Lithium amidoborane, highly chemoselective reagent for reduction of α,β-unsaturated ketones to allylic alcohols

Weiliang Xu, Yonggui Zhou, Ruimin Wang, Guotao Wu and Ping Chen*
pchen@dicp.ac.cn;

S1. Synthesis of α,β-unsaturated ketones (entry 3-6, entry 8, entry 9-14, Table 2)
In a 50 mL flask, corresponding aldehyde (10 mmol), corresponding ketone (10 mmol) and ethanol (20 ml) were placed, and the solution was stirred at room temperature. To the solution, NaOH aqueous solution (1.5M, 10ml) was slowly added. After 5 hrs, the reaction mixture was neutralized with 2M aqueous HCl solution. Crude α,β-unsaturated ketone was obtained after filtration. Then, the crude product was recrystallized from ethanol.

S2. Synthesis of α,β-unsaturated ketones (entry 2, entry 16)
In a 50 mL flask, corresponding aldehyde (10 mmol), corresponding ketone (10 mmol) and ethanol (20 ml) were placed, and the solution was stirred at room temperature. To the solution, NaOH aqueous solution (1.5M, 10ml) was added slowly. After 5 hrs, the reaction mixture was neutralized with 2M aqueous HCl solution. The solution was extracted with DCM (3 X 10 mL). The organic layer was washed with aqueous NaCl (2 X 10 mL) and dried over Na2SO4. The solvent was evaporated and the residue was purified by column chromatography with hexane/EtOAc (v/v,10/1) as an eluent to obtain α,β-unsaturated ketone.
S3. $^{11}$B NMR spectrum for synthesized LiAB

S4. $^2$H NMR result for LiND$_2$BH$_3$ (LiA(D)B) reacting chalcone in THF
S5. Characterization data for the isolated product after LiNH₂BD₃ (LiAB(D)) reacting with chalcone

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl₃, 25 °C; TMS): } & \delta = 2.05 \text{ (s, 1H; OH),} \\
& 5.39 \text{ (s, 0.13H; CH), 6.37-6.40 (m, 1H; CH), 6.69 (d, } J_{HH} = 15.80 \text{ Hz, 1H; CH),} \\
& 7.24-7.43 \text{ ppm (m, 10H; ArH); } ^{13}\text{C NMR (126 MHz, CDCl₃, 25°C; CDCl₃): } \delta = \\
& 74.70 \text{ (t, } J_{CD} = 22.08 \text{ Hz; CD), 126.32, 126.60, 127.76, 127.79, 128.54, 128.61, 130.59,} \\
& 131.48, 131.54, 136.53, 142.78 \text{ ppm; FT-IR (film): } \nu_{\text{max}} = 3348, 3077, 3059, 3026, \\
& 2128 \text{ (CD), 1600, 1493, 1448 cm}^{-1}; \text{ MS (EI): } m/z (\%) = 211 [M]^+ (10), 105 (100), 77 \\
& (40).
\end{align*}
\]
S6. $^1$H and $^{13}$C NMR spectra of products (entry 1, Table 2):
(entry 2, Table 2):
(entry 3, Table 2):
(entry 4, Table 2):
(entry 5, Table 2):
(entry 6, Table 2):
(entry 7, Table 2):
(entry 8, Table 2):

1H NMR no 856 LIAH amide chalcone

13C NMR no 856 LIAH amide chalcone
(entry 9, Table 2):
(entry 10, Table 2):
(entry 11, Table 2):
(entry 12, Table 2):
(entry 13, Table 2):
(entry 14, Table 2):
(entry 15, Table 2):
OH

(entry 16, Table 2):
(entry 17, Table 2):
(entry 16, Table 2):