

Terminal Hydrido Zinc Cation

Raju Chambehahalli,^a Alex P. Andrews,^a Florian Ritter,^b Jun Okuda^b and Ajay Venugopal ^{*a}

^a School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram,
Vithura, Thiruvananthapuram 695551, India.

^b Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany.

Supporting Information

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1. Synthetic Methods, Procedures and Characterisation

General Methods: All manipulations were performed under argon atmosphere using standard Schlenk and glove-box techniques.^[1] The starting materials, Me₆tren ^[3] and [Et₃NH][B{C₆H₃-3,5-(CF₃)₂}]₄ ^[4] were prepared according to the literature procedures, Et₂Zn was procured from Sigma Aldrich and used as received. (C₆H₅)₂CO was procured from Sigma Aldrich and dried under vacuum (10⁻³ mbar) at room temperature for 24 h. *N,N'*-Diisopropylcarbodiimide (DIC) was procured from Sigma Aldrich, distilled under vacuum (10⁻³ mbar) at 60 °C and used after drying on molecular sieves (3 Å) for one day. The solvents used for the synthesis and NMR experiments were dried, distilled and degassed prior to use by standard methods.^[2] NMR measurements were performed on Bruker 500 MHz spectrometer. The chemical shifts (δ ppm) in ¹H and ¹³C NMR spectra were referenced to the residual proton signals of the deuterated solvents. ¹⁹F & ¹¹B NMR spectra were referenced to CFCI₃ and NaBH₄ in D₂O respectively. Analytically pure compounds for elemental analysis were obtained by repeated crystallisation of the products. Elemental analyses were performed on Elemental Vario Micro Cube.

Compound 1

[Et₃NH][B{C₆H₃-3,5-(CF₃)₂}]₄ (0.375 mmol, 0.362 g) was added to a diethyl ether solution of Me₆tren (0.375 mmol, 0.100 mL). The reaction mixture was stirred for 2 min. 1 M solution of Et₂Zn in heptane (0.375 mmol, 0.375 mL) was slowly added to the reaction mixture using a syringe at room temperature then stirred for 1 min. All the volatiles were evaporated under vacuum (10⁻³ mbar) at room temperature to get a colourless powder of **1**, which was further purified by crystallisation using THF and *n*-pentane. Yield 0.410 g (93%); elemental analysis for C₄₆H₄₇BF₂₄N₄Zn: C, 46.50; H, 3.99; N, 4.72; Found: C, 46.48; H, 3.89; N, 4.60; ¹H NMR (CD₂Cl₂, 500 MHz): δ 0.22 (q, 2H, ³J_{H-H} = 10 Hz, CH₂Me₃), 1.28 (t, 3H, ³J_{H-H} = 10 Hz, CCH₃), 2.42 (s, 18H, NCH₃), 2.68 (t, 6H, ³J_{H-H} = 5 Hz, NCH₂), 2.89 (t, 6H, ³J_{H-H} = 5 Hz, NCH₂), 7.57 (s, 4H, *p*-C₆H₃) 7.79 (br, 8H, *o*-C₆H₃) (Figure S1); ¹³C{¹H} NMR (CD₂Cl₂, 126 MHz): δ -1.7 (CH₂Me), 13.9 (CCH₃), 46.7 (NCH₃), 52.1 (NCH₂), 56.5 (NCH₂), 118.0 (t, *p*-C), 128.4 (q, CF₃) 129.3 (m, *m*-C), 135.4 (s, *o*-C), 162.5 (q, *i*-C) (Figure S2); ¹¹B NMR (CD₂Cl₂, 128 MHz): δ -6.48 (Figure S3); ¹⁹F NMR (CD₂Cl₂, 471 MHz): δ -62.80 (Figure S4).

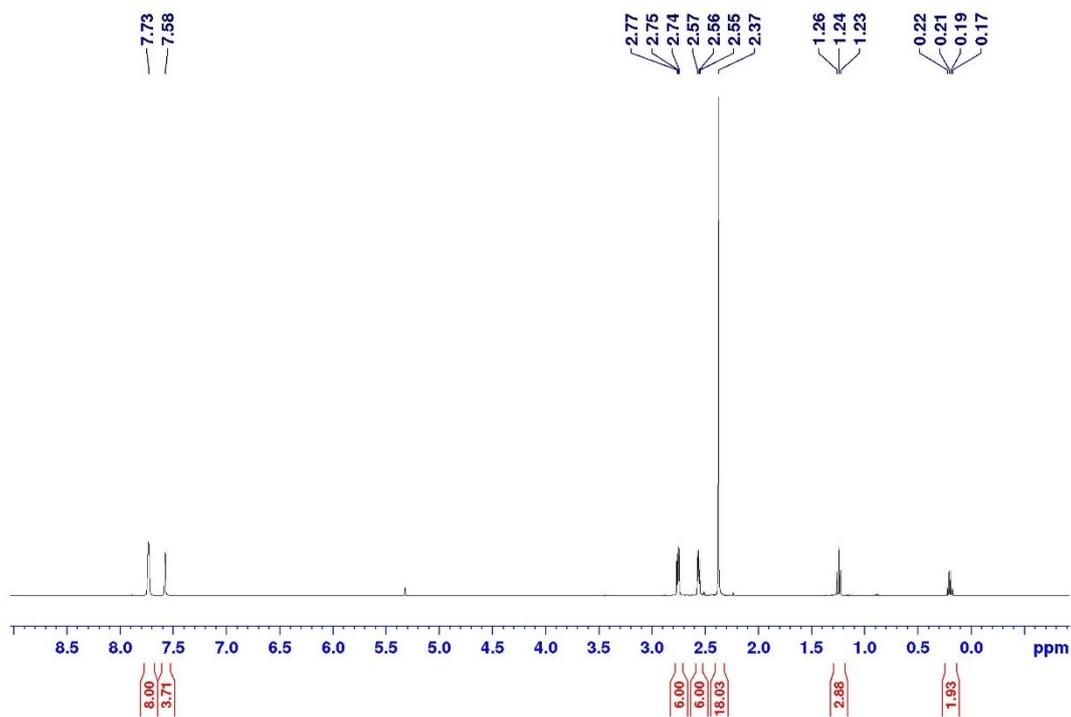


Figure S1. ^1H NMR spectrum of **1** recorded in CD_2Cl_2 .

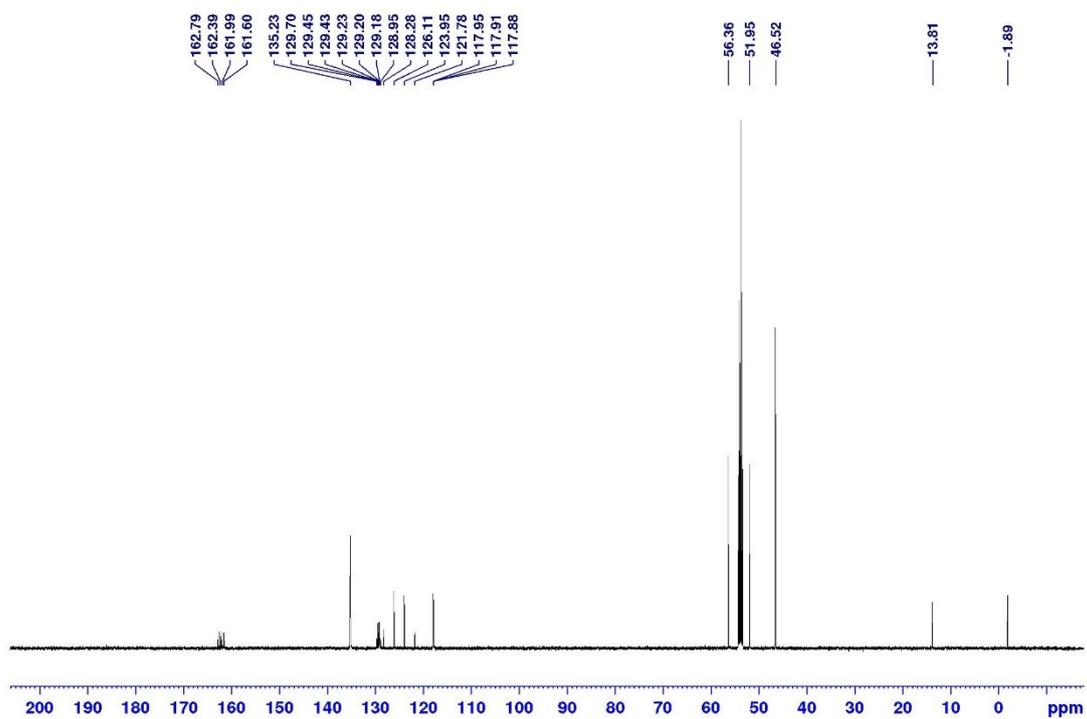


Figure S2. ^{13}C NMR spectrum of **1** recorded in CD_2Cl_2 .

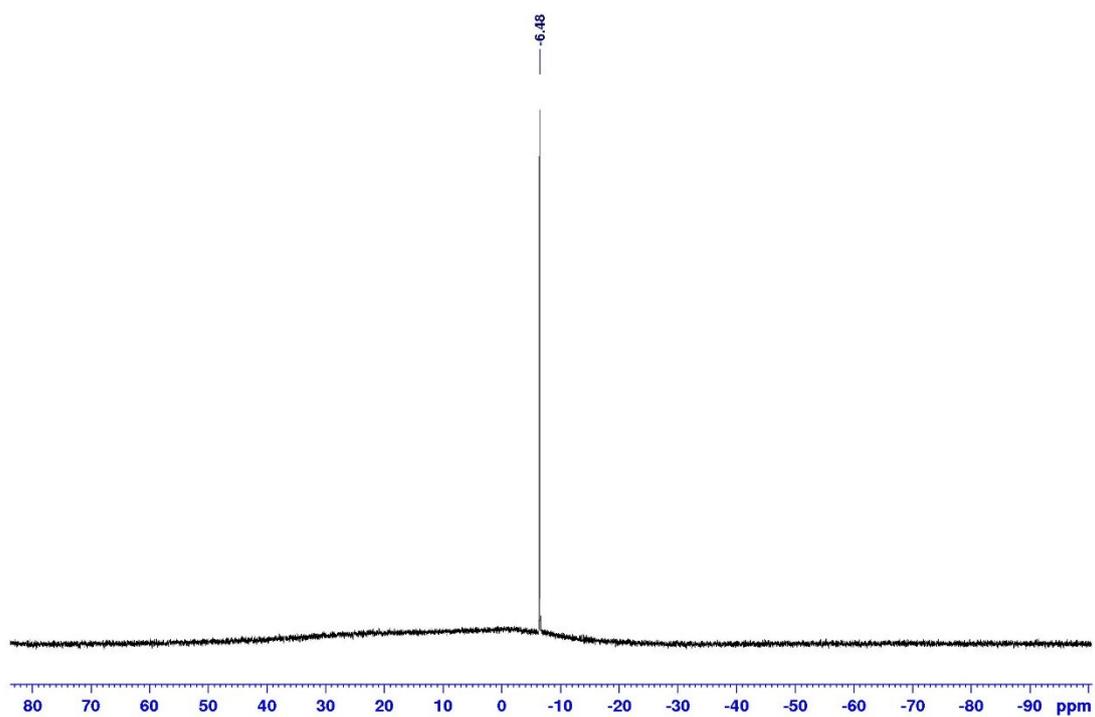


Figure S3. ^{11}B NMR spectrum of **1** recorded in CD_2Cl_2 .

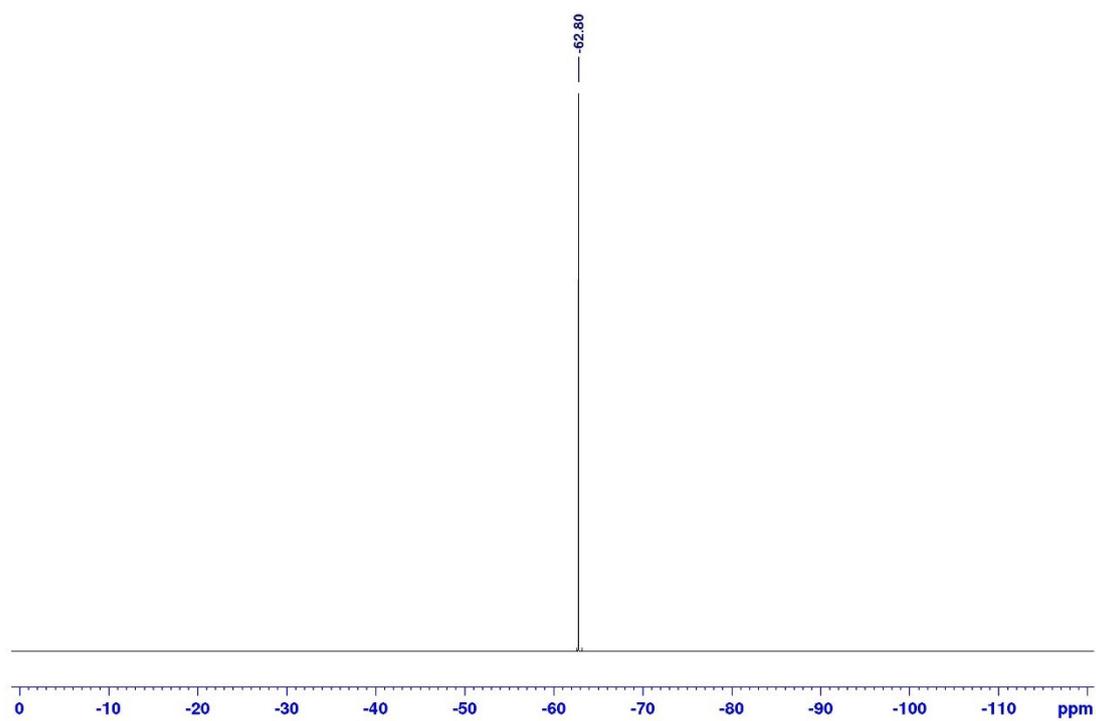


Figure S4. ^{19}F NMR spectrum of **1** recorded in CD_2Cl_2 .

[(Me₆tren)ZnOSiPh₃][B{C₆H₃(CF₃)₂]₄]

Compound **1** in 2 mL of diethylether (0.084 mmol, 0.100 g) was added to a solution of Ph₃SiOH in 2 mL diethylether (0.084 mmol, 0.023 g.). The reaction mixture was allowed to stir at room temperature for 24 h. All the volatiles were evaporated under vacuum (10⁻³ mbar) at room temperature to get a colourless powder of [(Me₆tren)ZnOSiPh₃][B{C₆H₃(CF₃)₂]₄]. Compound was further purified by crystallising at -30 °C in diethylether upon *n*-hexane layering. Yield: 0.110 g (91%); elemental analysis for C₆₂H₅₇BF₂₄N₄OSiZn: C, 51.92; H, 4.01; N, 3.91; found: C, 51.34; H, 3.98; N, 3.87; ¹H NMR (CD₂Cl₂, 500 MHz): δ 2.38 (s, 18H, NCH₃), 2.56 (t, 6H, ³J_{H-H} = 5 Hz, NCH₂), 2.72 (t, 6H, ³J_{H-H} = 5 Hz, NCH₂), 7.35 (m, 9H, *p*-, *m*-C₆H₅), 7.55 (s, 4H, *p*-C₆H₃), 7.57 (d, 6H, ³J_{H-H} = 5 Hz, *o*-C₆H₅), 7.72 (br, 8H, *o*-C₆H₃) (Figure S5); ¹³C{¹H} NMR (CD₂Cl₂, 126 MHz): δ 47.1 (NCH₃), 49.9 (NCH₂), 56.4 (NCH₂), 117.9 (t, *p*-C), 126.1 (q, CF₃), 129.3 (m, *m*-C), 135.2 (s, *o*-C), 162.2 (q, *i*-C), 128.0 (s, *p*-SiPh), 129.5 (s, *m*-SiPh), 135.5 (s, *o*-SiPh), 141.4 (s, *i*-SiPh) (Figure S6); ¹¹B NMR (CD₂Cl₂, 128 MHz): δ -6.56 (Figure S7); ¹⁹F NMR (CD₂Cl₂, 471 MHz): δ -62.80 (Figure S8).

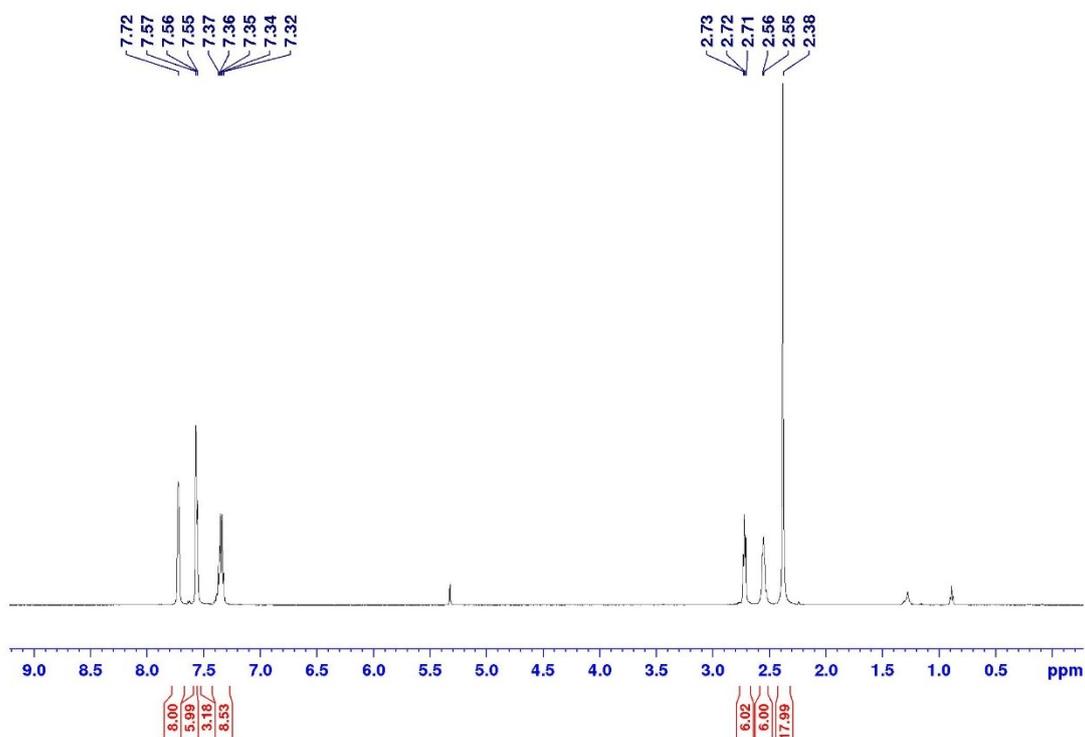


Figure S5. ¹H NMR spectrum of [(Me₆tren)ZnOSiPh₃][B{C₆H₃(CF₃)₂]₄ recorded in CD₂Cl₂.

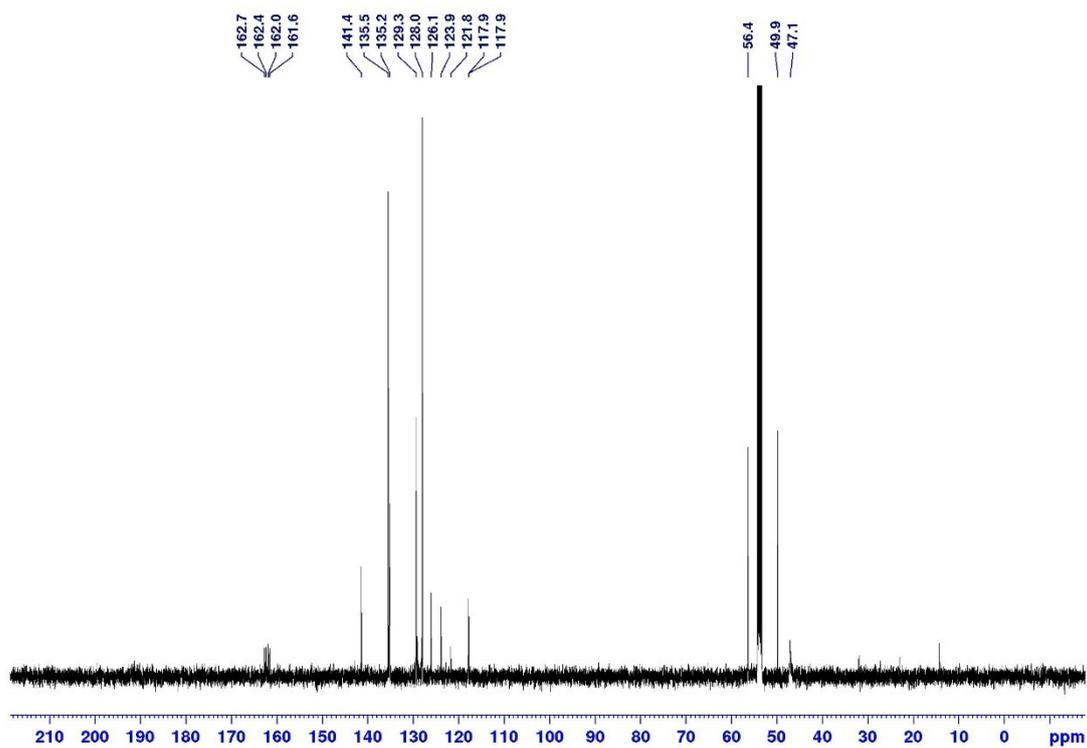


Figure S6. ^{13}C NMR spectrum of $[(\text{Me}_6\text{tren})\text{ZnOSiPh}_3][\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ recorded in CD_2Cl_2 .

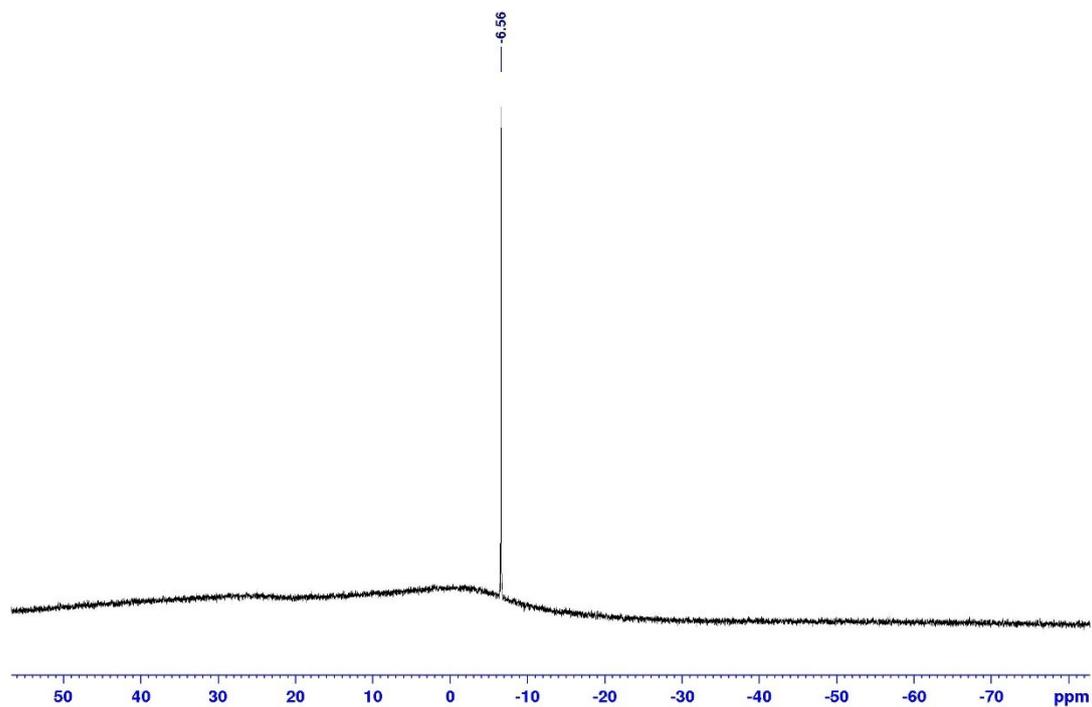


Figure S7. ^{11}B NMR spectrum of $[(\text{Me}_6\text{tren})\text{ZnOSiPh}_3][\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ recorded in CD_2Cl_2 .

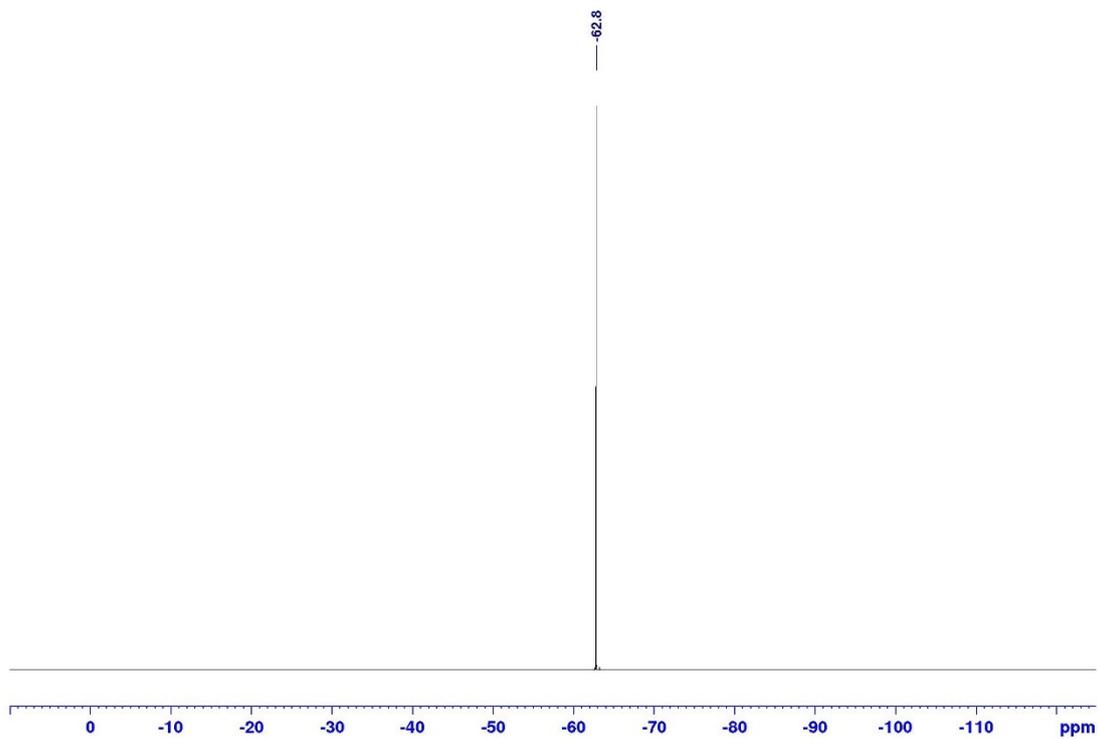


Figure S8. ^{19}F NMR spectrum of $[(\text{Me}_6\text{tren})\text{ZnOSiPh}_3][\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ recorded in CD_2Cl_2 .

Compound 2

Method A: $[(\text{Me}_6\text{tren})\text{ZnOSiPh}_3][\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]$ (0.069 mmol, 0.100 g) was dissolved in THF (2 mL). PhSiH_3 (0.140 mmol, 0.017 mL) was added to this solution. The reaction mixture was heated at 50 °C and stirred under argon for 6 h. A small amount of black precipitate was formed at the end of reaction which was filtered. The volatiles were dried under vacuum (10^{-3} mbar). The obtained residue was washed twice with *n*-hexane and dried to get a colourless powder of **2**. The compound was crystallised in THF upon layering with *n*-hexane. Yield: 0.075 g (93%); elemental analysis for $\text{C}_{44}\text{H}_{43}\text{BF}_{24}\text{N}_4\text{Zn}$: C, 45.56; H, 3.74; N, 4.83; found: C, 45.3; H, 3.73 N, 4.81; ^1H NMR (THF-D8, 500 MHz): δ 2.36 (s, 18H, NCH_3), 2.71 (t, 6H, $^3J_{\text{H-H}} = 5$ Hz, NCH_2), 2.84 (t, 6H, $^3J_{\text{H-H}} = 5$ Hz, NCH_2), 3.47 (s, 1H, ZnH), 7.58 (s, 4H, *p*- C_6H_3), 7.79 (br, 8H, *o*- C_6H_3) (Figure S9); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-D8, 126 MHz): δ 45.9 (NCH_3), 51.4 (NCH_2), 55.5 (NCH_2), 118.2 (t, *p*-C), 128.7 (q, CF_3), 120.2 (m, *m*-C), 135.6 (s, *o*-C), 162.3 (q, *i*-C) (Figure S10); ^{11}B NMR (THF-D8, 128 MHz): δ -6.47 (Figure S11); ^{19}F NMR (THF-D8, 471 MHz): δ -63.39 (Figure S12).

Method B: Me_6tren (0.800 mmol, 0.200 g) in THF was added to a stirred suspension of freshly prepared ZnH_2 (1 mmol, 0.070 g) in THF and stirred at ambient temperature for 5 min. Subsequently a THF solution of $[\text{Et}_3\text{NH}][\text{B}\{\text{C}_6\text{H}_3\text{-}3,5\text{-(CF}_3)_2\}_4]$ (0.800 mmol, 0.772 g) was added dropwise. After evolution of gas ceased, the reaction mixture was filtered and the filtrate was dried under *vacuo* (10^{-3} mbar) to remove all the volatiles. The obtained residue was washed twice with *n*-pentane and dried to get a colourless powder of **2**. Yield: 0.826 g (89%).

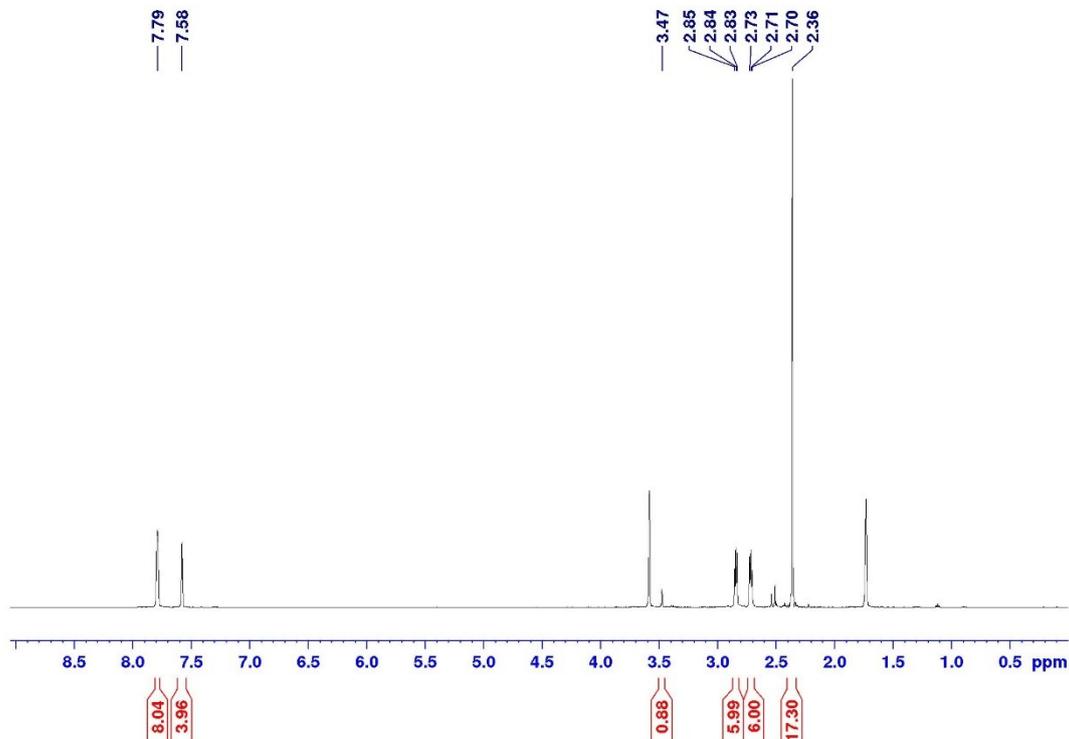


Figure S9. ^1H NMR spectrum of **2** recorded in THF (D8).

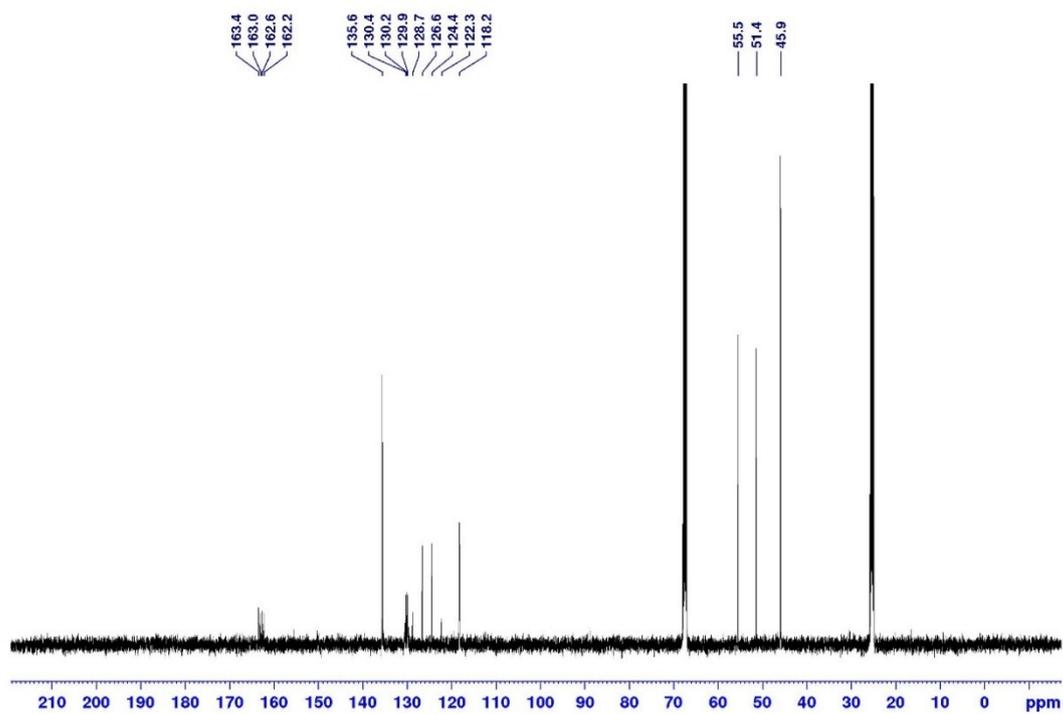


Figure S10. ^{13}C NMR spectrum of **2** recorded in THF (D8).

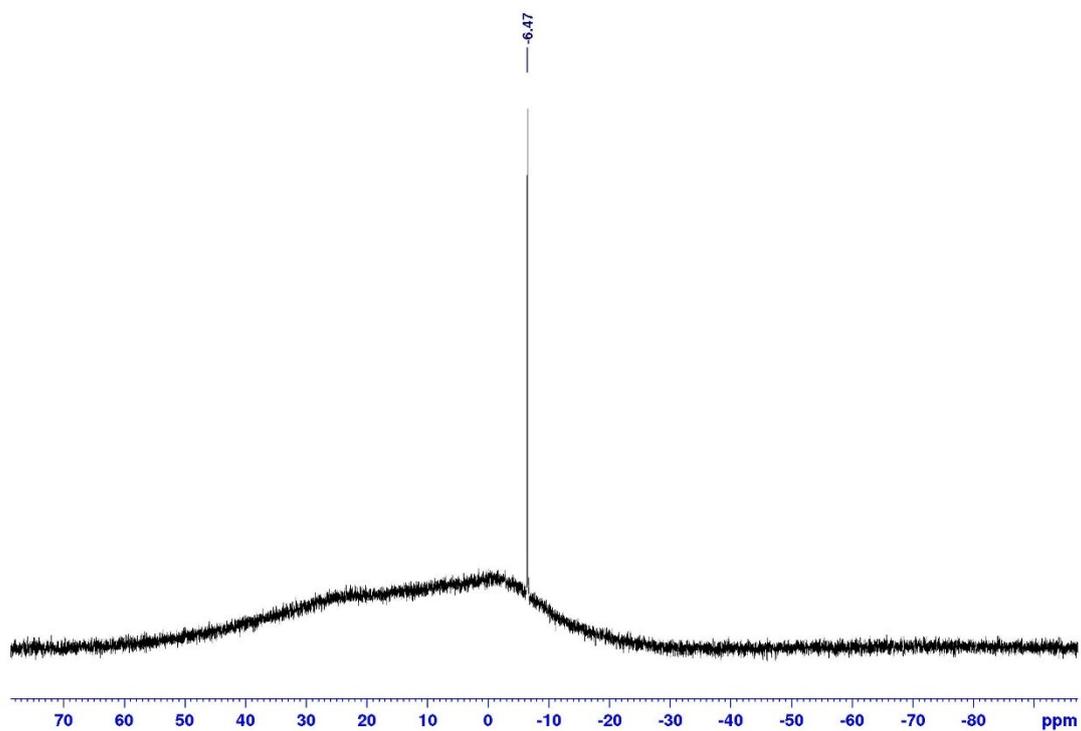


Figure S11. ^{11}B NMR spectrum of **2** recorded in THF (D8).

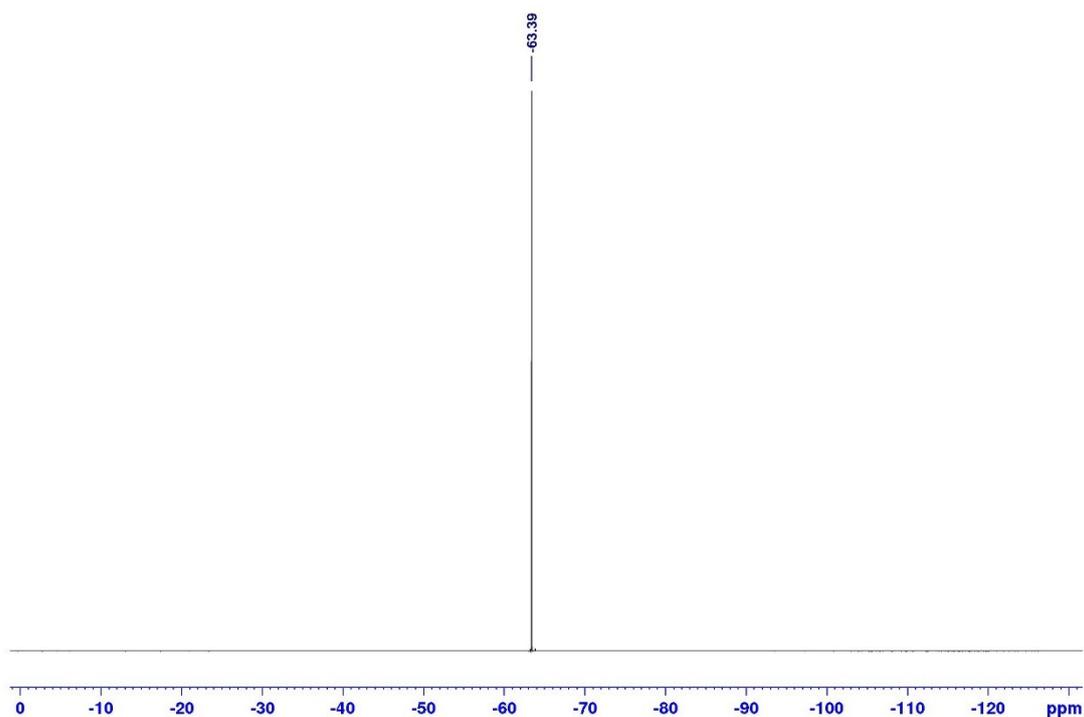


Figure S12. ^{19}F NMR spectrum of **2** recorded in THF (D8).

Compound 3

2 (0.086 mmol, 0.100 g) was dissolved in THF (5 mL) and pressurised with CO_2 (1 bar). The reaction mixture was stirred for 5 minutes. The volatiles were removed under vacuum (10^{-2} mbar) at room temperature, washed twice with *n*-hexane and dried to get a colourless powder of **3**. The compound was crystallised from diethylether/ *n*-hexane mixture. Yield: 0.098 g (93%); elemental analysis for $\text{C}_{46}\text{H}_{46}\text{BF}_{24}\text{N}_4\text{O}_2\text{Zn}$: C, 45.32; H, 3.80; N, 4.60; Found: C, 45.18; H, 3.75; N, 4.50; ^1H NMR (CD_2Cl_2 , 500 MHz): δ 2.55 (s, 18H, NCH_3), 2.64 (t, 6H, $^3J_{\text{H-H}} = 5$ Hz, NCH_2), 2.89 (t, 6H, $^3J_{\text{H-H}} = 5$ Hz, NCH_2), 7.57 (s, 4H, *p*- C_6H_3), 7.79 (br, 8H, *o*- C_6H_3) (Figure S13); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 126 MHz): δ -1.7 (CH_2Me), 13.9 (CCH3), 46.7 (NCH_3), 52.1 (NCH_2), 56.5 (NCH_2), 117.9 (t, *p*-C), 126.1 (q, CF_3), 129.2 (m, *m*-C), 135.2 (s, *o*-C), 162.0 (q, *i*-C) 167.7 (s, OCHO), (Figure S14); ^{11}B NMR (CD_2Cl_2 , 128 MHz): δ -6.49 (Figure S15); ^{19}F NMR (CD_2Cl_2 , 471 MHz): δ -62.80 (Figure S16).

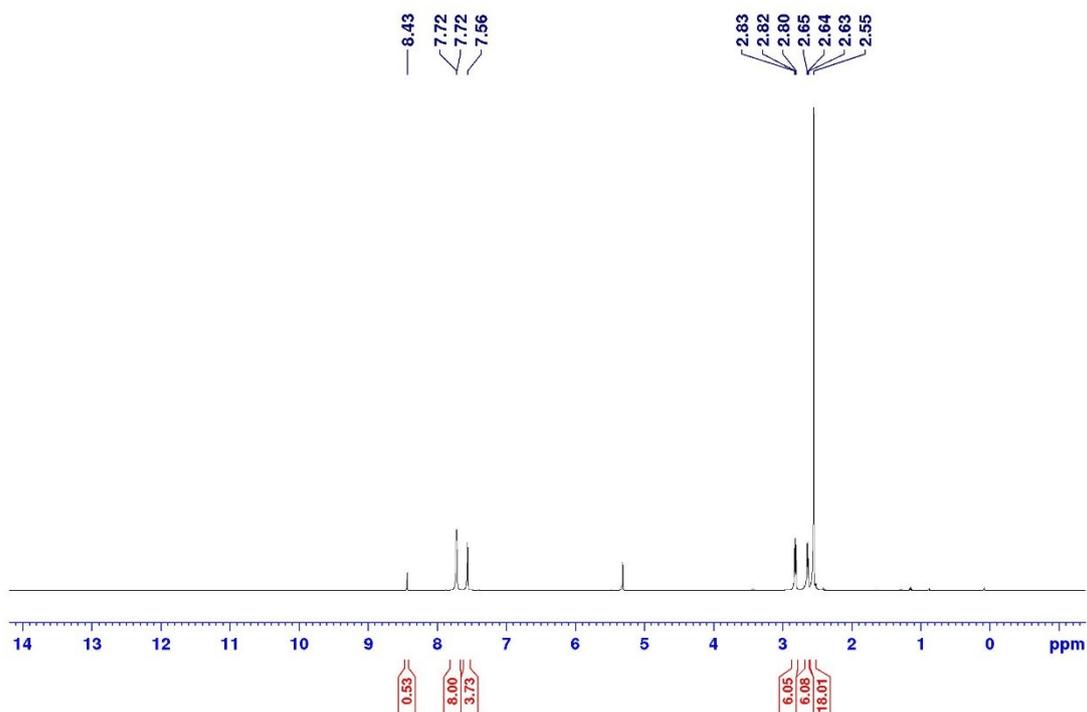


Figure S13. ^1H NMR spectrum of **3** recorded in CD_2Cl_2 .

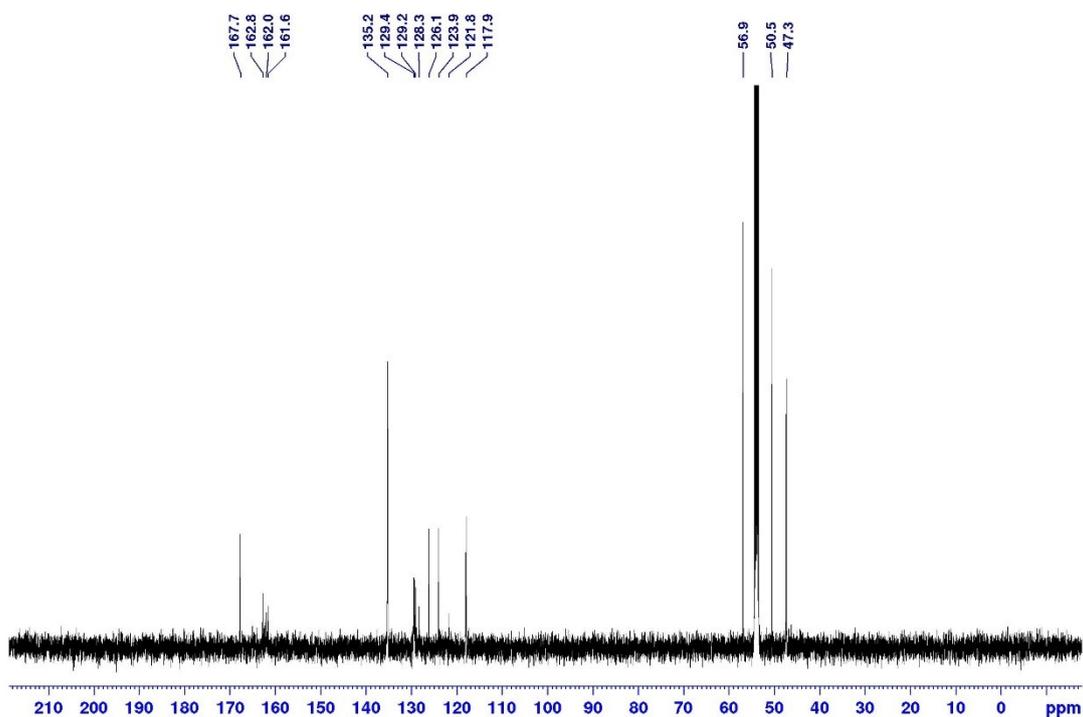


Figure S14. ^{13}C NMR spectrum of **3** recorded in CD_2Cl_2 .

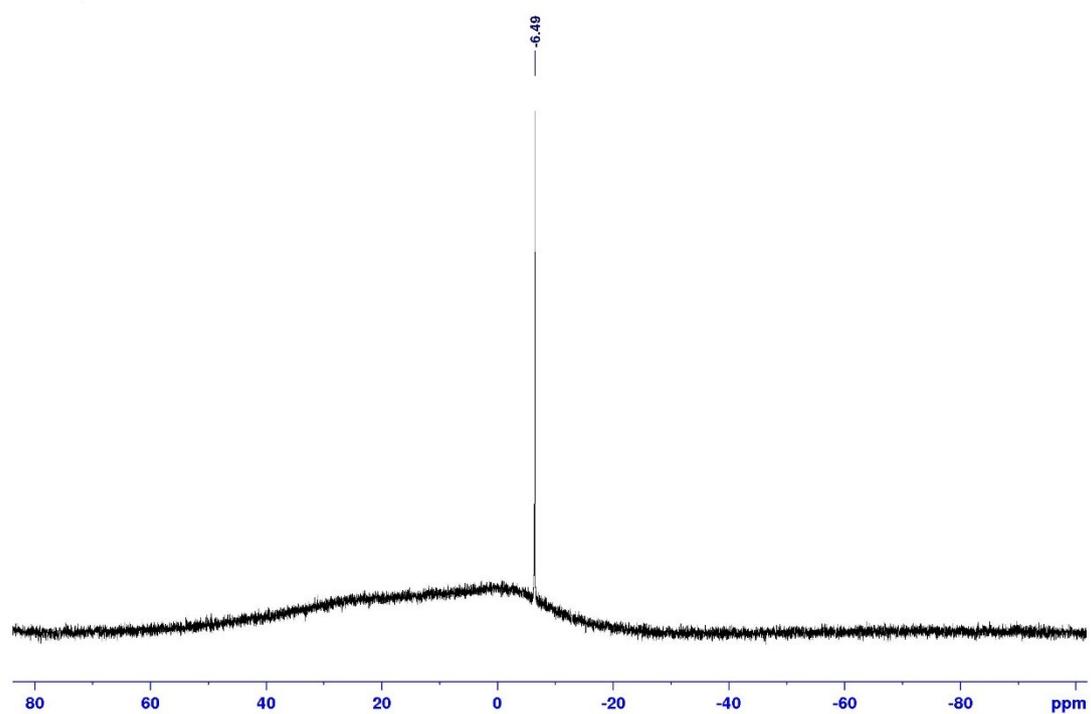


Figure S15. ^{11}B NMR spectrum of **3** recorded in CD_2Cl_2 .

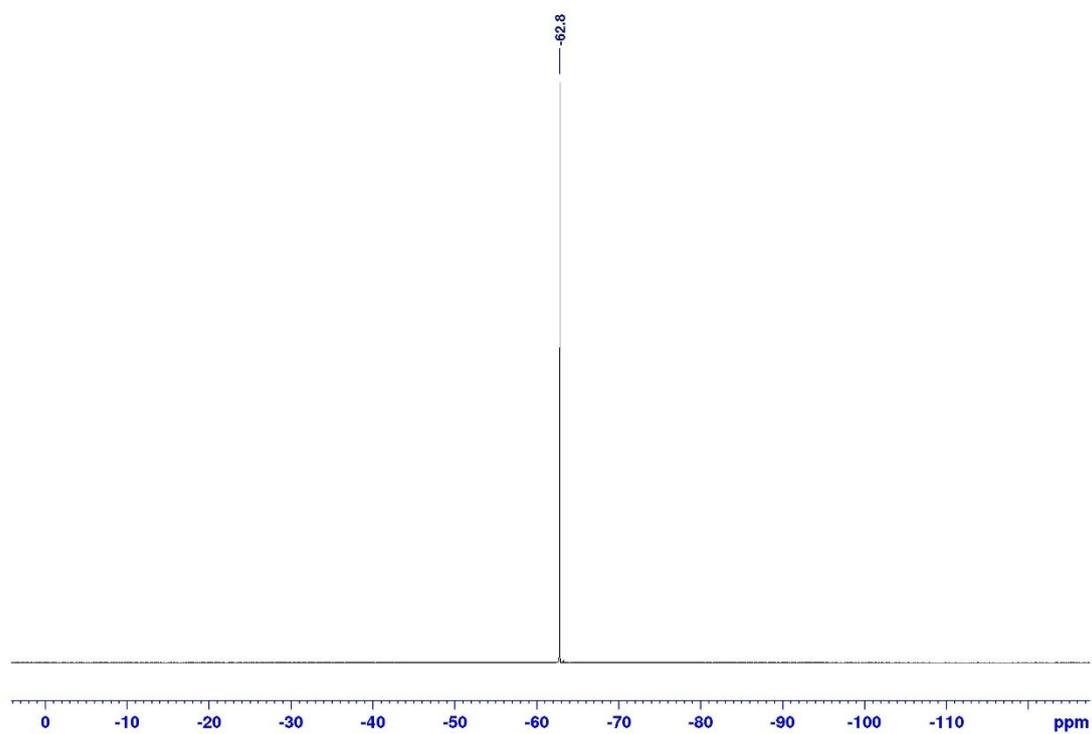


Figure S16. ^{19}F NMR spectrum of **3** recorded in CD_2Cl_2 .

Compound 4

2 (0.086 mmol, 0.100 g) was dissolved in THF (5 mL) and treated with N, N'-diisopropylcarbodiimide (0.086 mmol, 0.0134 mL). The reaction mixture was stirred at room temperature and the volatiles were subsequently evaporated under vacuum (10^{-3} mbar) leaving behind a colourless precipitate, which was washed twice with *n*-hexane and further dried to get a fine white powder of **4**. The compound was crystallised from a mixture of diethylether and *n*-hexane. Yield: 0.103 g (92%); elemental analysis for $C_{52}H_{60}BF_{24}N_6Zn$: C, 48.00; H, 4.65; N, 6.46; found: C, 47.71; H, 4.56; N, 6.45; 1H NMR (CD_2Cl_2 , 500 MHz): δ 1.10 (d, 12H, $^3J_{H-H} = 5$ Hz, CCH_3), 2.42 (s, 18H, NCH_3), 2.66 (t, 6H, $^3J_{H-H} = 5$ Hz, NCH_2), 2.98 (t, 6H, $^3J_{H-H} = 5$ Hz, NCH_2), 3.42 (m, 2H, $^3J_{H-H} = 5$ Hz, $NCHMe_2$), 7.57 (s, 4H, *p*- C_6H_3), 7.79 (br, 8H, *o*- C_6H_3), 7.82 (s, 1H, 7.82) (Figure S17); $^{13}C\{^1H\}$ NMR (CD_2Cl_2 , 126 MHz): δ 15.5 ($NCHMe_2$), 26.5 ($CH(CH_3)_2$), 46.5 (NCH_3), 50.0 (NCH_2), 55.9 (NCH_2), 117.9 (t, *p*-C), 125.0 (q, CF_3), 129.2 (m, *m*-C), 135.2 (s, *o*-C), 162.4 (q, *i*-C) (Figure S18); ^{11}B NMR (CD_2Cl_2 , 128 MHz): δ -6.64 (Figure S19); ^{19}F NMR (CD_2Cl_2 , 471 MHz): δ -62.80 (Figure S20).

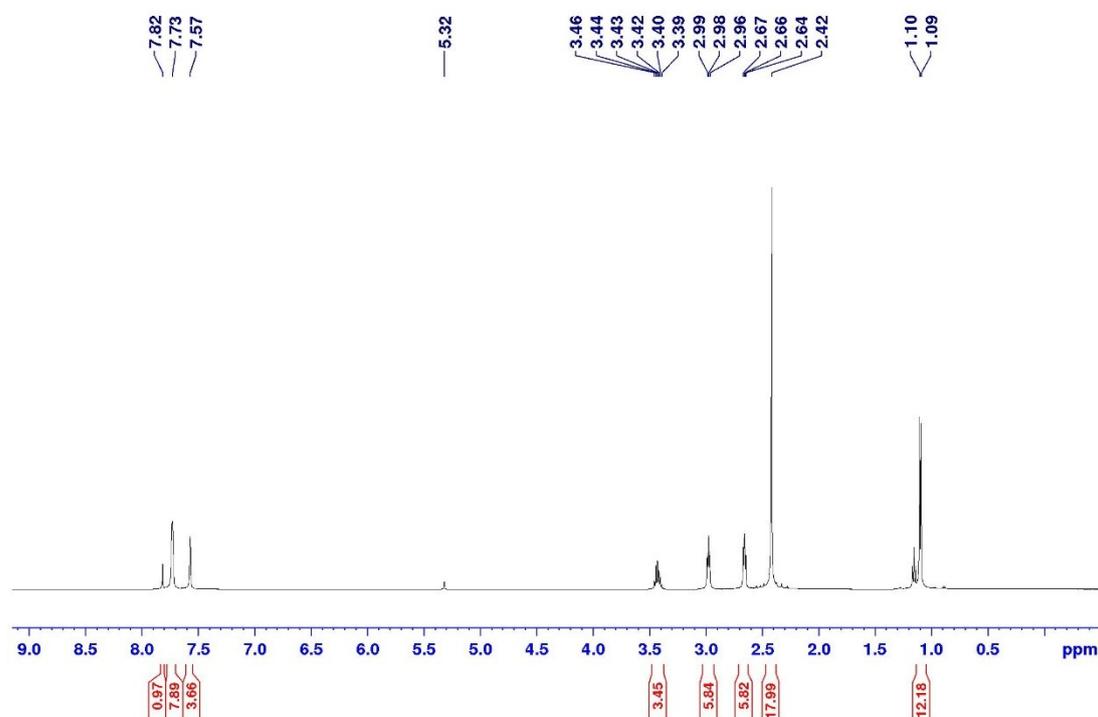


Figure S17. 1H NMR spectrum of **4** recorded in CD_2Cl_2 .

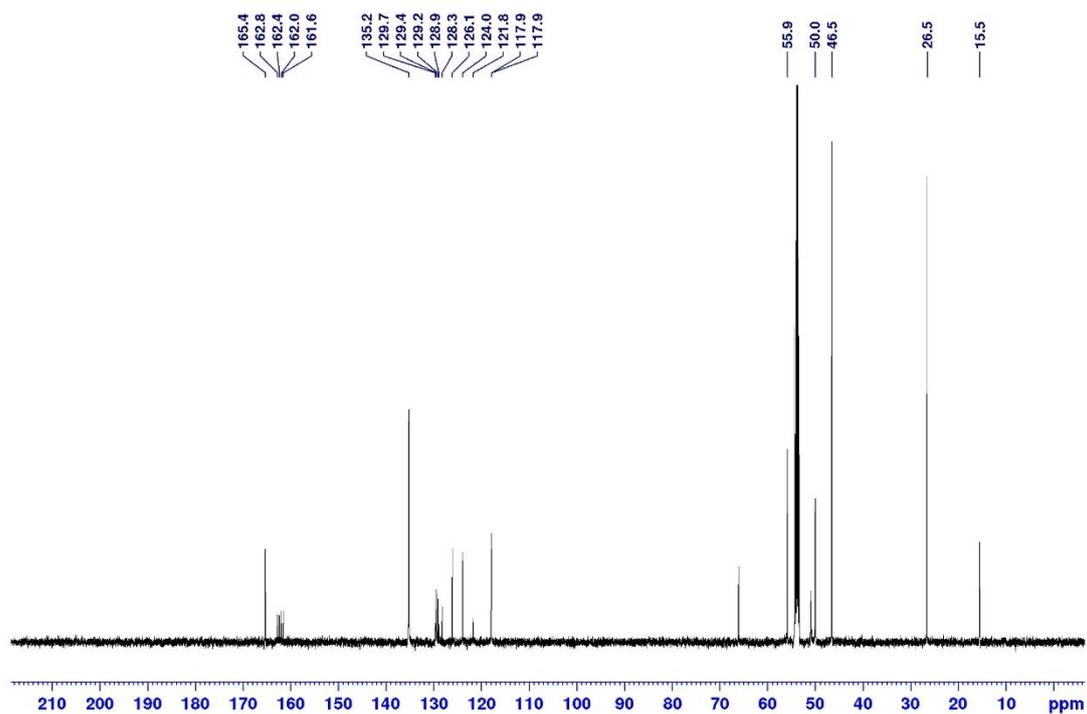


Figure S18. ¹³C NMR spectrum of **4** recorded in CD₂Cl₂.

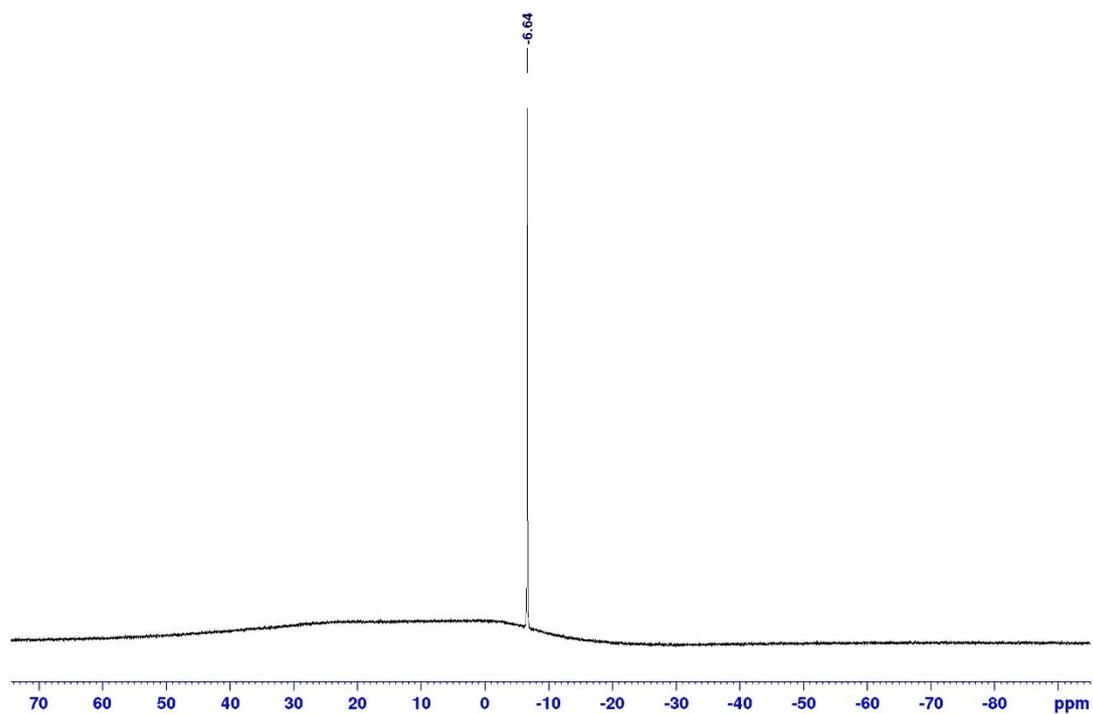


Figure S19. ¹¹B NMR spectrum of **4** recorded in CD₂Cl₂.

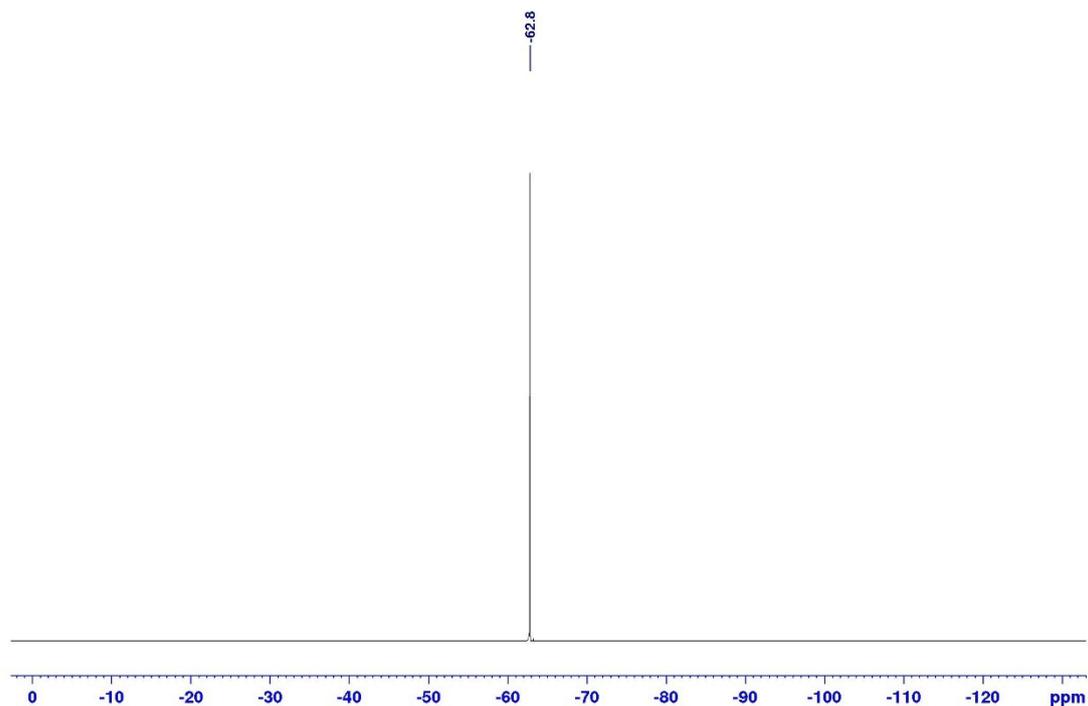


Figure S20. ^{19}F NMR spectrum of **4** recorded in CD_2Cl_2 .

Compound 5

2 (0.172 mmol, 0.200 g) was dissolved in THF (5 mL) and treated with benzophenone (0.172 mmol, 0.032 g). The reaction mixture was heated at 45 °C for 6 h followed by the evaporation of volatiles under vacuum (10^{-3} mbar). A colourless precipitate was formed which was washed once with ether and twice with *n*-hexane and then dried to obtain a colourless powder of **5**. The compound was crystallised from a mixture of THF and *n*-hexane. Yield: 0.207 g (90%); elemental analysis for $\text{C}_{57}\text{H}_{53}\text{BF}_{24}\text{N}_4\text{OZn}$: C, 51.01; H, 3.98; N, 4.17; found: C, 50.76; H, 3.83; N, 4.02; ^1H NMR (CD_2Cl_2 , 500 MHz): δ 2.44 (s, 18H, NCH_3), 2.55 (t, 6H, $^3J_{\text{H-H}} = 5$ Hz, NCH_2), 2.70 (t, 6H, $^3J_{\text{H-H}} = 5$ Hz, NCH_2), 5.94 (s, 1H, Ph_2CHO), 7.11 (t, 2H, $^3J_{\text{H-H}} = 5$ Hz, *p*- C_6H_5), 7.25 (t, 4H, *m*- C_6H_5), 7.11 (t, 2H, $^3J_{\text{H-H}} = 5$ Hz, *p*- C_6H_5), 7.51 (d, 4H, $^3J_{\text{H-H}} = 5$ Hz, *o*- C_6H_3), 7.58 (s, 4H, *p*- C_6H_3), 7.58 (br, 8H, *o*- C_6H_3) (Figure S21); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 126 MHz): δ -1.7 (CH_2Me), 13.9 (CCH_3), 46.6 (NCH_3), 52.1 (NCH_2), 56.5 (NCH_2), 81.7 (s, Ph_2CHO), 117.9 (t, *p*-C), 126.1 (q, CF_3), 129.2 (m, *m*-C), 135.2 (s, *o*-C), 162.0 (q, *i*-C), 125.9 (s, *p*- C_6H_5), 126.5 (s, *m*- C_6H_5), 128.6 (s, *o*- C_6H_5) 152.2 (s, *i*- C_6H_5) (Figure S22); ^{11}B NMR (CD_2Cl_2 , 128 MHz): δ -6.46 (Figure S23); ^{19}F NMR (CD_2Cl_2 , 471 MHz): δ -62.80 (Figure S24).

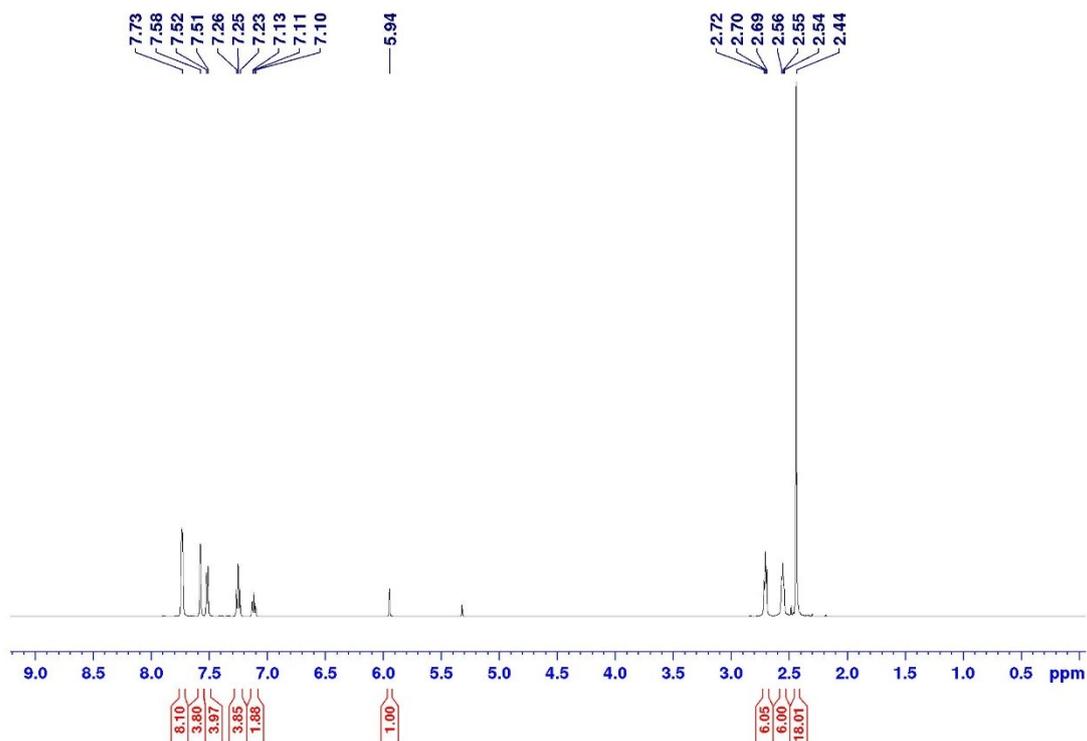


Figure S21. ^1H NMR spectrum of **5** recorded in CD_2Cl_2 .

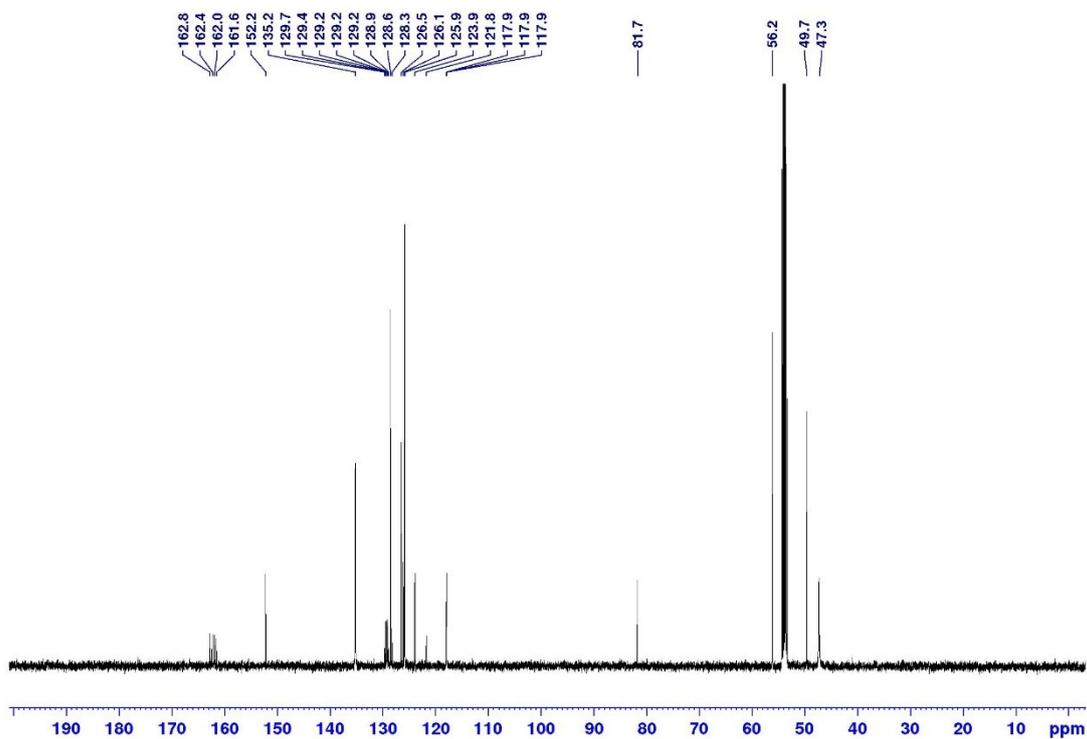


Figure S22. ^{13}C NMR spectrum of **5** recorded in CD_2Cl_2 .

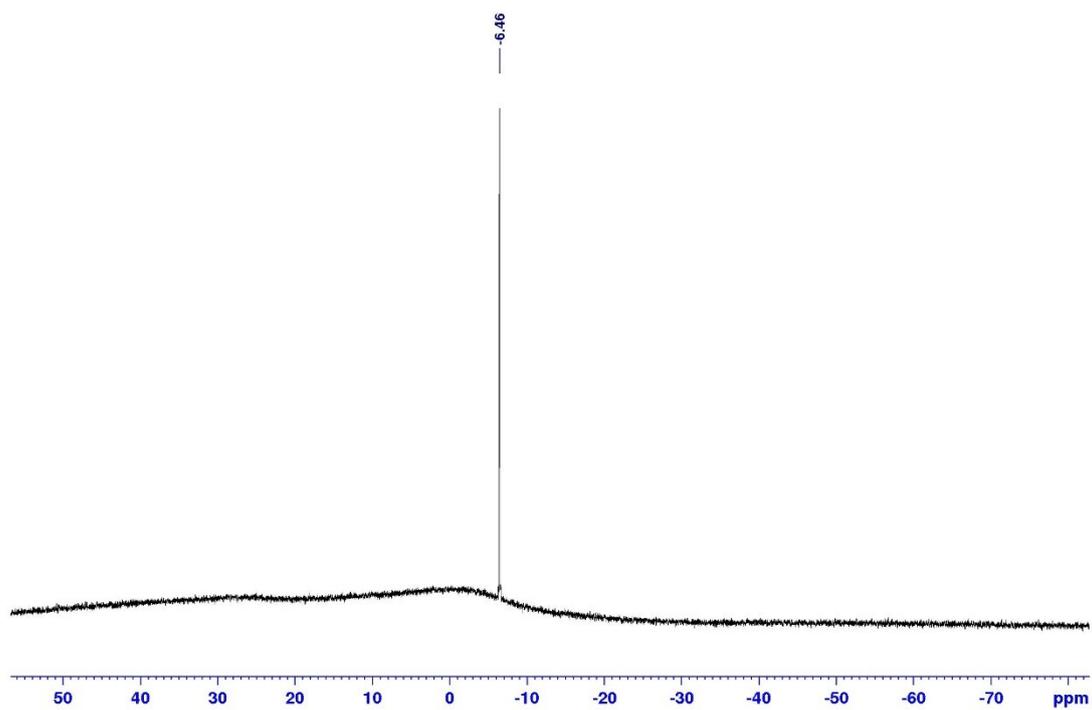


Figure S23. ^{11}B NMR spectrum of **5** recorded in CD_2Cl_2 .

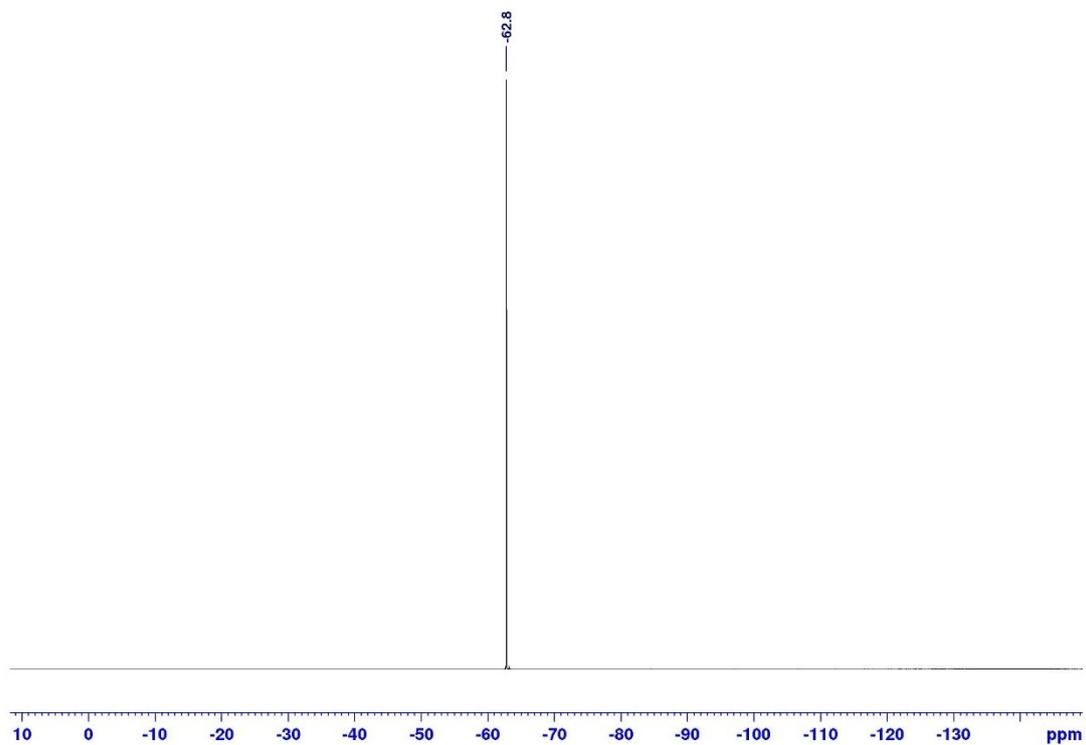


Figure S24. ^{19}F NMR spectrum of **5** recorded in CD_2Cl_2 .

Catalytic hydrosilylation of CO₂

An NMR tube equipped with a Young valve was charged with 0.0165 mmol of **2** (0.0195 g), and 0.0165 mmol of BPh₃ (0.0039 g). Acetonitrile[D₃] (0.500 mL) was added to this mixture followed by 0.324 mmol of PhSiH₃ (0.040 mL). The reaction mixture was degassed thrice and a constant pressure of CO₂ (1.5 bar) was maintained at 50 °C. The progress of the reaction was monitored by ¹H NMR spectroscopy and the complete consumption of PhSiH₃ (98% in 2h) was observed. TOF 29.1 h⁻¹

Catalytic hydrosilylation of Ph₂CO

An NMR tube equipped with a Young valve was charged with 0.0044 mmol of **2** (0.005 g), and 0.088 mmol of Ph₂CO (0.016 g). Acetonitrile[D₃] (0.500 mL) was added to this mixture followed by 0.029 mmol of PhSiH₃ (0.0036 mL). The NMR tube was heated at 60 °C and the reaction was monitored by ¹H NMR Spectroscopy for complete consumption of PhSiH₃ to form PhSi(OCHPh₂)₃ (6 h).

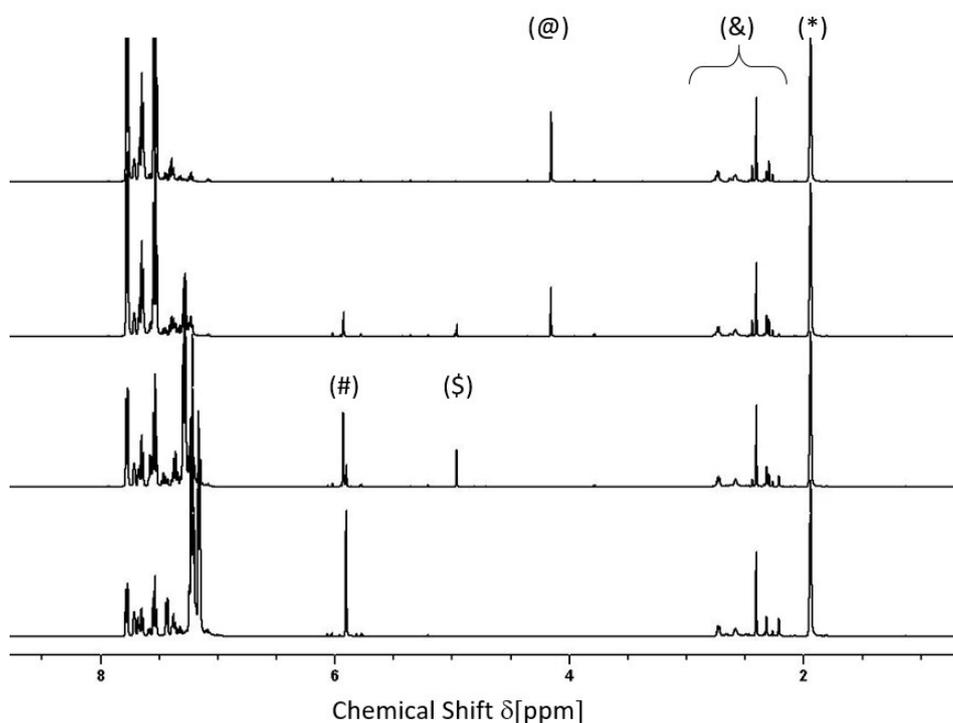


Figure S25. ¹H NMR spectra (stacked) of catalytic reduction of Ph₂CO during the course of reaction in acetonitrile-D₃. ‘(*)’ denotes CD₃CN; ‘(&)’ denotes Me₆tren; ‘(@)’ denotes PhSiH₃; ‘(\$)’ denotes PhSiH₂OCHPh₂; ‘(#)’ denotes PhSi(OCHPh₂)₃.

2. Crystallographic Data

Single-crystal X-ray crystallography for structural analysis was performed with a Bruker Kappa Apex-II CCD diffractometer at 298 K and with Mo-K α irradiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods with SIR-92, SHELXS-97 or SHELX-2013. Crystallographic data, details of data collection and structure refinement parameters for compounds **1-6** are presented below:

Table S1. Crystal data and structure refinement for **(1)**.

Identification code	Compound 1	
CCDC	1878262	
Empirical formula	C ₄₆ H ₄₇ B F ₂₄ N ₄ Zn	
Formula weight	1188.05	
Temperature	150(2) K	
Wavelength	0.71073 \AA	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.6025(3) \AA	$\alpha = 90^\circ$.
	b = 17.6868(4) \AA	$\beta = 93.6760(10)^\circ$.
	c = 22.9841(5) \AA	$\gamma = 90^\circ$.
Volume	5112.6(2) \AA^3	
Z	4	
Density (calculated)	1.543 Mg/m ³	
Absorption coefficient	0.606 mm ⁻¹	
F(000)	2408	
Crystal size	0.200 x 0.180 x 0.150 mm ³	
Theta range for data collection	1.454 to 24.999 $^\circ$.	
Index ranges	-14 \leq h \leq 14, -21 \leq k \leq 21, -27 \leq l \leq 26	
Reflections collected	38629	
Independent reflections	8977 [R(int) = 0.0378]	
Completeness to theta = 24.999 $^\circ$	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.915 and 0.888	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8977 / 199 / 809	
Goodness-of-fit on F ²	1.024	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0609, wR2 = 0.1562	
R indices (all data)	R1 = 0.0796, wR2 = 0.1721	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.807 and -0.841 e. \AA^{-3}	

Table S2. Crystal data and structure refinement for **(2)**

Identification code	compound 2	
CCDC	1878263	
Empirical formula	C ₄₄ H ₄₃ B F ₂₄ N ₄ Zn	
Formula weight	1160.00	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.1404(11) Å	$\alpha = 95.682(3)^\circ$.
	b = 12.1678(11) Å	$\beta = 103.794(3)^\circ$.
	c = 17.0313(16) Å	$\gamma = 95.983(3)^\circ$.
Volume	2410.0(4) Å ³	
Z	2	
Density (calculated)	1.599 Mg/m ³	
Absorption coefficient	0.640 mm ⁻¹	
F(000)	1172	
Crystal size	0.150 x 0.120 x 0.080 mm ³	
Theta range for data collection	2.266 to 24.999°.	
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20	
Reflections collected	54478	
Independent reflections	8492 [R(int) = 0.0516]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.950 and 0.911	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8492 / 6 / 677	
Goodness-of-fit on F ²	1.023	
Final R indices [I > 2σ(I)]	R1 = 0.0366, wR2 = 0.0833	
R indices (all data)	R1 = 0.0499, wR2 = 0.0905	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.615 and -0.448 e.Å ⁻³	

Table S3. Crystal data and structure refinement for **(3)**.

Identification code	compound 3	
CCDC	1878264	
Empirical formula	C ₅₀ H ₅₅ B F ₂₄ N ₄ O ₂ Zn	
Formula weight	1276.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 16.61(7) Å	$\alpha = 90^\circ$.
	b = 11.92(5) Å	$\beta = 90.62(3)^\circ$.
	c = 28.25(13) Å	$\gamma = 90^\circ$.
Volume	5596(42) Å ³	
Z	4	
Density (calculated)	1.515 Mg/m ³	
Absorption coefficient	0.561 mm ⁻¹	
F(000)	2600	
Crystal size	0.240 x 0.120 x 0.050 mm ³	
Theta range for data collection	0.721 to 24.999°.	
Index ranges	-19 ≤ h ≤ 19, -14 ≤ k ≤ 14, -33 ≤ l ≤ 33	
Reflections collected	39481	
Independent reflections	9851 [R(int) = 0.1291]	
Completeness to theta = 24.999°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.972 and 0.877	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9851 / 6 / 740	
Goodness-of-fit on F ²	1.021	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0730, wR2 = 0.1647	
R indices (all data)	R1 = 0.1407, wR2 = 0.2035	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.676 and -0.648 e.Å ⁻³	

Table S4. Crystal data and structure refinement for **(4)**

Identification code	compound 4	
CCDC	1878265	
Empirical formula	C ₅₄ H ₆₂ B F ₂₄ N ₆ Zn	
Formula weight	1327.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.312(4) Å	α = 99.762(9)°.
	b = 14.379(4) Å	β = 108.306(9)°.
	c = 17.415(5) Å	γ = 102.538(9)°.
Volume	2985.8(14) Å ³	
Z	2	
Density (calculated)	1.476 Mg/m ³	
Absorption coefficient	0.528 mm ⁻¹	
F(000)	1358	
Crystal size	0.240 x 0.150 x 0.150 mm ³	
Theta range for data collection	1.683 to 24.999°.	
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20	
Reflections collected	42361	
Independent reflections	10510 [R(int) = 0.0565]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.925 and 0.884	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10510 / 148 / 893	
Goodness-of-fit on F ²	1.036	
Final R indices [I > 2σ(I)]	R1 = 0.0673, wR2 = 0.1685	
R indices (all data)	R1 = 0.0888, wR2 = 0.1880	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.356 and -0.674 e.Å ⁻³	

Table S5. Crystal data and structure refinement for **(5)**.

Identification code	compound 5	
CCDC	1878266	
Empirical formula	C ₅₈ H ₅₅ B Cl ₂ F ₂₄ N ₄ O Zn	
Formula weight	1427.14	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.54(3) Å	α = 90°.
	b = 19.77(5) Å	β = 100.01(5)°.
	c = 26.08(6) Å	γ = 90°.
Volume	6369(28) Å ³	
Z	4	
Density (calculated)	1.488 Mg/m ³	
Absorption coefficient	0.582 mm ⁻¹	
F(000)	2896	
Crystal size	0.150 x 0.150 x 0.080 mm ³	
Theta range for data collection	1.586 to 24.999°.	
Index ranges	-14 ≤ h ≤ 14, -23 ≤ k ≤ 23, -31 ≤ l ≤ 26	
Reflections collected	61247	
Independent reflections	11193 [R(int) = 0.0629]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.955 and 0.918	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11193 / 0 / 826	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0555, wR2 = 0.1233	
R indices (all data)	R1 = 0.0878, wR2 = 0.1416	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.877 and -0.622 e.Å ⁻³	

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