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**PAPER**

# Comparative study on reducing aromatic aldehydes by using ammonia borane and lithium amidoborane as reducing reagents†

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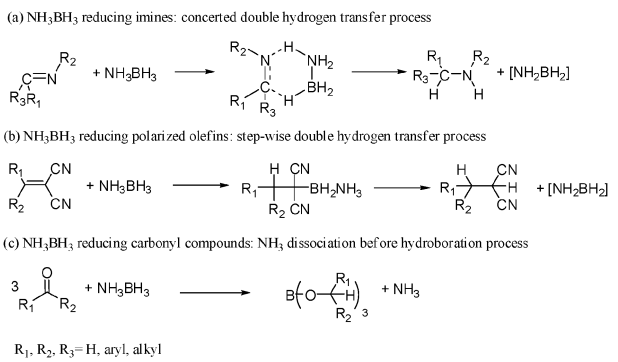
Lithium amidoborane ($LiNH_2BH_3$) and ammonia borane ($NH_3BH_3$) reduce aromatic aldehydes in tetrahydrofuran (THF) through two different pathways. $LiNH_2BH_3$ only transfers hydridic hydrogen on boron to aldehydes through a hydroboration process to achieve lithium aminoborate; ammonia borane, on the other hand, transfers both protic and hydridic hydrogens on N and B, respectively, to aldehydes to directly achieve corresponding alcohols. Mechanistic investigations confirm that protic H(N) and hydridic H(B) of ammonia borane participate in the reduction, in which the dissociation of both B–H and N–H bonds is likely to be involved in the rate-determining step.



## Introduction

Ammonia borane ($NH_3BH_3$) and lithium amidoborane ($LiNH_2BH_3$) have been intensively investigated as two promising solid-state hydrogen storage materials in the past few years.[1] $NH_3BH_3$ releases the first equiv. of $H_2$ at *ca.* 110 °C through the dissociation of both B–H and N–H bonds.[1b] With the assistance of additives or catalysts, the dehydrogenation can occur at lower temperature.[2] On the other hand, $LiNH_2BH_3$, the product obtained by substituting one of the protic hydrogens of $NH_3BH_3$ by lithium, can release hydrogen at *ca.* 90 °C in solid state or at 40 °C in tetrahydrofuran (THF) solution.[3] Owing to their high hydrogen content, $NH_3BH_3$ and $LiNH_2BH_3$ are also reducing reagents in organic synthesis. In the 1980's, $NH_3BH_3$ was reported to be a hydride reagent for converting aldehydes or ketones to alcohols in protic or aprotic solvents.[4] Hutchins and co-workers also reported that $NH_3BH_3$ was able to reduce 4-substitituted cyclohexyl imines, iminium salts and enamines.[5] In addition, $LiNH_2BH_3$ was reported to provide nucleophilic hydride in the reduction of tertiary amide to primary alcohol in 1996.[6]

However, in those previous studies, $NH_3BH_3$ and $LiNH_2BH_3$ were both treated as amine borane reagents which only transfer hydridic H on boron to unsaturated functional groups. The participation of protic H(N) of $NH_3BH_3$ or $LiNH_2BH_3$ in the reduction process was not taken into consideration. Recently, Ménard and Stephan reported that $NH_3BH_3$ reduces $CO_2$ to methanol with the assistance of an Al-based frustrated Lewis pair.[7] Theoretical investigations from Zimmerman *et al.* showed that $NH_3BH_3$ could reduce $CO_2$ through a double hydrogen transfer process.[8] Subsequently, Manner *et al.* reported that $NH_3BH_3$ can reduce the N=B double bond through this kind of process.[9] Berke and co-workers[10] also reported that $NH_3BH_3$ reduces imine through a concerted double hydrogen transfer process, where the protic H(N) and hydridic H(B) are transferred to the nitrogen and carbon ends of the imine group, respectively (Scheme 1(a)). Subsequently, a step-wise double hydrogen transfer mechanism was identified by the same group in the reaction of $NH_3BH_3$ and polarized olefins[11] (Scheme 1(b)). In the case of reduction of ketones and aldehydes by $NH_3BH_3$, however, a different process was proposed, *i.e.*, the dissociation of ammonia from $NH_3BH_3$ occurs before the hydroboration step due to which a broad signal is observed in the $^1H$ NMR at 0.4 ppm which belongs to free ammonia (Scheme 1(c)) during




**Scheme 1** Proposed mechanisms for reducing (a) imines, (b) polarized olefins, and (c) carbonyl compounds by using $NH_3BH_3$.[10–12]

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the reaction of $NH_3BH_3$ and ketones.[12] Therefore, the protic H(N)s on $NH_3BH_3$ do not participate in this specific reduction. The products obtained are borate esters based on the $^{11}B$ NMR observation. Although detailed mechanism studies by using benzophenone as representative were given, the deduction that reduction of aldehydes follows the same reaction procedure is questionable since the authors did not mention the observation of free ammonia in the reaction of $NH_3BH_3$ and aldehydes. However, in our research, we found that reduction of aldehydes by $NH_3BH_3$ takes place through a different route where a double hydrogen transfer process is the main path involved. Interestingly, reduction of aromatic aldehydes by $LiNH_2BH_3$, on the other hand, follows the hydroboration mechanism.

## Results and discussion

*In situ* FT-IR and NMR techniques were employed to monitor the reduction of $NH_3BH_3$ and benzaldehyde in anhydrous THF. It is interesting to find that the intensity of C=O stretch (at 1705 $cm^{-1}$) decreases while the intensity of O–H stretch (at 3438 $cm^{-1}$) increases with the progression of reduction from the *in situ* FT-IR measurement shown in Fig. 1. It should be noted that THF is an aprotic solvent. Therefore, the protic hydrogen which was transferred to the oxygen end of the carbonyl group must be from $NH_3BH_3$, not from solvent. Since the three Hs bonding with N of $NH_3BH_3$ are protic, this finding indicates that $NH_3BH_3$ transferred both protic and hydridic hydrogens to the carbonyl group.

To confirm this, $NH_3BD_3$ was employed to react with benzaldehyde in THF-$d_8$. From the $^1H$ NMR characterization (shown in Fig. 2(a)), a broad peak at 2.8 ppm attributed to O–H is observed. This finding confirms the participation of N–H in the reduction and the formation of O–H. However, free ammonia at 0.4 ppm which was observed in Berke's investigation on reduction of ketones by $NH_3BH_3$[12] does not appear in the spectrum. Moreover, a deuterated product at the carbon end of the C=O was obtained with the isolated yield of 79%, which evidences the transfer of deuterium on B of $NH_3BD_3$ to the carbon end of carbonyl group in the reduction ($^1H$ and $^{13}C$ NMR spectra of the product, α-deuterobenzenemethanol, are shown in ESI†). In a related experiment of reacting $ND_3BH_3$ and benzaldehyde in THF, a singlet at $\delta = 3.4$ ppm attributed to O–D was observed by $^2H$ NMR (the spectrum can be seen in Fig. 2(b)). Free $ND_3$ was also absent. All these isotopic labeling experimental results together with the high yield of phenylmethanol (entry 1, Table 1) confirm

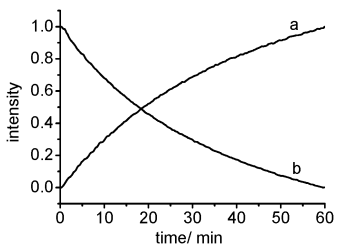



**Fig. 1** *In situ* FT-IR measurements of the reaction between 0.005 M $NH_3BH_3$ and 0.005 M benzaldehyde. The changes in intensities of OH stretch vibration at 3438 $cm^{-1}$ (a) and C=O stretch vibration at 1705 $cm^{-1}$ (b) were monitored with time.

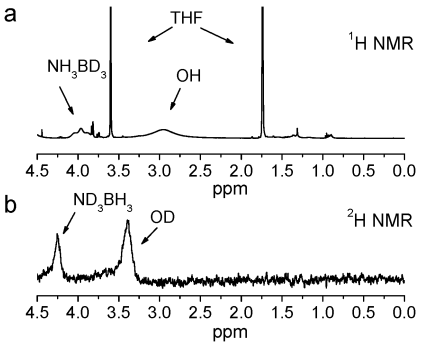
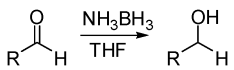
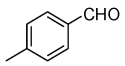
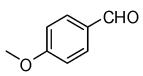
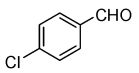
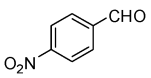
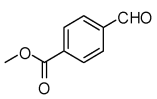



**Fig. 2** (a) $^1H$ NMR characterization of $NH_3BD_3$–benzaldehyde in THF-$d_8$. Singlet at 2.9 ppm attributed to O–H was observed; (b) $^2H$ NMR characterization for $ND_3BH_3$–benzaldehyde in THF. Singlet at 3.4 ppm attributed to O–D was observed.

**Table 1** Reactions of $NH_3BH_3$ and aldehydes in THF[a]

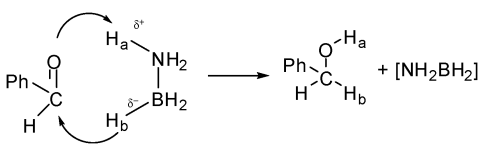



| Entry | Substrate | *t*/min | Yield[b] |
|---|---|---|---|
| 1 |  | 15 | 76 |
| 2 |  | 15 | 87 |
| 3 |  | 15 | 80 |
| 4 |  | 15 | 80 |
| 5 |  | 15 | 89 |
| 6 |  | 15 | 94 |

[a] The ratio of substrate and $NH_3BH_3$ is 1 : 1, and the concentration of $NH_3BH_3$ (or substrate) is 0.2 M. [b] Isolated overall yields.

that the main path for the reduction is *via* the double hydrogen transfer process, in which both H(N) and H(B) of $NH_3BH_3$ participate in the reaction and transfer to the O and C sites of carbonyl group, respectively (Scheme 2).

Borate ester, a key species in the mechanistic interpretation,[12] was also observed in our *in situ* $^{11}B$ NMR characterization (Fig. 3). However, it is a minor by-product which is too little to be isolated from the solution for quantification. The majority of B species is,




**Scheme 2** The reaction process of $NH_3BH_3$ reducing benzaldehyde: $NH_3BH_3$ transfers protic $H_a$ to oxygen end of carbonyl and hydridic $H_b$ to carbon end of carbonyl.

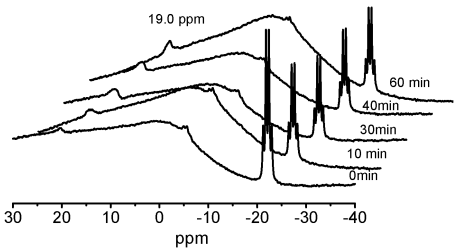



**Fig. 3** *In situ* $^{11}B$ NMR characterization of reacting $NH_3BH_3$ with one equiv. of benzaldehyde at room temperature. A small broad peak at 19.0 ppm, which belongs to borate ester, was observed. The quartet at −22.0 ppm is attributed to un-reacted $NH_3BH_3$.

on the other hand, precipitated from the reacting solution upon reduction, forming a white amorphous substance. The solute is, however, mainly composed of an alcohol product and un-reacted $NH_3BH_3$ or benzaldehyde. We, therefore, tentatively ascribe the formation of minor borate ester to the alcoholysis between ammonia borane and phenylmethanol.

Based on the results mentioned above, various aromatic aldehydes were chosen to react with $NH_3BH_3$. The results are shown in Table 1. The ratio of the substrate and $NH_3BH_3$ was 1 : 1. All the reactions were carried out in 15 min at room temperature (detected by GC). The isolated overall yields of corresponding primary alcohols are in between 76 and 94%.

Similar to $NH_3BH_3$, $LiNH_2BH_3$ also has protic H(N) and hydridic H(B) and may exhibit similar performance in reduction of aldehydes. However, to our surprise, a white precipitate was formed when benzaldehyde reacted with $LiNH_2BH_3$ in THF, and no phenylmethanol was detected by GC. On the other hand, high isolated yield of phenylmethanol can only be achieved after hydrolyzing the precipitate by aqueous HCl. In order to determine the composition of the white precipitate, we collected the sample of $LiNH_2BH_3$ with 3 equiv. of benzaldehyde for Raman and NMR characterizations. From the Raman spectrum shown in Fig. 4(a) we can find that B–H stretching vibrations in the range of 2140–2360 $cm^{-1}$ disappear. However, N–H vibrations are still observable at 3168 and 3210 $cm^{-1}$. Additionally, only one singlet signal at 2.0 ppm was observed by $^{11}B$ solid NMR as shown in Fig. 4(b). It is, therefore, very likely that the precipitate is lithium aminotribenzylborate of formula **a** (Scheme 3). The composition of **a** was further confirmed by $^{1}H$ NMR and $^{13}C$ NMR. However, the molecular weight cannot be determined due to the instability of the borate compound in GC-MS.[12]

Similar reactions were observed in the reduction of other aldehydes with $LiNH_2BH_3$. The results are shown in Table 2. The ratio of the substrate and $LiNH_2BH_3$ is 1 : 1. All aldehydes reacted rapidly with $LiNH_2BH_3$ to afford 100% conversion rate in 5 min at room temperature. The high isolated overall yields of corresponding primary alcohols were only achieved after hydrolysis of the borate ester in aqueous HCl solution.

Moreover, $LiND_2BH_3$ was also used to react with benzaldehyde in THF. During the reaction, a white precipitate was formed and deuterated benzenemethanol, $PhCH_2OD$, was not observed by GC-MS. In a similar reaction, after hydrolyzing the white precipitate from the reaction of $LiNH_2BD_3$ and benzaldehyde, α-deuterobenzenemethanol (PhCHDOH) was obtained with an isolated yield of 82%. Clearly, reduction of aldehydes by

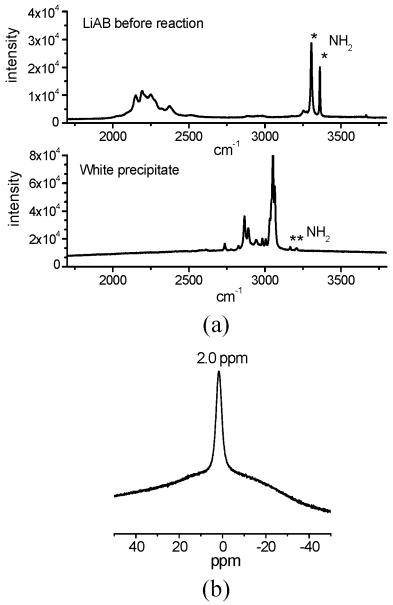
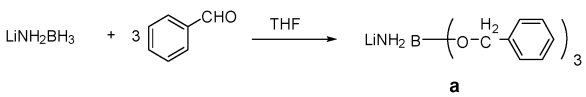
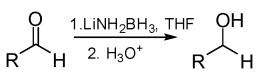


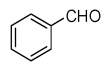
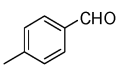
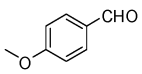
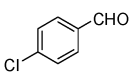
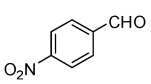
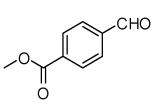

**Fig. 4** (a) Raman spectra for $LiNH_2BH_3$ (above) and white precipitate (below). The $NH_2$ vibrations in $LiNH_2BH_3$ at 3306 and 3364 $cm^{-1}$ shift to 3168 and 3210 $cm^{-1}$ in white precipitate. (b) $^{11}B$ solid NMR spectrum for white precipitate. Singlet at 2.0 ppm is observed.




**Scheme 3** The process of reduction of benzaldehyde by $LiNH_2BH_3$.

**Table 2** Reactions of $LiNH_2BH_3$ and aldehydes in THF[a]




| Entry | Substrate | *t*/min | Yield[b] (%) w/*t* hydrolysis | Yield[c] (%) after hydrolysis |
|---|---|---|---|---|
| 1 |  | 5 | N.A. | 85 |
| 2 |  | 5 | N.A. | 91 |
| 3 |  | 5 | N.A. | 93 |
| 4 |  | 5 | N.A. | 91 |
| 5 |  | 5 | N.A. | 88 |
| 6 |  | 5 | N.A. | 91 |

[a] The ratio of substrate and $LiNH_2BH_3$ is 1 : 1, and the concentration of $LiNH_2BH_3$ (or substrate) is 0.167 M. [b] Detected by GC. [c] Isolated overall yields.

**Table 3** Initial rates of formation of [OH] at different concentrations of $NH_3BH_3$ and benzaldehyde

| Entry | $[NH_3BH_3]$/M | [Benzaldehyde]/M | Initial rate of [OH]/M $min^{-1}$ |
|---|---|---|---|
| 1 | 0.0083 | 0.025 | 0.0011 |
| 2 | 0.0166 | 0.025 | 0.0020 |
| 3 | 0.0083 | 0.050 | 0.0020 |

$LiNH_2BH_3$ resembles the hydroboration of aldehyde by $NaBH_4$.[13] Both reagents only transfer hydridic H(B) to aldehydes. One possible explanation for the difference between $LiNH_2BH_3$ and $NH_3BH_3$ in reducing aldehydes is that the N–H bond distance (0.96 Å[3a]) in $LiNH_2BH_3$ is shorter than that in $NH_3BH_3$ (1.07 Å[14]). It makes the transfer of the protic hydrogen from $LiNH_2BH_3$ to the carbonyl group difficult.

The direct reduction of aldehydes to alcohols by $NH_3BH_3$ should be the consequence of dissociation of both B–H and N–H bonds followed by the addition of Hs to C═O, which resembles the double hydrogen transfer (DHT) hydrogenation of carbonyl compounds, which is *via* a dihydride route catalyzed by transition metals[15] or Meerwein–Ponndorf–Verley (MPV) reduction.[16] Ru,[17] Ir,[18] Rh[19] and aluminum alkoxides complexes[20] are effective catalysts for this process.

In order to further understand the reaction mechanism, detailed kinetic studies and computational simulations were carried out. Kinetic studies of the reaction of $NH_3BH_3$ and benzaldehyde were investigated in THF at room temperature by employing kinetic and quantitative FT-IR measurements.[21] Determination of reaction order is based on the initial formation rate of [OH] under different concentrations of $NH_3BH_3$ and benzaldehyde. The results (Table 3) show that the reaction obeys a second-order rate law, being first order to $[NH_3BH_3]$ and [benzaldehyde] respectively. According to the plot of 1/[benzaldehyde] *versus* time (Fig. 5(a)), the rate law at room temperature can be expressed as in eqn (1)

$$\nu = 5.62[NH_3BH_3][\text{benzaldehyde}] \quad (1)$$

Deuterium kinetic isotopic effects (DKIE) were analyzed to further understand the reaction process. Plots of 1/[benzaldehyde] *versus* time ($t$) based on the results of kinetic *in situ* FT-IR measurements of the reactions of benzaldehyde with $NH_3BH_3$, $ND_3BH_3$ or $NH_3BD_3$ are shown in Fig. 5, respectively. The DKIE value is 3.47 ($k_{NH_3BH_3}/k_{ND_3BH_3}$) for $ND_3BH_3$–benzaldehyde and 2.85 ($k_{NH_3BH_3}/k_{NH_3BD_3}$) for $NH_3BD_3$–benzaldehyde. Because those DKIE values are greater than 2 and close to each other, the dissociation of both N–H and B–H bonds is likely to be involved in the rate-determining step.[22]

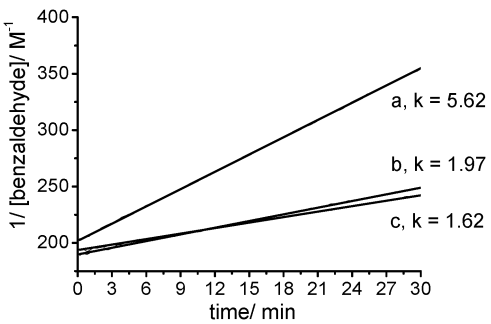



**Fig. 5** 1/[benzaldehyde] *versus* time plots for 0.005 M benzaldehyde reacting with 0.005 M $NH_3BH_3$ (a), 0.005 M $NH_3BD_3$ (b), 0.005 M $ND_3BH_3$ (c), respectively.

## Conclusions

In conclusion, $NH_3BH_3$ is an efficient reagent in reducing aromatic aldehydes. *In situ* FT-IR and NMR measurements evidence that the reduction is through double hydrogen transfer process, which is significantly different from the hydroboration mechanism proposed in previous investigations. $LiNH_2BH_3$ is also a powerful reagent in reducing aromatic aldehydes. However, in contrast to $NH_3BH_3$, $LiNH_2BH_3$ cannot transfer its protic hydrogen to aldehydes. The overall reduction process is identical to the hydroboration of aldehydes by $NaBH_4$. High yields of corresponding alcohols are achieved only after the hydrolysis step.

## Experimental section

### General remarks

Solvents and most of reagents were purchased commercially and used without further purification: THF (J&K, HPLC, dried over NaH), benzaldehyde (Sigma-Aldrich, 99%), 4-methylbenzaldehyde (Alfa Aesar, 98%), 4-methoxybenzaldehyde (J&K, 99%), 4-chlorobenzaldehyde (Acros, 99%), 4-nitrobenzaldehyde (J&K, 99%), methyl 4-formylbenzoate (Alfa, 98%), ammonia borane (Sigma-Aldrich, 97%), LiH (Alfa, 98%). $ND_3BH_3$ and $NH_3BD_3$ were synthesized according to Penner's work.[23] NMR spectra were recorded on a Bruker DRX-500 instrument. Chemical shifts, quoted in ppm, are relative to the internal or external standard (only for $^2H$ NMR and $^{11}B$ NMR): singlet $\delta$ = 0 ppm of TMS for $^1H$ NMR; the middle of $CDCl_3$ triplet $\delta$ = 77 ppm for $^{13}C$ NMR; singlet $\delta$ = 4.80 ppm of $D_2O$ for $^2H$ NMR; singlet $\delta$ = 0 ppm of $BF_3{\cdot}Et_2O$ for $^{11}B$ NMR. IR spectra were recorded on a Varian 3100 FT-IR spectrophotometer using Resolution Pro program. GC results were detected by RAMIN 2060 series. The model of capillary column was HP-5. MS analyses were performed on Agilent 6890-5973 GC-MS. Raman spectra were recorded on a Renishaw Raman microscope.

### Synthesis of $LiNH_2BH_3$

1 mmol $NH_3BH_3$ was firstly dissolved in 5 ml THF in a metal jar in a glove box. Then, 1 mmol LiH was quickly added into the solution and the jar cap was closed. The system was stirred at room temperature. After one equivalent of $H_2$ was released, as detected by a pressure gauge, clear 0.2 M $LiNH_2BH_3$ solution was obtained characterized by $^{11}B$ NMR. The solution can be directly used in reduction reaction without further purification.

### General experimental procedure for reducing aldehydes with $NH_3BH_3$

4 ml of 0.25 M $NH_3BH_3$ THF solution was added into 1 ml of 1 M aldehyde solution in THF in a closed glass bottle at room temperature. An FT-IR spectrometer was employed to monitor

the consumption of the carbonyl group and formation of the OH group. After the reaction, THF was evaporated, and then 10 ml hexane was added into the glass bottle to extract alcohol product three times. Then, clear hexane solution was collected after centrifugation. Next, hexane was evaporated and a transparent liquid residue was left. In the end, further column chromatography (silica gel, 200–300 mesh, elution by using ethyl acetate : hexane = 1 : 10 solution) was utilized to purify the alcohol product. Alcohol was characterized by $^1$H NMR, $^{13}$C NMR, FT-IR and MS.

### General experimental procedure for reducing aldehydes with $LiNH_2BH_3$

5 ml of 0.2 M $LiNH_2BH_3$ THF solution was added into 1 ml of 1 M aldehyde solution in THF in a closed glass bottle at room temperature. An FT-IR spectrometer was employed to monitor the consumption of the carbonyl group. The formation of a white precipitate was observed during the reaction. After the reaction, THF was evaporated, and then 5 ml of 2 M HCl aqueous solution was added into the glass bottle. The system was stirred at room temperature for 30 min. Next, the solution was extracted with 10 ml diethyl ether three times. The combined diethyl ether extracts were washed with brine, dried with $NaSO_4$ overnight and concentrated in vacuum. In the final step, the residue was purified by silica gel flash chromatography to obtain the desired product. The product was characterized by FT-IR, $^1$H NMR, $^{13}$C NMR and GC-MS.

### Product characterization

**α-Deuterobenzenemethanol.** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 2.2 (s, 1H; O–H), 4.6 (d, $^3J_{HH}$ = 9.90 Hz, 2H; $CH_2$), 7.3–7.4 ppm (m, 5H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CDCl_3$): $\delta$ = 64.9 (t, $J_{CD}$ = 21.84 Hz), 127.0, 127.6, 128.5, 140.8 ppm; FT-IR (film): $\nu_{max}$ = 3338, 3087, 3064, 3030, 2915, 2135, 1496, 1453, 1208, 1201, 734, 697 cm$^{-1}$; MS (EI): $m/z$ (%) 109 [M]$^+$ (80), 79 (100), 92 (20).

**Lithium aminotribenzylborate (a, Scheme 3).** $^1$H NMR (500 MHz, DMSO-$d_6$, 25 °C; TMS): $\delta$ = 3.3 (s, 2H; N–H), 4.4–4.5 (m, 6H; $CH_2$), 7.1–7.3 ppm (m, 15H; ArH); $^{13}$C NMR (126 MHz, DMSO-$d_6$, 25 °C; DMSO-$d_6$): $\delta$ = 63.4, 125.7, 126.8, 127.8, 128.4 ppm.

**Phenylmethanol (entry 1, Table 1).** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 2.8 (s, 1H; O–H), 4.6 (s, 2H; $CH_2$), 7.3–7.4 ppm (m, 5H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CDCl_3$): $\delta$ = 65.0, 126.9, 127.4, 128.4, 140.8 ppm; FT-IR (film): $\nu_{max}$ = 3335 (O–H), 3087, 3064, 3030, 2931, 2873, 1496, 1453, 1208, 1201, 734, 697 cm$^{-1}$; MS (EI): $m/z$ (%) 108 [M]$^+$ (94), 79 (100), 51 (19), 91 (16).

**4-Methylphenylmethanol (entry 2, Table 1).** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 1.9 (s, 1H; O–H), 2.4 (s, 3H; $CH_3$), 4.6 (s, 2H; $CH_2$), 7.2 (d, $^3J_{HH}$ = 7.89 Hz, 2H; ArH), 7.3 ppm (d, $^3J_{HH}$ = 8.08 Hz, 2H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CDCl_3$): $\delta$ = 21.2, 65.2, 127.1, 129.2, 137.7, 137.4 ppm; FT-IR (film): $\nu_{max}$ = 3334, 3048, 3021, 2950, 2919, 1518, 1445, 1032, and 802 cm$^{-1}$; MS (EI): $m/z$ (%) 122 [M]$^+$ (92), 107 (100), 91 (69), 79 (65).

**4-Methoxylphenylmethanol (entry 3, Table 1).** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 2.2 (s, 1H; O–H), 3.8 (s, 3H; $CH_3$), 4.6 (s, 2H; $CH_2$), 6.8–6.9 (m, 2H; ArH), 7.2–7.3 ppm (m, 2H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CDCl_3$): $\delta$ = 55.3, 64.9, 113.9, 128.6, 133.2, 159.2 ppm; FT-IR (film): $\nu_{max}$ = 3354, 3032, 3001, 2935, 2836, 1612, 1514, 1247, 1033, 816 cm$^{-1}$; MS (EI): $m/z$ (%) 138 [M]$^+$ (100), 109 (73), 121 (52), 77 (50), 94 (33).

**4-Chlorophenylmethanol (entry 4, Table 1).** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 2.1 (s, 1H; O–H), 4.6 (s, 2H; $CH_2$), 7.2–7.3 ppm (m, 4H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CHCl_3$): $\delta$ = 64.5, 128.3, 128.7, 133.3, 139.3 ppm; FT-IR (film): $\nu_{max}$ = 3342, 2953, 2920, 2855, 2731, 1597, 1491, 1450, 1405, 1086, 1012, 708 cm$^{-1}$; MS (EI): $m/z$ (%) 142 [M]$^+$ (60), 77 (100), 107 (68), 113 (18).

**4-Nitrophenylmethanol (entry 5, Table 1).** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 2.2 (s, 1H; O–H), 4.8 (s, 2H; $CH_2$), 7.5 (d, $^3J_{HH}$ = 8.86 Hz, 2H; ArH), 8.2 ppm (d, $^3J_{HH}$ = 8.76 Hz, 2H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CDCl_3$): $\delta$ = 64.0, 123.7, 127.0, 147.3, 148.3 ppm; FT-IR (film): $\nu_{max}$ = 3521, 3112, 2924, 2884, 1602, 1511, 1344, 1196, 1057, 736 cm$^{-1}$; MS (EI): $m/z$ (%) 153 [M]$^+$ (34), 77 (100), 107 (50), 89 (41), 51 (28), 136 (22).

**Methyl 4-(hydroxymethyl)benzoate (entry 6, Table 1).** $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; TMS): $\delta$ = 2.1 (s, 1H; O–H), 3.9 (s, 3H; $CH_3$), 4.7 (s, 2H; $CH_2$), 7.4–7.5 (m, 2H; ArH), 8.0–8.1 ppm (m, 2H; ArH); $^{13}$C NMR (126 MHz, $CDCl_3$, 25 °C; $CDCl_3$): $\delta$ = 52.0, 64.6, 126.4, 129.3, 129.8, 145.9, 166.9 ppm; FT-IR (film): $\nu_{max}$ = 3384, 3032, 3001, 2935, 2836, 1710, 1612, 816 cm$^{-1}$; MS (EI): $m/z$ (%) 166 [M]$^+$ (40), 77 (100), 107 (60), 136 (30).

## Notes and references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