Electronic Supplementary Information

for the article:

A Tunable Precious-Metal-Free System for Selective Oxidative Esterification of Biobased 5-(Hydroxymethyl)furfural

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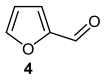
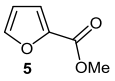
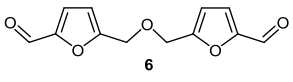
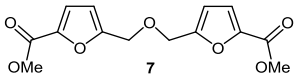
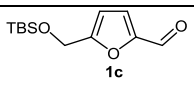
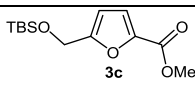
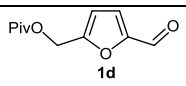
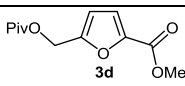
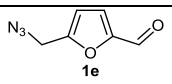
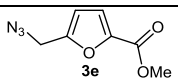
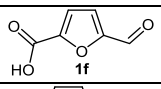
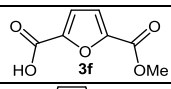
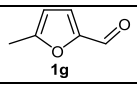
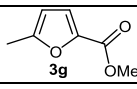
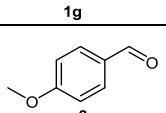
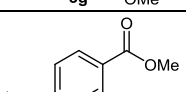
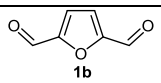
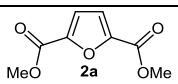
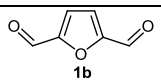
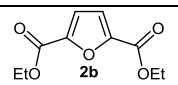
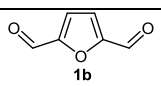
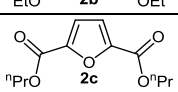
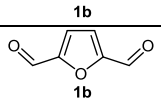
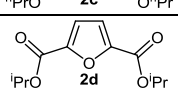
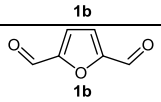
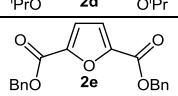
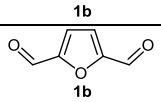
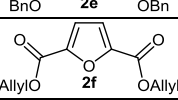
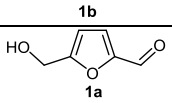
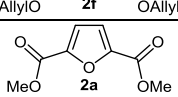
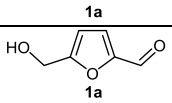
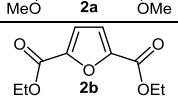
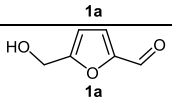
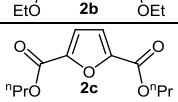
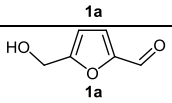
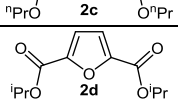
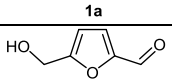
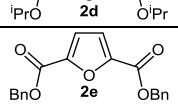
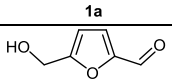
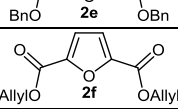
General information

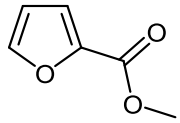
All reactions were performed in oven-dried (150 °C) glassware. Heating above boiling points of the solvents was performed in sealed Duran© culture tubes with screw caps. Chromatographic separations were performed on silica gel (Merck Kieselgel 230–400 mesh) with analytical grade solvents. Analytical TLC was per formed on Merck silica gel plates with QF-254 indicator. Visualization of TLC plates was accomplished with UV light and/or p-anisaldehyde–MeOH–H_2SO_4 and/or basic solution of $KMnO_4$. All reagents from commercial sources were used as received. Petroleum ether, EtOAc, EtOH were distilled without drying agents. The following solvents were distilled over the indicated drying agents: CH_2Cl_2 (CaH_2), MeOH (Mg).
NMR spectra were recorded on a Bruker Fourier™ 300 NMR spectrometer with residual solvent peak as an internal standard.
GC-MS analysis was performed on an Agilent Technologies 6890B gas chromatograph with MSD 5975 mass-selective detector (quadrupole mass-analyzer) using HP-5ms (30 m × 250 μm × 0.25 μm) capillary columns. Data analysis was performed using MSD ChemStation E.02.02.1431 software.
Mass spectra were recorded on a high-resolution time-of-flight Bruker maXis instrument using electrospray ionization (ESI-MS). The measurements were performed in positive ion mode, at 4.5 kV interface capillary voltage, effective m/z scan range 100 – 1200, external calibration (0.016 M sodium formate in MeCN-water 1:1 mixture or ESI-L Low Concentration Tuning Mix, Agilent Technologies), with direct syringe injection at a flow rate of 3 μL/min, nitrogen as dry gas at 4 L/min, at 180 °C interface temperature. The spectra were processed using Bruker Data Analysis 4.0 software package.
A target-oriented approach was utilized for optimization of the electron microscopy experiments.[1] For observation, the samples were mounted on 15 mm aluminum specimen stubs and fixed with carbon double-sided adhesive tape. Metal coating with a thin film (7 nm) of platinum/palladium alloy (80/20) was performed using a magnetron sputtering method as described earlier.[2] The observations were carried out using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). The images were acquired in secondary electron mode at 2 kV accelerating voltage and 8-10 mm working distance. Morphology of the samples was studied with regard to the possible influence of metal coating on the surface.[2] EDS-SEM studies were carried out using an Oxford Instruments X-max 80 EDS system at 30 kV accelerating voltage and 15 mm working distance.
Melting points were determined using a 1101D Mel-Temp apparatus and are uncorrected.

Table S1. Compound numbering and reaction conditions.

Substrate	ROH	Add. solvent	Time, h	Temp., °C	Yield, %	Product
 **4**	MeOH	-	12	40	89	 **5**
 **6**	MeOH	-	24	40	76	 **7**
 **1c**	MeOH	-	12	20	83	 **3c**
 **1d**	MeOH	-	4	20	61	 **3d**
 **1e**	MeOH	-	12	20	52	 **3e**
 **1f**	MeOH	-	24	20	42	 **3f**
 **1g**	MeOH	-	12	40	95	 **3g**
 **8**	MeOH	-	12	20	98	 **9**
 **1b**	MeOH	-	1	80	97	 **2a**
 **1b**	EtOH	-	12	80	84	 **2b**
 **1b**	n-PrOH	-	12	80	69	 **2c**
 **1b**	i-PrOH	-	72	100	38	 **2d**
 **1b**	BnOH	CH_2Cl_2	24	60	61	 **2e**
 **1b**	AllylOH	CH_2Cl_2	72	100	48	 **2f**
 **1a**	MeOH	CH_2Cl_2	4	100	83	 **2a**
 **1a**	EtOH	CH_2Cl_2	4	100	61	 **2b**
 **1a**	n-PrOH	CH_2Cl_2	4	100	54	 **2c**
 **1a**	i-PrOH	CH_2Cl_2	48	100	27	 **2d**
 **1a**	BnOH	CH_2Cl_2	24	100	49	 **2e**
 **1a**	AllylOH	CH_2Cl_2	48	100	33	 **2f**
1a	MeOH	H_2O	6	20	43	**3a**

Experimental procedures

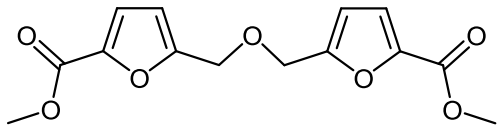
Synthesis of methyl furan-2-carboxylate (5)



Furfural (0.828 mL, 10 mmol) was dissolved in MeOH (20 mL), and sodium cyanide (196 mg, 4 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (1.74 g, 20 mmol, 2 equiv.) was added. The reaction mixture was stirred at 40 °C for 12 hours. Then CH_2Cl_2 (180 mL) was added and the resulting mixture was filtered through a 20 mm pad of silica gel to remove insoluble inorganic components. The filtrate was subsequently washed with water (2 x 50 mL) and saturated aqueous NaCl (1 x 50 mL). Organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give product **5** (1.126 g, 89%) as a brown oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (brs, 1H), 7.16 (d, 1H, *J* = 3.3 Hz), 6.49 (dd, 1H, *J* = 3.3, 1.5 Hz),
3.88 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 159.2, 146.4, 144.7, 118.0, 111.9, 52.0. HRMS (ESI) Calcd. for $C_6H_6O_3$ [M + Na^+] 149.0209, Found: 149.0211.

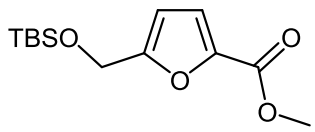
Synthesis of dimethyl 5,5'-(oxybis(methylene))bis(furan-2-carboxylate) (7)



5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde) (1.171 g, 5 mmol) was dissolved in MeOH (20 mL), and sodium cyanide (196 mg, 4 mmol, 0.8 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (1.304 g, 15 mmol, 3 equiv.) was added. The reaction mixture was stirred at 40 °C for 24 hours. Then CH_2Cl_2 (100 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. Filtrate was subsequently washed with water (2 x 30 mL), and saturated aqueous NaCl (1 x 30 mL). Organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Solid residue was recrystallized from Et_2O to give product **7** (1.117 g, 76%) as a brownish powder.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, 2H, *J* = 3.5 Hz), 6.46 (d, 2H, *J* = 3.5 Hz), 4.57 (s, 4H), 3.89 (s, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 159.2, 155.5, 144.9, 118.9, 111.5, 64.4, 52.1. HRMS (ESI) Calcd. for $C_{14}H_{14}O_7$ [M + H^+] 295.0812, Found: 295.0822. Melting point 154-156 °C (lit.[3] 155-156 °C).

Synthesis of methyl 5-(((tert-butyldimethylsilyl)oxy)methyl)furan-2-carboxylate (3c)



5-(((tert-butyldimethylsilyl)oxy)methyl)furan-2-carbaldehyde (2.404 g, 10 mmol) was dissolved in MeOH (20 mL), and sodium cyanide (196 mg, 4 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (1.74 g, 20 mmol, 2 equiv.) was added. The reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered

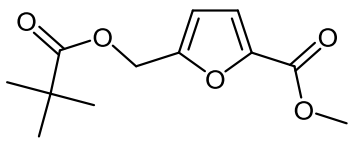
through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was diluted with Et_2O (150 mL) and washed with water (100 mL). Organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give product **3c** (2.253 g, 83%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.12 (d, 1H, *J* = 3.5 Hz), 6.35 (d, 1H, *J* = 3.5 Hz), 4.70 (s, 2H), 3.87 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 159.3, 148.9, 143.7, 119.1, 108.8, 58.7, 52.0, 25.9, 18.5, -5.2. HRMS (ESI) Calcd. for $C_{13}H_{22}O_4Si$ [M + H^+] 271.1360, Found: 271.1356.

Synthesis of compounds 3d, 3e

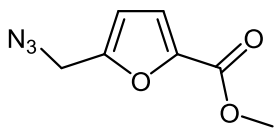
General procedure. Aldehyde (2 mmol) was dissolved in MeOH (4 mL), and sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (347 mg, 4 mmol, 2 equiv.) was added. The reaction mixture was stirred at room temperature for the time indicated in table S1. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. Additional purification by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)) was performed.

methyl 5-((pivaloyloxy)methyl)furan-2-carboxylate (3d)



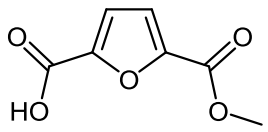
Yield 83%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10 (d, 1H, *J* = 3.7 Hz), 6.44 (d, 1H, *J* = 3.7 Hz), 5.06 (s, 2H), 3.03 (s, 3H), 1.17 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 178.0, 159.0, 154.1, 144.6, 118.8, 111.8, 58.0, 52.0, 38.9, 27.2. HRMS (ESI) Calcd. for $C_{12}H_{16}O_5$ [M + Na^+] 263.0890, Found: 263.0894.

methyl 5-(azidomethyl)furan-2-carboxylate (3e)



Yield 61%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, 1H, *J* = 3.7 Hz), 6.45 (d, 1H, *J* = 3.7 Hz), 4.37 (s, 2H), 3.89 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 158.9, 153.3, 145.0, 118.8, 111.0, 52.2, 47.0. HRMS (ESI) Calcd. for $C_7H_7N_3O_3$ [M + Na^+] 204.0380, Found: 204.0379.

Synthesis of 5-(methoxycarbonyl)furan-2-carboxylic acid (3f)

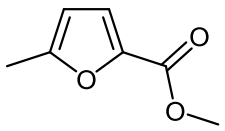


5-formylfuran-2-carboxylic acid (140 mg, 1 mmol) was dissolved in MeOH (4 mL), and sodium cyanide (19.6 mg, 0.4 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (174 mg, 2 mmol, 2 equiv.) was added. The reaction mixture was stirred at room temperature for 12 hours. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. The residue was purified by column chromatography (eluent

CH_2Cl_2:MeOH = 9:1 (v/v) + 2% AcOH) and dried *in vacuo* to give product **3f** (61 mg, 36%) as a bright-yellow solid.

^{1}H NMR (DMSO-d6, 300 MHz) δ 7.38 (d, 1H, *J* = 3.7 Hz), 7.30 (d, 1H, *J* = 3.7 Hz), 3.85 (s, 3H). ^{13}C {^{1}H} NMR (DMSO-d6, 75 MHz) δ 158.8, 158.0, 147.7, 145.6, 119.0, 118.2, 52.3. HRMS (ESI) Calcd. for $C_7H_6O_5$ [M + Na^+] 193.0107, Found: 193.0109. Melting point 197-199 °C (lit.[4] 200 °C).

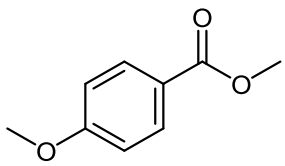
Synthesis of methyl 5-methylfuran-2-carboxylate (3g)



5-Methylfurfural (220 mg, 2 mmol) was dissolved in MeOH (4 mL), and sodium cyanide (39 mg, 0.8 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (348 mg, 4 mmol, 2 equiv.) was added. The reaction mixture was stirred at 40 °C for 12 hours. Then CH_2Cl_2 (10 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was subsequently washed with water (2 x 15 mL) and saturated aqueous NaCl (1 x 10 mL). Organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give product **3g** (267 mg, 95%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.05 (d, 1H, *J* = 3.3 Hz), 6.08 (d, 1H, *J* = 3.3 Hz), 3.84 (s, 3H), 2.34 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 159.3, 157.2, 143.1, 119.5, 108.5, 51.8, 14.0. HRMS (ESI) Calcd. for $C_7H_8O_3$ [M + Na^+] 163.0366, Found: 163.0366.

Synthesis of methyl 4-methoxybenzoate (9)



4-Anisaldehyde (1.361 g, 10 mmol) was dissolved in MeOH (20 mL), and sodium cyanide (196 mg, 4 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (1.74 g, 20 mmol, 2 equiv.) was added. The reaction mixture was stirred at room temperature for 12 hours. Then CH_2Cl_2 (180 mL) was added and the resulting mixture was filtered through a 20 mm pad of silica gel to remove insoluble inorganic components. The filtrate was subsequently washed with water (2 x 50 mL) and saturated aqueous NaCl (1 x 50 mL). Organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give product **9** (1.626 g, 98%) as white crystals.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98 (d, 2H, *J* = 8.8 Hz), 6.90 (d, 2H, *J* = 8.8 Hz), 3.88 (s, 3H), 3.85 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.0, 163.5, 131.7, 122.6, 113.7, 55.5, 52.0. HRMS (ESI) Calcd. for $C_9H_{10}O_3$ [M + Na^+] 189.0522, Found: 189.0521. Melting point 43-45 °C (lit.[5] 44-45°C).

Synthesis of compounds 2a-d from DFF

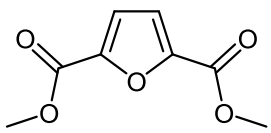
General procedure. DFF (248 mg, 2 mmol) was dissolved in the corresponding alcohol (4 mL), and sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (347 mg, 4 mmol, 2 equiv.) was added. The reaction mixture was stirred at 80 °C (100 °C for i-PrOH) for the time indicated in table S1. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove

insoluble inorganic components. The filtrate was evaporated to dryness. For products **2b-d** additional purification by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)) was performed.

Synthesis of compounds 2a-d from HMF

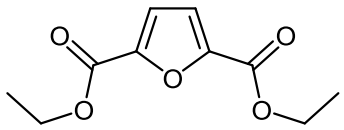
General procedure. HMF (252 mg, 2 mmol) was dissolved in CH_2Cl_2 (4 mL), and MnO_2 (347 mg, 8 mmol, 4 equiv.) was added. Mixture was stirred at 100 °C for 1 hour. Then the corresponding alcohol (4 mL) and sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) were added. The reaction mixture was stirred at 100 °C for the time indicated in table S1. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. For products **2b-d** additional purification by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)) was performed.

dimethyl furan-2,5-dicarboxylate (2a)



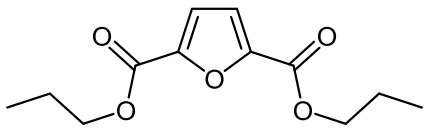
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20 (s, 2H), 3.91 (6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 158.5, 146.8, 118.6, 52.5. HRMS (ESI) Calcd. for $C_8H_8O_5$ [M + H^+] 185.0444, Found: 185.0448. Melting point 109-111 °C (lit.[6] 109-113°C).

diethyl furan-2,5-dicarboxylate (2b)



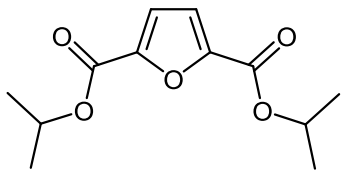
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18 (s, 2H), 4.38 (q, 4H, *J* = 7.2 Hz), 1.37 (t, 6H, *J* = 7.2 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 158.2, 147.0, 118.4, 61.7, 14.4. HRMS (ESI) Calcd. for $C_{10}H_{12}O_5$ [M + H^+] 213.0757, Found: 213.0765. Melting point 46-48 °C (lit.[7] 47°C).

dipropyl furan-2,5-dicarboxylate (2c)



^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18 (s, 2H), 4.28 (t, 4H, *J* = 6.8 Hz), 1.77 (m, 4H, *J* = 7.5, 6.8 Hz), 0.99 (t, 6H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 158.3, 147.0, 118.3, 61.1, 22.1, 10.4. HRMS (ESI) Calcd. for $C_{12}H_{16}O_5$ [M + Na^+] 263.0890, Found: 263.0894.

diisopropyl furan-2,5-dicarboxylate (2d)



^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.15 (s, 2H), 6.24 (sept., 2H, *J* = 6.2 Hz), 1.36 (d, 12H, *J* = 6.2 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 157.9, 147.3, 118.1, 69.6, 22.0. HRMS (ESI) Calcd. for $C_{12}H_{16}O_5$ [M + Na^+] 263.0890, Found: 263.0879.

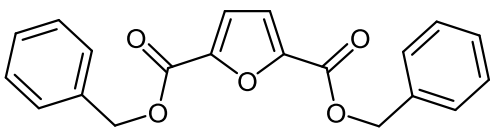
Synthesis of dibenzyl furan-2,5-dicarboxylate from DFF

DFF (248 mg, 2 mmol) was dissolved in CH_2Cl_2 (4 mL), and sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (347 mg, 4 mmol, 2 equiv.) was added and the mixture was stirred at room temperature for 20 minutes. Then benzyl alcohol (0.62 mL, 6 mmol, 3 equiv.) was added. The reaction mixture was stirred at 60 °C for 24 hours. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. Residue was reevaporated with water 3 times to remove traces of benzaldehyde. The product was purified by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)). Compound **2e** (411 mg, 61%) was obtained as a yellowish solid.

Synthesis of dibenzyl furan-2,5-dicarboxylate from HMF

HMF (252 mg, 2 mmol) was dissolved in CH_2Cl_2 (4 mL), and MnO_2 (347 mg, 8 mmol, 4 equiv.) was added. The mixture was stirred at 100 °C for 1 hour. Then sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) was added, and the mixture was stirred at room temperature for 20 minutes. Then benzyl alcohol (0.62 mL, 6 mmol, 3 equiv.) was added. The reaction mixture was stirred at 100 °C for 24 hours. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. Residue was reevaporated with water 3 times to remove traces of benzaldehyde. The product was purified by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)). Compound **2e** (327 mg, 49%) was obtained as a yellowish solid.

dibenzyl furan-2,5-dicarboxylate (2e)



^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51-7.35 (m, 10H), 7.22 (s, 2H), 5.37 (s, 4H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 157.6, 146.9, 135.3, 128.8, 128.7, 128.6, 118.8, 67.2. HRMS (ESI) Calcd. for $C_{20}H_{16}O_5$ [M + Na^+] 359.0890, Found: 359.0891.

Synthesis of diallyl furan-2,5-dicarboxylate (2f) from DFF

DFF (248 mg, 2 mmol) was dissolved in CH_2Cl_2 (4 mL), and sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) was added. The mixture was stirred at room temperature for 5 minutes. Then MnO_2 (347 mg, 4 mmol, 2 equiv.) was added and the mixture was stirred at room temperature for 20 minutes. Then allyl alcohol (0.408 mL, 6 mmol, 3 equiv.) was added. The reaction mixture was stirred at 100 °C for 72 hours. Then CH_2Cl_2 (40 mL) was added and the resulting mixture was filtered through a 10 mm pad of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. Residue was purified by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)) to give product **2f** (226 mg, 63%) as a yellowish oil.

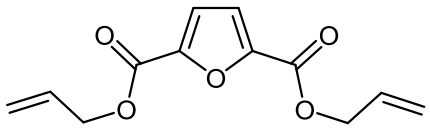
When reaction was occurred at decreased temperature (60 °C, 24 hours) allyl 5-formylfuran-2-carboxylate (**2f'**) was isolated as major product with 63% yield.

Synthesis of diallyl furan-2,5-dicarboxylate (2f) from HMF

HMF (252 mg, 2 mmol) was dissolved in CH_2Cl_2 (4 mL), and MnO_2 (347 mg, 8 mmol, 4 equiv.) was added. The mixture was stirred at 100 °C for 1 hour. Then sodium cyanide (39.2 mg, 0.8 mmol, 0.4 equiv.) was added, and the mixture was stirred at room temperature for 20 minutes. Then allyl alcohol (0.408 mL, 6 mmol, 3 equiv.) was added. The reaction mixture was stirred at 100 °C for 72 hours. Then CH_2Cl_2 (40 mL) was added, and the resulting mixture was filtered through a 10 mm pad

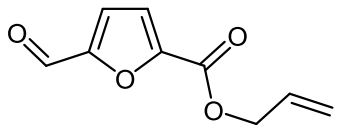
of silica gel to remove insoluble inorganic components. The filtrate was evaporated to dryness. Residue was purified by column chromatography (eluent petroleum ether:ethyl acetate = 4:1 (v/v)) to give product **2f** (155 mg, 33%) as a yellowish oil.

diallyl furan-2,5-dicarboxylate (2f)



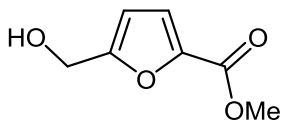
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.22 (s, 2H), 6.00 (ddt, 2H, *J* = 17.2, 10.3, 5.9 Hz), 5.40 (dd, 2H, *J* = 17.2, 1.1 Hz), 5.30 (dd, 2H, *J* = 10.3, 1.1 Hz), 4.82 (d, 4H, *J* = 5.9 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 157.8, 146.9, 131.6, 119.4, 118.7, 66.2. (ESI) Calcd. for $C_{12}H_{12}O_5$ [M + H^+] 237.0757, Found: 237.0758.

allyl 5-formylfuran-2-carboxylate (2f')



^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.80 (s, 1H), 7.28 (d, 1H, *J* = 3.6 Hz), 7.27 (d, 1H, *J* = 3.6 Hz), 6.01 (ddt, 1H, *J* = 17.2, 10.6, 5.9 Hz), 5.42 (dd, 1H, *J* = 17.2, 1.3 Hz), 5.32 (dd, 1H, *J* = 10.6, 1.3 Hz), 4.84 (d, 2H, *J* = 5.9 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 179.1, 157.7, 154.0, 147.7, 131.3, 119.6, 118.89, 118.86, 66.4. HRMS (ESI) Calcd. for $C_9H_8O_4$ [M + Na^+] 203.0315, Found: 203.0316.

Synthesis of methyl 5-(hydroxymethyl)furan-2-carboxylate (3a)



HMF (126 mg, 1 mmol) was dissolved in MeOH (4 mL); sodium cyanide (73.5 mg, 1.5 mmol, 1.5 equiv.) and water (0.2 mL) were added. The mixture was stirred at room temperature for 5 minutes, then MnO_2 (140 mg, 1.6 mmol, 1.6 equiv.) was added. The reaction mixture was stirred at room temperature for 6 hours. Then CH_2Cl_2 (50 mL) was added and the resulting mixture was filtered through a 10 mm pad of Celite to remove insoluble inorganic components. The filtrate was subsequently washed with water (2 x 20 mL) and saturated aqueous NaCl (1 x 20 mL). Organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give product **3a** (68 mg, 43%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11 (d, 1H, *J* = 3.3 Hz), 6.39 (d, 1H, *J* = 3.3 Hz), 4.65 (d, 2H, *J* = 5.5 Hz), 3.87 (s, 3H), 2.61 (t, 1H, *J* = 5.5 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 159.3, 158.6, 144.1, 119.0, 109.5, 57.6, 52.0. HRMS (ESI) Calcd. for $C_7H_8O_4$ [M + Na^+] 179.0315, Found: 179.0319.

NMR spectra of synthesized compounds

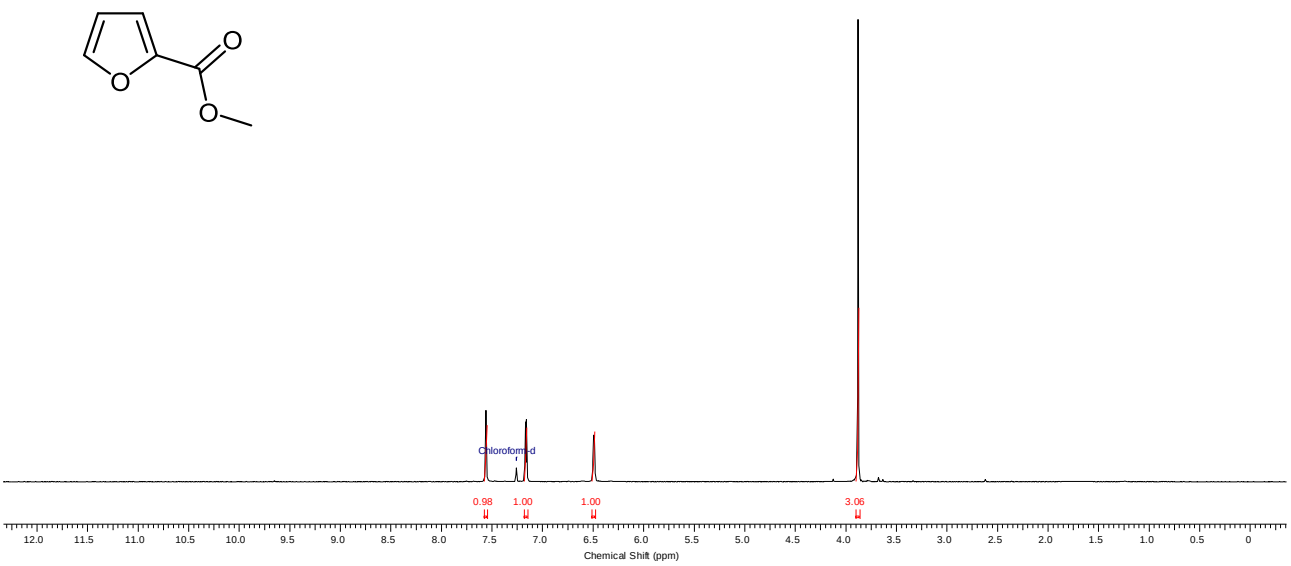


Figure S1. ^{1}H NMR spectrum of methyl furan-2-carboxylate **5**.

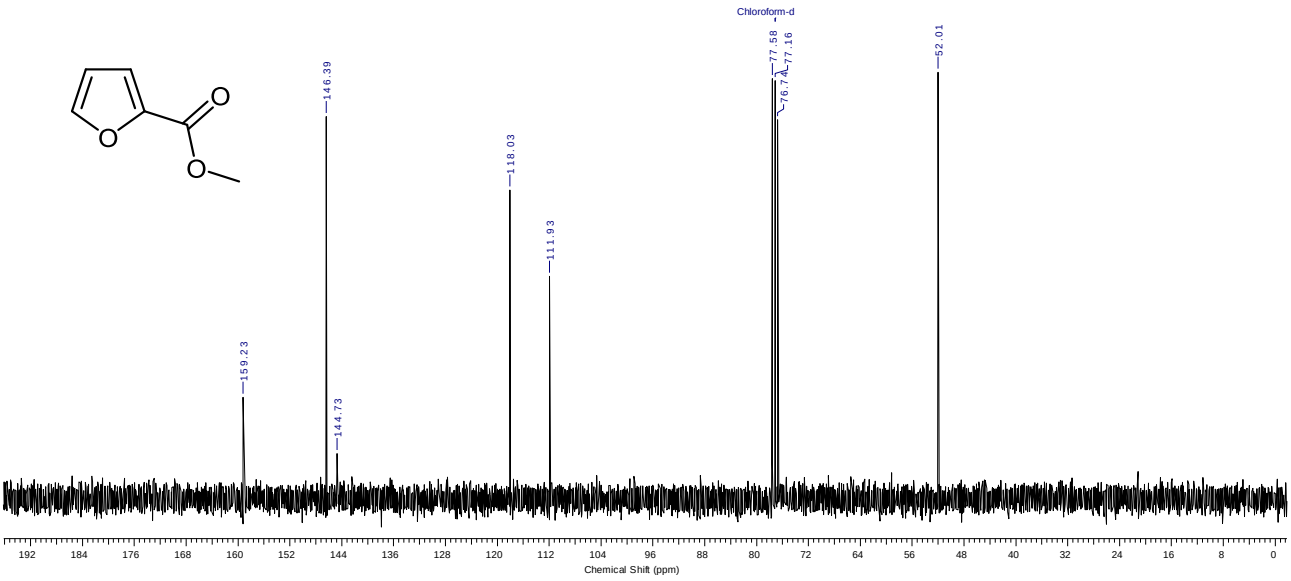


Figure S2. ^{13}C{^{1}H} NMR spectrum of methyl furan-2-carboxylate **5**.

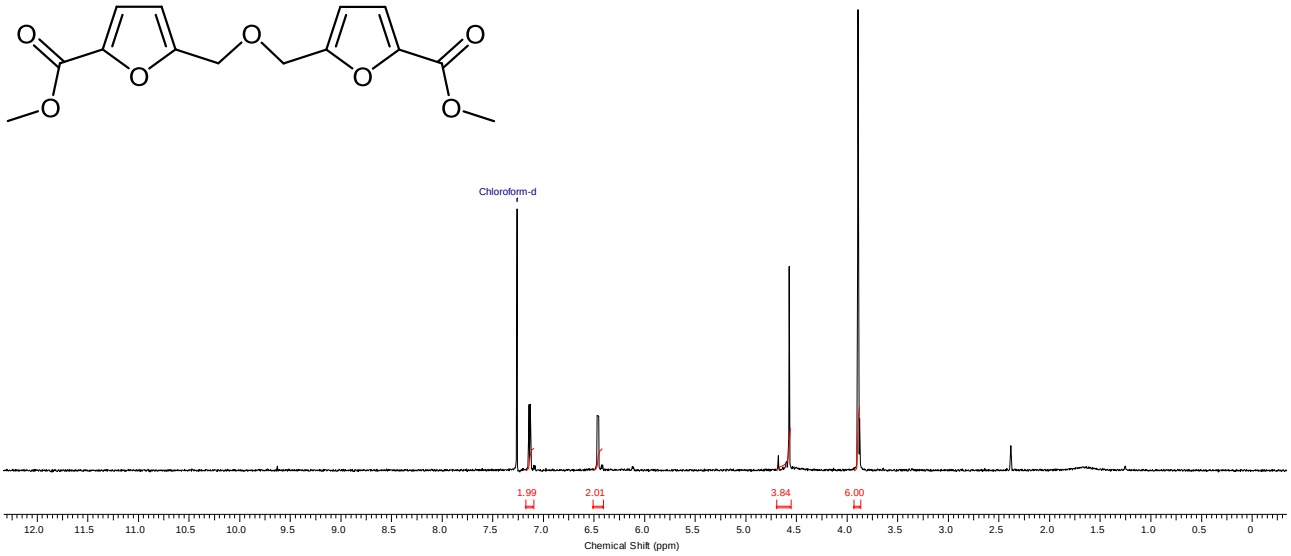


Figure S3. ^{1}H NMR spectrum of dimethyl 5,5'-(oxybis(methylene))bis(furan-2-carboxylate) **7.**

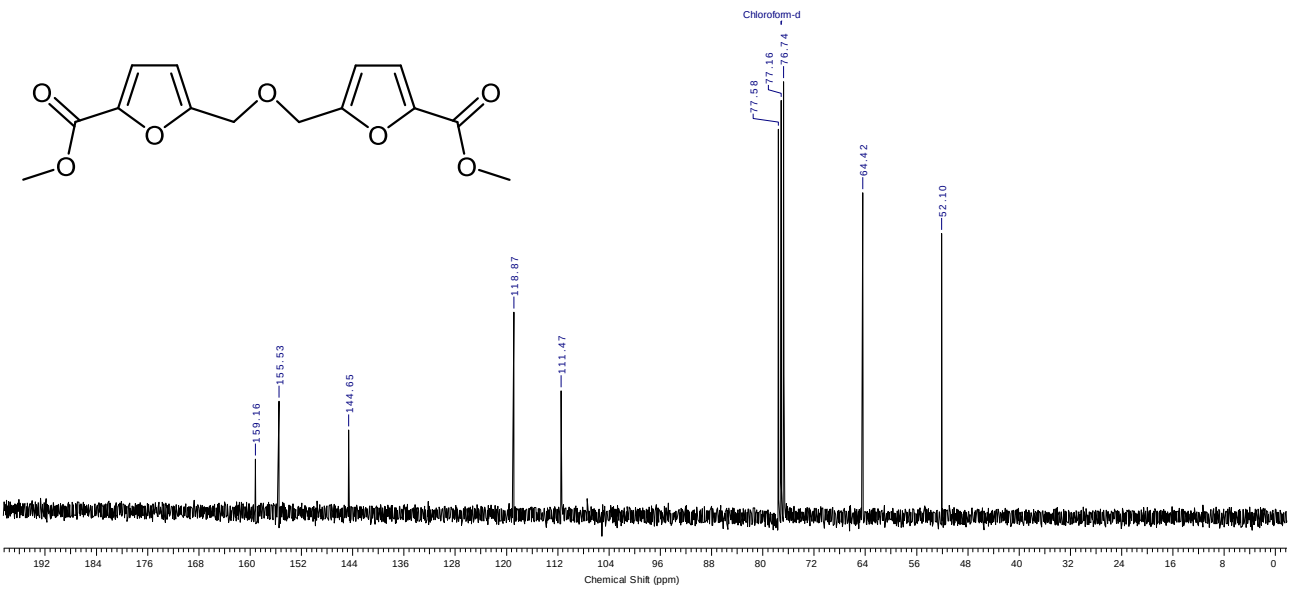


Figure S4. ^{13}C{^{1}H} NMR spectrum of dimethyl 5,5'-(oxybis(methylene))bis(furan-2-carboxylate) **7.**

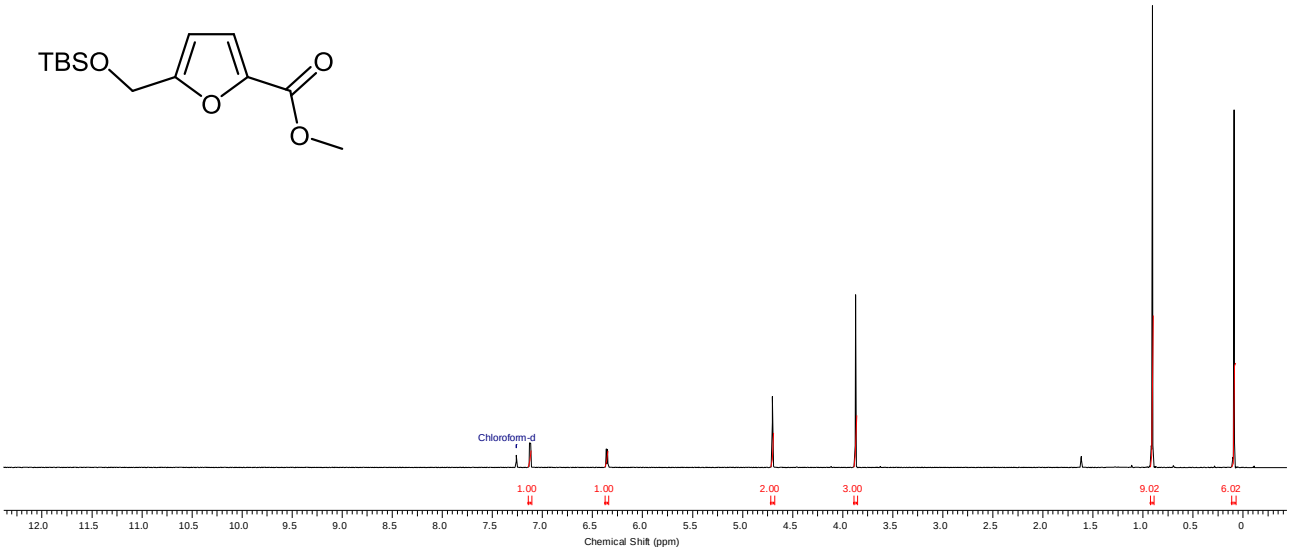


Figure S5. ^{1}H NMR spectrum of methyl 5-(((tert-butyldimethylsilyl)oxy)methyl)furan-2-carboxylate **3c**.

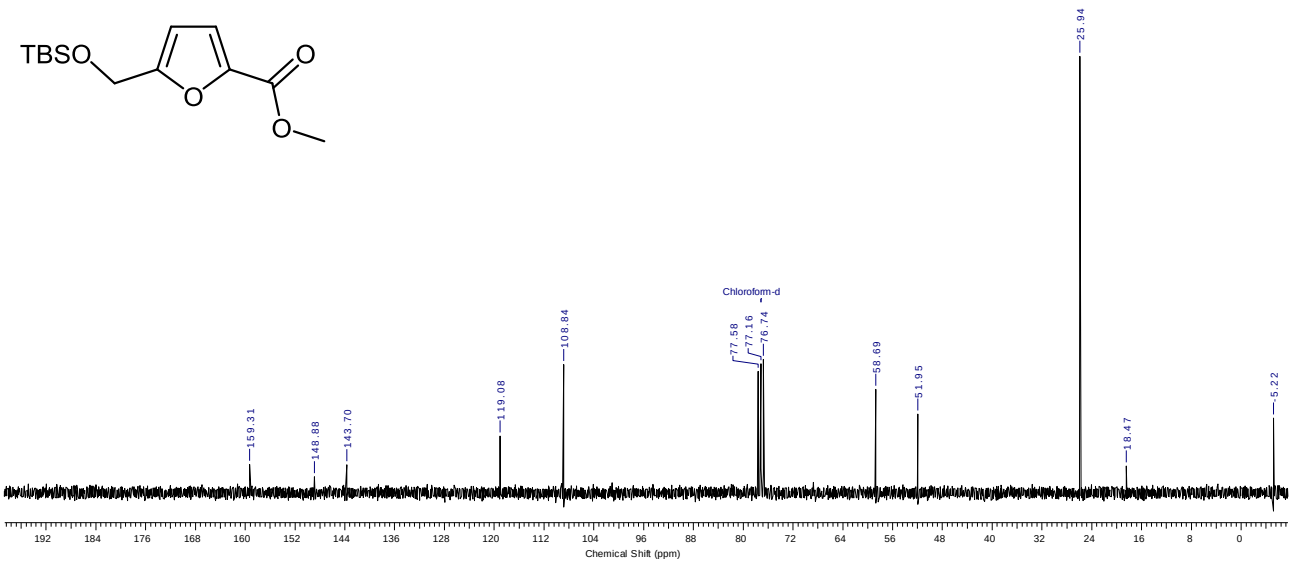


Figure S6. ^{13}C{^{1}H} NMR spectrum of methyl 5-(((tert-butyldimethylsilyl)oxy)methyl)furan-2-carboxylate **3c**.

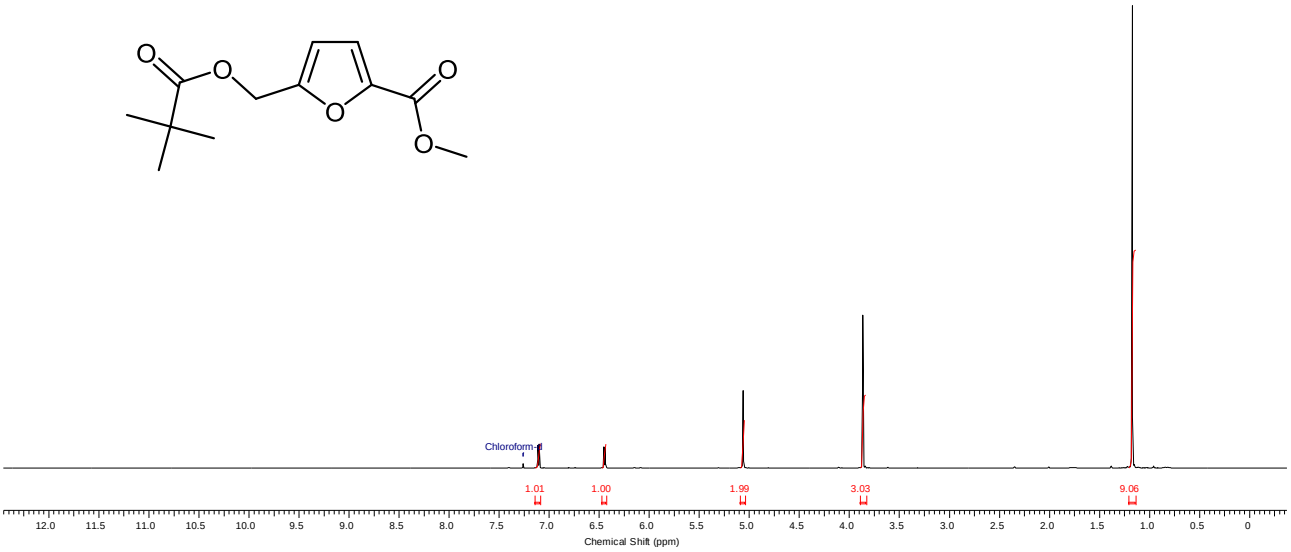


Figure S7. ^{1}H NMR spectrum of methyl 5-((pivaloyloxy)methyl)furan-2-carboxylate **3d**.

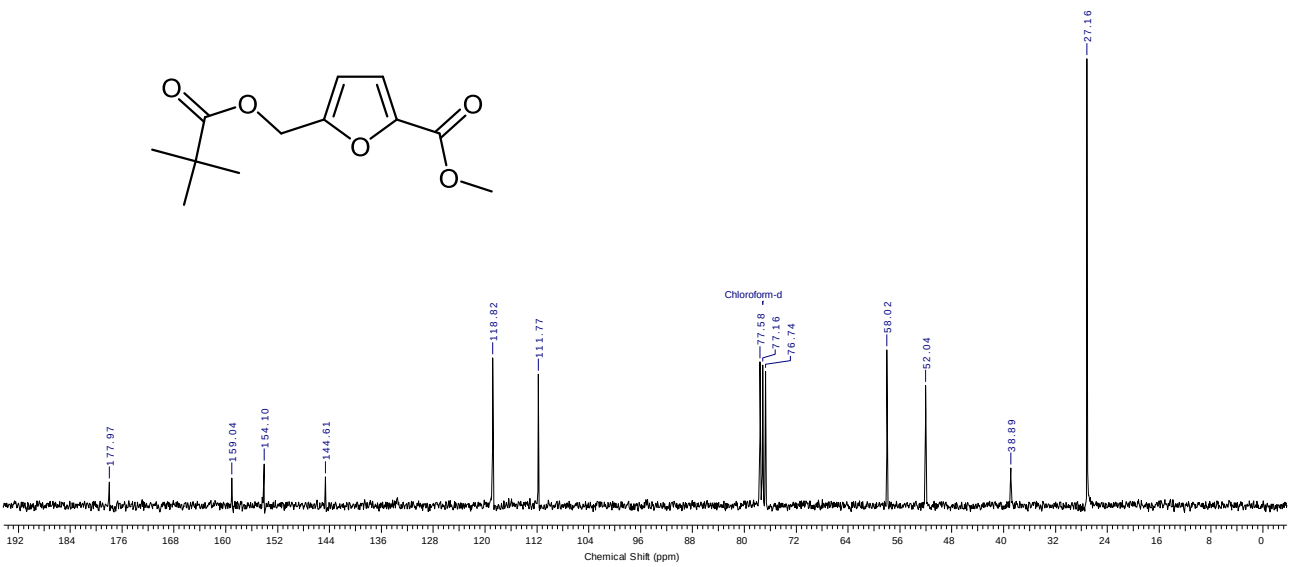


Figure S8. ^{13}C{^{1}H} NMR spectrum of methyl 5-((pivaloyloxy)methyl)furan-2-carboxylate **3d**.

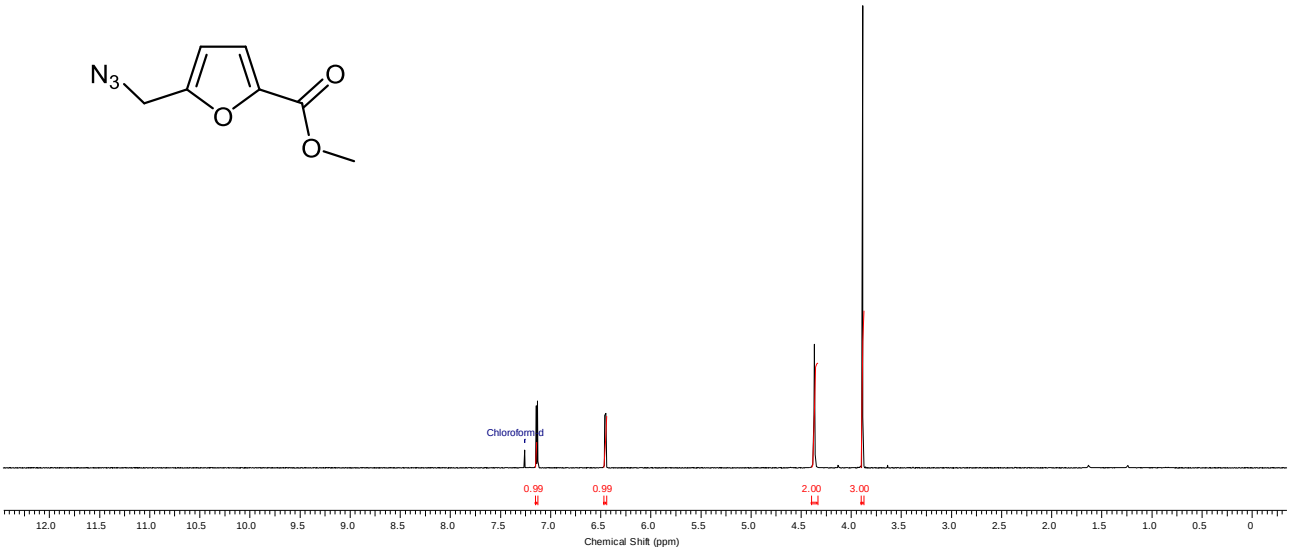


Figure S9. ^{1}H NMR spectrum of methyl 5-(azidomethyl)furan-2-carboxylate **3e**.

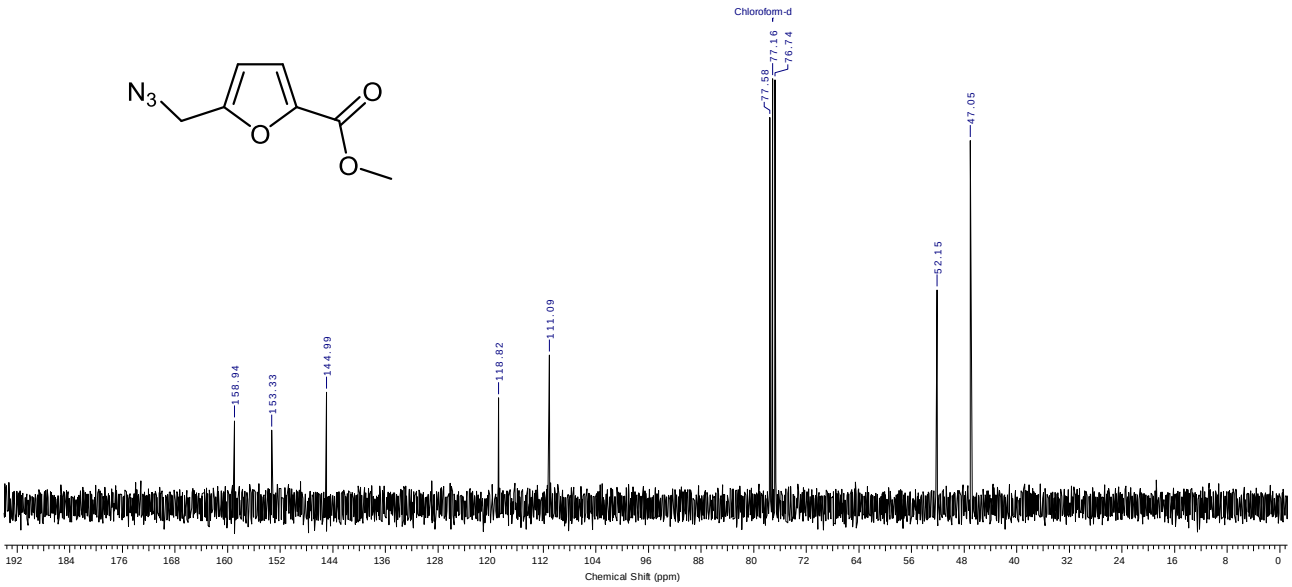


Figure S10. ^{13}C{^{1}H} NMR spectrum of methyl 5-(azidomethyl)furan-2-carboxylate **3e**.

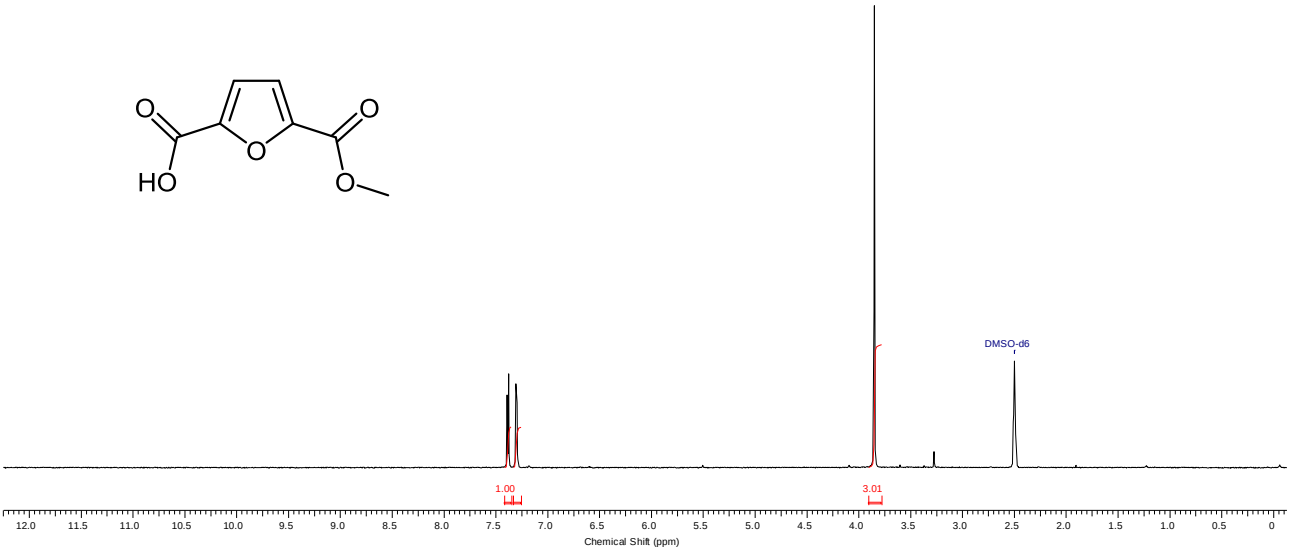


Figure S11. ^{1}H NMR spectrum of 5-(methoxycarbonyl)furan-2-carboxylic acid **3f**.

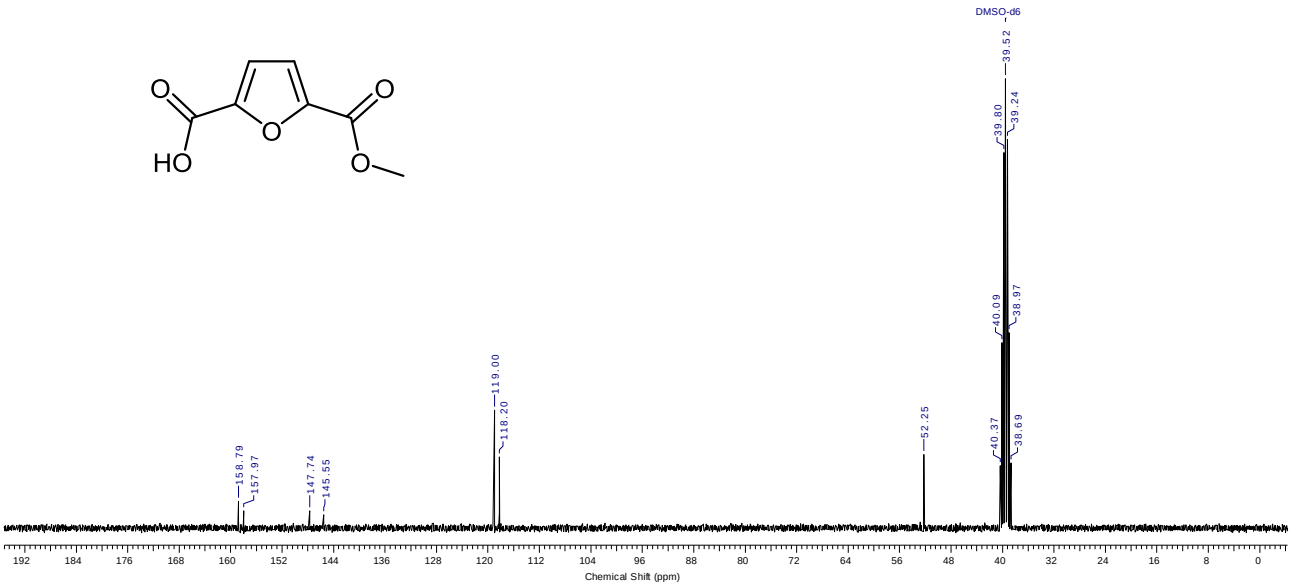


Figure S12. ^{13}C{^{1}H} NMR spectrum of 5-(methoxycarbonyl)furan-2-carboxylic acid **3f**.

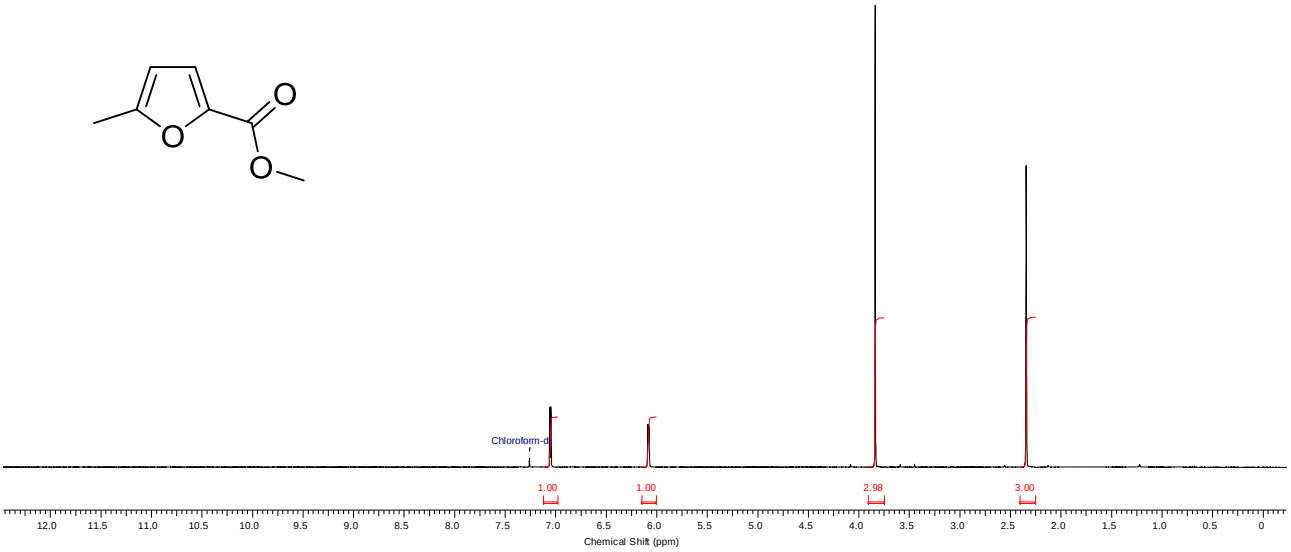


Figure S13. ^{1}H NMR spectrum of methyl 5-methylfuran-2-carboxylate **3g**.

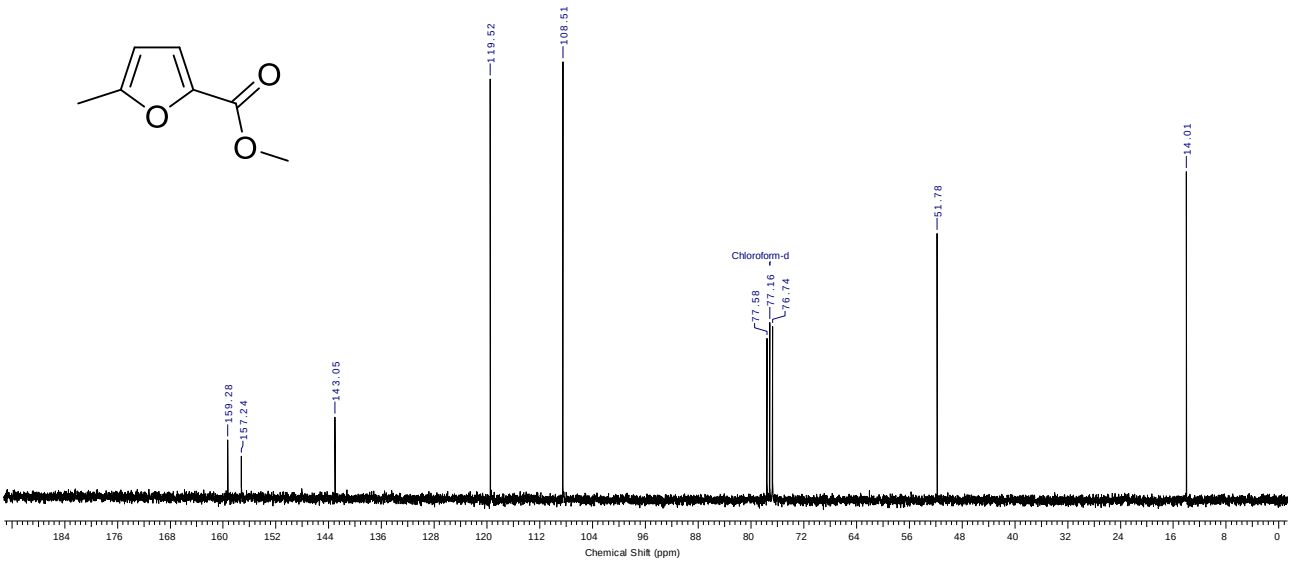


Figure S14. ^{13}C{^{1}H} spectrum of methyl 5-methylfuran-2-carboxylate **3g**.

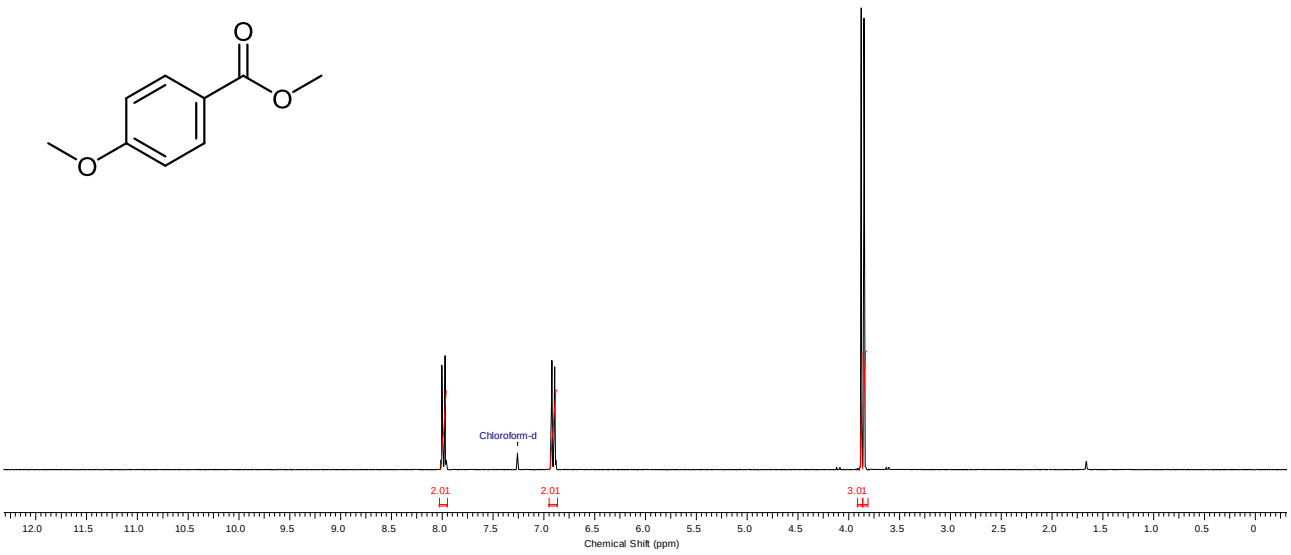


Figure S15. ^{1}H NMR spectrum of methyl 4-methoxybenzoate **9**.

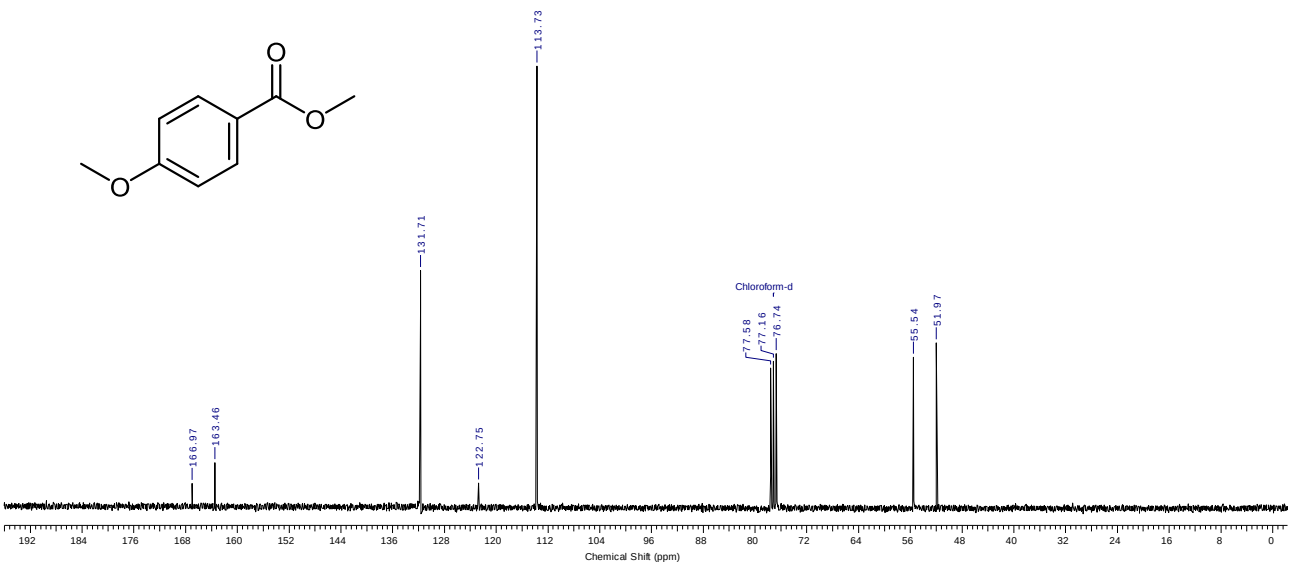


Figure S16. ^{13}C{^{1}H} NMR spectrum of methyl 4-methoxybenzoate **9**.

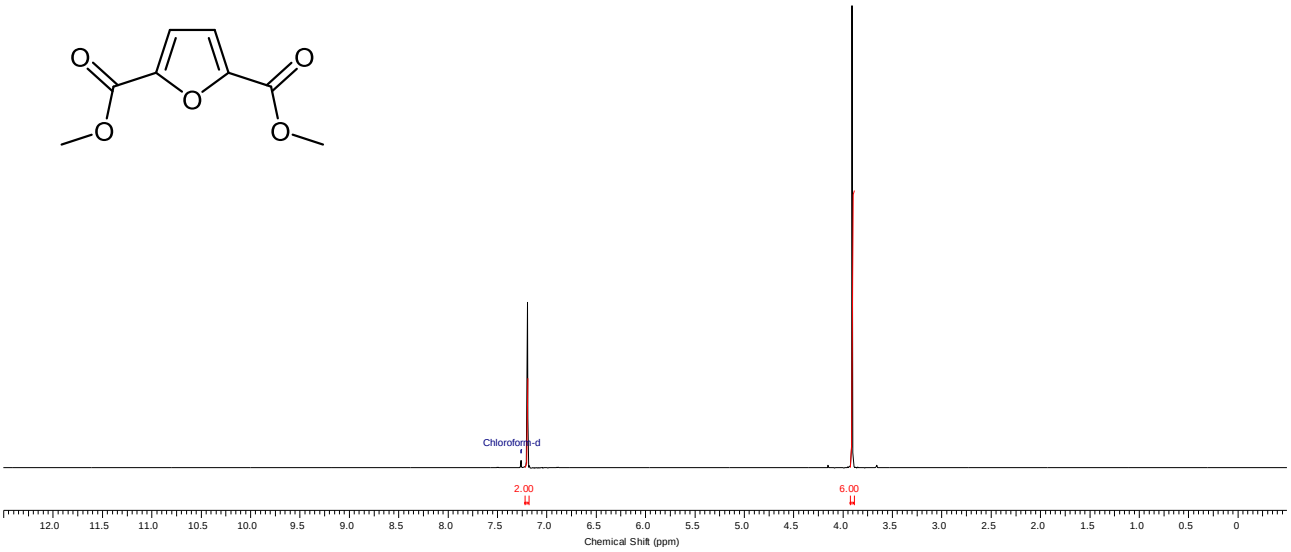


Figure S17. ^{1}H NMR spectrum of dimethyl furan-2,5-dicarboxylate **2a**.

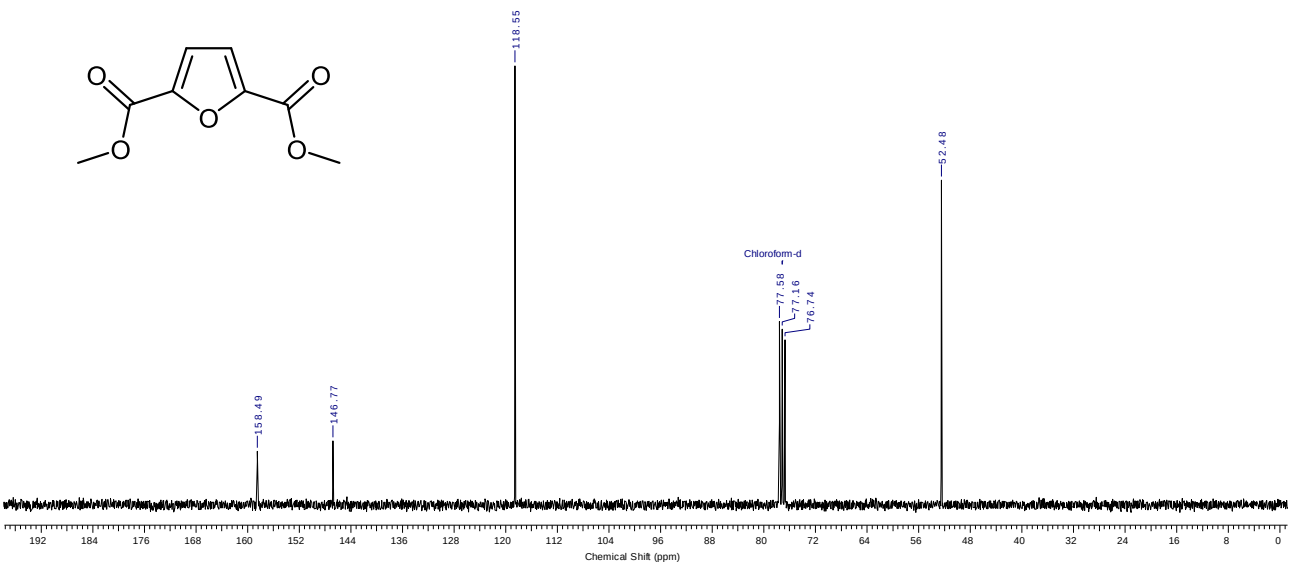


Figure S18. ^{13}C{^{1}H} NMR spectrum of dimethyl furan-2,5-dicarboxylate **2a**.

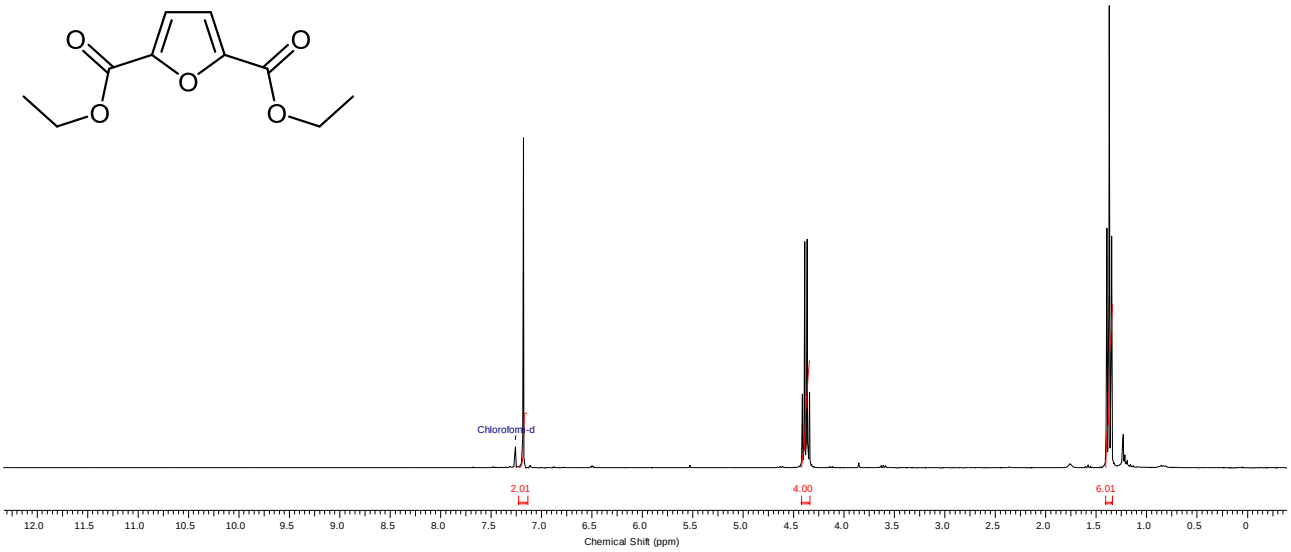


Figure S19. ^{1}H NMR spectrum of diethyl furan-2,5-dicarboxylate **2b**.

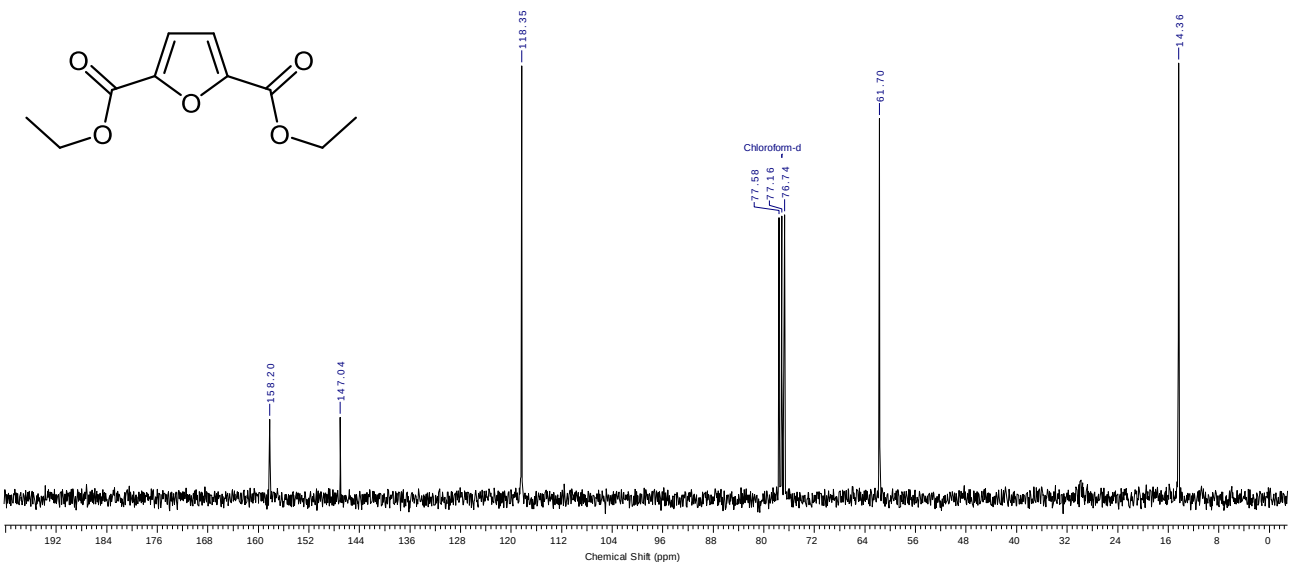


Figure S20. ^{13}C{^{1}H} NMR spectrum of diethyl furan-2,5-dicarboxylate **2b**.

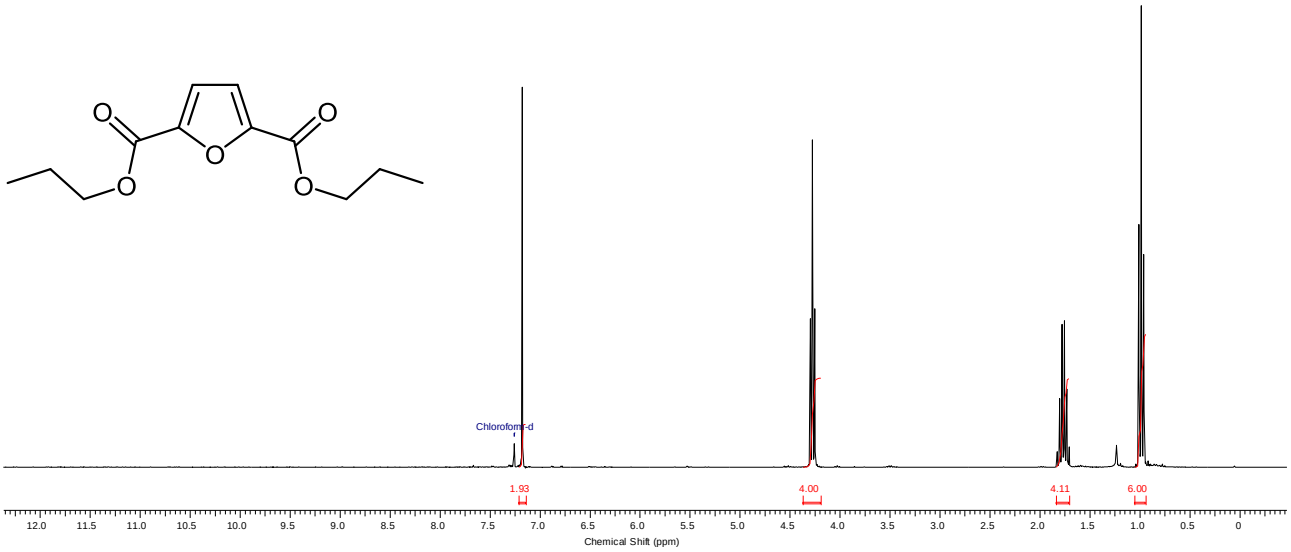


Figure S21. ^{1}H NMR spectrum of dipropyl furan-2,5-dicarboxylate **2c**.

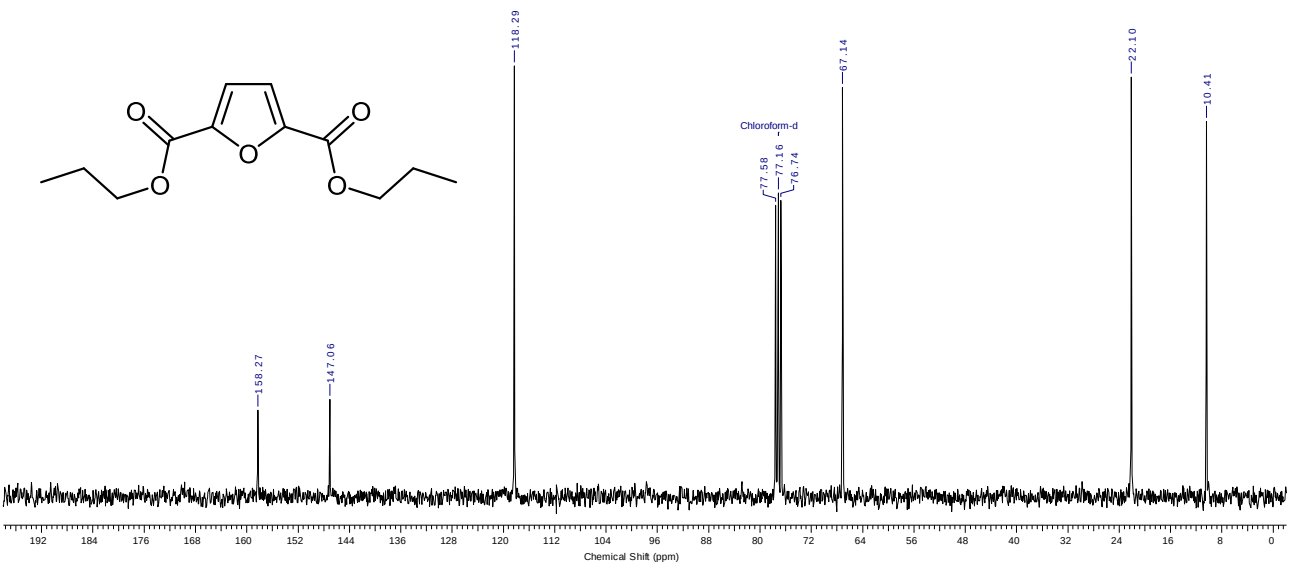


Figure S22. ^{13}C{^{1}H} NMR spectrum of dipropyl furan-2,5-dicarboxylate **2c**.

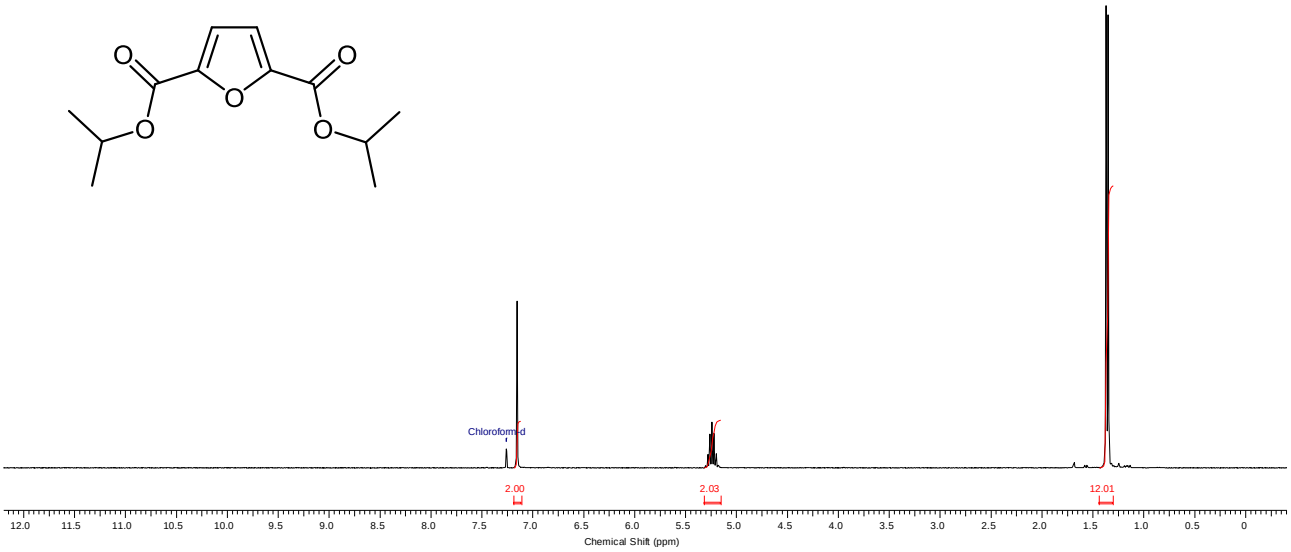


Figure S23. ^{1}H NMR spectrum of diisopropyl furan-2,5-dicarboxylate **2d**.

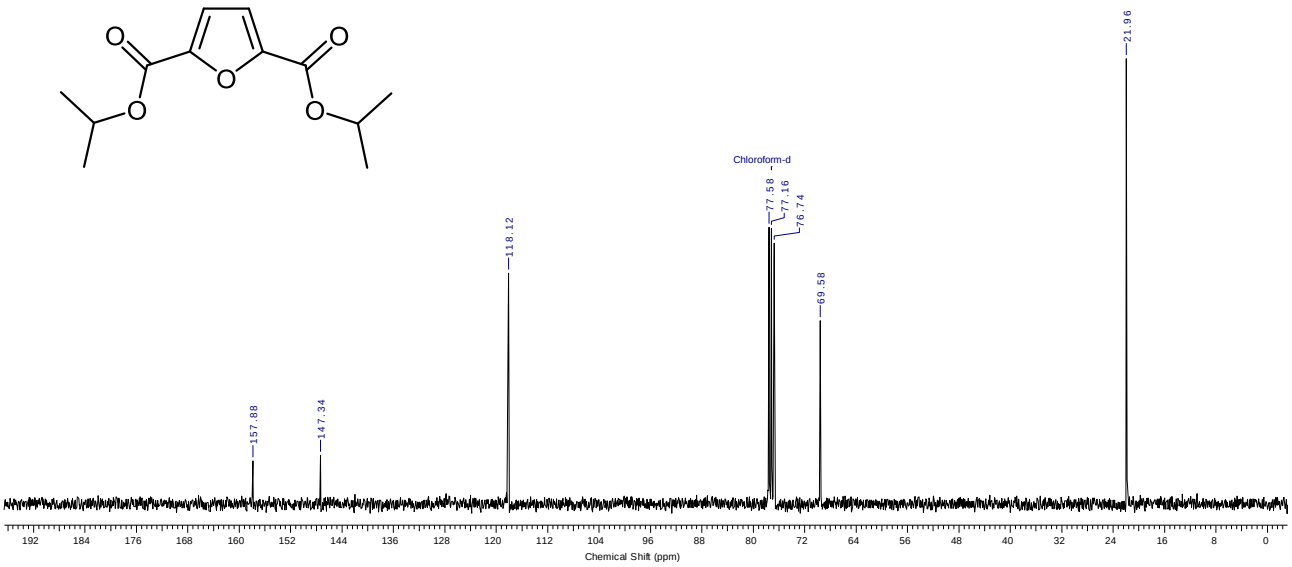


Figure S24. ^{13}C{^{1}H} NMR spectrum of diisopropyl furan-2,5-dicarboxylate **2d**.

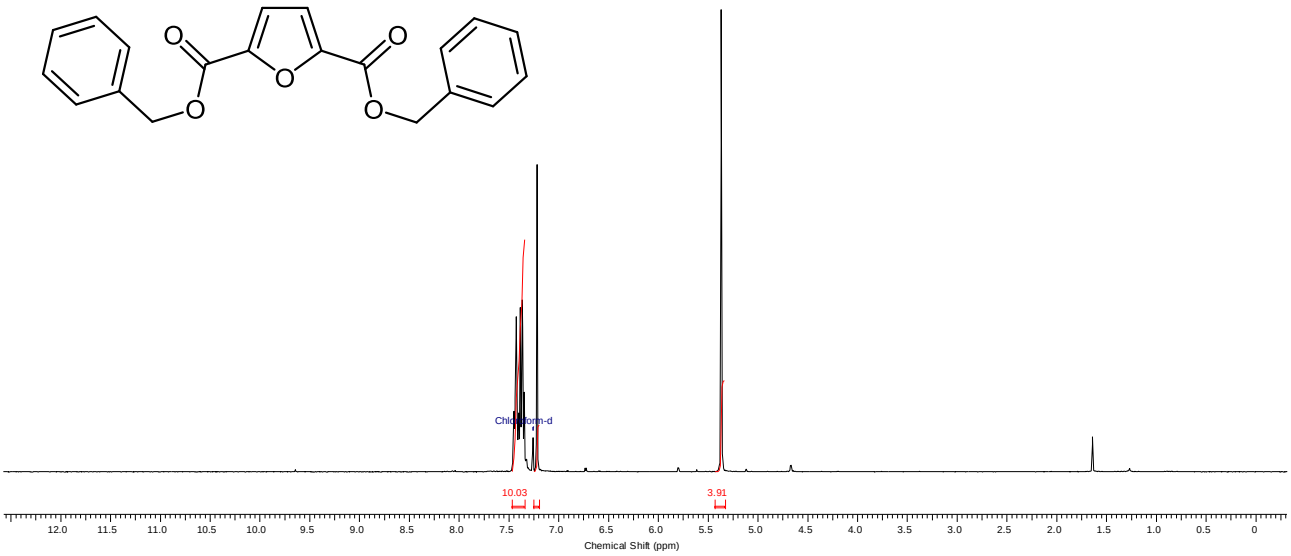


Figure S25. ^{1}H NMR spectrum of dibenzyl furan-2,5-dicarboxylate **2e**.

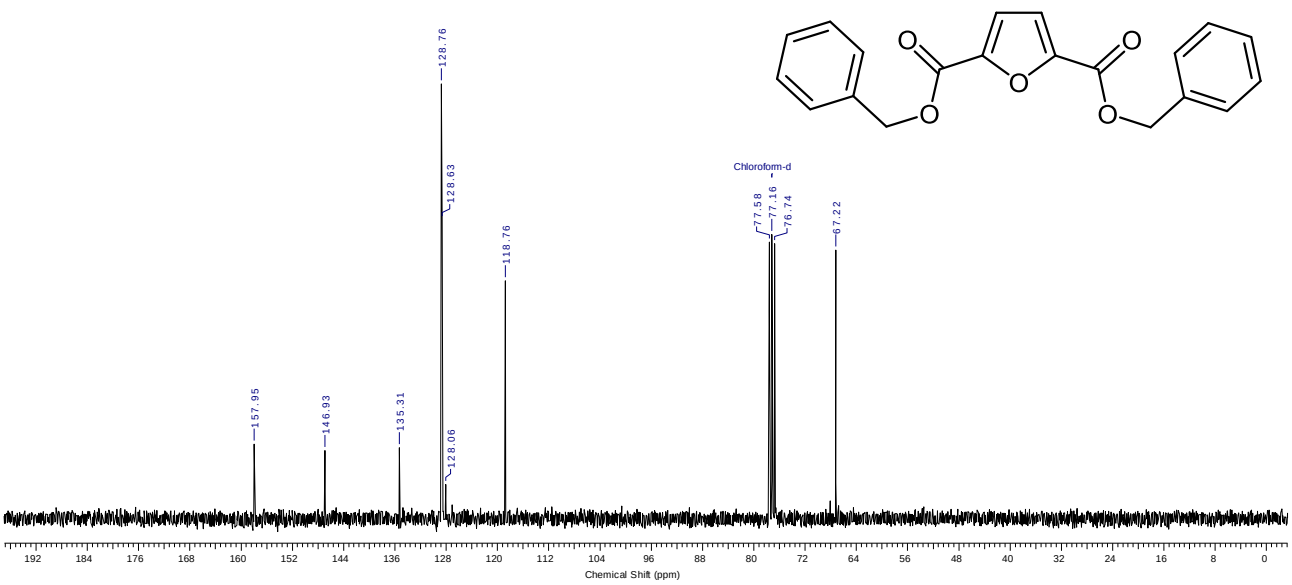


Figure S26. ^{13}C{^{1}H} NMR spectrum of dibenzyl furan-2,5-dicarboxylate **2e**.

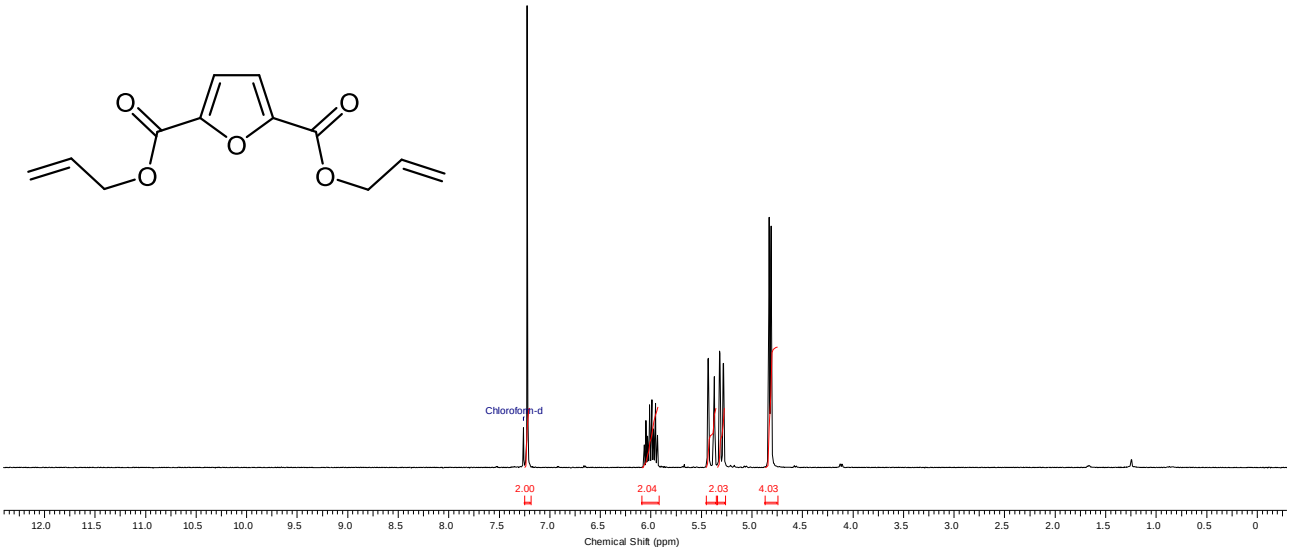


Figure S27. ^{1}H NMR spectrum of diallyl furan-2,5-dicarboxylate **2f**.

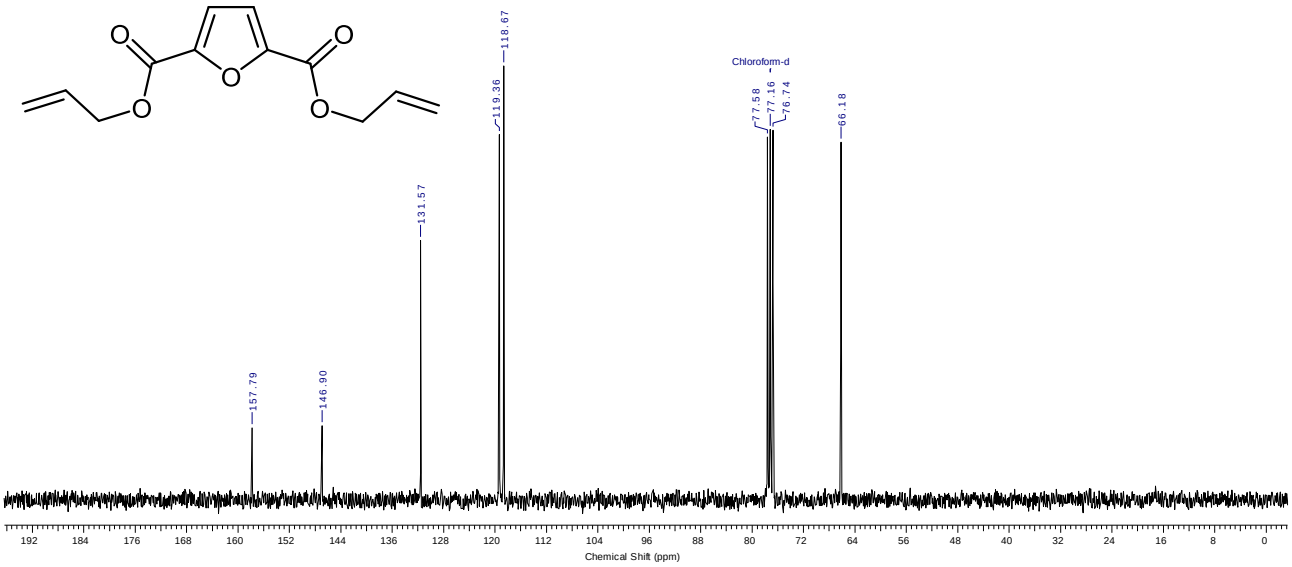


Figure S28. ^{13}C{^{1}H} NMR spectrum of diallyl furan-2,5-dicarboxylate **2f**.

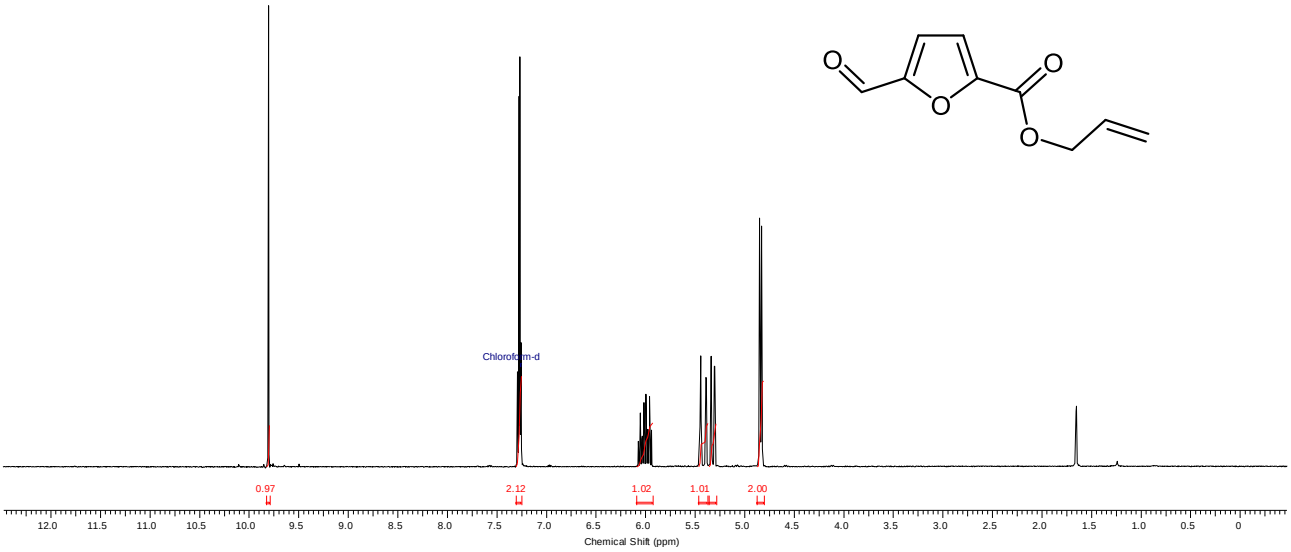


Figure S29. ^{1}H NMR spectrum of allyl 5-formylfuran-2-carboxylate **2f'**.

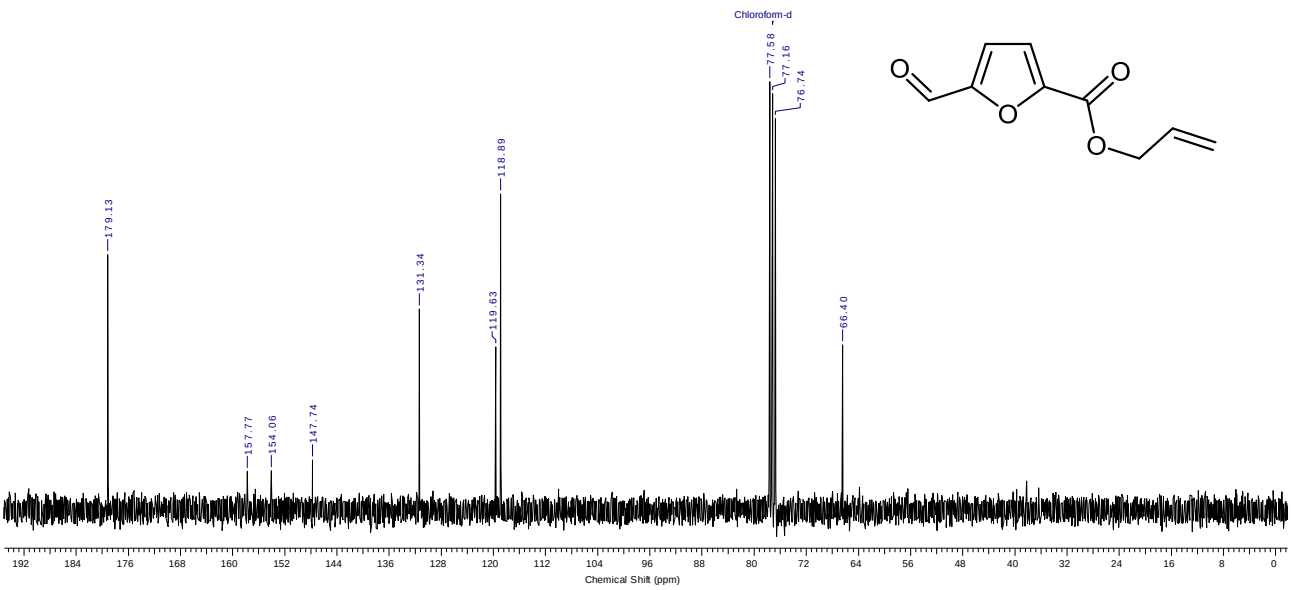


Figure S30. ^{13}C{^{1}H} NMR spectrum of allyl 5-formylfuran-2-carboxylate **2f'**.

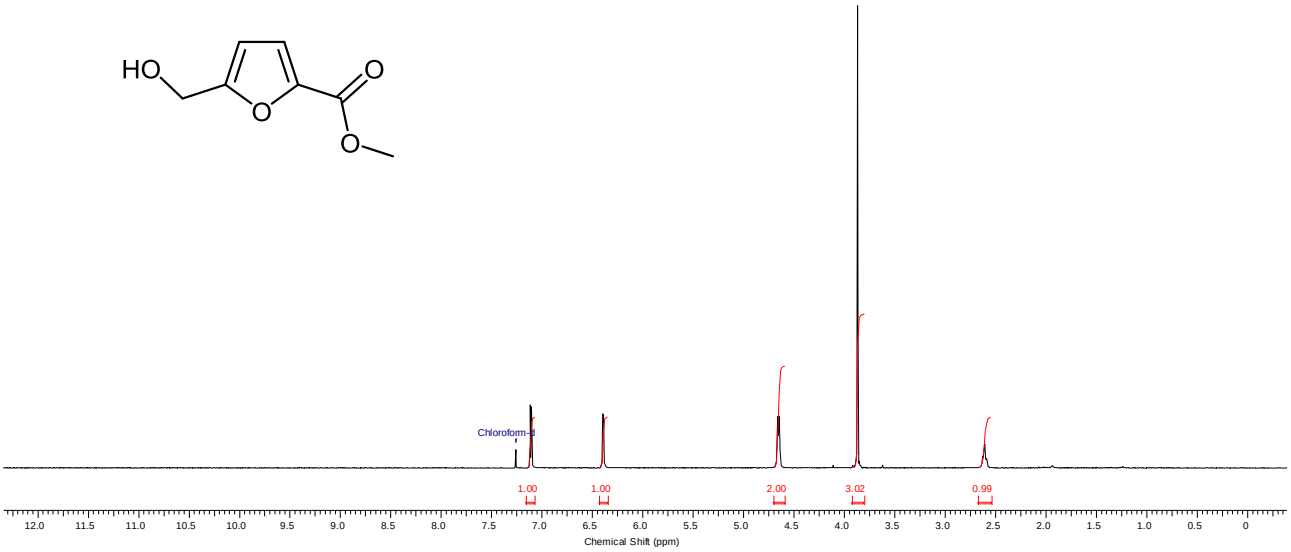


Figure S31. ^{1}H NMR spectrum of methyl 5-(hydroxymethyl)furan-2-carboxylate **3a**.

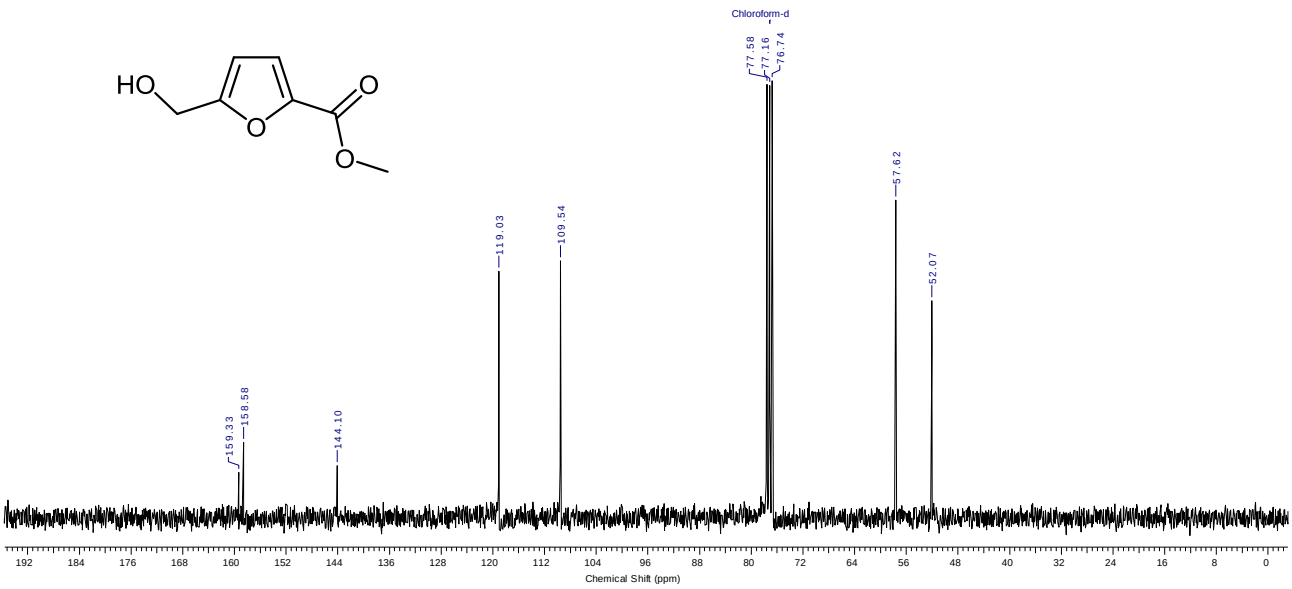


Figure S32. ^{13}C{^{1}H} NMR spectrum methyl 5-(hydroxymethyl)furan-2-carboxylate **3a**.

FE-SEM microscopy images

SEM images of MnO_2 prior to use:

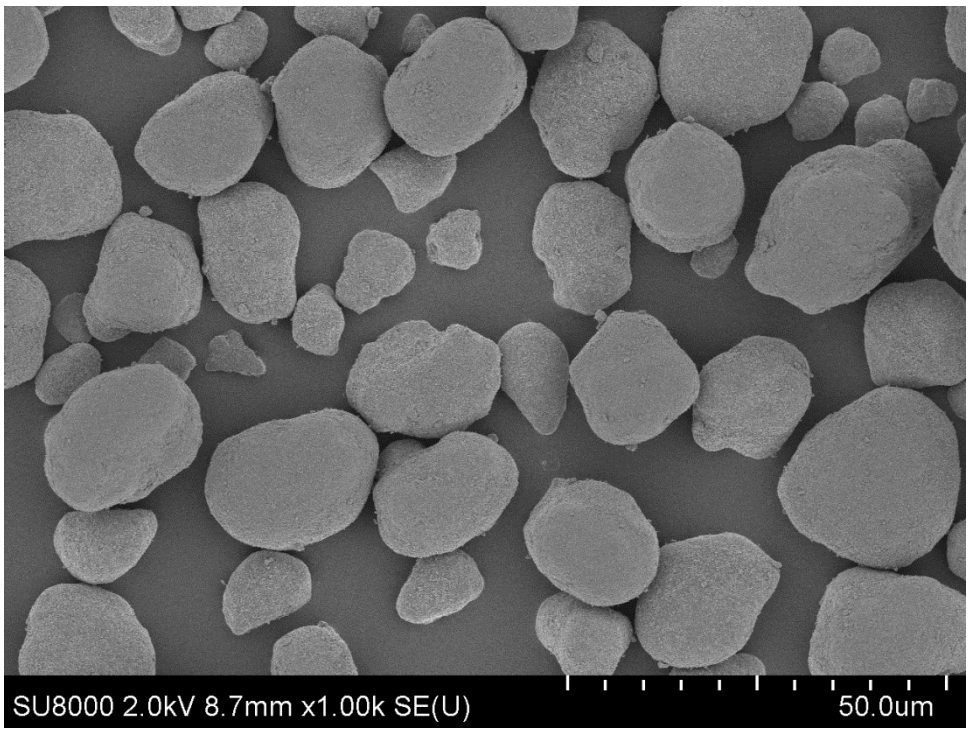


Figure S33. Microscopy image recorded at ×1000 magnification.

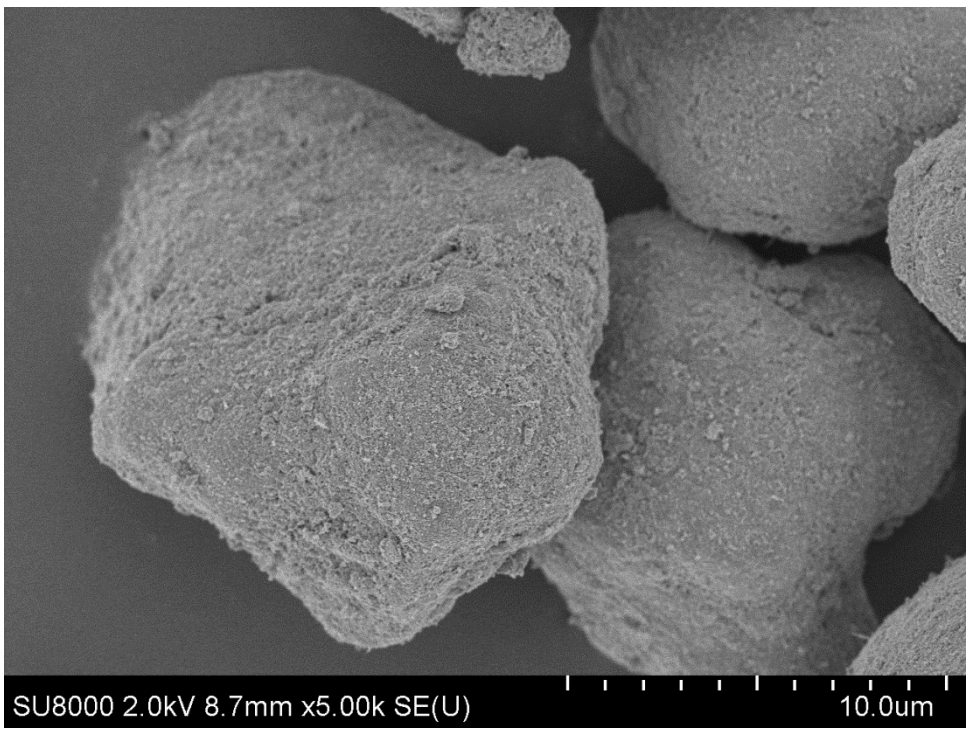


Figure S34. Microscopy image recorded at ×5000 magnification.

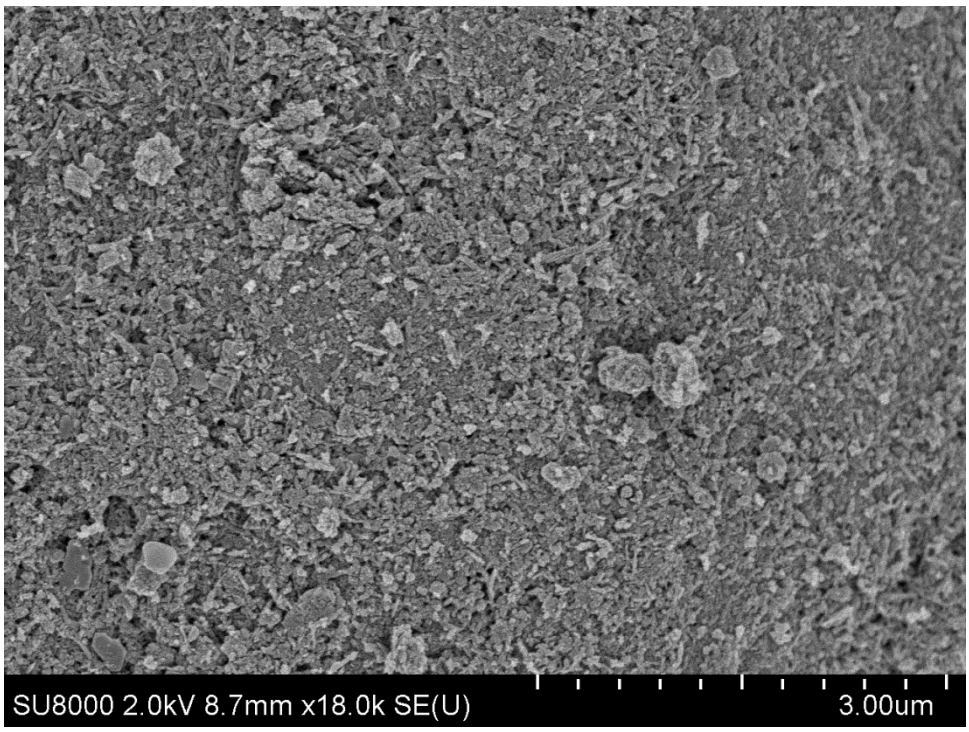


Figure S35. Microscopy image recorded at ×18 000 magnification.

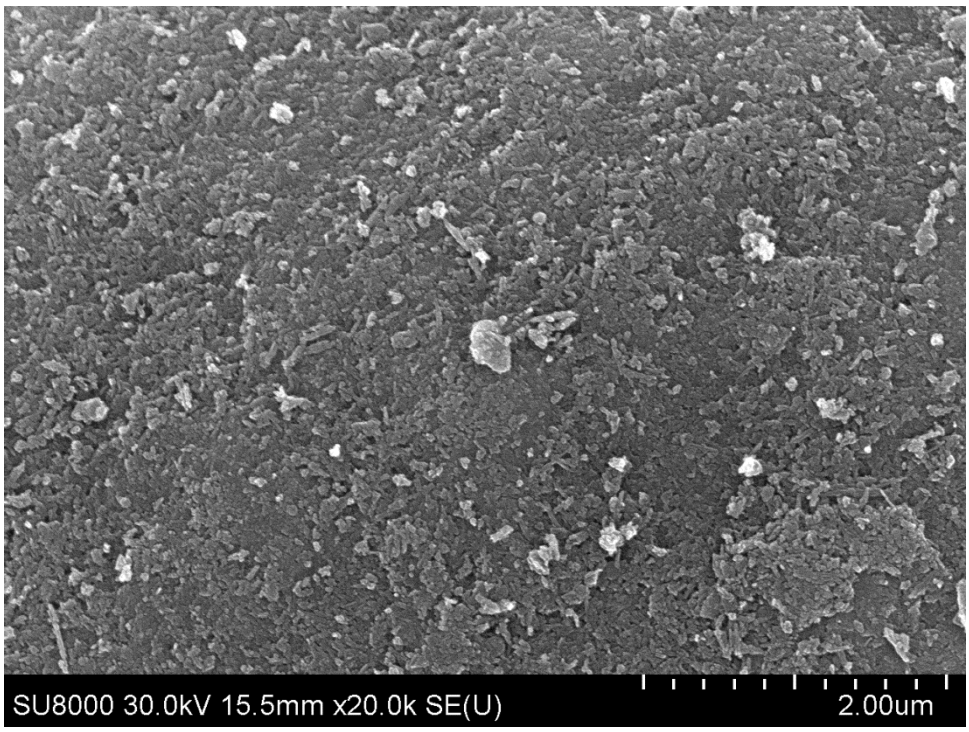


Figure S36. Microscopy image recorded at ×20 000 magnification.

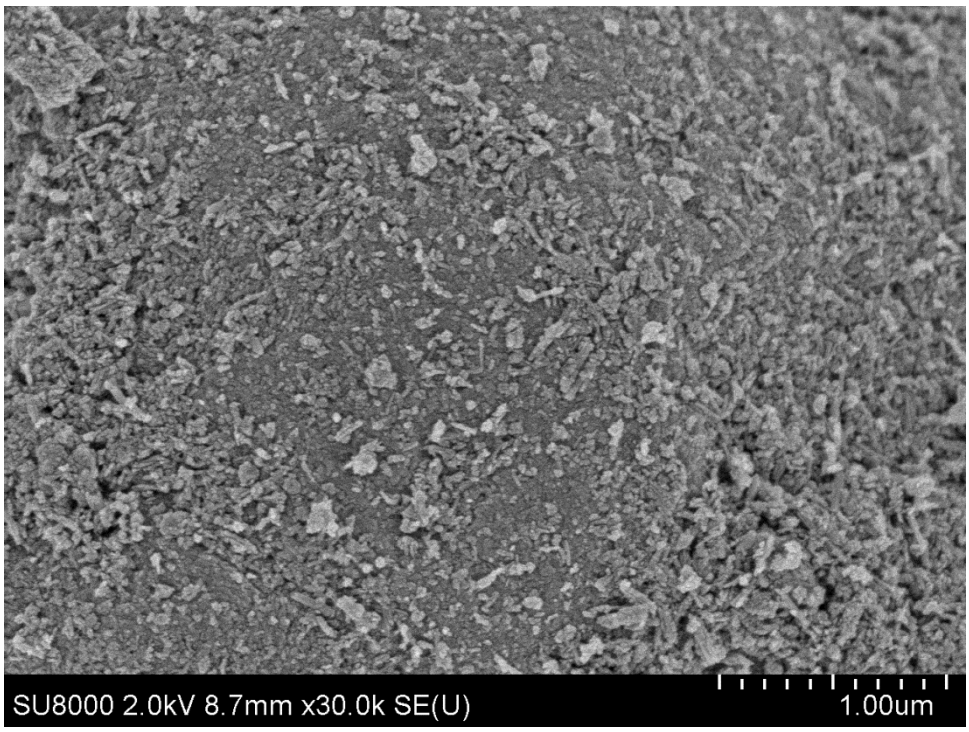


Figure S37. Microscopy image recorded at ×30 000 magnification.

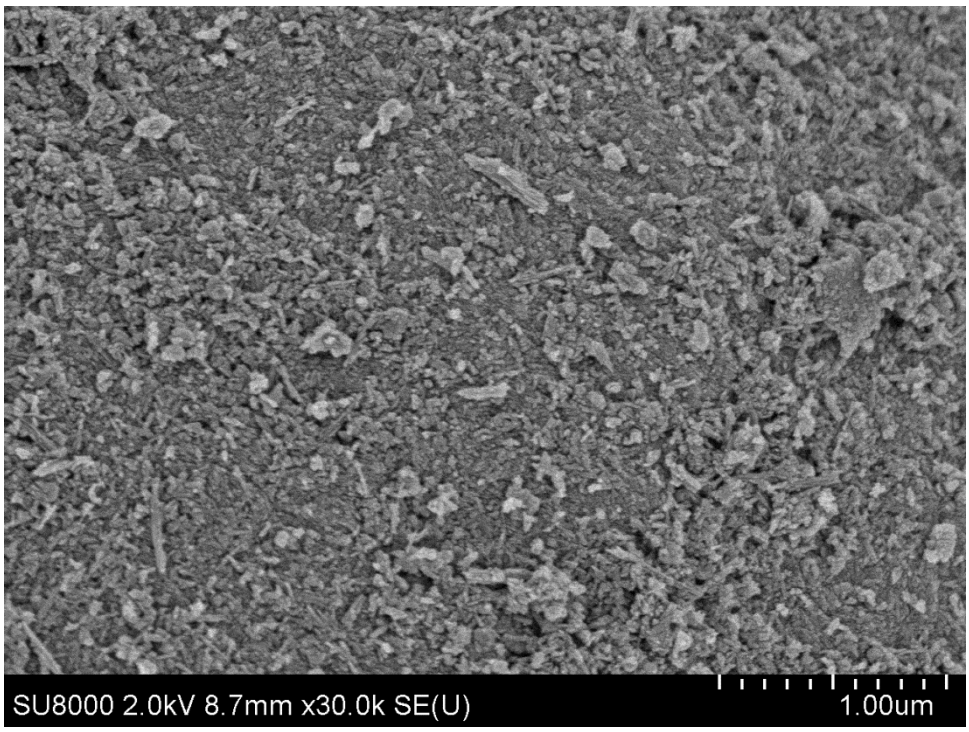


Figure S38. Microscopy image recorded at ×30 000 magnification.

SEM images of MnO_2 after reaction:

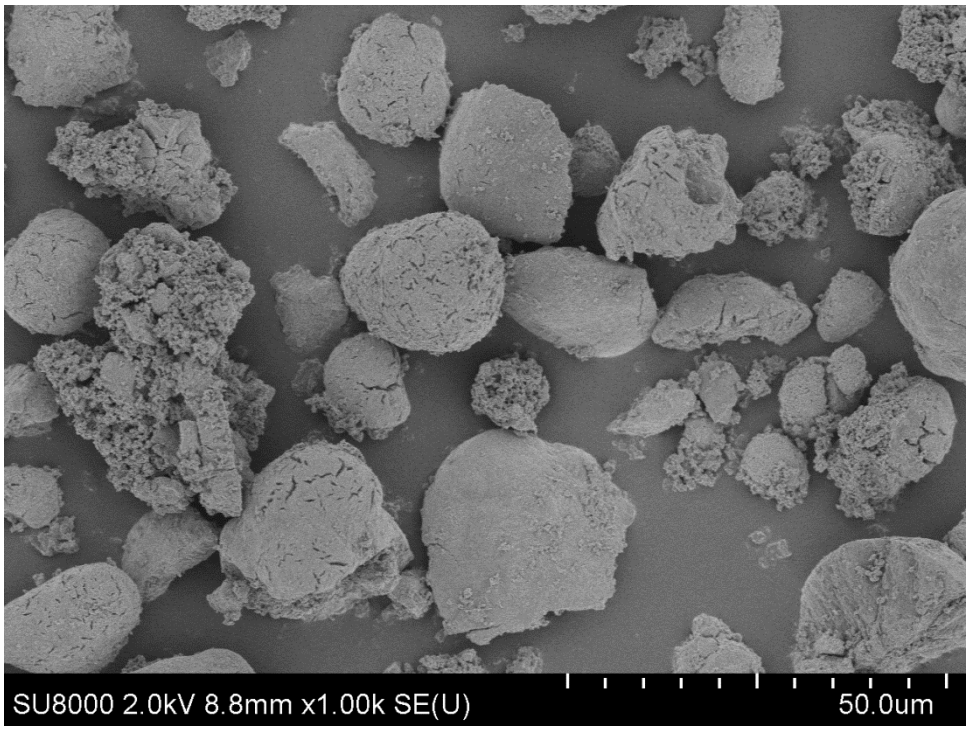


Figure S39. Microscopy image recorded at ×1000 magnification.

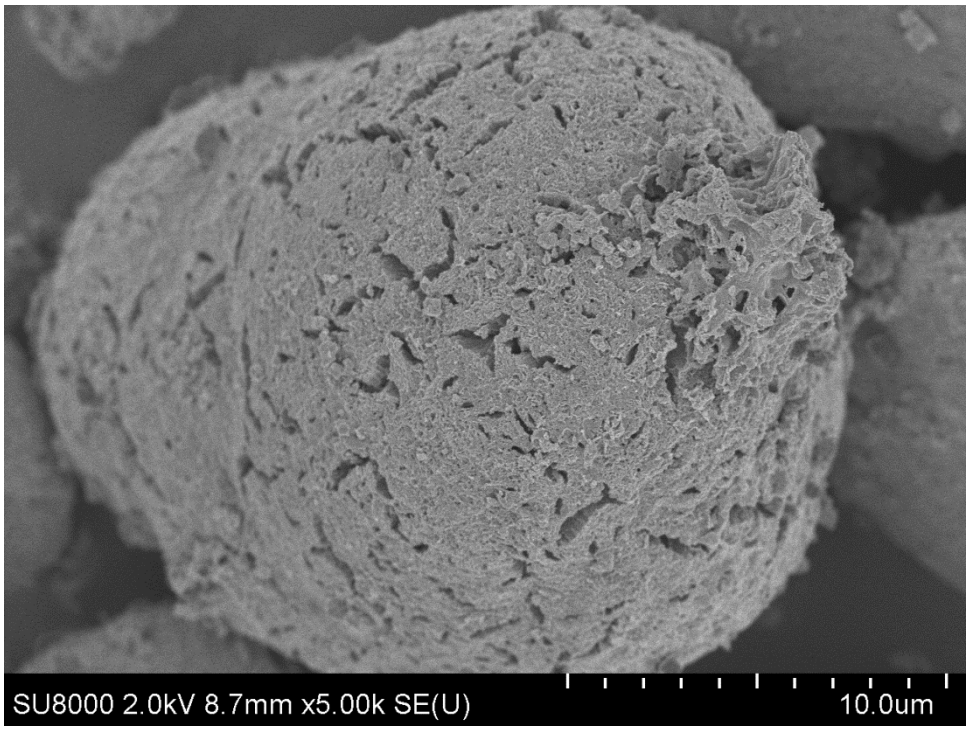


Figure S40. Microscopy image recorded at ×5000 magnification.

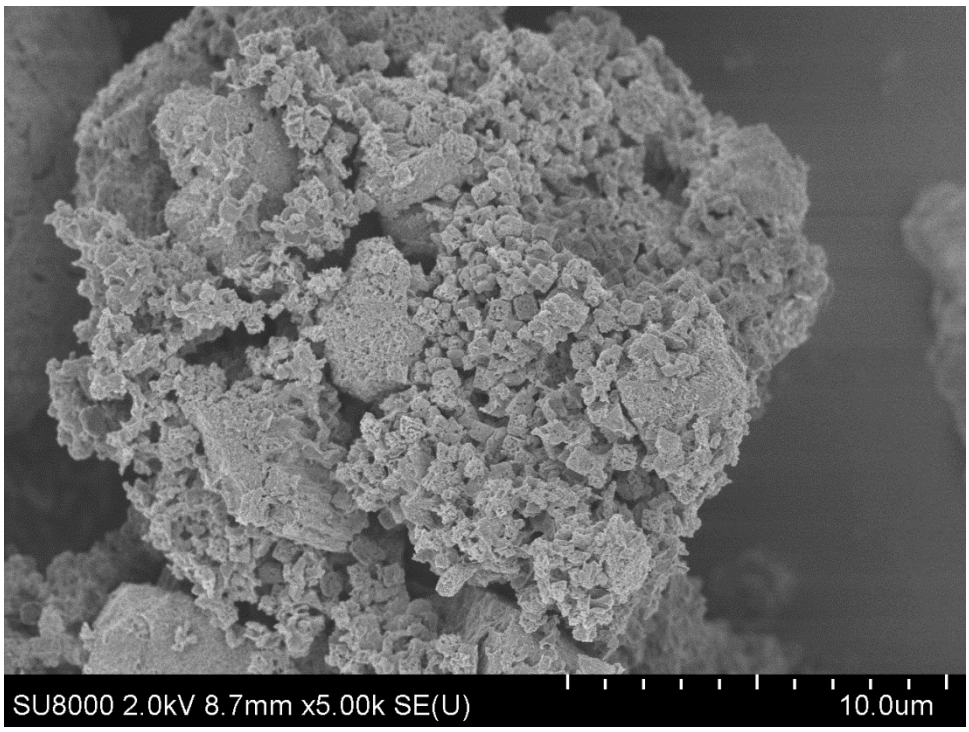


Figure S41. Microscopy image recorded at ×5000 magnification.

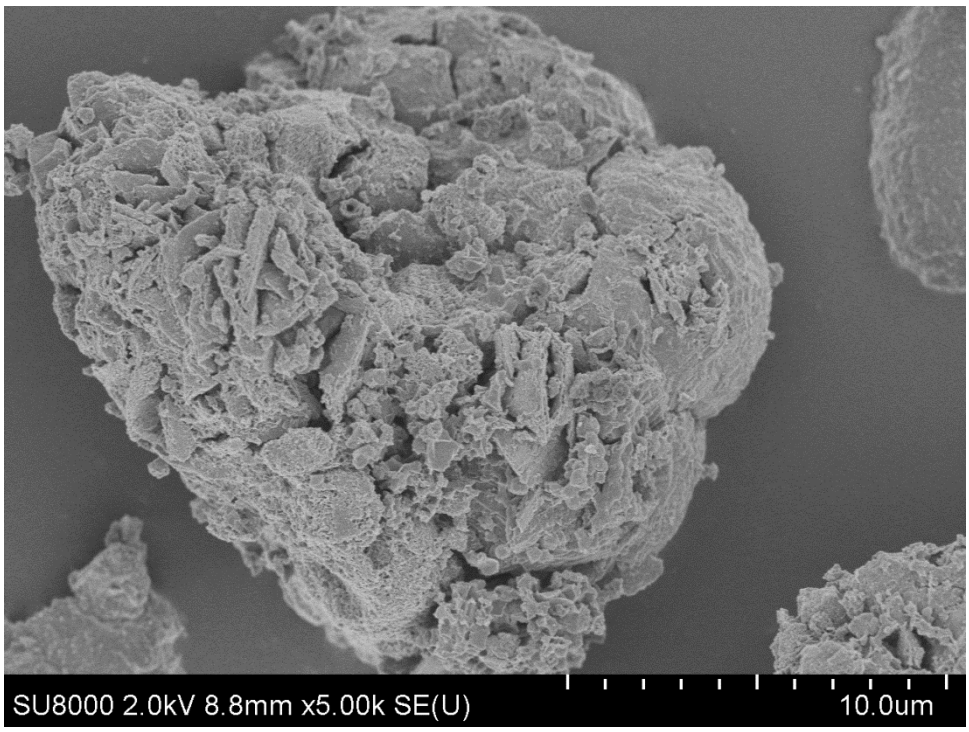


Figure S42. Microscopy image recorded at ×5000 magnification.

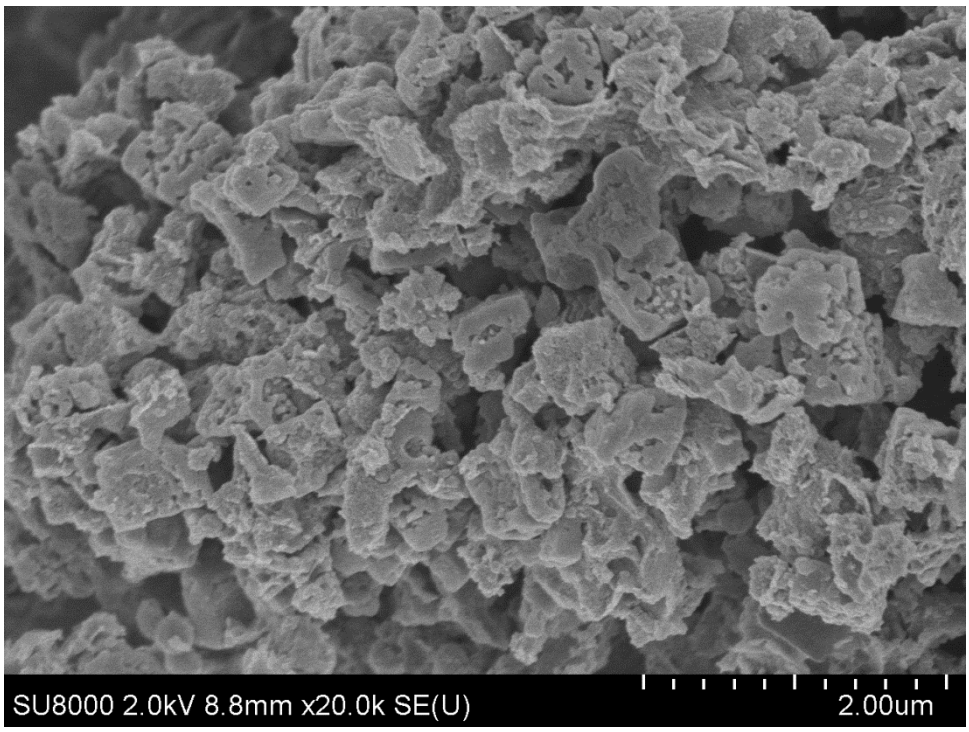


Figure S43. Microscopy image recorded at ×20 000 magnification.

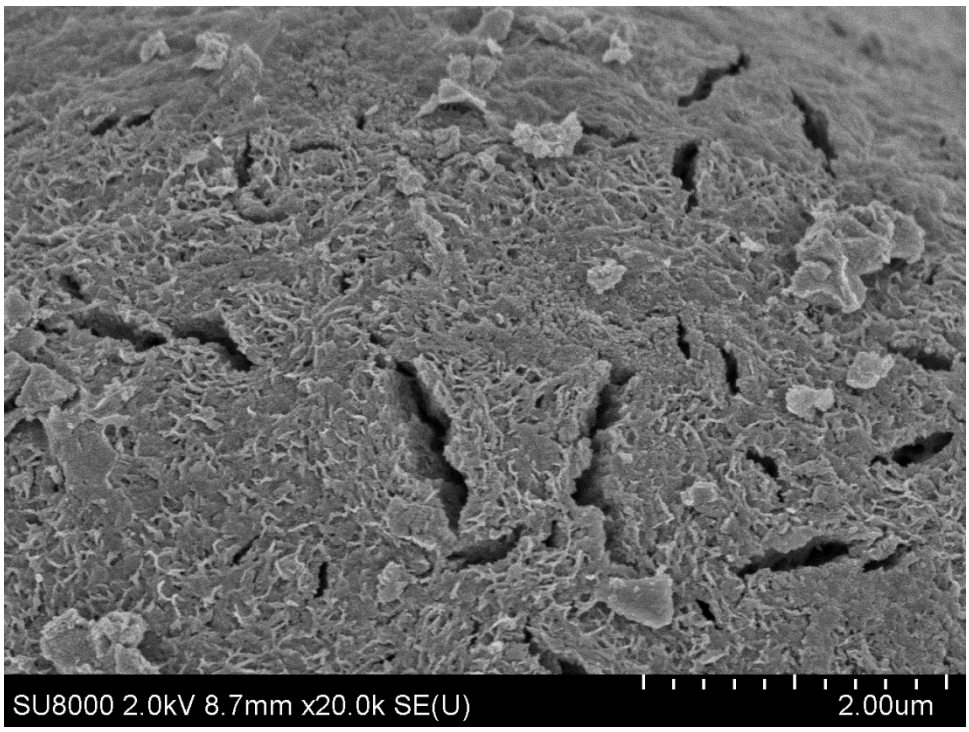


Figure S44. Microscopy image recorded at ×20 000 magnification.

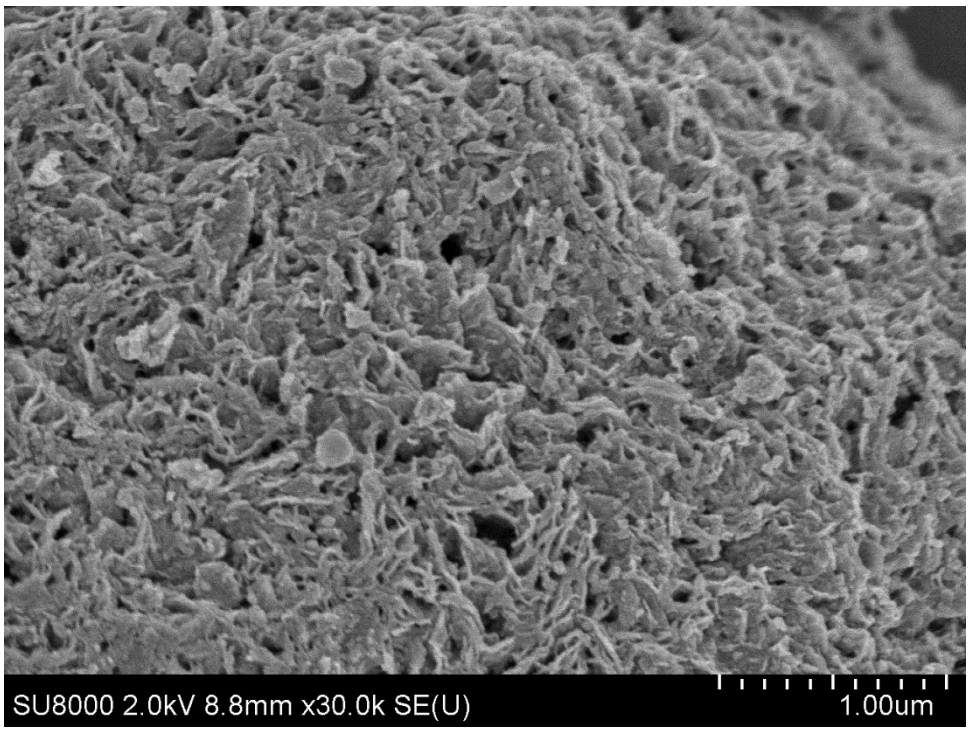


Figure S45. Microscopy image recorded at ×30 000 magnification.

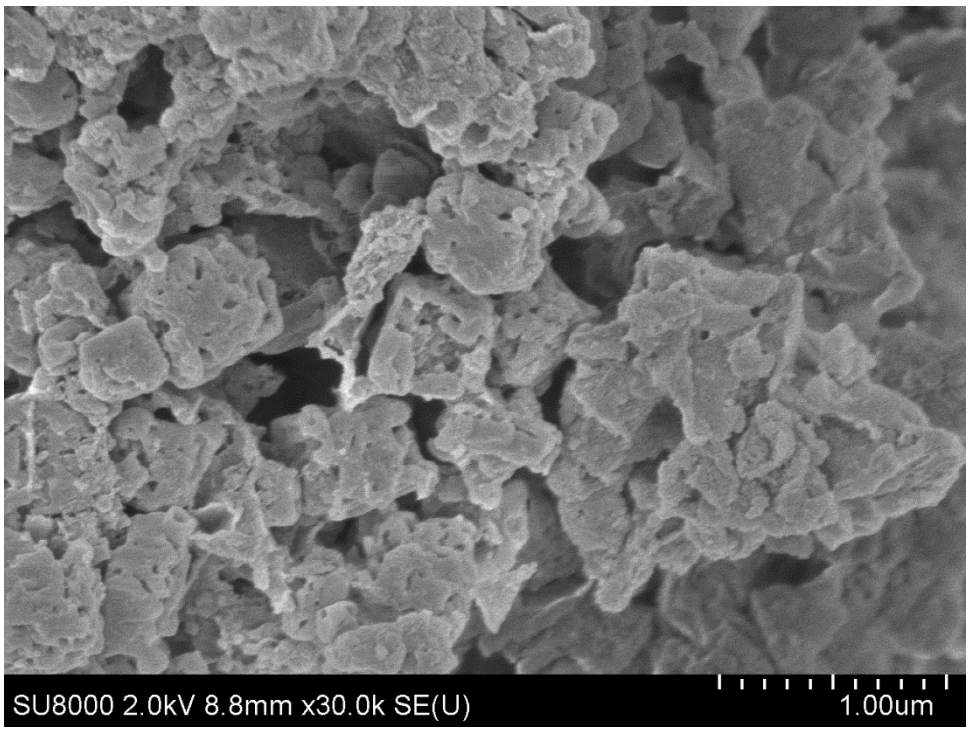


Figure S46. Microscopy image recorded at ×30 000 magnification.

SEM images of MnO_2 after drying:

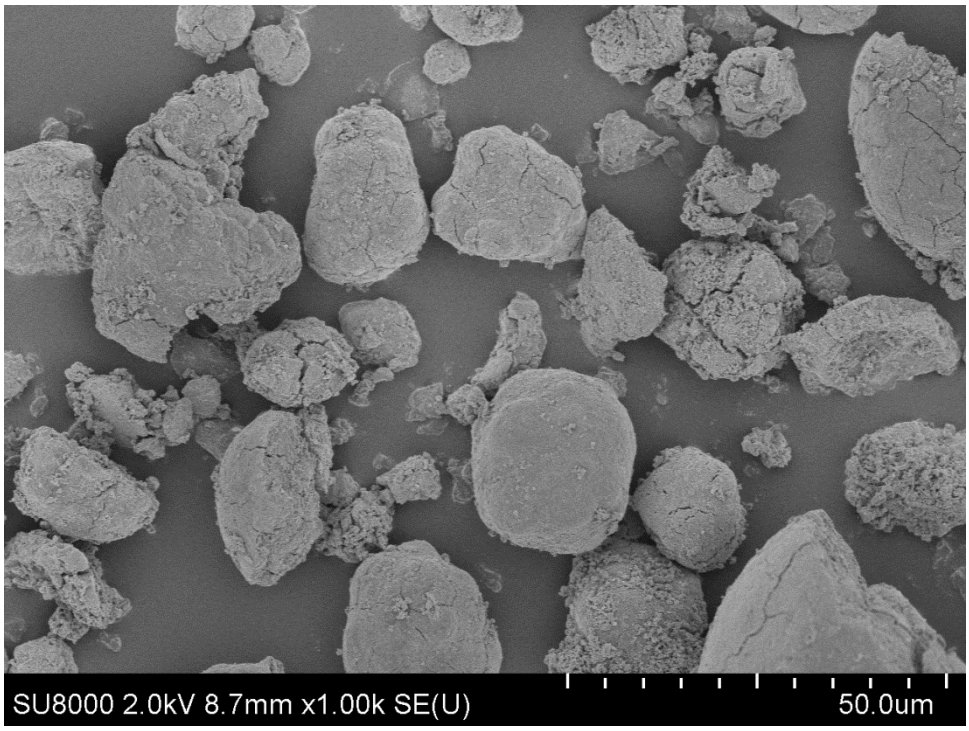


Figure S47. Microscopy image recorded at ×1000 magnification.

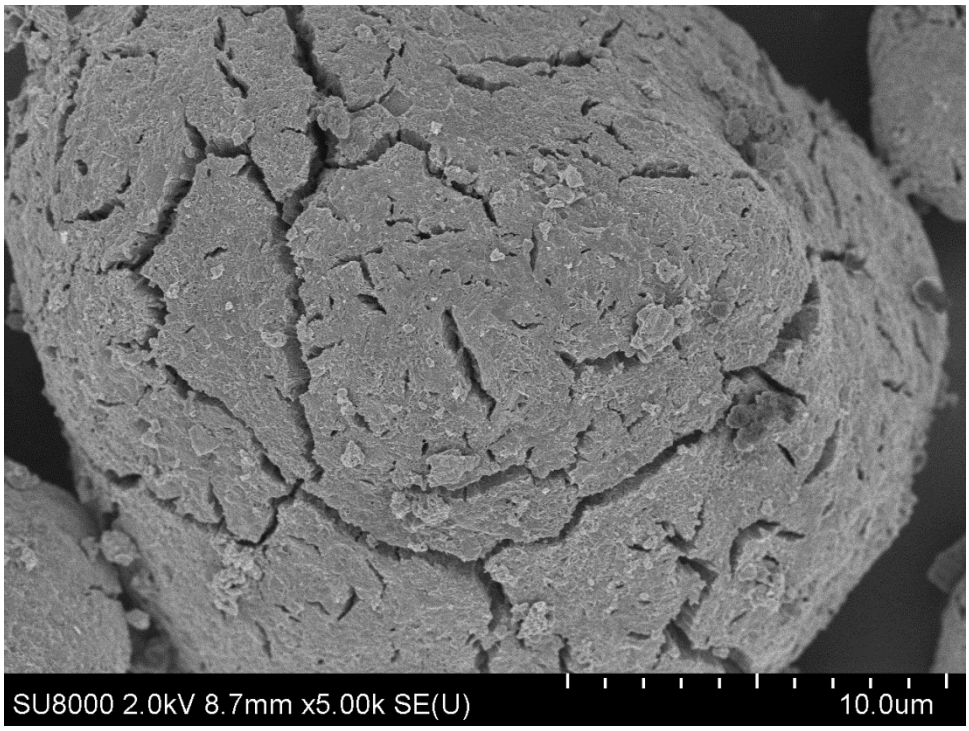


Figure S48. Microscopy image recorded at ×5000 magnification.

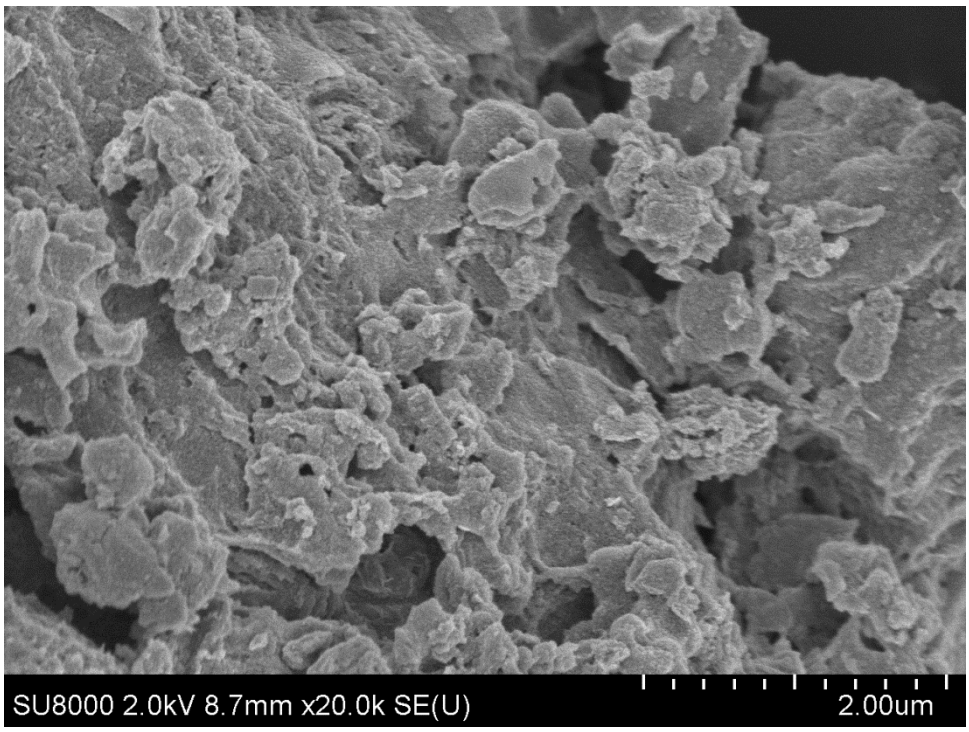


Figure S49. Microscopy image recorded at ×20 000 magnification.

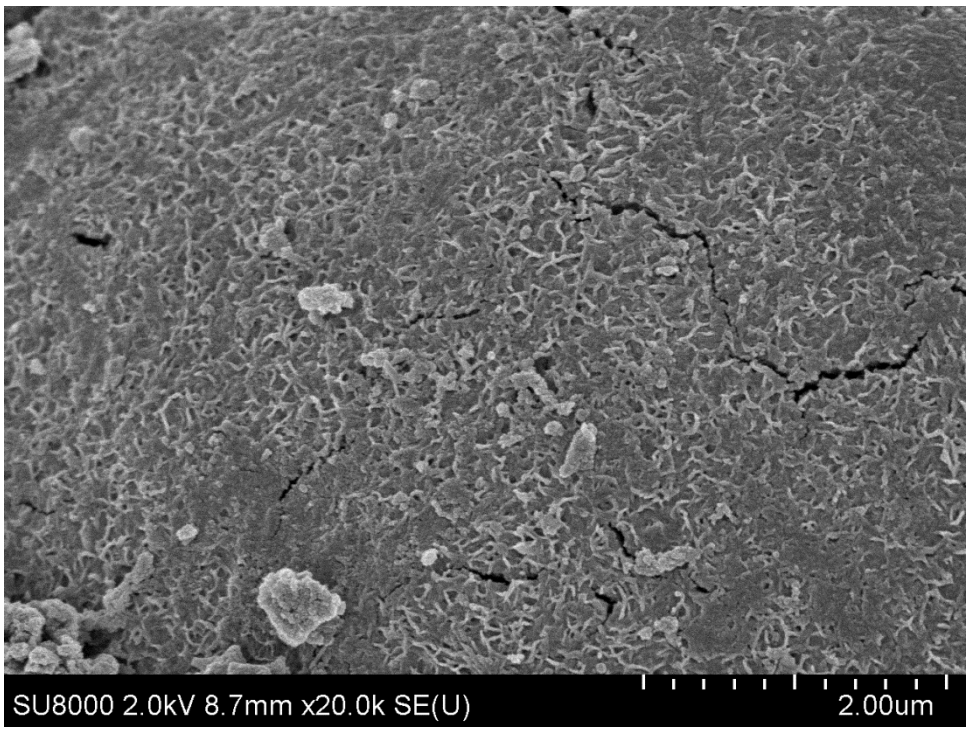


Figure S50. Microscopy image recorded at ×20 000 magnification.

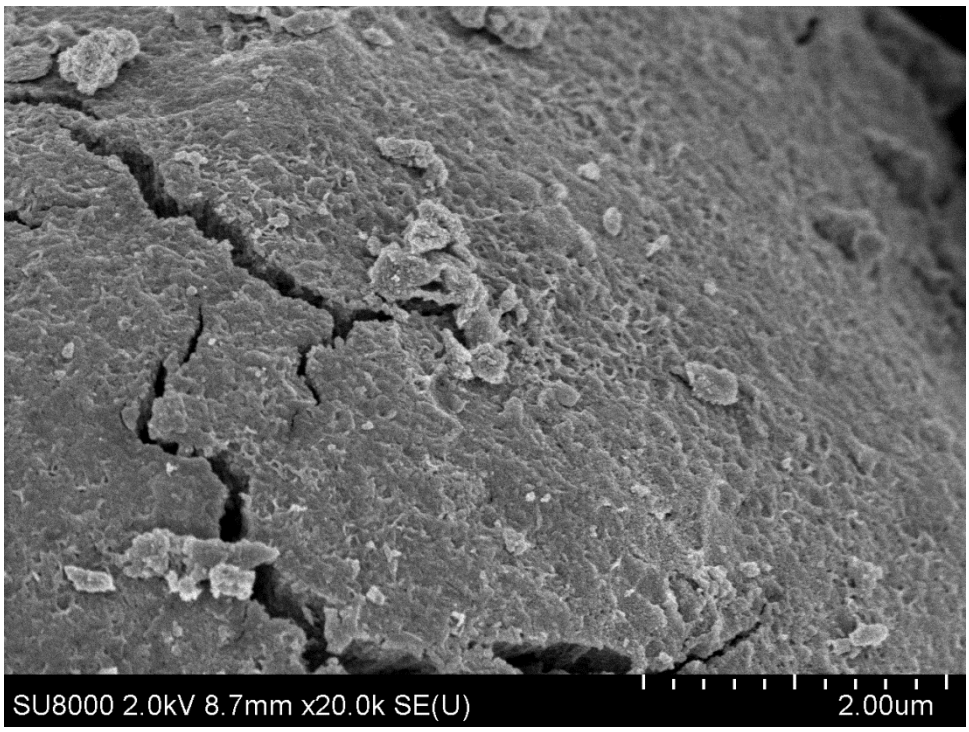


Figure S51. Microscopy image recorded at ×20 000 magnification.

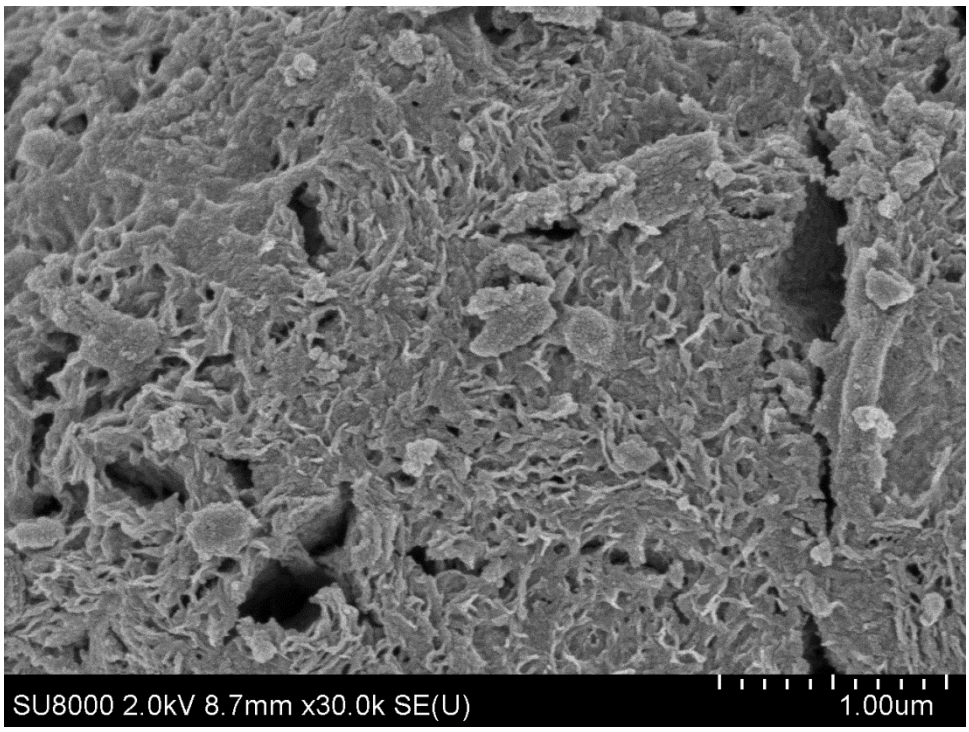


Figure S52. Microscopy image recorded at ×30 000 magnification.

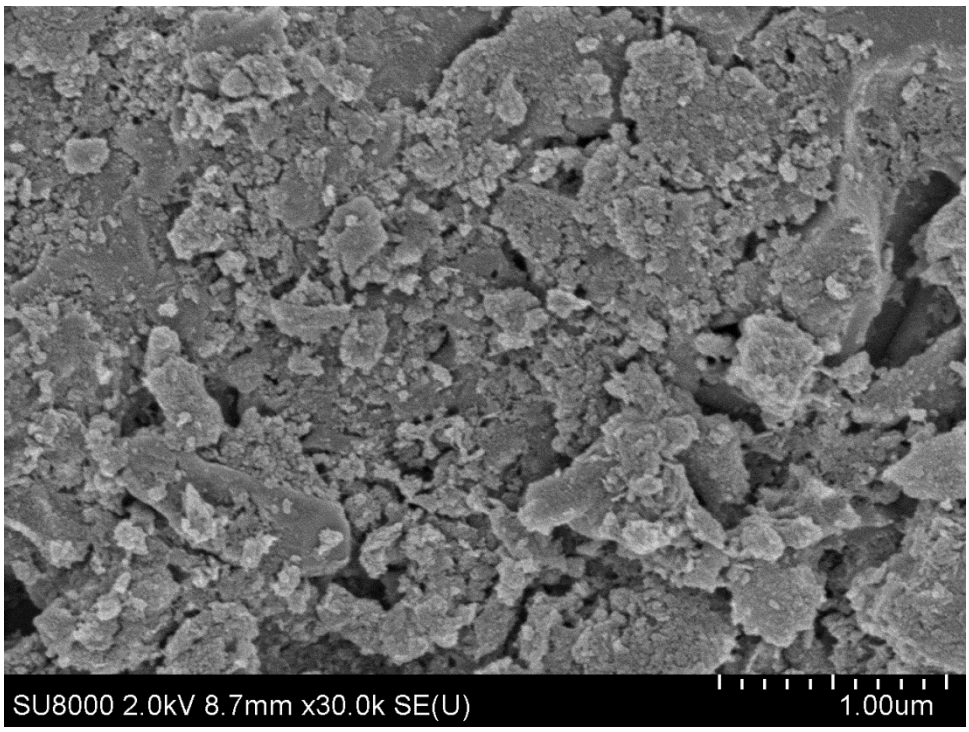


Figure S53. Microscopy image recorded at ×30 000 magnification.

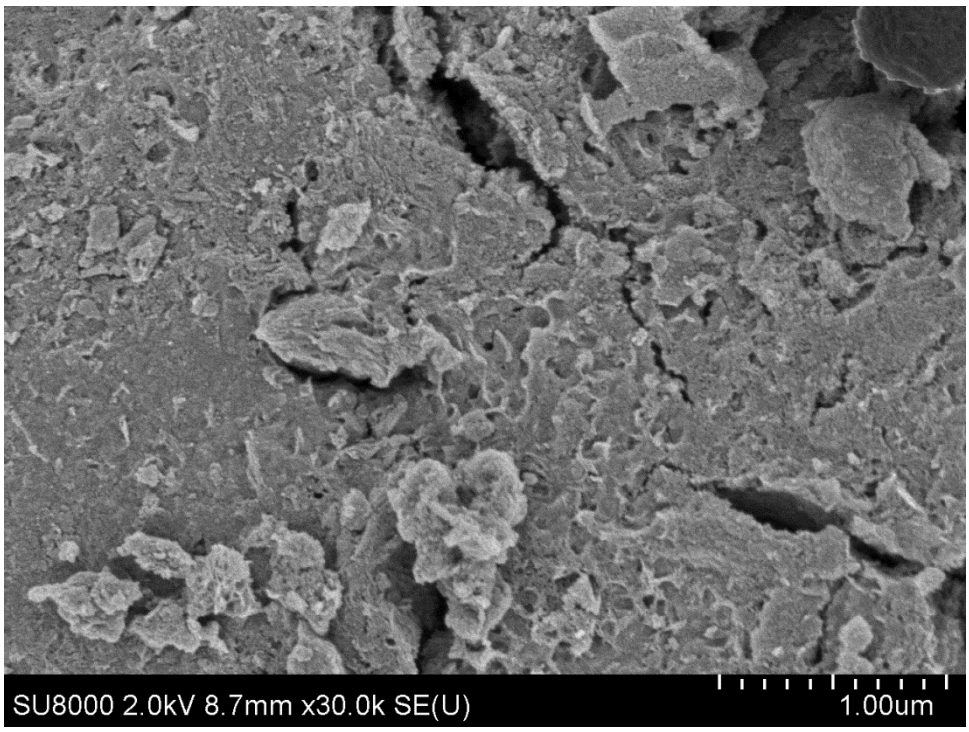


Figure S54. Microscopy image recorded at ×30 000 magnification.

EDX analysis of manganese dioxide

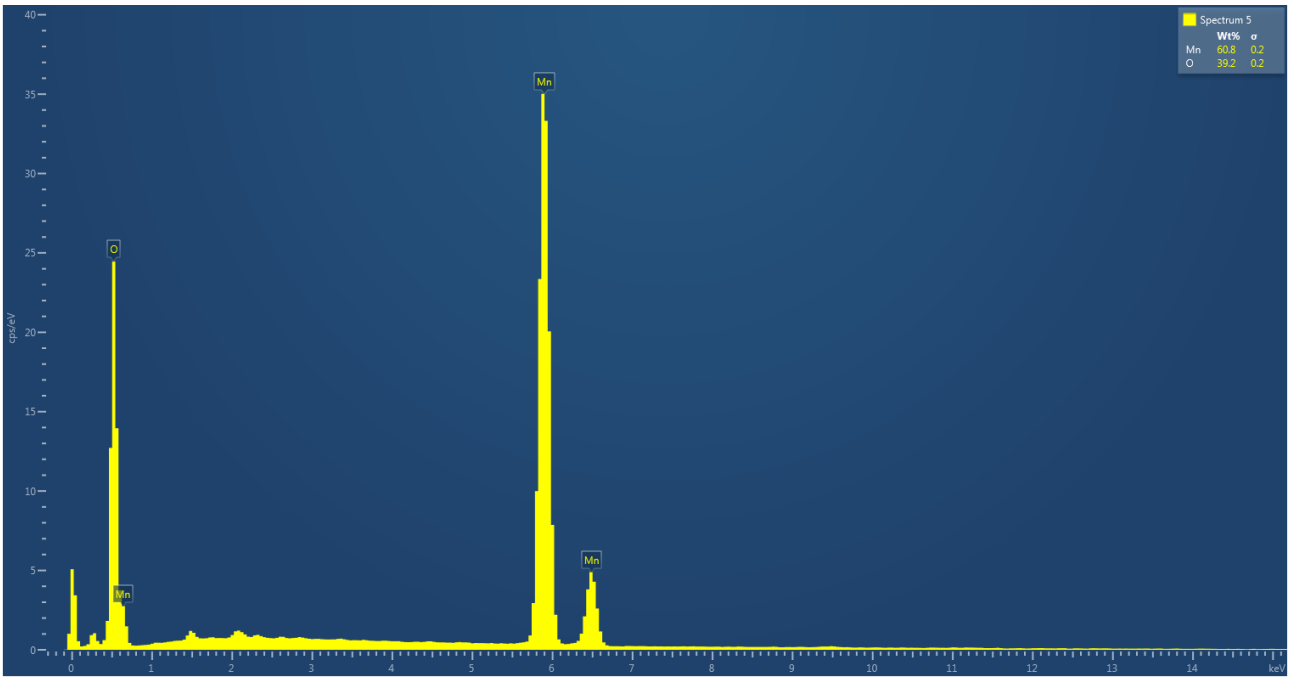


Figure S55. EDX of manganese dioxide prior to use.

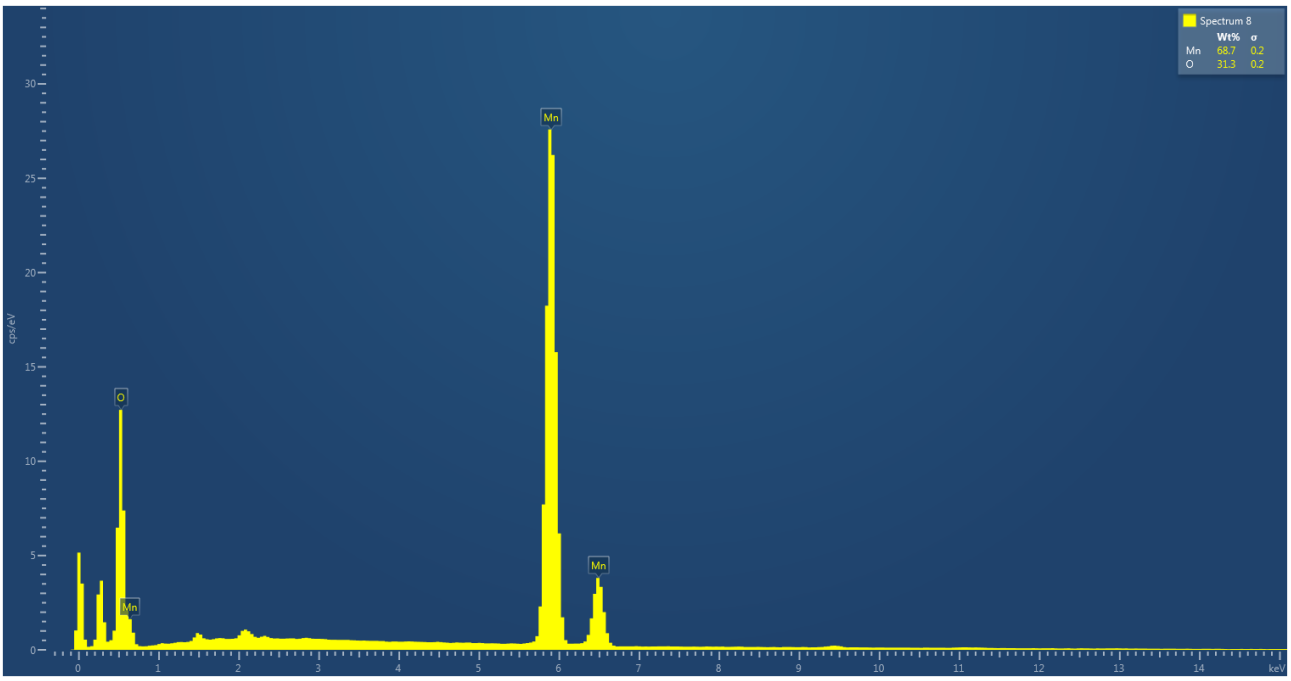


Figure S56. EDX of manganese dioxide after the reaction.

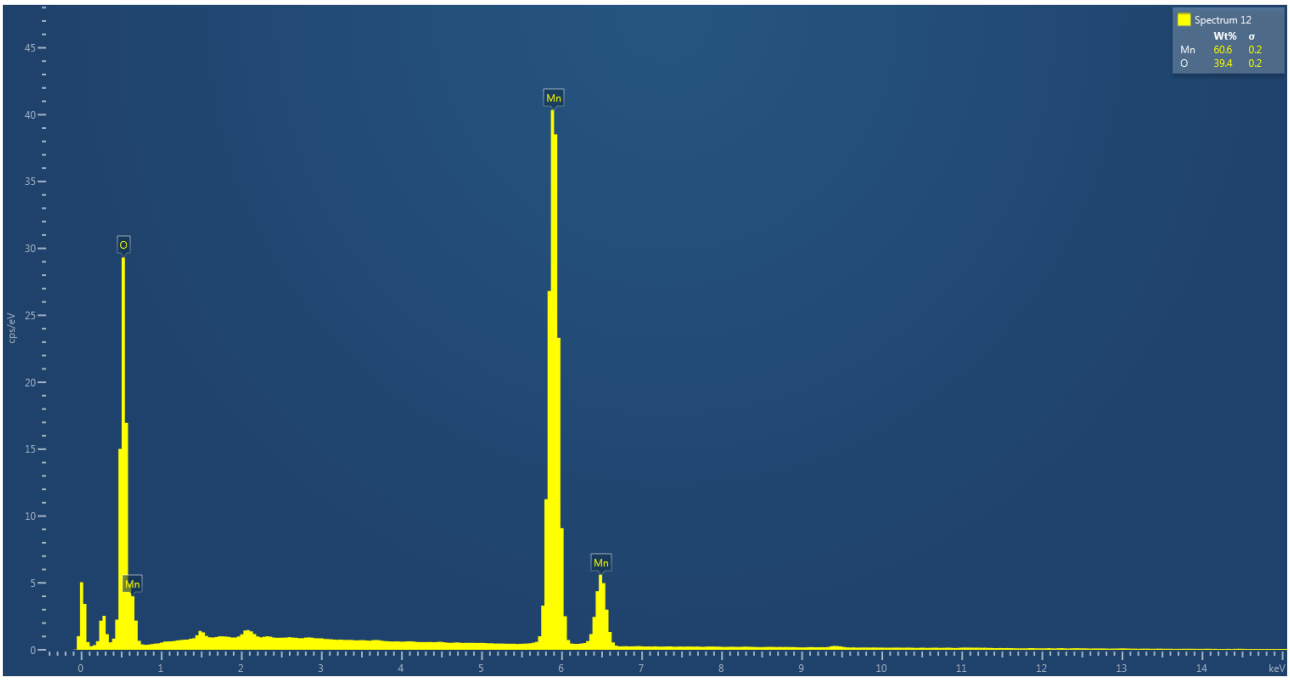


Figure S57. EDX of manganese dioxide after drying on air.

Regeneration of manganese dioxide

After the reaction, manganese dioxide (8 mmol) was filtered off and washed several times with methanol (3 x 30mL), water (4 x 50mL), and diethyl ether (2 x 30mL) and dried on air. Then MnO_2 was placed in a crucible and heated in an oven for 6 hours with a gradual increase in temperature from 100 °C to 180 °C.

For the reaction of DFF oxidative esterification with methanol recycling of the oxidant was performed 7 times. Obtained yields are shown in Table S2 and Figure S58.

Table S2. Recycling of MnO_2.

Cycle	Yield, %
1	95
2	97
3	93
4	98
5	97
6	92
7	96

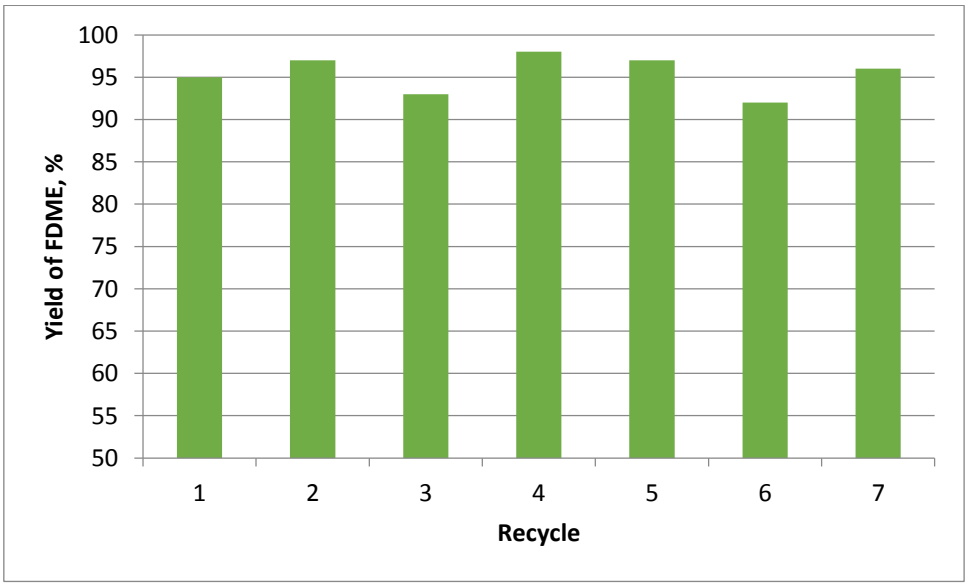


Figure S58. Recycling of MnO_2 in oxidative esterification.

Estimation of Green Chemistry metrics

Preliminary estimation of Green Chemistry metrics

Synthesis of FDME

Since solvents and manganese dioxide could be regenerated, simplified environmental factor can be calculated as follows:

$sEF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN}{m(FDME)} = \frac{39.2\ mg}{305.7\ mg} = 0.128$ – for the synthesis of FDME from HMF

$sEF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN}{m(FDME)} = \frac{39.2\ mg}{357.2\ mg} = 0.109$ – for the synthesis of FDME from DFF

If we estimate the loss of MnO_2 as 10 wt. %, calculation of EF will be following:

$EF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN + w_{loss}(MnO_2) \cdot m_{total}(MnO_2)}{m(FDME)} = \frac{39.2\ mg + 0.1 \cdot 347 mg}{305.7\ mg} = 0.242$ – for the synthesis of FDME from HMF

$EF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN + w_{loss}(MnO_2) \cdot m_{total}(MnO_2)}{m(FDME)} = \frac{39.2\ mg + 0.1 \cdot 347 mg}{357.2\ mg} = 0.207$ – for the synthesis of FDME from DFF

If we additionally estimate 10 wt. % loss of solvent, calculation of EF will be following:

$EF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN + w_{loss}\ MnO_2 \cdot m_{total}\ MnO_2 + w_{loss}\ MeOH \cdot m_{total}\ MeOH + w_{loss}\ DCM \cdot m_{total}\ DCM}{m(FDME)} = \frac{39.2\ mg + 0.1 \cdot 347 mg + 0.1 \cdot 3168\ mg + 0.1 \cdot 5320}{305.7\ mg} = 3.02$ – for the synthesis of FDME from HMF

$EF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN + w_{loss}\ MnO_2 \cdot m_{total}\ MnO_2 + w_{loss}(MeOH) \cdot m_{total}(MeOH)}{m(FDME)} = \frac{39.2\ mg + 0.1 \cdot 347 mg + 0.1 \cdot 3168\ mg}{357.2\ mg} = 1.09$ – for the synthesis of FDME from DFF

Synthesis of MHMFC

$EF = \frac{m(waste)}{m(product)} = \frac{m\ NaCN + w_{loss}(MnO_2) \cdot m_{total}(MnO_2)}{m(MHMFC)} = \frac{73.5\ mg + 0.1 \cdot 140\ mg}{68\ mg} = 1.29$

Estimations show that calculated environmental factors for described oxidative esterification of HMF and DFF are close to the range corresponding to bulk chemicals production (EF<1–5).[8] Only simplified estimation of the metrics is provided here, and more detailed analysis should be carried out if required.

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