Synthesis of homoallylic alcohols by allylation of aldehydes and ketones catalysed by a mesoporous material (MCM-41)-supported cyano palladium complex

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A variety of homoallylic alcohols has been conveniently synthesised in good to high yields by the allylation of aldehydes and ketones with allylic chlorides catalysed by an MCM-41-supported cyano palladium complex in DMF using $SnCl_2$ as reducing agent. This polymeric palladium complex can be recovered and reused with some loss of activity.

Keywords: homoallylic alcohol, allylation, supported catalyst, palladium, MCM-41

Homoallylic alcohols are versatile intermediates in the preparation of some materials, natural products, and bioactive compounds. The utilisation of π-allylpalladium complexes as nucleophiles has been exemplified by the transformation of allylic esters,[1-3] allylic alcohols[4-7] and allylic chlorides[8-10] with a palladium(0) catalyst into allylic metal compounds, which have then been applied to carbonyl allylation to prepare homoallylic alcohols. Some other carbonyl allylation reactions of aldehydes with different mechanisms can also afford homoallylic alcohols.[11-13] Masuyama *et al.*[14] reported that stannous chloride is more effective as a reducing agent than other low-valent metals in palladium-catalysed carbonyl allylation by allylic esters. However, in most cases, homogeneous palladium complexes such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and $Pd(PhCN)_2Cl_2$ are used for formation of π-allylpalladium complexes. The amount of palladium catalyst used is about 2 mol% of reactant and it is difficult to recover it from the products. Carbonyl allylation of aldehydes catalysed by homogeneous palladium complexes offers good to excellent yields of homoallylic alcohols,[15,16] but the non-recoverable expensive palladium metal restricts its use in industry. It is highly desirable to develop a new recoverable and reusable catalytic system with the same or better activity than the homogeneous system.

The high costs of transition-metal catalysts coupled with toxic effects associated with many transition metals has led to an increased interest in immobilising catalysts onto a support. This class of supported reagents can facilitate both the isolation and recycling of the catalysts by simple filtration, thus providing an environmentally, cleaner process.[17,18] Polymer-supported palladium catalysts have successfully been used for a variety of organic reactions.[19,20] Study of new types of supported palladium catalysts which might be suitable for carbonyl allylation of aldehydes or ketones has theoretical and practical significance. Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilisation of homogeneous catalysts.[21] MCM-41 has a regular pore diameter of *ca*50 Å and a specific surface area > 700 $m^2\ g^{-1}$.[22] Its pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach the surface of the channel.[23-25] It is generally believed that high surface area of heterogeneous catalysts results in high catalytic activity. Considering the fact that the MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that an MCM-41-supported palladium catalyst will exhibit high activity and good reusability. To date, a few palladium complexes on functionalised MCM-41 support have been prepared and used in organic reactions.[26-29] However, to the best of our knowledge, there has been no general study of carbonyl allylation reactions catalysed by an MCM-41-supported palladium complex catalyst described to date. In this paper, we report the synthesis of an MCM-41-supported cyano palladium complex catalyst [MCM-41-CN-Pd(II)] and its catalytic behaviour in the carbonyl allylation reactions of aldehydes or ketones.

The starting MCM-41 was easily prepared according to a reported procedure.[30] The MCM-41-supported cyano palladium complex catalyst [MCM-41-CN-Pd(II)] was conveniently synthesised from commercially available and cheap γ-cyanopropyltriethoxysilane by immobilisation on MCM-41, followed by reaction with palladium chloride in acetone (Scheme 1). The XRD analysis of MCM-41-CN-Pd(II) indicated that, in addition to an intense diffraction peak (100), two higher order peaks with lower intensities were also detected, and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41. Nitrogen adsorption studies demonstrated that a significant decrease in pore size by virtue of silylation of the MCM-41 channels had occurred. Additionally, upon modification the surface area and pore volume clearly decreased. These results are in good agreement with the fact that the surface modification indeed occurred inside the primary mesopores of the MCM-41. Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterise the MCM-41-supported cyano palladium complex [MCM-41-CN-Pd(II)]. The nitrogen and palladium content of the MCM-41-CN-Pd(II) was determined to be 0.73 and 0.23 $mmol^{-1}g$, respectively, and the N: Pd mole ratio of this complex was 3.17. The binding energy (337.5 eV) of $Pd_{3d5/2}$ of MCM-41-CN-Pd(II) was lower than the binding energy (338.3 eV) of $Pd_{3d5/2}$ of $PdCl_2$ and the binding energy (400.2 eV) of N_{1s} of MCM-41-CN-Pd(II) was higher than the binding energy (399.5 eV) of N_{1s} of MCM-41-CN. These results suggest that a coordination bond between N and Pd was formed in MCM-41-CN-Pd(II).

In order to test the catalytic activity of the MCM-41-CN-Pd(II), the carbonyl allylation of aldehydes and ketones with allylic chlorides was investigated (Scheme 2). The reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. The results are summarised in Table 1. The initial experimental was carried out with benzaldehyde and allyl chloride using 2 mol% MCM-41-CN-Pd(II) as catalyst and 1.5 equiv. $SnCl_2$ as reducing agent in DMF. The allylation reaction at 25°C required 48 h to go to completion and 1-phenylbut-3-en-1-ol (**3a**) was

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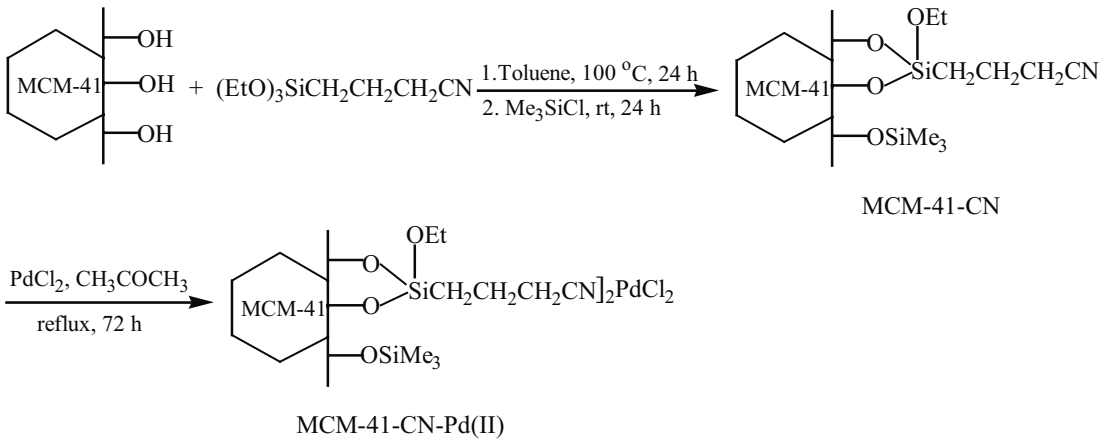


Scheme 1

obtained in 86% yield. When 2 mol% $PdCl_2(PhCN)_2$ was used, 1-phenylbut-3-en-1-ol was obtained in 81% yield under the same conditions. This polymeric palladium catalyst not only has high catalytic activity in the allylation of benzaldehyde, but also can be recovered by simple filtration. The activity of the recovered catalyst was tested for the allylation of benzaldehyde with allyl chloride for five recycles and it was found that 1-phenylbut-3-en-1-ol (**3a**) was formed in 85, 83, 79, 72 and 61% yield, respectively.

As shown in Table 1, the allylation reaction can tolerate a range of functional groups on the aromatic aldehydes; both strongly electron donating and withdrawing substituents can be present. The allylation of various aromatic aldehydes with allyl chloride has been achieved with good to high yields. The allylation of aliphatic aldehydes with allyl chloride also proceeded smoothly under the same conditions and the corresponding homoallylic alcohols were obtained in good yields. The allylation of aldehydes with methallyl chloride was slow at 25 °C under the same conditions and only trace amounts of products were formed after 48 h. However, the allylation reactions could proceed smoothly at 40 °C to give the corresponding homoallylic alcohols in good to high yields after 48 h. The reactivity of ketones was lower than that of aldehydes, but the allylation reactions of ketones with allyl chloride could also proceed at 40 °C and the corresponding homoallylic alcohols were obtained in good yields after 48 h (entries 12–14). Unfortunately, the allylation reaction of ketones with methallyl chloride did not occur at all at 40 or 60 °C.

In conclusion, we have described a MCM-41-supported cyano palladium complex catalyst whose preparation is simple and convenient. This complex has not only high activity for allylation of aldehydes and ketones with allylic chlorides, but also offers practical advantages such as easy handling, easy separation from the products and reuse for the preparation of homoallylic alcohols.

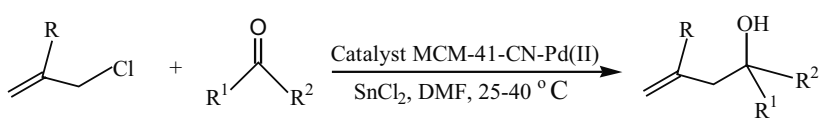
Experimental

IR spectra were obtained using a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P300 (300 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P300 (75 MHz) spectrometer using $CDCl_3$ as the solvent. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyser. DMF

Table 1 Allylation of aldehydes and ketones catalysed by MCM-41-CN-Pd(II)[a]

Entry	R	R^1	R^2	Temp./°C	Product	Yield [b]/%
1	H	Ph	H	25	**3a**	86
2	CH_3	Ph	H	40	**3b**	82
3	H	4-ClC_6H_4	H	25	**3c**	90
4	CH_3	4-ClC_6H_4	H	40	**3d**	87
5	H	4-$CH_3OC_6H_4$	H	25	**3e**	85
6	H	4-$O_2NC_6H_4$	H	25	**3f**	74
7	CH_3	2-HOC_6H_4	H	40	**3g**	77
8	CH_3	3,4-$CH_2O_2C_6H_3$	H	40	**3h**	84
9	H	3,4-$CH_2O_2C_6H_3$	H	25	**3i**	89
10	H	*n*-C_3H_7	H	25	**3j**	81
11	CH_3	*n*-C_6H_{13}	H	40	**3k**	79
12	H	Ph	CH_3	40	**3l**	73
13	H	Ph	CH_2Cl	40	**3m**	81
14	H	—$(CH_2)_5$—	—	40	**3n**	85

[a]Reactions were carried out with 1 mmol of aldehyde or ketone, 2 mmol of allylic chloride, 1.5 mmol of $SnCl_2$, 0.02 mmol of palladium catalyst in 3 ml of DMF for 48 h.
[b]Yield of isolated product **3** based on the aldehyde or ketone used.



1 **2** **3**

Scheme 2

was distilled before use, other reagents were used as received without further purification.

Preparation of MCM-41-CN: A solution of γ-cyanopropyltriethoxysilane (1.73 g, 7.5 mmol) in dry chloroform (12 mL) was added to a suspension of the mesoporous support MCM-41 (2.20 g) in dry toluene (120 mL). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered off and washed by $CHCl_3$ (2 × 20 mL), and dried under reduced pressure at 160 °C for 5 h. The dried white solid was soaked in a solution of Me_3SiCl (3.05 g, 28 mmol) in dry toluene (100 mL) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried under reduced pressure at 160 °C for 5 h to obtain 2.87 g of hybrid material MCM-41-CN. The nitrogen content was found to be 0.93 $mmol^{-1}g$ by elemental analysis.

Synthesis of MCM-41-CN-Pd(II): To a solution of $PdCl_2$ (0.135 g) in acetone (50 mL) was added MCM-41-CN (2.50 g). The mixture was refluxed under an argon atmosphere for 72 h. The product was allowed to cool and then filtered off. The resulting brown powder was washed with distilled water (3 × 10 mL) and acetone (3 × 10 mL) and then dried under reduced pressure to afford 2.47 g of MCM-41-CN-Pd(II). The nitrogen and palladium content was 0.73 and 0.23 $mmol^{-1}g$, respectively.

General procedure for the allylation of aldehydes and ketones with allylic chlorides: To a mixture of $SnCl_2$ (1.5 mmol), aldehyde or ketone (1 mmol), and allylic chloride (2 mmol) in DMF (3 mL) was added MCM-41-CN-Pd(II) (87 mg, 0.02 mmol Pd) at the temperature indicated in Table 1 under an argon atmosphere. After being stirred for 48 h, the mixture was filtered and the catalyst was washed with DMF (2 × 10 mL), diethyl ether (2 × 10 mL) and reused in the next run. The filtrate was diluted with 120 ml of a mixed solvent (diethyl ether/dichloromethane = 2:1) and washed successively with aqueous 10% HCl solution (2 × 10 mL), aqueous $NaHCO_3$ solution (10 mL), and water (3 × 10 mL). The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel (light petroleum: ethyl acetate = 7:1) to afford a colourless oil.

1-Phenylbut-3-en-1-ol (**3a**):[31] Oil. IR (film): ν (cm^{-1}) 3390, 3075, 3030, 2907, 1641, 1603, 1493, 1020, 750, 690; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.25 (m, 5H), 5.86–5.75 (m, 1H), 5.19–5.12 (m, 2H), 4.75–4.72 (m, 1H), 2.54–2.47 (m, 2H), 2.07 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 134.5, 128.4, 127.6, 125.8, 118.4, 73.3, 43.8; Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 80.89; H, 7.90%.

1-Phenyl-3-methylbut-3-en-1-ol (**3b**):[32] Oil. IR (film): ν (cm^{-1}) 3399, 3073, 3030, 2936, 1647, 1603, 1493, 1453, 1375, 1054, 891, 756, 699; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.27 (m, 5H), 4.93 (d, J = 1.6 Hz, 1H), 4.87 (d, J = 0.8 Hz, 1H), 4.82 (t, J = 6.8 Hz, 1H), 2.43 (d, J = 6.8 Hz, 2H), 2.15 (br, 1H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 142.4, 128.4, 127.5, 125.8, 114.1, 71.4, 48.4, 22.3; Anal. Calcd for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.22; H, 8.48%.

1-(4-Chlorophenyl)but-3-en-1-ol (**3c**):[33] Oil. IR (film): ν (cm^{-1}) 3387, 3078, 3028, 2907, 1641, 1597, 1492, 1411, 1051, 919, 830; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32–7.28 (m, 4H), 5.82–5.73 (m, 1H), 5.19–5.14 (m, 2H), 4.74–4.71 (m, 1H), 2.52–2.43 (m, 2H), 2.08 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3, 134.0, 128.5, 127.5, 127.2, 118.9, 72.6, 43.9; Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.75; H, 6.03. Found: C, 65.51; H, 5.83%.

1-(4-Chlorophenyl)-3-methylbut-3-en-1-ol (**3d**):[34] Oil. IR (film): ν (cm^{-1}) 3400, 3076, 3028, 2971, 2936, 1647, 1598, 1491, 1444, 1376, 1064, 1014, 894, 830; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (s, 4H), 4.94 (t, J = 1.6 Hz, 1H), 4.85 (d, J = 0.8 Hz, 1H), 4.79 (t, J = 6.8 Hz, 1H), 2.38 (d, J = 7.2 Hz, 2H), 2.15 (br, 1H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.5, 142.0, 133.1, 128.5, 127.2, 114.4, 70.7, 48.4, 22.3; Anal. Calcd for $C_{11}H_{13}OCl$: C, 67.18; H, 6.62. Found: C, 67.25; H, 6.56%.

1-(4-Methoxyphenyl)but-3-en-1-ol (**3e**):[33] Oil. IR (film): ν (cm^{-1}) 3386, 3072, 3019, 2930, 2850, 1640, 1600, 1500, 1450, 1380, 1240, 1175, 1030, 830; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.85–5.74 (m, 1H), 5.17–5.11 (m, 2H), 4.69 (t, J = 6.8 Hz, 1H), 3.80 (s, 3H), 2.52–2.48 (m, 2H), 1.99 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 136.1, 134.6, 127.1, 118.2, 113.8, 73.0, 55.3, 43.8; Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.27; H, 7.78%.

1-(4-Nitrophenyl)but-3-en-1-ol (**3f**): Oil. IR (film): ν (cm^{-1}) 3398, 3074, 3025, 2958, 1650, 1602, 1525, 1493, 1346, 845; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 5.84–5.74 (m, 1H), 5.22–5.17 (m, 2H), 4.89–4.86 (m, 1H), 2.60–2.54 (m, 1H), 2.49–2.42 (m, 1H), 2.13 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.1, 147.3, 133.2, 126.6, 123.7, 119.7, 72.2, 43.9; Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.18; H, 5.70, N, 7.25. Found: C, 61.89, H, 5.52, N, 7.08%.

1-(2-Hydroxyphenyl)-3-methylbut-3-en-1-ol (**3g**): Oil. IR (film): ν (cm^{-1}) 3396, 3070, 3026, 1638, 1601, 1495, 1443, 1200, 1030, 696; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.19–6.82 (m, 4H), 5.01 (t, J = 1.6 Hz, 1H), 4.97–4.93 (m, 1H), 4.91 (d, J = 0.8 Hz, 1H), 2.77 (s, 1H), 2.65–2.59 (m, 1H), 2.48–2.43 (m, 1H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 141.8, 129.0, 127.0, 126.2, 119.8, 117.3, 115.0, 72.9, 46.4, 22.2; Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 73.89; H, 7.74%.

1-(3,4-Methylenedioxyphenyl)-3-methylbut-3-en-1-ol (**3h**): Oil. IR (film): ν (cm^{-1}) 3365, 3060, 2881, 1630, 1601, 1489, 1440, 1375, 1243, 1040, 990, 870; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (d, J = 1.6 Hz, 1H), 6.82–6.75 (m, 2H), 5.94 (s, 2H), 4.90 (d, J = 1.6 Hz, 1H), 4.83 (s, 1H), 4.73–4.70 (m, 1H), 2.44–2.33 (m, 2H), 2.15 (br, 1H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.7, 146.9, 142.3, 138.2, 119.2, 114.0, 108.1, 106.4, 101.0, 71.4, 48.3, 22.4; Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.90; H, 6.80. Found: C, 69.71; H, 6.62%.

1-(3,4-Methylenedioxyphenyl)but-3-en-1-ol (**3i**):[31] Oil. IR (film): ν (cm^{-1}) 3360, 3070, 3024, 2880, 1640, 1600, 1490, 1440, 1240, 1030, 990, 870; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.87 (d, J = 1.6 Hz, 1H), 6.81–6.75 (m, 2H), 5.95 (s, 2H), 5.84–5.72 (m, 1H), 5.18–5.12 (m, 2H), 4.65 (t, J = 6.8 Hz, 1H), 2.49–2.44 (m, 2H), 1.91 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.8, 146.9, 138.0, 134.4, 119.2, 118.4, 108.1, 106.4, 101.0, 73.2, 43.8; Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.51; H, 6.30%.

1-Propylbut-3-en-1-ol (**3j**):[35] Oil. IR (film): ν (cm^{-1}) 3350, 2930, 2854, 1641, 1450, 1375, 1056, 1028; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89–5.78 (m, 1H), 5.16–5.12 (m, 2H), 3.70–3.62 (m, 1H), 2.36–2.27 (m, 1H), 2.19–2.09 (m, 1H), 1.63–1.24 (m, 5H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.9, 118.1, 70.4, 42.0, 39.0, 18.9, 14.1; Anal. Calcd for $C_7H_{14}O$: C, 73.68; H, 12.28. Found: C, 73.49; H, 12.07%.

1-Hexyl-3-methylbut-3-en-1-ol (**3k**):[36] Oil. IR (film): ν (cm^{-1}) 3358, 2930, 2857, 1641, 1442, 1375, 1054, 1025; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.89 (d, J = 1.6 Hz, 1H), 4.81 (d, J = 0.8 Hz, 1H), 3.75–3.67 (m, 1H), 2.27–2.18 (m, 1H), 2.13–2.04 (m, 1H), 1.77 (s, 3H), 1.72 (s, 1H), 1.54–1.23 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 114.6, 70.5, 48.6, 36.3, 31.8, 29.2, 25.7, 22.5, 22.3, 14.1. Anal. Calcd for $C_{11}H_{22}O$: C, 77.65; H, 12.94. Found: C, 77.48; H, 12.72%.

2-Phenylpent-4-en-2-ol (**3l**):[31] Oil. IR (film): ν (cm^{-1}) 3400, 3060, 2900, 1640, 1600, 1495, 1450, 1070, 760, 690; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.24 (m, 5H), 5.68–5.57 (m, 1H), 5.15–5.10 (m, 2H), 2.73–2.66 (m, 1H), 2.54–2.47 (m, 1H), 2.06 (br, 1H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.6, 133.7, 128.6, 128.2, 124.8, 119.5, 73.6, 48.5, 15.3; Anal. Calcd for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.25; H, 8.51%.

1-Chloro-2-phenylpent-4-en-2-ol (**3m**):[37] Oil. IR (film): ν (cm^{-1}) 3450, 3050, 2900, 1640, 1600, 1490, 1440, 760, 700; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.27 (m, 5H), 5.64–5.55 (m, 1H), 5.15–5.08 (m, 2H), 3.87–3.80 (m, 2H), 2.71 (d, J = 7.6 Hz, 2H), 2.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 132.4, 128.4, 127.5, 125.5, 119.7, 75.4, 53.8, 44.3; Anal. Calcd for $C_{11}H_{13}OCl$: C, 67.18; H, 6.62. Found: C, 66.91; H, 6.45%.

1-Allylcyclohexanol (**3n**):[31] Oil. IR (film): ν (cm^{-1}) 3350, 3060, 2870, 1637, 1030; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94–5.84 (m, 1H), 5.16–5.08 (m, 2H), 2.22 (d, J = 7.6 Hz, 2H), 1.64–1.25 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.7, 118.7, 71.0, 46.7, 37.4, 25.8, 22.2; Anal. Calcd for $C_9H_{16}O$: C, 77.14; H, 11.43. Found: C, 76.86; H, 11.21%.

We thank the National Natural Science Foundation of China (Project No. 20462002) and the Natural Science Foundation of Jiangxi Province in China (2007GZW0172) for financial support.

Received 23 February 2009; accepted 23 April 2009
Paper 09/0459 doi: 10.3184/030823409X460911
Published online: 22 June 2009

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