Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information (ESI) for

Catalytic aerial oxidation of 5-hydroxymethyl-2-furfural to furan-2,5-dicarboxylic acid over Ni-Pd nanoparticles supported on $Mg(OH)_2$ nanoflakes for synthesis of furan diesters

Kavita Gupta,[a] Rohit K. Rai,[a] and Sanjay K. Singh*[a,b]

[a]Discipline of Chemistry, [b]Discipline of Metallurgical Engineering and Materials Science, Indian Institute of Technology Indore, Indore 453 552, Madhya Pradesh, India. E-mail: sksingh@iiti.ac.in

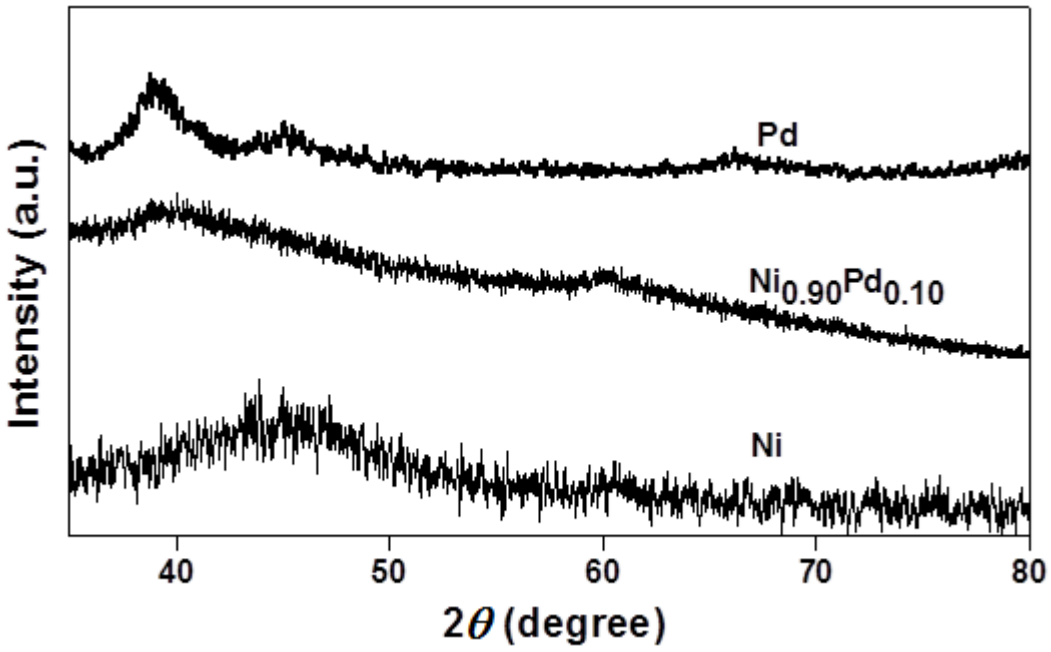


Figure S1 Powder X-ray diffraction pattern of unsupported bimetallic $Ni_{0.90}Pd_{0.10}$ alloy nanoparticles and monometallic Ni and Pd nanoparticles.

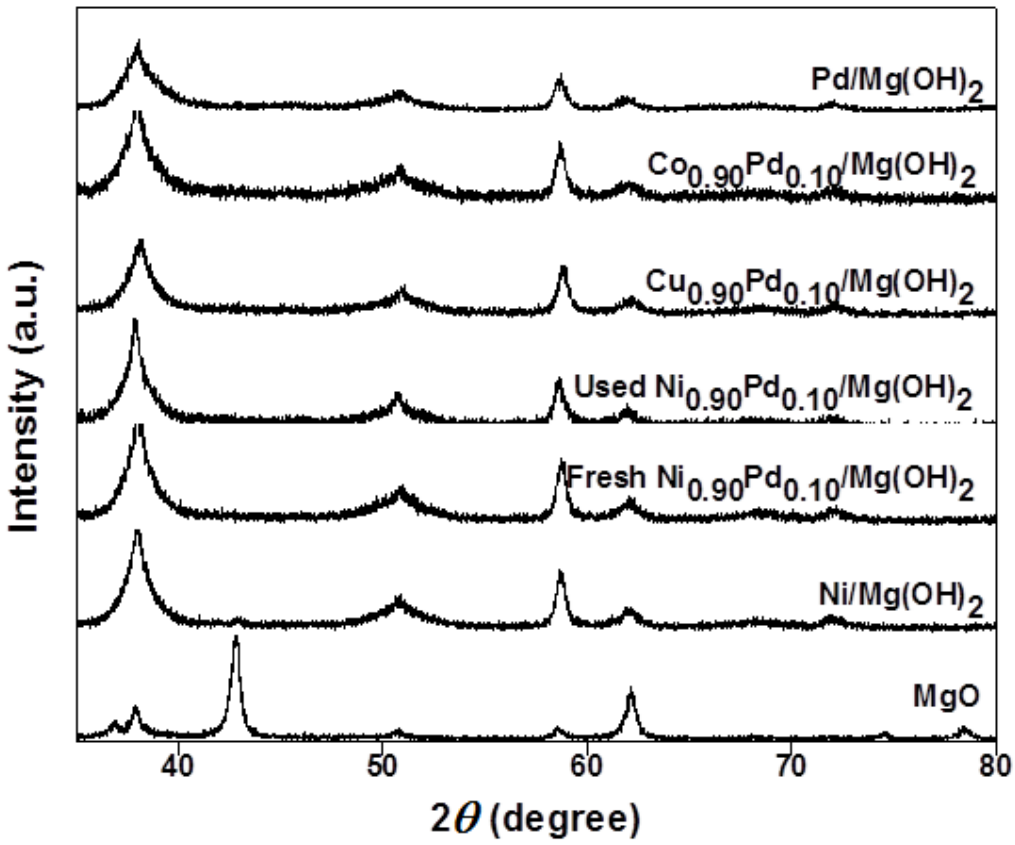


Figure S2 Powder X-ray diffraction pattern of studied $Mg(OH)_2$ supported bimetallic M-Pd (M = Ni, Cu or Co) alloy nanoparticles and monometallic Ni and Pd nanoparticles.

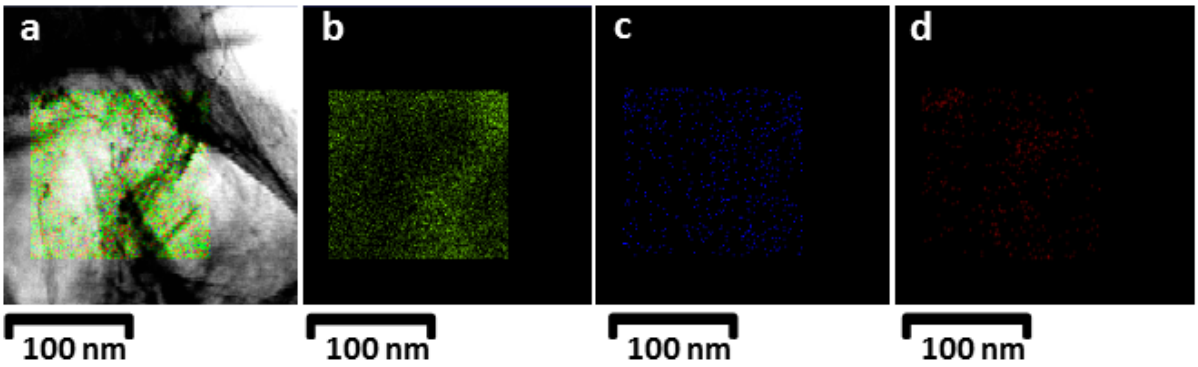


Figure S3 a) FEG-TEM image, b-d) their corresponding EDS elemental mapping showing b) Mg (green), c) Ni (blue) and d) Pd (red) for freshly prepared $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$.

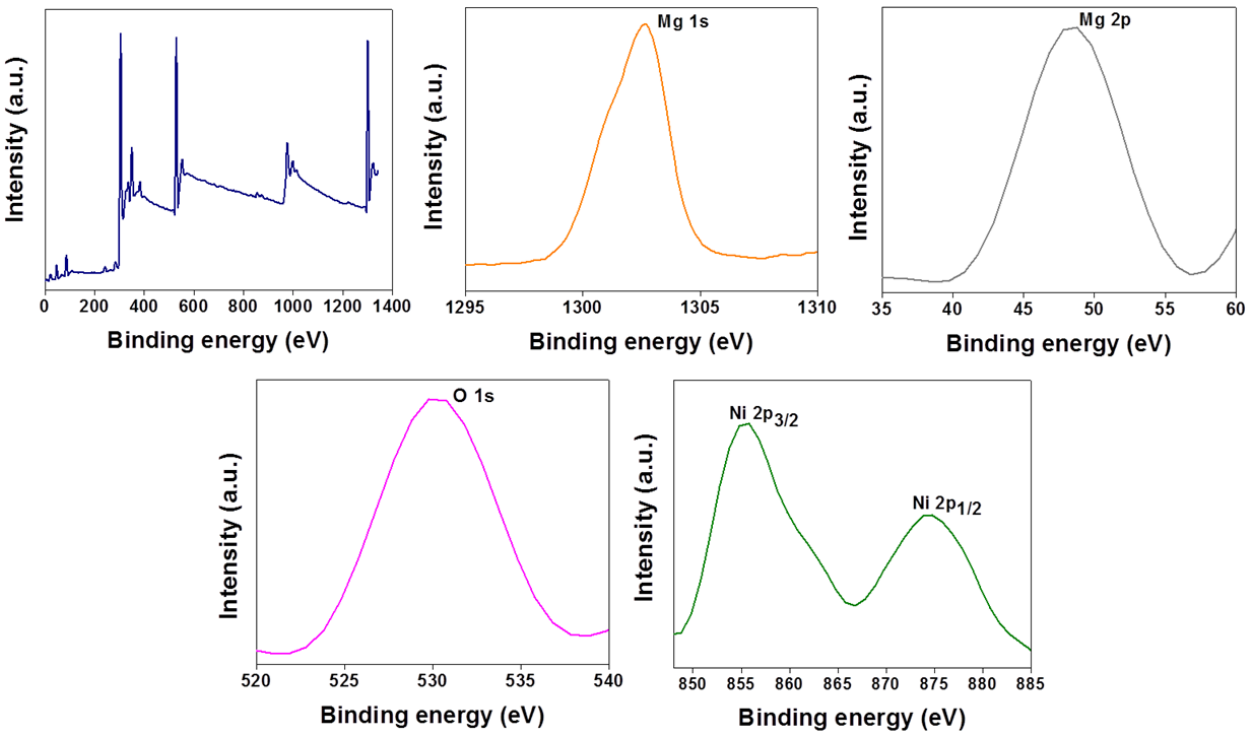


Figure S4 XPS analysis of $Ni_{0.90}$-$Pd_{0.10}/Mg(OH)_2$.

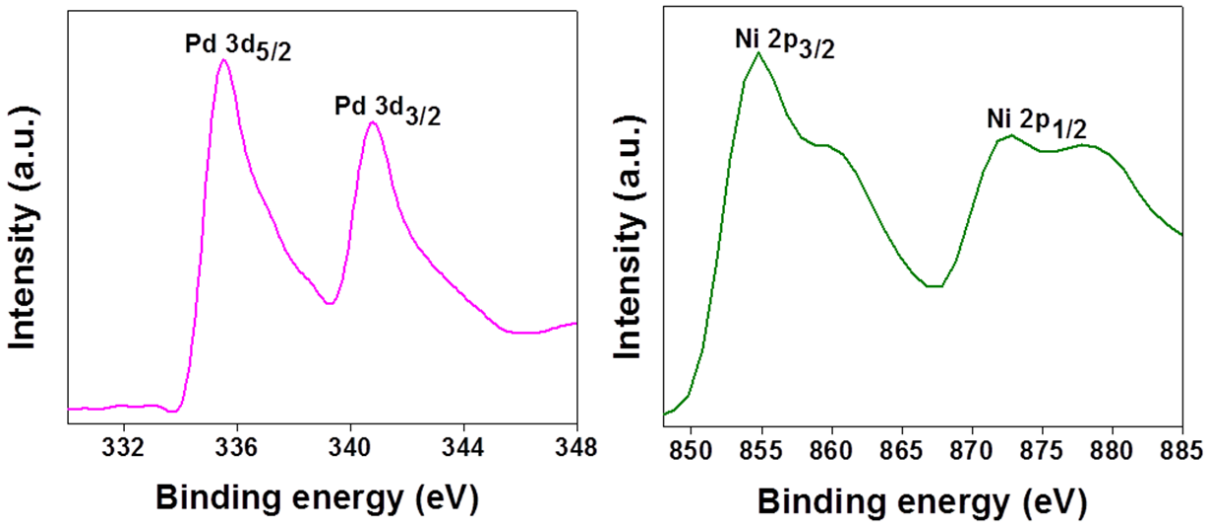


Figure S5 XPS analysis of unsupported bimetallic $Ni_{0.90}$-$Pd_{0.10}$ nanoparticles.

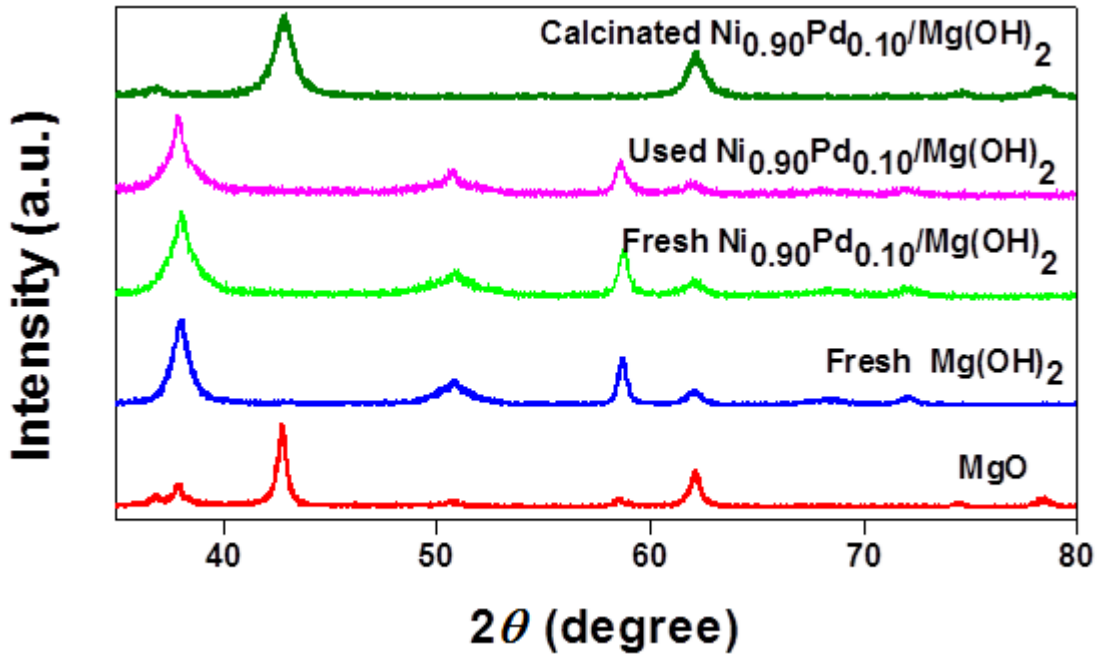


Figure S6 P-XRD analyses for MgO, $Mg(OH)_2$ and $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$.

Formulae for the calculations of Turnover number (TON) and turnover frequency (TOF)

$$\text{TON} = \frac{\text{mmol of product}}{\text{mmol of Pd in catalyst}}$$

$$\text{TOF} = \frac{\text{TON}}{\text{Time}}$$

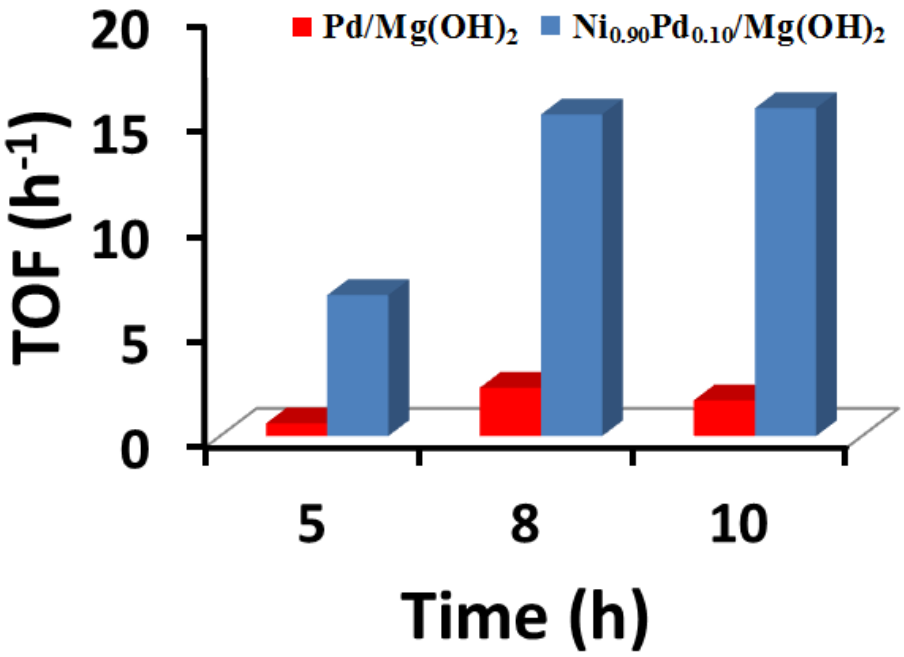


Figure S7 TOF (h^{-1}) for the catalytic oxidation of 5-HMF over $Pd/Mg(OH)_2$ and $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ at different time. TOF are on the basis of Pd content in the catalyst.

Gram-scale catalytic conversion of 5-HMF: A gram-scale oxidation of 5-HMF was achieved in a 100 mL two neck round bottom flask which was charged with 1.008 g (8 mmol) of 5-HMF and freshly prepared $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst (S/C = 40) dispersed in 40 mL water. The whole mixture was stirred in an oil bath at 100 °C with the continuous flow of air for 48 h. After the completion of catalytic reaction, catalyst was recovered from the reaction mixture by centrifugation at 6000 rpm for 10 min. To the reaction mixture 20 mL of brine solution and 40 mL of 1.2M HCl was added and then extracted using diethyl ether (20 x 20 mL). Organic layer was dried over anhydrous Na_2SO_4, filtered off and then solvent was removed under reduced pressure. Purification of FDCA was carried out with column chromatography using a mixture of dichloromethane and methanol, from 99.9:0.1 to 99:1 as an elute.

Poisoning experiment: To confirm the heterogeneity of $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst for the oxidation of 5-HMF, 10 mL aquesous suspension of $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ was stirred for 30 min with 5 mmol of CS_2 at optimized reaction temperature (100 °C), cool and collected by centrifugation at 6000 rpm for 10 min. The recovered $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ was re-dispersed in 10 mL distilled water and used for the oxidation of 5-HMF (1 mmol), under the flow of air at 100 °C for 10 h.

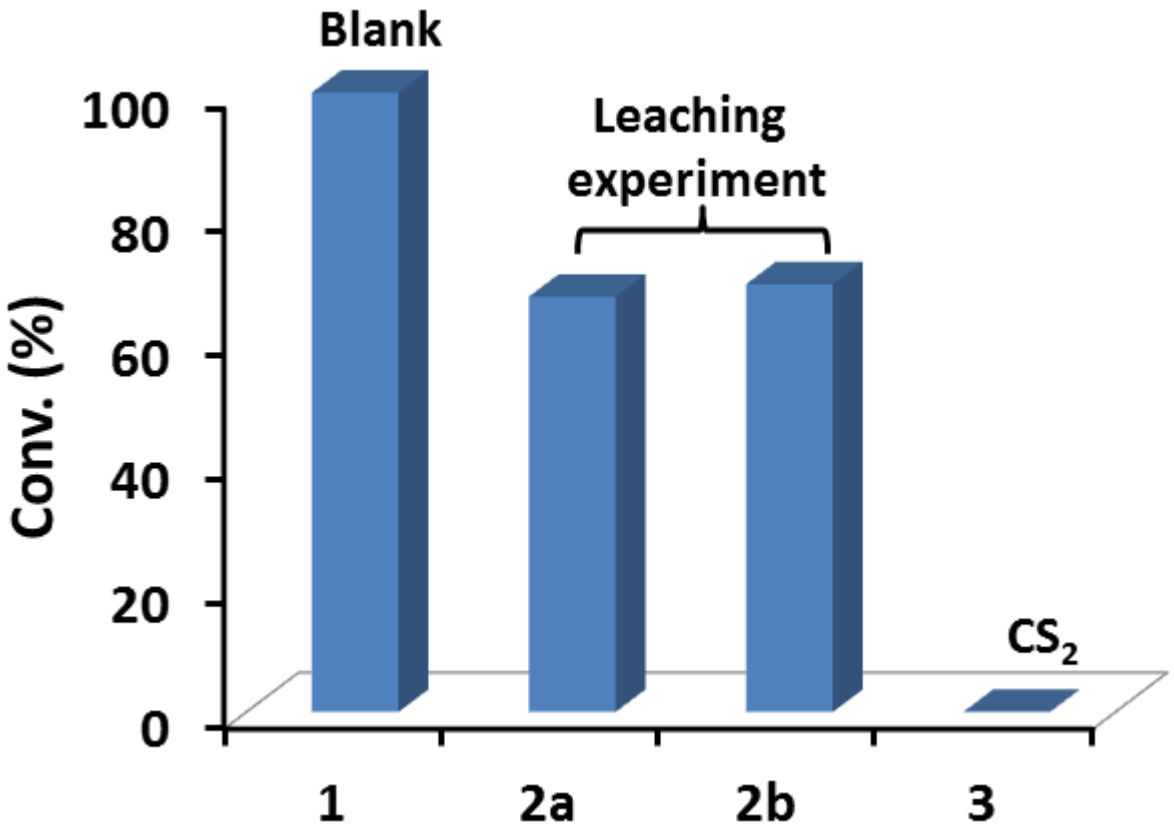


Figure S8 (1) Catalytic aerial oxidation of 5-HMF over $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ at 100 °C for 10 h, optimized reaction conditions. (2a-2b) Leaching experiments: catalytic aerial oxidation of 5-HMF over (2a) $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ at 100 °C for 5 h, and afterwards (2b) reaction mixture was centrifuged to separate the catalyst and reaction was extended for another 5 h at 100°C (without catalyst). (3) CS_2 poisoning experiment.

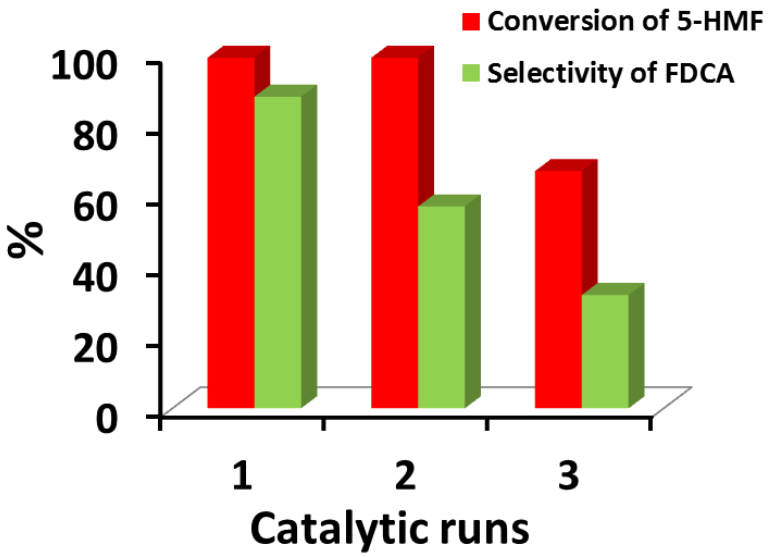
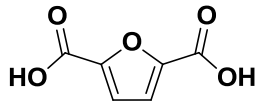


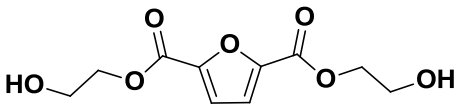
Figure S9 Recyclability of the $Ni_{0.90}Pd_{0.10}/Mg(OH)_2$ catalyst for the oxidation of 5-HMF.

Spectral data of furan-2,5-dicarboxylic Acid (FDCA) transformed by the catalytic aerial oxidation of 5-hydroxymethyl-furfural (5-HMF).

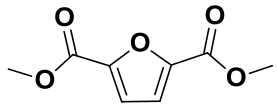


2,5-furandicarboxylic acid: ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.28 (s, 2H), 13.59 (b, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 118.39, 147.01, 158.88. HRMS (ESI) m/z: calculated 154.9975 [$C_6H_4O_5$ – 1H], found 154.9980 [$C_6H_4O_5$ – 1H].

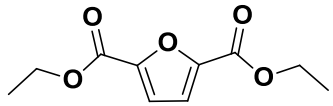
Spectral data of Bis(2-hydroxyethyl)furan-2,5-dicarboxylate and Dialkylfuran-2,5-dicarboxylates synthesized from FDCA (obtained by catalytic aerial oxidation of 5-HMF).



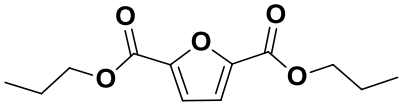
Bis(2-hydroxyethyl)furan-2,5-dicarboxylate: ^{1}H NMR (400 MHz, Acetone-d_6): δ (ppm) = 3.84 (t, 4H, *J* = 4.76 Hz), 4.18 (b, 2H), 4.38 (t, 4H, *J* = 4.76 Hz), 7.34 (s, 2H). ^{13}C NMR (100 MHz, Acetone-d_6): δ (ppm) = 60.54, 67.80, 119.38, 147.74, 158.55. HRMS (ESI) m/z: calculated 267.0475 [$C_{10}H_{12}O_7$ + 1Na], found 267.0483 [$C_{10}H_{12}O_7$ + 1Na].



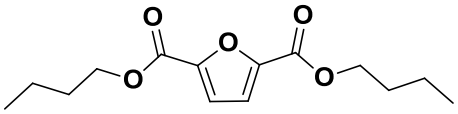
Dimethyl furan-2,5-dicarboxylate: ^{1}H NMR (400 MHz, Acetone-d_6): δ (ppm) = 3.88 (s, 6H), 7.30 (s, 2H). ^{13}C NMR (100 MHz, Acetone-d_6): δ (ppm) = 52.55, 119.26, 147.51, 158.82. HRMS (ESI) m/z: calculated 207.0264 [$C_8H_8O_5$ + 1Na], found 207.0264 [$C_8H_8O_5$ + 1Na].



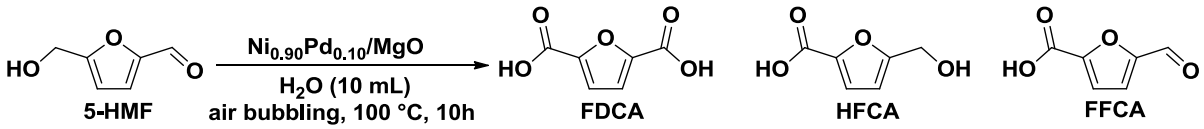
Diethyl furan-2,5-dicarboxylate: ^{1}H NMR (400 MHz, Acetone-d_6): δ (ppm) = 1.34 (t, 6H, *J* = 7.04 Hz), 4.33-4.38 (q, 4H, *J* = 7 Hz), 7.30 (s, 2H). ^{13}C NMR (100 MHz, Acetone-d_6): δ (ppm) = 14.45, 62.00, 119.14, 147.79, 158.41. HRMS (ESI) m/z: calculated 235.0577 [$C_{10}H_{12}O_5$ + 1Na], found 235.0586 [$C_{10}H_{12}O_5$ + 1Na].

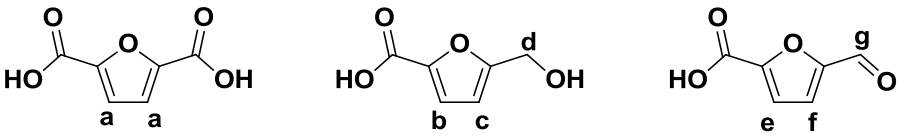


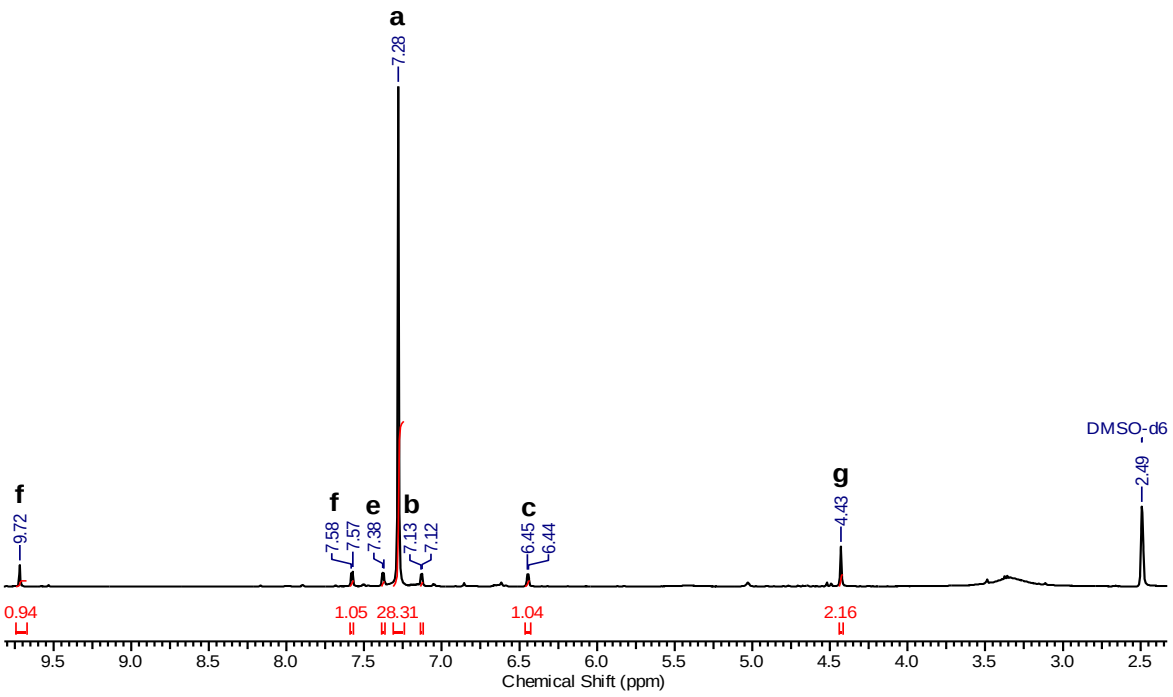
Dipropyl furan-2,5-dicarboxylate: ^{1}H NMR (400 MHz, Acetone-d_6): δ (ppm) = 0.98 (t, 6H, *J* = 7.24 Hz), 1.71-1.80 (m, 4H), 4.27 (t, 4H, *J* = 6.52 Hz), 7.31 (s, 2H). ^{13}C NMR (100 MHz, Acetone-d_6): δ (ppm) = 10.50, 22.63, 67.40, 119.14, 147.77, 158.47. HRMS (ESI) m/z: calculated 263.0890 [$C_{12}H_{16}O_5$ + 1Na], found 263.0890 [$C_{10}H_{12}O_5$ + 1Na].



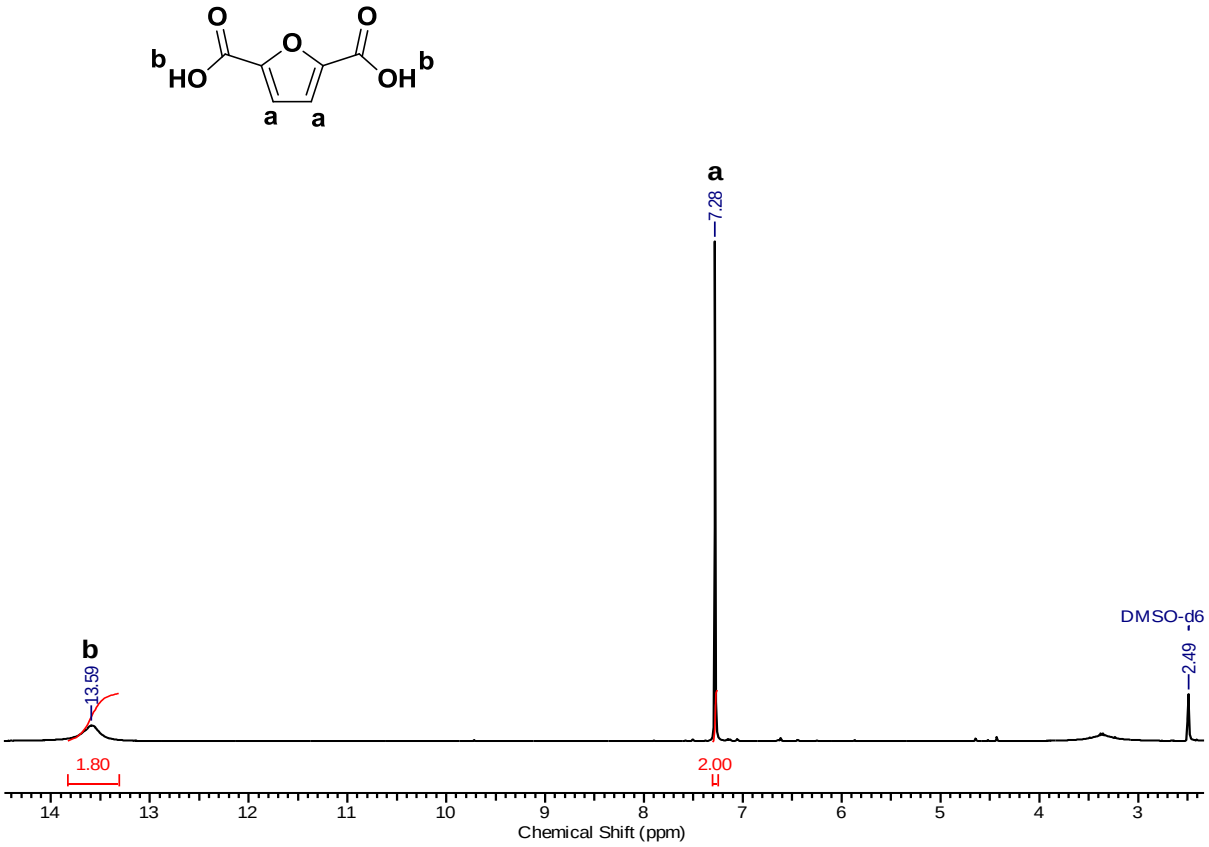
Dibutyl furan-2,5-dicarboxylate: ^{1}H NMR (400 MHz, Acetone-d_6): δ (ppm) = 0.95 (t, 6H, *J* = 7.28 Hz), 1.40-1.49 (m, 4H), 1.69-1.76 (m, 4H), 4.31 (t, 4H, J = 6.8 Hz), 7.31 (s, 2H). ^{13}C NMR (100 MHz, Acetone-d_6): δ (ppm) = 13.90, 19.71, 31.36, 65.72, 119.14, 147.80, 158.47. HRMS (ESI) m/z: calculated 291.1203 [$C_{14}H_{20}O_5$ + 1Na], found 291.1195 [$C_{10}H_{12}O_5$ + 1Na].



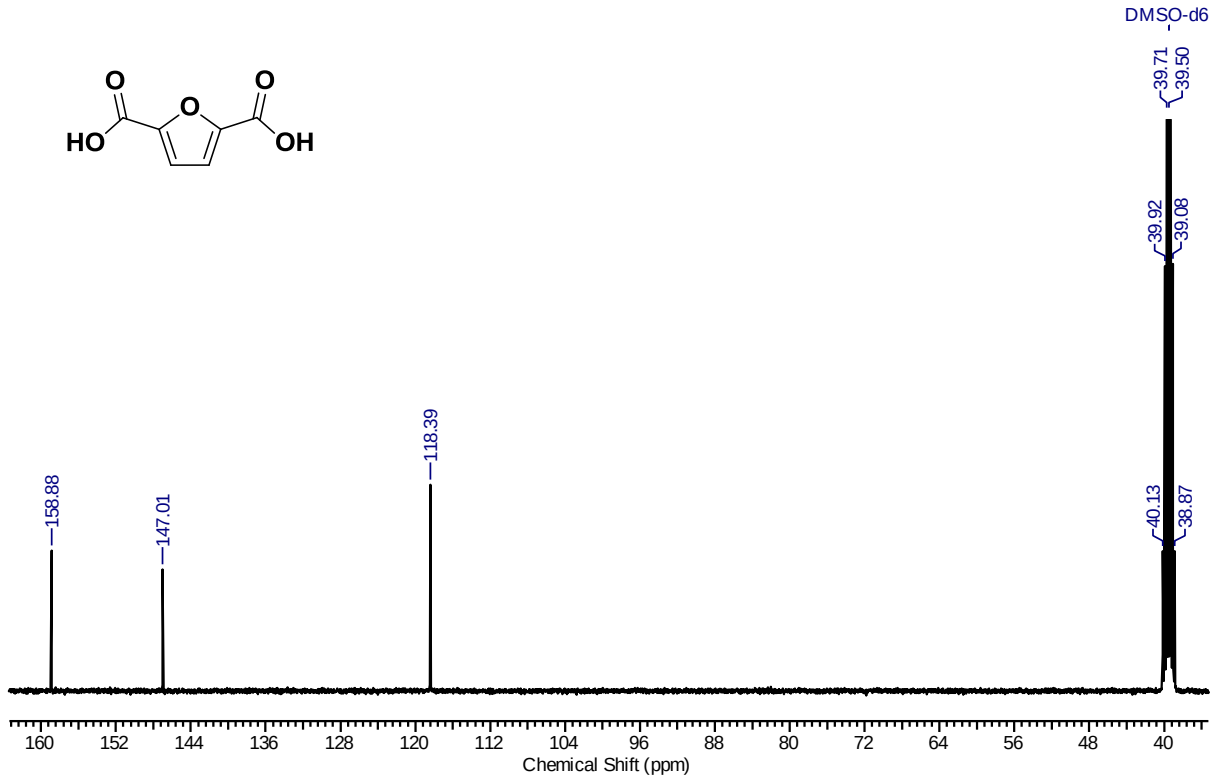




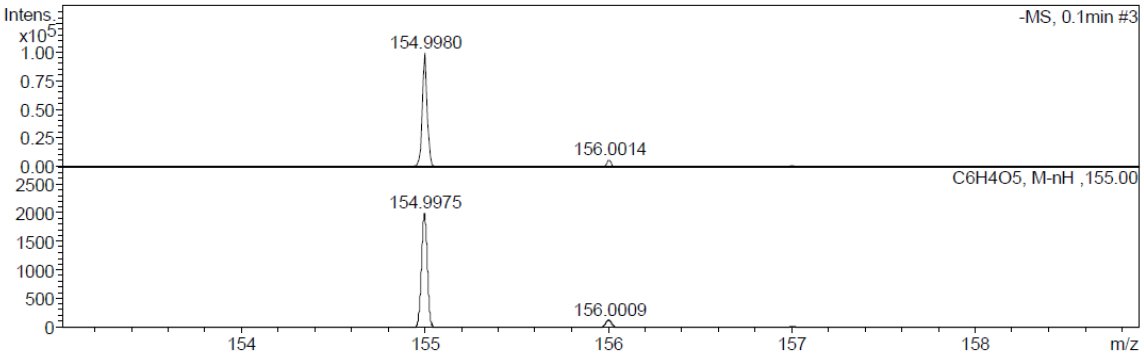
^{1}H NMR spectrum for carboxylic acids produced by the catalytic oxidation of 5-HMF in DMSO-d_6.



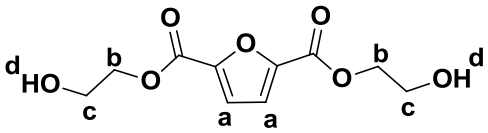
^{1}H NMR spectrum of purified 2,5-furandicarboxylic acid (FDCA) in DMSO-d_6.

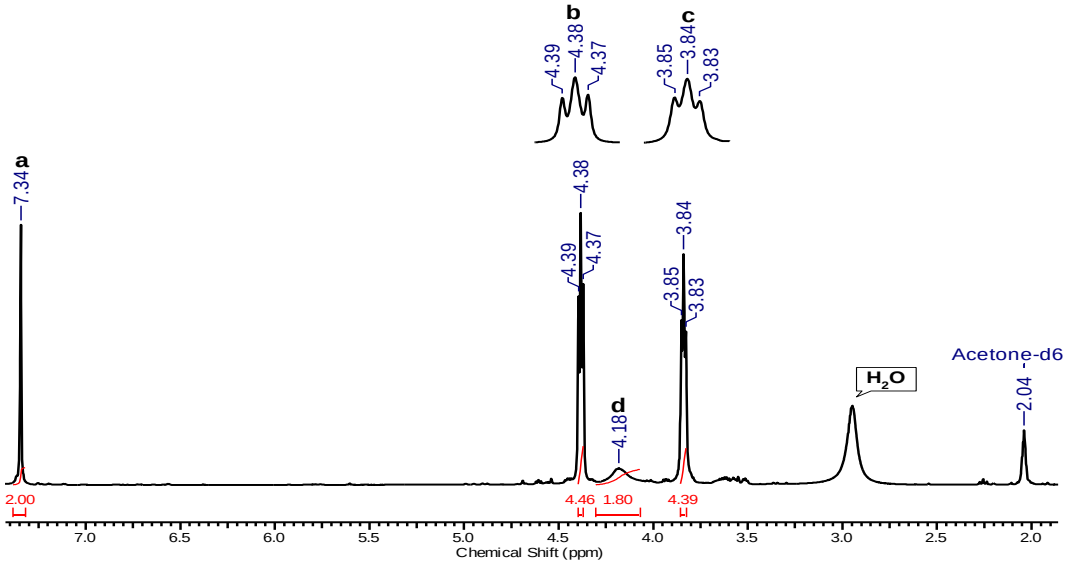


^{13}C NMR spectrum of purified 2,5-furandicarboxylic acid (FDCA) in DMSO-d_6.

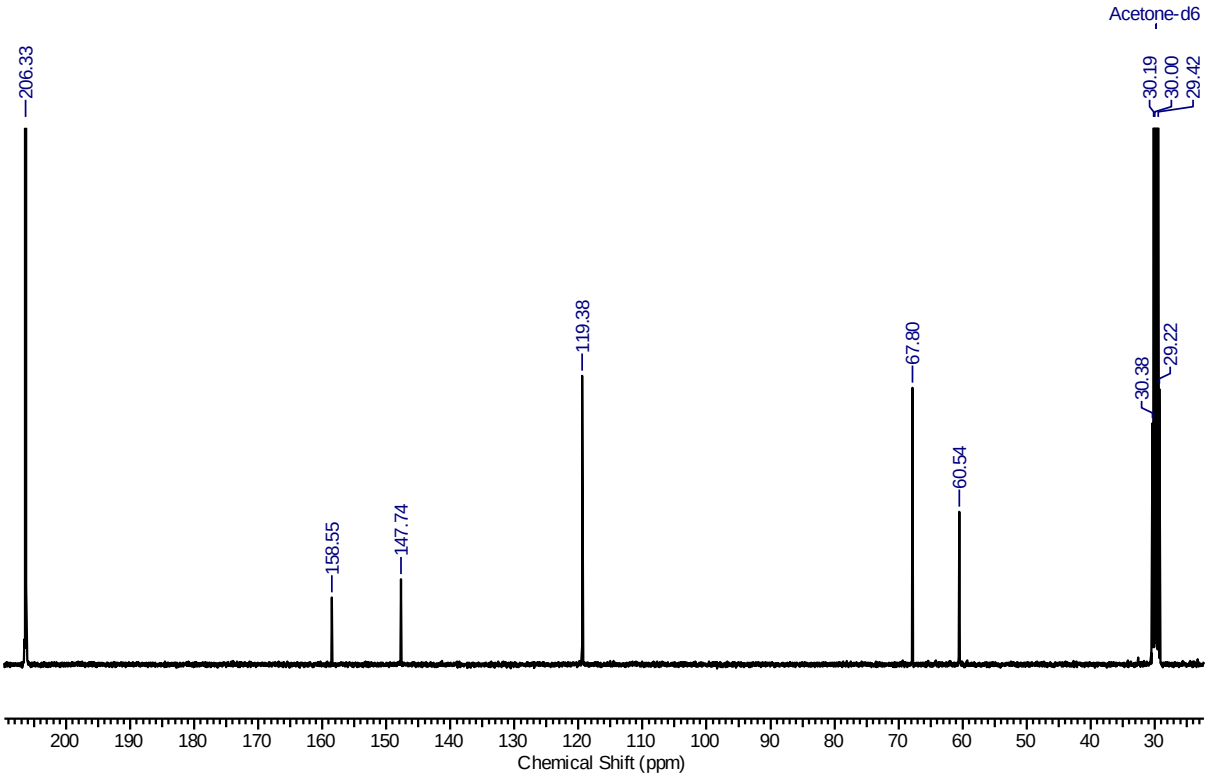


HRMS spectrum of purified 2,5-furandicarboxylic acid (FDCA).

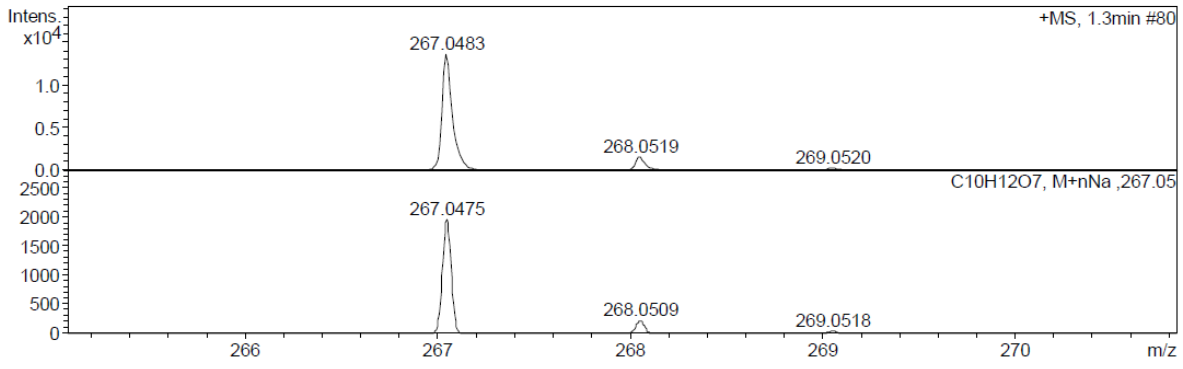




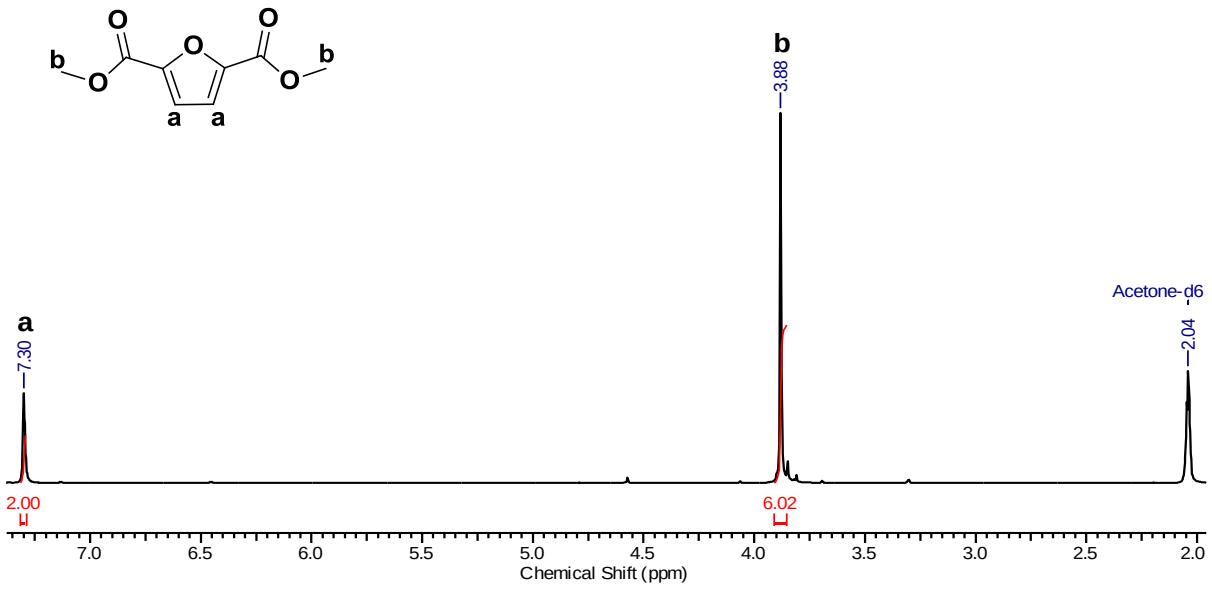
^{1}H NMR spectrum of bis(2-hydroxyethyl)furan-2,5-dicarboxylate in Acetone-d_6.



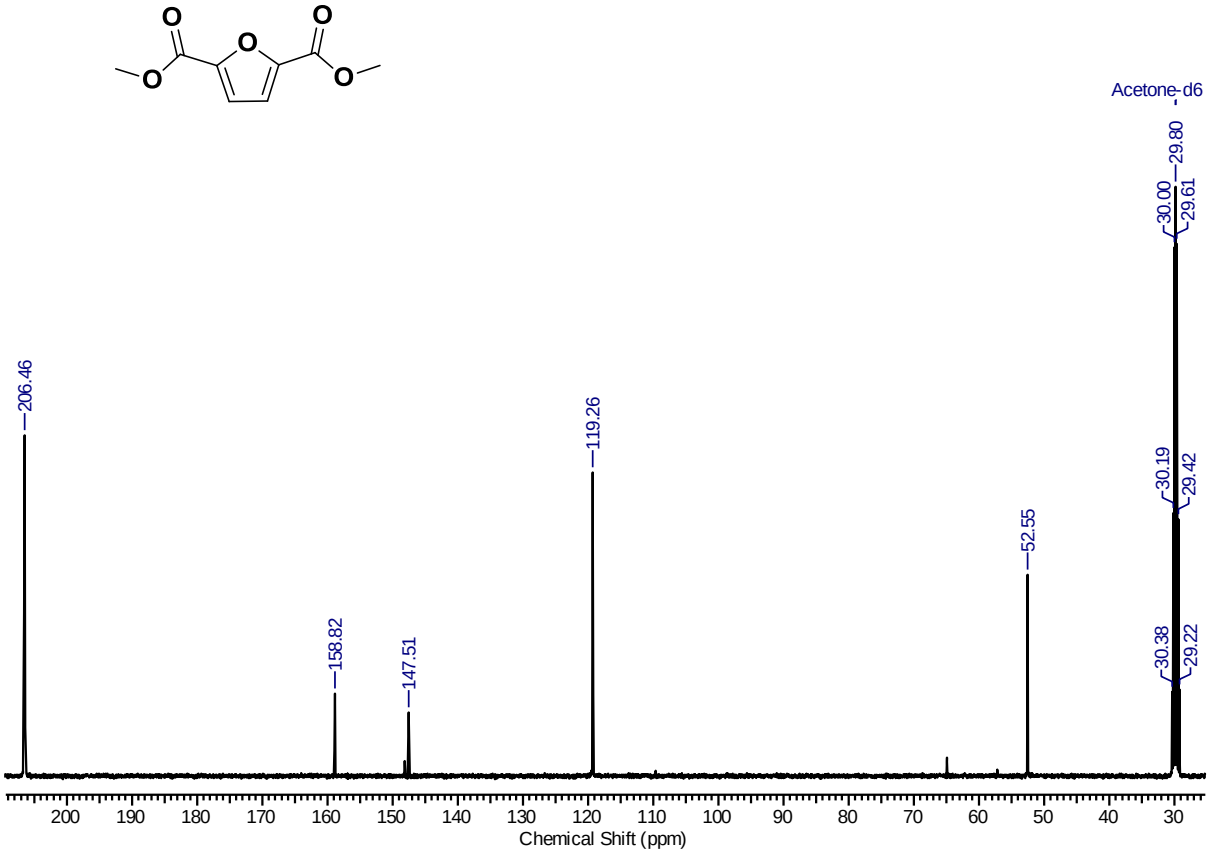
^{13}C NMR spectrum of bis(2-hydroxyethyl)furan-2,5-dicarboxylate in Acetone-d_6.



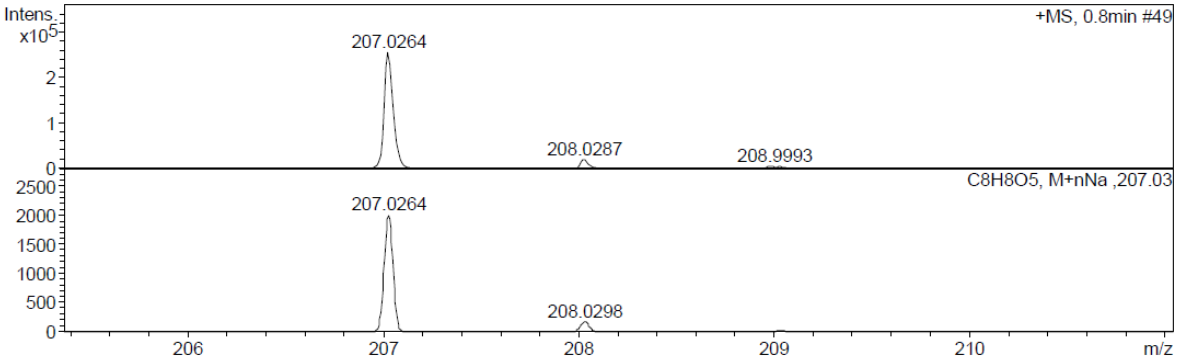
HRMS spectrum of bis(2-hydroxyethyl)furan-2,5-dicarboxylate.



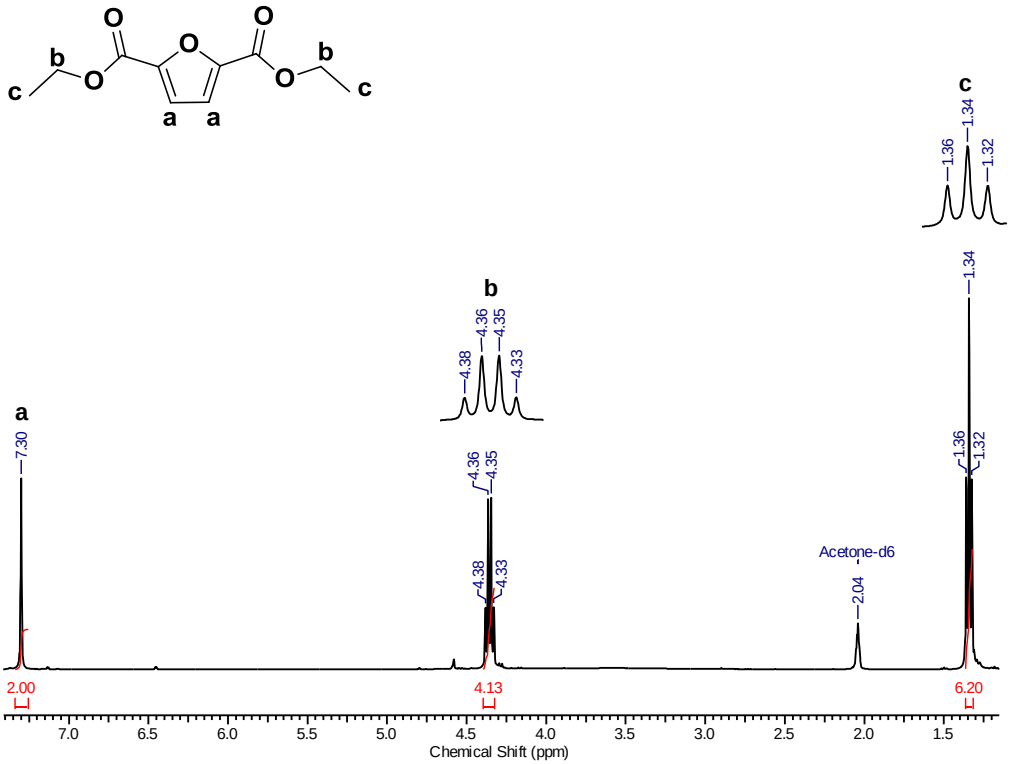
^{1}H NMR spectrum of Dimethyl furan-2,5-dicarboxylate in Acetone-d_6.



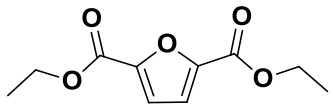
^{13}C NMR spectrum of Dimethyl furan-2,5-dicarboxylate in Acetone-d_6.

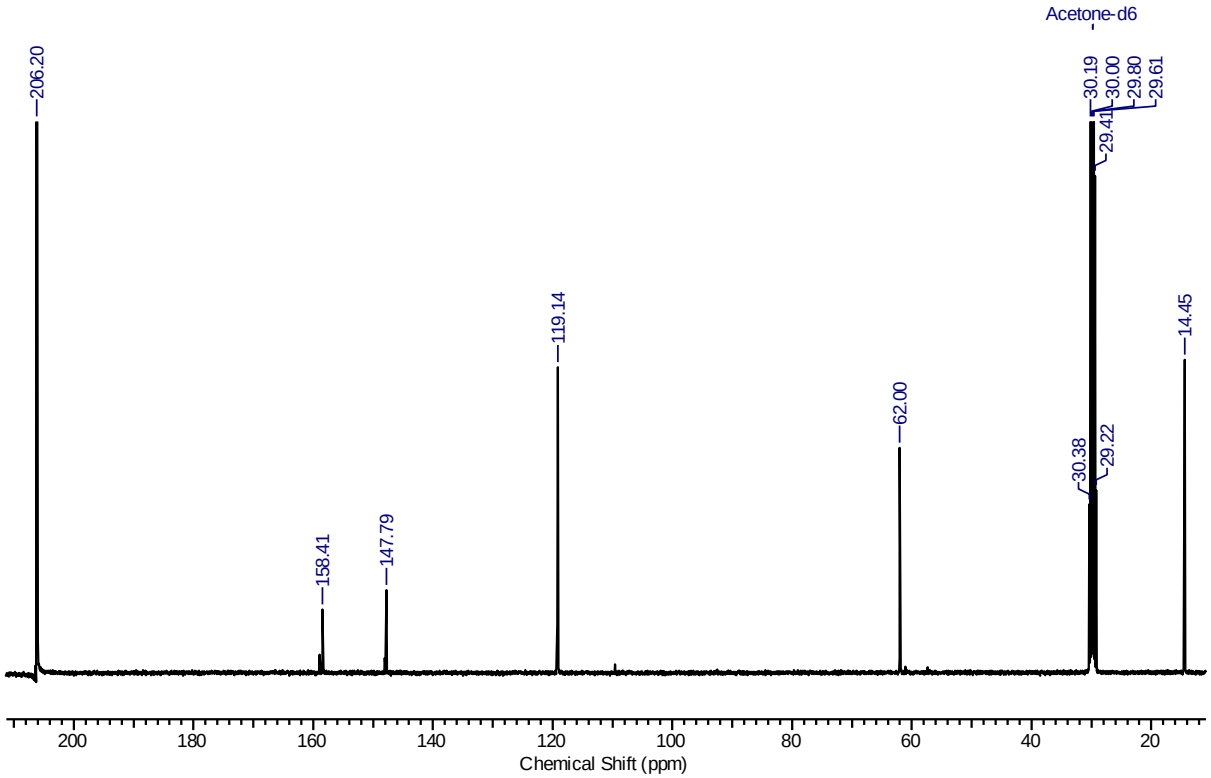


HRMS of Dimethyl furan-2,5-dicarboxylate.

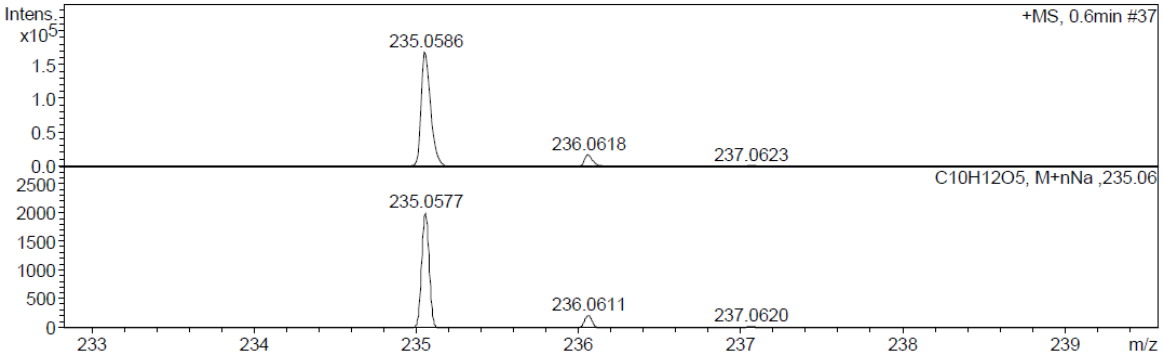


^{1}H NMR spectrum of Diethyl furan-2,5-dicarboxylate in Acetone-d_6.

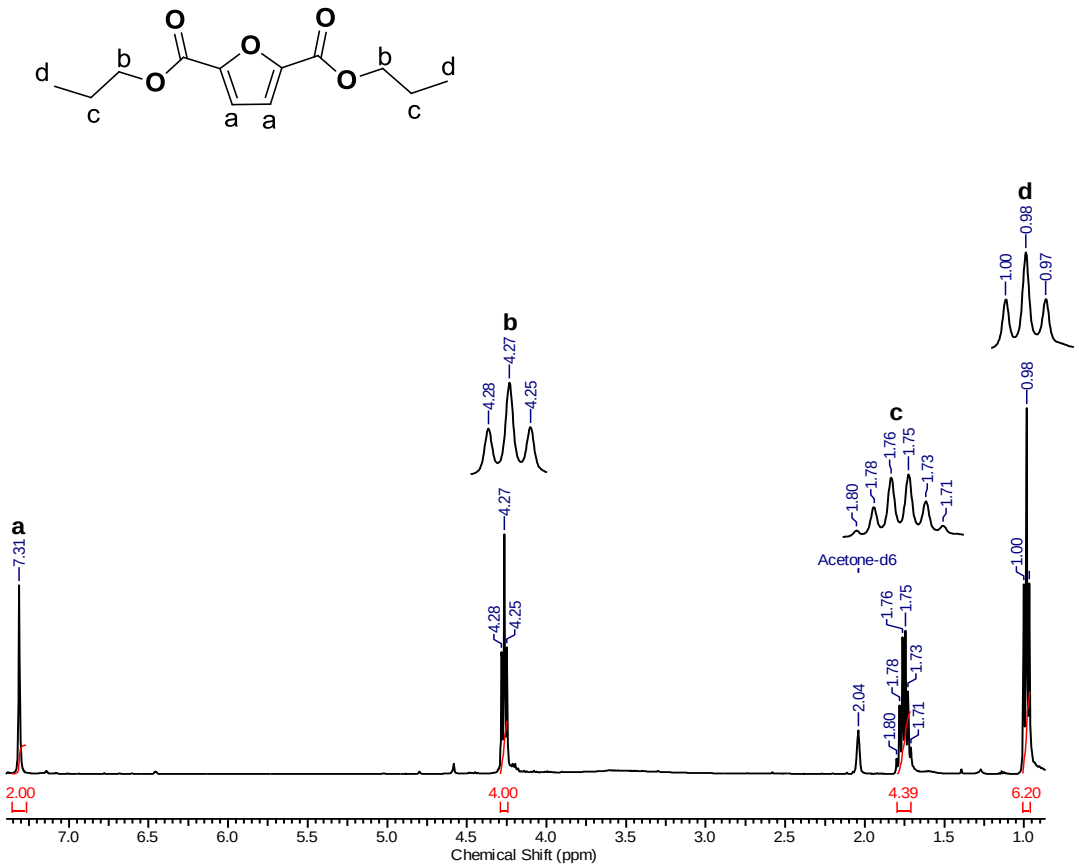




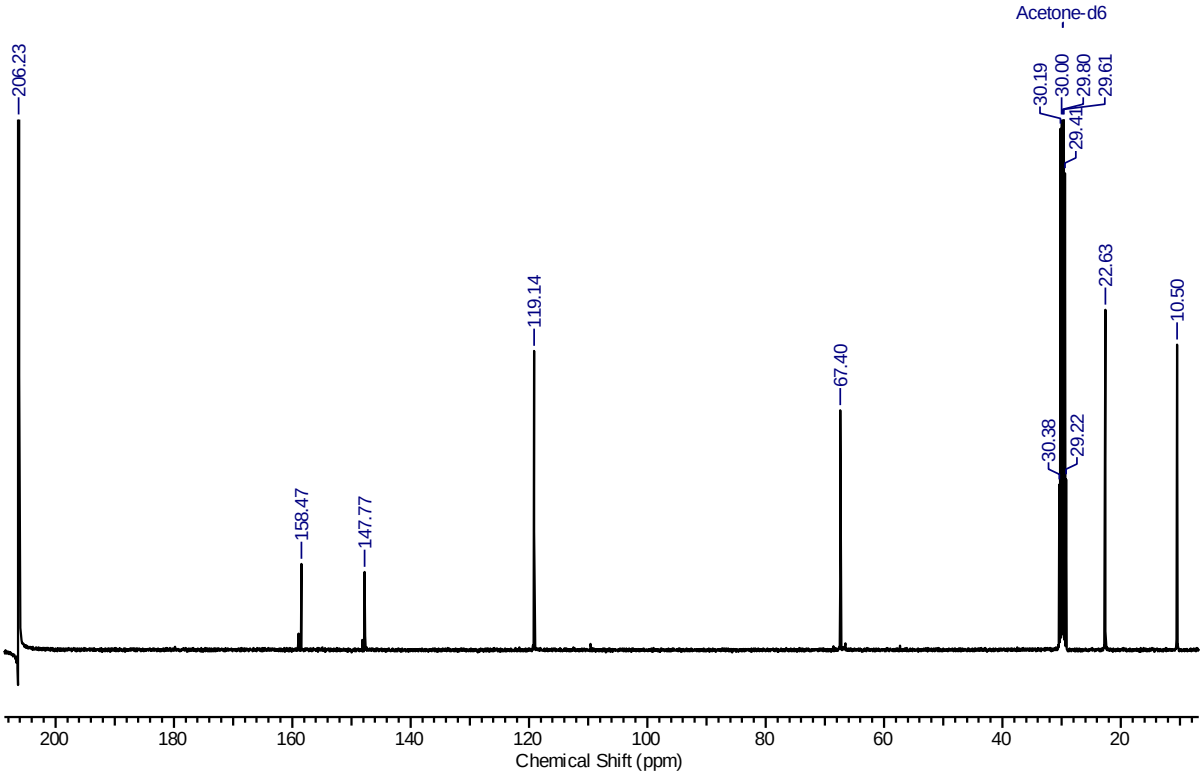
^{13}C NMR spectrum of Diethyl furan-2,5-dicarboxylate in Acetone-d_6.



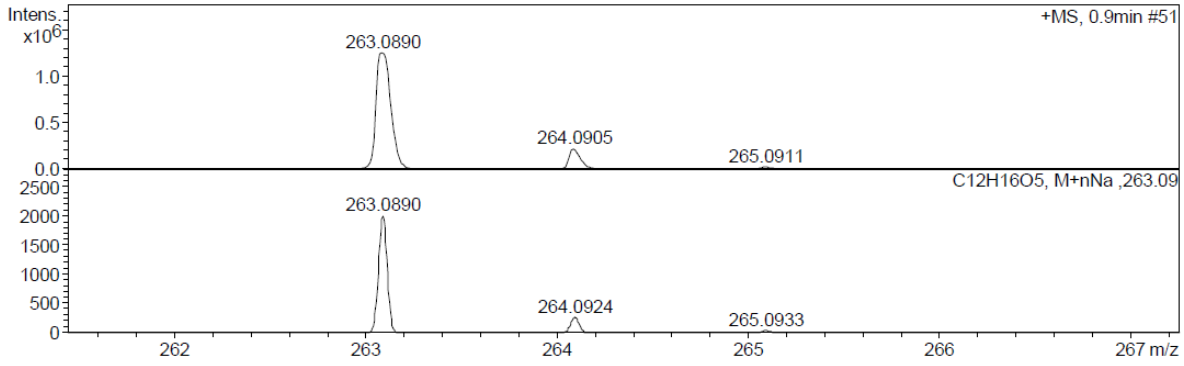
HRMS of Diethyl furan-2,5-dicarboxylate.



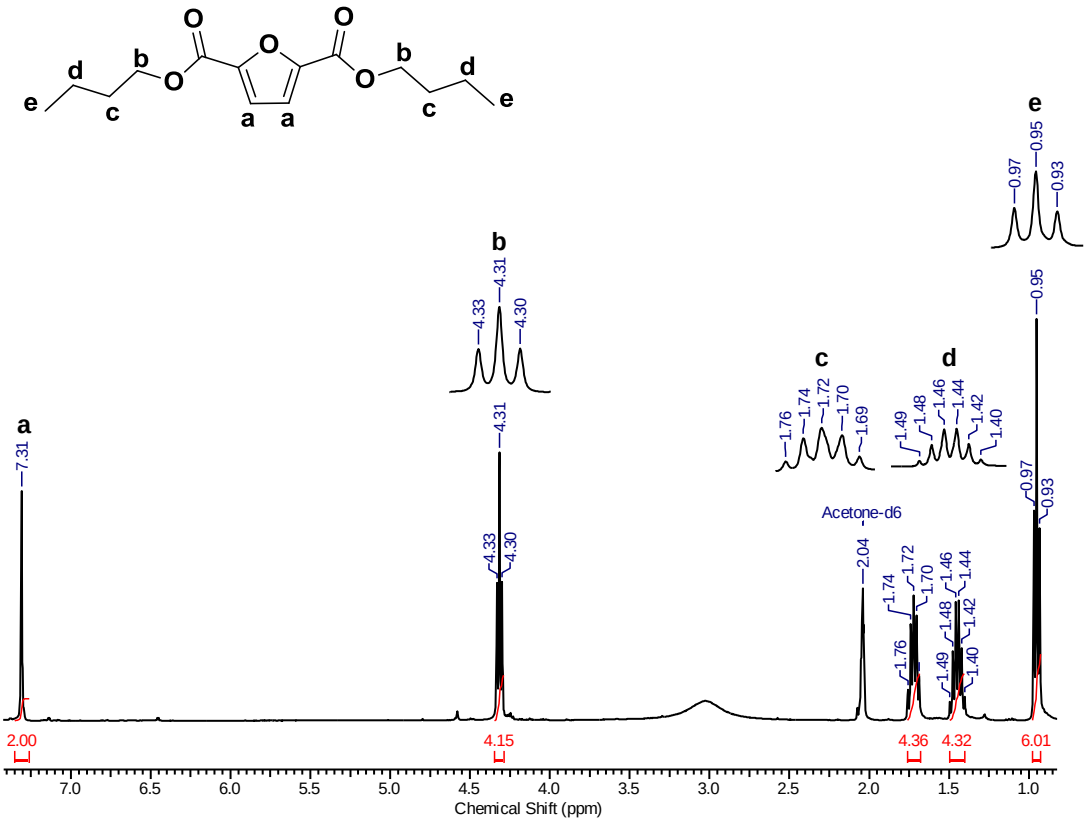
^{1}H NMR spectrum of Dipropyl furan-2,5-dicarboxylate in Acetone-d_6.



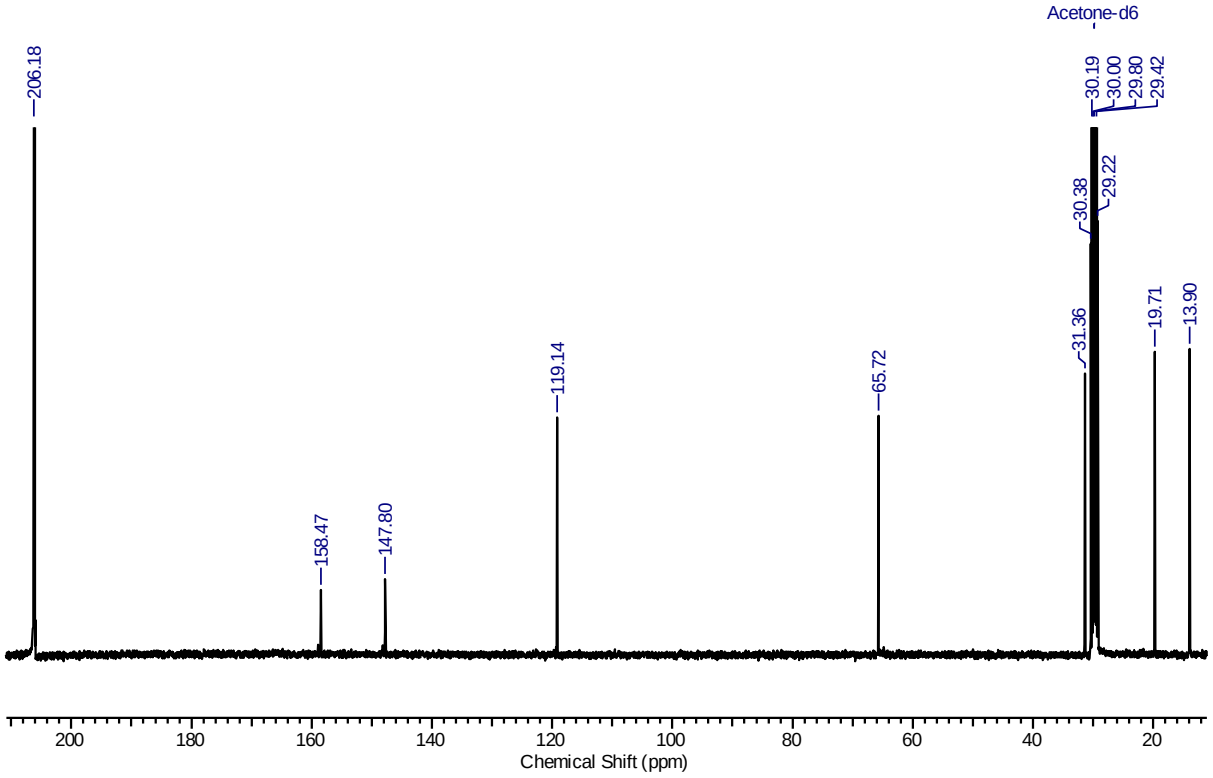
^{13}C NMR spectrum of Dipropyl furan-2,5-dicarboxylate in Acetone-d_6.



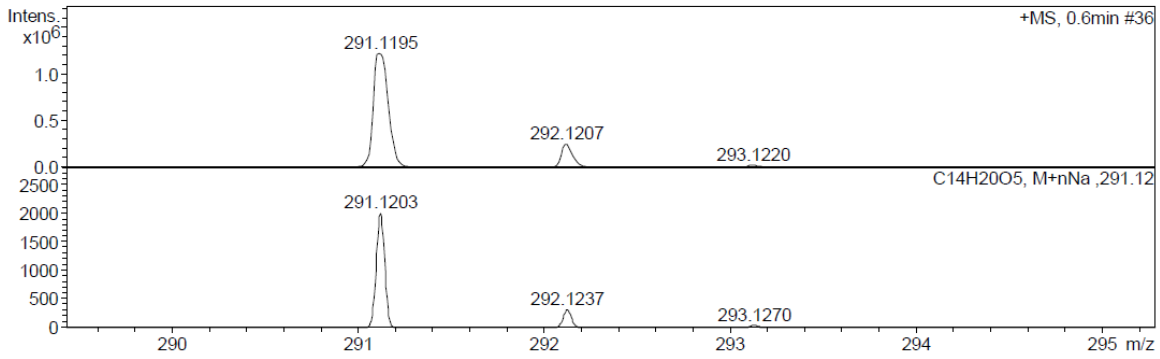
HRMS of Dipropyl furan-2,5-dicarboxylate.



^{1}H NMR spectrum of Dibutyl furan-2,5-dicarboxylate in Acetone-d_6.



^{13}C NMR spectrum of Dibutyl furan-2,5-dicarboxylate in Acetone-d_6.



HRMS of Dibutyl furan-2,5-dicarboxylate.