Supplementary Information (SI) for Green Chemistry.

Electronic Supplementary Information

Catalytic alkaline hydrolysis of PET and BPA-PC waste in minutes at atmospheric pressure without microwaves or organic solvents

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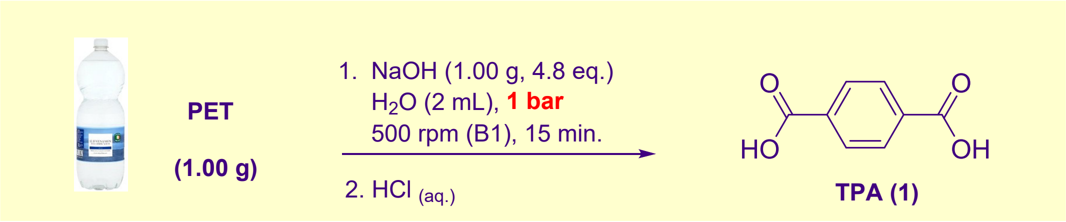
1. General information

Proton Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker DPX 400 MHz and Bruker Avance II 600MHz spectrometers, using $CDCl_3$ and DMSO-*d*$_6$ as solvents, and referenced relative to residual $CHCl_3$ (δ = 7.26 ppm) or DMSO (δ = 2.50 ppm). Carbon NMR spectra were recorded on the same instruments (101 MHz and 151 MHz respectively) with total proton decoupling. ESI mass spectra were acquired using a Waters Micromass LCT-time of flight mass spectrometer (TOF), interfaced to a Waters 2690 HPLC. The instrument was operated in either positive or negative mode as required. Hydrolysis experiments were carried out with Radleys Carousel 12 Plus Reaction Station or silicon oil bath. HPLC grade water was purchased from Sigma-Aldrich and used as the reaction medium for the basic hydrolysis of PET. Colourless polyethylene terephthalate (PET) bottles were purchased from a local supermarket chain and cut into flakes approximately 5 mm in size. Colourful waste PET fiber cloth was used and cut into small pieces, approximately 5 mm in size. Additionally, waste CDs, used as a polycarbonate source, were cut into flakes about 2.5 mm in size and pre-treated following a reported method.[33] Magnetic stirrer bars (Fisher UK, product codes B1 = 16235801, B2 = 16225781, B3 = 16390656, B4 = 10683012) were used to ensure uniform mixing during the reactions. Unless otherwise noted, all commercially available compounds were used as provided, without any further purification.

2. Optimisation study

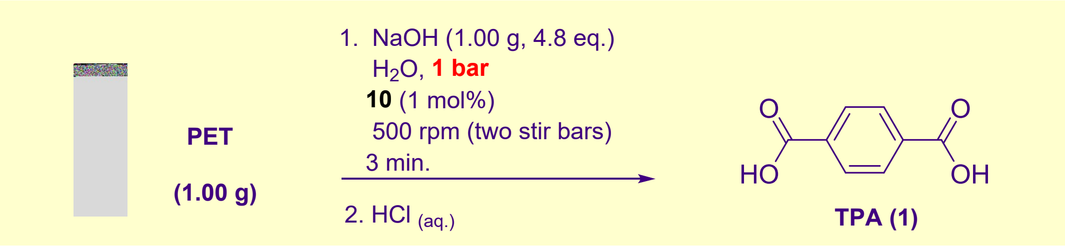
Table S1. Uncatalysed PET waste hydrolysis: the effect of temperature



Entry	Temp. (°C)	Time (min.)	Yield (%)[a]
1.	90	15	12.8
2.	100	15	18.4
3.	110	15	26.1
4.	120	15	52.0
5.	130	15	67.3
6.	138	15	72.4

[a]Isolated yield

Table S2. Phase transfer catalysed PET waste hydrolysis: higher temperatures and concentrations

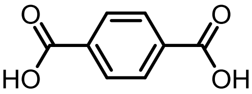


Entry	NaOH Conc. (% w/v) (4.8 equiv.)	H_2O (mL)	Temp. (°C)	Yield (%)[a]
1.	(50% NaOH)	2	138	93.2
2.	(55% NaOH)	1.81	142	88.6
3.	(60% NaOH)	1.66	147	84.9
4.	(65% NaOH)	1.53	152	75.2
5.	(70% NaOH)	1.41	160	70.4

[a]Isolated yield

3. PET hydrolysis and characterisation:

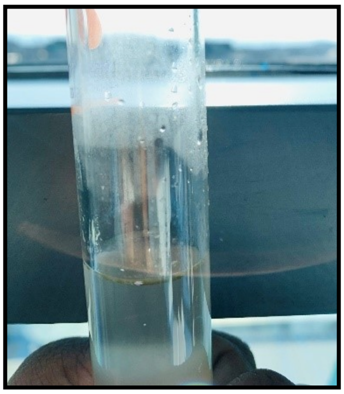
A) TPA isolated from bottle waste



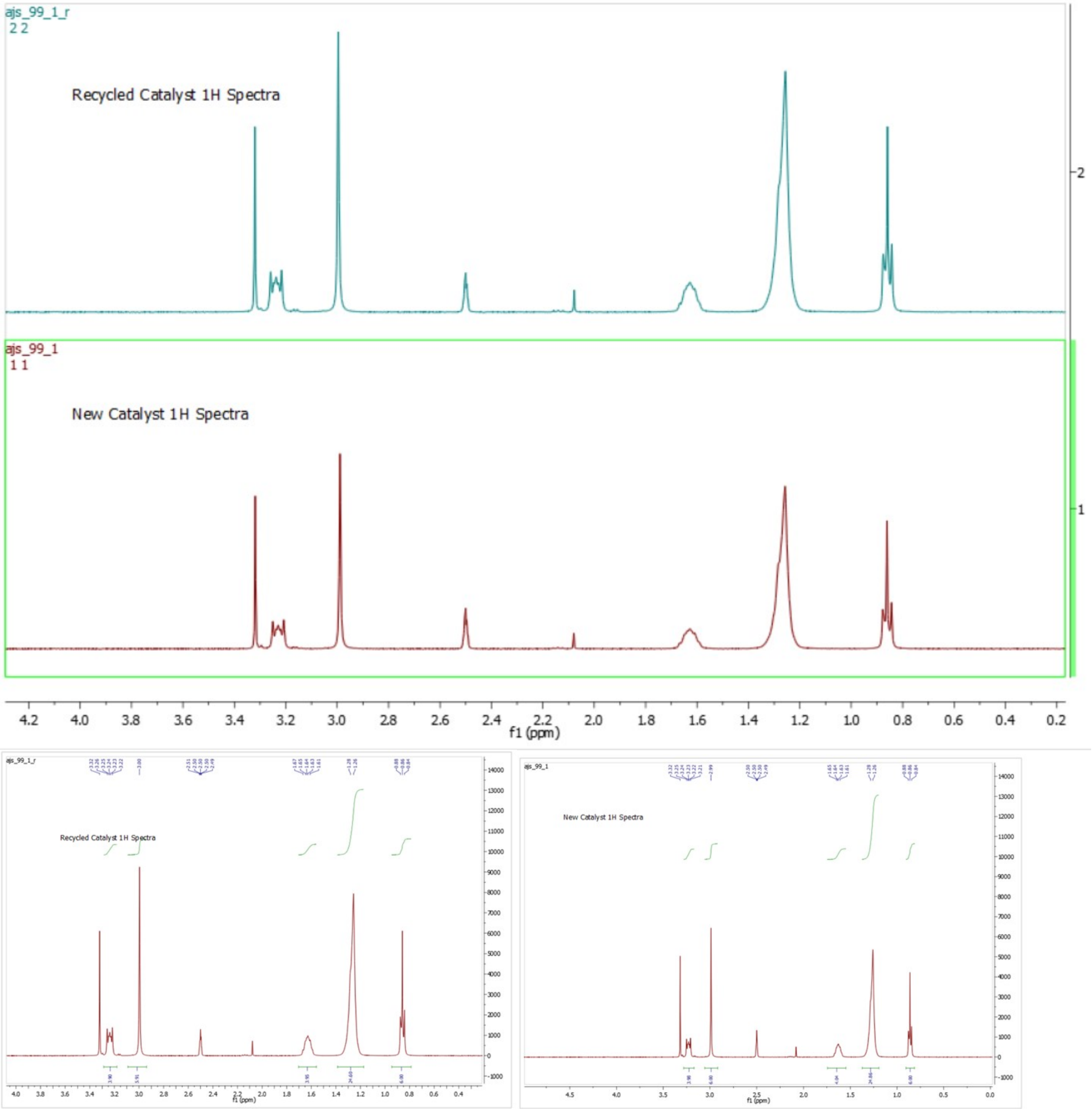
Caution: 50% NaOH is harmful to the skin and corrosive. Exercise appropriate care

An oven-dried carousel flask was charged with water (2 mL), sodium hydroxide (1.00 g), catalyst (1 mol%) and poly(ethylene terephthalate) flakes (*ca*. 5 mm squares, 1.00 g). [a] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred (500 RPM) at 138 °C with two stirrer bars for 4 min. The flask was removed from the carousel and cooled in an ice-bath for 10 min. The reaction mixture was diluted with 15 ml water and stirrer at rt until solid sodium terephthalate was dissolved then filtered, and the residue was washed with water (10 mL x 2). The filtrate was adjusted, with cooling, to pH 1-2 using dilute HCl and the resulting precipitate was filtered and washed with water (10 mL x 2). The product was dried for 4 h in a vacuum oven at 60 ˚C. The isolated yield was calculated by general formula (Actual yield/Theoretical Yield) and the NMR yield of terephthalic acid was determined by ^{1}H NMR spectroscopy using 4-iodoanisole as an internal standard: known masses of product (> 15 mg) and 4-iodoanisole (> 15 mg) were weighed into a sample vial and dissolved in DMSO-d_6.

Recycling of Catalyst:

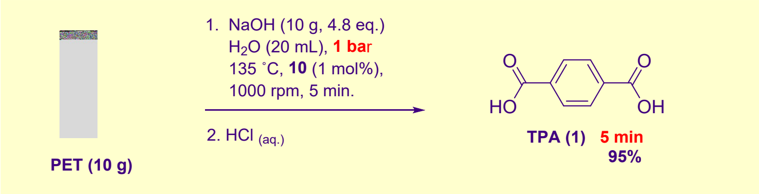


After PET hydrolysis and before neutralization, water was added to dissolve all the disodium-TPA. At this stage, an oily layer of the catalyst was visible on the surface. The catalyst was then extracted using DCM (2 × 5 mL), and the solvent was recovered using a rotary evaporator. After drying, the catalyst was characterized by ^{1}H NMR spectroscopy (recovered catalyst >99%) and reused for the next PET hydrolysis. TPA was isolated in 99.4% yield after 4 minutes from the recycled catalyst.



400 MHz 1H NMR spectrum (DMSO-d_6) of pure catalyst and recycled catalyst

B) TPA isolated from bottle waste (multigram scale)



An oven dried 100 mL round bottomed flask was charged with water (20 mL), sodium hydroxide (10.00 g) and catalyst **10** (196.8 mg, 1 mol %).[a] The flask was placed under an atmosphere of nitrogen (balloon), and the reaction was stirred at 135 °C at 1000 RPM using two stirrer bars until the solution reached the set temperature. Poly(ethylene terephthalate) flakes (*ca*. 5 mm squares, 10.00 g) were added and the mixture was stirred for 5 min. The flask was removed from the oil-bath and cooled in an ice-bath for 10 min. The reaction mixture was diluted with water (150 mL) and stirred at rt until solid sodium terephthalate was dissolved. The mixture was then filtered, and the residue was washed with water (50 mL x 2). The filtrate was adjusted, with cooling, to pH 1-2 using dilute HCl and the resulting precipitate was filtered and washed with water (30 mL x 2). The product was dried for 4 h in a vacuum oven at 60 ˚C. TPA was isolated in 95% (8.2 g) yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.28 (br s, 2H), 8.04 (s, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.7, 134.5, 129.5.

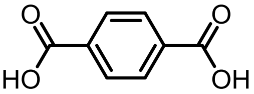
HRMS (m/z – ESI+): Found: 165.0192 (M+H) $C_8H_6O_4$-H Requires: 165.0193

[a] NaOH was dried in vacuum oven at 60 °C for 48 h and allowed to cool down under an nitrogen atmosphere. Mol% of catalyst is related to the number of moles of monomeric units (5.2 mmol) present in 1.0 g of polymer.

Note: Isophthalic acid (<0.75%) is an additive in commercial PET bottles – this could be identified by characteristic ^{1}H NMR resonances; these are not integrated during the determination of yield by ^{1}H NMR spectroscopy:

δ_H (400 MHz, DMSO-d_6): 8.48 (s, 1H), 8.16 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.7 Hz, 1H)

C) TPA isolated from textile fibre waste



An oven-dried round-bottomed flask (25 mL) was charged with water (2 mL), sodium hydroxide (1.00 g), catalyst **10** (19.68 mg, 1 mol %) and polyethylene terephthalate fibre (*ca*. 5 mm squares, 1.00 g).[a] The flask was placed under an N_2 atmosphere (balloon), and the reaction was stirred (1000 RPM) at 135 °C with two stirrer bars for 15 min. The flask was removed from the oil bath and cooled in an ice-bath for 10 min. The reaction mixture was diluted with 20 mL water and stirrer at rt until solid sodium terephthalate was dissolved. The mixture was filtered, and the residue washed with water (10 mL x 2). The filtrate was adjusted, with cooling, to pH 1-2 using dilute HCl and the resulting precipitate was filtered and washed with water (10 mL x 2). The product was dried for 4 h in a vacuum oven at 60 ˚C. The isolated yield was calculated by the general formula (actual yield/theoretical yield) and the NMR yield of terephthalic acid was determined by ^{1}H NMR spectroscopy using 4-iodoanisole as an internal standard: known masses of product (> 15 mg) and 4-iodoanisole (> 15 mg) were weighed into a sample vial and dissolved in DMSO-d_6. The integrals corresponding to TPA were used to determine yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.28 (br s, 2H), 8.04 (s, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.7, 134.5, 129.5.

HRMS (m/z – ESI+): Found: 165.0192 (M+H) $C_8H_6O_4$-H Requires: 165.0193

[a] NaOH was dried in vacuum oven at 60 °C for 48 h and cool down under a nitrogen atmosphere of nitrogen. Mol% of catalyst is related to the number of moles of monomeric units (5.2 mmol) present in 1.0 g of polymer.

4. Calculation of E-Factor, Energy Economy Coefficient, and Environmental Energy Impact Factor

For Entry 16 Table 1 E factor = $\frac{\text{Mass of waste}}{\text{Mass of Product}}$

Mass of waste = [mg of PET Remaining + mg of NaCl + mg of EG + mg of catalyst]

= {0+(1460) + (323) + (19.68)}

Mass of Product TPA = 863 mg

E_{Factor} = 1802.68/863 **= 2.09**

- Molar mass of NaCl = **58.44 g/mol**

So that the mass of NaCl = 24.98 X 58.44 = **1.46 g** = **1460 mg**

- **EG Produced:**

Moles of PET in **1 g** = **5.2 mmol**

Since 1 mol of PET releases 1 mol of EG,
5.2 mmol of PET will produce 5.2 mmol of EG.

So the Mass of EG produced = **5.2 mmol × 62.07 mg/mmol** = **0.323 g (323 mg)**

- **Molar Mass of isolated TPA**

Calculate Mass of TPA at 99.9% Yield

Mass of TPA = 5.2 mmol ×166.13 g × 0.999 = 863 mg

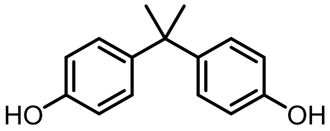
Energy Economy Coefficient (ε) = $\frac{Y}{T \text{ X } t} = \frac{0.99}{138 \text{ X } 4}$ = **0.00179**

Y is the yield of the main monomer in mass fraction; T is the reaction temperature in degrees Celsius; t is the reaction time (in minutes).

$$\xi = \frac{E_{\text{factor}}}{\varepsilon}$$

Environmental Energy Impact Factor ξ = $\frac{\text{E Factor}}{\varepsilon} = \frac{2.09}{0.00179}$ = **1167.6**

5. Polycarbonate hydrolysis and characterisation: *BPA isolated from CDs*



An oven-dried round-bottomed flask (25 mL) was charged with water (3 mL), sodium hydroxide (1.95 g), catalyst **8** (1 mol%) and poly(*bis*-phenol A carbonate) flakes (*ca*. 2.5 mm squares, 1.00 g).[a] The flask was placed under a nitrogen atmosphere (balloon), and the reaction was stirred (1000 RPM) at 135 °C for 30 min. The flask was removed from the oil bath and cooled in an ice-bath for 10 min. The reaction mixture was diluted with 25 mL water and stirred at rt until the solid disodium salt of bisphenol A was dissolved. The mixture was then filtered, and the residue was washed with water (10 mL x 2). The filtrate was adjusted, with cooling, to pH 7 using dilute HCl and the resulting precipitate was filtered and washed with water (5 mL x 2). The product was dried for 4 h in a vacuum oven at 60 ˚C. The isolated yield was calculated by the general formula (actual yield/theoretical yield) and the NMR yield of bisphenol A was determined by ^{1}H NMR spectroscopy using 4-iodoanisole as an internal standard: known masses of product (> 15 mg) and 4-iodoanisole (> 15 mg) were weighed into a sample vial and dissolved in DMSO-*d*$_6$. The integrals corresponding to BPA were used to determine yield.

BPA: ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.11 (s, 2H), 6.97 (d, *J* = 8.5 Hz, 4H), 6.63 (d, *J* = 8.5 Hz, 4H), 1.52 (s, 6H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 154.9, 141.0, 127.2, 114.5, 40.9, 30.9.

HRMS (m/z – ESI+): Found: 227.1072 (M+H) $C_{15}H_{15}O_2^-$ Requires: 227.1078

[a] NaOH was dried in vacuum oven at 60 °C for 48 h and cool down under a nitrogen atmosphere. Mol% of catalyst is related to the number of moles of monomeric units (3.94 mmol) present in 1.0 g of polymer.

6. Mixed recycling (PET+PC) and characterisation:

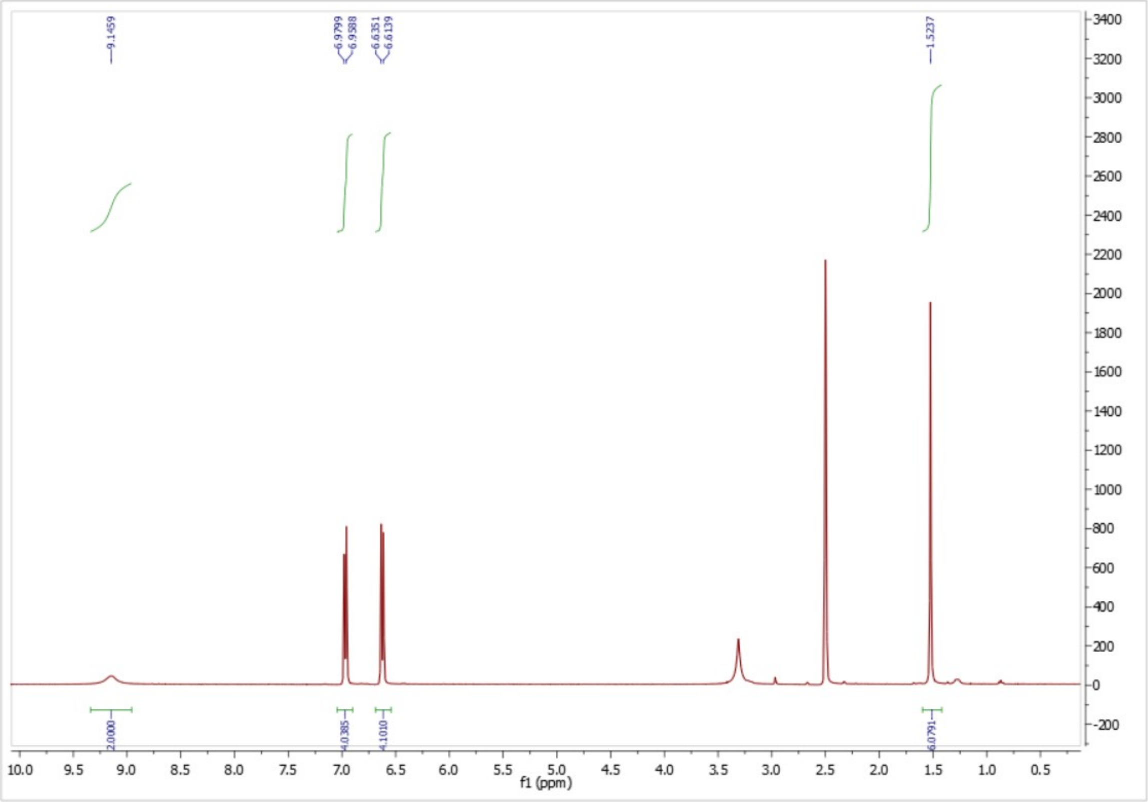
An oven-dried round-bottomed ed flask (25 ml) was charged with water (3 mL), sodium hydroxide (1.95 g), catalyst **8** (13.8 mg, 1 mol %) and polycarbonate flakes (*ca*. 2.5 mm squares, 0.5 g, 1.97 mmol) with polyethylene terephthalate flakes (*ca*. 5 mm squares, 3.5 g, 1.97 mmol).[a] The flask was placed under a nitrogen atmosphere (balloon), and the reaction was stirred (1000 RPM) at 145 °C for 30 min. The flask was removed from the oil bath and cooled in an ice-bath for 10 min. The reaction mixture was diluted with 25 mL water and stirred at rt until the solid disodium salts of BPA and TPA dissolved. The mixture was then filtered, and the residue was washed with water (10 mL x 2). The filtrate was diluted with 50 mL water and adjusted, with cooling, to pH 7.9 using dilute HCl and the resulting precipitate was filtered and washed with water (10 mL x 2) to give solid BPA. Then the remaining filtrate was again acidified with dilute HCl till pH 2 and the resulting precipitate was filtered and washed with water (10 mL x 2) to give solid TPA. Both the product was dried for 4 h in a vacuum oven at 60 ˚C. Both the product was characterized and calculate the isolated yield. The isolated BPA was 100% pure; however, the TPA was 99.9% pure, containing <0.1% BPA as an impurity. To obtain 100% pure TPA it was washed with ethanol.

BPA: ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 2H), 6.97 (d, *J* = 8.5 Hz, 4H), 6.63 (d, *J* = 8.5 Hz, 4H), 1.52 (s, 6H).

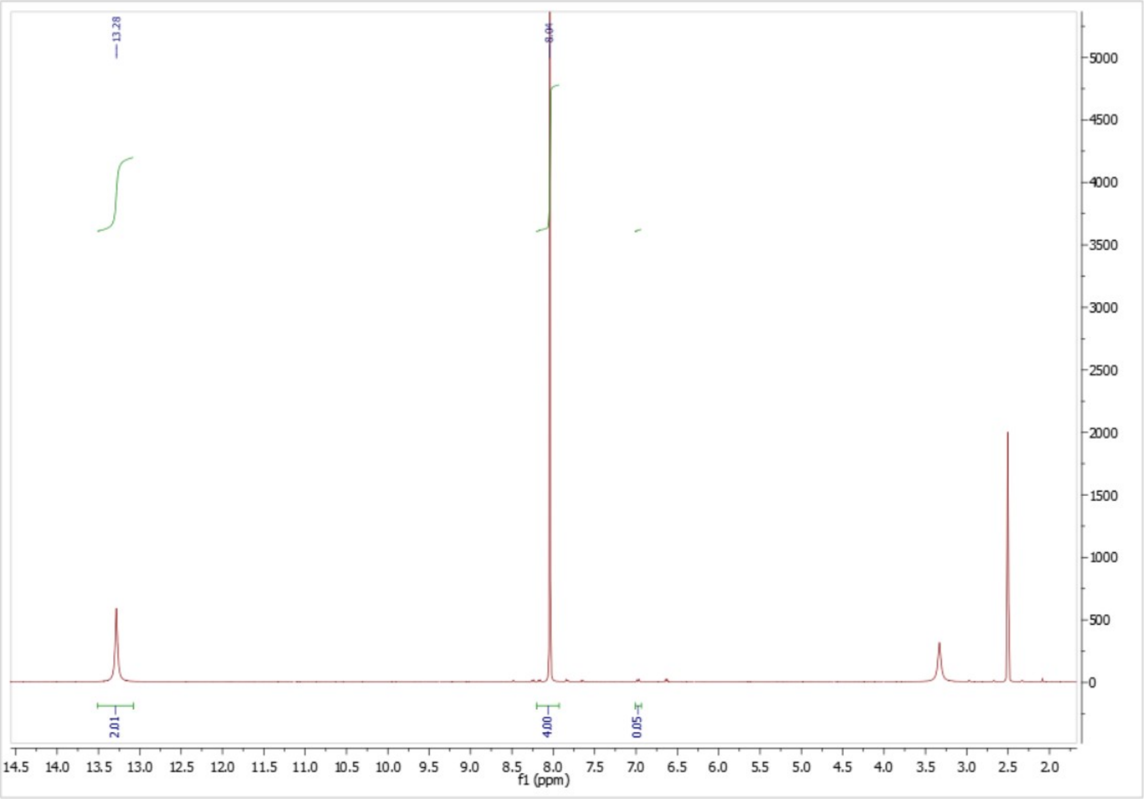
^{13}C NMR (101 MHz, DMSO-d_6) δ 154.9, 141.0, 127.2, 114.5, 40.9, 30.9.

TPA: ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.28 (br s, 2H), 8.04 (s, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 166.7, 134.5, 129.5.



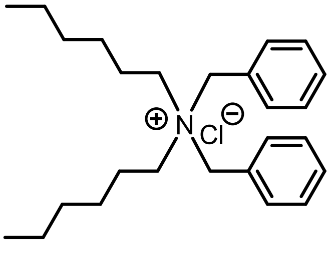
400 MHz ^{1}H NMR spectrum (DMSO-d_6) of isolated BPA (mixed stream)



400 MHz ^{1}H NMR spectrum (DMSO-d_6) of isolated TPA (mixed stream)

7. Catalysis synthesis and characterisation

Catalysts **2**, **3**, **6**, **9** and **11** were prepared following the literature procedure.[16k] Catalyst **8** and **12** were commercially available.

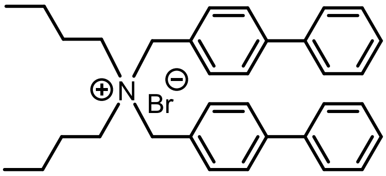


4

$[N\ 6,6,Bn,Bn]^+[Cl]^-$

Catalyst 4: A 25 mL round-bottomed flask equipped with a stirring bar was charged with dihexylamine (1.17 mL, 5 mmol), acetonitrile (5 mL) and potassium carbonate (1.73 g, 12.5 mmol). Benzyl chloride (1.44 mL, 12.5 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 48 h at 50 °C before the mixture was filtered. The solvent was removed under reduced pressure and the product was triturated in diethyl ether. The product was dried *in vacuo* yielding **4** as a white solid (1.79 g, 89%). M.p. 123-125 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 – 7.52 (m, 10H), 4.62 – 4.60 (m, 4H), 3.11 (s, 4H), 1.78 (s, 4H), 1.36 – 1.16 (m, 12H), 0.87 (t, *J* = 6.6 Hz, 6H).
^{13}C NMR (100 MHz, DMSO-d_6) δ 132.9, 130.3, 129.0, 128.1, 62.9, 57.6, 30.6, 25.5, 22.0, 21.8, 13.8.
HRMS (m/z – ESI+): Found: 366.3153 (M^+) $C_{26}H_{40}N$ Requires: 366.3155



5

[N 4,4,BiPh,BiPh]$^+$[Br]$^-$

Catalyst 5: A 25 mL round-bottomed flask equipped with a stirring bar was charged with dibutylamine (0.84 mL, 5.0 mmol), acetonitrile (5 mL) and potassium carbonate (1.73 g, 12.5 mmol). 4-Bromomethylbiphenyl (3.089 g, 12.5 mmol) was added at room temperature. The reaction mixture was stirred for 48 h before the mixture was filtered. The solvent was removed under reduced pressure and the product was triturated in diethyl ether. The product was dried *in vacuo* yielding **5** as a white solid (1.97 g, 94%). M.p. 155-157 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, *J* = 8.2 Hz, 4H), 7.73 (dd, *J* = 18.8, 7.8 Hz, 8H), 7.51 (t, *J* = 7.6 Hz, 4H), 7.42 (t, *J* = 7.3 Hz, 2H), 4.68 (s, 4H), 3.27 – 3.09 (m, 4H), 1.87 (s, 4H), 1.34 – 1.27 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 141.7, 138.9, 133.6, 129.1, 128.1, 127.1, 127.1, 126.8, 62.4, 57.4, 24.0, 19.4, 13.5.
HRMS (m/z – ESI+): Found: 462.3160 (M+) $C_{34}H_{40}N$ Requires: 462.3156

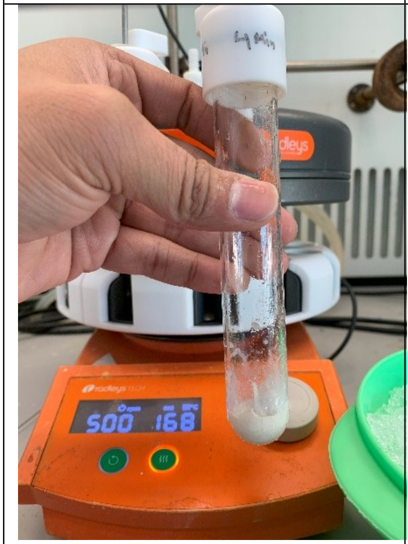
8. Pictures of reaction setup for PET hydrolysis

Depolymerisation of PET in a carousel

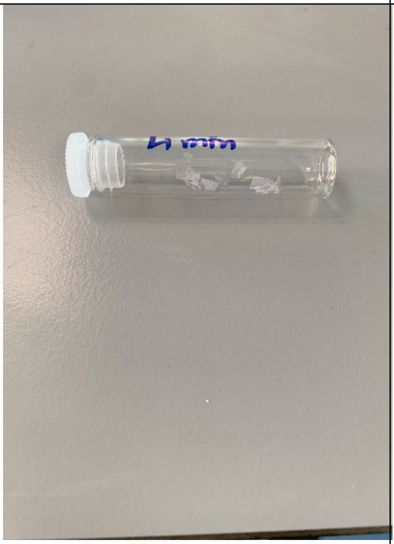
Initial Setup

T= 0 min

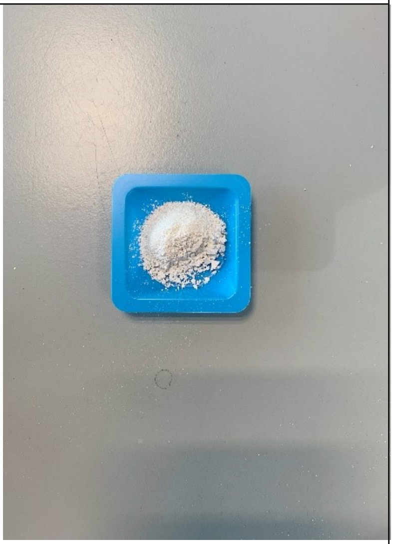
T= 4 min



After Reaction

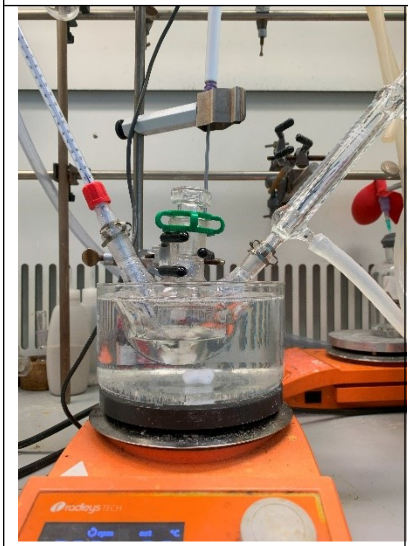
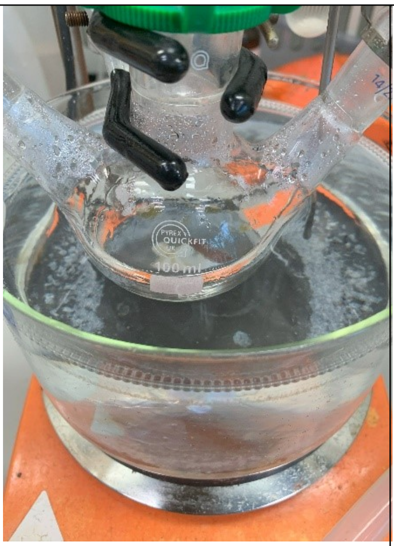
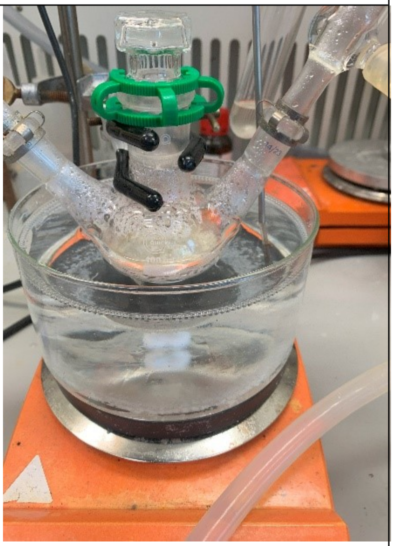
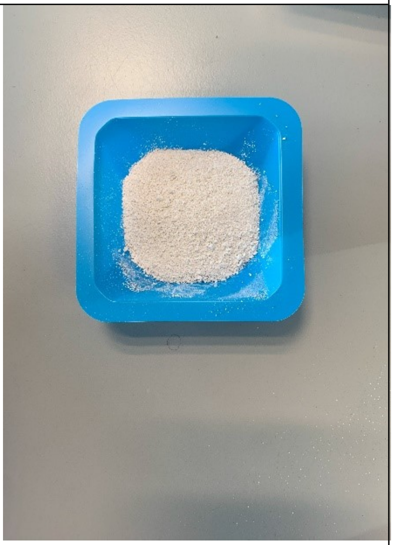


Remaining PET

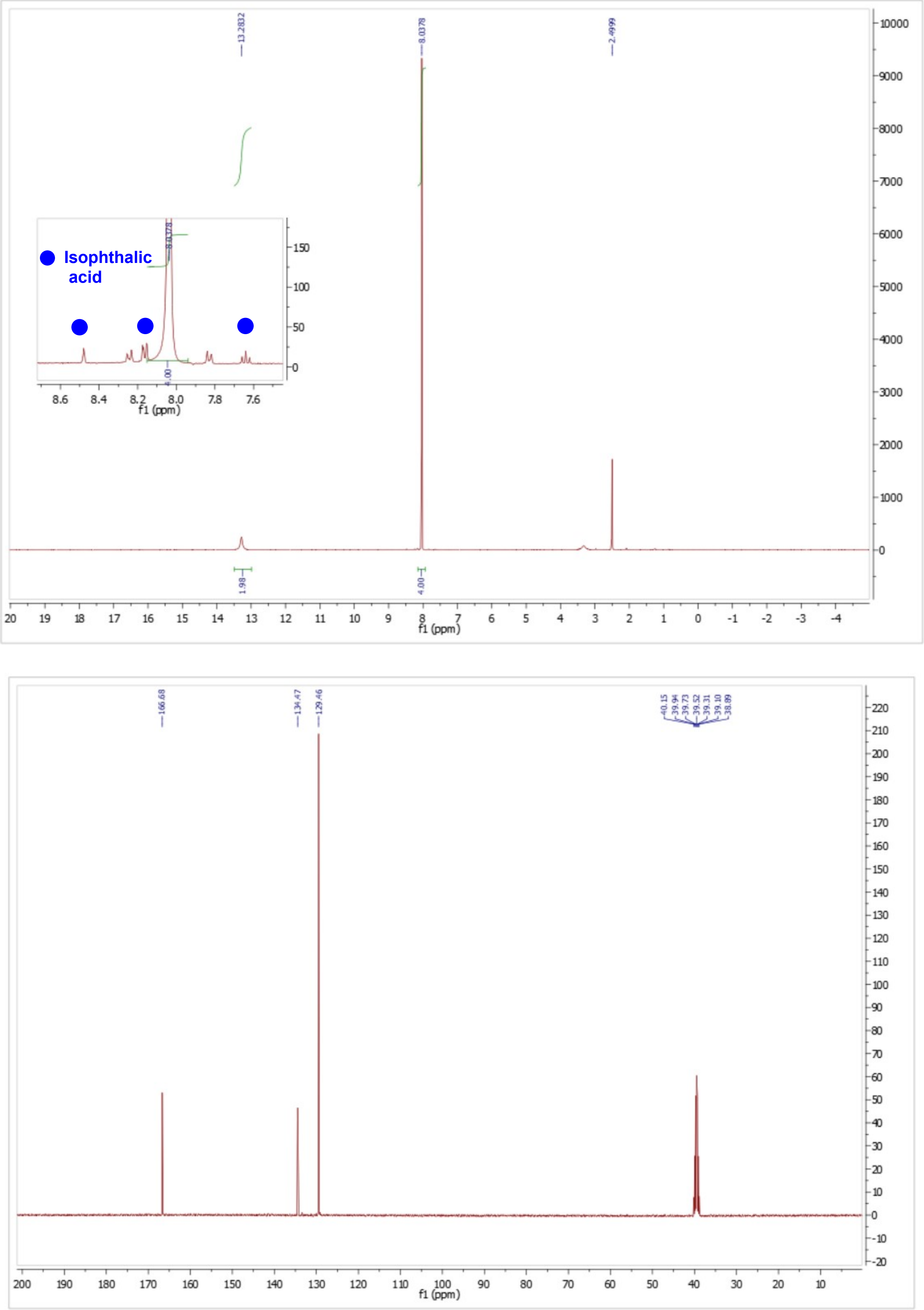


Isolated TPA

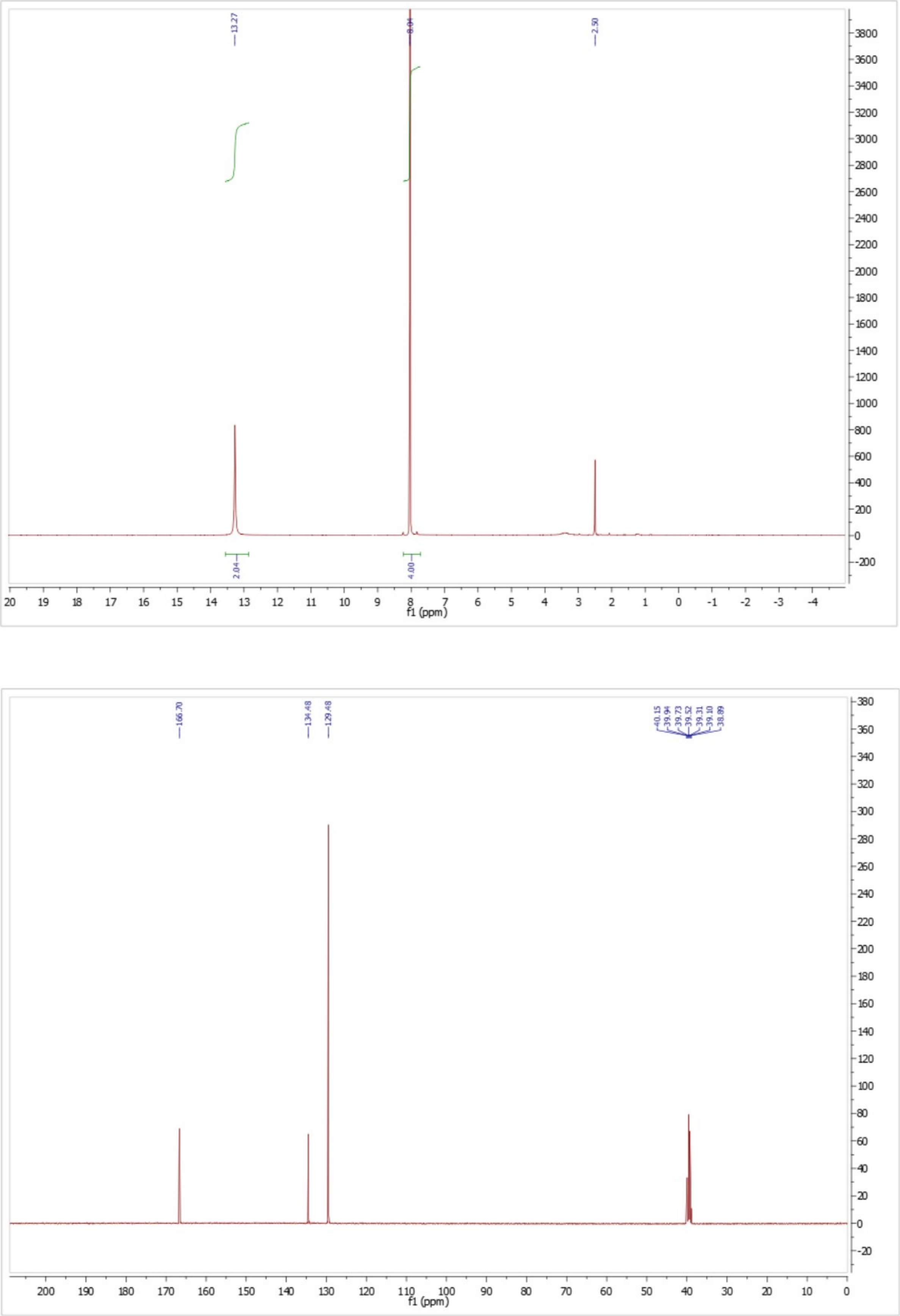
Depolymerisation of PET (10 g) in standard apparatus

		
Initial Setup	Insoluble Cat.	T = 0 min
		
After Reaction	Remaining PET	Isolated TPA

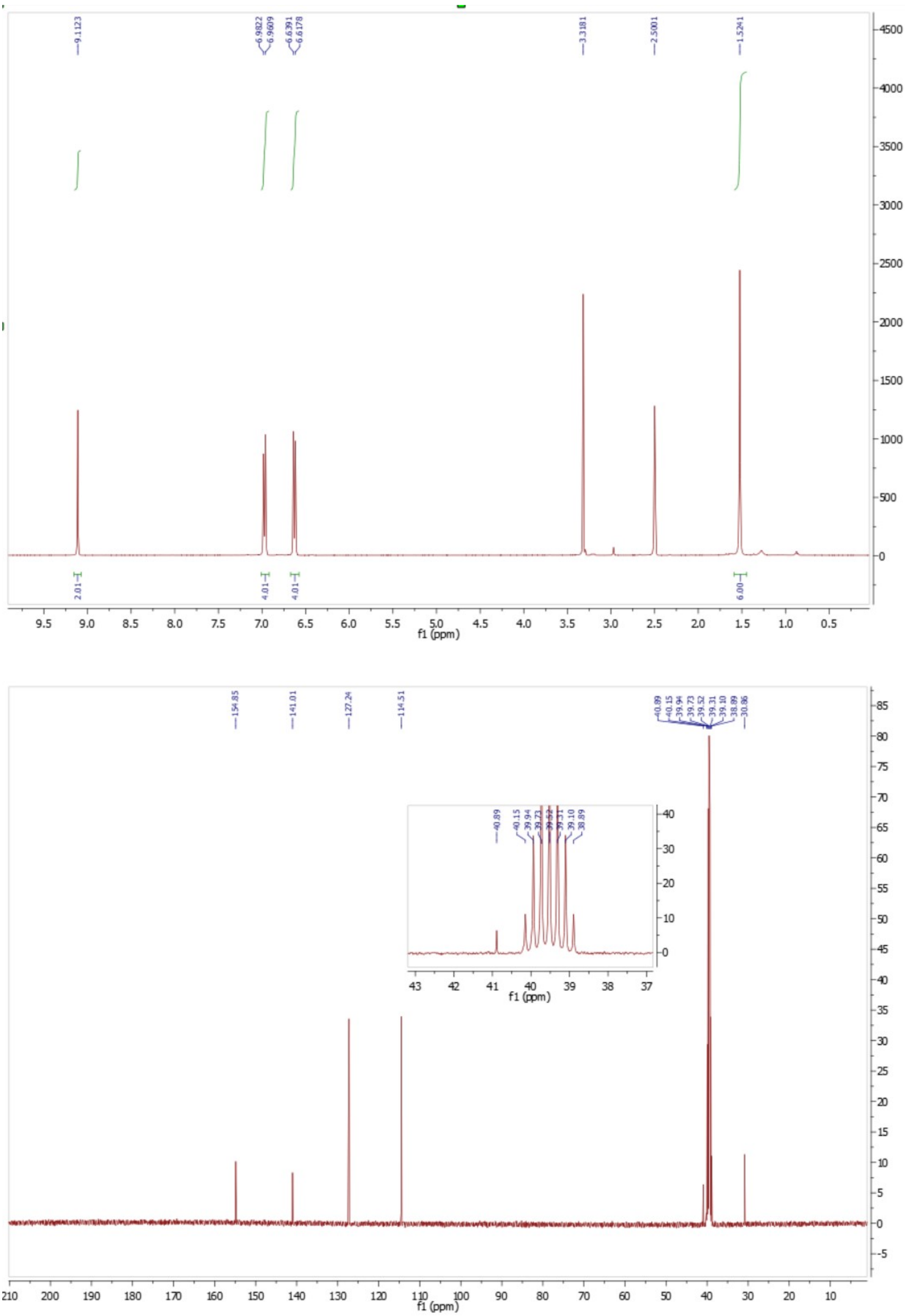
9. NMR spectra of catalysts and products



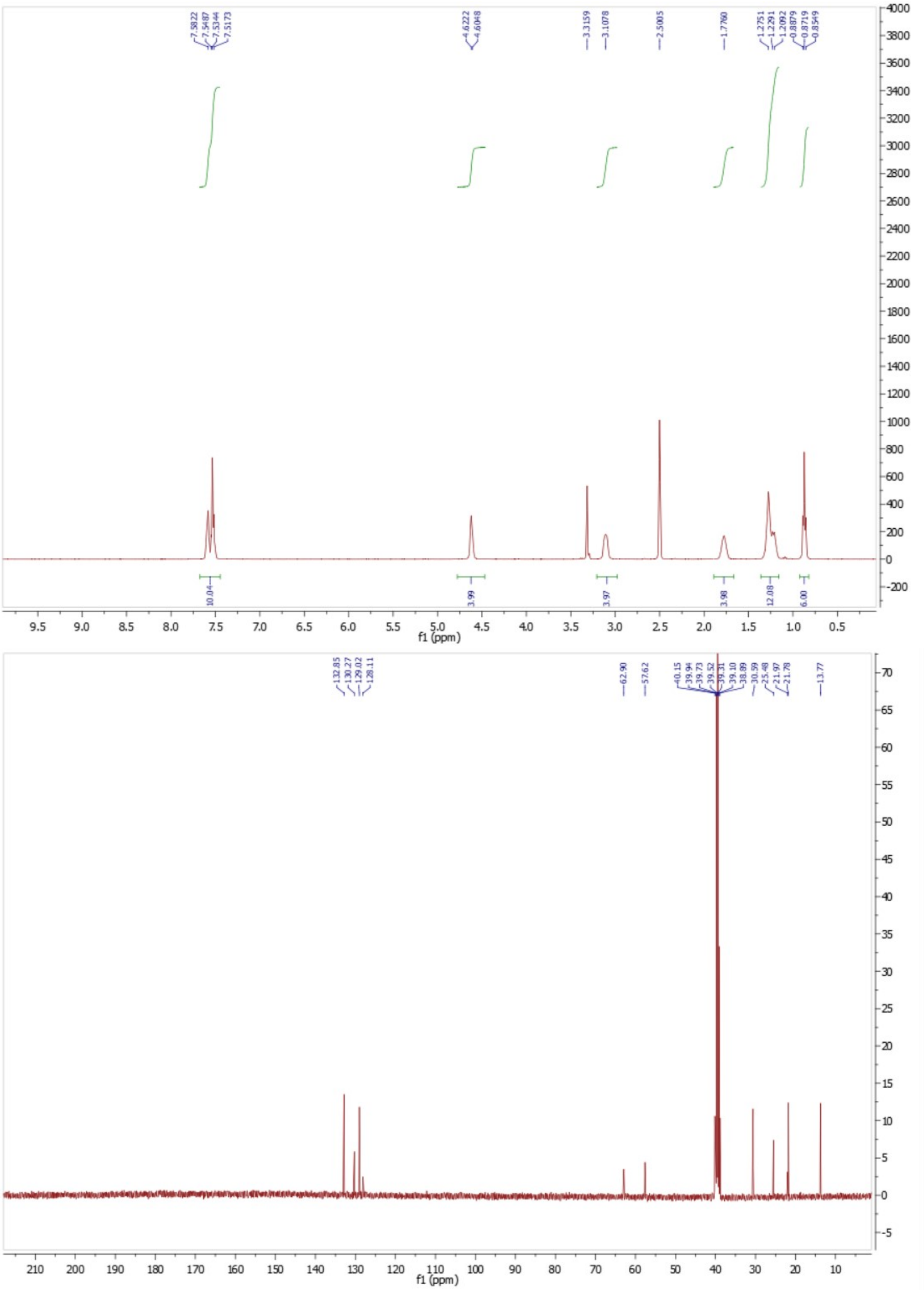
^{1}H NMR and 100 MHz ^{13}C NMR Spectra (DMSO-d_6) of TPA from bottle waste



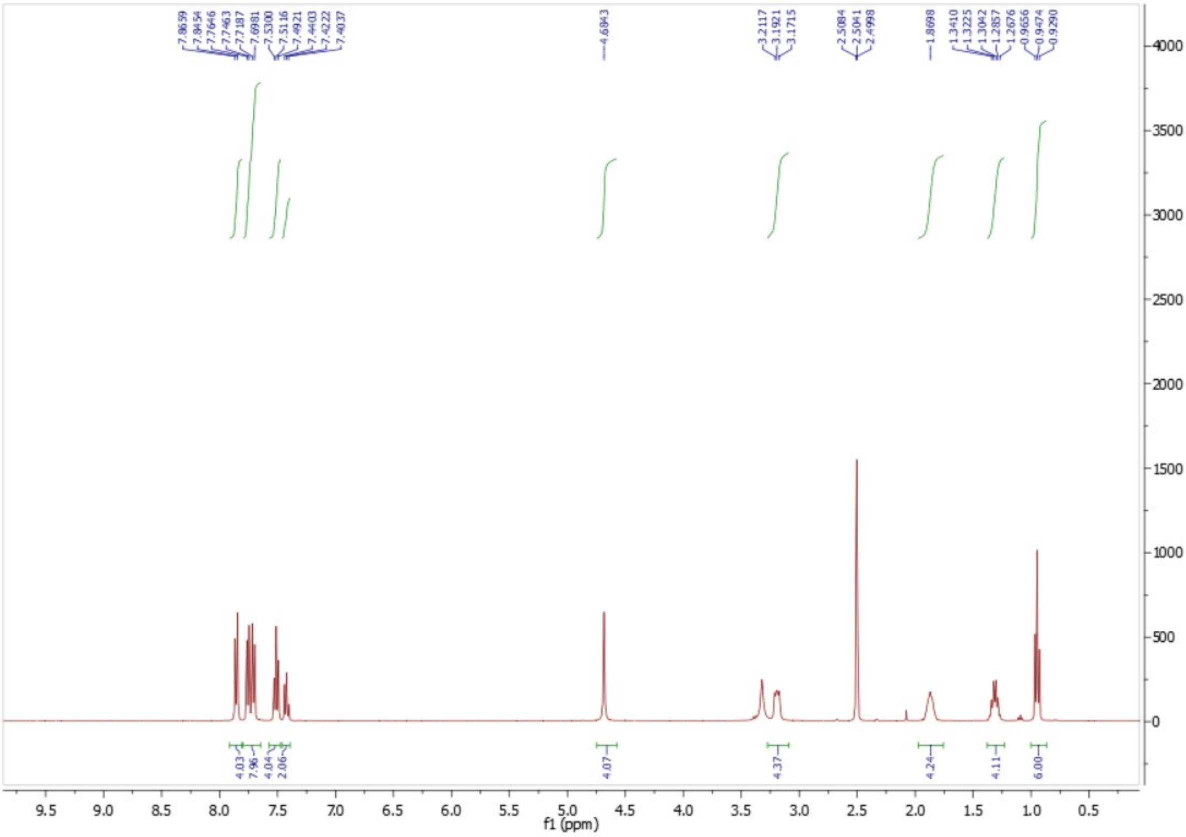
^{1}H NMR and 100 MHz ^{13}C NMR spectra (DMSO-d_6) of TPA from textile waste



^{1}H NMR and 100 MHz ^{13}C NMR spectra (DMSO-d_6) of BPA from CD waste



^{1}H NMR and 100 MHz ^{13}C NMR spectra (DMSO-d_6) of catalyst 4


7.8659
7.8454
7.7646
7.7463
7.7187
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7.5300
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7.4222
7.4037
4.6843
3.2117
3.1921
3.1715
2.5084
2.5041
2.4998
1.8698
1.3410
1.3225
1.3042
1.2857
1.2676
0.9656
0.9474
0.9290
4.03
7.96
4.04
2.06
4.07
4.37
4.24
4.11
6.00
4000
3500
3000
2500
2000
1500
1000
500
0
9.5
9.0
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8.0
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6.5
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5.0
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4.0
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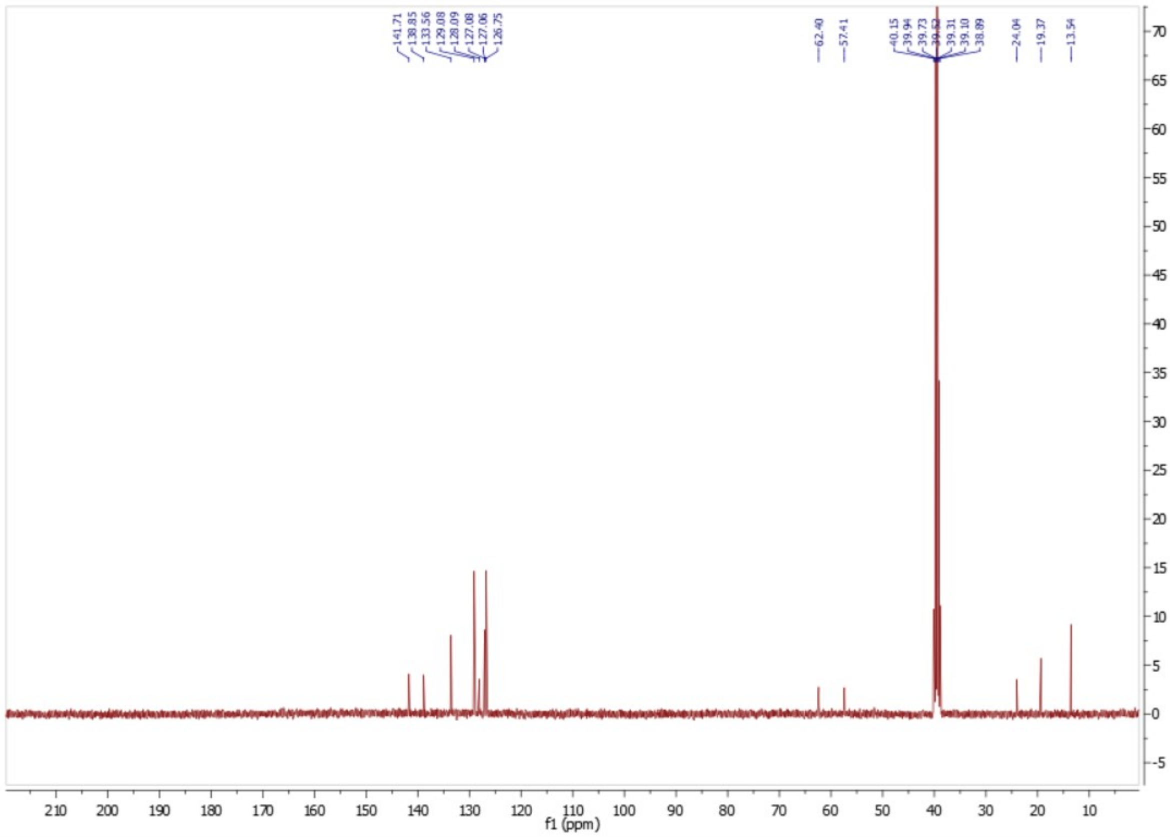
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



^{1}H NMR and 100 MHz ^{13}C NMR spectra (DMSO-*d*$_6$) of catalyst 5