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Synthesis of 2-Substituted Benzofurans from *o*-Iodophenols and Terminal Alkynes with a Recyclable Palladium Catalyst Supported on Nano-sized Carbon Balls under Copper- and Ligand-Free Conditions

Eul Kgun Yum, Ok-Kyung Yang, Ji-Eun Kim, and Hee Jung Park†,*

Department of Chemistry, Chungnam National University, Daejon 305-764, Korea
*†Korea Basic Science Institute, Seodaemun-gu, Seoul 120-750, Korea. *E-mail: hjpark8659@kbsi.re.kr*
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We have developed a one-step synthesis of benzofurans from *o*-iodophenol and various terminal alkynes, by using Pd catalyst supported on nano-sized carbon balls (NCB) under copper- and ligand free conditions. This recyclable catalyst could be reused more than 5 times in the same heteroannulation reaction. The results have demonstrated that diverse 2-substituted benzofurans with tolerant functional groups can be prepared simply and conveniently under these conditions.

Key Words : Benzofuran, Nano-sized carbon balls, Terminal alkynes, Recyclable, Palladium catalyst

Introduction

It can not be emphasized too much about the importance of developing environmentally benign and clean reaction media. In the Pd catalyzed processes, a number of approaches have been reported regarding green technologies, such as the development of recyclable Pd catalysts and efficient reaction methods. Concerning the recyclable heterogeneous Pd catalysts, diverse kinds of supports are used. *i.e.* polymer,[1] silica,[2] silica-carbon,[3] magnetic iron(II) diiron(III) oxide,[4] and carbon.[5] Specially, carbon materials have been used for long time because they can satisfy most of the desired properties for a suitable catalytic support. The surface, shape, and porosity of carbon can significantly influence catalytic activity and recyclability.[6]

We have paid attention to recently developed nano-sized carbon balls (NCBs), which are an interesting material for use as a heterogeneous catalyst support. The NCBs contain a hollow core and are mesoporous, ball-like structures with an average diameter of 500 nm, an average shell thickness of 40-50 nm, a specific surface area of at least 1,000 m^2/g, and a total pore volume of about 0.9 cm^3/g.[7] We previously reported the nano-sized carbon ball (NCB) which was utilized in the Sonogashira reaction of acetylene and an iodoarene to obtain a functionalized bisarylacetylene.[8]

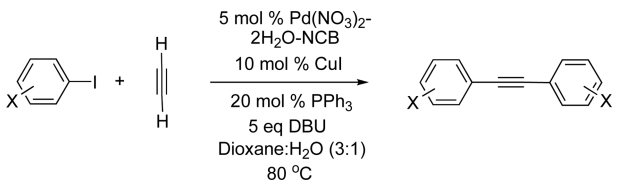
Many benzofuran derivatives of both natural or synthetic compounds have shown various biological properties for agrochemicals and pharmaceuticals.[9] Regarding to the synthesis of 2-substituted benzofurans, a number of various reaction conditions are documented including Sonogashira coupling and sequencial cyclization. Though typical examples employed Pd, copper, base, and ligand, several examples of different catalyst conditions were as follows. *i.e.* Ohtaka *et al.*;[10] PdO/ligand and copper free, Priyadarshini and Saejueng *et al.*;[11] copper(I) complex/Pd and phosphine free, Wang *et al.*;[12] Copper with ppb levels of Pd, Gil-M. *et al.*;[13] (dipyridin-2-ylmethyl)amine-derived $PdCl_2$ complex/copper free. Our results described herein provide an alternative recyclable methodology to Sonogashira coupling/cyclization reports.[14] In this methodology, the reaction proceed under relatively mild reaction conditions and tolerate variety of functional groups thus, avoiding protecting chemistry.

Herein, we report an efficient one step cyclization reaction affording 2-substituted benzofurans from *o*-iodophenol and various substituted terminal alkynes catalyzed by heterogeneous $Pd(OAc)_2$-NCB under copper and ligand free conditions. The reusability of the catalyst is also discussed.

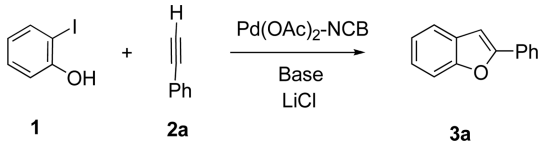
Results and Discussions

Our previous study demonstrated the very efficient synthesis of functionalized bisarylacetylenes from the Sonogashira coupling reaction of iodobenzenes and acetylene catalyzed by $Pd(NO_3)_2$-$2H_2O$-NCB as shown in Scheme 1.[8]

Iodobenzenes with various substituents at either the *m*- or *p*-position were employed in that study. *i.e.* 3-OH, 3-NO_2, 4-CH_3, 4-CO_2CH_3, 4-Br *etc*. Noteworthy in this reaction was that only symmetrical bisarylacetylenes were obtained without any other product. The result can be understood considering the low concentration of acetylene in the reaction mixture, which was achieved by stirring the reactants for 30 min, followed by introduction of acetylene gas from a balloon.[8] On the other hand, heteroannulation could be



Scheme 1. Functionalized symmetrical bisarylacetylenes using a $Pd(NO_3)$-$2H_2O$-NCB catalyst.



1 2a 3a

Scheme 2. Heteroannulation of *o*-iodophenol and phenylacetylene catalyzed by $Pd(NO_3)$-$2H_2O$-NCB.

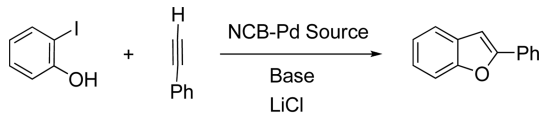
imagined by coupling of *o*-iodophenol and terminal alkynes under palladium catalyst supported NCB. With this in mind, we set out to carry out the Sonogashira coupling reactions of *o*-iodophenol and phenylacetylene as shown in Scheme 1.

Interestingly, the prototype reaction proceeded cleanly under ligand- and copper-free conditions affording 2-phenylbenzofuran. Hence, we investigated this reaction in more detail.

Table 1 shows the results of changing the reaction conditions by varying the Pd catalyst, base, temperature, and reaction times. Reactions were carried out using LiCl as an additive for stabilization of palladium intermediates. Yields were higher when $Pd(OAc)_2$ was used compared to other Pd sources (Table 1, entries 1, 4, 11, and 12). Reactions using Cs_2CO_3 as a base also produced good yields of the desired product (Table 1, entries 7-12). We also investigated the effect of different solvents under the same reaction conditions which were 1 equiv LiCl, 2 equiv phenylacetylene, 2 equiv Cs_2CO_3 and 5.0 mol % $Pd(OAc)_2$-NCB. The reactions using DMF as solvent produced good yields of the desired product, but the yield changed from moderate to dramatically lower in different solvents (Table 2).

From the results in Tables 1 and 2, the best results were obtained by using 1 equiv LiCl, 2 equiv Cs_2CO_3 and 5.0 mol % of $Pd(OAc)_2$-NCB in DMF at 110 °C. To synthesize diverse 2-substituted benzofurans with $Pd(OAc)_2$-NCB under Cu free condition, the reactions were run with *o*-iodophenol

Table 1. Optimization of the reaction conditions with an NCB-Pd catalyst



1 2a 3a

Entry[a]	Base	mol % Pd	Pd source in NCB-Pd	Temp (°C)	Reaction Time (h)	Isolated yields (%)
1	Cs_2CO_3	5	$Pd(OAc)_2$	110	15	87
2	KOAc	5	$Pd(OAc)_2$	110	15	52
3	Na_2CO_3	5	$Pd(OAc)_2$	110	15	31
4	K_2CO_3	5	$Pd(OAc)_2$	110	15	83
5	*i*-Pr_2NEt	5	$Pd(OAc)_2$	110	15	5
6	NEt_3	5	$Pd(OAc)_2$	110	15	3
7	Cs_2CO_3	5	$Pd(OAc)_2$	140	15	72
8	Cs_2CO_3	5	$Pd(OAc)_2$	80	48	-
9	Cs_2CO_3	2.5	$Pd(OAc)_2$	110	16	59
10	Cs_2CO_3	10	$Pd(OAc)_2$	110	16	69
11	Cs_2CO_3	5	$PdCl_2(PPh_3)_2$	110	16	65
12	Cs_2CO_3	5	$PdCl_2$	110	16	62

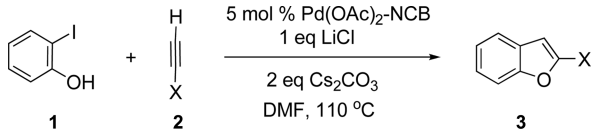
[a]A mixture of $Pd(OAc)_2$-NCB (5 mol %), *o*-iodophenol (0.5 mmol), LiCl (0.5 mmol), base (1.0 mmol) and phenylacetylene (1.0 mmol) was dissolved in 10 mL of DMF at a pressure tube.

Table 2. The effect of solvent on heteroannulation

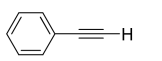
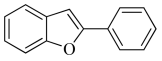
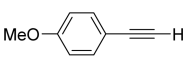
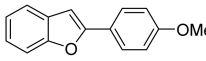
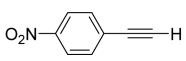
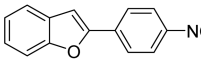
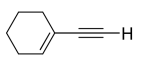
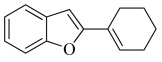
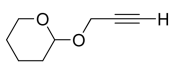
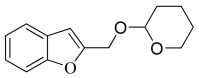
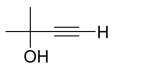
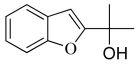
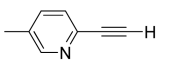
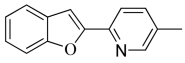
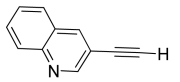
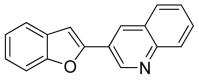
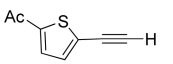
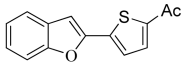
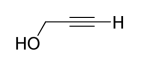
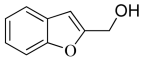
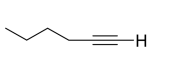
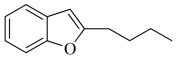
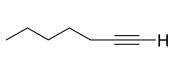
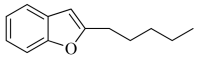
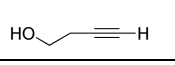
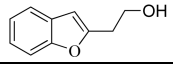
Entry[a]	Solvent	Reaction Time (h)	Isolated Yield (%)
1	DMF	15	87
2	DMA	15	77
3	NMP	15	52
4	1,4-Dioxane	15	-[b]

[a]Reaction conditions: 2 eq phenylacetylene, 1 eq LiCl, 2 eq Cs_2CO_3 and 5 mol % of $Pd(OAc)_2$- NCB at 110 °C. [b]trace

Table 3. Scope of the reaction



1 2 3

Entry	Alkyne		Reaction Time (h)	Product	Yields (%)
1		**2a**	15		**3a**/88
2		**2b**	15		**3b**/82
3		**2c**	15		**3c**/70
4		**2d**	15		**3d**/85
5		**2e**	14		**3e**/55
6		**2f**	14		**3f**/60
7		**2g**	48		**3g**/70
8		**2h**	20		**3h**/45
9		**2i**	7		**3i**/45
10		**2j**	15		**3j**/50
11		**2k**	15		**3k**/35
12		**2l**	15		**3l**/54
13		**2m**	15		**3m**/65

[a]A mixture of $Pd(OAc)_2$-NCB (5 mol %), *o*-iodophenol (0.5 mmol), LiCl (0.5 mmol), base (1.0 mmol) and terminal alkyne (1.0 mmol) was dissolved in 10 mL of DMF at a pressure tube.

Table 4. Synthesis of 2-phenylbenzofuran using recycled $Pd(OAc)_2$-NCB with *o*-iodophenol and phenylacetylene

Entry[a]	Recycling	Reaction Time (h)	Isolated Yield (%)
1	fresh	15	88
2	1st	15	88
3	2nd	20	87
4	3rd	24	65
5	4th	44	60
6	5th	48	55
7	6th	48	61

[a]All recycled reactions were run on 0.5 mmol scale without catalyst activation at 110 °C.

and various substituted terminal alkynes under the optimized reaction conditions. The results are summarized in Table 3.

After we explored optimal conditions for the formation of the benzofuran, the scope of this reaction was performed in more details as shown in Table 3. A variety of alkyl and aromatic terminal alkynes have been employed in this process. This reaction were smoothly heteroannulated for variation of electronic effect in phenyl group (H, NO_2, OCH_3), though electron rich methoxy containing acetylene afforded higher yields than electron poor nitro containing acetylene (entries 1-3). The results in Table 3 indicate that this ligand- and copper-free reaction condition could be applied for diverse functional groups, such as aryl, pyridyl, thiophene, alkyl, and hydroxyalkyl. The relatively lower yields when acyclic alkyl alkynes were employed (entries 5, 6 and 11-13) could be understood considering the chemical labilities of alkyl group.

The reusability of the $Pd(OAc)_2$-NCB catalyst was also evaluated. The used catalyst was recovered by membrane filtration, washed with methylene chloride, and dried in air. The results in Table 4 demonstrated that the catalyst could be reused more than 5 times, but requiring prolonged reaction times compared to those of the freshly prepared catalyst.

Conclusion

We have developed one-step method of synthesizing benzofurans from *o*-iodophenol and various terminal alkynes by using a Pd catalyst supported on nano-sized carbon balls (Pd-NCB) under free ligand- and Cu conditions. The recyclable catalyst could be reused more than 5 times for the same cyclization. The results have demonstrated that diverse 2-substituted benzofurans can be prepared simply under mild reaction conditions and reusable heterogeneous catalyst. This method obviously provides an efficient synthesis of heterocyclic compounds of biologically active compounds.

Experimental

Melting points were determined using a Thermo Scientific Electrothermal 9100 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 Spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) using $CDCl_3$ as the solvent and TMS as internal standard; chemical shifts are quoted in parts per million and J values are given in hertz. The GC-MS spectra are obtained using a Shimadzu QP 1000 GC-MS. Elemental analyses were carried out by Chungnam National University using an elemental analyzer (EA-1110). All chemicals were used as received without any further purification.

Procedure for the Preparation of 5 mol % $Pd(OAc)_2$-NCB. To a stirred solution of $Pd(OAc)_2$ (0.56 g, 2.5 mmol) in THF (200 mL) was added NCB (9.5 g). After the mixture was stirred for 1 day at room temperature, $Pd(OAc)_2$-NCB was filtered and washed with THF. The solid was dried at room temperature under vacuum. Mol % Pd contents at $Pd(OAc)_2$-NCB was determined using an inductively coupled plasma (ICP) spectrometer.

Synthesis of Terminal Alkynes. Preparation of the terminal alkynes was done according to the previous procedure of Sonogashira reaction by reacting aryl iodide/bromide with trimethylsilylacetylene.[15]

General Synthetic Procedure of 2-Substituted Benzofuran under $Pd(OAc)_2$-NCB Catalyzed Heteroannulation. A mixture of $Pd(OAc)_2$-NCB (5 mol %), *o*-iodophenol (0.5 mmol), LiCl (0.5 mmol), Cs_2CO_3 (1.0 mmol) and terminal alkyne (1.0 mmol) was dissolved in 10 mL of DMF in a pressure tube. After the resulting solution was stirred for an appropriate time at 110 °C, the reaction mixture was filtered and neutralized with saturated NH_4Cl. The mixture was extracted with ethyl acetate, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Further purification of the crude product was achieved by column chromatography using hexane and ethyl acetate as eluents.

2-Phenylbenzo[*b*]furan (3a): Yield; 88%, mp 112-114 °C (lit.[16] mp 108-112 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8 Hz, 1H, Ar-H), 7.57 (d, J = 8 Hz, 1H, Ar-H), 7.51 (d, J = 8 Hz, 1H, Ar-H), 7.43 (t, J = 8 Hz, 2H, Ar-H), 7.33 (t, J = 8 Hz, 2H, Ar-H), 7.30-7.19 (m, 2H, Ar-H), 7.01 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 154.7, 132.4, 128.6, 128.4, 128.3, 124.8, 124.1, 122.8, 120.8, 111.0, 101.2; MS (EI) (*m/z*, relative mass) 194 (M^+, 21), 165 (43), 101 (18), 82 (19). *Anal*. Calcd. For $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.47; H, 5.20.

2-(4-Methoxyphenyl)benzo[*b*]furan (3b): Yield; 82%, (lit.[17] mp 152-154 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dt, J = 8 Hz, 2, 4 Hz, 2H, Ar-H), 7.47-7.38 (m, 2H, Ar-H), 7.20-7.09 (m, 2H, Ar-H), 6.88 (dt, J = 8 Hz, 2, 4 Hz, 2H, Ar-H), 3,75 (s, 1H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 156.0, 154.6, 129.5, 126.4, 123.7, 123.3, 122.8, 120.5, 114.2, 110.9, 99.6, 55.3; MS (EI) (*m/z*, relative mass) 224 (M^+, 100), 207 (70), 181 (53), 152 (31).

2-(4-Nitrophenyl)benzo[*b*]furan (3c): Yield; 70%, (lit.[17] mp 182-183 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, J = 8.4 Hz, 2, 4 Hz, 2H, Ar-H), 7.64 -7.56 (m, 2H, Ar-H), 7.37-7.23 (m, 3H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 153.2, 147.2, 136.3, 128.6, 125.8, 125.2, 124.3, 123.5, 121.6, 111.5, 105.1; MS (EI) (*m/z*, relative mass) 209 (M^+, 25), 193 (21), 181 (25), 165 (100), 163 (35), 139 (11).

2-(1-Cyclohexenyl)benzo[*b*]furan (3d): Yield; 85%, mp 56-58 °C (lit.[18] mp 55-57 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.40 (d, *J* = 8 Hz, 1H, Ar-H), 7.22-7.13 (m, 2H, Ar-H), 6.60 (s, 1H, Ar-H), 6.49 (s, 1H, Ar-H), 2.38 (s, 2H, -CH_2-), 2.26 (s, 2H, -CH_2-), 1.78 (t, *J* = 6 Hz, 2H, -CH_2-), 1.69 (t, *J* = 6 Hz, 2H, -CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 154.2, 129.0, 127.0, 125.9, 123.6, 122.3, 120.4, 110.6, 99.9, 25.4, 24.9, 22.3, 22.1; MS (EI) (*m/z*, relative mass) 198 (M^+, 3), 170 (3), 86 (51), 84 (100); *Anal*. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12; Found: C, 84.80; H, 7.11.

2-[[(2-Tetrahydro-2*H*-pyran-2-yl)oxy]methyl]benzo[*b*]-furan (3e): Yield; 55%, yellow oil.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8 Hz, 1H, Ar-H), 7.47 (d, *J* = 8 Hz, 1H, Ar-H), 7.26 (t, *J* = 8 Hz, 1H, Ar-H), 7.20 (t, *J* = 8 Hz, 1H, Ar-H), 6.69 (s, 1H, Ar-H), 4.83-4.78 (m, 2H, -CH_2O-), 4.66 (d, *J* = 12 Hz, 1H, -O-CH-O-), 3.93 (t, *J* = 8 Hz, 1H, CH_2), 3.59-3.54 (m, 1H, CH_2), 1.90-1.53 (m, 6H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 154.2, 128.0, 124.1, 122.5, 120.9, 111.2, 105.5, 97.3, 61.9, 61.0, 30.3, 25.4, 19.1; MS (EI) (*m/z*, relative mass) 232 (M^+, 5), 131 (100), 85 (36), 77 (45); *Anal*. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; Found: C, 72.49; H, 6.83.

α,α-Dimethyl-2-benzo[*b*]furanmethanol (3f): Yield; 60%, yellow oil.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8 Hz, 1H, Ar-H), 7.44 (d, *J* = 9 Hz, 1H, Ar-H), 7.26-7.17 (m, 2H, Ar-H), 6.56 (s, 1H, Ar-H), 2.20 (br, 1H, OH), 1.67 (s, 6H, -C(CH_3)$_2$OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 154.5, 128.1, 123.8, 122.6, 120.8, 111.0, 100.2, 69.2, 28.7; MS (EI) (*m/z*, relative mass) 176 (M^+, 5), 161 (11), 58 (22), 43 (100); *Anal*. Calcd. for $C_{11}H_{12}O_2$: C, 74.89; H, 6.86; Found: C, 74.95; H, 6.79.

2-(2-Benzo[*b*]furanyl)-5-methylpyridine (3g): Yield; 70%, mp 112-113 °C (lit.[20] mp 112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H, Ar-H), 7.80 (d, *J* = 8 Hz, 1H, Ar-H), 7.63-7.53 (m, 3H, Ar-H), 7.36 (s, 1H, Ar-H), 7.31 (t, 1H, Ar-H), 7.23 (t, 1H, Ar-H), 2.38 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 150.1, 146.5, 137.1, 132.6, 128.8, 124.82, 122.9, 121.4, 119.9, 119.3, 111.3, 103.9, 18.4; MS (EI) (*m/z*, relative mass) 209 (M^+, 100), 180 (19), 90 (27), 76 (26); *Anal*. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69; Found: C, 80.46; H, 5.20; N, 6.60.

3-(2-Benzo[*b*]furanyl)quinoline (3h): Yield; 45%, mp 137-139 °C (lit.[21] mp 134-136 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H, Ar-H), 8.48 (s, 1H, Ar-H), 8.08 (d, *J* = 8 Hz, 1H, Ar-H), 7.81 (d, *J* = 8 Hz, 1H, Ar-H), 7.66 (t, *J* = 15.6 Hz, 1H, Ar-H), 7.59-7.50 (m, 3H, Ar-H), 7.30 (t, *J* = 15.6 Hz, 1H, Ar-H), 7.23 (t, *J* = 15.6 Hz, 1H, Ar-H), 7.15 (s, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.9, 147.3, 130.5, 129.6, 129.2, 128.7, 128.04, 127.5, 127.1, 124.8, 123.5, 123.1, 111.1, 102.8; MS (EI) (*m/z*, relative mass) 245 (M^+, 100), 216 (20), 123 (19), 94 (40); *Anal*. Calcd. for $C_{17}H_{11}NO$: C, 83.25; H, 4.25; N, 5.71; Found: C, 83.15; H, 4.50; N, 5.81.

2-(5-Acetyl-2-thienyl)benzo[*b*]furan (3i): Yield; 45%, mp 158-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 4 Hz, 1H, Ar-H), 7.57 (d, *J* = 8 Hz, 1H, Ar-H), 7.49 (d, *J* = 8 Hz, 1H, Ar-H), 7.44 (d, *J* = 4 Hz, 1H, Ar-H), 7.33-7.30 (m, 1H, Ar-H), 7.26-7.24 (m, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 2.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.27, 154.80, 149.84, 143.48, 140.77, 132.98, 128.55, 125.35, 124.73, 123.40, 121.22, 111.23, 103.93, 26.69; MS (EI) (*m/z*, relative mass) 242 (M^+, 19), 227 (26), 155 (13), 40 (100); *Anal*. Calcd. for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.16; Found: C, 69.35; H, 4.21.

2-Benzo[*b*]furanmethanol (3j): Yield; 50%, yellow oil.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8 Hz, 1H, Ar-H), 7.38 (d, *J* = 8 Hz, 1H, Ar-H), 7.21-7.11 (m, 2H, Ar-H), 6.57 (s, 1H, Ar-H), 4.68 (s, 2H, -CH_2OH), 2.07 (br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 154.9, 128.0, 124.2, 122.6, 121.0, 111.1, 104.0, 58.0; MS (EI) (*m/z*, relative mass) 148 (M^+, 27), 131 (56), 91 (100), 77 (24); *Anal*. Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44; Found: C, 72.90; H, 5.45.

2-Butylbenzo[*b*]furan (3k): Yield; 35%, yellow oil.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8 Hz, 1H, Ar-H), 7.36 (d, *J* = 8 Hz, 1H, Ar-H), 7.19-7.10 (m, 2H, Ar-H), 6.32 (s, 1H, Ar-H), 2.72 (t, 2H, CH_2), 1.72-1.64 (m, 2H, -CH_2), 1.48-1.33 (m, 2H, CH_2), 0.91 (t, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.5, 128.9, 122.9, 122.2, 120.0, 110.6, 101.6, 29.8, 28.1, 22.3, 13.8; MS (EI) (*m/z*, relative mass) 174 (M^+, 18), 131 (69), 61 (15), 43 (100); *Anal*. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10; Found: C, 82.62; H, 8.15.

2-Pentylbenzo[*b*]furan (3l): Yield; 54%, yellow oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8 Hz, 1H, Ar-H), 7.39 (d, *J* = 8 Hz, 1H, Ar-H), 7.20-7.13 (m, 2H, Ar-H), 6.35 (s, 1H, Ar-H), 2.75 (t, 2H, CH_2), 1.74 (t, 2H, CH_2), 1.37 (m, 4H, CH_2CH_2), 0.91 (t, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.5, 128.9, 122.9, 122.2, 120.0, 110.6, 101.6, 31.4, 28.4, 27.4, 22.4, 13.9; MS (EI) (*m/z*, relative mass) 188 (M^+, 3), 131 (58), 77 (21), 40 (100); *Anal*. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57; Found: C, 82.80; H, 8.61.

2-Benzo[*b*]furanethanol (3m): Yield; 65%, brown oil.[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8 Hz, 1H, Ar-H), 7.41 (d, *J* = 8 Hz, 1H, Ar-H), 7.24-7.16 (m, 2H, Ar-H), 6.50 (s, 1H, Ar-H), 3.98 (t, 2H, CH_2), 3.04 (t, 2H, CH_2), 1.72 (br, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 154.6, 128.5, 123.4, 122.5, 120.3, 110.7, 103.6, 60.7, 32.0; MS (EI) (*m/z*, relative mass) 162 (M^+, 21), 131 (100), 102 (18), 77 (45); *Anal*. Calcd. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21; Found: C, 74.16; H, 6.10.

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