

Communication

# Sustainable Catalytic Synthesis of 2,5-Diformylfuran from Various Carbohydrates

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**Abstract:** Versatile homogeneous and heterogeneous catalysts that convert carbohydrates to 2,5-diformylfuran (DFF) are essential for the development of sustainable processes for producing high-value chemicals from biomass-derived carbohydrates. An efficient catalytic system consisting of Br<sup>-</sup>, disulfide, and dimethylsulfoxide (DMSO) promoted the sustainable and selective synthesis of DFF in modest-to-good yields from various carbohydrates, such as fructose, glucose, mannose, galactose, and sucrose. Heterogeneous catalysts containing Br<sup>-</sup> also facilitated this reaction with recyclable high yields.

**Keywords:** biomass; carbohydrates; 2,5-diformylfuran; fructose; glucose



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## 1. Introduction

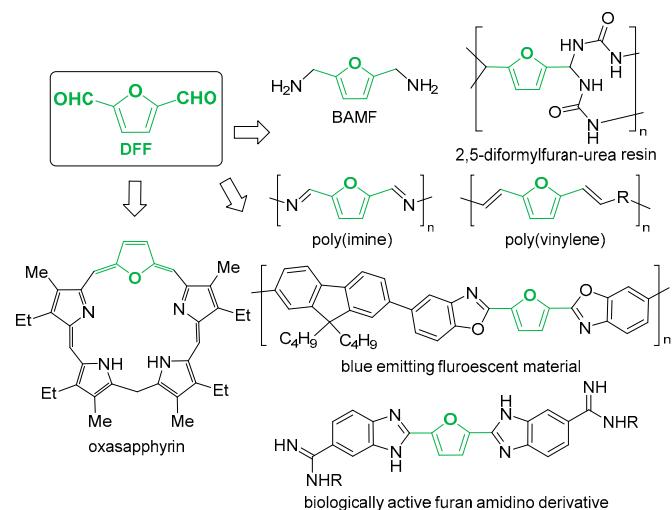
The valorization of biomass, which is a sustainable carbon source, has received increasing attention for many reasons. Biomass can be used to achieve net-zero carbon dioxide (CO<sub>2</sub>) emissions, decrease the fossil-fuel dependency of chemical processes, maintain the current consumption of chemical products, and save energy resources for the next generation. Lignocellulosic biomass, one of the most abundant biomass resources, has high functionality originating from its unique carbon skeleton and functional groups, which enable the production of a wide range of value-added chemicals. Several catalysts have been reported, which can be used for transforming the functional groups and for reorganizing the carbon skeleton of lignocellulosic biomass [1–7]. Among them, catalysts converting lignocellulose-derived carbohydrates to 2,5-diformylfuran (DFF) attracted our interest.

DFF has many uses in furan-based polymers (as a monomer), macrocyclic ligands (oxasapphyrins), blue emitting fluorescent materials, and biologically active compounds as described in Figure 1 [8–14]. In particular, furan-based polymers are considered sustainable replacements of petrochemical-based polymers in the chemical industry. DFF can replace the tere-/iso-phthalaldehydes, which are used in the synthesis of polyimines and phenolic resins [15]. DFF is also converted to 2,5-bis(aminomethyl)furan (BAMF), a monomer used for synthesizing biocompatible polymers [16–18].

The conversion of carbohydrates to DFF involves the following three key steps: (1) isomerization of carbohydrates (glucose, sugar, starch, and others) to fructose, (2) dehydration of fructose forming 5-hydroxymethylfurfural (HMF), and (3) selective oxidation of HMF to DFF [19,20]. While many articles report the facile oxidation of HMF to DFF [17,21–25], the direct synthesis of DFF from biomass-derived carbohydrates has generated interest due to the economic advantages of avoiding the use of expensive HMF and saving process costs by reducing the number of reaction steps.

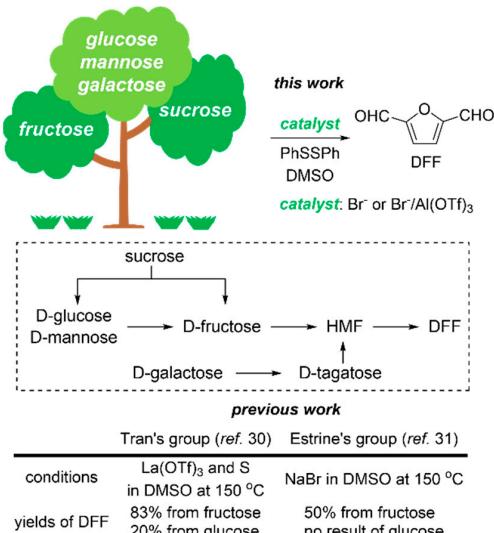
The conversion of fructose to DFF has been accomplished in the presence of various catalytic systems such as V<sub>2</sub>O<sub>5</sub>, hydrotalcite, amberlyst-15, metal-containing Keggin

heteropolyacids,  $\text{La}(\text{OTf})_3/\text{S}$ /dimethylsulfoxide (DMSO),  $\text{NaBr}/\text{DMSO}$ , and graphene oxide, exhibiting moderate yields at high temperatures [26–31]. The catalytic reactions of glucose, in which hydrotalcite-supported ruthenium catalysts or acid-base catalysts involving  $-\text{SO}_3\text{H}$  and  $-\text{NH}_2$  were used, afforded DFF in lower yields than the corresponding reactions of fructose [32,33]. This reactivity difference stems from the different carbohydrate structures. Glucose, mannose, and galactose reactions require an isomerization step to form fructose (or tagatose) before oxidation to DFF [34], and the sucrose (disaccharide) reaction must include several steps (glycosidic bond hydrolysis forming glucose and fructose, isomerization of glucose to fructose, and fructose-oxidation to DFF) to produce DFF [35].



**Figure 1.** Synthetic and industrial applications of DFF.

Reportedly, the oxidation of carbohydrates promotes the formation of DFF under conditions using  $\text{La}(\text{OTf})_3/\text{element sulfur}/\text{DMSO}$  or  $\text{NaBr}/\text{DMSO}$  at  $150\text{ }^\circ\text{C}$  (Scheme 1) [29,30]. The catalyst combination of  $\text{La}(\text{OTf})_3$ , sulfur, and DMSO afforded DFF in 83% yield and 20% yield from fructose and glucose, respectively [29]. The combination of  $\text{NaBr}$  and DMSO provided DFF from fructose in a 50% yield. However, no results were reported using glucose [30]. Accordingly, catalytic systems that are effective in general for various carbohydrate reactions must be investigated. In this study, we develop versatile homogeneous and heterogeneous catalysts capable of converting carbohydrates (fructose, glucose, mannose, galactose, and sucrose) to DFF in good yields under mild conditions (Scheme 1).



**Scheme 1.** Catalytic conversion of carbohydrates to DFF.

## 2. Results and Discussion

A combination of halides, disulfides, and DMSO was chosen for D-fructose reaction (Table 1). The reaction of sulfur and DMSO promoted the oxidation of fructose to form DFF in Tran's work, and halides with DMSO also induced the formation of DFF, albeit in low yields in Estrine's work (Scheme 1). Inspired by these previous reports, we employed sulfur–sulfur bonds of disulfides to induce the oxidation of fructose under mild reaction conditions [29,30]. DFF was obtained in 54% yield in the presence of NaBr (5 mol%), diphenyldisulfide (PhSSPh) (1 equiv), and DMSO at 120 °C (Table 1, entry 1). Changing the counter cation of the halide from  $\text{Na}^+$  and ammonium to phosphonium cations and increasing halide catalysts loadings to 10 mol% improved the DFF yield to 92% (entries 2–6). The reactions using tetrabutylphosphonium bromide (TBPBr), triphenylbutylphosphonium bromide (TPBPBr), and benzyltriphenylphosphonium bromide (BTPPBr) forms DFF in similar yields (entries 4–6). When benzyltriphenylphosphonium chloride (BTPPCl) was used instead of BTPPBr, the DFF yield dropped to 1%, exhibiting the critical role of  $\text{Br}^-$  in the oxidation (entries 6 and 7). The reaction without PhSSPh provided DFF and HMF in 20% and 30% yields, respectively, indicating the requirement of disulfides for the high yield of DFF (entry 8). The reaction conducted with only PhSSPh (without TBPBr) afforded only 2% DFF, along with 55% HMF (entry 9). The effect of PhSSPh was evaluated by replacing PhSSPh with other sulfides (diphenylsulfide (PhSPh) or dibenzylidisulfide (BnSSBn)), thus confirming the requirement of PhSSPh (entries 4, 10, and 11). The temperature was varied from 100 to 150 °C, showing the best yield at 120 °C (see Supplementary Materials, Table S1).

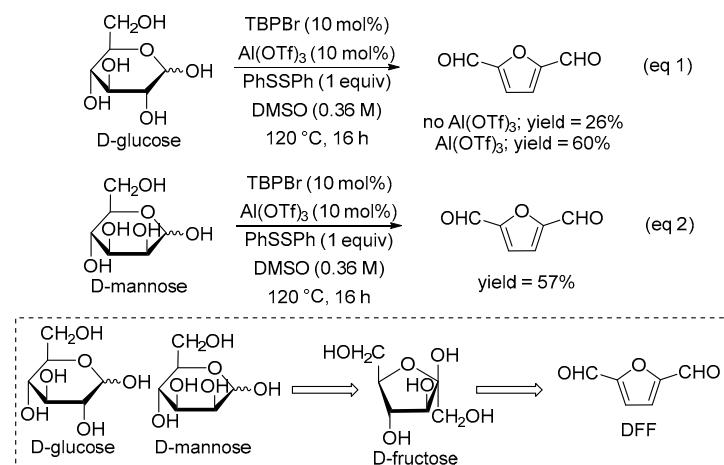
**Table 1.** Conversion of D-fructose to DFF.

Entry	Catalyst (Mol%)	Additive (Equiv)	Conversion of Fructose	Yield <sup>a</sup>
1	NaBr (5)	PhSSPh (1)	>99%	54%
2	TBAcBr (5)	PhSSPh (1)	>99%	70%
3	TBPBr (5)	PhSSPh (1)	>99%	65%
4	TBPBr (10)	PhSSPh (1)	>99%	92%
5	TPBPBr (10)	PhSSPh (1)	>99%	84%
6	BTPPBr (10)	PhSSPh (1)	>99%	80%
7	BTPPCl (10)	PhSSPh (1)	>99%	1% <sup>b,c</sup>
8	TBPBr (10)	-	>99%	20% <sup>b,d</sup>
9	-	PhSSPh (1)	>99%	2% <sup>b,e</sup>
10	TBPBr (10)	PhSPh (1)	>99%	31%
11	TBPBr (10)	BnSSBn (1)	>99%	62%

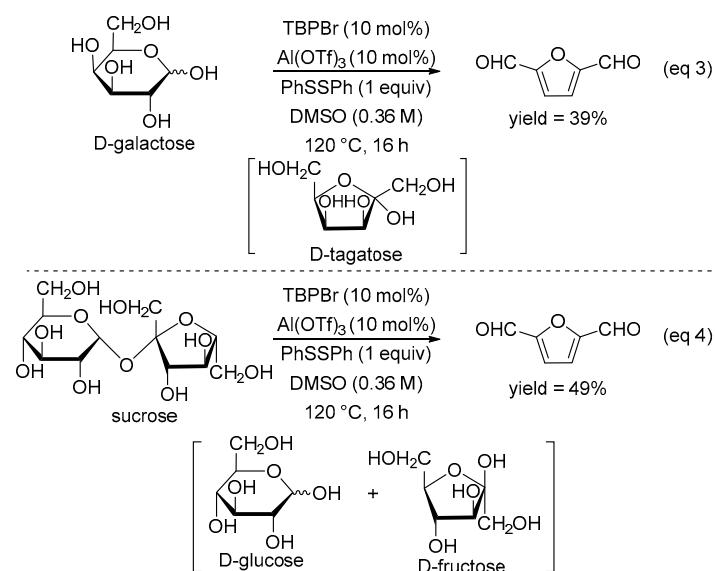
Reaction conditions: A mixture of fructose (0.25 mmol), catalysts, and additives in DMSO was heated at 120 °C for 16 h. <sup>a</sup> isolated yields, <sup>b</sup> yields measured by internal standard (1,3,5-trimethoxybenzene), <sup>c</sup> HMF 65%, <sup>d</sup> HMF 30%, <sup>e</sup> HMF 55%. TBAcBr (tetrabutylammonium bromide), TBPBr (tetrabutylphosphonium bromide), TPBPBr (triphenylbutylphosphonium bromide), BTPPBr (benzyltriphenylphosphonium bromide), BTPPCl (benzyltriphenylphosphonium chloride).

The glucose reactions were attempted in the presence of TBPBr and PhSSPh, and afforded DFF in a 26% yield (Scheme 2, Equation (1)). It was presumed that the conversion of glucose to fructose must be improved to give higher yields. First, the addition of a Lewis acid was tested;  $\text{Al}(\text{OTf})_3$ ,  $\text{In}(\text{OTf})_3$ ,  $\text{Cu}(\text{OTf})_2$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{Zn}(\text{OTf})_3$  were separately added to the catalytic reaction system, and only  $\text{Al}(\text{OTf})_3$  was found to promote the reaction (60% yield of DFF, Supplementary Materials, Table S2) [36,37]. PhSSPh is required to form DFF from glucose. The catalyst mixture of TBPBr (10 mol%) and  $\text{Al}(\text{OTf})_3$  (10 mol%) without PhSSPh converted glucose to 3% DFF and 58% HMF. A critical catalyst system, combining  $\text{Al}(\text{OTf})_3$ , TBPBr, and PhSSPh, which was used for the conversion of glucose, was also employed for the oxidation of mannose (Scheme 2, Equation (2)).

Mannose undergoes dehydration, forming fructose, which then undergoes facile oxidation to DFF. Since the dehydration pathway of mannose was similar to that of glucose, DFF was obtained with a 57% yield [34]. The reaction of galactose was attempted under the glucose oxidation conditions, forming DFF in a 39% yield (Scheme 3, Equation (3)). Unlike glucose and mannose, galactose was converted to a C-4 epimer of fructose (tagatose), resulting in less-efficient conversion to DFF [34]. Sucrose was subjected to the oxidation conditions, forming DFF in a 49% yield (Scheme 3, Equation (4)). A disaccharide, sucrose composed of glucose and fructose, should undergo the glycosidic hydrolysis before oxidation. The additional steps, including hydrolysis and isomerization of glucose to fructose, decreased the yield of DFF from sucrose.



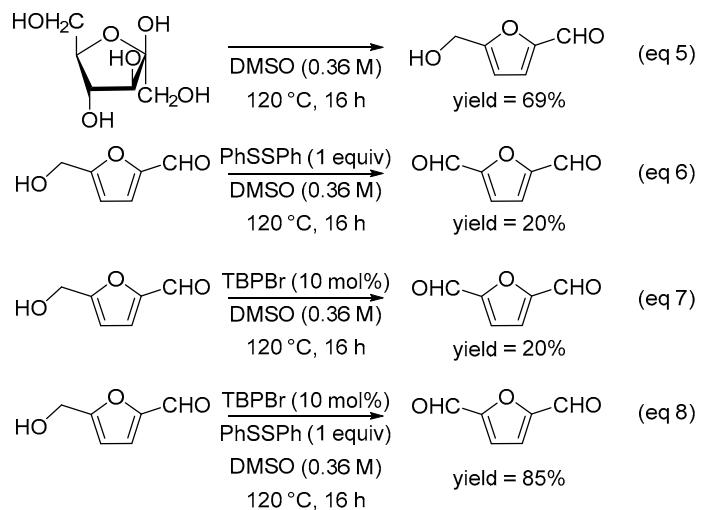
**Scheme 2.** Formation of DFF from D-glucose and D-mannose.



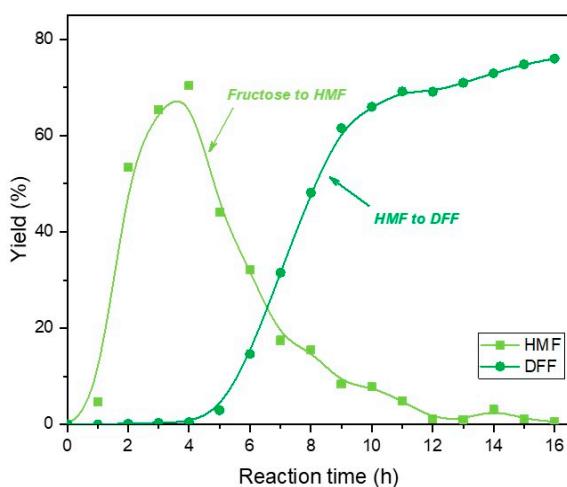
**Scheme 3.** Formation of DFF from D-galactose and sucrose.

The DFF reaction mechanism was probed by control experiments and by the reaction profile (Scheme 4 and Figure 2). Fructose was converted to HMF in a 69% yield in the absence of Br<sup>-</sup> and PhSSPh, and DFF was not observed (Scheme 4, Equation (5)). The conversion of HMF to DFF was poor in the presence of either PhSSPh or TBPBr (Equations (6) and (7)), but the addition of both TBPBr and PhSSPh to HMF increased the DFF yield to 85% (Equation (8)). Based on these results, the conversion of fructose to DFF occurs via DMSO-mediated dehydration of fructose to HMF, followed by the oxidation of HMF to DFF in the presence of TBPBr and PhSSPh. As illustrated in the reaction profile

(Figure 2), dehydration of D-fructose to form HMF occurs at the early stage, and HMF is subsequently converted to DFF.

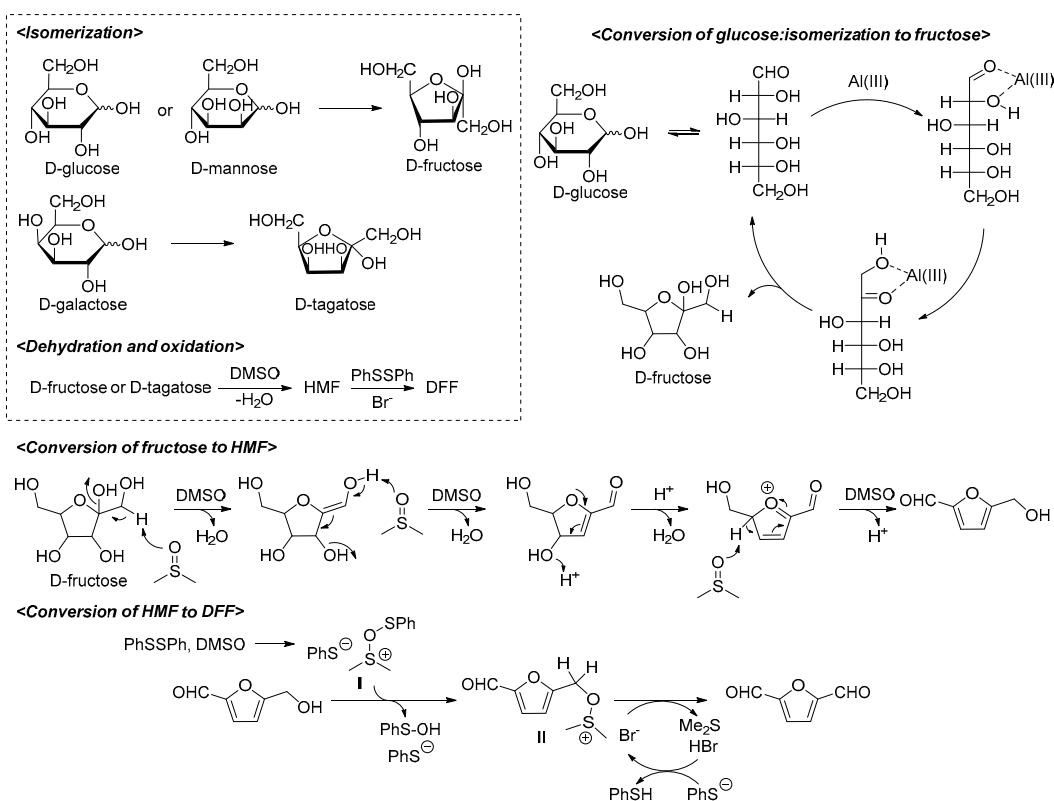


**Scheme 4.** Control experiments for probing the mechanism.



**Figure 2.** Reaction profile for converting D-fructose to DFF via HMF; TBPBr (10 mol%) and PhSSPh (1 equiv) were added to the solution of D-fructose in DMSO.

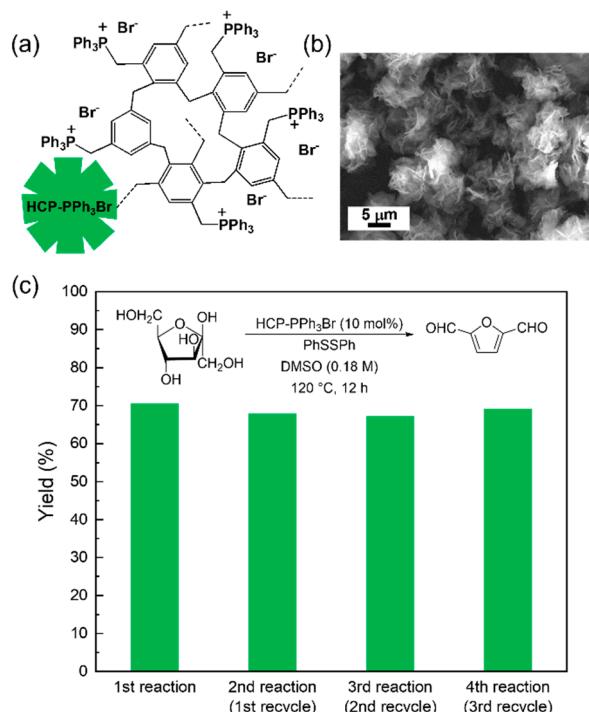
Based on control experiments and the reaction profile, a reaction mechanism is proposed in Scheme 5. Monosaccharides (glucose, mannose, and galactose) undergo isomerization, dehydration, and oxidation to afford DFF. As shown in Scheme 5, glucose and mannose forms fructose via isomerization, and galactose isomerizes to tagatose. A representative cycle of Al-catalyzed glucose conversion to fructose is described in Scheme 5. These five-membered ring carbohydrates are converted to HMF by DMSO-induced dehydration, which was confirmed by the results of the control experiments (Scheme 4, Equation (5)). However, Br<sup>-</sup>-mediated dehydration of fructose to HMF is not excluded because dehydration-induced by Br<sup>-</sup> as well as DMSO was reported [38,39]. The dehydration product (HMF) reacts with an adduct of PhSSPh and DMSO (intermediate I), forming intermediate II. Intermediate I is presumably formed via the cleavage of the S-S bond of PhSSPh upon the addition of DMSO [40–43]. The deprotonation of the  $\alpha$ -hydrogen of intermediate II by Br<sup>-</sup> affords DFF [29]. The generated by-product dimethylsulfide (Me<sub>2</sub>S) was observed in a gas-trapping experiment, supporting the proposed mechanism (see Supplementary Materials, Figures S1 and S2).



**Scheme 5.** Plausible mechanism for the synthesis of DFF from monosaccharides.

The recyclability of this catalytic system was examined using a heterogeneous catalyst, as illustrated in Figure 3. Recently, hypercross-linked polymers (HCPs) have emerged as versatile platforms for catalytic applications [44]. The HCPs have been prepared by the Friedel-Crafts reactions of organic building blocks, including arenes with multi-halomethylene moieties [45]. Considering the chemical structure of BTPPBr (entry 6 of Table 1), the HCP with triphenylphosphonium bromide species (HCP-PPh<sub>3</sub>Br) was designed and prepared as a heterogeneous catalyst through the FeCl<sub>3</sub>-catalyzed Friedel-Crafts reaction of 1,3,5-tri(bromomethyl)benzene and the following nucleophilic addition of triphenylphosphine to the benzyl bromide moieties (Figure 3a and see Supplementary Materials for detailed synthetic procedures and characterization data experimental procedure, Scheme S1 and Figures S3–S6). According to scanning (SEM) and transmission electron microscopy (TEM), the morphologies of HCP-PPh<sub>3</sub>Br were analyzed to be micron-sized particles consisting of nanosheets with thicknesses of 40~50 nm (Figure 3b and see Supplementary Materials, Figure S3). The energy-dispersive X-ray spectroscopy (EDS)-based elemental mapping studies of HCP-PPh<sub>3</sub>Br confirmed the homogeneous distribution of phosphorous and bromine over the materials. The infrared absorption (IR) spectroscopy of HCP-PPh<sub>3</sub>Br showed P<sup>+</sup>-C vibration peaks at 1436 and 1107 cm<sup>-1</sup>, indicating the successful incorporation of phosphonium bromide species (Supplementary Materials, Figure S4) [46]. According to inductively coupled plasma-optical emission (ICP-OES) and combustion ion chromatography, the contents of phosphorous and bromide in the HCP-PPh<sub>3</sub>Br were analyzed to be 0.89 and 0.74 mmol/g, respectively. Powder X-ray diffraction (PXRD) studies indicated that the HCP-PPh<sub>3</sub>Br has an amorphous feature (Supplementary Materials, Figure S5). Thermogravimetric analysis (TGA) showed that the HCP-PPh<sub>3</sub>Br is stable up to 248 °C (Supplementary Materials, Figure S6). Considering the phosphonium bromide species and the chemical stability of HCP-PPh<sub>3</sub>Br, we studied its performance as a heterogeneous catalyst in the fructose oxidation to DFF. When 10 mol% HCP-PPh<sub>3</sub>Br was used as a catalyst instead of BTPPBr, the fructose was converted to DFF with a yield of 71% (Figure 3c). The reaction conditions (the reaction time and the concentration) of heterogeneous reactions

were modified from the homogeneous reactions for the convenience of operation). Moreover, the recycling experiments showed that the yield of each experiment was maintained up to the third recycling test (Supplementary Materials, Table S3). The recyclable heterogeneous catalysts maintaining good catalytic activities can be applied to a continuous operation. This protocol, including recyclable catalysts, accords to develop sustainable catalytic processes.



**Figure 3.** (a) Structure of HCP-PPh<sub>3</sub>Br, (b) SEM image of HCP-PPh<sub>3</sub>Br, (c) the yield of each recycling experiment.

### 3. Conclusions

The selective one-pot synthesis of DFF from carbohydrates (fructose, glucose, mannose, galactose, and sucrose) was achieved using the combination of Br<sup>-</sup>, PhSSPh, and DMSO. The reaction mechanism for the conversion of fructose to DFF was elucidated, confirming the sequential process of fructose dehydration to HMF followed by HMF oxidation to DFF. Although isomerization or hydrolysis-isomerization is required in the reactions of glucose, mannose, galactose, and sucrose prior to the dehydration of fructose intermediates (or tagatose in the case of galactose), the combination of Br<sup>-</sup> catalysts, disulfide, and DMSO improved the yields of DFF compared to those of previously reported reactions using these carbohydrates. Furthermore, the heterogeneous catalyst containing Br<sup>-</sup> was recycled without a significant loss in its catalytic activity.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/catal12040360/s1>, Scheme S1: Synthesis of HCP-PPh<sub>3</sub>Br, Table S1: Reactions of D-fructose to form DFF, Table S2: Reactions of D-glucose to form DFF, Table S3: Recycling experiments, Figure S1: Experimental setup for the dimethyl sulfide trapping experiment, Figure S2: <sup>1</sup>H NMR spectra of dimethyl sulfide trapping experiment, Figure S3: (a–b) SEM images of HCP-Br and HCP-PPh<sub>3</sub>Br. (c) A TEM image of HCP-PPh<sub>3</sub>Br. (d–g) EDS-elemental mapping images of HCP-PPh<sub>3</sub>Br. (Red: Carbon, Green: Bromine, Teal: Phosphorus), Figure S4: IR spectra of HCP-Br and HCP-PPh<sub>3</sub>Br, Figure S5: PXRD patterns of HCP-Br and HCP-PPh<sub>3</sub>Br, Figure S6: TGA curves of HCP-Br and HCP-PPh<sub>3</sub>Br, Figure S7: <sup>1</sup>H spectrum of 2,5-diformylfuran, Figure S8: <sup>13</sup>C spectrum of 2,5-diformylfuran, Figure S9: <sup>1</sup>H spectra of (a) the reaction mixture of fructose, TBPBr (10 mol%), and PhSSPh in DMSO (the reaction mixture contains DFF, dimethyl sulfide, and intermediates derived from diphenyldisulfide), (b) fructose, (c) HMF, and (d) DFF. References [46–48] have been in the Supplementary Materials.

**Author Contributions:** Conceptualization, H.-Y.J.; investigations, S.A.K., K.S., J.Y.J. and S.B.; writing—original draft preparation, H.-Y.J.; writing—review and editing, S.U.S. and H.-Y.J. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data presented in this study are openly available in the Supplementary Materials at <https://www.mdpi.com/article/10.3390/catal12040360/s1>.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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