Palladium-Catalyzed Allylation of Carbonyl Compounds with Various Allylic Compounds Using In–$InCl_3$ in Aqueous Media

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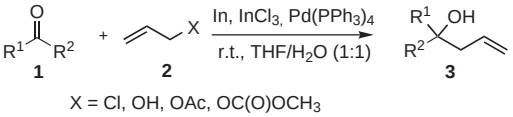
Received 15 February 2003

Abstract: Various allylic compounds can be effectively applied to palladium-catalyzed allylation of carbonyl compounds via the formation of π-allylpalladium(II) intermediates and their transmetalation with indium in the presence of indium trichloride in aqueous media.

Key words: allylation, palladium, indium, indium trichloride, aqueous

The chemistry of metallic indium is of current interest in organic synthesis due to its ability to mediate many organic transformations and its exceptional stability to air and water.[1] Among many indium mediated reactions, the Barbier-type allylation reaction is most widely applied in organic synthesis.[2] However, the allylating reagent has been limited to allylic halides, particularly allyl bromide and iodide. Allyl chloride also has been used with iodide salt via in situ generation of allyl iodide, and reported as an efficient allylating reagent in pure water under sonication or in a 1:1 mixture of water and *t*-butanol.[3] Our continuous efforts [4] in the area of indium chemistry led us to find out that various allylic compounds can be effectively applied to the indium-mediated allylation reaction of carbonyl compounds via the formation of π-allylpalladium(II) complexes, their transmetalation with indium in the presence of a catalytic amount of $Pd(PPh_3)_4$ and $InCl_3$ in aqueous media (Scheme 1). Thus allyl alcohol reacted with 2 equivalents of indium metal and benzaldehyde using 2 mol% of $Pd(PPh_3)_4$ and 0.5 equivalents of indium trichloride at room temperature in a 1:1 mixture of water and THF to afford the corresponding homoallylic alcohol in high yield.

Organopalladium compounds are known to undergo transmetalation with a number of metal salts, active metals, or organometallic compounds, such as Zn, $SnCl_2$, SmI_2, Et_3B, Et_2Zn and Me_6Sn_2.[5] The reaction transforms electrophilic palladium intermediates into nucleophilic organometallic compounds or umpolung type of compounds. Recently, allylic and allenic indium reagents have been prepared via transient organopalladium intermediates with indium or indium(I) iodide.[6] Our combined use of indium and indium(III) chloride in aqueous media was effective with various carbonyl compounds, gave a good diastereoselectivity, and had economical benefit than the use of indium(I) halide alone. Also the combination of indium with several other metal salts was possible.



Scheme 1

The results under various reaction conditions are summarized in Table 1. In the case of palladium-catalyzed reaction of benzaldehyde with indium and allyl alcohol, the optimized ratio of benzaldehyde, allyl alcohol and indium was 1:3:2. The addition of half equivalent of indium chloride as an additive in aqueous THF solution gave the best result (entry 6). The reaction hardly proceeds, if any, in THF or DMF (entry 2 and 3) and gave a lower yield in pure water (entry 4) under these Pd(0)–In–$InCl_3$ conditions. Without indium trichloride the reaction did not proceed even at 50 °C for 24 hours (entry 1), and when 0.1 equivalents of indium trichloride was used, the reaction of allyl alcohol gave the allylation product in lower yield (entry 5). When other Lewis acids, such as $SnCl_4$, $FeCl_3$, and CuCl (entry 8–10) instead of $InCl_3$, were used, the reactions of allyl alcohol provided the corresponding products in satisfactory yields respectively. But the reactions with other additives such as $SnCl_2$ (entry 7), $FeCl_2$ and $ZnCl_2$ gave a trace amount of the desired products. It should be noted that the reaction of allyl alcohol with 2 equivalents of InCl (entry 11) or InI (entry 12) instead of using In–$InCl_3$ afforded the allylation products in 50% and 55% yields respectively. The occurrence of these palladium catalyzed reactions with InCl instead of combining indium and $InCl_3$ suggests that active species might be InCl, which could be formed by the reaction of indium with metal chloride salts having higher reduction potentials than In(I).[7] The similar result was reported by us in the In–$InCl_3$ mediated cross-coupling reaction of methyl vinyl ketone and benzaldehyde.[8] The reaction in organic solvents with this combined use of indium and indium(III) chloride was unsuccessful probably due to slow generation of the InCl species through the reaction of In and $InCl_3$ in organic solvents.

Synthesis 2003, No. 5, Print: 01 05 2003.
Art Id.1437-210X,E;2003,0,05,0775,0779,ftx,en;C00403SS.pdf.

ISSN 0039-7881

Table 1 Palladium-catalyzed Allylation of Benzaldehyde with Indium and Allyl Alcohol under Various Conditions[a]

Entry	Additive (equiv)	Solvent	Time (h)	Temp (°C)	Yield (%)[b] of **3a**
1	–	THF–H_2O	24	50	NR[c]
2	$InCl_3$ (0.5)	DMF	24	r.t.	trace
3	$InCl_3$ (0.5)	THF	20	r.t.	12
4	$InCl_3$ (0.5)	H_2O	44	50	62
5	$InCl_3$ (0.1)	THF–H_2O	72	50	60
6	$InCl_3$ (0.5)	THF–H_2O	20	r.t.	94
7	$SnCl_2$ (1)	THF–H_2O	20	r.t.	5
8	$SnCl_4$ (1)	THF–H_2O	20	r.t.	76
9	$FeCl_3$ (1)	THF–H_2O	20	r.t.	87
10	CuCl (1)	THF–H_2O	20	r.t.	86
11	InCl (2)[d]	THF–H_2O	22	r.t.	50
12	InI (2)[d]	THF–H_2O	4	r.t.	55

[a] Reactions were carried out with 1 equiv of PhCHO, 3 equiv of allyl alcohol, 2 equiv of In, and 2 mol% of $Pd(PPh_3)_4$.
[b] Isolated yield.
[c] No reaction.
[d] Without indium.

As shown in Table 2, the In–$InCl_3$ system was also effective for the allylation of various carbonyl compounds such as aromatic aldehydes, heteroaromatic aldehydes, aliphatic aldehydes, and ketones with allyl alcohol in aqueous media.

Also, this reaction was effectively applicable to other allylic compounds with various leaving groups such as allyl trifluoroacetate, chloride, carbonate, acetate, and phenyl sulfone. The results are shown in Table 3. The reaction of allyl trifluoroacetate and chloride with benzaldehyde in the absence of $InCl_3$ under aqueous THF solution afforded the homoallyl alcohol in 80% and 91% yields respectively requiring longer reaction time (entry 1 and 2). However, the reaction of allyl carbonate and acetate in the absence of $InCl_3$ was very slow under the same conditions (entry 4 and 6).

As shown in Table 4, the palladium-catalyzed allylation reaction using the In–$InCl_3$ system was also effective for the allylation of various carbonyl compounds with allyl acetate in aqueous media.

The palladium-catalyzed allylation of benzaldehyde using the In–$InCl_3$ system with substituted allylic chlorides, acetates and alcohols afforded the corresponding branched homoallylic alcohols exclusively with the *anti*-selectivity in aqueous media (Table 5). In the case of cinnamyl alcohol and acetate, the reaction gave only *anti*-products (entry 7 and 8). The reaction of substituted allyl alcohols usually needed a higher reaction temperature.

Table 2 Palladium-catalyzed Allylation of Various Carbonyl Compounds with In–$InCl_3$ and Allyl Alcohol[a]

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1	PhCHO	20	**3a**	94
2	*o*-FPhCHO	20	**3b**	100
3	*m*-FPhCHO	20	**3c**	98
4	*p*-FPhCHO	20	**3d**	100
5	*o*-BrPhCHO	20	**3e**	98
6	*p*-MePhCHO	26	**3f**	99
7	*p*-*t*-BuPhCHO	72	**3g**	80
8	*p*-MeOPhCHO	72	**3h**	96
9	*p*-NCPhCHO	20	**3i**	76
10	*p*-MeO_2CPhCHO	48	**3j**	46
11	*p*-HO_2CPhCHO	20	**3k**	74
12	$CH_3(CH_2)_8CHO$	48	**3l**	79
13	Cinnamaldehyde	20	**3m**	63
14	3-Furaldehyde	20	**3n**	89
15	Nicotinaldehyde	20	**3o**	75
16	Cyclohexanone	20	**3p**	75
17	Acetophenone	96	**3q**	90
18	Ethylacetoacetate	2	**3r**	68[c]

[a] Reactions were carried out with 1 equiv of substrate, 3 equiv of allyl alcohol, 2 equiv of In, 0.5 equiv of $InCl_3$ and 2 mol% of $Pd(PPh_3)_4$ in THF–H_2O, 1:1 at r.t.
[b] Isolated yield.
[c] The bath temperature is 50 °C.

Table 3 Palladium-catalyzed Allyation of Benzaldehyde with In–$InCl_3$ and Various Allylic Compounds[a]

Entry	X	$InCl_3$ (equiv)	Time (h)	Yield (%)[b] of **3a**
1	$OC(O)CF_3$	–	24	80
2	Cl	–	27	91
3	Cl	0.5	4	94
4	$OC(O)OCH_3$	–	24	trace
5	$OC(O)OCH_3$	0.5	5	96
6	OAc	–	24	trace
7	OAc	0.5	4	94
8	SO_2Ph	0.5	40	54

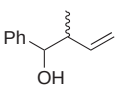
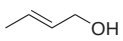
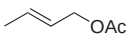
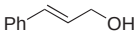
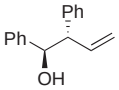
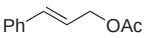
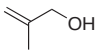
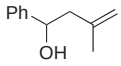
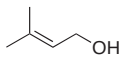
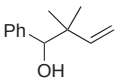
[a] Reactions were carried out with 1 equiv of PhCHO, 3 equiv of allyl alcohol, 2 equiv of In and 2 mol% of $Pd(PPh_3)_4$ in THF–H_2O, 1:1 at r.t.
[b] Isolated yield.

Table 4 Palladium-Catalyzed Allylation of Various Carbonyl Compounds with In–$InCl_3$ and Allyl Acetate[a]

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1	PhCHO	4	**3a**	94
2	*p*-FPhCHO	4	**3d**	94
3	$CH_3(CH_2)_8CHO$	12	**3l**	61
4	3-Furaldehyde	5	**3n**	89
5	Cyclohexanone	4	**3p**	76
6	Acetophenone	96	**3q**	49

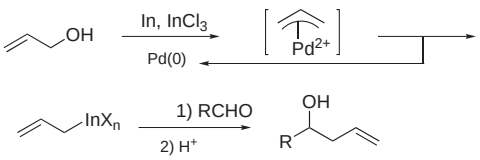
[a] Reactions were carried out with 1 equiv of substrate, 3 equiv of allyl acetate, 2 equiv of In, 0.5 equiv of $InCl_3$ and 2 mol% of $Pd(PPh_3)_4$ in THF–H_2O, 1:1 at r.t.
[b] Isolated yield.

Table 5 Palladium-catalyzed Allylation of Benzaldehyde with In–$InCl_3$ and Substituted Allylic Compounds[a]

Entry	Allylic comounds	Temp. (°C)	Time (h)	Product	Yield (%)[b] (*syn*:*anti*)[c]
1		r.t.	20		93 (50:50)
2		r.t.	3	**3s**	93 (63:37)[d]
3		50	20	**3s**	91 (22:78)
4		r.t.	20	**3s**	95 (36:64)[d]
5		50	15	**3s**	90 (28:72)
6		r.t.	5	**3s**	90 (26:74)[d]
7		50	20		78 (*anti* only)
8		50	20	**3t**	86 (*anti* only)
9		50	20	 **3u**	70
10		50	20	 **3v**	45

[a] Reactions were carried out with 1 equiv of substrate, 3 equiv of allyl alcohol, 2 equiv of In, 0.5 equiv of $InCl_3$ and 2 mol% of $Pd(PPh_3)_4$ in THF–H_2O, 1:1.
[b] Isolated yield.
[c] ^1H NMR ratio.
[d] α-Adduct only.

The probable mechanism for the palladium-catalyzed allylation of carbonyl compounds with the In–$InCl_3$ system is illustrated in Scheme 2. First of all, the reaction might proceed through the generation of π-allylpalladium(II) complexes. Unlike other palladium catalyzed allylation reactions, the direct formation of π-allylpalladium complexes from allylic alcohols usually requires severe reaction conditions[9] or a reagent such as $SnCl_2$,[10] Ph_3P,[11] Ph_3B,[12] and Ti(*i*-PrO)$_4$[13] to activate hydroxyl to serve as a leaving group. So the progress of the reaction of allyl alcohol is likely to be determined by the formation of π-allylpalladium complexes. In our results, the generation of π-allylpalladium complex from allyl chloride was accelerated in the presence of indium(III) chloride. And the generation of π-allylpalladium complexes from other allylic compounds, such as allyl alcohol, acetate, and carbonate, were practical when In–$InCl_3$, In–$FeCl_3$, In–CuCl, In–$SnCl_4$ or InCl were used. Subsequently, the complex reacted with indium in the presence of $InCl_3$ through the reductive transmetalation to allylindium species, which underwent the usual indium-mediated Barbier-type allylation of carbonyl compounds. In this reaction, indium(III) chloride have played a role in the formation of π-allylpalladium complexes from allylic compounds and/or in the in situ generation of the reactive In(I) chloride by reaction with indium(0) metal. Here, the structure of allylindium intermediates was not found in aqueous THF whereas allylindium(I) in pure water and allylindium(III) sesquihalides in organic solvents were reported.[14] The allylindium intermediates from allyl chloride in the presence of $Pd(PPh_3)_4$ (10%) was detected by ^1H NMR spectroscopy. The ^1H NMR spectra of the allylindium intermediates prepared from In–$InCl_3$ and InCl(I) in D_2O [allylic proton 1.57 ppm (d, J = 8.73 Hz)] and in $CDCl_3$ extracted from D_2O [allyl signals 6.11 (m, 1 H), 4.92 (dd, J = 1.76, 16.75 Hz, 1 H), 4.70 (dd, J = 1.98, 9.95 Hz, 1 H), and 2.07 ppm (d, J = 8.54 Hz, 2 H)] showed the same results respectively. But allylindium compounds from allyl chloride and indium(0) metal in the presence of $Pd(PPh_3)_4$ (10%) could not be detected in ^1H NMR spectrum because of its slow generation and decomposition.



Scheme 2

We were able to demonstrate that various allylic compounds had been successfully employed in indium-mediated Barbier-type allylation reactions with various carbonyl compounds using palladium catalyst and metal salts in aqueous media. We also managed to extend the scope of indium utility in organic synthesis. Further studies on the exact mechanism and use of this reaction conditions with various allylic compounds in aqueous media are in progress.

All compounds and solvents were obtained commercially and used in reactions without any further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 spectrometer and Varian Unity 300 spectrometer using TMS as internal standard. Electron-

impact mass spectra (EIMS) were recorded in the form of *m*/*z* on an Agilent GC-MSD (6850-5973) system. Flash column chromatography was performed on silica gel 60 (E. Merck).

Alcohols; General Procedure

A mixture of aldehyde (0.5 mmol), allyl alcohol (1.5 mmol), indium (1.0 mmol), indium(III) chloride (0.25 mmol) and $Pd(PPh_3)_4$ (2 mol%) in THF–H_2O, 1:1, 1 ml was stirred for 20 h at r.t. The reaction was quenched with 1N HCl (1 mL), EtOAc (1 mL), and the whole mixture was filtered through celite. After general work-up, purification by flash column chromatography on silica gel (hexane–EtOAc, 10:1) afforded the product.

1-Phenyl-3-buten-1-ol (3a)

^{1}H NMR ($CDCl_3$): δ = 7.21–7.35 (5 H, m), 5.69–5.83 (1 H, m), 5.08–5.15 (2 H, m), 4.66 (1 H, t, *J* = 6.6 Hz), 2.44–2.49 (2 H, m), 2.35 (1 H, br).

^{13}C NMR ($CDCl_3$): δ = 143.81, 134.46, 128.26, 127.39, 125.74, 118.11, 73.23, 43.62.

MS (EI, 70 eV): *m*/*z* (%) = 148 [M^+], 107 (100), 97, 77.

1-(2-Fluorophenyl)-3-buten-1-ol (3b)

^{1}H NMR ($CDCl_3$): δ = 7.43–7.48 (1 H, m), 7.19–7.27 (1 H, m), 7.10–7.16 (1 H, m), 6.97–7.04 (1 H, m), 5.74–5.87 (1 H, m), 5.11–5.18 (2 H, m), 5.04 (1 H, dd, *J* = 7.8, 5.1), 2.42–2.61 (2 H, m).

^{13}C NMR ($CDCl_3$): δ = 159.62, 134.07, 128.80, 128.69, 127.16, 124.13, 118.52, 115.22, 67.17, 42.48.

MS (EI, 70 eV): *m*/*z* (%) = 166 [M^+], 125(100), 97, 77.

1-(3-Fluorophenyl)-3-buten-1-ol (3c)

^{1}H NMR ($CDCl_3$): δ = 7.26–7.31 (1 H, m), 7.06–7.11 (2 H, m), 6.93–6.96 (1 H, m), 5.13–5.19 (1 H, m), 5.13–5.18 (1 H, m), 4.72 (1 H, dd, *J* = 7.7, 5.1 Hz), 2.40–2.54 (2 H, m), 2.16 (1 H, br).

^{13}C NMR ($CDCl_3$): δ = 162.91, 146.52, 133.90, 129.84, 121.35, 118.81, 114.26, 112.71, 72.56, 43.74.

MS (EI, 70 eV): *m*/*z* (%) = 166 [M^+], 125(100), 97, 77.

1-(4-Fluorophenyl)-3-buten-1-ol (3d)

^{1}H NMR ($CDCl_3$): δ = 7.25–7.33 (2 H, m), 6.97–7.05 (2 H, m), 5.69–5.83 (1 H, m), 5.10–5.17 (2 H, m), 4.68 (1 H, t, *J* = 6.5 Hz), 2.43–2.48 (2 H, m), 2.32(1 H, br).

^{13}C NMR ($CDCl_3$): δ = 162.08, 139.53, 134.11, 127.41, 118.52, 115.12, 72.60, 43.82.

MS (EI, 70 eV): *m*/*z* (%) = 166 [M^+], 125 (100), 97, 77.

1-(2-Bromophenyl)-3-buten-1-ol (3e)

^{1}H NMR ($CDCl_3$): δ = 7.48–7.54 (2 H, m), 7.28–7.34 (1 H, m), 7.08–7.13 (1 H, m), 5.79–5.93 (1 H, m), 5.14–5.20 (1 H, m), 5.08 (1 H, dd, *J* = 8.3, 3.8 Hz), 2.57–2.63 (1 H, m), 2.28–2.39 (2 H, m).

^{13}C NMR ($CDCl_3$): δ = 142.65, 134.18, 132.54, 128.71, 127.56, 127.26, 121.70, 118.52, 71.75, 41.97.

MS (EI, 70 eV): *m*/*z* (%) = 228 [M^+ + 2], 226 [M^+], 185 (100), 157, 77.

1-(4-Methylphenyl)-3-buten-1-ol (3f)

^{1}H NMR ($CDCl_3$): δ = 7.12–7.23 (4 H, m), 5.71–5.85 (1 H, m), 5.09–5.16 (2 H, m), 4.66 (1 H, t, *J* = 6.5 Hz), 2.47 (2 H, m), 2.33 (3 H, s), 2.14 (1 H, br).

^{13}C NMR ($CDCl_3$): δ = 140.88, 137.08, 134.56, 129.00, 125.72, 118.06, 73.14, 43.64, 21.03.

MS (EI, 70 eV): *m*/*z* (%) = 144 [M^+ – 18], 121 (100), 91, 77.

1-(4-*tert*-Butylphenyl)-3-buten-1-ol (3g)

^{1}H NMR ($CDCl_3$): δ = 7.26–7.38 (4 H, m), 5.75–5.88 (1 H, m), 5.11–5.19 (2 H, m), 4.69 (1 H, t, *J* = 6.5 Hz), 2.48–2.52 (2 H, m), 2.06 (1 H, br), 1.31 (9 H, s).

^{13}C NMR ($CDCl_3$): δ = 150.43, 140.86, 134.69, 125.52, 125.27, 118.12, 73.11, 43.58, 34.46, 31.32.

MS (EI, 70 eV): *m*/*z* (%) = 186 [M^+ – 18], 163 (100), 148, 133, 91, 77, 57.

1-(4-Methoxyphenyl)-3-buten-1-ol (3h)

^{1}H NMR ($CDCl_3$): δ = 7.23–7.27 (2 H, m), 6.84–6.88 (2 H, m), 5.70–5.84 (1 H, m), 5.08–5.16 (2 H, m), 4.64 (1 H, t, *J* = 6.5 Hz), 3.78 (3 H, s), 2.47 (2 H, m), 2.23 (1 H, br).

^{13}C NMR ($CDCl_3$): δ = 158.66, 135.80, 133.80, 134.34, 126.77, 117.76, 113.44, 72.68, 54.93, 43.38.

MS (EI, 70 eV): *m*/*z* (%) = 160 (100) [M^+ – 18], 144, 129, 115, 91, 77, 63.

4-(1-Hydroxy-but-3-enyl)-benzonitrile (3i)

^{1}H NMR ($CDCl_3$): δ = 7.61–7.63 (2 H, m), 7.45–7.48 (2 H, m), 5.70–5.84 (1 H, m), 5.11–5.18 (2 H, m), 4.80 (1 H, dd, *J* = 7.7, 5.0 Hz), 2.41–2.57 (3 H, m).

^{13}C NMR ($CDCl_3$): δ = 149.19, 133.29, 132.09, 119.19, 118.75, 110.91, 72.29, 43.66.

MS (EI, 70 eV) *m*/*z* (%) = 173 [M^+], 132 (100), 104, 77.

Methyl 4-(1-Hydroxy-but-3-enyl)-benzoate (3j)

^{1}H NMR ($CDCl_3$): δ = 8.01 (2 H, m), 7.42 (2 H, d, *J* = 8.4 Hz), 5.72–5.83 (1 H, m), 5.13–5.19 (2 H, m), 4.80 (1 H, dd, *J* = 7.7, 5.1 Hz), 3.91 (3 H, s), 2.44–2.54 (2 H, m), 2.29 (1 H, br).

^{13}C NMR ($CDCl_3$): δ = 166.94, 148.96, 133.79, 129.69, 129.22, 118.91, 125.70, 72.73, 52.05, 43.77.

MS (EI, 70 eV): *m*/*z* (%) = 175 [M^+ – 31], 165 (100), 133, 105, 91, 77, 59.

4-(1-Hydroxy-but-3-enyl)-benzoic acid (3k)

^{1}H NMR (CD_3OD): δ = 7.94 (2 H, m), 7.69 (2 H, d, *J* = 8.3 Hz), 5.70–5.79 (1 H, m), 4.95–5.02 (2 H, m), 4.70 (1 H, t, *J* = 6.5 Hz), 2.41–2.45 (2 H, m).

^{13}C NMR (CD_3OD): δ = 170.01, 151.10, 135.44, 130.72, 130.39, 127.01, 117.89, 74.23, 44.42.

MS (EI, 70 eV): *m*/*z* (%) = 193 [M^+ + 1], 175, 151 (100), 105, 79, 77.

Tridec-1-en-4-ol (3l)

^{1}H NMR ($CDCl_3$): δ = 5.76–5.90 (1 H, m), 5.09–5.17 (2 H, m), 3.60–3.68 (1 H, m), 2.16–2.34 (1 H, m), 2.09–2.19 (1 H, m), 1.71 (1 H, br), 1.27–1.46 (16 H, m), 0.88 (3 H, t, *J* = 6.6 Hz).

^{13}C NMR ($CDCl_3$): δ = 134.92, 117.95, 70.69, 36.81, 31.87, 29.63, 29.59, 29.54, 29.29, 25.64, 22.64, 14.06.

MS (EI, 70 eV): *m*/*z* (%) = 157 [M^+ – 51], 97, 83 (100), 69, 55.

(*E*)-1-Phenyl-1,5-hexadien-3-ol (3m)

^{1}H NMR ($CDCl_3$): δ = 7.23–7.39 (5 H, m), 6.60 (1 H, d, *J* = 15.9 Hz), 6.23 (1 H, dd, *J* = 15.9, 6.3 Hz), 5.78–5.92 (1 H, m), 5.14–5.20 (2 H, m), 4.35 (1 H, q, *J* = 5.7 Hz), 2.32–2.48 (2 H, m).

^{13}C NMR ($CDCl_3$): δ = 136.62, 133.99, 131.50, 130.35, 128.53, 127.62, 126.44, 118.40, 71.71, 41.94.

MS (EI, 70 eV): *m*/*z* (%) = 156 [M^+ – 18], 133 (100), 115, 105, 91, 77, 55.

1-(3-Furyl)-3-buten-1-ol (3n)
^{1}H NMR ($CDCl_3$): δ = 7.38–7.39 (2 H, m), 6.39–6.40 (1 H, m), 5.74–5.88 (1 H, m), 5.11–5.20 (2 H, m), 4.70 (1 H, t, *J* = 6.5 Hz), 2.47–2.53 (2 H, m).

^{13}C NMR ($CDCl_3$): δ = 143.19, 138.99, 134.04, 128.37, 66.04, 42.31.

MS (EI, 70 eV): *m*/*z* (%) = 138 [M^+], 120, 97 (100), 69.

1-(3-Pyridyl)-3-buten-1-ol (3o)
^{1}H NMR ($CDCl_3$): δ = 8.35–8.36 (1 H, m), 8.27–8.29 (1 H, m), 7.45–7.68 (1 H, m), 7.16–7.21 (1 H, m), 5.64–5.79 (1 H, m), 5.00–5.05 (2 H, m), 4.89 (1 H, br), 4.69 (1 H, t, *J* = 6.6 Hz), 2.42–2.48 (2 H, m).

^{13}C NMR ($CDCl_3$): δ = 147.89, 147.25, 133.93, 133,74, 123.32, 118.20, 70.74, 43.45.

MS (EI, 70 eV): *m*/*z* (%) = 149 [M^+], 108 (100), 80, 53.

1-Allyl-cyclohexanol (3p)
^{1}H NMR ($CDCl_3$): δ = 5.82–5.97 (1 H, m), 5.08–5.17 (2 H, m), 2.22 (2 H, dd, *J* = 7.8, 1.2 Hz), 1.26–1.66 (11 H, m).

^{13}C NMR ($CDCl_3$): δ = 133.71, 118.56, 46.67, 37.34, 25.72, 22.13.

MS (EI, 70 eV): *m*/*z* (%) = 122 [M^+ – 18], 99 (100), 81, 55.

2-Phenyl-pent-4-en-2-ol (3q)
^{1}H NMR ($CDCl_3$): δ = 7.41–7.46 (2 H, m), 7.29–7.36 (2 H, m), 7.19–7.26 (1 H, m), 5.54–5.69 (1 H, m), 5.08–5.16 (2 H, m), 2.64–2.72 (1 H, m), 2.45–2.53 (1 H, m), 2.05 (1 H, br), 1.54 (3 H, d, *J* = 2.7 Hz).

^{13}C NMR ($CDCl_3$): δ = 147.63, 133.65, 128.12, 126.57, 124.73, 119.33, 73.60, 48.44, 29.82.

EIMS (EI, 70 eV): *m*/*z* (%) = 144 [M^+ – 18], 121 (100), 105, 77.

Ethyl 3-Hydroxy-hex-5-enoate (3r)
^{1}H NMR ($CDCl_3$): δ = 5.79–5.93 (1 H, m), 5.06–5.14 (2 H, m), 4.18 (2 H, q, *J* = 7.2 Hz), 3.63 (1 H, br), 2.47 (2 H, q, *J* = 15.3 Hz), 2.30 (2 H, d, *J* = 7.8 Hz), 1.28 (3 H, t, *J* = 7.2 Hz), 1.25 (3 H, s).

^{13}C NMR ($CDCl_3$): δ = 133.67, 118.49, 70.68, 46.49, 44.40, 26.80, 14.13.

MS (EI, 70 eV) *m*/*z* (%) = 157 [M^+ – 15], 131, 103, 85 (100), 69.

2-Methyl-1-phenyl-but-3-en-1-ol (3s)
^{1}H NMR ($CDCl_3$): *syn* isomer, δ = 7.22–7.34 (5 H, m), 5.68–5.86 (1 H, m), 5.00–5.06 (2 H, m), 4.58 (1 H, d, *J* = 5.7 Hz), 2.41–2.60 (1 H, m), 2.10 (1 H, br), 1.00 (3 H, d, *J* = 6.9 Hz); *anti* isomer, δ = 7.22–7.34 (5 H, m), 5.68–5.86 (1 H, m), 5.15–5.21 (2 H, m), 4.34 (1 H, d, *J* = 7.8 Hz), 2.41–2.60 (1 H, m), 2.24 (1 H, br), 0.86 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR ($CDCl_3$): *syn* isomer, δ = 142.41, 140.32, 127.97, 127.25, 126.46, 115.3877.66, 44.45, 13.92; *anti* isomer, δ = 142.56, 140.61, 128.14, 127.55, 126.76, 116.62, 77.91, 46.10, 16.42.

MS (EI, 70 eV): *m*/*z* (%) = 144 [M^+ – 18], 128, 115, 107 (100), 79, 77.

1,2-Diphenyl-but-3-en-1-ol (3t)
^{1}H NMR ($CDCl_3$): *anti* isomer, δ = 7.10–7.29 (10 H, m), 6.25–6.37 (1 H, m), 5.24–5.34 (2 H, m), 4.89 (1 H, d, *J* = 7.8 Hz), 3.61 (1 H, t, *J* = 8.2 Hz), 2.57 (1 H, br).

^{13}C NMR ($CDCl_3$): *anti* isomer, δ = 141.84, 140.60, 137.78, 128.26, 127.80, 127.29, 126.59, 126.47, 118.20, 77.12, 59.01.

MS (EI, 70 eV): *m*/*z* (%) = 224 [M^+], 118 (100), 107, 91, 79, 77.

3-Methyl-1-phenyl-but-3-en-1-ol (3u)
^{1}H NMR ($CDCl_3$): δ = 7.23–7.38 (5 H, m), 4.90 (1 H, s), 4.83(1 H, m), 4.78 (1 H, t, *J* = 6.9 Hz), 2.41 (2 H, d, *J* = 6.9 Hz).

^{13}C NMR ($CDCl_3$): δ = 114.05, 142.32, 127.39, 125.70, 113.91, 71.44, 48.24, 22.28.

MS (EI, 70 eV): *m*/*z* (%) = 162 [M^+], 107 (100), 79, 77.

2,2-Dimethyl-1-phenyl-but-3-en-1-ol (3v)
^{1}H NMR ($CDCl_3$): δ = 7.28–7.31 (5 H, m), 5.92 (1 H, dd, *J* = 17.4, 10.8 Hz), 5.05–5.16 (2 H, m), 4.43 (1 H, s), 2.03 (1 H, br), 1.01 (3 H, s), 0.96 (3 H, s).

^{13}C NMR ($CDCl_3$): δ = 145.16, 140.80, 127.79, 127.48, 113.81, 80.66, 42.24, 24.44, 21.06.

MS (EI, 70 eV): *m*/*z* (%) = 176 [M^+], 107 (100), 79, 77, 70, 55.

Acknowledgments

This work was fully supported by the Korea Institute of Science & Technology and the Ministry of Science & Technology.

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