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Zeolite-catalyzed synthesis of 2,3-unsubstituted benzo[*b*]furans via the intramolecular cyclization of 2-aryloxyacetaldehyde acetals

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ABSTRACT

An efficient and environmentally benign heterogeneous catalytic process for the synthesis of 2,3-unsubstituted benzo[*b*]furans has been established via the intramolecular cyclization of 2-aryloxyacetaldehyde acetals. By utilizing tin-exchanged H-β zeolite (Sn-β) as catalyst, a wide range of functionalized 2,3-unsubstituted benzo[*b*]furans could be prepared in good to excellent yields. The Sn-β zeolite catalyst also exhibited excellent shape selectivity on the cyclization of *meta*-substituted 2-aryloxyacetaldehyde acetals, and 6-substituted isomers were preferably formed up to 97% regioselectivity. Moreover, Sn-β zeolite could be easily recovered and reused without any noticeable activity loss.

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1. Introduction

2,3-Unsubstituted benzo[*b*]furan is an important structural motif widely occurring in a number of natural products and biologically active molecules.[1] It also serves as versatile building block for the construction of complex benzo[*b*]furan derivatives.[2] Although 'naked' benzo[*b*]furan could be extracted from coal tar, a large number of functionalized 2,3-unsubstituted benzo[*b*]furans were only available through chemical synthesis. Over the past decades, many synthetic methods have been developed to prepare this class of compounds.[3] Among these reported methods, the acid-promoted intramolecular electrophilic cyclization of 2-aryloxyacetaldehyde acetals is perhaps the most straightforward and economic one, as the cyclization precursors can be easily accessible by the condensation of substituted phenols and bromoacetaldehyde diethyl acetal.[3l] So far, only a very limited number of acidic reagents have been reported to efficiently promote this transformation since the synthetic protocol was proposed a century ago.[4] An excessive amount of polyphosphoric acid (PPA) has been widely employed in this cyclization reaction to form 2,3-unsubstituted benzo[*b*]furans.[3l,5] Though inexpensive and readily available, PPA has several drawbacks including its high viscosity, tedious workup procedure and generation of large volume of aqueous waste. Furthermore, PPA was inefficient in the conversion of electron-deficient substrates due to its weak acidic strength. Recently, acidic resin (Amberlyst-15) was utilized by several research groups to promote this transformation for the synthesis of several special substituted 2,3-unsubstituted benzo[*b*]furans.[6] Stoichiometric amount of Amberlyst-15 was needed, and the reuse of Amberlyst-15 was problematic due to its weaker mechanical strength under the harsh reaction conditions (typically, 110–130 °C). In addition to PPA and Amberlyst-15, other Lewis acids or Bronsted acids have been tested for this transformation. A majority of them led to the competitive C–O bond cleavage of the aryloxyacetaldehyde acetals, and/or the subsequent polymerization of formed 2,3-unsubstituted benzo[*b*]furans, and thus failed to provide the desired cyclization products in reasonable yields.[7] Therefore, developing an efficient and environmentally sustainable catalyst system for this transformation is highly desired.

Over the past decades, catalysis by zeolites and related materials has received great attentions.[8] As an important type of solid acids, they have been widely used as replacement for highly toxic and corrosive mineral acids or inorganic Lewis acids in synthesis of fine chemicals.[9] By virtue of their nature, zeolites have well defined porous structures with large amount of acid sites (both Bronsted and Lewis type) present on the inner surface of these pores. In

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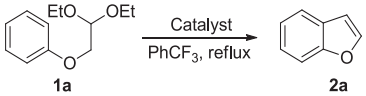
a catalytic reaction, each pore could be considered as a typical catalytic nanoreactor, where only the substrate with suitable size could access these pores, and thus be activated for the reactions. One of the most important properties of zeolites is the great variety of topologies and pore architectures, together with the possibility to adjust their acidity (type, concentration, and strength of acid sites). As a result, the catalysis activity of zeolites could be tailored for special chemical transformations. Additionally, their environmentally benign nature, high surface area, and adsorption capacity, as well as outstanding chemical and thermal stability, make them ideal candidates for heterogeneous catalysis. Due to our continuous interests in this area,[10] we herein reported the first zeolite-catalyzed intramolecular cyclization of 2-aryloxyacetaldehyde acetals for the preparation of 2,3-unsubstituted benzo[*b*]furans.

2. Results and discussion

Using the conversion of 2-phenyloxyacetaldehyde diethyl acetal (**1a**) to benzo[*b*]furan (**2a**) as a model reaction, we initiated our work by testing the catalytic activity of various commercially available zeolites, including H-ZSM-5, H-β, and H-Y.[11] The reaction was also carried out in the absence of catalyst. The results are summarized in Table 1. Without catalyst, the substrate **1a** was inert even after refluxing in trifluorotoluene for 6 h (entry 1, Table 1). The reaction proceeded smoothly in the presence of each one of the zeolites H-ZSM-5, H-β or H-Y, and the cyclization product benzo[*b*]furan **2a** was produced in moderate yields (58–77%) based on GC analysis (entries 2–4, Table 1). Zeolite H-β exhibited better catalytic activity than H-Y and H-ZSM-5. With H-β zeolite as catalyst and in refluxing trifluorotoluene, substrate **1a** could be completely converted in 0.5 h and benzo[*b*]furan **2a** was obtained in 77% yield (entry 4, Table 1). The better performance of H-β zeolite on this Friedel–Crafts type reaction could be attributed to its higher concentration of Bronsted acid sites and special three-dimensional large size porous structure.[12] Unfortunately, with H-β zeolite as catalyst, simply optimizing the reaction conditions, such as the solvent, reaction temperature, and the amount of catalyst, could not further improve the selectivity. Next, we turned our efforts to the metal-exchanged H-β zeolites, such as Fe-β, Zn-β, Sn-β, Zr-β, Ga-β, and In-β.[13] The various salts of these metal ions are widely used as Lewis acid catalyst in numerous acid-promoted organic transformations. To our delight, the zeolites Fe-β, Zn-β, Sn-β, and Zr-β exhibited significantly better catalysis performance than parent H-β. With each one of these metal-exchanged zeolites as catalyst, and under the identified reaction conditions, the reaction rate was the same as that of H-β, while the yields of **2a** were significantly improved to 93–96% (entries 5–8, Table 1). In particular, under the catalysis of zeolite Sn-β, the yield of benzo[*b*]furan **2a** reached to 96% (entry 7, Table 1). With the Ga-β zeolite as catalyst, moderate yield improvement was observed (84%), and a relatively longer reaction time (0.75 h) was needed for the completion of reaction (entry 9, Table 1). By contrast, In-β zeolite showed not only a much slower reaction rate, but also a lower selectivity than the parent H-β (entry 10, Table 1). Since Sn-β zeolite exhibited best catalysis performance in this transformation, it was selected as catalyst for our further research.

Table 1
The cyclization of 2-phenyloxyacetaldehyde diethyl acetal under the catalysis of different kinds of zeolites[a]



1a **2a**

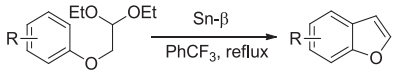
Entry	Catalyst	*T* (h)	Conv.[b] (%)	Yield[b] (%)
1	None	6	—	—
2	H-ZSM-5	6	>99	75
3	H-Y	2	>99	58
4	H-β	0.5	>99	77
5	Fe-β	0.5	>99	93
6	Zn-β	0.5	>99	92
7	*Sn-β*	*0.5*	*>99*	*96*
8	Zr-β	0.5	>99	93
9	Ga-β	0.75	>99	84
10	In-β	1	>99	52

[a] Reaction conditions: **1a** (1 mmol), catalyst (0.10 g), and trifluorotoluene (10 mL) at refluxing temperature.
[b] GC yields by internal standard method with naphthalene as internal standard.

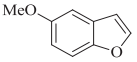
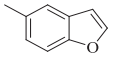
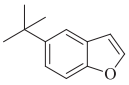
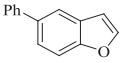
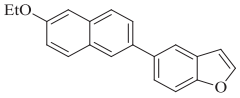
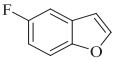
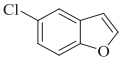
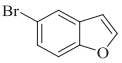
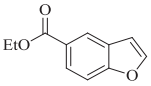
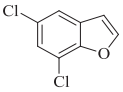
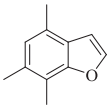
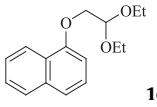
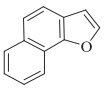
Then, we tried to demonstrate the generality of Sn-β zeolite for the synthesis of functionalized 2,3-unsubstituted benzo[*b*]furans via the intramolecular cyclization of 2-aryloxyacetaldehyde acetals. As shown in Table 2, a wide range of 2-aryloxyacetaldehyde diethyl acetals **1a**–**1o** can be smoothly converted to their corresponding 2,3-unsubstituted benzo[*b*]furans **2a**–**2o** in the presence of Sn-β zeolite catalyst. However, the reaction rate and selectivity were remarkably dependent on the electronic property and position of the substitute bearing on the substrates. Under identified reaction conditions, the substrates **1b**–**1f** bearing electron-donating groups (OMe, Me, *t*-Bu, Ph, and ethoxy-substituted naphthalenyl) at *para*-position exhibited similar reactivity as non-substituted **1a**, and the corresponding cyclization products **2b**–**2f** were obtained in 86–95% yield. Noteworthy, substituents (*t*-Bu and Ph) with moderate size showed no effects on both reaction rate and selectivity, indicating that the pore size of zeolite Sn-β was large enough to accommodate these molecules. However, much larger substituent (6-ethoxynaphthalen-2-yl) led to lower reaction rate, which was ascribed to its much slower diffusion rate in the pores of zeolite Sn-β. Nevertheless, the corresponding cyclization product **2f** could still be obtained in 88% yield. Both the reaction rate and yield were dramatically affected by the electron-withdrawing groups attached on the substrates. For instance, the substrates **1g**–**1j**, bearing F, Cl, Br, and ethoxycarboxyl group at *para*-position, exhibited slower reaction rate (1.5–4 h) and lower product yield (71–82%). As for substrate **1k**, bearing two chloro groups on the 2 and 4-positions of phenyl ring, it took 10 h for the complete conversion, and the cyclization product **2k** was obtained in only 30% yield. The substrates with strong electron-withdrawing groups (such as CN and NO_2) in phenyl ring could not afford the desired cyclization products. The above results were consistent with the basic electronic effect of Friedel–Crafts type reactions. It was noteworthy to point out that the main by-products detected by GC–MS in the reaction of those electron-deficient substrates were phenols, which undoubtedly resulted from the decomposition of these substrates under the reaction conditions. We are convinced that this competitive decomposition side-reaction led to the decreased yields of these 2,3-unsubstituted benzo[*b*]furans. Moreover, the cyclization reaction rate was also affected by the position of substituent on the phenyl ring. The substrates **1l** and **1m** bearing substituent at *ortho*-position required relatively longer reaction time than their analogs (**1b** and **1h**) with substituent at *para*-position. But the yields of **2l** and **2m** were similar with those of **2b** and **2h**. In addition, under the catalysis of Sn-β, the 2,3-unsubstituted benzo[*b*]furans with multiple substituents on phenyl ring and fused ring could also be prepared in excellent yields (**2n** and **2o**). The isolation yields of benzo[*b*]furan **2a** and 5-flourobenzo[*b*]furan **2g** were much lower than their GC assay yields due to their highly volatile character.

Considering that shape selectivity is a distinctive property of zeolites over other acid catalysts, we furthermore studied the cyclization reactions of *meta*-substituted 2-aryloxyacetaldehyde diethyl acetals under the catalysis of Sn-β zeolite, and the results were listed in Table 3. Under the identified reaction conditions, the substrates (**1p**–**1t**) bearing OMe, Me, Ph, Cl, and Br groups at *meta*-position exhibited similar reactivity as their *para*-substituted

Table 2
Preparation of various 2,3-unsubstituted benzo[*b*]furans from 2-aryloxyacetaldehyde diethyl acetals[a]



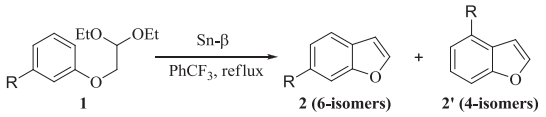
1 2

Entry	1[b] (R)	Product	2	Time[c] (h)	Yield[d] (%)
1	**1a** (R=H)		**2a**	0.5	78 (96)
2	**1b** (R=4-OMe)		**2b**	0.5	86
3	**1c** (R=4-Me)		**2c**	0.5	93
4	**1d** (R=4-*t*-Bu)		**2d**	0.5	92
5	**1e** (R=4-Ph)		**2e**	0.5	95
6	**1f** (R=6-ethoxynaphthalen-2-yl)		**2f**	2.5	88
7	**1g** (R=4-F)		**2g**	1.5	67 (82)
8	**1h** (R=4-Cl)		**2h**	2	80
9	**1i** (R=4-Br)		**2i**	3	77
10	**1j** (R=4-COOEt)		**2j**	4	71
11	**1k** (R=2, 4-diCl)		**2k**	10	30
12	**1l** (R=2-OMe)		**2l**	1	90
13	**1m** (R=2-Cl)		**2m**	4	75
14	**1n** (R=2, 3, 5-triMe)		**2n**	0.5	94
15	 **1o**		**2o**	0.5	95

[a] Reaction conditions: substrate **1** (1 mmol), Sn-β (0.10 g), and trifluorotoluene (10 mL) at refluxing temperature.
[b] The procedure for the synthesis of substrates **1** was present in Supplementary data.
[c] The time for the complete reaction.
[d] Isolated yields and the yields in parenthesis were the GC yields by internal standard method with naphthalene as internal standard.

analogs in respects of reaction rate and yield. As expected, all of these substrates afforded two isomeric products, 6-substituted benzo[*b*]furans (**2p**–**2t**) and 4-substituted benzo[*b*]furans (**2p′**–**2t′**), with 6-substituted product as predominant one (88–97%). In particular, when the substrate with a relatively larger phenyl group (**1r**) at *meta*-position, the selectivity of 6-isomer **2r** over 4-isomer **2r′** reached 97:3 (entry 3, Table 3). On the other hand, under the promotion of PPA, the ratio of **2r** to **2r′** and **2t** to

Table 3
Reaction of *meta*-substituted 2-aryloxyacetaldehyde diethyl acetals[a]



1 2 (6-isomers) 2' (4-isomers)

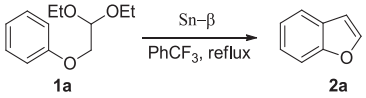
Entry	1[b] (R)	Time[c] (h)	Yield[d] (%)	Product (2/2')[e]
1	**1p** (R=OMe)	0.5	87	94:6
2	**1q** (R=Me)	0.5	91	88:12
3	**1r** (R=Ph)	0.5	93	97:3
4	**1s** (R=Cl)	2	80	96:4
5	**1t** (R=Br)	3	76	93:7

[a] Reaction conditions: substrate **1** (1 mmol), Sn-β (0.10 g), and trifluorotoluene (10 mL) at refluxing temperature.
[b] The procedure for the synthesis of substrates **1** was present in Supplementary data.
[c] The time for the complete reaction.
[d] Isolated yields.
[e] Determined by ^{1}H NMR analysis.

2t'was reported to 2:1 and 1:1, respectively.[3l,5a,14] It might be rationalized that the molecular size in vertical direction of 6-substituted benzo[*b*]furans was smaller than that of 4-substituted isomers, and have much greater diffusivity in pores of Sn-β. Therefore, more 6-substituted benzo[*b*]furans were generated in the pores of Sn-β zeolite.

We also tested the potential recycling ability of Sn-β in this 2,3-unsubstituted benzo[*b*]furan synthesis. With the cyclization of 2-phenyloxyacetaldehyde diethyl acetal (**1a**) to form corresponding benzo[*b*]furan (**2b**) as a model reaction, Sn-β could be recovered by simple filtration and maintained its catalytic activity. No obvious loss of the catalytic activity was observed even after five cycles (Table 4).

Table 4
Recycling tests of catalyst Sn-β[a]



1a 2a

Entry	Recycles	Time[b] (h)	Conv.[c] (%)	Yield[c] (%)
1	0	0.5	>99	96
2	1	0.5	>99	96
3	2	0.5	>99	92
4	3	0.5	>99	91
5	4	0.75	>99	90

[a] Reaction conditions: **1a** (1 mmol), Sn-β (0.10 g), and trifluorotoluene (10 mL) at refluxing temperature.
[b] The time for the complete reaction.
[c] GC yields by internal standard method and naphthalene used as internal standard.

Attempting to elucidate the peculiar catalytic performance of Sn-β zeolite on this transformation, the structures and acidity properties of the parent H-β zeolite and Sn-β zeolite were compared with classic methods, including X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature-programmed desorption (NH_3-TPD) ,and potentiometric titration analysis. The XRD patterns of H-β and Sn-β indicated that no obvious micro structural changes occurred after tin metal exchange (see Supplementary data, Fig. 1s). However, TEM analysis clearly showed that a number of well-formed nanoparticles (less than 5 nm) were present on the surface of Sn-β zeolite, while not found on that of H-β zeolite (Fig. 1). According to previous reports, these nanoparticles might be SnO_2 crystals formed during calcinations.[15] We assumed that these nanoparticles produced new catalytic sites on the surface of zeolite, and play a certain role in this transformation.

As expected, zeolite H-β and Sn-β exhibited difference in acidity property. The NH_3-TPD profile of H-β (Fig. 2a) showed that the zeolite H-β contained two types of acidic sites. The peak of desorption temperature at 255 °C was assigned to the weak acid site, and the peak of desorption temperature at 438 °C was assigned to the strong acid site. These two peaks shifted to 234 °C and 400 °C in the NH_3-TPD profile of Sn-β (Fig. 2b). The decrease of desorption temperature indicated that Sn-β had relatively lower acid strength than H-β. Considering that the cleavage of C–O bond of the substrates, 2-aryloxyacetaldehyde acetals were often observed under strong acidic conditions, it was not difficult to assume that a slight lower acid strength of zeolite Sn-β would benefit the stability of the substrate **1a**, and thus improve the cyclization reaction selectivity. In addition, NH_3-TPD profiles in Fig. 2 also showed that the amount of desorbed ammonia of Sn-β at both peaks of desorption temperature was remarkably lower than that of H-β. This indicated that the number of two acid sites in zeolite H-β was decreased after tin metal exchange. This decrease of acid sites was also confirmed by the potentiometric titration method.[16] With *n*-butylamine as titrant, the total acid capacities of the H-β and Sn-β were determined to be 0.79 mmol/g and 0.68 mmol/g, respectively (see Supplementary data, Fig. 2s). Although the total acid capacity of Sn-β was somewhat lower than that of H-β, it still could afford the similar reaction rate. Based on above results, the excellent catalytic ability of Sn-β on this transformation could be attributed to the combined effects of the newly generated Lewis acid sites by SnO_2 nanoparticles, and the decreased acid strength. Noteworthy, based on the total acid capacity of Sn-β, we also can calculate that the reaction was carried out under 6.8 mol % of acid catalyst. Thus an efficient catalytic process of transformation of aryloxyacetaldehyde diethyl acetal to its corresponding benzo[*b*]furan was successfully established.

In summary, we have successfully developed a heterogeneous catalytic system for the synthesis of 2,3-unsubstituted benzo[*b*]furans. Under the catalysis of tin-exchanged H-β Zeolite (Sn-β), a wide range of 2-aryloxyacetaldehyde acetals were smoothly converted to their corresponding 2,3-unsubstituted benzo[*b*]furans in good to excellent yields. Zeolite Sn-β also exhibited excellent shape selectivity on the cyclization of *meta*-substituted 2-aryloxyacetaldehyde acetals, and 6-substituted isomers were preferably formed in 88–97% selectivity. The heterogeneous catalyst Sn-β could be conveniently recovered and reused without obvious loss of the catalytic activity. Therefore, this work will pave an economic and environmental-benign way for the construction of various benzo[*b*]furan derivatives.

3. Experimental section

3.1. General

All proton and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500 MHz spectrometer in deuterium solvents with tetramethylsilane (TMS) as internal standard. GC–MS analyses were performed on a Thermo Trace ISQ instrument in EI mode (70 eV). GC analyses were performed on Thermo TRACE GC Ultra instrument with FID detector using an HP-5 capillary column (30 m×0.25 mm (i.d.), 0.25 μ). High-resolution mass spectra were recorded in the EI mode on Waters GCT Premier TOF mass spectrometer with an Agilent 6890 gas chromatography using a DB-XLB column (30 m×0.25 mm (i.d.), 0.25 μ). Melting points (uncorrected) were determined on BUCHI M-565 apparatus. X-ray powder diffraction (XRD) analyses were performed on a PANalytical X'Pert PRO diffractometer using Cu Kα radiation. Transmission electron

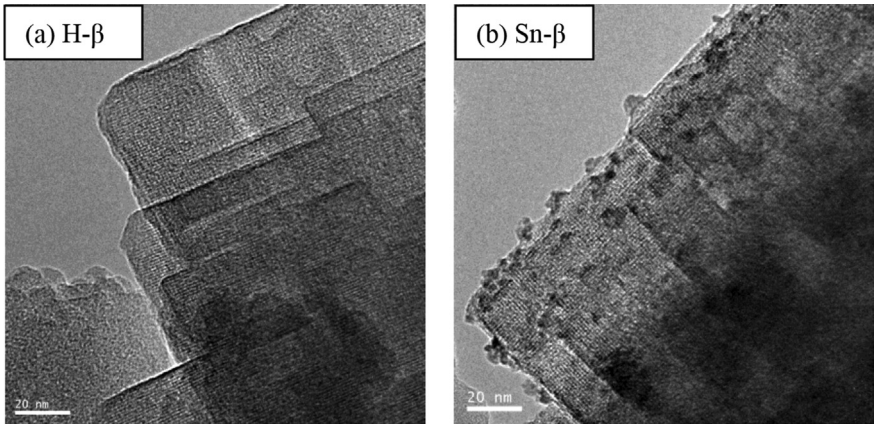


Fig. 1. TEM images of zeolites (a) H-β and (b) Sn-β.

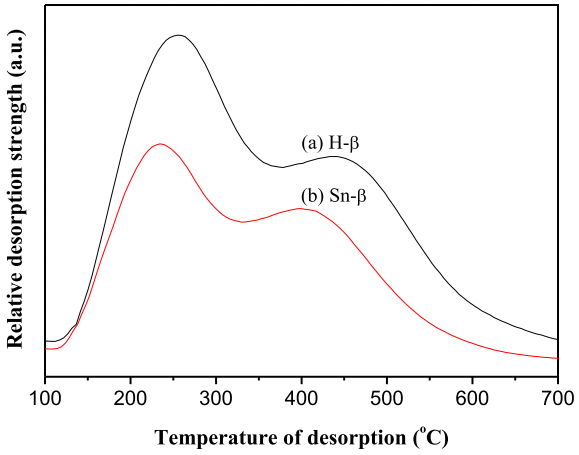


Fig. 2. NH_3-TPD profiles of zeolites (a) H-β and (b) Sn-β.

microscopy (TEM) analyses were performed on a Philips Tecnai G2 F30 microscope instrument at 200 kV using carbon coated copper grid. Temperature-programmed desorption for ammonia (NH_3-TPD) experiments were performed on a Hiden QIC-20 instrument. The acid capacity of H-β and Sn-β catalysts was determined by the potentiometric titration method on a Mettler Toledo T50 automatic titrator equipped with a Mettler Teledo DGi113-SC combined glass electrode. Flash column chromatography was performed on neutral SiO_2 (200–300 mesh) with ethyl acetate/petroleum as eluant. Trifluorotoluene was fresh distilled before use. Other solvents and reagents were directly used without further purification.

3.2. Preparation of the catalyst Sn-β

$SnCl_2 \cdot 2H_2O$ (0.34 g, 1.5 mmol) was dissolved in 150 mL of deionized water, followed by the addition of commercially available H-β zeolite (SiO_2/Al_2O_3=25, 1.5 g) over a period of 5 min. The slurry was stirred at room temperature for 24 h. The resulting solid was filtered, and washed with hot deionized water till free from Cl^- ions. Finally, the resulting solid was dried in an air oven at 80 °C and calcined at 550 °C for 4 h. The content of Sn in catalyst was 2.4 wt % based on ICP-MS analysis.

3.3. General procedure for the synthesis of 2,3-unsubstituted benzo[*b*]furans

A 25 mL round-bottomed flask was charged with 2-aryloxyacetaldehyde diethyl acetals (1 mmol), Sn-β (0.1 g), and trifluorotoluene (10 mL). The mixture was stirred under refluxing condition and monitored by GC. Upon completion, the mixture was cooled to room temperature, and the catalyst Sn-β was filtrate off. The filter cake was washed with trifluorotoluene (10 mL×3). The combined filtrate was concentrated under vacuum. The residue was purified by flash column chromatography on SiO_2 (petroleum ether/ethyl acetate) to afford the desired 2,3-unsubstituted benzo[*b*]furans.

3.3.1. Benzo[b]furan ***2a***. Yield 78%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.803–6.807 (m, 1H), 7.26–7.66 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.6, 111.4, 121.2, 122.7, 124.2, 127.4, 144.9, 154.9; GC–MS (EI): *m*/*z* 118 [M^+, 100%].

3.3.2. 5-Methoxy benzo[b]furan ***2b***. Yield 86%, white solid, mp 32.7 °C (lit.[5e] mp 32–33 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ=3.87 (s, 3H), 6.735–6.740 (m, 1H), 6.93–7.63 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=55.9, 103.6, 106.7, 111.8, 113.1, 128.0, 145.7, 150.0, 156.0; GC–MS (EI): *m*/*z* 148 [M^+, 100%].

3.3.3. 5-Methyl benzo[b]furan ***2c***. Yield 93%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=2.48 (s, 3H), 6.72–6.73 (m, 1H), 7.13–7.62 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=21.3, 106.3, 110.9, 121.0, 125.5, 127.5, 132.1, 145.0, 153.4; GC–MS (EI): *m*/*z* 132 [M^+, 100%].

3.3.4. 5-tert-Butyl benzo[b]furan ***2d***. Yield 92%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.44 (s, 9H), 6.780–6.785 (m, 1H), 7.40–7.66 (m, 4H), 7.63 (d, *J*=2.0 Hz, 1H), 7.65 (d, *J*=2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=31.9, 34.7, 106.7, 110.7, 117.3, 122.2, 127.1, 145.0, 145.8, 153.2; GC–MS (EI): *m*/*z* 174 [M^+, 89%], 159 (100).

3.3.5. 5-Phenyl benzo[b]furan ***2e***. Yield 95%, white solid, mp 66.1 °C (lit.[3b] mp 58–60 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.840–6.845 (m, 1H), 7.35–7.82 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.8, 111.5, 119.7, 124.0, 126.9, 127.5, 128.0, 128.8, 136.5, 141.7, 145.6, 154.6; GC–MS (EI) *m*/*z* 194 [M^+, 100%].

3.3.6. 5-(6-Ethoxynaphthalen-2-yl) benzo[b]furan ***2f***. Yield 88%; white solid, mp 133.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.52 (t, *J*=7.0 Hz, 3H), 4.20 (q, *J*=7.0 Hz, 3H), 6.859–6.863 (m, 1H), 7.18–8.01 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.8, 63.6, 106.63, 106.84, 111.6, 119.46, 119.77, 124.1, 125.8, 126.5, 127.2, 128.1, 129.3, 129.6, 133.7, 136.62, 136.85, 145.6, 154.6, 157.1; GC–MS (EI): *m*/*z* 288 [M, 100%]; EI-HRMS *m*/*z* calcd for $C_{20}H_{16}O_2$ $[M]^+$ 288.1150, found 288.1163.

3.3.7. 5-Fluoro benzo[b]furan ***2g***. Yield 67%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.760–6.766 (m, 1H), 7.02–7.68 (m, 4H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ=106.6 (d, J=25.2 Hz), 106.8 (d, J=3.54 Hz), 111.9 (d, J=4.0 Hz), 112.0 (d, J=11.8 Hz), 128.2 (d, J=10.6 Hz), 146.6, 151.2, 159.2 (d, J=236.6 Hz); GC–MS (EI) m/z 136 [M^+, 100%].

3.3.8. 5-Chloro benzo[b]furan ***2h***. Yield 80%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.738–6.742 (m, 1H), 7.26–7.66 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.3, 112.4, 120.8, 124.6, 128.4, 128.9, 146.4, 153.4; GC–MS (EI) m/z 152 [M^+, 100%], 154 (M+2, 34).

3.3.9. 5-Bromo benzo[b]furan ***2i***. Yield 77%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.73 (d, J=2.1 Hz, 1H), 7.38–7.75 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.1, 112.8, 115.8, 123.8, 127.2, 129.4, 146.1, 153.7; GC–MS (EI) m/z 196 [M^+, 100%], 198 (M+2, 97).

3.3.10. Ethyl benzo[b]furan-5-carboxylate ***2j***. Yield 71%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.43 (t, J=7.2 Hz, 3H), 4.42 (q, J=7.2 Hz, 2H), 6.851–6.856 (m, 1H), 7.53–8.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.4, 60.9, 107.1, 111.2, 123.7, 125.6, 126.0, 127.4, 146.2, 157.4, 166.8; GC–MS (EI) m/z 190[M^+, 38%], 145 (100).

3.3.11. 5,7-Dichloro benzo[b]furan ***2k***. Yield 30%, white solid, mp 57.2 °C (lit.[3d] mp 56.5–57 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.79 (s, 1H), 7.28–7.72 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=107.1, 117.6, 119.6, 124.6, 128.7, 129.8, 147.0, 149.5; GC–MS (EI) m/z 186 [M^+, 100%], 188 (M+2, 66), 190 (M+4, 11).

3.3.12. 7-Methoxy benzo[b]furan ***2l***. Yield 90%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=4.03 (s, 3H), 6.782–6.787 (m, 1H), 6.82–7.65 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=56.0, 106.4, 106.8, 113.5, 123.4, 129.1, 144.4, 144.9, 145.6; GC–MS (EI) m/z 148 [M^+, 100%].

3.3.13. 7-Chloro benzo[b]furan ***2m***. Yield 75%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.82–6.84 (m, 1H), 7.18–7.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=107.3, 117.0, 119.8, 123.7, 124.5, 129.1, 145.7, 150.8; GC–MS (EI) m/z 152 [M^+, 100%], 154 (M+2, 34).

3.3.14. 4,6,7-Trimethyl benzo[b]furan ***2n***. Yield 94%, white solid, mp 36.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=2.38 (s, 3H), 2.44 (s, 3H), 2.48 (s, 3H), 6.75 (d, J=2.2 Hz, 1H), 6.89 (s, 1H), 7.59 (d, J=2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=11.4, 18.2, 19.0, 105.3, 117.0, 124.5, 125.2, 127.3, 132.3, 143.7, 154.3; GC–MS (EI) m/z 160 [M^+, 98%], 145 (100); EI-HRMS m/z calcd for $C_{11}H_{12}O$ [M]$^+$ 160.0888, found: 160.0896.

3.3.15. Naphtho[1,2-b]furan ***2o***. Yield 95%, yellowish oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.95 (d, J=2.0 Hz, 1H), 7.53–8.39 (m, 7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=107.6, 119.74, 120.02, 121.5, 123.0, 123.4, 125.1, 126.3, 128.3, 131.5, 144.1, 150.6; GC–MS (EI) m/z 168[M^+, 100%].

3.3.16. 6-Methoxy benzo[b]furan ***2p***. Yield 87%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=3.88 (s, 3H), 6.71 (d, J=1.7 Hz, 1H), 6.91 (dd, J=2.2, 8.5 Hz, 1H), 7.07 (d, J=1.7 Hz, 1H), 7.47 (d, J=8.5 Hz, 1H), 7.55 (d, J=2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=55.71, 96.0, 106.3, 111.9, 120.7, 121.2, 144.0, 156.0, 158.0; GC–MS (EI) m/z 148 [M^+, 100%].

3.3.17. 6-Methyl benzofuran ***2q***. Yield 91%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=2.50 (s, 3H), 6.91 (dd, J=0.8, 2.2 Hz, 1H), 7.09 (d, J=8.0 Hz, 1H), 7.35 (s, 1H), 7.49 (d, J=8.0 Hz, 1H), 7.57 (d, J=2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=21.6, 106.3, 111.6, 120.6, 124.1, 124.9, 134.4, 144.3, 155.4; GC–MS (EI) m/z 132 [M^+, 100%].

3.3.18. 6-Phenyl benzo[b]furan ***2r***. Yield 93%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.838–6.841 (m, 1H), 7.39–7.42 (m, 1H), 7.49–7.52 (m, 2H), 7.55 (dd, J=1.4, 8.0 Hz, 1H), 7.69–7.71 (m, 4H), 7.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.5, 109.9, 121.2, 122.4, 126.6, 127.15, 127.40, 128.82, 138.0, 141.3, 145.46, 155.6; GC–MS (EI) m/z 194 [M^+, 100%].

3.3.19. 6-Chloro benzo[b]furan ***2s***. Yield 80%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.76 (d, J=2.0 Hz, 1H), 7.25 (dd, J=1.7, 8.3 Hz, 1H), 7.52 (d, J=8.3 Hz, 1H), 7.55 (s, 1H), 7.63 (d, J=2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.5, 112.0, 121.7, 123.6, 126.1, 130.2, 145.70, 155.1; GC–MS (EI) m/z 152 [M^+, 100%], 154 (M+2, 34).

3.3.20. 6-Bromo benzo[b]furan ***2t***. Yield 76%, colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.760–6.765 (m, 1H), 7.38 (dd, J=1.6, 8.3 Hz, 1H), 7.47 (d, J=8.3 Hz, 1H), 7.61 (d, J=2.0 Hz, 1H), 7.71 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=106.5, 114.9, 117.6, 122.1, 126.2, 126.5, 145.53, 155.3; GC–MS (EI) m/z 196 [M^+, 100%], 198 (M+2, 96).

3.4. Procedure for recovering of the catalyst Sn-β

After the reaction of 2-aryloxyacetaldehyde diethyl acetals was complete, the reaction mixture was cooled to room temperature. The catalyst Sn-β was filtered off and successively washed with trifluorotoluene (10 mL×3) and ethanol (5 mL×3), then dried at 100 °C for 2 h. The recovered catalyst was then reused directly in the next run.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.05.029.

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