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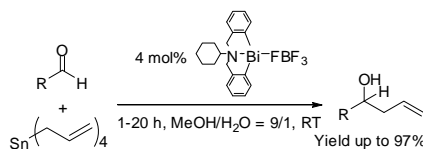
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The allylation of different aldehydes with tetraallyltin was successfully operated over hypervalent organobismuth (III) tetrafluoroborate catalyst in a medium of aqueous methanol, giving the corresponding homoallylic alcohols in excellent chemoselectivity and yields.

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Air-stable hypervalent organobismuth (III) tetrafluoroborate as effective and reusable catalyst for the allylation of aldehyde with tetraallyltin

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Abstract—Air-stable hypervalent organobismuth (III) tetrafluoroborate ($C_6H_{11}N(CH_2C_6H_4)_2BiBF_4$) was synthesized and characterized by spectroscopic and X-ray crystallographic techniques. The compound shows good catalytic efficiency in the allylation reaction of different aldehydes with tetraallyltin in a medium of aqueous methanol, giving the corresponding homoallylic alcohols in excellent chemoselectivity and yields. © 2011 Elsevier Science. All rights reserved

Keywords—Organobismuth, Tetrafluoroborate, Lewis acid, Catalysis, Allylation

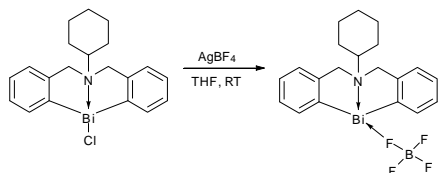
Bismuth compounds are not toxic and relatively cheap, and have been widely used in catalysis and organic synthesis. In the past two decades, bismuth(III) compounds (e.g., $BiCl_3$, $BiBr_3$, $Bi(OTf)_3$, $Bi(NO_3)_3$) have been used as catalysts in various organic reactions^{1,2}. However, up till now, there are only several reports on the use of organobismuth compounds as catalysts in organic synthesis, possibly due to the unstable nature of bismuth compounds³. With environmental concerns and ‘green reagents’ in mind, we have been synthesizing stable bismuth compounds for potential uses. For example, organobismuth oxide, hydroxide, methoxide and bismuth compounds bearing a sulfur-bridged bis(phenolato) ligand were synthesized and found to be good reagents and catalysts for CO_2 chemical fixation⁴. Very recently we reported that certain organobismuth chlorides and their triphenylgermylpropionate derivatives show good in vitro antiproliferative activity⁵, and that organobismuth perfluorooctanesulfonate

and perchlorate exhibit high catalytic efficiency towards one-pot Mannich-type reaction of ketones with aromatic aldehydes and aromatic amines in water⁶. We have also developed a series of novel Lewis acids by incorporating large electron-withdrawing groups (e.g., $-C_6F_5SO_3$, $-C_8F_{17}SO_3$) into organometallic (e.g., Ti, Zr, Hf) compounds, and found that they are catalytically active towards many organic reactions in aqueous media as well as in various organic solvents⁷. It is known that the Lewis acid-catalyzed allylation of carbonyl compounds to produce homoallylic alcohols is a versatile organic reaction⁸. The allylation reaction can be promoted by the addition of a Lewis acid⁹ or enhanced by the rise of reaction temperature or pressure¹⁰. On the other hand, there is a growing body of evidence that under certain circumstances, the solvent (THF-HCl^{8c} or methanol¹¹) and ionic liquids¹² can facilitate allyl transfer from tetraallylstannane to alkanals or alkanones.

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In this paper, we report the synthesis and characterization of an air-stable compound, viz. hypervalent organobismuth (III) tetrafluoroborate and its use in the allylation of carbonyl compounds with tetraallyl tin in aqueous media.

Shown in Scheme 1 is the synthesis of hypervalent organobismuth (III) tetrafluoroborate **1**. Treatment of $C_6H_{11}N(CH_2C_6H_4)_2BiCl$ with silver tetrafluoroborate ($AgBF_4$) (1 equiv) in THF yields the target complex¹³.



Scheme 1 Synthesis of compound **1**.

The crystal structure of compound **1** was confirmed by X-ray analysis technique. (For analysis condition, please see reference¹³). An ORTEP representation of the structure of compound **1**, as well as selected bonds and angles are shown in Fig. 1. One can see that the central bismuth-containing part shows a pseudo-trigonal bipyramidal (TBP) structure, where both the C(1) and C(8) atoms exist in the equatorial position of the TBP structure along with a lone electron pair of bismuth, and the N(1) and F(1) atoms are at the apical positions. The N(1)–Bi–F(1) bond angle is $153.9(3)^\circ$ while the C(1)–Bi–C(8) angle is $94.1(3)^\circ$. The Bi–C(1) and Bi–C(8) distance is $2.230(11)$ Å and $2.229(10)$ Å, respectively. As reported previously, the Bi–N coordination distance in 5,6,7,12-tetrahydridibenz[*c,f*][1,5]aza-

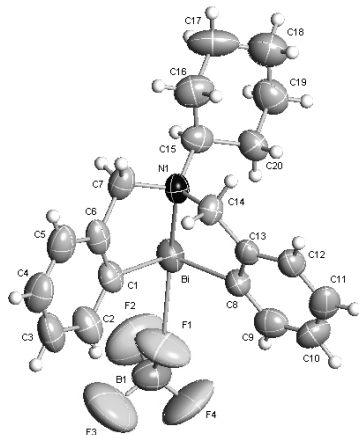


Fig. 1 Thermal ellipsoid plot of $C_6H_{11}N(CH_2C_6H_4)_2BiBF_4$ (50% probability level). Selected bond lengths (Å) and angles ($^\circ$): Bi–C(1) 2.230 (11); Bi–C(8) 2.229 (10); Bi–N(1) 2.394 (8); Bi–F(1) 2.502 (7); N(1)–C(14) 1.512 (10); N(1)–C(7) 1.506 (12); N(1)–C(15) 1.495 (12); F(1)–Bi(1) 1.35 (2); C(1)–Bi–C(8) $94.1(3)$; C(1)–Bi–N(1) $75.1(3)$; C(8)–Bi–N(1) $77.7(3)$; C(1)–Bi–F(1) $85.8(3)$; C(8)–Bi–F(1) $86.2(3)$; N(1)–Bi–F(1) $153.9(3)$; B(1)–F(1)–Bi $137.8(11)$; Bi–N(1)–C(15) $110.5(6)$.

bismocines flexibly changes in response to the electronic nature of bismuth¹⁴. The Bi–F bond is $2.502(7)$ Å in length,

longer than that ($2.190(4)$ Å) in ${}^iBuN(CH_2C_6H_4)_2BiF^{14a}$ and that ($2.088(8)$ Å) in $Ph_4BiF_4^{15}$, but shorter than the Bi⋯F distance in $[{}^iBuN(CH_2C_6H_4)_2Bi]^+[B(C_6F_5)_4]^-$ ($2.971(2)$ Å)^{14b}. The organobismuth tetrafluoroborate **1** remained as dry crystals and suffered no color change in a test of one year in air. It is apparent that it is resistant to moisture and oxygen. Attached to the Bi atom of compound **1** is a strongly electron-withdrawing tetrafluoroborate (BF_4), and compound **1** shows Lewis acid strength of $3.3 < H_0 \leq 4.8$, stronger than that of $(C_6H_{11}N(CH_2C_6H_4)_2Bi(OSO_2C_8F_{17}))^{6b}$. In addition, compound **1** is highly soluble in methanol and in aqueous solutions of common polar organic molecules. The thermal stability of compound **1** was investigated by TG-DSC analysis under N_2 atmosphere (Fig. 2). One can see that the material is stable up to about $259^\circ C$. With all these positive features in mind, we proceeded to evaluate compound **1** as a Lewis acid catalyst for the allylation of aldehydes and ketones with tetraallyl tin¹⁶.

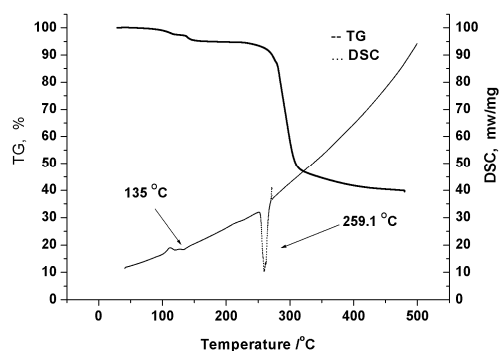
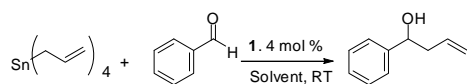


Fig. 2 TG-DSC curves of compound **1**.

In most cases of the utilization of metal reagents, the allylation reactions have to be conducted under dry condition and/or in an inert atmosphere. It is not so in the handling of tetraallyl tin. Another reason for adopting tetraallyl tin for allylation in this study is that the substance is inexpensive and readily available. The reaction of tetraallyl tin with benzaldehyde using 4 mol % of $C_6H_{11}N(CH_2C_6H_4)_2BiBF_4$ was examined in various solvents in a period of one hour (Table 1). One can see that the reaction occurs smoothly in solvents such as MeOH, C_2H_5OH , CH_3CN , DMSO, THF, CH_2Cl_2 (Table 1, entry 1, 2-4, 7-11), but slowly in hexane and toluene (Table 1, entries 12-13). In view of the facts that (i) methanol is relatively cheap, (ii) the effect of using water is positive (Table 1, entries 2-6), and (iii) the catalyst shows good air-tolerance, we conducted the reaction in aqueous MeOH solution. It was found that compound **1** is an excellent catalyst for the formation of 1-phenyl-3-buten-1-ol. After the usual work-up procedure, the yield of 1-phenyl-3-buten-1-ol can be as high as 97%.

In order to demonstrate the excellent catalytic activity of **1**, aliphatic aldehyde as well as aromatic aldehydes with electron-donating and electron-withdrawing groups were examined (Table 2). Allylation of both aromatic and

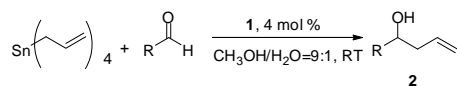
Table 1. Allylation of PhCHO with tetraallyltin catalyzed by **1** in various solvents^[a]

Entry	Solvent	Time (h)	Yield (%) ^[b]
1	MeOH	1	94
2	MeOH:H ₂ O = 9:1	1	97
3	MeOH:H ₂ O = 4:1	1	96
4	MeOH:H ₂ O = 7:3	1	90
5	MeOH:H ₂ O = 3:2	1	70
6	MeOH:H ₂ O = 1:1	1	58
7	C ₂ H ₅ OH	1	92
8	THF	1	90
9	CH ₃ CN	1	93
10	DMSO	1	84
11	CH ₂ Cl ₂	6	80
12	Toluene	6	56
13	Hexane	12	30

[a] PhCHO 1.0 mmol, tetraallyltin 0.3 mmol, **1**, 0.04 mmol, RT, 2.0 mL solvent.

[b] Isolated yield.

aliphatic aldehydes at ca. 30 °C in the presence of 4 mol% of the compound **1** proceeds smoothly to generate the corresponding homoallyl alcohols **2** in good to excellent yields. It is interesting to note that the aryl aldehydes with electron-withdrawing and electron-donating groups show similar allylation rate, suggesting that the presence of the electron-withdrawing or electron-donating group of the aldehydes has little effect on the reaction.

Table 2. Synthesis of homoallyl alcohols from aldehydes catalyzed by **1**^[a]

Entry	aldehyde	homoallylic alcohols	Reaction time(h)	Yield (%) ^[b]
1	PhCHO	2a	1	96
2	ⁱ C ₃ H ₇ CHO	2b	1	88
3	<i>p</i> -ClC ₆ H ₄ CHO	2c	1	93
4	<i>p</i> -CF ₃ C ₆ H ₄ CHO	2d	1	97
5	<i>p</i> -O ₂ NC ₆ H ₄ CHO	2e	1	92
6	<i>p</i> -CH ₃ OC ₆ H ₄ CHO	2f	1	94
7	<i>p</i> -CH ₃ C ₆ H ₄ CHO	2g	1	90
8	C ₇ H ₁₅ CHO	2h	1	95
9	PhCH ₂ CHO	2i	1	98
10	furan-2-carbaldehyde	2j	1	90

[a] PhCHO 1.0 mmol, tetraallyltin 0.3 mmol, **1** 0.04 mmol, RT, 2.0 mL solvent (CH₃OH/H₂O=9:1). All products are characterized by ¹H NMR.

[b] Isolated yield.

In Table 3, the catalytic performance of compound **1** is compared with those of the other bismuth compounds. After a blank run of 12 h, the isolated yield of homoallyl

alcohol is only 30%. When C₆H₁₁N(CH₂C₆H₄)₂Bi(BF₄) and [S(CH₂C₆H₄)₂Bi(OH₂)]⁺[ClO₄]⁻ are used as catalysts, the yields are above 90% after 1 h. The catalytic activity can be ranked in the order of C₆H₁₁N(CH₂C₆H₄)₂Bi(BF₄) > [S(CH₂C₆H₄)₂Bi(OH₂)]⁺[ClO₄]⁻ > C₆H₁₁N(CH₂C₆H₄)₂Bi[OCO(CH₂)₂GePh₃] > C₆H₅N(CH₂C₆H₄)₂Bi[OCO(CH₂)₂GePh₃] > ^tBuN(CH₂C₆H₄)₂Bi[OCO(CH₂)₂GePh₃] > C₆H₁₁N(CH₂C₆H₄)₂BiCl > S(CH₂C₆H₄)₂BiCl > Bi(OSO₂CF₃)₃ > BiCl₃. The poor catalytic activity of Bi(OSO₂CF₃)₃ and BiCl₃ could be attributed to the high sensitivity of the compounds towards moisture.

Table 3. Catalytic activity of different bismuth compounds in the allylation of PhCHO with tetraallyltin^[a]

Entry	Catalyst (4 mol %)	Time (h)	Yield (%) ^[b]
1	no Cat.	12	30
2	C ₆ H ₁₁ N(CH ₂ C ₆ H ₄) ₂ BiCl	4	80
3	C ₆ H ₁₁ N(CH ₂ C ₆ H ₄) ₂ BiBF ₄ (1)	1	96
4	[S(CH ₂ C ₆ H ₄) ₂ Bi(OH ₂)] ⁺ [ClO ₄] ⁻	1	94
5	C ₆ H ₁₁ N(CH ₂ C ₆ H ₄) ₂ Bi[OCO(CH ₂) ₂ GePh ₃]	4	88
6	C ₆ H ₅ N(CH ₂ C ₆ H ₄) ₂ Bi[OCO(CH ₂) ₂ GePh ₃]	4	85
7	^t BuN(CH ₂ C ₆ H ₄) ₂ Bi[OCO(CH ₂) ₂ GePh ₃]	4	75
8	Bi(OSO ₂ CF ₃) ₃	3	50
9	S(CH ₂ C ₆ H ₄) ₂ BiCl	4	77
11	BiCl ₃	3	68

[a] PhCHO 1.0 mmol, tetraallyltin 0.3 mmol, **1** 0.04 mmol, rt., 2 ml solvent (CH₃OH/H₂O=9:1).

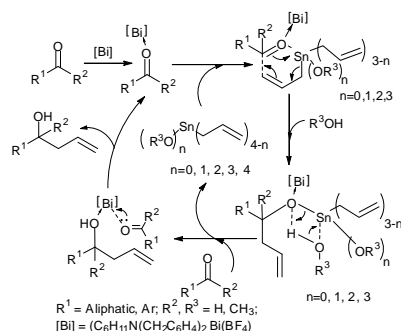
[b] Isolated yield.

To examine the reusability of the catalyst, compound **1** was subject to cycles of allylation reaction of benzaldehyde with tetraallyltin. In a test of 5 cycles, the change of product yield is minimal (isolated yield slightly declined from 96% to 94%), indicating that the catalyst is stable and reusable (details will be reported in a full paper).

Furthermore, we observed no formation of homoallylic alcohol in the case of acetophenone even after prolonged period of reaction (not shown). In other words, high chemoselectivity between aldehydes and ketones is possible in this approach of catalytic allylation. Such degree of chemoselectivity is impossible with the commonly used allylating reagents such as allylmagnesium bromide, allyllithium and allyltrityltin/BF₃·OEt₂^{8c}. It is apparent that compared to the catalysts reported in the literatures^{11d, 12}, compound **1** has the advantages of being high in activity, selectivity, stability, and reusability¹⁷.

According to the concepts suggested by Cokley *et al.*^{11b} and Lingaiah *et al.*¹⁸ and based on the experimental data reported so far, the mechanism of the allyllylation reaction over compound **1** in aqueous methanol solution is postulated (Scheme 2). With compound **1**, tetraallyltin and an aldehyde dissolved in aqueous methanol, the aldehyde coordinates with the bismuth atom and is activated. Then tetraallyltin attacks the activated aldehyde to form a six-membered intermediate. Meanwhile methanol and water coordinate to tin to form (RO)_nSn(CH₂-CH=CH₂)_{4-n} (*n* = 1,

2, 3, 4; R=H or CH₃), producing the homoallyl alcohol. With the cleavage of the coordinate bond, compound **1** is regenerated and is ready for the next catalytic cycle.



Scheme 2 Possible catalytic mechanism for the allylation of aldehyde catalyzed by compound **1**.

In summary, we have synthesized and characterized air-stable hypervalent organobismuth (III) tetrafluoroborate as efficient Lewis-acidity catalyst that shows high activity and good selective to homoallyl alcohols in the allylation of aromatic and aliphatic aldehydes with tetraallyltin in aqueous methanol.

Acknowledgements

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- Synthesis of compound **1**: C₆H₁₁N(CH₂C₆H₄)₂ BiCl (2.61 g, 5.0 mmol) was dissolved in 90.0 mL THF, then a solution of AgBF₄ (0.97 g, 5.0 mmol) in 60.0 mL THF was added. After the mixture was stirred in the dark at room temperature for 3 h, it was filtered. The filtrate mixed with 10.0 mL hexane was refrigerated for 24 h, giving colorless crystals (2.74 g, 95.6%). Compound **1**: ¹H NMR(D₆ acetone, 400 MHz, TMS): δ 1.19 (1H, td, J=13.6 Hz), 1.33-1.44(2H, m), 1.54-1.63 (3H, m), 1.84 (2H, d, J=11.2 Hz), 2.16 (2H, d, J=12.0 Hz), 3.50 (1H, t, J=12.0 Hz), 4.67 (2H, d, J=15.6 Hz), 5.02 (2H, d, J=15.6 Hz), 7.42 (2H, td, J=7.6 Hz), 7.58 (2H, t, J=7.6 Hz), 7.76 (2H, d, J=7.6 Hz), and 8.09 (2H, d, J=7.2 Hz); ¹³C NMR (D₆ acetone, 100 MHz): δ 25.89, 26.16, 26.29, 32.03, 65.07, 67.75, 68.06, 129.28, 129.55, 131.58, 137.77, and 154.44; ¹⁹F NMR (D₆ acetone, 376 MHz): -154.437(s); HRMS calcd for C₂₆H₃₅BBiF₄N: 657.3419, found: 657.3414; Crystallographic data for **1**: C₆H₁₁N(C₆H₄CH₂)₂BiBF₄·C₆H₁₂, colorless prism, formula weight 657.34, *Monoclinic*, P2(1)/n, a = 10.9011(12), b = 16.0649 (18), c = 14.2625 (15), V = 2457.3 (5), Z = 4, D_{calc} = 1.777 g·cm⁻³, R_{int} = 0.069, R_i = 0.056, wR₂ = 0.135, GOF = 0.86, CCDC No. 746982.
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- Typical procedure for the allylation reaction: To a solution of **1** (0.04 mmol, 23.9 mg) in 2.0 mL solvent (CH₃OH/H₂O = 9:1), PhCHO (106.1 mg, 1 mmol), and tetraallylstannane (0.3 mmol, 84.9 mg) were added. Then the mixture was stirred at room temperature and subject to TLC analysis for one hour. The resulted solution was subject to evaporation and the residue was dissolved in Et₂O (20 mL). The catalyst precipitated and was filtered out, and could be immediately reused in the next reaction. The organic layer was mixed with methanol and 2N HCl (1 mL) and stirred for 15 minutes, and then NaHCO₃ (10%) was added for neutralization. After filtration, the aqueous layer was extracted with Et₂O (10 mL × 3), and the organic layers were combined and washed with brine, then dried with Na₂SO₄. The resulted solution was subject to evaporation, whereas the residue was subject to silica gel column chromatograph (ethyl acetate/petroleum ether = 1/8). The collected colorless oil showed an isolated yield of 142.0 mg, 96%. All aldehydes, acetophenone and tetraallyltin are commercially available. All homoallylic alcohols **2a-2j** have been reported, and ¹H NMR spectra data of the products are consistent with our previously results (see references 7a,7b) and those of Jiang et al. and Zhao and Cai (see references 19a, 19b).
1-Phenyl-3-buten-1-ol (2a) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.01 (1H, bs), 2.49-2.58 (2H, m), 4.75 (1H, t, J =5.42 Hz), 5.14-5.20 (2H, m), 5.82 (1H, m), 7.25-7.43 (5H, m).
2-methylhex-5-en-3-ol (2b) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 0.91 (6H, d, J=7.2 Hz), 2.12-2.17(1H, m), 2.23-2.34(2H, m), 3.30-3.42(1H, m), 5.02(2H, d, J=7.8 Hz), 5.08(1H, S), 5.89-6.02(1H, m).

1-(p-Chlorophenyl)-3-buten-1-ol (2c) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.16 (1H, s), 2.41-2.50 (2H, m), 4.71(1H, dd, *J*=6.8 Hz), 5.13-5.17 (2H, m), 5.73-5.80 (1H, m), 7.26-7.32 (4H, m).

1-(p-Trifluoromethylphenyl)-3-buten-1-ol (2d) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.21(1H, s), 2.57-2.43 (2H, m), 4.80 (1H, m), 5.18 (2H, m), 5.75-5.83 (1H, m), 7.47 (2H, d, *J*=8.2 Hz), 7.61 (2H, d, *J*=8.2 Hz).

1-(4-nitrophenyl)but-3-en-1-ol (2e) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.13 (1H, br), 2.42-2.49 (1H, m), 2.54-2.60(1H, m), 4.86-4.89 (1H, m), 5.17-5.22(2H, m), 5.74-5.84(1H, m), 7.54(2H, d, *J*=8.8 Hz), 8.21 (2H, d, *J*=8.8 Hz).

1-(p-Methoxyphenyl)-3-buten-1-ol (2f) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 1.94 (1H, bs), 2.50 (2H, d, *J*=6.6 Hz), 3.81 (3H, s), 4.69 (1H, t, *J*= 6.3 Hz), 5.11-5.18 (2H, m), 5.80 (1H, m), 6.89 (2H, d, *J*= 8.8 Hz), 7.27 (2H, d, *J*=8.8 Hz).

1-(p-Methylphenyl)-3-buten-1-ol (2g) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 2.01 (1H, bs), 2.33 (3H, s), 2.48-2.51 (2H, m), 4.69 (1H, t, *J*= 6.6 Hz), 5.11-5.17 (2H, m), 5.76-5.81 (1H, m), 7.14 (2H, d, *J*= 7.8 Hz), 7.24 (2H, d, *J*=7.8 Hz).

Undec-1-en-4-ol (2h) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 0.88 (3H, t, *J*=7.0 Hz), 1.28 (12H, bs), 1.44-1.48 (2H, m), 1.84 (1H, s), 2.11-2.17 (1H, m, one proton of CH₂), 2.27-2.32 (1H, m, one proton of CH₂), 3.62-3.66 (1H, m), 5.11-5.15 (2H, m), 5.79-5.87 (1H, m).

1-Phenylpent-4-en-2-ol (2i) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 1.83 (1H, s), 2.20-2.26 (1H, m), 2.30-2.35 (1H, m), 2.72 (1H, dd, *J*= 13.6 Hz), 2.81 (1H, dd, *J*= 4.0 Hz), 3.87 (2H, m), 5.13-5.18 (2H, m), 5.86 (1H, m), 7.21-7.26 (3H, m), 7.29-7.34 (2H, m).

1-(furan-2-yl)but-3-en-1-ol (2j) ¹H NMR(CDCl₃, 400 MHz, TMS): δ 1.93-2.12 (1H, br), 2.61-2.66 (2H, m), 4.76 (1H, t, *J*=6.1 Hz), 5.14-5.22 (2H, m), 5.74-5.84 (1H, m), 6.25 (1H, d, *J*=2.6 Hz), 6.33 (1H, q, *J*= 2.6 Hz), 7.39(1H, d, *J*=1.5 Hz).

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