Supporting Information

Sulfonated Graphitic Carbon Nitride as Highly Selective and Efficient Heterogeneous Catalyst for Conversion of Biomass-derived Saccharides to 5-Hydroxymethylfurfural in Green Solvents

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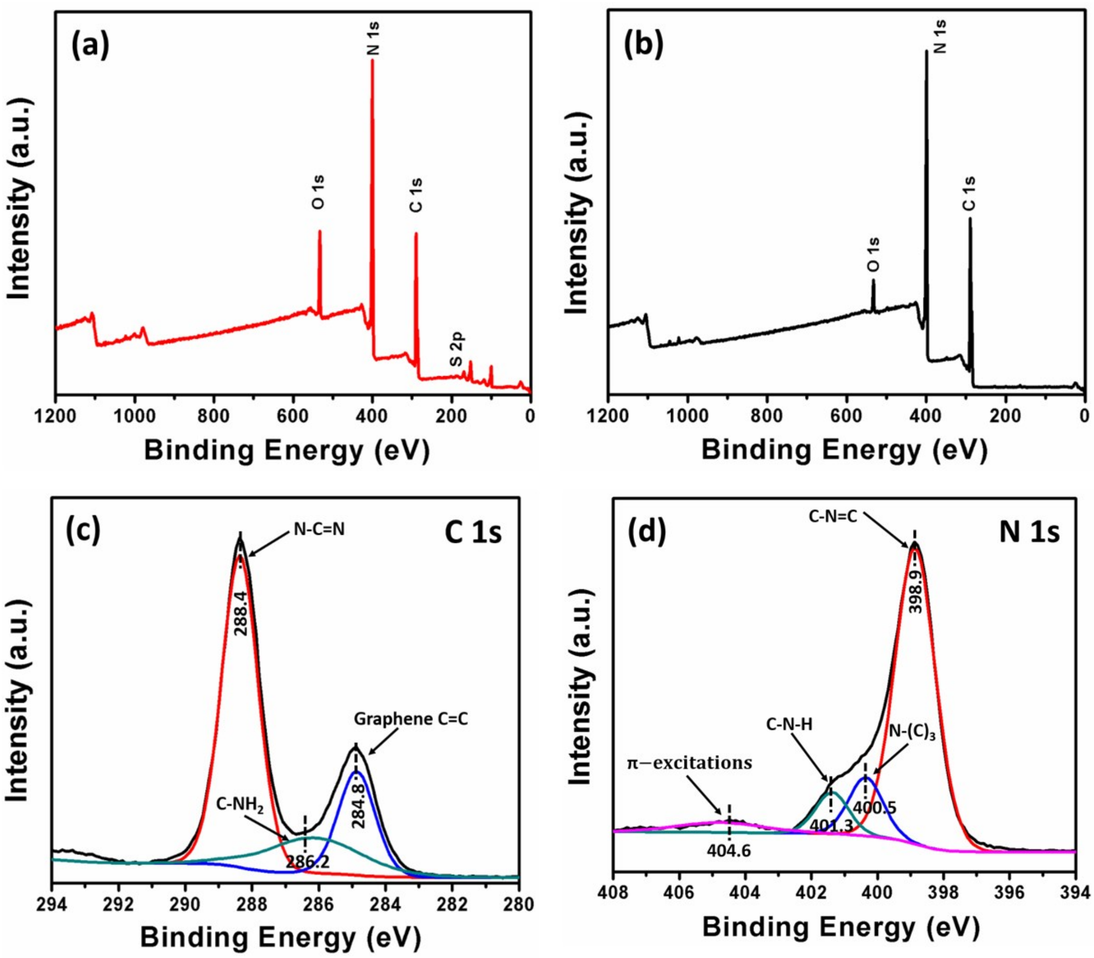

Figure S1. (a,b) Survey Spectrum for S-GCN and GCN. XPS for the GCN nanosheets (c) C 1s, (d) N 1s.

Table S1. Atomic percentage of elements in S-GCN catalyst from XPS analysis.

Sl. No.	Element	Binding Energy (eV)	Atomic (%)
1.	C-1s	288.79	42.07
2.	N-1s	399.35	41.22
3.	O-1s	532.65	13.44
4.	S-2p	168.70	3.27

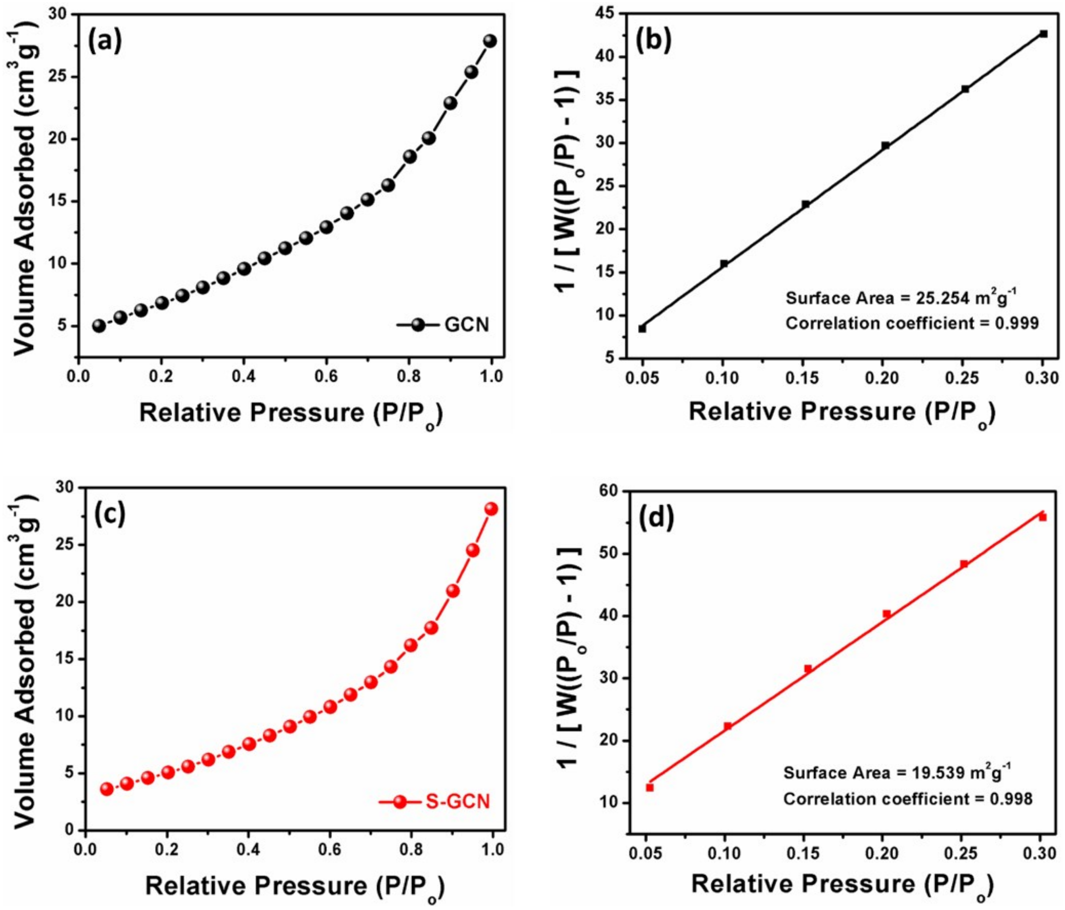

Figure S2. (a, c) N_2 adsorption isotherms and (b, d) BET surface area plots for GCN and S-GCN, respectively.

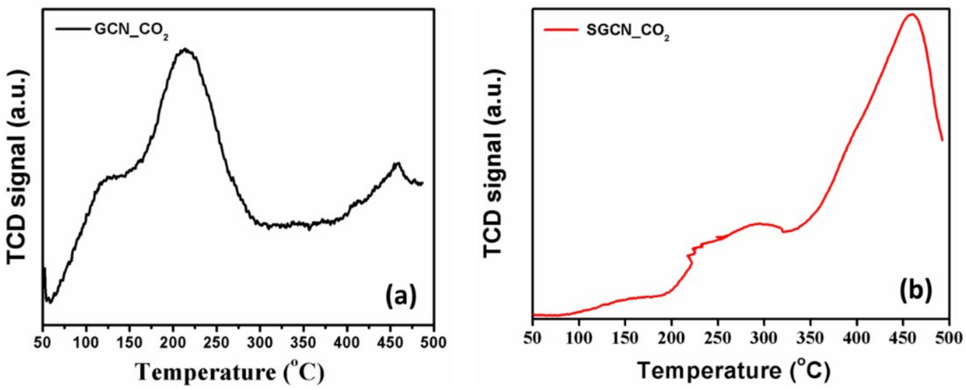

Figure S3. CO_2 TPD measurement of (a) GCN and (b) S-GCN nanosheets.

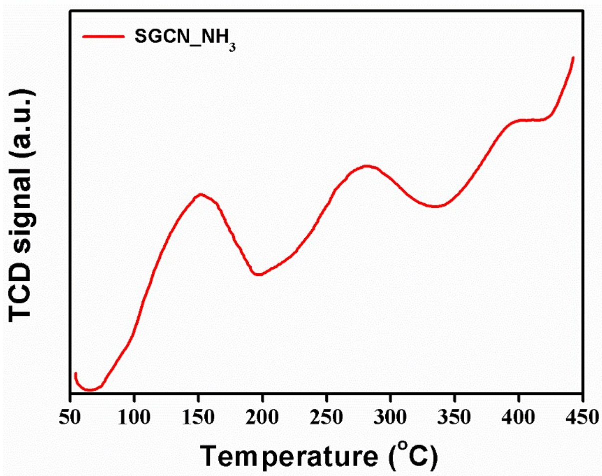

Figure S4. NH_3 TPD measurement of S-GCN nanosheets.

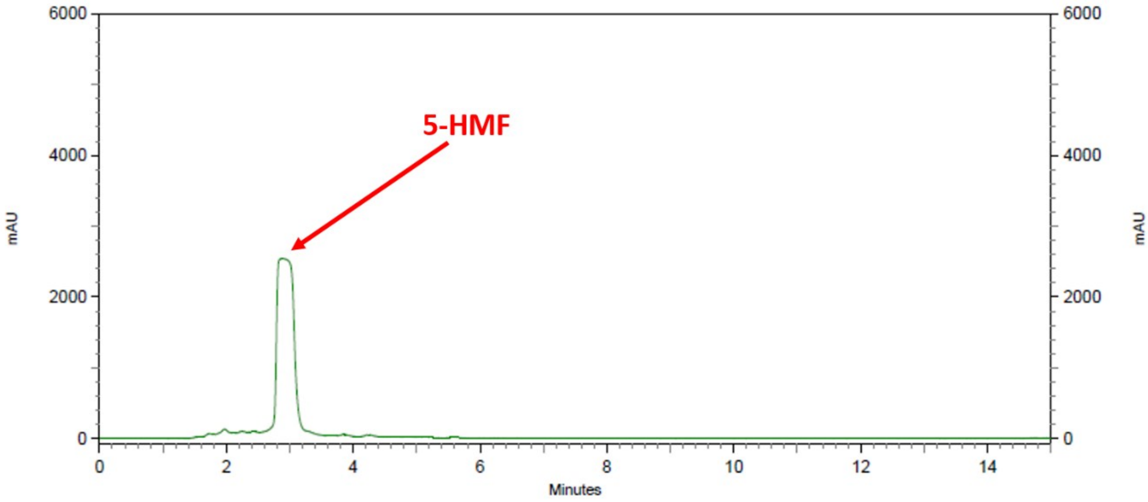

Figure S5: HPLC chromatogram of reaction mixture. Hydrothermal conditions: Glucose (100 mg), S-GCN (10 mg), water (10 mL), 200 ^{o}C for 5 h.

Product yield calculation

The product yield was calculated after purification of the product through column chromatography. The yield of the product was calculated by using the following formula.

Yield (%) = [Actual yield (in mg) / Theoretical yield (in mg)] * 100

Herein, Theoretical yield = Molecular weight of product * mmol of starting material

(Theoretical yield is the 100 % yield)

Table S2. Optimization table of fructose reaction.

Entries 1-6: Variation in time

Entries 7-10: Variation in catalyst amount

Entries 11-14: Variation in temperature

Sl. No.	Reactant (100 mg)	Catalyst amount (mg)	Temperature (°C)	Time (h)	Yield (%)
1	Fructose	10	200	1	12
2	Fructose	10	200	2	48
3	Fructose	10	200	3	54
4	Fructose	10	200	5	43
5	Fructose	10	200	7	33
6	Fructose	10	200	9	30
7	Fructose	5	200	3	62
8	Fructose	10	200	3	65
9	Fructose	20	200	3	59
10	Fructose	30	200	3	49
11	Fructose	10	125	3	No HMF
12	Fructose	10	150	3	46
13	Fructose	10	200	3	65
14	Fructose	10	225	3	53

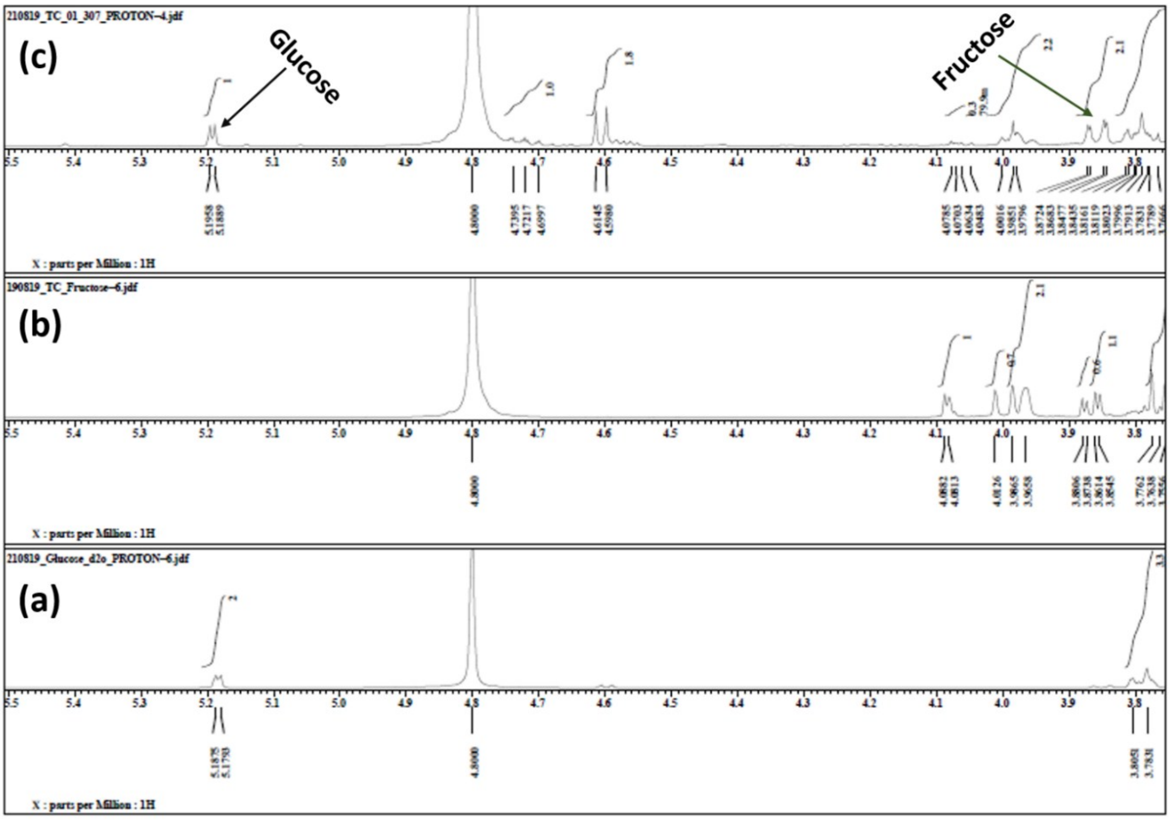

Figure S6. Stacked ^{1}H NMR spectra of (a) pure glucose (b) pure fructose and (c) reaction from glucose as starting material showing glucose to fructose conversion during the 5-HMF synthesis.

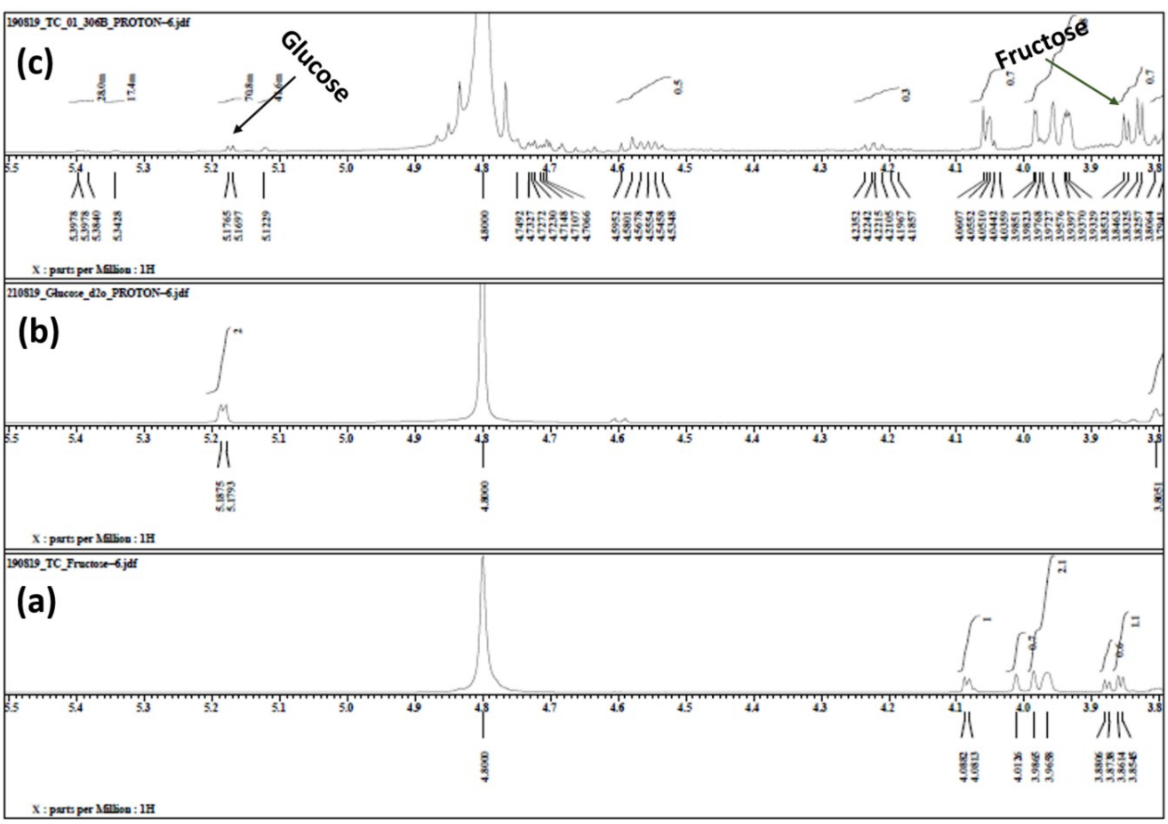

Figure S7. Stacked ^{1}H NMR spectra of (a) pure fructose (b) pure glucose and (c) reaction from fructose as starting material showing fructose to glucose back conversion, leading to less yield of 5-HMF.

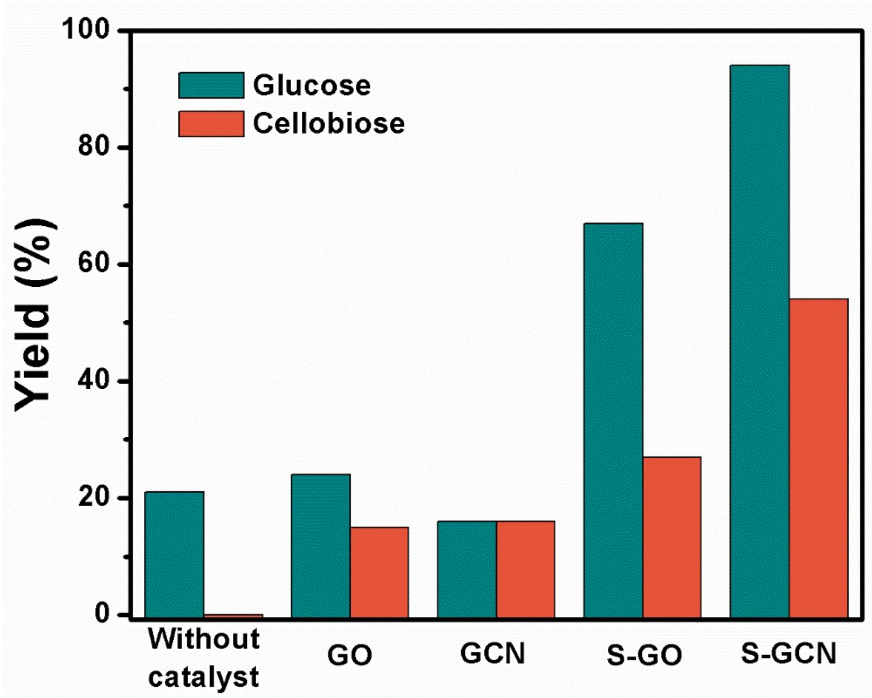

Figure S8. Catalytic performance for GO, GCN, S-GO, S-GCN and without catalyst. Reaction conditions: glucose = 0.1 g, catalyst = 0.01 g, distilled water = 10 mL at 200 ^{o}C for 5 h.

Green metrics calculations

Green chemistry metrics calculations were used to study the environment friendliness and sustainability of the chemical reaction (catalytic conversion of biomass to value added products). The various metrics used in this case have been detailed below.

1) Environmental factor or E-factor[1]

E = [Total mass of waste] / [Mass of final product]

Mass of waste = Total mass of reactant – Total mass of product

2) Mass intensity or MI[2]

MI = [Total mass in process] / [Mass of product]

3) Process mass intensity or PMI[2]

PMI = [Total mass in process (incl. solvent)] / [Mass of product]

4) Solvent intensity or SI[3]

SI = [Mass of solvents] / [Mass of product]

SI = [Mass of solvent (used in reaction)] / [Mass of 5-HMF (after purification)]

5) Atom economy or AE[4]

AE (%) = {[Mol wt. of product] / [Sum of mol wt. of reactants]} * 100

In case of Glucose, AE (%) = {[Molecular weight of 5-HMF] / [Molecular weight of Glucose]} * 100

6) Reaction mass efficiency or RME[5]

RME (%) = [Mass of product] / [Total mass of reactants] * 100

In case of Glucose, RM (%) = {[Mass of 5-HMF (after purification)] / [Mass of Glucose (used in reaction)]} * 100

7) Mass productivity or MP[3]

MP (%) = [Mass of product] / [Total mass (incl. solvents)] * 100

In case of Glucose, MP (%) = {[Mass of 5-HMF (after purification)] / [Mass of Glucose + Mass of solvent]} * 100

8) Carbon economy or CE[5]

CE (%) = [Carbon in product] / [Total carbon in reactant] * 100

= {[Number of moles of product*Number of C in product] / [Number of moles of reactant*Number of C in reactant]} * 100

Environmental factor or E factor tells us about the how much waste formed in a chemical process. Ideally, E factor should be zero for any greener chemical process. Higher E factor means more amount of waste which has a detrimental impact on our environment. In case of monosaccharides, reaction with glucose is greener than with fructose because its E factor has less value. In case of disaccharides, cellobiose shows more sustainable process for the production of 5-HMF because of its less E factor value than that of sucrose. Mass intensity or MI involves the ratio of the total mass involves in process to the mass of product. Lesser the value of mass intensity, more is the greener process as well as lesser is the cost of the process. Lesser value of mass intensity means either less amount of reactants are needed for given process or more amount of product are forming. In case of glucose, mass intensity value is less than that of fructose which means more amount of product are forming with the same reaction condition. Process Mass Intensity or PMI is same as Mass Intensity but it involves amount of solvent also. Cellobiose has less value of PMI than that of sucrose. Solvent Intensity or SI involves the ratio of amount of solvent to the amount of product. More the value of SI, more amount of solvent is needed for chemical process which means cost of process will increase. In case of water, glucose has lower value of SI than that of fructose. But we are using green solvents in our reaction which are recoverable, so in this chemical reaction, solvent has no negative impact on the environment. Atom Economy (AE) is the most simplest and popular green metrics. AE is a theoretical number by the use of exact stoichiometric quantities of starting materials which gives us the theoretical chemical yield. The highest yields in case of monosaccharides and disaccharides were found to be 70% and 74% respectively. Reaction Mass Efficiency (RME) is the percentage of mass of product with respect to the mass of the reactant. Glucose showed highest value of RME (66%) and fructose showed only 30%. Carbon Economy (CE) is the percentage of carbon content in the product with respect to the carbon content in reactant. Highest value of CE was calculated for glucose (94.55%).

Table S3. Green metrics calculations for ethanol.

Reaction conditions: Saccharides = 100 mg, S-GCN = 10 mg, Amount of ethanol = 10 mL, Density of ethanol = 0.8 gmL^{-1}, Mass of ethanol = 8000 mg, Time = 5 h and Temperature = 200 ^{o}C.

Sl. No.	Parameters	Glucose	Fructose	Cellobiose	Sucrose
1	Environmental factor	2.85	3.17	4.00	4.26
2	Mass intensity	3.85	4.17	5.00	5.26
3	Process mass intensity	311.54	337.50	405.00	426.32
4	Solvent intensity	307.70	333.33	400.00	421.10
5	Atom economy (%)	70	70	74	74
6	Reaction mass efficiency (%)	26	24	20	19
7	Mass productivity (%)	0.32	0.30	0.25	0.23
8	Carbon economy (%)	38.18	34.54	27.58	25.86

Table S4. Green metrics calculations for isopropyl alcohol.

Reaction conditions: Saccharides = 100 mg, S-GCN = 10 mg, Amount of IPA = 10 mL, Density of ethanol = 0.8 gmL^{-1}, Mass of IPA = 8000 mg, Time = 5 h and Temperature = 200 ^{o}C.

Sl. No.	**Parameters**	**Glucose**	**Fructose**	**Cellobiose**	**Sucrose**
1	Environmental factor	3.16	4.00	4.56	4.00
2	Mass intensity	4.16	5.00	5.56	5.00
3	Process mass intensity	337.50	405.00	450.00	405.00
4	Solvent intensity	333.33	400.00	444.44	400.00
5	Atom economy (%)	70	70	74	74
6	Reaction mass efficiency (%)	24	20	18	20
7	Mass productivity (%)	0.30	0.25	0.22	0.25
8	Carbon economy (%)	34.55	29.10	24.14	27.59

Table S5. Green metrics calculations for dimethyl carbonate.

Reaction conditions: Saccharides = 100 mg, S-GCN = 10 mg, Amount of DMC = 10 mL, Density of DMC = 1.1 gmL^{-1}, Mass of IPA = 11000 mg, Time = 5 h and Temperature = 200 ^oC.

Sl. No.	Parameters	Glucose	Fructose	Cellobiose	Sucrose
1	Environmental factor	5.25	7.33	7.33	4.00
2	Mass intensity	6.25	8.33	8.33	5.00
3	Process mass intensity	693.75	925.00	925.00	555.00
4	Solvent intensity	687.50	916.66	916.66	550.00
5	Atom economy (%)	70	70	74	74
6	Reaction mass efficiency (%)	16	12	12	20
7	Mass productivity (%)	0.14	0.11	0.11	0.18
8	Carbon economy (%)	23.64	18.18	17.24	27.59

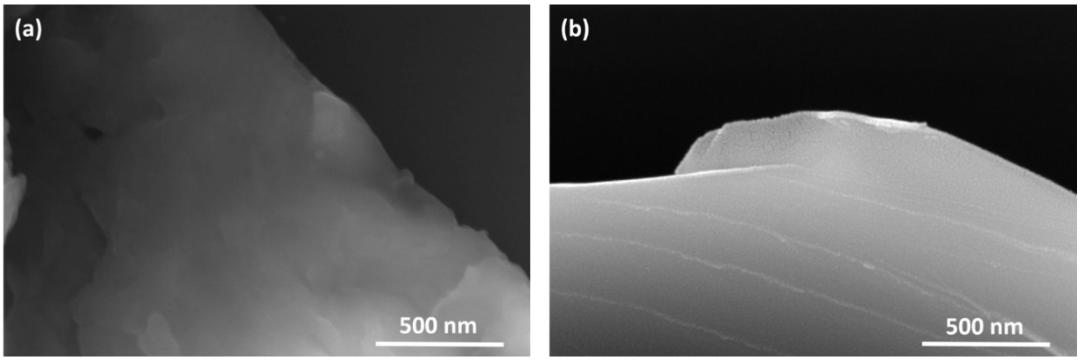

Figure S9. SEM image of (a) Fresh S-GCN, (b) Recycled S-GCN nanosheets.

NMR spectra of compounds

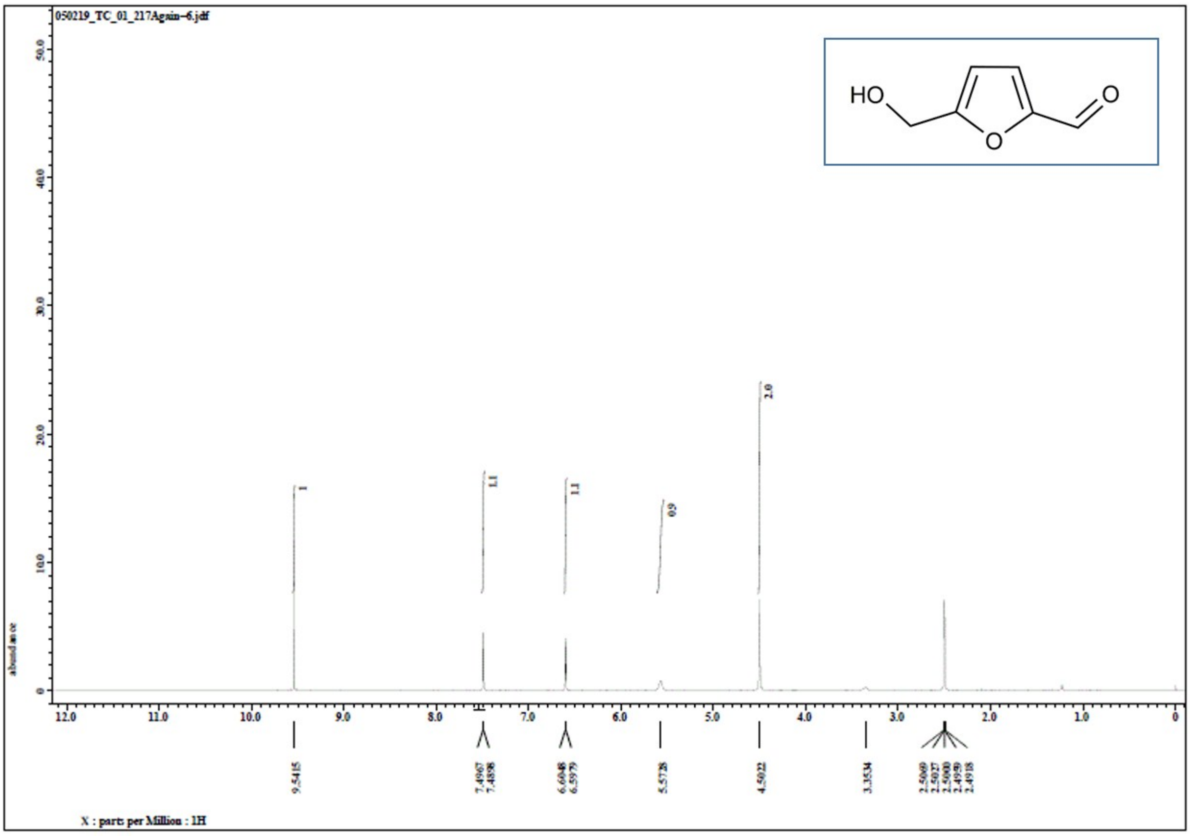

Figure S10. ^{1}H NMR spectrum of 5-(hydroxymethyl)furfural [DMSO-d_6, 500 MHz].

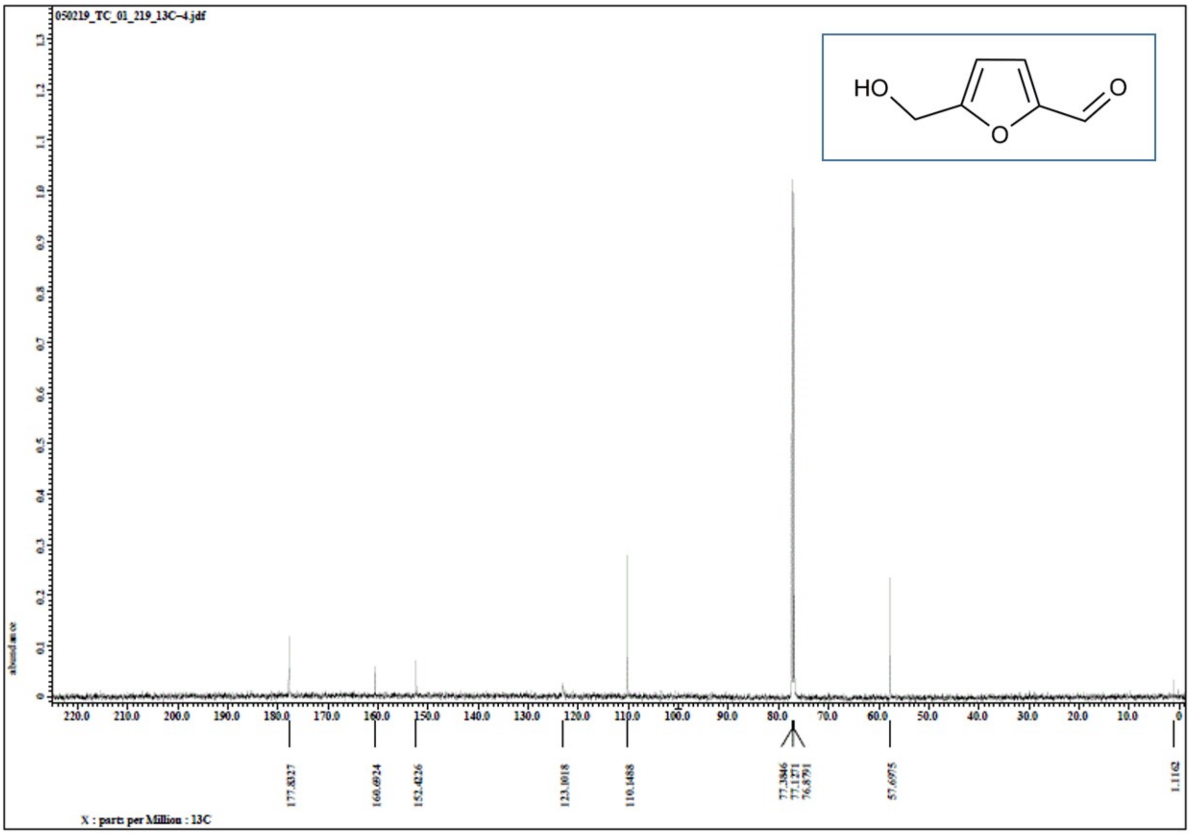

Figure S11. ^{13}C NMR spectrum of 5-(hydroxymethyl)furfural [DMSO-d_6, 125 MHz].

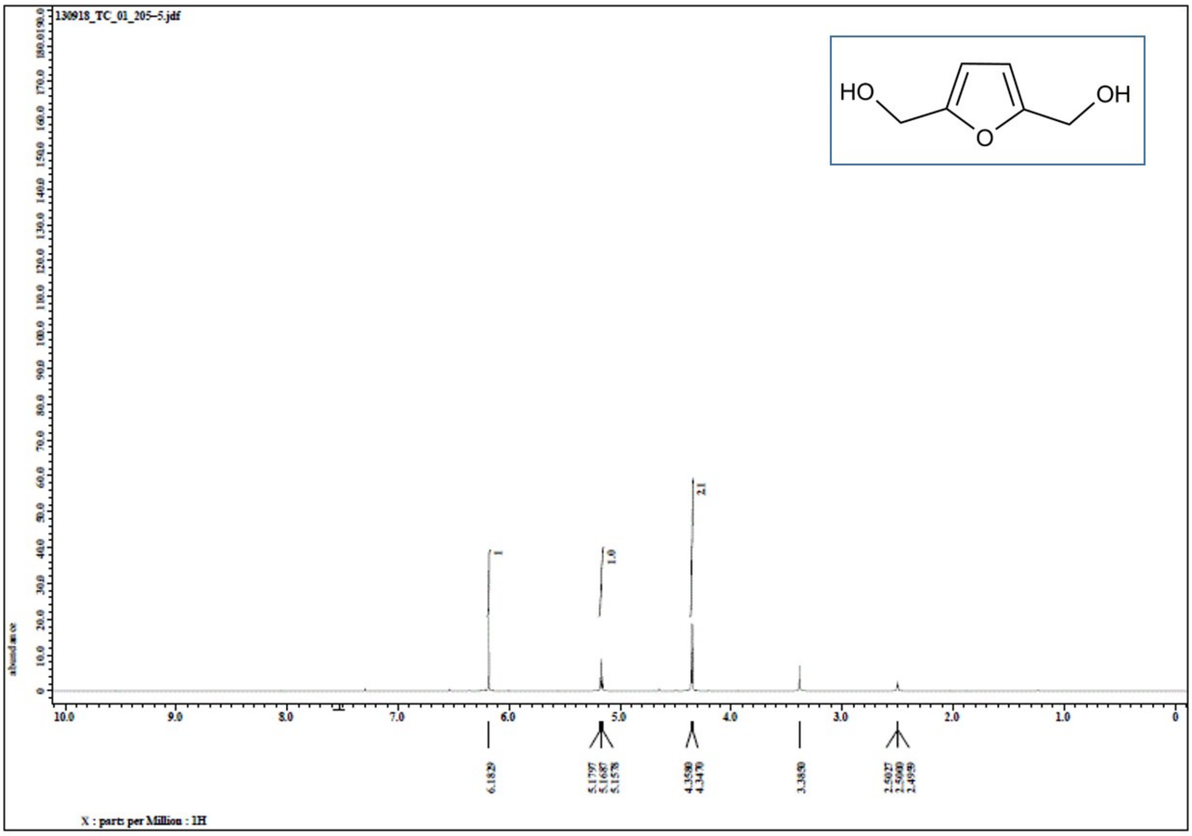

Figure S12. ^{1}H NMR spectrum of 2,5-bis(hydroxymethyl)furan [DMSO-d_6, 500 MHz].

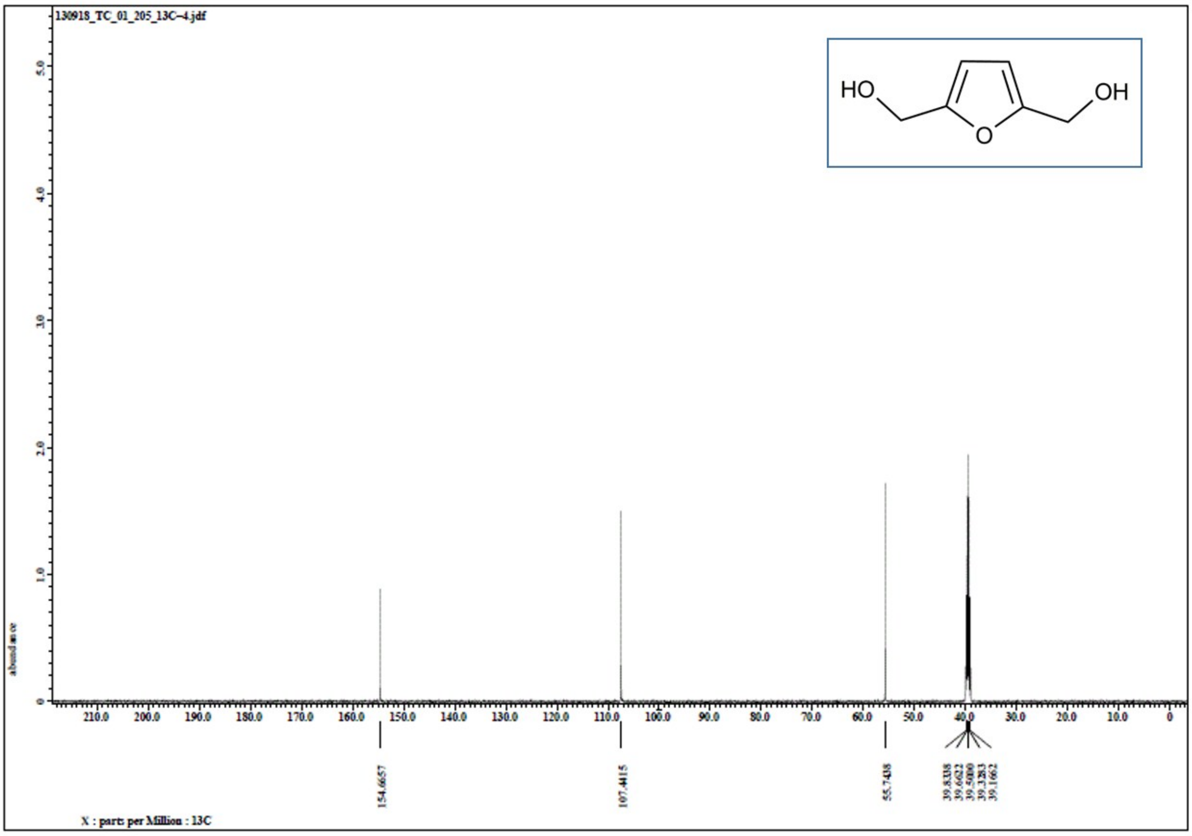

Figure S13. ^{13}C NMR spectrum of 2,5-bis(hydroxymethyl)furan [DMSO-d_6, 125 MHz].

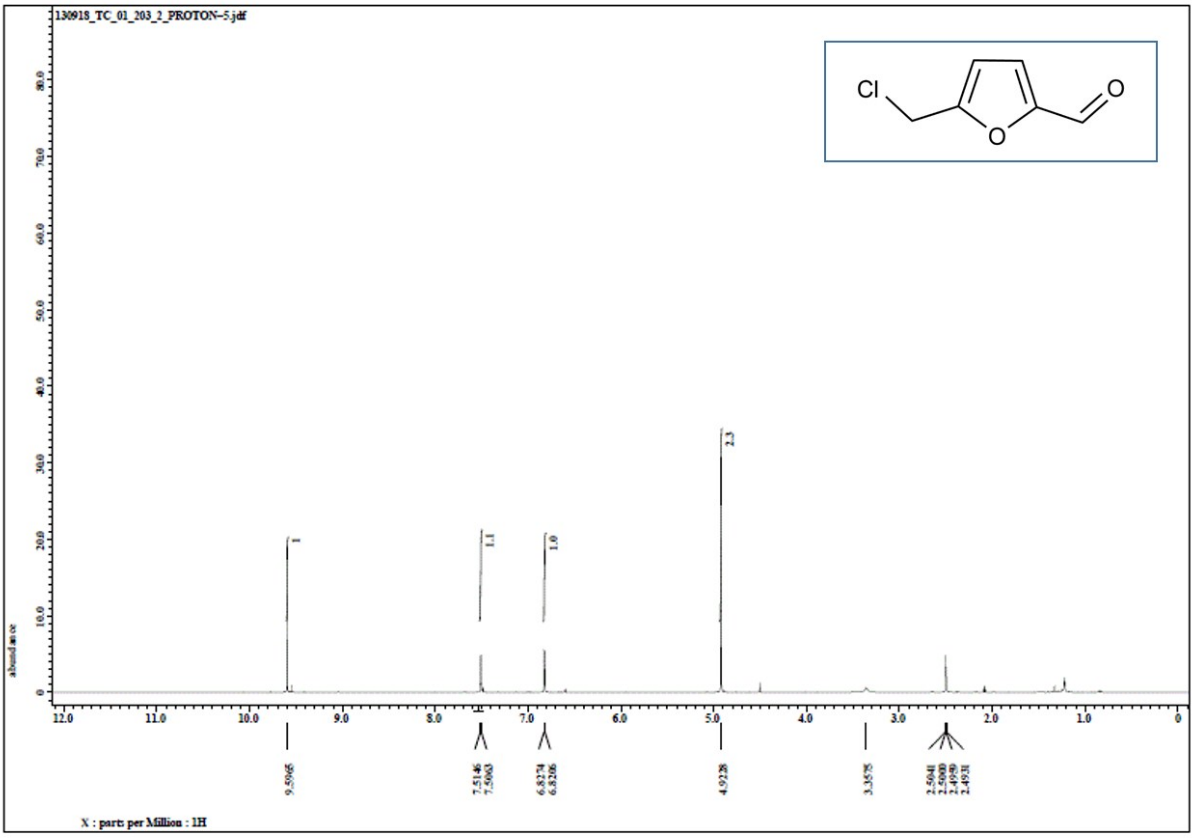

Figure S14. ^1H NMR spectrum of 5-(chloromethyl)furfural [DMSO-d_6, 500 MHz].

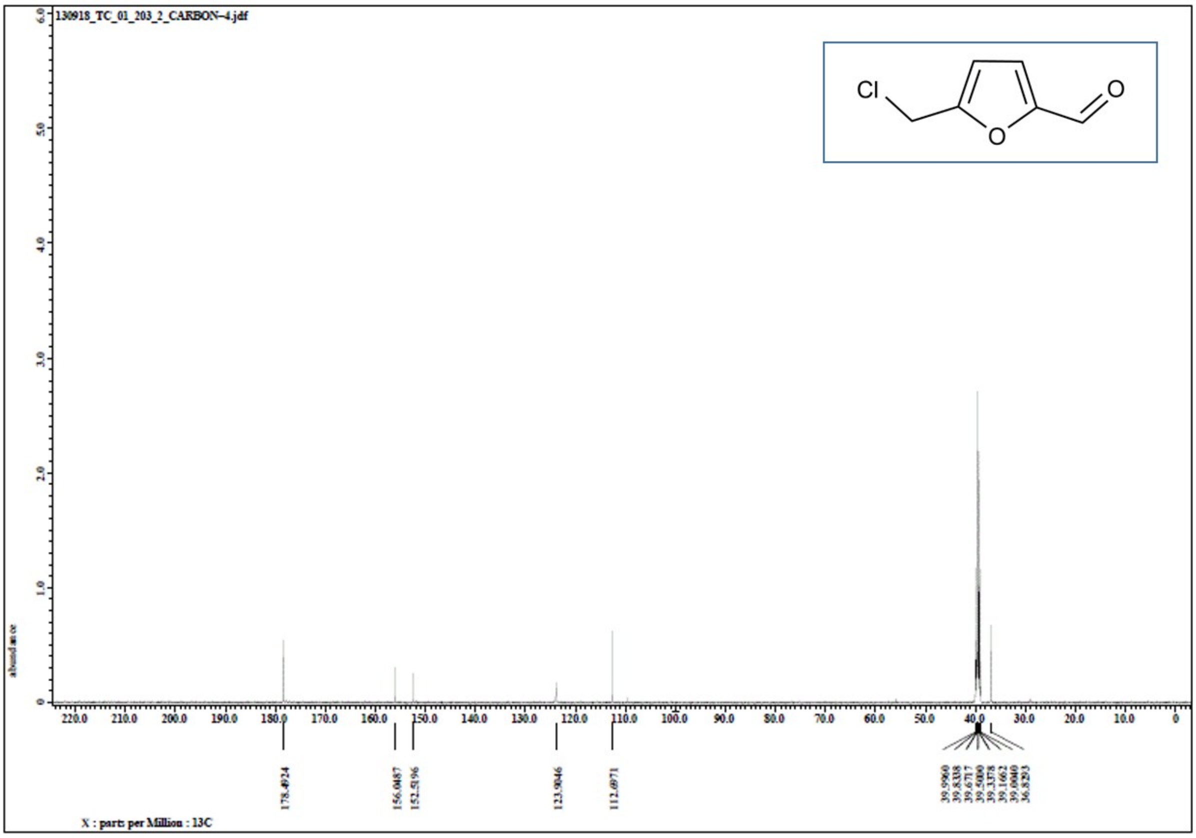

Figure S15. ^{13}C NMR spectrum of 5-(chloromethyl)furfural [DMSO-d_6, 125 MHz].

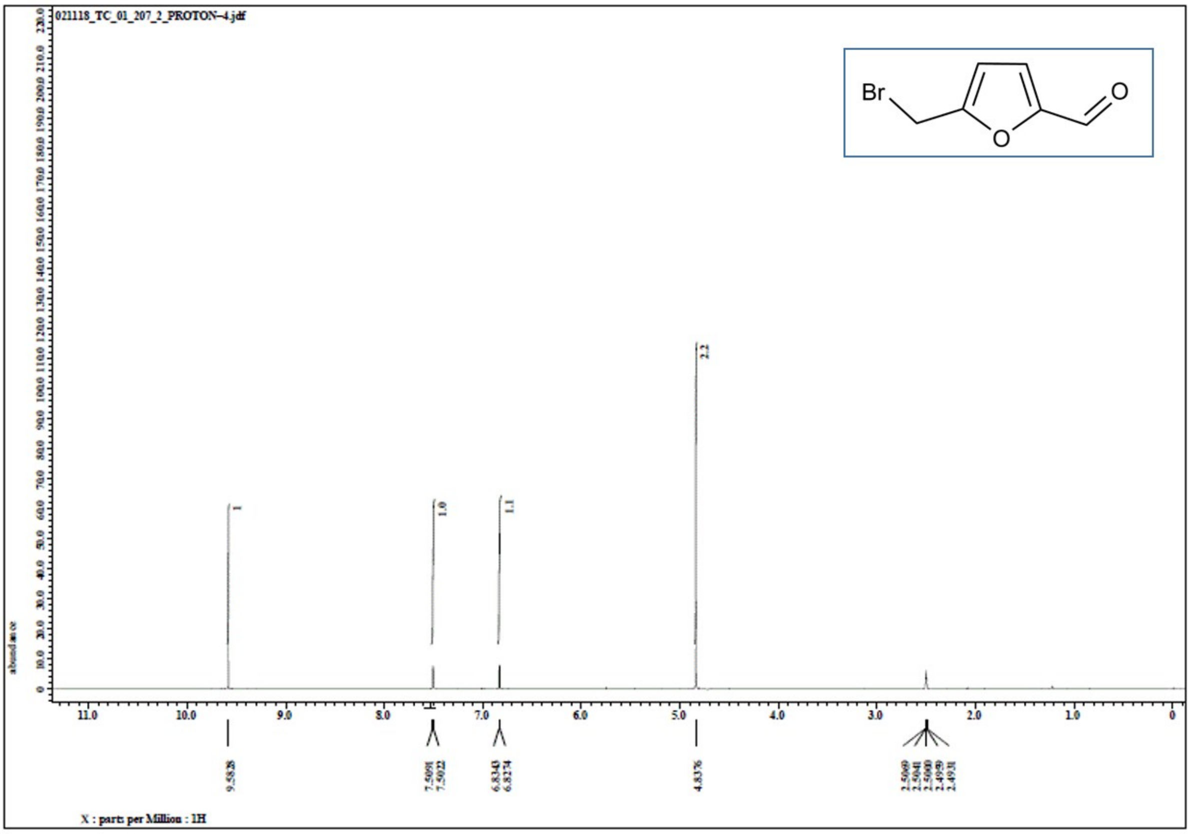

Figure S16. ^{1}H NMR spectrum of 5-(bromomethyl)furfural [DMSO-d_6, 500 MHz].

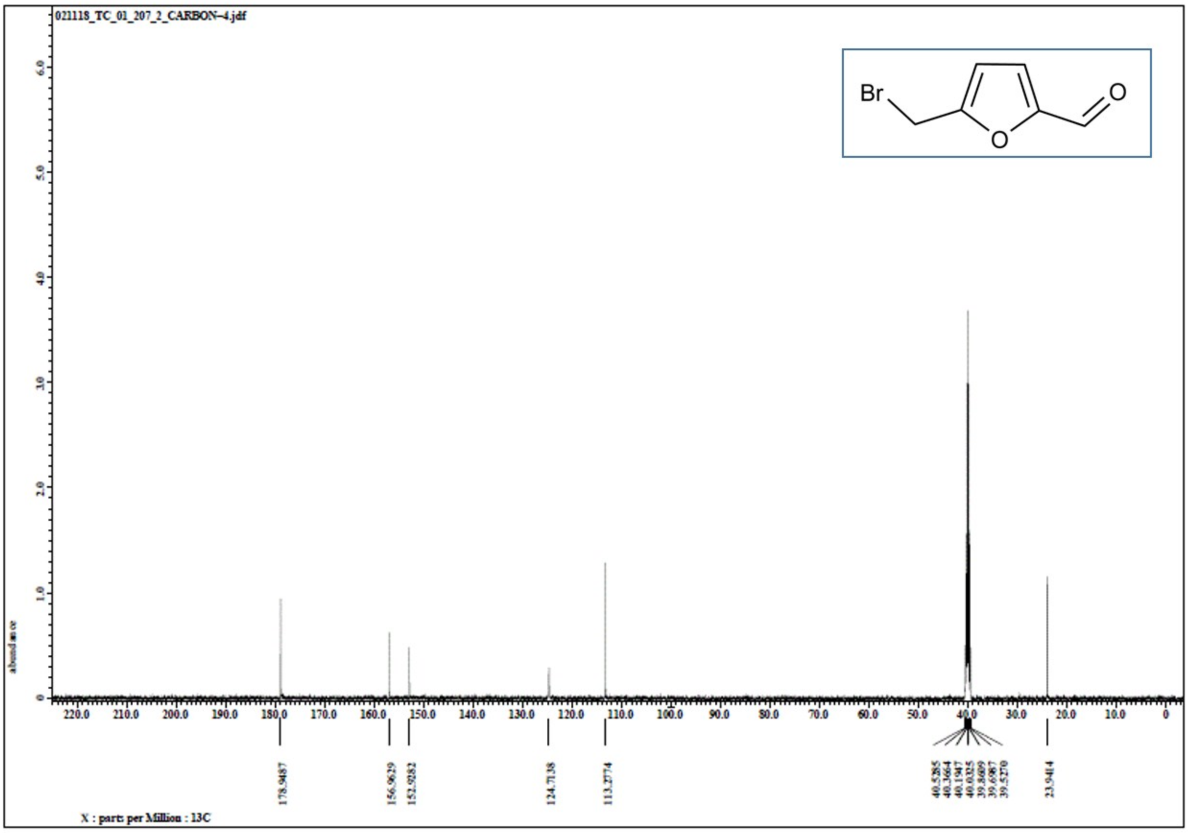

Figure S17. ^{13}C NMR spectrum of 5-(bromomethyl)furfural [DMSO-d_6, 125 MHz].

References

1. R. A. Sheldon, *Chem. Ind.* , 1992, 903-906.
2. C. Jimenez-Gonzalez, C. S. Ponder, Q. B. Broxterman and J. B. Manley, *Org. Process Res. Dev.*, 2011, 15, 912-917.
3. R. A. Sheldon, *ACS Sustainable Chem. Eng.*, 2017, 6, 32-48.
4. B. M. Trost, *Science*, 1991, 254, 1471-1477.
5. A. D. Curzons, D. J. Constable, D. N. Mortimer and V. L. Cunningham, *Green Chem.*, 2001, 3, 1-6.