

Heterogeneous Brønsted catalysis in the solvent-free and multigram-scale synthesis of polyalcohol acrylates: the case study of trimethylolpropane triacrylate

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Table S1. Protic ion exchange resin characteristics ^a.

	Amberlite™ 120 IR (H⁺)	Amberlyst® 15	DOWEX™ 50WX8	Units
Particle size	28-35	>50	50-100	mesh
	420-590	<300	150-300	µm
Matrix copolymer	Styrene-divinylbenzene (gel)	Styrene-divinylbenzene (macroreticular)	Styrene-divinylbenzene (gel)	–
Crosslinking degree	8	20	8	%
Water retention capacity	53-58	5	50-56	%
Total exchange capacity	1.8	1.7	1.1	meq/mL

^a Physical form: beads; ionic form: H⁺ (functional group: sulfonic acid)

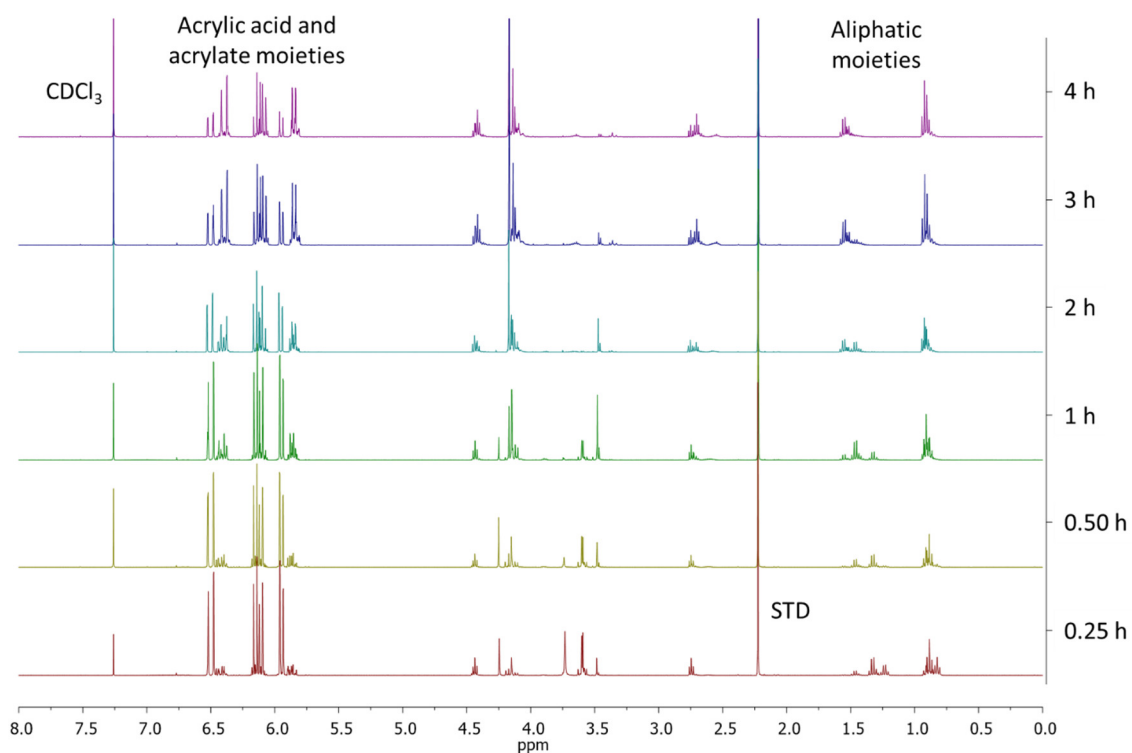


Figure S1. ^1H NMR spectra over reaction time.

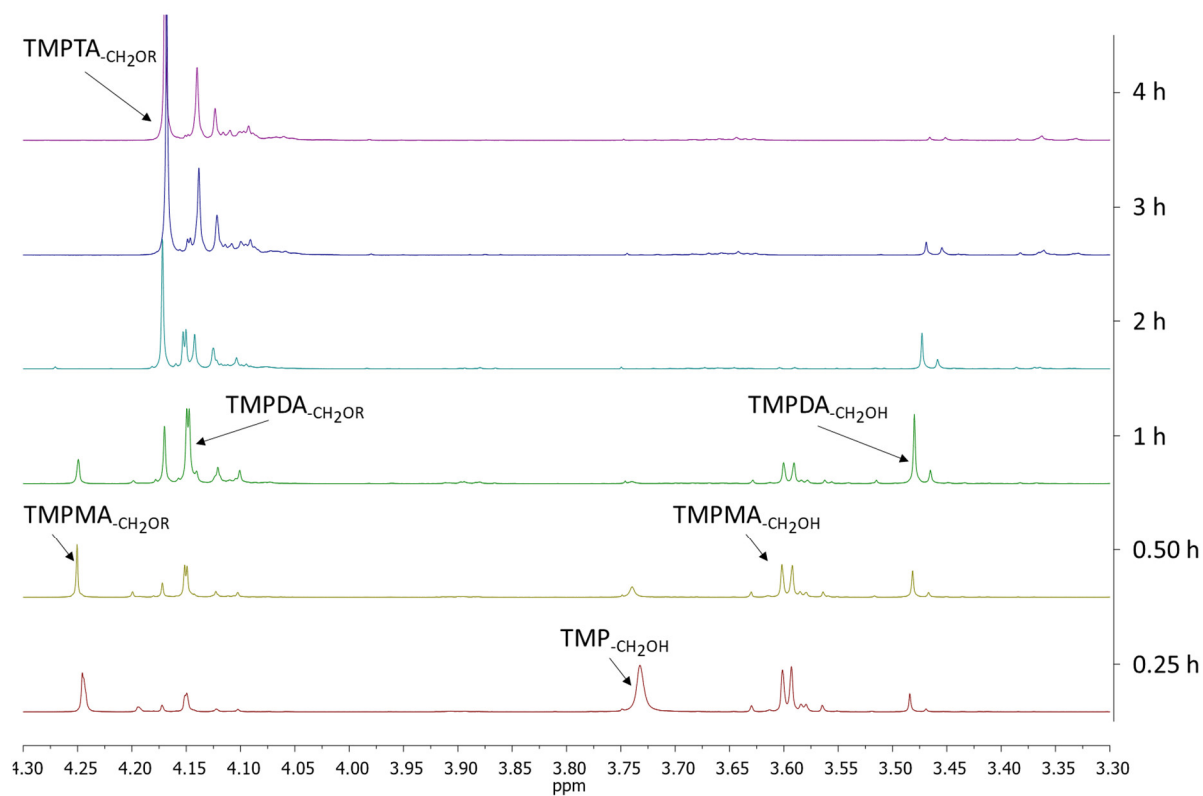


Figure S2. Relevant portion of ^1H NMR over reaction time.

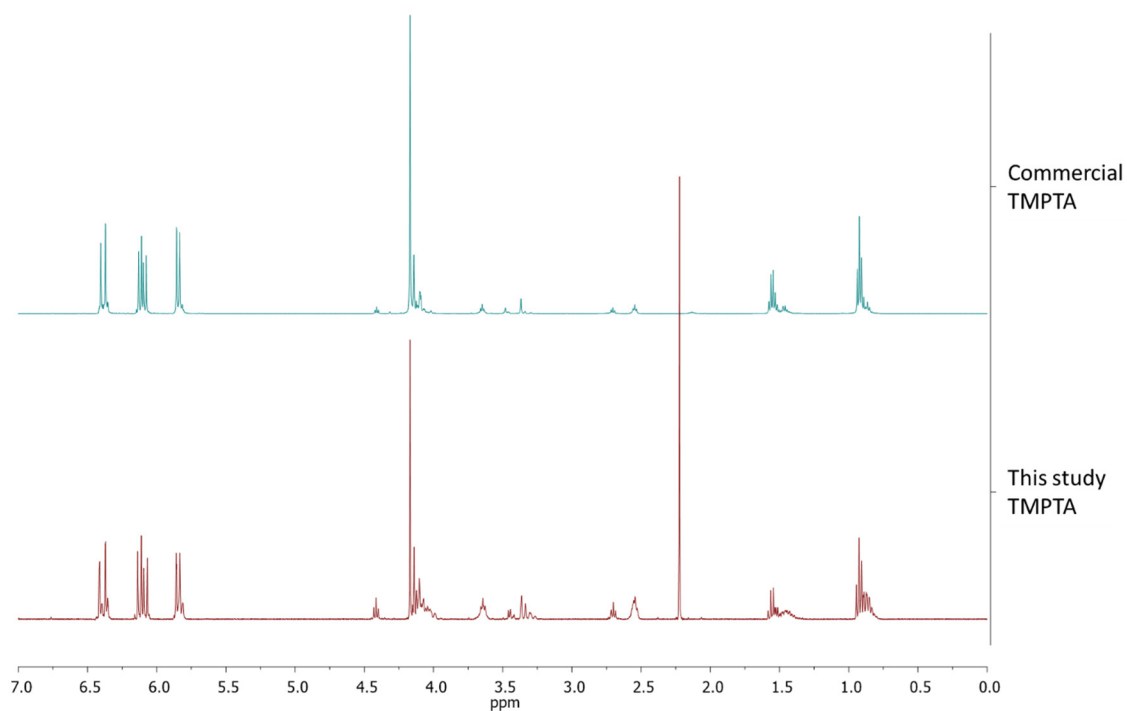


Figure S3. ^1H NMR spectra of the reaction mixture after 4 h in optimized conditions and acrylic acid distillation (bottom, red), and commercial TMPTA (top, cyan).

Signals at 4.42, 3.64, 2.70, 2.55 ppm (common in both spectra) are relative to acrylic contaminants: acrylic acid esteric dimers, and β -hydroxyacids (water addition to acrylic acid), which are ubiquitous contaminants in aged acrylic acid.

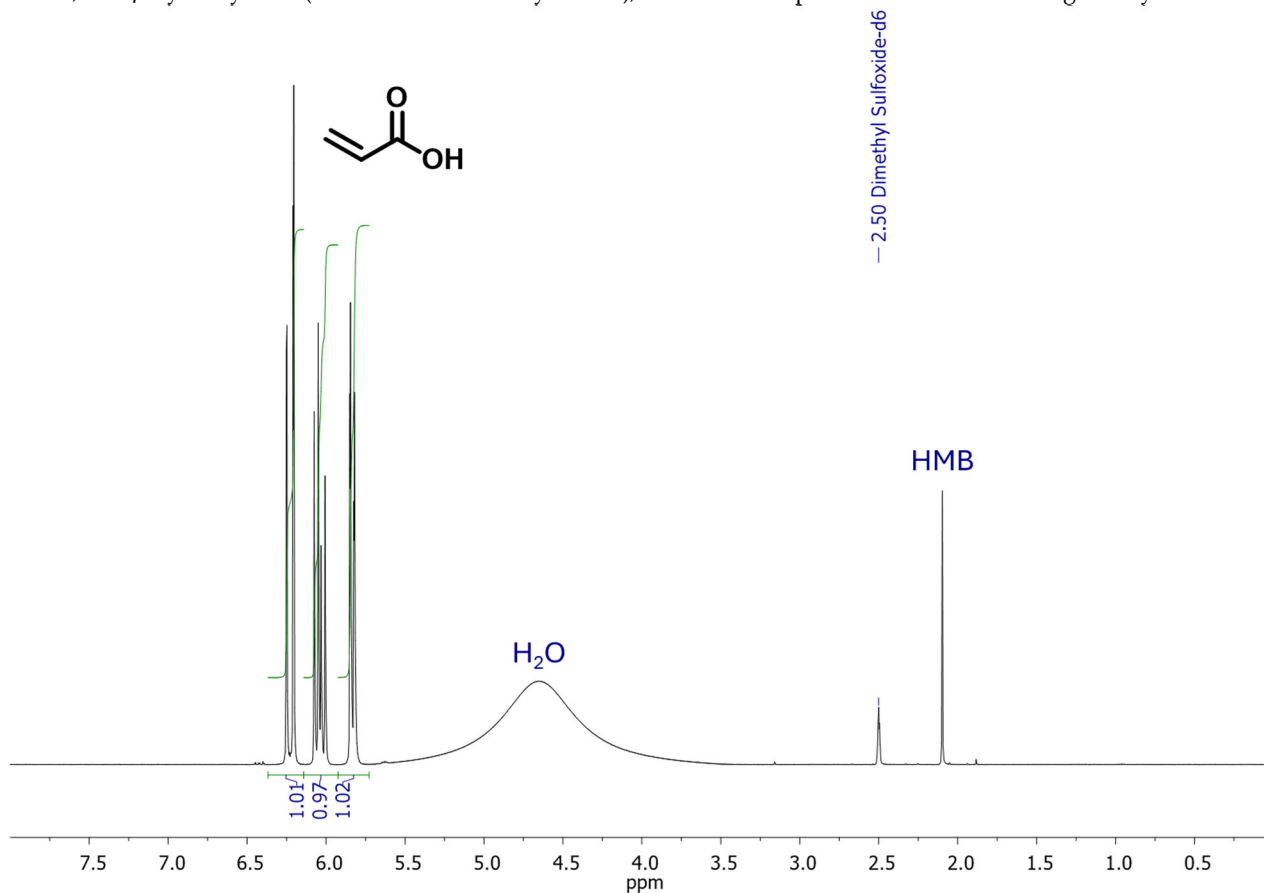


Figure S4. ^1H NMR of distilled acrylic acid after reaction time.

^1H NMR (400 MHz, DMSO) δ 6.23 (dd, $J = 17.3, 1.7$ Hz, 1H), 6.04 (dd, $J = 17.3, 10.3$ Hz, 1H), 5.83 (dd, $J = 10.3, 1.7$ Hz, 1H).

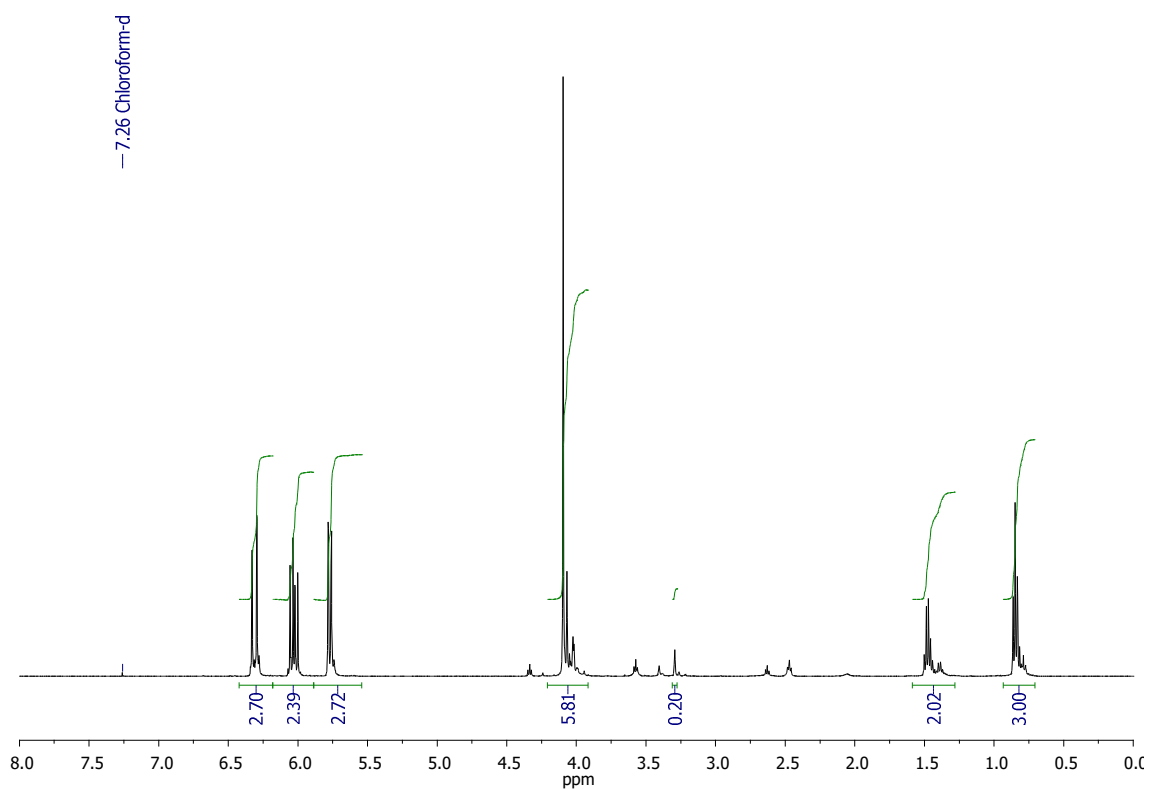


Figure S5. ¹H NMR of commercial TMPTA (Frimpeks TR, Turkey) used as reference 100 mg in 600 μ L CDCl₃. Estimated composition: 96% TMPTA, 4% TMPDA.

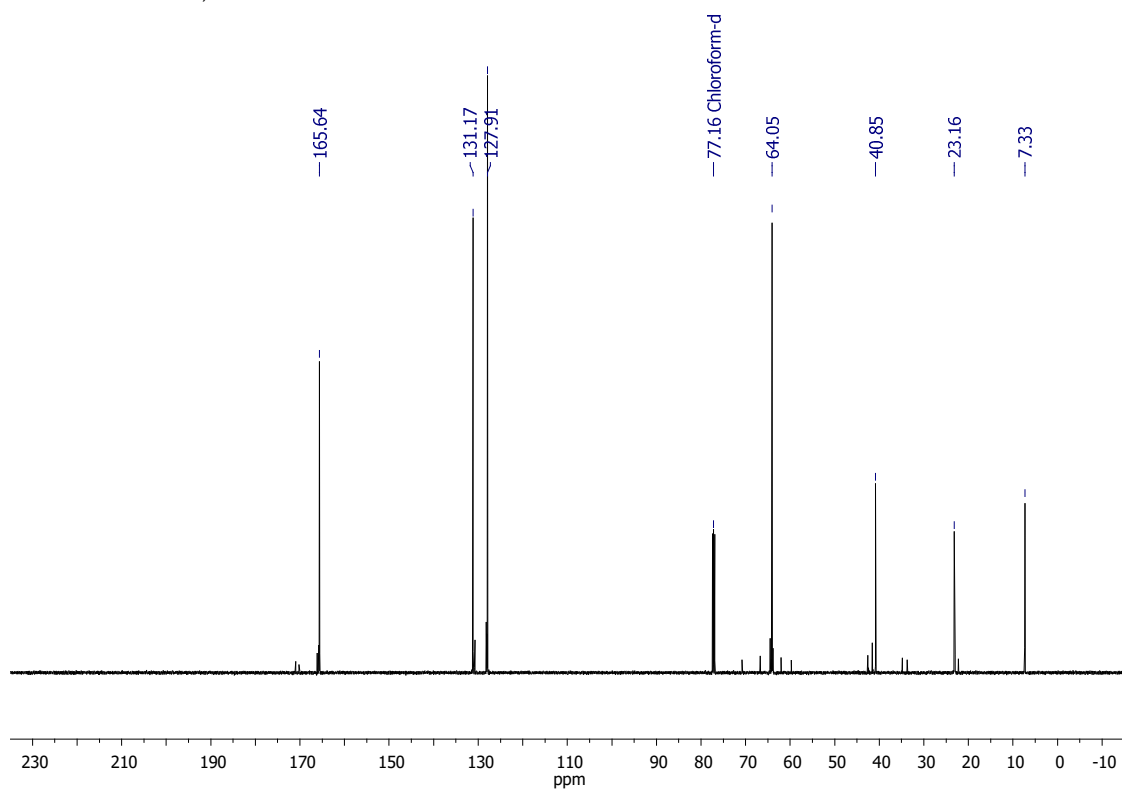


Figure S6. ¹³C NMR of commercial TMPTA (Frimpeks TR, Turkey,) used as reference, 100 mg in 600 μ L CDCl₃. Estimated composition: 96% TMPTA 4% TMPDA.

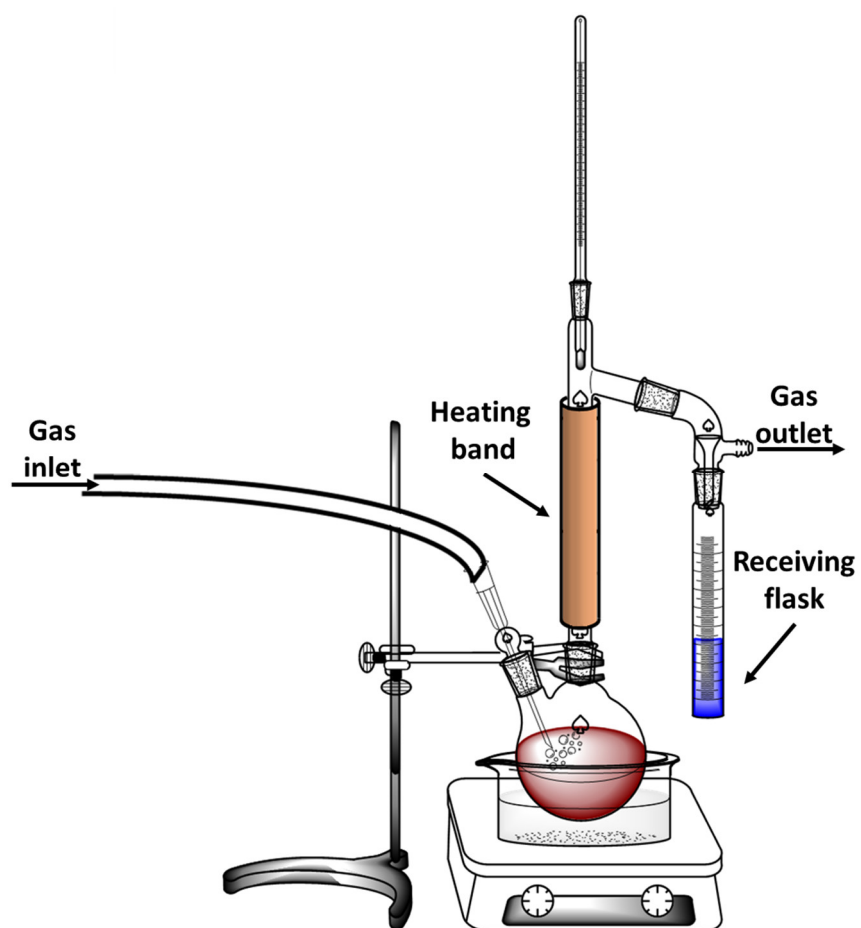


Figure S7. Reaction setup scheme with magnetic stirrer.

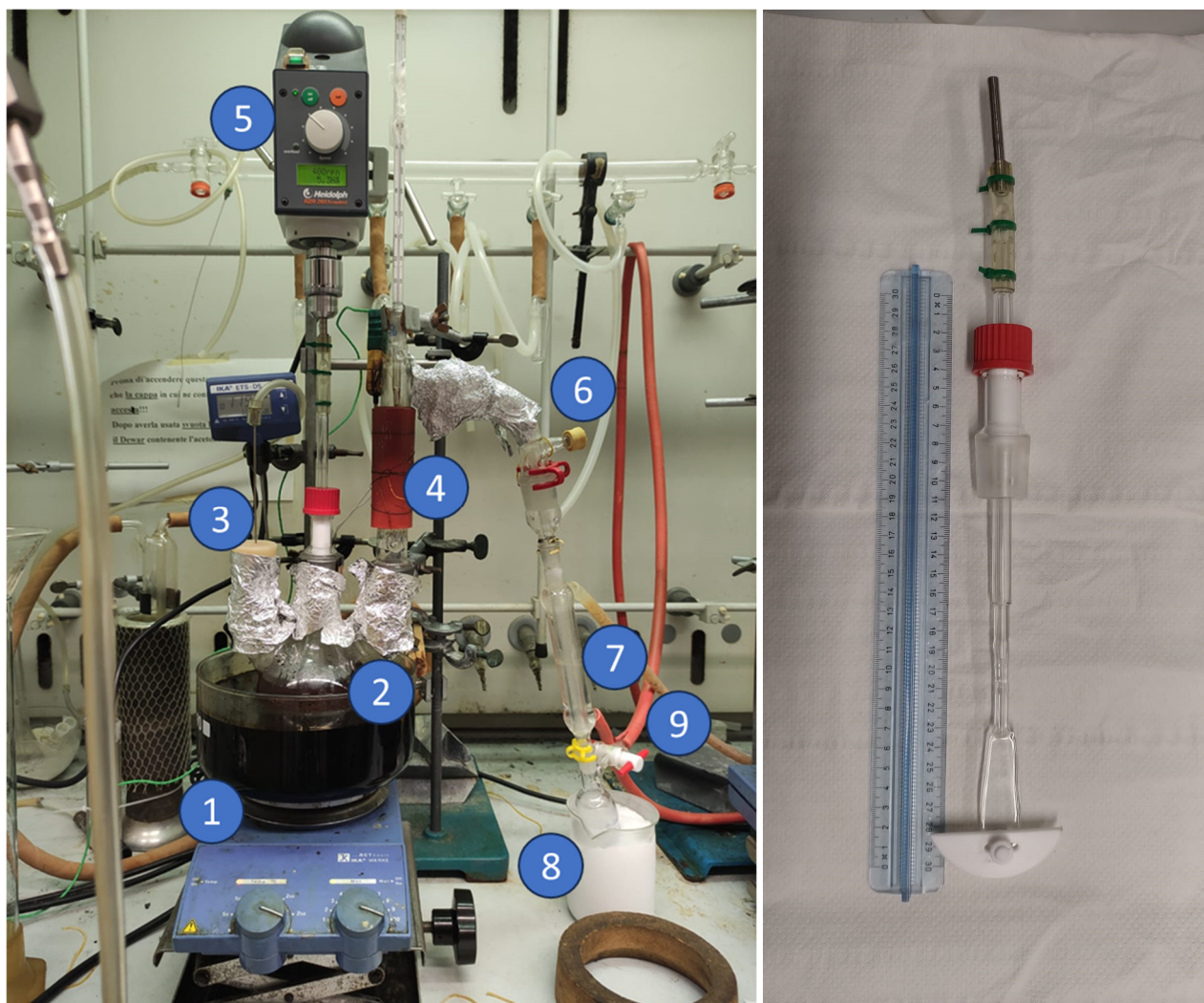


Figure S8. Left, reaction apparatus overview with a mechanical stirrer; right, details of mechanical stirrer used.

1) Heating plate; 2) round-bottom flask; 3) purging needle; 4) heating band; 5) mechanical stirrer; 6) vacuum hose connection (not connected in the picture); 7) water-condenser; 8) receiving flask in dry-ice bath; 9) vapor outlet hose.

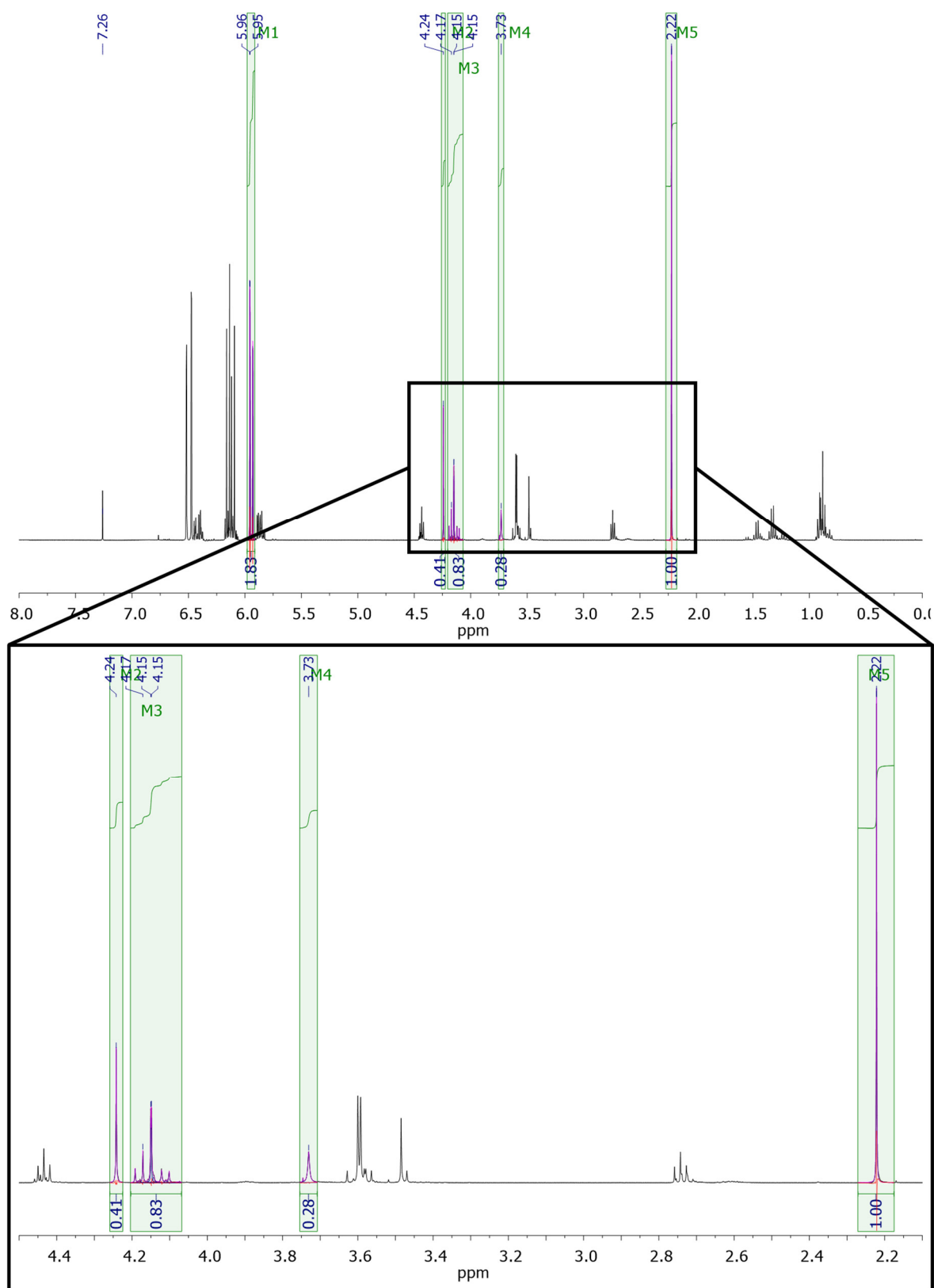


Figure S9. Example of ^1H NMR spectra analysis: integration and signal deconvolution.

A sample withdrawn from the reaction mixture after 30 min is diluted in CDCl_3 and analysed by ^1H NMR by the addition of a standard solution (hexamethylbenzene 0.1 M in CDCl_3). Here is reported the spectrum obtained (reaction conditions: cat IR 120 10%_{wt}, molar ratio TMP to AA 1 : 6, stripping condition, 0.5 h, 120 °C).