

HETEROCYCLES, Vol. 84, No. 2, 2012, pp. 775 - 783. © 2012 The Japan Institute of Heterocyclic Chemistry  
Received, 27th June, 2011, Accepted, 15th August, 2011, Published online, 17th August, 2011  
DOI: 10.3987/COM-11-S(P)55

## PREPARATION OF FURAN RING FROM 2-(OXIRAN-2-YL)-1-ALKYLETHANONE CATALYZED BY NAFION<sup>®</sup> SAC-13

Rihoko Tombe and Seijiro Matsubara\*

Department of Material Chemistry, Kyoto University, Kyoutodaigaku-katsura,  
Nishikyo, Kyoto 615-8510, Japan

E-mail: matsubar@orgrxn.mbox.media.kyoto-u.ac.jp

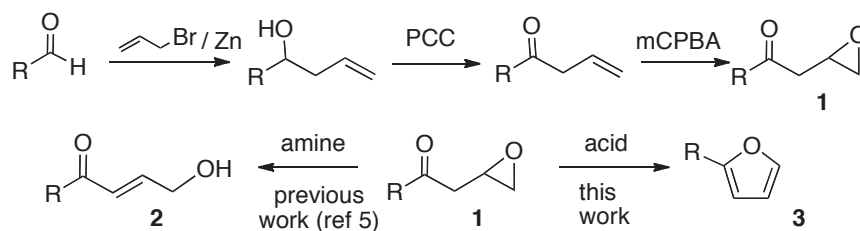
This paper is dedicated to Professor Dr. Albert Padwa as we celebrate his 75<sup>th</sup> birthday.

**Abstract** – Treatment of a 2-(oxiran-2-yl)-1-alkylethanone with Nafion<sup>®</sup> SAC-13 induced a cyclization reaction into furan ring. This method gave furans with a small amount of acid without aqueous work up.

### INTRODUCTION

Multisubstituted furans are of great importance because they can be found in many naturally occurring compounds and in many bioactive compounds.<sup>1</sup> There are many synthetic routes toward them. Among them, a cyclization reaction is one of the most reliable methods.<sup>2</sup> The method can be roughly classified into two groups. The one is acid-catalyzed condensation between oxygen-atom containing functional groups, such as alcohol, ketone or epoxide.<sup>3</sup> Another is transition-metal catalyzed cyclization reactions of alkynyl or allenyl derivatives.<sup>4</sup> While the transition-metal catalyzed reactions have been refined as a synthetic reaction, a reaction without metal catalyst is also important for a practical preparation of pharmaceuticals.

Recently, we had reported novel route to  $\gamma$ -hydroxy- $\alpha,\beta$ -unsaturated ketones **2** via a ring-opening reaction of  $\beta,\gamma$ -epoxyketones **1**, which had been prepared in three steps from aldehydes as shown in Scheme 1.<sup>5</sup> It was reported that treatment of  $\beta,\gamma$ -epoxyketones **1** with acid gave the corresponding furans;<sup>1d,6</sup> most cases required a stoichiometric amount of acid. The reaction condition using a large amount of acid is unfavorable, as the furans are acid sensitive. We tried to use a catalytic amount of polymer-supported acid, which may work effectively even in the presence of water formed in a dehydration process.



**Scheme 1.** Preparation of 2-(oxiran-2-yl)-1-alkylethanone **1** from an aldehyde and its transformation into alcohol **2** and furan **3**

## RESULTS AND DISCUSSION

Treatment of 2-(oxiran-2-yl)-1-phenylethanone (**1a**) with a catalytic amount of various acids was shown in Table 1. The results of the reactions of **1a** with a catalytic amount of trifluoromethylsulfonic acid gave **3a** in an excellent yield (entry 3). In addition, we also examined perfluorinated resin supported sulfonic acid, Nafion<sup>®</sup>.<sup>7</sup> Especially, a use of only a small amount of silica nanocomposite solid acid Nafion<sup>®</sup> SAC-13 (0.14–1.2 mol% as H<sup>+</sup> according to Equivalent Weight of Nafion<sup>®</sup> SAC-13<sup>8</sup>) gave the reasonable result (entry 12). As the work up of reaction using Nafion<sup>®</sup> can be done without a use of water, it is also favorable for isolation of a hydrophilic furan.

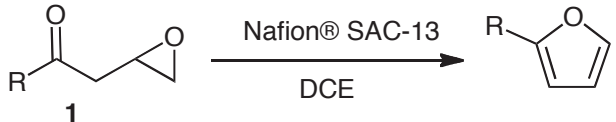
**Table 1.** Cyclization of 2-(oxiran-2-yl)-1-phenylethanone (**1a**) by means of various acid catalysts<sup>a</sup>

Entry	catalyst	solvent	h	<b>3</b> /%
1	TsOH (10 mol%)	DCE	21	76
2	CSA (10 mol%)	DCE	4	57
3	TfOH (10 mol%)	DCE	0.3	98
4	TfOH (5 mol%)	DCE	0.3	57
5	TfOH (0.5 mol%)	DCE	0.3	67
6	TfOH (10 mol%)	CH <sub>3</sub> CN	5	33
7	TfOH (10 mol%)	CH <sub>3</sub> NO <sub>2</sub>	0.7	20
8	TfOH (10 mol%)	CH <sub>3</sub> CN/H <sub>2</sub> O	10	40
9	ZnCl <sub>2</sub>	DCE	12	37
10	BF <sub>3</sub> •OEt <sub>2</sub>	DCE	0.3	46
11	TMSOTf	DCE	0.3	51
12	Nafion <sup>®</sup> SAC-13 <sup>b,c</sup> (0.25 mol%)	DCE	4	76
13	Nafion <sup>®</sup> SAC-13 <sup>c</sup> (0.25 mol%)	CH <sub>3</sub> CN/H <sub>2</sub> O	50	29
14	Nafion <sup>®</sup> NR-50 <sup>d</sup> (1.0 mol%)	DCE	5	33

<sup>a</sup>The substrate (0.5 mmol) and solvent (3.0 mL) were used. <sup>b</sup>According to Sigma-Aldrich data, Equivalent Weight of Nafion<sup>®</sup> SAC-13 is 0.12–1.0 meq/g. <sup>c</sup>6 mg of Nafion<sup>®</sup> SAC-13 was used. It was equal to an addition of 0.0007–0.006 mmol proton. <sup>d</sup>60 mg of Nafion<sup>®</sup> NR-50 was used. According to Sigma-Aldrich data, Equivalent Weight of Nafion<sup>®</sup> NR-50 is >0.8 meq/g.

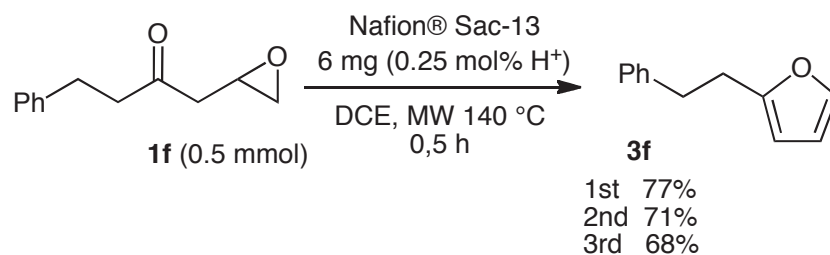
In Table 2, preparations of various 2-substituted furans using Nafion<sup>®</sup> SAC-13 as a catalyst were summarized. In these cases, irradiation of microwaves<sup>9</sup> was also examined, and gave the furans efficiently within a short reaction period (entries 1-4). The irradiation was performed without a mechanical stirring. As the mechanical stirring smashed the Nafion<sup>®</sup> SAC-13 in the reaction vessel, the procedure using microwaves made quantitative recovery of the catalyst possible. The reaction using the recovered catalyst was shown in Scheme 2.

**Table 2.** Preparation of 2-substituted furans<sup>a</sup>



entry	R	°C	Time / h	<b>3</b> / %
1	Ph ( <b>1a</b> )	85 °C	0.5	18 ( <b>3a</b> )
2	Ph ( <b>1a</b> )	85 °C	4	76 ( <b>3a</b> )
3	Ph ( <b>1a</b> )	MW, 140 °C	0.5	76 ( <b>3a</b> )
4	Ph ( <b>1a</b> )	MW, 140 °C	1	72 ( <b>3a</b> )
5	<i>p</i> -Tol ( <b>1b</b> )	85 °C	4	81 ( <b>3b</b> )
6	<i>p</i> -Tol ( <b>1b</b> )	MW, 140 °C	0.5	60 ( <b>3b</b> )
7	<i>p</i> -Tol ( <b>1b</b> )	MW, 140 °C	1	73 ( <b>3b</b> )
8	<i>o</i> -Tol ( <b>1c</b> )	85 °C	24	17 ( <b>3c</b> )
9	<i>o</i> -Tol ( <b>1c</b> )	MW, 140 °C	0.5	32 ( <b>3c</b> )
10	4-BrC <sub>6</sub> H <sub>4</sub> ( <b>1d</b> )	85 °C	5.0	76 ( <b>3d</b> )
11	4-BrC <sub>6</sub> H <sub>4</sub> ( <b>1d</b> )	MW, 140 °C	0.5	89 ( <b>3d</b> )
12	4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>1e</b> )	85 °C	24	15 ( <b>3e</b> )
13	4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>1e</b> )	MW, 140 °C	0.5	36 ( <b>3e</b> )
14	PhCH <sub>2</sub> CH <sub>2</sub> ( <b>1f</b> )	85 °C	0.8	97 ( <b>3f</b> )
15	PhCH <sub>2</sub> CH <sub>2</sub> ( <b>1f</b> )	MW, 140 °C	0.5	81 ( <b>3f</b> )
16	1-Naphtyl ( <b>1g</b> )	85 °C	4	76 ( <b>3g</b> )
17	1-Naphtyl ( <b>1g</b> )	MW, 140 °C	0.5	61( <b>3g</b> )

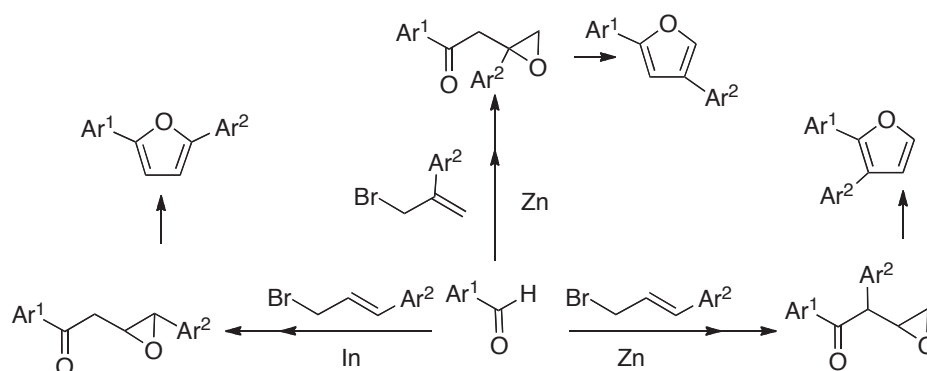
<sup>a</sup>The substrate (0.5 mmol), solvent (3.0 mL), and 6 mg of Nafion<sup>®</sup> SAC-13 were used. According to Sigma-Aldrich data, it was equal to an addition of 0.0007–0.006 mmol proton.



**Scheme 2.** Preparation of furan **3f** from **1f** with the recovered catalyst

Based on this method, we planned to prepare 2,3-, 2,4-, and 2,5-diarylfurans as shown in Scheme 3. As the regioselective allylation was already reported, the  $\beta,\gamma$ -epoxyketone derivatives, which are their

precursors, can be easily accessed.<sup>10</sup>



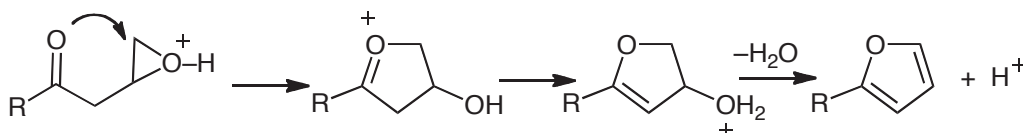
**Scheme 3.** Synthetic routes for 2,3-, 2,4-, 2,5-diarylfurans from an aromatic aldehyde

Treatment of these epoxyketones **1** with a catalytic amount Nafion<sup>®</sup> SAC-13 gave disubstituted furans in reasonable yields as shown in Table 3. Results with/without an irradiation of microwaves were shown. A simple heating for refluxing of the solvent (84 °C) was also effective for the cyclization, but their yields were improved by the procedure using microwaves.

**Table 3.** Preparation of disubstituted furan<sup>a</sup>

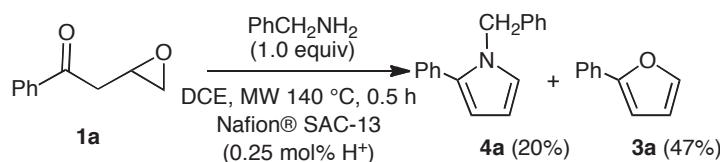
Entry	R <sup>1</sup> , R <sup>2</sup> , R <sup>3</sup> , R <sup>4</sup>				Condition	<b>3</b>	Recovery of <b>1</b>
	1						
1	Ph,	Ph,	H,	H ( <b>1h</b> )	85 °C, 6 h <sup>b</sup>	46% ( <b>3h</b> )	41%
2	Ph,	Ph,	H,	H ( <b>1h</b> )	140 °C, MW, 0.5 h <sup>b</sup>	33 ( <b>3h</b> )	64
3	Ph,	Ph,	H,	H ( <b>1h</b> )	140 °C, MW, 0.5 h <sup>c</sup>	52 ( <b>3h</b> )	43
4	Ph,	Ph,	H,	H ( <b>1h</b> )	140 °C, MW, 0.5 h <sup>d</sup>	74 ( <b>3h</b> )	16
5	Ph,	H,	Ph,	H ( <b>1i</b> )	85 °C, 4 h <sup>b</sup>	25 ( <b>3i</b> )	27
6	Ph,	H,	Ph,	H ( <b>1i</b> )	140 °C, MW, 0.5 h <sup>b</sup>	41 ( <b>3i</b> )	15
7	Ph,	H,	Ph,	H ( <b>1i</b> )	140 °C, MW, 0.5 h <sup>c</sup>	61 ( <b>3i</b> )	8
8	Ph,	H,	H,	Ph ( <b>1j</b> )	85 °C, 3 h <sup>b</sup>	88 ( <b>3j</b> )	0
9	Ph,	H,	H,	Ph ( <b>1j</b> )	140 °C, MW, 0.5 h <sup>b</sup>	94 ( <b>3j</b> )	0
10	Ph,	Me,	H,	H ( <b>1k</b> )	85 °C, 4 h <sup>b</sup>	99 ( <b>3k</b> )	0
11	Ph,	Me,	H,	H ( <b>1k</b> )	140 °C, MW, 0.5 h <sup>c</sup>	95 ( <b>3k</b> )	0
12	<i>o</i> -TMSC <sub>6</sub> H <sub>4</sub> ,	Me,	H,	H ( <b>1l</b> )	85 °C, 4 h <sup>b</sup>	70 ( <b>3l</b> )	0
13	<i>o</i> -TMSC <sub>6</sub> H <sub>4</sub> ,	Me,	H,	H ( <b>1l</b> )	140 °C, MW, 0.5 h <sup>b</sup>	52 ( <b>3l</b> )	0
14	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> ,	Ph,	H,	H ( <b>1m</b> )	85 °C, 4 h <sup>b</sup>	38 ( <b>3m</b> )	60
15	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> ,	Ph,	H,	H ( <b>1m</b> )	140 °C, MW, 0.5 h <sup>b</sup>	35 ( <b>3m</b> )	65
16	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> ,	Ph,	H,	H ( <b>1m</b> )	140 °C, MW, 0.5 h <sup>d</sup>	85 ( <b>3m</b> )	15

<sup>a</sup>The substrate (0.5 mmol), solvent (3.0 mL), and a catalytic amount of Nafion<sup>®</sup> SAC-13 were used. <sup>b</sup>6 mg of Nafion<sup>®</sup> SAC-13 were used. <sup>c</sup>12 mg of Nafion<sup>®</sup> SAC-13 were used. <sup>d</sup>18 mg of Nafion<sup>®</sup> SAC-13 were used.



**Scheme 4.** Plausible reaction pathway for the formation of furans

The reaction pathway was supposed as shown in Scheme 4. In this pathway, a generation of an equimolar amount of water is accompanied simultaneously, and may cause the low performance of metal Lewis acids (entries 9-11 in Table 1). According to the plausible pathway, an addition of amine may lead to a formation of pyrrole *via* an imine. As shown in Scheme 5, an addition of benzylamine to the reaction gave the corresponding pyrrole in 20% yield. Although we tried an optimization for the formation of pyrrole, the improved yield has not been realized.



**Scheme 5.** Reaction with benzylamine

Thus, we showed a preparation of a furan from a  $\beta,\gamma$ -epoxyketone using Nafion<sup>®</sup> SAC-13 as a catalyst under an irradiation of microwaves. As the method offered us convenient procedure without an aqueous work up, it may be useful method for the systematic preparation of furan derivatives.

## EXPERIMENTAL

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (<sup>1</sup>H, 500 MHz; <sup>13</sup>C, 125.7 MHz) spectrometer using tetramethylsilane for <sup>1</sup>H NMR as an internal standard ( $\delta = 0$  ppm), CDCl<sub>3</sub> for <sup>13</sup>C NMR as an internal standard ( $\delta = 77.0$  ppm). <sup>1</sup>H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet), coupling constants (Hz), and integration. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100  $\mu\text{m}$ ). Unless otherwise noted, commercially available reagents were used without purification. Nafion<sup>®</sup> SAC-13 was purchased from Sigma-Aldrich. In our reaction, microwaves were irradiated using Biotage Initiator in a 10-mL vial. Power varied automatically between 0–100W to maintain the temperature.

### Preparation of Furan 3a by Nafion<sup>®</sup> SAC-13 Catalyst under an Irradiation of Microwaves.

In a sealed glass vial (10 mL), 2-(oxiran-2-yl)-1-phenylethanone (**1a**, 81 mg, 0.5 mmol), 6 mg of Nafion<sup>®</sup> SAC-13, and dichloroethane (3 mL) were placed. According to Sigma-Aldrich data, Equivalent Weight of Nafion<sup>®</sup> SAC-13 is 0.12–1.0 meq/g. A use of 6 mg of Nafion<sup>®</sup> SAC-13 was equal to an addition of

0.0007–0.006 mmol proton. Microwaves were irradiated using Biotage Initiator. Power varied automatically between 0–100W to maintain 140 °C. During the irradiation, the mixture was not stirred by an electronic stirrer which is equipped in the Biotage machine. After irradiated for 0.5 h, the mixture was diluted with 10 mL of ethyl acetate and filtered through a short silica gel column. The recovered Nafion<sup>®</sup> SAC-13 was reused after it was washed with acetone and dried in vacuo. The filtrate was concentrated in vacuo, and purified by a silica-gel column chromatography. The corresponding furan **3a** was obtained in 76% yield.

**2-Phenylfuran (3a)<sup>11</sup>: CAS RN [17113-33-6]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.48 (1H, dd, *J*=2.0, 3.5 Hz), 6.66 (1H, dd, *J*=1.0, 3.5 Hz), 7.25–7.29 (1H, m), 7.37–7.42 (2H, m), 7.48 (1H, dd, *J*=1.0, 2.0 Hz), 7.69 (m, 2H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 104.9, 111.6, 123.8, 127.3, 128.6, 130.9, 142.0, 154.0. The product was identified with the authentic sample.

**2-*p*-Tolyl-furan (3b)<sup>11</sup>: CAS RN [17113-32-5]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.36 (3H, s), 6.45 (1H, dd, *J*=2.0, 3.5 Hz), 6.59 (1H, dd, *J*=0.5, 3.5 Hz), 7.19 (2H, m), 7.44 (1H, dd, *J*=0.5, 2.0 Hz), 7.57 (2H, td, *J*=2.0, 8.5 Hz); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 21.2, 104.2, 111.5, 123.8, 128.3, 129.3, 137.1, 141.6, 154.3. The product was identified with the authentic sample.

**2-*o*-Tolylfuran (3c)<sup>11</sup>: CAS RN [38527-54-7]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.51 (3H, s), 6.51 (1H, dd, *J*=1.5, 3.5 Hz), 6.55 (1H, dd, *J*=0.5, 3.5 Hz), 7.21–7.28 (3H, m) 7.51 (1H, dd, *J*=0.5, 1.5 Hz), 7.70 (1H, d, *J*=8.0Hz); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 21.8, 108.4, 111.3, 125.9, 127.1, 127.4, 130.3, 131.1, 134.6, 141.6, 153.6. The product was identified with the authentic sample.

**2-(4-Bromophenyl)furan (3d)<sup>11</sup>: CAS RN [14297-34-8]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.47–6.48 (1H, m), 6.65 (1H, d, *J*=3.5 Hz), 7.47–7.55 (5H, m); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 105.5, 111.8, 121.1, 125.3, 129.8, 131.8, 142.4, 153.0. The product was identified with the authentic sample.

**2-(4-Methoxyphenyl)furan (3e)<sup>11</sup>: CAS RN [17113-31-4]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.84 (3H, s), 6.44 (1H, dd, *J*=1.5, 3.5 Hz), 6.51 (1H, dd, *J*=0.5, 3.5 Hz), 6.92 (2H, dt, *J*=2.0, 8.5 Hz), 7.42 (1H, dd, *J*=0.5, 1.5 Hz), 7.60 (2H, dt, *J*=2.5, 8.5 Hz); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 55.3, 103.4, 111.5, 114.1, 124.1, 125.2, 141.4, 154.1, 159.0. The product was identified with the authentic sample.

**2-Phenethylfuran (3f): CAS RN [36707-30-9]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.96 (4H, m), 5.98 (1H, td, *J*=1.0, 3.0 Hz), 6.29 (1H, dd, *J*=1.5, 3.0 Hz),

7.18–7.23 (3H, m), 7.28–7.32 (2H, m), 7.34(1H, dd,  $J=0.5, 2.0$  Hz);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  29.9, 34.4, 105.1, 110.1, 126.0, 128.3, 128.4, 140.9, 141.2, 155.4; HRMS(EI) Calcd. for  $\text{C}_{12}\text{H}_{12}\text{O}$  172.0888, found 172.0891.

**2-(1-Naphthalenyl)furan (3g)<sup>12</sup>: CAS RN [51792-32-6]**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.60 (1H, dd,  $J=2.0, 3.5$  Hz), 6.74 (1H, dd,  $J=1.0, 3.5$  Hz), 7.51–7.57 (3H, m), 7.64 (1H, dd,  $J=1.0, 1.5$  Hz), 7.75 (1H, dd,  $J=1.0, 7.0$  Hz), 7.85 (1H, d,  $J=8.0$  Hz), 7.90 (1H, dd,  $J=2.0, 7.5$  Hz), 8.41–8.43 (1H, m);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  109.2, 111.3, 125.3, 125.5, 125.9, 126.1, 126.5, 128.5, 128.5, 128.6, 130.4, 133.9, 142.4, 153.5. The product was identified with the authentic sample.

**2,3-Diphenylfuran (3h)<sup>13</sup>: CAS RN [954-55-2]**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.56 (1H, d,  $J=1.5$  Hz), 7.22–7.33 (4H, m), 7.35–7.38 (2H, m), 7.41–7.43 (2H, m), 7.51 (1H, d,  $J=1.5$  Hz), 7.52–7.55 (2H, m);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  114.0, 122.3, 126.3, 127.1, 127.5, 128.4, 128.6, 128.7, 131.2, 134.4, 141.5, 148.6. The product was identified with the authentic sample.

**2,4-Diphenylfuran (3i)<sup>14</sup>: CAS RN [5369-55-1]**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97 (1H, d,  $J=2.0$  Hz), 7.29 (2H, tdd,  $J=2.0, 4.0, 7.5$  Hz), 7.39–7.43 (4H, m), 7.53–7.55 (2H, m), 7.73 (2H, dt,  $J=1.5, 8.5$  Hz), 7.76 (1H, d,  $J=1.0$  Hz);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  104.0, 123.9, 125.8, 127.1, 127.6, 128.4, 128.7, 128.8, 130.7, 132.4, 137.9, 154.9. The product was identified with the authentic sample.

**2,5-Diphenylfuran (3j)<sup>13</sup>: CAS RN [955-83-9]**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.75 (2H, s), 7.28 (2H, tt,  $J=1.0, 7.5$  Hz), 7.41 (4H, t,  $J=7.5$  Hz), 7.74–7.76 (4H, m);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  107.2, 123.7, 127.3, 128.7, 130.8, 153.4. The product was identified with the authentic sample.

**3-Methyl-2-phenylfuran (3k)<sup>15</sup>: CAS RN [30078-92-3]**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (3H, s), 6.33 (1H, t,  $J=1.5$  Hz), 7.25–7.28 (1H, m), 7.38–7.43 (3H, m), 7.62–7.65 (2H, m);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  11.6, 114.8, 116.0, 125.1, 126.4, 128.2, 131.6, 140.4, 148.4. The product was identified with the authentic sample.

**3-Methyl-2-(2-Trimethylsilylphenyl)furan (3l):**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.10 (9H, d,  $J=0.5$  Hz), 2.08 (3H, s), 6.36 (1H, s), 7.33–7.41 (4H, m), 7.66 (1H, d,  $J=7.5$  Hz);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.54, 10.6, 114.2, 116.0, 127.1, 128.5, 129.6, 135.2, 136.6, 140.0, 140.5, 151.3; HRMS(EI) Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OSi}$  230.1127, found 230.1121.

**2-(4-Bromophenyl)-3-phenylfuran (3m):**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.55 (1H, d,  $J=2.0$  Hz), 7.31–7.42 (9H, m), 7.50 (1H, d,  $J=1.5$  Hz);  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ )  $\delta$  114.2, 121.4, 122.9, 127.4, 127.7, 128.6, 128.7, 130.1, 131.6, 134.0, 141.8,

147.5; HRMS(EI) Calcd. for C<sub>16</sub>H<sub>11</sub>BrO 297.9993, found 297.9997. The product was identified with the authentic sample.

**1-Benzyl-2-phenyl-1H-pyrrole (4a)<sup>16</sup>: CAS RN [78979-71-2]**

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.17 (2H, s), 6.30 (2H, d, *J*=2.5Hz), 6.77 (1H, t, *J*=2.5Hz), 7.03–7.04 (2H, m), 7.25–7.36 (8H, m); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>) δ 50.6, 108.5, 108.9, 122.9, 126.5, 126.9, 127.3, 128.3, 128.6, 128.9, 133.3, 135.0, 138.8.

## ACKNOWLEDGEMENTS

This work was supported financially by the Japanese Ministry of Education, Culture, Sports, Science and Technology.

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