Supplementary Information (SI) for RSC Sustainability.

Electronic Supporting Information

Upcycle to recycle: triglyceride-derived magnesium soaps as stable, sustainable and efficient catalysts for poly(ethylene terephthalate) glycolysis

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1. General procedures

Cooking oil-derived catalyst synthesis

A 50 mL round bottomed flask was charged with a stirring bar, 5.00 g of oil, 2.00 g of NaOH, and 10 mL of deionised water. The mixture was stirred at 90 °C for 3 h, during which time the oil disappears due to saponification. The reaction mixture was then poured into a 500 mL beaker and diluted with 300 mL of deionised water. The temperature of the beaker liquid was brought to 90 °C. Once the solution reached this temperature, the pH was adjusted to ca. 9 with aqueous NaOH. Next, a solution of 2.00 g of $MgCl_2$ in 20 mL of deionised water was added dropwise to the vigorously stirred hydrolysed oil solution. As the addition progressed, a solid precipitate began to form. After complete addition, the mixture was cooled to 0 °C, and the solid was washed with deionised water and filtered. The collected solid was dried in a vacuum oven at 60 °C overnight, yielding the oil-derived magnesium soap.

Catalytic PET glycolysis - isolation of BHET

An oven-dried carousel flask was charged with polyethylene terephthalate flakes (1.0000 g ± 0.0050 g, 5 mm x 5 mm), ethylene glycol (3.6 mL, 4 g) and catalyst.[a,b] The flask was placed under a nitrogen atmosphere (balloon), and the reaction was stirred (800 rpm) for the time and temperature indicated. The flask was removed from the carousel and was left to cool for 5 min. The reaction mixture was then diluted with deionised water (400 mL), and the resulting aqueous mixture was vigorously stirred for 20 min. Utilising a Bucker funnel the mixture was filtered and the pre-weighed filter paper was dried overnight in a vacuum oven at 60 °C to determine levels of unreacted PET residue and oligomers. The filtrate was concentrated *in vacuo* to a total of 50 mL and cooled to 4 °C overnight to enhance crystallisation. The resulting crystals were filtered and dried overnight in a vacuum oven at 60 °C to obtain BHET as a crystalline white solid.

[a] Glycolysis experiments were accomplished with Radleys Carousel 12 Plus Reaction Station.
[b] Mol% of catalyst is related to the number of moles of monomeric units (5.2 mmol) present in 1 g of polymer.

Catalytic PET glycolysis - determination of yield by ^1H NMR spectroscopy

An oven-dried carousel flask was charged with polyethylene terephthalate flakes (1.0000 g ± 0.0050 g, 5 mm x 5 mm), ethylene glycol (3.6 mL, 4 g) and catalyst.[a,b] The flask was placed under a nitrogen atmosphere (balloon), and the reaction was stirred for the time and temperature indicated. The flask was removed from the carousel and was left to cool for 5 min. The reaction mixture was transferred in a 50 mL beaker, the internal standard was added ((*E*)-stilbene, 2 mmol, 0.3605 g) and the mixture was diluted by adding 15 mL of DMSO-d_6. The cloudy suspension was vigorously stirred while keeping the plate temperature at 50 °C until a clear solution save a small amount of insoluble catalyst was obtained. A sample of the reaction mixture (~ 3 drops) was diluted to ca. 1 mL with DMSO-d_6. The obtained sample was analysed by qH{^{13}C}NMR to determine BHET yield.[c,d]

[a] Glycolysis experiments were accomplished with Radleys Carousel 12 Plus Reaction Station.
[b] Mol% of catalyst is related to the number of moles of monomeric units (5.2 mmol) present in 1 g of polymer.

[c] qH{^{13}C}NMR, 400 MHz, D1 = 15 s, GARP-mediated ^{13}C decoupling.

[d] Yield was calculated by subtraction of the integrals associated with the soluble oligomeric fraction 4.68 ppm (4H) from the integral associated with the -CH_2- signal at 3.72 ppm (4H).

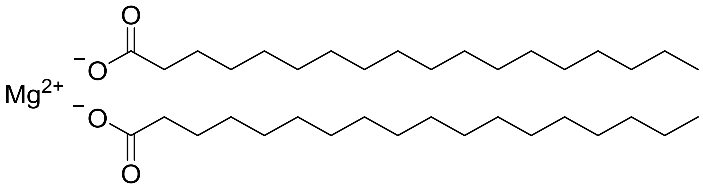
Resonances relevant for yield calculation:

A	3.72 ppm	BHET (4H) + BHET dimer (4H)
B	4.68 ppm	BHET dimer (4H)
C	7.38 ppm	(*E*)-stilbene (4H)
	(set as reference integration to 1.00)	

$$\%yield = \frac{(int.A - int.B)}{theoretical\, mmol} \times \frac{C\, mmol}{int.C} \times 100$$

$$= \frac{(int.A - int.B)}{5.2\, mmol} \times 2\, mmol \times 100$$

Synthesis of magnesium stearate (11) using dibutylmagnesium

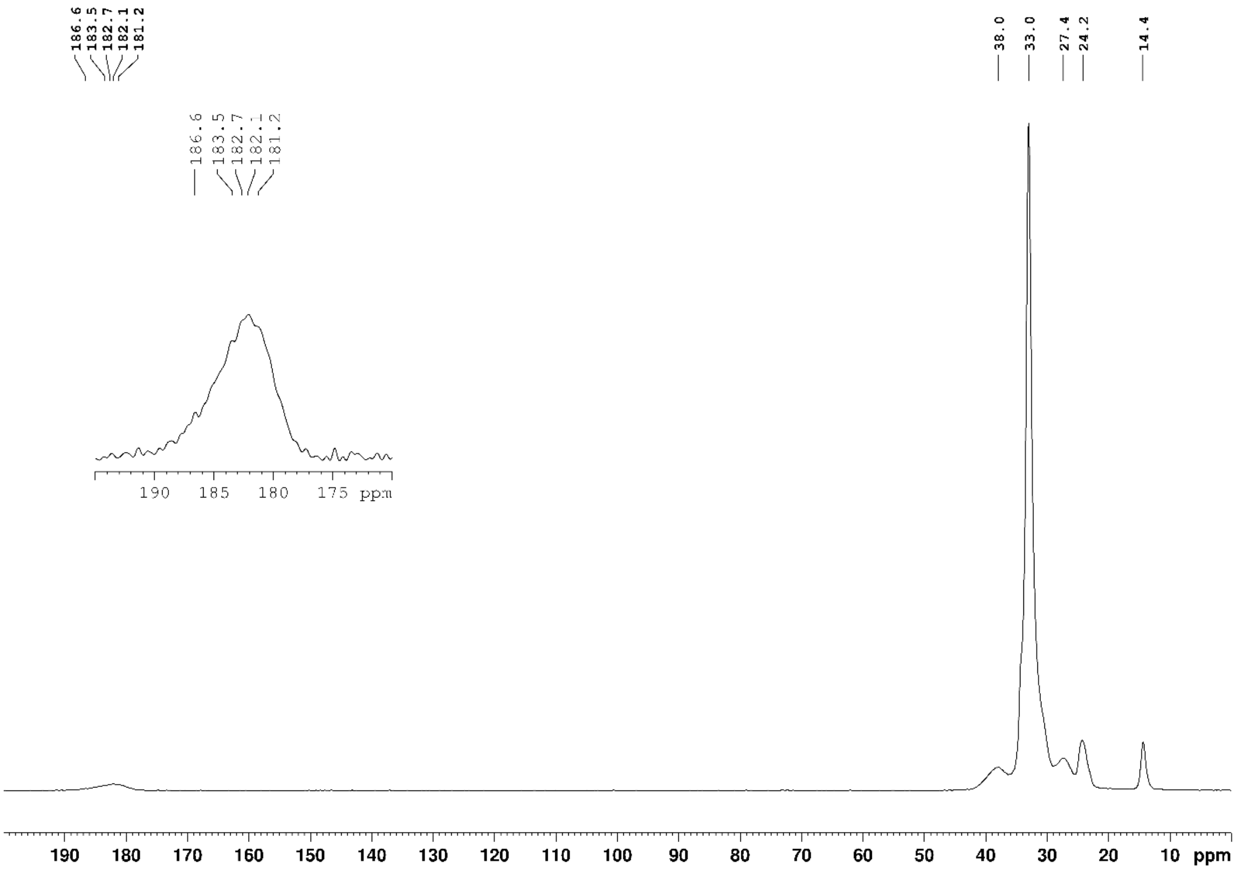


An oven-dried round-bottomed flask was charged with stearic acid (0.28 g, 1 mmol) and anhydrous Et_2O (40 mL), the mixture was kept under argon atmosphere, it was stirred until complete dissolution of the acid and cooled to 0 °C. A solution of dibutylmagnesium (0.47 mL, 0.47 eq., 1 M in heptane) was added dropwise and formed a white precipitate. The resulting suspension was stirred for 1 h at room temperature and it was filtered with a Buckner funnel. The residue was washed with $CHCl_3$ (3 x 20 mL) and was dried in a vacuum oven for 4 h at 60° C to yield **11** as a white solid (0.21 g, 74%). Dec.p. 359.2 °C (Measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 182.1, 38.0, 33.0, 27.4, 24.2, 14.4 ppm.

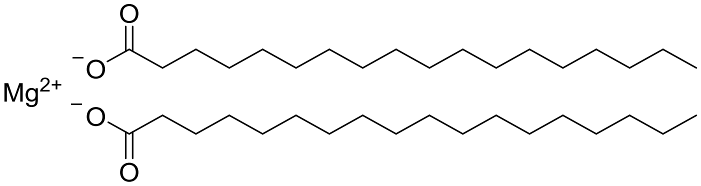
HRMS (*m/z* – DIP APCI$^-$): Found: 283.2687 (M^-) $C_{18}H_{35}O_2^-$ Requires: 283.2643.

ν_{MAX} (neat)/cm^{-1}: 2956, 2917, 2850, 1580, 1461, 1315, 1265, 1116, 885, 825, 767, 720.



^{13}C CP/MAS SSNMR spectrum of 11 synthesised using dibutylmagnesium (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.5 ms, 80 kHz proton decouple)

Synthesis of magnesium stearate (11) using $MgCl_2$

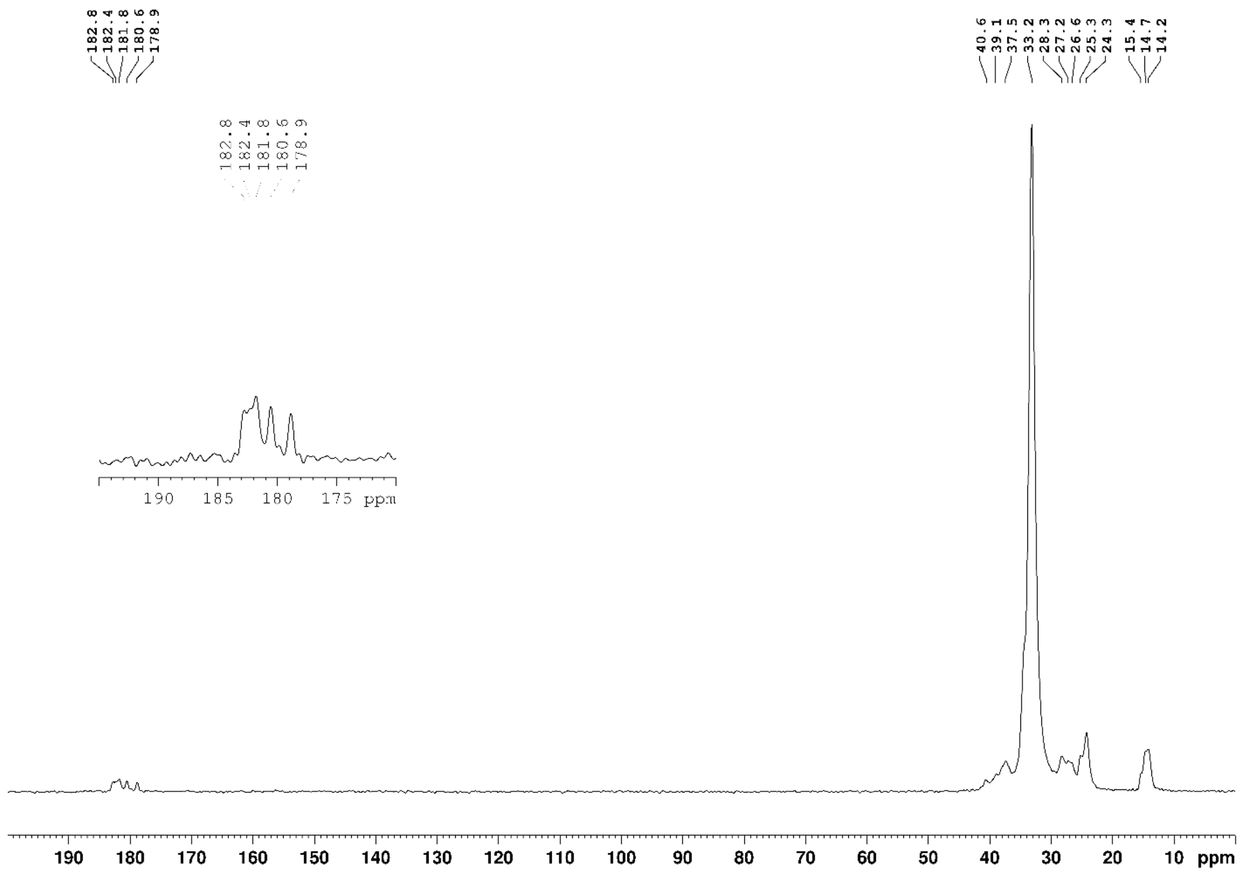


A 400 mL beaker was charged with deionised H_2O (300 mL) and stearic acid (1.42 g, 5 mmol), heated to 90 °C, and adjusted to pH 10. The suspension was stirred until full solubilisation of the acid was achieved. In a separate beaker, $MgCl_2$ (0.29 g, 3 mmol) was dissolved in H_2O (20 mL), and the solution was added dropwise to the first beaker at a rate of 1 mL per minute using a syringe pump to yield the precipitation of a white solid. The resulting suspension was gradually cooled to room temperature to favour flocculation of the precipitate. The solid was filtered, washed with H_2O (2 x 50 mL), and dried in a vacuum oven for 8 h at 60 °C to yield **11** as a white solid (1.46 g, 99%). Dec.p. 339.9 °C (measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 182.8, 182.4, 181.8, 180.6, 178.9, 40.6, 39.1, 37.5, 33.2, 28.3, 27.2, 26.6, 25.3, 24.3, 15.4, 14.7, 14.2 ppm.

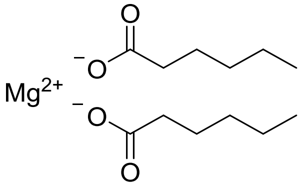
HRMS (*m/z* – DIP APCI$^-$): Found: 283.2675 (M^-) $C_{18}H_{35}O_2^-$ Requires: 283.2643.

ν_{MAX} (neat)/cm^{-1}: 2916, 2850, 1574, 1459, 1336, 1305, 1265, 1038, 877, 721, 687.



^{13}C CP/MAS SSNMR spectrum of 11 synthesised using $MgCl_2$ (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.5 ms, 80 kHz proton decouple)

Synthesis of magnesium hexanoate (12)

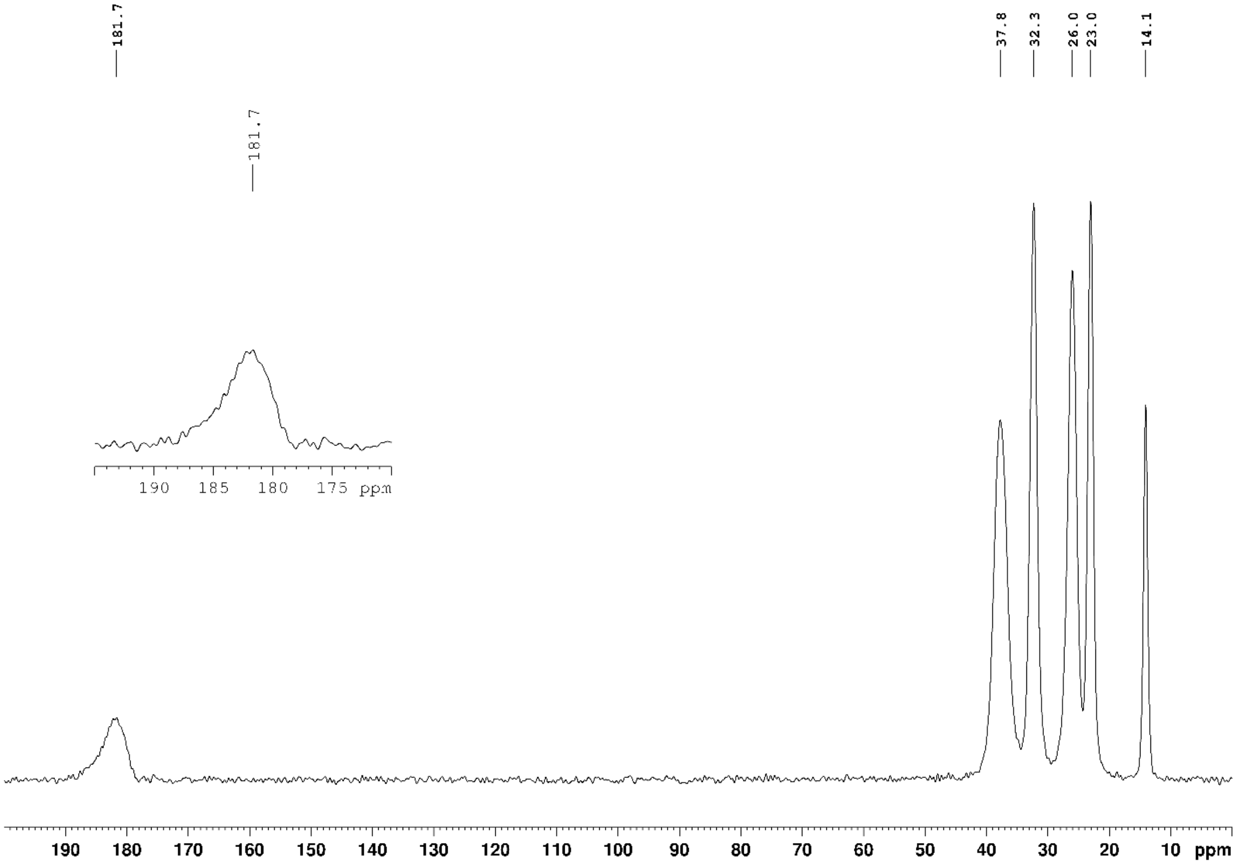


An oven-dried round-bottomed flask was charged with hexanoic acid (0.25 mL, 2 mmol) and anhydrous Et_2O (80 mL), the mixture was kept under argon atmosphere, it was stirred until complete dissolution of the acid and cooled to 0 °C. A solution of dibutylmagnesium (0.96 mL, 0.96 eq., 1 M in heptane) was added dropwise and formed a white precipitate. The resulting suspension was stirred for 1 h at room temperature and the solvent evaporated under reduced pressure. The residue was triturated with $CHCl_3$ (20 mL) and the resulting solid was filtered, washed with $CHCl_3$ (20 mL) and dried in a vacuum oven for 4 h at 60° C to yield **12** as a white solid (0.22 g, 88%). Dec.p. 332.6 °C (measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 181.7, 37.8, 32.3, 26.0, 23.0, 14.1 ppm.

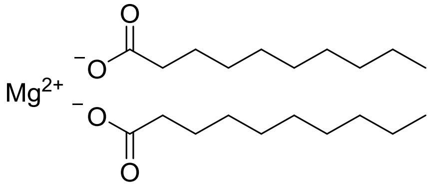
HRMS (*m/z* – DIP APCI$^-$): Found: 115.0783 (M^-) $C_6H_{11}O_2^-$ Requires: 115.0765.

ν_{MAX} (neat)/cm^{-1}: 2957, 2930, 2866, 1569, 1422, 1343, 1318, 1228, 1193, 1110, 963, 893, 850, 778, 731, 672.



^{13}C CP/MAS SSNMR spectrum of 12 (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.0 ms, 80 kHz proton decouple)

Synthesis of magnesium decanoate (13)

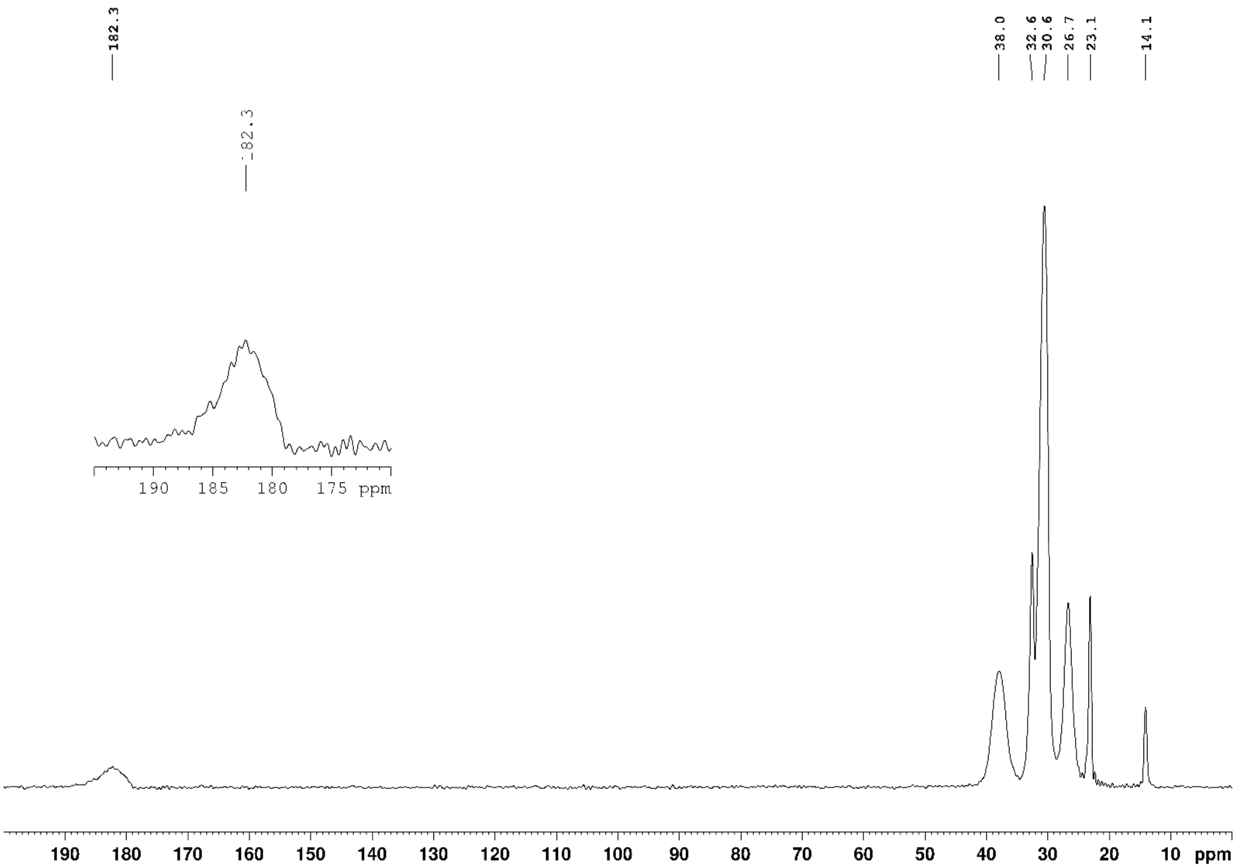


An oven-dried round-bottomed flask was charged with decanoic acid (0.35 g, 2 mmol) and anhydrous Et_2O (80 mL), the mixture was kept under argon atmosphere, it was stirred until complete dissolution of the acid and cooled to 0 °C. A solution of dibutylmagnesium (0.96 mL, 0.96 eq., 1 M in heptane) was added dropwise and formed a white precipitate. The resulting suspension was stirred for 1 h at room temperature and the solvent evaporated under reduced pressure. The residue was triturated with $CHCl_3$ (20 mL) and the resulting solid was filtered, washed with $CHCl_3$ (20 mL) and dried in a vacuum oven for 4 h at 60° C to yield **13** as a white solid (0.34 g, 97%). Dec.p. 327.1 °C (measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 182.3, 38.0, 32.6, 30.6, 26.7, 23.1, 14.1 ppm.

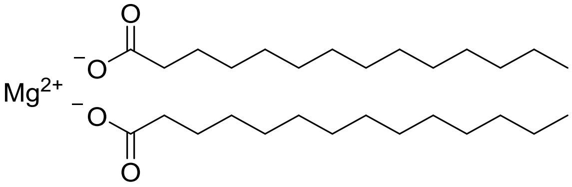
HRMS (m/z – DIP APCI$^-$): Found: 171.1384 (M$^-$) $C_{10}H_{19}O_2^-$ Requires: 171.1391.

ν_{MAX} (neat)/cm^{-1}: 2957, 2922, 2853, 1572, 1433, 1314, 1115, 720.9, 670.



^{13}C CP/MAS SSNMR spectrum of 13 (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.0 ms, 80 kHz proton decouple)

Synthesis of magnesium tetradecanoate (14)

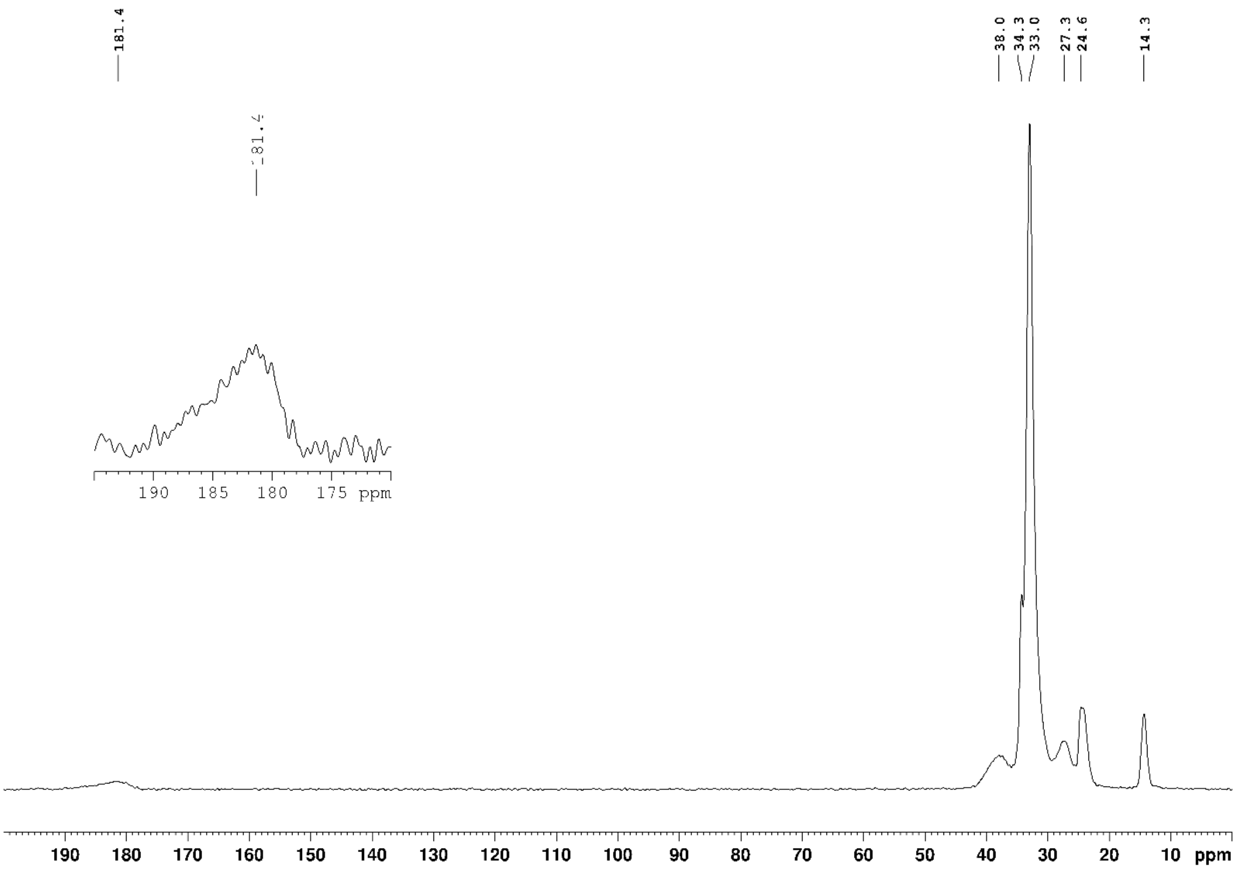


An oven-dried round-bottomed flask was charged with tetradecanoic acid (0.46 g, 2 mmol) and anhydrous Et_2O (40 mL), the mixture was kept under argon atmosphere, it was stirred until complete dissolution of the acid and cooled to 0 °C. A solution of dibutylmagnesium (0.96 mL, 0.96 eq., 1 M in heptane) was added dropwise and formed a white precipitate. The resulting suspension was stirred for 1 h at room temperature and the solvent evaporated under reduced pressure. The residue was triturated with $CHCl_3$ (20 mL) and the resulting solid was filtered, washed with $CHCl_3$ (20 mL) and dried in a vacuum oven for 4 h at 60° C to yield **14** as a white solid (0.30 g, 65%). Dec.p. 321.0 °C (measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 181.4, 38.0, 34.3, 33.0, 27.3, 24.6, 14.3 ppm.

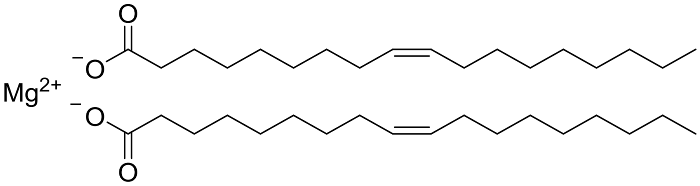
HRMS (*m/z* – DIP APCI$^-$): Found: 227.2070 (M^-) $C_{14}H_{27}O_2^-$ Requires: 227.2017.

ν_{MAX} (neat)/cm^{-1}: 2957, 2918, 2850, 1574, 1454, 1318, 1244, 1115, 721.



^{13}C CP/MAS SSNMR spectrum of 14 (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.0 ms, 80 kHz proton decouple)

Synthesis of magnesium oleate (15)

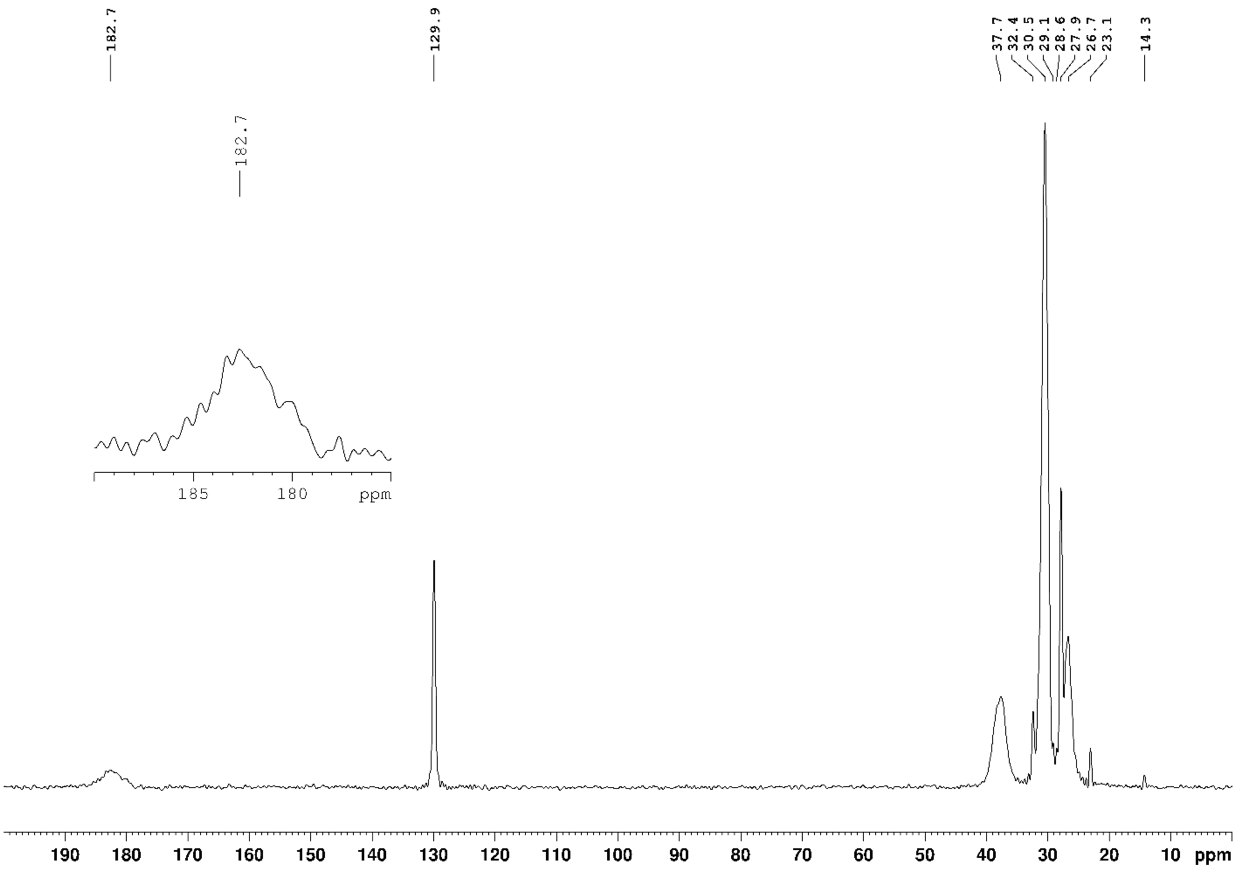


A 200 mL beaker was charged with deionised H_2O (100 mL) and oleic acid (0.32 mL, 1 mmol), heated to 90 °C, and adjusted to pH 10. The suspension was stirred until full solubilisation of the acid was achieved. In a separate beaker, $MgCl_2$ (0.07 g, 0.75 mmol) was dissolved in H_2O (10 mL), and the solution was added dropwise to the first beaker at a rate of 1 mL per minute using a syringe pump to yield the precipitation of a white solid. The resulting suspension was gradually cooled to room temperature to favour flocculation of the precipitate. The solid was filtered, washed with H_2O (2 x 25 mL), and dried in a vacuum oven for 8 h at 60 °C to yield **15** as a white solid (0.29 g, 99%). Dec.p. 325.0 °C (measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 182.7, 129.9, 37.7, 32.4, 30.5, 29.1, 28.6, 27.9, 26.7, 23.1, 14.3 ppm.

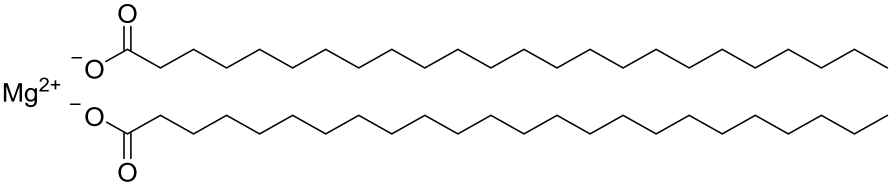
HRMS (*m/z* – DIP APCI$^-$): Found: 281.2540 (M^-) $C_{18}H_{33}O_2^-$ Requires: 281.2486.

ν_{MAX} (neat)/cm^{-1}: 2922, 2853, 1575, 1441, 1314, 721.



^{13}C CP/MAS SSNMR spectrum of 15 (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.0 ms, 80 kHz proton decouple)

Synthesis of magnesium tetraeicosanoate (16)

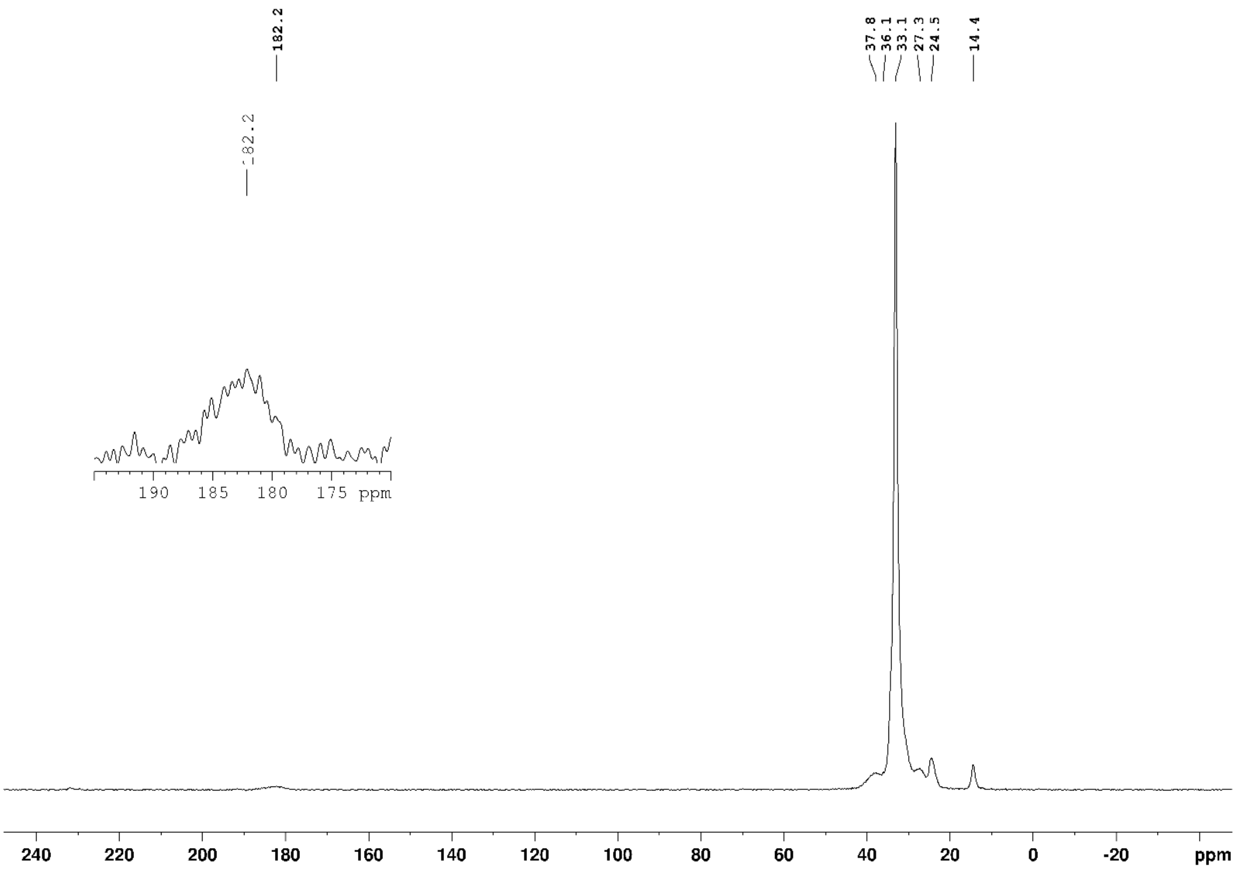


An oven-dried round-bottomed flask was charged with stearic acid (0.18 g, 0.5 mmol) and anhydrous Et_2O (20 mL), the mixture was kept under argon atmosphere, it was stirred until complete dissolution of the acid and cooled to 0 °C. A solution of dibutylmagnesium (0.47 mL, 0.47 eq., 1 M in heptane) was added dropwise and formed a white precipitate. The resulting suspension was stirred for 1 h at room temperature and it was filtered with a Buckner funnel. The residue was washed with $CHCl_3$ (3 x 10 mL) and was dried in a vacuum oven for 4 h at 60° C to yield **16** as a white solid (0.17 g, 88%). Dec.p. 350.4 °C (measured at the onset of a TGA spectrum)

δ_C (101 MHz, CP/MAS SSNMR) 182.2, 37.8, 36.1, 33.1, 27.3, 24.5, 14.4 ppm.

HRMS (*m/z* – DIP APCI$^-$): Found: 367.3640 (M$^-$) $C_{24}H_{47}O_2^-$ Requires: 367.3582.

ν_{MAX} (neat)/cm^{-1}: 2916, 2850, 1576, 1466, 1319, 1114, 719.



^{13}C CP/MAS SSNMR spectrum of 16 (100.6 MHz, 20 °C, spin rate 20 kHz, contact time 1.0 ms, 80 kHz proton decouple)

2. Supplementary glycolysis experimental procedures and associated NMR spectra

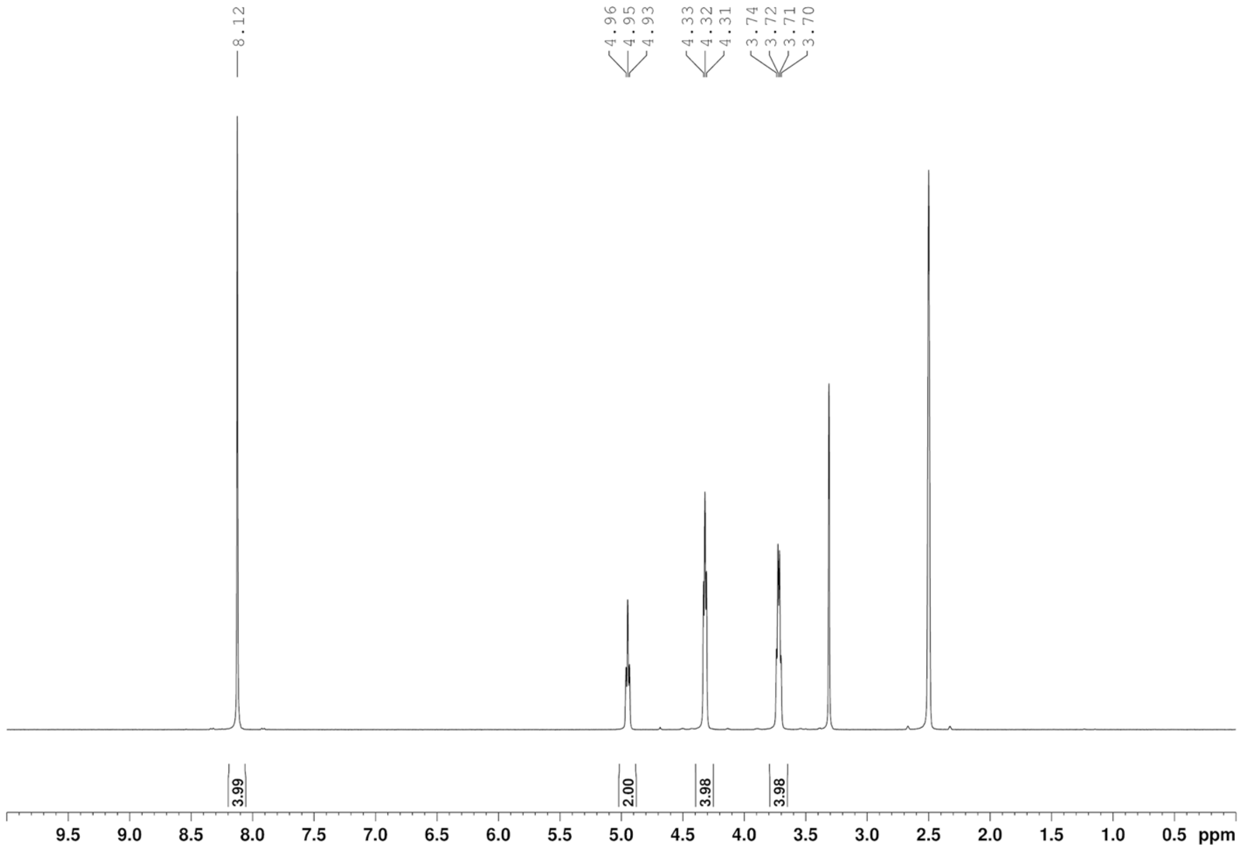
PET:EG (1:10, *wt:wt*) experimental procedure

An oven dried carousel flask was charged with polyethylene terephthalate flakes (0.5000 g ± 0.0025 g, 5 mm x 5 mm), ethylene glycol (4.5 mL, 5 g) and magnesium stearate (0.0077 g, 0.013 mmol, 0.5 mol%).[a,b] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred for 4 h at 180 °C. The flask was removed from the carousel and was left to cool for 5 min. The reaction mixture was then diluted with deionised water (200 mL), and the resulting aqueous mixture was vigorously stirred for 20 min. Utilising a Bucker funnel the mixture was filtered and the pre weighed filter paper was dried overnight in a vacuum oven at 60 °C to determine levels of unreacted PET residue and oligomers. The filtrate was evaporated to a total of 30 mL and cooled to 4 °C overnight to crystallise *bis*(2-hydroxyethyl)terephthalate (BHET). The resulting crystals were filtered and dried overnight in a vacuum oven at 60 °C to obtain BHET as a crystalline white solid (0.5276 g, 80%).

The mother liquor from the crystallisation process was evaporated to remove water and ethylene glycol; qH NMR analysis was performed using (*E*)-stilbene as the internal standard (1 mmol, 0.1803 g) to reveal the presence of 11% yield of BHET remaining in the crystallisation filtrate.

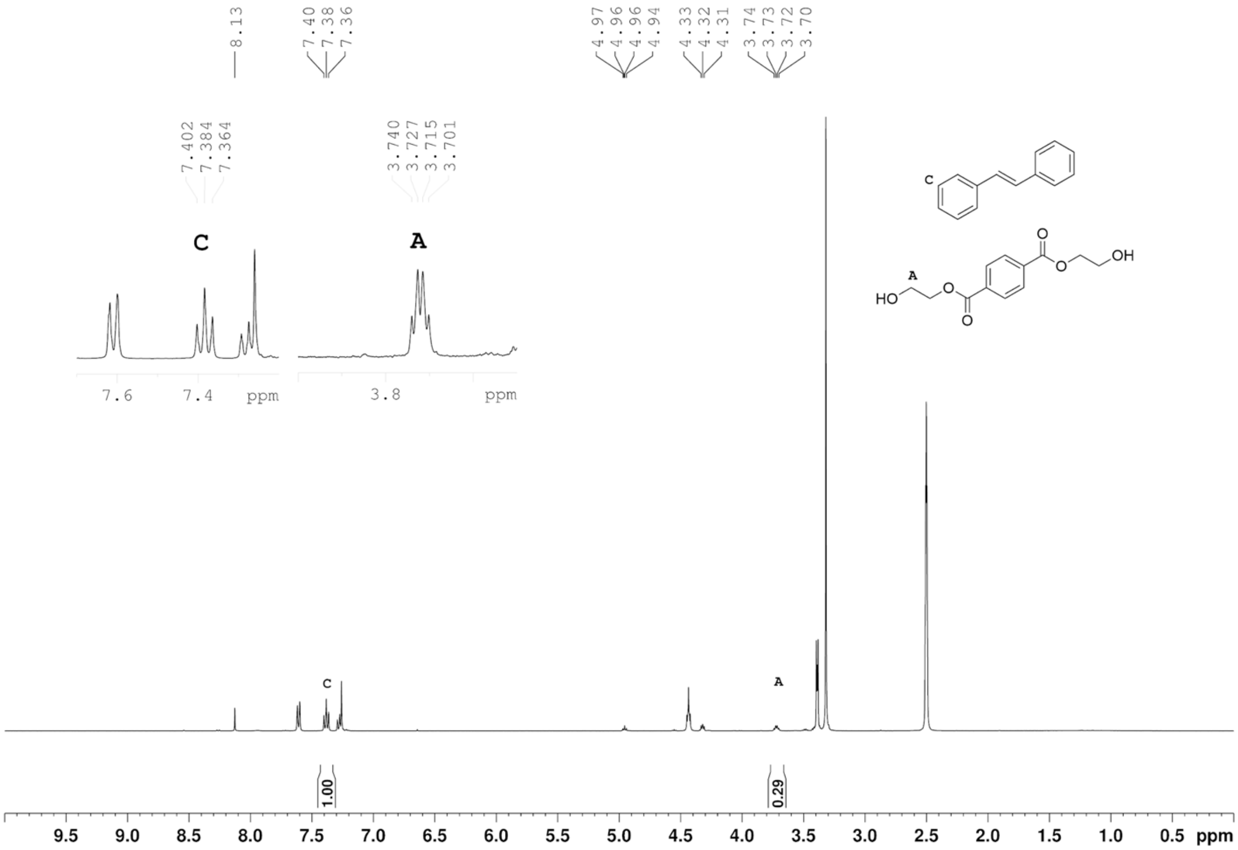
[a] Glycolysis experiments were accomplished with Radleys Carousel 12 Plus Reaction Station.

[b] Mol% of catalyst is related to the number of moles of monomeric units (2.6 mmol) present in 0.5 g of polymer.



^{1}H NMR spectrum (400 MHz) of isolated BHET from the PET:EG (1:10, *wt:wt*) experiment

(Table 2, entry 7)



qH NMR (400 MHz, D1 = 15s) spectrum from the PET:EG (1:10, *wt:wt*) experiment: post crystallisation mother liquor analysis (Table 2, entry 7)

PET:EG (1:10, *wt:wt*) experimental procedure to determine the yield by ^{1}H NMR spectroscopy

An oven dried carousel flask was charged with polyethylene terephthalate (PET) flakes (0.5000 g ± 0.0025 g, 5 mm x 5 mm), ethylene glycol (4.5 mL, 5 g) and magnesium stearate (0.0077 g, 0.013 mmol, 0.5 mol%).[a,b] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred for 4 h at 180 °C. The flask was removed from the carousel and was left to cool for 5 min. The reaction mixture was transferred in a 50 mL beaker, the internal standard was added ((*E*)-stilbene, 1 mmol, 0.1803 g) and the mixture was diluted by adding 10 mL of DMSO-d_6. The cloudy suspension was vigorously stirred while keeping the plate temperature to 50 °C until a clear solution save a small amount of insoluble catalyst. A sample of the reaction mixture (~ 3 drops) was diluted to ca. 1 mL with DMSO-d_6. The obtained sample was analysed by qH{^{13}C}NMR to determine BHET yield (95%).[c,d]

[a] Glycolysis experiments were accomplished with Radleys Carousel 12 Plus Reaction Station.

[b] Mol% of catalyst is related to the number of moles of monomeric units (2.6 mmol) present in 0.5 g of polymer.

[c] qH{^{13}C}NMR, 400 MHz, D1 = 15 s, GARP-mediated ^{13}C decoupling.[1]

[d] Yield value was calculated by subtraction of the -CH$_2$- signal at 3.72 ppm (4H) with the resonance associated with the soluble oligomeric fraction 4.68 ppm (4H).[2]

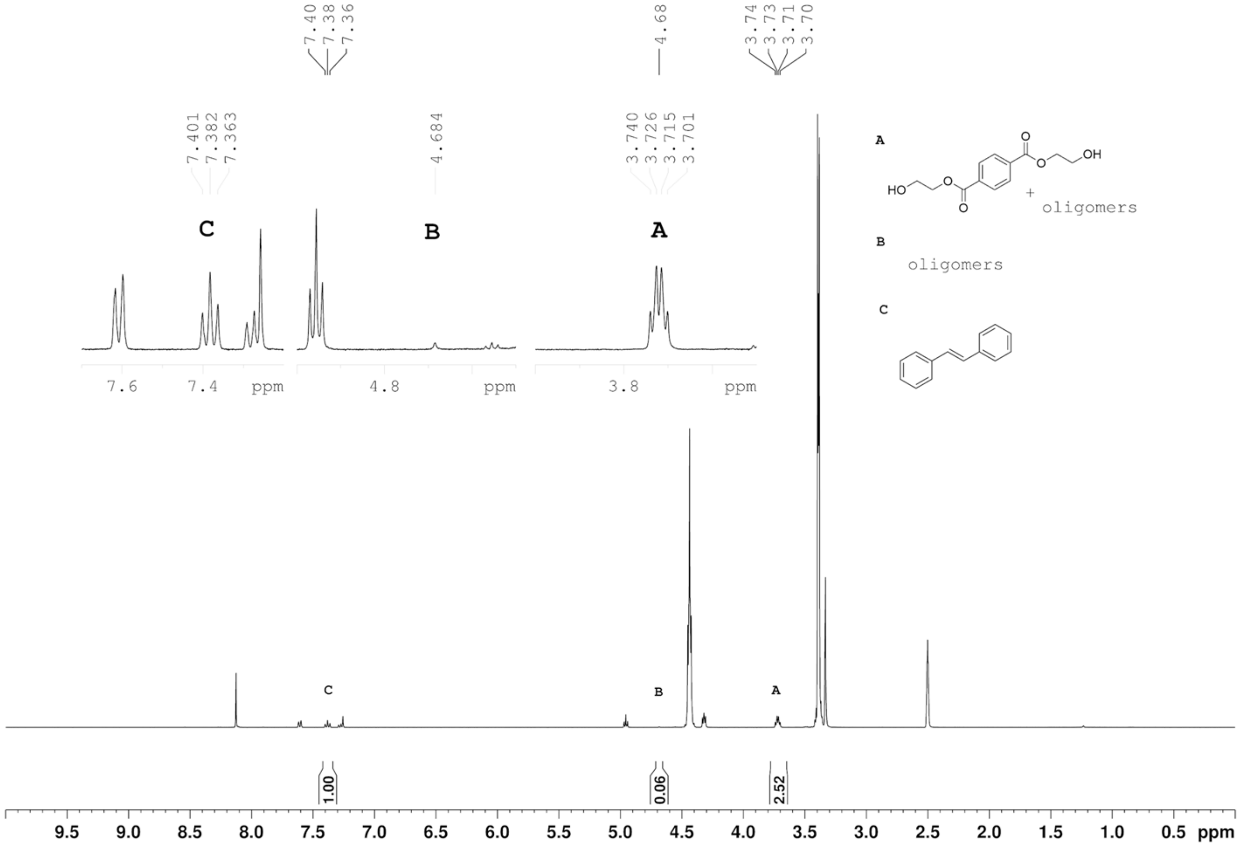
Resonances relevant for yield calculation:

A - 3.72 ppm BHET (4H) + BHET dimer (4H)

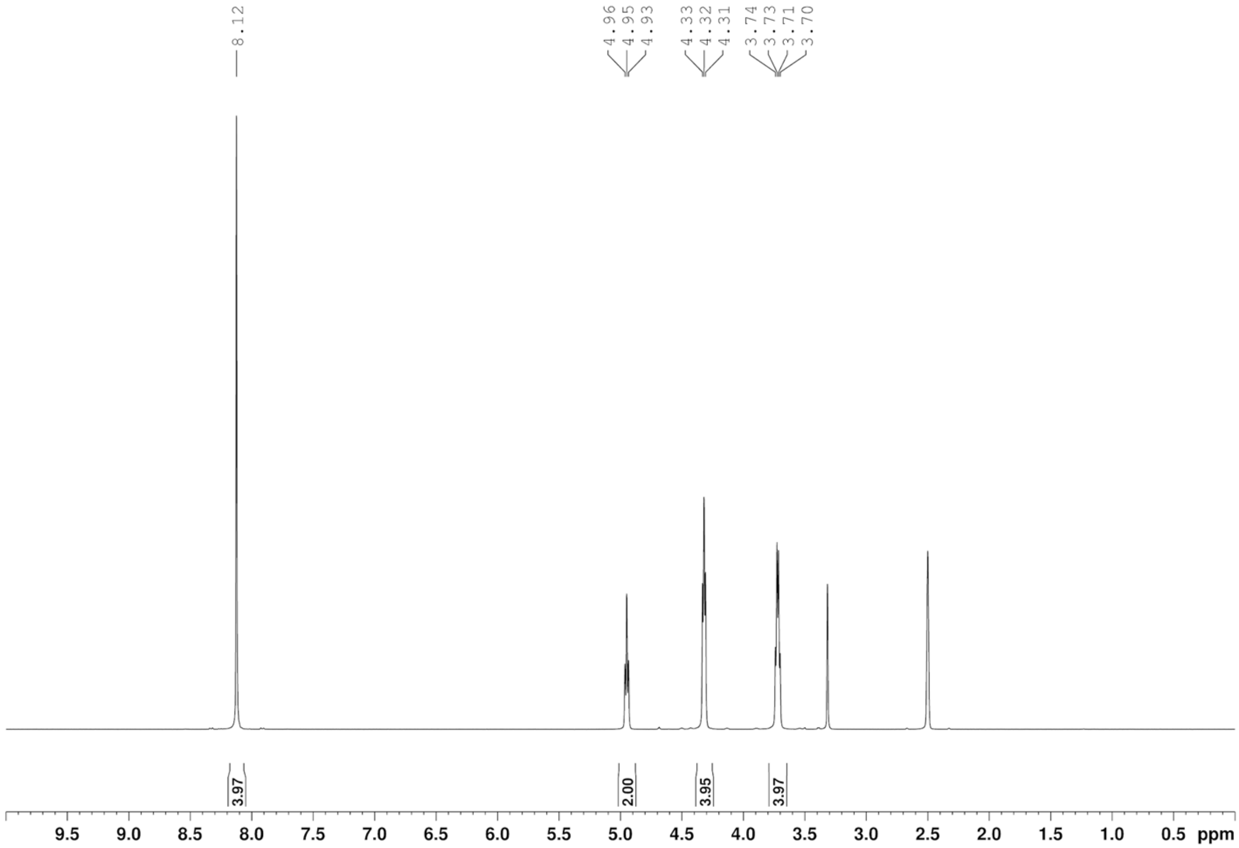
B - 4.68 ppm BHET dimer (4H)

C - 7.38 ppm (*E*)-stilbene (4H) - set integration to 1.00

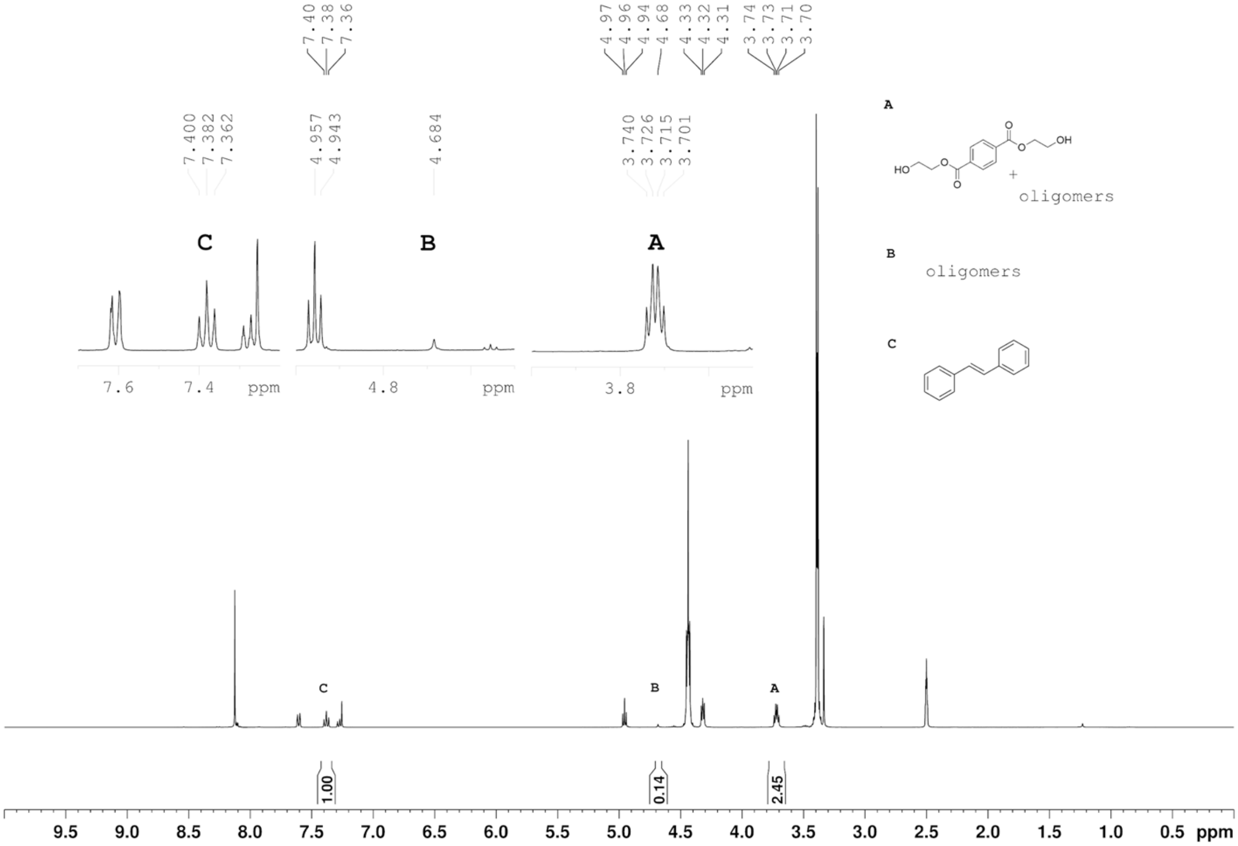
$$\%yield = \frac{(int.\,A - int.B)}{theoretical\,mmol} \times \frac{C\,mmol}{int.C} * 100 = \frac{(int.\,A - int.\,B)}{2.6\,mmol} \times 1\,mmol * 100 = \ 95\%$$



qH{^{13}C}NMR (400 MHz, D1 = 15 s, GARP-mediated ^{13}C decoupling) of PET:EG (1:10, *wt:wt*) experiment for NMR yield calculation, internal standard (*E*)-stilbene (Table 2, entry 8)



^{1}H NMR (400 MHz) spectrum of BHET from the PET:EG (1:4, *wt:wt*) experiment (Table 2, entry 1)



qH{^{13}C}NMR (400 MHz, D1 = 15 s, GARP-mediated ^{13}C decoupling) of the PET:EG (1:4, *wt:wt*) experiment for NMR yield calculation, internal standard (*E*)-stilbene (Table 2, entry 2)

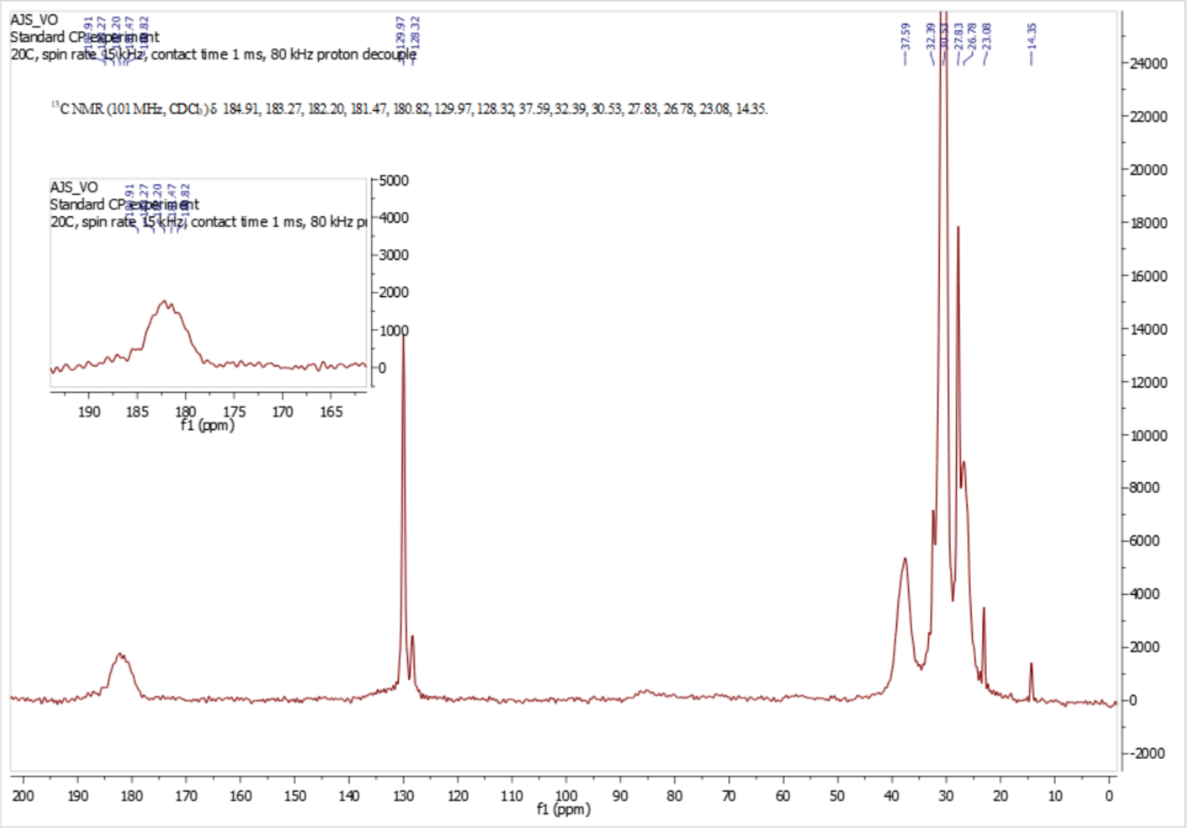
3. Cooking oil catalyst characterisation and associated spectra

RS-cat (rapeseed oil-derived)

δ_C (101 MHz, CP/MAS SSNMR) 184.9, 183.3, 182.2, 181.5, 180.8, 130.0, 128.3, 37.6, 32.4, 30.5, 27.8, 26.8, 23.1, 14.4 ppm.

ν_{MAX} (neat)/cm^{-1}: 3008, 2923, 2853, 1746, 1574, 1449, 1239, 1162, 1050, 858, 721.

Dec.p. 318.9 °C (measured at the onset of a TGA spectrum)



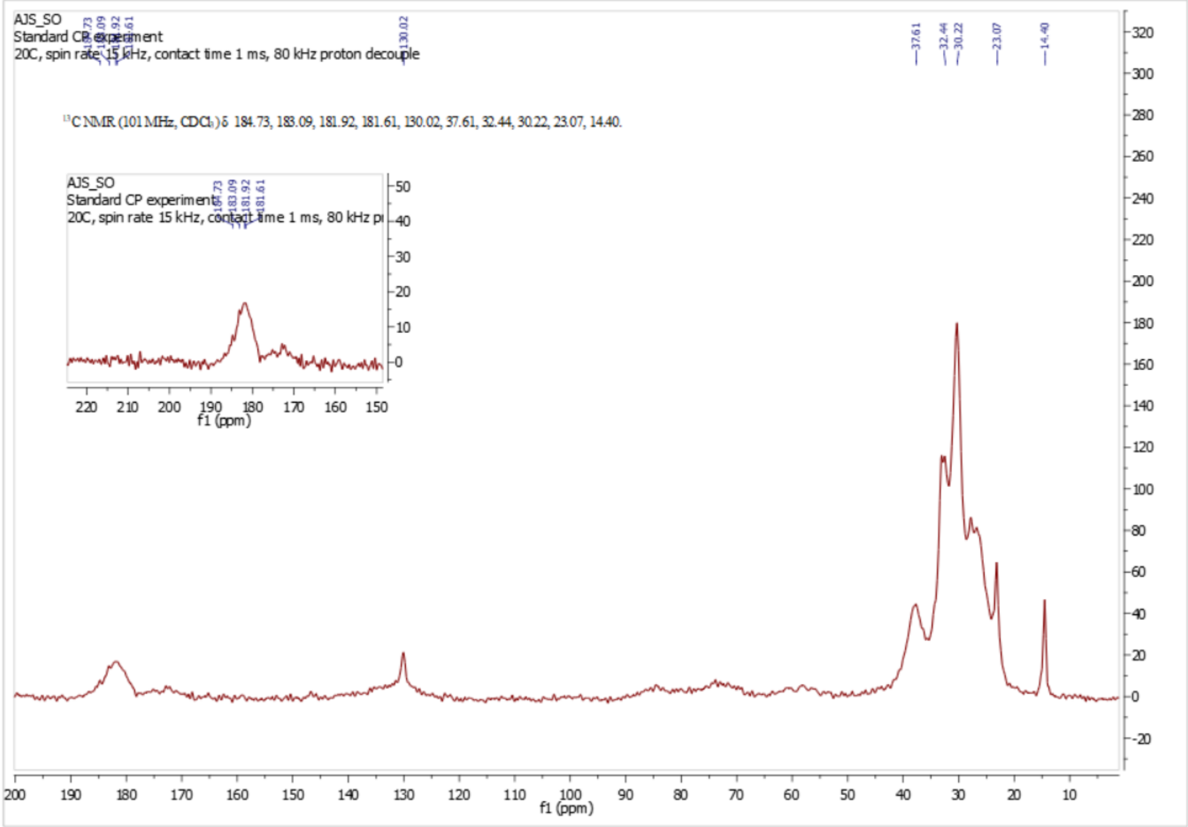
CP/MAS SSNMR (101 MHz) spectrum of RS-cat

SF-cat (sunflower oil-derived)

δ_C (101 MHz, CP/MAS SSNMR) δ 184.7, 184.1, 182.0, 182.6, 130.0, 37.6, 32.4, 30.2, 23.1, 14.4 ppm.

ν_{MAX} (neat)/cm^{-1}: 3053, 2923, 2853, 1744, 1577, 1437, 1315, 1056, 1004, 886, 722

Dec.p. 319.5 °C (measured at the onset of a TGA spectrum)



^{13}C NMR (101 MHz, CDCl$_3$) δ 184.73, 183.09, 181.92, 181.61, 130.02, 37.61, 32.44, 30.22, 23.07, 14.40.

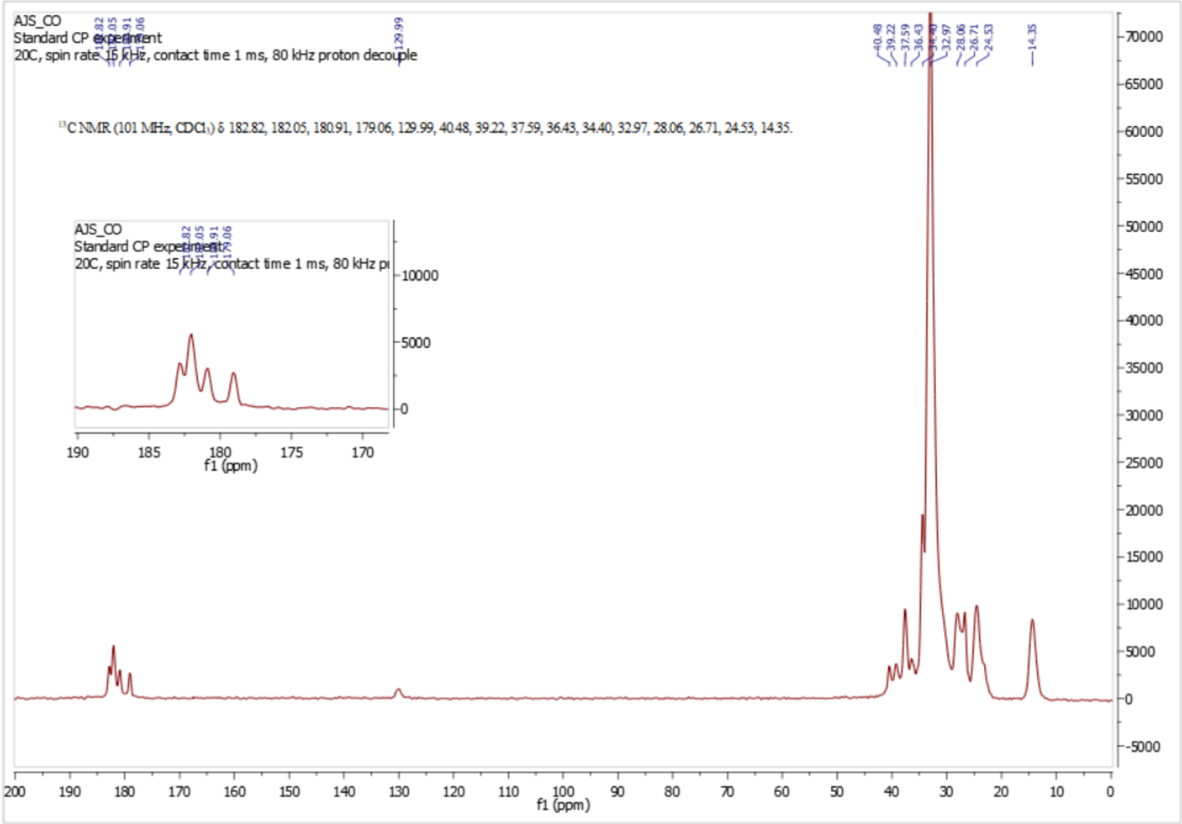
CP/MAS SSNMR (101 MHz) spectrum of SF-cat

CO-cat (coconut oil-derived)

δ_C (101 MHz, CP/MAS SSNMR) δ 182.8, 182.1, 180.9, 179.1, 130.0, 40.5, 39.2, 37.6, 36.4, 34.4, 33.0, 28.1, 26.7, 24.5, 14.4 ppm.

ν_{MAX} (neat)/cm^{-1}: 2957, 2919, 2851, 1574, 1450, 1378, 1316, 1337, 1114, 1029, 933, 87, 790, 720.

Dec.p. 336.1 °C (measured at the onset of a TGA spectrum)



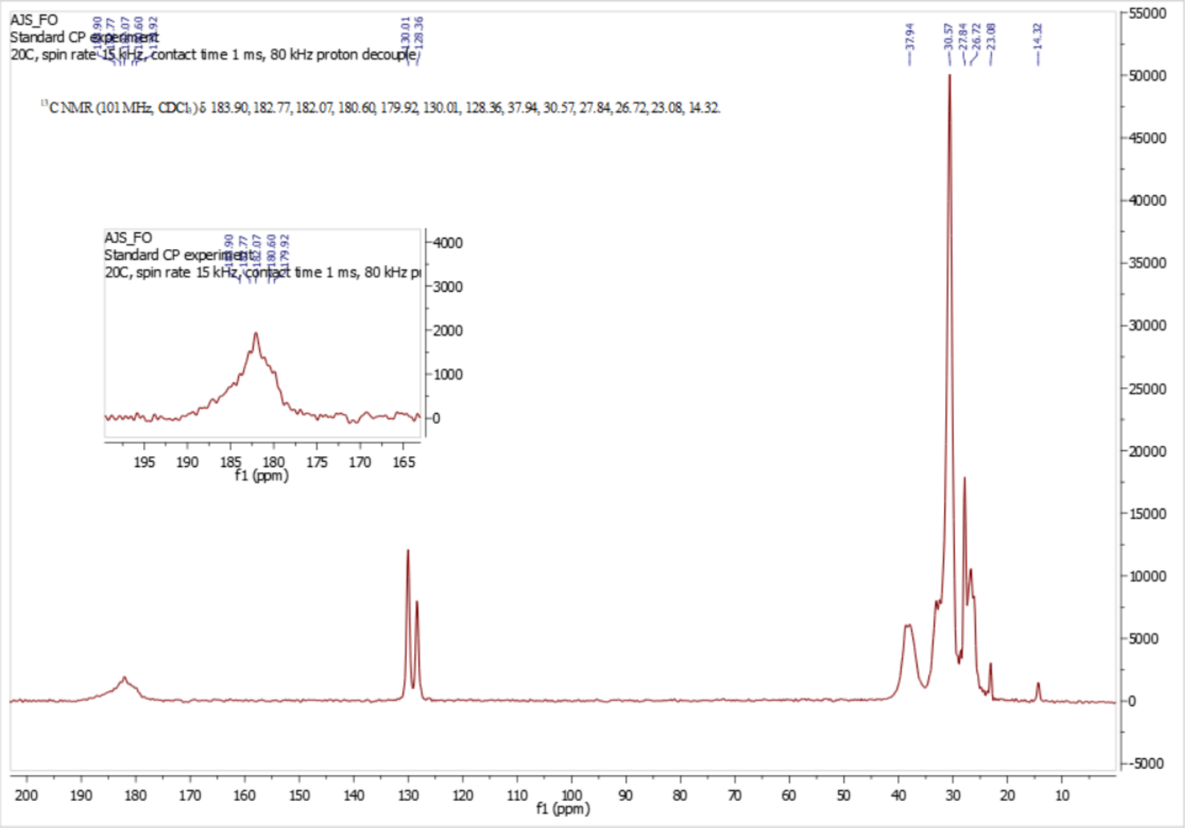
CP/MAS SSNMR (101 MHz) spectrum of CO-cat

RES-cat (restaurant vegetable oil-derived)

δ_C (101 MHz, CP/MAS SSNMR) δ 183.9, 182.8, 182.1, 180.6, 179.9, 130.0, 128.4, 38.0, 30.6, 27.9, 26.7, 23.1, 14.3 ppm.

ν_{MAX} (neat)/cm^{-1}: 3010, 2922, 2852, 1567, 1442, 1316, 720.

Dec.p. 326.7 °C (measured at the onset of a TGA spectrum)



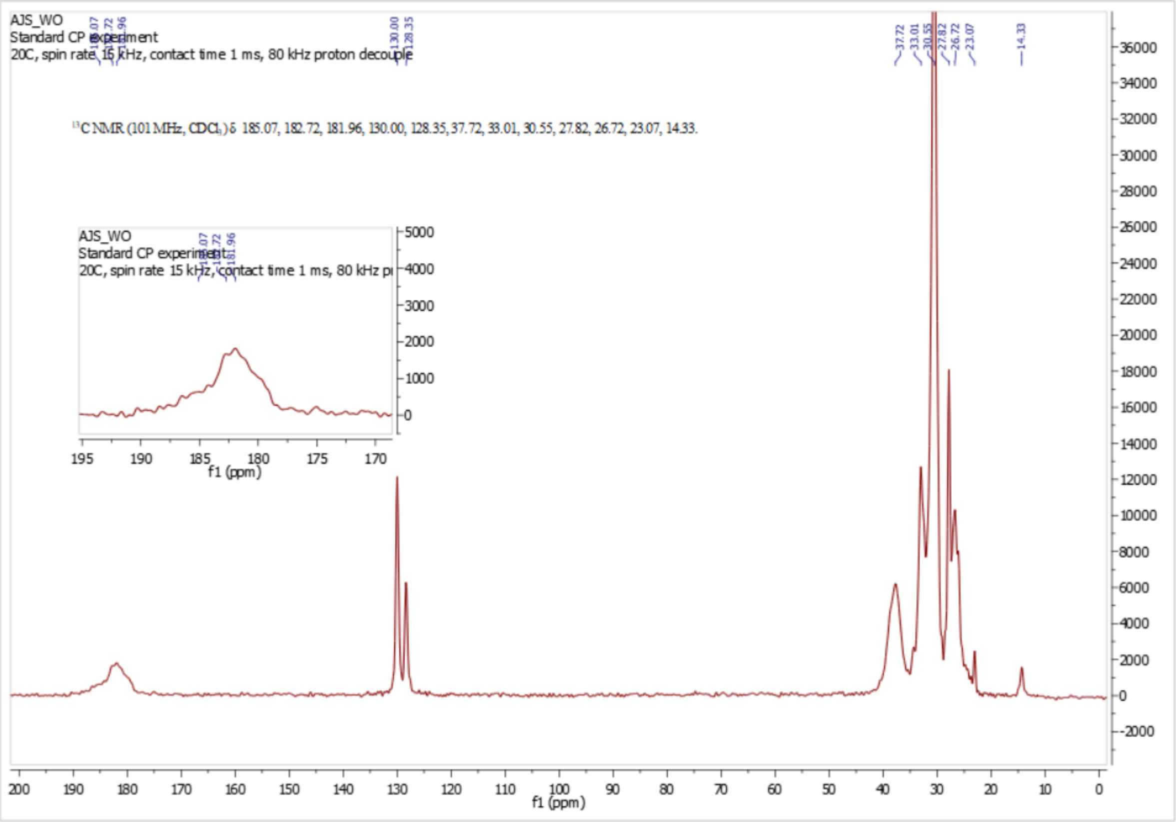
CP/MAS SSNMR (101 MHz) spectrum of RES-cat

W-RES-cat (waste restaurant vegetable oil-derived)

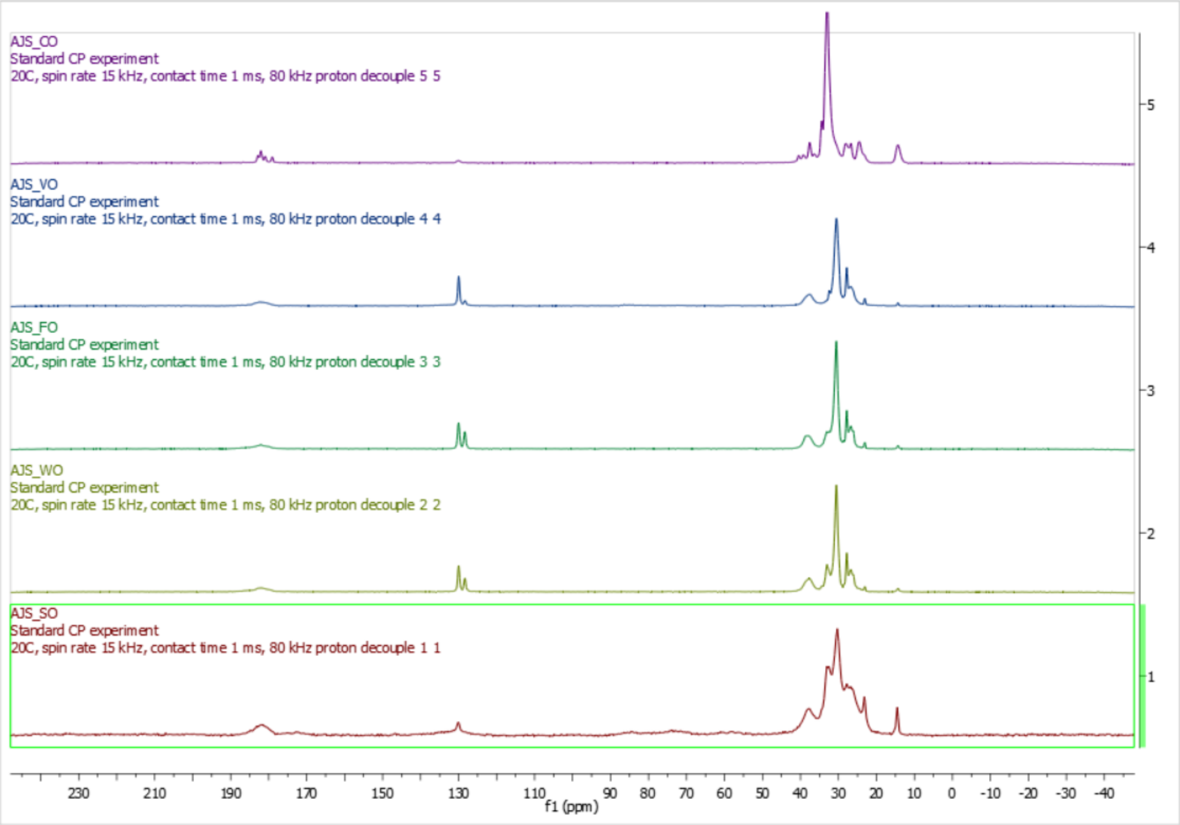
δ_C (101 MHz, CP/MAS SSNMR) δ 185.1, 182.7, 182.0, 130.0, 128.4, 37.7, 33.0, 30.6, 27.8, 26.7, 23.1, 14.3 ppm.

ν_{MAX} (neat)/cm^{-1}: 3010, 2922, 2852, 1573, 1446, 1312, 720.

Dec.p. 333.2 °C (measured at the onset of a TGA spectrum)



CP/MAS SSNMR (101 MHz) spectrum of W-RES-cat



Comparison of the CP/MAS SSNMR (101 MHz) spectra associated with the cooking oil catalysts (Bottom to top: SF-cat, W-RES-cat, RES-cat, RS-cat, CO-cat)

Cat	Carbonyl Region (ppm)	Olefinic Region (ppm)	Aliphatic Region (ppm)	Observations
CO-cat	182.8–179.1	130.00	40.5–14.4	Higher saturation, shorter-chain fatty acids.
RS-cat	184.9–180.8	130.0, 128.3	37.6–14.4	High unsaturation, long-chain fatty acids.
RES-cat	183.9–179.9	130.0, 128.4	38.0–14.3	Distinct profile from the others, possibly soya content
W-RES-cat	185.1–182.0	130.0, 128.4	37.7–14.3	Possible thermal degradation evident in upfield carbonyl shifts.
SF-cat	184.7–181.6	130.0	37.6–14.4	High linoleic acid content

4. Supplementary glycolysis experimental procedures using cooking oil-derived catalysts (Table 4) and associated NMR spectra

Glycolysis of PET using the waste oil-derived catalyst:

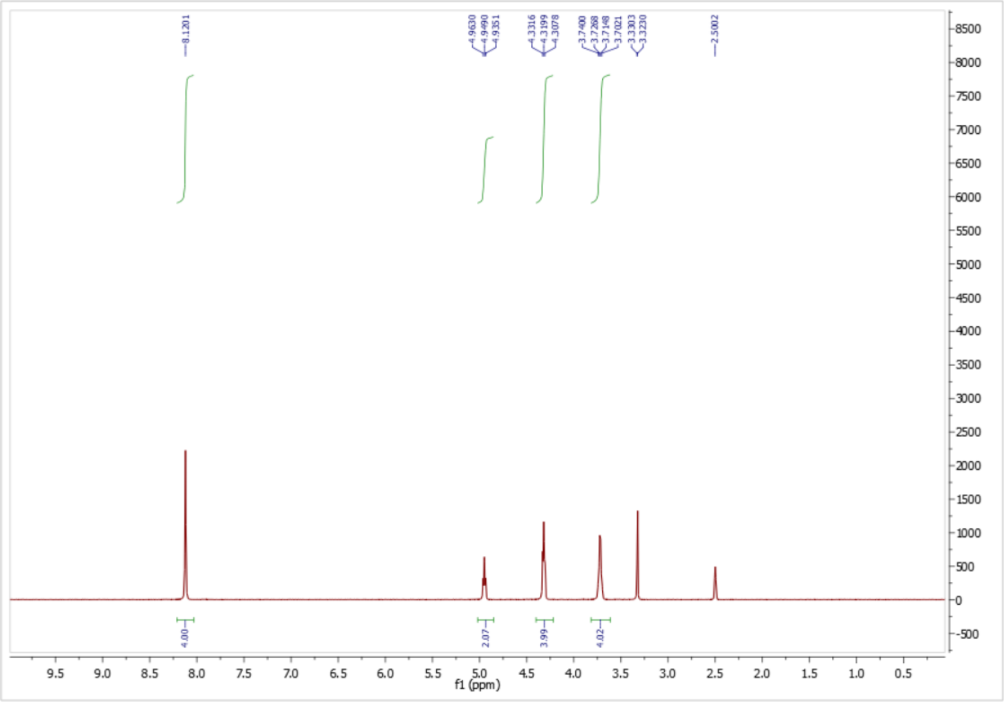
An oven-dried carousel flask was charged with polyethylene terephthalate flakes (1.0 g, 5 mm x 5 mm), ethylene glycol (3.6 mL, 4 g) and oil-derived catalyst (1.5 w/w%, 15 mg).[a] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred (800 rpm) for 50 min at 190 °C. The flask was removed from the carousel and was left to cool for 5 min. The reaction mixture was then diluted with deionised water (400 mL), and the resulting aqueous mixture was vigorously stirred for 20 min. Utilising a Bucker funnel the mixture was filtered and the pre-weighed filter paper was dried overnight in a vacuum oven at 60 °C to determine levels of unreacted PET residue and oligomers. The filtrate was then concentrated under vacuum to a total volume of 50 mL and cooled to 4 °C overnight to promote crystallisation. . The resulting crystals were filtered and subsequently dried overnight in a vacuum oven at 60 °C to obtain BHET as a crystalline white solid (1.10 g, 83% yield).

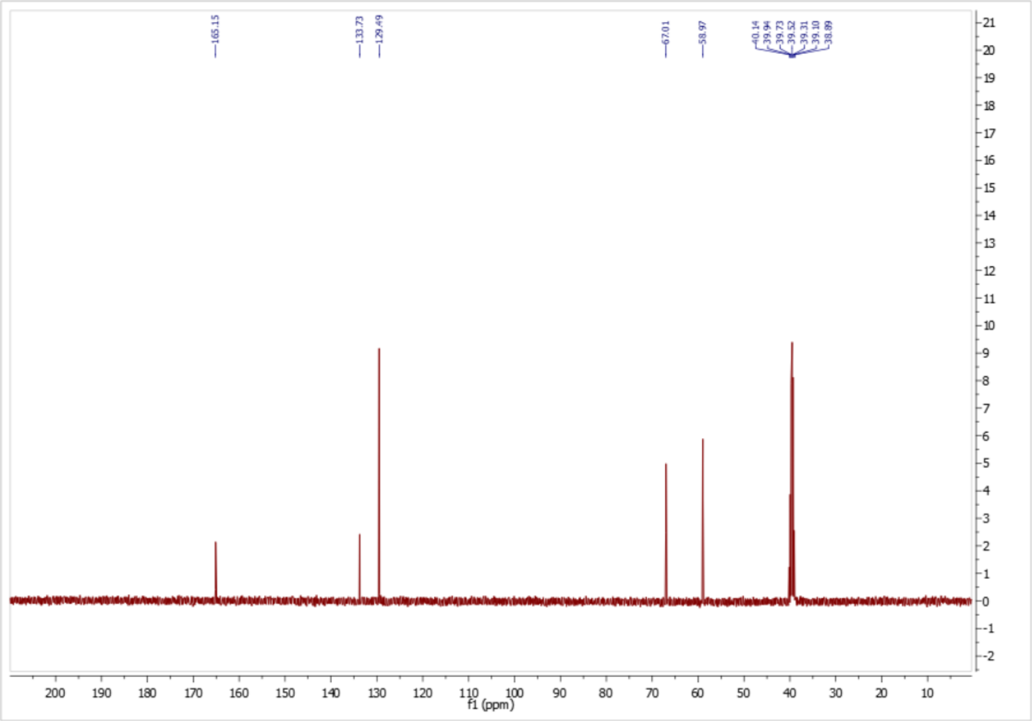
Glycolysis of textile waste using waste oil catalysts:

An oven-dried carousel flask was charged with textile cuttings (1.0 g, 5 mm x 5 mm), ethylene glycol (3.6 mL, 4 g) and oil-derived catalyst (1.5 w/w%, 15 mg).[a] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred for 50 min. at 190 °C. The flask was removed from the carousel and was left to cool for 5 min. The reaction mixture was then diluted with deionised water (400 mL), and the resulting aqueous mixture was vigorously stirred for 20 min. Utilising a Bucker funnel the mixture was filtered and the pre weighed filter paper was dried overnight in a vacuum oven at 60 °C to determine levels of unreacted textile residue and oligomers. The filtrate was then concentrated under vacuum to a total volume of 50 mL and cooled to 4 °C overnight to promote crystallisation. The resulting crystals were filtered, and dried overnight in a vacuum oven at 60 °C to obtain BHET as a crystalline white solid (1.06 g, 80% yield).

Glycolysis of PET using waste oil catalyst at gram scale:

An oven-dried thick-walled glass tube was charged with polyethylene terephthalate flakes (5.0 g, 5 mm x 5 mm), ethylene glycol (18 mL, 20 g) and **W-RES-cat** (1.5 w/w%, 75 mg).[a] The flask was placed under an atmosphere of nitrogen (balloon) with septum, and the reaction was stirred (800 rpm) for 1 h at 190 °C. The thick-walled glass tube was removed from the oil bath and was left to cool for 5 min. The reaction mixture was then diluted with deionised water (2.0 L), and the resulting aqueous mixture was vigorously stirred for 20 min. Utilising a Bucker funnel the mixture was filtered and the pre-weighed filter paper was dried overnight in a vacuum oven at 60 °C to determine levels of unreacted PET residue and oligomers. The filtrate was then concentrated under vacuum to a total volume of 300 mL and cooled to 4 °C overnight to promote crystallisation. The resulting crystals were filtered, the mother liquor further concentrated under vacuum to 25 mL and cooled again to 4 °C overnight. The resulting crystals were filtered, combined with the first crop and dried overnight in a vacuum oven at 60 °C to obtain BHET as a crystalline white solid (5.43 g, 82% yield).





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra (DMSO-d_6) of BHET synthesised with W-RES-cat

5. Magnesium stearate recycling: procedure and associated spectra

A two-necked 25 mL round bottomed flask equipped with a thermometer was charged with polyethylene terephthalate flakes (1.0000 g ± 0.0050 g, 5 mm x 5 mm), ethylene glycol (9.0 mL) and magnesium stearate (0.0615 g, 0.104 mmol, 2 mol%).[a] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred for 4 h at 180 °C (a clear transparent solution was obtained). The reaction vessel was left to cool for 5 min. The reaction mixture was then diluted with deionised water (400 mL), and the resulting aqueous mixture was vigorously stirred and heated to 90 °C. Utilising a pre-heated filter the insoluble catalyst was filtered, recovered from the mixture (0.0382 g, 62 %) and dried overnight in a vacuum oven at 60 °C. The filtrate was cooled to room temperature and traces of insoluble oligomeric material were removed by filtration. The filtrate was concentrated in vacuo to a total volume of 50 mL and cooled to 4 °C overnight to crystallise *bis*(2-hydroxyethyl)terephthalate (BHET). The resulting crystals were filtered and dried overnight in a vacuum oven to obtain BHET as a crystalline white solid (0.9601 g, 73%).

To assess the recyclability of the catalyst, a second experiment was performed in a carousel tube on 50% scale. The carousel tube was charged with polyethylene terephthalate flakes (0.5000 g ± 0.0025 g, 5 mm x 5 mm), magnesium stearate (0.0308 g, 0.052 mmol, 2 mol%) and ethylene glycol (4.5 mL).[b] The tube was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred for 4 h at 180 °C.[c] The reaction mixture was dilute with water (200 mL) and worked up using the previously stated procedure outlined above. Crystallisation was performed in 30 mL of aqueous solution at a temperature of 4 °C overnight. BHET was isolated as a crystalline white solid (0.5441 g, 82%).[d] M.p. 103.0-104.5 °C (lit.,[3] M.p. 103.1-107.4 °C).

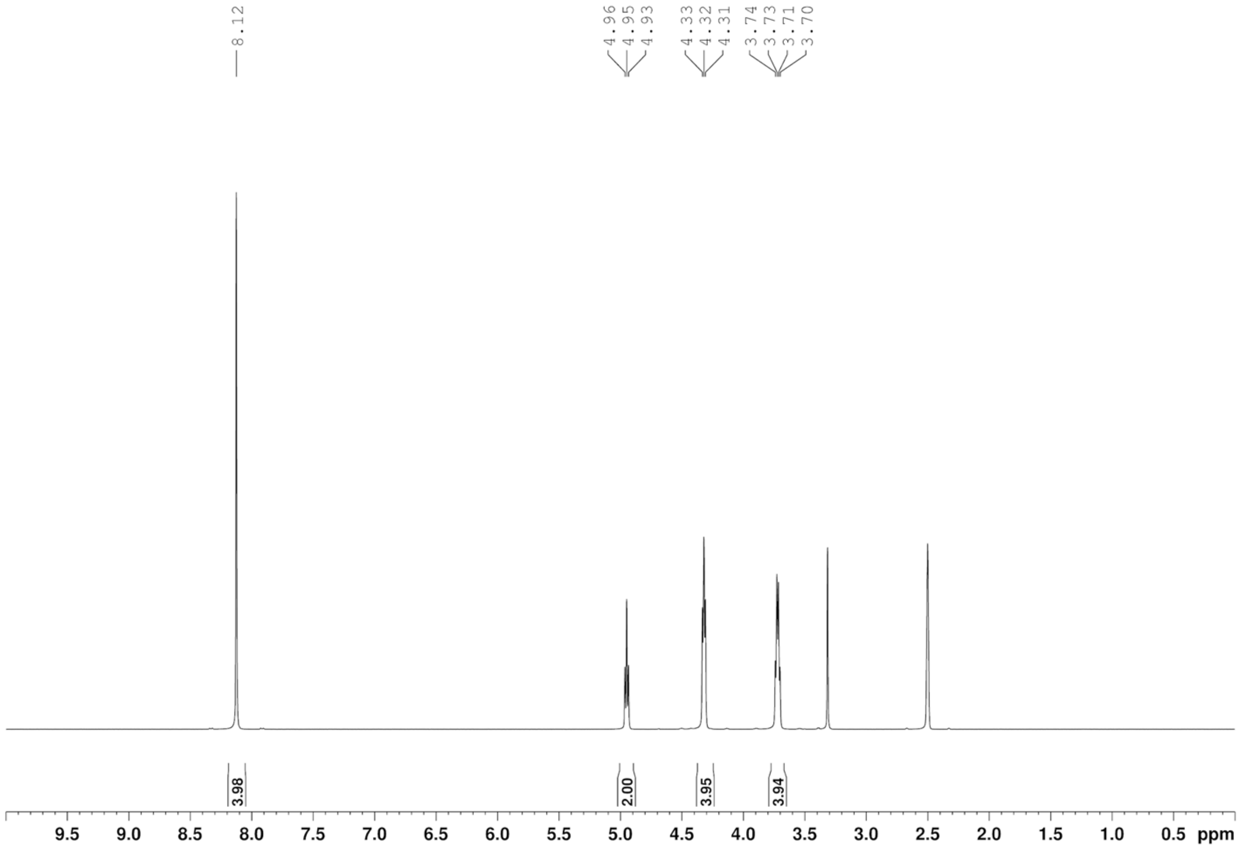
^{1}H NMR (400 MHz, DMSO-d_6): δ_H = 8.12 (s, 4H), 4.95 (t, 2H, *J* 5.3 Hz), 4.32 (t, 4H, *J* 4.7 Hz), 3.72 (dt, 4H, *J* 5.3 Hz, *J* 4.7 Hz) ppm.

[a] Mol% of catalyst is related to the number of moles of monomeric units (5.2 mmol) present in 1 g of polymer.

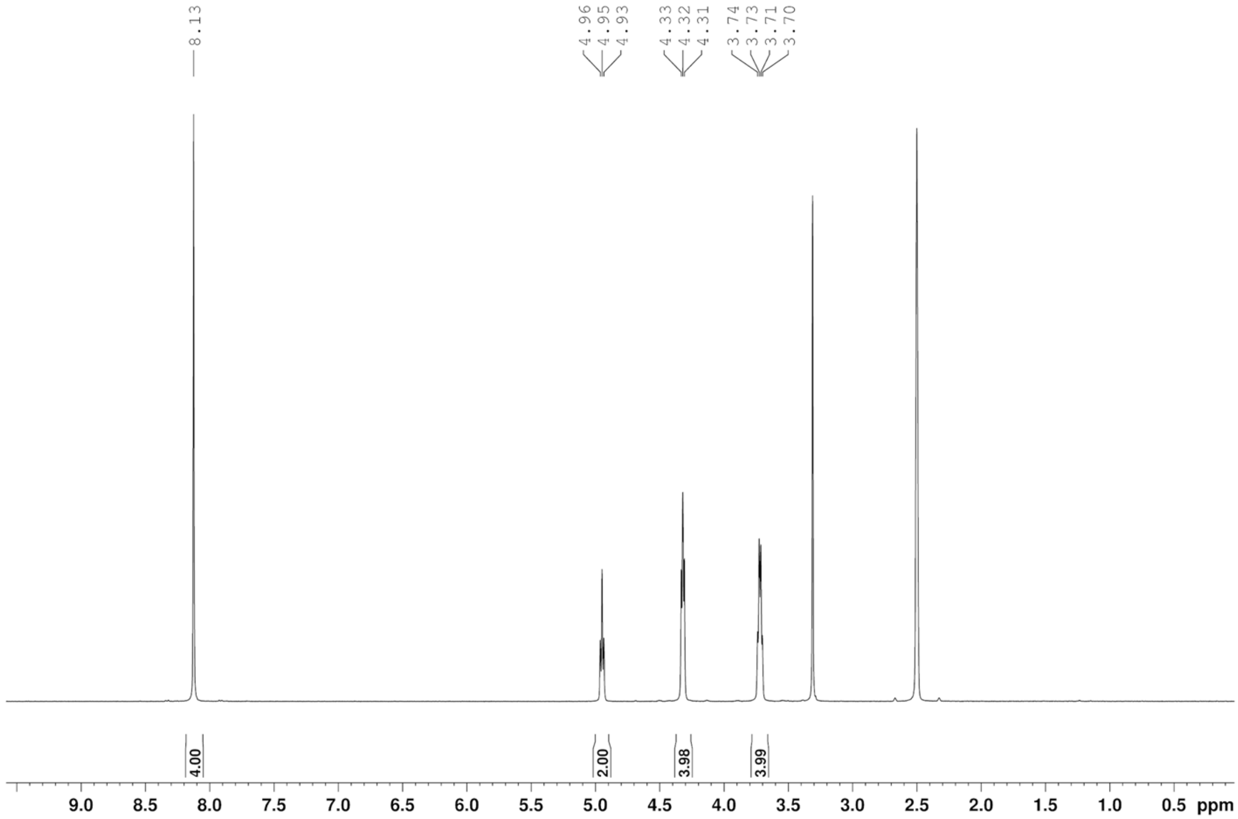
[b] Glycolysis experiments were carried out with Radleys Carousel 12 Plus Reaction Station.

[c] Temperature was measured in an adjacent carousel flask filled with the equivalent amount of ethylene glycol and equipped with a thermometer.

[d] From a duplicate experiment quantitative recovery of the catalyst was detected by gravimetry — however a considerable amount of the catalyst was lost stuck in the pores of the filter.



^{1}H NMR spectrum (400 MHz) of isolated BHET from the catalyst recyclability experiment (1st run)



^{1}H NMR spectrum (400 MHz) of isolated BHET from the catalyst recyclability experiment (2nd run)

6. Pictures of the oils and oil-derived magnesium soap catalysts

Supermarket-purchased oil (RS, CO, SF)

Restaurant oil (RES, W-RES)

Oil-derived catalysts

SF cat. W-RES cat. CO cat. RES cat. RS cat.

7. Cooking oil-derived magnesium soap catalysts: fatty acid analysis

Five samples (Table 1) were analysed for total fatty acid profile by gas chromatography flame ionisation detection (GC-FID). Samples were analysed in triplicate.

FAME preparation was carried out as described by Ichihara and Fukubayashi[4] with some modifications. Into a 2 ml amber GC vial 5 mg of salt sample was weighed out and 50 µL of internal standard, undecanoic acid at 1000 mg/L in heptane, was added. 0.5 ml methanol and 0.5 ml BF_3/methanol (12% *v/v*) was added. The vial was capped with a screw cap containing a PFTE/silicone septa. The vial was heated to 80 ˚°C for 90 min and then allowed to cool to room temperature. Water (0.5 mL) and hexane (0.5 mL) were added and the vial vortexed to extract the esters into the hexane layer. The top layer was transferred into vial with a 250 µL insert and 1 µL was injected for GC analysis.

GC-FID Analysis was carried out on a Thermo Trace 1600 gas chromatograph (Thermo Fisher Scientific, Altrincham, United Kingdom) equipped with a flame ionisation detector. Sample introduction was accomplished using Triplus RSH autosampler to a PTV inlet containing a wool packed liner. The injector was set at 250 °C with a 1:50 split. FAMEs were separated on a select FAME column (Agilent Technologies, Little Island, Cork, Ireland, 100 m x 250 µm x 0.25 m). The column oven was set at 80 °C, held for 8 min, increased to 160 °C at a rate of 20 °C/min, increased to 198°C at a rate of 1 °C/min, held for 10 min and then increased to 250 °C/min at a rate of 5 °C/min and held for 15 min. Total runtime was 85.4 min. the carrier gas was helium and set at a constant flow rate of 1 mL/min. The FID was set at 250 °C.

Fatty acid information

Chain length	Bond position	Configuration	Group[a]	Systematic name	Trivial name	Abbreviation
C4:0			SFA	Butanoic	Butyric	
C6:0			SFA	Hexanoic	Caproic	
C8:0			SFA	Octanoic	Caprylic	
C10:0			SFA	Decanoic	Capric	
C12:0			SFA	Dodecanoic	Lauric	
C14:0			SFA	Tetradecanoic	Myristic	
C14:1	ɯ-5 or 5-n	Cis	MUFA	Δ9-Tetradecenoic	Myristoleic	
C15:0			SFA	Pentadecanoic		
C15:1	ɯ-5 or 5-n	cis	MUFA	Δ10-Pentadecenoic		
C16			SFA	Hexadecanoic	Palmitic	
C16:1	ɯ-7 or 7-n	Cis	MUFA	Δ9-Hexadecenoic	Palmitoleic	
C17			SFA	Heptadecaoic		
C17:1	ɯ-7 or 7-n	Cis	MUFA	Δ10-Heptadecenoic		
C18:0			SFA	Octadecanoic	Stearic	
C18:1 TFA		trans		Sum of C18:1 trans isomers	All trans 4 to 16 octadecenoic	
C18:1	ɯ-9 or 9-n	Cis	MUFA	Δ9-Octadecenoic	Oleic	
C18:2 TFA		trans		Sum of C18:2 trans isomers	All trans 9,12 Octadecadienoic in deodorized oils and	

Chain length	Bond position	Configuration	Group[a]	Systematic name	Trivial name	Abbreviation
					trans originated from milk fat (i.e. C18:2 cis-9, trans 13, C18:2 trans-8,cis-12 and C18:2 trans-11, cis 15)	
C18:2	ɯ-6 or 6-n	cis	PUFA	Δ9,12 Octadecadienoic	Linoleic	LA
C18:2CLA	ɯ-7 or 7-n	Cis/trans	PUFA	Δ9,11 Octadecadienoic	Rumeric	CLA
C18:3	ɯ-6 or 6-n	Cis	PUFA	Δ6,9,12 Octadecatrienoic	Gamma- Linoleic	
C18:3 TFA		trans		Sum of C18:2 trans isomers	All trans 9,12,15 Octadecatrienoic	
C18:3	ɯ-3 or 3-n	Cis	PUFA	9,12,15 Octadecatrienoic	Linolenic	ALA
C20:0			SFA	Eicosanoic	Arachidic	
C20:1	ɯ-6 or 6-n	Cis	MUFA	Δ11- Eicosenoic	Gondoic	
C20:2	ɯ-6 or 6-n	Cis	PUFA	Δ11,14-Eicosadienoic		
C20:3	ɯ-3 or 3-n	Cis	PUFA	Δ8,11,14-Eicosatrienoic	Dihomo-gamma-linolenic (DHGLA)	
C20:3	ɯ-6 or 6-n	Cis	PUFA	Δ8,14,17-Eicosatrienoic		
C20:4	ɯ-3 or 3-n	Cis	PUFA	Δ5,8,11,14-Eicosatetraenoic	Arachidonic	ARA
C20:5			SFA	Δ5,8,11,14,17-Eicosapentaenoic	Eicosapentaenoic	EPA
C21:0			SFA	Heneicosanoic		
C22:0			SFA	Docosanoic	Behenic	
C22:1	ɯ-9 or 9-n	Cis	MUFA	Δ13-Docosenoic	Erucic	
C22:2	ɯ-6 or 6-n	Cis	PUFA	Δ13,16-Docosadienoic		
C22:6	ɯ-3 or 3-n	Cis	PUFA	Δ4,7,10,13,16,19-Docosahexaenoic	Docosahexaenoic	DHA
C24:0			SFA	Tetracosanoic	Lignoceric	
C24:1	ɯ-9 or 9-n	Cis	MUFA	Δ15-Tetracosenoic	Nervonic	

[a] Do not include trans fatty acids in MUFA and PUFA sums.

Results: fatty acids identified in the catalyst samples

Fatty acid[a]	CO-cat	RES-cat	W-RES-cat	SF-cat	RS-cat
C4:0	0 +/- 0	0.11 +/- 0.02	0.09 +/- 0.04	0.06 +/- 0.01	0.06 +/- 0
C6:0	0 +/- 0	1.97 +/- 0.08	2.17 +/- 0.02	4.68 +/- 0.04	1.26 +/- 0.02
C8:0	0.56 +/- 0.01	0.93 +/- 0.05	0.78 +/- 0.02	1.52 +/- 0.04	1.5 +/- 0.01
C10:0	4.4 +/- 0.05	0.06 +/- 0.02	0.07 +/- 0	0.11 +/- 0	0.17 +/- 0.01
C11:0	0.84 +/- 0.04	1.71 +/- 0.17	1.64 +/- 0.08	2.28 +/- 0.2	1.7 +/- 0.05
C12:0	46.22 +/- 0.13	0.04 +/- 0	0.07 +/- 0.01	0.03 +/- 0	0.04 +/- 0.02
C13:0	0.04 +/- 0	0.05 +/- 0.01	0.03 +/- 0	0.02 +/- 0	0.02 +/- 0
C14:0	21.39 +/- 0.1	0.26 +/- 0.01	0.37 +/- 0.01	0.27 +/- 0.01	0.13 +/- 0.01
C14:1	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0
C15:0	0.01 +/- 0	0.07 +/- 0.01	0.08 +/- 0	0.08 +/- 0	0.07 +/- 0
C15:1	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0
C16:0	10.18 +/- 0.03	27.79 +/- 0.25	29.18 +/- 0.16	20.69 +/- 0.55	10.3 +/- 0.04
C16:1	0.01 +/- 0	0.08 +/- 0	0.09 +/- 0	0.08 +/- 0	0.14 +/- 0
C17:0	1.6 +/- 0.07	3.7 +/- 0.34	3.49 +/- 0.15	4.43 +/- 0.36	3.34 +/- 0.12
C18:0	5.33 +/- 0.01	15.11 +/- 0.21	12.53 +/- 0.08	15.28 +/- 0.42	4.76 +/- 0.04
C18:1 CFA	7.92 +/- 0.03	33.66 +/- 0.72	35.7 +/- 0.21	34.98 +/- 0.71	54.83 +/- 0.26
C18:1 TFA	0 +/- 0	0.52 +/- 0.03	0.43 +/- 0.03	0.39 +/- 0.02	1.33 +/- 0.02
C18:2 t10,c12	0 +/- 0	0.05 +/- 0	0.05 +/- 0	0.1 +/- 0	0.3 +/- 0.01
C18:2 c9,t11	0 +/- 0	0.31 +/- 0.01	0.45 +/- 0.05	0.43 +/- 0.02	1.12 +/- 0.04
C18:2 TFA	0 +/- 0	1.03 +/- 0	0.83 +/- 0.04	1.16 +/- 0.04	0.71 +/- 0.06
C18:2n6c	1.18 +/- 0.01	4.05 +/- 0.23	2.23 +/- 0.03	0.03 +/- 0	0.06 +/- 0
C18:3 TFA	0 +/- 0	0.07 +/- 0.02	0.1 +/- 0.03	0.07 +/- 0.02	0.18 +/- 0.01
C18:3n3	0 +/- 0	0.38 +/- 0.02	0.25 +/- 0.02	0.09 +/- 0	0.25 +/- 0.01
C18:3n6	0 +/- 0	0.07 +/- 0	0.04 +/- 0.01	0.04 +/- 0.02	0.14 +/- 0.01
C19:0	0.01 +/- 0	0.05 +/- 0	0.04 +/- 0	0.05 +/- 0.01	0.08 +/- 0
C20:0	0.15 +/- 0.01	1.45 +/- 0.02	1.49 +/- 0.04	1.31 +/- 0.08	1.9 +/- 0.01
C20:1	0.04 +/- 0.01	0.36 +/- 0.01	0.37 +/- 0.01	0.19 +/- 0.02	1.3 +/- 0.01
C20:2	0 +/- 0	1.74 +/- 0.09	2.55 +/- 0.09	3.88 +/- 1.58	7.48 +/- 0.13
C20:3n3	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0
C20:3n6	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0	0.04 +/- 0
C20:4n6	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0	0 +/- 0
C20:5	0 +/- 0	0 +/- 0	0 +/- 0	0.04 +/- 0	0.15 +/- 0.01
C21:0	0 +/- 0	0.92 +/- 0.01	1.04 +/- 0.02	1.12 +/- 0.03	2.61 +/- 0.09
C22:0	0.02 +/- 0.01	1.87 +/- 0.01	2.08 +/- 0.01	4.23 +/- 0.1	2.15 +/- 0.01
C22:1	0.02 +/- 0.01	0.06 +/- 0.01	0.09 +/- 0.02	0.13 +/- 0.01	0.36 +/- 0
C22:2	0 +/- 0	0.06 +/- 0.01	0.04 +/- 0.01	0.26 +/- 0.04	0.27 +/- 0.02
C22:6n3	0 +/- 0	0.08 +/- 0	0.06 +/- 0.01	0.21 +/- 0.06	0.11 +/- 0.05
C23:0	0 +/- 0	0.27 +/- 0.01	0.24 +/- 0.04	0.21 +/- 0.01	0.13 +/- 0
C24:0	0.05 +/- 0.02	0.65 +/- 0.01	0.77 +/- 0.06	1.34 +/- 0.04	0.73 +/- 0.04
C24:1n9	0 +/- 0	0.48 +/- 0.05	0.51 +/- 0.05	0.19 +/- 0.25	0.31 +/- 0.01

[a] Values are presented as average (n=3) g/100g fat.

8. References

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