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Mild and efficient barbier allylation reaction mediated by magnesium powder under solvent-free conditions

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ABSTRACT

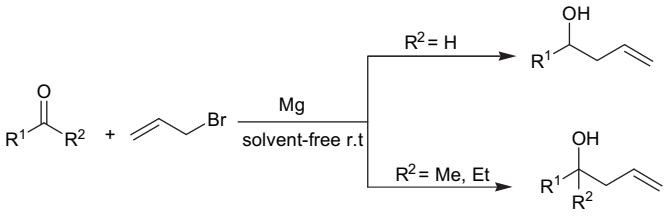
A novel and highly efficient synthesis of homoallylic alcohols is achieved by the allylation of carbonyl compounds using magnesium powder as mediator under solvent-free conditions. A series of aldehydes and ketones are converted to the corresponding homoallylic alcohols, the yields of the reaction is considerably high (85–98%). The procedure is environment benign, operationally simple and easy to scale up at room temperature.

1. Introduction

Over recent years, the allylation of carbonyl compounds has attracted tremendous interest in building blocks for the construction of various biologically active compounds and pharmaceutical chemistry.[1] Therefore, numerous reagents and methods have been applied to accomplish synthetically useful homoallylic alcohols.[2] Examples include various Lewis acids,[3] metal salts,[4] catalysts,[5] β-cyclodextrin,[6] organometallic reagents in organic media, aqueous media,[7,8] ionic liquids,[9] and PEG.[10] However, because of economical and environmental concerns, organic chemists have been confronted with a new challenge of finding novel methods in organic synthesis that can reduce and finally eliminate the impact of volatile organic solvents and hazardous toxic chemicals on the environment.[11] This new challenge attracts considerable attention because of increasing public interest in green chemistry.[12]

Within the last several years, various metals have been exploited for mediating allylation of carbonyl compounds. Including In,[13] Sb,[14] Pb,[15] Mn,[16] Fe,[17] Mg,[7,18] Zn,[8b,19] Sn,[11,20,9b,8a] Ga,[21] Bi[22] or organometallic compounds, such as allylmercurybromide,[23] triallylaluminum,[24a] and allyltributylstannanes [24b] mediated Barbier reactions in aqueous medium are well known in the literature. Though using of aqueous medium has a number of advantages,[25] it is notable that not all of the above aqueous Barbier reactions could be conducted in fully aqueous media. Most of these reactions require long reaction time to improve the yields. In addition, many allylmagnesium and allyllithium reagents are often very difficult to handle, and the reactions have to be performed under strictly anhydrous, oxygen-free, low-temperature conditions for prolonged lengths times and the use of a great deal of organic solvents can potentially lead to some environmental pollution. So, the development of more improved synthetic methods for the preparation of homoallylic alcohols remains an active research area.

Previously our program reported the allylation of carbonyl compounds under solvent-free conditions.[19a,26] In this paper, we focus on the potential use of magnesium metal in solvent-free allylation reactions, we are interested in finding the allylation of carbonyl compounds mediated by magnesium powder under solvent-free conditions to synthesize the homopropargyl alcohols (Scheme 1) possessed the following advantages: high yields, short reaction time, low costs, reduced pollution, simplicity in process and handling.



R^1 = Ph, Aryl, Heterocyclic, Aliphatic

Scheme 1. Magnesium powder mediated allylation of carbonyl compounds with allylbromide under solvent-free conditions.

2. Results and discussion

In order to exploit the effect of different metals and solvents on the yields of the reaction, a mixture of benzaldehyde, allylbromide, solvent, and metal was stirred at room temperature. The results were presented in Table 1.

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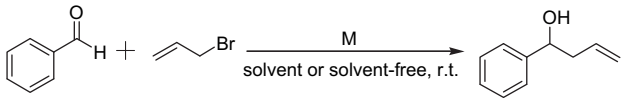
Table 1
.Allylation of aldehyde mediated by various metals under different conditions[a]



Entry	Mediator	Solvent	Time (h)	Yield (%)[b]
1	Ni	—	6	NR[c]
2	Mn	—	4	NR[c]
3	Co	—	7	NR[c]
4	Fe	—	15	NR[c]
5	Al	—	16	NR[c]
6	W	—	17	NR[c]
7	Pb	—	17	NR[c]
8	Ti	—	19	NR[c]
9	Mg	—	0.14	85
10	Sn	—	1	78
11	Zn	—	0.25	81
12	Mg	H_2O	24	NR[c]
13	Mg	CH_2Cl_2	20	NR[c]
14	Mg	DMSO	16	NR[c]
15	Mg	EtOH	8	20
16	Mg	Et_2O	6	38
17	Mg	DMF	4	46
18	Mg	THF	0.21	78

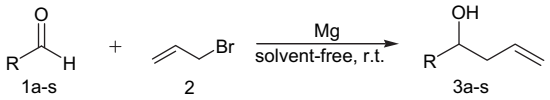
[a] Reaction conditions: benzaldehyde (2 mmol), allylbromide (3 mmol), metal (3 mmol), solvent (2 mL), at room temperature.
[b] Isolated yield.
[c] NR: no reaction. Almost all of the benzaldehyde was recycled.

We first probed into different metals to mediate the reaction. From Table 1, it was obvious that most metals, such as Ni, Mn, Co, Fe, Al, W, Pb, and Ti did not give the desired product even after prolonged stirring time (Table 1, entries 1–8) under solvent-free conditions. When mediated by magnesium, the allylation went on smoothly and the desired product was obtained under solvent-free conditions (Table 1, entry 9). With tin powder as mediators in the absence of solvent, the homoallylic alcohol was gained in 78% yield after 1 h (Table 1, entry 10). For zinc powder, the allylation yield was further enhanced to 81% at room temperature after 0.25 h (Table 1, entry 11).

Then we explored the allylation of benzaldehyde mediated by magnesium under different solvents. We found that the desired products were not observed after prolonged stirring time, when distilled water, dimethyl sulfoxide or methylene dichloride was used as solvent (Table 1, entries 12–14). And the solvent was ethanol, diethyl ether or *N*,*N*-dimethylformamide (Table 1, entries 15–17), the product was produced in low yields while the use of magnesium powder in THF, the allylation yield was further enhanced to 78% at room temperature after 0.21 h (Table 1, entry 18). It is obvious that product yield was higher (85%) under solvent-free conditions in comparison to that (78%) in THF. Among the different metals and solvents studied, magnesium powder was found to be the most ideal metal for this allylation (Table 1, entry 9). So the solvent-free conditions were necessary for the successful allylation of benzaldehyde, which is a great improvement in reducing chemical pollution.

In an effort to obtain improver yields, we conducted Table 1 mediated by magnesium powder at different temperatures under solvent-free condition. As a result, we found that at 0 °C no significant formation of the desired product even after prolonged stirring. When the reactions were performed under higher temperature conditions, the products led to the generation of complicated mixtures. Subsequently, it was found that allylation of benzaldehyde proceeded smoothly at room temperature under solvent-free condition. Then a variety of aldehydes were examined using this allylation method (Scheme 1). The results are listed in Table 2.

Table 2
Allylation of aldehydes mediated by magnesium powder under solvent-free conditions[a]



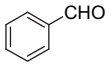
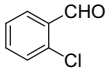
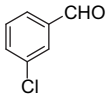
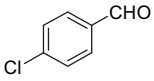
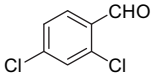
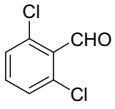
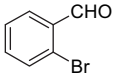
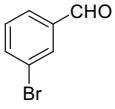
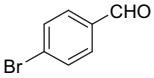
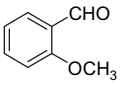
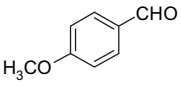
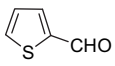
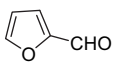
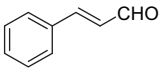
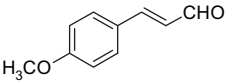
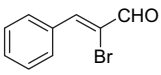
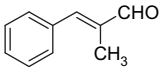
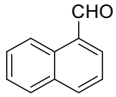
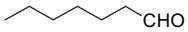
Entry	RCHO	Product[b]	Time/(min)	Yield/(%)[c]
1		**3a**	8(15[d])	85(81[d])
2		**3b**	5(10[d])	90(91[d])
3		**3c**	5	87
4		**3d**	6	91
5		**3e**	6	86
6		**3f**	5	94
7		**3g**	6	90
8		**3h**	5	92
9		**3i**	5(12[d])	91(82[d])
10		**3j**	10	94
11		**3k**	10(15[d])	95(86[d])
12		**3l**	12(20[d])	93(84[d])
13		**3m**	12(15[d])	91(82[d])
14		**3n**	6(15[d])	86(77[d])
15		**3o**	6	88
16		**3p**	5	89

Table 2 (*continued*)

Entry	RCHO	Product[b]	Time/(min)	Yield/(%)[c]
17		**3q**	6	90
18		**3r**	7	91
19		**3s**	10(20[d])	82(80[d])

[a] Reaction conditions: aldehydes (2 mmol), allylbromide (3 mmol), magnesium powder (3 mmol).
[b] All products were characterized by IR ^{1}H NMR, ^{13}C NMR, MS, and elemental analyses for all new compound.
[c] Isolated yield.
[d] The yields in brackets are from the reaction mediated by zinc powder.[19a]

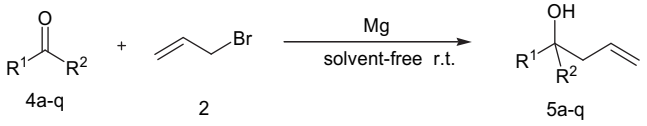
From the results shown in Table 2, it can be seen that most of the reactions were complete in high yields within a short reaction time. TLC analysis of the ether extract clearly showed a spot that corresponds to the desired allylation product. In general, allylation of various aldehydes (Table 2, entries 2, 4, 6–13, 17, 18) gave the corresponding products in good to excellent yields, but reaction times were shorter than allylation of aldehydes by zinc powder[19a] under solvent-free conditions. Moreover, the reaction conditions were sufficiently mild not to affect the phenyl (Table 2, entry l), chloro (Table 2, entries 2–6), bromide (Table 2, entries 7–9), and methoxy (Table 2, entries 10 and 11) functionalities. As for thiophene-2-carbaldehyde (Table 2, entry 12) and furan-2-carbaldehyde (Table 2, entry 13) afforded moderate yields of the corresponding homoallylic alcohols after long reaction times. It was noteworthy that α,β-unsaturated aldehydes were also allylated in good yields, only the 1,2-addition products were obtained regioselectively (Table 2, entries 14–17). Aliphatic aldehyde was also allylated smoothly under same conditions in good yield (Table 2, entry 19). In addition, substituent on the phenyl ring, whether electron-donating or electron-withdrawing, has no significant influence on the reactions. Moreover, the position of the substituents on the phenyl ring also has little effect on the product yields.

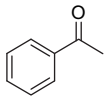
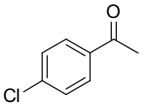
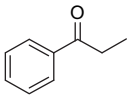
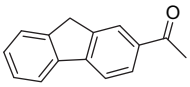
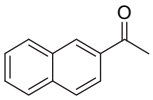
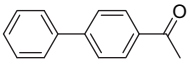
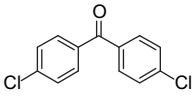
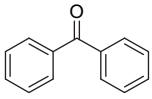
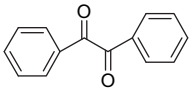
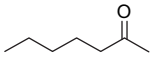
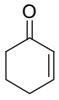
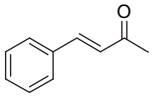
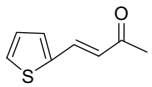
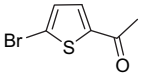
Thus far, the successful examples for allylation of ketones were much less than those for aldehydes. It is possible that the lower electrophilicity of the carbonyl carbon, are not so active in Barbier type allylation as aldehydes.[27,28]

In our further investigations, it was found that not only aldehydes but also ketones can be applied under the same conditions, furnishing various homoallylic alcohols in good to excellent yields. The allylation results of a series of ketones were summarized in Table 3.

From Table 3, it is evident that the most of ketones were complete after 4–9 min at room temperature, and side reactions, such as couplings has been not observed under solvent-free conditions. Aromatic ketones reacted with allylbromide and generated the corresponding homoallylic alcohols in good yields (Table 3, entries 1–3). The allylation of 1-(9*H*-fluoren-7-yl)ethanone (Table 3, entry 4), 1-(naphthalen-6-yl)ethanone (Table 3, entry 5), 1-(4-biphenyl)-ethanone (Table 3, entry 6), bis(4-chlorophenyl)methanone (Table 3, entry 7), and benzophenone (Table 3, entry 8) could be carried out very well. Then benzyl has been allylated under the same conditions, the allylation proceeded smoothly and give the single addition product (Table 3, entry 9). If the substrates were aliphatic ketones, the corresponding homoallylic alcohols were obtained in good yields (Table 3, entries 10 and 11). For α,β-unsaturated ketones, only

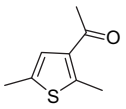
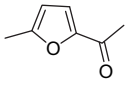
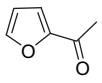
Table 3
Allylation of ketones mediated by magnesium powder under solvent-free conditions[a]



Entry	Ketones	Products[b]	Time/(min)	Yield/(%)[c]
1		**5a**	8(20[d])	94(85[d])
2		**5b**	9	92
3		**5c**	9(30[d])	89(77[d])
4		**5d**	7	95
5		**5e**	8	94
6		**5f**	7	92
7		**5g**	6	98
8		**5h**	9(30[d])	94(80[d])
9		**5i**	13	94
10		**5j**	7(20[d])	91(74[d])
11		**5k**	6(20[d])	88(78[d])
12		**5l**	5	92
13		**5m**	5	92
14		**5n**	4	91

(*continued on next page*)

Table 3 (*continued*)

Entry	Ketones	Products[b]	Time/(min)	Yield/(%)[c]
15		**5o**	6	96
16		**5p**	6	88
17		**5q**	8	91

[a] Reaction conditions: ketones (2 mmol), allylbromide (3 mmol), magnesium powder (3 mmol).
[b] All products were characterized by IR ^{1}H NMR, ^{13}C NMR, MS.
[c] Isolated yield.
[d] The yields in brackets are from the reaction mediated by zinc powder.[19a]

the 1,2-addition products were obtained regioselectively in good yields (Table 3, entries 12 and 13). Indeed, heterocyclic ketones react almost as well as aromatic ketones (Table 3, entries 14–17).

3. Conclusion

In conclusion, magnesium powder was found to be an effective metal for mediating allylation of carbonyl compounds under solvent-free conditions at room temperature. This method reported here compared with previously reported methods[19a] has the following advantages: (a) the high yields (the yields is rise height to 85–98% from 77 to 91%); (b) the reaction time is shortened to 4–13 min from 10 to 30 min; (c) easy to handle.

4. Experimental

4.1. General remarks

^{1}H NMR spectra were recorded on a Brucker AM-400 MHz and Brucker AC-E 200 MHz spectrometers in $CDCl_3$ with TMS as an internal standard. ^{13}C NMR spectra were obtained on a Brucker AM-400 operating at 100 MHz or a Brucker AC-E 200 operating at 50 MHz. IR spectra were recorded on an Alpha Centauri FI-IR spectrometer. Mass spectra were recorded on an HP 5988A and GC/MS/DS instruments. Elemental analyses were carried out on Carlo Erba-1106 instruments. Purification of products was performed via flash chromatography with 200–400 mesh silica gel (15:1 petroleum/diethyl ether). All substrates and reagents were obtained commercially, which were prepared by standard procedures.

4.2. Typical experimental procedure for the synthesis of homoallylic alcohols

Magnesium powder (3 mmol) was placed in a flame dried round bottom flask (50 mL). Then carbonyl compounds (2 mmol) and allybromide (3 mmol) were added. The resulting mixture was stirred at room temperature and the reaction was monitored by TLC. After complete conversion, saturated NH_4Cl solution (15 mL) was poured into the mixture. The mixture was extracted with Et_2O (3×10 mL) and the organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated. The pure products were obtained by column chromatograph of the crude mixture on silica gel using petroleum/ethyl acetate as an eluent. All the isolated products were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS, and elemental analysis for all the new compounds.

4.2.1. 1-Phenylbut-3-en-1-ol ***3a***. Oil,[19a] IR (ν/cm^{-1}): 3372, 3073, 2907, 1641, 1493, 1445, 1043, 997, 917, 757, 701; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39–7.23 (m, 5H), 5.84–5.74 (m, 1H), 5.18–5.12 (m, 2H), 4.72 (t, J=8 Hz, 1H), 2.532.45 (m, 2H), 2.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.8, 134.4, 128.3, 127.5, 125.8, 118.3, 73.2, 43.7; EI-MS (m/z, %) 148 (M^+), 131, 107, 91, 79, 77, 51, 39.

4.2.2. 1-(2-Chloro-phenyl)but-3-en-1-ol ***3b***. Oil,[5b] IR (ν/cm^{-1}): 3419, 3074, 2938, 1637, 1472, 1435, 1348, 1254, 1068, 914, 751; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.58–7.18 (m, 4H), 5.92–5.82 (m, 1H), 5.22–5.14 (m, 3H), 2.67–2.34 (m, 2H), 2.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.1, 134.2, 131.6, 129.3, 128.4, 127.0, 118.7, 76.6, 69.5, 42.0; EI-MS (m/z, %) 182 (M^+), 147, 141, 113, 105, 77.

4.2.3. 1-(3-Chloro-phenyl)but-3-en-1-ol ***3c***. Oil,[9b] IR (ν/cm^{-1}): 3377, 3075, 2927, 1709, 1641, 1574, 1429, 1196, 994, 919; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36–7.17 (m, 4H), 5.84–5.73 (m, 1H), 5.19–5.10 (m, 2H), 4.72–4.68 (m, 1H), 2.55–2.43 (m, 2H), 2.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.8, 134.2, 133.8, 129.6, 127.5, 125.9, 123.9, 118.9, 72.5, 43.8; EI-MS (m/z, %) 182 (M^+), 165, 141, 113, 77.

4.2.4. 1-(4-Chloro-phenyl)but-3-en-1-ol ***3d***. Oil,[5b] IR (ν/cm^{-1}) 3374, 3077, 2980, 2908, 1642, 1597, 1490, 1411, 1091, 919, 829; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.24 (m, 4H), 5.83–5.72 (m, 1H), 5.19–5.14 (m, 2H), 4.73–4.69 (m, 1H), 2.54–2.41 (m, 2H), 2.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.2, 133.9, 133.1, 128.5, 127.1, 118.8, 72.5, 43.8; EI-MS (m/z, %) 182 (M^+), 165, 141, 113, 77.

4.2.5. 1-(2,4-Dichlorphenyl)but-3-en-1-ol ***3e***. White solid,[5b] mp 60–61 °C, IR (ν/cm^{-1}) 3278, 3080, 2938, 1639, 1470, 1071, 1045, 985, 926; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52–7.26 (m, 3H), 5.87–5.81 (m, 1H), 5.20–5.09 (m, 3H), 2.63–2.57 (m, 1H), 2.37–2.29 (m, 1H), 2.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.7, 133.7, 133.4, 132.2, 129.0, 128.0, 127.3, 119.1, 69.1, 41.9; EI-MS (m/z, %) 216 (M^+), 199, 175, 147, 111, 75, 51, 39.

4.2.6. 1-(2,6-Dichloro-phenyl)but-3-en-ol ***3f***. Oil, IR (ν/cm^{-1}): 3415, 3076, 2978, 2918, 1641, 1562, 1435, 1182, 1083, 918, 869, 769; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.29–7.15 (m, 3H), 5.89–5.78 (m, 1H), 5.52–5.46 (m, 1H), 5.17–5.08 (m, 2H), 2.95–2.84 (m, 2H), 2.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.1, 134.2, 133.8, 129.3, 128.9, 118.1, 71.4, 39.9; EI-MS (m/z, %) 216 (M^+), 216, 199, 175, 147, 111, 75, 39. Anal. Calcd for $C_{10}H_{10}OCl_2$: C, 55.33; H, 4.64. Found C, 55.46; H, 4.53.

4.2.7. 1-(2-Bromo-phenyl)but-3-en-1-ol ***3g***. White solid,[5a] mp 33–34 °C, IR (ν/cm^{-1}):3297, 3070, 2933, 1640, 1498, 1465, 1433, 1065, 984, 913; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.58–7.51 (m, 1H), 7.33–7.18 (m, 3H), 5.90–5.82 (m, 1H), 5.22–5.14 (m, 3H), 2.66–2.60 (m, 1H), 2.42–2.34 (m, 1H), 2.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.1, 134.2, 131.6, 129.3, 128.4, 127.0, 118.7, 69.5, 41.9; EI-MS (m/z, %) 226 (M^+), 226, 209, 185, 157, 77, 51, 39.

4.2.8. 1-(3-Bromo-phenyl)but-3-en-1-ol ***3h***. Oil,[5a] IR (ν/cm^{-1}): 3373, 3076, 2978, 2906, 1643, 1433, 1166, 1035, 919, 701; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52 (s, 1H), 7.41–7.28 (m, 1H), 7.27–7.19 (m, 2H), 5.84–5.72 (m, 1H), 5.19–5.14 (m, 2H), 4.72–4.68 (m, 1H), 2.54–2.40 (m, 2H), 2.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.1, 133.8, 130.5, 129.9, 128.9, 124.4, 119.0, 109.7, 72.4, 43.8; EI-MS (m/z, %) 226 (M^+), 209, 185, 157, 105, 77, 51, 39.

4.2.9. 1-(4-Bromo-phenyl)but-3-en-1-ol ***3i***. Oil,[5a] IR (ν/cm^{-1}): 3376, 3076, 2926, 2906, 1642, 1486, 1405, 1062, 1005, 919, 870; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.48–7.43 (m, 2H), 7.26–7.18 (m, 2H),

5.82–5.72 (m, 1H), 5.18–5.14 (m, 2H), 4.71–4.68 (m, 1H), 2.51–2.40 (m, 2H), 2.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.7, 133.9, 131.4, 127.5, 121.2, 118.9, 72.5, 43.8; EI-MS (*m*/*z*, %) 226 (M^+), 209, 185, 157, 105, 77, 51, 39.

4.2.10. 1-(2-Methoxy-phenyl)but-3-en-1-ol ***3j***. Oil,[26b] IR (ν/cm^{-1}): 3412, 3072, 2938, 2837, 1640, 1596, 1462, 1240, 1045, 754; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.34–7.23 (m, 2H), 6.99–6.85 (m, 2H), 5.89–5.79 (m, 1H), 5.15–5.08 (m, 2H), 4.98–4.93 (m, 1H), 3.85 (s, 3H), 2.63–2.58 (m, 2H), 2.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=156.3, 135.1, 131.6, 128.2, 126.7, 120.6, 117.5, 110.3, 69.6, 55.2, 41.8; EI-MS (*m*/*z*, %) 178 (M^+), 161, 147, 137, 121, 107, 94, 77.

4.2.11. 1-(4-Methoxy-phenyl)but-3-en-1-ol ***3k***. Oil,[5b] IR (ν/cm^{-1}) 3398, 3072, 2932, 1886, 1611, 1512, 1456, 1247, 1036, 917, 831; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.28–7.25 (m, 2H), 6.89–6.86 (m, 2H), 5.83–5.76 (m, 1H), 5.16–5.11 (m, 2H), 4.70–4.66 (m, 1H), 3.81 (s, 3H), 2.51–2.47 (m, 2H), 2.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.9, 136.0, 134.6, 127.0, 118.2, 113.7, 72.9, 55.2, 43.7; EI-MS (*m*/*z*, %) 178 (M^+), 161, 144, 137, 109, 94, 77, 51, 39.

4.2.12. 1-(Thiophen-2-yl)but-3-en-1-ol ***3l***. Oil,[19a] IR (ν/cm^{-1}) 3362, 3026, 2906, 1641, 1438, 1030, 917, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.22–7.25 (m, 1H), 6.97–6.94 (m, 2H), 5.87–5.77 (m, 1H), 5.21–5.14 (m, 2H), 5.00–4.96 (m, 1H), 2.63–2.56 (m, 2H), 2.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.7, 133.7, 126.5, 124.5, 123.6, 118.7, 69.3, 43.7; EI-MS (*m*/*z*, %) 154 (M^+), 137, 113, 85, 58, 39.

4.2.13. 1-(Furan-2-yl)but-3-en-1-ol ***3m***. Oil,[5a] IR (ν/cm^{-1}) 3370, 3078, 2918, 1841, 1643, 1431, 1029, 920; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.38–7.26 (m, 1H), 6.34–6.25 (m, 2H), 5.86–5.77 (m, 1H), 5.20–5.13 (m, 2H), 4.75 (t, *J*=6.8 Hz, 1H), 2.67–2.57 (m, 2H), 2.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.9, 141.9, 133.6, 118.5, 110.0, 105.0, 66.8, 40.0; EI-MS (*m*/*z*, %) 138 (M^+), 121, 97, 84, 69, 55, 39.

4.2.14. (E)-1-Phenylhexa-1,5-dien-3-ol ***3n***. Oil,[4] IR (ν/cm^{-1}): 3371, 3078, 2915, 1641, 1431, 1009, 920, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.41–7.21 (m, 5H), 6.60 (d, *J*=16.0 Hz, 1H), 6.25 (d, *J*=16.0 Hz, 1H), 5.91–5.80 (m, 1H), 5.22–5.13 (m, 2H), 4.36 (d, *J*=5.6 Hz, 1H), 2.36–2.24 (m, 2H), 1.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.5, 133.9, 131.5, 130.2, 128.5, 127.6, 126.4, 118.4, 71.6, 41.9; EI-MS (*m*/*z*, %) 174 (M^+), 157, 133, 115, 91, 77, 55, 39.

4.2.15. (E)-1-(4-Methoxypheny)hexa-1,5-dien-3-ol ***3o***. Oil, IR (ν/cm^{-1}): 3413, 3074, 2929, 1712, 1605, 1512, 1448, 1294, 1176, 1032, 971, 919; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.26 (m, 2H), 6.89–6.83 (m, 2H), 6.54 (d, *J*=16.0 Hz, 1H), 6.11 (d, *J*=16.4 Hz 1H), 5.89–5.81 (m, 1H), 5.22–5.17 (m, 2H), 4.34–4.29 (m, 1H), 3.82 (s, 3H), 2.46–2.33 (m, 2H), 1.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.2, 134.1, 129.9, 129.3, 129.3, 127.6, 118.3, 113.9, 71.8, 55.2, 42.0; EI-MS (*m*/*z*, %) 204 (M^+), 187, 173, 163, 145, 121, 107, 91, 77, 55, 39; Anal. Calcd. For $C_{13}H_{16}O_2$: C, 74.13; H, 7.92. Found C, 74.04; H, 7.86.

4.2.16. (Z)-2-Bromo-1-phenylhexa-1,5-dien-3-ol ***3p***. Oil,[26b] IR (ν/cm^{-1}): 3541, 3376, 3074, 2915, 1640, 1441, 1038, 920, 864; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.59 (m, 2H), 7.38–7.23 (m, 3H), 7.08 (s, 1H), 5.86–5.76 (m, 1H), 5.23–5.15 (m, 2H), 4.35–4.30 (m, 1H), 2.64–2.49 (m, 2H), 2.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=134.9, 133.6, 133.2, 129.0, 128.9, 128.2, 128.1, 118.7, 76.4, 40.3; EI-MS (*m*/*z*, %) 252 (M^+), 252, 211, 193, 131, 103, 77, 51, 39.

4.2.17. (E)-2-Methyl-1-phenylhexa-1,5-dien-3-ol ***3q***. Oil,[26b] IR (ν/cm^{-1}): 3400, 3052, 2923, 1664, 1441, 1031, 917, 733, 704; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.35–7.20 (m, 5H), 6.53 (s, 1H), 5.85–5.80 (m, 1H), 5.21–5.14 (m, 2H), 4.23 (dd, *J*=7.2, 5.6 Hz, 1H), 2.48–2.39 (m, 2H), 1.93(s, 1H), 1.86–1.61 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.4, 137.4, 134.5, 128.9, 128.0, 126.4, 125.7, 118.0, 76.5, 40.0, 13.6; EI-MS (*m*/*z*, %) 188 (M^+), 171, 147, 129, 115, 91, 77, 51, 39.

4.2.18. 1-(Naphthalen-6-yl)but-3-en-1-ol ***3r***. Oil,[6] IR (ν/cm^{-1}): 3547, 3382, 3069, 2932, 1639, 1511, 1431, 1161, 1056, 917, 799, 778; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.08–7.46 (m, 7H), 5.98–5.88 (m, 1H), 5.55–5.51 (m, 1H), 5.25–5.17 (m, 2H), 2.75–2.56 (m, 2H), 2.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.4, 134.7, 133.7, 130.2, 128.9, 127.9, 126.0, 125.5, 125.4, 122.9, 122.8, 118.4, 69.9, 42.8; EI-MS (*m*/*z*, %) 198 (M^+), 157, 127, 115, 91, 77, 51, 39.

4.2.19. Dec-1-en-4-ol ***3s***. Oil,[4] IR (ν/cm^{-1}): 3363, 3074, 2927, 2857, 1828, 1641, 1458, 1377, 995, 912; ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.88–5.78 (m, 1H), 5.15–5.11 (m, 2H), 3.67–3.61 (m, 1H), 2.33–2.12 (m, 2H), 1.79 (s, 1H), 1.49–1.29 (m, 10H), 0.88 (t, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=134.9, 118.0, 70.6, 41.9, 36.8, 31.8, 29.3, 25.6, 22.6, 14.0; EI-MS (*m*/*z*, %) 139 (M^+–OH), 115, 97, 69, 55, 41.

4.2.20. 2-Phenylpent-4-en-2-ol ***5a***. Oil,[9b] IR (ν/cm^{-1}): 3440, 3069, 2977, 1641, 1444, 1371, 1068, 916, 765, 699; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.21 (m, 5H), 5.66–5.56 (m, 1H), 5.16–5.08 (m, 2H), 2.71–2.46 (m, 2H), 2.08 (s, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.5, 133.6, 128.1, 126.5, 124.7, 119.4, 73.5, 48.4, 29.8; EI-MS (*m*/*z*, %) 162 (M^+), 145, 121, 105, 77, 51, 43.

4.2.21. 2-(4-Chloro-phenyl)pent-4-en-2-ol ***5b***. Oil,[9b] IR (ν/cm^{-1}) 3431, 3076, 2977, 1641, 1490, 1094, 1007, 923, 828; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.36 (m, 2H), 7.33–7.26 (m, 2H), 5.64–5.53 (m, 1H), 5.15–5.12 (m, 2H), 2.67–2.45 (m, 2H), 2.07 (s, 1H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.1, 133.1, 132.3, 128.2, 126.3, 119.8, 73.3, 48.3, 29.8; EI-MS (*m*/*z*, %) 196 (M^+), 181, 155, 139, 111, 77, 43.

4.2.22. 3-Phenylhex-5-en-3-ol ***5c***. Oil,[26b] IR (ν/cm^{-1}): 3475, 3067, 2934, 1684, 1445, 978, 761; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.53–7.19 (m, 5H), 5.62–5.51 (m, 1H), 5.14–5.07 (m, 2H), 2.73–2.46 (m, 2H), 2.07 (s, 1H), 1.90–1.78 (m, 2H), 0.76 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.6, 133.5, 127.9, 126.3, 125.3, 119.4, 75.9, 46.8, 35.1, 7.7; EI-MS (*m*/*z*, %) 159 (M^+–OH), 147, 135, 117, 105, 91, 77, 57, 41, 39.

4.2.23. 2-(9H-Fluoren-7-yl)pent-4-en-2-ol ***5d***. White solid,[26a] mp 72–74 °C, IR (ν/cm^{-1}): 3475, 2976, 1670, 1456, 1269, 1101, 920, 771, 738; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.84–7.23 (m, 7H), 5.70–5.59 (m, 1H), 5.18–5.09 (m, 2H), 3.88 (m, 2H), 2.76–2.51 (m, 2H), 2.14 (s, 1H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.3, 143.3, 143.2, 141.4, 140.2, 133.7, 126.6, 126.5, 124.9, 123.4, 121.4, 119.7, 119.4, 73.8, 48.6, 36.9, 30.0, 26.7; EI-MS (*m*/*z*, %) 250 (M^+), 209, 193, 165, 43, 39.

4.2.24. 2-(Naphthalen-6-yl)pent-4-en-2-ol ***5e***. Oil,[26a] IR (ν/cm^{-1}): 3432, 3058, 2976, 1637, 1438, 1127, 918, 820, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.91–7.43 (m, 7H), 5.66–5.55 (m, 1H), 5.17–5.09 (m, 2H), 2.82–2.55 (m, 2H), 2.21 (s, 1H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.9, 133.5, 133.1, 132.2, 128.1, 127.8, 127.4, 126.0, 125.6, 123.5, 123.1, 119.6, 73.7, 48.2, 29.9; EI-MS (*m*/*z*, %) 212 (M^+), 197, 171, 127, 43, 39.

4.2.25. 2-(4-Biphenyl)pent-4-en-2-ol ***5f***. Oil,[26a] IR (ν/cm^{-1}): 3433, 3070, 2976, 1639, 1486, 1075, 919, 840, 696; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.60–7.25 (m, 9H), 5.70–5.64 (m, 1H), 5.19–5.14 (m, 2H), 2.75–2.51 (m, 2H), 2.08 (s, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.6, 140.7, 133.6, 128.7, 127.1, 127.0, 126.8, 125.2, 119.6, 73.5, 48.3, 29.9; EI-MS (*m*/*z*, %) 238 (M^+), 221, 197, 165, 152, 77, 43, 39.

4.2.26. 1,1-Bis(4-chloro-phenyl)but-3-en-1-ol ***5g***. Oil,[26a] IR (ν/cm^{-1}): 3548, 3077, 2926, 1639, 1489, 1094, 1006, 824; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.37–7.24 (m, 8H), 5.64–5.57 (m, 1H),

5.27–5.19 (m, 2H), 3.00 (d, *J*=6.8 Hz, 2H), 2.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=144.5, 132.9, 132.5, 128.4, 127.3, 121.3, 76.1, 46.4; EI-MS (*m*/*z*, %) 251 (M^+), 139, 135, 111, 75, 55, 41, 39.

4.2.27. 1,1-Diphenylbut-3-en-1-ol ***5h***. Oil,[19a] IR (ν/cm^{-1}): 3551, 3061, 1812, 1651, 1444, 1167, 995, 919, 700; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.49–7.18 (m, 10H), 5.71–5.60 (m, 1H), 5.26–5.15 (m, 2H), 3.08–3.06 (m, 2H), 2.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.4, 133.3, 128.1, 126.8, 125.9, 120.5, 76.8, 46.6; EI-MS (*m*/*z*, %) 224 (M^+), 207, 183, 165, 105, 91, 77, 51, 39.

4.2.28. 2-Hydroxy-1,2-diphenylpent-4-en-1-one ***5i***. White solid,[26a] mp 91–92 °C, IR (ν/cm^{-1}): 3462, 3062, 1672, 1443, 1359, 1219, 995, 932, 699, 513; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.74–7.24 (m, 10H), 5.78–5.68 (m, 1H), 5.13–4.98 (m, 2H), 4.19 (s, 1H), 3.16–2.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=200.7, 141.7, 134.4, 132.7, 132.2, 130.1, 128.8, 128.0, 128.0, 125.5, 120.3, 81.3, 43.8; EI-MS (*m*/*z*, %) 252 (M^+), 235, 211, 181, 163, 105, 77, 51, 39.

4.2.29. 4-Methylnon-1-en-4-ol ***5j***. Oil,[19a] IR (ν/cm^{-1}): 3392, 3073, 2935, 1642, 1454, 1149, 1002, 917; ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.91–5.81 (m, 1H), 5.15–5.08 (m, 2H), 2.23–2.19 (m, 2H), 1.65 (s,1H), 1.48–1.25 (m, 8H), 1.16 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=134.1, 118.5, 72.1, 46.2, 41.8, 32.3, 26.6, 23.5, 22.6, 14.0; EI-MS (*m*/*z*, %) 139 (M^+–OH), 115, 99, 83, 71, 55, 43.

4.2.30. 1-Allylcyxlohex-2-enol ***5k***. Oil,[19a] IR (ν/cm^{-1}): 3406, 3073, 2934, 1668, 1434, 1172, 984, 732; ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.93–5.80 (m, 2H), 5.63–5.61 (m, 1H), 5.15–5.10 (m, 2H), 2.31 (d, *J*=7.2 Hz, 2H), 2.07–2.00 (m, 1H), 1.74–1.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=133.6, 132.1, 130.0, 118.4, 69.0, 46.6, 35.4, 25.1, 18.8; EI-MS (*m*/*z*, %) 120 (M^+–H_2O), 97, 79, 67, 55, 41.

4.2.31. (E)-3-Methyl-1-phenylhexa-1,5-dien-3-ol ***5l***. Oil,[26a] IR (ν/cm^{-1}): 3398, 3072, 2974, 1641, 1445, 1104, 970, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.39–7.20 (m, 5H), 6.61 (d, *J*=16.4 Hz, 1H), 6.32 (d, *J*=16 Hz, 1H), 5.87–5.78 (m, 1H), 5.18–5.14 (m, 2H), 2.47–2.33 (m, 2H), 1.82 (s, 1H), 1.69 (s, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=136.8, 136.1, 133.5, 128.5, 127.3, 126.3, 119.3, 72.3, 47.2, 27.8; EI-MS (*m*/*z*, %) 188 (M^+), 171, 147, 129, 115, 77, 43, 39.

4.2.32. (E)-3-methyl-1-(thiophen-2-yl)hexa-1,5-dien-3-ol ***5m***. Oil,[26a] IR (ν/cm^{-1}): 3405, 3074, 2974, 1641, 1370, 1108, 960, 920, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.14–6.92 (m, 3H), 6.74 (d, *J*=16 Hz, 1H), 6.15 (d, *J*=16 Hz, 1H), 5.87–5.77 (m, 1H), 5.18–5.13 (m, 2H), 2.44–2.30 (m, 2H), 1.84 (s, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.0, 135.8, 133.3, 127.3, 125.5, 123.9, 120.8, 119.4, 72.1, 47.1, 27.8; EI-MS (*m*/*z*, %) 194 (M^+), 192, 177, 161, 153, 135, 122, 109, 97, 43, 39.

4.2.33. 2-(5-Bromothiophen-2-yl)pent-4-en-2-ol ***5n***. Oil,[26a] IR (ν/cm^{-1}): 3406, 3077, 2977, 1644, 1439, 1372, 1114, 923, 796; ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.87 (d, *J*=3.6 Hz, 1H), 6.63 (d, *J*=3.6 Hz, 1H), 5.77–5.67 (m, 1H), 5.19–5.12 (m, 2H), 2.66–2.48 (m, 2H), 2.33 (s, 1H), 1.57 (s 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.5, 132.7, 129.5, 122.4, 120.1, 110.4, 72.9, 48.7, 30.1; EI-MS (*m*/*z*, %) 246 (M^+), 231, 229, 207, 43, 39.

4.2.34. 2-(2,5-Dimethylthiophen-3-yl)pent-4-en-2-ol ***5o***. Oil,[26a] IR (ν/cm^{-1}): 3439, 3072, 2922, 1662, 1445, 1369, 1142, 917, 829; ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.54 (s, 1H), 5.77–5.67 (m, 1H), 5.16–5.12 (m, 2H), 2.50–2.14 (m, 8H), 2.03 (s, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.1, 134.2, 133.9, 131.2, 125.6, 119.1, 73.6, 47.6, 30.8, 29.2, 14.9; EI-MS (*m*/*z*, %) 196 (M^+), 181, 155, 139, 113, 59, 43, 41, 39.

4.2.35. 2-(5-Methylfuran-2-yl)pent-4-en-2-ol ***5p***. Oil,[26a] IR (ν/cm^{-1}): 3411, 3077, 2981, 1684, 1373, 1097, 921, 786; ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.05 (s, 1H), 5.87 (s, 1H), 5.72–5.67 (m, 1H), 5.15–5.11 (m, 2H), 2.68–2.51 (m, 2H), 2.27 (s, 3H), 2.13 (s, 1H), 1.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=157.3, 151.2, 133.4, 118.9, 105.8, 105.3, 70.5, 46.0, 26.3, 13.5; EI-MS (*m*/*z*, %) 166 (M^+), 149, 135, 125, 109, 95, 43, 39.

4.2.36. 2-(Furan-2-yl)pent-4-en-2-ol ***5q***. Oil,[26a] IR (ν/cm^{-1}): 3415, 3077, 2981, 1672, 1367, 1159, 921, 737; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.26 (s, 1H), 6.31–6.18 (m, 2H), 5.71–5.62 (m, 1H), 5.15–5.10 (m, 2H), 2.70–2.51 (m, 2H), 2.22 (s, 1H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.1, 141.5, 133.2, 119.2, 109.9, 104.6, 70.7, 46.1, 26.4; EI-MS (*m*/*z*, %) 151 (M^+–H), 135, 120, 111, 95, 79, 43, 39.

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