Electronic Supplementary Information

Heterogeneous catalysed production of isosorbide *tert*-butyl ethers

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Experimental Details

All chemicals (isosorbide (98%, Alfa Aesar), Amberlyst-15 (hydrogen form and dry (moisture <1.5%), Sigma-Aldrich), *tert*-butanol (99.5%, Merck), ethyl acetate (technical grade), tetrahydrofuran (99.9%, Sigma Aldrich), dioxan (>99%, TCI), dimethyl carbonate (99%, Alfa Aesar), metyl undecanoate (>98%, Roth), isobutene (2.0, Westfalen Gas)) have been used as received.

The etherification of isosorbide with *tert*-butanol was carried out as follows unless stated otherwise: Isosorbide (1 g, 6.8 mmol) is dissolved in *tert*-butanol (4 g, 54.0 mmol). Amberlyst-15 (0.1 g) is added to the solution in a round bottom flask equipped with a reflux condenser. The mixture is continuously stirred with a magnetic stirring bar and heated to the above mentioned temperatures for 8 h.

For the recycling experiments, the catalyst has been separated and re-used without further modification.

The etherification of isosorbide with isobutene has been carried out as follows unless stated otherwise: Isosorbide (5 g, 34.2 mmol) is dissolved in ethyl acetate (20 ml). Amberlyst-15 (0.2 g) is added to the solution in a 50 ml stainless steel autoclave equipped with a manometer, temperature sensor, gas inlet and a magnetic stirring bar. Isobutene (7 ml, 78.6 mmol) is condensed into a scaled *Schlenk* tube using liquid nitrogen or a dry ice/acetone bath and subsequently recondensed into the sealed autoclave. Upon heating to temperatures below 100 °C, the pressure does not exceed 20 bar. For reactions under ambient pressure, excess amounts of isobutene were bubbled through the isosorbide solution containing the catalyst.

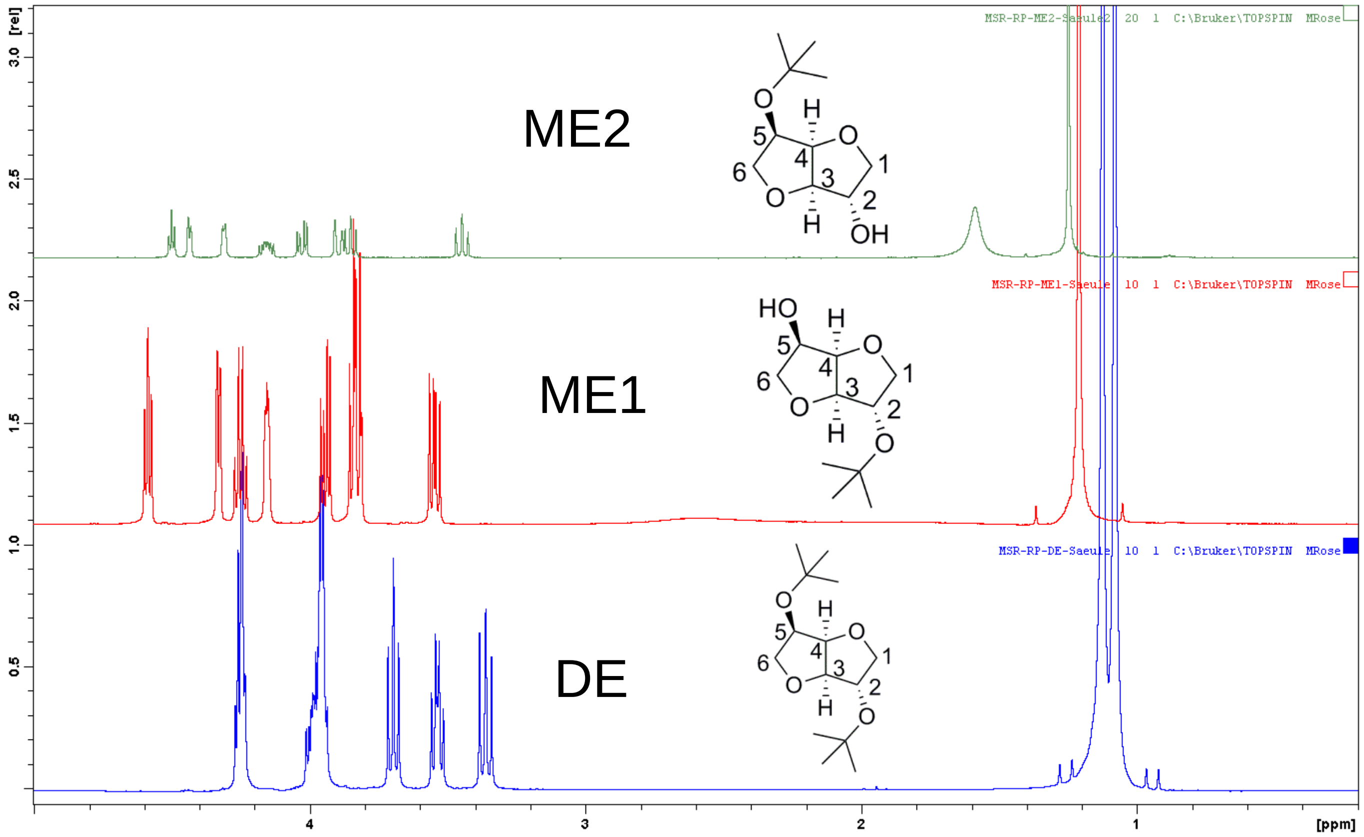
For the recycling experiments with isobutene, the catalyst has been separated, washed with DMC, dried in air at 50 °C for 15 min and re-used without further modification.

The pure mono- and diethers used for calibration were obtained by column chromatography using silica gel (60Å) with particle sizes of 0.04-0.063 mm from the company *Roth* as stationary phase and a hexane/ethyl acetate (1:4) mixture as mobile phase. The pure products were characterized measuring NMR spectra (^{1}H, ^{13}C, HSQC) on a *Bruker Avance 400* in $CDCl_3$ solutions. The two different monoethers were identified in solutions of equal concentrations and temperature by comparison of the chemical shift of the hydroxyl group protons of the two ethers with the spectrum of isomannide with two *endo* configured hydroxyl groups.

The identification of the reaction products was carried out using GC/MS analysis on a *Focus GC* chromatograph of *Thermo Scientific* equipped with a 30m Rtx-5Sil column and coupled with a *Varian* mass spectrometer. Quantification of the ITBE derivatives was carried out on a *Focus GC* chromatograph of *Thermo Scientific* equipped with a 30m Rtx-5Sil-MS column (inner diameter: 0.28mm, film thickness: 0.25 µm, Inlet: 250°C, SplitFlow:

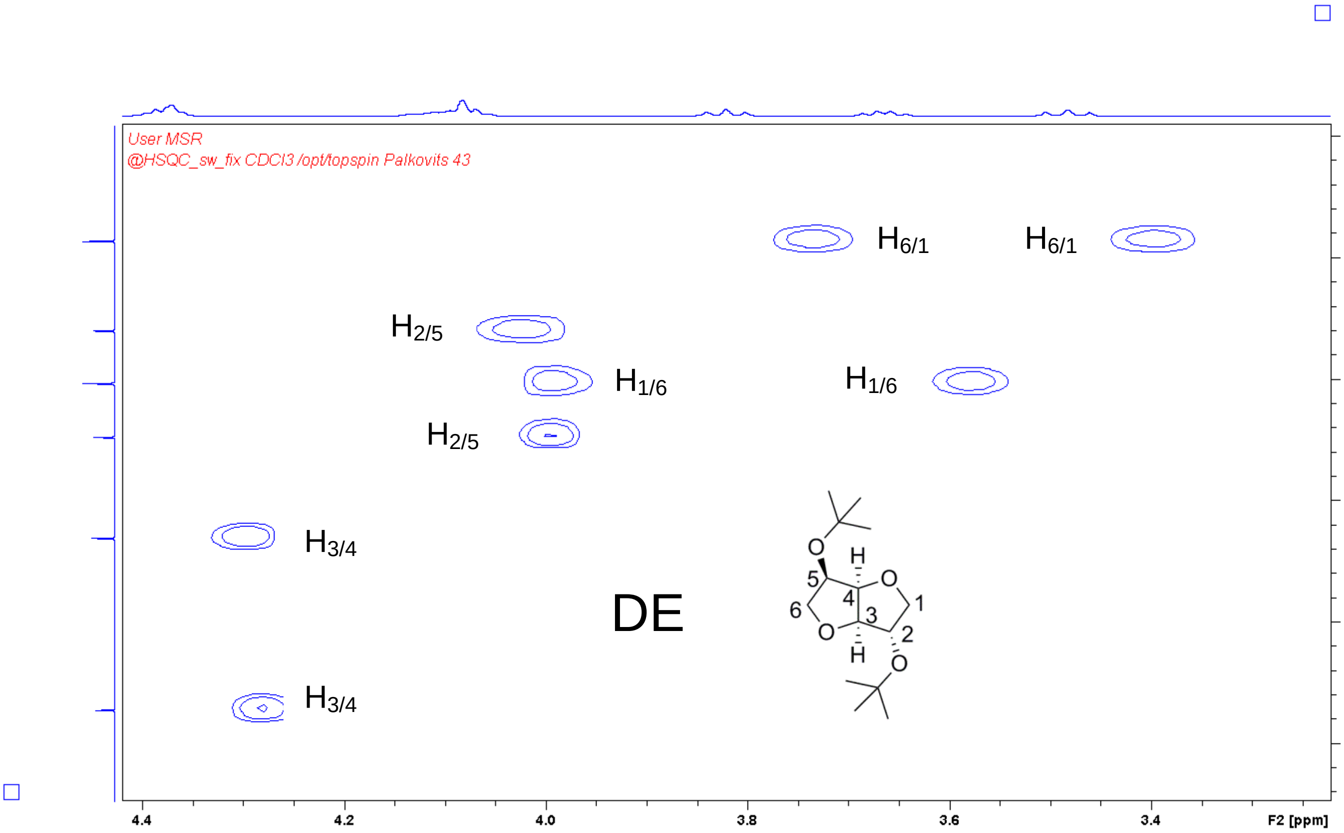
54ml/min, Injection Volume: 1µl, Carrier gas: Helium 1.5 ml/min, Detector: FID(250°C), Range:10, Temperature program: 80°C, 8°C/min to 300°C, 15min). Methyl undecanoate has been used as an internal standard for quantification of the total yields of the isosorbide derivatives via GC analysis. It was added to the reaction mixture prior to the GC analysis. The GC correction factors for the ITBE derivatives were determined as follows: ME1=1.68, ME2=1.79, DE=1.4. The GC correction factor of isosorbide was determined to be 2.69. However, a quantification of the isosorbide conversion is not shown since isosorbide results in a broad GC peak often underestimating the conversion of isosorbide in comparison to the amount of different products in the reaction mixture. Thus, only the yields of the three isosorbide ether derivatives are used for quantification with a good reproducibility.

FT-IR spectra of the novel compounds were recorded using a Platinum-ATR (attenuated total reflectance) unit with a diamond crystal on a Bruker Vertex-70 IR spectrometer.

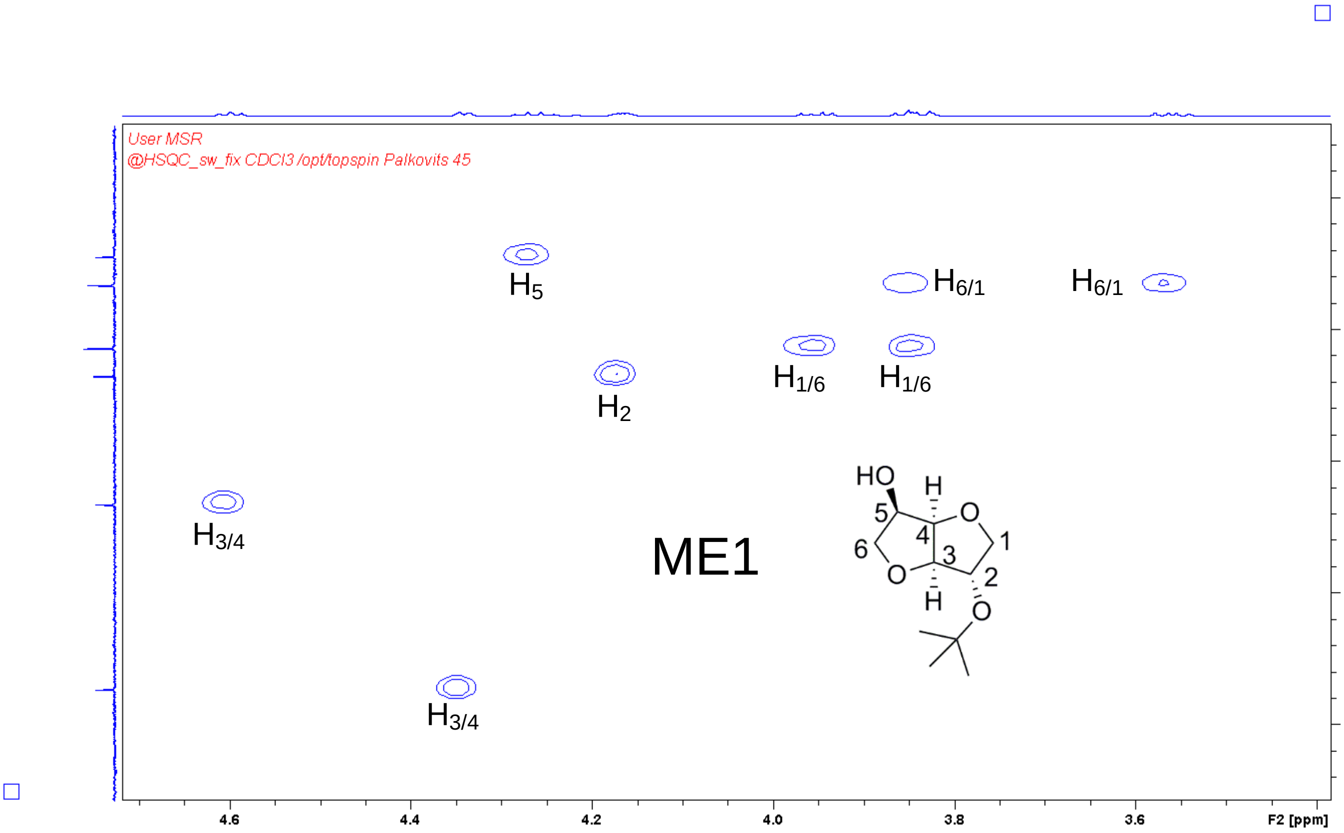


ME1		ME2		DE	
δ / ppm	**Quantity / Position**	**δ / ppm**	**Quantity / Position**	**δ / ppm**	**Quantity / Position**
4.52	1H / $H_{3/4}$	4.43	1H / $H_{3/4}$	4.25	2H / H_{3+4}
4.27	1H / $H_{3/4}$	4.37	1H / $H_{3/4}$	3.96	3H / H_{2+5} & $H_{1/6}$
4.19	1H / H_5	4.24	1H / H_2	3.69	1H / $H_{6/1}$
4.09	1H / H_2	4.09	1H / H_5	3.54	1H / $H_{1/6}$
3.88	1H / $H_{1/6}$	3.96	1H / $H_{1/6}$	3.36	1H / $H_{6/1}$
3.78	2H / $H_{1/6+6/1}$	3.80	2H / $H_{1/6+6/1}$	1.12	9H / 2/5-O-C(CH_3)$_3$
3.48	1H / $H_{6/1}$	3.38	1H / $H_{6/1}$	1.08	9H / 2/5-O-C(CH_3)$_3$
1.15	9H / 2-O-C(CH_3)$_3$	1.18	9H / 5-O-C(CH_3)$_3$		

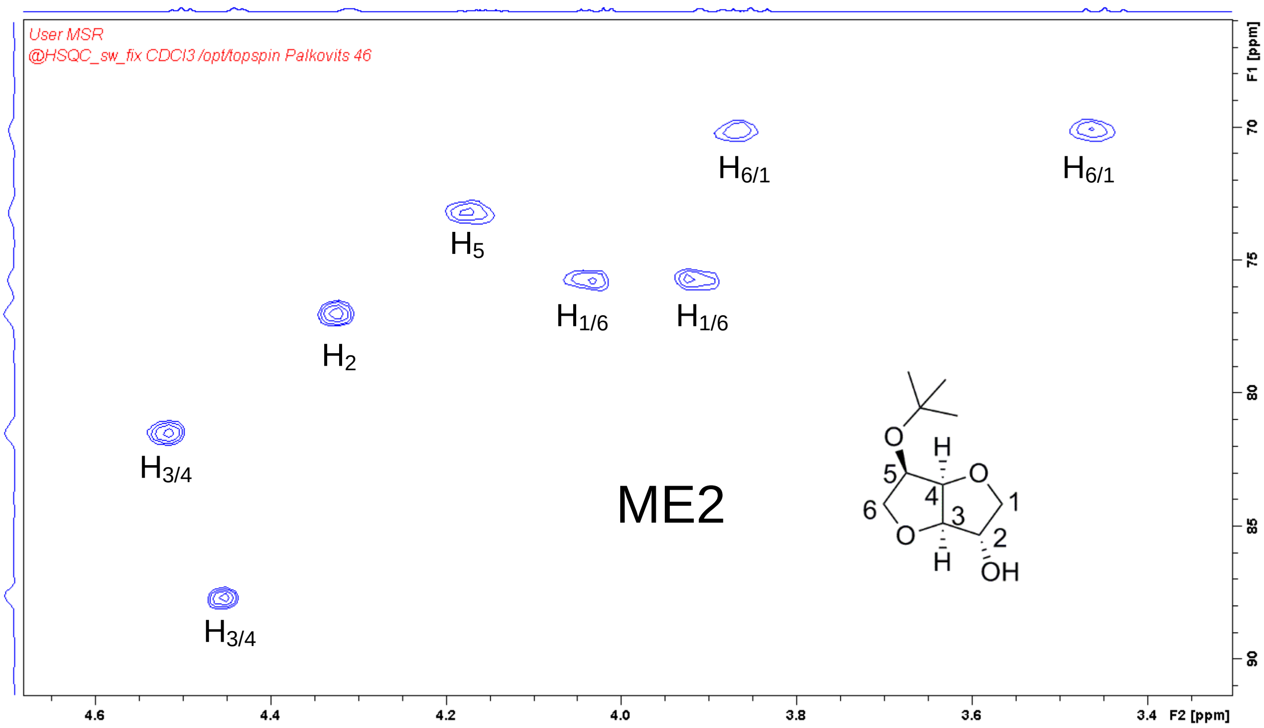
S1a. NMR spectra and data of DE (blue, bottom), ME1 (red, middle) and ME2 (green, top) measured in $CDCl_3$. $H_{x/y}$ denotes a proton in position x or y.



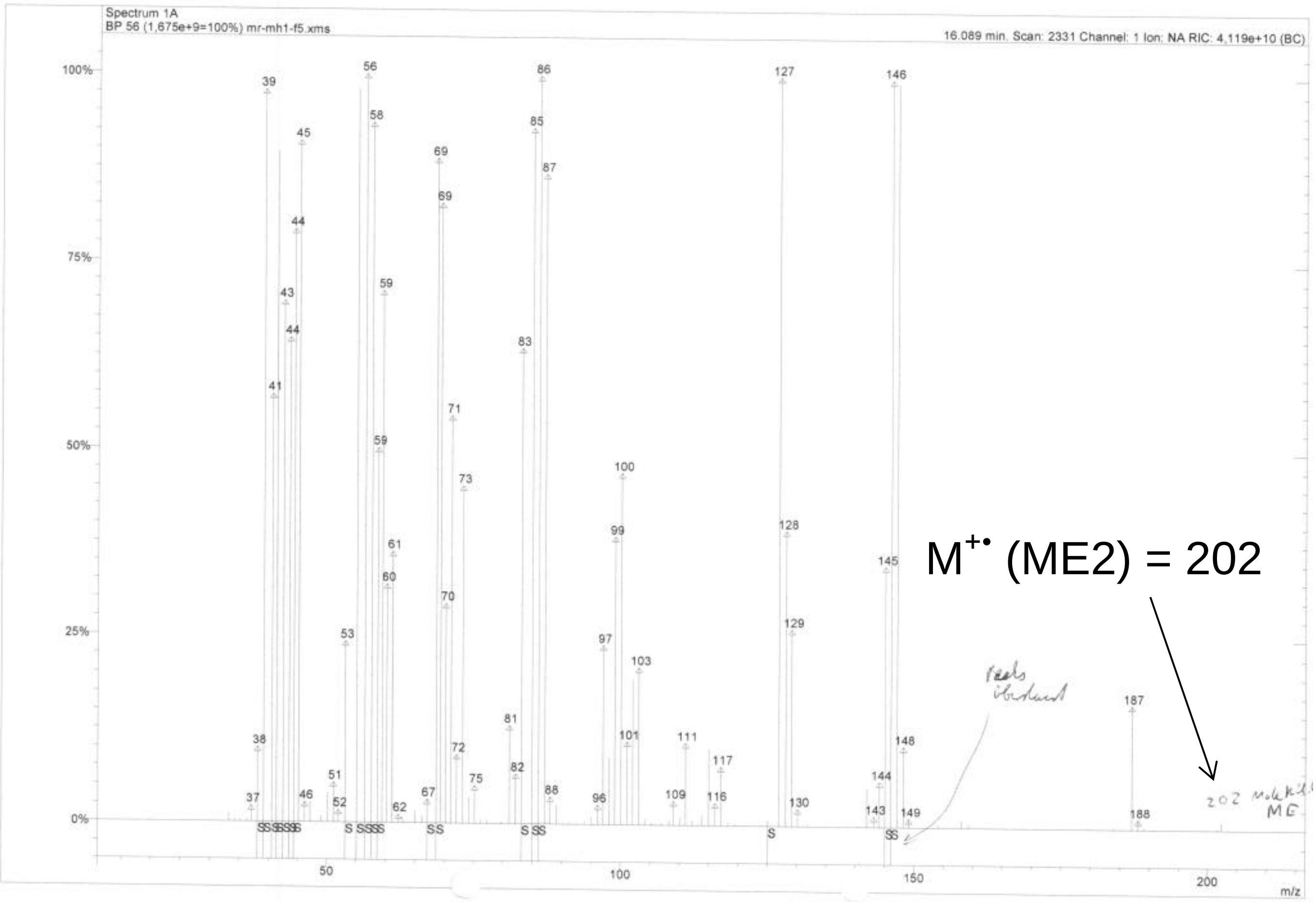
S1b. HSQC NMR spectra of DE. $H_{x/y}$ denotes a proton in position x or y.

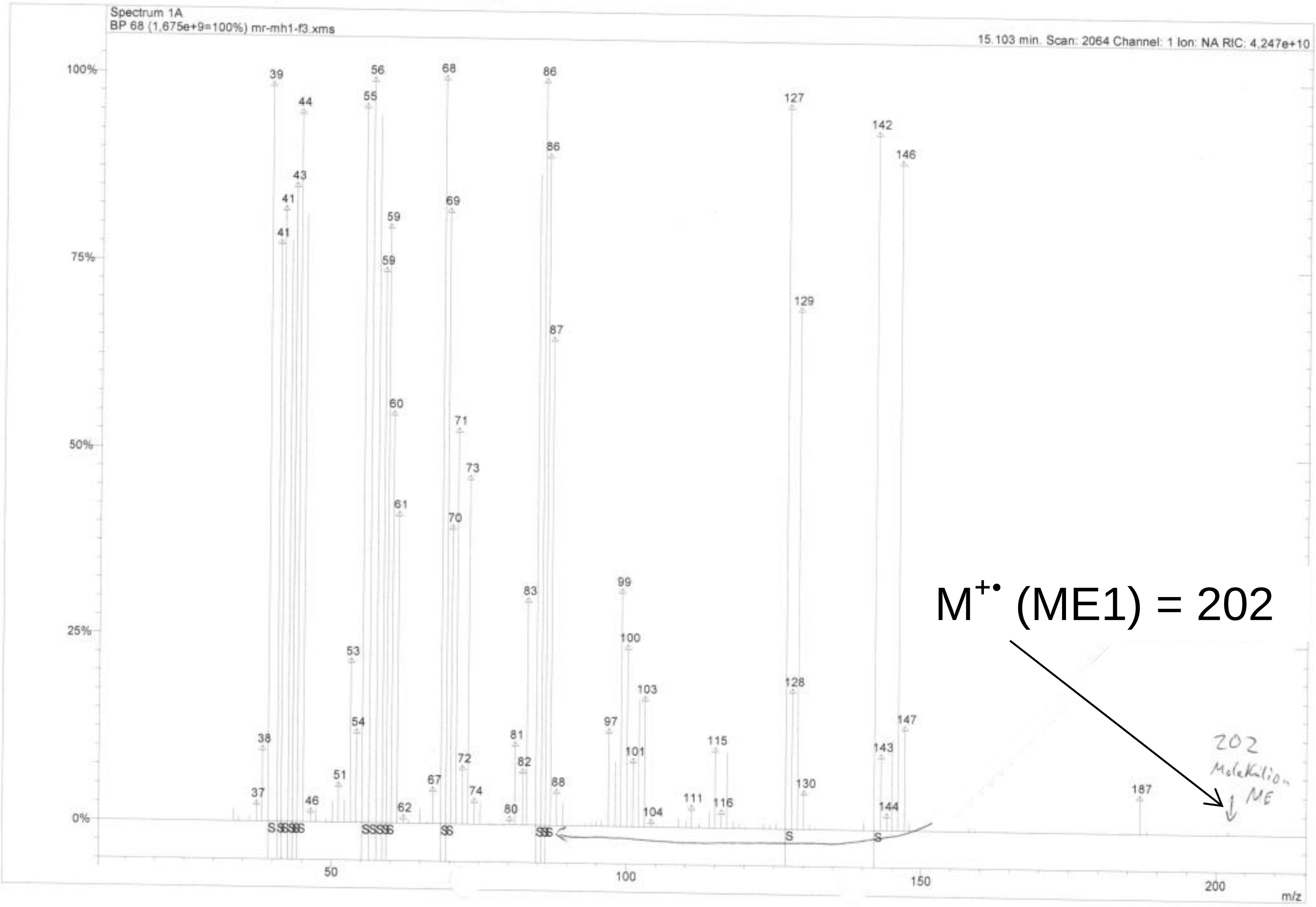


S1c. HSQC NMR spectra of ME1. $H_{x/y}$ denotes a proton in position x or y.



S1b. HSQC NMR spectra of ME2. $H_{x/y}$ denotes a proton in position x or y.


Spectrum 1A
BP 56 (1,675e+9=100%) mr-mh1-f5.xms
16.089 min. Scan: 2331 Channel: 1 Ion: NA RIC: 4,119e+10 (BC)
100%
75%
50%
25%
0%
39
56
58
86
85
87
127
146
45
69
69
44
43
44
59
83
41
71
59
73
100
99
128
61
60
145
70
53
129
97
103
38
81
101
111
148
72
82
117
51
75
88
144
37
46
52
62
67
96
109
116
130
143
149
187
188
50
100
150
200
m/z
M+• (ME2) = 202
Peaks überlagert
202 Molekülion ME


Spectrum 1A
BP 68 (1,675e+9=100%) mr-mh1-f3.xms
15.103 min. Scan: 2064 Channel: 1 Ion: NA RIC: 4,247e+10
100%
75%
50%
25%
0%
39
56
68
86
55
44
127
142
86
146
43
41
69
41
59
59
129
87
60
71
73
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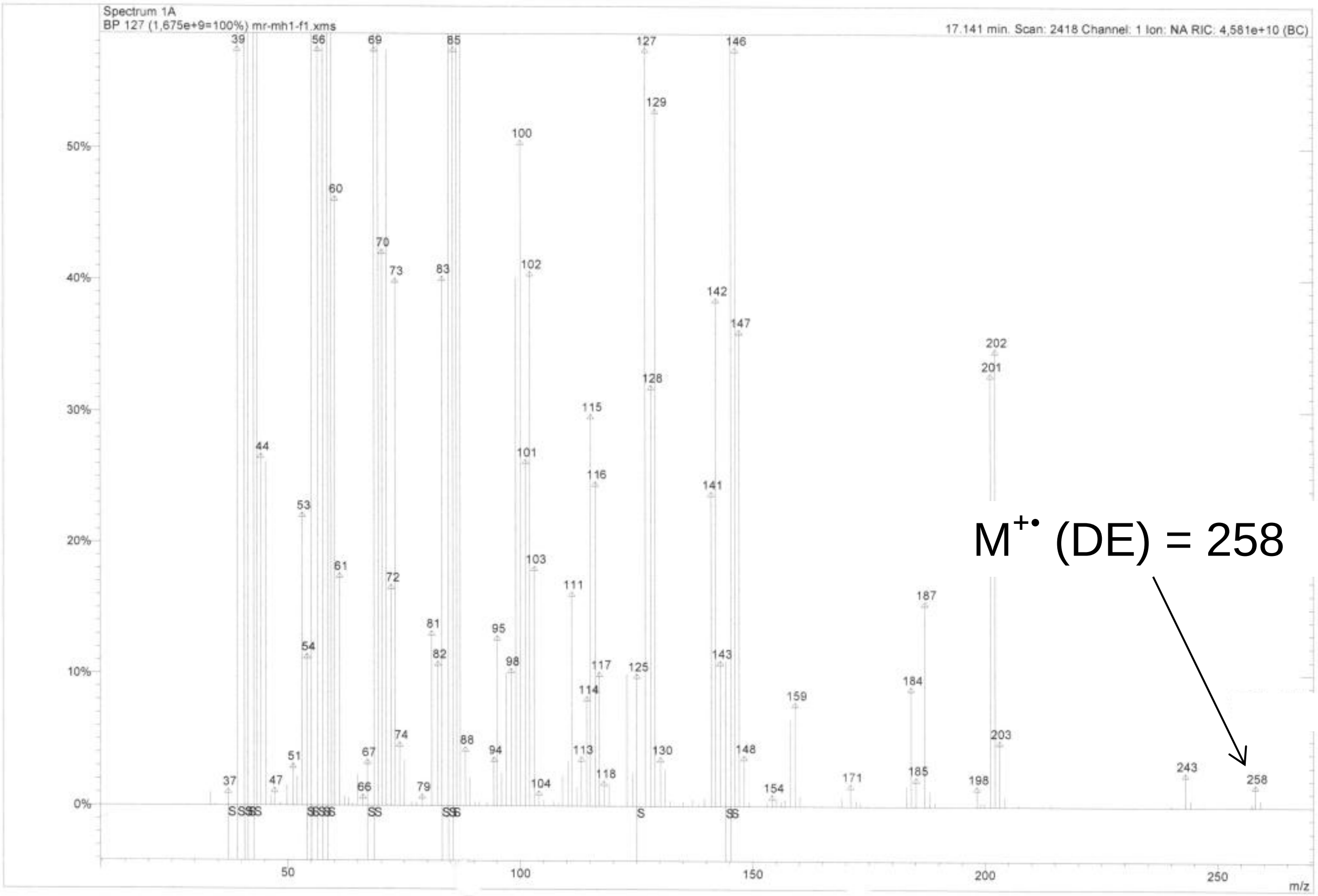
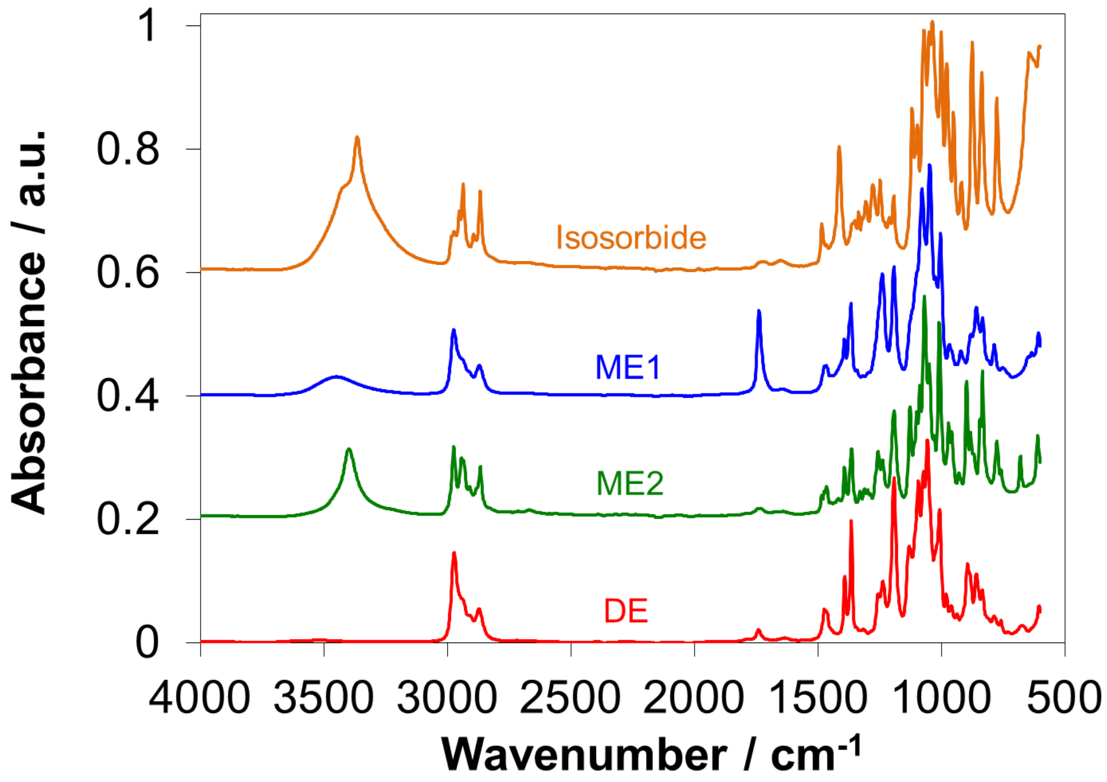
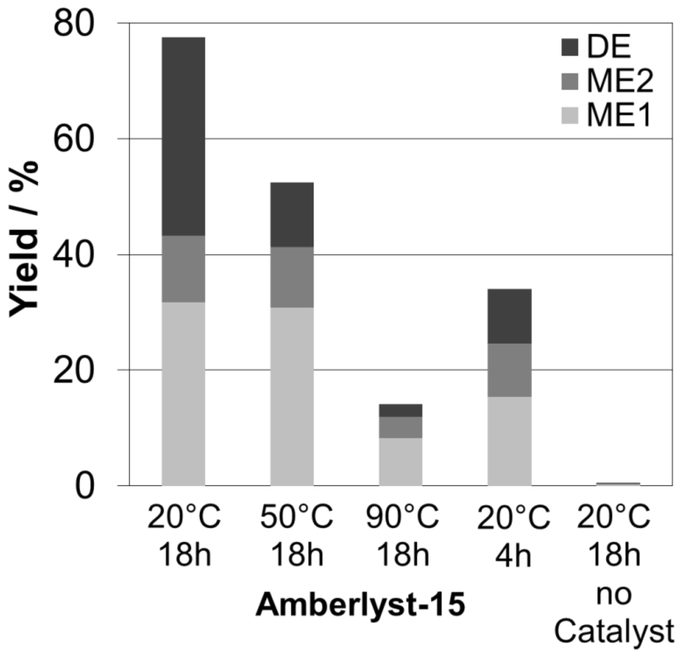
99
83
100
53
128
103
54
97
147
38
81
115
143
101
72
82
130
51
67
74
88
111
116
144
187
37
46
62
80
104
50
100
150
200
m/z
M+• (ME1) = 202
202 Molekülion ME



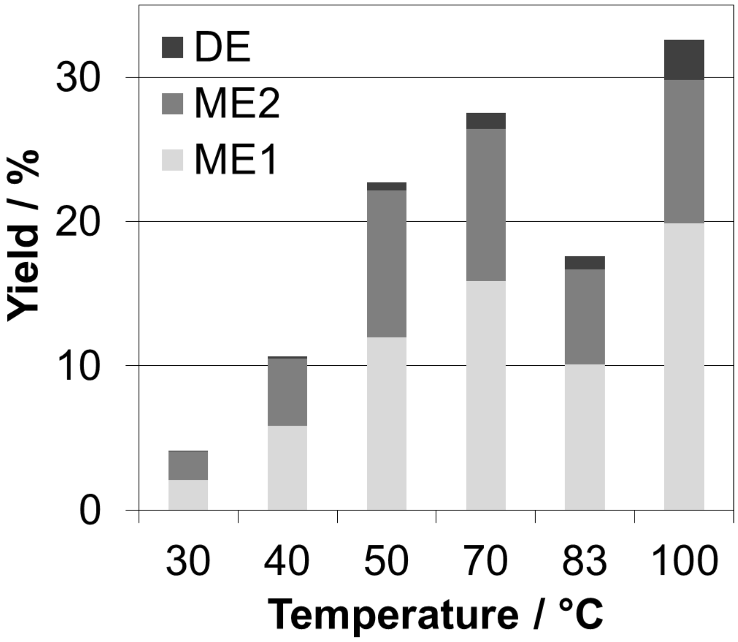
S2. Mass spectra of DE (bottom), ME1 (middle) and ME2 (top).



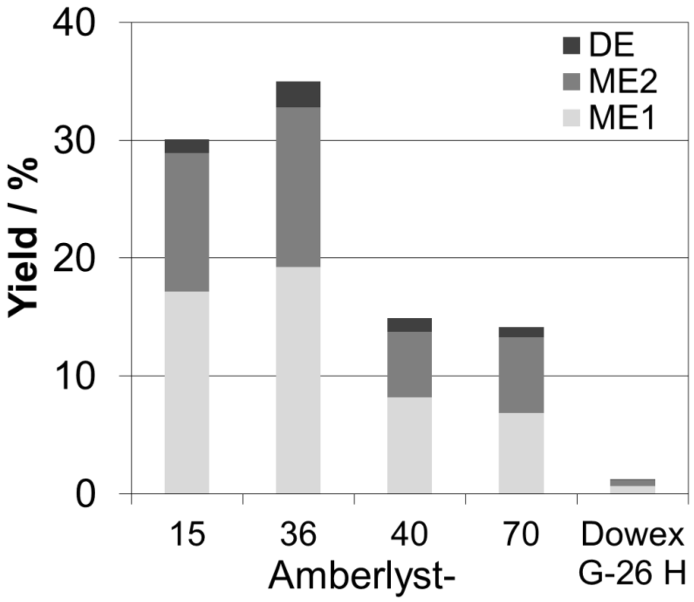
S3. FT-IR-Spectra of isosorbide (offset: 0.6), ME1 (offset: 0.4), ME2 (offset: 0.2) and DE (no offset).



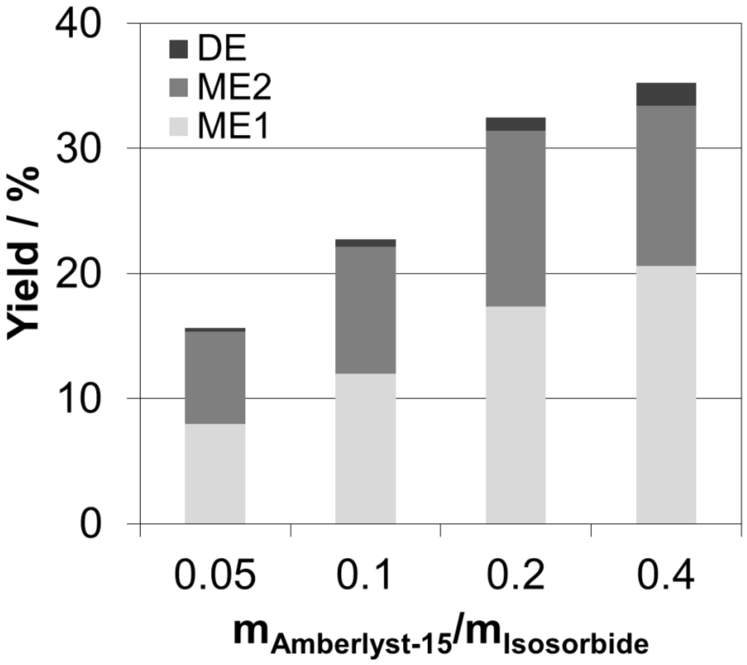
S4. Yields of the isosorbide ether derivatives using isobutene and a solution of isosorbide in ethylacetate in an autoclave reaction under different reaction conditions.



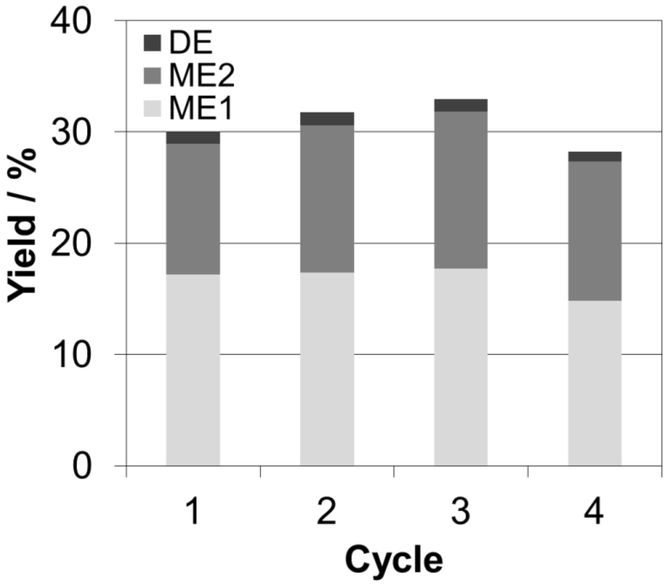
S5. Yields of the isosorbide ether derivatives from isosorbide and *tert*-butanol using Amberlyst-15 as catalyst at different reaction temperatures after 8 h. The reaction at 100°C was carried out in an autoclave while the other reactions up to the boiling point were carried out under atmospheric pressure with a reflux condenser.



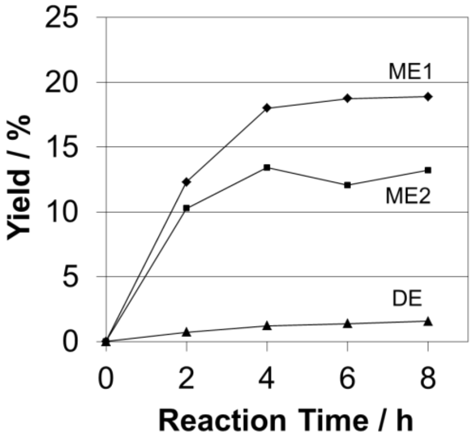
S6. Yields of the isosorbide ether derivatives at a reaction temperature of 70 °C after 4 h using different acidic ion exchange resins.



S7. Yields of the isosorbide ether derivatives from isosorbide and *tert*-butanol using different ratios of Amberlyst-15 and isosorbide at 70 °C for 8 h.



S8. Yields of the isosorbide ether derivatives from isosorbide and *tert*-butanol in recycling experiments of Amberlyst-15 at 70°C for 8 h.



S9. Kinetic investigation of the yields of the isosorbide ether derivatives at a reaction temperature of 70 °C using Amberlyst-15.