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Mahmoud Abdul-Aziz

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078

Judith V. Auping and Michael A. Meador

Polymers Branch, Materials Division, NASA Lewis Research Center, Cleveland, Ohio 44135-3191

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A series of substituted 2,3,5,6-tetraarylbenzo[1,2-*b*:5,4-*b*′]difurans **1** was synthesized. This synthesis is based upon the photocyclization of 2,5-dibenzoylresorcinol dibenzyl ethers to the corresponding tetrahydrobenzo[1,2-*b*:5,4-*b*′]difurans. Treatment of the photoproducts with methanesulfonyl chloride in pyridine afforded **1** in overall yields ranging from 30–72%. A number of these compounds have high fluorescence quantum yields (ϕ_f = 0.76–0.90), and their fluorescence spectra exhibit large solvatochromic shifts . These compounds may be suitable for use as fluorescent probes.

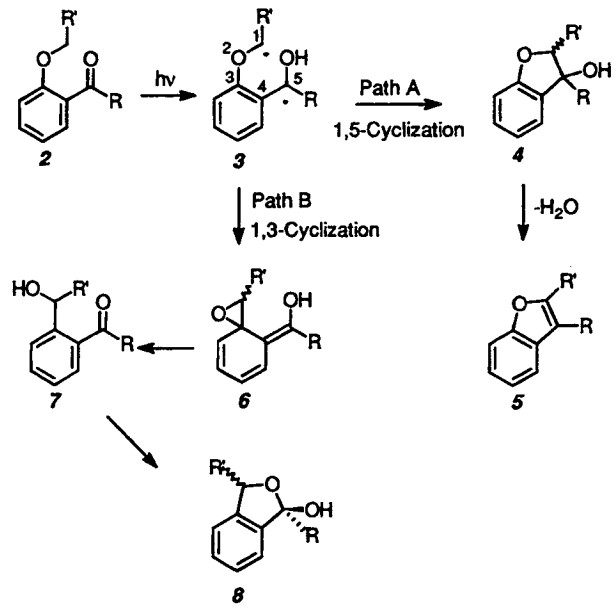
Introduction

Intramolecular hydrogen abstractions are among some of the best studied reactions in organic photochemistry.[2] The most prevalent examples of these involve abstraction of a γ-hydrogen, i.e., the Norrish Type II reaction.[3] However, a number of cases of both δ- and ϵ-hydrogen abstraction have been reported.[4,5] Higher forms of hydrogen abstraction, such as these, have attracted a fair amount of recent interest, not only because they provide useful insight into ketone photochemistry and biradical behavior, but many have potential synthetic utility in the construction of five- and six-membered rings.

One example of a δ-hydrogen abstraction which has found some applications in synthesis is the photocyclization of *o*-alkoxyphenyl ketones **2** to 2,3-disubstituted-3-hydroxy-2,3-dihydrobenzofurans **4** (Scheme 1).[6,7] Irradiation of ketone **2** leads to the formation of a biradical intermediate, **3**, via a triplet state intramolecular abstraction of a benzyloxy hydrogen by the carbonyl oxygen. This biradical intermediate can undergo a 1,5 cyclization to **4** (path A). In some cases, a competing 1,3-cyclization can occur (path B) to produce a spiro-epoxide intermediate, **6**, which rearranges to the corresponding 2-acylbenzyl alcohol **7**, or its hemiketal, **8**.

For *o*-(benzyloxy)acetophenone, **2** (R′ = Ph, R = CH_3), 1,3-cyclization predominates leading to formation of 2-acetylbenzyl alcohol.[8] Similar results have been reported for *o*-(cyclopropylmethoxy)acetophenone,[9] other *o*-alkoxyacetophenones, and *o*-alkoxybenzaldehydes.[10]

Scheme 1. Photocyclization of *o*-Alkoxyphenyl Ketones



On the other hand, *o*-(benzyloxy)benzophenone, **2** (R, R′ = Ph), photocyclizes exclusively (100% yield) to 3-hydroxy-2,3-diphenyl-2,3-dihydrobenzofuran, **4** (R,R′ = Ph), with a high quantum efficiency (0.95).[11] Dehydration of the dihydrobenzofuranol photoproduct with HCl produces 2,3-diphenylbenzofuran, **5** (R, R′ = Ph), in 100% yield.[6] High chemical yields have also been reported for the photocyclization of *o*-(allyloxy)- and *o*-(propargyloxy)-benzophenones and their subsequent dehydration to substituted benzofurans.[12] This photochemistry has also been used in the synthesis of aflatoxin M_2.[13] Thus, this

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(1) Mahmoud Abdul-Aziz came to the U. S. in 1983 to escape the war in his native country of Lebanon. He obtained his B.S. in Chemistry from Cleveland State University and was close to finishing his Ph.D. at Case Western Reserve University when he was tragically shot and killed in downtown Cleveland on January 7, 1992. Mahmoud was an outstanding human being and an extremely gifted and hard-working chemist. We wish to dedicate this paper to his memory.

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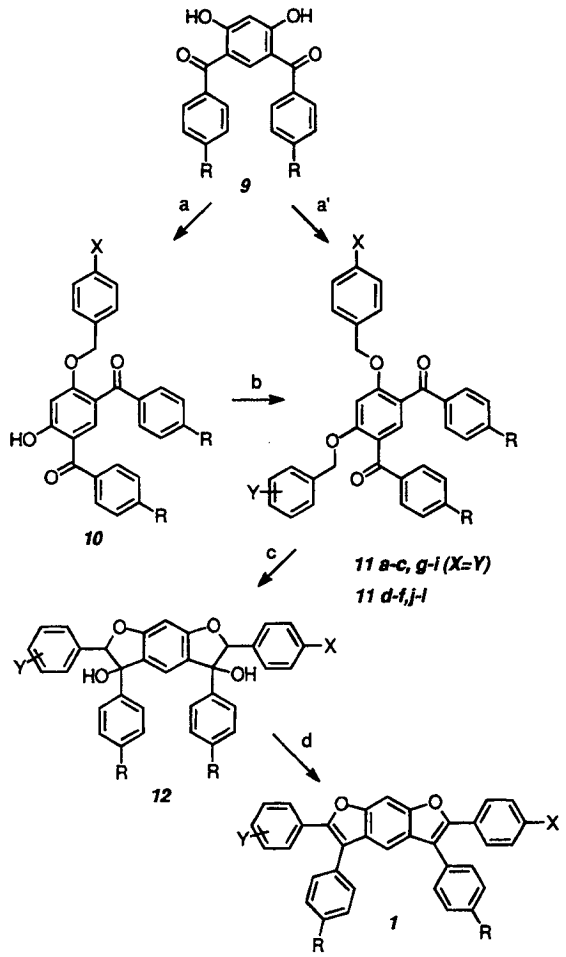
Scheme 2. Synthesis of 1



(a) 1.) K_2CO_3, KI, Bu_4NHSO_4/H_2O, 2.) $ArCH_2Z$/1,2-$EtCl_2$, reflux N_2, 18 h; (a') 1.) K_2CO_3, KI, Bu_4NHSO_4/H_2O, 2.) $2ArCH_2Z$/1,2-$EtCl_2$, reflux N_2, 18 h; (b) 1.) K_2CO_3, KI, Bu_4NHSO_4/H_2O, 2.) $2Ar'CH_2Z$/1,2-$EtCl_2$, reflux N_2, 18 h: (c) hv/ C_6H_6, N_2, Pyrex Filter; (d) $MeSO_2Cl$/pyridine

method constitutes a simple, high yield approach to substituted benzofurans.

We have been applying this chemistry to the synthesis of highly substituted benzofurans and have recently examined this photocyclization in polymers containing *o*-(benzyloxy)benzoyl chromophores.[14] We have now used this photochemistry in the synthesis of a series of substituted tetraarylbenzo[1,2-*b*:5,4-*b*']difurans, **1** (Scheme 2). Through this method, symmetrically and unsymmetrically substituted benzodifurans were prepared, including donor/acceptor substituted systems. We now report the results of these efforts.

Results and Discussion

2,3,5,6-Tetraarylbenzo[1,2-*b*:5,4-*b*']difurans **1** were prepared from substituted 1,3-dihydroxy-2,5-dibenzoylbenzenes **9**, according to the synthesis outlined in Scheme 2. Symmetrically and unsymmetrically substituted 2,5-diaroylresorcinol dibenzyl ethers **11** were prepared in one or two steps from **9** via a modified Williamson ether synthesis under phase transfer conditions. Yields for the synthesis of **11** are presented in Table 1.

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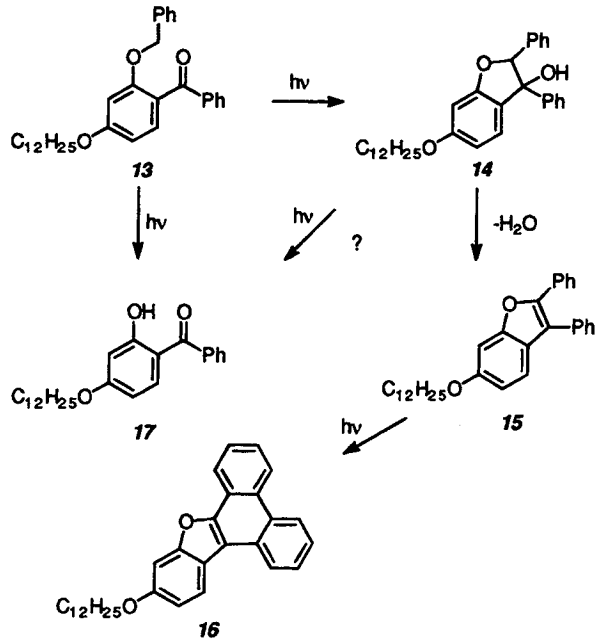
Table 1. Yields for Synthesis of 2,3,5,6-Tetraarylbenzo[1,2-*b*:5,4-*b*']difurans 1 and 1,3-Bis(benzyloxy)-4,6-dibenzoylbenzenes 11

	X	Y	R	% yield, 11	% yield, 1
a	H	H	H	80	69
b	4-CN	4-CN	H	90	80
c	4-MeO	4-MeO	H	60	63
d	3,5-$(MeO)_2$	3,5-$(MeO)_2$	H	58	62
e	4-CN	4-MeO	H	49[a]	70
f	4-CN	3,5-$(MeO)_2$	H	52[a]	62
g	H	H	Me	83	68
h	4-CN	4-CN	Me	92	76
i	4-MeO	4-MeO	Me	62	63
j	3,5-$(MeO)_2$	3,5-$(MeO)_2$	Me	64	57
k	4-CN	4-MeO	Me	52 (82)[a]	61
l	4-CN	3,5-$(MeO)_2$	Me	53 (82)[a]	56

[a] Formed in two steps from the corresponding monoether (**10a** or **10b**), overall yields from **9** reported first, yields from **10a** or **10b** are given in parentheses.

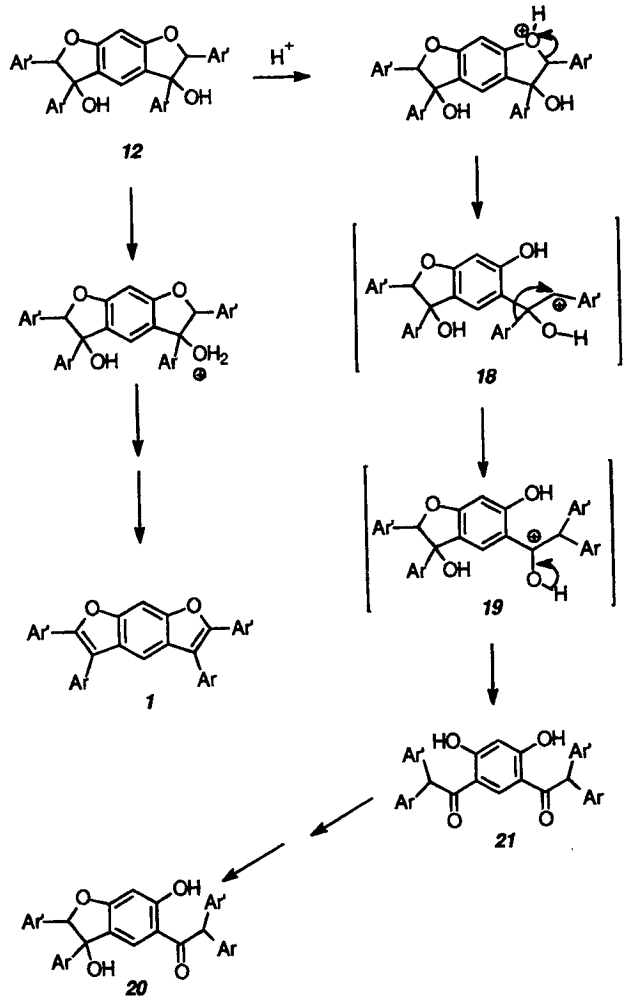
Photolysis of ~0.01M benzene solutions of **11** under nitrogen produced the desired 2,6-dihydroxy-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b*']difuran, **12**, as a mixture of stereoisomers in quantitative yield. Spectral data are consistent with the formation of the desired products. Competing reactions have been observed in the photocyclization of *o*-alkoxyacetophenones leading to the formation of *o*-acylbenzyl alcohols (Scheme 1).[9] Photolysis of 2-(benzyloxy)-4-(dodecyloxy)benzophenone, **13**, leads to photocleavage product **17** and benzo[*b*]phenanthro-[9,10-*d*]furan, **16**, as well as dihydrobenzofuranol, **14** (eq 1).[7] However, ^{1}H- and ^{13}C-NMR reveal no evidence of unreacted starting materials, unwanted side products, or secondary photoproducts in the present systems.



Attempts to convert the photoproducts into the corresponding benzo[1,2-*b*:5,4-*b*'] difurans through an acid-catalyzed dehydration were unsuccessful. Unlike simple 3-hydroxy-2,3-dihydrobenzofurans, treatment of **12** with a trace amount of HCl in benzene or diethyl ether produced a significant amount of side products. Attempts to use other acids (mineral, organic, or Lewis) either resulted in no dehydration or led to the formation of the same side products.

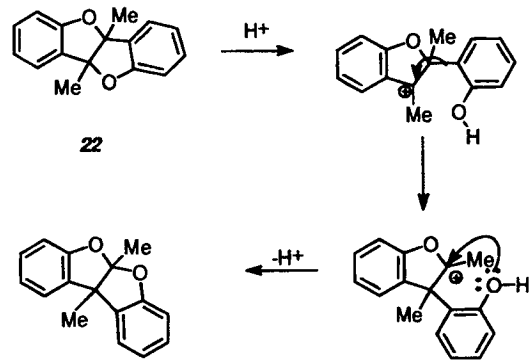
No attempt was made to isolate and purify these side products. However, ^{1}H-NMR of the crude product mix-

Scheme 3. Pinacol Rearrangement of 12

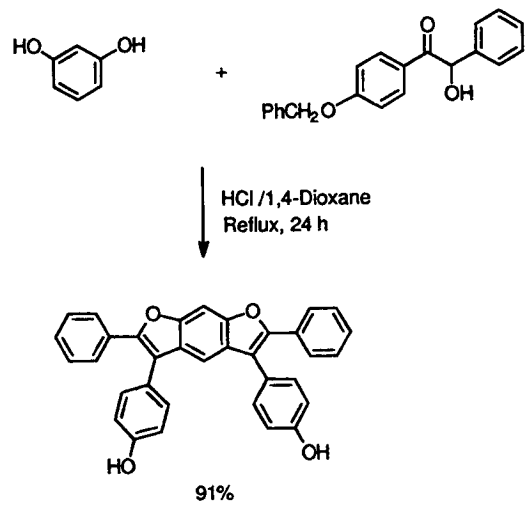


ture from these dehydrations revealed the presence of phenolic protons. This suggests that under acidic conditions **12** undergoes protonation at a furan oxygen leading to a pinacol–pinacolone rearrangement to form a compound we tentatively identify as either **20** or **21** (Scheme 3). While these results are disappointing, they are not altogether surprising. Pinacol rearrangements such as this have been reported for triphenylethylene oxides and 1,2-diethers.[15] The acid-catalyzed ring-opening and rearrangement of benzofuran **22** has also been reported.[16] Acid-catalyzed cleavage and rearrangement of benzyl phenyl ethers[17–19] is a fairly facile process and should compete with dehydration. For example, the rate constant for cleavage of α-phenethyl phenyl ether in HCl/i-BuOH at 40 °C[18] is comparabe to that for dehydration of 1,2-diphenylethanol in H_2SO_4/EtOH at 45 °C[20] ($3.2 \times 10{-}5$ s^{-1} vs $2.72 \times 10{-}5$ s^{-1}).

As an alternative, base-catalyzed eliminations were examined. Treatment of the crude photolysate with an excess (4 equiv) of methanesulfonyl chloride in pyridine produced the corresponding benzodifuran **1** in 56–80% yield after purification by flash chromatography (Table 1).



To our knowledge only one other synthesis of tetraphenylbenzo[1,2-*b*;5,4-*b'*]difurans has been reported in the literature.[21] This involved an acid-catalyzed cyclocondensation of resorcinol with *p*-(benzyloxy)benzoin in refluxing 1,4-dioxane (eq 2). The method that we have described in this paper employs considerably milder conditions than these, with slightly lower overall yields. Overall yields for the preparation of **1** from dibenzoylresorcinols **9** range from 30 to 72%, with the symmetrically substituted derivatives having the highest yields.



Another strength of the present procedure is that it provides a route to donor/acceptor substituted compounds which may have some use as fluorescent probes in biological[22] and polymeric systems. Requirements for these probes are a high fluorescence quantum yield and a sensitivity of the fluorescence spectrum to the polarity of its environment.

Fluorescence quantum yields for **1** in methylcyclohexane are quite high, ranging from 0.76 to 0.98 (Table 2). Quantum yields varied slightly with substituents. Donor/acceptor substituted compounds, e.g. **1e** and **1f**, had the lowest values. Emission spectra of donor/acceptor substituted **1** were measured in solvents of varying polarity (Table 3). Fluorescence emission spectra were red shifted in solvents of increasingly higher polarity. These solvatochromic shifts are large, as much as 100 nm for **1e** in methylcyclohexane vs DMSO. The photophysics of these compounds is currently under investigation.

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Table 2. Fluorescence Data for 1 in Methylcyclohexane

1	X	Y	R	λ_{Em}[a]	ϕ_f[b]
a	H	H	H	387	0.95
b	4-CN	4-CN	H	407	0.98
e	4-CN	4-MeO	H	421	0.81
f	4-CN	3,5-$(MeO)_2$	H	411	0.88
g	H	H	Me	387	0.98
h	4-CN	4-CN	Me	391	0.92
k	4-CN	4-MeO	Me	423	0.76
l	4-CN	3,5-$(MeO)_2$	Me	413	0.84

[a] Longest wavelength band, nm. [b] Anthracene used as the actinometer ($\phi_f = 0.27$).

Table 3. Solvent Dependence of Fluorescence Emission Maxima[a] for 1

solvent[b]	1b	1e	1f	1h	1k	1l
DMSO	495	527	441	451	518	487
CH_3CN	471	522	427	443	498	478
1,2-$EtCl_2$	452	453	422	423	491	449
THF	441	479	415	420	465	439
$CHCl_3$	440	465	420	421	468	438
MCH	411	421	407	391	423	413

[a] Longest wavelength band, values in nm. [b] 1,2-Cl_2Et = 1,2-dichloroethane, MCH = methylcyclohexane.

Conclusions

We have described a simple route to symmetrically and unsymmetrically substituted 2,3,5,6-tetraphenylbenzo-[1,2-*b*;5,4-*b'*]difurans **1**. Reaction conditions are relatively mild and should be suitable for a variety of substituents beyond those investigated. Fluorescence studies indicate that some of these compounds may have potential use as fluorescent probes.

Experimental Section

All reagents and solvents were purchased from Aldrich Chemical Co. and used as received. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were acquired at 300.133 and 75.469 MHz, respectively, in deuterated chloroform ($CDCl_3$) solution using tetramethylsilane as an internal standard. Chemical shifts are reported in ppm (δ). Fluorescence quantum yields were measured on solutions having an optical density of 0.05. An ethanol solution of anthracene of matched optical density was used as an actinometer (ϕ_f = 0.27[23]). Elemental analyses were performed by Spang Microanalytical Laboratory in Eagle Harbor, Michigan.

General Friedel–Crafts Procedure. A dichloromethane solution of 1,3-dimethoxybenzene (1.0 equiv) and aroyl chloride (2.10 equiv) was added dropwise to a stirred suspension of aluminum chloride (2.10 equiv) in dichloromethane under nitrogen. Once addition was complete, the reaction mixture was left to stir at room temperature for 72 h. The resulting solution was then poured over a mixture of crushed ice and concd HCl (3:1). The organic layer was separated and washed with an aqueous 5% KOH solution (6 × 25 mL). The base extracts were combined, neutralized with concd HCl, and extracted with diethyl ether. The ether extracts were dried ($MgSO_4$), and solvent was removed under reduced pressure. The resulting residue was triturated with methanol to afford 1,3-dihydroxy-4,6-diaroylbenzene as a crude solid.

1,3-Dihydroxy-4,6-dibenzoylbenzene (9a). Sublimation in vacuo (0.1 Torr, 120–135 °C), followed by recrystallization from MeOH (57%), afforded cream colored crystals, mp 147–149 °C: ^1H NMR δ 6.63 (s, 1H), 7.25–7.60 (m, 5H), 8.01 (s, 1H), 12.88 (s, 1H); ^{13}C NMR δ 105.37, 112.73, 128.37, 128.8, 132.11, 137.24, 142.63, 169.76, 199.91. Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.36; H, 4.49.

(23) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker, Inc.: New York, 1993.

1,3-Dihydroxy-4,6-di(4-methylbenzoyl)benzene (9b): pale green crystals (55%) from EtOH, mp 172–173 °C; ^1H NMR δ 2.41 (s, 3H), 6.61 (s, 1H), 7.25–7.53 (m, 4H), 12.89 (s, 1H); ^{13}C NMR δ 21.56, 105.24, 112.74, 129.01, 134.6, 142.16, 142.87, 169.56, 199.6. Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 76.43; H, 5.26.

General Synthesis of Benzyl Ethers. Potassium carbonate (4.5 equiv), potassium iodide (1.25 equiv), **9** (1.0 equiv), benzyl halide (2.0 equiv), and tetrabutylammonium hydrogen sulfate (0.05 equiv) were combined in 1,2-dichloroethane and distilled water (1:1) and refluxed under N_2 with stirring for 18 h. The organic layer of the resulting solution was separated, washed with a saturated aqueous $NaHCO_3$ solution, and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was triturated with methanol to afford the corresponding 1,3-bis(benzyloxy)-4,6-diaroylbenzene as a crude solid.

1-Hydroxy-3-[(4-cyanobenzyl)oxy]-4,6-dibenzoylbenzene (10a): fluffy white needles (60%) from EtOH, mp 190–191 °C; ^1H NMR δ 5.10 (s, 2H), 6.63 (s, 1H), 7.02–7.82 (m, 10H), 7.88 (s, 1H), 12.98 (s, 1H); ^{13}C NMR δ 69.71, 101.47, 112.26, 113.68, 118.83, 121.47, 127.26, 128.97, 129.36, 129.78, 129.96, 132.63, 133.24, 133.38, 137.62, 137.77, 139.09, 140.73, 162.66, 168.64, 194.70, 200.53. Anal. Calcd for $C_{28}H_{19}O_4N$: C, 77.62; H, 4.38; N, 3.23. Found: C, 77.73; H, 4.33; N, 3.17.

1-Hydroxy-3-[(4-cyanobenzyl)oxy]-4,6-bis(4-methylbenzoyl)benzene (10b): pale yellow powder (63%) from EtOH, mp 205–206 °C; ^1H NMR δ 2.40 (s, 3H), 5.0 (s, 2H), 6.59 (s, 1H), 7.02 (d, 1H, J = 6), 7.16–7.22 (d, 1H, J = 6 Hz), 7.26 (d, 1H, J = 6 Hz), 7.49 (d, 1H, J = 6 Hz), 7.58 (d, 1H, J = 6 Hz), 7.67 (d, 1H, J = 6 Hz), 7.86 (s, 1H), 7.84 (s, 1H), 12.94 (s, 1H); ^{13}C NMR δ 69.52, 101.34, 112.10, 113.65, 118.78, 121.55, 127.21, 129.20, 129.31, 129.41, 129.54, 132.48, 134.99, 137.09, 140.83, 143.28, 144.11, 162.29, 168.26, 194.34, 200.17. Anal. Calcd for $C_{30}H_{23}O_4N$: C, 78.11; H, 4.98; N, 3.04. Found: C, 77.21; H, 5.03; N, 2.99.

1,3-Bis(benzyloxy)-4,6-dibenzoylbenzene (11a): white crystals (80%) from $CHCl_3$/MeOH (1:3), mp 151–153 °C; ^1H NMR δ 5.02 (s, 2H), 6.63–7.81 (m, 12H); ^{13}C NMR δ 70.62, 98.38, 121.93, 126.66, 127.95, 128.24, 128.48, 129.61, 132.64, 133.27, 135.64, 138.66, 160.46, 194.92. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.9; H, 5.26. Found: C, 81.71; H, 5.31.

1,3-Bis[(4-cyanobenzyl)oxy]-4,6-dibenzoylbenzene (11b): white crystals (90%) from $CHCl_3$/MeOH (1:3), mp 215–216.5 °C; ^1H NMR δ 5.09 (s, 2H), 6.60 (s, 1H), 7.11 (d, 1H, J = 9 Hz), 7.45–7.55 (m, 10H), 7.70 (s, 1H), 7.78 (d, 1H, J = 9 Hz); ^{13}C NMR δ 69.62, 97.87, 111.97, 118.38, 122.45, 126.88, 126.91, 128.41, 129.54, 132.28, 133.37, 138.43, 140.58, 159.88, 194.38. Anal. Calcd for $C_{36}H_{24}N_2O_4$: C, 78.82; H, 4.41; N, 5.11. Found: C, 78.76; H, 4.39; N, 5.11.

1,3-Bis[(4-methoxybenzyl)oxy]-4,6-dibenzoylbenzene (11c): white crystals (60%) from EtOH, mp 136–137.5 °C; ^1H NMR δ 3.77 (s, 3H), 4.95 (s, 2H), 6.64 (s, 1H), 6.77 (d, 1H, J = 6), 6.96 (d, 1H, J = 9 Hz), 7.24 (s, 1H), 7.38–7.56 (m, 10H), 7.62 (s, 1H), 7.78 (d, 1H, J = 9 Hz); ^{13}C NMR δ 55.26, 70.50, 98.59, 113.91, 127.72, 128.26, 128.39, 129.61, 132.58, 133.15, 138.71, 159.42, 160.53, 194.97. Anal. Calcd for $C_{36}H_{30}O_6$: C, 77.44; H, 5.37. Found: C, 77.28; H, 5.33.

1,3-Bis[(3,5-dimethoxybenzyl)oxy]-4,6-dibenzoylbenzene (11d): light cream colored powder (58%) from MeOH, mp 142–143 °C; ^1H NMR δ 3.71 (s, 3H), 4.98 (s, 2H), 6.32 (d, 1H, J = 6), 6.64 (s, 1H), 7.39–7.58 (m, 10H), 7.82 (d, 1H, J = 6 Hz); ^{13}C NMR δ 55.41, 70.79, 98.91, 100.09, 104.53, 122.02, 128.34, 129.79, 132.91, 138.18, 138.32, 160.27, 161.06, 194.82. Anal. Calcd for $C_{38}H_{34}O_8$: C, 73.81; H, 5.49. Found: C, 73.71; H, 5.40.

1-[(4-Cyanobenzyl)oxy]-3-[(4-methoxybenzyl)oxy]-4,6-dibenzoylbenzene (11e): shiny white crystals (82%) from EtOH, mp 173–174 °C. ^1H NMR δ 3.76 (s, 3H), 4.97 (s, 2H), 5.05 (s, 2H), 6.62 (s, 1H), 6.75 (d, 1H, J = 9), 6.94 (d, J = 9 Hz), 7.08 (d, 1H, J = 9 Hz), 7.40–7.57 (m, 10H), 7.67 (s, 1H), 7.78 (d, 1H, J = 9 Hz); ^{13}C NMR δ 55.69, 69.93, 71.13, 98.84, 112.25, 114.40, 118.86, 122.21, 123.09, 127.36, 127.93, 128.70, 128.77, 129.97, 132.65, 133.17, 133.74, 138.89, 139.10, 141.34, 159.95, 160.20, 161.02, 194.96, 195.15. Anal. Calcd for

$C_{36}H_{27}O_5N$: C, 78.14; H, 4.88; N, 2.53. Found: C, 78.13; H, 4.79; N, 2.43.

1-[(4-Cyanobenzyl)oxy]-3-[(3,5-dimethoxybenzyl)oxy]-4,6-dibenzoylbenzene (11f): cream colored crystals (86%) from EtOH, mp 169–171 °C; ^{1}H NMR δ 3.72 (s, 3H), 5.02 (s, 2H), 5.04 (s, 2H), 6.29 (s, 1H), 6.30 (s, 1H), 6.35 (s, 1H), 6.58 (s, 1H), 7.06 (d, 1H, J = 9 Hz), 7.04–7.64 (m, 5H), 7.78 (s, 1H), 7.79-7.82 (m, 5H); ^{13}C NMR δ 55.37, 69.23, 69.47, 98.47, 99.88, 104.47, 111.81, 118.51, 121.79, 122.55, 126.91, 128.305, 129.49, 129.59, 132.26, 133.01, 133.22, 133.49, 138.05, 138.58, 140.85, 159.63, 160.09, 160.39, 161.08, 194.57. Anal. Calcd for $C_{37}H_{27}O_6N$: C, 76.44; H, 4.64; N, 2.41. Found: C, 76.57; H, 4.89; N, 2.49.

1,3-Bis(benzyloxy)-4,6-bis(4-methylbenzoyl)benzene (11g): white crystals (83%) from $CHCl_3$/MeOH (1:3), mp 161–162.5 °C; ^{1}H NMR δ 2.40 (s, 3H), 5.06 (s, 2H), 6.63 (s, 1H), 6.97–7.27 (m, 10H), 7.56 (d, 1H, J = 9 Hz), 7.65 (d, 1H, J = 9 Hz), 7.82 (s, 1H); ^{13}C NMR δ 70.69, 98.77, 122.26, 126.72, 127.85, 128.39, 128.88, 129.82, 132.77, 135.84, 136.12, 143.41, 160.11, 194.56. Anal. Calcd for $C_{36}H_{30}O_4$: C, 82.11; H, 5.74. Found: C, 82.27; H, 5.80.

1,3-Bis[(4-cyanobenzyl)oxy]-4,6-bis(4-methylbenzoyl)benzene (11h): white crystals (92%) from $CHCl_3$/MeOH (1:3), mp 290–292 °C; ^{1}H NMR δ 2.41 (s, 3H), 5.10 (s, 2H), 6.61 (s, 1H), 7.10 (d, 1H, J = 9 Hz), 7.22 (d, 1H, J = 9 Hz), 7.49 (d, 1H, J = 9 Hz), 7.69 (d, 1H, J = 9 Hz); ^{13}C NMR δ 22.06, 70.0, 98.52, 112.22, 118.84, 123.01, 127.34, 129.48, 130.18, 132.59, 133.63, 136.16, 141.22, 144.35, 159.98, 194.52. Anal. Calcd for $C_{38}H_{28}N_2O_4$: C, 79.15; H, 4.89; N, 4.86. Found: C, 78.91; H, 4.85; N, 4.88.

1,3-Bis[(4-methoxybenzyl)oxy]-4,6-bis(4-methylbenzoyl)benzene (11i): shiny white crystals (62%) from EtOH, mp 165–166 °C; ^{1}H NMR δ 2.39 (s, 3H), 3.77 (s, 3H), 4.95 (s, 2H), 6.74 (s, 1H), 6.77 (d, 2H, J = 9), 6.98 (d, 2H, J = 9 Hz), 7.20 (d, 2H, J = 6 Hz), 7.56 (s, 1H), 7.68 (d, 2H, J = 9 Hz); ^{13}C NMR δ 21.61, 55.29, 70.67, 99.19, 113.97, 122.37, 128.03, 128.48, 128.91, 129.88, 132.70, 136.18, 143.37, 159.52, 160.22, 194.62. Anal. Calcd for $C_{38}H_{34}O_6$: C, 77.84; H, 5.79. Found: C, 77.81; H, 5.88.

1,3-Bis[(3,5-dimethoxybenzyl)oxy]-4,6-bis(4-methylbenzoyl)benzene (11j): fluffy off-white powder (64%) from EtOH, mp 159–161 °C; ^{1}H NMR δ 2.40 (s, 3H), 3.60 (s, 3H), 4.98 (s, 2H), 6.28 (s, 1H), 6.34 (s, 1H), 6.62 (s, 1H), 7.20 (d, 1H, J = 9 Hz), 7.54 (s, 1H), 7.72 (d, 1H, J = 9 Hz); ^{13}C NMR δ 21.64, 55.29, 70.67, 98.83, 99.95, 104.45, 122.24, 128.98, 129.96, 132.53, 135.68, 138.24, 143.68, 159.84, 160.96, 194.49. Anal. Calcd for $C_{40}H_{38}O_8$: C, 74.33; H, 5.88. Found: C, 74.13; H, 5.82.

1-[(4-Cyanobenzyl)oxy]-3-[(4-methoxybenzyl)oxy]-4,6-bis(4-methylbenzoyl)benzene (11k): shiny white crystals (82%) from EtOH, mp 164–165 °C; ^{1}H NMR δ 2.41 (s, 3H), 3.79 (s, 3H), 5.00 (s, 2H), 5.07 (s, 2H), 6.74 (s, 1H), 6.77 (d, 1H, J = 9), 6.98 (d, 1H, J = 9 Hz), 7.19 (d, 1H, J = 9 Hz), 7.56 (s, 1H), 7.69 (d, 1H, J = 9 Hz); ^{13}C NMR δ 21.62, 55.22, 69.36, 70.55, 98.37, 111.64, 113.82, 118.49, 121.79, 122.64, 126.87, 127.56, 128.28, 128.92, 128.96, 129.12, 129.80, 132.16, 132.97, 135.69, 135.86, 141.02, 143.63, 143.70, 159.37, 160.20, 194.31, 194.48. Anal. Calcd for $C_{38}H_{31}O_5N$: C, 78.51; H, 5.33; N, 2.41. Found: C, 78.47; H, 5.28; N, 2.38.

1-[(4-Cyanobenzyl)oxy]-3-[(3,5-dimethoxybenzyl)oxy]-4,6-bis(4-methylbenzoyl)benzene (11l): white powder (91%) from EtOH/EtOAc (2:1), mp 182–183 °C; ^{1}H NMR δ 2.39 (s, 3H), 2.40 (s, 3H), 3.70 (s, 3H), 5.00 (s, 2H), 5.05 (s, 2H), 6.28 (s, 1H), 6.25 (s, 1H), 6.59 (s, 1H), 7.12 (d, 1H, J = 9 Hz), 7.22 (d, 1H, J = 9 Hz), 7.51 (d, 1H, J = 6 Hz), 7.58 (s, 1H), 7.71 (t, 1H, J = 12); ^{13}C NMR δ 22.05, 55.71, 69.98, 71.17, 98.98, 100.20, 104.88, 112.10, 118.94, 122.43, 123.12, 127.31, 129.43, 130.24, 130.33, 132.59, 133.22, 135.87, 136.30, 138.54, 141.46, 144.16, 144.30, 159.73, 160.40, 161.42, 194.72. Anal. Calcd for $C_{39}H_{33}O_6N$: C, 76.62; H, 5.39; N, 2.29. Found: C, 76.78; H, 5.43; N, 2.31.

General Photolysis Procedure. A 500 mL benzene solution containing 2.0 g of **3** was vigorously degassed under nitrogen for 1 h and irradiated under nitrogen using light from a 450 W Hanovia mercury lamp fitted with a Pyrex glass filter. ^{1}H NMR was used to monitor the course of the reaction by following the disappearance of the OCH_2Ar protons. Once the reaction had gone to completion, the solvent was removed under reduced pressure to afford a mixture of isomers of **4** as yellow powder. In all cases, spectral data and elemental analysis revealed that the crude photoproduct mixture required no further purification.

2,6-Dihydroxy-2,3,5,6-tetraphenyl-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12a): ^{1}H NMR δ 5.75 (s, 1H), 6.4–7.45 (m, 22H); ^{13}C NMR δ 82.81, 93.86, 96.19, 109.23, 116.12, 117.42, 117.79, 126.59–132.92, 142.72, 150.34, 150.84, 152.78, 155.64, 158.77. Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.9; H, 5.26. Found: C, 83.88; H, 5.14.

2,6-Dihydroxy-2,6-bis(4-cyanophenyl)-3,5-diphenyl-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12b): ^{1}H NMR δ 5.73 (s, 1H), 6.2–7.6 (m, 20H); ^{13}C NMR δ 82.79, 86.97, 91.16, 95.35, 100.01, 101.39, 110.69, 112.09, 115.81, 118.14, 120.93, 121.39, 126.45–142.32, 147.90, 155.34, 159.07, 162.32, 167.90. Anal. Calcd for $C_{36}H_{24}N_2O_4$: C, 78.82; H, 4.41; N, 5.11. Found: C, 78.76; H, 4.39; N, 5.14.

2,6-Dihydroxy-2,6-bis(4-methoxyphenyl)-3,5-diphenyl-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12c): ^{1}H NMR δ 3.77 (s, 3H), 5.66 (s, 1H), 6.3–7.8 (m, 20H); ^{13}C NMR δ 55.52, 82.75, 83.0, 94.03, 94.11, 96.38, 96.58, 114.14, 116.13, 122.32, 123.68, 125.65–130.02, 142.7, 143.21, 158.85, 159.85, 160.23, 162.87. Anal. Calcd for $C_{36}H_{30}O_6$: C, 77.44; H, 5.37. Found: C, 77.31; H, 5.34.

2,6-Dihydroxy-2,6-bis(3,5-dimethoxyphenyl)-3,5-diphenyl-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12d): ^{1}H NMR δ 3.43–3.82 (ms, 3H), 5.69 (s, 1H), 6.31–7.45 (m, 18H); ^{13}C NMR δ 55.23, 82.88, 93.87, 96.14, 99.40, 100.95, 101.06, 101.2, 104.32, 104.46, 104.55, 107.17, 107.23, 116.23, 126.41, 126.75, 126.96, 127.65–136.10, 142.78, 155.48, 160.61, 160.66, 160.71, 160.9, 161.04. Anal. Calcd for $C_{38}H_{34}O_8$: C, 73.81; H, 5.49. Found: C, 73.92; H, 5.41.

2,6-Dihydroxy-2-(4-cyanophenyl)-6-(4-methoxyphenyl)-3,5-diphenyl-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12e): ^{1}H NMR δ 3.78 (s, 3H), 5.66 (s, 1H), 6.76–7.38 (m, 20H); ^{13}C NMR δ 55.54, 83.42 (ms), 9413, 94.33, 95.71, 95.86, 96.59, 96.70, 112.38–132.94, 140.18, 142.20, 150.4, 155.2, 156, 159.98, 160.33, 163.1, 163.9. Anal. Calcd $C_{36}H_{27}O_5N$: C, 78.14; H, 4.88; N, 2.53. Found: C, 78.04; H, 4.75; N, 2.44.

2,6-Dihydroxy-2-(4-cyanophenyl)-6-(3,5-dimethoxyphenyl)-3,5-diphenyl-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12f): ^{1}H NMR δ 3.54–3.81 (ms, 3H), 5.64 (ms, 1H), 6.31–7.65 (m, 19H); ^{13}C NMR δ 55.35, 96.79, 97.35, 98.32, 99.4, 100.99, 101.08, 104.48, 107.50, 112.5, 117.1, 118.71, 121.12, 126.41–132.03, 142.62, 160.23, 167.92. Anal. Calcd for $C_{37}H_{27}O_6N$: C, 76.44; H, 4.64; N, 2.41. Found: C, 76.44; H, 4.69; N, 2.34.

2,6-Dihydroxy-2,6-diphenyl-3,5-bis(4-methylphenyl)-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12g): ^{1}H NMR δ 3.38, 2.41 (ms, 3H), 5.73 (s, 1H), 6.76–7.65 (m, 10H); ^{13}C NMR δ 93.79, 96.24, 109.40, 116.20, 117.44, 126.57–129.88, 130.92, 133.96, 150.68, 152.82. Anal. Calcd for $C_{36}H_{30}O_4$: C, 82.11; H, 5.74. Found: C, 83.97; H, 5.67.

2,6-Dihydroxy-2,6-bis(4-cyanophenyl)-3,5-bis(4-methylphenyl)-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12h): ^{1}H NMR δ 2.17–2.42 (m, 3H), 5.69 (s, 1H), 6.73–7.67 (m, 10H); ^{13}C NMR δ 20.97, 21.2, 21.57, 83.4, 94.05, 95.43, 112.2, 113.1, 116.44, 118.53, 121.2–146.2, 148.1, 156.1, 156.8, 164.2. Anal. Calcd for $C_{38}H_{28}N_2O_4$: C, 79.15; H, 4.89; N, 4.86. Found: C, 79.29; H, 4.94; N, 4.84.

2,6-Dihydroxy-2,6-bis(4-methoxyphenyl)-3,5-bis(4-methylphenyl)-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12i): ^{1}H NMR δ 2.37 (s, 3H), 2.36 (s, 3H), 3.73 (s, 3H), 5.66 (s, 1H), 6.50–7.60 (m, 18H); ^{13}C NMR δ 21.31, 21.52, 93.93, 96.34, 99.0, 102.0, 108.94, 114.10, 116.13, 120.0–137.0 (m), 137.38, 140.10, 150.0–160.18. Anal. Calcd for $C_{38}H_{34}O_6$: C, 77.84; H, 5.79. Found: C, 77.73; H, 5.68.

2,6-Dihydroxy-2,6-bis(3,5-dimethoxyphenyl)-3,5-bis(4-methylphenyl)-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]difuran (12j): ^{1}H NMR δ 2.41 (s, 3H), 3.63–3.85 (ms, 3H), 5.68 (s, 1H), 6.37–7.36 (m, 16H); ^{13}C NMR δ 21.06, 55.24, 82.78, 93.77, 93.08, 100.86, 100.99, 101.21, 104.33, 104.33, 104.51, 104.58, 116.29, 118.37, 125.70, 126.31, 126.54, 126.63, 128.78–

137.44, 155.44, 158.70, 160.64, 160.68, 160.87, 160.94, 161.01. Anal. Calcd for $C_{38}H_{34}O_8$: C, 73.81; H, 5.49. Found: C, 74.45; H, 5.81.

2,6-Dihydroxy-2-(4-cyanophenyl)-6-(4-methoxyphenyl)-3,5-bis(4-methylphenyl)-2,3,5,6-tetrahydrobenzo[1,2-*b*:5,4-*b'*]-difuran (12k): ^{1}H NMR δ 2.41 (s, 3H), 2.44 (s, 3H), 3.80 (s, 3H), 5.66 (s, 1H), 6.50–7.80 (m, 18H); ^{13}C NMR δ 21.05, 55.25, 83.10, 93.79, 93.99, 95.35, 109.62, 110.82, 113.93, 114.31, 115.46, 115.71, 118.84, 120.76, 123.33, 126.59, 127.1, 127.60–138.13, 151.31, 152.75, 153.27, 159.71. Anal. Calcd for $C_{38}H_{31}O_5N$: C, 78.51; H, 5.33; N, 2.41. Found: C, 78.47; H, 5.17; N, 2.38.

2,6-Dihydroxy-2-(4-cyanophenyl)-6-(3,5-dimethoxyphenyl)-3,5-bis(4-methylphenyl)-2,3,5,6-tetrahydrobenzo-[1,2-*b*:5,4-*b'*]difuran (12l): ^{1}H NMR δ 2.33–2.39 (ms, 3H)), 3.66–3.75 (ms, 3H), 5.69 (s, 1H), 6.36–7.32 (m, 17H); ^{13}C NMR δ 21.09, 55.35, 82.50, 82.64, 93.85, 94.06, 95.48, 95.57, 96.24, 96.31, 100.86, 101.07, 104.49, 104.57, 112.08, 116.94, 118.76, 121.37, 126.33, 126.6, 126.87, 127.43, 127.59, 127.65–143.1, 155.90, 159.47, 160.67, 160.90, 162.14, 162.50. Anal. Calcd for $C_{39}H_{33}O_6N$: C, 76.62; H, 5.39; N, 2.29. Found: C, 76.80; H, 5.36; N, 2.24.

General Dehydration Procedure. A pyridine solution of **12** (1.0 equiv) and methanesulfonyl chloride (4.0 equiv) was stirred under nitrogen at room temperature for 18 h. The solvent was then removed under reduced pressure, and the crude product was dissolved in dichloromethane and washed three times with a saturated solution of aqueous $NaHCO_3$. The organic layer was separated, dried ($MgSO_4$), and solvent removed under reduced pressure. The residue was triturated with methanol and filtered to afford **1** as crude product. Flash chromatography on silica gel (Aldrich, Merck grade 60, 230–240 mesh, 60 Å) using 2:8 (dichloromethane:hexane) as the eluent followed by solvent removal under reduced pressure. The residue was triturated with methanol and filtered to afford pure **1** as a fluffy powder.

2,3,5,6-Tetraphenylbenzo[1,2-*b*:5,4-*b'*]difuran (1a): light cream solid (69%), mp 220–221.5 °C; ^{1}H NMR δ 7.30–7.67 (m, 12H); ^{13}C NMR δ 93.91, 109.32, 117.55, 126.91, 127.59, 127.70, 128.23, 128.43, 129.08, 129.94, 130.84, 133.06, 150.99, 152.92. Anal. Calcd for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79. Found: C, 88.25; H, 4.88.

2,6-Bis(4-cyanophenyl)-3,5-diphenylbenzo[1,2-*b*:5,4-*b'*]-difuran (1b): light cream solid (80%), mp 340–341 °C; ^{1}H NMR δ 7.39 (s, 1H), 7.41–7.48 (m, 10H), 7.56 (d, 1H, J = 9), 7.73 (s, 1H), 7.75 (d, 1H, J = 6); ^{13}C NMR δ 93.91, 109.33, 117.55, 126.91, 127.59, 127.70, 128.23, 128.43, 129.08, 129.94, 130.85, 133.06, 150.99, 152.92. Anal. Calcd for $C_{36}H_{20}N_2O_2$: C, 84.36; H, 3.93; N, 5.46. Found: C, 84.27; H, 3.99; N, 5.50.

2,6-Bis(4-methoxyphenyl)-3,5-diphenylbenzo[1,2-*b*:5,4-*b'*]difuran (1c): cream colored solid (63%), mp 212–214 °C; ^{1}H NMR δ 3.82 (s, 3H), 6.85 (d, 1H, J = 9), 7.37–7.50 (m, 5H), 7.58 (d, J = 9), 7.68 (s, 1H); ^{13}C NMR δ 55.21, 93.64, 108.48, 113.85, 115.85, 123.42, 127.39, 127.70, 128.24, 128.95, 129.84, 133.18, 150.90, 152.40, 159.55. Anal. Calcd for $C_{36}H_{26}O_4$: C, 82.78; H, 4.98. Found: C, 83.54; H, 5.01.

2,6-Bis(3,5-dimethoxyphenyl)-3,5-diphenylbenzo[1,2-*b*:5,4-*b'*]difuran (1d): white solid (63%), mp 210–212 °C; ^{1}H NMR δ 3.84 (s, 3H), 6.82 (s, 1H), 6.85 (s, 1H), 7.37–7.49 (m, 10H), 7.55 (s, 1H), 7.58 (s, 1H), 7.67 (s, 1H); ^{13}C NMR δ 55.71, 94.15, 108.99, 114.36, 116.35, 123.92, 127.90, 128.76, 129.46, 130.35, 133.68, 152.90, 160.04. Anal. Calcd for $C_{38}H_{30}O_6$: C, 78.37; H, 5.15. Found: C, 78.51; H, 4.62.

2-(4-Cyanophenyl)-6-(4-methoxyphenyl)-3,5-diphenylbenzo[1,2-*b*:5,4-*b'*]difuran (1e): pale yellow solid (70%), mp 284–286 °C. ^{1}H NMR δ 3.81 (s, 3H), 6.84 (d, 1H, J = 9), 7.38 (s, 1H), 7.40–7.58 (m, 10H), 7.02 (d, 1H, J = 6), 7.71 (s, 1H); ^{13}C NMR δ 55.28, 93.91, 109.52, 111.00, 113.97, 115.76, 118.80, 126.67, 127.03, 127.62, 128.21, 128.33, 128.37, 129.08, 129.37, 129.70, 129.86, 132.17, 135.0, 148.30, 151.55, 152.78, 153.30, 159.81. Anal. Calcd for $C_{36}H_{23}NO_3$: C, 83.58; H, 4.44; N, 2.71. Found: C, 83.63; H, 4.42; N, 2.73.

2-(4-Cyanophenyl)-6-(3,5-dimethoxyphenyl)-3,5-diphenylbenzo[1,2-*b*:5,4-*b'*]difuran (1f): light cream solid (62%), mp 250–251 °C; ^{1}H NMR δ 3.66 (s, 6H), 6.39 (s, 1H), 6.79 (d, 1H, J = 4), 7.37 (s, 1H), 7.41–7.53 (m, 10H), 7.54 (s, 1H), 7.58 (s, 1H), 7.70 (d, 1H, J = 4), 7.75 (s, 1H); ^{13}C NMR δ 55.28, 93.98, 101.46, 104.53, 109.92, 111.05, 117.81, 118.78, 120.63, 126.66, 127.21, 127.87, 128.06, 128.36, 129.06, 129.39, 129.66, 130.00, 132.00, 132.06, 132.15, 132.70, 134.88, 148.43, 151.04, 153.01, 153.19, 160.62. Anal. Calcd for $C_{37}H_{25}NO_4$: C, 81.19; H, 4.57; N, 2.56. Found: C, 81.15; H, 4.53; N, 2.55.

2,6-Diphenyl-3,5-bis(4-methylphenyl)benzo[1,2-*b*:5,4-*b'*]difuran (1g): white solid (68%), mp 216–217 °C; ^{1}H NMR δ 2.43 (s, 3H), 7.24–7.67 (m, 10H); ^{13}C NMR δ 21.35, 93.78, 109.39, 117.44, 126.78, 127.57, 128.07, 128.37, 129.70, 129.78, 129.86, 130.90, 137.35, 150.66, 152.80. Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.14; H, 5.34. Found: C, 88.15; H, 5.47.

2,6-Bis(4-cyanophenyl)-3,5-bis(4-methylphenyl)benzo-[1,2-*b*:5,4-*b'*]difuran (1h): pale yellow solid (76%), mp 340–342 °C; ^{1}H NMR δ 2.44 (s, 3H), 7.25–7.32 (m, 4H), 7.39 (s, 1H), 7.57 (d, 1H, J = 9), 7.74 (d, 1H, J = 9), 7.76 (s, 1H); ^{13}C NMR δ 21.00, 93.72, 110.38, 110.83, 118.38, 120.23, 126.35, 127.45, 128.40, 129.11, 129.78, 131.82, 134.50, 137.98, 148.32, 153.16. Anal. Calcd for $C_{38}H_{24}N_2O_2$: C, 84.43; H, 4.47; N, 5.18. Found: C, 84.20; H, 4.49; N, 5.21.

2,6-Bis(4-methoxyphenyl)-3,5-bis(4-methylphenyl)benzo[1,2-*b*:5,4-*b'*]difuran (1i): light cream solid (63%), mp 214–215 °C; ^{1}H NMR δ 2.42 (s, 3H), 3.81 (s, 3H), 6.83 (d, 1H, J = 9), 7.15 (s, 1H), 7.23–7.38 (m, 8H), 7.57 (d, 1H, J = 9), 7.65 (s, 1H); ^{13}C NMR δ 21.14, 55.08, 93.42, 99.40, 108.49, 113.71, 115.70, 123.50, 128.05, 128.80, 129.39, 129.97, 136.93, 150.55, 152.27, 159.35. Anal. Calcd for $C_{38}H_{30}O_4$: C, 82.92; H, 5.45. Found: C, 83.04; H, 5.40.

2,6-Bis(3,5-dimethoxyphenyl)-3,5-bis(4-methylphenyl)-benzo[1,2-*b*:5,4-*b'*]difuran (1j): light cream solid (57%), mp 234–235 °C; ^{1}H NMR δ 2.40 (s, 3H), 3.67 (s, 6H), 6.38 (s, 1H), 6.81–7.39 (m, 7H), 7.69 (s, 1H); ^{13}C NMR δ 21.86, 55.79, 94.33, 101.77, 105.10, 110.02, 118.50, 125.36, 128.22, 130.23, 130.43, 133.94, 137.99, 141.43, 145.32, 153.27, 162.74. Anal. Calcd for $C_{40}H_{34}O_6$: C, 78.71; H, 5.57. Found: C, 78.79; H, 5.53.

2-(4-Cyanophenyl)-6-(4-methoxyphenyl)-3,5-bis(4-methylphenyl)benzo[1,2-*b*:5,4-*b'*]difuran (1k): pale yellow solid (61%), mp 270–271 °C; ^{1}H NMR δ 2.43 (s, 3H), 2.45 (s, 3H), 3.82 (s, 3H), 6.84 (d, 1H, J = 9), 7.24–7.61 (m, 11H), 7.67 (s, 1H), 7.72 (d, 1H, J = 9); ^{13}C NMR δ 20.95, 20.98, 54.87, 93.42, 109.23, 110.42, 113.55, 115.31, 118.48, 120.37, 122.94, 126.20, 126.71, 127.90, 128.70, 129.13, 129.29, 129.41, 129.69, 131.74, 134.75, 136.93, 137.74, 147.70, 150.91, 152.36, 152.87, 159.32. Anal. Calcd for $C_{38}H_{27}NO_3$: C, 83.68; H, 4.95. Found: C, 83.50; H, 5.05.

2-(4-Cyanophenyl)-6-(3,5-dimethoxyphenyl)-3,5-bis(4-methylphenyl)benzo[1,2-*b*:5,4-*b'*]difuran (1l): pale yellow solid (56%), mp 240–242 °C; ^{1}H NMR δ 2.42 (s, 3H), 2.44 (s, 3H), 3.67 (s, 3H), 6.40 (s, 1H), 6.81 (s, 1H), 6.82 (s, 1H), 7.15–7.76 (m, 14H); ^{13}C NMR δ 21.32, 55.26, 93.93, 101.84, 104.59, 109.6, 110.09, 110.91, 118.06, 118.90, 120.06, 126.65, 127.32, 128.18, 129.01, 129.53, 129.64, 129.72, 129.77, 129.88, 130.15, 132.21, 135.08, 137.61, 138.23, 148.26, 150.84, 153.22, 160.66. Anal. Calcd for $C_{39}H_{29}NO_4$: C, 81.41; H, 5.04; N, 2.43. Found: C, 81.69; H, 5.00; N, 2.30.

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