



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

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ARTICLE INFO

Article history:

Received 21 September 2009

Revised 20 October 2009

Accepted 22 October 2009

Available online 27 October 2009

Keywords:

Organobismuth
Tetrafluoroborate
Lewis acid
Catalysis
Allylation

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.

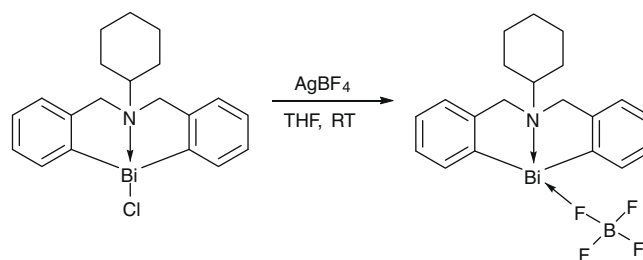
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Bismuth compounds are not toxic and relatively cheap, and have been widely used in catalysis and organic synthesis. In the past two decades, bismuth(III) compounds (e.g., $BiCl_3$, $BiBr_3$, $Bi(OTf)_3$, and $Bi(NO_3)_3$) have been used as catalysts in various organic reactions.^{1,2} However, up till now, there are not that many reports on the use of organobismuth compounds as catalysts in organic synthesis, possibly due to the unstable nature of bismuth compounds.³ 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 fixation.⁴ Very recently we reported that certain organobismuth chlorides and their triphenylgermylpropionate derivatives show good in vitro antiproliferative activity,⁵ and that organobismuth perfluorooctanesulfonate and perchlorate exhibit high catalytic efficiency toward one-pot Mannich-type reaction of ketones with aromatic aldehydes and aromatic amines in water.⁶ We have also developed a series of novel Lewis acids by incorporating large electron-withdrawing groups (e.g., $-C_6F_5SO_3$ and $-C_8F_{17}SO_3$) into organometallic (e.g., Ti, Zr, and Hf) compounds, and found that they are catalytically active toward many organic reactions in aqueous media as well as in various organic solvents.⁷ It is known that the Le-

wis acid-catalyzed allylation of carbonyl compounds to produce homoallylic alcohols is a versatile organic reaction.⁸ The allylation reaction can be promoted by the addition of a Lewis acid⁹ or enhanced by the rise of reaction temperature or pressure.¹⁰ On the other hand, there is a growing body of evidence that under certain circumstances, the solvent (THF– HCl ^{8e} or methanol¹¹) and ionic liquids¹² can facilitate allyl transfer from tetraallylstannane to alkanals or alkanones.

In this Letter, 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 tetraallyltin in aqueous media.

Scheme 1 shows the synthesis of hypervalent organobismuth(III) tetrafluoroborate **1**. Treatment of $C_6H_{11}N(CH_2C_6H_4)_2BiCl$



Scheme 1. Synthesis of compound **1**.

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with silver tetrafluoroborate (AgBF_4) (1 equiv) in THF yields the target complex.¹³ The crystal structure of compound **1** was confirmed by X-ray analysis technique (for analysis condition, please see Ref. 13). An ORTEP representation of the structure of compound **1**, as well as selected bonds and angles are shown in Figure 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 $2.230(11) \text{ \AA}$ and $2.229(10) \text{ \AA}$, respectively. As reported previously, the Bi–N coordination distance in 5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azabismocines flexibly changes in response to the electronic nature of bismuth.¹⁴ The Bi–F bond is $2.502(7) \text{ \AA}$ in length, longer than that ($2.190(4) \text{ \AA}$) in $[\text{BuN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiF}]^{14a}$ and that ($2.088(8) \text{ \AA}$) in Ph_4BiF_4 ,¹⁵ but shorter than the Bi–F distance in $[\text{BuN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]^+[\text{C}_6\text{F}_5)_4]^-$ ($2.971(2) \text{ \AA}$).^{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 $(\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}(\text{OSO}_2\text{C}_6\text{F}_5))$.^{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°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 tin.¹⁶

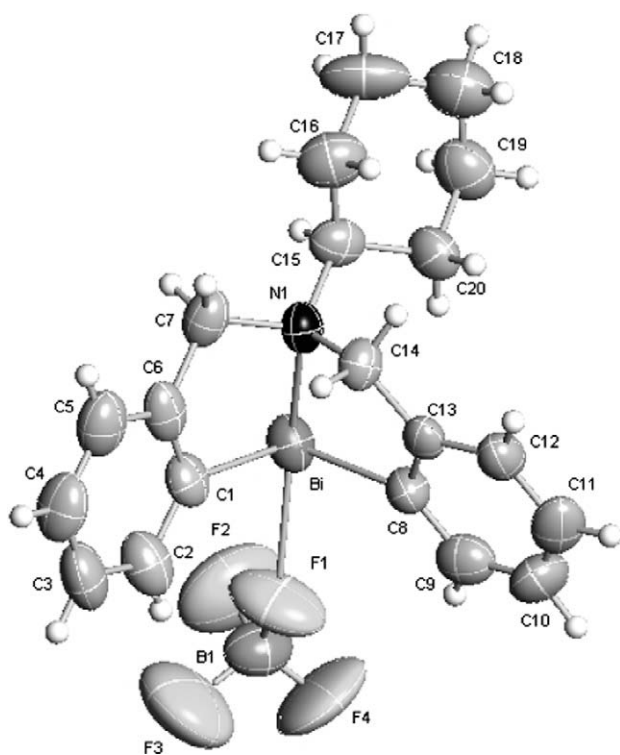


Figure 1. Thermal ellipsoid plot of $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBF}_4$ (50% probability level). Selected bond lengths (\AA) and angles ($^\circ$): Bi–C(1) $2.230(11)$; Bi–C(8) $2.229(10)$; Bi–N(1) $2.394(8)$; Bi–F(1) $2.502(7)$; N(1)–C(14) $1.512(10)$; N(1)–C(7) $1.506(12)$; 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) $110.5(6)$.

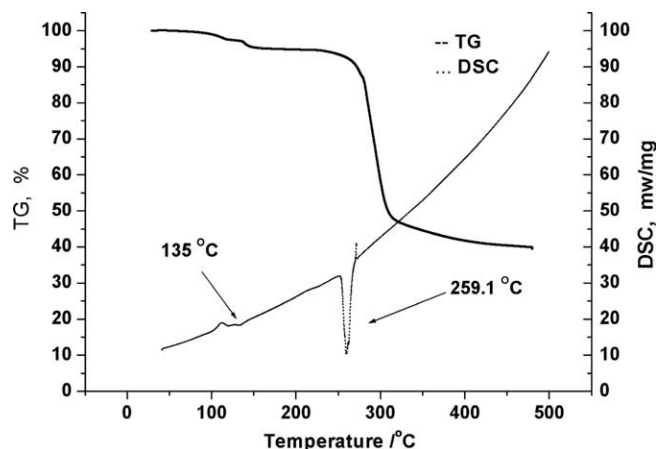


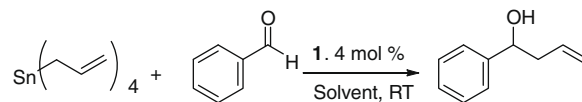
Figure 2. TG–DSC curves of compound **1**.

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 $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBF}_4$ was examined in various solvents in a period of 1 h (Table 1). One can see that the reaction occurs smoothly in solvents such as MeOH, $\text{C}_2\text{H}_5\text{OH}$, CH_3CN , DMSO, THF, and CH_2Cl_2 (Table 1, entries 1, 2–4, and 7–11), but slowly in hexane and toluene (Table 1, entries 12 and 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 was examined (Table 2). Allylation of both aromatic and 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 alde-

Table 1

Allylation of PhCHO with tetraallyl tin 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	$\text{C}_2\text{H}_5\text{OH}$	1	92
8	THF	1	90
9	CH_3CN	1	93
10	DMSO	1	84
11	CH_2Cl_2	6	80
12	Toluene	6	56
13	Hexane	12	30

^a PhCHO 1.0 mmol, tetraallyl tin 0.3 mmol, **1**, 0.04 mmol, rt, 2.0 mL solvent.

^b Isolated yield.

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>i</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.

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.

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 toward moisture.

To examine the reusability of the catalyst, compound **1** was subject to cycles of allylation reaction of benzaldehyde with tetraallyltin. In a test of five 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).

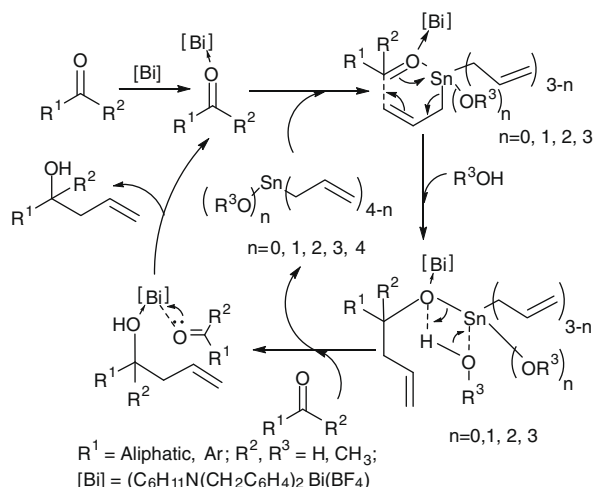
Furthermore, we observed no formation of homoallylic alcohol in the case of acetophenone even after prolonged period of reaction (not shown). In other words, high chemoselectivity between aldehydes and ketones is possible in this approach of catalytic allyla-

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
10	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.



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

tion. Such degree of chemoselectivity is impossible with the commonly used allylating reagents such as allylmagnesium bromide, allyllithium, and allyltrityltin/BF₃·OEt₂.^{8e} 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 reusability.¹⁷

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 allylation 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 = 1–4; 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.

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

Acknowledgments

This work was financially supported by the National Science Foundation of China (Nos. 20507005 and 20873038) and the National 863 Program of China (2009AA05Z319). C.-T. Au thanks the Hunan University for an adjunct professorship.

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13. *Synthesis of compound 1*: $C_6H_{11}N(CH_2C_6H_4)_2BiCl$ (2.61 g, 5.0 mmol) was dissolved in 90.0 mL THF, then a solution of $AgBF_4$ (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 (acetone- d_6 , 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); ^{13}C NMR (acetone- d_6 , 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; ^{19}F NMR (acetone- d_6 , 376 MHz): δ -154.437(s); HRMS calcd for $C_{26}H_{35}BBiF_4N$: 657.3419, found: 657.3414; *Crystallographic data for 1*: $C_6H_{11}N(C_6H_4CH_2)_2BiBF_4 \cdot C_6H_{12}$, colorless prism, formula weight 657.34, monoclinic, $P2(1)/n$, $a = 10.9011(12)$, $b = 16.0649(18)$, $c = 14.2625(15)$, $V = 2457.3(5)$, $Z = 4$, $D_{calcd} = 1.777$ g cm^{-3} , $R_{int} = 0.069$, $R_1 = 0.056$, $wR_2 = 0.135$, GOF = 0.86, CCDC No. 746982.
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16. *Typical procedure for the allylation reaction*: To a solution of **1** (0.04 mmol, 23.9 mg) in 2.0 mL solvent ($CH_3OH/H_2O = 9:1$), 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 1 h. The resulted solution was subject to evaporation and the residue was dissolved in Et_2O (20 mL). The catalyst was precipitated and was filtered out, and could be immediately reused in the next reaction. The organic layer was mixed with methanol and 2 N HCl (1 mL) and stirred for 15 min, and then $NaHCO_3$ (10%) was added for neutralization. After filtration, the aqueous layer was extracted with Et_2O (10 mL \times 3), and the organic layers were combined and washed with brine, then dried with Na_2SO_4 . 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–j** have been reported, and 1H NMR spectra data of the products are consistent with our previous results (see Refs. 7a,b) and those of Jiang et al. and Zhao and Cai (see Refs. 19a,b).
- 1-Phenyl-3-buten-1-ol (2a)*: 1H NMR ($CDCl_3$, 400 MHz, TMS): δ 2.01 (1H, br s), 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 ($CDCl_3$, 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 ($CDCl_3$, 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 ($CDCl_3$, 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 ($CDCl_3$, 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 ($CDCl_3$, 400 MHz, TMS): δ 1.94 (1H, br s), 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 ($CDCl_3$, 400 MHz, TMS): δ 2.01 (1H, br s), 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 ($CDCl_3$, 400 MHz, TMS): δ 0.88 (3H, t, $J = 7.0$ Hz), 1.28 (12H, br s), 1.44–1.48 (2H, m), 1.84 (1H, s), 2.11–2.17 (1H, m, one proton of CH_2), 2.27–2.32 (1H, m, one proton of CH_2), 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 ($CDCl_3$, 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 ($CDCl_3$, 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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