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PAPER

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

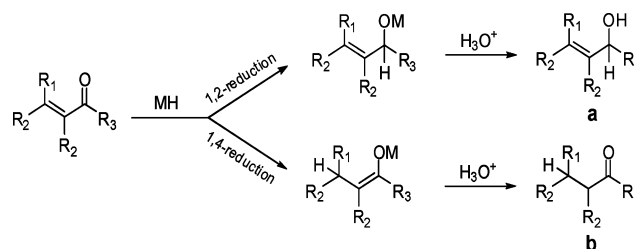**Weiliang Xu,[b] Yonggui Zhou,[a] Ruimin Wang,[c] Guotao Wu[a] and Ping Chen*[a]**

Lithium amidoborane ($LiNH_2BH_3$, LiAB for short), is capable of chemoselectively reducing α,β-unsaturated ketones to the corresponding allylic alcohols at ambient temperature. A mechanistic study shows that the reduction is *via* a double hydrogen transfer process. The protic H(N) and hydridic H(B) in amidoborane add to the O and C sites of the carbonyl group, respectively.

Introduction

The chemoselective reduction of α,β-unsaturated carbonyl compounds to allylic alcohols is one of the important processes in synthetic organic chemistry.[1] Catalytic hydrogenation,[2] transfer hydrogenation[3] and borohydride reduction[1a] are traditional methods that can be applied for this transformation. Metal borohydrides, such as $NaBH_4$, are usually employed as the primary choice due to its low cost and convenient operation.[1a] Reduction of α,β-unsaturated ketones by metal borohydrides generally gives two possible products, *i.e.*, the corresponding allylic alcohol **a** through a 1,2-reduction and the corresponding saturated carbonyl compound **b** after a 1,4-reduction (Scheme 1). Which product is formed depends on the steric hindrance of the double bonds and the reaction conditions.[4] Meanwhile, a substantial amount of fully reduced alcohols are also produced in some cases.[5] Improved 1,2-selective reductions of α,β-unsaturated carbonyl groups can be achieved by introducing additives, such as stoichiometric lanthanide chlorides ($CeCl_3$) developed by Luche and his co-workers,[6] to the $NaBH_4$ reaction system. One of the disadvantages of such a process is the formation of toxic cerium byproducts. Besides lanthanide chlorides, other additives such as calcium chloride ($CaCl_2$),[7] guanidine chloride[8] and pentafluorophenol,[9] are also employed to achieve high selectivity towards the 1,2-reduction route. Another reliable reagent for the 1,2-reduction of conjugated carbonyl compounds is a lithium aminoborohydride ($LiNRR'BH_3$), such as lithium pyrrolidinoborohydride,[10] which can be applied to most of the α,β-unsaturated carbonyl compounds with an essentially quantitative yield of allylic alcohols upon hydrolysis/solvolysis of the intermediate borates. Herein, we report an effective chemoselective reagent, lithium amidoborane ($LiNH_2BH_3$, or LiAB for short), which can directly reduce

Scheme 1 1,2- and 1,4-reduction of α,β-unsaturated ketones.

α,β-unsaturated carbonyl compounds to allylic alcohols under ambient conditions.

Ammonia borane (NH_3BH_3, AB for short), a promising solid-state hydrogen storage material,[11] has been used to reduce unsaturated organic functional groups for a long time.[12] Berke and his co-workers recently reported that AB reduces C≡N groups[13a] and polarizes C≡C groups[13b] at 60 °C or room temperature through a double hydrogen transfer process, due to the coexistence of a protic H(N) and hydridic H(B) in the AB structure. Recently, metal amidoboranes ($M(NH_2BH_3)_n$, or MAB for short), which are synthesized by substituting one of the protic hydrogen atoms of AB by an alkali or alkaline-earth element, have been investigated intensively for hydrogen storage due to their high hydrogen content and mild dehydrogenation conditions.[14] LiAB can release hydrogen at *ca.* 90 °C in the solid-state[15] or at *ca.* 40 °C when in a THF solution.[15a] Notably, lithium amidoborane can be conveniently obtained by reacting LiH with AB in THF (Reaction (1)).

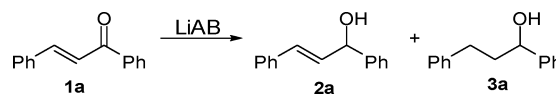$$LiH + NH_3BH_3 \xrightarrow{THF} LiNH_2BH_3 + H_2 \qquad (1)$$

In comparison with lithium aminoborohydrides, LiAB has two protic Hs bonded with N. It is of interest to figure out whether the dissociation of the B–H and N–H of LiAB, and the transfer of those oppositely charged Hs to unsaturated functional groups can be realized.

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Table 1 Reducing **1a** by LiAB in different solvents[a]

Entry	Solvent	Time/h	Conv. %	**2a/3a**
1	CH_2Cl_2	3	78	52/26
2	$CHCl_3$	3	45	26/19
3	CCl_4	3	25	2/23
4	Et_2O	3	93	36/57
5	Glyme	3	93	85/8
6	THF	0.5	>99	> 99/1

[a] Reaction conditions: 1 mmol of **1a** reacted with 0.5 mmol of LiAB in 5 ml of solvent at ambient temperature. Conversion rates of **1a** and **2a/3a** were determined by GC analysis.
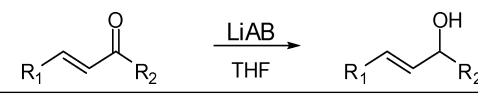
Results and Discussion

We first performed the reduction of chalcone **1a** by LiAB in a number of common solvents to figure out the solvent effect. The results are listed in the Table 1. Protic solvents, such as methanol, are unsuitable due to the solvolysis of LiAB. Ether solvents (Table 1, entries 4–6) gave higher conversion rates of **1a** than others which is probably due to the facile solubility of LiAB in those solvents. 1,3-Diphenylpropanol **3a**, the fully reduced product, was observed in most cases (Table 1, entries 1–5). However, the THF mediated reaction showed the best performance, *i.e.*, fastest reaction rate, highest chemoselectivity and **3a** was almost undetectable.

In light of this result, a series of α,β-unsaturated ketones were chosen to react with LiAB in THF at ambient temperature. The molar ratio of ketone and LiAB was 2:1. The results are listed in Table 2. In all the cases, it took *ca.* half an hour to reach 99% conversion rates of ketones giving rise to the corresponding allylic alcohols regardless of the steric and electronic effect of substituents R_1 and R_2.

In 1996, Myers and his co-workers reported that LiAB provides a nucleophilic hydride that reduces tertiary amides into primary alcohols.[16] To the best of our knowledge, this is the first report on using LiAB to selectively reduce α,β-unsaturated ketones to allylic alcohols.

It is noted that the selective reduction of α,β-unsaturated ketones can also be carried out on an enlarged scale. We up-scaled the reduction to 30 mmol of **1a** and 15 mmol of LiAB under the same conditions and obtained an 87% isolated yield of **2a** in 30 min. Noting that LiAB can be facilely produced, it can be considered that the method demonstrated here may be a practical and viable route for the selective reduction of conjugated ketones.
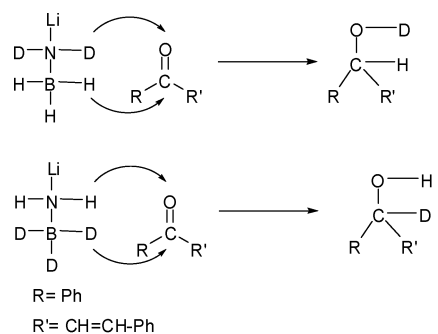
As discussed in the introduction section, the distinction of LiAB and LiNRR′BH₃ lies in the presence of two protic Hs in LiAB. Moreover, allylic alcohols were obtained directly from ketones–LiAB without hydrolysis. Therefore, it can be deduced that the protic H(N) of LiAB transfers to the O site of the carbonyl group. In order to prove this deduction, LiND₂BH₃ (LiA(D)B) was employed to react with **1a** in THF. A singlet at δ = 0.45 ppm, attributed to O–D, was observed in the ²H NMR spectrum evincing the transfer of deuterium from N to the O of the carbonyl group upon reduction (see ESI†). In a related experiment, reacting LiNH₂BD₃ (LiAB(D)) and **1a** in THF, a deuterated product at the carbon end of the C=O bond, which was of 88% isolated yield,

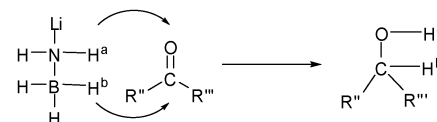**Table 2** Reduction of α,β-unsaturated ketones by LiAB[a]

Entry	R_1/R_2	Time/h	Yield %[b]
1	Ph/Ph	0.5	85[c]
2	$o\text{-MeC}_6H_4$/Ph	0.5	86
3	$m\text{-MeC}_6H_4$/Ph	0.5	87
4	$p\text{-MeC}_6H_4$/Ph	0.5	88
5	$p\text{-MeOC}_6H_4$/Ph	0.5	92
6	$p\text{-ClC}_6H_4$/Ph	0.5	90
7	$p\text{-NO}_2C_6H_4$/Ph	0.5	80
8	$p\text{-CH}_3C(O)NHC_6H_4$/Ph	0.5	78
9	Ph/$p\text{-MeC}_6H_4$	0.5	82
10	Ph/$p\text{-MeOC}_6H_4$	0.5	88
11	Ph/$p\text{-ClC}_6H_4$	0.5	91
12	Ph/$p\text{-NO}_2C_6H_4$	0.5	90
13	Ph/$p\text{-CNC}_6H_4$	0.5	90
14	Ph–CH=CH/Ph	0.5	93
15	Ph/CH_3	0.5	86
16	$n\text{-C}_5H_{11}$/$n\text{-C}_4H_9$	0.5	88
17		0.5	86
18		0.5	90

[a] The ratio of substrate and LiAB was 2 to 1 and the concentration of LiAB was 0.083 M. [b] Isolated overall yields. [c] The yield of the allylic alcohol was 87% when the molar ratio of LiAB and chalcone was 1:1.

was obtained (see ESI†). It shows the transfer of the deuterium on the B of the LiAB to the C of the carbonyl group in the reduction. These experimental results confirm that both the protic H(N) and hydridic H(B) in LiAB participate in the reduction and add directly to the O and C sites of the ketone, respectively (Scheme 2). Our interpretation is that the first step of the reduction may be the dissociation of the B–H bond of LiAB with the assistance of the metal cation.[17] According to the HSAB (hard and soft acids and bases) concept, the hard nucleophile hydride has a higher chance

R= Ph
R'= CH=CH-Ph

Overall reaction model for LiAB with ketone

Scheme 2 The deuterium labelling study and the reaction model for LiAB with ketones.

of bonding with the C of the C=O, which is a hard electrophile, giving rise to the 1,2-reduction product.[6a]

The direct reduction of ketones to alcohols by LiAB through a dissociation of both the B–H and N–H bonds resembles the double hydrogen transfer (DHT) hydrogenation of carbonyl compounds, which is *via* a dihydride route catalyzed by transitional metals[18] or the Meerwein–Ponndorf–Verley (MPV) reduction.[19] 2-Propanol, formic acid and its salts, and the Hantzsch ester are traditional hydrogen donors in hydrogen transfer reactions which provide two hydrogens to the reactants.[20] However, vigorous conditions or catalysts are needed to complete the reduction. LiAB rapidly transfers two hydrogens to the ketones at ambient temperature without the employment of catalysts, showing superior performances in both reactivity and selectivity.

Conclusion

In summary, the highly chemoselective reduction of α,β-unsaturated ketones to allylic alcohols was successfully achieved by using lithium amidoborane as the reducing reagent. High reducibility, double hydrogen transfer and chemoselectivity makes this approach practical for the synthesis of allylic alcohols. Efforts into exploring the use of MAB in other chemoselective reductions of organic compounds are ongoing.

Experimental section

General remarks

Solvents and some of the reagents were purchased commercially and used without further purification: THF (Honywell, HPLC, further dried over NaH), diethyl ether (Honeywell, HPLC), hexane (Beijing HuaGong, AR), EtOAc (Beijing HuaGong, AR), ammonia borane (Sigma–Aldrich, 97%), lithium hydride (Alfa, 98%), chalcone (Table 2, entry 1, Alfa, 97%), 4-nitrochalcone (Table 2, entry 7, Alfa, 99%), 4′-methoxychalcone (Table 2, entry 10, Alfa, 97%), 3-methyl-2-cyclohexen-1-one (Table 2, entry 17, Alfa, 98%), 2-benzylidenecyclohexanone (Table 2, entry 18, Alfa, 98%), 4-phenyl-3-buten-2-one (Table 2, entry 15, Sigma–Aldrich, 99%). Other α,β-unsaturated ketones were synthesized from corresponding aldehydes and ketones. The synthetic procedures are mentioned in the ESI†.

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 ^{2}H NMR): singlet $\delta = 0$ ppm of TMS for ^{1}H NMR; the middle of the CDCl$_3$ triplet $\delta = 77$ ppm for ^{13}C NMR; singlet $\delta = 7.26$ ppm of CDCl$_3$ for ^{2}H NMR. IR spectra were obtained by a Varian 3100 FTIR spectrophotometer using a Resolution Pro program. GC results were detected using the RAMIN 2060 series. The model of the capillary column was HP-5. MS analyses were performed on an Agilent 6890–5973 GC–MS.

Synthesis of LiAB, LiA(D)B and LiAB(D)

1 mmol NH$_3$BH$_3$, ND$_3$BH$_3$ or NH$_3$BD$_3$ was first dissolved in 10 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 and detected by a pressure gauge, a clear 1 M LiAB solution was obtained and characterized by ^{11}B NMR.

The solution can be directly used in the reducing reaction without further purification.

General experimental procedure for reducing α,β-unsaturated ketones with LiAB

5 ml 0.1 M LiAB solution (THF as solvent) was added to 1 ml 1 M ketone solution (THF as solvent) at room temperature in a closed glass bottle under argon gas protection. A FT-IR spectrometer was used to monitor the consumption of the C=O group and the formation of the OH group. After the reaction was complete the THF was evaporated. Then diethyl ether (3 × 10 ml) was added to the glass bottle to extract the alcohol. The diethyl ether solution also underwent centrifugation to remove any suspended substances. Next, the diethyl ether mixture was evaporated to leave a transparent liquid residue which was further purified by column chromatography (silica gel, 200–300 mesh, hexane/EtOAc (v/v, 10 : 1) as an eluent). Alcohol products were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and GC-MS.

Products characterization

1,3-Diphenylprop-2-en-1-ol (entry 1, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): $\delta = 2.07$ (s, 1H; OH), 5.38 (s, 1H; CH), 6.36–6.40 (m, 1H; CH), 6.68 (d, $^3J_{HH} = 15.80$ Hz, 1H; CH), 7.24–7.42 ppm (m, 10H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): $\delta = 75.11$, 126.32, 126.59, 127.75, 127.77, 128.54, 128.60, 130.56, 131.51, 136.53, 142.78 ppm; FT-IR (film): $\nu_{max} = 3342$, 3077, 3059, 3027, 1599, 1449, 1493, 1092, 1067, 1009, 966, 744, 695 cm^{-1}; MS (EI): m/z (%) 209 [M–H]$^+$ (47), 105 (100), 191 (67), 178 (27), 77 (33), 115 (30).

1-Phenyl-3-*o*-tolylprop-2-en-1-ol (entry 2, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): $\delta = 2.07$ (s, 1H; OH), 2.37 (s, 3H; CH$_3$), 5.41 (s, 1H; CH), 6.30–6.40 (m, 1H; CH), 6.92 (d, $^3J_{HH} = 15.60$ Hz, 1H; CH), 7.15–7.44 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): $\delta = 19.78$, 75.33, 125.79, 126.06, 126.34, 127.65, 127.77, 128.41, 128.61, 130.28, 132.87, 135.62, 142.86 ppm; FT-IR (film): $\nu_{max} = 3349$, 3061, 3062, 2969, 2863, 1601, 1487, 1463 cm^{-1}; MS (EI): m/z (%) 224 [M]$^+$ (3), 105 (100), 206 (16), 77 (26).

1-Phenyl-3-*m*-tolylprop-2-en-1-ol (entry 3, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): $\delta = 2.16$ (s, 1H; OH), 2.34 (s, 3H; CH$_3$), 5.38 (s, 1H; CH), 6.37–6.40 (m, 1H; CH), 6.66 (d, $^3J_{HH} = 15.55$ Hz, 1H; CH), 7.07–7.44 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): $\delta = 21.35$, 75.16, 123.81, 126.34, 127.30, 127.76, 128.46, 128.60, 130.68, 131.36, 136.48, 138.11, 142.85 ppm; FT-IR (film): $\nu_{max} = 3350$, 3056, 3028, 2955, 2919, 2862, 1602, 1491, 1453 cm^{-1}; MS (EI): m/z (%) 224 [M]$^+$ (15), 105 (100), 119 (36), 77 (33).

1-Phenyl-3-*p*-tolylprop-2-en-1-ol (entry 4, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): $\delta = 1.99$ (s, 1H; OH), 2.33 (s, 3H; CH$_3$), 5.38 (s, 1H; CH), 6.31–6.36 (m, 1H; CH), 6.66 (d, $^3J_{HH} = 15.80$ Hz, 1H; CH), 7.11–7.44 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): $\delta = 21.71$, 75.23, 126.31, 126.51, 127.73, 128.58, 129.25, 130.50, 130.59, 133.78, 137.66, 142.88 ppm; FT-IR (film): $\nu_{max} = 3342$, 2081, 3026, 2919, 2859, 1513, 1493, 1451 cm^{-1}; MS (EI): m/z (%) 223 [M–H]$^+$ (47), 105 (100), 207 (50), 119 (60), 77 (40).

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3-(4-Methoxyphenyl)-1-phenylprop-2-en-1-ol (entry 5, Table 2).
^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.04 (s, 1H; OH), 3.80 (s, 3H; CH3), 5.37 (s, 1H; CH), 6.23–6.27 (m, 1H; CH), 6.63 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 6.84 (d, $^3J_{HH}$ = 8.35 Hz, 2H; ArH), 7.29–7.44 ppm (m, 7H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 55.27, 75.30, 113.98, 126.28, 127.69, 127.81, 128.57, 129.26, 129.40, 130.26, 142.99, 159.38 ppm; FT-IR (film): ν_{max} = 3374, 3060, 3030, 3005, 2956, 2935, 2836, 1606, 1511, 1250 cm^{-1}; MS (EI): m/z (%) 239 [M–H]$^+$ (43), 121 (100), 222 (36), 178 (36), 77 (38), 105 (37).

3-(4-Chlorophenyl)-1-phenylprop-2-en-1-ol (entry 6, Table 2).
^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.07 (s, 1H; OH), 5.37 (d, $^3J_{HH}$ = 6 Hz, 1H; CH), 6.33–6.37 (m, 1H; CH), 6.64 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.25–7.42 (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 74.99, 126.32, 127.79, 127.93, 128.69, 128.71, 129.19, 132.16, 133.40, 135.05, 142.58 ppm; FT-IR (film): ν_{max} = 3338, 3060, 3029, 2958, 2924, 2856, 1593, 1491, 1452, 1404 cm^{-1}; MS (EI): m/z (%) 244 [M]$^+$ (37), 105 (100), 139 (32), 190 (27), 77 (33).

3-(4-Nitrophenyl)-1-phenylprop-2-en-1-ol (entry 7, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.15 (s, 1H; OH), 5.44 (s, 1H; CH), 6.55–6.58 (m, 1H; CH), 6.78 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.33–8.17 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 74.68, 123.97, 126.40, 127.10, 127.85, 128.24, 128.85, 136.23, 142.03, 143.12, 147.02 ppm; FT-IR (film): ν_{max} = 3392, 3105, 3062, 3030, 2931, 2850, 1596, 1514, 1342 cm^{-1}; MS (EI): m/z (%) 254 [M–H]$^+$ (30), 105 (100), 178 (12), 77 (35).

N-(4-(3-Hydroxy-3-phenylprop-1-enyl)phenyl)acetamide (entry 8, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.04 (s, 1H; OH), 2.15 (s, 3H; CH$_3$), 2.19 (s, 1H; NH), 5.36 (s, 1H; CH), 6.29–6.33 (m, 1H; CH), 6.63 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.25–7.58 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 24.52, 75.13, 119.85, 125.89, 126.31, 127.20, 127.74, 128.45, 129.41. 129.91, 130.85, 132.69, 142.86 ppm; FT-IR (film): ν_{max} = 3303, 3113, 3030, 2975, 2871, 1669, 1597, 1534, 1513, 1410 cm^{-1}; MS (EI): m/z (%) 267 [M]$^+$ (30), 105 (100).

3-Phenyl-1-p-tolylprop-2-en-1-ol (entry 9, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 1.98 (d, $^3J_{HH}$ = 3.45 Hz, 1H; OH), 2.35 (s, 3H; CH$_3$), 5.36 (t, $^3J_{HH}$ = 4.52 Hz, 1H; CH), 6.36–6.41 (m, 1H; CH), 6.68 (d, $^3J_{HH}$ = 15.85 Hz, 1H; CH), 7.18–7.39 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 21.11, 74.96, 136.31, 126.58, 127.70, 128.53, 129.30, 130.31, 131.66, 136.60, 137.56, 139.86 ppm; FT-IR (film): ν_{max} = 3338, 3083, 3026, 2971, 2919, 1599, 1578, 1509 cm^{-1}; MS (EI): m/z (%) 223 [M–H]$^+$ (47), 119 (100), 206 (98), 105 (60), 191 (70), 77 (40).

1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-ol (entry 10, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 1.96 (s, 1H; OH), 3.81 (s, 3H; CH$_3$), 5.35 (s, 1H; CH), 6.36–6.41 (m, 1H; CH), 6.67 (d, $^3J_{HH}$ = 15.85 Hz, 1H; CH), 6.91 (d, $^3J_{HH}$ = 7.90 Hz, 2H; ArH), 7.23–7.39 ppm (m, 7H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 55.31, 74.66, 114.01, 126.57, 127.69, 128.54, 130.20, 131.69, 135.01, 136.61, 159.28 ppm; FT-IR (film): ν_{max} = 3379, 3059, 3026, 2956, 2908, 2835, 1610, 1511, 1449 cm^{-1}; MS (EI): m/z (%) 239 [M–H]$^+$ (43), 223 (100), 135 (85), 178 (50), 77 (35).

1-(4-Chlorophenyl)-3-phenylprop-2-en-1-ol (entry 11, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.04 (s, 1H; OH), 5.37 (s, 1H; CH), 6.31–6.35 (m, 1H; CH), 6.67 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.25–7.27 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 74.48, 126.62, 127.69, 127.97, 128.61, 128.71, 131.03, 131.08, 133.49, 136.25, 141.16 ppm; FT-IR (film): ν_{max} = 3334, 3078, 3059, 3027, 2957, 2925, 2870, 1597, 1490, 1449, 1404 cm^{-1}; MS (EI): m/z (%) 244 [M]$^+$ (36), 139 (100), 105 (60), 192 (60), 77 (33).

1-(4-Nitrophenyl)-3-phenylprop-2-en-1-ol (entry 12, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.19 (s, 1H; OH), 5.49 (s, 1H; CH), 6.27–6.32 (m, 1H; CH), 6.73 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.25–7.37 ppm (m, 5H; ArH), 7.61 (d, $^3J_{HH}$ = 7.90 Hz, 2H; ArH), 8.22 (d, $^3J_{HH}$ = 7.85 Hz, 2H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 74041, 123.76, 126.69, 126.96, 128.34, 128.69, 130.07, 132.30, 135.82, 147.39, 149.71 ppm; FT-IR (film): ν_{max} = 3427, 3107, 3081, 3027, 1855, 1600, 1519, 1345 cm^{-1}; MS (EI): m/z (%) 237 [M–H$_2$O]$^+$ (98), 105 (100), 150 (65), 77 (40).

4-(1-Hydroxy-3-phenylallyl)benzonitrile (entry 13, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.31 (s, 1H; OH), 5.43 (d, $^3J_{HH}$ = 6.85 Hz, 1H; CH), 6.26–6.31 (m, 1H; CH), 6.70 (d, $^3J_{HH}$ = 15.80 Hz, 1H; CH), 7.26–7.65 ppm (m, 9H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 74.51, 111.37, 118.78, 126.68, 126.89, 128.26, 128.68, 130.25, 132.05, 132.37, 135.92, 147.87 ppm; FT-IR (film): ν_{max} = 3426, 3059, 3027, 2924, 2229, 1607, 1494, 967 cm^{-1}; MS (EI): m/z (%) 235 [M]$^+$ (100), 105 (98), 217 (50), 130 (60), 91 (50).

1,5-Diphenylpenta-2,4-dien-1-ol (entry 14, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 2.01 (s, 1H; OH), 5.32 (d, $^3J_{HH}$ = 6.35 Hz, 1H; CH), 5.98–6.02 (m, 1H; CH), 6.45–6.50 (m, 1H; CH), 6.58 (d, $^3J_{HH}$ = 15.65 Hz, 1H; CH), 6.75–6.81 (m, 1H; CH), 7.21–7.42 ppm (m, 10H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 74.86, 126.30, 126.39, 127.65, 127.78, 128.07, 128.60, 130.98, 133.23, 135.49, 137.08, 142.79 ppm; FT-IR (film): ν_{max} = 3290, 3080, 3059, 3026, 1599, 1492, 1449 cm^{-1}; MS (EI): m/z (%) 235 [M–H]$^+$ (25), 105 (100), 217 (90), 128 (50), 202 (50), 77 (33).

4-Phenylbut-3-en-2-ol (entry 15, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; CHCl$_3$): δ = 1.36 (d, $^3J_{HH}$ = 6.39 Hz, 3H; CH$_3$), 1.56 (s, 1H; O–H), 4.47–4.45 (m, 1H; CH), 6.23–6.28 (m,1H, CH), 6.56 (d, $^3J_{HH}$ = 15.93 Hz, 1H; CH), 7.21–7.38 ppm (m, 5H; ArH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 23.42, 68.94, 126.46, 127.64, 128.59, 129.41, 133.58, 136.72 ppm; FT-IR (film): ν_{max} = 3342, 3078, 3058, 3026, 2972, 2926, 2871, 1493, 1449, 1141, 1059, 967, 748, 693 cm^{-1}; MS (EI): m/z (%) 148 [M]$^+$ (50), 129 (100), 105 (67), 115 (50), 132 (25), 77 (25), 91 (33).

Dodec-6-en-5-ol (entry 16, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 0.8 (s, 6H), 1.29–1.33 (m, 12H), 2.01–2.07 (m, 4H), 4.02 (s, 2H; OH), 5.39 ppm (s, 1H; CH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 13.94, 13.98, 22.53, 22.84, 27.38, 27.76, 29.42, 30.83, 31.56, 67.30, 127.09, 139.09 ppm; FT-IR (film): ν_{max} = 3344, 2928, 2397, 1378, 1331, 1086 cm^{-1}; MS (EI): m/z (%) 184 [M]$^+$ (9), 57 (100), 81 (39), 71 (76), 94 (35).

3-Methylcyclohex-2-enol (entry 17, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 1.38 (s, 1H; CH), 1.55–1.61 (m, 2H, CH$_2$), 1.68 (s, 3H; CH$_3$), 1.72–1.92 (m, 4H), 4.17 (s, 1H; OH), 5.49 (s, 1H, CH); ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 18.89, 23.60, 30.06, 31.67, 65.86, 124.23, 138.72 ppm; FT-IR

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(film): ν_{max} = 3342, 2935, 2862, 1447, 1376, 1033 cm^{-1}; MS (EI): m/z (%) 112 [M]$^+$ (30), 97 (100), 79 (80), 69 (25).

2-Benzylidenecyclohexanol (entry 18, Table 2). ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C; TMS): δ = 1.48–1.68 (m, 5H), 1.85–2.12 (m, 3H), 2.72 (s, 1H; OH), 4.24 (s, 1H; CH), 6.52 (s, 1H; CH); 7.22–7.32 (m, 5H; ArH) ^{13}C NMR (126 MHz, CDCl$_3$, 25 °C; CDCl$_3$): δ = 23.18, 26.96, 27.34, 36.58, 73.74, 120.81, 126.21, 128.07, 128.91, 137.66, 144.34 ppm; FT-IR (film): ν_{max} = 3360, 3058, 3020, 2938, 2853, 1598, 1494 cm^{-1}; MS (EI): m/z (%) 188 [M]$^+$ (36), 91(100), 115 (40), 97 (80).

Acknowledgements

Notes and references

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