dissolved in $CDCl_3$ and the E/Z ratio was determined as 2:3 using ^{1}H NMR (Figure S61).

Data for E/Z (1-cyclohexylethene-1,2-diyl)dibenzene (**4i**):

^{1}H NMR (300 MHz, d6-benzene, 25 °C): δ (ppm) 7.35 – 7.12 (m, 5H, Ar*H*), 7.11 – 6.84 (m, 5.4H, Ar*H* (E)*H*C=, overlapping signals), 6.43 (s, 0.6H, (Z)*H*C=), 1.84 – 1.51 (m, 6H, CH_2), 1.32 – 1.07 (m, 5H, CH_2).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.39 – 7.22 (m, 6H, Ar*H*), 7.11 – 7.00 (m, 3H, Ar*H*), 6.85 – 6.82 (m, 1H, Ar*H*), 6.37 (s, 0.6H, Z-*H*C=), 6.30 (s, 0.4H, E-*H*C=), 1.86 – 1.53 (m, 6H, CH_2), 1.35 – 1.10 (m, 6H, CH_2).

NMR data are consistent with literature.[12]

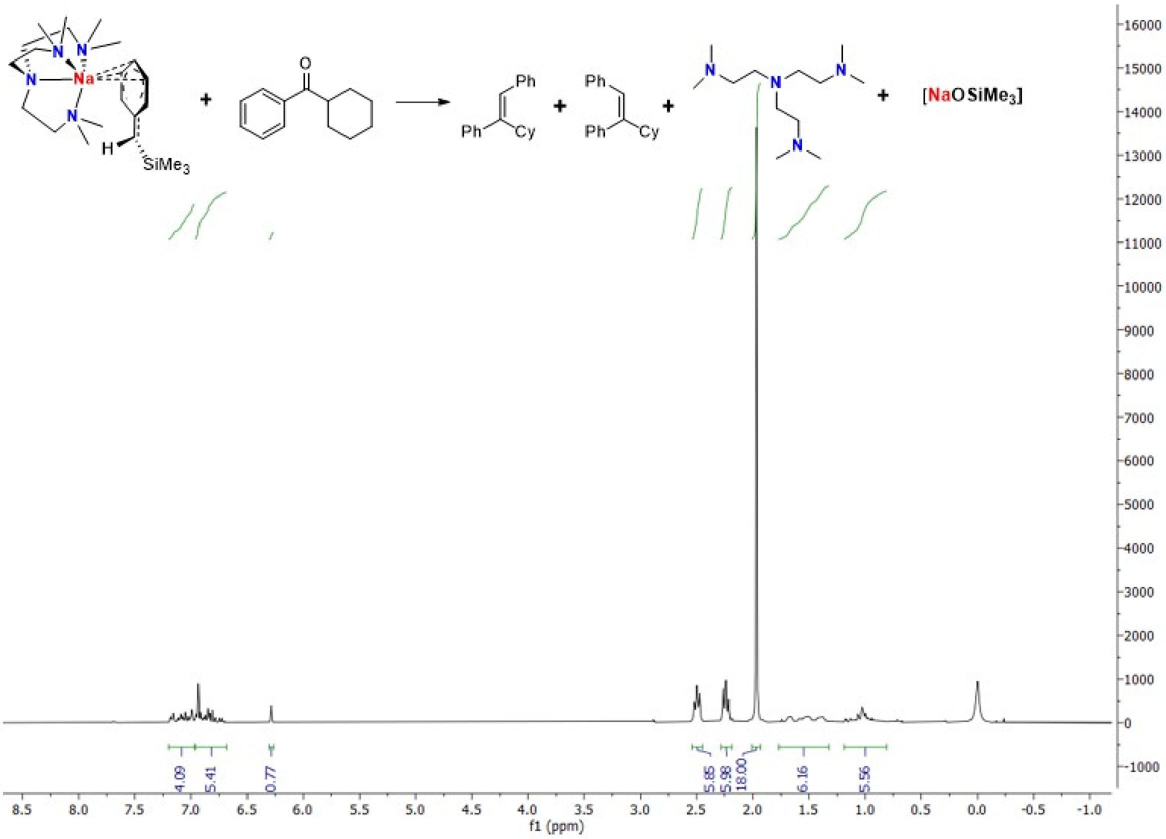

Figure S60. ^{1}H NMR (d_6-benzene, 25 ˚C, 300 MHz) for an NMR scale reaction between **2**-Na and phenylcyclohexyl ketone (**3i**).

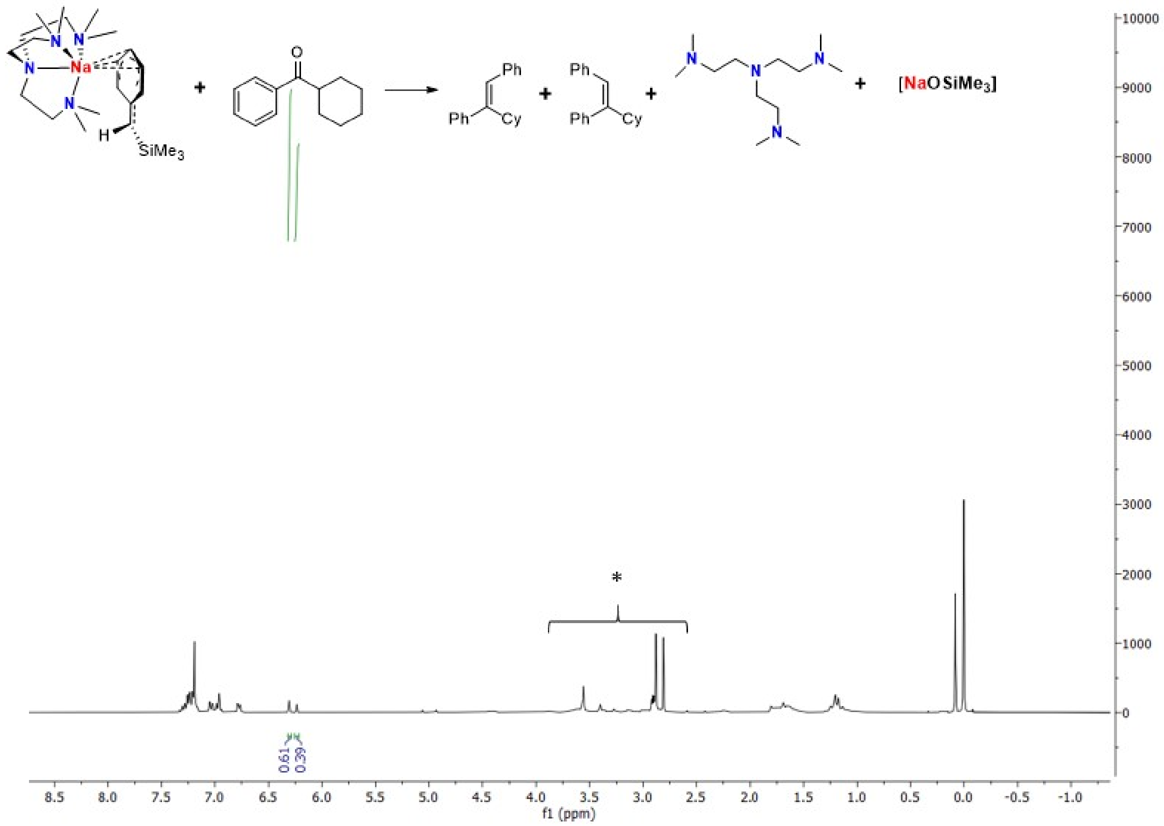

Figure S61. ^{1}H NMR ($CDCl_3$, 25 ˚C, 300 MHz) for the products from an NMR scale reaction between **2**-Na and phenylcyclohexylketone (**3i**) carried out in benzene. *Me_6Tren and unidentified products.

1.9 Single-crystal X-ray diffraction (SCXRD) Details

Crystal structures data for **2-**Li and **2**-Na were collected on a XtaLAB Synergy, Dualflex, HyPix-Arc 100 diffractometer equipped with an micro-focus sealed X-ray tube (λ Cu Kα = 1.54184 Å) and an Oxford Cryosystems CryostreamPlus open-flow N_2 cooling device. Cell refinement, data collection and data reduction were undertaken via software CrysAlisPro 1.171.42.63a (Rigaku OD, 2022). Intensities were corrected for absorption using CrysAlisPro 1.171.42.63a (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Using Olex2 (Dolomanov, 2009), the structure was solved using SHELXT 2014/5 (Sheldrick, 2014) and refined by XL (Sheldrick, 2008).

Compound	**2**-Li	**2**-Na
Empirical formula	$C_{22}H_{45}LiN_4Si$	$C_{22}H_{45}N_4NaSi$
Formula weight	400.65	416.70
Temperature/K	150(2)	150(2)
Crystal system	monoclinic	Monoclinic
Space group	$P2_{1/n}$	$P2_{1/c}$
a/Å	9.8325(3)	14.0881(6)
b/Å	15.3730(5)	9.6060(4)
c/Å	17.1794(5)	20.0799(8)
α/°	90	90
β/°	93.668(3)	102.389(4)
γ/°	90	90
Volume/Å3	2591.43(14)	2654.14(19)
Z	4	4
ρcalcg/cm3	1.027	1.043
μ/mm-1	0.876	1.026
F(000)	888.0	920.0
Crystal size/mm3	0.18 × 0.13 × 0.12	0.19 × 0.13 × 0.11
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.724 to 156.906	6.424 to 156.704
Index ranges	-12 ≤ h ≤ 12, -18 ≤ k ≤ 10, -21 ≤ l ≤ 20	-17 ≤ h ≤ 17, -11 ≤ k ≤ 11, -24 ≤ l ≤ 24
Reflections collected	17608	18205
Independent reflections	5136 [Rint = 0.0279, Rsigma = 0.0288]	5237 [R_{int} = 0.0232, R_{sigma} = 0.0236]
Data/restraints/parameters	5136/0/266	5237/0/263
Goodness-of-fit on F2	1.037	1.034
Final R indexes [I>=2σ (I)]	R1 = 0.0398, wR2 = 0.1067	R_1 = 0.0373, wR_2 = 0.0996
Final R indexes [all data]	R1 = 0.0479, wR2 = 0.1117	R_1 = 0.0428, wR_2 = 0.1029
Largest diff. peak/hole / e Å-3	0.30/-0.19	0.33/-0.19

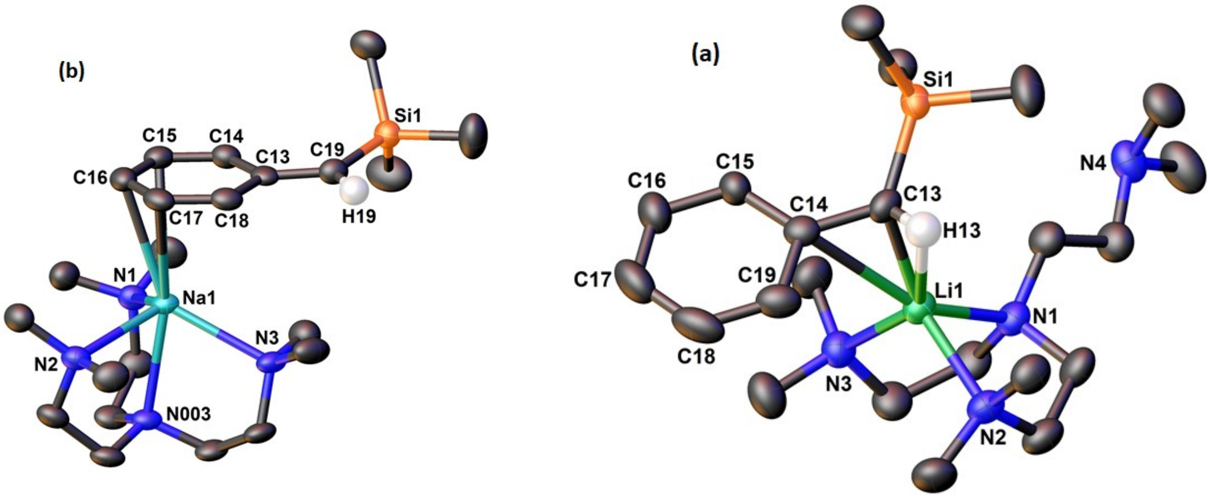

Figure S62. Single-crystal X-ray diffraction (SCXRD) molecular structures of **2**-Li (**a**) and **2**-Na (**b**) measured at 150 K. Key bond distances (Å): **2**-Li: Li1–C13 2.219(3); Li1–C14 2.759(3); Li1–N1 2.182(3); Li1–N2 2.197(3); Li1–N3 2.090(3); Li1–H13 2.322(17); C13–C14 1.437(2); C13–H13 0.940(17). **2**-Na: Na1–C15 3.0017(15); Na1–C16 2.8179(15); Na1–C17 2.9066(15); Na1–N1 2.5949(12); Na1–N2 2.5834(12); Na1–N3 2.4849(12); Na1–N003 2.5466(12); C13–C14 1.429(2); C14–C15 1.372(2); C15–C16 1.399(2); C16–C17 1.392(2); C17–C18 1.383(2); C18–C13 1.4469(19); C13–C19 1.4038(19).

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