Supporting Information

Ohmic Heating-Assisted Regioselective Sulfonation of Aniline: Synthesis of Sulfanilic Acid

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1. Chromatogram of the reference sample

From the analysis of the reference sample by HPLC (Figure S1) it was possible to identify the retention time of each compound, thus making easier to determine the composition of the reaction product obtained in each experiment.

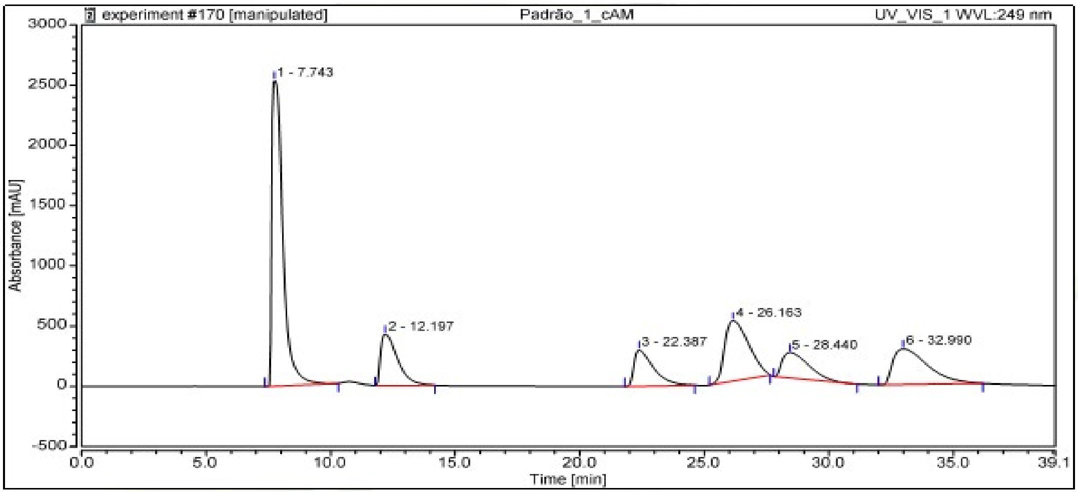


Figure S1.

Chromatogram of the reference sample at 259 nm. Relative area: **2** (40.4%), **3** (10.46%), **1** (8.5%), **5** (17.4%), **6** (8.2%), **4** (15.1%) (the relative areas are presented in the increasing order of the retention time of the compounds).[1]

Table S1 indicates the compounds present in the reference sample, their retention times, and the absorption wavelength. The percentage of SA (**2**) was calculated based on the relative areas of the peaks observed in the HPLC chromatograms of the reaction mixture and it was assumed that there is no degradation but only transformation of aniline (**1**) into other products.

Table S1. Compounds present in the reference sample, their retention times (min.) and absorption wavelengths (nm)

$compound$	$t\ (min)$	$\lambda_{máx}\ (nm)$
Sulfanilic acid (**2**)	7.7	249
3-Aminobenzenesulfonic acid (**3**)	12.2	237
Aniline (**1**)	22.4	230
4-Aminobenzene-1,3-disulfonic acid (**5**)	26.2	256
2-Aminobenzene-1,4-disulfonic acid (**6**)	28.4	218
2-Aminobenzenesulfonic acid (**4**)	33.0	239

2. Calculation of the average temperature of heating

Ohmic heating process depends on the electrical impedance, more precisely the AC resistance of the reaction medium and the applied voltage. On the other hand, the applied voltage depends on the input power from the amplifier, which also depends on the AC resistance of the reaction medium. As the distance between electrodes is fixed, the field strength applied will vary from experiment to experiment.

Since our current prototype is not fully automated, the input power was manually adjusted during the experiment to maintain the desired temperature. Therefore, an average temperature value is indicated for each experiment.

The methodology followed to determine the average temperature of heating, for each experiment, was based on the analysis of the corresponding heating curves [T = f(t)] recorded by the reactor software, as exemplified in Figure S2. To calculate the average temperature of heating, only the values corresponding to the time interval where the temperature remains almost constant were considered; the temperature values of the initial heating ramp were excluded.

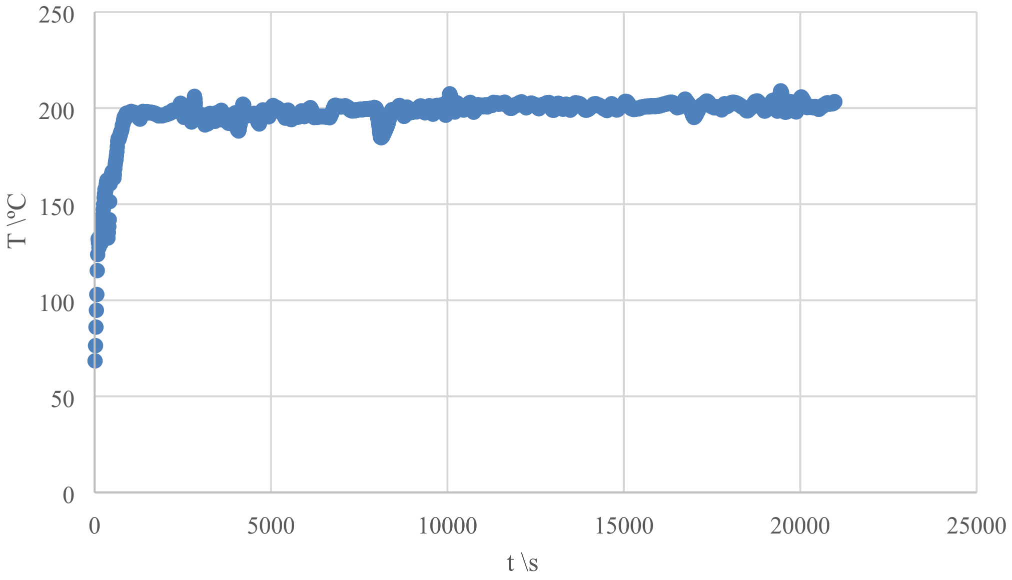


Figure S2. Graphical representation of the temperature during the heating time [T = f (t)] for the experiment 9.

3. Images of experiments 7, 9 and 13

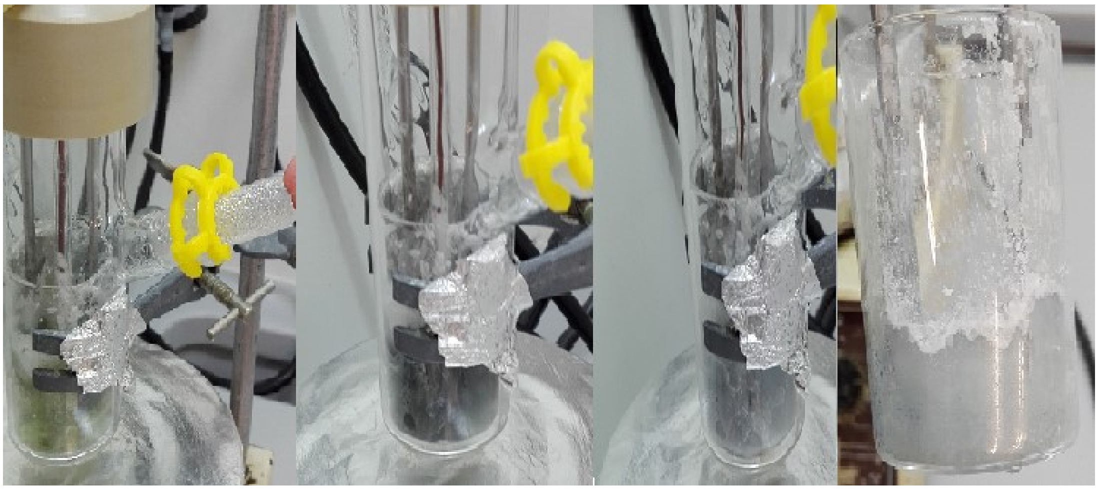


Figure S3. Images of experiment 7 at 21 min., 40 min., 1.20 h and 6.00 h (from left to right).

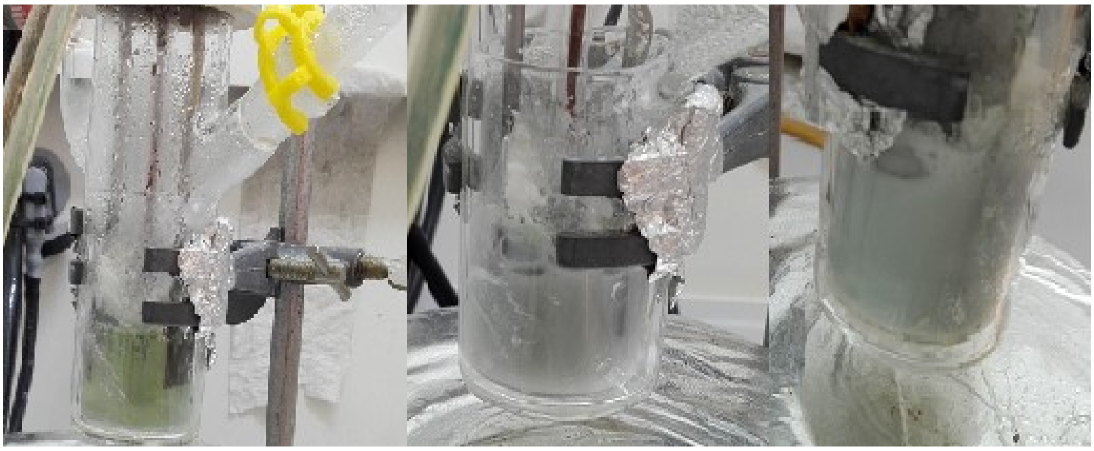
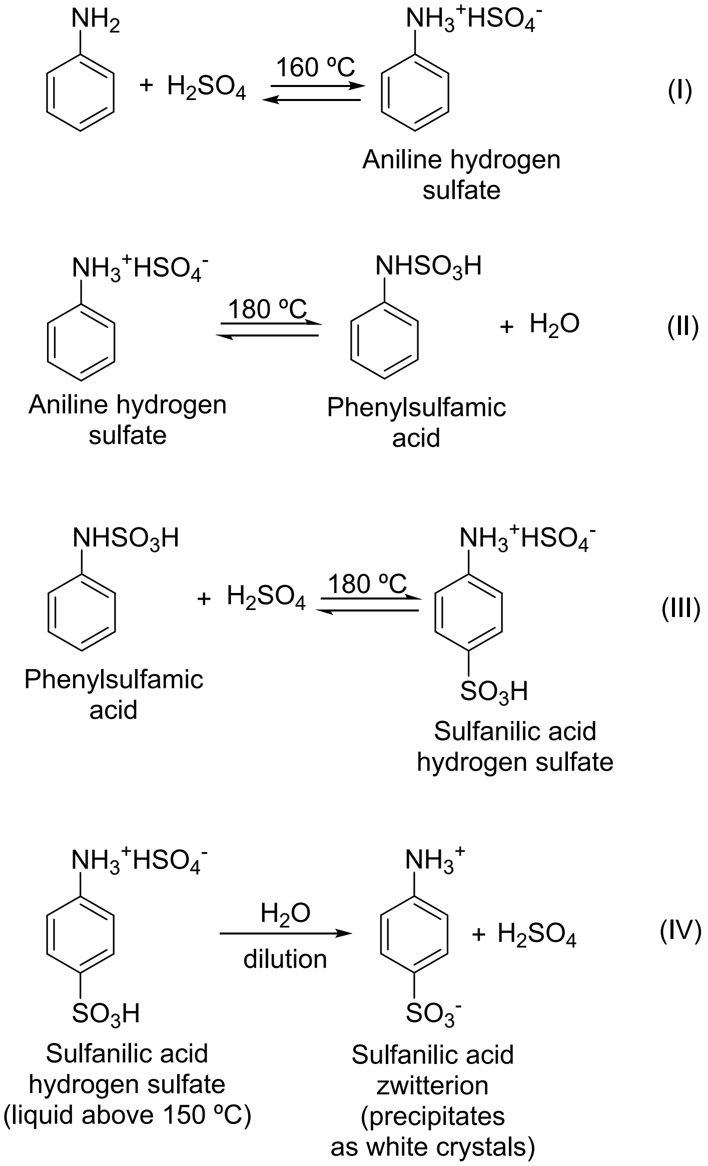


Figure S4. Images of experiment 9 at 6 min., 19 min. and 4.39 h (from left to right).

Figure S5. Images of experiment 13 at 0 h, 18 min., 30 min., 52 min., 1.36 h and 5.5 h (from left to right).

4. Four-stage reaction sequence for the synthesis of sulfanilic acid in sulfuric acid solvent [aniline: sulfuric acid ratio (1:2.65)][1]



5. Images of the sulfanilic acid obtained in experiments 10, 11 and 13

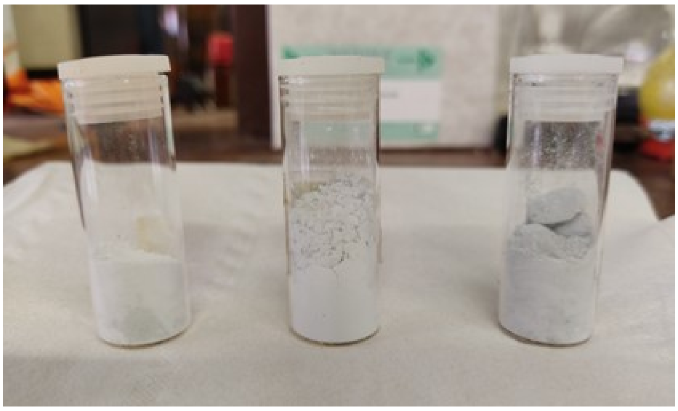


Figure S6. Sulfanilic acid obtained in experiments 10, 11 and 13 (from left to right) after dilution with water and filtration of the precipitated SA as the insoluble zwitterion.

6. NMR spectra

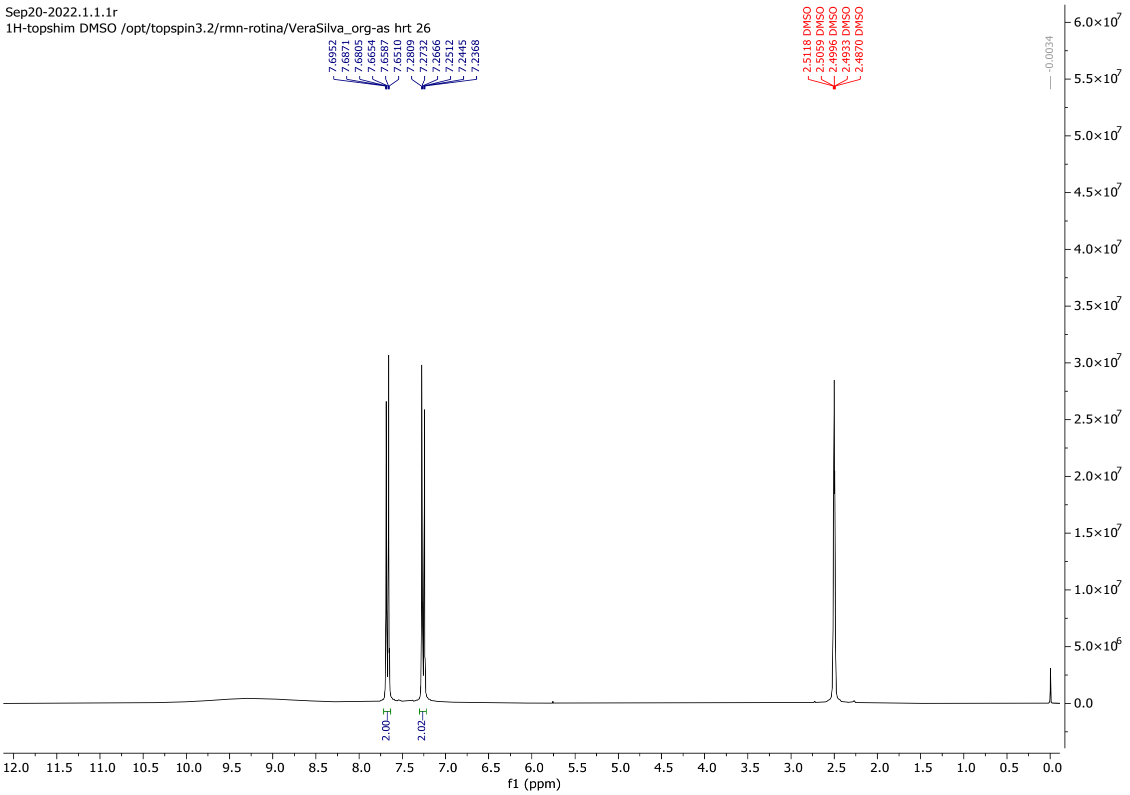


Figure S7. ^{1}H-NMR spectrum of pure sulfanilic acid used as reference (300.13 MHz, DMSO-d_6).

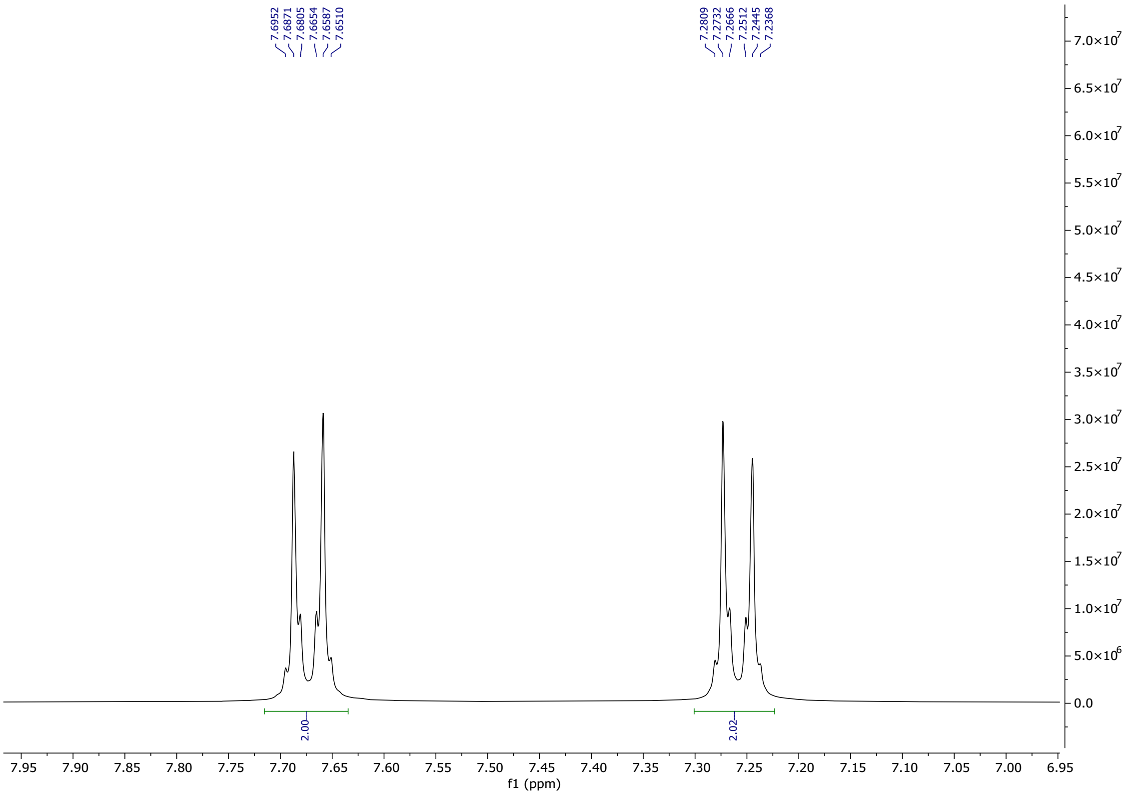


Figure S8. Expansion of the ^{1}H-NMR spectrum of pure sulfanilic acid used as reference (300.13 MHz, DMSO-d_6).

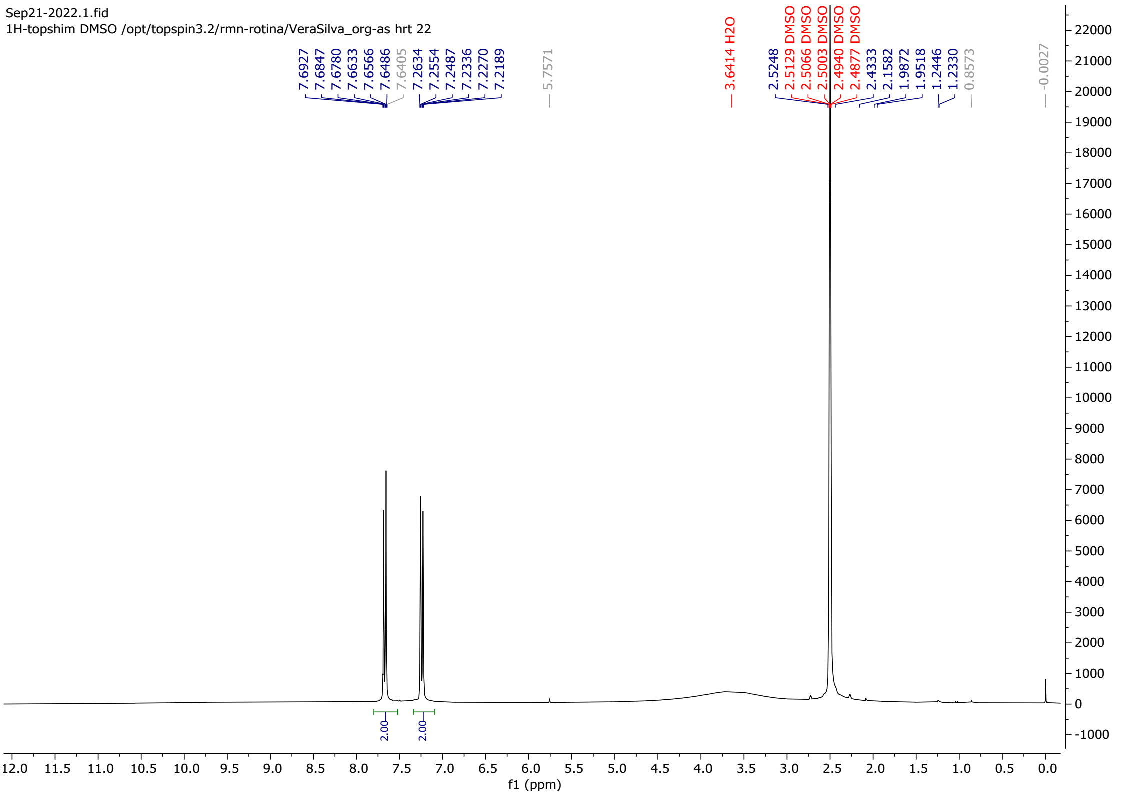


Figure S9. ^{1}H-NMR spectrum of sulfanilic acid isolated in the experiment 11 (300.13 MHz, DMSO-d_6).

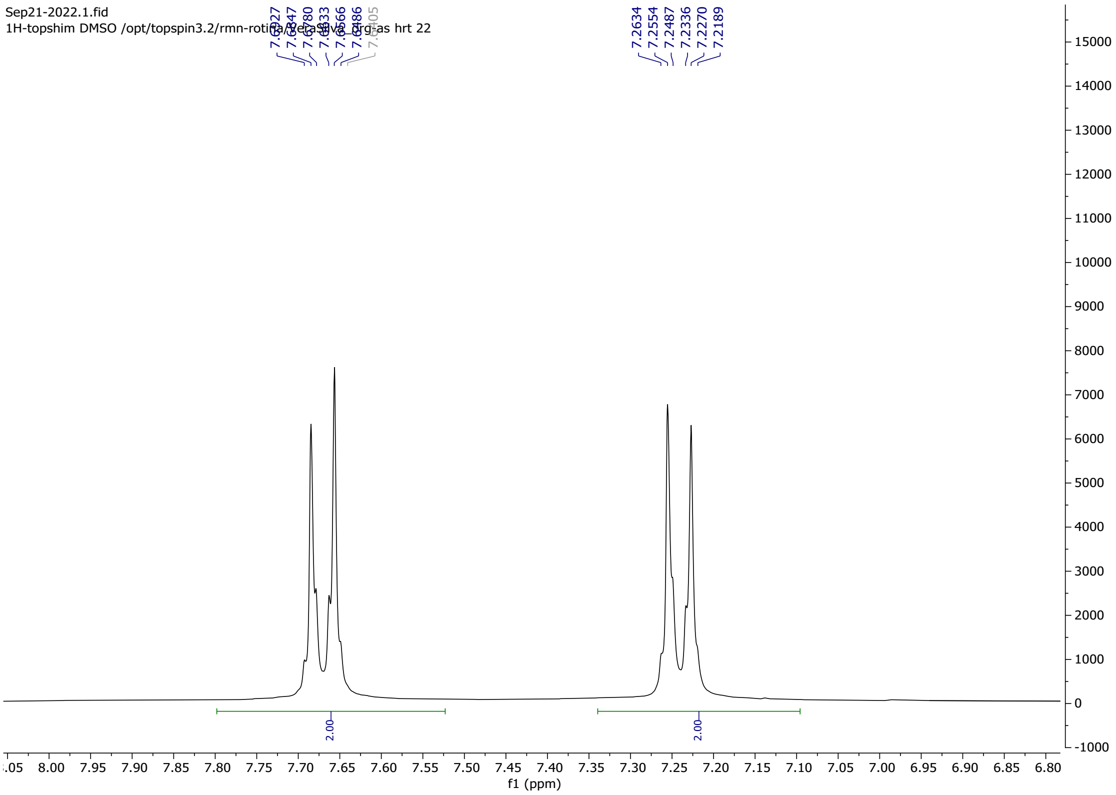


Figure S10. Expansion of ^{1}H-NMR spectrum of sulfanilic acid isolated in the experiment 11 (300.13 MHz, DMSO-d$_6$).

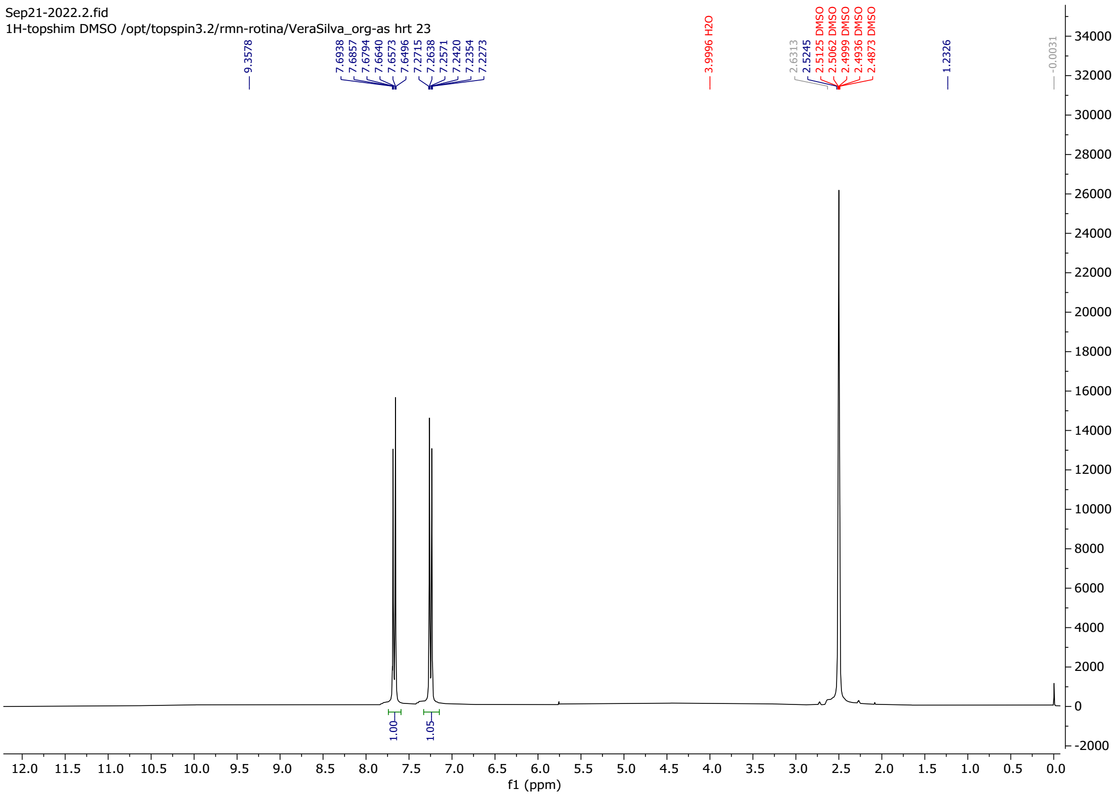


Figure S11. ^{1}H-NMR spectrum of sulfanilic acid isolated in the experiment 13 (300.13 MHz, DMSO-d$_6$).

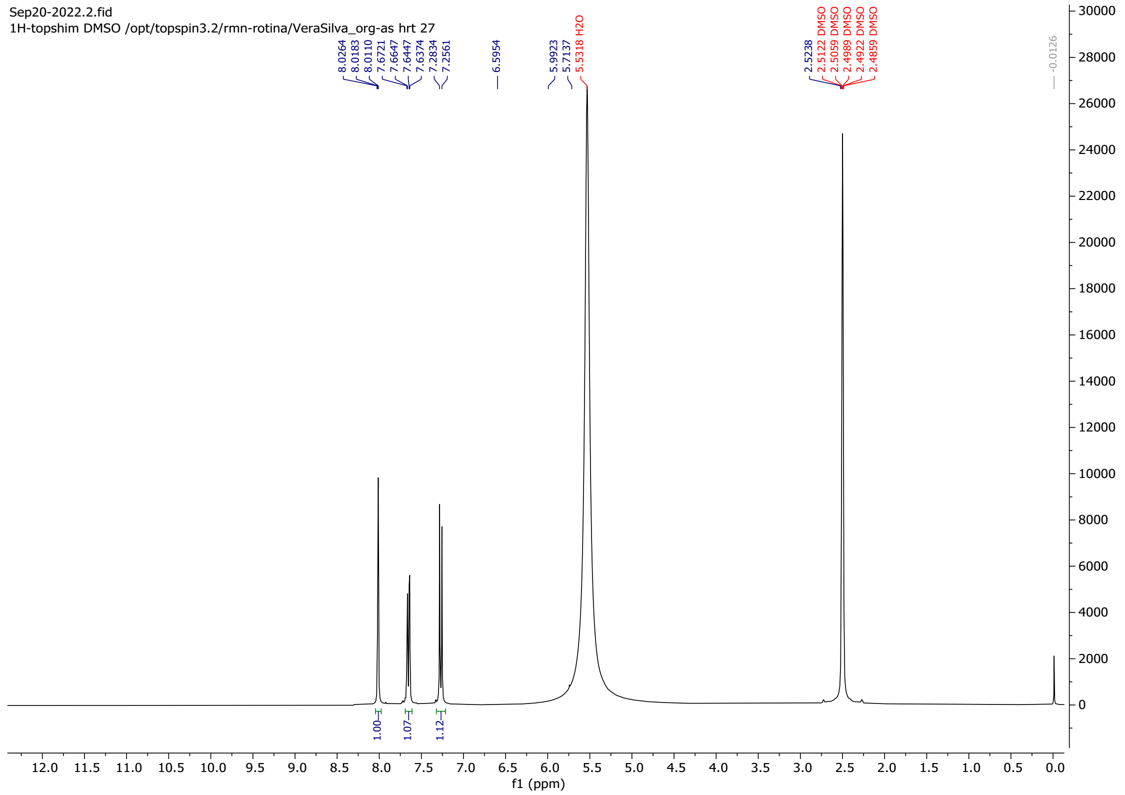


Figure S12. ^{1}H-NMR spectrum of pure 4-aminobenzene-1,3-disulfonic acid used as reference (300.13 MHz, DMSO-d$_6$).

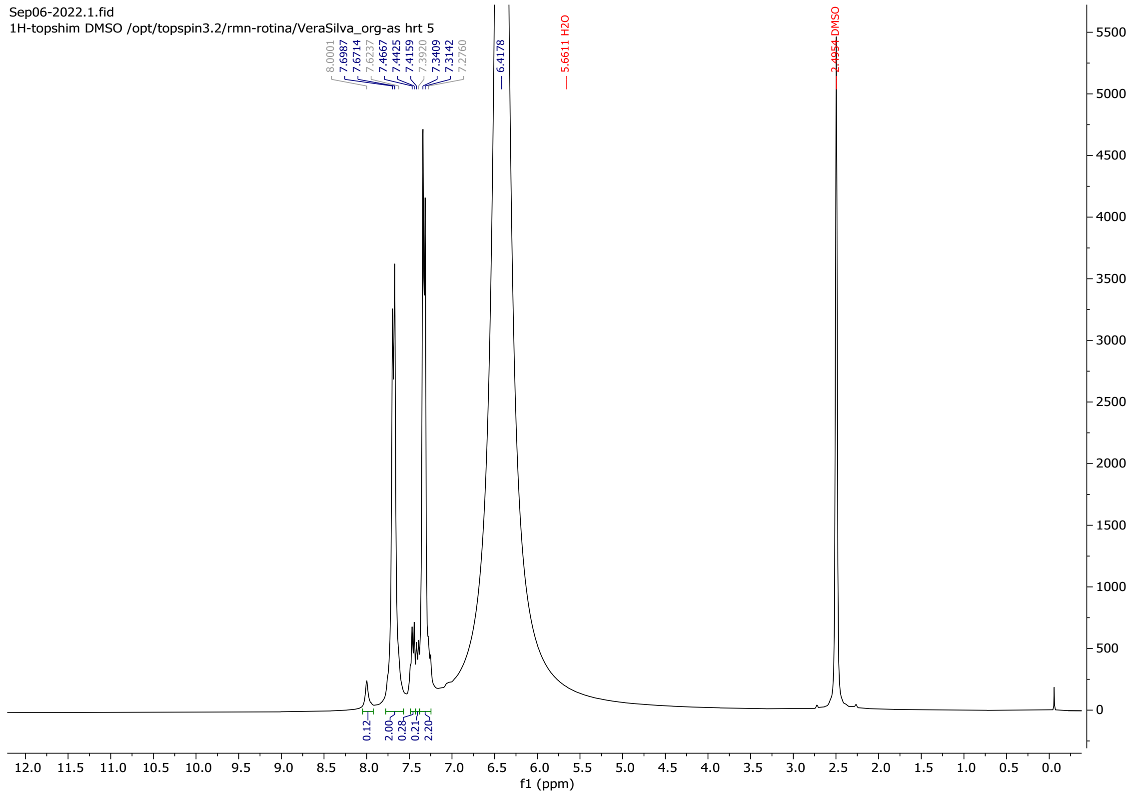
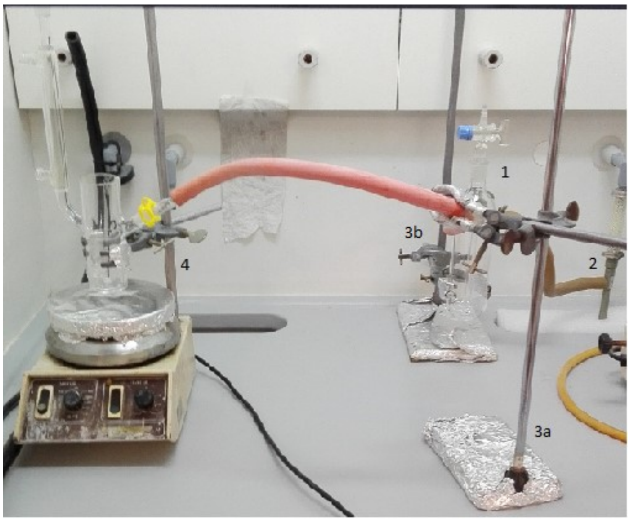


Figure S13. ^{1}H-NMR spectrum of the product obtained in experiment 10 (300.13 MHz, DMSO-d$_6$).

7. Experimental setup of the experiments using vacuum



1 – Trap

2 – Vacuum System

3a e 3b – Supports

4 – Adapter

Figure S14. Experimental setup for the experiments performed using vacuum to promote the splitting of water.

8. Images of the electrodes

Figure S15. Rectangular (left) and cylindrical (right) stainless steel 316 electrodes.

9. Structure of sulfanilic acid

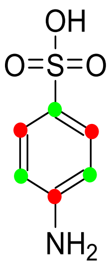


Figure S16. Directing effects of the substituent groups in the structure of sulfanilic acid.

10. Images of the sulfonation of aniline using conventional heating

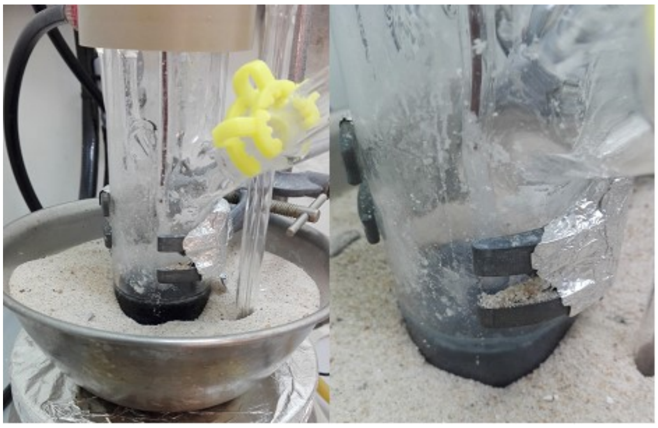


Figure S17. Sulfonation of aniline using the conventional heating method.

11. Chromatograms of experiments 1-13

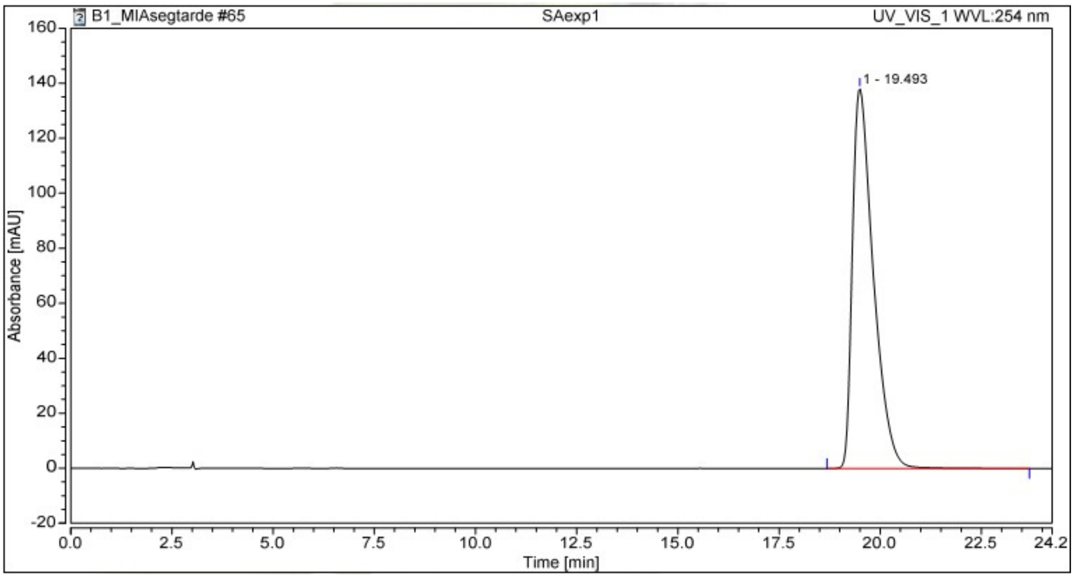


Figure S18. Chromatogram of the product obtained in experiment 1. Relative area: 100% of aniline (**1**).

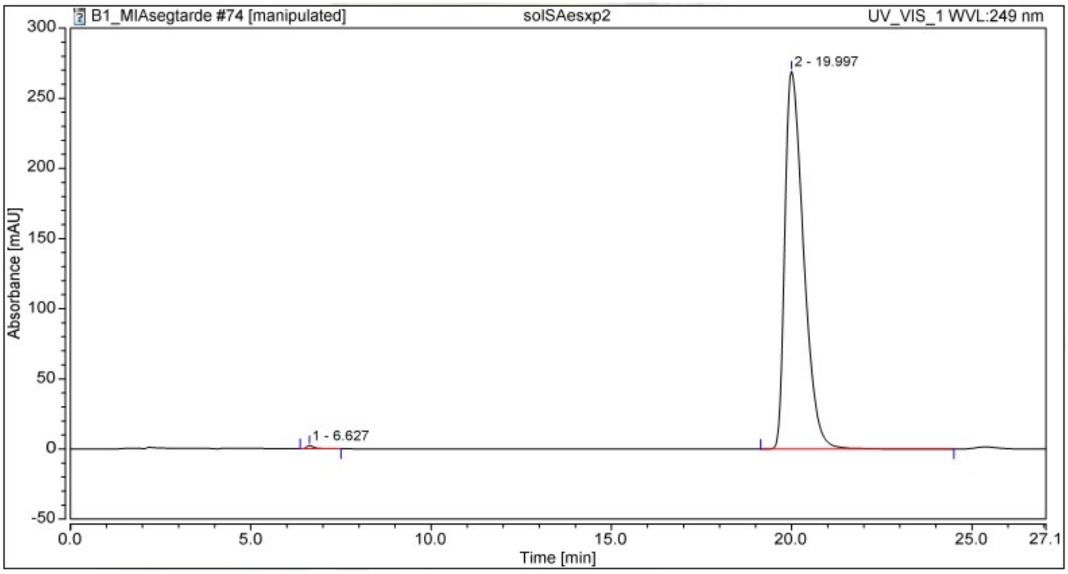


Figure S19. Chromatogram of the product obtained in experiment 2. Relative areas: SA (**2**) (0.3%) and aniline (**1**) (99.7%) .

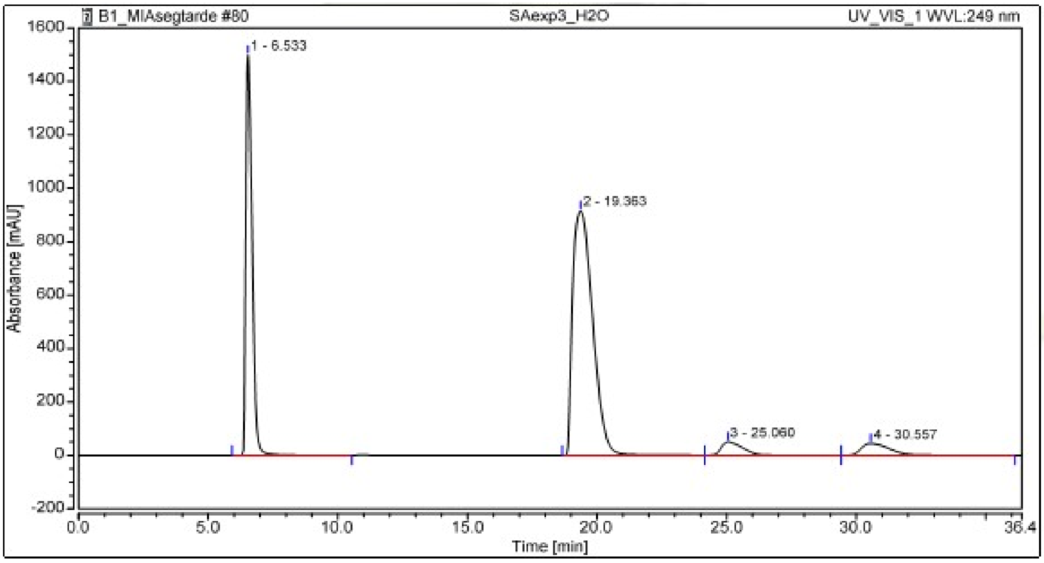


Figure S20. Chromatogram of the product obtained in experiment 3. Relative areas: SA (**2**) (28.3%), aniline (**1**) (65.5%), 1,3-ADS (**5**) (2.9%) and 2-aminobenzenesulfonic acid (**4**) (3.3%).

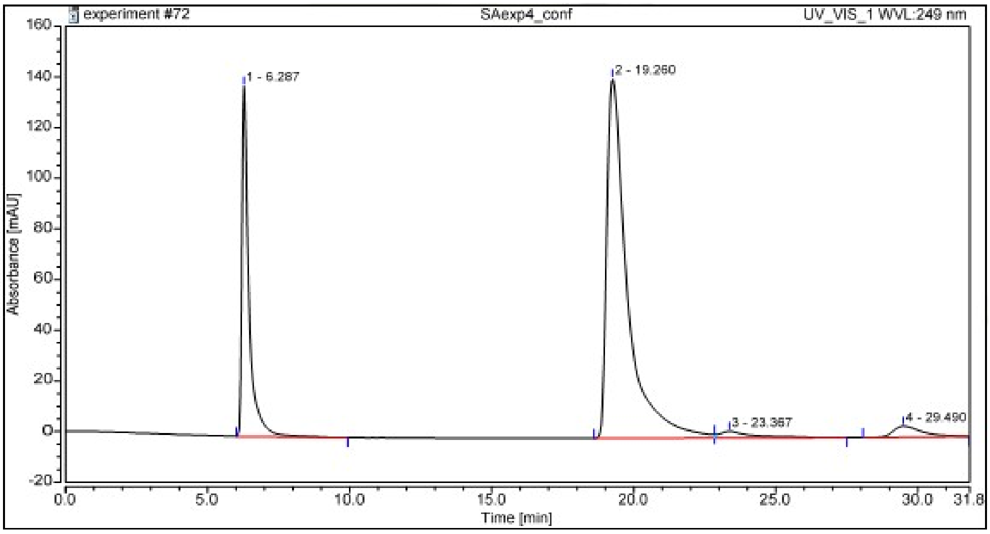


Figure S21. Chromatogram of the product obtained in experiment 4. Relative area: SA (**2**) (23.4%), aniline (**1**) (71.5%), 1,3-ADS (**5**) (2.1%) and 2-aminobenzenesulfonic acid (**4**) (3.0%).

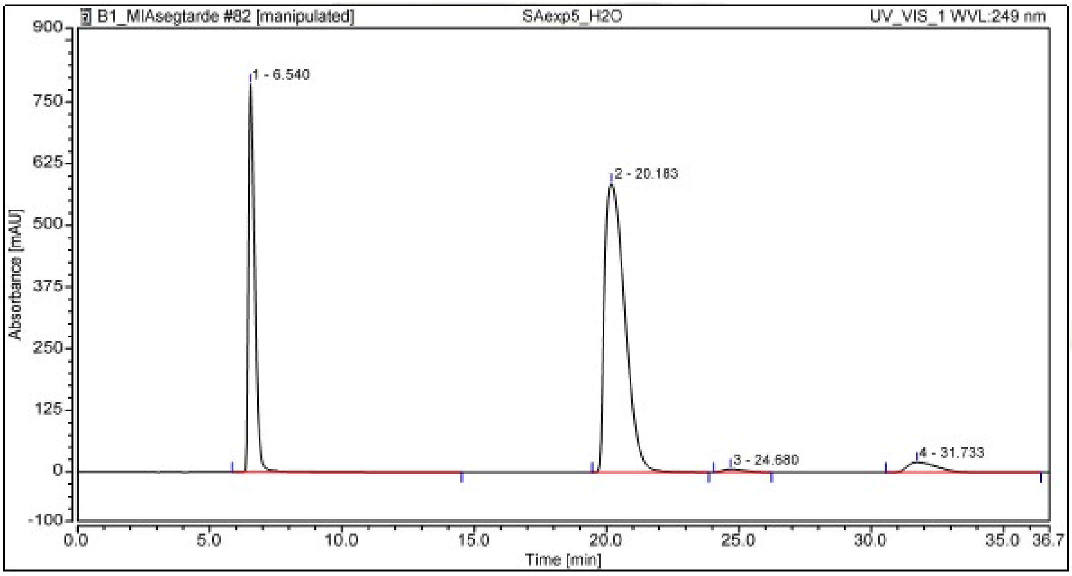


Figure S22. Chromatogram of the product obtained in experiment 5. Relative areas: SA (**2**) (28.1%), aniline (**1**) (67.5%), 1,3-ADS (**5**) (0.8%) and 2-aminobenzenesulfonic acid (**4**) (3.7%).

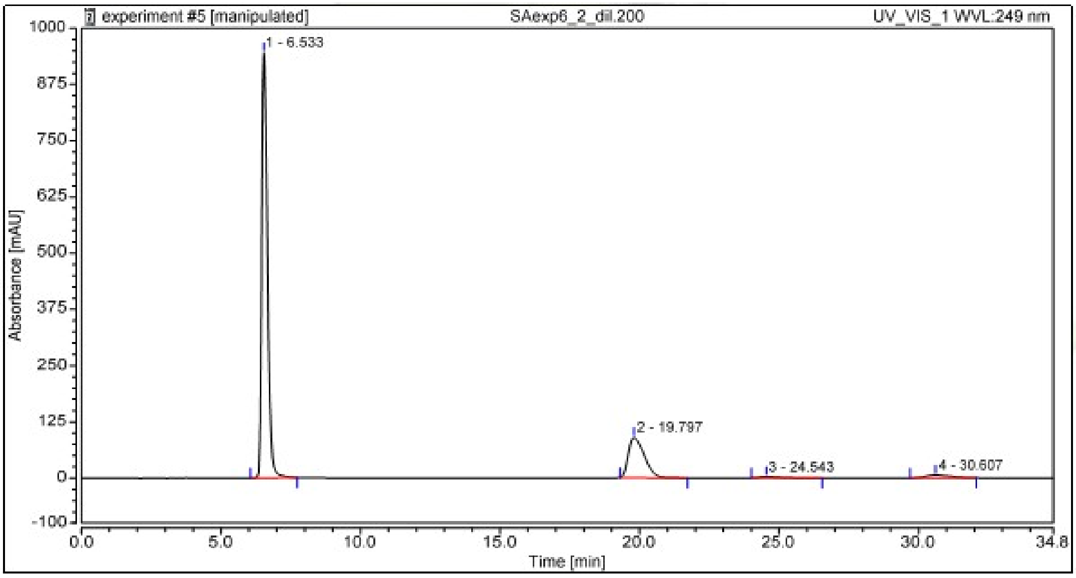


Figure S23. Chromatogram of the product obtained in experiment 6. Relative areas: SA (**2**) (76.6%), aniline (**1**) (20.4%), 1,3-ADS (**5**) (0.8%) and 2-aminobenzenesulfonic acid (**4**) (2.2%).

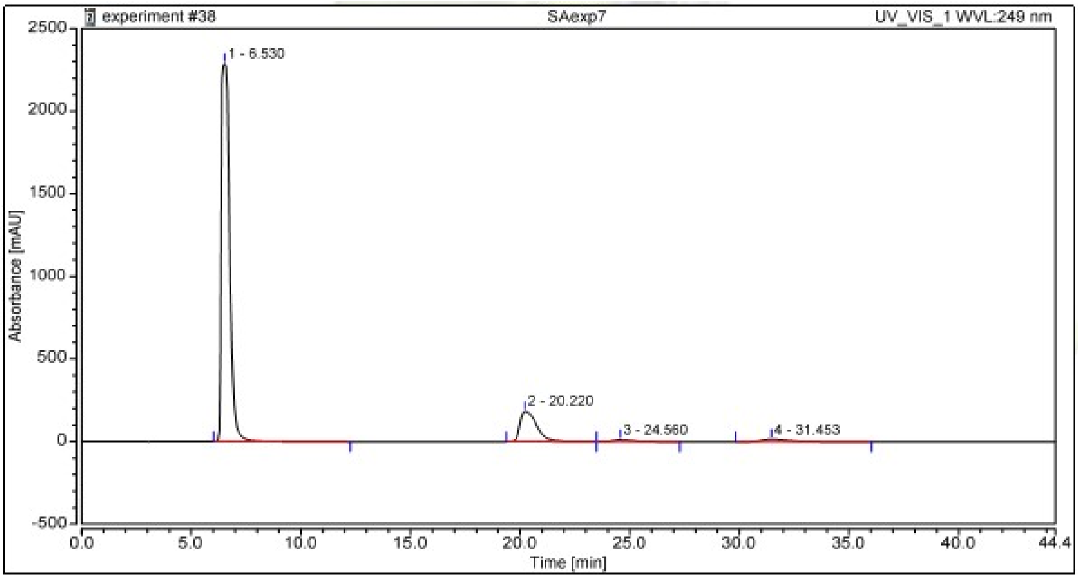


Figure S24. Chromatogram of the product obtained in experiment 7. Relative areas: SA (**2**) (83.8%), aniline (**1**) (13.5%), 1,3-ADS (**5**) (0.9%) and 2-aminobenzenesulfonic acid (**4**) (1.8%).

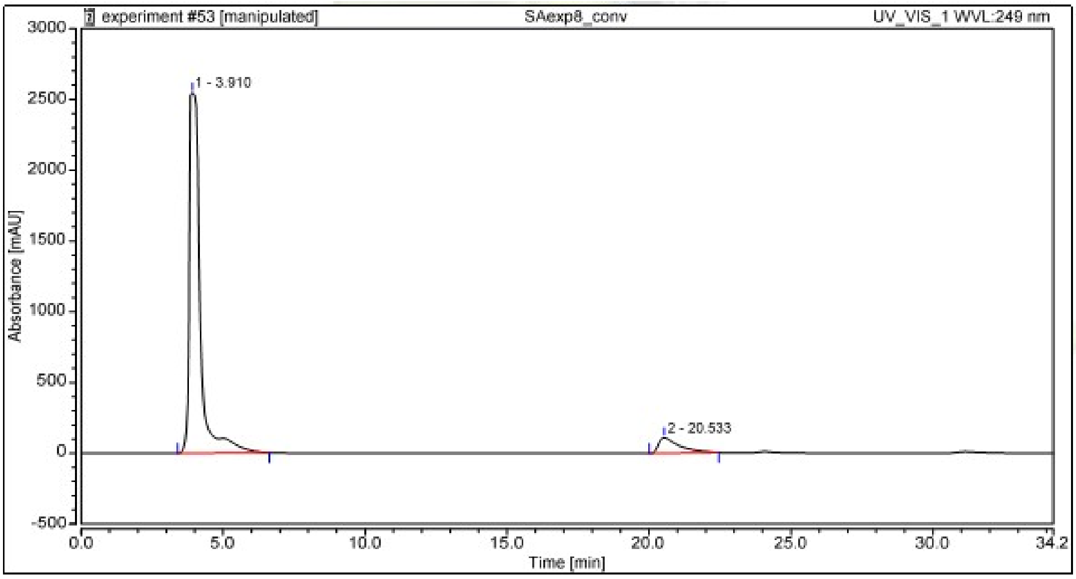


Figure S25. Chromatogram of the product obtained in experiment 8. Relative areas: SA (**2**) (93.2%) and aniline (**1**) (6.8%).

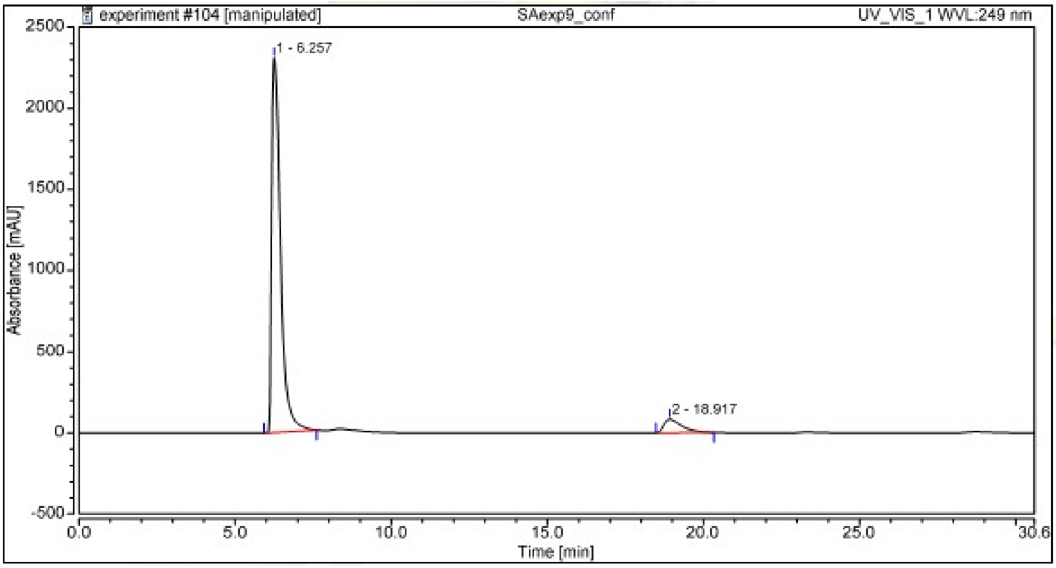


Figure S26. Chromatogram of the product obtained in experiment 9. Relative areas: SA (**2**) (91.3%) and aniline (**1**) (7.6%) and 2-aminobenzenesulfonic acid (**4**) (1.1%).

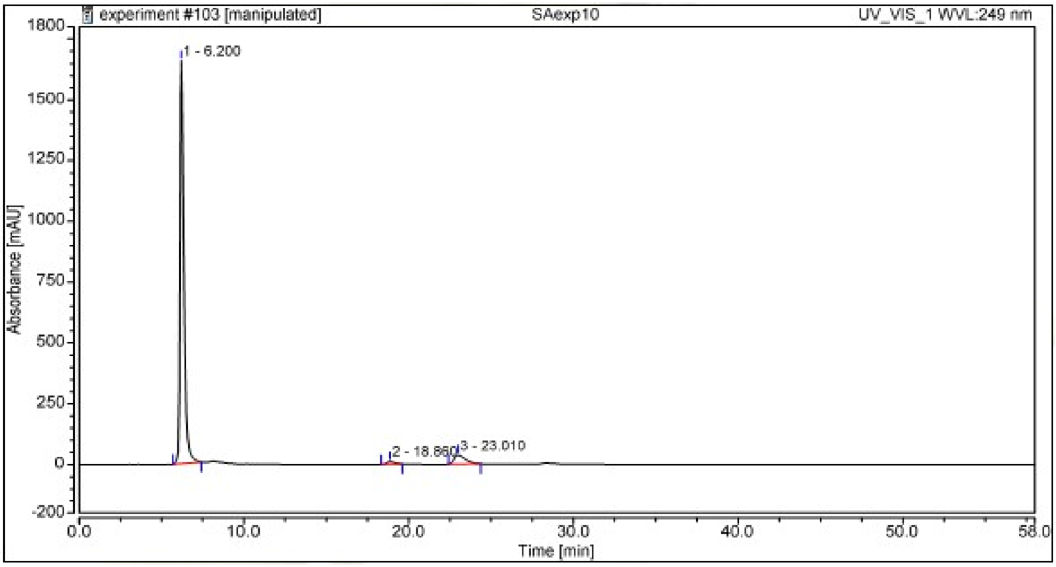


Figure S27. Chromatogram of the product obtained in experiment 10. Relative area: SA (**2**) (92.3%), aniline (**1**) (1.3%) and 1,3-ADS (**5**) (6.4%).

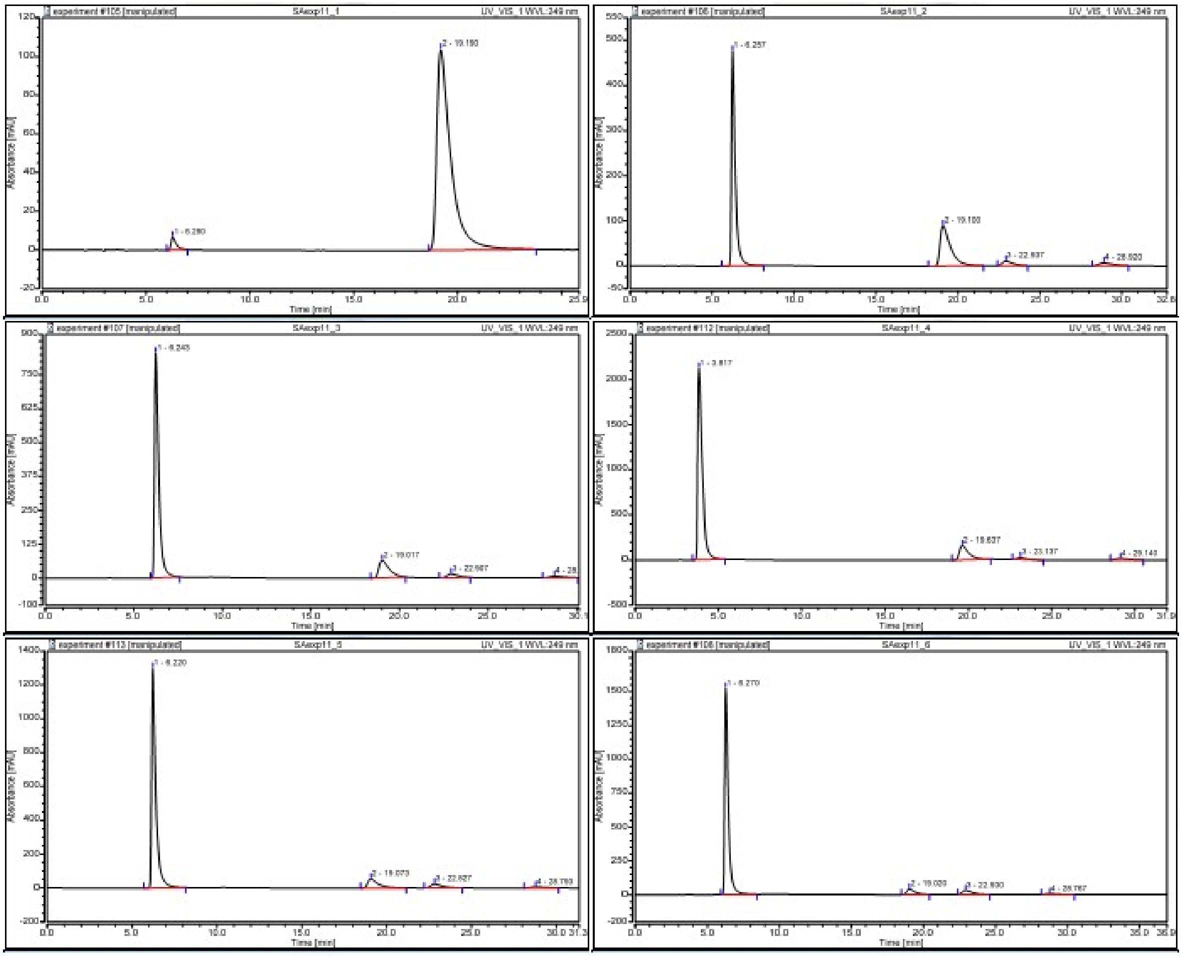


Figure S28. Chromatograms of the samples analyzed during experiment 11. Samples taken every 30 min until 2.5 h of heating.[1]

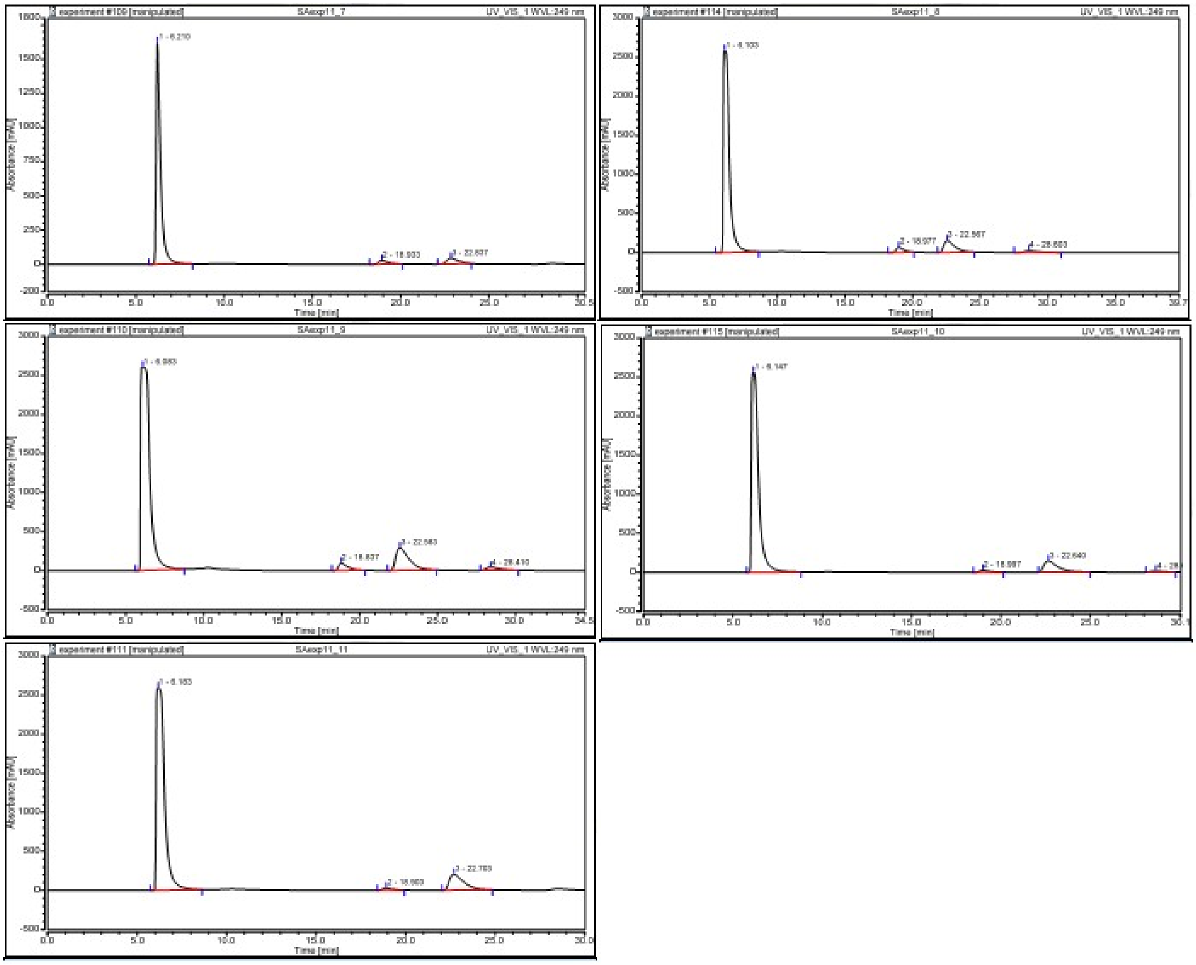


Figure S29. Chromatograms of the samples analyzed during experiment 11. Samples taken every 30 min from 3 h to 5 h of heating.[1]

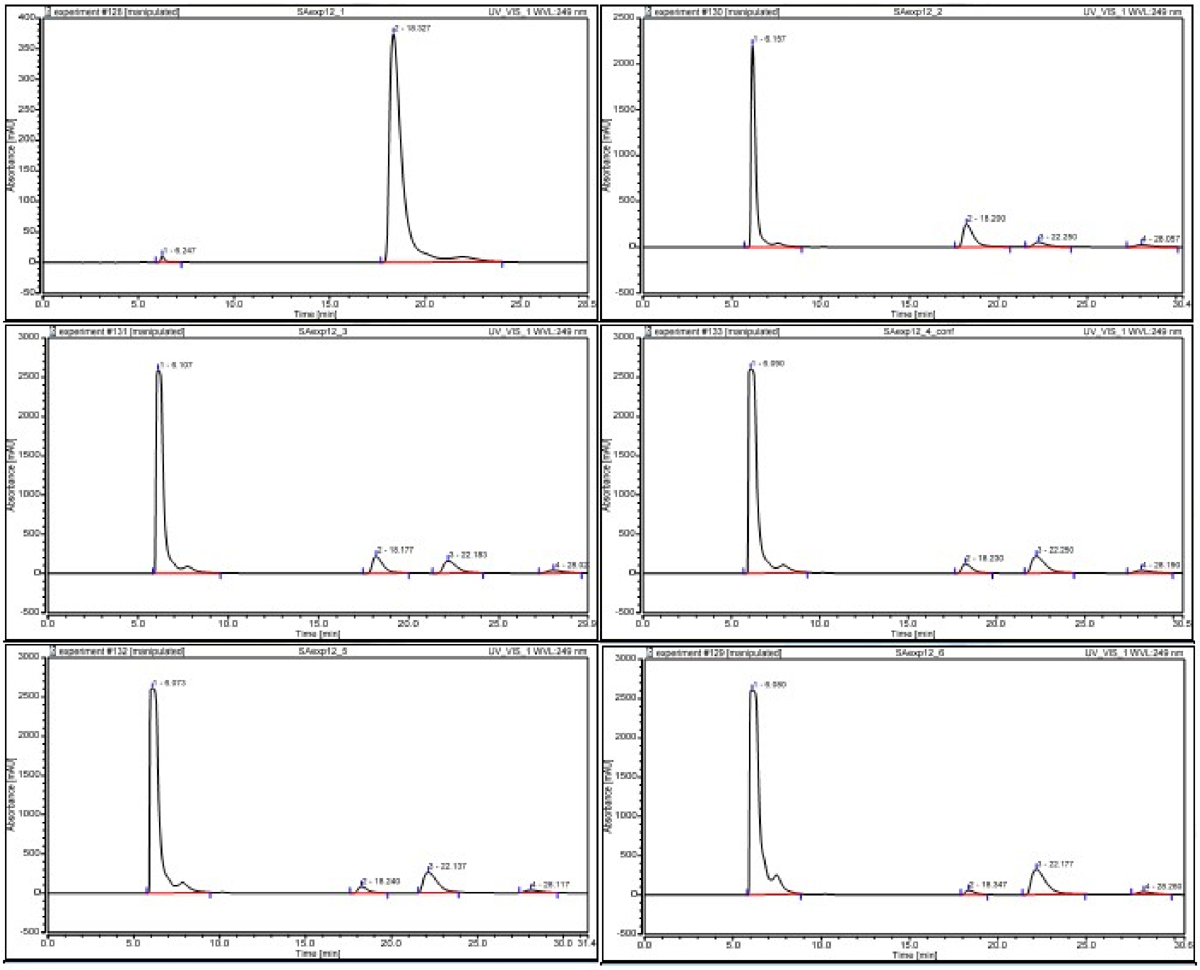


Figure S30. Chromatograms of the samples analyzed during experiment 12. Samples taken every 1 h until 5 h of heating.[1]

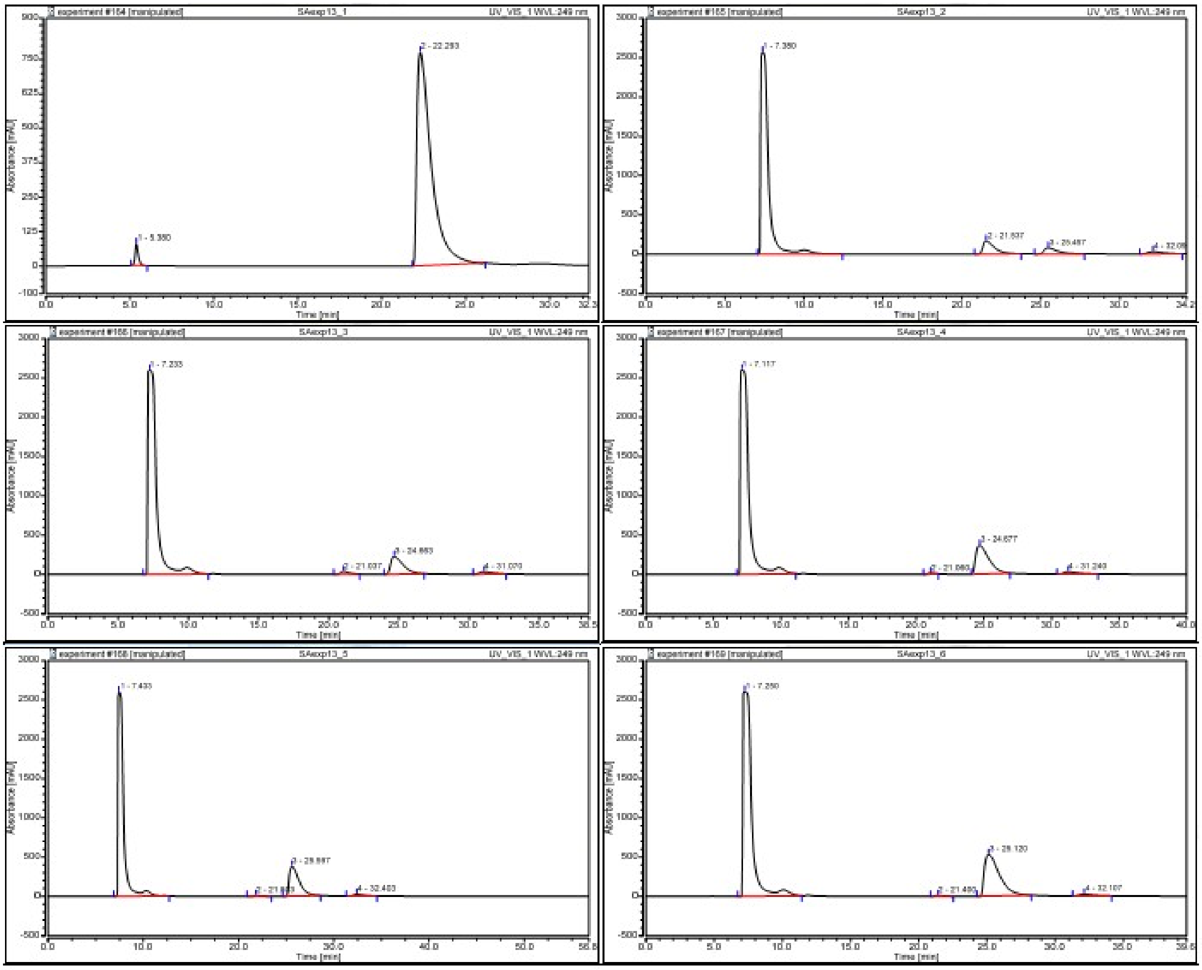


Figure S31. Chromatograms of the samples analyzed during experiment 13. Samples taken every 1 h until 5.29 h of heating.[1]

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[1] The chromatograms of Figures S28-S31, are organized by increasing reaction time from left to right and up to down. Peaks in all chromatograms are numbered sequentially and those numbers do not correspond to the compounds' numbers given in the paper.

12. References

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[1] Lund, R. B.; Pass, M. C. Production of sulfonated amines, Patent US4808342A, 1989.