Supporting Information for

Hydroborative reduction of amides to amines mediated by $La(CH_2C_6H_4NMe_2\text{-}o)_3$

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1. Table S1. Optimization of the reaction conditions for the reduction of N,N-dimethylbenzamide[a].

Entry	Catalyst	[cat.]/[Amide] (mol%)	T/°C	t/h	Yield/%[b]
1	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	25	4	95
2	$Y(CH_2C_6H_4NMe_2\text{-}o)_3$	5	25	4	54
3	$Sc(CH_2C_6H_4NMe_2\text{-}o)_3$	5	25	4	45
4	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	3	25	4	56
5	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	1	25	4	23

[a]Reaction conditions: Amide (0.25 mmol), and HBpin (1.25 mmol, 5 equiv) in C_6D_6 (1 mL total volume). [b]yields of amine products calculated by integration vs a 1,3,5-trimethylbenzene internal standard.

1. Table S2. Optimization of the reaction conditions for the reduction of 4-Fluorobenzamide[a].

Entry	Catalyst	[cat.]/[Amide] (mol%)	T(°C)	T(h)	Yield(%)[b]
1	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	1	120	24	51
2	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	3	120	24	75
3	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	120	24	98
4	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	25	24	-
5	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	60	24	23
6	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	80	24	52
7	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	100	24	87
8	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	100	24	85[c]
9	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	100	24	71[d]
10	$La(CH_2C_6H_4NMe_2\text{-}o)_3$	5	100	24	35[e]
11	$Y(CH_2C_6H_4NMe_2\text{-}o)_3$	5	120	24	79
12	$Sc(CH_2C_6H_4NMe_2\text{-}o)_3$	5	120	24	71
13	No catalyst	-	120	36	52

[a]Reaction conditions: Amide (0.25 mmol), and HBpin (1.25 mmol, 5 equiv) in C_6D_6 (1 mL total volume). [b]yields of amine products calculated by integration vs a 1,3,5-trimethylbenzene internal standard. [c]8 equiv HBpin. [d]4 equiv HBpin. [e]2 equiv HBpin.

2. ^{1}H NMR monitoring of the reaction between La($CH_2C_6H_4NMe_2$-*o*)$_3$ and HBpin.

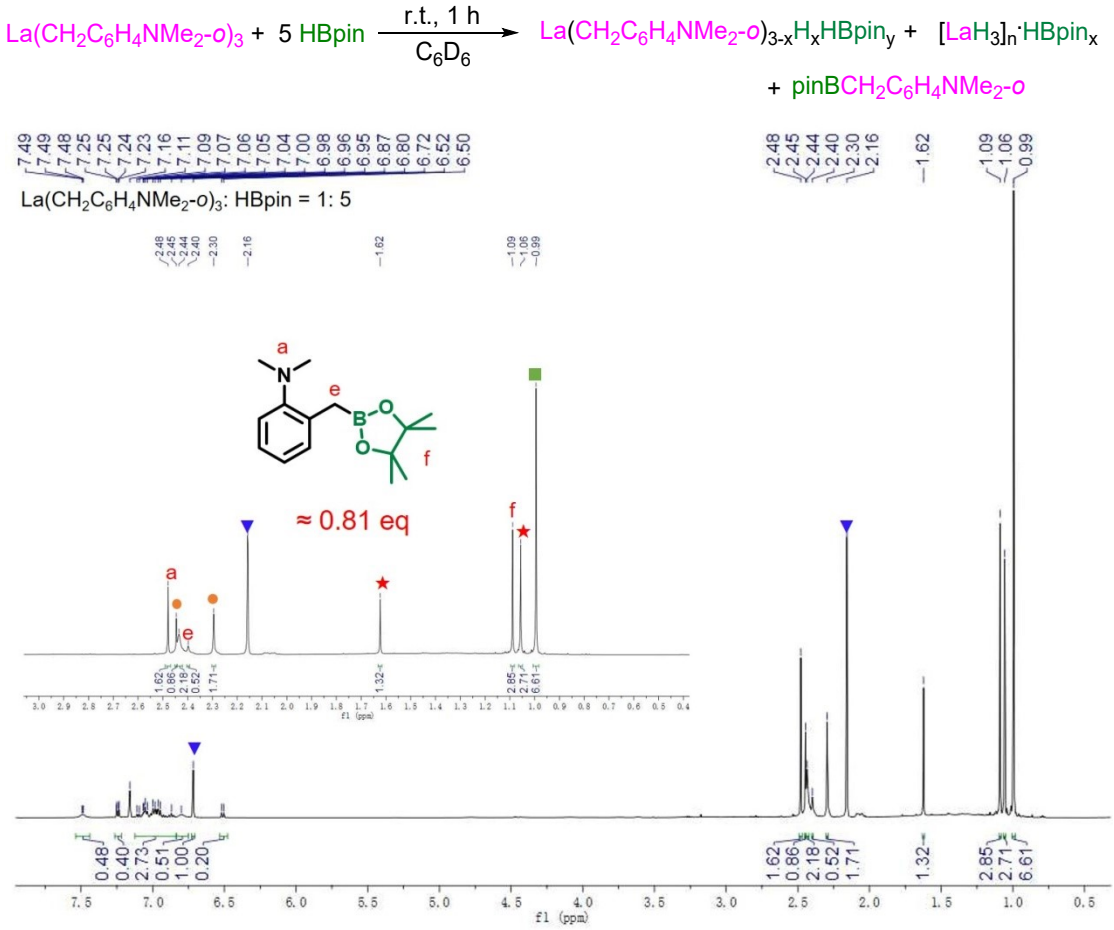


Fig. S1. ^{1}H NMR spectrum of the reaction of La($CH_2C_6H_4NMe_2$-*o*)$_3$ with 5 equiv HBpin for 1 h, ● = La($CH_2C_6H_4NMe_2$-*o*)$_{3-x}H_xHBpin_y$, ★ = $B_2(OC(CH_3)_2C(CH_3)_2O)_3$, ■ = excess HBpin, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C).

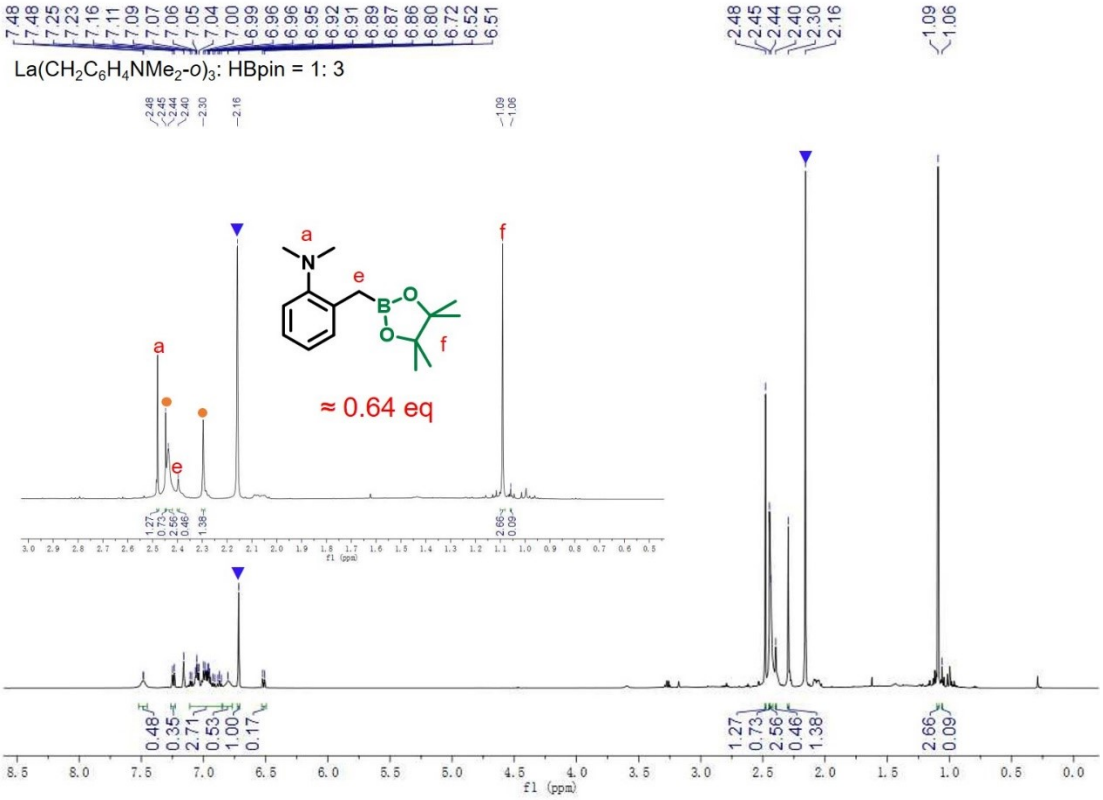


Fig. S2. ^{1}H NMR spectrum of the reaction of La($CH_2C_6H_4NMe_2$-*o*)$_3$ with 3 equiv HBpin for 1 h, ● = La($CH_2C_6H_4NMe_2$-*o*)$_{3-x}H_xHBpin_y$, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C).

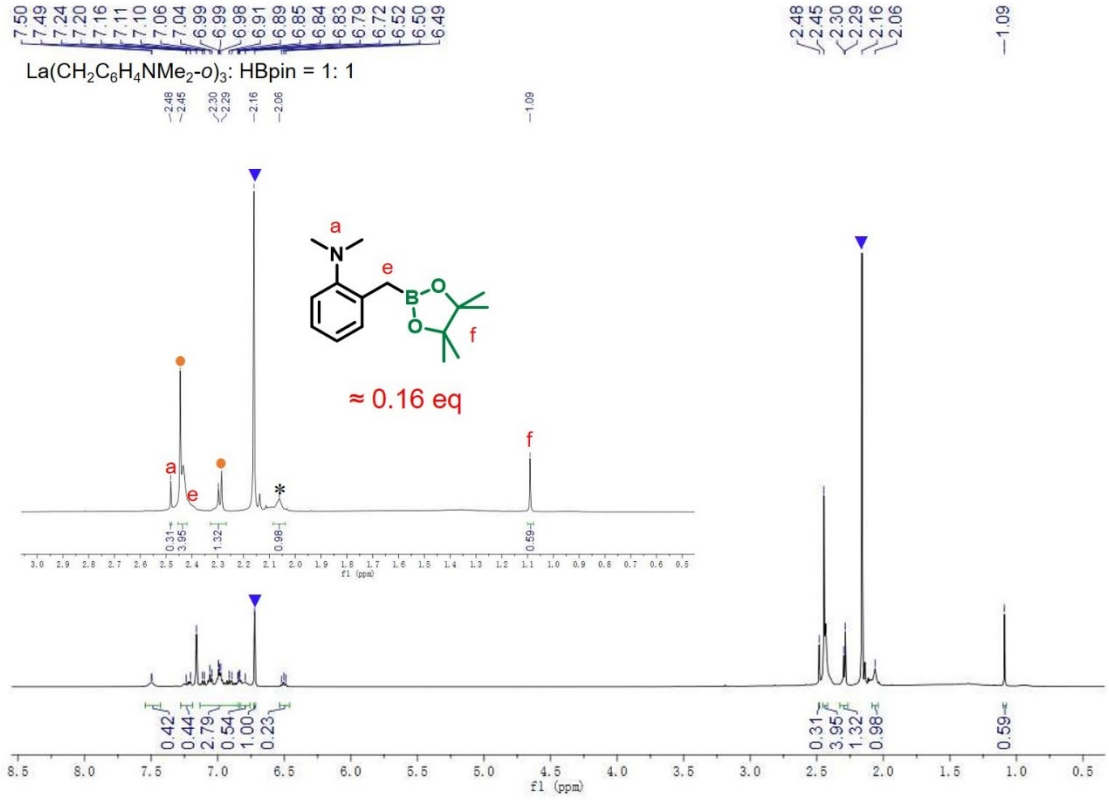


Fig. S3. ^{1}H NMR spectrum of the reaction of La($CH_2C_6H_4NMe_2$-*o*)$_3$ with 1 equiv HBpin for 1 h, ● = La($CH_2C_6H_4NMe_2$-*o*)$_{3-x}H_xHBpin_y$, * = La($CH_2C_6H_4NMe_2$-*o*)$_3$, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C).

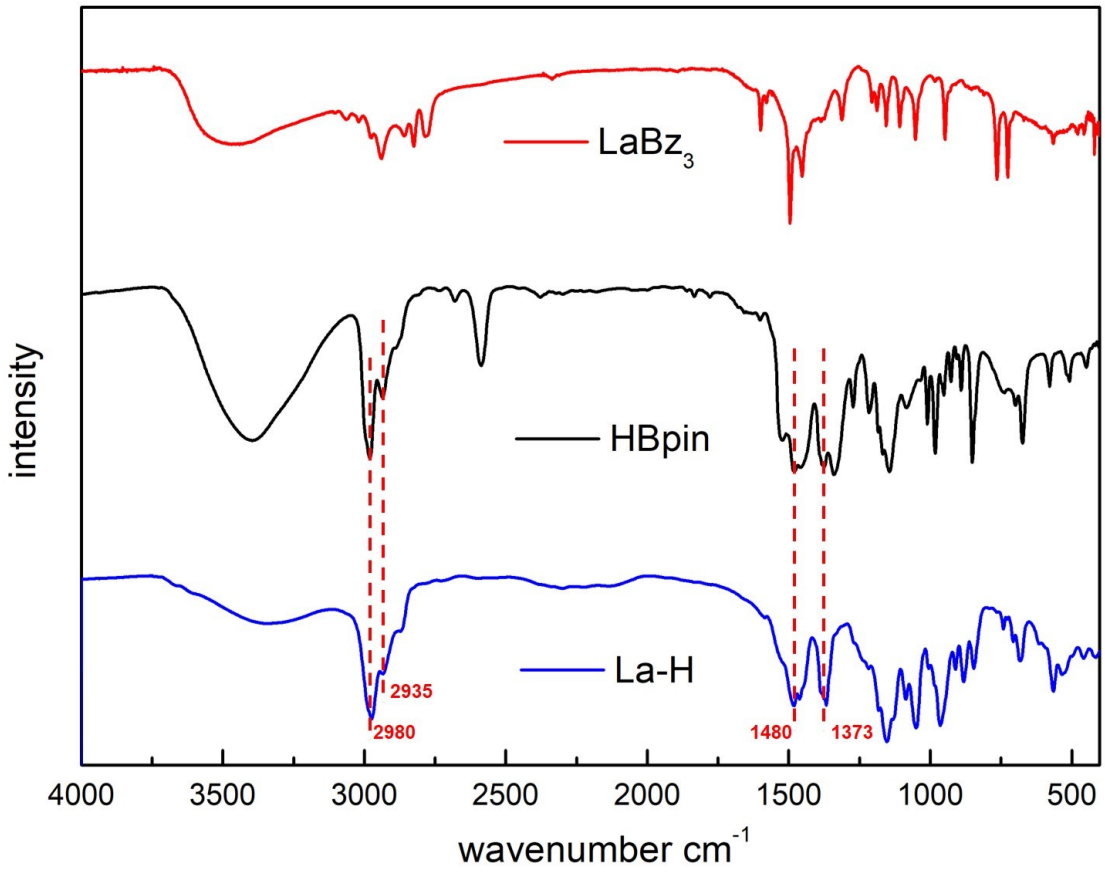


Fig. S4. The FT-IR spectra (KBr) of the insoluble materials ($La(CH_2C_6H_4NMe_2\text{-}o)_{3-x}H_xHBpin_y$ or $[LaH_3]_n{\cdot}HBpin_x$) from the reaction of $La(CH_2C_6H_4NMe_2\text{-}o)_3$ with HBpin (5 eq).

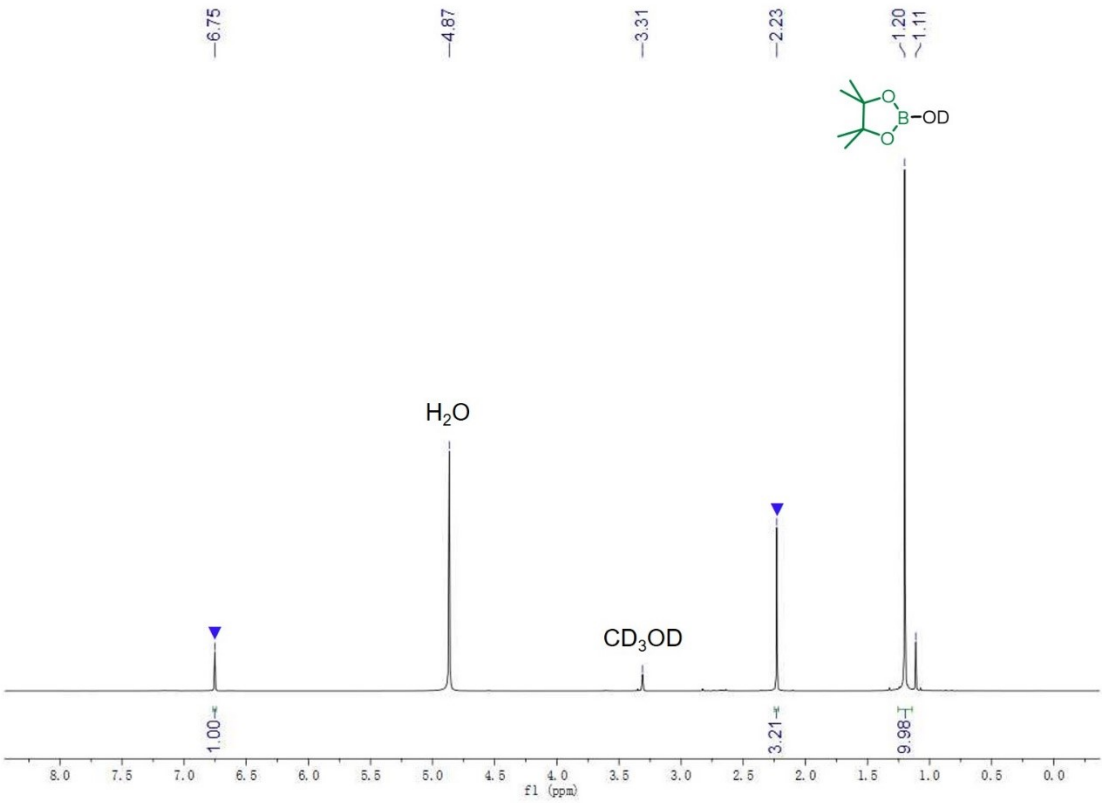


Fig. S5. ^{1}H NMR spectrum of the hydrolysis product of the insoluble material with CD_3OD. ▼ = 1,3,5-trimethylbenzene (500 MHz, CD_3OD, 25 °C).

3. ^{1}H NMR monitoring of the reaction between La($CH_2C_6H_4NMe_2$-*o*)$_3$ and secondary amide.

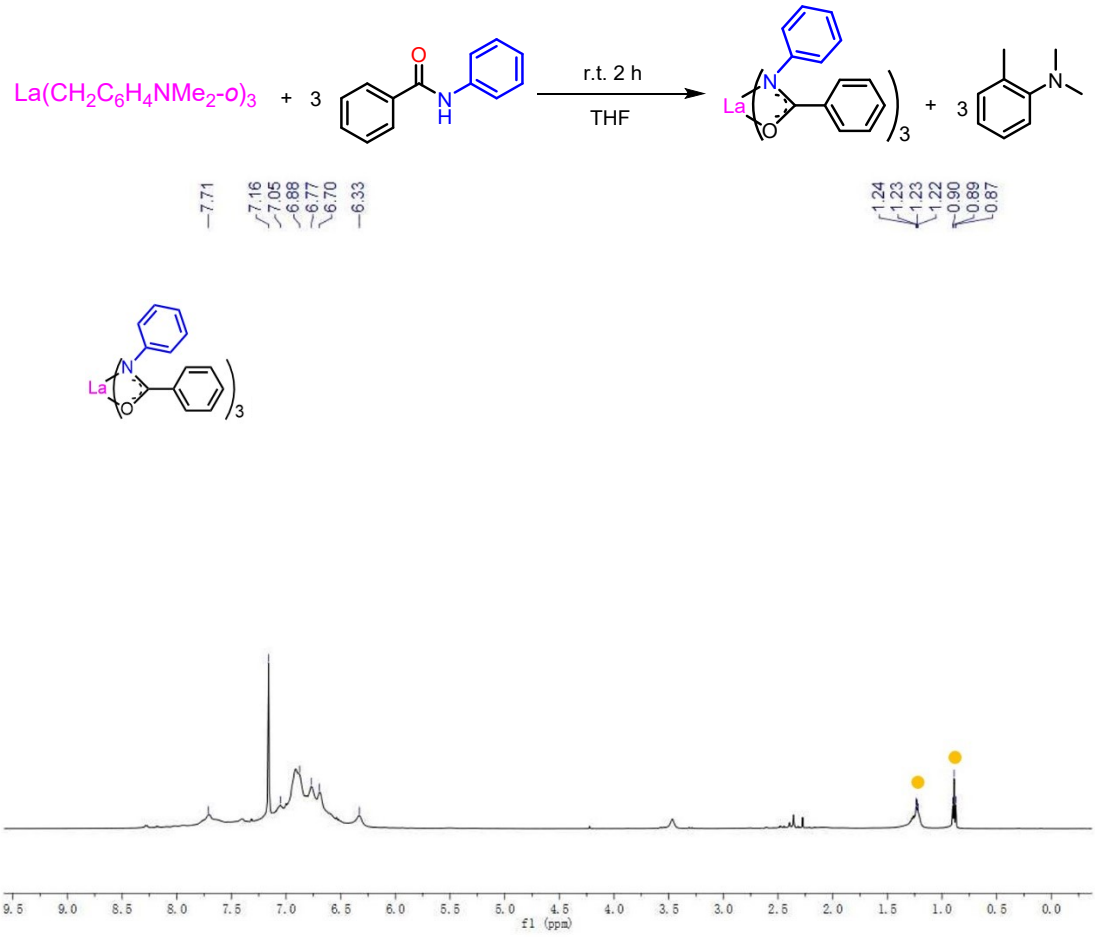


Fig. S6. ^{1}H NMR spectrum of lanthanum tris-amidate complex. ● = residual n-hexane (500 MHz, C_6D_6, 25 °C).

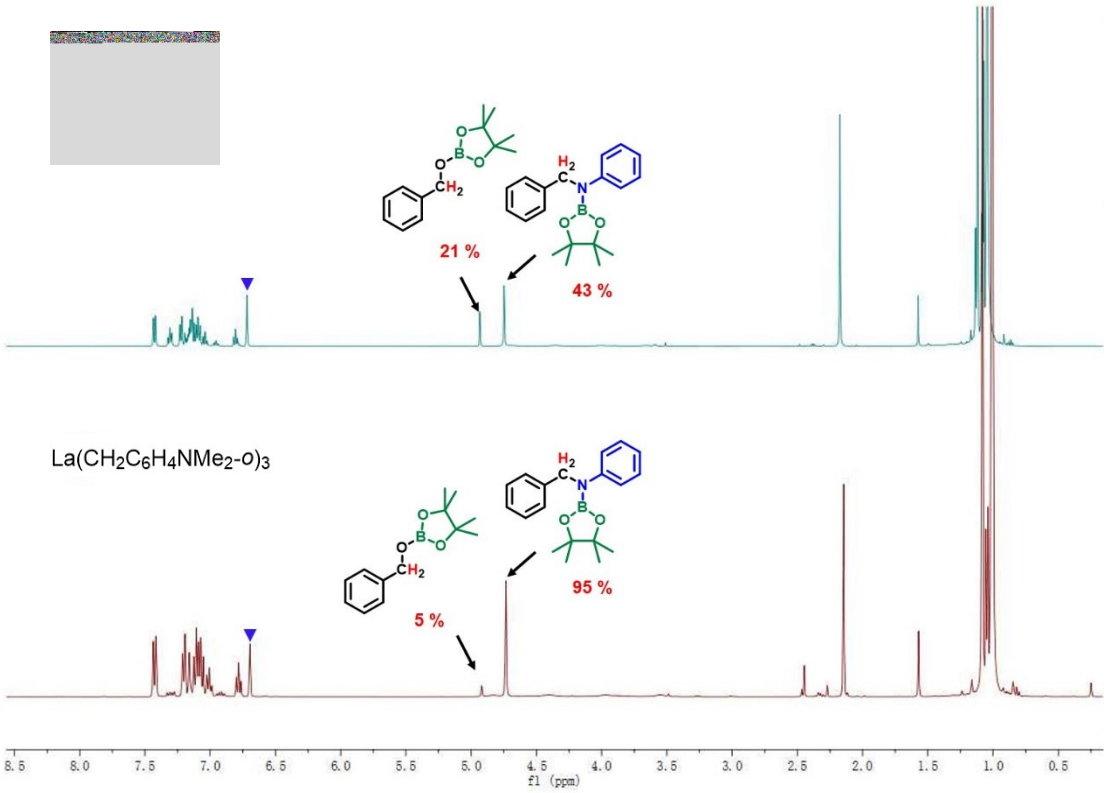


Fig. S7. ^{1}H NMR spectrum of the reduction products of N-phenylbenzamide with HBpin using lanthanum tris-amidate complex or La($CH_2C_6H_4NMe_2$-*o*)$_3$. ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C).

4. ^{1}H NMR monitoring of the reaction between La($CH_2C_6H_4NMe_2$-*o*)$_3$ and primary amide.

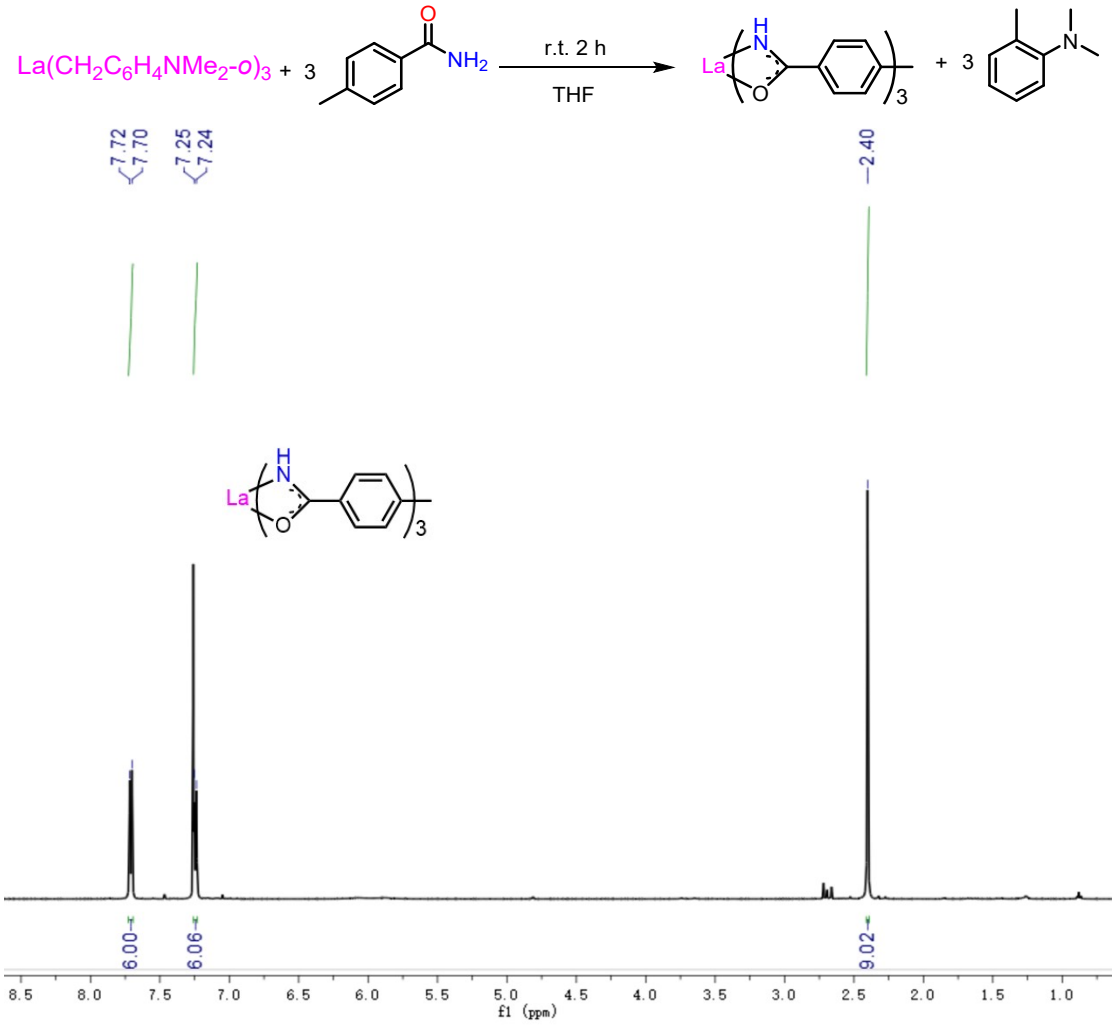


Fig. S8. ^{1}H NMR spectrum of lanthanum tris-amidate complex (500 MHz, $CDCl_3$, 25 ^{o}C).

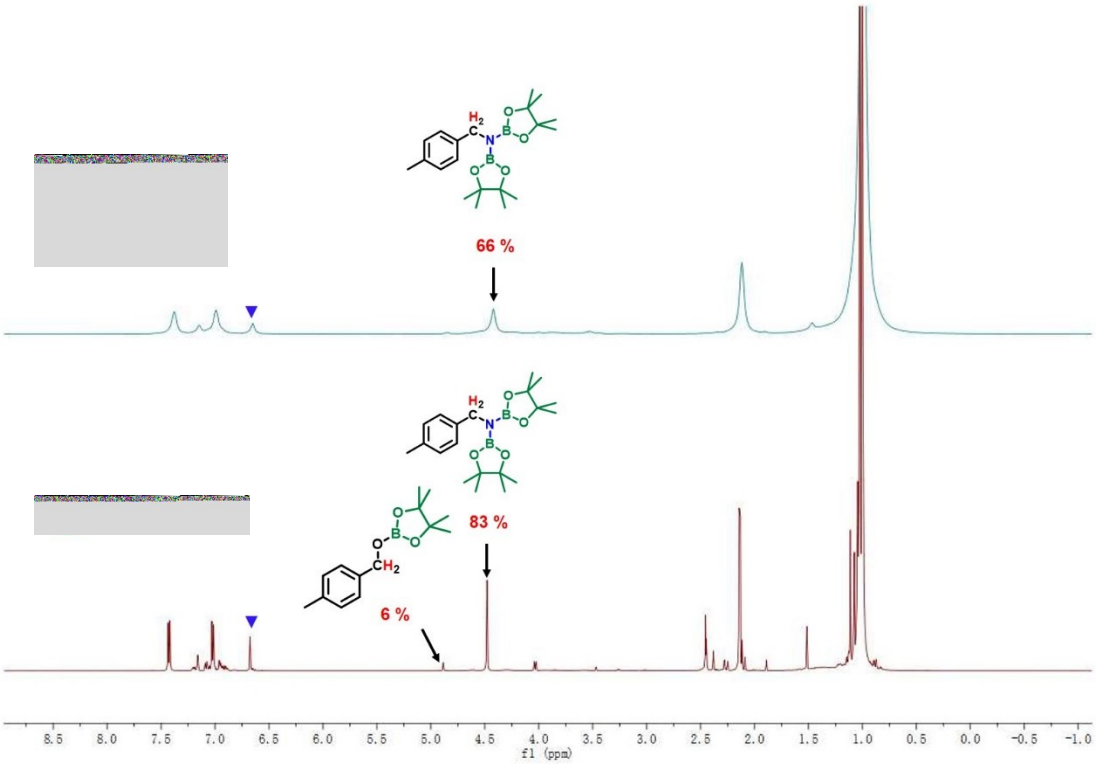


Fig. S9. ^{1}H NMR spectrum of the reduction products of 4-methylbenzamide with HBpin using lanthanum tris-amidate complex or La($CH_2C_6H_4NMe_2$-*o*)$_3$. ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C).

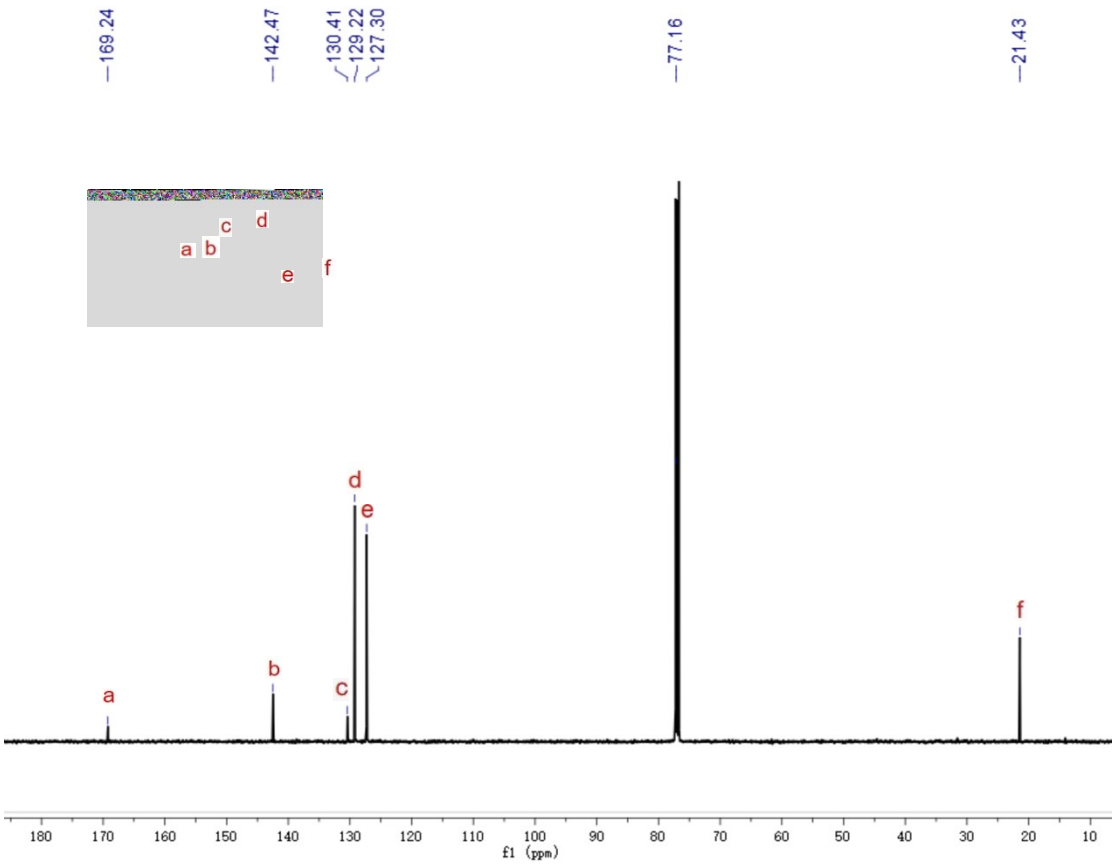


Fig. S10.^{13}C NMR spectrum of lanthanum tris-amidate complex (126 MHz, $CDCl_3$, ppm): δ 169.24 (-O*C*N), 142.47 (-C_6H_4), 130.41 (-C_6H_4), 129.22 (-C_6H_4), 127.30 (-C_6H_4), 21.43 (-CH_3).

5. Control experiments of N-Phenylbenzamide with pinacolborane catalyzed by $La(CH_2C_6H_4NMe_2\text{-}o)_3$

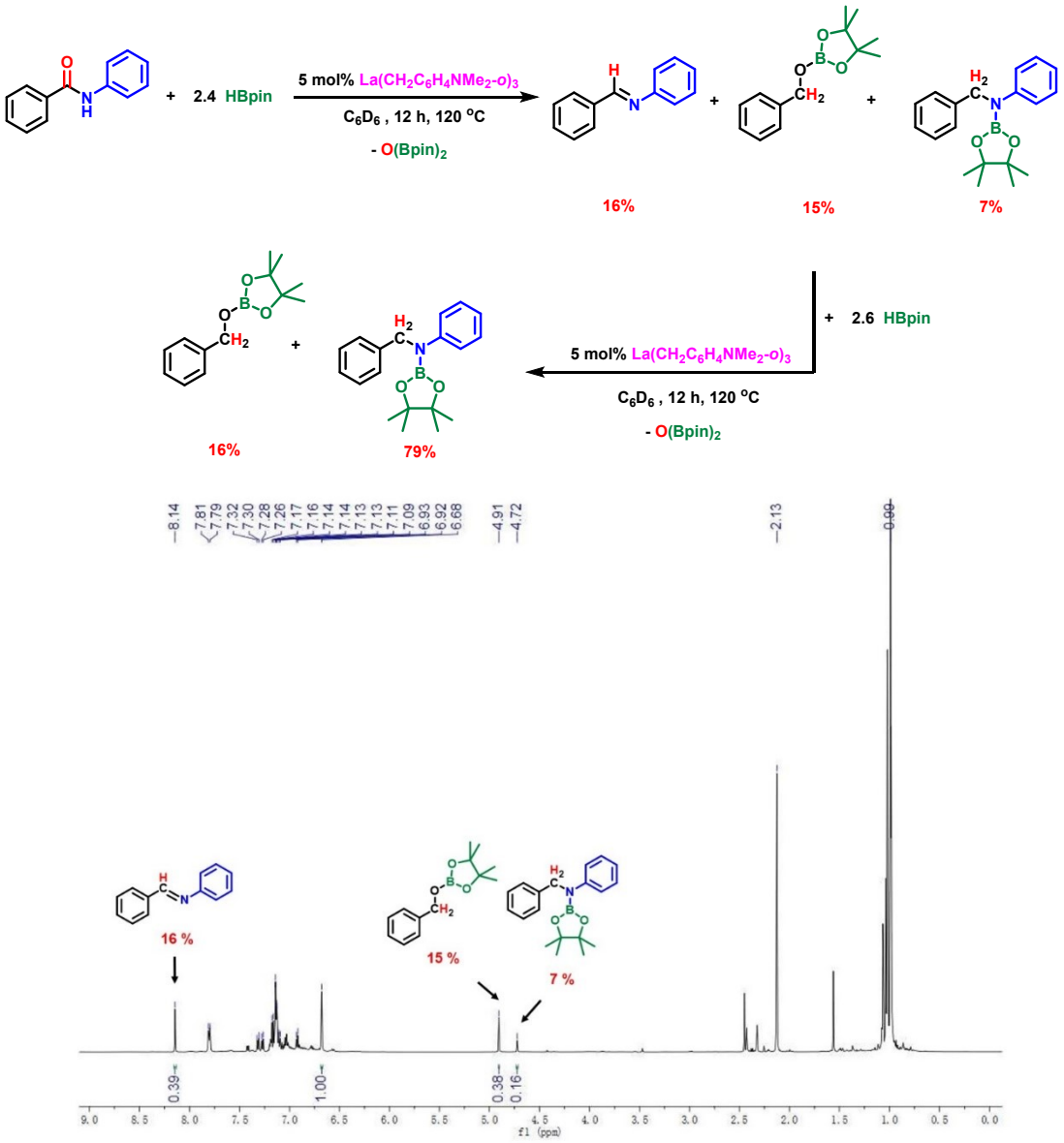


Fig. S11. ^{1}H NMR spectrum of the products generated in situ from the reaction of N-phenylbenzamide with 2.4 equiv pinacolborane catalyzed by $La(CH_2C_6H_4NMe_2\text{-}o)_3$ (500 MHz, C_6D_6, 25 °C).

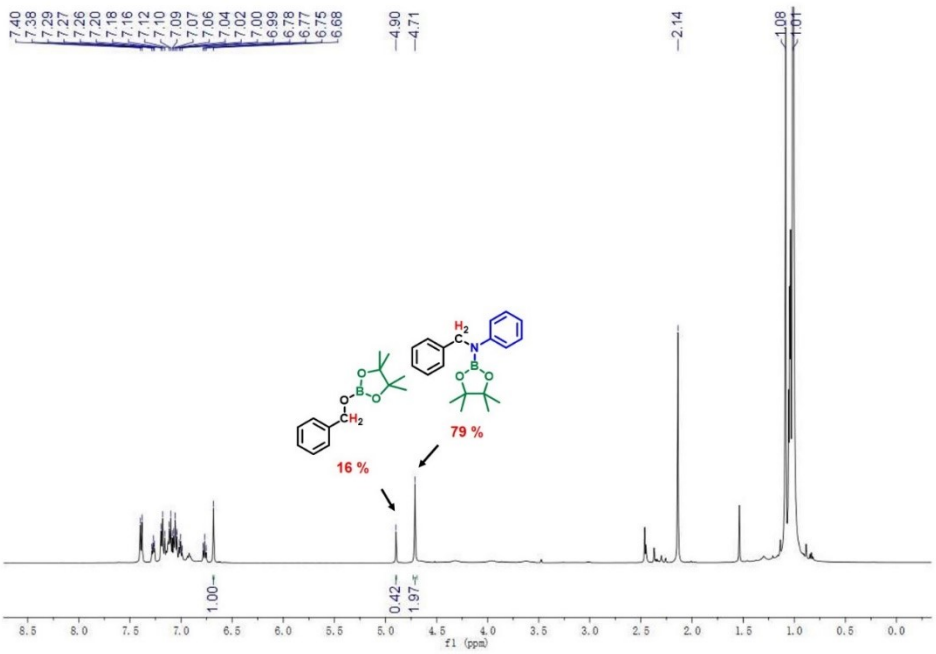
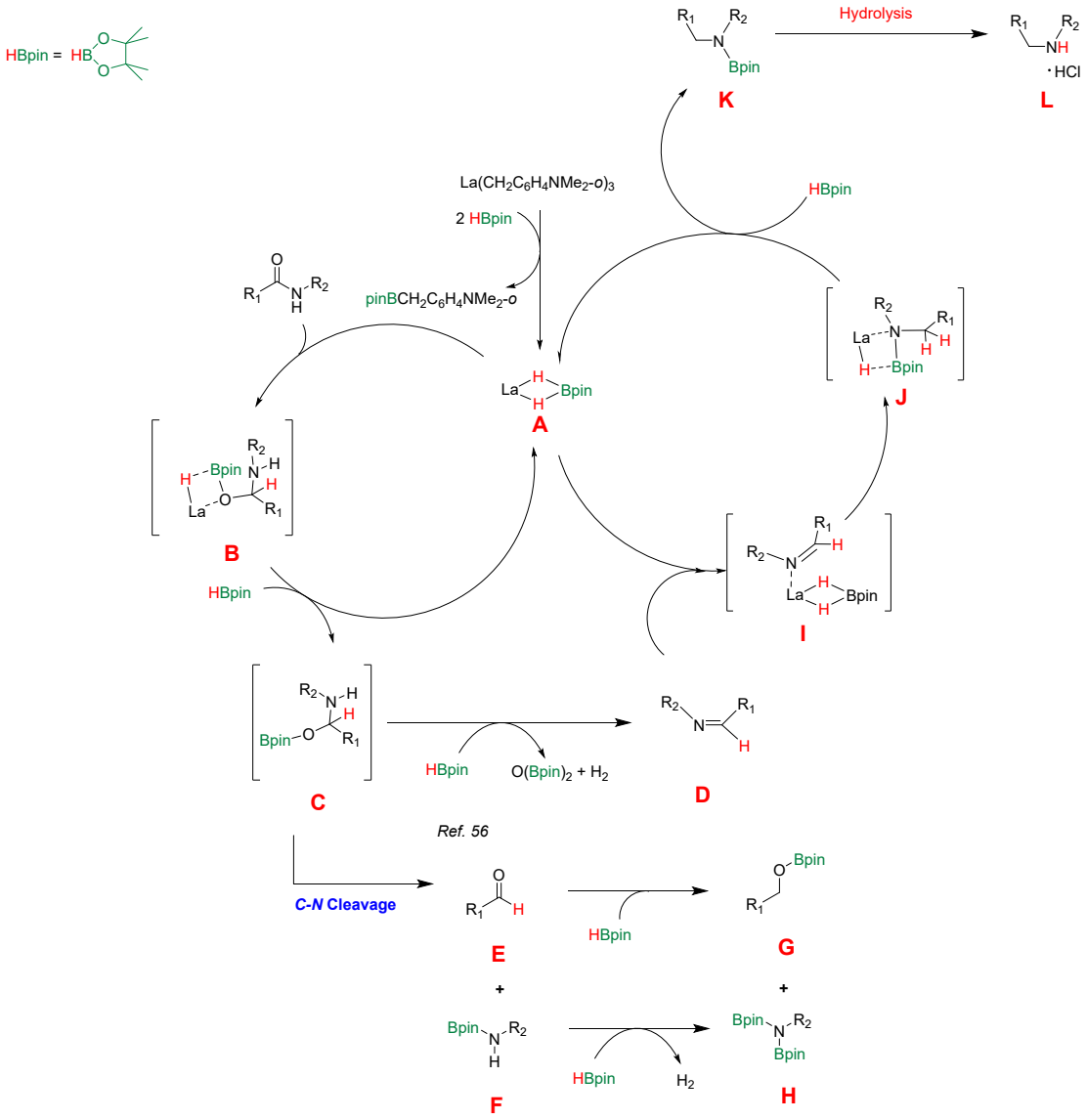
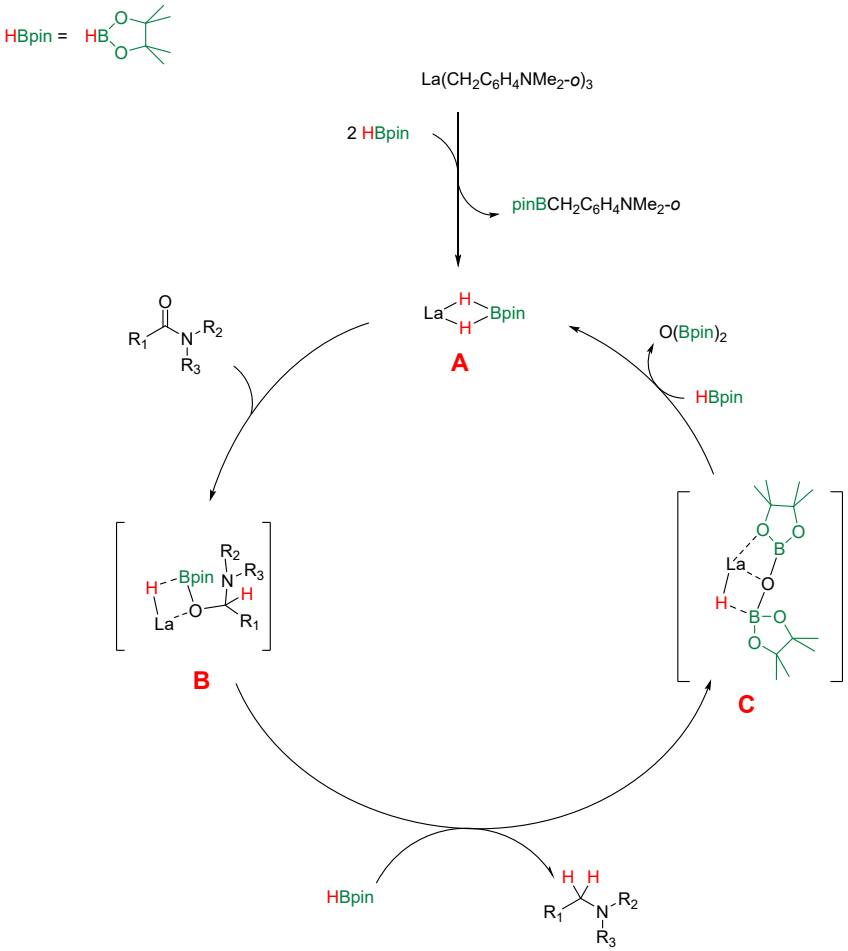


Fig. S12. ^{1}H NMR spectrum of the products generated in situ from the reaction of the resulting mixture with 2.6 equiv pinacolborane catalyzed by La($CH_2C_6H_4NMe_2$-*o*)$_3$ (500 MHz, C_6D_6, 25 °C).

6. Proposed mechanism for the deoxygenative reduction of secondary and tertiary amides.



Scheme S1. Proposed mechanism for the deoxygenative reduction of secondary amides catalyzed by $La(CH_2C_6H_4NMe_2\text{-}o)_3$.



Scheme S2. Proposed mechanism for the deoxygenative reduction of tertiary amides catalyzed by $La(CH_2C_6H_4NMe_2\text{-}o)_3$.

7. ^{1}H NMR spectra of the products on gram-scale preparation.

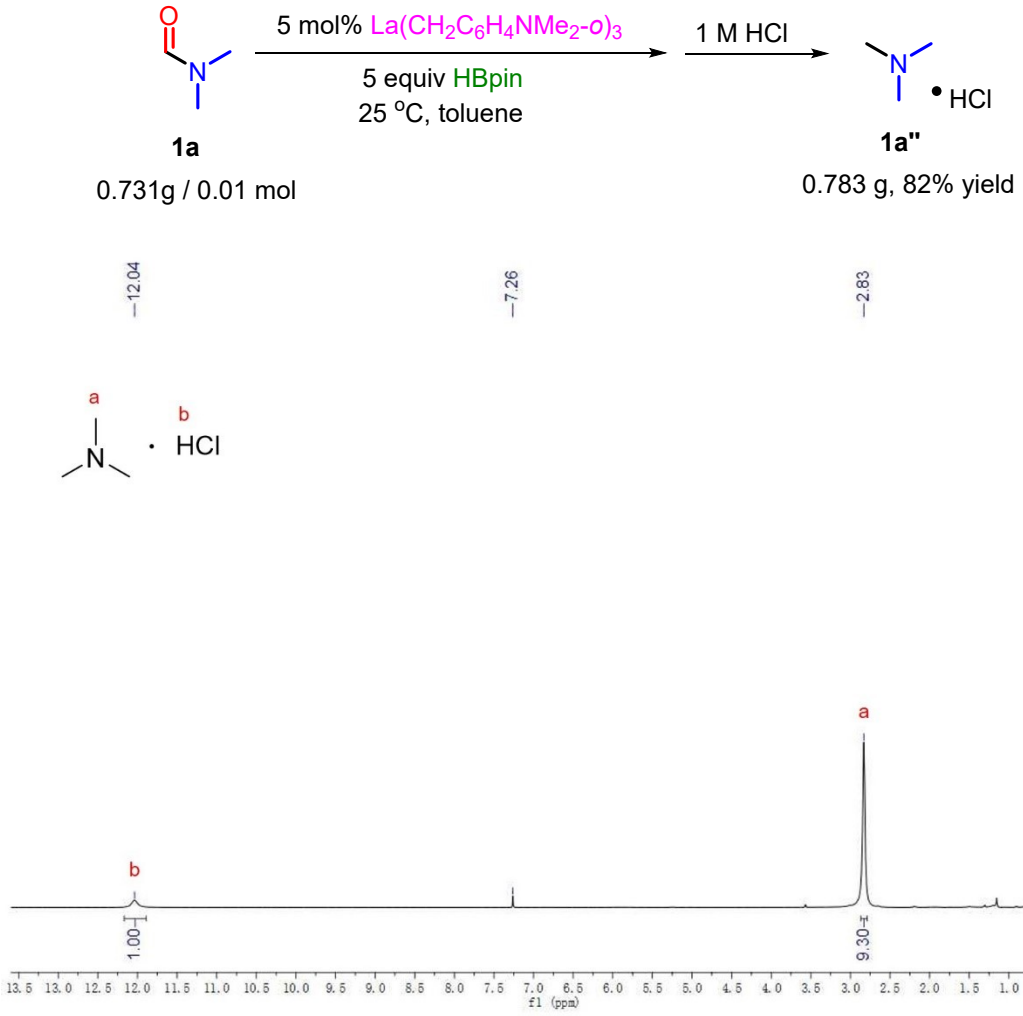


Fig. S13. ^{1}H NMR spectrum of trimethylamine hydrochloride (400 MHz, $CDCl_3$, 25 °C, **1a**, Table 1).

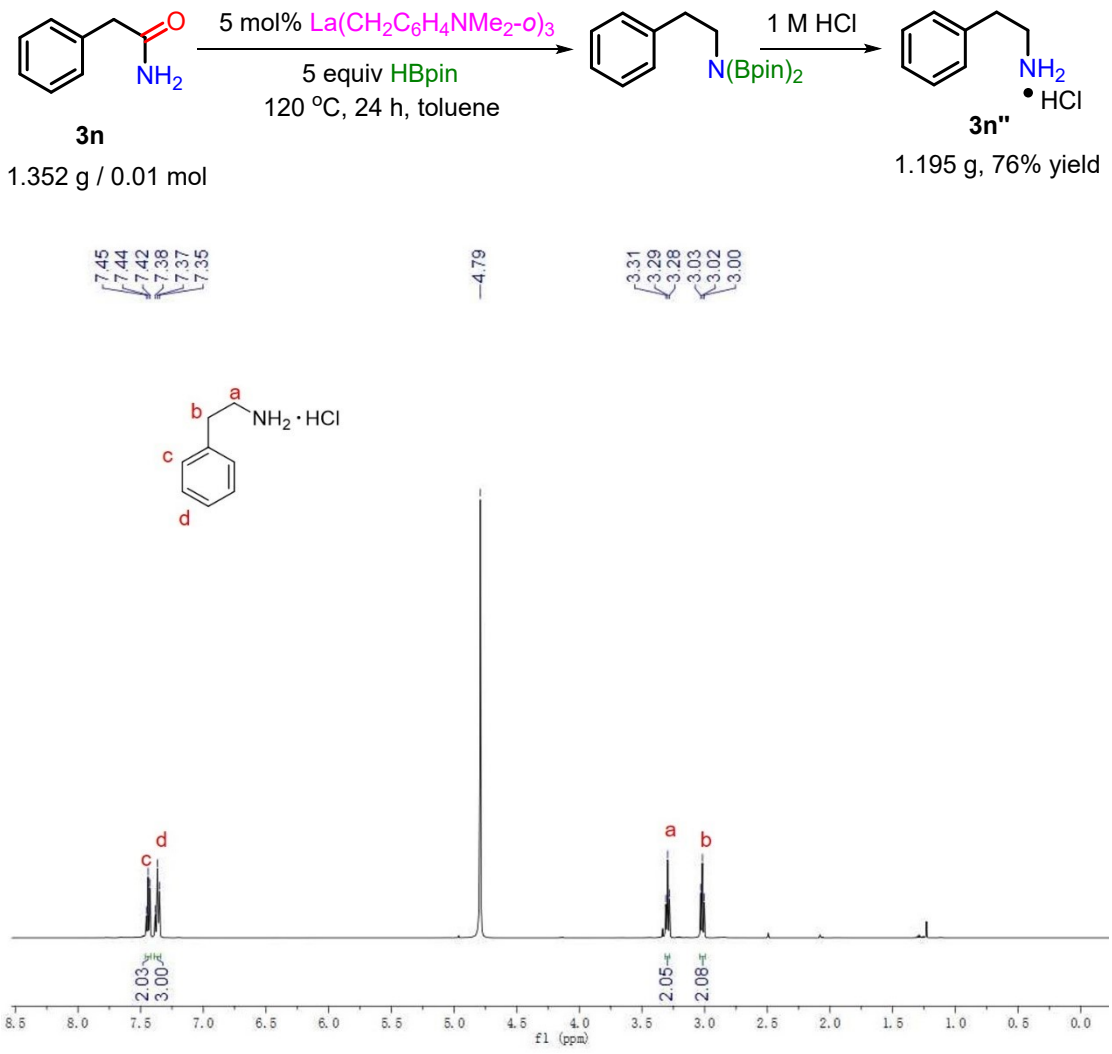


Fig. S14. ^{1}H NMR spectrum of 2-phenylethan-1-amine hydrochloride (500 MHz, D_2O, 25 °C, **3n**, Table 3).

8. ^{1}H NMR spectroscopy of amines.

All amide reduction products were characterized by ^{1}H NMR, and compared with the previous literature.

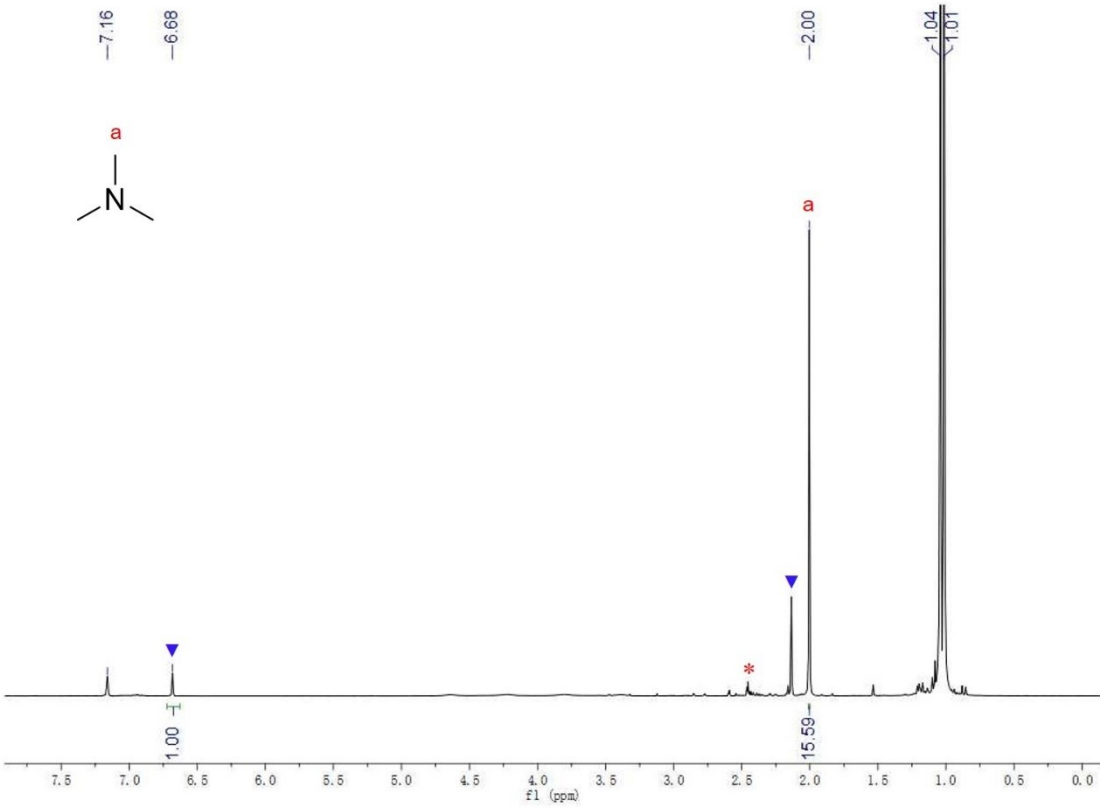


Fig. S15. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dimethylformamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 25 °C for 1 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 °C, **1a**, Table 1).

Trimethylamine.[1] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 2.00 (s, 9H, -NC*H*$_3$).

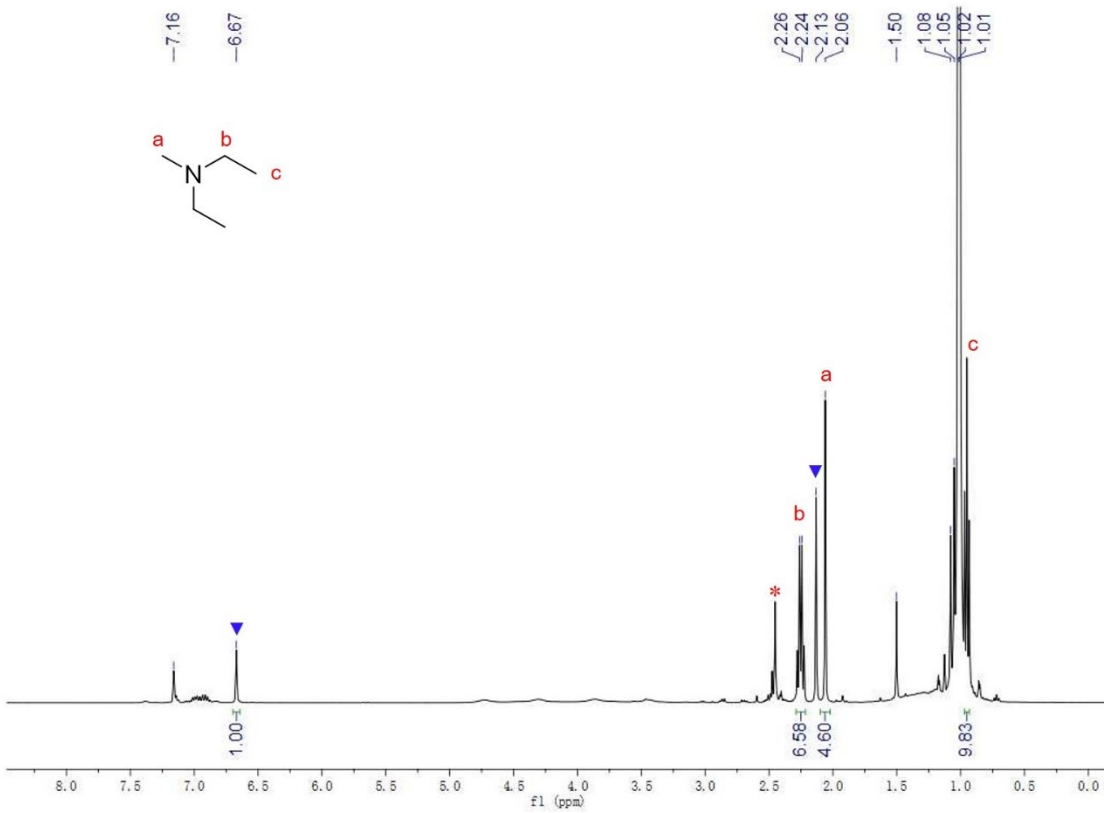


Fig. S16. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-diethylformamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 25 ^{o}C for 2 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 ^{o}C, **1b**, Table 1).

N,N-Diethylmethylamine.[2] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 2.25 (d, J = 7.1 Hz, 4H, -N(CH_2CH_3)$_2$), 2.06 (s, 3H, -NCH_3), 0.95 (t, J = 7.1 Hz, 6H, -N(CH_2CH_3)$_2$).

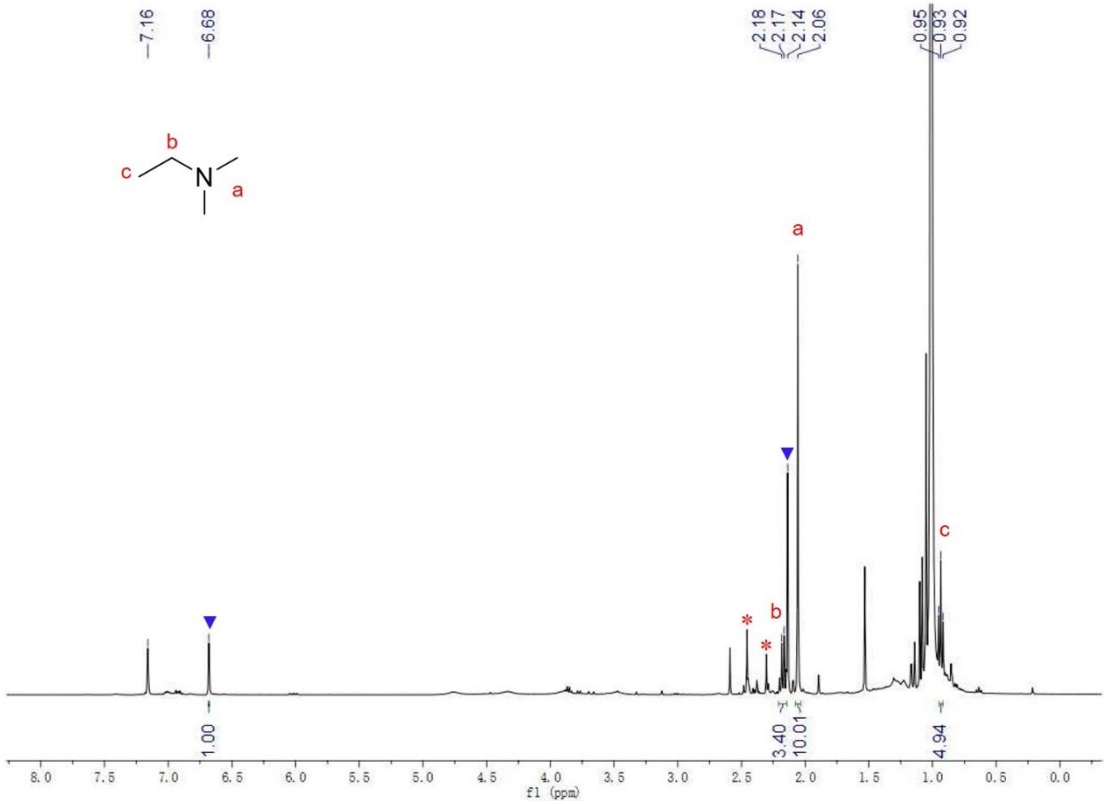


Fig. S17. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dimethylacetamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 25 °C for 2 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 °C, **1c**, Table 1).

N,N-Dimethylethanamine.[3] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 2.17 (d, *J* = 7.3 Hz, 2H, -NC*H*$_2$CH$_3$), 2.06 (s, 6H, -N(C*H*$_3$)$_2$), 0.93 (t, *J* = 7.2 Hz, 3H, -NCH$_2$C*H*$_3$).

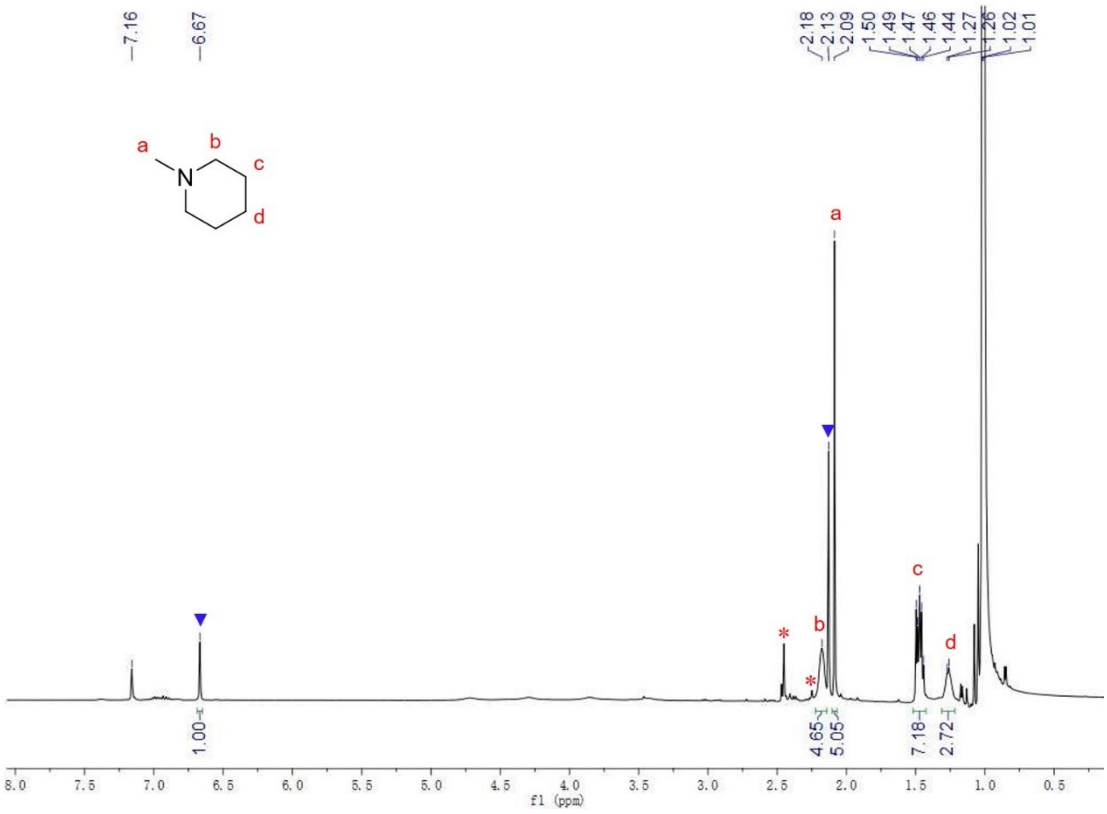


Fig. S18. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of piperidine-1-carbaldehyde catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 25 °C for 1 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 °C, **1d**, Table 1).

1-Methylpiperidine.[4] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 2.18 (s, 4H, -NC_5H_{10}), 2.09 (s, 3H, -NCH_3), 1.51 - 1.43 (m, 4H, -NC_5H_{10}), 1.27 (s, 2H, -NC_5H_{10}).

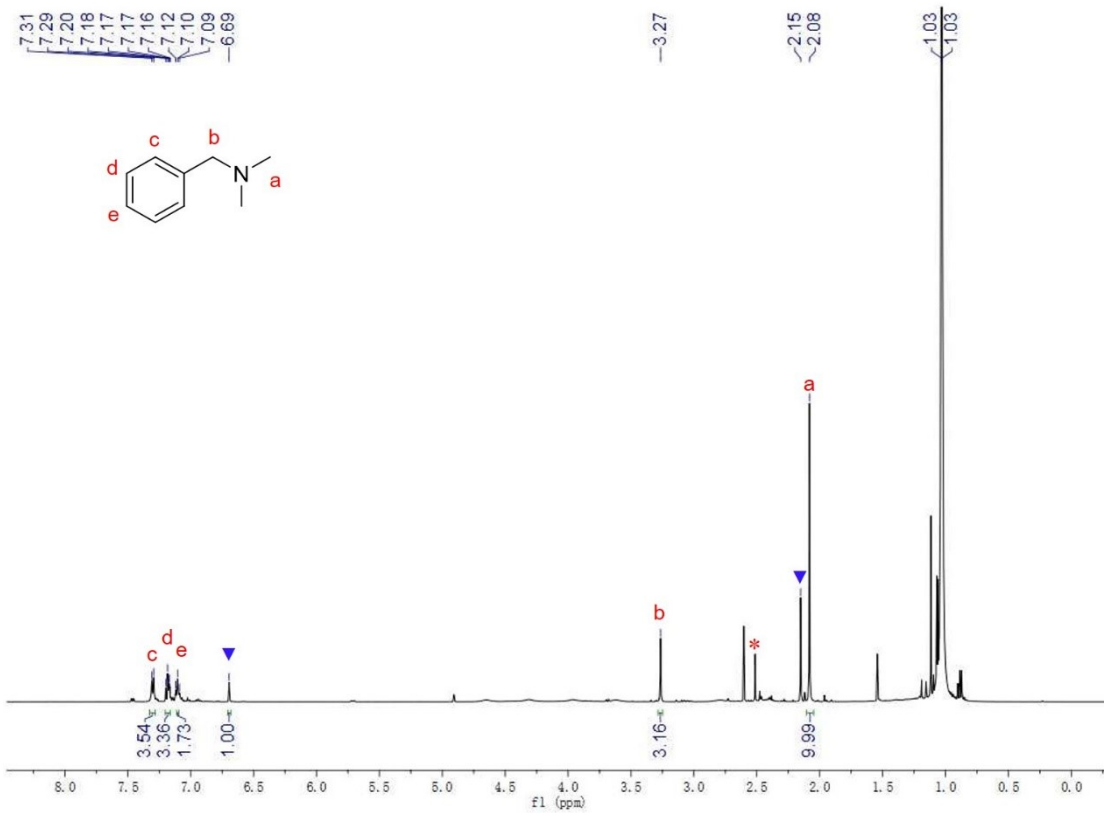


Fig. S19. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dimethylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 25 ^{o}C for 4 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 ^{o}C, **1e**, Table 1).

N,N-Dimethylbenzylamine.[5] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.30 (d, *J* = 7.4 Hz, 2H, -NCH_2*Ph*), 7.20 - 7.17 (m, 2H, -NCH_2*Ph*), 7.14 - 7.07 (m, 1H, -NCH_2*Ph*), 3.27 (s, 2H, -NCH_2Ph), 2.08 (s, 6H, -N(CH_3)$_2$).

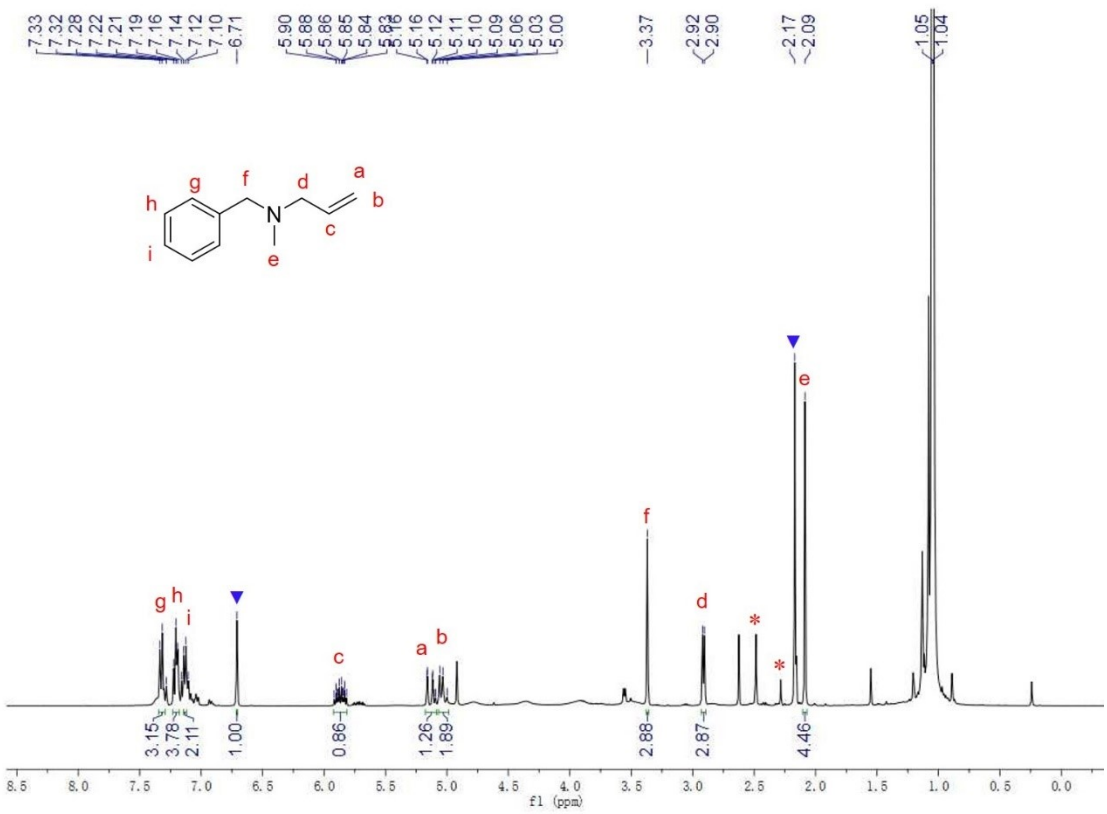


Fig. S20. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-allyl-N-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 60 ^{o}C for 1 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 ^{o}C, **1f**, Table 1).

N-Allyl-N-Methylbenzylamine.[3] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.33 (d, *J* = 7.5 Hz, 2H, -NCH_2*Ph*), 7.21 (t, *J* = 6.6 Hz, 2H, -NCH_2*Ph*), 7.13 (d, *J* = 7.0 Hz, 1H, -NCH_2*Ph*), 5.87 (ddt, *J* = 16.5, 10.2, 6.3 Hz, 1H, -NCH_2CHCH_2), 5.14 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H, -NCH_2CHCH_2), 5.05 (dd, *J* = 10.2 Hz, 0.8 Hz, 1H, -NCH_2CHCH_2), 3.37 (s, 2H, -NCH_2Ph), 2.91 (d, *J* = 6.3 Hz, 2H, -NCH_2CHCH_2), 2.09 (s, 3H, -NCH_3).

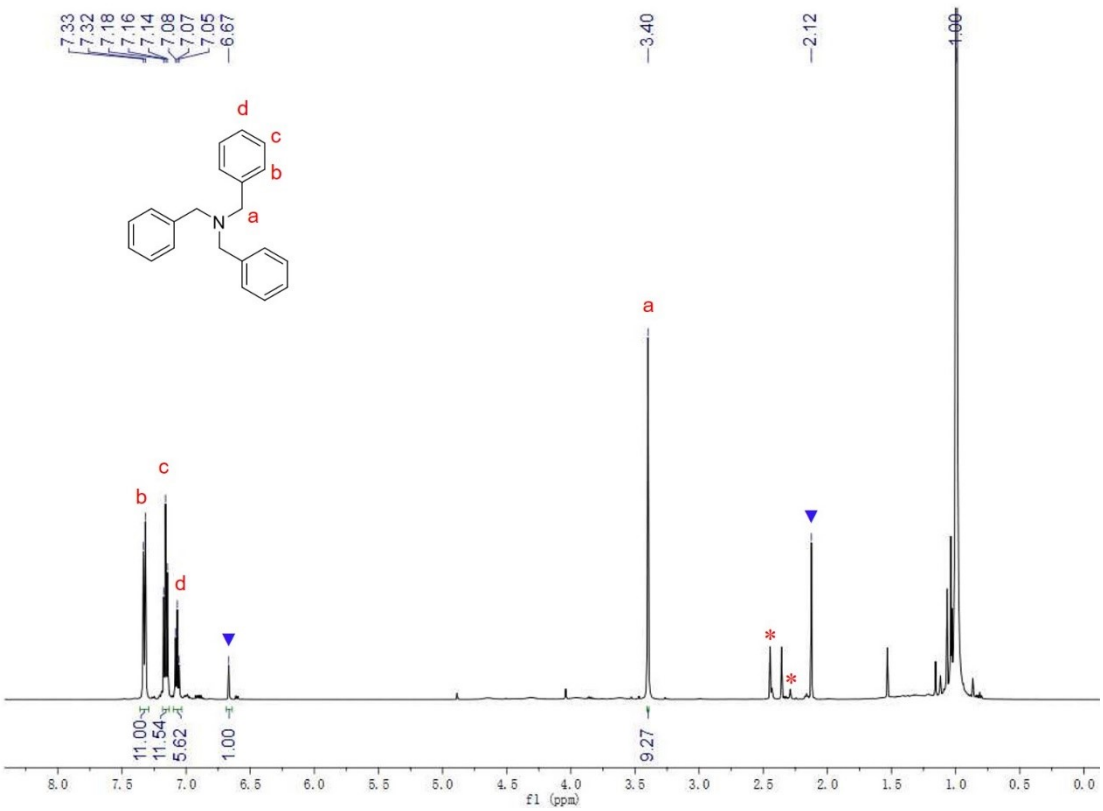


Fig. S21. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 ^{o}C, **1g**, Table 1).

Tribenzylamine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.33 (d, *J* = 7.6 Hz, 6H, -NCH_2*Ph*), 7.19 - 7.16 (m, 6H, -NCH_2*Ph*), 7.07 (t, *J* = 7.3 Hz, 3H, -NCH_2*Ph*), 3.40 (s, 6H, -NCH_2Ph).

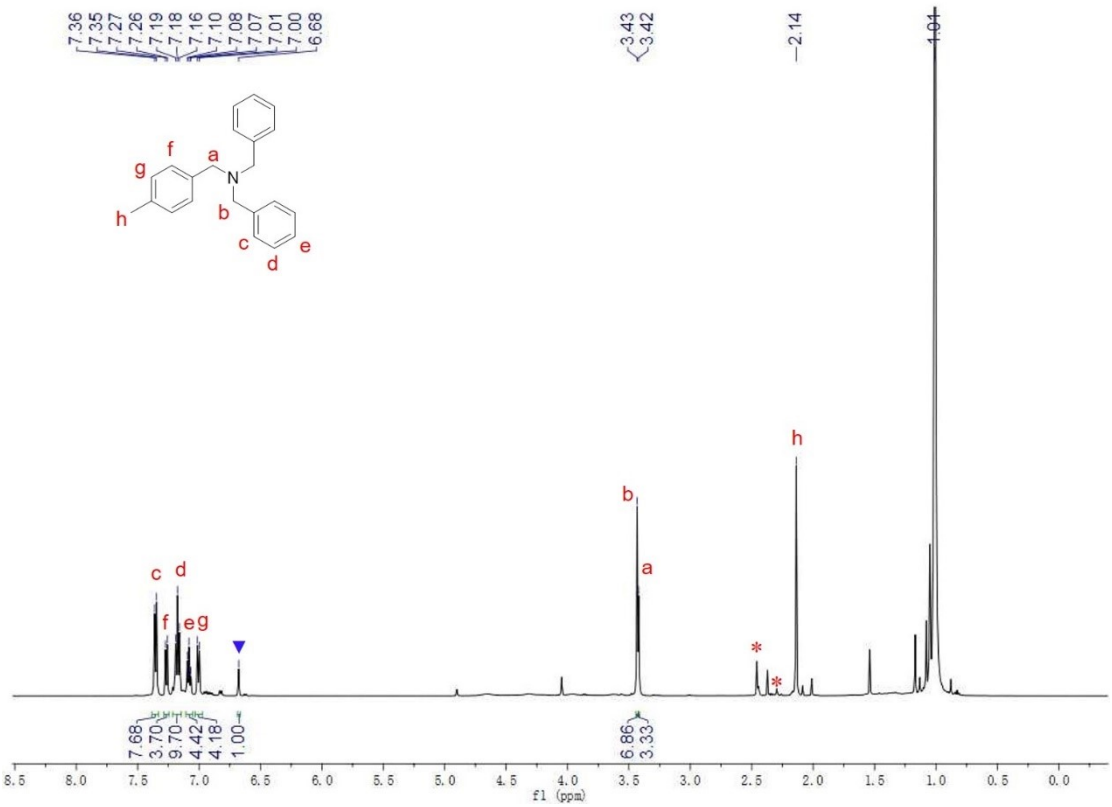


Fig. S22. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzyl-4-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1h**, Table 1).

N,N-Dibenzyl(4-Methylbenzyl)Amine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.35 (d, *J* = 7.6 Hz, 4H, -NCH_2*Ph*), 7.27 (d, *J* = 7.8 Hz, 2H, -NCH_2*Ph*CH_3), 7.20 - 7.18 (m, 4H, -NCH_2*Ph*), 7.08 (t, *J* = 7.3 Hz, 2H, -NCH_2*Ph*), 7.01 (d, *J* = 7.7 Hz, 2H, -NCH_2*Ph*CH_3), 3.43 (s, 4H, -N*C*H_2Ph), 3.42 (s, 2H, -N*C*H_2PhCH_3), 2.14 (s, 3H, -NCH_2Ph*C*H_3).

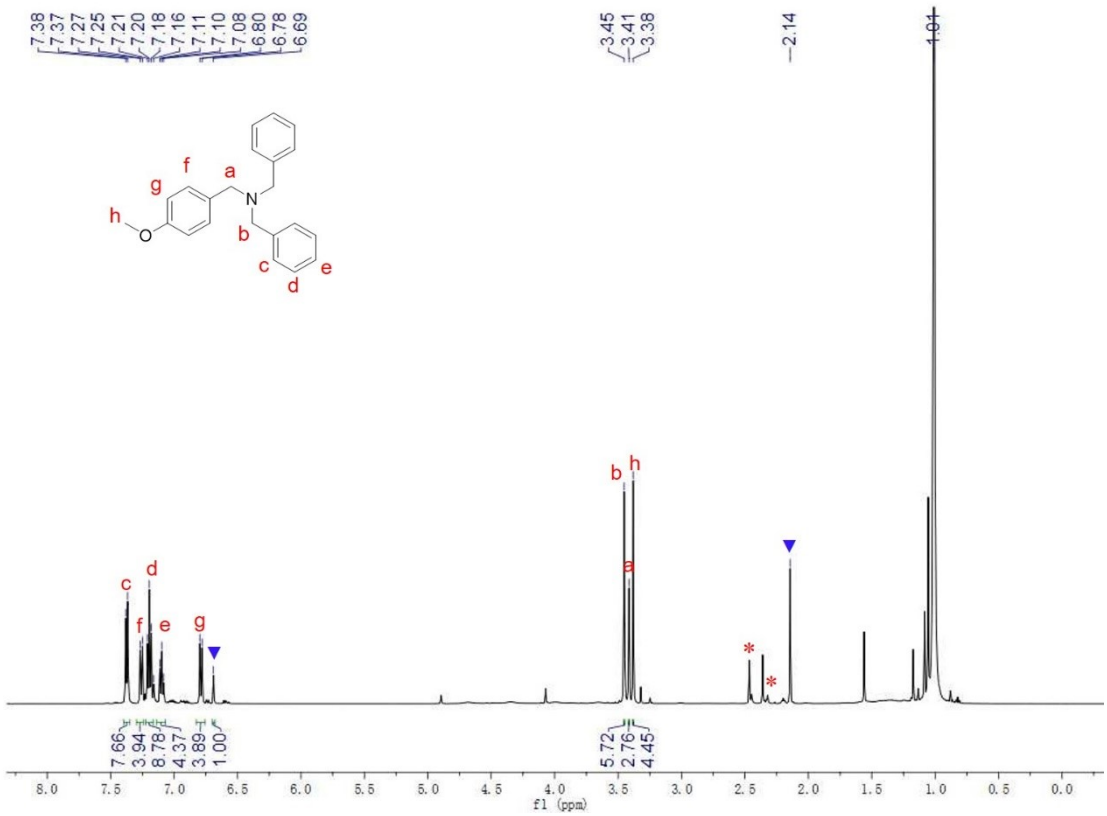


Fig. S23. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzyl-4-methoxybenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1i**, Table 1).

N,N-Dibenzyl(4-Methoxybenzyl)Amine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.37 (d, *J* = 7.5 Hz, 4H, -NCH_2*Ph*), 7.26 (d, *J* = 8.5 Hz, 2H, -NCH_2*Ph*OCH_3), 7.20 (t, *J* = 7.6 Hz, 4H, -NCH_2*Ph*), 7.10 (t, *J* = 7.3 Hz, 2H, -NCH_2*Ph*), 6.79 (d, *J* = 8.5 Hz, 2H, -NCH_2*Ph*OCH_3), 3.45 (s, 4H, -NCH_2Ph), 3.41 (s, 2H, -$NCH_2$$PhOCH_3$), 3.38 (s, 3H, -$NCH_2PhOCH_3$).

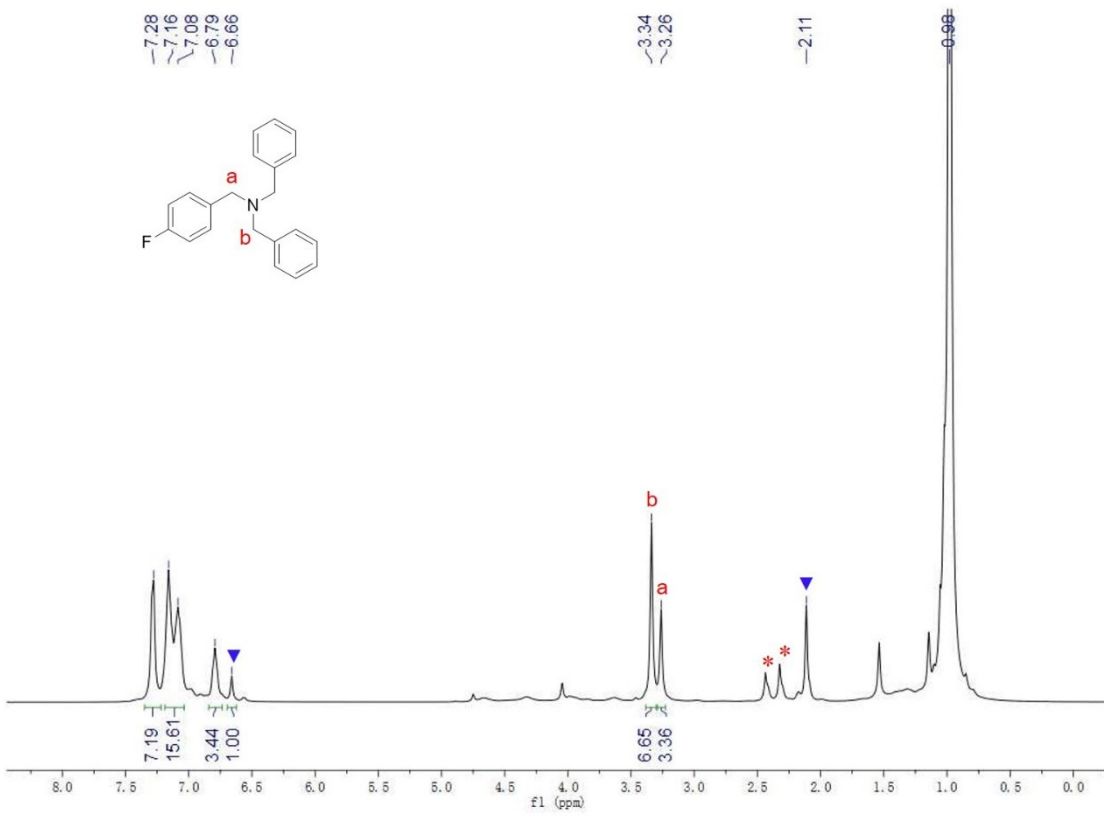


Fig. S24. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzyl-4-fluorobenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1j**, Table 1).

N,N-Dibenzyl(4-Fluorobenzyl)Amine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.28 (s, 4H, -NCH$_2$*Ph*), 7.12 (d, *J* = 37.5 Hz, 8H, -NCH$_2$*Ph*), 6.79 (s, 2H, -NCH$_2$*Ph*), 3.34 (s, 4H, -NC*H*$_2$Ph), 3.26 (s, 2H, -NC*H*$_2$PhF).

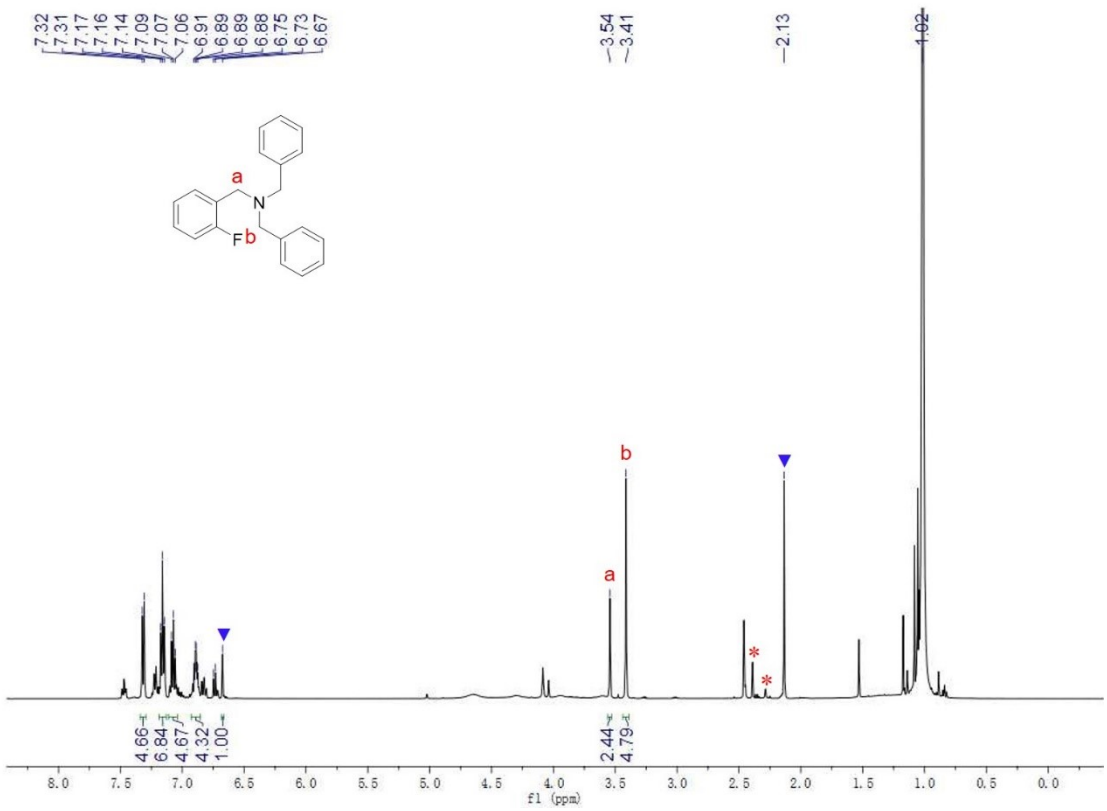


Fig. S25. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzyl-2-fluorobenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1k**, Table 1).

N,N-Dibenzyl(2-Fluorobenzyl)Amine.[7] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.32 (d, *J* = 7.2 Hz, 4H, -NCH$_2$*Ph*), 7.16 (t, *J* = 7.5 Hz, 4H, -NCH$_2$*Ph*), 7.07 (t, *J* = 7.3 Hz, 4H, -NCH$_2$*Ph*), 6.91 - 6.87 (m, 2H, -NCH$_2$*Ph*), 3.54 (s, 2H, -NC*H*$_2$PhF), 3.41 (s, 4H, -NC*H*$_2$Ph).

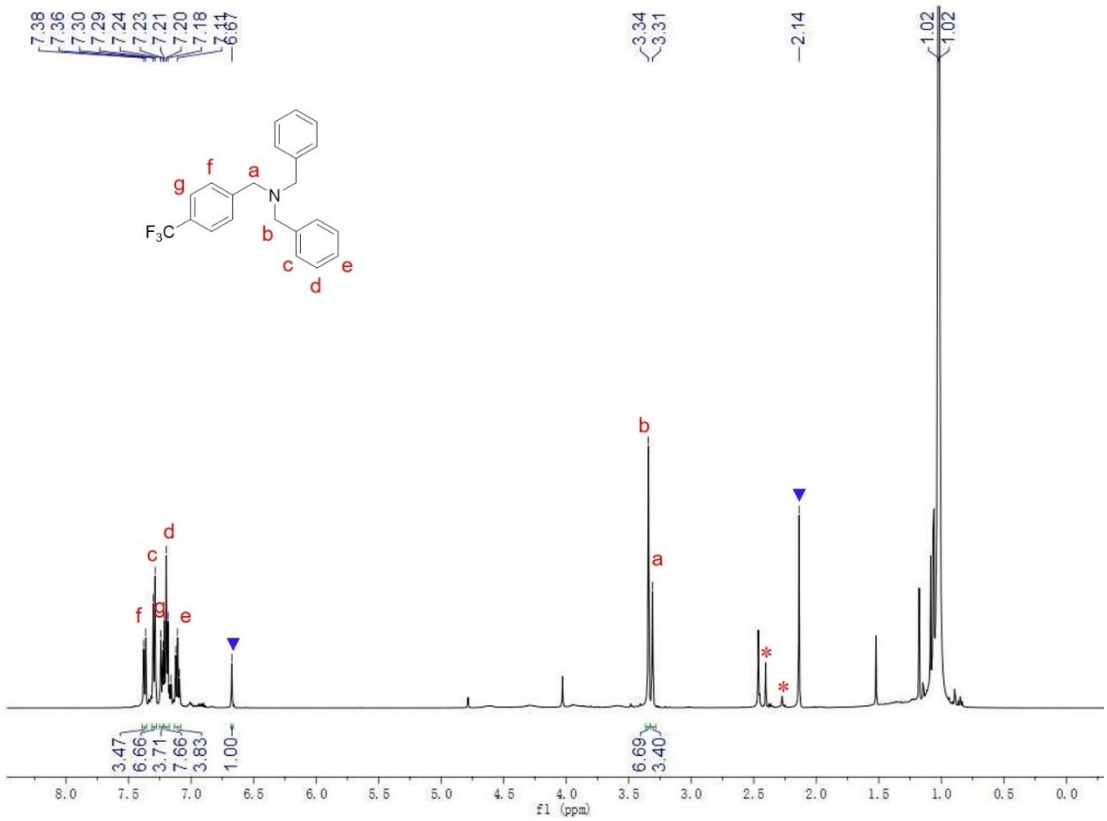


Fig. S26. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzyl-4-(trifluoromethyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1l**, Table 1).

N,N-Dibenzyl(4-Trifluoromethylbenzyl)Amine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.37 (d, *J* = 8.1 Hz, 2H, -NCH_2*Ph*CF_3), 7.30 (d, *J* = 7.3 Hz, 4H, -NCH_2*Ph*), 7.23 (d, *J* = 8.0 Hz, 2H, -NCH_2*Ph*CF_3), 7.20 (t, *J* = 7.6 Hz, 4H, -NCH_2*Ph*), 7.11 (t, *J* = 7.4 Hz, 2H, -NCH_2*Ph*), 3.34 (s, 4H, -N*C*H_2Ph), 3.31 (s, 2H, -N*C*H_2PhCF_3).

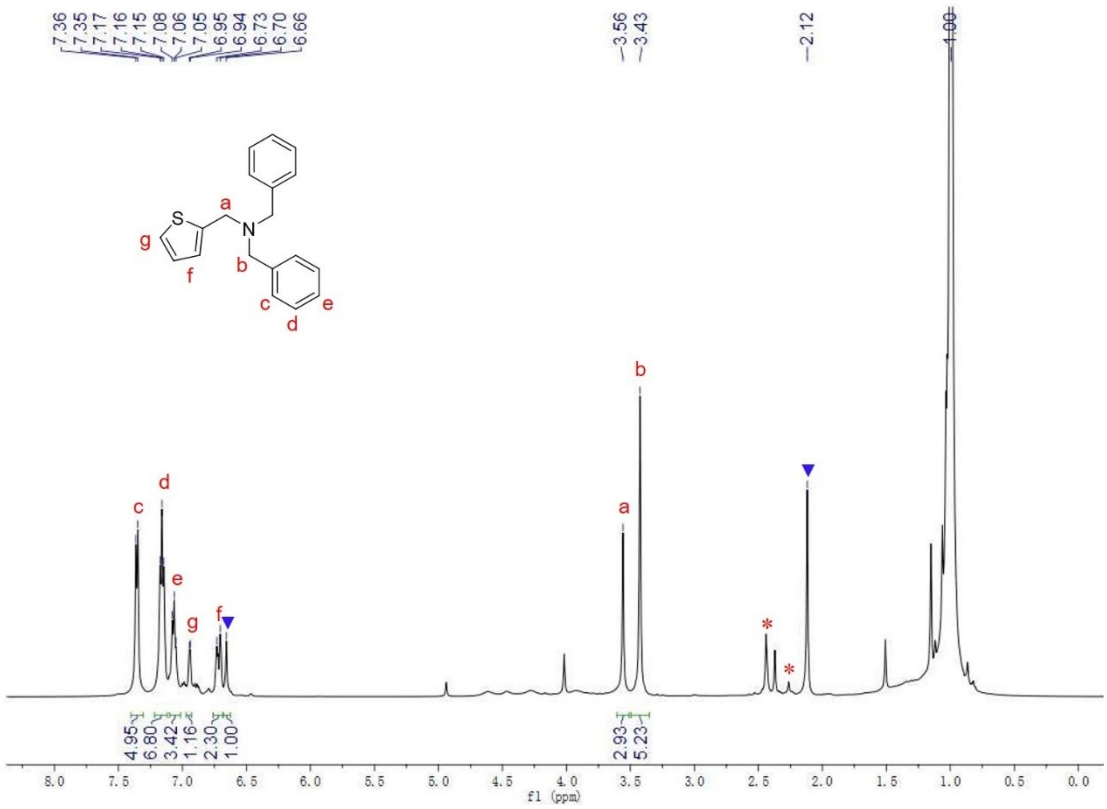


Fig. S27. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzylthiophene-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1m**, Table 1).

N,N-Dibenzyl-2-Thiophenemethylamine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.36 (d, *J* = 7.3 Hz, 4H, -NCH_2*Ph*), 7.19 - 7.12 (m, 4H, -NCH_2*Ph*), 7.06 (t, *J* = 7.0 Hz, 2H, -NCH_2*Ph*), 6.94 (d, *J* = 4.5 Hz, 1H, -NCH_2C_4*H*$_3$S), 6.72 (d, *J* = 13.1 Hz, 2H, -NCH_2C_4*H*$_3$S), 3.56 (s, 2H, -NC*H*$_2C_4H_3$S), 3.43 (s, 4H, -NC*H*$_2$Ph).

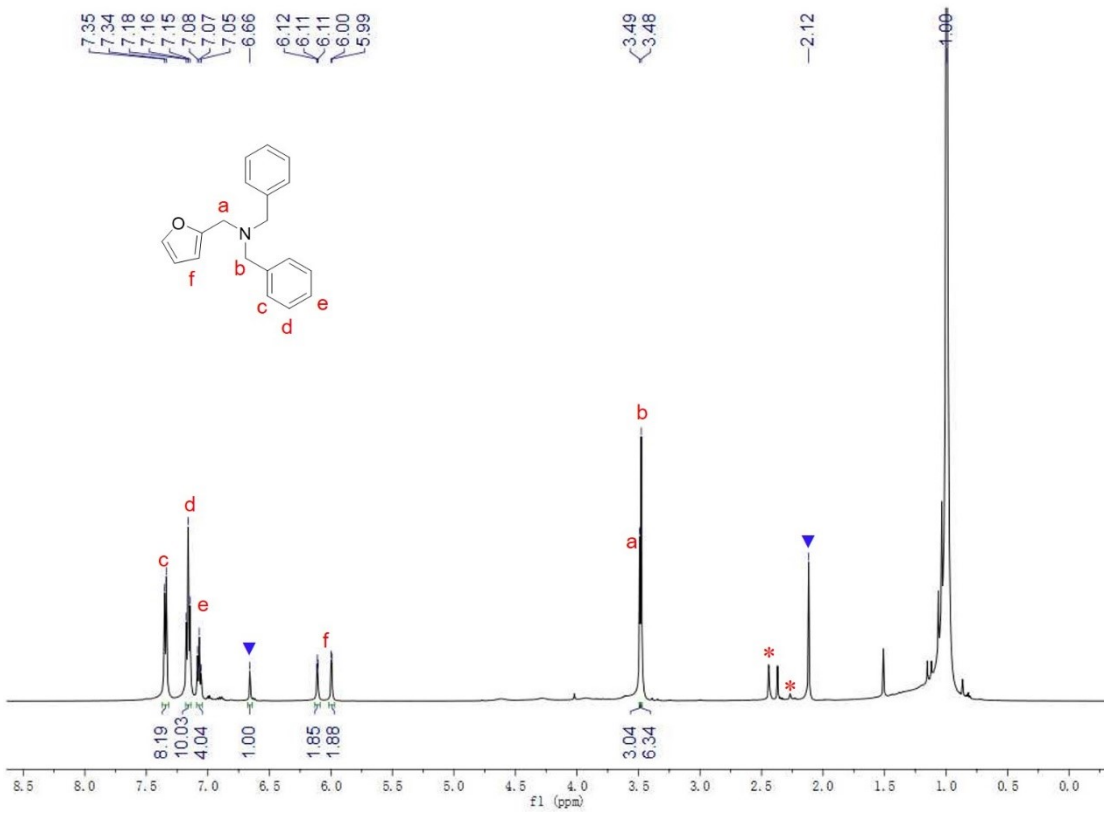


Fig. S28. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzylfuran-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1n**, Table 1).

N,N-Dibenzyl-2-Furanmethylamine.[6] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.34 (d, *J* = 7.4 Hz, 4H, -NCH_2*Ph*), 7.16 (t, *J* = 7.6 Hz, 4H, -NCH_2*Ph*), 7.07 (t, *J* = 7.3 Hz, 2H, -NCH_2*Ph*), 6.14 - 6.08 (m, 1H, -NCH_2C_4*H*$_3$O), 6.00 (d, *J* = 3.0 Hz, 1H, -NCH_2C_4*H*$_3$O), 3.49 (s, 2H, -NC*H*$_2C_4H_3O$), 3.48 (s, 4H, -NC*H*$_2$Ph).

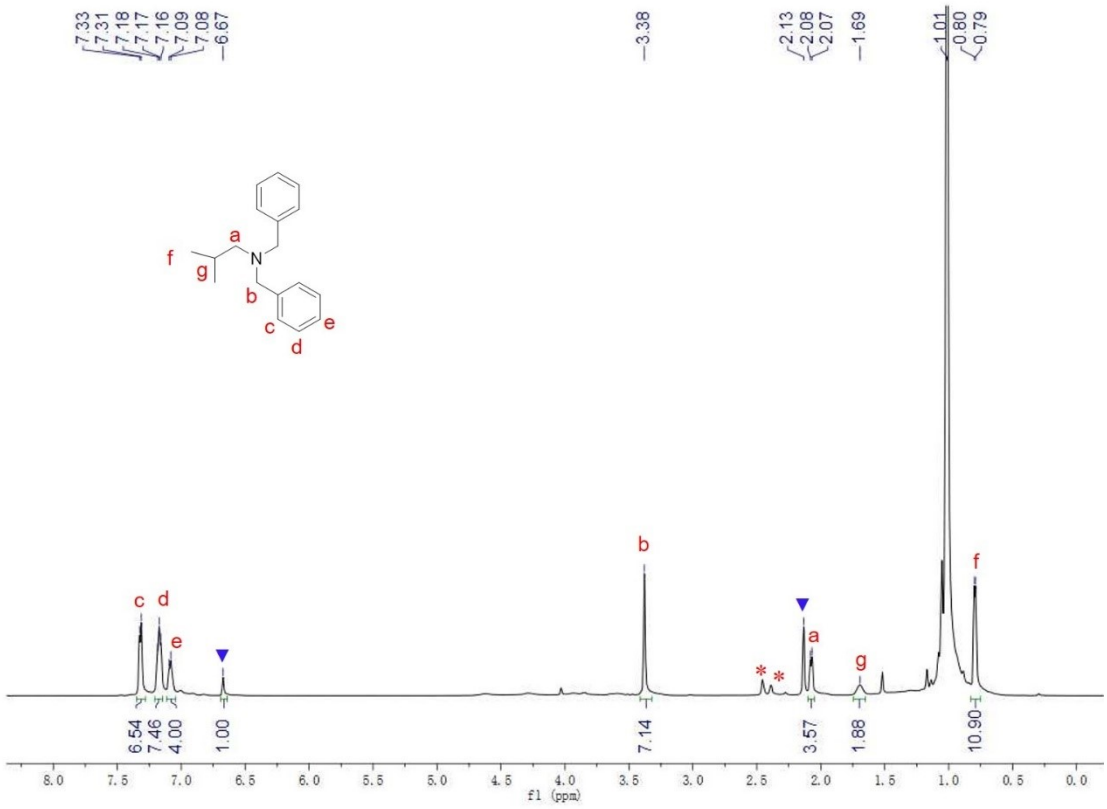


Fig. S29. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-dibenzylisobutyramide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 ^{o}C, **1o**, Table 1).

N,N-Dibenzyl-2-Methylpropan-1-Amine.[8] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.32 (d, *J* = 6.8 Hz, 4H, -NCH$_2$*Ph*), 7.22 - 7.15 (m, 4H, -NCH$_2$*Ph*), 7.09 (d, *J* = 6.1 Hz, 2H, -NCH$_2$*Ph*), 3.38 (s, 4H, -NC*H*$_2$Ph), 2.07 (d, *J* = 5.4 Hz, 2H, -NC*H*$_2$CH(CH$_3$)$_2$), 1.69 (s, 1H, -NCH$_2$C*H*(CH$_3$)$_2$), 0.79 (d, *J* = 4.0 Hz, 6H, -NCH$_2$CH(C*H*$_3$)$_2$).

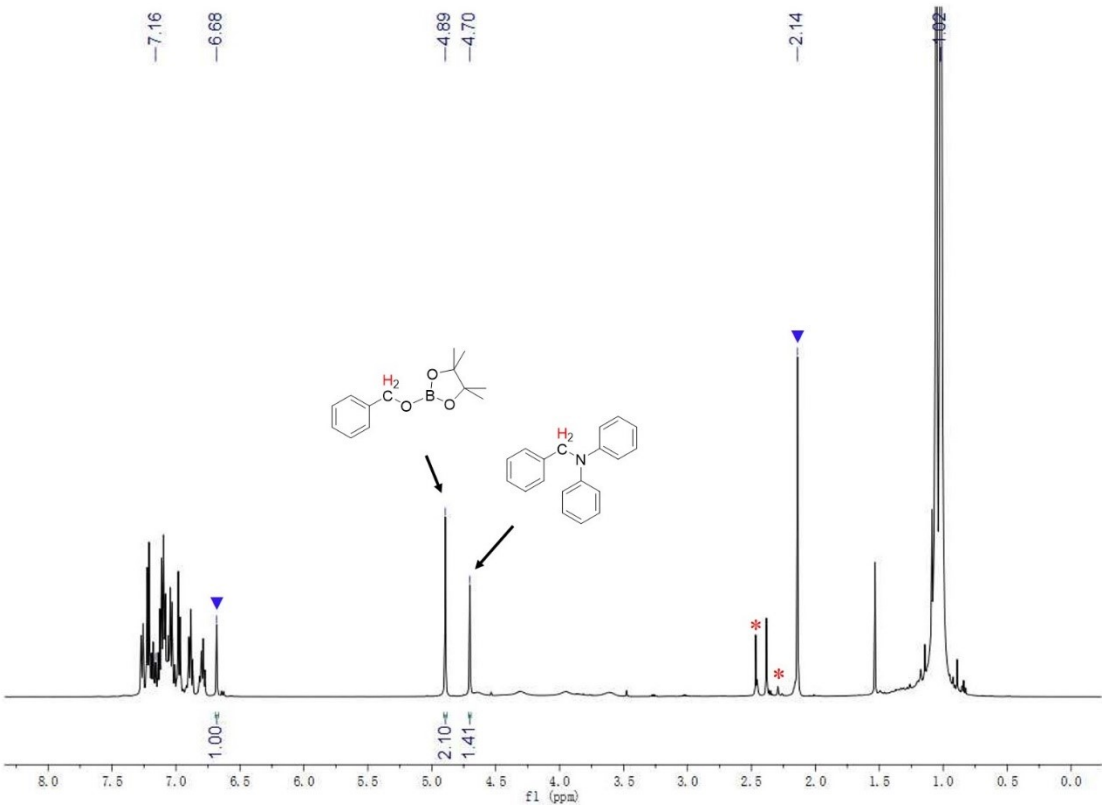


Fig. S30. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,N-diphenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1p**, Table 1).

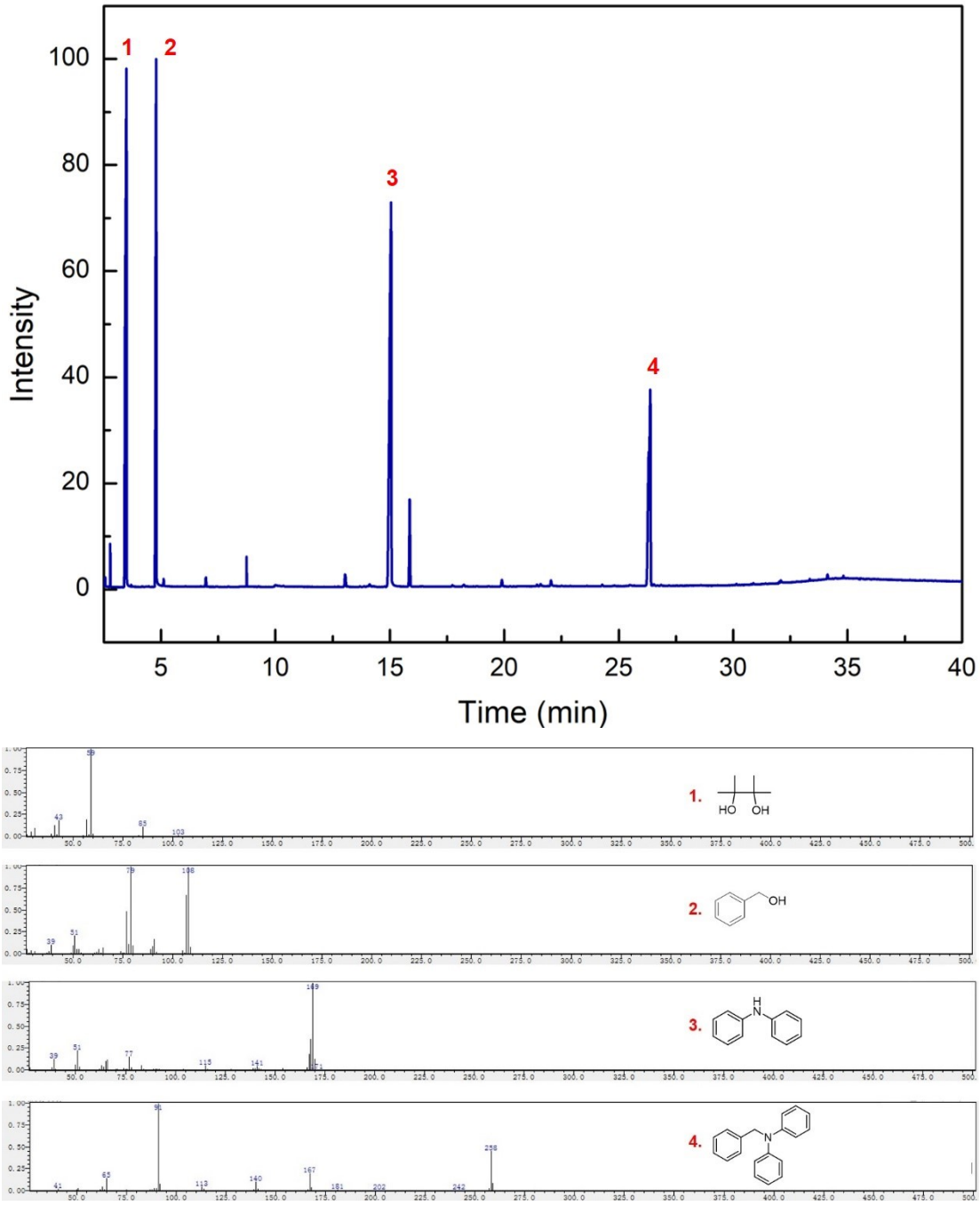


Fig. S31. GC-MS of 2,3-dimethylbutane-2,3-diol, phenylmethanol, diphenylamine and N-benzyl-N-phenylaniline.

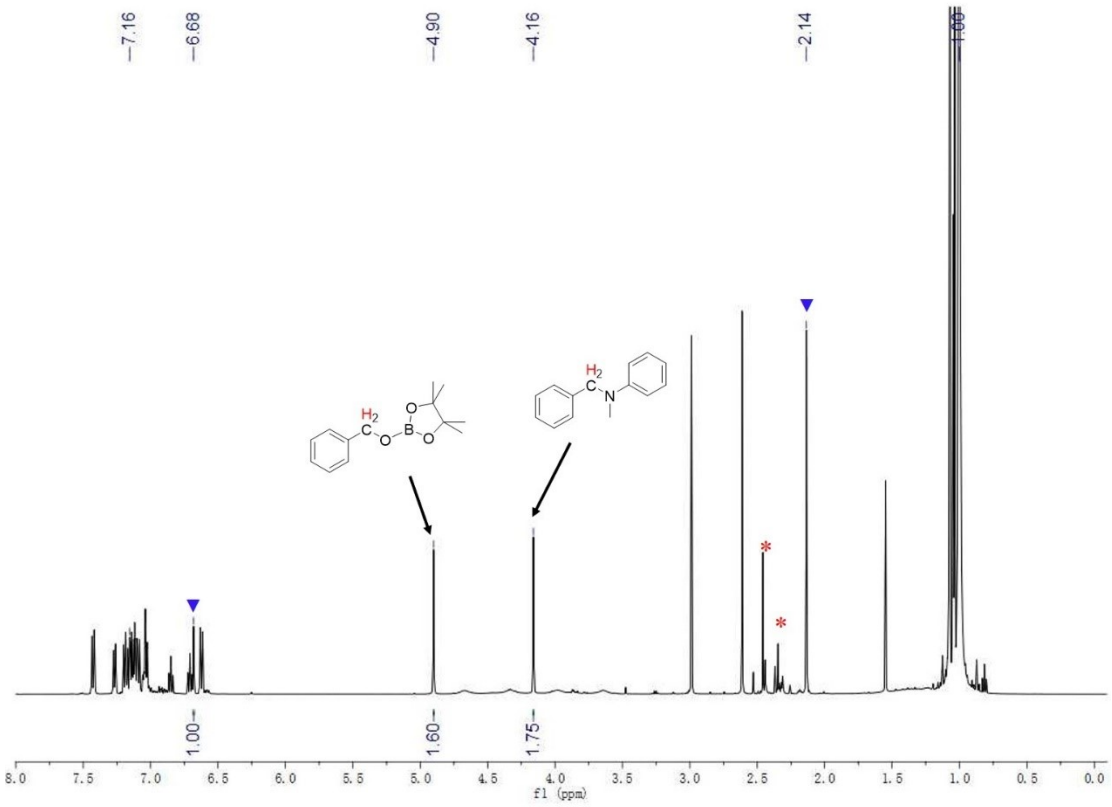


Fig. S32. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-methyl-N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 80 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (500 MHz, C_6D_6, 25 °C, **1q**, Table 1).

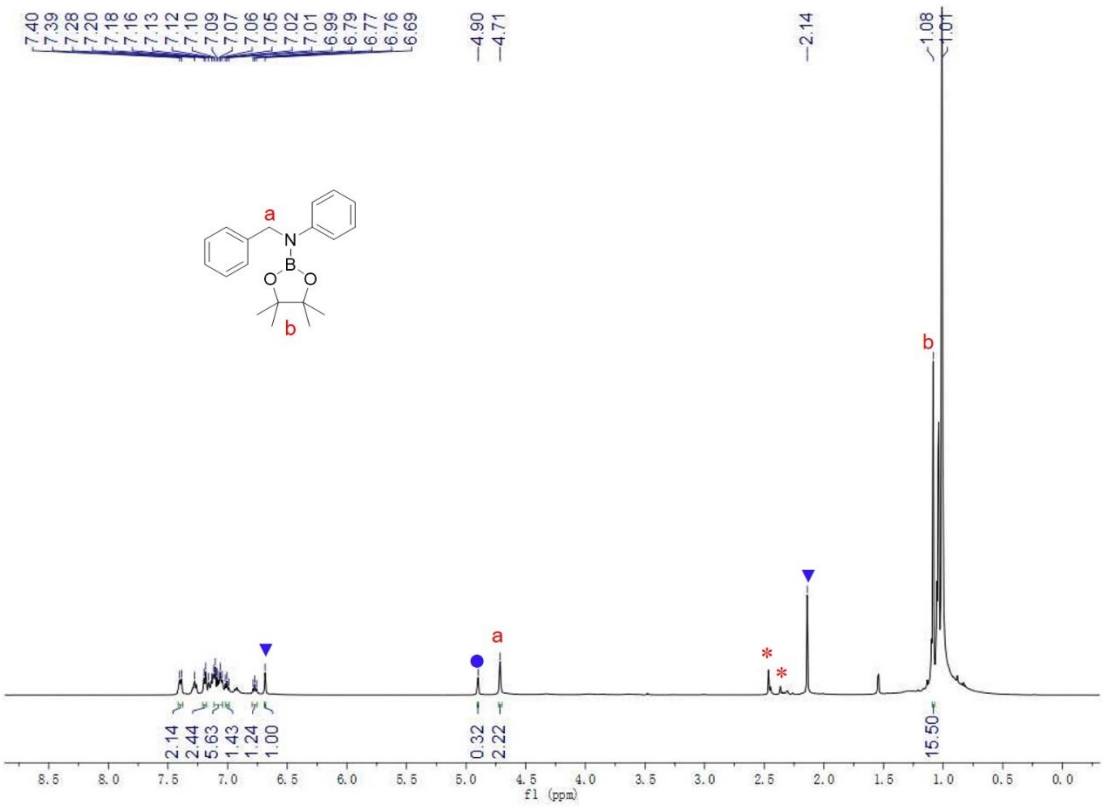


Fig. S33. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_5$ (400 MHz, C_6D_6, 25 ^{o}C, **2a**, Table 2).

N-Benzyl-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[9] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.40 (d, *J* = 8.7 Hz, 2H, -*Ph*), 7.19 (d, *J* = 7.3 Hz, 2H, -*Ph*), 7.15 - 7.03 (m, 4H, -*Ph*), 7.00 (t, *J* = 7.3 Hz, 1H, -*Ph*), 6.77 (t, *J* = 7.3 Hz, 1H, -*Ph*), 4.71 (s, 2H, -NC*H*$_2$Ph), 1.08 (s, 12H, -NB*pin*).

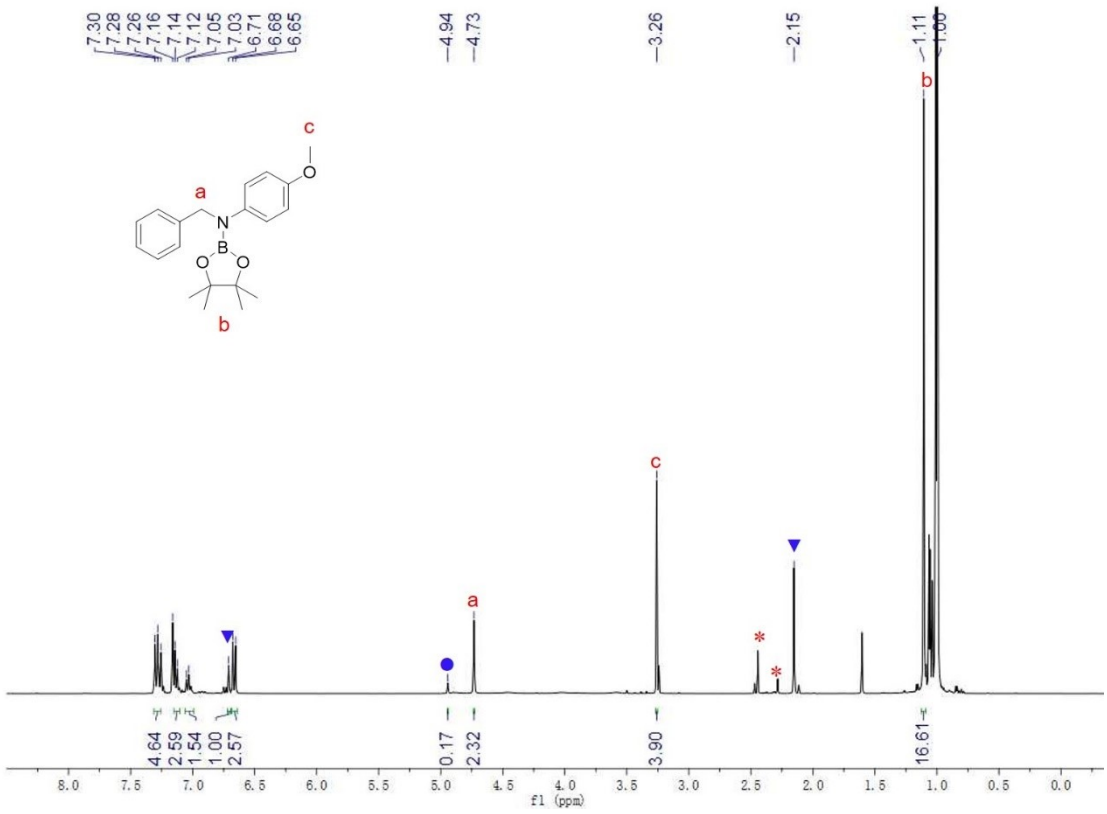


Fig. S34. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-(4-methoxyphenyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinB$OCH_2C_6H_5$ (400 MHz, C_6D_6, 25 °C, **2b**, Table 2).

N-Benzyl-N-(4-Methoxyphenyl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[9]
^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.32 - 7.24 (m, 4H, -*Ph*), 7.13 (d, *J* = 7.7 Hz, 2H, -*Ph*), 7.03 (t, *J* = 7.4 Hz, 1H, -*Ph*), 6.66 (d, *J* = 9.1 Hz, 2H, -*Ph*), 4.73 (s, 2H, -NCH_2Ph), 3.26 (s, 3H, -NPhOCH_3), 1.11 (s, 12H, -NB*pin*).

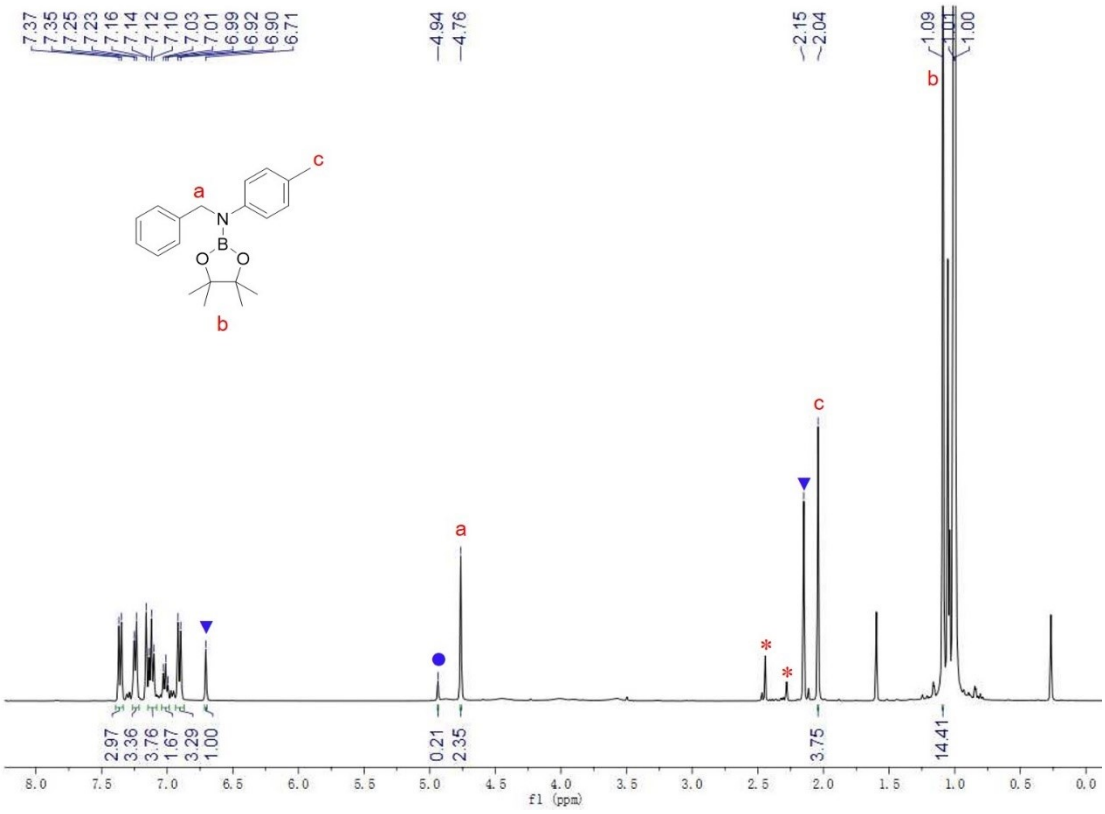


Fig. S35. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-(p-tolyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_5$ (400 MHz, C_6D_6, 25 ^{o}C, **2c**, Table 2).

N-Benzyl-N-(p-Tolyl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[10] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.36 (d, *J* = 8.4 Hz, 2H, -*Ph*), 7.24 (d, *J* = 7.4 Hz, 2H, -*Ph*), 7.12 (t, *J* = 7.6 Hz, 2H, -*Ph*), 7.01 (t, *J* = 7.3 Hz, 1H, -*Ph*), 6.91 (d, *J* = 8.2 Hz, 2H, -*Ph*), 4.76 (s, 2H, -NC*H*$_2$Ph), 2.04 (s, 3H, -NPhC*H*$_3$), 1.09 (s, 12H, -NB*pin*).

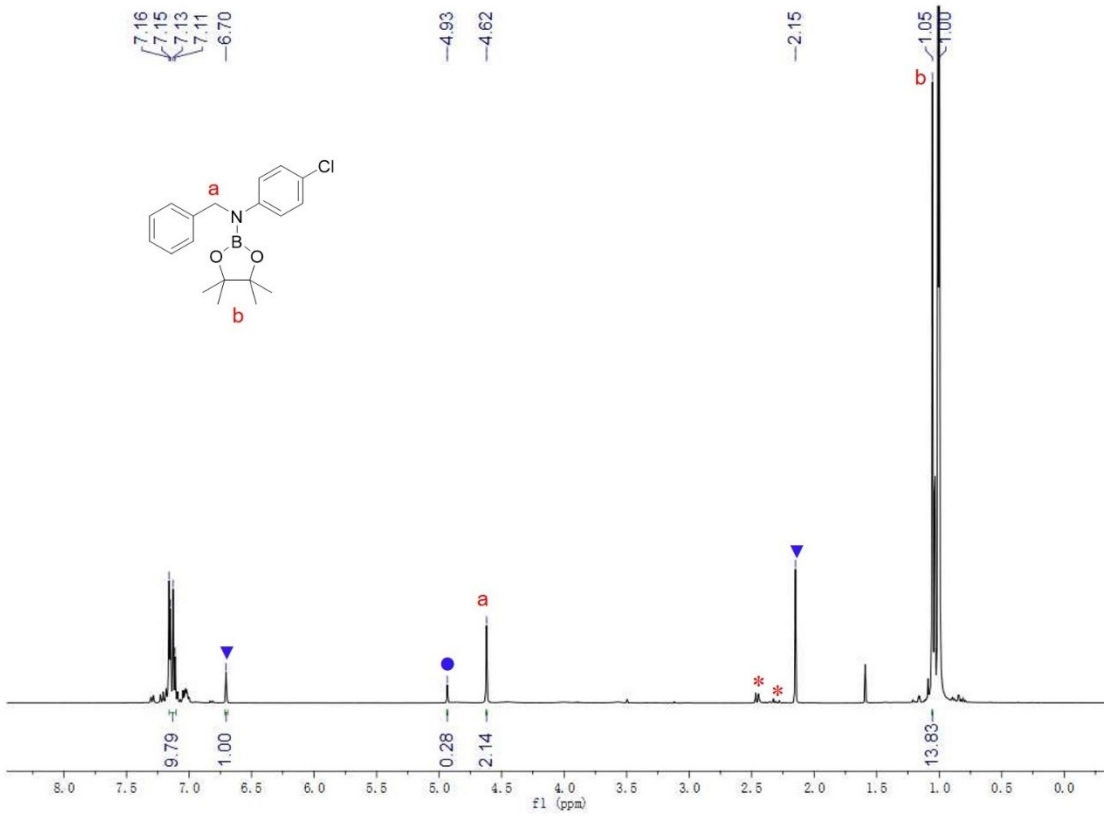


Fig. S36. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-(4-chlorophenyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_5$ (400 MHz, C_6D_6, 25 °C, **2d**, Table 2).

N-Benzyl-N-(4-Chlorophenyl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[10] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.15 -7.10 (m, 9H, -*Ph*), 4.62 (s, 2H, -NC*H*$_2$Ph), 1.05 (s, 12H, -NB*pin*).

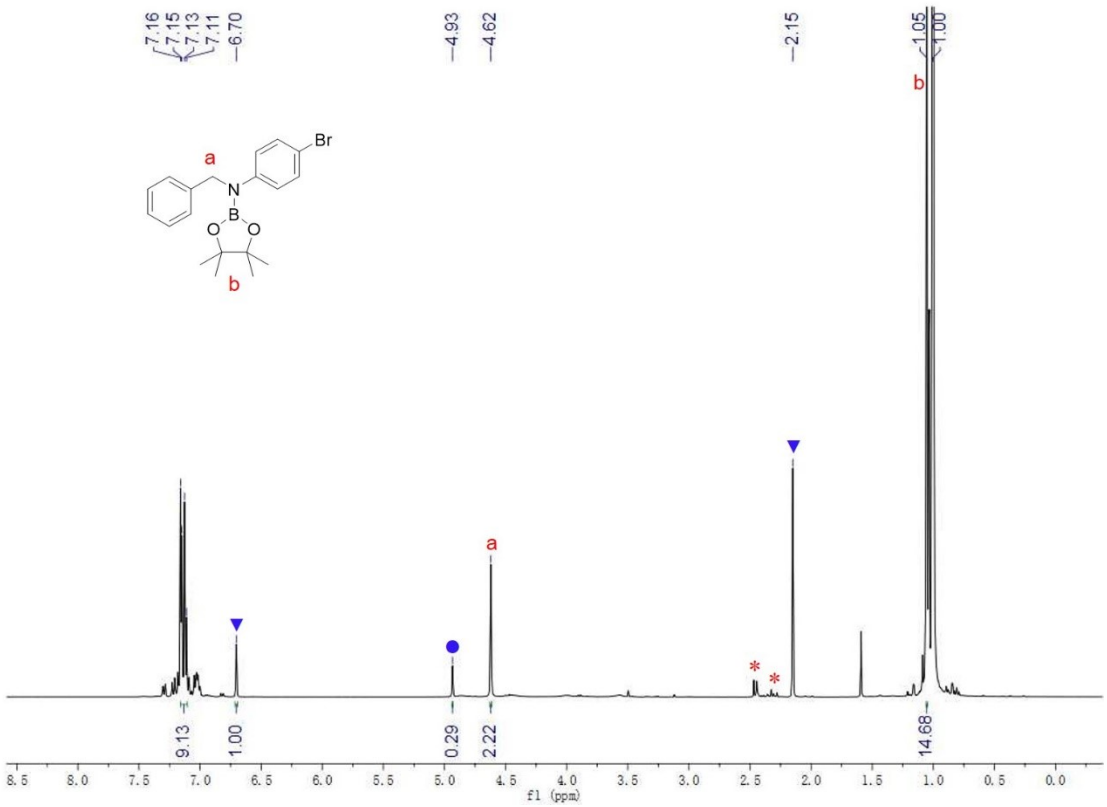


Fig. S37. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-(4-bromophenyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_5$ (400 MHz, C_6D_6, 25 °C, **2e**, Table 2).

N-Benzyl-N-(4-Bromophenyl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[11] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.16 - 7.11 (m, 9H, -*Ph*), 4.62 (s, 2H, -NC*H*$_2$Ph), 1.05 (s, 12H, -NB*pin*).

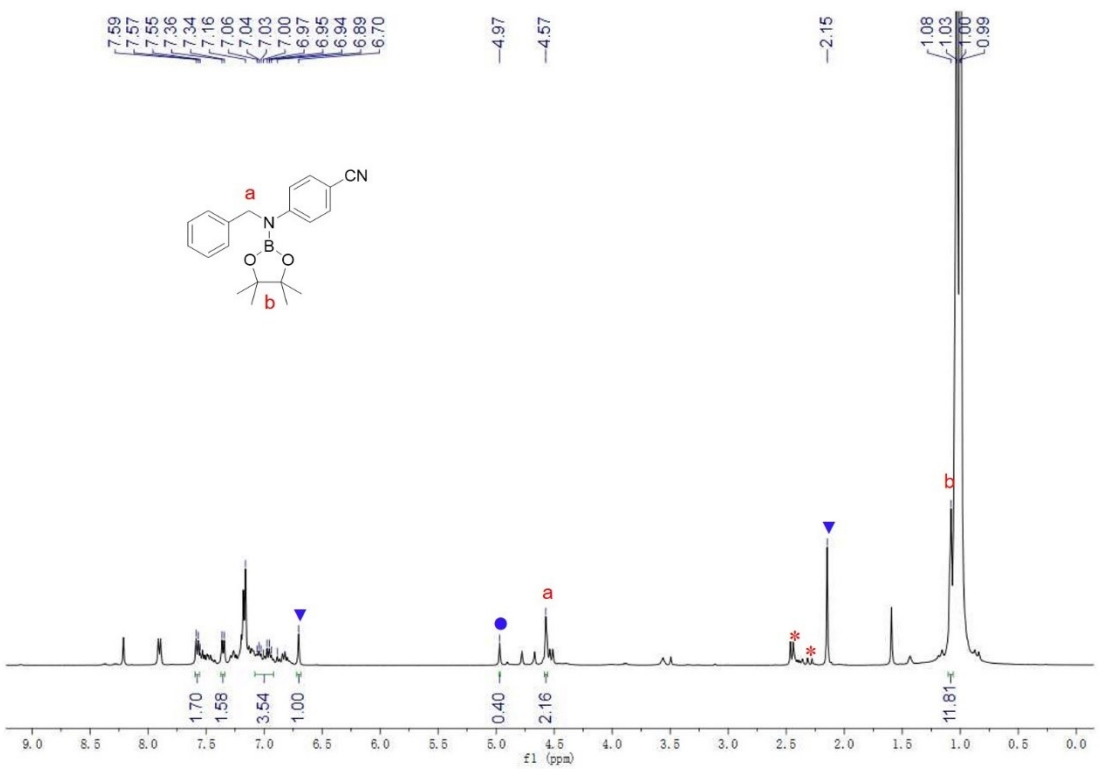


Fig. S38. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-(4-cyanophenyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_5$ (400 MHz, C_6D_6, 25 °C, **2f**, Table 2).

4-(Benzyl(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-yl)Amino)Benzonitrile. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.58 (d, *J* = 7.9 Hz, 2H, -*Ph*), 7.35 (d, *J* = 7.7 Hz, 2H, -*Ph*), 7.06 - 6.89 (m, 5H, -*Ph*), 4.57 (s, 2H, -NC*H*$_2$Ph), 1.08 (s, 12H, -NB*pin*).

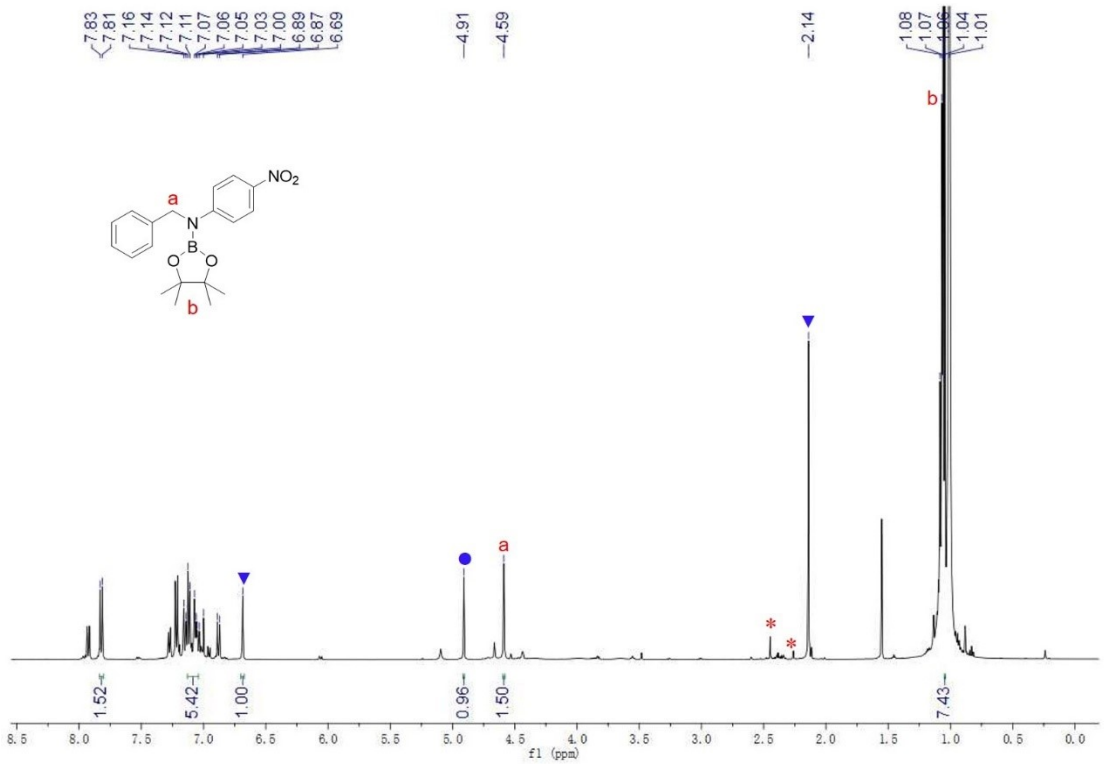


Fig. S39. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-(4-nitrophenyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_5$ (400 MHz, C_6D_6, 25 °C, **2g**, Table 2).

N-Benzyl-N-(4-Nitrophenyl)-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.82 (d, *J* = 9.4 Hz, 2H, -*Ph*), 7.14 - 7.03 (m, 7H, -*Ph*), 4.59 (s, 2H, -NC*H*$_2$Ph), 1.08 (s, 12H, -NB*pin*).

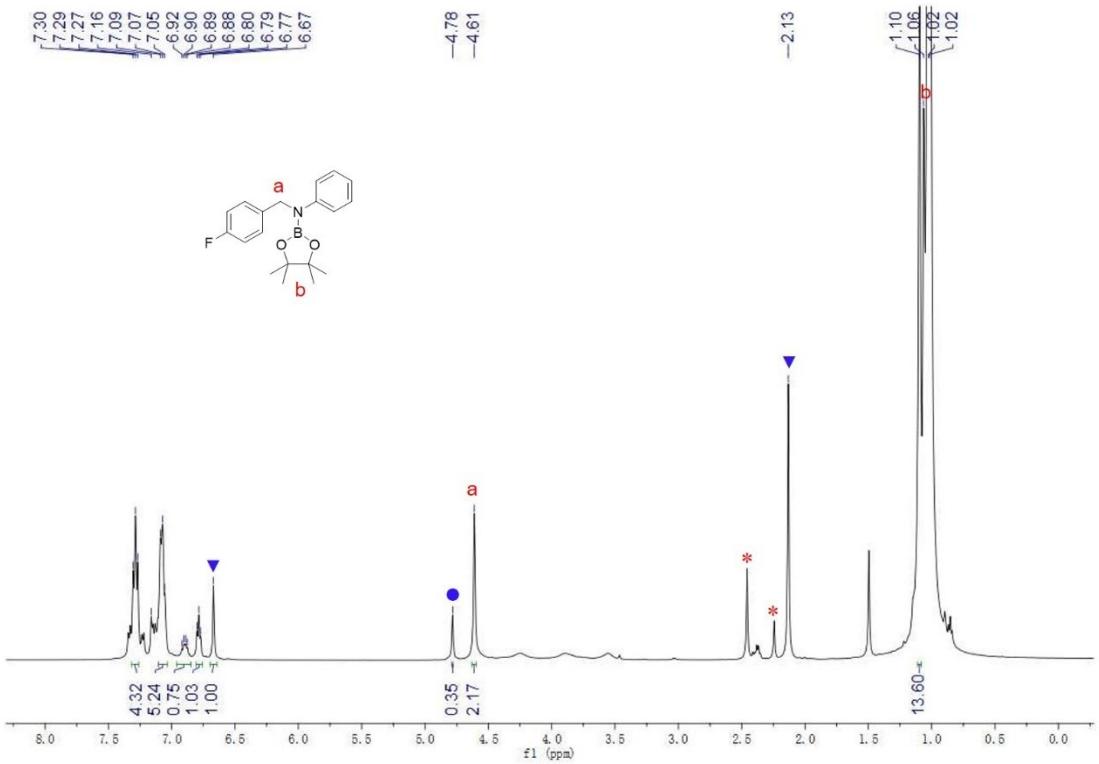


Fig. S40. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-fluoro-N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4F$-*p* (500 MHz, C_6D_6, 25 °C, **2h**, Table 2).

N-(4-Fluorobenzyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[11] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.29 (d, *J* = 9.1 Hz, 2H, -*Ph*), 7.10 - 7.03 (m, 5H, -*Ph*), 6.90 (dd, *J* = 13.4, 7.2 Hz, 1H, -*Ph*), 6.79 (t, *J* = 7.0 Hz, 1H, -*Ph*), 4.61 (s, 2H, -NCH_2PhF), 1.10 (s, 12H, -NB*pin*).

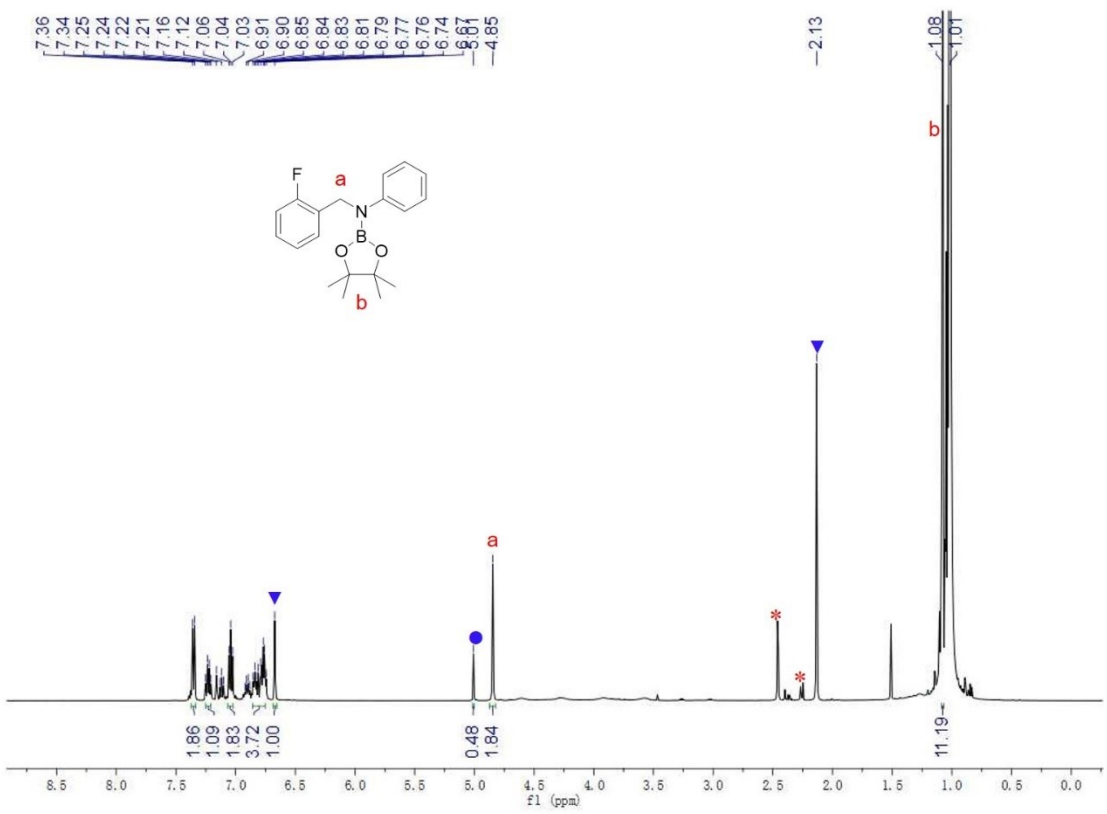


Fig. S41. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 2-fluoro-N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_4F$-*o* (500 MHz, C_6D_6, 25 °C, **2i**, Table 2).

N-(2-Fluorobenzyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[12] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.35 (d, *J* = 8.1 Hz, 2H, -*Ph*), 7.23 (dd, *J* = 14.9, 7.5 Hz, 1H, -*Ph*), 7.04 (t, *J* = 7.9 Hz, 2H, -*Ph*), 6.78 - 6.76 (m, 4H, -*Ph*), 4.85 (s, 2H, -NCH_2PhF), 1.08 (s, 12H, -NB*pin*).

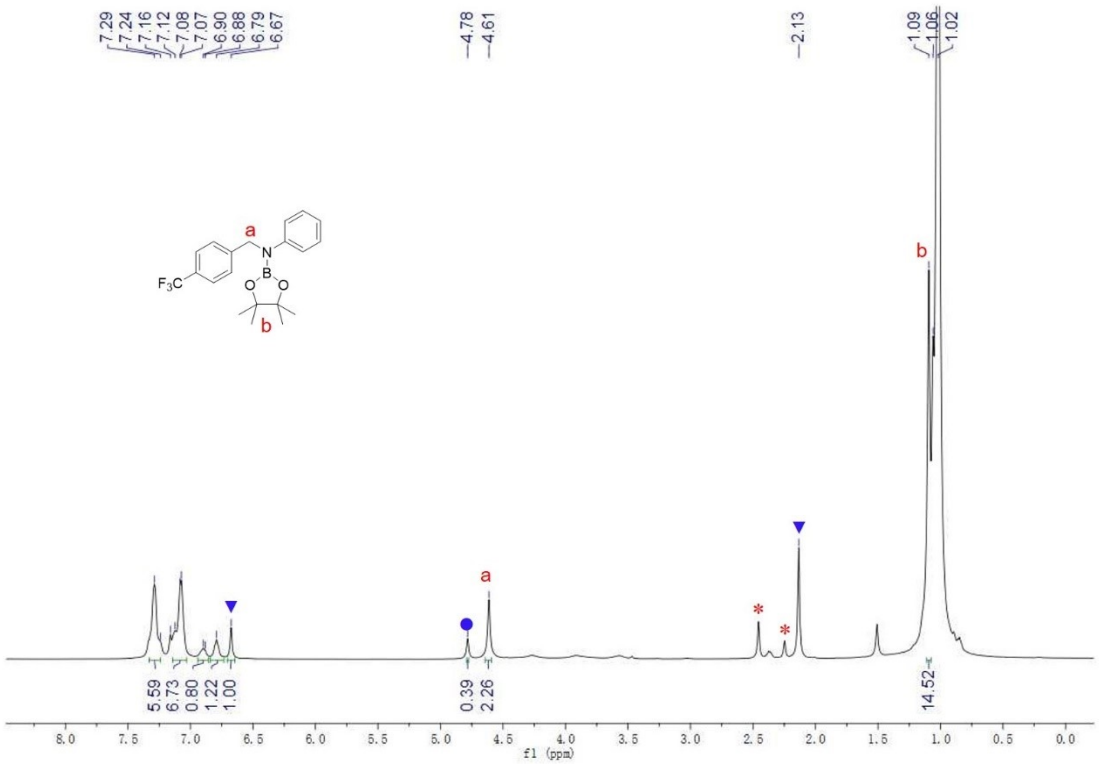


Fig. S42. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-phenyl-4-(trifluoromethyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_4CF_3$-*p* (500 MHz, C_6D_6, 25 °C, **2j**, Table 2).

N-(4-(Trifluoromethyl)Benzyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-A-mine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.26 (d, *J* = 24.3 Hz, 3H, -*Ph*), 7.14 - 7.03 (m, 4H, -*Ph*), 6.89 (d, *J* = 7.0 Hz, 1H, -*Ph*), 6.79 (s, 1H), 4.61 (s, 2H, -N*C*H_2PhCF_3), 1.09 (s, 12H, -NB*pin*).

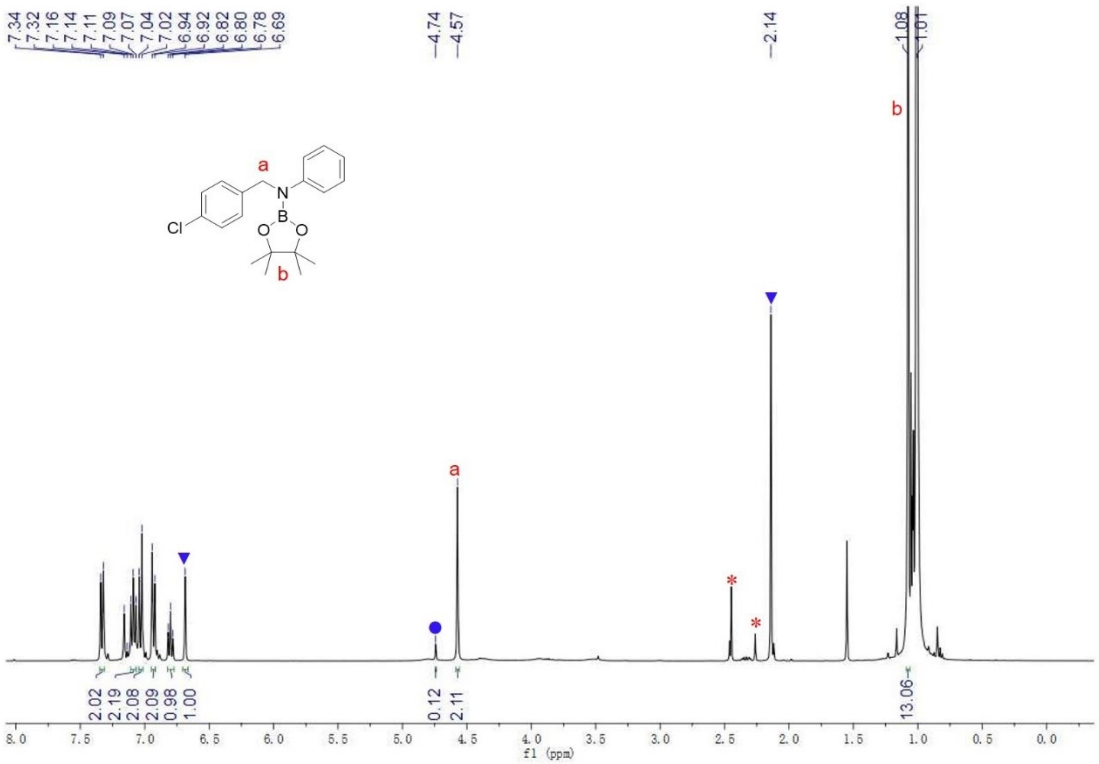


Fig. S43. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-chloro-N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4Cl$-*p* (400 MHz, C_6D_6, 25 °C, **2k**, Table 2).

N-(4-Chlorobenzyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[11] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.33 (d, *J* = 7.9 Hz, 2H, -*Ph*), 7.12 - 7.06 (m, 2H, -*Ph*), 7.03 (d, *J* = 8.4 Hz, 2H, -*Ph*), 6.93 (d, *J* = 8.4 Hz, 2H, -*Ph*), 6.80 (t, *J* = 7.3 Hz, 1H, -*Ph*), 4.57 (s, 2H, -NC*H*$_2$PhCl), 1.08 (s, 12H, -NB*pin*).

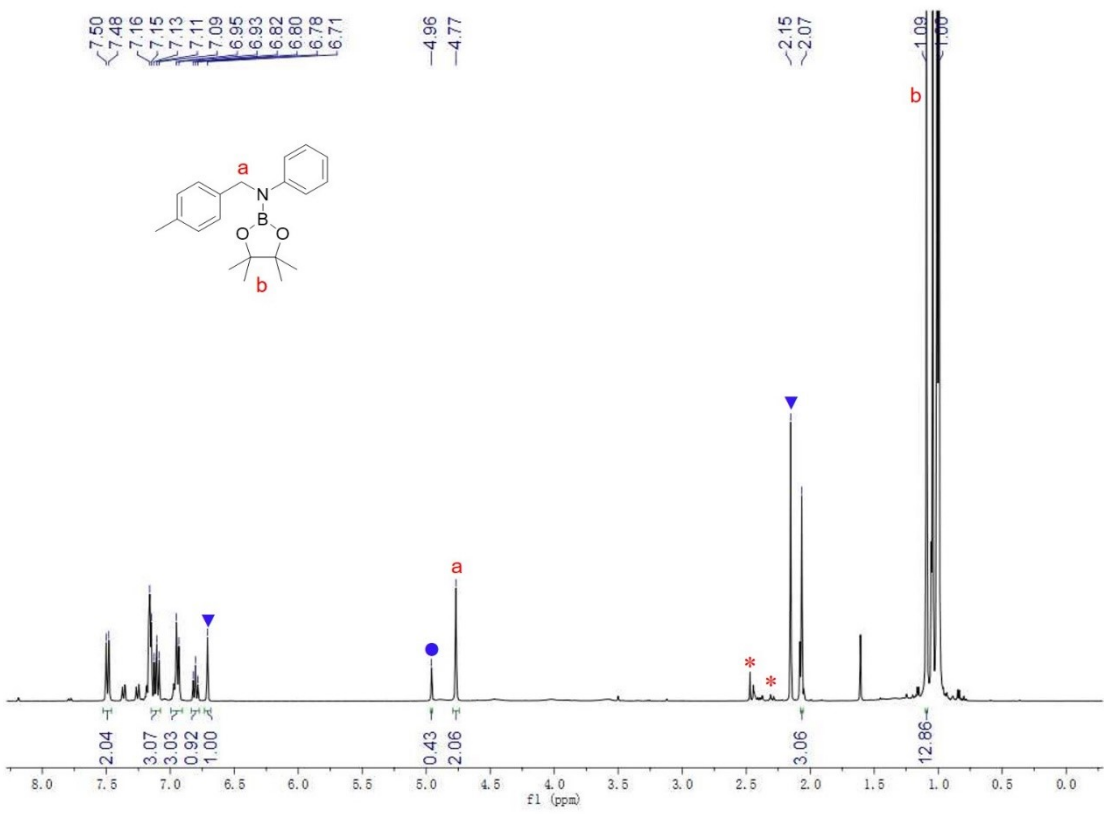


Fig. S44. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-methyl-N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_4$Me-*p* (400 MHz, C_6D_6, 25 °C, **2l**, Table 2).

N-(4-Methylbenzyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[11] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.49 (d, *J* = 7.8 Hz, 2H, -*Ph*), 7.13 - 7.08 (m, 3H, -*Ph*), 6.94 (d, *J* = 7.9 Hz, 3H, -*Ph*), 6.80 (t, *J* = 7.3 Hz, 1H, -*Ph*), 4.77 (s, 2H, -NC*H*$_2$PhCH$_3$), 2.07 (s, 3H, -NCH$_2$PhC*H*$_3$), 1.09 (s, 12H, -NB*pin*).

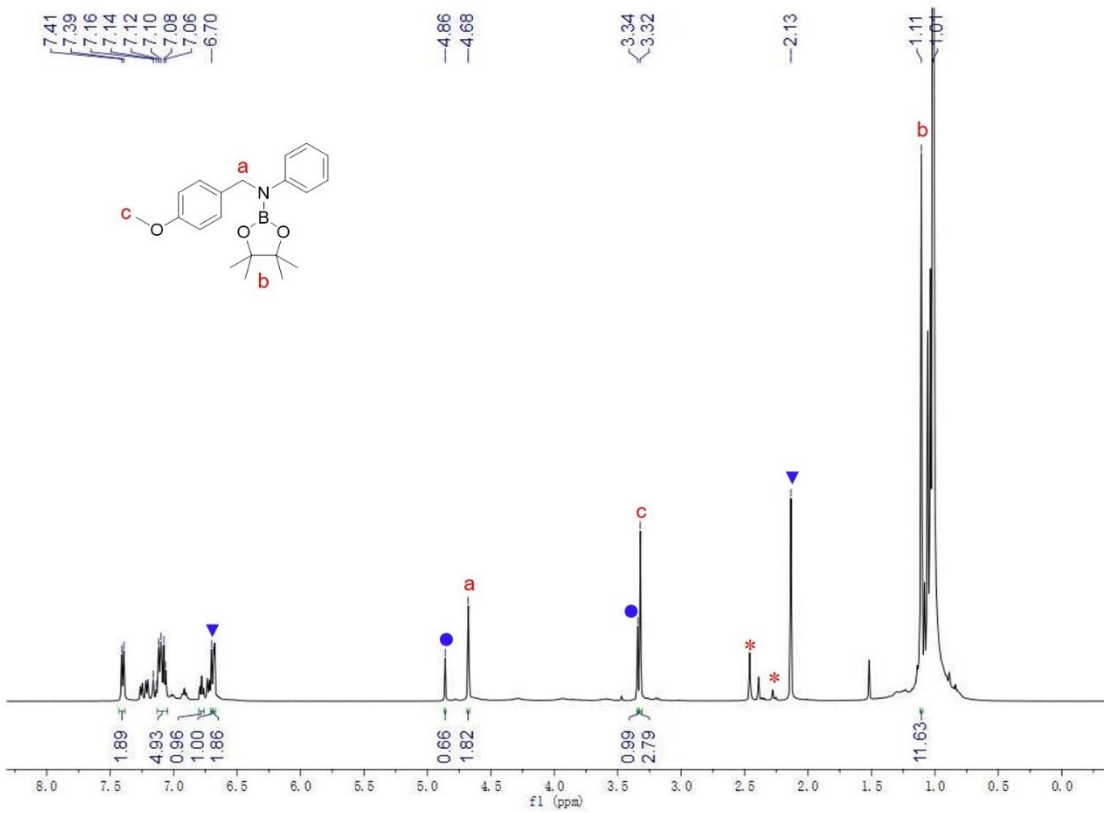


Fig. S45. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-methoxy-N-phenylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinB$OCH_2C_6H_4OMe$-*p* (500 MHz, C_6D_6, 25 °C, **2m**, Table 2).

N-(4-Methoxybenzyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[11]

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.40 (d, *J* = 8.3 Hz, 2H, -*Ph*), 7.16 - 7.03 (m, 5H, -*Ph*), 6.78 (td, *J* = 7.4, 0.8 Hz, 1H, -*Ph*), 6.68 (d, *J* = 3.6 Hz, 2H, -*Ph*), 4.68 (s, 2H, -NCH_2PhOCH_3), 3.32 (s, 3H, -NCH_2PhOCH_3), 1.11 (s, 12H, -NB*pin*).

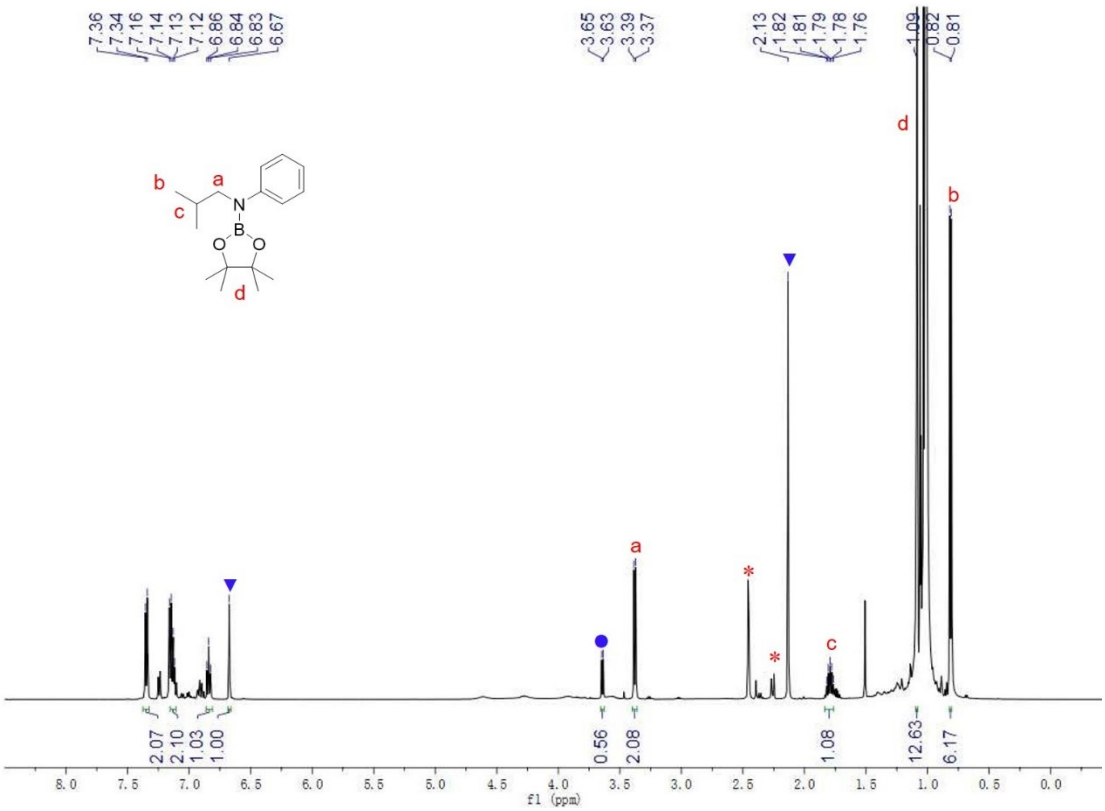


Fig. S46. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-phenylisobutyramide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2CH(CH_3)_2$ (500 MHz, C_6D_6, 25 °C, **2n**, Table 2).

N-Isobutyl-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.35 (d, *J* = 8.0 Hz, 2H, -*Ph*), 7.15 - 7.10 (m, 2H, -*Ph*), 6.84 (t, *J* = 7.3 Hz, 1H, -*Ph*), 3.38 (d, *J* = 7.3 Hz, 2H, -N*C*H_2CH$(CH_3)_2$), 1.79 (dt, *J* = 13.6, 6.8 Hz, 1H, -NCH$_2$C*H*$(CH_3)_2$), 1.09 (s, 12H, -NB*pin*), 0.81 (d, *J* = 6.7 Hz, 6H, -NCH$_2$CH(CH_3)$_2$).

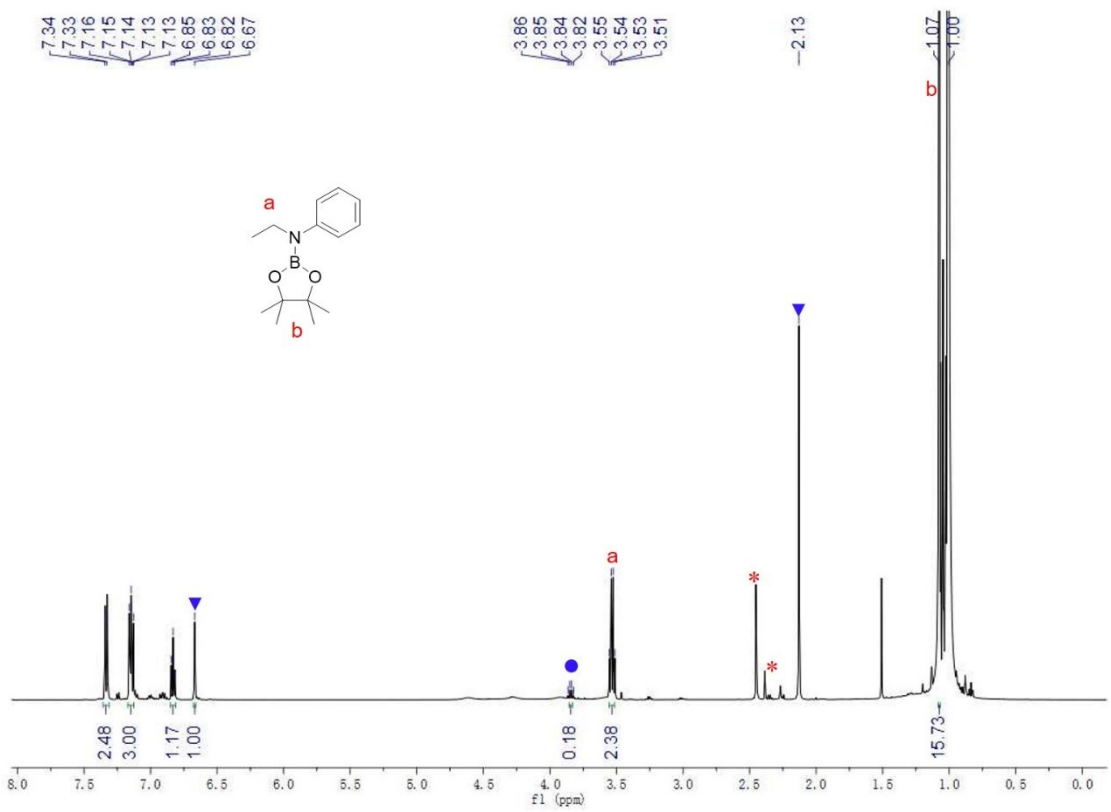


Fig. S47. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-phenylacetamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2CH_3$ (500 MHz, C_6D_6, 25 ^{o}C, **2o**, Table 2).

N-Propyl-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[13] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.34 (d, *J* = 7.9 Hz, 2H, -*Ph*), 7.17 - 7.12 (m, 2H, -*Ph*), 6.83 (t, *J* = 6.8 Hz, 1H, -*Ph*), 3.53 (q, *J* = 7.0 Hz, 2H, -NC*H*$_2$CH$_3$), 1.07 (s, 12H, -NB*pin*).

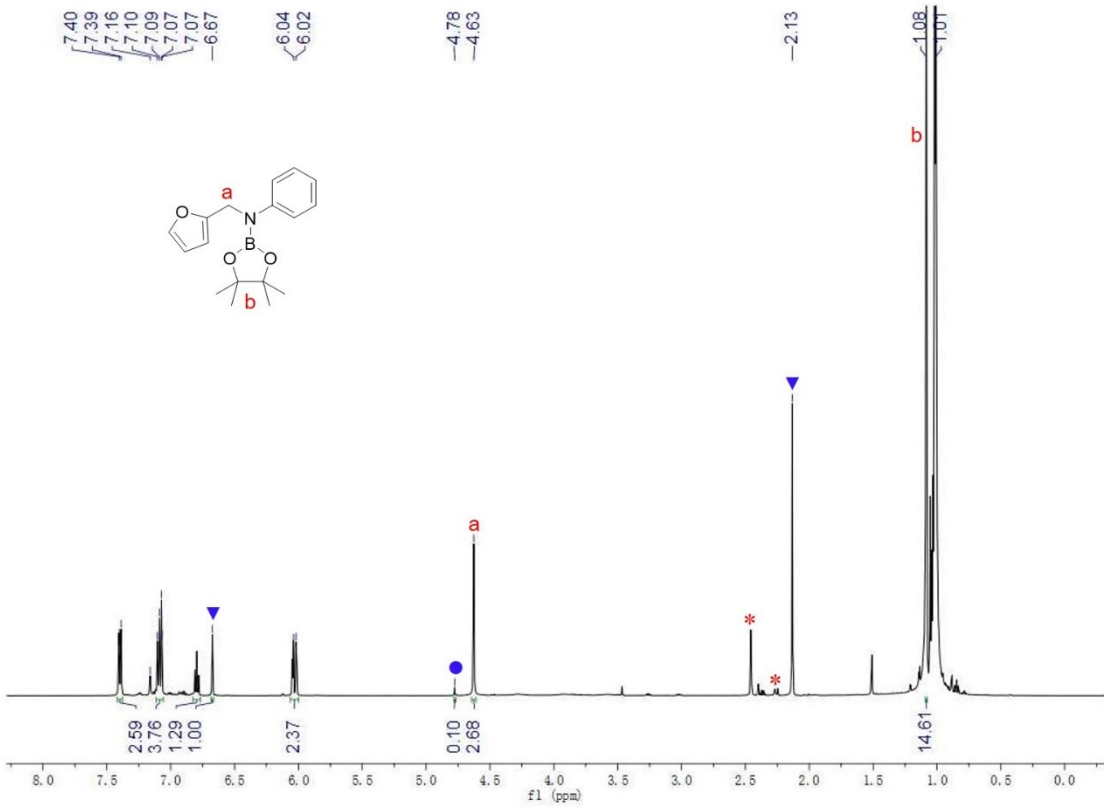


Fig. S48. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-phenylthiophene-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinB$OCH_2C_4H_3O$ (500 MHz, C_6D_6, 25 °C, **2p**, Table 2).

N-(Furan-2-Ylmethyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.40 (d, *J* = 7.8 Hz, 2H, -*Ph*), 7.11 - 7.07 (m, 3H, -*Ph*), 6.82 - 6.77 (m, 1H, -NC$H_2C_4H_3O$), 6.03 (d, *J* = 9.2 Hz, 2H, -NC$H_2C_4H_3O$), 4.63 (s, 2H, -NC$H_2C_4H_3O$), 1.08 (s, 12H, -NB*pin*).

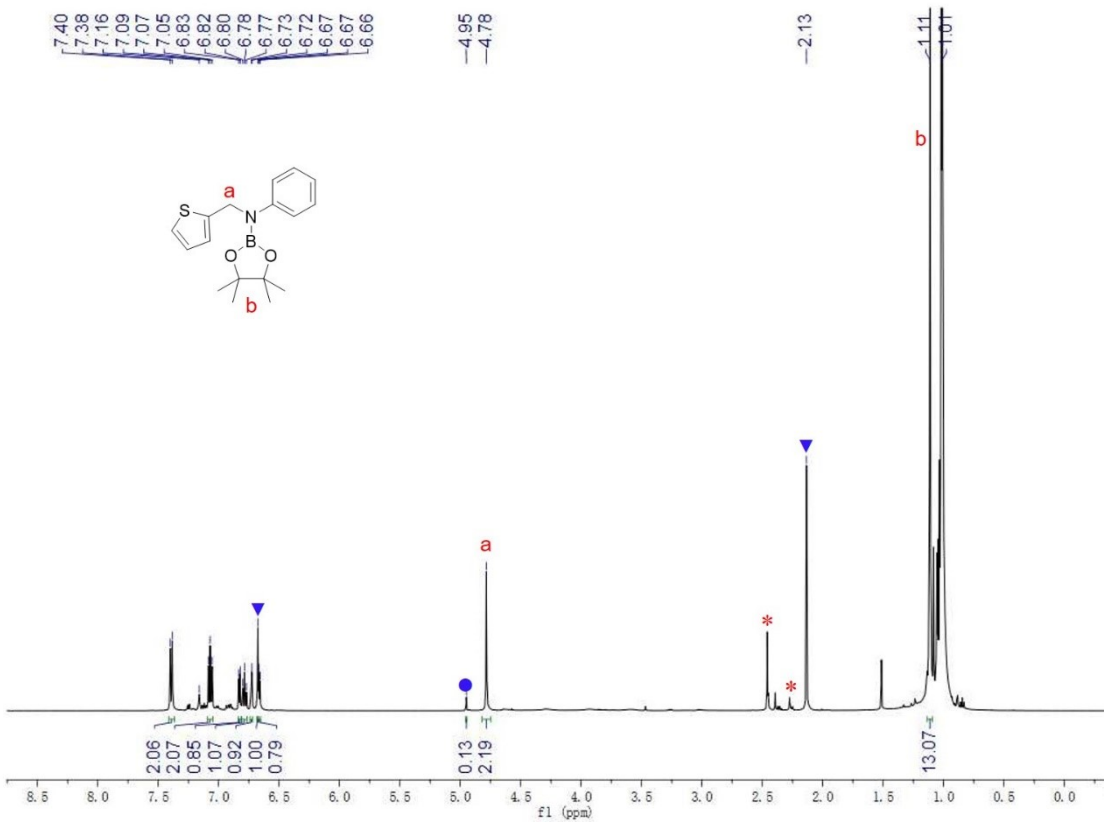


Fig. S49. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-phenylfuran-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_4H_3S$ (500 MHz, C_6D_6, 25 °C, **2q**, Table 2).

N-(Thiophen-2-Ylmethyl)-N-Phenyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.39 (d, *J* = 7.9 Hz, 2H, -*Ph*), 7.09 - 7.04 (m, 2H, -*Ph*), 6.83 (d, *J* = 6.0 Hz, 1H, -$NCH_2C_4H_3S$), 6.78 (t, *J* = 7.3 Hz, 1H, -*Ph*), 6.73 (d, *J* = 2.5 Hz, 1H, -$NCH_2C_4H_3S$), 6.66 (d, *J* = 5.0 Hz, 1H, -$NCH_2C_4H_3S$), 4.78 (s, 2H, -$NCH_2C_4H_3S$), 1.11 (s, 12H, -NB*pin*).

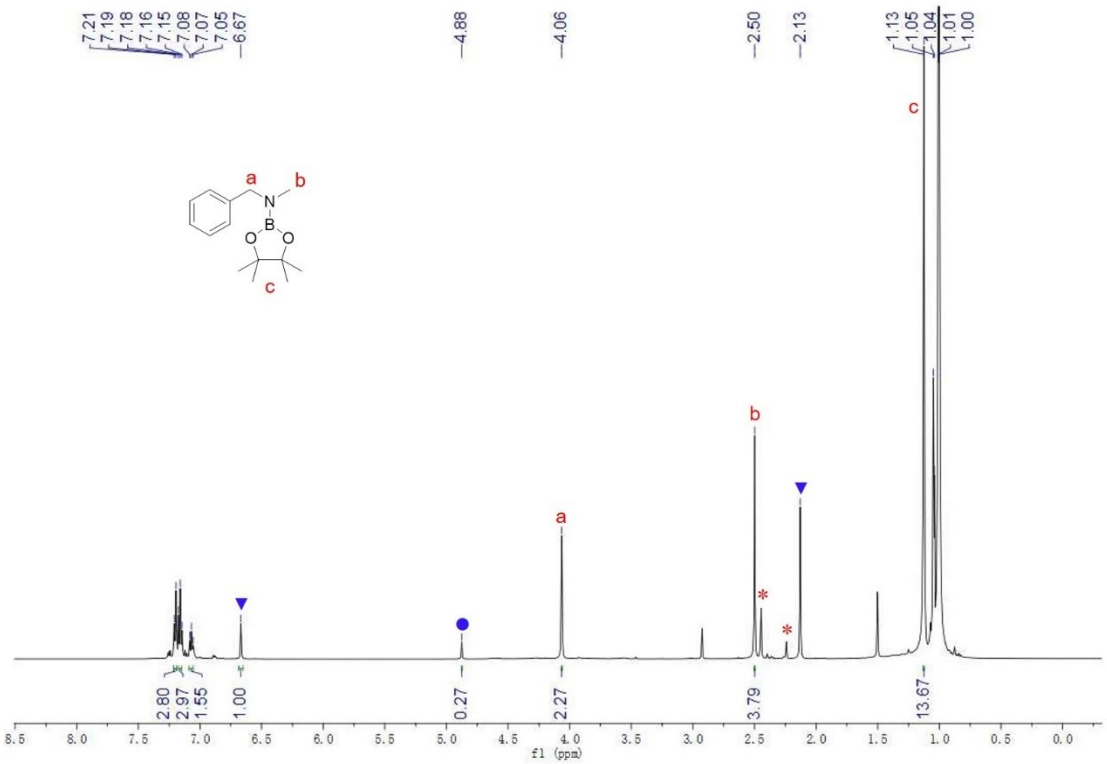


Fig. S50. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_5$ (500 MHz, C_6D_6, 25 ^{o}C, **2r**, Table 2).

N-Benzyl-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine.[3] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.20 (d, *J* = 7.2 Hz, 2H, -*Ph*), 7.16 (t, *J* = 7.5 Hz, 2H, -*Ph*), 7.07 (t, *J* = 7.1 Hz, 1H, -*Ph*), 4.06 (s, 2H, -NC*H*$_2$Ph), 2.50 (s, 3H, -NC*H*$_3$), 1.13 (s, 12H, -NB*pin*).

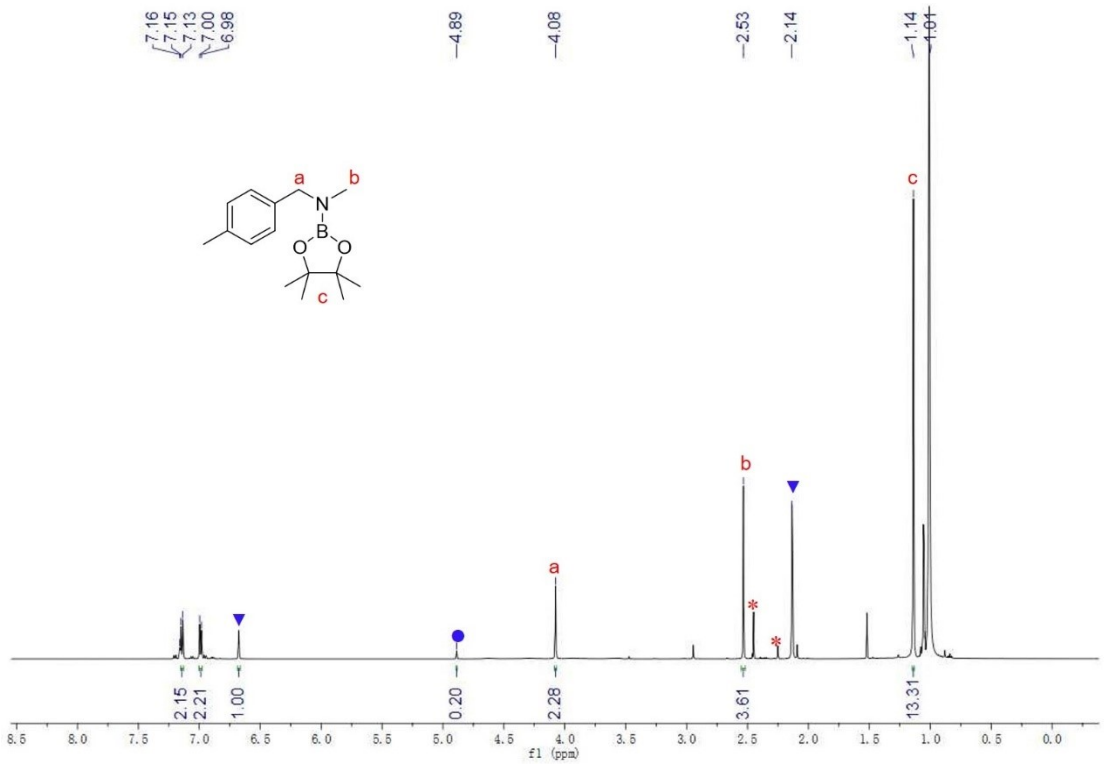


Fig. S51. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N,4-dimethylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4Me$-*p* (500 MHz, C_6D_6, 25 °C, **2s**, Table 2).

N-(4-Methylbenzyl)-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.14 (d, *J* = 7.9 Hz, 2H, -*Ph*), 6.99 (d, *J* = 7.8 Hz, 2H, -*Ph*), 4.08 (s, 2H, -NCH_2PhCH_3), 2.53 (s, 3H, -NCH_3), 1.14 (s, 12H, -NB*pin*).

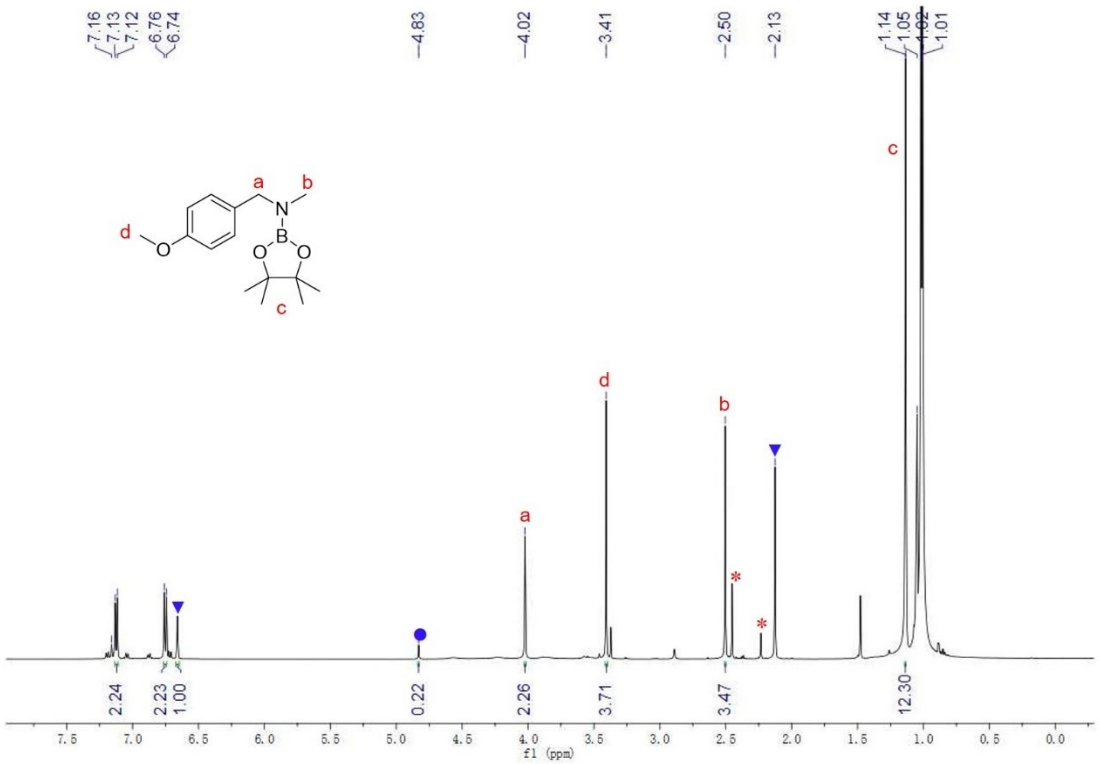


Fig. S52. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-methoxy-N-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinB$OCH_2C_6H_4OMe$-*p* (500 MHz, C_6D_6, 25 °C, **2t**, Table 2).

N-(4-Methoxybenzyl)-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine.[14] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.12 (d, *J* = 8.5 Hz, 2H, -*Ph*), 6.75 (d, *J* = 8.6 Hz, 2H, -*Ph*), 4.02 (s, 2H, -NC*H*$_2$PhOCH_3), 3.41 (s, 3H, -NCH$_2$PhOC*H*$_3$), 2.50 (s, 3H, -NC*H*$_3$), 1.14 (s, 12H, -NB*pin*).

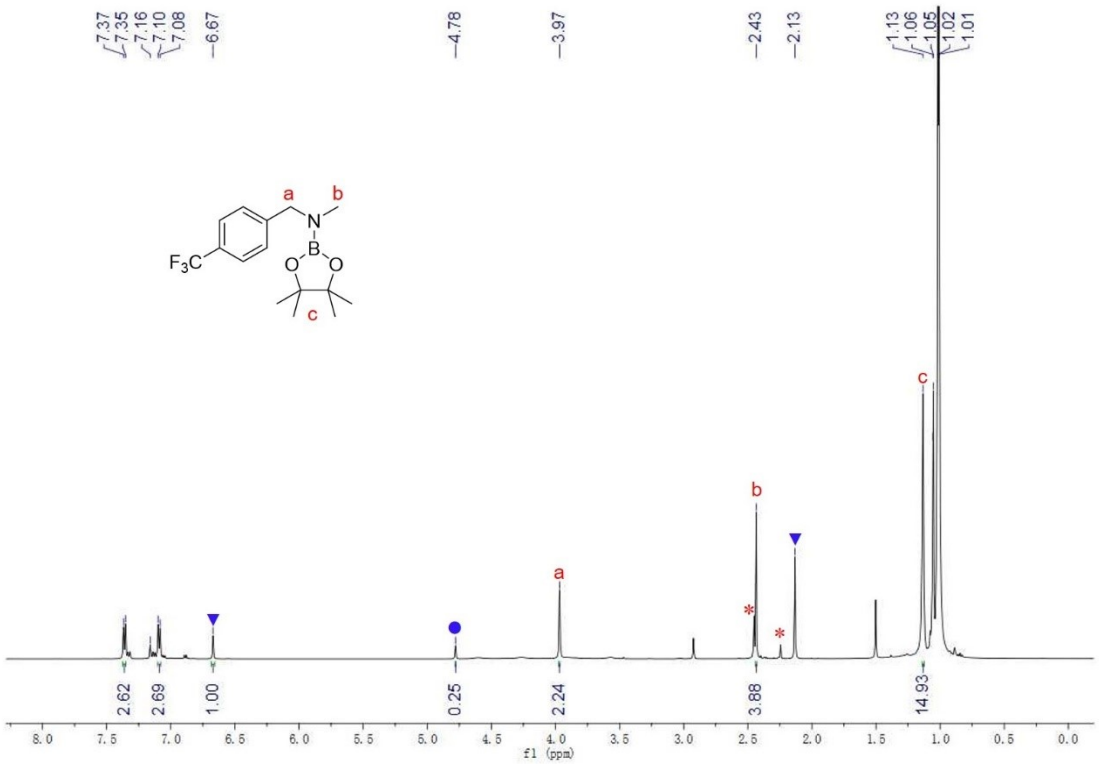


Fig. S53. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-methyl-4-(trifluoromethyl)benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_4CF_3$-*p* (500 MHz, C_6D_6, 25 °C, **2u**, Table 2).

N-(4-(Trifluoromethyl)benzyl)-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.36 (d, *J* = 8.0 Hz, 2H, -*Ph*), 7.09 (d, *J* = 7.9 Hz, 2H, -*Ph*), 3.97 (s, 2H, -NCH_2PhCF$_3$), 2.43 (s, 3H, -NCH_3), 1.13 (s, 12H, -NB*pin*).

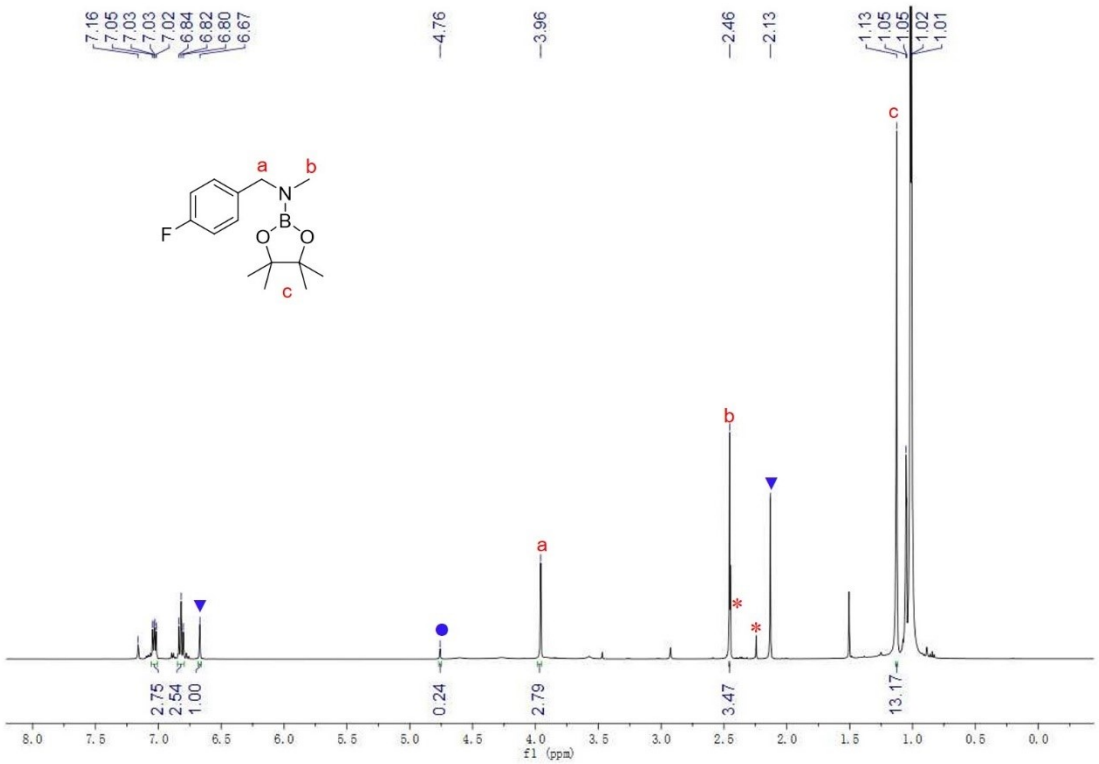


Fig. S54. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-fluoro-N-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4F$-*p* (500 MHz, C_6D_6, 25 °C, **2v**, Table 2).

N-(4-Fluorobenzyl)-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.03 (dd, *J* = 8.6, 5.5 Hz, 2H, -*Ph*), 6.82 (t, *J* = 8.7 Hz, 2H, -*Ph*), 3.96 (s, 2H, -NCH_2PhF), 2.46 (s, 3H, -NCH_3), 1.13 (s, 12H, -NB*pin*).

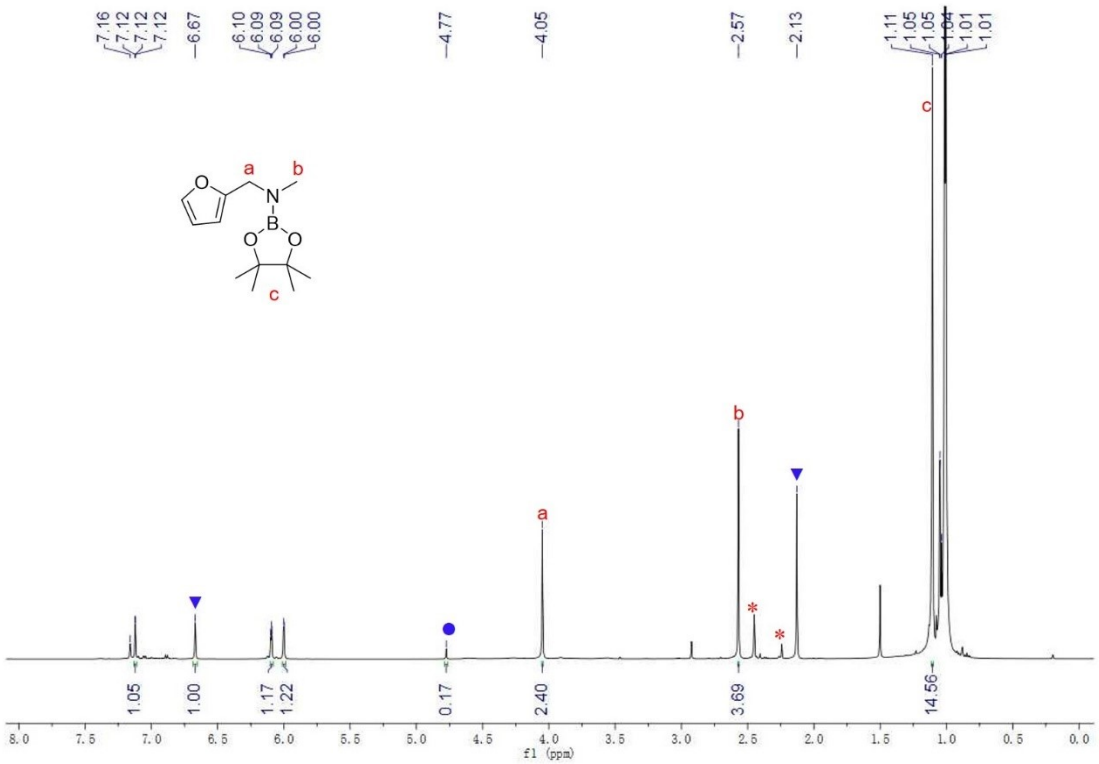


Fig. S55. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-methylfuran-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_4H_3O$ (500 MHz, C_6D_6, 25 °C, **2w**, Table 2).

N-(Furan-2-Ylmethyl)-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.14 - 7.10 (m, 1H, -$NCH_2C_4H_3O$), 6.11 - 6.08 (m, 1H, -$NCH_2C_4H_3O$), 6.00 (d, *J* = 3.1 Hz, 1H, -$NCH_2C_4H_3O$), 4.05 (s, 2H, -$NCH_2C_4H_3O$), 2.57 (s, 3H, -NCH_3), 1.11 (s, 12H, -NB*pin*).

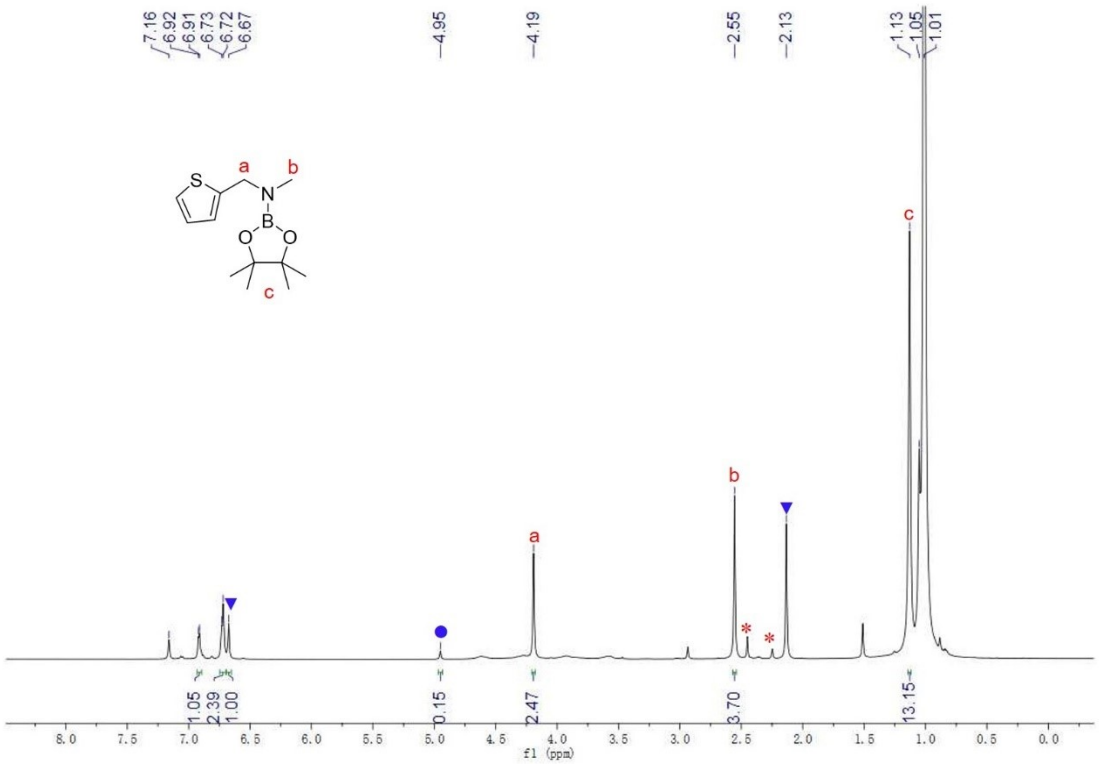


Fig. S56. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-methylthiophene-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_4H_3S$ (500 MHz, C_6D_6, 25 °C, **2x**, Table 2).

N-(Thiophen-2-Ylmethyl)-N,4,4,5,5-Pentamethyl-1,3,2-Dioxaborolan-2-Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 6.92 (d, *J* = 4.3 Hz, 1H, -NCH$_2$C$_4$*H*$_3$S), 6.72 (d, *J* = 5.1 Hz, 2H, -NCH$_2$C$_4$*H*$_3$S), 4.19 (s, 2H, -NC*H*$_2$C$_4$H$_3$S), 2.55 (s, 3H, -NC*H*$_3$), 1.13 (s, 12H, -NB*pin*).

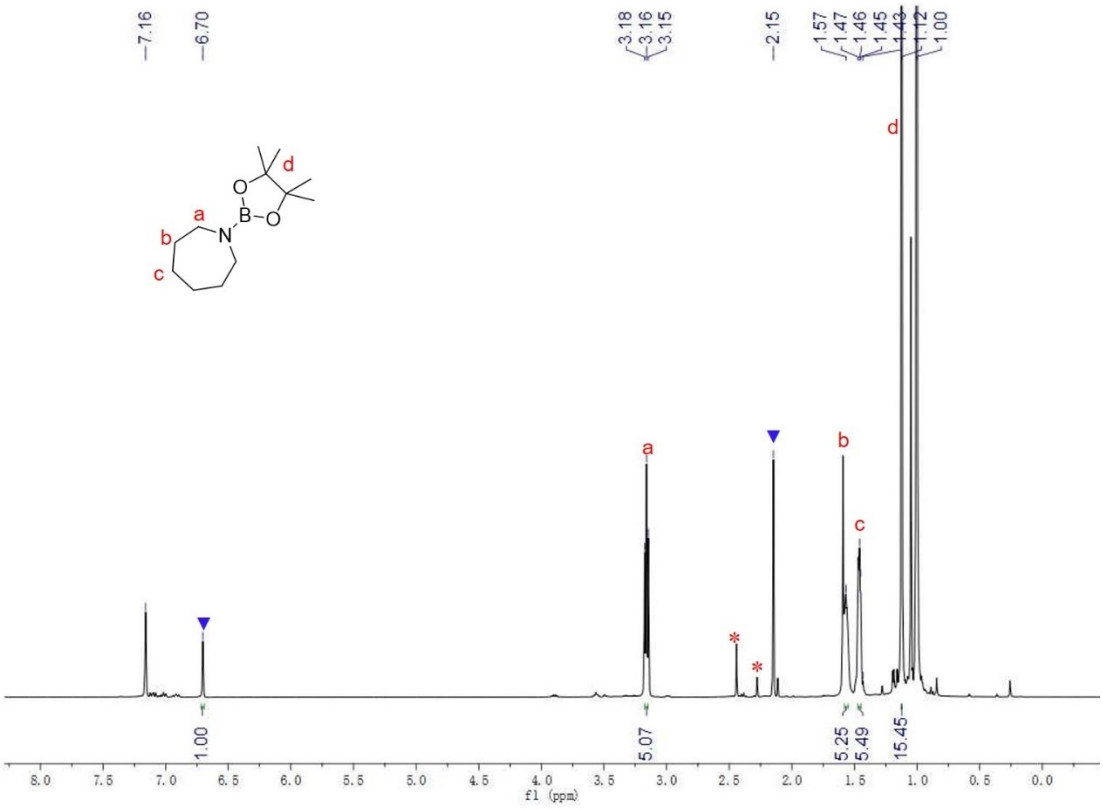


Fig. S57. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of azepan-2-one catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 °C, **2y**, Table 2).

1-(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)Azepane.[3] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 3.16 (t, *J* = 6.0 Hz, 4H, -NC_6H_{12}), 1.57 (s, 4H, -NC_6H_{12}), 1.50 - 1.44 (m, 4H, -NC_6H_{12}), 1.12 (s, 12H, -NB*pin*).

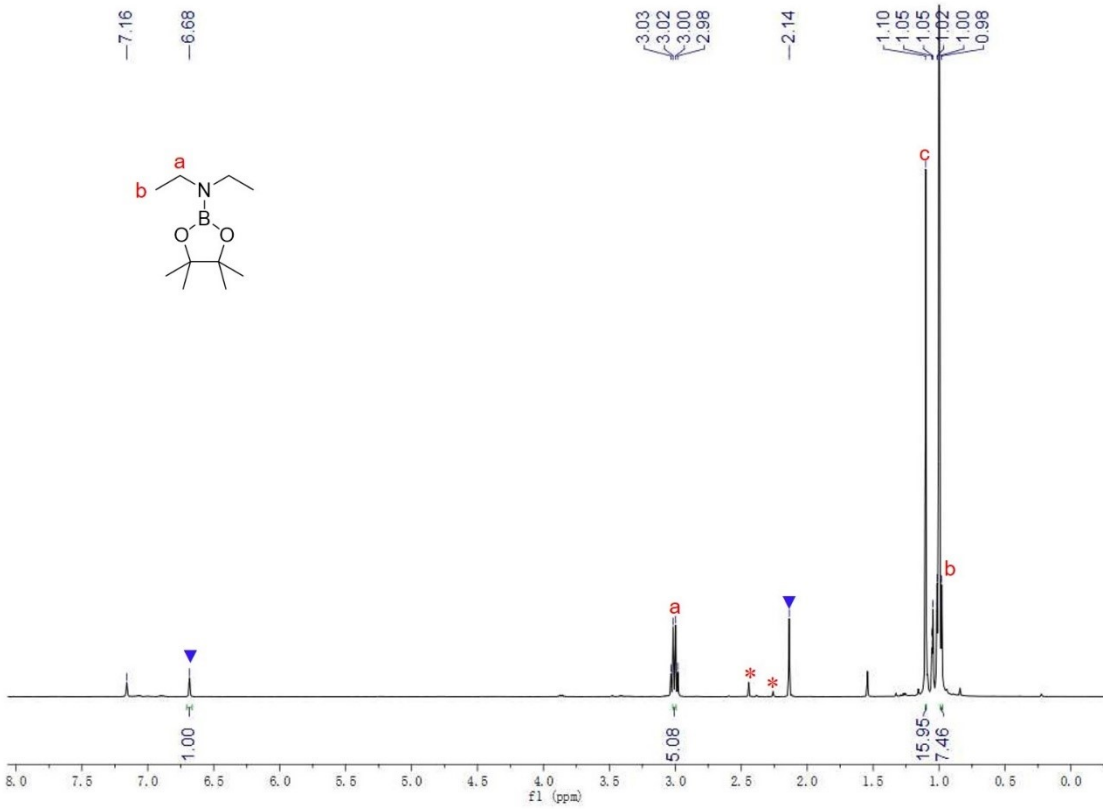


Fig. S58. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of N-ethylacetamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene (400 MHz, C_6D_6, 25 °C, **2z**, Table 2).

N,N-Diethyl-4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Amine.[3] ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 3.01 (q, *J* = 7.1 Hz, 4H, -N(CH_2CH_3)$_2$), 1.10 (s, 12H, -NB*pin*), 1.00 - 0.98 (m, 6H, -N(CH_2CH_3)$_2$).

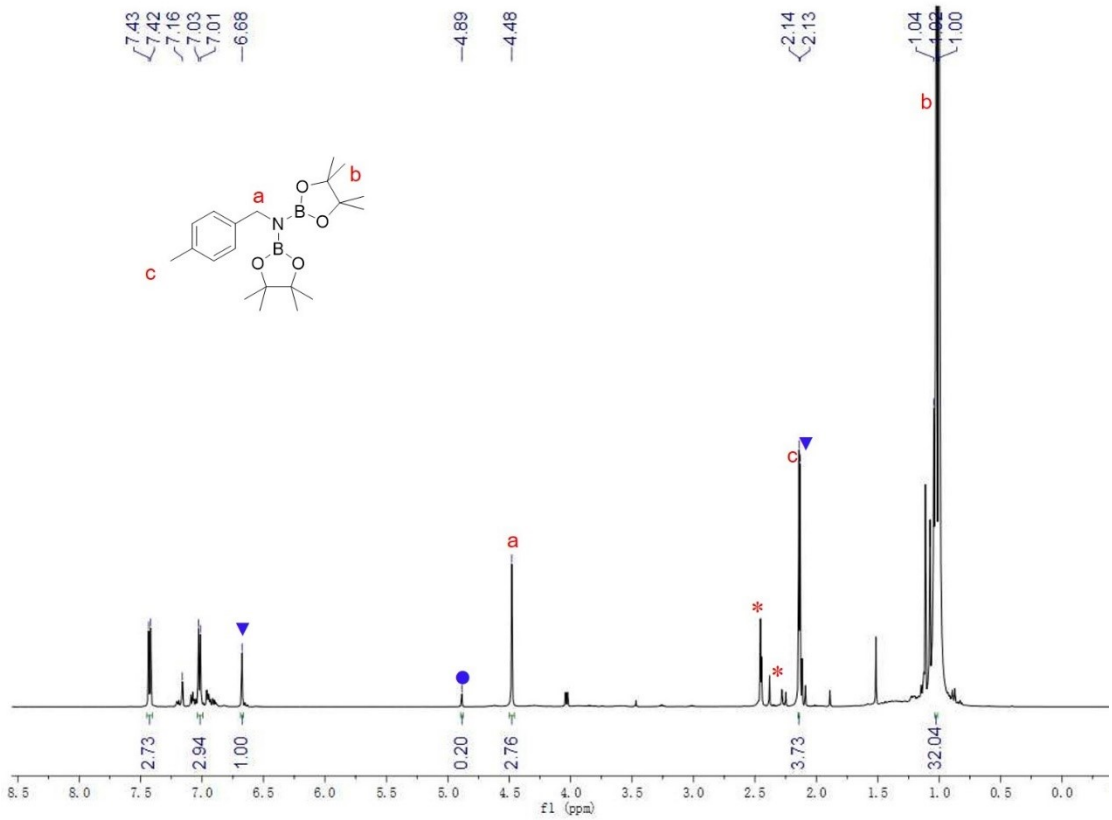


Fig. S59. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4Me$-*p* (500 MHz, C_6D_6, 25 ^{o}C, **3a**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(4-Methylbenzyl)Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.43 (d, *J* = 7.8 Hz, 2H, -*Ph*), 7.02 (d, *J* = 7.8 Hz, 2H, -*Ph*), 4.48 (s, 2H, -NC*H*$_2$PhCH$_3$), 2.14 (s, 2H, -NCH$_2$PhC*H*$_3$), 1.02 (s, 24H, -N(B*pin*)$_2$).

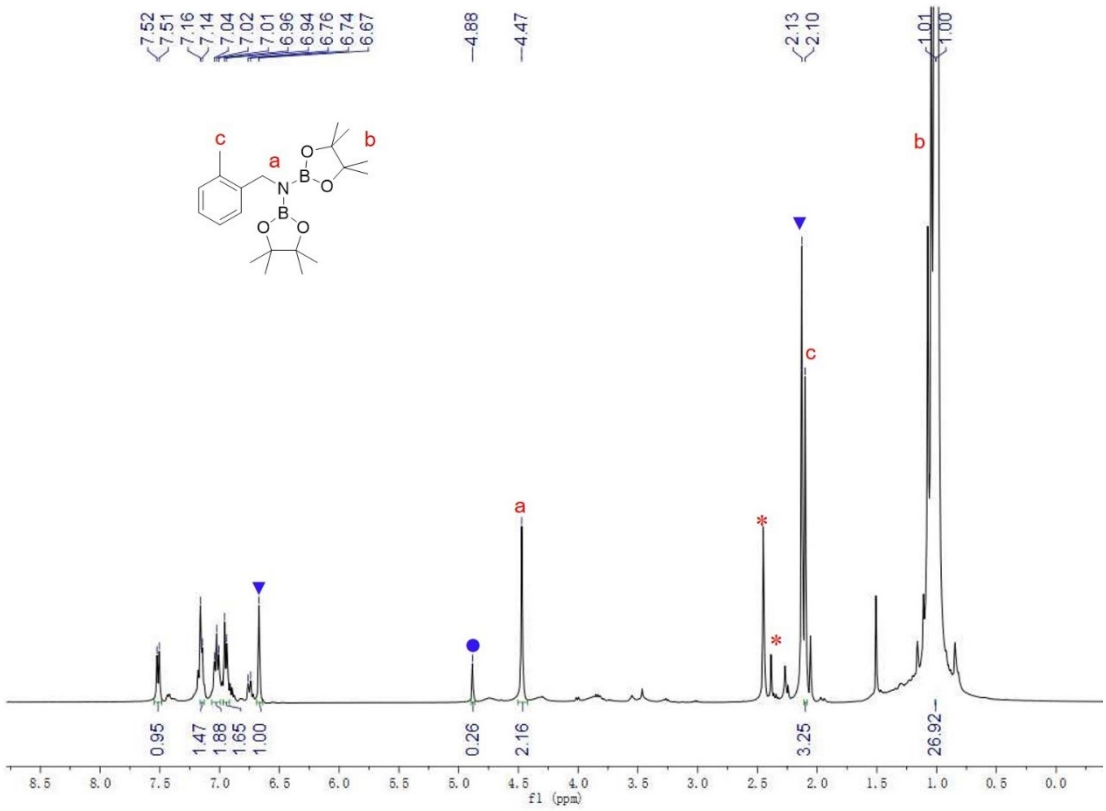


Fig. S60. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 2-methylbenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4Me$-*o* (400 MHz, C_6D_6, 25 ^{o}C, **3b**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(2-Methylbenzyl)Amine. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.51 (d, *J* = 7.6 Hz, 1H, -*Ph*), 7.14 (s, 1H, -*Ph*), 7.03 (t, *J* = 7.3 Hz, 1H, -*Ph*), 6.95 (d, *J* = 7.3 Hz, 1H, -*Ph*), 4.47 (s, 2H, -NC*H*$_2$PhCH$_3$), 2.10 (s, 3H, -NCH$_2$PhC*H*$_3$), 1.01 (s, 24H, -N(B*pin*)$_2$).

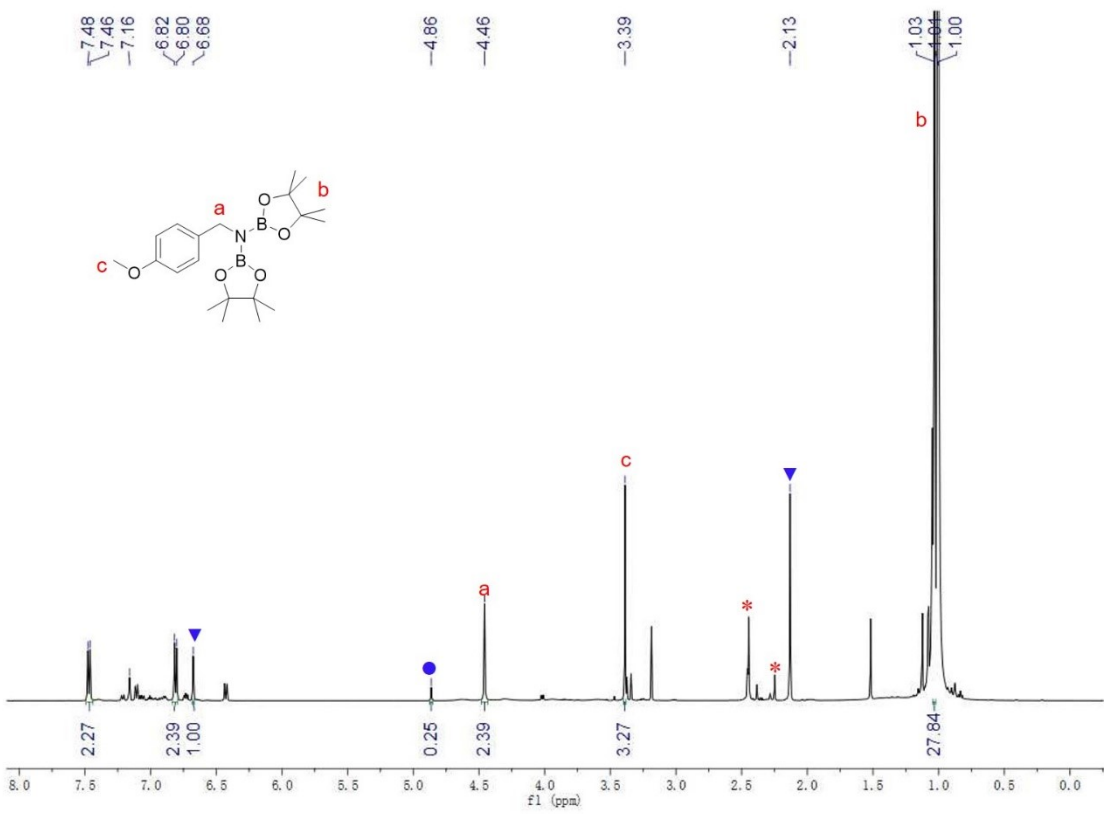


Fig. S61. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-methoxybenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4OMe$-*p* (500 MHz, C_6D_6, 25 ^{o}C, **3c**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(4-Methoxybenzyl)Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.47 (d, *J* = 8.5 Hz, 2H, -*Ph*), 6.81 (d, *J* = 8.5 Hz, 2H, -*Ph*), 4.46 (s, 2H, -NC*H*$_2$PhOCH$_3$), 3.39 (s, 3H, -NCH$_2$PhOC*H*$_3$), 1.03 (s, 24H, -N(B*pin*)$_2$).

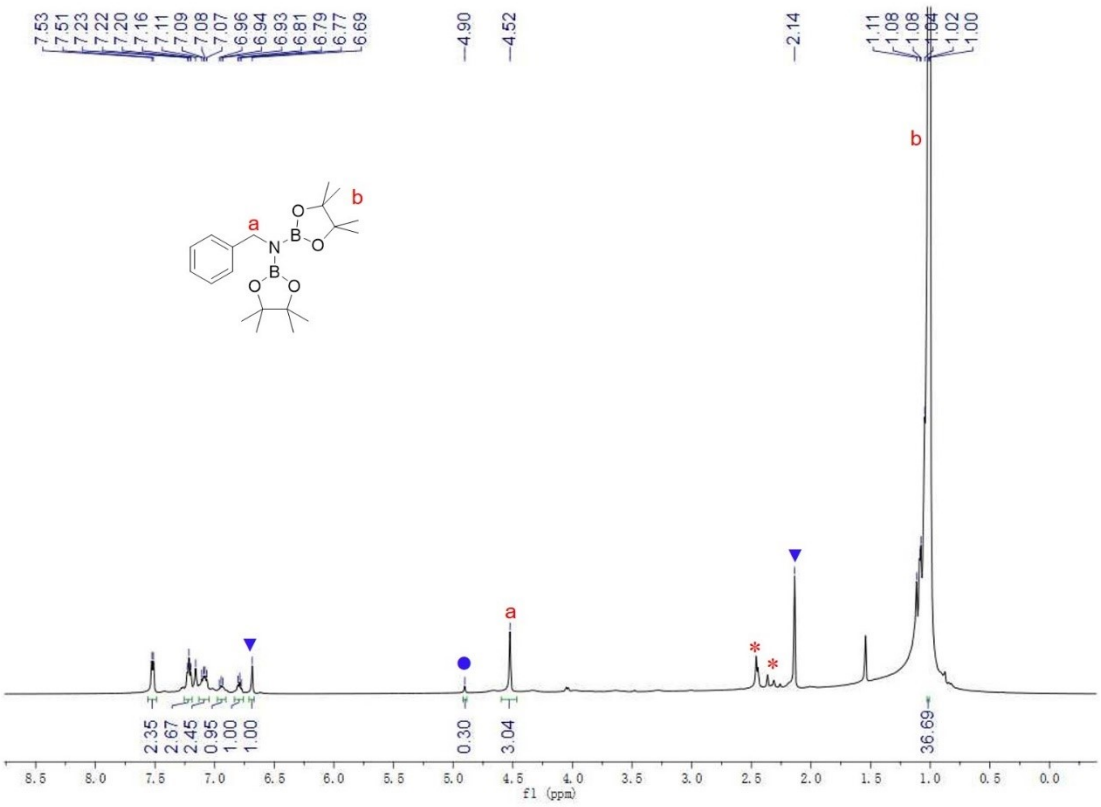


Fig. S62. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_5$ (500 MHz, C_6D_6, 25 °C, **3d**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)Benzylamine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.52 (d, *J* = 7.2 Hz, 2H, -*Ph*), 7.22 (t, *J* = 7.3 Hz, 1H, -*Ph*), 7.09 (dd, *J* = 13.7, 7.2 Hz, 2H, -*Ph*), 4.52 (s, 2H, -NC*H*$_2$Ph), 1.02 (s, 24H, -N(B*pin*)$_2$).

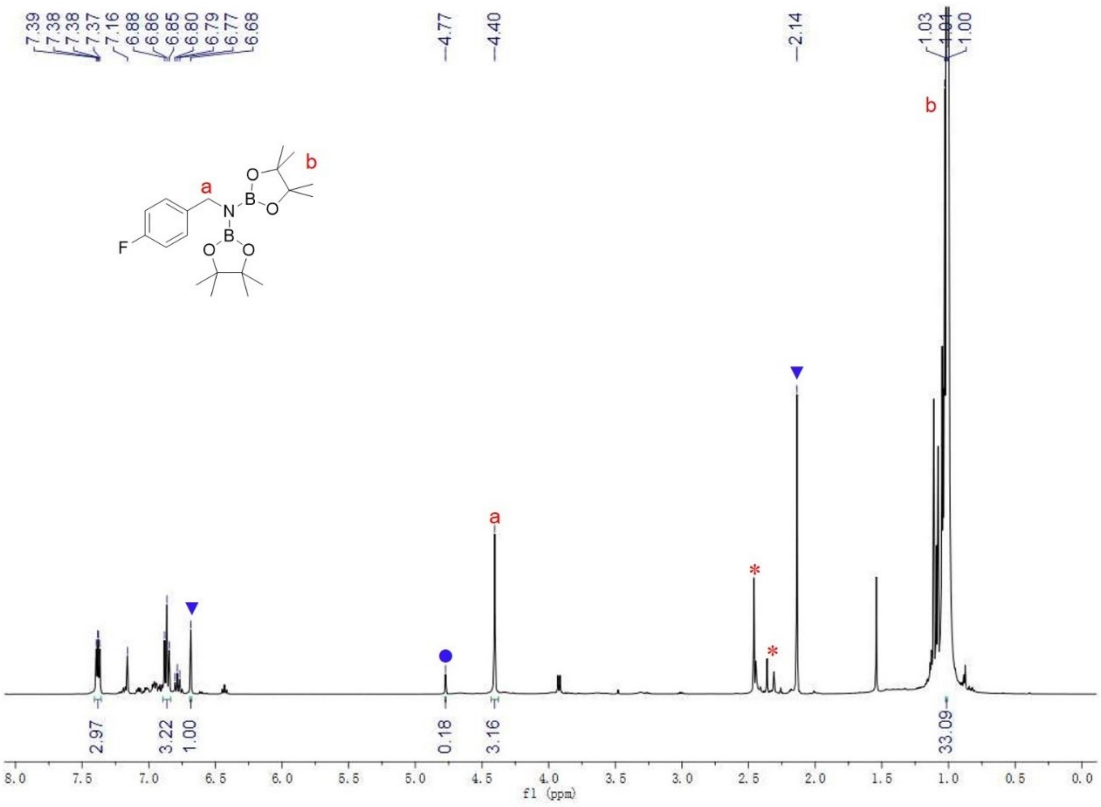


Fig. S63. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of benzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinBO$CH_2C_6H_4$F-*p* (500 MHz, C_6D_6, 25 °C, **3e**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(4-Fluorobenzyl)Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.38 (dd, *J* = 8.3, 5.7 Hz, 2H, -*Ph*), 6.86 (t, *J* = 8.7 Hz, 2H, -*Ph*), 4.40 (s, 2H, -NC*H*$_2$PhF), 1.01 (s, 24H, -N(B*pin*)$_2$).

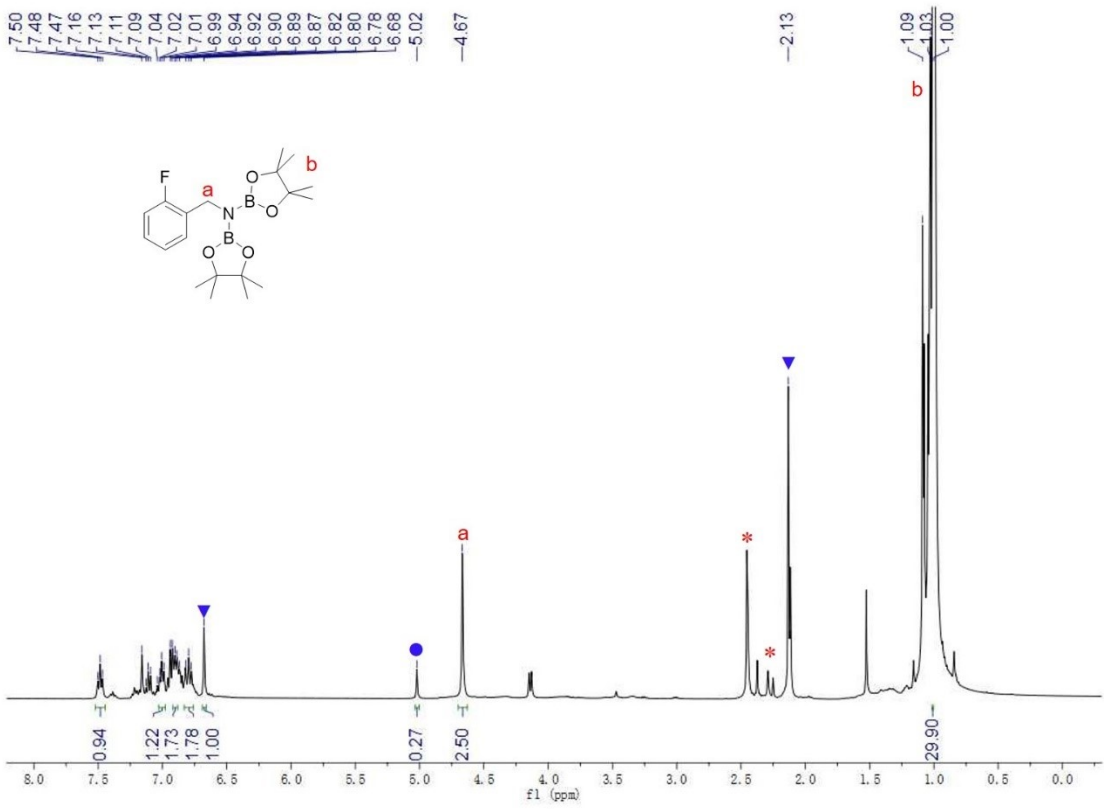


Fig. S64. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 2-fluorobenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4F$-*o* (400 MHz, C_6D_6, 25 ^{o}C, **3f**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(2-Fluorobenzyl)Amine. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.48 (t, *J* = 7.2 Hz, 1H, -*Ph*), 7.01 (t, *J* = 6.6 Hz, 1H, -*Ph*), 6.90 (dd, *J* = 14.4, 8.4 Hz, 1H, -*Ph*), 6.80 (t, *J* = 8.6 Hz, 1H, -*Ph*), 4.67 (s, 2H, -NCH_2PhF), 1.03 (s, 24H, -N(B*pin*)$_2$).

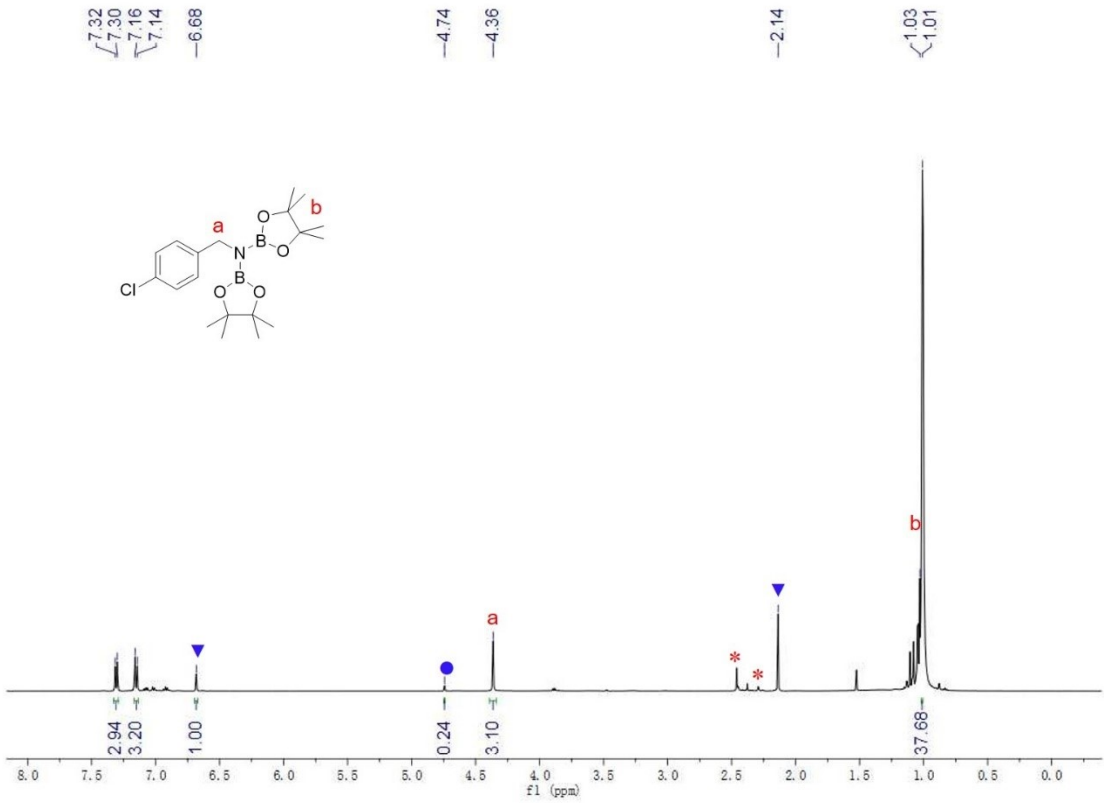


Fig. S65. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-chlorobenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4Cl$-*p* (500 MHz, C_6D_6, 25 ^{o}C, **3g**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(4-Chlorobenzyl)Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.31 (d, *J* = 8.3 Hz, 2H, -*Ph*), 7.15 (d, *J* = 8.4 Hz, 2H, -*Ph*), 4.36 (s, 2H, -NC*H*$_2$PhCl), 1.01 (s, 24H, -N(B*pin*)$_2$).

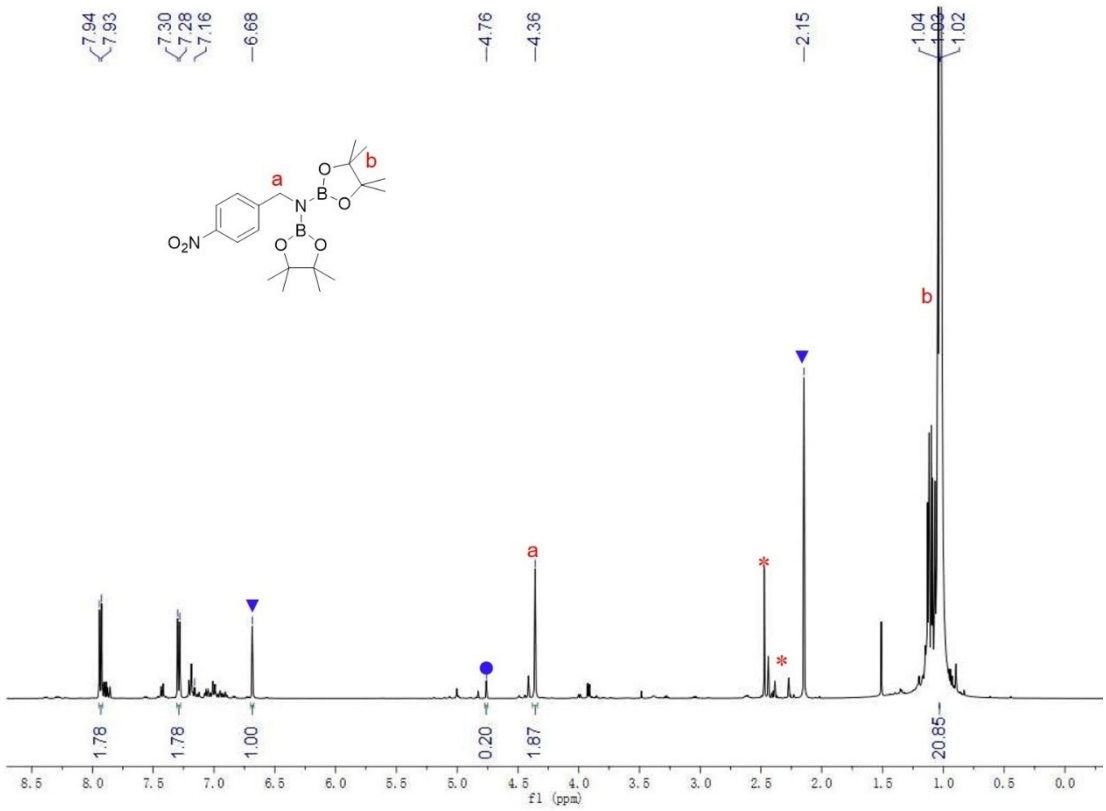


Fig. S66. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 4-nitrobenzamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_4NO_2$-*p* (500 MHz, C_6D_6, 25 °C, **3h**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(4-Nitrobenzyl)Amine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.93 (d, *J* = 8.8 Hz, 2H, -*Ph*), 7.29 (d, *J* = 8.8 Hz, 2H, -*Ph*), 4.36 (s, 2H, -NC*H*$_2$PhNO_2), 1.03 (s, 24H, -N(B*pin*)$_2$).

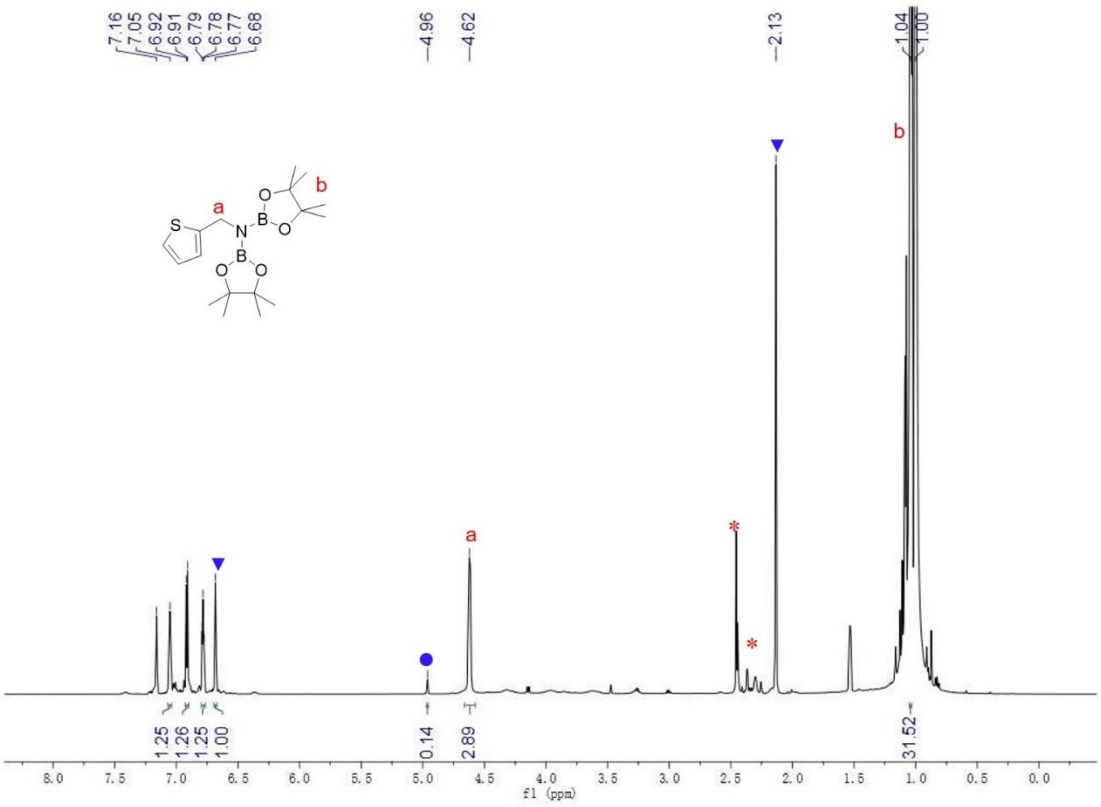


Fig. S67. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of thiophene-2-carboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_4H_3S$ (500 MHz, C_6D_6, 25 °C, **3i**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)-2-Thiophenemethylamine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.05 (s, 1H, -*Ph*), 6.91 (d, *J* = 5.1 Hz, 1H, -*Ph*), 6.78 (t, *J* = 4.0 Hz, 1H, -*Ph*), 4.62 (s, 2H, -NC*H*$_2$C$_4$H$_3$S), 1.04 (s, 24H, -N(B*pin*)$_2$).

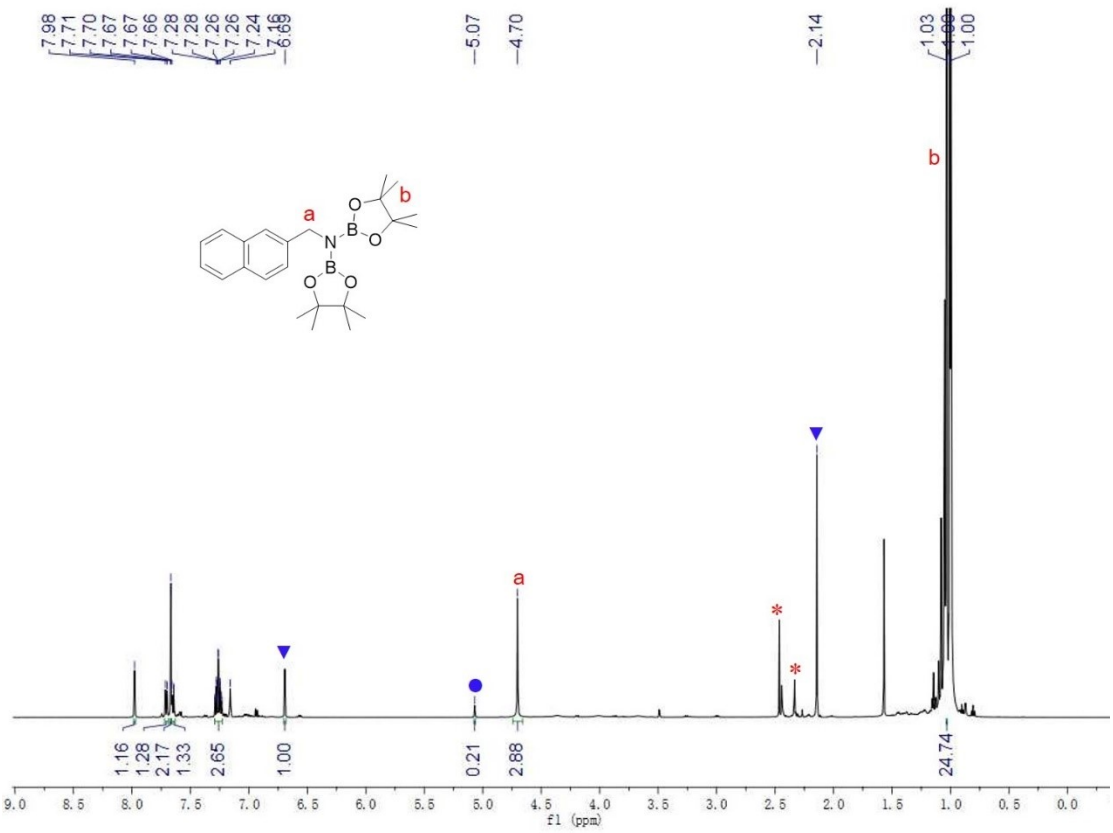


Fig. S68. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 2-naphthamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pinB$CH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pinB$OCH_2C_{10}H_7$ (500 MHz, C_6D_6, 25 °C, **3j**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)-1-(Naphthalen-2-Yl)Methanamine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.98 (s, 1H, -*Ph*), 7.71 (d, *J* = 7.3 Hz, 1H, -*Ph*), 7.67 (d, *J* = 1.1 Hz, 2H, -*Ph*), 7.66 - 7.64 (m, 1H, -*Ph*), 7.29 - 7.23 (m, 2H, -*Ph*), 4.70 (s, 2H, -NC*H*$_2$C$_{10}$H$_7$), 1.03 (s, 24H, -N(B*pin*)$_2$).

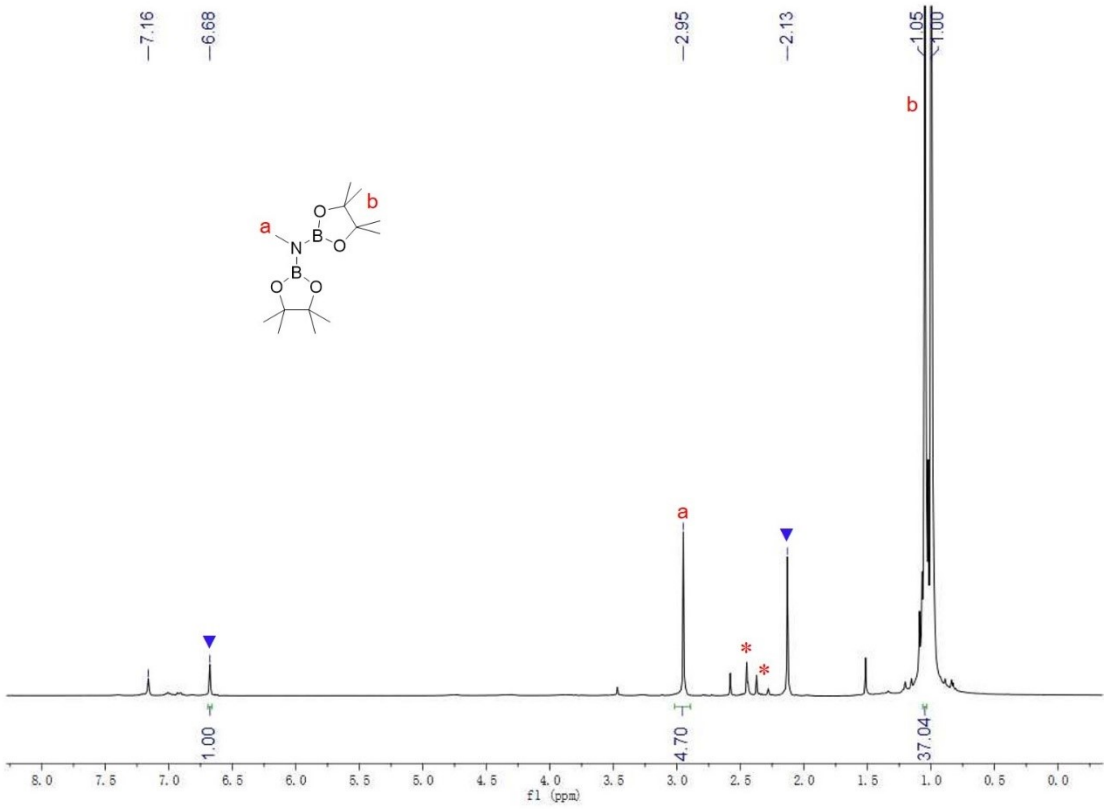


Fig. S69. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of acetamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, (400 MHz, C_6D_6, 25 °C, **3k**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)Methylamine. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 2.95 (s, 3H, -NC*H*$_3$), 1.05 (s, 24H, -N(B*pin*)$_2$).

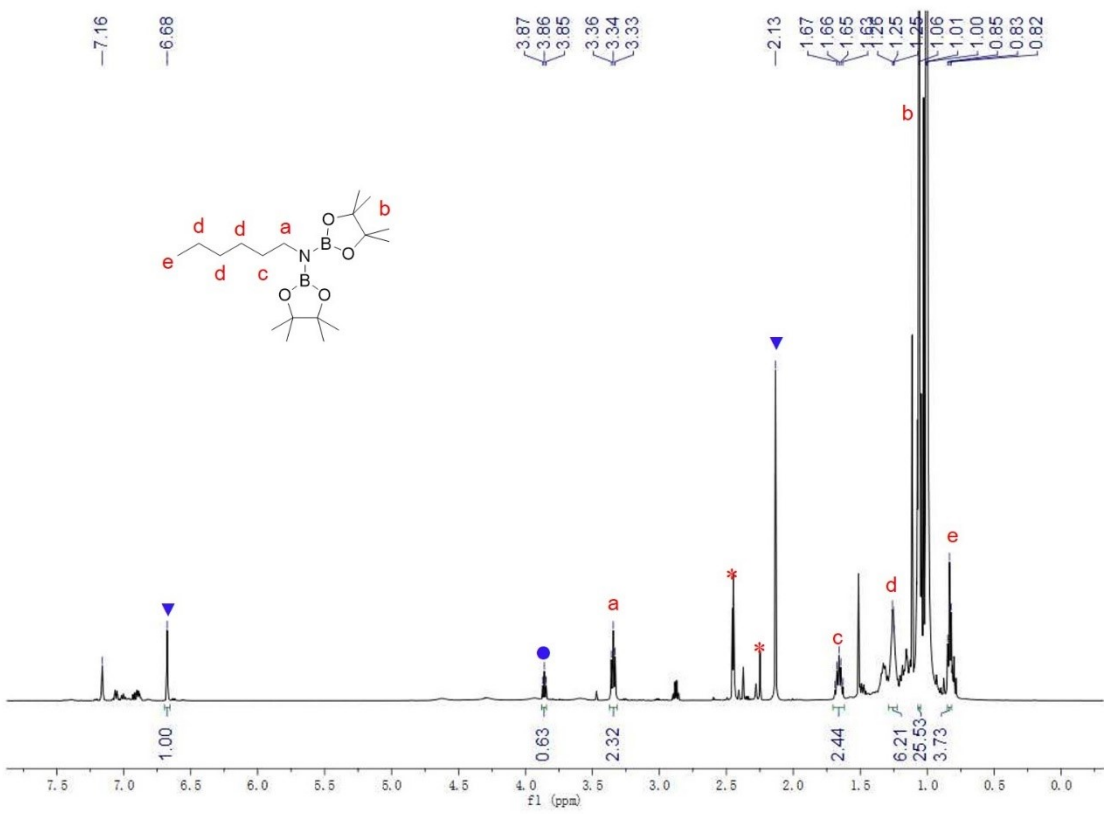


Fig. S70. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of hexanamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BO(CH_2)_5CH_3$ (500 MHz, C_6D_6, 25 °C, **3l**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)Hexylamine.[15] ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 3.34 (t, *J* = 7.1 Hz, 2H, -N(CH_2)$_5CH_3$), 1.70 - 1.61 (m, 2H, -N(CH_2)$_5CH_3$), 1.28 - 1.23 (m, 6H, -N(CH_2)$_5CH_3$), 1.06 (s, 24H, -N(B*pin*)$_2$), 0.83 (t, *J* = 6.9 Hz, 3H, -N$(CH_2)_5CH_3$).

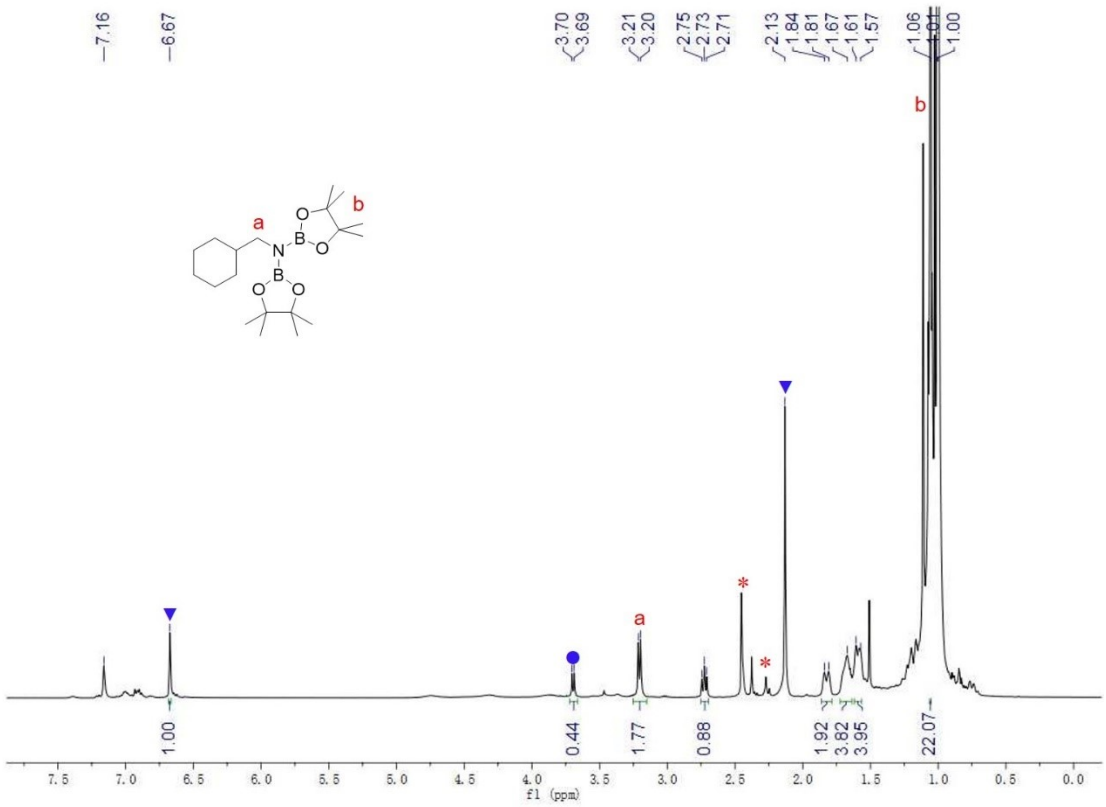


Fig. S71. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of cyclohexanecarboxamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 °C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BOCH_2C_6H_{11}$ (400 MHz, C_6D_6, 25 °C, **3m**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)-1-Cyclohexyl-Methenamine.

^{1}H NMR (400 MHz, C_6D_6, ppm): δ 3.21 (d, *J* = 7.1 Hz, 2H, -NC*H*$_2C_6H_{11}$), 2.73 (t, *J* = 7.2 Hz, 1H, -$NCH_2C_6H_{11}$), 1.82 (d, *J* = 12.5 Hz, 2H, -$NCH_2C_6H_{11}$), 1.67 (s, 4H, -$NCH_2C_6H_{11}$), 1.59 (d, *J* = 13.5 Hz, 4H, -$NCH_2C_6H_{11}$), 1.06 (s, 24H, -N(B*pin*)$_2$).

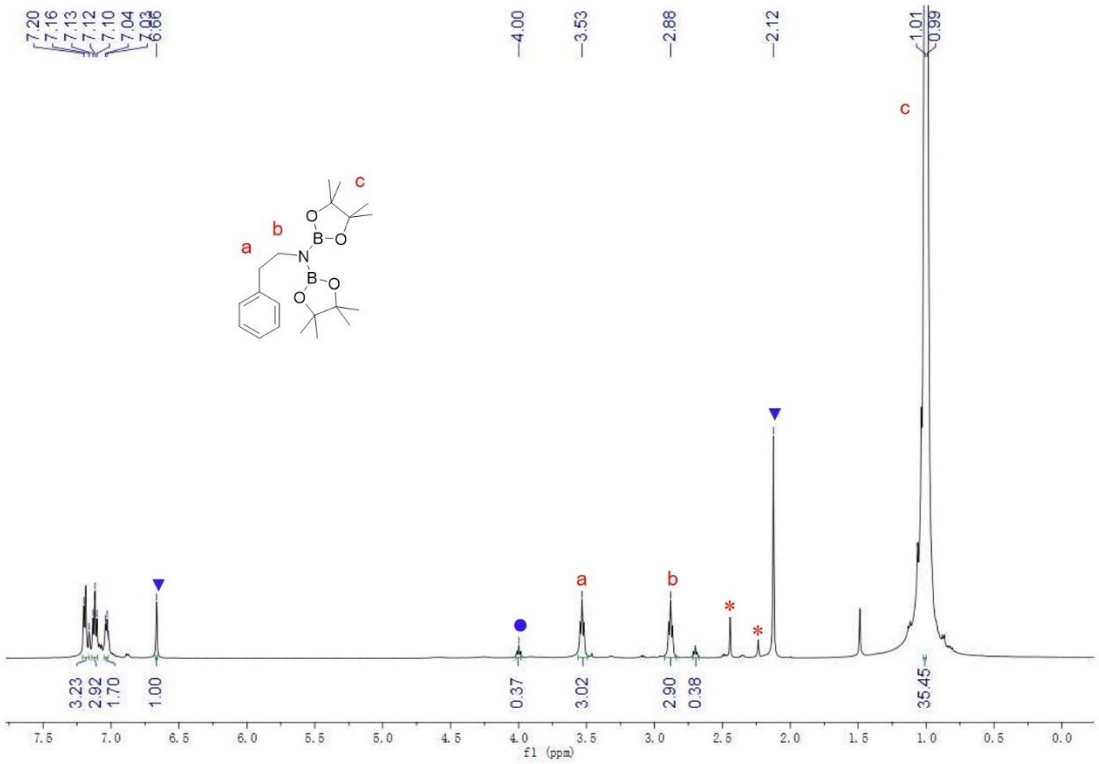


Fig. S72. Quantitative ^{1}H NMR spectrum of the products of the deoxygenative reduction of 2-phenylacetamide catalyzed by 5 mol% La($CH_2C_6H_4NMe_2$-*o*)$_3$ at 120 ^{o}C for 24 h. * = pin$BCH_2C_6H_4NMe_2$-*o*, ▼ = 1,3,5-trimethylbenzene, ● = pin$BO(CH_2)_2C_6H_5$ (500 MHz, C_6D_6, 25 ^{o}C, **3n**, Table3).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)-2-Phenethylamine. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.18 (d, *J* = 20.1 Hz, 2H, -*Ph*), 7.12 (t, *J* = 7.5 Hz, 2H, -*Ph*), 7.05 - 7.00 (m, 1H, -*Ph*), 3.53 (t, *J* = 7.2 Hz, 2H, -N(CH_2)$_2$Ph), 2.88 (t, *J* = 7.2 Hz, 2H, -N(CH_2)$_2$Ph), 1.01 (s, 24H, -N(B*pin*)$_2$).

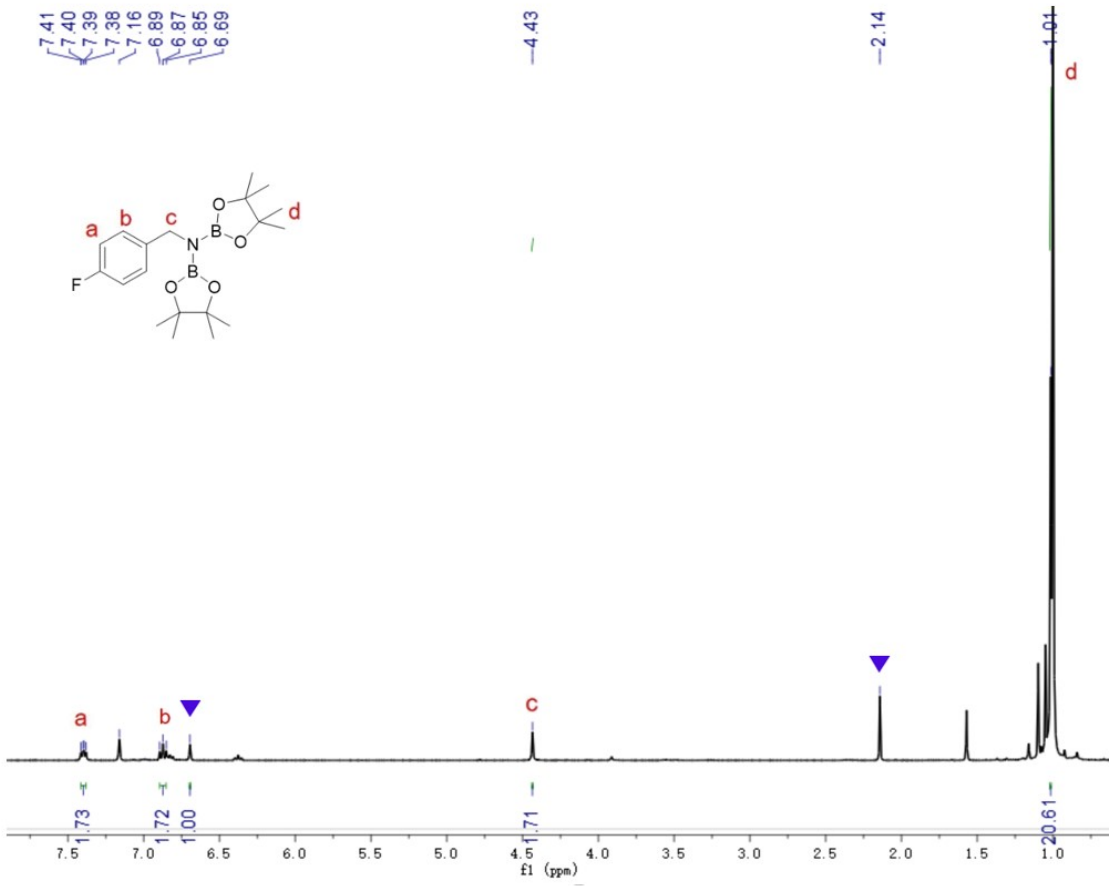


Fig. S73. Quantitative ^{1}H NMR spectrum of the products generated in situ from the reaction of 4-Fluorobenzamide with HBpin at 120 °C for 36 h without using the catalyst. ▼ = 1,3,5-trimethylbenzene. (400 MHz, C_6D_6, 25 °C).

N,N-Di(4,4,5,5-Tetramethyl-1,3,2-Dioxaborolan-2-Yl)(4-Fluorobenzyl)Amine. ^{1}H NMR (400 MHz, C_6D_6, ppm): δ 7.40 (dd, *J* = 8.4 Hz, 5.7 Hz, 2H, -*Ph*), 6.87 (t, *J* = 8.7 Hz, 2H, -*Ph*), 4.43 (s, 2H, -NC*H*$_2$PhF), 1.01 (s, 24H, -N(B*pin*)$_2$).

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