Supporting information

Friedel-Crafts Alkylation over Zr-Mont Catalyst for the Production of Diesel Fuel Precursors

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Content

1. Catalyst Characterisation

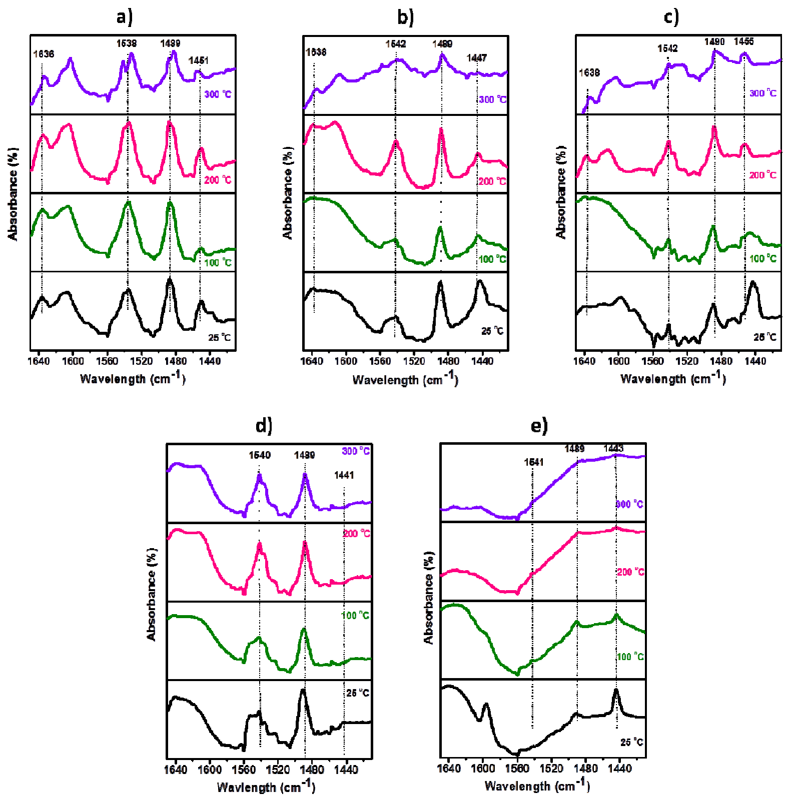


Figure S1. Py-FTIR of a) Sn-Mont, b) Zr-Mont, c) Al-Mont, d) Fe-Mont and e) Mont evacuated at different temperatures.

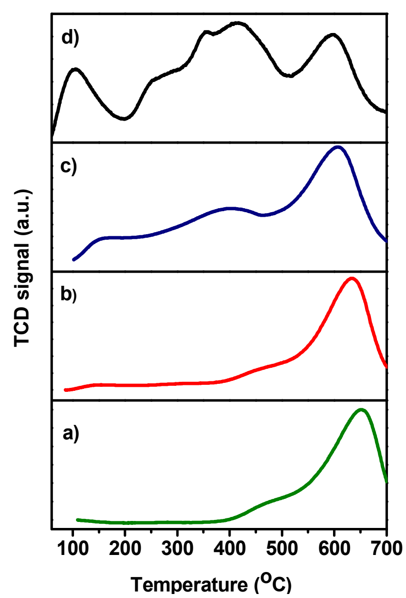


Figure S2. NH_3-TPD of a) Fe-Mont, b) Al-Mont, c) Zr-Mont and d) Sn-Mont

2. Experimental procedure for synthesis of HMF derivatives

1.1 Synthesis of 5-(formyloxymethyl)furfural from HMF

In a typical experiment[1], mixture of HMF (0.2 g) and formic acid (98%, 10 mL) was stirred at room temperature for 3 h. After completion of reaction it was neutralized with saturated solution of $NaHCO_3$. Further reaction mixture diluted with ethyl acetate (20 mL) and washed with water (10 mL x 1), brine (10 mL x 1). The organic layer was finally dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Residue was purified using column chromatography by eluating in ethyl acetate: pet ether (90: 10) mobile phase. After purification yellow oil of 5-(formyloxymethyl)furfural (0.212 g, 87%) was obtained.

1.2 Synthesis of 5-(acetyloxymethyl)furfural from HMF

In a typical experiment, mixture of HMF (0.2 g) and acetic acid (98%, 10 mL) was stirred at 50 °C for 4 h. After completion of reaction, it was neutralized with saturated solution of $NaHCO_3$. Further reaction mixture diluted with ethyl acetate (20 mL) and washed with water (10 mL x 1), brine (10 mL x 1). The organic layer was finally dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. Residue was purified using column chromatography by eluating in ethyl acetate: pet ether (90: 10) mobile phase. After purification yellow oil of 5-(acetoxymethyl)furfural (0.218 g, 82%) was obtained.

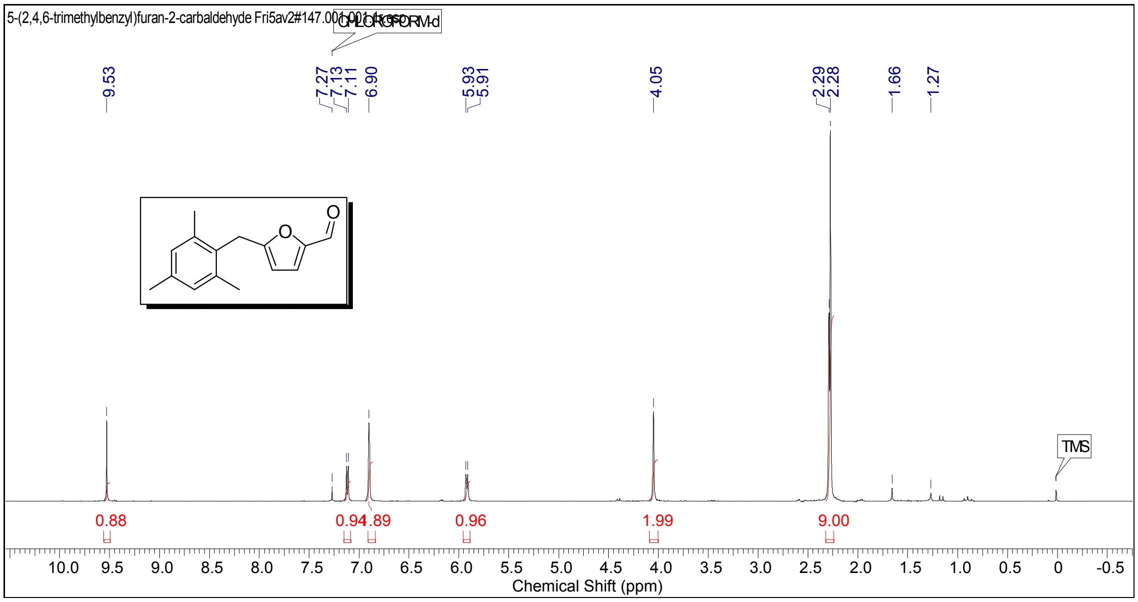
1.3 Synthesis of 5-(chloromethyl)furfural from HMF

In typical experiment[2], HMF (0.252 g, 2 mmol) was dissolved in CH_2Cl_2 (10 mL) and HCl (aq. 37%, 5 mL) was added drop wise. Biphasic reaction mixture was stirred at room temperature for 24 h, then organic layer was separated, and acidic fraction was extracted with CH_2Cl_2 (3 x 20 mL). Organic fractions were combined, dried over Na_2SO_4, and evaporated. Residue was purified by filtering through short silica gel column (ethyl acetate: pet ether, 90:10) to yield, 0.23 g (80%) as yellowish crystals.

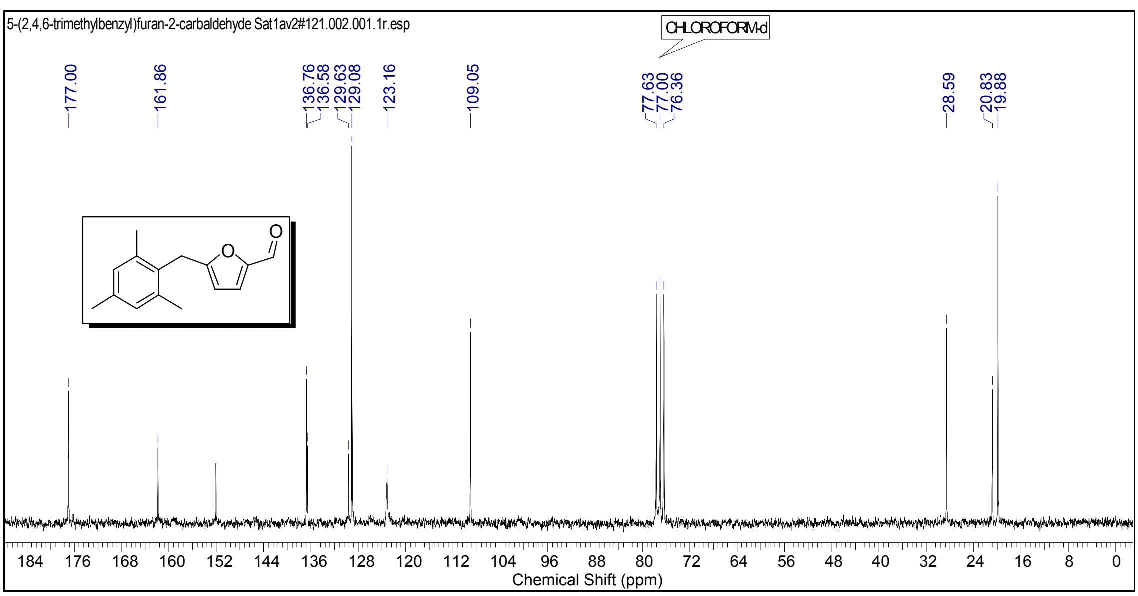
1.4 Synthesis of 5-(bromomethyl)furfural from HMF

In a typical experiment[2], HMF (0.252 g, 2 mmol) was dissolved in 1,2-dichloroethane (7 mL) and HBr (aq. 48%, 7 mL) was added drop wise. Biphasic reaction mixture was stirred at room temperature for 24 h, then organic layer was separated, and acidic fraction was extracted with CH_2Cl_2 (3 x 20 mL). Organic fractions were combined, dried with Na_2SO_4, and evaporated. Residue was purified by filtering through short silica gel column (ethyl acetate: pet ether, 90:10) to yield, 0.319 g (85%) as yellowish crystals.

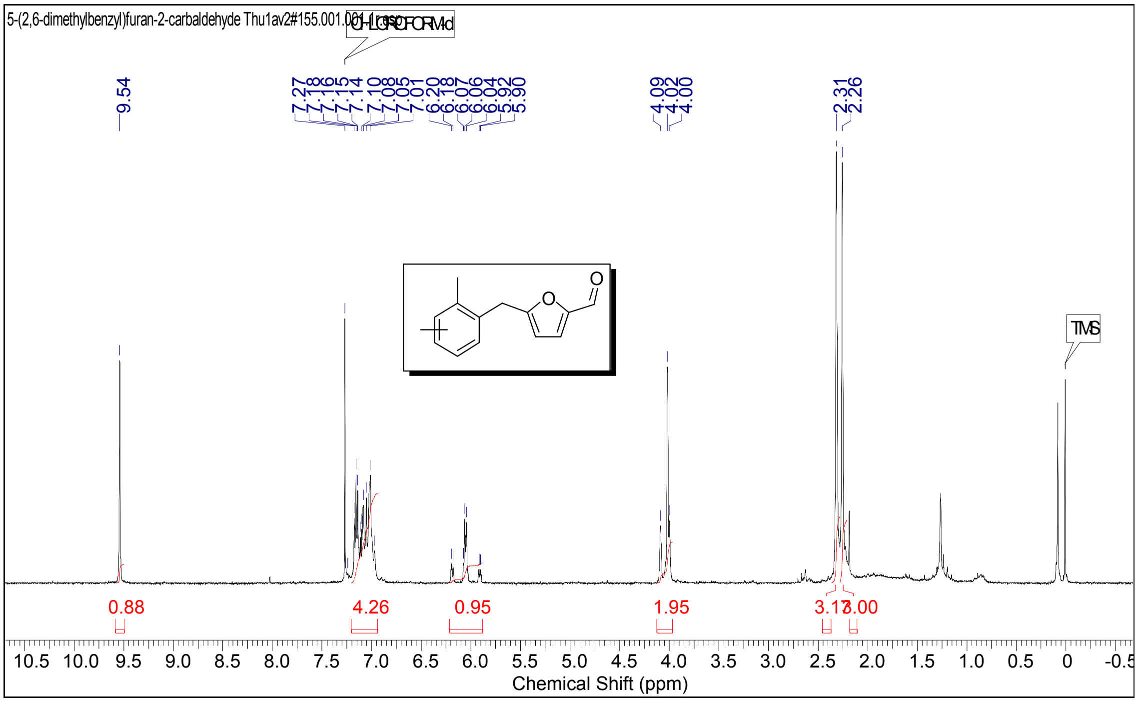
3. Characterisation of pure products: ^{1} H NMR and ^{13} C NMR



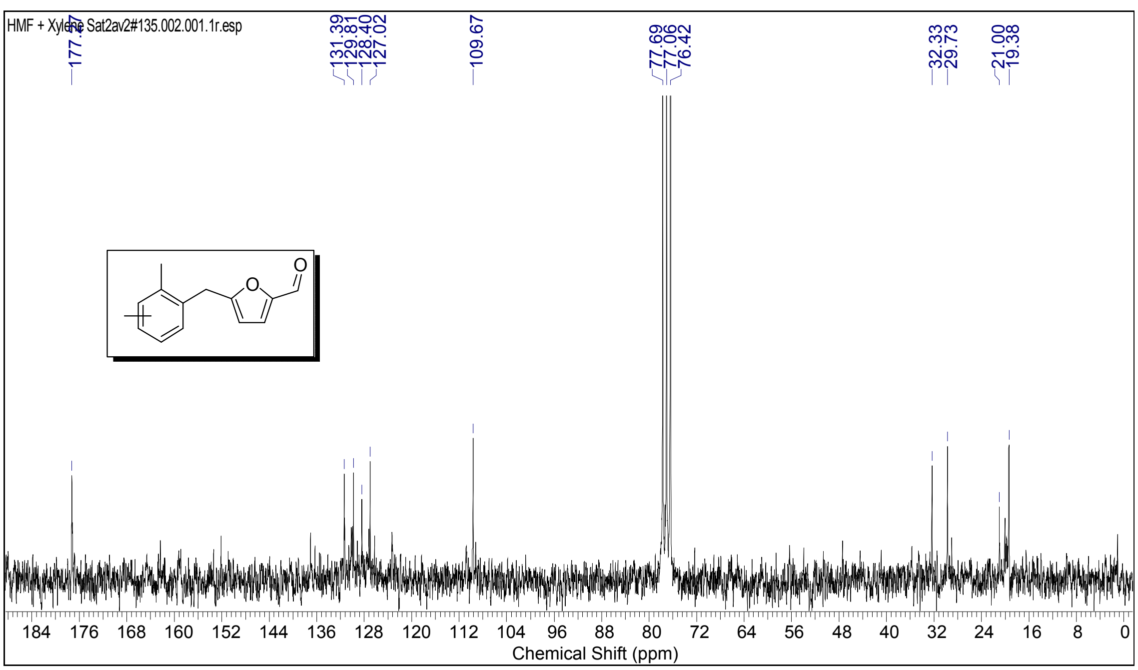
5-(2,4,6-trimethylbenzyl)furan-2-carbaldehyde: ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 2.28 - 2.29 (m, 9 H) 4.05 (s, 2 H) 5.91-5.93 (d, *J*=3.54 Hz, 1 H) 6.90 (s, 2 H) 7.11-7.13 (d, *J*=3.54 Hz, 1 H) 9.53 (s, 1 H)



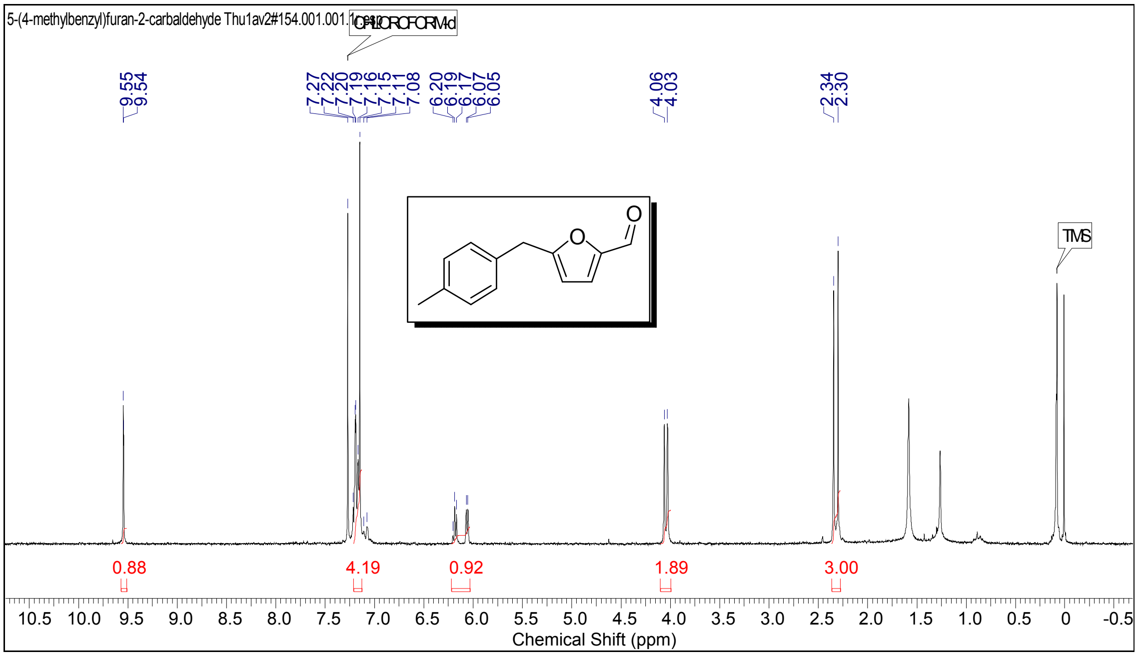
5-(2,4,6-trimethylbenzyl)furan-2-carbaldehyde: ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 19.88, 20.83, 28.59, 109.05, 123.16, 129.08, 129.63, 136.58, 136.76, 161.86, 177.00



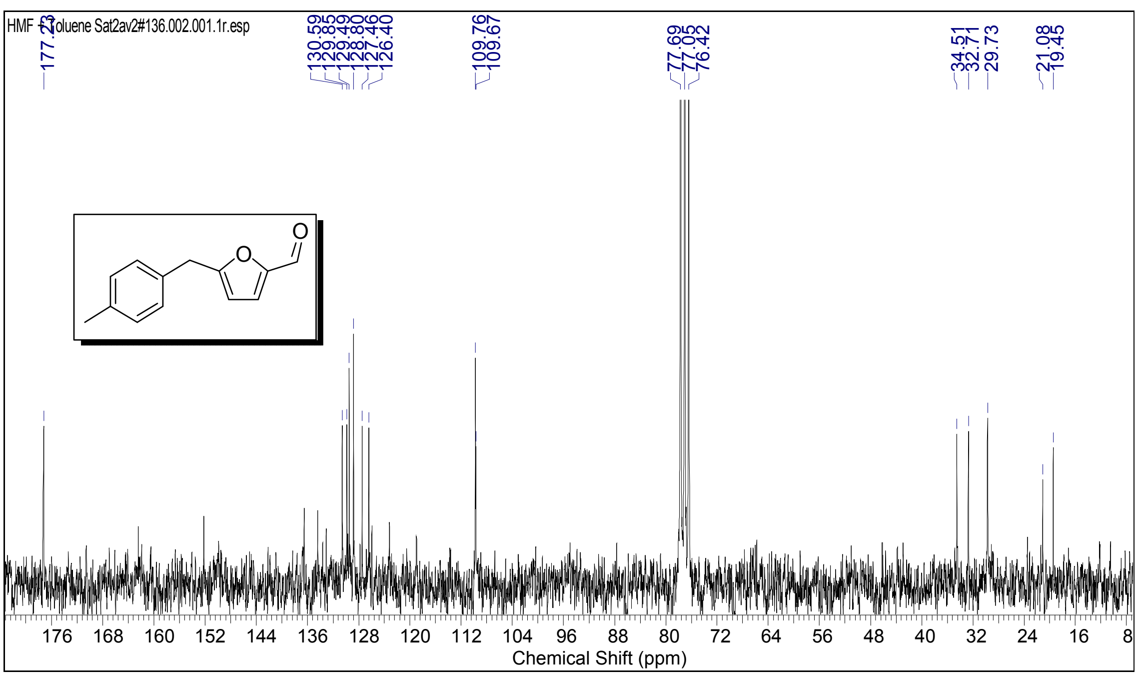
5-(2, 6-dimethylbenzyl)furan-2-carbaldehyde: ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 2.26 (s, 3 H) 2.31 (s, 3 H) 4.00 - 4.09 (m, 2 H) 5.90 - 6.20 (m, 1 H) 6.97 - 7.18 (m, 5 H) 9.54 (s, 1 H)



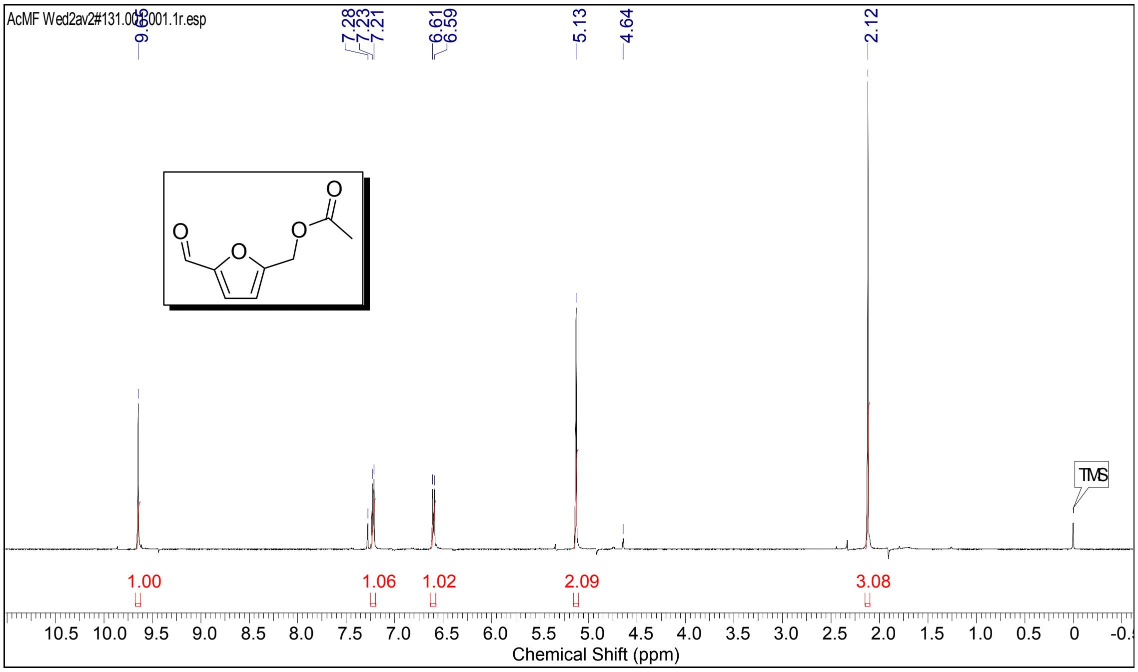
5-(2, 6-dimethylbenzyl)furan-2-carbaldehyde: ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 19.38, 21.00, 29.73, 32.33, 109.67, 127.02, 128.40, 129.81, 131.39, 177.27



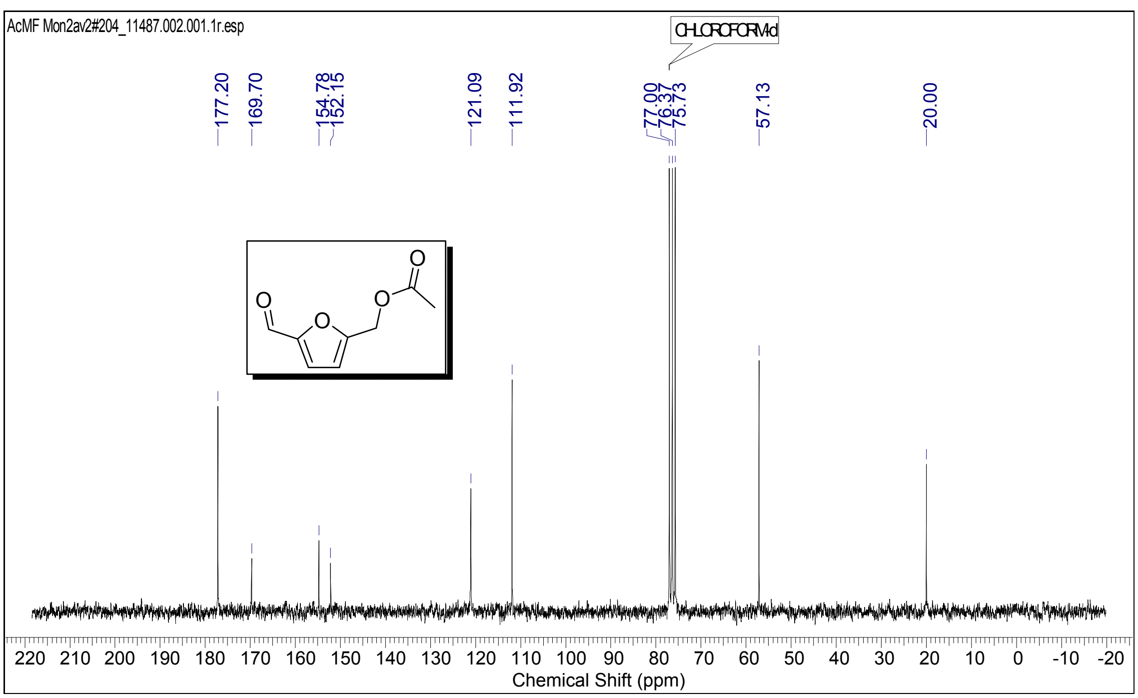
5-(4-methylbenzyl)furan-2-carbaldehyde: ^{1}H NMR (200 MHz, CHLOROFORM-*d*) δ ppm 2.30-2.34 (d, *J*=8.97 Hz, 3 H) 4.03-4.04 (d, *J*=6.57 Hz, 2 H) 6.05 - 6.20 (m, 1 H) 7.15 - 7.20 (m, 4 H) 9.54-9.55 (d, *J*=0.88 Hz, 1 H)



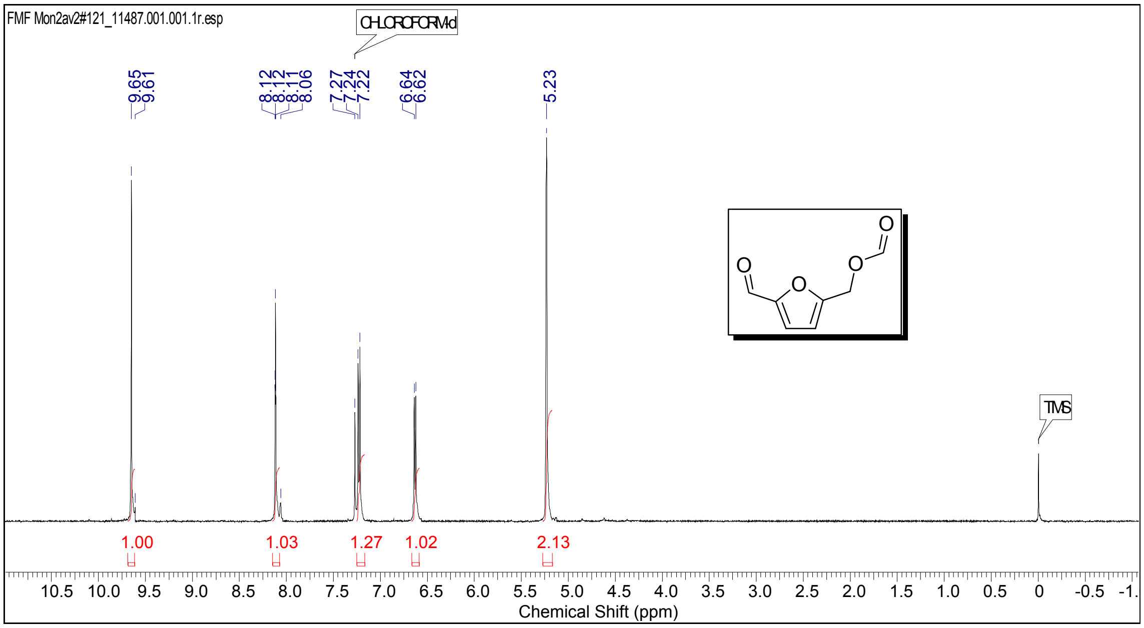
5-(4-methylbenzyl)furan-2-carbaldehyde: ^{13}C NMR (50 MHz, CHLOROFORM-*d*) δ ppm 19.45, 21.08, 29.73, 32.71, 34.51, 109.67 109.76, 126.40, 127.46, 128.80, 129.49, 129.85, 130.59, 177.23



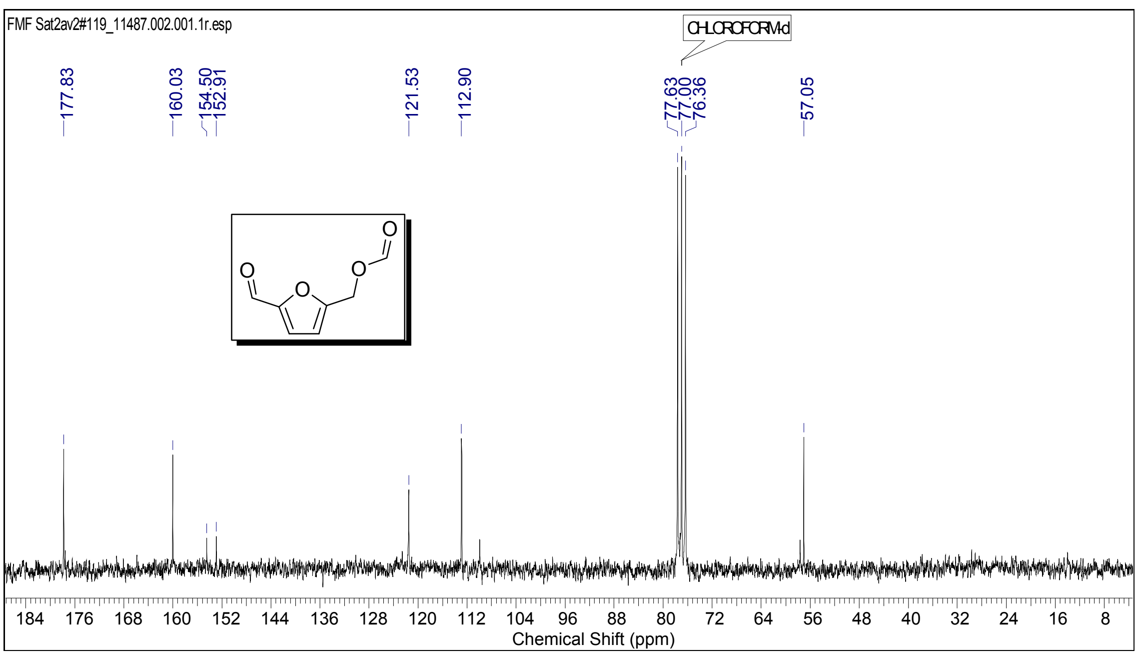
5-(acetoxymethyl)furfural: ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 2.12 (s, 3 H) 5.13 (s, 2 H) 6.60 (d, J=3.54 Hz, 1 H) 7.22 (d, J=3.54 Hz, 1 H) 9.65 (s, 1 H)



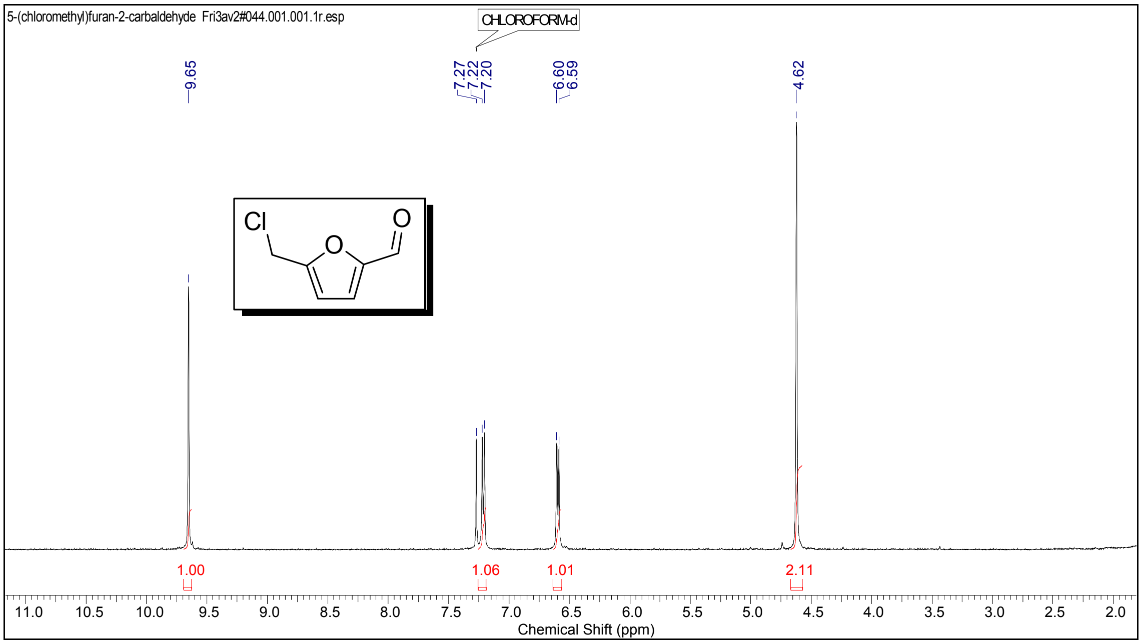
5-(acetoxymethyl)furfural: ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm 20.00, 57.13, 111.92, 121.09, 152.15, 154.78, 169.70, 177.20.



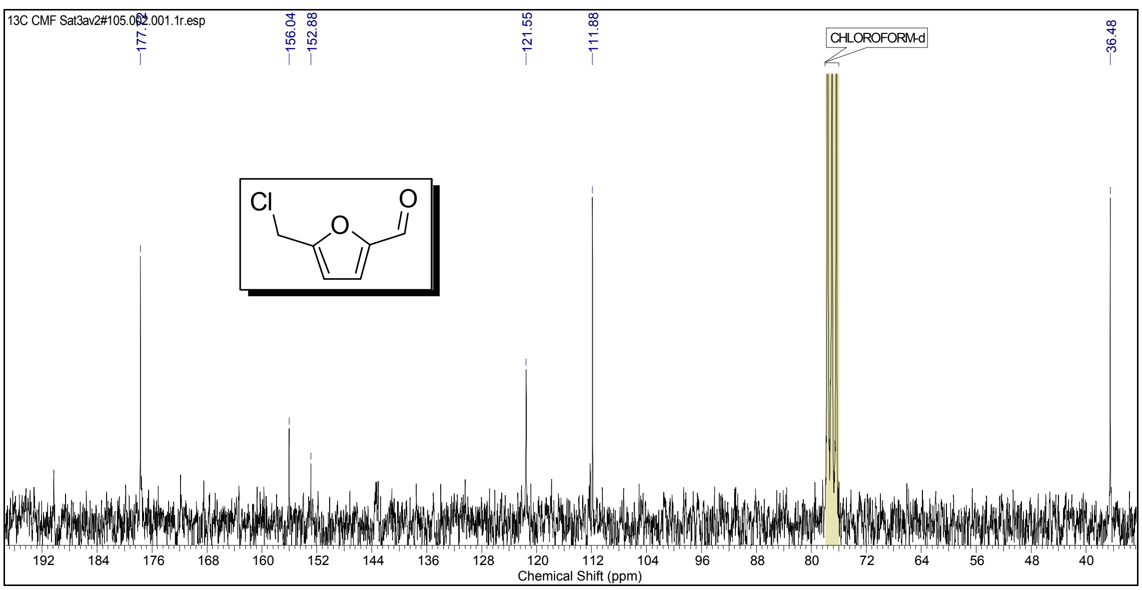
5-(formyloxymethyl)furfural: ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 2.12 (s, 3 H) 5.13 (s, 2 H) 6.60 (d, J=3.54 Hz, 1 H) 7.22 (d, J=3.54 Hz, 1 H) 9.65 (s, 1 H)



5-(formyloxymethyl)furfural: ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm 57.05, 112.90, 121.53, 152.91, 154.50, 160.03, 177.83



5-(chloromethyl)furfural: ^{1}H NMR (200 MHz, $CDCl_3$): 4.62 (s, 2H, CH_2Cl), 6.59-6.60 (d, *J*=3.54Hz, 1H, ArH), 7.20-7.22 (d, *J*=3.54, 1H, ArH), 9.65 (s, 1H, CHO).



5-(chloromethyl)furfural: ^{13}C NMR (50 MHz, $CDCl_3$): 36.48 (CH_2-Cl), 111.88 (Ar-CH), 121.55 (Ar-CH), 152.88 (Ar-C), 156.04 (Ar-C) and 177.72 (CHO).

References

1. X. Zhou, T. B. Rauchfuss, *ChemSusChem* **2013**, *6*, 383–388.
2. A. Bredihhin, U. Mäeorg, L. Vares, Carbohy. Res. **2013**, *375*, 63–67.