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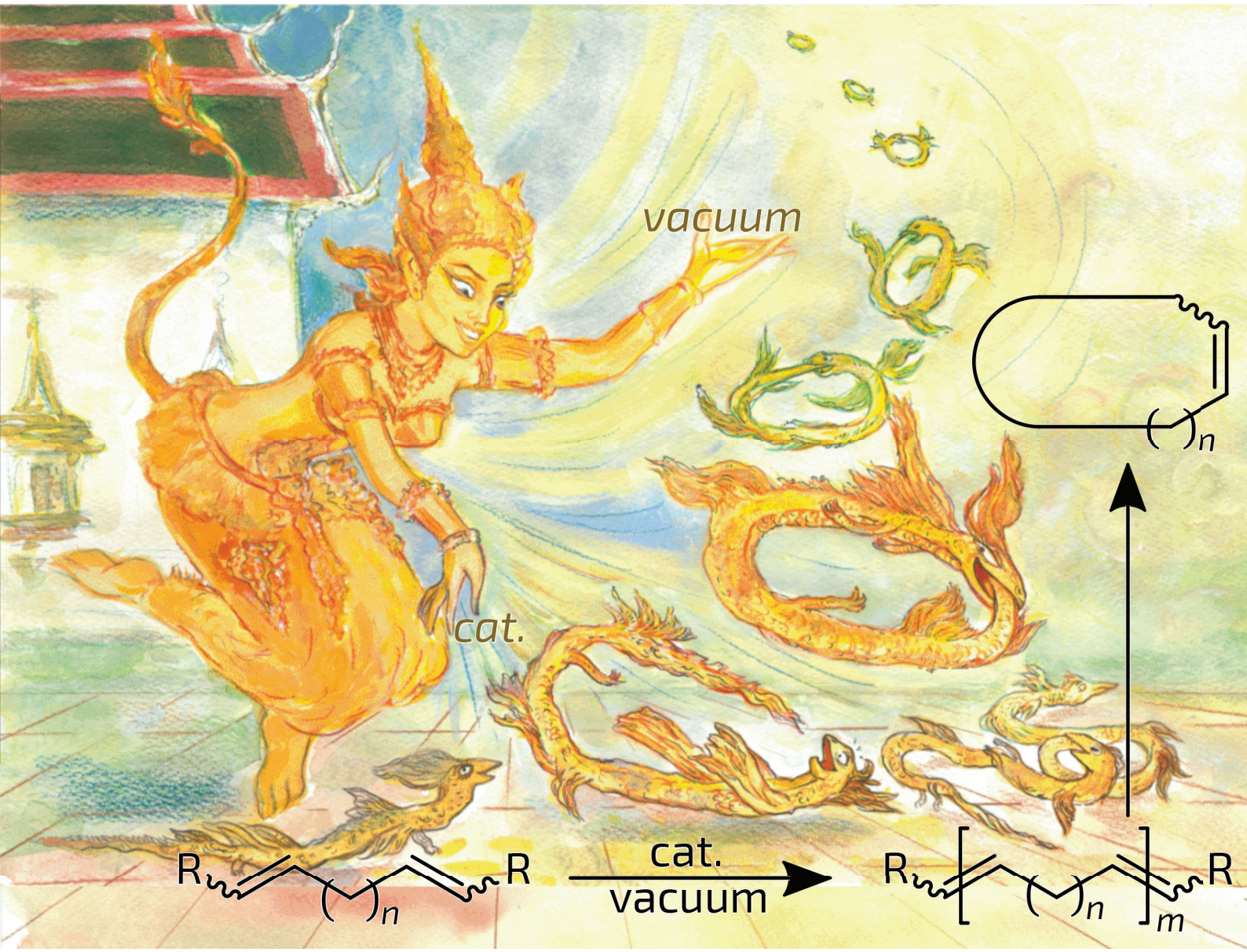

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Karol Grela, Anna Kajetanowicz *et al.*
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Schrock molybdenum alkylidene catalyst enables selective formation of macrocyclic unsaturated lactones by ring-closing metathesis at high-concentration†

Adrian Sytniczuk, ‡ Mariusz Milewski, ‡ Michał Dąbrowski, Karol Grela * and Anna Kajetanowicz *

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A set of macrocyclic unsaturated musk compounds was obtained from unbiased dienes *via* ring-closing metathesis at 20–40 times higher concentration than recommended in state-of-the-art, proceeding *via* formation of oligomers and then by a backbiting metathesis reaction. As the commercial Schrock catalyst **Mo1** does not lead to the parasitic C–C double bond migration process, the above reactive distillation proceeded with very high chemical selectivity, leading to pure macrocyclic musk products in 24–92% yield and selectivity around 90% or higher. It was also shown that this process can be performed under user-friendly conditions, using Schrock catalyst **Mo1** suspended in paraffin tablet, cheap PAO-6 engine oil as a diluent, on air, in simple distillation glassware, and with a standard laboratory vacuum pump. In addition, most of the substrates were obtained from bio-sourced oleic acid, making the high-concentration RCM (HC-RCM) process even more environmentally friendly.

Introduction

Unsaturated macrocyclic musk compounds play an important role in the flavour and fragrance industry.[1,2] These compounds can be obtained from natural sources such as animals (*e.g.* Siberian musk deer, African civet), plants (*e.g. Abelmoschus moschatus*), or they can be synthesized. In the latter case, the catalytic olefin metathesis is one of the preferred methods of forming the macrocycle.[1] However, one of the key problems in ring-closing metathesis macrocyclisation of *unbiased dienes* (molecules defined by Fürstner as the dienes that lack structural motifs that could help to achieve effective macrocyclisation at reasonable concentration)[3] is related to the unfavourable entropic effect of such a transformation, making—especially in more concentrated solutions—the process of oligomerisation dominate over the desired macrocyclisation (Scheme 1a). Therefore, ever since the very first reports from the academia (1980),[4] and industry (1984)[5] to the most recent publications,[6–12] the preparation of medium and large rings by RCM of unbiased dienes was always conducted under the so-called *high dilution conditions* (usually 1–5 mM). Sadly, this makes RCM macrocyclisation (mRCM) technology very problematic from an industrial perspective, because of the high environmental and economic costs of utilising and disposing of large volumes of carefully purified organic solvents.[13] Interestingly, such a cardinal problem in the olefin metathesis methodology remained unsolved for almost 40 years![14,15] Some approaches, based on using of specialised catalysts[16] or techniques[17–20] such as membrane pervaporation and continuous flow can allow to increase concentration up to 10–20 mM. However, when RCM of unbiased dienes is conducted at >20 mM concentration, the macrocycle yield is usually visibly reduced. Recently, some original solutions to this problem have been proposed, *i.e.* by using specially designed homogeneous catalysts[21] or tailored ruthenium complexes covalently bound to mesoporous silica with defined pore diameters.[22–25] Another approach was related to the use of cavitands.[26] In contrast, we decided to make use of the intriguing observation by Fogg *et al.*, that macrocyclisation *via* RCM always involves oligomerisation being in equilibrium with the *backbiting* and RCM processes.[14,15] As a result, using a reactive distillation technique, we achieved a successful RCM at concentration of 0.2–0.7 M (Scheme 1b).[27] Notably, this was only possible with a very few Ru olefin metathesis catalysts bearing unsymmetrical NHC ligands as all standard commercially available Ru-complexes with symmetrical NHCs led to severe isomerisation of the obtained musk products, making this process impractical (Scheme 1c).[27]

Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland.
E-mail: prof.grela@gmail.com, a.kajetanowicz@uw.edu.pl

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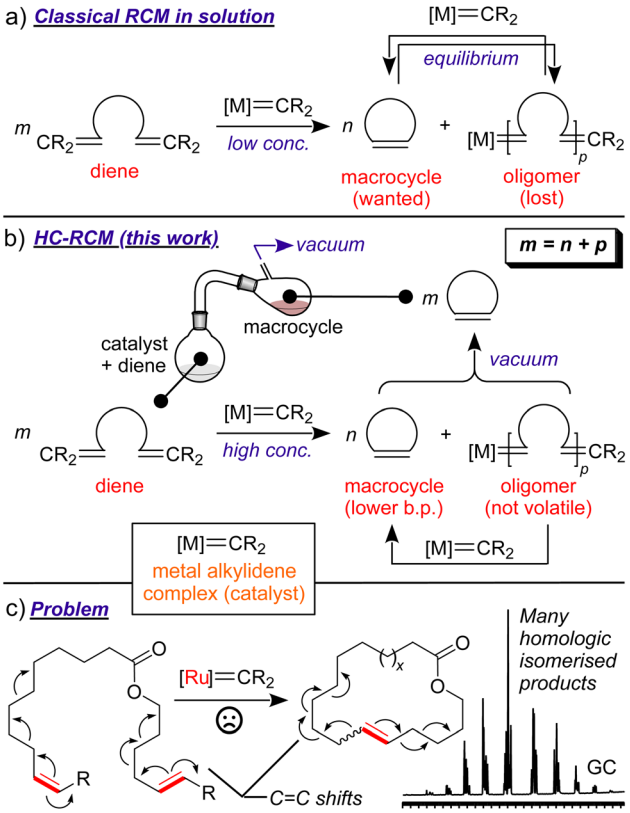
‡These authors contributed equally.



Scheme 1 (a) Classical RCM macrocyclisation (mRCM) of unbiased dienes in solution; (b) high-concentration polymerisation-depolymerisation process (HC-RCM); (c) problems resulted from the use of popular Ru metathesis catalysts in HC-RCM. Low concentration = 0.001–0.01 M; high concentration ≥0.2 M.

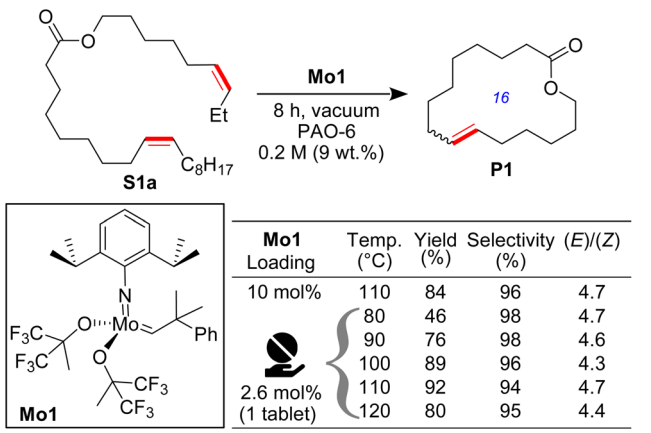
Our goal was to search for conditions that allow the selective synthesis of unsaturated macrocyclic products of a valued musky smell *via* RCM of unbiased dienes at a high concentration utilising *easily available commercial catalysts*, but at the same time avoiding the previously observed low selectivity caused by unwanted C–C double bond shifts.[27] The latter process, resulting in formation of a very complex mixture of isomerised products, was observed with several of popular commercially available Ru catalysts[27] and unfortunately made this method unusable in the context of the flavour and fragrance industry.

Results

As molybdenum alkylidene catalysts[28] tend to be less prone to unwanted C–C double bond isomerisation,[29–31] we decided to test them in the high-concentration RCM process. In contrast to classic RCM macrocyclisation in solution, the HC-RCM technique does not require a solvent.[27] However, to keep the distillation flask content liquid, a minimal amount of a non-volatile diluent is needed. In this role, we opt to use a low cost synthetic engine oil constituent—poly-α-olefin (PAO-6)[32]—keeping the initial diene concentration at 5–9 wt% (*ca.* 0.25 mol kg^{-1}, *ca.* 200 mM). Reactive distillation of a model unbiased diene (**S1a**) leading to a 16-membered unsaturated Exaltolide™ analogue (**P1**) was conducted in a standard Hickmann apparatus[33] at 110 °C on the 0.5 mmol scale using an oil diffusion pump as a vacuum source (the nominal pressure at the pump inlet was set at 10^{-6} mbar, Scheme 2). Under such conditions, the Schrock catalyst **Mo1** (weighted and handled in a glovebox) was tested. After a number of exploratory experiments, it was found that 10 mol% of **Mo1** after 8 hours of distillation allowed one to collect in the receiver of the Hickmann apparatus an oily, musk-smelling distillate in an amount that corresponds to 84% of yield. Subsequent GC and NMR analysis of this product showed that it contains practically pure macrocyclic lactone **P1** formed with an excellent selectivity of 96% (Scheme 2).

For comparison, and to underline the uniqueness of the Mo-complex, it should be noted that virtually all popular Ru-based catalysts, such as Grubbs and Hoveyda–Grubbs second generation complexes, gave in the same process selectivity levels of 13–47%,[27] causing a substantial C–C double bond migration during the process, which results in a complicated mixture of 12 to 20-membered diversely unsaturated macrocycles—an outcome which is unfortunately useless in the industrial production context. With **Mo1**, the selectivity was in the range of 96–98%, which means that the only process to take place was a fully selective formation of sixteen-membered lactone with the double bond situated at C-9 position (Scheme 2).

Having an experimental proof that the Mo-alkylidene catalyst **Mo1** offers an almost ideal selectivity in HC-RCM, we sought to making the process more user-friendly. We see that air- and moisture-sensitivity of molybdenum alkylidene complexes is a barrier to more practical procedure that could be more widely adopted without the need for special training.[34] To avert this potential problem, we turned our attention to the



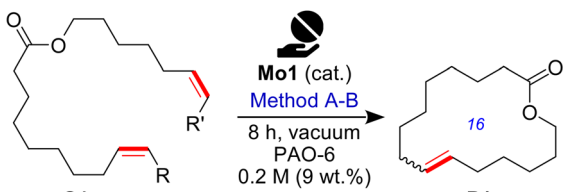
Mo1 Loading	Temp. (°C)	Yield (%)	Selectivity (%)	(*E*)/(*Z*)
10 mol%	110	84	96	4.7
2.6 mol% (1 tablet)	80	46	98	4.7
	90	76	98	4.6
	100	89	96	4.3
	110	92	94	4.7
	120	80	95	4.4

Scheme 2 Optimisation of HC-RCM process catalysed by **Mo1** in pure form or as a paraffin tablet. Oil diffusion pump with simple Hickman distillation adapter was used. Selectivity = (integration of (*E*)-**P1** + (*Z*)-**P1**)/(integration of all products) × 100%; determined by GC. Isolated yields of pure compounds.

Mo1 catalyst suspended in solid paraffin tablets that were recently made commercially available.[34,35] On the reaction scale used by us (0.5 mmol) one of such tablets was equal to 2.6 mol% of Schrock catalyst **Mo1** (10 mg of Mo-complex in 200 mg of paraffin§). Next, a range of temperatures was tested to find the optimal distillation parameters. Although the temperature of 80 and 90 °C was not high enough to promote efficient distillation of the formed macrocycle, the HC-RCM made at 100–120 °C was found to yield ≥80% of macrocyclic lactone **P1** with very good selectivity ≥97% (Scheme 2). Importantly, the set-up of the reaction can now be done outside of the glovebox, as short exposures to air do not cause any significant reduction in conversion and product selectivity.

Oleic acid—a widely-available natural feedstock—an internal olefin, possesses a C_8H_{17} alkene fragment at the end of the olefinic bond. To check the influence of the end-groups present at the C–C double bond of the substrate, a small set of dienes (**S1a–S1c**) have been synthesized and tested in HC-RCM under the previously established conditions (coded as "Method A", Scheme 3).

In this experiment, substrate **S1a** derived from oleic acid and (*Z*)-6-nonenol was compared with a diene containing a terminal and an internal C–C double bond (**S1b**) and with a bis(terminal) substrate (**S1c**, Scheme 3). In the last two cases, the predicted boiling point of a diene was similar to that of product **P1**, and we observed co-distillation of the substrate together with the cyclic product. To avoid this problem, we gradually increased the temperature over time to polymerise substrates **S1b–S1c** into non-volatile ADMET (acyclic diene metathesis) oligomers before the distillation began,[36] and the whole process required three tablets (7.8 mol% of **Mo1**) to complete the mRCM reaction during the same distillation time (for optimisation of loading and other parameters, see ESI†). However, we were pleased to find that under these conditions ("Method B") even terminal diene **S1c** can be used in mRCM at high concentration and it can provide a high selectivity of 95%. However, we noted that in the case of lighter substrates (**S1b–S1c**) slightly lower yields of musk compound **P1** (57–67%) were obtained.



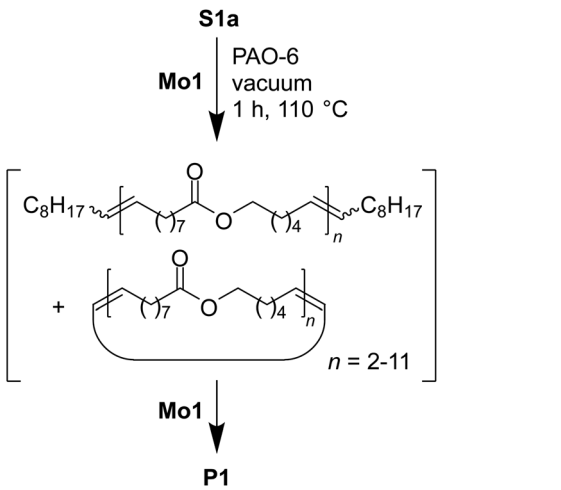
Entry	R	R'	Method	Diene	Yield (%)	Selectivity (%)	(*E*)/(*Z*)
1	C_8H_{17}	Et	A	**S1a**	92	94	4.7
2	H	Et	B	**S1b**	67	95	4.6
3	H	H	B	**S1c**	57	94	4.4

Scheme 3 Influence of C–C double bond substitution on the HC-RCM process catalysed by **Mo1**. Method A = **Mo1** (2.6 mol%, 1 tablet), constant temp. of 110 °C; method B = **Mo1** (7.8 mol%, 3 tablets), temperature increase 40 → 110 °C during the process. Oil diffusion pump with simple Hickman distillation adapter was used. Isolated yields of pure compounds.

To prove that the HC-RCM with **Mo1** indeed proceeds *via* polymeric intermediates, one experiment performed with diene **S1a** under standard reaction conditions ("Method A") was interrupted after one hour ($\frac{1}{8}$ of the standard time) and the reaction mixture was analysed by matrix-assisted laser desorption-ionisation (MALDI) mass spectrometry (Scheme 4).

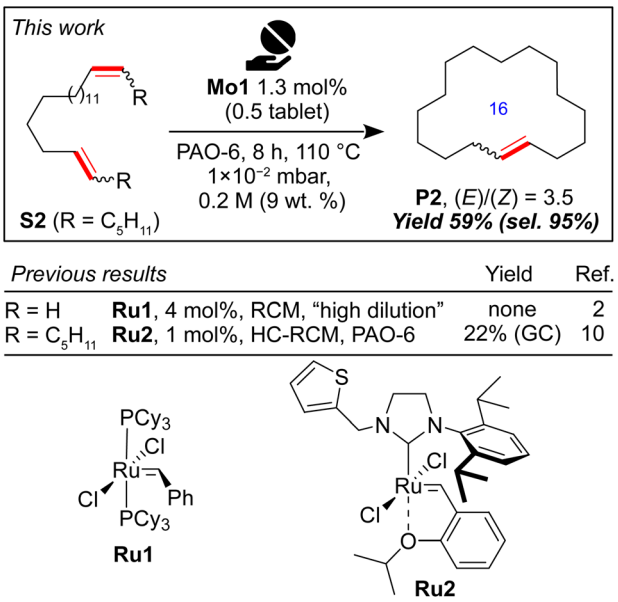
The observed positive mono-charged ions $[M + H]^+$ or $[M + Li]^+$ signals were in the range of 761 to 3000 Da and could be associated with cyclic and linear dimers, trimers, and higher oligomers (n = 2–11) possessing repeating $-CH(CH_2)_7C(O)O(CH_2)_5CH-$ unit (of 238 Da). Because the substrate **S1a** possesses two differently substituted alkene groups—one with an ethyl group and the other one with a larger *n*-octyl substituent—we expected the presence of both of these groups at the outermost positions of the linear oligomers. To our surprise, the mass spectrometry data suggest that the oligomers contain mostly *n*-octyl groups and not, as expected, mixture of *n*-octyl and ethyl groups as in the substrate **S1a** (see ESI for details of oligomers MALDI analysis†). These results suggest—in perfect agreement with Fogg's hypothesis for mRCM in solution[14,15]—that also high-concentration RCM starts with polymerisation, and so formed oligomers are further backbiten by **Mo1** catalyst during the reaction, forming the macrocyclic product that can eventually be distilled-off (Scheme 4).

To better present the unique catalytic activity of the Schrock Mo-catalyst in macrocyclisation at high concentration, we attempted to form 16-membered macrocycle **P2** from unbiased precursor **S2** (Scheme 5). It is prudent to note that this purely hydrocarbon macrocycle was first described by Fürstner as impossible to form in classical RCM using Grubbs catalyst

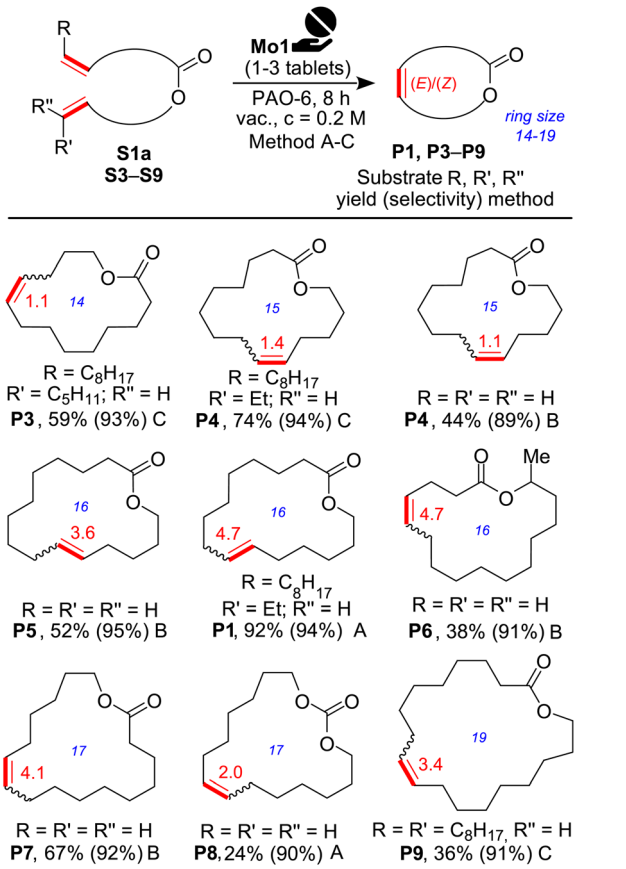


Scheme 4 Observed oligomerisation *en route* to mRCM of diene **S1a** (conditions as in "Method A"). Oligomers analysed by MALDI.

§ The amount of paraffin from tablets was added to the calculated volume of the reaction medium (see ESI for details†).



Scheme 5 Catalysed by **Mo1** HC-RCM formation of macrocyclic cycloalkene **P2** that was unobtainable in classical mRCM in solution. Rotary vain pump was used as the source of vacuum. Isolated yields of pure compounds.



Scheme 6 Scope and limitations of the HC-RCM promoted by **Mo1**. Method A = **Mo1** (2.6 mol%, 1 tablet), 110 °C; Method B = **Mo1** (7.8 mol%, 3 tablets), 40 → 110 °C. Method C = **Mo1** (7.8 mol%, 3 tablets), 110 °C. In all experiments oil diffusion pump with simple Hickman distillation adapter was used. Isolated yields of pure compounds.

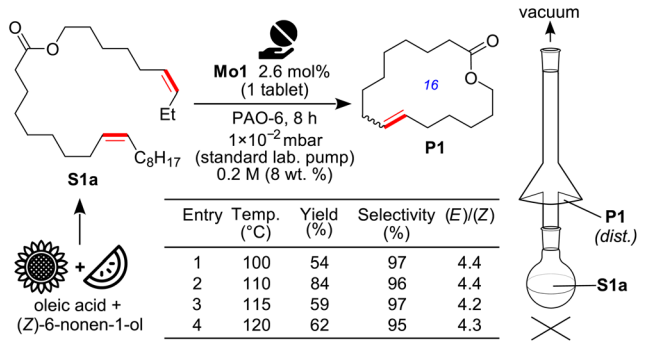
Ru1 at high dilution because of the lack of the so-called *templating effect*.[37] To our delight, **P2** was formed in 59% yield and excellent selectivity of 95% in the presence of 1.3 mol% of **Mo1** ($\frac{1}{2}$ tablet) at 0.2 M concentration. We recently demonstrated synthesis of **P2** using a specialised ruthenium complex **Ru2** under HC-RCM conditions, although with a much lower yield (22%).[27]

In order to map out the scope and limitations of the macro-RCM reaction catalysed by **Mo1** tablets, a small library of dienes was subjected to the reactive distillation process (Scheme 6). Most of tested dienes underwent a smooth macrocyclisation that led to the corresponding 14–17 membered musk products in moderate to good isolated yields (38–85%). Importantly, both terminal and internal dienes can be used in the HC-RCM process with **Mo1**. The larger, 19-memberd ring was also formed, albeit in a lower yield (36%, **P9**, Scheme 6). To our delight, all macrolactones were formed with an almost perfect selectivity (91–98%), which is a better result than the one previously reported for the Ru-catalysts (81–97%).[27]

Interestingly, the carbonate –OC(O)O– moiety present in a diene **S8** remained inert during the reaction and no carbonyl group olefination products were observed with **Mo1**,[38] but the yield of **P8** was rather low (24%).

To further explore the practical prospects and the green chemistry angle[39] of HC-RCM reaction, we focused on substrate **S1a** which can be derived from renewable feedstocks—bio-sourced oleic acid and (*Z*)-6-nonenol.[40] Therefore, we decided to test the practicality of unsaturated Exaltolide analogue **P1** manufacturing using the studied HC-RCM method. To do so, we attempted the reactive distillation of **S1a** using fully user-friendly conditions, which included a standard laboratory rotary vain vacuum pump, and as before, the preparation of the reaction took place entirely in the air. To our satisfaction, the macrocyclisation at high concentration proceeded with **Mo1** tablet with a very high selectivity (96–98%), giving the highest isolated yield of 84% in the reactive distillation run at 110 °C (Scheme 7).

Thanks to reactive distillation employed in this study, much less solvent (diluent) was needed compared to the volume of solvent that is usually used in a standard RCM macrocyclisation in solution. Therefore, we were interested to quantify this difference with the help of green chemistry metrics, such as EcoScale and the environmental (*E*) factor.[41,42] First, we compared the *E* factor—defined by the ratio of the mass of waste per mass of product—for the reaction of **S1** performed under classic conditions in solution (c = 1.5 mM in toluene)[11] and the same reaction performed at high concentration (0.2 M in PAO-6) using the Schrock catalyst **Mo1** (used as a tablet). In the latter case, the value of 224 was calculated, while the process performed in a classic high dilution gave *E*-factor around 13 000 which is almost 60 times higher (for detailed calculations, see ESI†). When we compared other important green



Entry	Temp. (°C)	Yield (%)	Selectivity (%)	(E)/(Z)
1	100	54	97	4.4
2	110	84	96	4.4
3	115	59	97	4.2
4	120	62	95	4.3

Scheme 7 Practical promise of HC-RCM promoted by **Mo1** in synthesis of musk **P1**. Substrate was synthesised from renewable oleic acid and kosher (*Z*)-6-nonenol (flavour & fragrance grade). Standard laboratory rotary vain oil vacuum pump with simple Hickman distillation adapter was used.

metrics parameter, the EcoScale, which evaluates the total effectiveness of a synthetic reaction in terms of cost, safety, technical set-up, energy, and purification aspects, we observed that the high concentration mRCM reaction is still more environmentally friendly (total score for HC-RCM reaction was equal to 75, while for mRCM in solution it was 68; for details see ESI†).

In addition to the green metrics analysis (for full details of them see ESI†), the present methodology has a viable advantage over the previously described HC-RCM distillation with ruthenium complexes,[27] as it uses the commercially available general purpose catalyst **Mo1**, instead of the specialised and non-commercial ruthenium catalysts.

Conclusions

In summary, utilising commercial Schrock catalyst **Mo1**, a number of 14- to 19-membered unsaturated macrocyclic musk compounds were selectively obtained from terminal and internal dienes in moderate to good isolated yield, making it the second example of reactive distillation in mRCM reaction described in the literature.[27] Using these conditions, challenging macrocyclisation reactions of *unbiased dienes* can be made at a concentration 20–40 times higher than recommended in state-of-the-art. Since molybdenum alkylidenes did not cause the parasitic C–C double bond shifting process (even at 100–120 °C), the title reaction proceeded with a very high selectivity, leading to well-defined unsaturated macrocyclic musk compositions. This constitutes a significant improvement over the previously reported process which was either completely non-selective when commercial general purpose ruthenium metathesis catalysts were utilised or it required the use of specialised Ru-complexes.[27] We believe that this process offers a premise for practical applications as it can be made with inexpensive PAO-6 synthetic engine oil as a diluent and a standard laboratory vacuum pump, on air, using dienes obtained from bio-based substrates.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 A. Sytniczuk, M. Milewski, A. Kajetanowicz and K. Grela, *Russ. Chem. Rev.*, 2020, **89**, 469–490.
2 N. Armanino, J. Charpentier, F. Flachsmann, A. Goeke, M. Liniger and P. Kraft, *Angew. Chem., Int. Ed.*, 2020, **59**, 16310–16344.
3 A. Fürstner and K. Langemann, *J. Org. Chem.*, 1996, **61**, 3942–3943.
4 D. Villemin, *Tetrahedron Lett.*, 1980, **21**, 1715–1718.
5 W. J. Wiegers, A. G. Van Loveren, M. R. Hanna, D. J. Luccarelli, D. R. Bowen and M. H. Vock, Macrocyclic carbonates, processes for preparing same, organoleptic uses thereof and intermediates used in said process. US4490544A, 1984.
6 L. E. Rosebrugh, M. B. Herbert, V. M. Marx, B. K. Keitz and R. H. Grubbs, *J. Am. Chem. Soc.*, 2013, **135**, 1276–1279.
7 D. L. Nascimento, A. Gawin, R. Gawin, P. A. Guńka, J. Zachara, K. Skowerski and D. E. Fogg, *J. Am. Chem. Soc.*, 2019, **141**, 10626–10631.
8 C. S. Higman, D. L. Nascimento, B. J. Ireland, S. Audörsch, G. A. Bailey, R. McDonald and D. E. Fogg, *J. Am. Chem. Soc.*, 2018, **140**, 1604–1607.
9 T. S. Ahmed, T. P. Montgomery and R. H. Grubbs, *Chem. Sci.*, 2018, **9**, 3580–3583.
10 R. Gawin, A. Tracz, M. Chwalba, A. Kozakiewicz, B. Trzaskowski and K. Skowerski, *ACS Catal.*, 2017, **7**, 5443–5449.
11 A. Sytniczuk, A. Leszczyńska, A. Kajetanowicz and K. Grela, *ChemSusChem*, 2018, **11**, 3157–3166.
12 A. Sytniczuk, G. Forcher, D. B. Grotjahn and K. Grela, *Chem. – Eur. J.*, 2018, **24**, 10403–10408.
13 T. Nicola, M. Brenner, K. Donsbach and P. Kreye, *Org. Process Res. Dev.*, 2005, **9**, 513–515.
14 B. J. van Lierop, J. A. M. Lummiss and D. E. Fogg, in *Olefin Metathesis: Theory and Practice*, John Wiley & Sons, Inc., 2014, 85–152.

15 S. Monfette and D. E. Fogg, *Chem. Rev.*, 2009, **109**, 3783–3816.
16 A. Tracz, A. Gawin, M. Bieniek, T. K. Olszewski and K. Skowerski, *New J. Chem.*, 2018, **42**, 8609–8614.
17 É. Morin, J. Sosoe, M. Raymond, B. Amorelli, R. M. Boden and S. K. Collins, *Org. Process Res. Dev.*, 2019, **23**, 283–287.
18 C. P. Breen, C. Parrish, N. Shangguan, S. Majumdar, H. Murnen, T. F. Jamison and M. M. Bio, *Org. Process Res. Dev.*, 2020, **24**, 2298–2303.
19 J. Morvan, T. McBride, I. Curbet, S. Colombel-Rouen, T. Roisnel, C. Crévisy, D. L. Browne and M. Mauduit, *Angew. Chem., Int. Ed.*, 2021, **60**, 19685–19690.
20 K. Skowerski, S. J. Czarnocki and P. Knapkiewicz, *ChemSusChem*, 2014, **7**, 536–542.
21 R. S. Phatake, N. B. Nechmad, O. Reany and N. G. Lemcoff, *Adv. Synth. Catal.*, 2022, **364**, 1465–1472.
22 F. Ziegler, J. Teske, I. Elser, M. Dyballa, W. Frey, H. Kraus, N. Hansen, J. Rybka, U. Tallarek and M. R. Buchmeiser, *J. Am. Chem. Soc.*, 2019, **141**, 19014–19022.
23 U. Tallarek, J. Hochstrasser, F. Ziegler, X. Huang, C. Kübel and M. R. Buchmeiser, *ChemCatChem*, 2021, **13**, 281–292.
24 F. Ziegler, T. Roider, M. Pyschik, C. P. Haas, D. Wang, U. Tallarek and M. R. Buchmeiser, *ChemCatChem*, 2021, **13**, 2234–2241.
25 S. T. Emmerling, F. Ziegler, F. R. Fischer, R. Schoch, M. Bauer, B. Plietker, M. R. Buchmeiser and B. V. Lotsch, *Chem. – Eur. J.*, 2022, **28**, e202104108.
26 N.-W. Wu, I. D. Petsalakis, G. Theodorakopoulos, Y. Yu and J. Rebek, *Angew. Chem., Int. Ed.*, 2018, **57**, 15091–15095.
27 A. Sytniczuk, M. Dąbrowski, Ł. Banach, M. Urban, S. Czarnocka-Śniadała, M. Milewski, A. Kajetanowicz and K. Grela, *J. Am. Chem. Soc.*, 2018, **140**, 8895–8901.
28 R. R. Schrock, *Angew. Chem., Int. Ed.*, 2006, **45**, 3748–3759.
29 M. Yu, C. Wang, A. F. Kyle, P. Jakubec, D. J. Dixon, R. R. Schrock and A. H. Hoveyda, *Nature*, 2011, **479**, 88–93.
30 C. Wang, M. Yu, A. F. Kyle, P. Jakubec, D. J. Dixon, R. R. Schrock and A. H. Hoveyda, *Chem. – Eur. J.*, 2013, **19**, 2726–2740.
31 Y. Mu, F. W. W. Hartrampf, E. C. Yu, K. E. Lounsbury, R. R. Schrock, F. Romiti and A. H. Hoveyda, *Nat. Chem.*, 2022, **14**, 640–649.
32 N. Dolatabadi, R. Rahmani, H. Rahnejat, C. P. Garner and C. Brunton, *Lubricants*, 2020, **8**, 17.
33 P. Ridgway Watt, *Vacuum*, 1956, **6**, 113–160.
34 L. Ondi, G. M. Nagy, J. B. Czirok, A. Bucsai and G. E. Frater, *Org. Process Res. Dev.*, 2016, **20**, 1709–1716.
35 J. E. Dander, N. A. Weires and N. K. Garg, *Org. Lett.*, 2016, **18**, 3934–3936.
36 Y. Chen, M. M. Abdellatif and K. Nomura, *Tetrahedron*, 2018, **74**, 619–643.
37 A. Fürstner, O. R. Thiel and C. W. Lehmann, *Organometallics*, 2002, **21**, 331–335.
38 For a recent example of a ketone olefination with **Mo1**, see: D. J. Nasrallah, T. E. Zehnder, J. R. Ludwig, D. C. Steigerwald, J. J. Kiernicki, N. K. Szymczak and C. S. Schindler, *Angew. Chem., Int. Ed.*, 2022, **61**, e202112101.
39 P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.
40 (*Z*)-6-Nonen-1-ol occurs naturally in melon fruits, such as honeydew and muskmelon, see: D. Kourkoutas, J. S. Elmore and D. S. Mottram, *Food Chem.*, 2006, **97**, 95–102.
41 A. Lapkin and D. J. C. Constable, *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*, Blackwell Publishing Ltd, 2008.
42 R. A. Sheldon, *ACS Sustainable Chem. Eng.*, 2018, **6**, 32–48.