

Electronic Supplementary Information for

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

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I. Experimental procedures

General information

D-Fructose, D-glucose, anhydrous DMSO, and tetrabutylammonium bromide, $\text{Al}(\text{OTf})_3$ were received from Sigma Aldrich (Korea). Diphenyl disulfide, D-mannose, D-galactose, and sucrose were received from TCI (Korea). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a JEOL Resonance ECZ600R (600 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the singlet at 2.50 ppm for DMSO-d_6 . Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a JEOL Resonance ECZ600R (151 MHz). Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the multiplet at 39.52 ppm for DMSO-d_6 . High resolution mass spectra were obtained with a magnetic sector-electric sector double focusing mass analyzer equipment. IR spectra were recorded with a Bruker VERTEX 70 IF-IR spectrometer. Melting points of the compounds were checked in open capillary and were uncorrected. Elemental analyses were performed by a Flash 2000 (Thermo Scientific). SEM images were obtained by a JSM7100F. TEM and EDS-elemental mapping images were obtained by a JEOL 2100F. ICP-OES analysis was conducted by a 5900 ICP-OES. Combustion ion chromatograph was conducted by a AQF-2100H. PXRD patterns were obtained by a Rigaku MAX-2200. TGA curves were obtained by a Seiko Exstar 7300.

Experimental procedure for the synthesis of DFF from fructose

Fructose (0.25 mmol), PhSSPh (0.25 mmol), TBPBr (10 mol%), and DMSO (0.7 ml) were added into the sealed tube. The mixture was heated at 120 °C for 16 h. After the reaction, the mixture was cooled down to ambient temperature, and the solvent was evaporated. The product was isolated by flash column chromatography with EtOAc/hexane as an eluent.

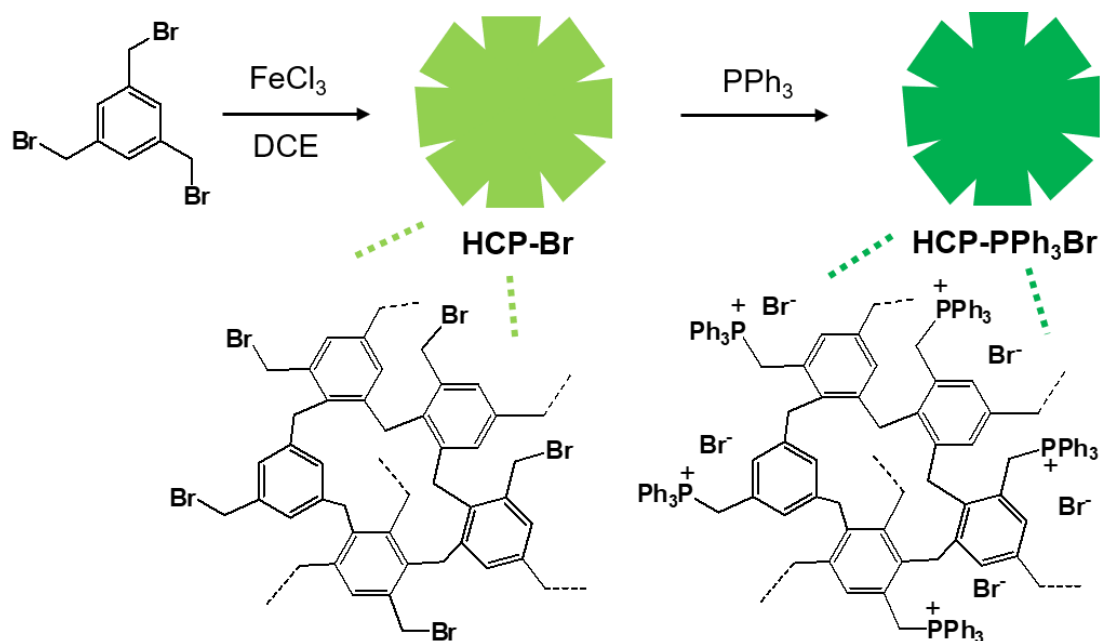
Experimental procedure for the synthesis of DFF from glucose

Glucose (0.25 mmol), $\text{Al}(\text{OTf})_3$ (10 mol%), PhSSPh (0.25 mmol), TBPBr (10 mol%), and DMSO (0.7 ml) were added into the sealed tube. The mixture was heated at 120 °C for 16 h. After the reaction, the mixture was cooled down to ambient temperature, and the solvent was evaporated. The product was isolated by flash column chromatography with EtOAc/hexane as an eluent.

Experimental procedure for the synthesis of DFF from various carbohydrates

Carbohydrate (0.25 mmol), $\text{Al}(\text{OTf})_3$ (10 mol%), PhSSPh (0.25 mmol), TBPBr (10 mol%), and DMSO (0.7 ml) were added into the sealed tube. The mixture was heated at 120 °C for 16 h. After the reaction, the mixture was cooled down to ambient temperature, and the solvent was evaporated. The product was isolated by flash column chromatography with EtOAc/hexane as an eluent.

Synthetic procedure of heterogeneous catalysts



Scheme S1. Synthesis of *HCP-PPh₃Br*

Preparation of HCP-Br

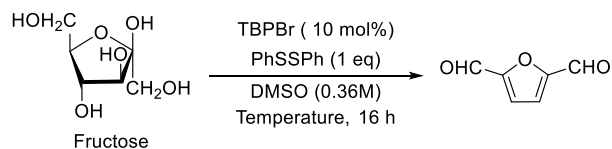
1,3,5-Tri(bromomethyl)benzene (0.36 g, 1.0 mmol) and 1,2-dichloroethane (240 ml) were added into a flame-dried 500 ml round bottom flask under Ar atmosphere. After the reaction mixture was stirred at room temperature, FeCl₃ (0.65 g, 4.0 mmol) was added. After the mixture was heated at 80 °C for 24 hours, it was cooled to room temperature. The powder (HCP-Br) was isolated by centrifugation, washed with a mixture of dichloromethane (15 ml), methanol (15 ml), and acetone (15 ml) 10 times, and dried under vacuum.

Synthesis of HCP-PPh₃Br

HCP-Br (70 mg), toluene (20 ml), and triphenylphosphine (0.26 mg, 1.0 mmol) were added into a flame-dried 50 ml two-neck Schlenk flask under Ar atmosphere. After the mixture was heated at 80 °C for 24 hours, it was cooled to room temperature. The powder (HCP-PPh₃Br) was isolated by centrifugation, washed with a mixture of dichloromethane (15 ml), methanol (15 ml), and acetone (15 ml) 10 times, and dried under vacuum. The contents of phosphorus and bromine in HCP-PPh₃Br were analyzed to be 0.89 mmol/g and 0.74 mmol/g by the ICP-OES and combustion ionic chromatography, respectively.

II. Conversion of carbohydrates to DFF

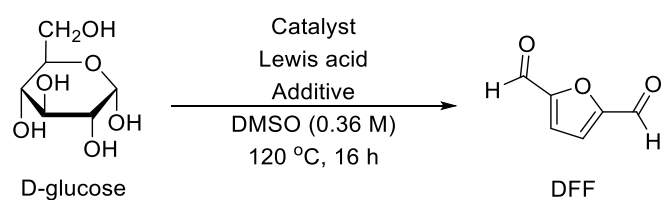
Table S1. Reactions of D-fructose to form DFF.



Entry	Temperature (°C)	DFF yield (%) ^a
1	100	25
2	120	92
3	150	50

^aIsolated yields.

Table S2. Reactions of D-glucose to form DFF.



Entry	Catalyst (mol%)	Lewis acid (mol%)	Additive (eq.)	HMF yield (%) ^a	DFF yield (%) ^b	Conversion (%)
1	TBPBr (10)	-	PhSSPh (1 eq)	-	26	>99
2	TBPBr (10)	Al(OTf) ₃ (10)	PhSSPh (1 eq)	-	60	>99
3	TBPBr (10)	In(OTf) ₃ (10)	PhSSPh (1 eq)	37	-	>99
4	TBPBr (10)	Cu(OTf) ₂ (10)	PhSSPh (1 eq)	13	-	>99
5	TBPBr (10)	AlCl ₃ ·6H ₂ O (10)	PhSSPh (1 eq)	-	-	>99
6	TBPBr (10)	Zn(OTf) ₂ (10)	PhSSPh (1 eq)	-	-	>99
7	TBPBr (10)	Al(OTf) ₃ (10)	-	58	3	>99

^aH NMR yields using 1,3,5-trimethoxybenzene as an internal standard. ^bIsolated yields.

III. Dimethyl sulfide trapping experiment

Procedure: Fructose (0.25 mmol), PhSSPh (0.25 mmol), TBPBr (10 mol%), and DMSO (0.7 ml) were added into a round bottom flask. The flask was connected with a bubbler filled with CHCl_3 . The mixture was heated at 120 °C for 16 hours. Dimethyl sulfide in CHCl_3 (0.5 ml) was mixed with 0.15 ml of CDCl_3 for the ^1H NMR analysis.

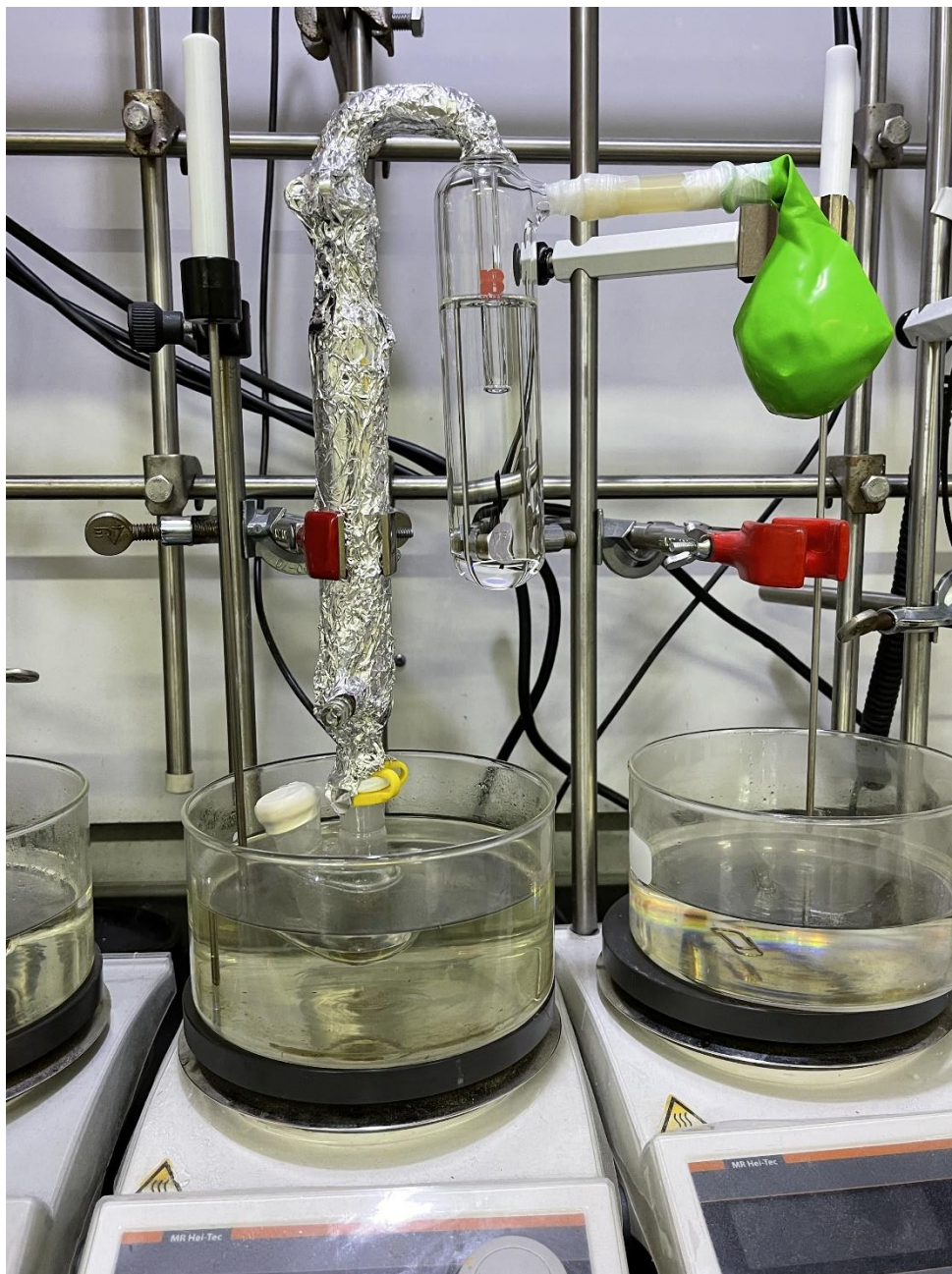


Figure S1. Experimental setup for the dimethyl sulfide trapping experiment.

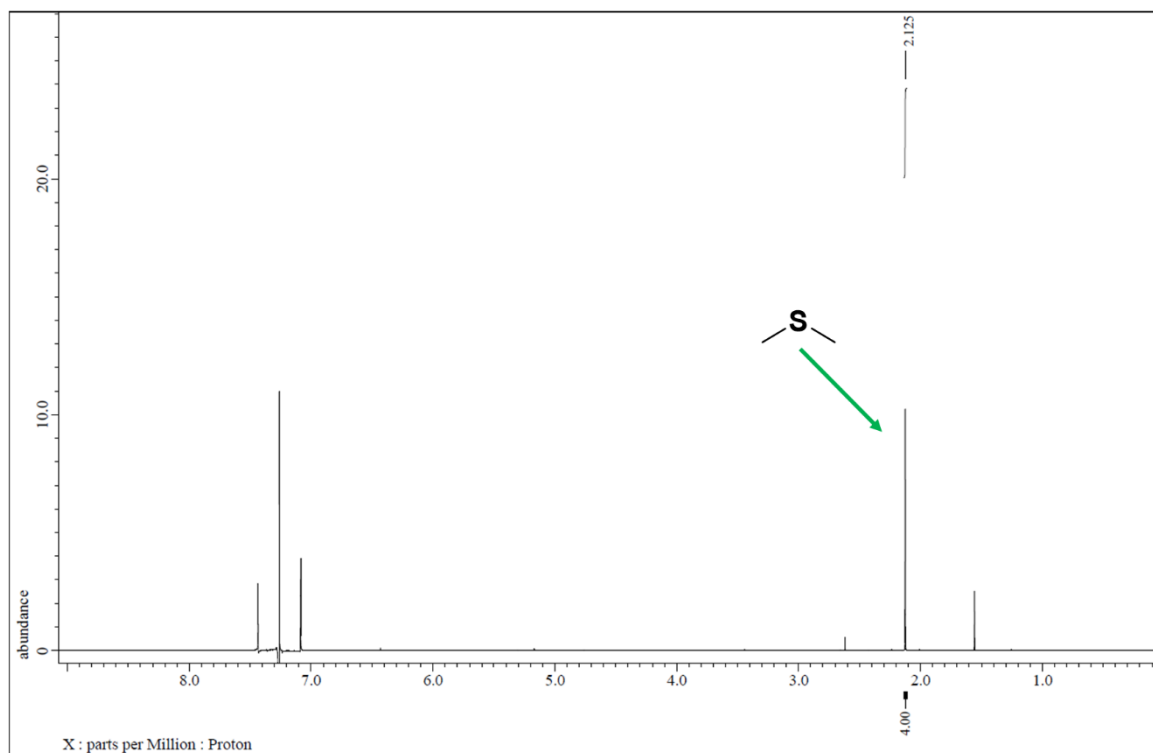


Figure S2. ^1H NMR spectra of dimethyl sulfide trapping experiment.¹

¹ S. Song.; X. Huang.; Y.-F. Liang.; C. Tang.; X. Li.; N. Jiao.; From simple organobromides or olefins to highly value added bromohydrins: a versatile performance of dimethyl sulfoxide. *Green Chem.*, **2015**, *17*, 2727-2731. <https://doi.org/10.1039/C5GC00184F>.

IV. Characterization of HCP-Br and HCP-PPh₃Br

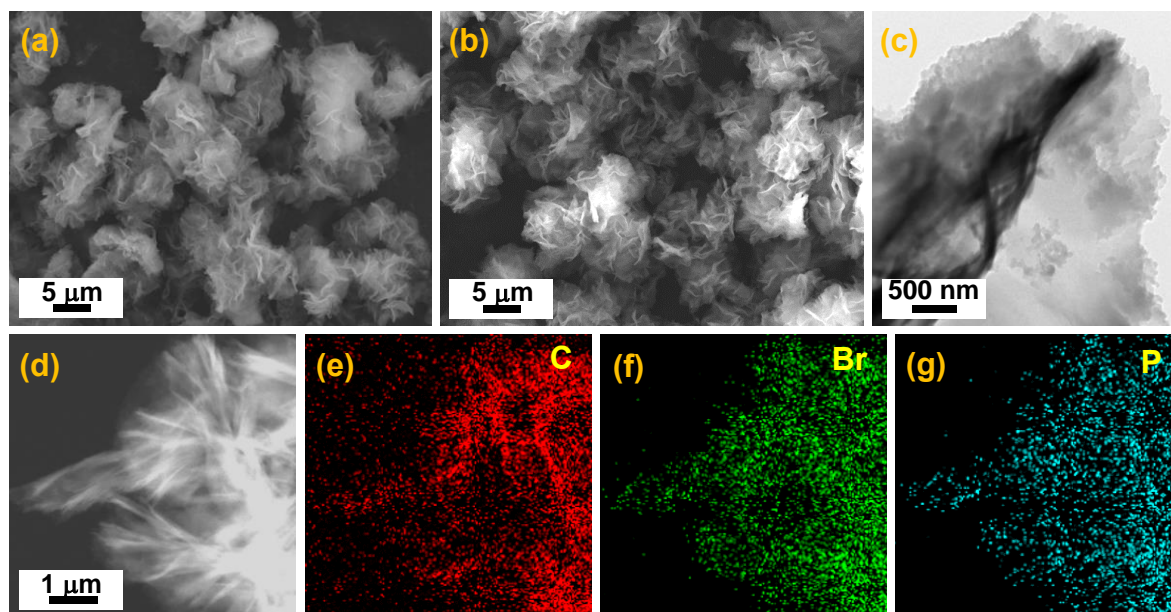


Figure S3. (a–b) SEM images of HCP-Br and HCP-PPh₃Br. (c) A TEM image of HCP-PPh₃Br. (d–g) EDS-elemental mapping images of HCP-PPh₃Br. (Red: Carbon, Green: Bromine, Blue: Phosphorus)

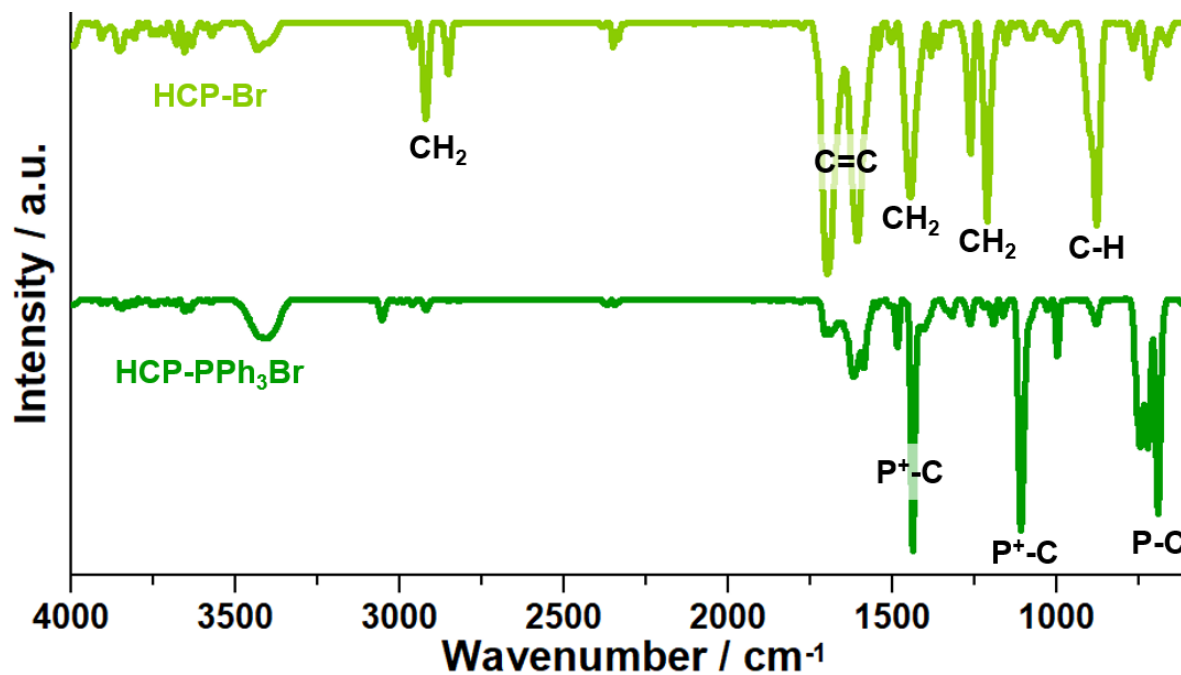


Figure S4. IR spectra of HCP-Br and HCP-PPh₃Br^{2,3}

² D. Chakraborty.; S. Nandi.; M. A. Sinnwell.; J. Liu.; R. Kushwaha.; P. K. Thallapally.; R. Vaidhyanathan. Hyper-cross-linked porous organic frameworks with ultramicropores for selective xenon capture. *ACS Appl. Mater. Interfaces*. **2019**, *11*, 13279–13284. <https://doi.org/10.1021/acsami.9b01619>.

³ M. Arroyo.; R.V. Rufino.; M.A. Lopez-Manchado.; J. F. Fernandez. Relevant features of bentonite modification with a phosphonium salt. *J. Nanosci. Nanotechnol.* **2006**, *6*, 2151-2154. <https://doi.org/10.1166/jnn.2006.346>.

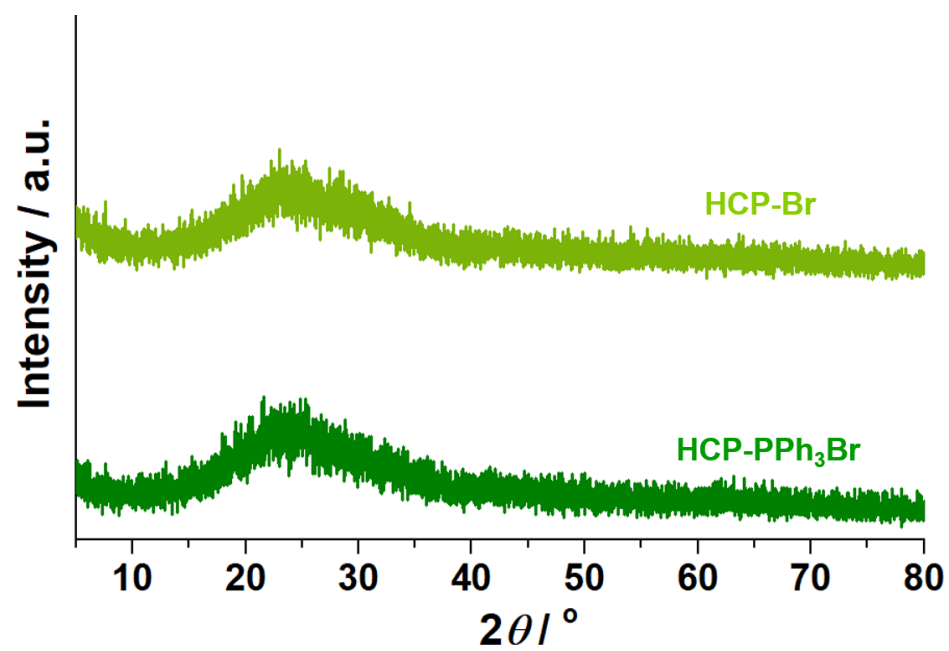


Figure S5. PXRD patterns of HCP-Br and HCP-PPh₃Br.

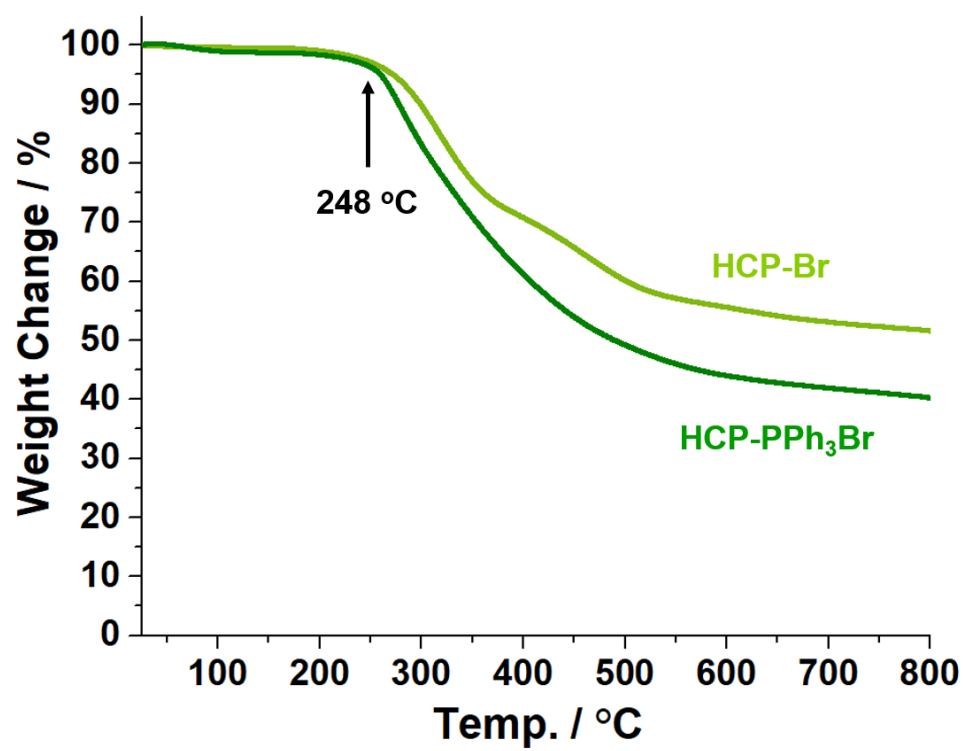


Figure S6. TGA curves of HCP-Br and HCP-PPh₃Br

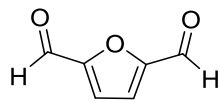
V. Recycling experiment

Catalytic procedure: Fructose (0.25 mmol), PhSSPh (0.25 mmol), HCP-PPh₃Br (10 mol% Br⁻), and DMSO (1.4 ml) were added into the sealed tube. The mixture was heated at 120 °C for 12 h. After the reaction, substrates and solvent were added subsequently for the next cycle.

Table S3. Recycling experiments.

Entry	Cycle	DFP yield (%)
1	1	70.6
2	2	67.8
3	3	67.1
4	4	69.1

VI. Spectral data of 2,5-diformylfuran



¹H NMR (DMSO-d₆, 600 MHz): δ 9.81 (s, 2H), 7.66 (s, 2H) ppm.

¹³C NMR (DMSO, 150 MHz): δ 180.7, 153.6, 122.0 ppm.

HRMS *m/z* (EI⁺): C₆H₄O₃ calcd: 124.02, found: 124.016.

FTIR (neat, cm⁻¹): 3130, 2874, 1668, 1562, 1173, 961 cm⁻¹.

Mp (°C): 112 °C.

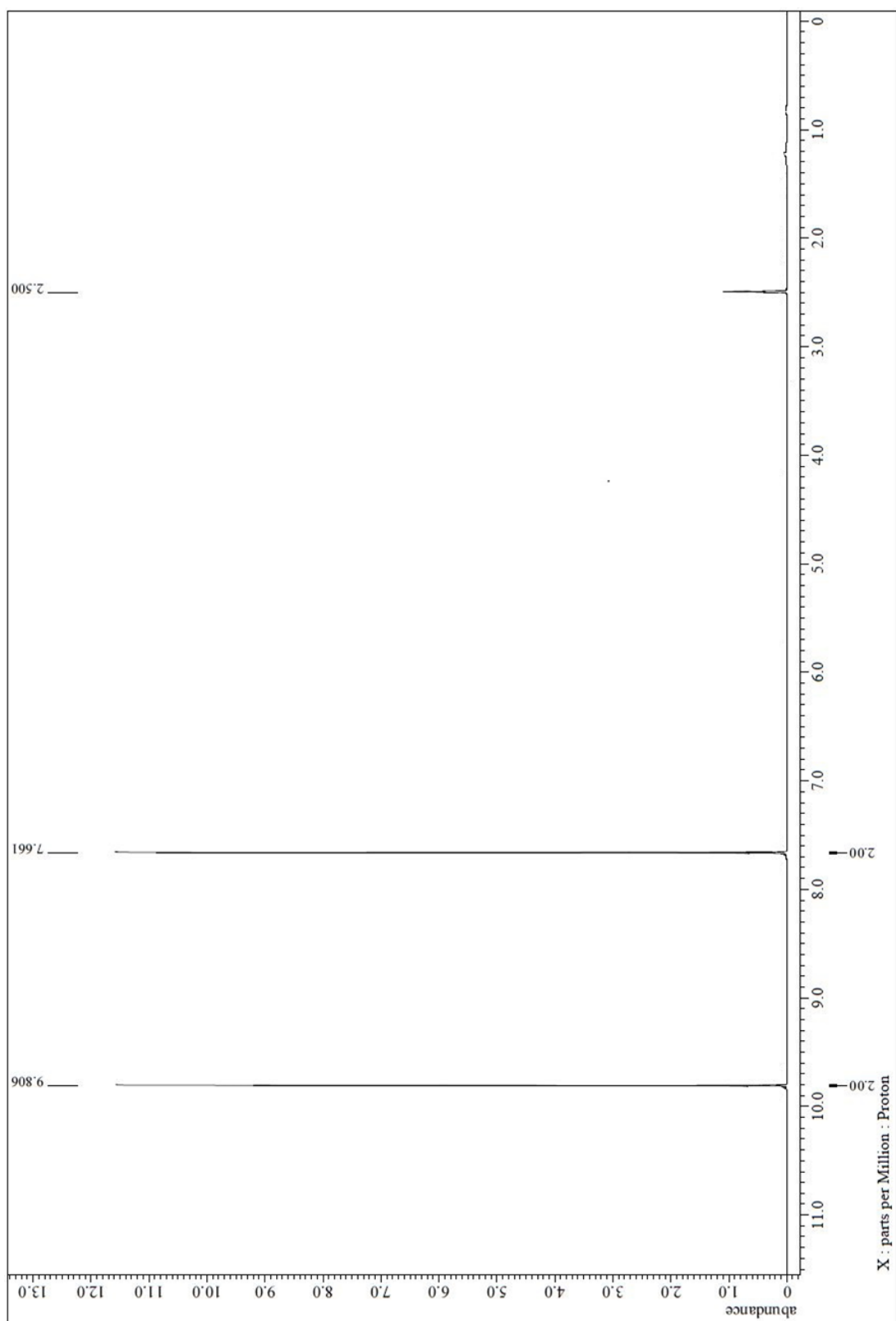


Figure S7. ¹H spectrum of 2,5-diformylfuran.

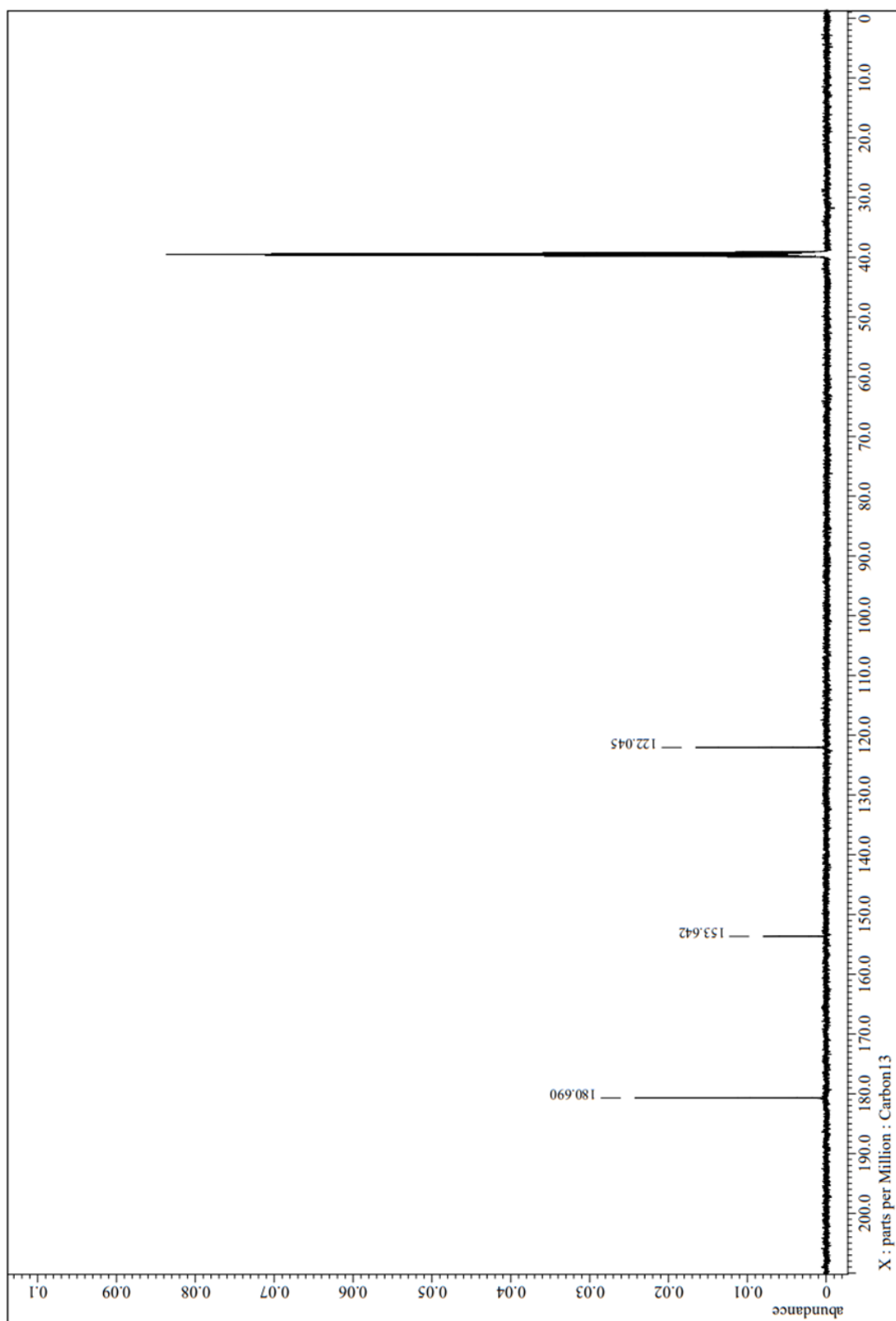


Figure S8. ^{13}C spectrum of 2,5-diformylfuran.

VII. ^1H NMR of the reaction mixture using fructose

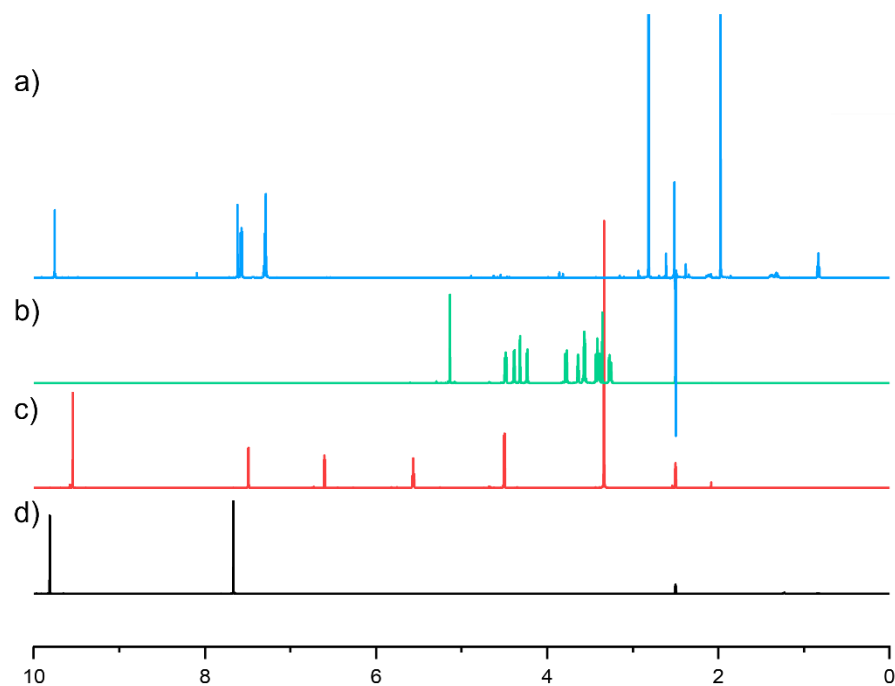


Figure S9. ^1H spectra of **a)** the reaction mixture of fructose, TBPBr (10 mol%), and PhSSPh in DMSO (the reaction mixture contains DFF, dimethyl sulfide, and intermediates derived from diphenyldisulfide), **b)** fructose, **c)** HMF, and **d)** DFF