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General Methods

All the reactions and manipulation were performed under protective Argon atmosphere; using the standard Schlenk technique or Glovebox MBraun equipped with a gas purification and recirculation unit. Hexane was dried over alumina column of Solvent Purification System (a MBraun MBSPS 5) and stored over activated 4 Å molecular sieves collection and under argon atmosphere Tetrahydrofuran were dried over sodium and benzophenone ketyl and purified by distillation under argon atmosphere, after the collection it was stored over activated 4 Å molecular sieves and argon atmosphere. $\text{Ph}_2\text{Si}(\text{NAr}^*)_2$ [$\{\text{Ph}_2\text{Si}(\text{NAr}^*)(\text{NAr}^*)\text{K}\}_\infty$] were prepared as reported in literature.^[1,2]

NMR spectra were performed in J. Young's NMR tube, prior oven dried and flushed with argon. NMR spectra were recorded using a Bruker AV 400 spectrometer operating at 400.13 MHz for ^1H and ^{19}F , 100.62 MHz for $^{13}\text{C}\{^1\text{H}\}$ or a Bruker AV 400 spectrometer operating at 300 MHz for ^1H and ^{19}F , 75 MHz for $^{13}\text{C}\{^1\text{H}\}$. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were calibrated against the appropriate solvent signal. All the deuterated solvents for NMR were dried and distilled over $\text{NaK}_{2,8}$ and stored over activated 4 Å molecular sieves and argon atmosphere.

Synthetic Procedures

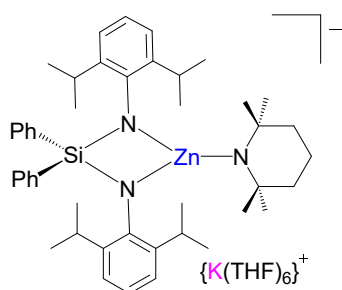
Synthesis of ZnTMP_2

2.72 mL of 2,2,6,6-tetramethylpiperidine (16 mmol) were solubilized in 10 mL of THF and then 10 mL of $n\text{BuLi}$ solution (1.6 M in hexane) were added drop by drop affording a yellow solution. 1.09 g of ZnCl_2 (8 mmol) were added, instantaneously a white precipitate was formed. The mixture was allowed to stir at room temperature for 1h. All the volatiles were removed under reduced pressure affording a yellow waxy solid. 30 mL of Hexane were added affording a white suspension. The suspension was filtered through celite and the mother liquor was evaporated furnishing $\text{Zn}(\text{TMP})_2$ as white solid (2700 mg 98%). The solid can be further purified via sublimation as reported in the literature.^[3]

$^1\text{H-NMR}$ (300.1 MHz, $\text{D}_8\text{-THF}$, 298 K) $\delta(\text{ppm})$: 1.68 (m, 4H, $\gamma\text{-CH}_2$), 1.32 (m, 8H, $\beta\text{-CH}_2$), 1.22 (s, 24H, $\alpha\text{-CH}_3$)

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (75.5 MHz, $\text{D}_8\text{-THF}$, 298 K) $\delta(\text{ppm})$: 53.3 (C_q), 39.8 ($\beta\text{-CH}_2$), 36.8 ($\alpha\text{-CH}_3$) 19.7 ($\gamma\text{-CH}_2$)

Synthesis of [$\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{K}(\text{THF})_6\}^+$] (**1**)



572 mg of freshly prepared [$\{\text{Ph}_2\text{Si}(\text{NAr}^*)(\text{NAr}^*)\text{K}\}_\infty$] (**1**)^[2] (1 mmol) and 346 mg of $\text{Zn}(\text{TMP})_2$ (1 mmol) were solubilized in 10 mL of THF and the solution was allowed to stir at reflux overnight. Volatiles were removed under

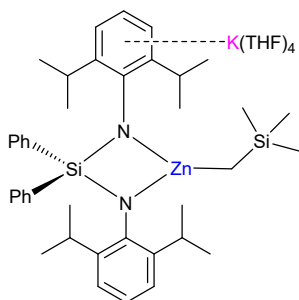
vacuum, the white residue was dissolved in 5 mL of hexane and 2 mL of THF, affording a pale-yellow solution. Storage in freezer (-33°C) for two days furnished colourless crystal of **1** (641.6 mg 67%).

¹H-NMR (D₈-THF; 298K; 400 MHz) δ(ppm): 7.28 [m, 4H, Ph], 6.93 [m, 4H, Ar*], 6.71 [m, 6H, Ph], 6.45 [t, 2H, Ar*], 4.14 [sept., 4H, CH ⁱPr], 3.61 [m, 10H, O-CH₂ THF], 1.77 [m, 10H, CH₂ THF], 1.55[m, 2H, γ-CH₂ TMP], 1.17 [m, 4H,β-CH₂ TMP], 0.97 [s, 12H, CH₃ TMP] ¹H NMR integration revealed that approximately four molecules of the solvating THF present in **1** were removed under vacuum when drying the crystals

¹³C{¹H}-NMR (D₈-THF; 298K, 100 MHz) δ(ppm): 152.6, 148.2, 145.7 [C_{quaternary} Ar* and Ph], 136.3, 126.5, 122.4, 117.5 [CH, Ar* and Ph], 68.4 [O-CH₂ of THF], 53.2 [C_{quaternary} TMP], 42.0[β-CH₂ TMP], 37.0 [CH₃ TMP], 28.2 [CH ⁱPr], 26.5 [CH₃ ⁱPr], 20.8 [γ-CH₂ TMP]

Elemental analysis: analytical calculated: C₆₁H₉₄KN₃O₄SiZn C 68.73, H 8.89, N 3.94. Found: C 68.51, H 8.72, N 3.93.

Synthesis of [**Ph₂Si(NAr*)₂Zn(CH₂SiMe₃)⁻{K(THF)₄}⁺** (**2**)



126 mg of KCH₂SiMe₃ (1mmol), 346 mg of ZnTMP₂ (1mmol) and 10 mL of hexane were added to a flushed Schlenk tube. The white suspension was left stirring for 2 hours until it becomes a fine suspension to which 1 mmol of Ph₂Si(NHAr*)₂ (530 mg) and 1 mL of THF were added, the yellowish suspension was gently heated and allowed to stir overnight. Volatiles were removed under vacuum and to the white residue 7 mL of hexane and 0.7 mL of THF was added, affording a pale-yellow suspension. The mixture was heated under reflux and let

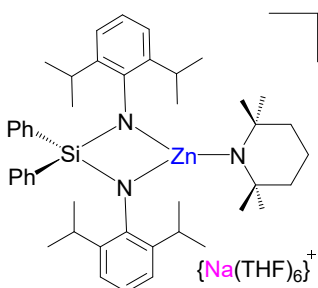
slowly cool down at room temperature depositing a crop of colourless crystals of **2** after 24h at room temperature. (550 mg, yield 76%). The synthesis of this compound can be achieved using a different procedure reported in literature before.^[2]

¹H-NMR (D₈-THF; 298K; 600 MHz) δ (ppm): 7.27 [m, 4H,Ph], 6.94 [m, 6H, Ph], 6.7 [d, 4H Ar*], 6.42 [t, 2H, Ar*], 4.15 [sept, 4H, CH ⁱPr], 0.8 [d, 24H, CH₃ ⁱPr], -0.14 [s, 9H, CH₃ CH₂SiMe₃], -0.9 [s, 2H, CH₂ CH₂SiMe₃]. ¹H NMR integration revealed that approximately three THF molecules in **2** were removed under vacuum when drying the crystals.

¹³C{¹H}-NMR (D₈-THF; 298K; 150 MHz) δ (ppm): 153.3, 148.2, 144.8 [C_{quaternary} Ar* and Ph], 136.1, 126.66, 126.5 [CH Ph], 122.2, 117.0 [CH of Ar*], 28.3 [CH ⁱPr], 25.0 [CH₃ ⁱPr], 3.4 [CH₃, CH₂SiMe₃], -6.1 [CH₂ CH₂SiMe₃].

Elemental analysis: analytical calculated: C₄₄H₆₃KN₂OSi₂Zn C 66.34, H 7.97, N 3.52. Found: C 66.27, H 7.42, N 3.64.

Synthesis of [**Ph₂Si(NAr*)₂Zn(TMP)⁻{Na(THF)₆}⁺** (**3**)



278 mg of freshly prepared [**Ph₂Si(NHAr*)(NAr*)Na**]₂^[1] (0.5 mmol) and 176 mg of Zn(TMP)₂ (0.5 mmol) were solubilized in 5 mL of THF and the

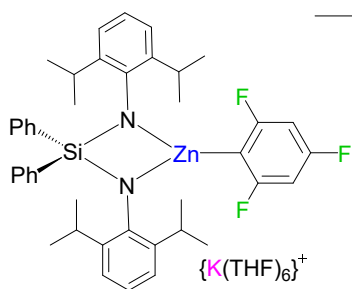
solution was allowed to stir at reflux overnight. Volatiles were removed under vacuum, the white residue was dissolved in 2.5 mL of hexane and 1 mL of THF, affording a pale-yellow solution. Storage in freezer (-33°C) for two days furnished colourless crystal of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$ (541.5 mg 65%).

¹H-NMR (D_8 -THF; 298K; 400 MHz) δ (ppm): 7.29 [m, 4H, Ph], 6.93 [m, 4H, Ar*], 6.72 [m, 6H, Ph], 6.45 [t, 2H, Ar*], 4.14 [sept., 4H, CH ⁱPr], 3.62 [m, 5H, O-CH₂ THF], 1.78 [m, 5H, CH₂ THF], 1.55 [m, 2H, γ -CH₂ TMP], 1.17 [m, 4H, β -CH₂ TMP], 0.97 [s, 12H, CH₃ TMP] ¹H NMR integration revealed that approximately five THF molecules in this compound were removed under vacuum when drying the crystals.

¹³C{¹H}-NMR (D_8 -THF; 298K, 100 MHz) δ (ppm): 152.5, 148.2, 145.7 [$\text{C}_{\text{quaternary}}$ Ar* and Ph], 136.3, 126.6, 126.4, 122.4, 117.4 [CH, Ar* and Ph], 68.4 [O-CH₂ of THF], 53.2 [$\text{C}_{\text{quaternary}}$ TMP], 42.0 [β -CH₂ of TMP], 37.0 [CH₃ TMP], 28.2 [CH ⁱPr], 26.5 [CH₃ ⁱPr], 20.8 [γ -CH₂ TMP]

Elemental analysis: analytical calculated: C₆₁H₉₀NaN₃O₄SiZn C 70.05, H 8.67, N 4.02. Found: C 69.83, H 8.94, N 4.09

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{K}(\text{THF})_6\}^+]$ (**3a**):



388 mg of **1** (0.5 mmol) was solubilized in 5 mL of THF, 0.05 mL of 1,3,5 trifluorobenzene (0.5 mmol) were added. The resulting yellow solution was allowed to stir at room temperature for 48 h. All the volatiles were removed under reduced pressure. The white solid was solubilized with 2.5 mL of hexane and 1.5 mL of THF. Overnight storage in freezer (-33°C) furnished colourless crystal of **3a**. (676.6 mg, 85%). The yield determined in NMR scale reaction using hexamethylbenzene as internal standard in ¹H-NMR

spectrum was 90%.

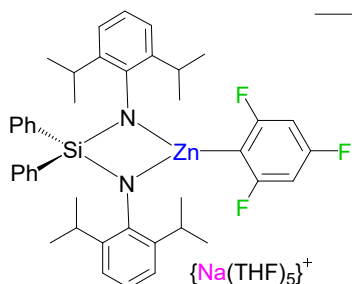
¹H-NMR (D_8 -THF; 298K; 400 MHz) δ (ppm): 7.33 [m, 4H, Ph], 6.97 [m, 6H, Ph], 6.72 [d, 4H, Ar*], 6.46 [t, 2H, Ar*], 6.33 [m, 2H, C₆H₂F₃], 4.19 [sept., 4H, CH ⁱPr], 3.61 [m, 6H, O-CH₂ THF], 1.77 [m, 6H, CH₂ THF], 0.82 [d, 24H, CH₃ ⁱPr] ¹H NMR integration revealed that approximately five THF molecules in **3a** were removed under vacuum when drying the crystals.

¹³C{¹H}-NMR (D_8 -THF; 298K, 100 MHz) δ (ppm): 170.9, 168.8 [m, C-F C₆H₂F₃], 165.2 [Zn-C, C₆H₂F₃], 152.5, 147.2, 145.0 [$\text{C}_{\text{quaternary}}$ Ar*, C₆H₂F₃ and Ph], 136.1, 127.0, 126.6, 122.2, 117.7 [CH, Ar* and Ph], 98.36 [CH, C₆H₂F₃], 28.5 [CH ⁱPr], 24.7 [CH₃ ⁱPr]

¹⁹F-NMR (D_8 -THF; 298K; 400 MHz) δ (ppm): -83.45 [m, 2F], -116.0 [m, 1F]

Elemental analysis: analytical calculated: C₁₀₄H₁₂₇F₆K₂N₄O₅Si₂Zn₂ C 66.01, H 6.77, N 2.96. Found: C 65.78, H 7.11, N 2.99

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$:



523 mg of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$ (0.94 mmol) was solubilized in 5 mL of THF, 0.097 mL of 1,3,5 trifluorobenzene (0.94

mmol) were added. The resulting yellow solution was allowed to stir at reflux for 3 h. All the volatiles were removed under reduced pressure. the white solid was solubilized with 5 mL of hexane and 3 mL of THF, that was gently heated until a yellow solution was obtained. Colourless crystals of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$ were obtained after slow cooling of this solution (474 mg, 53%). $^1\text{H-NMR}$ analysis of the filtrate of the reaction showed that this complex is the only organometallic species present in

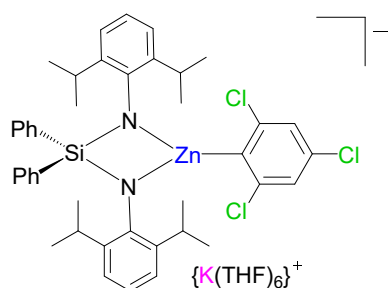
$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) $\delta(\text{ppm})$: 7.33 [m, 4H, Ph], 6.97 [m, 6H, Ph], 6.71 [d, 4H, Ar*], 6.45 [t, 2H, Ar* $J=7.5$ Hz], 6.32 [m, 2H, $\text{C}_6\text{H}_2\text{F}_3$] 4.19 [sept., 4H, CH ^iPr], 3.62 [m, 10H, O- CH_2 THF], 1.77 [m, 10H, CH_2 THF], 0.82 [d, 24H, CH_3 ^iPr] ^1H NMR integration revealed that approximately four THF molecules in this compound were removed under vacuum when drying the crystals.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 100 MHz) $\delta(\text{ppm})$: 152.5, 147.2, 145.0 [$\text{C}_{\text{quaternary}}$ Ar*, $\text{C}_6\text{H}_2\text{F}_3$ and Ph], 136.1, 127.0, 126.6, 122.2, 117.7 [CH, Ar* and Ph], 98.36 [CH, $\text{C}_6\text{H}_2\text{F}_3$], 68.4 [O- CH_2 THF], 28.5 [CH ^iPr], 26.5 [CH $_2$ THF] 24.7 [CH $_3$ ^iPr]. Relevant signals for the Zn-C and for the C-F of the $\text{C}_6\text{H}_2\text{F}_3$ could not be detected.

$^{19}\text{F}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) $\delta(\text{ppm})$: -83.4 [d, 2F], -116.1 [t, 1F]

Elemental analysis: analytical calculated: $\text{C}_{58}\text{H}_{74}\text{F}_3\text{N}_2\text{NaO}_4\text{SiZn}$ C 67.20, H 7.20, N 2.70. Found: C 67.36, H 7.65, N 2.79

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{Cl}_3)\}^- \{\text{K}(\text{THF})_6\}^+]$ (**3b**):



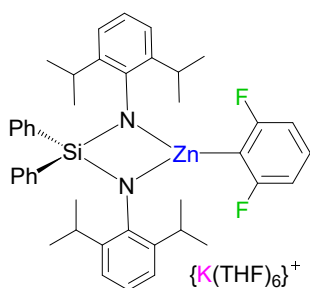
388 mg of **1** (0.5 mmol) was solubilized in 5 mL of THF, 90 mg of 1,3,5 trichlorobenzene (0.5 mmol) were added. The resulting yellow solution was allowed to stir at reflux for 21 h. All the volatiles were removed under reduced pressure. The white solid was solubilized with 3 mL of hexane and 1.5 mL of THF. Overnight storage in freezer (-33°C) furnished colourless crystals of **3b** (265mg, 65%). The yield determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard was 96%.

$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) $\delta(\text{ppm})$: 7.36 [m, 4H, Ph], 6.97 [m, 8H, Ph and $\text{C}_6\text{H}_2\text{Cl}_3$], 6.72 [d, 4H, Ar*], 6.46 [t, 2H, Ar*], 4.19 [sept., 4H, CH ^iPr], 3.61 [m, 9H, O- CH_2 THF], 1.77 [m, 9H, CH_2 THF], 0.79 [d, 24H, CH_3 ^iPr] ^1H NMR integration revealed that approximately four THF molecules in **3b** were removed under vacuum when drying the crystals.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 100 MHz) $\delta(\text{ppm})$: 152.5, 147.3, 145.8, 145.1 [$\text{C}_{\text{quaternary}}$ Ar*, $\text{C}_6\text{H}_2\text{Cl}_3$ and Ph], 136.3, 126.9, 126.6, 125.5, 122.3, 117.7 [CH, Ar*, Ph and $\text{C}_6\text{H}_2\text{Cl}_3$], 68.4 [O- CH_2 THF], 28.4 [CH ^iPr], 26.5 [CH $_2$ THF], 25.0 [CH $_3$ ^iPr]. Relevant signals for the Zn-C and for the C-Cl of the $\text{C}_6\text{H}_2\text{Cl}_3$ group could not be detected.

Elemental analysis: analytical calculated: $\text{C}_{134}\text{H}_{152}\text{Cl}_9\text{K}_3\text{N}_6\text{O}_2\text{Si}_3\text{Zn}_3$ C 62.01, H 5.90, N 3.24. Found: C 61.81, H 6.04, N 3.25

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_3\text{F}_2)\}^- \{\text{K}(\text{THF})_6\}^+]$ (**3c**):



388 mg of **1** (0.5 mmol) was solubilized in 5 mL of THF, 0.1 mL of 1,3-difluorobenzene (0.5 mmol) were added. The resulting yellow solution was allowed to stir at reflux for 5 h. All the volatiles were removed under reduced pressure. The white solid was solubilized with 2.5 mL of Hexane and 1.5 mL of THF. Overnight storage in freezer (-33°C) furnished colourless crystals of **3c**. (448 mg, 54%). The yield determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard was 90%.

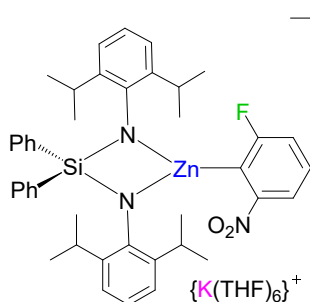
$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) δ (ppm): 7.35 [m, 4H, Ph], 6.98 [m, 6H, Ph], 6.92 [m, 1H, $\text{C}_6\text{H}_3\text{F}_2$], 6.71 [d, 4H, Ar^*], 6.5 [m, 2H, $\text{C}_6\text{H}_3\text{F}_2$], 6.45 [t, 2H, Ar^*], 4.21 [sept., 4H, CH^iPr], 0.83 [d, 24H, CH_3^iPr]. ^1H NMR integration revealed that approximately five THF molecules in **3c** were removed under vacuum when drying the crystals.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 100 MHz) δ (ppm): 152.7, 147.4, 145.1 [$\text{C}_{\text{quaternary}} \text{Ar}^*$, $\text{C}_6\text{H}_3\text{F}_2$ and Ph], 136.2, 126.9, 126.6, 122.2, 117.6 [CH, Ar^* and Ph], 109.9, 109.5 [CH, $\text{C}_6\text{H}_3\text{F}_2$], 28.5 [CH ^iPr], 24.7 [CH_3^iPr]. Relevant signals for the Zn-C and for the C-F of the $\text{C}_6\text{H}_3\text{F}_2$ could not be detected.

$^{19}\text{F}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) δ (ppm): -85.75 [s, 2F]

Elemental analysis: analytical calculated: $\text{C}_{46}\text{H}_{54}\text{F}_2\text{KN}_2\text{OSiZn}$ C 67.25, H 6.63, N 3.41. Found: C 67.22, H 6.31, N 3.73

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_3\text{FNO}_2)\}^- \{\text{K}(\text{THF})_6\}^+]$ (**3d**):



398 mg of **1** (0.5 mmol) was solubilized in 5 mL of THF. 0.05 mL of 3-fluoronitrobenzene (0.5 mmol) were added. The resulting deep red solution was allowed to stir at room temperature for 16 h. All the volatiles were removed under reduced pressure. The resulting red waxing solid was washed with 10 mL of hexane. The red solid was solubilized in 1 mL of THF and 3 mL of Hexane. Overnight storage in freezer (-33°C) furnishing red crystals of **3d** (205mg 46%). The yield determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard was 69%.

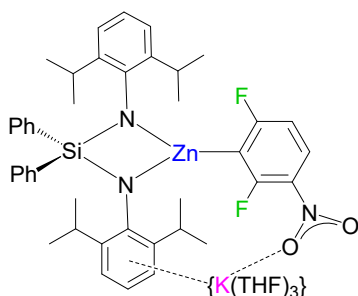
$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) δ (ppm): 7.94 [m, 1H, CH $\text{C}_6\text{H}_3\text{FNO}_2$], 7.48 [m, 4H, Ph], 7.16 [m, 1H, CH $\text{C}_6\text{H}_3\text{FNO}_2$], 6.97 [m, 6H, Ph], 6.67 [d, 4H, Ar^*], 6.40 [t, 2H, Ar^*], 4.36 [sept., 4H, CH ^iPr], 3.62 [m, 6H, O- CH_2 THF], 1.77 [m, 6H, CH_2 THF], 0.79 [d, 24H, CH_3^iPr]. ^1H NMR integration revealed that approximately five THF molecules in **3d** were removed under vacuum when drying the crystals.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 75 MHz) δ (ppm): 147.6, 144.9 [$\text{C}_{\text{quaternary}} \text{Ar}^*$, $\text{C}_6\text{H}_3\text{FNO}_2$ and Ph], 136.3, 129.4, 126.3, 126.1, 121.9, 117.1 [CH, Ar^* , $\text{C}_6\text{H}_3\text{FNO}_2$ and Ph], 68.0 [O- CH_2 THF], 28.0 [CH ^iPr], 26.2 [CH_2 THF], 24.6 [CH_3^iPr]. Relevant signals for the Zn-C and for the C-F of the $\text{C}_6\text{H}_3\text{FNO}_2$ could not be detected.

$^{19}\text{F-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: -82.26 [s, 1F]

Due to the high air and moisture sensitivity of **3c** it was not possible to obtain satisfactory elemental analysis

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_2\text{NO}_2)\}^- \{\text{K}(\text{THF})_3\}^+]$ (**3e**):



778 mg of **1** (1 mmol) was solubilized in 3.6 mL of THF in a Schlenk bottle wrapped in tin foil to prevent the contact with light. 0.11 mL of 2,4 difluoronitrobenzene (1 mmol) were added. The resulting deep red solution was allowed to stir at room temperature for 30 minutes. 6 mL of hexane were slowly added to the solution and then the mixture was stored overnight in freezer (-33°C) furnishing yellow crystals of **3e** (520mg 55%). The yield determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard was 90%.

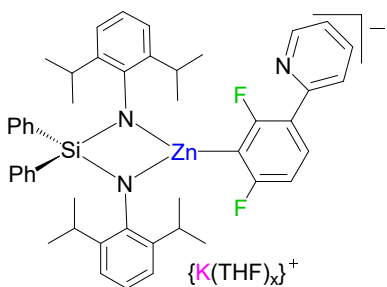
$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: 7.79 [m, 1H, CH $\text{C}_6\text{H}_2\text{F}_2\text{NO}_2$], 7.35 [m, 4H, Ph], 6.99 [m, 6H, Ph], 6.74 [m, 5H, Ar^* and $\text{C}_6\text{H}_2\text{F}_2\text{NO}_2$], 6.48 [t, 2H, Ar^*], 4.19 [sept., 4H, CH ^iPr], 3.62 [m, 9H, O- CH_2 THF], 1.77 [m, 9H, CH_2 THF], 0.82 [d, 24H, CH_3 ^iPr]. ^1H NMR integration revealed that approximately five THF molecules in **3d** were removed under vacuum when drying the crystals.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 75 MHz) $\delta(\text{ppm})$: 152.7, 147.4, 145.1 [$\text{C}_{\text{quaternary}}$ Ar^* , $\text{C}_6\text{H}_2\text{F}_2\text{NO}_2$ and Ph], 136.2, 126.9, 126.6, 122.2, 117.6 [CH, Ar^* and Ph], 109.9, 109.5 [CH, $\text{C}_6\text{H}_2\text{F}_2\text{NO}_2$] 28.5 [CH ^iPr], 24.7 [CH_3 ^iPr]. Relevant signals for the Zn-C and for other quaternary C of the $\text{C}_6\text{H}_2\text{F}_2\text{NO}_2$ fragment could not be detected

$^{19}\text{F-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: -85.75 [s, 2F]

Elemental analysis: analytical calculated: $\text{C}_{50}\text{H}_{62}\text{F}_2\text{KN}_3\text{O}_4\text{SiZn}$ C 63.61, H 6.65, N 4.47. Found: C 63.26, H 6.91, N 4.12

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_{11}\text{H}_6\text{F}_2\text{N})\}^- \{\text{K}(\text{THF})_x\}^+]$ (**3f**):



338 mg of **1** (0.44 mmol) was solubilized in 5 mL of THF, 99.5 mg of 2-(2,4-difluorophenyl)pyridine (0.5 mmol) were added. The resulting yellow solution was allowed to stir at reflux for 3 h. All the volatiles were removed under reduced pressure. 10 mL of hexane was added affording a white suspension. The suspension was filtered through celite and a white solid of **3f** was isolated (195 mg, 54%). The yield determined in NMR scale reaction using hexamethylbenzene as internal standard in $^1\text{H-NMR}$ spectrum was

95%.

$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) $\delta(\text{ppm})$: 8.51 [m, 1H, CH $\text{C}_{11}\text{H}_6\text{F}_2\text{N}$], 7.78 [m, 1H, CH $\text{C}_{11}\text{H}_6\text{F}_2\text{N}$], 7.74 [m, 1H, CH $\text{C}_{11}\text{H}_6\text{F}_2\text{N}$], 7.64 [m, 1H, CH $\text{C}_{11}\text{H}_6\text{F}_2\text{N}$], 7.36 [m, 4H, Ph], 7.08 [dd, 1H, CH $\text{C}_{11}\text{H}_6\text{F}_2\text{N}$], 6.99 [m, 6H, Ph], 6.72 [d, 4H, Ar^*], 6.65 [m, 1H, $\text{C}_{11}\text{H}_6\text{F}_2\text{N}$], 6.46 [t, 2H, Ar^*], 4.24 [sept., 4H, CH ^iPr], 0.84 [d, 24H,

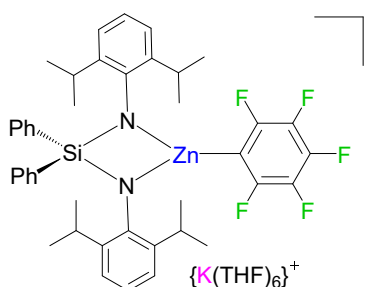
CH₃ ⁱPr]. ¹H NMR integration revealed that approximately five THF molecules in **3f** were removed under vacuum when drying the crystals.

¹³C{¹H}-NMR (D₈-THF; 298K, 75 MHz) δ(ppm): 152.7 [C_{quaternary} Ar*, Ph, C₁₁H₆F₂N], 150.1 [CH C₁₁H₆F₂N], 147.3, 145.1 [C_{quaternary} Ar*, Ph, C₁₁H₆F₂N], 136.2, 131.6 [CH Ph and C₁₁H₆F₂N], 126.7 [C_{quaternary} Ar*, Ph, pyr or C₁₁H₆F₂N], 126.6, 125.0, 122.3, 122.0 117.7, 110.6 [CH Ar*, Ph, C₁₁H₆F₂N], 28.5 [CH ⁱPr], 24.8 [CH₃ ⁱPr]. Relevant signals for the Zn-C and for other quaternary C of the C₁₁H₆F₂N₂ fragment could not be detected

¹⁹F{¹H}-NMR (D₈-THF; 298K; 400 MHz) δ(ppm): -85.32 [d, 1F], -87.31 [d, 1F]

Due to the sensitivity of **3f** it was not possible to obtain satisfactory elemental analysis

Synthesis of [$\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{F}_5)\}^- \{\text{K}(\text{THF})_6\}^+\]$ (**3h**)



493 mg of **19** (0.46 mmol) were solubilized in 5 mL of THF. The solution was cooled down to -40°C. 0.05 mL of pentafluorobenzene (0.5 mmol) were added. The mixture was allowed to stir for 30 minutes at room temperature. All the volatiles were removed under reduced pressure. The resulting waxy solid was suspended in 10 mL of hexane and the suspension was filtered through celite. The remaining yellow-white solid was solubilized in 3 mL of hexane and 0.8 mL of THF. Overnight storage in the freezer (-15°C)

furnishing yellow crystals of **3h**. Any attempt in isolating the pure product was unsuccessful due to the co-crystallization of [K(THF)_xZn(C₆F₅)₃] and Ph₂Si(NHAr*)₂. The yield determined in NMR scale reaction using hexamethylbenzene as internal standard in ¹H-NMR spectrum was 91%.

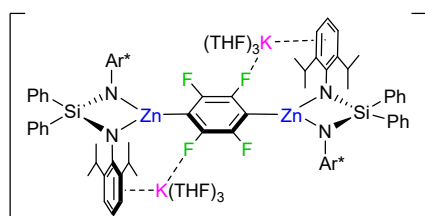
¹H-NMR (D₈-THF; 298K; 300 MHz) δ(ppm): 7.33 [m, 4H, Ph], 6.99 [m, 6H, Ph], 6.73 [d, 4H, Ar*], 6.48 [t, 2H, Ar*], 4.16 [sept., 4H, CH ⁱPr], 3.61 [m, 6H, O-CH₂ THF], 1.77 [m, 6H, CH₂ THF], 0.81 [d, 24H, CH₃ ⁱPr] ¹H NMR integration revealed that approximately five THF molecules in **3h** were removed under vacuum when drying the crystals.

¹³C{¹H}-NMR (D₈-THF; 298K, 75 MHz) δ(ppm): 151.7, 146.3 144.7 [C_{quaternary} Ar*, C₆F₅ and Ph], 135.8, 126.8, 126.4 [CH Ph] 122.0, 117.8 [CH Ar*], 68.0 [O-CH₂ THF], 28.2 [CH ⁱPr], 26.2 [CH₂ THF], 24.3 [CH₃ ⁱPr]. Relevant signals of the C₆F₅ fragment could not be detected.

¹⁹F-NMR (D₈-THF; 298K; 300 MHz) δ(ppm): -114.4 [m, 2F], -160.5 [t, 1F], -164.4 [m, 2F]

Compound **3h** could not be isolated as a pure compound. Hence not satisfactory elemental analysis could be obtained.

Synthesis of [(THF)₆K₂Zn₂{Ph₂Si(NAr*)₂}(C₆F₄)] (**3j**):



397 mg of **1** (0.39 mmol) were solubilised in 5 mL of THF. The solution was cooled down to -40°C and 0.02 mL of 1,2,4,5 tetrafluorobenzene (0.1 mmol) were added dropwise. The resulting solution was allowed

to stir at room temperature for 30 minutes. The solution was then left to stir at reflux for 16h. The next day all the volatiles were removed under reduced pressure. The obtained white solid was washed with 6 mL of hexane and solubilized in 2 ml of THF. Layering 1.5 mL of hexane on the yellow solution furnished colourless crystals of **3j** (59 mg, 11%). The yield determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard was 84%.

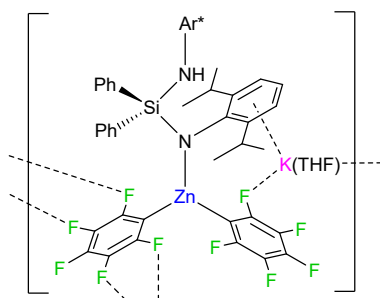
$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: 7.29 [m, 8H, Ph], 6.97 [m, 12H, Ph], 6.74 [d, 8H, Ar*], 6.48 [t, 4H, Ar*], 4.13 [sept., 8H, CH ^iPr], 3.61 [m, 10H, O-CH₂ THF], 1.77 [m, 10H, CH₂ THF], 0.78 [d, 48H, CH₃ ^iPr].

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 100 MHz) $\delta(\text{ppm})$: 152.5, 146.4 144.9 [$\text{C}_{\text{quaternary}}$ Ar*, C_6F_4 and Ph], 135.7, 126.8, 126.3 [CH Ph] 122.0, 117.3 [CH, Ar*], 68.0 [O-CH₂ THF], 28.1 [CH ^iPr], 26.2 [CH₂ THF], 24.2 [CH₃ ^iPr]. Relevant signals of the C_6F_4 fragment could not be detected.

$^{19}\text{F-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: -119.0 [s, 4F]

Elemental analysis: analytical calculated: $\text{C}_{106}\text{H}_{137}\text{F}_4\text{K}_2\text{N}_4\text{O}_7\text{Si}_2\text{Zn}_2$ C 65.03, H 7.19, N 2.92. Found: C 65.17, H 7.41, N 3.03

Synthesis of [$\{\text{Ph}_2\text{Si}(\text{NHAr}^*)(\text{NAr}^*)\text{KZn}(\text{C}_6\text{F}_5)_2\}_n$] (**4**):



398 mg of **1** (0.5 mmol) were solubilized in 5 mL of THF. The solution was cooled down to -40°C . 0.17 mL of pentafluorobenzene (1.5 mmol) were added. The mixture was allowed to stir for 1h at room temperature. All the volatiles were removed under reduced pressure. The resulting yellow solid was solubilized in 1 mL of fluorene and 1.2 mL of hexane. Overnight storage in fridge (4°C) furnishing red crystals of **4** which was isolated with variable amounts of $([\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_6)_3])$ and $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$. Despite

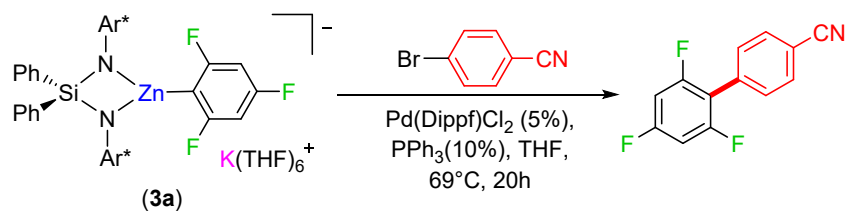
numerous attempts **4** could not be isolated as a pure compound which precluded the collection of satisfactory elemental analysis data or a meaningful ^{13}C NMR spectrum.

$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: 7.67 [m, 4H, Ph], 7.05 [m, 6H, Ph], 6.92 [d, 2H, Ar*], 6.76 [t, 1H, Ar*], 6.72 [d, 2H, Ar*], 6.59 [t, 1H, Ar*], 4.13 [sept., 2H, CH ^iPr], 3.61 [m, 6H, O-CH₂ THF], 2.55 [sept., 2H, CH ^iPr], 1.77 [m, 6H, CH₂ THF], 0.88 [d, 12H, CH₃ ^iPr], 0.55 [d, 12H, CH₃ ^iPr] It should be noted that the resonance for the NH is overlapping with the residual signal of the solvent.

$^{19}\text{F-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 300 MHz) $\delta(\text{ppm})$: -115.5 [m, 2F], -163.5 [t, 1F], -165.2 [m, 2F]

Studies on C-C bond forming reactions using **3a**

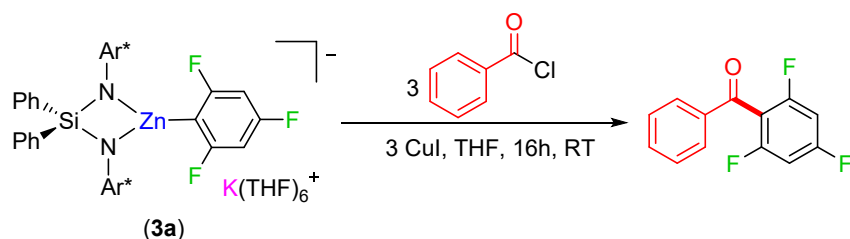
2',4',6'-trifluoro-[1,1'-biphenyl]-4-carbonitrile



384 mg of **3a** (0.5 mmol), 18.3 mg of [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($\text{Pd}(\text{dppf})\text{Cl}_2$) (0.025 mmol, 5%), 13 mg of triphenylphosphine (0.05 mmol, 10%) and 82 mg of 4-Bromobenzonitrile (0.45 mmol) were solubilized in 10 mL of THF. The mixture was let stir for 20h at 66°C. The reaction were quenched with a saturated solution NH_4Cl and extract with Et_2O . The combined organic layers were washed with HCl, dried with MgSO_4 and concentrated. 11.7 mg of hexamethylbenzene were added as internal standard (NMR yield 0.28 mmol, 63%). The compound was purified by chromatographic column (silica gel, hexane:ethyl acetate, 80:20) affording an isolate yield of 49%. The ^1H -NMR and ^{19}F -NMR spectra fully agreed with those reported in literature.^[4]

^1H -NMR (CDCl_3 ; 298K; 400 MHz) δ (ppm): 7.75 [d, 2H], 7.55 [d, 2H], 6.80 [m, 2H,] $^{19}\text{F}\{^1\text{H}\}$ -NMR (CDCl_3 ; 298K; 400 MHz) δ (ppm): -106.4 [t, 1F], -110.0 [d, 2F]

Phenyl(2,4,6-trifluorophenyl)methanone



384 mg of **3a** (0.5mmol) were solubilized in 5 mL of THF. The mixture was cooled down to -20°C . 286 mg of CuI (1.5 mmol) and 0.18 mL of benzoylchloride (1.5 mmol) were added. The flask was removed from the bath and the mixture was allowed to reach the room temperature. The mixture was let stir for 16h, affording a red-brown solution. The reaction was quenched with a saturated solution NH_4Cl and extract with Et_2O . The combined organic layers were washed with HCl, dried with MgSO_4 and concentrated. 10.2 mg of Hexamethylbenzene were added as internal standard (NMR yield 0.35 mmol, 70%). The compound was purified by chromatographic column (silica gel, hexane:ethyl acetate, 80:20), despite the attempt of a complete purification impurities were still present together with the products. ^1H -NMR and ^{19}F -NMR spectra are in agreement with those previously reported in literature for this compound.^[5]

^1H -NMR (CDCl_3 ; 298K; 400 MHz) δ (ppm): 7.86 [d, 2H], 7.64 [m, 1H], 7.50 [t, 2H], 6.78 [m, 2H,]

^{19}F -NMR (CDCl_3 ; 298K; 400 MHz) δ (ppm): -103.6 [m, 1F], -108.1 [t, 2F]

General Experimental Procedure for the ¹H NMR Monitoring of the Zn-H Exchange Reactions

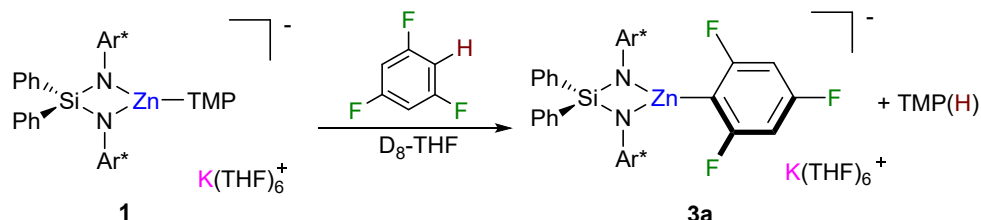
In a glovebox, a J. Young's NMR tube was filled with 78 mg of **1** (0.1 mmol), 16 mg of hexamethylbenzene (0.09 mmol) as internal standard and 0.45 mL of D₈-THF. The initial ratio of base calculated by integration in ¹H-NMR spectrum relative to the Hexamethylbenzene. 0.1 mmol of fluoroarene was introduced and the mixture was heated at 69°C in an oil bath (when needed). The reactions times were measured from this point in regular intervals of time until full conversion by ¹H NMR spectrum. All the yields were calculated by integration of the products relative to the hexamethylbenzene in the ¹H NMR spectrum.

NMR monitoring of the reaction of **1** with 1,3,5 trifluorobenzene

75.7 mg of **1** (0.1 mmol) and 18.6 mg of hexamethylbenzene were solubilized in 0.5 mL of D₈-THF together with a precise amount of Hexamethylbenzene (used as internal standard) in a Young j tube. 9.8 μL of 1,3,5 trifluorobenzene (**2a**) were added to the mixture. ¹H-NMR spectrum was recorded 5' minutes after the addition of the fluorarene (**Figure S 1**). The mixture was heated for 3 hours at 69°C in an oil bath. New NMR spectrum was recorded after the heating (**Figure S 2**). The amount of the component of the mixture were calculated against the mass of the internal standard according to the following equation:

$$n_c = \frac{\int \text{signal}}{N_H} * \frac{m_{hex.}}{MM_{hex.}} \text{equation 1}$$

n_c = number of moles of the compounds N_H = number of the proton assigned to the chosen resonance $m_{hex.}$ = mass of hexamethylbenzene $MM_{hex.}$ = molecular mass of hexamethylbenzene



1	5 min. RT	3h 69°C
1	0.1 mmol	0
1,3,5 trifluorobenzene	0.8 mmol	0
3a	0.01 mmol (1%) ^a	0.9 mmol (90%) ^a
TMP(H)	0.03 mmol	0.11 mmol

Scheme S 1 Metalation of 1,3,5 trifluorobenzene monitored by NMR spectroscopy. The spectra re recorded after the addition of trifluorobenzene and after 3h at 69°C. The number of moles are calculated against Hexamethylbenzene. (a= NMR yield)

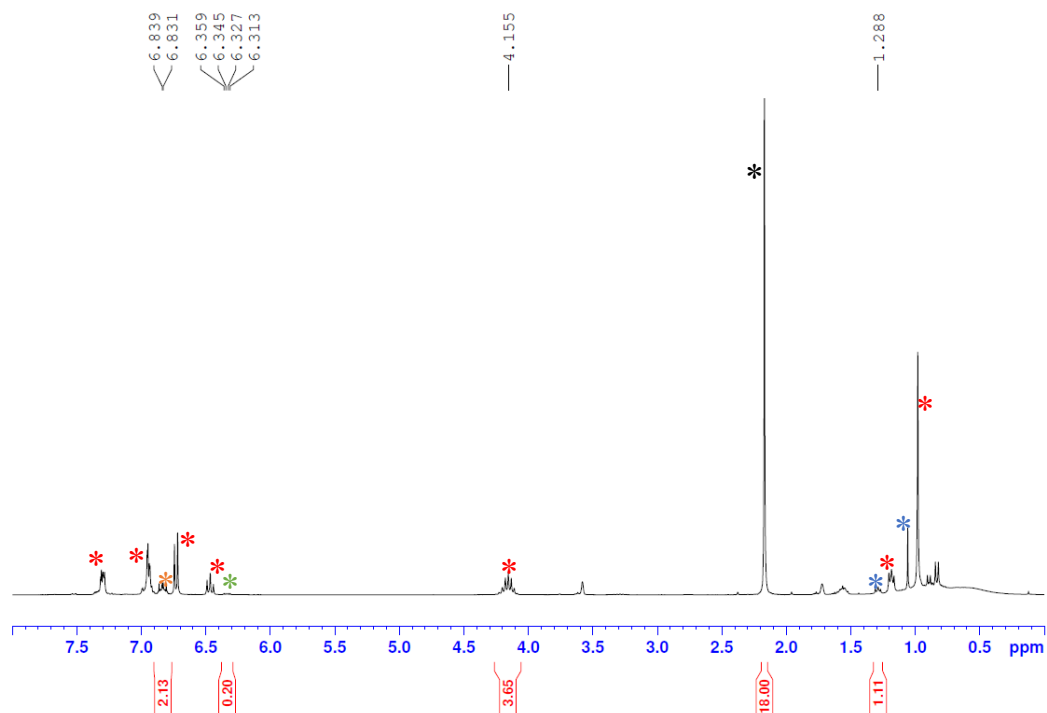


Figure S 1 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 400 MHz, 298 K) spectrum of reaction between **1** and 1,3,5 trifluorobenzene, after 5 minutes at room temperature. (*= hexamethylbenzene, * = **1**, * = **3a**, * = **TMP(H)**, * = 1,3,5 trifluorobenzene)

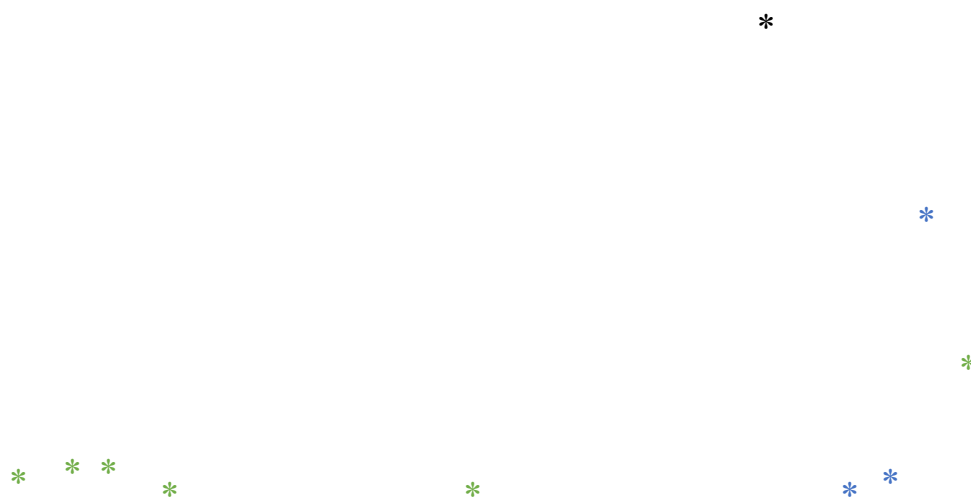


Figure S 2 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 400 MHz, 298 K) spectrum of reaction between **1** and 1,3,5 trifluorobenzene, after 3 hours at 69°C. (*= hexamethylbenzene, * = **3a**, * = **TMP(H)**)

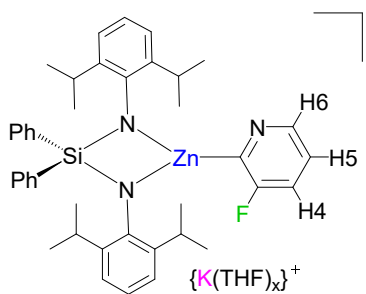
Reaction of **1** with 1,3,5 trifluorobenzene (**2a**) in presence of [2.2.2]cryptand

38 mg of **1** (0.05 mmol) and 8.8 mg of hexamethylbenzene (0.05 mmol), used as internal standard, were solubilised in 0.45 mL D₈-THF affording a light yellow mixture. 19.6 mg of [2.2.2]cryptand (0.05 mmol) and 5.4 μL of 1,3,5 trifluorobenzene (0.05 mmol) were added to the solution. The mixture was heated in a hot bath at 69°C for 3h. **3a** was found formed in 96% yield, by integration against hexamethylbenzene in ¹H-NMR spectrum.

Reaction of [(PMDETA)KZn(TMP)Et₂] with 2,4-difluoronitrobenzene

47 mg of [(PMDETA)KZn(TMP)Et₂] (0.1 mmol) freshly prepared, according to the method reported in the literature,^[6] were solubilized in 0.45 mL of C₆D₆ affording a light yellow solution. 3 μL of hexafluorobenzene (0.025 mmol) and 7.7 mg of hexamethylbenzene (0.05 mmol) were added as internal standards. 11 μL of 2,4-difluoronitrobenzene (0.1 mmol) were added dropwise to the mixture. After the addition an insoluble dark precipitate appears instantaneously. The ¹⁹F-NMR spectrum shows two signals compatible with metalation in C3 position, their yield was calculated in 8% yield by integration against hexafluorobenzene. The ¹H-NMR spectrum shows an intractable mixture of products.

Synthesis of [$\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_5\text{H}_3\text{FN})\}^- \{\text{K}(\text{THF})_x\}^+$] (**3g**)



34.6 mg of **1** (0.05 mmol) and 6.9 mg of hexamethylbenzene (0.04 mmol), as internal standard, were solubilised in 0.45 mL of D₈-THF affording a yellow solution, 4.1 μL of 3-Fluoropyridine (0.05 mmol). The mixture was heated at 69°C for 16h. The yield determined using hexamethylbenzene as internal standard was 89%.

¹H-NMR (D₈-THF; 298K; 400 MHz) δ(ppm): 7.96 [d, 1H, H6], 7.92 [t, 1H, H5], 7.32 [m, 4H, Ph], 7.23 [m, 1H, H4], 6.99 [m, 6H, Ph], 6.75 [d, 4H, Ar*], 6.50 [t, 2H, Ar*], 4.20 [sept., 4H, CH ⁱPr], 0.86 [d, 24H, CH₃ ⁱPr]

¹³C{¹H}-NMR (D₈-THF; 298K, 75 MHz) δ(ppm): 168.3, 152.2, 146.8, 144.5 [C_{quaternary} Ar*, Ph, C₅H₃FN], 143.8 [CH C6 C₅H₃FN], 135.9 [CH Ph], 135.2 [CH C5 C₅H₃FN], 134.9 [CH C4 C₅H₃FN], 126.4 [CH Ph], 122.0, 117.5 [CH Ar*], 49.9 [C_{quaternary} TMP(H)], 38.9 [β-CH₂ TMP(H)], 32.2 [CH₃ TMP(H)], 28.1 [CH ⁱPr], 24.2 [CH₃ ⁱPr], 19.4 [γ-CH₂ TMP(H)],

¹⁹F{¹H}-NMR (D₈-THF; 298K; 400 MHz) δ(ppm): -102.2 [s, 1F]

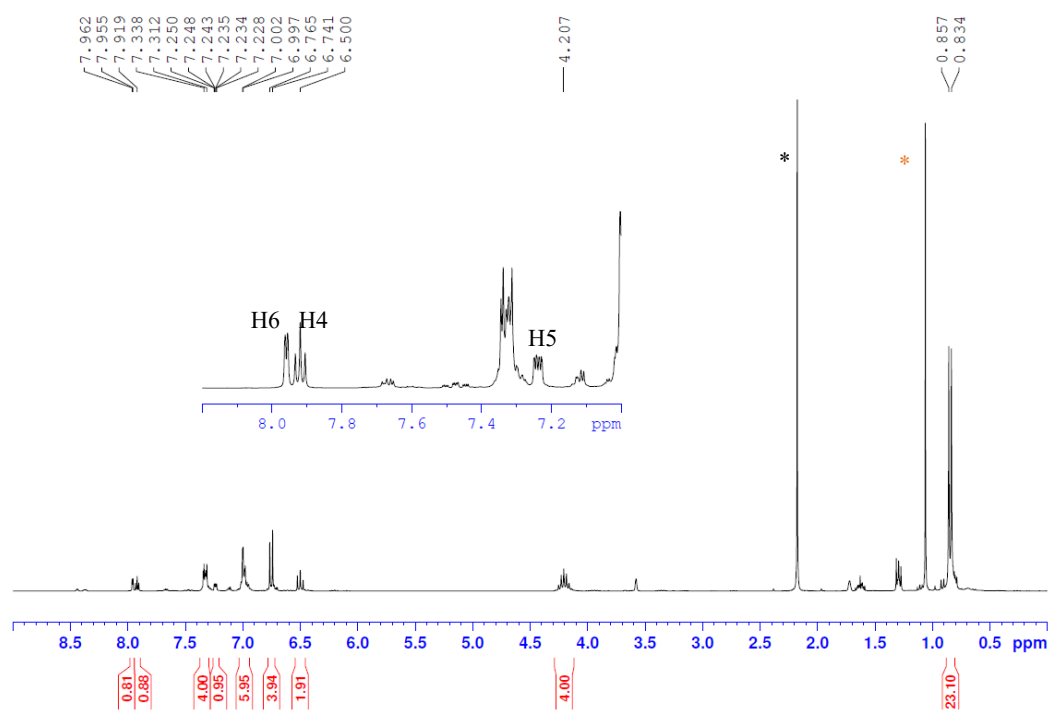


Figure S 3 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 400 MHz, 298 K) spectrum of reaction between **1** and 3-fluoropyridine, after 16 hours at 69°C . The spectrum was magnified in the area between 8.2 and 7.5 ppm. (* = hexamethylbenzene, * = TMP(H))

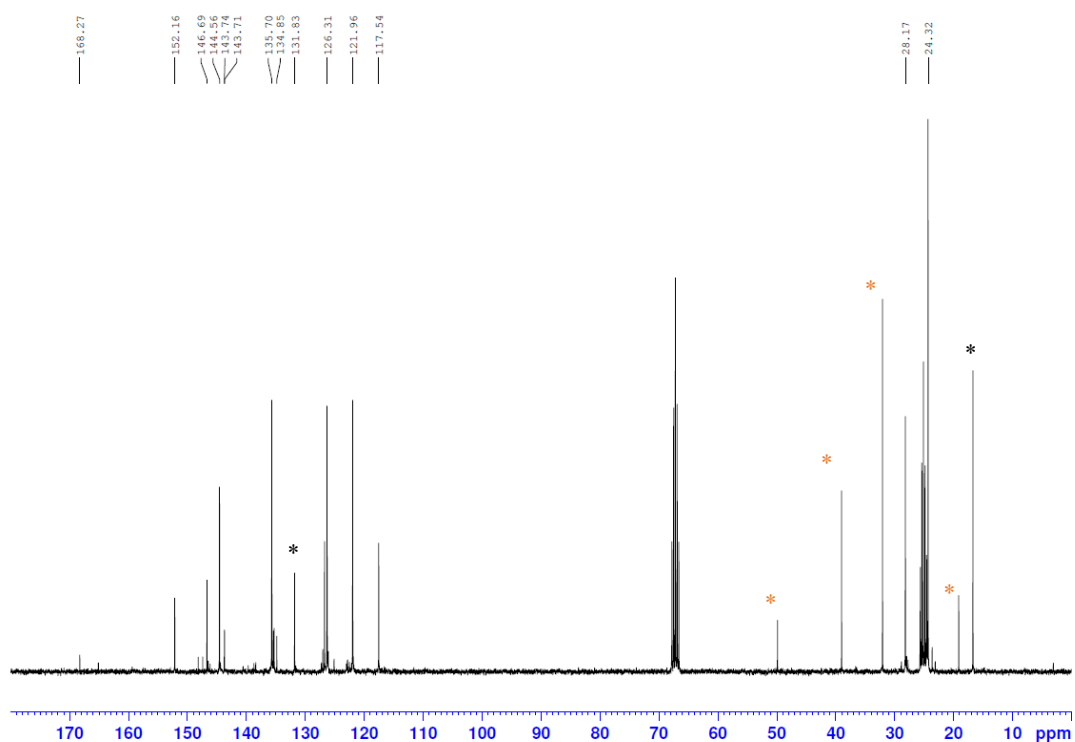


Figure S 4 $^{13}\text{C}\{^1\text{H}\}$ -NMR ($D_8\text{-THF}$, 75 MHz, 298 K) spectrum of reaction between **1** and 3-fluoropyridine, after 16 hours at 69°C . (* = hexamethylbenzene, * = TMP(H))

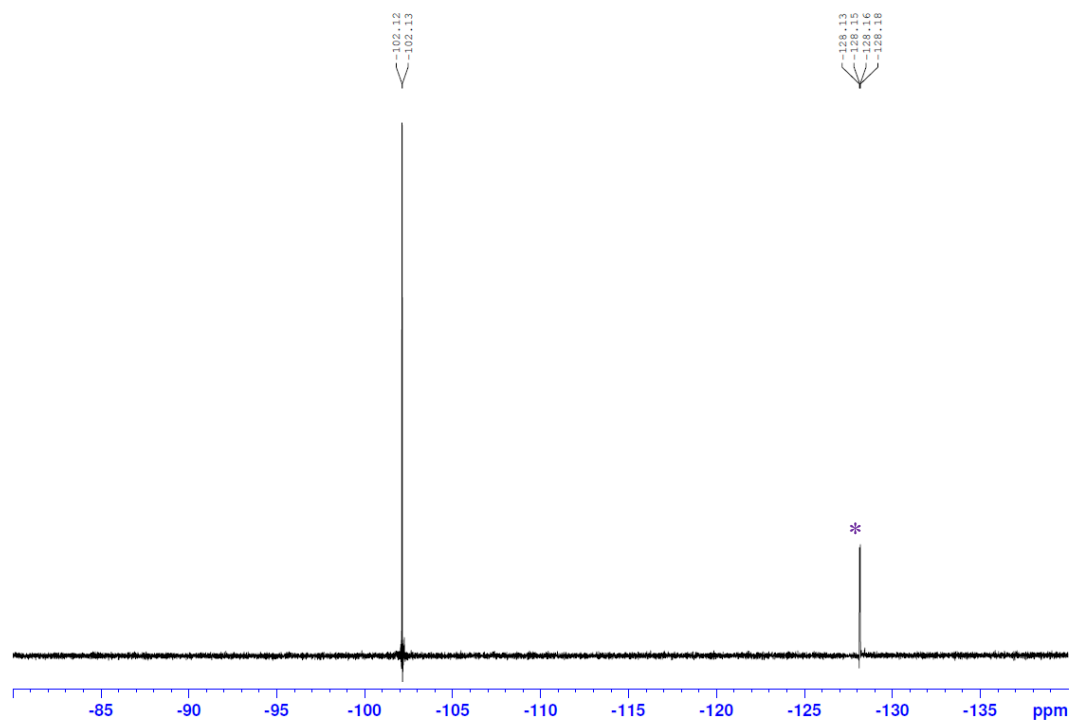


Figure S 5 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of reaction between **1** and 3-fluoropyridine, after 16 hours at 69°C. (*= 1,2,4,5-tetrafluorobenzene)

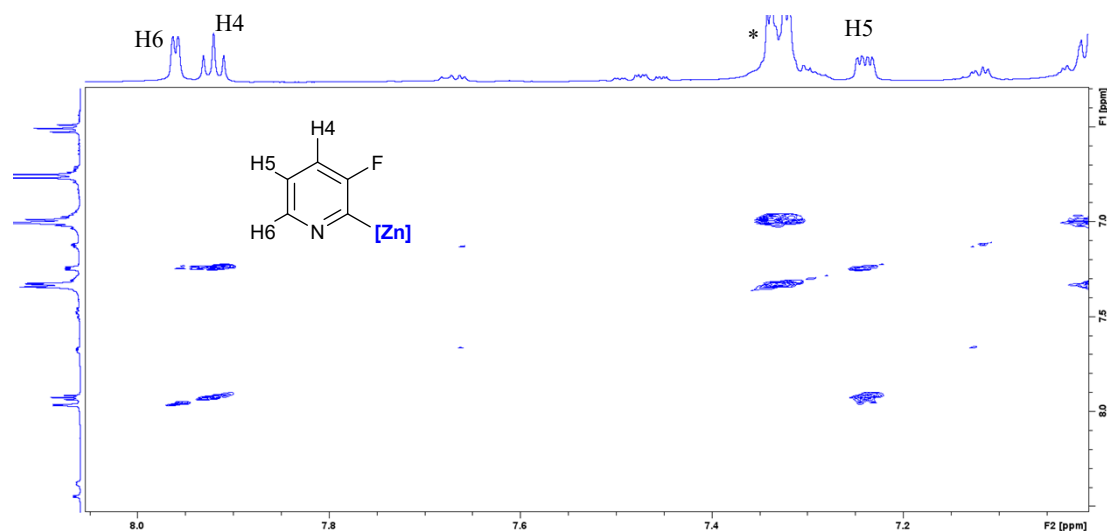
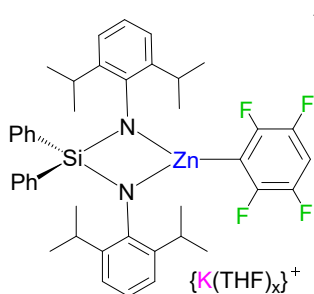


Figure S 6 ^1H -COSY (D_8 -THF, 300.1 MHz, 298 K) spectrum of **3g** magnified between 8.2 and 7.0 ppm, in the spectrum it is possible notice the correlation between the proton H5 and both the protons H4 and H6. The resonance of the proton in C4 appears as a triplet due to the coupling with the fluorine atom. ($[\text{Zn}] = [\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}\}^-]$, *)

Synthesis of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_5\text{HF}_4)\}^- \{\text{K}(\text{THF})_x\}^+]$ (**3i**)



34.2 mg of **1** (0.05 mmol), were solubilised in 0.45 mL D_8 -THF affording a light yellow mixture, 4 μL of α,α,α trifluorotoluene (0.032 mmol) and 10.1 mg of hexamethylbenzene (0.06 mmol) were added as internal standards. The tube was placed in cold bath at -40°C and 5 μL of 1,2,4,5 tetrafluorobenzene

(0.05 mmol, 1 eq.) were added to the mixture. The yield determined using hexamethylbenzene as internal standard was 89%.

$^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) $\delta(\text{ppm})$: 7.37 [m, 4H, Ph], 7.00 [m, 6H, Ph], 6.80 [m, 1H, C_5HF_4] 6.75 [d, 4H, Ar^*], 6.50 [t, 2H, Ar^*], 4.20 [sept., 4H, CH^iPr], 0.84 [d, 24H, CH_3^iPr]

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K, 75 MHz) $\delta(\text{ppm})$: 151.9, 146.6, 144.7 [$\text{C}_{\text{quaternary}} \text{Ar}^*$, Ph, C_5HF_4], 135.9, 126.4 [CH Ph], 122.0, 117.7 [CH Ar^*], 28.2 [CH ^iPr], 24.3 [CH_3^iPr]

$^{19}\text{F}\{^1\text{H}\}\text{-NMR}$ ($\text{D}_8\text{-THF}$; 298K; 400 MHz) $\delta(\text{ppm})$: -116.4 [m, 2F], -142.1 [m, 2F]

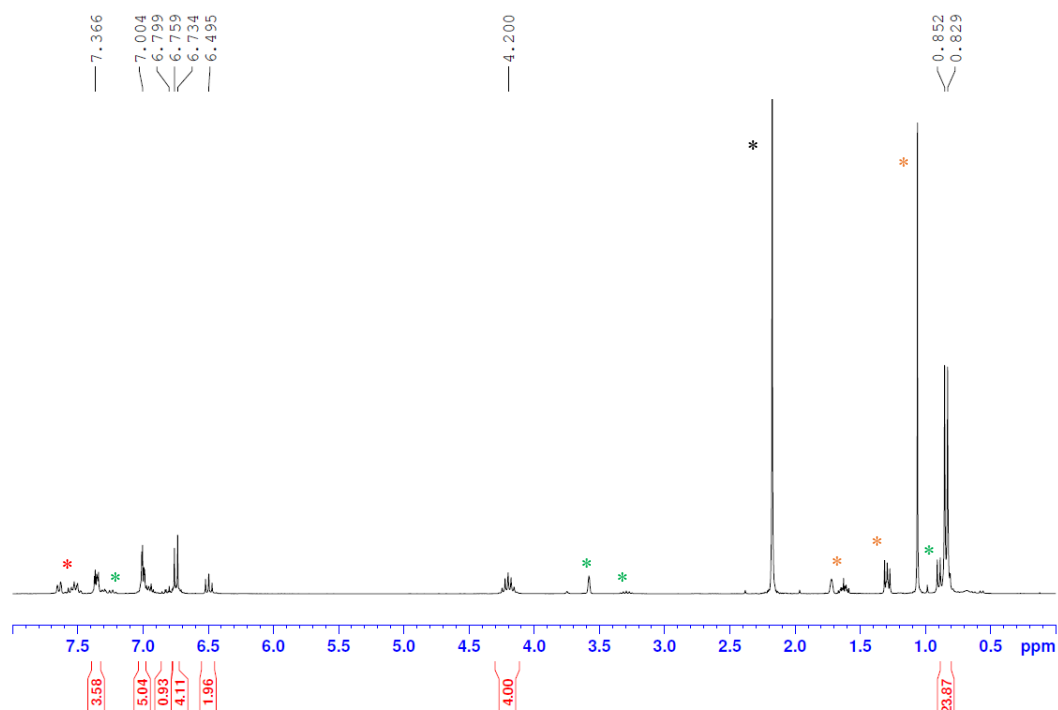


Figure S 7 $^1\text{H-NMR}$ ($\text{D}_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of 1,2,4,5 tetrafluorobenzene. (* = hexamethylbenzene, * = TMP(H) , * = tetrafluorotoluene * = $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$)

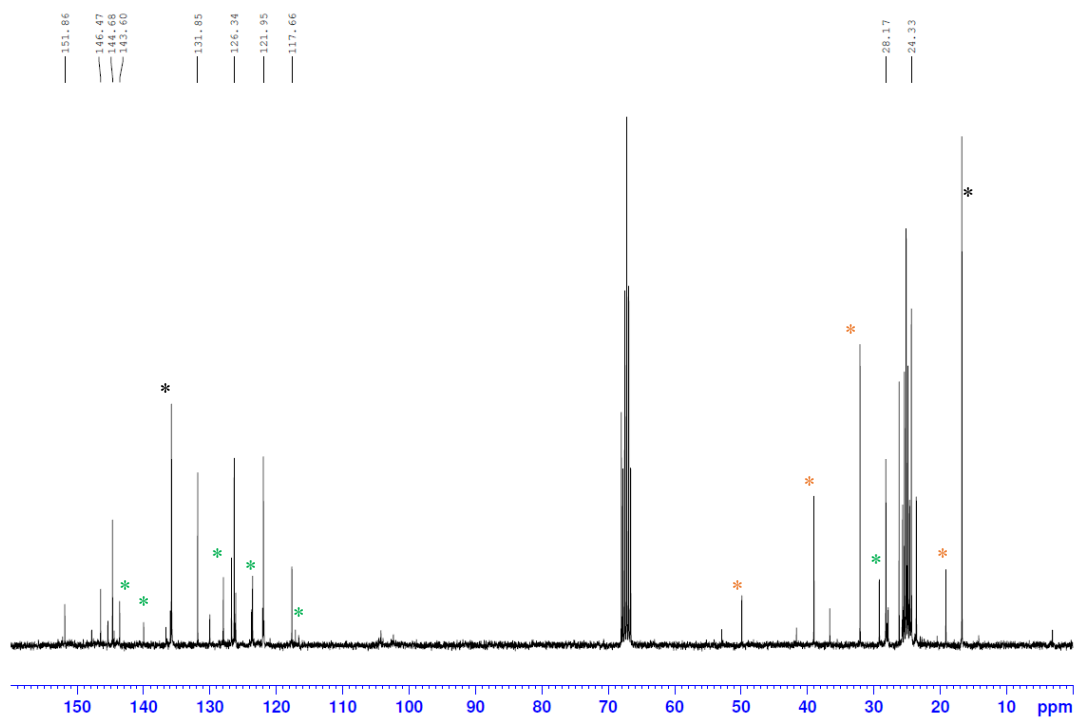


Figure S 8 $^{13}\text{C}\{^1\text{H}\}$ -NMR (D_8 -THF, 75 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of 1,2,4,5 tetrafluorobenzene. (* = hexamethylbenzene, * = TMP(H), * = $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$)

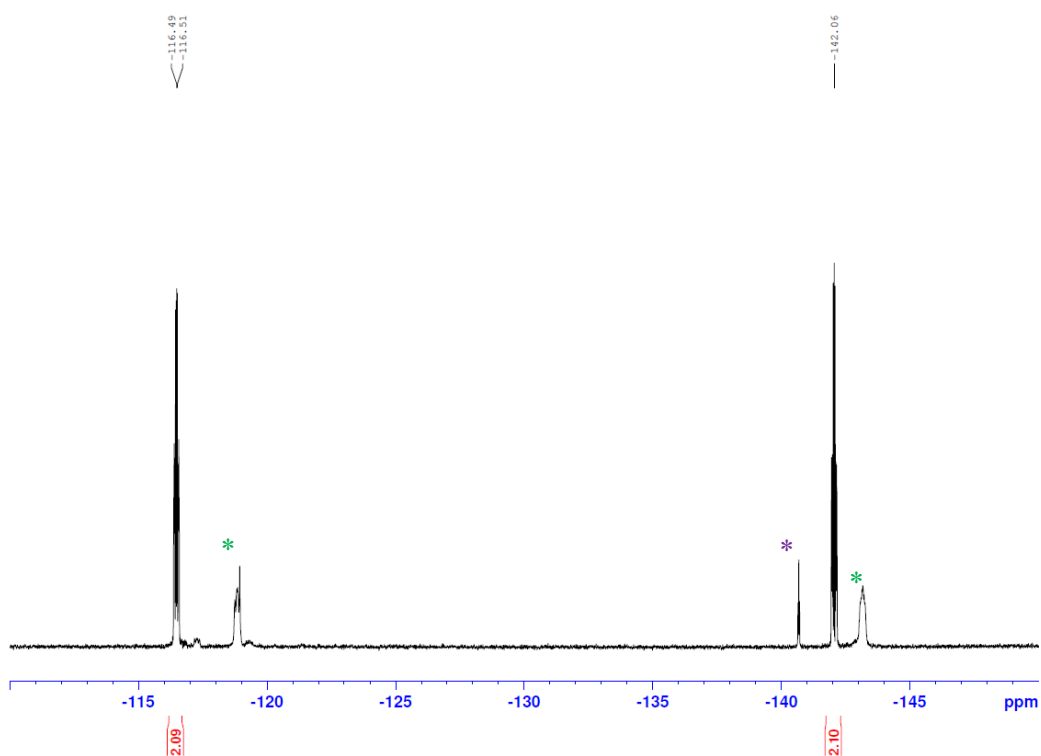
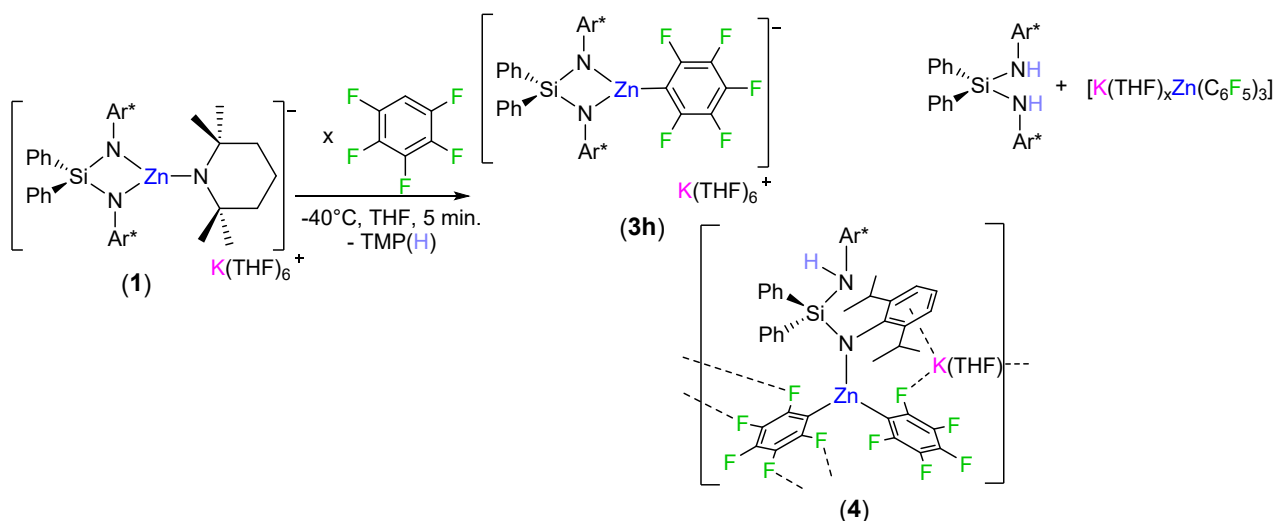


Figure S 9 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of 1,2,4,5-tetrafluorobenzene, after 5 minutes. (* = $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_4\text{H})_3]$, * = 1,2,4,5-tetrafluorobenzene)

Reaction of **1** with variable amounts of pentafluorobenzene

51 mg of **1** (0.07 mmol), were solubilised in 0.45 mL D₈-THF affording a light yellow mixture, 4.4 μL of α,α,α-trifluorotoluene (0.036 mmol) and 8.8 mg of hexamethylbenzene (0.05 mmol) were added as internal standards. The tube was placed in cold bath at -40°C and 7.8 μL of pentafluorobenzene (0.07 mmol, 1 eq.) were added to the mixture. The solution was allowed to warm up at room temperature for 5 minutes before the analysis with multinuclear NMR spectroscopy was performed. The addition of pentafluorobenzene were repeated in total 3 times. The products are summarized in **Scheme S 2**



Scheme S 2 Metalation of the pentafluorobenzene using **1** as base.

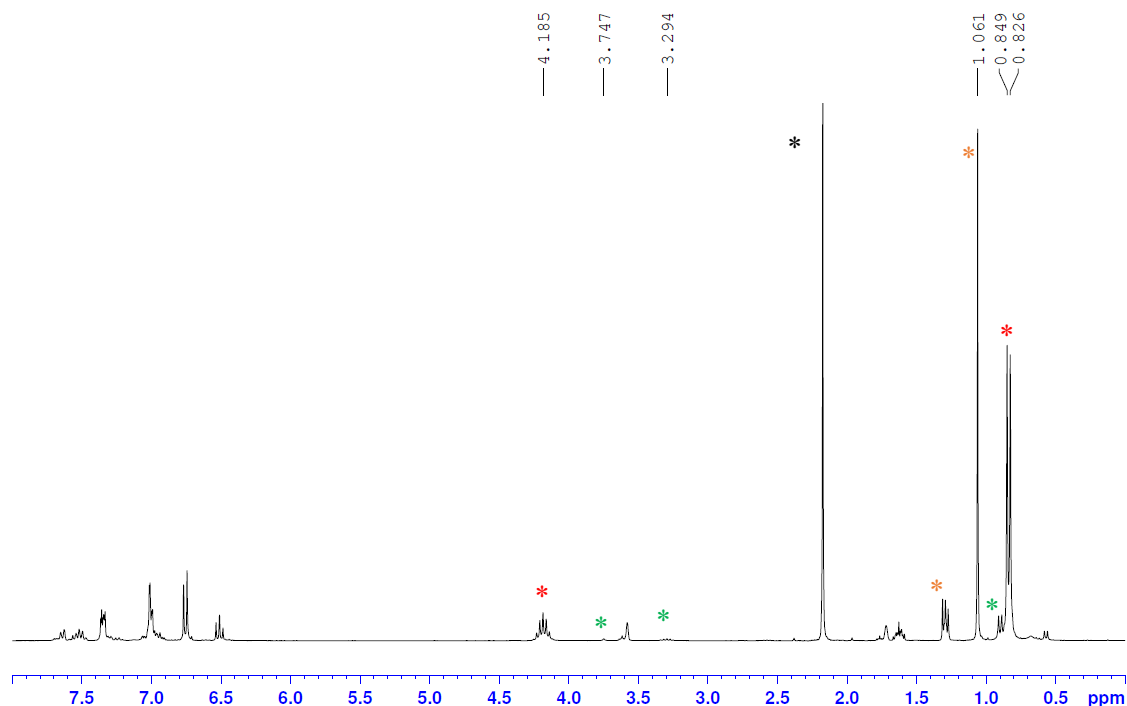


Figure S 10 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of pentafluorobenzene, after 5 minutes. (* = **3h**, * = $\text{Ph}_2\text{Si}(\text{NAr}^*)_2$, * = hexamethylbenzene, * = $\text{TMP}(\text{H})$)

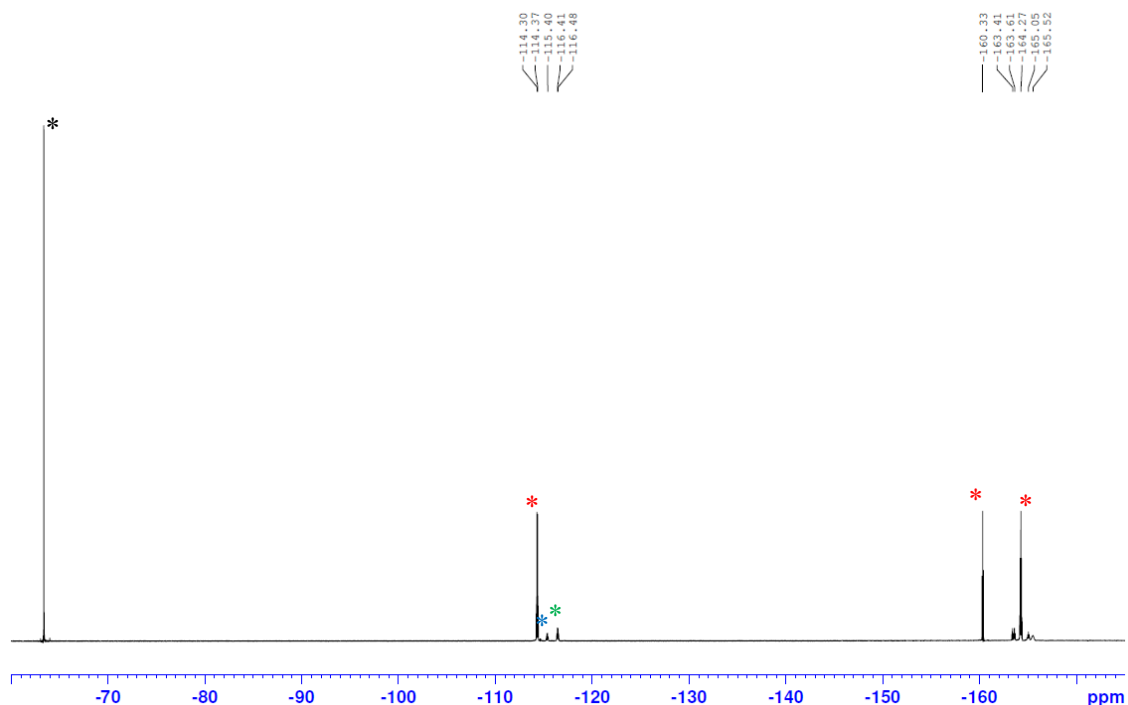


Figure S 11 $^{19}\text{F-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of pentafluorobenzene, after 5 minutes. (* = **3h**, * = **4**, * = $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_6)_3]$, * = trifluorotoluene)

The addition of the first equivalent of pentafluorobenzene, leads to a complete conversion of **1** in **3h**. The reaction proceeds with concomitant formation of $\text{TMP}(\text{H})$ (as shown in **Figure S 5**). The $^{19}\text{F-NMR}$

spectrum confirms the presence of only **3h**, as the major product of the reaction (**4** and $[K(THF)_xZn(C_6F_5)_3]$ are present only in traces) (**Figure S 6**)

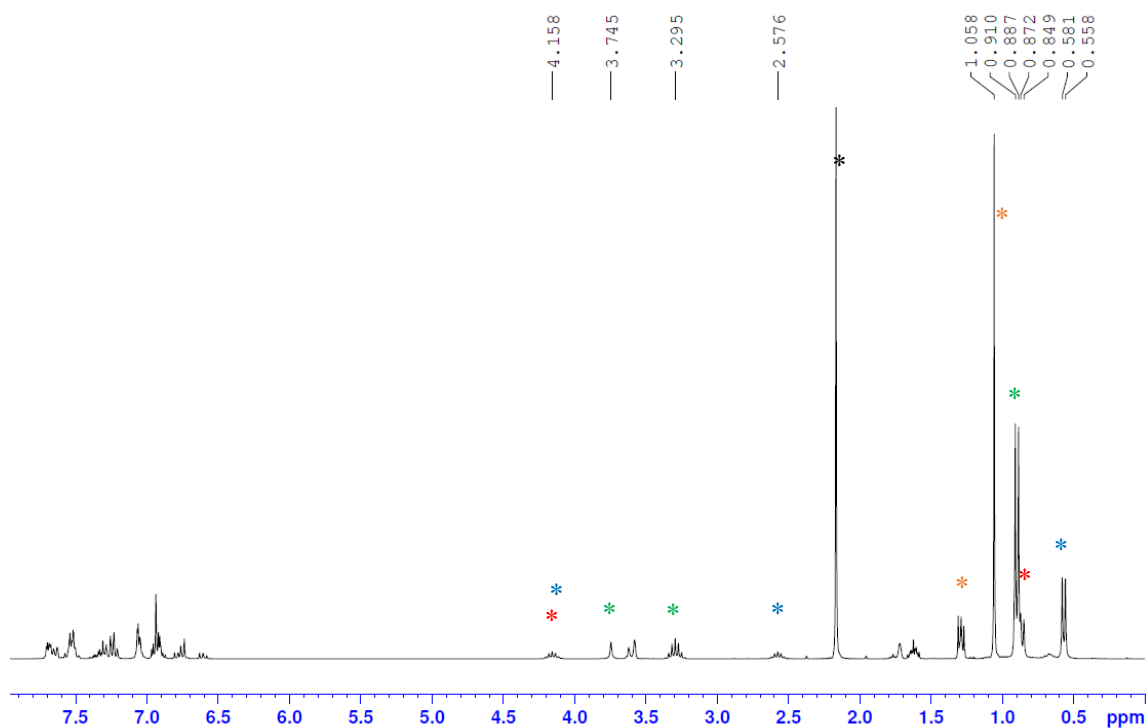


Figure S 12 1H -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of pentafluorobenzene, after 5 minutes. (* = **3h**, * = **4**, * = $Ph_2Si(NHAr^*)_2$, * = hexamethylbenzene, * = TMP(H))

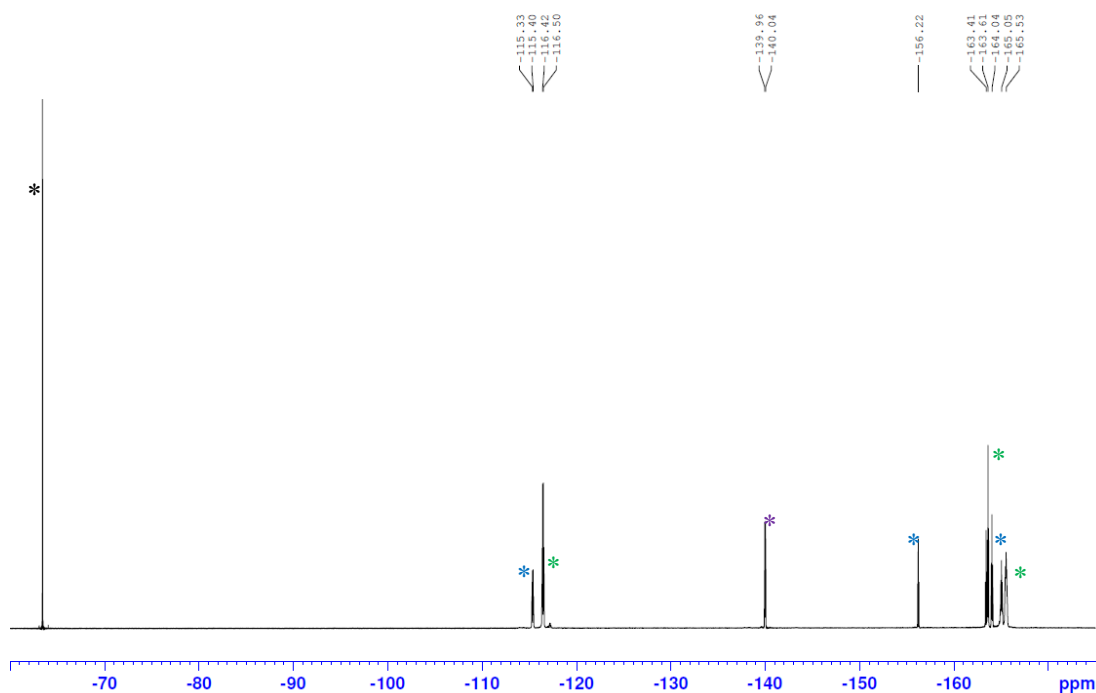


Figure S 13 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of pentafluorobenzene, after 5 minutes. (* = **3h**, * = **4** * = $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_6)_3]$, * = trifluorotoluene, * = pentafluorobenzene)

Adding a three fold excess of pentafluorobenzene **1** exhibits a polybasicity. **3h** further reacts through the silyl bis(amido) ligand, generating **4** and $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$ (**Figure S 7**). Notably the reaction did not proceed stepwise and **4** and $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$ were generated with almost the same ratio. Pentafluorobenzene is still present in the mixture (**Figure S 8**) after 5 minutes due to the slower reactivity of $[\text{Ph}_2\text{Si}(\text{NHAr}^*)_2]^{2-}$ towards protonation. After 16h the reaction goes to completion consuming all the pentafluorobenzene and having $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$ (**Figure S 9**) $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_6)_3]$ (**Figure S 10**) as only products.

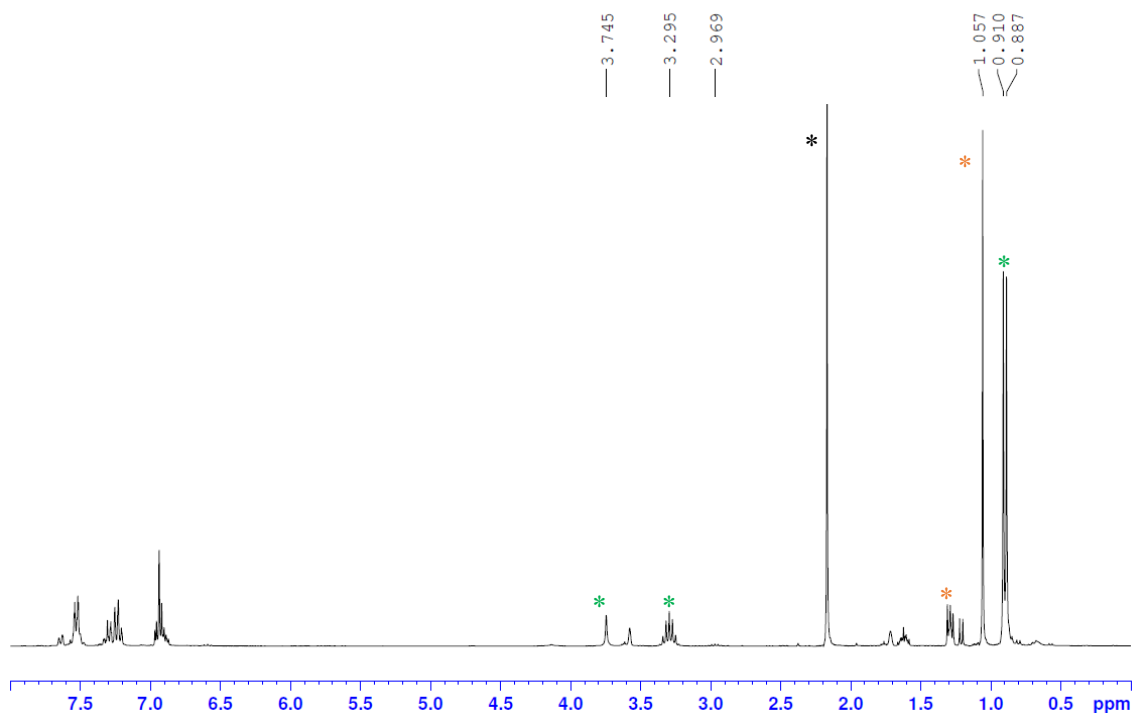


Figure S 14 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of pentafluorobenzene, after 16 hours. (*= $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$, *=hexamethylbenzene, *= TMP(H))

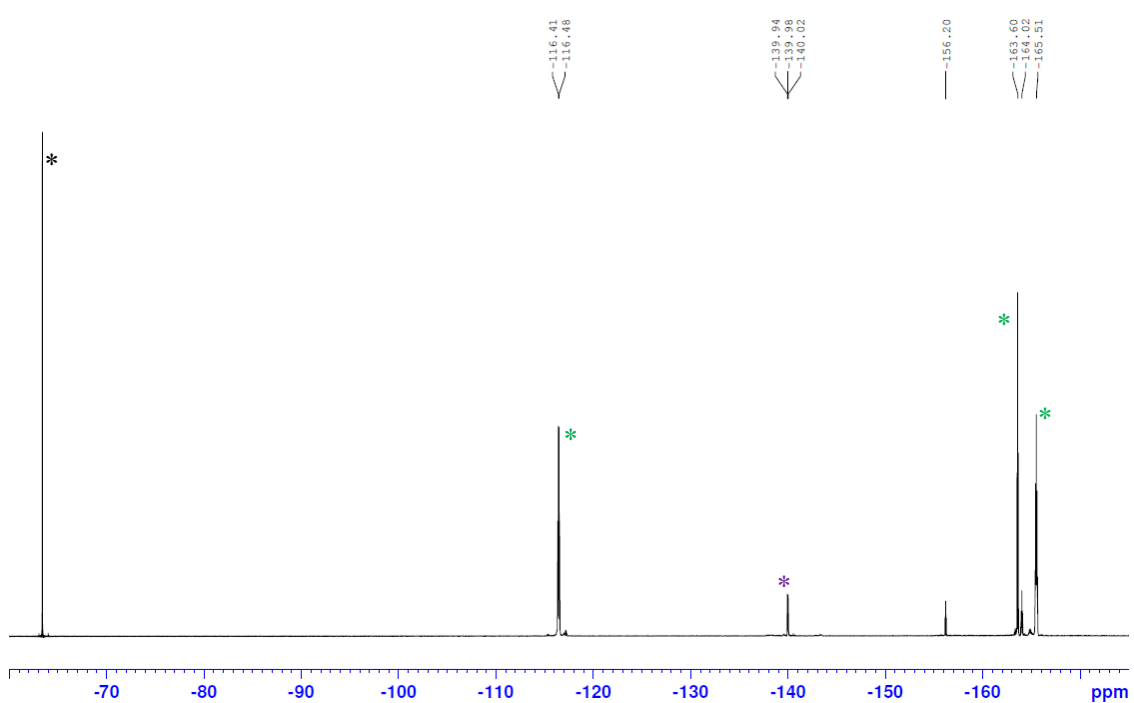
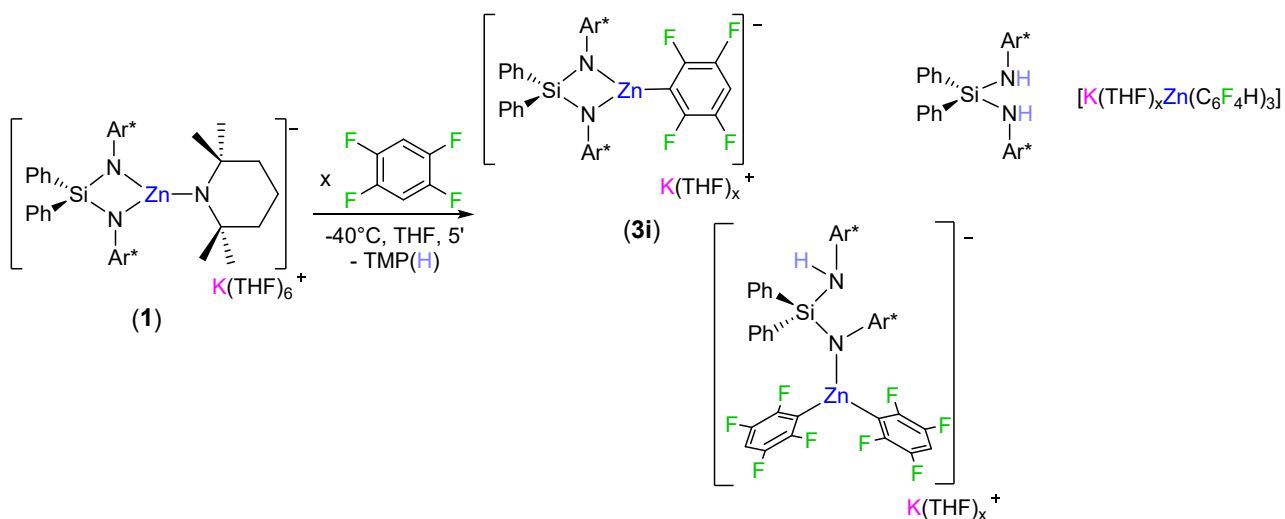


Figure S 15 $^{19}\text{F-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of pentafluorobenzene, after 16 hours. (*= $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_5)_3]$, *=trifluorotoluene, *=pentafluorobenzene)

Reaction of **1** with variable amount of 1,2,4,5-tetrafluorobenzene

34.2 mg of **1** (0.05 mmol), were solubilised in 0.45 mL D₈-THF affording a light yellow mixture, 4 μL of α,α,α-trifluorotoluene (0.032 mmol) and 10.1 mg of hexamethylbenzene (0.06 mmol) were added as internal standards. The tube was placed in cold bath at -40°C and 5 μL of 1,2,4,5 tetrafluorobenzene (0.05 mmol, 1 eq.) were added to the mixture. The solution was allowed to warm up at room temperature for 5 minutes before the analysis with multinuclear NMR spectroscopy was performed. The addition of tetrafluorobenzene were repeated in total 3 times. The products are summarized in **Scheme S 3**..



Scheme S 3 Metalation of the 1,2,4,5 tetrafluorobenzene using **1** as base

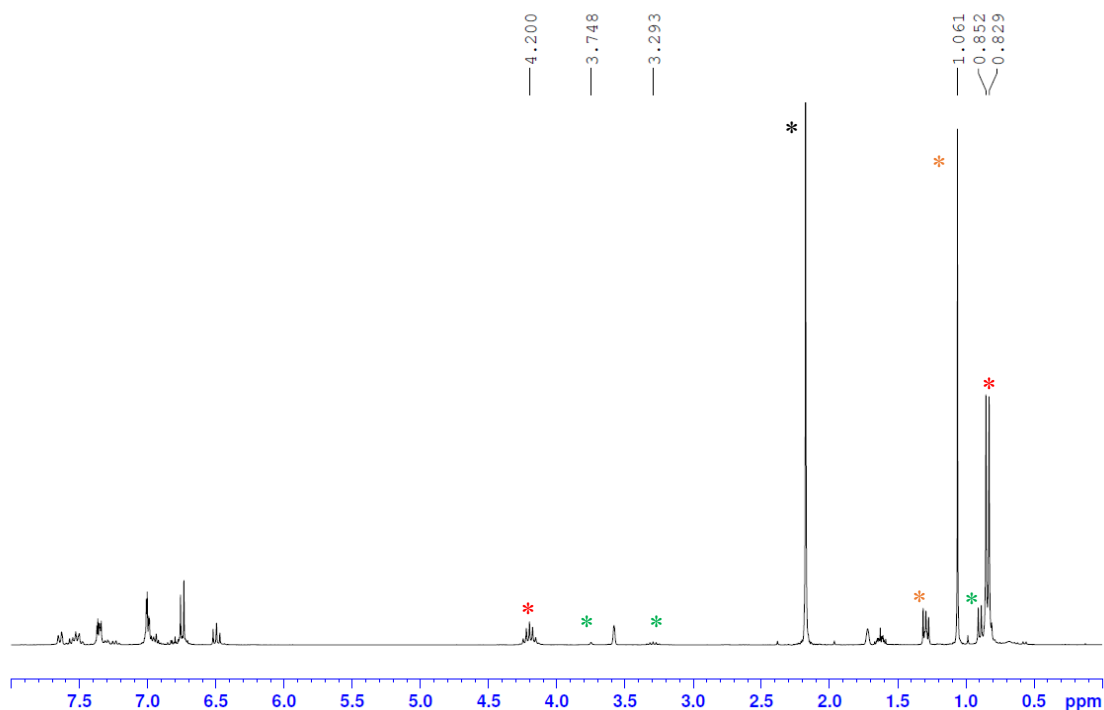


Figure S 16 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of 1,2,4,5-tetrafluorobenzene, after 5 minutes. (*= **3i**, *= $\text{Ph}_2\text{Si}(\text{NAr}^*)_2$, *=hexamethylbenzene, *= $\text{TMP}(\text{H})$)

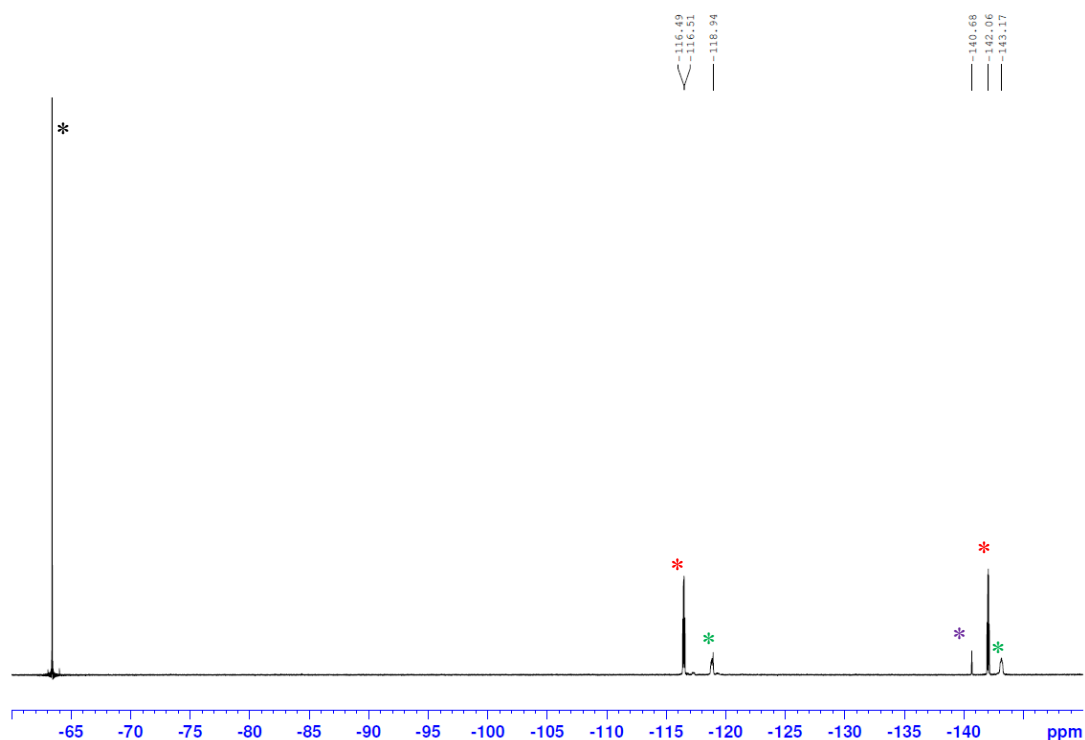


Figure S 17 $^{19}\text{F-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 1 eq. of 1,2,4,5-tetrafluorobenzene, after 5 minutes. (*= **3i**, *= $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_4\text{H})_3]$, *=trifluorotoluene, *= 1,2,4,5-tetrafluorobenzene)

The addition of the first equivalent of 1,2,4,5-tetrafluorobenzene, leads to a complete conversion of **1** in **3i**.

The reaction proceeds via liberation of $\text{TMP}(\text{H})$ (as shown in **Figure S 11**). The $^{19}\text{F-NMR}$ spectrum confirms

the presence of **3i**, as the principle product of the reaction ($[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_4\text{H})_3]$) and unreacted tetrafluorobenzene are present only in traces (**Figure S 12**)

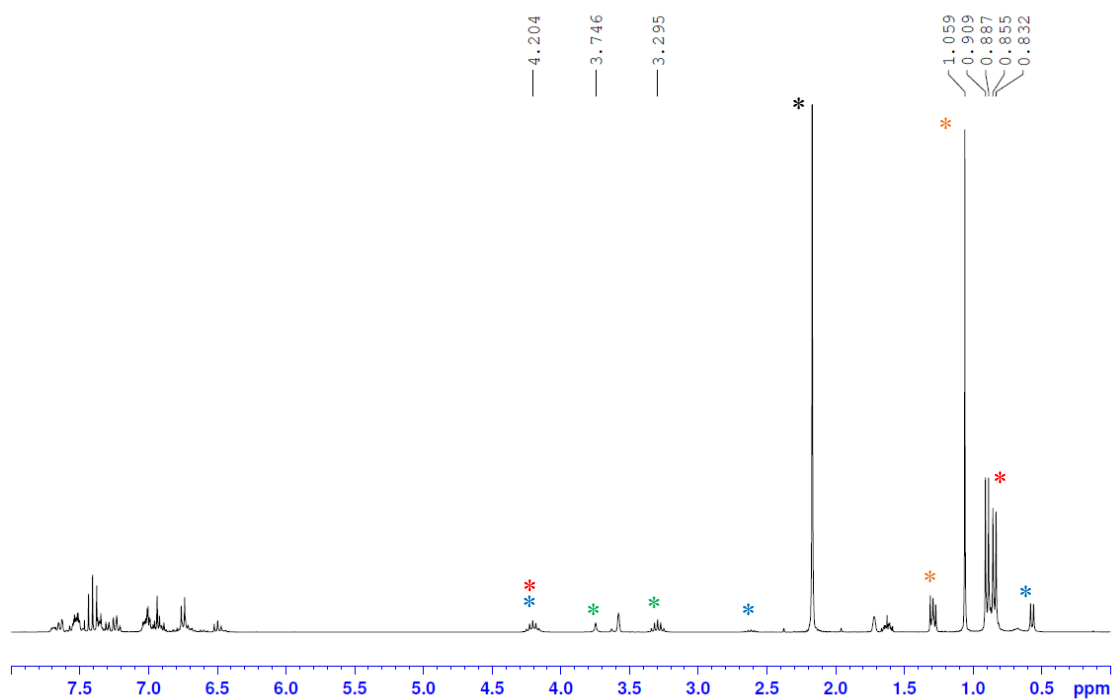


Figure S 18 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of 1,2,4,5-tetrafluorobenzene, after 5 minutes. (* = **3i**, * = $[\text{K}(\text{THF})_x\text{Zn}\{\text{Ph}_2\text{Si}(\text{NHAr}^*)(\text{NAr}^*)\}(\text{C}_6\text{F}_4\text{H})_2]$, * = $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$, * = hexamethylbenzene, * = $\text{TMP}(\text{H})$)

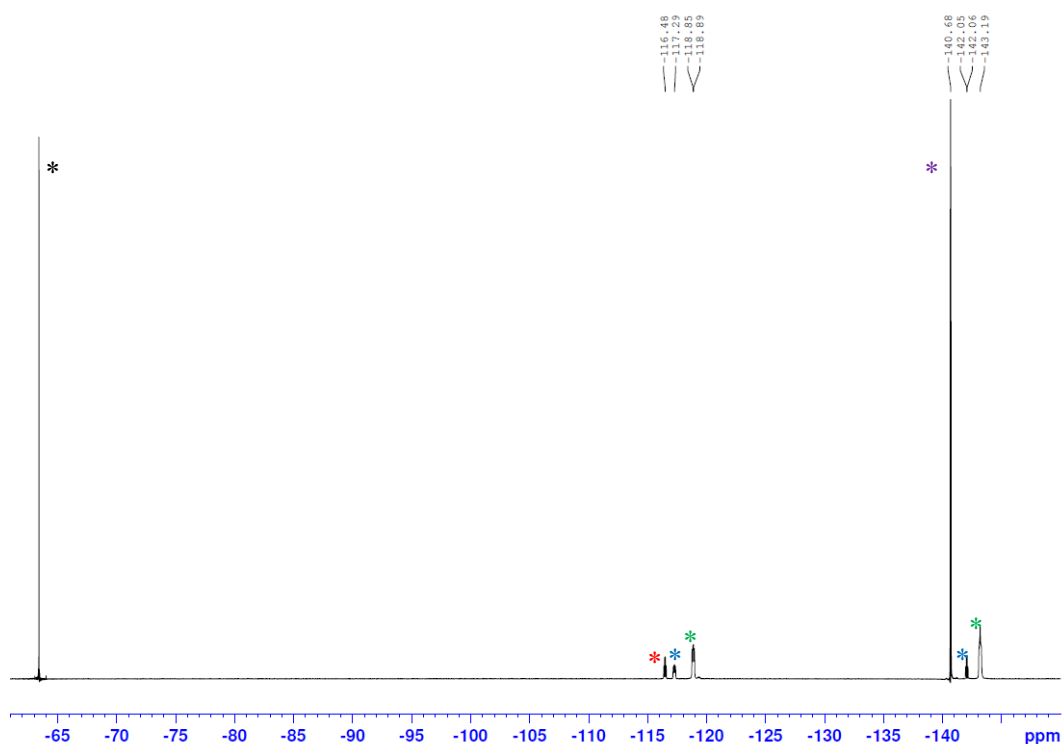


Figure S 19 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of 1,2,4,5-tetrafluorobenzene, after 5 minutes. (*= **3i**, *= $[\text{K}(\text{THF})_x\text{Zn}\{\text{Ph}_2\text{Si}(\text{NHAr}^*)(\text{NAr}^*)\}(\text{C}_6\text{F}_4\text{H})_2]$ *= $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_4\text{H})_3]$, *=trifluorotoluene, *=1,2,4,5-tetrafluorobenzene)

Adding a threefold excess of 1,2,4,5-tetrafluorobenzene **1** exhibits a polybasicity, in fact **3i** further reacts through the silyl bis(amido) ligand, generating $[\text{K}(\text{THF})_x\text{Zn}\{\text{Ph}_2\text{Si}(\text{NHAr}^*)(\text{NAr}^*)\}(\text{C}_6\text{F}_4\text{H})_2]$ and $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$ (**Figure S 13**). 1,2,4,5-tetrafluorobenzene is still present in the mixture (**Figure S 14**) after 5 minutes due to the slower reactivity of $[\text{Ph}_2\text{Si}(\text{NHAr}^*)_2]^{2-}$ towards protonation. After 16h the reaction goes to completion consuming most of the 1,2,4,5-tetrafluorobenzene and having $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$ (**Figure S 15**) $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_6)_3]$ (**Figure S 16**) as only products.

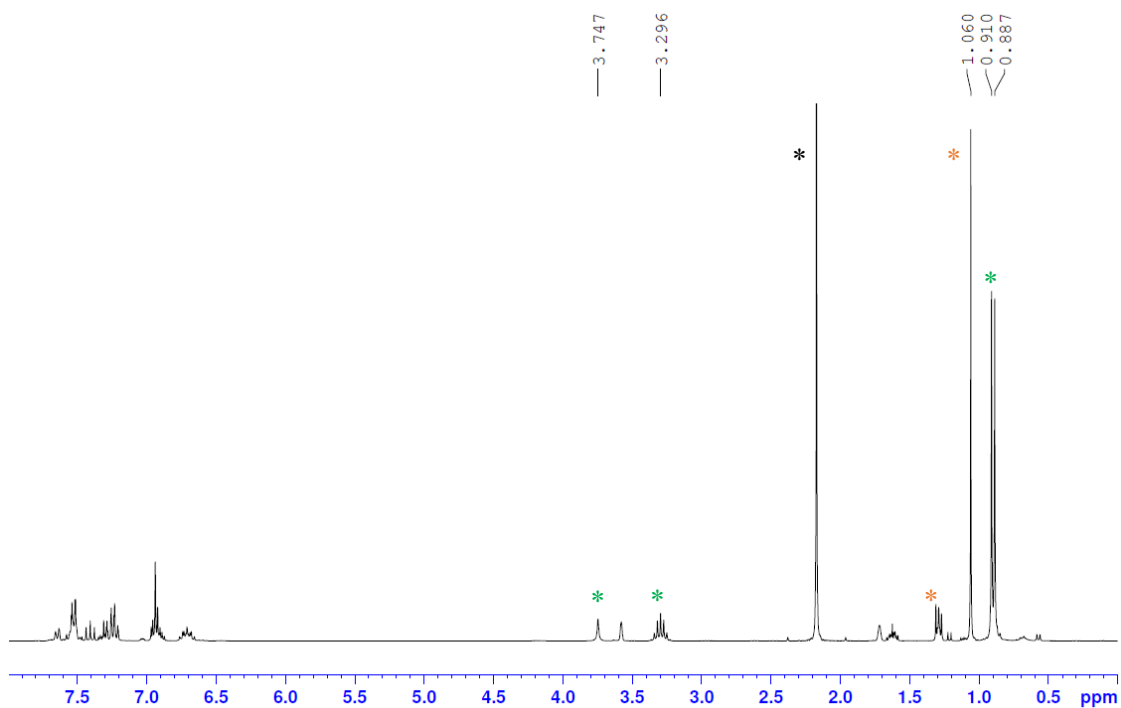


Figure S 20 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of 1,2,4,5-tetrafluorobenzene, after 16 hours. (*= $\text{Ph}_2\text{Si}(\text{NHAr}^*)_2$), *= hexamethylbenzene , *= $\text{TMP}(\text{H})$)

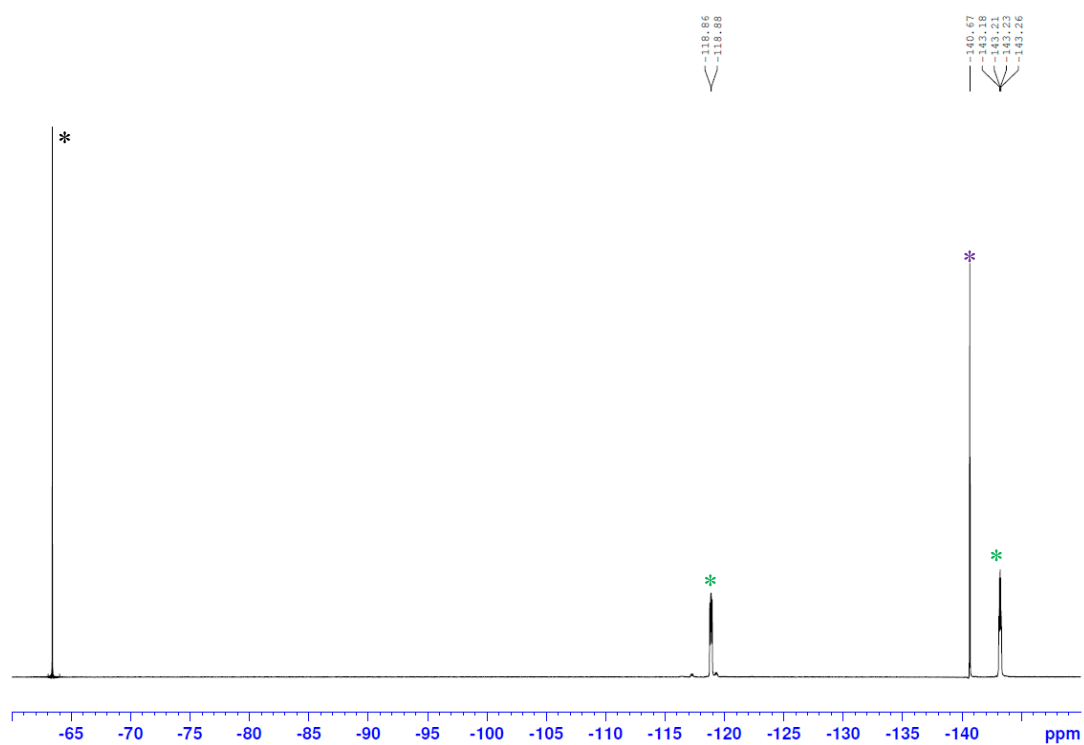


Figure S 21 $^{19}\text{F-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of reaction between **1** and 3eq. of 1,2,4,5-tetrafluorobenzene, after 16 hours. (*= $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_4\text{H})_3]$), *= trifluorotoluene , *= $1,2,4,5\text{-tetrafluorobenzene e}$)

X-ray Crystallography

A crystal of **1** or **3a-j** is immersed in parabar oil was mounted at ambient conditions and transferred into the stream of nitrogen (100 K for **3b**, **3d**, **3e**, **3h**, **3j** and $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{F}_5)_2\}^- \{\text{K}(\text{THF})_1\}^+]$, 123 K for **1**, **3a**, **3c**, $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$ and $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$). All measurements were made on a RIGAKU Synergy S area-detector diffractometer and Oxford Diffraction Gemini S or Xcalibur E⁶ using mirror optics monochromated Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) or Mo K α ($\lambda = 0.71073 \text{ \AA}$). The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of reflections in the range:

- $3.398^\circ < \theta < 73.102^\circ$ for **1**. A total of 2192 frames were collected using ω scans, with 1.335 second exposure time (15 s for high-angle reflections and 5.33 s for medium-angle reflections), a rotation angle of 1° per frame, a crystal-detector distance of 45.0 mm, at $T = 123.35(10) \text{ K}$

- $3.7300^\circ < \theta < 73.1710^\circ$ for $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$ A total of 2097 frames were collected using ω scans, with 1.53 second exposure time (15 s for high-angle reflections and 6.115 s for medium-angle reflections), a rotation angle of 1° per frame, a crystal-detector distance of 45.0 mm, at $T = 123(2) \text{ K}$

- $4.3560^\circ < \theta < 72.5470^\circ$ for **3a**. A total of 1388 frames were collected using ω scans, with 2.71 second exposure time (35 s for high-angle reflections and 10.84 s for medium-angle reflections), a rotation angle of 1° per frame, a crystal-detector distance of 45.0 mm, at $T = 123(2) \text{ K}$

- $3.8130^\circ < \theta < 73.1290^\circ$ for $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$. A total of 2674 frames were collected using ω scans, with 1 second exposure time (9 s for high-angle reflections and 3 s for medium-angle reflections), a rotation angle of 1° per frame, a crystal-detector distance of 45.0 mm, at $T = 123(2) \text{ K}$

- $3.4490^\circ < \theta < 71.4310^\circ$ for **3b**. A total of 3684 frames were collected using ω scans, with 0.5 second exposure time (2.75 s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 34.0 mm, at $T = 100(2) \text{ K}$.

- $2.296^\circ < \theta < 76.484^\circ$ for **3c**. A total of 11258 frames were collected using ω scans, with 2 second exposure time (12 s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 34.0 mm, at $T = 173.15(10) \text{ K}$

- $3.487^\circ < \theta < 68.084^\circ$ for **3d**. A total of 3020 frames were collected using ω scans, with 5 second exposure time (12 s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 34.0 mm, at $T = 84.8(6) \text{ K}$.

- $2.7800^\circ < \theta < 76.7790^\circ$ for **3e**. A total of 3332 frames were collected using ω scans, with 0.1 second exposure time (0.25 s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 34.0 mm, at $T = 100.00(10) \text{ K}$.

- $3.098^\circ < \theta < 77.579^\circ$ for **3h**. A total of 6512 frames were collected using ω scans, with 0.7 second exposure time (4 s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 34.0 mm, at $T = 100.0(5)$ K.

- $2.965^\circ < \theta < 79.598^\circ$ for **3j**. A total of 6306 frames were collected using ω scans, with 0.8 second exposure time (3 s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 34.0 mm, at $T = 100.01(10)$ K.

- $2.860^\circ < \theta < 76.442^\circ$ for **4**. A total of 5894 frames were collected using ω scans, with 0.8 second exposure time (3.1s for high-angle reflections), a rotation angle of 0.5° per frame, a crystal-detector distance of 65.0 mm, at $T = 173.00(10)$ K.

Data reduction was performed using the *CrysAlisPro* program^[7]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in *CrysAlisPro*^[7] was applied.

The structures were solved by direct methods using *SHELXT*^[8], which revealed the positions of all non-hydrogen atoms of the title compound. All non-hydrogen atoms were refined anisotropically. H-atoms were assigned in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent atom (1.5U_{eq} for methyl groups).

refinement of the structures was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the *SHELXL-2014/7*^[9] program in OLEX2.4^[10]

The X-ray crystal structure determination service unit of the Department of Chemistry and Biochemistry of the University of Bern is acknowledged for measuring, solving, refining and summarizing the structures of compounds **3b**, **3c**, **3d**, **3e**, **3h**, **3j** and **4**. The Synergy diffractometer was partially funded by the Swiss National Science Foundation (SNF) within the R'Equip programme (project number 206021_177033).

Selected crystallographic data are presented in **Table S1-S4** and full details in cif format can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif

Table S 1 Crystal data and structure refinement details for compounds **1**, **3a**, **3b**

Compound	1	3a	3b
CCDC number	2151990	2151992	2151994
Empirical formula	C ₆₉ H ₁₁₀ KN ₃ O ₆ SiZn	C ₇₀ H ₁₀₂ F ₃ KN ₂ O ₇ SiZn	C ₇₀ H ₁₀₂ Cl ₃ KN ₂ O ₇ SiZn
Formula weight	1210.15	1273.09	1322.44
Temperature/K	123(2)	123(2)	100.00(10)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	C2/c	P2 ₁ /n

a/Å	15.8130(1)	35.0797(7)	20.6110(6)
b/Å	16.9447(1)	15.7345(3)	15.6044(5)
c/Å	25.5040(2)	25.6152(4)	23.2737(8)
α /°	90	90	90
β /°	91.405(1)	98.473(2)	109.050(3)
γ /°	90	90	90
Volume/Å ³	6831.65(8)	13984.3(4)	7075.4(4)
Z	4	8	4
ρ_{calc} /g/cm ³	1.177	1.209	1.241
μ /mm ⁻¹	1.597	1.658	2.613
F(000)	2624.0	5456.0	2824.0
Crystal size/mm ³	1.0 × 0.5 × 0.3	0.8 × 0.6 × 0.6	0.264 × 0.083 × 0.067
Radiation	CuK α (λ = 1.54184)	CuK α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for refinement data/°	6.262 to 146.178	6.9 to 146.252	6.946 to 129.306
Index ranges	-18 ≤ h ≤ 19, -20 ≤ k ≤ 19, 31 ≤ l ≤ 28	-43 ≤ h ≤ 41, -19 ≤ k ≤ 14, 31 ≤ l ≤ 30	-23 ≤ h ≤ 24, -17 ≤ k ≤ 18, 27 ≤ l ≤ 27
Reflections collected	60911	37197	75990
Independent reflections	13559 [R _{int} = 0.0482, R _{sigma} = 0.0306]	13808 [R _{int} = 0.0552, R _{sigma} = 0.0492]	11930 [R _{int} = 0.1091, R _{sigma} = 0.1368]
Data/restraints/parameters	13559/33/781	13808/397/923	11930/556/822
Goodness-of-fit on F ²	1.030	1.014	1.414
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0439, wR ₂ = 0.1123	R ₁ = 0.0813, wR ₂ = 0.2241	R ₁ = 0.1244, wR ₂ = 0.3502
Final R indexes [all data]	R ₁ = 0.0507, wR ₂ = 0.1186	R ₁ = 0.1002, wR ₂ = 0.2547	R ₁ = 0.1547, wR ₂ = 0.3854
Largest diff. peak/hole / e Å ⁻³	0.62/-0.29	0.83/-0.63	1.05/-0.62

Table S 2 Crystal data and structure refinement details for compounds **3c**, **3d**, **3e**

Compound	3c	3d	3e
CCDC number	2151995	2151996	2151997
Empirical formula	C ₆₆ H ₉₅ F ₂ KN ₂ O ₆ SiZn	C ₇₀ H ₁₀₃ FKN ₃ O ₉ SiZn	C ₅₄ H ₇₀ F ₂ KN ₃ O ₅ SiZn
Formula weight	1182.99	1282.11	1011.69
Temperature/K	173.15(10)	84.8(6)	100.00(10)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /c	P2 ₁ /c
a/Å	18.6356(2)	22.630(3)	11.68683(6)
b/Å	18.8587(3)	15.7650(10)	14.09772(9)
c/Å	18.8788(3)	20.4853(17)	31.61154(15)
α /°	90.4963(14)	90	90
β /°	93.1729(12)	108.879(12)	91.4303(5)
γ /°	92.1929(12)	90	90
Volume/Å ³	6619.39(18)	6915.2(13)	5206.62(5)
Z	4	4	4
ρ_{calc} /g/cm ³	1.187	1.231	1.291

μ/mm^{-1}	1.681	1.664	2.043
F(000)	2536.0	2752.0	2144.0
Crystal size/ mm^3	$0.168 \times 0.13 \times 0.085$	$0.304 \times 0.217 \times 0.122$	$0.17 \times 0.12 \times 0.09$
Radiation	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)	CuK α ($\lambda = 1.54184$)
2 θ range for refinement data/ $^\circ$	4.688 to 138.264	6.962 to 95.676	5.594 to 154.234
Index ranges	$-22 \leq h \leq 22, -22 \leq k \leq 22, -22 \leq l \leq 22$	$-21 \leq h \leq 21, -14 \leq k \leq 15, -19 \leq l \leq 16$	$-14 \leq h \leq 12, -16 \leq k \leq 17, -39 \leq l \leq 39$
Reflections collected	236341	38045	55788
Independent reflections	24646 [$R_{\text{int}} = 0.0897, R_{\text{sigma}} = 0.0399$]	6426 [$R_{\text{int}} = 0.1321, R_{\text{sigma}} = 0.0636$]	10802 [$R_{\text{int}} = 0.0366, R_{\text{sigma}} = 0.0268$]
Data/restraints/parameters	24646/520/1456	6426/515/778	10802/0/622
Goodness-of-fit on F^2	1.338	1.035	1.039
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1143, wR_2 = 0.3376$	$R_1 = 0.1316, wR_2 = 0.3393$	$R_1 = 0.0358, wR_2 = 0.0873$
Final R indexes [all data]	$R_1 = 0.1576, wR_2 = 0.3734$	$R_1 = 0.1510, wR_2 = 0.3580$	$R_1 = 0.0412, wR_2 = 0.0908$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.12/-0.83	1.15/-0.62	0.62/-0.50

Table S 3 Crystal data and structure refinement details for compounds **3h**, **3j**, **4**

Compound	3h	3j	4
CCDC number	2151998	2151999	2152000
Empirical formula	$\text{C}_{70}\text{H}_{100}\text{F}_5\text{KN}_2\text{O}_7\text{SiZn}$	$\text{C}_{110}\text{H}_{152}\text{F}_4\text{K}_2\text{N}_4\text{O}_8\text{Si}_2\text{Zn}_2$	$\text{C}_{52}\text{H}_{52}\text{F}_{10}\text{KN}_2\text{OSiZn}$
Formula weight	1309.07	1999.47	1043.51
Temperature/K	100.0(5)	100.01(10)	173.00(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	P2 ₁ /n	P-1
a/ \AA	35.1874(3)	12.14746(7)	10.92365(17)
b/ \AA	15.60249(10)	29.80377(15)	15.3180(4)
c/ \AA	25.53322(18)	15.17589(8)	15.4312(2)
$\alpha/^\circ$	90	90	86.8366(16)
$\beta/^\circ$	99.1052(7)	105.0495(6)	86.8944(13)
$\gamma/^\circ$	90	90	72.2944(17)
Volume/ \AA^3	13841.39(17)	5305.84(5)	2454.12(8)
Z	8	2	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.256	1.252	1.412
μ/mm^{-1}	1.733	1.976	2.363
F(000)	5584.0	2132.0	1078.0
Crystal size/ mm^3	$0.263 \times 0.215 \times 0.161$	$0.254 \times 0.088 \times 0.068$	$0.15 \times 0.1 \times 0.05$
Radiation	Cu K α ($\lambda = 1.54184$)	Cu K α ($\lambda = 1.54184$)	CuK α ($\lambda = 1.54184$)
2 θ range for refinement data/ $^\circ$	6.21 to 150.04	5.93 to 135.146	5.74 to 154.742
Index ranges	$-44 \leq h \leq 40, -19 \leq k \leq 19, -31 \leq l \leq 31$	$-14 \leq h \leq 14, -35 \leq k \leq 35, -17 \leq l \leq 18$	$-13 \leq h \leq 12, -19 \leq k \leq 19, -19 \leq l \leq 19$
Reflections	140186	100664	47554

collected			
Independent reflections	14236 [$R_{\text{int}} = 0.0487$, $R_{\text{sigma}} = 0.0524$]	9576 [$R_{\text{int}} = 0.0412$, $R_{\text{sigma}} = 0.0452$]	10199 [$R_{\text{int}} = 0.0666$, $R_{\text{sigma}} = 0.0347$]
Data/restraints/parameters	14236/233/976	9576/99/818	10199/77/597
Goodness-of-fit on F^2	1.044	1.030	1.054
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0727$, $wR_2 = 0.1995$	$R_1 = 0.0359$, $wR_2 = 0.0965$	$R_1 = 0.0659$, $wR_2 = 0.1950$
Final R indexes [all data]	$R_1 = 0.0793$, $wR_2 = 0.2065$	$R_1 = 0.0372$, $wR_2 = 0.0975$	$R_1 = 0.0716$, $wR_2 = 0.2012$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.71/-0.66	0.52/-0.49	1.14/-1.02

Table S 4 Crystal data and structure refinement details for compounds $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$, $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$

Compound	$[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$	$[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$
CCDC number	2151991	2151993
Empirical formula	$\text{C}_{69}\text{H}_{110}\text{N}_3\text{NaO}_6\text{SiZn}$	$\text{C}_{62}\text{H}_{86}\text{F}_3\text{N}_2\text{NaO}_5\text{SiZn}$
Formula weight	1194.04	1112.77
Temperature/K	123(2)	123(2)
Crystal system	triclinic	monoclinic
Space group	P-1	$\text{P}2_1/\text{c}$
$a/\text{\AA}$	10.47530(10)	16.8242(2)
$b/\text{\AA}$	35.3408(5)	15.0900(2)
$c/\text{\AA}$	37.5660(5)	25.0756(4)
$\alpha/^\circ$	87.6370(10)	90
$\beta/^\circ$	82.6610(10)	109.534(2)
$\gamma/^\circ$	88.9470(10)	90
Volume/ \AA^3	13780.3(3)	5999.71(16)
Z	8	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.151	1.232
μ/mm^{-1}	1.104	1.293
F(000)	5184.0	2376.0
Crystal size/ mm^3	$0.9 \times 0.6 \times 0.6$	$1.0 \times 0.6 \times 0.4$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2θ range for refinement data/ $^\circ$	9.922 to 146.38	6.95 to 146.36
Index ranges	$-11 \leq h \leq 12$, $-39 \leq k \leq 43$, $-45 \leq l \leq 46$	$-18 \leq h \leq 20$, $-18 \leq k \leq 18$, $-31 \leq l \leq 30$
Reflections collected	125953	67540
Independent reflections	54223 [$R_{\text{int}} = 0.0380$, $R_{\text{sigma}} = 0.0441$]	11935 [$R_{\text{int}} = 0.0362$, $R_{\text{sigma}} = 0.0182$]
Data/restraints/parameters	54223/423/3056	11935/37/724
Goodness-of-fit on F^2	1.023	1.029
Final R indexes	$R_1 = 0.0615$, $wR_2 = 0.1656$	$R_1 = 0.0432$, $wR_2 = 0.1154$

[I] \geq 2 σ (I)]
 Final R indexes [all data] $R_1 = 0.0738$, $wR_2 = 0.1776$ $R_1 = 0.0458$, $wR_2 = 0.1184$
 Largest diff. peak/hole / e \AA^{-3} 1.31/-0.53 0.47/-0.36

Crystal Structure of **1**

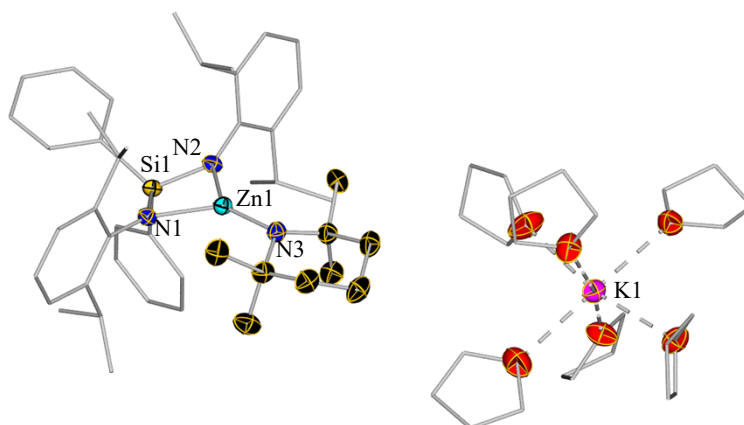


Figure S 22 Crystal structure of **1**. Thermal ellipsoids are rendered at 50% probability. Hydrogen atoms and disordered components in THF are omitted, carbon atoms of Aryl and THF fragments are drawn as wire frames for clarity. Selected bond distances (\AA) and angles ($^\circ$) N2-Zn1 1.9828(13), N1-Zn1 2.0123(14), Zn1-N3 1.8899(14), N2-Zn1-N1 79.50(5), N2-Zn1-N3 140.06(6), N1-Zn1-N3 139.51(5)

Crystal Structure of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$

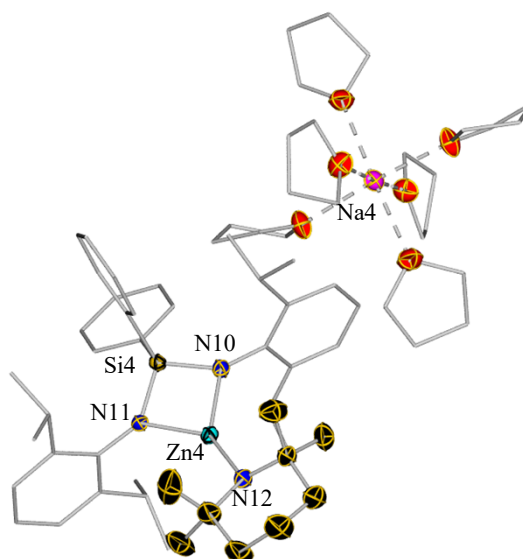


Figure S 23 Crystal structure of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$. Thermal ellipsoids are rendered at 50% probability. Hydrogen atoms are omitted, and carbon atoms of aryl and THF fragments are drawn as wireframes for clarity. The asymmetric unit contains 4 different anions and 4 cations all in general positions which are very similar, and therefore only one was represented (the one with least disorder), the selected bond and angle distances reported referred only to this structure. Selected bond distance (\AA) and angles ($^\circ$): N10-Zn4 1.9814(19), N11-Zn4 2.0080(18), Zn4-N12 1.887(19), N10-Zn4-N11 80.26(8), N10-Zn4-N12 138.43(8), N11-Zn4-N12 139.96(8), N10-Si4-N11 97.94(9), Si4-N10-Zn4 90.68(9), Si4-N11-Zn4 89.61(8).

Crystal Structure of **3a**

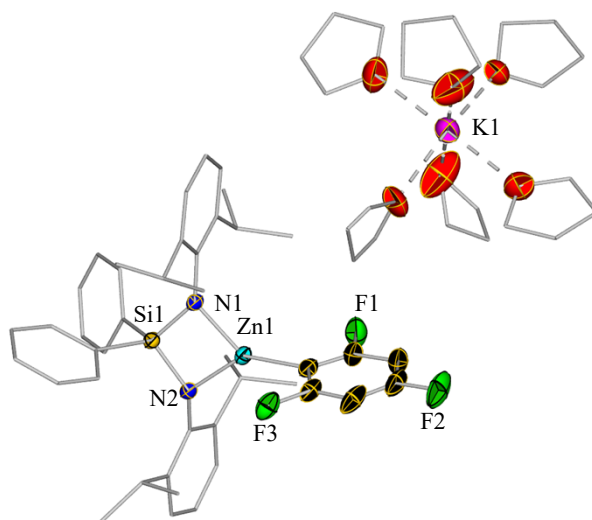


Figure S 24 Crystal structure of **3a**. Thermal ellipsoids are rendered at 50% probability. Hydrogen atoms and disordered components in THF are omitted, and carbon atoms of Ar*, phenyl ring and THF fragments are drawn as wire frames for clarity. Selected bond distances (Å) and angles (°) N2-Zn1 1.969(3), N1-Zn1 1.952(2), Zn1-C37 1.970(3), N2-Si1-N1 96.74(13), N2-Zn1-N1 81.01(11), Si1-N1-Zn1 91.32(11), Si1-N2-Zn1 90.71(12), N2-Zn1-C37 140.66(13), N1-Zn1-C37 137.56(13)

Crystal Structure of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$

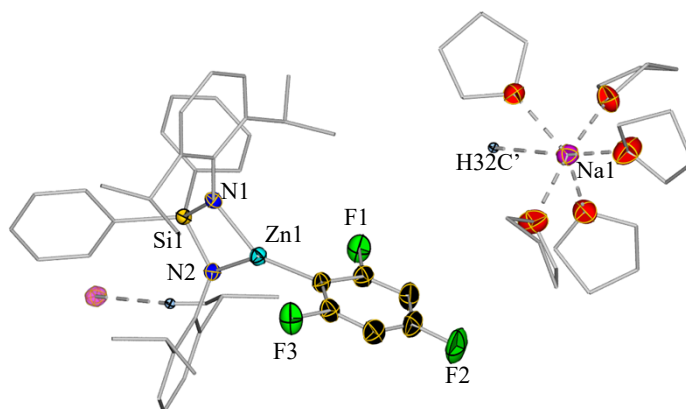


Figure S 25 Crystal structure of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$. Thermal ellipsoids are rendered at 50% probability. Hydrogen atoms (with the exception of H32C') and disordered components in THF are omitted, and carbon atoms of Ar*, phenyl ring and THF fragments are drawn as wireframes for clarity. Symmetry transformations used to generate symmetrical atoms: 1-x, 1-y, 1-z. Selected bond distances (Å) and angles (°) N2-Zn1 1.9799(13), N1-Zn1 1.9547(13), Zn1-C37 1.9596(17), N2-Si1-N1 97.12(6), N2-Zn1-N1 81.19(5), Si1-N1-Zn1 90.53(6), Si1-N2-Zn1 90.13(6), N2-Zn1-C37 135.49(6), N1-Zn1-C37 142.55(6).

Crystal Structure of **3b**

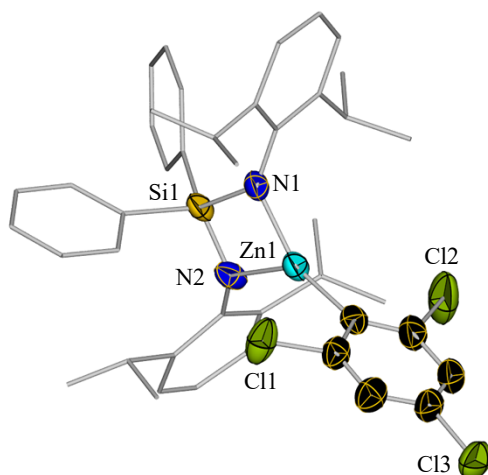


Figure S 26 Anionic moiety of **3b**. Thermal ellipsoids are rendered with 30% probability. Hydrogen atoms are omitted and carbon atoms of $\text{Ph}_2\text{Si}(\text{NAr}^*)_2^{2-}$ are drawn as wireframe for clarity. The asymmetric unit is neutral by the presence of two half $\text{K}(\text{THF})_6$ units, where both half occupied K atoms are sitting on a special position (inversion centre) not shown here.

Crystal Structure of **3c**

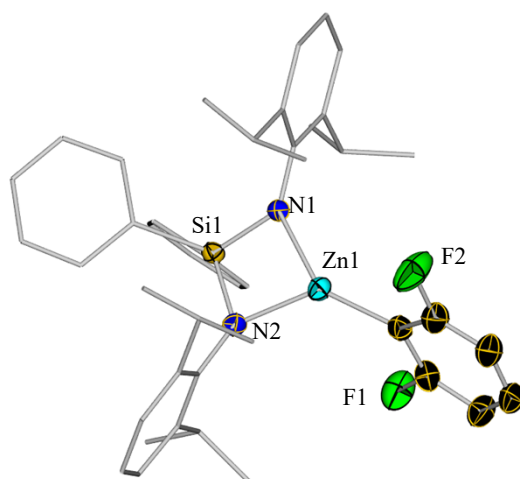


Figure S 27 Anionic moiety of **3c**. Thermal ellipsoids are rendered with 30% probability. Hydrogen atoms are omitted and carbon atoms of $\text{Ph}_2\text{Si}(\text{NAr}^*)_2^{2-}$ are drawn as wireframe for clarity. The asymmetric unit has 2 different molecular structures very similar, so only one was represented

Crystal Structure of **3d**

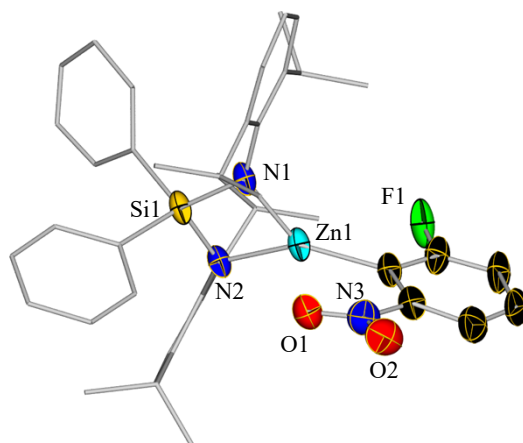


Figure S 28 Anionic Moiety of **3d**. Hydrogen atoms and disorder in the ⁱPr group are omitted for clarity. Carbon atoms of $\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{J}^{2-}$ are drawn as wireframe. Thermal ellipsoids are rendered at 20% probability. The asymmetric unit is neutral by the presence of two half $\text{K}(\text{THF})_6$ units, where both half occupied K atoms are sitting on a special position (inversion centre) not shown here.

Crystal Structure of **3e**

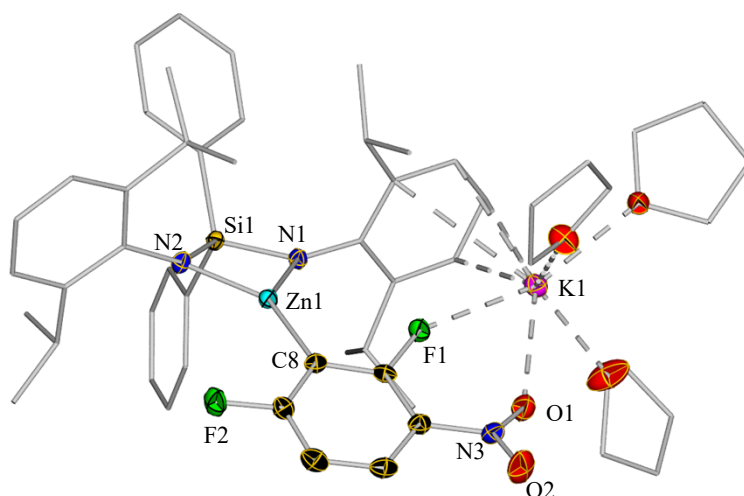


Figure S 29 Crystal structure of **3e**, ellipsoids are rendered with 50% probability. Hydrogen atoms and disordered components in THF are omitted, carbon atoms of Aryl and THF fragments are drawn as wireframe for clarity. Selected bond distances (Å) and angles (°): Zn1-C8 1.9648(16), N1-Zn1 1.9633(13), N2-Zn1 1.9536(14), K1-F1 2.7149(10), K1-O1 2.8946(13), K1-C_{aryl} ranging from 3.1875(17) to 3.5912(16), Si1-N2-Zn1 90.52(6), N2-Zn1-N1 81.58(6), N1-Zn1-C8 129.41(6), N2-Zn1-C8 146.70(6), Si1-N1-Zn1 90.05(6)

Crystal Structure of 3h

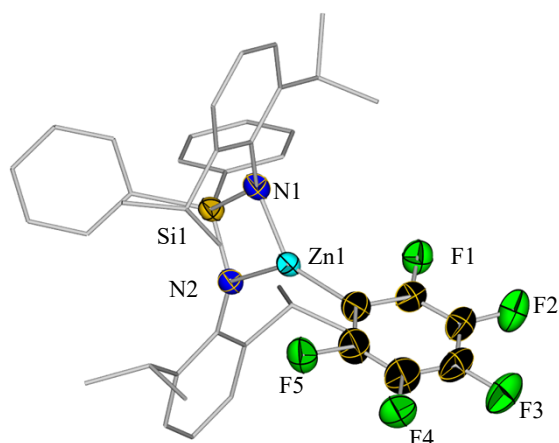


Figure S 30 Crystal structure of anionic moiety of **3h**. Hydrogens atoms are omitted and carbon atoms (except for the pentafluoroaryl anion) are drawn as wireframe for clarity. Disorder components of fluorine atoms were omitted for clarity. The asymmetric unit is neutral by the presence of two half $K(THF)_6$ units, where both half occupied K atoms are sitting on a special position (inversion centre and a two fold axis) not shown here. Selected bond distances (\AA) and angles ($^\circ$): N1-Zn1 1.921(4), N2-Zn1 1.988(4), Zn1-C1 1.984(5), Si1-N1-Zn1 40.97(10), Si1-N2-Zn1 40.80(9), N1-Zn1-N2 81.75(16), N1-Zn1-C1 141.5(2), N2-Zn1-C1 135.1(2)

Crystal Structure of 3j

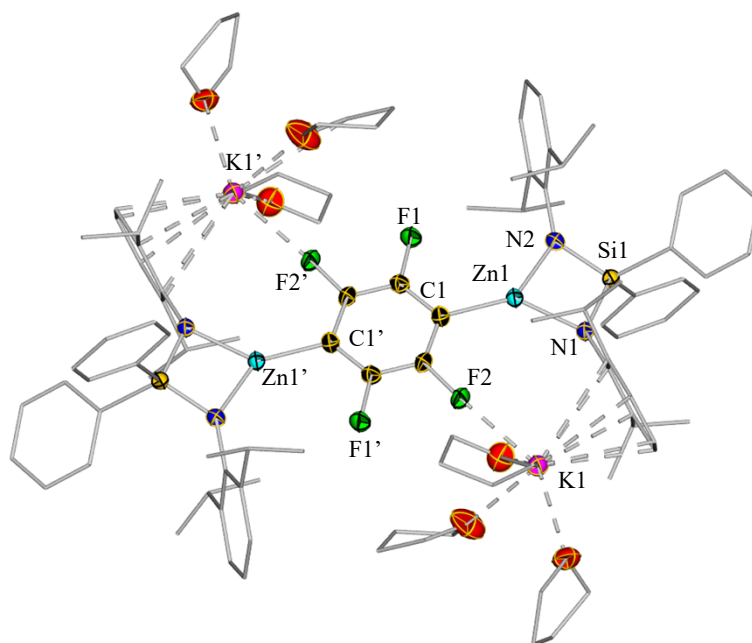


Figure S 31 Crystal structure of **3j**, ellipsoids are rendered with 50% probability. Hydrogen atoms and disordered components in THF, ^iPr group and phenyl are omitted, carbon atoms of Aryl (except for the tetrafluoro dianion) and THF fragments are drawn as wireframes for clarity. Symmetry transformations used to generate symmetrical atoms: $1-x, 1-y, 1-z$. Selected bond distances (\AA) and angles ($^\circ$): N1-Zn1 1.9872(14), N2-Zn1 1.9474(14), Zn1-C1 1.9689(17), K1-F2 2.6792(13), K1- C_{Ar^*} ranging from 3.080(2) to 3.2702(19), Si1-N1-Zn1 90.03(6), Si1-N2-Zn1 91.66(6), N1-Zn1-N2 81.12(6), N1-Zn1-C1 139.39(6), N2-Zn1-C1 138.88(7)

Crystal Structure of 4

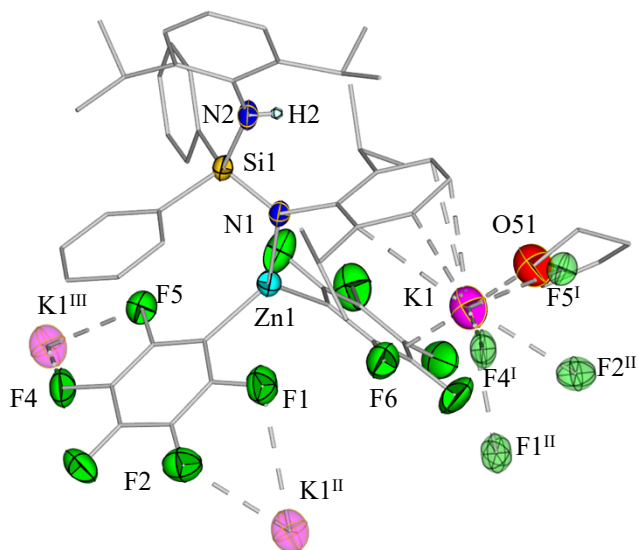


Figure S 32 Crystal structure of **4**. Ellipsoids are rendered with 50% probability. Hydrogen atoms and disordered components in THF are omitted, and carbon atoms of Aryl and THF fragments are drawn as wire frames for clarity. Symmetry transformations used to generate symmetrical atoms I: $1+x, y, z$; II: $1-x, 1-y, 1-z$; III: $-1+x, y, z$. Selected bond distances (\AA) and angles ($^\circ$): N1-Zn1 1.940(2), Zn1-C39 2.022(3), Zn1-C45 2.033(3), K1-F ranging from 2.681(3) to 3.436(3), K1-C_{Ar*} 3.061(3) to 3.536(3), N1-Zn1-C39 123.11(11), N1-Zn1-C45 120.01(11), C39-Zn1-C45 116.69(12)

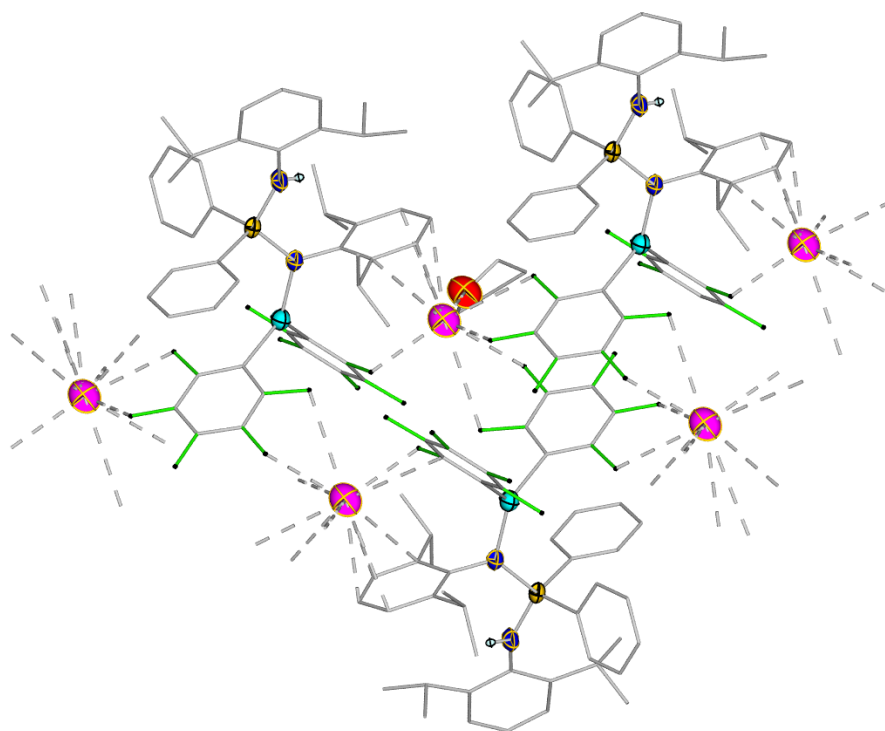


Figure S 33 Polymeric structure of **4**. Ellipsoids are rendered with 50% probability. Hydrogen atoms and disordered components in THF are omitted, fluorine and carbon atoms are drawn as wire frames for clarity. Symmetry transformations used to generate symmetrical atoms $1-x, 1-y, -z$; $1+x, y, z$; $1-x, 1-y, 1-z$; $-x, 1-y, -z$; $x, y, 1+z$; $2-x, 1-y, -z$; $1+x, y, 1+z$.

NMR spectra of the reported compounds

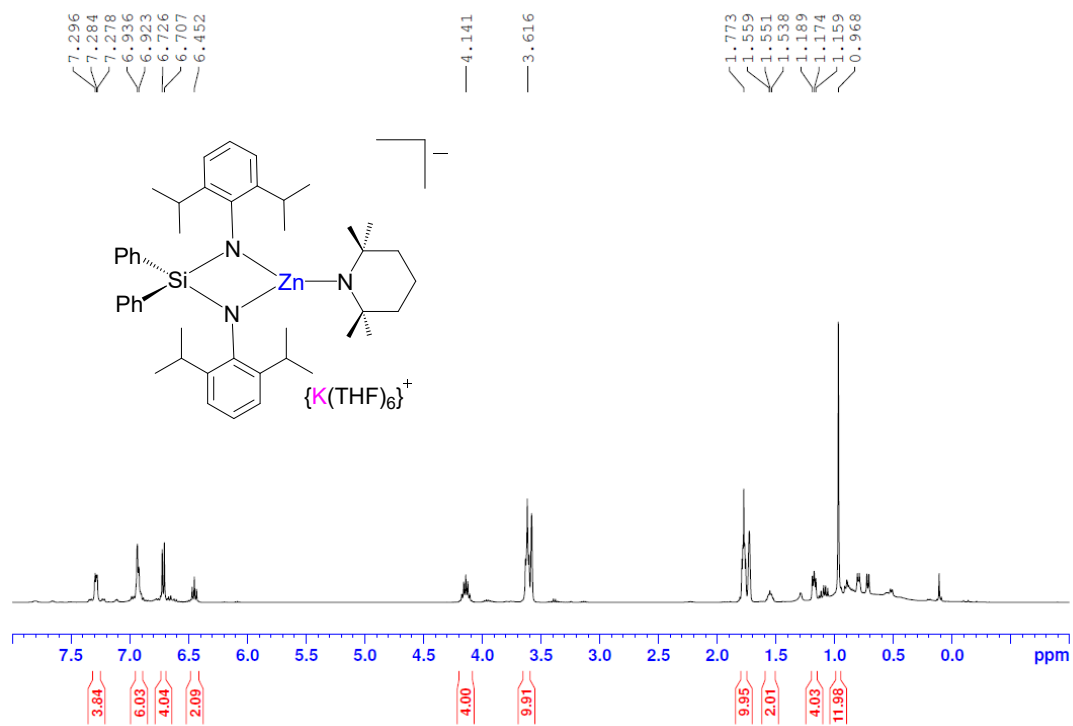


Figure S 34 ¹H-NMR (*D*₈-THF, 400 MHz, 298 K) spectrum of **1**

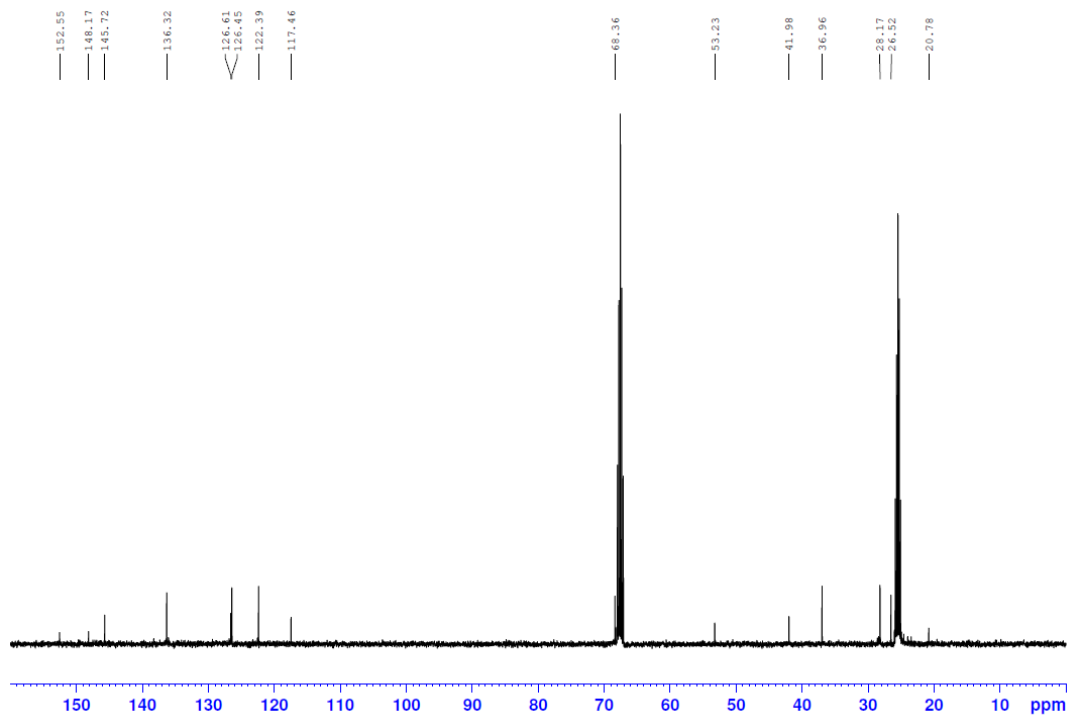


Figure S 35 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 100 MHz, 298 K) of **1**

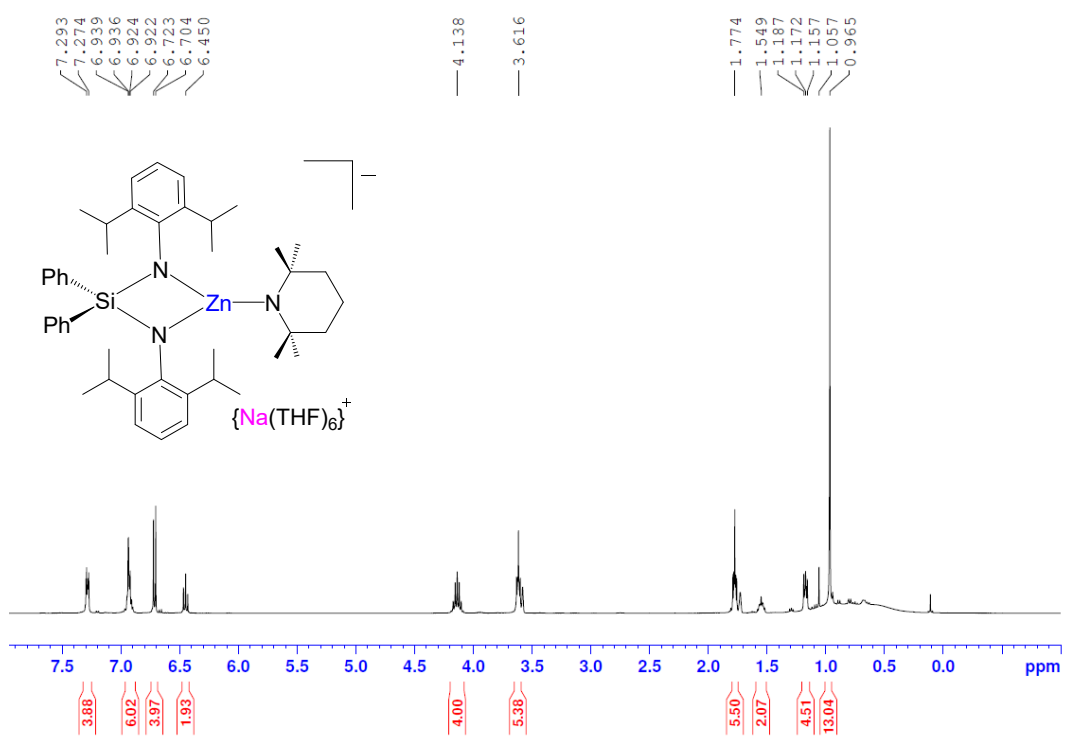


Figure S 36 ^1H -NMR (D_8 -THF, 400 MHz, 298 K) spectrum of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}]^- \{\text{Na}(\text{THF})_6\}^+$

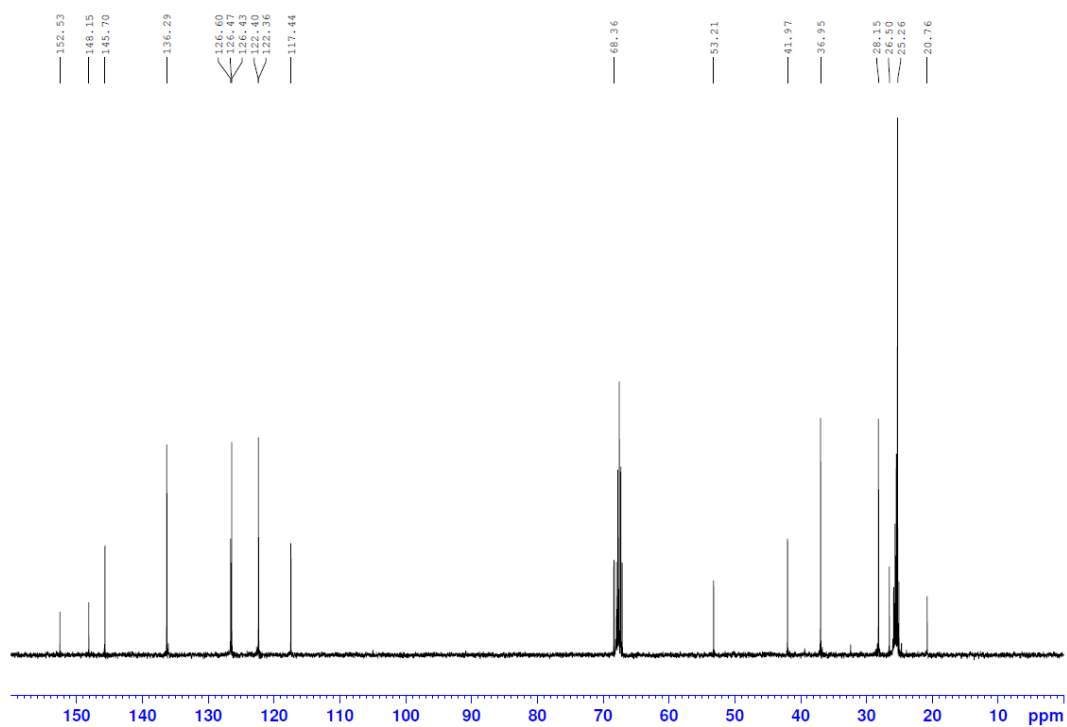


Figure S 37 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 100 MHz, 298 K) of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{TMP})\}^- \{\text{Na}(\text{THF})_6\}^+]$

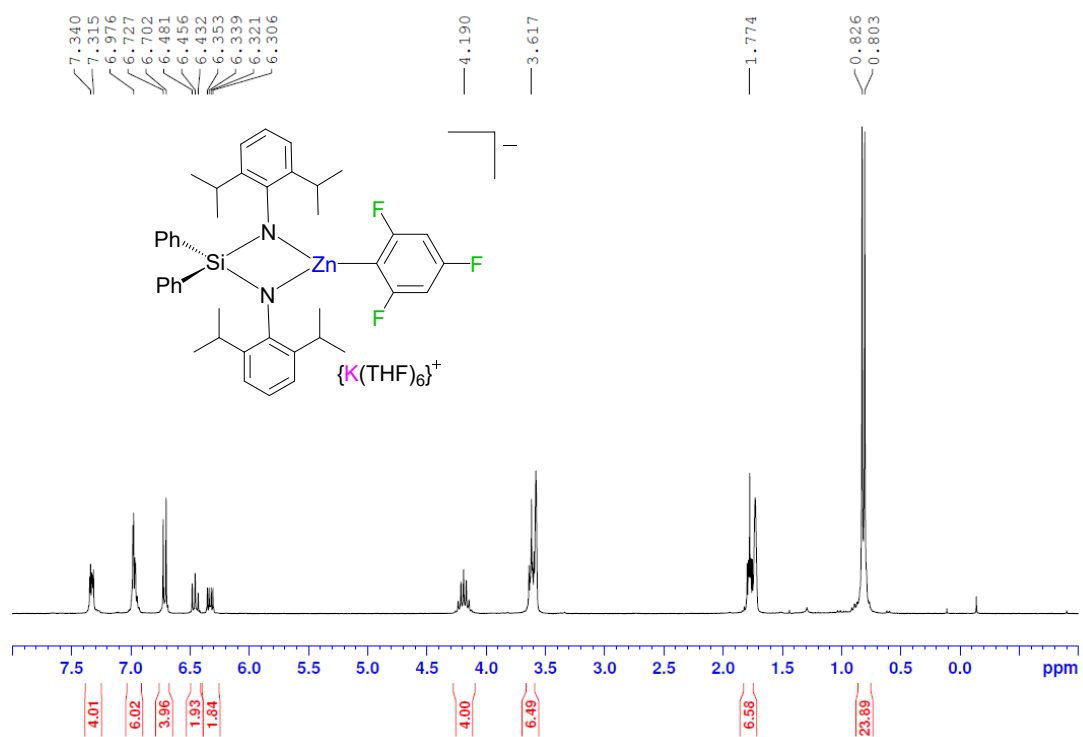


Figure S 38 ^1H -NMR (D_8 -THF, 400 MHz, 298 K) spectrum of **3a**

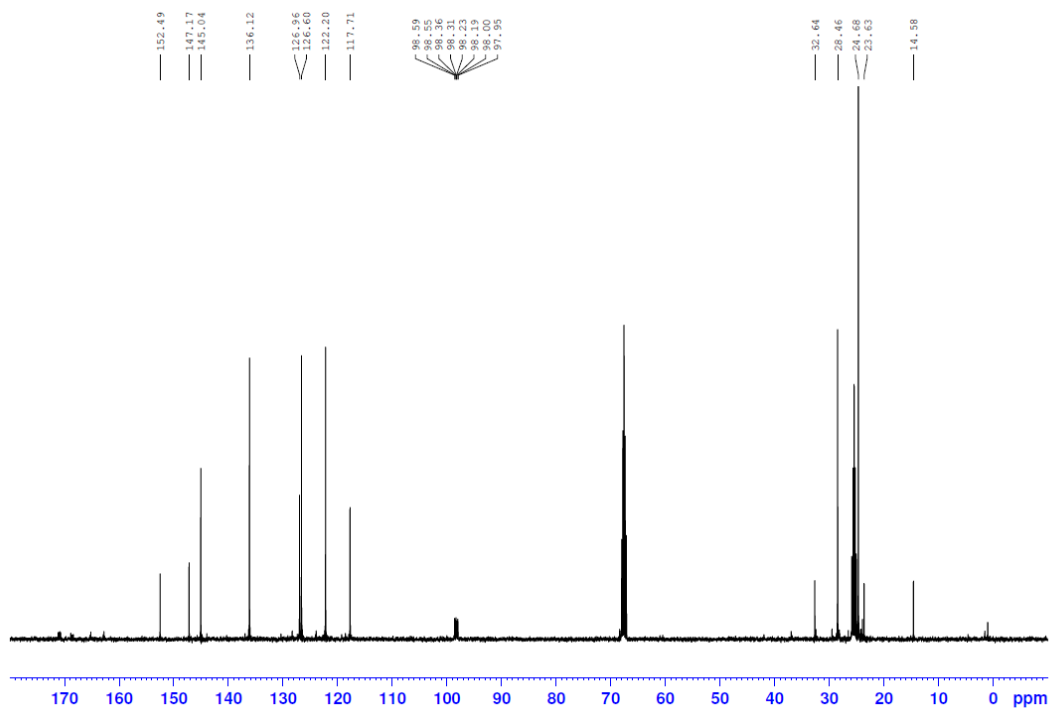


Figure S 39 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 100 MHz, 298 K) of **3a**

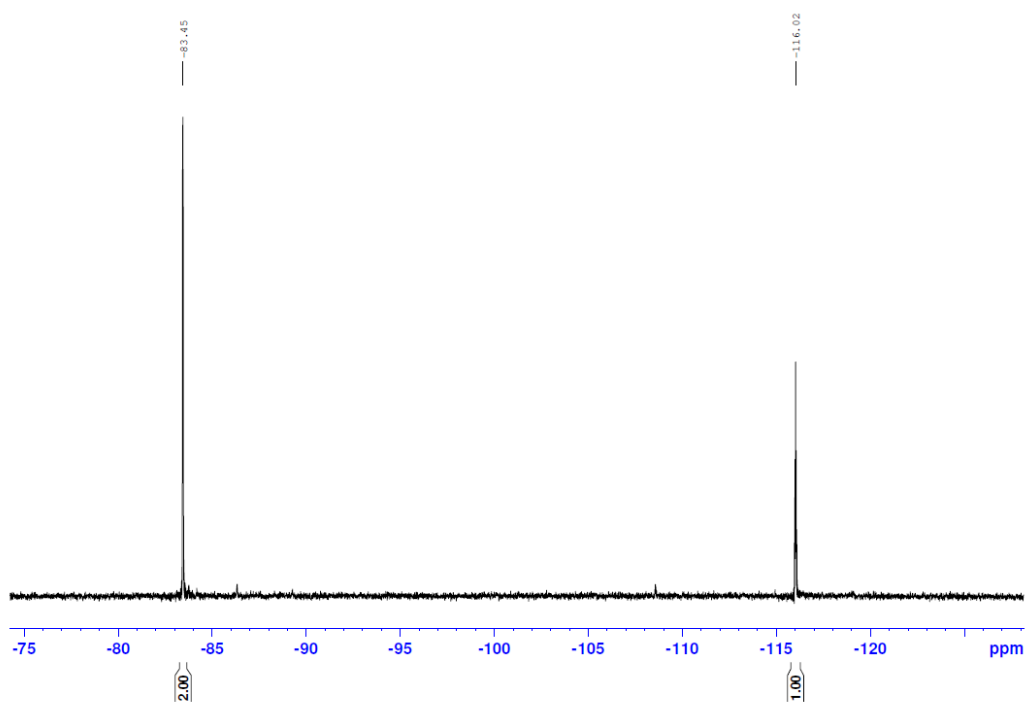


Figure S 40 ^{19}F -NMR (D_8 -THF, 400 MHz, 298 K) spectrum of **3a**

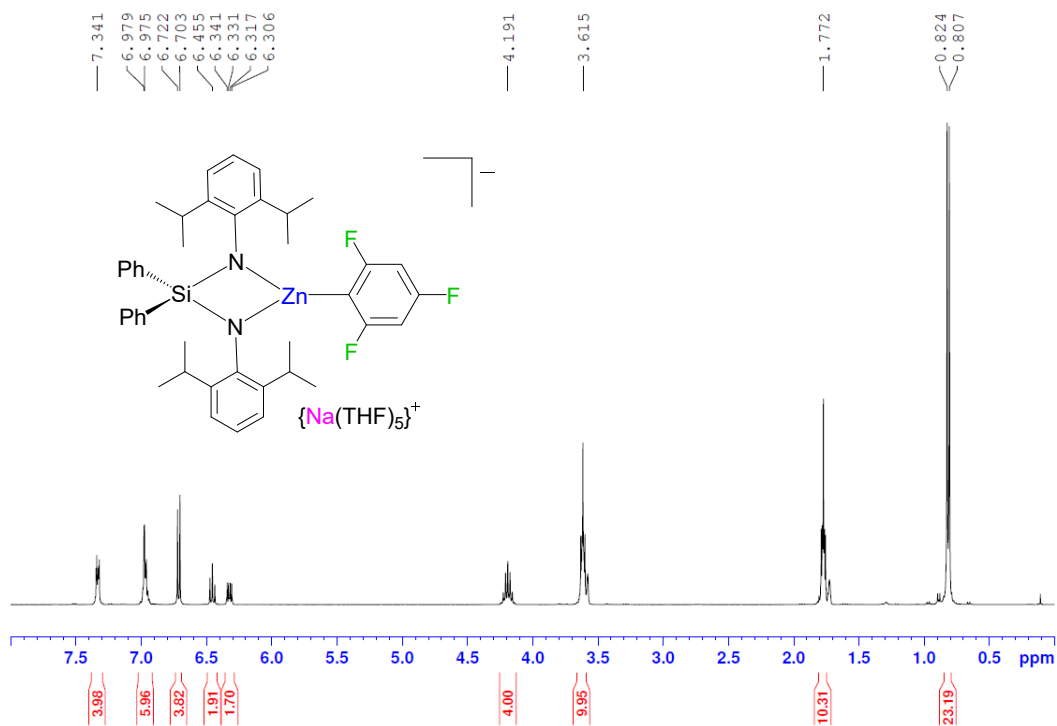


Figure S 41 1H -NMR (D_8 -THF, 400 MHz, 298 K) spectrum of $[\{Ph_2Si(NAr^*)_2Zn(C_6H_2F_3)\}^- \{Na(THF)_5\}^+]$

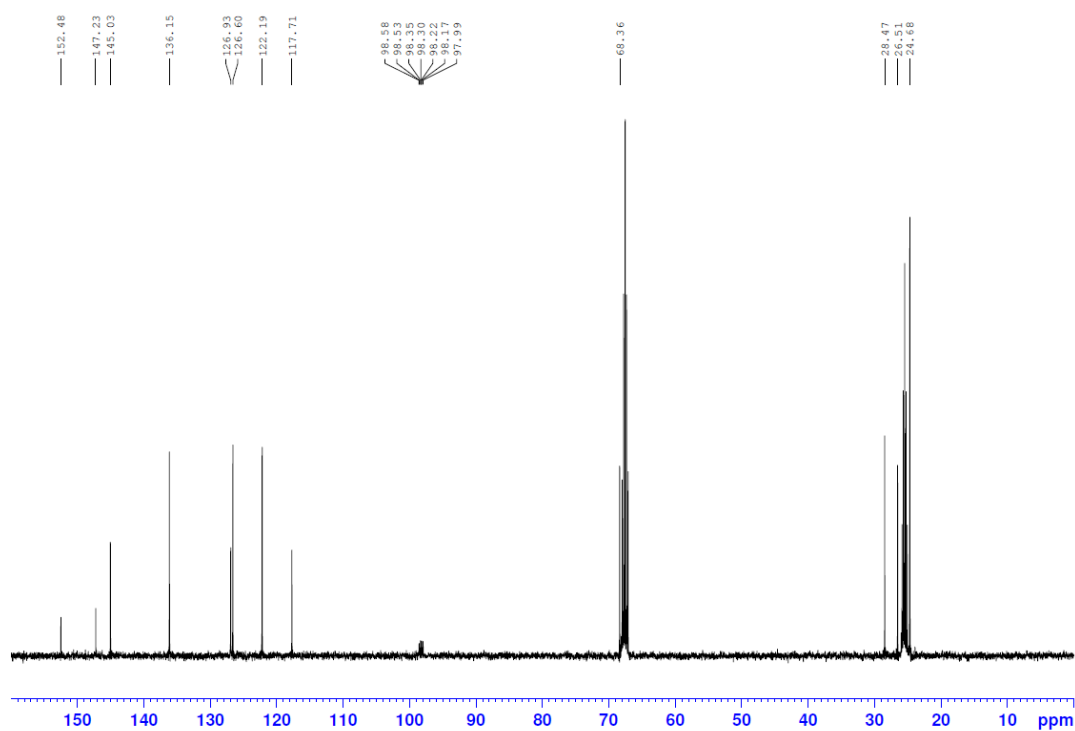


Figure S 42 $^{13}C\{H\}$ -NMR spectrum (D_8 -THF, 75 MHz, 298 K) of $[\{Ph_2Si(NAr^*)_2Zn(C_6H_2F_3)\}^- \{Na(THF)_5\}^+]$

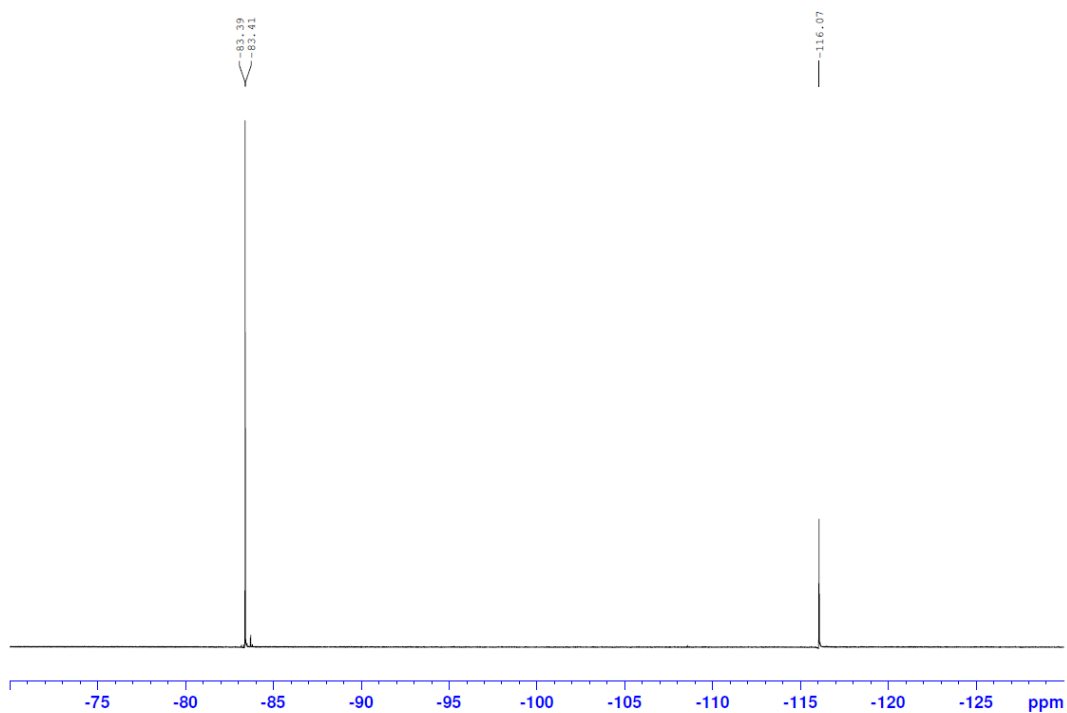


Figure S 43 ^{19}F -NMR (D_8 -THF, 400 MHz, 298 K) spectrum of $[\{\text{Ph}_2\text{Si}(\text{NAr}^*)_2\text{Zn}(\text{C}_6\text{H}_2\text{F}_3)\}^- \{\text{Na}(\text{THF})_5\}^+]$

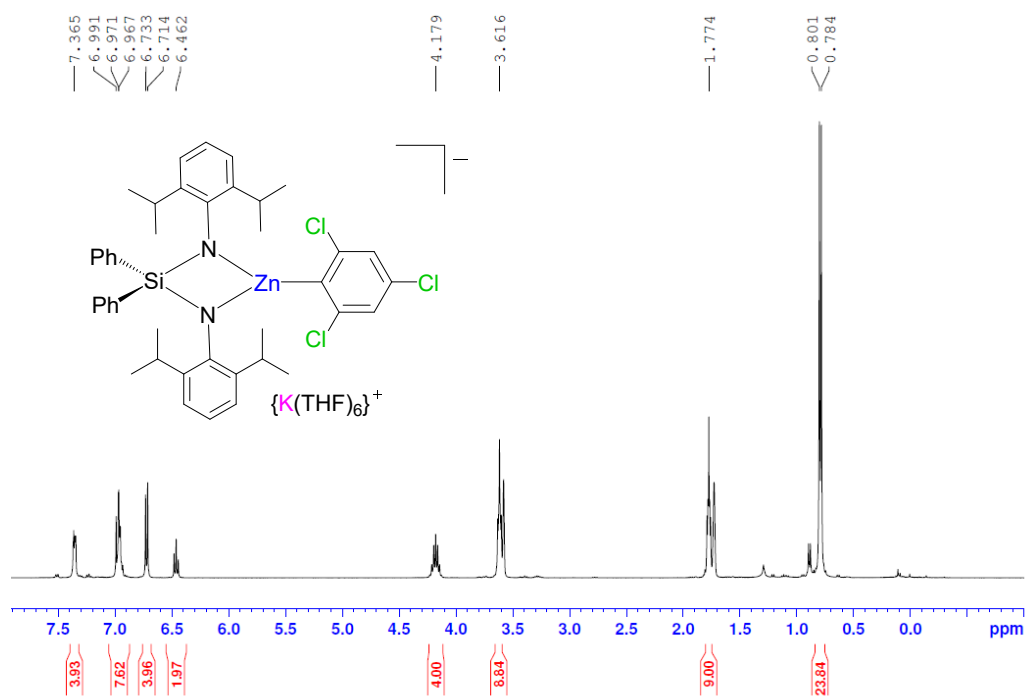


Figure S 44 ^1H -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3b**

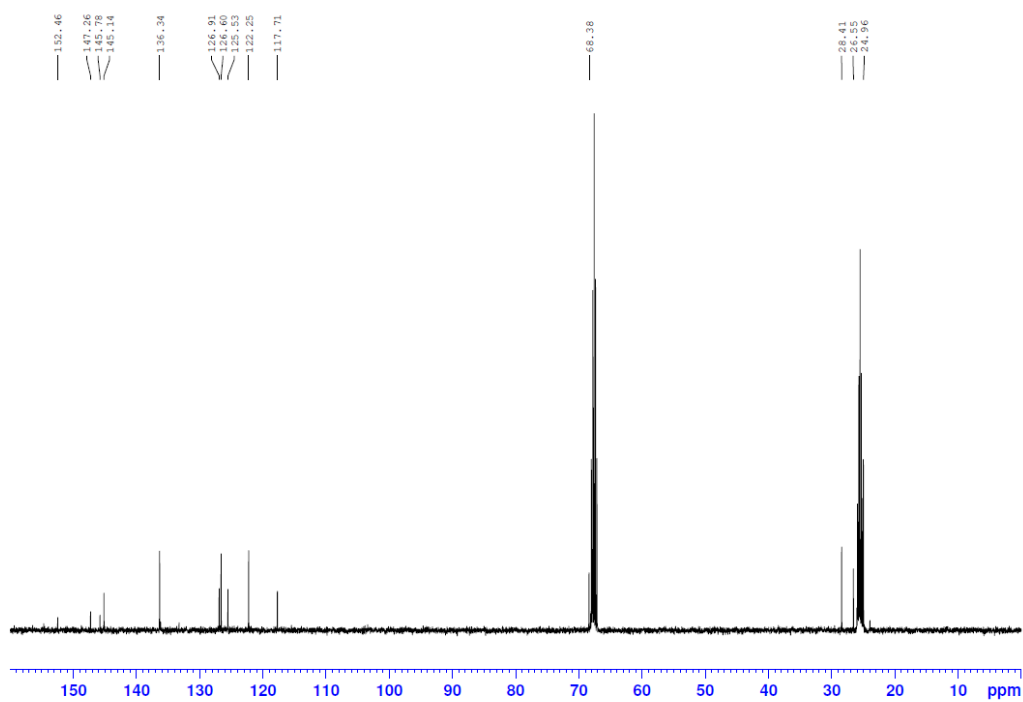


Figure S 45 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 75 MHz, 298 K) of **3b**

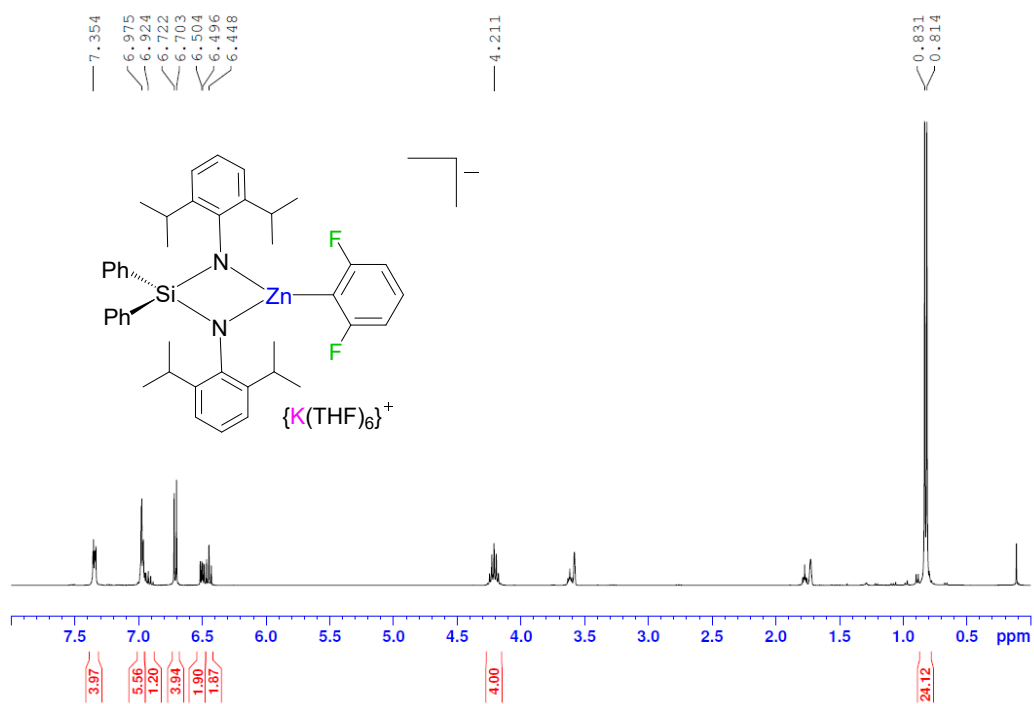


Figure S 46 ^1H -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3c**

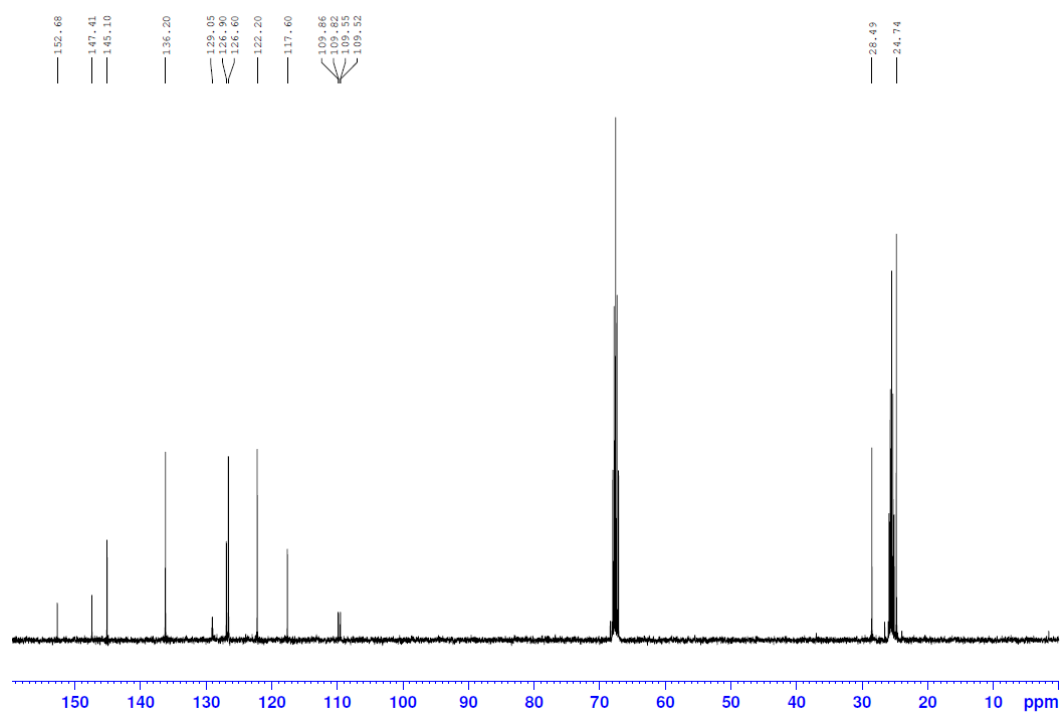


Figure S 47 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 75 MHz, 298 K) of **3c**

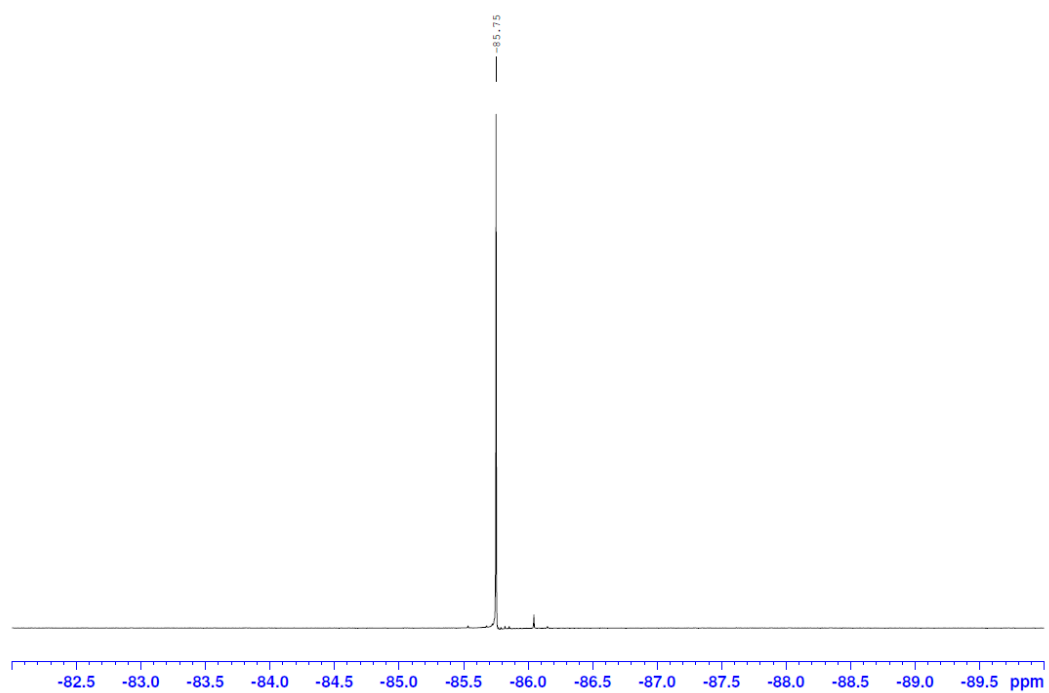


Figure S 48 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3c**

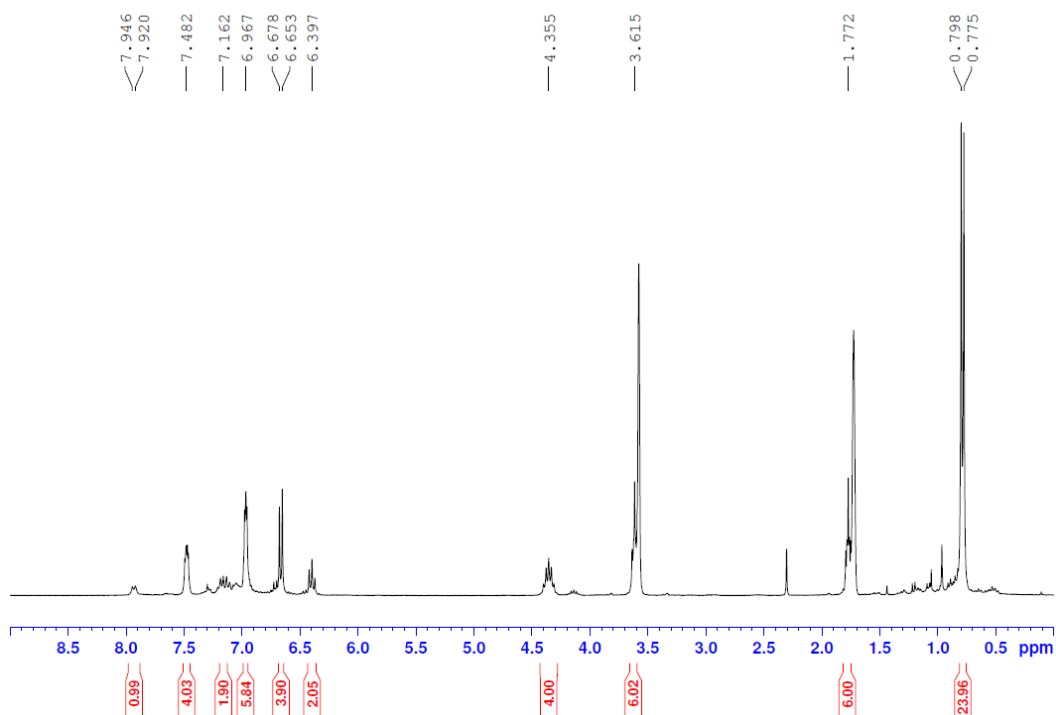


Figure S 49 $^1\text{H-NMR}$ ($D_8\text{-THF}$, 300 MHz, 298 K) spectrum of **3d**

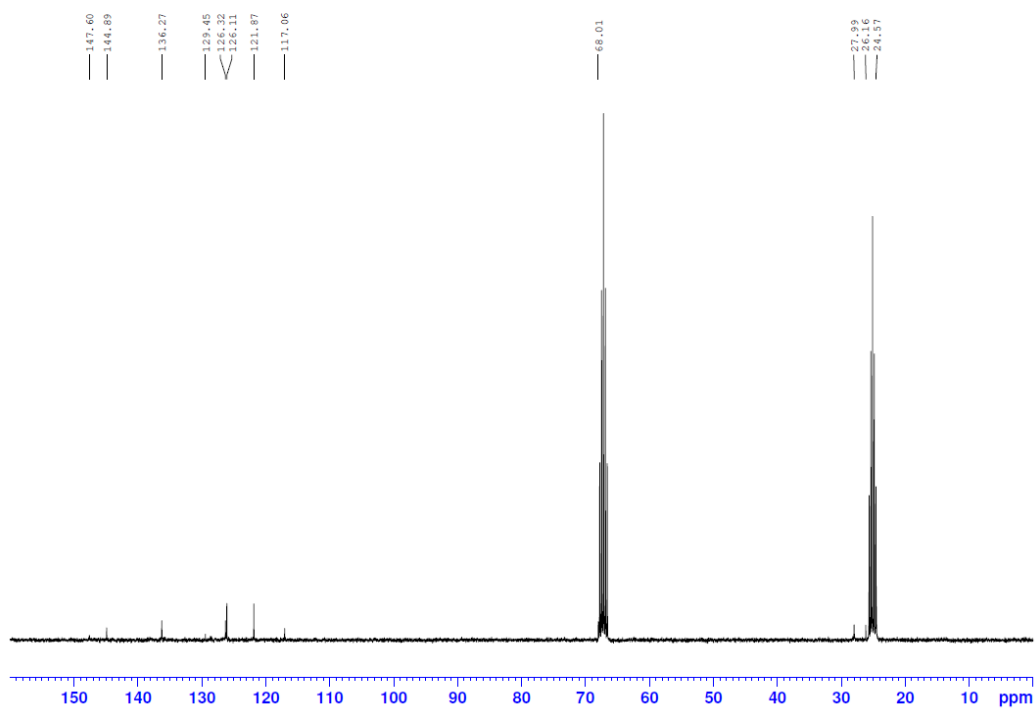


Figure S 50 $^{13}\text{C}\{\text{H}\}\text{-NMR}$ spectrum ($D_8\text{-THF}$, 75 MHz, 298 K) of **3d**

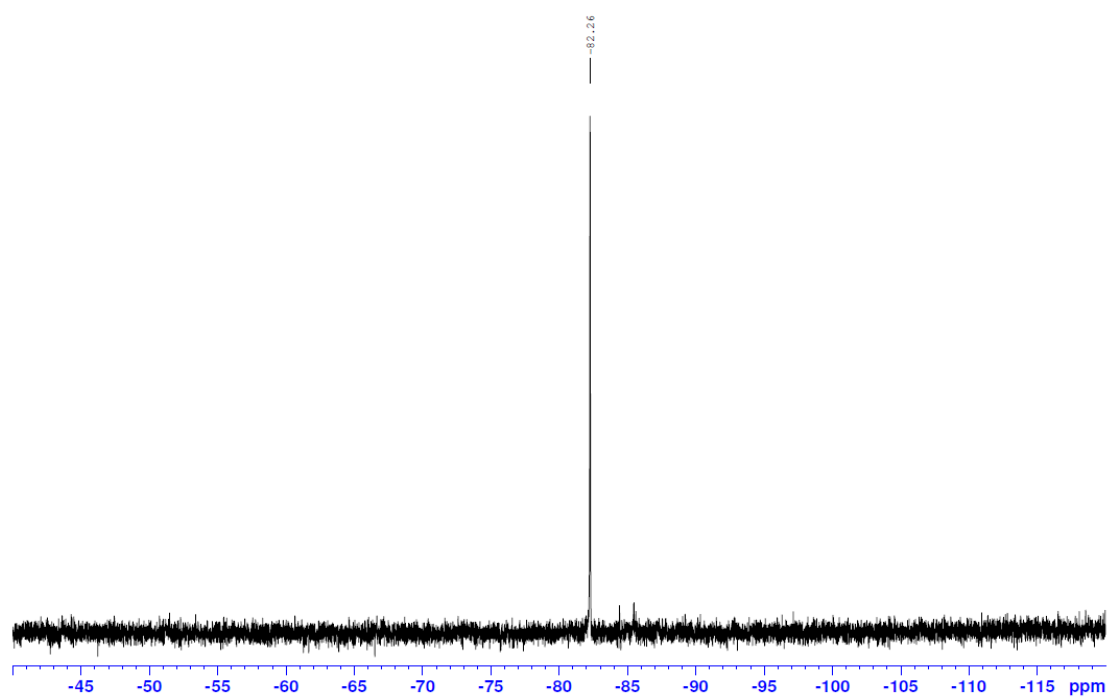


Figure S 51 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3d**

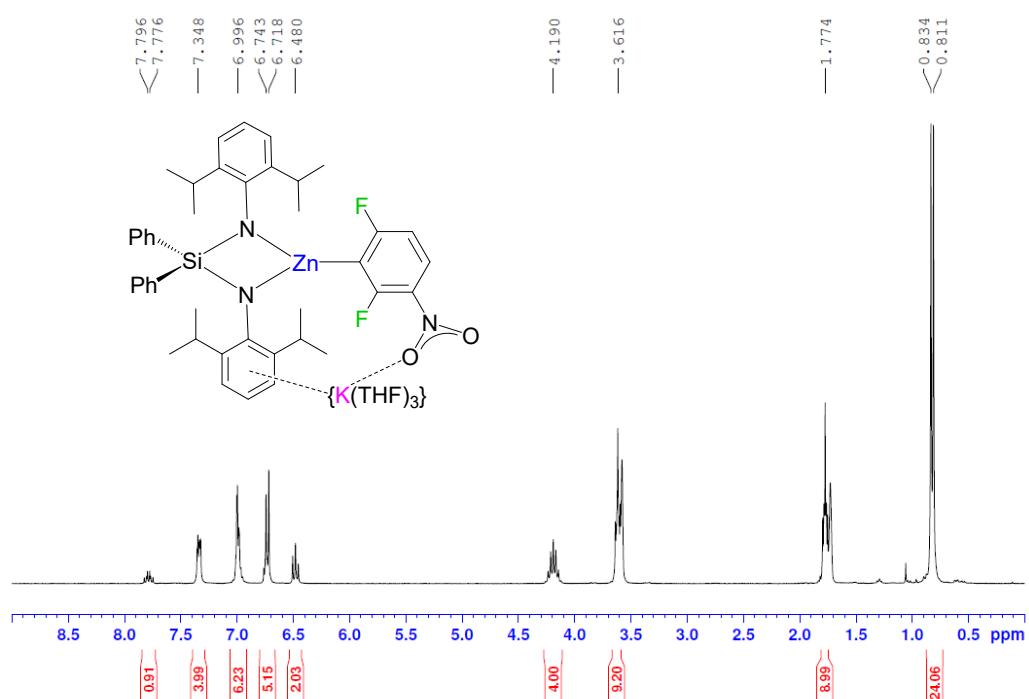


Figure S 52 ^1H -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3e**

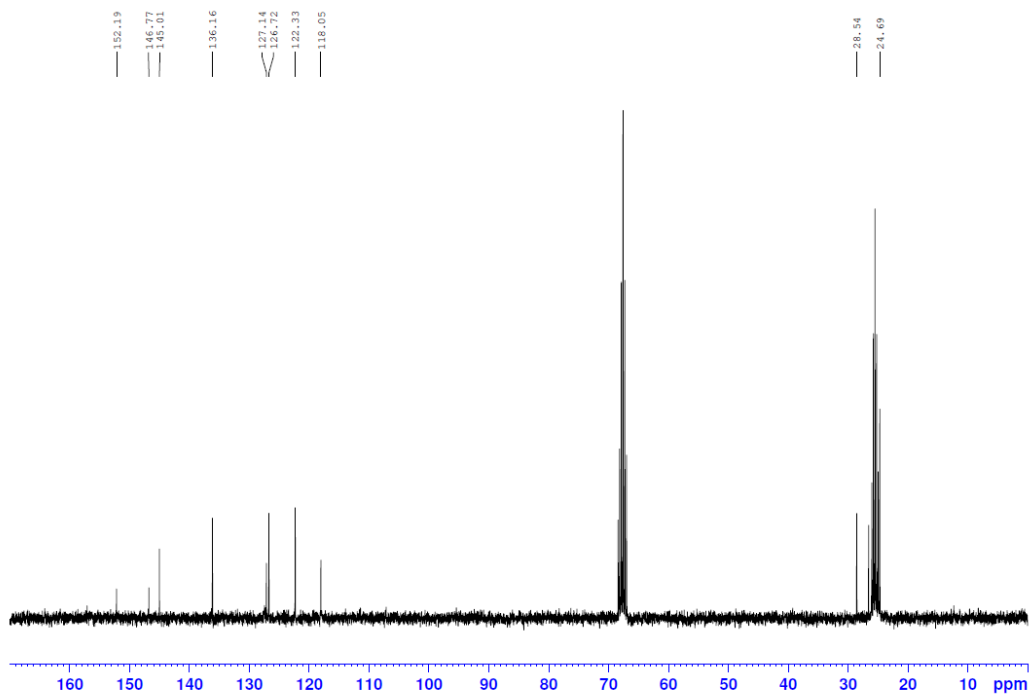


Figure S 53 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 75 MHz, 298 K) of **3e**

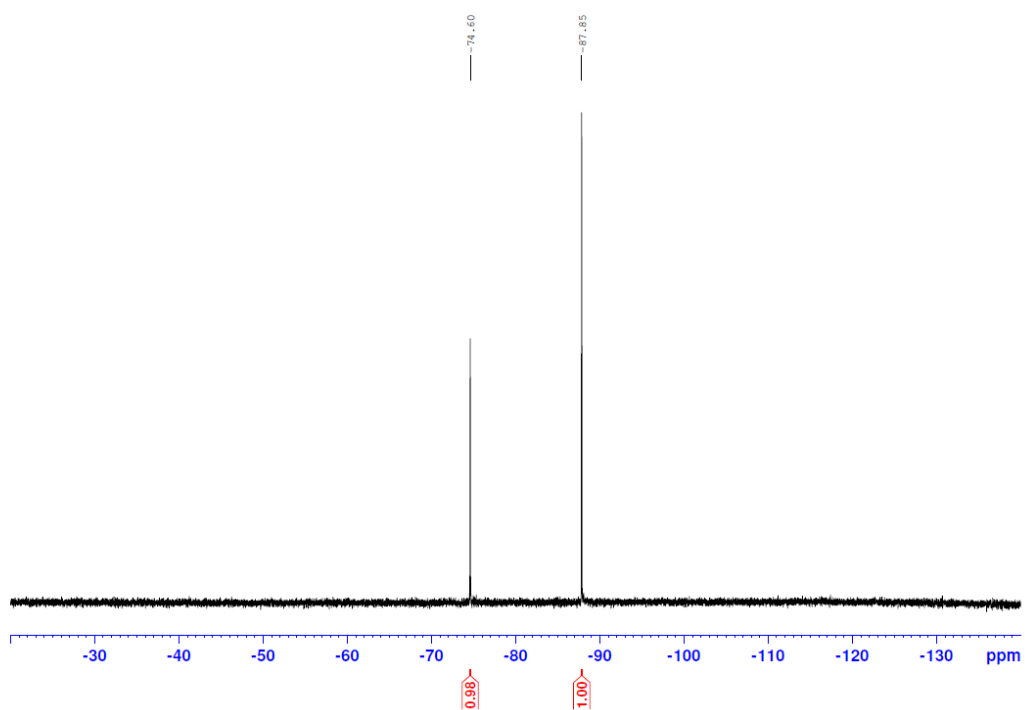


Figure S 54 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3e**

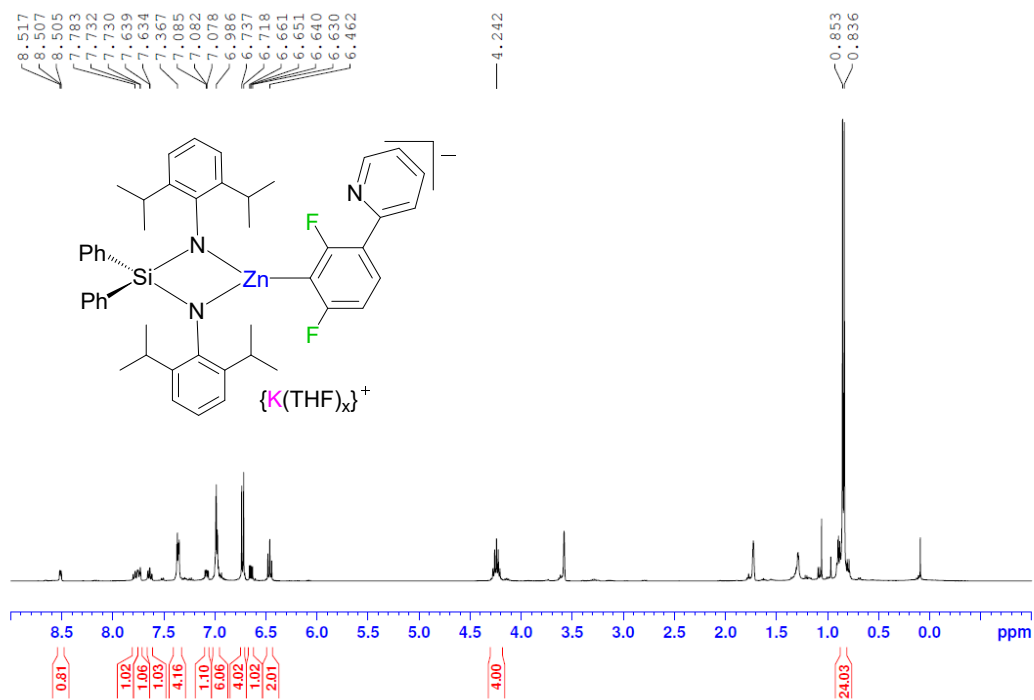


Figure S 55 1H -NMR (D_8 -THF, 400 MHz, 298 K) spectrum of **3f**

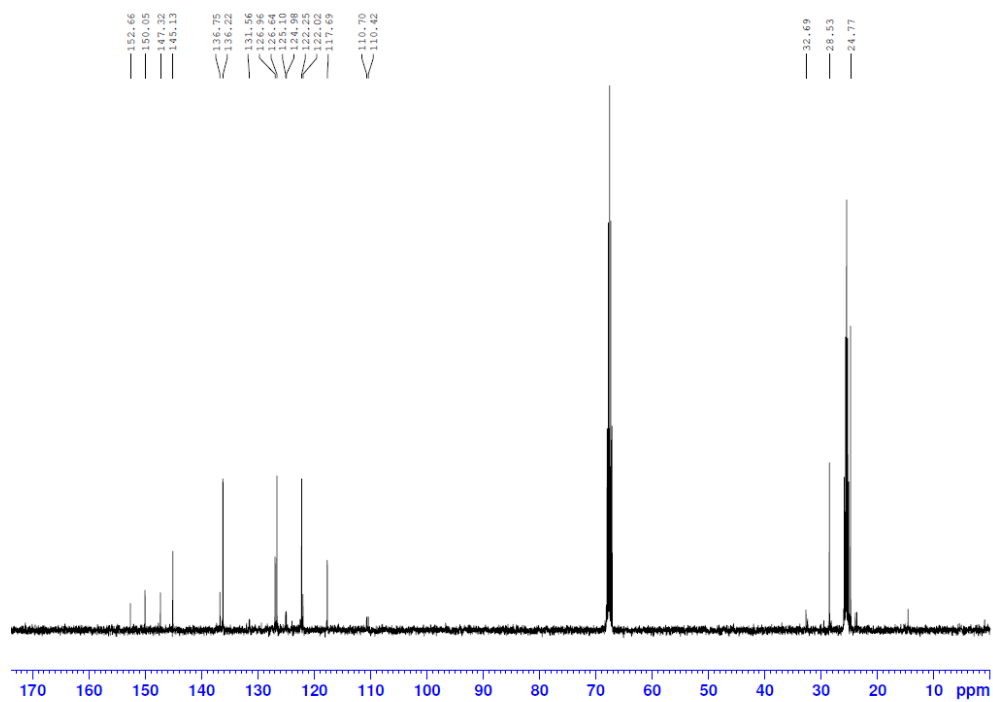


Figure S 56 $^{13}C\{^1H\}$ -NMR spectrum (D_8 -THF, 100 MHz, 298 K) of **3f**

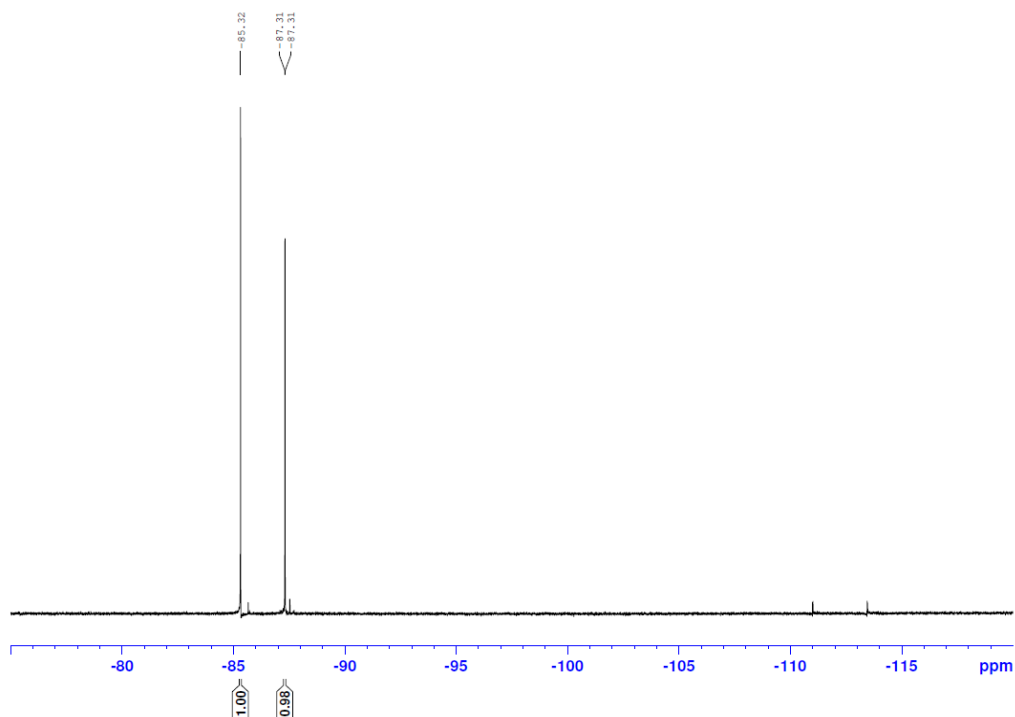


Figure S 57 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3f**

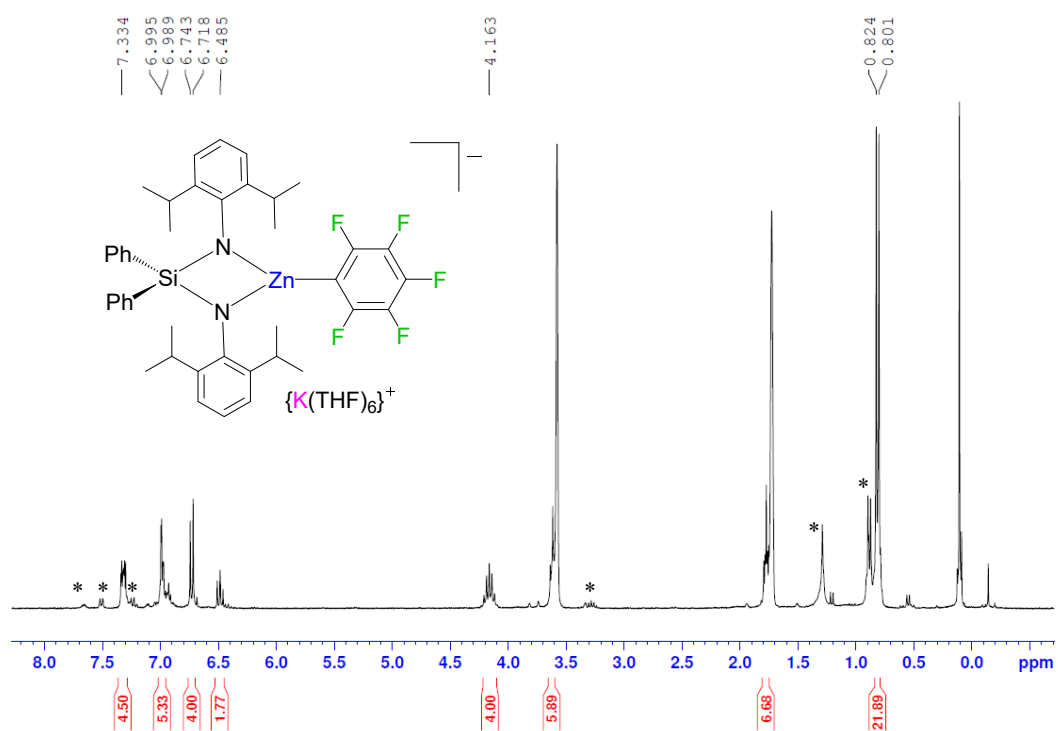


Figure S 58 ^1H -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3h**. Some impurities (*) are present due to the polibasicity reactivity of **1** towards pentafluorobenzene.

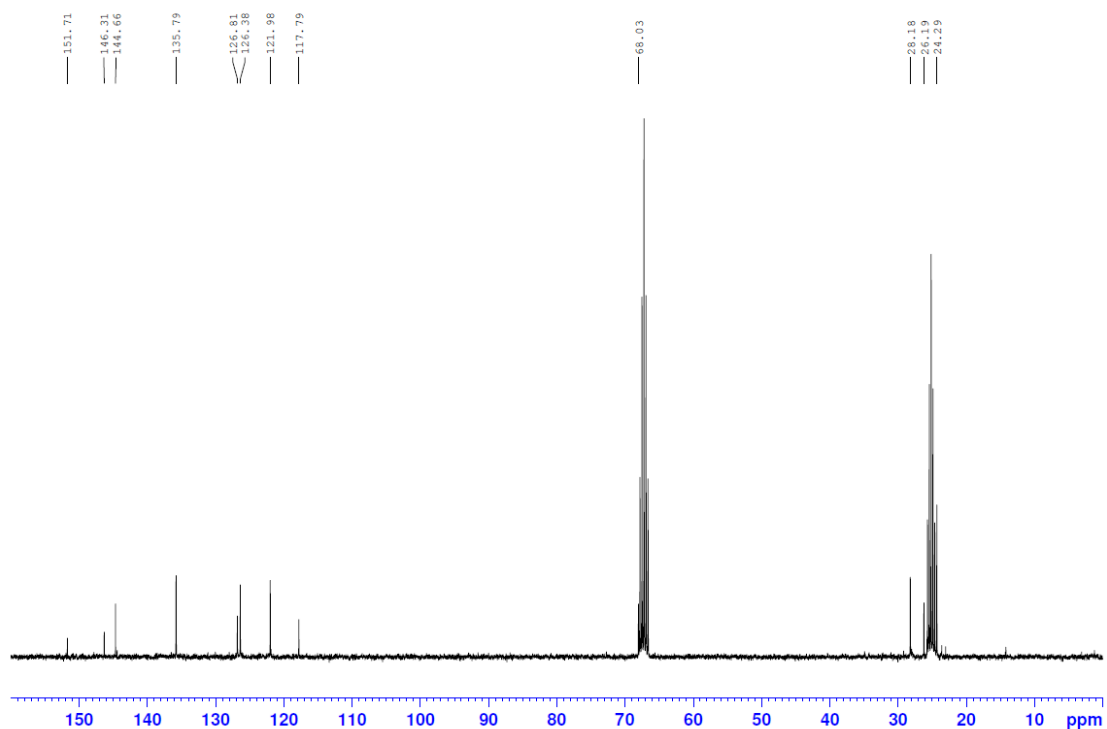


Figure S 59 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (D_8 -THF, 75 MHz, 298 K) of **3h**

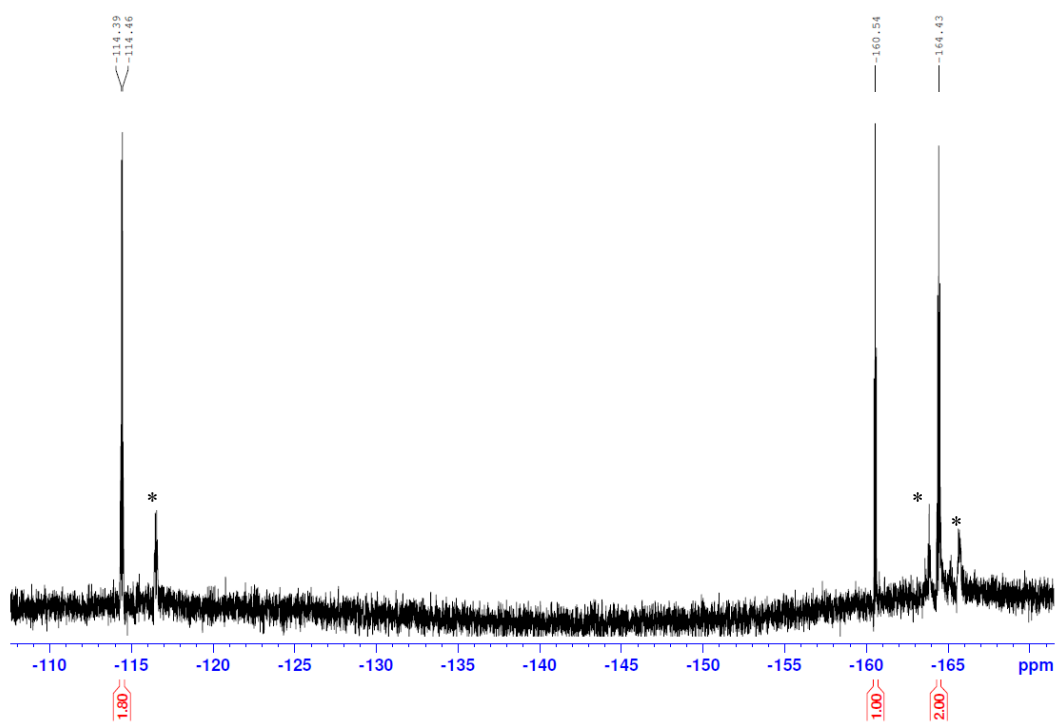


Figure S 60 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3h**. Some impurities (*) are present due to the polibasicity reactivity of **1** towards pentafluorobenzene.

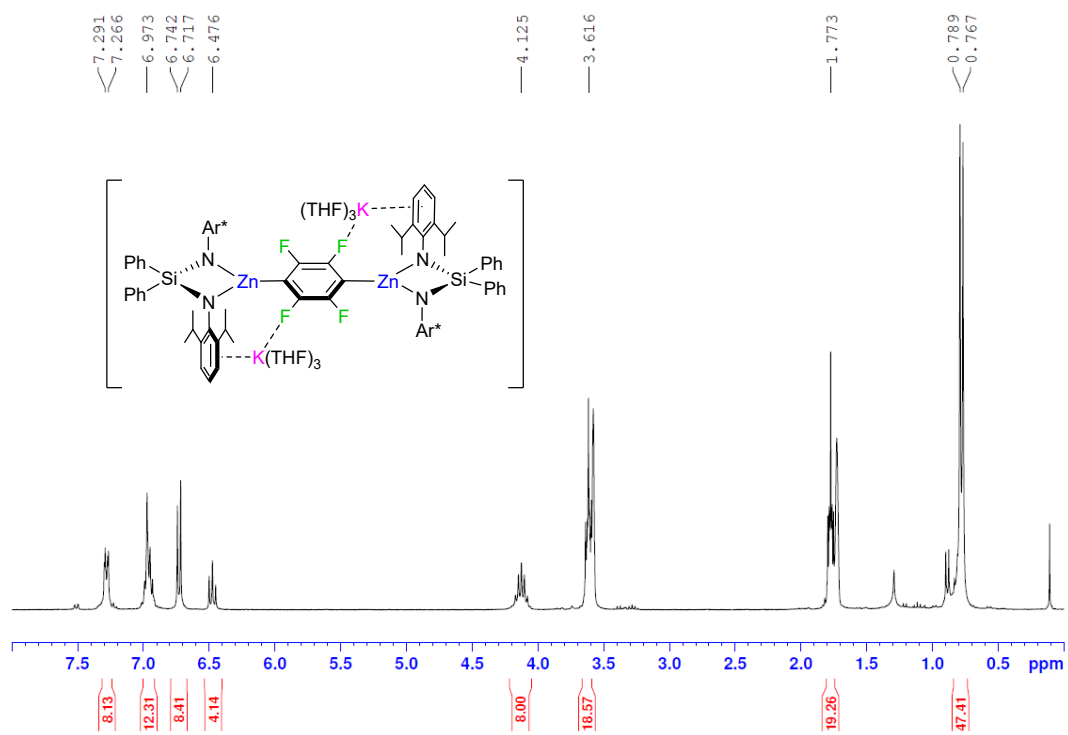


Figure S 61 ¹H-NMR (D₈-THF, 300 MHz, 298 K) spectrum of **3j**

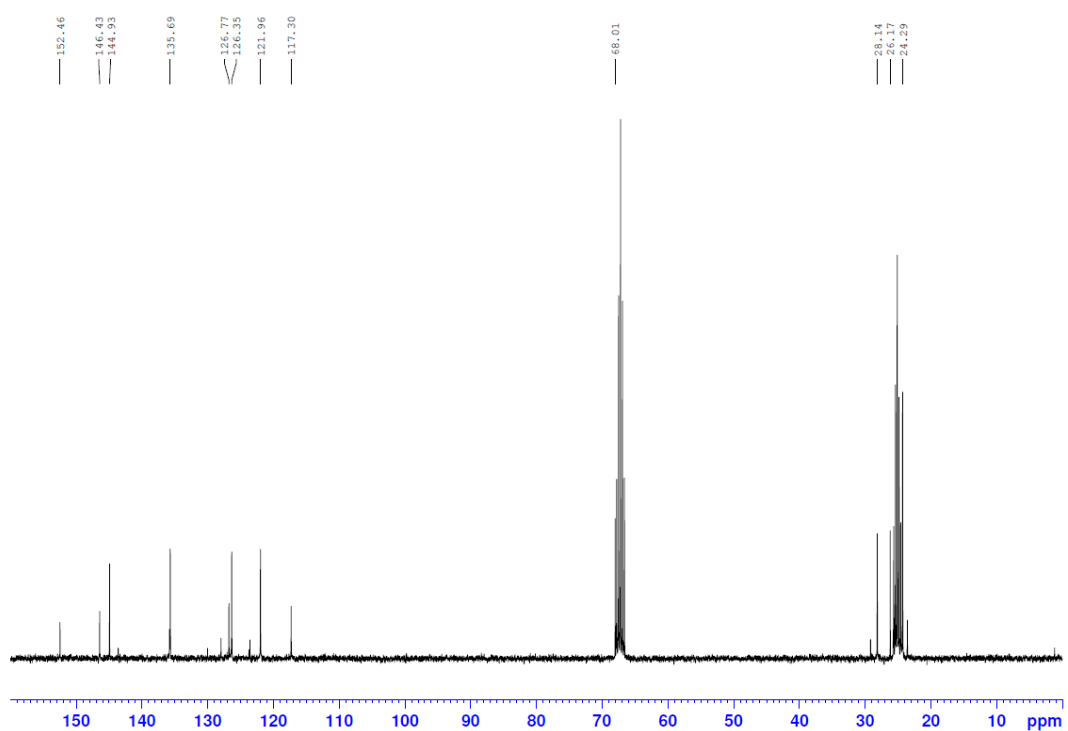


Figure S 62 ¹³C{H}-NMR spectrum (D₈-THF, 75 MHz, 298 K) of **3j**

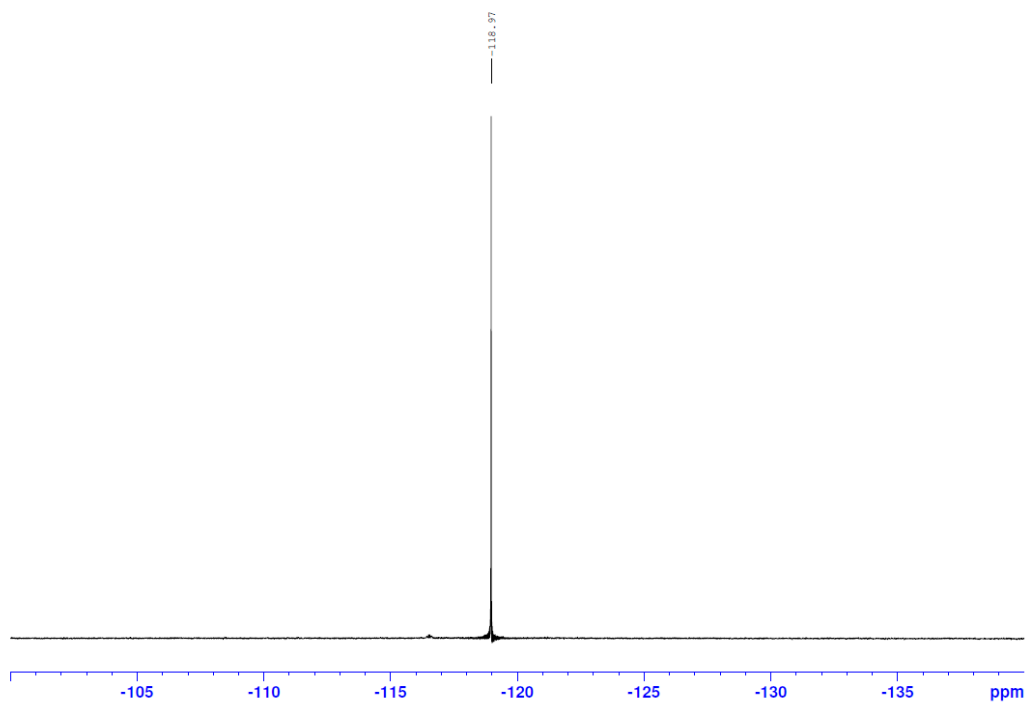


Figure S 63 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **3j**

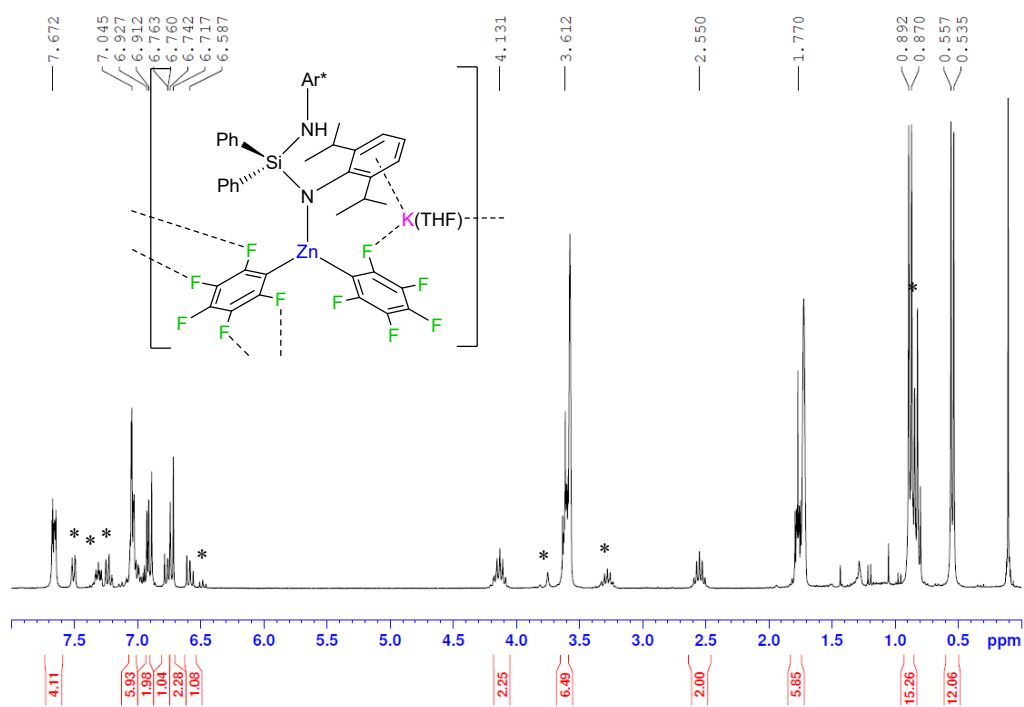


Figure S 64 ^1H -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **4** (*= $[\text{Ph}_2\text{Si}(\text{NAr}^*)_2]$ impurity)

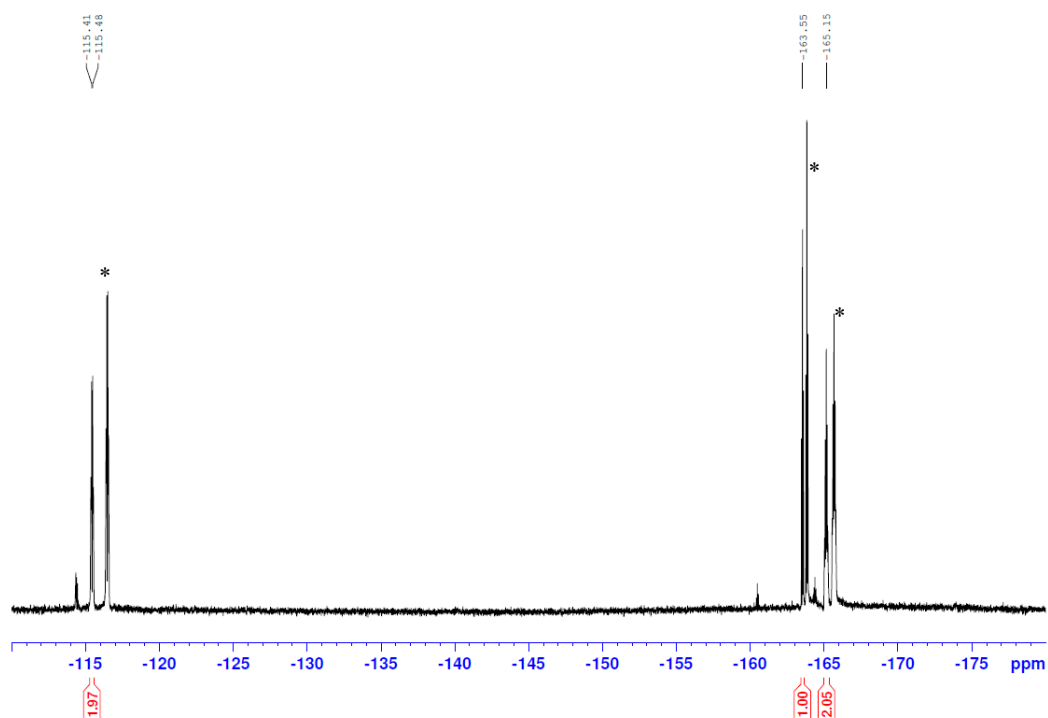


Figure S 65 ^{19}F -NMR (D_8 -THF, 300 MHz, 298 K) spectrum of **4** (*= $[\text{K}(\text{THF})_x\text{Zn}(\text{C}_6\text{F}_6)_3]$)

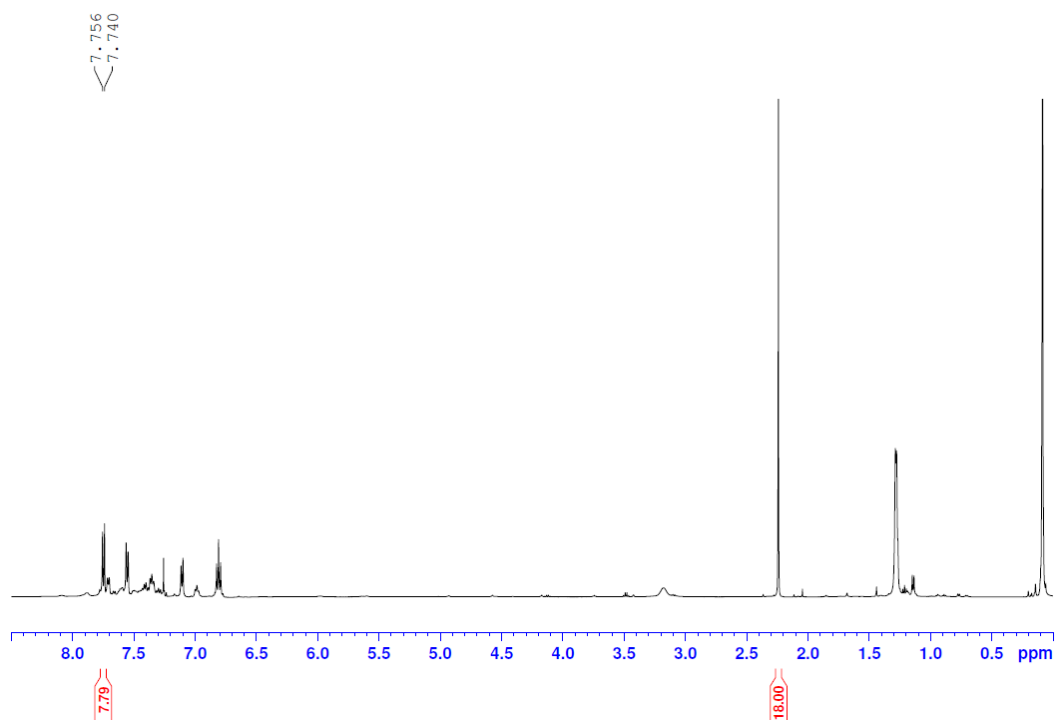


Figure S 66 ^1H -NMR (CDCl_3 , 400 MHz, 298 K) spectrum of the crude of the synthesis of 2',4',6'-trifluoro-[1,1'-biphenyl]-4-carbonitrile. The NMR yield was calculated against the integral of hexamethylbenzene, using the **equation 1**. The calculated yield is 63% (using as limiting reagent 4-Bromobenzonitrile, 0.45 mmol)

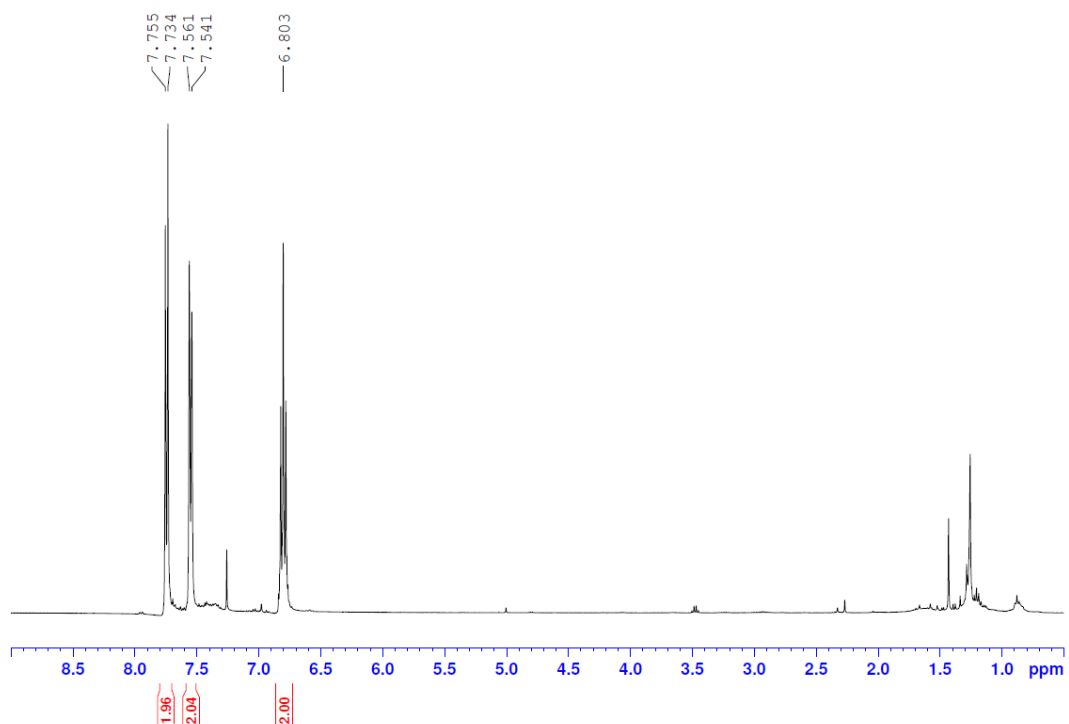


Figure S 67 $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 298 K) spectrum of the crude of the synthesis of 2',4',6'-trifluoro-[1,1'-biphenyl]-4-carbonitrile, after purification via silica-gel column

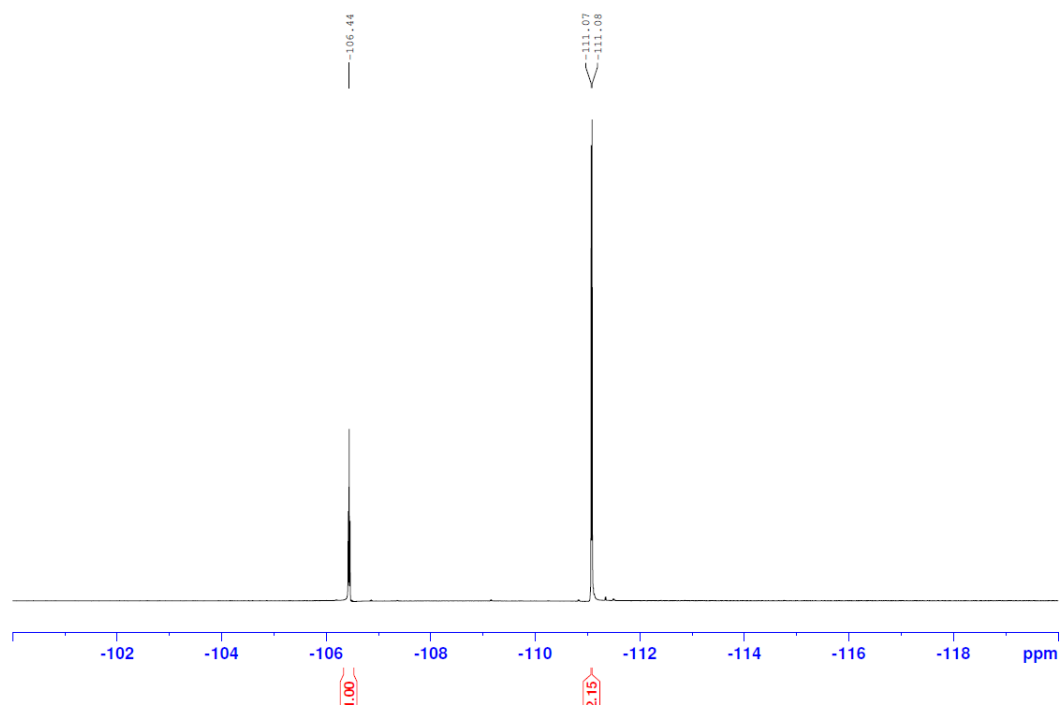


Figure S 68 $^{19}\text{F-NMR}$ (CDCl_3 , 400 MHz, 298 K) spectrum of the crude of the synthesis of 2',4',6'-trifluoro-[1,1'-biphenyl]-4-carbonitrile, after purification via silica-gel column

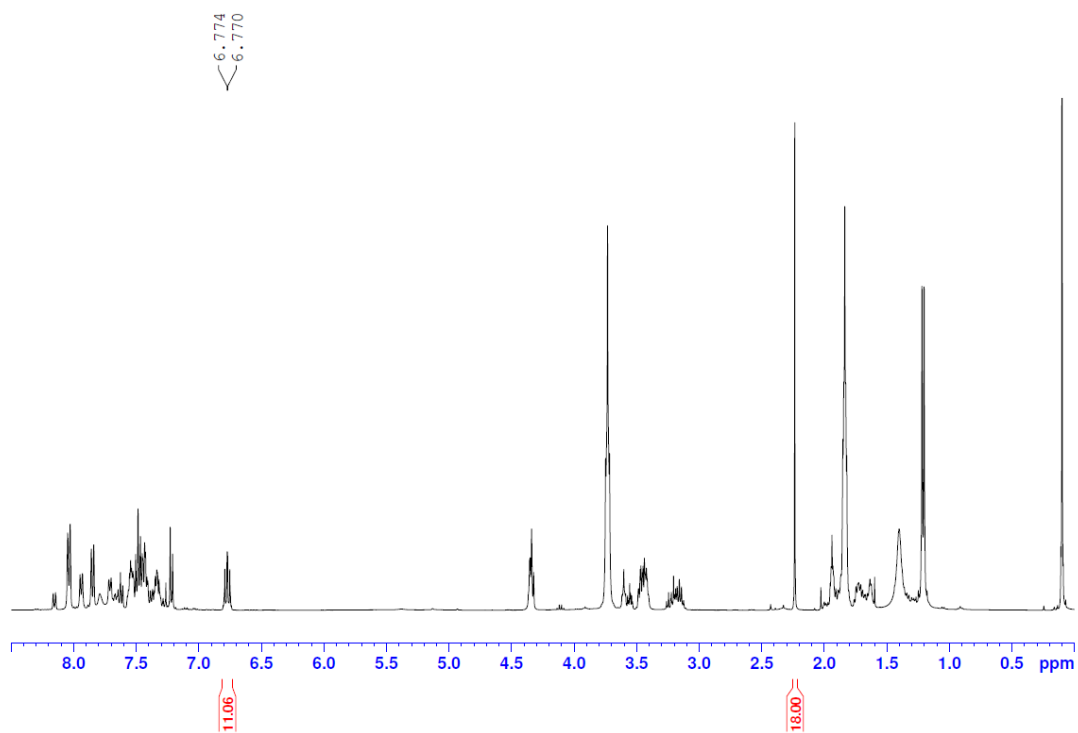


Figure S 69 $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 298 K) spectrum of the crude of the synthesis of Phenyl(2,4,6-trifluorophenyl)methanone. The NMR yield was calculated against the integral of hexamethylbenzene, using the **equation 1**. The calculated yield is 70%

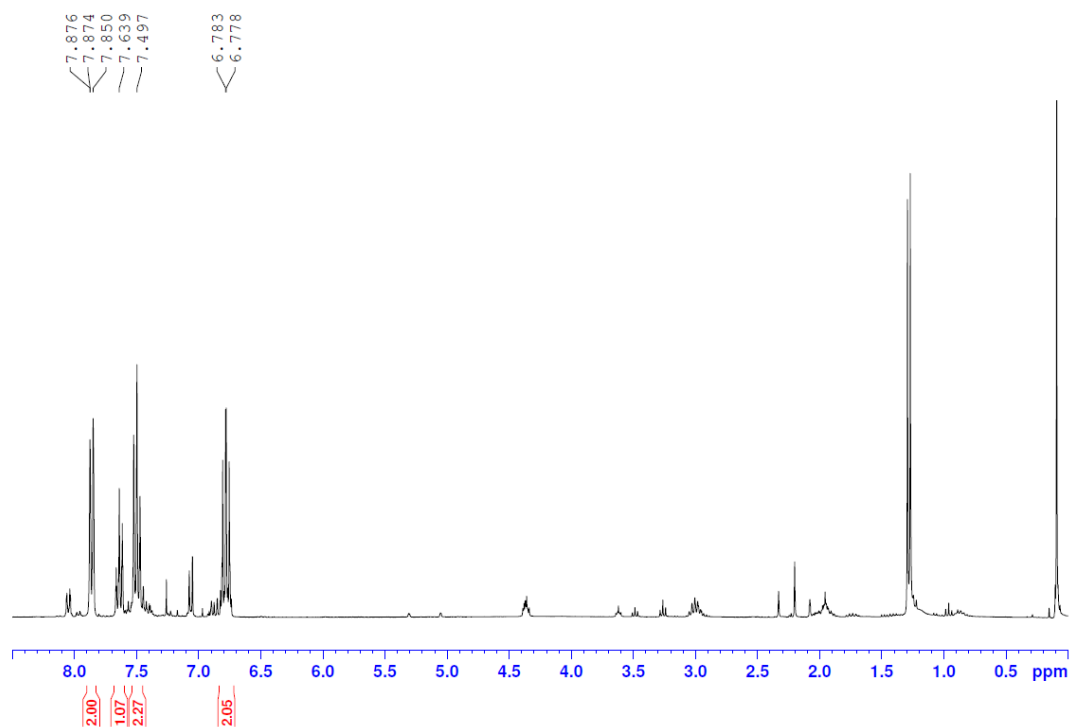


Figure S 70 $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, 298 K) spectrum of the crude of the synthesis of Phenyl(2,4,6-trifluorophenyl)methanone. after gel purification column.

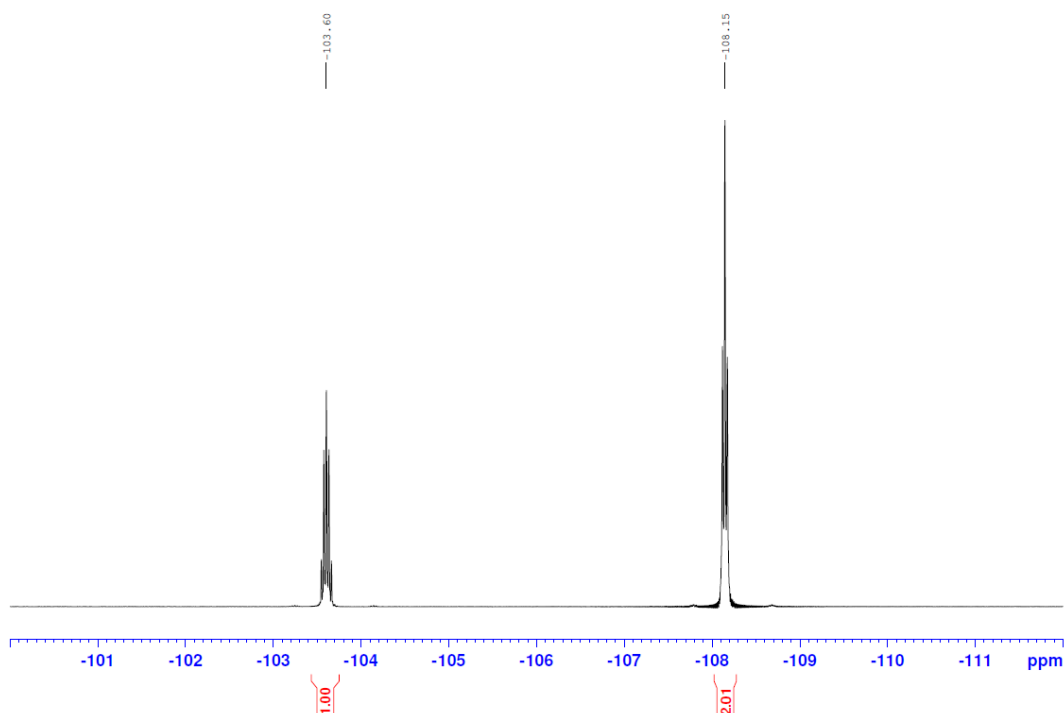


Figure S 71 ^{19}F -NMR (CDCl_3 , 400 MHz, 298 K) spectrum of the crude of the synthesis of Phenyl(2,4,6-trifluorophenyl)methanone. after gel purification column.

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