Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Unique pathway to platform chemicals – aldaric acids as stable intermediates for synthesis of furandicarboxylic acid esters

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1 General considerations

Gas chromatography GC-FID analyses were done with Shimadzu GC-1020 Plus Gas Chromatograph. The column used was ZB-5HT Inferno and the temperature program 100°C/ 1 min -> 10°C/min to 280°C/ hold time 1 min-> 30°C/min to 350°C/ hold time 5 min. Injector temperature 320°C, detector temperature 380°C, carrier gas helium, pressure 100.2 kPa, total flow 103.8 ml/ min, column flow 1.00 ml/ min, linear velocity 27.5 cm/ sec, purge flow 3.0 ml/ min, injection volume 1.0 µl, split ratio 100. All GC samples from the reactions were silylated with BSTFA prior to analysis.

Gas chromatography mass spectrometry The GC/MS analyses of the trimethylsilylated ester (substrate) and FDCA samples were performed with an Agilent 6890 series GC system, equipped with an Agilent 5973 mass selective detector and a DB-5 MS capillary column (30 m x 0.25 mm, film thickness 0.25 µm). The applied temperature program was 1 min at 80 °C, 10 °C min^{-1} to 300 °C, and 10 min at 300 °C. The injection split ratio was 25:1. The MS identifications were based on the use of relevant literature, an in-house MS library, and the commercial Wiley database. Selected identifications are briefly described in Section 3.3 Catalyst preparation

2 Catalyst preparation

2.1 Sulfated zirconia

Sulfated zirconia was prepared according to procedure reported by Saravan *et al*.[1] Zirconium IV hydroxide (2.0 g, 12.56 mmol) and sulfuric acid 1N (30 ml) were stirred at room temperature (23 °C) for 3 hours and vacuum filtered through number 2 Whatman paper. The residual solid was dried at 45 °C / 160 mbar until constant weight (72 h) to afford an off-white solid (0.78 g, 30% yield). The product was crushed-up and calcinated at 600 °C for 2 hours.

2.2 Sulfated alumina

Prepared with modified procedure by Nicholas *et al.*[2] *p*-toluenesulfonic acid (1.34 g, 7.36 mmol) was added to a slurry of γ-alumina (3.0 g, 29.42 mmol) in water (2.2 ml) and heated to 140 °C for 4 hours with water-condenser. Cool water (5 ml) was added and the slurry vacuum filtered through number 2 Whatman paper. The residual solid was dried at 45 °C / 160 mbar until constant weight (72 h) to afford a purple powder after grinding (2.50 g, 83 % weight recover from alumina).

2.3 Sulfonic acid silica

Prepared with modified procedure by Dacquin *et al.*[3] MCM-41 silica was calcined at 550 °C for 6 h. In the reaction flask was charged calcinated MCM-41 silica (2.0 g), toluene (60 ml) and (3-mercaptopropyl)trimethoxysilane (2.0 ml). The reaction mixture was heated to reflux for 24 h and filtrated. The solids were washed three times with methanol and dried in vacuum at 80°C overnight. The dried solids (2.5 g) were charged to the reaction flask and hydrogen peroxide (30%, 40 ml) was added and the reaction stirred for 4 h at room temperature. The mixture was filtrated and the solids washed three times with methanol and dried in vacuum at 80°C overnight. The product (2.3 g) was a white solid.

3 Esterification of aldaric acids

*3.1 Galactaric acid dibutyl ester **1b***

Esterification of aldaric acids was carried out using acid catalysts, e.g. Si-tosic acid. In a typical procedure, galactaric acid (238.7 mmol) and *n*-butanol (500ml) were placed in a three-neck flask and stirred with magnetic stirrer. To this was added Si-tosic acid (21 mol%) and the reaction heated to reflux for 24h. Once complete the reaction was hot filtered (80 °C) over a porosity 3 sinter. Evaporation of solvent (45 °C, less than 20 mbar) afforded an off-white crystalline product at 91 mol% recovery. According to GC analyses, the product contained 91% diester **1b**, 5% monoester and 4% **1a**. The product was used in aromatisation without further purification.

^{1}H (500 MHz, DMSO-d_6): δ = 4.29 (s, 2H, 2C*H*), 4.07 (m, 4H, 2CH_2) 3.78 (s, 2H, 2C*H*), 1.57 (m, 4H, 2CH_2), 1.34 (m, 4H, 2CH_2), 0.89 (t, 6H, 2CH_3); ^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 174.2, 71.8, 70.6, 64.2, 30.7, 19.0.

*3.2 Esterified glucaric acid **4***

Esterification of glucaric acid potassium salt was carried out by using a homogeneous acid catalysts. In a typical procedure, glucaric acid potassium salt (403.26 mmol) and *n*-butanol (1000 ml) were placed in a three-neck flask and stirred with magnetic stirrer. To this sulfuric acid (27 mol%) was added and the reaction heated to reflux for 24h. Once complete the reaction was hot filtered (80 °C) over a porosity 3 sinter. Evaporation of solvent (45 °C, less than 20 mbar) afforded a viscous light-brown product with 62 mol% recovery. According to GC-MS, the esterified glucaric acid contained 39% dibutyl glucarate, 51% monobutyl glucarolactones, 5% monobutylglucaric acids, 4% glucaro-1,4:6,3-dilactone and small amounts of isomeric glucarolactones. Based on these, the average molecular weight of mixture **4** is 274.12 g/mol, which was used to calculate the substrate conversion and selectivities. The product was used in aromatisation without further purification.

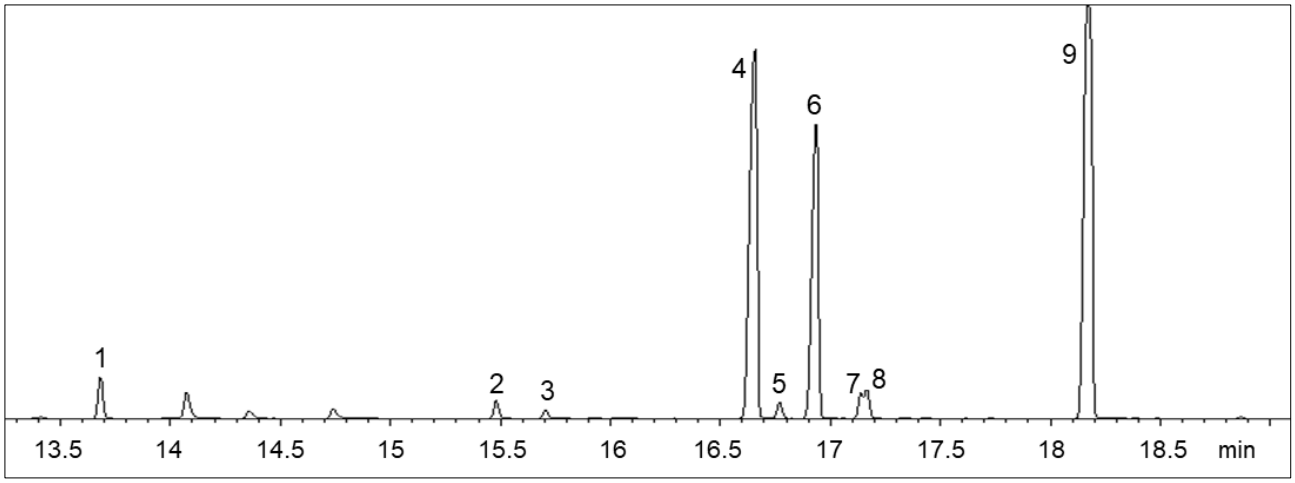


Figure S1. Total ion chromatogram from the GC-MS analysis of the esterified glucaric acid **4**. Identification of peaks: 1, (tentative) glucaro-1,4:6,3-dilactone; 2-3, isomeric glucarolactones (apparently 1,4- and 6,3-lactones); 4-6, isomeric monobutylglucarolactones (apparently 1,4-, 1,5- and 6,3-lactones); 7-8, isomeric monobutylglucaric acids; and 9, dibutyl glucarate.

3.3 Identification of selected esterification products

From the reaction mixtures, the identification of trimethylsilylated mono- and dibutyl galactarates and glucarates was a straightforward task. As described in detail by Petersson,[4] fully trimethylsilylated hexaric acids show (together with all other aliphatic 2,3-dihydroxy acids) an abundant, characteristic m/z 292 McLafferty rearrangement ion. The introduction of one butyl ester to a hexaric acid will readily result in the formation of two different McLafferty ions, m/z 276 from the butyl ester and 292 from the TMS ester. Analogously, for the trimethylsilylated dibutyl hexarates, only the abundant 276 ion is possible (Figure S2).

Other characteristic features that fully support these identifications include low intensity M–15 ions at m/z 611 and 595, for mono- and dibutyl esters, respectively. In addition, fragmentation between the C-2 and C-3 (or C-4-and C-5) carbon atoms produces highly characteristic ions. In case of fully trimethylsilylated hexaric acid, this route gives rise to the formation of m/z 423 and 333 (423–TMSOH) ions.[4] For the monobutyl ester, two different series of the corresponding ions are possible, at m/z 423 and 333, and 407 and 317. For the dibutyl ester, only the latter set of ions can be formed. As can be seen, the m/z 317 ion forms the base peak in the spectrum of the dibutyl ester, in a good agreement with the m/z 275 base peak in the mass spectrum of the trimethylsilylated dimethyl glucarate.[5] It is also noteworthy that monobutylation of glucaric acid produces two chromatographically separated (partially overlapping) stereoisomers (Figure S1), but in case of galactaric acid only one isomer is possible.

Several lactone compounds were found after butylation of glucaric acid. The peaks 4–6 (Figure S1) were readily identified as lactones of monobutyl glucarates, with the help of apparent M and M–15 ions at m/z 464 and 449, respectively (Figure S2). There are also other similarities between these mass spectra and those reported for the trimethylsilylated lactones of monomethyl glucaric acids.[6] It is now justified to assume that the dominating peaks 4 and 6 represent 1,4- and 6,3-lactones, and the minor peak refers to the presence of a 1,5-lactone. However, due to the lack of authentic model compounds, their final isomer-specific identification is not currently possible. It can also be concluded that the two potential stereoisomers of the 1,4- and 6,3-lactones are apparently co-eluting together, although their open-chain forms were at least partially separated (Figure S1).

The two glucarolactones (peaks 2–3) were readily identified from the apparent M and M–15 ions at m/z 480 and 465, respectively. The identification of the dilactone (peak 1) is still tentative, although the m/z 303 peak (as apparent M-15 ion) and some similarities with the spectra of the glucarolactones would now support the identification.

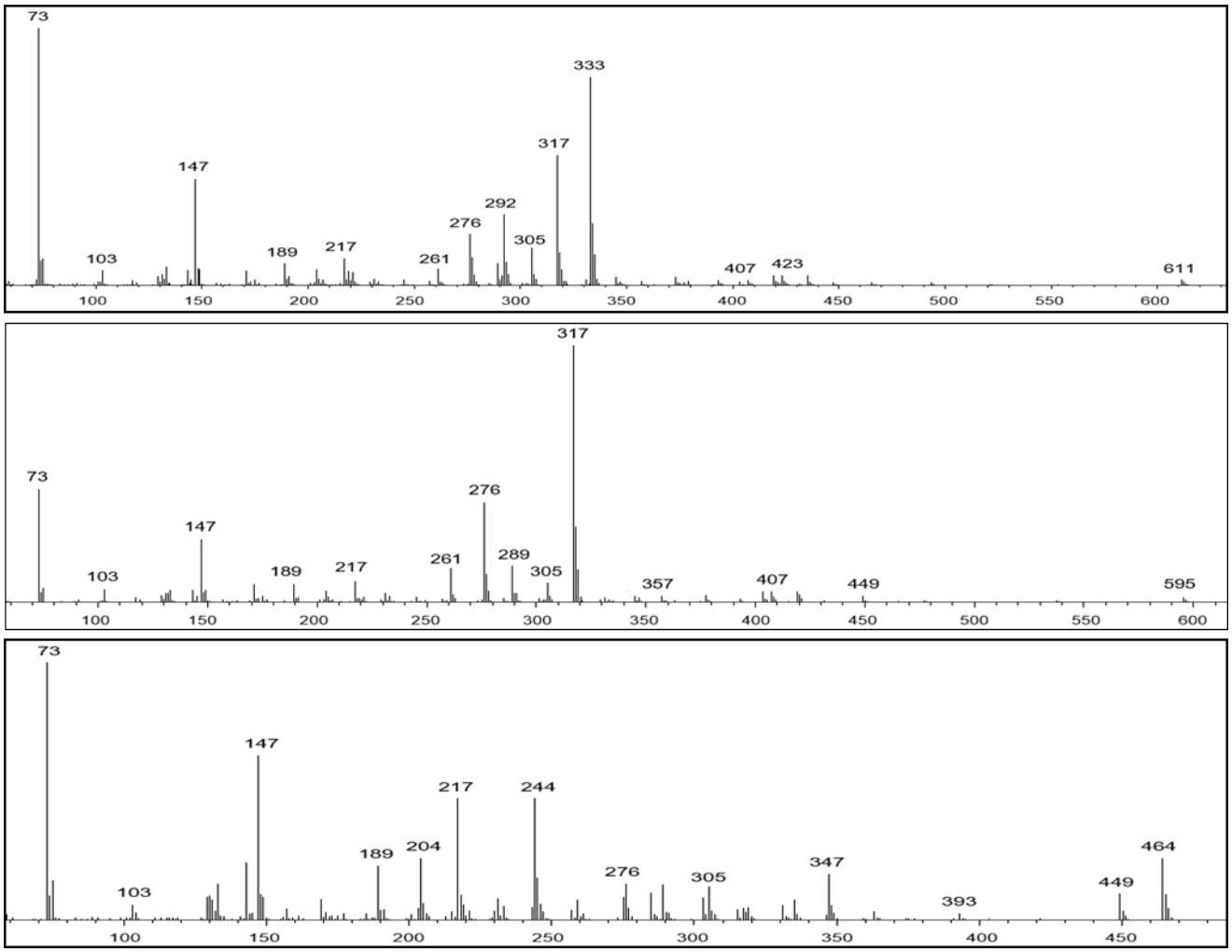


Figure S2. Mass spectra at 70 eV of the trimethylsilyl derivatives of monobutyl glucarate (top), dibutyl glucarate (middle) and a monobutyl glucarate lactone (peak 4, bottom). The mass spectrum of the other main monobutyl glucarate lactone (peak 6) was otherwise very similar, but the intensity of the m/z 244 ion was significantly lower.

4 Optimisation of reaction conditions

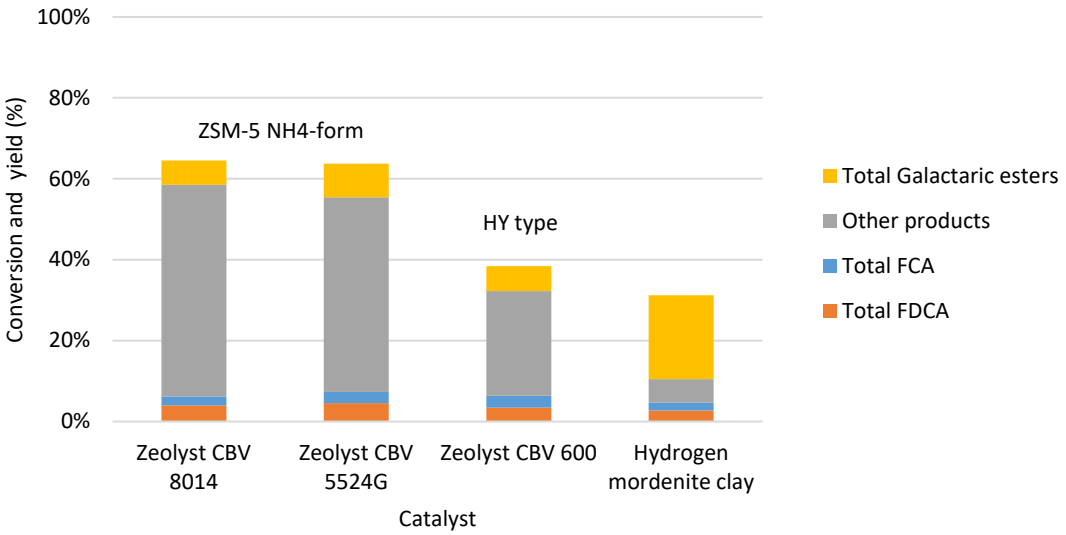


Figure S3. Initial screening of catalysts in galactaric acid **1a** aromatisation. Reaction conditions: 9.5 mmol substrate, 50 wt% catalyst, 20 ml *n*-BuOH, 210 °C (oil bath temperature), 4 h.

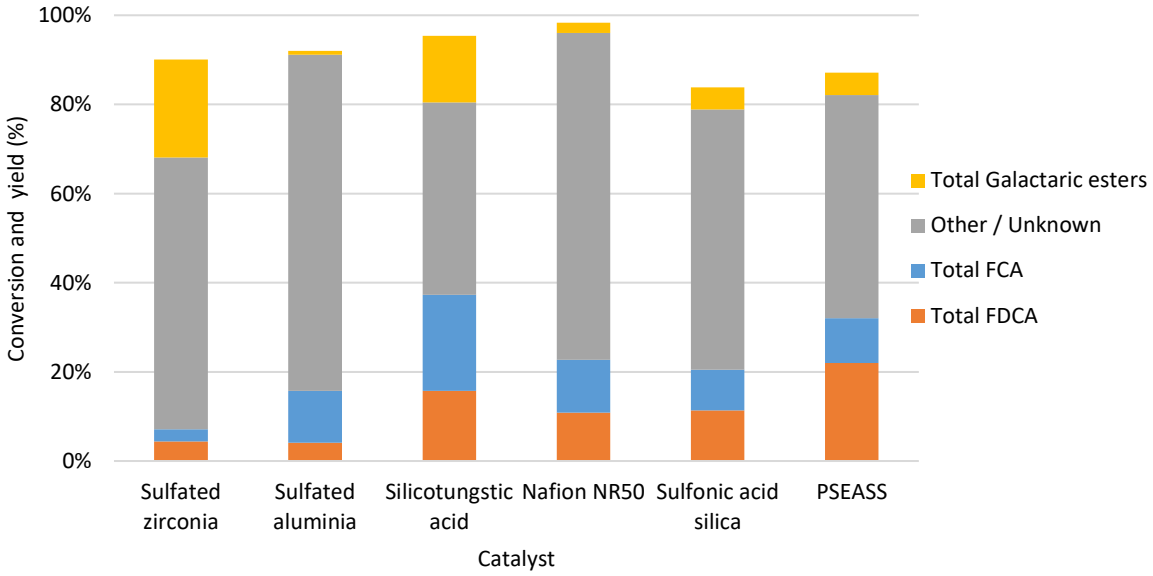
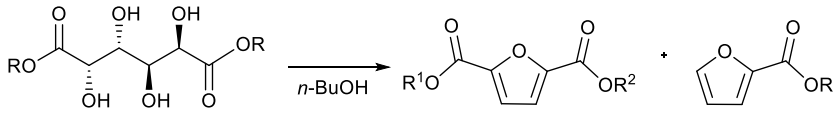


Figure S4. Initial screening of catalysts in galactaric acid **1a** aromatisation. Reaction conditions: 9.5 mmol substrate, 50 wt% catalyst, 20 ml *n*-BuOH, 230 °C (oil bath temperature), 2 h.

Table S1. Blanc experiments without catalyst.



1a: R = H
1b: R = ^{n}Bu

2a: R^1, R^2 = H
2b: R^1= H, R^2 = ^{n}Bu
2c: R^1, R^2 = ^{n}Bu

3a: R = H
3b: R = ^{n}Bu

Entry	Substrate (mmol)	T (°C)	t (h)	Conv. (mol%)	Yield (mol%)				
					2a	**2b**	**2c**	**3a**	**3b**
1	**1b** (6.3)	220	4	17	0	0	7	0	0
2[a]	**1a** (9.6)	120 + 220	24 + 4	10	0	0	0	0	0

[a] Diester **1b** was produced with 7 mol% yield.

5 Product analyses

5.1 NMR

Monobutyl 2,5-furandicarboxylate **2b**

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.42 (d, 1H, C*H*), 7.36 (d, 1H, C*H*), 4.32 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 0.96 (t, 3H, CH_3); ^{13}C NMR (125.8 MHz, DMSO-d_6): δ = 159.8, 158.5, 148.3, 146.8, 119.9, 119.4, 65.8, 31.1, 19.5, 14.5.

Dibutyl 2,5-furandicarboxylate[7] **2c**

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.19 (s, 2H, 2C*H*), 4.34 (t, 4H, 2CH_2), 1.75 (m, 4H, 2CH_2), 1.45 (m, 4H, 2CH_2), 0.95 (t, 6H, 2CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 158.2, 146.9, 118.2, 65.4, 30.6, 19.1, 13.7.

Butyl 2-furancarboxylate[8] **3b**

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (m, 1H, C*H*), 7.15 (d, 1H, C*H*), 6.48 (m, 1H, C*H*), 4.28 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.43 (m, 2H, CH_2), 0.94 (t, 3H, CH_3); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 158.9, 146.2, 144.8, 117.7, 111.8, 64.8, 30.7, 19.1, 13.7.

5.2 GC-FID

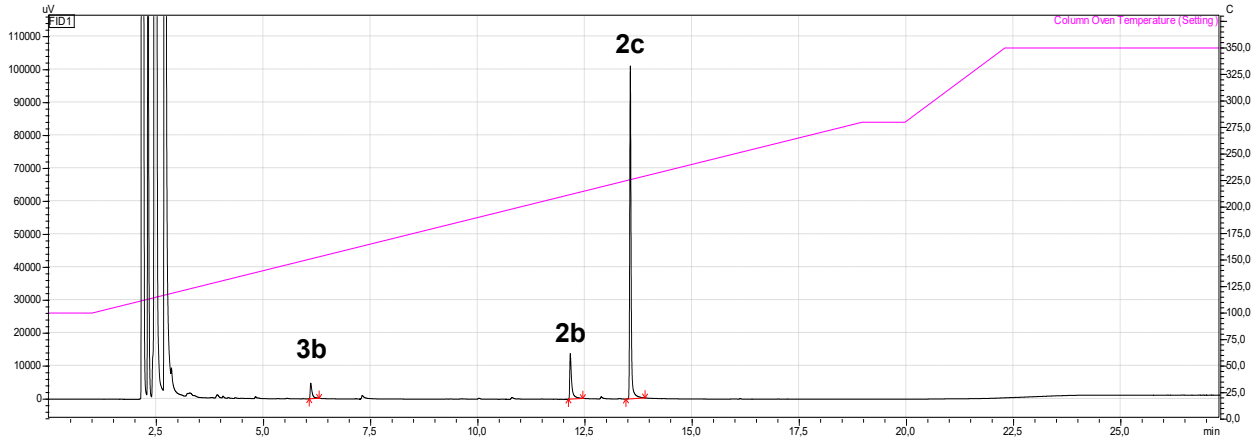


Figure S4. Sample chromatogram of product mixture after **1b** aromatisation with 5 wt% Si-tosic acid (Table 1, entry 10).

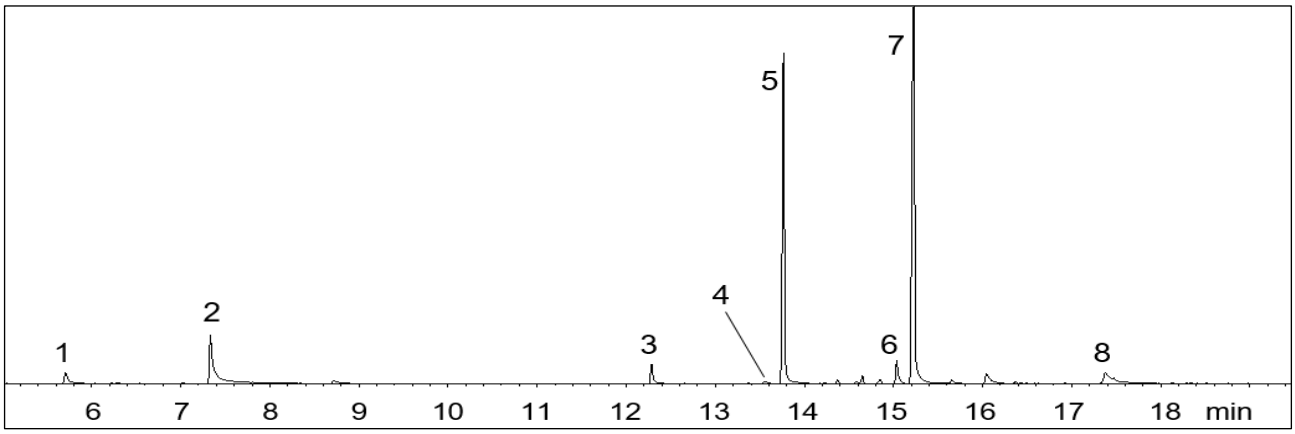


Figure S5. Total ion chromatogram from the GC-MS analysis of trimethylsilylated product mixture after **1b** aromatisation. 1, 2-furancarboxylic acid **3a**; 2, butyl 2-furancarboxylate **3b**; 3, 2,5-furandicarboxylic acid **2a**; 4, a furandicarboxylic acid; 5, monobutyl 2,5-furandicarboxylate **2b**; 6, a monobutyl furandicarboxylate; 7, dibutyl 2,5-furandicarboxylate **2c**; and 8, a dibutyl furandicarboxylate.

6 References

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