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Microwave-Assisted Ruthenium-Catalysed Olefin Metathesis in Fluorinated Aromatic Hydrocarbons: A Beneficial Combination

Cezary Samojłowicz,[a] Etienne Borré,[b,c] Marc Mauduit,[b,c,*] and Karol Grela[a,*]

[a] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
Fax: (+48)-22-343-2109; phone: (+48)-22-343-2108; e-mail: klgrela@gmail.com
[b] Sciences Chimiques de Rennes, UMR 6226, CNRS – Equipe Chimie Organique et Supramoléculaire, Ecole Nationale Supérieure de Chimie de Rennes, Av. du Général Leclerc, CS 50837, 35708 Rennes cedex 7, France
[c] Université européenne de Bretagne, 35000 Rennes, France
Fax: (+33)-2-2323-8108; phone: (+33)-2-2323-8112; e-mail: marc.mauduit@ensc-rennes.fr

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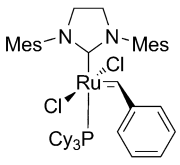
Abstract: High conversions in ruthenium-based olefin metathesis of demanding substrates are commonly forced by using a high loading of a catalyst and conducting reactions at elevated temperature for extended times. However, in many cases this approach is not fully effective. In this article we present that fluorinated aromatic hydrocarbons (FAH) combined with microwave (MW) irradiation using a commercially available ruthenium-based pre-catalyst creates attractive reaction conditions for promoting challenging olefin metathesis transformations.

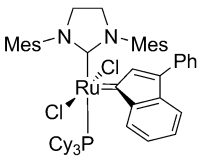
Keywords: fluorinated aromatic hydrocarbons; microwave irradiation; N-heterocyclic carbenes; olefin metathesis; ruthenium

Introduction

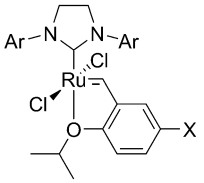
Functionalised olefins are important building blocks in organic synthesis.[1] Catalytic olefin cross-metathesis (CM), ring-closing metathesis (RCM) and en-yne metathesis are convenient routes to obtain functionalised molecules from simple alkene, diene and en-yne precursors.[1] With the advent of stable, commercially available 2nd generation ruthenium complexes (**1a**–**e**, **g**),[1–4] that combine high catalytic activity and excellent functional group tolerance, olefin metathesis reactions have emerged as one of the most attractive and powerful tools for the formation of new carbon-carbon double bonds (Figure 1). Although a wide range of functionalised di- or trisubstituted olefins can be used efficiently in olefin metathesis transformations,[2–4] some sterically or electronically deactivated substrates are still challenging and typically require high loadings of the Ru complexes and extended reaction times.[4] Recently, through an important effort in the design of N-heterocyclic carbene (NHC) ligands, Grubbs et al. have reported attractive new Ru complexes (**1e**, **1f**) enabling one to improve significantly the yield in RCM[4] and CM transformations.[5] However, in some cases, the efficiency of these catalysts takes place to the detriment of stability in the reaction media (catalyst lifetime).[4,5]



1a



1b



1c Ar = Mes, X = H
1d Ar = Mes, X = NO_2
1e Ar = Tol, X = H
1f Ar = 3,6-(*t*-Bu)$_2$C$_6$H$_3$, X = H
1g Ar = Mes, X = NH-CO-CF_3

Figure 1. Ruthenium-based olefin metathesis initiators. Cy = cyclohexyl; Mes = 2,4,6-trimethylphenyl; Tol = 2-methylphenyl.

Very recently, another approach based on modifications of the reaction conditions, by use of fluorinated aromatic hydrocarbons (FAH), e.g., C_6F_6 and $C_6F_5CF_3$, to dope the activity of standard ruthenium 2nd generation commercially available initiators has been published.[6–8] This approach was found to be quite successful in the case of a wide range of difficult olefin metathesis substrates, including biologically active compounds.[7]

The use of microwave (MW) irradiation is a well known practice in modern organic synthesis as an alternative way to optimise the thermal activation.[9] In many cases, the main profit is a dramatic reduction of reaction time limiting the premature degradation of the catalyst and/or formation of by-products and enhancing the yields for demanding substrates.[9] However, it should be quoted that the beneficial effect of microwave irradiation in general, and particularly on olefin metathesis reactions is poorly understood.[9b,c] Nevertheless, in view of these improvements, we decided to examine if a synergistic effect could be observed in difficult metathesis transformations promoted by commercially available ruthenium complexes **1a–d**, **g** and conducted in FAH solvents under microwave irradiation.

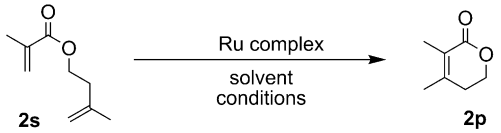
Results and Discussion

The first demanding substrate, which has been selected by us, was diene **2s** leading to the formation of six-membered lactone **2p**, bearing a tetrasusbtituted C–C bond (Table 1). The presence of such a lactone as a structural subunit in numerous natural products makes the possibility of accessing it *via* RCM very attractive.[10] As reported by Grubbs and co-workers in 2007, despite the higher reactivity of new modified NHC complexes **1e** and **1f**, the ring closing of **2s** was unproductive under "classical" thermal conditions (5 mol%, C_6D_6, 0.1 M, 60 °C, 24 h; entry 1).[4] In the meantime, D'Annibal and co-workers have reported the isolation of lactone **2p** in a low yield of 40% but requiring a large amount of Ru complex **1a** (20 mol%, entry 2).[10a]

We started our study by confirming, indeed, the absence of reactivity of **2s** with 2 mol% of **1b** in C_6D_6, where no product was observed at 100 °C over 24 h (the reaction was conducted in a sealed vial, entry 3). Interestingly, with the same catalyst loading, using hexafluorobenzene, 15% formation of desired product **2p** was observed at 100 °C after only 15 min (entry 4). However, when the same reaction mixture was heated *via* microwave irradiation (100 °C, 200 W), 31% conversion of **2s** has been obtained (entry 5). In the next step, we used octafluorotoluene at 120 °C and after 15 min (entry 6) we observed 33% conversion of **2s**. Octafluorotoluene in combination with microwave irradiation (120 °C, 200 W, entry 7) led to improved conversion up to 57%. Remarkably, under fully optimised conditions (e.g., 2×2 mol% of **1b**, 2×15 min of microwave irradiation, entry 8), the expected lactone **2p** was obtained in 80% isolated yield.[6b]

It is worth noting that while the increase of catalyst activity in FAH solvents was clearly demonstrated in practically all cases tested,[6,7] the additional benefit of microwave irradiation was not observed for all hindered substrates. As showed in Figure 2, the formation of cyclic olefin **3p** bearing a tetrasubstituted C=C double bond at 100 °C within 5 min in hexafluorobenzene gave improved results compared to "classical" solvent (63% *vs.* 23%, respectively), however, microwave irradiation has not improved the yield significantly. Interestingly, repeated heating did not allow us to increase the conversion, attesting the

Table 1. RCM leading to lactone **2p**.



Entry	Solvent (conc.)	Complex (mol%)	Conditions	Conversion [%][a]
1a	C_6D_6 (0.1 M)	**1e** (5)	60 °C, 24 h	0[4a]
1b	C_6D_6 (0.1 M)	**1f** (5)	60 °C, 24 h	0[4a]
2	CH_2Cl_2 (0.01 M)	**1a** (20)	40 °C, 48 h	(40)[10a]
3	C_6D_6 (0.2 M)	**1b** (2)	100 °C, 24 h	0
4	C_6F_6 (0.2 M)	**1b** (2)	100 °C, 15 min	15
5	C_6F_6 (0.2 M)	**1b** (2)	100 °C, 15 min, MW (200 W)	31
6	$C_6F_5CF_3$ (0.2 M)	**1b** (2)	120 °C, 15 min	33
7	$C_6F_5CF_3$ (0.2 M)	**1b** (2)	120 °C, 15 min, MW (200 W)	57
8	$C_6F_5CF_3$ (0.2 M)	**1b** (2×2)[b]	120 °C, 2×15 min, MW (200 W)	81 (80)

[a] Determined by ^{1}H NMR spectroscopy. In parenthesis are isolated yields of analytically pure product.
[b] MW irradiation has been repeated using 2 mol% of pre-catalysts.

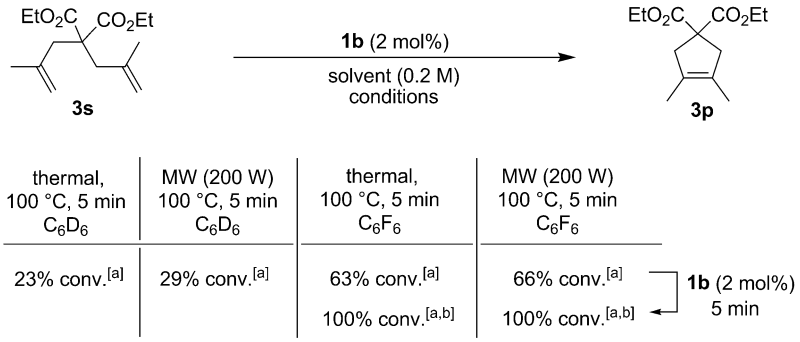


Figure 2. RCM of **3s** leading to tetrasubstituted olefin **3p**. [a] Determined by ^{1}H NMR. [b] Reaction protocol has been repeated.

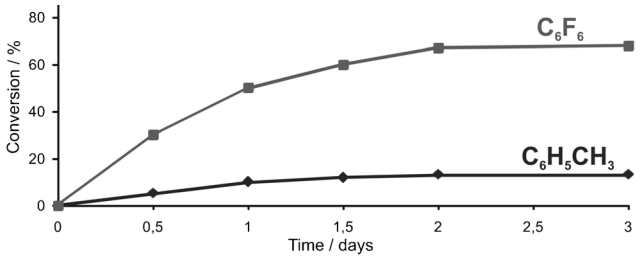


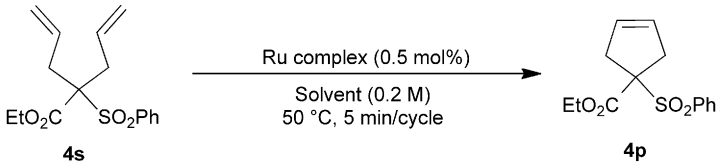
Figure 3. Reaction profile of RCM with **3s**. *Reaction conditions:* 5 mol% of **1b**, 0.2 M, 40 °C, 3 days.

probable rapid deactivation of the Ru active species.[1d,e] Therefore, we have attempted to study an RCM reaction profile with catalyst **1b** in FAH *vs.* a non-fluorinated aromatic solvent (Figure 3). The reaction profiles of RCM of **3s** in C_6F_6 and in toluene at 40 °C promoted by pre-catalyst[11] **1b** (5 mol%) differ dramatically, suggesting that the lifetime of the active catalytic species is prolonged in the FAH media. Indeed, the formation of **3p** increased continually in C_6F_6 until 48 h reaching a maximum of 70% whereas a premature degradation of pre-catalyst **1b** occurred in toluene, stopping the transformation (reaching only 13% conversion of **3s**) at the beginning of the reaction.

In the next experiment we decided to examine further the stability of the Ru pre-catalysts and the catalytically active species in the presence of diene **4s**. The straightforward starting material was selected for the RCM transformation (Table 2) using C_6D_6 and C_6F_6 as solvents. The reaction was performed with low loadings (0.5 mol% at 50 °C) of well established Ru complexes of both types of pre-catalyst: Grubbs 2nd generation (**1a**) and the more stable Hoveyda 2nd generation (**1c**). After each 5 min of the reaction its progress has been measured using ^{1}H NMR spectroscopy and a fresh amount of **4s** was added into the reaction mixture.

Interestingly, in RCM of **4s** more catalytic cycles took place in FAHs compared to "classical" solvent (Table 2) for both ruthenium complexes. In the case of **1a** we observed 500 and 1000 catalytic turnover numbers (TONs) in C_6D_6 and C_6F_6, respectively, whereas for **1c** TONs reached 1400 and 1800, respectively. These results can suggest that FAH solvents prevent quick degradation of the Ru propargating species.

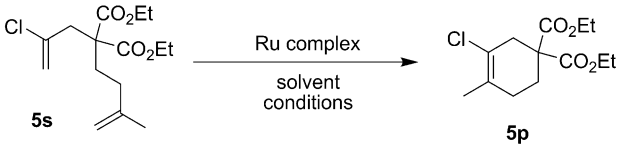
Table 2. Stability of **1a** and **1c** in C_6D_6 and C_6F_6.



		Reaction Cycle/Conversion [%][a]										
Complex	Solvent	1	2	3	4	5	6	7	8	9	10	Σ TON
1a	C_6D_6	>99	>99	47	-	-	-	-	-	-	-	500
1a	C_6F_6	>99	>99	>99	95	63	26	-	-	-	-	1000
1c	C_6D_6	>99	>99	92	86	75	60	33	15	-	-	1400
1c	C_6F_6	>99	>99	>99	>99	>99	83	69	50	31	10	1800

[a] Determined by ^{1}H NMR spectroscopy.

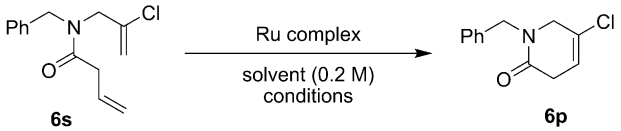
Table 3. RCM to form tetrasubstituted chloro-olefin **5p**.



Entry	Solvent (conc.)	Complex (mol%)	Conditions	Conversion [%][a]
1	C_6D_6 (0.1 M)	**1e** (5)	60 °C, 18 h	24[13b]
2	$C_6D_5CD_3$ (0.2 M)	**1b** (5)	120 °C, 24 h	35
3	C_6D_6 (0.2 M)	**1b** (2)	100 °C, 10 min, MW (200 W)	15
4	C_6F_6 (0.2 M)	**1b** (2)	100 °C, 10 min, MW (200 W)	34
5	$C_6F_5CF_3$ (0.2 M)	**1b** (2)	120 °C, 10 min, MW (200 W)	50
6	$C_6F_5CF_3$ (0.2 M)	**1b** (2×2)[b]	120 °C, 2×10 min MW (200 W)	82 (78)

[a] Determined by ^{1}H NMR spectroscopy. In parenthesis are isolated yields of analytically pure product.
[b] MW irradiation has been repeated using each time 2 mol% of pre-catalyst **1b.**

Table 4. RCM leading to lactam **6p**.



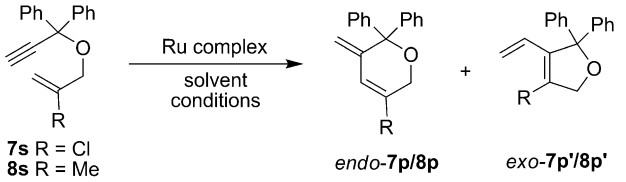
Entry	Solvent[a]	Complex (mol%)	Conditions	Conversion [%][a]
1	$C_6D_5CD_3$	**1b** (6)	100 °C, 24 h	0
2	C_6F_6	**1b** (3×2)[b]	100 °C, 3×5 min	29
3	C_6F_6	**1b** (3×2)[b]	100 °C, 3×5 min, MW (200 W)	69 (61)

[a] Determined by ^{1}H NMR spectroscopy. In parenthesis are isolated yields of analytically pure product.
[b] The reaction protocol has been repeated three times using each time a fresh portion (2 mol%) of pre-catalyst **1b**.

Having these results in hand, we decided to test our newly developed conditions towards some even more reluctant dienes, such as **5s**, a precursor of the tetrasubstituted chloro-olefin **5p** (Table 3). The reluctance of this kind of substrate is well documented,[12] and is probably related to both the electronic and steric deactivating effects of the olefin function. The total synthesis of an Elatol (that belongs to chamigrene subclass of sesquiterpenes, characterised by a spiro-[5.5]undecane core) involving such a difficult RCM, has been recently executed by Stolz et al. using the more reactive, NHC modified catalyst **1e**.[13] In our model study, we used **5s** as a closely related substrate, that has been recently described by the same authors as even more challenging for catalyst **1e** (Table 3, entry 1) than the Elatol precursor.[13] The "classical" conditions in combination with standard pre-catalyst **1b** under both thermal condition (120 °C, 24 h) or microwave irradiation (100 °C, 200 W, 10 min), gave only low conversions of the cyclic product **5p**, 35% and 15%, respectively (entries 2 and 3). In hexafluorobenzene using microwave irradiation, the conversion was slightly improved, reaching 34% (entry 4). A more significant doping of activity was observed when octafluorotoluene was combined with microwave irradiation effect (entry 5) giving a 50% conversion of **5s**. Finally, when 4 mol% of the catalyst (added in two consecutive portions) was used over 20 min, the desired tetrasubstituted chloro-olefin **5p** was isolated in a remarkable yield of 78% after purification (entry 6).

Next, we focused our attention on the amide[14] **6s** bearing also a chloro-substituted C=C double bond (Table 4). Its corresponding RCM product, lactam **6p**, is an important fragment for the construction of building blocks through cross-coupling reactions.[15] However, the problem related to this substrate is not only the presence of the electronically deactivating chloro substituent, but also the ability of the amide function to neutralise the 14-electron Ru active species by chelation.[16] Due to the mentioned factors, **6s** in toluene remained completely inert towards 6 mol% of **1b** under "classical" thermal conditions, even after a prolonged heating (100 °C, 24 h, entry 1). Under thermal conditions in C_6F_6, only 29% of the expected lactam **6p** was formed after 15 min at 100 °C (entry 2). Interestingly, in hexafluorobenzene using microwave

Table 5. En-yne metathesis leading to *endo*/*exo* products.



Entry (Substrate)	Solvent (conc.)	Complex (mol%)	Conditions	*endo*/*exo*	Conversion [%][a]
1 (**7s**)	CH_2Cl_2 (0.01 M)	**1b** (10)	40 °C, 24 h	–	0
2 (**7s**)	$C_6H_5CH_3$ (0.1 M)	**1b** (10)	120 °C, 24 h	–	0
3 (**7s**)	$C_6F_5CF_3$ (0.1 M)	**1b** (2×5)[b]	120 °C, 2×15 min MW (200 W)	100/0	25
4 (**7s**)	$C_6F_5CF_3$ (0.1 M)	**1c** (2×5)[b]	120 °C, 2×15 min MW (200 W)	100/0	33
5 (**7s**)	$C_6F_5CF_3$ (0.1 M)	**1d** (2×5)[b]	120 °C, 2×15 min MW (200 W)	100/0	75 (60)
6 (**7s**)	$C_6F_5CF_3$ (0.1 M)	**1d** (2×5)[b]	120 °C, 2×15 min	100/0	17
7 (**8s**)	$C_6H_5CH_3$ (0.02 M)	**1a** (5)	70 °C, 14 h	0/100	(73)[19a]
8 (**8s**)	$C_6F_5CF_3$ (0.2 M)	**1a** (5)	120 °C, 24 h	0/100	80
9 (**8s**)	$C_6F_5CF_3$ (0.2 M)	**1a** (2×2)[b]	120 °C, 2×5 min MW (200 W)	0/100	79 (75)

[a] Determined by ^{1}H NMR spectroscopy. In parenthesis are isolated yields of analytically pure product.
[b] The reaction protocol has been repeated two times using each time a fresh portion (2 or 5 mol%) of the pre-catalyst.

irradiation at 100 °C, the conversion was significantly improved reaching up to 69% conversion and 61% isolated yield after only 15 min (entry 3).

A similar beneficial effect was also observed in the en-yne metathesis of **7s** bearing also a chloro-alkene function (Table 5, entries 1–6). Indeed, under "classical" thermal conditions, using **1b** in dichloromethane at 40 °C or in toluene at 120 °C, only the starting material was present after 24 h (entries 1 and 2). When the reaction was conducted in octafluorotoluene at 120 °C under microwave irradiation (**1b** at 2×5 mol% over 2×15 min, entry 3), only 25% of the cyclised product was formed. Interestingly, we have identified by ^{1}H NMR that the formed metathesis product was the six-membered *endo*-carbocyclic diene **7p** instead of the expected five-membered *exo*-diene **7p′**. It is worthy of mention that such a high *endo*-selectivity is quite rare in ruthenium-catalysed en-yne reactions,[17] but typical in those catalysed by molybdenum complexes.[18] We have also tried the Hoveyda pre-catalyst **1c** under similar conditions and observed a slight improvement of the conversion (33%, entry 4). Finally, the best activity was obtained with the activated "nitro" pre-catalyst **1d** allowing us to obtain the *exo*-diene **7p** with a remarkable 75% conversion and in 60% isolated yield (Table 5, entry 5).

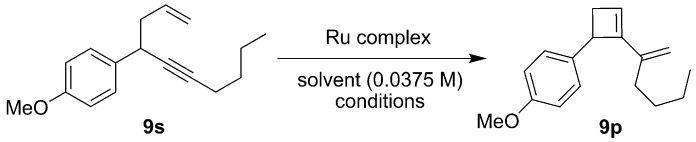
The less pronounced, but still beneficial, effect of the FAH/MW combination was also visible in the case of another challenging substrate, methallyl en-yne **8s**, leading to the expected *exo*-carbocyclic diene **8p′** (Table 5, entries 7–9). However, except for the reduction of the reaction time (10 min *vs.* 14 h) and the catalyst loading (4 mol% *vs.* 5 mol%),[19] no significant differences were noted between "classical" and FAH/MW conditions, under which similar isolated yields were observed (73% and 75%, respectively).

Another highly reluctant substrate, recently reported by Campagne and Debleds, is 1,5-enyne **9s**, affording the strained cyclobutene **9p** (Table 6).[20] Hoveyda pre-catalyst **1c** (20 mol%) employed under microwave irradiation at 70 °C in dichloromethane lead to 53% of isolated yield (entry 1).[20a] Remarkably, using the same catalyst loading of **1c**, under optimised conditions in hexafluorobenzene at 100 °C gave full conversion and 76% isolated yield after 35 min of microwave irradiation (entry 2).

The positive results of the above experiments encouraged us to examine even more challenging cross-metathesis reactions. The first type of a reluctant starting material was olefin **10**, bearing bulky substituents in the allylic position (Table 7). As reported by Grubbs and co-workers,[5] CM of **10** with allylbenzene (**11**) or with 5-acetoxy-1-pentene (**12**), promoted by pre-catalyst **1c** gave the expected products **13** and **14** in moderate yields after 6 h in refluxing dichloromethane (entries 1 and 5). By using the newly developed, less hindered catalyst **1e**, the yields were improved up to 91% and 89%, respectively (entries 2 and 6).[5] In FAH, where the lifetime of the catalysts is extended (see Figure 3 and Table 2), **1b** showed excellent reactivity at 120 °C, giving **13** and **14** in 69% and 90% conversion (entries 3 and 7). Conversion could be improved up to 91% and 95%, respectively, by using octafluorotoluene in combination with microwave irradiation as the optimal conditions (entries 4 and 8, 82% and 86% isolated yields, respectively).

The second type of reluctant CM substrates tested were 1,1′-disubstituted olefins, such as compounds **15**

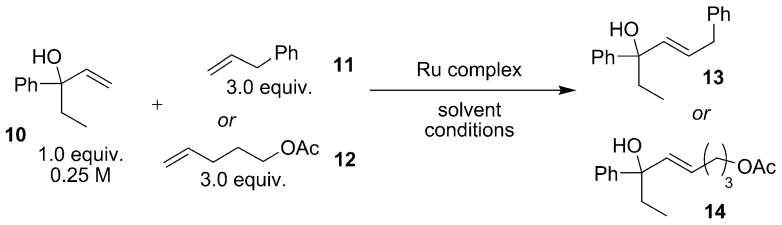
Table 6. 1,5-enyne cycloisomerization.



Entry	Solvent	Complex (mol%)	Conditions	Conversion [%][a]
1	CH_2Cl_2	**1c** (20)	70 °C, 35 min, MW (200 W)	(53)[20a]
2	C_6F_6	**1c** (20)	100 °C, 35 min, MW (200 W)	100 (76)

[a] Determined by ^{1}H NMR spectroscopy. In parenthesis are isolated yields of analytically pure product.

Table 7. Formation of disubstituted olefins in CM with **10**.



Entry (Olefin)	Solvent	Complex (mol%)	Conditions	Product[a]/Conversion [%][b]
1 (**11**)	CH_2Cl_2	**1c** (5)	40 °C, 6 h	**13**/(64)[5]
2 (**11**)	CH_2Cl_2	**1e** (5)	40 °C, 6 h	**13**/(91)[5]
3 (**11**)	$C_6F_5CF_3$	**1b** (3×2)[c]	120 °C, 3×10 min	**13**/69
4 (**11**)	$C_6F_5CF_3$	**1b** (3×2)[c]	120 °C, 3×10 min MW (200 W)	**13**/91 (82)
5 (**12**)	CH_2Cl_2	**1c** (5)	40 °C, 6 h	**14**/(70)[5]
6 (**12**)	CH_2Cl_2	**1e** (5)	40 °C, 6 h	**14**/(89)[5]
7 (**12**)	$C_6F_5CF_3$	**1b** (3×2)[c]	120 °C, 3×10 min	**14**/90
8 (**12**)	$C_6F_5CF_3$	**1b** (3×2)[c]	120 °C, 3×10 min MW (200 W)	**14**/95 (86)

[a] $E/Z > 20/1$ in all cases.
[b] Determined by ^{1}H NMR. In parenthesis are isolated yields of analytically pure product.
[c] Reaction protocol has been repeated three times using each time a fresh portion (2 mol%) of pre-catalyst **1b**.

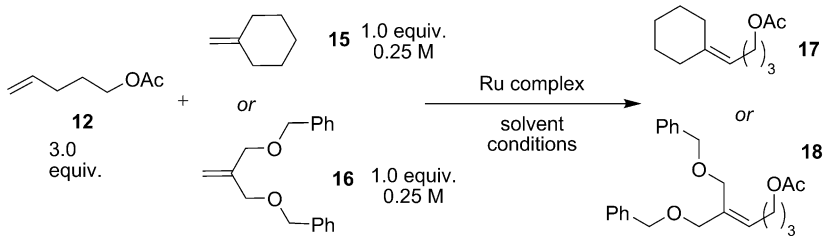
and **16** (Table 8). It has been reported that under "classical" conditions these olefins in CM with 5-acetoxy-1-pentene (**12**) promoted by **1c**, gave products **17** and **18** in 78% and 32% yield, respectively (entries 1 and 4).[2b,5] We decided to evaluate the phosphine-containing complex **1b** under optimised conditions. Unfortunately, in spite of the higher loading of pre-catalyst **1b** (8 mol% instead of 5 mol%) at elevated temperature (120 °C), we obtained only 50% and 41% of conversion for **17** and **18** in FAH solvent (entries 2 and 5; $C_6F_5CF_3$, 40 min.). The use of microwave irradiation led to increased conversions in both cases – up to 61% and 67% (entries 3 and 6).

Another challenging molecule that has been modified in the CM reaction was *S*-(+)-carvone (**20**), a terpene derivative (Figure 4). Regrettably, after an optimisation process of the CM between **19** and **20** catalysed by 20 mol% of **1b** in optimal reaction conditions (microwave irradiation in $C_6F_5CF_3$ at 120 °C) the reaction led only to a 33% isolated yield of **21**.

Finally, the last demanding molecule that has been tested in CM reaction involved synthetic ethyl chrysanthemate **22** (Figure 5). The challenge of this transformation is related to substantial steric hindrance around the geminally disubstituted alkene fragment of **22**, bearing additionally a bulky substituent in the allylic position. As expected, only a low conversion of **22** in the CM reaction was observed under "classical" conditions (toluene-d_8, 120 °C, sealed vial). However, the desired olefin **23** was obtained as a mixture of isomers ($E/Z = 4.5:1$) in 64% NMR yield by applying microwave irradiation in $C_6F_5CF_3$ at 120 °C. The possibility of modifying the prenyl fragment ($CH{=}CMe_2$) *via* CM[21] opens a new and promising approach in the elaboration of new building blocks based on the naturally occurring compounds.

These CM reactions show that, indeed, there are still a number of attractive olefinic building blocks, which are unfortunately, very challenging substrates for metathetical transformations. Therefore, the con-

Table 8. Formation of trisubstituted olefins in CM with **12**.



Entry (Olefin)	Solvent	Complex (mol%)	Conditions	Product/Conversion [%][a]
1 (**15**)	CH_2Cl_2	**1c** (5)	40 °C, 24 h	**17**/(78)[5]
2 (**15**)	$C_6F_5CF_3$	**1b** (4×2)[b]	120 °C, 4×10 min	**17**/50
3 (**15**)	$C_6F_5CF_3$	**1b** (4×2)[b]	120 °C, 4×10 min MW (200 W)	**17**/61 (56)
4 (**16**)	CH_2Cl_2	**1c** (5)	40 °C, 24 h	**18**/(32)[2b]
5 (**16**)	$C_6F_5CF_3$	**1b** (4×2)[b]	120 °C, 4×10 min	**18**/41
6 (**16**)	$C_6F_5CF_3$	**1b** (4×2)[b]	120 °C, 4×10 min MW (200 W)	**18**/67 (62)

[a] Determined by ^{1}H NMR spectroscopy. In parenthesis are isolated yields of analytically pure product.
[b] Reaction protocol has been repeated four times using each time a fresh portion (2 mol%) of pre-catalyst **1b**.

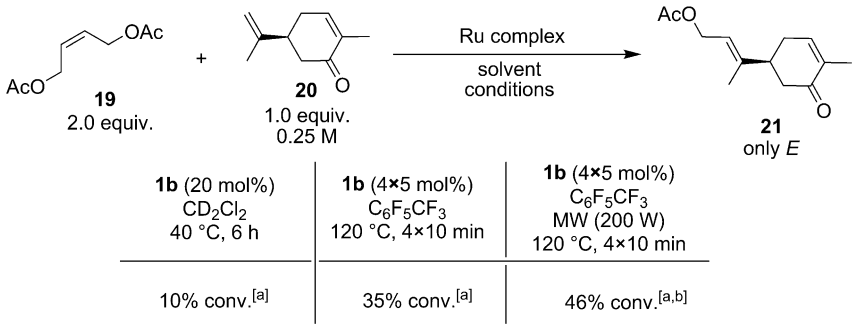


Figure 4. Modification of terpene scaffold. [a] Determined by ^{1}H NMR spectroscopy. [b] Isolated yields 33%.

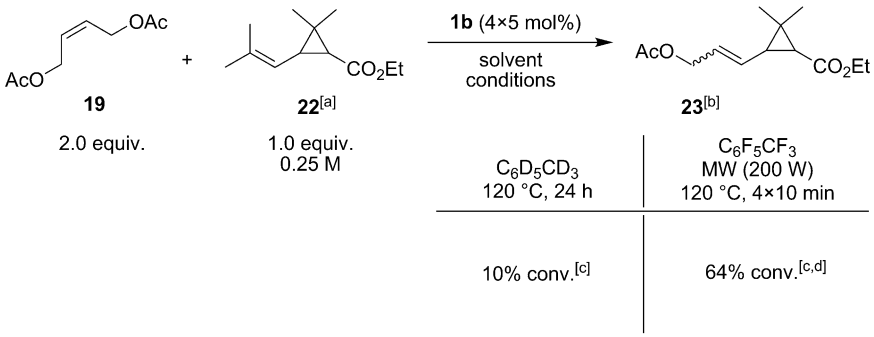


Figure 5. Modification of ethyl chrysanthemate scaffold. [a] 1:10 mixture of *cis*/*trans* isomers. [b] $E/Z = 4.5/1$ in all cases. [c] Determined by ^{1}H NMR spectroscopy. [d] Isolated yields 51%.

tinuous search for new reaction conditions as well as improvements of ruthenium pre-catalyst structures is of vital importance for the further development of olefin metathesis methodology.

Conclusions

In conclusion, we have demonstrated that fluorinated aromatic hydrocarbons used as solvent in ruthenium-catalysed olefin metathesis are able to give higher isolated yields in the challenging metathesis transformations compared to reactions performed in "classical" solvents.[28] Combining the activating effects of fluori-

nated aromatic hydrocarbons and microwave irradiation, we have developed new attractive reaction conditions for the efficient metathetical transformation of a wide range of reluctant precursors. Especially, RCM and en-yne cycloisomerisations of difficult substrates have been enhanced under FAH/MW conditions. Although we succeeded in showing that the combination of FAH/MW conditions gives a better outcome, each reaction needs to be studied carefully to find optimal reaction conditions. The still existing limitations in the synthesis of challenging molecules by olefin metathesis, require further research in this field.

Experimental Section

General Considerations

Microwave-assisted reactions were performed with a CEM Microwaves Discovery (200 W) using an infrared temperature detector. The reactions were performed in sealed vials using MW as well as conventional heating. The solvents: octafluorotoluene (FluoroChem), hexafluorobenzene (FluoroChem), toluene (Fluka), dichloromethane (Merck) and 1,2-dichloroethane (Aldrich) were dried by distillation over CaH_2 under argon and stored under an argon atmosphere. Analytical thin-layer chromatography (TLC) of all reactions was performed on silica gel 60 F_{254} TLC plates. Visualisation was performed with standard potassium permanganate stains or UV light. Flash column chromatographies were performed using silica gel 60 (230–400 mesh). NMR spectra were recorded using Bruker or Varian machines. Mass (EI) spectra were recorded on an AMD 604 Intectra GmbH spectrometer. Mass (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc. instrument. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer with a diamond ATR accessory. Elemental analyses were performed by Institute of Organic Chemistry, PAS, Warsaw. Glassware was either oven dried or flame dried, and reactions were performed under an argon atmosphere unless otherwise noted. All reagents were used as received. Catalysts were purchased and used as received: **1a**, **1b**, **1c**, **1e** (Aldrich), **1d** (Apeiron-Catalysts) and **1g** (Ωcat SYSTEM®). The following substrates (**2s**,[10a] **3s**,[22] **5s**,[13b] **8s**,[24] **9s**,[25] **10**[26] and **16**[27]) were prepared according to the literature procedures. The following products (**2p**,[10a] **3p**,[23] **5p**,[13b] **8p′**,[19c] **9p**,[20a] **13**,[5a] **14**,[5a] **17**[5a] and **18**[5a]) have been described previously and were identified by comparison of their physical and spectroscopic data (^{1}H and ^{13}C NMR, MS) with those in the cited references and their purities were confirmed by GC analysis.

Procedure for the Stability Studies

A Schlenk apparatus was filled with the pre-catalyst (0.002 mmol) and the C_6D_6 or C_6F_6 solvent (2 mL) under an argon atmosphere and then substrate **4s** (0.4 mmol) was added. After 5 min of reaction, a small amount (50 μL) of the reaction media was taken for NMR monitoring followed by another loading of **4s** (0.4 mmol). This procedure was repeated every 5 min until a significant amount of unconsumed starting material was detected. All the aliquots were diluted in C_6D_6 (400 μL) and the conversion of **4s** was measured by ^{1}H NMR spectroscopy.

General Procedure for the RCM Reactions

Reactions performed using conventional heating: A Schlenk flask was filled under argon with diene (0.4 mmol) and solvent (2 mL) before the addition of the pre-catalyst **1b** (0.008 mmol) as a solid. Progress of the reaction was monitored by TLC and ^{1}H NMR. The solvent was removed under vacuum and the crude residue was purified by flash chromatography.

Microwave heating: A microwave vial was filled with olefin (0.4 mmol) and solvent (2 mL) before the addition of the pre-catalyst **1b** (0.008 mmol). The vial was flushed with argon and then placed in a microwave reactor and heated for the reported time. Progress of the reaction was monitored by TLC and ^{1}H NMR. The procedure was repeated until disappearance of the starting material. The vial content was then transferred to a round-bottom flask where the solvent was removed under vacuum and the crude residue was purified by flash column chromatography to obtain the analytically pure product.

Ethyl 1-phenylsulfonyl-cyclopent-3-enecarboxylate (4p): The general procedure for RCM using conventional heating after flash chromatography on silica gel (*c*-hexane:EtOAc = 4:1, $R_f = 0.3$) afforded the title compound **4p** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.87$ (d, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.55 (dd, $J = 7.5$, 8.0 Hz, 2H), 5.62 (s, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.22 (AB, $J_{AB} = 16.0$ Hz, 4H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 168.5$ (C), 136.8 (C), 134.0 (CH), 129.9 (CH), 128.7 (CH), 127.5 (CH), 78.0 (C), 62.6 (CH_2), 38.8 (CH_2), 13.7 (CH_3): IR (film): $\nu = 3066$, 2984, 2939, 1732, 1584, 1478, 1448, 1367, 1309, 1269, 1206, 1147, 1084, 1055, 1016, 952, 861, 759, 722, 689, 632, 595, 556 cm^{-1}; HR-MS (ESI$^+$): $m/z = 303.0649$ $[M+Na]^+$, calcd. for $C_{14}H_{16}O_4SNa$: 303.0662; elem. anal. calcd. for $C_{14}H_{16}O_4S$: C 59.98, H 5.75, S 11.44; found: C 60.04, H, 5.58, S 11.33.

***N*-Benzyl-5-chloro-1,6-dihydropyridin-2(3*H*)-one (6p):** The general procedure for RCM using microwave heating after flash chromatography on silica gel (*c*-hexane/EtOAc = 9:1; $R_f = 0.2$) afforded the title compound **6p** as colorless crystals; mp 64–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.56$–7.27 (m, 5H), 5.83 (m, 1H), 4.64 (s, 2H), 3.88 (m, 2H), 3.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 165.5$ (C), 135.9 (C), 128.7 (CH), 128.2 (CH), 127.8 (CH), 123.6 (C), 120.1 (CH), 51.9 (CH_2), 49.6 (CH_2), 32.7 (CH_2). IR (KBr): $\nu = 2923$, 1650, 1487, 1453, 1408, 1360, 1332, 1289, 1254, 1204, 1174, 1095, 1076, 1029, 1015, 944, 877, 816, 766, 736, 700, 642, 500 cm^{-1}; HR-MS (EI$^+$): $m/z = 221.0600$ $[M]^{+\bullet}$, calcd. for $C_{12}H_{12}NO^{35}Cl$: 221.0607.

General Procedure for the En-Yne Reactions

Microwave heating: A microwave vial was filled with en-yne precursor (0.5 mmol) and solvent (5 mL) before the addition of the pre-catalyst (0.01 mmol). The vial was flushed with argon and then placed in a microwave reactor and heated for the reported time. Progress of the reaction was monitored by TLC and ^{1}H NMR. The procedure was repeated until disappearance of the starting material. The vial con-

tent was then transferred to a round-bottom flask where the solvent was removed under vacuum and the crude residue was purified by flash column chromatography to obtain the analytically pure product.

5-Chloro-3-methylene-2,2-diphenyl-3,6-dihydro-2*H*-pyran (7p): The general procedure yielded after flash chromatography on silica gel (pentane, $R_f = 0.1$) afforded the title compound **7p** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.40–7.30 (m, 10H), 6.20 (s, 1H), 5.83 (s, 1H), 5.32 (s, 1H), 4.46 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.5$ (C), 142.3 (C), 142.2 (C), 128.1 (CH), 128.0 (CH), 127.9 (CH), 117.8 (CH), 111.4 (CH_2) , 92.4 (C), 69.9 (CH_2). IR (film): $\nu = 3405$, 3096, 3071, 2955, 1881, 1782, 1643, 1624, 1595, 1583, 1493, 1461, 1376, 1323, 1279, 1226, 1202, 1192, 1175, 1135, 1093, 1074, 1007, 959, 827, 669, 639, 628, 509 cm^{-1}; HR-MS (EI$^+$): $m/z = 282.0806$ [M]$^{+\cdot}$, calcd. for $C_{18}H_{15}O^{35}Cl$: 282.0811.

General Procedure for the CM Reactions

Microwave heating: A microwave vial was filled with olefin (1 mmol), deactivated olefin partner (0.5 mmol) and solvent (2 mL) before the addition of the pre-catalyst **1b** (0.025 mmol). The vial was flushed with argon and then placed in a microwave reactor and heated for the reported time. Progress of the reaction was monitored by TLC and ^{1}H NMR. The procedure was repeated until disappearance of the starting material. The vial content was then transferred to a round-bottom flask where the solvent was removed under vacuum and the crude residue was purified by flash column chromatography to obtain the analytically pure product.

(*S*,*E*)-3-(4-Methyl-5-oxocyclohex-3-enyl)-but-2-enyl acetate (21): The general procedure yielded after flash chromatography on silica gel (*c*-hexane:EtOAc = 9:1; $R_f = 0.1$) afforded the title compound **21** as a brownish oil. ^{1}H NMR (600 MHz, $CDCl_3$) $\delta =$ 6.76–6.43 (m, 1H), 5.40 (tt, $J = 1.2$, 6.9 Hz, 1H), 4.61 (d, $J = 6.9$ Hz, 2H), 2.73–2.67 (m, 1H), 2.56 (ddd, $J = 1.6$, 3.8, 15.9 Hz, 1H), 2.44–2.28 (m, 3H), 2.06 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 199.4$ (C), 170.9 (C), 144.4 (CH), 142.4 (C), 135.5 (C), 119.1 (CH), 61.1 (CH_2), 43.9 (CH), 42.8 (CH_2), 30.9 (CH_2), 20.9 (CH_3), 15.7 (CH_3), 14.6 (CH_3); IR (film): $\nu = 2953$, 2924, 1981, 1935, 1738, 1674, 1435, 1368, 1232, 1112, 1024, 958, 903, 799, 706, 607, 494, 444 cm^{-1}; HR-MS (EI$^+$): $m/z = 222.1250$ [M]$^{+\cdot}$, calcd. for $C_{13}H_{18}O_3$: 222.1256.

(*E*/*Z*)-Ethyl 3-(3-Acetoxyprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (23): The general procedure yielded after flash chromatography on silica gel (*c*-hexane-EtOAc = 20:1; $R_f = 0.1$) afforded the title compound **23** as a brownish oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.75$ (td, $J = 6.5$, 15.3 Hz, 1H), 5.53 (dd, $J = 8.7$, 15.3 Hz, 1H), 4.53 (d, $J =$ 6.5 Hz, 2H), 4.18–4.07 (m, 2H), 2.06 (s, 3H), 1.57 (d, $J =$ 5.3 Hz, 1H), 1.29–1.24 (m, 7H), 1.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 171.7$ (C), 170.8 (C), 133.1 (CH), 125.9 (CH), 64.8 (CH_2), 60.4 (CH_2), 35.3 (CH_3), 34.2 (CH), 28.7 (C), 22.1 (CH_3), 21.0 (CH), 20.2 (CH_3), 14.3 (CH_3); IR (film): $\nu = 2981$, 2953, 2876, 1741, 1726, 1668, 1459, 1448, 1430, 1380, 1341, 1277, 1231, 1177, 1148, 1115, 1096, 1075, 1057, 1026, 967, 844, 607 cm^{-1}; HR-MS (ESI$^+$): $m/z =$ 263.1264 [M + Na]$^+$, calcd. for $C_{13}H_{20}O_4Na$: 263.1254 ; elem. anal. calcd. for $C_{13}H_{20}O_4$: C 64.98, H 8.39; found: C 64.99, H 8.24.

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