

Catalytically transforming legacy phthalate esters from plastic waste into benzoic acid and benzoate plasticizers

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Material

All chemicals were used as received, unless otherwise specified. Phthalic acid (Alfa Aesar, > 99%), Benzoic acid (Acros Organics, 99%), Benzene (Chem-Lab, > 99.7%), Methanol (VWR, > 99.8%), 2-Ethyl-1-hexanol (Sigma-Aldrich, > 99%), Isononanol (Evonik, > 99%), 1-Octene (Thermo scientific, 97%+), Ortho-phosphoric acid (VWR, 85%), Nitric acid (Acros organics, > 68%), Tetrahydrofuran (Acros organics, 99%), N₂ (Air Liquide, α 1), Bis(2-ethylhexyl) phthalate (J&K scientific, 99%), Poly(vinyl chloride) (Sigma-Aldrich, average MW ~43.000, average MN ~22,000), Bis(2-ethylhexyl) adipate (Fisher scientific, 99%), N,O-Bis(trimethylsilyl)trifluoroacetamide (Sigma-Aldrich, BSTFA + TCMS 99:1), Sodium hydroxide (Chemsolute, 99.5%), Ethyl acetate (Fisher scientific, \geq 99.8%), Hydrochloric acid (VWR, 37% HCl solution), Sulfuric acid (Acros Organics, 95%), H-Beta 75 (Clariant, CZB 150), Pt/C (Acros Organics, 5 wt% Pt), Copper(I) oxide (Thermo scientific, 97%), Copper(II) sulfate pentahydrate (Fisher scientific, >98%).

Experimental set-up

Hydrolysis-decarboxylation

All reactions were performed in a 50 mL high-pressure Parr® reactor vessel (Series 5500, Stainless Steel 316, Model 4848 temperature controller). In a typical decarboxylation experiment, the reactor was consecutively loaded with the aromatic acid (3 mmol), the metal catalyst (x mol% metal relative to the aromatic acid) and deionized water (25 mL). Subsequently, the reactor was sealed, purged three times with N₂ and then pressurized with 8 bar N₂ at room temperature. Finally, the reactor was heated to 150 – 250 °C (30 min induction time) and stirred at 500 rpm using a magnetically driven impeller. Reactions were quenched by stopping the stirrer and by cooling of the reactor in an ice-in-water bath. Finally, the samples were homogenized by addition of tetrahydrofuran, after which solid catalyst particles were removed from the liquid mixture by centrifugation (3000 rpm, 5 min).

The one-pot hydrolysis-decarboxylation reactions were conducted in a similar manner to that described above, with the substrate changed to phthalate plasticizers and the addition of H-Beta 75 to the reaction mixture as the extra hydrolysis catalyst.

Benzoic acid purification

After the complete hydrolysis-decarboxylation of legacy phthalate plasticizers (procedure described above), the benzoic acid was isolated from the reaction mixture to enable its subsequent use in e.g. the production of benzoate plasticizers. This purification was achieved by completely dissolving the carboxylic acid in the aqueous phase at room temperature by the addition of 400 mg of NaOH (no prior homogenization with tetrahydrofuran), followed by the addition ethyl acetate (5 mL) to dissolve the hydrolyzed sidechain fragments. The mixture was centrifugated (5000 rpm, 5 min) to facilitate a clear separation of the solid, aqueous and organic phase. Afterwards, both the zeolite and organic phase were washed three additional times with basic water (150 mg NaOH, 10 mL H₂O) to extract residual benzoic acid. The aqueous phases were then collected in a round bottom flask (500 mL) and aqueous HCl (2750 μ L, 37 wt% HC) was added to precipitate the benzoic acid. Finally, the suspension was filtered and dried (70 °C, 16 h) to remove the water.

Esterification

A glass vial (11 mL) was loaded with the purified benzoic acid (approximately 2.82 mmol), isononyl alcohol (1.05 eq.), sulfuric acid (5 mol%) and a magnetic stirring bar. Then, the mixture was heated to 100 °C and continuously stirred (200 rpm) under air for the desired reaction time (30 min - 4 h). The esterification was stopped by quickly cooling the glass vial in an ice-in-water bath. When the mixture was back at room temperature, tetrahydrofuran was added to homogenize the reaction sample.

Product identification and quantification

Product identification - GC/MS analysis

The assignment of the different peaks detected on HPLC chromatograms was established by gas chromatography mass spectrometry (GC/MS) analyses on an Agilent 6890 GC instrument, equipped with a HP-1 MS column and an Agilent 5973 MSD mass spectrometer. Prior to the analysis, reaction mixtures were silylated (60 °C, 3 h) with a threefold excess of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). Spectra of essential compounds are provided below (Figures S1 – S7).



Figure S1: 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).

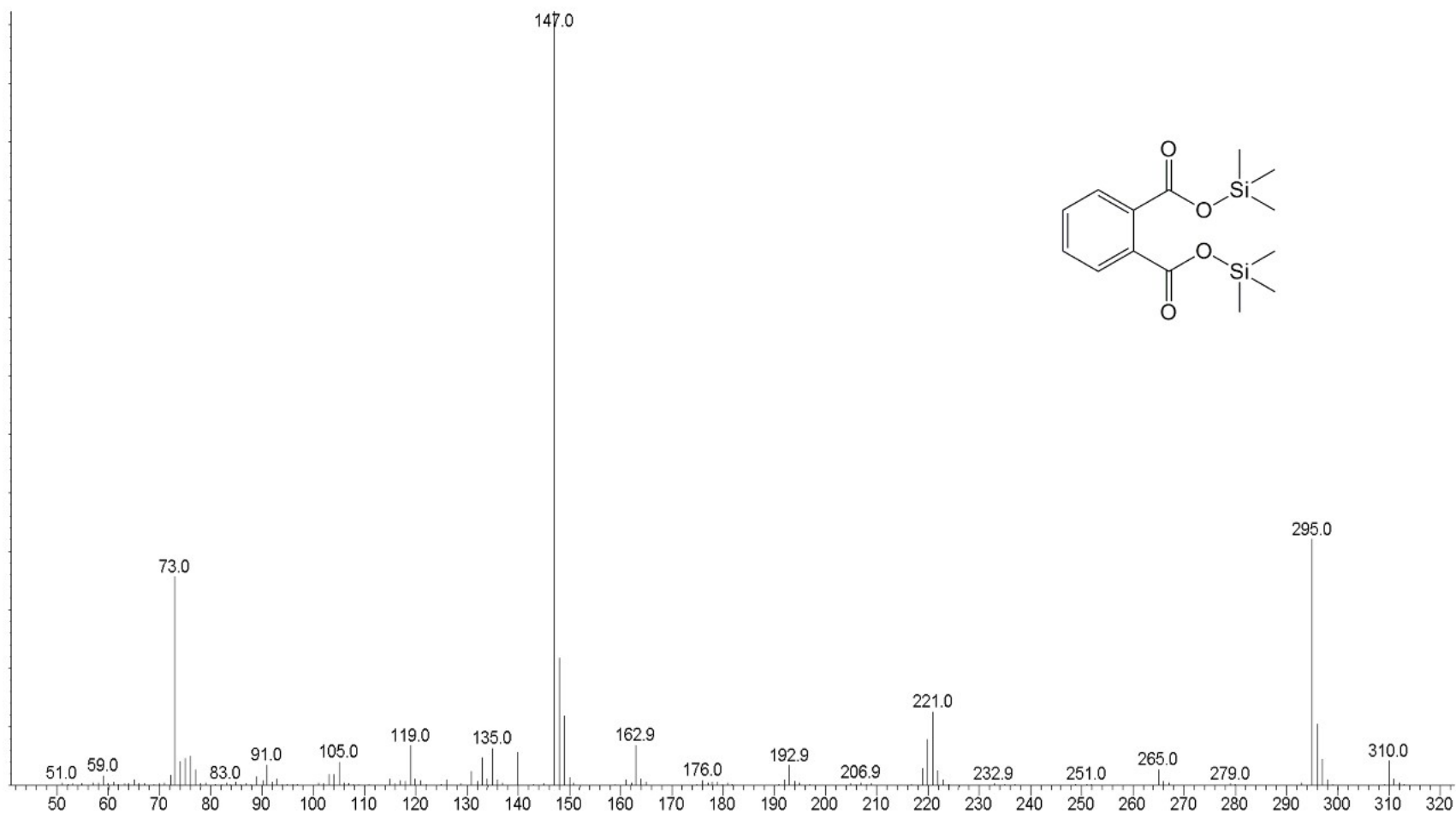


Figure S2: GC-MS spectrum of phthalic acid (MW = 166 g mol⁻¹) – bis(trimethylsilyl) phthalate (MW = 310 g mol⁻¹).
 GC-MS (EI, 70 eV): m/z (rel. int., %): 310 (3), 297 (3), 296 (8), 295 (32), 265 (2), 222 (2), 221 (10), 220 (6), 219 (2), 193 (3), 163 (5), 149 (9), 148 (16), 147 (100), 140 (4), 135 (5), 133 (4), 119 (5), 105 (3), 91 (3), 77 (2), 76 (4), 75 (4), 74 (3), 73 (27).

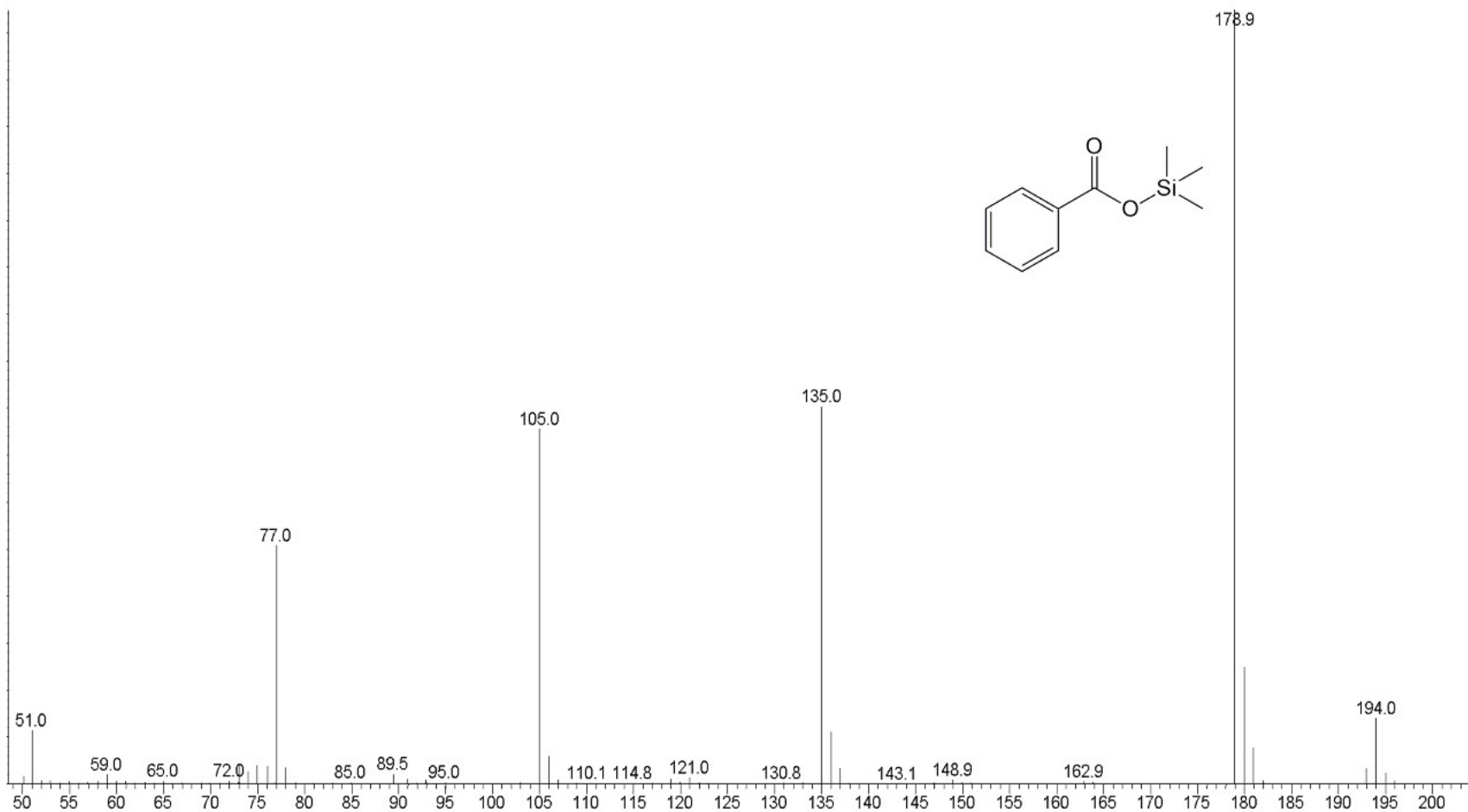


Figure S3: GC-MS spectrum of benzoic acid (MW = 122 g mol⁻¹) – trimethylsilyl benzoate (MW = 194 g mol⁻¹).
 GC-MS (EI, 70 eV): m/z (rel. int., %): 194 (8), 181 (5), 180 (15), 179 (100), 137 (2), 136 (7), 135 (48), 106 (3), 105 (46), 78 (2), 77 (30), 76 (2), 75 (2), 72 (2), 51 (7).

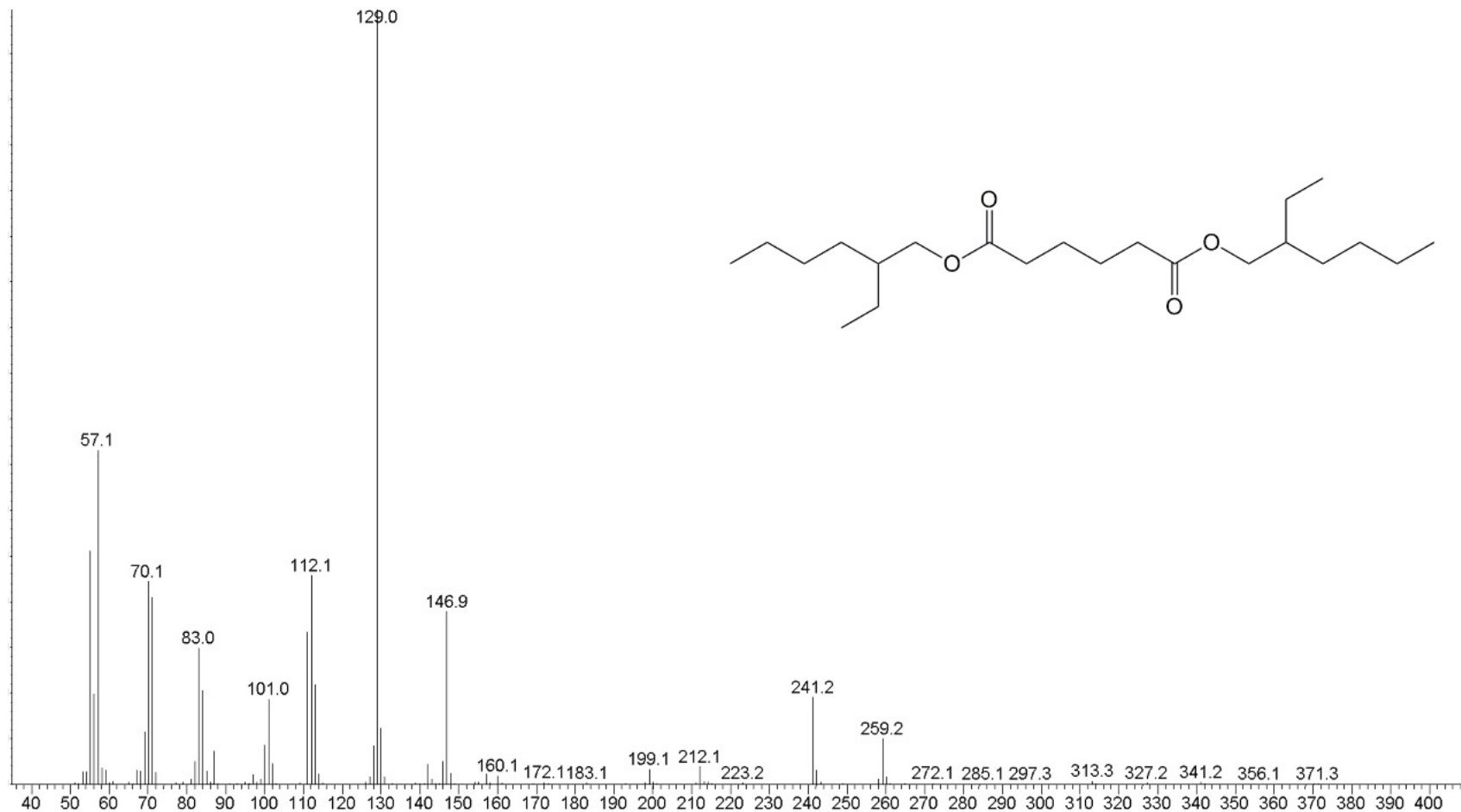


Figure S4: GC-MS spectrum Bis(2-ethylhexyl) adipate (MW = 371 g mol⁻¹).

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).

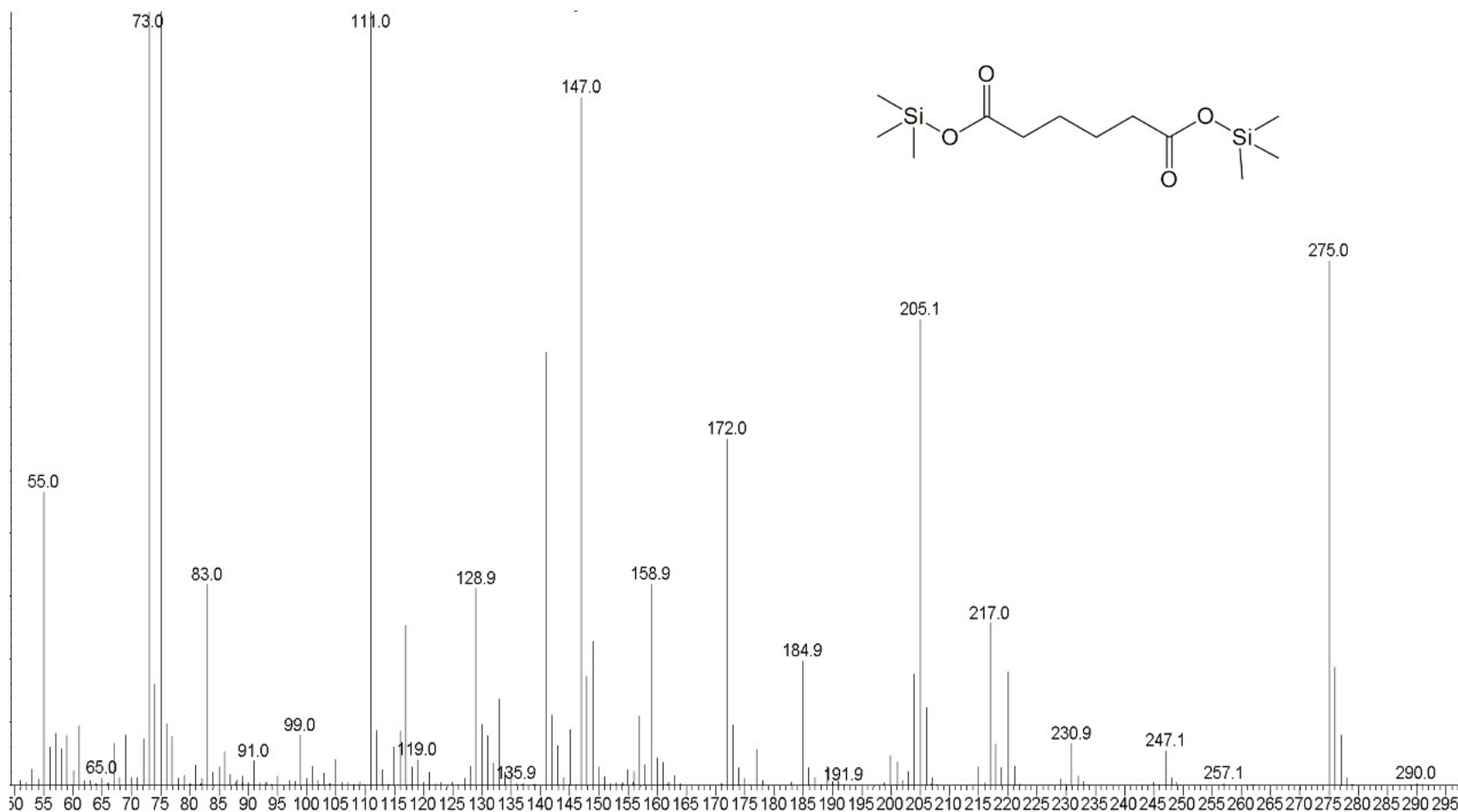


Figure S5: GC-MS spectrum of adipic acid (MW = 146 g mol⁻¹) - bis(trimethylsilyl) adipate (MW = 290 g mol⁻¹).

GC-MS (EI, 70 eV): m/z (rel. int., %): 290 (trace), 277 (7), 276 (15), 275 (68), 247 (4), 231 (6), 221 (3), 220 (15), 219 (2), 218 (5), 217 (21), 215 (3), 206 (10), 205 (60), 204 (15), 201 (3), 200 (3), 189 (3), 186 (2), 185 (16), 177 (6), 173 (8), 172 (45), 161 (3), 160 (3), 159 (26), 158 (2), 157 (9), 156 (52), 155 (2), 150 (2), 149 (18), 148 (14), 147 (89), 145 (7), 143 (5), 142 (9), 141 (56), 135 (2), 134 (2), 133 (11), 132 (3), 131 (6), 130 (8), 129 (25), 128 (2), 121 (2), 119 (3), 118 (2), 117 (21), 116 (7), 115 (5), 113 (2), 112 (7), 111 (99), 105 (3), 101 (2), 99 (6), 91 (4), 86 (4), 85 (2), 84 (2), 83 (26), 81 (3), 77 (6), 76 (8), 75 (99), 74 (13), 73 (100), 72 (6), 69 (6), 67 (5), 61 (7), 59 (6), 58 (5), 57 (7), 56 (5), 55 (38), 53 (2).

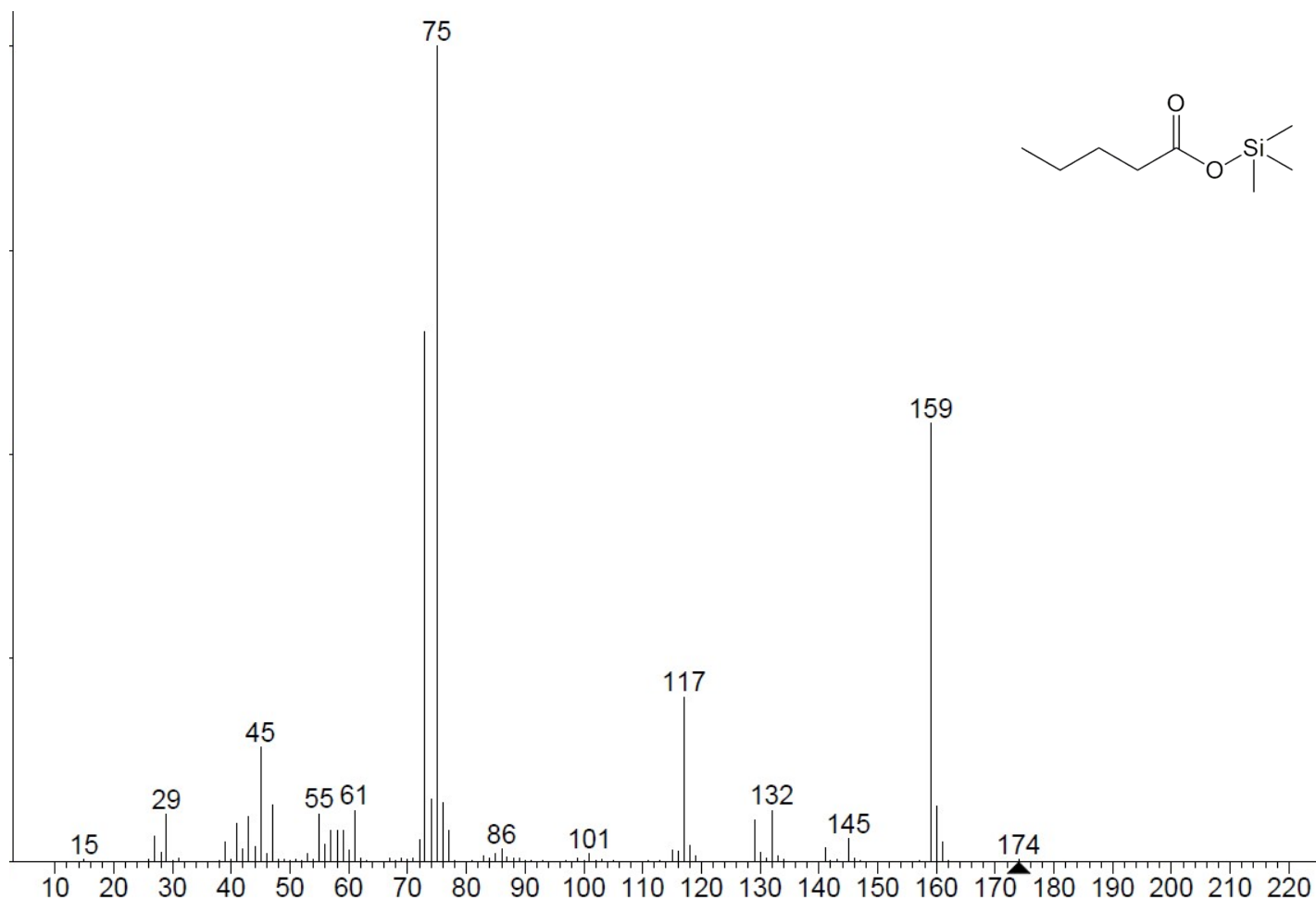


Figure S6: GC-MS spectrum of valeric acid (MW = 102 g mol⁻¹) - trimethylsilyl pentanoate (MW = 174 g mol⁻¹).

GC-MS (EI, 70 eV): m/z (rel. int., %): 174 (trace), 161 (2), 161 (3), 160 (7), 159 (57), 144 (3), 141 (2), 132 (6), 129 (5), 118 (2), 117 (20), 86 (2), 77 (4), 76 (7), 75 (100), 74 (7), 73 (65), 72 (3), 61 (6), 59 (4), 58 (4), 57 (4), 56 (3), 55 (6), 47 (7), 45 (14), 44 (2), 43 (6), 42 (2), 41 (5), 39 (3), 29 (6), 27 (3).

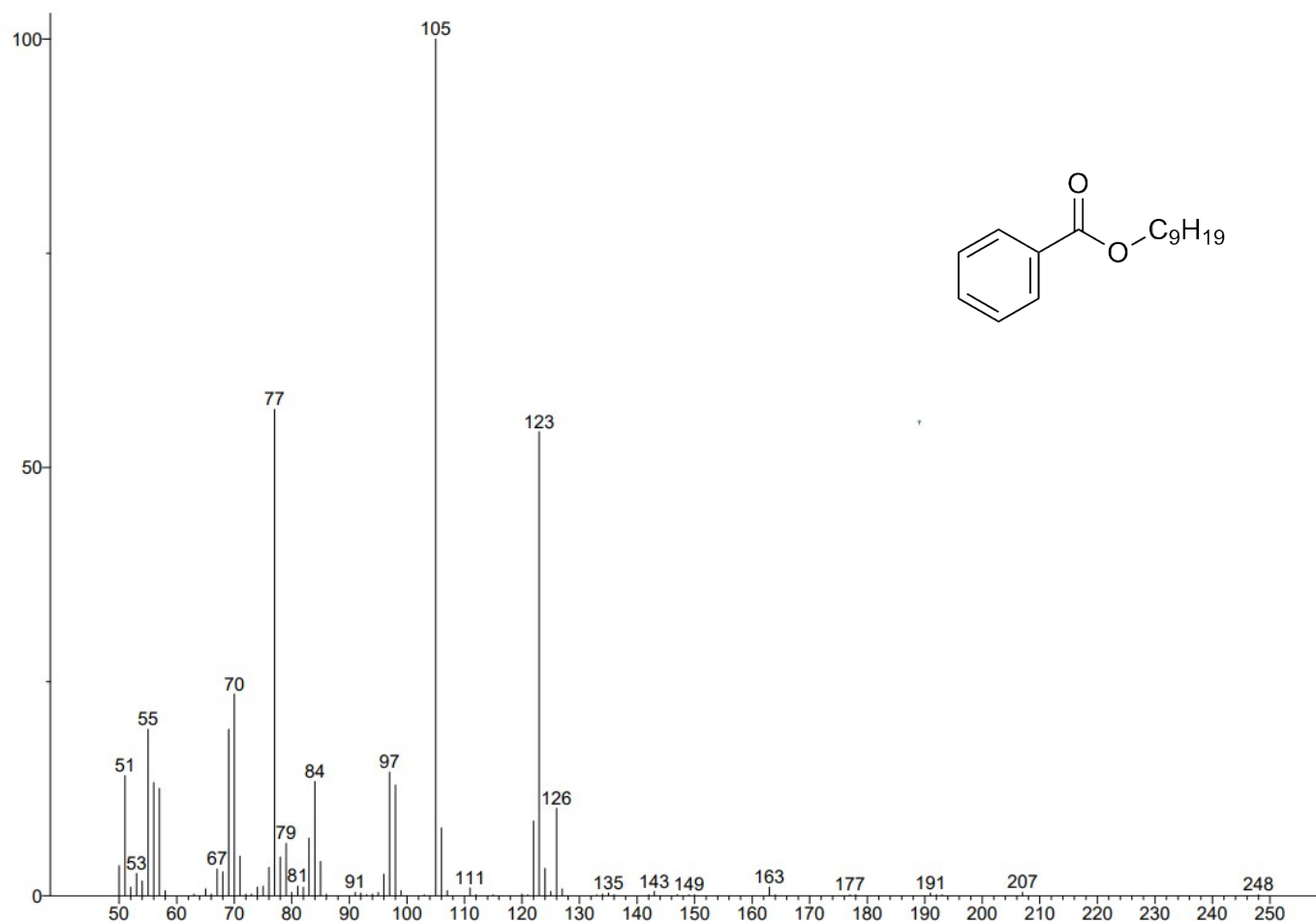


Figure S7: GC-MS spectrum of isononyl benzoate (MW = 248 g mol⁻¹).

GC-MS (EI, 70 eV): m/z (rel. int., %): 248 (trace), 126 (10), 124 (3), 123 (54), 122 (9), 106 (8), 105 (100), 98 (13), 97 (14), 96 (3), 85 (4), 84 (13), 83 (7), 79 (6), 78 (4), 77 (57), 76 (3), 71 (5), 70 (24), 69 (19), 68 (3), 67 (3), 57 (13), 56 (13), 55 (19), 54 (2), 53 (3), 51 (14), 50 (3).

Product identification - Gas phase Fourier Transform Infrared Spectroscopy

The gas phase of reactions containing bis(2-ethylhexyl) adipate were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) in order to characterize volatile products, aiding in closing the mass balance. The gas samples were taken at room temperature, injected in a N₂ flow and measured on a Gasetm DX4000 FTIR detector. The data was processed with Calcmet software.

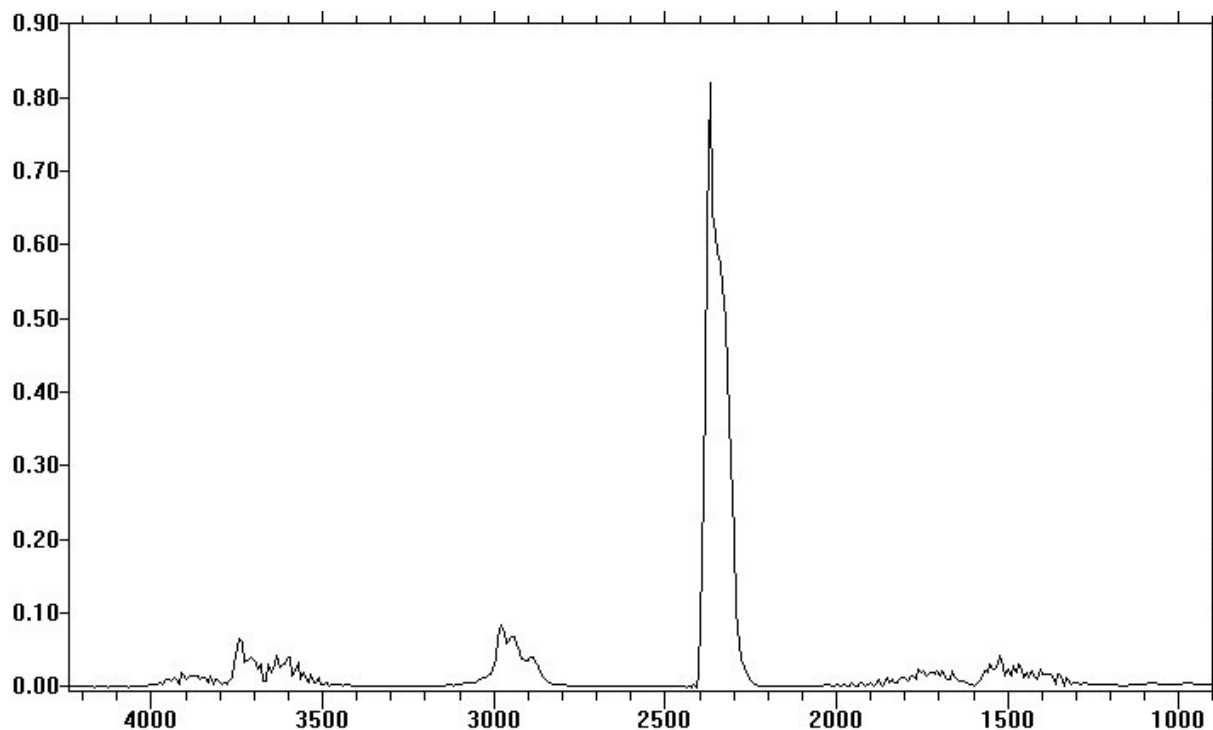


Figure S8: Gas phase FTIR spectra of the hydrolysis-decarboxylation experiment with bis(2-ethylhexyl) adipate in water (1500 cm⁻¹) forming pentanoic acid (not volatile), butane (2850 - 3050 cm⁻¹) and CO₂ (2250 - 2400 cm⁻¹ and 3550 - 3800 cm⁻¹). Reaction conditions: DEHA (3 mmol), H₂O (V_{tot} = 25 mL), Cu₂O (7 mol% metal), H-Beta 75 (150 wt%), 8 bar N₂, 200 °C for 2.5 h.

Product quantification - HPLC analysis

The reaction samples were analyzed by high-pressure liquid chromatography (HPLC) analysis in order to determine the conversion and product distributions in revalorisation experiments. The measurements were performed on an Agilent 1200 Series SL quaternary system equipped with a G1322A degasser, a G1311A quaternary pump, a G1367A automated sample injector, a G1316A thermostatted column compartment, and a G1314A variable wavelength detector. The injection volume was 5 μL and chromatograms were recorded at 254 nm. Product separation was achieved on an Agilent Eclipse XDB-C18 column (4.6 mm i.d. x 250 mm, 5.0 μm particles), which was heated to 40 $^{\circ}\text{C}$. The mobile phase composition consists of 1 wt% H_3PO_4 in milli-Q water (Acidic water) and methanol of which the ratio was gradually adjusted in accordance with [Table S1](#). The flow rate was kept constant at 0.6 mL min^{-1} . A typical chromatogram of the reaction mixture is shown in [Figure S9](#), with the following retention times being characteristic for the different compounds: DEHP (34.5 min), PA (6.5 min), BA (11.8 min). All products were quantified based on calibration curves.

Table S1: HPLC mobile phase composition gradient

Time (min)	Acidic water [%]	Methanol [%]
0	70	30
8	50	50
14	10	90
40	0	100

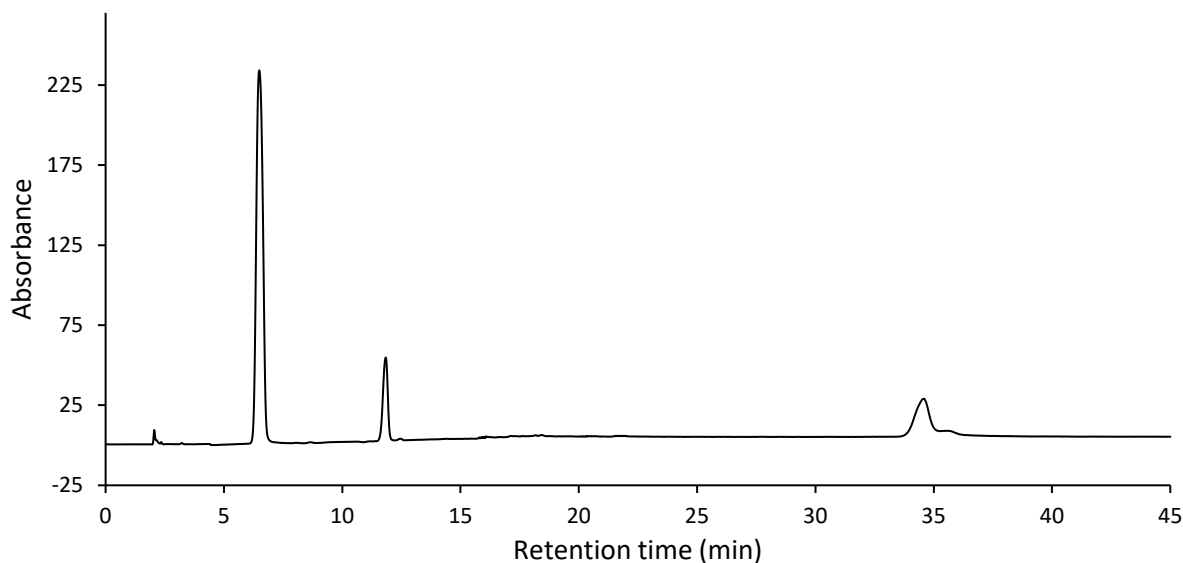


Figure S9: Typical HPLC chromatogram obtained in the tandem hydrolysis-decarboxylation of DEHP (34.5 min). Products are PA (6.5 min) and BA (11.8 min).

Inductively Coupled Plasma - Optical Emission spectrometry

The copper content in the reaction mixtures was analyzed by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) at a wavelength of 327.393 nm on a Perkin-Elmer Optima 8300. After the catalytic experiments, the insoluble solids were removed from the aqueous reaction mixture (no homogenization with tetrahydrofuran) by centrifugation at 3000 rpm for 5 min. The aqueous phase was then 30 times diluted using a HNO_3 in water solution (0.42 N).

Additional catalytic results

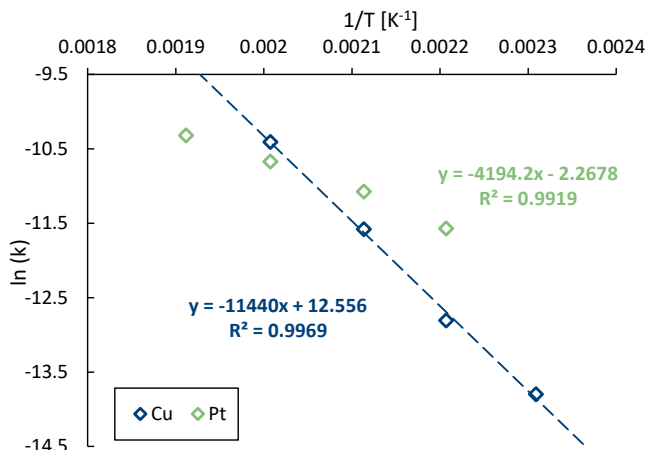


Figure S10: Arrhenius plot of the decarboxylation of PA with Cu_2O (blue) and Pt/C (green). Reaction conditions: PA (3 mmol), H_2O ($V_{\text{tot}} = 25$ mL), Cu_2O (7 mol% metal) or Pt/C (2.5 mol% metal, 5 wt% metal on carbon), 8 bar N_2 .

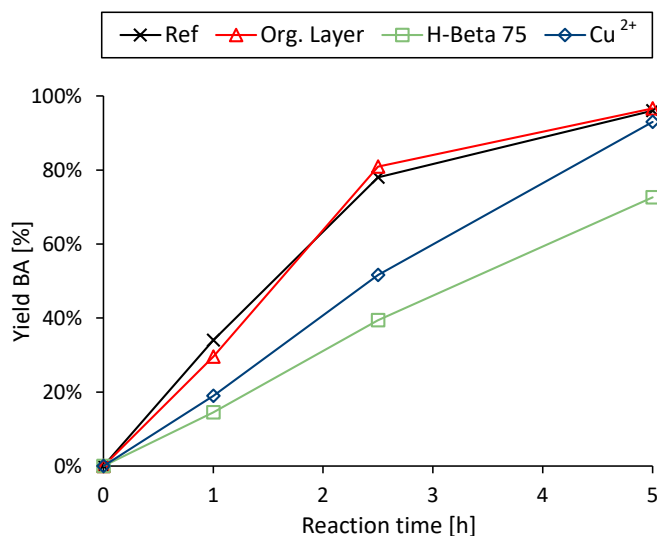


Figure S11: Time profiles of some control experiments of the decarboxylation of PA to BA with Cu-catalysts. Reaction conditions: PA (3 mmol), H_2O ($V_{\text{tot}} = 25$ mL), Cu_2O (7 mol% metal), 8 bar N_2 , 200 °C. Entry Org. Layer: Addition of 2-EH (0.6 mmol) and 1-octene (5.4 mmol). Entry H-Beta 75: Addition of H-Beta 75 (150 wt%). Entry Cu^{2+} : $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ used instead of Cu_2O .

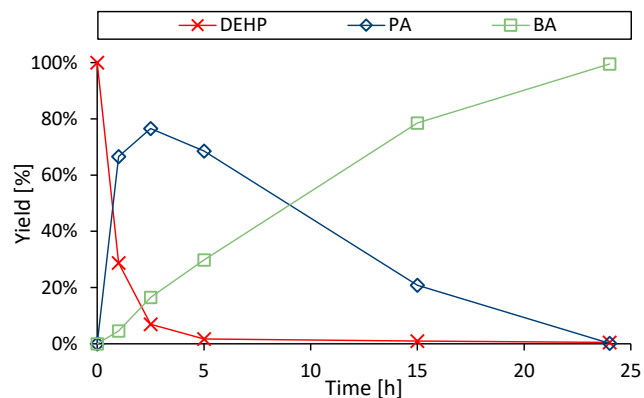


Figure S12: Time profiles of the one-pot hydrolysis-decarboxylation of DEHP to PA and BA. Reaction conditions: DEHP (3 mmol), H₂O ($V_{tot} = 25$ mL), Cu₂O (7 mol% Cu), H-Beta 75 (150 wt%), 8 bar N₂, 200 °C for the indicated reaction time.

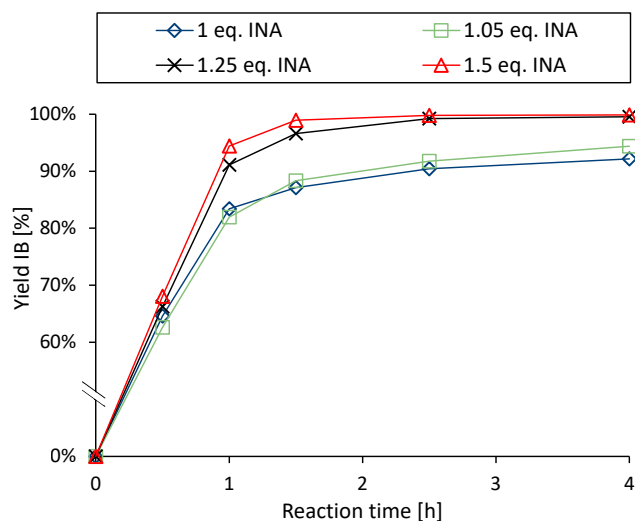


Figure S13: Time profiles of the esterification of virgin BA to IB using different amounts of INA. Reaction conditions: BA (3 mmol), INA (defined amount: 1 to 1.5 eq.), H₂SO₄ (5 mol%) in air at 100 °C for the defined reaction time (30 min to 4 h).