Electronic Supporting Information for

# Sustainable Production of Dimethyl Adipate by Non-Heme Iron(III) Catalysed Oxidative Cleavage of Catechol

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## Contents

## S1 $^{1}$H NMR spectrum of oxygenated products

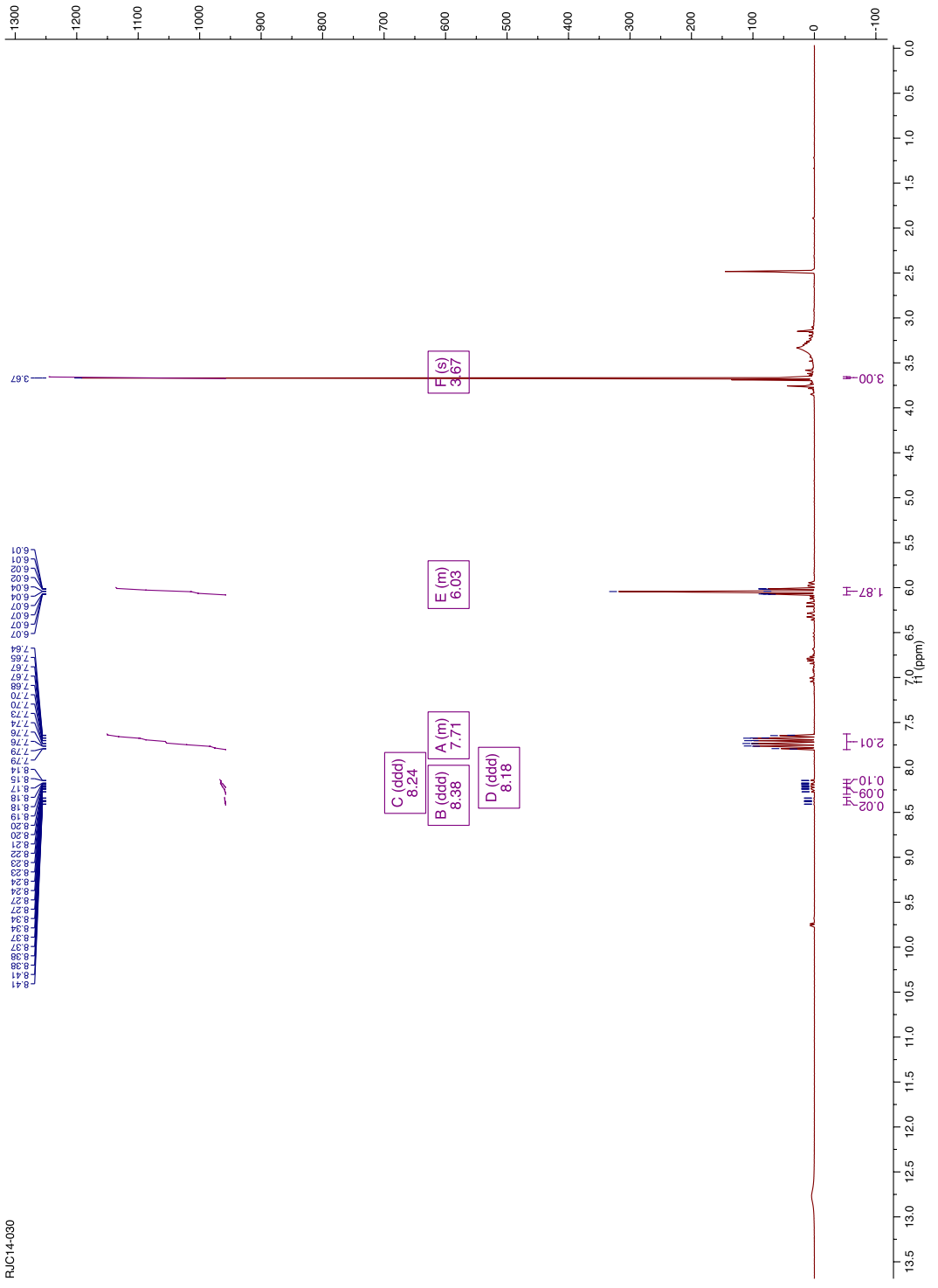


*Figure S1: $^{1}$H NMR spectrum of oxygenated products*

## S2 $^{1}$H NMR spectrum of hydrogenated products

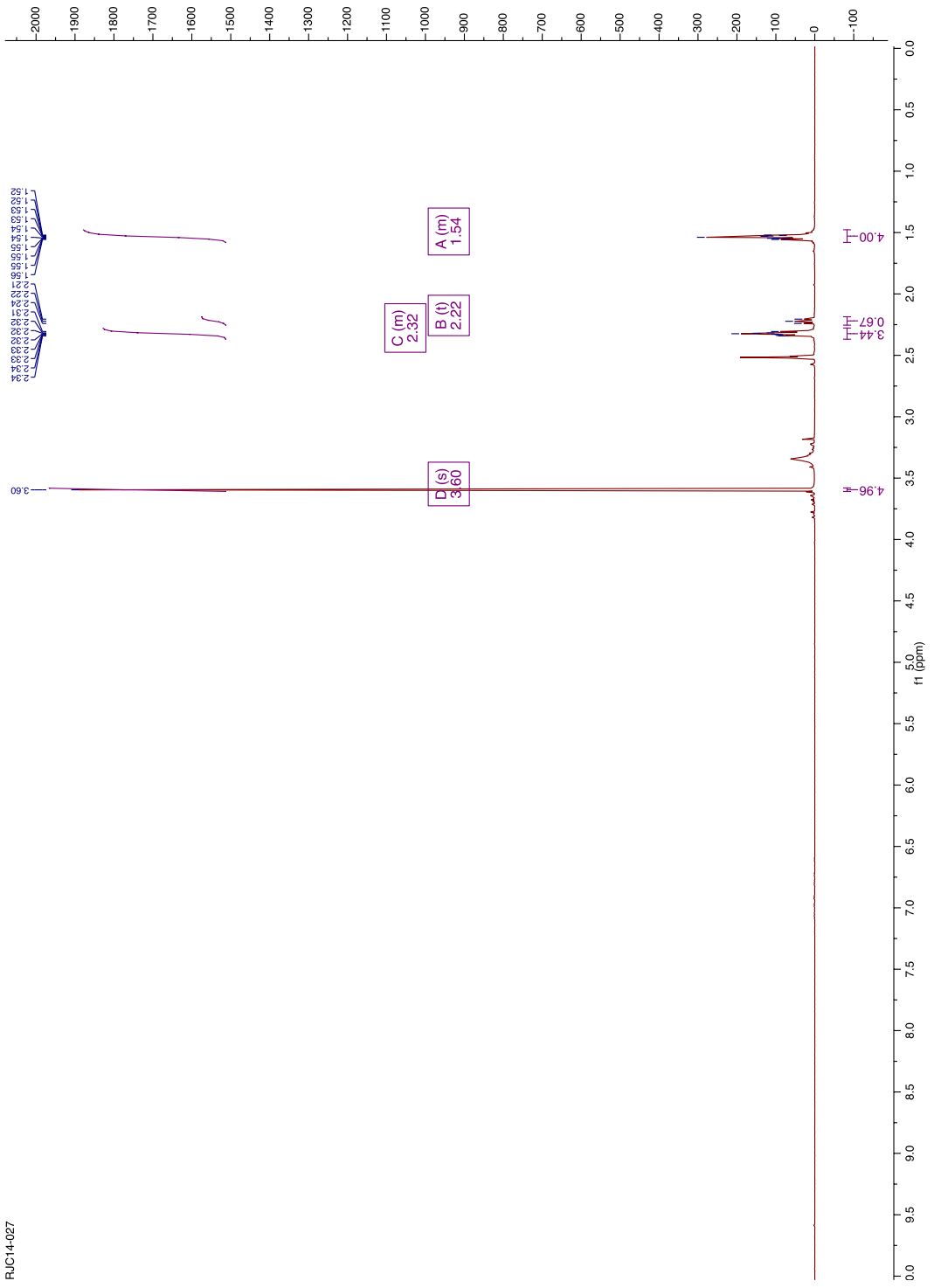


*Figure S2: $^{1}$H NMR spectrum of hydrogenated products*

## S3 Analytical data for dimethyl adipate

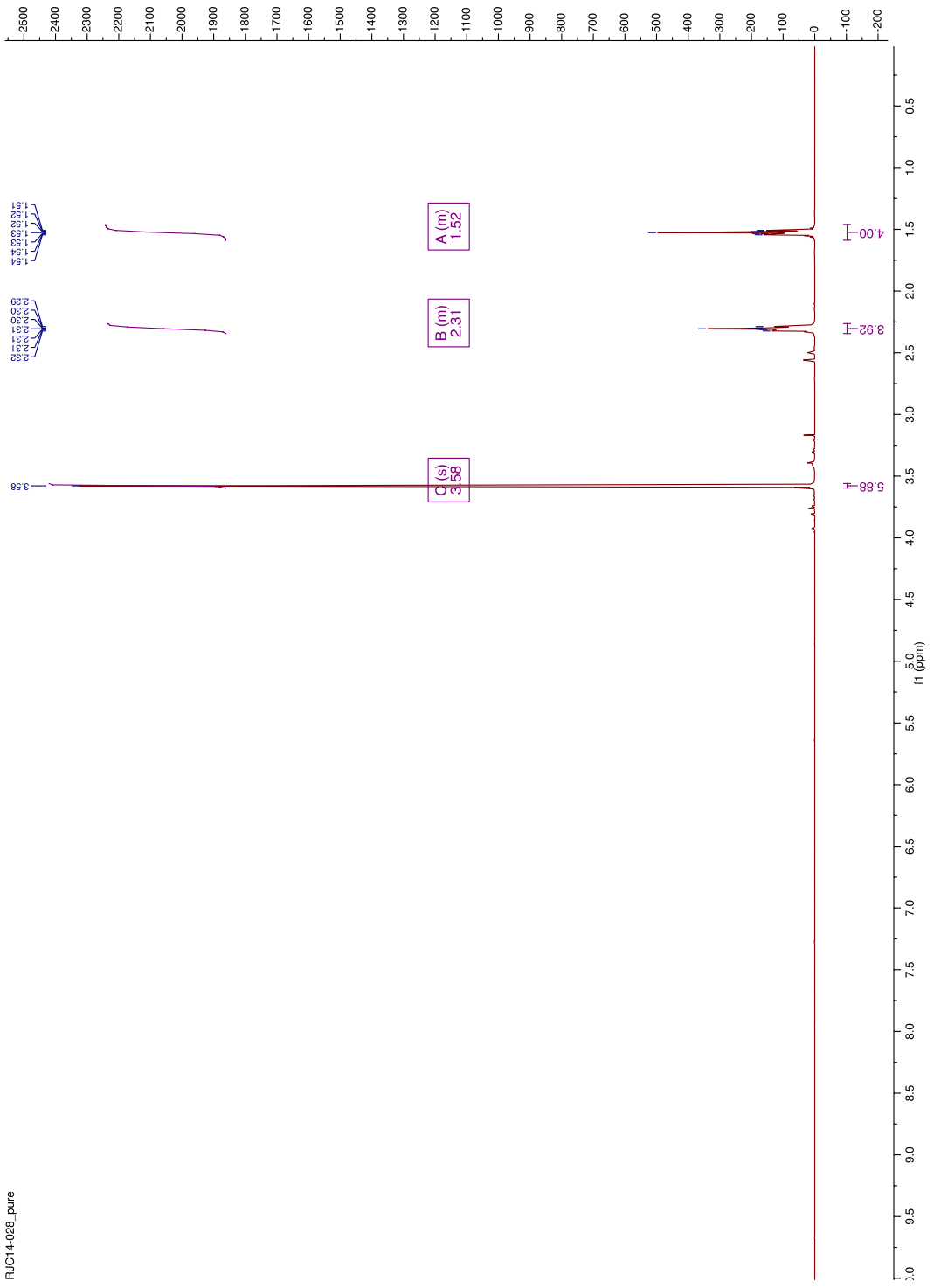


*Figure S3: 1H NMR spectrum of dimethyl adipate after vacuum distillation*

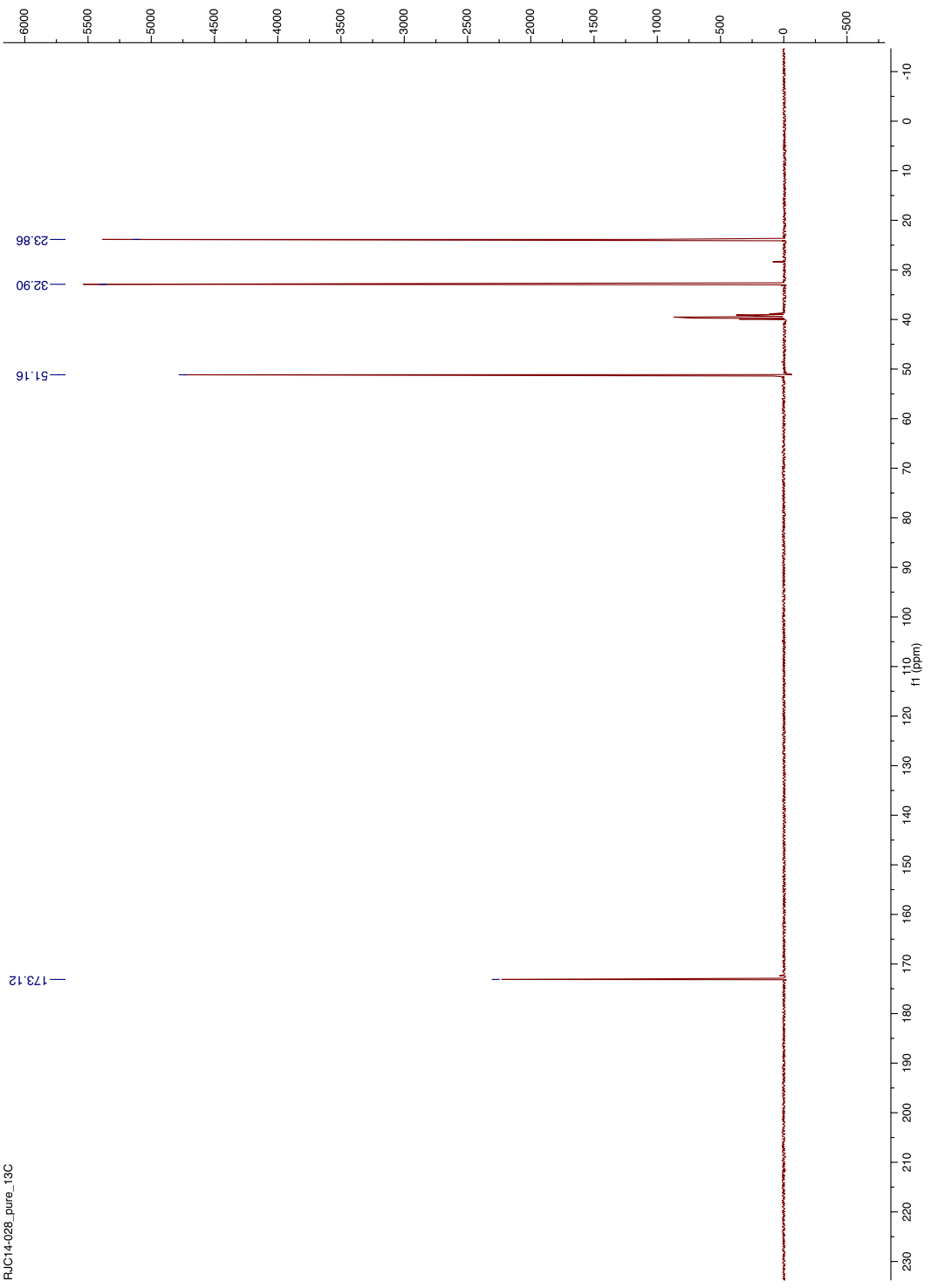


*Figure S4: $^{13}C$ NMR spectrum of dimethyl adipate after vacuum distillation*

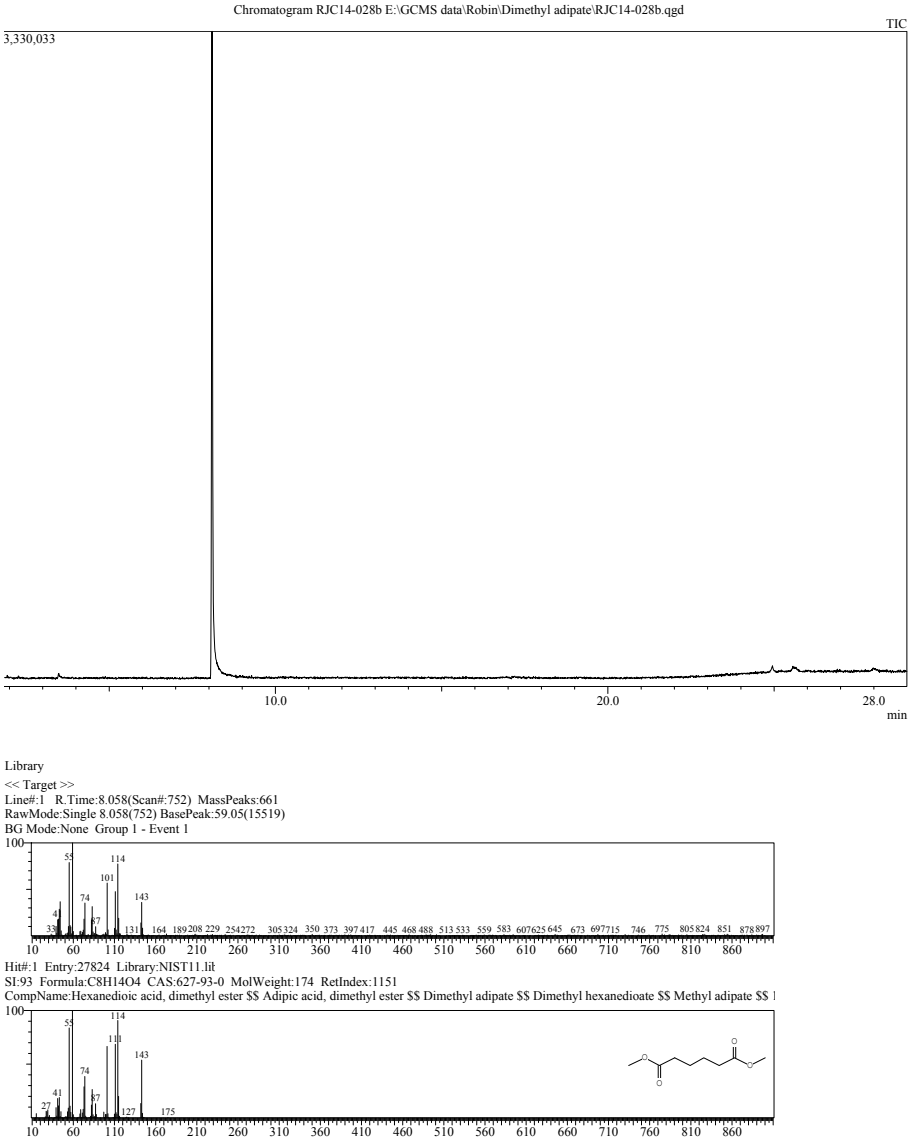


*Figure S5: GC-MS chromatogram and mass spectrum of dimethyl adipate after vacuum distillation.*

## S4 $^{1}$H NMR spectrum of distillation residue

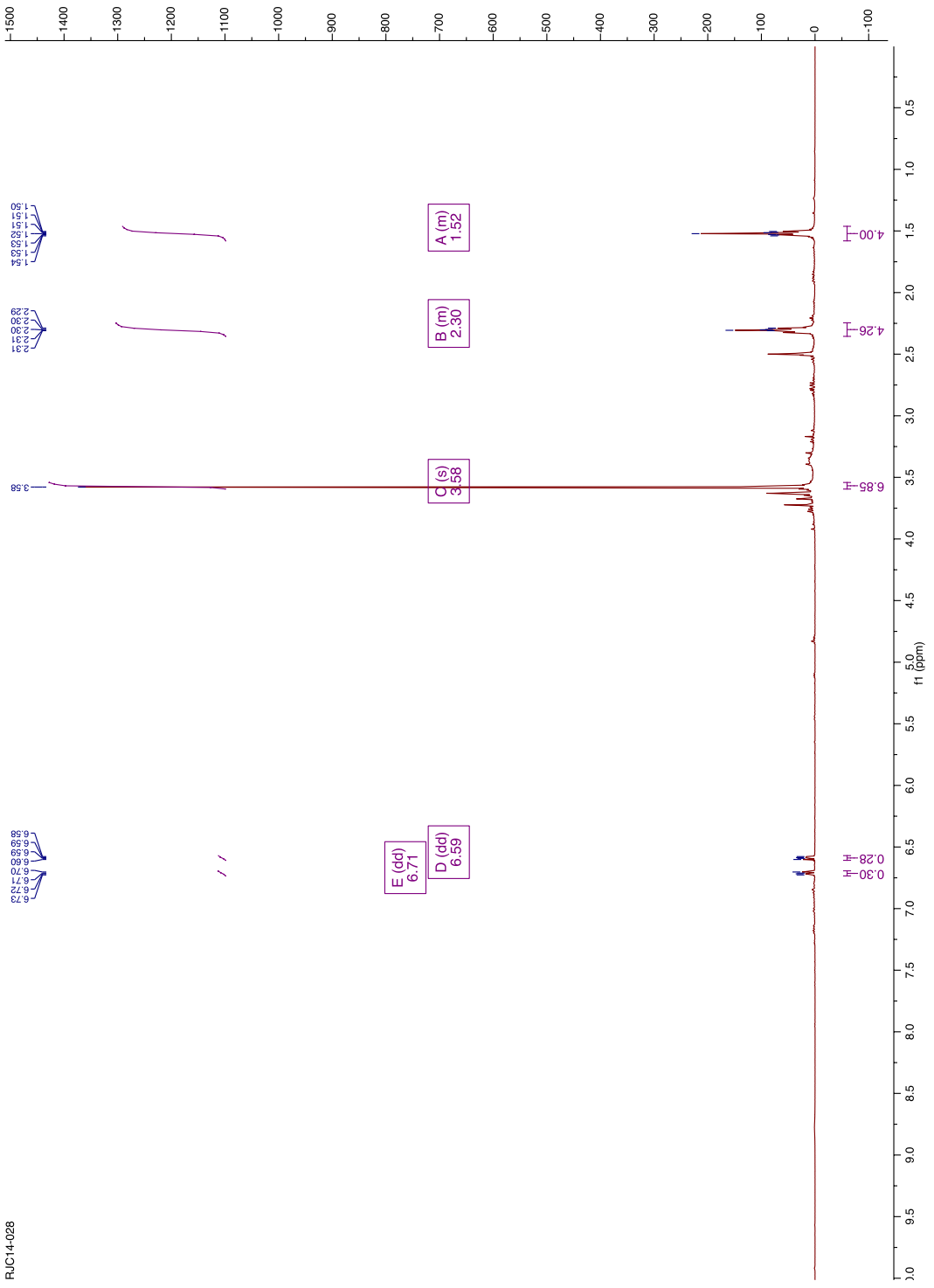


*Figure S6: $^{1}$H NMR spectrum of the vacuum distillation resdue. The peaks at 1.52, 2.30 and 3.58 ppm are indicative of dimethyl adipate, whereas the peaks at 6.59 and 6.71 correspond to catechol.*

**S5 UV-Visible spectrum of post-extraction aqueous layer**

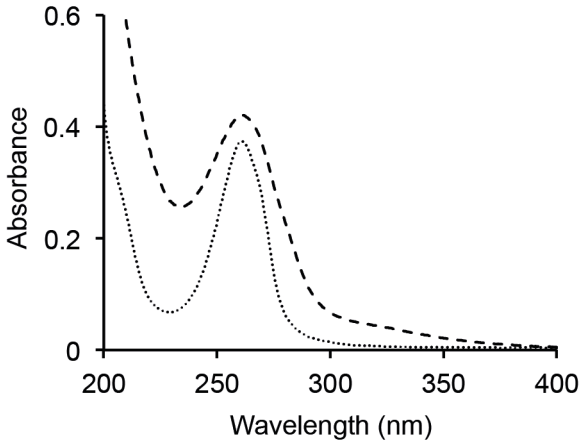


*Figure S7. UV-Vis spectrum of TPA (dotted, 23.2 µM in 4 mM HCl) and the aqueous phase after product extraction (dashed, 10x diluted). Subtracting the known absorbance of the TPA ligand in the aqueous phase at 264 nm, the residual muconate content of the aqueous phase must be < 1 % of the original catechol intake.*

**S6 Absolute energies for calculated structures**

| | *cis,cis isomer* | *transition state* | *cis,trans isomer* |
|---|---|---|---|
| Electronic energy (kcal/mol) | -2729.1 | -2707.0 | -2731.1 |
| Internal energy (kcal/mol) | 86.3 | 85.0 | 86.3 |
| Entropy (cal/mol/K) | 110.3 | 100.6 | 111.4 |
| Gibbs Free Energy[1] (kcal/mol) | -2675.6 | -2652.0 | -2678.0 |

[1] *At 298 K*

## S7 Cartesian coordinates for calculated structures

*cis,cis isomer*

| | | | |
|---|---|---|---|
| C | 1.368498000 | -0.011499000 | 0.201812000 |
| C | 0.011830000 | -0.045717000 | 0.162801000 |
| C | -0.829698000 | 1.114199000 | -0.014441000 |
| C | -2.186842000 | 1.142535000 | -0.077227000 |
| H | 1.901071000 | -0.960573000 | 0.305802000 |
| H | -0.490464000 | -1.009605000 | 0.251049000 |
| H | -0.303345000 | 2.067146000 | -0.093776000 |
| H | -2.687285000 | 2.102783000 | -0.206510000 |
| C | 2.272111000 | 1.181722000 | 0.006473000 |
| O | 1.919835000 | 2.325930000 | 0.436632000 |
| O | 3.364452000 | 0.920181000 | -0.603228000 |
| C | -3.085008000 | -0.014257000 | 0.014020000 |
| O | -2.779994000 | -1.200586000 | 0.148983000 |
| O | -4.387159000 | 0.400579000 | -0.076200000 |
| C | -5.372760000 | -0.661895000 | -0.003340000 |
| H | -5.276218000 | -1.204624000 | 0.943547000 |
| H | -6.342369000 | -0.162399000 | -0.064128000 |
| H | -5.242980000 | -1.355773000 | -0.841592000 |

*cis,trans isomer*

| | | | |
|---|---|---|---|
| C | 1.312563000 | 0.016992000 | -0.151227000 |
| C | -0.042707000 | 0.037222000 | -0.110822000 |
| C | -0.880008000 | 1.206064000 | 0.010077000 |
| C | -2.230616000 | 1.124462000 | 0.045547000 |
| H | 1.802965000 | -0.956958000 | -0.221924000 |
| H | -0.567138000 | -0.922676000 | -0.163442000 |
| H | -0.386543000 | 2.177088000 | 0.062751000 |
| H | -2.738448000 | 0.159668000 | -0.012089000 |
| C | 2.270355000 | 1.178300000 | -0.035773000 |
| O | 1.877080000 | 2.359997000 | -0.293640000 |
| O | 3.453128000 | 0.852547000 | 0.329975000 |
| C | -3.080031000 | 2.314285000 | 0.153623000 |
| O | -2.700171000 | 3.483661000 | 0.230460000 |
| O | -4.399558000 | 1.962826000 | 0.156274000 |
| C | -5.329583000 | 3.074136000 | 0.248889000 |
| H | -5.212435000 | 3.736429000 | -0.616153000 |
| H | -6.323238000 | 2.620537000 | 0.254781000 |
| H | -5.155493000 | 3.637020000 | 1.172436000 |

*transition state*

| | | | |
|---|---|---|---|
| C | 1.223272000 | -0.265788000 | -0.700066000 |
| C | 0.177594000 | 0.077517000 | -1.467462000 |
| C | -0.391262000 | 1.384377000 | -1.009641000 |
| C | -1.814292000 | 1.292972000 | -0.542711000 |
| H | 1.834045000 | -1.163806000 | -0.742645000 |
| H | -0.272627000 | -0.471017000 | -2.289886000 |
| H | -0.193490000 | 2.171996000 | -1.763751000 |
| H | -2.075501000 | 1.813643000 | 0.377160000 |
| C | 1.426868000 | 0.779955000 | 0.306614000 |
| O | 0.473490000 | 1.751958000 | 0.133040000 |
| O | 2.268743000 | 0.866133000 | 1.201940000 |
| C | -2.792470000 | 0.697121000 | -1.319146000 |
| O | -2.686197000 | 0.138579000 | -2.456240000 |
| O | -4.085263000 | 0.758861000 | -0.710230000 |
| C | -5.128678000 | 0.118628000 | -1.460982000 |
| H | -4.929839000 | -0.953820000 | -1.595483000 |
| H | -6.041921000 | 0.250861000 | -0.869978000 |
| H | -5.258596000 | 0.580574000 | -2.449198000 |