Hydroboration of carbon dioxide enabled by molecular zinc dihydrides

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Supporting Information

General Procedures: All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported as δ units with reference to the residual solvent resonance or an external standard. The assignments of NMR data were supported by 1D and 2D NMR experiments. Elemental analysis data was recorded on a Carlo-Erba EA-1110 instrument. 2,6-Diisopropylphenol, HBpin, HBcat and 9-BBN were purchased from Strem. $BH_3{\cdot}SMe_2$, $ZnEt_2$, and $PhSiH_3$ were purchased from Adamas. Ligand precursors **NHC^a·HBr** [**NHC^a·HBr** = 1-(2-diphenylphosphinoethyl)-3-(2,6-diisopropylphenyl)imidazolium bromide] and **NHC^b·HBr** [**NHC^b·HBr** = 1-(2-diphenylphosphinoethyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide] were synthesized by following the literature procedures.[1] Zinc hydride complexes $[(IPr)ZnH_2]_2$,[2] $[(IMes)ZnH_2]_2$,[2] and (DIPP-nacnac)ZnH[3] were synthesized following the literature procedures.

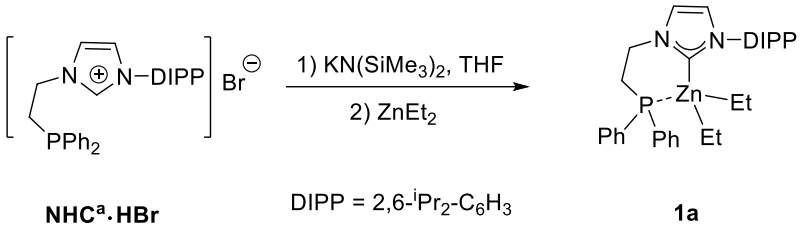
References

[1] J. Wolf, A. Labande, M. Natella, J. C. Daran and R. Poli, *J. Mol. Catal. A: Chem.*, 2006, **259**, 205-212.

[2] A. Rit, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem. Int. Ed.*, 2013, **52**, 4664-4667.

[3] J. Spielmann, D. Piesik, B. Wittkamp, G. Jansen and S. Harder, *Chem. Commun.*, 2009, 3455-3456.

Preparation of complex 1a



NHC^{a}·HBr DIPP = 2,6-^{i}Pr$_2$-C$_6$H$_3$ **1a**

Scheme S1.

K[N(SiMe$_3$)$_2$] (2.5 mL, 1.0 M in THF) was slowly added to a solution of **NHC^{a}·HBr** (1.30 g, 2.50 mmol) in 15 mL of THF at -78 ℃. After stirring at -78 ℃ for 30 min, ZnEt$_2$ (2.5 mL, 1.0 M in n-hexane) was slowly added to the reaction mixture and the reaction mixture was allowed to stir at room temperature for 8 h. The resulting mixture was filtered and all the volatiles were removed under vacuum. The residue was washed with hexane (4 * 2 mL) to finally give **1a** as a pale yellow solid (1.16 g, 82% yield).

Elemental Analysis: calcd. for $C_{33}H_{43}N_2PZn$: C, 70.27; H, 7.68; N, 4.97. Found: C, 70.89; H, 7.12; N, 4.71.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.38 (m, 4H, *o*-*Ph*$_2$P), 7.21 (m, 1H, *p*-N*Ar*), 7.11 (m, 2H, *p*-*Ph*$_2$P), 7.10 (m, 4H, *m*-*Ph*$_2$P), 7.08 (m, 2H, *m*-N*Ar*), 6.33 (m, 1H, ArNC*H*), 6.24 (m, 1H, ArNCH=C*H*), 4.01 (m, 2H, NC*H*$_2$), 2.56 (sp, $^{3}J_{HH}$ = 6.8 Hz, 2H, NArC*H*Me$_2$), 2.27 (m, 2H, PC*H*$_2$), 1.66 (t, $^{3}J_{HH}$ = 8.1 Hz, 3H, ZnCH$_2$C*H*$_3$), 1.27 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, NArCH*Me*$_2$), 0.97 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, NArCH*Me*$_2$), 0.35 (q, $^{3}J_{HH}$ = 8.1 Hz, 2H, ZnC*H*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 190.2 (d, $^{2}J_{PC}$ = 8.0 Hz, N*C*N), 145.9 (*o*-N*Ar*), 137.9 (d, $^{1}J_{PC}$ = 10.4 Hz, *i*-*Ph*$_2$P), 135.8 (*i*-N*Ar*), 133.1 (d, $^{2}J_{PC}$ = 18.8 Hz, *o*-*Ph*$_2$P), 130.2 (*p*-N*Ar*), 129.2 (*p*-*Ph*$_2$P), 129.0 (d, $^{3}J_{PC}$ = 6.9 Hz, *m*-*Ph*$_2$P), 124.1 (*m*-N*Ar*), 123.1 (ArN*C*H), 119.9 (ArNCH=*C*H), 47.4 (d, $^{2}J_{PC}$ = 20.3 Hz, N*C*H$_2$), 31.5 (d, $^{1}J_{PC}$ = 13.4 Hz, P*C*H$_2$), 28.5 (NAr*C*HMe$_2$), 25.4 (NArCH*Me*$_2$), 23.5 (NArCH*Me*$_2$), 14.9 (ZnCH$_2$*C*H$_3$), 4.6 (Zn*C*H$_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -22.5.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.38 / 133.1 (*o*-*Ph*$_2$P), 7.21 / 130.2 (*p*-N*Ar*), 7.11 / 129.2 (*p*-*Ph*$_2$P), 7.10 / 129.0 (*m*-*Ph*$_2$P), 7.08 /

124.1 (*m*-N*Ar*), 6.33 / 123.1 (ArN*CH*), 6.24 / 119.9 (ArNCH=*CH*), 4.01 / 47.4 (N*CH*$_2$), 2.56 / 28.5 (NAr*CH*Me$_2$), 2.27 / 31.5 (P*CH*$_2$), 1.66 / 14.9 (ZnCH$_2$*CH*$_3$), 1.27 / 23.5 (NArCH*Me*$_2$), 0.97 /25.4 (NArCH*Me*$_2$), 0.35 / 4.6 (Zn*CH*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.38 / 129.3 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.08 / 135.8, 28.5 (*m*-N*Ar* / *i*-N*Ar*, NAr*C*HMe$_2$), 4.01 / 190.2, 119.9, 31.5 (NC*H*$_2$ / N*C*N, ArNCH=*C*H, P*C*H$_2$), 2.56 / 145.9, 135.8, 124.1, 25.4, 23.5 (NArC*H*Me$_2$ / *o*-N*Ar*, *i*-N*Ar*, *m*-N*Ar*, NArCH*Me*$_2$, NArCH*Me*$_2$), 2.27 / 137.9, 47.4 (PC*H*$_2$ / *i*-*Ph*$_2$P, N*C*H$_2$).

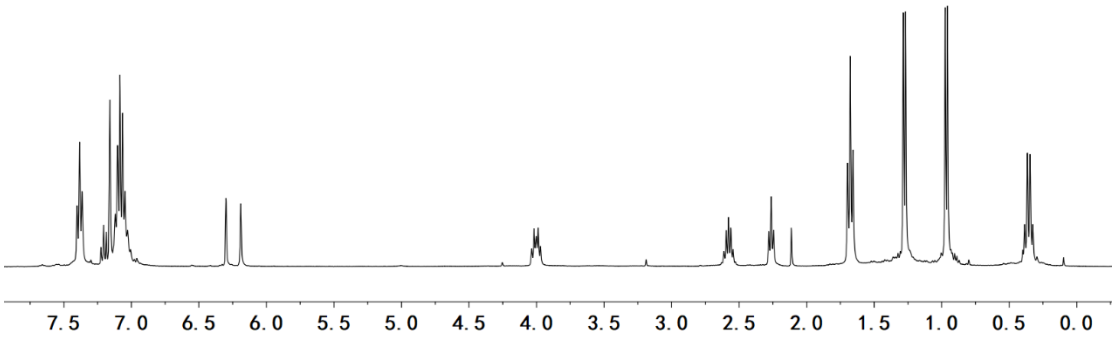


Fig. S1. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

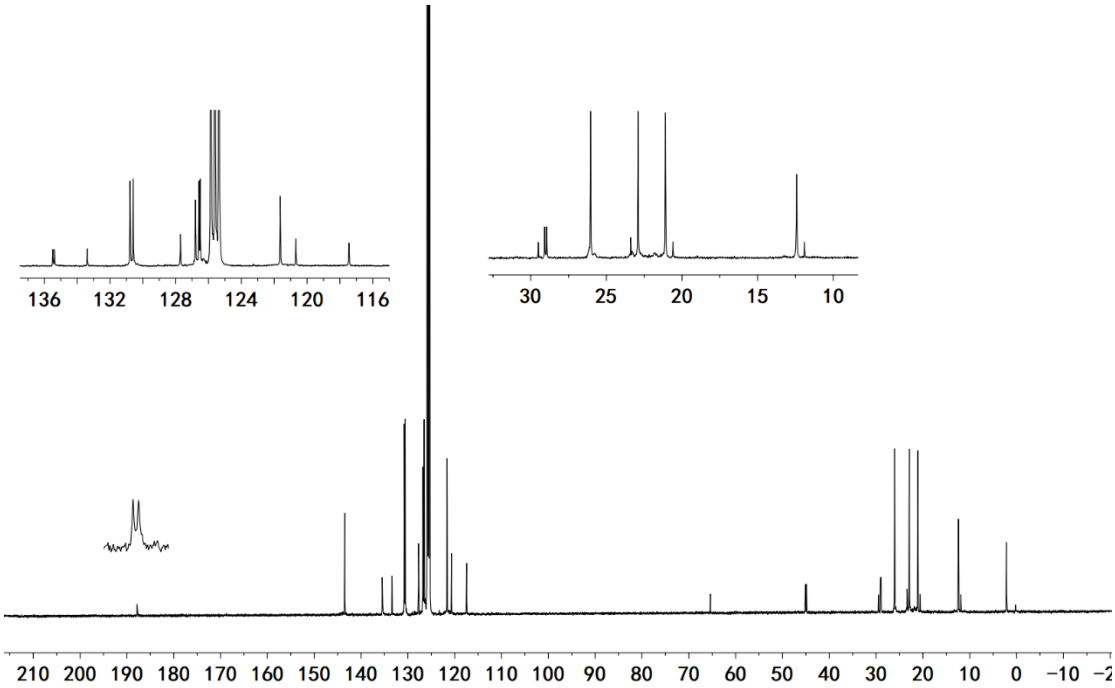


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K).

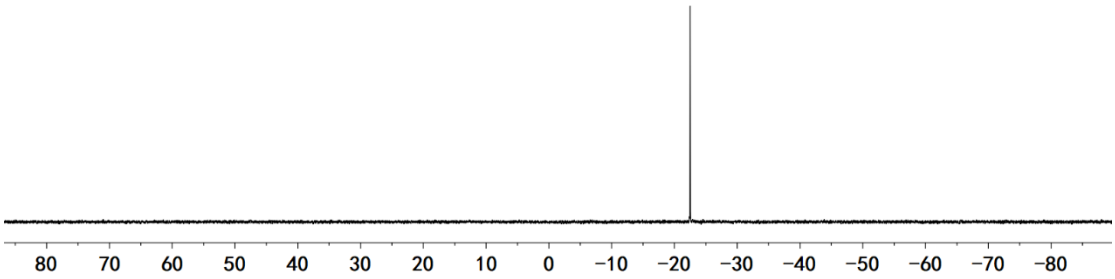
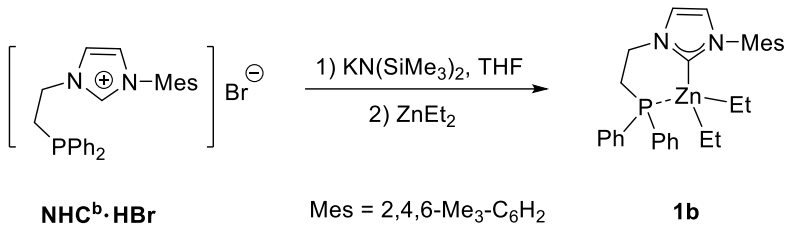


Fig. S3. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

Preparation of complex 1b



NHC^{b}·HBr Mes = 2,4,6-Me_3-C_6H_2 **1b**

Scheme S2.

Following the procedure described for **1a**, reaction of **NHC^{b}·HBr** (719 mg, 1.50 mmol), K[N($SiMe_3$)$_2$] (1.5 mL, 1.0 M in THF) and $ZnEt_2$ (1.5 mL, 1.0 M in n-hexane) gave **1b** as a pale yellow solid (626 mg, 80% yield).

Elemental Analysis: calcd. for $C_{30}H_{37}N_2PZn$: C, 69.03; H, 7.14; N, 5.37. Found: C, 69.25; H, 6.66; N, 5.32.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.42 (m, 4H, *o*-*Ph*$_2$P), 7.11 (m, 4H, *m*-*Ph*$_2$P), 7.06 (m, 2H, *p*-*Ph*$_2$P), 6.71 (m, 2H, *m*-N*Ar*), 6.18 (m, 1H, ArNC*H*), 6.00 (m, 1H, ArNCH=C*H*), 3.91 (m, 2H, NCH_2), 2.34 (m, 2H, PCH_2), 2.05 (s, 3H, *p*-NAr*Me*),1.92 (s, 6H, *o*-NAr*Me*), 1.67 (t, $^{3}J_{HH}$ = 8.1 Hz, 3H, $ZnCH_2CH_3$), 0.43 (q, $^{3}J_{HH}$ = 8.1 Hz, 2H, $ZnCH_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 190.0 (N*C*N), 138.9 (*p*-N*Ar*), 137.7 (d, $^{1}J_{PC}$ = 11.4 Hz, *i*-*Ph*$_2$P), 136.0 (*o*-N*Ar*), 135.2 (*i*-N*Ar*), 133.2 (d, $^{2}J_{PC}$ = 18.9 Hz, *o*-*Ph*$_2$P), 129.4 (*m*-N*Ar*), 129.3 (*p*-*Ph*$_2$P), 129.0 (d, $^{3}J_{PC}$ = 6.9 Hz, *m*-*Ph*$_2$P), 121.2 (ArN*C*H), 120.3 (ArNCH=*C*H), 47.6 (d, $^{2}J_{PC}$ = 21.4 Hz, N*C*H$_2$), 31.1 (d, $^{1}J_{PC}$ = 13.7 Hz, P*C*H$_2$), 21.0 (*p*-NAr*Me*), 17.7 (*o*-NAr*Me*), 14.9 ($ZnCH_2CH_3$), 4.6 ($ZnCH_2$).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -22.1.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.42 / 133.2 (*o*-*Ph*$_2$P), 7.11 / 129.0 (*m*-*Ph*$_2$P), 7.06 / 129.3 (*p*-*Ph*$_2$P), 6.71 / 129.4 (*m*-N*Ar*), 6.18 / 121.2 (ArN*CH*), 6.00 / 120.3 (ArNCH=*CH*), 3.91 / 47.6 (N*C*H$_2$), 2.34 / 31.1 (P*C*H$_2$), 2.05 / 21.0 (*p*-NAr*Me*), 1.92 / 17.7 (*o*-NAr*Me*), 1.67 / 14.9 ($ZnCH_2CH_3$), 0.43 / 4.6 ($ZnCH_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.42 / 129.3 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 6.71 / 135.2, 21.0, 17.7 (*m*-N*Ar* / *i*-N*Ar*, *p*-NAr*Me*, *o*-NAr*Me*), 3.91 / 190.0, 120.3, 31.1 (NCH_2 / N*C*N, ArNCH=*C*H, P*C*H$_2$), 2.05 / 138.9,

129.4 (*p*-NAr*Me* / *p*-N*Ar*, *m*-N*Ar*), 1.92 / 135.2, 129.4 (*o*-NAr*Me* / *i*-N*Ar*, *m*-N*Ar*).

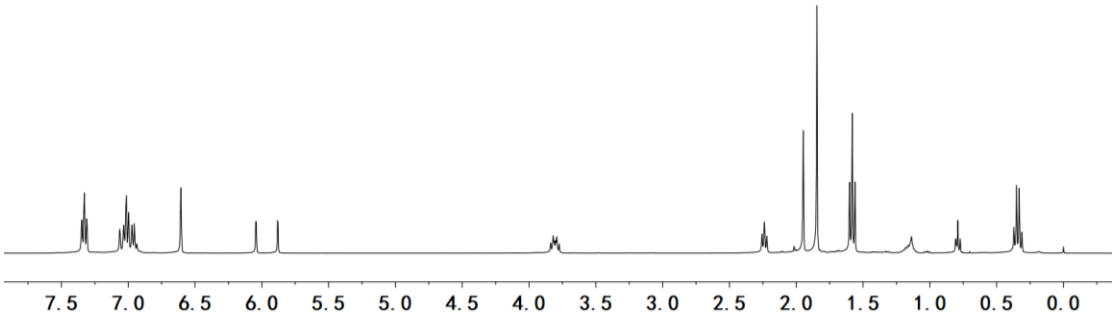


Fig. S4. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

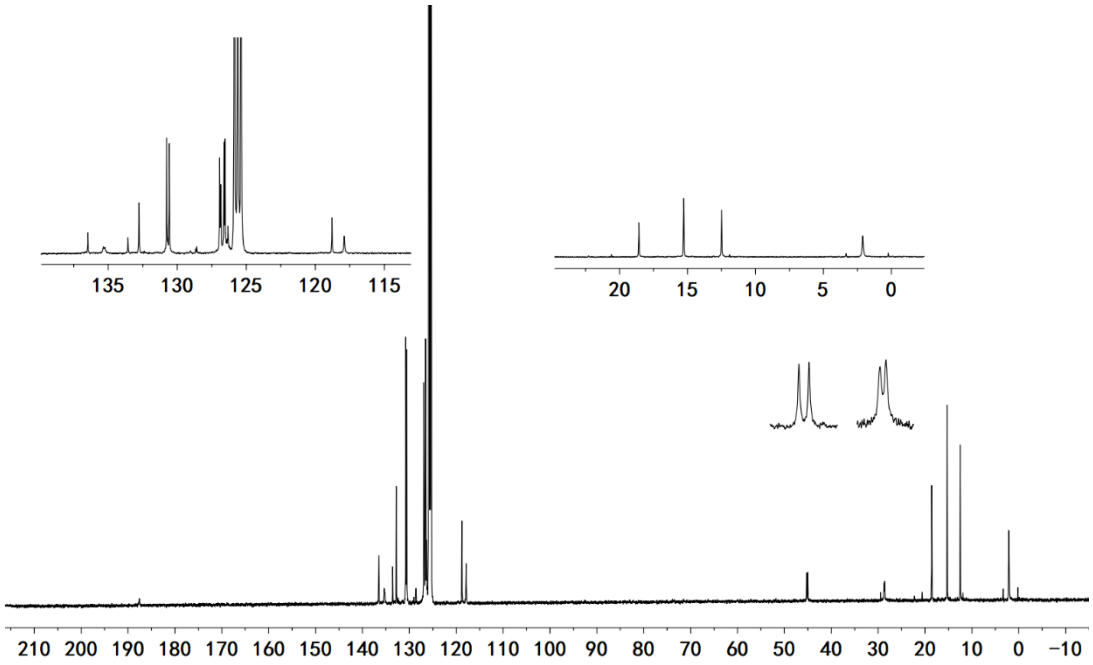


Fig. S5. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K).

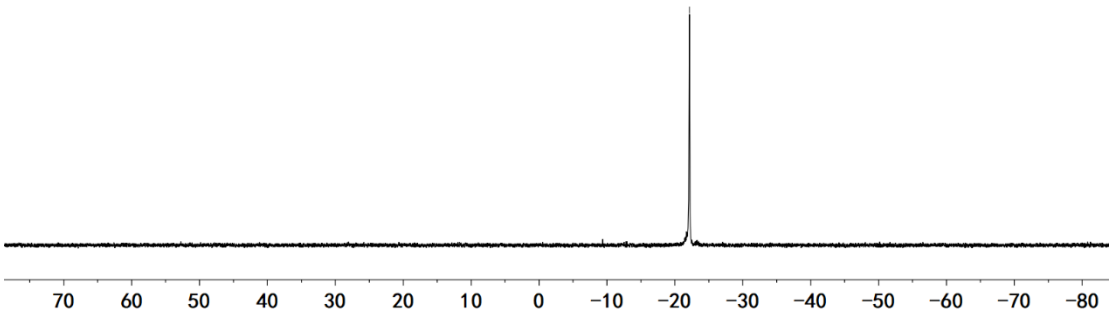
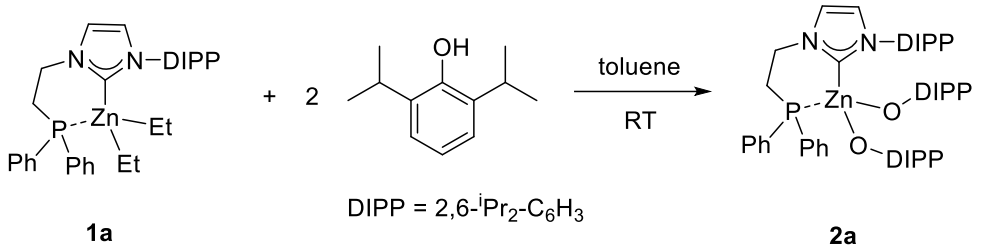


Fig. S6. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K).

Preparation of complex 2a



Scheme S3.

2,6-Diisopropylphenol (196 mg, 1.10 mmol) was added to a solution of **1a** (310 mg, 0.55 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 8 h. The volatiles were removed under vacuum and then the residue was washed with hexane (3 * 2 mL) to eventually give **2a** as a colorless solid (440 mg, 93% yield).

Elemental Analysis: calcd. for $C_{53}H_{67}N_2O_2PZn$: C, 73.98; H, 7.85; N, 3.26. Found: C, 73.40; H, 7.80; N, 3.07.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.33 (m, 4H, *o*-*Ph*$_2$P), 7.19 (m, 1H, *p*-N*Ar*), 7.12 (m, 4H, *m*-O*Ar*), 7.08 (m, 4H, *m*-*Ph*$_2$P), 7.05 (m, 2H, *m*-N*Ar*), 7.02 (m, 2H, *p*-*Ph*$_2$P), 6.90 (m, 2H, *p*-O*Ar*), 6.10 (m, 1H, ArNC*H*), 5.93 (m, 1H, ArNCH=C*H*), 4.12 (m, 2H, NC*H*$_2$), 3.25 (m, 4H, OArC*H*Me$_2$), 2.46 (m, 2H, NArC*H*Me$_2$), 2.15 (m, 2H, PC*H*$_2$), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NArCH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 6.8 Hz, 24H, OArCH*Me*$_2$), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 175.5 (d, $^2J_{PC}$ = 37.8 Hz, N*C*N), 161.3 (*i*-O*Ar*)[1], 145.9 (*o*-N*Ar*), 137.2 (*o*-O*Ar*), 135.4 (*i*-*Ph*$_2$P), 134.8 (*i*-N*Ar*), 133.5 (d, $^2J_{PC}$ = 16.0 Hz, *o*-*Ph*$_2$P), 131.1 (*p*-N*Ar*), 129.9 (*p*-*Ph*$_2$P), 129.0 (d, $^3J_{PC}$ = 7.7 Hz, *m*-*Ph*$_2$P), 125.2 (ArN*C*H), 124.5 (*m*-N*Ar*), 123.0 (*m*-O*Ar*), 121.4 (ArNCH=*C*H), 115.6 (*p*-O*Ar*)[1], 48.7 (d, $^2J_{PC}$ = 12.8 Hz, N*C*H$_2$), 30.5 (P*C*H$_2$), 28.8 (NAr*C*HMe$_2$), 27.3 (OAr*C*HMe$_2$), 25.5 (NArCH*Me*$_2$), 24.0 (OArCH*Me*$_2$), 23.7 (NArCH*Me*$_2$). [[1]from the ^{1}H, ^{13}C GHMBC experiment].

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -23.8.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.33 / 133.5 (*o*-*Ph*$_2$P), 7.19 / 131.1 (*p*-N*Ar*), 7.12 / 123.0 (*m*-O*Ar*), 7.08 / 129.0 (*m*-*Ph*$_2$P), 7.05 /

124.5 (*m*-N*Ar*), 7.02 / 129.9 (*p*-*Ph*$_2$P), 6.90 / 115.6 (*p*-O*Ar*), 6.10 / 125.2 (ArN*CH*), 5.93 / 121.4 (ArNCH=*CH*), 4.12 / 48.7 (N*CH*$_2$), 3.25 / 27.3 (OAr*CH*Me$_2$), 2.46 / 28.8 (NAr*CH*Me$_2$), 2.15 / 30.5 (P*CH*$_2$), 1.34 / 23.7 (NArCH*Me*$_2$), 1.14 / 24.0 (OArCH*Me*$_2$), 0.88 / 25.5 (NArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.33 / 129.9 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P), 7.19 / 145.9 (*p*-N*Ar* / *o*-N*Ar*), 7.05 / 134.8 (*m*-N*Ar* / *i*-N*Ar*), 1.34 / 145.9, 28.8 (NArCH*Me*$_2$ / *o*-N*Ar*, NAr*C*HMe$_2$), 1.14 / 137.2, 27.3 (OArCH*Me*$_2$ / *o*-O*Ar*, OAr*C*HMe$_2$), 0.88 / 145.9, 28.8 (NArCH*Me*$_2$ / *o*-N*Ar*, NAr*C*HMe$_2$).

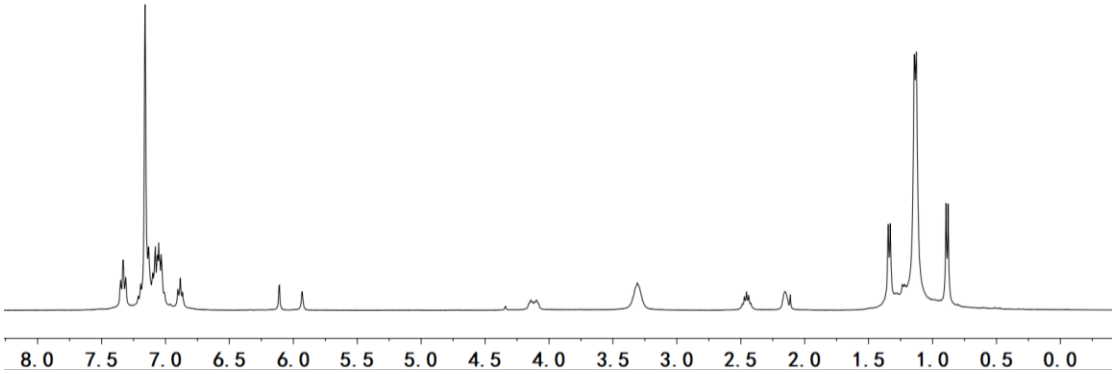


Fig. S7. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

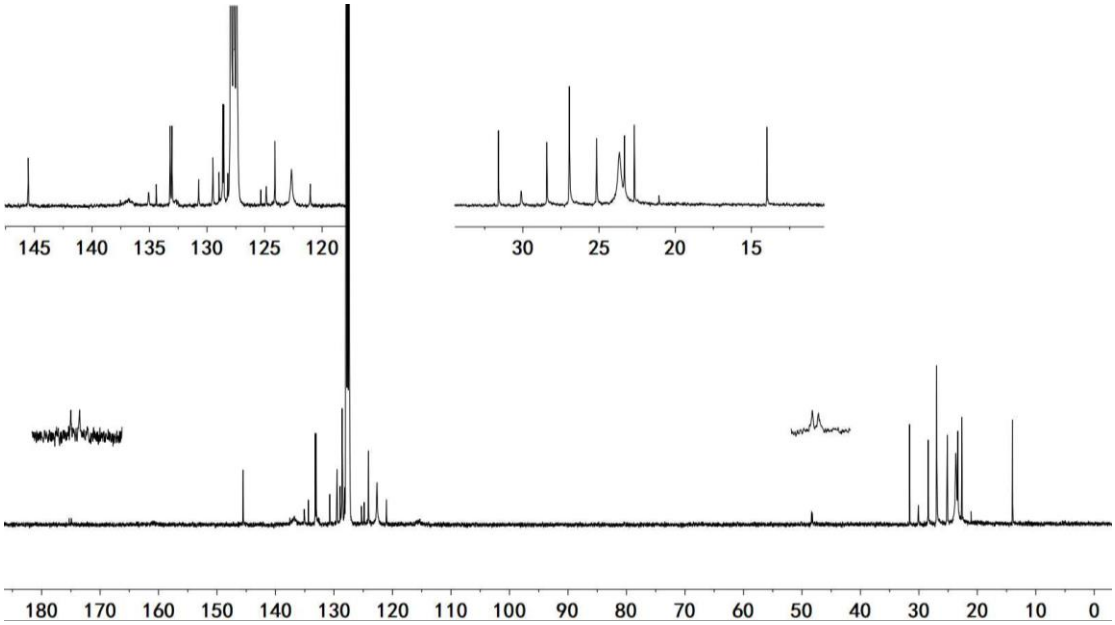


Fig. S8. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K).

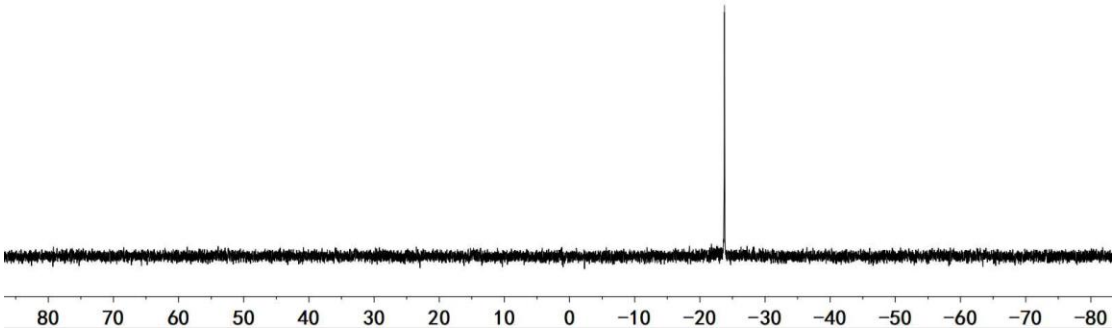
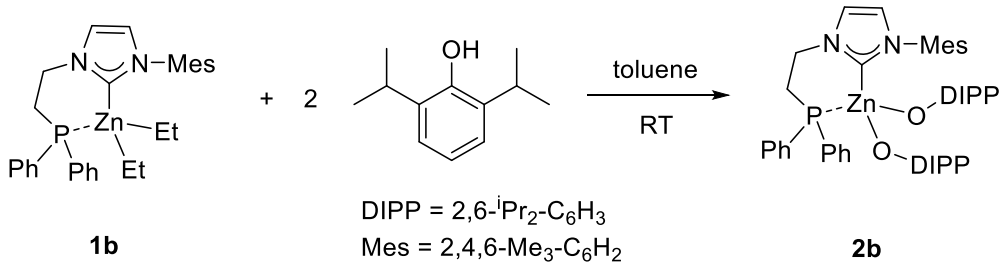


Fig. S9. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

Preparation of complex 2b



1b

DIPP = 2,6-$^{i}Pr_2$-C_6H_3
Mes = 2,4,6-Me_3-C_6H_2

2b

Scheme S4.

Following the procedure described for **2a**, reaction of 2,6-diisopropylphenol (232 mg, 1.30 mmol) and **1b** (340 mg, 0.65 mmol) gave **2b** as a colorless solid (436 mg, 82% yield). Crystals suitable for the X-ray crystal structure analysis were grown from a layered dichloromethane / hexane (v/v: 1:2) solution at -30 °C.

Elemental Analysis: calcd. for $C_{50}H_{61}N_2O_2PZn$: C, 73.38; H, 7.51; N, 3.42. Found: C, 72.97; H, 7.83; N, 3.11.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.45 (m, 4H, *o*-*Ph*$_2$P), 7.38 (m, 4H, *m*-*Ph*$_2$P), 7.36 (m, 2H, *p*-*Ph*$_2$P), 7.29 (m, 1H, ArNCH=C*H*), 6.93 (m, 1H, ArNC*H*), 6.76 (m, 2H, *m*-N*Ar*), 6.73 (m, 4H, *m*-O*Ar*), 6.42 (m, 2H, *p*-O*Ar*), 4.97 (m, 2H, NC*H*$_2$), 3.06 (m, 4H, OArC*H*Me$_2$), 2.76 (m, 2H, PC*H*$_2$), 2.23 (s, 3H, *p*-NAr*Me*),1.75 (s, 6H, *o*-NAr*Me*), 0.84 (br, 24H, OArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 174.5 (d, $^{2}J_{PC}$ = 48.7 Hz, N*C*N), 161.4 (*i*-O*Ar*), 139.8 (*p*-N*Ar*), 137.3 (*o*-O*Ar*), 135.0 (*i*-*Ph*$_2$P), 134.8 (*i*-N*Ar*), 133.3 (d, $^{2}J_{PC}$ = 15.5 Hz, *o*-*Ph*$_2$P), 130.2 (*p*-*Ph*$_2$P), 129.6 (*m*-N*Ar*), 129.4 (*o*-N*Ar*), 129.2 (d, $^{3}J_{PC}$ = 8.1 Hz, *m*-*Ph*$_2$P), 124.2 (ArNCH), 122.5 (ArNCH=*C*H), 122.3 (*m*-O*Ar*), 114.5 (*p*-O*Ar*), 48.8 (d, $^{2}J_{PC}$ = 13.0 Hz, N*C*H$_2$), 29.5 (P*C*H$_2$), 27.2 (OAr*C*HMe$_2$), 23.4 (OArCH*Me*$_2$), 21.2 (*p*-NAr*Me*), 17.6 (*o*-NAr*Me*).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ = -23.9.

^{1}H, ^{1}H GCOSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{1}H = 7.45 / 7.38 (*o*-*Ph*$_2$P / *m*-*Ph*$_2$P), 6.73 / 6.41 (*m*-O*Ar* / *p*-O*Ar*), 4.97 / 2.76 (NC*H*$_2$ / PC*H*$_2$), 3.06 / 0.84 (OArC*H*Me$_2$ / OArCH*Me*$_2$).

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.45 / 133.3 (*o*-*Ph*$_2$P), 7.38 / 129.2 (*m*-*Ph*$_2$P), 7.36 / 130.2 (*p*-*Ph*$_2$P), 7.29 / 122.5 (ArNCH=*CH*),

6.93 / 124.2 (ArNC*H*), 6.76 / 129.6 (*m*-N*Ar*), 6.73 / 122.3 (*m*-O*Ar*), 6.42 / 114.5 (*m*-O*Ar*), 4.97 / 48.8 (NCH_2), 3.06 / 27.2 (OAr*C*HMe_2), 2.76 / 29.5 (PCH_2), 2.23 / 21.2 (*p*-NAr*Me*), 1.75 / 17.6 (*o*-NAr*Me*), 0.84 / 23.4 (OArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.45 / 135.0, 130.2 (*o*-*Ph*$_2$P / *i*-*Ph*$_2$P, *p*-*Ph*$_2$P), 7.29 / 174.5, 124.2 (ArNCH=C*H* / N*C*N, ArN*C*H), 6.93 / 174.5, 122.5 (ArNC*H* / N*C*N, ArNCH=*C*H), 6.73 / 161.4, 27.2 (*m*-O*Ar* / *i*-O*Ar*, OAr*C*HMe$_2$), 4.97 / 174.5, 122.5, 29.5 (NC*H*$_2$ / N*C*N, ArNCH=*C*H, P*C*H$_2$), 3.06 / 137.3, 122.3, 23.4 (OArC*H*Me$_2$ / *o*-O*Ar*, *m*-O*Ar*, OArCH*Me*$_2$), 2.76 / 135.0, 48.8 (PC*H*$_2$ / *i*-*Ph*$_2$P, N*C*H$_2$), 1.75 / 134.8, 129.6 (*o*-NAr*Me* / *i*-N*Ar*, *m*-N*Ar*).

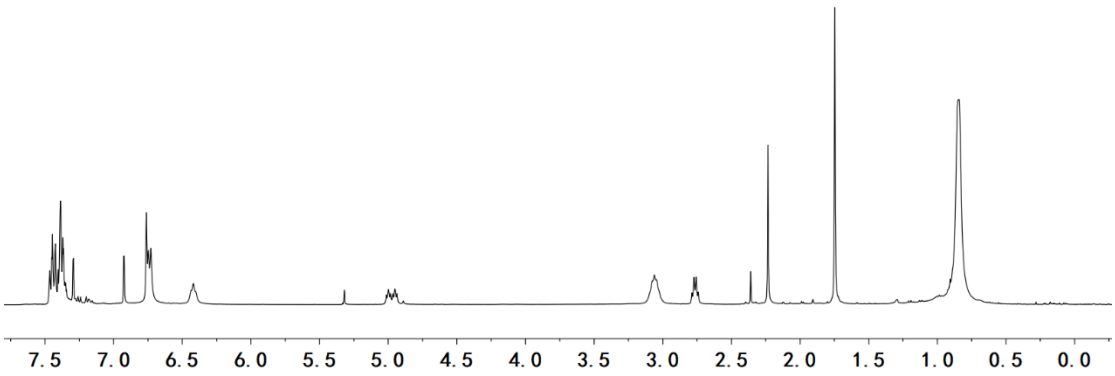


Fig. S10. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K).

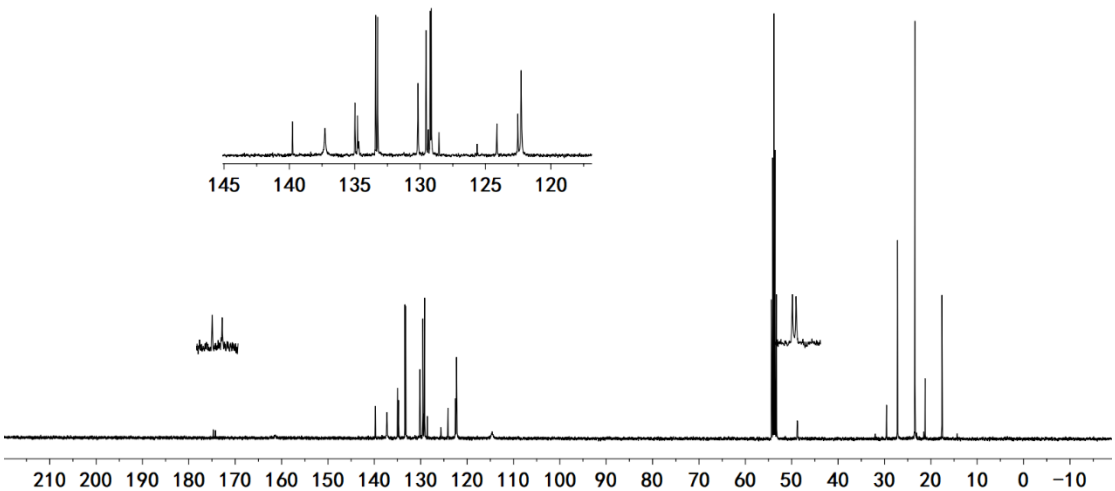


Fig. S11. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K).

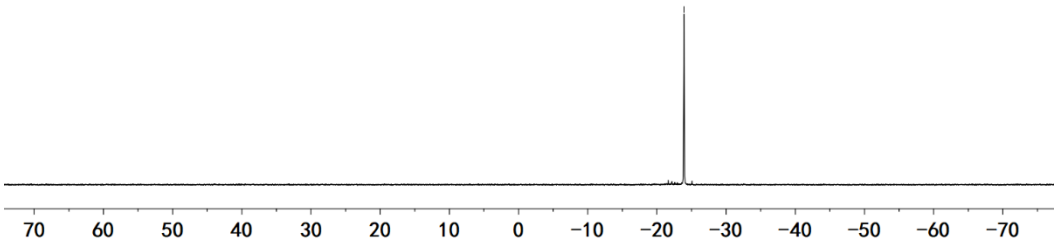


Fig. S12. $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 298 K).

X-ray crystal structure analysis of complex 2b: formula $C_{50}H_{61}N_2O_2PZn$, M = 818.34 $gmol^{-1}$, colorless, 0.28 x 0.25 x 0.14 mm, Monoclinic, space group $P2_1/n$, a = 21.0915(10), b = 10.6678(4), c = 40.3216(18) Å, β = 104.462(2)°, V = 8784.9(7) $Å^3$, ρ_{calc} = 1.237 gcm^{-3}, μ = 0.636 mm^{-1}, empirical absorption correction ($0.6322 \leq T \leq 0.7456$), Z = 8, λ = 0.71073 Å, T = 120 K, 142705 reflections collected ($-27 \leq h \leq 26$, $-13 \leq k \leq 13$, $-52 \leq l \leq 52$), 20209 independent (R_{int} = 0.0645) and 15241 observed reflections [$I>2\sigma(I)$], 1060 refined parameters, the final R_1 was 0.0391 ($I > 2\sigma(I)$) and wR_2 was 0.1008 (all data). max. (min.) residual electron density 0.56 (-0.51) $e.Å^{-3}$, hydrogen atoms were placed in calculated positions and refined using a riding model.

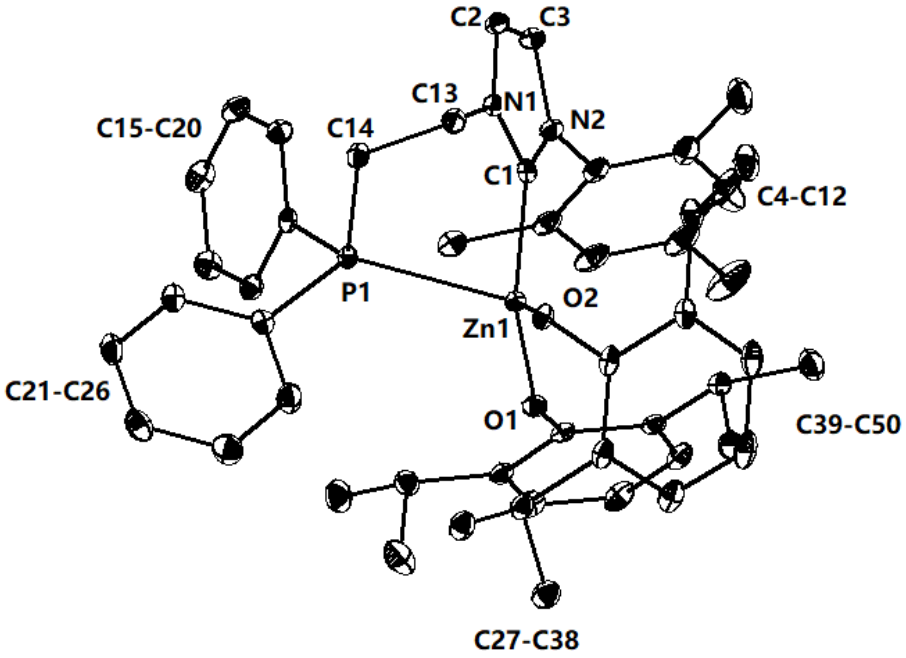
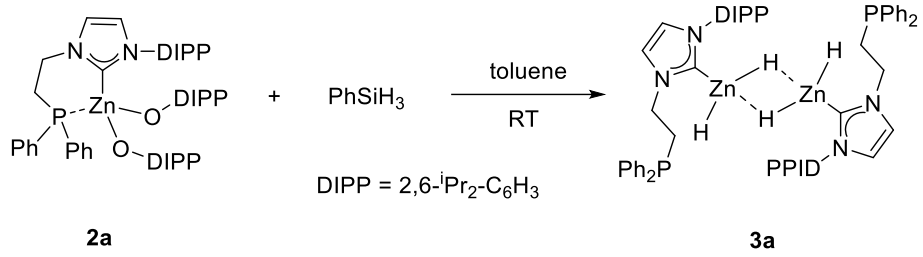


Fig. S13. Molecular structure of complex **2b**.

Preparation of complex 3a



Scheme S5.

$PhSiH_3$ (126 mg, 1.16 mmol) was added to a solution of **2a** (499 mg, 0.58 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 1 h. The volatiles were removed under vacuum, and then the residue was washed with hexane (3 * 2 mL) to eventually give **3a** as a colorless solid (242 mg, 82% yield).

Elemental Analysis: calcd. for $C_{58}H_{70}N_4P_2Zn_2$: C, 68.57; H, 6.95; N, 5.51. Found: C, 68.04; H, 7.18; N, 4.91.

^{1}H NMR (400 MHz, d_8-toluene, 243 K): δ = 7.40 (m, 8H, *o*-*Ph*$_2$P), 7.22 (m, 2H, *p*-N*Ar*), 7.12 (m, 4H, *m*-N*Ar*), 7.08 (m, 8H, *m*-*Ph*$_2$P), 7.05 (m, 4H, *p*-*Ph*$_2$P), 6.22 (m, 2H, ArNC*H*), 6.13 (m, 2H, ArNCH=C*H*), 4.27 (m, 4H, NC*H*$_2$), 4.15 (s, 2H, Zn-*H*), 3.50 (s, 2H, Zn-*H*), 2.85 (m, 4H, PC*H*$_2$), 2.66 (m, 4H, ArC*H*Me$_2$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 12H, ArCH*Me*$_2$), 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 12H, ArCH*Me*$_2$).

^{1}H NMR (400 MHz, d_8-toluene, 298 K): δ = 7.42 (m, 8H, *o*-*Ph*$_2$P), 7.21 (m, 2H, *p*-N*Ar*), 7.10 (m, 4H, *m*-N*Ar*), 7.06 (m, 8H, *m*-*Ph*$_2$P), 7.04 (m, 4H, *p*-*Ph*$_2$P), 6.30 (m, 2H, ArNC*H*), 6.29 (m, 2H, ArNCH=C*H*), 4.35 (m, 4H, NC*H*$_2$), 2.82 (m, 4H, PC*H*$_2$), 2.64 (m, 4H, ArC*H*Me$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12H, ArCH*Me*$_2$), 0.98 (d, $^3J_{HH}$ = 6.9 Hz, 12H, ArCH*Me*$_2$), n. o. (Zn-*H*). [n. o.: not observed]

^{13}C{^{1}H} NMR (101 MHz, d_8-toluene, 298 K): δ = 186.6 (N*C*N), 146.3 (*o*-N*Ar*), 139.1 (d, $^1J_{PC}$ = 14.0 Hz, *i*-*Ph*$_2$P), 136.2 (*i*-N*Ar*), 133.4 (d, $^2J_{PC}$ = 19.0 Hz, *o*-*Ph*$_2$P), 129.8 (*p*-N*Ar*), 129.1 (overlapped with solvent, *p*-*Ph*$_2$P), 128.7 (overlapped with solvent, *m*-*Ph*$_2$P), 123.8 (*m*-N*Ar*), 122.5 (ArN*C*H), 120.8 (ArNCH=*C*H), 48.6 (d, $^2J_{PC}$ = 21.2 Hz, N*C*H$_2$), 31.5 (d, $^1J_{PC}$ = 14.0 Hz, P*C*H$_2$), 28.5 (Ar*C*HMe$_2$), 25.5 (ArCH*Me*$_2$), 23.7 (ArCH*Me*$_2$).

^{31}P{^{1}H} NMR (162 MHz, d_8-toluene, 298 K): δ = -20.0.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, d_8-toluene, 298 K): δ ^{1}H / δ ^{13}C = 7.42 / 133.4 (*o*-*Ph*$_2$P), 7.21 / 129.8 (*p*-N*Ar*), 7.10 / 123.8 (*m*-N*Ar*), 7.06 / 128.7 (*m*-*Ph*$_2$P), 7.04 / 129.1 (*p*-*Ph*$_2$P), 6.30 / 122.5 (ArN*CH*), 6.29 / 120.8 (ArNCH=*CH*), 4.35 / 48.6 (N*CH*$_2$), 2.82 / 31.5 (P*CH*$_2$), 2.64 / 28.5 (Ar*CH*Me$_2$), 1.37 / 23.7 (ArCH*Me*$_2$), 0.98 / 25.5 (ArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, d_8-toluene, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.42 / 129.1, 128.7 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P, *m*-*Ph*$_2$P), 7.10 / 136.2, 129.8, 28.5 (*m*-N*Ar* / *i*-N*Ar*, *p*-N*Ar*, NAr*C*HMe$_2$), 4.35 / 186.6, 120.8, 31.5 (NC*H*$_2$ / N*C*N, ArNCH=*C*H, P*C*H$_2$), 2.82 / 139.1, 48.6 (PC*H*$_2$ / *i*-*Ph*$_2$P, N*C*H$_2$), 2.64 / 146.3, 136.2, 123.8, 25.5, 23.7 (NArC*H*Me$_2$ / *o*-N*Ar*, *i*-N*Ar*, *m*-N*Ar*, NArCH*Me*$_2$, NArCH*Me*$_2$), 1.37 / 146.3 (NArCH*Me*$_2$ / *o*-N*Ar*), 0.98 / 146.3 (NArCH*Me*$_2$ / o-N*Ar*).

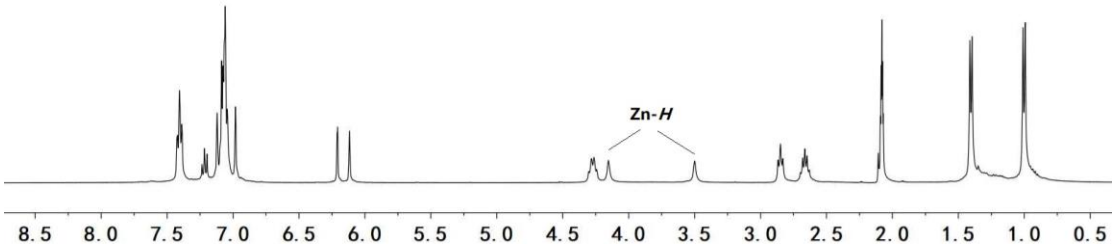


Fig. S14. ^{1}H NMR (400 MHz, d_8-toluene, 243 K).

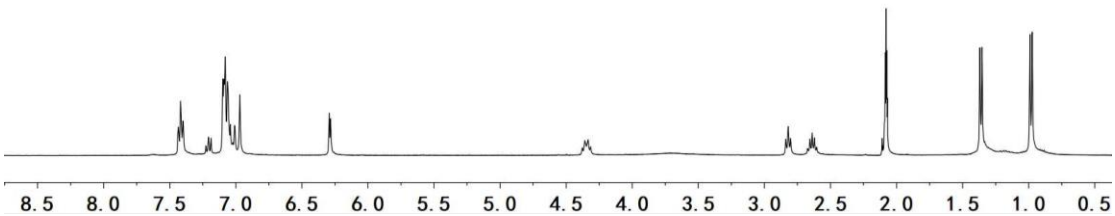


Fig. S15. ^{1}H NMR (400 MHz, d_8-toluene, 298 K).

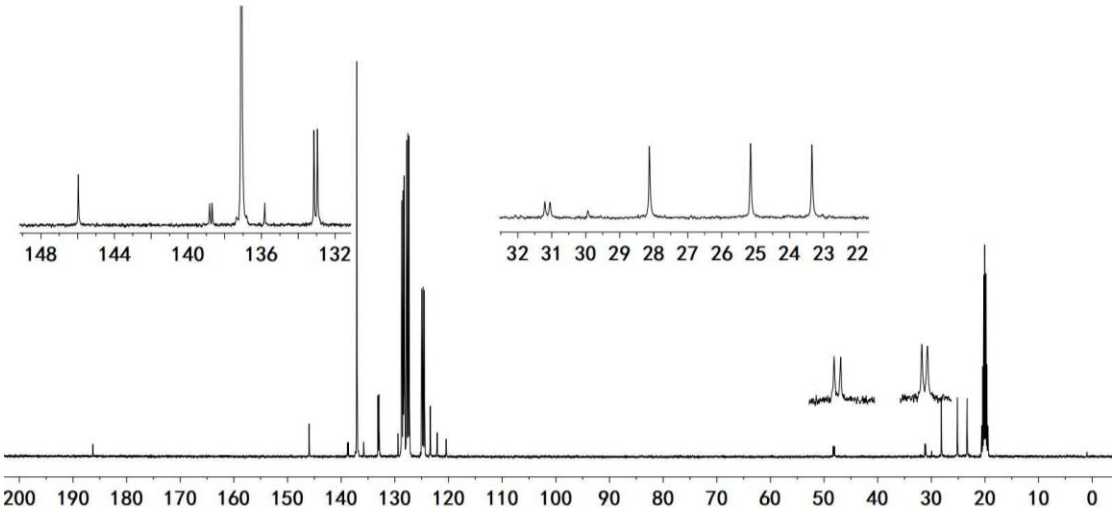


Fig. S16. $^{13}C\{^{1}H\}$ NMR (101 MHz, d_8-toluene, 298 K).

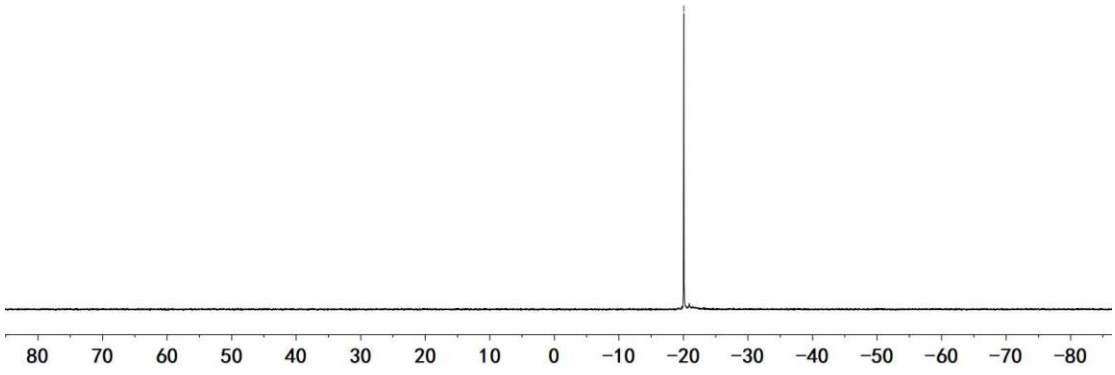


Fig. S17. $^{31}P\{^{1}H\}$ NMR (162 MHz, d_8-toluene, 298 K).

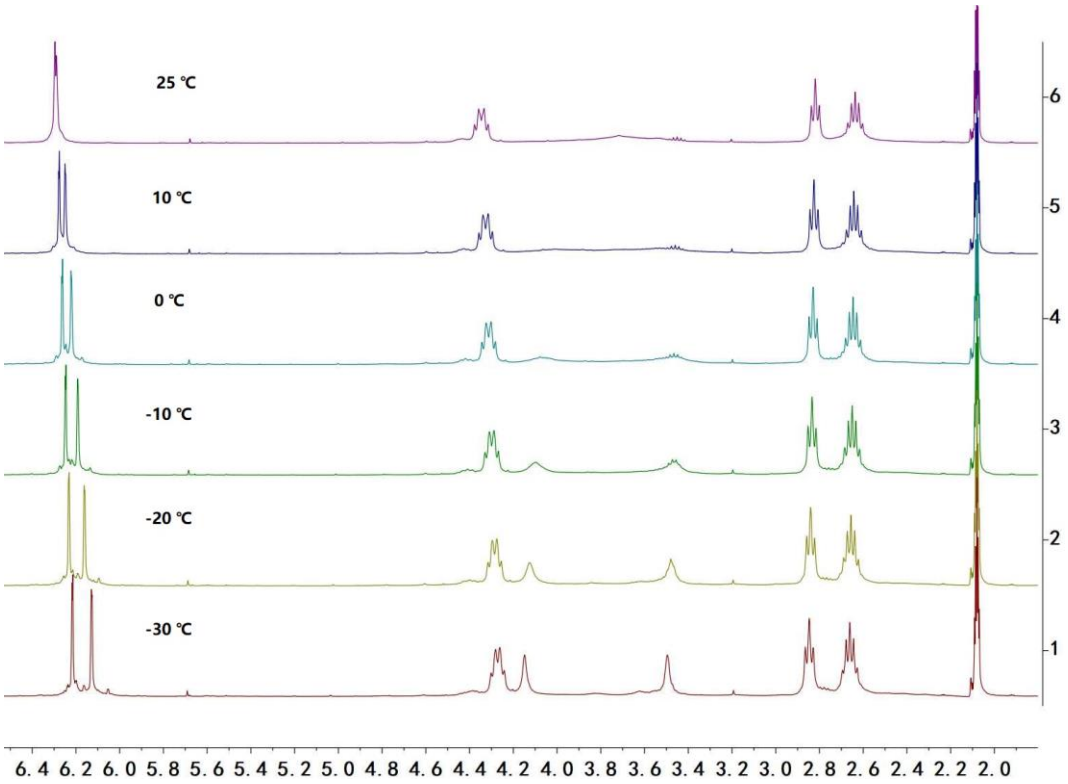
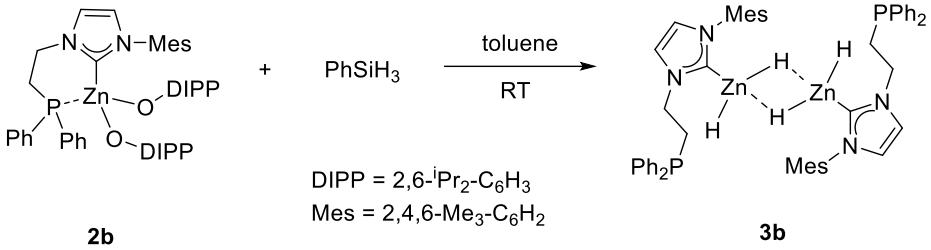


Fig. S18. Variable-temperature ^{1}H NMR spectra of **3a** in d_8-toluene.

Preparation of complex 3b



2b **3b**

Scheme S6.

Following the procedure described for **3a**, reaction of $PhSiH_3$ (173 mg, 1.60 mmol) with **2b** (655 mg, 0.80 mmol) gave **3b** as a colorless solid (283 mg, 76% yield).

Elemental Analysis: calcd. for $C_{52}H_{58}N_4P_2Zn_2$: C, 67.03; H, 6.27; N, 6.01. Found: C, 67.06; H, 6.90; N, 5.21.

^{1}H NMR (400 MHz, d_8-toluene, 243 K): δ = 7.45 (m, 8H, *o*-*Ph*$_2$P), 7.11 (m, 8H, *m*-*Ph*$_2$P), 7.05 (m, 4H, *p*-*Ph*$_2$P), 6.67 (s, 4H, *m*-N*Ar*), 6.03 (m, 2H, ArNCH=C*H*), 5.80 (m, 2H, ArNC*H*), 4.32 (s, 2H, Zn-*H*), 4.18 (m, 4H, NC*H*$_2$), 3.46 (s, 2H, Zn-*H*), 2.77 (m, 4H, PC*H*$_2$), 2.08 (s, 12H, *o*-NAr*Me*), 2.06 (s, 6H, *p*-NAr*Me*).

^{13}C{^{1}H} NMR (101 MHz, d_8-toluene, 243 K): δ = 184.6 (N*C*N), 139.0 (d, $^1J_{PC}$ = 13.6 Hz, *i*-*Ph*$_2$P), 138.1 (*o*-N*Ar*), 136.2 (*i*-N*Ar*), 135.5 (*p*-N*Ar*), 133.4 (d, $^2J_{PC}$ = 18.7 Hz, *o*-*Ph*$_2$P), 129.1 (*m*-N*Ar*), 129.0 (overlapped with solvent, *p*-*Ph*$_2$P), 128.7 (overlapped with solvent, *m*-*Ph*$_2$P), 120.9 (ArNCH=*C*H), 120.3 (ArN*C*H), 48.1 (d, $^2J_{PC}$ = 22.6 Hz, N*C*H$_2$), 31.4 (d, $^1J_{PC}$ = 14.7 Hz, P*C*H$_2$), 21.2 (*p*-NAr*Me*), 18.4 (*o*-NAr*Me*).

^{31}P{^{1}H} NMR (162 MHz, d_8-toluene, 243 K): δ = -19.5.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, d_8-toluene, 243 K): δ ^{1}H / δ ^{13}C = 7.45 / 133.4 (*o*-*Ph*$_2$P), 7.11 / 128.7 (*m*-*Ph*$_2$P), 7.05 / 129.0 (*p*-*Ph*$_2$P), 6.67 / 129.1 (*m*-N*Ar*), 6.03 / 120.9 (ArNCH=*CH*), 5.80 / 120.3 (ArN*CH*), 4.18 / 48.1 (N*C*H$_2$), 2.77 / 31.4 (P*C*H$_2$), 2.08 / 18.4 (*o*-NAr*Me*), 2.06 / 21.2 (*p*-NAr*Me*).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, d_8-toluene, 243 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.45 / 129.0, 128.7 (*o*-*Ph*$_2$P / *p*-*Ph*$_2$P, *m*-*Ph*$_2$P), 7.11 / 139.0 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P), 6.67 / 136.2, 21.2, 18.4 (*m*-N*Ar* / *i*-N*Ar*, *p*-NAr*Me*, *o*-NAr*Me*), 2.08 / 138.1, 136.2, 129.1 (*o*-NAr*Me* / *i*-N*Ar*, *o*-N*Ar*, *m*-NAr), 2.06 / 135.5, 129.1 (*p*-NAr*Me* / *p*-N*Ar*, *m*-N*Ar*).

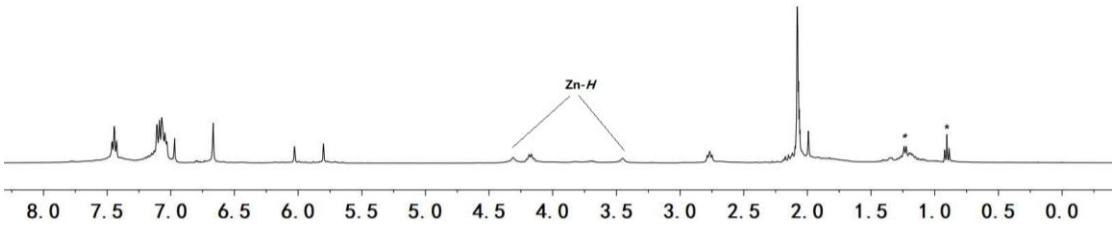


Fig. S19. ^{1}H NMR (400 MHz, d_8-toluene, 243 K) [*: hexane].

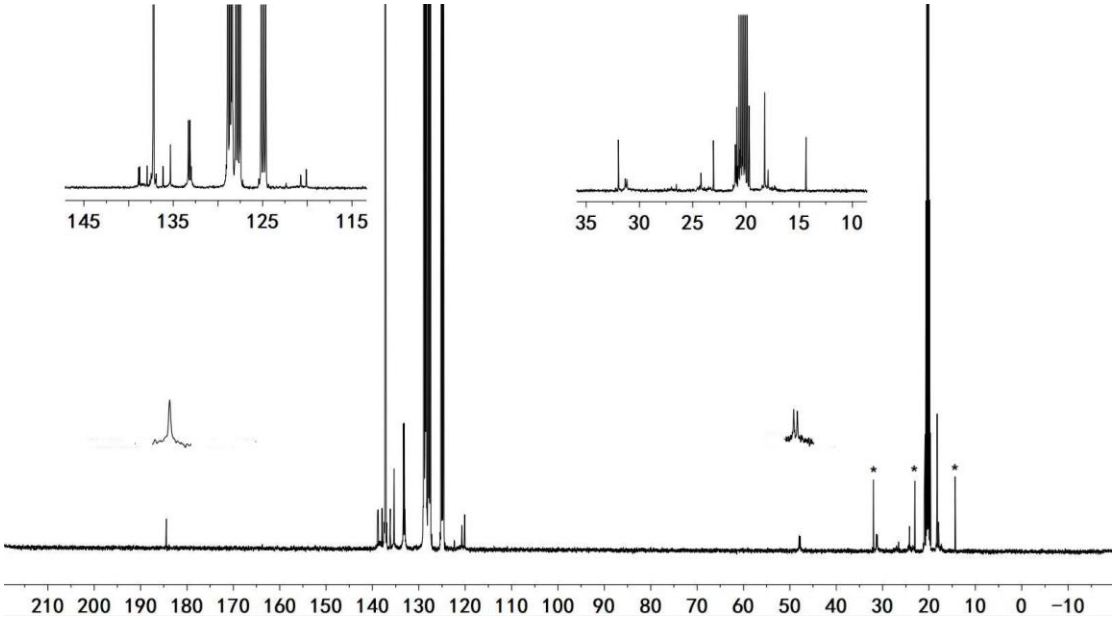


Fig. S20. ^{13}C{^{1}H} NMR (101 MHz, d_8-toluene, 243 K) [*: hexane].

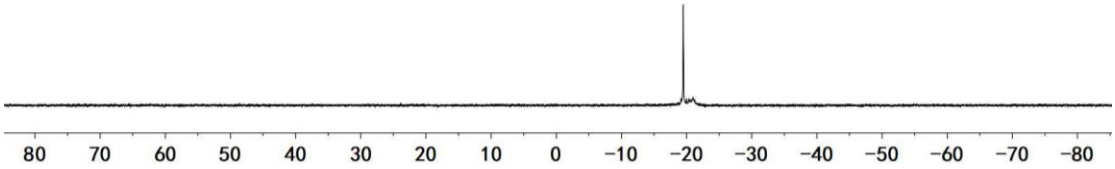
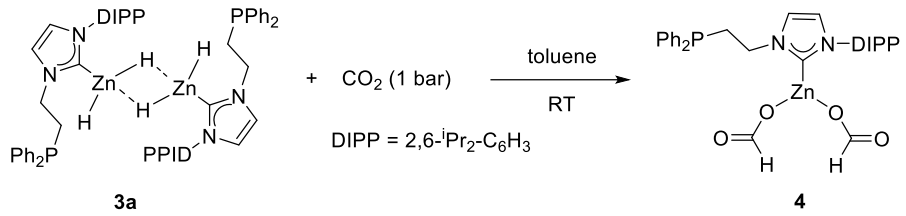


Fig. S21. ^{31}P{^{1}H} NMR (162 MHz, d_8-toluene, 243 K).

Preparation of complex 4a



Scheme S7.

A solution of **3a** (102 mg, 0.10 mmol) in 3 mL toluene was pressurized with 1 bar of CO_2 at room temperature for 1 h. The resulting mixture was filtered to remove minor impurities and all the volatiles of reaction mixture were removed in vacuo. The residue was washed with hexane (4 * 1 mL) to finally give **4** as a colorless solid (82 mg, 69% yield).

Elemental Analysis: calcd. for $C_{31}H_{35}N_2O_4PZn$: C, 62.47; H, 5.92; N, 4.70. Found: C, 62.44; H, 5.78; N, 4.02.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.31 (br s, 2H, OC*H*O), 7.54 (m, 4H, *o*-*Ph*$_2$P), 7.15 (m, 1H, *p*-N*Ar*), 7.13 (m, 2H, *p*-*Ph*$_2$P), 7.07 (m, 4H, *m*-*Ph*$_2$P), 7.05 (m, 2H, *m*-N*Ar*), 6.28 (m, 1H, ArNC*H*), 6.22 (m, 1H, ArNCH=C*H*), 4.61 (br, 2H, NC*H*$_2$), 2.93 (br, 2H, PC*H*$_2$), 2.64 (br, 2H, NArC*H*Me$_2$), 1.35 (br, 6H, NArCH*Me*$_2$), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 6H, NArCH*Me*$_2$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 175.6 (N*C*N)[1], 167.6 (O*C*HO), 146.6 (*o*-N*Ar*), 138.7 (d, $^1J_{PC}$ = 15.2 Hz, *i*-*Ph*$_2$P), 135.2 (*i*-N*Ar*), 133.4 (d, $^2J_{PC}$ = 19.2 Hz, *o*-*Ph*$_2$P), 130.4 (*p*-N*Ar*), 129.0 (*p*-*Ph*$_2$P), 128.9 (d, $^3J_{PC}$ = 6.7 Hz, *m*-*Ph*$_2$P), 124.0 (*m*-N*Ar*), 123.5 (ArNCH=*C*H), 121.1 (ArN*C*H), 49.0 (d, $^2J_{PC}$ = 23.6 Hz, N*C*H$_2$), 30.6 (d, $^1J_{PC}$ = 14.4 Hz, P*C*H$_2$), 28.3 (NAr*C*HMe$_2$), 25.9 (NArCH*Me*$_2$), 23.2 (NArCH*Me*$_2$). [[1]from the ^{1}H, ^{13}C GHMBC experiment]

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -20.1.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 7.54 / 133.4 (*o*-*Ph*$_2$P), 7.15 / 130.4 (*p*-N*Ar*), 7.13 / 129.0 (*p*-*Ph*$_2$P), 7.07 / 128.9 (*m*-*Ph*$_2$P), 7.05 / 124.0 (*m*-N*Ar*), 6.28 / 121.1 (ArN*CH*), 6.22 / 123.5 (ArNCH=*CH*), 4.61 / 49.0 (N*C*H$_2$), 2.93 / 30.6 (P*C*H$_2$), 2.64 / 28.3 (NAr*CH*Me$_2$) 1.35 / 23.2 (NArCH*Me*$_2$), 0.93 / 25.9 (NArCH*Me*$_2$).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.54 / 138.7, 128.9 (*o*-*Ph*$_2$P / *i*-*Ph*$_2$P, *m*-*Ph*$_2$P), 7.15 / 146.6 (*p*-N*Ar* / *o*-N*Ar*), 7.05 / 135.2, 28.3 (*m*-N*Ar* / *i*-N*Ar*, NAr*C*HMe$_2$), 6.22 / 175.6, 121.1 (ArNCH=C*H* / N*C*N, ArN*C*H), 2.64 / 146.6, 135.2, 124.0 (NArC*H*Me$_2$ / *o*-N*Ar*, *i*-N*Ar*, *m*-N*Ar*), 1.35 / 146.6, 28.3 (NArCH*Me*$_2$ / *o*-N*Ar*, NAr*C*HMe$_2$), 0.93 / 146.6, 28.3 (NArCH*Me*$_2$ / *o*-N*Ar*, NAr*C*HMe$_2$).

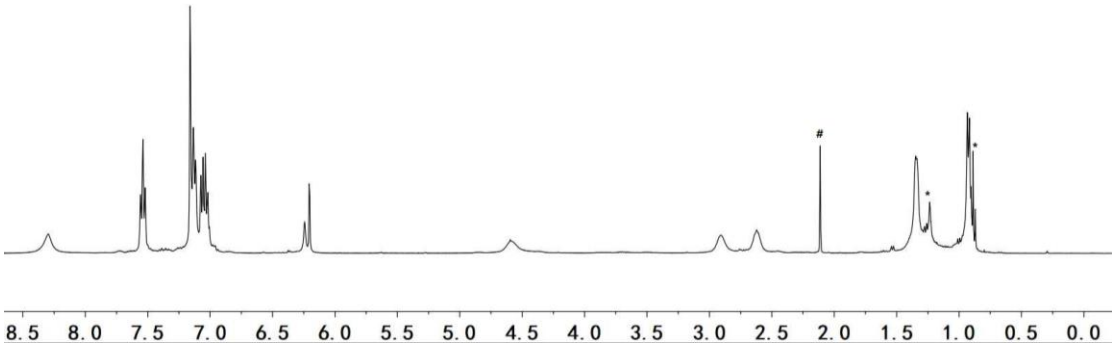


Fig. S22. ^{1}H NMR (400 MHz, C_6D_6, 298 K) [*: hexane, #: toluene].

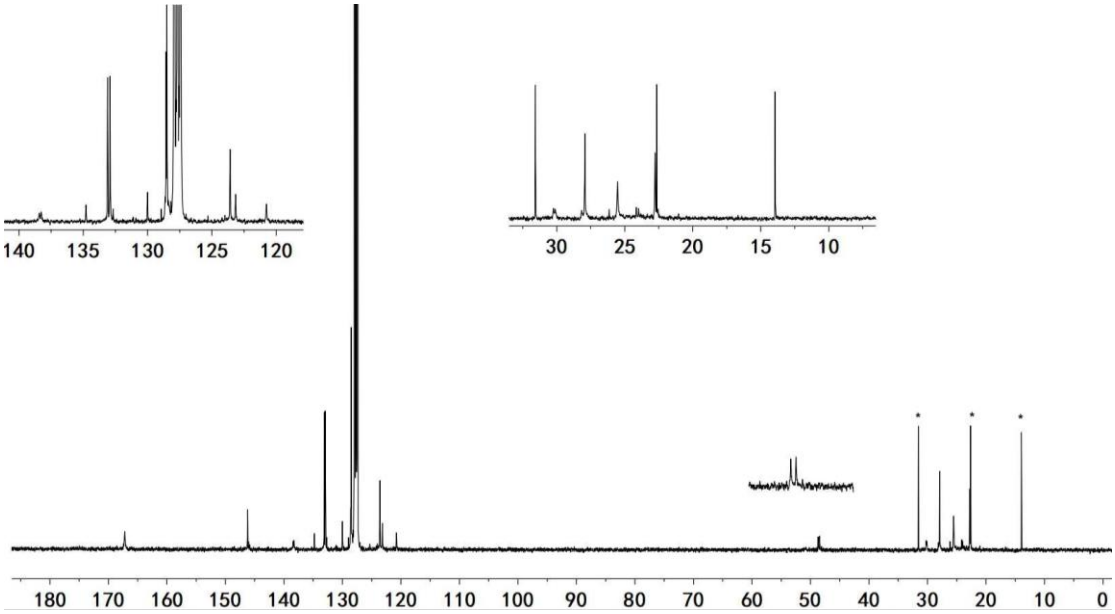


Fig. S23. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) [*: hexane].

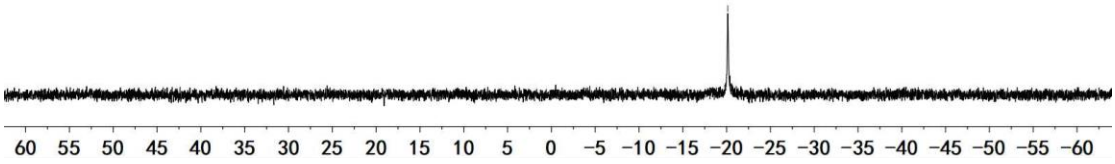
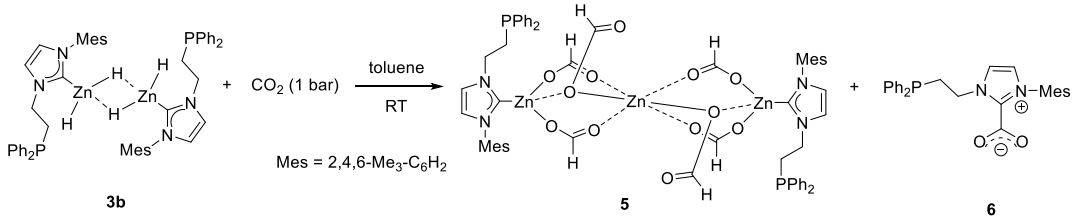


Fig. S24. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K).

Preparation of complexes 5 and 6



Scheme S8.

A solution of **3b** (373 mg, 0.40 mmol) in 3 mL toluene was pressurized with 1 bar of CO_2 at room temperature for 1 h, which resulted in the precipitation of colorless crystals overnight. The crystals were isolated and washed with 1 mL toluene and dried under reduced pressure to give **5** as a colorless crystalline solid (270 mg, 53% yield based on **NHC^b**). The filtrates were combined and all the volatiles were evaporated to dryness. The remaining residue was washed with pentane and dried under reduced pressure to give **6** as a white solid (132 mg, 37% yield based on **NHC^b**). Crystals of **5** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane to a saturated solution of **5** in THF at room temperature.

For complex **5**:

Elemental Analysis: calcd. for $C_{58}H_{60}N_4O_{12}P_2Zn_3$: C, 55.15; H, 4.79; N, 4.44. Found: C, 54.90; H, 5.28; N, 4.18.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.96 (s, 6H, OC*H*O), 7.48 (m, 8H, *o*-*Ph*$_2$P), 7.36 (m, 4H, *p*-*Ph*$_2$P), 7.34 (m, 8H, *m*-*Ph*$_2$P), 7.16 (m, 2H, ArNCH=C*H*), 6.91 (m, 4H, *m*-N*Ar*), 6.89 (m, 2H, ArNC*H*), 4.46 (m, 4H, NCH_2), 2.78 (m, 4H, PCH_2), 2.29 (s, 6H, *p*-NAr*Me*),1.95 (s, 12H, *o*-NAr*Me*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ = 172.4 (N*C*N), 168.1 (O*C*HO), 139.6 (*p*-N*Ar*), 137.0 (d, $^1J_{PC}$ = 11.0 Hz, *i*-*Ph*$_2$P), 135.7 (*o*-N*Ar*), 134.5 (*i*-N*Ar*), 133.0 (d, $^2J_{PC}$ = 19.0 Hz, *o*-*Ph*$_2$P), 129.2 (*m*-N*Ar*), 128.9 (*p*-*Ph*$_2$P), 128.8 (d, $^3J_{PC}$ = 6.9 Hz, *m*-*Ph*$_2$P), 122.7 (ArN*C*H), 121.9 (ArNCH=*C*H), 48.6 (d, $^2J_{PC}$ = 23.6 Hz, N*C*H$_2$), 30.4 (d, $^1J_{PC}$ = 14.7 Hz, P*C*H$_2$), 21.2 (*p*-NAr*Me*), 17.6 (*o*-NAr*Me*).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ = -20.4.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, $CDCl_3$, 298 K): δ ^{1}H / δ ^{13}C = 7.96 / 168.1 (OC*H*O), 7.48 / 133.0 (*o*-*Ph*$_2$P), 7.36 / 128.9 (*p*-*Ph*$_2$P), 7.34 / 128.8 (*m*-*Ph*$_2$P), 7.16 /

121.9 (ArNCH=*CH*), 6.91 / 129.2 (*m*-N*Ar*), 6.89 / 122.7 (ArN*CH*), 4.46 / 48.6 (N*CH*$_2$), 2.78 / 30.4 (P*CH*$_2$), 2.29 / 21.2 (*p*-NAr*Me*), 1.95 / 17.6 (*o*-NAr*Me*).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, $CDCl_3$, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.48 / 137.0, 128.9, 128.8 (*o*-*Ph*$_2$P / *i*-*Ph*$_2$P, *p*-*Ph*$_2$P, *m*-*Ph*$_2$P), 7.34 / 137.0 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P), 7.16 / 172.4 / 122.7 (ArNCH=C*H* / N*C*N, ArN*C*H), 6.89 / 172.4, 121.9 (ArNC*H* / N*C*N, ArNCH=*C*H), 4.46 / 172.4, 121.9, 30.4 (NC*H*$_2$ / N*C*N, ArNCH=*C*H, P*C*H$_2$), 2.78 / 137.0, 48.6 (PC*H*$_2$ / *i*-*Ph*$_2$P, N*C*H$_2$), 2.29 / 139.6, 129.2 (*p*-NAr*Me* / *p*-N*Ar*, *m*-N*Ar*), 1.95 / 135.7, 129.2 (*o*-NAr*Me* / *o*-N*Ar*, *m*-N*Ar*).

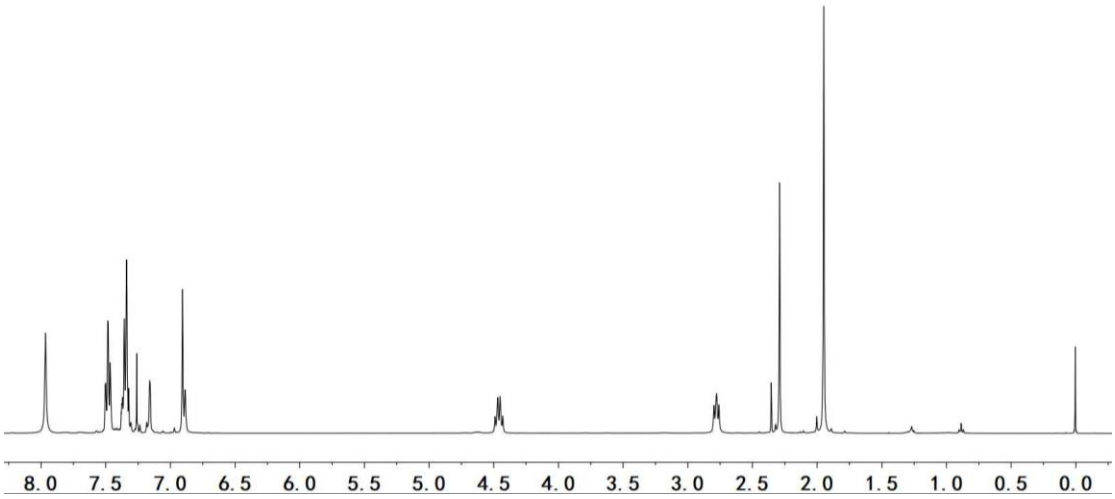


Fig. S25. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

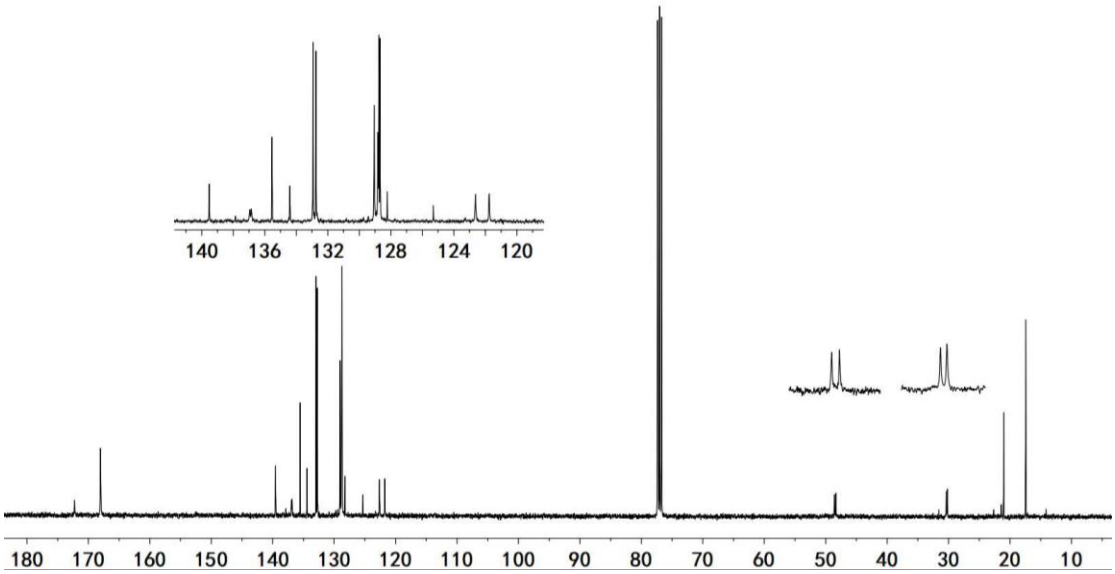


Fig. S26. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K).

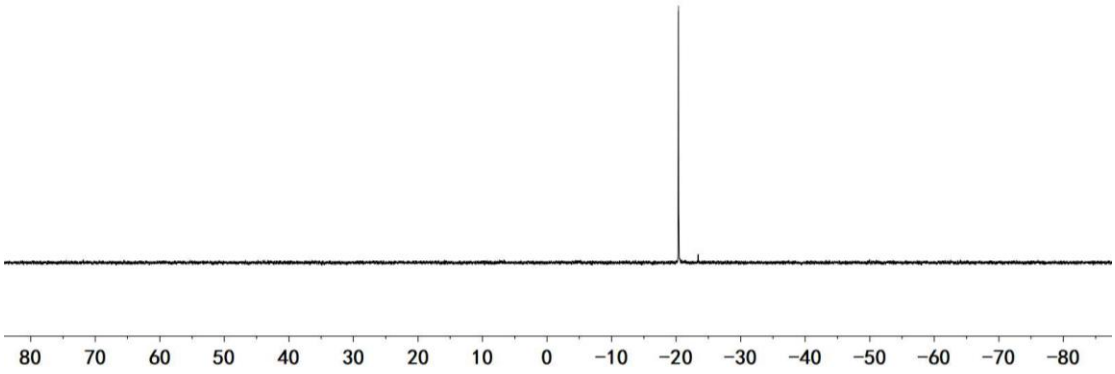


Fig. S27. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 298 K).

X-ray crystal structure analysis of complex 5: formula $C_{58}H_{60}N_4O_{12}P_2Zn_3$, M = 1263.15 $gmol^{-1}$, colorless, 0.11 x 0.1 x 0.09 mm, Monoclinic, space group $P2_1/n$, a = 13.1607(14), b = 11.9411(12), c = 19.722(2) Å, β = 107.396(3)°, V = 2957.6(6) $Å^3$, ρ_{calc} = 1.418 gcm^{-3}, μ = 1.324 mm^{-1}, empirical absorption correction ($0.4737 \leq T \leq 0.7456$), Z = 2, λ = 0.71073 Å, T = 193 K, 32857 reflections collected ($-17 \leq h \leq 17$, $-15 \leq k \leq 15$, $-25 \leq l \leq 24$), 6791 independent (R_{int} = 0.1017) and 4251 observed reflections [$I>2\sigma(I)$], 361 refined parameters, the final R_1 was 0.0464 ($I > 2\sigma(I)$) and wR_2 was 0.0985 (all data). max. (min.) residual electron density 0.34 (-0.63) $e.Å^{-3}$, hydrogen atoms were placed in calculated positions and refined using a riding model.

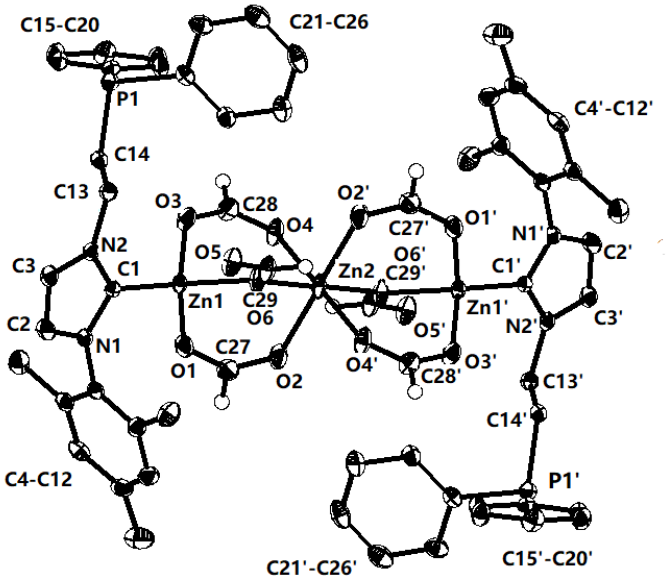


Fig. S28. Molecular structure of complex **5**.

For complex **6**:

Elemental Analysis: calcd. for $C_{27}H_{27}N_2O_2P$: C, 73.29; H, 6.15; N, 6.33. Found: C, 73.65; H, 6.65; N, 5.99.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.08 (m, 1H, ArNCH=C*H*), 7.59 (m, 4H, *o*-*Ph*$_2$P), 7.14 (m, 4H, *m*-*Ph*$_2$P), 7.06 (m, 2H, *p*-*Ph*$_2$P), 6.61 (m, 2H, *m*-N*Ar*), 6.32 (m, 1H, ArNC*H*), 4.66 (m, 2H, NC*H*$_2$), 2.87 (m, 2H, PC*H*$_2$), 2.04 (s, 3H, *p*-NAr*Me*), 1.93 (s, 6H, *o*-NAr*Me*).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ = 154.6 (O*C*O), 145.4 (N*C*N), 139.2 (*p*-N*Ar*), 138.2 (d, $^1J_{PC}$ = 13.2 Hz, *i*-*Ph*$_2$P), 134.8 (*o*-N*Ar*), 134.3 (*i*-N*Ar*), 133.4 (d, $^2J_{PC}$ = 19.1 Hz, *o*-*Ph*$_2$P), 129.3 (*m*-N*Ar*), 128.9 (*p*-*Ph*$_2$P), 128.8 (d, $^3J_{PC}$ = 8.0 Hz, *m*-*Ph*$_2$P), 123.3 (ArNCH=*C*H), 121.0 (ArN*C*H), 47.7 (d, $^2J_{PC}$ = 26.9 Hz, N*C*H$_2$), 30.2 (d, $^1J_{PC}$ = 15.4 Hz, P*C*H$_2$), 21.1 (*p*-NAr*Me*), 17.8 (*o*-NAr*Me*).

^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K): δ = -21.0.

^{1}H, ^{13}C GHSQC (400 MHz / 101 MHz, C_6D_6, 298 K): δ ^{1}H / δ ^{13}C = 8.08 / 123.3 (ArNCH=*CH*), 7.59 / 133.4 (*o*-*Ph*$_2$P), 7.14 / 128.8 (*m*-*Ph*$_2$P), 7.06 / 128.9 (*p*-*Ph*$_2$P), 6.61 / 129.3 (*m*-N*Ar*), 6.32 / 121.0 (ArN*CH*), 4.66 / 47.8 (N*CH*$_2$), 2.87 / 30.2 (P*CH*$_2$), 2.04 / 21.1 (*p*-NAr*Me*), 1.93 / 17.8 (*o*-NAr*Me*).

^{1}H, ^{13}C GHMBC (400 MHz / 101 MHz, C_6D_6, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.59 / 138.2, 128.9, 128.8 (*o*-*Ph*$_2$P / *i*-*Ph*$_2$P, *p*-*Ph*$_2$P, *m*-*Ph*$_2$P), 7.14 / 138.2, 133.4,

128.9 (*m*-*Ph*$_2$P / *i*-*Ph*$_2$P, *o*-*Ph*$_2$P, *p*-*Ph*$_2$P), 6.61 / 134.3, 21.1, 17.8 (*m*-N*Ar* / *i*-N*Ar*, *p*-NAr*Me*, *o*-NAr*Me*), 2.87 / 138.2, 47.8 (PC*H*$_2$ / *i*-*Ph*$_2$P, N*C*H$_2$), 2.04 / 139.2, 129.3 (*p*-NAr*Me* / *p*-N*Ar*, *m*-N*Ar*), 1.93 / 134.8, 129.3 (*o*-NAr*Me* / *o*-N*Ar*, *m*-N*Ar*).

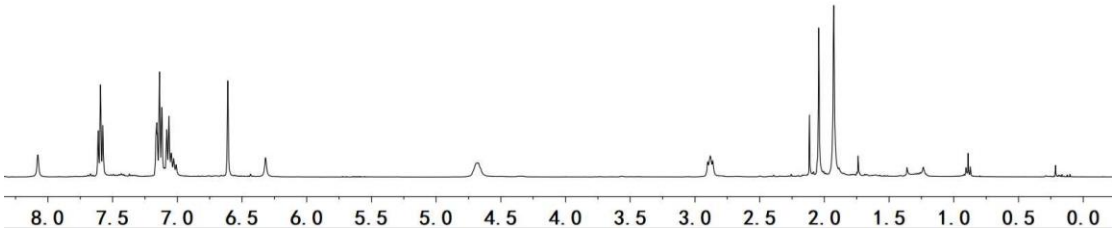


Fig. S29. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

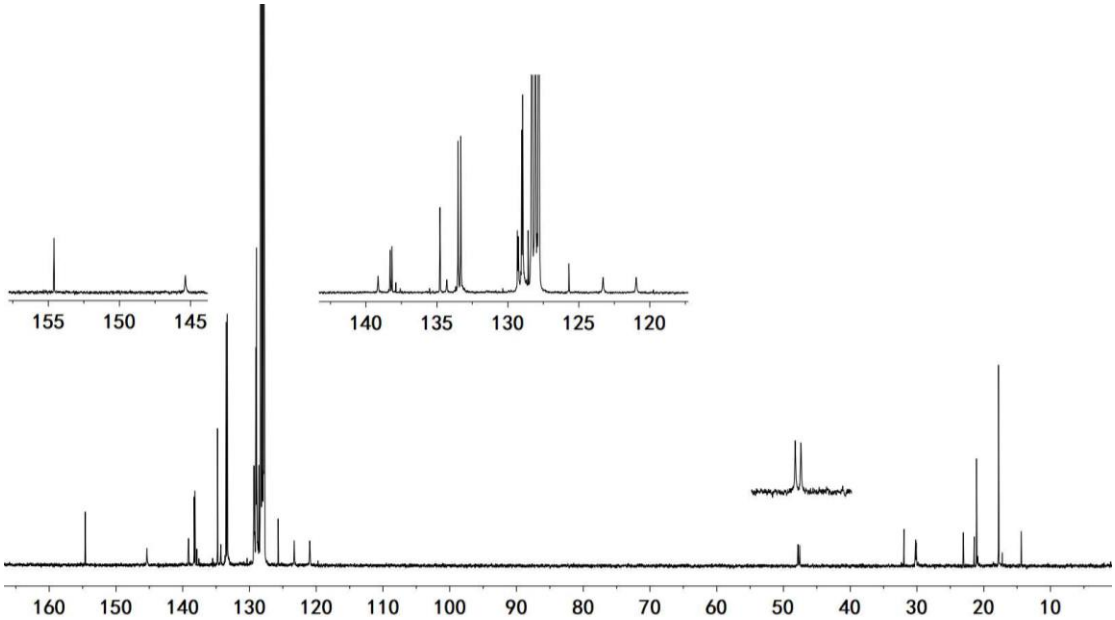


Fig. S30. ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K).

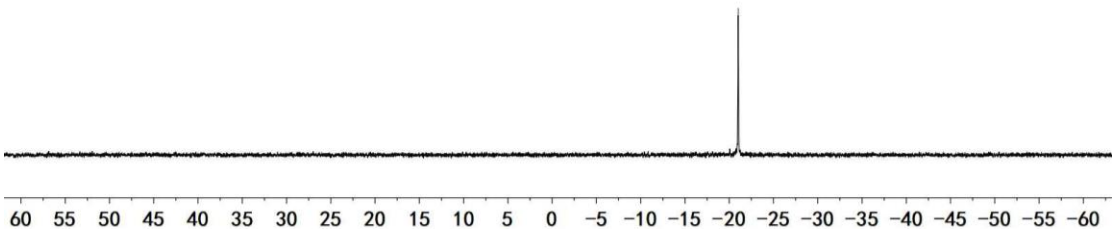
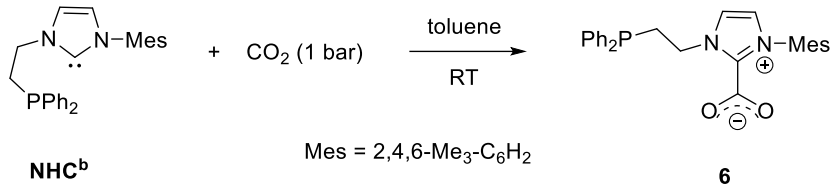


Fig. S31. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K).

Independent reaction of NHC^b with CO_2



Scheme S9.

Freshly prepared **NHC^b** (104 mg, 0.26 mmol) was dissolved in toluene (4 mL). The resulting mixture was degassed by a freeze-pump-thaw cycle for three times and placed under 1 bar CO_2 at room temperature for 1 h. All the volatiles of reaction mixture were removed in vacuo and the residue was washed with hexane (3 * 1 mL) to finally give **6** as a colorless solid (102 mg, 89% yield).

^{1}H DOSY NMR experiments

^{1}H DOSY experiments were measured on a Bruker 400 MHz spectrometer running TopSpin2 and equipped with a z-gradient PABBO 5 mm probe and a BSMS GAB 10 A gradient amplifier providing a maximum gradient output of 5.35 G/cmA. The spectra were collected at a frequency of 400.13 MHz with a spectral width of 4006.41 Hz and 64k data points. The pulse sequence ledbpgp2s was employed and main related parameters as followed: relaxation delay of 1 s, diffusion time (large delta) of 20 ms, bipolar gradient pulses (little delta) of 2.3 ms and homospoil gradient pulses of 0.6 ms. Sixteen experiments were collected with the bipolar gradient strength, initially at 2% (first experiment) and linearly increased to 98% (16th experiment). The data were processed using Topspin dosy module.

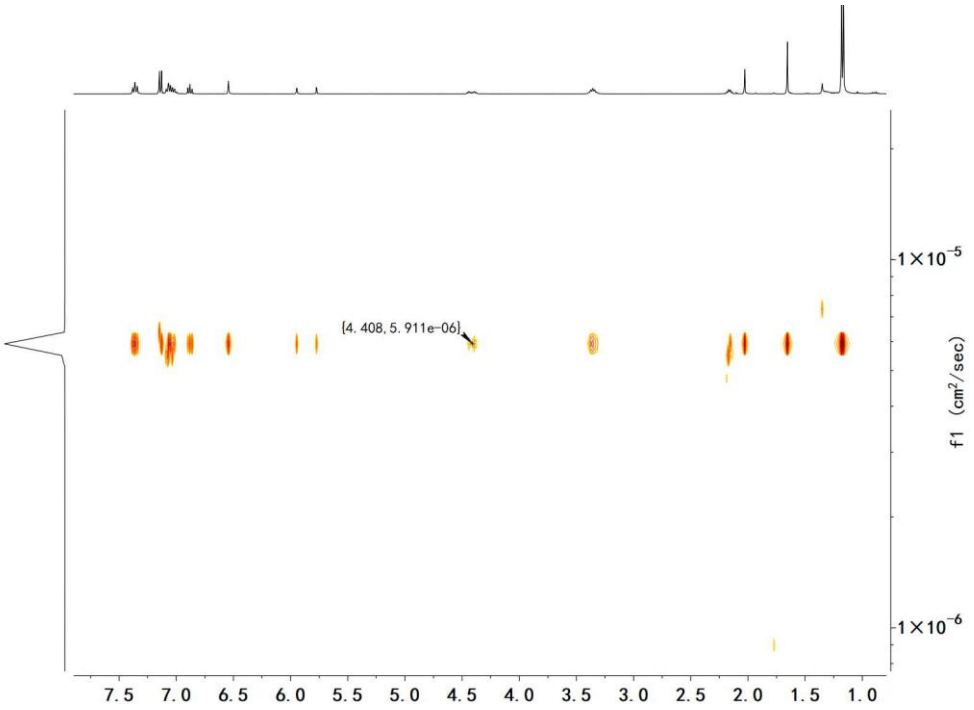


Fig. S32. ^{1}H DOSY NMR spectrum of complex **2b** in C_6D_6 at 298 K

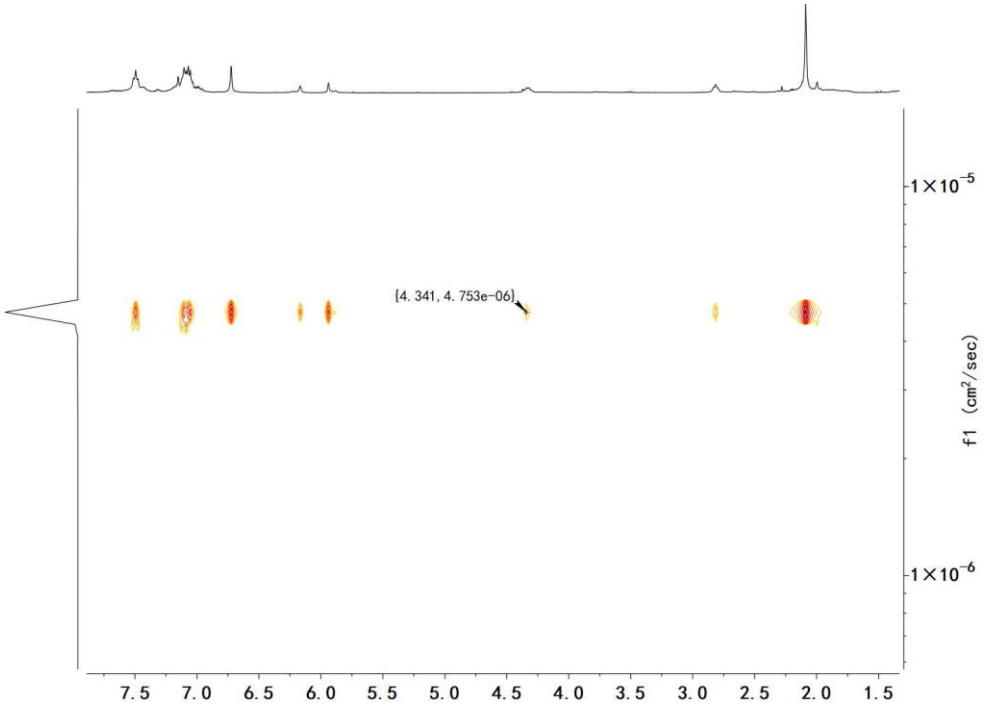


Fig. S33. ^{1}H DOSY NMR spectrum of complex **3b** in C_6D_6 at 298 K

General procedure for catalytic hydroboration of CO_2

In a glovebox, zinc catalyst (0.0075 mmol, based on Zn), C_6Me_6 (0.015 mmol), and borane (0.15 mmol) were mixed in C_6D_6 (0.5 mL) and transferred to an oven-dried J-Young NMR tube. The mixture was degassed by a freeze-pump-thaw cycle for three times and placed under 1 atm CO_2 at room temperature. The yields of products were determined by ^1H and ^{11}B NMR. Each catalytic run was repeated to give at least two sets of values per complex.

Reaction of HBpin with CO_2 (1 bar) in the presence of 3a (entry 1)

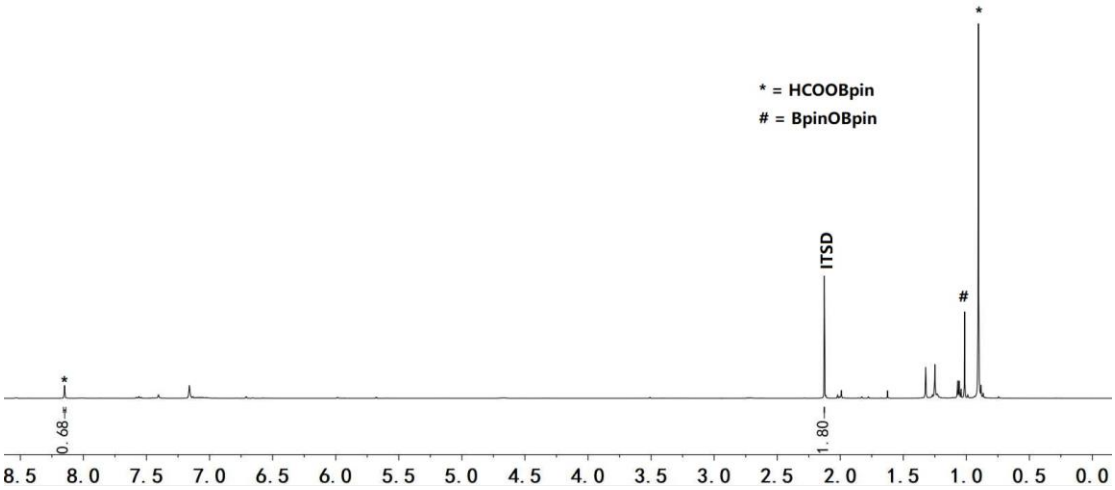


Fig. S34. ^1H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol **3a**, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

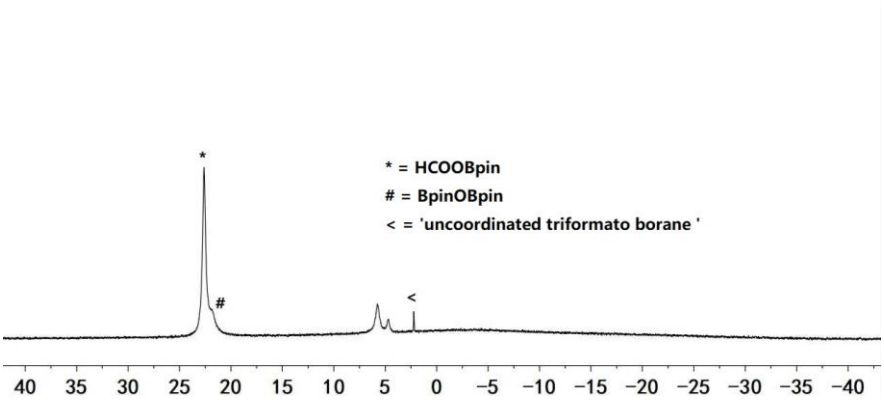


Fig. S35. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol **3a**, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Reaction of HBpin with CO_2 (1 bar) in the presence of 3b (entry 2)

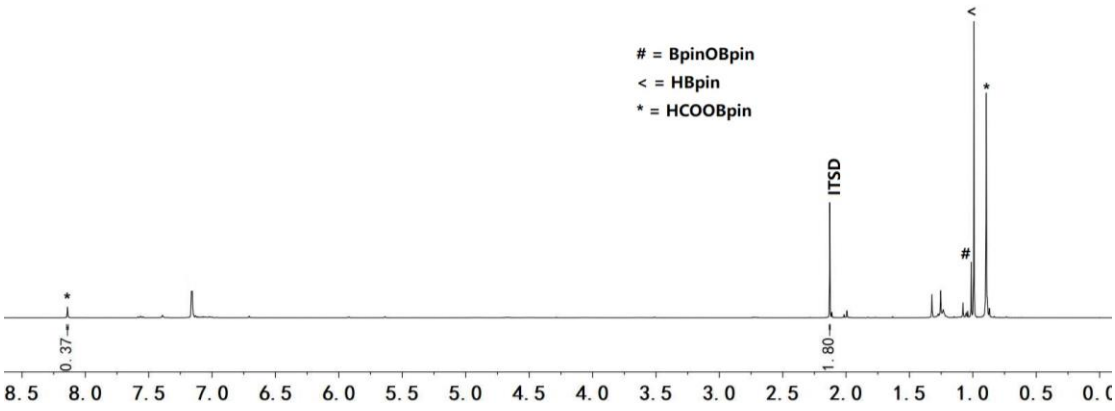


Fig. S36. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol **3b**, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

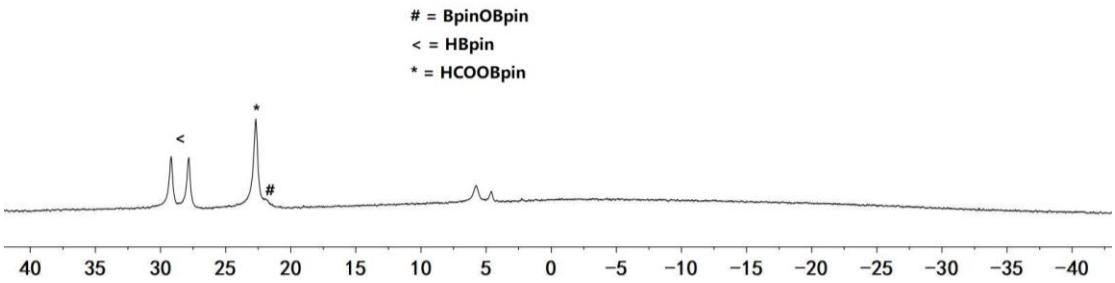


Fig. S37. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol **3b**, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Reaction of HBpin with CO_2 (10 bar) in the presence of 3a (entry 3)

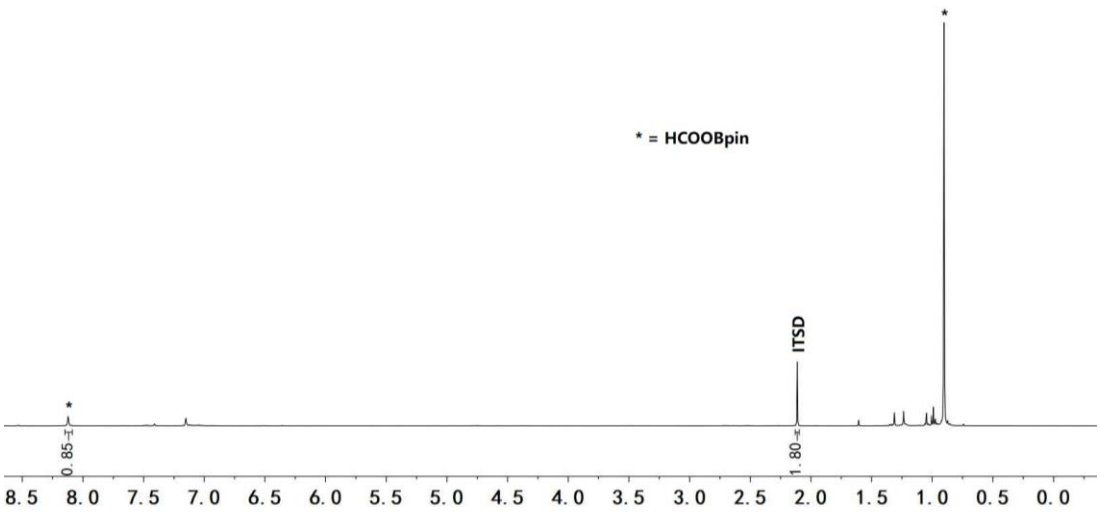


Fig. S38. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0075 mmol **3a**, 0.30 mmol HBpin, 1.0 mL C_6D_6, 10 bar CO_2, 0.03 mmol C_6Me_6, RT, 12 h.

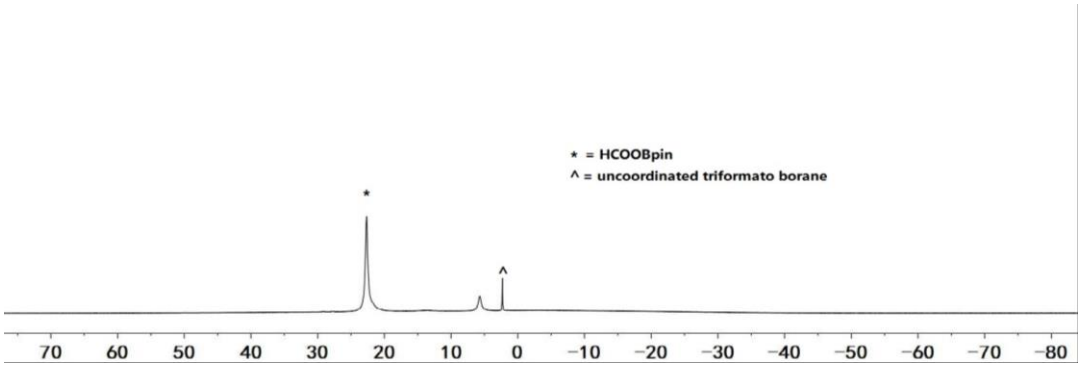
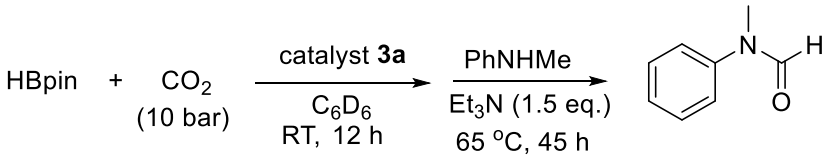


Fig. S39. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0075 mmol **3a**, 0.30 mmol HBpin, 1.0 mL C_6D_6, 10 bar CO_2, 0.03 mmol C_6Me_6, RT, 12 h.

Direct *N*-formylation of *N*-methyl aniline



After the hydroboration reaction was complete, Et_3N (0.45 mmol) and PhNHMe (0.3 mmol) were directly added and then the reaction mixture was stirred for 45 h at 65 °C under argon. The reaction mixture was directly passed through a pad of silica gel with

EtOAc/hexane = 1/4 to afford *N*-formylation product (29 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.48 (s, 1H, *H*CO), 7.42 (m, 2H, *Ph*), 7.28 (m, 1H, *Ph*), 7.17 (m, 2H, *Ph*), 3.33 (s, 3H, N*Me*).

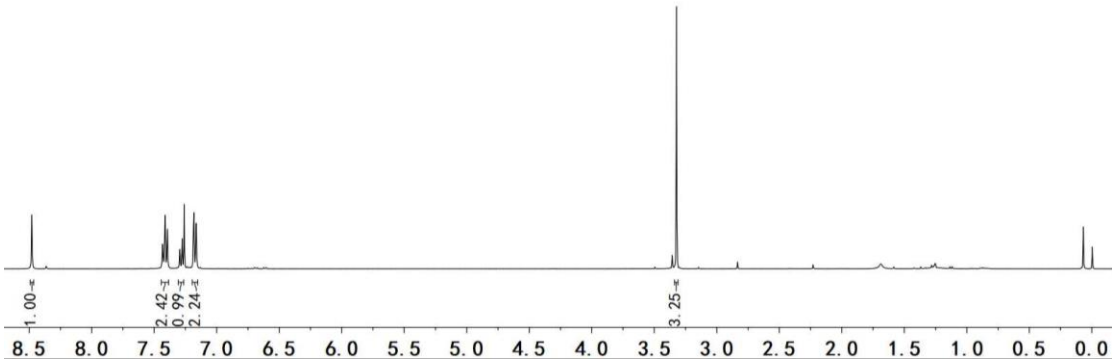


Fig. S40. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)

Reaction of HBpin with CO_2 (10 bar) in the presence of 4 (entry 4)

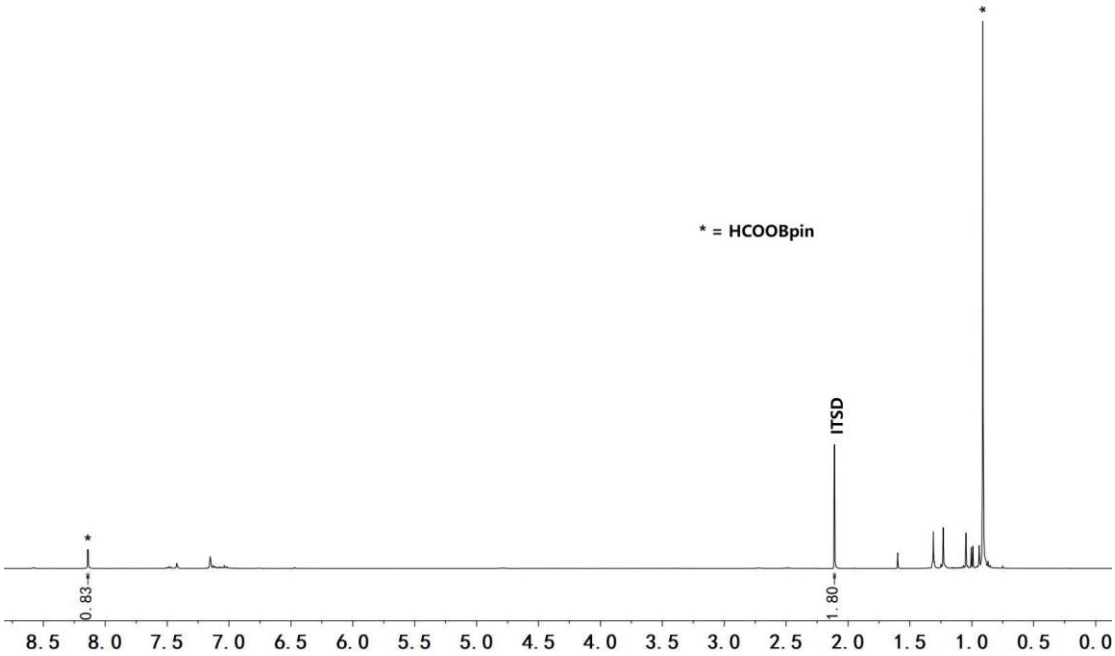


Fig. S41. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.015 mmol **4**, 0.30 mmol HBpin, 1.0 mL C_6D_6, 10 bar CO_2, 0.03 mmol C_6Me_6, RT, 12 h.

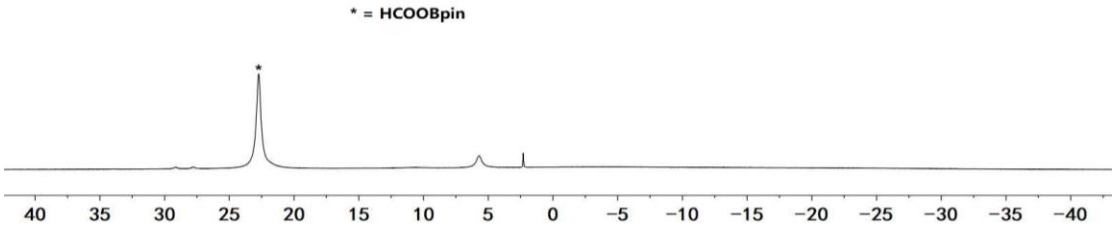


Fig. S42. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.015 mmol **4**, 0.30 mmol HBpin, 1.0 mL C_6D_6, 10 bar CO_2, 0.03 mmol C_6Me_6, RT, 12 h.

Reaction of HBpin with CO_2 (1 bar) in the presence of NHC[a] (entry 5)

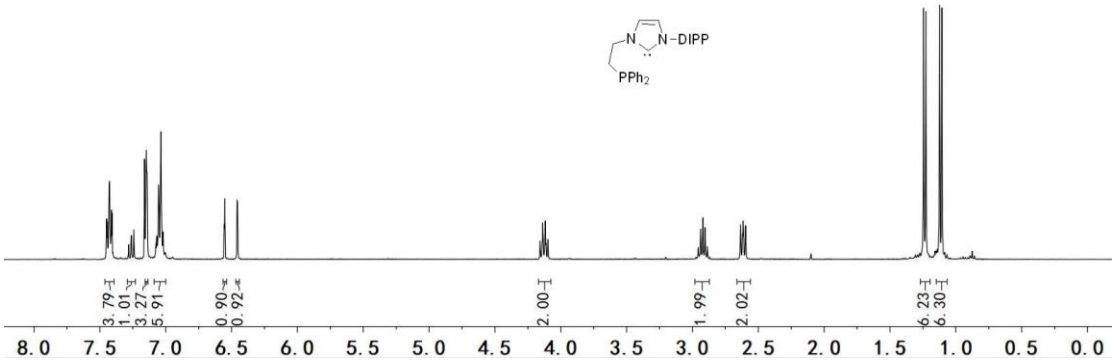


Fig. S43. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

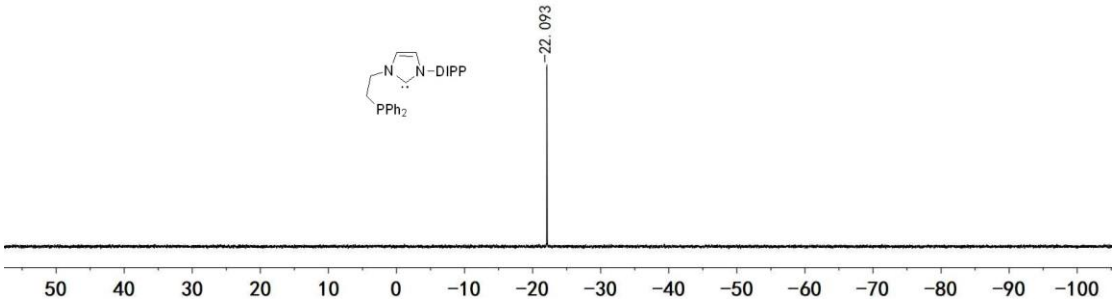


Fig. S44. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K).

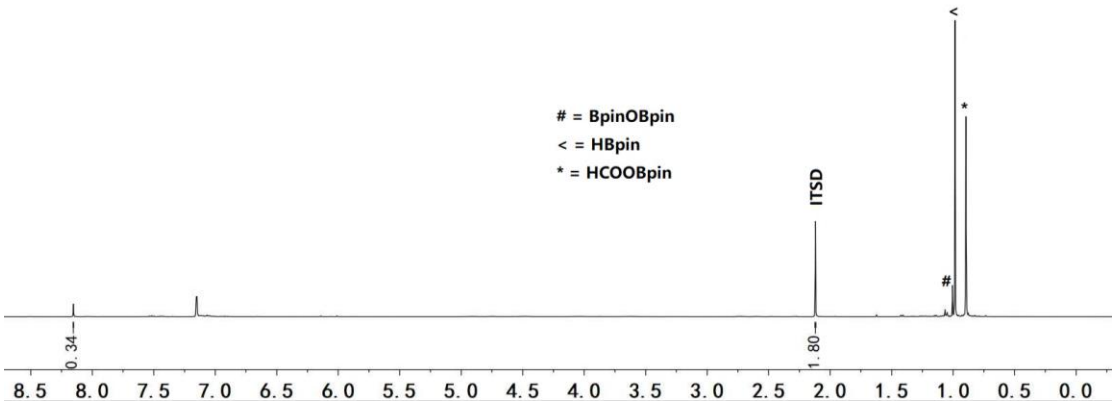


Fig. S45. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0075 mmol **NHC[a]**, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

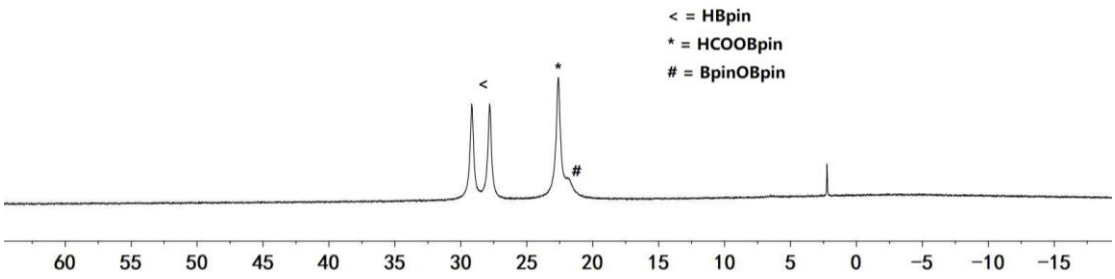


Fig. S46. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0075 mmol **NHC[a]**, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Reaction of HBpin with CO_2 (1 bar) in the presence of $[(IMes)ZnH_2]_2$ (entry 6)

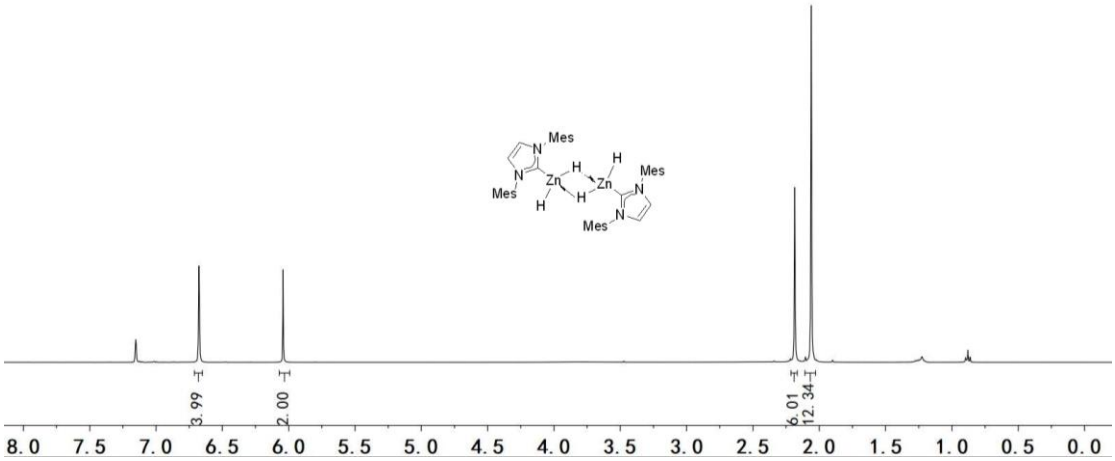


Fig. S47. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

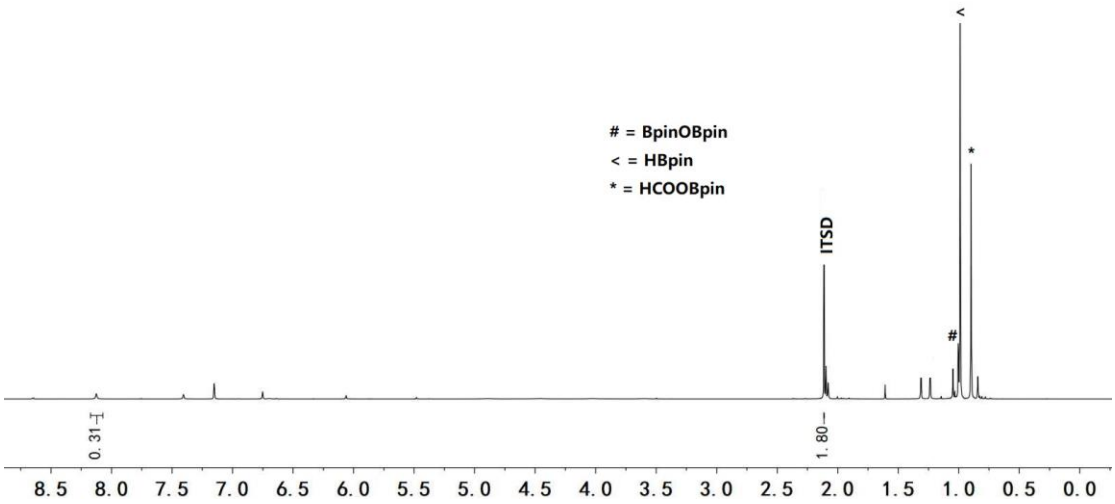


Fig. S48. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol $[(IMes)ZnH_2]_2$, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

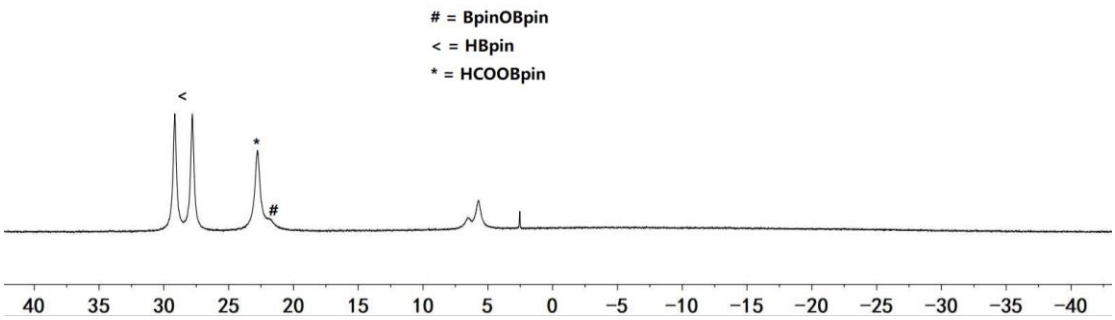


Fig. S49. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol $[(IMes)ZnH_2]_2$, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Reaction of HBpin with CO_2 (1 bar) in the presence of $[(IPr)ZnH_2]_2$ (entry 7)

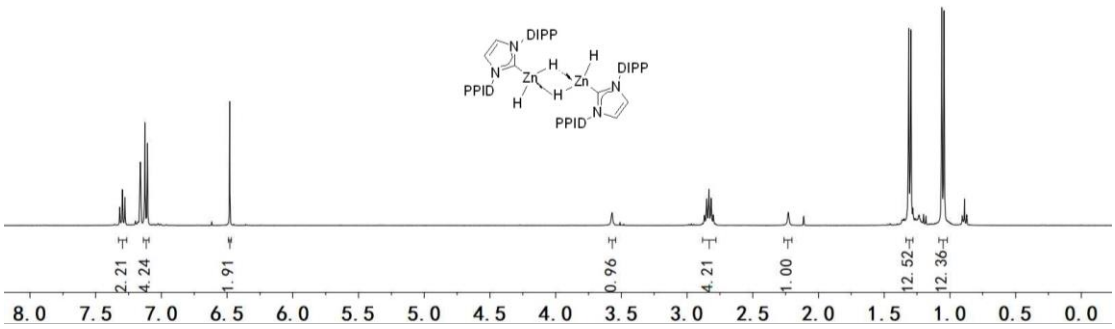


Fig. S50. ^{1}H NMR (400 MHz, C_6D_6, 298 K).

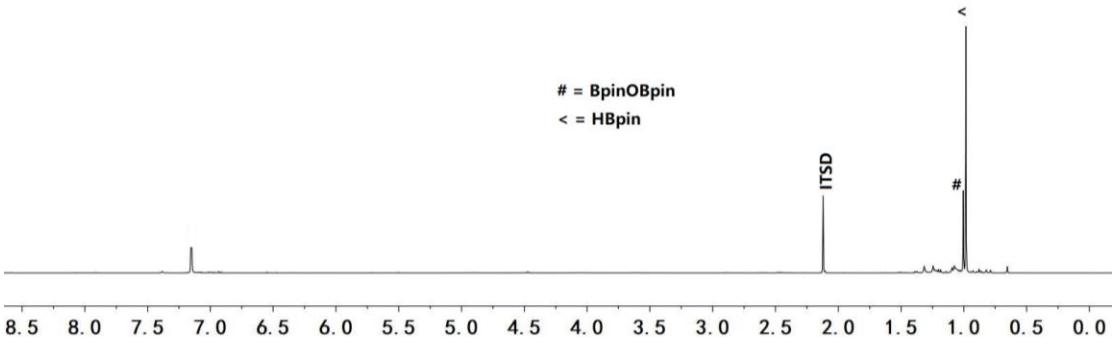


Fig. S51. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin.

Conditions: 0.0038 mmol $[(IPr)ZnH_2]_2$, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

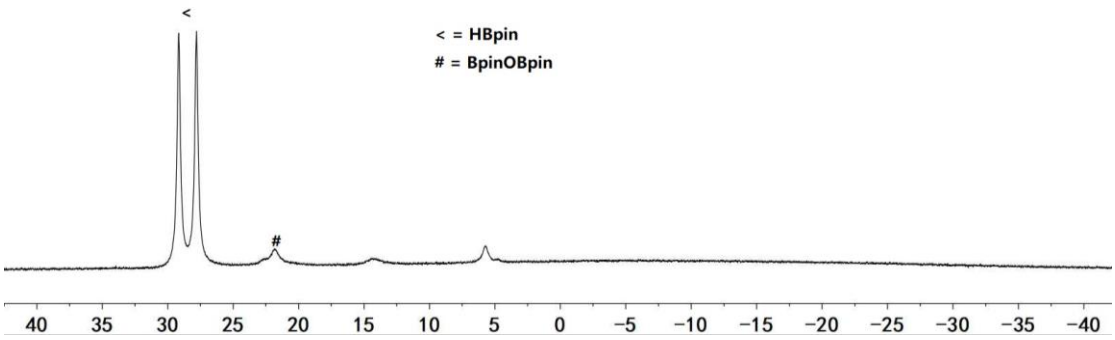


Fig. S52. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0038 mmol $[(IPr)ZnH_2]_2$, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Reaction of HBpin with CO_2 (1 bar) in the presence of (DIPP-nacnac)ZnH (entry 8)

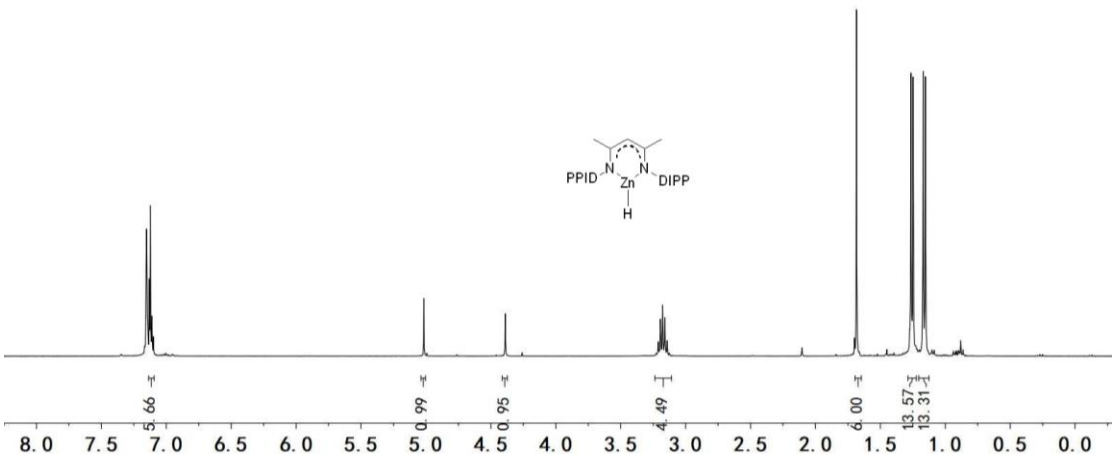


Fig. S53. ^1H NMR (400 MHz, C_6D_6, 298 K).

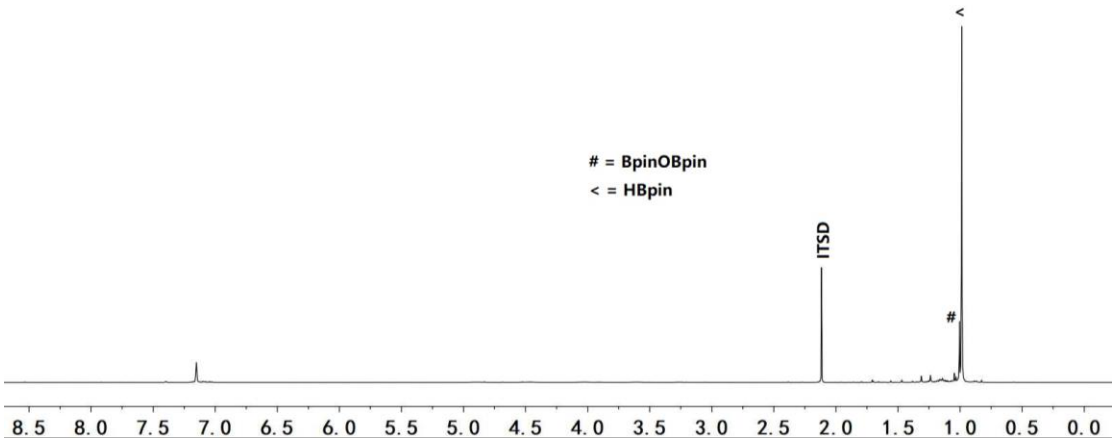


Fig. S54. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0075 mmol (DIPP-nacnac)ZnH, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

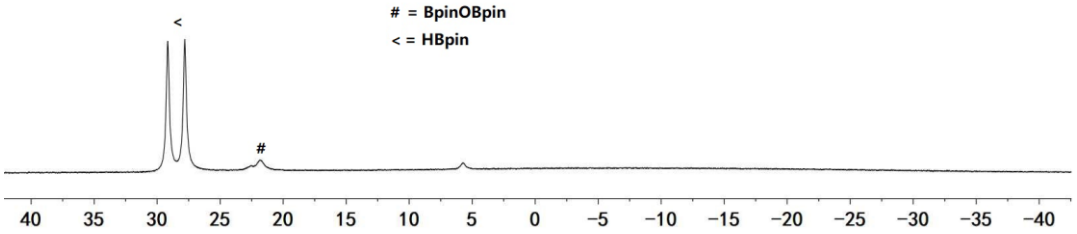


Fig. S55. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBpin. Conditions: 0.0075 mmol (DIPP-nacnac)ZnH, 0.15 mmol HBpin, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Reaction of HBcat with CO_2 (1 bar) in the presence of 3a (entry 9)

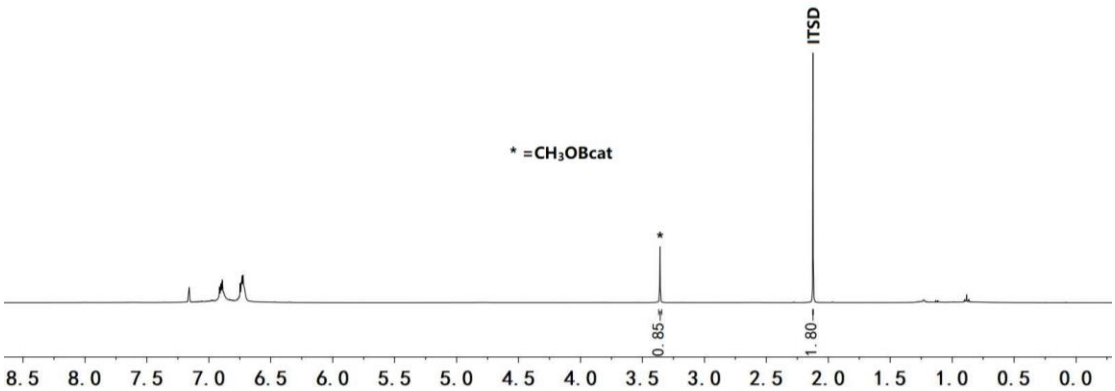


Fig. S56. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBcat.

Conditions: 0.0038 mmol **3a**, 0.15 mmol HBcat, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 12 h.

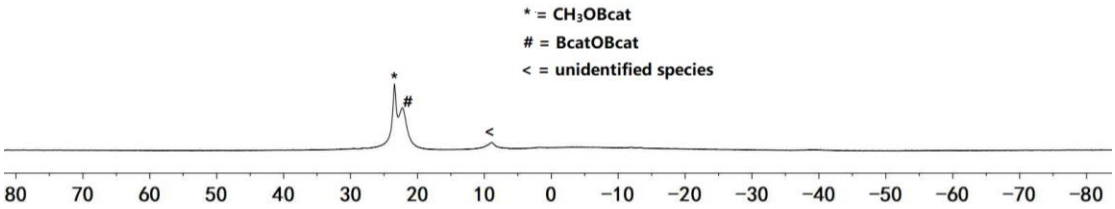


Fig. S57. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBcat. Conditions: 0.0038 mmol **3a**, 0.15 mmol HBcat, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 12 h.

Direct hydrolysis of CH_3OBcat to generate CH_3OH with one-pot reaction

After the hydroboration reaction was complete, distilled water (500 μL) was added via syringe and the resulting mixture was stirred at room temperature under an argon atmosphere for 24 h. The volatiles were vacuum transferred (60 ^oC) into a Schlenk tube and mixed with hexamethylbenzene (2.4 mg, 0.015 mmol) as the internal standard in an NMR tube. The isolated yield for CH_3OH was determined to 61%.

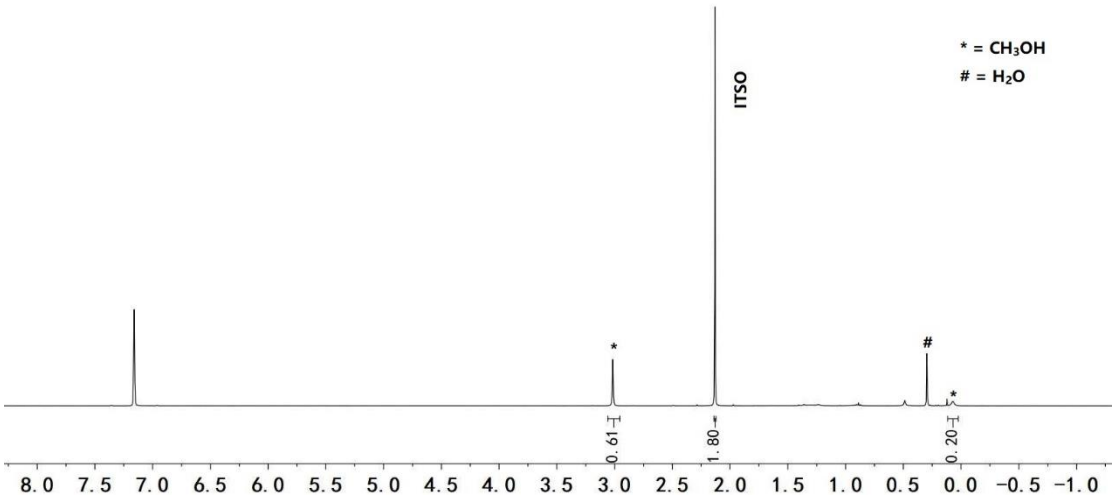


Fig. S58. ^1H NMR (400 MHz, C_6D_6, 298 K)

Reaction of HBcat with CO_2 (1 bar) in the presence of NHC[a]

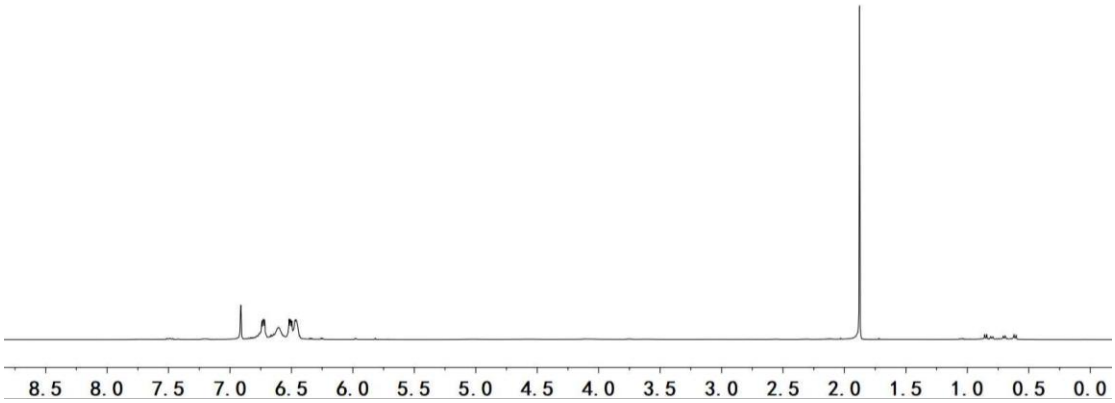


Fig. S59. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with HBcat. Conditions: 0.0075 mmol **NHC[a]**, 0.15 mmol HBcat, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 12 h.

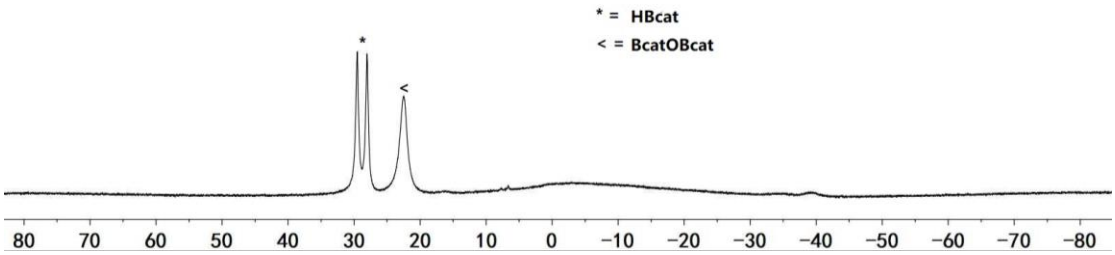


Fig. S60. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with HBcat. Conditions: 0.0075 mmol **NHC[a]**, 0.15 mmol HBcat, 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 12 h.

Reaction of 9-BBN with CO_2 (1 bar) in the presence of 3a (entry 10)

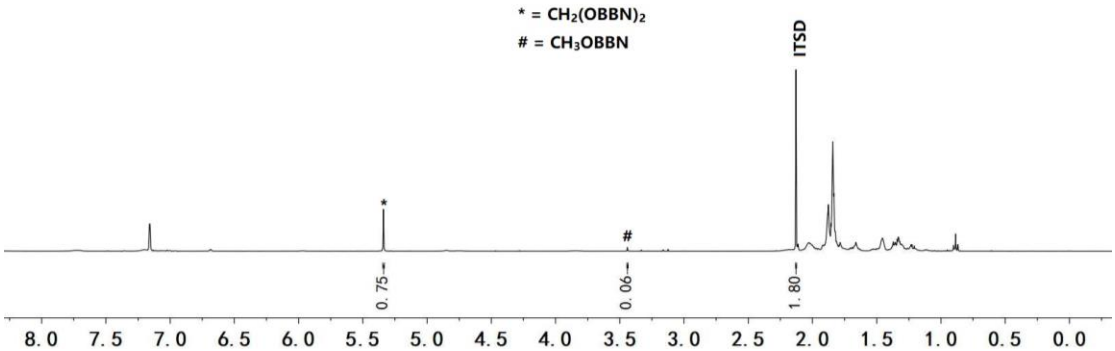


Fig. S61. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with 9-BBN. Conditions: 0.0038 mmol **3a**, 0.15 mmol 9-BBN (based on B-H), 0.5 mL C_6D_6, 1 bar

CO_2, 0.015 mmol C_6Me_6, RT, 4 h.

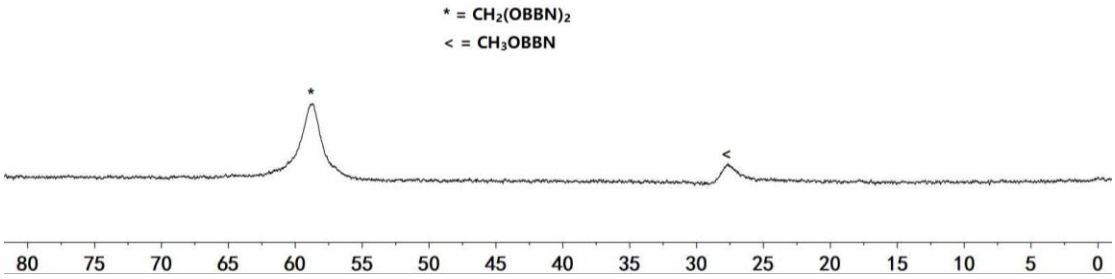


Fig. S62. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with 9-BBN. Conditions: 0.0038 mmol **3a**, 0.15 mmol 9-BBN (based on B-H), 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 4 h.

Reaction of BH_3·SMe_2 with CO_2 (1 bar) in the presence of 3a (entry 11)

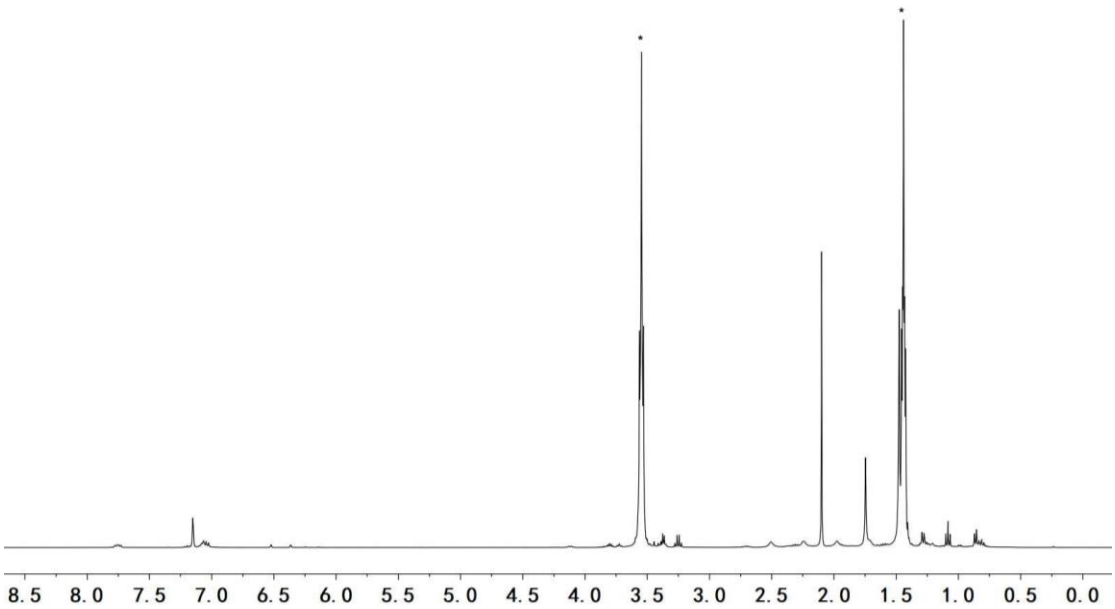


Fig. S63. ^{1}H NMR spectrum of the catalytic hydroboration of CO_2 with BH_3·SMe_2. Conditions: 0.0038 mmol **3a**, 0.15 mmol BH_3·SMe_2 (1 M in THF), 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h. (*: THF)

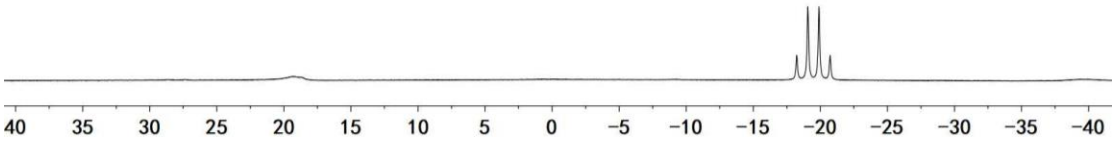
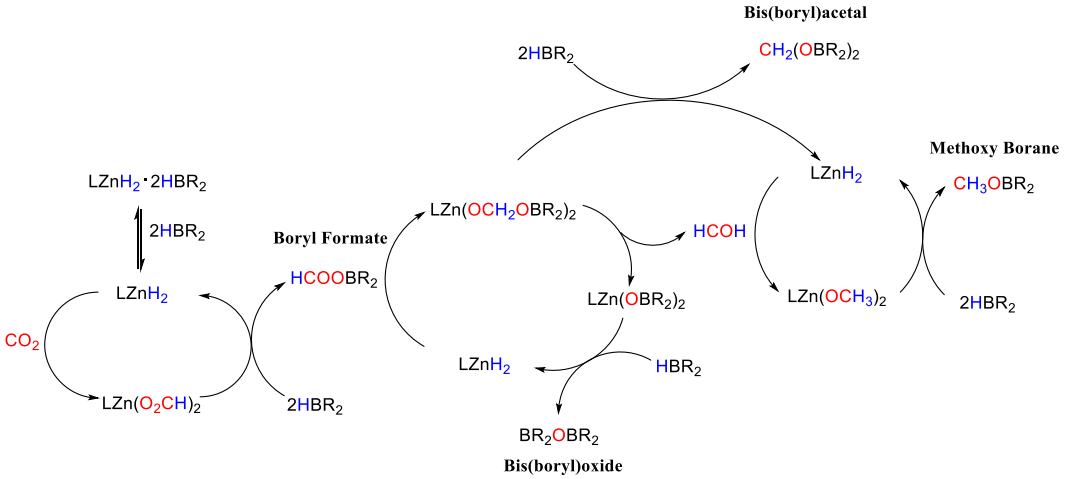


Fig. S64. ^{11}B NMR spectrum of the catalytic hydroboration of CO_2 with BH_3·SMe_2. Conditions: 0.0038 mmol **3a**, 0.15 mmol BH_3·SMe_2 (1 M in THF), 0.5 mL C_6D_6, 1 bar CO_2, 0.015 mmol C_6Me_6, RT, 48 h.

Proposed mechanism for the catalytic hydroboration of CO_2



Scheme S10. Proposed pathway for zinc dihydride-catalyzed CO_2 hydroboration.