

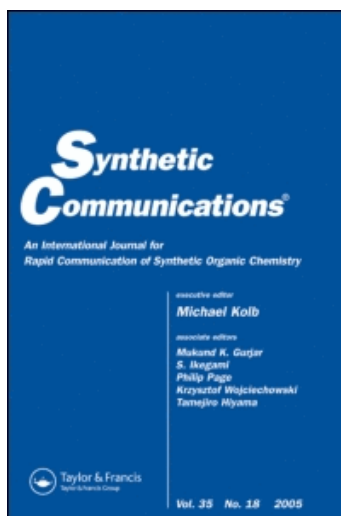
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### Efficient Procedure for the Preparation of 2-Bromofuran and Its Application in the Synthesis of 2-Arylfurans

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## EFFICIENT PROCEDURE FOR THE PREPARATION OF 2-BROMOFURAN AND ITS APPLICATION IN THE SYNTHESIS OF 2-ARYLFURANS

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*A simple, straightforward, and scalable procedure for the preparation of 2-bromofuran using N-bromosuccinimide (NBS) in dimethylformamide (DMF) is reported. The described preparation is conducted on a 20 to 50 g scale and does not require extractive workup procedures or chromatographic purifications. To illustrate the synthetic applications of 2-bromofuran, palladium-catalyzed Suzuki coupling reactions of the prepared 2-bromofuran with various aryl boronic acids were investigated, and moderate to good yields of 2-arylfurans were obtained.*

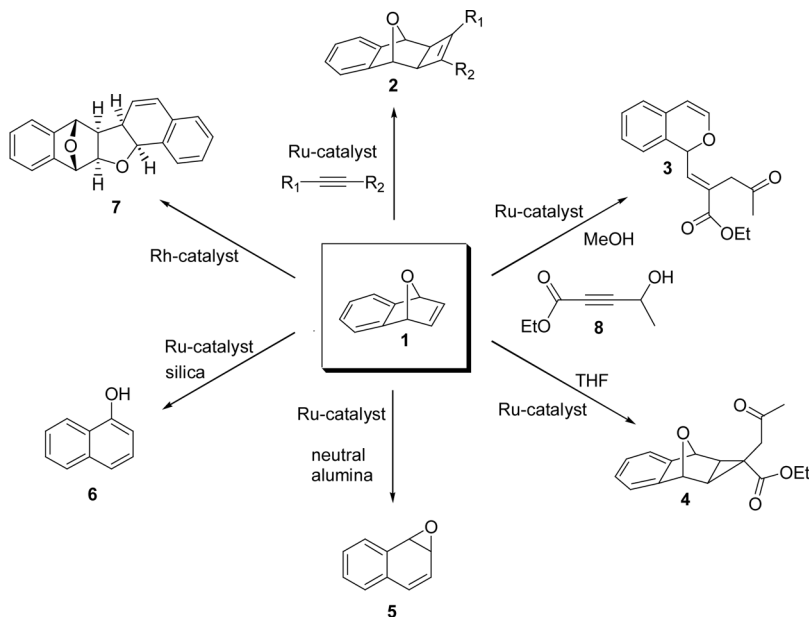
**Keywords:** Bromination; 2-bromofuran; N-bromosuccinimide; steam distillation; Suzuki coupling

### INTRODUCTION

We have recently investigated different modes of transition metal-catalyzed reactions of oxabenzonorbornadiene **1** and found that, depending on the reaction conditions, several products (**2–7**) could be obtained (Scheme 1). For example, when 7-oxabenzonorbornadiene **1** is treated with an alkyne in the presence of the ruthenium catalyst, Cp<sup>\*</sup>Ru(COD)Cl, a [2 + 2] cycloaddition is observed and cyclobutene cycloadduct **2** is formed.<sup>[1]</sup> When oxabenzonorbornadiene **1** is treated with the secondary propargylic alcohol **8** in the presence of the neutral Ru catalyst, Cp<sup>\*</sup>Ru(COD)Cl, in MeOH or using a cationic Ru catalyst (e.g., [CpRu(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub>), isochromene **3** is formed.<sup>[2]</sup> On the other hand, if the same reaction between oxabenzonorbornadiene **1** and the secondary propargylic alcohol **8** is carried out with Cp<sup>\*</sup>Ru(COD)Cl in tetrahydrofuran (THF), cyclopropane **4** is produced.<sup>[3]</sup> More recently, we have observed that in the absence of an alkyne, Cp<sup>\*</sup>Ru(COD)Cl catalyzes the isomerization of oxabenzonorbornadiene **1** to the corresponding naphthalene oxide **5** or naphthol **6**.<sup>[4]</sup> We have also reported that asymmetric cationic rhodium(I)-catalyzed cyclodimerization of oxabenzonorbornadiene **1** to produce dimers **7** in excellent enantioselectivity (up to 99% ee).<sup>[5]</sup>

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**Scheme 1.** Transition metal-catalyzed reactions of oxabenzonorbornadiene **1**.

Because oxabenzonorbornadiene **1** is symmetrical, no regiochemical information could be gain from these studies. To explore the regioselectivity of these reactions, we plan to synthesize C1-substituted oxabenzonorbornadiene **11** by the Diels–Alder reaction of benzyne **9** and 2-substituted furans **10** (Scheme 2). Although some 2-substituted furans are commercially available (such as  $R = \text{Me}$ ,  $^t\text{Bu}$ ,  $\text{COOMe}$  etc.), 2-substituted furans with  $R = \text{Br}$  and aryl groups are not commercially available. During the course of our efforts to prepare a series of 2-aryl furans **10** ( $R = \text{Ar}$ ), we required large quantities of 2-bromofuran **12**. Several methods have been described in literature for bromination of furan to 2-bromofuran.<sup>[6]</sup> Bromination of furan using hexabromocyclopentadiene,<sup>[6b]</sup> dioxane dibromide,<sup>[6d]</sup> and microwave-assisted bromination using 2,4,4,6-tetrabromo-2,5-cyclohexadienone<sup>[6g]</sup> are unsuitable for the preparation of 2-bromofuran **12** in large quantities. The two methods developed by Brandsma are much more effective and provided 2-bromofuran **12** in 70–80% yield: (i) the metallation of furan with  $\text{EtLi}$ , followed by the reaction with  $\text{Br}_2$ , in ether at  $-80\text{ }^\circ\text{C}$ <sup>[6d]</sup> and (ii) the bromination of furan with  $\text{Br}_2$  in dimethylformamide (DMF).<sup>[6e]</sup> However, we and others<sup>[6g]</sup> found that these methods are difficult to work with and the isolation of the product is troublesome. In this article, we describe



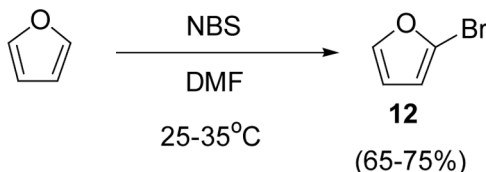
**Scheme 2.** Synthesis of C1-substituted oxabenzonorbornadiene **11**.

a new and practical procedure for the bromination of furan, which offers simplified workup and isolation techniques for large-scale preparation (20–50 g) of 2-bromofuran using safe, inexpensive, and readily available reagents. The described preparation does not require extractive workup procedures or chromatographic purifications.

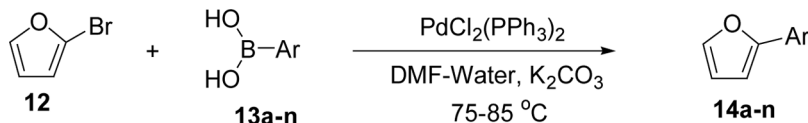
## RESULTS AND DISCUSSION

We initially followed Keegstra et al.'s procedure for the synthesis of 2-bromofuran **12** involving treatment of furan with  $\text{Br}_2$  in DMF.<sup>[6e]</sup> We encountered difficulties similar to those mentioned by Gupta et al. in isolation of bromofuran.<sup>[6g]</sup> We modified the isolation step by effecting direct steam distillation of the reaction mixture to isolate bromofuran in moderate yields (50–55%). The residual reaction mass contained a green, dense, tarry solid. This is not surprising in view of the unusual sensitivity of furan toward mineral acids. It was also found that the addition of  $\text{Br}_2$  to DMF is highly exothermic, and it is very difficult to control the reaction temperature in the large-scale reaction (20–30 g). Furthermore, elemental bromine itself is not easy to handle because of its highly corrosive nature. Therefore, we modified the procedure of bromination using readily available and easy to handle N-bromosuccinimide (NBS) (Scheme 3). Interestingly, we found that addition of NBS to DMF is not exothermic. Bromination of furan was done by controlled addition of NBS–DMF solution at room temperature followed by stirring the reaction mixture at room temperature overnight. Direct steam distillation of the reaction mixture resulted in isolation of 2-bromofuran **12** in 65–75% yields.

To illustrate the synthetic applications of 2-bromofuran **12**, palladium-catalyzed Suzuki coupling reactions with various aryl boronic acids were carried out, and the results are shown in Table 1. In the presence of 2 mol% of  $\text{PdCl}_2(\text{PPh}_3)_2$  and 2.5 equivalents of  $\text{K}_2\text{CO}_3$  in DMF/ $\text{H}_2\text{O}$  (3:1), the Suzuki coupling reaction between 2-bromofuran **12** and phenylboronic acid **13a** ( $\text{Ar} = \text{Ph}$ ) occurred smoothly at 80 °C, providing 2-phenylfuran **14a** in 62% isolated yield after column chromatography (entry 1). Suzuki coupling reactions of 2-bromofuran **12** worked well with boronic acids containing both electron-donating groups attached to the Ar ring ( $\text{Ar} = \text{CH}_3$ , entries 2–4;  $\text{Ar} = \text{OCH}_3$ , entries 5–7;  $\text{Ar} = \text{Et}$ , entry 11) as well as with electron-withdrawing groups attached to the Ar ring ( $\text{Ar} = \text{Cl}$ , entries 8–10;  $\text{Ar} = \text{Ac}$ , entry 12). The position of the substituent on the Ar ring (*ortho*, *meta*, or *para*) showed little effect on the yields of the Suzuki coupling reactions (compare entries 2 to 4, entries 5–7, and entries 8–10). In general, all the palladium-catalyzed Suzuki coupling reactions of 2-bromofuran **12** occurred smoothly, giving moderate to good



**Scheme 3.** Synthesis of 2-bromofuran using NBS in DMF.

**Table 1.** Synthesis of 2-aryl boronic acids by palladium-catalyzed Suzuki cross-coupling reactions between 2-bromofuran **12** and aryl boronic acids

| Entry | Boronic acid <b>13</b> | Ar   | Furan <b>14</b> | Yield (%) <sup>a</sup> |
|-------|------------------------|--|-----------------|------------------------|
| 1     | <b>13a</b>             | C <sub>6</sub> H <sub>5</sub>                        | <b>14a</b>      | 62                     |
| 2     | <b>13b</b>             | 4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>     | <b>14b</b>      | 56                     |
| 3     | <b>13c</b>             | 3-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>     | <b>14c</b>      | 80                     |
| 4     | <b>13d</b>             | 2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>     | <b>14d</b>      | 78                     |
| 5     | <b>13e</b>             | 4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>    | <b>14e</b>      | 57                     |
| 6     | <b>13f</b>             | 3-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>    | <b>14f</b>      | 72                     |
| 7     | <b>13g</b>             | 2-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>    | <b>14g</b>      | 63                     |
| 8     | <b>13h</b>             | 4-Cl-C <sub>6</sub> H <sub>4</sub>                   | <b>14h</b>      | 65                     |
| 9     | <b>13i</b>             | 3-Cl-C <sub>6</sub> H <sub>4</sub>                   | <b>14i</b>      | 67                     |
| 10    | <b>13j</b>             | 2-Cl-C <sub>6</sub> H <sub>4</sub>                   | <b>14j</b>      | 70                     |
| 11    | <b>13k</b>             | 4-Et-C <sub>6</sub> H <sub>4</sub>                   | <b>14k</b>      | 56                     |
| 12    | <b>13l</b>             | 4-C(O)CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> | <b>14l</b>      | 59                     |
| 13    | <b>13m</b>             | 4-Biphenyl   | <b>14m</b>      | 77                     |
| 14    | <b>13n</b>             | 1-Naphthyl   | <b>14n</b>      | 85                     |

<sup>a</sup>Isolated yield after column chromatography.

yields of the 2-arylfurans. These 2-arylfurans synthesized (**14a-n**) are useful precursors for the synthesis of C1-substituted oxabenzonorbornadiene **11** (Scheme 2), which will be useful in the investigation of various regiochemical issues in various metal-catalyzed reactions (Scheme 1).

## CONCLUSION

In conclusion, we have investigated a new, simple, straightforward, and scalable procedure for the preparation of 2-bromofuran using NBS in DMF. The described preparation was conducted on a 20 to 50 g scale and does not require extractive workup procedures or chromatographic purifications. We have also illustrated the synthetic applications of the prepared 2-bromofuran by the palladium-catalyzed Suzuki coupling reactions with various aryl boronic acids, and moderate to good yields of 2-arylfurans were obtained. The use of 2-bromofuran and 2-arylfurans for the synthesis of C1-substituted oxabenzonorbornadiene **11** are in progress in our laboratories.

## EXPERIMENTAL

### General Considerations

All reactions are done in septum-sealed, flame-dried flasks under a nitrogen atmosphere. All commercial reagents were used as received from their respective suppliers. Reagent-grade furan and NBS purchased from Aldrich were used without

additional purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at 300/400 and 75/100 MHz, respectively. Chemical shifts are reported in parts per million ( $\delta$ ) using internal solvent signals as references, and coupling constants are reported in hertz (Hz).

### Preparation of Bromofuran

A solution of NBS (20 g, 0.112 mol) in DMF (60 mL) was added via addition funnel to a solution of furan (15.3 g, 0.225 mol) in DMF (40 mL) in a 500-mL, three-necked, round-bottomed flask over a period of 40–60 min, keeping internal temperature between 25 and 35 °C under constant stirring. Addition of NBS solution to reaction mixture was found to be exothermic. During addition, the reaction mixture went from brown solution to dark green. After the addition was complete, the reaction mixture was stirred at ambient temperature for an additional 2–4 h. The resulting clear brown solution was heated gradually to 100–110 °C to distill out some of the unreacted furan. After maintaining 100–110 °C temperature for 0.5–1 h, the reaction mixture was exposed to a constant jet of steam generated by heating distilled water to 100–120 °C in a separate two-necked, round-bottomed flask. Distillate consisting of water and bromofuran was collected in a receiver. The initial few drops contained mostly residual unreacted furan and were therefore collected separately. Distillation continued until no organic product was present in the distillate. The distillate was transferred to a separatory funnel along with water (20–30 mL). The suspension was shaken well to force traces of DMF to the aqueous layer. After layer separation, the bromofuran **12** settled down as a colorless lower layer, which was collected and stored in a dry bottle containing anhydrous  $\text{K}_2\text{CO}_3$  (11.5 g, 70%).

### 2-Bromofuran, **12**

Colorless liquid, yield = 70% (11.5 g); IR ( $\text{CH}_2\text{Cl}_2$ ): 3140, 2930, 1679, 1472, 1386, 1161,  $1052\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.28 (dd,  $J = 3.3, 2.3$  Hz, 1H), 6.35 (dd,  $J = 4.9, 3.6$  Hz, 1H), 7.40 (dd,  $J = 2.1, 1.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 111.5, 114.0, 124.0, 141.3; HRMS (EI) calcd. for  $\text{C}_4\text{H}_4\text{BrO}$  ( $\text{M}^+$ ): 146.9446; found: 146.9452.

### General Procedure for Suzuki Coupling with Bromofuran

Under a nitrogen atmosphere, arylboronic acid (1.0 mmol) was suspended in a DMF–water (3 mL/1 mL) mixture, followed by the addition of bromofuran (1.7 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.02 mmol), and  $\text{K}_2\text{CO}_3$  (2.5 equiv.). The mixture was heated to 75–85 °C for 16–20 h. After reaction completion, the mixture was cooled to room temperature, followed by quenching by addition of 15–20 mL water. The obtained suspension was extracted with ether (10 mL  $\times$  3), and then the combined organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated using rotary evaporation. The crude product was purified by column chromatography (EtOAc–hexanes mixtures) to give the product.

## Data

**2-Phenylfuran, 14a.** Colorless oil. Yield = 62% (90.0 mg);  $R_f$  = 0.38 (hexanes); IR ( $\text{CH}_2\text{Cl}_2$ ): 3054, 1608, 1507, 1477, 1265, 1023  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.45–6.57 (m, 1H), 6.66 (d,  $J$  = 3.4 Hz, 1H), 7.26 (t,  $J$  = 7.2 Hz, 1H), 7.39 (t,  $J$  = 7.8 Hz, 2H), 7.47–7.48 (m, 1H), 7.69 (d,  $J$  = 7.8 Hz, 2H);  $^{13}\text{C}$  (APT) NMR ( $\text{CDCl}_3$ , 75 MHz): 104.9 (CH), 111.6 (CH), 123.8 (CH), 127.3 (CH), 128.6 (CH), 130.9 (qC), 142.0 (CH), 154.0 (qC). HRMS (EI) calcd. for  $\text{C}_{10}\text{H}_8\text{O}$  ( $\text{M}^+$ ): 144.0575; found: 144.0579.

**2-(4-Methylphenyl)furan, 14b.** Colorless oil. Yield = 56% (83.3 mg);  $R_f$  = 0.65 (EtOAc/hexanes = 30:70); IR ( $\text{CH}_2\text{Cl}_2$ ): 3290, 1620, 1509, 1455, 1380, 1260, 1100, 1052  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.24 (s, 3H), 6.33 (m, 1H), 6.47 (d,  $J$  = 3.2 Hz, 1H), 7.07 (d,  $J$  = 8.0 Hz, 2H), 7.32 (br s, 1H), 7.46 (d,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  (APT) NMR ( $\text{CDCl}_3$ , 100 MHz): 21.0 ( $\text{CH}_3$ ), 104.0 (CH), 111.4 (CH), 123.6 (CH), 128.1 (qC), 129.2 (CH), 136.9 (qC), 141.5 (CH), 154.0 (qC). HRMS (EI) calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}$  ( $\text{M}^+$ ): 158.0732; found: 158.0735.

**2-(3-Methylphenyl)furan, 14c.** Colorless oil. Yield = 80% (119.6 mg);  $R_f$  = 0.63 (EtOAc/hexanes = 30:70); IR ( $\text{CH}_2\text{Cl}_2$ ): 3288, 1622, 1521, 1447, 1382, 1260, 1105, 1059  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.54 (s, 3H), 6.61 (m, 1H), 6.79 (m, 1H), 7.23 (d,  $J$  = 7.5 Hz, 1H), 7.43 (td,  $J$  = 7.7, 1.5 Hz, 1H), 7.60 (br s, 1H), 7.54–7.76 (m, 2H);  $^{13}\text{C}$  (APT) NMR ( $\text{CDCl}_3$ , 100 MHz): 21.4 ( $\text{CH}_3$ ), 104.7 (CH), 111.5 (CH), 120.9 (CH), 124.3 (CH), 128.0 (CH), 128.5 (CH), 130.7 (qC), 138.1 (qC), 141.8 (CH), 154.0 (qC). HRMS (EI) calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}$  ( $\text{M}^+$ ): 158.0732; found: 158.0737.

**2-(2-Methylphenyl)furan, 14d.** Colorless oil. Yield = 78% (114.4 mg);  $R_f$  = 0.67 (EtOAc/hexanes = 30:70); IR ( $\text{CH}_2\text{Cl}_2$ ): 3034, 1617, 1510, 1479, 1266, 1043  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.37 (s, 3H), 6.36 (dd,  $J$  = 3.4, 1.8 Hz, 1H), 6.43 (d,  $J$  = 3.4 Hz, 1H), 7.06–7.15 (m, 3H), 7.37 (d,  $J$  = 1.6 Hz, 1H), 7.59 (d,  $J$  = 7.7 Hz, 1H);  $^{13}\text{C}$  (APT) NMR ( $\text{CDCl}_3$ , 100 MHz): 21.8 ( $\text{CH}_3$ ), 108.4 (CH), 111.2 (CH), 125.9 (CH), 127.1 (CH), 127.4 (CH), 130.2 (qC), 131.0 (CH), 134.5 (qC), 141.6 (CH), 153.5 (qC). HRMS (EI) calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}$  ( $\text{M}^+$ ): 158.0732; found: 158.0736.

**2-(4-Methoxyphenyl)furan, 14e.** White solid. Yield = 57% (100.0 mg);  $R_f$  = 0.26 (EtOAc/hexanes = 5:95); IR ( $\text{CH}_2\text{Cl}_2$ ): 2959, 2937, 1617, 1218, 1047  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.82 (s, 3H), 6.43 (dd,  $J$  = 3.4, 1.7 Hz, 1H), 6.51 (d,  $J$  = 2.8 Hz, 1H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 7.41 (d,  $J$  = 1.3 Hz, 1H), 7.61–7.56 (m, 2H);  $^{13}\text{C}$  (APT) NMR ( $\text{CDCl}_3$ , 75 MHz): 55.2 ( $\text{CH}_3$ ), 103.3 (CH), 111.5 (CH), 114.1 (CH), 124.0 (qC), 125.2 (CH), 141.3 (CH), 154.0 (qC), 159.0 (qC). HRMS (EI) calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}_2$  ( $\text{M}^+$ ): 174.0681; found: 174.0686.

**2-(3-Methoxyphenyl)furan, 14f.** Brown oil. Yield = 72% (126.0 mg);  $R_f$  = 0.45 (EtOAc/hexanes = 5:95); IR ( $\text{CH}_2\text{Cl}_2$ ): 2938, 1605, 1504, 1290, 1226, 1038  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.77 (s, 3H), 6.38 (dd,  $J$  = 3.4, 1.8 Hz, 1H), 6.56 (d,  $J$  = 3.4 Hz, 1H), 6.71–6.75 (m, 1H), 7.13–7.21 (m, 3H), 7.37 (d,  $J$  = 1.7 Hz, 1H);  $^{13}\text{C}$  (APT) NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  55.3 ( $\text{CH}_3$ ), 105.3 (CH), 109.2 (CH), 111.7 (CH), 113.2 (CH), 116.4 (CH), 129.8 (CH), 132.2 (qC), 142.1

(CH), 153.8 (qC), 159.9 (qC). HRMS (EI) calcd. for  $C_{11}H_{10}O_2$  ( $M^+$ ): 174.0681; found: 174.0679.

**2-(2-Methoxyphenyl)furan, 14g.** Brown oil. Yield = 63% (110.0 mg);  $R_f$  = 0.42 (EtOAc/hexanes = 10:90); IR ( $CH_2Cl_2$ ): 3002, 2940, 2837, 1602, 1464, 1083  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  3.93 (s, 3H), 6.48–6.50 (m, 1H), 6.93–7.04 (m, 3H), 7.20–7.27 (m, 1H), 7.46 (d,  $J$  = 0.7 Hz, 1H), 7.85 (dd,  $J$  = 7.7, 1.3 Hz, 1H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  55.4 ( $CH_3$ ), 109.8 (CH), 111.0 (CH), 111.6 (CH), 119.9 (qC), 120.7 (CH), 126.0 (CH), 128.0 (CH), 141.1 (CH), 150.3 (qC), 155.3 (qC). HRMS (EI) calcd. for  $C_{11}H_{10}O_2$  ( $M^+$ ): 174.0681; found: 174.0685.

**2-(4-Chlorophenyl)furan, 14h.** White solid. Yield = 65% (116.0 mg);  $R_f$  = 0.29 (hexanes); IR ( $CH_2Cl_2$ ): 3054, 2987, 1487, 1422, 1265, 1093, 1020  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  6.42–6.49 (m, 1H, CH), 6.62 (d,  $J$  = 2.9 Hz, 1H), 7.33 (d,  $J$  = 8.5 Hz, 2H), 7.45 (s, 1H), 7.58 (d,  $J$  = 8.5 Hz, 2H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  105.4 (CH), 111.8 (CH), 125.0 (CH), 128.9 (CH), 129.4 (qC), 133.0 (qC), 142.3 (CH), 153.0 (qC). HRMS (EI) calcd. for  $C_{10}H_7ClO$  ( $M^+$ ): 178.0185; found: 178.0188.

**2-(3-Chlorophenyl)furan, 14i.** Colorless oil. Yield = 67% (119.0 mg);  $R_f$  = 0.29 (hexanes); IR ( $CH_2Cl_2$ ): 3371, 1603, 1582, 1282, 1013  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  6.44 (dd,  $J$  = 3.42, 1.83 Hz, 1H), 6.63 (d,  $J$  = 3.4 Hz, 1H), 7.15–7.38 (m, 2H), 7.46 (d,  $J$  = 1.71 Hz, 1H), 7.49–7.52 (m, 1H), 7.64 (t,  $J$  = 1.77 Hz, 1H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  106.0 (CH), 111.7 (CH), 121.8 (CH), 123.8 (CH), 127.2 (CH), 130.0 (CH), 132.5 (qC), 134.7 (qC), 142.5 (CH), 152.5 (qC). HRMS (EI) calcd. for  $C_{10}H_7ClO$  ( $M^+$ ): 178.0185; found: 178.0182.

**2-(2-Chlorophenyl)furan, 14j.** Colorless oil. Yield = 70% (70.0 mg);  $R_f$  = 0.29 (hexanes); IR ( $CH_2Cl_2$ ): 3065, 1599, 1499, 1470, 1031  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  6.53 (dd,  $J$  = 3.5, 1.8 Hz, 1H), 7.14 (dd,  $J$  = 3.5, 0.6 Hz, 1H), 7.19 (dd,  $J$  = 7.4, 1.7 Hz, 1H), 7.31 (td,  $J$  = 3.9, 1.4 Hz, 1H), 7.44 (dd,  $J$  = 7.9, 1.2 Hz, 1H), 7.51 (dd,  $J$  = 1.8, 0.6 Hz, 1H), 7.87 (dd,  $J$  = 7.9, 1.7 Hz, 1H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  110.9 (CH), 111.7 (CH), 126.9 (CH), 127.9 (CH), 128.0 (CH), 129.3 (CH), 130.1 (qC), 130.7 (qC), 142.1 (CH), 150.2 (qC). HRMS (EI) calcd. for  $C_{10}H_7ClO$  ( $M^+$ ): 178.0185; found: 178.0181.

**2-(4-Ethylphenyl)furan, 14k.** Brown oil. Yield = 56% (96.0 mg);  $R_f$  = 0.5 (EtOAc/hexanes = 5:95); IR ( $CH_2Cl_2$ ): 3023, 2965, 2931, 1516, 1457, 1157, 1007  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  1.24 (t,  $J$  = 7.6 Hz, 3H), 2.65 (q,  $J$  = 7.6 Hz, 2H), 6.44 (dd,  $J$  = 3.3, 1.8 Hz, 1H), 6.58 (d,  $J$  = 3.3 Hz, 1H), 7.21 (d,  $J$  = 8.2 Hz, 2H); 7.43 (d,  $J$  = 1.6 Hz, 1H), 7.59 (d,  $J$  = 8.2 Hz, 2H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  15.5 ( $CH_3$ ), 28.6 ( $CH_2$ ), 104.2 (CH), 111.5 (CH), 123.8 (CH), 128.1 (CH), 128.5 (qC), 141.6 (CH), 143.5 (qC), 154.2 (qC); HRMS (EI) calcd. for  $C_{12}H_{12}O$  ( $M^+$ ): 172.0888; found: 172.0886.

**2-(4-Acetylphenyl)furan, 14l.** White solid. Yield = 59% (110.0 mg);  $R_f$  = 0.24 (EtOAc/hexanes = 20:80); IR ( $CH_2Cl_2$ ): 1668, 1475, 1416, 1079, 1020  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  2.59 (s, 3H), 6.46–6.54 (m, 1H), 6.78 (d,  $J$  = 3.3 Hz, 1H), 7.51 (s, 1H), 7.72 (d,  $J$  = 8.4 Hz, 2H), 7.95 (d,  $J$  = 8.4 Hz, 2H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  26.5 ( $CH_3$ ), 107.5 (CH), 112.1 (CH), 123.5 (CH), 128.9 (CH), 134.9 (qC),

135.5 (qC), 143.3 (CH), 152.8 (qC), 197.3 (CO); HRMS (EI) calcd. for  $C_{12}H_{10}O_2$  ( $M^+$ ): 186.0681; found: 186.0687.

**2-(4-Biphenyl)furan, 14m.** White solid. Yield = 77% (170.0 mg);  $R_f$  = 0.33 (EtOAc/hexanes = 5:95); IR ( $CH_2Cl_2$ ): 3054, 2987, 1600, 1478, 1265, 1158  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz):  $\delta$  6.42–6.40 (m, 1H), 6.69 (d,  $J$  = 3.3 Hz, 1H), 7.32–7.37 (m, 1H), 7.33–7.50 (m, 3H), 7.62 (d,  $J$  = 8.4 Hz, 4H), 7.75 (d,  $J$  = 8.4 Hz, 2H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  105.1 (CH), 111.7 (CH), 124.2 (CH), 126.9 (CH), 127.3 (CH), 128.8 (CH), 129.9 (qC), 140.0 (qC), 140.6 (qC), 142.1 (CH), 153.8 (qC). RMS (EI) calcd. for  $C_{16}H_{12}O$  ( $M^+$ ): 220.0888; found: 220.0885.

**2-(1-Naphthyl)furan, 14n.** Colorless oil. Yield = 85% (165.0 mg);  $R_f$  = 0.45 (EtOAc/hexanes = 10:90); IR ( $CH_2Cl_2$ ): 3054, 2987, 1512, 1422, 1265, 1015  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 300 MHz): 6.58 (dd,  $J$  = 3.3, 1.9 Hz, 1H), 6.71 (d,  $J$  = 3.3 Hz, 1H), 7.40–7.56 (m, 3H), 7.61 (d,  $J$  = 1.7 Hz, 1H), 7.71 (dd,  $J$  = 7.2, 1.0 Hz, 1H), 7.80–7.89 (m, 2H), 8.37–8.41 (m, 1H);  $^{13}C$  (APT) NMR ( $CDCl_3$ , 75 MHz):  $\delta$  109.2 (CH), 111.3 (CH), 125.3 (CH), 125.6 (CH), 125.9 (CH), 126.2 (CH), 126.5 (CH), 128.5 (CH), 128.6 (CH), 128.7 (qC), 130.4 (qC), 134.0 (qC), 142.4 (CH), 153.4 (qC). HRMS (EI) calcd. for  $C_{14}H_{10}O$  ( $M^+$ ): 194.0732; found: 194.0726.

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