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Supporting Information

Molecular Zinc Hydride Cations $[ZnH]^+$: Synthesis, Structure, and CO_2 Hydrosilylation Catalysis

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Supporting Information

General Remarks

All reactions were performed under dry argon atmosphere using standard Schlenk technique or under argon in a glovebox, unless otherwise stated. Prior to use, glassware were dried at 130 °C overnight. Solvents were dried, distilled and degassed using standard methods or using a *MB SPS-800* solvent purification system. TMEDA (*N*,*N*,*N′*,*N′*-tetramethylethylenediamine) and TEEDA (*N*,*N*,*N′*,*N′*-tetraethylethylenediamine) were purchased from Sigma-Aldrich. $[ZnH_2]_n$,[S1] $[NEt_3H][B(3,5-(CF_3)_2C_6H_3)_4]$,[S2] Et_3SiH,[S3] and $B(3,5-(CF_3)_2C_6H_3)_3$[S4] were synthesized following literature procedures. ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on a *Bruker Avance II 400* or *Bruker Avance III HD 400* spectrometer in J. Young style NMR tubes at ambient temperature unless otherwise stated. Chemical shifts (δ in ppm) in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced internally to the residual signals of the deuterated solvents. Chemical shifts in the $^{11}B\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ spectra were referenced externally to $BF_3(OEt_2)$ or tetramethylsilane, respectively. The resonances in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were assigned based on two-dimensional NMR experiments (COSY, HSQC, HMBC). Abbreviations for multiplicities of NMR signals are as follows: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), br (broad). IR spectra were recorded as KBr pellets using an *AVATAR 360 FT-IR* spectrometer. Elemental analysis were performed on an *elementar vario EL* machine.

Experimental Procedures and Spectroscopic Data

Synthesis of [(TMEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (1a).

To a stirred solution of [NEt_3H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (1.50 g, 1.55 mmol) in Et_2O (5 mL) was added dropwise TMEDA (0.27 g, 2.32 mmol) in Et_2O (2 mL) and the mixture was stirred overnight at room temperature. The solution was concentrated *in vacuo*. Addition of *n*-pentane resulted in the precipitation of a solid. The supernatant was decanted off, the residue was washed with *n*-pentane (2 × 3 mL) and dried *in vacuo* to give [(TMEDA)H][B(3,5-$(CF_3)_2C_6H_3)_4$] as colorless solid (1.50 g, 1.52 mmol). Yield: 98%.

^{1}H NMR (400 MHz, [D_3]acetonitrile): δ = 2.46 (s, N-C*H*$_3$, 12H), 2.75 (s, N-C*H*$_2$, 4H), 3.64 (br, NH, 1H), 7.67 (s, *para*-C_6H_3, 4H), 7.69 (s, *ortho*-C_6H_3, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D_3]acetonitrile): δ = 44.86 (N-*C*H$_3$), 55.27 (N-*C*H$_2$), 118.72 (*para*-C_6H_3), 124.16 (q, $^1J_{C\text{-}F}$ = 271.6 Hz, *C*F$_3$), 130.08 (qq, $^2J_{C\text{-}F}$ = 31.6 Hz, $^3J_{C\text{-}B}$ = 2.8 Hz, *meta*-C_6H_3), 135.70 (*ortho*-C_6H_3), 162.66 (q, $^1J_{B\text{-}C}$ = 50.1 Hz, *ipso*-C_6H_3) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D_3]acetonitrile): δ = -6.67 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D_3]acetonitrile): δ = -63.27 ppm.

IR (KBr): ν = 2973 cm^{-1} (br, NH).

Anal. Calcd. for $C_{38}H_{29}N_2BF_{24}$ (980.44 g · mol^{-1}): C, 46.55; H, 2.98; N, 2.86. Found: C, 46.77; H, 3.05; N, 3.21%.

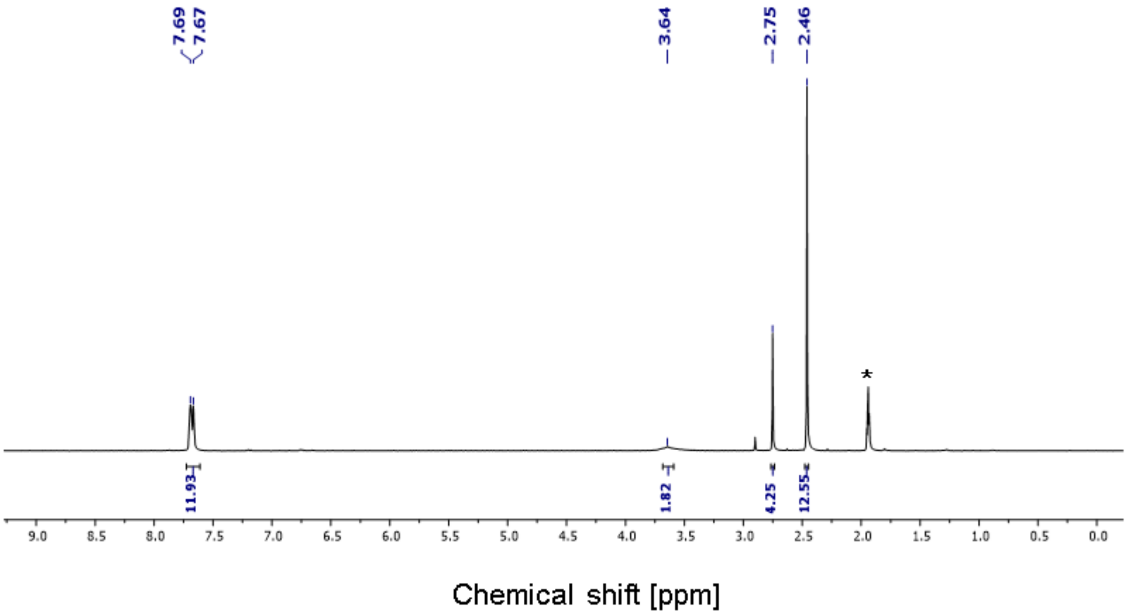


Figure S1: ^{1}H NMR spectrum of [(TMEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1a**) in [D_3]acetonitrile (*).

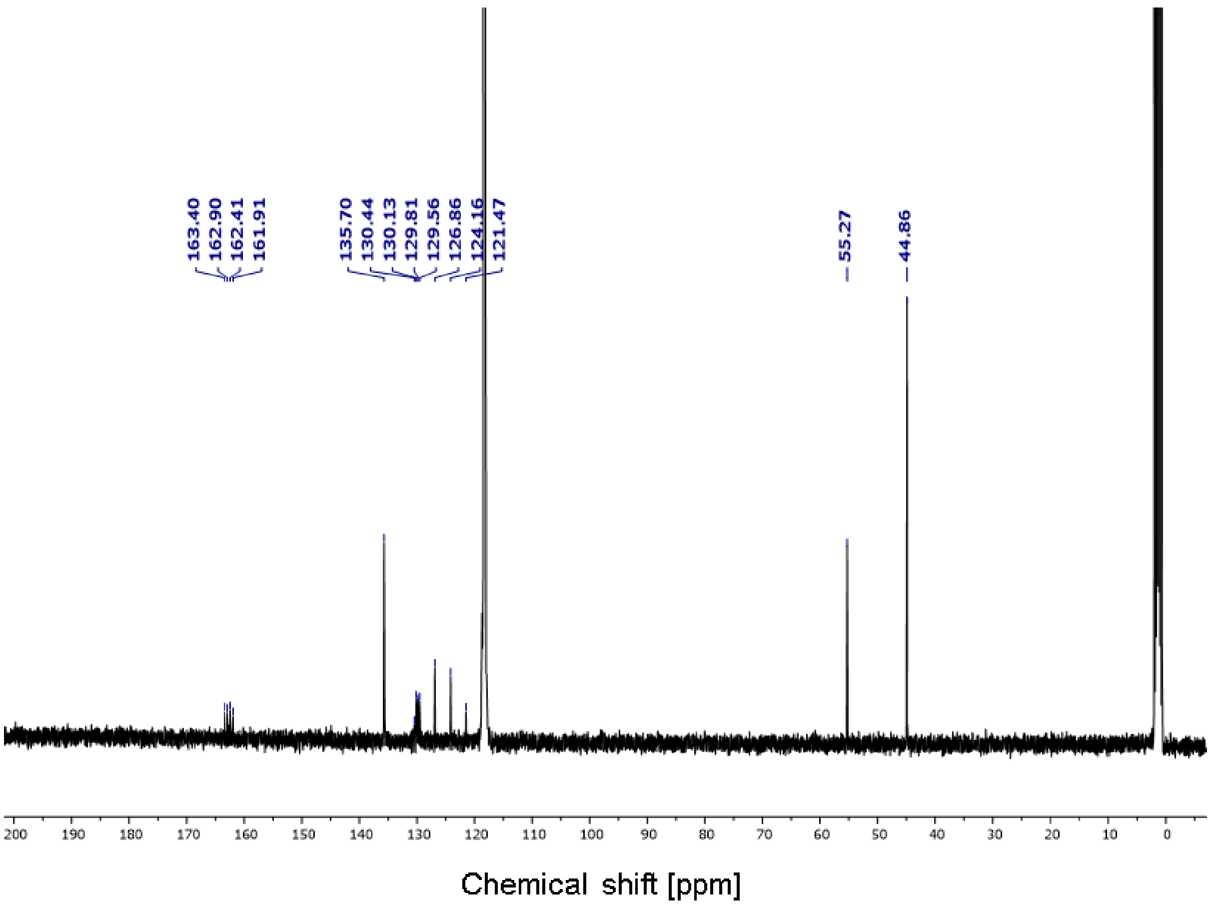


Figure S2: $^{13}C\{^1H\}$ NMR spectrum of [(TMEDA)H][B(3,5-$(CF_3)_2C_6H_3)_4$] (**1a**) in [D_3]acetonitrile.

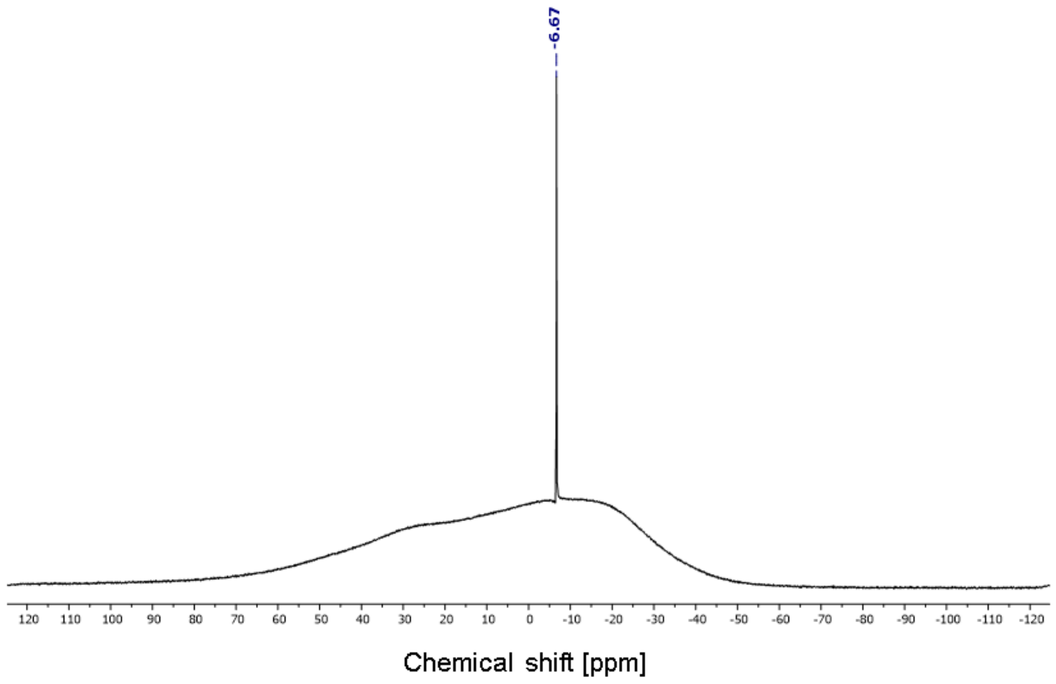


Figure S3: $^{11}B\{^1H\}$ NMR spectrum of [(TMEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1a**) in [D_3]acetonitrile.

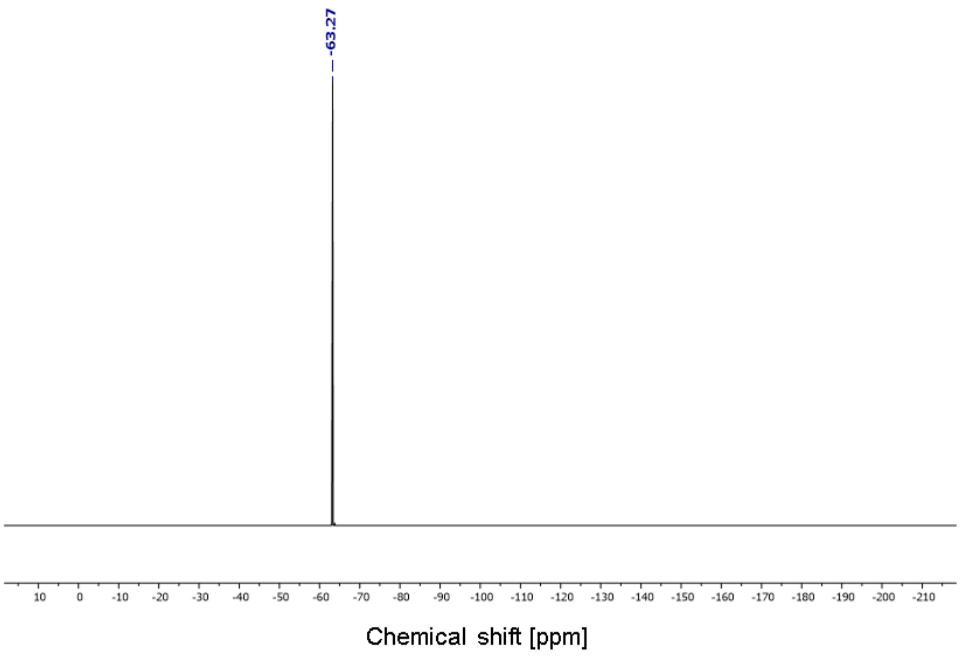


Figure S4: $^{19}F\{^1H\}$ NMR spectrum of [(TMEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1a**) in [D_3]acetonitrile.

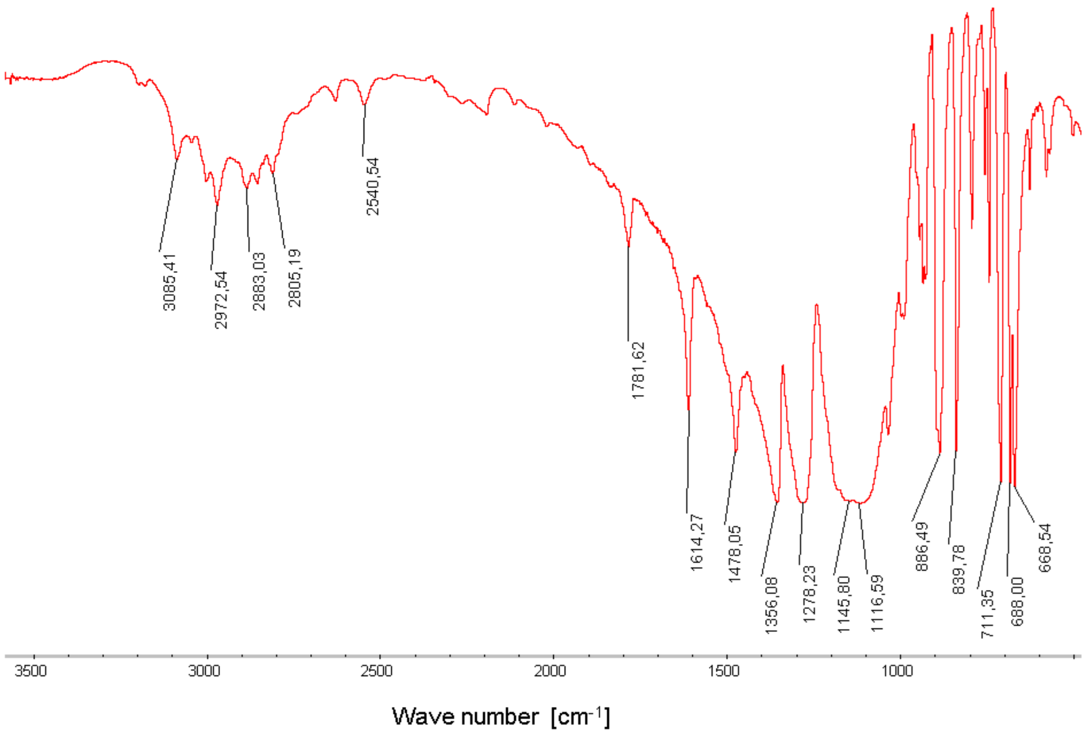


Figure S5: IR spectrum (KBr pellet) of [(TMEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1a**).

Synthesis of [(TEEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (1b).

To a stirred solution of [NEt_3H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (0.500 g, 0.517 mmol) in Et_2O (5 mL) was added a solution of TEEDA (0.131 g, 0.760 mmol) in Et_2O (2 mL) and the mixture was stirred overnight at room temperature. The solution was concentrated *in vacuo*. Addition of n-pentane resulted in the precipitation of a solid. The supernatant was decanted off, the residue washed with *n*-pentane (2 × 3 mL) and dried *in vacuo* to give [(TEEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] as a colorless solid (0.523 g, 0.504 mmol). Yield: 97%.

^{1}H NMR (400 MHz, [D_3]acetonitrile): δ = 1.13 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, N-$CH_2C\mathit{H}_3$, 12H), 2.51 (q, $^3J_{C\text{-}H}$ = 7.2 Hz, N-$C\mathit{H}_2CH_3$, 8H), 2.89 (s, N-$C\mathit{H}_2C\mathit{H}_2$, 4H), 4.92 (br, NH, 1H), 7.67 (s, *para*-C_6H_3, 4H), 7.70 (s, *ortho*-C_6H_3, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D_3]acetonitrile): δ = 10.27 (N-$CH_2\mathit{C}H_3$), 47.57 (N-$\mathit{C}H_2CH_3$), 48.75 (N-$\mathit{C}H_2$), 118.71 (*para*-C_6H_3), 125.49 (q, $^1J_{C\text{-}F}$ = 271.7 Hz, $\mathit{C}F_3$), 129.95 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{C\text{-}B}$ = 2.8 Hz, *meta*-C_6H_3), 135.68 (*ortho*-C_6H_3), 162.63 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-C_6H_3) ppm.

^{13}B{^{1}H} NMR (128 MHz, [D_3]acetonitrile): δ = -6.67 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D_3]acetonitrile): δ = -63.67 ppm.

IR (KBr): ν = 2976 cm^{-1}(br, NH).

Anal. Calcd. for $C_{42}H_{37}N_2BF_{24}$ (1036.54 g · mol^{-1}): C, 48.67; H, 3.60; N, 2.70. Found: C, 48.16; H, 4.05; N, 2.94%.

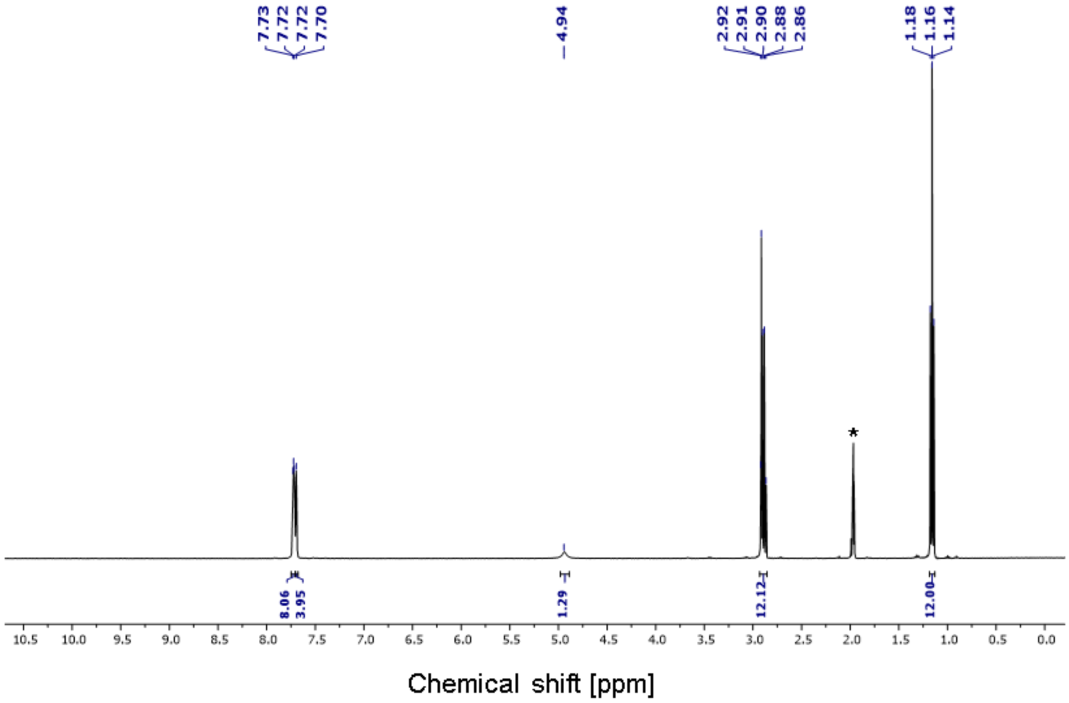


Figure S6: ^{1}H NMR spectrum of [(TEEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1b**) in [D_3]acetonitrile (*).

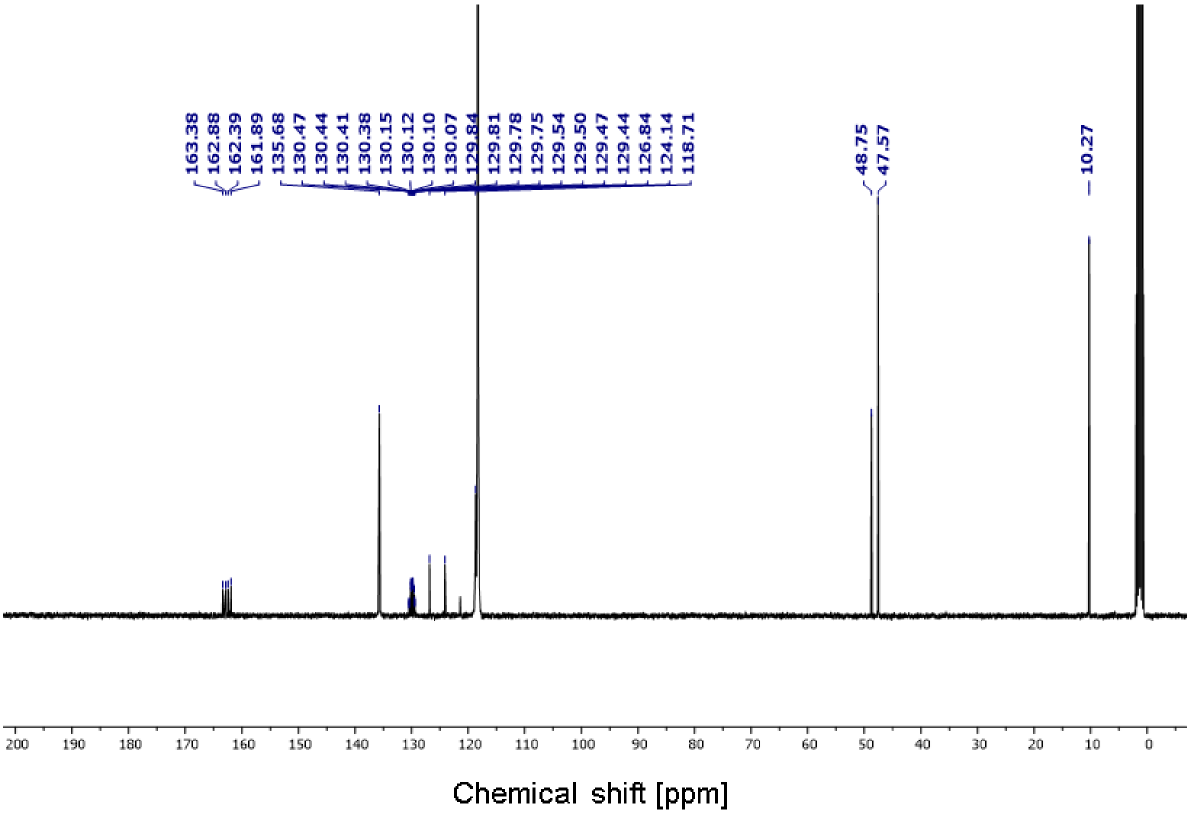


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of [(TEEDA)H][B(3,5-$(CF_3)_2$-C_6H_3)$_4$] (**1b**) in [D_3]acetonitrile.

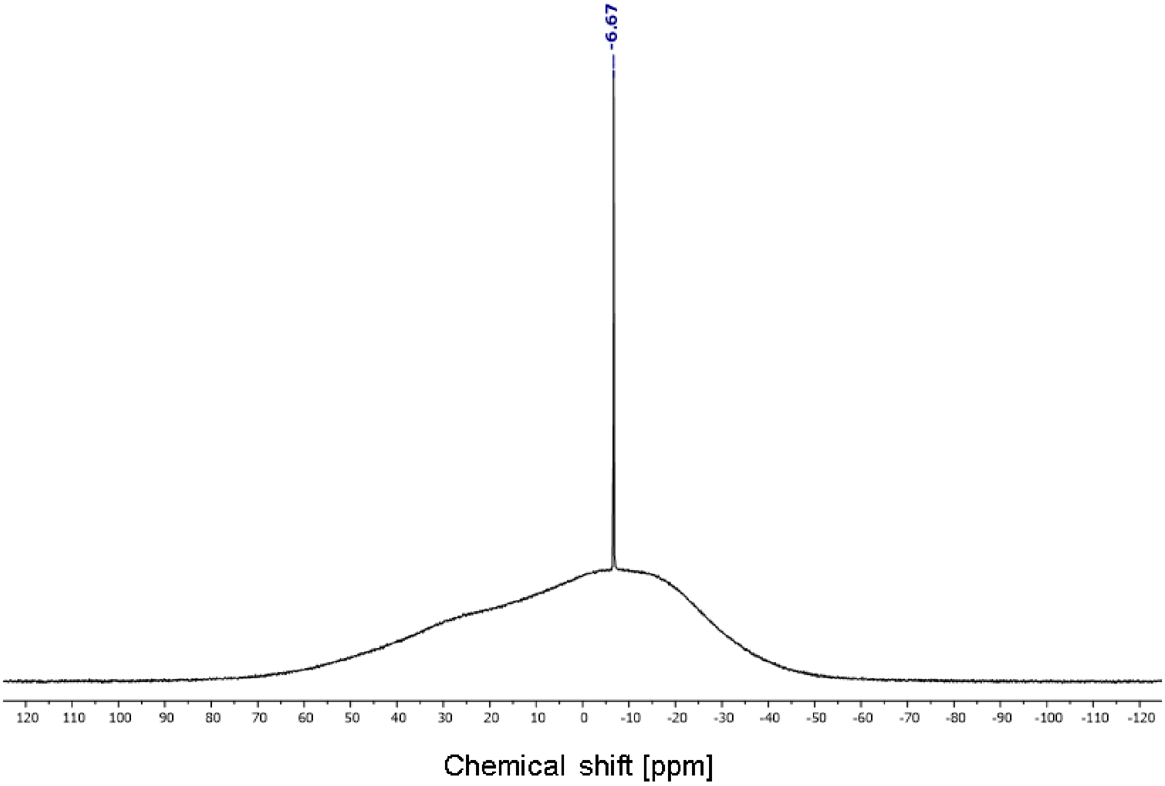


Figure S8: $^{11}B\{^{1}H\}$ NMR spectrum of [(TEEDA)H][B(3,5-$(CF_3)_2$-C_6H_3)$_4$] (**1b**) in [D_3]acetonitrile.

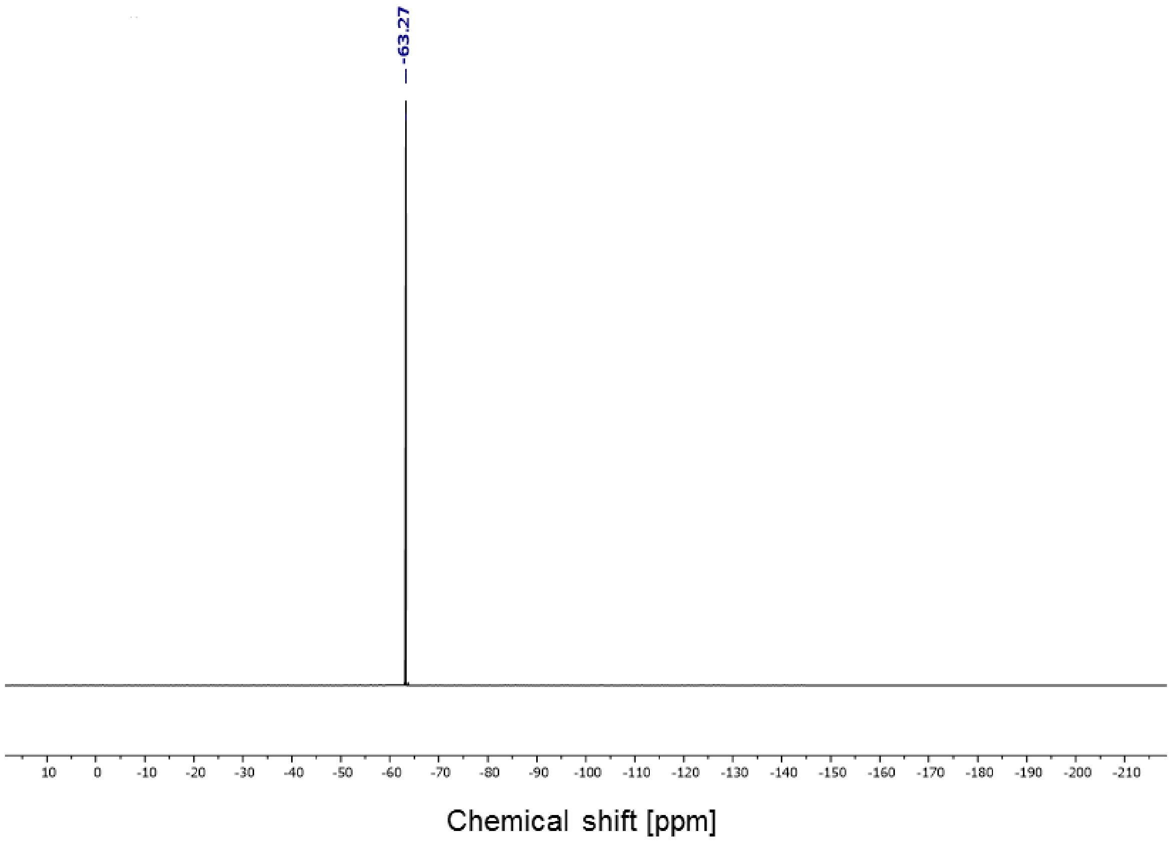


Figure S9: $^{19}F\{^{1}H\}$ NMR spectrum of [(TEEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1b**) in [D_3]acetonitrile.

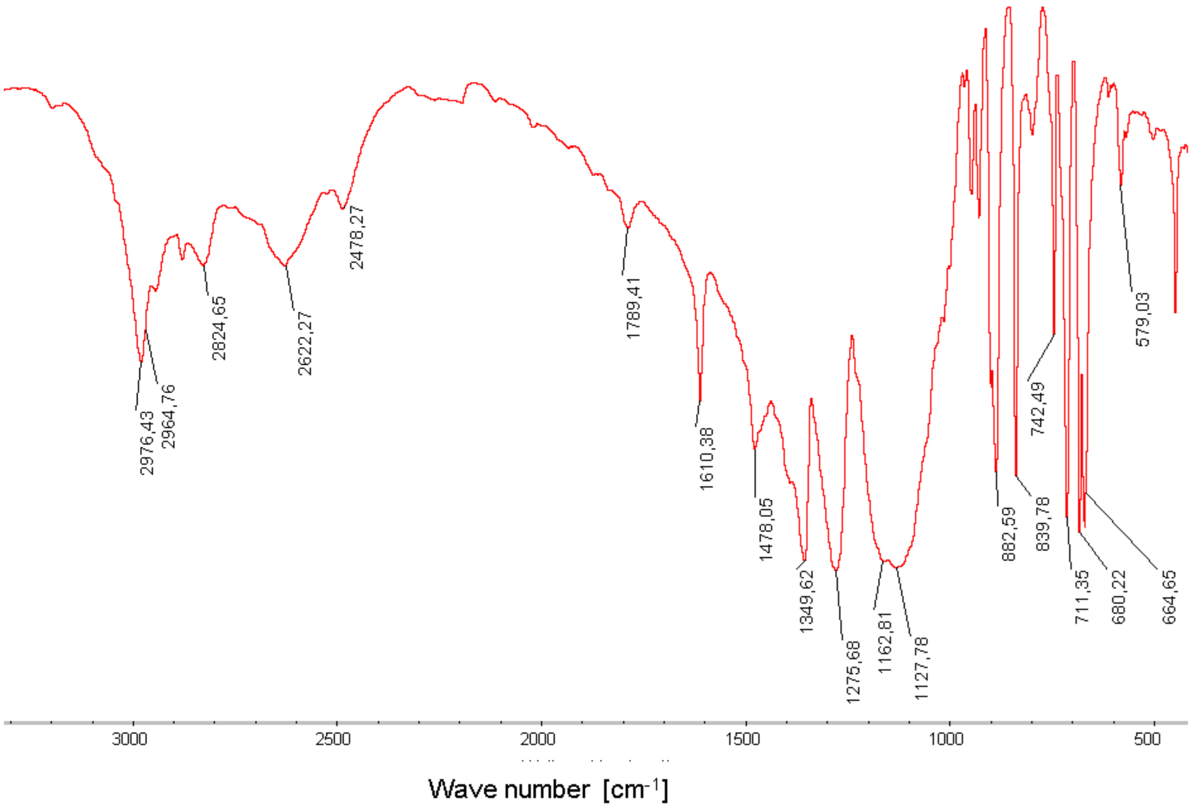


Figure S10: IR spectrum (KBr pellet) of [(TEEDA)H][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**1b**).

Synthesis of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (2a).

To a suspension of $[ZnH_2]_n$ (34 mg, 0.51 mmol) in THF (5 mL) was added dropwise a solution of [(TMEDA)H][B(3,5-$(CF_3)_2$-C_6H_3)] (0.500 g, 0.51 mmol) in THF (5 mL) at room temperature. After gas evolution had ceased (approximately 15 min) the reaction mixture was filtered. The solution was concentrated in *vacuo* and subsequent addition of *n*-pentane resulted in the precipitation of a colorless solid. The solvent was removed by decantation. Drying under reduced pressure gave [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] as a colorless solid (535 mg, 0.48 mmol). Yield: 94%.

^1H NMR (400 MHz, [D8]THF): δ = 1.78 (m, THF, 4H), 2.60 (s, N-C*H*$_3$, 12H), 2.87 (s, N-C*H*$_2$, 4H), 3.65 (m, THF, 4H), 3,68 (s, Zn-*H*, 1H) 7.59 (s, *para*-C_6H_3, 4H), 7.80 (s, *ortho*-C_6H_3, 8H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, [D8]THF): δ = 26.43 (thf), 47.37 (N-*C*H$_3$), 57.97 (N-*C*H$_2$*C*H$_2$), 68.27 (thf), 118.26 (*para*-C_6H_3), 125.58 (q, $^1J_{C\text{-}F}$ = 272 Hz, *C*F$_3$), 130.08 (qq, $^2J_{C\text{-}F}$ = 31.6 Hz, $^3J_{C\text{-}B}$ = 3.5 Hz, *meta*-C_6H_3), 135.66 (*ortho*-C_6H_3), 162.88 (q, $^1J_{B\text{-}C}$ = 50 Hz, *ipso*-C_6H_3).ppm.

$^{11}B\{^1H\}$ NMR (128 MHz, [D8]THF): δ = -6.48 ppm.

$^{19}F\{^1H\}$ NMR (377 MHz, [D8]THF): δ = 63.42 ppm.

^1H NMR (400 MHz, CD_2Cl_2): δ = 1.99 (m, THF, 4H), 2.56 (s, N-C*H*$_3$, 12H), 2.75 (s, N-C*H*$_2$, 4H), 3.56 (s, Zn-*H*, 1H), 4.03 (m, THF, 4H), 7.58 (s, *para*-C_6H_3, 4H), 7.73 (s, *ortho*-C_6H_3, 2.1, 8H) ppm.

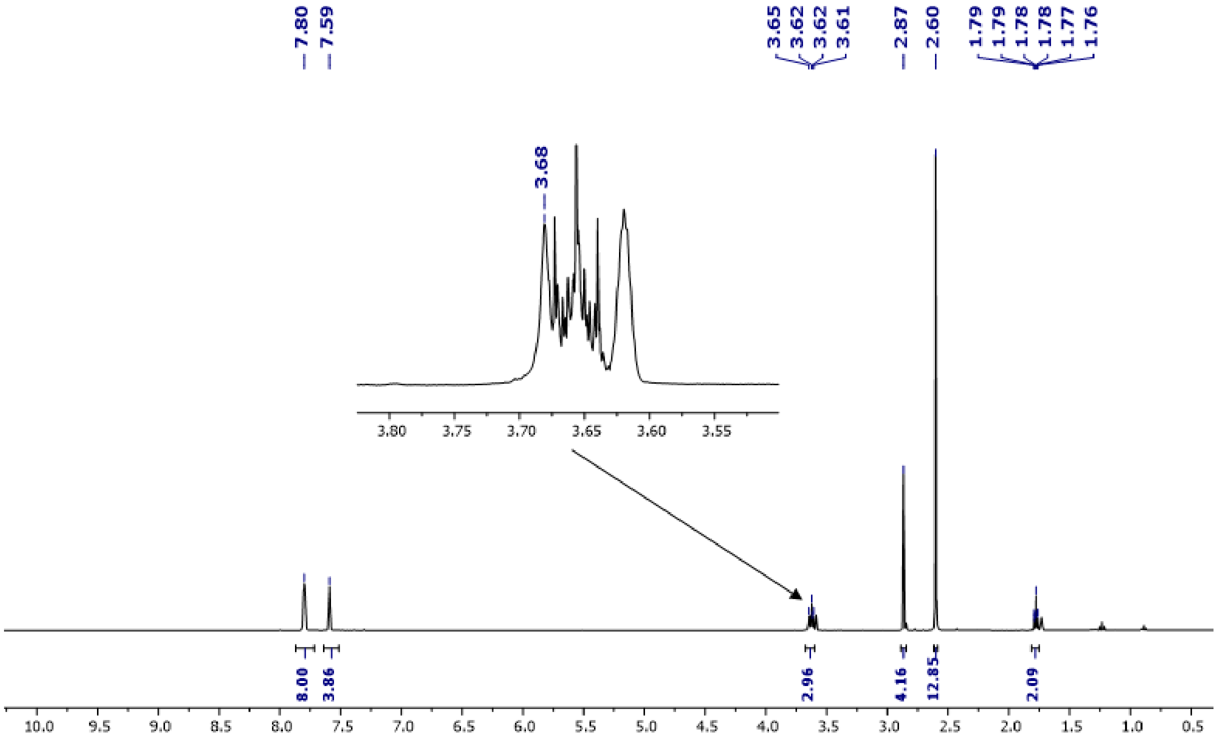
$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 25.87 (THF), 47.97 (N-*C*H$_3$), 57.84 (N-*C*H$_2$), 72.61 (THF), 118.12 (*para*-C_6H_3), 125.24 (q, $^1J_{C\text{-}F}$ = 272.4 Hz, *C*F$_3$), 129.46 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{C\text{-}B}$ = 2.5 Hz, *meta*-C_6H_3), 135.44 (*ortho*-C_6H_3), 162.39 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-C_6H_3) ppm.

$^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ = -6.47 ppm.

$^{19}F\{^1H\}$ NMR (377 MHz, CD_2Cl_2): δ = -63.42 ppm.

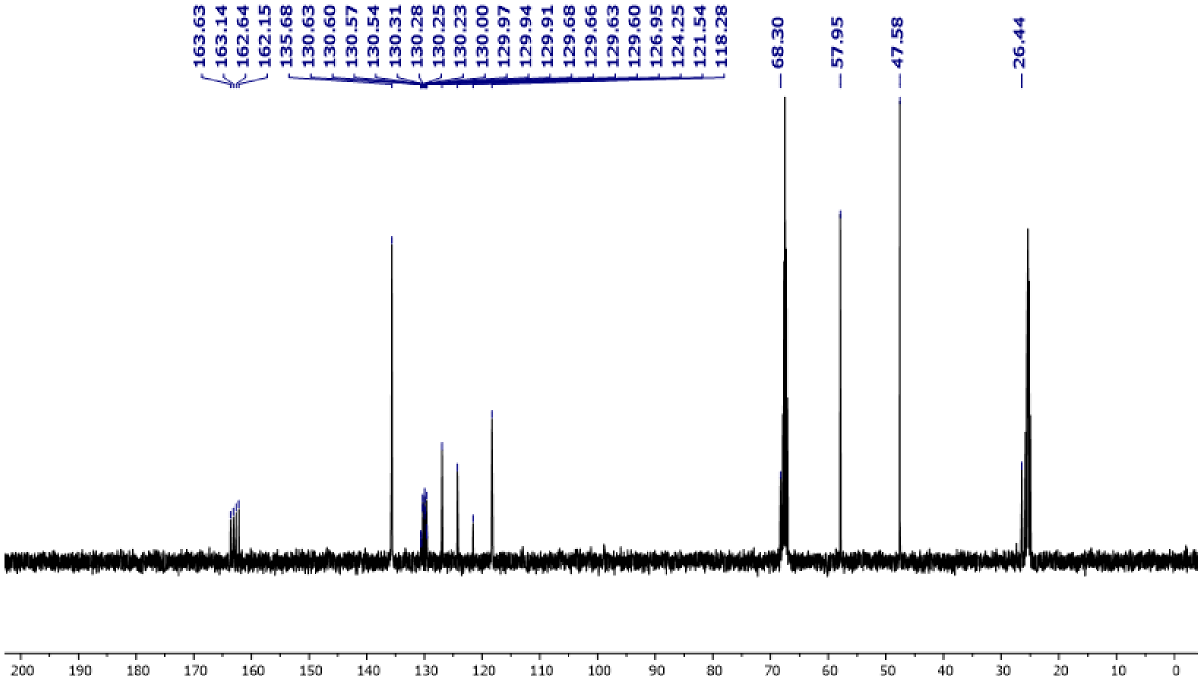
IR (KBr): ν = 1804, 1609 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{42}H_{37}BF_{24}ON_2Zn$ (1117.92 g · mol^{-1}): C, 45.12; H, 3.34; N, 2.51. Found: C, 44.41; H, 3.68; N, 2.98%.



Chemical shift [ppm]

Figure S11: ^{1}H NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**2a**) in [D8]THF.



Chemical shift [ppm]

Figure S12: ^{13}C{^{1}H} NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**2a**) in [D8]THF.

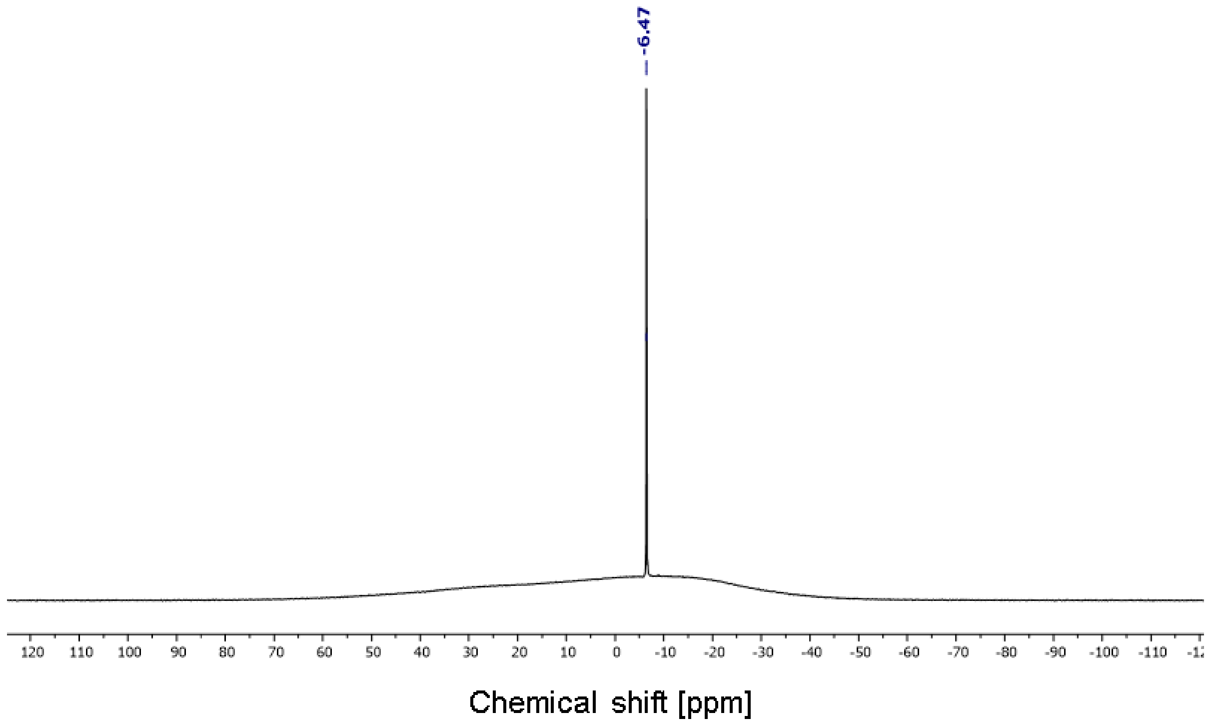


Figure S13: $^{11}B\{^1H\}$ NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**2a**) in [D8]THF.

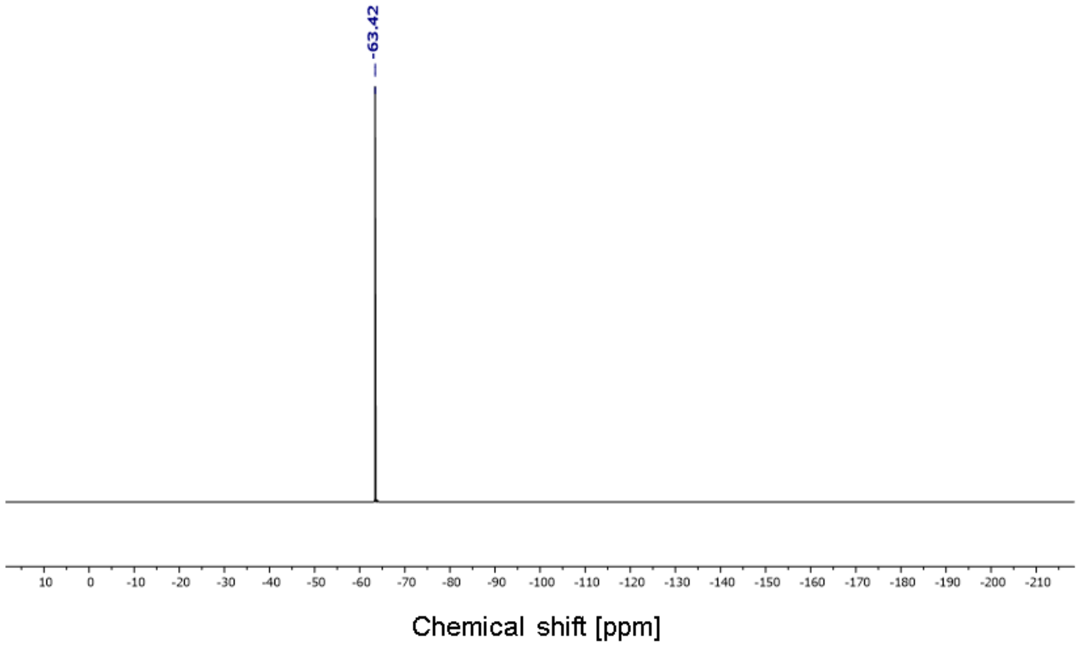


Figure S14: $^{19}F\{^1H\}$ NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**2a**) in [D8]THF.

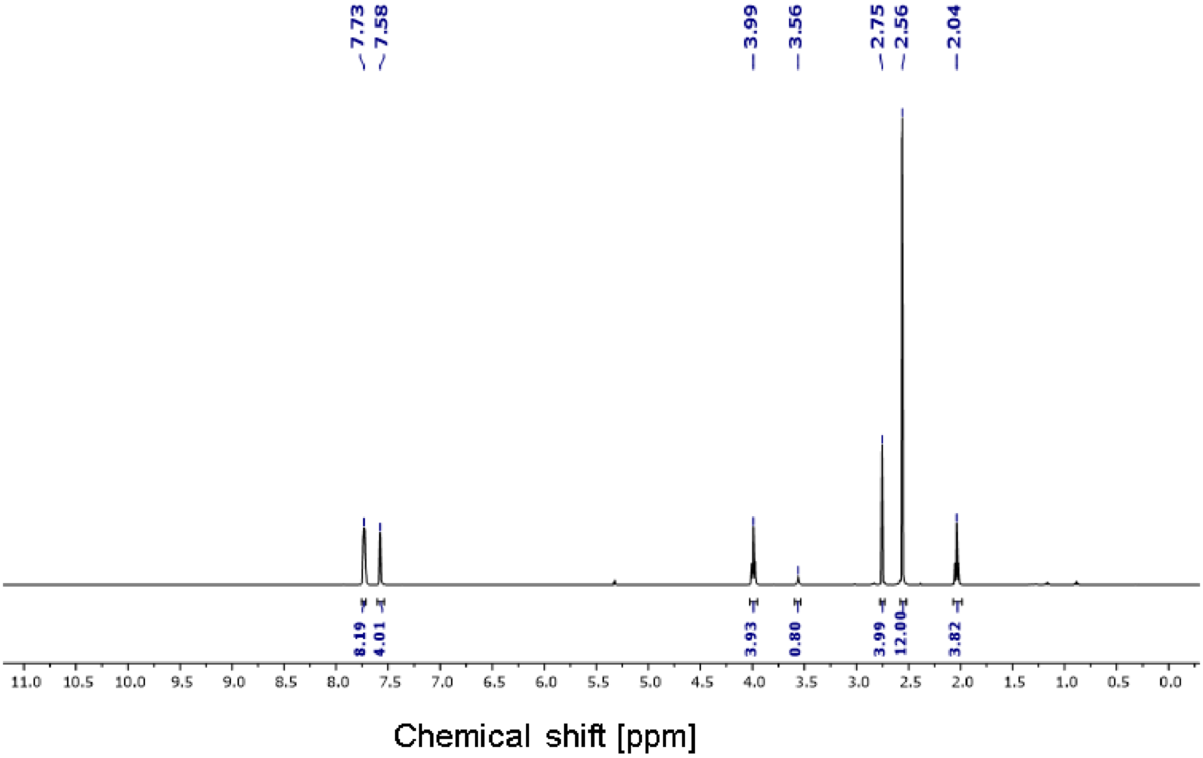


Figure S15: ^{1}H NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-C_6H_3)$_4$] (**2a**) in CD_2Cl_2.

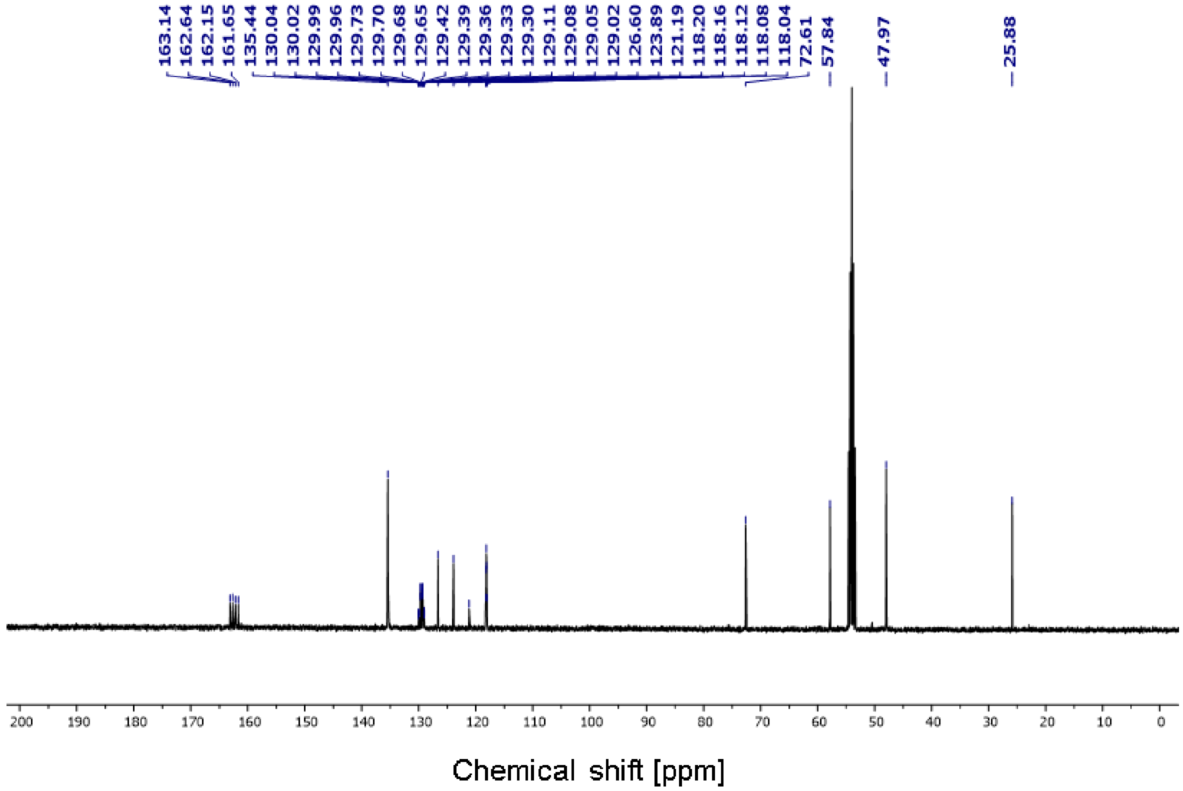


Figure S16: $^{13}C\{^1H\}$ NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-C_6H_3)$_4$] (**2a**) in CD_2Cl_2.

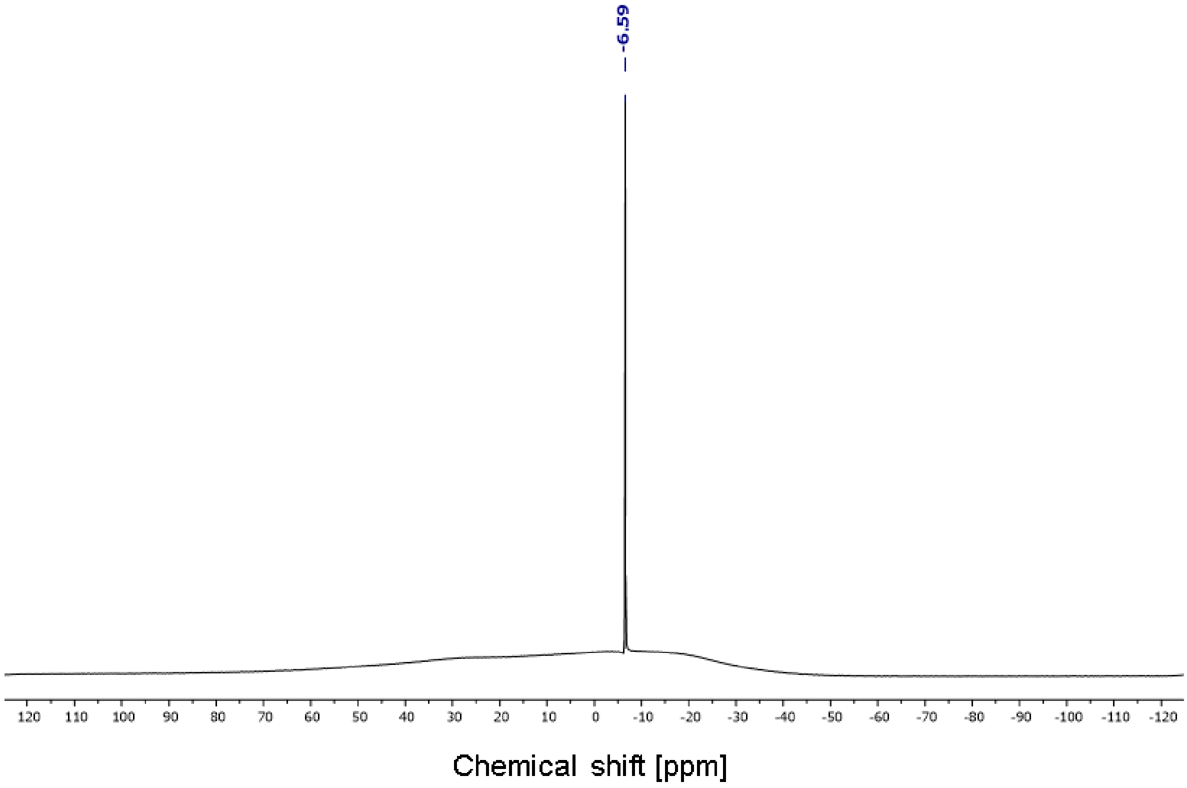


Figure S17: $^{11}B\{^1H\}$ NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**2a**) in CD_2Cl_2.

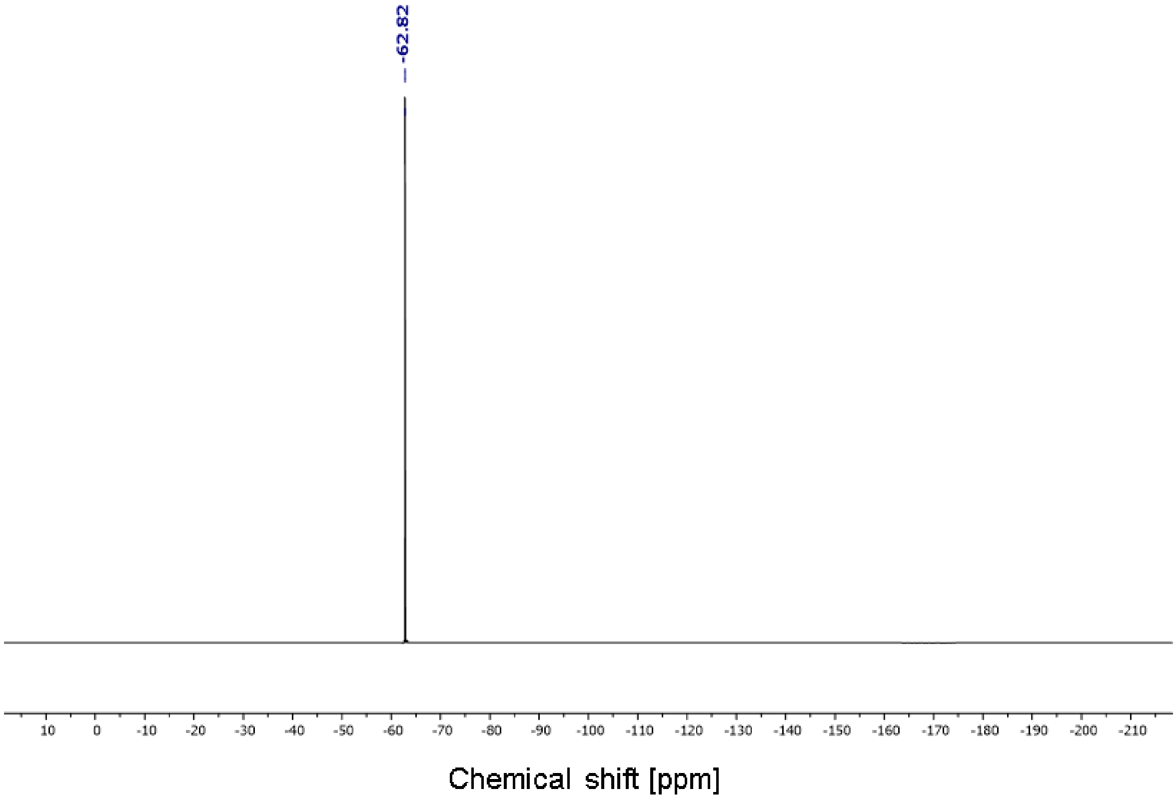


Figure S18: $^{19}F\{^1H\}$ NMR spectrum of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-$C_6H_3)_4$] (**2a**) in CD_2Cl_2.

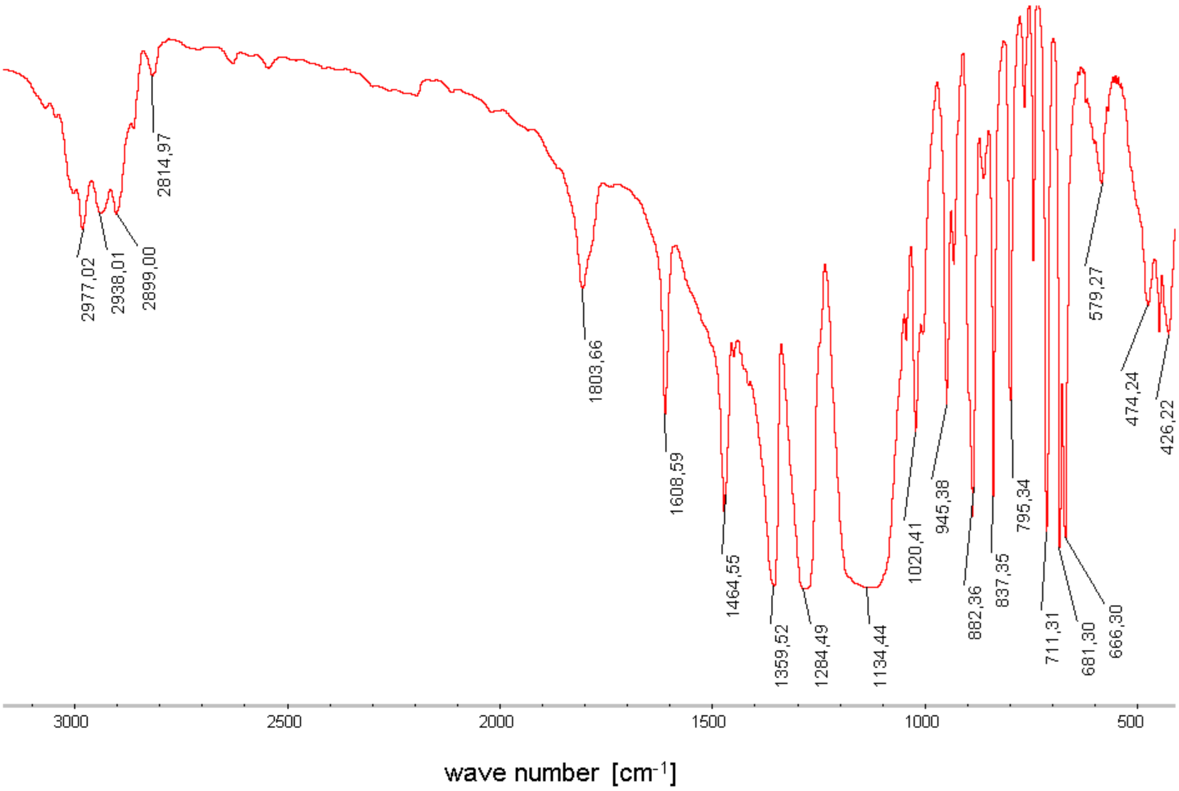


Figure S19: IR spectrum (KBr pellet) of [(TMEDA)ZnH(thf)][B(3,5-$(CF_3)_2$-C_6H_3)] (**2a**).

Synthesis of [(TEEDA)ZnH]$_2$[B(3,5-$(CF_3)_2$-C_6H_3)$_4$]$_2$ (2b).

To a suspension of $[ZnH_2]_n$ (26 mg, 385 µmol) in THF (5 mL) was added dropwise a solution of [(TEEDA)H][B(3,5-$(CF_3)_2$-C_6H_3)] (400 mg, 385 µmol) in THF (5 mL) at room temperature. After gas evolution had ceased (approximately 15 min) the reaction mixture was filtered and the solvent volume reduced in *vacuo*. Addition of *n*-pentane resulted in the precipitation of a colorless solid which could be isolated by decantation and subsequent drying under reduced pressure. The title complex was recrystallized by layering a solution of [(TEEDA)ZnH]$_2$[B(3,5-$(CF_3)_2$-C_6H_3)$_4$]$_2$ in CD_2Cl_2 with n-pentane at –30 °C to give colorless crystals (392 mg, 355 µmol). Yield: 92%.

^{1}H NMR (400 MHz, [D8]THF): δ = 1.17 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, N-CH_2CH_3, 24H), 2.84 – 2.95 (AA'BB', N-CH_2CH_3, 8H), 2.96 (s, N-CH_2CH_2, 8H), 2.98 – 3.11 (AA'BB', N-CH_2CH_3, 8H), 3.73 (s, Zn-*H* , 2H), 7.59 (s, *para*-C_6H_3, 8H), 7.80 (s, *ortho*-C_6H_3, 16H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 8.87 (N-CH_2CH_3), 46.97 (N-CH_2CH_3), 51.64 (N-CH_2CH_2), 118.28 (*para*-C_6H_3), 125.61 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, CF_3), 129.99 (qq, $^2J_{C\text{-}F}$ = 31.52 Hz, $^3J_{C\text{-}B}$ = 2.81 Hz, *meta*-C_6H_3), 135.69 (*ortho*-C_6H_3), 162.89 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-C_6H_3) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.50 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF): δ = -63.44 ppm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.23 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, N-CH_2CH_3, 24H), 2.95 (p, $^{3}J_{H\text{-}H}$ =7.1 Hz, N-CH_2CH_3, 16H), 3.03 (s, N-CH_2CH_2, 8H), 4.28 (s, Zn-*H*, 2H), 7.58 (s, *para*-C_6H_3, 8H), 7.73 (s, *ortho*-C_6H_3, 16H). ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 10.92 87 (N-CH_2CH_3), 50.14 (N-CH_2CH_3), 51.64 (N-CH_2CH_2), 118.12 (*para*-C_6H_3), 125.24 (q, $^{1}J_{C\text{-}F}$ = 272.4 Hz, CF_3), 129.50 (qq, $^{2}J_{C\text{-}F}$ = 31.66 Hz, $^{3}J_{C\text{-}B}$ = 2.90 Hz, *meta*-C_6H_3), 135.44 (*ortho*-C_6H_3), 162.37 (q, $^{1}J_{B\text{-}C}$ = 49.9 Hz, *ipso*-C_6H_3) ppm.

^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = -6.60 ppm.

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): δ = -63.44 pp.

IR (KBr): ν = 1798, 1607 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{84}H_{74}B_2F_{48}N_4Zn_2$ (2203.85 g · mol^{-1}): C, 45.78; H, 3.38; N, 2.54. Found: C, 44.42; H, 4.82; N, 3.32%.

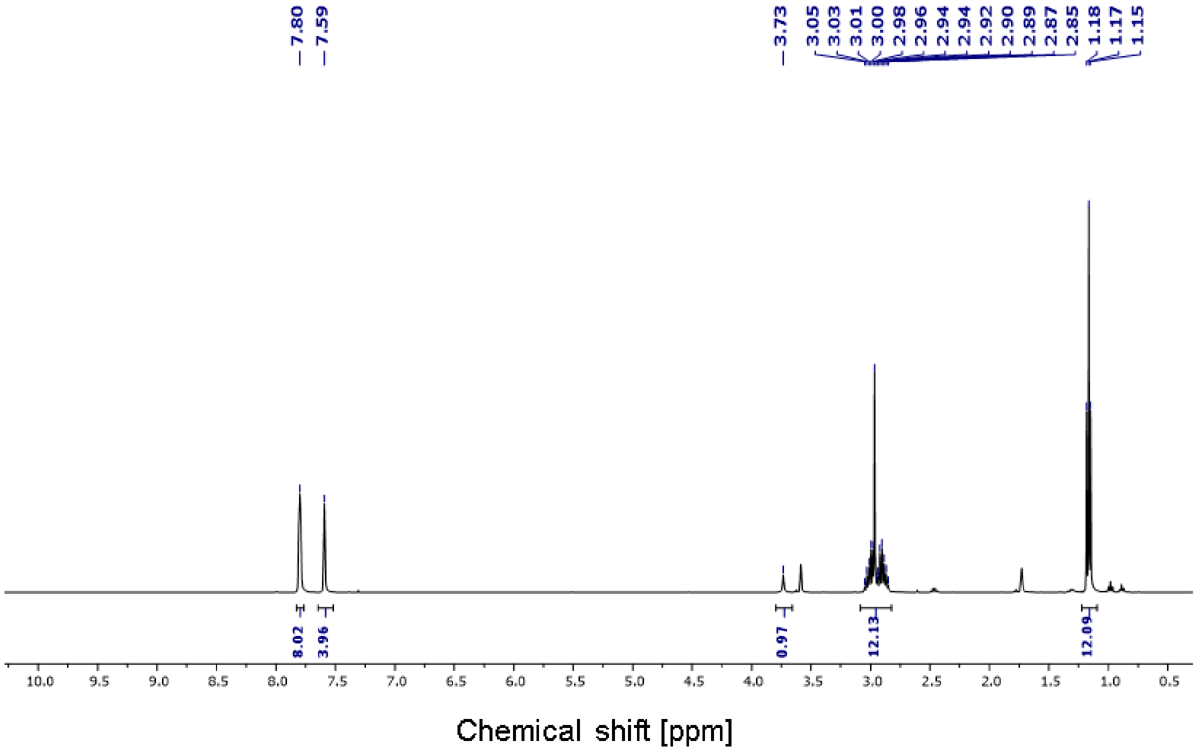


Figure S20: ^{1}H NMR spectrum of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**2b**) in [D8]THF.

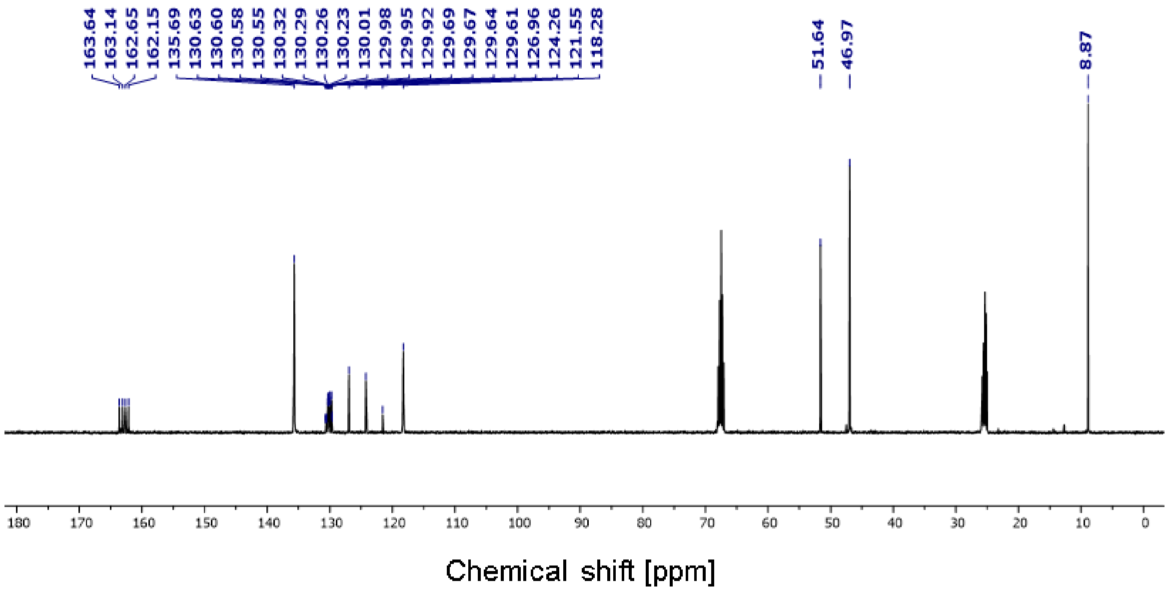


Figure S21: $^{13}C\{^1H\}$ NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (**2b**) in [D8]THF.

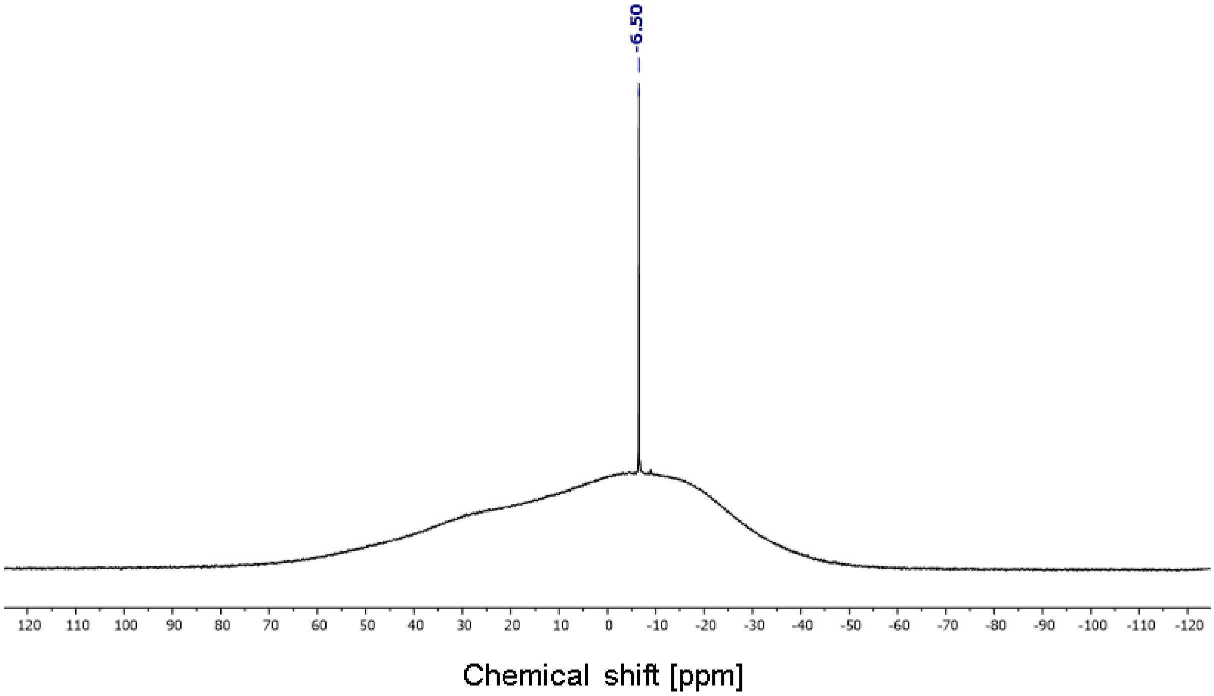


Figure S22: $^{11}B\{^1H\}$ NMR spectrum of [(TEEDA)ZnH]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (**2b**) in [D8]THF.

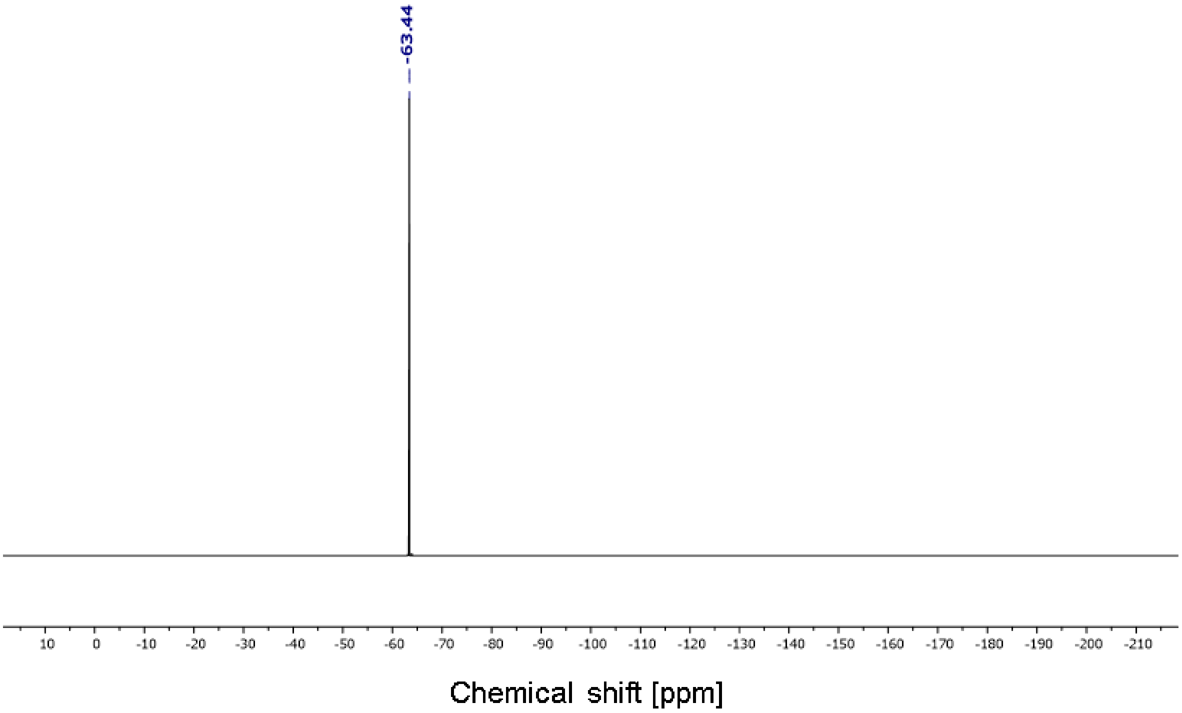


Figure S23: $^{19}F\{^1H\}$ NMR spectrum of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**2b**) in [D8]THF.

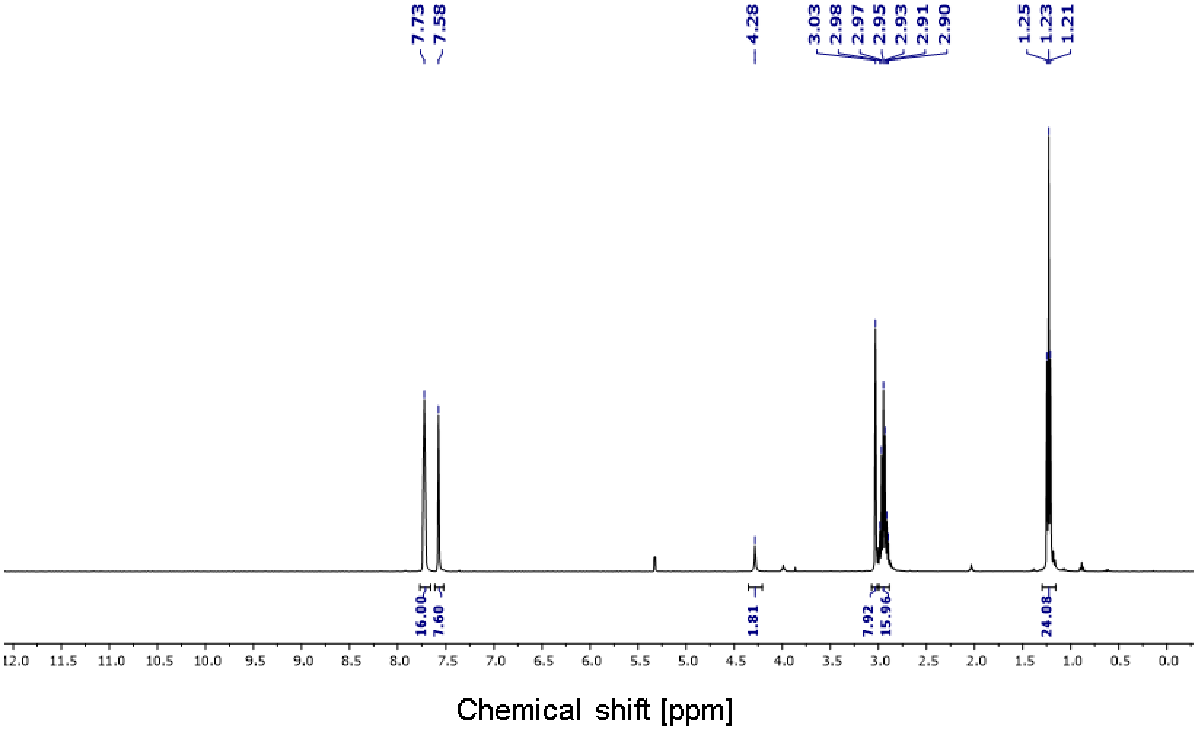


Figure S24: ^1H NMR spectrum of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**2b**) in CD_2Cl_2.

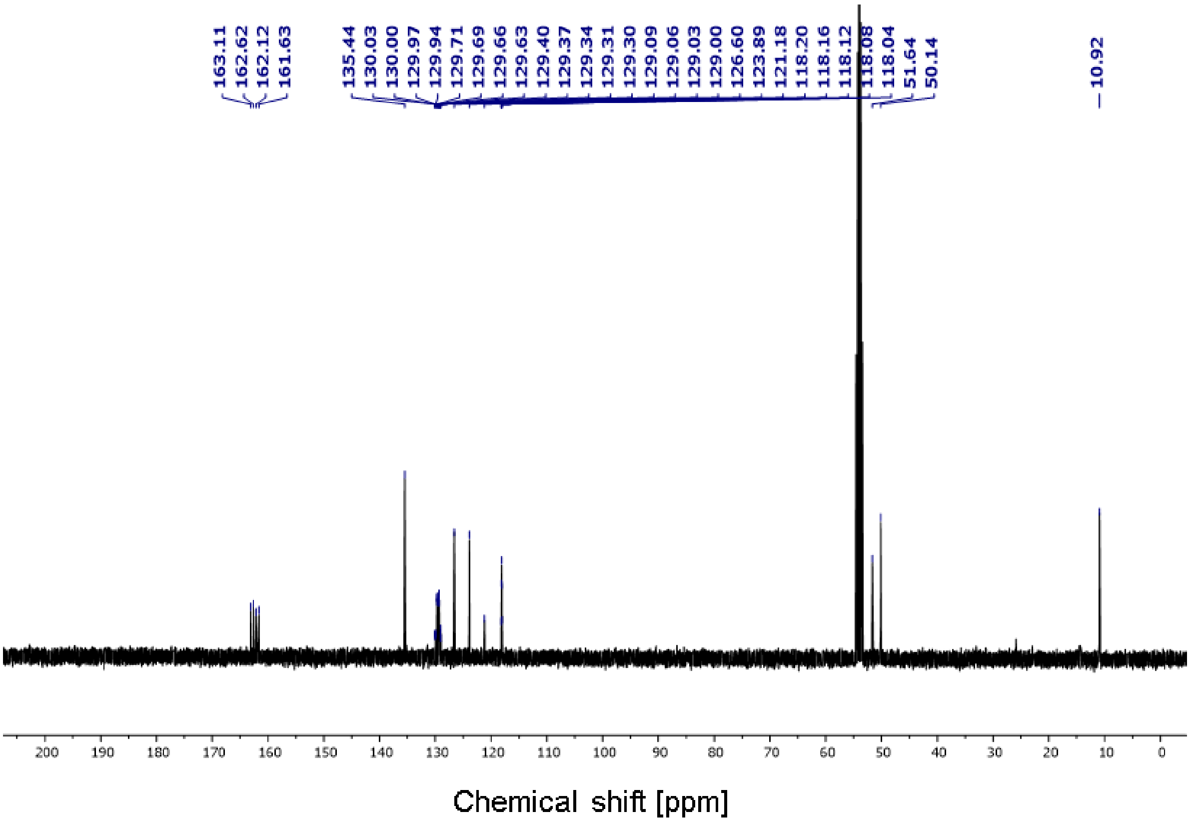


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**2b**) in CD_2Cl_2.

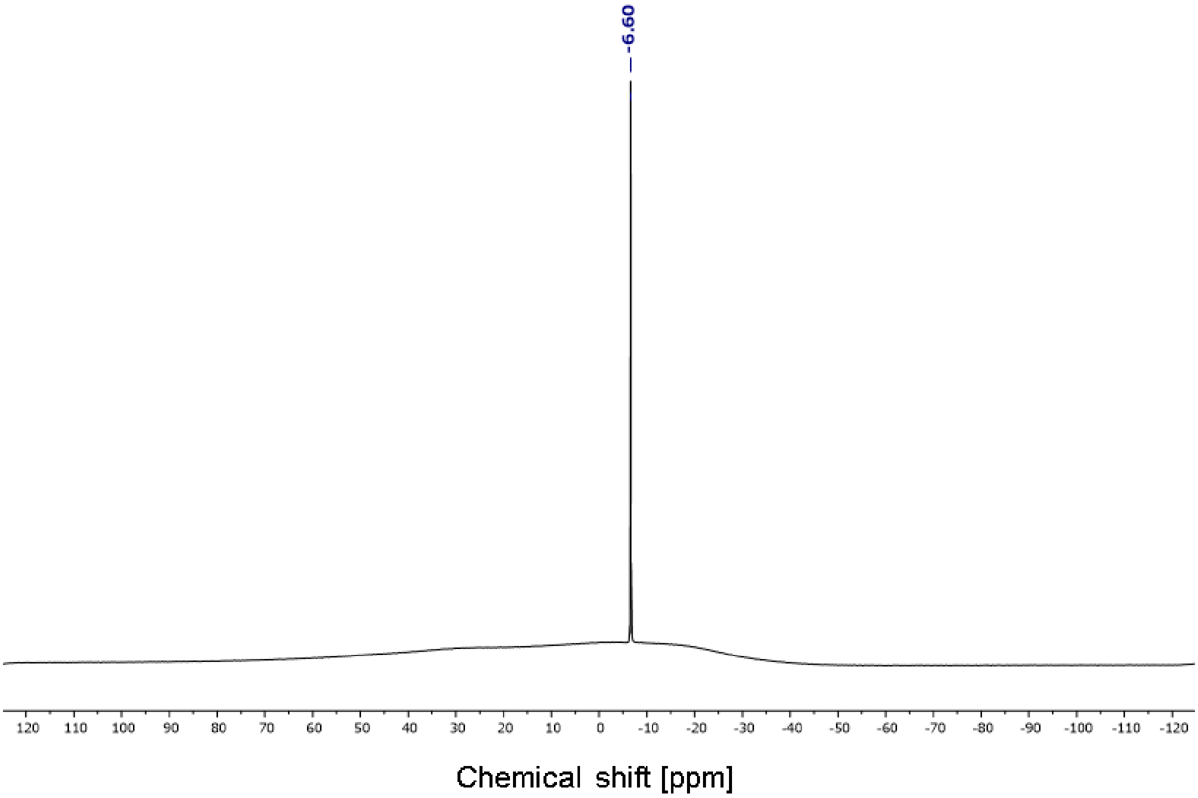


Figure S26: $^{11}B\{^{1}H\}$ NMR spectrum of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**2b**) in CD_2Cl_2.

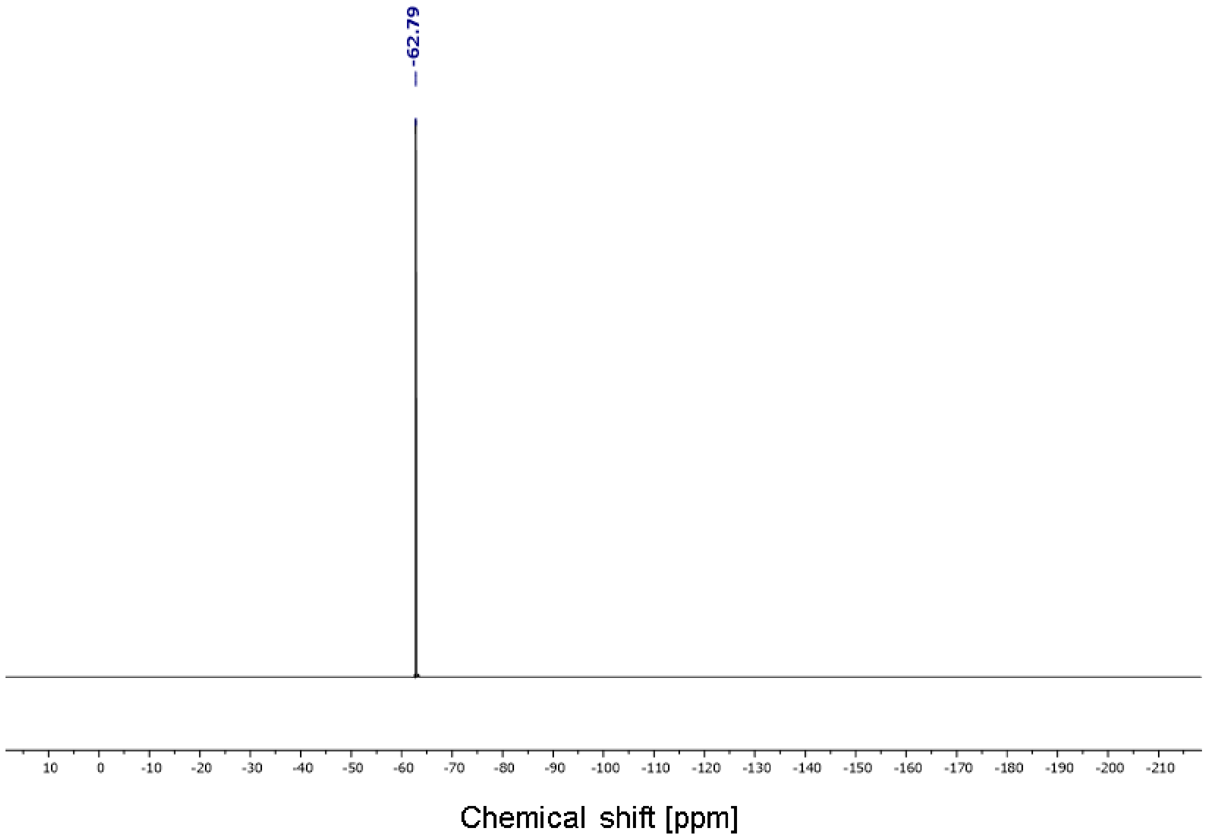


Figure S27: $^{19}F\{^{1}H\}$ NMR spectrum of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**2b**) in CD_2Cl_2.

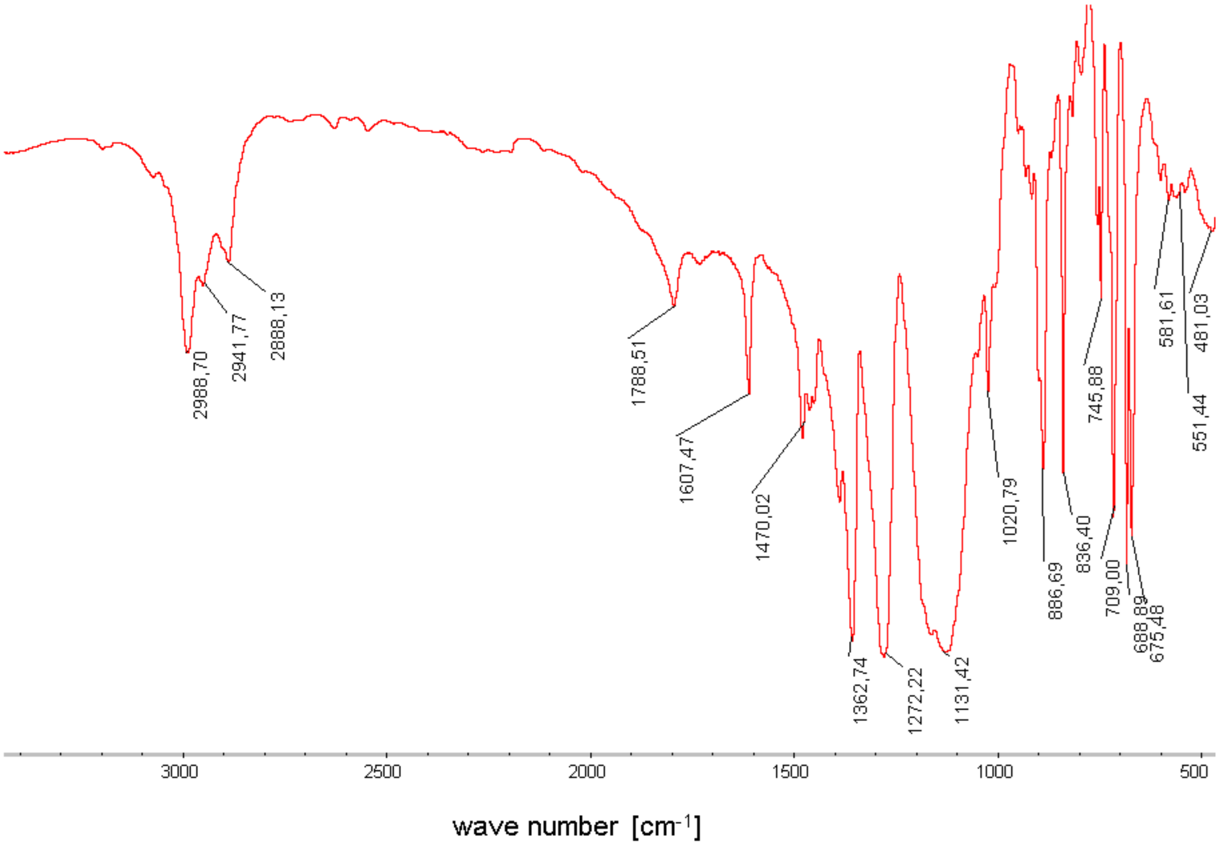


Figure S28: IR spectrum (KBr pellet) of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**2b**).

Synthesis of $[(TMEDA)_2Zn_2H_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (3a).

Method A: To a suspension of $[ZnH_2]_n$ (70 mg, 1.03 mmol) in THF (5 mL) was added dropwise a solution of $[(TMEDA)H][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]$ (500 mg, 0.51 mmol) and TMEDA (59 mg, 0.51 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature until gas evolution ceased (approximately 15 min). The reaction mixture was filtered and the filtrate concentrated in *vacuo.* Addition of *n*-pentane resulted in the precipitation of a colorless solid which could be isolated by decantation and subsequent drying under reduced pressures. Recrystallization from CD_2Cl_2/*n*-pentane at -30 °C gave $[(TMEDA)_2Zn(H)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ as a colorless solid (554 mg, 0.45 mmol). Yield: 88%.

Method B: To a suspension of $[ZnH_2]_n$ (6 mg, 89 µmol) and TMEDA (10 mg, 89 µmol) in THF (5 mL) was added a THF solution of $[(TMEDA)ZnH(thf)][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]$ (**1a**) (100 mg, 89 µmol). The solvent was removed *in vacuo* and the residue was recrystallized from CD_2Cl_2/n-pentane at -30 °C. The supernatant was decanted off and the crystalline solid was dried under reduced pressure a colorless solid (105 mg, 85 µmol). Yield: 96%.

^{1}H NMR (400 MHz, [D8]THF): δ = 2.58 (s, N-C*H*$_3$, 24H), 2.83 (s, N-C*H*$_2$, 8H), 3.68 (s, Zn-*H*, 3H), 7.59 (s, *para*-C_6H_3, 4H), 7.80 (s, *ortho*-C_6H_3, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 48.10 (N-*C*H$_3$), 58.01 (N-*C*H$_2$), 118.25 (*para*-C_6H_3), 125.58 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, *C*F$_3$), 130.13 (qq, $^2J_{C\text{-}F}$ = 31.2 Hz, $^3J_{B\text{-}C}$ = 3.4 Hz, *meta*-C_6H_3), 135.66 (*ortho*-C_6H_3), 163.37 (q, $^1J_{B\text{-}C}$ = 50.1 Hz, *ipso*-C_6H_3) ppm

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.52 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF): δ = -63.42 ppm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.56 (s, N-C*H*$_3$, 24H), 2.74 (s, N-C*H*$_2$, 8H), 3.58 (s, Zn-*H*, 3H), 7.58 (s, *para*-C_6H_3, 4H), 7.73 (s, *ortho*-C_6H_3, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 48.59 (N-*C*H$_3$), 57.82 (N-*C*H$_2$), 117.97 (*para*-C_6H_3), 125.24 (q, $^1J_{C\text{-}F}$ = 272.3 Hz, *C*F$_3$), 129.48 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{B\text{-}C}$ = 2.8 Hz, *meta*-C_6H_3), 135.44 (*ortho*-C_6H_3), 162.40 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-C_6H_3) ppm.

^{13}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ = -6.60 ppm.

^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): δ = -62.80 ppm.

IR (KBr): ν = 1758 (m, ZnH), 1606 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{44}H_{47}BF_{24}N_4Zn_2$ (1229.42 g · mol^{-1}): C, 42.99; H, 3.85; N; 4.56. Found: C, 43.61; H, 4.46; N, 4.61%.

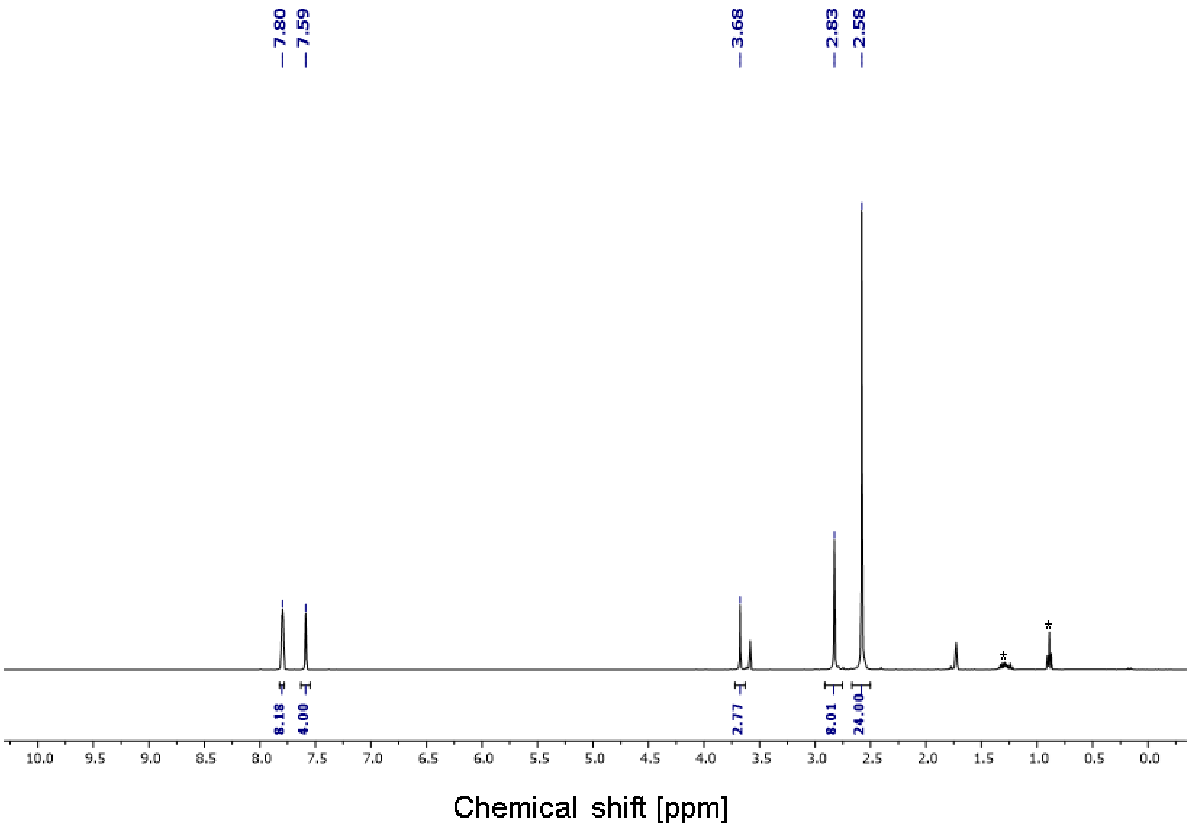


Figure S29: ^{1}H NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**3a**) in [D8]THF (* denotes *n*-pentane).

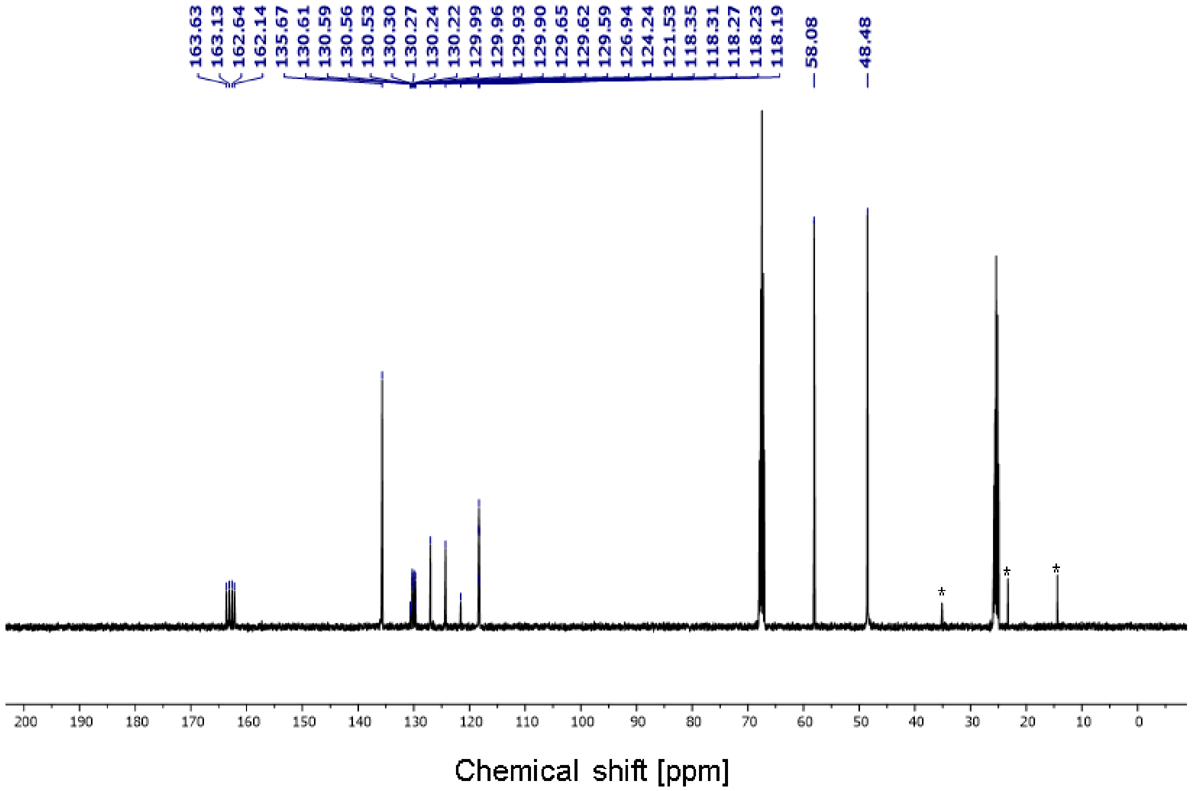


Figure S30: ^{13}C{^{1}H} NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**3a**) in [D8]THF (* denotes *n*-pentane.

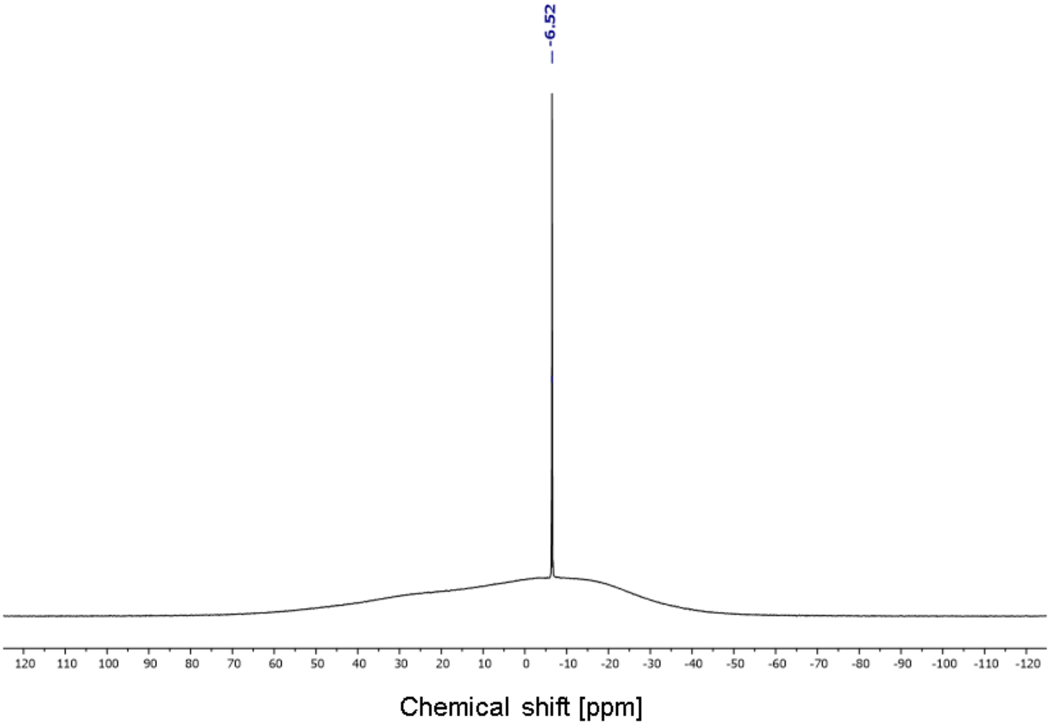


Figure S31: $^{11}B\{^1H\}$ NMR spectrum of $[(TMEDA)_2Zn_2H_3][B(3,5-(CF_3)_2-C_6H_3)_4]$ (**3a**) in [D8]THF.

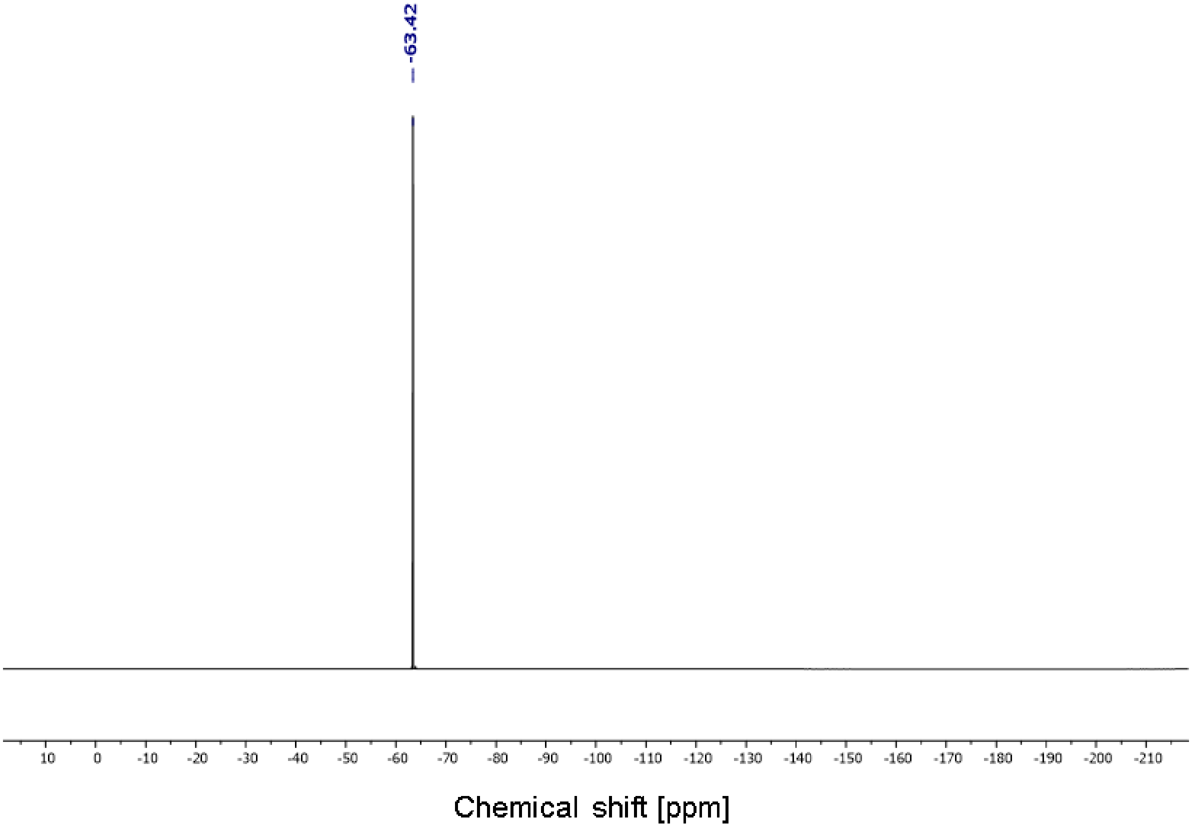


Figure S32: $^{19}F\{^1H\}$ NMR spectrum of $[(TMEDA)_2Zn_2H_3][B(3,5-(CF_3)_2-C_6H_3)_4]$ (**3a**) in [D8]THF.

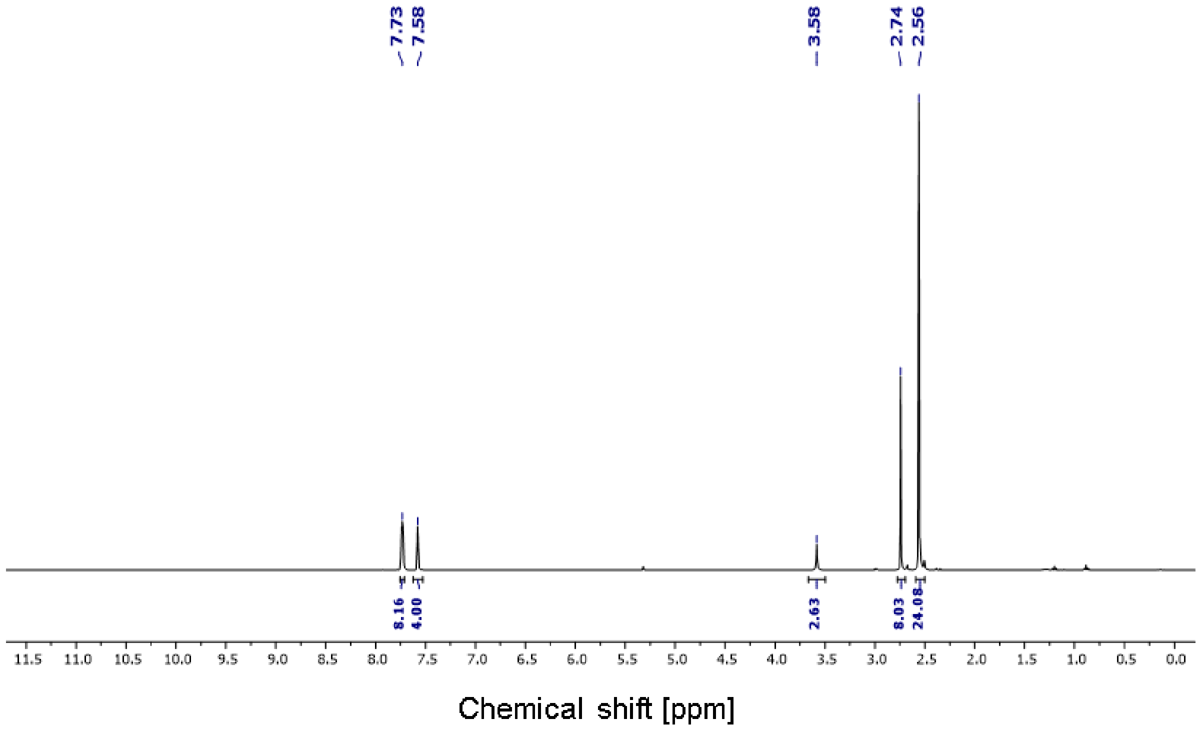


Figure S33: ^{1}H NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**3a**) in CD$_2$Cl$_2$.

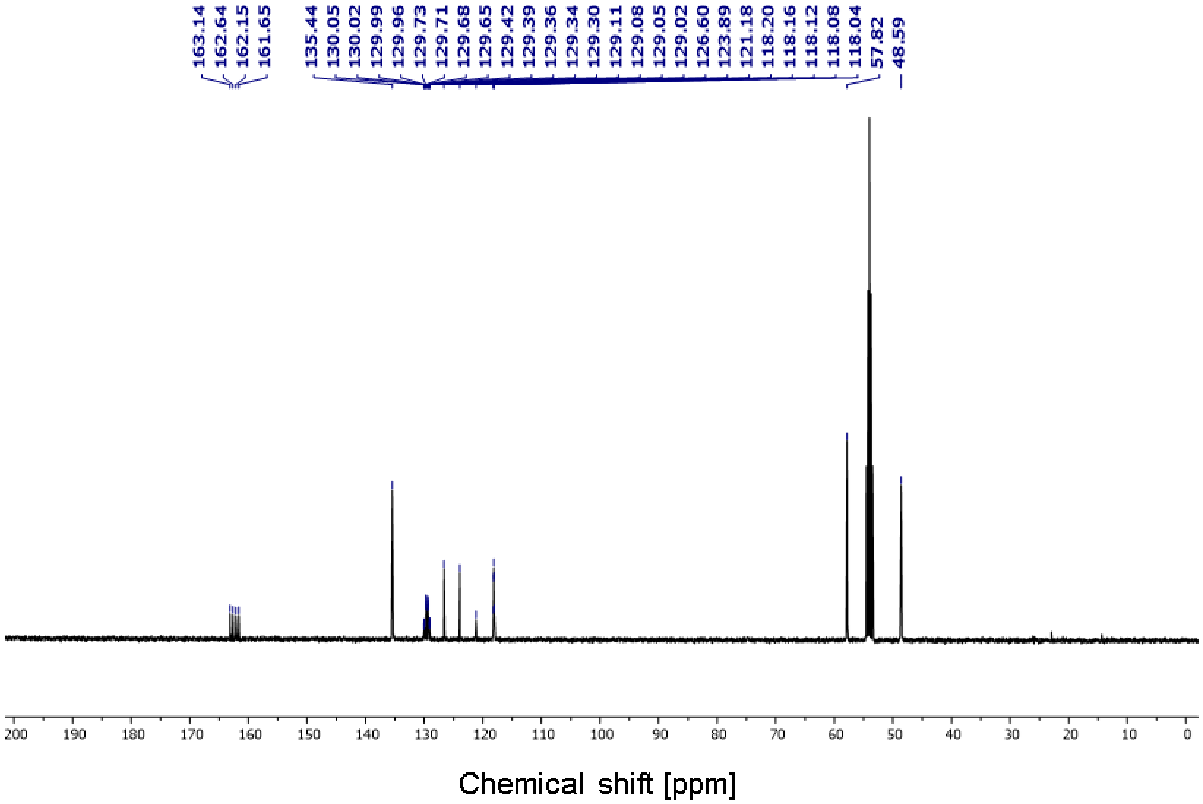


Figure S34: ^{13}C{^{1}H} NMR spectrum of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**3a**) in CD$_2$Cl$_2$.

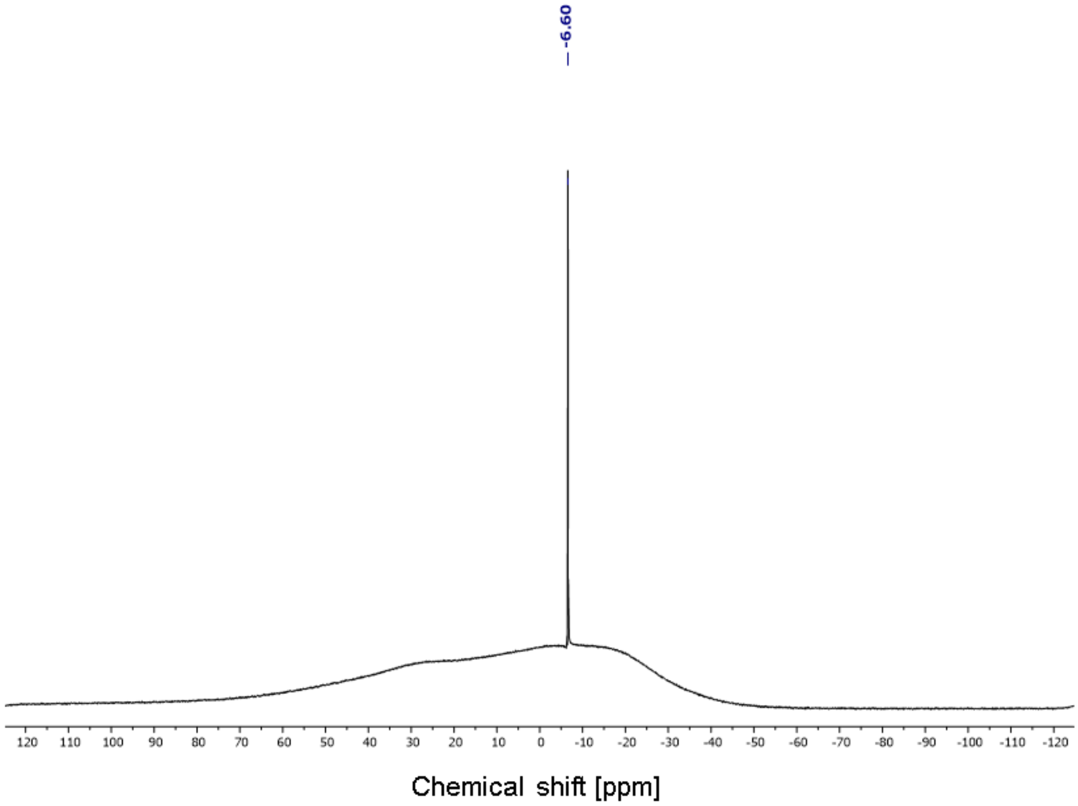


Figure S35: $^{11}B\{^1H\}$ NMR spectrum of $[(TMEDA)_2Zn_2H_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**3a**) CD_2Cl_2.

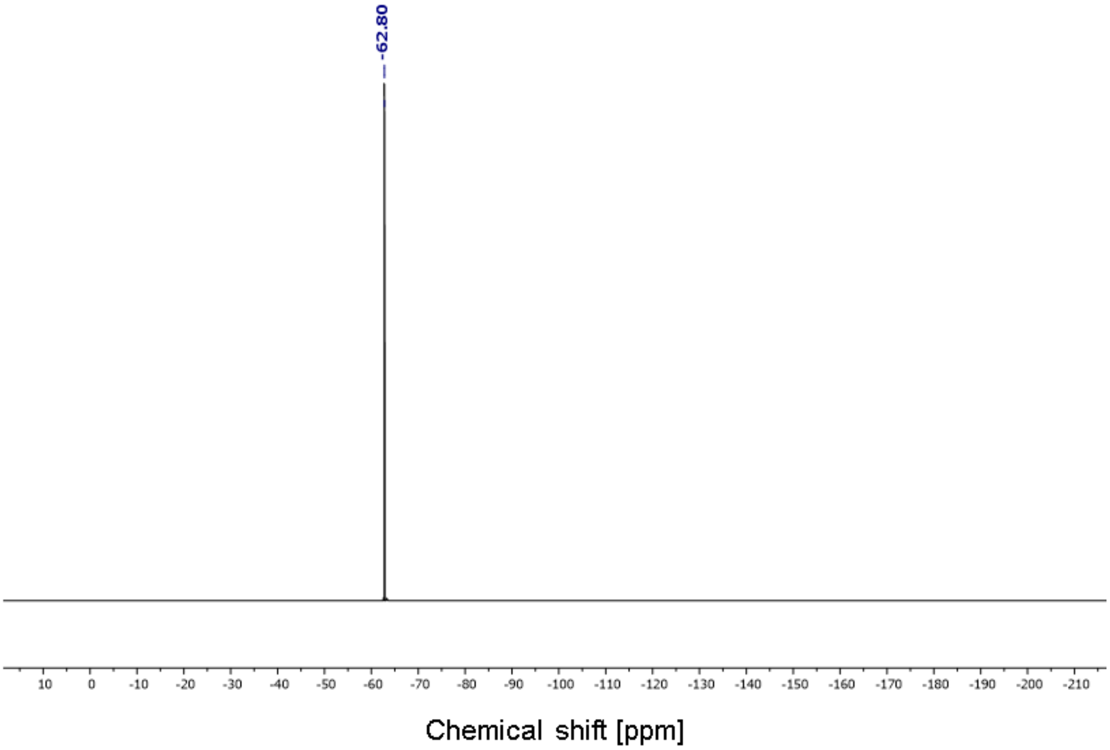


Figure S36: $^{19}F\{^1H\}$ NMR spectrum of $[(TMEDA)_2Zn_2H_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**3a**) in CD_2Cl_2.

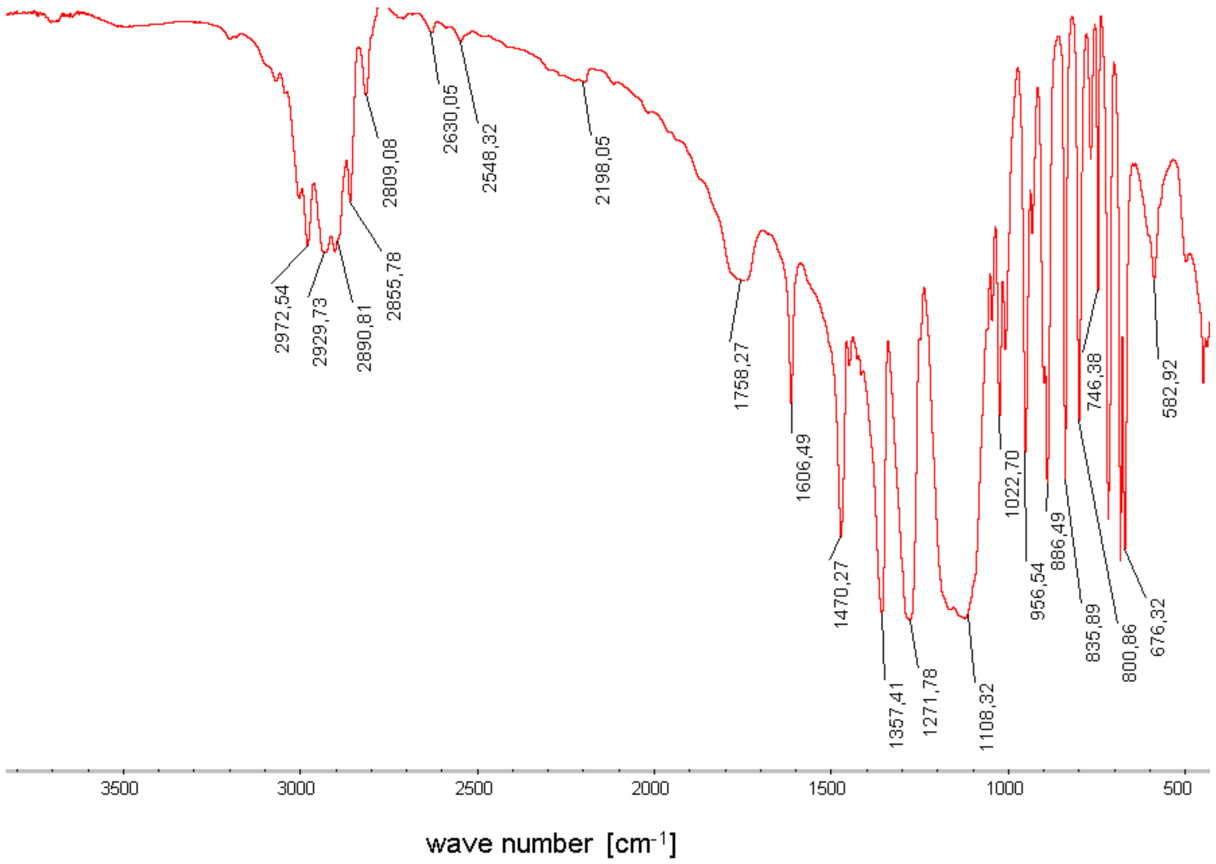


Figure S37: IR spectrum (KBr pellet) of [(TMEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**3a**).

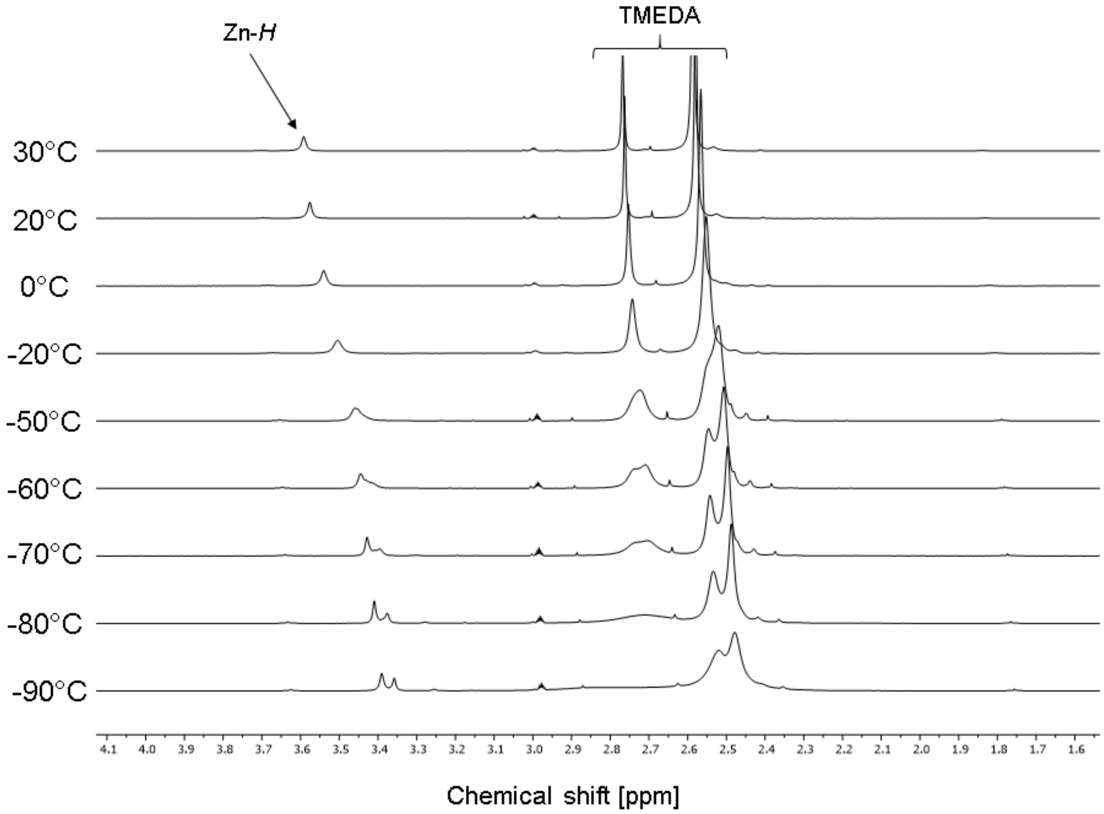


Figure S38: Variable-temperature ^{1}H NMR spectrum of [(TMEDA)$_2$ZnH$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**3a**) in CD$_2$Cl$_2$.

Synthesis of $[(TEEDA)_2Zn_2H_3][B(3,5-(CF_3)_2-C_6H_3)_4]$ (3b).

Method A: To a suspension of $[ZnH_2]_n$ (26 mg, 385 µmol) in THF (5 mL) was added dropwise a solution of $[(TEEDA)H][B(3,5-(CF_3)_2-C_6H_3)]$ (200 mg, 192 µmol) and TEEDA (33.2 mg, 192 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature until gas evolution had ceased (approximately 15 min), filtered and concentrated in *vacuo.* Addition of *n*-pentane resulted in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressures. Recrystallization from toluene/*n*-pentane at -30 °C gave $[(TEEDA)_2ZnH_3][B(3,5-(CF_3)_2-C_6H_3)_4]$ as a colorless solid (284 mg, 211 µmol). Yield: 74%.

Method B: To a suspension of $[ZnH_2]_n$ (6 mg, 91 µmol) and TEEDA (16 mg, 91 µmol) in THF (5 mL) was added a solution of $[(TEEDA)ZnH]_2[B(3,5-(CF_3)_2-C_6H_3)]_2$ (100 mg, 45 µmol) in THF (mL). After stirring the reaction mixture for 15 min at room temperature, the solvent was removed *in vacuo*. The residue was recrystallized from CD_2Cl_2/n-pentane at -30 °C. The supernatant was decanted off and the crystalline solid was dried under reduced pressureto give olorless crystals (121 mg, 90 µmol). Yield: 98%.

^{1}H NMR (400 MHz, [D8]THF): δ = 1.14 (t, $^3J_{H-H}$ = 7.1 Hz, N-CH_2-CH_3, 24H), 2.83 (m, N-C$H_2$$CH_3$, 8H), 2.90 (s, N-C$H_2$, 8H), 3.06 (m, N-C$H_2$$CH_3$, 8H), 3.65 (s, Zn-*H*, 3H), 7.60 (s, *para*-C_6H_3, 4H), 7.81 (s, *ortho*-C_6H_3, 8H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 9.19 (N-CH_2CH_3), 47.78 (N-CH_2CH_3), 51.72 (N-CH_2CH_2), 118.28 (*para*-C_6H_3), 125.62 (q, $^1J_{C-F}$ = 272.2 Hz, CF_3), 130.27 (qq, $^2J_{C-F}$ = 31.5 Hz, $^3J_{B-C}$ = 2.8 Hz, *meta*-C_6H_3), 135.70 (*ortho*-C_6H_3), 162.90 (q, $^1J_{B-C}$ = 49.8 Hz, *ipso*-C_6H_3) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.50 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF): δ = -63.44 ppm.

IR (KBr): ν = 1758 (m, ZnH), 1610 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{82}H_{76}B_2F_{48}N_6Zn_3$ (2209.86 g · mol^{-1}): C, 46.55; H, 4.73; N, 4.18. Found: C, 46.02; H, 4.52; N, 4.22%.

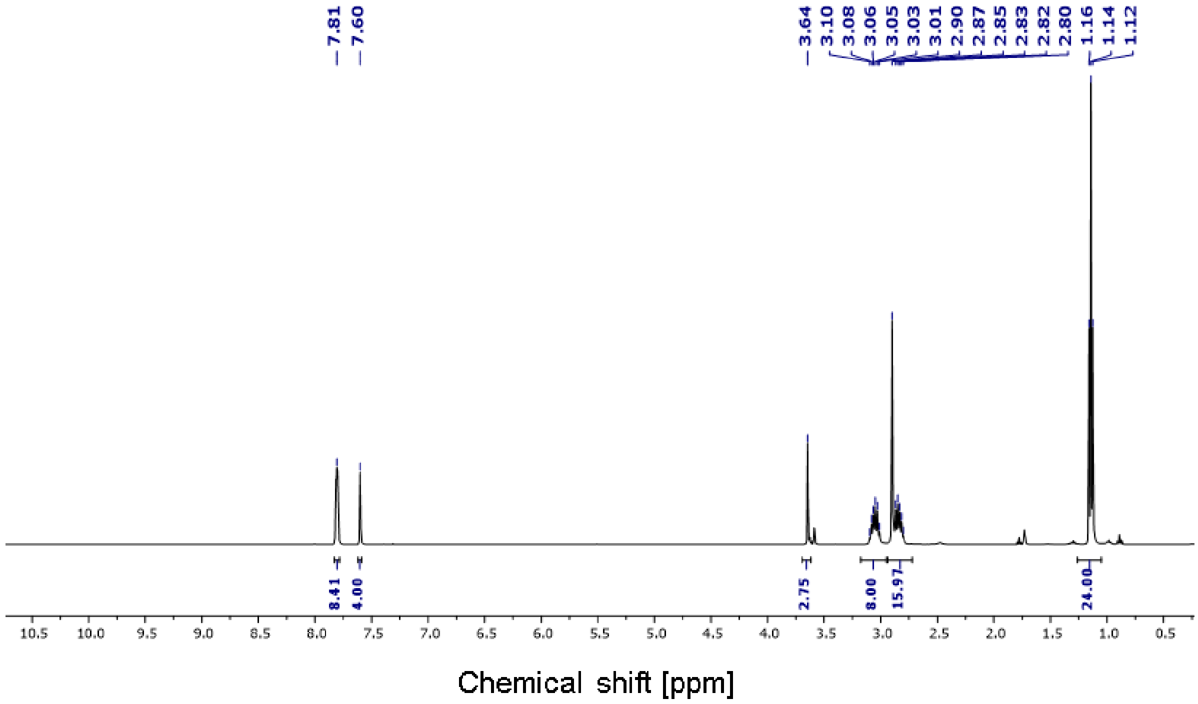


Figure S39: ^{1}H NMR spectrum of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (**3b**) in [D8]THF.

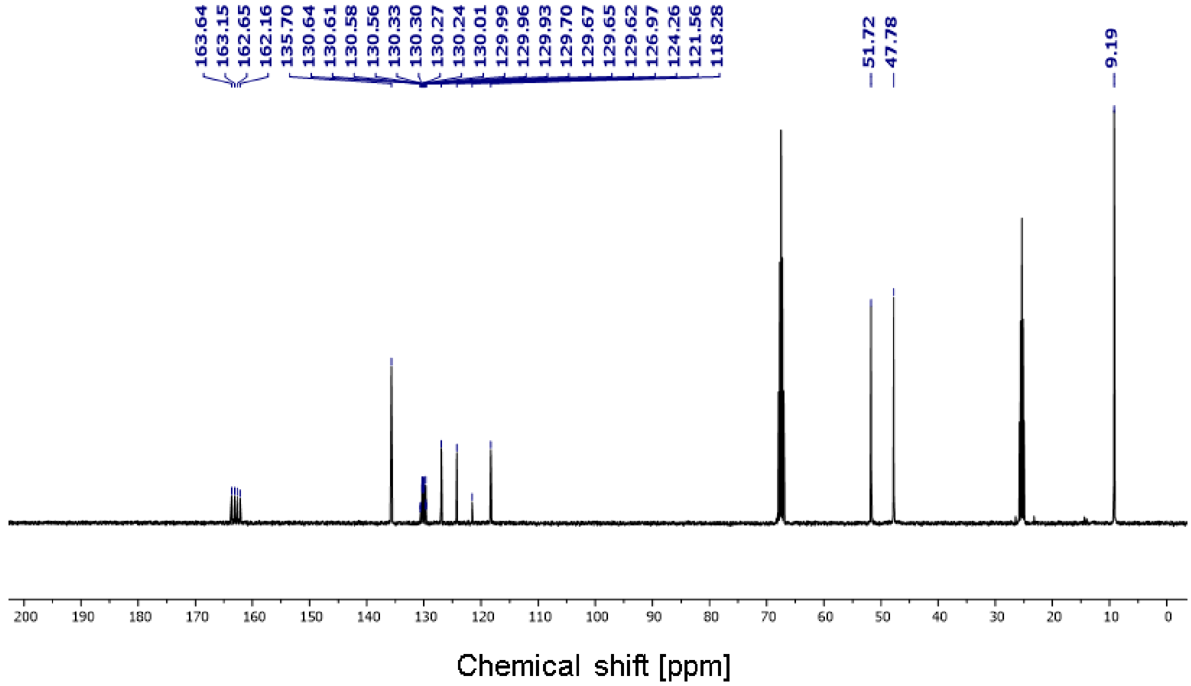


Figure S40: ^{13}C{^{1}H} NMR spectrum of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)] (**3b**) in [D8]THF.

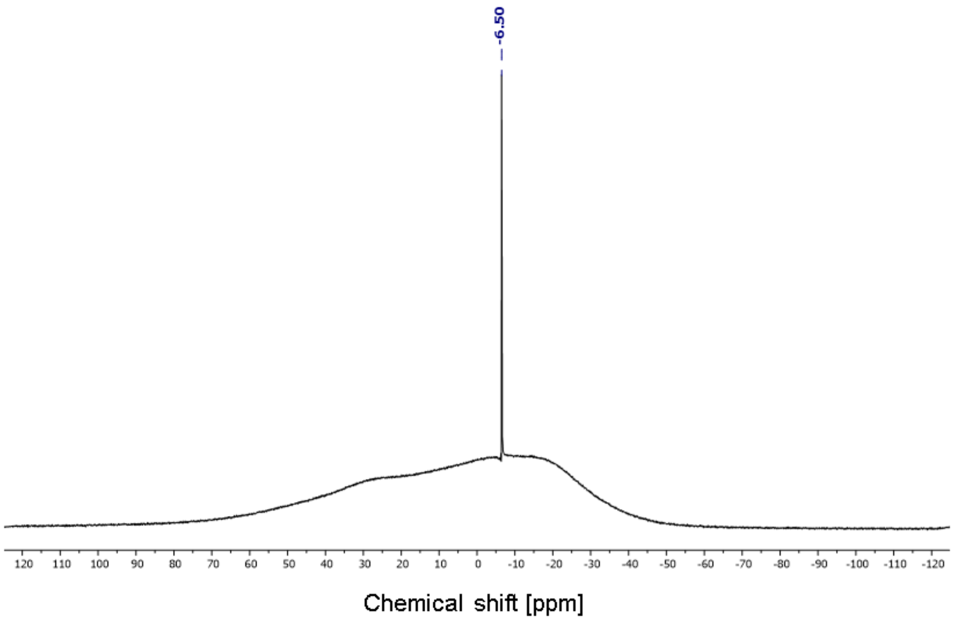


Figure S41: $^{11}B\{^1H\}$ NMR spectrum of $[(TEEDA)_2Zn_2H_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]$ in [D8]THF.

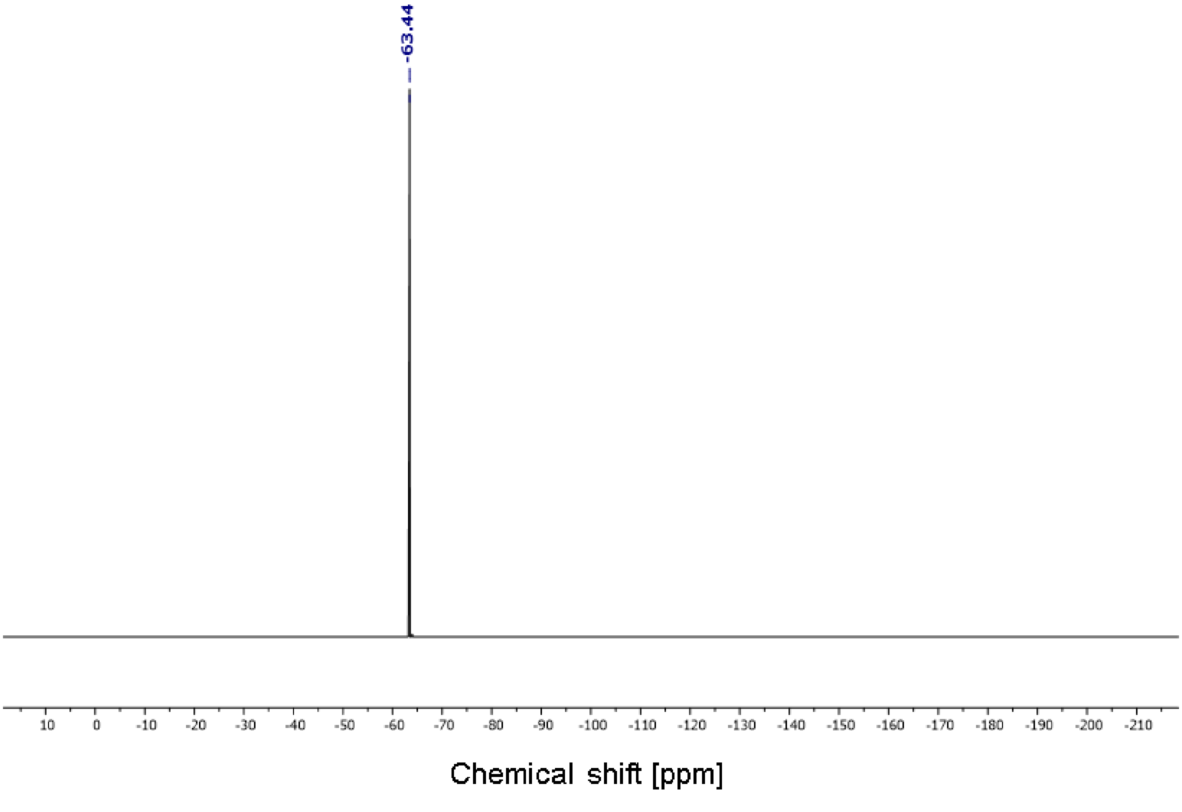


Figure S42: $^{19}F\{^1H\}$ NMR spectrum of $[(TEEDA)_2Zn_2H_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]$ (**3b**) in [D8]THF.

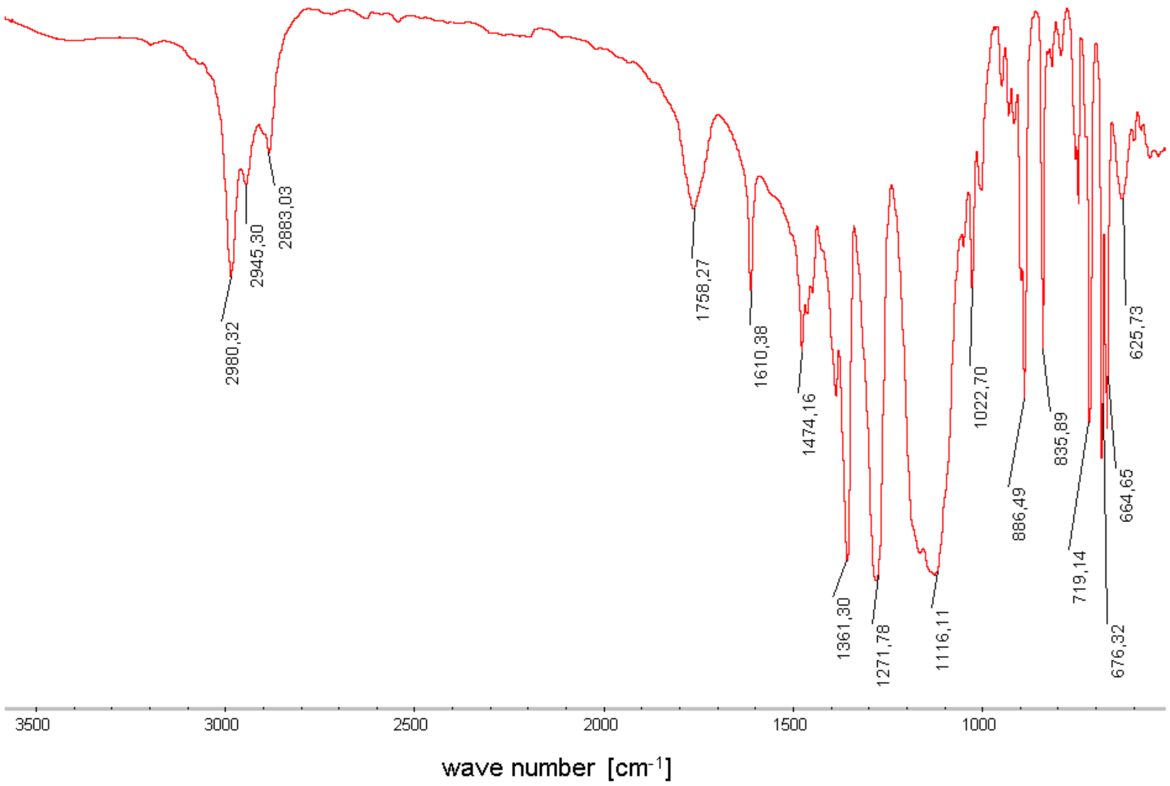


Figure S43: IR spectrum (KBr pellet) of $[(TEEDA)_2Zn_2H_3]$ $[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]$ (**3b**).

Synthesis of $[(TMEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (4a).

Method A: To a suspension of $[ZnH_2]_n$ (21 mg, 306 µmol) in THF (5 mL) was added a solution of $[(TMEDA)H][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (200 mg, 204 µmol) and TMEDA (12 mg, 102 µmol) in THF (5 mL). After gas evolution had ceased (ca. 15 min), the reaction mixture was filtered and the volume of the filtrate reduced in *vacuo*. Addition of *n*-pentane resulted in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressure zo give colorless platelets (201 mg, 91 µmol). Yield: 90%.

Method B: To a suspension of $[ZnH_2]_n$ (3 mg. 44 µmol) and TMEDA (5 mg, 44 µmol) in THF (5 mL) was added a solution containing $[(TMEDA)ZnH(thf)][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (100 mg, 89 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 30 min. After filtration the solvent was removed in *vacuo* to give $[(TMEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ as colorless platelets (92 mg, 42 µmol). Yield:, 94%.

^1H NMR (400 MHz, [D8]THF): δ = 2.50 (s, N-CH_3, 36H), 2.73 (s, N-CH_2, 12H), 3.62 (s, Zn-*H*, 4H), 7.60 (s, *para*-C_6H_3, 8H), 7.80 (s, *ortho*-C_6H_3, 16H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, [D8]THF): δ = 47.52 (N-CH_3), 58.26 (N-CH_2), 118.29 (*para*-C_6H_3), 125.61 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, CF_3), 130.12 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{B\text{-}C}$ = 2.8 Hz, *meta*-C_6H_3), 135.68 (*ortho*-C_6H_3), 162.90 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-C_6H_3) ppm.

$^{11}B\{^1H\}$ NMR (128 MHz, [D8]THF): δ = -6.50 ppm.

$^{19}F\{^1H\}$ NMR (377 MHz, [D8]THF): δ = -63.42 ppm.

IR (KBr): ν = 1778 (m, ZnH), 1606 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{82}H_{76}B_2F_{48}N_6Zn_3$ (2209.86 g · mol^{-1}): C, 44.57; H, 3.47; N, 3.80. Found: C, 44.17; H, 4.36; N, 4.69%.

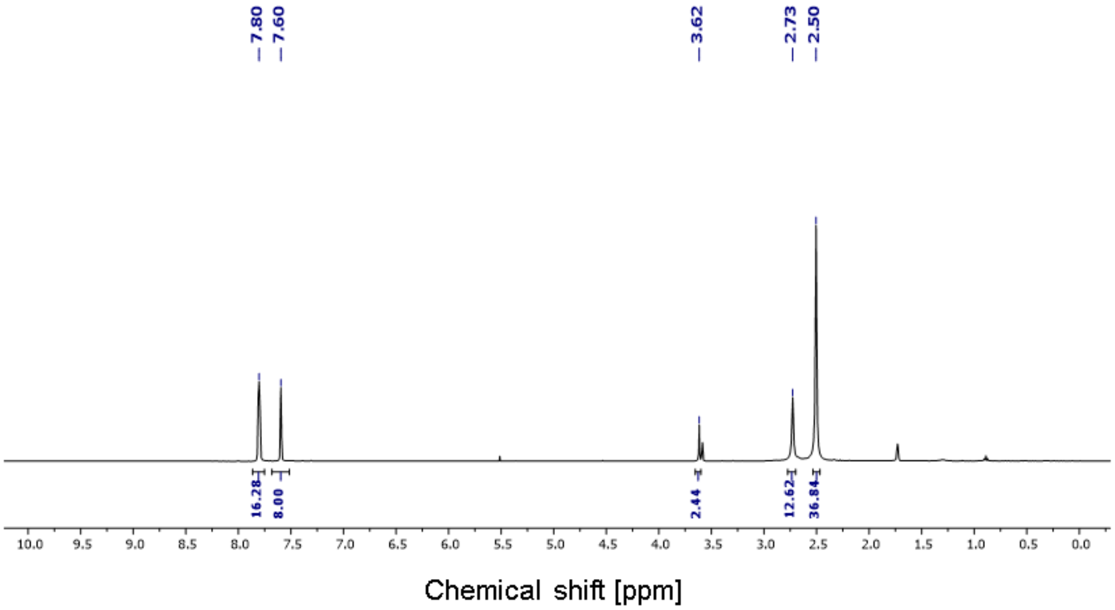


Figure S44: ^1H NMR spectrum of $[(TMEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4a**) in [D8]THF.

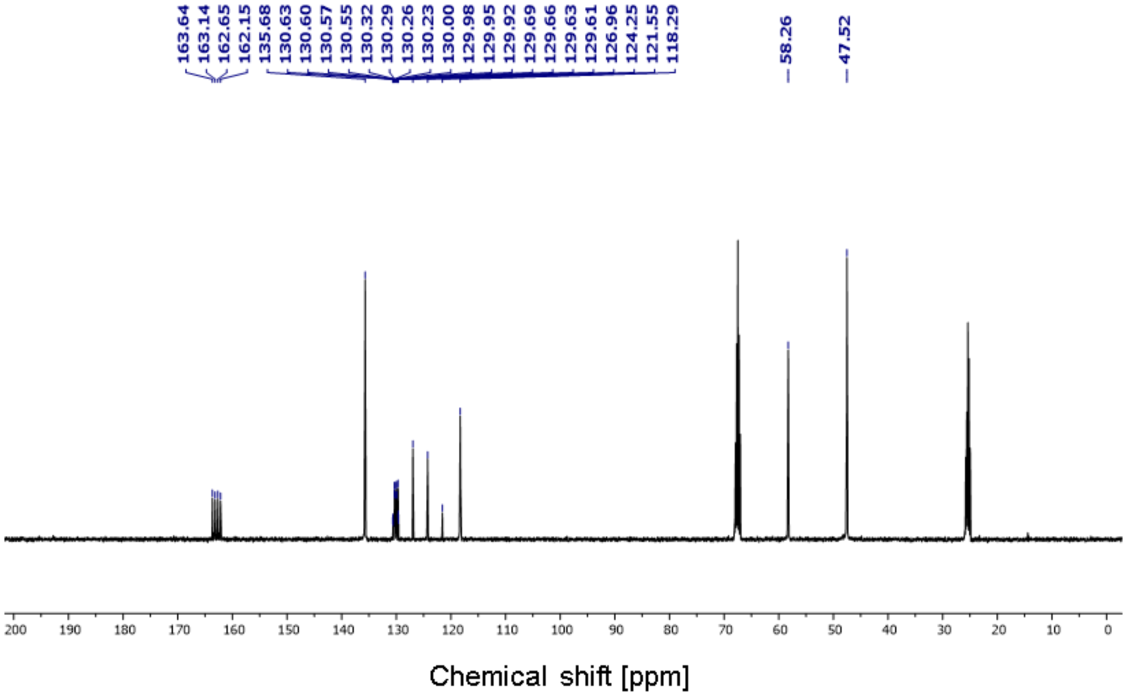


Figure S45: $^{13}C\{^1H\}$ NMR spectrum of $[(TMEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4a**) in [D8]THF.

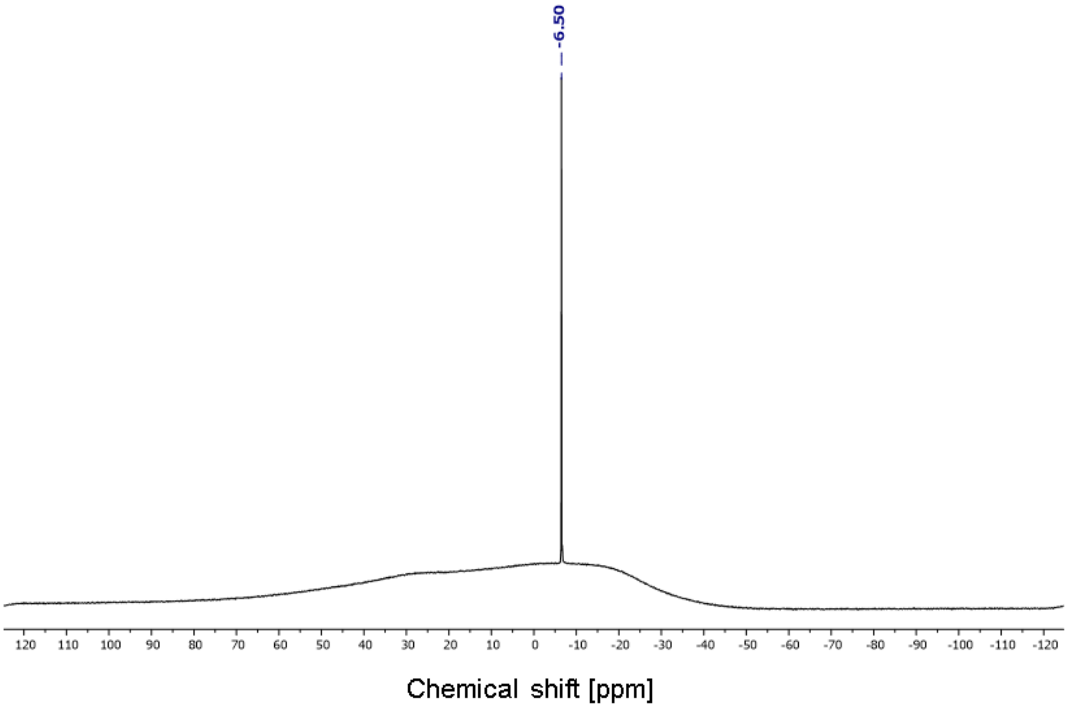


Figure S46: $^{11}B\{^{1}H\}$ NMR spectrum of $[(TMEDA)_3Zn_3H_4][B(3,5-(CF_3)_2-C_6H_3)]_2$ (**4a**) in [D8]THF.

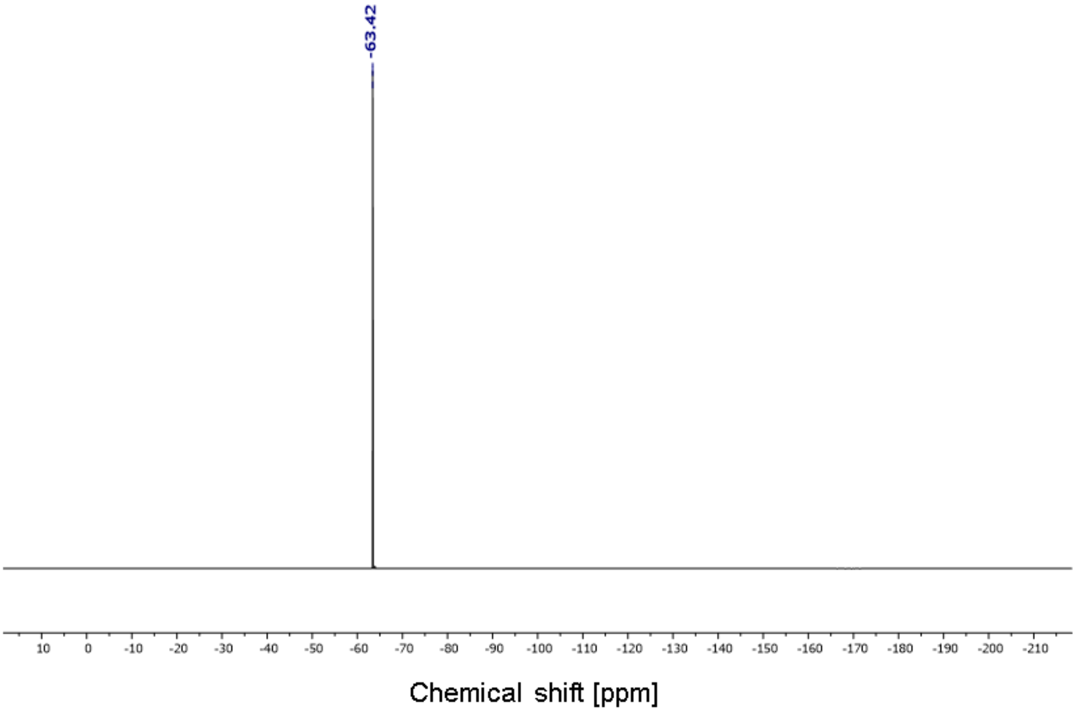


Figure S47: $^{19}F\{^{1}H\}$ NMR spectrum of $[(TMEDA)_3Zn_3H_4][B(3,5-(CF_3)_2-C_6H_3)]_2$ (**4a**) in [D8]THF.

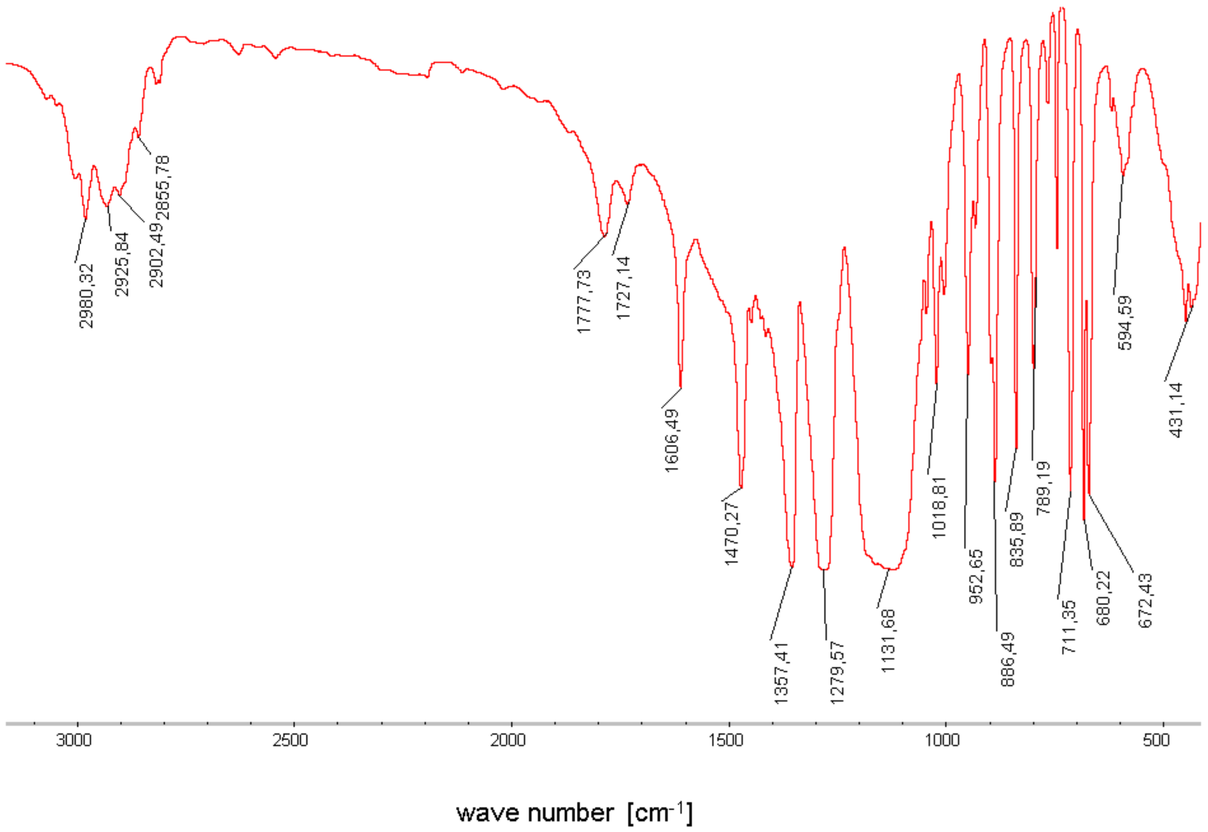


Figure S48: IR spectrum (KBr pellet) of $[(TMEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4a**).

Synthesis of $[(TEEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (4b).

Method A: To a suspension of $[ZnH_2]_n$ (19 mg, 289 µmol) in THF (5 mL) was added dropwise a solution containing $[(TEEDA)H][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]$ (200 mg, 192 mmol) and TEEDA (17 mg, 96 µmol) in THF (5 mL). After gas evolution had ceased (approximately 15 min) the reaction mixture was filtered and the volume of the filtrate reduced in *vacuo*. Addition of *n*-pentane results in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressure to give a colorless solid (217 mg, 89 µmol). Yield: 92%.

Method B: To a suspension of $[ZnH_2]_n$ (3 mg, 45 µmol) and TEEDA (8 mg, 45 µmol) in THF (5 mL) was added a solution of $[(TEEDA)ZnH]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (100 mg, 45 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 30 min. After filtration the solvent was removed in *vacuo* giving $[(TEEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ as a colorless solid (103 mg, 42 µmol). Yield: 98%.

^1H NMR (400 MHz, [D8]THF): δ = 1.15 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, N-CH_2-CH_3, 36H), 2.88 (m, N-C$H_2$$CH_3$, 12H), 2.92 (s, N-C$H_2$, 12H), 3.03 (m, N-C$H_2$$CH_3$, 12H), 3.66 (s, Zn-*H*, 4H), 7.58 (s, *para*-C_6H_3, 8H), 7.79 (s, *ortho*-C_6H_3, 16H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, [D8]THF): δ = 9.09 (N-CH_2*C*H_3), 47.46 (N-*C*H_2CH_3), 51.67 (N-*C*H_2*C*H_2), 118.26 (*para*-C_6H_3), 125.59 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, *C*F_3), 130.09 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{B\text{-}C}$ = 2.8 Hz, *meta*-C_6H_3), 135.67 (*ortho*-C_6H_3), 162.88 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-C_6H_3) ppm.

$^{11}B\{^1H\}$ NMR (128 MHz, [D8]THF): δ = -6.48 ppm.

$^{19}F\{^1H\}$ NMR (377 MHz, [D8]THF): δ = -63.42 ppm.

IR (KBr): ν = 1766 (m, ZnH), 1610 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{94}H_{100}B_2F_{48}N_6Zn_3$ (2443.56 g · mol^{-1}): C, 46.20; H, 4.13; N, 3.44. Found: C, 46.10; H, 4.71; N, 3.59%.

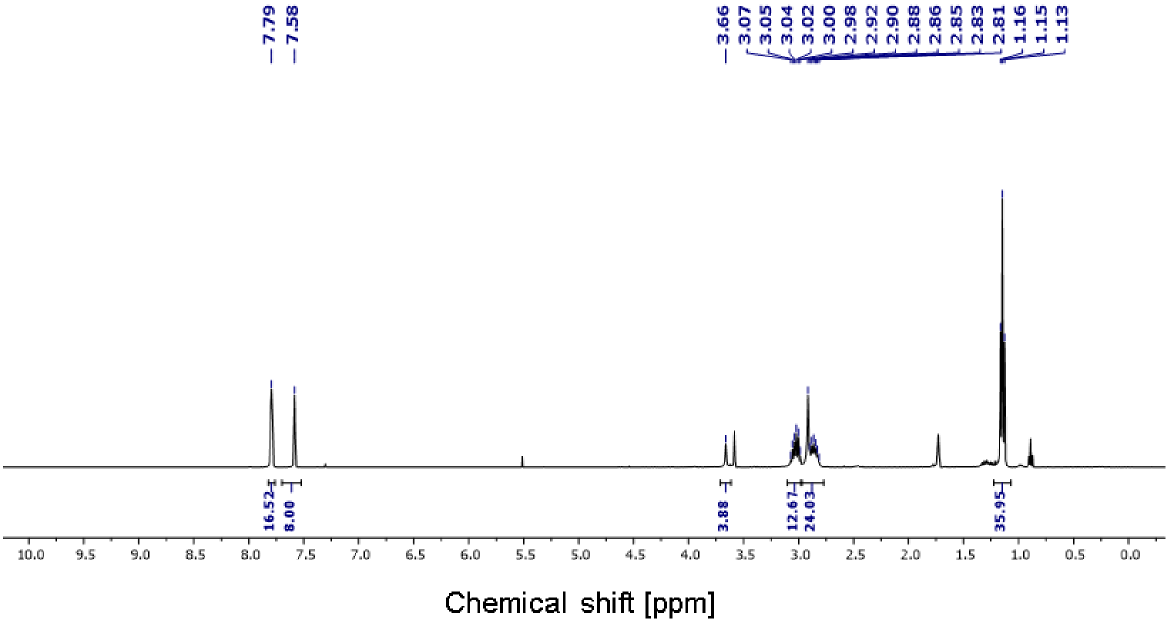


Figure S49: ^{1}H NMR spectrum of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)]$_2$ (**4b**) in [D8]THF.

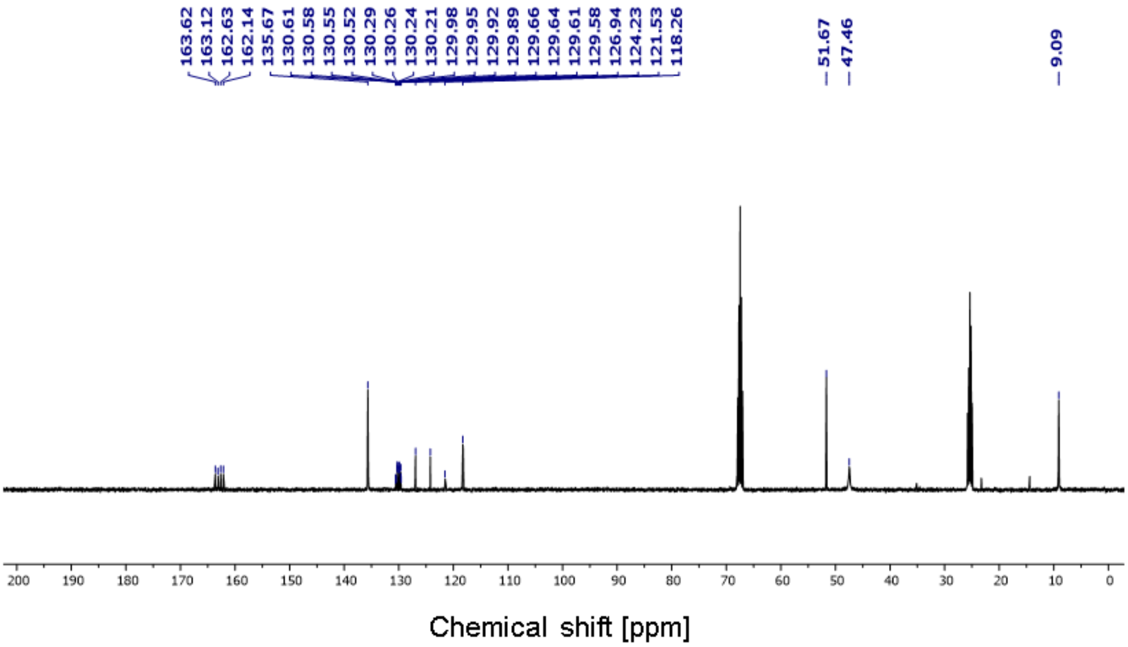


Figure S50: $^{13}C\{^1H\}$ NMR spectrum of $[(TEEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4b**) in [D8]THF.

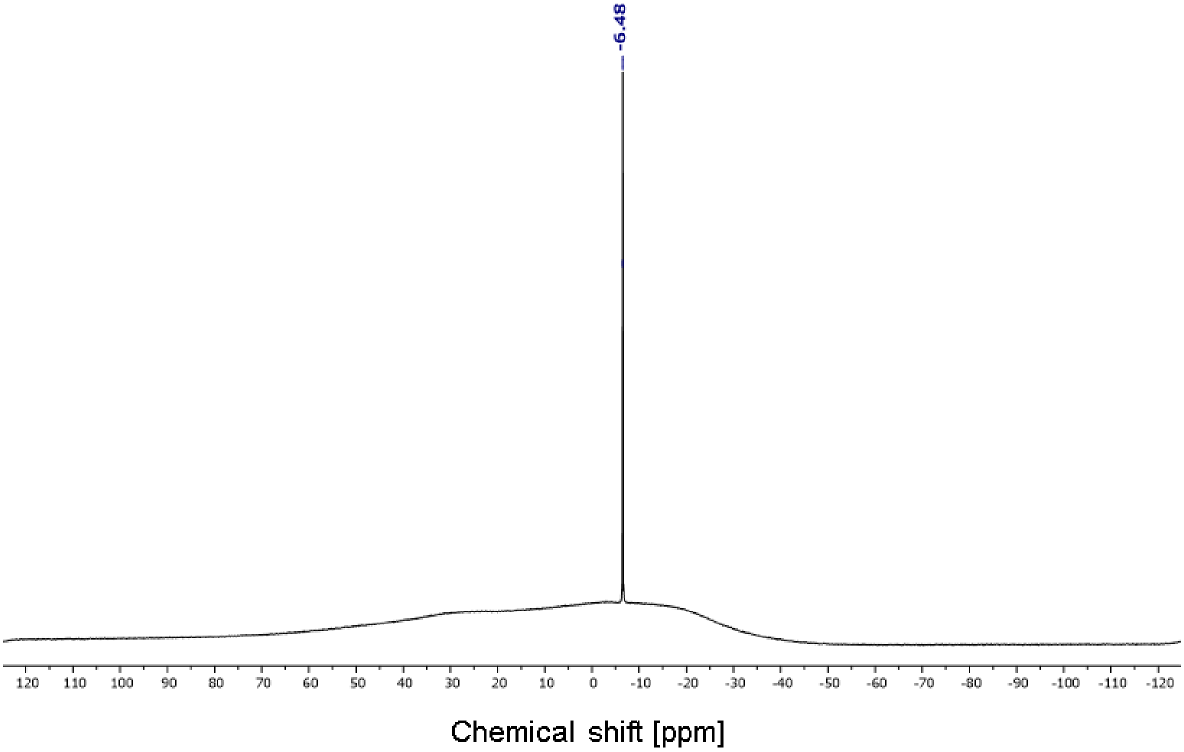


Figure S51: $^{11}B\{^1H\}$ NMR spectrum of $[(TEEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4b**) in [D8]THF.

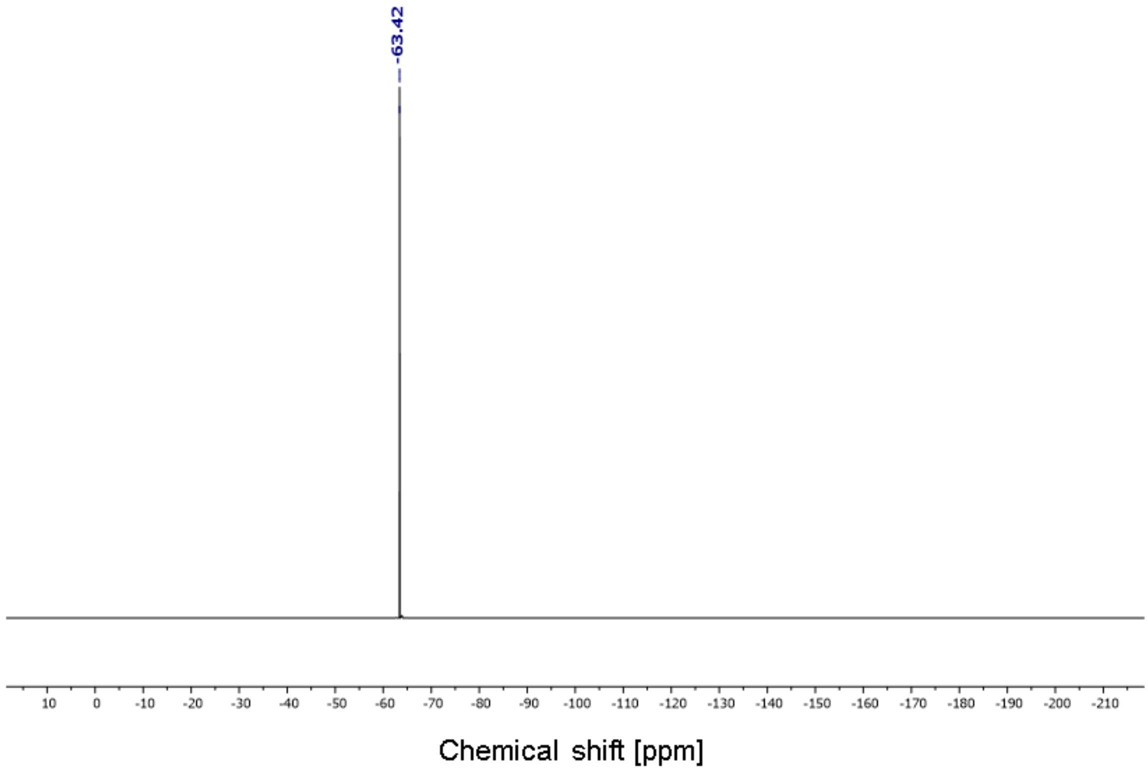


Figure S52: $^{19}F\{^1H\}$ NMR spectrum of $[(TEEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4b**) in [D8]THF.

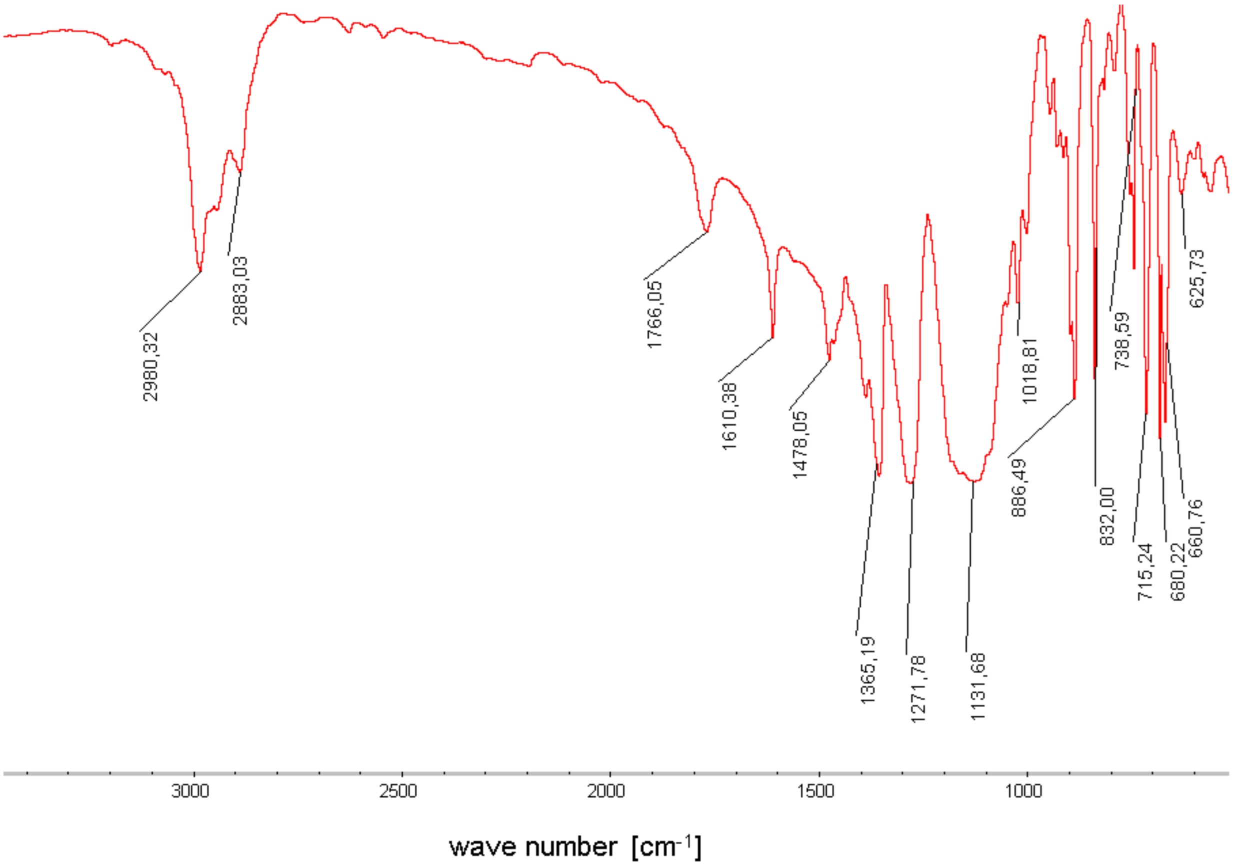


Figure S53: IR spectrum (KBr pellet) of $[(TEEDA)_3Zn_3H_4][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4b**).

Synthesis of [{(TEEDA)Zn(μ-H_2)}{(TMEDA)ZnH$)_2$}][B(3,5-($CF_3$$)_2$-$C_6H_3$)]$_2$ (4c).

To a suspension of [ZnH_2]$_n$ (3 mg, 45 µmol) and TEEDA (8 mg, 45 µmol) THF (5 mL) was added a solution of [(TMEDA)ZnH(thf)][B(3,5-($CF_3$$)_2$-$C_6H_3$$)_4$] (100 mg, 89 µmol) in THF (5 mL). The reaction mixture was stirred at room temperature until all solid material had dissolved (approximately 15 min). The solvent volume was reduced in *vacuo*. Addition of *n*-pentane resulted in the precipitation of a colorless solid which was isolated by decantation and subsequent drying under reduced pressure to give colorless solid (102 mg, 43 µmol). Yield:, 95%.

^{1}H NMR (400 MHz, [D8]THF): δ = 1.14 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, N-$CH_2C\mathit{H}_3$, 12H), 2.59 (s, N-$C\mathit{H}_3$, 24H), 2.84 (s, N-$C\mathit{H}_2$, 8H), 2.86 – 2.90 (m, N-$C\mathit{H}_2CH_3$, 4H), 2.92 (s, N-$C\mathit{H}_2$, 4H), 2.97 – 3.09 (m, N-$C\mathit{H}_2CH_3$, 4H), 3.67 (s, Zn-*H*, 4H), 7.59 (s, *para*-C_6H_3, 8H), 7.80 (s, *ortho*-C_6H_3, 16H).

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 9.14 (N-$CH_2\mathit{C}H_3$), 47.58 (N-$\mathit{C}H_2CH_3$), 48.13 (N-$\mathit{C}H_3$), 51.71 (N-$\mathit{C}H_2$), 58.02 (N-$\mathit{C}H_2$), 118.28 (*para*-C_6H_3), 125.60 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, $\mathit{C}F_3$), 130.06 (qq, $^1J_{C\text{-}F}$ = 31.5 Hz, $^3J_{B\text{-}C}$ = 2.8 Hz, *meta*-C_6H_3), 135.68 (*ortho*-C_6H_3), 162.89 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-C_6H_3) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.49 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF) : δ = -63.38 ppm.

IR (KBr): ν = 1774 (m, ZnH), 1611 cm^{-1} (m, ZnH).

Anal. Calcd. for $C_{86}H_{84}B_2F_{48}N_6Zn_3$ (2331.34 g · mol^{-1}): C, 44.31; H, 3.63; N, 3.60. Found: C, 42.99; H, 3.79; N, 3.74%.

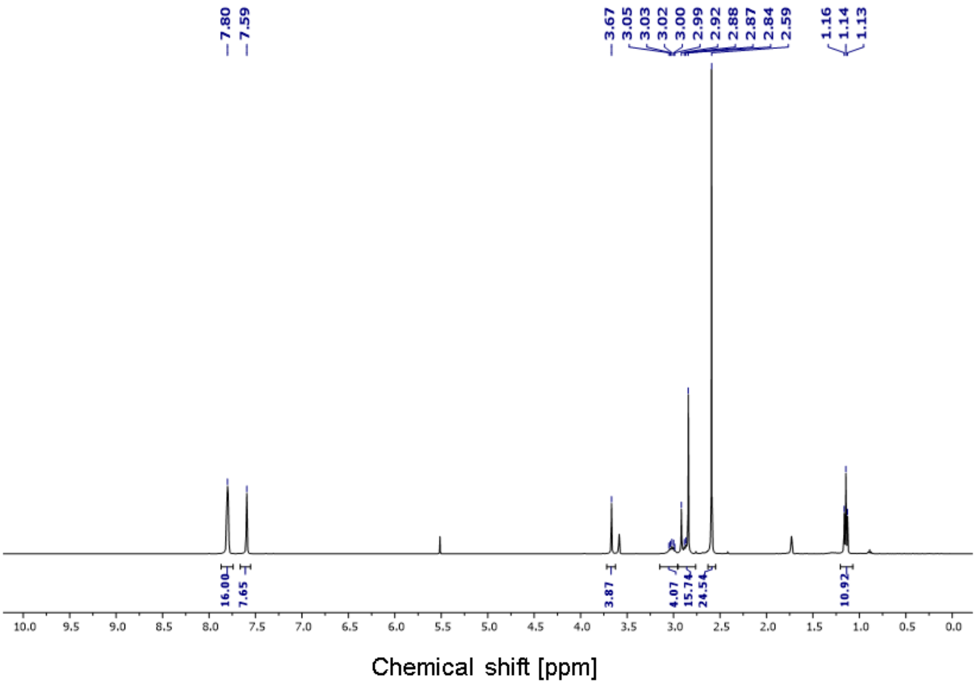


Figure S54: ^{1}H NMR spectrum of [{(TEEDA)Zn(μ-H_2)}{(TMEDA)ZnH)$_2$}][B(3,5-(CF_3)$_2$-C_6H_3)]$_2$ (**4c**) in [D8]THF.

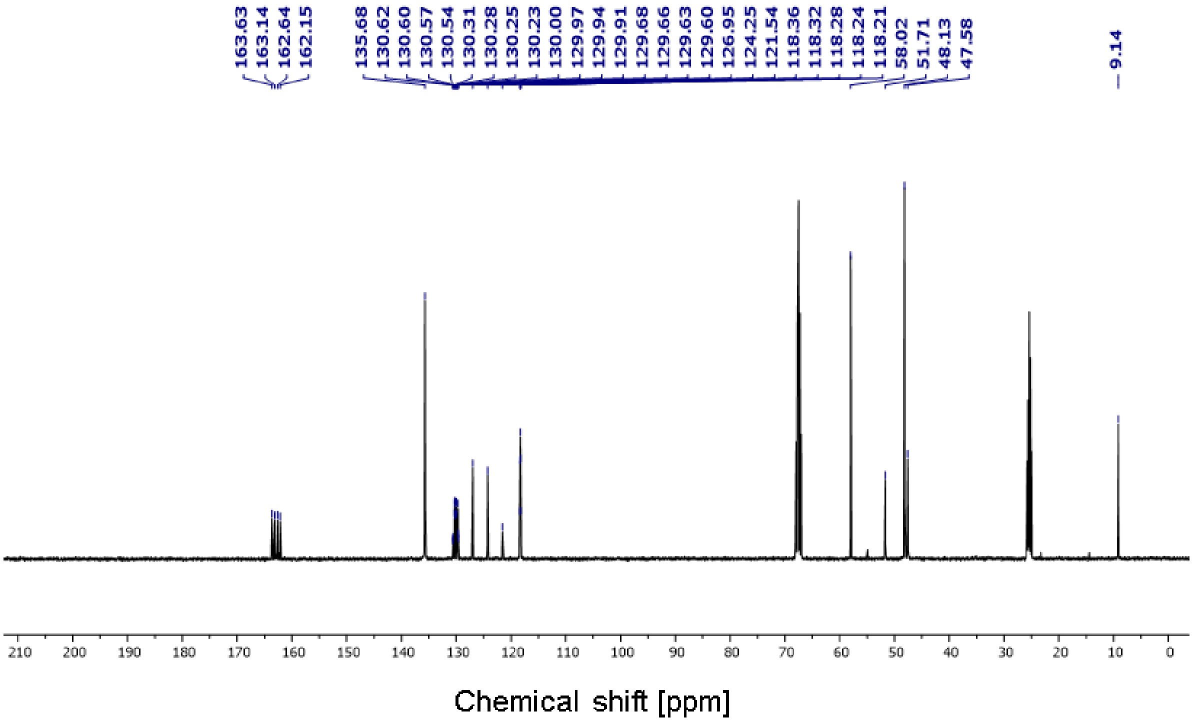


Figure S55: $^{13}C\{^1H\}$ NMR spectrum of [{(TEEDA)Zn(μ-H_2)}{(TMEDA)ZnH)$_2$}][B(3,5-(CF_3)$_2$-C_6H_3)]$_2$ (**4c**) in [D8]THF.

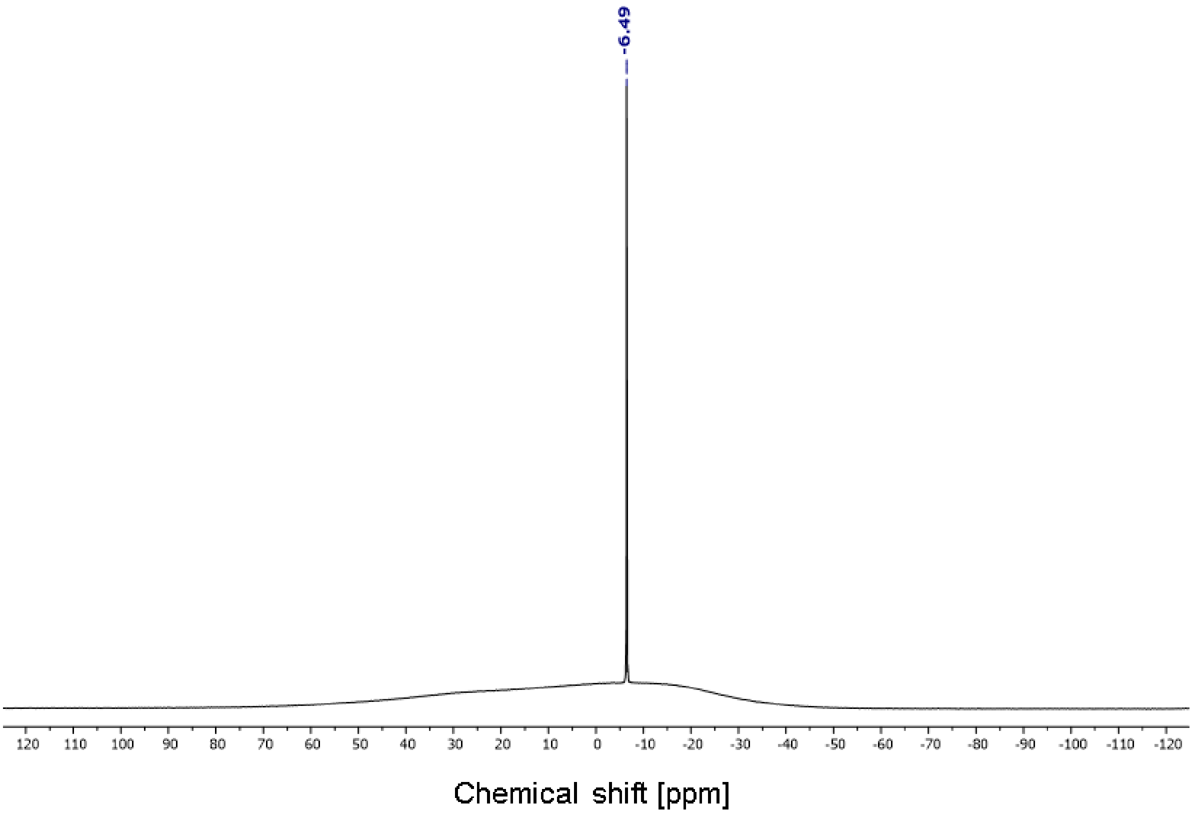


Figure S56: $^{11}B\{^{1}H\}$ NMR spectrum of $[\{(TEEDA)Zn(\mu\text{-}H_2)\}\{(TMEDA)ZnH)_2\}][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4c**) in [D8]THF.

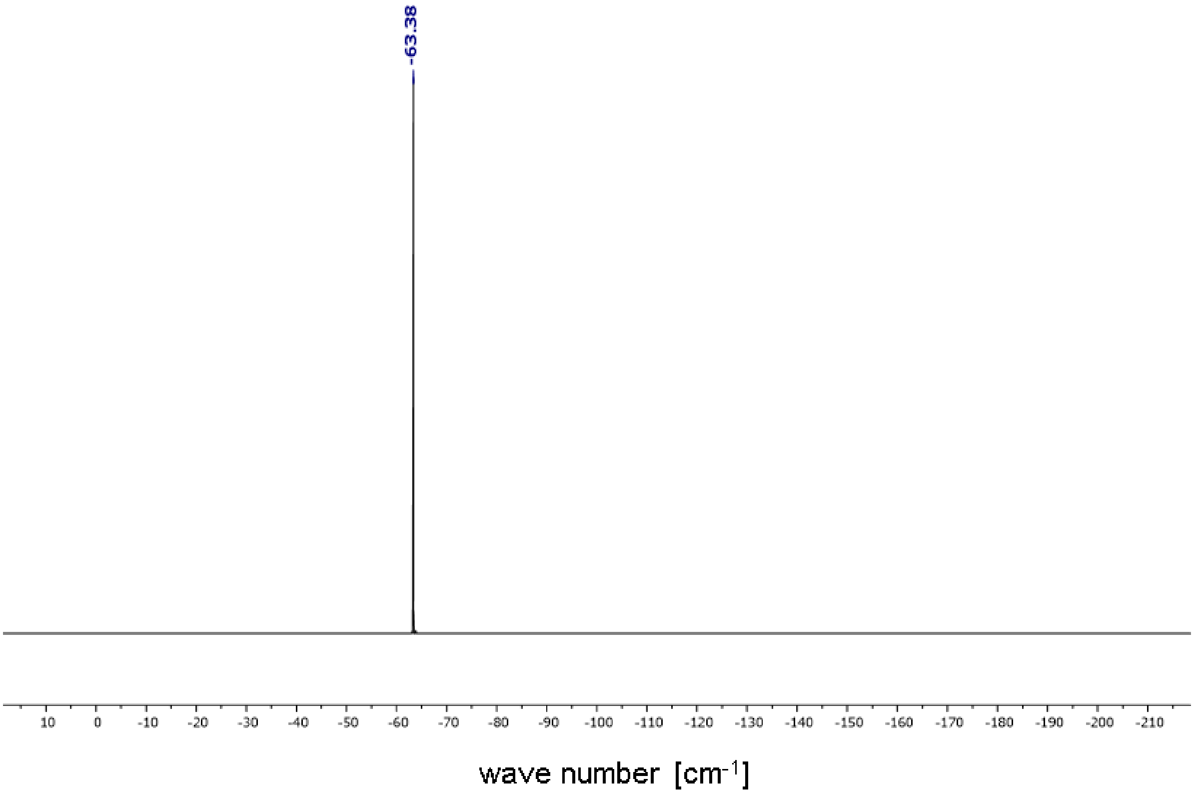


Figure S57: $^{19}F\{^{1}H\}$ NMR spectrum of $[\{(TEEDA)Zn(\mu\text{-}H_2)\}\{(TMEDA)ZnH)_2\}][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)]_2$ (**4c**) in [D8]THF.

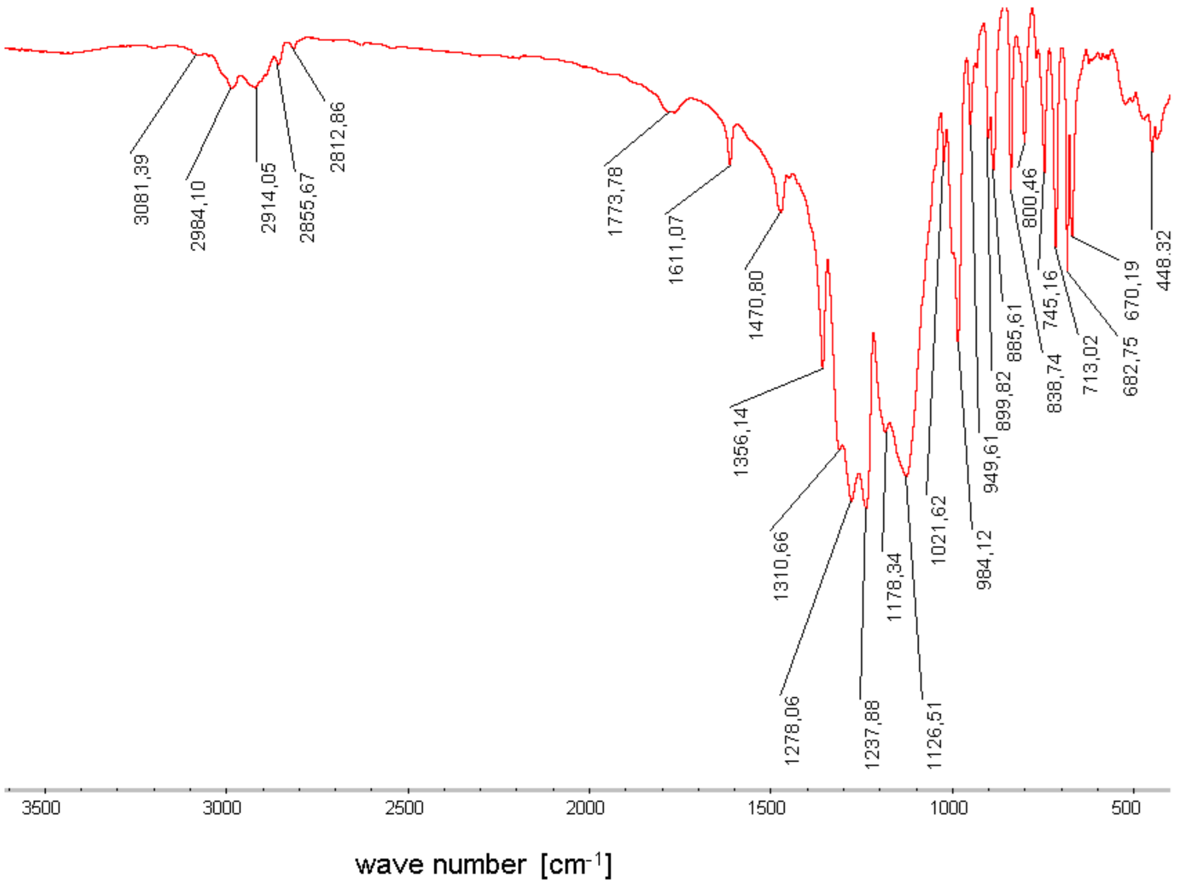
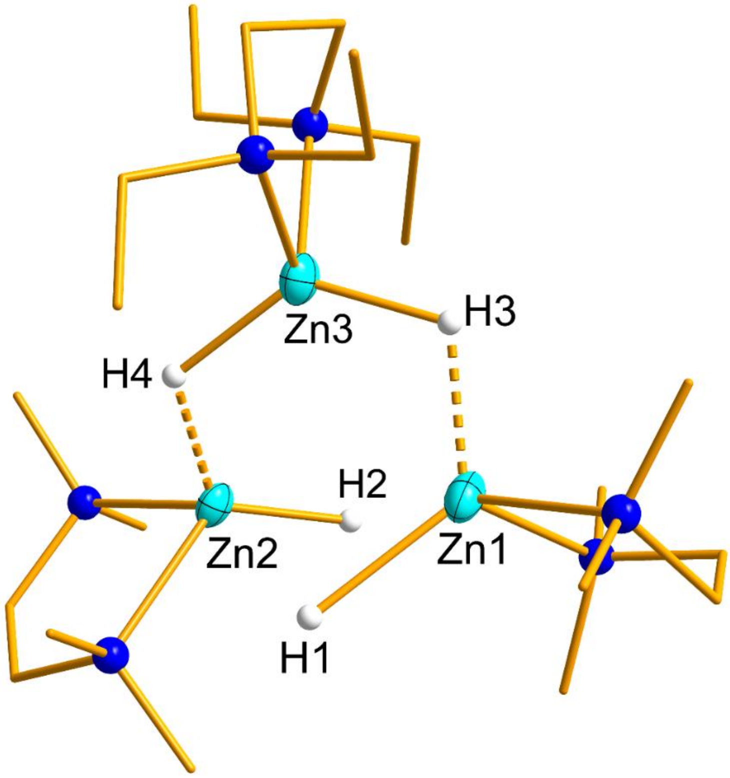


Figure S58: IR spectrum (KBr pellet) [{(TEEDA)Zn(μ-H)$_2$}{(TMEDA)ZnH)$_2$}][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)]$_2$ (**4c**).



Molecular structure of **4c**. Displacement parameters of the zinc and nitrogen atoms are set at 40% probability level. The borate anions and hydrogen atoms except of H1, H2, H3 and H4 are omitted for clarity. Selected bond distances [Å] and angles [°]: Zn1-H1 1.75(6), Zn1-H3 1.89(2), Zn3-H3 1.78(6), Zn3-H4 1.62(6), Zn2-H4 1.78(2), Zn2-H2 1.61(6), H1-Zn1-H3 125(3), H3-Zn3-H4 130(3), H4-Zn2-H2 118(3)..

Synthesis of $[(TMEDA)Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2$ (5a).

A solution of $[(TMEDA)_2ZnH(thf)][B(3,5-(CF_3)_2-C_6H_3)_4]$ (200 mg, 179 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO_2 (1 bar). The reaction mixture was layered with *n*-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying *in vacuo* to give $[(TMEDA)_2Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2$ as a colorless solid (185 mg, 84 µmol). Yield:, 94 %.

^{1}H NMR (400 MHz, [D8]THF): δ = 2.62 (s, N-CH_3, 24H), 2.91 (s, N-CH_2, 8H), 7.58 (s, *para*-C_6H_3, 4H), 7.79 (s, *ortho*-C_6H_3, 8H), 8.26 (s, Zn-OC*H*O, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 47.34 (N-CH$_3$), 57.60 (N-CH$_2$), 118.24 (*para*-C_6H_3), 125.59 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, CF_3), 130.27 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^3J_{B\text{-}C}$ = 2.9 Hz, *meta*-C_6H_3), 135.67 (*ortho*-C_6H_3), 162.88 (q, $^1J_{B\text{-}C}$ = 49.8 Hz, *ipso*-C_6H_3), 171.87 (Zn-O*C*HO) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.48 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF) : δ = -63.41 ppm.

IR (KBr): ν = 1649 cm^{-1} (s, ZnOCHO).

Anal. Calcd. for $C_{78}H_{58}B_2F_{48}N_4O_4Zn_2$ (2179.65 g · mol^{-1}): C, 42.98; H, 2.68; N, 2.57. Found: C, 43.62; H, 3.67; N, 2.38%.

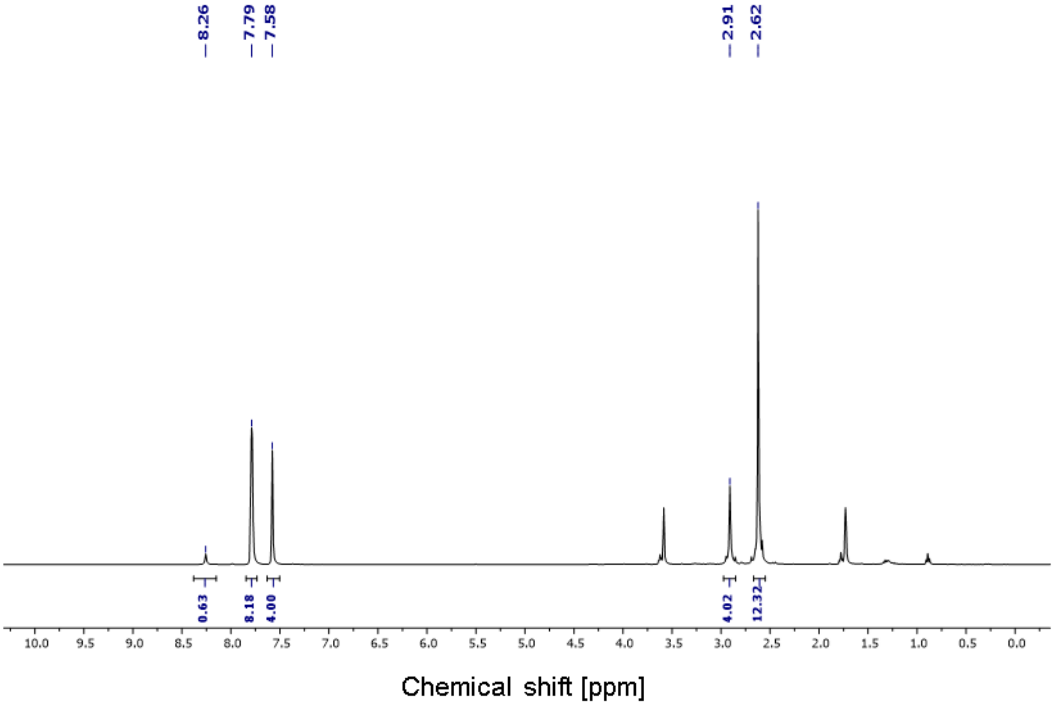


Figure S59: ^{1}H NMR spectrum of $[(TMEDA)Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2$ (**5a**) in [D8]THF.

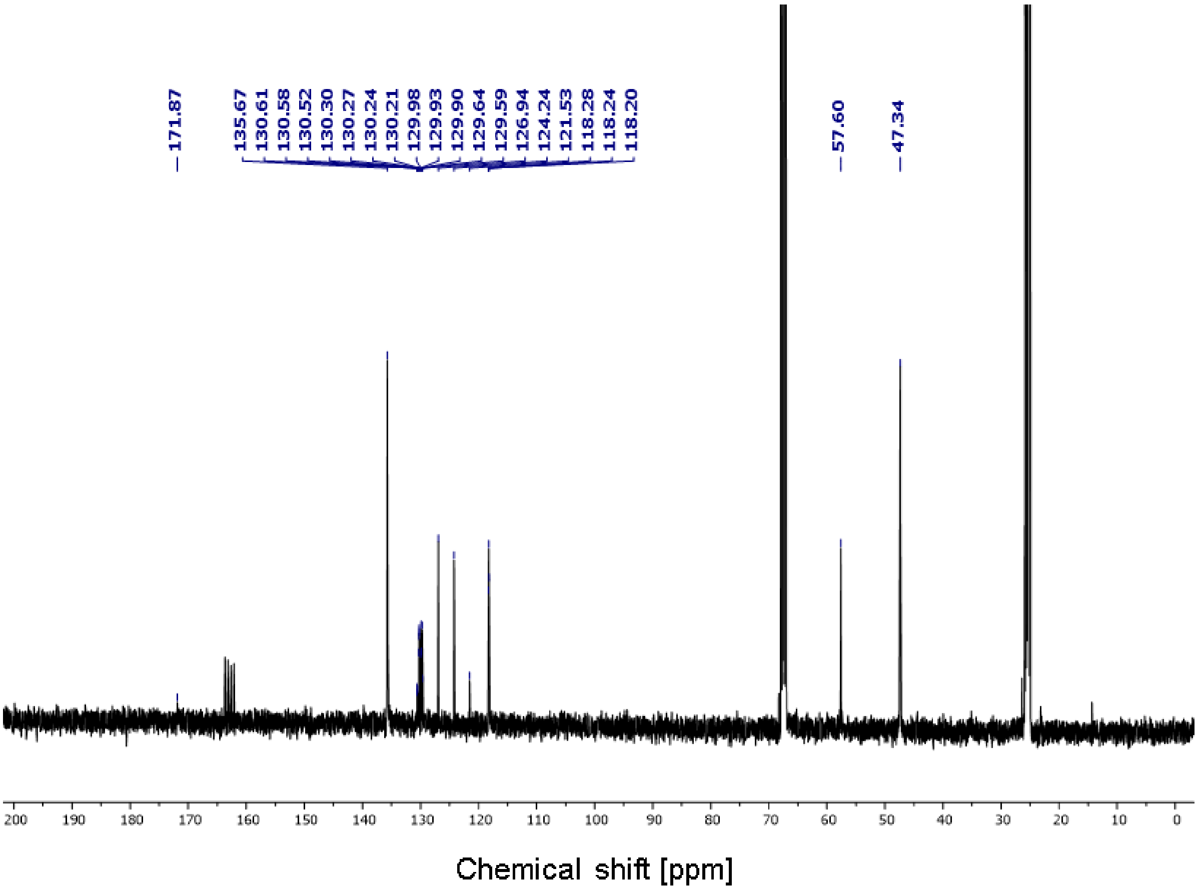


Figure S60: $^{13}C\{^1H\}$ NMR spectrum of $[(TMEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5a**)in [D8]THF.

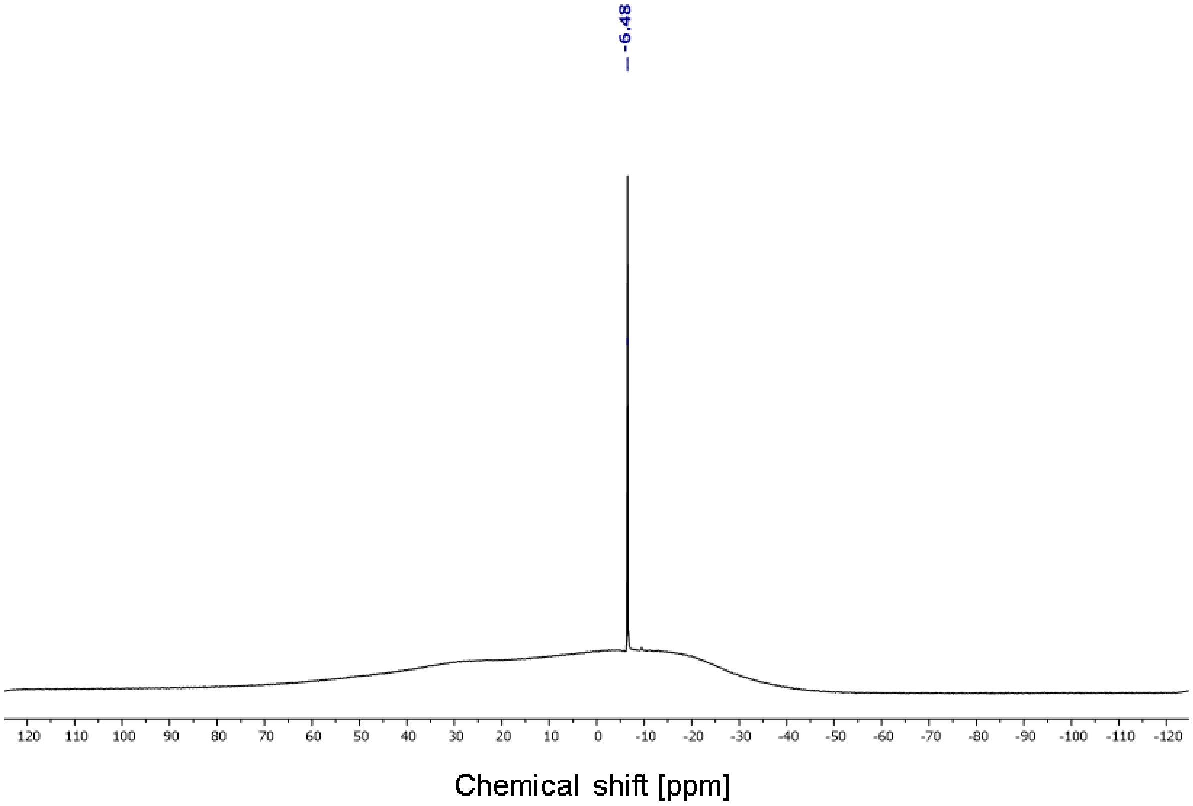


Figure S61: $^{11}B\{^1H\}$ NMR spectrum of $[(TMEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5a**)in [D8]THF.

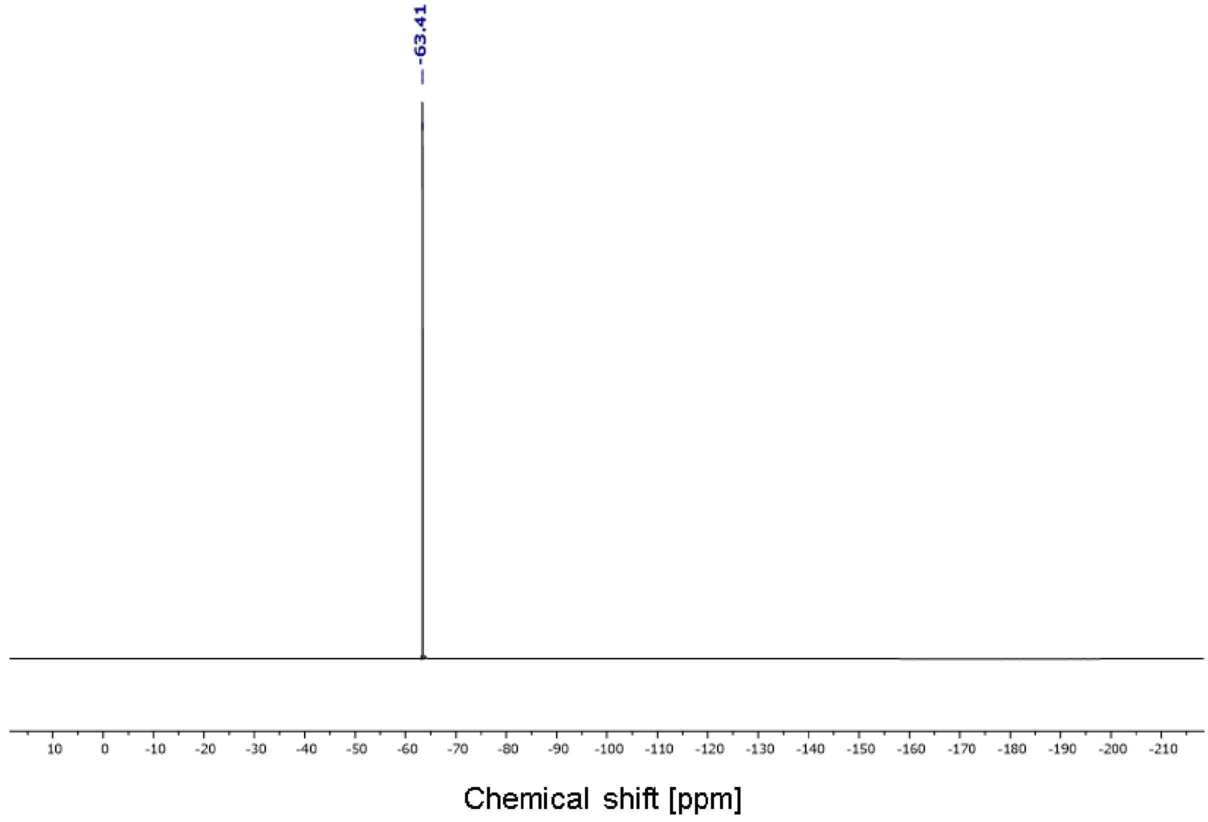


Figure S62: $^{19}F\{^{1}H\}$ NMR spectrum of $[(TMEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5a**)in [D8]THF.

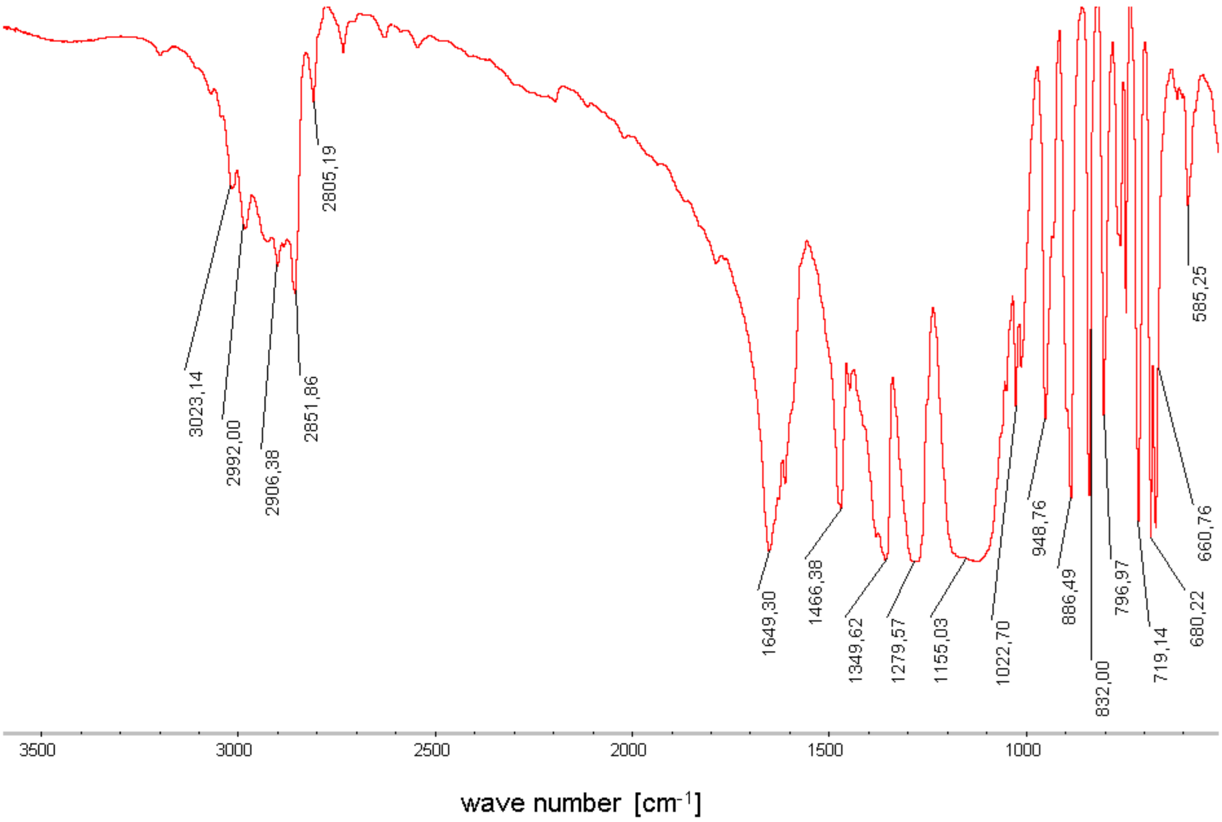


Figure S63: IR spectrum (KBr pellet) of $[(TMEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5a**).

Synthesis of $[(TEEDA)Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2$ (5b).

A solution of $[(TEEDA)ZnH]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2$ (200 mg, 91 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO_2 (1 bar). The reaction mixture was layered with *n*-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying *in vacuo.* to give $[(TEEDA)_2Zn(OCHO)]_2[B(3,5-(CF_3)_2-C_6H_3)_4]_2$ as a colorless solid (201 mg, 88 µmol). Yield: 96 %.

^{1}H NMR (400 MHz, [D8]THF): δ = 1.16 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, N-CH_2CH_3, 24H), 3.02 (m br., N-CH_2CH_3, 16H), 3.07 (s, N-CH_2CH_2, 8H), 7.59 (s, *para*-C_6H_3, 4H), 7.79 (s , *ortho*-C_6H_3, 8H), 8.23 (s, Zn-OC*H*O, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 7.74 (N-CH_2CH_3), 46.06 (N-CH_2CH_3), 50.34 (N-CH_2CH_2), 117.21 (*para*-C_6H_3), 124.53 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, CF_3), 129.04 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{C\text{-}B}$ = 2.8 Hz ,*meta*-C_6H_3), 134.61 (*ortho*-C_6H_3), 161.82 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-C_6H_3), 170.19 (Zn-O*C*HO) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = - 6.48 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF) : δ = -63.39 ppm.

IR (KBr): ν = 1625 cm^{-1} (s, ZnOCHO).

Anal. Calcd. for $C_{86}H_{74}B_2F_{48}N_4O_4Zn_2$ (2291.87 g · mol^{-1}): C, 45.07; H, 3.25; N, 2.44. Found: C, 45.28; H, 3.44; N, 2.79%.

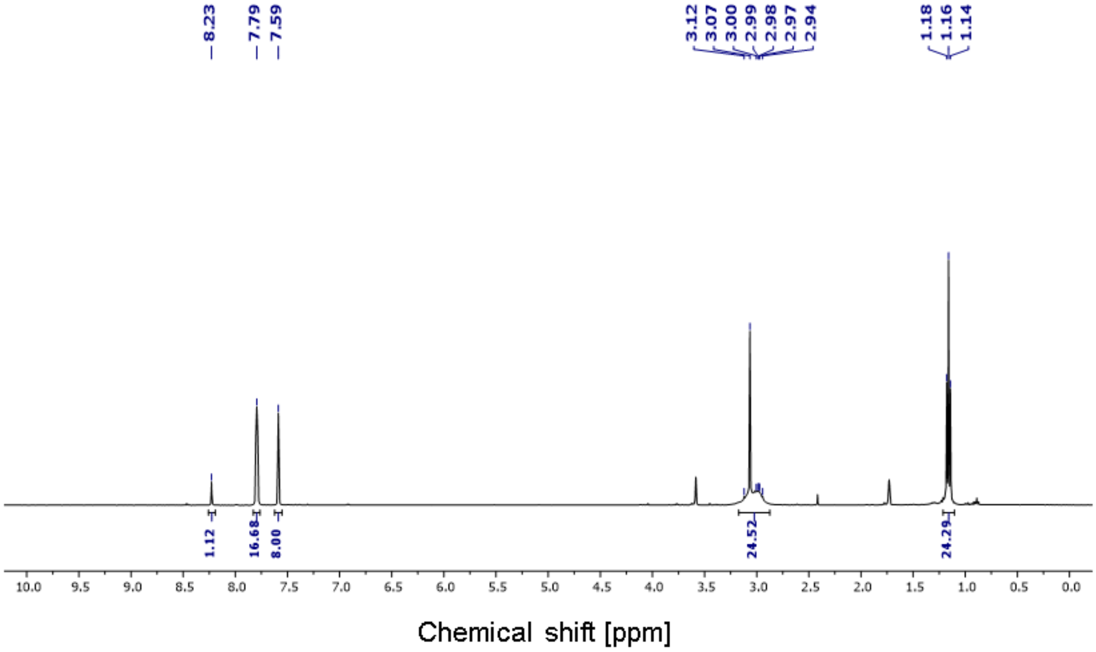


Figure S 64: ^{1}H NMR spectrum of [(TEEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (**5b**) in [D8]THF.

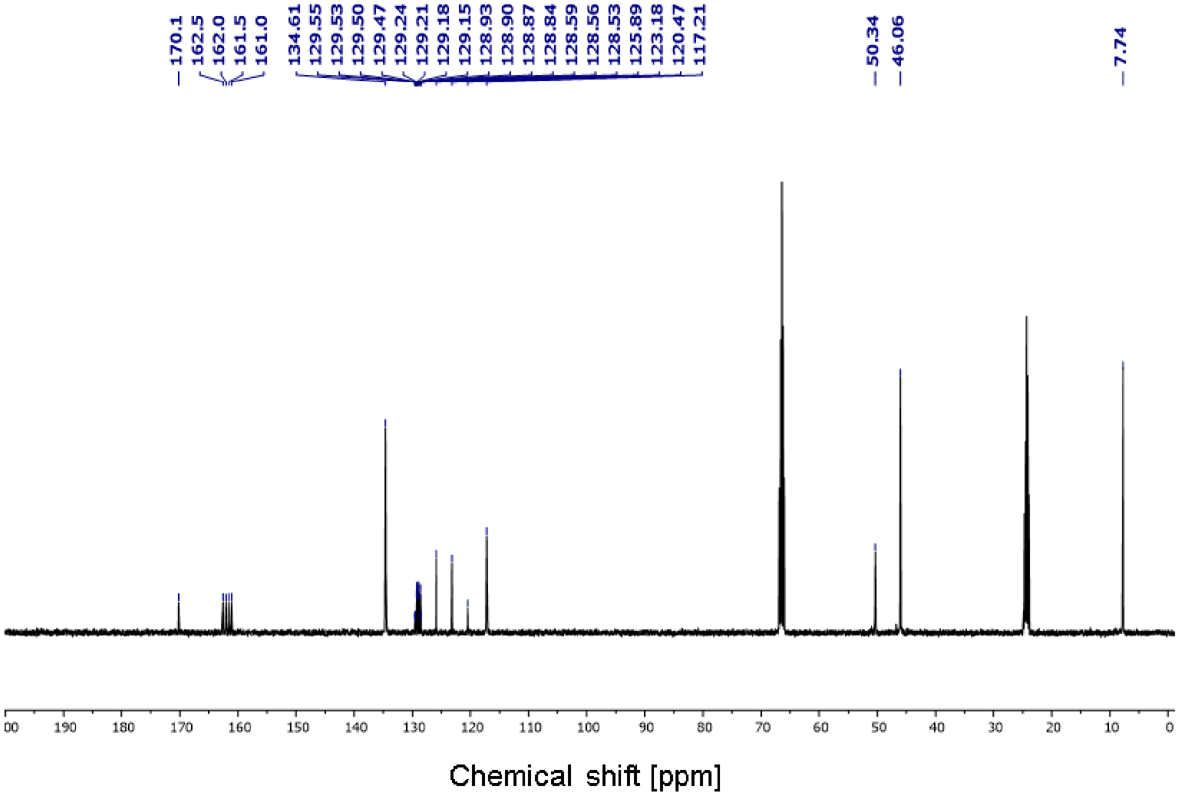


Figure S65: ^{13}C{^{1}H} NMR spectrum of [(TEEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (**5b**) in [D8]THF.

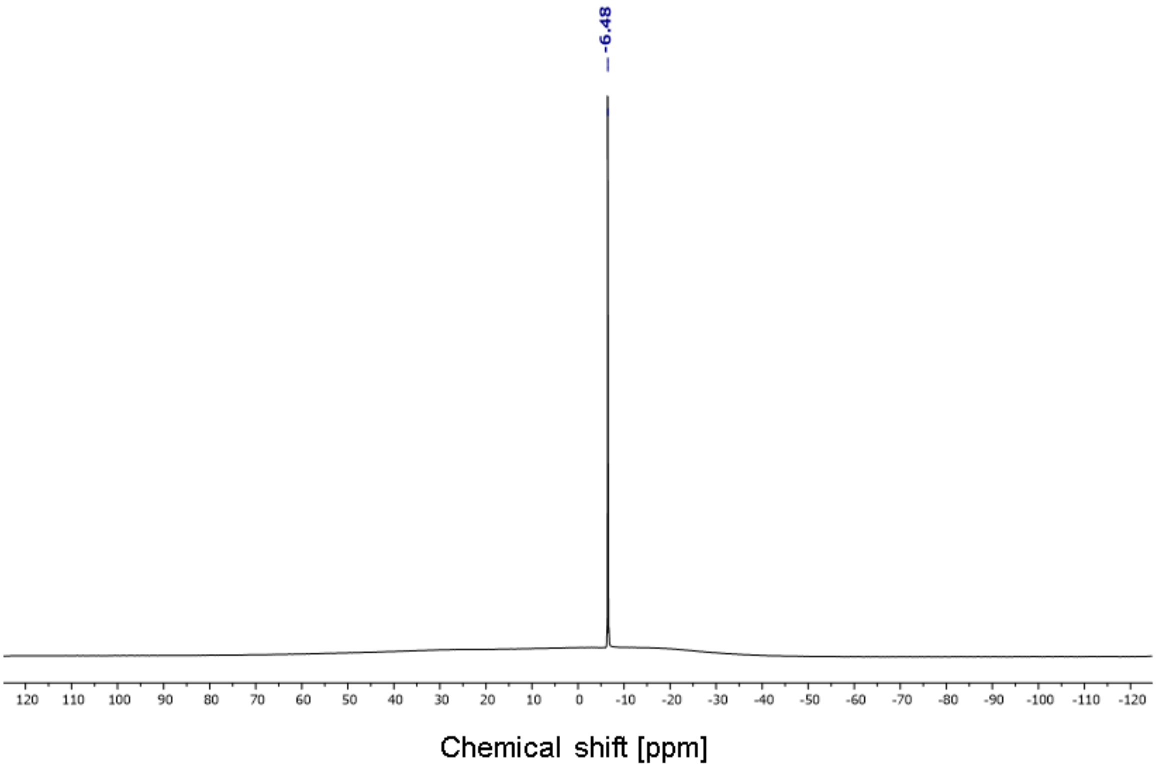


Figure S66: $^{11}B\{^{1}H\}$ NMR spectrum of $[(TEEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5b**) in [D8]THF.

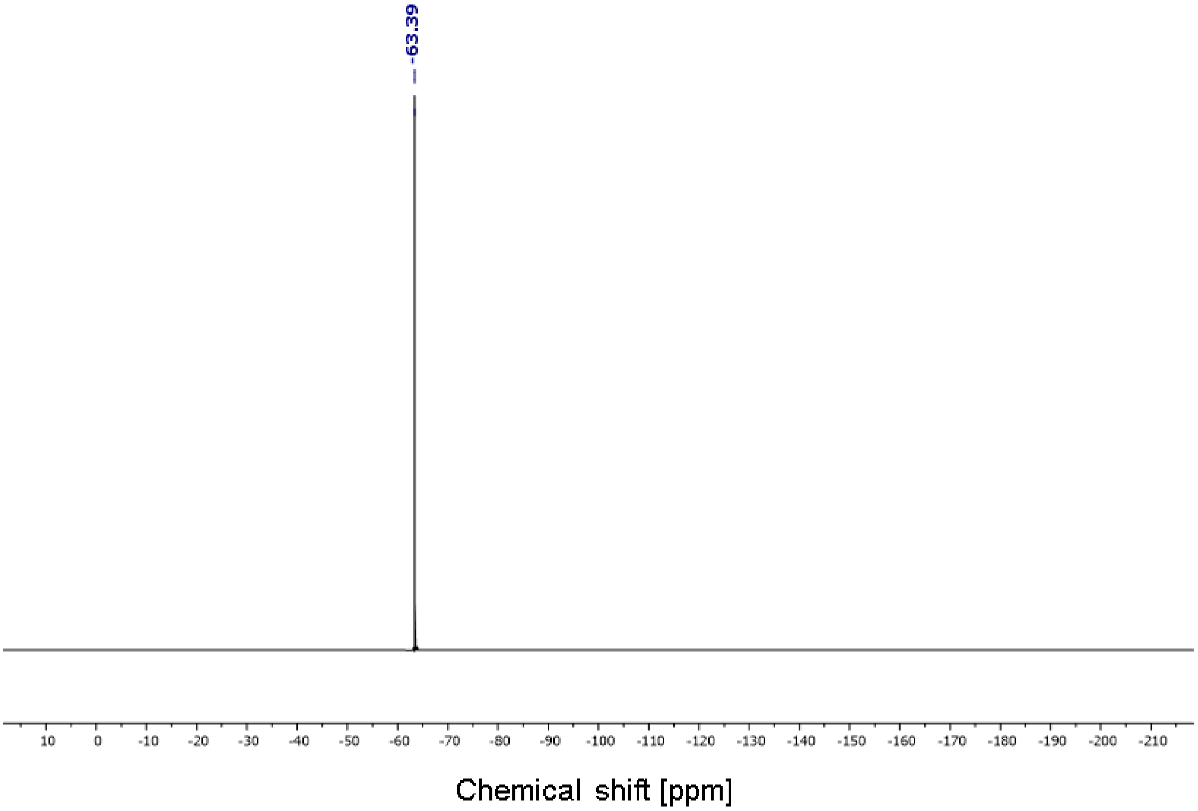


Figure S67: $^{19}F\{^{1}H\}$ NMR spectrum of $[(TEEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5b**) in [D8]THF.

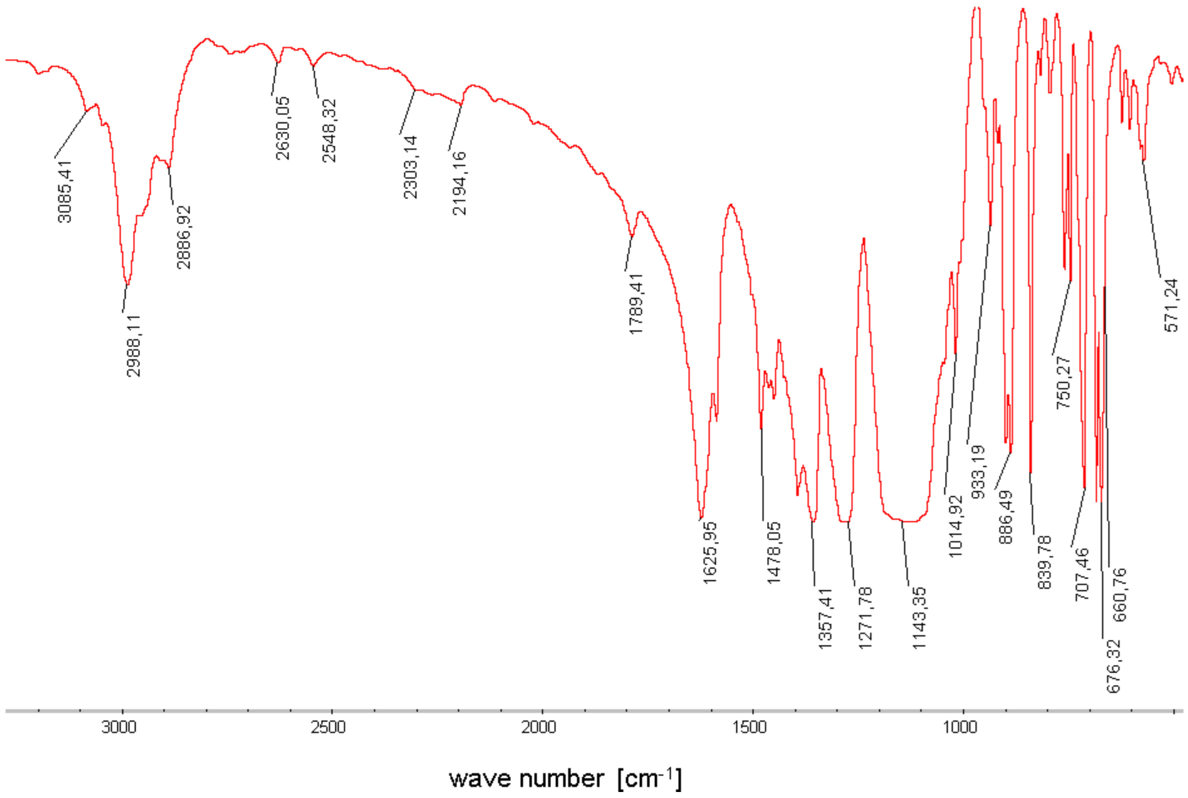


Figure S68: IR spectrum (KBr pellet) of $[(TEEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ (**5b**).

Synthesis of $[(TMEDA)_2Zn(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (6a).

A solution of $[(TMEDA)_2Zn_2H_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (200 mg, 163 µmol) in THF (1 mL)was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO_2 (1 bar). The reaction mixture was layered with *n*-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying *in vacuo* to give $[(TMEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ as colorless rods (212 mg, 156 µmol). Yield: 92 %.

^{1}H NMR (400 MHz, [D8]THF): δ = 2.49 (s, N-CH_3, 24H), 2.76 (s, N-CH_2, 8H), 7.58 (s, *para*-C_6H_3, 4H), 7.79 (s, *ortho*-C_6H_3, 8H), 8.26 (s, Zn-OC*H*O, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 47.04 (N-*C*H_3), 57.02 (N-*C*H_2), 118.23 (*para*-C_6H_3), 125.58 (q, $^1J_{C\text{-}F}$ = 272.2 Hz, *C*F_3), 130.10 (qq, $^2J_{C\text{-}F}$ = 31.5 Hz, $^3J_{B\text{-}C}$ = 2.8 Hz, *meta*-C_6H_3), 135.66 (*ortho*-C_6H_3), 162.88 (q, $^1J_{B\text{-}C}$ = 49.9 Hz, *ipso*-C_6H_3), 170.70 (Zn-O*C*HO) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.60 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF) : δ = -63.43 ppm.

IR (KBr): ν = 1653 cm^{-1} (s, ZnH).

Anal. Calcd. for $C_{47}H_{47}BF_{24}N_4O_6Zn_2$ (1361.45 g · mol^{-1}): C, 41.96; H, 3.48; N, 4.12. Found: C, 41.55; H, 3.96; N, 4.14%.

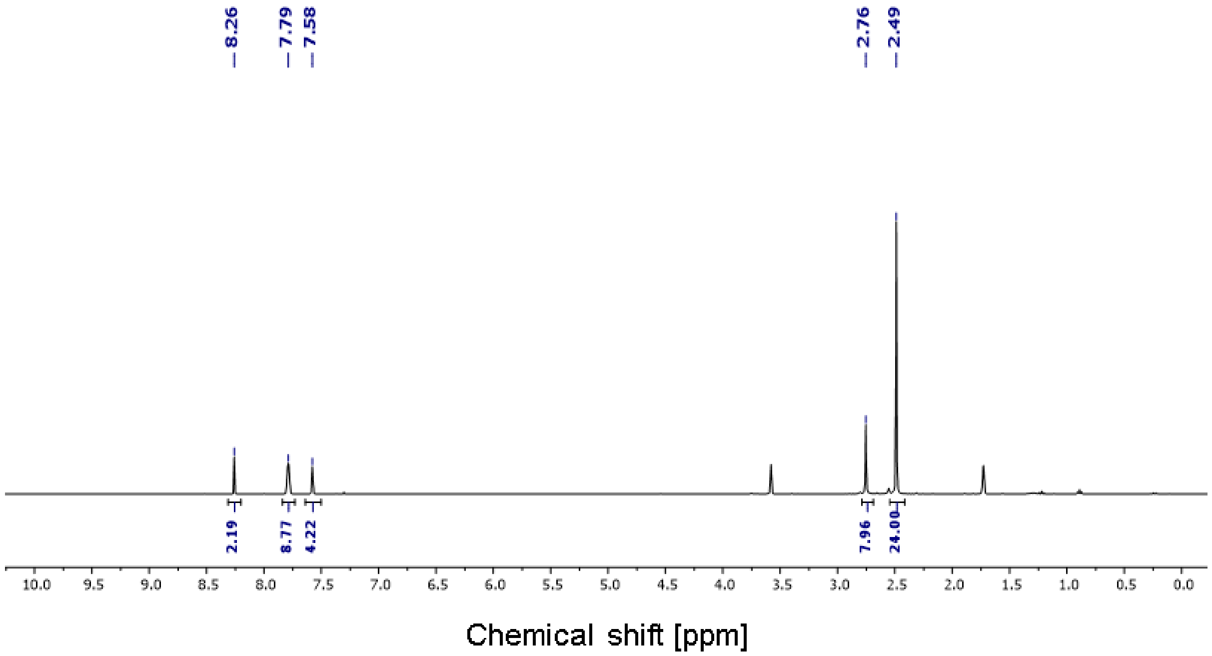


Figure S69: ^{1}H NMR spectrum of [(TMEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**6a**) in [D8]THF.

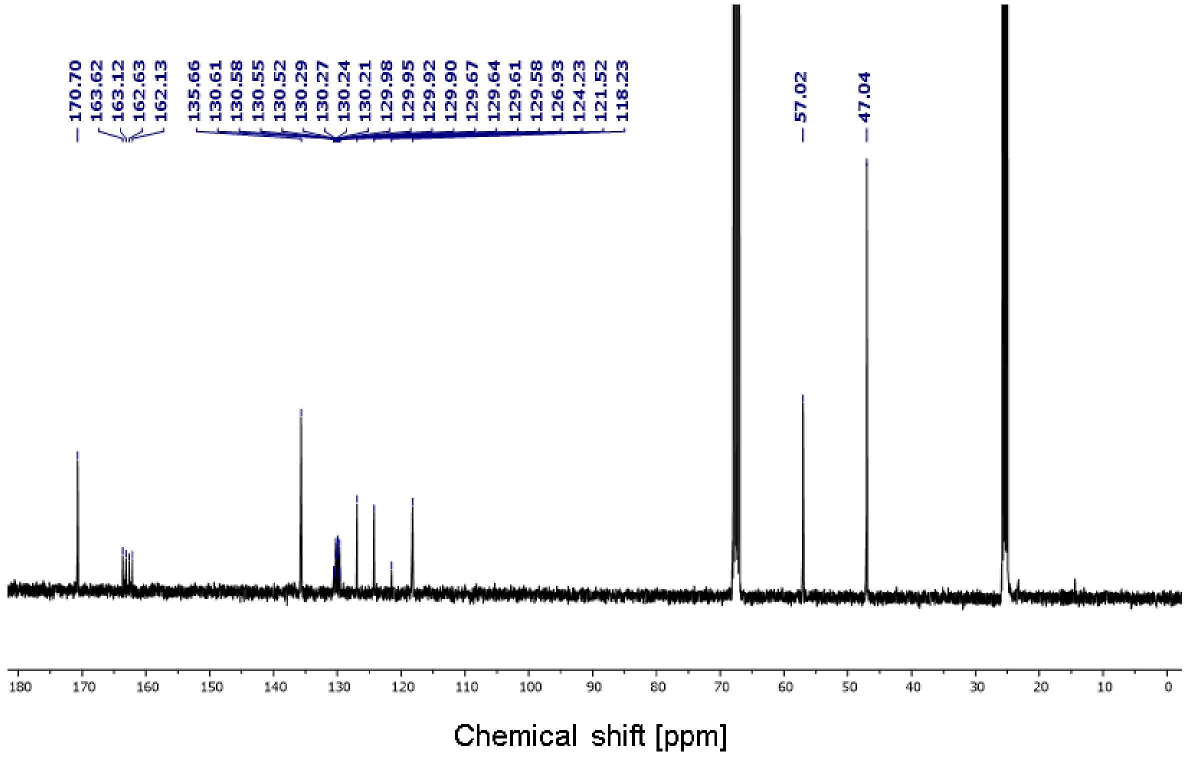


Figure S70: ^{13}C{^{1}H} NMR spectrum of [(TMEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**6a**) in [D8]THF.

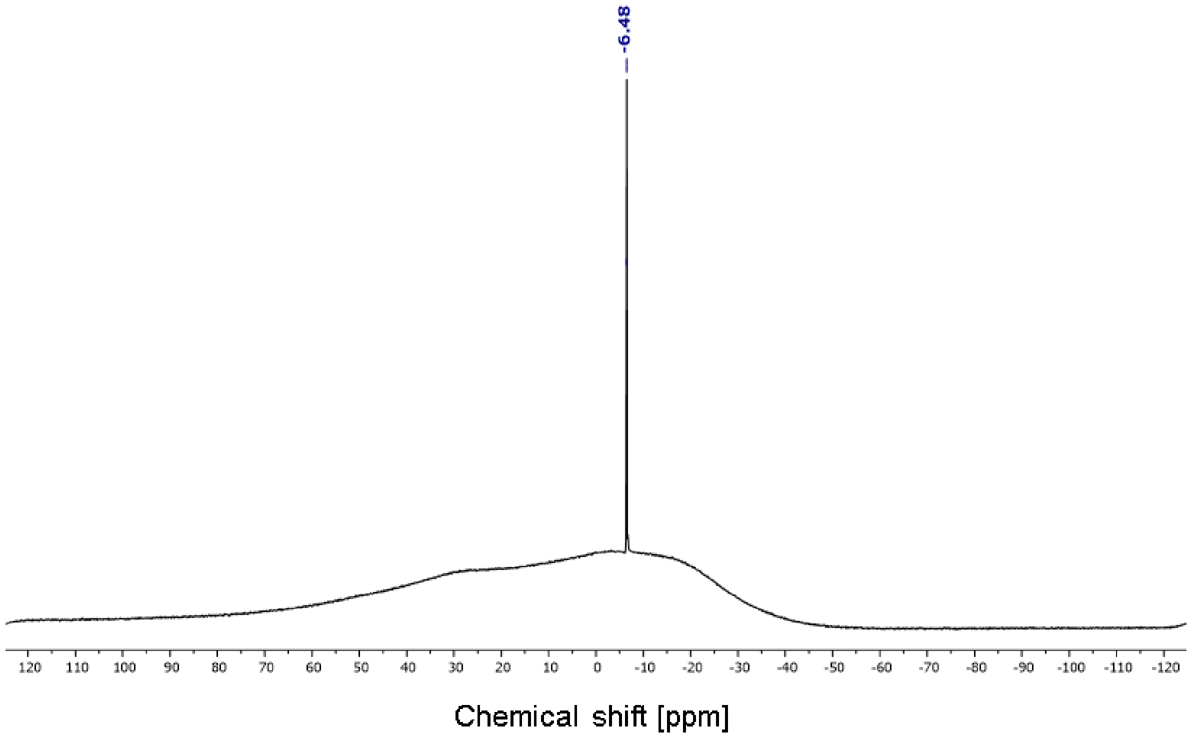


Figure S71: $^{11}B\{^{1}H\}$ NMR spectrum of $[(TMEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**6a**) in [D8]THF.

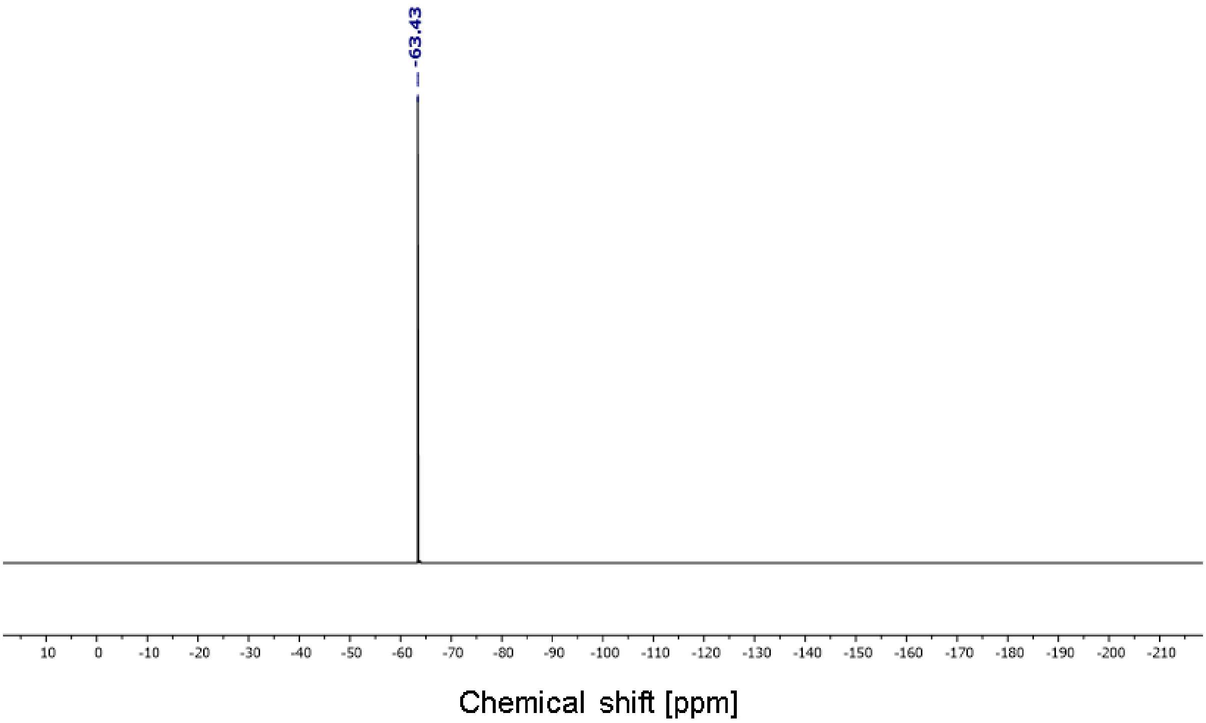


Figure S72: $^{19}F\{^{1}H\}$ NMR spectrum of $[(TMEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**6a**) in [D8]THF.

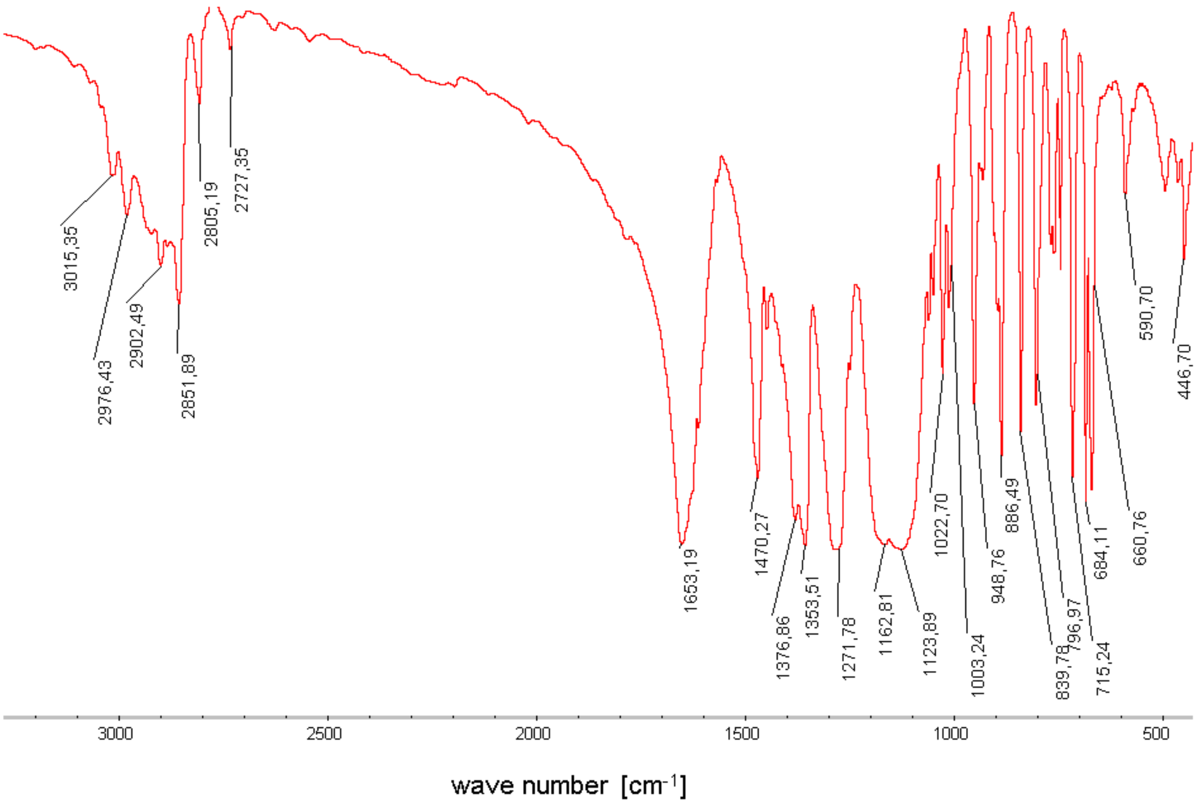


Figure S73: IR spectrum (KBr pellet) of [(TMEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**6a**).

Synthesis of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (6b).

A solution of [(TEEDA)$_2$Zn$_2$H$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (200 mg, 149 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO$_2$ (1 bar). The reaction mixture was layered with *n*-pentane and placed in the freezer at -30 °C. After standing overnight crystals formed which were isolated by decantation of the mother liquor and subsequent drying *in vacuo.* to give [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] as a colorless solid (204 mg, 138 µmol). Yield: 96 %.

^{1}H NMR (400 MHz, [D8]THF): δ = 1.11 (t, $^3J_{\text{H-H}}$ = 7.1 Hz, N-CH$_2$C*H*$_3$, 24H), 2.97 (m, N-C*H*$_2$, 24H), 7.60 (s, *para*-C$_6$H$_3$, 4H), 7.81 (s , *ortho*-C$_6$H$_3$, 8H), 8.30 (s, Zn-OC*H*O, 3H) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D8]THF): δ = 8.84 (N-CH$_2$*C*H$_3$), 46.94 (N-*C*H$_2$CH$_3$), 50.97 (N-*C*H$_2$*C*H$_2$), 118.28 (*para*-C$_6$H$_3$), 125.62 (q, $^1J_{\text{C-F}}$ = 272.2 Hz, *C*F$_3$), 130.13 (qq, $^2J_{\text{C-F}}$ = 31.5 Hz, $^3J_{\text{C-B}}$ = 2.8 Hz ,*meta*-C$_6$H$_3$), 135.70 (*ortho*-C$_6$H$_3$), 162.90 (q, $^1J_{\text{B-C}}$ = 49.8 Hz, *ipso*-C$_6$H$_3$), 171.45 (Zn-O*C*HO) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D8]THF): δ = -6.48 ppm.

^{19}F{^{1}H} NMR (377 MHz, [D8]THF) : δ = -63.38 ppm.

IR (KBr): ν = 1594 cm^{-1} (s, ZnH).

Anal. Calcd. for $C_{55}H_{63}BF_{24}N_4O_6Zn_3$ (1473.66 g · mol^{-1}): C, 44.83; H, 4.13; N 3.80. Found: C, 44.73; H, 4.27; N, 3.78%.

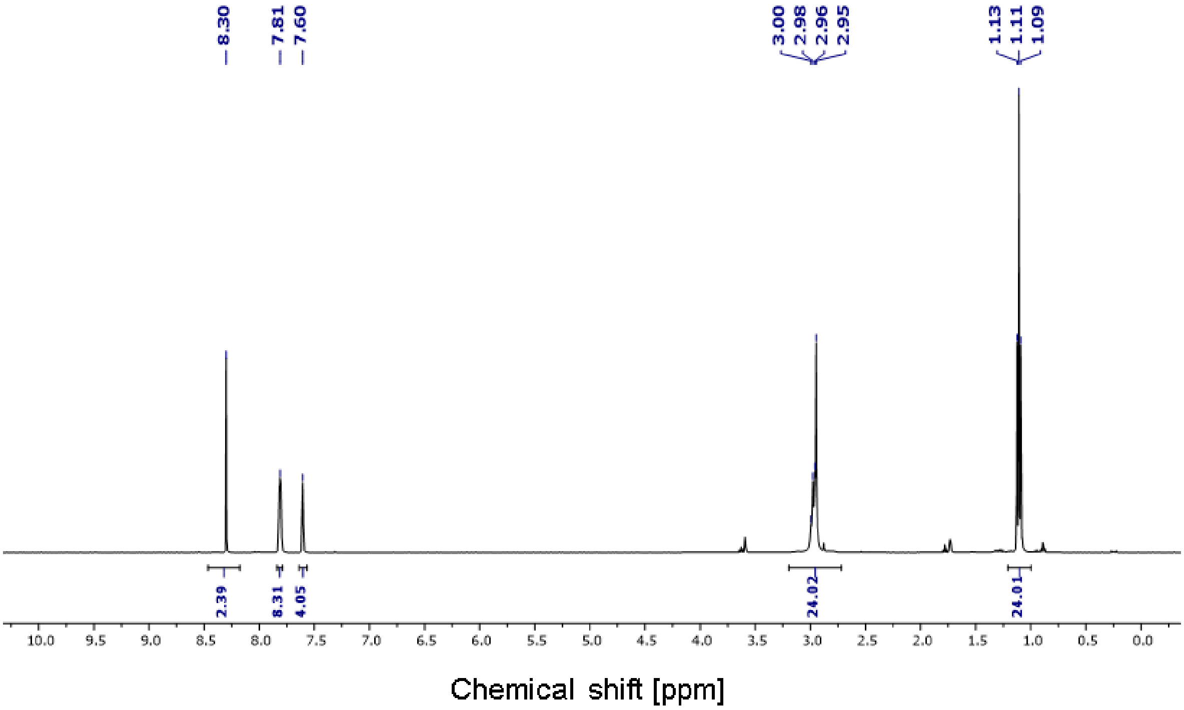


Figure S74: ^1H NMR spectrum of $[(TEEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**6b**) in [D8]THF.

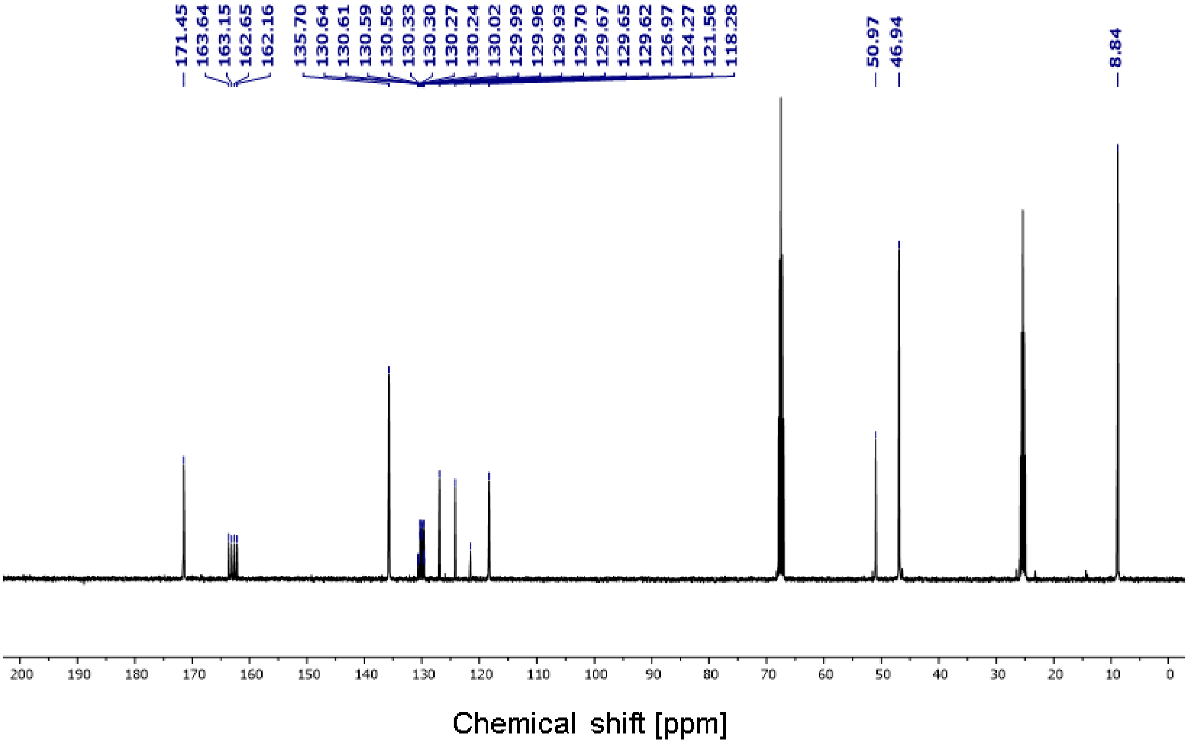


Figure S75: $^{13}C\{^1H\}$ NMR spectrum of $[(TEEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**6b**) in [D8]THF.

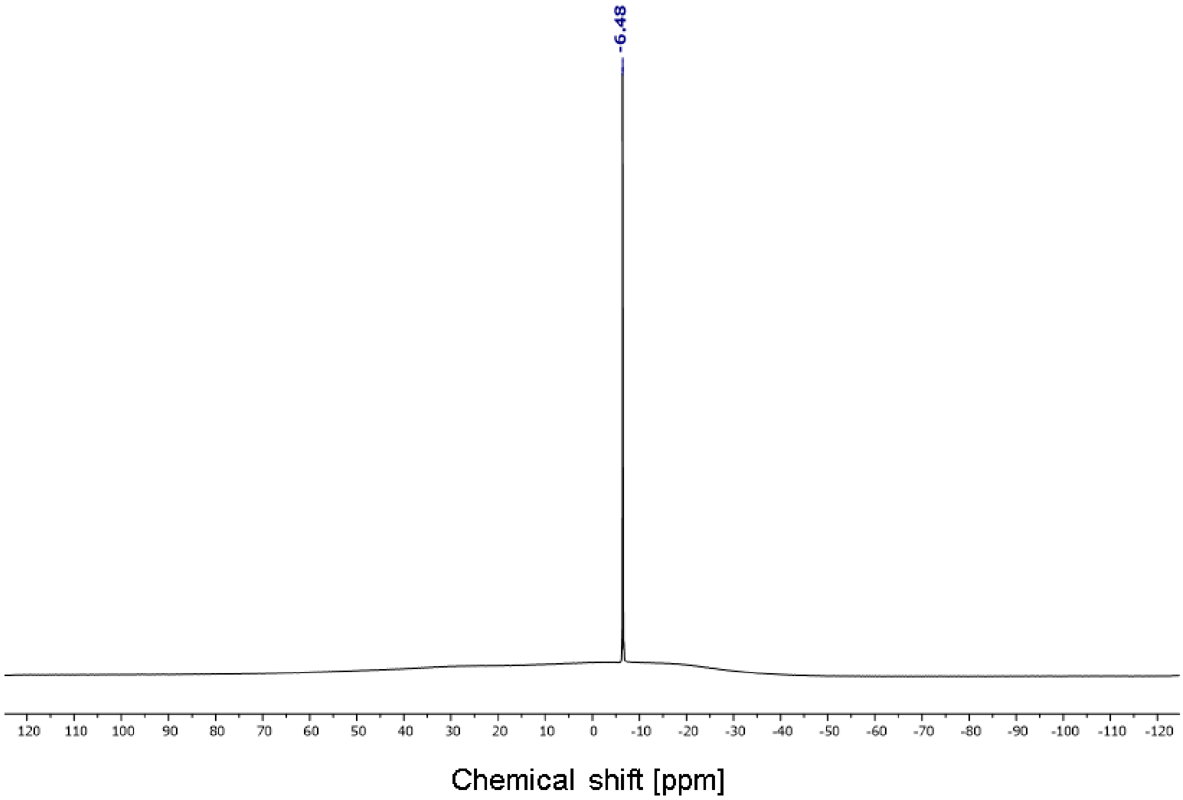


Figure S76: $^{11}B\{^1H\}$ NMR spectrum of $[(TEEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**6b**) in [D8]THF.

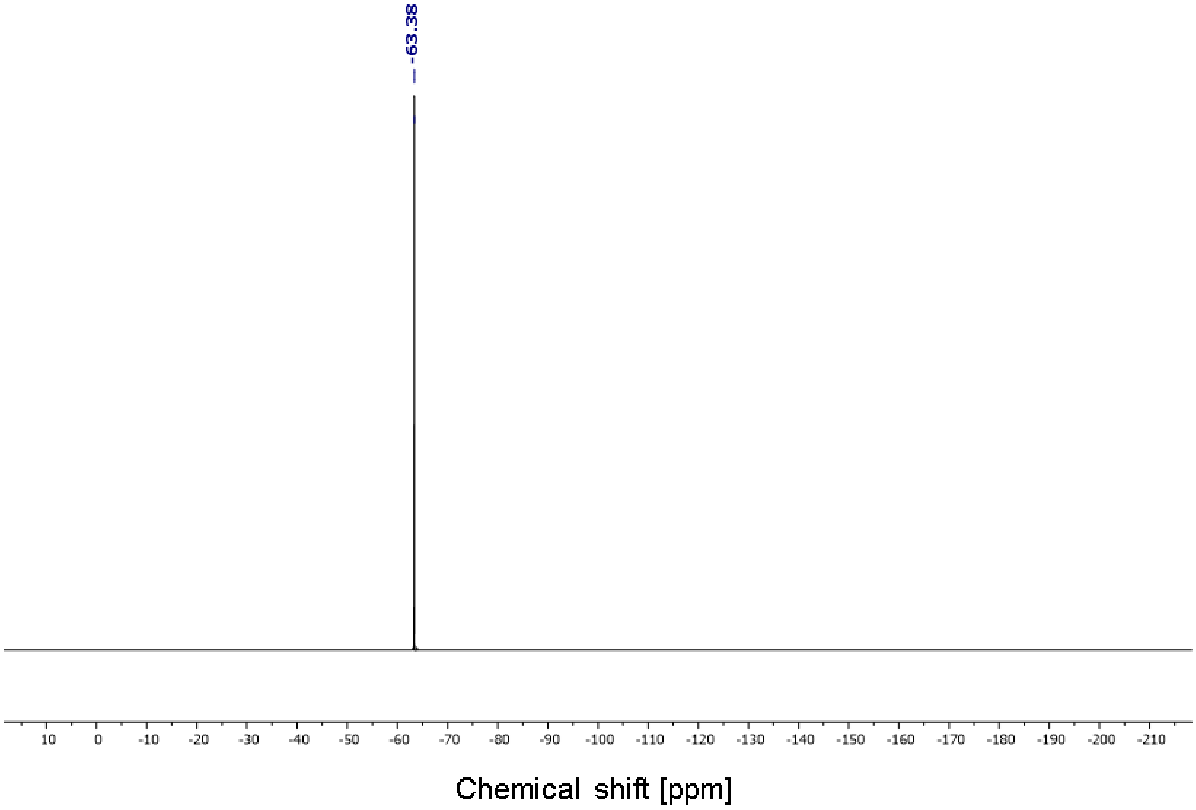


Figure S77: $^{19}F\{^1H\}$ NMR spectrum of $[(TEEDA)_2Zn_2(OCHO)_3][B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]$ (**6b**) in [D8]THF.

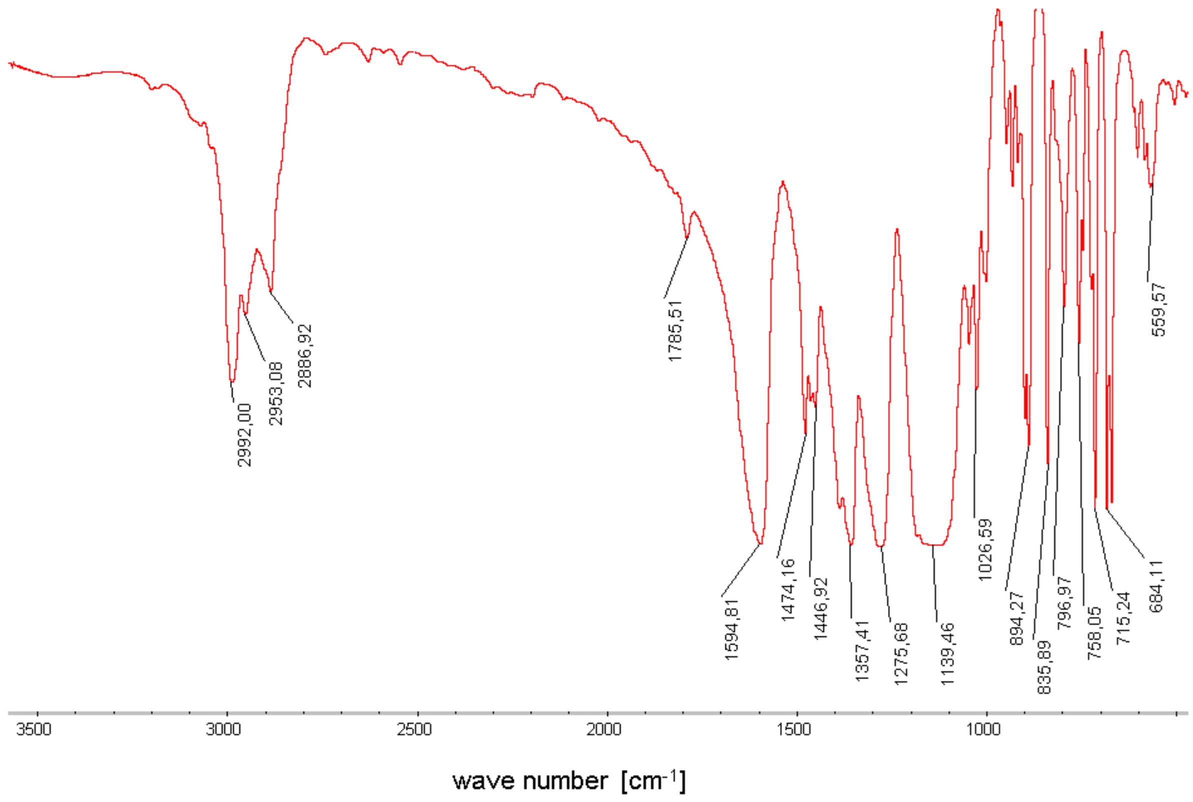


Figure S78: IR spectrum (KBr pellet) of [(TEEDA)$_2$Zn$_2$(OCHO)$_3$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] (**6b**).

Synthesis of [(TMEDA)Zn(OCHO)$_2$] (7a).

Method A: A solution of [(TMEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (200 mg, 88 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO$_2$ (1 bar). The solvent was removed in vacuo and the residue was extracted with benzene (3 x 3 mL) The solvent was removed in vacuo and the residue was extracted with diethyl ether (3 x 3 mL) to separate the title compound [(TMEDA)Zn(OCHO)]$_2$[B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ from 5a. The combined ethereal extracts were filtered and the solvent removed *in vacuo*. Repeated recrystallization and drying under reduced pressure gave [(TEMDA)$_2$Zn(OCHO)$_2$] as a solid (19 mg, 70 µmol). Yield: 80 % (based on the maximum theoretical yield).

Method B: A suspension of [ZnH$_2$]$_n$ (20 mg, 296 µmol) and TMEDA (35 mg, 296 µmol) in CH$_2$CH$_2$ (2 mL) was transferred into a Schlenk tube equippded with a stir bar, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO$_2$ (1 bar). The suspension was stirred at rommtemperature until all solid material had dissolved (approximately 20 min). The solvent was removed *in vacuo* to give [(TEEDA)Zn(OCHO)$_2$] as a colorless solid (79 mg, 290 µmol). Yield: 98 %.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.53 (s, N-C*H*$_3$, 12H), 2.73 (s, N-C*H*$_2$, 4H), 8.29 (s, Zn-OC*H*O, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ = 47.12 (N-*C*H$_3$), 57.27 (N-*C*H$_2$), 169.70 (Zn-O*C*HO) ppm.

IR (KBr): ν = 1608 cm^{-1} (s, ZnOCHO).

Anal. Calcd. for $C_8H_{18}N_2O_4Zn$ (271.62 g · mol^{-1}): C, 35.38; H, 6.68; N 10.31. Found: C, 35.11; H, 6.60; N, 10.45%.

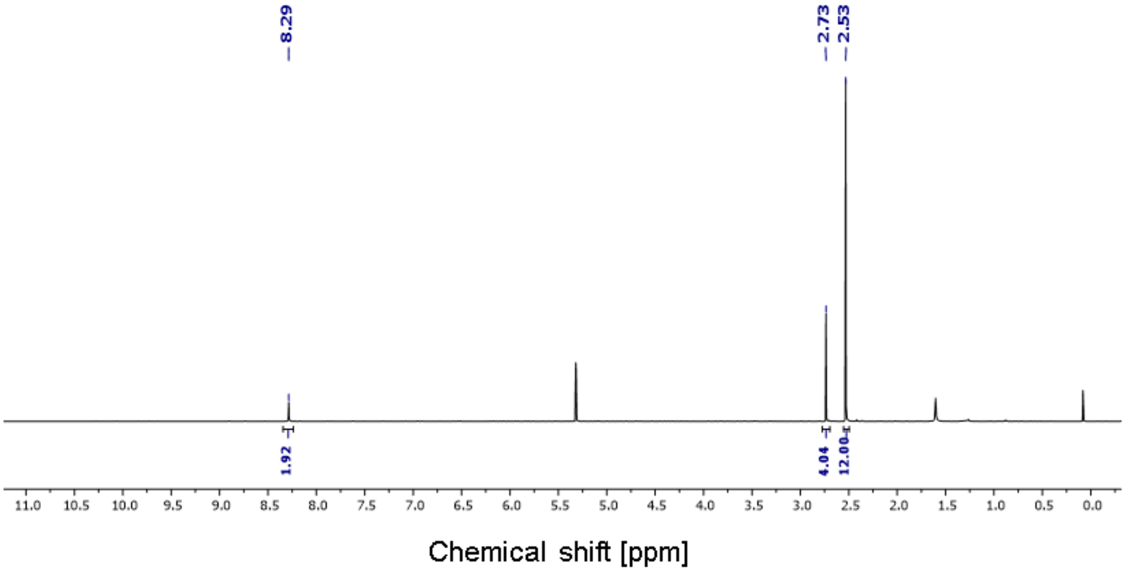


Figure S79: ^{1}H NMR spectrum of [(TMEDA)Zn(OCHO)$_2$] (**7a**) in CD_2Cl_2.

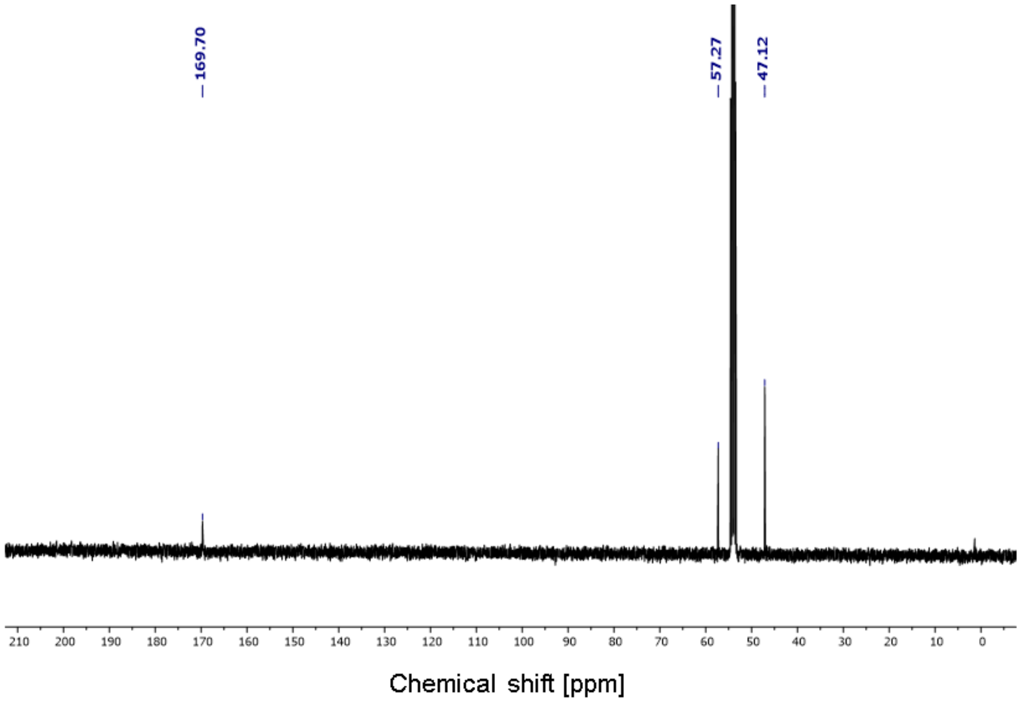


Figure S80: ^{13}C{^{1}H} NMR spectrum of [(TMEDA)Zn(OCHO)$_2$] (**7a**) in CD_2Cl_2.

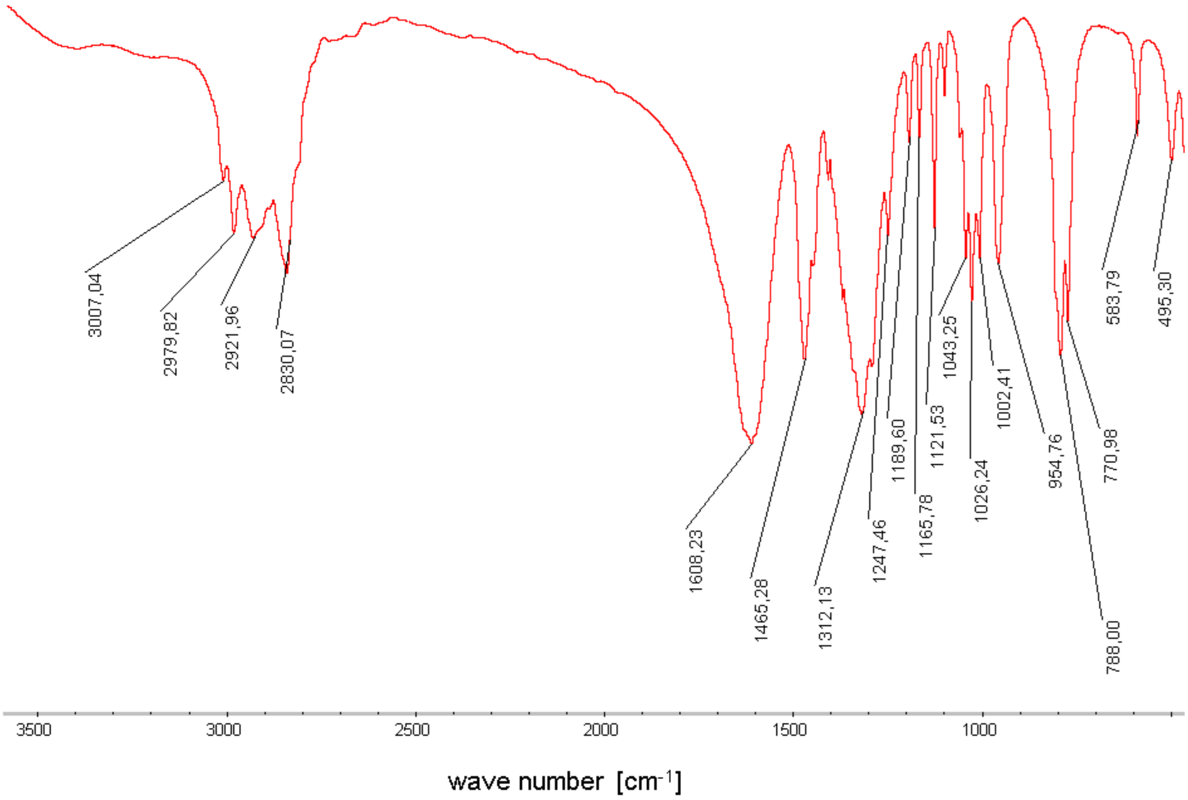
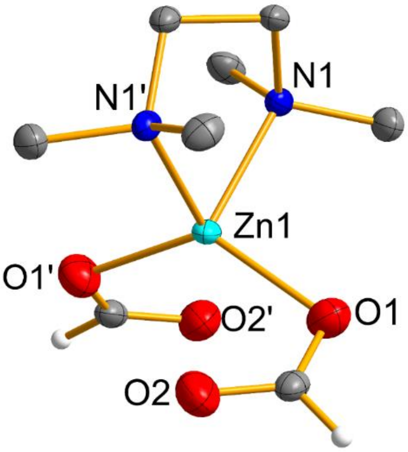


Figure S81: IR spectrum (KBr pellet) of [(TMEDA)Zn(OCHO)$_2$] (**7a**).



Molecular structure of **7a**. Displacement parameters atoms are set at 50% probability level. The hydrogen atoms except of the formate hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Zn1-O1 1.986(3), Zn1-N1 2.101(4), N1-Zn1-O1 102.89(14), N1'-Zn1-O1 113.13(15).[S5]

Synthesis of [(TEEDA)Zn(OCHO)$_2$] (7b).

A solution of [(TEEDA)$_3$Zn$_3$H$_4$][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$]$_2$ (200 mg, 82 µmol) in THF (1 mL) was transferred into a Schlenk tube, degassed by three cycles of "freeze-pump-thaw" and pressurized with CO_2 (1 bar). The solvent was removed in vacuo and the residue was extracted with diethyl ether (3 x 3 mL) to separate the title compound $[(TEEDA)Zn(OCHO)]_2[B(3,5\text{-}(CF_3)_2\text{-}C_6H_3)_4]_2$ from **5b**. . The combined ethereal extracts were filtered and the solvent removed in vacuo. Repeated recrystallization and drying under reduced pressure gave $[(TEEDA)_2Zn(OCHO)_2]$ as colorless solid (12 mg, 68 µmol). Yield: 83 % (based on the maximum theoretical yield).

Method B: A suspension of $[ZnH_2]_n$ (20 mg, 296 µmol) and TEEDA (51 mg, 296 µmol) in CH_2CH_2 (2 mL) was transferred into a Schlenk tube equippded with a stir bar, degassed by three cycles of “freeze-pump-thaw” and pressurized with CO_2 (1 bar). The suspension was stirred at rommtemperature until all solid material had dissolved (approximately 20 min). The solvent was removed *in vacuo* to give $[(TEEDA)Zn(OCHO)_2]$ as a colorless solid (94 mg, 287 µmol). Yield: 98 %.

^1H NMR (400 MHz, CD_2Cl_2): δ = 1.08 (t, $^3J_{H\text{-}H}$ = 7.1 Hz, N-$CH_2C\mathit{H}_3$, 12H), 2.79 (m, N-$C\mathit{H}_2CH_3$, 4H), 2.87 (s, N-$C\mathit{H}_2$, 4H), 3.17 (m, N-$C\mathit{H}_2CH_3$, 4H), 8.31 (s, Zn-OC*H*O, 2H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ = 8.78 (N-$CH_2\mathit{C}H_3$), 46.18 (N-$\mathit{C}H_2CH_3$), 51.02 (N-$\mathit{C}H_2\mathit{C}H_2$), 168.48 (Zn-O*C*HO) ppm.

IR (KBr): ν = 1633 cm^{-1} (s, ZnOCHO).

Anal. Calcd. for $C_{12}H_{26}N_2O_4Zn$ (327.73 g · mol^{-1}): C, 43.98; H, 8.00; N 8.55. Found: C, 42.84; H, 7.68; N, 8.60%.

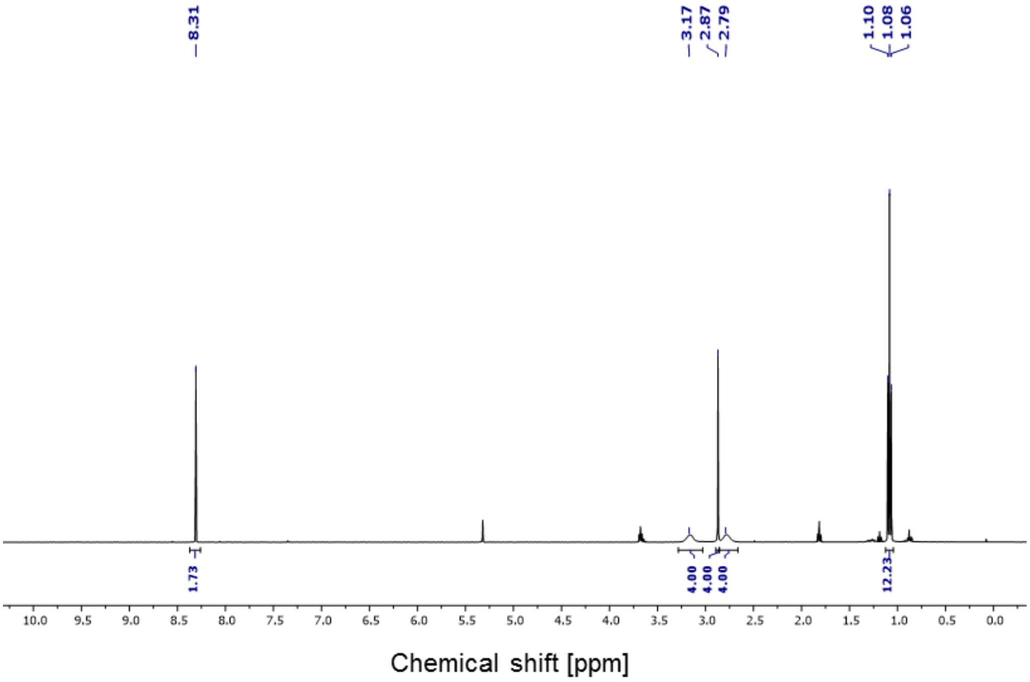


Figure S82: ^1H NMR spectrum of $[(TEEDA)Zn(OCHO)_2]$ (**7b**) in CD_2Cl_2.

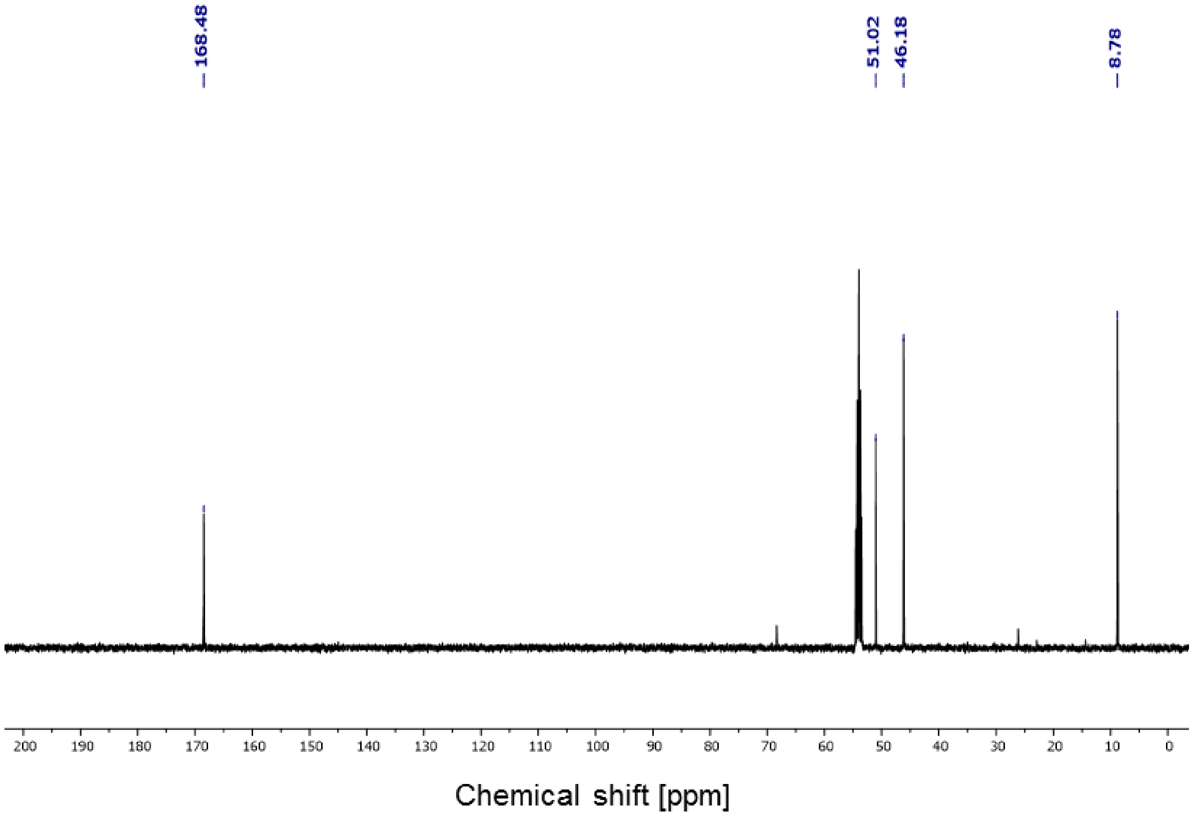


Figure S83: $^{13}C\{^{1}H\}$ NMR spectrum of [(TEEDA)Zn(OCHO)$_2$] (**7b**) in CD_2Cl_2.

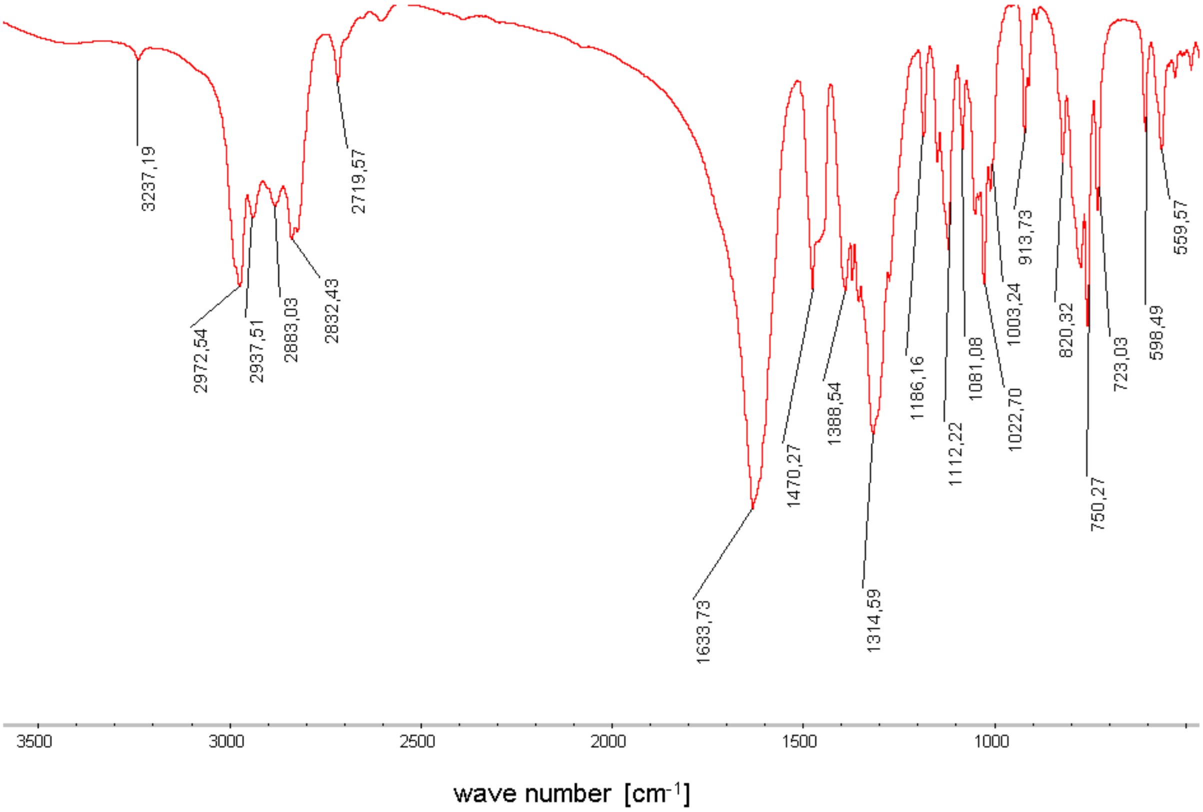


Figure S84: IR spectrum (KBr pellet) of [(TEEDA)Zn(OCHO)$_2$] (**7b**).

Synthesis of silanes

Synthesis of ^{n}BuMe$_2$SiH[S6]

To a suspension of LiAlH$_4$ (302 mg, 7,9 mmol) tetraglyme was added dropwise ^{n}BuMe$_2$SiCl (1000 mg, 6.6 mmol) and stirred over night at roomtemperature. The title compound was distilled directly from the reaction mixture under reduced preassure as a colorless liquid. Yield: 740 mg, 6.4 mmol, 96%.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.06 (d, $J_{\text{H-H}}$ = 3.7 Hz, 6H, Si-CH_3), 0.44 – 0.63 (m, 2H, Si-CH_2CH$_2$CH$_2$CH$_3$), 0.89 (t, $J_{\text{H-H}}$ = 7.0 Hz, 3H, Si-CH$_2$CH$_2$CH$_2$CH_3), 1.18 – 1.44 (m, 6H, Si-CH2CH_2CH_2CH$_3$), 3.84 (hept, J = 3.6 Hz, 1H, Si-*H*) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = -4.28 (Si-*C*H$_3$), 13.96 (Si-CH_2CH$_2$CH$_2$CH$_3$), 14.02 (Si-CH$_2$CH$_2$CH$_2$CH_3), 26.33(Si-CH2CH_2CH_2CH$_3$), 26.75 (Si-CH2CH_2CH_2CH$_3$) ppm.

^{29}Si{^{1}H} (DEPT 45) NMR (79 MHz, CDCl$_3$): δ = -13.06 ppm.

^{29}Si{^{1}H} (inverse gated) NMR (79 MHz, CDCl$_3$): δ = -13.06 ppm.

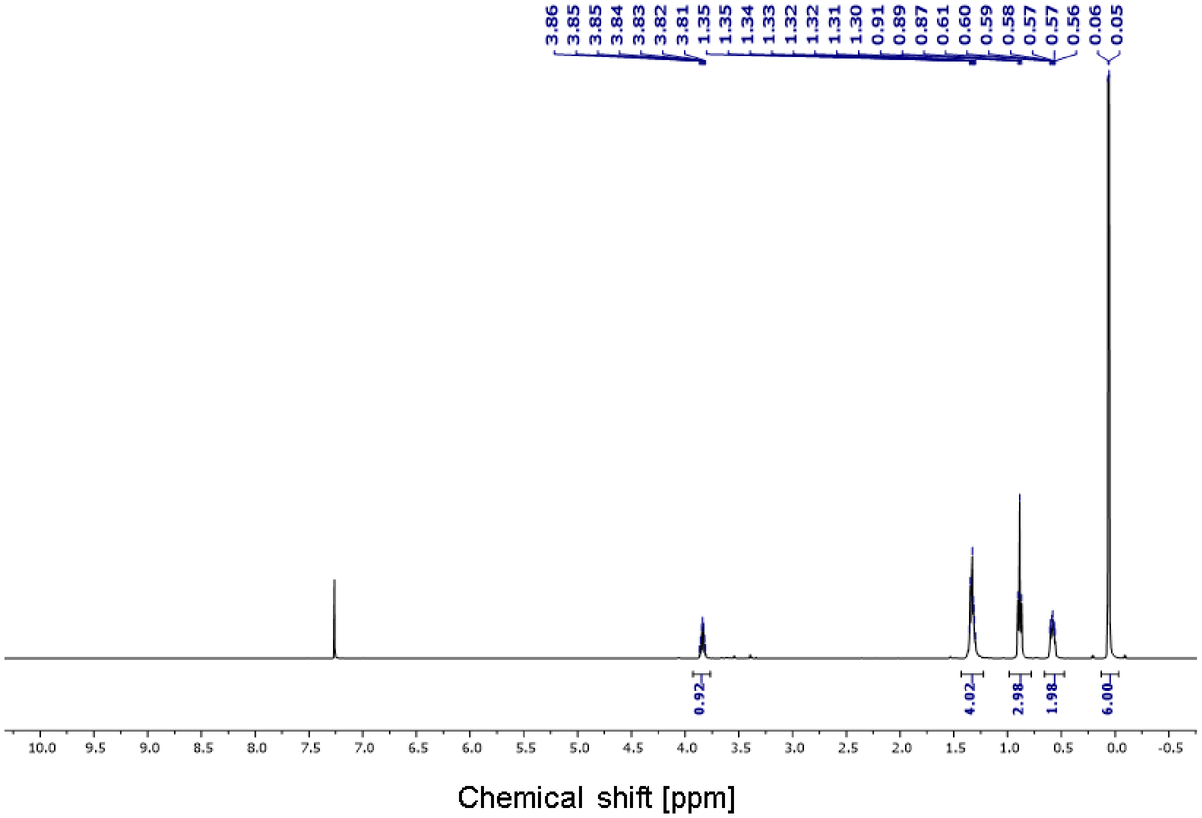


Figure S85: ^{1}H NMR spectrum of ^{n}BuMe$_2$SiH in CDCl$_3$.

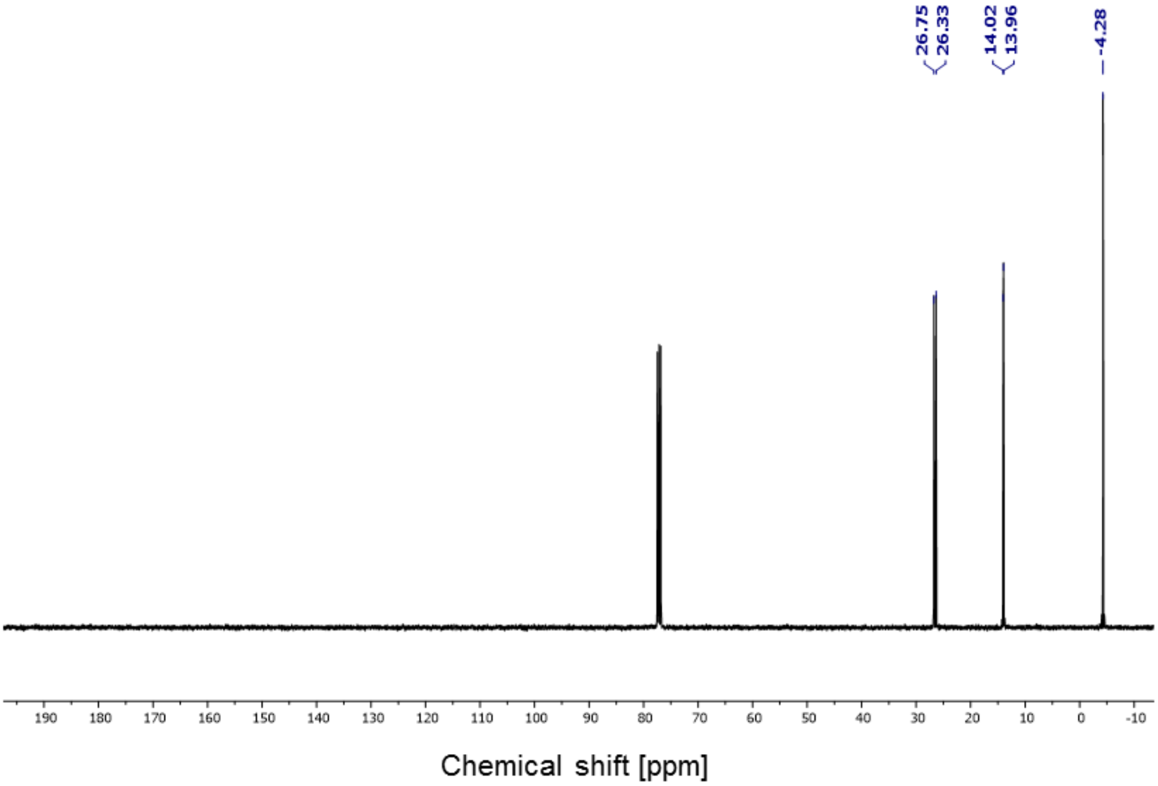


Figure S86: $^{13}C\{^{1}H\}$ NMR spectrum of ${}^{n}BuMe_2SiH$ in $CDCl_3$.

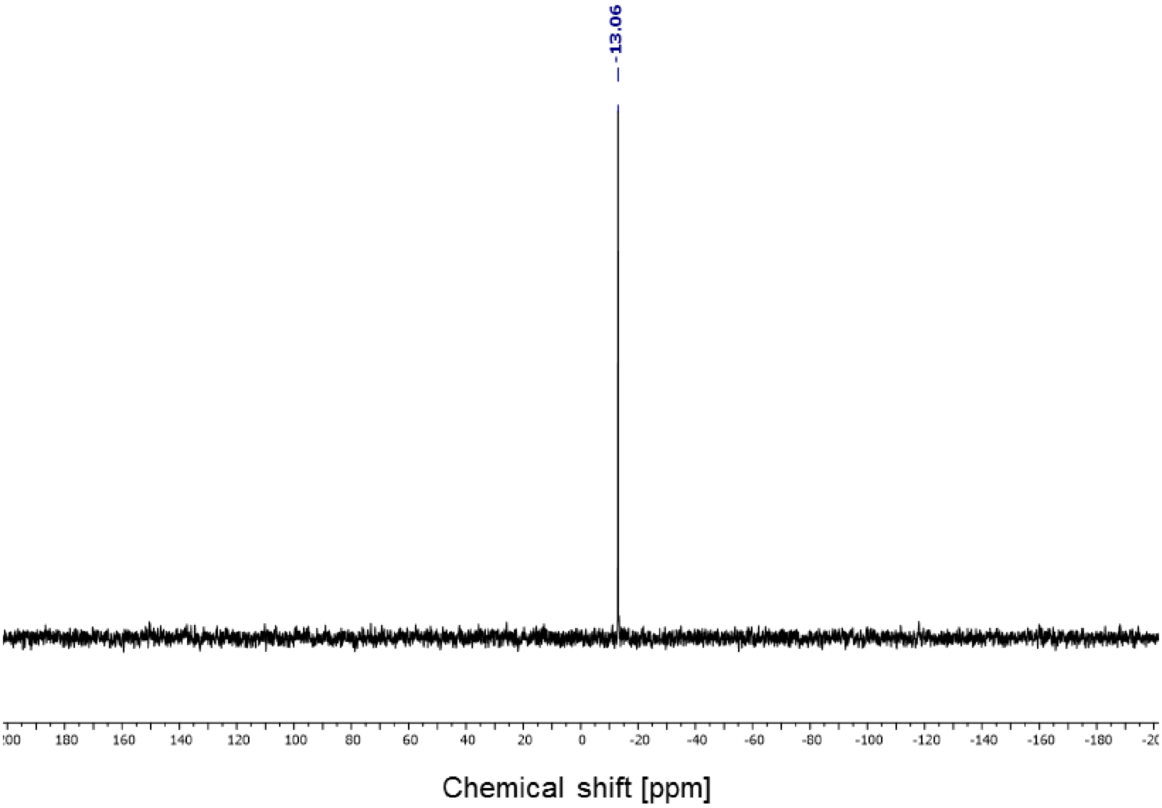


Figure S87: $^{29}Si\{^{1}H\}$ NMR spectrum (DEPT 45) of ${}^{n}BuMe_2SiH$ in $CDCl_3$.

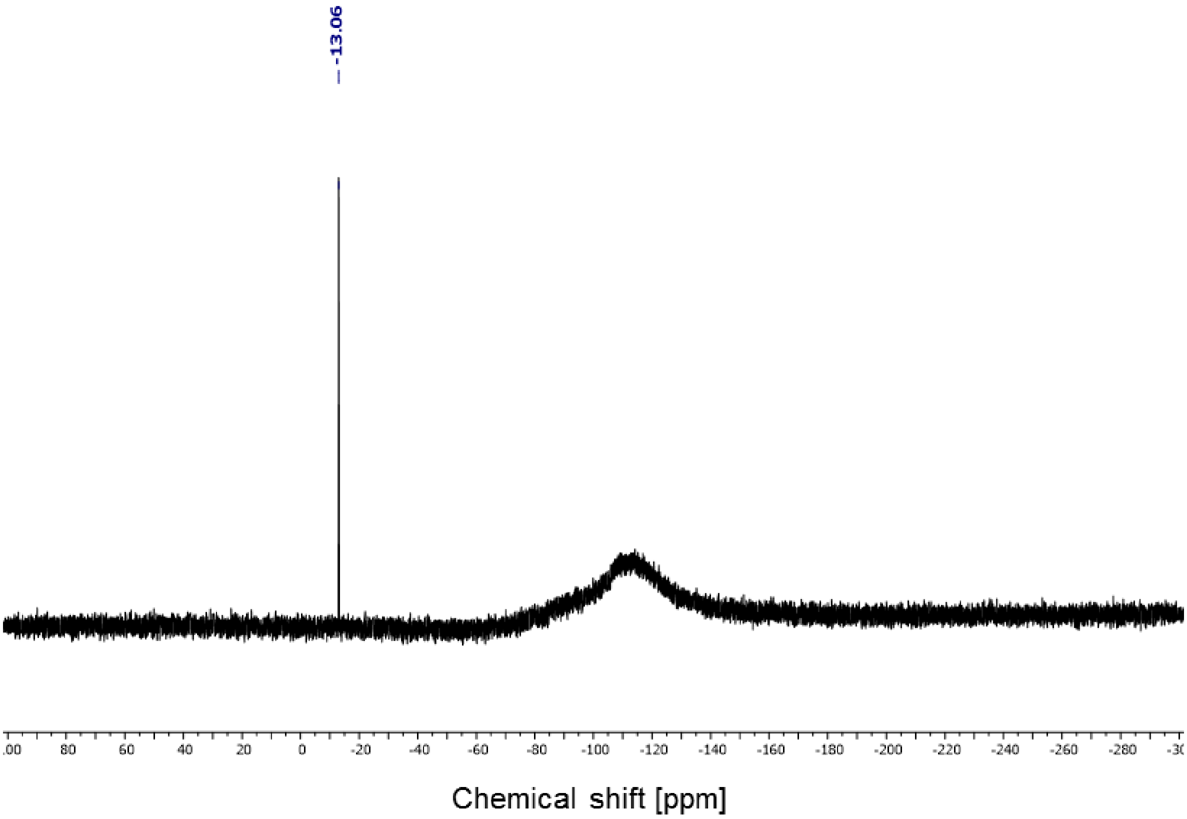


Figure S88: ^{29}Si{^{1}H} NMR spectrum (inverse gated) of ^{n}BuMe$_2$SiH in CDCl$_3$.

Synthesis of ^{n}BuMe$_2$Si(OCHO)[S7]

To Na(OCHO) (541 mg, 7.9 mmol) in tetraglyme was added ^{n}BuMe$_2$SiCl (1000 mg, 6.6 mmol) and reaction mixture was stirred for 48 h at 90°C. The title compound was distilled direct from the reaction mixture as a colorless liquid. Yield: 999 mg, 6.2 mmol, 94%.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.30 (s, 6H, Si-C*H*$_3$), 0.74 – 0.82 (m, 2H, Si-C*H*$_2$CH$_2$CH$_2$CH$_3$), 0.85 – 0.95 (m, 3H), 1.28 – 1.42 (m, 4H, Si-CH$_2$CH$_2$CH$_2$C*H*$_3$), 8.08 (s, 1H, Si-OC*H*O) ppm.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = -1.64 (Si-*C*H$_3$), 13.83 (Si-C*H*$_2$CH$_2$CH$_2$CH$_3$), 15.82 (Si-CH$_2$CH$_2$CH$_2$C*H*$_3$), 25.01 (Si-CH2C*H*$_2$C*H*$_2$CH$_3$), 26.25 (Si-CH2C*H*$_2$C*H*$_2$CH$_3$), 161.19 (Si-O*C*HO) ppm.

^{29}Si{^{1}H} (DEPT 20) NMR (79 MHz, CDCl$_3$): δ = 26.19 ppm.

^{29}Si{^{1}H} (inverse gated) NMR (79 MHz, CDCl$_3$): δ = 26.19 ppm.

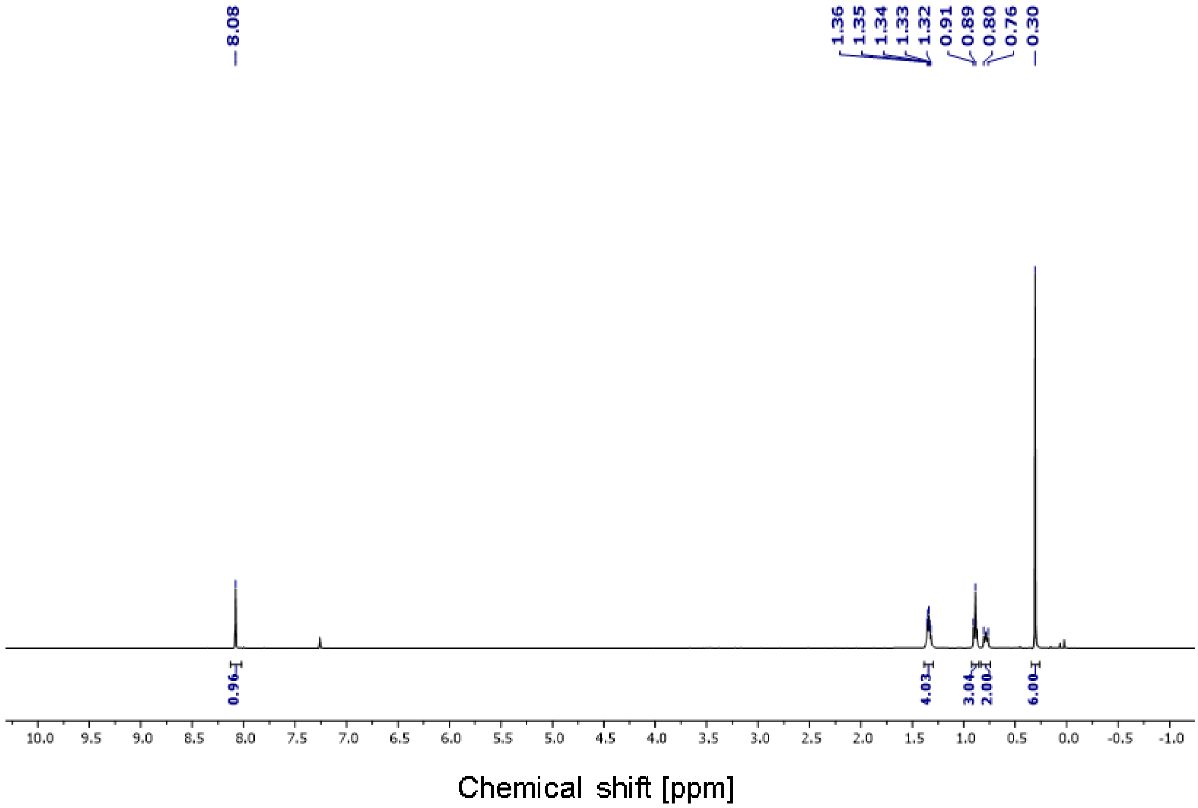


Figure S89: ^{1}H NMR spectrum of ^{n}BuMe$_2$Si(OCHO) in CDCl$_3$.

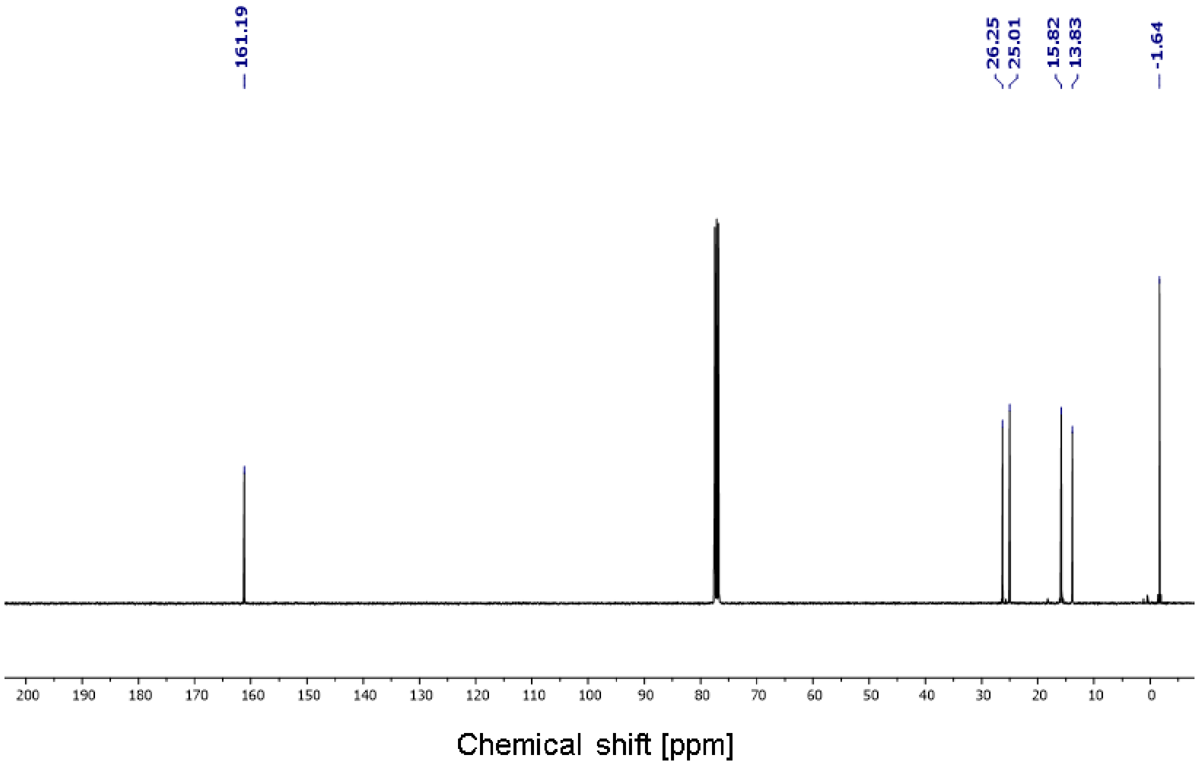


Figure S90: ^{13}C{^{1}H} NMR spectrum of ^{n}BuMe$_2$Si(OCHO) in CDCl$_3$.

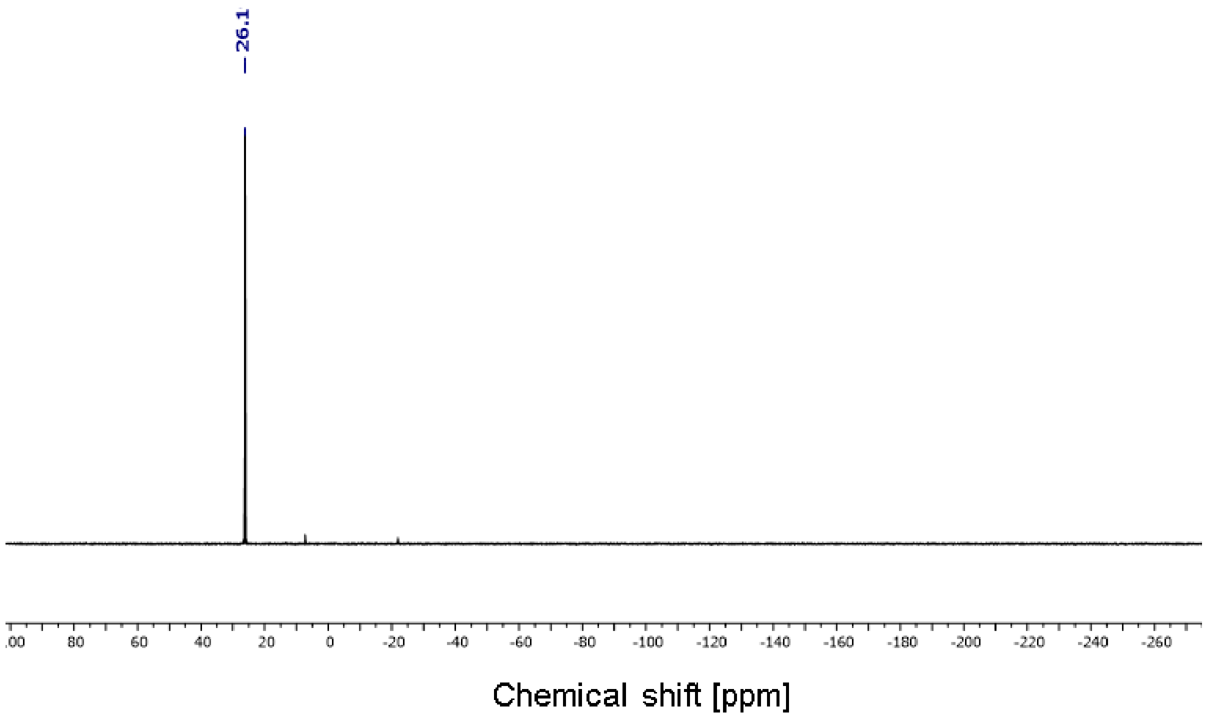


Figure S91: $^{29}Si\{^{1}H\}$ NMR spectrum (DEPT 20) of $^{n}BuMe_2Si(OCHO)$ in $CDCl_3$.

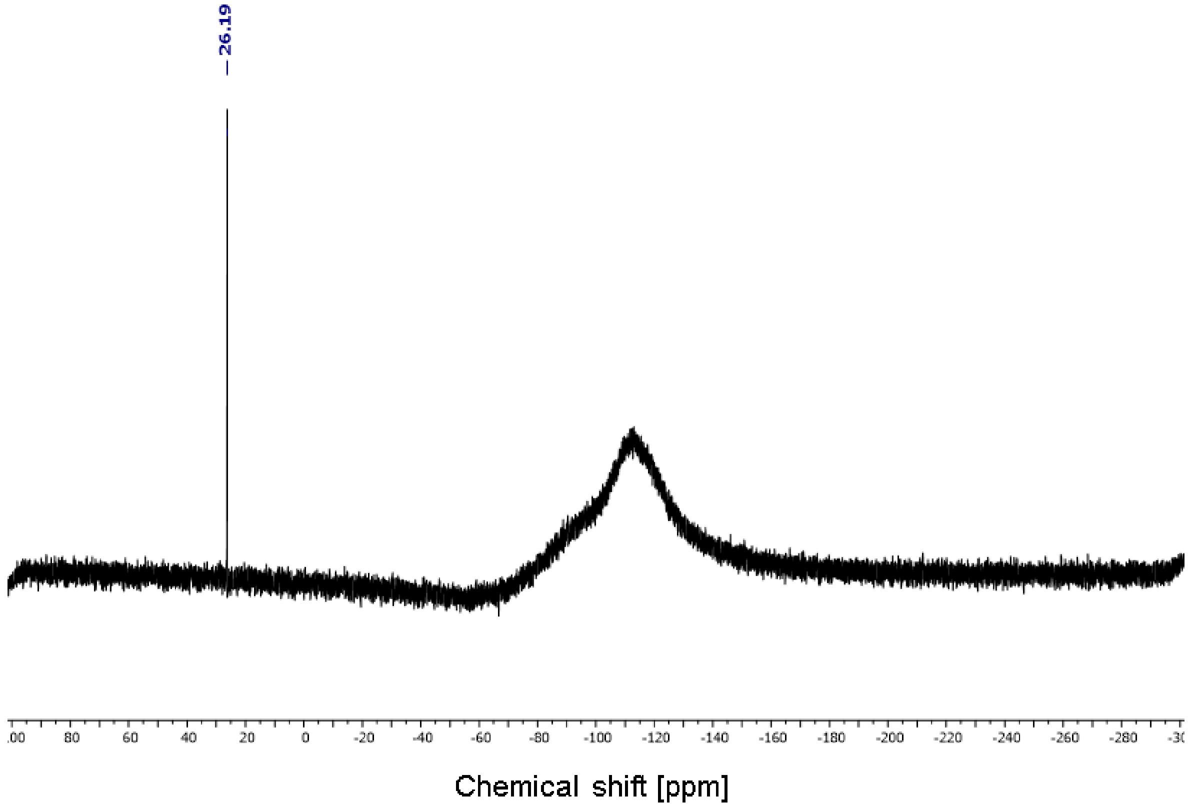


Figure S92: $^{29}Si\{^{1}H\}$ NMR spectrum (inverse gated) of $^{n}BuMe_2Si(OCHO)$ in $CDCl_3$.

Synthesis of $^{n}\mathrm{BuMe_2Si(OCH_3)}$[S8]

To $\mathrm{NaOCH_3}$ (430 mg, 7.9 mmol) in tetraglyme was added dropwise $^{n}\mathrm{BuMe_2SiCl}$ (1000 mg, 6.6 mmol) and stirred for 48 h at 80°C. The title compound was direct destilled from the reaction mixture as a colorless liquid. Yield: 912 mg, 6.2 mmol, 94%.

^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 0.09 (s, 6H, $\mathrm{Si{-}C}H_3$), 0.54 – 0.65 (m, 2H, $\mathrm{Si{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 0.83 – 0.95 (m, 3H, $\mathrm{Si{-}CH_2CH_2CH_2C}H_3$), 1.23 – 1.43 (m, 4H, $\mathrm{Si{-}CH2C}H_2\mathrm{C}H_2\mathrm{CH_3}$), 3.42 (s, 3H, $\mathrm{Si{-}OC}H_3$) ppm.

^{13}C{^{1}H} NMR (101 MHz, $\mathrm{CDCl_3}$): δ = -2.54 ($\mathrm{Si{-}}C\mathrm{H_3}$), 13.93 ($\mathrm{Si{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 15.73 ($\mathrm{Si{-}CH_2CH_2CH_2}C\mathrm{H_3}$), 25.50 ($\mathrm{Si{-}CH_2}C\mathrm{H_2CH_2CH_3}$), 26.54 ($\mathrm{Si{-}CH_2CH_2}C\mathrm{H_2CH_3}$), 50.41 ($\mathrm{Si{-}O}C\mathrm{H_3}$) ppm.

^{29}Si{^{1}H} (DEPT 20) NMR (79 MHz, $\mathrm{CDCl_3}$): δ = 19.79 ppm.

^{29}Si{^{1}H} (inverse gated) NMR (79 MHz, $\mathrm{CDCl_3}$): δ = 19.80 ppm.

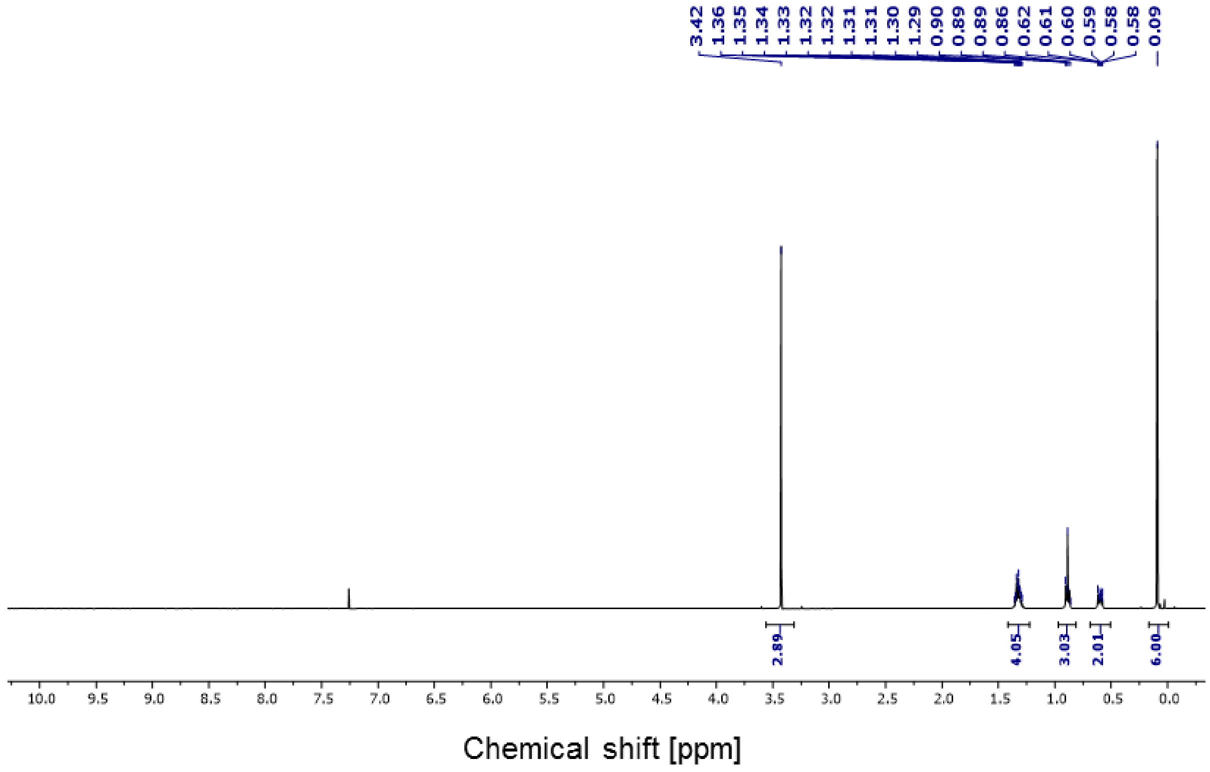


Figure S93: ^{1}H NMR spectrum of $^{n}\mathrm{BuMe_2Si(OCH_3)}$ in $\mathrm{CDCl_3}$.

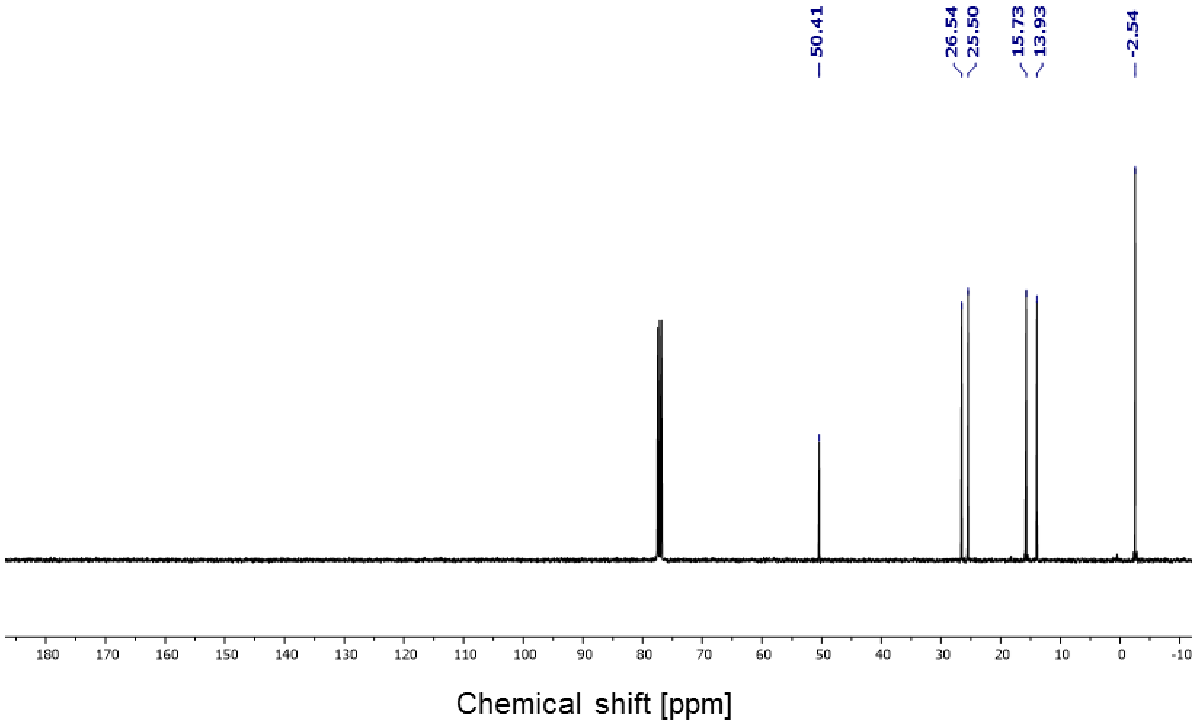


Figure S94: $^{13}C\{^{1}H\}$ NMR spectrum of $^{n}BuMe_2Si(OCH_3)$ in $CDCl_3$.

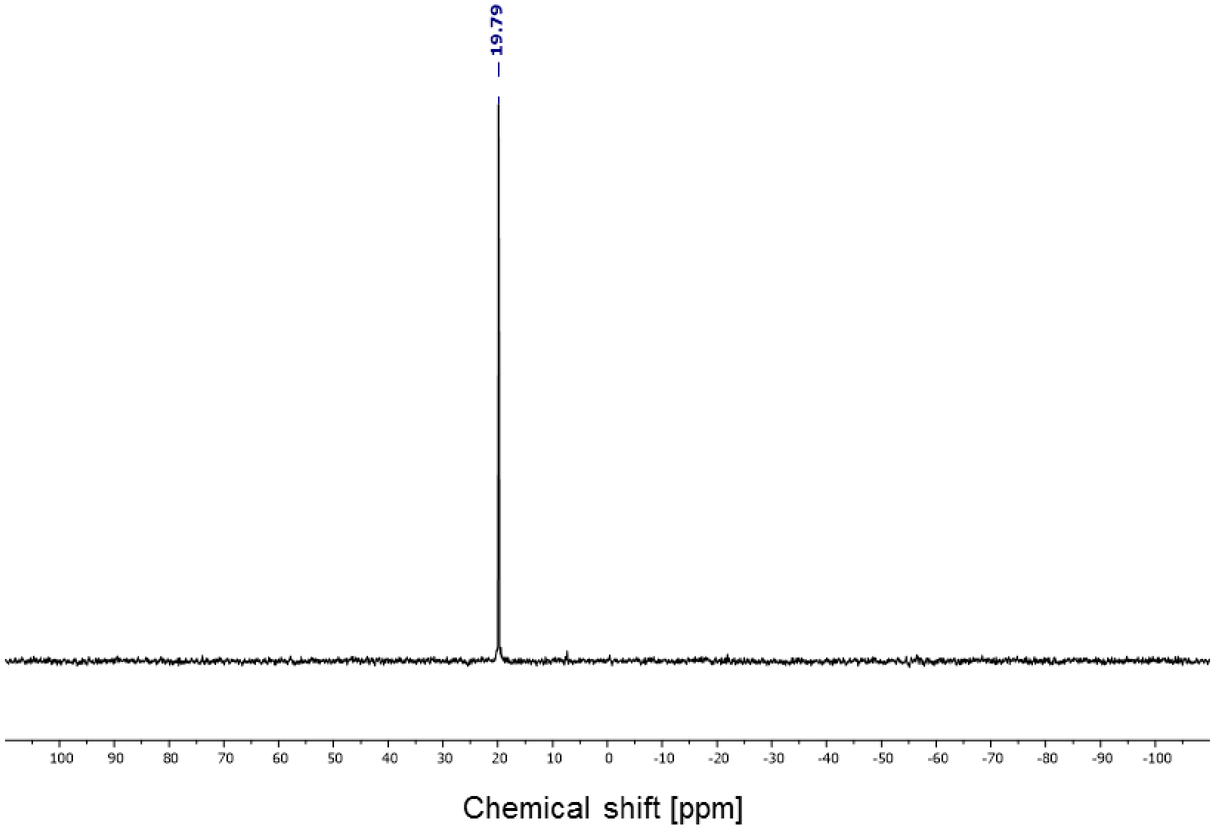


Figure S95: $^{29}Si\{^{1}H\}$ NMR spectrum (DEPT20) of $^{n}BuMe_2Si(OCH_3)$ in $CDCl_3$.

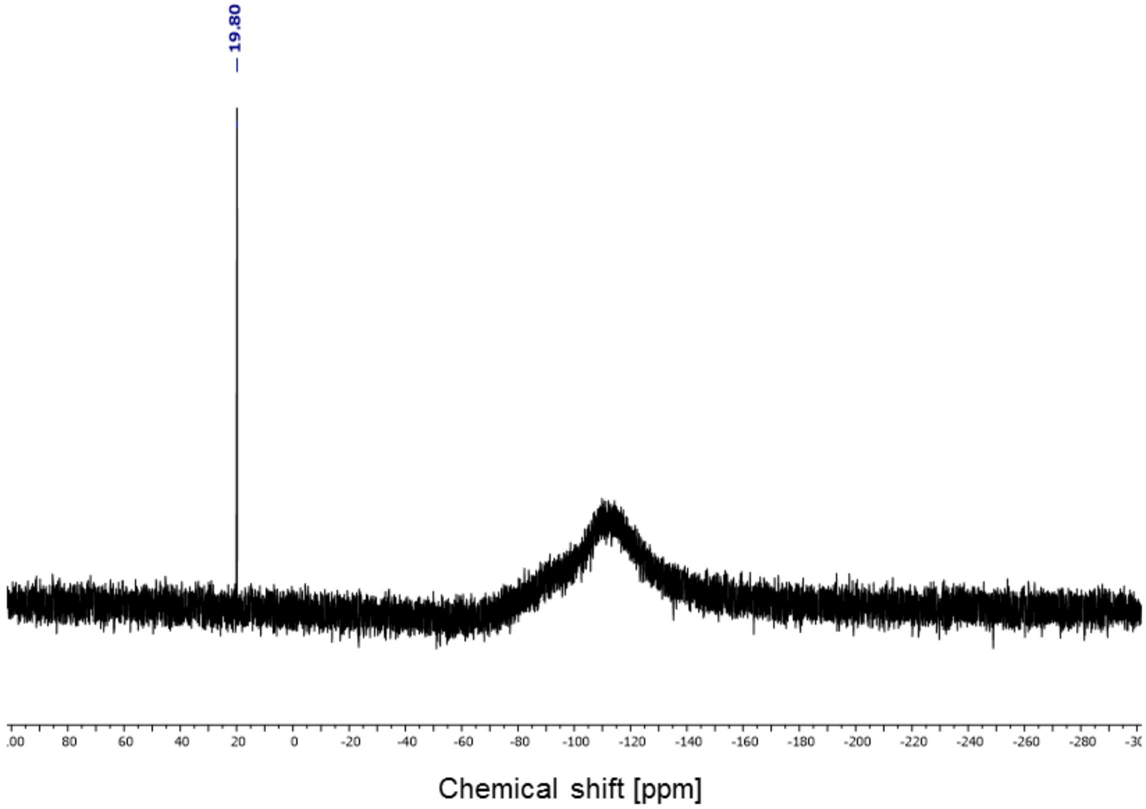


Figure S96: ^{29}Si{^{1}H} NMR spectrum (inverse gated) of ^{n}BuMe$_2$Si(OCH$_3$) in CDCl$_3$.

Catalysis of CO_2 Hydrosilylation

Typical procedure for CO_2 hydrosilylation

In a glovebox, a J. Young-style NMR tube was charged with hydrosilane (0.18 mmol) and hexamethylbenzene (0.06 mmol). 0.5 mL of a catalyst stock solution in [D8]THF was added. The mixture was degassed by three cycles of "freeze-pump-thaw" and pressurized with 1 bar of CO_2. The reaction progress was monitored by NMR spectroscopy. Selected spectra of the catalytic reaction mixture are provided below.

Typical procedure for twostep CO_2 hydrosilylation

In a glovebox, a J. Young-style NMR tube was charged with silane (0.18 mmol) and hexamethylbenzene (0.06 mmol). 0.5 mL of a catalyst stock solution in [D8]THF was added. The mixture was degassed by three cycles of "freeze-pump-thaw" and pressurized with 1 bar of CO_2. When hydrosilane was consumed CO_2 was removed by three cycles of "freeze-pump-thaw" and the reaction mixture charged with silane. The reaction progress was monitored by NMR spectroscopy. Selected spectra of the catalytic reaction mixture are provided below.

Catalytic hydrosilylation using $^{n}BuMe_2SiH$:

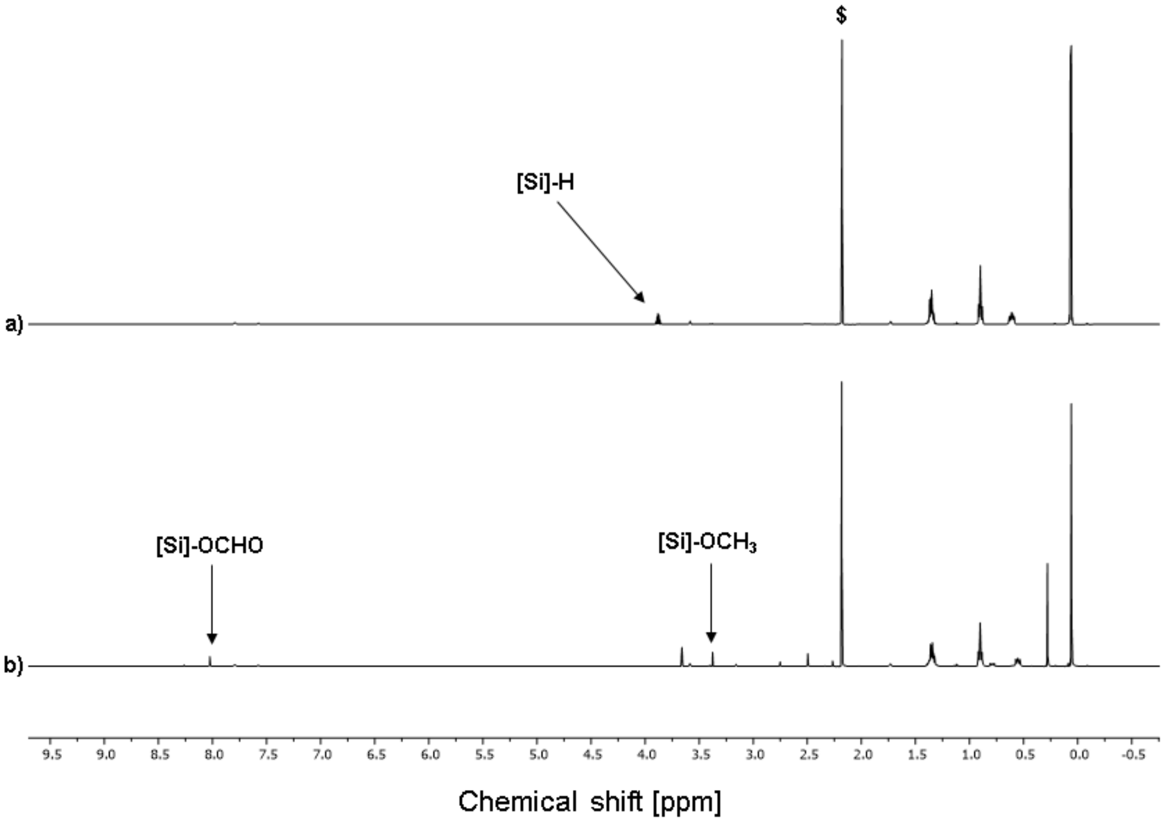


Figure S97: ^{1}H NMR spectra of the catalytic reaction mixture with $^{n}BuMe_2SiH$ ($: hexamethylbenzene as internal standard); a): at the start, b) after 6h.

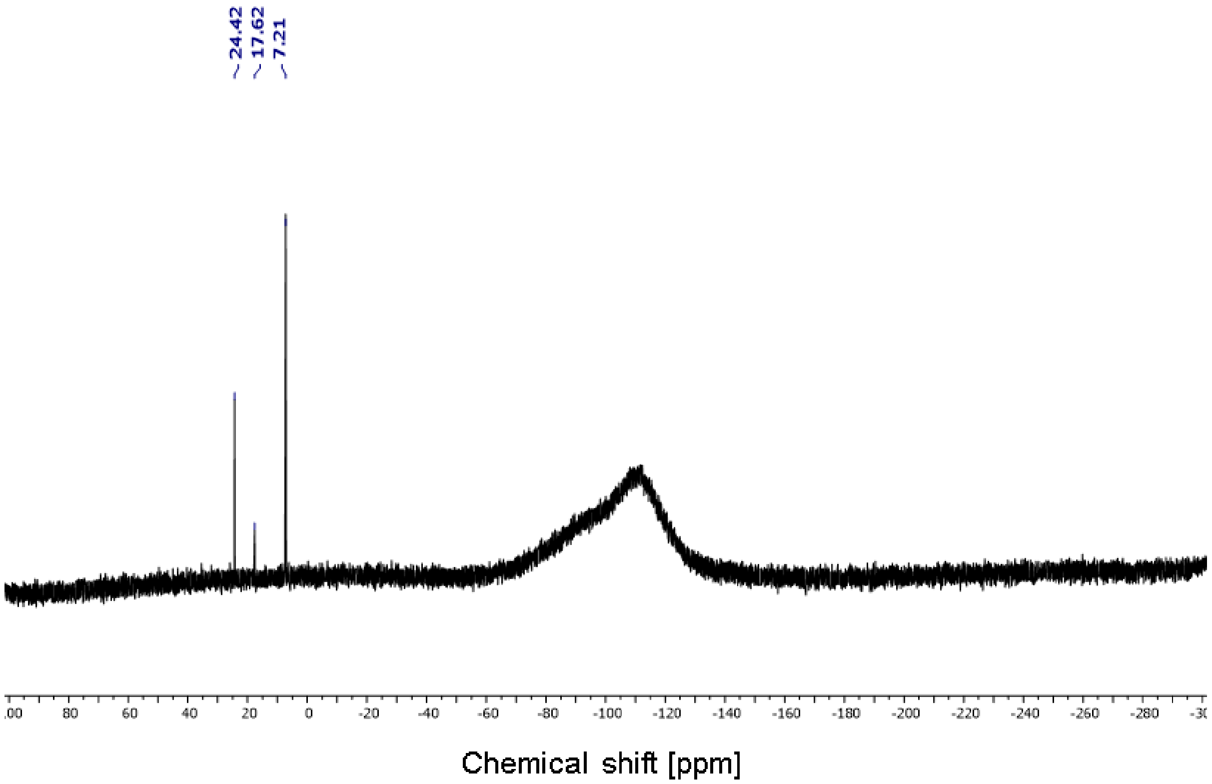


Figure S98: $^{29}Si\{^1H\}$ NMR spectrum (inverse gated) of the catalytic reaction mixture using $^nBuMe_2SiH$ after 6 h.

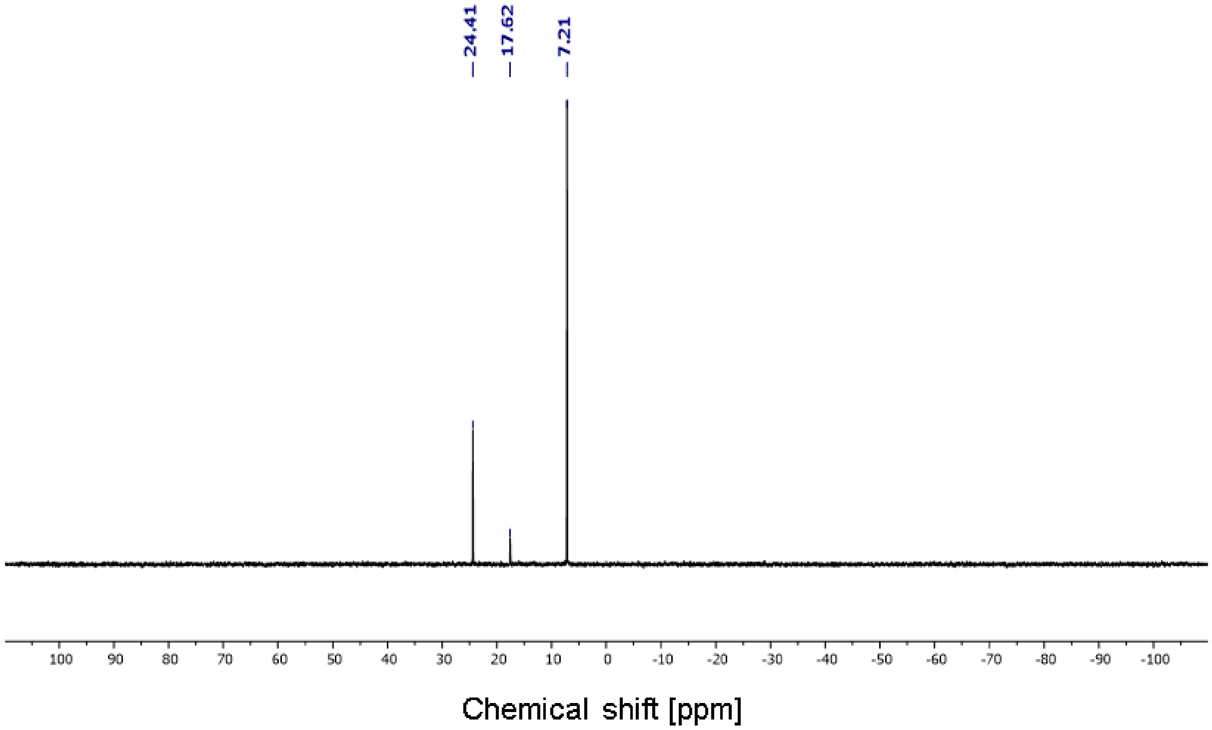


Figure S99: $^{29}Si\{^1H\}$ NMR spectrum (DEPT20) of the catalytic reaction mixture using $^nBuMe_2SiH$ after 6 h.

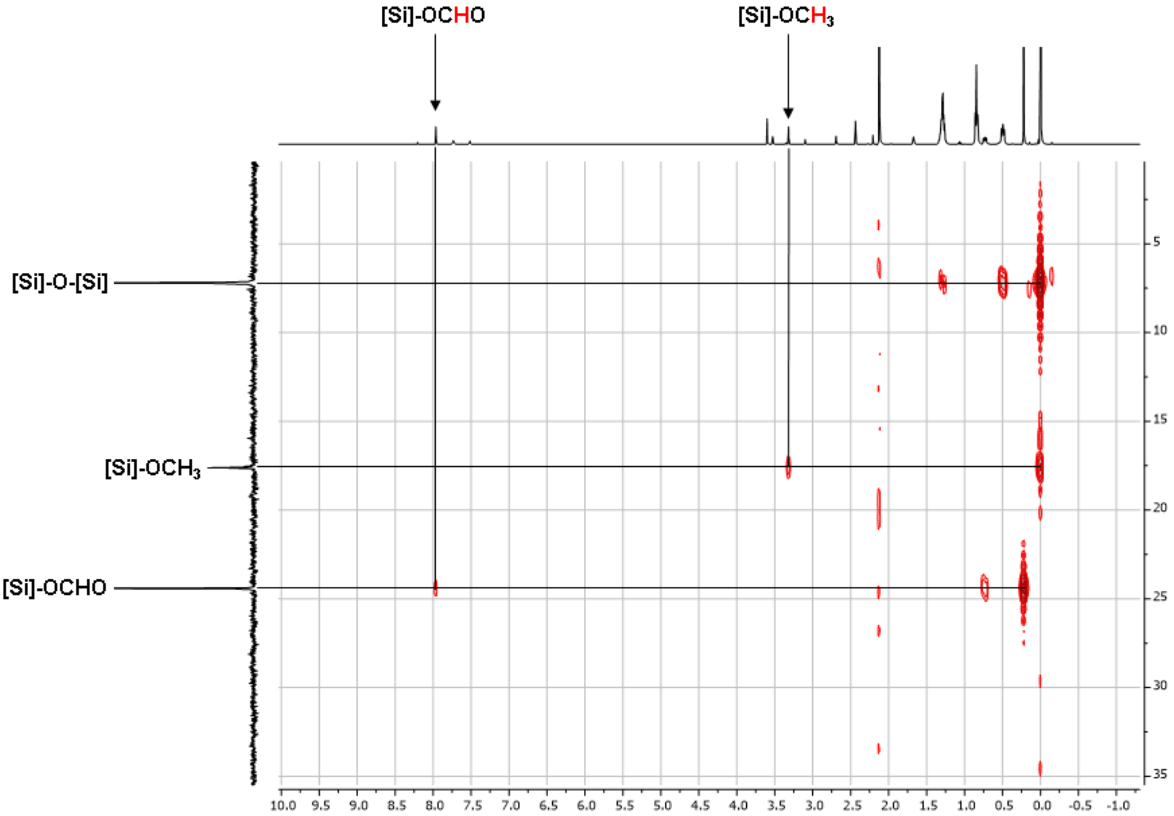


Figure S100: $^{29}Si^{1}H$ HMBC spectrum of the catalytic reaction mixture using $^{n}BuMe_2SiH$ after 6 h.

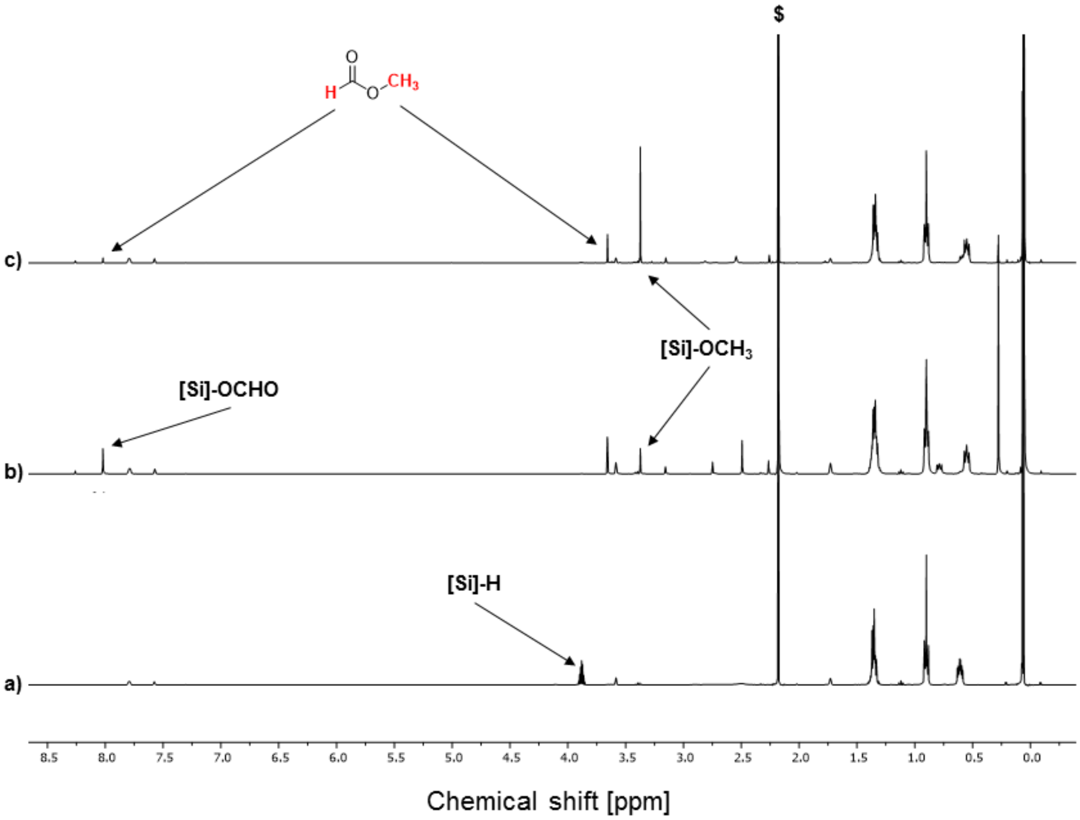


Figure S101: ^{1}H NMR spectra of the catalytic reaction mixture with $^{n}BuMe_2SiH$ ($: hexamethylbenzene as internal standard). a): Start of the reaction; b): after 6 h and full consumption of silane; c): 16 h and addition of 1 equiv. silane and catalyst.

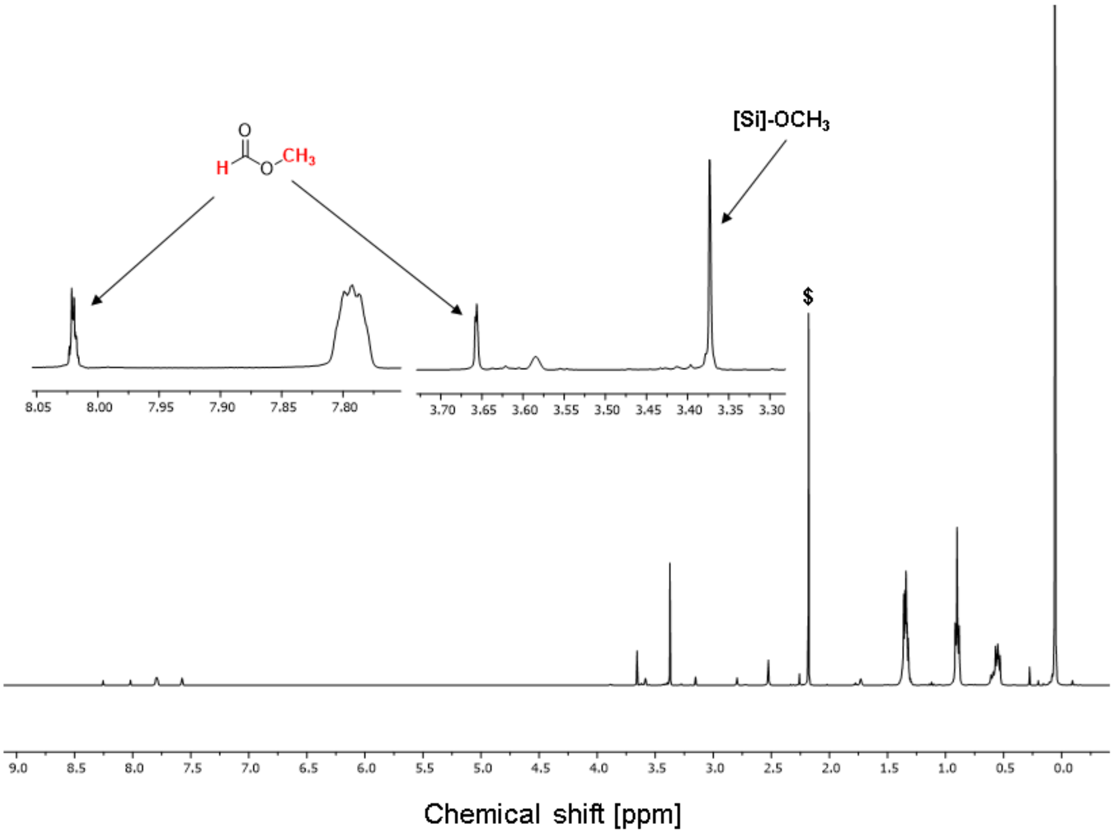


Figure S102: ^{1}H NMR spectrum after 16 h of the catalytic reaction mixture with $^{n}BuMe_2SiH$ ($: hexamethylbenzene as internal standard).

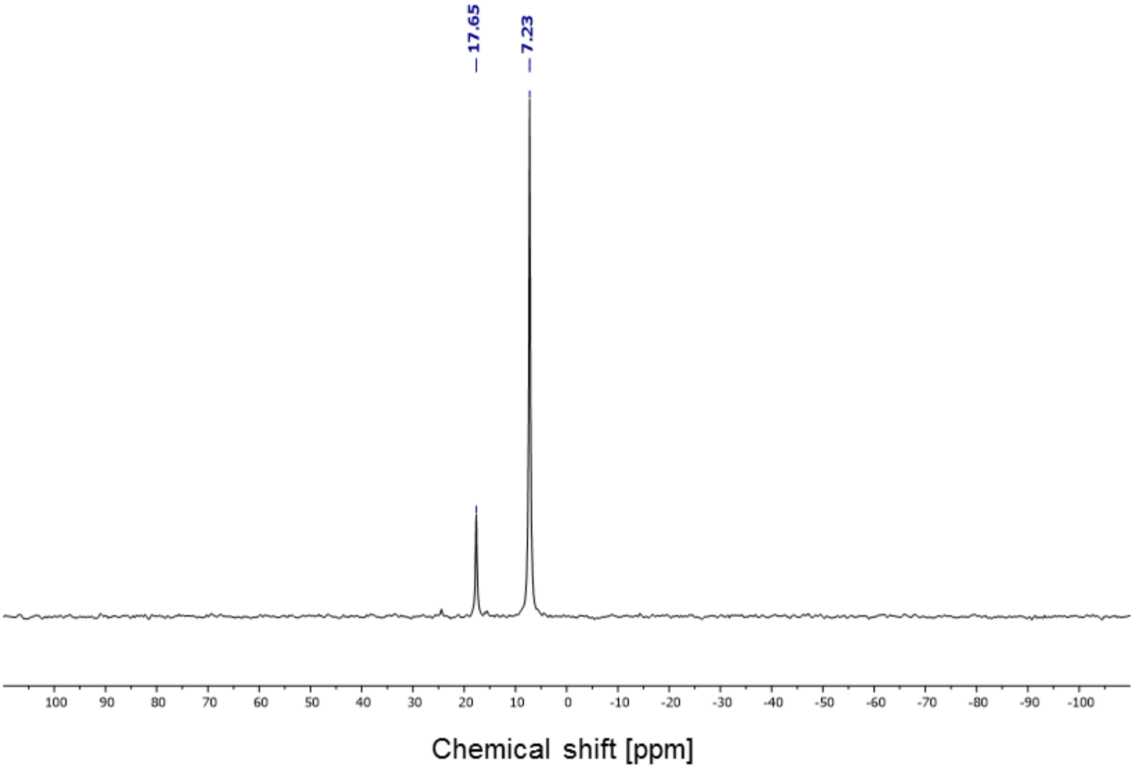


Figure S103: $^{29}Si\{^{1}H\}$ NMR spectrum (DEPT20) of the catalytic reaction mixture using $^{n}BuMe_2SiH$ after 16 h.

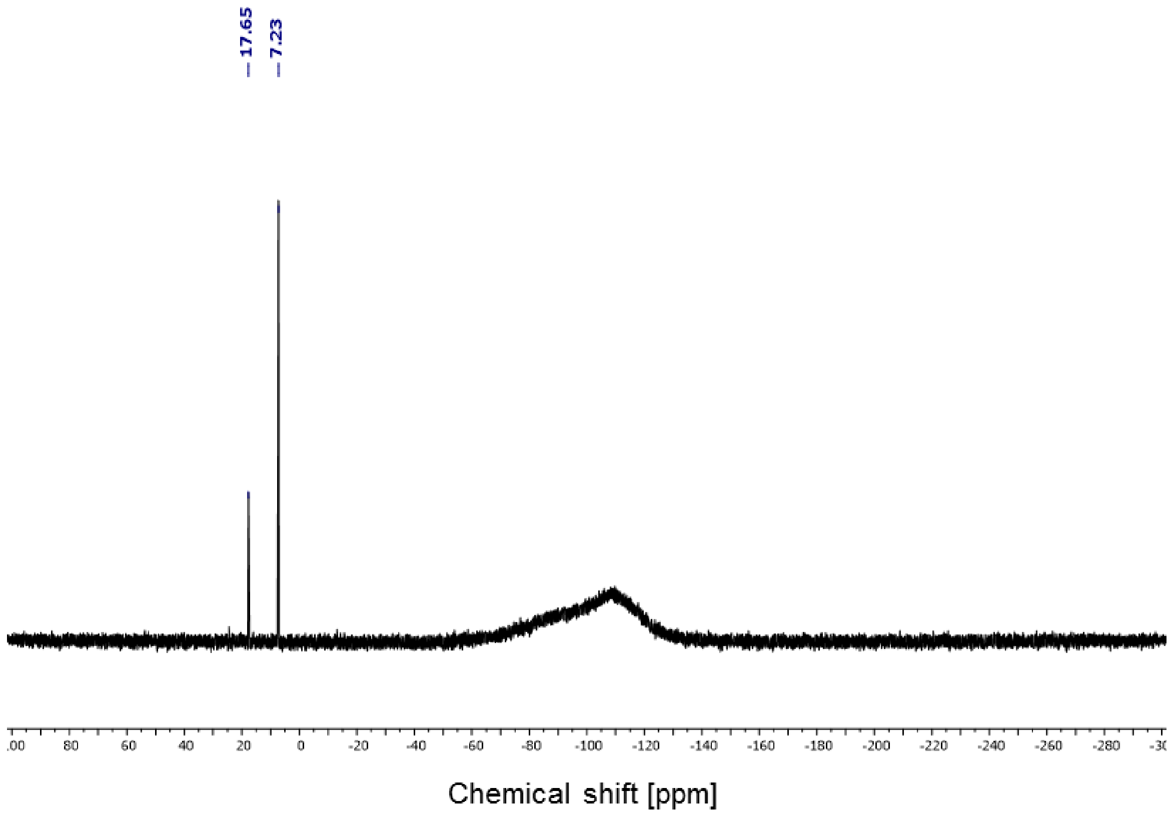


Figure S104: $^{29}Si\{^1H\}$ NMR spectrum (inverse gated) of the catalytic reaction mixture using $^nBuMe_2SiH$ after 16 h.

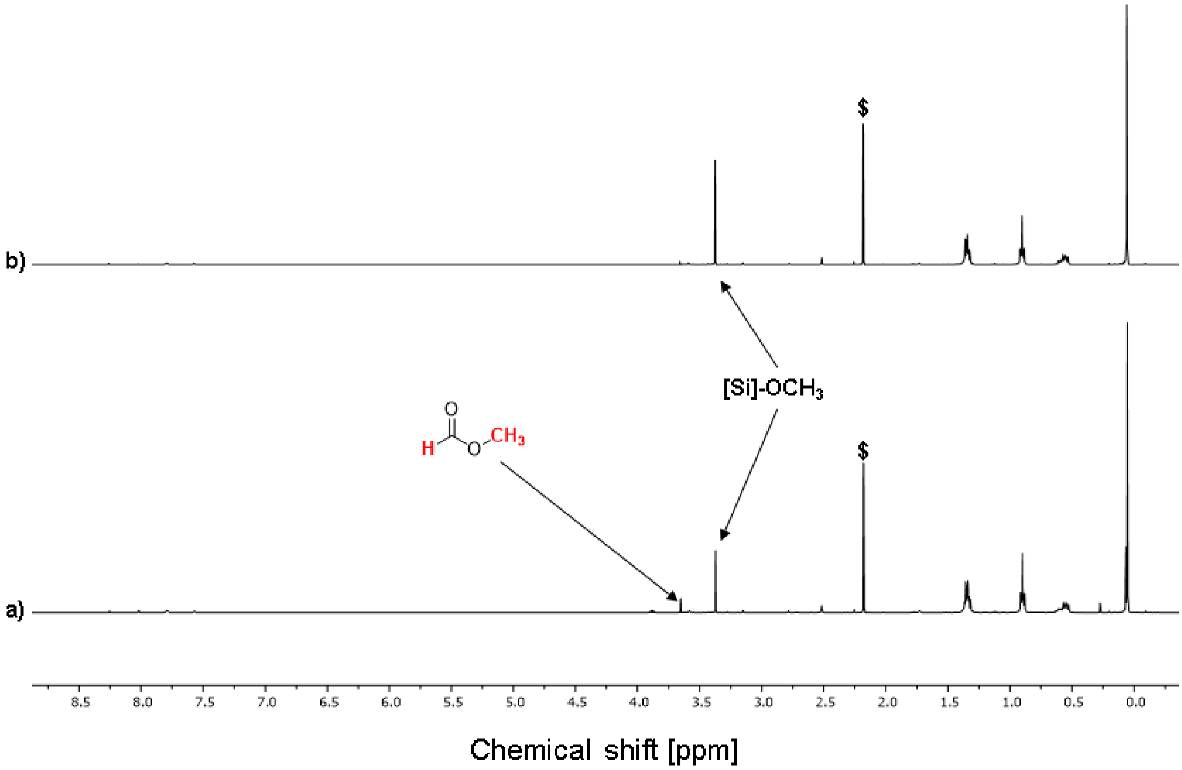


Figure S105: ^1H NMR spectra of the catalytic reaction mixture with $^nBuMe_2SiH$ ($: hexamethylbenzene as internal standard). a): reaction mixture after 16 h and added silane and catalyst; b): after 2 4h and excess silane (2 equiv.) and catalyst.

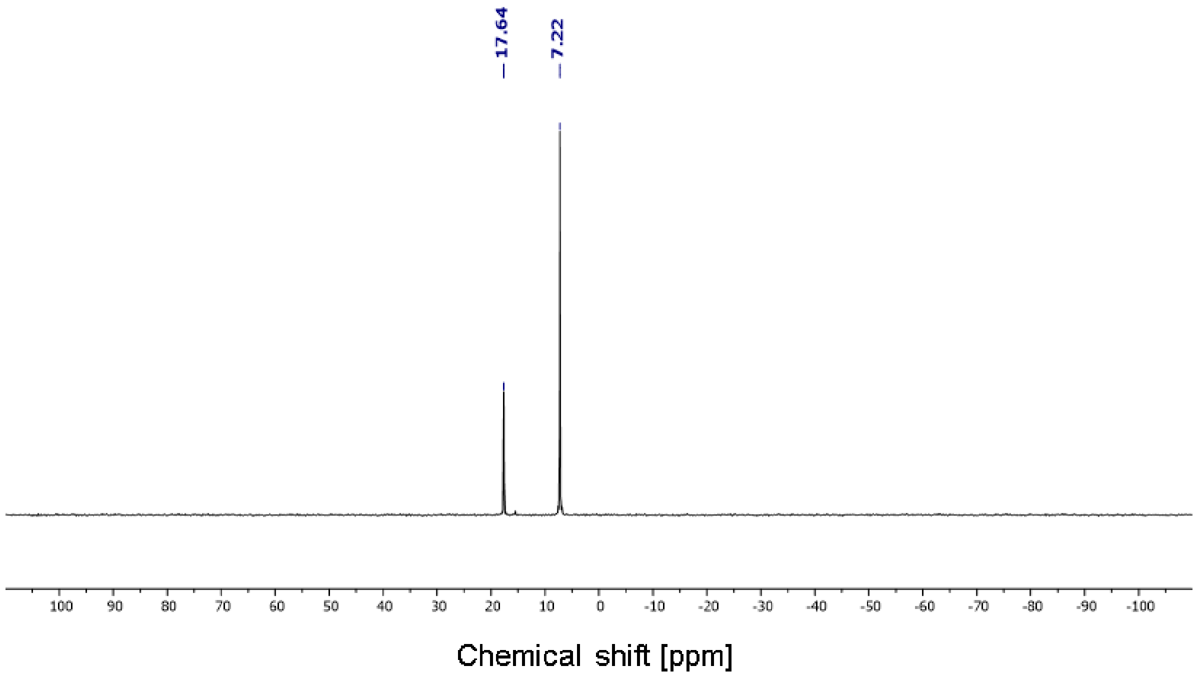


Figure S106: ^{29}Si{^{1}H} NMR spectrum (DEPT20) of the catalytic reaction mixture using ^{n}BuMe$_2$SiH after 24 h.

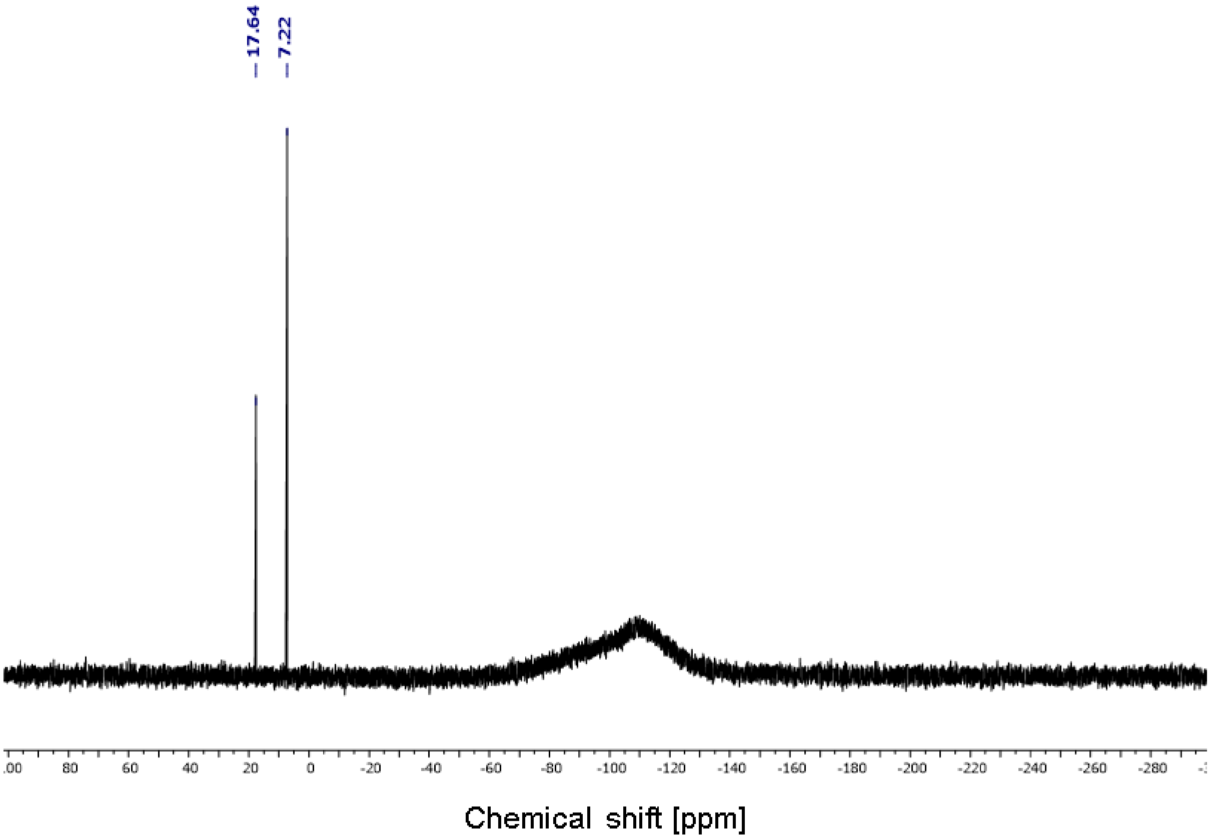


Figure S107: ^{29}Si{^{1}H} NMR spectrum (inverse gated) of the catalytic reaction mixture using ^{n}BuMe$_2$SiH after 24 h.

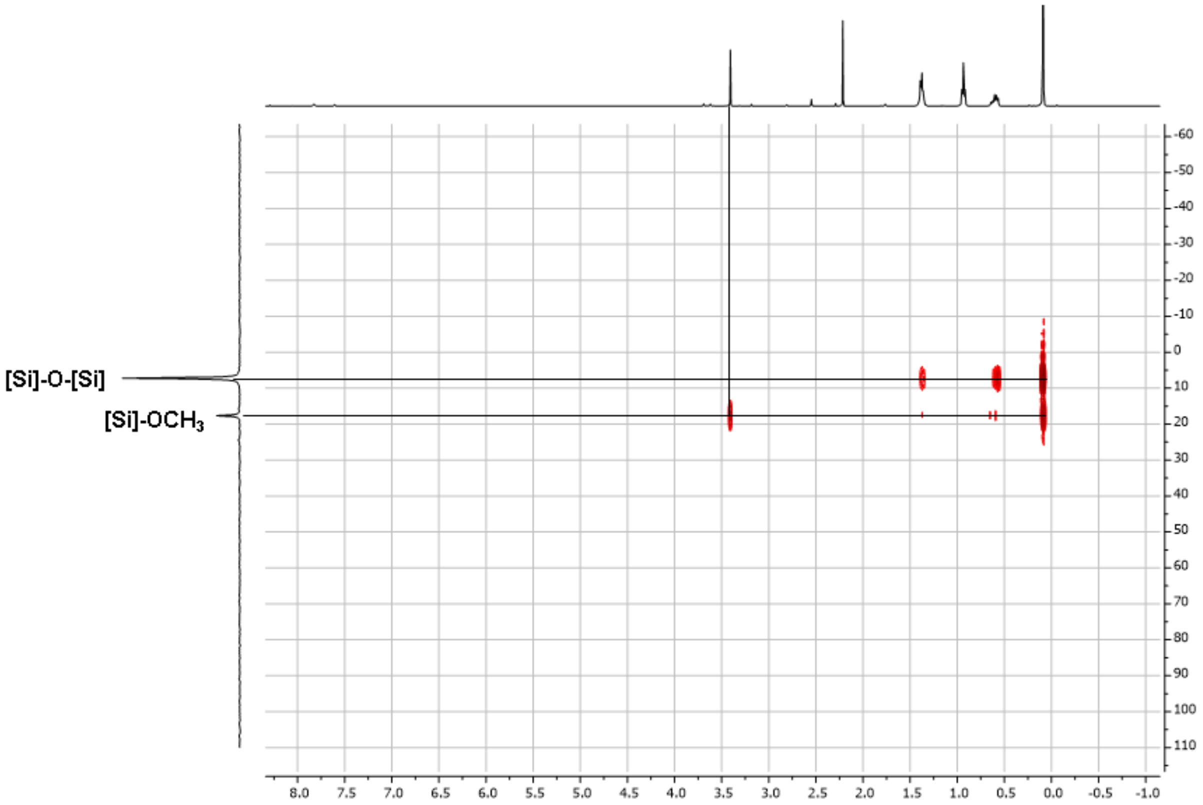


Figure S108: ^{29}Si^{1}H HMBC spectrum of the catalytic reaction mixture using ^{n}BuMe$_2$SiH after 24 h and addtioin of excess silane (2 equiv.) and catalyst.

Catalytic hydrosilylation using $EtMe_2SiH$:

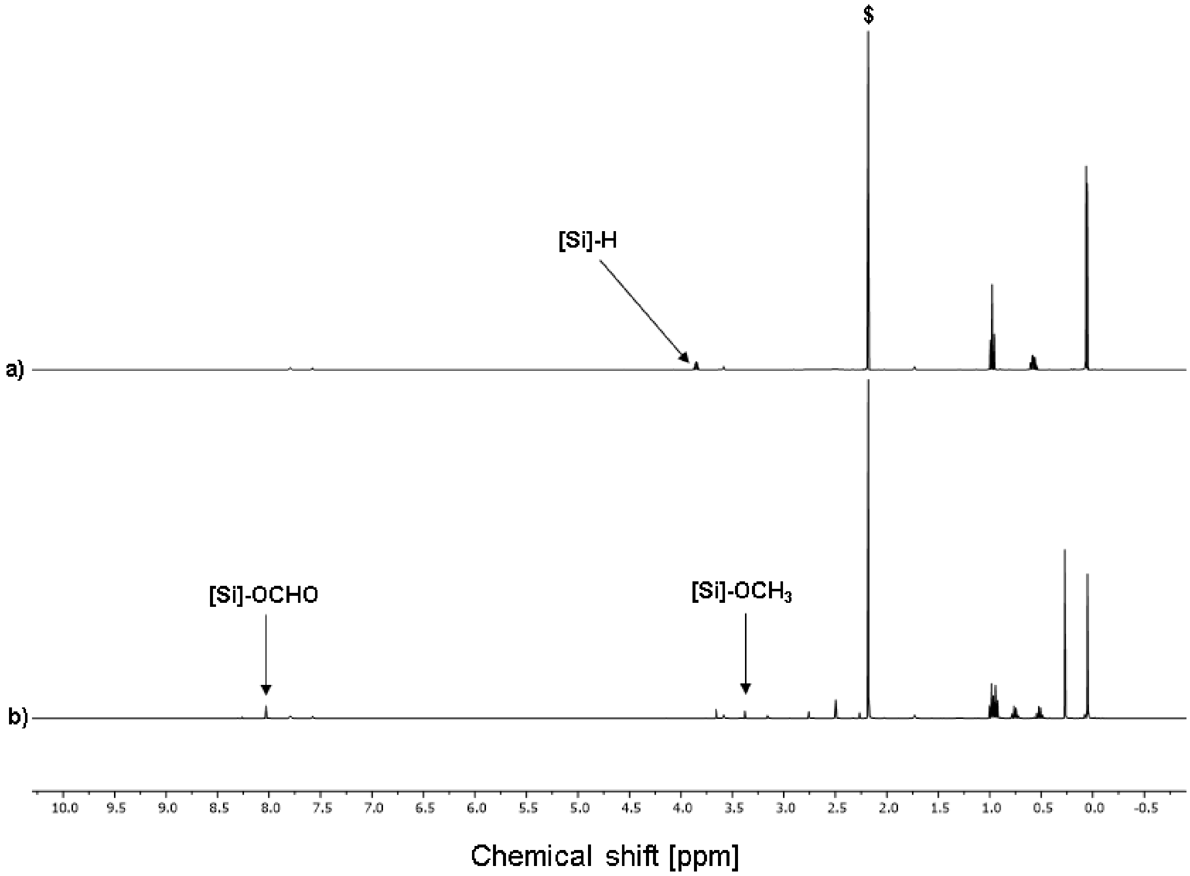


Figure S109: ^1H NMR spectra of the catalytic reaction mixture with $EtMe_2SiH$ ($: hexamethylbenzene as internal standard); a): at the start; b): after 4h.

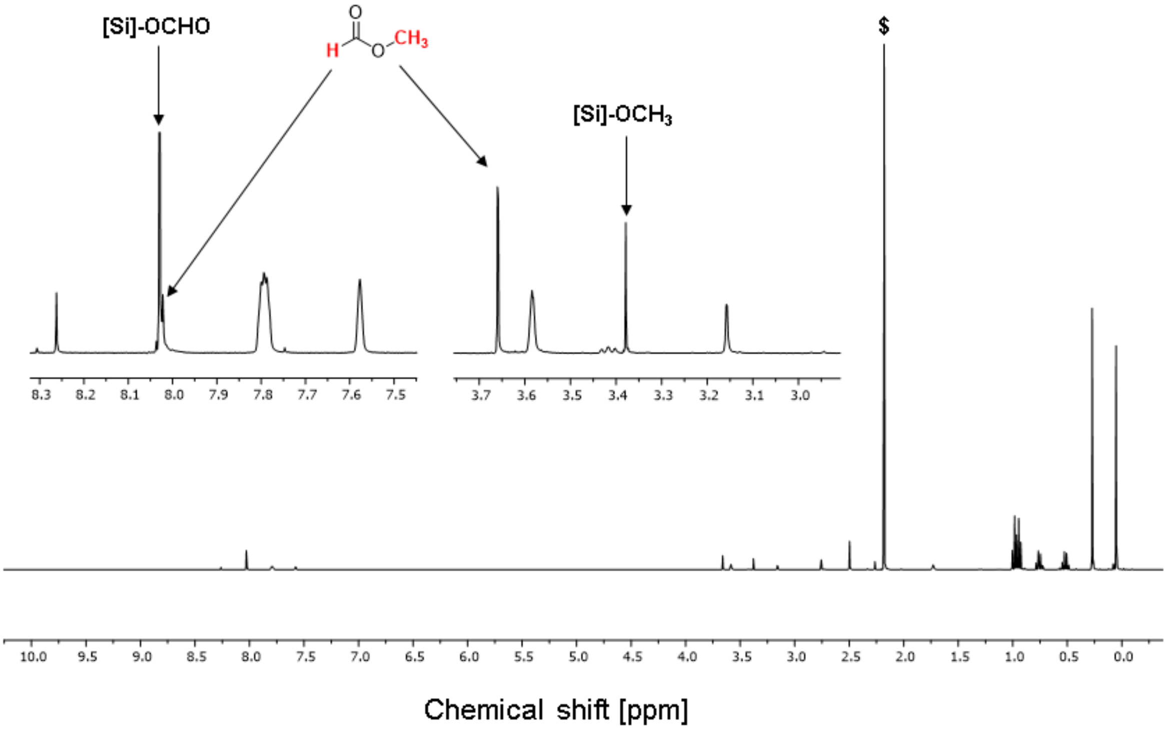


Figure S110: ^1H NMR spectra of the catalytic reaction mixture with $EtMe_2SiH$ ($: hexamethylbenzene as internal standard) after 4h.

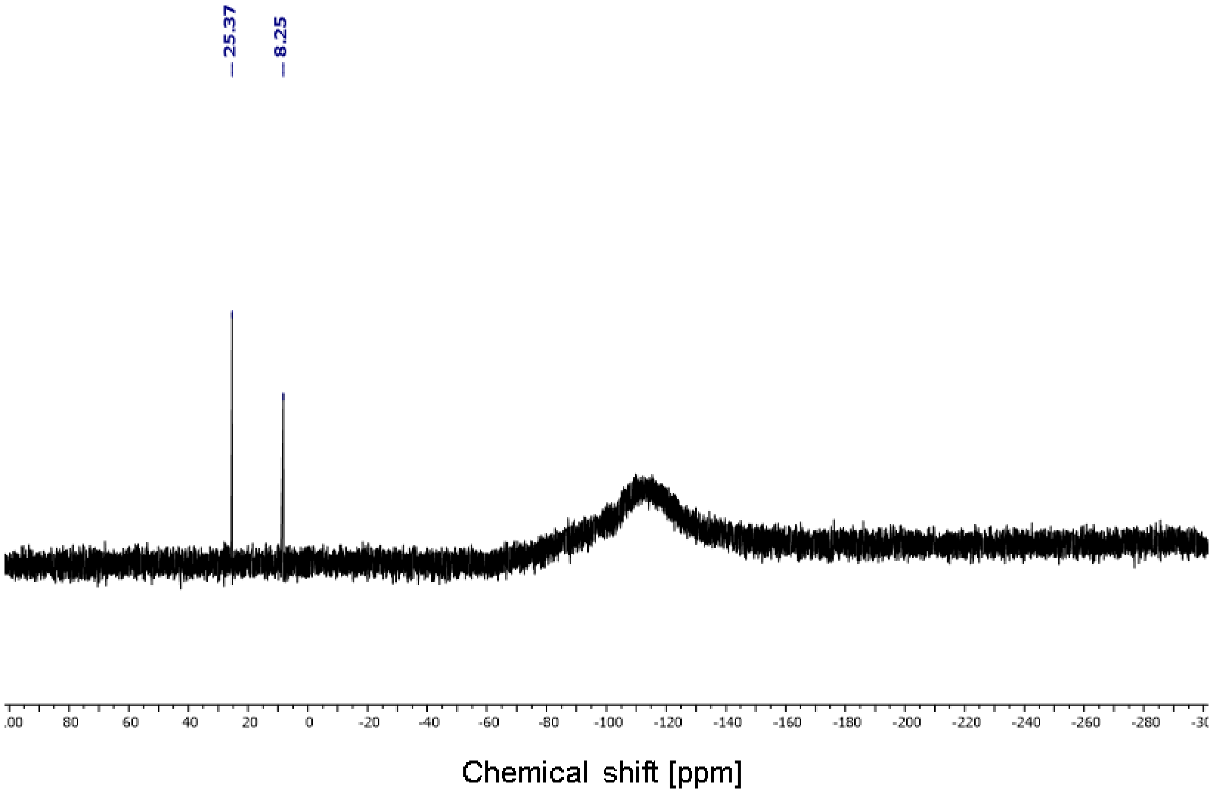


Figure S111: $^{29}Si\{^{1}H\}$ NMR spectrum (inverse gated) of the catalytic reaction mixture using $EtMe_2SiH$ after 4h.

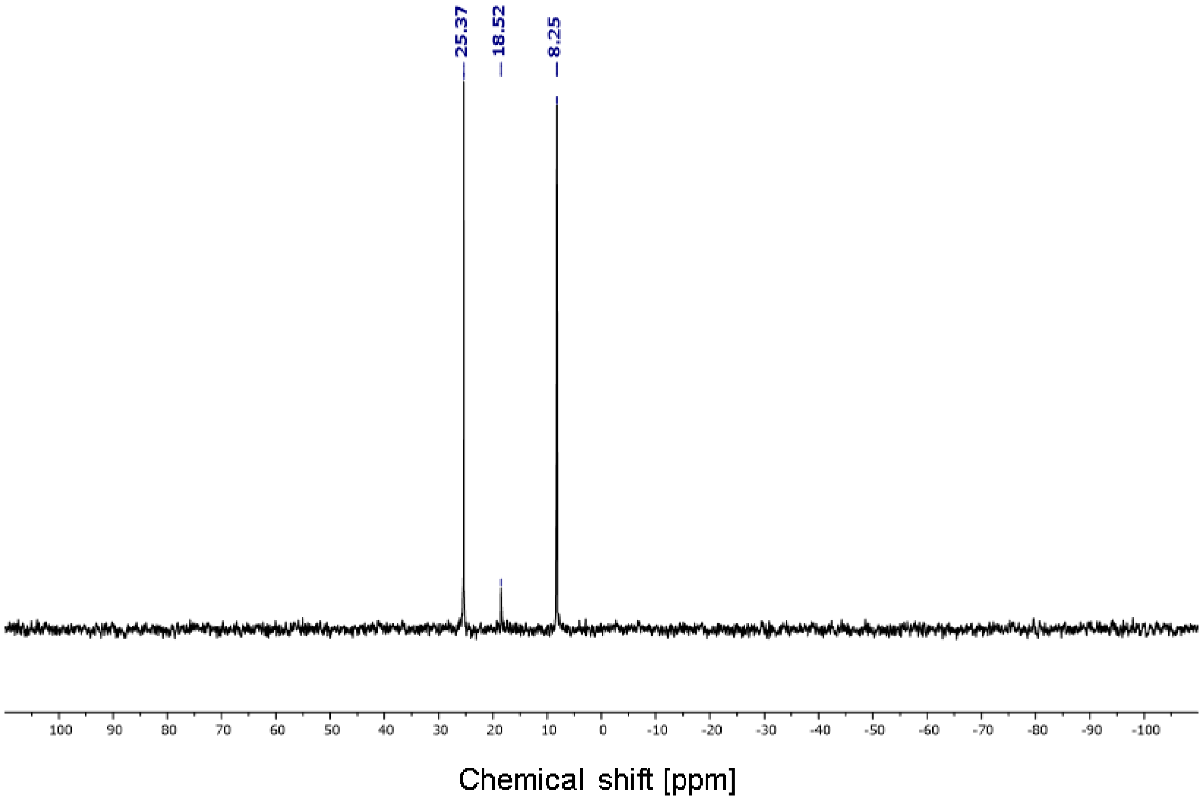


Figure S112: $^{29}Si\{^{1}H\}$ NMR spectrum (DEPT20) of the catalytic reaction mixture using $EtMe_2SiH$ after 4h.

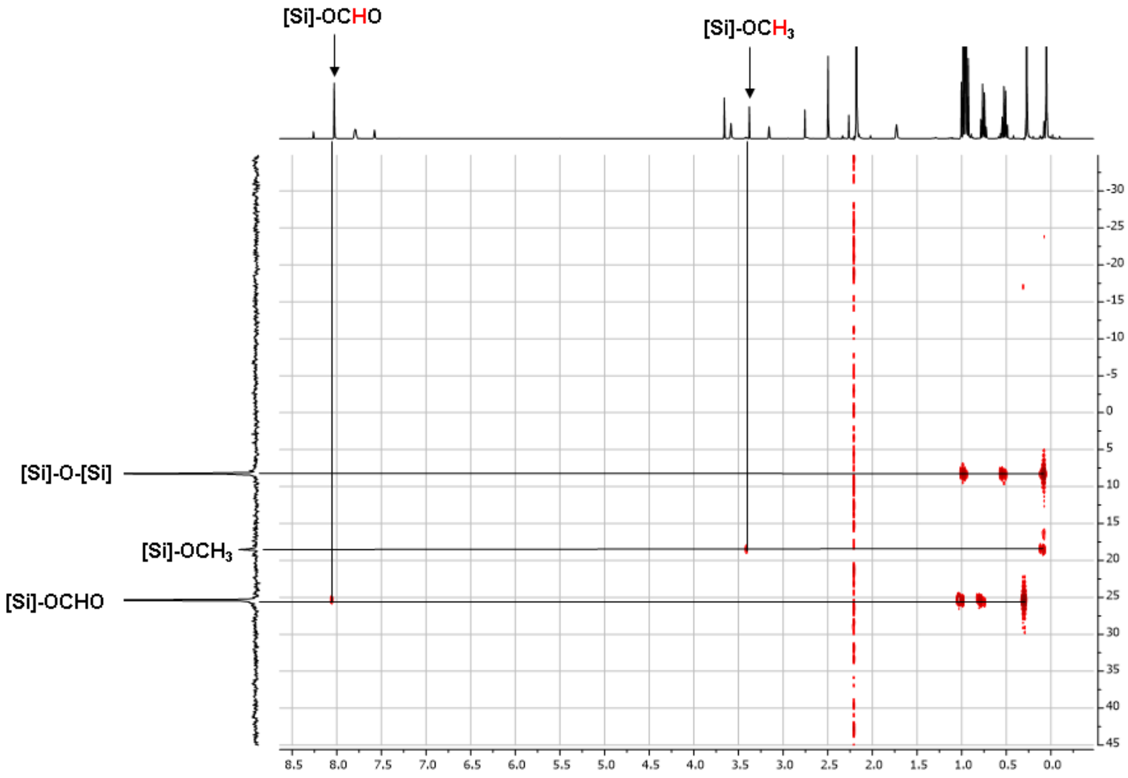


Figure S 113: ^{29}Si^{1}H HMBC spectrum of the catalytic reaction mixture using EtMe$_2$SiH after 4h.

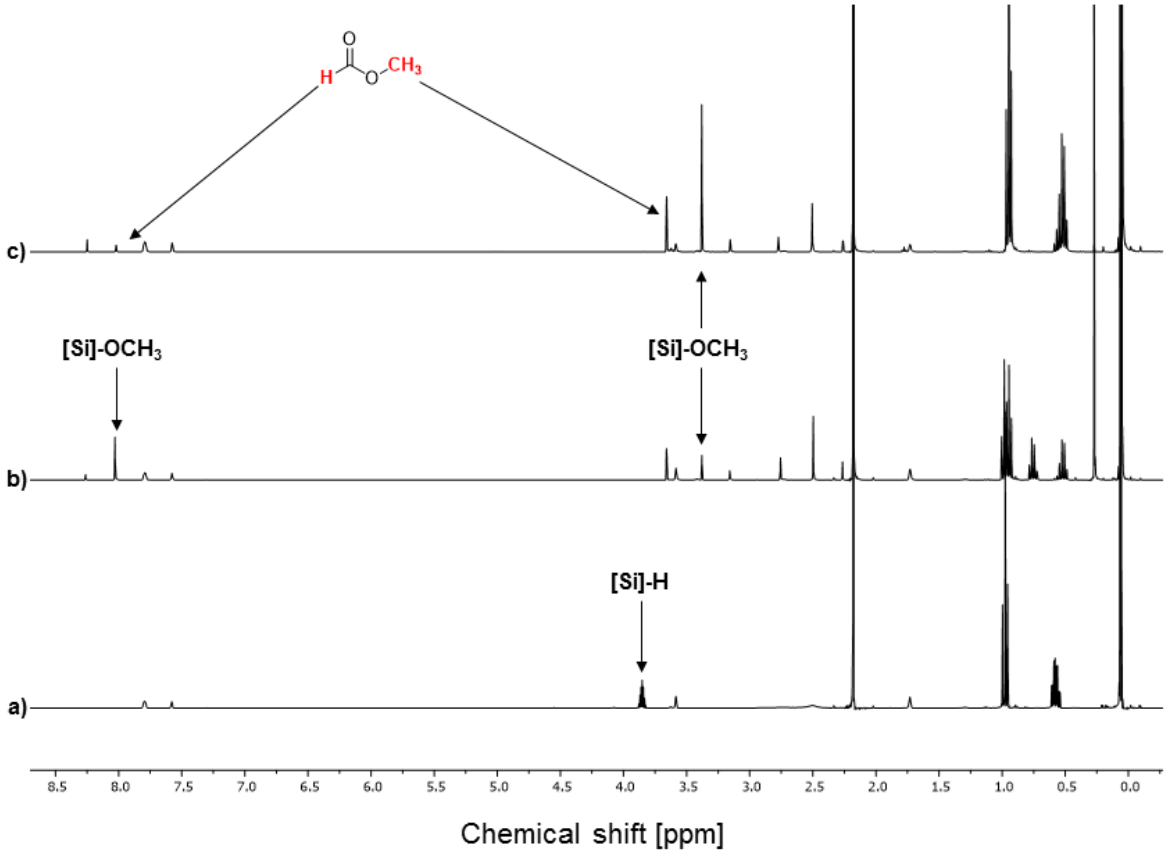


Figure S114: ^{1}H NMR spectra of the catalytic reaction mixture with EtMe$_2$SiH ($: hexamethylbenzene as internal standard). a): Start of the reaction; b): after 4h and full consumption of silane; c): after 8 h and addition of silane and catalyst.

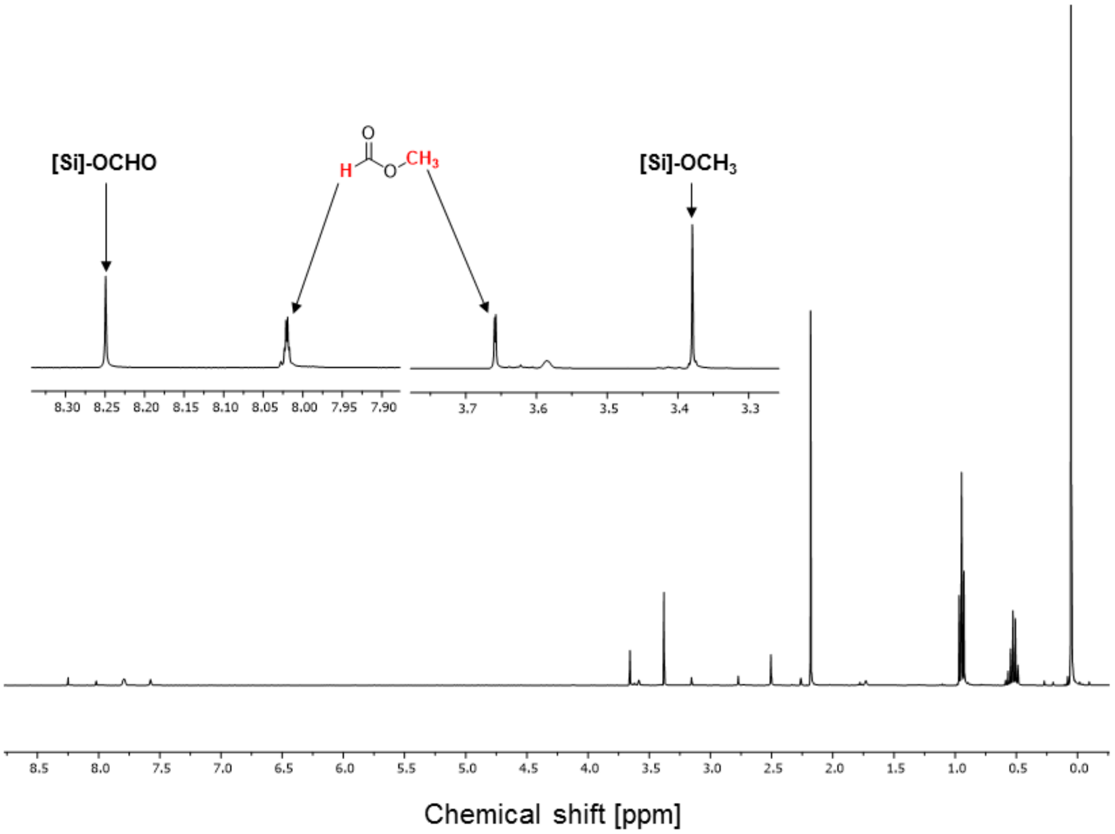


Figure S115: ^{1}H NMR spectrum after 8h of the catalytic reaction mixture with $EtMe_2SiH$ ($: hexamethylbenzene as internal standard).

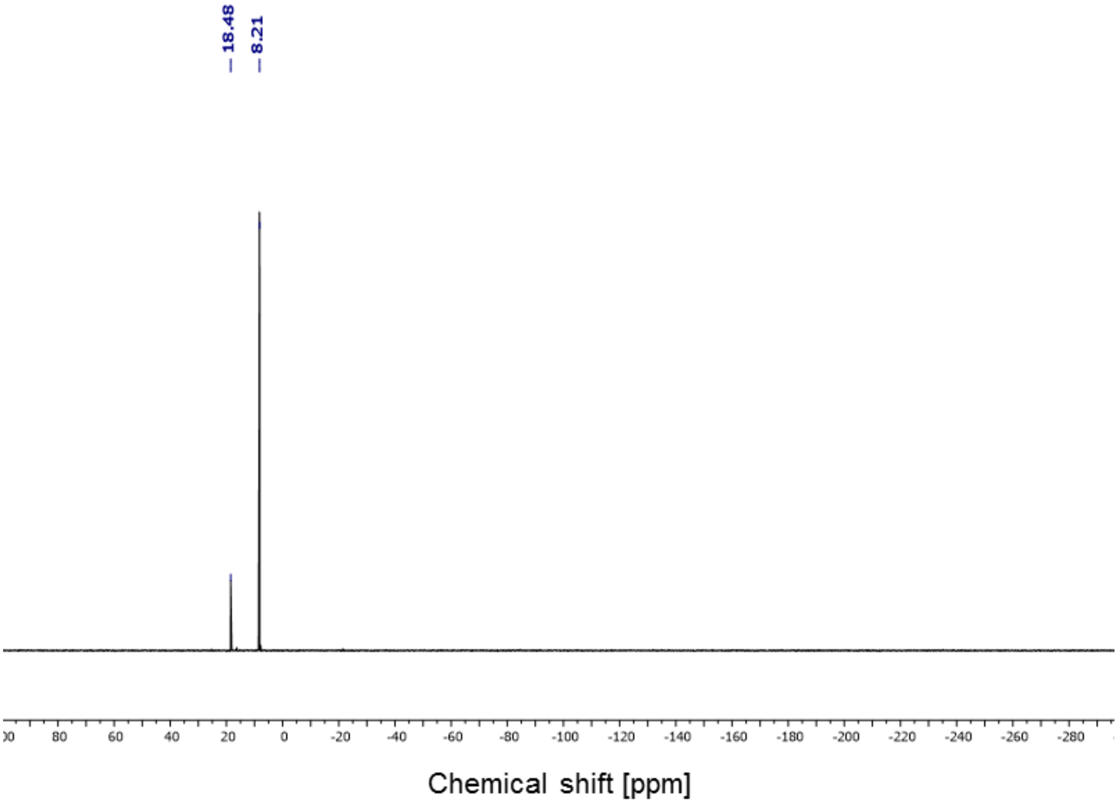


Figure S116: $^{29}Si\{^1H\}$ NMR spectrum (DEPT 20) of the catalytic reaction mixture using $EtMe_2SiH$ after 8 h.

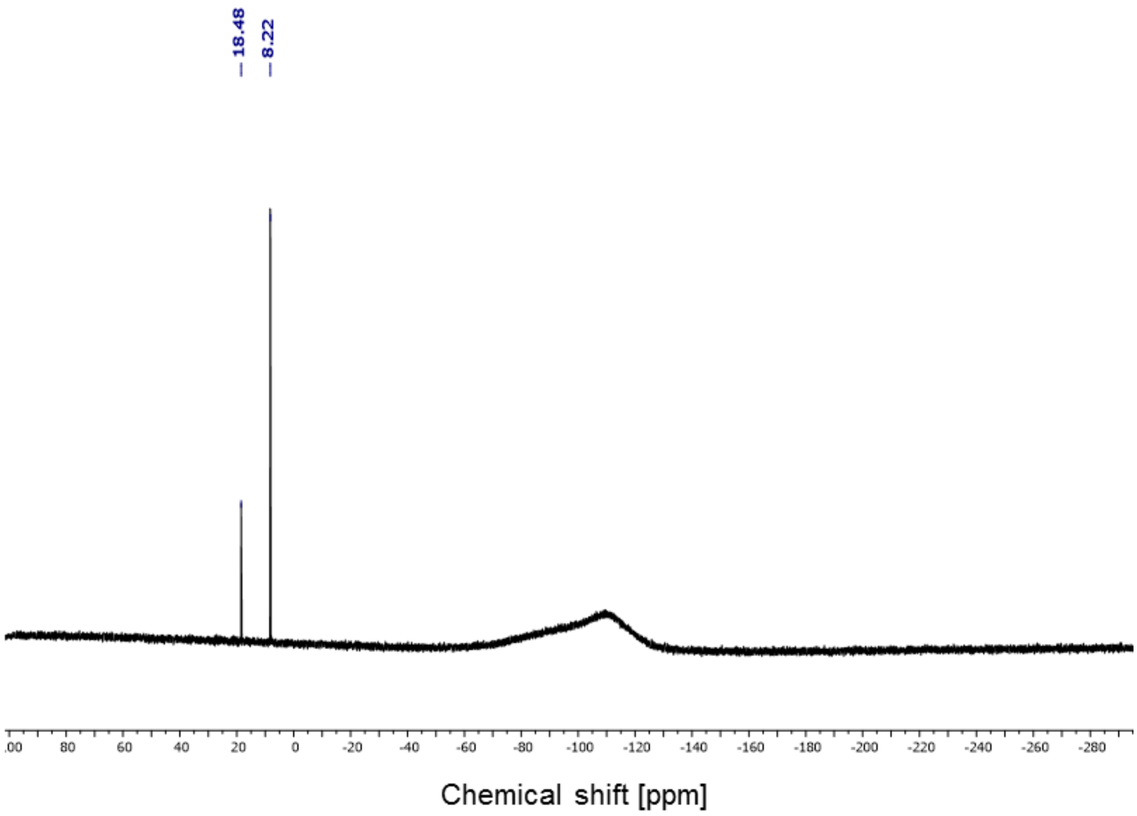


Figure S117: $^{29}Si\{^1H\}$ NMR spectrum (inverse gated) of the catalytic reaction mixture using $EtMe_2SiH$ after 8 h.

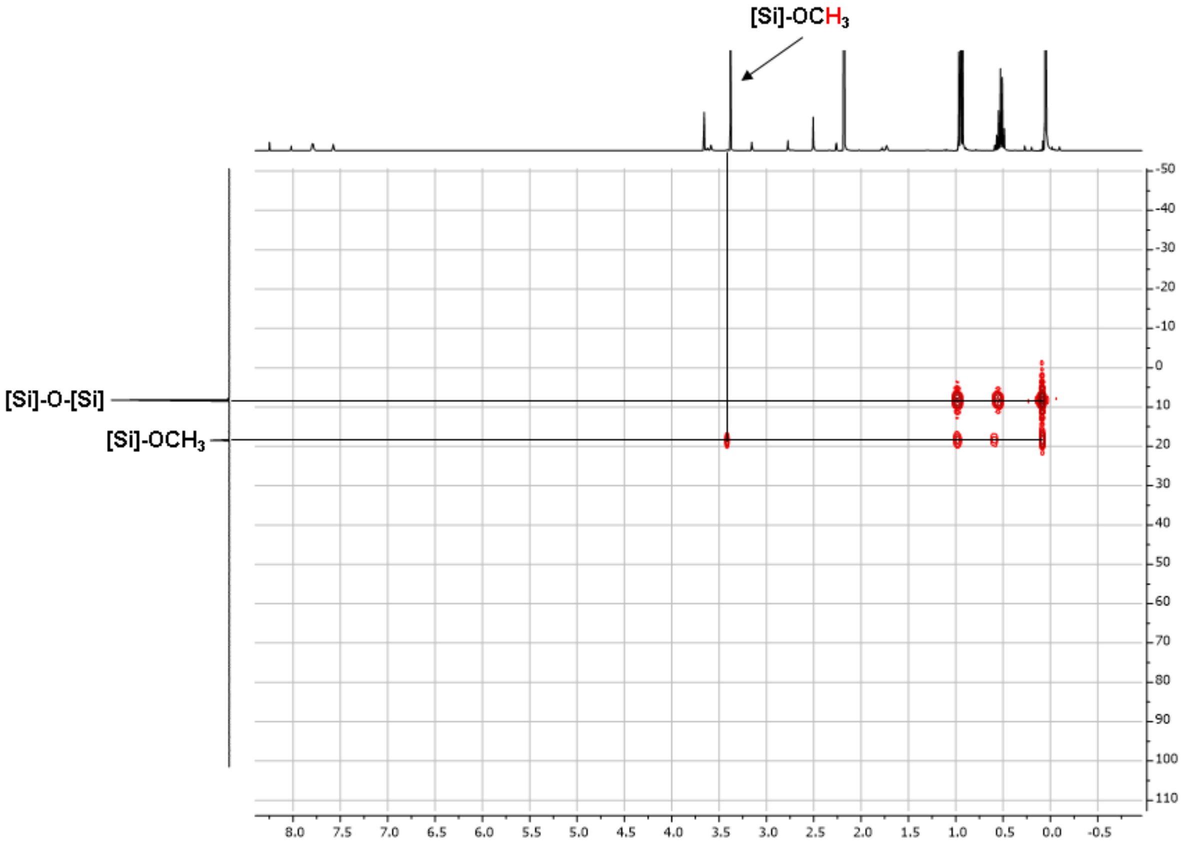


Figure S118: $^{29}Si^1H$ HMBC spectrum of the catalytic reaction mixture using $EtMe_2SiH$ after 8h.

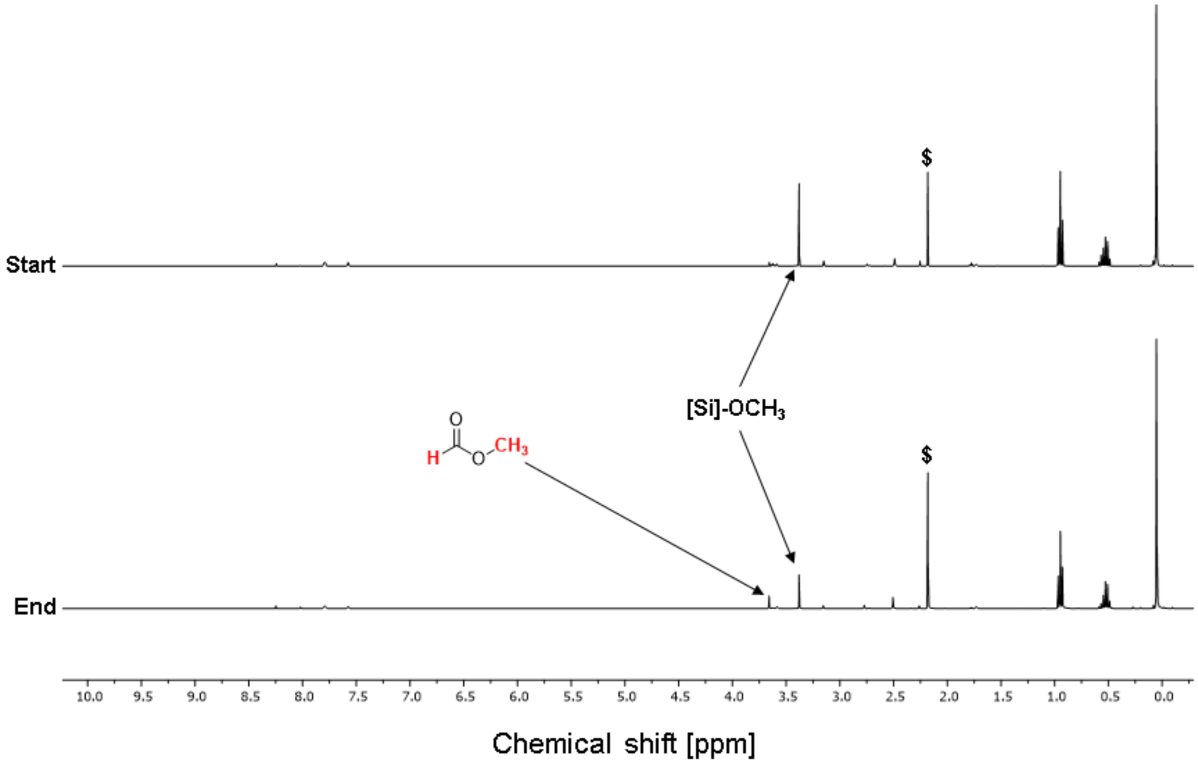


Figure S119: ^{1}H NMR spectra of the catalytic reaction mixture with EtMe$_2$SiH ($: hexamethylbenzene as internal standard). a): reaction mixture after 8 h and added silane and catalyst; b): after 14 h and excess silane (2 equiv.) and catalyst.

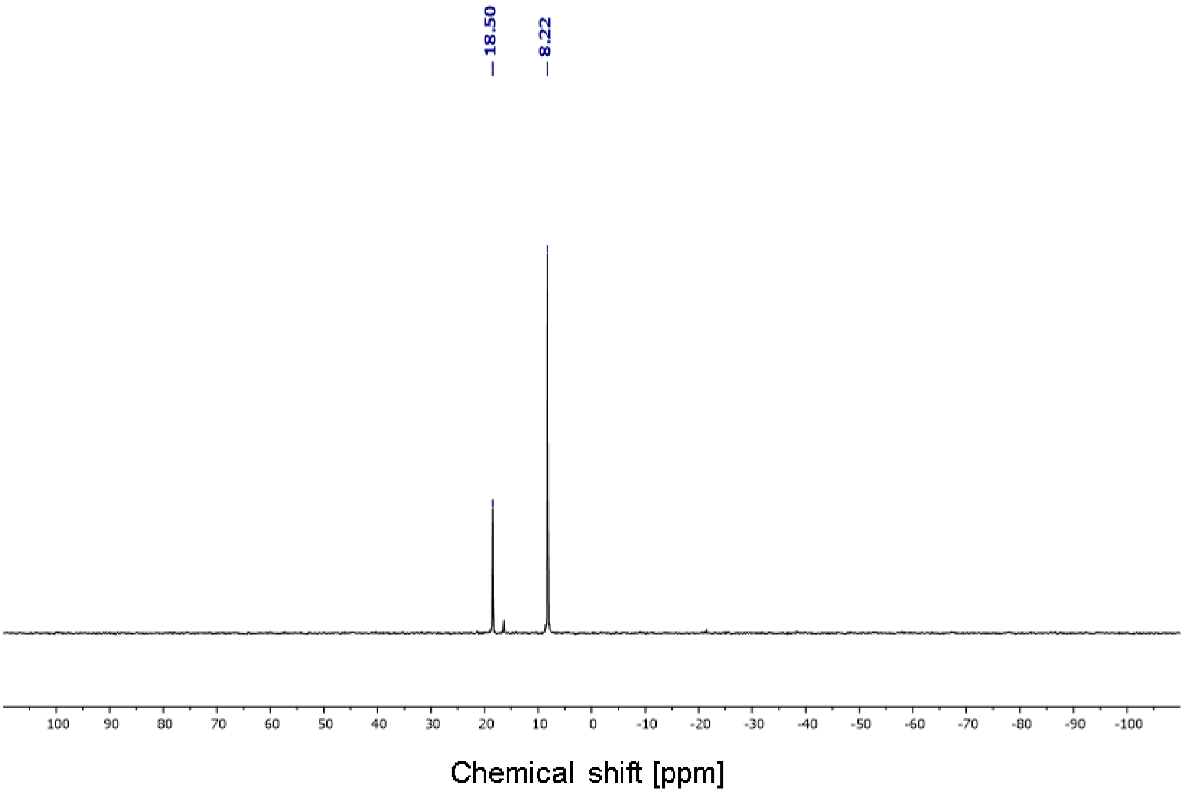


Figure S120: ^{29}Si{^{1}H} NMR spectrum (DEPT 20) of the catalytic reaction mixture using EtMe$_2$SiH after 14 h.

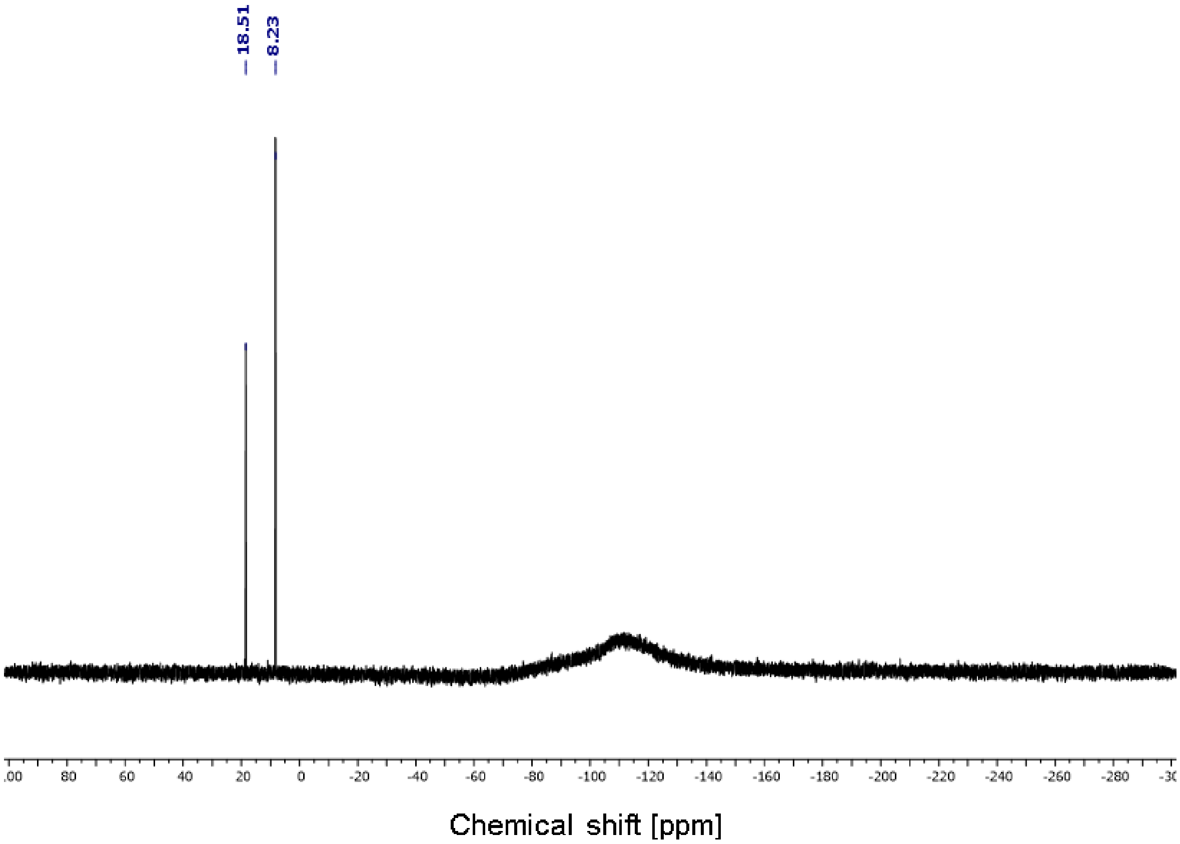


Figure S121: ^{29}Si{^{1}H} NMR spectrum (inverse gated) of the catalytic reaction mixture using $EtMe_2SiH$ after 14 h.

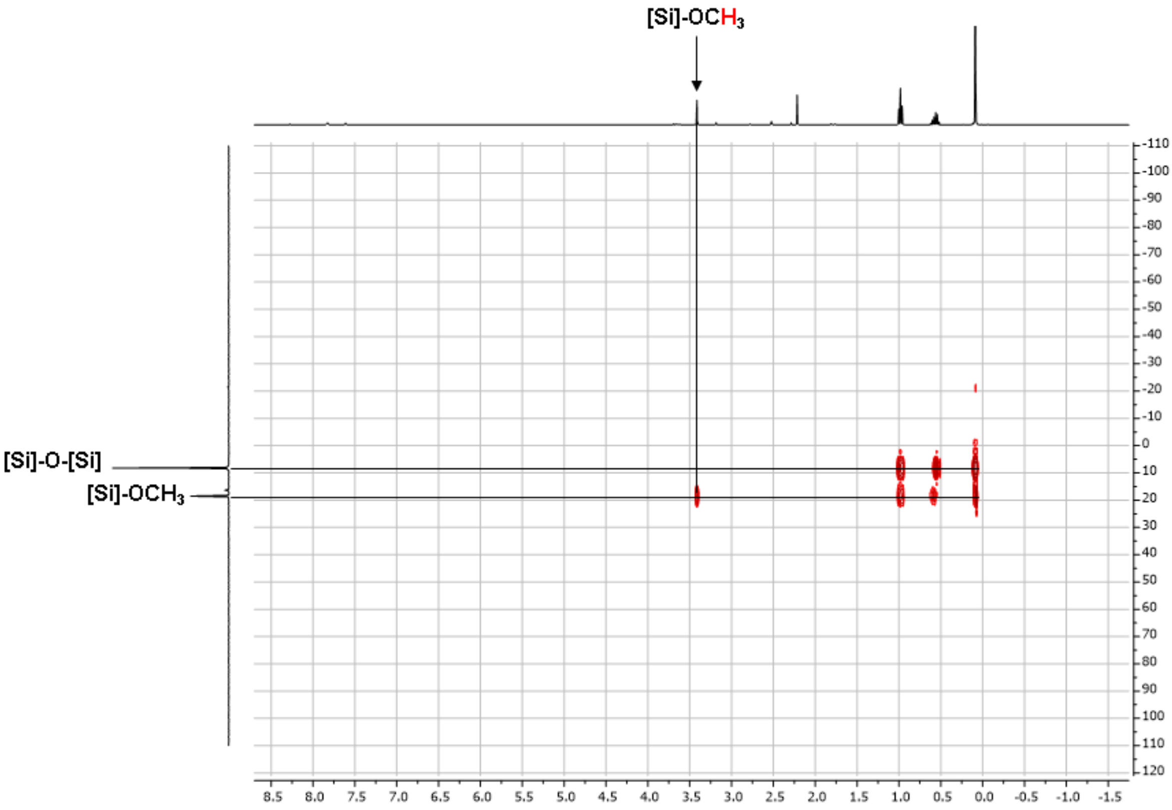


Figure S122: ^{29}Si^{1}H HMBC spectrum of the catalytic reaction mixture using $EtMe_2SiH$ after 14 h.

Catalytic hydrosilylation using Et_3SiH:

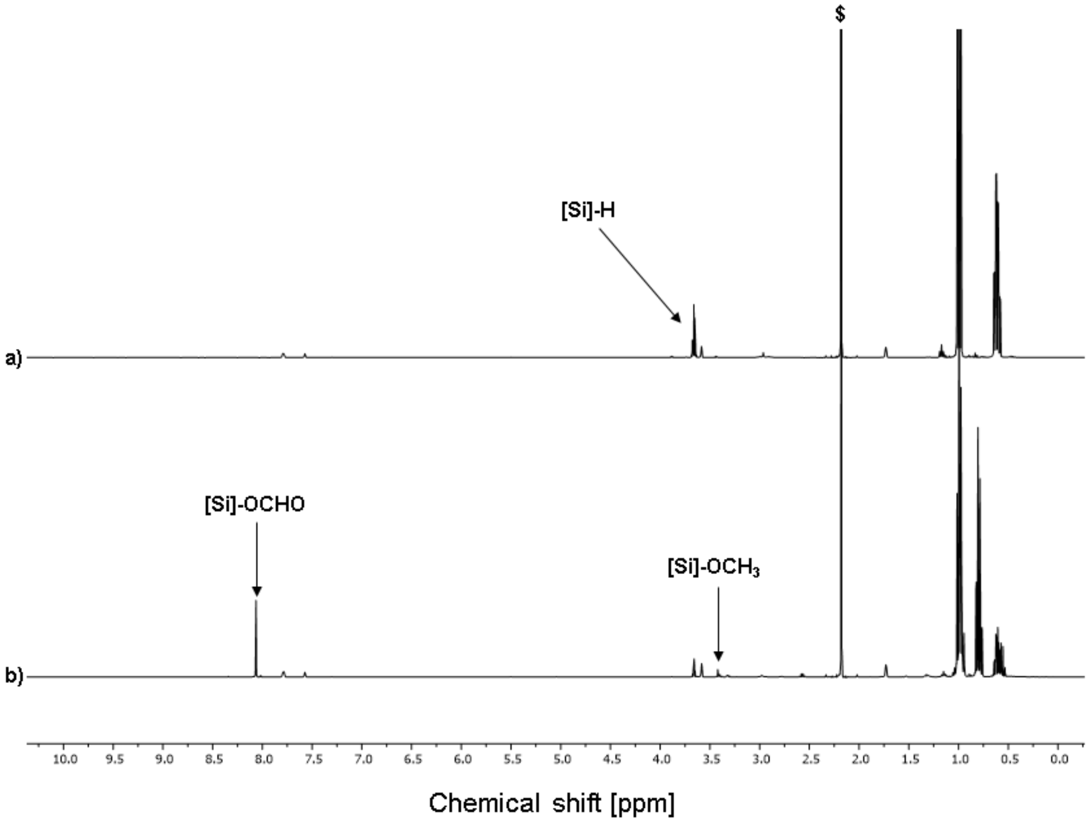


Figure S123: ^1H NMR spectra of the catalytic reaction mixture with Et_3SiH ($: hexamethylbenzene as internal standard); a): at the start; b): after 48 h.

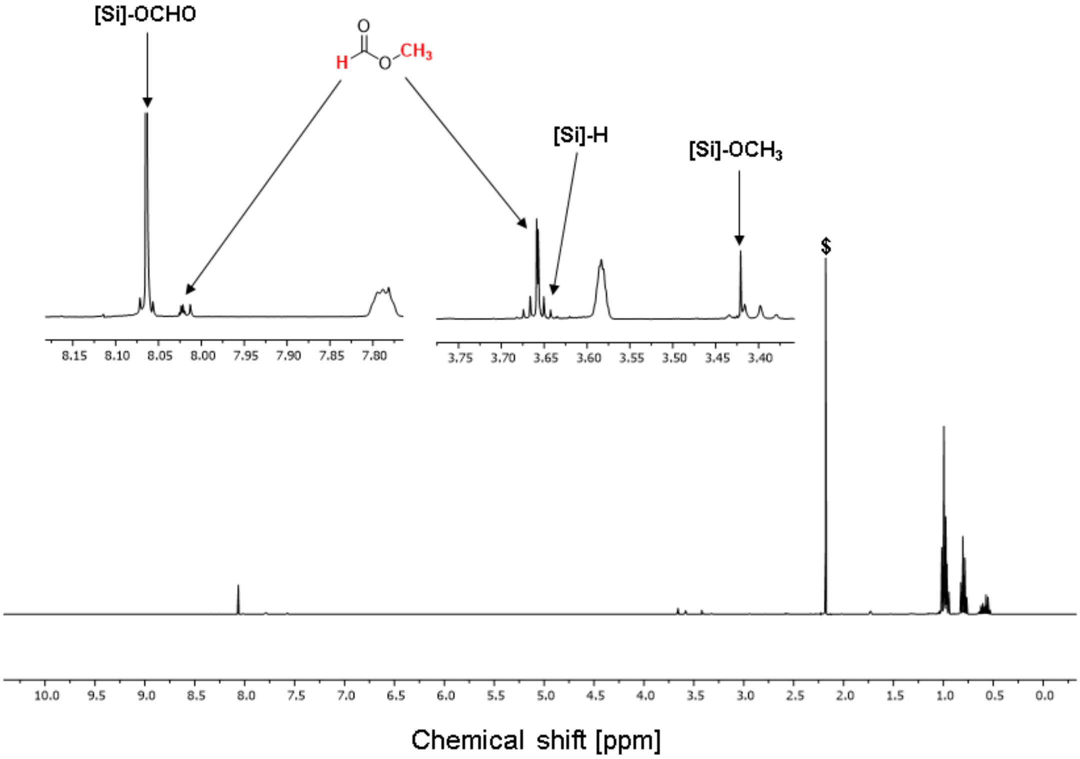


Figure S124: ^1H NMR spectra at the after 48 h of the catalytic reaction mixture with Et_3SiH ($: hexamethylbenzene as internal standard).

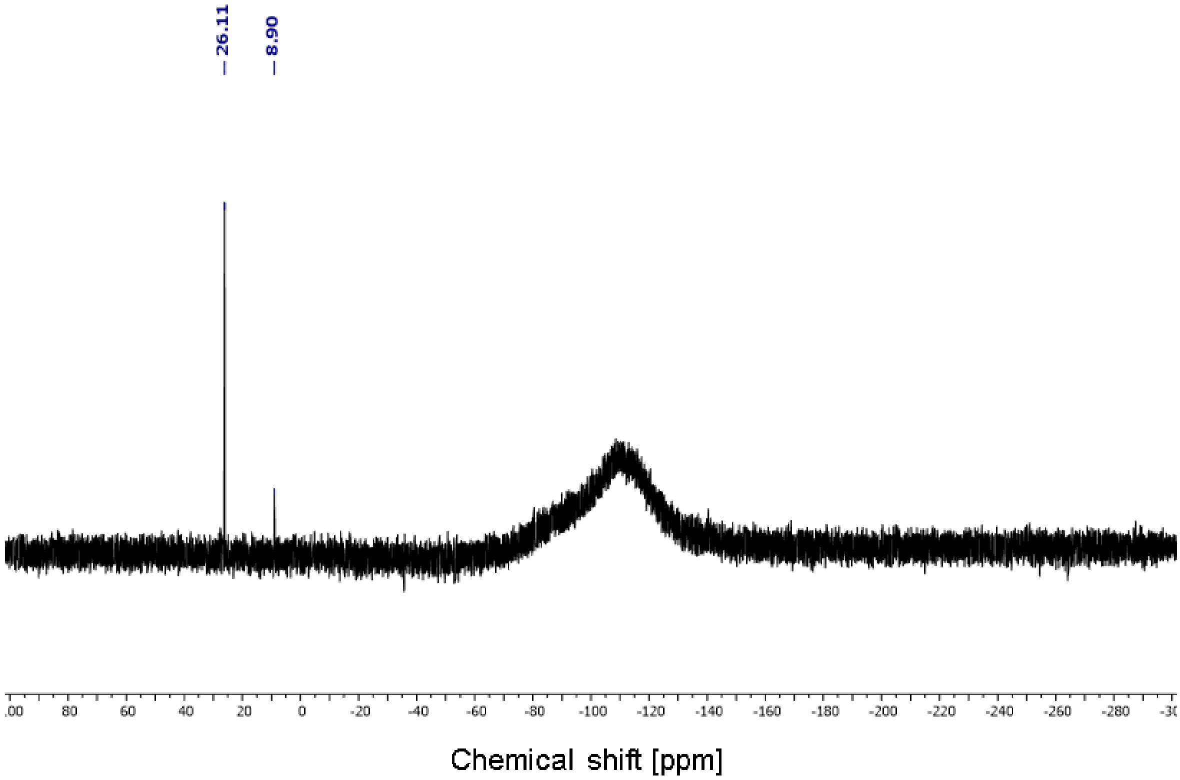


Figure S125: $^{29}Si\{^1H\}$ NMR spectrum (inverse gated) of the catalytic reaction mixture using Et_3SiH after 48 h.

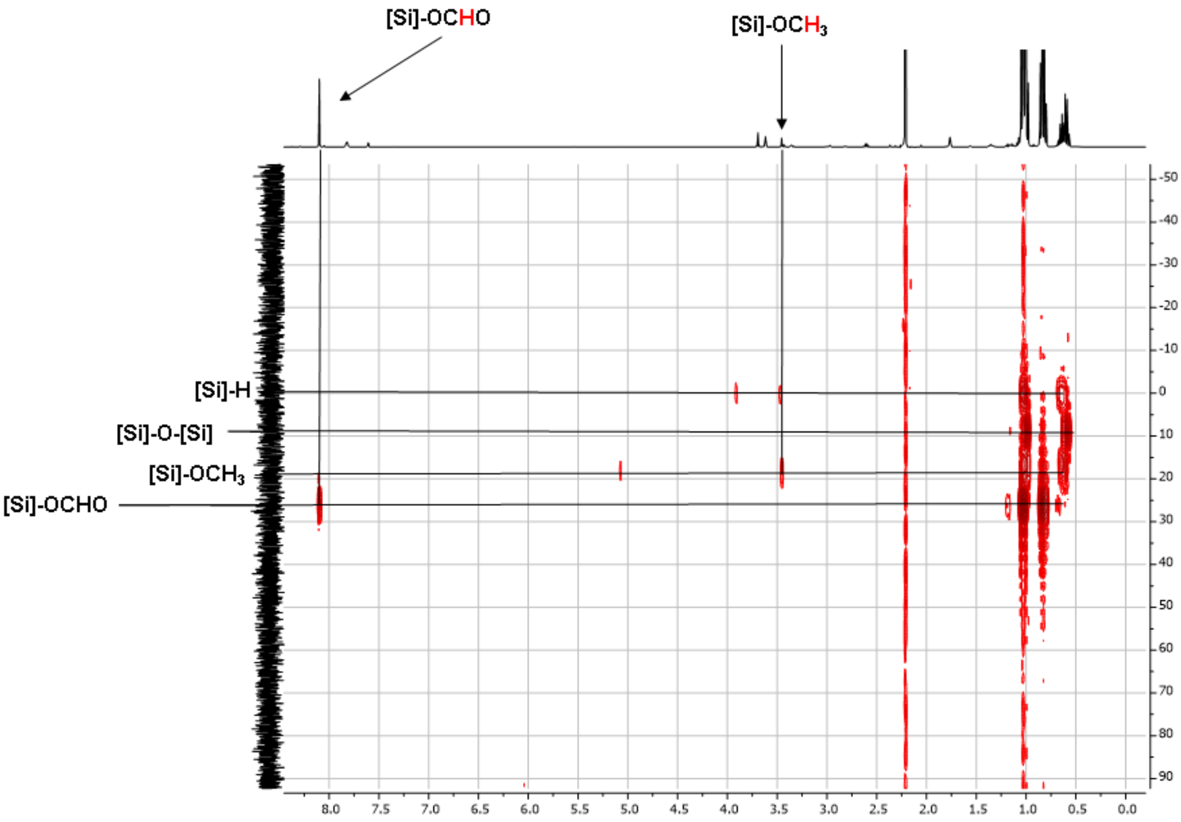


Figure S126: $^{29}Si^1H$ HMBC spectrum of the catalytic reaction mixture using Et_3SiH after 48 h.

Background Catalysis

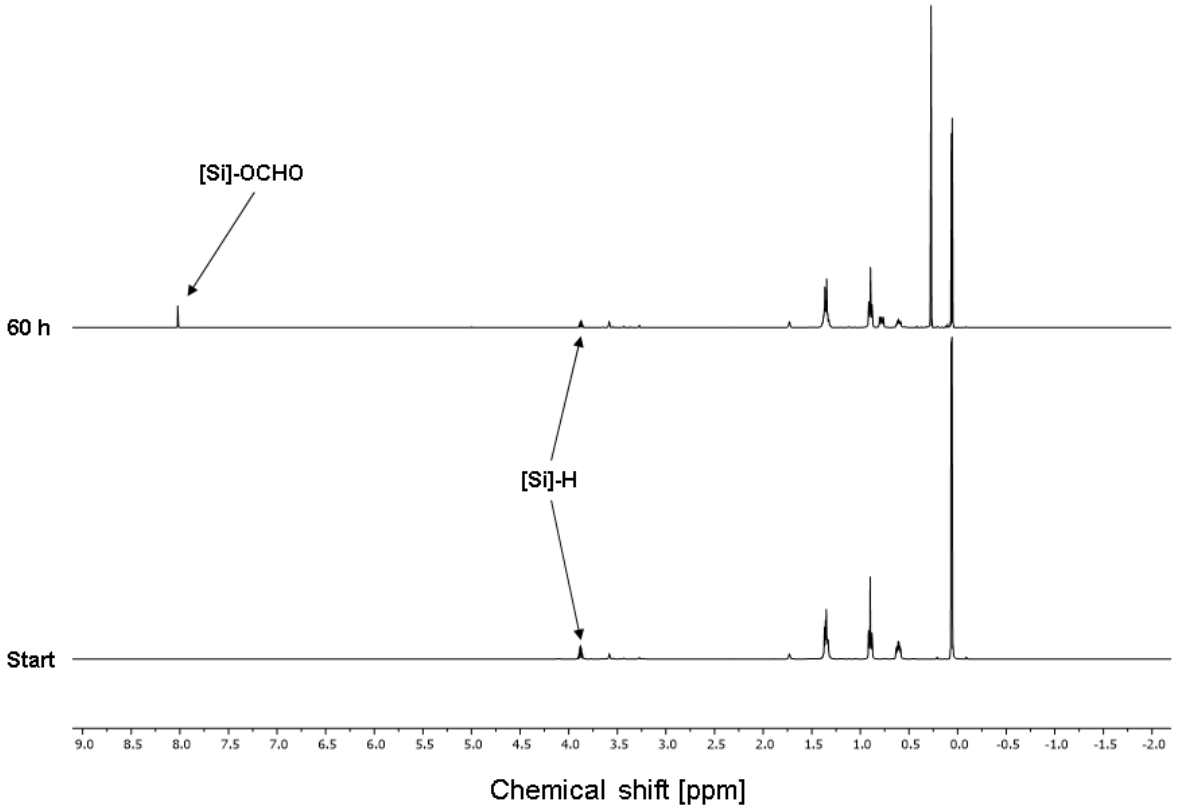


Figure S127: ^{1}H NMR spectra at the start and after 60 h of the catalytic reaction mixture with ^{n}BuMe$_2$SiH [Zn(OTf)$_2$] (10 mol%) as catalyst.

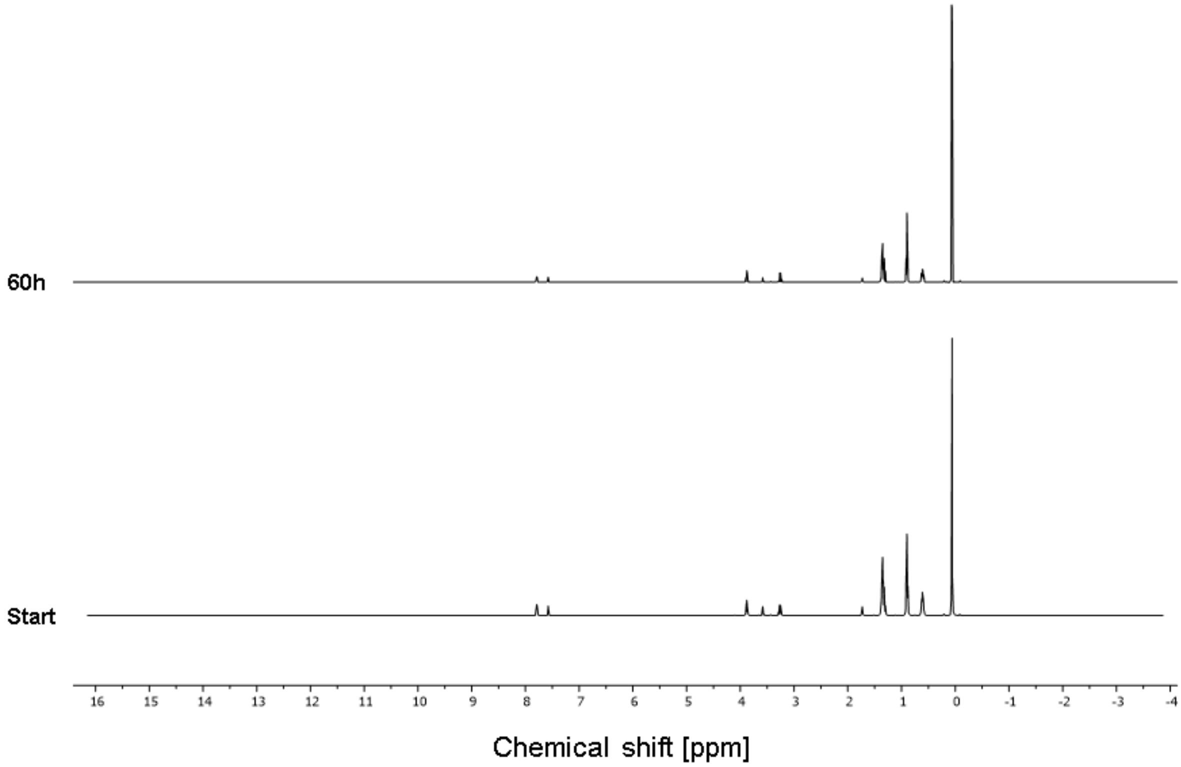


Figure S128: ^{1}H NMR spectra at the start and after 60 h of the catalytic reaction mixture with ^{n}BuMe$_2$SiH [NEt$_3$H][B(3,5-CF$_3$-C$_6$H$_3$)$_4$] (10mol%) as catalyst.

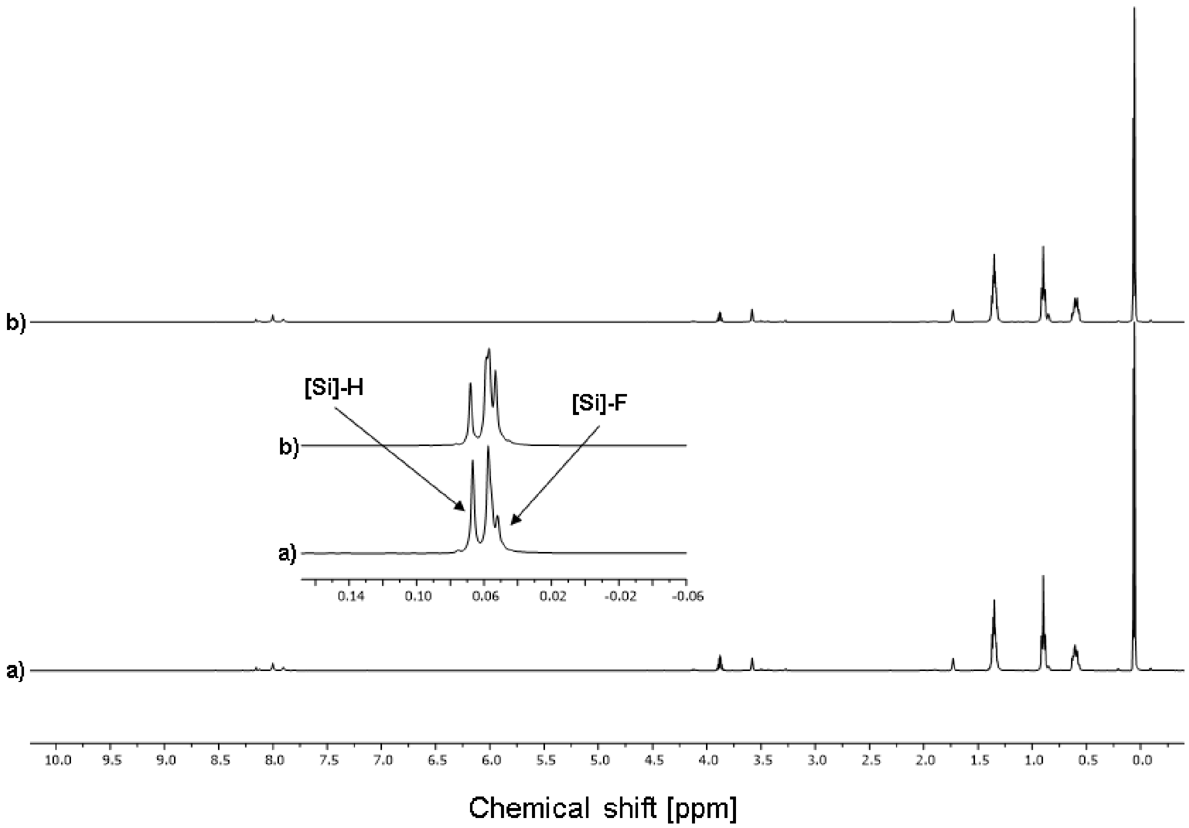


Figure S 129: ^{1}H NMR spectra of with ^{n}BuMe$_2$SiH and B(3,5-CF$_3$-C$_6$H$_3$)$_3$ (10mol%) as catalyst: a) immediately after mixing; b) 20 min after mixing.

Stoichiometric reaction

Reaction of formate complex **2a** with 1 equiv. of ^{n}BuMe$_2$Si(OCHO):

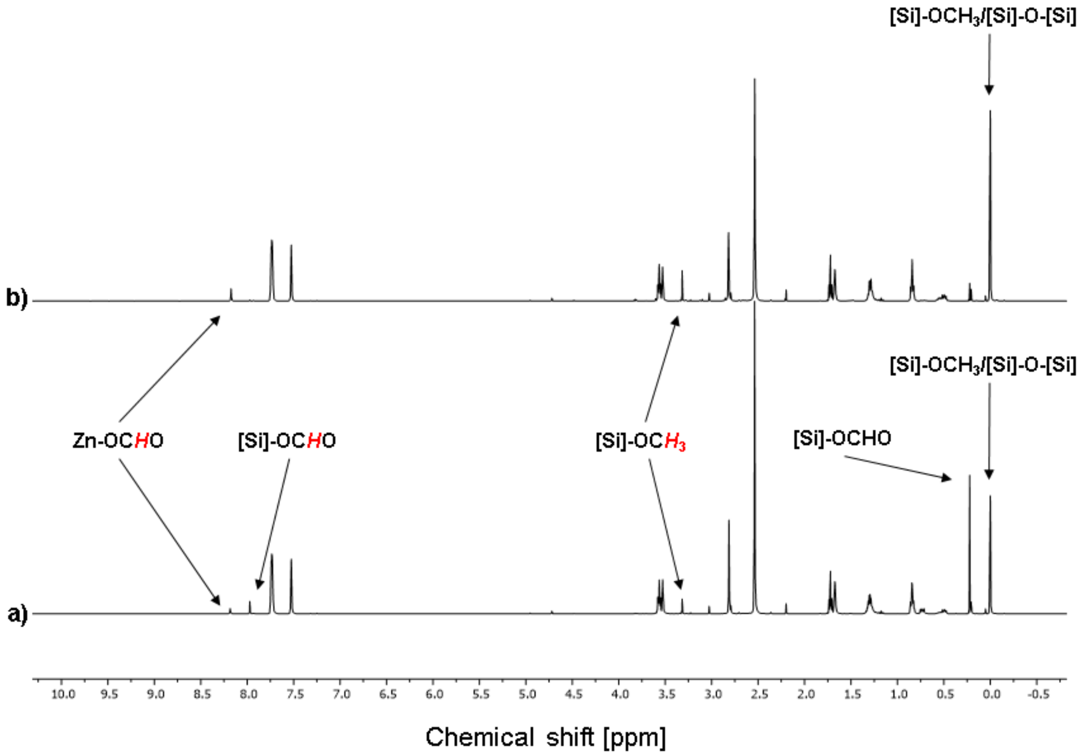


Figure S130: ^{1}H NMR spectra of the reaction of 1 eq. **2a** with 1 equiv. of ^{n}BuMe$_2$S(OCHO) (a): 10 min after mixing; b): 20 min after mixing) in [D8]THF.

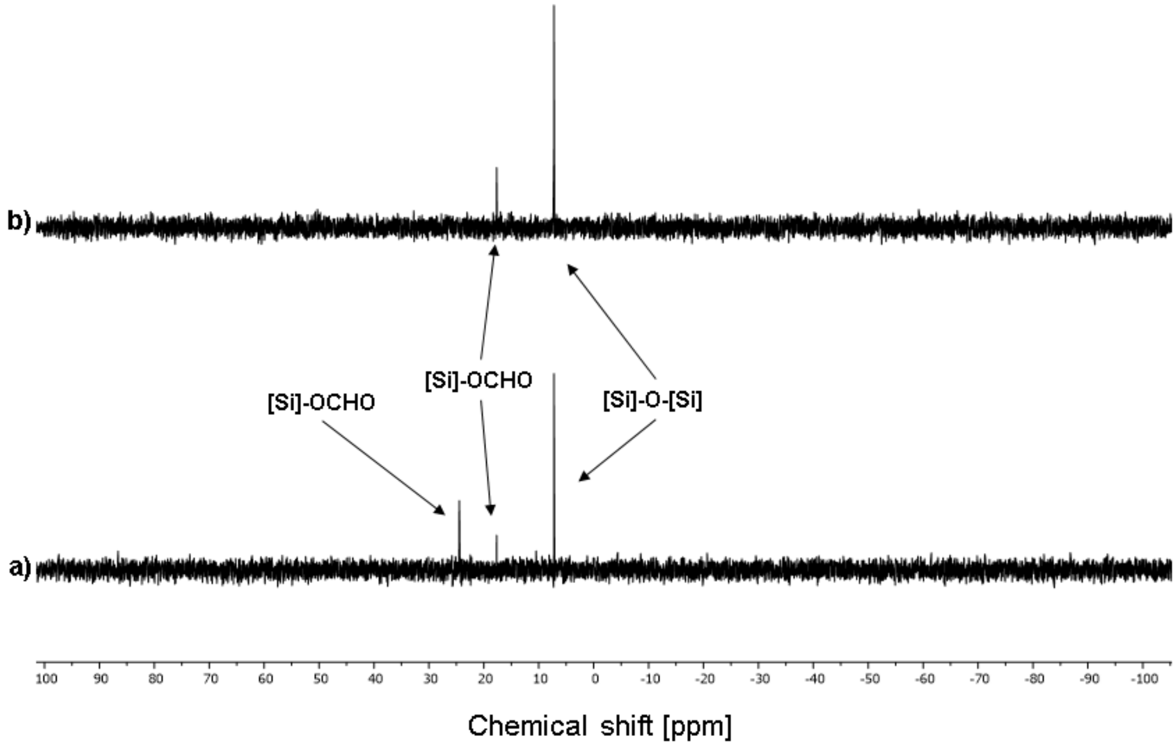


Figure S131: ^{29}Si NMR spectra (DEPT 20) of the reaction of 1 equiv. **2a** with 1 equiv. of ^{n}BuMe$_2$SiH (a): 10 min after mixing; b): 20 min after mixing) in [D8]THF.

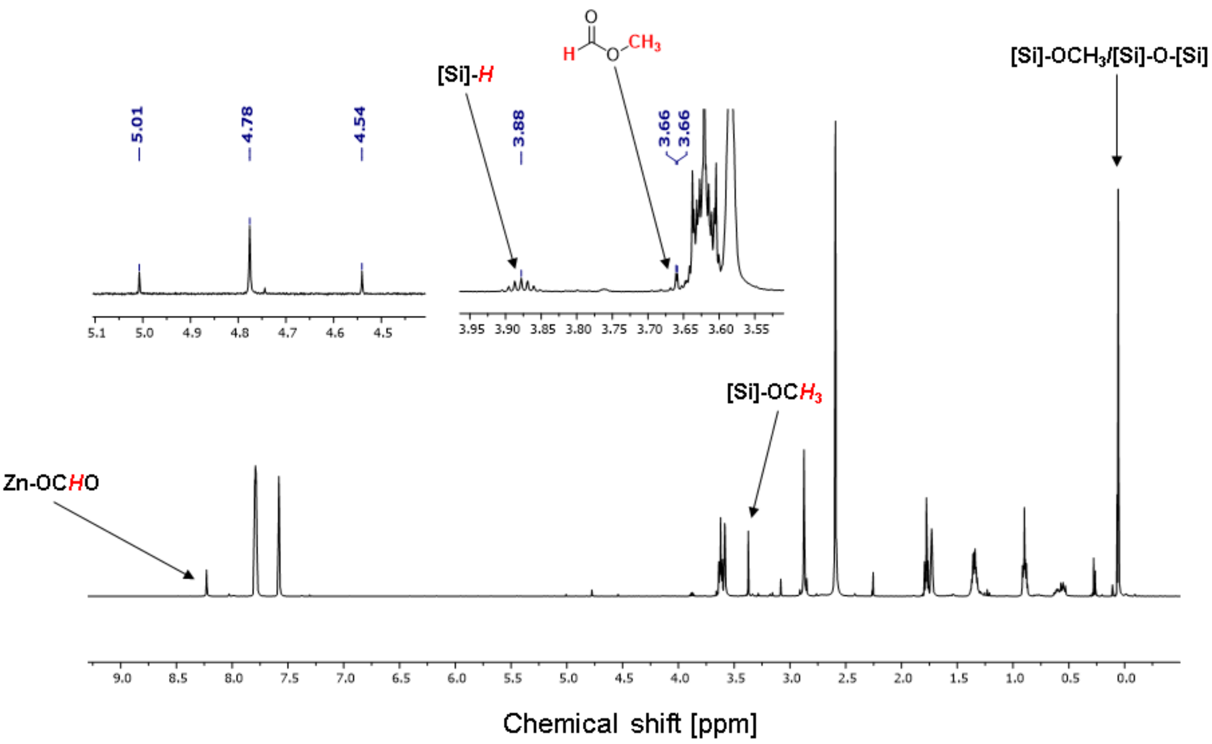


Figure S132: ^{1}H NMR spectrum of the reaction of 1 equiv. **2a** with 1 equiv. of ^{n}BuMe$_2$SiH: 20 min after mixing in [D8]THF.

Reaction of **2a** with 1 equiv. of ^{n}BuMe$_2$Si(OCH$_3$):

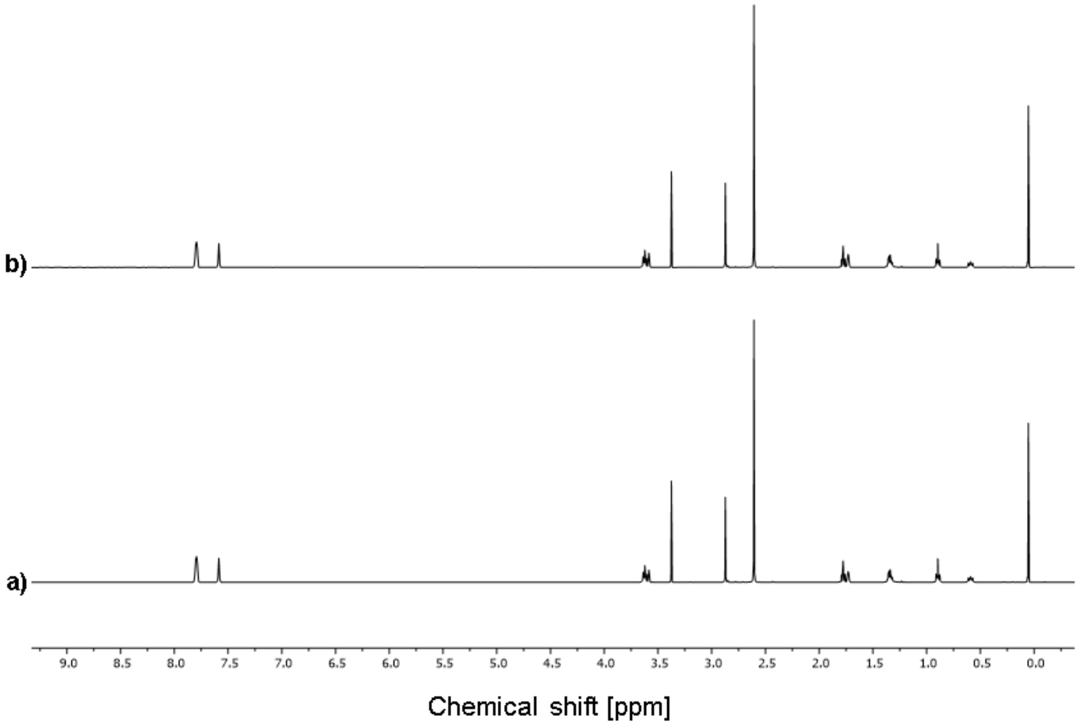


Figure S133: ^{1}H NMR spectra of ^{n}BuMe$_2$Si(OCH$_3$) and **2a** in [D8]THF; (a): 10 min after mixing; b):6 h after mixing.

Reaction of ^{n}BuMe$_2$Si(OCHO) and ^{n}BuMe$_2$Si(OCH$_3$) in presence of **2a**:

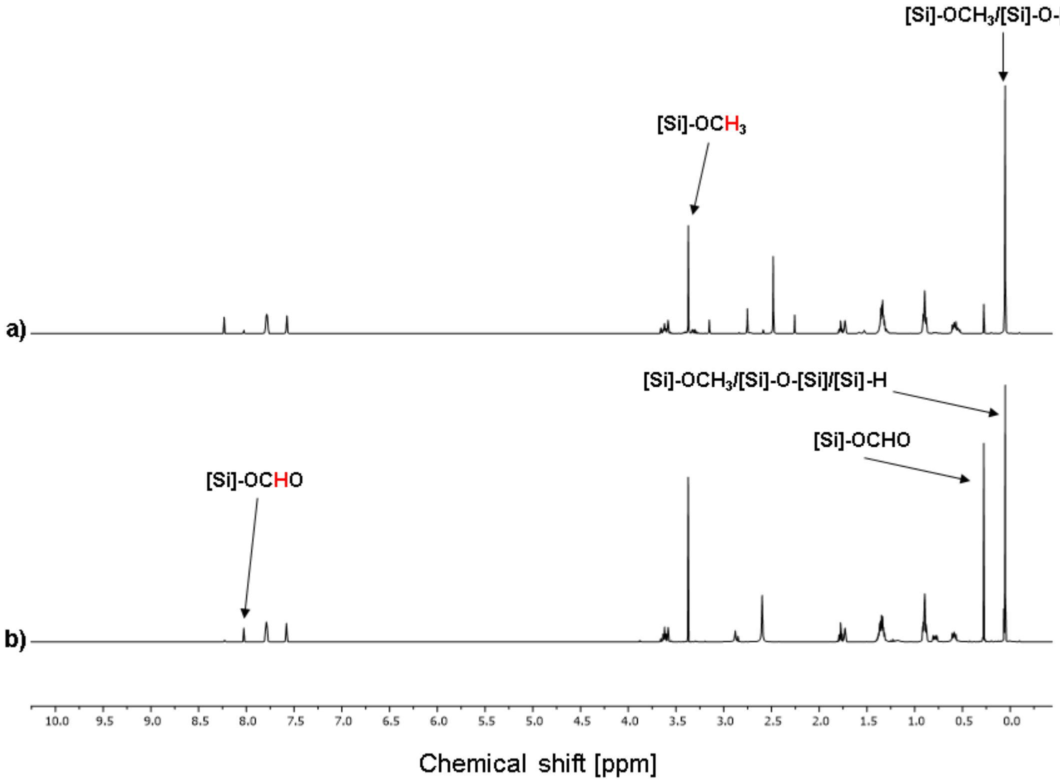


Figure S134: ^{1}H NMR spectra of the reaction of ^{n}BuMe$_2$S(OCH$_3$) with of ^{n}BuMe$_2$S(OCHO) in the presence of **2a** in [D8]THF; (a): 10 min after mixing; b): 24 h at 70 °C.

Reaction of ^{n}BuMe$_2$Si(OCHO) and ^{n}BuMe$_2$Si(OCH$_3$) in presence of **5a**:

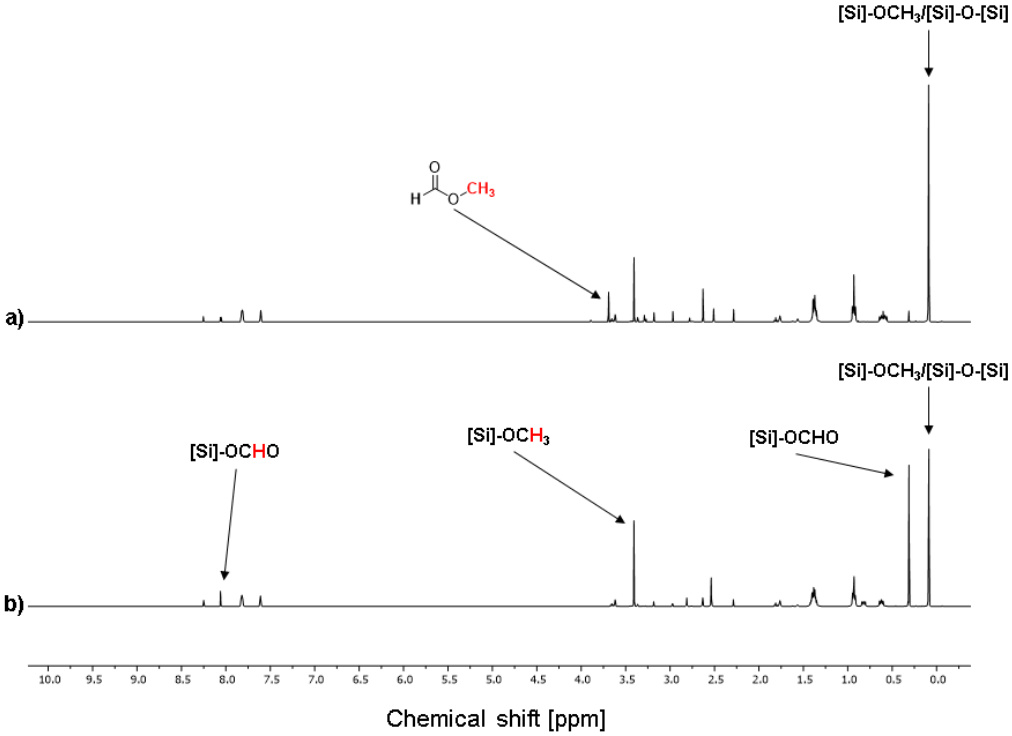


Figure S135: ^{1}H NMR spectra of the reaction of ^{n}BuMe$_2$S(OCH$_3$) with of ^{n}BuMe$_2$S(OCHO) in the presence of **5a** in [D8]THF; (a): 10 min after mixing; b): 3 d at 70 °C.

Reaction of ^{n}BuMe$_2$Si(OCHO) and ^{n}BuMe$_2$Si(OCH$_3$) without presence of a catalyst:

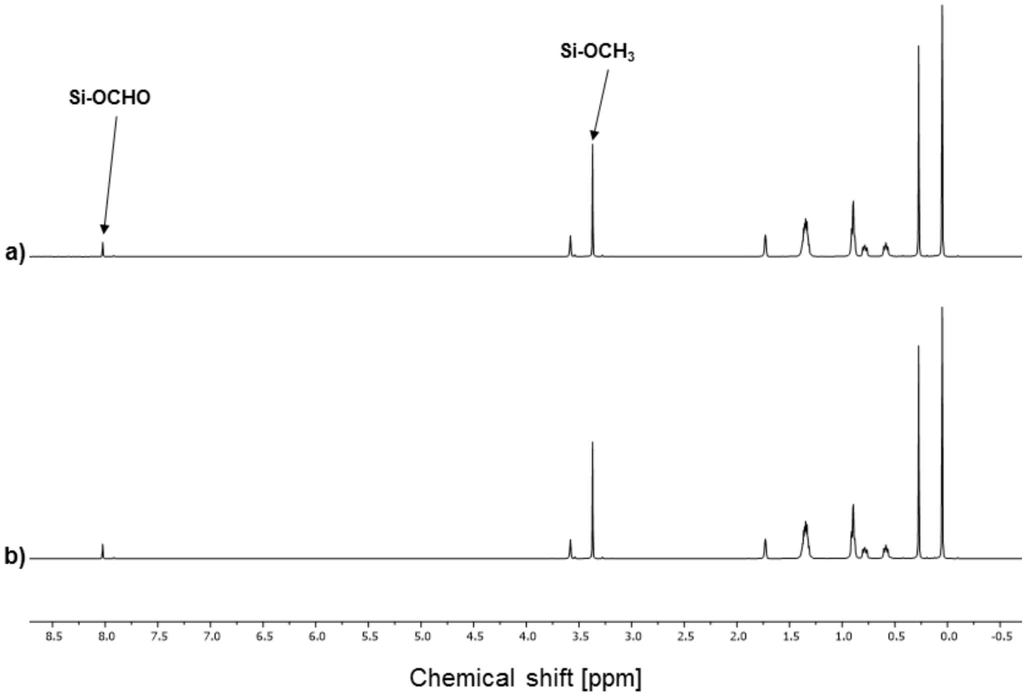


Figure S136: ^{1}H NMR spectra of ^{n}BuMe$_2$Si(OCH$_3$) of ^{n}BuMe$_2$Si(OCHO) in [D8]THF; (a): 10 min after mixing; b): 7 d at 70 °C.

Single Crystal X-ray Diffraction

X-ray diffraction data were collected at 100 K on an Eulerian 4-circle diffractometer STOE STADIVARI in ω-scan mode with Cu-Kα radiation (**2a**, **2b**, **3a**, **4a**, **4c**, **5a**, **6a**) or with Mo-Kα radiation (**7a**). The structures were solved by direct methods using SHELXT[S9] and all refinements were carried out against F^2 with SHELXL[S10] as implemented in the program system Olex2.[S11] The packing of **2b** contains CH_2Cl_2, the packing of **3a** contains co-crystallized *n*-hexane, the packing of **4a** contains co-crystallized CH_2Cl_2, and the packing of **4c** contains co-crystallized *n*-pentane. The co-crystallized solvent in **6a** could not be modelled reasonably well; in this case the routine "solvent mask" as implied in Olex2 was used. The molecular cation in **2b** shows crystallographic $\bar{1}$ symmetry, the molecular cation in **6a** shows crystallographic C_2 symmetry with the C_2 axis through the atoms C1 and C2, and the molecule **7a** shows crystallographic C_2 symmetry with the C_2 axis through the metal atom Zn1. The packing of **3a** contains two crystallographically independent molecules, of which one $C_{12}H_{35}N_4Zn_2$ unit is disordered (involving the atoms Zn4, N8, C54 and C55). The disorder was resolved by using split positions, also for the for CF_3 groups involving atoms F22, F23 and F24 in **2a**, F13, F14 and F15 in **2b**, F10, F11, F12 and F13, F14 and F15 in **3a**. Further disorder that was resolved involved the carbon atoms C10 and C11, the fluorine atoms F1, F2, F3, F4, F5, F6, F7, F8, F9, F10, F12, F22, F23, F24, F40, F41, F42, F44, F45 in **4a**, the fluorine atoms F46, F47 F48 in **4c**, as well as the fluorine atoms F22, F23, F24 in **5a** and the carbon atoms C4, C5, C6, C7, C8 in **6a**. The carbon atoms of the co-crystallized solvent molecule *n*-pentane in **4c** (C88 – C91) were also refined with split positions. All non-hydrogen atoms were refined with anisotropic displacement parameters. Only the disordered atoms C54B, C55B, C56B in **3a**, F46, F47, F48 in **4c**, C4, C5, C6, C7, C8 in **6a**, as well as those of the solvent molecule *n*-pentane in **4c** (C88 – C91) were refined with isotropic displacement parameters, because attempted refinement with anisotropic displacement parameters did not lead to physically meaningful values. The reflections 2 0 0, 2 0 2, 2 0 4 and 1 0 4 in **2a**, as well as 1 0 1 in **4a** were omitted from the refinement, because they were most likely affected by the beam stop. The hydrogen atoms were included in calculated positions and treated as riding throughout the refinement. Only the hydride atoms H1 in **2a**, H1 in **2b**, H1, H2 and H3 in **3a**, as well as H1, H2, H3 and H4 in **4a** were located in a Fourier difference map and were refined with isotropic displacement parameters. For the refinement of the anisotropic displacement parameters of the fluorine atoms of disordered CF_3 groups, restraints were used (F13, F14 and F15 in **2b**, F10, F13, F14, F15, F46 and F47 in **3a**, F1, F2, F3, F4, F5, F6, F9, F10, F11, F12, F22, F23, F24, F40, F41, F42, F44, F45 in **4a**). Restraints were also used in the refinement of the anisotropic displacement parameters of Zn4 in **3a**. Distance restraints were employed in the refinement of **3a** (involving the carbon atoms C53, C54, C89, C90, C91, C92, C93 and C94), in the refinement of **4c** (involving the fluorine atoms F46, F47, F48 and the carbon atoms of the co-crystallized solvent molecule *n*-pentane (C87 – C91)) and in the rerfinement of **6a** (involving the nitrogen atoms N1, N2 and the carbon atoms C7 and C8). Refinement results are given in Tables S1 – S3. Graphical representations were performed with the program DIAMOND.[S12] CCDC 2022679 – 2022686 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data of **2a**, **2b** and **3a**.

	2a	**2b**	**3a**
formula	$C_{10}H_{25}N_2OZn$, $C_{32}H_{12}BF_{24}$	$C_{10}H_{25}N_2Zn$, $C_{32}H_{12}BF_{24}$, CH_2Cl_2	$2(C_{12}H_{35}N_4Zn_2)$, $2(C_{32}H_{12}BF_{24})$, C_6H_{14}
Fw / g·mol^{-1}	1117.91	1186.84	2544.98
cryst. color, habit	colorless plate	colorless plate	colorless block
crystal size / mm	0.05 × 0.11 × 0.22	0.08 × 0.14 × 0.21	0.15 × 0.21 × 0.33
crystal system	orthorhombic	triclinic	triclinic
space group	$Pbca$	$P\bar{1}$	$P\bar{1}$
a / Å	18.8785(3)	13.7238(4)	12.6330(2)
b / Å	19.1191(3)	13.7498(5)	18.7331(4)
c / Å	25.6643(4)	13.8331(5)	23.7463(4)
α / °		79.572(3)	89.246(2)
β / °		67.574(3)	87.985(2)
γ / °		85.890(3)	80.892(2)
V / Å^3	926.3(3)	2373.03(15)	5545.24(18)
Z	8	2	2
d_{calc} / Mg·m^{-3}	1.603	1.661	1.524
μ(CuKα) / mm^{-1}	1.963	2.950	2.130
F(000)	4496	1192	2580
θ range / °	4.63, 72.17	3.48, 72.00	3.55, 71.99
index ranges	$-23 \leq h \leq 15$, $-22 \leq k \leq 19$, $-31 \leq l \leq 26$	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-17 \leq l \leq 12$	$-15 \leq h \leq 11$, $-22 \leq k \leq 19$, $-29 \leq l \leq 26$
refln.	33170	20641	54441
independ. reflns (R_{int})	8754 (0.0401)	8723 (0.0238)	20267 (0.0186)
observed reflns	6570	7291	15543
data/ restr./ param.	8754 / 0 / 677	8723 / 42 / 693	20267 / 77 / 1549
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0558, 0.1508	0.0547, 0.1416	0.0546, 0.1515
R_1, $wR2$ (all data)	0.0720, 0.1604	0.0658, 0.1512	0.0682, 0.1574
GooF on F^2	1.019	1.049	1.078
largest diff. peak, hole / e·Å^3	0.980, -0.795	0.647, -0.960	2.287, -1.089
CCDC number	2022679	2022680	2022681

Table S2. Crystallographic data of **4a**, **4c** and **5a**.

	4a	**4c**	**5a**
formula	$C_{18}H_{52}N_6Zn_3$, $2(C_{32}H_{12}BF_{24})$, CH_2Cl_2	$2(C_{22}H_{56}N_6Zn_3)$, $4(C_{32}H_{12}BF_{24})$, C_5H_{12}	$C_{15}H_{35}N_4O_6Zn_2$, $C_{32}H_{12}BF_{24}$
Fw /g·mol^{-1}	2360.14	4726.72	1361.43
cryst. color, habit	colorless plate	colorless plate	colorless plate
crystal size / mm	0.04 × 0.18 × 0.34	0.07 × 0.28 × 0.45	0.04 × 0.16 × 0.33
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	13.6357(4)	12.6823(12)	10.4089(3)
b / Å	17.9663(4)	17.7306(16)	16.4176(4)
c / Å	21.9342(5	23.497(3)	16.7899(4)
α / °	71.9835(17)	96.087(8)	75.5669(19)
β / °	76.0546(19)	91.887(9)	82.161(2)
γ / °	71.3749(18)	103.611(7)	89.192(2)
V / Å^3	4781.7(2)	5097.1(9)	2752.10(13)
Z	2	1	2
d_{calc} / Mg·m^{-3}	1.639	1.540	1.643
μ(CuKα) / mm^{-1}	2.672	2.037	2.278
F(000)	2368	2382	1372
θ range / °	2.15, 72.09	2.58, 71.41	2.64, 71.89
index ranges	$-16 \leq h \leq 12$, $-22 \leq k \leq 21$, $-27 \leq l \leq 26$	$-15 \leq h \leq 15$, $-16 \leq k \leq 20$, $-28 \leq l \leq 27$	$-9 \leq h \leq 12$, $-19 \leq k \leq 20$, $-20 \leq l \leq 20$
refln.	50574	42734	24803
Independ. reflns (R_{int})	17716 (0.0490)	18149 (0.0223)	10009 (0.0175)
observed reflns	10530	14082	8299
data/ restr./ param.	17716 / 198 / 1528	18149 / 37 / 1346	10009 / 0 / 793
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0376, 0.0751	0.0779, 0.2149	0.0439, 0.1206
R_1, $wR2$ (all data)	0.0691, 0.0796	0.0946, 0.2277	0.0520, 0.1243
GooF on F^2	0.784	1.076	1.098
largest diff. peak, hole / e·Å^3	0.511, -0.543	2.140, -1.125	0.910, -0.762
CCDC number	2022682	2022683	2022684

Table S3. Crystallographic data of **6a** and **7a**.

	6a	**7a**
Formula	0.5($C_{14}H_{34}N_4O_4Zn_2$), $C_{32}H_{12}BF_{24}$ [+ solvent]	$C_8H_{18}N_2O_4Zn_3$
Fw /g·mol^{-1}	1089.92	271.61
cryst. color, habit	colorless rod	colorless plate
crystal size / mm	0.05 × 0.14 × 0.29	0.05 × 0.11 × 0.19
crystal system	monoclinic	monoclinic
space group	*C2/c*	*C2/c*
a / Å	24.289(5)	14.6808(19)
b / Å	14.3638(6)	7.1067(6)
c / Å	28.4787(6)	12.0225(16)
β / °	92.8825(18)	109.443(10)
V / Å^3	9923(3)	1182.8(3)
Z	8	4
d_{calc} / Mg·m^{-3}	1.459	1.525
μ(CuKα) / mm^{-1}	1.835	
μ(MoKα) / mm^{-1}		2.074
F(000)	4352	568
θ range / °	3.11, 72.02	2.94, 30.42
index ranges	$-29 \le h \le 29$, $-17 \le k \le 13$, $-35 \le l \le 34$	$-20 \le h \le 17$, $-9 \le k \le 9$, $-15 \le l \le 16$
refln.	48330	4076
Independ. reflns (R_{int})	9500 (0.0297)	1600 (0.0672)
observed reflns	5854	857
data/ restr./ param.	9500 / 6 / 622	1600 / 0 / 71
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0638, 0.1873	0.0614, 0.1386
R_1, $wR2$ (all data)	0.0902, 0.1980	0.1087, 0.1499
GooF on F^2	1.05	0.863
largest diff. peak, hole / e·Å^3	1.210, -0.878	0.849, -1.276
CCDC number	2022685	2022686

DFT Calculations

Computational details: Zinc was treated with a Stuttgart–Dresden pseudopotential in combination with their adapted basis set.[S13] The basis set has been augmented by a set of polarization functions (*f* for Zn).[S14] All other atoms have been described with a 6–31G(d,p) double–ζ basis set.[S15] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[S16,S17] Geometry optimizations were carried out without any symmetry restrictions, the nature of the extrema (minimum) was verified with analytical frequency calculations. All these computations have been performed with the Gaussian 09[S18] suite of programs. The bonding situation was analyzed using the NBO technique.[S19]

[(TMEDA)ZnH(thf)]$^+$

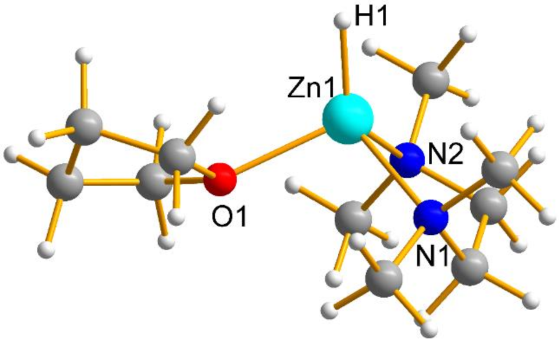
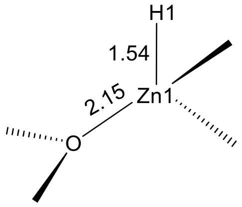


Figure S137: DIAMOND representation of the optimized molecular structure of [(TMEDA)ZnH(thf)]$^+$.



Natural Charge: Zn = 1.00
H = -0.39

Wiberg Bond Index: Zn1–H1: 0.77

Bond: (1.86963) BD(1) Zn1–H1

(25.52%) 0.5051*Zn1 *s*(38.53%)*p*1.53(58.77%)*d*0.07(2.70%)*f*0.00(0.00%)
(74.48%) 0.8630*H1 *s*(99.98%)*p*0.00(0.02%)

Analysis of the Bonding:
This is a classical terminal Zn–H bond as found in the two species presented below; Wiberg bond indices and bond description are similar (see below).

Optimized Molecular Coordinates

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$ZnC_{10}N_2H_{25}O$

Zn1	12.685256000	16.027308000	14.085514000
O1	13.983852000	17.490842000	14.973146000
N1	12.098397000	14.904403000	15.826862000
N2	10.659244000	16.771158000	14.084535000
C1	15.371290000	17.034615000	15.057001000
C2	13.958536000	18.906963000	14.630808000
C3	10.752106000	15.421711000	16.169726000
C4	13.007069000	15.039875000	16.982637000
C5	12.034342000	13.481237000	15.424661000
C6	9.954238000	15.766054000	14.919252000
C7	10.145781000	16.730676000	12.696366000
C8	10.466101000	18.129493000	14.630098000
C9	16.205604000	18.161411000	14.470382000
C10	15.382628000	19.397674000	14.838499000
H1	13.367513000	15.423531000	12.839856000
H2	15.450448000	16.095040000	14.503219000
H3	15.597854000	16.860766000	16.114316000
H4	13.225314000	19.393542000	15.278156000
H5	13.647844000	19.007108000	13.583858000
H6	10.885584000	16.312648000	16.790784000
H7	10.197263000	14.691068000	16.774832000
H8	13.986625000	14.632655000	16.723174000
H9	12.623692000	14.491476000	17.853231000
H10	13.121125000	16.094115000	17.242670000
H11	11.368965000	13.351021000	14.569143000
H12	11.675039000	12.857576000	16.254015000
H13	13.028740000	13.143008000	15.126962000
H14	9.805923000	14.870779000	14.307956000
H15	8.955626000	16.128606000	15.200091000
H16	10.669658000	17.474398000	12.092492000
H17	9.069541000	16.945475000	12.667951000
H18	10.328737000	15.746249000	12.260426000
H19	10.850273000	18.196837000	15.649818000
H20	9.401395000	18.399055000	14.637627000
H21	11.000288000	18.851040000	14.009261000
H22	17.216497000	18.179740000	14.883840000
H23	16.282991000	18.056548000	13.383370000
H24	15.545141000	19.674436000	15.885232000
H25	15.610297000	20.267082000	14.217443000

$[(TEEDA)Zn_2H_2]^{2+}$

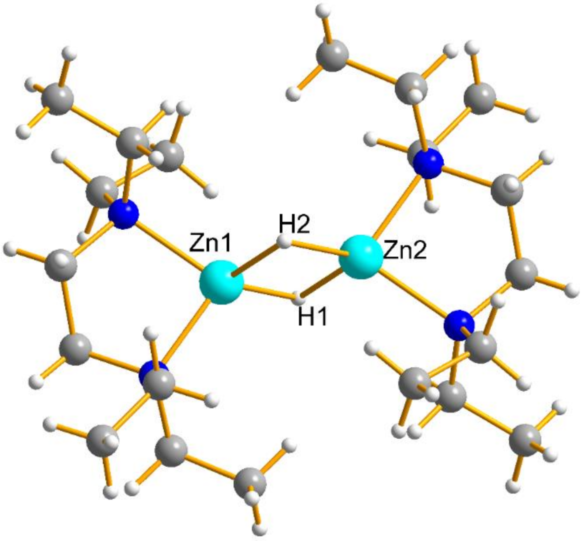
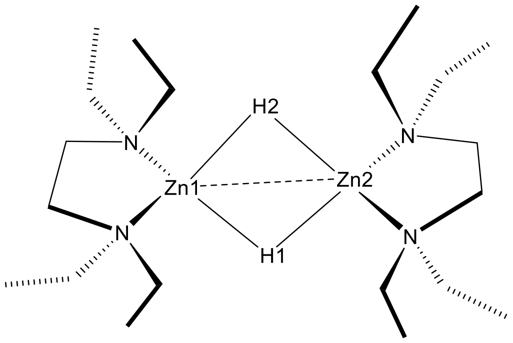


Figure S138: DIAMOND representation of the optimized molecular structure of $[(TEEDA)Zn_2H_2]^{2+}$.



Natural Charge:

Zn1 = 0.91761
Zn2 = 0.91761
H1 = -0.36259
H2 = -0.36259

Natural Electron Configuration:

Zn1	[core]4*s*(0.49)3*d*(9.97)4*p*(0.58)5*s*(0.01)4*d*(0.01)5*p*(0.01)5*d*(0.01)
Zn2	[core]4*s*(0.49)3*d*(9.97)4*p*(0.58)5*s*(0.01)4*d*(0.01)5*p*(0.01)5*d*(0.01)

Wiberg Bond Indices:

Zn1–Zn2: 0.2829
Zn1–H1: 0.3904
Zn1–H2: 0.3846
Zn2–H1: 0.3846
Zn2–H2: 0.3846
Zn1: 1.8583
Zn2: 1.8584
H1: 0.8720
H2: 0.8720

Bond:

1. (1.65185) BD(1) Zn2–H1

(18.26%) Zn2 *s*(32.49%)*p*2.02(65.73%)*d*0.05(1.77%)*f*0.00(0.00%)
(81.74%) H1 *s*(99.98%)*p*0.00(0.02%)

2. (1.65720) BD(1) Zn2–H2

(18.60%) Zn2 *s*(35.16%)*p*1.79(62.97%) *d*0.05(1.87%)*f*0.00(0.00%)
(81.40%) H2 *s*(99.98%)*p*0.00(0.02%)

Donation:

Donation from *s* orbitals Zn1 → Zn2: 9,02 kcal/mol
Donation from *s* orbitals of Zn2 → Zn1: 33,8 kcal/mol
Donation from *d* orbitals of Zn2 → Zn1: 2,74 kcal/mol
Donation from the bond Zn2–H1 → Zn1: 283,91 kcal/mol
Donation from the bond Zn2–H2 → Zn1: 266,48 kcal/mol

Optimized Molecular Coordinates

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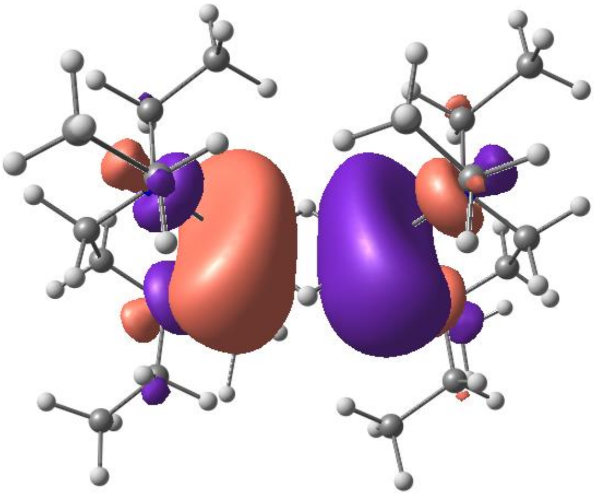
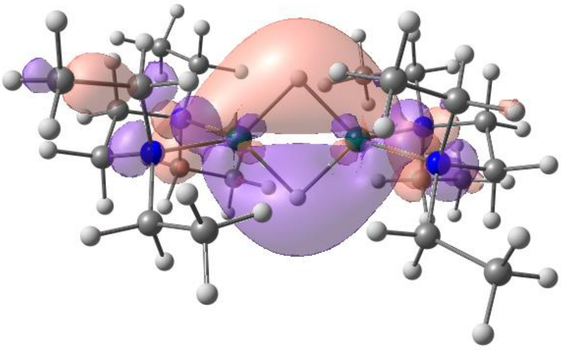
$C_{20}H_{50}N_4Zn_2$

Zn1	13.77827	12.95281	0.20210
Zn2	15.64070	14.47647	-0.20210
N1	11.73827	13.16377	0.20550
N2	13.55915	10.90184	0.23324
N3	17.68070	14.26551	-0.20550
N4	15.85982	16.52744	-0.23324
C1	11.30515	11.81773	0.70476
C2	11.31336	13.40716	-1.21033
C3	11.17130	14.19353	1.13720
C4	14.32291	10.26631	-0.89514
C5	12.08335	10.70665	0.03026
C6	13.94524	10.30214	1.55578
C7	18.11382	15.61154	-0.70476
C8	18.10561	14.02212	1.21033
C9	18.24766	13.23575	-1.13720
C10	15.09606	17.16297	0.89514
C11	17.33562	16.72263	-0.03026
C12	15.47373	17.12714	-1.55578
C13	9.82142	13.35100	-1.47761
C14	11.55618	15.60680	0.78419
C15	13.95529	8.81708	-1.20907
C16	15.32498	10.69973	2.03360
C17	19.59755	14.07827	1.47761
C18	17.86279	11.82247	-0.78419
C19	15.46368	18.61219	1.20907
C20	14.09399	16.72955	-2.03360
H1	14.84034	14.03522	1.65285
H2	14.57863	13.39406	-1.65285
H3	10.35854	11.69917	0.53078
H4	11.44058	11.77010	1.66420
H5	11.74972	12.75053	-1.77641
H6	11.63761	14.28201	-1.47887
H7	11.47454	14.00169	2.03865
H8	10.20296	14.12252	1.13090
H9	15.26752	10.30327	-0.68459
H10	14.18112	10.79749	-1.69572

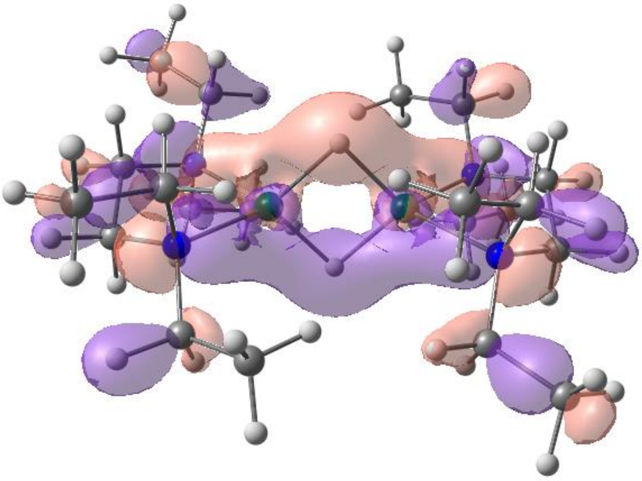
H11	11.81515	9.85022	0.39966
H12	11.88497	10.69975	-0.91909
H13	13.90780	9.33523	1.48265
H14	13.29569	10.57261	2.22272
H15	19.06042	15.73010	-0.53078
H16	17.97839	15.65917	-1.66420
H17	17.66925	14.67875	1.77641
H18	17.78136	13.14726	1.47887
H19	17.94443	13.42759	-2.03865
H20	19.21601	13.30676	-1.13090
H21	14.15144	17.12600	0.68459
H22	15.23785	16.63178	1.69572
H23	17.60382	17.57906	-0.39966
H24	17.53399	16.72952	0.91909
H25	15.51117	18.09404	-1.48265
H26	16.12328	16.85667	-2.22272
H27	9.65502	13.53425	-2.40553
H28	9.37460	14.00474	-0.93674
H29	9.49121	12.47564	-1.26076
H30	11.16026	15.84727	-0.05673
H31	12.51214	15.67094	0.71737
H32	11.24289	16.20508	1.46752
H33	14.52924	8.48454	-1.90248
H34	13.04146	8.77449	-1.50156
H35	14.06384	8.28145	-0.41857
H36	15.98276	10.39429	1.40322
H37	15.49464	10.29998	2.88966
H38	15.37410	11.65492	2.11051
H39	19.76395	13.89503	2.40553
H40	20.04437	13.42454	0.93674
H41	19.92776	14.95364	1.26076
H42	18.25871	11.58200	0.05673
H43	16.90682	11.75834	-0.71737
H44	18.17608	11.22420	-1.46752
H45	14.88973	18.94474	1.90248
H46	16.37751	18.65479	1.50156
H47	15.35513	19.14783	0.41857
H48	13.43620	17.03499	-1.40322
H49	13.92433	17.12930	-2.88966
H50	14.04487	15.77436	-2.11051



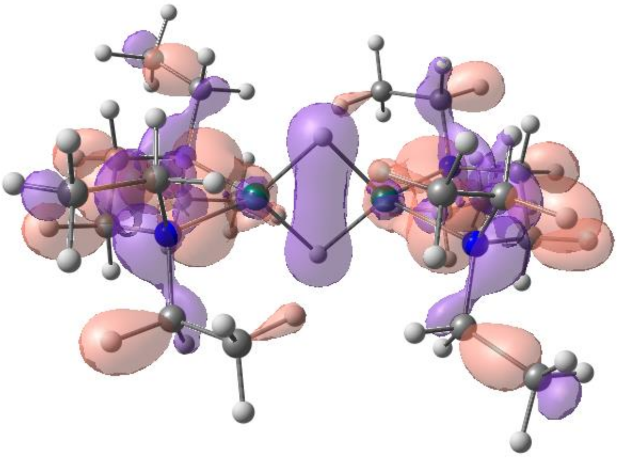
LUMO, E = -0.2414



HOMO$_{-1}$, E = -0.4921



HOMO$_{-2}$, E = -0.4948



HOMO$_{-3}$, E = -0.5082

The HOMO is not shown because it involves mainly the interaction between the metal centers and the ligands TEEDA.

$[(TMEDA)_2Zn_2H_3]^+$

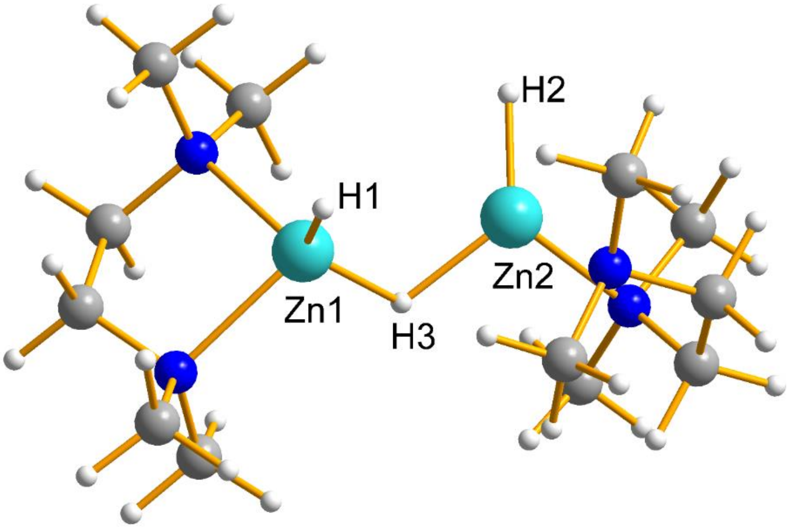
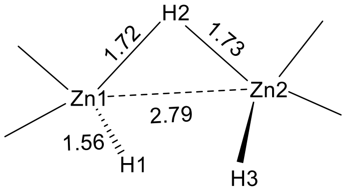


Figure S139: DIAMOND representation of the optimized molecular structure of $[(TMEDA)_2Zn_2H_3]^+$.



Natural Charge:
Zn1: 0.76
Zn2: 0.76
H1: -0.36
H2: -0.40
H3: -0.36

Wiberg Bond Indices:
Zn1–H1: 0.76
Zn1–H2: 0.37
Zn2–H2: 0.37
Zn2–H3: 0.76

Bond:
(1.89755) BD(1) Zn1–H1
(28.71%) 0.5358*Zn1 *s*(43.09%)*p*1.29(55.39%)*d*0.04(1.52%)*f*0.00(0.00%)
(71.29%) 0.8444*H1 *s*(99.98%)*p*0.00(0.02%)

(1.90166) BD(1) Zn2–H3
(28.87%) 0.5373*Zn2 *s*(43.84%) *p*1.25(54.59%)*d*0.04(1.57%)*f*0.00(0.00%)
(71.13%) 0.8434*H3 *s*(99.98%)*p*0.00(0.02%)

Second Order Study:
Donation from lone pair of the bridging H2 to an empty *sp* orbital (7.6%*s*, 91.3%*p*) at Zn1: 81.98 kcal/mol
Donation from lone pair of the bridging H2 to an empty *sp* orbital (7.6%*s*, 91.3%*p*) at Zn2: 79.18 kcal/mol

Analysis of the Bonding:
Donation from the *s* lone pair of the bridging H2 to the empty *sp* orbitals of Zn1 and Zn2 leads to a 3*c*-2*e* bond between Zn1–H2–Zn2. In line with a 3*c*-2*e* bond, the Wiberg bond indices of 0.37 correspond to half of that of a normal 2*c*-2*e* Zn–H bond.

Optimized Structure

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$Zn_2C_{12}N_4H_{35}$

Zn1	2.223870000	0.004002000	14.511442000
Zn2	-0.038889000	-1.433080000	15.318682000
N1	4.272935000	0.324455000	15.187741000
N2	1.900508000	2.052461000	15.170133000
N3	-0.556291000	-2.880354000	16.876005000
N4	0.056049000	-3.167495000	14.020782000
C1	4.373963000	1.800822000	15.225822000
C2	4.546765000	-0.265434000	16.509786000
C3	5.221956000	-0.223953000	14.199631000
C4	3.147557000	2.433332000	15.870522000
C5	0.738136000	2.230560000	16.060958000
C6	1.703976000	2.866867000	13.952487000
C7	-0.331898000	-4.200425000	16.246698000
C8	-1.982028000	-2.683777000	17.205955000
C9	0.249996000	-2.745469000	18.100976000
C10	-0.709245000	-4.188676000	14.770000000
C11	-0.614124000	-2.852068000	12.742330000
C12	1.429506000	-3.626939000	13.744394000
H1	2.090063000	-0.245331000	12.973405000
H2	1.590304000	-1.031965000	15.727508000
H3	-1.172288000	-0.404584000	15.012871000
H4	5.279752000	2.116324000	15.764625000
H5	4.479442000	2.150710000	14.194292000
H6	3.836613000	0.104705000	17.251174000
H7	5.567363000	-0.032022000	16.844988000
H8	4.435150000	-1.350171000	16.450727000
H9	5.136828000	-1.312717000	14.178934000
H10	6.258026000	0.042349000	14.451136000
H11	4.980746000	0.157551000	13.205358000
H12	3.059896000	2.106030000	16.910988000
H13	3.265599000	3.526524000	15.891745000
H14	-0.169282000	1.913229000	15.544038000
H15	0.631299000	3.280260000	16.368233000
H16	0.858588000	1.609876000	16.951898000
H17	2.544478000	2.744003000	13.267163000
H18	1.598073000	3.930793000	14.206665000
H19	0.803405000	2.529842000	13.435937000
H20	0.727491000	-4.449413000	16.361008000
H21	-0.900953000	-4.984295000	16.767637000
H22	-2.126028000	-1.678034000	17.605366000
H23	-2.318550000	-3.420295000	17.949221000
H24	-2.598631000	-2.772573000	16.310131000
H25	1.311091000	-2.836486000	17.857998000
H26	-0.015276000	-3.510790000	18.843909000

H27	0.077800000	-1.760966000	18.542360000
H28	-1.772555000	-3.956006000	14.655767000
H29	-0.552766000	-5.188632000	14.339482000
H30	-1.613918000	-2.458366000	12.937318000
H31	-0.690921000	-3.743601000	12.104665000
H32	-0.038976000	-2.086607000	12.217291000
H33	1.971049000	-2.834392000	13.223490000
H34	1.423721000	-4.530536000	13.118266000
H35	1.956279000	-3.847955000	14.675059000

$[(TMEDA)_3Zn_3H_4]^{2+}$

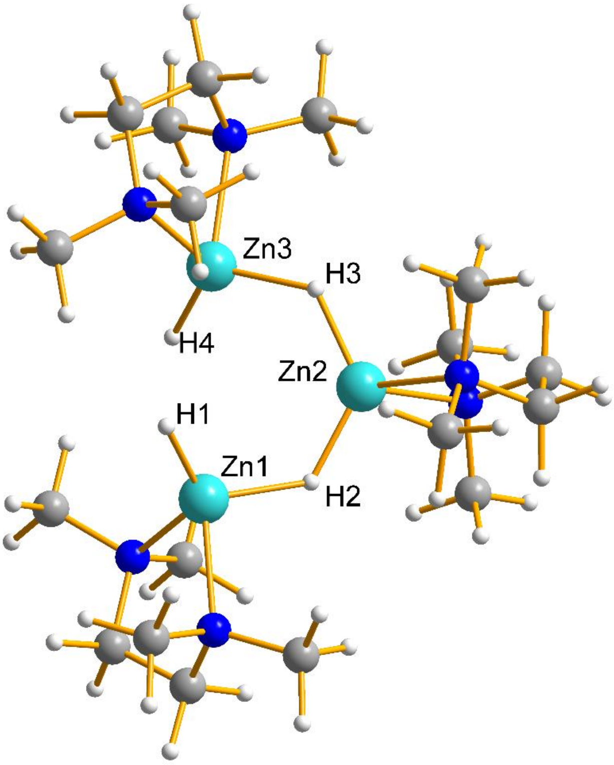
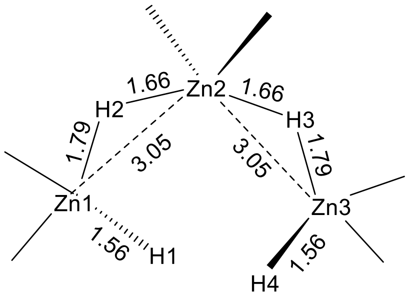


Figure S140: DIAMOND representation of the optimized molecular structure of $[(TMEDA)_3Zn_3H_4]^{2+}$.



Natural Charge:

Zn1= 0.87
Zn2= 0.97
Zn3= 0.87
H1= -0.39
H2= -0.45
H3= -0.45
H4= -0.39

Wiberg Bond Indices:

Zn1–H1: 0.70
Zn1–H2: 0.29
Zn2–H2: 0.40
Zn2–H3: 0.40
Zn3–H3: 0.29
Zn3–H4: 0.70
Zn1–Zn2: 0.12
Zn2–Zn3: 0.12

NBO Analysis:

(1.92788) BD(1) Zn1–H1
(29.32%) 0.5415*Zn1 *s*(74.12%)p0.33(24.57%)*d*0.02(1.31%)*f*0.00(0.00%)
(70.68%) 0.8407*H1 *s*(99.98%)*p*0.00(0.02%)

(1.73783) BD(1) Zn2–H2
(17.17%) Zn2 *s*(43.41%)*p*(55.32%)*d*(1.27%)
(82.83%) H2 *s*(99.99%)*p*(0.01%)

A bond exists between Zn2 and H2.

Second Order Study for H2:

→ Donation from the Zn2–H2 bond to the empty *sp* orbital (25%s, 75%p) at Zn1: 75.58 kcal/mol

(1.92839) BD(1) Zn3–H4
(29.32%) 0.5414*Zn3 *s*(74.13%)*p*0.33(24.56%)*d*0.02(1.31%)*f*0.00(0.00%)
(70.68%) 0.8407*H4 *s*(99.98%)*p*0.00(0.02%)

(1.73764) BD(1) Zn2–H3
(17.21%) Zn2 *s*(43.57%)*p*(55.14%)*d*(1.29%)
(82.79%) H3 *s*(99.99%)*p*0.00(0.01%)

A bond exists between Zn2 and H3.

Second Order Study for H3:

→ Donation from the Zn2–H3 bond to the empty *sp* orbital (25%s, 75%p) at Zn3: 75.82 kcal/mol.

Analysis of the Bonding:

The structure can be defined as an adduct between a neutral ZnH_2 fragment and two $[ZnH]^+$ cations. The two Zn-H bonds of the Zn_3H_2 (Zn2–H1 and Zn2–H3) moiety are weakened because of the donation to the empty *sp* orbitals of the Zn cations (Zn1 and Zn3).

Optimized Structure

79

$Zn_3C_{18}N_6H_{52}$

Zn1	21.689880000	7.529445000	6.452191000
Zn2	24.109301000	9.252877000	5.767868000
Zn3	21.808262000	11.100681000	4.986130000
N1	20.596890000	6.636427000	4.836727000
N2	21.844086000	5.513451000	7.224777000
N3	25.708618000	9.024864000	4.348404000
N4	25.652735000	9.412606000	7.257376000

N5	20.707132000	12.053347000	6.563246000
N6	22.089433000	13.103961000	4.217857000
C1	20.282709000	5.263915000	5.310781000
C2	21.392071000	6.591890000	3.591660000
C3	19.341749000	7.378322000	4.575926000
C4	21.444846000	4.656655000	6.082882000
C5	20.885315000	5.389936000	8.346859000
C6	23.185082000	5.125359000	7.700116000
C7	25.545956000	9.869206000	3.145897000
C8	26.912147000	9.448216000	5.109871000
C9	25.824786000	7.611503000	3.927140000
C10	25.802962000	10.818644000	7.692037000
C11	25.405359000	8.569468000	8.446345000
C12	26.872995000	8.948681000	6.547699000
C13	21.457446000	12.053062000	7.836635000
C14	20.486278000	13.441755000	6.082520000
C15	19.404741000	11.381173000	6.776677000
C16	21.168401000	13.273692000	3.070638000
C17	21.704917000	13.981912000	5.348443000
C18	23.460729000	13.421480000	3.778033000
H1	21.117649000	8.644068000	7.383256000
H2	23.332935000	7.788726000	5.794798000
H3	23.408541000	10.754396000	5.703808000
H4	21.211846000	10.016324000	4.034589000
H5	20.019356000	4.615140000	4.464477000
H6	19.395372000	5.324762000	5.947377000
H7	21.634864000	7.612637000	3.288524000
H8	20.827355000	6.105225000	2.785486000
H9	22.321117000	6.040864000	3.752751000
H10	18.760302000	7.455292000	5.497402000
H11	18.738245000	6.869372000	3.813218000
H12	19.587046000	8.383587000	4.228105000
H13	21.173338000	3.649130000	6.428030000
H14	22.316853000	4.546142000	5.430480000
H15	21.190630000	6.053792000	9.157856000
H16	20.851411000	4.358041000	8.720275000
H17	19.882789000	5.685823000	8.034095000
H18	23.914816000	5.254366000	6.897072000
H19	23.203502000	4.078119000	8.029953000
H20	23.466625000	5.755961000	8.546371000
H21	24.648882000	9.563399000	2.602786000
H22	26.410375000	9.775779000	2.475789000
H23	25.440835000	10.914821000	3.441767000
H24	26.951947000	10.541422000	5.089120000
H25	27.826478000	9.087805000	4.619046000
H26	25.942487000	6.959063000	4.794189000
H27	26.685473000	7.472921000	3.260116000
H28	24.916826000	7.315899000	3.398145000
H29	25.985250000	11.469511000	6.835036000
H30	26.636621000	10.921328000	8.398665000
H31	24.883449000	11.146320000	8.180609000
H32	24.497172000	8.906984000	8.950728000
H33	26.242284000	8.627083000	9.154218000
H34	25.273910000	7.530006000	8.139498000
H35	26.876727000	7.854766000	6.569881000
H36	27.776782000	9.279179000	7.077549000
H37	21.634779000	11.020307000	8.144562000
H38	20.890109000	12.567526000	8.623512000
H39	22.419618000	12.554534000	7.712014000
H40	20.233587000	14.104276000	6.921287000

H41	19.617727000	13.431485000	5.417941000
H42	18.852621000	11.338864000	5.835155000
H43	18.803657000	11.920605000	7.520121000
H44	19.581943000	10.363087000	7.128651000
H45	21.461499000	12.593746000	2.268554000
H46	21.196537000	14.305371000	2.696006000
H47	20.144311000	13.029039000	3.356840000
H48	21.502667000	15.003705000	4.997708000
H49	22.561193000	14.040372000	6.027968000
H50	24.160697000	13.262532000	4.601980000
H51	23.540305000	14.464174000	3.442945000
H52	23.733835000	12.771689000	2.943645000

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