Organic Aluminum Hydrides Catalyze Nitrile Hydroboration

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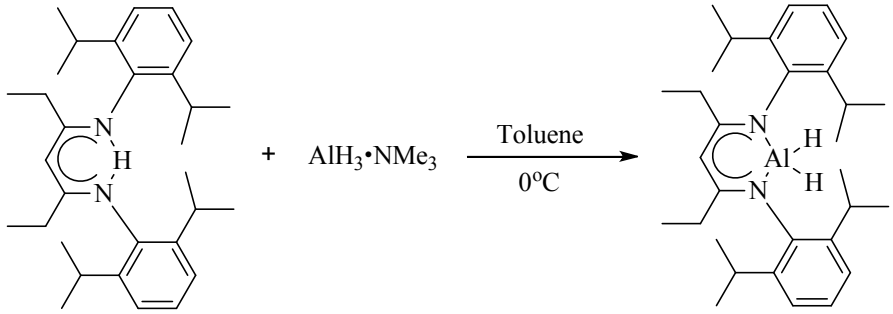
General considerations: All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glove box. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from J&K chemical or Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercury Plus 400 MHz or Bruker Avance III 600 MHz spectrometer. The elemental analyses were performed by the Analytical Instrumentation Center of the Beijing Institute of Technology. Melting points were measured in sealed glass tubes. Compound $L'AlH_2$ ($L' = HC(CMeNAr)_2$, Ar = 2,6- $Et_2C_6H_3$) (**1**) was prepared according to the literature procedure.[1] CCDC- 1891212 (**2**) and CCDC-1899546 (**3**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Synthesis of Aluminum Hydrides 2 and 3

Scheme S1. Synthesis of Aluminum Hydride Complex **2**



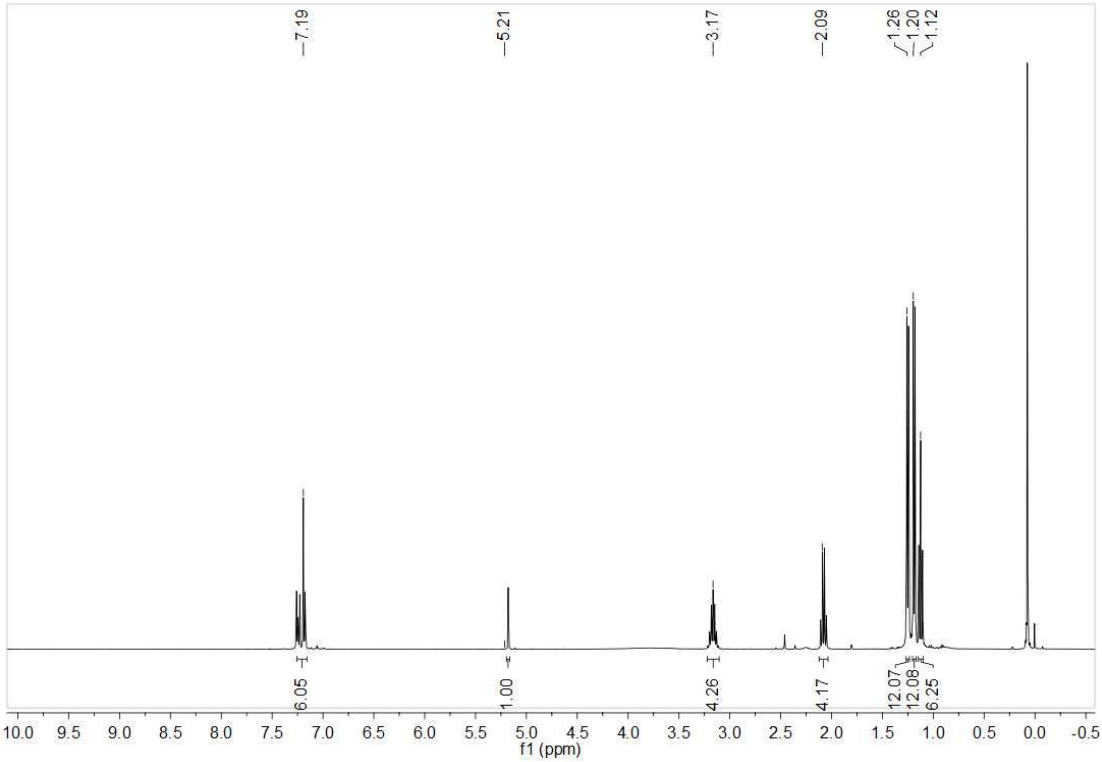
2

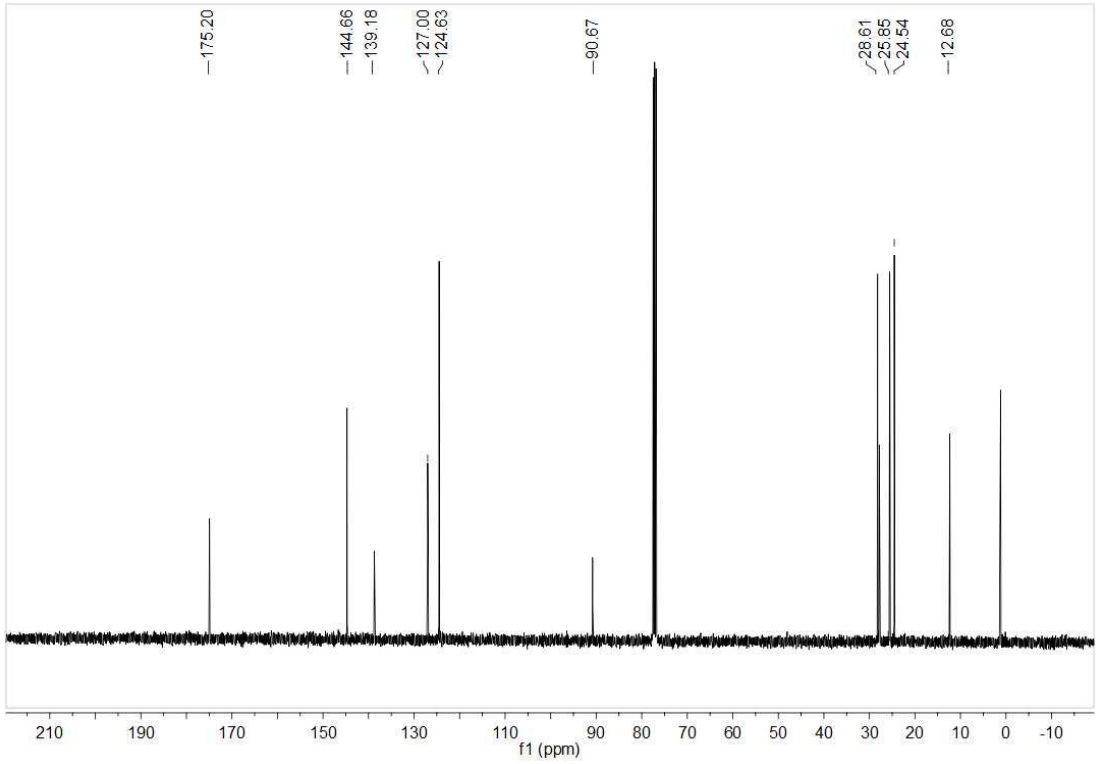
Method for preparation of L″AlH$_2$: A solution of L″H (L″= HC(CEtNAr)$_2$, Ar = 2,6- *i*Pr$_2$C$_6$H$_3$) (0.434g, 1 mmol) in toluene (10 mL) was added at ice bath to a solution of AlH$_3$·NMe$_3$ (0.089 g, 1 mmol) in toluene (2 mL) under nitrogen atmosphere, and the reaction mixture was stirred for additional 24 h, concentrated to 5 mL and stored overnight at -32 ℃. The crude product was crystallized from toluene to afford colorless crystals of **2** and dried in vacuo. (0.38 g, yield 80% based on L″H); m.p. 153~157 °C

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.16-7.28 (m, 6H, aromatic of Ar group), 5.21 (s, 1H, γ-CH), 3.17 (sept, 4H, *CH*Me$_2$), 2.09 (q, 4H, *CH$_2$*Me), 1.26, 1.20 (dd, 24H, CH*Me$_2$*), 1.12 (t, 6H, CH$_2$*Me*);

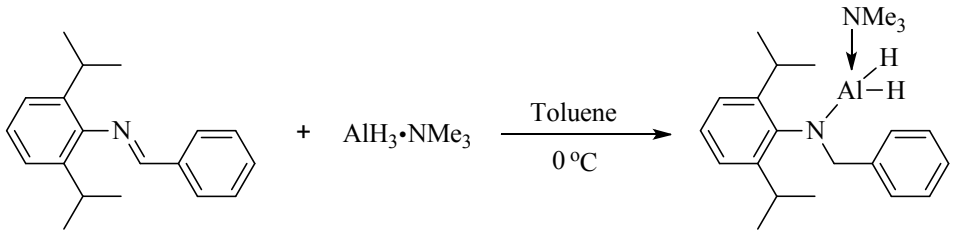
^{13}C NMR (101 MHz, CDCl$_3$, 298 K): δ 175.20 (CN), 144.66, 139.18, 127.00, 124.63 (Ar), 90.67 (γ-CH), 28.61 (*CH*Me$_2$), 25.85 (CH*Me$_2$*), 24.54 (*CH$_2$*Me), 12.68 (CH$_2$*Me*).

Scheme S2. ^{1}H (top) and ^{13}C NMR (bottom) ($CDCl_3$, 298 K) of Complex **2**





Scheme S3. Synthesis of Aluminum Hydride Complex **3**



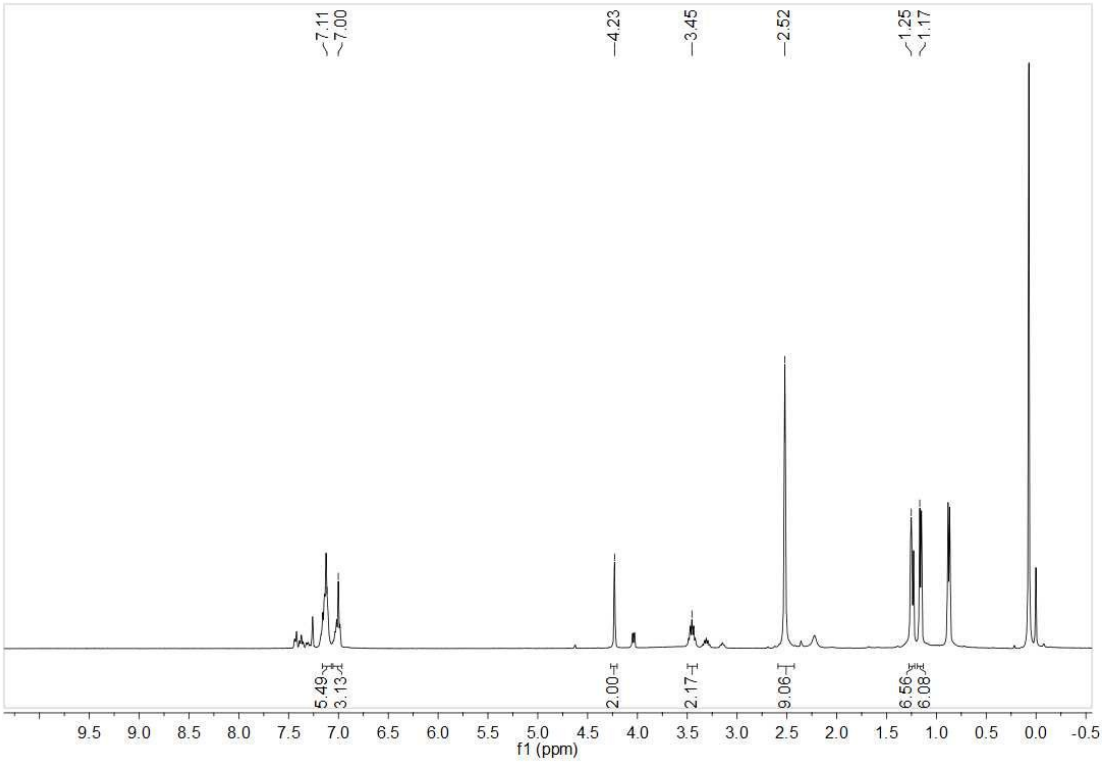
3

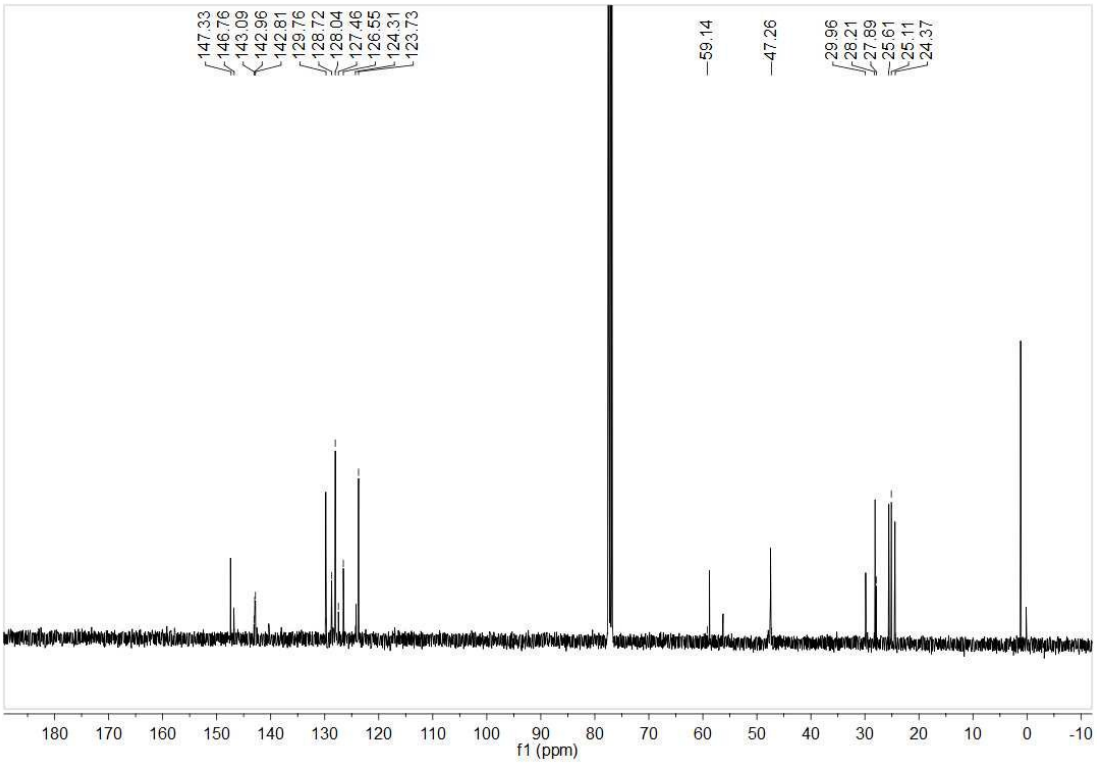
Method for preparation of [BnN(2,6- *i*Pr$_2$C$_6$H$_3$)]AlH$_2$(NMe$_3$): A solution of PhCH=N(2,6-*i*Pr$_2$C$_6$H$_3$) (0.265g, 1 mmol) in toluene (10 mL) was added at ice bath to a solution of AlH$_3$·NMe$_3$ (0.089 g, 1 mmol) in toluene (2 mL) under nitrogen atmosphere, and the reaction mixture was stirred for additional 24 h, concentrated to 5 mL and stored overnight at -32 °C. The crude product was crystallized from toluene to afford colorless crystals of **3** and dried in vacuo. (0.27 g, yield 76%); m.p. 191.3~192.5 °C

^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.11 (m, 5H, Ar-H), 7.00 (m, 3H, Ar-H), 4.23 (s, 2H, N*CH$_2$*), 3.45 (sept, 2H, *CH*Me$_2$), 2.52 (s, 9H, N*Me$_3$*), 1.25, 1.17 (dd, 12H, CH*Me$_2$*);

^{13}C NMR (101 MHz, CDCl$_3$, 298 K): δ 147.33, 146.76, 143.09, 142.96, 142.81, 129.76, 128.72, 128.04, 127.46, 126.55, 124.31, 123.73(Ar), 59.14 (N*C*H$_2$), 47.26 (N*Me$_3$*), 29.96, 28.21 (*C*HMe$_2$), 27.89, 25.61, 25.11, 24.37 (CH*Me$_2$*).

Scheme S4. ^{1}H (top) and ^{13}C NMR (bottom) ($CDCl_3$, 298 K) of Complex **3**





Single Crystal X-ray Structure and Refinement

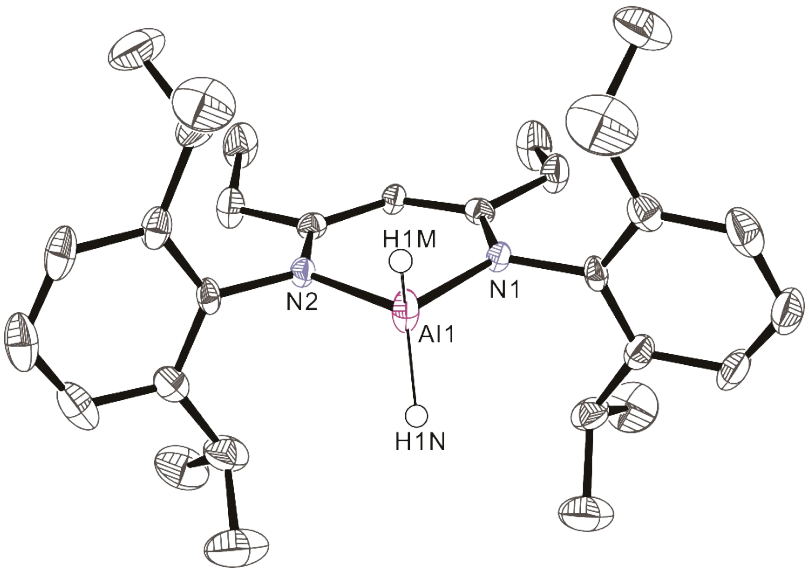


Figure S1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity except those at the aluminum. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 1.898(3), Al(1)-N(2) 1.904(3), Al(1)-H(1M) 1.475(14), Al(1)-H(1N) 1.459(14).

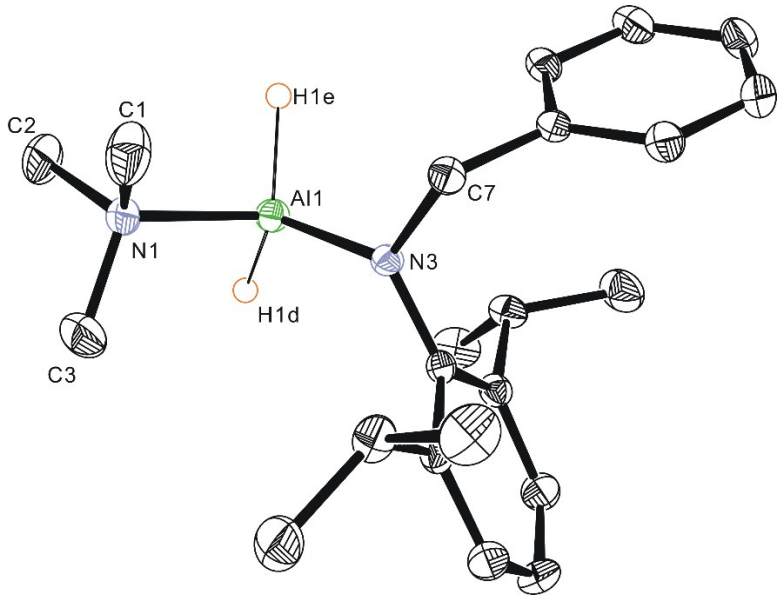


Figure S2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% level and the hydrogen atoms are omitted for clarity except those at the aluminum. Selected bond distances (Å) and angles (deg): Al(1)-N(1) 2.0262(13), Al(1)-N(3) 1.8254(12), N(3)-C(7) 1.4760(18), N(1)-Al(1)-N(3) 109.90(5), N(1)-Al(1)-H(1e) 98.7(6), N(1)-Al(1)-H(1d) 98.8(7), N(3)-Al(1)-H(1e) 111.5(6), N(3)-Al(1)-H(1d) 115.0(7).

The single crystal of **2** and **3** were mounted with glue on a glass fiber and crystal data were collected on the Rigaku AFC10 Saturn724 + (2 × 2 bin mode) diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption correction was applied using the SADABS program.[2] The structure was solved by direct methods[3] and refined by full-matrix least squares on F^2 using the SHELXL-97 program.[4] The summary of the crystal data were given in Table S**1.**

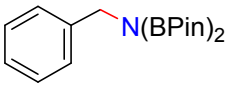
Table S**1**	**2**	**3**
Empirical formula	C_{31} H_{47} Al N_2	C_{22} H_{35} Al N_2
Formula weight	474.68	354.50
Temperature (K)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C* 2	*P* 21/n
a (Å)	27.963(5)	15.4104(4)
b (Å)	16.952(3)	18.6531(5)
c (Å)	12.983(2)	15.4547(4)
α (°)	90	90
β (°)	107.713(5)	96.7470(10)
γ (°)	90	90
V (Å^3)	5862.2(16)	4411.7(2)
Z	8	8
ρ_c (g/cm^3)	1.076	1.067
Absorption coefficient (mm^{-1})	0.089	0.098
F(000)	2080	1552
Crystal size(mm^3)	0.20×0.15×0.10	0.20×0.15×0.10
θ range for data collection(°)	2.35 to 24.48	2.56 to 28.84
Index ranges	-35≤h≤35	-21≤h≤22
	-21≤k≤21	-26≤k≤27

	-16≤l≤16	-22≤l≤22
Reflections collected	32161	60774
R (int)	0.0496	0.0547
Data / restraints / parameters	12340/5/632	13689/4/467
Goodness-of-fit on F^2	1.012	1.019
$R1^a$, $wR2^b$(I >2σ(I))	0.0511, 0.1230	0.0522, 0.1188
$R1^a$, $wR2^b$(all data)	0.0711, 0.1333	0.1105, 0.1412
Largest diff. peak/hole [eÅ^{-3}]	-0.251/0.277	-0.287/0.364

General Catalytic Procedure for the Hydroboration of Nitriles

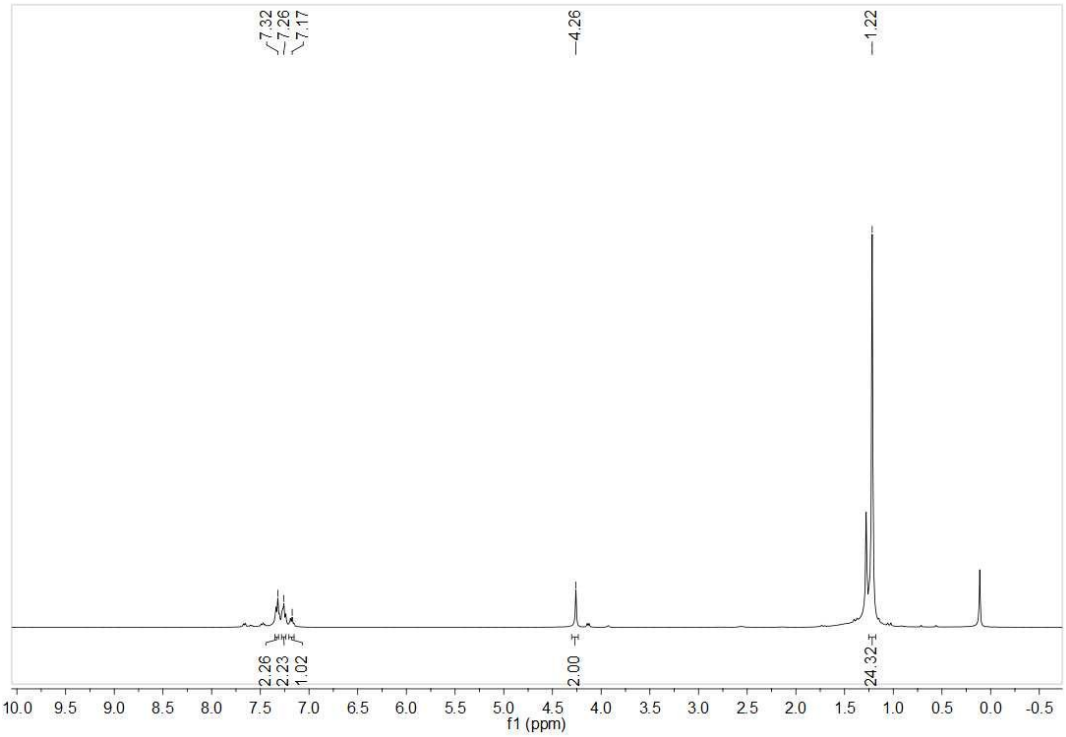
All reactions were carried out under nitrogen atmosphere. Catalyst **1** (5 mol%), nitriles (0.5 mmol) and pinacolborane (1.05 mmol) were sealed in a 10 mL Schlenk flask equipped with a magnetic stir bar inside the glove box. The reaction mixture was stirred at 80°C for 6-24 hours depending on the nature of the starting materials. The progress of the reaction was monitored by ^{1}H NMR spectroscopy using anisole (10 mol%) as an internal standard. The corresponding diborylamines (4a-4k) can be further purified by crystallization in n-hexane solution.

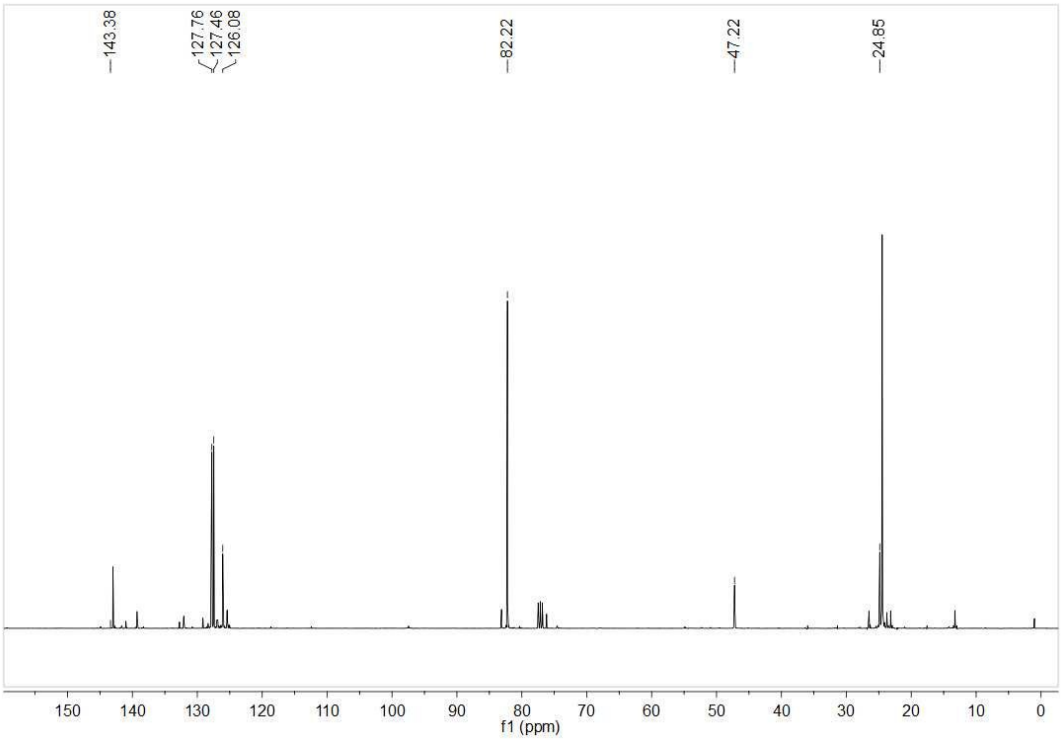
The NMR Spectra of Products from Nitrile Hydroboration

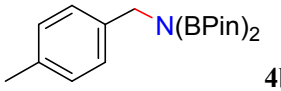


4a (99% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.32 (m, 2H, *o*-C_6H_5), 7.26 (m, 2H, *m*-C_6H_5), 7.17 (m, 1H, *p*-C_6H_5), 4.26 (s, 2H, NCH_2), 1.22 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 143.38 (s, *i*-*C*), 127.76 (s, *p*-*C*), 127.46 (s, *o*-*C*), 126.08 (s, *m*-*C*), 82.22 (s, Bpin-*ipso*), 47.22 (s, N-CH_2), 24.85 (s, Bpin-CH_3). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 26.11 (br).

Scheme S5. ^{1}H (top) and ^{13}C NMR (bottom) of **4a**

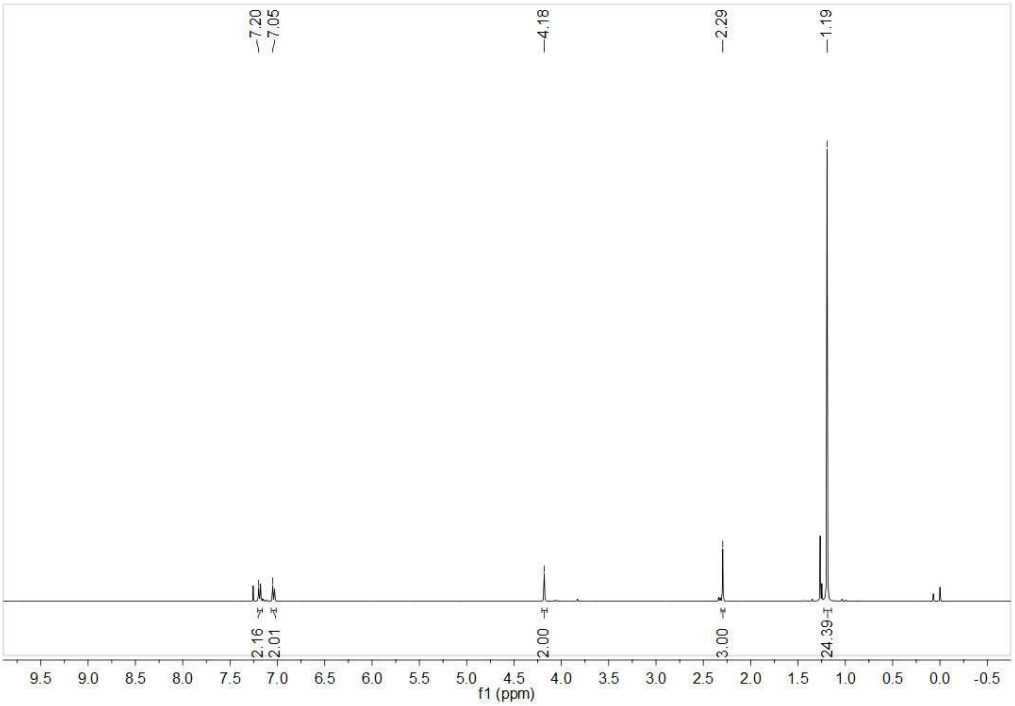


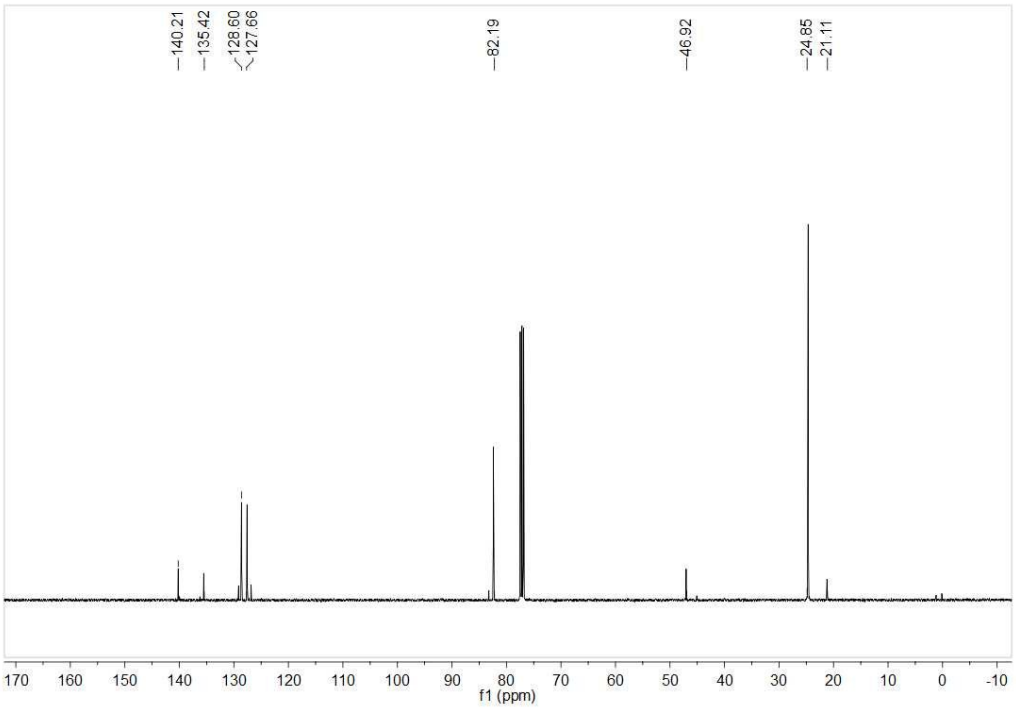


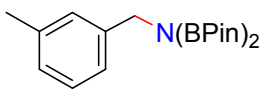


4b (99% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.20(d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, *p*-(CH_3)C_6H_4), 7.05 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, *p*-(CH_3)C_6H_4), 4.18 (s, 2H, NCH_2), 2.29 (s, 3H, *p*-(CH_3)C_6H_4), 1.19 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 140.21 (s, *p*-Tol-*ipso*), 135.42 (s, *p*-Tol-*ipso*), 128.60 (s, *p*-Tol), 127.66 (s, *p*-Tol), 82.19 (s, Bpin-*ipso*), 46.92 (s, N-CH_2), 24.85 (s, Bpin-CH_3), 21.11 (s, *p*-(CH_3)C_6H_4). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.81 (br).

Scheme S6. ^{1}H (top) and ^{13}C NMR (bottom) of **4b**



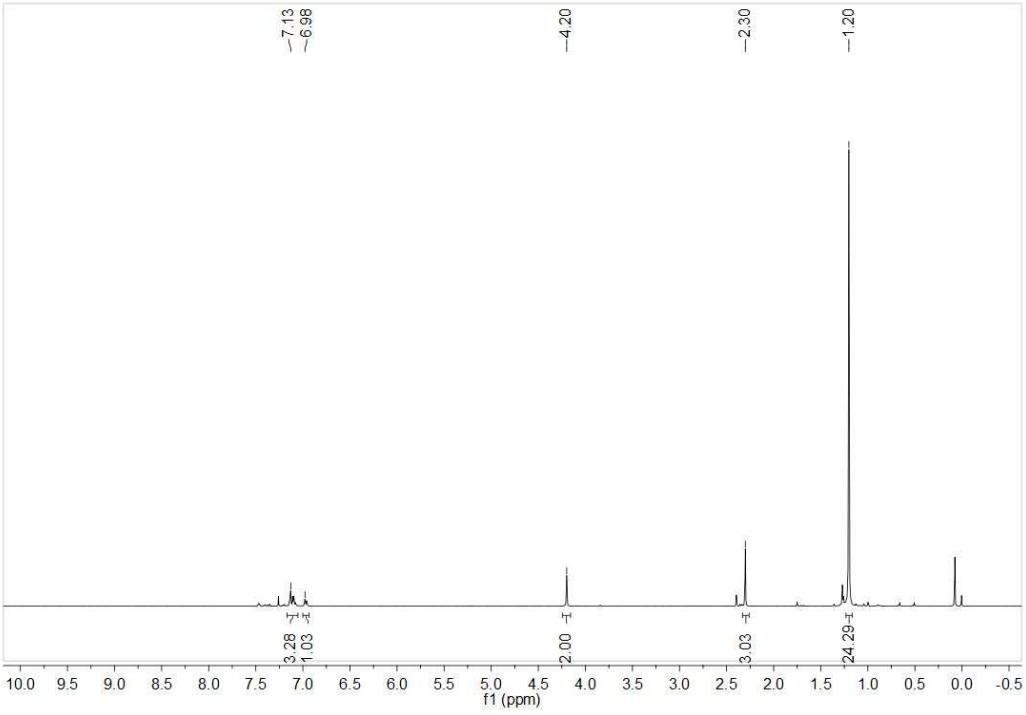


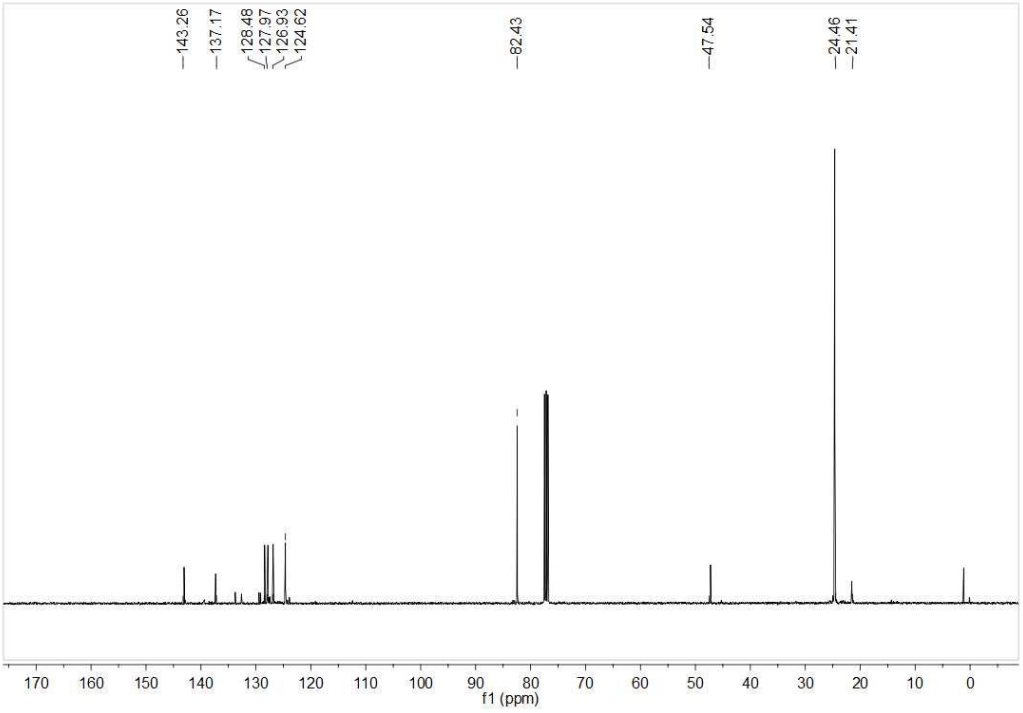


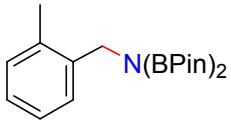
4c (99% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.15-6.96 (m, 4H, *m*-$(CH_3)C_6H_4$), 4.20 (s, 2H, NCH_2), 2.30 (s, 3H, *m*-$(CH_3)C_6H_4$), 1.20 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 143.26 (s, *m*-Tol-*ipso*), 137.17 (s, *m*-Tol-*ipso*), 128.48 (s, *m*-Tol), 127.97 (s, *m*-Tol), 126.93 (s, *m*-Tol), 124.62 (s, *m*-Tol), 82.43 (s, Bpin-*ipso*),

47.54 (s, N-CH_2), 24.46 (s, Bpin-CH_3), 21.41 (s, *m*-(CH_3)C_6H_4). ^{11}B {^1H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.81 (br).

Scheme S7. ^1H (top) and ^{13}C NMR (bottom) of **4c**

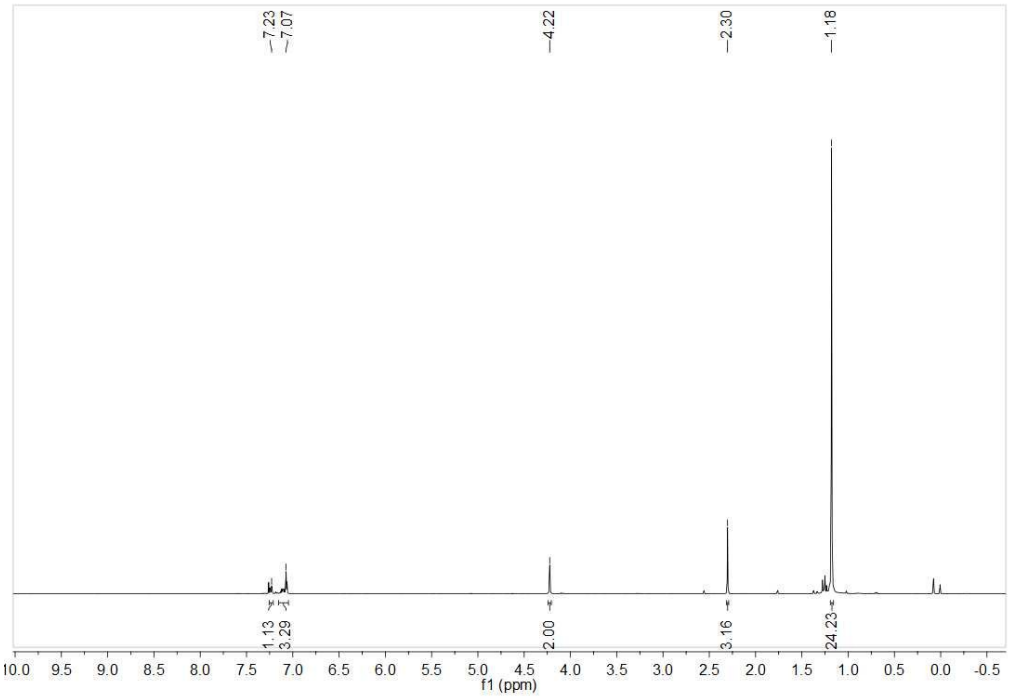


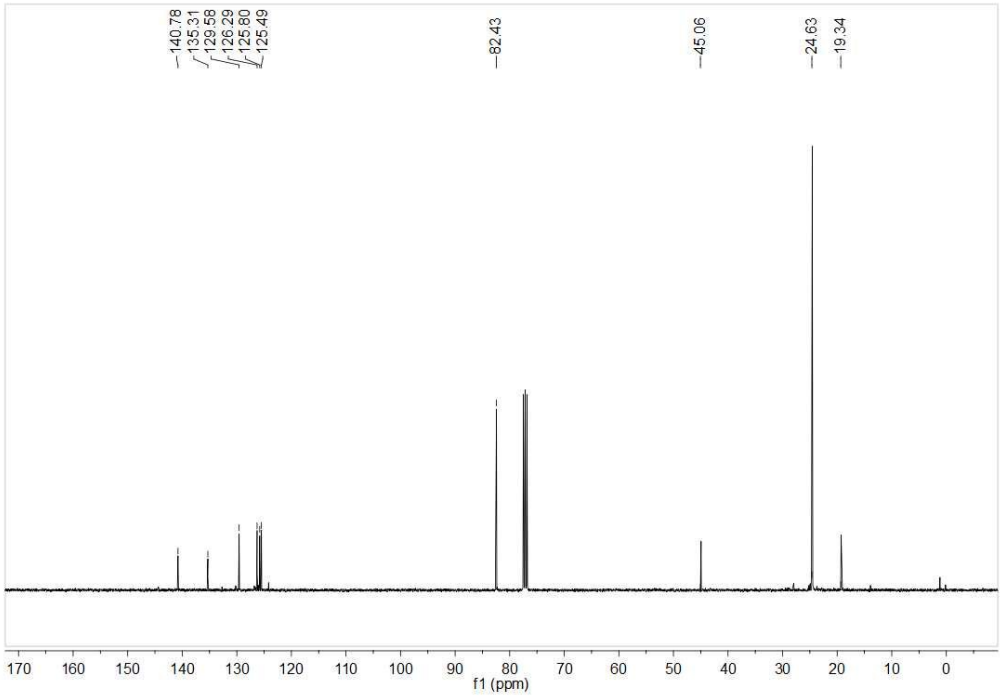


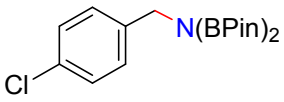


4d (85% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.23-7.07 (m, 4H, *o*-(CH_3)C_6H_4), 4.22 (s, 2H, NCH_2), 2.30 (s, 3H, *o*-(CH_3)C_6H_4), 1.18 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 140.78 (s, *o*-Tol-*ipso*), 135.31 (s, *o*-Tol-*ipso*), 129.58 (s, *o*-Tol), 126.29 (s, *o*-Tol), 125.80 (s, *o*-Tol), 125.49 (s, *o*-Tol), 82.43 (s, Bpin-*ipso*), 45.06 (s, N-CH_2), 24.63 (s, Bpin-CH_3), 19.34 (s, *o*-(CH_3)C_6H_4). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 26.05 (br).

Scheme S8. ^{1}H (top) and ^{13}C NMR (bottom) of **4d**

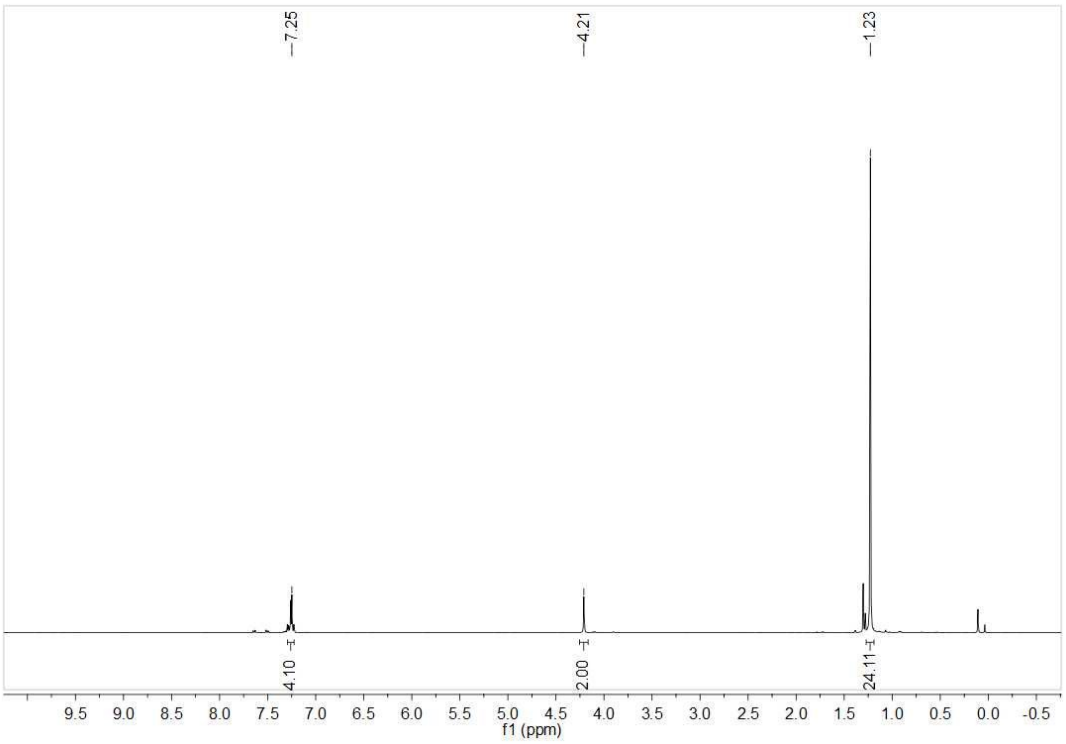


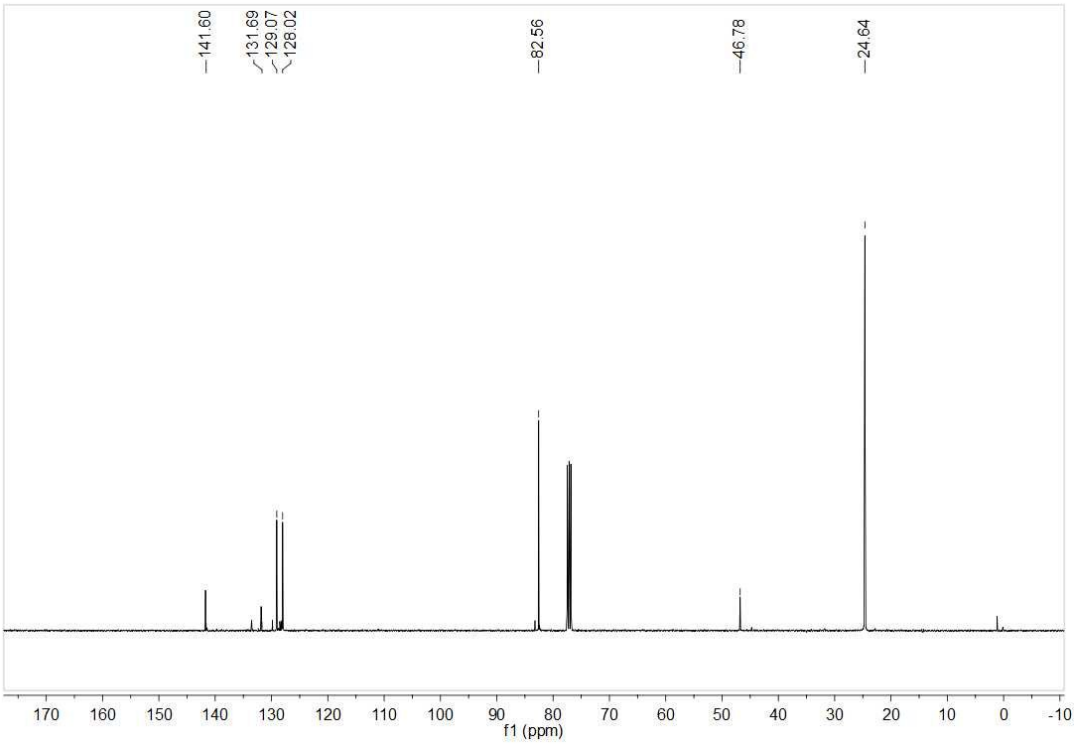


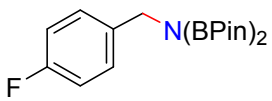


4e (99% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.25 (m, 4H, *p*-Cl-C_6H_4), 4.21 (s, 2H, NCH_2), 1.23 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 141.60 (s, *i*-*C*), 131.69 (s, *p*-*C*), 129.07 (s, *o*-*C*), 128.02 (s, *m*-*C*), 82.56 (s, Bpin-*ipso*), 46.78 (s, N-CH_2), 24.64 (s, Bpin-CH_3). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.76 (br).

Scheme S9. ^{1}H (top) and ^{13}C NMR (bottom) of **4e**



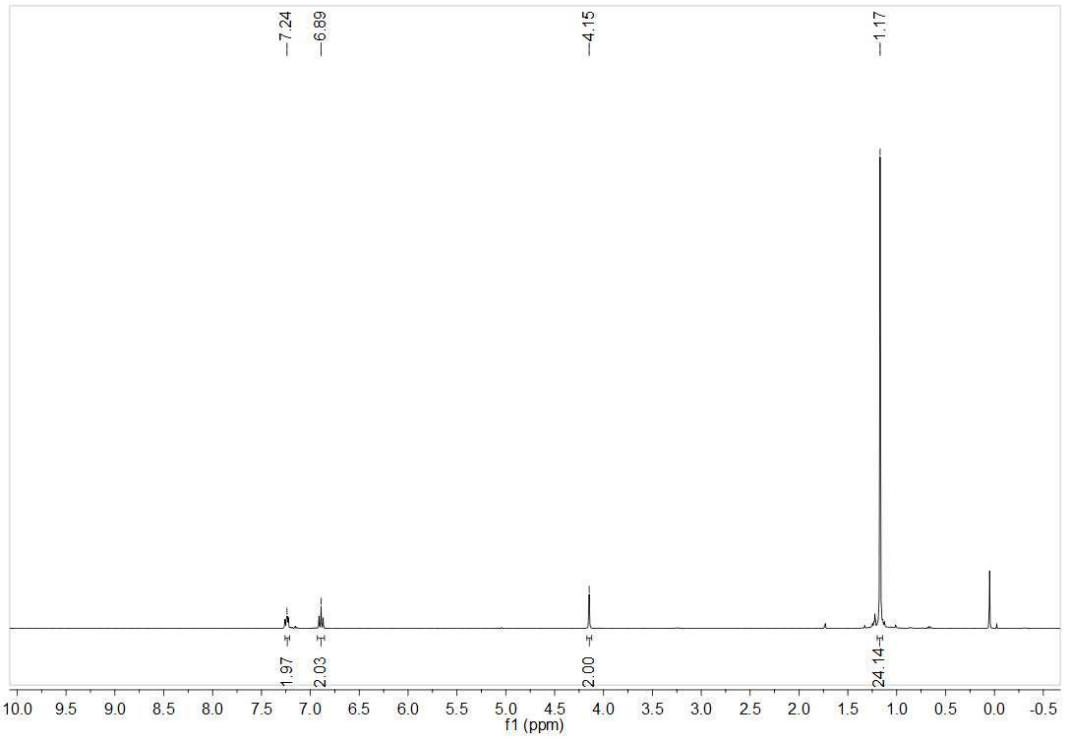


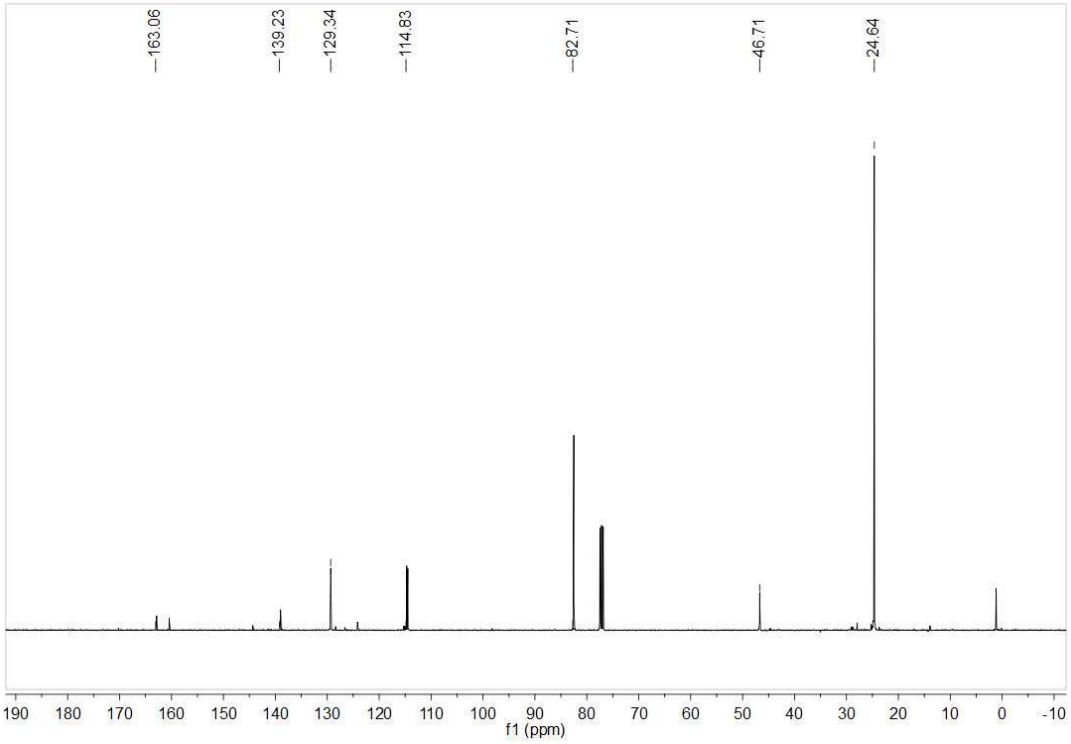


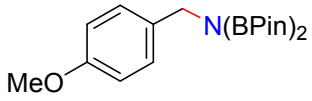
4f (99% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.24 (m, 2H, *o*-C_6H_4), 6.89 (m, 2H, *o*-C_6H_4), 4.15 (s, 2H, NCH_2), 1.17 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 163.06 (s, *i-C*), 139.23 (s, *p-C*), 129.34 (s, *o-C*), 114.83 (s, *m-*

C), 82.71 (s, Bpin-*ipso*), 46.71 (s, N-CH_2), 24.64 (s, Bpin-CH_3). ^{11}B {^1H} NMR (128 MHz, $CDCl_3$, 298K): δ 26.04 (br).

Scheme S10. ^1H (top) and ^{13}C NMR (bottom) of **4f**

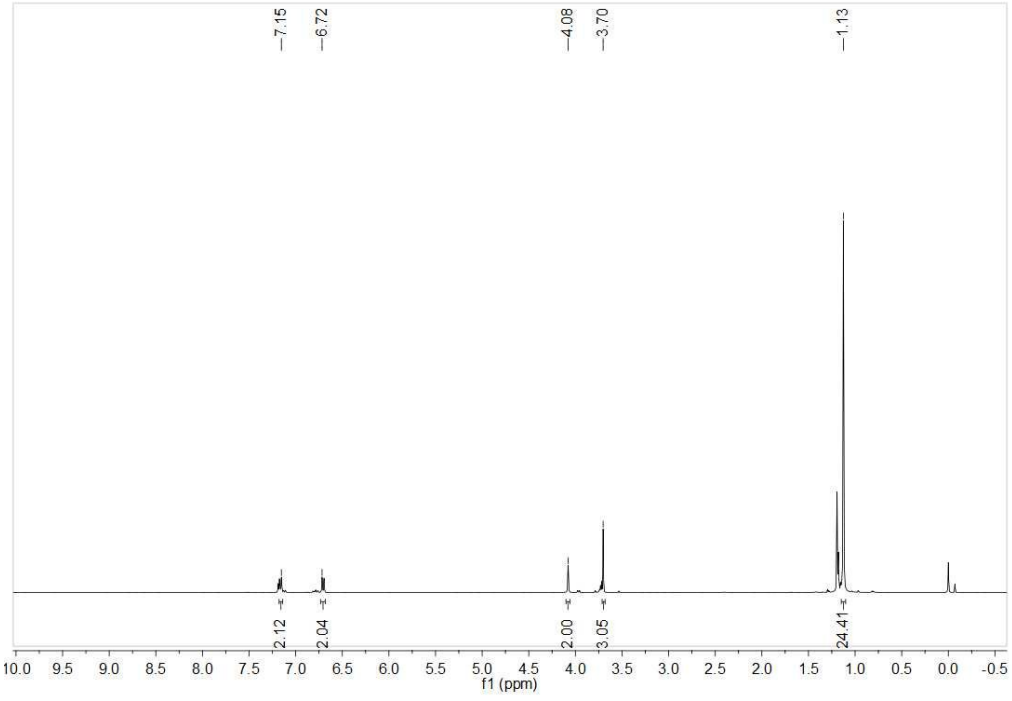


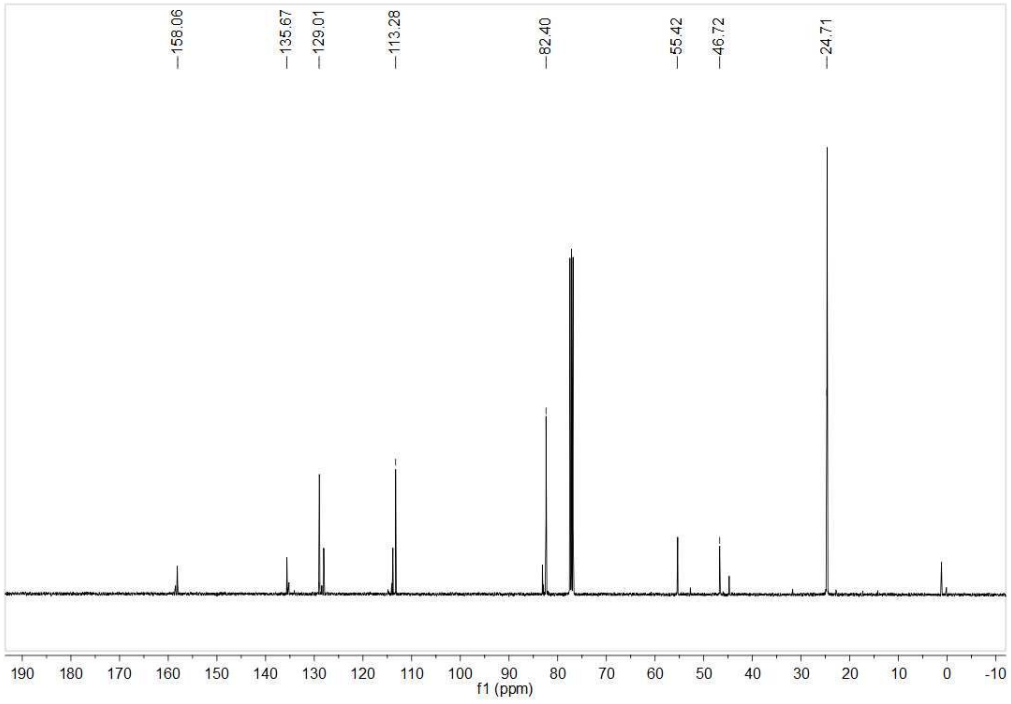


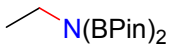


4g (61% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.16 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, *p*-(OCH_3)C_6H_4), 6.71 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, *p*-(OCH_3)C_6H_4), 4.08 (s, 2H, NCH_2), 3.70 (s, 3H, *p*-(OCH_3)C_6H_4), 1.13 (s, 24H, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 158.06 (s, *i*-*C*), 135.67 (s, *p*-*C*), 129.01 (s, *o*-*C*), 113.28 (s, *m*-*C*), 82.40 (s, Bpin-*ipso*), 55.42 (s, *p*-(OCH_3)C_6H_4), 46.72 (s, N-CH_2), 24.71 (s, Bpin-CH_3). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.83 (br).

Scheme S11. ^{1}H (top) and ^{13}C NMR (bottom) of **4g**

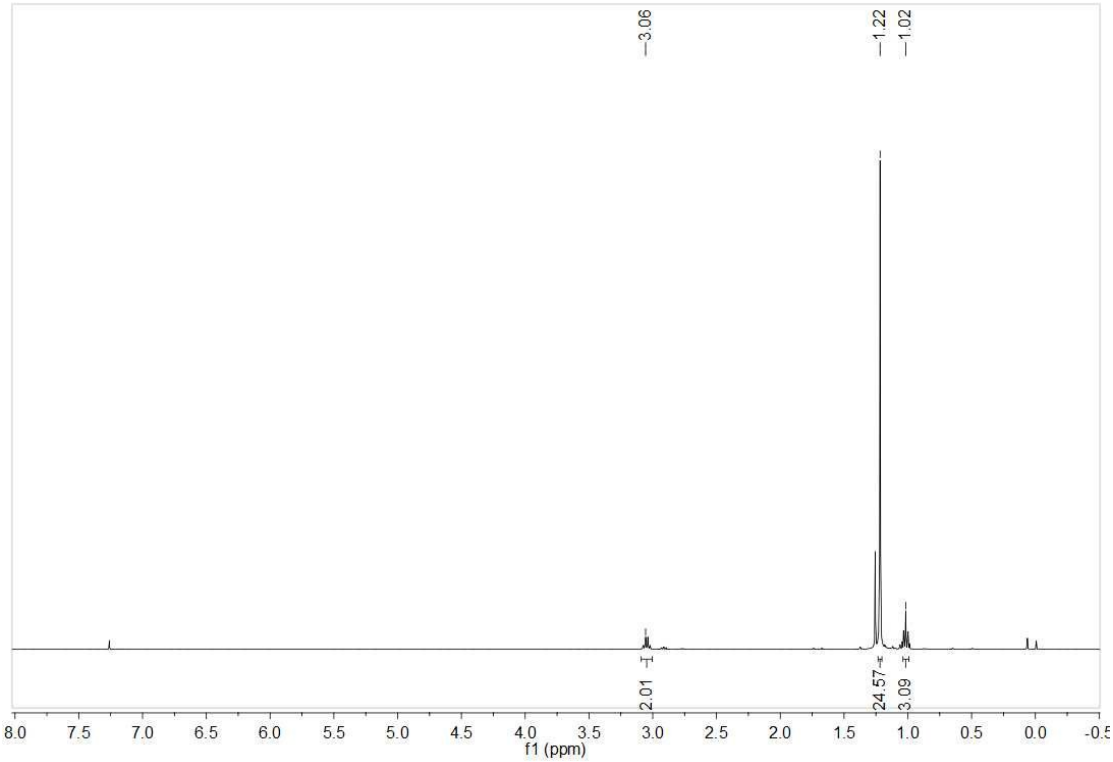


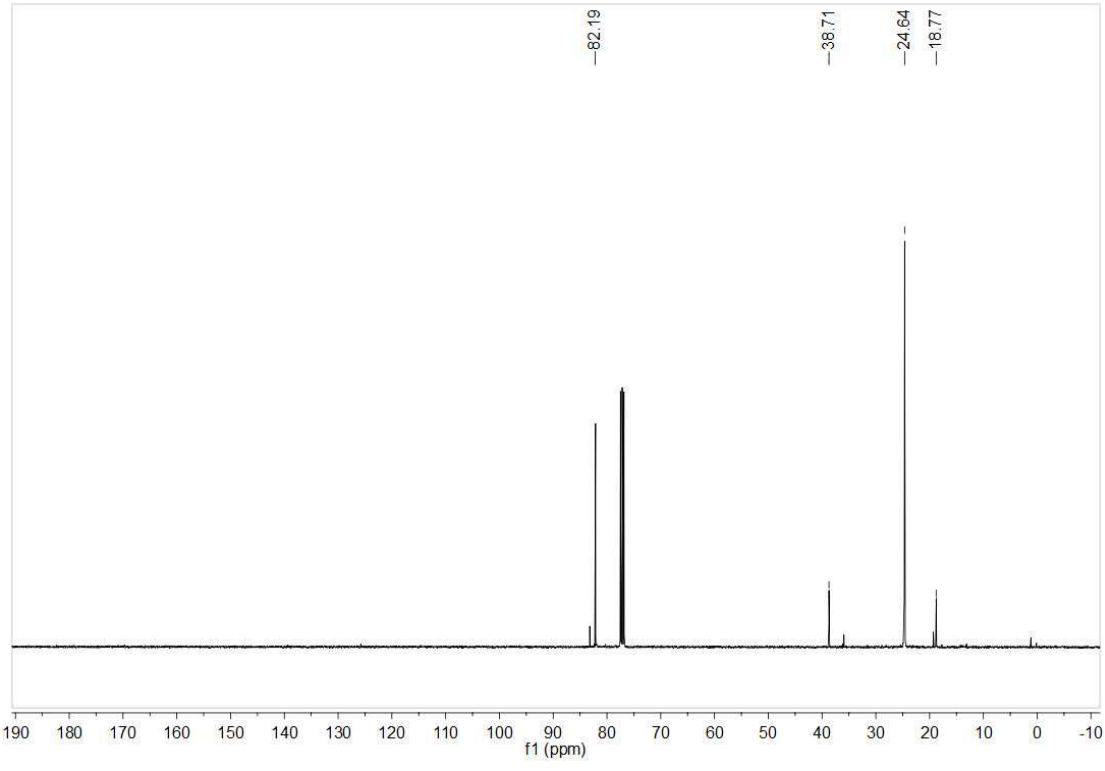


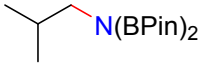


4h (99% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.06 (q, 2H, $J_{H\text{-}H}$ = 8 Hz, NCH_2CH$_3$), 1.22 (s, 24H, Bpin), 1.02 (t, 3H, $J_{H\text{-}H}$ = 7.2 Hz, CH$_2$CH_3). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.19 (s, Bpin-*ipso*), 38.71(s, NCH$_2$CH$_3$), 24.64 (s, Bpin-CH$_3$), 18.77 (s, NCH$_2$CH$_3$). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.87 (br).

Scheme S12. ^{1}H (top) and ^{13}C NMR (bottom) of **4h**



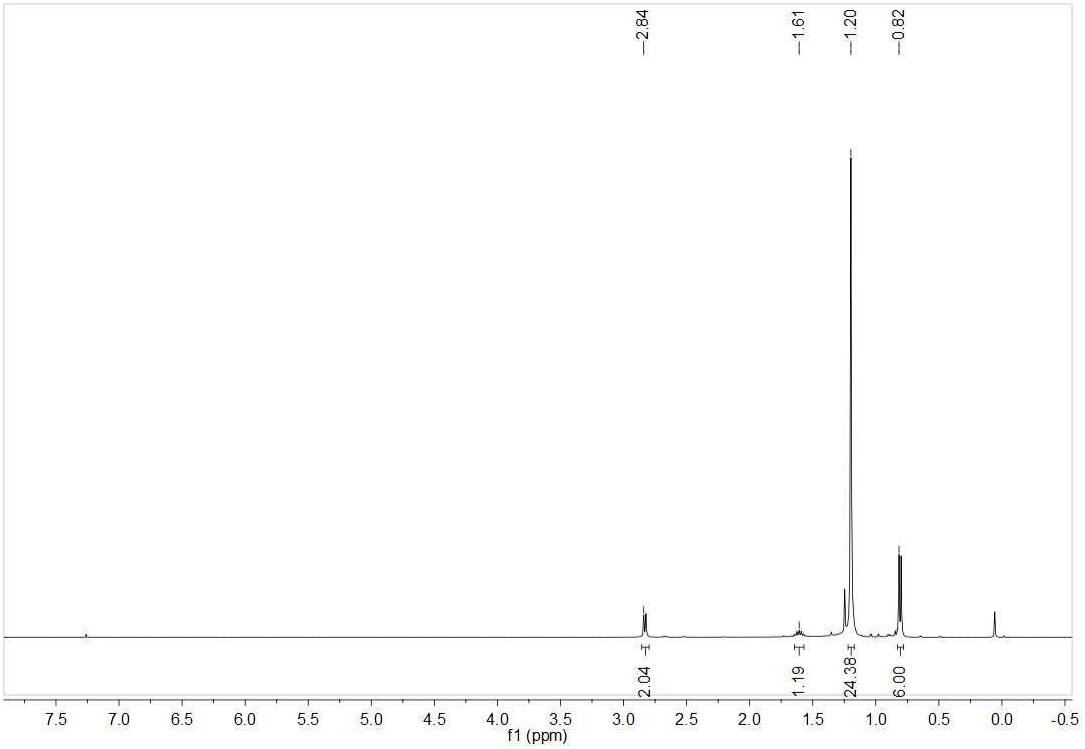


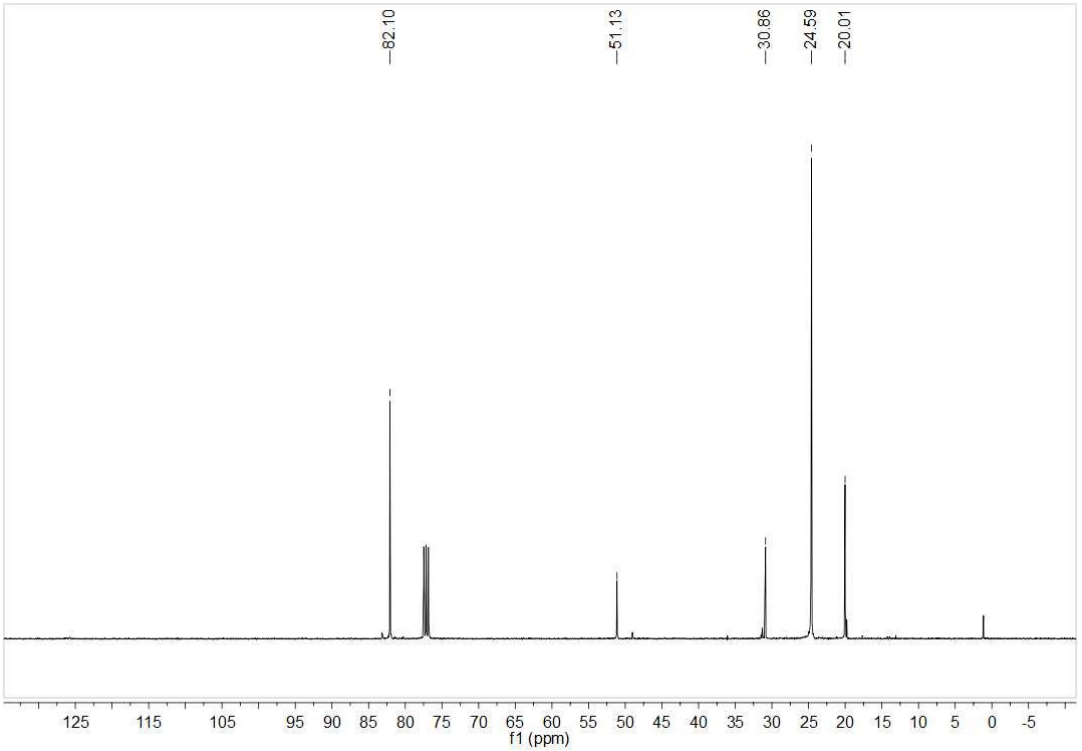


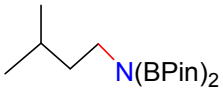
4i (88% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.84-2.82 (d, 2H, $J_{H\text{-}H}$ = 8 Hz, $NCH_2CH(CH_3)_2$), 1.61-1.59 (m, 1H, $J_{H\text{-}H}$ = 8 Hz, $CH(CH_3)_2$), 1.20 (24H, s, Bpin), 0.82-0.80 (d, 6H, $J_{H\text{-}H}$ = 8 Hz, $NCH_2CH(CH_3)_2$). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298

K): δ 82.10 (s, Bpin-*ipso*), 51.13 (s, N*C*H_2CH(CH_3)$_2$), 30.86 (s, NCH$_2$*C*H(CH_3)$_2$), 24.59 (s, Bpin-*C*H_3), 20.01 (s, NCH$_2$CH(*C*H_3)$_2$). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.83(br).

Scheme S13. ^{1}H (top) and ^{13}C NMR (bottom) of **4i**

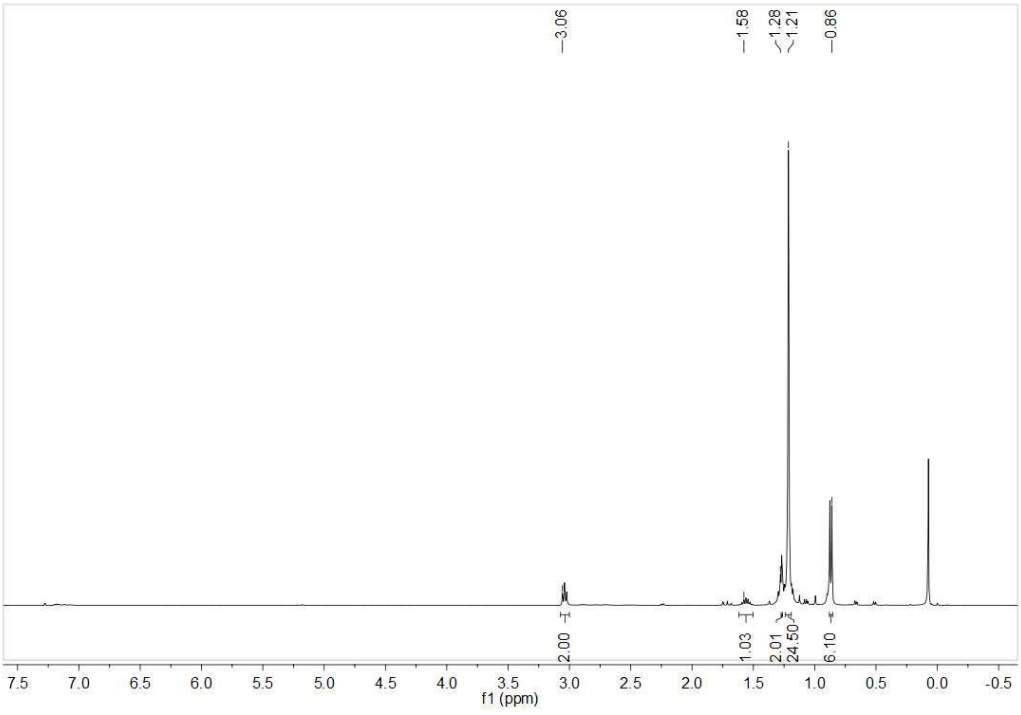


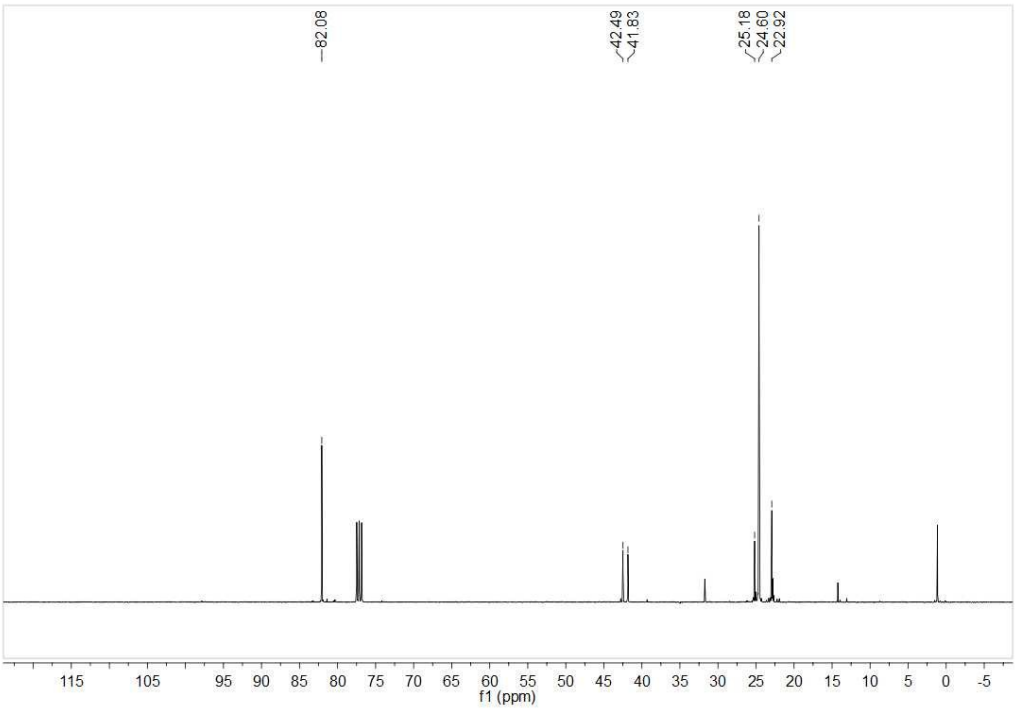


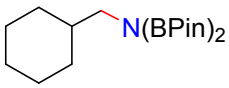


4j (76% yield, colorless liquid) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.02 (d, 2H, $J_{H\text{-}H}$ = 8 Hz, $NCH_2CH_2CH(CH_3)_2$), 1.56-1.54 (m, 1H, $J_{H\text{-}H}$ = 8 Hz, $NCH_2CH_2CH(CH_3)_2$), 1.28-1.27 (m, 2H, $J_{H\text{-}H}$ = 4 Hz, $NCH_2CH_2CH(CH_3)_2$), 1.21 (24H, s, Bpin), 0.88-0.86 (d, 6H, $J_{H\text{-}H}$ = 8 Hz, $NCH_2CH_2CH(CH_3)_2$). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.08 (s, Bpin-*ipso*), 42.49 (s, $NCH_2CH_2CH(CH_3)_2$), 41.83 (s, $NCH_2CH_2CH(CH_3)_2$), 25.18 (s, $NCH_2CH_2CH(CH_3)_2$), 24.60 (s, Bpin-CH_3), 22.92 (s, $NCH_2CH_2CH(CH_3)_2$). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.83(br).

Scheme S14. ^{1}H (top) and ^{13}C NMR (bottom) of **4j**

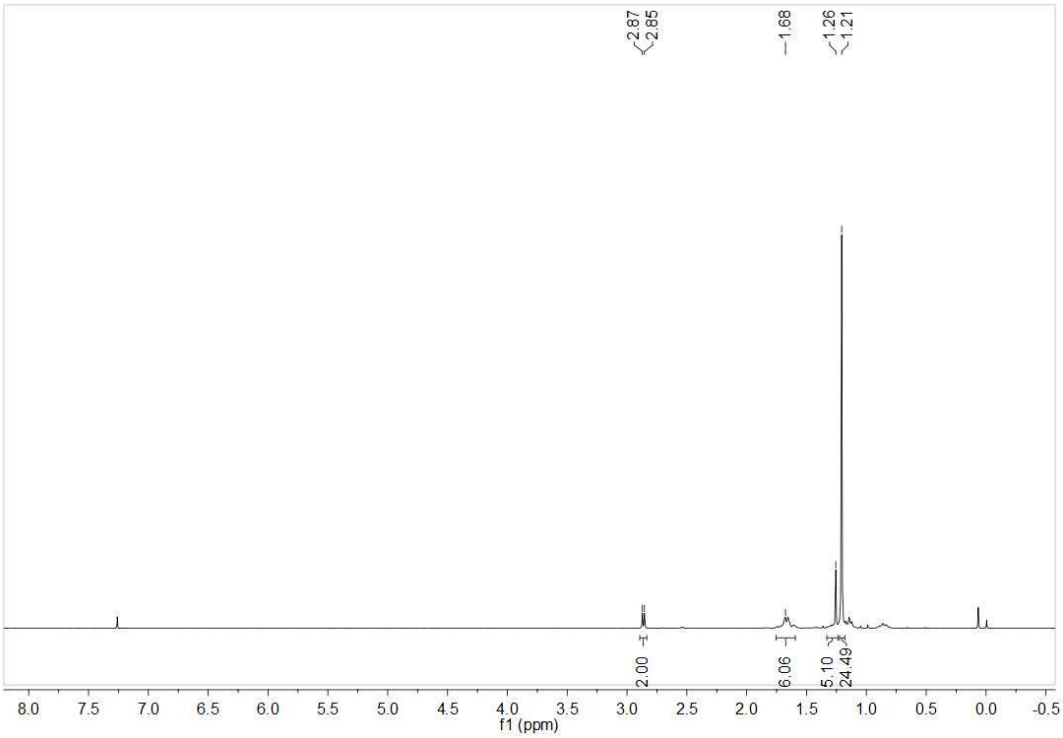


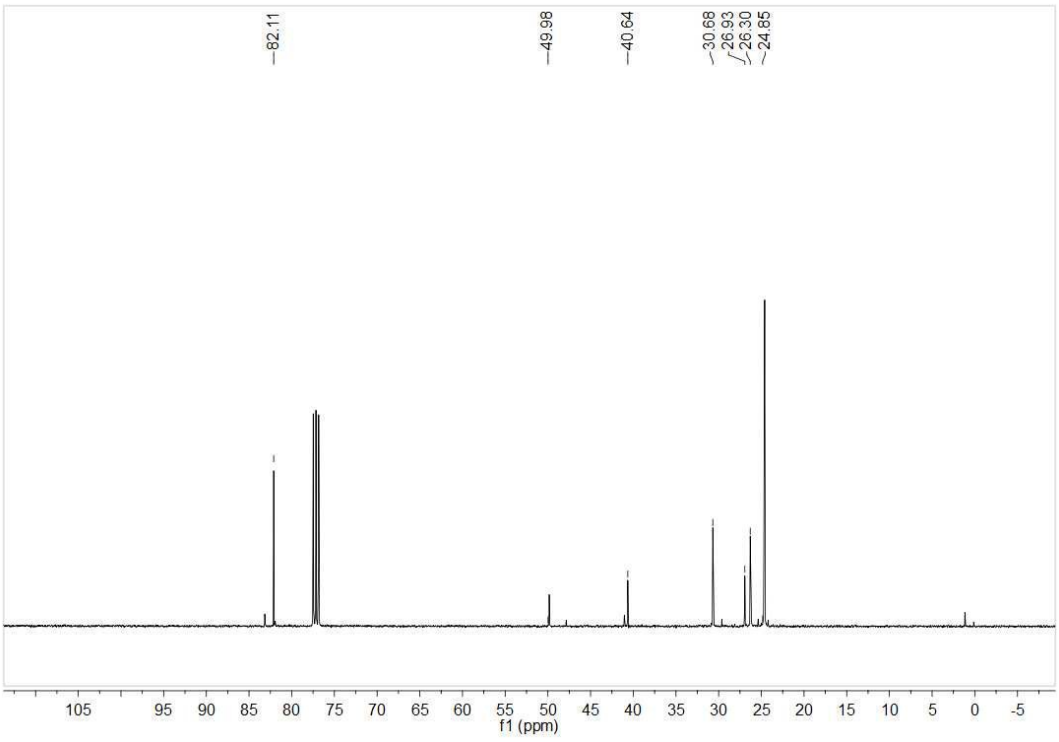




4k (90% yield, colorless crystal) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.86 (d, 2H, $J_{H\text{-}H}$ = 8 Hz, NCH_2), 1.68 (m, 6H, Cy-*H*), 1.26 (m, 5H, Cy-*H*), 1.21 (24H, s, Bpin). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.11 (s, Bpin-*ipso*), 49.98 (s, N-*C*H_2), 40.64 (s, Cy-C), 30.68 (s, Cy-C), 26.93 (s, Cy-C), 26.30 (s, Cy-C), 24.85 (s, Bpin-*C*H_3). ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.62 (br).

Scheme S15. ^{1}H (top) and ^{13}C NMR (bottom) of **4k**



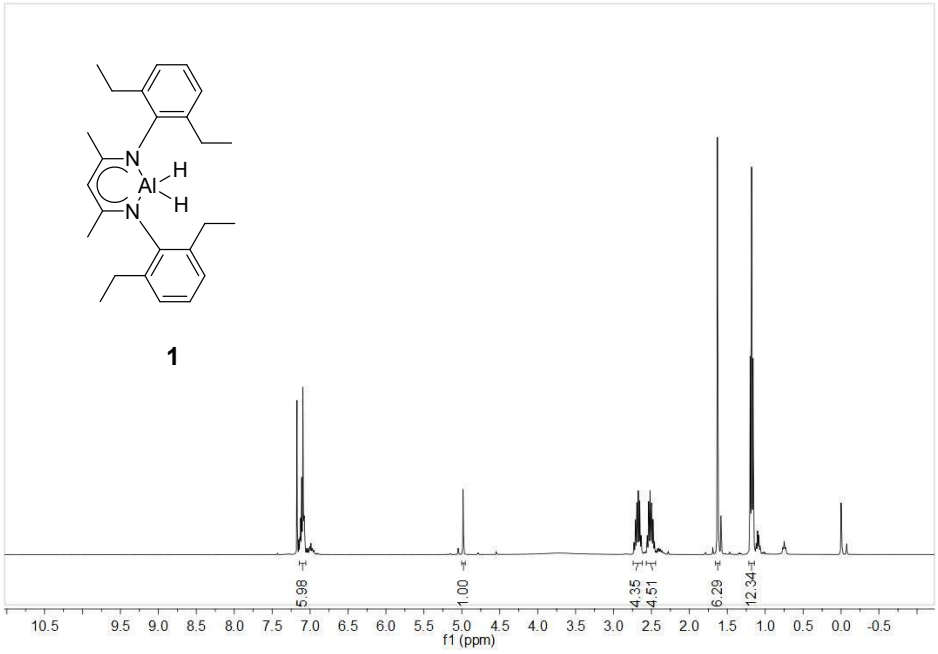


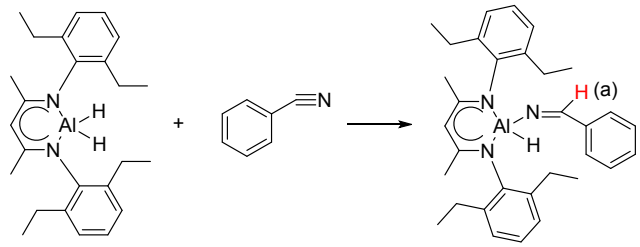
Mechanism Experiment

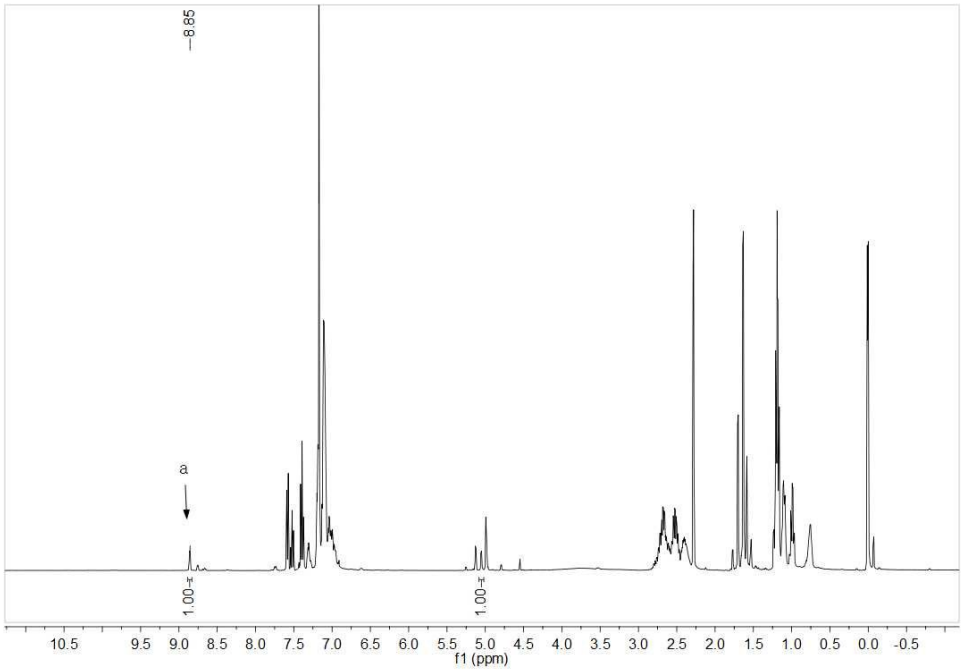
The stoichiometric reaction of **1** with PhCN (1:1) was performed at 80°C for 24 h under nitrogen atmosphere, solvent toluene was removed in vacuo resulting in a solid containing a mixture of

products.

Scheme S16. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K). Top spectrum, starting material of **1**, bottom spectrum of the crude product from the reaction of **1** with PhCN.







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