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Photochemical Aerobic Upcycling of Polystyrene Plastics to Commodity Chemicals Using Anthraquinone as the Photocatalyst

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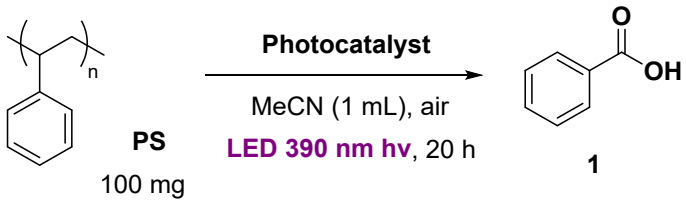
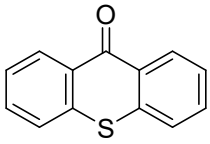
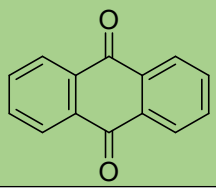
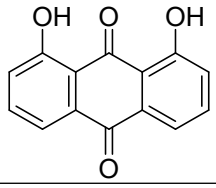
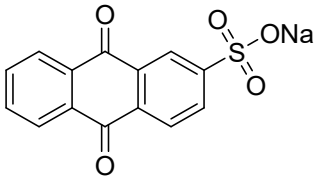
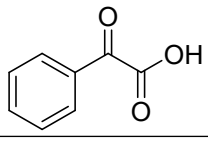
General Remarks

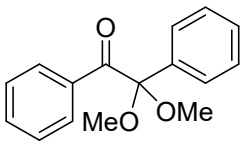
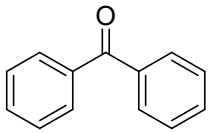
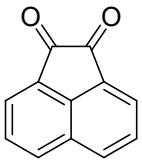
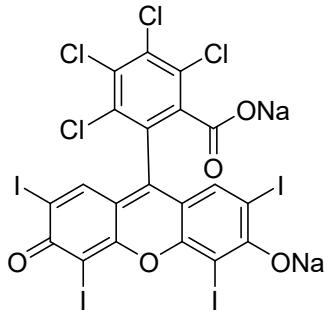
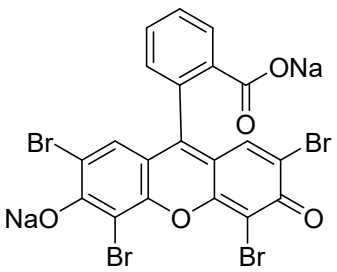
Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatograms was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Brucker Avance-400 (400 MHz and 100 MHz) spectrometer in $CDCl_3$ and are internally referenced to residual solvent signals. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad signal), coupling constant and assignment. Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm). A Varian® Cary 50 UV-Vis spectrophotometer was used as the light source for the quantum yield measurements and the UV-Vis spectra. A Scinco® FS-2 fluorescence spectrometer was used for the fluorescence studies. Kessil lamps PR160L were used as the irradiation source. For all experiments, the intensity of Kessil lamps was controlled in the maximum level with power consumption: 370 nm (max 43W), 390 nm (max 52W), 427 nm & 440 nm (max 45W), 456 nm (max 50W), 467 nm (max 44 W) and 525 nm (max 44W).

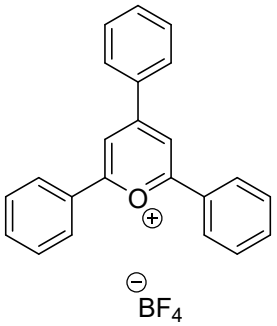
Photochemical Aerobic Upcycling of Polystyrene:

Photocatalyst Study



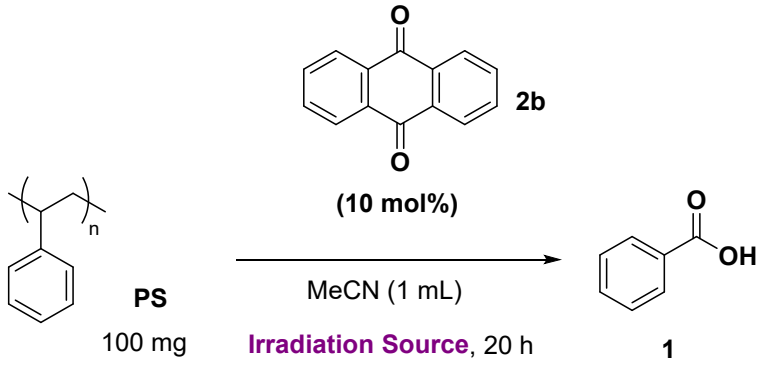
Entry	Photocatalyst	Yield (%)[a]
1	Thioxanthone (10 mol%) (**2a**) 	6.0
2	Anthraquinone (10 mol%) (**2b**) 	18.8
3	1,8-Dihydroxyanthraquinone (10 mol%) (**2c**) 	1.0
4	Sodium anthraquinone-2-sulfonate (10 mol%) (**2d**) 	1.6
5	Phenylglyoxylic acid (10 mol%) (**2e**) 	6.0

6	2,2-Dimethoxy-2-phenylacetophenone (10 mol%) (**2f**) 	6.5
7	Benzophenone (10 mol%) (**2g**) 	4.8
8	Acenaphthenequinone (10 mol%) (**2h**) 	1.5
9	Rose Bengal (2 mol%) (**2i**) 	traces
10	Eosin Y (2 mol%) (**2j**) 	2.6

11	TPP (5 mol%) (**2k**) 	6.0
12	$[Ru(bpy)_3]Cl_2$ (5 mol%) (**2l**)	3.4
13	TBADT (Tetra-*n*-butylammonium decatungstate) (1 mol%) (**2m**)	2.4
14	$CeCl_3$ (20% w/w)-TBACl (20% w/w) (**2n**)	2.1
15	$FeCl_3$ (20% w/w) (**2o**)	4.0
16	TsOH (20% (w/w) (**2p**)	0.4
17	$(NH_4)_2S_2O_8$ (3 equiv.) in H_2O:MeCN (1 mL:1 mL)	0

[a] Yield of isolated product, after base-acid wash and extractions.

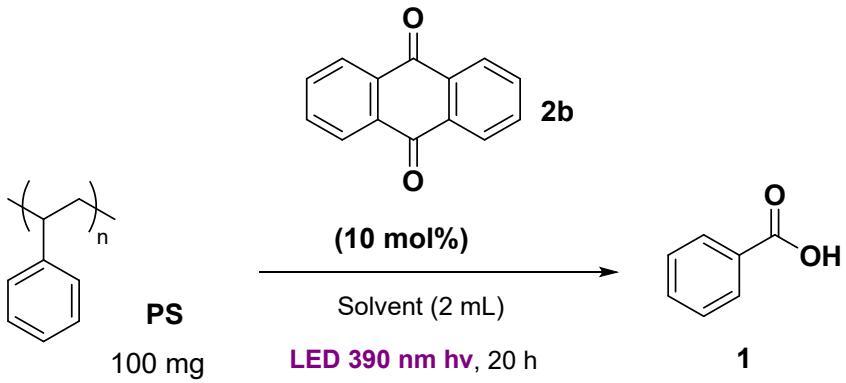
Photochemical Aerobic Upcycling of Polystyrene: Irradiation Source Study



Entry	Irradiation Source	Yield (%)[a]
1	CFL lamps	0.4
2	370 nm	6.2
3	390 nm	18.8
4	427 nm	2.8
5	440 nm	1.4
6	456 nm	0.6
7	467 nm	0.4
8	525 nm	0.3

[a] Yield of isolated product, after base-acid wash and extractions.

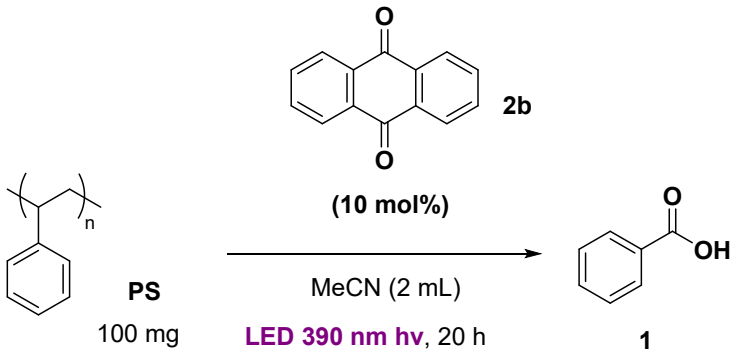
Photochemical Aerobic Upcycling of Polystyrene: Solvent Study



Entry	Solvent	Yield (%)[a]
1	MeCN[b]	18.8
2	MeCN	21.3
3	CH_2Cl_2	6.0
4	$CHCl_3$	traces
5	AcOEt	traces
6	Acetone	4.4
7	Benzene	21.1
8	THF	traces
9	2-Me-THF	traces
10	DMF	n.d.
11	DMSO	n.d.

[a] Yield of isolated product, after base-acid wash and extractions.
[b] 1 mL of MeCN was used.

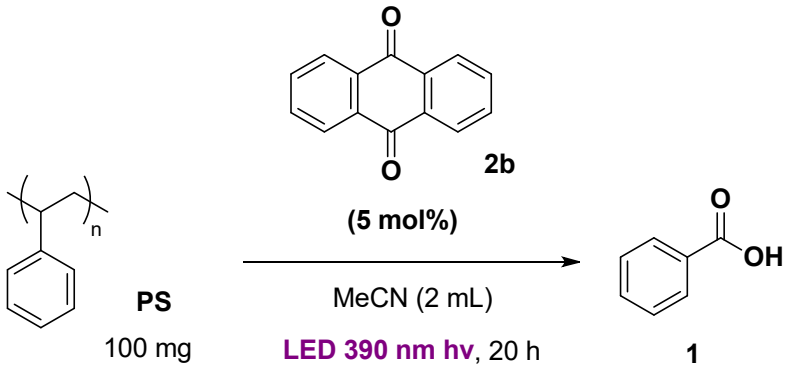
Photochemical Aerobic Upcycling of Polystyrene: Variations from the Optimum Reaction Conditions



Entry	Variation from optimum conditions	Yield (%)[a]
1	none	21.3
2	O_2 atmosphere	17.1
3	48 h reaction time	24.8
4	Anthraquinone (20 mol%)	15.0
5	Anthraquinone (5 mol%)	11.1
6	Anthraquinone (5 mol%), 48 h reaction time	28.2
7	Anthraquinone (5 mol%), 48 h reaction time, O_2 atmosphere	27.6
8	Anthraquinone (5 mol%), 48 h reaction time, MeCN (1 mL), CH_2Cl_2 (1 mL)	28.1

[a] Yield of isolated product, after base-acid wash and extractions.

Photochemical Aerobic Upcycling of Polystyrene: Control Experiments

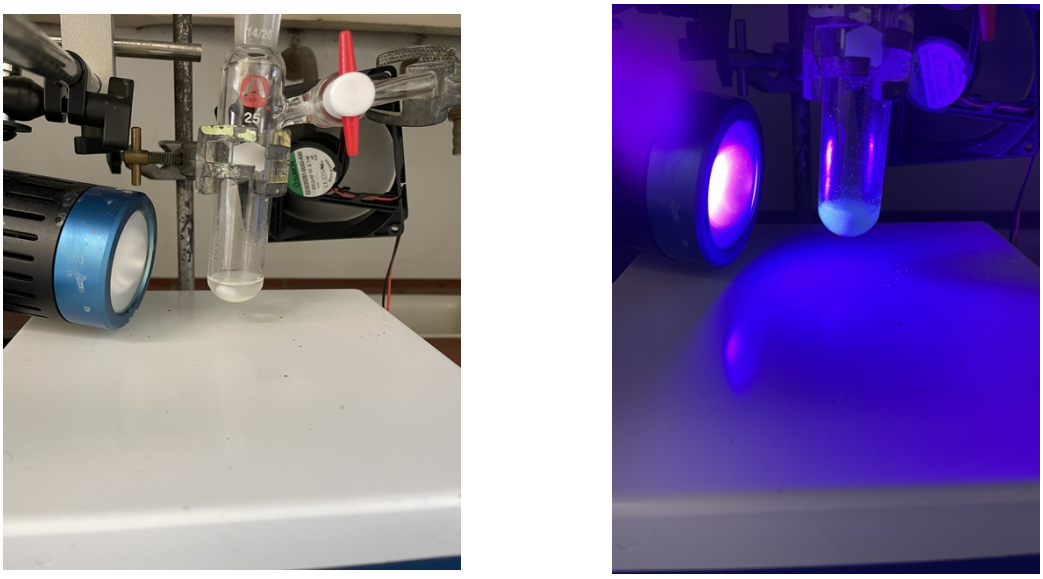


Entry	Quenchers - Control	Yield (%)[a]
1	Under argon	0
2	Reaction on the bench	0
3	Under dark	0
4	No catalyst	0
5	No hv, at 50 °C	0
6	Hydrogen peroxide solution (5 equiv.)	0
7	1,4-Dimethoxybenzene (DMB) (1 mmol)	traces
8	NaN_3 (1 mmol)	traces
9	DABCO (1 mmol)	3.0
10	Extraction and filtration with EtOAc	3.0

[a] Yield of isolated product, after base-acid wash and extractions.

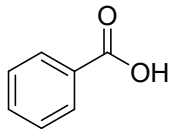
General Procedure for the Photochemical Aerobic Upcycling of Commercially Available Polystyrene

In an open Schlenk flask loaded with polystyrene (100 mg, 0.96 mmol based on the repeated group, CAS Number: 9052-95-3), anthraquinone (10 mg, 0.05 mmol, 5 mol%) and MeCN (2 mL) were added and the reaction mixture was stirred upon irradiation (35W 390 nm Kessil Lamp) for 48 h. Upon reaction completion, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and vacuum filtered to remove the insoluble residues. The filtrate was then concentrated *in vacuo.* Then, CH_2Cl_2 (10 mL) and aq. NaOH 1N (5 mL) were added to flask and stirred for 15 min. The layers were separated in a separatory funnel. The aqueous phase was then acidified with concentrated HCl until pH = 1. Then, the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*, affording the desired benzoic acid.

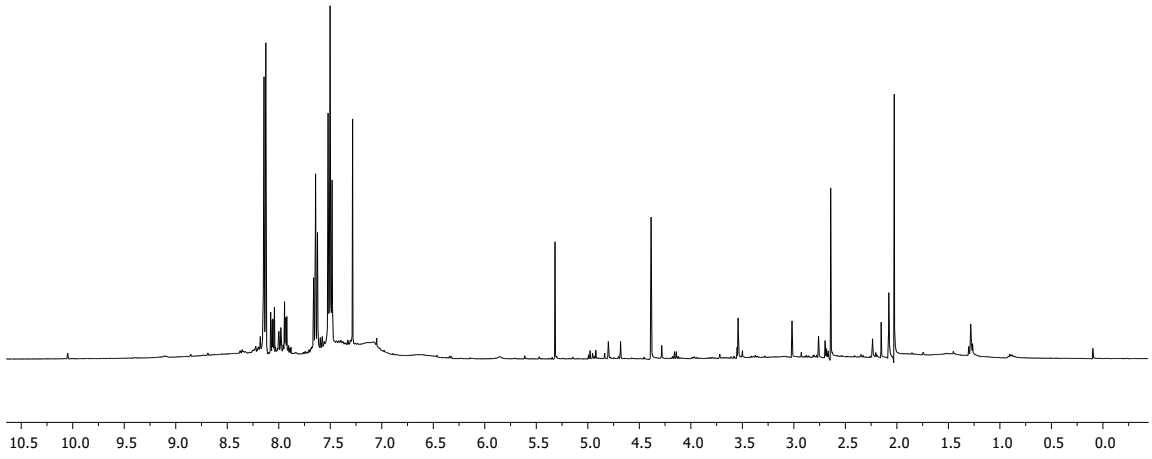


Scheme S1. **A**: Reaction mixture setup. The Schlenk flask is placed 5 cm away from the irradiation source. **B**: End of the reaction, the particles that are dispersed in the solvent are a lot thinner than the starting material, and in most cases, pass through the frit of the Buchner funnel.

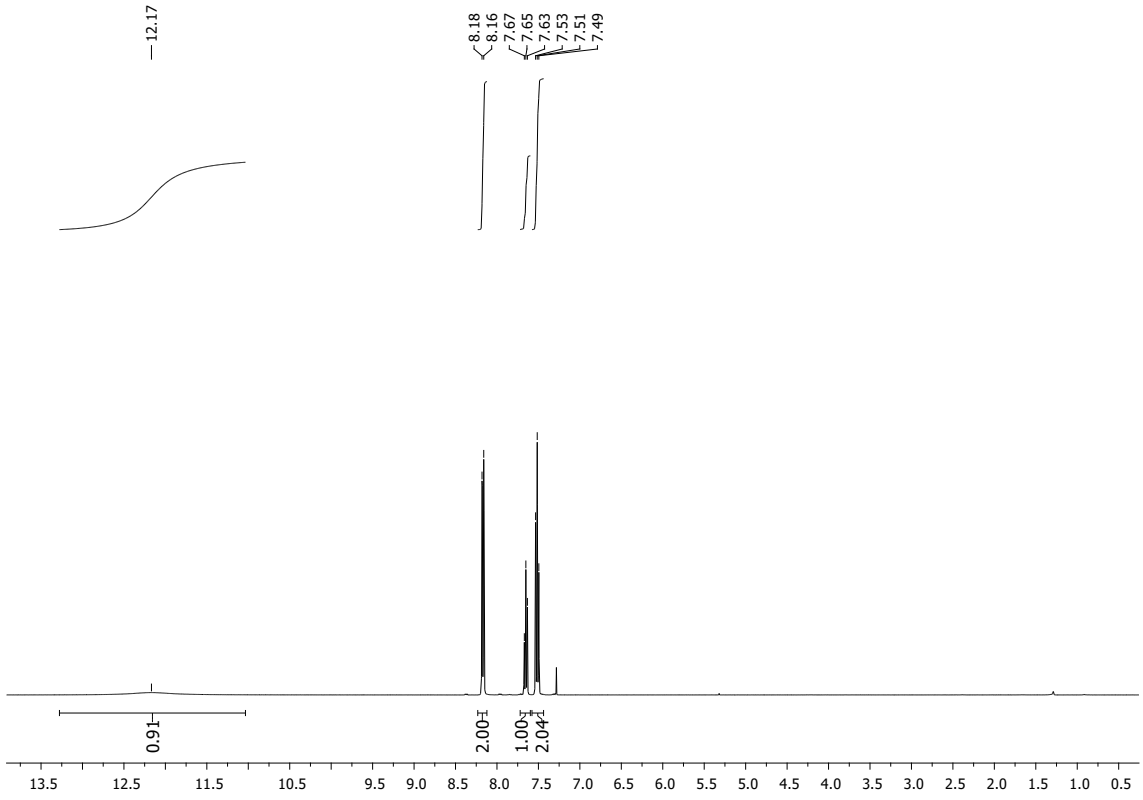
Benzoic acid (1)[1]



White solid; mp: 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 12.15 (1H, br s, COOH), 8.15 (2H, d, J = 7.7 Hz, ArH), 7.63 (1H, t, J = 7.7 Hz, ArH), 7.49 (2H, t, J = 7.7 Hz, ArH); **^{13}C NMR** ($CDCl_3$) δ: 172.5, 133.8, 130.2, 129.3, 128.5; **MS (ESI)** *m/z* 121 $[M-H]^-$.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the crude reaction mixture, upon filtration and solvent evaporation



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the isolated benzoic acid, after acid-base workup

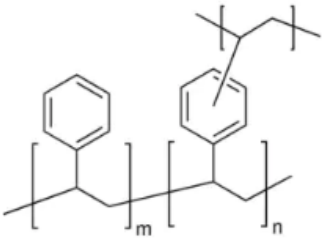
General Procedure for the Photochemical Aerobic Upcycling of Polystyrene Products

In an open Schlenk flask loaded with polystyrene product (100 mg, assumed as before 0.96 mmol), anthraquinone (10 mg, 0.05 mmol, 5 mol%), MeCN (1 mL) and CH_2Cl_2 (1 mL) were added and the reaction mixture was stirred upon irradiation (35W 390 nm Kessil Lamp) for 48 h. Upon reaction completion, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and vacuum filtered to remove the insoluble residues. The filtrate was concentrated *in vacuo.* Then, CH_2Cl_2 (10 mL) and NaOH 1N (5 mL) were added to a flask and stirred for 15 min. The layers were separated in a separatory funnel. The aqueous phase was then acidified with concentrated HCl until pH = 1. Then, the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*, affording the desired benzoic acid (**1**).

Polystyrene Resins

Polystyrene (CAS Number: 9052-95-3)

200-400 mesh



Yield of benzoic acid (28.2%)

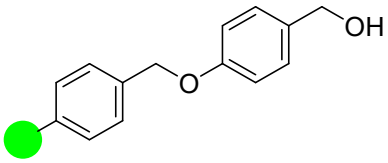
(Aminomethyl)polystyrene Resin (CAS Number: 89551-24-6)

100-200 mesh, HL, substitution: 0.81 mmol/g

Yield of benzoic acid (28.1%)

Wang Resin (CAS Number: 65307-53-1)

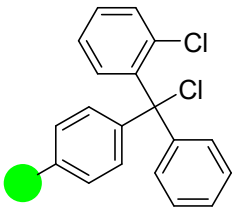
extent of labeling ca. 1.0 mmol/g loading



Yield of benzoic acid (25.6%)

Chlorotrityl Chloride Resin (CAS Number: 42074-68-0)

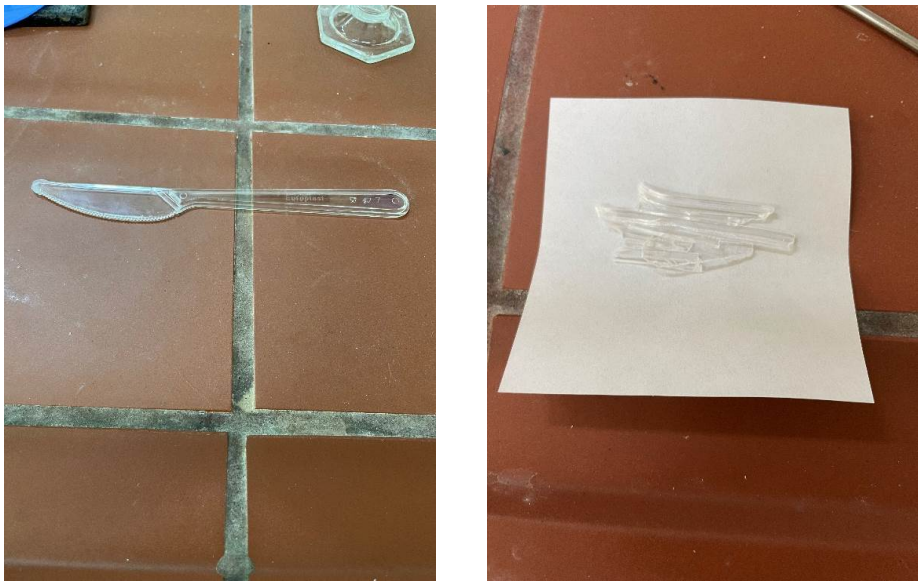
(1.0 mmol/g loading)



Yield of benzoic acid (13.1%)

Plastic Polystyrene Daily Products

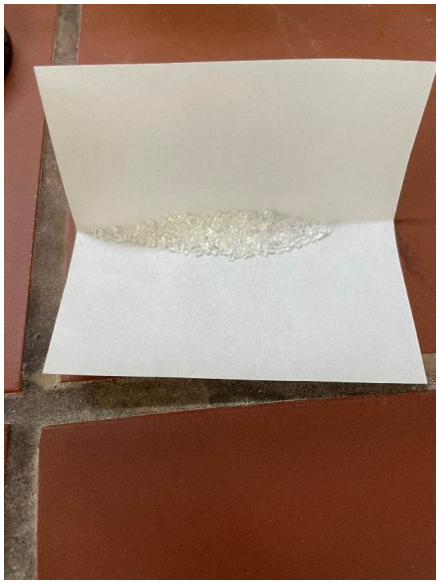
Polystyrene Knife



Polystyrene knife (100 mg)

Yield of benzoic acid (31.5%)

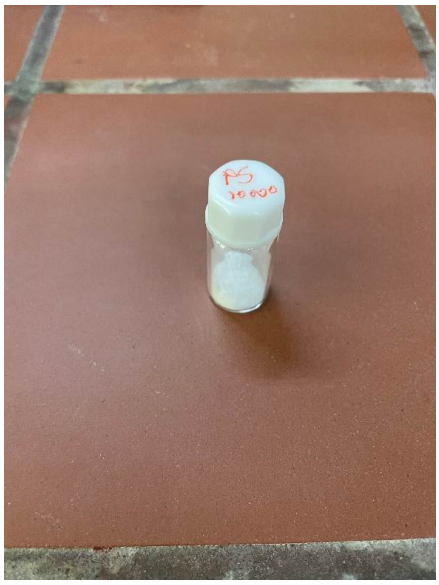
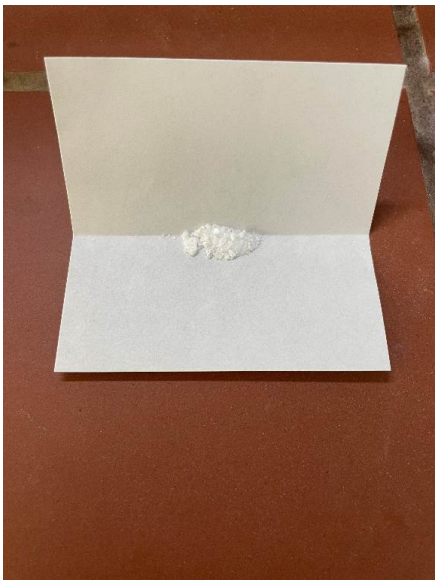
Polystyrene Beads



Polystyrene beads (100 mg)

Yield of benzoic acid (41.8%)

Polystyrene (MW: 10.000)

Polystyrene (MW: 10.000) (100 mg)

Yield of benzoic acid (49.2%)

Polystyrene Plastic Coffee Cup

Polystyrene plastic coffee cup (100 mg)

Yield of benzoic acid (29.6%)

Polystyrene Plastic Cup

Polystyrene plastic cup (100 mg)

Yield of benzoic acid (50.6%)

Yellow Polystyrene Plastic Cup

Yellow Polystyrene plastic cup (100 mg)

Yield of benzoic acid (38.8%)

Polystyrene Plastic Spoon

Polystyrene plastic spoon (100 mg)

Yield of benzoic acid (51.4%)

Polystyrene Foam

Polystyrene foam (100 mg)

Yield of benzoic acid (49.5%)

Polystyrene Foam

Polystyrene foam (100 mg)

Yield of benzoic acid (43.5%)

CD Case

CD Case (100 mg)

Yield of benzoic acid (24.9%)

Polystyrene Microwavable Food Container

Polystyrene microwavable food container (100 mg)

Yield of benzoic acid (31.1%)

Polystyrene Big Cup

Polystyrene big cup (100 mg)

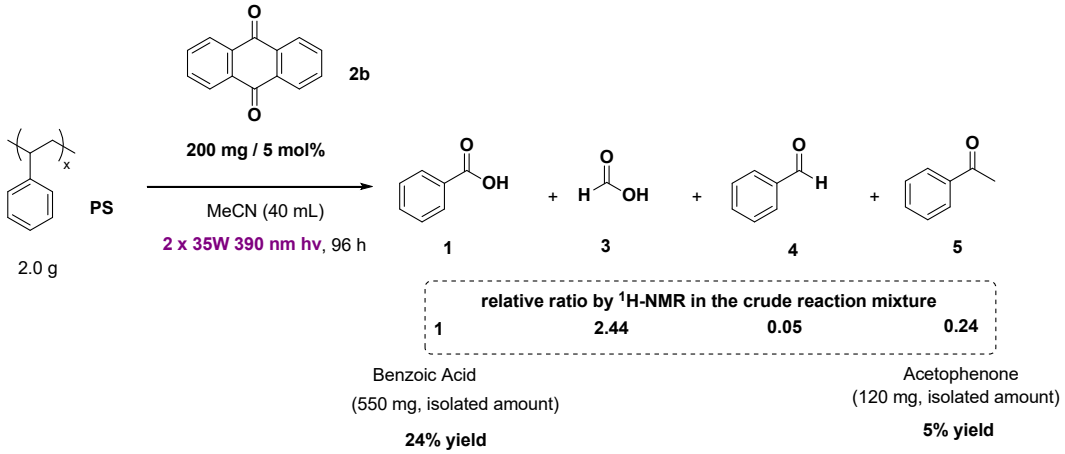
Yield of benzoic acid (26.8%)

Polystyrene Big Transparent Cup

Polystyrene big transparent cup (100 mg)

Yield of benzoic acid (58.8% yield)

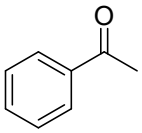
Large Scale Photochemical Aerobic Upcycling of Polystyrene



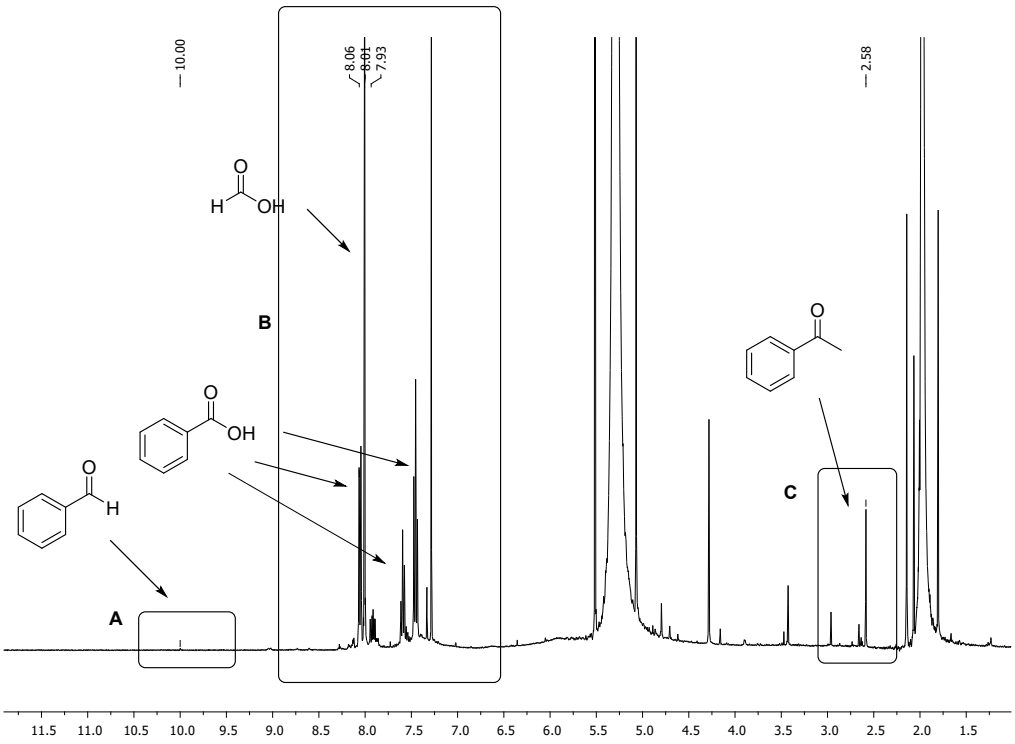
In an open Schlenk flask loaded with polystyrene (2.0 g, 19.20 mmol based on the repeated group), anthraquinone (200 mg, 0.96 mmol, 5 mol%) and MeCN (40 mL) were added and the reaction mixture was stirred upon irradiation of (2 x 35W 390 nm Kessil Lamps) for 96 h. Upon reaction completion, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and vacuum filtered to remove the insoluble residues (100 mg). The filtrate was concentrated *in vacuo.* Then, CH_2Cl_2 (100 mL) and NaOH 1N (100 mL) were added to flask and stirred for 15 min. The aqueous phase was separated in a separatory funnel. The aqueous phase was then acidified with concentrated HCl until pH = 1. After that, the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*, affording the desired benzoic acid (**1**) (550 mg, 4.50 mmol). The first organic layer (CH_2Cl_2) was also concentrated and acetophenone (**5**) (120 mg, 1.00 mmol) was isolated upon column chromatography. Formic acid (**3**) and benzaldehyde (**4**) were also detected in the NMR spectrum of the crude reaction mixture.

Scheme S2. **A**: Reaction setup for the large-scale experiment. **B**: Beginning of the reaction.

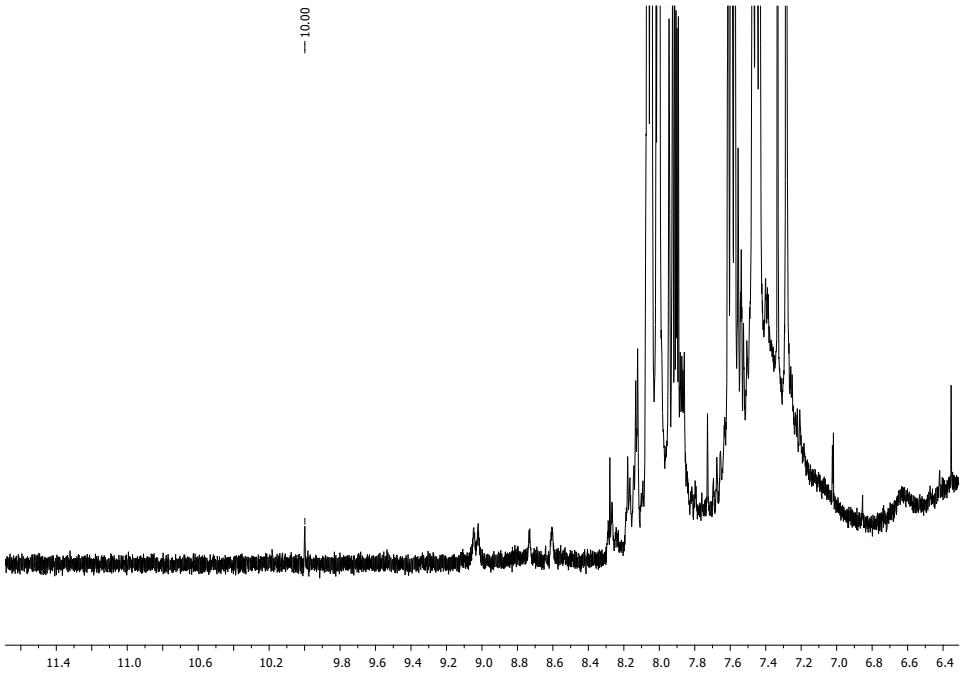
Acetophenone (5)[2]



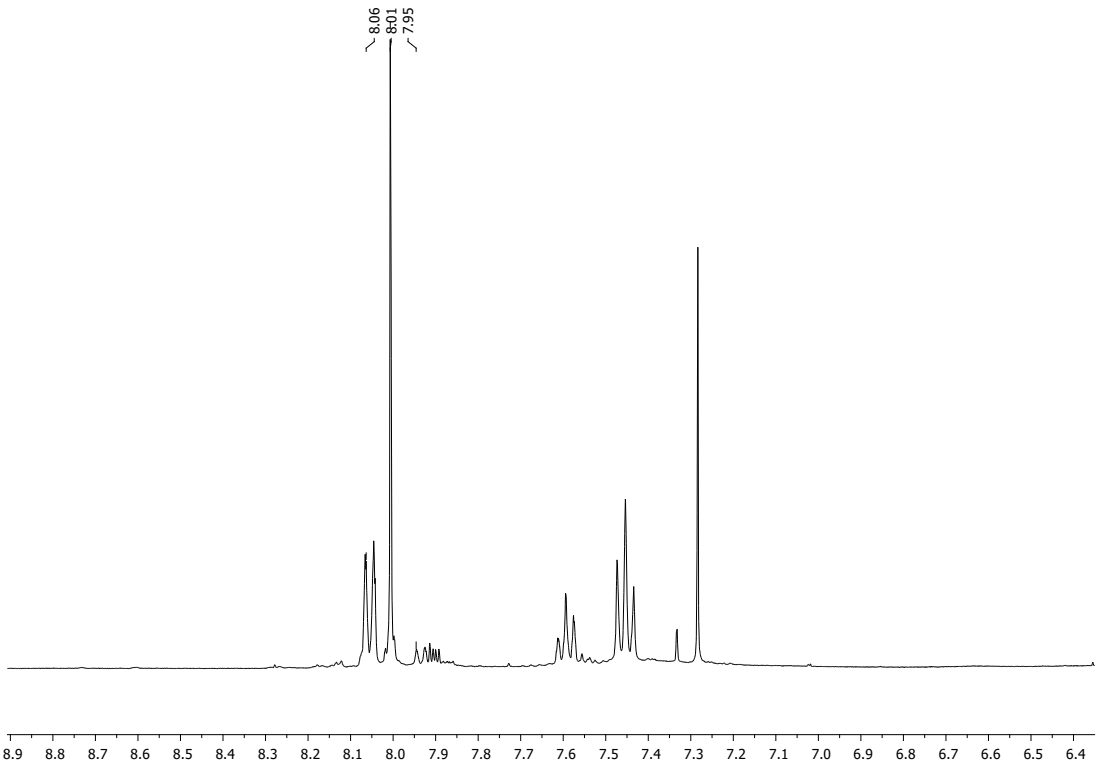
Colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.95 (2H, d, J = 7.5 Hz, ArH), 7.55 (2H, t, J = 7.5 Hz, ArH), 7.45 (2H, t, J = 7.5 Hz, ArH), 2.59 (3H, s, CH_3); **^{13}C NMR** ($CDCl_3$) δ: 198.0, 137.1, 133.0, 128.5, 128.2, 26.5; **MS (ESI)** *m/z* 121 $[M+H]^+$.



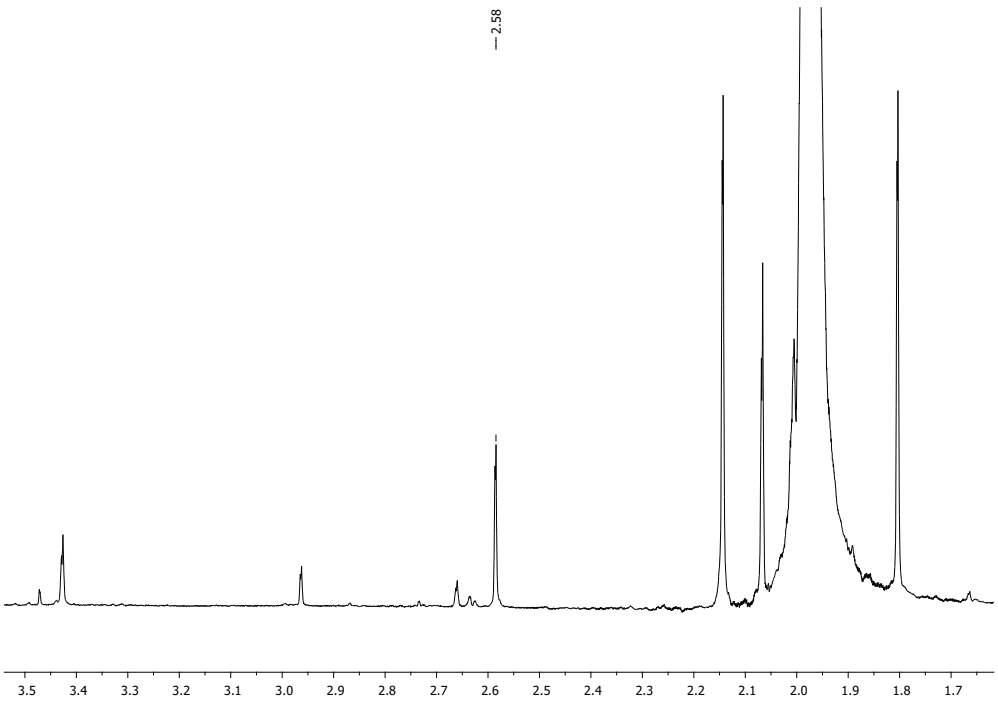
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude reaction mixture from the large-scale reaction: Identifying the presence of benzoic acid (**1**), formic acid (**3**), benzaldehyde (**4**), and acetophenone (**5**) as the major products of the photochemical aerobic upcycling process.



Zoom in ^{1}H NMR (400 MHz, $CDCl_3$) spectrum from 11.50 to 6.40 ppm (Section A) of the large-scale reaction, presenting benzaldehyde (**4**).



Zoom in ^{1}H NMR (400 MHz, $CDCl_3$) spectrum from 8.90 to 6.40 ppm (Section B) of the large-scale reaction, presenting benzoic acid (**1**) and formic acid (**3**).



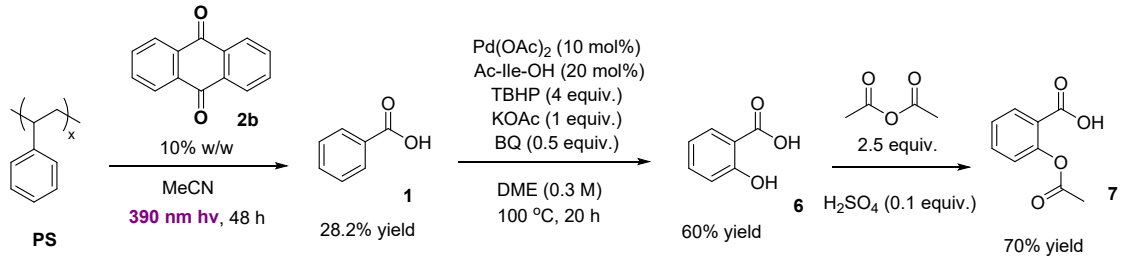
Zoom in ^{1}H NMR (400 MHz, $CDCl_3$) spectrum from 3.50 to 1.70 ppm (Section C) of the large-scale reaction, presenting acetophenone (**5**).

Catalyst Recycling Experiments

Experiments focusing on the recycling of the anthraquinone photocatalyst were conducted. A series of experiments took place, where consecutive additions of PS (100 mg per load) occurred. In an open Schlenk flask loaded with PS (100 mg, assumed as before 0.96 mmol), anthraquinone (10 mg, 0.05 mmol, 5 mol%), MeCN (1 mL) and CH_2Cl_2 (1 mL) were added and the reaction mixture was stirred upon irradiation (35W 390 nm Kessil Lamp) for 48 h. The addition of CH_2Cl_2 as co-solvent facilitates the solubility of the aggregates that are formed during the addition of extra amount of PS. The addition of each load was followed by a 48 h reaction time before the next load was added. Then, a new load of PS (100 mg) was added in the flask and the cycles were repeated. Upon reaction completion, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and vacuum filtered to remove the insoluble residues. The filtrate was concentrated *in vacuo.* Then, CH_2Cl_2 (10 mL) and NaOH 1N (5 mL) were added to a flask and stirred for 15 min. The layers were separated in a separatory funnel. The aqueous phase was then acidified with concentrated HCl until pH = 1. Then, the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*, affording the desired benzoic acid (**1**). The final yield of the benzoic acid was determined through the isolation of the benzoic acid by acid-base workup. The yield of each load was calculated by: amount of total benzoic acid minus amount of previous recycling experiment.

Entry	Number of Loads	Yield of Benzoic acid (%)
1	1	33 mg (28.1)
2	2	29 mg [62 - 33 mg] (24.7)
3	3	26 mg [88 - 62 mg] (22.2)
4	4	24 mg [112 - 88 mg] (20.5)
5	5	22 mg [134 -112 mg] (18.8)

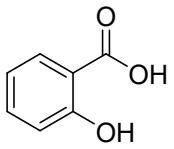
Synthetic Application in the Synthesis of Acetylsalicylic Acid



Benzoic acid (**1**) was produced and isolated following the General Procedure and was directly subjected to *ortho*-hydroxylation and acetylation to yield the desired aspirin **7**.

Hydroxylation procedure: A pressure vessel was loaded with benzoic acid (432 mg, 3.60 mmol), $Pd(OAc)_2$ (80 mg, 0.36 mmol, 10 mol%), Ac-Ile-OH (96 mg, 0.72 mmol, 20 mol%), TBHP (70% w/w in H_2O) (1.84 mL, 14.40 mmol, 4 equiv.), KOAc (348 mg, 3.60 mmol, 1 equiv.), benzoquinone (192 mg, 1.80 mmol, 0.5 equiv.) and 1,2-dimethoxyethane (12 mL) and the reaction mixture was heated at 100 °C for 20 h. The crude reaction mixture was allowed to cool and acidified with HCl 1N (40 mL) and extracted with EtOAc (3 x 30 mL). The organic layers were combined and washed with brine (1 x 90 mL) and dried over Na_2SO_4. The desired product **6** was isolated by column chromatography (60% yield).

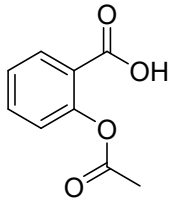
Salicylic acid (6)[3]



White solid; mp: 158-160 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 10.35 (1H, s, OH), 7.94 (1H, d, J = 8.0 Hz, ArH), 7.54 (1H, t, J = 8.0 Hz, ArH), 7.02 (1H, d, J = 8.0 Hz, ArH), 6.95 (1H, t, J = 8.0 Hz, ArH); **^{13}C NMR** ($CDCl_3$) δ: 175.0, 162.2, 137.0, 131.0, 119.6, 117.9, 111.3; **MS (ESI)** *m/z* 137 $[M-H]^-$.

Acetylation reaction: Sallicylic acid (**6**) (276 mg, 2.00 mmol), acetic anhydride (0.5 mL) and sulfuric acid 96% (1 drop) were heated at 70 °C for 30 min. The reaction mixture was cooled at room temperature, water (10 mL) was added and the reaction mixture was further cooled at 0 °C. The desired acetylsalicylic acid precipitated. The reaction mixture was vacuum filtered and the crystals of the product were washed with cold water. Acetylsalicylic acid was isolated without the need for further purification (70% yield).

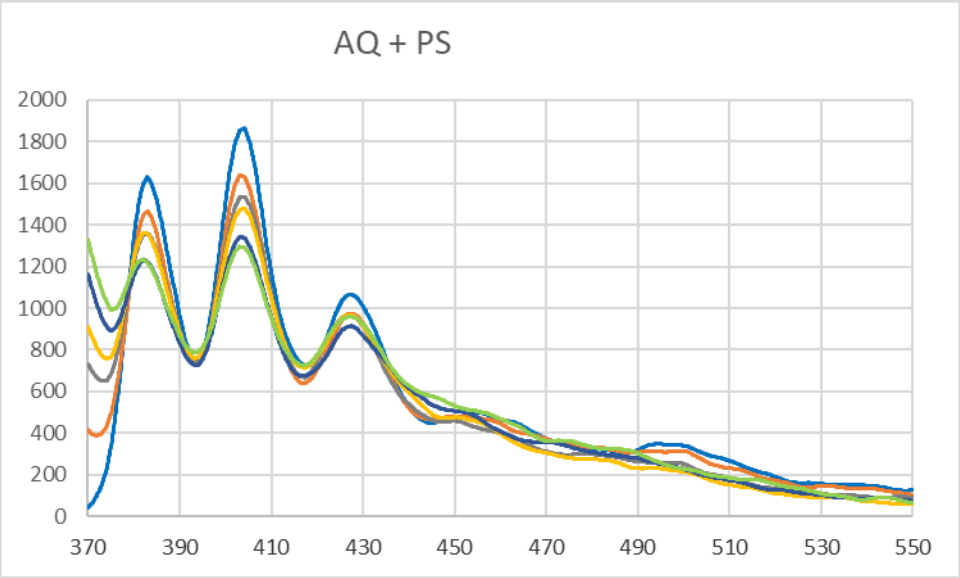
Acetyl salicylic acid (7)[4]

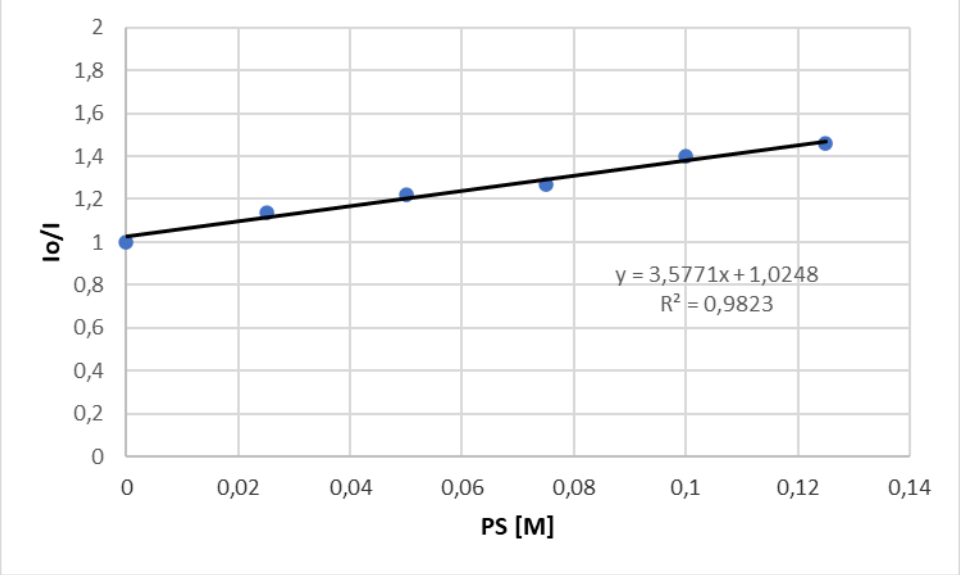


White solid; mp: 138-140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 10.56 (1H, br s, COOH), 8.12 (1H, d, J = 7.1 Hz, ArH), 7.62 (1H, t, J = 7.1 Hz, ArH), 7.35 (1H, t, J = 7.1 Hz, ArH), 7.14 (1H, d, J = 7.1 Hz, ArH), 2.35 (3H, s, CH_3); **^{13}C NMR** ($CDCl_3$) δ: 170.1, 169.7, 151.3, 134.9, 132.5, 126.1, 124.0, 122.2, 21.0; **MS (ESI)** *m/z* 179 $[M-H]^-$.

Fluorescence Quenching Studies

After irradiation of anthraquinone (**2b**) (1 mM in MeCN) at 358 nm, its fluorescence was measured at 404 nm. Increasing the added amount of polystyrene, a decrease in the fluorescence intensity was observed. The corresponding Stern-Volmer plot is presented below.





Determination of the Quantum Yield

Determination of the photon flux

A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure[5] outlined in the *Handbook of Photochemistry*.[6] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to the concentration and wavelength.

The solutions were prepared and stored under dark:

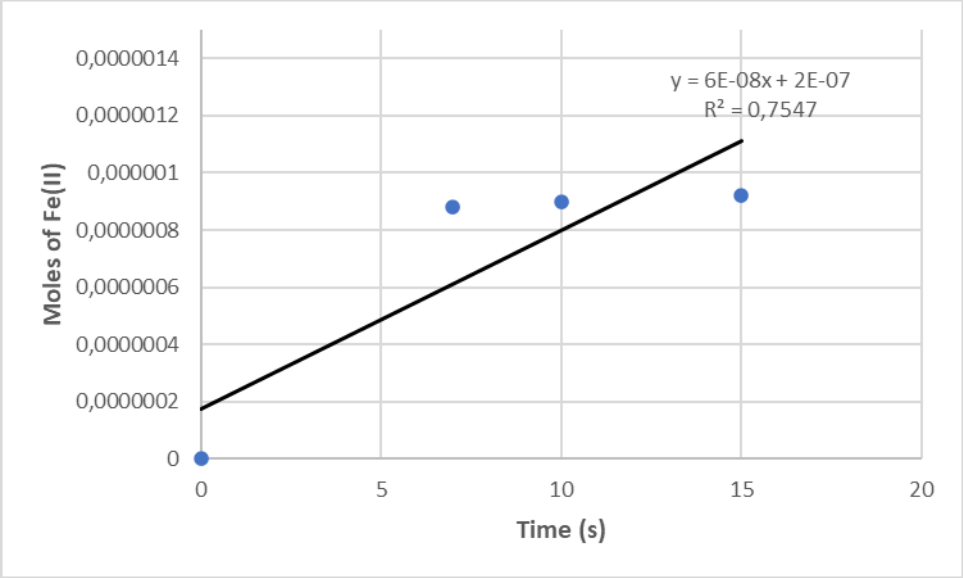
1. **Potassium ferrioxalate solution 0.012M**: 147.4 mg of potassium ferrioxalate and 69.5 μL of sulfuric acid (96%) were added to a 25 mL volumetric flask and filled to the mark with water (HPLC grade).
2. **Phenanthroline solution**: 0.2% by weight of 1,10-phenanthroline in water (100 mg in 50 mL volumetric flask or 50 mg in 25 mL).
3. **Buffer solution**: to a 100 mL volumetric flask 4.94 g of NaOAc and 1.0 mL of sulfuric acid (96%) were added and filled to the mark with water (HPLC grade).

A cuvette was loaded with 1.0 mL of potassium ferrioxalate solution and placed under Kessil 390 nm lamp irradiation. Three different actinometer solutions were irradiated in sequence for 5 s, 10 s and 15 s, respectively. After each irradiation, the actinometer solutions were carefully transferred into a 10 mL volumetric flask, then 0.5 mL of phenanthroline solution and 2.0 mL of buffer solution were added and the flask was filled up with water. The absorbance of the final solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The moles of Fe^{2+} formed for each sample are determined using Beers' Law (Eq. 1):

$$\text{Moles of Fe (II)} = \frac{V_1 \times V_3 \times \Delta A\ (510\ nm)}{10^3 \times V_2 \times l \times \varepsilon\ (510\ nm)} \qquad \text{(Eq. 1)}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), ΔA (510 nm) is the optical difference in absorbance between the irradiated solution and the one stored in the dark, ε (510 nm) is the extinction coefficient the complex $Fe(phen)_3^{2+}$ at 510 nm (11100 L mol^{-1} cm^1). The moles of Fe^{2+} formed (x) are plotted as a function of time (t).



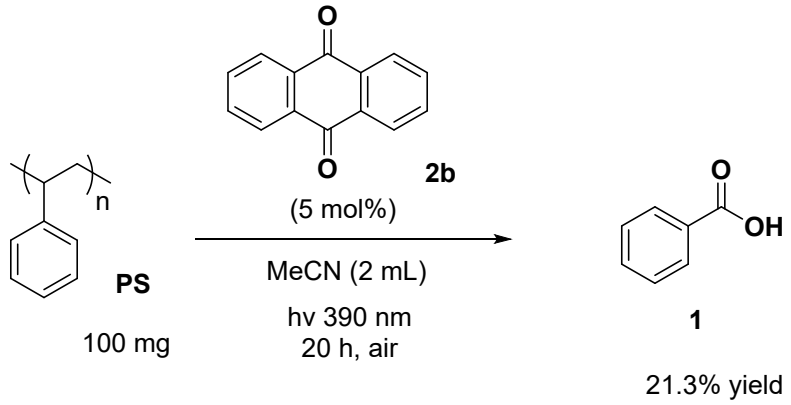
The slope of this line was correlated to the moles of incident photons by unit of time ($q^0_{n,p}$) by the use of the following Equation 2:

$$\Phi(\lambda) = \frac{dx/dt}{q^0_{n,p} \times [1 - 10^{-A(\lambda)}]} \qquad \text{(Eq. 2)}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), the quantum yield (Φ) for Fe^{2+} at 390 nm is 1.21,[7] $[1\text{-}10^{-A(\lambda)}]$ is the ratio of absorbed photons by the solution, and A(λ) is the absorbance of the actinometer at the wavelength used to carry out the experiments (390 nm). The absorbance at 390 nm (A(390)) was 0.5218.

The photon flux, which is $q^0_{n,p}$, was determined to 7.09 x 10^{-8} einstein s^{-1}.

Determination of the quantum yield for the photochemical aerobic oxidation of polystyrene to benzoic acid:



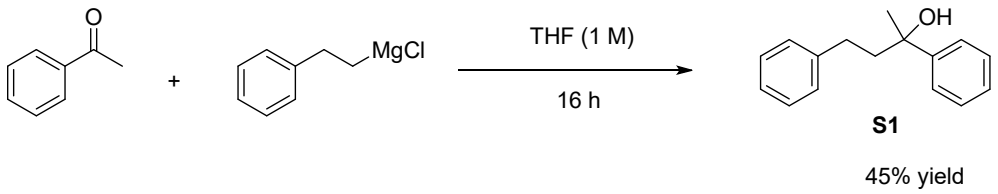
A Schlenk flask loaded with PS (100 mg, 0.96 mmol), anthraquinone (10 mg, 0.05 mmol, 5 mol%) and MeCN (2 mL). The reaction mixture was stirred and irradiated using Kessil lamp 390 nm for 72000 s (20 h). After irradiation, the yield of the product was determined by acid-base extractions (21.3% yield). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{2 \times 10^{-4}\,\text{mol}}{7.09 \times 10^{-8}\,\text{einstein}\,s^{-1} \times 72000\,s \times 0.5218} = 0.08$$

Mechanistic Investigation Using Model Reaction

Model Substrate Synthesis

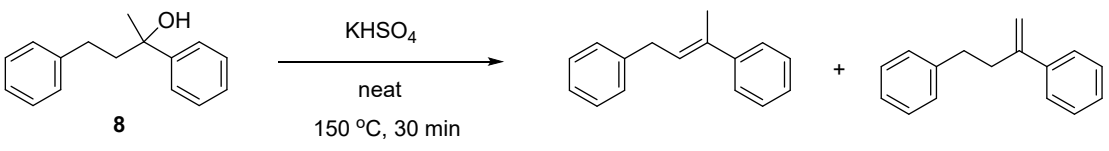
2,4-Diphenylbutan-2-ol (S1)[8]



To a round bottomed flask charged with acetophenone (1.44 g, 12.00 mmol, 1.2 equiv.) dissolved in dry THF (10 mL), phenethylmagnesium chloride solution (10.00 mmol, 10 mL, 1M in THF) was added dropwise. The reaction mixture was stirred at r.t. for 16 h. Upon reaction completion, the mixture was quenched by NH_4Cl saturated aqueous solution (5 mL) and the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The organic phase was evaporated *in vacuo*. The desired product **S1** was isolated by column chromatography (45% yield).

Colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.52 (2H, d, J = 7.5 Hz, ArH), 7.41 (2H, t, J = 7.5 Hz, ArH), 7.34-7.24 (3H, m, ArH), 7.23-7.12 (3H, m, ArH), 2.72-2.61 (1H, m, PhCH*H*), 2.54-2.41 (1H, m, PhCH*H*), 2.24-2.09 (2H, m, CH_2), 1.81 (1H, br s, OH), 1.65 (3H, s, CH_3); **^{13}C NMR** ($CDCl_3$) δ: 147.5, 142.2, 128.4, 128.3, 128.2, 126.6, 125.7, 124.7, 74.7, 45.9, 30.5, 30.4; **MS (ESI)** *m/z* 227 $[M+H]^+$.

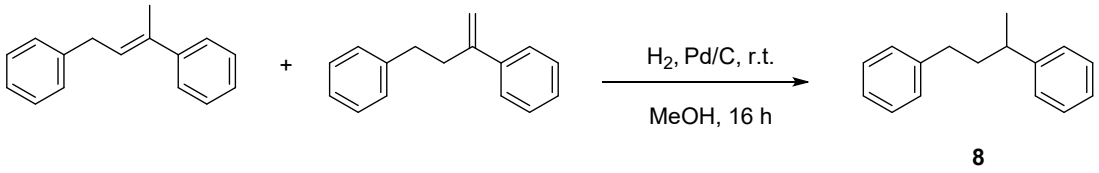
(*E*)-But-2-ene-1,3-diyldibenzene and But-3-ene-1,3-diyldibenzene (S2)



S1 (452 mg, 2.00 mmol) was added to a round bottom flask, charged with $KHSO_4$ (490 mg, 3.60 mmol, 1.8 equiv.) and heated neat at 150 °C for 30 min. Upon reaction completion, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and filtered

through celite. The filtrate was evaporated *in vacuo* and the crude product mixture was utilized directly without further purification to the next step (50% yield).

Butane-1,3-diyldibenzene (8)[9]

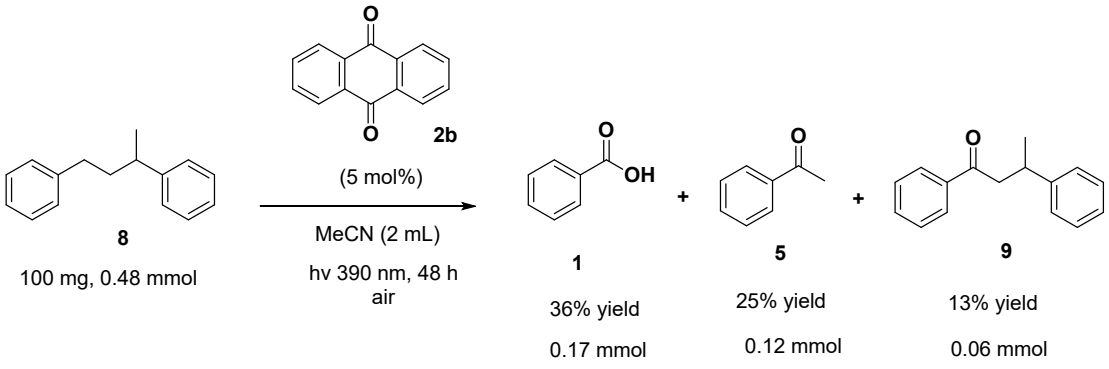


99% yield

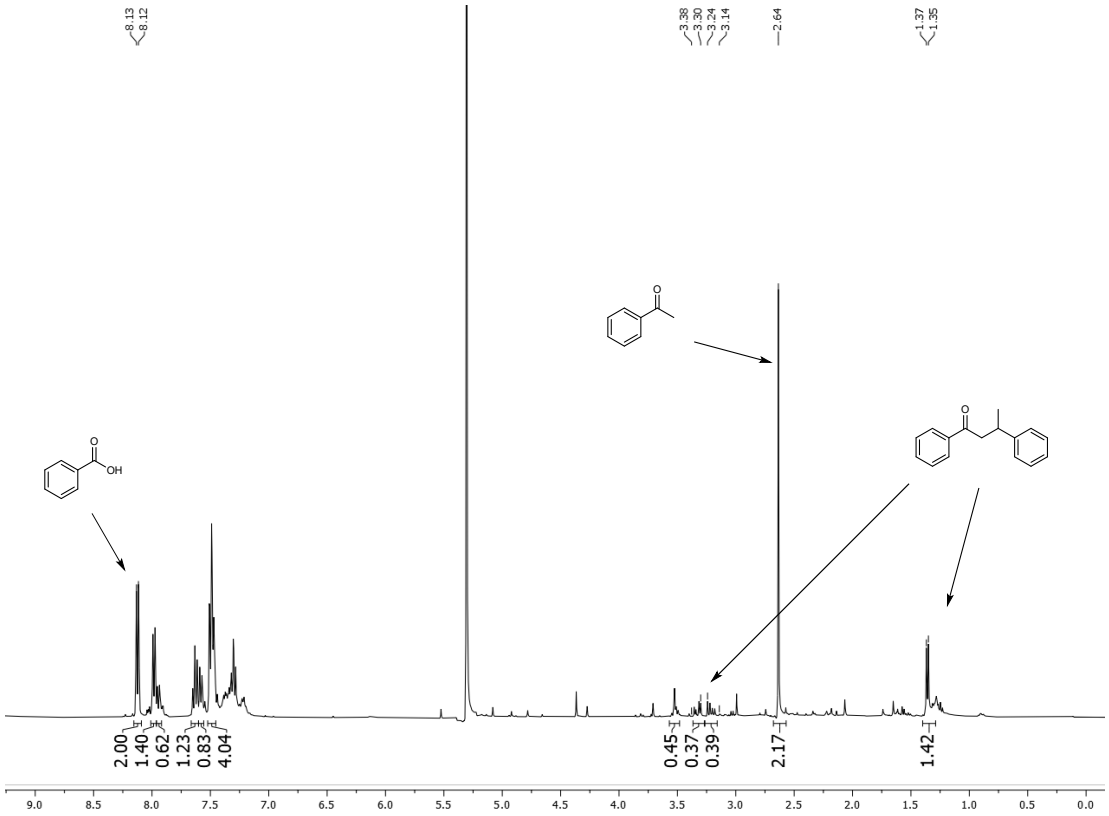
To a round bottomed flask charged with mixture of products **S2** (208 mg, 1.00 mmol) methanol (10 mL) was added and catalytic amount of Pd/C (10% w/w, 30 mg). The reaction mixture was stirred at r.t. for 16 h under a hydrogen atmosphere. Upon reaction completion, the reaction mixture was diluted with methanol (20 mL) and filtered through celite. The solvent was removed *in vacuo* and the desired product **8** was isolated by column chromatography (99% yield). Colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.56-7.23 (10H, m, ArH), 2.95-2.82 (1H, m, PhCH), 2.75-2.62 (2H, m, $PhCH_2$), 2.19-2.01 (2H, m, CH_2), 1.47-1.45 (3H, d, J = 7.0 Hz, CH_3); **^{13}C NMR** ($CDCl_3$) δ: 147.2, 142.5, 128.4, 128.3, 128.2, 127.0, 125.9, 125.6, 39.9, 39.5, 33.9, 22.5; **MS (ESI)** *m/z* 211 $[M+H]^+$.

Mechanistic Investigation Using Model Reaction

In order to shed light in the oxidation pathway that is followed in this anthraquinone-promoted protocol, we utilized the developed protocol for the oxidation of 1,3-diphenylbutane (**8**), which behaves as a model substrate for the oxidation of polystyrene as it mimics its repeated unit.[1,10] The reaction was performed according to the general photochemical aerobic upcycling protocol. In an open Schlenk flask loaded with 1,3-diphenylbutane (**8**) (100 mg, 0.48 mmol), anthraquinone (**2b**) (5 mg, 0.024 mmol, 5 mol%) and MeCN (2 mL) were added and the reaction mixture was irradiated for 48 h. The reaction mixture was then concentrated in *vacuo* and the yield of the products was determined by ^{1}H-NMR.

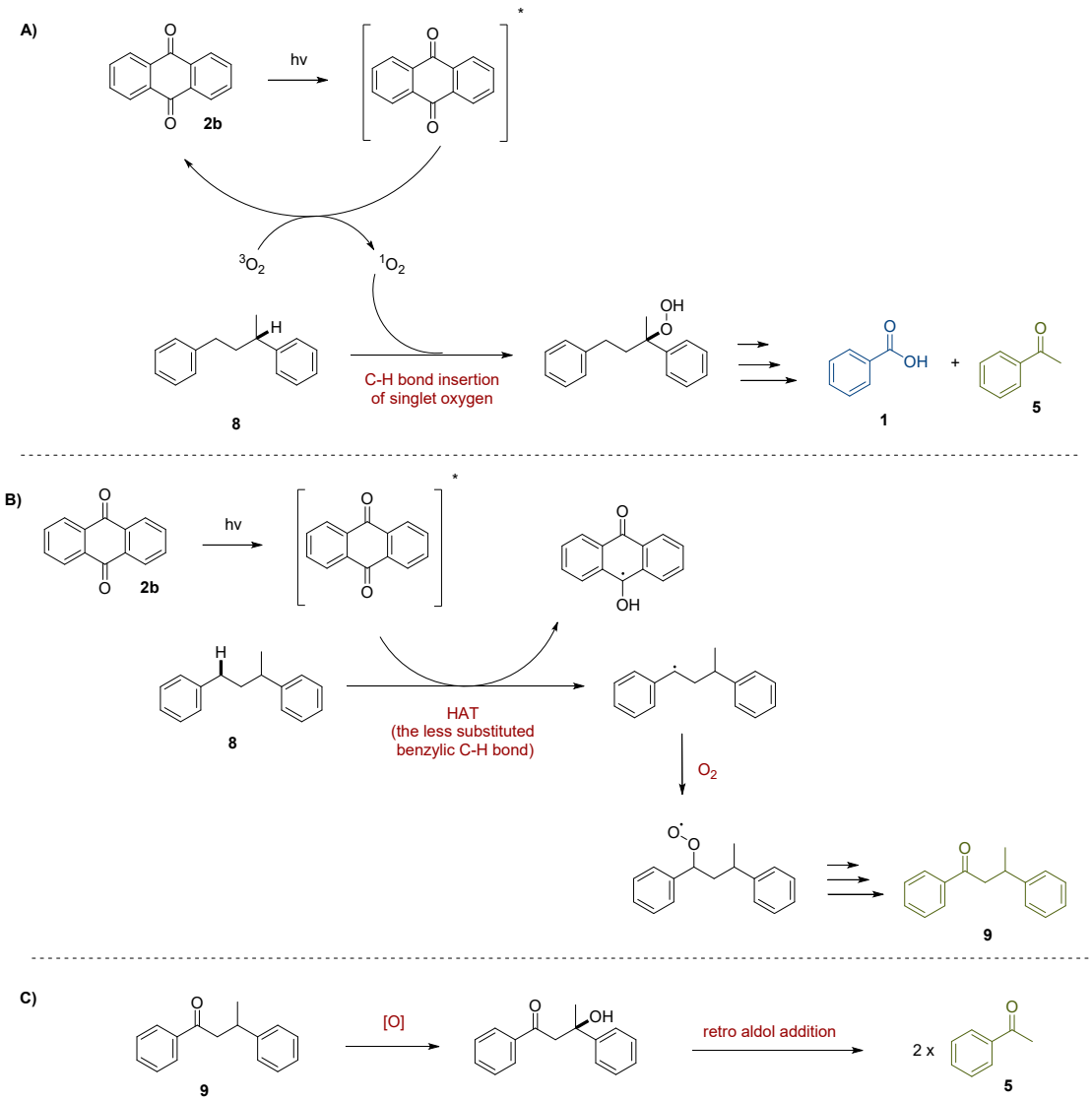


Along with the formation of **1** and **5**, formation of **9** indicates that singlet oxygen is not the only pathway responsible for the oxidation of 1,3-diphenylbutane (**8**).



^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of the crude reaction mixture of the oxidation of 1,3-diphenylbutan-1-one (8), where the presence of the major oxidation products was indicated.

According to literature, the insertion of singlet oxygen is favored to the most substituted benzylic position (Scheme below, Pathway A). Hydrogen atom abstraction from the less substituted benzylic position of the model substrate **8** by the excited form of anthraquinone is a plausible explanation for the generation of **9** (Scheme below, Pathway B). Ketone **9** can be further oxidized in its second available benzylic position, leading to keto alcohols, which can break down through retro-aldol reactions, forming two molecules of acetophenone (**5**) (Scheme below, pathway C). In literature,[1,10] it is supported, through DFT calculations that the more susceptible position for the hydrogen atom abstraction in compound **8** is the tertiary substituted benzylic position. In both examples of literature,[1,10] the formation of compound **9** is not presented, indicating that in the case of this anthraquinone upcycling protocol, the catalyst can also perform the HAT in the less activated benzylic position.


A)
2b
hv
$^3O_2$
$^1O_2$
8
C-H bond insertion
of singlet oxygen
1
5
B)
2b
hv
8
HAT
(the less substituted
benzylic C-H bond)
O_2
9
C)
9
[O]
retro aldol addition
2 x
5

Direct Infusion-High Resolution Mass Spectrometry (DI-HRMS) Mechanistic Studies

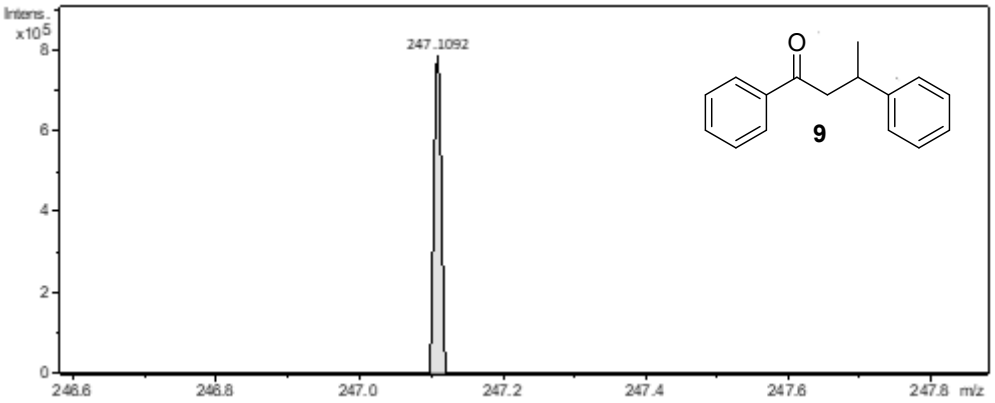
Instrumentation

High Resolution Mass Spectra were recorded with a Q-TOF (Time of Flight Mass Spectrometer) Bruker Maxis Impact with electrospray ionization (ESI) source. N_2 was used as collision gas and positive ionization mode was used for all MS experiments. The data acquisition was carried out with Data Analysis from Bruker Daltonics (version 4.1). Acetonitrile LC-MS gradient was obtained from Carlo Erba Reagents (Chaussée du Vexin, France). Source conditions: End plate offset 500V, Capillary 4500V, Nebulizer 0.4 bar, dry gas 4.0 L/min, dry temperature 180 ^{o}C and Quadrupole conditions: Ion energy 5 eV, Collision energy 10 eV, Transfer time 143 μs, Collision ion RF 3500 vpp, Pre pulse storage 1μs.
HRMS studies were performed with an ESI source in positive-ionization mode. The annotation of the intermediates was based on the exact mass high accuracy (mass error lower than 5 ppm).

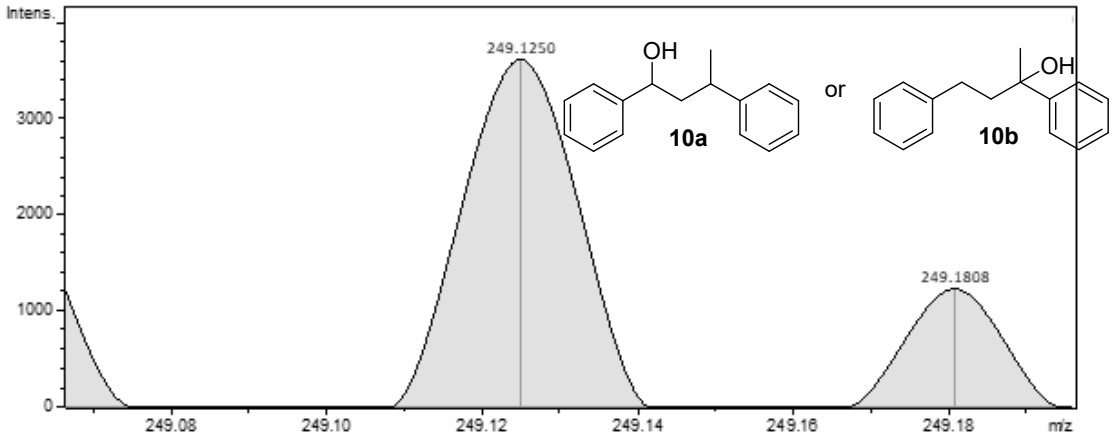
Products of the oxidation of 1,3-diphenylbutan-1-one (8) under LED 390 nm irradiation

The products of the oxidation of 1,3-diphenylbutan-1-one (**8**), upon irradiation with KESSIL LED 390 nm, were monitored for 24 hours by DI-HRMS. 1,3-Diphenylbutane-1-one (**8**) (42 μL, 0.20 mmol) and anthraquinone (**2b**) (2 mg, 0.01 mmol, 5 mol%) were dissolved in MeCN (0.8 mL) and the reaction mixture was left stirring under irradiation at 390 nm at room temperature. At the specific time of study (1h, 2h, 3h and 24h), a sample of the reaction mixture (20 μL) was first diluted with 980 μL methanol and 100 μL of that sample were further diluted with 900 μL of methanol. Finally, 100 μL were injected for DI-HRMS analysis.

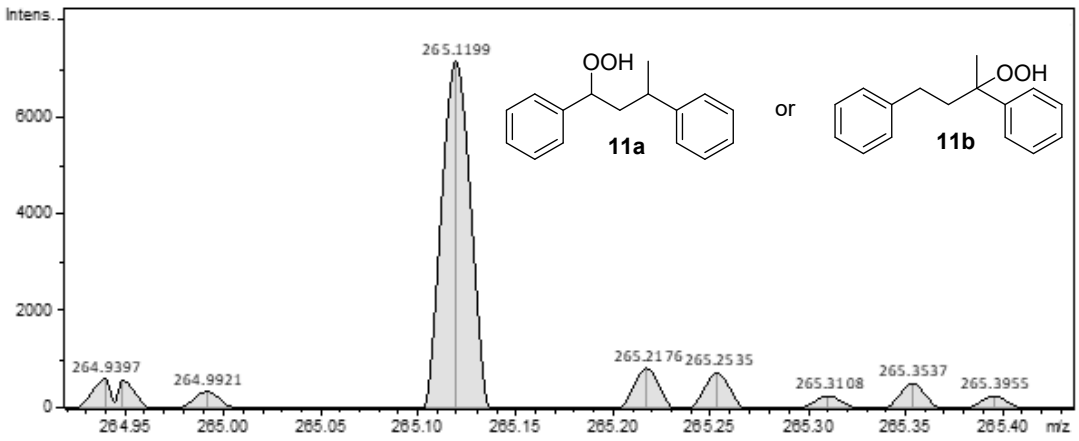
Monitoring the full scan spectrum of the reaction mixture, our attention was captured in the following oxygenated intermediates **9**, **10** and **11**.



Exact mass calculated for $[M+Na]^+(C_{16}H_{16}NaO^+)$	Exact mass found for $[M+Na]^+(C_{16}H_{16}NaO^+)$
247.1093	247.1092

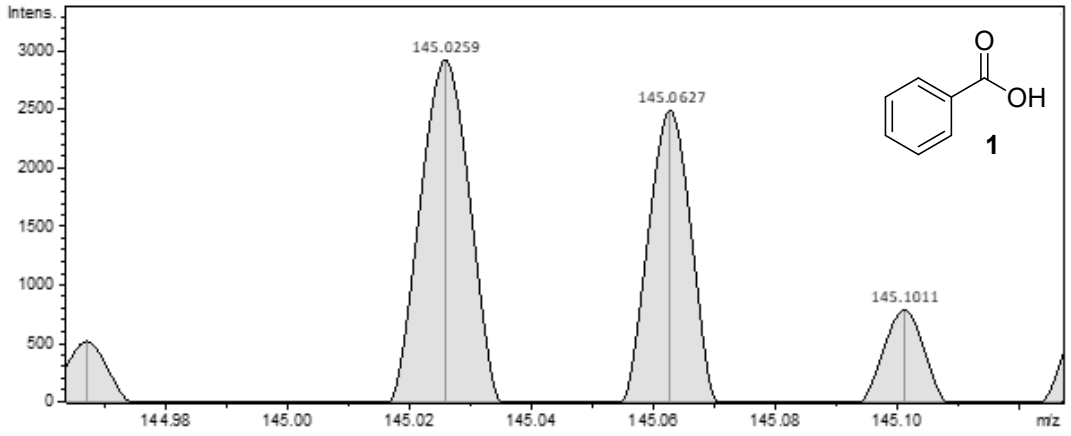


Exact mass calculated for $[M+Na]^+(C_{16}H_{18}NaO^+)$	Exact mass found for $[M+Na]^+(C_{16}H_{18}NaO^+)$
249.1250	249.1250

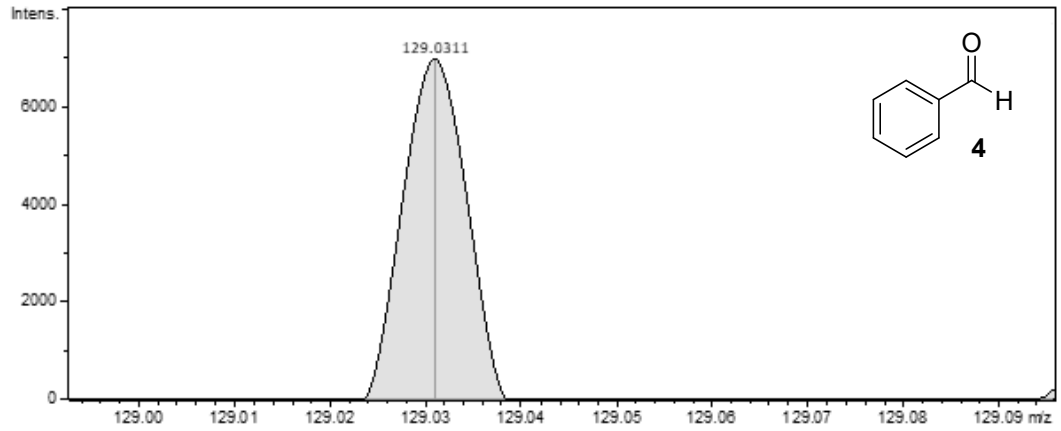


Exact mass calculated for $[M+Na]^+(C_{16}H_{18}NaO_2^+)$	**Exact mass found for $[M+Na]^+(C_{16}H_{18}NaO_2^+)$**
265.1199	265.1199

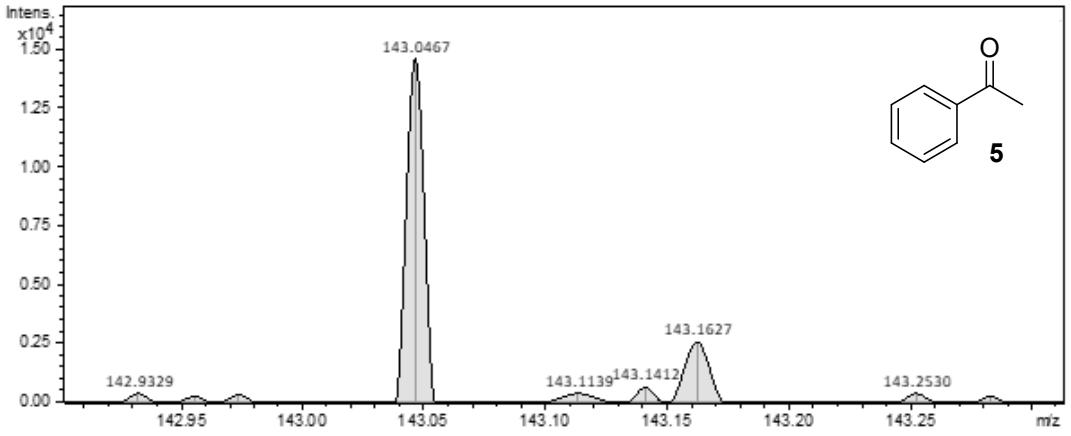
Additionally, we were able to identify intermediates **1**, **4**, **5**, **I**-**IV**, derived from the photochemical disconnection of 1,3-diphenylbutan-1-one.



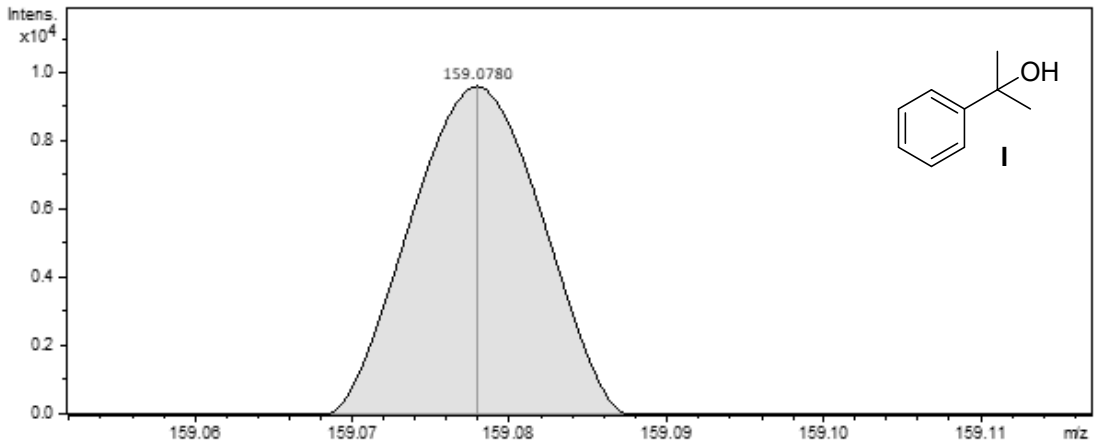
Exact mass calculated for $[M+Na]^+(C_7H_6NaO_2^+)$	**Exact mass found for $[M+Na]^+(C_7H_6NaO_2^+)$**
145.0260	145.0259



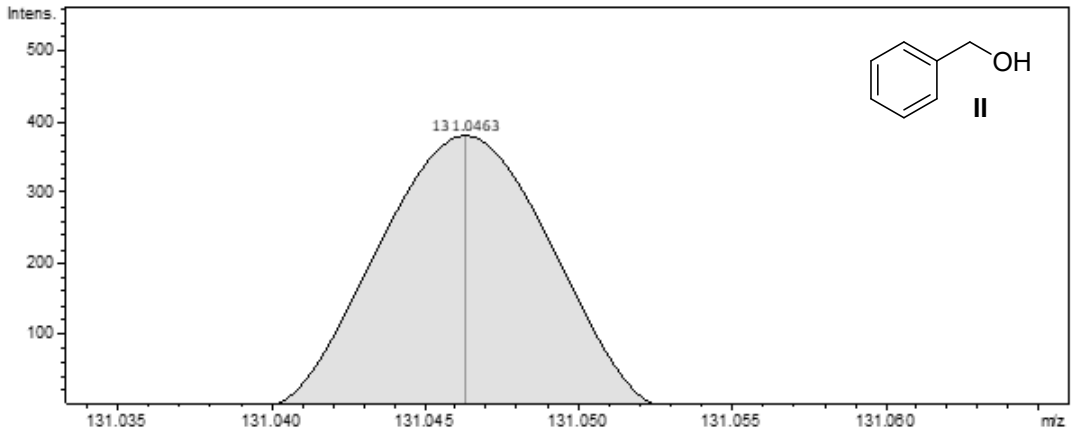
Exact mass calculated for $[M+Na]^+(C_7H_6NaO^+)$	Exact mass found for $[M+Na]^+(C_7H_6NaO^+)$
129.0311	129.0311



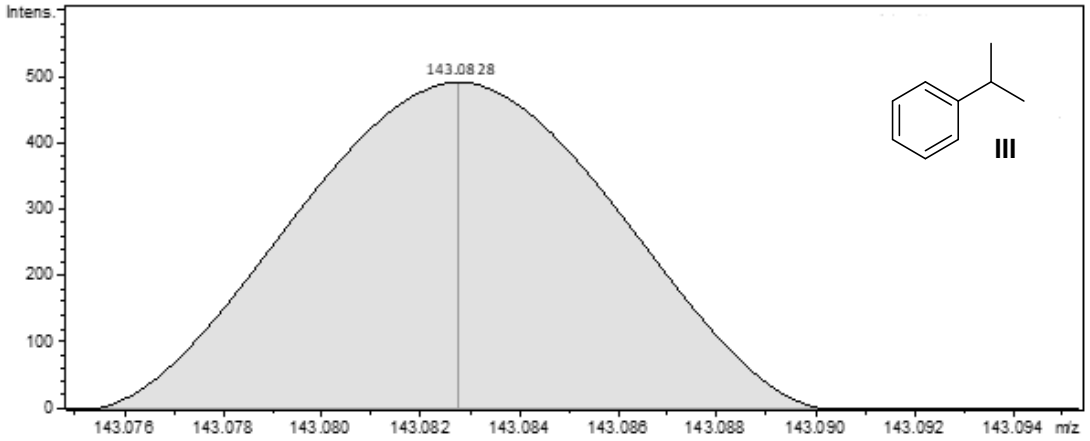
Exact mass calculated for $[M+Na]^+(C_8H_8NaO^+)$	Exact mass found for $[M+Na]^+(C_8H_8NaO^+)$
143.0467	143.0467



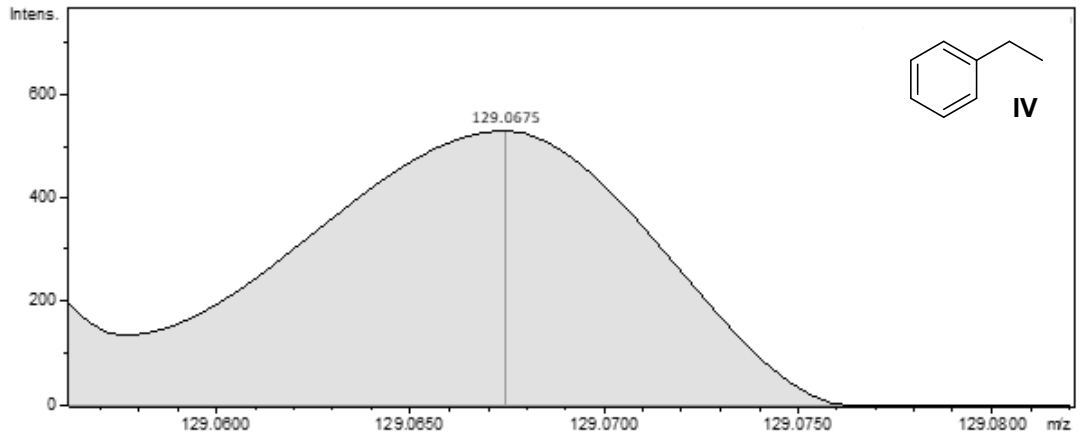
Exact mass calculated for $[M+Na]^+(C_9H_{12}NaO^+)$	**Exact mass found for $[M+Na]^+(C_9H_{12}NaO^+)$**
159.0780	159.0780



Exact mass calculated for $[M+Na]^+(C_7H_8NaO^+)$	**Exact mass found for $[M+Na]^+(C_7H_8NaO^+)$**
131.0467	131.0463



Exact mass calculated for $[M+Na]^+(C_9H_{12}Na^+)$	**Exact mass found for $[M+Na]^+(C_9H_{12}Na^+)$**
143.0831	143.0828

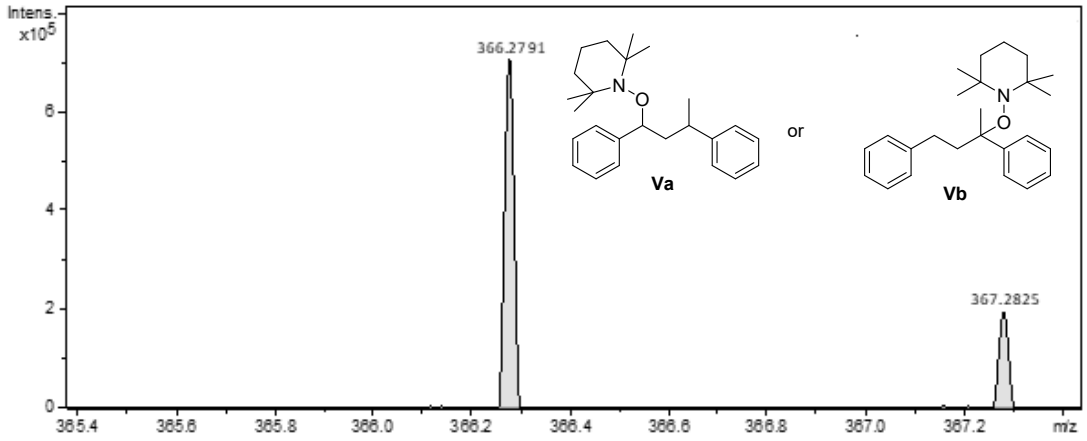


Exact mass calculated for $[M+Na]^+(C_8H_{10}Na^+)$	**Exact mass found for $[M+Na]^+(C_8H_{10}Na^+)$**
129.0675	129.0675

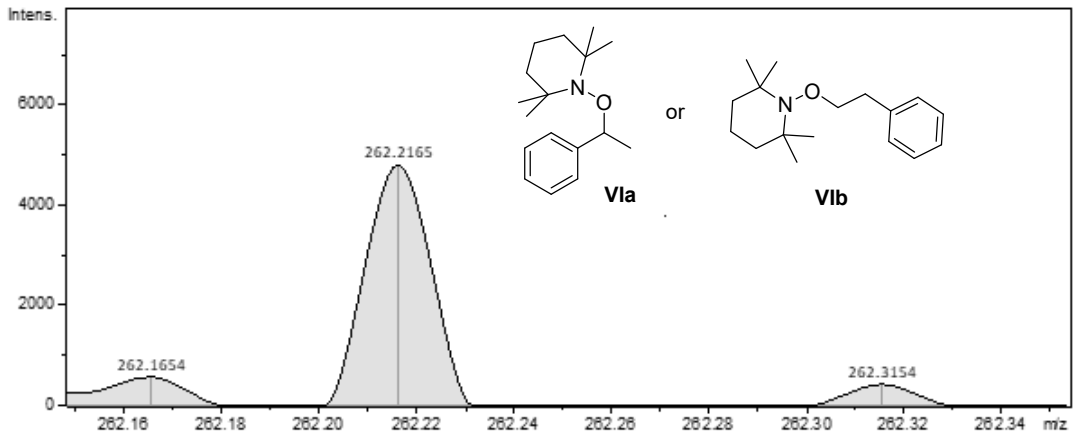
Products of the oxidation of 1,3-diphenylbutan-1-one (8) under LED 390 nm irradiation in the presence of TEMPO as the radical scavenger

The products of the oxidation of 1,3-diphenylbutan-1-one (**8**), upon irradiation with KESSIL LED 390 nm in the presence of TEMPO as the radical scavenger, were monitored for 24 hours by DI-HRMS. 1,3-Diphenylbutane-1-one (**8**) (42 μL, 0.20 mmol), TEMPO (31 mg, 0.20 mmol) and anthraquinone (**2b**) (2 mg, 0.01 mmol, 5 mol%) were dissolved in MeCN (0.8 mL) and the reaction mixture was left stirring under irradiation at 390 nm at room temperature. At the specific time of study (1h, 2h, 3h and 24h), a sample of the reaction mixture (20 μL) was first diluted with 980 μL methanol and 100 μL of that sample were further diluted with 900 μL of methanol. Finally, 100 μL were injected for DI-HRMS analysis.

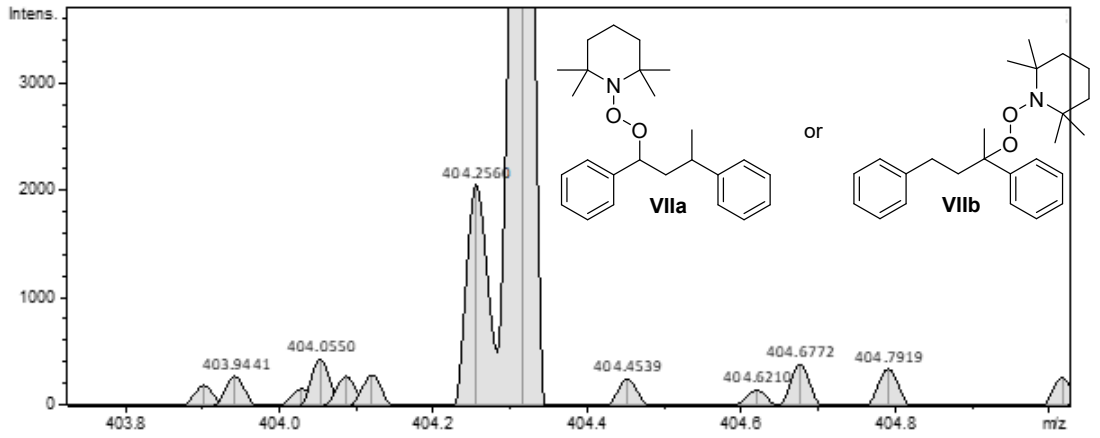
Monitoring the full scan spectrum of the reaction mixture, our attention was captured in the following TEMPO-adducts **V**-**VIII**.



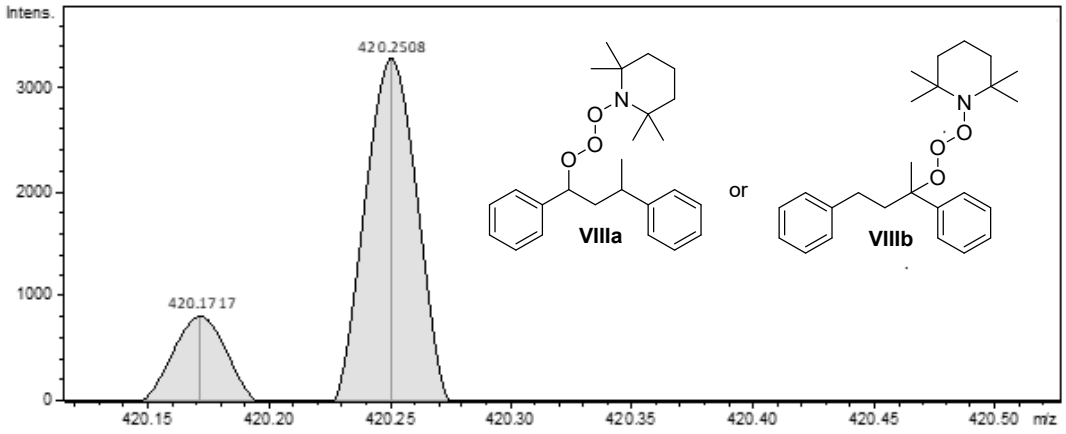
Exact mass calculated for $[M+Na]^+$ ($C_{25}H_{35}NNaO^+$)	Exact mass found for $[M+Na]^+$ ($C_{25}H_{35}NNaO^+$)
366.2791	366.2791



Exact mass calculated for $[M+Na]^+$ ($C_{17}H_{27}NNaO^+$)	Exact mass found for $[M+Na]^+$ ($C_{17}H_{27}NNaO^+$)
262.2165	262.2165



Exact mass calculated for $[M+Na]^+$ ($C_{25}H_{35}NNaO_2^+$)	Exact mass found for $[M+Na]^+$ ($C_{25}H_{35}NNaO_2^+$)
404.2560	404.2560



Exact mass calculated for $[M+Na]^+$ ($C_{25}H_{35}NNaO_2^+$)	**Exact mass found for $[M+Na]^+$ ($C_{25}H_{35}NNaO_2^+$)**
420.2509	420.2508

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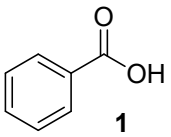
NMR traces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OH

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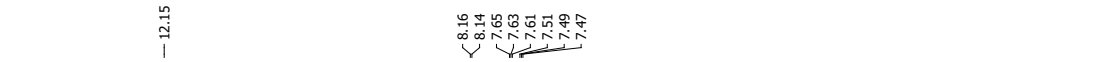
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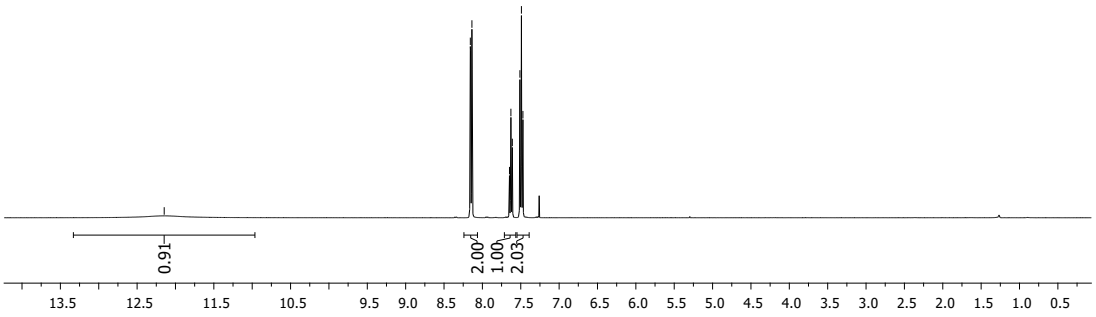
8.14
7.65
7.63
7.61
7.51
7.49
7.47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2.00
1.00
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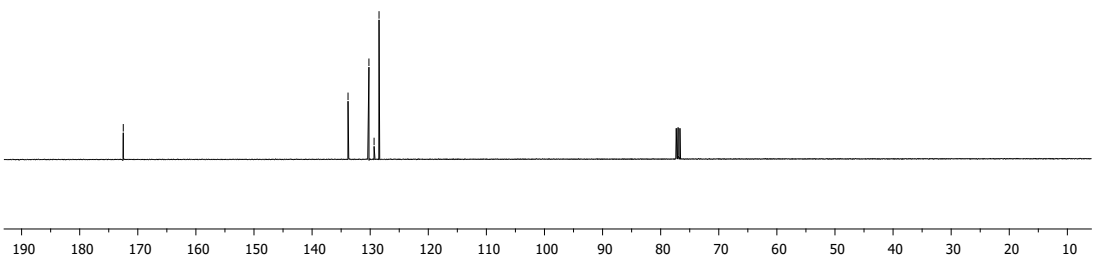
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

172.5
133.8
130.2
129.3
128.5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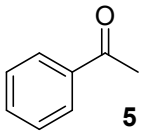
10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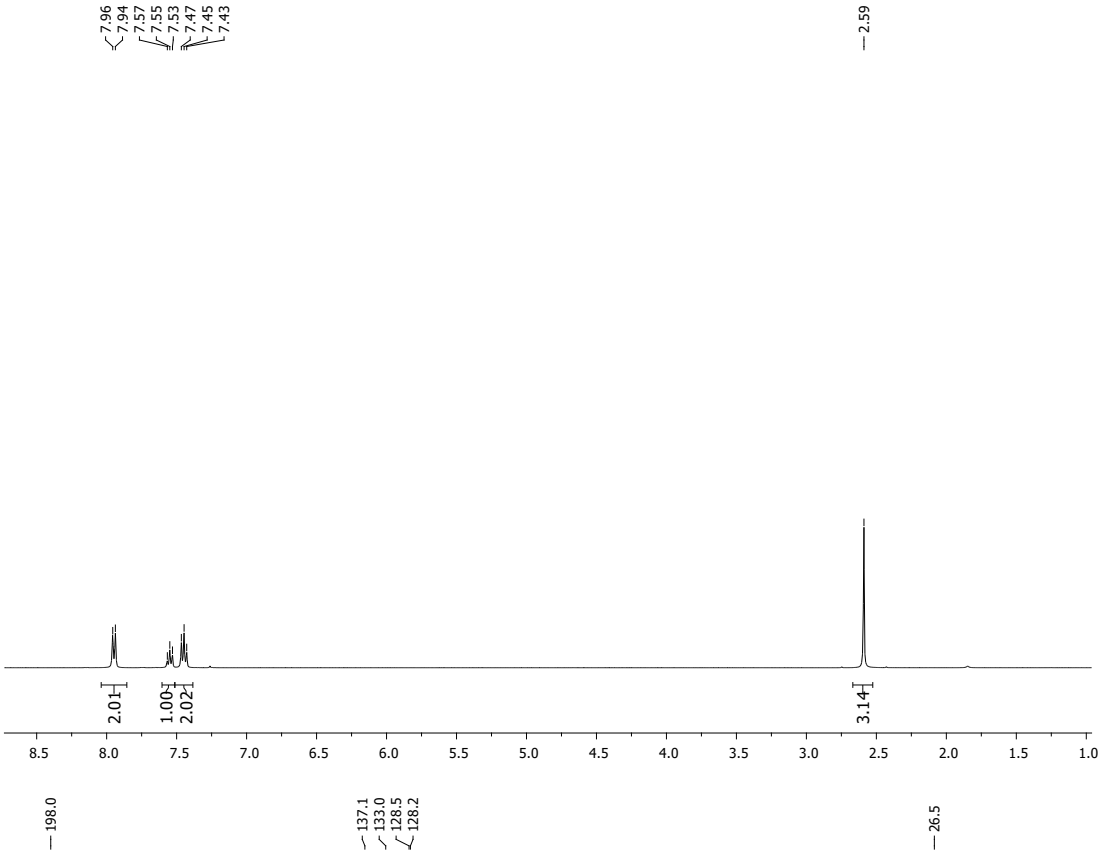
5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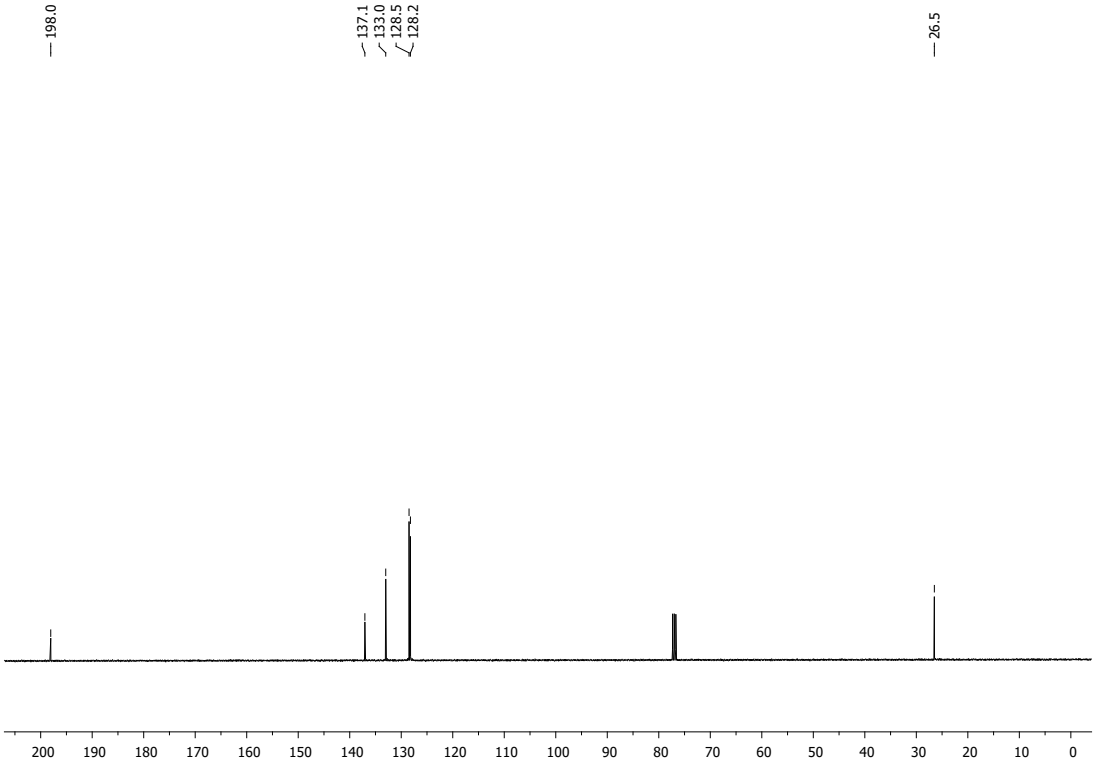
1.5
1.0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30
20
10
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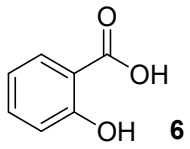
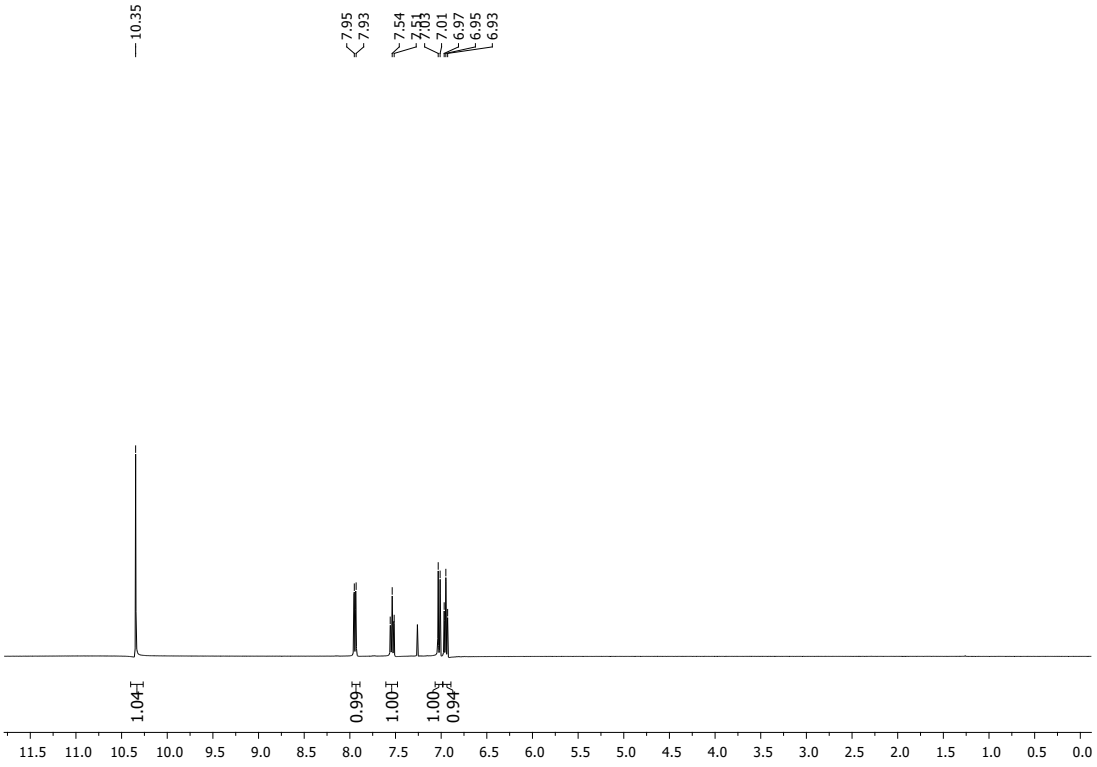

O
OH
OH

6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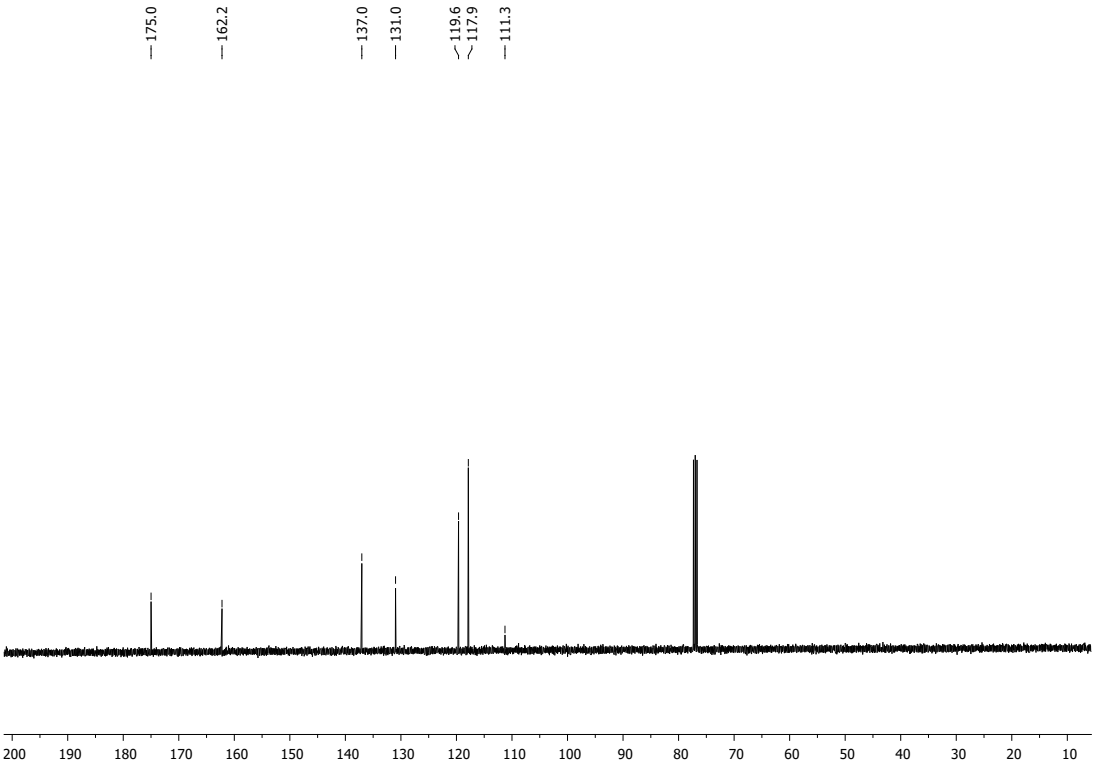
1.00
1.00
0.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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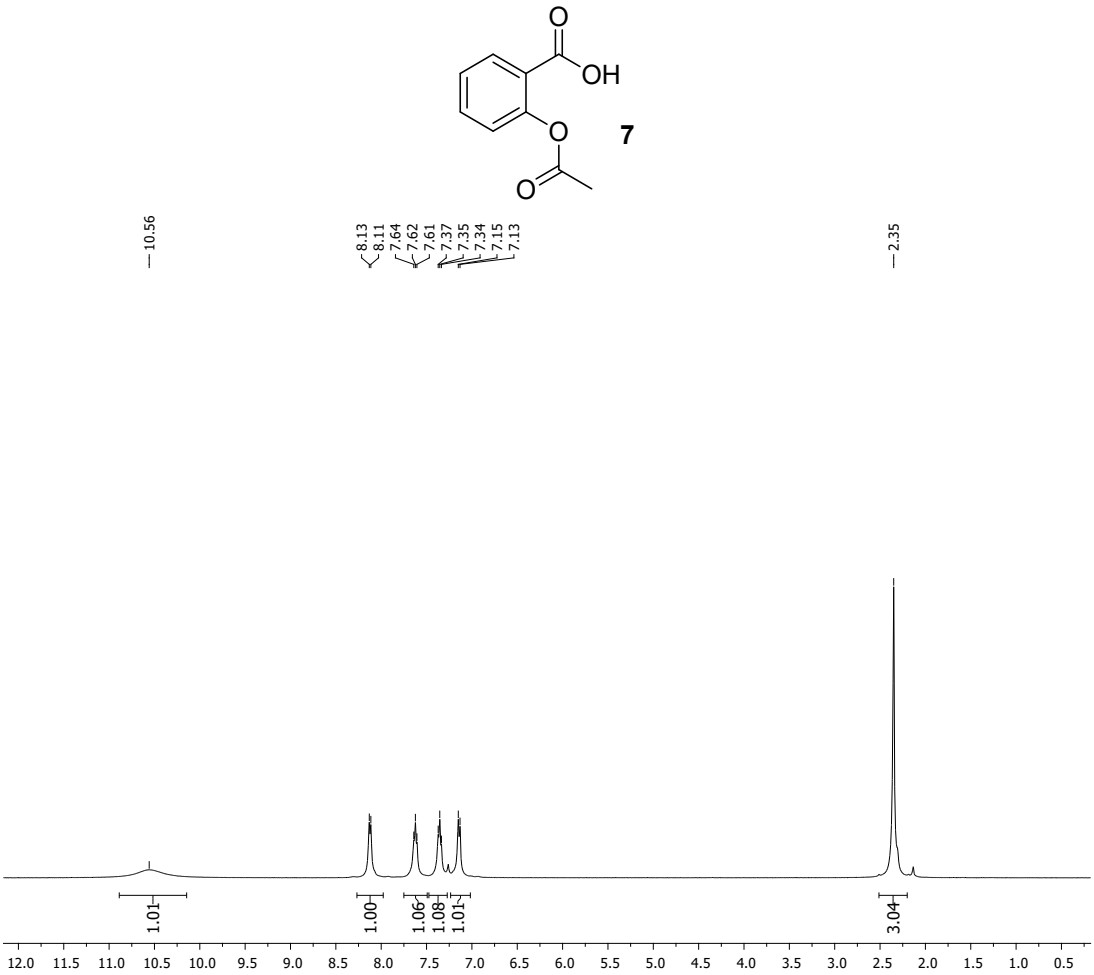
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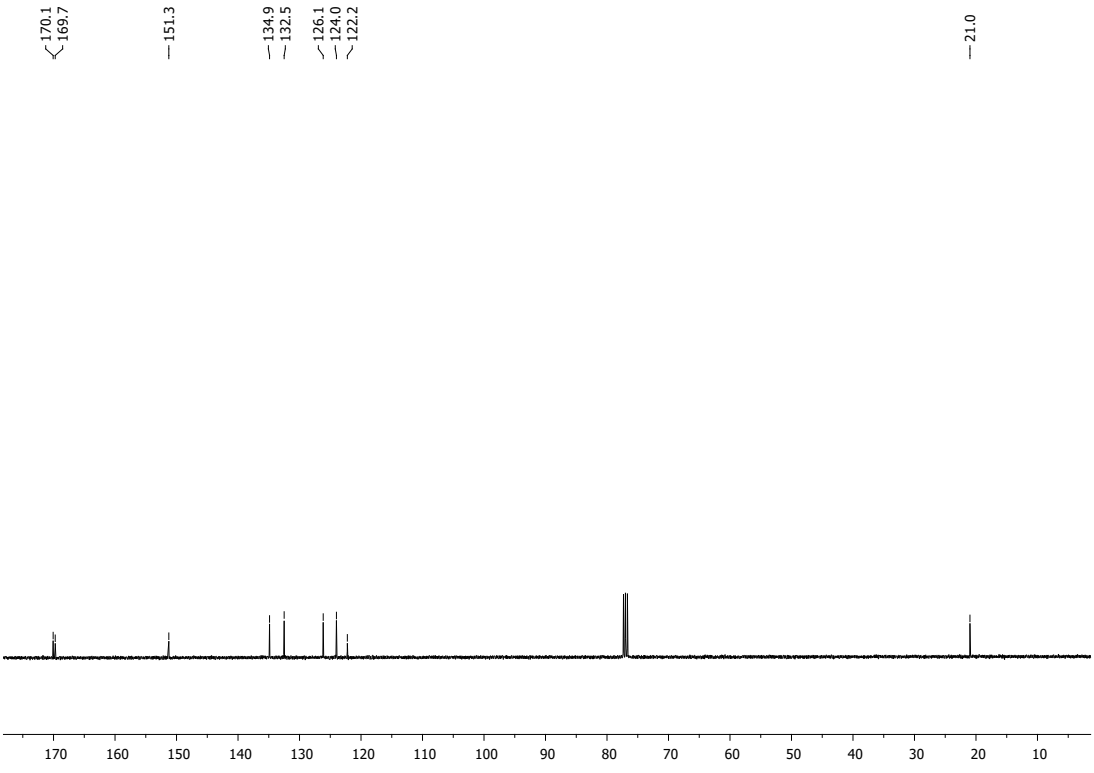
7.13
2.35
1.01
1.00
1.06
1.08
1.01
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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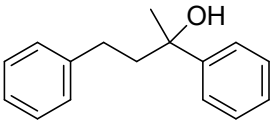
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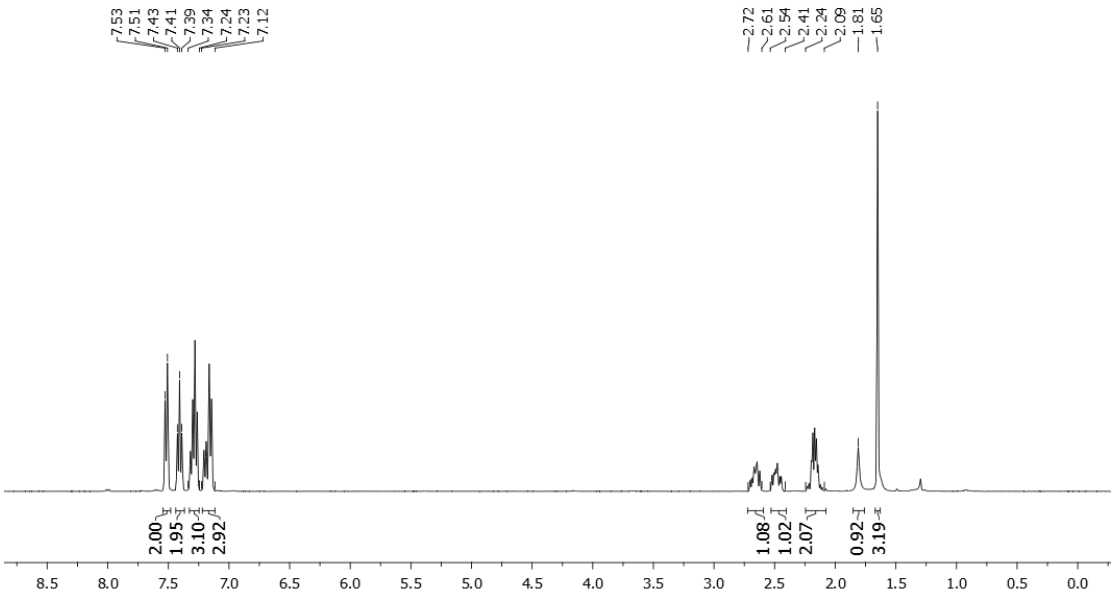
S1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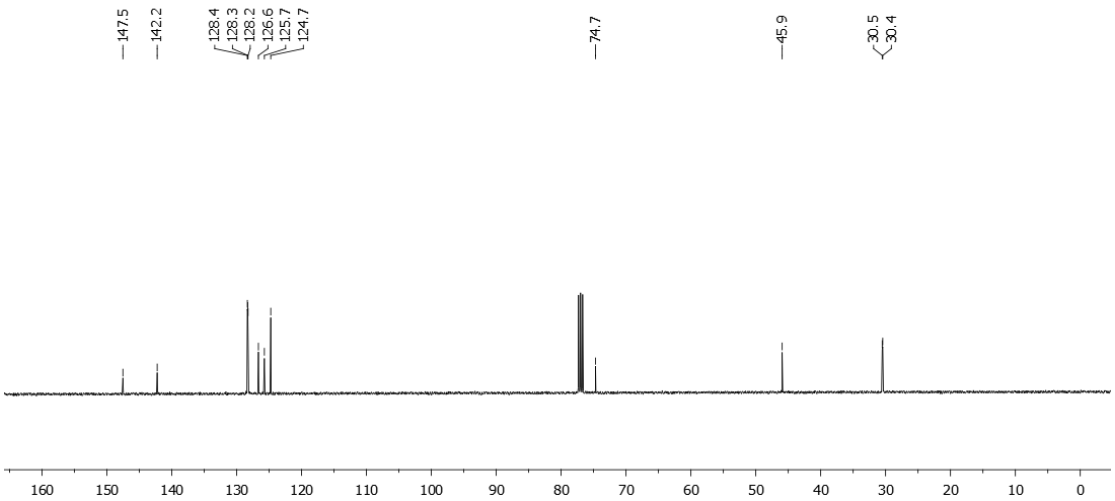
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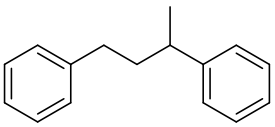

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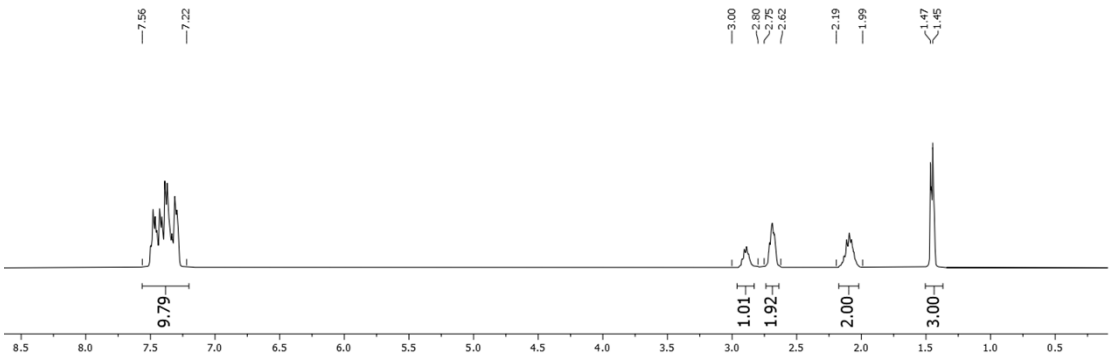
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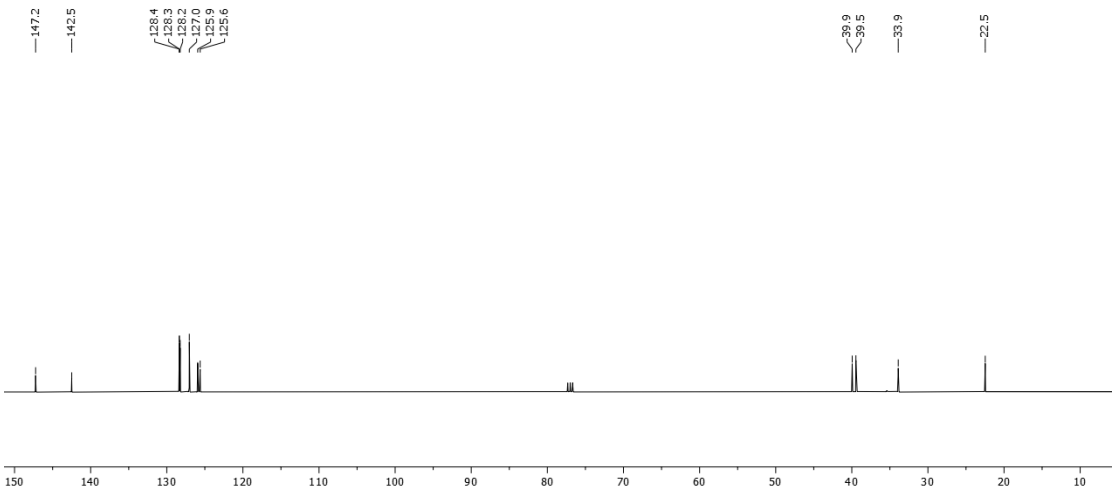
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