SUPPORTING INFORMATION

Microwave-Assisted Ring-Closing Metathesis Revisited. On the Question of the Non- Thermal Microwave Effect

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Contents: Experimental Section

Figure S1

Figure S1. Heating profiles for quartz (a) and glass (b) vessels filled with 2 mL of microwave transparent CCl_4 (100 W constant microwave power). Temperatures were recorded on the outer surface of the vial by an IR sensor.

Experimental Section

General. For general methods, see ref.^{S1,S2} All RCM products and starting materials have previously been described and identified.^{S3} Metathesis catalyst **3** was obtained from commercial sources, catalyst **4** was prepared according to ref.^{S4}

General Procedure for the RCM of Substrates **1a-f** under Microwave

Conditions. A) For Catalyst 4: A solution of the corresponding diene **1a-f** (0.1 mmol) and catalyst **4** (1.8 or 3.4 mg, 0.002 or 0.004 mol, 2 or 4 mol%, Table 1) in DCM (0.5 mL; freshly distilled) with stirring was irradiated under Ar for 20 min at 100-140 °C (temperature control, fixed hold time off, absorbtion level normal, see Table 1). Experiments were carried out in 2.5 mL (small) sealed microwave glass process vials. **B) For Catalyst 3:** A solution of the corresponding diene **1a-f** (0.1 mmol) and catalyst **3** (0.43 mg, 0.0005 mol, 0.5 mol%) in DCM (2.0 mL; freshly distilled) with stirring was irradiated 2 min at 60 °C (temperature control, fixed hold time off, absorbtion level normal). Experiments were carried out in 5.0 mL (large) sealed microwave glass or quartz process vials. For both methods, after active gas jet cooling to rt (ca 1 min) the reaction mixture was immediately filtered through a small

pad of silica to remove the catalyst. Evaporation of the solvent produced products **2a-2f**. The conversions were analyzed by both HPLC (215 nm) and ^1H NMR (360 MHz), with the exception of **2d** where because of volatility conversions were analyzed by HPLC only.

1-(Toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole (2a). ^1H NMR (CDCl_3 , 360 MHz): 2.4 (s, 3H, CH_3), 4.1 (s, 4H, CH_2), 5.63 (m, 2H, CH), 7.3 (d, 2H, $J = 8.2\text{Hz}$, *o*-ArH), 7.7 (d, 2H, $J = 8.2\text{Hz}$, *m*-ArH). MS m/z (%): 224.1 (MH^+ , 100%).

1-(Toluene-4-sulfonyl)-1,2,3,6-tetrahydro-pyridine (2b). ^1H NMR (CDCl_3 , 360 MHz): 2.2 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 3.16 (t, 2H, CH_2), 3.57 (m, 2H, CH_2), 5.67 (m, 2H, CH), 7.3 (d, 2H, $J = 8.25\text{Hz}$, *o*-ArH), 7.66 (d, 2H, $J = 8.25\text{Hz}$, *m*-ArH). MS m/z (%): 238.2 (MH^+ , 100%).

1-(Toluene-4-sulfonyl)-2,3,6,7-tetrahydro-1H-azepine (2c). ^1H NMR (CDCl_3 , 360 MHz): 2.24-2.34 (m, 4H, CH_2), 2.41 (s, 3H, CH_3), 3.2-3.3 (m, 4H, CH_2), 5.72 (t, 2H, CH), 7.27 (d, 2H, $J = 8.23\text{Hz}$, *o*-ArH), 7.66 (d, 2H, $J = 8.23\text{Hz}$, *m*-ArH). MS m/z (%): 252.3 (MH^+ , 100), 198 (37), 155.1 (45).

Toluene-4-sulfonic acid cyclopent-3-enyl ester (2e). ^1H NMR (CDCl_3 , 360 MHz) 2.47 (s, 3H, CH_3), 2.51-2.6 (m, 4H, CH_2), 5.1-5.21 (m, 1H, CH), 5.63 (m, 2H, CH), 7.35 (d, 2H, $J = 8.01\text{Hz}$, *o*-ArH), 7.8 (d, 2H, $J = 8.01\text{Hz}$, *m*-ArH). ^{13}C NMR (CDCl_3 , 90MHz) 22.2, 40.5, 82.4, 119.4, 128.3, 130.4, 134.9, 145.01.

Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester (2f). ^1H NMR (CDCl_3 , 360 MHz) 1.2 (t, $J = 7\text{Hz}$, 6H, CH_3) 2.58 (s, 4H, CH_2) 4.13 (q, $J = 7\text{Hz}$, 4H, CH_2) 5.6 (s, 2H, CH). MS m/z (%): 213.2 (MH^+ , 100), 167 (35), 139 (10).

Thermal Control Reaction for RCM of Substrate 1a using Grubbs Catalyst 3 in DCM. A solution of diene **1a** (25.2 mg, 0.1 mmol) in DCM (1.8 mL; freshly distilled) prepared in a 5 mL sealed microwave Pyrex glass vial (Teflon septum) was immersed in a preheated oil bath (60°C) with stirring. After an equilibration period of 30 min a solution of the catalyst (0.43 mg, 0.0005 mmol, 0.5 mol%) in DCM (0.2 mL; freshly distilled) was injected in the diene solution. Upon standing for 2 min with stirring in

the preheated oil bath, the Pyrex tube was removed immediately from the oil bath and cooled in a cold water bath for 1 min. The mixture was subsequently filtered through a pad of silica to remove the catalyst, the solvent evaporated to give the product **2a** and the conversion analyzed by ^1H NMR (360 MHz) (Table 2).

Microwave (A) and Thermal Control Reaction (DCM Reflux Conditions) (B) for RCM of Substrate 1a Using Catalyst 3. (A) A freshly prepared solution of the diene **1a** (25.2 mg, 0.1 mmol) and the catalyst **3** (0.43 mg, 0.0005 mmol, 0.5 mol%) suspended in a Teflon sealed Pyrex glass tube was microwave irradiated at 40 °C for 5 min. The mixture was subsequently filtered through a pad of silica to remove the catalyst, the solvent evaporated and conversion determined by HPLC (215 nm). Similarly, individual runs were conducted for 10 min and 20 min respectively by preparing fresh samples of diene **1a** and the catalyst **3** and conversions (see Table 2) determined as above. (B) A solution of diene **1a** (25.2 mg, 0.1 mmol) in DCM (1.8mL, freshly distilled) prepared in a 5 mL round bottom flask equipped with a reflux condenser was immersed in an oil bath (preset to 50 °C) and the solution allowed to reflux gently. To this mixture, catalyst **3** (0.43 mg, 0.0005 mmol, 0.5 mol%) in DCM (0.2 mL, freshly distilled) was injected. The progress of the reaction was monitored by HPLC by taking aliquots at regular. Upon maintaining reflux for 20 minutes, the reaction gave complete conversion to product **2a** determined by HPLC and ^1H NMR (Table 2).

Microwave (A) and Thermal Control (B) Reaction for RCM of 1a Using Catalyst 3 in Doped DCM (Figure 1). (A) A solution of the diene **1a** (25.2 mg, 0.1 mmol) and catalyst **3** (0.43 mg, 0.0005 mmol, 0.5 mol%) was prepared in a Teflon sealed Pyrex glass process vial in doped DCM (2.0 mL, 0.04 M bmimPF₆) and microwave irradiated with stirring at 300 W power for 15 seconds. Subsequently, the mixture was filtered through a pad of silica to remove the catalyst and the solvent evaporated to give product **2a** with virtually quantitative conversion as determined by HPLC and ^1H NMR. (B) A freshly prepared solution of the diene **1a** (25.2 mg, 0.1 mmol) in doped

DCM (1.8 mL, 0.04 M bmimPF₆) contained in Teflon sealed Pyrex glass process vial was immersed with stirring in a preheated oil bath (80 °C) and the temperature allowed to equilibrate. To this suspension, catalyst **3** (0.43 mg, 0.0005 mmol, 0.5 mol%) in DCM (0.2 mL 0.1M bmimPF₆) was injected and the process vial maintained in the oil bath. Upon standing for 15 seconds, the vial was immediately removed and cooled in a cold water bath and the catalyst removed by filtration through a pad of silica and the solvent evaporated to give product **2a** with virtually quantitative conversion as determined by HPLC and ¹H NMR.

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