Synthesis of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans using *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2 as an efficient and reusable catalyst

Mohammad Akrami Abarghooei[a], Razieh Mohebat[a]*, Zahed Karimi-Jaberi[b] and Mohammad Hossein Mosslemin[a]

[a]*Department of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran*
[b]*Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, Fars, Iran*

A new and convenient method is described for the synthesis of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans by the reaction of various α-bromoketones with phenols and 2-naphthols in the presence of *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2. All products were obtained in high yields and short reaction times using solvent-free conditions and a reusable catalyst.

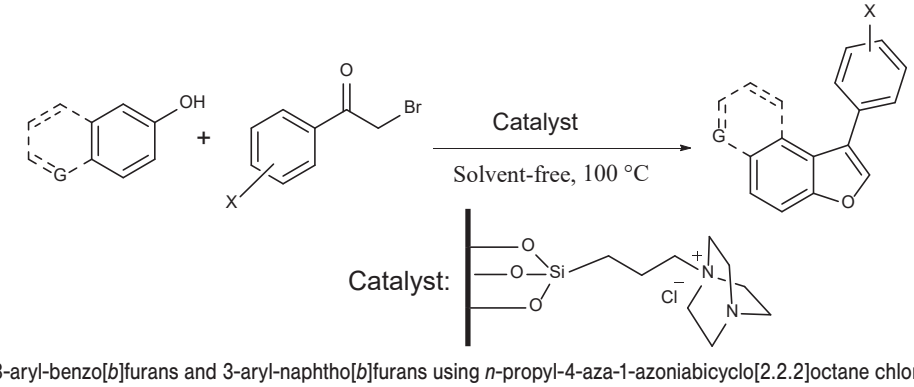
Keywords: benzo[*b*]furan, naphtho[*b*]furans, α-bromoketones, phenol, 2-naphthol, solvent-free conditions

Benzofuran is a common structural unit in natural products as well as pharmaceutical compounds and heterocycles with a 3-arylbenzofuran framework can be found in a series of pharmacologically relevant structures such as iantheran A.[1–3] Naphthofuran is a core structure in several natural products and biologically active compounds such as furomollugin[4] and 7-methoxy-2-nitronaphtho[2,1-*b*]furan.[5] Naphthofuran is also a key structure in some compounds with anticancer activities[6] and in imaging agents for B-amyloid plaques in the brain.[7] Owing to the remarkable biological properties of compounds with benzofuran and naphthofuran frameworks, a plethora of synthetic methods have been published for the synthesis of these potentially bioactive structures,[8–11] but most of these are associated with transition metal-catalysed annulation reactions.[12–15] The most common strategy for the synthesis of benzofurans and naphthofurans is Sonogashira reaction of terminal alkynes with *ortho* iodo- or bromophenols and naphthols, respectively.[16] However, most of these reactions need prolonged reaction times or external additives. Consequently, the development of an efficient and convenient method using a reusable catalyst for the synthesis of these widely used heterocyclic compounds is highly desirable. In recent years, ionic liquids have received significant attention because of their unique chemical and physical properties, such as undetectable vapour pressure, non-flammability, high thermal stability, wide liquid range, and the ability to dissolve many organic and inorganic substances. These compounds have also found many applications in sensors, batteries, plasticisers, electrolytes, lubricants, energetic materials, extraction and absorption. In addition, ionic liquids have been examined extensively in organic synthesis as reaction media or as catalysts.[17,18] Although the ability of ionic liquids as solvent and catalyst have successfully been demonstrated, there are several drawbacks with ionic liquids, such as possible environmental concerns, separation and reusability limitations, restricting their widespread practical application. However, these limitations can be overcome by the immobilisation of ionic liquids on solid supports, which provides the advantages of both ionic liquids and heterogeneous catalysts, including ease of handling, enhanced reaction rates, greater selectivity, simple work-up, reusability of the catalyst and the use of smaller amounts of ionic liquid in the potential process.[19,20]

Herein we report a new and convenient method for the synthesis of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans through the reaction of various α-bromoketones with phenols and 2-naphthols in the presence of *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2 as an efficient and reusable catalyst under solvent-free conditions (Scheme 1).

Results and discussion

The results of the optimisation study are shown in Table 1. The best result was achieved when we used *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2 (NPABOC@SiO_2) and this was found to be the most efficient catalyst for this reaction (Table 1, entry 8). When the reaction was carried out in the absence of the catalyst, there was no reaction (Table 1, entry 1), which shows that the presence of the catalyst is necessary for this reaction. The influence of catalyst loading on the model reaction was then investigated using 0.2–0.4 mmol of catalyst and the best yield was obtained in the presence of 0.3 mmol of catalyst. Finally, the effect of temperature was evaluated for the model reaction in the range of 90–110 °C and 100 °C was found to be the optimum temperature.



Scheme 1 Synthesis of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans using *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2.

* Correspondent. E-mail: mohebat@iauyazd.ac.ir; raziehmohebat@yahoo.com

Table 1 Optimisation of reaction condition for the synthesis of 3-phenylbenzofuran[a]

Entry	Catalyst (mmol)	Time (h)	Yield (%)[d]
1	No catalyst	12	–
2	[Bmim]BF_4	2	25
3	[Bmim]OTf	2	30
4	[Hmim]NO_3	2	30
5	[Bmim]Cl	2	25
6	DABCO	2	38
7	NPABOC@SiO_2 (0.2)	2	55
8	NPABOC@ SiO_2 (0.3)	2	93
9	NPABOC@SiO_2 (0.4)	2	93
10[b]	NPABOC@SiO_2 (0.3)	2	85
11[c]	NPABOC@SiO_2 (0.3)	2	93

[a]α-bromoketone (1 mmol), phenol (1 mmol), *n*-propyl-4-aza-1-azoniabicyclo[2.2.2] octane chloride immobilised on SiO_2 (NPABOC@SiO_2) (0.3 mmol), solvent free, 100 °C.
[b]Reaction was performed at 90 °C.
[c]Reaction was performed at 110 °C.
[d]Isolated yield.

To probe the efficiency and scope of our method, we decided to employ different α-bromoketones with phenols and β-naphthols for the synthesis of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans, respectively, and the results are shown in Table 2. The desired pure products were characterised by comparing the spectra (IR, ^{1}H NMR and ^{13}C NMR) and elemental analysis with the literature for the known compounds (Table 2, entries 1–4, 7, 8 and 11), while the structures of new compounds were deduced from their satisfactory elemental and spectral studies (Table 2, entries 5, 6, 9, 10 and 12–14). The mass spectra of the new compounds displayed molecular ion peaks at the appropriate *m*/*z* values.

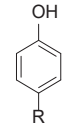
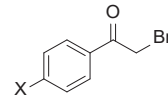
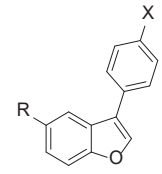
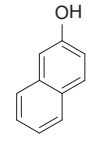
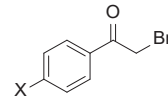
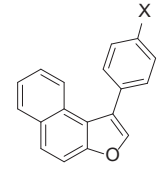
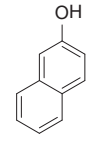
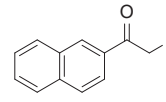
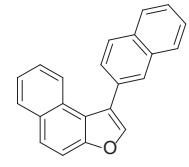
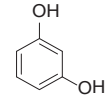
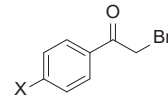
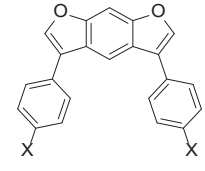
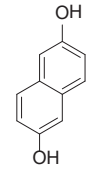
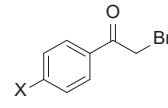
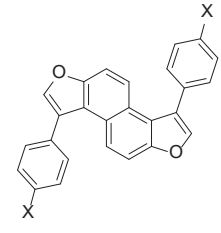
As shown in Table 2, the reaction of β-naphthol, phenol and phenol bearing electron-donating as well as electron-withdrawing functionalities proceeded smoothly and cleanly with α-bromoketone under thermal conditions, and the corresponding 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*] furans were obtained in high yields (Table 2, entries 1–10).

To screen the scope of application of this protocol, we then studied the synthesis of bis-derivatives of 3-aryl-benzo[*b*] furans and bis-derivatives of 3-aryl-naphtho[*b*]furans. Reaction of resorcinol (1 mmol) or 2,6-naphthalenediol (1 mmol) with an α-bromoketone (2 mmol) in the presence of NPABOC@SiO_2 (0.3 mmol) as a catalyst under solvent-free conditions at 100 °C was performed and the corresponding products were obtained in high yields (Table 2, entries 11–14). To the best of our knowledge, the present report is the first example of the synthesis of bis-derivatives of these compounds. Consequently, this new procedure is of practical importance and can be considered as a useful achievement in the synthesis of these fundamental heterocycles.

Based on the proposed mechanism for the synthesis of 3-aryl-benzo[*b*]furan catalysed by NPABOC@SiO_2, initially, condensation of phenol and α-bromoketone in the presence of NPABOC@SiO_2 leads to the 2-phenoxy-1-phenylethanone. Then, activation of the carbonyl group of 2-phenoxy-1-phenylethanone with NPABOC@SiO_2 catalyst followed by intramolecular nucleophilic attack and cyclisation leads to 3-phenyl-2,3-dihydrobenzo[*b*]furan-3-ol. Finally, dehydration of this intermediate in the presence of the catalyst NPABOC@ SiO_2 furnishes the desired 2-arylquinoxaline and releases the catalyst for the next catalytic cycle.

To evaluate the catalytic activity and the recycling potential, the reusability of the catalyst in the synthesis of benzo[*b*]furan by the reaction of α-bromoketones with phenol was explored and the results are summarised in Table 3. After reaction completion, the mixture was cooled to room temperature and ethyl acetate (5 mL) was added. The catalyst was recovered by simple filtration, washed with DCM and dried under vacuum to remove the residual solvent. Then, the recovered catalyst was reused for subsequent experiments. As can be seen in Table 3, the catalyst could be reused five times with a minimal loss of activity.

Table 2 Synthesis of 3-aryl-benzo[*b*]furans, 3-aryl-naphtho[*b*]furans and their bis-derivatives using n-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2 (NPABOC@SiO_2) as a catalyst

Entry	Ar–OH	α-Bromoketone	Product	Yield[ref, c]
				
1[a]	R = H	X = H	R = H, X = H	93[21]
2[a]	R = Me	X = Br	R = Me, X = Br	92[22]
3[a]	R = H	X = Br	R = H, X = Br	91[23]
4[a]	R = H	X = Cl	R = H, X = Cl	88[24]
5[a]	R = F	X = Br	R = F, X = Br	85
6[a]	R = Cl	X = Br	R = Cl, X = Br	84
				
7[a]		X = H	X = H	92[25]
8[a]		X = Br	X = Br	81[25]
9[a]		X = C_6H_5	X = C_6H_5	89
10[a]				86
				
11[b]		X = H	X = H	65[26]
12[b]		X = Br	X = Br	67
				
13[b]		X = H	X = H	74
14[b]		X = Br	X = Br	76

[a]α-bromo ketone (1 mmol), aromatic alcohol (1 mmol), catalyst (0.3 mmol), 100 °C.
[b]α-bromoketone (2 mmol), aromatic alcohol (1 mmol), catalyst (0.35 mmol), 100 °C.
[c]Isolated yield.

Table 3 Recycling of NPABOC@SiO_2 catalyst in the reaction of phenol with α-bromoketone[a]

Yield (%)[b]	Cycle	Run
93	0	1
90	1	2
90	2	3
88	3	4
87	4	5
87	5	6

[a]α-bromoketone (1 mmol), phenol (1 mmol), catalyst (0.3 mmol), 100 °C
[b]Isolated yield

Conclusion

We have demonstrated a convenient and efficient method for the synthesis of 3-aryl-benzo[*b*]furans, 3-aryl-naphtho[*b*]furans and their bis-derivatives catalysed by NPABOC@SiO_2. To the best of our knowledge, this is the first example of synthesising bis-derivatives of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans. Mild reaction conditions, environmental compatibility, ease of isolation of product and excellent reusability of the catalyst are the salient features of this protocol.

Experimental

Elemental analyses were performed with a CHN CORDER MT-3 (Yanaco). FTIR spectra were recorded on a Jasco 460 instrument in the range of 360–4000 cm^{-1}. ^1H NMR and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ solution. Mass spectra were recorded on an Agilent Technology (HP) spectrometer operating at an ionisation potential of 70 eV.

Synthesis of n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2 (NPABOC@SiO_2)*

The synthesis of the catalyst was performed in two steps, as illustrated in Scheme 2. First, the silica (25.0 g) was suspended in dry toluene (300 mL), and then an excess amount of 3-chloropropyltrimethoxysilane (25.0 mL) and triethylamine (as a catalyst, 2.5 mL) was added. The suspension was mechanically stirred and refluxed for 48 h. Afterwards, the reaction mixture was cooled to room temperature, transferred to a vacuum glass filter, and washed with toluene, ethanol–water mixture and deionised water in turn and finally with methanol. The resulting solid was dried under vacuum at 60 °C for 4 h to give *n*-propyl chloride@SiO_2. Then, 3-chloropropyl silica (1 g) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.56 g, 5 mmol) were added to a 50 mL round-bottomed flask containing dry acetone (30 mL) connected to a reflux condenser, and refluxed for 36 h. Finally, the reaction mixture was cooled to room temperature, transferred to a vacuum glass filter, and washed with acetone, ethanol and methanol in turn. The resulting solid was dried under vacuum at 50 °C for 4 h to give NPABOC@SiO_2 as a white powder.[19] The catalyst was characterised by FTIR spectroscopy, elemental analysis and chlorimetery.

For NPABOC@SiO_2, the IR spectra shows C–N^+ stretching at 1660 cm^{-1}, C–N stretching at 1155 cm^{-1}, CH_2 bending at 1477 cm^{-1} and Si–O stretching at 1070 cm^{-1} as a broad bond. These characteristic bands are not observed in the FTIR spectrum of silica and silica-bonded *n*-propyl chloride. We also determined the loading level of DABCO (1.24 mmol g^{-1}) based on the chlorine content by titrimetric analysis, which is shown to be in good agreement with the results obtained from elemental analysis. Nitrogen content of the silica-bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride was 3.54% by elemental analysis. These results prove that the DABCO was successfully linked to the silica bonded *n*-propyl chloride to give NPABOC@SiO_2.

*Synthesis of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans catalysed by NPABOC@SiO_2; general procedure*

In a 25 mL round-bottomed flask, a mixture of phenol or β-naphthol (1 mmol), α-bromoketone (1 mmol) and NPABOC@SiO_2 catalyst (0.3 mmol) was prepared according to Table 2 and the reaction mixture was stirred at 100 °C until the reaction completion. The progress of the reaction was monitored by TLC (eluent: ethyl acetate/petroleum ether, 1:15). After reaction completion, ethyl acetate (5 mL) was added and the catalyst was separated by simple filtration. Evaporation of the solvent followed by purification of the crude product by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:15) afforded the pure product.

*Synthesis of bis-derivatives of 3-aryl-benzo[*b*]furans and 3-aryl-naphtho[*b*]furans catalysed by NPABOC@SiO_2; general procedure*

Resorcinol (1 mmol) or 2,6-naphthalendiol (1 mmol) was reacted with an α-bromoketone (2 mmol) in the presence of NPABOC@SiO_2 catalyst (0.3 mmol) under solvent-free conditions according to Table 2 and the resulting mixture was stirred at 100 °C until the reaction completion. The progress of the reaction was monitored by TLC (eluent: ethyl acetate/petroleum ether, 1:15). The work-up was performed as described in the abovementioned general procedure and the crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:15) to afford the pure product.

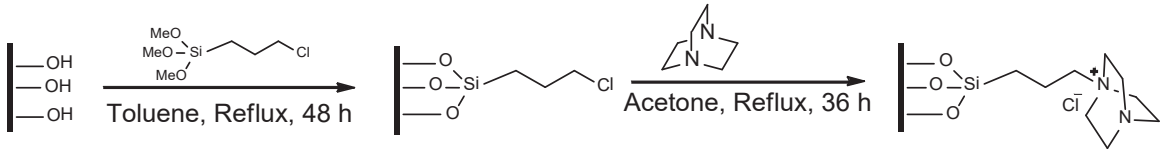
Analytical and spectroscopic data for the known compounds

3-Phenylbenzofuran[21] (Table 2, entry 1): Yellow oil; yield 0.180 g (93%); IR (KBr) (υ cm^{-1}): 3053, 1665, 1601, 1483, 1447; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.71 (d, J = 7.0 Hz, 2H), 7.54–7.49 (m, 2H), 7.47–7.43 (m, 2H), 7.29 (td, J_1 = 7.2, J_2 = 1.3 Hz, 1H), 7.24 (td, J_1 = 7.3, J_2 = 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 141.4, 132.1, 131.0, 129.0, 127.6, 126.1, 124.8, 123.2, 121.4, 120.2, 111.9; MS *m*/*z* (%): 194 (M^+). Anal. calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19; found: C, 86.39; H, 5.28%.

3-(4-Bromophenyl)-5-methylbenzofuran[22] (Table 2, entry 2): Yellow oil; yield 0.263 g (92%); IR (KBr) (υ cm^{-1}): 3048, 2980, 1667, 1608, 1458; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 143.0, 132.0, 131.7, 130.4, 129.7, 128.9, 127.9, 127.0, 125.0, 123.0, 112.7, 22.65; MS *m*/*z* (%): 286 (M^+). Anal. calcd for $C_{15}H_{11}BrO$: C, 62.74; H, 3.86; found: C, 62.56; H, 3.91%.

3-(4-Bromophenyl)benzofuran[23] (Table 2, entry 3): Yellow oil; yield 0.247 g (91%); IR (KBr) (υ cm^{-1}): 3051, 1660, 1601, 1482, 1446; ^1H NMR (400MHz, $CDCl_3$): δ 7.99 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H); 7.36 (t, J = 7.7 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155. 8, 141.5, 132.1, 131.0, 129.0, 126.1, 124.8, 123.2, 121.4, 121.3, 120.1, 111.9; MS *m*/*z* (%): 271 (M^+). Anal. calcd for $C_{14}H_9BrO$: C, 61.57; H, 3.32; found: C, 61.72; H, 3.27%.

3-(4-Chlorophenyl)benzofuran[24] (Table 2, entry 4): Yellow oil; yield 0.201 g (88%); IR (KBr) (υ cm^{-1}): 2935, 1741, 1658, 1607, 1489, 1452; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 2H), 7.73 (s, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 143.5,



Scheme 2 Preparation of *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride immobilised on SiO_2.

132.1, 131.0, 129.0, 126.1, 124.8, 123.2, 121.4, 121.3, 120.1, 111.9; MS *m/z* (%): 228 (M^+). Anal. calcd for $C_{14}H_9ClO$: C, 73.53; H, 3.97; found: C, 73.70; H, 4.07%.

*1-Phenylnaphtho[2,1-*b*]furan*[25] (Table 2, entry 7): Yellow oil; yield 0.224 g (92%,); IR (KBr) (υ cm^{-1}): 3039, 1661, 1602, 1479, 1405; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.73 (s, 1H), 7.66 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.59–7.52 (m, 3H), 7.49 (td, *J* = 7.8, 1.2 Hz, 1H), 7.41 (td, *J* = 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 141.7, 133.1, 130.9, 129.9, 128.9, 128.6, 128.4, 127.9, 126.0, 125.9, 124.5, 124.4, 123.4, 120.8, 112.7; MS *m/z* (%): 244 (M^+). Anal. calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95; found: C, 88.69; H, 5.02%.

*1-(4-Bromophenyl)naphtho[2,1-*b*]furan*[25] (Table 2, entry 8): Yellow oil; yield 0.260 g (81%); IR (KBr) (υ cm^{-1}): 3050, 1657, 1604, 1481, 1451; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.31–7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 141.7, 132.4, 131.8, 131.5, 131.0, 130.0, 129.4, 129.0, 127.9, 126.2, 126.1, 125.0, 124.5, 123.2, 112.7; MS *m/z* (%): 322 (M^+). Anal. calcd for $C_{18}H_{11}BrO$: C, 66.89; H, 3.43; found: C, 66.71; H, 3.38%.

*3,5-Diphenylbenzo[1,2-*b*:5,4-*b′*]difuran*[26] (Table 2, entry 11): Yellow oil; yield 0.202 g (65%); IR (KBr) (υ cm^{-1}): 3014, 1659, 1601, 1481, 1405; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 2H), 7.86 (s, 1H), 7.77 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 4H), 7.50 (m, 4H), 7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 151.7, 130.3, 129.1, 128.9, 127.9, 127.4, 125.1, 121.9, 118.5; MS *m/z* (%): 310 (M^+). Anal. calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55; found: C, 85.31; H, 4.48 %.

Analytical and spectroscopic data for the unknown compounds

3-(4-Bromophenyl)-5-fluorobenzofuran (Table 2, entry 5): Yellow oil; yield 0.246 g (85%); IR (KBr) (υ cm^{-1}): 3041, 1676, 1648, 1579, 1476, 1461; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.73 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.35–7.29 (m, 1H), 6.96–6.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 150.2, 142.5, 132.0, 131.7, 130.3, 129.1, 128.1, 117.5, 113.2, 110.0, 109.7; MS *m/z* (%): 289 (M^+). Anal. calcd for $C_{14}H_8BrFO$: C, 57.76; H, 2.77; found: C, 57.58; H, 2.82%.

3-(4-Bromophenyl)-5-chlorobenzofuran (Table 2, entry 6): Yellow oil; yield 0.256 g (84%); IR (KBr) (υ cm^{-1}): 3051, 1635, 1605, 1489, 1451; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 1H), 7.66 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 142.0, 140.3, 132.1, 131.7, 129.7, 126.8, 125.5, 123.5, 123.1, 121.7, 112.0; MS *m/z* (%): 305 (M^+). Anal. calcd for $C_{14}H_8BrClO$: C, 54.67; H, 2.62; found: C, 54.80; H, 2.70%.

*1-(Biphenyl-4-yl)naphtho[2,1-*b*]furan* (Table 2, entry 9): Yellow oil; yield 0.285 g (89%); IR (KBr) (υ cm^{-1}): 3026, 1669, 1486, 1460; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.70–7.60 (m, 9H), 7.44–7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 141.8, 132.0, 130.9, 130.8, 130.4, 130.2, 129.0, 128.9, 127.7, 127.5, 127.3, 127.1, 126.0, 125.3, 124.4, 124.1, 123.4, 112.7; MS *m/z* (%): 320 (M^+). Anal. calcd for $C_{24}H_{16}O$: C, 89.97; H, 5.03; found: C, 89.78; H, 4.95%.

*1-(Naphthalen-2-yl)naphtho[2,1-*b*]furan* (Table 2, entry 10): Yellow oil; yield 0.253 g (86%); IR (KBr) (υ cm^{-1}): 3002, 1659, 1605, 1392; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.88–7.85 (m, 2H), 7.83–7.81 (m, 1H) 7.72–7.63 (m, 4H), 7.49–7.46 (m, 2H) 7.36–7.32 (m, 1H), 7.24–7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 141.9, 133.5, 132.9, 129.6, 130.8, 130.6, 128.9, 128.5, 128.2, 128.1, 127.9, 126.5, 126.3, 126.1, 126.0, 124.4, 123.2, 112.7; MS *m/z* (%): 294 (M^+). Anal. calcd for $C_{22}H_{14}O$: C, 89.77; H, 4.79; found: C, 89.59; H, 4.84%.

*3,5-Bis(4-bromophenyl)benzo[1,2-*b*:5,4-*b′*]difuran* (Table 2, entry 12): Yellow oil; yield 0.312 g (67%); IR (KBr) (υ cm^{-1}): 3018, 1667, 1607, 1491, 1452; ^1H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 2H), 7.78 (d, *J* = 8.4 Hz, 4H); 7.66 (d, *J* = 8.4 Hz, 4H), 7.57 (s, 1H), 7.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 140.2, 132.3, 132.2, 131.9, 129.4, 129.3, 129.2, 124.2, 115.9; MS *m/z* (%): 465 (M^+). Anal. calcd for $C_{22}H_{12}Br_2O_2$: C, 56.44; H, 2.58; found: C, 56.61; H, 2.53%.

*3,8-Diphenylnaphtho[2,1-*b*:6,5-*b′*]difuran* (Table 2, entry 13): Brown oil; yield 0.266 g (74%); IR (KBr) (υ cm^{-1}): 3011, 1669, 1489, 1464; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.64–7.57 (m, 3H), 7.47–7.41 (m, 2H), 7.39–7.35 (m, 1H), 7.24–7.21 (m, 3H), 7.17–7.10 (m, 2H), 7.08–7.04 (m, 2H), 6.96–6.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 141.4, 132.1, 131.0, 129.0, 126.1, 124.8, 123.2, 121.3, 120.1, 111.9; MS *m/z* (%): 360 (M^+). Anal. calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47; found: C, 86.48; H, 4.35%.

*3,8-Bis(4-bromophenyl)naphtho[2,1-*b*:6,5-*b′*]difuran* (Table 2, entry 14): Brown oil; yield 0.391 g (76%); IR (KBr) (υ cm^{-1}): 3009, 1669, 1491, 1466; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.72–7.60 (m, 7H), 7.44–7.41 (m, 2H), 7.38–7.34 (m, 1H), 7.33–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 141.1, 132.0, 131.7, 125.1, 124.6, 123.9, 123.2, 122.4, 117.4, 109.9; MS *m/z* (%): 515 (M^+). Anal. calcd for $C_{26}H_{14}Br_2O_2$: C, 60.26; H, 2.72; found: C, 60.48; H, 2.67%.

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