

SUPPORTING INFORMATION

An Investigation of Wall Effects in Microwave-Assisted Ring-Closing Metathesis and Cyclotrimerization Reactions

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General Experimental Details: ^1H NMR and ^{13}C NMR spectra were recorded on a 300/360 MHz instrument at 300/360 and at 75/90 MHz, respectively. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, t, q and m are used to indicate singlet, doublet, triplet, quadruplet and multiplet. Low resolution mass spectra were obtained on a LC/MS instrument using atmospheric pressure chemical ionization (APCI) in positive or negative mode. Analytical HPLC analysis was carried out on a C18 reversed-phase (RP) analytical column (119×3 mm, particle size 5 mm) or a reversed-phase column (150×4.6 mm, particle size 5 mm) at $25\text{ }^\circ\text{C}$ using a mobile phase A (water/acetonitrile 90:10 (v/v) + 0.1 % TFA) and B (MeCN + 0.1 % TFA) at a flow rate of 1 mL/min. The following gradient was applied: linear increase from solution 30% B to 100 % B in 6 min, hold at 100% solution B for 2.2 min. GC-MS conditions were as follows: splitless injection, injection temperature $250\text{ }^\circ\text{C}$, HP-5 MS column ($30\text{m} \times 0.25\text{mm}$ ID, $0.25\text{ }\mu\text{m}$ film); carrier gas helium 5.0, flow 1 mL/min, temperature gradient programmed from 60 to $300\text{ }^\circ\text{C}$ at $20\text{ }^\circ\text{C}/\text{min}$ after an initial time of 6min. The MS conditions were as follows: positive EI ionization, ionization energy 70 eV, ionization source temperature $280\text{ }^\circ\text{C}$, emission current $100\text{ }\mu\text{A}$. Melting points were obtained on a standard melting point apparatus in open capillary tubes. TLC analyses were performed on pre-coated (silica gel 60 HF₂₅₄) plates. Chromatographic purifications were done using silica gel automated flash chromatography.

Starting materials **2**,^{S1} **6**,^{S2} **8**,^{S3} **10**^{S4} were synthesized according to known procedures; characterization data (^1H NMR/MS) are in agreement with literature values. All anhydrous solvents (stored over molecular sieves), and chemicals were obtained from standard commercial vendors and were used without any further purification except where stated otherwise. Importantly, DCE needs to be purchased from Acros in 99.8%, extra dry, AcroSeal, quality (Cat.No. 326840010). It was used without prior degassing. Extra dry toluene (99.85%, water <50 ppm, AcroSeal) was purchased from Acros (Cat.No. 364410010). $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ (98%, Cat.No. 280100) and $\text{CpCo}(\text{CO})_2$ (min. 95%, Cat.No. 270550) were purchased from Strem Chemicals Inc. Grubbs I (**1a**) (Cat.No. 579726), Grubbs II (**1b**) (Cat.No. 569747) and Hoveyda-Grubbs II (**1c**) (Cat.No. 69755) catalysts were obtained from Aldrich. Stock solutions were prepared by weighing the catalysts into oven-dried microwave vials, capping them and purging them for 5 min with Ar. Then the DCE was added and the vial was purged for additional 5 min with Ar. The vials were kept under Ar for further use.

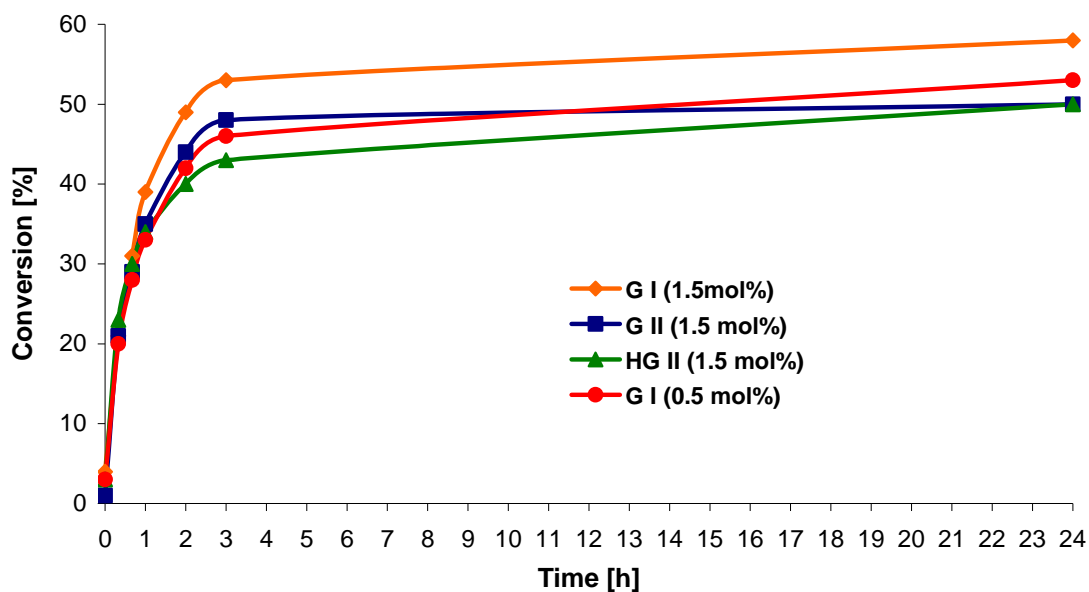


Figure S1. Conversion over time for the room temperature ring-closing metathesis of 1,2-bis(allyloxy)benzene (**2**) to metathesis product **3** with Ru catalysts **1a**, **1b** and **1c** (Scheme 1). Conditions: DCE (0.02 M), rt, closed vessel (10 mL round bottom flask). HPLC peak area percent (215 nm).

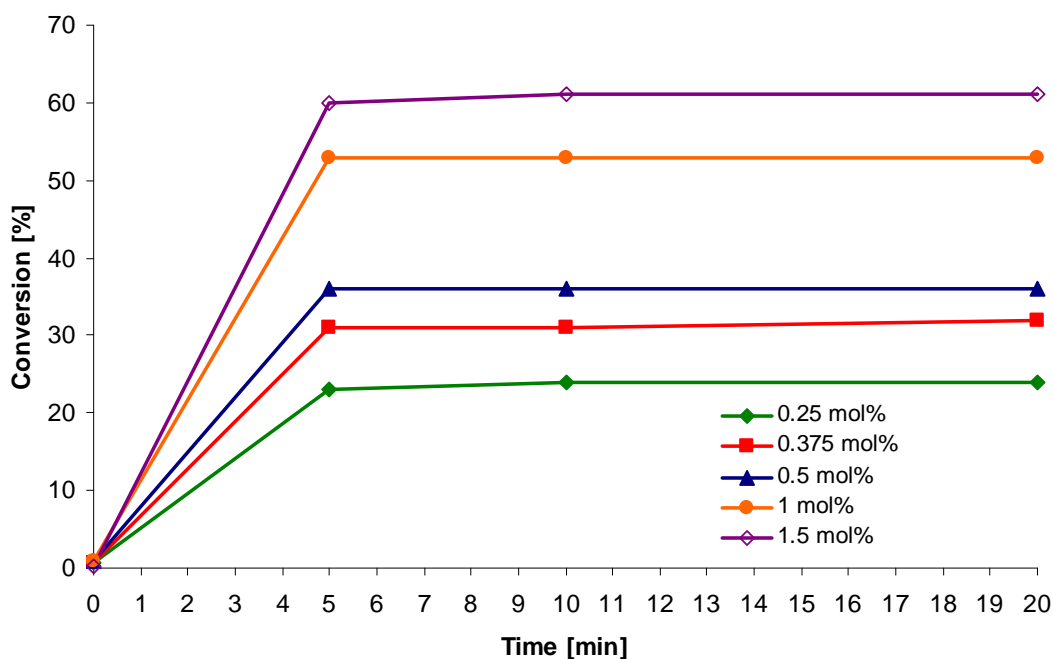


Figure S2. Conversion over time for sealed vessel ring-closing metathesis of 1,2-bis(allyloxy)benzene (**2**) to metathesis product **3** with Ru catalyst **1a** at different concentrations (Scheme 1). Conditions: DCE (0.02 M), closed vessel, 10 mL microwave vial, 83 °C set temperature. HPLC peak area percent (215 nm).

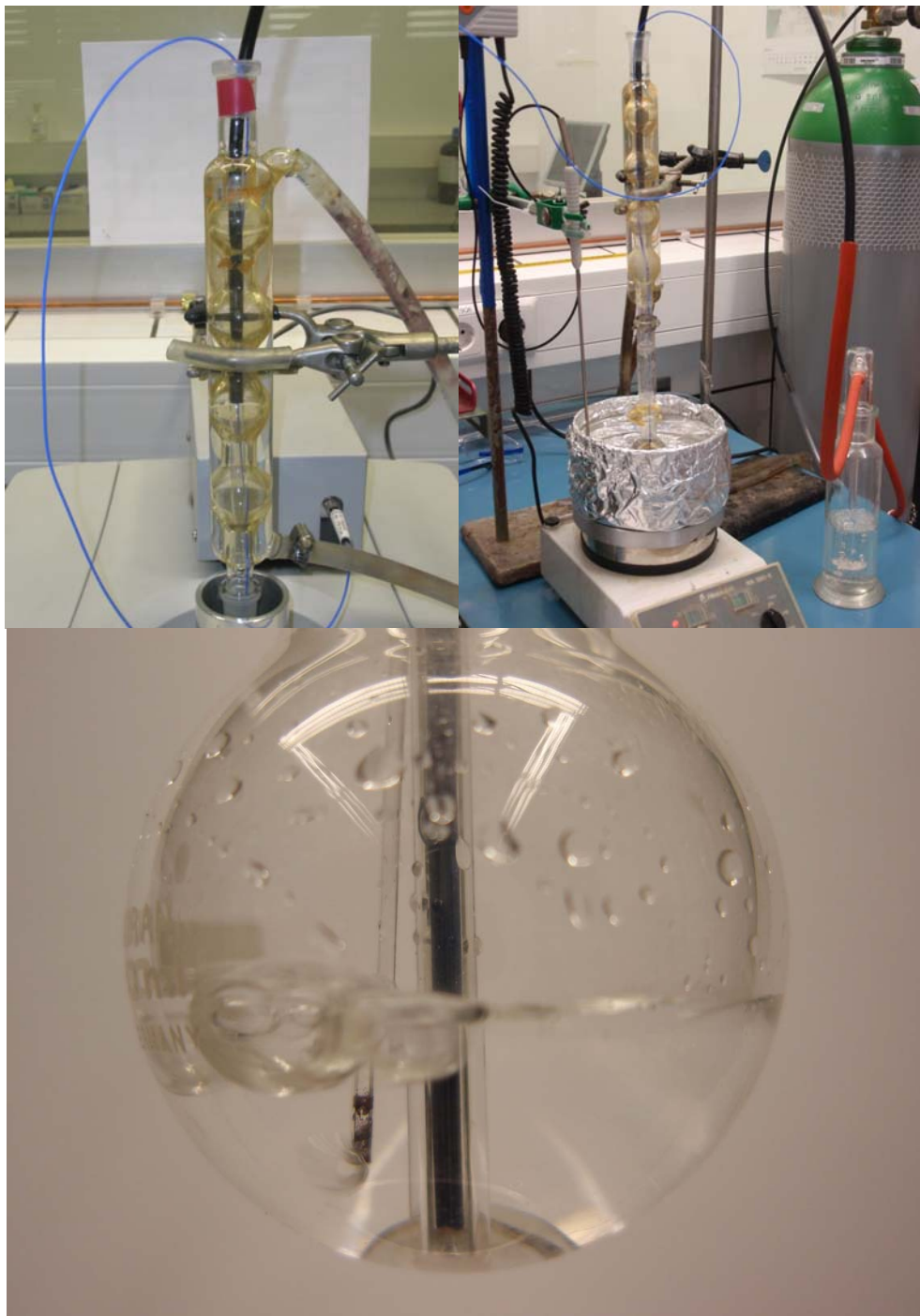


Figure S3. Experimental set-up for open-vessel microwave (left) and oil-bath (right) experiments with internal FO temperature measurement and Ar sparging. Bottom: close up with glass capillary for Ar sparging (left) and FO probe. Also seen is the magnetic stir bar at the bottom.

Table S1. Selectivity for open-vessel ring-closing metathesis of 1,2-bis(allyloxy)benzene (2) to metathesis products 3-5 (Scheme 1) with 0.5 mol% of Ru catalyst 1a under microwave heating.

Time [min]	Starting Material (2) ^b	Product (3) ^b	Linear Dimer (4) ^b	Cyclic Dimer (5) ^b
1	43	44	8	5
2	23	62	6	9
3	16	70	4	10
4	13	73	3	11
5	11	74	3	12

^a Conditions: DCE (0.02 M), open vessel microwave heating (150 W constant power), 83 °C reflux, Ar sparging. ^b HPLC-UV peak area percent (215 nm). Conversions to metathesis products **3-5**.

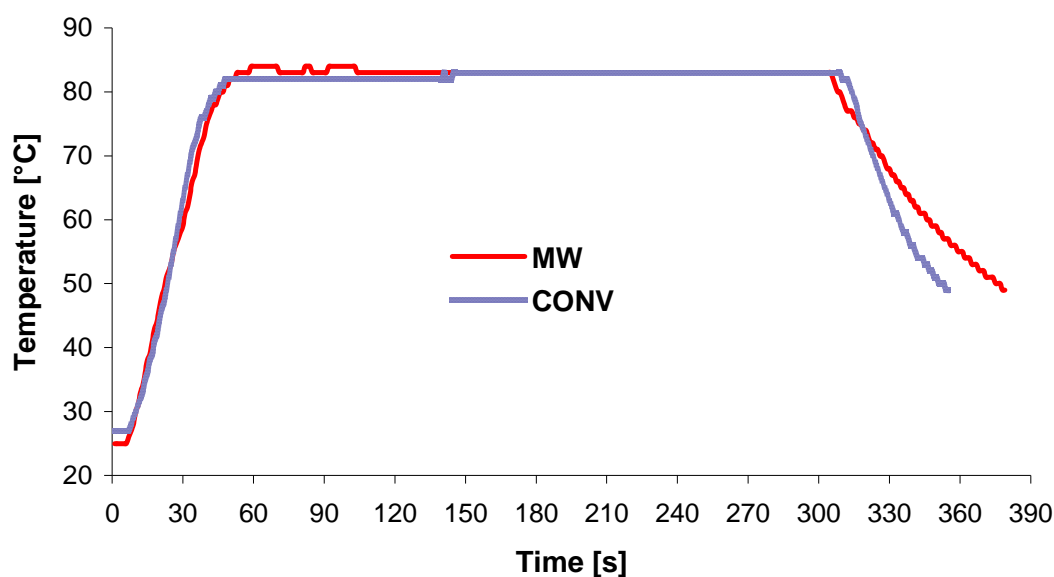


Figure S4. Heating profiles for open-vessel microwave (MW) and oil-bath (CONV) experiments. As can be seen, the ramp and the cooling profile are nearly identical. Conditions: DCE (0.02 M), open-vessel, 10 mL round-bottom flask, 150 W constant power, reflux at 83 °C, 0.5 mol% Ru-catalyst **1a**.

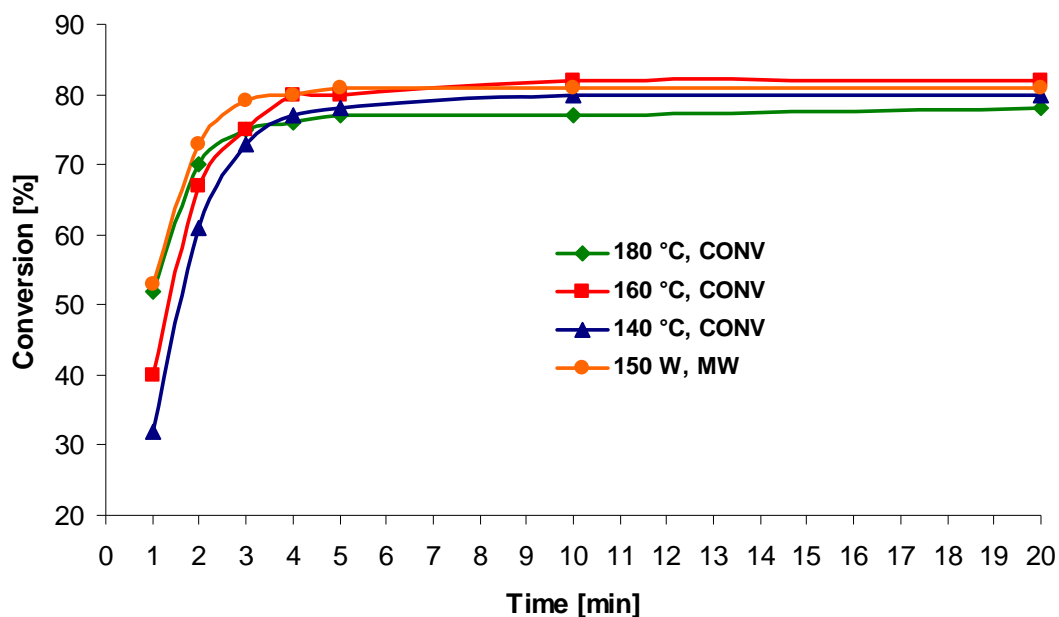


Figure S5. Overall conversion over time for open-vessel ring-closing metathesis of 1,2-bis(allyloxy)benzene (**2**) to metathesis product **3** with 0.5 mol% of Ru catalyst **1a** at different oil-bath temperatures (CONV) and microwave heating (MW, 150 W constant power) (Scheme 1). Conditions: DCE (0.02 M), open-vessel, 10 mL round-bottom flask, reflux at 83 °C. HPLC peak area percent (215 nm).

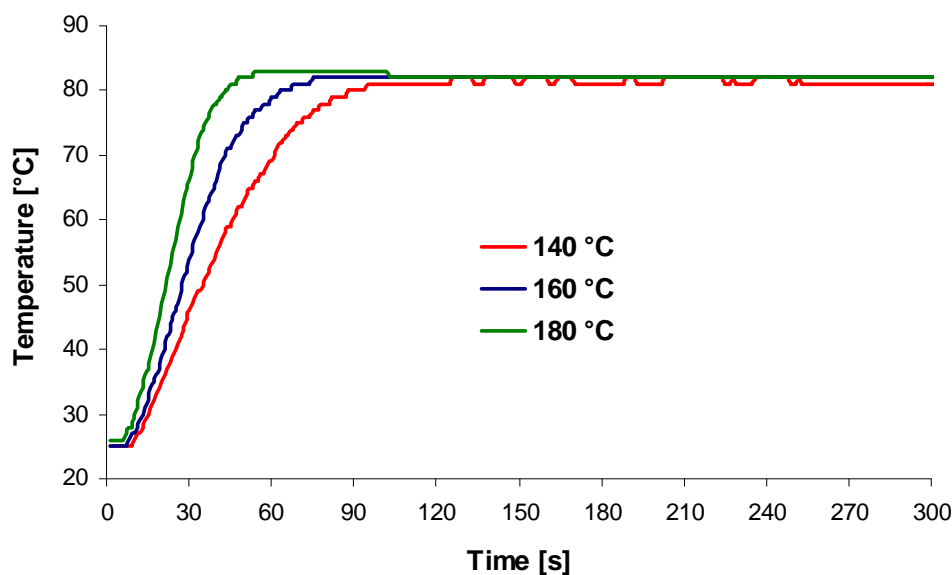


Figure S6. Heating profiles for 5 mL of DCE under open-vessel oil-bath heating at different oil-bath temperatures. When lower oil bath temperatures were used (140 °C and 160 °C), the heating ramp to 83 °C was slower compared to 180 °C, therefore also the rate of the metathesis reaction was slower during the first 1-2 min but finally reached nearly the same conversion levels as the 180 °C bath temperature experiments (see Figure S5).

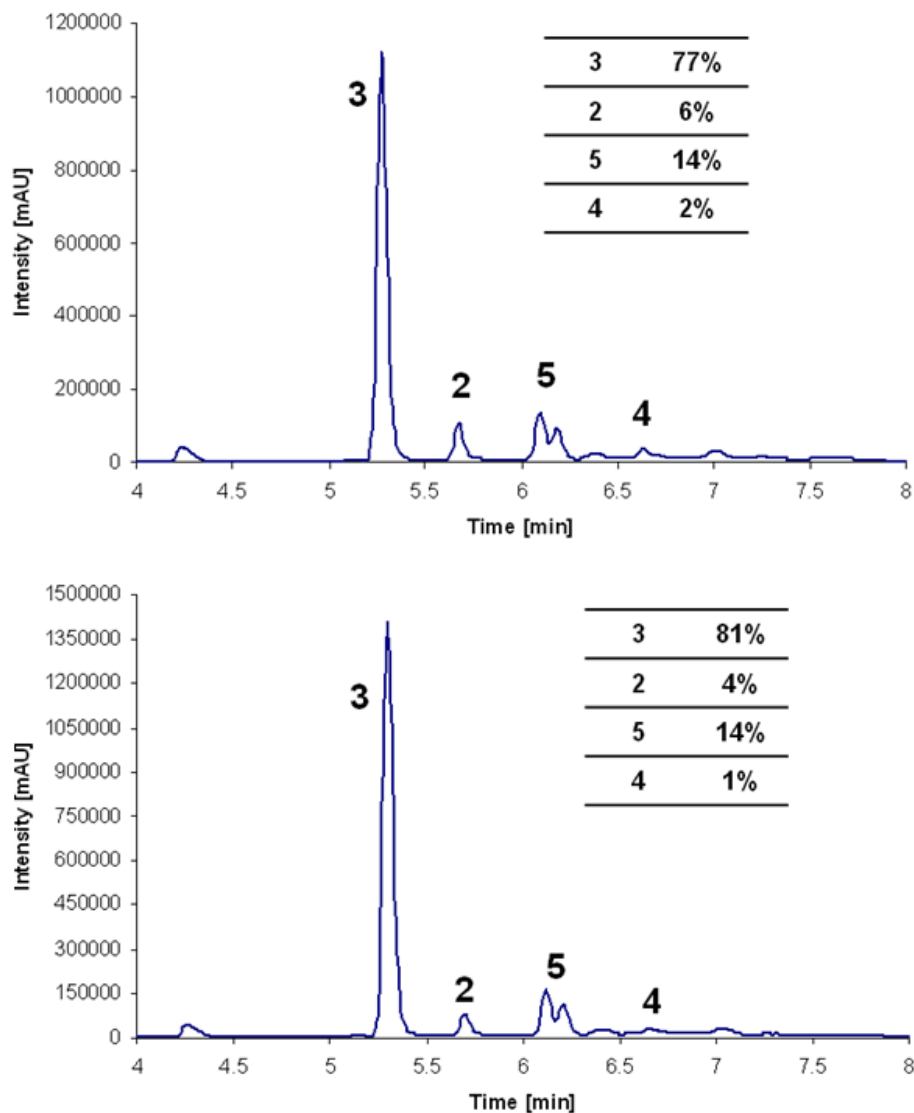


Figure S7. HPLC-UV traces (215 nm) obtained from the crude reaction mixtures of oil-bath heating at 180 °C bath temperature (top) and microwave heating at 150 W constant power (bottom). The product distributions (see Scheme 1) were virtually identical. Conditions: 0.5 mol% catalyst **1a**, 5 min, DCE (0.02 M), open-vessel, 10 mL round-bottom flask, reflux at 83 °C.

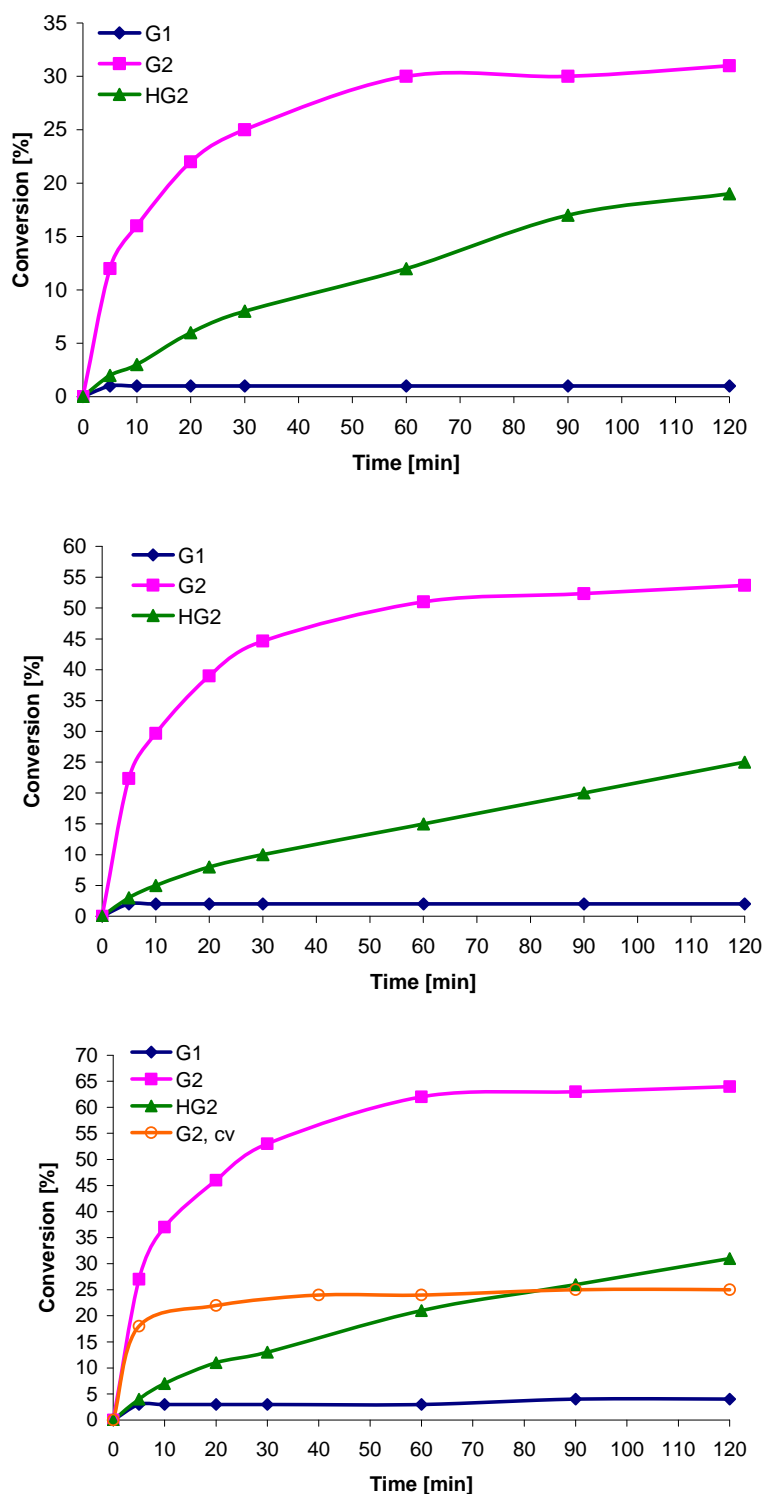


Figure S8. Conversion over time for the ring-closing metathesis of 1,2-bis(2-methylallyloxy)benzene (**6**) to metathesis product **7** (Scheme 2) with Ru catalysts **1a**, **1b** and **1c** at different concentrations (top: 1.5 mol%, center: 5 mol%, bottom: 10 mol%). For the 10 mol% catalyst loading also the closed vessel experiment (G2, cv) was performed. Conditions: DCE (0.02 M), 10 mL round-bottom flask, open vessel microwave heating (150 W constant power), 83 °C reflux, Ar sparging. HPLC peak area percent (215 nm).

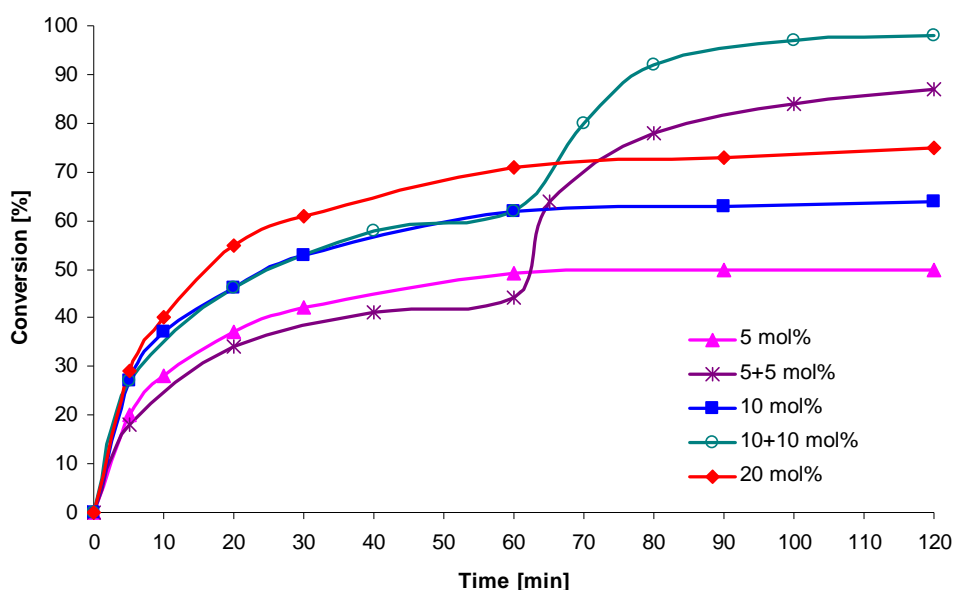


Figure S9. Conversion over time for the ring-closing metathesis of 1,2-bis(2-methylallyloxy)benzene (**6**) to metathesis product **7** (Scheme 2) with Ru catalyst **1b** at different concentrations. For the 5+5 and 10+10 mol% experiments, fresh catalyst is added after 1 h microwave heating and cooling to 50 °C. Then the reaction mixture is heated again for an additional hour. Conditions: DCE (0.02 M), 10 mL round-bottom flask, open vessel microwave heating (150 W constant power), 83 °C reflux, Ar sparging. HPLC peak area percent (215 nm).

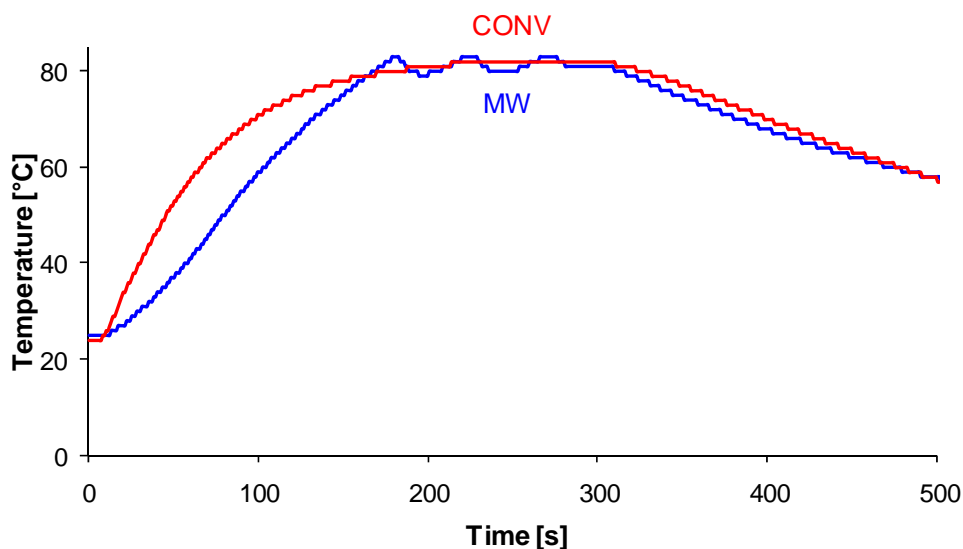


Figure S10. Temperature profiles obtained with internal FO sensors for conventionally (CONV) and microwave (MW) heated [2+2+2] cyclotrimerizations of diethyl dipropargyl malonate (**8**) with 1-hexyne in toluene (Scheme 3a). Conditions: 300 W maximum microwave power, 82 °C set temperature; 86 °C oil bath temperature. Ramp time 3 min, hold time 2 min, cooling time 4 min. In the microwave experiments cooling by compressed air was disabled in order to match the cooling profile of the oil bath experiment. For further details see the Experimental Section.

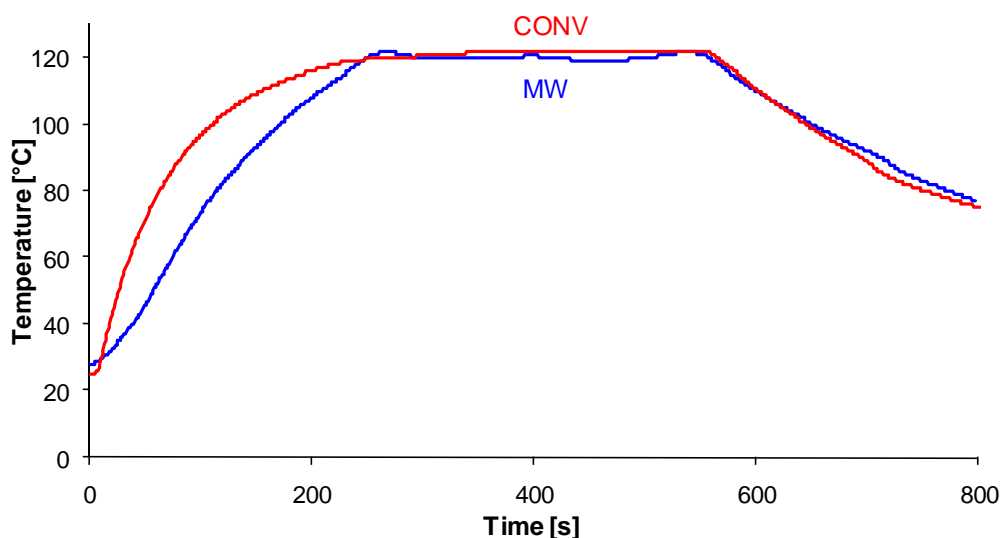


Figure S11. Temperature profiles obtained with internal FO sensors for conventionally (CONV) and microwave (MW) heated [2+2+2] cyclotrimerizations of 1,2-dipropargylbenzene (**10**) with propargyl alcohol in toluene (Scheme 3b). Conditions: 300 W maximum microwave power, 120 °C set temperature; 135 °C oil bath temperature. Ramp time 4 min, hold time 5 min, cooling time 4 min. In the microwave experiments cooling by compressed air was disabled in order to match the cooling profile of the oil bath experiment. For further details see the Experimental Section.

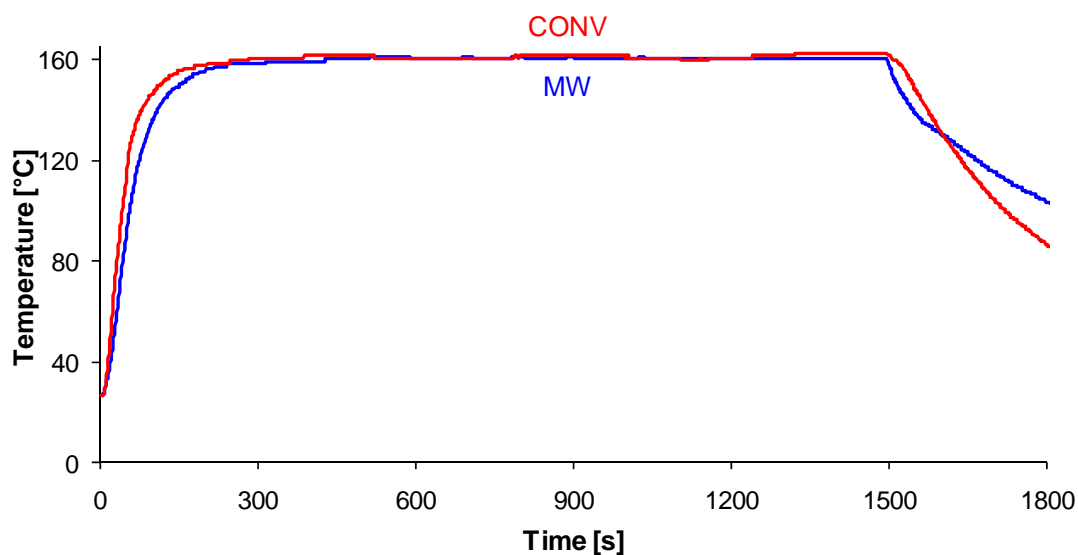


Figure S12. Temperature profiles obtained with internal FO sensors for conventionally (CONV) and microwave (MW) heated [2+2+2] cyclotrimerizations of 1,2-dipropargylbenzene (**10**) with benzonitrile in toluene (Scheme 3c). Conditions: 300 W maximum microwave power, 160 °C set temperature; 180 °C oil bath temperature. Ramp time 4 min, hold time 20 min, cooling time 5 min. In the microwave experiments cooling by compressed air was disabled in order to match the cooling profile of the oil bath experiment. For further details see the Experimental Section.

References

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