

Ultrasonic activation of Nozaki-Hiyama-Kishi reaction in the presence of phase transfer catalysis

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Abstract: The addition of compounds organochromium with aldehydes originally described by Nozaki-Hiyama-Kishi has evolved to become a very powerful method leads to the formation of C-C bonds. We present a process that allows the coupling of aldehydes with organic halides under Ultrasonic irradiation and in the presence of phase transfer catalysis in a medium consisting of anhydrous CrCl_2 and an amount of Mn in combination with trimethylsilane chloride $(\text{Me})_3\text{SiCl}$ to finally produce secondary alcohols. Yields are increased through the ultrasonic irradiation in the presence of the phase transfer catalyst at ambient temperature and for a very short duration. The isolated product has a high purity.

Keywords: Nozaki-Hiyama-Kishi, organochromium, Ultrasonic irradiation, phase transfer catalysis, C-C bond formation.

INTRODUCTION

The formation of carbon-carbon bonds is important in processes such as bioactives molecule synthesis, drugs and agrochemical synthesis. In the last years, catalytic reactions were increasingly used for reactions involving C-C bond formation, because they represent processes respectful to environment [1-4]. Among them, we find the reaction of Nozaki-Hiyama Kishi (NHK), which was of great importance in C-C bond formation [4-7]. The Nozaki-Hiyama-Kishi reaction is an addition of alkenyl, alkynyl or vinyl chromium(III) compounds to aldehydes and ketones [7-11]. This type of reaction was used for a large number of features [12,13]. In the last years, ultrasound has been used to accelerate organic reactions. They are defined as acoustic waves with frequencies in the 20-100 MHz range [14,15]. The effects of ultrasound on organic reactions are due to cavitation, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid. Cavitation induces very high

local temperatures and pressures inside the bubbles, leading to a turbulent flow in the liquid and enhanced mass transfer [16].

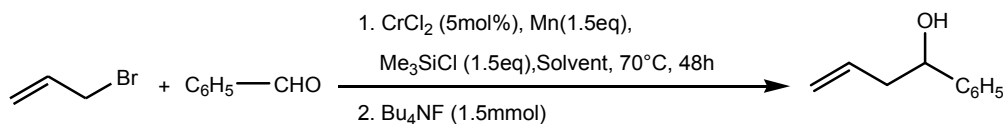
The aim of this study was to investigate the effects of the phase transfer catalysis combined with the ultrasonic irradiation on the evolution of the coupling reaction of aldehydes with organic halides. A reaction mechanism is proposed to rationalize the results.

RESULTS AND DISCUSSION

We examined in this study several effects (solvent, addition of phase transfer catalyst, ultrasonic irradiation) in the Nozaki-Hiyama-Kishi reaction.

1. Solvent effect

The solvent selected for dissolving the reactants is not believed to participate in the chemical reaction but it is susceptible to dissolve varying amounts of solutes whose concentration is an important factor on the evolution of the reaction. Solvent may indeed



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**Table I.** Influence of the solvent on Nozaki-Hiyama-Kishi reaction of benzaldehyde and allyl bromide.

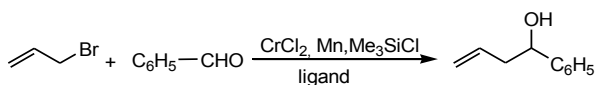
Solvent	H ₂ O	CH ₃ CN	DMF	H ₂ O/DMF	CH ₂ Cl ₂	THF	Ether	C ₆ H ₅ CH ₃
ϵ at 25°C	87	37.5	36.7	-	9.08	7.58	4.5	2.38
Yield (%)	65	63	61	64	36	29	25	21

interact with the reagents through its polarization interactions and Van der Waals and hydrogen bonds is promoted or prevent their contact.

The Nozaki Hiyama Kishi reaction evolves with appreciable yields in solvents with high dielectric constants (Table I). A higher dielectric constant is associated with an improved yield. Yields are 65, 63 and 61% in water, acetonitrile and N,N-dimethylformamide, respectively. Solvent having a high dielectric constant results in the activation of the basic entity, through the dissociation of the cation-anion of the binding base. The results are in agreement with those reported in the case of Wittig, Baylis Hillman and Sonogashira reactions [17,18].

2. Influence of the nature of ligands on the yield of coupling NHK's reaction

In order to understand and visualize the role of the ligand in the NHKs' reaction, we undertook a study involving allyl bromide with benzaldehyde in the presence of different types of ligands. The results are summarized in Table 2.

**Table II.** Cross-coupling reaction between NHK allyl bromide and benzaldehyde in various ligands.

Ligand	Cone angle Θ (°)	Yield (%)
P(Ph) ₃	145	68
P(<i>p</i> -CH ₃ C ₆ H ₄) ₃	145	64
P(<i>p</i> -CH ₃ OC ₆ H ₄) ₃	143.6	71
As(Ph) ₃	163.5	26
P(<i>p</i> -ClC ₆ H ₄) ₃	176.6	18

Allyl Bromide (1.5mmol), benzaldehyde (1mmol), CrCl₂ (0.05mmol), Me₃SiCl (0.75mmol), Mn (0.75mmol), (H₂O/DMF): (1mL/1mL), ligand (5mol %), TBAF (1.5mmol), T= 70°C, t= 48h.
















It appears that the yield was proportional to the value of the cone angle Θ (Table 2). Thereafter, the ability of the phosphorus in coordinating to a metal center is also dependent on the distance at which it can approach this center. This distance is all higher and thus force connecting M-P most low this means that the steric bulk of the phosphorus ligand is more important. This bulk is measured by the opening of Tolman cone which depends both of the pyramidal geometry phosphorus and also occupies the space of intrinsic substituent grafted on this angle metal [19].

The angle of Tolman allows also quantifying a hindered trisubstituted phosphine. For monophosphines, more clutter is important most Θ is large. These results allow us to improve the efficiency of coupling NHKs' reaction. Indeed, the results shown in Table II allowed that the yield dependent on steric effects and electronic ligands. It increased gradually as the basicity of the substituents on the phosphorus graft increased. In general, phosphorus ligands played a role in a steric combined electronic effect on the metal.

3. Biactivation NHK reaction by PTC under ultrasound

To increase the reaction yield of NHK, we chose the biactivation through Aliquat-336 associated with ultrasonic irradiation. The results reported in table 3 emphasize that NHKs' reaction activated by phase transfer catalysis type Aliquat-336 under ultrasonic irradiation at room temperature tends to promote the yield in comparison with the conventional conditions. The addition of Aliquat-336 generates a remarkable reactivity stage insofar where it improves the yield. We also highlighted the positive effect of ultrasound on the yield of the coupling product (Table III). When submitting the Nozaki-Hiyama-Kishis' reaction to ultrasonic waves at 20°C, we observed a significant increase in yields for a very short duration (7 min). We have acceded to the synthesis of secondary alcohols with good yields

Table III. Biactivation NHK reaction by PTC under ultrasonic irradiation

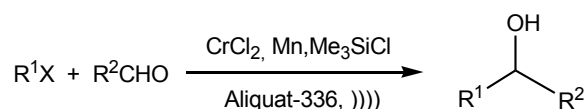
R ¹ X	R ² CHO	Product	Yield (%)		
			*	**	***
C ₆ H ₅ I	CH ₃ (CH ₂) ₆ CHO	1	45	57	78
C ₆ H ₅ I	PhCHO	2	56	79	93
	CH ₃ (CH ₂) ₆ CHO	3	53	66	79
	CH ₃ (CH ₂) ₆ CHO	4	59	74	88
	PhCHO	5	64	80	96
	<i>o</i> -CH ₃ OC ₆ H ₄ CHO	6	64	75	92
	<i>m</i> -CH ₃ OC ₆ H ₄ CHO	7	63	73	91
	<i>p</i> -CH ₃ OC ₆ H ₄ CHO	8	60	71	90
	<i>p</i> -ClC ₆ H ₄ CHO	9	68	77	89
	<i>m</i> -ClC ₆ H ₄ CHO	10	70	79	93
	<i>o</i> -ClC ₆ H ₄ CHO	11	67	72	87
	<i>p</i> -CNC ₆ H ₄ CHO	12	66	72	90
	<i>m</i> -CNC ₆ H ₄ CHO	13	51	69	77
	<i>o</i> -CNC ₆ H ₄ CHO	14	59	70	86
	<i>p</i> -CH ₃ C ₆ H ₄ CHO	15	65	81	90
	<i>m</i> -CH ₃ C ₆ H ₄ CHO	16	59	72	87
	<i>o</i> -CH ₃ C ₆ H ₄ CHO	17	70	85	94

*: halogenated derivative (1.5mmol), aldehyde (1mmol), CrCl₂ (0.05 mmol), Me₃SiCl (0.75mmol), Mn (0.75mmol), (H₂O/DMF): (1mL/1mL), TBAF (1.5mmol), T= 70°C, t= 48h.

** : halogenated derivative (1.5mmol), aldehyde (1mmol), CrCl₂ (0.05mmol), Me₃SiCl (0.75mmol), Mn (0.75mmol), (H₂O/DMF): (1mL/1mL), Aliquat-336 (0.5mmol), T= 70°C, t= 48h.

***: halogenated derivative (1.5mmol), aldehyde (1mmol), CrCl₂ (0.05mmol), Me₃SiCl (0.75mmol), Mn (0.75mmol), (H₂O/DMF): (1mL/1mL), Aliquat-336 (0.5mmol), Ultrasonic irradiation: T=20°C, t=7 min.

(77-96%). Not only are the yields markedly improved, but we note that the purity of the isolated products has increased.



The activation of the reaction under ultrasound is probably due to the chemical effects of cavitation, i.e, the formation of bubbles in the liquid growth after undergoing implosion. These bubbles constitute chemical microreactors, when temperatures are reached and a very high pressure at

final stage of implosion which causes the release of high energy. This allows having such a kind of agitation of the reaction medium, an activation of the catalytic system and the approximation of the reagents by increasing their specific surface and a mixing of liquid layers located in the vicinity. As a Result an increase in the contact between the reactants which promotes the formation of the product for a short time with a very increased yields.

Development of a process that is catalytic in chromium would reduce the amount of potentially toxic chromium waste. Several obstacles needed to be overcome before a catalytic cycle could be realized. The chromium (III) needs to be released

from the product and then reduced to chromium (II) in order to complete the catalytic cycle. The first NHK reaction catalytic in chromium was described by Fürstner and Shi [6]. The release of the chromium (III) from the product was facilitated by the use of trimethylsilyl halide (Figure 1). This silicon reagent is more oxophilic than the chromium and thus provides the silyl ether product. However, a competition between chromium and silicon for the product was still observed at low chromium loadings, requiring that 5 mol% of chromium be used. The chromium (III) could then be reduced to chromium (II) by addition of a co-reductant; manganese (0) was suitable for reducing the chromium without effecting the reaction (Figure 1).

The phenomenon consists of the formation of bubbles within the liquid whose collapse produce high local energies. The bubbles serve in fact as chemical microreactors [20]. Thus, in the cross-coupling reaction Nozaki-Hiyama-Kishi catalyzed CrCl_2 in the presence of Aliquat-336 Ultrasonic, have been observed in very high yields. However, the bi-anion and sonochemical activation also provides purer products with better performance.

CONCLUSION

In summary, the cross-coupling of Nozaki-Hiyama-Kishi was performed at room temperature with improved reaction rates by the combined use of Aliquat-336 as a phase transfer catalyst and under ultrasonic irradiation. The product of coupling depends on the phenomenon of acoustic cavitation which the appearance and maintenance in a medium depends on a number of factors,

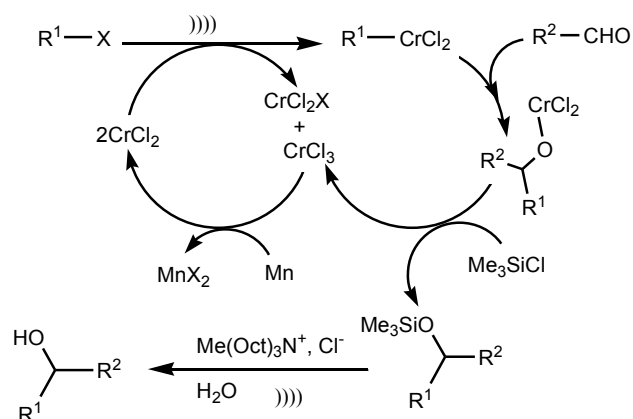


Figure 1. Proposed Mechanism of cross-coupling reaction of Nozaki-Hiyama-Kishi catalyzed by CrCl_2 in the presence of Aliquat-336 under ultrasound.

including temperature, pressure, viscosity, and especially the presence of various particles microbubbles and acting as cavitation nuclei.

EXPERIMENTAL

1. Classical procedure without ultrasound

In a steel pipe, we introduced vinyl or allyl organometallic (1.5 mmol), aldehyde (1 mmol) in the presence of CrCl_2 (8 mg, 0.05 mmol), Me_3SiCl (95 mL, 0.75 mmol) and Mn (83 mg, 0.75 mmol), which were made in the solvent (2 mL). The reaction mixture was formed in a steel tube carried out by a magnetic stirrer continuously in an oil bath maintained at 70°C for 48 hours. After filtration and evaporation, the residue was dissolved in DMF (2 mL) while TBAF (1.5 mmol) was added slowly. The solution was stirred for 30 min. The mixture is then diluted in diethylene ether (15 mL), we proceed extracted with a solution of hydrochloric acid HCl (2N). The residue is extracted with Et_2O and the organic phase was dried using anhydrous magnesium sulfate. The solvent was evaporated and the product was purified by column chromatography on silica gel using a mixture of hexane / dichloromethane as eluent.

2. Procedure with phase transfer activation

The addition of nucleophilic vinyl or allyl organometallic (1.5 mmol) to aldehyde (1 mmol) in the presence of CrCl_2 (8 mg, 0.05 mmol), Me_3SiCl (95 mL, 0.75 mmol) and Mn (83 mg, 0.75 mmol) were carried out in the solvent (2 ml) and Aliquat-336 (0.5 mmol). The reaction was carried out in a steel pipe supported by a continuous magnetic stirrer in an oil bath maintained at 70°C for 48 hours. After filtration and evaporation, the mixture was then diluted in diethylene ether (15 mL), we proceed extracted with a solution of hydrochloric acid HCl (2N). The residue was extracted with Et_2O and the organic phase was dried using anhydrous magnesium sulfate. The solvent was evaporated; the product was purified by column chromatography on silica gel using a mixture of hexane / dichloromethane as eluent.

3. Procedure with Ultrasonic irradiation

The ultrasonic probe was immersed directly in the reactor. An ultrasonic generator (sonics VC 505 300 W) emits the sound vibration into the reaction mixture. Sonification was achieved at low frequencies of 20 kHz (amplitude

of 50%) at room temperature for 7 min. The allyl organometallic (1.5 mmol) to aldehyde (1 mmol) in the presence of CrCl_2 (8 mg, 0.05 mmol), Me_3SiCl (95 mL, 0.75 mmol) and Mn (83 mg, 0.75 mmol) were carried out in the solvent (2 mL) and Aliquat-336 (0.5 mmol) are placed in a reactor. After reaction, the mixture is extracted (three times) with diethyl ether. The latter is dried on MgSO_4 and the solvent removed under vacuum. The coupling product is finally isolated by silica gel chromatography. The yields of the reactions were determined by gas chromatography on a Shimadzu 2014-GC apparatus. The capillary column was DB-5 and the carrier gas was helium.

4. Characterization

All the products were characterized by IR, ^1H NMR spectra, ^{13}C NMR spectra and mass spectra. The IR spectra were recorded in KBr with a SHIMADZUE IR spectrometer, with a precision of $\pm 2\text{cm}^{-1}$ in the range $400\text{-}4000\text{ cm}^{-1}$. The ^1H NMR spectra (300MHz) and ^{13}C NMR spectra (75MHz) were obtained on a Bruker AC300 spectrometer using CDCl_3 as solvent and TMS as an internal standard, chemical shift are given in ppm. The multiplicities of the signals are indicated by the following abbreviations: s: singlet; d: doublet; t: triplet; b: band; m: multiplet. The coupling constants are expressed in Hz. Mass spectra were performed by GC-MS (Hewlett-Packard computerised system consisting of a 5890 gas chromatograph coupled to a 5971A mass spectrometer.

Melting points were taken on a Reichert-Heizbank apparatus.

1-phenyloctan-1-ol (1). IR: ν (cm^{-1}): 1599, 3025. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 0.71-0.93 (t, 3H, CH_3), 1.19-1.31 (m, 10H), 1.65-1.78 (m, 2H), 2.00 (b, 1H, OH), 4.50-4.69 (t, 1H, CH-OH), 7.29 (s, 5H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 13.9, 22.5, 24.0, 29.2, 30.0, 31.9, 38.9, 75.4, 126.0, 127.8 (2 CH aromatic), 128.6 (2 CH aromatic), 141.0 (C_q aromatic). HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{10}\text{H}_{22}\text{O}$, 206.1676; found, 206.1670.

Diphenylmethanol (2). IR: ν (cm^{-1}): 1600, 3023. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.00 (b, 1H, OH), 5.80 (s, 1H, CH-OH), 7.21 (s, 10H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 76.3, 126.0 (2 CH aromatic), 128.2 (4 CH aromatic), 129.7 (4 CH aromatic), 149.9 (2 C_q aromatic). GC-MS m/z (relative intensity, %): 184 (M^+ , 100). HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{O}$, 184.0889; found, 184.0882.

Undec-1-en-4-ol (3). IR: ν (cm^{-1}): 2945, 2867. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 0.85 (t, 3H, CH_3), 1.21 (m, 10H), 1.43 (m, 2H), 2.03-2.34 (m, 3H), 3.41 (m, 1H, CH-OH), 5.07 (m, 1H), 5.17 (m, 1H), 5.83 (m, 1H, $\text{CH}_2=\text{CH}$). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 14.0, 22.6, 23.5, 28.9, 29.3, 31.7, 36.4, 41.7, 70.8, 117.6, 134.5. HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{11}\text{H}_{22}\text{O}$, 170.1678; found, 170.1676.

1-(thiophen-2-yl) octan-1-ol (4). IR: ν (cm^{-1}): 2952, 2872. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 0.95 (t, 3H, CH_3), 1.30 (m, 10H), 1.84 (m, 2H), 2.04 (b, 1H, OH), 4.74-4.77 (t, 1H, CH-OH), 6.69-6.71 (m, 2H), 7.14-7.15 (m, 1H). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 14.0, 22.6, 23.1, 29.2, 29.9, 31.7, 40.0, 70.1, 122.8, 125.4, 126.8, 142.5. HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{20}\text{OS}$, 212.1239; found, 212.1234.

1-phenylbut-3-en-1-ol (5). IR: ν (cm^{-1}): 1596, 3028. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.10 (b, 1H, OH), 2.42-2.53 (m, 2H), 4.54-4.71 (m, 1H, CHOH), 5.00-5.15 (m, 2H, $\text{CH}=\text{CH}_2$), 5.70-5.85 (m, 1H, $\text{CH}=\text{CH}_2$), 7.19-7.31 (m, 5H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 43.0, 75.3, 116.8, 127.0 (2 CH aromatic), 127.7, 128.9 (2 CH aromatic), 134.4, 140.9 (C_q aromatic). GC-MS m/z (relative intensity, %): 148 (M^+ , 20), 107 (100), 79 (88), 77 (48), 51 (12). HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}$, 148.0888; found, 148.0882.

1-(2-Methoxy-phenyl)-but-3-en-1-ol (6). IR: ν (cm^{-1}): 3417, 3073, 3002, 2937, 2836, 1639, 1601, 1588. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.48-2.64 (m, 3H), 3.85 (s, 3H), 4.94-4.98 (m, 1H), 5.09-5.17 (m, 2H), 5.81-5.87 (m, 1H), 6.86-6.98 (m, 2H), 7.22-7.35 (m, 2H). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 41.9, 55.2, 69.6, 110.4, 117.5, 120.7, 126.8, 128.3, 131.8, 135.2, 156.3. GC-MS m/z (relative intensity, %): 178 (M^+ , 6), 160 (10), 137(100), 109 (40), 94 (31), 77 (27). HRMS-EI (m/z): $[\text{M}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$,



178.0994; found, 178.0995.

1-(3-methoxyphenyl)-but-3-en-1-ol (7). IR: ν (cm^{-1}): 3417, 3073, 3010, 2937, 2836, 1641, 1601, 1587. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.05 (b, 1H, OH), 2.35-2.56 (m, 2H), 3.76 (s, 3H), 4.57 (s, 1H, CHOH), 4.99-5.18 (m, 2H, CH=CH₂), 5.69-5.81 (m, 1H, CH=CH₂), 6.71-6.79 (m, 1H, CH_{ar}), 6.80-6.84 (m, 2H, 2CH_{ar}), 7.07-7.09 (t, J = 4.5 Hz, 1H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 42.5, 55.4, 76.6, 111.3, 113.1, 116.8, 119.7, 130.0, 134.4, 141.9 (C_q aromatic), 160.1 (C_q aromatic). GC-MS m/z (relative intensity, %): 178 (M⁺, 7), 137 (91), 109(100), 94 (42), 77 (42), 66 (19). HRMS-EI (m/z): [M]⁺ calcd for C₁₁H₁₄O₂, 178.0994; found, 178.0990.

1-(4-Methoxy-phenyl)-but-3-en-1-ol (8). IR: ν (cm^{-1}): 3417, 3082, 2934, 2830, 1641, 1612, 1587. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.04 (b, 1H, OH), 2.46-2.53 (t, J = 7.5 Hz, 2H), 3.79 (s, 3H), 4.70-4.67 (t, J = 4.5 Hz, 1H), 5.11-5.18 (m, 2H, CH=CH₂), 5.71-5.86 (m, 1H, CH=CH₂), 6.91-6.87 (m, 2H, 2CH_{ar}), 7.29-7.25 (m, 2H, 2CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 43.5, 55.9, 74.0, 114.4 (2CH aromatic), 116.6, 128.1 (2CH aromatic), 134.6 (C_q aromatic), 136.0, 159.2 (C_q aromatic). GC-MS m/z (relative intensity, %): 178 (M⁺, 4), 137 (100), 109 (38), 94 (29), 77 (31). HRMS-EI (m/z): [M]⁺ calcd for C₁₁H₁₄O₂, 178.0990; found, 178.0995.

1-(4-chlorophenyl) but-3-en-1-ol (9). IR: ν (cm^{-1}): 3389, 3077, 2992, 2907, 1641, 1596. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.18 (b, 1H, OH), 2.34-2.48 (m, 2H), 4.57-4.69 (m, 1H, CHOH), 5.02-5.15 (m, 2H, CH=CH₂), 5.70-5.80 (m, 1H, CH=CH₂), 7.19-7.32 (m, 4H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 43.2, 73.0, 116.9, 127.8 (2CH aromatic), 129.0 (2CH aromatic), 133.1 (C_q aromatic), 134.4, 140.9 (C_q aromatic). GC-MS m/z (relative intensity, %): 182 (M⁺, 17), 143 (31), 141 (100), 113 (19), 77 (69). HRMS-EI (m/z): [M]⁺ calcd for C₁₀H₁₁ClO, 182.0498; found, 182.0491.

1-(3-Chloro-phenyl)-but-3-en-1-ol (10). IR: ν (cm^{-1}): 3389, 3082, 3010, 2974, 2938, 2911, 1642, 1600, 1574. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.04 (b, 1H, OH), 2.32-2.40 (m, 1H), 2.55-2.58 (m, 1H), 4.54-4.74 (m, 1H, CHOH), 4.97-5.19 (m, 2H, CH=CH₂), 5.70-5.82 (m, 1H, CH=CH₂), 7.13-7.21 (m, 3H, CH_{ar}), 7.34 (s, 1H, CH_{ar}). ^{13}C NMR:

(CDCl_3 , 75MHz): δ (ppm): 42.9, 75.1, 116.8, 125.0 (CH aromatic), 126.7 (CH aromatic), 127.6 (CH aromatic), 130.2 (CH aromatic), 133.9, 134.5 (C_q aromatic), 143.3 (C_q aromatic). GC-MS m/z (relative intensity, %): 182 (M⁺, 7), 143 (29), 141 (89), 113 (45), 77 (100), 51 (18). HRMS-EI (m/z): [M]⁺ calcd for C₁₀H₁₁ClO, 182.0498; found, 182.0495.

1-(2-Chloro-phenyl)-but-3-en-1-ol (11). IR: ν (cm^{-1}): 3389, 3073, 2983, 2920, 2857, 1637, 1600, 1573. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.06 (b, 1H, OH), 2.32-2.39 (m, 1H), 2.57-2.61 (m, 1H), 4.54-4.83 (m, 1H, CHOH), 4.99-5.20 (m, 2H, CH=CH₂), 5.70-5.83 (m, 1H, CH=CH₂), 7.07-7.45 (m, 4H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 42.1, 69.6, 116.7, 127.1 (CH aromatic), 128.6 (CH aromatic), 129.4 (2CH aromatic), 132.3 (C_q aromatic), 134.2, 140.8 (C_q aromatic). GC-MS m/z (relative intensity, %): 182 (M⁺, 8), 143 (24), 141 (100), 113 (37), 78 (9). HRMS-EI (m/z): [M]⁺ calcd for C₁₀H₁₁ClO, 182.0498; found, 182.0502.

4-(1-Hydroxy-but-3-enyl)-benzonitrile (12). IR: ν (cm^{-1}): 3834, 3442, 3076, 2979, 2908, 2348, 2229, 1928, 1840, 1642, 1609, 1572. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.19 (b, 1H, OH), 2.37-2.57 (m, 2H), 4.61-4.79 (t, J = 4.0 Hz, 1H, CHOH), 5.11-5.20 (m, 2H, CH=CH₂), 5.71-5.80 (m, 1H, CH=CH₂), 7.37-7.46 (d, J = 4.0 Hz, 2H, CH_{ar}), 7.48-7.52 (t, J = 6.0 Hz, 2H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 43.2, 74.3, 111.5 (C_q aromatic), 115.8 (CN), 116.9, 127.4 (2CH aromatic), 132.4 (2CH aromatic), 134.3, 145.0 (C_q aromatic). GC-MS m/z (relative intensity, %): 173 (M⁺, 8), 132(100), 104 (43), 77 (20). HRMS-EI (m/z): [M]⁺ calcd for C₁₁H₁₁NO, 173.0846; found, 173.0841.

3-(1-Hydroxy-but-3-enyl)-benzonitrile (13). IR: ν (cm^{-1}): 3443, 3073, 3010, 2983, 2924, 2230, 1642, 1605, 1587. ^1H NMR (CDCl_3 , 300MHz): δ (ppm): 2.12 (b, 1H, OH), 2.41-2.57 (m, 2H), 4.54-4.78 (m, 1H, CHOH), 4.98-5.17 (m, 2H, CH=CH₂), 5.70-5.82 (m, 1H, CH=CH₂), 7.37-7.43 (t, J = 6.0 Hz, 1H, CH_{ar}), 7.44-7.54 (m, 2H, CH_{ar}), 7.57 (s, 1H, CH_{ar}). ^{13}C NMR: (CDCl_3 , 75MHz): δ (ppm): 43.1, 74.7, 112.4 (C_q aromatic), 115.8 (CN), 118.2, 129.1 (CH aromatic), 130.3 (CH aromatic), 130.9 (CH aromatic), 131.5 (CH aromatic), 134.4, 142.3 (C_q aromatic). GC-MS m/z (relative intensity, %): 173 (M⁺, 13), 132 (100),

104 (6). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{11}NO$, 173.0846; found, 173.0848.

2-(1-Hydroxy-but-3-enyl)-benzotrile (14). IR: ν (cm^{-1}): 3293, 3077, 2978, 2910, 2222, 1940, 1840, 1763, 1681, 1614. 1H NMR ($CDCl_3$, 300MHz): δ (ppm): 2.03 (b, 1H, OH), 2.38-2.77 (m, 2H), 4.54-4.83 (m, 1H, CHOH), 4.97-5.19 (m, 2H, CH=CH₂), 5.71-5.83 (m, 1H, CH=CH₂), 7.34-7.37 (d, $J = 8.0$ Hz, 1H, CH_{ar}), 7.44-7.52 (m, 1H, CH_{ar}), 7.52-7.58 (m, 1H, CH_{ar}), 7.75-7.83 (d, $J = 8.0$ Hz, 1H, CH_{ar}). ^{13}C NMR: ($CDCl_3$, 75MHz): δ (ppm): 41.9, 72.7, 115.4 (C_q aromatique), 117.1 (CN), 118.6, 128.2 (CH aromatic), 129.3 (CH aromatic), 131.9 (CH aromatic), 133.5 (CH aromatique), 134.8, 146.7 (C_q aromatique). GC-MS m/z (relative intensity, %): 173 (M^+ , 12), 133 (100), 105 (40), 77 (40), 51 (17). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{11}NO$, 173.0846; found, 173.0849.

1-p-Tolyl-but-3-en-1-ol (15). IR: ν (cm^{-1}): 3390, 3075, 3009, 2977, 2922, 1902, 1640, 1615. 1H NMR ($CDCl_3$, 300MHz): δ (ppm): 2.07 (b, 1H, OH), 2.35 (s, 3H), 2.49-2.52 (m, 2H), 4.64-4.71 (m, 1H, CHOH), 5.12-5.19 (m, 2H, CH=CH₂), 5.73-5.85 (m, 1H, CH=CH₂), 7.11-7.16 (d, $J = 8.0$ Hz, 2H, CH_{ar}), 7.22-7.26 (9, $J = 8.0$ Hz, 2H, CH_{ar}). ^{13}C NMR: ($CDCl_3$, 75MHz): δ (ppm): 23.3, 43.6, 75.2, 117.2, 126.8 (2CH aromatic), 129.3 (2CH aromatic), 134.4, 137.3 (C_q aromatic), 138.9 (C_q aromatic). GC-MS m/z (relative intensity, %): 162 (M^+ , 13), 121 (100), 93(35), 91 (30), 77 (25). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1046.

1-m-Tolyl-but-3-en-1-ol (16). IR: ν (cm^{-1}): 3388, 3074, 3023, 2977, 2920, 2866, 1641, 1608, 1590. 1H NMR ($CDCl_3$, 300MHz): δ (ppm): 1.96 (b, 1H, OH), 2.36 (s, 3H), 2.47-2.57 (m, 2H), 4.54-4.69 (m, 1H, CHOH), 4.97-5.16 (m, 2H, CH=CH₂), 5.70-5.78 (m, 1H, CH=CH₂), 7.00-7.06 (d, $J = 8.0$ Hz, 1H, CH_{ar}), 7.10-7.14 (t, $J = 8.0$ Hz, 2H, CH_{ar}), 7.19-7.22 (d, $J = 8.0$ Hz, 1H, CH_{ar}). ^{13}C NMR: ($CDCl_3$, 75MHz): δ (ppm): 22.4, 42.6, 76.3, 117.9, 124.2 (CH aromatic), 128.3 (CH aromatic), 128.9 (CH aromatic), 129.1 (CH aromatic), 134.4, 138.0 (C_q aromatic), 142.9 (C_q aromatic). GC-MS m/z (relative intensity, %): 162 (M^+ , 13), 121 (100), 93 (80), 91 (48), 77 (34). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1050.

1-o-Tolyl-but-3-en-1-ol (17). IR (KBr): ν (cm^{-1}):

3379, 3073, 3023, 2976, 2932, 1640, 1605. 1H NMR ($CDCl_3$, 300MHz): δ (ppm): 1.99 (b, 1H, OH), 2.34 (s, 3H), 2.42-2.54 (m, 2H), 4.96-5.01 (m, 1H), 5.14-5.21 (m, 2H, CH=CH₂), 5.73-5.87 (m, 1H, CH=CH₂), 7.16-7.45 (m, 3H, 3CH_{ar}), 7.45-7.50 (m, 1H, 1CH_{ar}). ^{13}C NMR: ($CDCl_3$, 75MHz): δ (ppm): 19.0, 42.6, 69.3, 116.9, 126.1 (CH aromatic), 127.1 (CH aromatic), 128.0 (CH aromatic), 129.9 (CH aromatic), 134.4, 135.0 (C_q aromatic), 141.9 (C_q aromatic). GC-MS m/z (relative intensity, %): 162 (M^+ , 14), 121 (100), 93 (25), 91(14), 77 (7). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{14}O$, 162.1045; found, 162.1052.

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