

# AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub>-Catalyzed [3+2] Cycloaddition of Cyclic Diazodicarbonyl Compounds: Efficient Synthesis of 2,3-Dihydrofurans and Conversion to 3-Acyfurans

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A novel and efficient method for the synthesis of 2,3-dihydrofurans bearing a variety of substituents on the dihydrofuran ring was achieved by the reaction of cyclic diazodicarbonyl compounds with styrene and vinyl acetate. The key strategy was AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub>-catalyzed [3+2] cycloaddition. The synthesized dihydrofurans with an acetate group were further converted to the corresponding 3-acylfurans.

**Key Words** : AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub>, [3+2] cycloaddition, Diazodicarbonyls, 2,3-Dihydrofurans

## Introduction

2,3-Dihydrofurans are one of the most commonly observed classes of structural units in natural and unnatural products with biological properties and activities.<sup>1</sup> Molecules with the 2,3-dihydrofuran moiety are widely used in the pharmaceutical, flavour, insecticidal, and fish antifeedant industries.<sup>2</sup> Their importance in biological activity and usefulness as synthetic intermediates for natural product synthesis have prompted a search for better method of synthesis.

Several methods for the synthesis of 2,3-dihydrofurans have already been developed, the majority of which have been accomplished through ionic<sup>3</sup> or radical<sup>4</sup> pathways through the oxidative addition of 1,3-dicarbonyl compounds to the appropriate olefins. In addition, the reaction between iodonium ylides of β-diketones and olefins in the presence of Cu(acac)<sub>2</sub> as a catalyst results in complex mixtures of inseparable products at higher temperatures.<sup>5</sup> In the case of CAN- and the Mn(OAc)<sub>3</sub>-mediated oxidative cycloaddition of β-dicarbonyl compounds to substituted styrenes, dihydrofurans are produced in low yields. This may be due to the polymerization of styrenic olefins, which requires an excess amount of styrene to complete the reaction.<sup>6</sup> In particular, the use of more than two equivalents of metal reagents usually made the separation difficult.

Successful methods for the synthesis of 2,3-dihydrofurans from cyclic diazodicarbonyl compounds were achieved utilizing the Rh(II) complex by us<sup>7</sup> and others.<sup>8</sup> Nevertheless, the Rh(II) complex is very expensive, so cheaper catalysts are desirable. Among these, silver (I) catalysts have garnered much attention due to their mild reaction conditions and successful usage in several homogeneous and heterogeneous reactions.<sup>9</sup> We report a simple and facile synthesis for 2,3-dihydrofurans by AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub>-catalyzed [3+2] cycloaddition of diazodicarbonyls to olefins (Scheme 1). We also describe a conversion of 2,3-dihydrofurans to 3-acylfurans.

Several Ag(I)-catalysts were first investigated for the synthesis of 2,3-dihydrofurans starting from 2-diazo-5,5-di-



**Scheme 1.** AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub>-catalyzed [3+2] cycloaddition of diazodicarbonyls with olefins.

methylcyclohexanedione (**1**) and styrene. The results are summarized in Table 1. Among the silver(I) catalysts (10 mol %) tested, Ag<sub>2</sub>O, Ag<sub>2</sub>CO<sub>3</sub>, AgNO<sub>3</sub>, AgClO<sub>4</sub>, and AgSO<sub>2</sub>CF<sub>3</sub> in toluene at 70 °C for 10 h gave no cycloadducts. With AgBF<sub>4</sub> (10 mol %) as a catalyst, reactions in methylene

**Table 1.** Reaction of 2-diazo-5,5-dimethylcyclohexanedione (**1**) with styrene under several Ag(I) catalysts

Catalysts	Solvent	Temp.	Time (h)	Yield (%)
Ag <sub>2</sub> O	toluene	70 °C	10	0
Ag <sub>2</sub> CO <sub>3</sub>	toluene	70 °C	10	0
AgNO <sub>3</sub>	toluene	70 °C	10	0
AgClO <sub>4</sub>	toluene	70 °C	10	0
AgSO <sub>2</sub> CF <sub>3</sub>	toluene	70 °C	10	0
AgBF <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	rt	48	0
AgBF <sub>4</sub>	THF	rt	48	0
AgBF <sub>4</sub>	acetonitrile	rt	48	0
AgBF <sub>4</sub>	toluene	rt	48	22
AgBF <sub>4</sub>	toluene	70 °C	10	47
AgBF <sub>4</sub> /[Bmim]BF <sub>4</sub>	benzene	70 °C	5	60
AgBF <sub>4</sub> /[Bmim]BF <sub>4</sub>	toluene	70 °C	5	71
AgSbF <sub>6</sub> /[Bmim]BF <sub>4</sub>	toluene	70 °C	10	30
[Bmim]BF <sub>4</sub>	toluene	70 °C	12	0

<sup>a</sup>All reactions were carried out with **1** (1.0 mmol) and styrene (5.0 mmol) in the presence of catalyst (0.10 mmol) in solvent (2.0 mL). [Bmim]BF<sub>4</sub> (0.1 mL) was used in this reaction. <sup>b</sup>Isolated yields.

**Table 2.** Synthesis of 2,3-dihydrofurans starting from cyclic diazodicarbonyls with styrene and vinyl acetate in the presence of AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub><sup>a</sup>

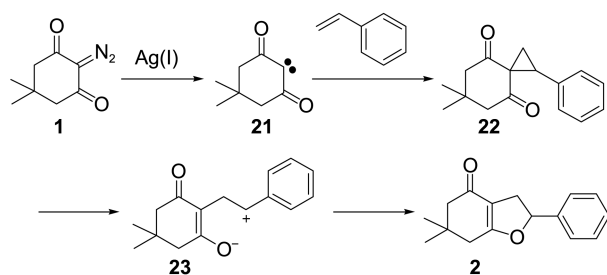
Entry	Diazodicarbonyls	Olefins	Condition	Products <sup>b</sup>	Yield (%) <sup>c</sup>
1			rt, 24 h		61
2			70 °C, 5 h		74
3			rt, 24 h		59
4			50 °C, 5 h		68 <sup>d</sup>
5			rt, 24 h		52 <sup>d</sup>
6			70 °C, 5 h		57 <sup>d</sup>
7			rt, 24 h		61 <sup>d</sup>
8			70 °C, 5 h		69 <sup>d</sup>
9			rt, 24 h		60 <sup>d</sup>
10			70 °C, 5 h		60 <sup>d</sup>
11			rt, 24 h		58 <sup>d</sup>
12			70 °C, 5 h		54

<sup>a</sup>Reaction conditions: cyclic diazodicarbonyl compound **1** (1.0 mmol), olefin (5.0 mmol), toluene (2.0 mL), using AgBF<sub>4</sub> (0.10 mmol)/[Bmim]BF<sub>4</sub> (8 drops) as a catalyst under a nitrogen atmosphere. <sup>b</sup>All products gave satisfactory spectral data. <sup>c</sup>Isolated yields. <sup>d</sup>A 1:1 mixture of diastereomers.

chloride, THF, and acetonitrile solvents at room temperature for 48 h did not give any cycloadducts. However, with toluene at room temperature for 48 h, the expected product **2** was produced in 22% yield. Upon raising the temperature to 70 °C, the yield of **2** increased to 47%. Surprisingly, significant increases in yield were observed with addition of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF<sub>4</sub>). Treatment of **1** with styrene in the presence of AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub> in benzene or toluene at 70 °C for 5 h provided **2** in 60 and 71% yields, respectively. This result may be due to the increase in solubility of the Ag(I) salt by added ionic liquids. Ag(I) catalysts have been shown to be activated after stabilization with ionic liquids.<sup>10</sup> In this case, any C-H insertion products of toluene produced by the rhodium-catalyzed

reaction were undetected. With AgSbF<sub>6</sub>/[bmim]BF<sub>4</sub> as the other catalyst, cycloadduct **2** was also obtained in 30% yield. However, with only [Bmim]BF<sub>4</sub>, **2** was not produced.

Next, additional reactions of a variety of cyclic diazodicarbonyl compounds with styrene and vinyl acetate were attempted in the presence of AgBF<sub>4</sub> (10 mol %)/[Bmim]BF<sub>4</sub>. The results are collected in Table 2. Reaction of **1** with vinyl acetate at room temperature for 24 h provided cycloadduct **9** in 61% yield (entry 1). Similarly, treatment of **3** with styrene and vinyl acetate gave products **10** and **11** in 74 and 59% yield, respectively (entries 2 and 3). Reactions of diazo compounds **4-7**, with methyl, isopropyl, phenyl and aryl substituents on the cyclohexanedione ring, were successful. In these cases, cycloadducts **12-19** were produced as a 1:1



Scheme 2

mixture of diastereomers (entries 4-11). Reaction of **4** with styrene and vinyl acetate provided cycloadducts **12** and **13** in 68 and 52% yield, respectively, whereas that of **5** gave **14** and **15** in 57 and 61% yields, respectively. Similarly, treatment of **6** and **7** with styrene and vinyl acetate afforded cycloadducts **16-19** in 69, 60, 60, and 58% yield, respectively (entries 8-11). Treatment of 2-diazophenylene-1,3-dione (**8**) with styrene afforded cycloadduct **20** in 54% yield (entry 12).

A plausible mechanism for the formation of **2** is shown in Scheme 2 in light of the reported Rh(II)-catalyzed reaction.<sup>11,7a</sup> Diazo compound **1** first gives carbene **21** through the loss of a nitrogen by Ag(I)/[Bmim]BF<sub>4</sub>. Carbene **21** then reacts with styrene to give the cyclopropane **22**, which undergoes bond cleavage to give zwitterion **23**. Ring closure of intermediate **23** then gives dihydrofuran **2**.

As an application of this methodology, the conversion of dihydrofurans with an acetate group to the corresponding 3-acylfuran was next attempted. The results are depicted in Table 3. Treatment of **9** and **11** with *p*-TsOH in refluxing toluene for 2 h gave 3-acylfurans **24** and **25** in 89 and 81%

yield, respectively. Similarly, reactions of other dihydrofurans, **13**, **15**, **17**, and **19** as a 1:1 mixture of diastereomers provided 3-acylfurans **25-29** in 80-85% yield.

In summary, AgBF<sub>4</sub>/[Bmim]BF<sub>4</sub>-catalyzed [3+2] cycloaddition reactions of diazodicarbonyl compounds with styrene and vinyl acetate were carried out. These reactions provided rapid entry to the synthesis of 2,3-dihydrofurans in moderate yields. This method has the advantages of mild reaction conditions and simple manipulation. The dihydrofurans with an acetate group were further converted to the corresponding 3-acylfurans.

## Experimental

All experiments were carried out in a nitrogen atmosphere. Merck, pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Model ARX (300 and 75 MHz, respectively) spectrometer in CDCl<sub>3</sub> as the solvent. IR spectra were recorded on a Jasco FTIR 5300 spectrophotometer. HRMS and MS were carried out at the Korea Basic Science Institute.

### General Procedure for the Synthesis of 2,3-Dihydrofurans.

To a solution of cyclic diazodicarbonyl compound **1** (1.0 mmol) and the corresponding olefins (5.0 mmol) in toluene (2.0 mL) was added silver tetrafluoroborate (0.10 mmol) and [Bmim]BF<sub>4</sub> (0.1 mL) at room temperature. The reaction mixture was stirred at r.t. for 24 h or 70 for 5 h and then cooled to room temperature. Water (20 mL) was added and the solution was extracted with ethyl acetate (20 mL × 3). Evaporation of the solvent and purification by column chromatography on silica gel using hexane-ethyl acetate (4:1) gave products.

**6,6-Dimethyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (2).** Yield: 71%, a yellow oil; IR (neat): 3064, 2959, 1640, 1403, 1220, 1165, 1045, 961, 758, 701, 628 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.35-7.23 (m, 5H), 5.70 (dd, *J* = 10.2, 7.5 Hz, 1H), 3.27-3.18 (m, 1H), 2.83-2.77 (m, 1H), 2.31 (s, 2H), 2.06 (s, 2H), 1.08 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.8, 176.1, 140.6, 128.8, 128.5, 125.8, 111.4, 86.5, 50.9, 37.7, 34.1, 33.8, 28.8, 28.5.

**6,6-Dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (9).** Yield: 61%, a yellow oil; IR (neat): 2960, 2879, 1760, 1649, 1407, 1212, 1165, 1052, 946, 849, 780, 734 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.68 (dd, *J* = 7.5, 2.4 Hz, 1H), 3.02 (dd, *J* = 16.2, 7.5 Hz, 1H), 2.74 (dd, *J* = 16.2, 2.4 Hz, 1H), 2.30 (d, *J* = 8.1 Hz, 2H), 2.20 (d, *J* = 5.4 Hz, 2H), 2.06 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.5, 174.2, 169.4, 110.8, 98.8, 50.8, 37.2, 34.2, 31.7, 28.9, 28.2, 20.9.

**2-Phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (10).** Yield: 74%, a yellow oil; IR (neat): 3032, 2948, 1634, 1495, 1454, 1402, 1289, 1231, 1182, 1061, 1022, 997, 907, 760, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32-7.21 (m, 5H), 5.66 (dd, *J* = 10.5, 8.1 Hz, 1H), 3.23-3.14 (m, 1H), 2.81-2.73 (m, 1H), 2.45-2.39 (m, 2H), 2.32-2.28 (m, 2H), 2.02-1.94

Table 3. Synthesis of 3-acylfurans **24-29** from dihydrofurans

Entry	Dihydrofurans	Condition	Products <sup>b</sup>	Yield (%) <sup>c</sup>
1		<i>p</i> -TsOH toluene reflux, 2 h		89
2		<i>p</i> -TsOH toluene reflux, 3 h		81
3		<i>p</i> -TsOH toluene reflux, 3 h		85
4		<i>p</i> -TsOH toluene reflux, 3 h		84
5		<i>p</i> -TsOH toluene reflux, 3 h		85
6		<i>p</i> -TsOH toluene reflux, 3 h		80

(m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.6, 177.5, 140.4, 128.6, 128.3, 125.7, 112.8, 86.2, 36.2, 33.7, 23.7, 21.5.

**4-Oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (11).** Yield: 59%, a yellow oil; IR (neat): 2951, 1760, 1649, 1407, 1216, 1165, 1053, 938, 872, 775 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.67 (d, *J* = 7.5 Hz, 1H), 3.01 (dd, *J* = 16.2, 6.6 Hz, 1H), 2.75 (d, *J* = 16.2 Hz, 1H), 2.52-2.46 (m, 2H), 2.35-2.31 (m, 2H), 2.07 (s, 3H), 2.04-1.98 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.2, 175.3, 169.4, 112.2, 98.5, 36.4, 31.9, 23.4, 21.5, 20.9.

**6-Methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (12).** Yield: 68%, a yellow oil; IR (neat): 3034, 2957, 1634, 1495, 1454, 1402, 1248, 1211, 1138, 1053, 1028, 924, 901, 760, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33-7.18 (m, 5H), 5.71-5.64 (m, 1H), 3.24-3.13 (m, 1H), 2.82-2.72 (m, 1H), 2.52-2.45 (m, 1H), 2.41-2.23 (m, 2H), 2.17-2.04 (m, 2H), 1.05 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.5, 177.4, 140.4, 130.2, 128.5, 125.8, 112.4, 86.7, 44.7, 33.7, 31.8, 29.8, 20.9.

**6-Methyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (13).** Yield: 52%, a yellow oil; IR (neat): 2928, 1736, 1633, 1404, 1205, 1142, 1049, 736 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.70-6.66 (m, 1H), 3.04-2.97 (m, 1H), 2.77-2.70 (m, 1H), 2.52-2.48 (m, 2H), 2.43-2.34 (m, 2H), 2.07 (s, 3H), 2.06-2.03 (m, 1H), 1.09-1.06 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.9, 175.0, 169.4, 111.9, 98.7, 45.0, 31.9, 31.5, 31.3, 29.8, 20.9; HRMS *m/z* (M<sup>+</sup>) calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>: 210.0892, Found 210.0894.

**6-Isopropyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (14).** Yield: 57%, a yellow oil; IR (neat): 2959, 1640, 1452, 1402, 1248, 1209, 1049, 758, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37-7.28 (m, 5H), 5.79-5.71 (m, 1H), 3.28-3.21 (m, 1H), 2.90-2.83 (m, 1H), 2.55-2.46 (m, 2H), 2.34-2.08 (m, 2H), 2.03-2.00 (m, 1H), 1.68-1.60 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.6, 177.9, 140.4, 128.8, 128.5, 125.9, 112.5, 86.9, 41.3, 40.6, 33.8, 32.0, 29.7, 27.6, 19.6; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>: 256.1463, Found 256.1466.

**6-Isopropyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (15).** Yield: 61%, a yellow oil; IR (neat): 2961, 1761, 1651, 1404, 1226, 1202, 1049, 939 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.72-6.67 (m, 1H), 3.07-2.96 (m, 1H), 2.79-2.71 (m, 1H), 2.52-2.39 (m, 2H), 2.46-2.13 (m, 2H), 2.09 (s, 3H), 2.00-1.96 (m, 1H), 1.67-1.58 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 195.2, 175.6, 169.3, 112.0, 98.7, 41.0, 40.6, 31.8, 31.7, 26.9, 20.8, 19.7, 19.5; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: 238.1205, Found 238.1209.

**2,6-Diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (16).** Yield: 69%, a yellow oil; IR (neat): 2944, 1632, 1402, 1248, 1207, 1046, 932, 764, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32-7.26 (m, 5H), 7.23-7.19 (m, 5H), 5.78-5.71 (m, 1H), 3.49-3.38 (m, 1H), 3.33-3.21 (m, 1H), 2.92-2.82 (m, 1H), 2.72-2.65 (m, 2H), 2.62-2.59 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.0, 176.5, 142.6, 140.5, 128.9, 128.6, 127.2, 126.8, 126.0, 125.8, 112.9, 87.0, 43.9, 40.5, 33.9, 31.5; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>: 290.1307, Found

290.1308.

**4-Oxo-6-phenyl-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (17).** Yield: 60%, a yellow oil; IR (neat): 3030, 2932, 1761, 1647, 1495, 1404, 1364, 1258, 1227, 1202, 1165, 1049, 939, 856, 764, 702, 621 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.20 (d, *J* = 7.2 Hz, 2H), 7.15-7.12 (m, 3H), 6.65 (dd, *J* = 7.5, 2.4 Hz, 1H), 3.41-3.24 (m, 1H), 3.03-2.92 (m, 1H), 2.75-2.68 (m, 1H), 2.61-2.56 (m, 2H), 2.52-2.48 (m, 2H), 1.99 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 193.2, 174.2, 168.8, 141.9, 128.3, 126.6, 126.2, 111.9, 98.4, 43.2, 39.6, 31.4, 30.4, 20.4.

**6-(Benzo[d][1,3]dioxol-5-yl)-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (18).** Yield: 60%, a yellow oil; IR (neat): 3027, 2926, 1736, 1603, 1491, 1450, 1246, 1041, 739, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.38-7.27 (m, 5H), 6.75-6.60 (m, 3H), 5.90 (s, 2H), 5.80-5.73 (m, 1H), 3.40-3.23 (m, 2H), 2.92-2.83 (m, 1H), 2.69-2.63 (m, 2H), 2.58-2.54 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 193.7, 176.3, 147.7, 146.4, 140.4, 136.4, 128.7, 128.4, 125.7, 119.7, 112.7, 108.3, 107.0, 100.9, 86.6, 44.3, 40.0, 33.7, 31.7; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>: 334.1205, Found 334.1201.

**6-(Benzo[d][1,3]dioxol-5-yl)-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (19).** Yield: 58%, a yellow oil; IR (neat): 2922, 1759, 1645, 1491, 1443, 1404, 1246, 1200, 1040, 980, 853, 810, 775, 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.75-6.64 (m, 4H), 5.92 (s, 2H), 3.43-3.26 (m, 1H), 3.11-3.01 (m, 1H), 2.83-2.73 (m, 1H), 2.67-2.63 (m, 2H), 2.57-2.53 (m, 2H), 2.09 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 193.6, 174.4, 169.3, 147.9, 146.5, 136.1, 119.7, 112.1, 108.4, 107.0, 101.0, 98.8, 44.3, 40.2, 31.9, 31.4, 20.9; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>17</sub>H<sub>16</sub>O<sub>6</sub>: 316.0947, Found 316.0947.

**9-Phenyl-8,9-dihydro-7H-phenaleno[1,2-*b*]furan-7-one (20).** Yield: 54%, a yellow oil; IR (neat): 2926, 1734, 1636, 1580, 1435, 1379, 1325, 1219, 1020, 878, 845, 777, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.59 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.11-8.03 (m, 2H), 7.74-7.67 (m, 1H), 7.61-7.55 (m, 1H), 7.44-7.36 (m, 5H), 6.04-5.98 (m, 1H), 3.72-3.63 (m, 1H), 3.27-3.19 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 181.6, 166.7, 140.8, 135.3, 135.1, 134.1, 133.3, 133.0, 130.0, 128.8, 128.5, 127.4, 126.8, 126.7, 126.4, 125.9, 114.8, 86.8, 35.3; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>21</sub>H<sub>14</sub>O<sub>2</sub>: 298.0994, Found 298.0996.

**6,6-Dimethyl-6,7-dihydrobenzofuran-4(5H)-one (24).** Yield: 89%, a colorless oil; IR (neat): 3132, 2952, 2878, 1678, 1596, 1514, 1445, 1370, 1281, 1228, 1174, 1118, 1042 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 1.9 Hz, 1H), 6.67 (d, *J* = 1.9 Hz, 1H), 2.76 (s, 2H), 2.39 (s, 2H), 1.15 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 194.0, 166.2, 142.7, 119.5, 106.0, 51.7, 37.1, 35.1, 28.3, 28.3; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: 164.0837, Found: 164.0840.

**6,7-Dihydrobenzofuran-4(5H)-one (25).** Yield: 81%, a colorless oil; IR (neat): 3131, 2948, 1677, 1595, 1516, 1447, 1414, 1294, 1242, 1184, 1119, 1026 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 2.89 (m, 2H), 2.50 (m, 2H), 2.18 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 193.9, 166.7, 142.2, 120.6, 105.9, 37.2,

22.8, 22.2; MS (EI) 136 ( $M^+$ ), 121, 108, 94, 80, 77, 63, 55, 52.

**6-Methyl-6,7-dihydrobenzofuran-4(5H)-one (26).** Yield: 85%, a colorless oil; IR (neat): 2953, 1678, 1594, 1448, 1413, 1285, 1219, 1119, 1039  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 1.9$  Hz, 1H), 6.66 (d,  $J = 1.9$  Hz, 1H), 3.00-2.25 (m, 5H), 1.18 (d,  $J = 6.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  194.6, 167.1, 142.8, 121.0, 106.3, 46.1, 31.4, 30.8, 21.0.

**6-Isopropyl-6,7-dihydrobenzofuran-4(5H)-one (27).** Yield: 84%, a colorless oil; IR (neat): 3124, 2961, 2875, 1681, 1598, 1450, 1389, 1371, 1281, 1216, 1119, 1040, 993, 739, 690, 631  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 1.8$ , 1H), 6.65 (d,  $J = 1.8$ , 1H), 2.88-2.81 (m, 1H), 2.56-2.45 (m, 2H), 2.23-2.14 (m, 1H), 2.04-1.97 (m, 1H), 1.66-1.58 (m, 1H), 0.90 (d,  $J = 6.9$ , 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  194.2, 167.2, 142.6, 120.5, 106.0, 41.9, 41.7, 31.7, 26.7, 19.6, 19.4; HRMS calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_4$ : 178.0994, Found 178.0995.

**6-Phenyl-6,7-dihydrobenzofuran-4(5H)-one (28).** Yield: 85%, a yellow oil; IR (KBr): 3150, 3123, 3061, 3029, 2952, 2900, 1682, 1600, 1515, 1499, 1450, 1413, 1278, 1215, 1120, 1038, 996, 897, 854, 765, 701, 615, 543, 503  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.33 (m, 3H), 7.29-7.27 (m, 3H), 6.70 (d,  $J = 1.5$ , 1H), 3.57-3.46 (m, 1H), 3.18-2.97 (m, 2H), 2.75-2.72 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  192.7, 166.0, 142.8, 142.1, 128.5, 126.9, 126.5, 120.6, 106.2, 44.6, 40.9, 30.8.

**6-(Benzo[d][1,3]dioxol-5-yl)-6,7-dihydrobenzofuran-4(5H)-one (29):** Yield: 80%, a colorless oil; mp 145-146  $^\circ\text{C}$ ; IR (KBr): 3140, 3121, 2915, 2872, 1676, 1588, 1506, 1455, 1413, 1289, 1269, 1248, 1213, 1116, 1033, 925, 858, 770, 696, 632, 608, 582  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 2.1$ , 1H), 6.77-6.72 (m, 2H), 6.71 (d,  $J = 1.8$ , 1H), 6.68 (d,  $J = 2.1$ , 1H), 5.93 (s, 2H), 3.51-3.40 (m, 1H), 3.16-3.09 (m, 1H), 3.01-2.92 (m, 1H), 2.70-2.67 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  193.0, 166.2, 149.7, 146.6, 143.1, 136.3, 120.9, 119.8, 108.4, 107.1, 106.4, 101.1, 45.2, 41.1, 31.5; HRMS  $m/z$  ( $M^+$ ) calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_4$ : 256.0736. Found 256.0734.

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