Catalytic upcycling of PVC waste-derived phthalate esters into safe, hydrogenated plasticizers

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Content of the Electronic Supplementary Information

Materials

All chemicals were used as received, unless otherwise specified: Dibutyl phthalate (J&K scientific, 99%), Diisobutyl phthalate (TCI Europe, > 98 %), Benzyl butyl phthalate (TCI Europe, > 97%), Bis(2-ethylhexyl) phthalate (J&K scientific ,99%), Diisononyl phthalate (TCI Europe, purity not specified), Monobutyl phthalate (TCI Europe, >95%), Tetrahydrofuran (Acros organics, 99%), Tetrahydrofuran-d$_8$ (Sigma-Aldrich, ≥ 99.5% atom% D), 2-Methyltetrahydrofuran (Sigma-Aldrich, anhydrous ≥ 99%), Cyclopentyl methyl ether (VWR Chemicals, > 99.9%), Cyclohexanone (Sigma-Aldrich, ≥ 99.5%), Butanone (Acros Organics, 99+%), γ-Valerolactone (Acros organincs, 98%), 2-Ethyl-1-hexanol (Sigma-Aldrich, > 99%), *tert*-amyl methyl ether (Sigma-Aldrich, > 99%), Isononanol (Evonik, > 99%), Diisononyl cyclohexane-1,2-dicarboxylate (Evonik, 99%, Elatur® CH), Sulfuric acid (Acros Organics, 95%), N,O-Bis(trimethylsilyl)trifluoroacetamide (Sigma-Aldrich, BSTFA + TCMS 99:1), Anisole (Sigma-Aldrich, ReagentPlus®, 99%), Poly(vinyl chloride) (Sigma-Aldrich, average MW ~43.000, average MN ~22,000), Maleic acid (TCI Europe, > 99%), bis (2-ethylhexyl) adipate (Fisher scientific, 99 %), Calcium carbonate (Sigma-Aldrich, ≥ 99%), Ruthenium(III)nitrosylnitrate (Alfa Aesar, Ru 31.3% min), SiO_2 (Evonik, Aerosil 380), SiO_2-Al_2O_3 (Grace Silica GmbH, 13% Al_2O_3), Al_2O_3 (acidic, CONDEA Chemie, Puralox NGa-150), Al_2O_3 (neutral, Sigma-Aldrich, Type 507 C Brockmann I), Al_2O_3 (basic, Sigma-Aldrich, Brockmann I), TiO_2 (Sigma-Aldrich, Aeroxide © P25), ZrO_2 (Alfa Aesar, 1/8" pellets) and activated carbon (Alfa Aesar; Carbon powder, activated, Norit GSX, steam activated, acid washed). Commercial hydrogenation catalysts include 5 wt.% Pt/C (Alfa Aesar), 5 wt.% Pd/C (Alfa Aesar), 5 wt.% Ru/C (Alfa Aesar) and 5 wt.% Rh/C (Alfa Aesar, Type 87L, dry).

Temperature programmed reduction

The sample was prepared via incipient wetness impregnation of the Al_2O_3 [acidic] support with an aqueous solution of the Ru precursor salt, i.e. $RuNO(NO_3)_3$. The impregnated support was then dried at 60 °C for 16 h (overnight), after which the dry materials were granulated to particles sizes between 250 and 500 µm. Prior to the temperature programmed reduction (TPR) experiment, the sample (200 mg) was treated with N_2 at 200 °C in a quartz U-tube (120 min, 10 °C min^{-1}, 20 mL N_2 min^{-1}), after which the TPR (20 mL min^{-1} of 5 % H_2 in Ar, 10 °C min^{-1}) was recorded on a Quantachrome ChemBET pulsar, equipped with a thermal conductivity detector (TCD).

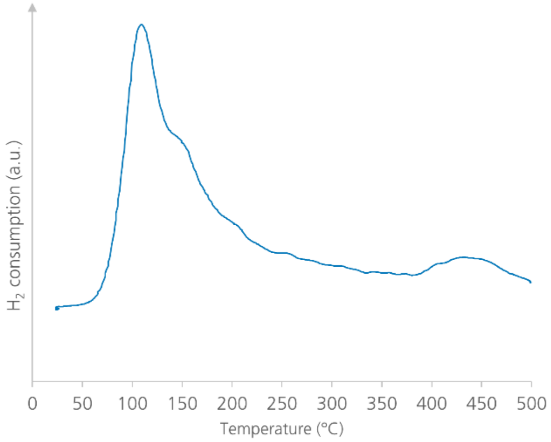

Figure S1: The temperature programmed reduction profile of a 0.5 wt.% Ru/Al_2O_3 [acidic] sample.

Product identification and quantification (GC/GC-MS)

The assignment of the different peaks detected on GC chromatograms, was established by GC-MS analyses. In agreement with Guo *et al.*[SI1] and Yin *et al.*[SI2], the compounds were identified by the analysis of the molecular ion and the base peak of the component. The fragmentation pattern served as an additional tool for the identification of the product. The base peak is (generally) the protonated phthalic anhydride or the (partially) hydrogenated analogue, producing the characteristic m/z ratios of 149 (phthalate), 153 (H4-intermediate) or 155 (H6-product).

Reaction mixtures containing a considerable amount of carboxylic acids were silylated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) prior to the GC analysis. To that end, BSTFA was added in a 3-fold excess, after which the samples were placed at 60 °C for 3 h.

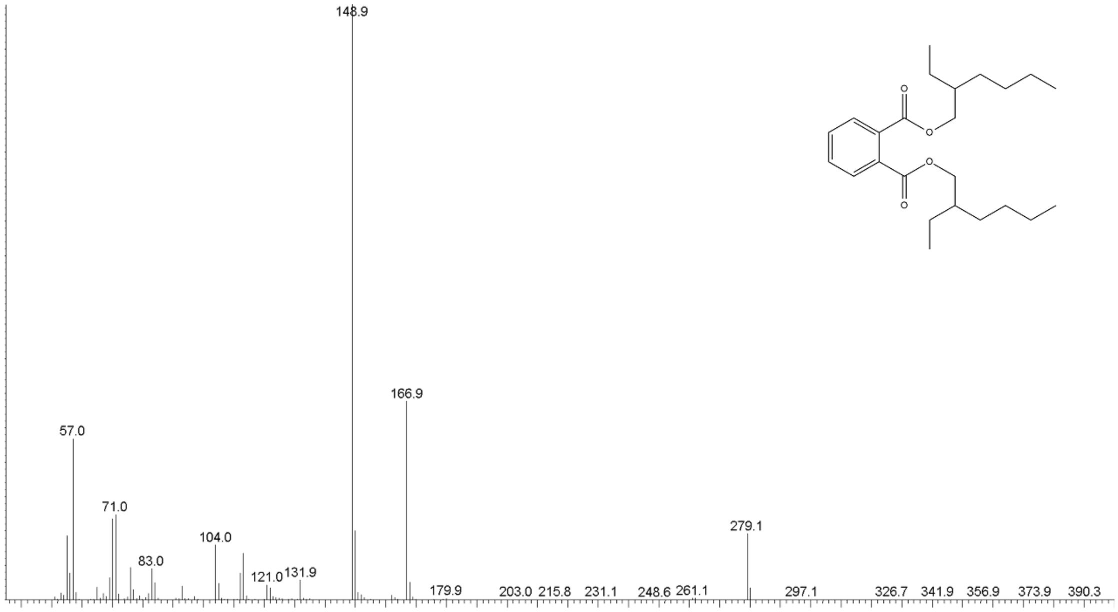

Figure S2: GC-MS spectrum of bis(2-ethylhexyl) phthalate (MW = 390 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 390 (trace), 280 (3), 279 (12), 168 (3), 167 (35), 150 (12), 149 (100), 132 (2), 122 (2), 121 (2), 113 (8), 112 (5), 105 (2), 104 (6), 93 (2), 84 (3), 83 (5), 82 (1), 77 (1), 76 (3), 72 (1), 71 (14), 70 (13), 69 (3), 65 (1), 57 (20), 56 (4), 55 (8).

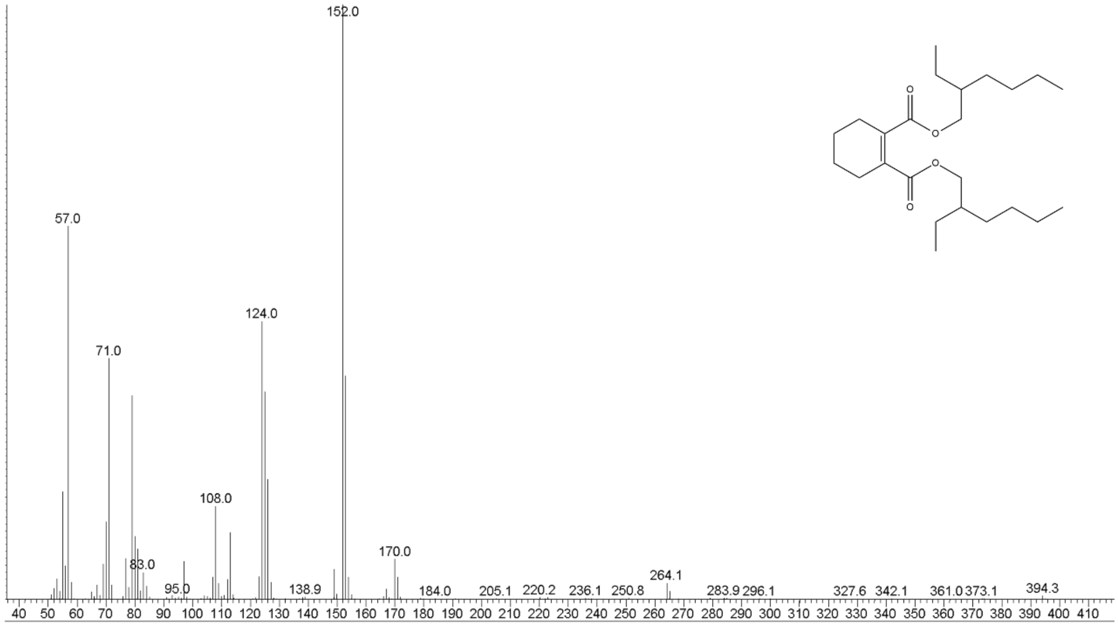

Figure S3: GC-MS spectrum of bis(2-ethylhexyl) 1,2-cyclohexene dicarboxylate ester (MW = 394 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 394 (trace), 283 (2), 282 (2), 281(1), 265 (1), 264 (2), 207 (3), 171 (3), 170 (6), 155 (12), 154 (4), 153 (37), 152 (100), 127 (3), 126 (20), 125 (30), 124 (41), 123 (3), 113 (11), 112 (3), 109 (2), 108 (10), 107 (2), 97 (4), 84 (2), 83 (4), 82 (1), 81 (7), 80 (7), 79 (20), 77 (4), 72 (2), 71 (34), 70 (9), 69 (5), 67 (1), 58 (2), 57 (44), 56 (4), 55 (12).

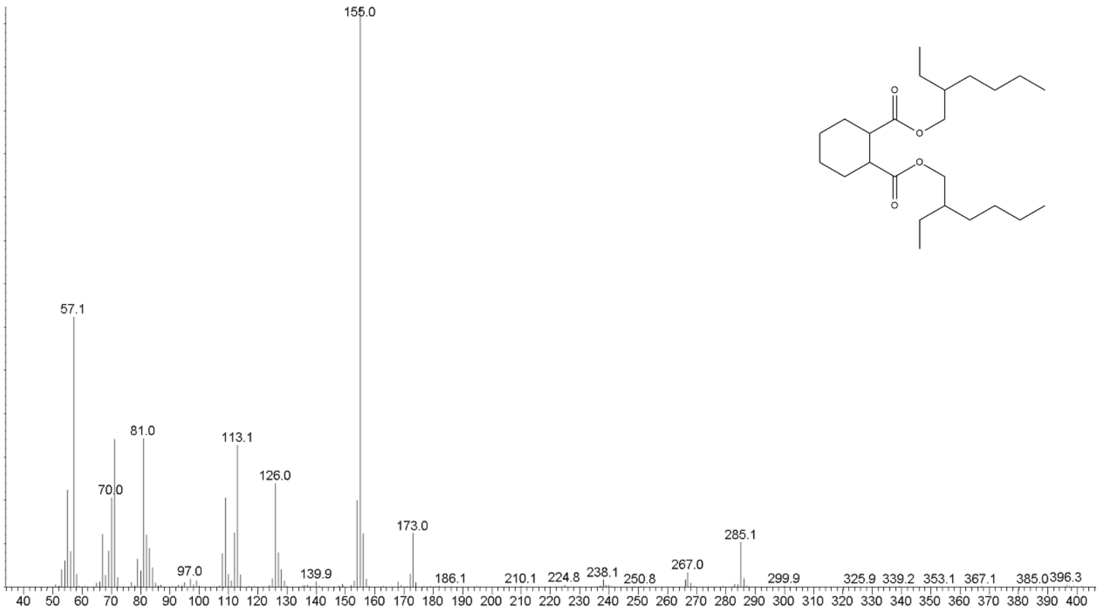

Figure S4: GC-MS spectrum of bis(2-ethylhexyl) 1,2-cyclohexane dicarboxylate ester (MW = 396 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 396 (2), 286 (2), 285 (10), 268 (1), 267 (5), 266 (1), 238 (1), 173 (10), 172 (2), 157 (2), 156 (9), 155 (100), 154 (15), 128 (3), 127 (6), 12 (16), 125 (1), 123 (3), 114 (2), 113 (23), 6112 (9), 109 (13), 108 (4), 97 (1), 84 (3), 83 (6), 82 (6), 81 (17), 80 (2), 79 (2), 72 (1), 71 (20), 70 (11), 69 (2), 68 (1), 67 (5), 58 (1), 57 (26), 56 (4), 55 (9), 54(2).

Figure S5: GC-MS spectrum of dibutyl phthalate (MW = 278 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 278 (trace), 223 (9), 205 (2), 167 (4), 150 (10), 149 (100), 132 (2), 122 (1), 121 (2), 105 (2), 104 (8), 93 (2), 77(1), 76 (6), 75 (1), 65 (3), 57 (13), 56 (3), 55 (1).

Figure S6: GC-MS spectrum of dibutyl 1,2-cyclohexane dicarboxylate ester (MW = 284 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 284 (trace), 229 (3); 212 (3), 211 (23), 210 (7), 183 (2), 182 (14), 156 (9), 155 (100), 154 (8), 128 (3), 127 (9), 126 (34), 125 (3), 110 (2), 109 (23), 108 (13), 82 (9), 81 (32), 80 (4), 79 (6), 68 (2), 67 (10), 57 (30), 56 (5), 55 (5), 54 (5), 53 (3).

Figure S7: GC-MS spectrum of diisononyl phthalate (MW = 418 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 418 (trace), 294 (6), 293 (29), 167 (12), 150 (11), 149 (100), 128 (2), 127 (16), 126 (3), 120 (2), 105 (2), 104 (4), 98 (4), 97 (6), 93 (2), 85 (14), 84 (4), 83 (4), 76 (4), 71 (23), 70 (7), 69 (12), 68 (2), 67 (2), 57 (24), 56 (5), 55 (13).

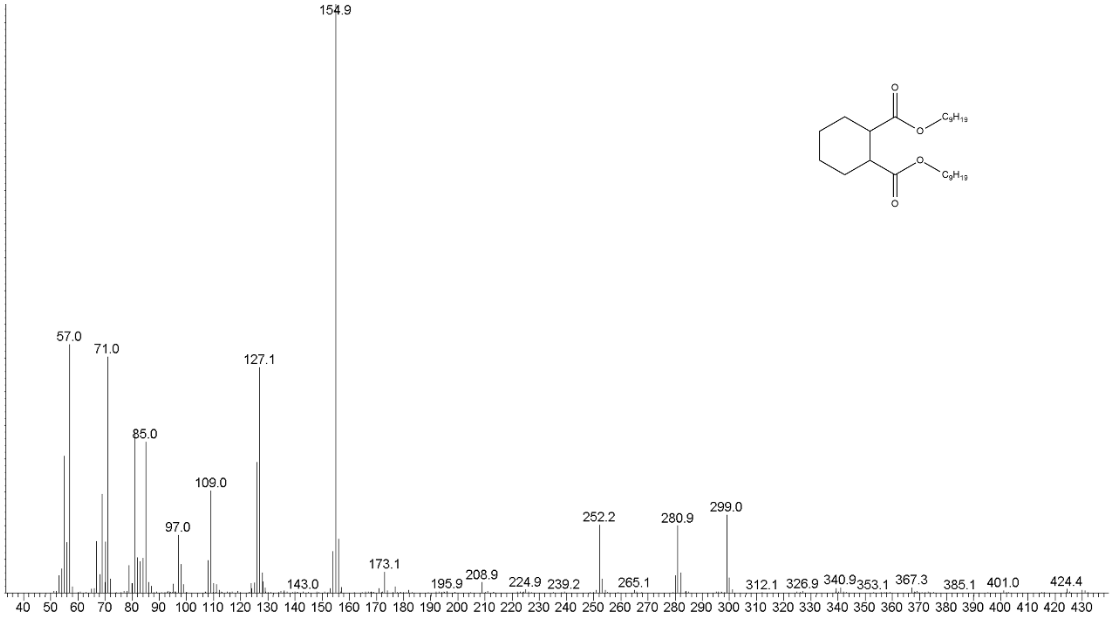

Figure S8: GC-MS spectrum of diisononyl 1,2-cyclohexane dicarboxylate ester (MW = 424 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 424 (trace), 300 (3), 299 (16), 283 (2), 282 (6), 281 (29), 280 (3), 253 (2), 252 (11), 209 (2), 173 (4), 156 (9), 155 (100), 154 (7), 128 (6), 127 (41), 126 (22), 125 (3); 124 (2), 110 (2), 109 (17), 108 (5), 98 (3), 97 (10), 96 (3), 95 (2), 86 (2), 85 (27), 84 (6), 83 (6), 82 (6), 81 (28), 80 (4), 79 (6), 73 (3), 72 (3), 71 (42), 70 (11), 69 (17), 68 (3), 67 (9), 58 (2), 57 (44), 56 (9), 55 (24), 54 (4), 53 (3).

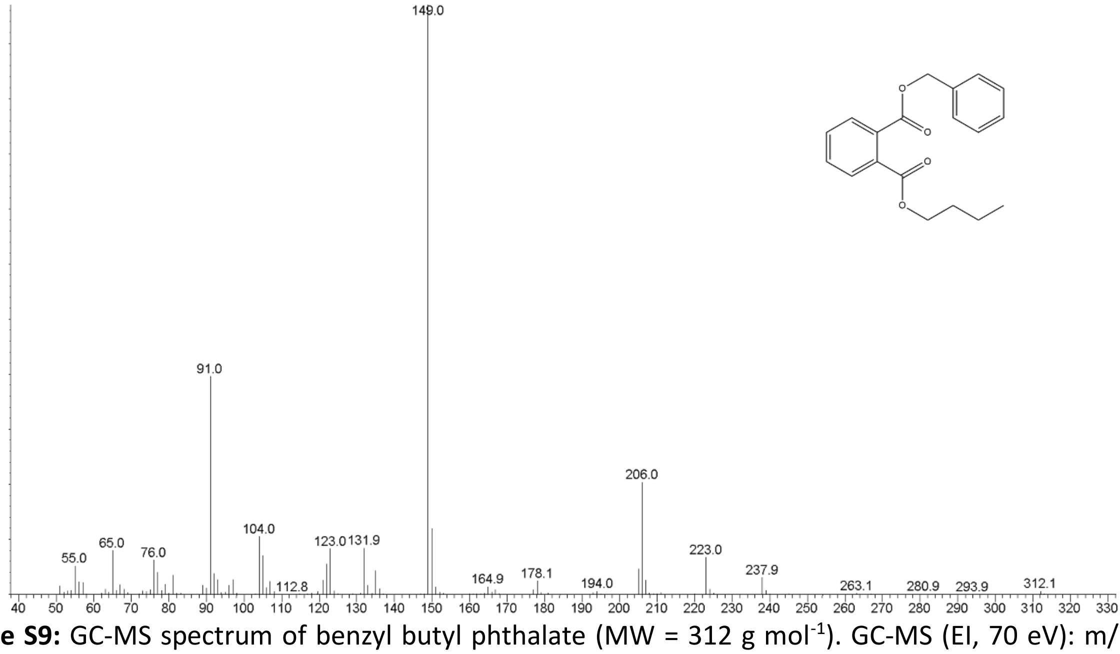

Figure S9: GC-MS spectrum of benzyl butyl phthalate (MW = 312 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 312 (1), 239 (1), 238 (4), 207 (4), 206 (28), 205 (4), 194 (1), 178 (3), 177 (1), 165 (2), 151 (1), 150 (12), 149 (100), 136 (2), 135 (6), 133 (2), 123 (12), 122 (7), 121 (3), 120 (1), 107 (4), 106 (2), 105 (10), 103 (13), 93 (3), 92 (6), 91 (61), 90 (2), 89 (3), 79 (2), 78 (1), 77 (5), 75 (1), 74 (1), 73 (1), 65 (11), 57 (3), 56 (3), 51 (2).

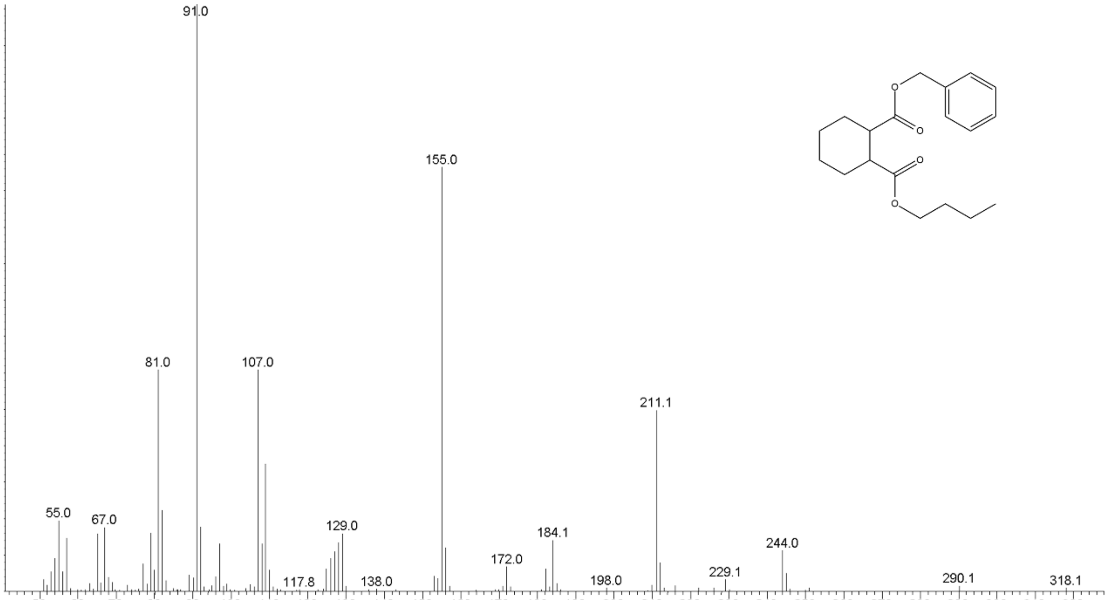

Figure S10: GC-MS spectrum of benzyl butyl 1,2 cyclohexane dicarboxylate ester (MW = 318 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 318 (1), 290 (1), 245 (3), 244 (7), 212 (4), 211 (29), 206 (1), 185 (1), 184 (1), 182 (2), 172 (4), 157 (1), 156 (6), 155 (61), 153 (3), 130 (1), 129 (10), 128 (8), 127 (5), 126 (2), 125 (4), 111 (3), 109 (20), 108 (7), 107 (38), 108 (7), 97 (3), 92 (11), 91 (100), 89 (2), 83 (2), 82 (13), 81 (30), 80 (3), 79 (9), 78 (1), 77 (4), 73 (3), 68 (2), 67 (8), 66 (1), 65 (10), 63 (1), 57 (7), 56 (3), 55 (6), 54 (4), 53 (3), 51 (2).

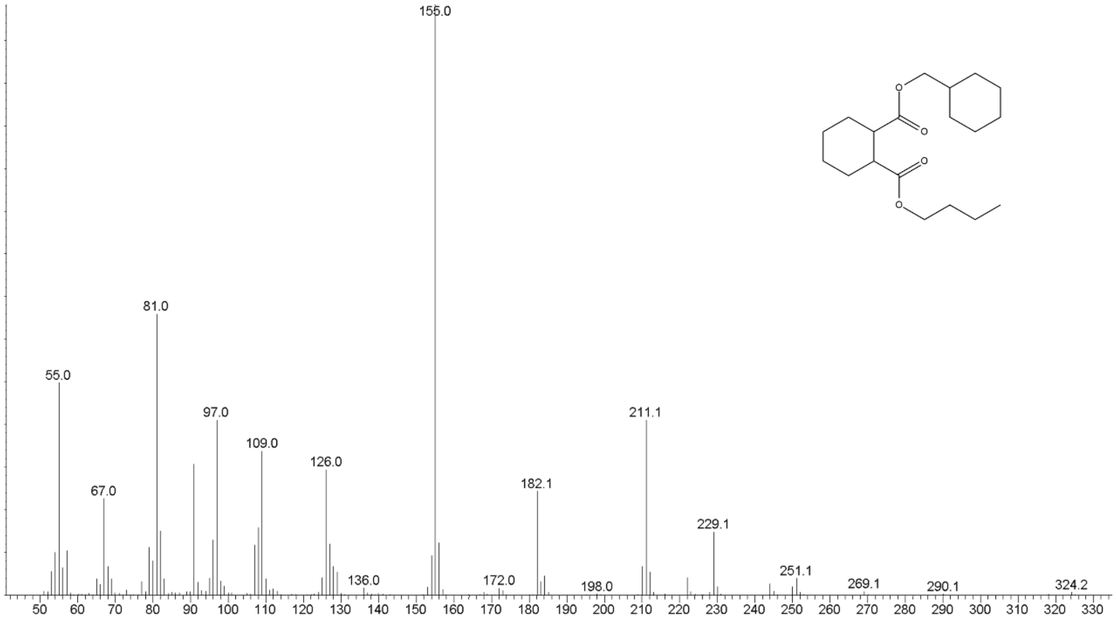

Figure S11: GC-MS spectrum of cyclohexyl butyl 1,2 cyclohexane dicarboxylate ester (MW = 324 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 324 (1), 281 (1), 251 (3), 250 (2), 244 (2), 229 (11), 222 (4), 212 (4), 211 (28), 210 (6), 207 (2), 184 (3), 183 (2), 182 (18), 156 (8), 155 (100), 154 (7), 153 (1), 136 (1), 129 (3), 128 (5), 127 (9), 126 (21), 125 (4), 110 (3), 109 (25), 108 (12), 107 (7), 98 (2), 97 (29), 96 (10), 95 (3), 83 (3), 82 (10), 81 (45), 80 (6), 79 (7), 77 (2), 73 (1), 68 (5), 67 (14), 66 (1), 65 (2), 57 (7), 56 (4), 55 (34), 54 (7), 53 (4).

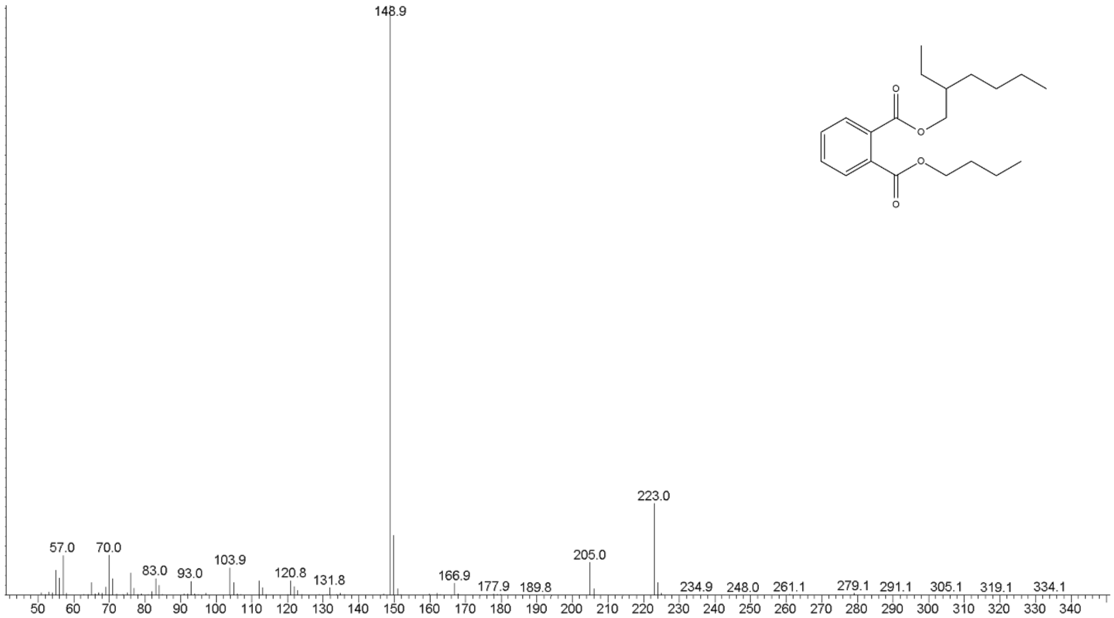

Figure S12: GC-MS spectrum of 2-ethylhexyl butyl phthalate (MW = 334 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 334 (trace), 224 (2), 223 (17), 205 (6), 167 (2), 150 (10), 149 (100), 132 (2), 121 (2), 113 (1), 112 (2), 105 (2), 104 (5), 93 (2), 84 (2), 83 (3), 77 (1), 76 (4), 71 (3), 70 (6), 65 (2), 57 (6), 55 (4), 56 (3).

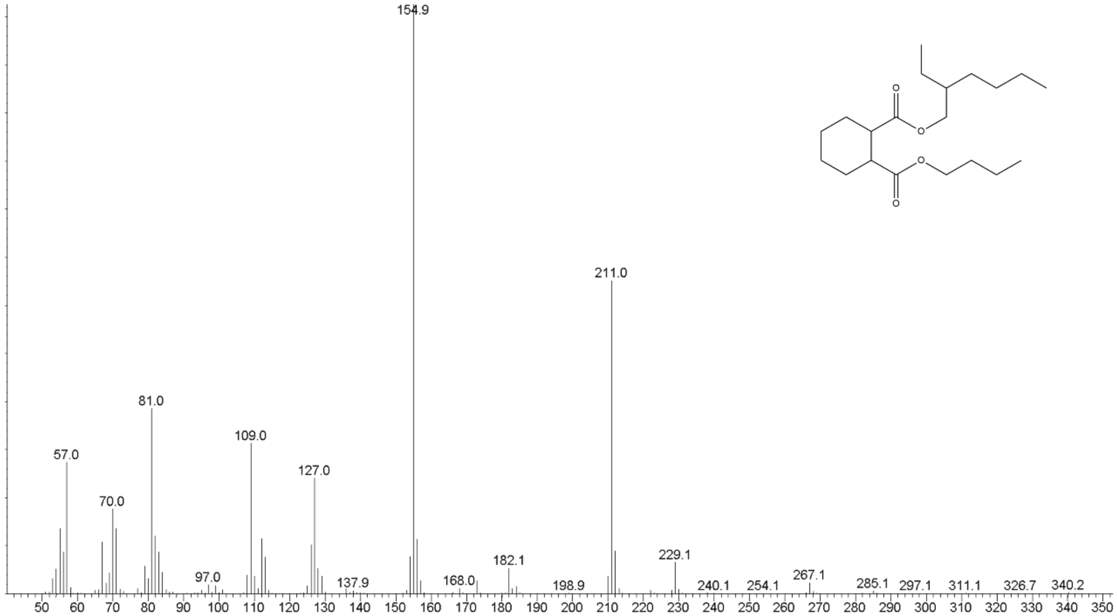

Figure S13: GC-MS spectrum of 2-ethylhexyl butyl 1,2 cyclohexane dicarboxylate ester (MW = 340 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 340 (2), 268 (1), 229 (7), 212 (4), 211 (32), 210 (6), 183 (2), 182 (19), 173 (1), 157 (1), 156 (9), 155 (100), 154 (9), 136 (1), 129 (2), 128 (3), 127 (9), 126 (22), 125 (2), 113 (10), 112 (6), 110 (2), 109 (23), 108 (11), 99 (1), 84 (2), 83 (5), 82 (8), 81 (33), 80 (5), 79 (6), 77 (1), 71 (12), 70 (10), 69 (3), 68 (2), 67 (9), 58 (1), 57 (24), 56 (6), 55 (11), 54 (4), 53 (3).

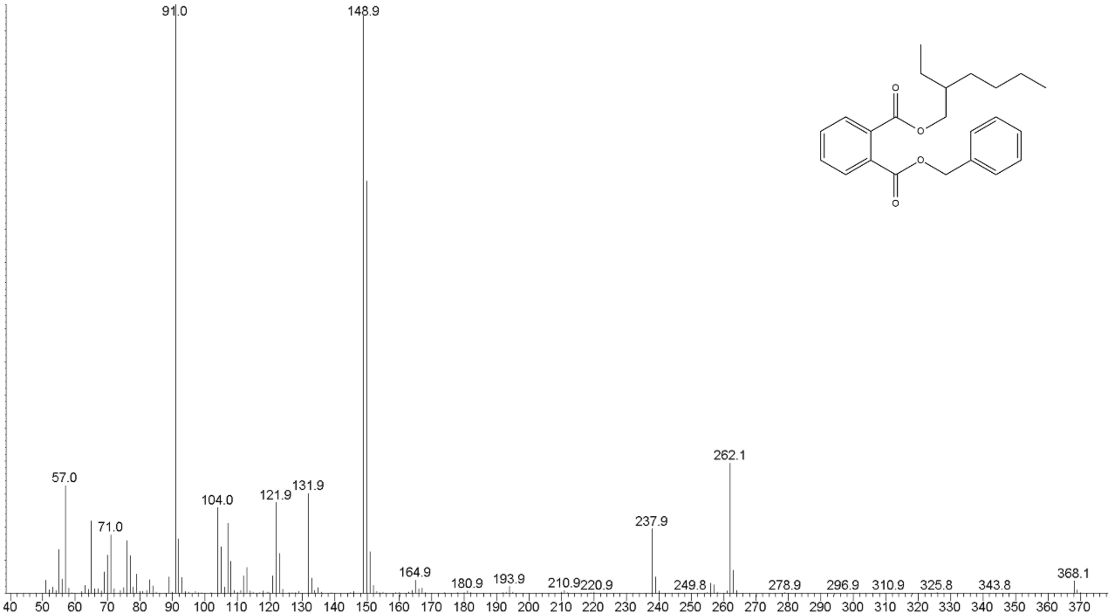

Figure S14: GC-MS spectrum of benzyl 2-ethylhexyl phthalate (MW = 368 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 368 (2), 341 (1), 282 (1), 281 (5), 263 (4), 262 (20), 256 (2), 255 (2), 239 (3), 238 (10), 208 (2), 207 (9), 194 (1), 193 (1), 191 (1), 165 (5), 151 (7), 150 (69), 149 (97), 147 (1), 133 (4), 132 (17), 123 (7), 122 (15), 121 (3), 113 (5), 108 (6), 107 (12), 104 (15), 93 (3), 92 (9), 91 (100), 85 (3), 83 (2), 78 (1), 77 (6), 76 (9), 73 (3), 71 (11), 70 (7), 69 (4), 65 (12), 63 (1), 57(19), 56 (3), 55 (8).

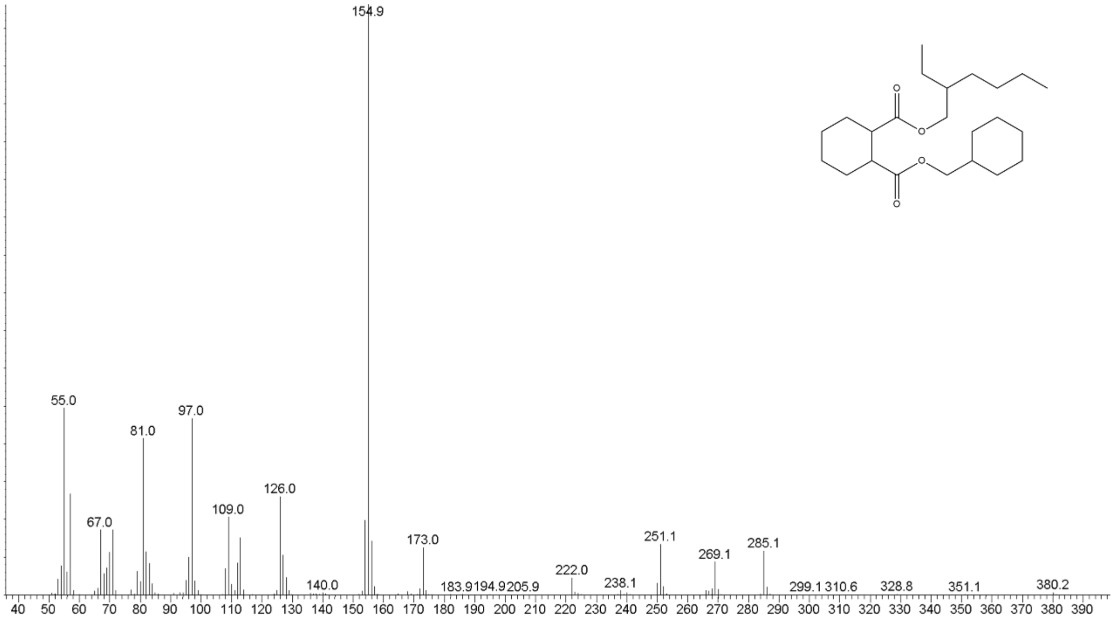

Figure S15: GC-MS spectrum of cyclohexyl 2-ethylhexyl 1,2 cyclohexane dicarboxylate ester (MW = 380 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 380 (trace), 341 (1), 286 (1), 285 (7), 251 (8), 250 (2), 173 (8), 157 (1), 156 (9), 155 (100), 154 (13), 128 (3), 127 (6), 126 (17), 125 (1), 113 (9), 112 (5), 109 (12), 108 (5), 98 (2), 97 (31), 96 (11), 95 (3), 84 (2), 83 (5), 82 (7), 81 (26), 79 (4), 73 (10), 72 (1), 71 (12), 70 (8), 69 (5), 68 (4), 67 (11), 66 (1), 57 (17), 56 (5), 55 (31), 54 (5), 53 (3).

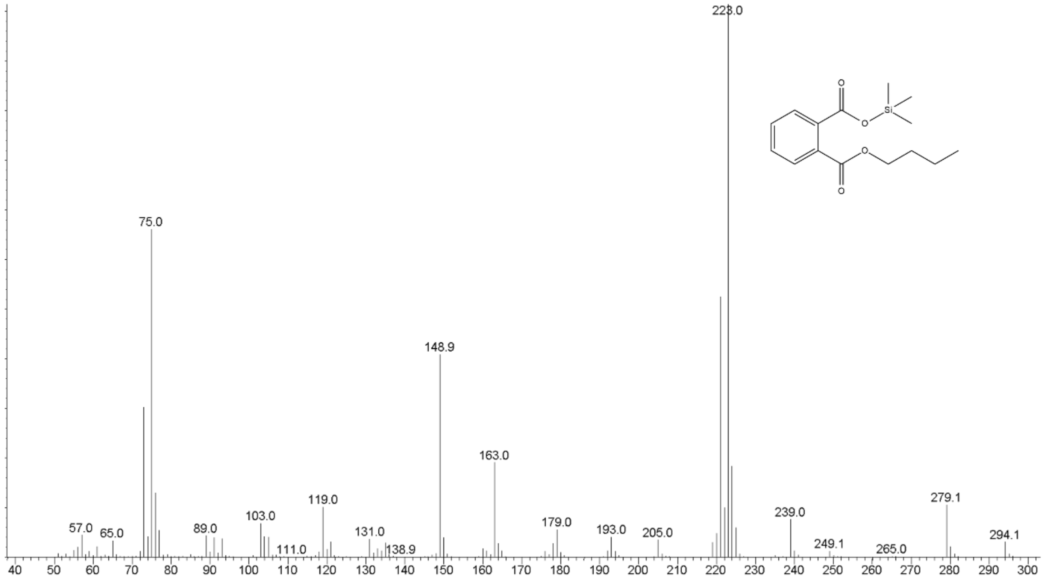

Figure S16: GC-MS spectrum of monobutyl phthalate (MW = 222 g mol^{-1}) - butyl trimethylsilyl phthalate (MW = 294 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 294 (3), 279 (10), 239 (9), 224 (16), 223 (100), 222 (9), 221 (47), 220 (4), 219 (3), 205 (3), 194 (1), 193 (4), 192 (1), 179 (5), 178 (3), 176 (1), 165 (1), 164 (2), 161 (1), 160 (2), 150 (3), 149 (36), 135 (2), 134 (1), 133 (1), 131 (3), 121 (3), 119 (9), 105 (4), 104 (4), 103 (6), 93 (3), 91 (3), 89 (4), 77 (5), 76 (12), 75 (58), 74 (4), 73 (27), 72 (1), 65 (3), 61 (2), 59 (1), 57 (4), 56 (2), 55 (1).

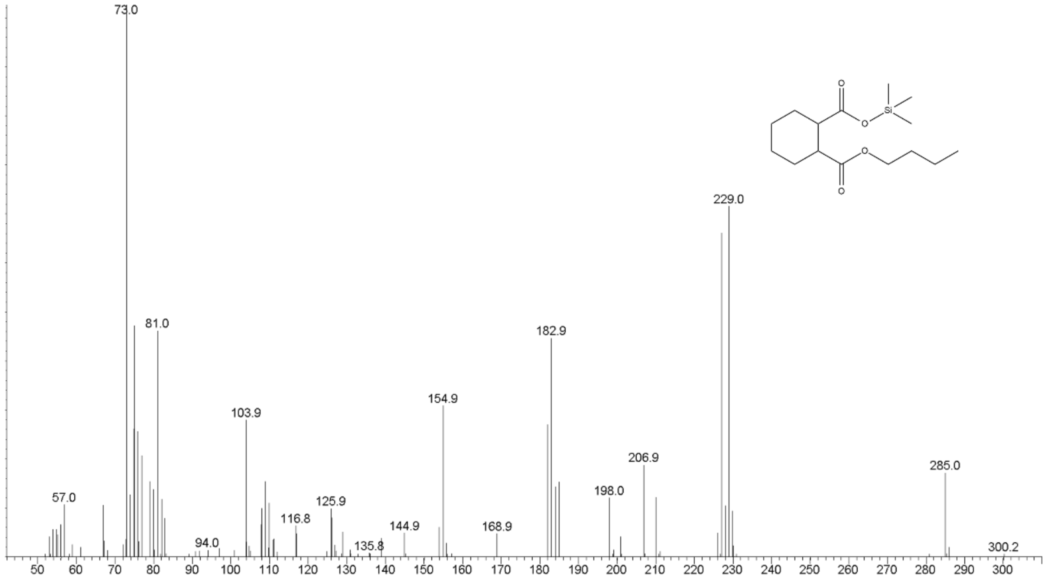

Figure S17: GC-MS spectrum of 1,2-cyclohexanedicarboxylic acid, monobutyl ester (MW = 228 g mol^{-1}) – Butyl trimethylsilyl 1,2 cyclohexane dicarboxylate ester (MW = 300 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 300 (2), 286 (3), 285 (15), 256 (1), 231 (3), 230 (9), 229 (59), 228 (9), 227 (54), 226 (5), 211 (3), 210 (11), 201 (5), 200 (3), 199 (3), 198 (11), 186 (2), 185 (13), 184 (13), 183 (37), 182 (27), 173 (2), 171 (1), 170 (1), 169 (5), 157 (1), 156 (4), 155 (24), 154 (7), 145 (6), 142 (2), 139 (4), 136 (3), 131 (3), 130 (1), 128 (6), 127 (4), 125 (15), 123 (3), 119 (2), 117 (8), 116 (2), 112 (2), 111 (7), 110 (11), 109 (11), 108 (13), 103 (2), 101 (3), 99 (3), 97 (2), 95 (1), 94 (3), 92 (2), 91 (2), 90 (2), 83 (6), 82 (10), 81 (37), 80 (10), 79 (9), 77 (5), 76 (4), 75 (58), 74 (9), 73 (100), 72 (3), 67 (9), 61 (4), 59 (3), 58 (2), 57 (10), 56 (4), 55 (6), 54 (5), 53 (4).

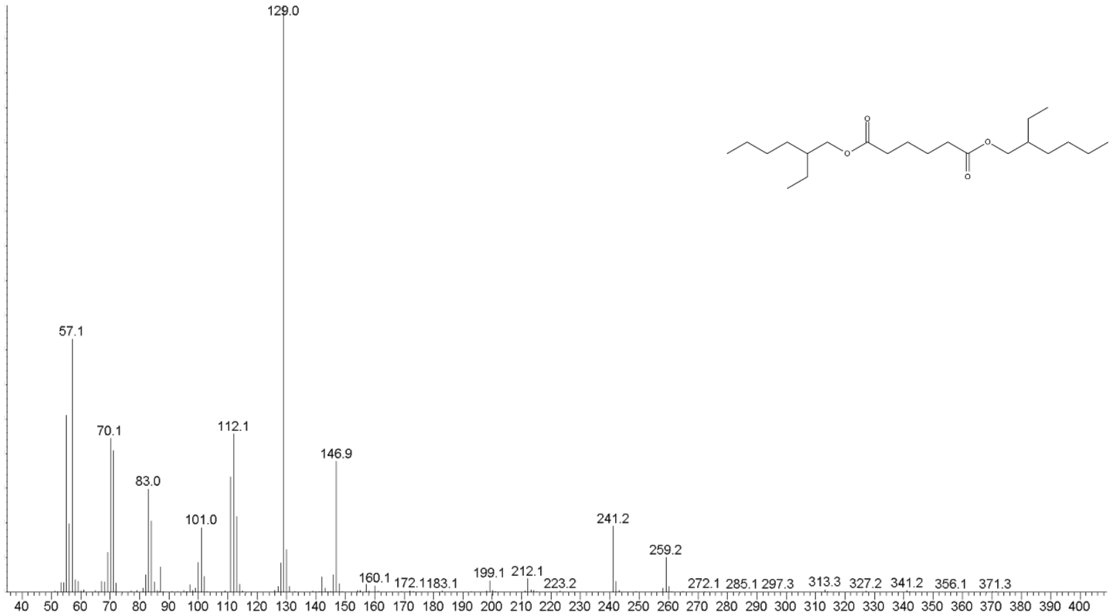

Figure S18: GC-MS spectrum of bis(2-ethylhexyl) hexanedioate (MW = 371 g mol^{-1}). GC-MS (EI, 70 eV): m/z (rel. int., %): 371 (trace), 259 (6), 242 (2), 241 (11), 212 (2), 199 (2), 148 (2), 147 (23), 146 (3), 130 (7), 129 (100), 128 (5), 113 (13), 112 (27), 111 (20), 102 (3), 101 (11), 100 (5), 87 (4), 84 (12), 83 (17), 82 (3), 72 (2), 71 (24), 70 (26), 69 (7), 68 (2), 67 (2), 58 (2), 57 (43), 56 (12), 55 (30), 54 (2), 53 (2).

Product identification and quantification (^{1}H-NMR)

Maleic acid was used as the external standard in ^{1}H-NMR measurements (δ = 6.20 ppm, s, 2H). Phthalate esters were then quantified based on their characteristic aromatic proton signals at 7.50 – 7.55 ppm (m, 2H) and 7.64 – 7.70 ppm (m, 2H). The formed products, i.e. dialkyl 1,2-cyclohexanedicarboxylate esters, were quantified based on the signals at 2.78 (*cis*-configuration) and 2.55 ppm (*trans*-configuration) (br, 2H). These signals represent the hydrogen atoms in the alpha position relative to the ester functionality (Figure S19). The amount of residual PVC could be determined on the basis of the three, partially overlapping broad signals at 4.3- 4.7 ppm (3H).

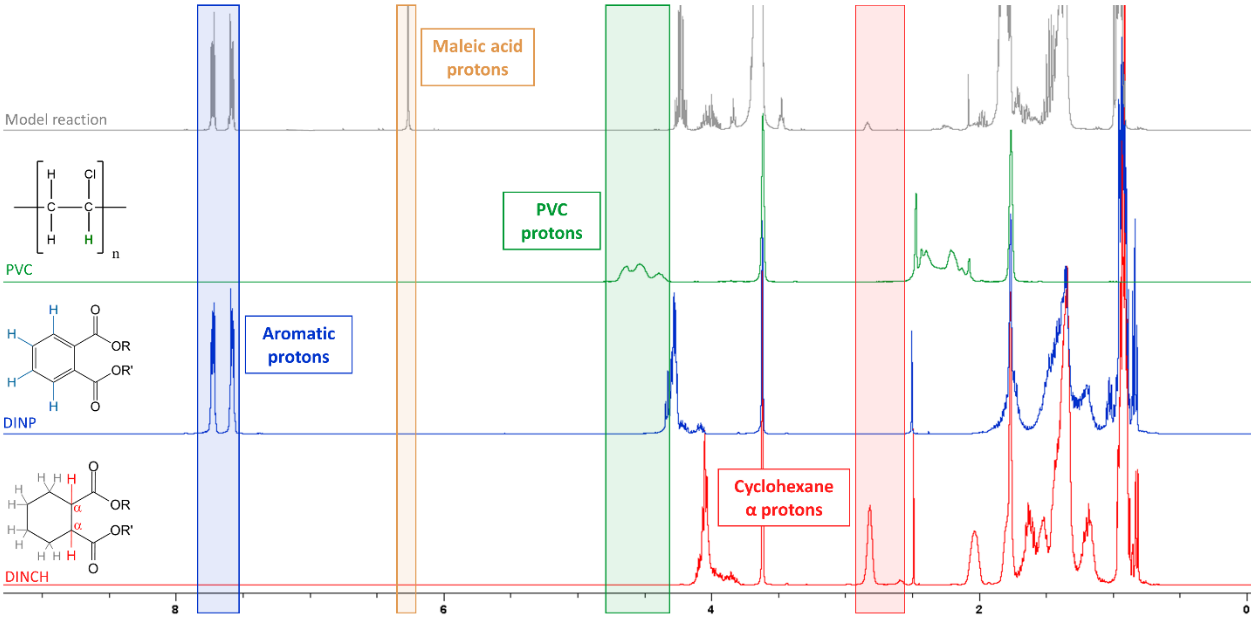

Figure S19: ^{1}H-NMR spectra of diisononyl 1,2- cyclohexane dicarboxylate ester (red), diisononyl phthalate (blue), PVC (green) and an sample of a model reaction in THF (grey), all dissolved in d^8-THF. The proton peak of the used standard, i.e. maleic acid, is featured in orange.

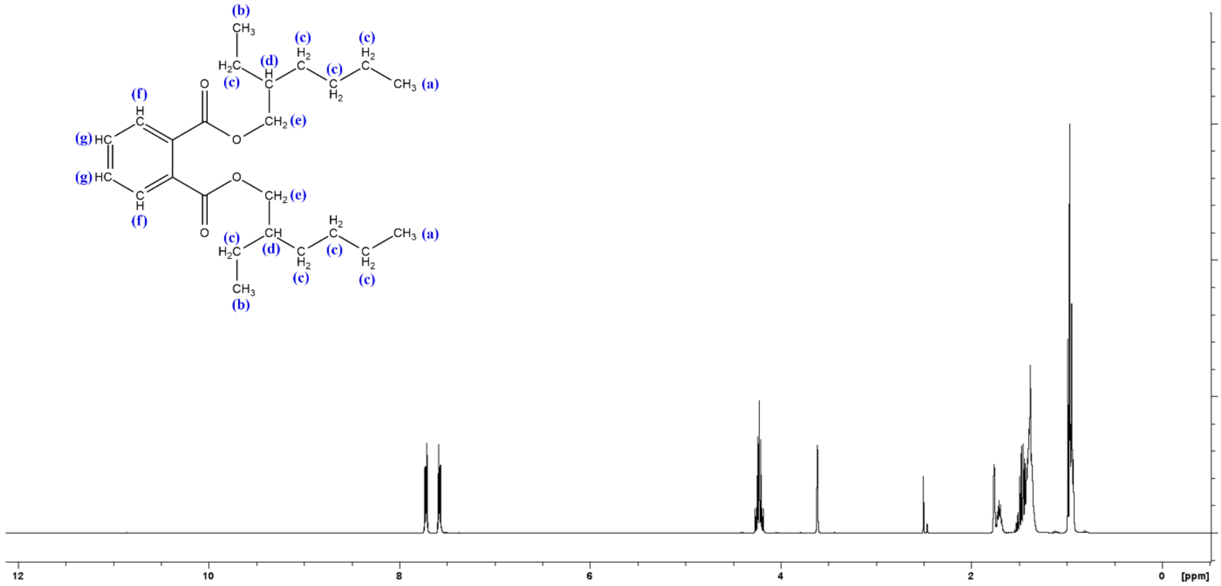

Figure S20: ^{1}H-NMR spectrum of bis(2-ethylhexyl) phthalate. ^{1}H-NMR (400 MHz, d^8-THF), δ (ppm): 0.93 - 1.00 (m, 12H; a and b), 1.35 – 1.52 (m, 16H; c), 1.71 (septet, 2H; d), 4.23 (dd, 4H; e), 7.58 (dd, 2H; g), 7.72 (dd, 2H; f). Impurity peaks at 1.72 and 3.59 ppm originate from d^8-THF, while the peak at 3.61 ppm is from H_2O.

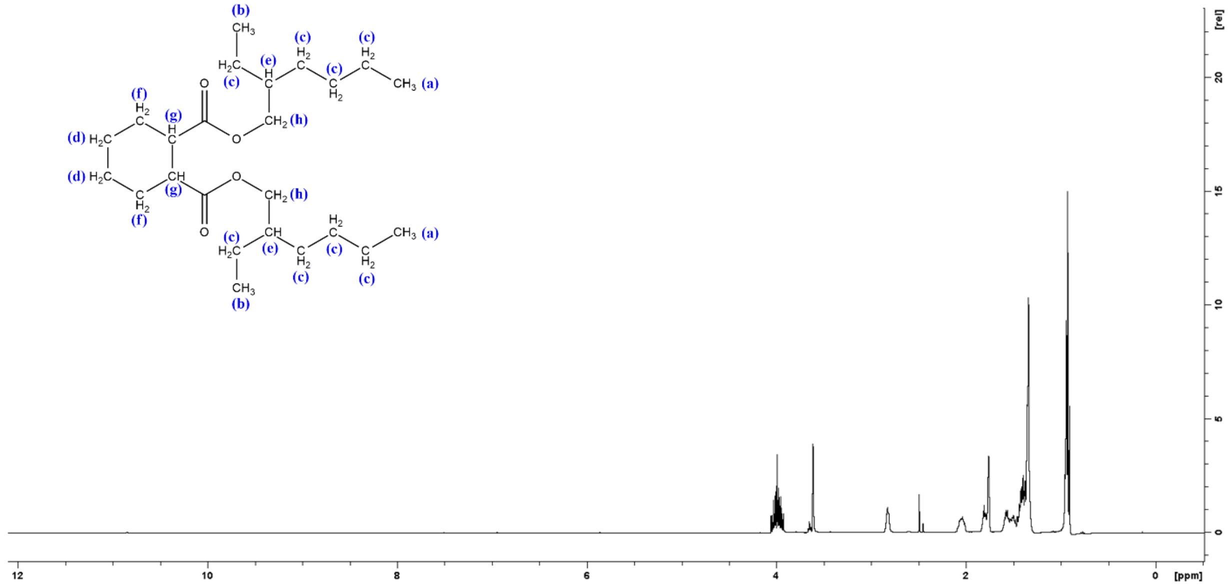

Figure S21: ^{1}H-NMR spectrum of bis(2-ethylhexyl) 1,2-cyclohexane dicarboxylate ester. ^{1}H-NMR (400 MHz, d^8-THF), δ (ppm): 0.91 – 0.97 (m, 12H; a and b), 1.32 – 1.61 (m, 22H; c, d and e), 1.80 and 2.01 (br, 4H; f), 2.82 (br, 2H; g), 4.00 (m, 4H; h). Impurity peaks at 1.72 and 3.59 ppm originate from d^8-THF, while the peak at 3.61 ppm is from H_2O.

Kinetics

For the hydrogenation of phthalates into 1,2-cyclohexanedicarboxylate esters (H6-phthalate) in the liquid phase using a catalyst can be chemically represented as:

$$Phthalate + 3\ H_2 \xrightarrow{Catalyst} H_6\text{-}phthalate \tag{1}$$

The reaction rate v is defined as the conversion of the substrate (phthalate) over time (2). The most general form of the rate equation is displayed in (3), with k the rate constant:

$$v = -\frac{d[phthalate]}{dt} \tag{2}$$

$$v = k\ [phthalate]^a\ [p_{H_2}]^b\ [H_2SO_4]^c \tag{3}$$

In order to determine the partial reaction orders $a, b\ and\ c$, a set of experiments are conducted, in which the influence of the components on the conversion rate is individually investigated. Therefore, all concentrations (except the parameter to be investigated) are kept constant per reaction set, allowing the simplification of (3) to for example:

$$v = k'\ [phthalate]^a \qquad \text{(4)}$$

$$with\ k' = k\ [p_{H_2}]^b [H_2SO_4]^c$$

In a zero order reaction (*a*=0) , the conversion rate is independent of the substrate's concentration and, thus, a straight line is observed in the [substrate] - time plot (Figure 7 of the main paper). Mathematically this becomes, with *a* = 0:

$$\begin{gathered} v_{a=0} = -\frac{d[phthalate]}{dt} = k'\ [phthalate]^0 = k' \\ \Rightarrow \frac{[phthalate]_t}{[phthalate]_0} = -k't + 1 \end{gathered} \tag{5}$$

In order to quantitatively determine other partial reaction orders (H_2 pressure and H_2SO_4), the log of the conversion rate is plotted in function of the log of the parameter to be investigated; the slope of this curve represents the value of the partial reaction order. Mathematically this becomes:

$$v = -\frac{d[phthalate]}{dt} = k\ [phthalate]^0\ \left[p_{H_2}\right]^b\ [H_2SO_4]^c \tag{6}$$

$$\Rightarrow -\frac{d[phthalate]}{dt} = k_b'\ [p_{H_2}]^b \tag{7}$$

$$\Rightarrow \log\left(-\frac{d[phthalate]}{dt}\right) = b\ \log\left[p_{H_2}\right] + k_b'' \tag{8}$$

Additional results

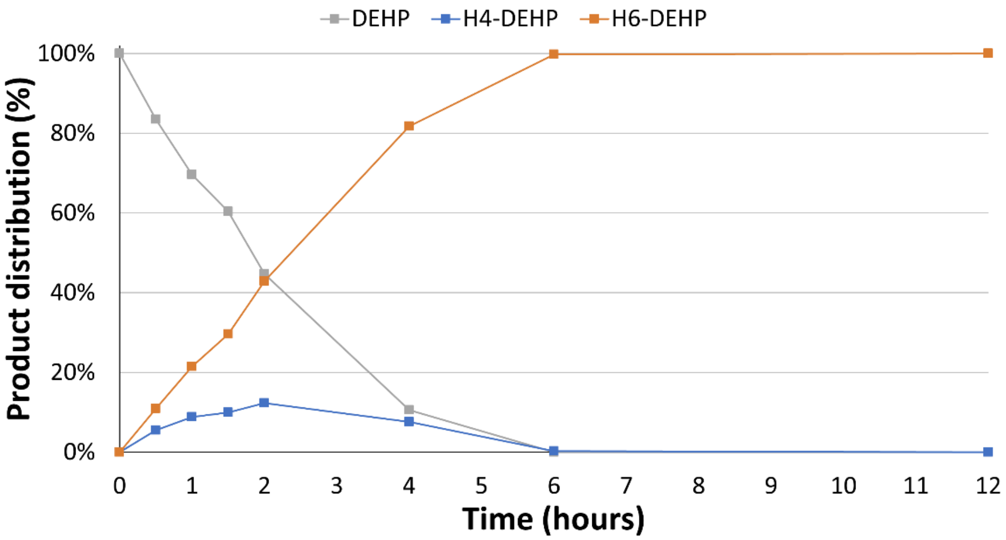

Figure S22: Time profile of the hydrogenation of bis(2-ethylhexyl) phthalate. **Reaction conditions:** 0.5 mol/L DEHP in THF (V_{tot}= 25 mL), 0.1 mol% Ru/C (5 wt.%), under 50 bar H_2 at 80 °C. **Legend**: bis(2-ethylhexyl) phthalate (grey), bis(2-ethylhexyl) 1,2-cyclohexenedicarboxylate (blue) and bis (2-ethylhexyl) 1,2-cyclohexanedicarboxylate (orange).

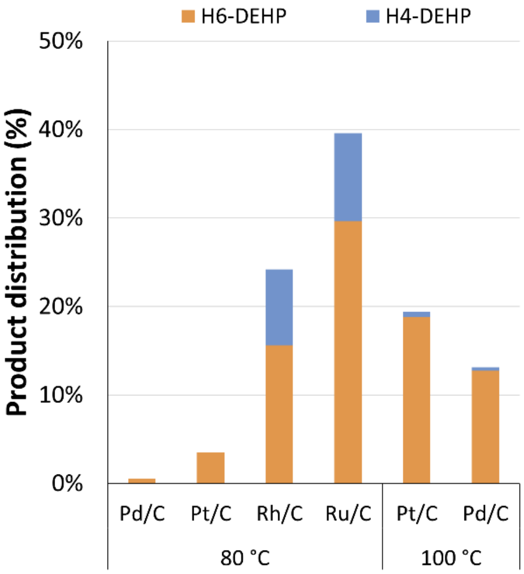

Figure S23: Product distributions obtained in the hydrogenation of bis(2-ethylhexyl) phthalate using several noble metal catalysts. **Reaction conditions:** 0.5 mol/L DEHP in THF (V_{tot}= 25 mL), 0.1 mol% metal (5 wt.% metal loading), under 50 bar H_2 at 80 or 100 °C for 90 min. **Legend:** bis(2-ethylhexyl) 1,2-cyclohexenedicarboxylate (blue) and bis(2-ethylhexyl) 1,2-cyclohexanedicarboxylate (orange).

Table S1: CO chemisorption results

Catalyst	CO uptake (µmol CO /$g_{catalyst}$)	Dispersion (%)[a]	Crystal size (nm)
0.1 wt.% Ru/Al_2O_3	5.39	87	1.5
0.5 wt.% Ru/Al_2O_3	30.74	99	1.4
1 wt.% Ru/Al_2O_3	49.06	79	1.7
2.5 wt.% Ru/Al_2O_3	88.27	57	2.3
5 wt.% Ru/Al_2O_3	210.33	68	2.0

[a] Assuming stoichiometry 0.6 CO:Ru and spherical metal particles.[SI3, SI4]

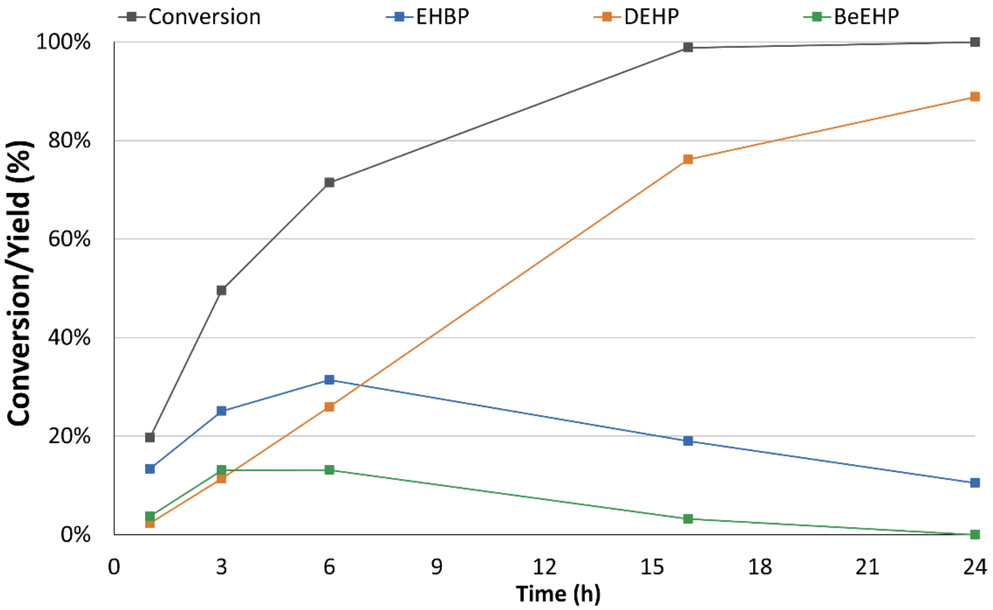

Figure S24: Time profile of the transesterification reaction of BeBP with 2-EH and H_2SO_4 as catalyst. **Reaction conditions:** 0.5 mol/L BEBP in 2-EH (V_{tot}= 25 mL), 5 mol% H_2SO_4 under N_2 atmosphere at 140 °C for 24 hours of reaction time.

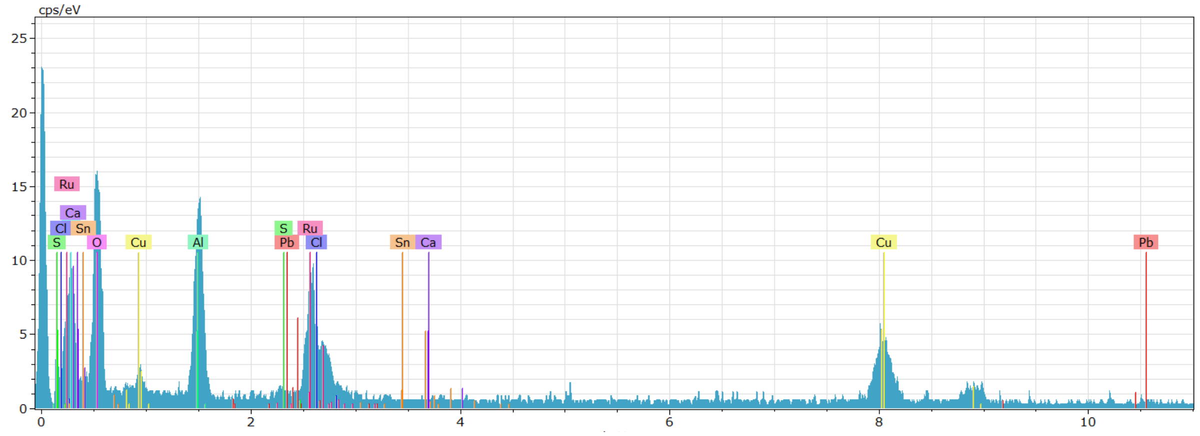

Figure S25: EDX spectrum of extract-spent Ru catalyst. Cu signals arise from the TEM grid.

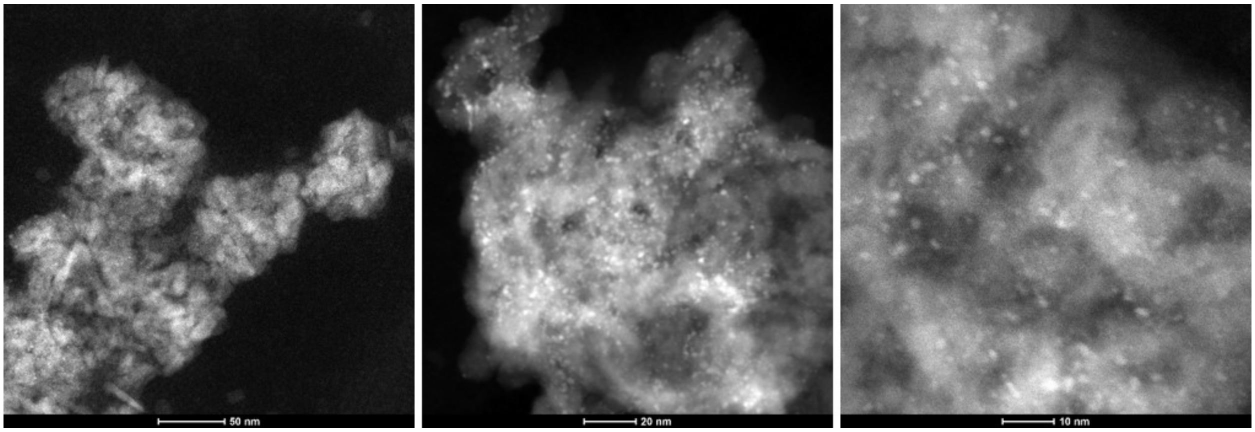

Figure S26. HAADF-STEM images of 1 wt.% Ru/Al_2O_3 taken at increasing magnifications (left to right). The size of Ru nanoparticles is in the range of 1-5 nm.

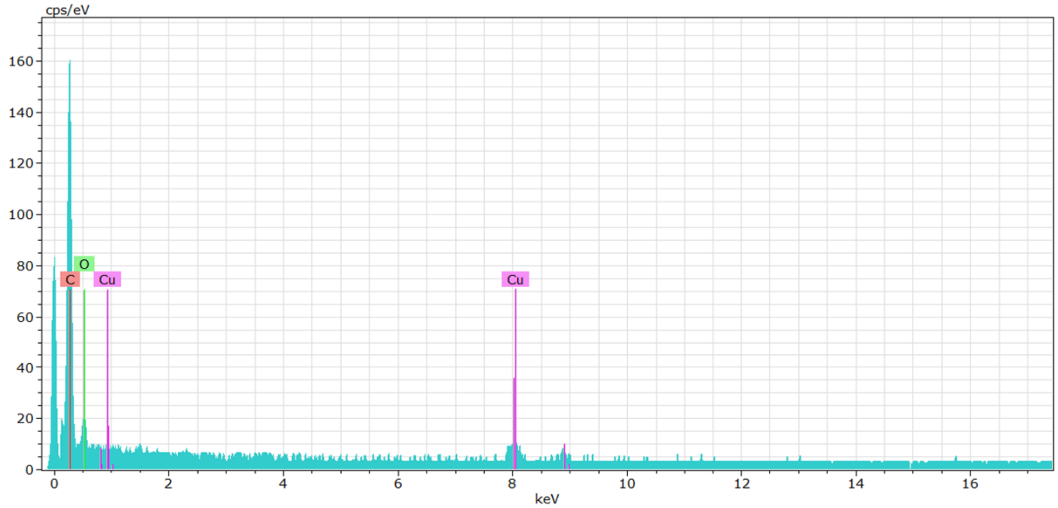

Figure S27: EDX spectrum of fresh activated carbon sample. Cu signals come from the TEM grid.

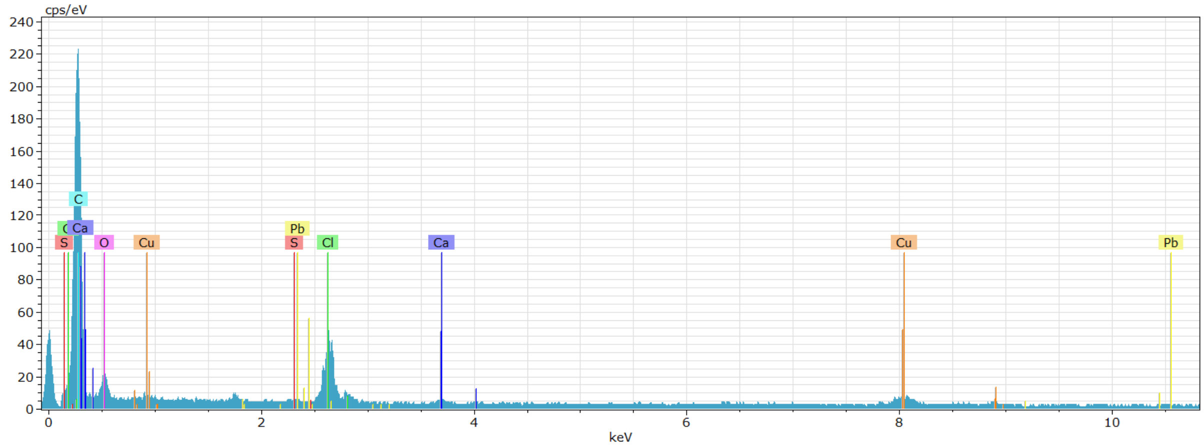

Figure S28: EDX spectrum of extract-spent activated carbon sample. Cu signals come from the TEM grid.

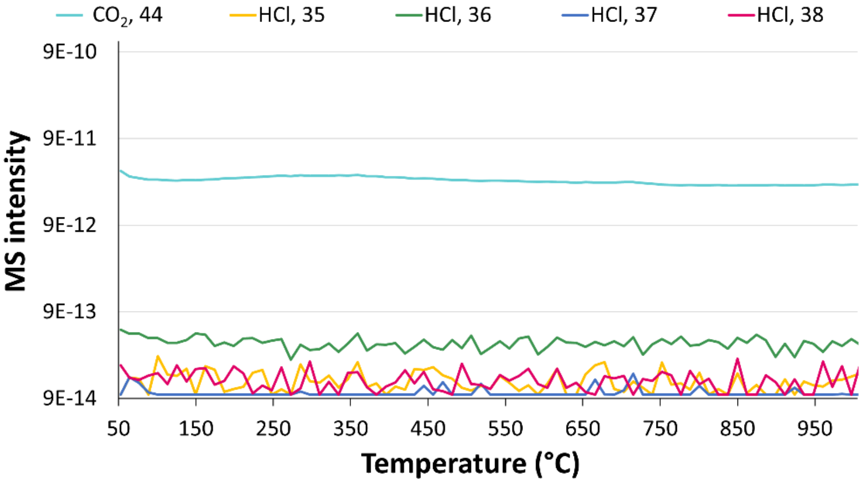

Figure S293: Mass spectrum of the thermogravimetric analysis of the recovered Ru-catalyst from a model reaction.

References supporting info

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SI4. A.M. Ruppert, M. Jędrzejczyk, O. Sneka-Platek, N. Keller, A. S. Dumon, C. Michel, P. Sautet and J. Grams, *Green Chem.*, 2016, **18**, pp. 2014 – 2028.