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Facile synthesis of regio-isomeric naphthofurans and benzodifurans

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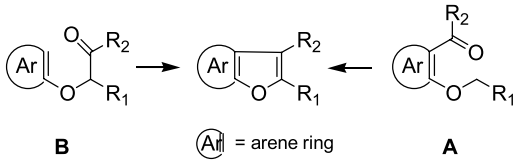
Abstract—Naphtho[1,2-*b*]furans **1a–f**, naphtho[2,1-*b*]furans **2a–f**, benzo[1,2-*b*:5,4-*b*′]difurans **3a–b**, benzo[1,2-*b*:4,5-*b*′]difurans **4a–b**, and benzo[1,2-*b*:4,3-*b*′]difurans **5a–b** were synthesized by base-catalyzed cyclization reaction of the corresponding *o*-alkoxybenzoylarene derivatives. The *o*-alkoxybenzoylarenes were obtained from the etherification reaction of the *o*-hydroxybenzoylarenes, which were prepared either by the reaction of methoxyarenes with benzoyl chloride in the presence of aluminum chloride or by photo-Fries rearrangement of aryl benzoates.

1. Introduction

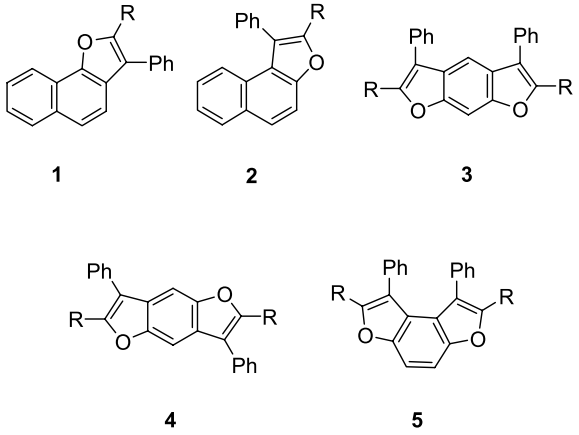
Arene ring-fused furans have attracted widespread interest in view of their presence in natural products, and their biological and pharmacological activities.[1–4] Among arenofurans, benzofurans have been the subject of the most extensive studies and numerous synthetic methods have been developed for them.[1,2,5–7] Compared to benzofurans, the reports on the synthesis of naphthofurans[3,5,8] and benzodifurans[4,9–11] are rather limited, though many of the extended arenofurans exhibit interesting biological properties[3,4] and have potential applications as fluorescent dyes and probes, and as photosensitizers.[9,12]

A major route for the synthesis of various arene ring-fused furan derivatives is the intramolecular formation of a furan moiety starting from properly substituted arene compounds via dehydrative cyclization of either *o*-alkoxycarbonyl compounds of type **A**[2,4b–d,6,7a,8b–e,9–11] or α-aryloxycarbonyl compounds of type **B** (Scheme 1).[5b–d] For the efficient synthesis of variously substituted benzodifurans and naphthofurans, availability of the corresponding starting materials **A** or **B** and facile methods of dehydrative cyclization reaction of the precursors are the key factors.



Scheme 1. A major route for the synthesis of arene ring-fused furan derivatives.

We have been interested in the preparation of various alkoxybenzoylarene derivatives **A** and their photocyclization reaction leading to benzo[*b*]furan[6] and benzodifuran ring systems.[10,11] However, we could not obtain naphthofurans and benzodifurans other than benzo[1,2-*b*:5,4-*b*′]difuran from the photocyclization reactions of the corresponding alkoxybenzoylarenes.[11] In this paper, we describe facile syntheses of regioisomeric naphthofurans **1–2** and benzodifurans **3–5** by base-catalyzed dehydrative cyclization reaction of appropriate *o*-alkoxybenzoylarene derivatives.



Keywords: Naphtho[1,2-*b*]furan; Naphtho[2,1-*b*]furan; Benzo[1,2-*b*:4,5-*b*′]difuran; Benzo[1,2-*b*:5,4-*b*′]difuran; Benzo[1,2-*b*:4,3-*b*′]difuran.
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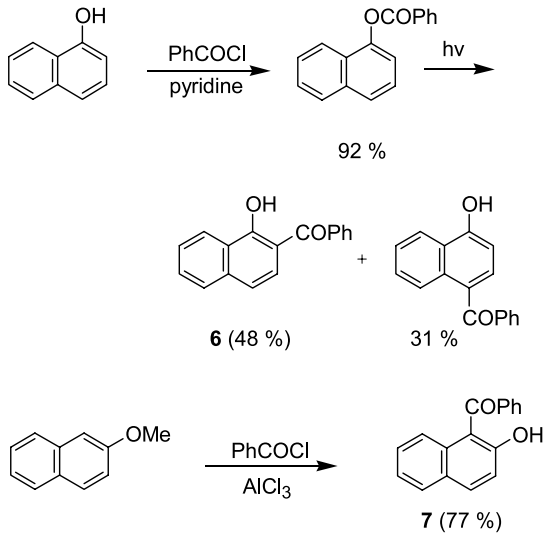
2. Results and discussion

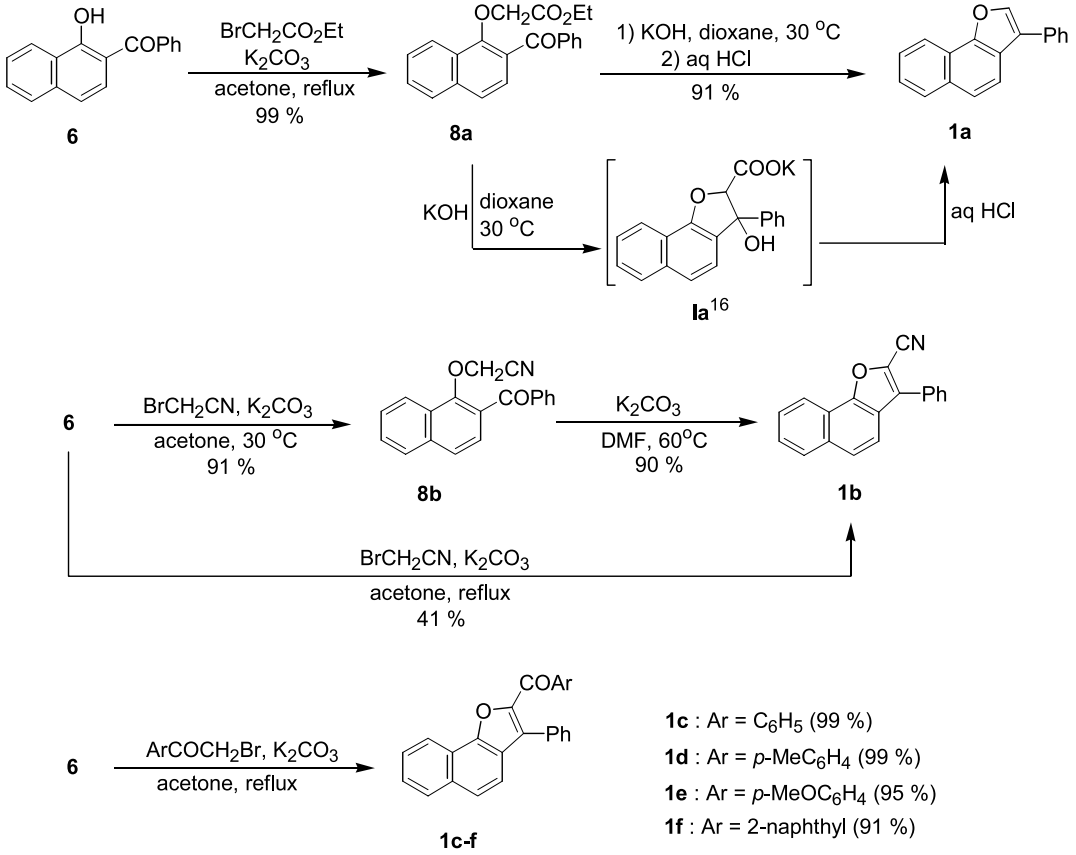
2.1. Synthesis of naphthofurans 1 and 2

Regioisomeric *o*-hydroxybenzoylnaphthalenes **6** and **7**, the starting materials for the naphthofurans **1** and **2**, were prepared as shown in Scheme 2. 2-Benzoyl-1-naphthol **6** was prepared in 48% yield from photo-Fries rearrangement of 1-naphthyl benzoate in methanol, which also gave the *p*-isomer, 4-benzoyl-1-naphthol as a co-product in 31% yield: Crouse et al. reported that photoirradiation of 1-naphthyl benzoate gave the *o*-isomer **6** with 47% yield without the *para* isomer,[13] while Gu et al. reported that both isomers were obtained with 1:1 ratio.[14] 1-Benzoyl-2-naphthol **7** was obtained in 77% yield from the reaction of 2-methoxynaphthalene with benzoyl chloride in the presence of $AlCl_3$. The corresponding reaction of 1-methoxynaphthalene gave 4-benzoyl-1-methoxynaphthalene in 94% yield without formation of any 2-benzoylated products. It is noteworthy that the $AlCl_3$-catalyzed benzoylation reaction of 2-methoxynaphthalene gives demethylated product **7**, while the same reaction of 1-methoxynaphthalene gives non-demethylated product, 4-benzoyl-1-methoxynaphthalene. Such selective demethylation of methoxy group *ortho* to carbonyl group had previously been reported in the reaction of aryl methyl ether with $AlCl_3$.[15]

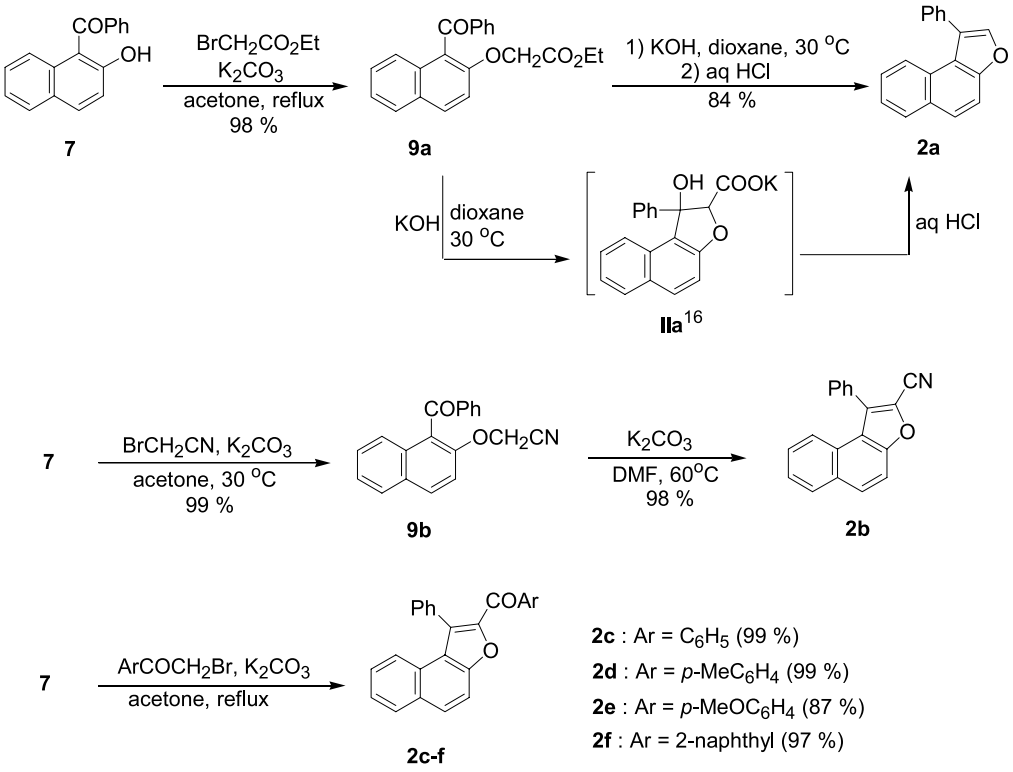


Scheme 2. Preparation of *o*-benzoylhydroxynaphthalenes **6** and **7**.

o-Alkoxybenzoylnaphthalenes **8** and **9** were prepared with 91–99% yields by reacting *o*-benzoylnaphthols **6** and **7** with alkyl halide in the presence of potassium carbonate in acetone. It is known that *o*-alkoxy-substituted benzophenones photocyclize readily to benzo[*b*]furans via intramolecular δ-hydrogen abstraction.[6,9–11] Thus, we attempted photocyclization reaction of **8a** and **9a** to obtain the corresponding naphthofurans. However, irradiation of a solution of **8a** or **9a** in various solvents (benzene, methanol, *t*-butanol, or cyclohexane) with either 350 or 254 nm lamps did not produce any significant amounts of cyclized products and most of the starting materials were recovered. The failure of the photocyclization reaction made us to try base-catalyzed cyclization reaction and the reaction



Scheme 3. Synthesis of naphtho[1,2-*b*]furan derivatives **1a–f**.

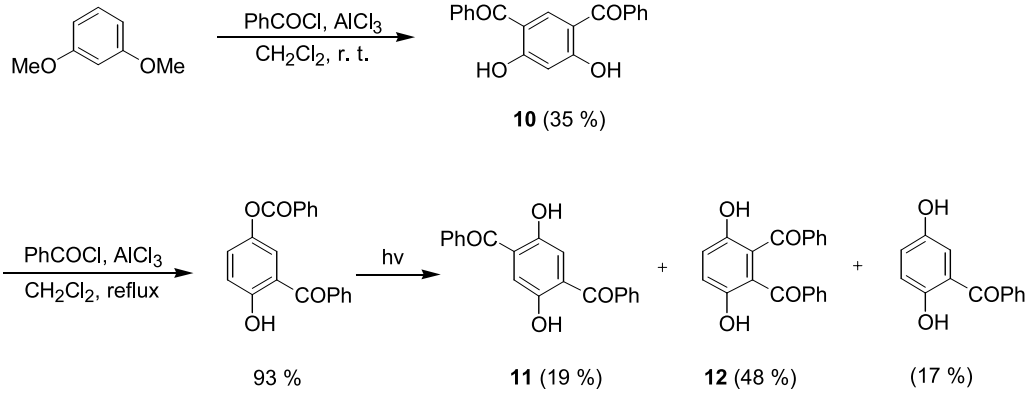


Scheme 4. Synthesis of naphtho[2,1-*b*]furan derivatives **2a–f**.

provided naphthofurans **1** and **2** in excellent yields (84–99%). The synthetic routes are summarized in Schemes 3 and 4.

Depending on the α-substituent in the alkyl halide, the reactions of **6** and **7** with alkyl halides in the presence of K_2CO_3 in acetone either stop at the alkylation stage or further proceed to the cyclization/dehydration step. When the α-substituent is ethoxycarbonyl, *o*-alkoxybenzoylnaphthalene **8a** and **9a** were obtained at reflux temperature of acetone. Treatment of **8a** and **9a** with KOH in dioxane at 30 °C produced **Ia** and **IIa**, respectively.[16] Acidification of the salts **Ia** and **IIa** with aq HCl resulted in decarboxylative dehydroxylation to provide 3-phenylnaphtho[1,2-*b*]furan **1a** and 1-phenylnaphtho[2,1-*b*]furan **2a**, respectively: **1a** and/or **2a** had been previously prepared either by cyclodehydration of the corresponding 2-naphthyloxy-1-phenylethanone, type **B** starting material,[5b–d] or by cyclofragmentation of epoxysulfone.[5a] Chatterjea et al. reported that **9a** is cyclized to 2-ethoxycarbonyl-1-phenylnaphtho[2,1-*b*]furan by sodium/ethanol.[8d] However, repetition of the reaction by us gave not only the reported product, but also its hydrolyzed product, 1-phenylnaphtho[2,1-*b*]furan-2-carboxylate and decarboxylated product **2a** with poorly reproducible products ratios.

The naphthofurans **1b** and **2b** were obtained in overall yields of 82 and 97% yields, respectively, from the two-step reactions of **6** and **7** with bromoacetonitrile involving isolated **8b** and **9b** intermediates. The one-step reaction of **6** to produce **1b** in refluxing acetone solution without isolating the intermediate **8b** gave much low yield, 41%. When the α-substituents in the alkyl halide are benzoyl and napthoyl groups, alkylation and then cyclization/dehydration



Scheme 5. Preparation of dibenzoyldihydroxybenzenes **10–12**.[9,10,15]

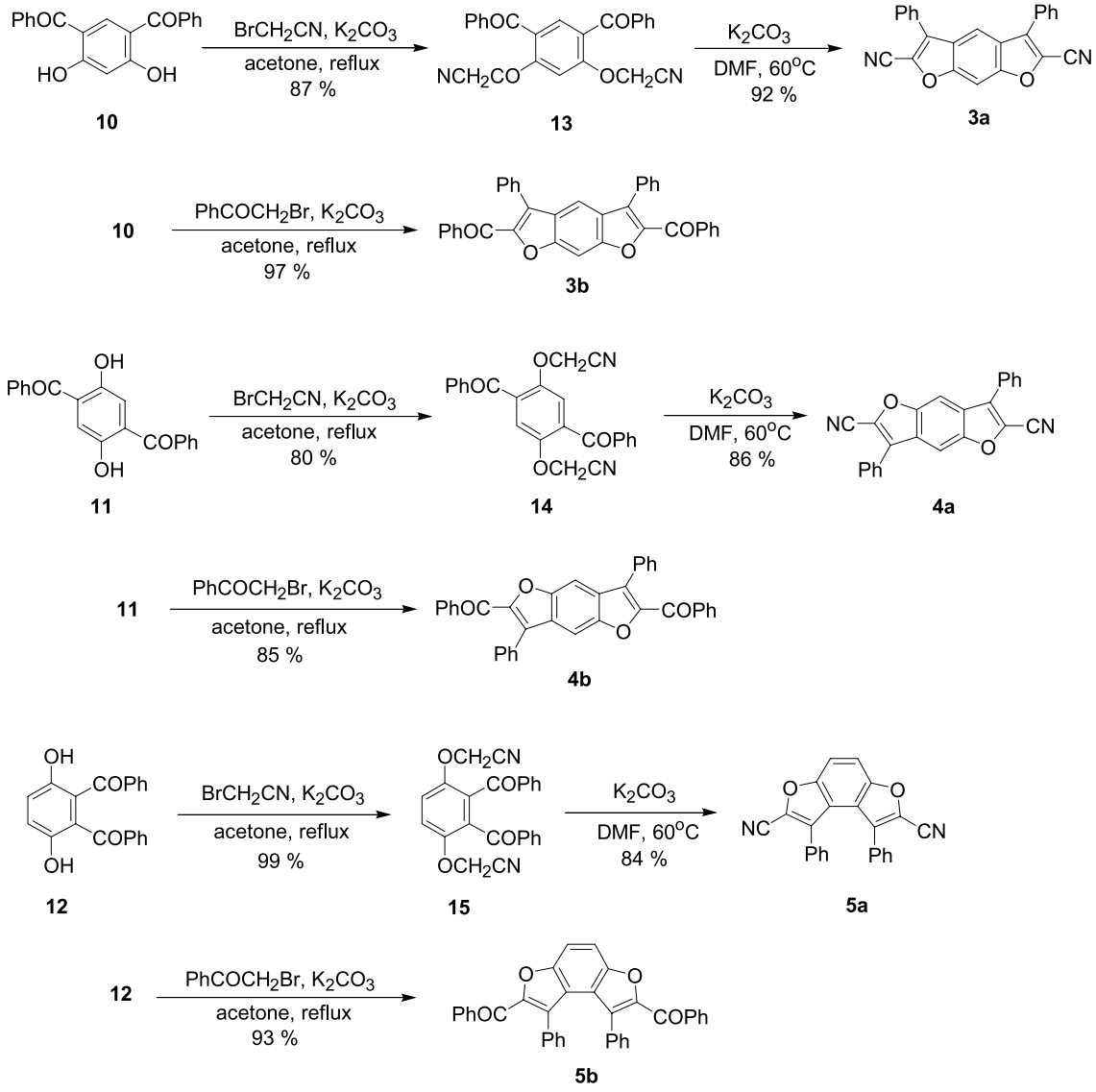
reactions proceeded in one pot at refluxing temperature of acetone to give the corresponding naphthofurans **1c–f** and **2c–f** in 87–99% yields.[17]

2.2. Synthesis of regioisomeric benzodifuran derivatives 3–5

Regioisomeric dihydroxydibenzoylbenzenes **10–12**, starting materials for the synthesis of the benzodifurans **3–5**, were prepared by the reported procedures (Scheme 5).[9,10,15] The reaction of 1,3-dimethoxybenzene with benzoyl chloride in the presence of aluminum chloride provided 1,5-dibenzoyl-2,4-dihydroxybenzene **10** in 35% yield.[9,10] 2,5-Dibenzoyl-1,4-dihydroxybenzene **11** and 2,3-dibenzoyl-1,4-dihydroxybenzene **12** were obtained in two steps from 1,4-dimethoxybenzene and separated.[15]

Alkylation of **10–12** to dialkoxydibenzoylbenzenes **13–15** and subsequent dehydrative cyclization reactions of **13–15** to produce **3–5** were carried out in the same manner described for the synthesis of naphthofurans **1** and **2**, which are shown in Scheme 6. For cyano-derivatives **3a–5a**, alkylated intermediates **13–15** were isolated and cyclization/dehydration of the intermediates gave the desired products with the overall yields of 69–83%. For **3b–5b**, alkylation and dehydrative cyclization reactions proceeded in one pot at refluxing temperature of acetone to give the corresponding benzodifurans in 85–97% yields: the synthesis of **3b** from the same starting materials, but by phase transfer catalytic method or microwave irradiation had been reported.[4d]

The symmetrical nature of the compounds **3–5** is manifested in their NMR spectra. Based on the symmetry of the compounds, the expected number of ^{13}C NMR peaks is 11 for **3a**, 10 for **4a** and **5a**, 15 for **3b**, and 14 for **4b** and **5b**. The actual carbon numbers present in the compounds are 24 for the **a** series and 36 for the **b** series. The observed number of peaks in the ^{13}C NMR spectra exactly matches the expected number or one less number due to overlapping.



Scheme 6. Synthesis of various regioisomeric benzodifurans **3–5**.

3. Conclusions

Facile synthetic methods for various regioisomeric naphthofurans **1** and **2** and benzodifurans **3–5** have been developed. The starting materials for the syntheses, regioisomeric *o*-hydroxybenzoylarenes, were prepared either by the reaction of methoxyarenes with benzoyl chloride in the presence of aluminum chloride or by photo-Fries rearrangement of aryl benzoates, depending on the positions of the substituents. The allkylation of *o*-hydroxybenzoylarenes followed by cyclization/dehydration reactions afforded the desired arenofurans in excellent yields.

4. Experimental

4.1. General

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained at 400 and 100 MHz, respectively, using tetramethylsilane (in $CDCl_3$) or residual undeuterated solvent (in DMSO-d_6 and D_2O) as an internal standard.

4.2. Preparation of 2-benzoyl-1-naphthol 6

Benzoyl chloride (3.51 g, 25.0 mmol) in dichloromethane (50 mL) was added slowly to a solution of 1-naphthol (3.00 g, 20.8 mmol) and pyridine (6.58 g, 83.2 mmol) in dichloromethane (250 mL) and refluxed for 3 h under nitrogen atmosphere. The reaction mixture was washed with 10% aqueous HCl and then dried with anhydrous sodium sulfate. The concentrated reaction mixture was purified by silica gel column chromatography (eluent: 9:1 hexane–ethyl acetate) to give 1-naphthyl benzoate (4.75 g, 92%): mp 58–59 °C (lit.[13] 47–48 °C). A methanol solution (870 mL) of 1-naphthyl benzoate (4.75 g, 19.1 mmol) in a quartz vessel was purged with nitrogen for 1 h and then irradiated under nitrogen with 254 nm mercury lamps using RPR-100 photochemical reactor (Southern New England Ultraviolet Company) for 17 h. The reaction mixture was concentrated and purified by silica gel column chromatography eluting with 9:1 hexane–ethyl acetate to provide 2.28 g (48%) of 2-benzoyl-1-naphthol **6** and 1.47 g (31%) of 4-benzoyl-1-napththol.

2-Benzoyl-1-naphthol **6**: mp 70–72 °C (lit. 63–64 °C;[13] 70.85 °C[18]); ^{1}H NMR ($CDCl_3$) δ 13.95 (s, 1H), 8.52 (d, 1H, J=8 Hz), 7.75 (d, 1H, J=8 Hz), 7.71 (d, 2H, J=8 Hz), 7.64 (t, 1H, J=8 Hz), 7.61–7.49 (m, 5H), 7.21 (d, 1H, J=9 Hz).

4-Benzoyl-1-napththol: mp 164–165 °C (lit. 166–167 °C[19]); ^{1}H NMR (DMSO-d_6) δ 11.10 (br s, 1H), 8.33 (d, 1H, J=8 Hz), 8.26 (dd, 1H, J=8, 2 Hz), 7.71 (d, 2H, J=8 Hz), 7.63 (t, 1H, J=8 Hz), 7.60–7.49 (m, 5H), 6.92 (d, 1H, J=8 Hz).

4.3. Reaction of 2-methoxynaphthalene with benzoyl chloride: preparation of 7

A solution of 2-methoxynaphthalene (1.00 g, 6.32 mmol) and benzoyl chloride (1.06 g, 7.58 mmol) in dichloromethane (30 mL) was added slowly to the suspension of $AlCl_3$ (1.80 g, 13.9 mmol) in dichloromethane (30 mL), and stirred for 20 h at room temperature under nitrogen atmosphere. Then the reaction mixture was poured to a beaker containing ice water (45 mL) and conc HCl (15 mL) and stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with dichloromethane three times. The organic layers were combined, dried with anhydrous sodium sulfate and concentrated. The residue was purified by silica gel column chromatography (eluent: 5:1 hexane–ethyl acetate) and then recrystallization from dichloromethane to afford 1-benzoyl-2-naphthol **7** (1.22 g, 77%): mp 139–141 °C (lit. 141.05 °C;[18] 135–137 °C[8d]); ^{1}H NMR ($CDCl_3$) δ 11.20 (s, 1H), 7.93 (d, 1H, J=9 Hz), 7.74 (d, 1H, J=8 Hz), 7.62 (d, 2H, J=8 Hz), 7.55 (t, 1H, J=7 Hz), 7.40 (t, 2H, J=8 Hz), 7.31–7.22 (m, 3H), 7.15 (t, 1H, J=8 Hz).

The same reaction using 1-methoxynaphthalene (0.200 g, 1.26 mmol) instead of 2-methoxynapthalene gave 94% yield (0.309 g) of 4-benzoyl-1-methoxynaphthalene:[20] ^{1}H NMR ($CDCl_3$) δ 8.39–8.33 (m, 2H), 7.83 (d, 2H, J=8 Hz), 7.61–7.42 (m, 6H), 6.78 (d, 1H, J=8 Hz), 4.05 (s, 3H).

4.4. Preparation of 1a and 2a

A solution of ethyl bromoacetate (1.21 g, 7.25 mmol) in acetone (50 mL) was added to the reaction mixture of benzoylnaphthol (**6** or **7**, 1.50 g, 6.04 mmol) and potassium carbonate (3.34 g, 24.2 mmol) in acetone (100 mL) and heated at reflux for 2 h under nitrogen atmosphere. After removing potassium carbonate by filtration, the reaction mixture was concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: 5:1 hexane–ethyl acetate) to give the alkylated compound, **8a** or **9a**.

4.4.1. Compound 8a. Yield, 99%; mp 68–70 °C; ^{1}H NMR ($CDCl_3$) δ 8.43 (dd, 1H, J=6, 3 Hz), 7.90–7.85 (m, 3H), 7.68 (d, 1H, J=8 Hz), 7.61–7.56 (m, 3H), 7.47–7.42 (m, 3H), 4.59 (s, 2H), 4.18 (q, 2H, J=7 Hz), 1.23 (t, 3H, J=7 Hz); ^{13}C NMR ($CDCl_3$) δ 196.16, 168.41, 153.47, 137.17, 135.77, 133.26, 130.08, 128.33, 127.90, 127.76, 127.64, 127.01, 126.79, 125.72, 123.99, 123.30, 72.36, 61.15, 14.11. IR (KBr): 1758, 1662, 1281, 1196, 1100 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43%. Found: C, 75.46; H, 5.41%.

4.4.2. Compound 9a. Yield, 98%; mp 78–80 °C (lit.[8d] oil); ^{1}H NMR ($CDCl_3$) δ 7.93–7.88 (m, 3H), 7.85–7.81 (m, 1H), 7.57–7.52 (m, 2H), 7.44–7.35 (m, 4H), 7.18 (d, 1H, J=9 Hz), 4.63 (s, 2H), 4.16 (q, 2H, J=7 Hz), 1.20 (t, 3H, J=7 Hz); ^{13}C NMR ($CDCl_3$) δ 197.08, 168.46, 152.22, 137.69, 133.42, 131.60, 131.04, 129.67, 129.22, 128.43, 128.02, 127.43, 124.49, 124.20, 123.87, 113.63, 66.47, 61.30, 14.11.

To the reaction flask containing potassium hydroxide (0.280 g, 5.00 mmol) in dioxane (20 mL), **8a–9a** (0.500 g, 1.50 mmol) was added and stirred at 30 °C for 1 h. The reaction mixture was concentrated under reduced pressure to give a solid residue. The solid residue was dissolved in water (10 mL), acidified with aq HCl, stirred for 1 h at 80 °C, and then extracted with ether. The ether layers were

dried, concentrated, and then purified by silica gel column chromatography (eluent: 5:1 hexane–ethyl acetate) to give **1a**–**2a**.

4.4.3. Compound 1a. Yield, 91%; mp 111–113 °C; ^{1}H NMR ($CDCl_3$) δ 8.33 (d, 1H, J=8 Hz), 7.93 (d, 1H, J=8 Hz), 7.90 (s, 1H), 7.86 (d, 1H, J=9 Hz), 7.71–7.66 (m, 3H), 7.59 (t, 1H, J=8 Hz), 7.52–7.45 (m, 3H), 7.37 (t, 1H, J=8 Hz); ^{13}C NMR ($CDCl_3$) δ 151.31, 140.38, 132.11, 131.40, 128.91, 128.18, 127.58, 127.39, 126.35, 125.27, 123.57, 123.42, 121.83, 121.53, 120.03, 118.66. IR (KBr): 1558, 1521, 1445, 1387, 1128 cm^{-1}. Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95%. Found: C, 88.52; H, 4.92%.

4.4.4. Compound 2a. Yield, 84%; oil; ^{1}H NMR ($CDCl_3$) δ 7.98 (d, 1H, J=8 Hz), 7.93 (d, 1H, J=8 Hz), 7.76 (d, 1H, J=9 Hz), 7.69 (d, 1H, J=9 Hz), 7.68 (s, 1H), 7.62–7.58 (m, 2H), 7.53–7.46 (m, 3H), 7.42 (t, 1H, J=8 Hz), 7.34 (t, 1H, J=8 Hz); ^{13}C NMR ($CDCl_3$) δ 153.04, 141.59, 133.02, 130.72, 129.79, 128.82, 128.51, 128.24, 127.78, 125.89, 125.86, 124.37, 124.27, 123.30, 120.65, 112.58. IR (KBr): 1525, 1489, 1386, 1225, 1109 cm^{-1}. Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95%. Found: C, 88.64; H, 4.84%.

When the solid residues obtained from the reaction of **8a** and **9a** with KOH were washed with abs. ethanol several times to remove potassium hydroxide, the potassium salts of 3-hydroxy-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylic acid **Ia** and 1-hydroxy-1-phenyl-1,2-dihydronaphtho[2,1-*b*]furan-2-carboxylic acid **IIa** were obtained, respectively.[16]

4.4.5. Compound Ia. Mp 303 °C (dec); ^{1}H NMR (D_2O) δ 8.13 (d, 1H, J=8 Hz), 7.79 (d, 1H, J=8 Hz), 7.58 (t, 1H, J=8 Hz), 7.52 (t, 1H, J=8 Hz), 7.35–7.27 (m, 6H), 6.94 (d, 1H, J=9 Hz), 4.95 (s, 1H); ^{13}C NMR (D_2O) δ 174.98, 167.37, 156.55, 144.97, 136.51, 129.92, 129.69, 129.25, 128.94, 127.89, 126.09, 123.47, 123.35, 123.23, 121.94, 95.67, 85.23. IR (KBr): 3500–2500 (broad), 1607, 1399, 1064 cm^{-1}. Anal. Calcd for $C_{19}H_{13}KO_4$: C, 66.26; H, 3.80%. Found: C, 66.05; H, 3.95%.

4.4.6. Compound IIa. Mp 280–281 °C (dec); ^{1}H NMR (D_2O) δ 7.80 (d, 1H, J=9 Hz), 7.67 (d, 1H, J=8 Hz), 7.30–7.25 (m, 3H), 7.16–7.08 (m, 4H), 7.03 (t, 1H, J=7 Hz), 6.94 (t, 1H, J=7 Hz), 4.98 (s, 1H); ^{13}C NMR (D_2O) δ 175.07, 159.07, 145.75, 134.11, 131.75, 130.83, 130.67, 130.01, 128.95, 128.76, 127.46, 125.03, 123.74, 122.46, 114.26, 96.13, 85.49. IR (KBr): 3500–2500 (broad), 1601, 1408, 1239 cm^{-1}. Anal. Calcd for $C_{19}H_{13}KO_4$: C, 66.26; H, 3.80%. Found: C, 66.28; H, 3.79%.

4.5. Preparation of 1b and 2b

A solution of bromoacetonitrile (0.116 g, 0.967 mmol) in acetone (5 mL) was added dropwise to the reaction mixture of benzoylnaphthol, **6**–**7** (0.200 g, 0.806 mmol) and potassium carbonate (0.446 g, 3.22 mmol) in acetone (10 mL) and stirred at 30 °C for 3–6 h under nitrogen atmosphere. After removing potassium carbonate by filtration, the reaction mixture was concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: 5:1 hexane–ethyl acetate) to give **8b**–**9b**.

4.5.1. Compound 8b. Yield, 91%; oil; ^{1}H NMR ($CDCl_3$) δ 8.29–8.26 (m, 1H), 7.94–7.91 (m, 1H), 7.84–7.81 (m, 2H), 7.76 (d, 1H, J=8 Hz), 7.68–7.58 (m, 3H), 7.49–7.43 (m, 3H), 4.84 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 195.68, 152.25, 136.97, 135.81, 133.59, 130.15, 128.47, 128.26, 128.08, 127.55, 127.48, 125.59, 125.22, 122.61,115.11, 60.57 (one sp^2 carbon is missing due to overlap). IR (neat): 1662, 1597, 1447, 1338, 1281, 1246, 1090 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88%. Found: C, 79.50; H, 4.63; N, 4.85%.

4.5.2. Compound 9b. Yield, 99%; mp 90–91 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (d, 1H, J=9 Hz), 7.90–7.87 (m, 1H), 7.84–7.81 (m, 2H), 7.59 (t, 1H, J=7 Hz), 7.55–7.52 (m, 1H), 7.47–7.39 (m, 5H), 4.75 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 196.31, 150.69, 137.35, 133.90, 131.55, 131.46, 130.04, 129.56, 128.72, 128.19, 127.81, 125.61, 125.43, 124.52, 114.85, 114.31, 55.35. IR (KBr): 1665, 1592, 1579, 1509, 1281, 1242, 1219 cm^{-1}. Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88%. Found: C, 79.46; H, 4.63; N, 4.89%.

The reaction mixture of potassium carbonate (0.385 g, 2.78 mmol) and **8b**–**9b** (0.200 g, 0.696 mmol) in DMF (8 mL) was stirred at 60 °C for 3.5 h. After removing potassium carbonate by filtration, the filtrate was concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: 2:1 hexane–dichloromethane for **1b**; 2:1 hexane–ethyl acetate for **2b**) to give **1b**–**2b**.

4.5.3. Compound 1b. Yield, 90%; mp 163–164 °C; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, 1H, J=8 Hz), 7.96 (d, 1H, J=8 Hz), 7.80–7.76 (m, 4H), 7.70–7.56 (m, 4H), 7.55–7.50 (m, 1H); ^{13}H NMR ($CDCl_3$) δ 152.47, 134.18, 133.16, 129.45, 129.31, 128.66, 128.41, 128.30, 127.40, 127.27, 125.54, 122.80, 120.88, 120.81, 120.71, 118.31, 112.72. IR (KBr): 2217, 1459, 1444, 1378, 1197, 1077 cm^{-1}. Anal. Calcd for $C_{19}H_{11}NO$: C, 84.74; H, 4.12; N, 5.20%. Found: C, 84.76; H, 4.12; N, 5.04%.

4.5.4. Compound 2b. Yield, 98%; mp 99–102 °C; ^{1}H NMR ($CDCl_3$) δ 7.96–7.90 (m, 3H), 7.68–7.56 (m, 6H), 7.51 (t, 1H, J=8 Hz), 7.41 (t, 1H, J=8 Hz); ^{13}C NMR ($CDCl_3$) δ 154.19, 135.37, 130.99, 130.53, 129.54, 129.48, 129.39, 129.17, 129.05, 127.82, 127.26, 125.57, 124.51, 122.95, 119.58, 112.20, 112.07. IR (KBr): 2229, 1584, 1530, 1444, 1262, 1218 cm^{-1}. Anal. Calcd for $C_{19}H_{11}NO$: C, 84.74; H, 4.12; N, 5.20%. Found: C, 84.71; H, 4.12; N, 5.18%.

4.6. Preparation of 1c–f and 2c–f

A solution of the corresponding bromoacetophenone or bromoacetonaphthone (0.484 mmol) in acetone (4 mL) was added dropwise to the reaction mixture of benzoylnaphthol, **6**–**7** (0.100 g, 0.403 mmol) and potassium carbonate (0.223 g, 1.61 mmol) in acetone (4 mL) and heated at reflux for 2–6 h under nitrogen atmosphere until the benzoylnaphthol disappeared. After removing potassium carbonate

by filtration, the reaction mixture was concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: dichloromethane for **1c** and **1e**; 1:1 hexane–dichloromethane for **1d**, **1f**, **2d**, and **2e**; 2:1 hexane–ethyl acetate for **2c** and **2f**) to give the corresponding naphthofurans.

4.6.1. Compound 1c. Yield, 99%; mp 119–120 °C; ^{1}H NMR ($CDCl_3$) δ 8.42 (d, 1H, J=8 Hz), 7.98–7.94 (m, 3H), 7.72 (d, 1H, J=9 Hz), 7.67–7.55 (m, 5H), 7.51 (t, 1H, J=7 Hz), 7.44–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 184.75, 151.09, 146.91, 137.51, 133.35, 132.39, 130.97, 130.85, 130.00, 129.82, 128.40, 128.26, 127.99, 126.98, 126.87, 124.86, 123.73, 121.23, 120.99, 119.17 (one carbon is missing due to overlap). IR (KBr): 1643, 1539, 1490, 1339, 1288, 1213 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_2$: C, 86.19; H, 4.63%. Found: C, 86.13; H, 4.72%.

4.6.2. Compound 1d. Yield, 99%; mp 157–160 °C; ^{1}H NMR ($CDCl_3$) δ 8.41 (d, 1H, J=8 Hz), 7.95 (d, 1H, J=8 Hz), 7.92 (d, 2H, J=8 Hz), 7.71 (d, 1H, J=8 Hz), 7.67–7.56 (m, 5H), 7.45–7.35 (m, 3H), 7.21 (d, 2H, J=8 Hz), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 184.36, 150.91, 147.13, 143.25, 134.88, 133.27, 131.08, 130.42, 130.06, 129.99, 128.76, 128.39, 128.25, 128.16, 126.87, 126.82, 124.77, 123.76, 121.27, 120.94, 119.19, 21.73. IR (KBr): 1637, 1605, 1545, 1385, 1340, 1165 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%. Found: C, 86.16; H, 5.08%.

4.6.3. Compound 1e. Yield, 95%; mp 180–181 °C; ^{1}H NMR ($CDCl_3$) δ 8.42 (d, 1H, J=8 Hz), 8.04 (d, 2H, J=9 Hz), 7.96 (d, 1H, J=8 Hz), 7.72 (d, 1H, J=8 Hz), 7.68–7.57 (m, 5H), 7.45–7.35 (m, 3H), 6.90 (d, 2H, J=9 Hz), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 183.24, 163,14, 150.78, 147.24, 133.20, 132.13, 131.17, 130.18, 130.01, 129.97, 128.40, 128.29, 128.14, 126.79, 124.72, 123.74, 121.27, 120.89, 119.17, 113.40, 55.46 (one sp^2 carbon is missing due to overlap). IR (KBr): 1626, 1596, 1543, 1508, 1488, 1165 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_3$: C, 82.52; H, 4.79%. Found: C, 82.58; H, 4.67%.

4.6.4. Compound 1f. Yield, 91%; mp 162–164 °C; ^{1}H NMR ($CDCl_3$) δ 8.55 (s, 1H), 8.42 (d, 1H, J=8 Hz), 8.04 (dd, 1H, J=8, 2 Hz), 7.97 (d, 1H, J=7 Hz), 7.88–7.84 (m, 3H), 7.75–7.55 (m, 7H), 7.51 (t, 1H, J=7 Hz), 7.38 (t, 2H, J=7 Hz), 7.32–7.28 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 184.59, 151.14, 147.15, 135.18, 134.71, 133.38, 132.23, 132.01, 131.04, 130.85, 129.99, 129.46, 128.44, 128.30, 128.24, 127.87, 127.63, 127.00, 126.93, 126.46, 125.42, 124.91, 123.82, 121.31, 120.98, 119.23 (one carbon is missing due to overlap). IR (KBr): 1739, 1635, 1545, 1361, 1292, 1191 cm^{-1}. Anal. Calcd for $C_{29}H_{18}O_2$: C, 87.42; H, 4.55%. Found: C, 87.44; H, 4.63%.

4.6.5. Compound 2c. Yield, 99%; mp 140–143 °C (lit.[8e] 137 °C); ^{1}H NMR ($CDCl_3$) δ 7.95–7.90 (m, 4H), 7.73 (d, 1H, J=9 Hz), 7.68 (d, 1H, J=8 Hz), 7.51–7.42 (m, 7H), 7.39–7.30 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 184.59, 152.85, 147.67, 137.35, 132.73, 132.28, 131.39, 130.99, 130.25, 129.77, 129.62, 129.15, 128.69, 128.47, 128.25, 127.97, 126.92, 125.14, 123.19, 121.91, 112.65. IR (KBr): 1653, 1646, 1545, 1342, 1333, 1014 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_2$: C, 86.19; H, 4.63%. Found: C, 86.21; H, 4.71%.

4.6.6. Compound 2d. Yield, 99%; mp 122–124 °C (lit.[8e] 105 °C); ^{1}H NMR ($CDCl_3$) δ 7.92 (t, 2H, J=8 Hz), 7.87 (d, 2H, J=8 Hz), 7.73 (d, 1H, J=9 Hz), 7.68 (d, 1H, J=8 Hz), 7.52–7.43 (m, 6H), 7.33 (t, 1H, J=8 Hz), 7.19 (d, 2H, J=8 Hz), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 184.14, 152.66, 147.87, 143.14, 134.73, 132.87, 130.99, 130.98, 130.00, 129.85, 129.75, 129.11, 128.72, 128.68, 128.46, 128.14, 126.85, 125.09, 123.21, 121.94, 112.64, 21.72. IR (KBr): 1635, 1606, 1545, 1343, 1182, 1013 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01%. Found: C, 86.14; H, 5.03%.

4.6.7. Compound 2e. Yield, 87%; mp 144–145 °C (lit.[8e] 180 °C); ^{1}H NMR ($CDCl_3$) δ 8.01 (d, 2H, J=9 Hz), 7.92 (t, 2H, J=9 Hz), 7.73 (d, 1H, J=9 Hz), 7.68 (d, 1H, J=8 Hz), 7.53–7.42 (m, 6H), 7.32 (t, 1H, J=8 Hz), 6.88 (d, 2H, J=9 Hz), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 182.91, 163.03, 152.52, 147.98, 132.96, 132.14, 130.95, 130.64, 130.04, 129.81, 129.76, 129.09, 128.64, 128.46, 128.14, 126.80, 125.04, 123.19, 121.90, 113.36, 112.58, 55.43. IR (KBr): 1643, 1600, 1550, 1489, 1255, 1180 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_3$: C, 82.52; H, 4.79%. Found: C, 82.47; H, 4.96%.

4.6.8. Compound 2f. Yield, 97%; mp 139–142 °C; ^{1}H NMR ($CDCl_3$) δ 8.48 (s, 1H), 7.96 (dd, 1H, J=9, 2 Hz), 7.92 (d, 1H, J=8 Hz), 7.91 (d, 1H, J=9 Hz), 7.86 (d, 1H, J=8 Hz), 7.81 (d, 1H, J=8 Hz), 7.80 (d, 1H, J=8 Hz), 7.74 (d, 1H, J=9 Hz), 7.70 (d, 1H, J=8 Hz), 7.57–7.30 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 184.41, 152.85, 147.86, 135.05, 134.54, 132.75, 132.05, 131.60, 131.33, 130.97, 130.19, 129.71, 129.40, 129.14, 128.68, 128.44, 128.14, 128.12, 127.82, 127.59, 126.89, 126.37, 125.18, 125.12, 123.17, 121.92, 112.64. IR (KBr): 1647, 1623, 1559, 1491, 1361, 1336 cm^{-1}. Anal. Calcd for $C_{29}H_{18}O_2$: C, 87.42; H, 4.55%. Found: C, 87.38; H, 4.69%.

4.7. Preparation of 3a, 4a and 5a

Dibenzoyldihydroxybenzenes **10–12** are available from our earlier studies.[10,15] A solution of bromoacetonitrile (0.166 g, 1.38 mmol) in acetone (5 mL) was added dropwise to the reaction mixture of dibenzoyldihydroxybenzene **10–12** (0.200 g, 0.628 mmol) and potassium carbonate (0.694 g, 5.02 mmol) in acetone (10 mL) and heated at reflux for 2–12 h under nitrogen atmosphere until the dibenzoyldihydroxybenzene disappeared. After removing potassium carbonate by filtration, the reaction mixture was concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: 1:1 hexane–dichloromethane for **13**; 1:9 hexane–ethyl acetate for **15**) to give **13** and **15** with 87 and 99% yields, respectively. In case of **14**, the reaction mixture was concentrated and the residue was washed with water to remove potassium carbonate. Further washing of the residue with cold methanol provided **14** with 80% yield.

4.7.1. Compound 13. Mp 179–180 °C; ^{1}H NMR (DMSO-d_6) δ 7.75 (d, 4H, J=7 Hz), 7.66 (t, 2H, J=7 Hz), 7.53 (t, 4H, J=7 Hz), 7.52 (s, 1H), 7.31 (s, 1H), 4.09 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 193.05, 156.88, 136.84, 133.45, 131.38,

129.19, 128.58, 122.76, 115.45, 99.38, 54.29. IR (KBr): 1661, 1600, 1447, 1262, 1196, 1040 cm^{-1}. Anal. Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07%. Found: C, 72.74; H, 4.03; N, 7.04%.

4.7.2. Compound 14. Mp 245–247 °C; ^1H NMR (DMSO-d_6) δ 7.82 (d, 4H, $J=8$ Hz), 7.72 (t, 2H, $J=7$ Hz), 7.57 (t, 4H, $J=7$ Hz), 7.47 (s, 2H), 5.13 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 193.42, 148.14, 135.95, 134.03, 131.37, 129.39, 128.82, 115.82, 114.20, 54.37. IR (KBr): 1664, 1596, 1448, 1411, 1217, 1049 cm^{-1}. Anal. Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07%. Found: C, 72.89; H, 4.11; N, 6.92%.

4.7.3. Compound 15. Mp 147–150 °C; ^1H NMR ($CDCl_3$) δ 7.70 (d, 4H, $J=8$ Hz), 7.53 (t, 2H, $J=8$ Hz), 7.39 (t, 4H, $J=8$ Hz), 7.25 (s, 2H), 4.63 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 193.44, 149.29, 136.73, 133.80, 131.78, 129.41, 128.44, 115.74, 114.30, 54.77. IR (KBr): 1739, 1669, 1597, 1470, 1450, 1292 cm^{-1}. Anal. Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72; H, 4.07; N, 7.07%. Found: C, 72.74; H, 4.05; N, 7.05%.

The reaction mixture of potassium carbonate (0.558 g, 4.04 mmol) and **13–15** (0.200 g, 0.504 mmol) in DMF (8 mL) was stirred at 60 °C for 2–20 h until the starting material disappeared. After concentrating the reaction mixture, the residue was washed with water and then cold methanol to give **3a** and **4a** with 92 and 86% yields, respectively. In case of **5a**, the reaction mixture was filtered to remove potassium carbonate and then concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: 2:1 hexane–dichloromethane) to give **5a** with 84% yield.

4.7.4. Compound 3a. Mp 295–297 °C; ^1H NMR ($CDCl_3$) δ 8.15 (s, 1H), 7.81 (s, 1H), 7.73 (d, 4H, $J=8$ Hz), 7.63–7.52 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 155.78, 133.16, 129.94, 129.59, 128.39, 127.86, 125.01, 123.93, 114.21, 111.86, 96.15. IR (KBr): 2221, 1626, 1568, 1448, 1342, 1200 cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_2O_2$: C, 79.99; H, 3.36; N, 7.77%. Found: C, 79.96; H, 3.28; N, 7.65%.

4.7.5. Compound 4a. Mp 290–291 °C; ^1H NMR ($CDCl_3$) δ 7.96 (s, 2H), 7.75 (d, 4H, $J=8$ Hz), 7.63–7.53 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 152.91, 133.14, 129.99, 129.59, 128.26, 127.79, 126.83, 125.53, 111.93, 104.14. IR (KBr): 2227, 1571, 1483, 1445, 1419, 1221 cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_2O_2$: C, 79.99; H, 3.36; N, 7.77%. Found: C, 79.95; H, 3.34; N, 7.67%.

4.7.6. Compound 5a. Mp 211–214 °C; ^1H NMR ($CDCl_3$) δ 7.80 (s, 2H), 7.12–7.06 (m, 6H), 6.94 (t, 4H, $J=8$ Hz); ^{13}C NMR ($CDCl_3$) δ 153.65, 134.18, 129.17, 128.55, 128.25, 128.05, 126.16, 118.95, 113.23, 111.71. IR (KBr): 2226, 1559, 1462, 1447, 1412, 1050 cm^{-1}. Anal. Calcd for $C_{24}H_{12}N_2O_2$: C, 79.99; H, 3.36; N, 7.77%. Found: C, 79.91; H, 3.34; N, 7.64%.

4.8. Preparation of 3b, 4b and 5b

A solution of bromoacetophenone (0.413 g, 2.07 mmol) in acetone (5 mL) was added dropwise to the reaction mixture of dibenzoyldihydroxybenzene **10–12** (0.300 g, 0.942 mmol) and potassium carbonate (1.04 g, 7.54 mmol) in acetone (10 mL) and heated at reflux for 15–24 h under nitrogen atmosphere until the starting material disappeared. After concentrating the reaction mixture, the residue was washed with water and then recrystallized from 2:1 acetone–CH_2Cl_2 to give **3b** and **4b** with 97 and 85% yields, respectively. In case of **5b**, the reaction mixture was filtered to remove potassium carbonate and then concentrated. To the residue, water was added and extracted with dichloromethane. The organic layer was dried, concentrated, and then purified by silica gel column chromatography (eluent: 1:1 hexane–dichloromethane) to give **5b** with 93% yield.

4.8.1. Compound 3b. Mp 228–230 °C (lit.[4d] 208–209 °C); ^1H NMR ($CDCl_3$) δ 7.90 (s, 1H), 7.86 (s, 1H), 7.85 (d, 4H, $J=7$ Hz), 7.49–7.43 (m, 6H), 7.36–7.30 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 185.29, 154.83, 148.04, 136.84, 132.67, 130.37, 129.85, 129.67, 129.09, 128.41, 128.00, 126.38, 115.01, 95.61 (one carbon is missing due to overlap). IR (KBr): 1653, 1542, 1445, 1331, 1236 cm^{-1}. Anal. Calcd for $C_{36}H_{22}O_4$: C, 83.38; H, 4.28%. Found: C, 83.39; H, 4.30%.

4.8.2. Compound 4b. Mp 259–260 °C; ^1H NMR ($CDCl_3$) δ 7.91 (d, 4H, $J=8$ Hz), 7.88 (s, 2H), 7.54 (dd, 4H, $J=8$, 2 Hz), 7.49 (t, 2H, $J=7$ Hz), 7.45–7.33 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 185.26, 151.71, 148.59, 136.87, 132.81, 130.42, 129.80, 129.69, 129.08, 128.52, 128.46, 128.06, 104.17 (one carbon is missing due to overlap). IR (KBr): 1640, 1554, 1445, 1333, 1235 cm^{-1}. Anal. Calcd for $C_{36}H_{22}O_4$: C, 83.38; H, 4.28%. Found: C, 83.34; H, 4.25%.

4.8.3. Compound 5b. Mp 185–187 °C; ^1H NMR ($CDCl_3$) δ 7.82 (s, 2H), 7.70 (d, 4H, $J=7$ Hz), 7.40 (t, 2H, $J=8$ Hz), 7.25 (t, 4H, $J=8$ Hz), 6.90 (d, 4H, $J=7$ Hz), 6.85 (t, 2H, $J=8$ Hz), 6.69 (t, 4H, $J=8$ Hz); ^{13}C NMR ($CDCl_3$) δ 185.60, 152.16, 148.67, 136.90, 132.41, 131.21, 129.57, 129.48, 127.93, 127.85, 127.26, 121.66, 112.94 (one carbon is missing due to overlap). IR (KBr): 1653, 1545, 1377, 1268, 1243 cm^{-1}. Anal. Calcd for $C_{36}H_{22}O_4$: C, 83.38; H, 4.28%. Found: C, 83.44; H, 4.32%.

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16. The stereochemistry of the intermediates **Ia** and **IIa** is not clear. However, based on the reports that the corresponding *cis* isomer is preferentially formed from the base-catalyzed cyclization of ethyl 2-acylphenoxyacetates[21,22] and the fact that only one singlet peak at δ 5.0 (C*H*COOK) is observed in their ^{1}H NMR spectra (see Section 4), it can be safely assumed that the structures of **Ia** and **IIa** are *cis* (2-carboxy group and 3-hydroxyl group of the furan ring are *cis*).
17. The synthesis of **2c–e** by the same method, but using ethanol instead of acetone as a solvent had been reported (the reported yield of **2e** was 57% and the yields of **2c** and **2d** were not mentioned).[8e]
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