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Visible-Light Promoted Synthesis of Dibenzofuran Derivatives

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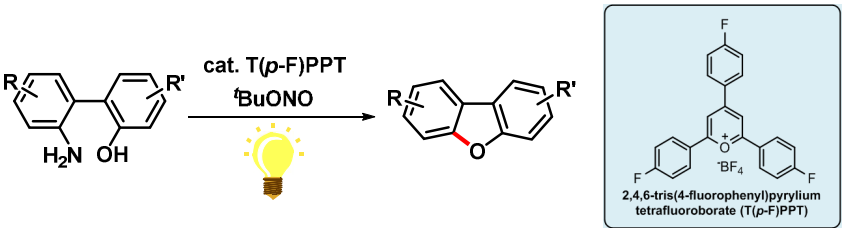
Abstract: Dibenzofurans are naturally-occurring molecules that have received considerable attention for a variety of practical applications, such as in pharmaceuticals and electronic materials. Herein, an efficient and eco-friendly method for the synthesis of dibenzofuran derivatives via intramolecular C-O bond formation, which involves the *in situ* production of a diazonium salt, is described. The transformation requires a diazotizing agent and is promoted by the use of an organic photosensitizer under visible-light irradiation.



INTRODUCTION

Dibenzofuran structural motifs are widely found in natural products and are used in pharmaceuticals, as well as in material sciences, owing to their unique properties, such as weak biochemical stress response and high heat resistance.[1, 2] Accordingly, a variety of

functional molecules contain the dibenzofuran skeleton, such as biologically active cotonefurans[3], furobufen[4], DB03682[5], fortuneanoside L[6], and the photoelectronic materials used in phosphorescent organic light-emitting diodes (PhOLEDs)[7] (**Figure 1**).

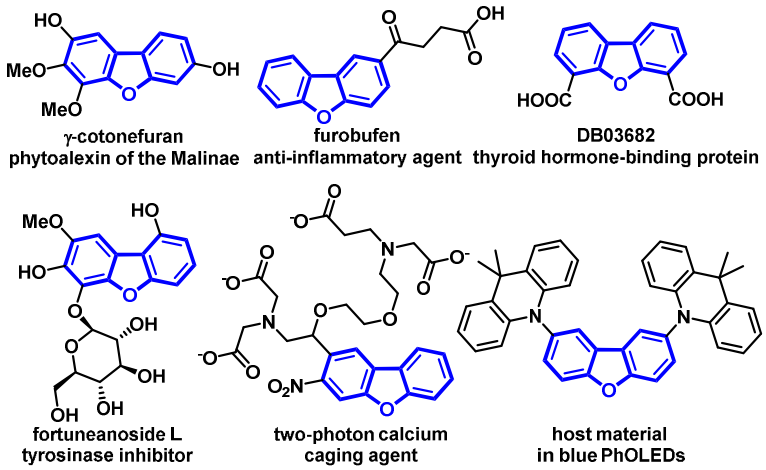
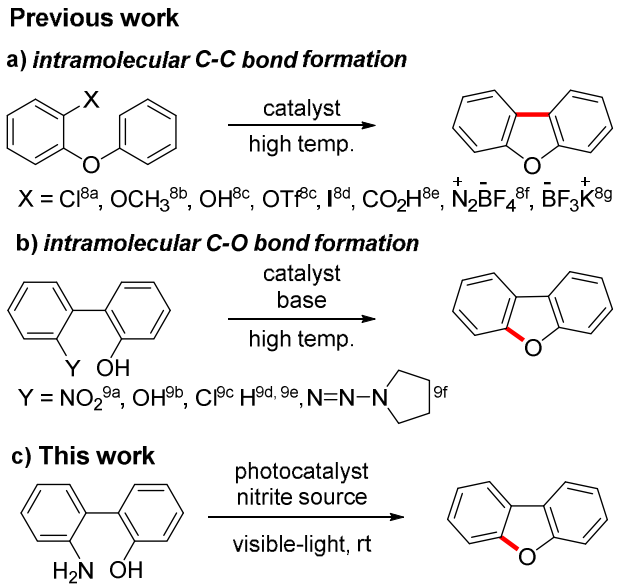


Figure 1. Examples of functional molecules containing the dibenzofuran structural motif.

Due to their importance, several methodologies for the construction of dibenzofuran derivatives have been developed based on numerous intermolecular and intramolecular reactions. Approaches based on intramolecular ring closure through formation of C-C bonds using functionalized diaryl ethers[8] [**Scheme 1**(a)] and formation of C-O bonds using functionalized biaryls[9] have been extensively developed [**Scheme 1**(b)]. Intramolecular C-O bond formation by C-H activation is particularly attractive in terms of efficiency as this approach can furnish various kinds of dibenzofuran motifs from less-functionalized starting substrates.[9d, 9e] Nonetheless, despite the efficiency, these methods are often restricted in that they require harsh reaction conditions and the use of transition-metal catalysts such as

copper[9c] and palladium.[9d, 9e] Therefore, the search for synthetic methods employing mild reaction conditions is ongoing.

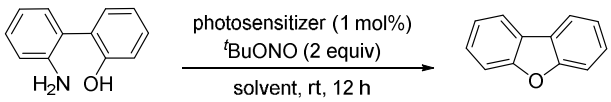
Scheme 1. Intramolecular synthesis of dibenzofuran derivatives



Diazonium salts are easily prepared and handled and have been widely used as effective substrates in a variety of organic transformations.[10] Recently, we utilized diazonium salts generated *in situ* from amino substrates using nitrite sources for the synthesis of various heteroaromatic compounds.[11] With the continued interest in the use of diazonium salts for the synthesis of valuable polycyclic heteroaromatic compounds, we attempted to develop a practical dibenzofuran synthetic method utilizing 2-(2′-aminoaryl)phenol derivatives through *in situ* diazotization of the amino group, followed by intramolecular C-O cyclization under mild conditions.

RESULTS AND DISCUSSION

Table 1. Optimization studies with 1a[a]



1a **2a**

entry	photosensitizer[b]	solvent (conc.)	variations	yield (%)[c]
1	-	TFE (0.05 M)	no ^{t}BuONO	0
2	-	TFE (0.05 M)		43
3	-	TFE (0.05 M)	60 °C	44
4	$[Ru(bpy)_3]Cl_2$	TFE (0.05 M)		56
5	*fac*-$Ir(ppy)_3$	TFE (0.05 M)		53
6	Eosin Y	TFE (0.05 M)		52
7	TPPT	TFE (0.05 M)		52
8	T(*p*-F)PPT	TFE (0.05 M)		64
9	T(*p*-Cl)PPT	TFE (0.05 M)		56
10	T(*p*-Br)PPT	TFE (0.05 M)		60
11	T(*p*-Me)PPT	TFE (0.05 M)		53
12	T(*p*-OMe)PPT	TFE (0.05 M)		60
13	T(*p*-F)PPT	TFE (0.05 M)	isopentyl nitrite instead of ^{t}BuONO	62
14	T(*p*-F)PPT	DCE (0.05 M)		42
15	T(*p*-F)PPT	DCM (0.05 M)		44
16	T(*p*-F)PPT	DMF (0.05 M)		61
17	T(*p*-F)PPT	DMSO (0.05 M)		42
18	T(*p*-F)PPT	MeCN (0.05 M)		45
19	T(*p*-F)PPT	THF (0.05 M)		31
20	T(*p*-F)PPT	MeOH (0.05 M)		21
21	T(*p*-F)PPT	Acetone (0.05 M)		0
22	T(*p*-F)PPT	TFE (0.05 M)	1.5 equiv. ^{t}BuONO	70
23	T(*p*-F)PPT	TFE (0.05 M)	3.0 equiv. ^{t}BuONO	57
24	T(*p*-F)PPT	TFE (0.05 M)	0.25 mol% F-TPT	58
25	T(*p*-F)PPT	TFE (0.05 M)	0.5 mol% F-TPT	60
26	T(*p*-F)PPT	TFE (0.05 M)	2 mol% F-TPT	60
27	T(*p*-F)PPT	TFE (0.005 M)	1.5 equiv. ^{t}BuONO	63
28	T(*p*-F)PPT	TFE (0.01 M)	1.5 equiv. ^{t}BuONO	72
29	T(*p*-F)PPT	**TFE (0.02 M)**	**1.5 equiv. ^{t}BuONO**	**80**
30	T(*p*-F)PPT	TFE (0.1 M)	1.5 equiv. ^{t}BuONO	44
31	-	TFE (0.02 M)	1.5 equiv. ^{t}BuONO	59[d]

[a]Reaction scale: 0.1 mmol; [b]photosensitizer was used under 23 W CFL; [c]yields were determined by ^{1}H NMR spectroscopy using 4-chloroanisole as the internal standard.; [d]77%

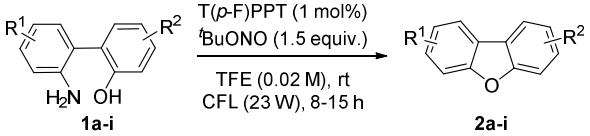
after 36 h.

The investigation was initiated by using 2-(2′-aminophenyl)phenol (**1a**) as the model substrate with *tert*-butyl nitrite (^{t}BuONO) as a diazotizing agent in 2,2,2-trifluroroethanol (TFE) to construct dibenzofuran (**2a**) (**Table 1**). As expected, the reaction did not proceed at all in the absence of ^{t}BuONO (**Table 1**, entry 1) but provided **2a** through *in situ* diazotization followed by simple nucleophilic substitution in the presence of ^{t}BuONO, despite the unsatisfactory yield (**Table 1**, entry 2). Increasing the reaction temperature to 60 °C did not improve the efficiency of the process (**Table 1**, entry 3). To improve the efficiency of intramolecular C-O bond formation, the introduction of visible-light photocatalysis was proposed, where photocatalysis have recently emerged as a powerful synthetic tool owing to their environmental benignity and mechanistic versatility in promoting a large number of organic reactions [**Scheme 1**(c)].[12] Notably, diazonium salts have been successfully utilized in a variety of visible-light promoted photocatalytic reactions.[10b, 11a, 11c, 11d] First, the most widely used photosensitizers $[Ru(bpy)_3]Cl_2$ and *fac*-$Ir(ppy)_3$ (bpy = 2,2'-bipyridine; ppy = 2-phenlypyridine) were employed under visible-light irradiation using a compact fluorescent lamp (CFL, 23W); however, no improvement of the reaction efficiency was achieved (**Table 1**, entries 4 and 5). Several types of organic photosensitizers were also explored, including Eosin Y and triphenylpyrylium tetrafluoroborate (TPPT) derivatives (**Table 1**, entries 6−12). Notably, the use of an organic photosensitizer can minimize the drawbacks associated with transition metals, including toxicity and threshold values in pharmaceutical products.[13] The use of 2,4,6-tris(4-fluorophenyl)pyrylium tetrafluoroborate (T(*p*-F)PPT) successfully increased the reaction efficiency to provide **2a** in 64% yield (**Table 1**, entry 8), plausibly due to the high oxidizing potential of its photoexcited state (E^*[T(*p*-F)PPT*/T(*p*-F)PPT$^-$]= +2.28 V *vs*. SCE)[14] and good solubility in TFE. The reaction atmosphere did not affect the reactivity in that the reactions under argon and oxygen provided similar yields of **2a**. Changing the

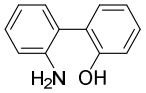
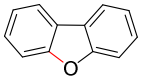
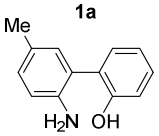
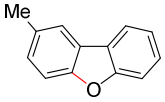
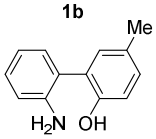
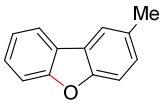
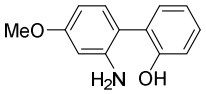
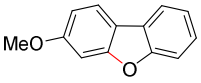
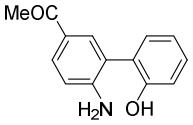
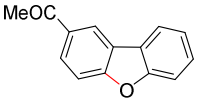
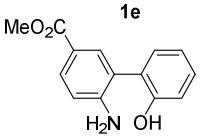
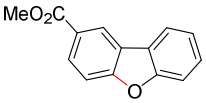
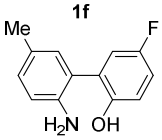
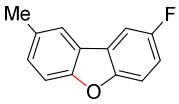
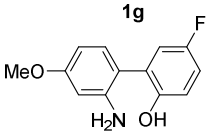
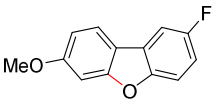
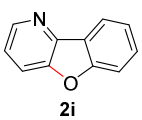
nitrite source and solvent system did not improve the reaction efficiency (**Table 1**, entries 13−22). After extensive screening of the stoichiometry of the reagents and reaction concentration (**Table 1**, entries 23−30), the reaction of **1a** provided the best result, furnishing **2a** in 80% yield with 1 mol% of T(*p*-F)PPT, 1.5 equiv. ^{t}BuONO, and 0.02 M TFE (**Table 1**, entry 29).

Using the optimized conditions, the scope of various 2-(2′-aminoaryl)phenol substrates (**1**) was then investigated (**Table 2**). One advantage of this approach is that regardless of the substituent pattern on the two aryl rings (aniline or phenol rings) of the mono-substituted substrate, the same product could be obtained in similar yields so that the more-easily prepared substrate could be used. The reactions of substrates with the substituent located at different positions generated the same dibenzofuran derivative (**Table 2**, entries 2 and 3, **1b** *vs*. **1c**) with nearly equal efficiencies, confirming that the efficiency of the approach was not significantly altered by the position of the aryl ring substituents.[15] The reactions of substrates containing substituents on both rings (**1g** and **1h**) also proceeded to give the corresponding dibenzofuran derivatives (**Table 2**, entries 7 and 8). Heteroatom-containing substrates also worked well for the transformation. A pyridyl-containing substrate, 2-(3-aminopyridin-2-yl)phenol (**1i**) smoothly underwent C−O cyclization to produce the tricyclic product **2i** in 60% yield (**Table 2**, entry 9). The reaction also produced nitrodibenzofurans (1%−5%) as side products, through overreaction with the nitro group present in the reaction medium. Notably, the reaction conditions were amenable to gram-scale reaction, where the product **2a** was prepared on a 6 mmol-scale with yield similar to that of the 0.5 mmol-scale reaction (**Table 2**, entry 1).

Table 2. Substrate scope for synthesis of dibenzofuran derivatives[a]



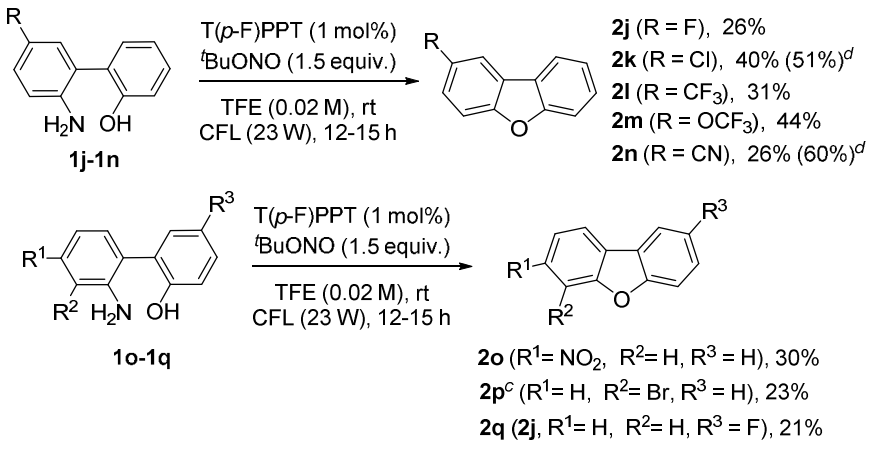
1a-i 2a-i

Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **2a**	74 76[c]
2	 **1b**	 **2b**	65
3	 **1c**	 **2b**	70
4	 **1d**	 **2d**	85
5	 **1e**	 **2e**	68
6	 **1f**	 **2f**	43
7	 **1g**	 **2g**	53
8	 **1h**	 **2h**	65
9	 **1i**	 **2i**	60

[a]Reaction scale: 0.5 mmol; [b]Isolated yield (products are generally volatile[2]); [c]6.0 mmol-scale.

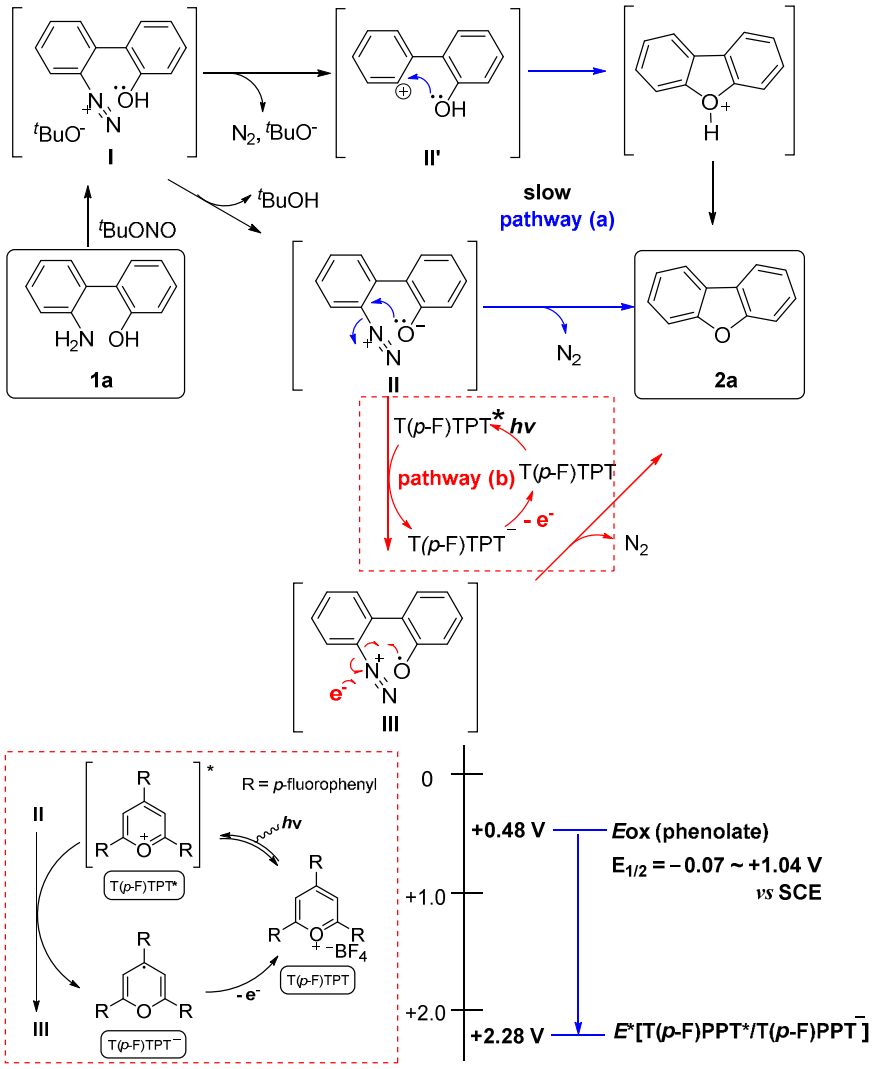
Substrates containing electron donating substituents generally underwent C-O cyclization smoothly to give the corresponding dibenzofuran derivatives in good yields, whereas reactions of substrates with electron withdrawing substituents provided lower yields of the desired dibenzofurans. Other substrates with various electron withdrawing substituents such as -F, -Cl, -Br, -CF_3, -OCF_3, -CN, and -NO_2 were explored, but reactions showed lower reactivity, providing low to moderate yields of the dibenzofuran products (**Scheme 2**).[16]

Scheme 2. Reactions with substrates containing electron withdrawing substituents[a,b]



[a]Reaction scale: 0.5 mmol; [b]Isolated yield (products are generally volatile[2]); [c]DMF (0.1 M) was used as a solvent due to the insolubility of **1p** in TFE; [d]Reaction yields at 60 °C.

Scheme 3. Proposed reaction mechanism



A plausible mechanism for the intramolecular C-O cyclization with **1a** is shown in **Scheme 3**. *In situ* diazotization of **1a** by ^{t}BuONO produces the corresponding diazonium salt **I**. The desired product **2a** can be synthesized simply by nucleophilic substitution through either **II** or **II'** [pathway (a)][17] where the driving force for the process is the formation of stable nitrogen gas, as well as the tricyclic heterocycle, dibenzofuran. However, the process is very slow and

not sufficiently efficient to generate a high yield of **2a**, as described above (see entry 2 of **Table 1**). The use of T(*p*-F)PPT as a photosensitizer under visible-light irradiation was found herein to increase the reaction efficiency, indicating the involvement of another photocatalytic process. The photoexcited state of T(*p*-F)PPT has a sufficiently high oxidizing potential (E^*[T(*p*-F)PPT*/T(*p*-F)PPT$^-$]= +2.28 V *vs*. SCE)[14] to oxidize the phenolate of the intermediate **II** (approximately $E_{1/2}$ = −0.07 ~ +1.04 V *vs*. SCE)[18] with highly positive driving force through a single-electron-transfer process under visible-light irradiation, providing the oxyradical intermediate **III** [pathway (b)]. Moreover, in pathway (b), formation of the aryl radical from the diazonium salt moiety can be facilitated by single electron reduction from T(*p*-F)PPT$^-$, regenerating T(*p*-F)PPT in the photocatalytic cycle. Subsequent intramolecular C-O cyclization to give the desired product **2a**.

In conclusion, a visible-light-promoted method was developed for the synthesis of dibenzofuran derivatives under mild reaction conditions. Intramolecular C-O bond formation through the diazonium intermediate formed *in situ* from 2-(2′-aminoaryl)phenol could be facilitated by visible-light photocatalysis utilizing T(*p*-F)PPT as the photosensitizer. The high excited oxidizing potential of T(*p*-F)PPT accounts for formation of the oxyradical intermediate, leading to efficient C-O bond formation. Moreover, the practicality of the process was demonstrated by producing various functionalized dibenzofuran derivatives, even on the gram-scale.

EXPERIMENTAL SECTION

General Information. All reagents and solvents including ^{t}BuONO and 2,2,2-trifluoroethanol (TFE) were purchased from Sigma-Aldrich, Alfa Aesar, TCI, and Combi

Blocks chemical companies. Flash column chromatography was performed using Merck silica gel 60 (70-230 mesh). The 2'-amino[1,1'-biphenyl]-2-ol derivatives and dibenzofuran products were characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Bruker 600 MHz instrument (600 MHz for ^{1}H NMR and 151 MHz for ^{13}C NMR). Copies of ^{1}H and ^{13}C NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) or residual DMSO (2.50 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm) or deuterated DMSO (39.52 ppm), and all were obtained with ^{1}H decoupling. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Tensor 27 Bruker FT-IR spectrometer. Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. The mass analyzer type used for HRMS measurements is EI-quadrupole. Melting points of unknown solid compounds were recorded on a Stuart SMP30 apparatus.

Experimental Details

1. Preparation of triphenylpyrylium tetrafluoroborate(TPPT) derivatives

All of triphenylpyrylium tetrafluoroborate (TPPT) derivatives were synthesized following a reported procedure.[19]

2. Preparation of 2'-amino[1,1'-biphenyl]-2-ol derivatives (1a-1p)

For the synthesis of **1a-1p**, we followed a slightly modified synthetic procedure that was reported by our group for the synthesis of 2,2′-diaminobiaryls[11d], the Ritter group for the synthesis of 2-(2-pyridinyl)aniline[20], and the Yoshikai group for [1,1'-biphenyl]-2-ol[9d].

An oven-dried 250 mL round bottom flask equipped with a magnetic stir bar was charged with 2-iodoaniline (10 mmol, 2.23 g) and (2-hydroxyphenyl)boronic acid (12 mmol, 1.71 g) in ethylene glycol dimethyl ether (18 mL) mixed with distilled water (18 mL). 5 mol% $Pd(PPh_3)_4$ (0.5 mmol, 0.60 g) and K_2CO_3 (40 mmol, 5.53 g) were added to it. The round bottom flask connected with a reflux column was placed in the oil bath and heated for 16 h at 120 °C. The progress of the reaction was monitored by TLC and gas chromatography. The flask was cooled to room temperature, the reaction mixture was diluted with dichloromethane, and the aqueous phase was extracted with dichloromethane. The combined organic layers were dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography using hexane and ethyl acetate as the eluent to give the desired product **1a** (1.44 g, 78%). Other substrates **1b–1q** are synthesized similarly to the synthesis of **1a** by Suzuki-Miyaura coupling process using the corresponding substituted 2-haloanilines and (2-hydroxyphenyl)boronic acid (on 5 or 10 mmol scale).

3. A Representative Experimental Procedure for the Synthesis of Dibenzofuran derivatives (2a-2p)

An oven-dried 50 mL round bottom flask with a magnetic stir bar was charged with the 2-(2′-aminoaryl)phenol derivative (**1**, 0.5 mmol) and T(*p*-F)PPT (0.005 mmol, 2.3 mg) in 2,2,2-trifluoroethanol (TFE) (25 mL, 0.02 M). ^{t}BuONO (1.5 mmol, 99 μL) was added to the solution, considering the purity of ^{t}BuONO (90% purity). The flask was then irradiated with visible-light using a CFL (23 W) at room temperature. The reaction progress was monitored by TLC. After completion of the reaction, the solvent was evaporated and the reaction mixture was purified by flash column chromatography to give the corresponding dibenzofuran product **2**.

Analytic Data for 2'-Amino[1,1'-biphenyl]-2-ol Derivatives

2'-amino-[1,1'-biphenyl]-2-ol (1a):[21] beige solid (10 mmol scale: 1.57 g, 85%); mp 92−94 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.31 – 7.28 (m, 2H), 7.24 – 7.20 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.01 (ddd, *J* = 7.7, 7.5, 1.3 Hz, 1H), 6.96 (ddd, *J* = 7.5, 7.4, 1.2 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 3.76 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.9, 142.0, 132.0, 131.3, 129.7, 129.2, 126.3, 126.2, 121.4, 121.2, 118.3, 117.4; **IR (neat)** ν_{max} = 3380, 3308, 3060, 1613, 1479, 753 cm^{-1}; $\mathbf{R}_f$ 0.57 (hexane/EtOAc, 2/1)

2'-amino-5'-methyl-[1,1'-biphenyl]-2-ol (1b): pale yellow solid (0.64 g, 64%); mp 104−106 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.31 (ddd, *J* = 8.0, 7.5, 1.7 Hz, 1H), 7.08 (d, *J* = 1.4 Hz, 1H), 7.06 (dd, *J* = 8.0, 2.1 Hz, 1H) 7.05 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.03 (ddd, *J* = 7.5, 7,4, 1.3 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 3.71 (bs, 2H), 2.32 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.0, 139.1, 132.5, 131.3, 130.8, 129.7, 129.5, 126.9, 126.7, 121.3, 118.5, 117.8, 20.8; **HRMS** *m/z* calc. for $C_{13}H_{13}NO$ [M+] 199.0997, found 199.0999; **IR (neat)** ν_{max} = 3381, 3301, 3027, 2919, 1602, 1483, 754 cm^{-1}; $\mathbf{R}_f$ 0.44 (hexane/EtOAc, 2/1)

2'-amino-5-methyl-[1,1'-biphenyl]-2-ol (1c): light brown solid (0.53 g, 53%); mp 95−96 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.22 (d, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.09 (s, 1H), 6.95 (dd, *J* = 7.6, 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 3.79 (bs, 2H), 2.32 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 151.6, 142.0, 131.9, 131.6, 130.5, 130.2, 129.0, 126.3, 126.0, 121.0, 118.0, 117.3, 20.7; **HRMS** *m/z* calc. for $C_{13}H_{13}NO$ [M+] 199.0997, found 199.0998; **IR (neat)** ν_{max} = 3381, 3310, 3026, 2920, 1614, 1491, 907, 818, 752 cm^{-1}; $\mathbf{R}_f$ 0.44 (hexane/EtOAc, 2/1)

2'-amino-4'-methoxy-[1,1'-biphenyl]-2-ol (1d):[21] light brown solid (0.51 g, 47%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.25 – 7.20 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H)

6.96 (dd, *J* = 7.5, 7.4 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.33 (d, *J* = 2.5 Hz, 1H), 3.74 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 215.1, 160.5, 153.7, 143.6, 132.7, 131.3, 129.2, 125.9, 121.2, 118.2, 117.6, 106.4, 102.6, 55.4; **IR (neat)** ν_{max} = 3378, 2936, 2835, 1605, 1480, 1203, 728 cm^{-1}; $\mathbf{R}_f$ 0.53 (hexane/EtOAc, 1/1)

1-(6-amino-2'-hydroxy-[1,1'-biphenyl]-3-yl)ethan-1-one (1e): yellow solid (0.83 g, 73%); mp 165−166 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.33 (ddd, *J* = 8.4, 7.2, 1.5 Hz, 1H), 7.25 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.03 (dd, *J* = 7.2, 7.5 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.84 (bs, 1H), 4.27 (bs, 2H), 2.51 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 196.8, 153.5, 148.4, 133.1, 131.3, 130.4, 130.2, 129.1, 124.5, 122.6, 121.6, 117.3, 115.5, 26.4; **HRMS** *m/z* calc. for $C_{14}H_{13}NO_2$ [M+] 227.0946, found 227.0945; **IR (neat)** ν_{max} = 3367, 1615, 1585, 1449, 1248, 729 cm^{-1}; $\mathbf{R}_f$ 0.42 (hexane/EtOAc, 1/1)

methyl 6-amino-2'-hydroxy-[1,1'-biphenyl]-3-carboxylate (1f):[22] brown solid (0.46 g, 38%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 1.7 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.24 (dd, *J* = 7.5, 7.0 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.68 (bs, 3H), 3.80 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.3, 153.5, 148.3, 133.6, 131.3, 131.0, 129.8, 124.7, 123.2, 121.2, 120.5, 117.1, 115.4, 51.9; **IR (neat)** ν_{max} = 3380, 2951, 1692, 1616, 1436, 1245 cm^{-1}; $\mathbf{R}_f$ 0.59 (hexane/EtOAc, 1/1)

2'-amino-5-fluoro-5'-methyl-[1,1'-biphenyl]-2-ol (1g): beige solid (0.36 g, 33%); mp 92−94 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.70 (bs, 1H), 7.08 (d, *J* = 2.9 Hz, 1H), 7.07 (s, 1H), 7.04 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 3.75 (bs, 2H), 2.32 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.4 (d, $^{1}J_{C\text{-}F}$ = 238.6 Hz), 150.1, 138.7, 132.4, 131.3, 130.0, 127.8 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 126.5, 119.7 (d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 118.2, 117.1 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 116.0 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 20.8; **HRMS** *m/z* calc. for $C_{13}H_{12}FNO$ [M+]

217.0903, found 217.0905; **IR (neat)** ν_{max} = 3303, 1621, 1489, 1263, 1164 cm^{-1}; $\mathbf{R}_f$ 0.40 (hexane/EtOAc, 2/1)

2'-amino-5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-ol (1h): off-white solid (0.24 g, 21%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.13 (d, *J* = 8.5 Hz, 1H), 6.99 – 6.96 (m, 3H), 6.55 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.42 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.2 (d, $^1J_{C\text{-}F}$ = 238.6 Hz), 149.6 (d, $^5J_{C\text{-}F}$ = 2.1 Hz), 142.9, 132.5, 131.9 (d, $^3J_{C\text{-}F}$ = 10.6 Hz), 128.9 (d, $^3J_{C\text{-}F}$ = 12.6 Hz), 126.9 (d, $^4J_{C\text{-}F}$ = 7.8 Hz), 118.8 (d, $^4J_{C\text{-}F}$ = 8.4 Hz), 116.9 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 106.7, 102.9, 55.5; **HRMS** *m/z* calc. for $C_{13}H_{12}FNO_2$ [M+] 233.0852, found 233.0854; **IR (neat)** ν_{max} = 3312, 2935, 1616, 1482, 1263, 1168 cm^{-1}; $\mathbf{R}_f$ 0.50 (hexane/EtOAc, 1/1)

2-(3-aminopyridin-2-yl)phenol (1i): yellow solid (0.47 g, 50%); mp 123−125 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (dd, *J* = 4.6, 1.5 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.27 (ddd, *J* = 7.7, 7.5, 1.6 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.92 (ddd, *J* = 7.8, 7.5 1.6 Hz, 1H), 4.08 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.5, 142.9, 140.8, 137.7, 130.4, 127.2, 125.1, 123.0, 120.9, 119.1, 118.5; **HRMS** *m/z* calc. for $C_{11}H_{10}N_2O$ [M+] 186.0793, found 186.0791; **IR (neat)** ν_{max} = 3357, 3060, 1609, 1455, 1443, 757 cm^{-1}; $\mathbf{R}_f$ 0.41 (hexane/EtOAc, 2/1)

2'-amino-5'-fluoro-[1,1'-biphenyl]-2-ol (1j): brown viscous oil (0.60 g, 59%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.63 (bs, 1H), 7.33 (dd, *J* = 8.5 Hz, $^3J_{H\text{-}F}$ = 7.3 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.05 (d, $^3J_{H\text{-}F}$ = 8.1 Hz, 1H), 7.05 – 7.02 (m, 1H), 7.00 (dd, *J* = 9.3, 2.9 Hz, 1H), 6.95 (ddd, *J* = 8.1, 7.5, 2.9 Hz, 1H), 6.81 (dd, *J* = 8.5 Hz, $^4J_{H\text{-}F}$ = 4.9 Hz, 1H), 3.87 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.7 (d, $^1J_{C\text{-}F}$ = 238.6 Hz), 153.8, 137.5 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 131.2, 130.0, 129.0 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 125.8 (d, $^4J_{C\text{-}F}$ = 1.5 Hz), 121.4, 118.9 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 118.8, 118.1 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 22.5 Hz); **HRMS** *m/z* calc. for

$C_{12}H_{10}FNO$ [M+] 203.0746, found 203.0744; **IR (neat)** ν_{max} = 3311, 1591, 1484, 1266, 1174, 903, 726 cm^{-1}; $\mathbf{R}_f$ 0.67 (hexane/EtOAc, 1/1)

2'-amino-5'-chloro-[1,1'-biphenyl]-2-ol (1k): light brown solid (0.56 g, 51%); mp 102−103 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (ddd, *J* = 7.6, 7.5, 1.4 Hz 1H), 7.27 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.22 (d, *J* = 2.3 Hz, 1H), 7.18 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.78 (dd, *J* = 7.9, 7.6 Hz, 1H), 4.68 (bs, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.7, 140.8, 131.4, 131.2, 130.1, 128.9, 127.7, 125.6, 125.2, 121.5, 118.5, 118.4; **HRMS** *m/z* calc. for $C_{12}H_{10}ClNO$ [M+] 219.0451, found 219.0453; **IR (neat)** ν_{max} = 3382, 3314, 3060, 1612, 1483, 754 cm^{-1}; $\mathbf{R}_f$ 0.69 (hexane/EtOAc, 1/1)

2'-amino-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-ol (1l): yellow viscous oil (0.19 g, 15%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H) 7.34 (ddd, *J* = 8.1, 7.1, 1.7 Hz, 1H), 7.26 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.06 (ddd, *J* = 8.1, 8.0, 1.1, Hz, 1H), 7.05 (dd, *J* = 7.1, 1.1 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.02 (bs, 1H), 4.03 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.6, 146.0, 131.3, 130.4, 129.1(q, $^3J_{C\text{-}F}$ = 3.0 Hz), 126.5 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 125.7 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 124.5, 124.2, 122.2 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 121.7, 117.8, 116.2; **HRMS** *m/z* calc. for $C_{13}H_{10}F_3NO$ [M+] 253.0714, found 253.0716; **IR (neat)** ν_{max} = 3386, 1625, 1488, 1335, 1111 cm^{-1}; $\mathbf{R}_f$ 0.41 (hexane/EtOAc, 2/1)

2'-amino-5'-(trifluoromethoxy)-[1,1'-biphenyl]-2-ol (1m): yellow viscous oil (1.08 g, 80%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 (ddd, *J* = 7.8, 7.7, 1.3 Hz, 1H), 7.28 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.14 (d, *J* = 1.9 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.06 – 7.04 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 4.09 (bs, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.5, 142.8 (q, $^3J_{C\text{-}F}$ = 2.0 Hz), 140.6, 131.1, 130.1, 127.3, 124.9, 124.5, 121.8, 121.4, 120.6 (q, $^1J_{C\text{-}F}$ = 256.7 Hz), 118.3, 117.8; **HRMS** *m/z* calc. for $C_{13}H_{10}F_3NO_2$ [M+] 269.0664, found 269.0667; **IR (neat)** ν_{max} = 3327, 1622, 1485, 1251, 1214, 1164 cm^{-1}; $\mathbf{R}_f$ 0.41 (hexane/EtOAc, 2/1)

6-amino-2'-hydroxy-[1,1'-biphenyl]-3-carbonitrile (1n): orange solid (0.81 g, 77%); mp 128−129 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.34 (ddd, *J* = 8.1, 7.6, 1.4 Hz, 1H), 7.20 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.04 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.85 (bs, 1H), 4.24 (bs, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.3, 147.8, 135.9, 133.4, 131.2, 130.7, 123.8, 123.3, 121.8, 119.7, 117.4, 116.0, 102.0; **HRMS** *m/z* calc. for $C_{13}H_{10}N_2O$ [M+] 210.0793, found 210.0790; **IR (neat)** ν_{max} = 3373, 2219, 1620, 1497, 756 cm^{-1}; $\mathbf{R}_f$ 0.53 (hexane/EtOAc, 1/1)

2'-amino-4'-nitro-[1,1'-biphenyl]-2-ol (1o): yellow solid (0.59 g, 51%); mp 147−149 °C; **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.74 (s, 1H), 7.61 (d, *J* = 1.2 Hz, 1H), 7.42 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.9, 7.4 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.90 (dd, *J* = 7.4, 7.4 Hz, 1H), 5.22 (bs, 2H); **^{13}C NMR (151 MHz, DMSO-d_6)** δ 154.3, 147.4, 147.1, 131.8, 130.8, 130.7, 129.4, 124.4, 119.5, 116.0, 110.4, 108.4; **HRMS** *m/z* calc. for $C_{12}H_{10}N_2O_3$ [M+] 230.0691, found 230.0693; **IR (neat)** ν_{max} = 3377, 3284, 2361, 1608, 1585, 1484, 1351 cm^{-1}; $\mathbf{R}_f$ 0.39 (hexane/EtOAc, 2/1)

2'-amino-3'-bromo-[1,1'-biphenyl]-2-ol (1p):[23] light brown solid (0.26 g, 20%); mp 148−150 °C; **^{1}H NMR (600 MHz, DMSO-d_6)** δ 9.66 (bs, 1H), 7.38 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.22 (dd, *J* = 8.1, 7.3 Hz 1H), 7.08 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.89 (dd, *J* = 7.3, 7.2 Hz, 1H), 6.60 (dd, *J* = 7.8, 7.5 Hz, 1H), 4.54 (bs, 2H); **^{13}C NMR (151 MHz, DMSO-d_6)** δ 154.3, 142.7, 131.3, 131.1, 130.3, 129.0, 126.2, 125.6, 119.5, 117.7, 115.8, 108.7; **IR (neat)** ν_{max} = 3370, 3272, 1506, 1436, 1108, 1038, 637 cm^{-1}; $\mathbf{R}_f$ 0.48 (hexane/EtOAc, 4/1)

2'-amino-5-fluoro-[1,1'-biphenyl]-2-ol (1q):[24] brown viscous oil (0.38 g, 37%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.25 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.03 (dd, $^3J_{H\text{-}F}$ = 9.1 Hz, *J* = 3.1 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.96 (dd, *J* = 8.8 Hz, $^4J_{H\text{-}F}$ = 5.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.03 (bs, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** 157.3 (d, $^1J_{C\text{-}F}$ = 238.6

Hz), 149.8, 141.6, 131.7, 129.4, 127.6 (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 125.9, 121.4, 119.4 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 117.8, 117.0 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 22.7 Hz); **IR (neat)** ν_{max} = 1482, 1261, 1175, 905, 722 cm^{-1}; $\mathbf{R}_f$ 0.43 (hexane/EtOAc, 2/1)

Analytic Data for Dibenzofuran Products

dibenzo[*b,d*]furan (2a):[8d] white solid (0.5 mmol scale: 62 mg, 74%, 6 mmol scale: 0.77g, 76%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.47 (dd, *J* = 8.2, 7.4 Hz, 2H), 7.36 (dd, *J* = 7.7, 7.4 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.4, 127.3, 124.4, 122.9, 120.7, 111.9; **IR (neat)** ν_{max} = 3047, 1444, 1195, 723 cm^{-1}; $\mathbf{R}_f$ 0.57 (hexane)

2-methyldibenzo[*b,d*]furan (2b):[9d, 8e] white solid (59 mg, 65%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.77 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.2 Hz 1H), 7.48 (dd, *J* = 8.2, 7.6 Hz, 1H), 7.36 (dd, *J* = 7.7 ,7.6 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 2.55 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.7, 154.7, 132.3, 128.4, 127.1, 124.5, 124.4, 122.7, 120.8, 120.7, 111.8, 111.3, 21.5; **IR (neat)** ν_{max} = 3044, 2921, 1481, 1447, 1192, 744 cm^{-1}; $\mathbf{R}_f$ 0.57 (hexane)

3-methoxydibenzo[*b,d*]furan (2d):[9d, 9e] white solid (84 mg, 85%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.32 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.0 Hz, 1H), 3.91 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** 160.1, 157.7, 156.5, 125.9, 124.6, 122.9, 121.1, 112.0, 117.5, 111.5, 111.1, 96.7, 55.9; **IR (neat)** ν_{max} = 2983, 1458, 1236, 1043, 750 cm^{-1}; $\mathbf{R}_f$ 0.60 (hexane/EtOAc, 8/1)

1-(dibenzo[*b,d*]furan-2-yl)ethan-1-one (2e):[9e] white solid (71 mg, 68%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.38 (dd, *J* = 7.6, 7.4 Hz,

1H), 2.70 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 197.5, 159.1, 157.1, 132.7, 128.2, 128.1, 124.8, 124.0, 123.6, 121.8, 121.2, 112.1, 111.8, 27.0; **IR (neat)** ν_{max} = 3064, 2926, 1677, 1599, 1476 cm^{-1}; **R_f** 0.47 (hexane/EtOAc, 4/1)

methyl dibenzo[*b,d*]furan-2-carboxylate (2f):[8d, 8g] white solid (49 mg, 43%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.67 (dd, *J* = 1.8, 0.5 Hz, 1H), 8.18 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.99 (ddd, *J* = 7.7, 1.3, 0.6 Hz, 1H), 7.59 (ddd, *J* = 8.3, 0.9, 0.6 Hz, 1H), 7.58 (dd, *J* = 8.6, 0.5 Hz, 1H), 7.50 (ddd, *J* = 8.3, 7.4, 1.3 1H), 7.38 (ddd, *J* = 7.7, 7.4, 0.9 Hz, 1H), 3.98 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.2, 159.1, 157.0, 129.1, 128.1, 125.2, 124.6, 123.9, 123.5, 123.1, 121.2, 112.1, 111.7, 52.4; **IR (neat)** ν_{max} = 3066, 2951, 1718, 1603, 1435, 1249 cm^{-1}; **R_f** 0.58 (hexane/EtOAc, 6/1)

2-fluoro-8-methyldibenzo[*b,d*]furan (2g): white solid (53 mg, 53%); mp 69−70 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.69 (s, 1H), 7.56 (dd, $^3J_{H\text{-}F}$ = 8.2 Hz, *J* = 2.6 Hz, 1H), 7.47 (dd, *J* = 8.9 Hz, $^4J_{H\text{-}F}$ = 4.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.15 (ddd, $^3J_{H\text{-}F}$ = 9.0 Hz, *J* = 8.9, 2.6 Hz, 1H), 2.51 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.1 (d, $^1J_{C\text{-}F}$ = 238.6 Hz), 155.8, 152.7, 132.5, 129.1, 125.3 (d, $^3J_{C\text{-}F}$ = 10.6 Hz), 124.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 121.0, 114.4 (d, $^2J_{C\text{-}F}$ = 25.7 Hz), 112.4 (d, $^3J_{C\text{-}F}$ = 10.6 Hz), 111.6, 106.7 (d, $^2J_{C\text{-}F}$ = 25.7 Hz), 21.5; **HRMS** *m/z* calc. for $C_{13}H_9FO$ [M+] 200.0637, found 200.0635; **IR (neat)** ν_{max} = 2921, 1596, 1487, 1456, 1137, 810 cm^{-1}; **R_f** 0.40 (hexane)

2-fluoro-7-methoxydibenzo[*b,d*]furan (2h): light yellow solid (70 mg, 65%); mp 92−93 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.5 Hz, 1H), 7.50 (dd, $^3J_{H\text{–}F}$ = 8.3 Hz, *J* = 2.6 Hz, 1H), 7.43 (dd, *J* = 8.9 Hz, $^4J_{H\text{–}F}$ = 4.1 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 7.07 (ddd, $^3J_{H\text{–}F}$ = 9.0 Hz, *J* = 8.9, 2.6 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.90 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 160.2, 159.4 (d, $^1J_{C\text{-}F}$ = 239.1 Hz), 158.8, 152.5, 125.6 (d, $^3J_{C\text{-}F}$ = 10.3 Hz), 121.4, 117.3 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 113.0 (d, $^2J_{C\text{-}F}$ = 25.8 Hz), 112.1 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 111.5, 106.2 (d,

$^{2}J_{C\text{-}F}$ = 25.4 Hz), 96.7, 56.0; **HRMS** *m/z* calc. for $C_{13}H_9FO_2$ [M+] 216.0587, found 216.0584; **IR (neat)** ν_{max} = 2965, 1637, 1501, 1275, 1147 cm^{-1}; $\mathbf{R}_f$ 0.60 (hexane/EtOAc, 6/1)

benzofuro[3,2-*b*]pyridine (2i): [25] yellow solid (51 mg, 60%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.56 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.44 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.37 (dd, *J* = 8.3, 4.8 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.6, 149.9, 145.4, 144.5, 129.4, 123.8, 123.5, 121.5, 121.4, 118.8, 112.3; **IR (neat)** ν_{max} = 3061, 1631, 1593, 1449, 1401, 1189 cm^{-1}; $\mathbf{R}_f$ 0.45 (hexane/EtOAc, 2/1)

2-fluorodibenzo[*b,d*]furan (2j): [8e, 8g] white solid (24 mg, 26%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.61 (dd, $^{3}J_{H\text{-}F}$ = 8.6 Hz, *J* = 2.7 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.35 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.17 (ddd, *J* = 8.7, 2.7 Hz, $^{3}J_{H\text{-}F}$ = 8.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 159.2 (d, $^{1}J_{C\text{-}F}$ = 238.6 Hz), 157.4, 152.4, 128.0, 125.3 (d, $^{3}J_{C\text{-}F}$ = 10.6 Hz), 124.2 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 123.0, 121.1, 114.6 (d, $^{2}J_{C\text{-}F}$ = 25.7 Hz), 112.5 (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 112.1, 106.9 (d, $^{2}J_{C\text{-}F}$ = 25.7 Hz); **IR (neat)** ν_{max} = 2926, 1599, 1478, 1447, 1162 cm^{-1}; $\mathbf{R}_f$ 0.57 (hexane)

2-chlorodibenzo[*b,d*]furan (2k): [9d] white solid (41 mg, 40%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 2.2 Hz, 1H), 7.91 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.57 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H) 7.41 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.36 (ddd, *J* = 7.6, 7.3, 0.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.0, 154.7, 128.4, 128.1, 127.4, 125.9, 123.6, 123.2, 121.0, 120.7, 112.9, 112.1; **IR (neat)** ν_{max} = 3063, 1624, 1440, 1199, 725 cm^{-1}; $\mathbf{R}_f$ 0.48 (hexane)

2-(trifluoromethyl)dibenzo[*b,d*]furan (2l): [8g] white solid (37 mg, 31%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.53 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.40 (dd, *J* = 7.7, 7.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.8, 157.1, 128.4, 125.6 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 124.8,

124.8 (q, $^{1}J_{C\text{-}F}$ = 272.1 Hz), 124.4 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.6, 123.5, 121.2, 118.5 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 112.3 112.2; **IR (neat)** ν_{max} = 2927, 1332, 1272, 1107, 731 cm^{-1}; $\mathbf{R}_f$ 0.50 (hexane)

2-(trifluoromethoxy)dibenzo[*b,d*]furan (2m): white solid (55 mg, 44%); mp 59−60 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.80 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.51 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.38 (dd, *J* = 7.7, 7.5 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.4, 154.4, 145.0 (q, $^{3}J_{C\text{-}F}$ = 1.8 Hz), 128.3, 125.4, 123.9, 123.3, 121.1, 120.9 (q, $^{1}J_{C\text{-}F}$ = 256.8 Hz), 120.7, 113.8, 112.6, 112.2; **HRMS** *m/z* calc. for $C_{13}H_7F_3O_2$ [M+] 252.0398, found 252.0399; **IR (neat)** ν_{max} = 1590, 1477, 1447, 1258, 1160, 747 cm^{-1}; $\mathbf{R}_f$ 0.58 (hexane)

dibenzo[*b,d*]furan-2-carbonitrile (2n):[9e] off-white solid (25 mg, 26%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 1.7 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.75 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.56 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.43 (dd, *J* = 7.7, 7.3 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.2, 157.0, 131.1, 129.0, 125.6, 125.5, 124.0, 122.8, 121.3, 119.4, 113.1, 112.3, 106.8; **IR (neat)** ν_{max} = 2225, 2699, 1474, 1448, 1247, 752 cm^{-1}; $\mathbf{R}_f$ 0.52 (hexane/EtOAc, 6/1)

3-nitrodibenzo[*b,d*]furan (2o): white solid (32 mg, 30%); mp 175−177 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.44 (d, *J* = 1.9 Hz, 1H), 8.28 (dd, *J* = 8.5, 1.9 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.44 (dd, *J* = 7.8, 7.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.5, 155.3, 147.0, 130.4, 124.0, 122.7, 122.0, 120.8, 112.5, 108.2; **HRMS** *m/z* calc. for $C_{12}H_7NO_3$ [M+] 213.0426, found 213.0428; **IR (neat)** ν_{max} = 2851, 1628, 1523, 1457, 1343 cm^{-1}; $\mathbf{R}_f$ 0.45 (hexane/EtOAc, 5/1)

4-bromodibenzo[*b,d*]furan (2p): [26] yellow solid (28 mg, 23%); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.38 (dd, *J* = 7.6, 7.5 Hz, 1H), 7.23 (dd, *J* = 7.9, 7.7 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.3, 153.5, 130.3, 128.1, 125.9, 124.4, 124.2,

123.5, 121.3, 119.9, 112.3, 104.7, 77.4; **IR (neat)** ν_{max} = 1576, 1447, 1417, 1195, 650 cm^{-1}; $\mathbf{R}_f$ 0.55 (hexane/EtOAc, 20/1)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra for ^{1}H NMR and ^{13}C NMR spectra of 2'-amino[1,1'-biphenyl]-2-ol derivatives and dibenzofuran derivatives (**PDF**)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Kokubun, T.; Harborne, J. B.; Eagles, J.; Waterman, P. G., *Phytochemistry* **1995,** *39*, 1039.

(2) Collin, G.; Höke, H., Benzofurans. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA2000; Vol. 5, pp 325.

(3) Chizzali, C.; Beerhues, L., *Beilstein J. Org. Chem.* **2012,** *8*, 613.

(4) Martel, R. R.; Rochefort, J. G.; Klicius, J.; Dobson, T. A., *Can. J. Physiol. Pharmacol.* **1974,** *52*, 669.

(5) Petrassi, H. M.; Johnson, S. M.; Purkey, H. E.; Chiang, K. P.; Walkup, T.; Jiang, X.; Powers, E. T.; Kelly, J. W., *J. Am. Chem. Soc.* **2005,** *127*, 6662.

(6) Lin, R.-D.; Chen, M.-C.; Liu, Y.-L.; Lin, Y.-T.; Lu, M.-K.; Hsu, F.-L.; Lee, M.-H., *Int. J. Mol. Sci.* **2015,** *16*, 28598.

(7) Zhang, L.; Zhang, Y.-X.; Hu, Y.; Shi, X.-B.; Jiang, Z.-Q.; Wang, Z.-K.; Liao, L.-S., *ACS Appl. Mater. Interfaces* **2016,** *8*, 16186.

(8) (a) Henderson Jr, W. A.; Zweig, A., *Tetrahedron Lett.* **1969,** *10*, 625. (b) Ejlx, J.; Murphy, D.; Sargent, M., *Synth. Commun.* **1972,** *2*, 427. (c) Wang, J.-Q.; Harvey, R. G., *Tetrahedron* **2002,** *58*, 5927. (d) Liu, Z.; Larock, R. C., *Org. Lett.* **2004,** *6*, 3739. (e) Wang, C.; Piel, I.; Glorius, F., *J. Am. Chem. Soc.* **2009,** *131*, 4194. (f) Du, Z.; Zhou, J.; Si, C.; Ma, W., *Synlett* **2011,** *2011*, 3023. (g) Lockner, J. W.; Dixon, D. D.; Risgaard, R.; Baran, P. S., *Org. Lett.* **2011,** *13*, 5628.

(9) (a) Maevskii, Y. V.; Migachev, G., *Chem. Heterocycl. Compd.* **1986,** *22*, 676. (b) Yamato, T.; Hideshima, C.; Prakash, G. K. S.; Olah, G. A., *J. Org. Chem.* **1991,** *56*, 3192. (c) Liu, J.; Fitzgerald, A. E.; Mani, N. S., *J. Org. Chem.* **2008,** *73*, 2951. (d) Wei, Y.; Yoshikai, N., *Org. Lett.* **2011,** *13*, 5504. (e) Xiao, B.; Gong, T.-J.; Liu, Z.-J.; Liu, J.-H.; Luo, D.-F.; Xu, J.; Liu, L., *J. Am. Chem. Soc.* **2011,** *133*, 9250. (f) Yang, W.; Zhou, J.; Wang, B.; Ren, H., *Chem. Eur. J.* **2011,** *17*, 13665.

(10) (a) Roglans, A.; Pla-Quintana, A.; Moreno-Manas, M., *Chem. Rev.* **2006,** *106*, 4622. (b) Hari, D. P.; König, B., *Angew. Chem. Int. Ed.* **2013,** *52*, 4734.

(11) (a) Chatterjee, T.; Choi, M. G.; Kim, J.; Chang, S. K.; Cho, E. J., *Chem. Commun.* **2016,** *52*, 4203. (b) Choi, Y.; Chatterjee, T.; Kim, J.; Kim, J. S.; Cho, E. J., *Org. Biomol. Chem.* **2016,** *14*, 6804. (c) Chatterjee, T.; Lee, D. S.; Cho, E. J., *J. Org. Chem.* **2017,** *82*, 4369. (d) Chatterjee, T.; Roh, G. B.; Shoaib, M. A.; Suhl, C. H.; Kim, J. S.; Cho, C. G.; Cho, E. J., *Org. Lett.* **2017,** *19*, 1906.

(12) Some recent reviews on visible light photocatalysis, see: (a) Narayanam, J. M. R.; Stephenson, C. R. J., *Chem. Soc. Rev.* **2011,** *40*, 102. (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., *Chem. Rev.* **2013,** *113*, 5322. (c) Schultz, D. M.; Yoon, T. P., *Science* **2014,** *343*, 1239176. (d) Cambié, D.; Bottecchia, C.; Straathof, N. J. W.; Hessel, V.; Noël, T., *Chem. Rev.* **2016,** *116*, 10276. (e) Romero, N. A.; Nicewicz, D. A., *Chem. Rev.* **2016,** *116*, 10075.

(13) Sun, C.-L.; Shi, Z.-J., *Chem. Rev.* **2014,** *114*, 9219.

(14) Martiny, M.; Steckhan, E.; Esch, T., *Chem. Ber.* **1993,** *126*, 1671.

(15) The e□ciency of reactions can depend on the substitution pattern of the biaryls, see: Cho, S. H.; Yoon, J.; Chang, S., *J. Am. Chem. Soc.* **2011,** *133*, 5996.

(16) The diazonium salt intermediates remained after reaction.

(17) Ramanathan, M.; Liu, S.-T., *J. Org. Chem.* **2015,** *80*, 5329.

(18) Li, C.; Hoffman, M. Z., *J. Phys. Chem. B*, **1999**, *103*, 6653.

(19) Ortgies, S.; Depken, C.; Breder, A., *Org. Lett.* **2016,** *18*, 2856.

(20) Lee, E.; Hooker, J. M.; Ritter, T., *J. Am. Chem. Soc.* **2012,** *134*, 17456.

(21) Kumar, A.; Sattar, M.; Verma, A.; Dara, A.; Kumar, S., *RSC Adv.* **2015**, *5*, 44728.

(22) Chauhan, J.; Wang, H.; Yap, J. L.; Sabato, P. E.; Hu, A.; Prochownik, E. V.; Fletcher, S., *ChemMedChem* **2014**, *9*, 2274.

(23) Gao, H.; Ess, D. H.; Yousufuddin, M.; Kürti, L., *J. Am. Chem. Soc.* **2013**, *135*, 7086.

(24) Liu, B.; Yin, M.; Gao, H.; Wu, W.; Jiang, H., *J. Org. Chem.* **2013**, *78*, 3009.

(25) Abramovitch, R. A.; Inbasekaran, M. N.; Kato, S.; Radzikowska, T. A.; Tomasik, P., *J. Org. Chem.* **1983,** *48*, 690.

(26) Unger, Y.; Meyer, D.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T., *Angew. Chem. Int. Ed.* **2010,** *49*, 10214.