Supporting Information

Comment on "Catalyst- and additive-free sunlight-induced autoxidation of aldehydes to carboxylic acids" by H. Shi, J. Li, T. Wang, M. Rudolph and A. S. K. Hashmi, *Green Chem.*, 2022, 24, 5835[1]

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1 General information

1.1 Chemicals

Acetone, benzaldehyde, benzoic acid, ethanol, 2-ethylhexanoic acid (I.S.), 4-methoxybenzaldehyde, methyl p-tolyl sulfide, and methyl p-tolyl sulfoxide were used as obtained from the suppliers. Aldehydes and methyl p-tolyl sulfide were stored at 4°C with protection from light.

1.2 Analytical procedure

The composition of the GC vials was analyzed using Shimadzu GC/FID Nexis GC-2030 and Shimadzu GC-MS QP2010 SE systems, both equipped with DB-HeavyWax columns (Agilent Technologies).

2-ethylhexanoic acid was used as the internal standard (I.S.). The product of the reaction is a carboxylic acid, so a trace amount of I.S. will not influence the reaction rate or selectivity. Furthermore, the I.S. is soluble in acetone, is not volatile, and is adapted to DB-HeavyWax columns (see Figure S 3, Figures S 5 to S 8).

The concentration of peracid **1** in the solution was determined using methyl p-tolyl sulfide **2** (Figure S 1). We have shown previously that in the presence of peracid **1**, methyl p-tolyl sulfide **2** was quantitatively oxidized into methyl p-tolyl sulfoxide **4**. The latter could be precisely quantified by GC/FID.[2,3]

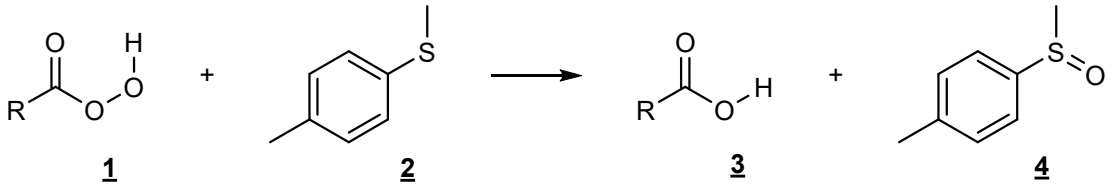

*Figure S 1. Quantification of peracid **1** by ex situ analysis using methyl p-tolyl sulfide **2** and quantitative formation of the corresponding carboxylic acid **3** and methyl p-tolyl sulfoxide **4**.*

1.3 Experimental conditions

The experiments were performed in Villeurbanne (France) on 29.07.2022 and 02.08.2022. Weather (sunny); outdoor temperature (28-34 °C); humidity (53%); barometer (1019 mbar); wind 7 km/h (02.08.2022).

2 General procedure for the evaluation of sunlight-induced autoxidation of aldehydes to carboxylic acids

Solution A: In a volumetric flask of 10 mL, 4-methoxybenzaldehyde (1.361 g, 10 mmol, 1 M) and 2-ethylhexanoic acid (0.144g, 1 mmol, I.S.) were precisely weight, and the flask was filled with analytical grade solvent and mixed.

Solution B: In a volumetric flask of 20 mL, methyl p-tolyl sulfide (1.382 g, 10 mmol, 0.5 M) was precisely weight, and the flask was filled with analytical grade acetone and mixed.

Using 2.5 mL Hamilton Syringes with PTFE luer lock, 5 x 0.5 mL of solution A were added in 5 different test tubes (6 mL, 7.5 cm height, i.d. 1 cm). PTFE stir bar was added. The tubes were left stirring under sunlight outside at room temperature (Figure S 2). Under those conditions, a regular stirring is obtained for the 12 tubes per magnetic stirrer (reaction test + blank and duplicate). The test tube stand was periodically rotated according to the sun's position to maximize light shining (see the shadow on the right of the test tube stand in figure S2). Compared to the experimental setup described for 8 test tubes (Hashmi et al.[1], Supporting information page S2), one could expect that the test tube stand could make some shadow even if stirring efficiency could be more homogeneous in our case. However, preliminary experiments with tubes held by clamps under the same weather conditions gave similar results.

At a given time (t=0, 30 60, 120, 180 or 240 min), 0.5 mL of solution B (0.5 M methyl p-tolyl sulfide solution) was add to a test tube. The resulting solution was mixed and added to amber GC vials equipped with a 250 µL insert. The vials without oxygen were stored under light protection and analyzed by GC/FID and GC/MS. This procedure enables us to follow the composition of the solution as a function of time. Sometimes, after ~2h under sunlight, crystals could be found on the tube walls. These crystals were carefully dissolved using the methyl p-tolyl sulfide solution.

For one experiment (Figure S 5), the p-tolyl sulfide solution was replaced with acetone.

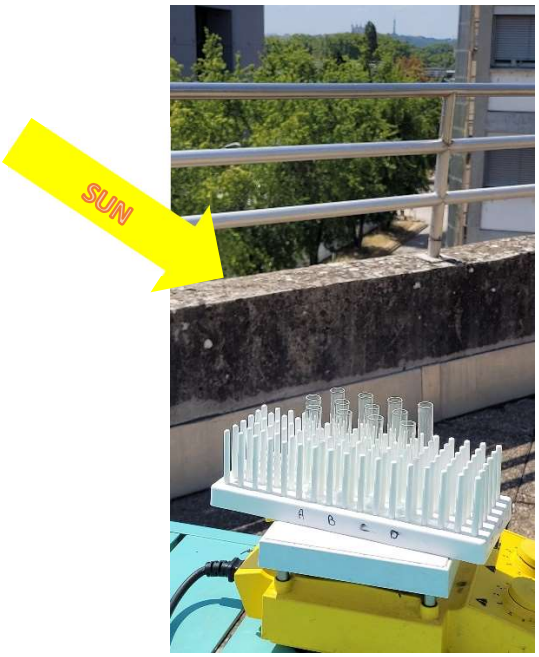

Figure S 2. Reaction setup with 12 test tubes.

2.1 Sunlight-induced autoxidation of 4-methoxybenzaldehyde 5 in acetone with quantification of peracid using methyl p-tolyl sulfide 2.

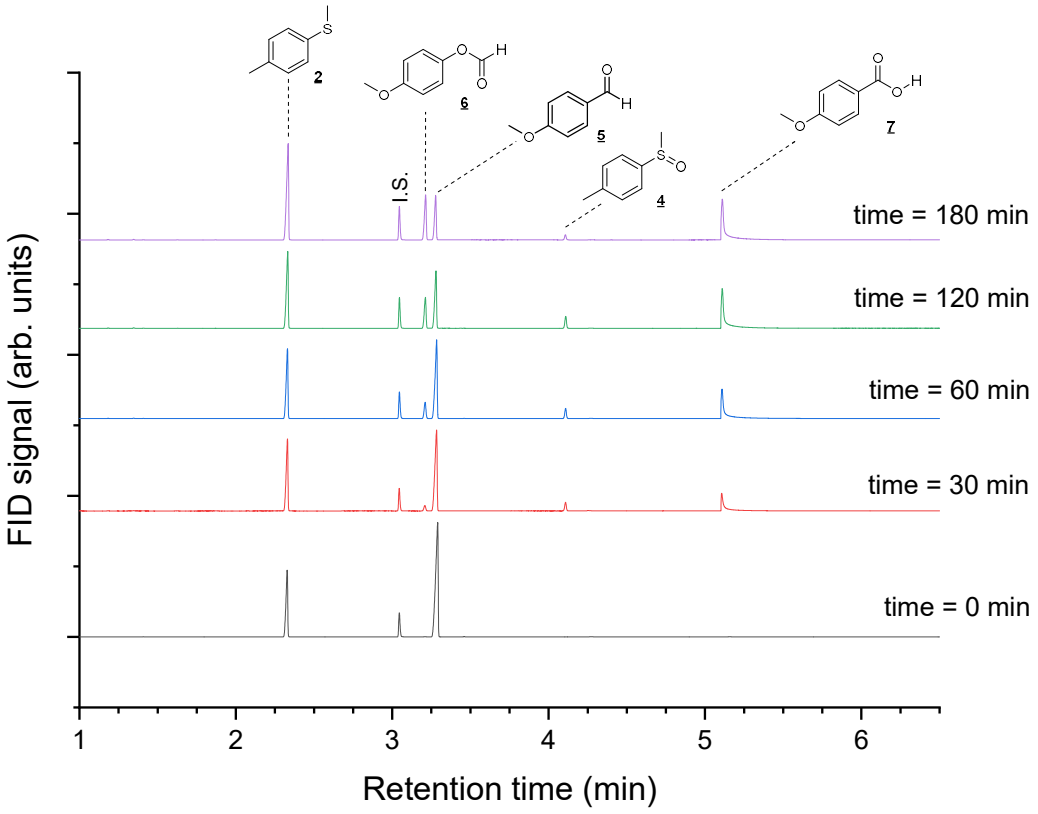

*Figure S 3. Comparison of the GC/FID chromatogram as a function of time during the sunlight-induced autoxidation of 4-methoxybenzaldehyde **5**. Reaction conditions: 4-methoxybenzaldehyde **5** in acetone (1 M), 0.5 mL in test tube, open-air, outdoor temperature (28-34 °C); humidity (53%); barometer (1019 mbar); wind 7 km/h. 2-ethylhexanoic acid is used as an internal standard (I.S.). Samples were diluted with 0.5 mL of methyl p-tolyl sulfide in acetone (0.5 M).*

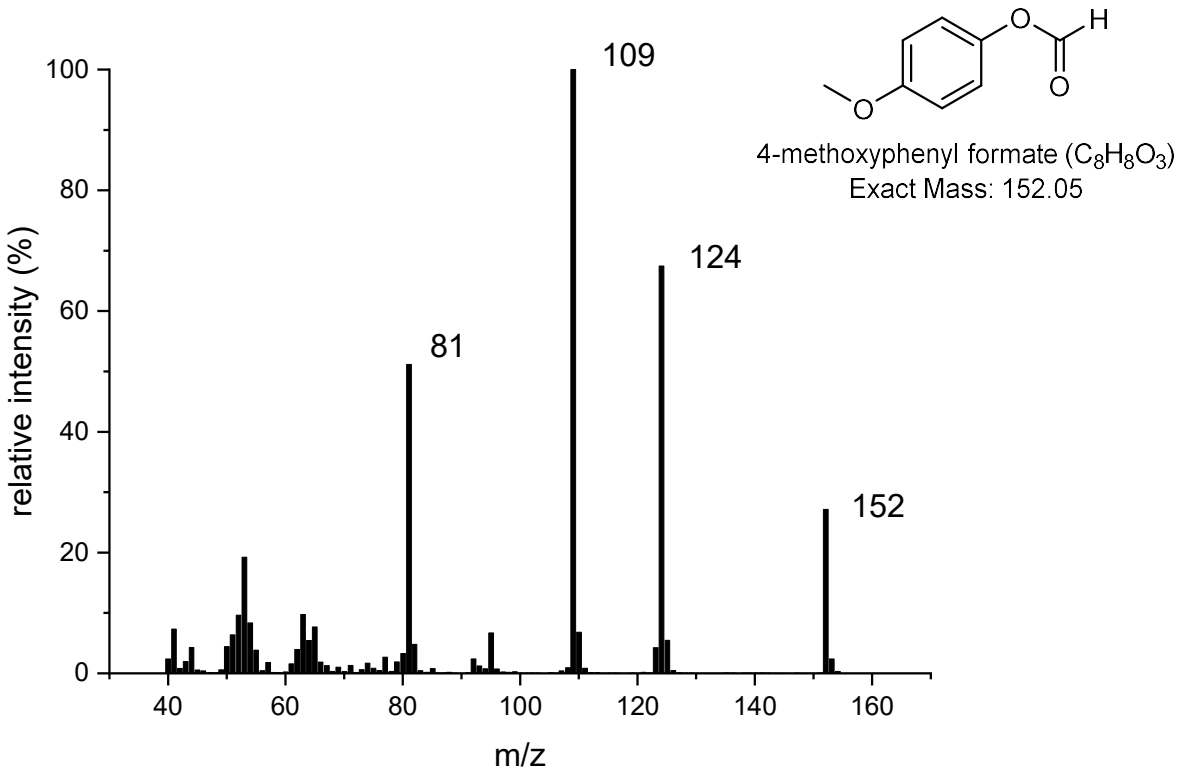

Figure S 4. EI mass spectrum for the compound with a retention time of 3.212 min.

2.2 Sunlight-induced autoxidation of 4-methoxybenzaldehyde 5 in acetone

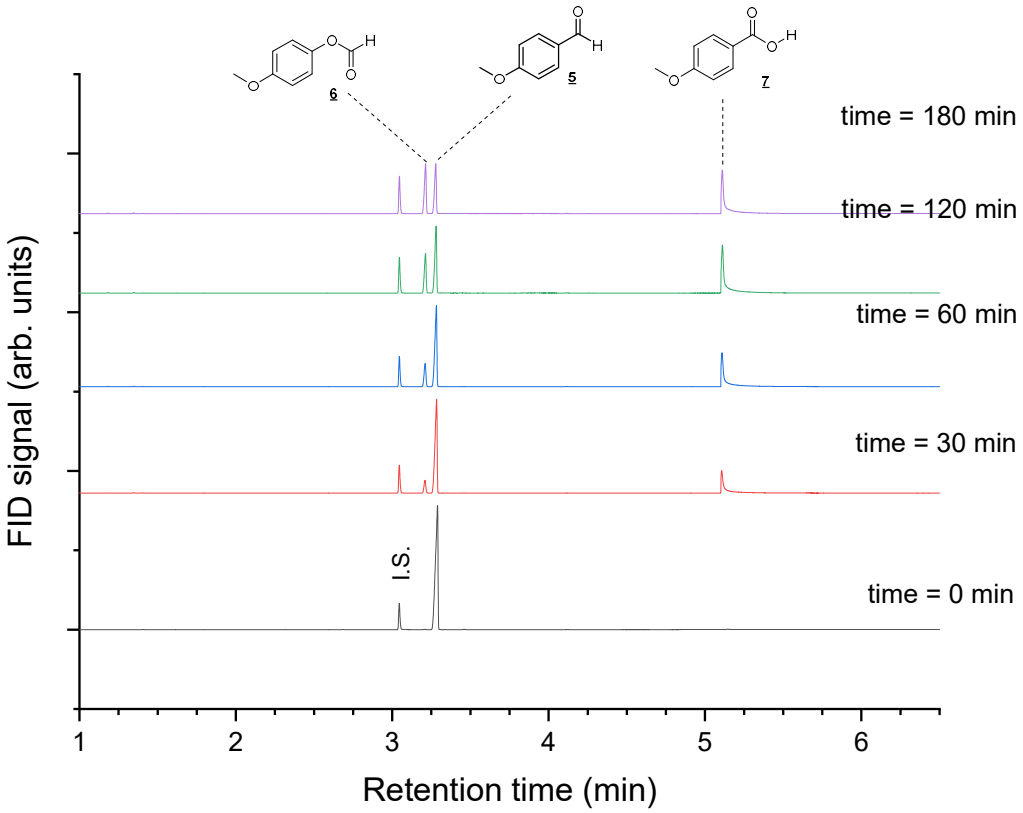

*Figure S 5. Comparison of the GC/FID chromatogram as a function of time during the sunlight-induced autoxidation of 4-methoxybenzaldehyde **5**. Reaction conditions: 4-methoxybenzaldehyde **5** in acetone (1 M), 0.5 mL in test tube, open-air, outdoor temperature (28-34 °C); humidity (53%); barometer (1019 mbar); wind 7 km/h. 2-ethylhexanoic acid is used as an internal standard (I.S.). Samples were diluted with 0.5 mL volume of acetone.*

2.3 Sunlight-induced autoxidation of benzaldehyde 8 in acetone with quantification of peracid using methyl p-tolyl sulfide 2.

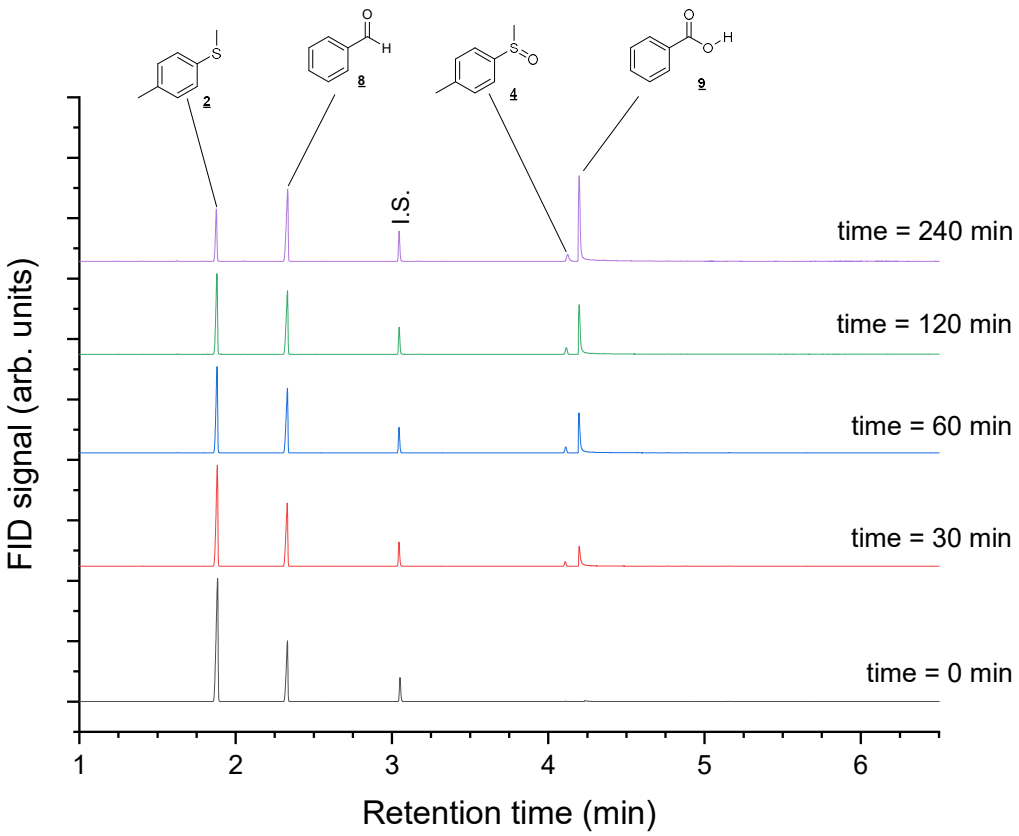

*Figure S 6. Comparison of the GC/FID chromatogram as a function of time during the sunlight-induced autoxidation of benzaldehyde **8**. Reaction conditions: benzaldehyde **8** in acetone (1 M), 0.5 mL in test tube, open-air, outdoor temperature (28-34 °C); humidity (53%); barometer (1019 mbar); wind 7 km/h. 2-ethylhexanoic acid is used as an internal standard (I.S.). The samples were diluted with 0.5 mL of methyl p-tolyl sulfide in acetone (0.5 M).*

2.4 Sunlight-induced autoxidation of 4-methoxybenzaldehyde 5 in ethanol with quantification of peracid using methyl p-tolyl sulfide 2.

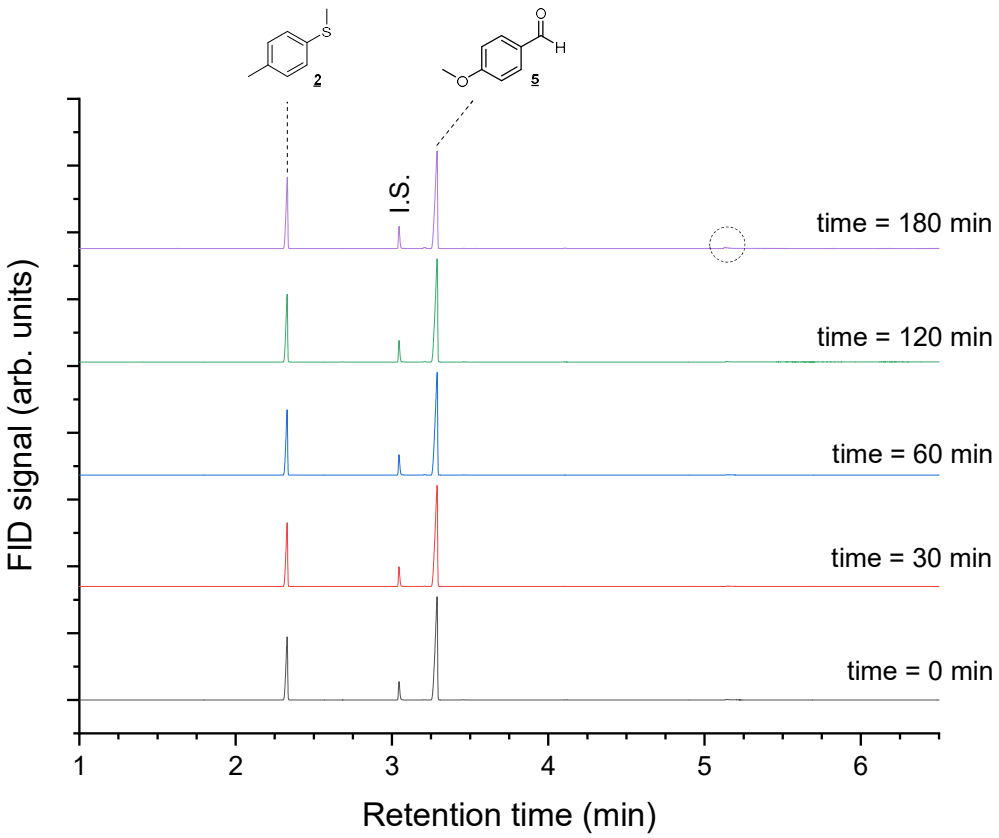

*Figure S 7. Comparison of the GC/FID chromatogram as a function of time during the sunlight-induced autoxidation of 4-methoxybenzaldehyde **5**. Reaction conditions: 4-methoxybenzaldehyde **5** in ethanol (1 M), 0.5 mL in test tube, open-air, outdoor temperature (28-34 °C); humidity (53%); barometer (1019 mbar); wind 7 km/h. 2-ethylhexanoic acid is used as an internal standard (I.S.). The samples were diluted with 0.5 mL of methyl p-tolyl sulfide in acetone (0.5 M).*

2.5 Sunlight-induced autoxidation of 4-methoxybenzaldehyde 5 in THF with quantification of peracid using methyl p-tolyl sulfide 2.

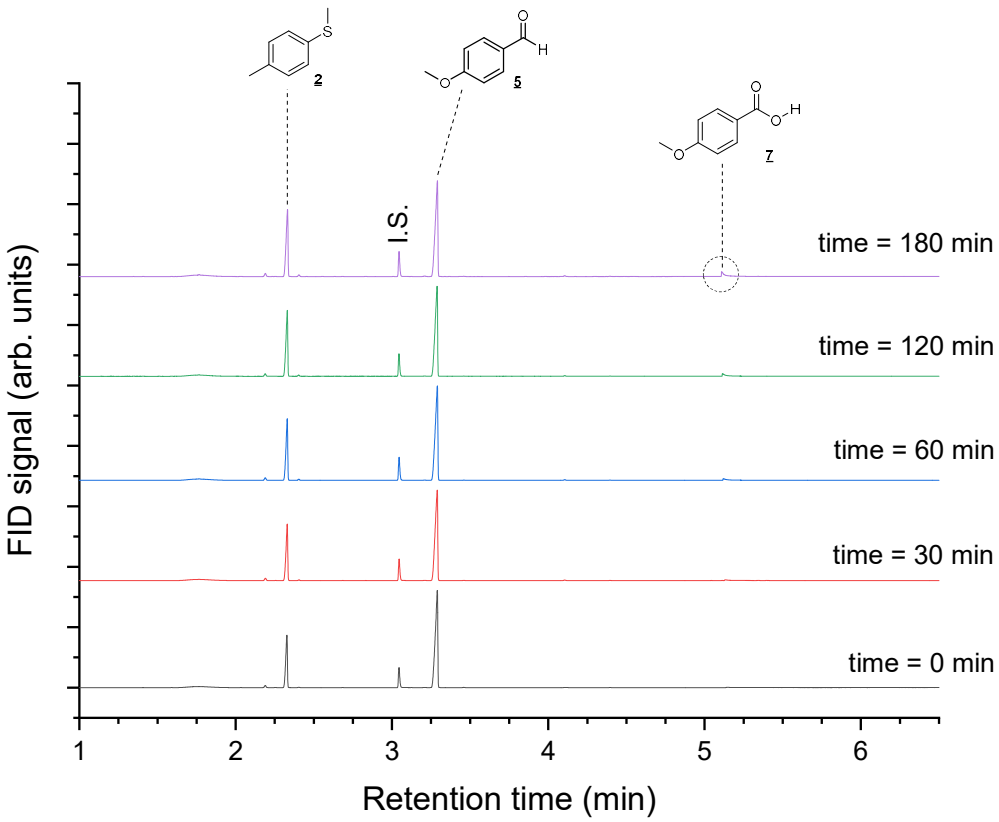

*Figure S 8. Comparison of the GC/FID chromatogram as a function of time during the sunlight-induced autoxidation of 4-methoxybenzaldehyde **5**. Reaction conditions: 4-methoxybenzaldehyde **5** in THF (1 M), 0.5 mL in test tube, open-air, outdoor temperature (28-34 °C); humidity (53%); barometer (1019 mbar); wind 7 km/h. 2-ethylhexanoic acid is used as an internal standard (I.S.). The samples were diluted with 0.5 mL of methyl p-tolyl sulfide in acetone (0.5 M).*

3 References

1. H. Shi, J. Li, T. Wang, M. Rudolph and A. S. K. Hashmi, *Green Chem.*, 2022, **24**, 5835-5841.
2. L. Vanoye and A. Favre-Réguillon, *Org. Process Res. Dev.*, 2022, **26**, 335-346.
3. L. Vanoye, M. Abdelaal, K. Grundhauser, B. Guicheret, P. Fongarland, C. De Bellefon and A. Favre-Réguillon, *Org. Lett.*, 2019, **21**, 10134-10138.