Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Synthesis of *Bis*(2-pyridylthio)methyl Zinc Hydride and Catalytic Hydrosilylation and Hydroboration of CO_2

Daniel G. Shlian, Erika Amemiya and Gerard Parkin,*

Department of Chemistry,

Columbia University,

New York, New York 10027, USA.

Received xxxx xx, 2021.

Experimental Section

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified.[1] Solvents were purified and degassed by using standard procedures. ^{1}H NMR spectra were measured on Bruker AVIII 300, Bruker 400 Cyber-enabled Avance III and Bruker 500 DMX spectrometers. ^{1}H chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C_6D_5H).[2] ^{13}C NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 128.06 for C_6D_6).[2] Coupling constants are given in hertz. Mesitylene is added to NMR samples as an internal standard when deemed appropriate. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode, and are reported in reciprocal centimeters. [Bptm]H was prepared by the literature method.[3]

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[4] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2127030-2127039).

Synthesis of [Bptm]ZnN(SiMe$_3$)$_2$

A solution of [Bptm]H (500 mg, 2.13 mmol) in benzene (*ca.* 2 mL) was treated with $Zn[N(SiMe_3)_2]_2$ (900 mg, 2.36 mmol). The solution was heated at 60˚C overnight and then lyophilized to remove volatile components to give [Bptm]ZnN(SiMe$_3$)$_2$ (980 mg, 99% yield). Large colorless crystals suitable for X-ray diffraction were obtained by (i) diffusion of pentane into a solution of [Bptm]ZnN(SiMe$_3$)$_2$ in benzene and (ii) evaporation of a solution in pentane. ^{1}H NMR (C_6D_6): 0.34 [s, 18H,

$(C_5H_4NS)_2HCZnN(Si\underline{Me}_3)_2]$, 3.28 [s, 1H, $(C_5H_4NS)_2\underline{H}CZnN(SiMe_3)_2]$, 6.15 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnN(SiMe_3)_2]$, 6.42 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnN(SiMe_3)_2]$, 6.60 [dt, $^2J_{H\text{-}H}$ = 1 Hz, $^3J_{H\text{-}H}$ = 8 Hz, 2H, $(C_5\underline{H}_4NS)_2HCZnN(SiMe_3)_2]$, 8.24 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnN(SiMe_3)_2]$. $^{13}C\{^1H\}$ NMR (C_6D_6): 6.5 [6H, $(C_5H_4NS)_2HCZnN(Si\underline{Me}_3)_2]$, 19.3 [1C, $(C_5H_4NS)_2H\underline{C}ZnN(SiMe_3)_2]$, 119.1 [2C, $(\underline{C}_5H_4NS)_2HCZnN(SiMe_3)_2]$, 122.7 [2C, $(\underline{C}_5H_4NS)_2HCZnN(SiMe_3)_2]$, 137.4 [2C, $(\underline{C}_5H_4NS)_2HCZnN(SiMe_3)_2]$, 146.8 [2C, $(\underline{C}_5H_4NS)_2HCZnN(SiMe_3)_2]$, 165.3 [2C, $(\underline{C}_5H_4NS)_2HCZnN(SiMe_3)_2]$. IR Data (ATR, cm^{-1}): 2953 (w), 1589 (s), 1553 (m), 1453 (s), 1414 (vs), 1280 (w), 1250 (w), 1180 (w), 1128 (s), 1089 (w), 1044 (w), 1009 (w), 930 (m), 881 (m), 840 (m), 754 (vs), 721 (s), 669 (w), 643 (w), 618 (w), 483 (s).

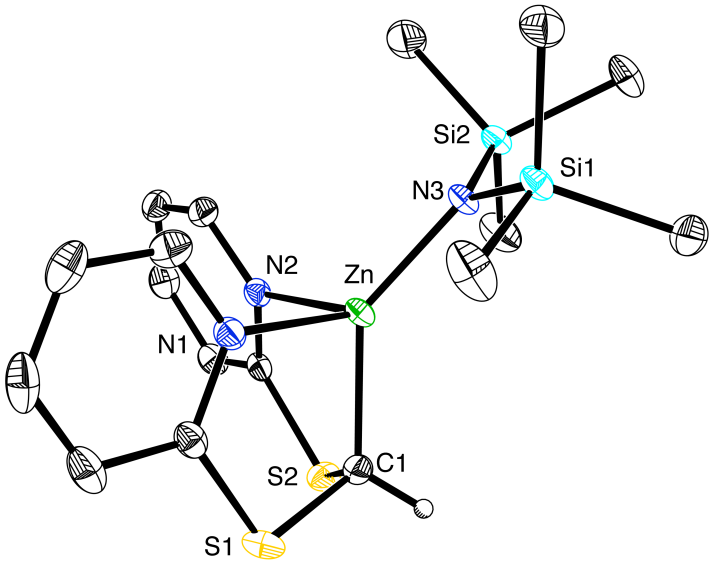

Figure S1. Molecular Structure of $[Bptm]ZnN(SiMe_3)_2$

Synthesis of $[Bptm]ZnOSiPh_3$

A solution of $[Bptm]ZnN(SiMe_3)_2$ (400 mg, 0.87 mmol) in benzene (*ca.* 2 mL) was treated with Ph_3SiOH (240 mg, 0.87 mmol). The solution was lyophilized to remove volatile components after 5 minutes at room temperature to give $[Bptm]ZnOSiPh_3$ (430 mg, 86% yield). Colorless crystals suitable for X-ray diffraction were obtained *via* diffusion of

pentane into a solution of [Bptm]ZnOSiPh$_3$ in benzene. Anal. Calcd. for [Bptm]ZnOSiPh$_3$: C, 60.7%; H, 4.2%; N, 4.9%. Found: C, 59.9%; H, 4.3%; N, 4.6%. ^{1}H NMR (C_6D_6): 3.24 [s, 1H, $(C_5H_4NS)_2\underline{H}CZnOSiPh_3$], 6.06 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnOSiPh_3$], 6.43 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnOSiPh_3$], 6.55 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnOSiPh_3$], 7.19-7.25 [m, 9H, $(C_5H_4NS)_2HCZnOSi\underline{Ph}_3$], 7.99 [m, 6H, $(C_5H_4NS)_2HCZnOSi\underline{Ph}_3$], 8.12 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnOSiPh_3$]. ^{13}C{^{1}H} NMR ($C_6D_6$): 16.24 [1C, $(C_5H_4NS)_2H\underline{C}ZnOSiPh_3$], 119.18 [2C, $(\underline{C}_5H_4NS)_2HCZnOSiPh_3$], 121.83 [2C, $(\underline{C}_5H_4NS)_2HCZnOSiPh_3$], 127.80 [6C, $(C_5H_4NS)_2HCZnOSi\underline{Ph}_3$], 128.83 [3C, $(C_5H_4NS)_2HCZnOSi\underline{Ph}_3$], 135.69 [6C, $(C_5H_4NS)_2HCZnOSi\underline{Ph}_3$], 137.85 [2C, $(\underline{C}_5H_4NS)_2HCZnOSiPh_3$], 142.45 [3C, $(C_5H_4NS)_2HCZnOSi\underline{Ph}_3$], 147.10 [2C, $(\underline{C}_5H_4NS)_2HCZnOSiPh_3$], 164.49 [2C, $(\underline{C}_5H_4NS)_2HCZnOSiPh_3$].. IR Data (ATR, cm^{-1}): 3060 (w), 2996 (w), 2216 (vw), 1962 (vw), 1892 (vw), 1834 (vw), 1590 (m), 1556 (w), 1457 (w), 1418 (m), 1283 (w), 1256 (w), 1130 (w), 1109 (m), 1032 (w), 1006 (m), 889 (w), 751 (m), 703 (s), 673 (w), 645 (w), 548 (w), 510 (s), 468 (w), 429 (w).

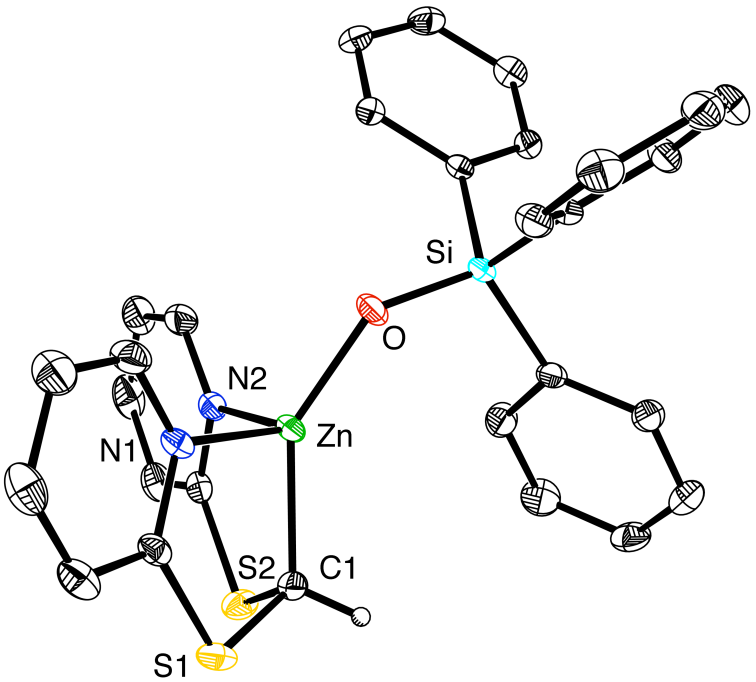

Figure S2. Molecular Structure of [Bptm]ZnOSiPh$_3$

Synthesis of [Bptm]ZnH

(i) A solution of [Bptm]ZnN(SiMe$_3$)$_2$ (297 mg, 0.647 mmol) in C_6H_6 (5 mL) was treated with HBpin (125 mg, 0.977 mmol). The solution was lyophilized to remove volatile components after a period of 5 minutes and the solid obtained was washed with pentane (5 mL) and dried *in vacuo* to give [Bptm]ZnH as a white solid (165 mg, 64% yield). Crystals suitable for X-ray diffraction were obtained by evaporation from a solution in pentane (monoclinic) or benzene (orthorhombic). ^{1}H NMR (C_6D_6): 3.48 [s, 1H, ($C_5H_4NS)_2$<u>H</u>CZnH], 5.48 [s, 1H, ($C_5H_4NS)_2$HCZn<u>H</u>], 6.11 [m, 2H, (C_5<u>H</u>$_4$NS)$_2$HCZnH], 6.45 [m, 2H, (C_5<u>H</u>$_4$NS)$_2$HCZnH], 6.66 [m, 2H, (C_5<u>H</u>$_4$NS)$_2$HCZnH], 8.16 [m, 2H, (C_5<u>H</u>$_4$NS)$_2$HCZnH]. ^{13}C{^{1}H} NMR (C_6D_6): 20.76 [1C, ($C_5H_4NS)_2$H<u>C</u>ZnH], 118.83 [2C, (<u>C</u>$_5$H$_4$NS)$_2$HCZnH], 121.67 [2C, (<u>C</u>$_5$H$_4$NS)$_2$HCZnH], 137.19 [2C, (<u>C</u>$_5$H$_4$NS)$_2$HCZnH], 146.80 [2C, (<u>C</u>$_5$H$_4$NS)$_2$HCZnH], 166.08 [2C, (<u>C</u>$_5$H$_4$NS)$_2$HCZnH]. IR Data (ATR, cm^{-1}): 3038 (vw), 2922 (w), 2852 (w), 1742 (m), 1588 (s), 1555 (m), 1459 (m), 1416 (s), 1128 (s), 1009 (w), 890 (w), 756 (vs), 722 (m), 546 (m), 525 (m), 486 (s), 411 (m).

(ii) A solution of [Bptm]ZnOSiPh$_3$ (10 mg, 0.017 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with PhSiH$_3$ (30 mg, 0.278 mmol). The solution was lyophilized to remove volatile components after 5 minutes at room temperature to give [Bptm]ZnH, as identified by ^{1}H NMR spectroscopy.

(iii) A solution of [Bptm]ZnOSiPh$_3$ (1.5 mg, 0.003 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with HBpin (15 mg, 0.118 mmol) and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Bptm]ZnH.

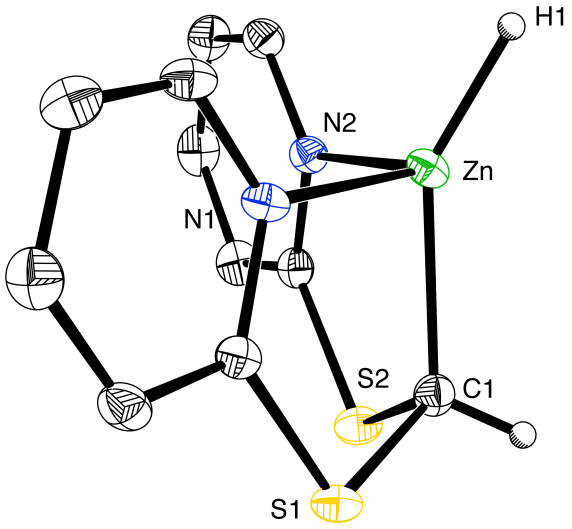

Figure S3. Molecular Structure of [Bptm]ZnH (Orthorhombic Form)

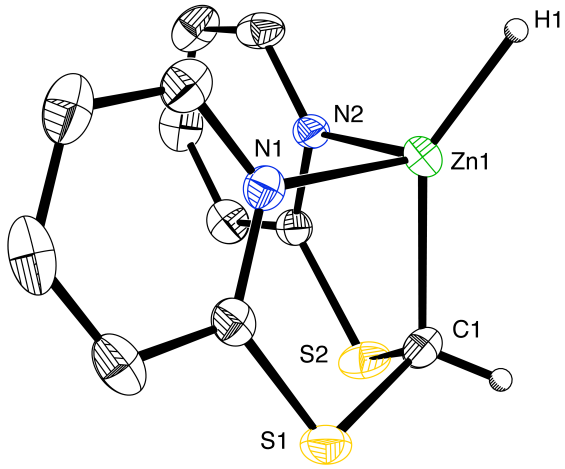

Figure S4. Molecular Structure of [Bptm]ZnH (Monoclinic Form)

Synthesis of [Bptm]ZnO$_2$CH

A solution of [Bptm]ZnH (20 mg, 0.065 mmol) in C_6D_6 (ca. 0.5 mL) was treated with CO_2 (1 atm). The solution was lyophilized to remove volatile components after 5 minutes at room temperature to give [Bptm]ZnO$_2$CH as a white solid (15 mg, 67% yield). Colorless crystals suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into a solution of [Bptm]ZnO$_2$CH in benzene. ^{1}H NMR (C_6D_6): 3.30 [s, 1H, $(C_5H_4NS)_2\underline{H}CZnO_2CH$], 6.13 [m, 2H, $(C_5\underline{H}_4NS)_2HCZnO_2CH$], 6.42 [m, 2H,

($C_5\underline{H}_4NS)_2HCZnO_2CH$], 6.57 [m, 2H, ($C_5\underline{H}_4NS)_2HCZnO_2CH$], 8.93 [m, 2H, ($C_5\underline{H}_4NS)_2HCZnO_2CH$], 8.98 [s, 1H, ($C_5H_4NS)_2HCZnO_2C\underline{H}$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 15.02 [1C, ($C_5H_4NS)_2H\underline{C}ZnO_2CH$], 119.33 [2C, ($\underline{C}_5H_4NS)_2HCZnO_2CH$], 121.81 [2C, ($\underline{C}_5H_4NS)_2HCZnO_2CH$], 138.00 [2C, ($\underline{C}_5H_4NS)_2HCZnO_2CH$], 148.66 [2C, ($\underline{C}_5H_4NS)_2HCZnO_2CH$], 165.25 [2C, ($\underline{C}_5H_4NS)_2HCZnO_2CH$], 170.03 [1C, ($C_5H_4NS)_2HCZnO_2\underline{C}H$]. Anal. Calcd. for [Bptm]ZnO_2CH: C, 41.9%; H, 2.9%; N, 8.2%. Found: C, 42.9%; H, 3.2%; N, 7.5%. IR Data (ATR, cm^{-1}): 2970 (vw), 2838 (w), 1614 (vs), 1592 (s), 1553 (m), 1457 (m), 1415 (s), 1359 (w), 1311 (m), 1283 (m), 1132 (m), 1092 (w), 1045 (w), 1013 (w), 907 (w), 758 (vs), 721 (m), 669 (w), 647 (w), 484 (w), 444 (w), 408 (m).

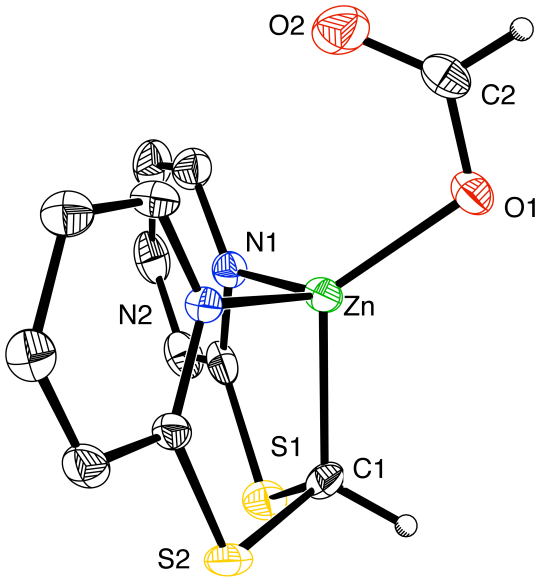

Figure S5. Molecular Structure of [Bptm]ZnO_2CH

Synthesis of [Bptm]ZnNCO

(i) A solution of [Bptm]$ZnN(SiMe_3)_2$ (10 mg, 0.022 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with CO_2 (1 atm). The sample was monitored by ^1H NMR spectroscopy over 2 weeks and lyophilized to remove volatile components to give *inter alia* [Bptm]ZnNCO. Colorless crystals of [Bptm]ZnNCO were obtained *via* vapor diffusion of pentane into a solution in benzene.

(ii) A suspension of [Bptm]ZnH (5 mg, 0.017 mmol) in C_6D_6 was treated with Me_3SiNCO (15 mg, 0.130 mmol). The sample was monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of [Bptm]ZnNCO over a period 2 weeks at room temperature. The sample was lyophilized to remove volatile components to give [Bptm]ZnNCO as a white solid (2 mg) which includes some [Bptm]H impurity. ^1H NMR (C_6D_6): 3.10 [s, 1H, $(C_5H_4NS)_2C\underline{H}ZnNCO$], 6.09 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnNCO$], 6.43 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnNCO$], 6.51 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnNCO$], 7.95 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnNCO$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 16.38 [s, 1C, $(C_5H_4NS)_2\underline{C}HZnNCO$], 119.46 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnNCO$], 121.83 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnNCO$], not observed [s, 2C, $(C_5H_4NS)_2CHZnN\underline{C}O$], 138.08 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnNCO$], 146.59 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnNCO$], 164.70 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnNCO$].

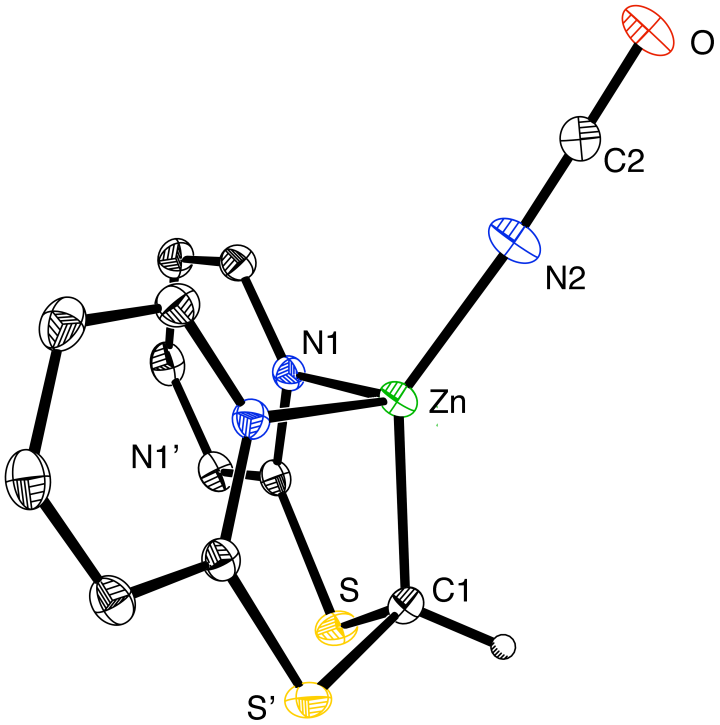

Figure S6. Molecular Structure of [Bptm]ZnNCO

Synthesis of [Bptm]ZnCl

(i) A solution of [Bptm]ZnN$(SiMe_3)_2$ (21 mg, 0.045 mmol) in C_6D_6 (ca. 0.5 mL) was treated with Me_3SnCl (9 mg, 0.045 mmol), thereby resulting in the deposition of

colorless crystals over a period of 1 week at room temperature. The crystals were isolated, washed with pentane (1 mL) and dried to give [Bptm]ZnCl as a white solid (14 mg, 93% yield).

(ii) A solution of [Bptm]ZnN($SiMe_3$)$_2$ (6 mg, 0.013 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with Me_3SiCl (15 mg, 0.138 mmol), resulting in the deposition of colorless crystals of [Bptm]ZnCl over a period of two weeks.

(iii) A suspension of [Bptm]ZnH (3.5 mg, 0.012 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with Me_3SnCl (2.5 mg, 0.013 mmol), and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Bptm]ZnCl.

^{1}H NMR (C_6D_6): 3.27 [s, 1H, ($C_5H_4NS)_2\underline{H}CZnCl$], 6.10 [m, 2H, ($C_5\underline{H}_4NS)_2HCZnCl$], 6.43 [m, 2H, ($C_5\underline{H}_4NS)_2HCZnCl$], 6.53 [dt, $^2J_{H\text{-}H}$ = 1 Hz, $^3J_{H\text{-}H}$ = 8 Hz, 2H, ($C_5\underline{H}_4NS)_2HCZnCl$], 8.32 [m, 2H, ($C_5\underline{H}_4NS)_2HCZnCl$]. $^{13}C\{^1H\}$ NMR (C_6D_6): 17.11 [1C, ($C_5H_4NS)_2H\underline{C}ZnCl$], 119.37 [2C, ($\underline{C}_5H_4NS)_2HCZnCl$], 121.77 [2C, ($\underline{C}_5H_4NS)_2HCZnCl$], 138.10 [2C, ($\underline{C}_5H_4NS)_2HCZnCl$], 146.97 [2C, ($\underline{C}_5H_4NS)_2HCZnCl$], 164.76 [2C, ($\underline{C}_5H_4NS)_2HCZnCl$]. Anal. Calcd. for [Bptm]ZnCl: C, 39.4%; H, 3.0%; N, 8.4%. Found: C, 39.4%; H, 2.8%; N, 8.1%. IR Data (ATR, cm^{-1}): 3084 (w), 3057 (w), 3012 (w), 2944 (w), 2743 (w), 1590 (vs), 1552 (vs), 1475 (m), 1460 (vs), 1415 (vs), 1285 (vs), 1252 (m), 1188 (m), 1155 (m), 1129 (vs), 1090 (s), 1045 (s), 1012 (vs), 993 (s), 874 (vs), 755 (vs), 720 (vs), 666 (vs), 646 (vs), 536 (m), 482 (s), 441 (s), 409 (vs).

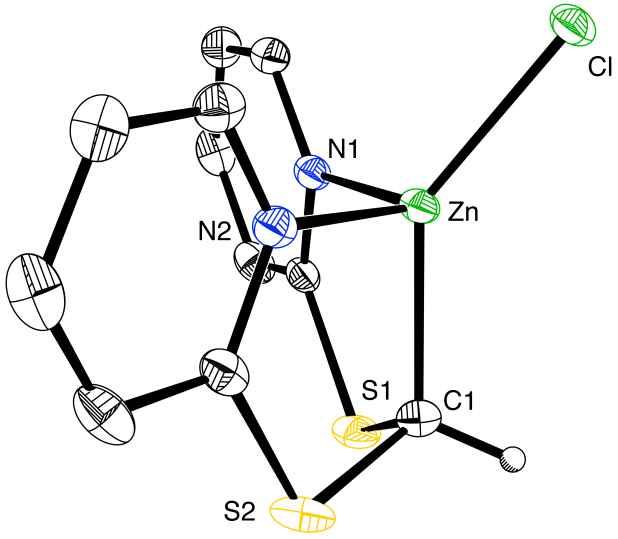

Figure S7. Molecular Structure of [Bptm]ZnCl

Synthesis of [Bptm]ZnBr

(i) A solution of [Bptm]ZnN(SiMe$_3$)$_2$ (26 mg, 0.057 mmol) in C$_6$H$_6$ (*ca.* 0.5 mL) was treated with Me$_3$SiBr (15 mg, 0.098 mmol), resulting in the deposition of colorless crystals over a period of two weeks. The crystals were isolated, washed with pentane (1 mL) and dried to give [Bptm]ZnBr as a white solid (6 mg, 28% yield).
^{1}H NMR (C$_6$D$_6$): 3.29 [s, 1H, (C$_5$H$_4$NS)$_2$HCZnBr], 6.10 [m, 2H, (C$_5$H$_4$NS)$_2$HCZnBr], 6.41 [m, 2H, (C$_5$H$_4$NS)$_2$HCZnBr], 6.51 [dt, $^2J_{H\text{-}H}$ = 1 Hz, $^3J_{H\text{-}H}$ = 8 Hz, 2H, (C$_5$H$_4$NS)$_2$HCZnBr], 8.33 [m, 2H, (C$_5$H$_4$NS)$_2$HCZnBr]. ^{13}C{^{1}H} NMR (C$_6$D$_6$): 17.61 [1C, (C$_5$H$_4$NS)$_2$HCZnBr], 119.39 [2C, (C$_5$H$_4$NS)$_2$HCZnBr], 121.76 [2C, (C$_5$H$_4$NS)$_2$HCZnBr], 138.10 [2C, (C$_5$H$_4$NS)$_2$HCZnBr], 146.94 [2C, (C$_5$H$_4$NS)$_2$HCZnBr], 164.89 [2C, (C$_5$H$_4$NS)$_2$HCZnBr]. Anal. Calcd. for [Bptm]ZnBr: C, 34.9%; H, 2.4%; N, 7.4%. Found: C, 35.4%; H, 2.3%; N, 7.3%. IR Data (ATR, cm^{-1}): 3084 (w), 1591 (vs), 1554 (m), 1459 (s), 1416 (vs), 1286 (m), 1255 (w), 1213 (w), 1191 (w), 1152 (m), 1132 (s), 1095 (w), 1044 m), 1014 (m), 991 (w), 960 (w), 882 (m), 848 (w), 758 (vs), 722 (s), 698 (w), 666 (m), 647 (m), 617 (w), 532 (w), 498 (w), 482 (m), 462 (w), 444 (w), 409 (s).

(ii) A solution of [Bptm]ZnN(SiMe$_3$)$_2$ (7 mg, 0.015 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with Me$_3$SnBr (15 mg, 0.062 mmol), resulting in the deposition of colorless crystals over 1 week, which were isolated *via* decantation and dried to give [Bptm]ZnBr.

(iii) A suspension of [Bptm]ZnH (6 mg, 0.020 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with Me$_3$SiBr (15 mg, 0.098 mmol) and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Bptm]ZnBr. The solution was lyophilized to remove volatile components to give [Bptm]ZnBr as a white solid (5 mg, 66% yield).

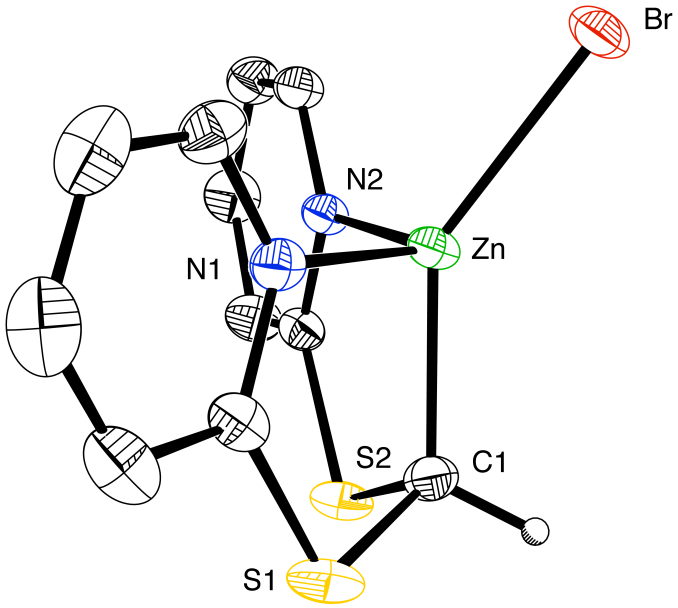

Figure S8. Molecular Structure of [Bptm]ZnBr

Synthesis of [Bptm]ZnI

(i) A solution of [Bptm]ZnN(SiMe$_3$)$_2$ (26 mg, 0.057 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with Me$_3$SnI (20 mg, 0.069 mmol), resulting in the deposition of colorless crystals over a period of one week. The crystals were isolated, washed with pentane (1 mL) and dried to give [Bptm]ZnI as a white solid (11 mg, 45% yield).

^{1}H NMR (C_6D_6): 3.32 [s, 1H, $(C_5H_4NS)_2$HCZnI], 6.09 [m, 2H, $(C_5H_4NS)_2$HCZnI], 6.38 [m, 2H, $(C_5H_4NS)_2$HCZnI], 6.50 [dt, $^{2}J_{H\text{-}H}$ = 1 Hz, $^{3}J_{H\text{-}H}$ = 8 Hz, 2H, $(C_5H_4NS)_2$HCZnI], 8.35 [m, 2H, $(C_5H_4NS)_2$HCZnI]. ^{13}C{^{1}H} NMR (C_6D_6): 18.60 [1C, $(C_5H_4NS)_2$HCZnI], 119.40 [2C, $(C_5H_4NS)_2$HCZnI], 121.75 [2C, $(C_5H_4NS)_2$HCZnI], 138.09 [2C, $(C_5H_4NS)_2$HCZnI], 146.85 [2C, $(C_5H_4NS)_2$HCZnI], 165.04 [2C, $(C_5H_4NS)_2$HCZnI]. Anal. Calcd. for [Bptm]ZnI: C, 31.0%; H, 2.1%; N, 6.6%. Found: C, 31.3%; H, 2.2%; N, 6.5%. IR Data (ATR, cm^{-1}): 3071 (w), 3054 (w), 3011 (w), 2945 (w), 1593 (vs), 1553 (s), 1480 (m), 1457 (s), 1416 (vs), 1280 (s), 1188 (m), 1153 (m), 1130 (s), 1094 (m), 1044 (s), 1015 (s), 963 (m), 887 (m), 878 (s), 761 (vs), 720 (vs), 665 (s), 647 (s), 538 (m), 482 (s), 443 (m), 412 (s).

(ii) A solution of [Bptm]ZnN(SiMe$_3$)$_2$ (11 mg, 0.024 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with Me_3SiI (15 mg, 0.075 mmol), resulting in the deposition of colorless crystals over 2 weeks.

(*iii*) A suspension of [Bptm]ZnH (4 mg, 0.013 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with Me_3SnI (10 mg, 0.034 mmol) and monitored by ^{1}H NMR spectroscopy, thereby demonstrating the formation of [Bptm]ZnI.

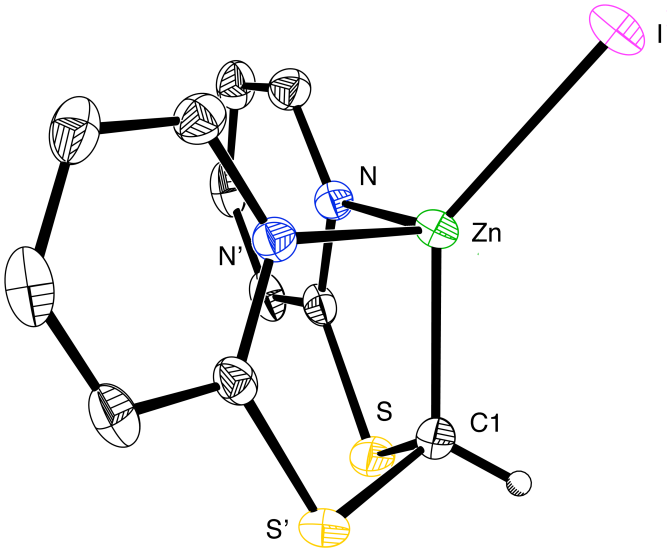

Figure S9. Molecular Structure of [Bptm]ZnI

Synthesis of [Bptm]ZnMe

A solution of [Bptm]H (53 mg, 0.226 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with Me_2Zn (20 mg, 0.209 mmol). The solution was heated at 100˚C for 40 days and then lyophilized to remove volatile components to give [Bptm]ZnMe as a brown solid. Colorless crystals were obtained *via* diffusion of pentane into benzene. ^{1}H NMR (C_6D_6): 0.00 [s, 3H, $(C_5H_4NS)_2CHZnC\underline{H}_3$], 3.47 [s, 1H, $(C_5H_4NS)_2C\underline{H}ZnCH_3$], 6.15 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnCH_3$], 6.50 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnCH_3$], 6.69 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnCH_3$], 8.00 [m, 2H, $(C_5\underline{H}_4NS)_2CHZnCH_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): -14.44 [s, 1C, $(C_5H_4NS)_2CHZn\underline{C}H_3$], 20.86 [s, 1C, $(C_5H_4NS)_2\underline{C}HZnCH_3$], 118.83 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnCH_3$], 121.58 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnCH_3$], 137.12 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnCH_3$], 146.48 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnCH_3$], 165.85 [s, 2C, $(\underline{C}_5H_4NS)_2CHZnCH_3$].

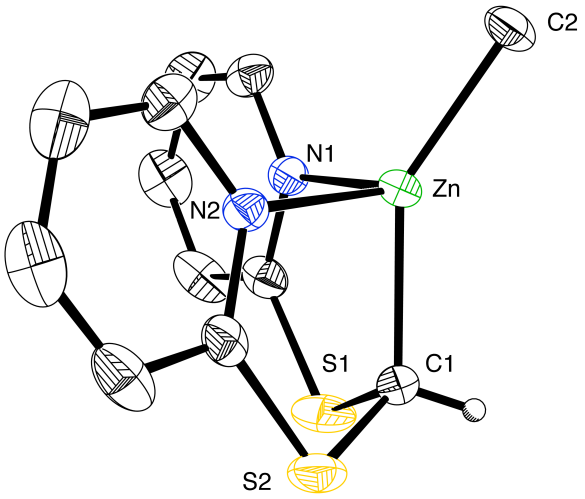

Figure S10. Molecular Structure of [Bptm]ZnMe

Hydrosilylation of CO_2 by $(MeO)_3SiH$ as catalyzed by [Bptm]ZnH

A mixture of [Bptm]ZnH (0.3 mg, 0.001 mmol), $(MeO)_3SiH$ (21 mg, 0.172 mmol), and mesitylene (10 mg, 0.083 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with CO_2 (1 atm), heated at 60°C, and monitored by ^{1}H NMR spectroscopy over the course of 23 hours, thereby demonstrating the formation of $(MeO)_3SiO_2CH$ (Table S1).

Hydrosilylation of CO_2 by $(EtO)_3SiH$ as catalyzed by [Bptm]ZnH

A mixture of [Bptm]ZnH (0.3 mg, 0.001 mmol), $(EtO)_3SiH$ (28 mg, 0.170 mmol), and mesitylene (10 mg, 0.083 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with CO_2 (1 atm), heated at 80°C, and monitored by ^1H NMR spectroscopy over the course of 2 days, thereby demonstrating the formation of $(EtO)_3SiO_2CH$ (Table S1).

Hydroboration of CO_2 by HBpin as catalyzed by [Bptm]ZnH

A mixture of [Bptm]ZnH (1.5 mg, 0.005 mmol), HBpin (22 mg, 0.172 mmol), and mesitylene (10 mg, 0.083 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with CO_2 (1 atm) and monitored by ^1H NMR spectroscopy over the course of 2 days, thereby demonstrating the formation of $pinBO_2CH$ (Table S1).

Hydrosilylation of Ph_2CO by $PhSiH_3$ as catalyzed by [Bptm]ZnH

A mixture of Ph_2CO (95 mg, 0.521 mmol), $PhSiH_3$ (56 mg, 0.517 mmol) and mesitylene (15 mg, 0.125 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with [Bptm]ZnOSiPh$_3$ (3 mg, 0.005 mmol), as a precursor to [Bptm]ZnH, and monitored by ^1H NMR spectroscopy over the course of 10.5 hours, thereby demonstrating the consumption of $PhSiH_3$ accompanied by the formation of $PhSiH_2(OCHPh_2)$[5] (3%) and $PhSiH(OCHPh_2)_2$ (97%); Table S1.[6] Selected ^1H NMR signals for $PhSiH(OCHPh_2)_2$: 5.33 [s, 1H, $PhSi\underline{H}(OCHPh_2)_2$], 5.92 [s, 2H, $PhSiH(OC\underline{H}Ph_2)_2$].

Hydrosilylation of PhC(O)Me by $PhSiH_3$ as catalyzed by [Bptm]ZnH

A mixture of PhC(O)Me (63 mg, 0.525 mmol), $PhSiH_3$ (56 mg, 0.517 mmol) and mesitylene (15 mg, 0.125 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with [Bptm]ZnOSiPh$_3$ (3 mg, 0.005 mmol), as a precursor to [Bptm]ZnH, and monitored by ^1H NMR spectroscopy over the course of 9 hours, thereby demonstrating the consumption of

$PhSiH_3$ accompanied by the formation of $PhSiH_2$[OCH(Ph)Me] (3%) and $PhSiH[OCH(Ph)Me]_2$ (97%); Table S1.[5]

Hydroboration of Ph_2CO by HBpin as catalyzed by [Bptm]ZnH

A mixture of Ph_2CO (35 mg, 0.192 mmol) and HBpin (25 mg, 0.195 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with [Bptm]ZnH (0.4 mg, 0.001 mmol) and monitored by ^1H NMR spectroscopy over 8 hours, thereby demonstrating the formation of $pinBOCHPh_2$[7] (Table S1).

Hydroboration of PhC(O)Me by HBpin as catalyzed by [Bptm]ZnH

A mixture of PhC(O)Me (25 mg, 0.208 mmol) and HBpin (24 mg, 0.188 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with [Bptm]ZnH (0.4 mg, 0.001 mmol) and monitored by ^1H NMR spectroscopy over 5 hours, thereby demonstrating the formation of pinBOCHPhMe[7] (Table S1).

Hydroboration of PhCHO by HBpin as catalyzed by [Bptm]ZnH

A mixture of PhCHO (36 mg, 0.339 mmol) and HBpin (45 mg, 0.352 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with [Bptm]ZnH (0.3 mg, 0.001 mmol) and monitored by ^1H NMR spectroscopy over 15 hours, thereby demonstrating the formation of $pinBOCH_2Ph$[7] (Table S1).

Reduction of HCO_2Bpin to MeOBpin by HBpin

A mixture of [Bptm]ZnH (2 mg, 0.007 mmol) and HBpin (20 mg, 0.156 mmol) in C_6D_6 (*ca*. 0.5 mL) was treated with CO_2 (1 atm) and monitored by ^1H NMR spectroscopy over a period of 2 days, thereby demonstrating the partial formation of HCO_2Bpin (TON = 6.5, TOF = 0.14 h^{-1}). The sample was degassed and placed under N_2. After standing at room temperature for 2 days, the sample was heated at 60°C for 3 days and monitored

by ^{1}H NMR spectroscopy, thereby demonstrating the formation of MeOBpin accompanied by $O(Bpin)_2$[8] (TON = 4.2, TOF = 0.06 h^{-1}).

Reaction of [Bptm]ZnO_2CH with HBpin to form MeOBpin

A solution of [Bptm]ZnO_2CH (2.5 mg, 0.007 mmol) in C_6D_6 (*ca.*0.5 mL) was treated with HBpin (15 mg, 0.117 mmol) and monitored by ^{1}H NMR spectroscopy over the course of 4 days, thereby demonstrating the formation of MeOBpin accompanied by $O(Bpin)_2$.

Competition of hydrosilylation and hydroboration of Ph_2CO as catalyzed by [Bptm]ZnH

A mixture of Ph_2CO (40 mg, 0.220 mmol), HBpin (28 mg, 0.219 mmol), and $PhSiH_3$ (24 mg, 0.222 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with [Bptm]ZnH (0.3 mg, 0.001 mmol) and monitored by ^{1}H NMR spectroscopy over 2 days, thereby demonstrating that formation of $pinBOCHPh_2$ (TON = 104, TOF = 2.2 h^{-1}) was more facile than that of $PhSiH(OCHPh_2)_2$ (TON = 17, TOF = 0.35 h^{-1}).[5]

Competition of hydrosilylation and hydroboration of PhC(O)Me as catalyzed by [Bptm]ZnH

A mixture of [Bptm]ZnH (0.3 mg, 0.001 mmol), HBpin (33 mg, 0.258 mmol), and $PhSiH_3$ (24 mg, 0.259 mmol) in C_6D_6 (*ca.* 0.5 mL) was treated with PhC(O)Me (37 mg, 0.308 mmol) and monitored by ^{1}H NMR spectroscopy over 2 hours, thereby demonstrating that formation of pinBOCH(Ph)Me (TON = 40, TOF = 20 h^{-1}) was more facile than that of $PhSiH[OCH(Ph)Me]_2$ (TON = 25, TOF = 12 h^{-1}).[5]

Table S1. Catalytic reduction of CO_2 and R_2CO.

Silane or borane	**Substrate**	**Temp. (°C)**	**Catalyst loading (%)**	**Products**	**TON**	**TOF (h^{-1})**
$(MeO)_3SiH$	CO_2	60	0.5	$(MeO)_3SiO_2CH$	97	4.2
$(EtO)_3SiH$	CO_2	80	0.5	$(EtO)_3SiO_2CH$	114	2.4
HBpin	CO_2	rt	3	HCO_2Bpin	11	0.43
$PhSiH_3$	Ph_2CO	rt	1	$PhSiH_2(OCHPh_2)$ (3%) $PhSiH(OCHPh_2)_2$ (97%)	53	5
$PhSiH_3$	PhC(O)Me	rt	1	$PhSiH_2$[OCH(Ph)Me] (3%) $PhSiH[OCH(Ph)Me]_2$ (97%)	54	6
HBpin	Ph_2CO	rt	0.5	$pinBOCHPh_2$	77	10
HBpin	PhC(O)Me	rt	0.5	pinBOCH(Ph)Me	43	9
HBpin	PhCHO	rt	0.3	$pinBOCH_2Ph$	328	22

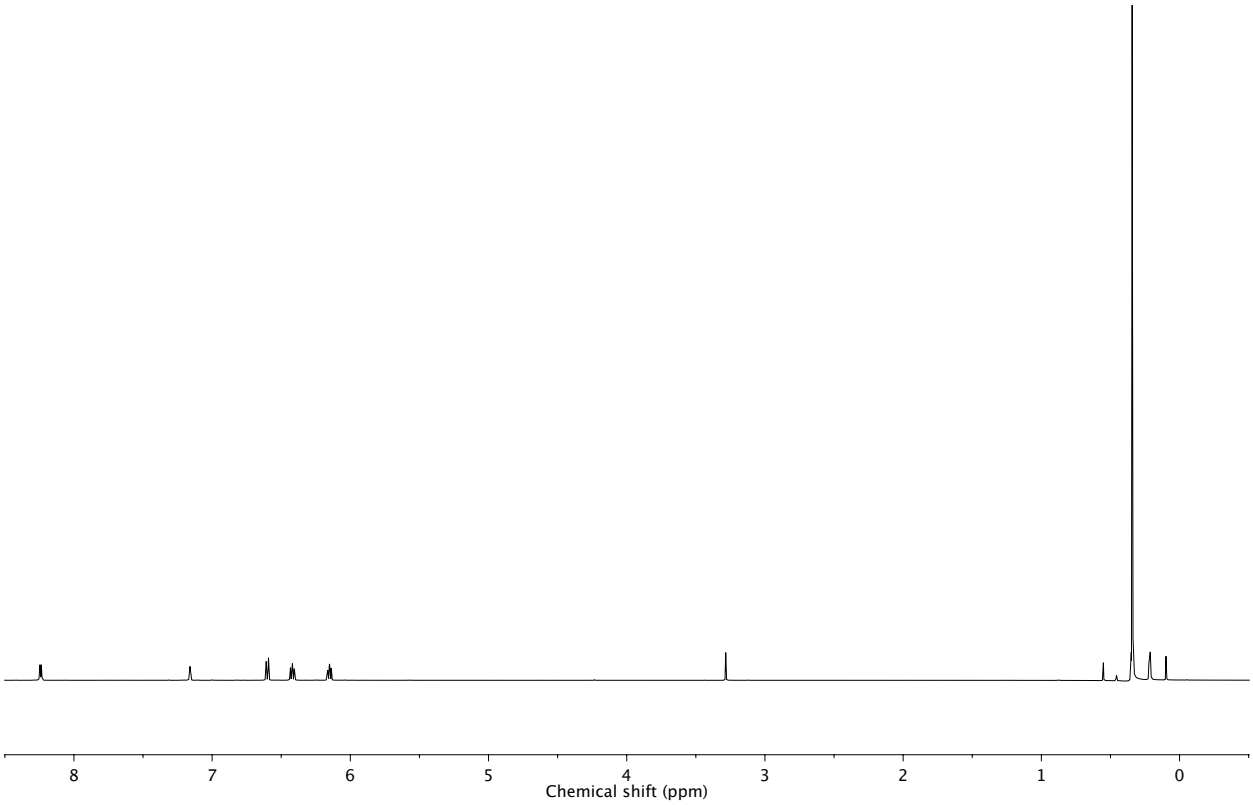

Figure S11. ^{1}H NMR spectrum of [Bptm]ZnN(SiMe$_3$)$_2$ in C_6D_6.

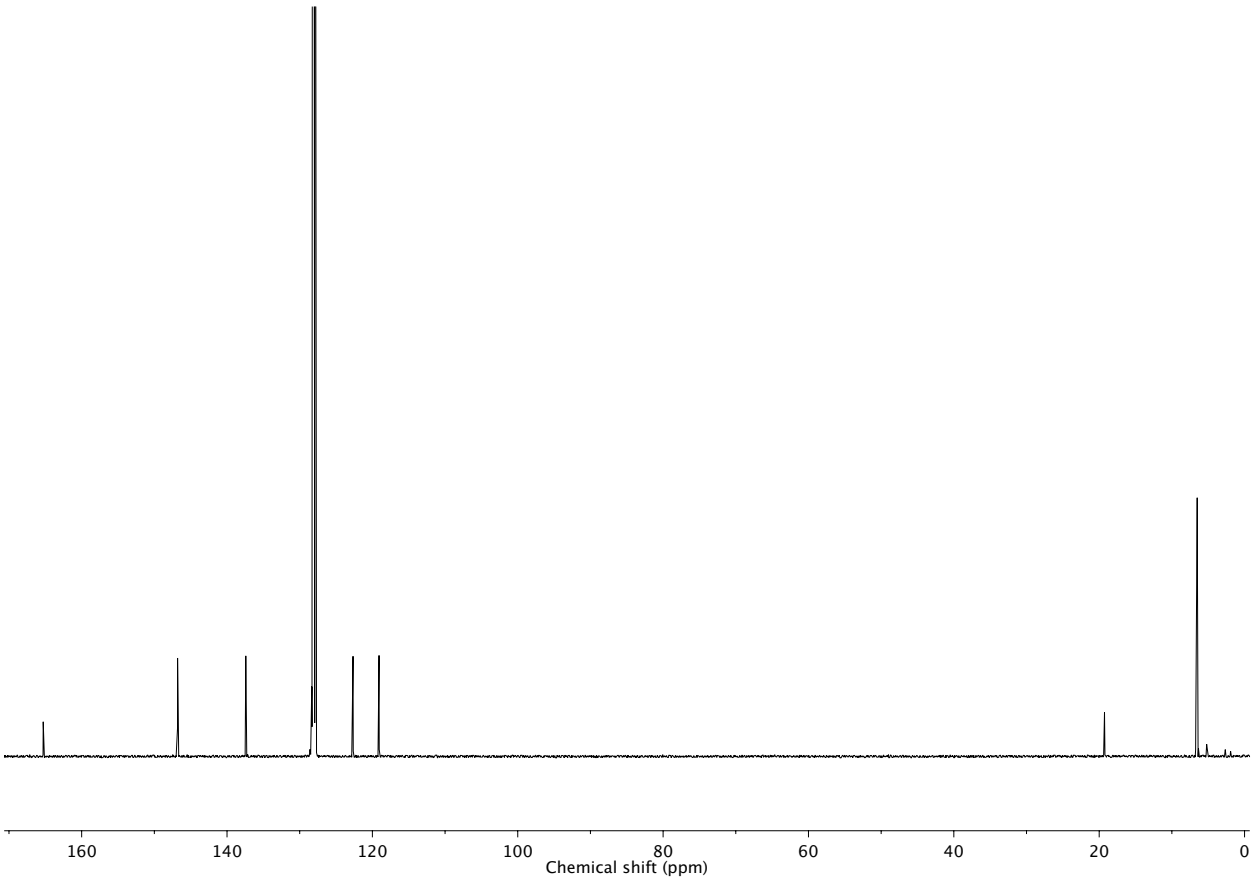

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnN($SiMe_3$)$_2$ in C_6D_6.

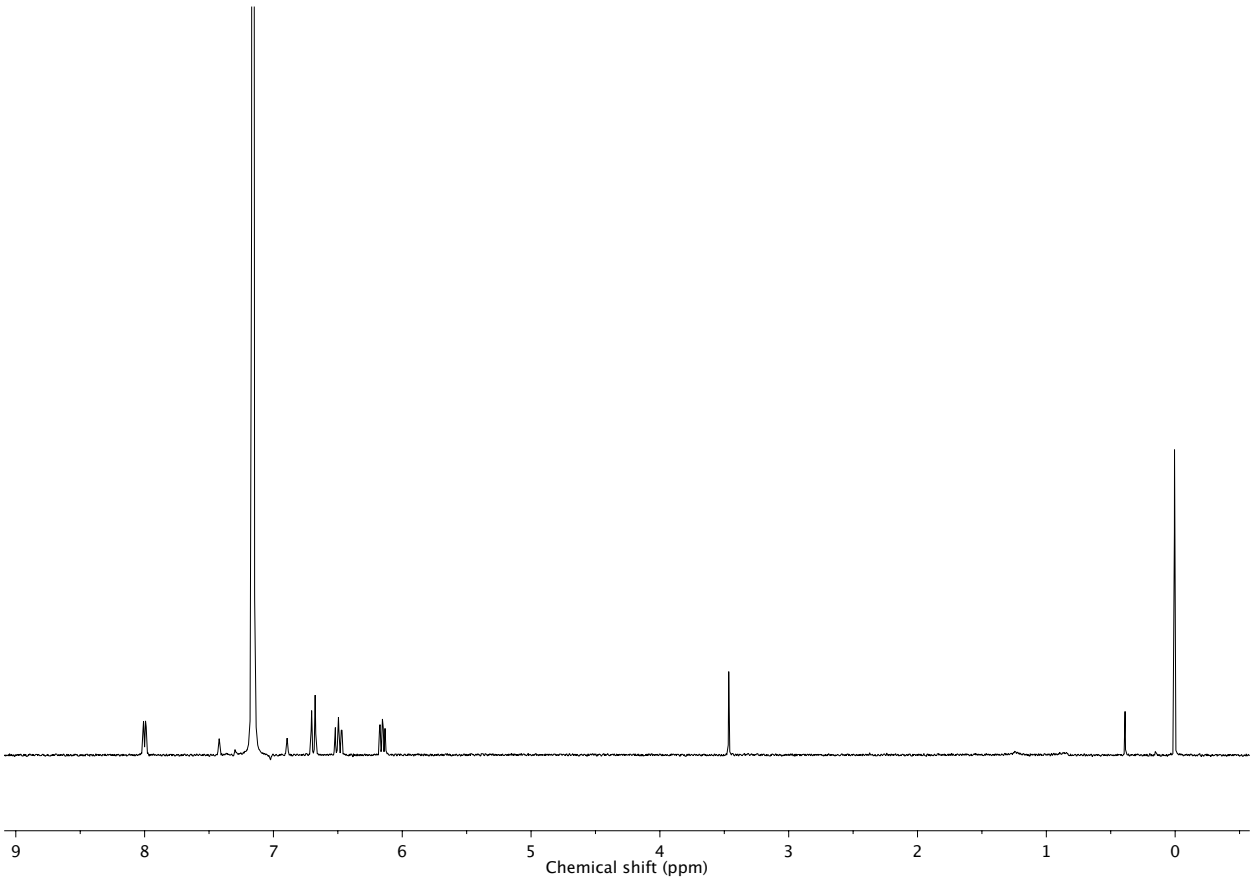

Figure S13. ^{1}H NMR spectrum of [Bptm]ZnMe in C_6D_6.

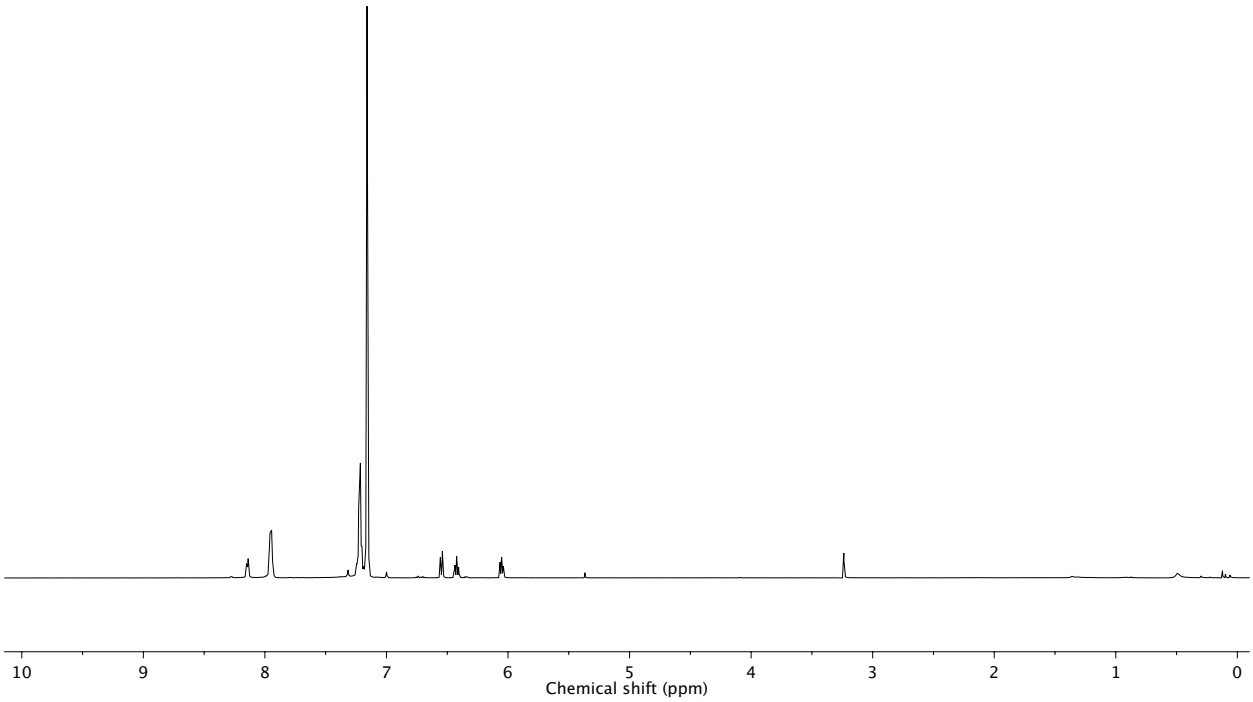

Figure S14. ^{1}H NMR spectrum of [Bptm]ZnOSiPh$_3$ in C_6D_6.

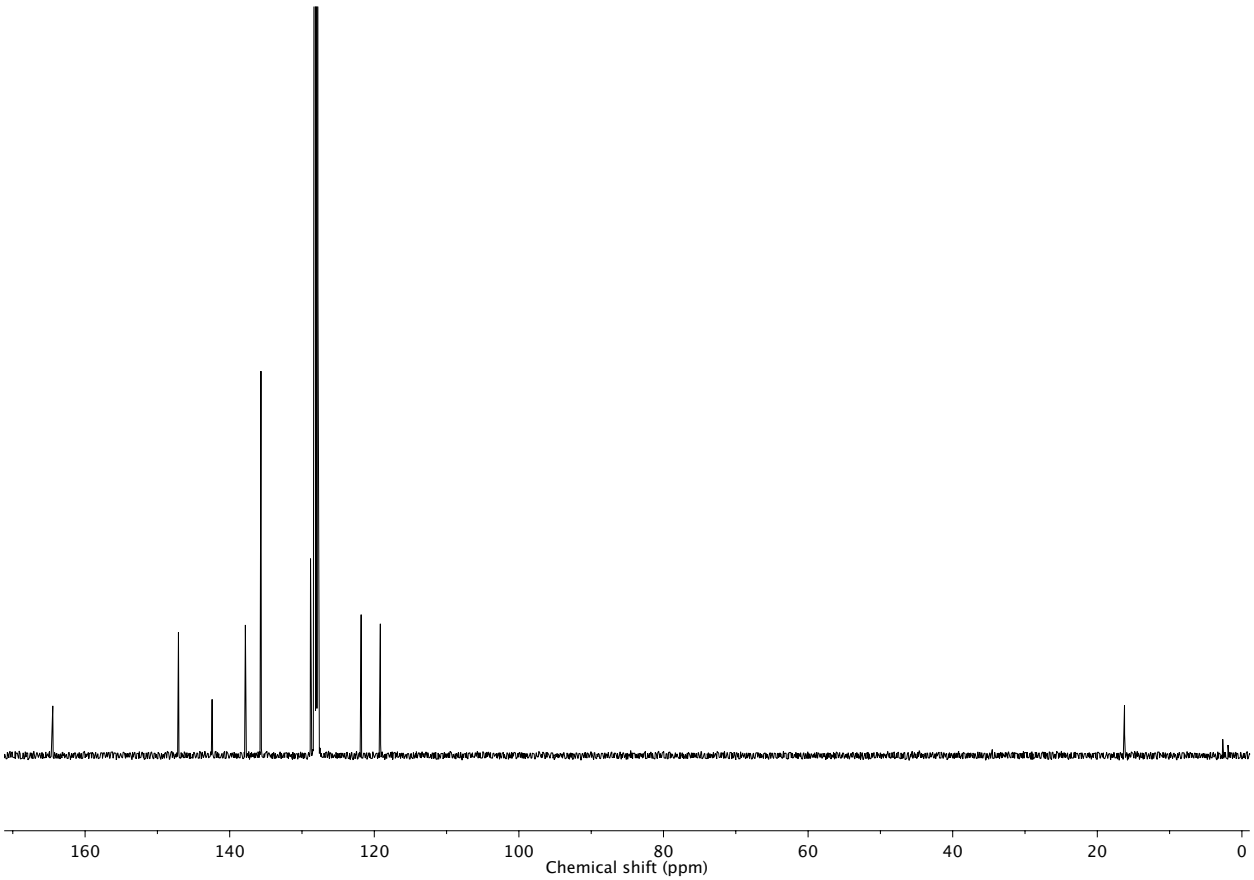

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnOSiPh$_3$ in C_6D_6.

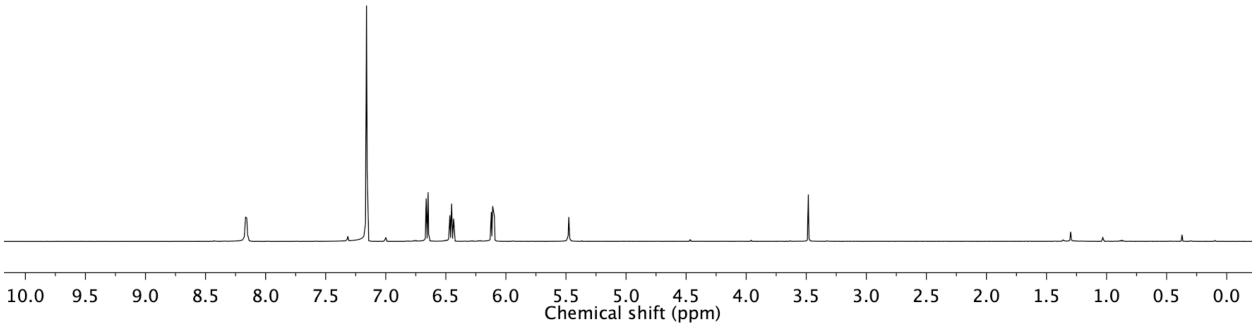

Figure S16. ^{1}H NMR spectrum of [Bptm]ZnH in C_6D_6.

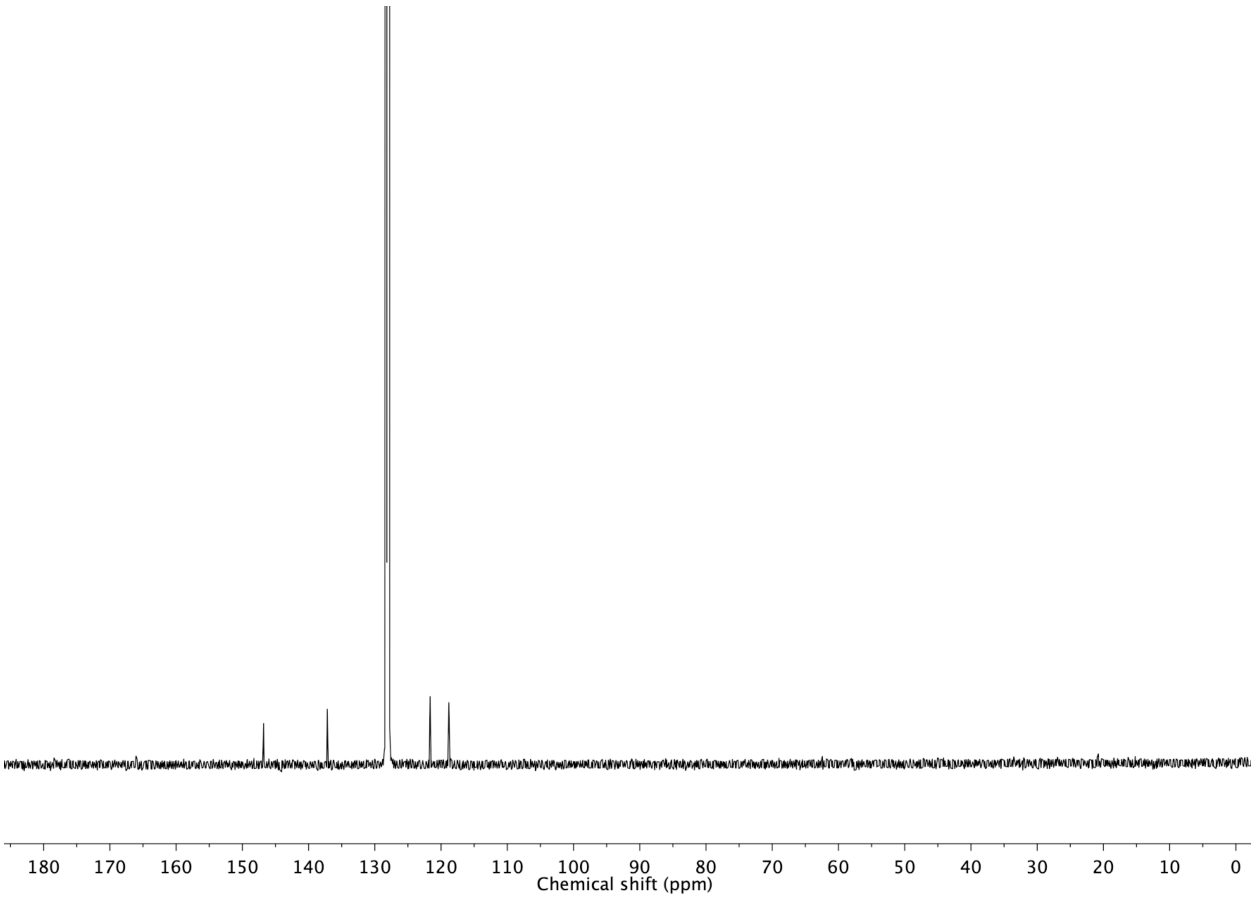

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnH in C_6D_6.

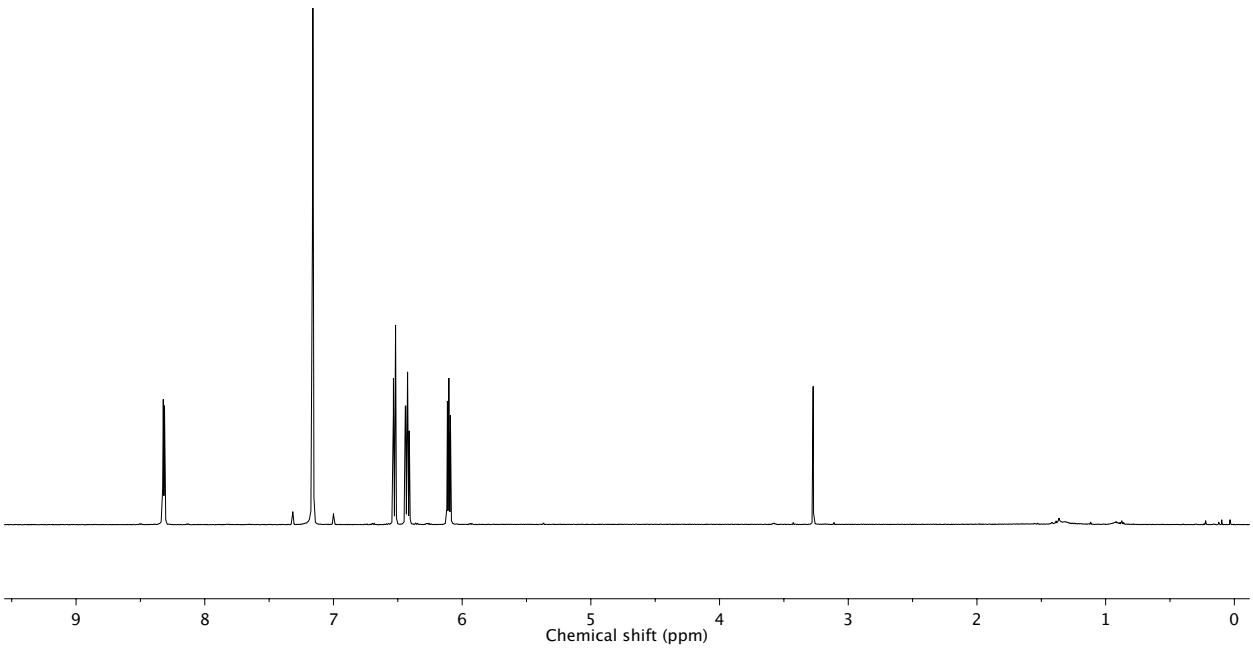

Figure S18. ^{1}H NMR spectrum of [Bptm]ZnCl in C_6D_6.

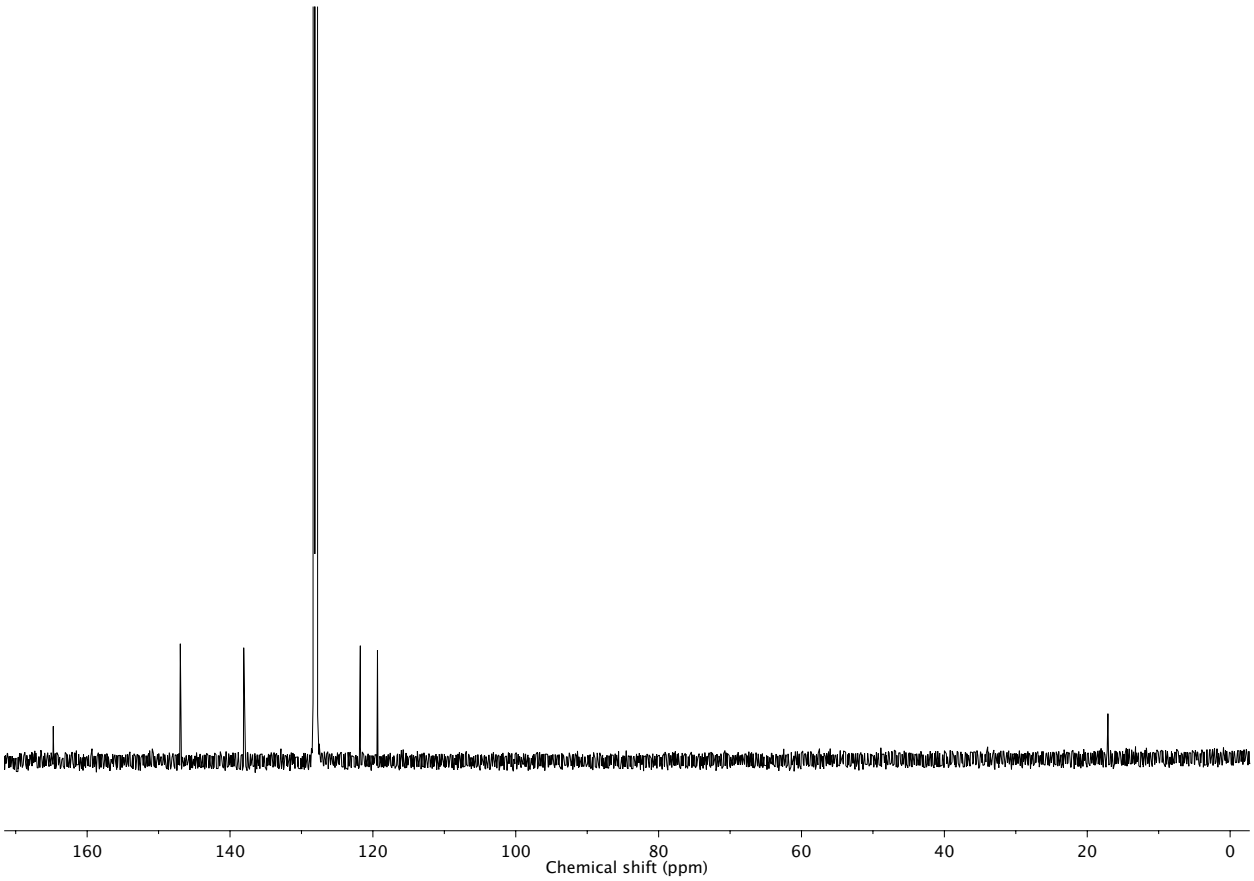

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnCl in C_6D_6.

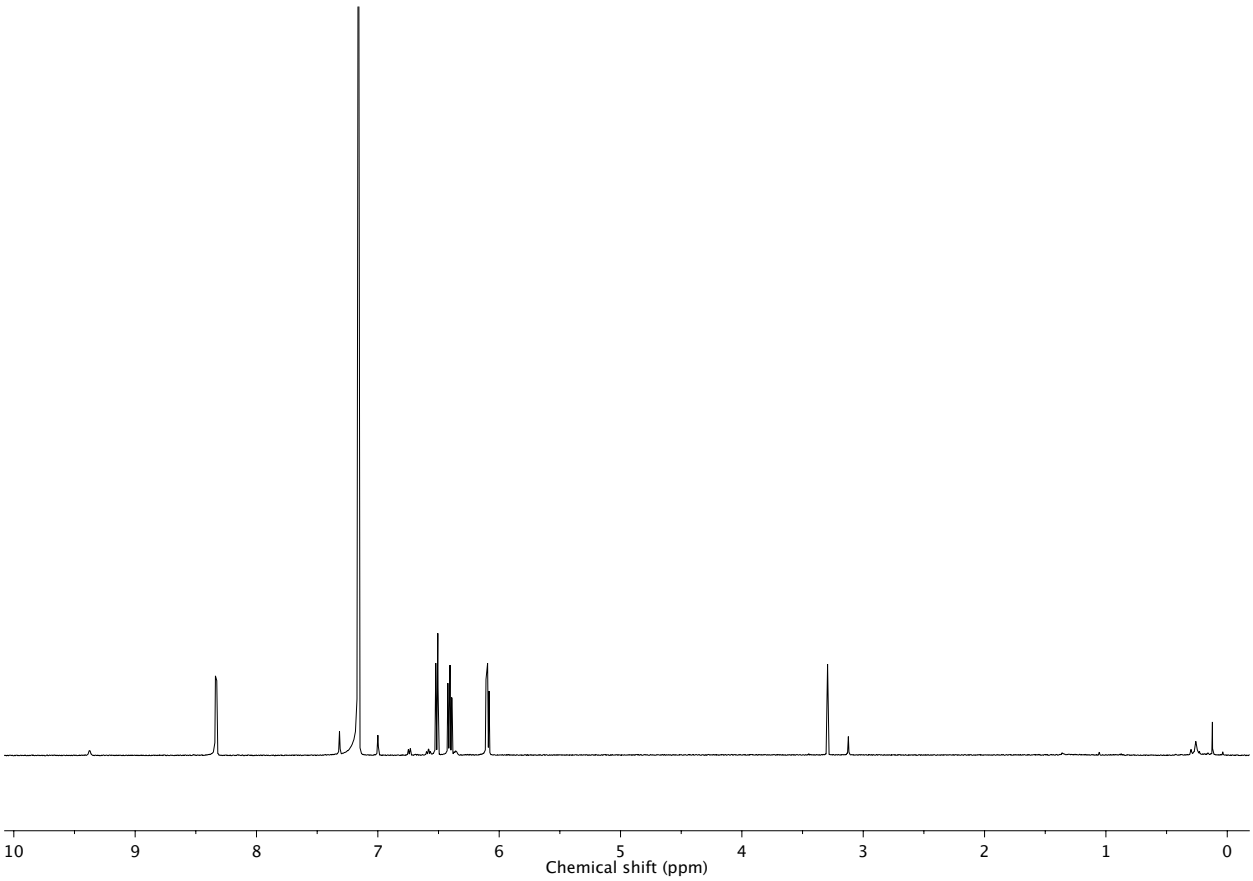

Figure S20. ^{1}H NMR spectrum of [Bptm]ZnBr in C_6D_6.

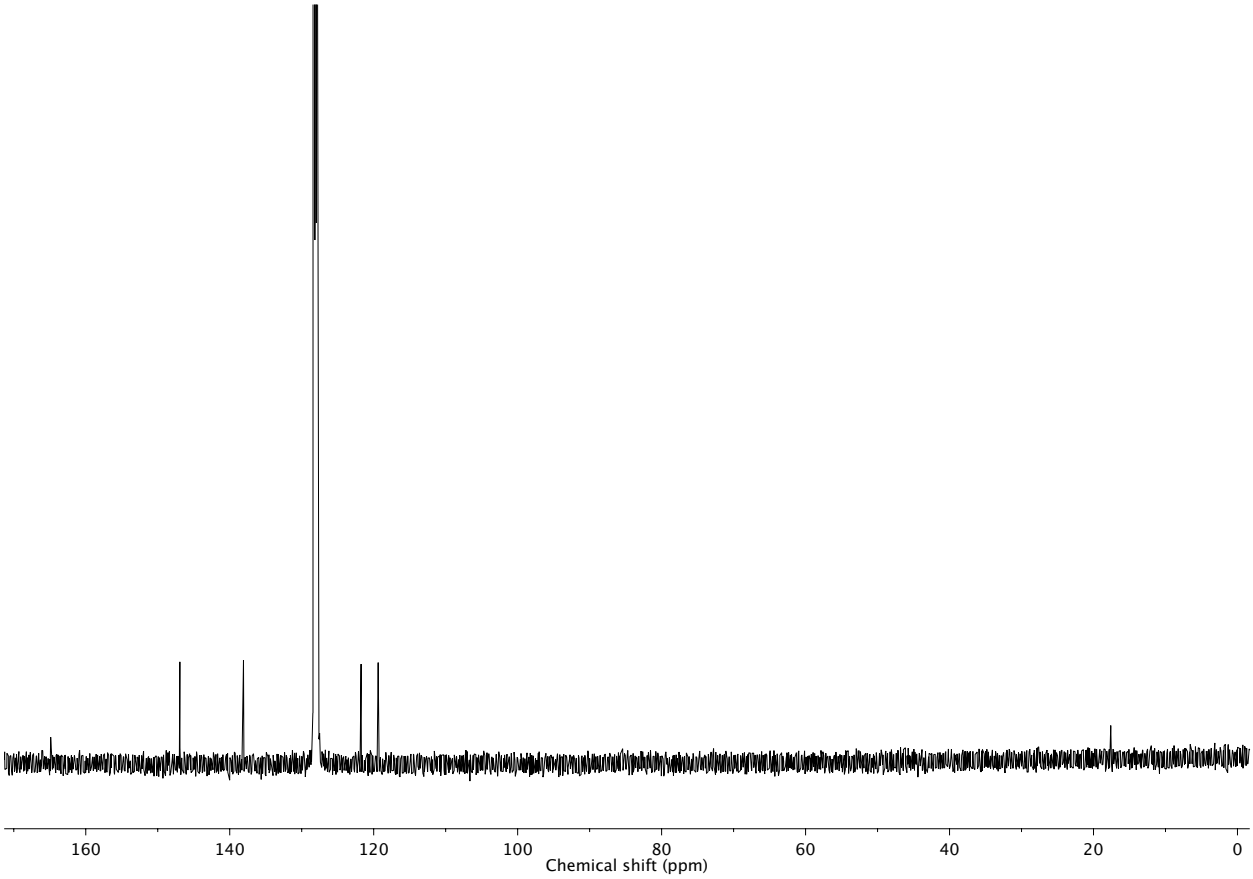

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnBr in C_6D_6.

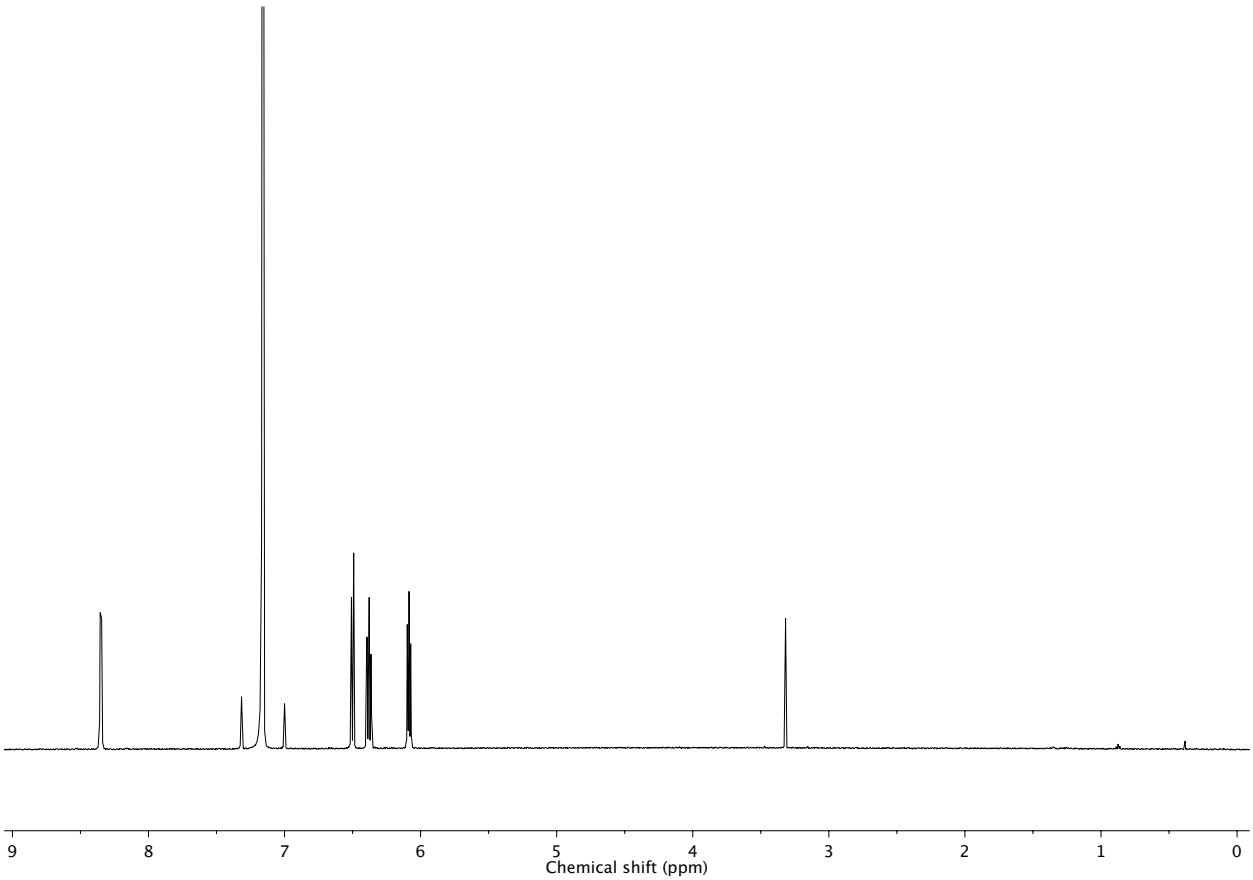

Figure S22. ^{1}H NMR spectrum of [Bptm]ZnI in C_6D_6.

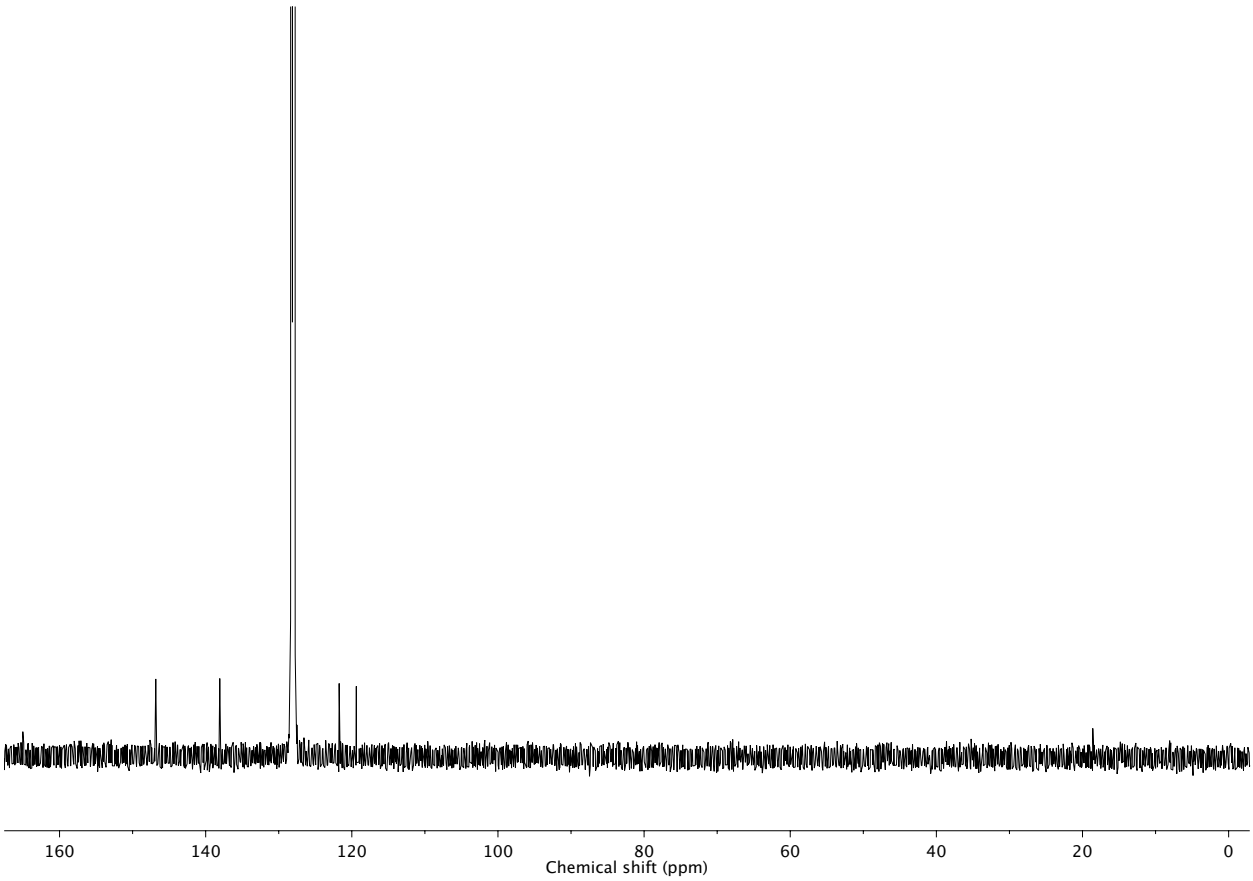

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnI in C_6D_6.

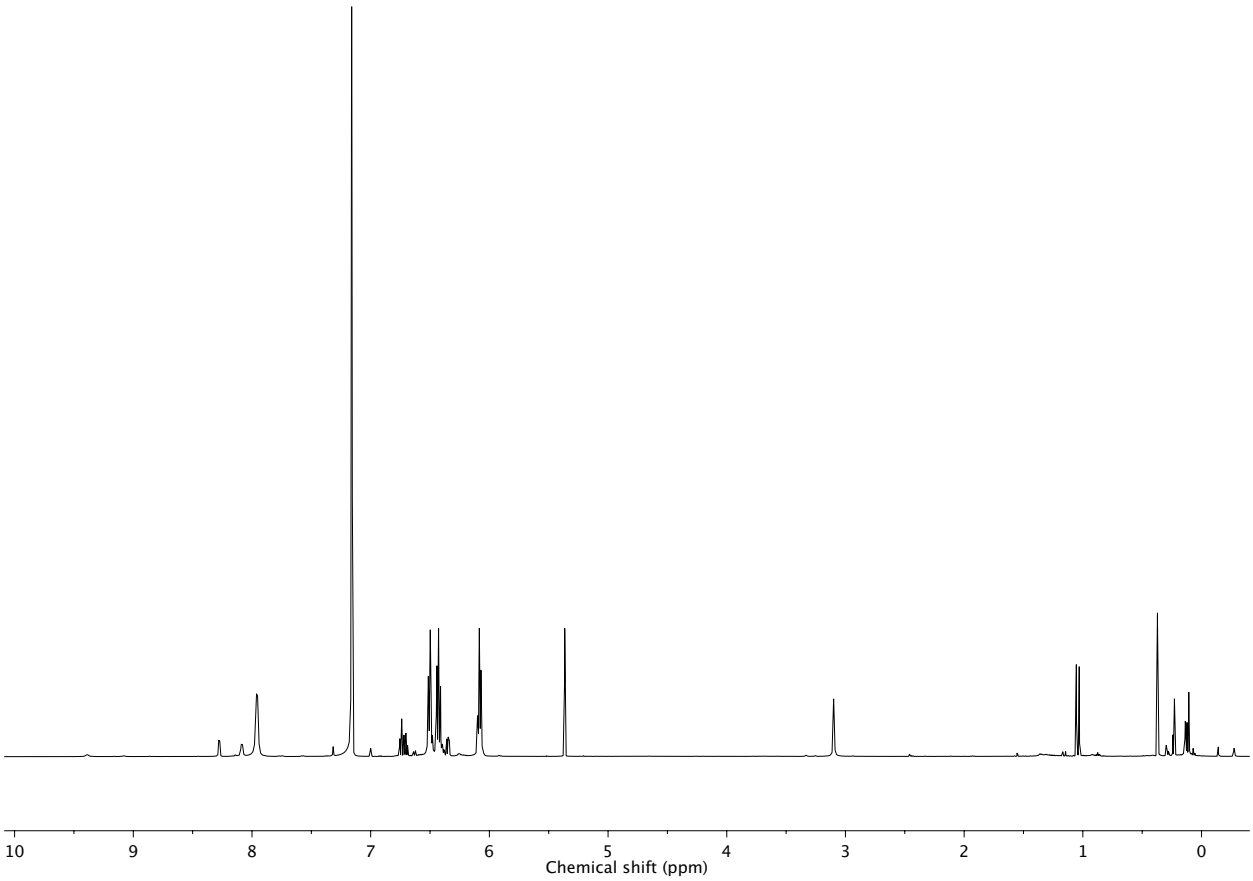

Figure S24. ^{1}H NMR spectrum of [Bptm]ZnNCO in C_6D_6 (signals due to [Bptm]H are observed at δ 5.35, 6.36, 6.69 – 6.76, and 8.27 ppm).

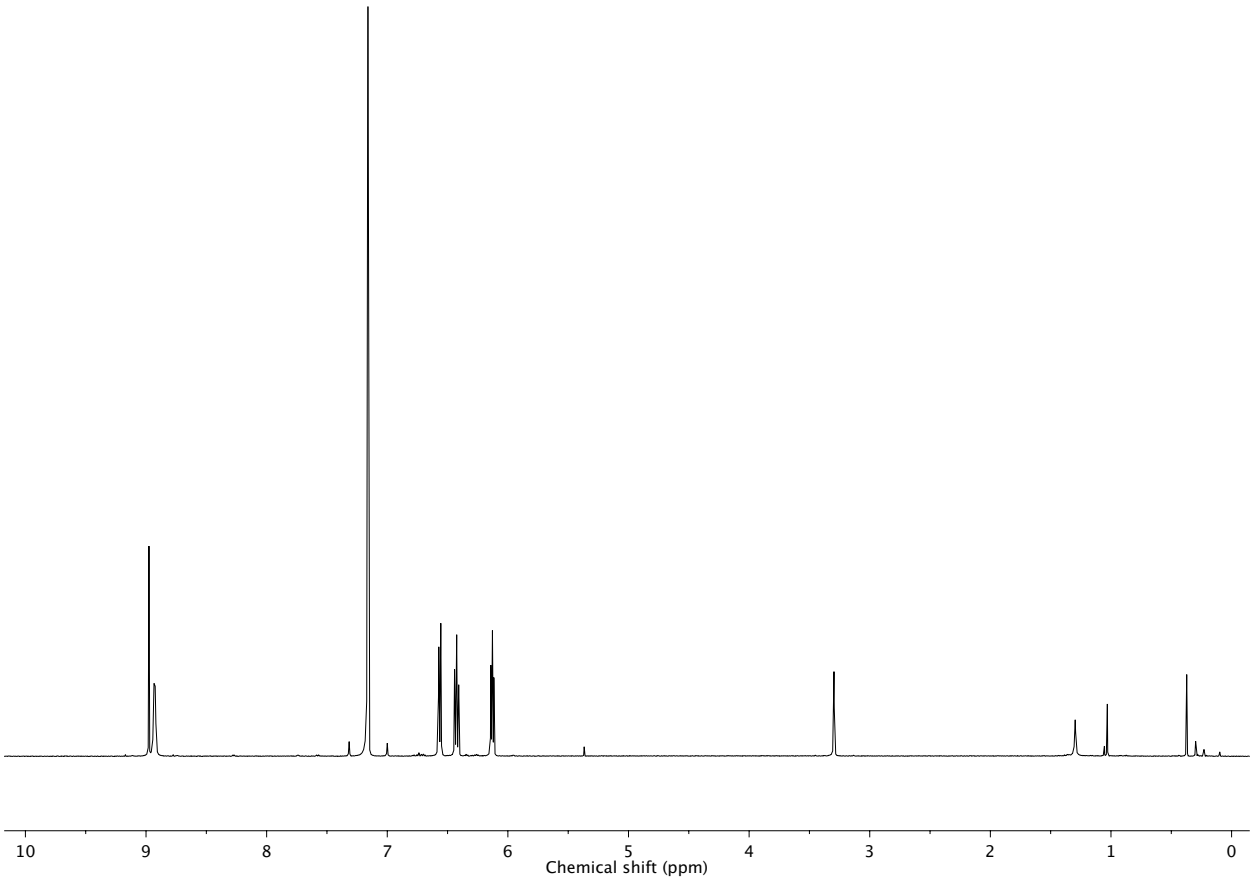

Figure S25. ^{1}H NMR spectrum of [Bptm]ZnO_2CH in C_6D_6.

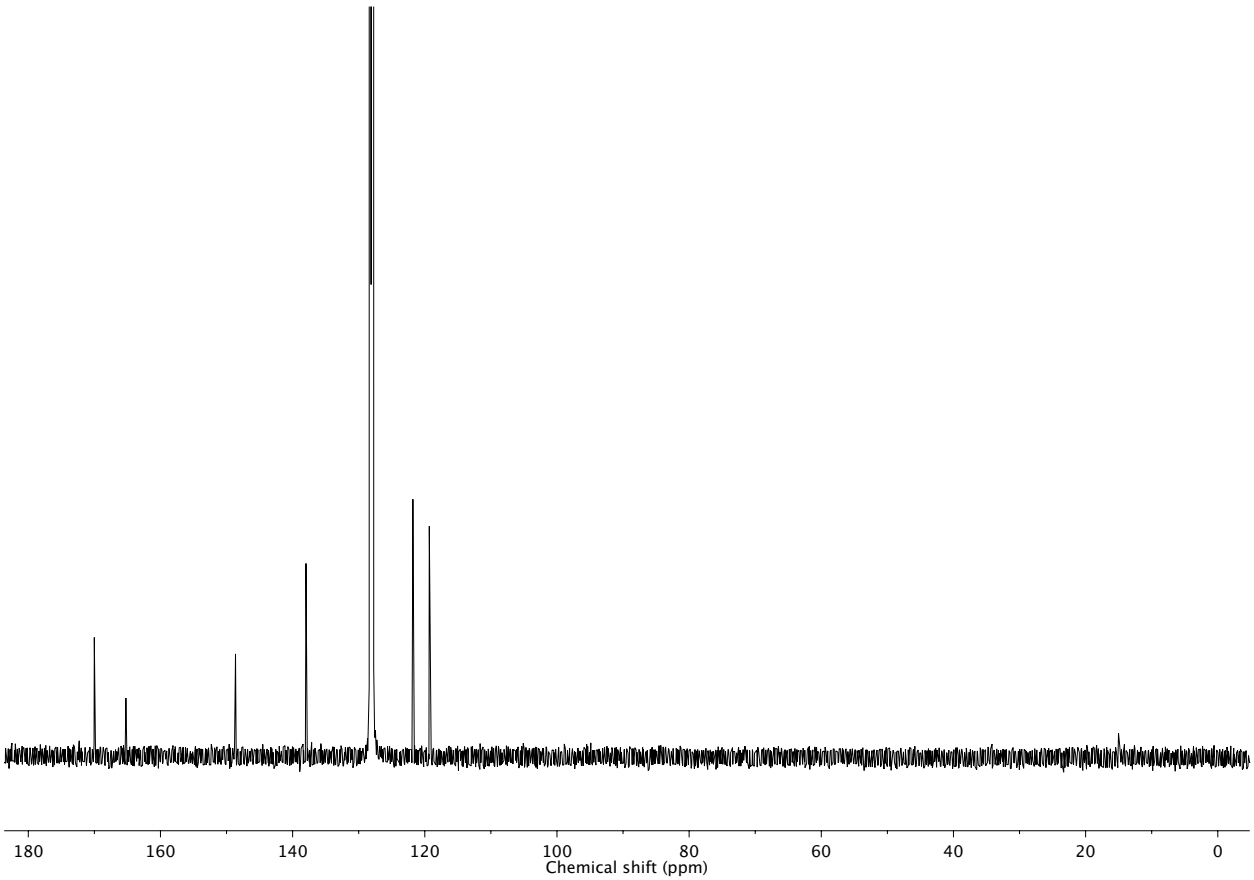

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of [Bptm]ZnO_2CH in C_6D_6.

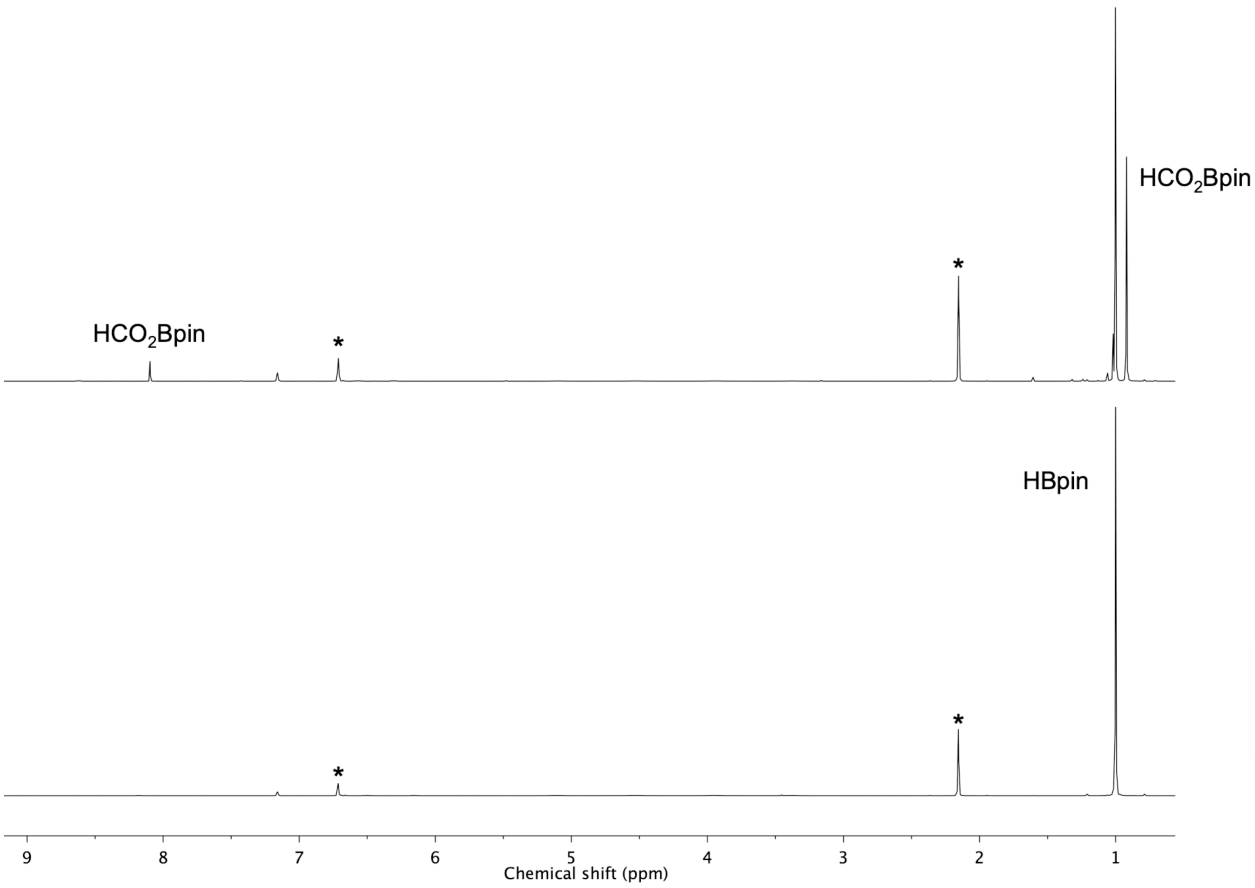

Figure S27. ^{1}H NMR spectrum demonstrating hydroboration of CO_2 by HBpin in the presence of [Bptm]ZnH in C_6D_6 at room temperature (mesitylene as an internal standard is indicated *).

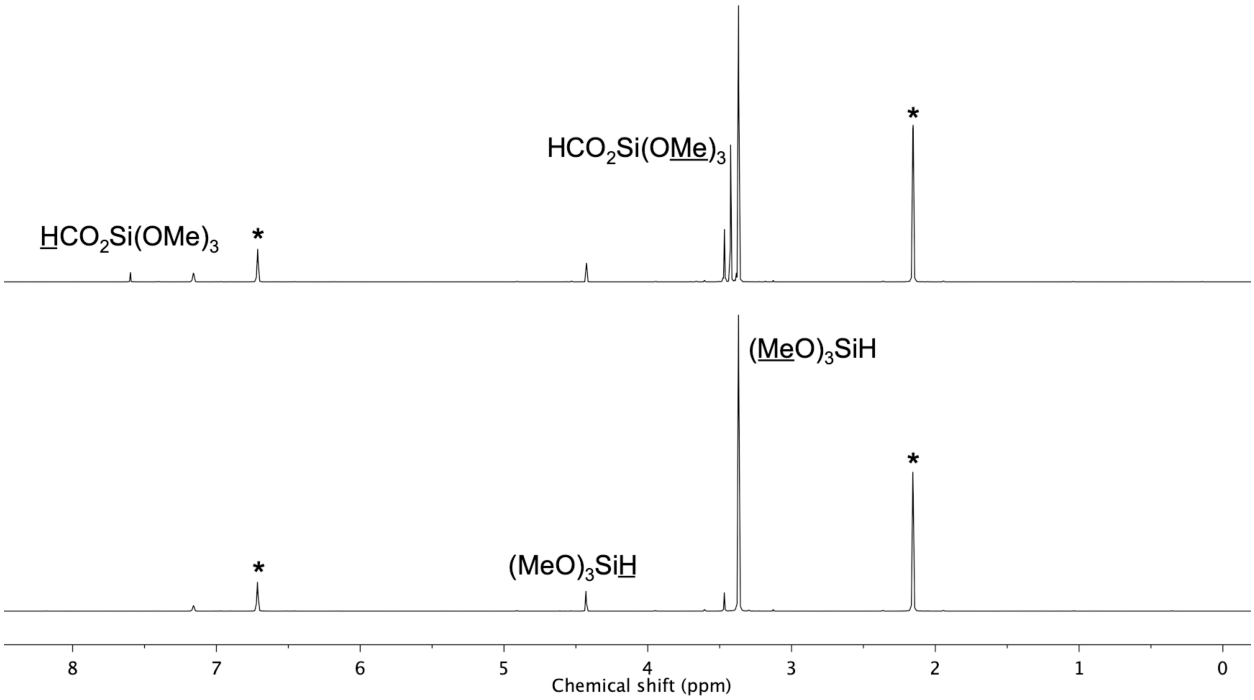

Figure S28. ^{1}H NMR spectrum demonstrating hydrosilylation of CO_2 by $(MeO)_3SiH$ in the presence of [Bptm]ZnH in C_6D_6 at 60˚C (mesitylene as an internal standard is indicated *).

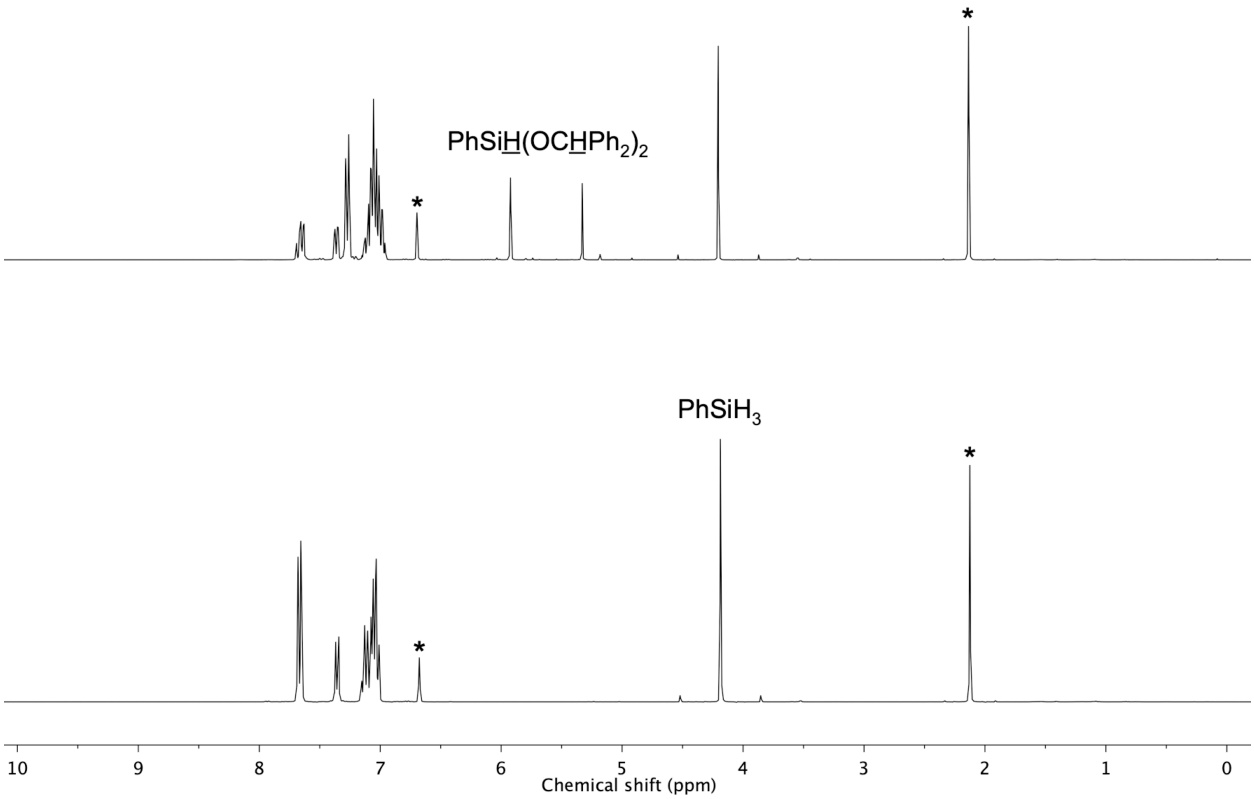

Figure S29. ^{1}H NMR spectrum demonstrating hydrosilylation of Ph_2CO by $PhSiH_3$ in the presence of [Bptm]ZnH in C_6D_6 (mesitylene as an internal standard is indicated *).

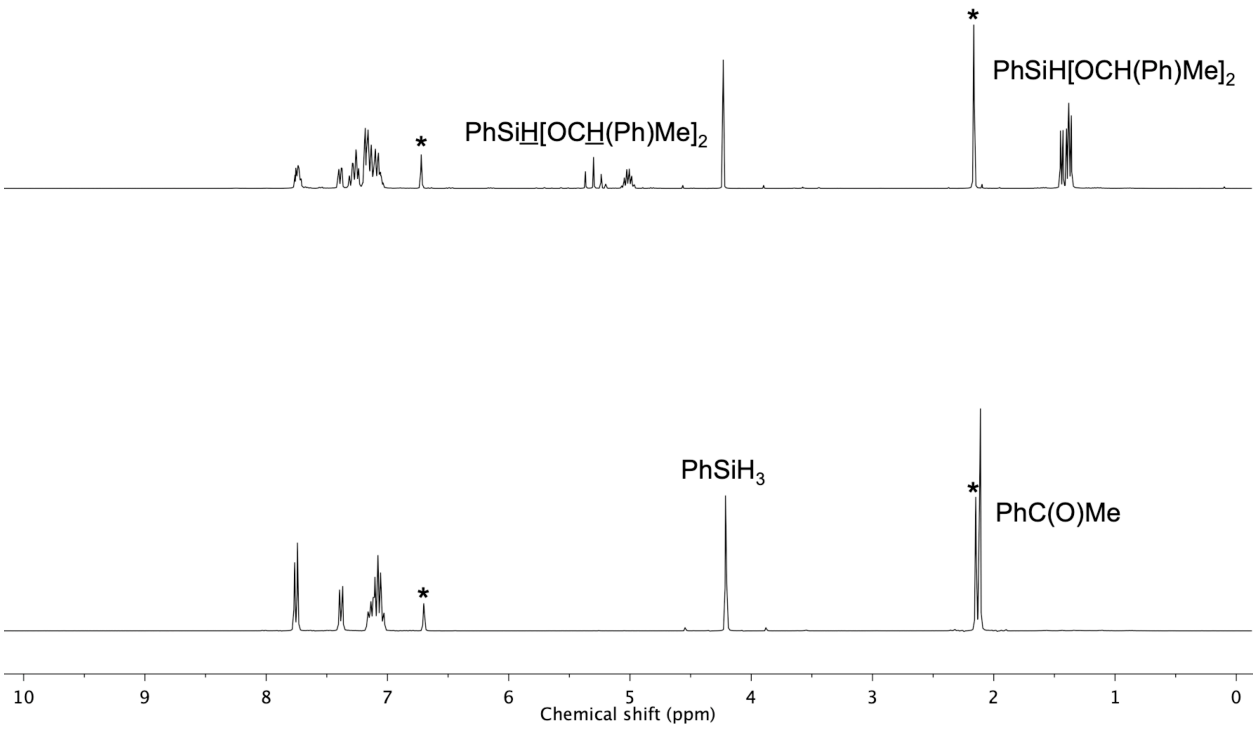

Figure S30. ^{1}H NMR spectrum demonstrating hydrosilylation of PhC(O)Me by $PhSiH_3$ in the presence of [Bptm]ZnH in C_6D_6 (mesitylene as an internal standard is indicated *).

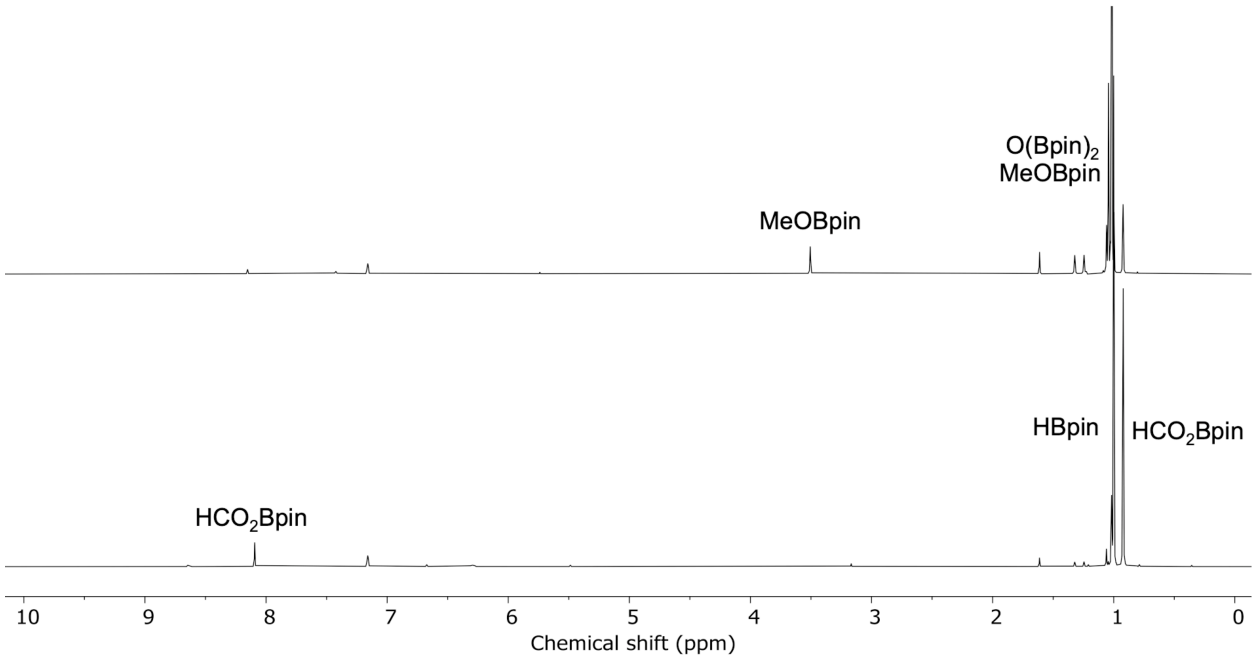

Figure S31. ^{1}H NMR spectroscopic evidence demonstrating hydroboration of HCO_2Bpin by HBpin in the presence of [Bptm]ZnH in C_6D_6.

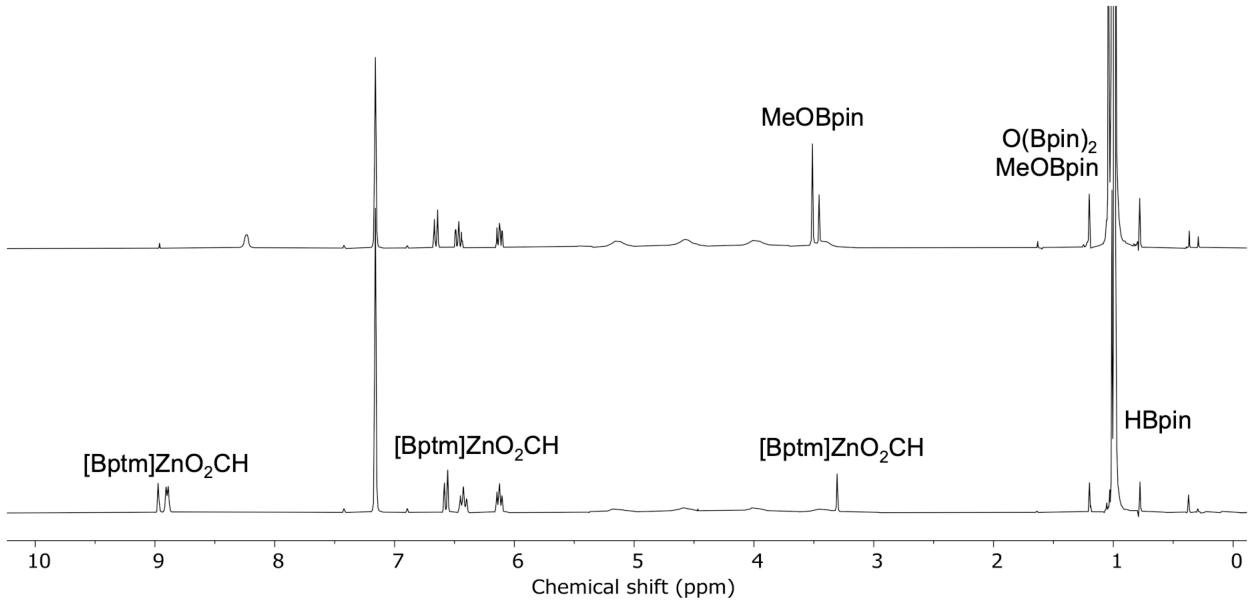

Figure S32. ^{1}H NMR spectroscopic evidence demonstrating the reaction of [Bptm]ZnO_2CH with HBpin to form MeOBpin in C_6D_6.

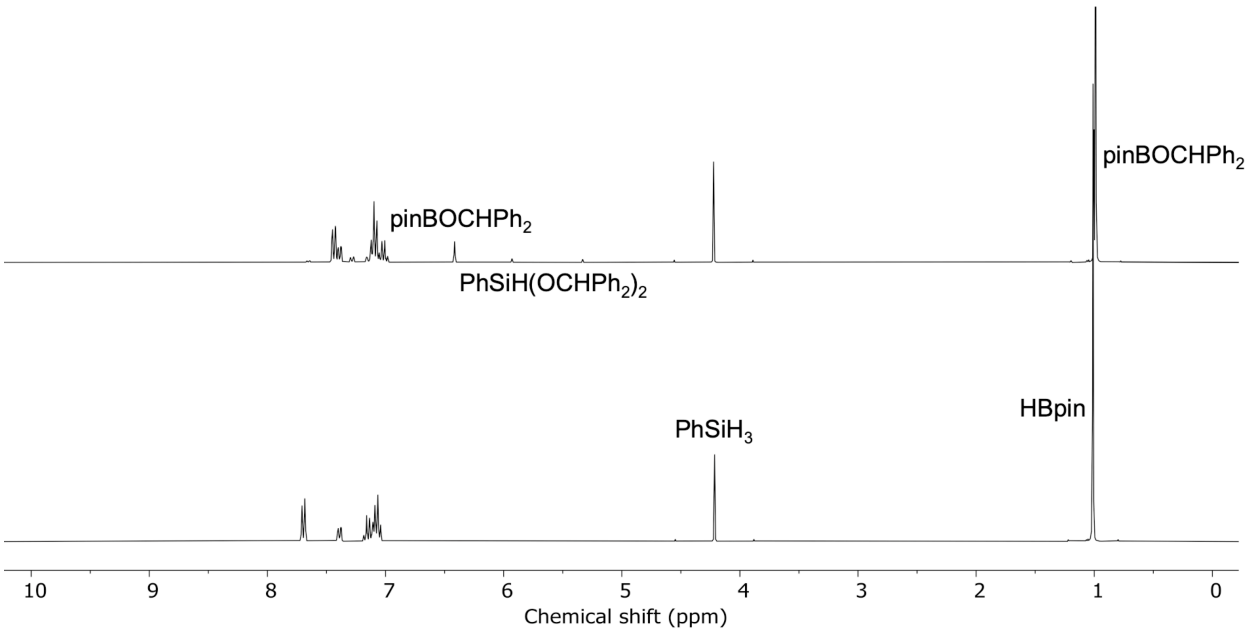

Figure S33. ^{1}H NMR spectroscopic evidence for more facile hydroboration than hydrosilylation of Ph_2CO catalyzed by [Bptm]ZnH in C_6D_6.

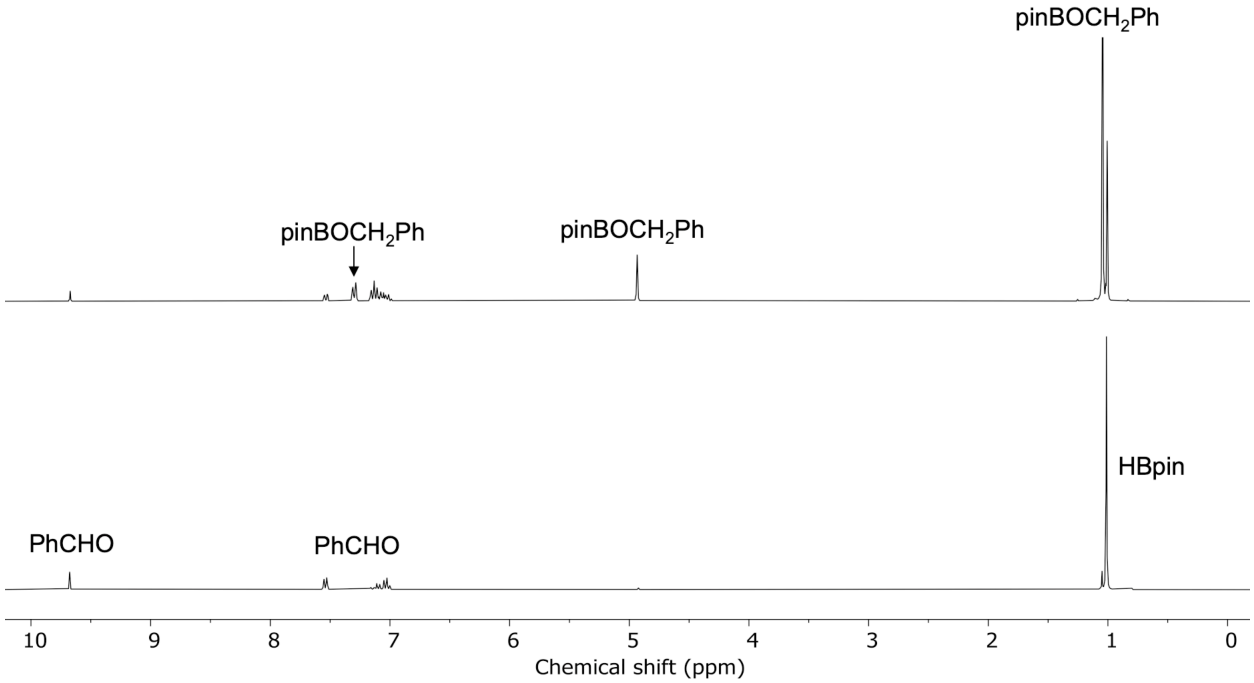

Figure S34. ^{1}H NMR spectrum demonstrating hydroboration of PhCHO by HBpin in the presence of [Bptm]ZnH in C_6D_6.

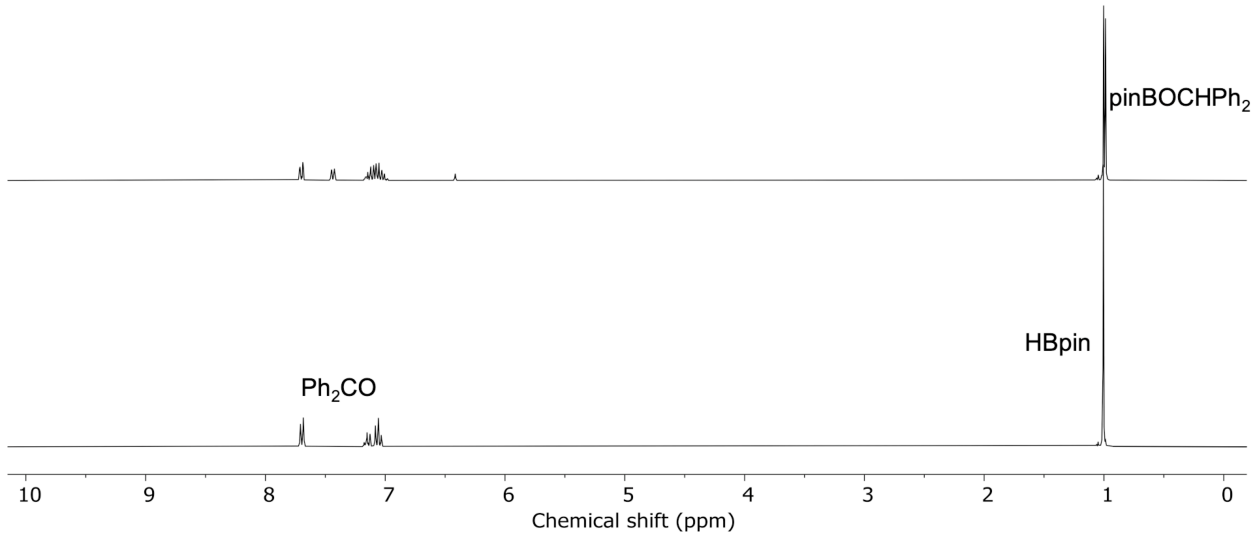

Figure S35. ^{1}H NMR spectrum demonstrating hydroboration of Ph_2CO by HBpin in the presence of [Bptm]ZnH in C_6D_6.

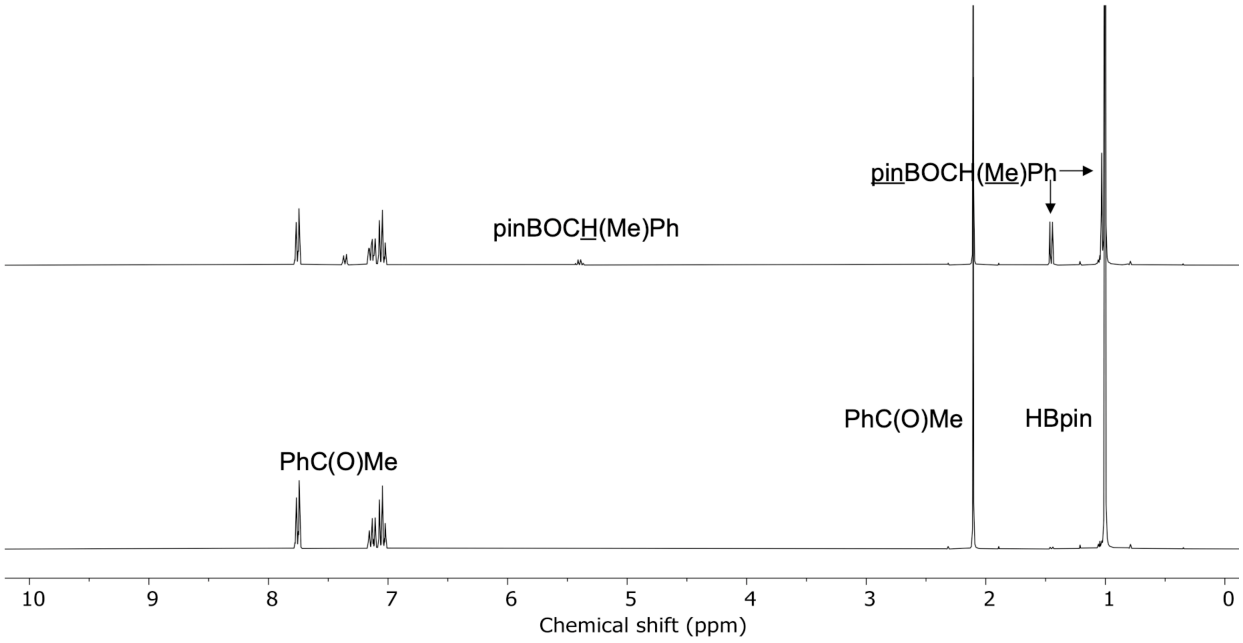

Figure S36. ^{1}H NMR spectrum demonstrating hydroboration of PhC(O)Me by HBpin in the presence of [Bptm]ZnH in C_6D_6.

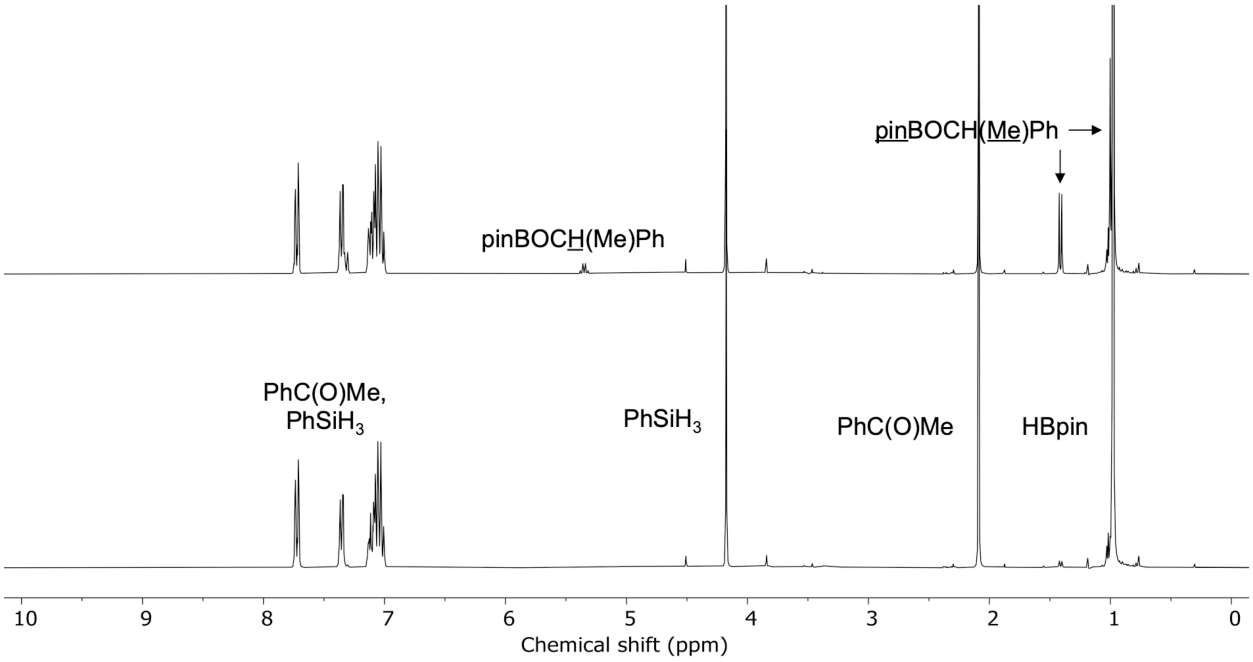

Figure S37. ^{1}H NMR spectroscopic evidence for more facile hydroboration than hydrosilylation of PhC(O)Me catalyzed by [Bptm]ZnH in C_6D_6.

REFERENCES

(1) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic* Chemistry, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23.
(b) Burger, B.J.; Bercaw, J. E. in Experimental Organometallic Chemistry; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.
(c) Shriver, D. F.; Drezdzon, M. A.; The Manipulation of Air-Sensitive Compounds, 2nd Edition; Wiley-Interscience: New York, 1986.

(2) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512-7515.

(3) de Castro, V. D.; de Lima, G. M.; Filgueiras, C. A. L.; Gambardella, M. T. P. "The molecular structure and spectral studies of mercaptopyridyl-based ligands" *J. Mol. Struct.* **2002,** *609*, 199-203.

(4) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.
(b) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
(c) Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8.

(5) Sattler, W.; Ruccolo, S.; Chaijan, M. R.; Allah, T. N.; Parkin, G. *Organometallics* **2015**, *34*, 4717-4731.

(6) For other examples of competitive mono and di-insertion of ketones into Si–H bonds, see reference 5 and
(a) Findlay, A. E.; Leelasubcharoen, S.; Kuzmina, L. G.; Howard, J. A. K.; Nikonov, G. I. *Dalton Trans.* **2010**, *39*, 9264-9269.
(b) McLeod, N. A.; Kuzmina, L. G.; Korobkov, I.; Howard, J. A. K.; Nikonov, G. I. *Dalton Trans.* **2016**, *45*, 2554-2561.

(7) Anga, S.; Acharya, J.; Chandrasekhar, V. *J. Org. Chem.* **2021**, *86*, 2224-2234.

(8) Sokolovicz, Y. C. A.; Faza, O. N.; Specklin, D.; Jacques, B.; Lopez, C. S.; dos Santos, J. H. Z.; Schrekker, H. S.; Dagorne, S. *Catal. Sci. Technol.* **2020,** *10*, 2407-2414.