Upgrading Biogenic Furans: Blended C_{10}-C_{12} Platform Chemicals via Lyase-Catalyzed Carboligations and Formation of Novel C_{12} – Choline Chloride-Based Deep-Eutectic-Solvents.**

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SUPPLEMENTARY INFORMATION

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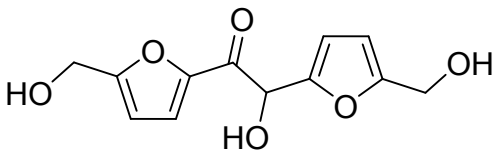
Analysis of products.

NMR-Spectroscopy. NMR spectra for HMF coupled products were recorded on a 300 MHz (^{1} H-NMR: 300 MHz, ^{13}C-NMR: 75 MHz) Bruker device from BioSpin GmbH at 20 °C. ^{1}H NMR spectra for HMF-furfural cross coupled products were recorded on a 500 MHz Bruker Ultrashield Plus device. Chemical shifts are relative to the used solvents (acetone-d_6: ^{1}H: δ = 2.09 ppm, ^{13}C: δ = 30.6 ppm (CD$_3$)), indicated in ppm.

Mass Spectrometry. EI Mass spectra for coupled furfural products were measured with a "Finnigan SSQ 7000" device. Spectra for HMF-furfural coupled products were recorded using a “Bruker MicrOTOF” ESI-TOF device.

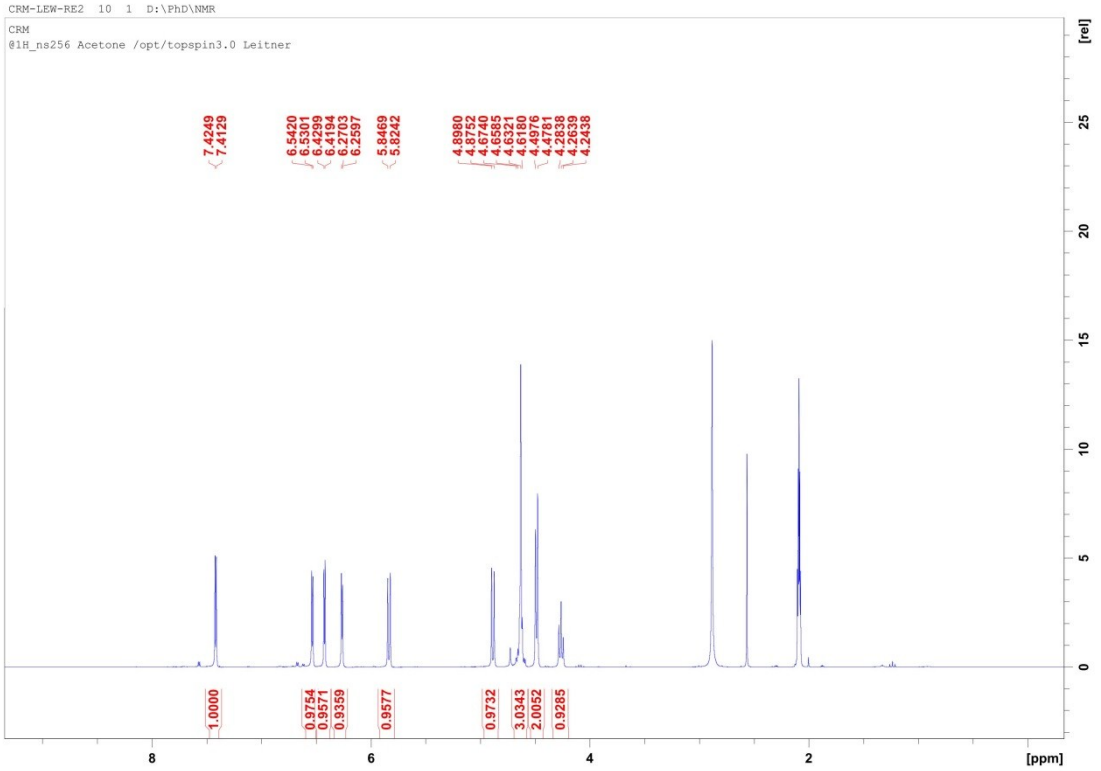
IR Spectroscopy. IR spectra were measured with a "Perkin-Elmer 100FT-IR" spectrometer and detected with an "UATR Diamond/KRS-5" device. The measurement was per-formed as differance spectra versus $CHCl_3$. The unit of the absorption signals is cm^{-1}. Signal intesities are characterized by following abbreviations: vs = very strong (0 - 20 %), s = strong (21 - 40 %), m = medium (41 - 60 %), w = weak (61 - 80 %), vw = very weak (81 - 90 %).

2-hydroxy-1,2-bis(5-(hydroxymethyl)furan-2-yl)ethanone



^{1}H NMR(acetone-d_6): δ 7.42 (d, J = 3.6 Hz, 1 H), 6.54 (d, J = 3.5 Hz, 1 H), 6.42 (d, J = 3.1 Hz, 1 H), 6.27 (d, J = 3.2 Hz, 1 H), 5.84 (d, J = 6.8 Hz, 1 H), 4.67 – 4.62 (m, 3 H), 4.49 (d, J = 5.9 Hz, 1 H), 4.26 (t, J = 6.0 Hz, 1 H) ppm.

^{13}C NMR (acetone-d_6): δ 185.9, 163.1, 157.7, 153.6, 150.7, 122.8, 111.0, 110.8, 109.5, 71.3, 58.3, 58.0 ppm;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6.5420
6.5301
6.4299
6.4194
6.2703
6.2597
5.8469
5.8242
4.8980
4.8752
4.6740
4.6585
4.6321
4.6160
4.4976
4.4781
4.2838
4.2639
4.2438
1.0000
0.9754
0.9571
0.9359
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0.9732
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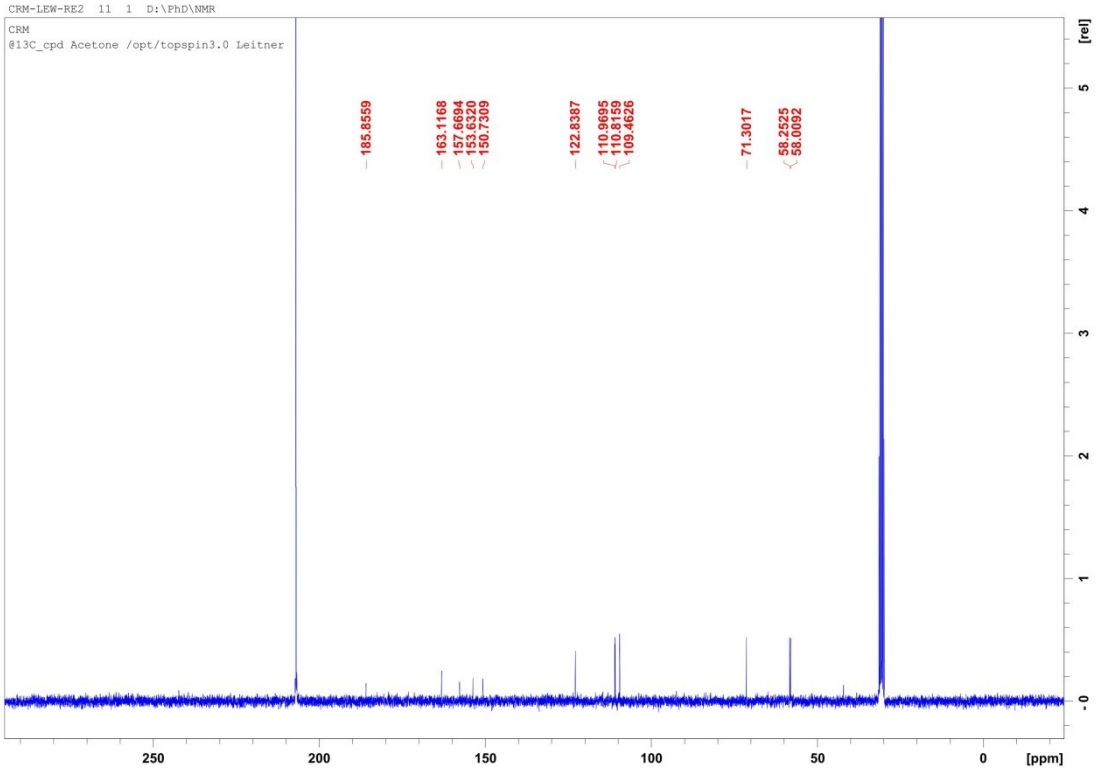
2.0052
0.9285
8
6
4
2
[ppm]
[rel]


CRM-LEW-RE2 11 1 D:\PhD\NMR
CRM
@13C_cpd Acetone /opt/topspin3.0 Leitner
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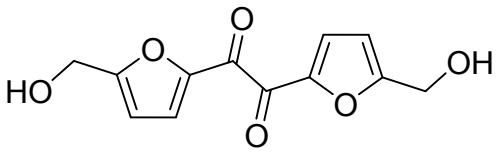
163.1168
157.6694
153.6320
150.7309
122.8387
110.9695
110.8159
109.4626
71.3017
58.2525
58.0092
250
200
150
100
50
0
[ppm]
[rel]

1,2-bis(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione



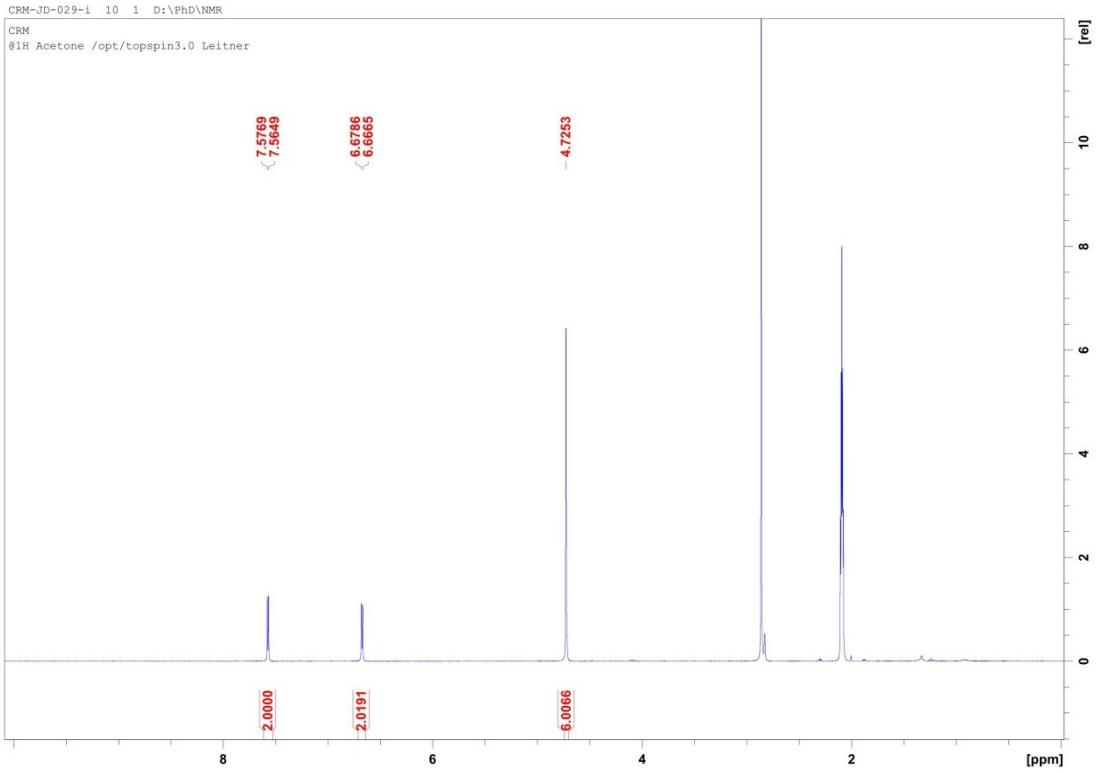
^{1}H NMR(acetone-d_6): δ 7.57 (d, J = 3.6 Hz, 2 H), 6.67 (d, J = 3.6 Hz, 2 H), 4.73 (m, 6 H) ppm;

^{13}C NMR (acetone-d_6): δ 179.3, 165.4, 150.4, 127.0, 111.5, 58.4 ppm;

IR (KBr): ν = 3249 (s), 3120 (m), 2942 (vw), 2104 (vw), 1739 (m), 1633 (vs), 1497 (vs), 1437 (m), 1387 (m), 1339 (w), 1273 (m), 1231 (w), 1190 (s), 1019 (vs), 949 (vs), 822 (vs), 781 (vs), 685 (w) cm^{-1};

MS (EI, 100 eV): m/z (%) = 250 ([M]+, 15), 233 (43), 125 ($[C_6H_5O_3]^+$, 100), 69 (19), 52 (18), 51 (23), 50 (20).

HRMS (ESI): [M]+Na^+ calculated for $[C_{12}H_{10}O_6Na]^+$: 273.03696, found: 273.03699.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6.6665
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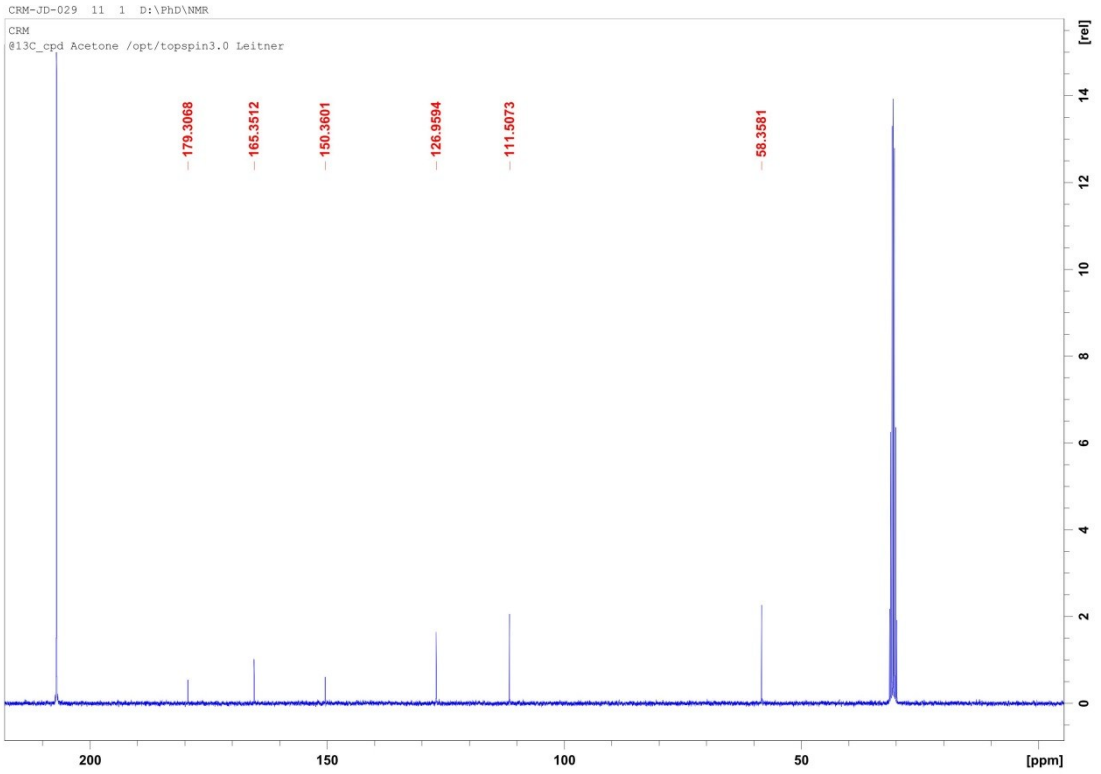
2.0000
2.0191
6.0066
[rel]
[ppm]


CRM-JD-029 11 1 D:\PhD\NMR
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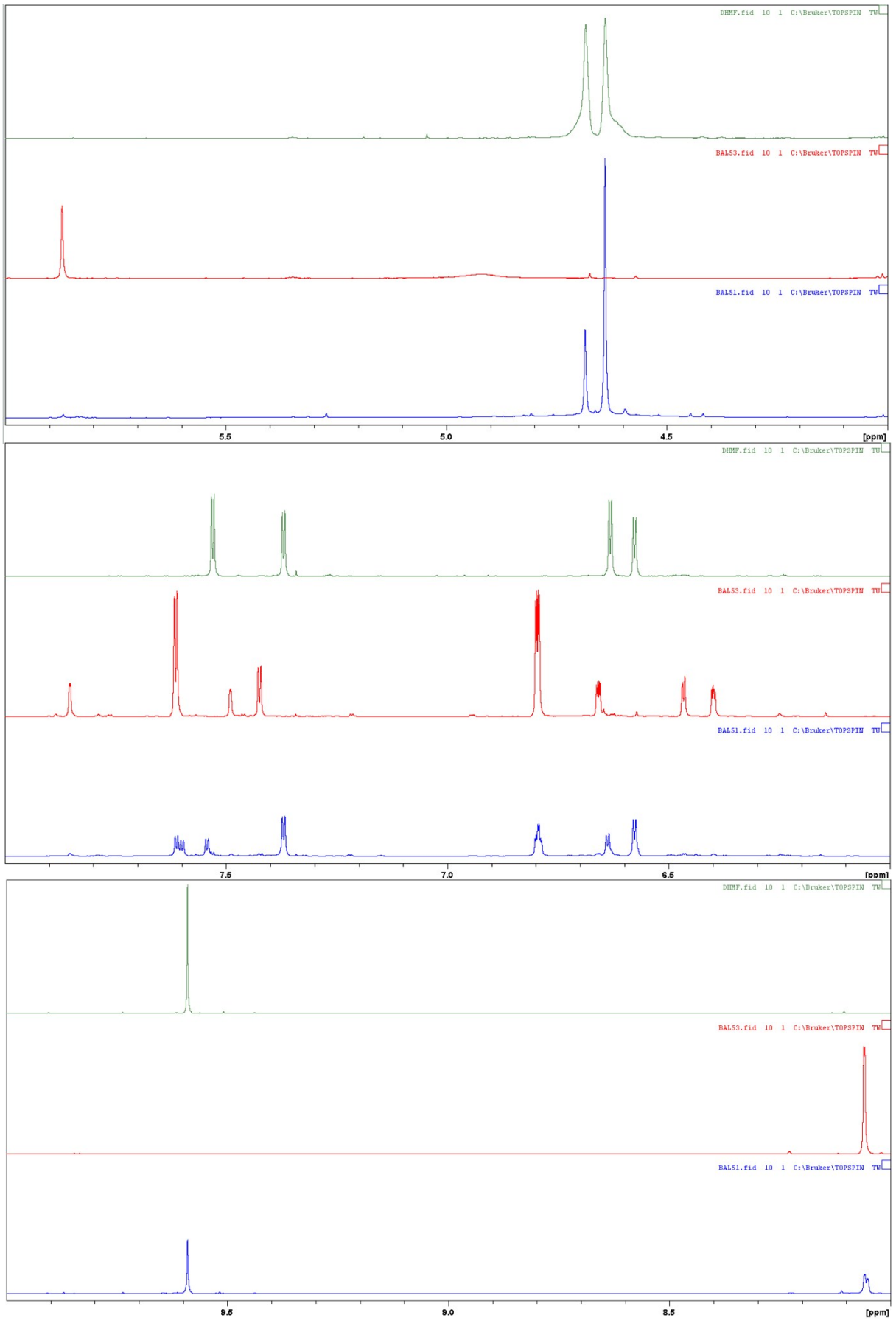
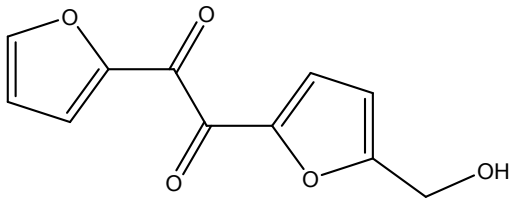
150.3601
126.9594
111.5073
58.3581
[rel]
[ppm]

^{1}H NMR spectra for coupling reactions with HMF/Furfural substrate ratios of 100/0 (green), 0/100 (red) and 50/50 (blue)


DHMF.fid 10 1 C:\Bruker\TOPSPIN TW
BAL53.fid 10 1 C:\Bruker\TOPSPIN TW
BAL51.fid 10 1 C:\Bruker\TOPSPIN TW
5.5
5.0
4.5
[ppm]
DHMF.fid 10 1 C:\Bruker\TOPSPIN TW
BAL53.fid 10 1 C:\Bruker\TOPSPIN TW
BAL51.fid 10 1 C:\Bruker\TOPSPIN TW
7.5
7.0
6.5
DHMF.fid 10 1 C:\Bruker\TOPSPIN TW
BAL53.fid 10 1 C:\Bruker\TOPSPIN TW
BAL51.fid 10 1 C:\Bruker\TOPSPIN TW
9.5
9.0
8.5
[ppm]

Conversions were calculated by identification of product peaks through comparison to substrate spectra and spectra of isolated coupled HMF products. Subsequent integration of relevant peaks yielded relative quantities of each product.

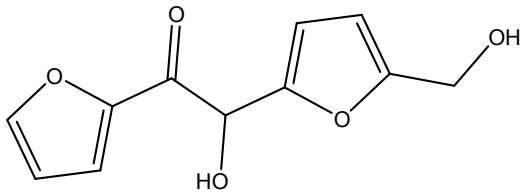
1-(furan-2-yl)-2-(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione



^{1}H NMR (500 MHz, acetone-*d6*): 4.68 ((br)s, 2H) 6.64 (dt, *J*= 3.7, 0.7 Hz, 1H) 6.79 (dd, *J*= 3.6, 1.7 Hz, 1H) 7.55 (dt, *J*= 3.6, 0.4 Hz, 1H) 7.60 (dd, 3.7, 0.7 Hz, 1H) 8.05 (dd, *J*= 1.7, 0.8 Hz, 1H)

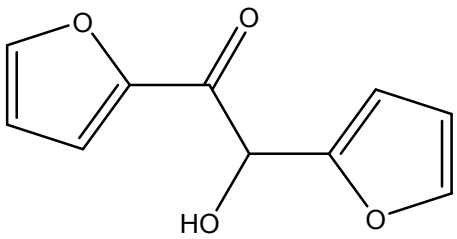
HRMS (ESI): $[M]+Na^{+}$ calculated for $[C_{11}H_8O_5Na]^{+}$: 243.0298, found: 243.0255.

1-(furan-2-yl)-2-hydroxy-2-(5-(hydroxymethyl)furan-2-yl)ethanone



HRMS (ESI): $[M]+Na^{+}$ calculated for $[C_{11}H_{10}O_5Na]^{+}$: 245.0398, found: 245.0407.

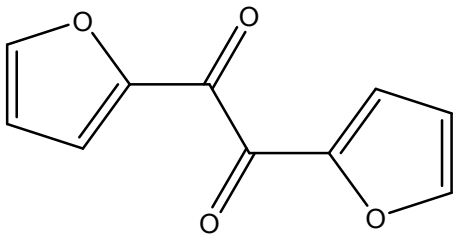
1,2-di(furan-2-yl)-2-hydroxyethanone



^{1}H NMR (500 MHz, acetone-d_6): 5.87 (s, 1H) 6.40 (ddd, *J*= 3.3, 1.8, 0.3 Hz, 1H) 6.47 (ddd, *J*= 3.3, 0.8, 0.4 Hz, 1H) 6.66 (dd, *J*=3.6, 1.7 Hz, 1H) 7.43 (dd, *J*= 3.6, 0.7 Hz, 1H) 7.49 (dd, *J*= 1.8, 0.8 Hz, 1H) 7.85 (dd, *J*= 1.7, 0.7 Hz, 1H)

HRMS (ESI): $[M]+Na^+$ calculated for $[C_{10}H_8O_4Na]^+$: 215.0298, found: 215.0278.

1,2-di(furan-2-yl)ethane-1,2-dione



^{1}H NMR (500 MHz, acetone-d_6): 6.80 (dd, *J*= 3.7, 1.7 Hz, 2H) 7.62 (dd, *J*= 3.7, 0.7 Hz, 2H) 8.06 (dd, *J*= 1.7, 0.7 Hz, 2H)

HRMS (ESI): $[M]+Na^+$ calculated for $[C_{10}H_6O_4Na]^+$: 213.0198, found:213.0161.