5-Hydroxymethylfurfural-Derived Boron-Dipyrromethene Immobilized on Resin Support as a Sustainable Catalyst for C–H Arylation of Heterocycles

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*S Supporting Information

ABSTRACT: 5-Hydroxymethylfurfural (HMF) was used as a sustainable raw material in the development of a resin-supported boron-dipyrromethene (BODIPY)-based photocatalyst. In the development of the catalyst, the brominated product (HMF-BODIPY-Br) and photocatalyst (HMF-BODIPY-Br-Suc) were isolated under a chromatography-free condition. The photocatalyst was loaded on polymeric resin by bridging alcohol functionality in HMF and amine functionality in polymeric resin using succinic anhydride. The resin-supported photocatalyst was used in light-mediated C–H arylation of various heterocycles using aryldiazonium salt. For representative examples, diazotization and photoarylation were carried out in one pot, and arylated furans were obtained in very good yields. C–H arylation was found to proceed via a photogenerated radical intermediate, and the radical intermediate was trapped by forming an adduct with TEMPO.

INTRODUCTION

The ever-increasing demand for fossil-sourced energy and chemical products results in depletion of fossil fuel reserves, impacting environmental harmony. Intense research is being carried out on developing many plant-sourced organic matters as energy alternates to be used in internal combustion engines, for example, ethanol, biodiesel, and 2,5-dimethylfuran. Considering the demand for fine chemicals, various HMF-derived chemicals have been utilized as plant-sourced sustainable raw materials (Table 1). HMF-derived 2,5-diformylfuran (DFF) has been utilized as a raw material in accessing pharmaceutical intermediates and antifungal agents. 2,5-Furandicarboxylic acid (FDCA) accessed by oxidation of HMF is an alternate for fossil-derived terephthalic acid in making polymers. 2,5-Bis(hydroxymethyl)furan (BHF) obtained by reduction of HMF is used as a monomer in the synthesis of polyurethane foams and polyesters. 2,5-Bis(aminomethyl)furan (BAF) is used as a monomer in the synthesis of polyamides and polyurethanes. Caprolactone, an important molecule in polymer industry, can be obtained from HMF. HMF-derived 1,6-hexanediol has been utilized as a monomer in the synthesis of polyurethane foams and polyesters. HMF can also be utilized in the synthesis of adipic acid, a monomer utilized in the production of nylon. To date, HMF has been converted into many simple molecules of industrial importance, including DFF, FDCA, etc. The use of HMF in developing complex functional molecules has not been explored much. Herein, we have taken a step ahead to utilize HMF beyond its conventional usage of accessing simple molecules. We have developed a functionalized photocatalyst accessible from sustainable raw materials such as HMF and 2,4-dimethylpyrrole. The photocatalyst has been immobilized on polymeric resin to facilitate its complete recovery after the reaction. The immobilized photocatalyst has been utilized in light-mediated arylation of various arenes. Recovery and reusability of the resin-supported photocatalyst have been demonstrated.

Table 1. 5-Hydroxymethylfurfural (HMF)-Derived Fine Chemicals

| entry | fine chemical | utilization |
|-------|---------------|-------------|
| 1     | DFF           | pharmaceutical intermediates and antifungal agents |
| 2     | FDCA          | biorenewable alternate for fossil-derived terephthalic acid |
| 3     | BHF           | monomer for polyurethane foams and polyesters |
| 4     | BAF           | monomer for polyamides and polyurethanes |
| 5     | caprolactone  | monomer for production of nylon-6 |
| 6     | 1,6-hexanediol| monomer for polyurethane foams and polyesters |
| 7     | adipic acid   | monomer for production of nylon |

* Supporting Information

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RESULTS AND DISCUSSION

Previously, we have developed a facile method to access HMF from fructose at room temperature, utilizing silica as a solid support, mitigating humin formation, and facilitating selective extraction of HMF.26 Also, we have strategically utilized 2,4-dimethylpyrrole (DMP) in developing a colorimetric naked-eye chemosensor for copper(II) ions.27,28 Here, we have utilized these two sustainable raw materials (HMF and DMP) in developing a sustainable photocatalyst with an objective to mitigate our dependency on fossil-based chemicals. A retrosynthetic scheme originating from sustainable raw materials including 5-hydroxymethylfurfural (HMF), succinic anhydride, and 2,4-dimethylpyrrole was designed to access the photocatalyst (Scheme 1).

HMF was converted into BODIPY alcohol (HMF-BODIPY) in a three-step process (Scheme 2). In the first step, HMF was converted into corresponding 1,3,7,9-tetramethyl-dipyrrromethane (TM-DPM). The formed TM-DPM was further oxidized into corresponding dipyrrin using chloranil as an oxidant and then treated with excess BF3·OEt2 in basic media. All these three steps are low yielding synthetic steps. On carrying out these three steps in one pot, HMF-BODIPY was obtained in 5% overall yield. Our attempts to increase the yield of HMF-BODIPY did not succeed. Hence, we proceeded further for functionalization of HMF-BODIPY and immobilization of the photocatalyst on polymeric resin.

Visible light-mediated reactions attract considerable attention.29−31 BODIPY derivatives have been previously utilized as photocatalysts in various organic transformations.32,33 In general, bromination of BODIPY increases the population at the triplet excited state by spin−orbital coupling.34−36 Hence, we have brominated HMF-BODIPY in positions 2 and 6 using N-bromosuccinimide under chromatography-free synthesis and obtained HMF-BODIPY-Br in a quantitative yield (Scheme 3). The byproduct, succinimide, was removed by washing with water. Then, acid functionality was introduced into HMF-BODIPY-Br by treating with excess succinic anhydride. Complete consumption of HMF-BODIPY-Br was confirmed by TLC analysis. Excess succinic anhydride was removed by washing with warm water. Trituration of the organic layer with hexanes yielded HMF-BODIPY-Br-Suc in pure form (63% yield), without any chromatographic purification.

The UV−vis spectrum of the photocatalyst showed maximum absorption at 545 nm. Coupling reagents that used to immobilize the photocatalyst on resin did not show any absorption near 545 nm (Supporting Information). Hence, we decided to utilize this absorption characteristics of HMF-BODIPY-Br-Suc (ε = 35,100 M−1 cm−1) to estimate the extent of loading in the process of immobilization of the photocatalyst on polymeric resin, aminomethyl polystyrene (Scheme 3). The amino functionality on the resin was coupled with acid functionality of HMF-BODIPY-Br-Suc via an amide linkage utilizing peptide-coupling reagents. The extent of immobilization on polymeric resin was calculated based on (i) absorbance of unreacted HMF-BODIPY-Br-Suc present in a reaction medium and (ii) change in the weight of resin after BODIPY loading.

HMF-BODIPY-Br-Suc shows strong absorption at 545 nm (ε = 35,100 M−1 cm−1) in the free state and after immobilization on polymeric resin (Supporting Information). Hence, we have used green LED, emitting in the range between 495 and 555 nm with a maximum at 520 nm, as a light source for photocatalysis (Figure 1).

The immobilized photocatalyst was utilized in green light-mediated arylation of heteroarenes and arenes using aryl diazonium tetrafluoroborate, furan, and the photocatalyst in a solvent was irradiated with green LED at 30 °C for 2 h. We have observed in a solvent screening study that the yield of the photoarylation product is directly depending on the solubility of aryl diazonium salt. Initially, photoarylation was explored in furan. In a typical experiment, a mixture of aryl diazonium tetrafluoroborate, furan, and the photocatalyst in a solvent was irradiated with green LED at 30 °C for 2 h. We have observed in a solvent screening study that the yield of the photoarylation product is directly depending on the solubility of aryl diazonium salt. 4-Bromobenzenediazonium tetrafluoroborate is completely soluble in dimethylsulfoxide (DMSO), least soluble in halogenated solvents such as dichloroethane (DCE) and dichloromethane (DCM), and moderately soluble in other polar solvents such as acetone, acetonitrile, and ethanol. Among the various solvents utilized for photoarylation of
furan, better yields were obtained in the DMSO solvent (Table 2). Control experiments were carried out in the absence of the photocatalyst or without irradiation. The formation of the product in a very low yield (10%) in the absence of the photocatalyst confirmed the importance of the photocatalyst in mediating photoarylation (Table 2, entry 7). In the absence of light and both photocatalyst and light, the product was obtained in traces (Table 2, entries 8 and 9).

To study the substrate scope of this photoarylation, experiments were carried out using different arenes and diazonium salts (Table 3). The reaction condition utilized in the photoarylation of furan using 4-bromobenzene diazonium tetrafluoroborate (Table 2, entry 5) was adopted in the arylation of furan using other diazonium salts (Table 3, entries 1–6). Corresponding 2-arylfurans were obtained in moderate to good yields. Further, we extended this methodology to arylate thiophene. In the case of arylation of thiophene using 4-chlorobenzene diazonium tetrafluoroborate, the arylated product was obtained in a low yield (30%) upon 2 h irradiation (Table 2, entry 7). Extending the irradiation time to 4 h increased the product yield (Table 3, entries 8 and 9). We further explored the photoarylation of benzene as a
representative example of simple arenes using different diazonium salts (Table 3, entries 10–14). Photoarylation of benzene was sluggish, and even after 12 h irradiation, different biphenyls were obtained in lower yields (Table 3, entries 12–14). The photocatalyst system was found to be effective in light-mediated arylation of heteroarenes. In photoarylation using a radical scavenger TEMPO, the radical-scavenged product 2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine was obtained in 80% yield. This experiment affirmed that the photoarylation proceeds via a radical intermediate (Scheme 4).

Recoverability and recyclability are another attracting features of the immobilized catalyst system. We have studied the recyclability of the newly developed pseudo-homogeneous immobilized photocatalyst (Table 4). In a solvent medium, the immobilized photocatalyst swells and behaves as a homogeneous-like system. After the completion of the reaction, the photocatalyst was recovered by simple filtration. The recovered catalyst was reused in four recycles of photoarylation and found to be effective in catalyzing photoarylation with out any deterioration in yield (Table 4).

Further, we have explored the in situ diazotization and photoarylation in one pot for representative substituted anilines (Table 5). tert-Butyl nitrite was used to diazotize p-substituted anilines. In our first exploration on in situ diazotization and photoarylation, a mixture containing 4-chloroaniline, the resin-supported photocatalyst, and furan in DMSO was irradiated using green LED at 30 °C for 2 h. It is interesting to note that the product 2-(4-chlorophenyl)furan was obtained in 56% yield (Table 5, entry 1). When we treat 4-nitroaniline with furan under the same reaction condition, 2-(4-nitrophenyl)furan was obtained in 71% yield (Table 5, entry 2). In the photoarylation using diazonium salt, we are constrained to use DMSO due to poor solubility of diazonium salt in other solvents. In in situ diazotization and photoarylation, we have explored the use of dichloromethane.

Table 3. Substrate Scope in Immobilized BODIPY-Catalyzed Photoarylation

| entry | -R | arene | time (h) | product | yield (%) |
|-------|----|-------|----------|---------|-----------|
| 1     | H  | 2     |          |         | 56        |
| 2     | F  | 2     |          |         | 73        |
| 3     | Cl | 2     |          |         | 76        |
| 4     | Br | 2     |          |         | 73        |
| 5     | OMe| 2     |          |         | 70        |
| 6     | NO2| 2     |          |         | 70        |
| 7     | Cl | 4     |          |         | 30        |
| 8     | Cl | 4     |          |         | 55        |
| 9     | NO2| 4     |          |         | 68        |
| 10    | NO2| 2     |          |         | 20        |
| 11    | NO2| 4     |          |         | 32        |
| 12    | NO2| 12    |          |         | 46        |
| 13    | Cl | 12    |          |         | 30        |
| 14    | NO2| 12    |          |         | 26        |
| 15    | NO2| 12    |          |         | 80        |

“*A mixture of aryldiazonium tetrafluoroborate (0.25 mmol), photocatalyst (5 mg, ~3.6 μmol), and furan/benzene (1.0 mL) or thiophene (1.25 mmol) in DMSO (2.0 mL) stirred under green LED at 30 °C for stipulated time.

Table 4. Catalyst Recyclability in Photoarylation of Furan

| entry | cycle number | yield (%) |
|-------|--------------|-----------|
| 1     | fresh catalyst | 76        |
| 2     | I recycle | 78        |
| 3     | II recycle | 76        |
| 4     | III recycle | 71        |
| 5     | IV recycle | 71        |

“*A mixture of 4-chlorobenzenediazonium tetrafluoroborate (57 mg, 0.25 mmol), fresh/recovered catalyst (5 mg, ~3.6 μmol), and furan (1.0 mL) in DMSO (2.0 mL) stirred under green LED at 30 °C for 2 h.

Table 5. In Situ Diazotization in Photoarylation of Furan

| entry | R  | solvent | yield (%) |
|-------|----|---------|-----------|
| 1     | Cl | DMSO    | 56        |
| 2     | NO2| DMSO    | 71        |
| 3     | NO2| DCM     | 62        |
| 4     | NO2| DCM     | not formed |

“*A mixture of p-substituted aniline (0.25 mmol), t-BuONO (57 μL, 0.50 mmol), resin-supported photocatalyst (5 mg, ~3.6 μmol), and furan (1.0 mL) in a solvent (2.0 mL) stirred under green LED at 30 °C for 2 h. In the absence of t-BuONO.
Column chromatography was carried out using silica gel provided by Merck. The spots were visualized using UV light. Measured on a Shimadzu-Kratos-Axima CFR+ MALDI-TOF.

We have developed a pseudo-homogeneously immobilized BODIPY-based photocatalyst from sustainable raw materials, 5-hydroxymethylfurfural and 2,4-dimethylpyrrole. The extent of loading was measured based on optical intensity of the unreacted photocatalyst present in a reaction medium. The immobilized photocatalyst was employed in C–H arylation of heteroarenes and simple arenes. The catalyst was recovered from a reaction medium by simple filtration. The recovered catalyst was found to be effective in all four recycles tested. DMSO was used as a solvent to facilitate the dissolution of diazonium salt. By adopting in situ diazotization and photoarylation strategies, the use of DMSO as a solvent can be avoided.

EXPERIMENTAL SECTION

General Information. 1H NMR (300 MHz) spectra were recorded using a Bruker 300 AVANCE II spectrometer, with chloroform-d as a solvent and tetramethylsilane (TMS) as a reference (δ = 0 ppm). The chemical shifts are expressed in δ downfield from the signal of internal TMS. Mass spectra were measured on a Shimadzu-Kratos-Axima CFR+ MALDI-TOF spectrometer. Analytical thin layer chromatographic tests were carried out on aluminium sheets coated with silica gel GF provided by Merck. The spots were visualized using UV light. Column chromatography was carried out using silica gel (230–400 mesh). All yields reported are of isolated materials judged to be homogeneous using TLC and NMR spectroscopy. Aryldiazonium tetrafluoroborates,18 HMF,26,39 and 2,4-dimethylpyrrole30 were synthesized by a reported procedure. (Aminomethyl)polystyrene (70–90 mesh, 1% cross-linked) was purchased from Sigma-Aldrich.

8-(5-Hydroxymethyl-2-furanyl)-1,3,5,7-tetramethyl-BODIPY (HMF-BODIPY). A solution of HMF (8.0 mmol, 1.0 g) in CH2Cl2 (5.0 mL) was added to drops to a mixture containing 2,4-dimethylpyrrole (24 mmol, 2.4 mL), celite (50 mg), and CH2Cl2 (10 mL) and stirred for 1 h at 30 °C. After the complete consumption of HMF as evidenced by TLC analysis, the reaction mixture was diluted with hexane (20 mL) and filtered. The filtrate was concentrated under reduced pressure.

The resulting reddish brown solid was dissolved in toluene (100 mL) and then treated with chloranil (8.8 mmol, 2.2 g, 1.1 equiv) at 30 °C for 45 min. To the reaction mixture, Et3N (7.8 mL, 56 mmol, 7.0 equiv) was added and stirred for 10 min. After 10 min, BF3·OEt2 (7.1 mL, 56 mmol, 7.0 equiv) was added in drops to the cooled reaction mixture. The stirring was continued for 15 h, and the corresponding BODIPY formation was confirmed by TLC analysis using a hexane/EtOAc (1:1, v/v) mixture as an eluent. Then, the toluene layer from the reaction mixture was decanted. The remaining viscous mass in the reaction flask was washed with toluene (2 × 25 mL). The combined toluene extract was washed with water, saturated with NaCl solution, dried with anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure. The resulting solid was purified by column chromatography [silica, (30% EtOAc + 70% hexane)] to obtain the title compound as a red color solid (138 mg, 5% yield).

1H NMR (300 MHz, CDCl3, δ): 1.65 (s, 6H), 2.55 (s, 6H), 4.68 (s, 2H), 6.02 (s, 2H), 6.42 (dd, J1 = 11.4 Hz, J2 = 3.0 Hz, 2H); 13C NMR (75 MHz, CDCl3, δ): 13.2, 14.7, 57.3, 109.3, 112.2, 121.4, 127.9, 132.8, 143.0, 145.0, 155.1, 157.0; MALDI-TOF-MS obsd 344.5851, calc 344.1508 (M = C16H16BF3N2O2).

2,6-Dibromo-8-(5-hydroxymethyl-2-furanyl)-1,3,5,7-tetramethyl-BODIPY (HMF-BODIPY-Br). N-Nitrosoureas (171 mg, 0.96 mmol, 3.0 equiv) was added to a stirred solution of 8-(5-hydroxymethyl-2-furanyl)-1,3,5,7-tetramethyl-BODIPY (110 mg, 0.32 mmol) in dry CH2Cl2 at 0 °C. The resulting reaction mixture was warmed to 30 °C and stirred for 30 min under N2. Then, the reaction mixture was washed with water and saturated with NaCl solution. The organic layer was dried with sodium sulfate, and the solvent was removed by rotary evaporation under reduced pressure to obtain 2,6-dibromo-8-(5-hydroxymethyl-2-furanyl)-1,3,5,7-tetramethyl-BODIPY (159 mg, 99% yield). The sample was pure enough to proceed to the next step as judged by NMR analysis.

1H NMR (300 MHz, CDCl3, δ): 1.64 (s, 6H), 2.60 (s, 6H), 4.70 (s, 2H), 6.46 (dd, J1 = 13.8 Hz, J2 = 3.0 Hz, 2H); 13C NMR (75 MHz, CDCl3, δ): 12.7, 13.9, 57.3, 109.5, 112.1, 113.0, 128.2, 131.7, 140.5, 142.2, 155.4, 155.7; MALDI-TOF-MS obsd 502.7312, calc 501.9697 (M = C22H19BF2N2O2).

2,6-Dibromo-1,3,5,7-tetramethyl-8-(5-succinylmethyl-2-furanyl)BODIPY (HMF-BODIPY-Br-Suc). For the epsilon value calculation, a stock solution (200 μM) was dissolved in CH2Cl2 (25 mL). Solutions of HMF-BODIPY-Br-Suc were prepared from stock solution. The epsilon value was determined to be 35,100 M−1 cm−1.
Loading of HMF-BODIPY-Br-Suc on Resin. DIPEA (21 μL, 120 μmol, 2.0 equiv) was added to a stirred suspension of (aminomethyl)polystyrene resin (40 mg, 60 μmol), HMF-BODIPY-Br-Suc (36 mg, 60 μmol), and HBTU (34 mg, 90 μmol, 1.5 equiv) in dry CH₂Cl₂ (2.0 mL). The reaction mixture was stirred at 30 °C under N₂ for 12 h. The change in the color of resin from translucent to dark red affirmed the loading of BODIPY on resin. The extent of loading of BODIPY on resin was calculated by measuring the absorbance of the reaction mixture. After 12 h, the resin loaded with BODIPY was separated by filtration. On the basis of the absorbance value of the filtrate at 545 nm, the amount of unreacted BODIPY was found to be 8.5 μmol. Hence, the percentage of loading was found to be 85.8%. The resin loaded with BODIPY was washed thoroughly and dried under reduced pressure to obtain BODIPY immobilized on resin (72 mg). On the basis of the increase in the weight of resin, the percentage of loading was found to be 88%. This loading value was utilized in calculating the amount of BODIPY present in 5 mg of immobilized photocatalyst as 3.6 μmol.

**General Procedure for Arylation of Furan.** Aryldiazonium tetrafluoroborate (0.25 mmol) was added to a stirred suspension of furan (1.0 mL) and HMF-BODIPY-loaded resin (5 mg, ~3.6 μmol) in DMSO (2.0 mL). The reaction mixture was stirred under irradiation of green LED at 30 °C for 4 h. Then, the catalyst was separated by filtration and washed with diethyl ether for further reuse. The combined filtrate was diluted with diethyl ether, washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting residue was purified using column chromatography to obtain arylated furan in pure form.

**2-Phenylfuran.** (20 mg, 56%); ¹H NMR (300 MHz, CDCl₃, δ): 6.47 (dd, J₁ = 1.8 Hz, J₂ = 3.3 Hz, 1H), 6.58 (d, J = 3.6 Hz, 1H), 7.04–7.11 (m, 1H), 7.45 (d, J = 1.2 Hz, 1H), 7.60–7.66 (m, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 104.6, 111.7, 115.5, 115.8, 125.5, 125.6, 127.3, 142.0, 153.2, 160.5, 163.8. Spectral data are exactly matching with the reported literature data.¹⁰,¹¹

**2-(4-Fluorophenyl)furan.** (34 mg, 76%); ¹H NMR (300 MHz, CDCl₃, δ): 6.48 (dd, J₁ = 1.8 Hz, J₂ = 3.3 Hz, 1H), 6.64 (d, J = 3.3 Hz, 1H), 7.35 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 12 Hz, 1H), 7.60 (d, J = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 105.4, 111.8, 125.0, 128.9, 129.4, 133.0, 142.3, 152.9. Spectral data are exactly matching with the reported literature data.¹²

**2-(4-Chlorophenyl)furan.** (41 mg, 73%); ¹H NMR (300 MHz, CDCl₃, δ): 6.47 (dd, J₁ = 1.8 Hz, J₂ = 3.3 Hz, 1H), 6.66 (d, J = 3.3 Hz, 1H), 7.47–7.56 (m, 5H); ¹³C NMR (75 MHz, CDCl₃, δ): 105.6, 111.8, 121.1, 125.3, 129.8, 131.8, 142.4, 153.0. Spectral data are exactly matching with the reported literature data.¹²

**2-(4-Bromophenyl)furan.** (31 mg, 70%); ¹H NMR (300 MHz, CDCl₃, δ): 3.83 (s, 3H), 6.45 (dd, J₁ = 1.8 Hz, J₂ = 3.3 Hz, 1H), 6.51 (d, J = 3.3 Hz, 1H), 6.92 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 0.9 Hz, 1H), 7.60 (d, J = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 55.3, 103.4, 111.5, 114.1, 124.0, 125.2, 141.4, 154.0, 159.0. Spectral data are exactly matching with the reported literature data.²⁹,¹¹

**2-(4-Nitrophenyl)furan.** (33 mg, 70%); ¹H NMR (300 MHz, CDCl₃, δ): 6.56 (dd, J₁ = 1.8 Hz, J₂ = 3.3 Hz, 1H), 6.88 (d, J = 3.6 Hz, 1H), 7.58 (d, J = 1.5 Hz, 1H), 7.79 (d, J = 9.0 Hz, 2H), 8.25 (d, J = 9.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 109.0, 112.5, 123.9, 124.3, 136.4, 144.2, 146.4, 151.7. Spectral data are exactly matching with the reported literature data.²⁹,¹¹

**General Procedure for Arylation of Thiophene.** Aryldiazonium tetrafluoroborate (0.25 mmol) was added to a stirred suspension of thiophene (1.25 mmol, 5.0 equiv) and HMF-BODIPY-loaded resin (5 mg, ~3.6 μmol) in DMSO (2.0 mL). The reaction mixture was stirred under irradiation of green LED at 30 °C for 4 h. Then, the catalyst was separated by filtration and washed with diethyl ether for further reuse. The combined filtrate was diluted with diethyl ether, washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting residue was purified using column chromatography to obtain arylated thiophene in pure form.

**2-(4-Chlorophenyl)thiophene.** (27 mg, 55%); ¹H NMR (300 MHz, CDCl₃, δ): 7.07–7.09 (m, 1H), 7.29–7.30 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 123.5, 125.2, 127.1, 128.1, 129.0, 133.0, 133.2, 143.1. Spectral data are exactly matching with the reported literature data.³³

**General Procedure for Arylation of Benzene.** Aryldiazonium tetrafluoroborate (0.25 mmol) was added to a stirred suspension of benzene (1.0 mL) and HMF-BODIPY-loaded resin (5 mg, ~3.6 μmol) in DMSO (2.0 mL). The reaction mixture was stirred under green LED at 30 °C for 12 h. Then, the catalyst was separated by filtration and washed with diethyl ether for further reuse. The combined filtrate was diluted with diethyl ether, washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting residue was purified using column chromatography to obtain arylated benzene in pure form.

**4-Fluoro-1,1′-biphenyl.** (13 mg, 30%); ¹H NMR (300 MHz, CDCl₃, δ): 7.13 (t, J = 8.4 Hz, 2H), 7.32–7.34 (m, 1H), 7.41–7.46 (m, 2H), 7.52–7.57 (m, 4H); ¹³C NMR (75 MHz, CDCl₃, δ): 115.5, 115.8, 127.1, 127.3, 128.7, 128.8, 128.9, 137.3, 140.3, 160.9, 164.1. Spectral data are exactly matching with the reported literature data.³⁴

**4-Nitro-1,1′-biphenyl.** (23 mg, 46%); ¹H NMR (300 MHz, CDCl₃, δ): 7.43–7.54 (m, 3H), 7.62–7.65 (m, 2H), 7.75 (d, J = 9.0 Hz, 2H), 8.31 (d, J = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃, δ): 124.1, 127.4, 127.8, 128.9, 129.2, 138.4, 147.1, 147.6. Spectral data are exactly matching with the reported literature data.³⁴

**4-Chloro-1,1′-biphenyl.** (12 mg, 26%); ¹H NMR (300 MHz, CDCl₃, δ): 7.33–7.39 (m, 1H), 7.42–7.47 (m, 4H), 7.51–7.57 (m, 4H); ¹³C NMR (75 MHz, CDCl₃, δ): 127.0, 127.6, 128.4, 128.91, 128.93, 133.4, 139.7, 140.0. Spectral data are exactly matching with the reported literature data.³³
Radical Scavenger Reaction. 4-Nitrobenzenediazonium tetrafluoroborate (59 mg, 0.25 mmol) was added to a stirred suspension of TEMPO (78 mg, 0.50 mmol, 2.0 equiv) and HMF-BODIPY-loaded resin (5 mg, ~3.6 μmol) in DMSO (2.0 mL). The reaction mixture was stirred under green LED at 30 °C for 2 h. Then, the catalyst was separated by filtration and washed with diethyl ether. The combined filtrate was diluted with diethyl ether, washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting residue was purified using column chromatography to obtain 2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine in pure form.

2,2,6,6-Tetramethyl-1-(4-nitrophenoxy)piperidine. (56 mg, 80%); 1H NMR (300 MHz, CDCl₃, δ): 0.99 (s, 6H), 1.25 (s, 6H), 1.43–1.46 (m, 1H), 1.58–1.66 (m, 5H), 7.31–7.34 (m, 2H), 8.15 (d, J = 9.3 Hz, 2H); 13C NMR (75 MHz, CDCl₃, δ): 16.9, 20.5, 32.3, 39.7, 60.9, 114.2, 125.6, 141.1, 168.7. Spectral data are exactly matching with the reported literature data.29,41

General Procedure for Catalyst Recyclability. 4-Chlorobenzenediazonium tetrafluoroborate (57 mg, 0.25 mmol) was added to a stirred suspension of furan (1.0 mL) in DMSO (2.0 mL) and HMF-BODIPY-loaded resin (5 mg, ~3.6 μmol). The reaction mixture was stirred under green LED at 30 °C for 2 h. Then, the catalyst was separated by filtration and washed with diethyl ether for further reuse. The combined filtrate was diluted with diethyl ether, washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting residue was purified using column chromatography to obtain 2-(4-chlorophenyl)furan in pure form.

General Procedure for in Situ Diazotation and Photoarylation. t-Butyl nitrite (57 μL, 0.50 mmol) was added to a stirred suspension of furan (1.0 mL), substituted aniline (0.25 mmol), and BODIPY-loaded resin (5 mg) in CH₂Cl₂ (2.0 mL). The reaction mixture was stirred under irradiation of green LED at 30 °C for 2 h. Then, the catalyst was separated by filtration and washed with diethyl ether. The combined filtrate was diluted with diethyl ether, washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting residue was purified using column chromatography to obtain aryalted furan in pure form.

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REFERENCES

1. Cooney, C. P.; Yeliana; Worm, J. J.; Naber, J. D. Combustion Characterization in an Internal Combustion Engine with Ethanol-Gasoline Blended Fuels Varying Compression Ratios and Ignition Timing. Energy Fuels 2009, 23, 2319–2324.
2. Chiatti, G.; Chiavola, O.; Palmieri, F.; Albertini, S. Combustion and Emissions Characterization of Biodiesel Blends in a City-Car Engine. Energy Fuels 2014, 28, 5076–5085.
3. Cheung, C. S.; Cheng, C.; Chan, T. L.; Lee, S. C.; Yao, C.; Tsang, K. S. Emissions Characteristics of a Diesel Engine Fueled with Biodiesel and Fumigation Methanol. Energy Fuels 2008, 22, 906–914.
4. Haas, M. J.; Scott, K. M.; Allem, T. L.; McCormick, R. L. Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstock: A High Quality Renewable Fuel Produced from a Waste Feedstock. Energy Fuels 2001, 15, 1207–1212.
5. Nguyen, D. C.; Dong, V. H. 2,5-Dimethylfuran Produced from Internal Combustion Engines: Potential and Development. Eur. J. Eng. Res. Sci. 2018, 3, 106–111.
6. Tian, G.; Daniel, R.; Li, H.; Xu, H.; Shuai, S.; Richards, P. Laminar Burning Velocities of 2,5-Dimethylfuran Compared with Ethanol and Gasoline. Energy Fuels 2010, 24, 3898–3905.
7. Zhong, S.; Daniel, R.; Xu, H.; Zhang, J.; Turner, D.; Wyszynski, M. L.; Richards, P. Combustion and Emissions of 2,5-Dimethylfuran in a Direct-Injection Spark-Ignition Engine. Energy Fuels 2010, 24, 2891–2899.
8. Hulsey, M. J.; Yang, H.; Yao, N. Sustainable Routes for the Synthesis of Renewable Heteroatom-Containing Chemicals. ACS Sustainable Chem. Eng. 2018, 6, 5694–5707.
9. Fornasiero, P.; Graziani, M. Renewable Resources and Renewable Energy: A Global Challenge; Second Ed., CRC Press: Boca Raton, 2012.
10. Fang, R.; Luque, R.; Li, Y. Selective aerobic oxidation of biomass-derived HMF to 2,5-diformylfuran using a MOF-derived magnetic hollow Fe–Co nonocatalyst. Green Chem. 2016, 18, 3152–3157.
11. Antonyraj, C. A.; Jeong, J.; Kim, B.; Shin, S.; Kim, S.; Lee, K.-Y.; Cho, J. K. Selective oxidation of HMF to DFF using Ru/γ-alumina catalyst in moderate boiling solvents toward industrial production. J. Ind. Eng. Chem. 2013, 19, 1056–1059.
12. Tong, X.; Sun, Y.; Bai, X.; Li, Y. Highly efficient aerobic oxidation of biomass-derived 5-hydroxymethyl furfural to produce 2,5-diformylfuran in the presence of copper salts. RSC Adv. 2014, 4, 44307–44311.
13. Motagamwala, A. H.; Won, W.; Sener, C.; Alonso, D. M.; Maravelias, C. T.; Dumesic, J. A. Toward biomass-derived renewable plastics: Production of 2,5-furandicarboxylic acid from fructose. Sci. Adv. 2018, 4, eaap9722.
14. Sousa, A. F.; Vilela, C.; Fonseca, A. C.; Matos, M.; Freire, C. S. R.; Gruter, G.-J. M.; Coelho, J. F. J.; Silvestre, A. J. D. Biobased polyesters and other polymers from 2,5-furandicarboxylic acid: a tribute to furan excellency. Polym. Chem. 2015, 6, 5961–5983.
15. Yi, G.; Teong, S. P.; Zhang, Y. The Direct Conversion of Sugars into 2,5-Furandicarboxylic Acid in a Triphasic System. ChemSusChem 2015, 8, 1151–1155.
16. Bosell, J. J.; Petersen, G. R. Technology development for the production of biobased products from biorefinery carbohydrates—the
(35) Sabatini, R. P.; McCormick, T. M.; Lazarides, T.; Wilson, K. C.; Eisenberg, R.; McCamant, D. W. Intersystem Crossing in Halogenated Bodipy Chromophores Used for Solar Hydrogen Production. *J. Phys. Chem. Lett.* 2011, 2, 223–227.

(36) Gorman, A.; Killoran, J.; O’Shea, C.; Kenna, T.; Gallagher, W. M.; O’Shea, D. F. In Vitro Demonstration of the Heavy-Atom Effect for Photodynamic Therapy. *J. Am. Chem. Soc.* 2004, 126, 10619–10631.

(37) He, L.; Qiu, G.; Gao, Y.; Wu, J. Removal of amino groups from anilines through diazonium salt-based reactions. *Org. Biomol. Chem.* 2014, 12, 6965.

(38) Cheng, K.; Zhao, B.; Hu, S.; Zhang, X.-M.; Qi, C. Pd-catalyzed cross-coupling reactions of arenediazonium salts with arylsilanes and aryltrifluoroborates in water. *Tetrahedron Lett.* 2013, 54, 6211–6214.

(39) Simeonov, S. P.; Afonso, C. A. M. Batch and Flow Synthesis of 5-Sulfooxymethylfulvalene (SOMF) from Fructose as a Bioplatfrom Intermediate: An Experiment for the Organic or Analytical Laboratory. *J. Chem. Educ.* 2013, 90, 1373–1375.

(40) Meng, G.; Zheng, M.-L.; Wang, M. An Improved Two-step Preparation of 2, 4-Dimethylpyrrole. *Org. Prep. Proced. Int.* 2011, 43, 308–311.

(41) Zhou, C.-Y.; Chan, P. W. H.; Che, C.-M. Gold(III) Porphyrin-Catalyzed Cycloisomerization of Allenones. *Org. Lett.* 2006, 8, 325–328.

(42) Guchhait, S.; Kashyap, M.; Saraf, S. Direct C-H Bond Arylation of (Hetero)arenes with Aryl and Heteroarylboronic Acids. *Synthesis* 2010, 2010, 1166–1170.

(43) Peretti, M. D.; Monzón, D. M.; Crisóstomo, F. P.; Martin, V. S.; Carrillo, R. Radical C–H arylation of {hetero}arenes catalysed by gallic acid. *Chem. Commun.* 2016, 52, 9036–9039.

(44) Crisóstomo, F. P.; Martin, T.; Carrillo, R. Ascorbic Acid as an Initiator for the Direct C-H Arylation of (Hetero)arenes with Anilines Nitrosated In Situ. *Angew. Chem., Int. Ed.* 2014, 53, 2181–2185.

US Department of Energy’s “Top 10” revisited. *Green Chem.* 2010, 12, 539–554.

(17) Lăcătuș, M. A.; Bencze, L. C.; Toșa, M. I.; Paizs, C.; Irimie, F.-D. Eco-Friendly Enzymatic Production of 2,5-Bis(hydroxymethyl)-furan Fatty Acid Diesters, Potential Biodiesel Additives. *ACS Sustainable Chem. Eng.* 2018, 6, 11333–11339.

(18) Li, Y.-M.; Zhang, X.-Y.; Li, N.; Xu, P.; Lou, W.-Y.; Zong, M.-H. Biocatalytic Reduction of HMF to 2,5-Bis(hydroxymethyl)furan by HMF-Tolerant Whole Cells. *ChemSusChem* 2016, 10, 372–378.

(19) Xu, Y.; Jia, X.; Ma, J.; Gao, J.; Xia, F.; Li, X.; Xu, J. Selective synthesis of 2,5-bis(aminomethyl)furan via rhodium-catalysed hydrogenation of 2,5-diformylfuran dioxide. *Green Chem.* 2018, 20, 2697–2701.

(20) Le, N.-T.; Buyu, A.; Han, Y.; Lee, K.-I.; Kim, H. Preparation of 2,5-Bis(aminomethyl)furan by Direct Reductive Amination of 2,5-Diformylfuran over Nickel-Raney Catalysts. *Green Sustainable Chem.* 2015, 05, 115–127.

(21) Buntara, T.; Noel, S.; Phua, P. H.; Melián-Cabrera, I.; de Vries, J. G.; Heeres, H. J. Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurufural into Caprolactone. *Angew. Chem., Int. Ed.* 2011, 50, 7083–7087.

(22) Xiao, B.; Zheng, M.; Li, X.; Pang, J.; Sun, R.; Wang, H.; Pang, X.; Wang, A.; Wang, X.; Zhang, T. Synthesis of 1,6-hexanediol from HMF over double-layered catalysts of Pd/SiO2 + Ir-ReOx/SiO2 in a fixed-bed reactor. *Green Chem.* 2016, 18, 2175–2184.

(23) Tuteja, J.; Choudhary, H.; Nishimura, S.; Ebitani, K. Direct Synthesis of 1,6-Hexanediol from HMF over a Heterogeneous Pd/ZrP Catalyst using Formic Acid as Hydrogen Source. *ChemSusChem* 2014, 7, 96–100.

(24) Gilkey, M. J.; Mironenko, A. V.; Vlachos, D. G.; Xu, B. Adipic Acid Production via Metal-Free Selective Hydrogenolysis of Biomass-Derived Tetrahydrofuran-2,5-Diacrylic Acid. *ACS Catal.* 2017, 7, 6619–6634.

(25) Mika, L. T.; Cséfalvay, E.; Németh, Á. Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. *Chem. Rev.* 2018, 118, 505–613.

(26) Rajmohan, R.; Gayathri, S.; Vairaparaksh, P. Facile synthesis of 5-hydroxymethylfurfural: a sustainable raw material for the synthesis of key intermediates toward 21,23-dioxopyrophosphine. *RSC Adv.* 2015, 5, 100401–100407.

(27) Rajmohan, R.; Ahmed, K. B. A.; Sangeetha, S.; Anbazhagan, V.; Vairaparaksh, P. C–H oxidation and chelation of a dipyrromethane mediated rapid colorimetric nakeyde Cu(II) chemosensor. *Analyst* 2017, 142, 3346–3351.

(28) Rajaswathi, K.; Jayanthi, M.; Rajmohan, R.; Anbazhagan, V.; Vairaparaksh, P. Simple admiixture of 4-nitrobenzaldehyde and 2,4-dimethylpyrrole for efficient colorimetric sensing of copper(II) ions. *Spectrochim. Acta, Part A* 2019, 212, 308–314.

(29) Hari, D. P.; Schroll, P.; König, B. Metal-Free, Visible-Light-Mediated Direct C–H Arylation of Heteroarenes with Aryl Diazonium Salts. *J. Am. Chem. Soc.* 2012, 134, 2958–2961.

(30) Xuan, J.; Xiao, W.-J. Visible-Light Photoredox Catalysis. *Angew. Chem., Int. Ed.* 2012, 51, 6828–6838.

(31) Hari, D. P.; König, B. The Photocatalyzed Meerwein Arylation: Classic Reaction of Aryl Diazonium Salts in a New Light. *Angew. Chem., Int. Ed.* 2013, 52, 4734–4743.

(32) Guo, S.; Zhang, H.; Huang, L.; Guo, Z.; Xiong, G.; Zhao, J. Porous material-immobilized iodo-Bodipy as an efficient photocatalyst for photoredox catalytic organic reaction to prepare pyrrolo[2,1-a]isoquinoline. *Chem. Commun.* 2013, 49, 8689.

(33) Huang, L.; Zhao, J. Iodo-Bodips as visible-light-absorbing dual-functional photoredox catalysts for preparation of highly functionalized organic compounds by formation of C–C bonds via reductive and oxidative quenching catalytic mechanisms. *RSC Adv.* 2013, 3, 23377.

(34) Zhao, J.; Xu, K.; Yang, W.; Wang, Z.; Zhong, F. The triple excited state of Bodipy: formation, modulation and application. *Chem. Soc. Rev.* 2015, 44, 8904–8939.