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Olefin Metathesis

Hoveyda-Type Quinone-Containing Complexes – Catalysts to Prevent Migration of the Double Bond under Metathesis Conditions

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Abstract: Three new quinone-containing Hoveyda-type complexes have been synthesised and fully characterised. Their ability to suppress undesired double-bond migration along the carbon chain during metathesis reactions was examined. It was proved that these catalysts decrease the amounts of undesired side-products with a shifted double bond in the reaction mixture.

Introduction

The role of olefin metathesis in organic chemistry has grown enormously over the last four decades because this reaction is a very efficient and elegant method for the formation of C=C double bonds.[1–3] What is more, recent developments in the field have significantly facilitated 1) the control of *E*/*Z* selectivity,[4–8] 2) the synthesis of enantiopure cyclic olefins in ring-closing metathesis,[9–13] 3) the application of metathesis for the conversion of biomass into useful products[14–19] and 4) decreasing the amount of ruthenium in the final product.[20] The latter is of key importance for the pharmaceutical industry, which increasingly utilises metathesis as a key step in the total synthesis of biologically active compounds.[21–25] Olefin metathesis is used not only in small-scale laboratory research, but can also be applied in large-scale industrial production,[26] mostly because of the easy access to the efficient well-defined catalysts produced in large quantity and which are stable towards impurities in industrial-grade solvents. Despite these great achievements, suppressing the isomerisation of the double bonds during the metathesis reactions is still problematic.[27,28]

Although in some cases the isomerisation of a double bond can be a useful synthetic methodology,[29–32] in many cases it is an undesired side-reaction that can significantly alter the product distribution and decrease the yield of the desired product.

During a metathesis reaction, a mixture of products can be formed due to alkene C=C double-bond migration, which can occur both in the substrates and products. The isomerisation products can also undergo metathesis and therefore three major groups of products can be identified in the reaction mixture (Scheme 1): the primary metathesis products (PMP), isomerisation products (IP) and secondary metathesis products (SMP), which leads to a decrease in the yield of the desired products. Additionally, the side-products resulting from unwanted isomerisation are frequently difficult to remove by standard purification techniques. Moreover, evidence has been provided that undesired double-bond isomerisation can lead to the accumulation of isomers that can act as catalyst inhibitors.[33]

Various researchers have conducted mechanistic studies of the isomerisation processes occurring during metathesis reactions by using both in vitro[34–38] and in silico[39] methods. It has been found that ruthenium hydrides like **A**,[40] **B**[41,42] or **C**[43,44] as well as ruthenium nanoparticles[45] (Figure 1), which can be formed as decomposition products from metathesis catalysts, can act as isomerisation agents. These species can be removed from the reaction mixtures by reaction with various additives, for example, quinones,[46–49] acetic acid,[46,47] chlorocatecholborane[50] and phenylphosphoric acids,[51] however, the effectiveness of suppressing the undesired migration of a double bond is not always sufficient.

Grubbs and co-workers investigated the influence of 1,4-benzoquinones and other additives on the isomerisation of C=C double bonds in a number of olefin metathesis reactions of allylic ethers and amines as well as long-chain aliphatic alkenes in the presence of ruthenium catalysts.[46,47] In most reactions investigated, quinones and acetic acid were the most effective agents for suppressing undesirable double-bond migration, whereas radical scavengers, such as BHT (butylated 4-hydroxytoluene), TEMPO [2,2,6,6-tetramethylpiperidin-1-yl)oxyl], phenol and 4-methoxyphenol, were, in general, much less effective. Quinones were also utilised by Rutjes and co-workers in the ring-closing metathesis of homoallylic derivatives of dehydroamino acids.[48] Although 1,4-benzoquinone significantly inhibited the isomerisation of the allylic ether fragments of all the

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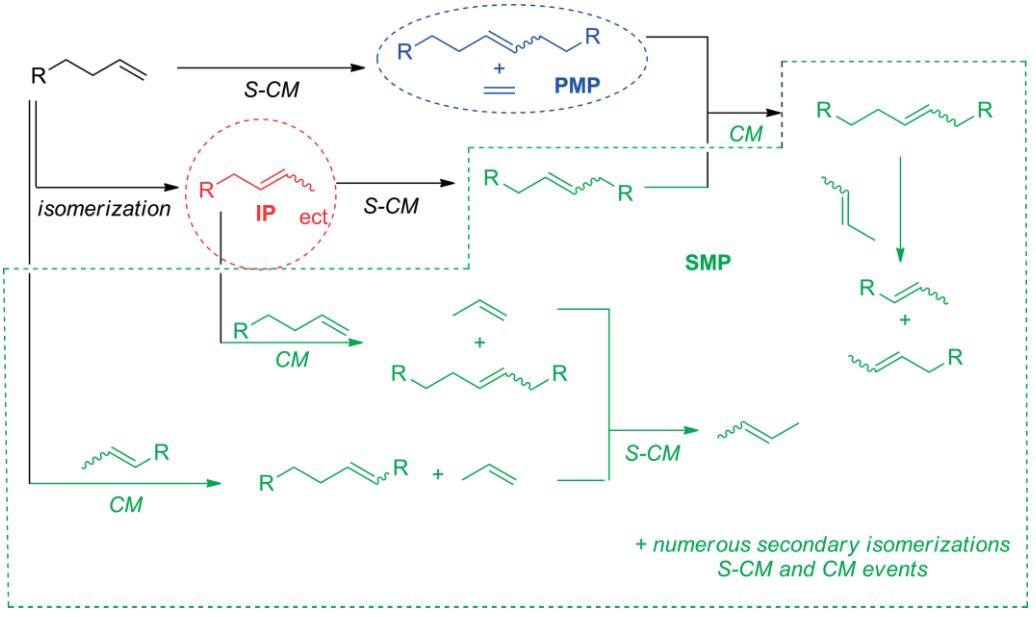


Scheme 1. Possible reactions of linear alkenes in the presence of a metathesis catalyst. (CM = cross metathesis, S–CM = self-metathesis. Colour codes: blue: primary metathesis products (PMP), red: isomerisation products (IP), and green: secondary metathesis products (SMP).

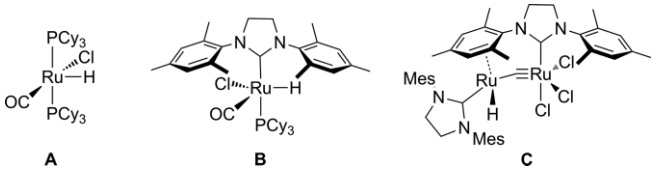


Figure 1. Examples of ruthenium hydrides active in the isomerisation of double bonds. Cy = cyclohexyl, Mes = mesityl.

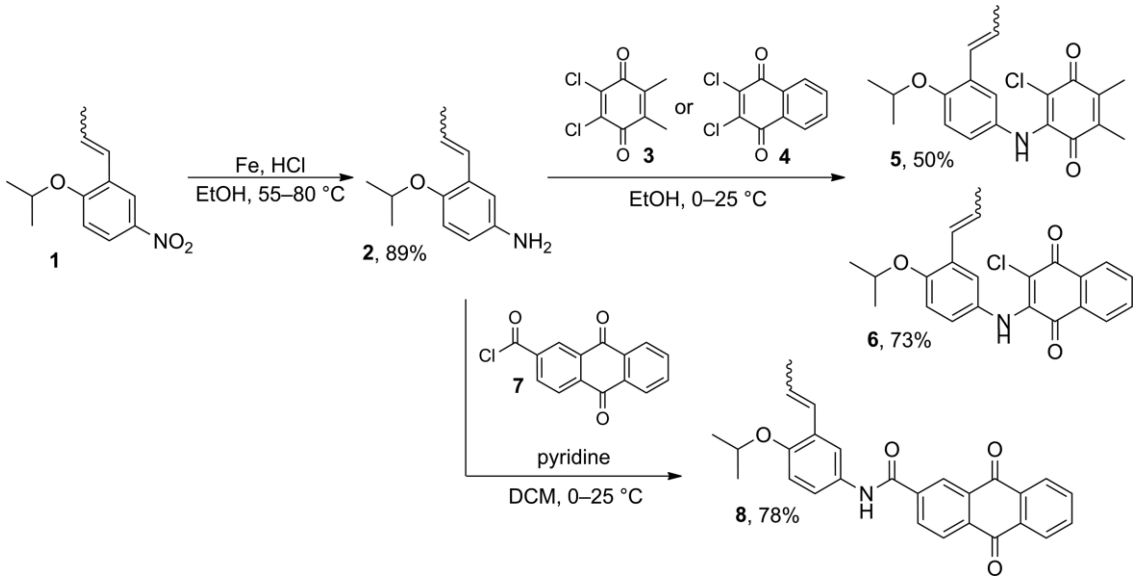
used substrates, the absolute yields of the products did not always increase, because the additive scavenged the ruthenium hydride or other decomposition products but did not necessarily inhibit catalyst decomposition. Howell and co-workers examined the cross-metathesis reactions of α-methylene-γ-butyrolactone with different olefinic partners.[49] Even though lactone underwent a rapid and efficient olefin isomerisation in the presence of second-generation metathesis catalysts, it was possible to obtain the desired products in good yields in the presence of 2,6-dichlorobenzoquinone. The same lactone was exploited by Cossy and co-workers in the presence of a broad spectrum of additives, for example, derivatives of phosphines (Cy_2PCl and Ph_2PCl), phosphine oxides (Cy_3PO and Ph_3PO), 2,6-dichloro-1,4-benzoquinone and chlorocatecholborane.[50] This borane was found to be the most effective agent in suppressing the migration of the double bond; it also led to the highest yield (91 % in comparison with the 86 % obtained in the presence of the quinone derivative). Vilar and co-workers successfully utilised phenylphosphoric acid and its derivatives in the metathesis reactions of alkenes containing hydrogen-bonding substituents (urea and thiourea groups) and found that the isomerisation of these alkenes can be suppressed by the addition of phenylphosphoric acid to the reaction mixture.[51] Other tested isomerisation inhibitors, for example, benzoic acid, salts of phosphoric acid and 2,6-dichloro-1,4-benzoquinone, suppressed the isomerisation of the double bond almost completely, but the yields of the desired products were relatively low (ca. 50 %). In the case of Schrock-type complexes, migration of the double bond was not observed.[2,3]

Herein we report on the synthesis and evaluation of the catalytic performance of three new Hoveyda–Grubbs-type metathesis (pre)catalysts containing the quinone moiety in their structures. We found that this structural modification increases the stability of the complexes and facilitates the formulation of the catalyst/quinone system. Furthermore, by introducing the quinone moiety directly into the catalyst molecule, the amount of byproducts in the reaction mixture was reduced in comparison with the reactions in which catalysts without such a structural modification were utilised. This, as well as the elimination of one of the reactants (quinone) from the reaction mixture, made product purification easier.

Results and Discussion

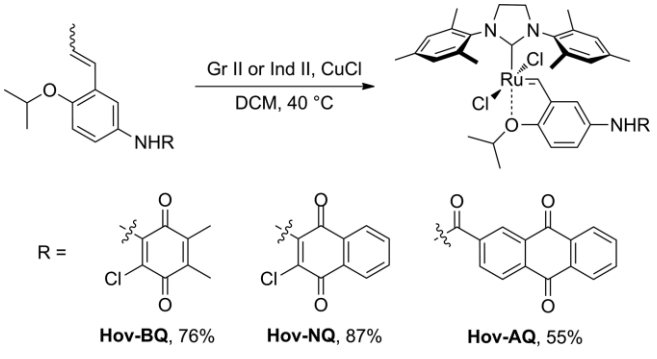
The first part of the study involved the synthesis of ruthenium complexes containing a quinone moiety in the benzylidene ligand. The three ligands were synthesised as shown in Scheme 2. First, 1-isopropoxy-4-nitro-2-propenylbenzene (**1**)[52] was reduced[53] with iron powder in the presence of hydrochloric acid to produce amine **2**, which was then subjected to reaction with either 2,3-dichloro-5,6-dimethyl-1,4-benzoquinone (**3**) or 2,3-dichloro-1,4-naphthoquinone (**4**) to provide the desired ligands **5** and **6** in yields of 50 and 73 %, respectively. When amine **2** was treated with 9.10-dioxo-9,10-dihydroanthracene-2-carbonyl chloride (**7**), the desired ligand **8** was synthesised in a yield of 78 %.

The prepared ligands **5**, **6** and **8** containing a quinone moiety were utilised in the preparation of the Hoveyda–Grubbs-



Scheme 2. Synthesis of quinone-containing benzylidene ligands.

type catalysts (Scheme 3). For **Hov-BQ** and **Hov-NQ** the ruthenium source was the second-generation Grubbs catalyst (Gr II), for **Hov-AQ** it was the second-generation indenylidene catalyst (Ind II), and the required complexes were synthesised by a ligand-exchange method according to already established procedures.[54] The benzo- and naphthoquinone derivatives (**Hov-BQ** and **Hov-NQ**, respectively) were obtained as purple crystals in yields of 76 and 87 %, respectively, whereas the complex with the anthraquinone moiety, **Hov-AQ**, was obtained in a yield of 55 % as a green powder. The ^{1}H NMR spectra of these materials show singlet peaks at 16.43, 16.47 and 16.55 ppm, respectively, which is characteristic of Hoveyda–Grubbs-type complexes.



Scheme 3. Synthesis of quinone-containing complexes.

X-ray Diffraction

Single crystals of **Hov-BQ** and **Hov-NQ** were obtained to study their structures by X-ray diffraction at 100 K.[55] Their crystal data as well as the details of data collection and structure refinement are summarised in Table 7. The conformations of the single molecules as well as the arrangements of the molecules in both crystal structures are presented in Figure 6 and Figure 7.

Single crystals of both investigated compounds were recrystallized from dichloromethane (DCM), and as a result both crystals contained molecules of this solvent embedded in their structures. The DCM molecules are located in cavities between the main molecules and are noticeably disordered. In each structure, the main molecules as well as the solvent molecules are located in general positions. The clearest difference between the two structures is the orientation of the benzo- and naphthoquinone substituents with respect to the core structure of the molecule (see Figure 2).

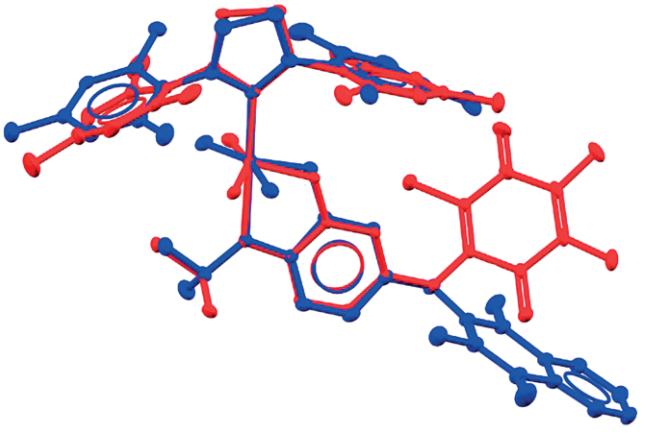


Figure 2. Overlay of the molecular structures of **Hov-BQ** (red molecule) and **Hov-NQ** (blue molecule). Hydrogen atoms have been omitted for clarity.

The different orientations of the benzo- and naphthoquinone substituents can be attributed to the presence or absence of intermolecular hydrogen bonds. In the case of **Hov-NQ**, short N3–H3···O2 hydrogen bonds (2.219 Å) link molecules into dimers (Figure 3), whereas no such interactions exist in **Hov-BQ**.

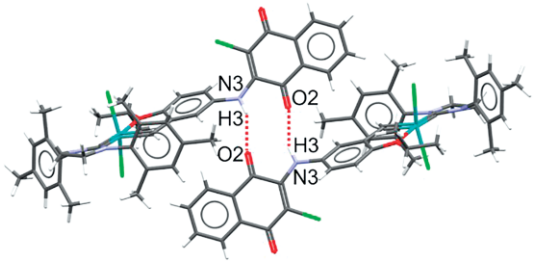


Figure 3. Dimers of **Hov-NQ** interconnected by intermolecular N3–H3···O2 hydrogen bonds (red dotted lines).

Activity Studies of Quinone-Containing Complexes

Prior to testing the sensitivity of substrates to isomerisation, the general influence of the structural modification on the catalytic activity of the complexes containing the quinone moiety was examined. The results obtained with the complexes developed in this work were compared with those obtained in reactions with the commercially available Hoveyda–Grubbs second-generation catalyst (**Hov II**). The structures of all the tested complexes are presented in Figure 4.

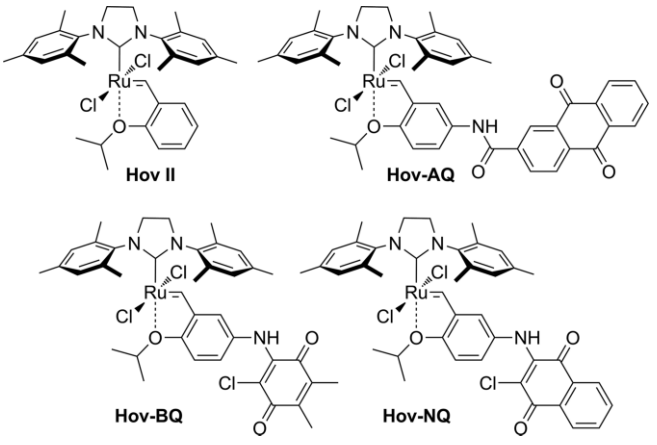
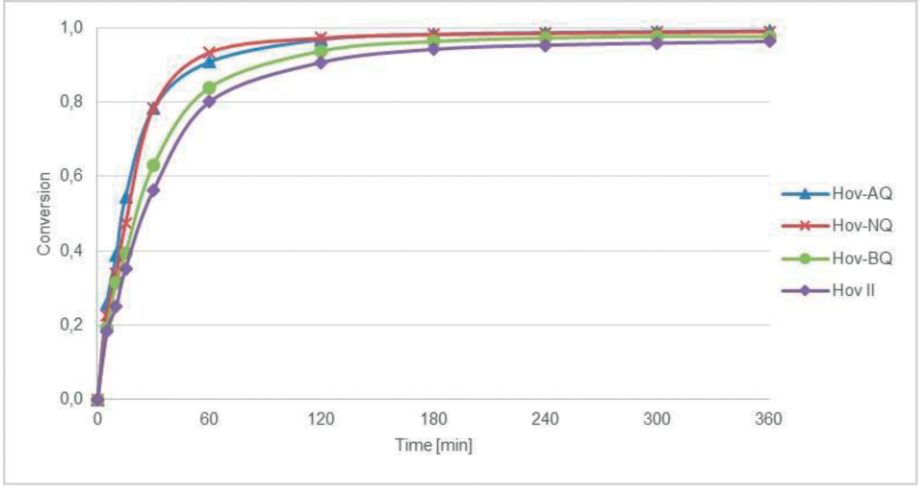
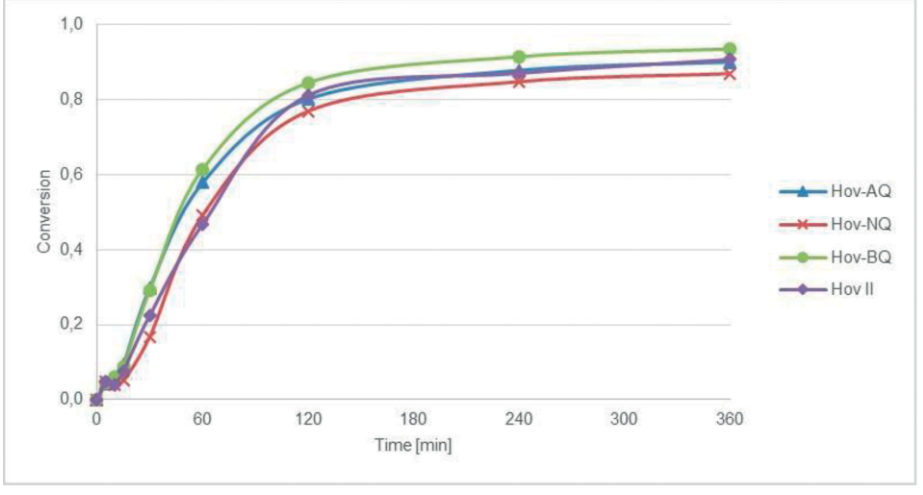


Figure 4. Structures of the Hoveyda–Grubbs-type complexes utilised in this study.



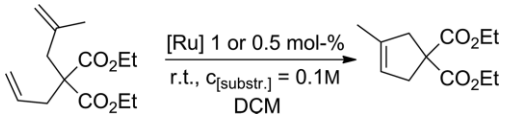
(a)



(b)

Figure 5. Time/conversion curves for the RCM reaction of diethyl 2-allyl-2-(methylallyl)malonate with (a) 1 mol-% of Ru complexes and (b) 0.5 mol-% of Ru complexes.

The first process to be tested was the ring-closing metathesis (RCM) of diethyl 2-allyl-2-(methylallyl)malonate (Scheme 4). As can be seen in Figure 5, the quinone-containing Hoveyda-type complexes exhibited similar activity to the Hoveyda–Grubbs catalyst, however, they initiated the RCM reaction slightly faster than the commercially available **Hov II**. When 1 mol-% of the Ru complexes was used, almost full conversion of the substrate was reached within the first hour. The reaction proceeded more slowly in the presence of 0.5 mol-% of the catalysts, but here also the substrate was almost fully consumed after 2–3 h and no significant difference in the activities of the complexes was observed. Similar reactivity was observed for all the tested complexes in further RCM reactions, including those with more demanding substrates with a substituted double bond (Table 1, rows 1 and 2) as well as ene-yne metathesis (Table 1, row 3) and cross-metathesis reactions (Table 1, rows 4 and 5). These results clearly demonstrate that introducing substituted aminocarbonyl groups (Hov-AQ) onto the benzylidene ring of Hoveyda–Grubbs-type complexes did not decrease the activity of the quinone-containing complexes. In that respect, the amide function bearing a quinone can be seen as an analogue of the very effective Umicore M71 and M73 catalysts designed by Mauduit and co-workers.[56]



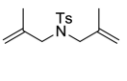
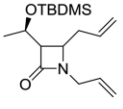
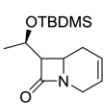
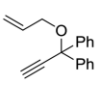
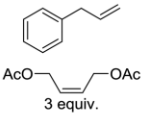
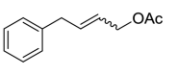
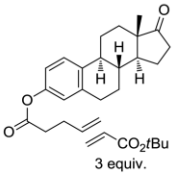
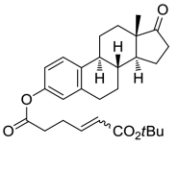
Scheme 4. Model RCM reaction of diethyl 2-allyl-2-(methylallyl)malonate.

After the initial study presented above, the catalytic performances of the quinone-bearing Hoveyda–Grubbs-type complexes (**Hov-BQ**, **Hov-NQ** and **Hov-AQ**) as well as the commercially available Hoveyda–Grubbs second-generation catalyst (**Hov II**) were evaluated in more demanding reactions, namely the self-metathesis reactions of dodec-1-ene (**9**) and methyl oleate (**11**) as well as the cross-metathesis of methyl oleate (**11**) with (*Z*)-but-2-ene-1,4-diol diacetate (**14**) and the RCM reactions of diallyl ether (**17**) and the diene **20**.

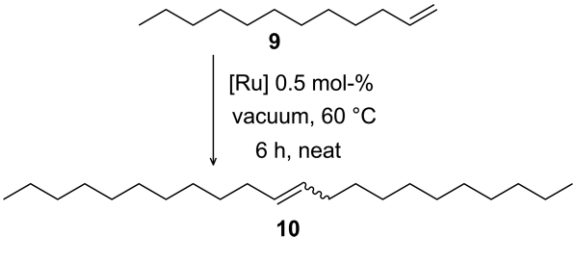
The study of the effectiveness of the suppression of isomerisation of the double bond started with the homo-dimerisation of dodec-1-ene (**9**; Scheme 5) in the presence of the previously obtained complexes as well as the commercially available Hoveyda–Grubbs second-generation catalyst **Hov II**. All the reactions were performed neat at elevated temperature with 0.5 mol-% of the ruthenium catalyst under a pressure of 40 mbar,[57] which was necessary to remove the ethylene released during the reaction. As a result of the metathesis of **9**, not only the desired product **10** was observed in the reaction mixture, but also its homologues with longer and shorter carbon chains, obtained as a result of the migration of the double bond in the substrate.

As can be seen from the data in Table 2, **Hov II** utilised in the self-metathesis reaction of dodec-1-ene (**9**) without any additive not only gave the worst selectivity, but also the conversion of **9** was relatively poor, reaching only 69 % (Table 2, entry 1). When the reaction was performed in the presence of the same catalyst with 2,3,5,6-tetrafluoro- or 2,6-dichloro-1,4-

Table 1. Metathesis reactions catalysed by ruthenium complexes.[a]

Substrate(s)	Product	Conditions	[Ru], yield [%], *E*/*Z*[b]
		toluene 80 °C, 24 h	**Hov II**, 83 **Hov-BQ**, 86 **Hov-NQ**, 67 **Hov-AQ**, 79
		DCM r.t., 3 h	**Hov II**, 89 **Hov-BQ**, 89 **Hov-NQ**, 90 **Hov-AQ**, 85
		DCM r.t., 5 h	**Hov II**, 80 **Hov-BQ**, 83 **Hov-NQ**, 89 **Hov-AQ**, 82
		DCM r.t., 3 h	**Hov II**, 84 10:1 **Hov-BQ**, 86 9:1 **Hov-NQ**, 83 7:1 **Hov-AQ**, 81 8:1
		toluene 40 °C, 24 h	**Hov II**, 57 20:1 **Hov-BQ**, 48 20:1 **Hov-NQ**, 50 20:1 **Hov-AQ**, 64 20:1

[a] 1 mol-% of [Ru] was used. [b] Isolated yields.



Scheme 5. Homo-dimerisation of dodec-1-ene (**9**).

benzoquinone as additive (Table 2, entries 2 and 3), both conversion and selectivity increased, giving conversions of 74 and 82 % and selectivities of 88 and 92 %, respectively. These results confirmed previous observations[43,44] that quinones can effectively prevent isomerisation in olefin metathesis reactions. Additionally, it seems that their presence suppressed the decomposition of the catalysts, which in turn resulted in higher conversion of the substrate. When complexes bearing a benzylidene ligand substituted with either a benzo- or naphthoquinone derivative, namely **Hov-BQ** and **Hov-NQ**, were employed, a substantial increase in both the conversion and selectivity was observed (Table 2, entries 4 and 5). The highest conversion, almost

95 %, was observed when **Hov-NQ** was utilised, whereas **Hov-BQ** gave 89 % conversion. The third synthesised quinone-containing complex, namely **Hov-AQ**, exhibited lower activity, giving only 48 % conversion of dodec-1-ene (**9**), which can be attributed to the poor solubility of the complex in the reaction mixture. On the other hand, **Hov-AQ** showed higher selectivity than that obtained with **Hov II** (Table 2, entry 6).

Table 2. Homo-dimerisation of dodec-1-ene (**9**) in the presence of ruthenium complexes.[a]

Entry	[Ru]	Additive	Conversion [%][b]	Selectivity. [%][b,c]
1	**Hov II**	–	69	70
2	**Hov II**	2,3,5,6-Tetrafluoro-1,4-benzoquinone	74	88
3	**Hov II**	2,6-Dichloro-1,4-benzoquinone	82	92
4	**Hov-BQ**	–	89	95
5	**Hov-NQ**	–	94	95
6	**Hov-AQ**	–	48	89

[a] Reaction conditions: 0.5 mol-% of Ru complex, 1 mol-% of additive, neat, 60 °C, 40 mbar, 6 h. [b] Determined by GC, calculated for a mixture of *E* and *Z* isomers. [c] Selectivity was calculated as the ratio of the desired product to all the products obtained in the reaction (main product + its homologues).

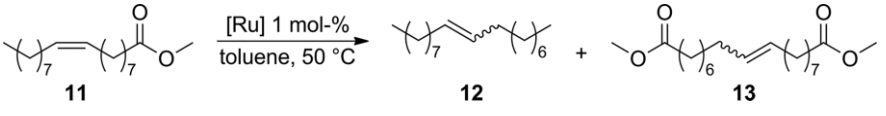
The next reaction tested was the self-metathesis of methyl oleate (**11**; Scheme 6) performed in the presence of **Hov-BQ**, **Hov-NQ** and **Hov-AQ** as well as the benchmark second-generation Hoveyda–Grubbs catalyst **Hov-II**. The results are shown in Table 3. The self-metathesis reaction of methyl oleate (**11**) gave mainly octadec-9-ene (**12**) and dimethyl octadec-9-enedioate (**13**) along with a small amount of their homologues with longer or shorter carbon chains; the products were formed as a mixture of *E* and *Z* isomers. In this reaction all the examined complexes, including the commercially available second-generation Hoveyda–Grubbs catalyst (used alone or in the presence of 2 equivalents of 2-chloro-1,4-benzoquinone), led to the maximum conversion within the first hour (Table 3) owing to the nature of the reaction; the metathesis process is energetically neutral and thus reversible, therefore a mixture of substrate and products is obtained in the thermodynamic equilibrium. Also after 1 hour, a selectivity of 100 % was observed with each of the tested ruthenium complexes with only the desired products observed in the reaction mixture (Table 3, entries 1, 4, 7, 10 and 13). After an additional 4 h, isomerisation products were only detected with the **Hov II** catalyst (Table 3, entry 2), whereas with all the complexes bearing the quinone moiety, the reaction was selective towards the desired products **12** and **13** (Table 3, entries 8, 11 and 14). Moreover, the isomerisation process was slowed down when **Hov II** was used in the self-metathesis reaction of methyl oleate (**11**) in the presence of 2-chloro-1,4-benzoquinone (Table 3, entry 5), however, some undesired byproducts possessing longer or shorter carbon chains were still detected in the reaction mixture. When the reaction time was extended to 24 h, isomerisation occurred with all the catalysts, although to varying degrees (Table 3, entries 3, 6, 9, 12 and 15). When **Hov-BQ** or **Hov-NQ** were utilised, the desired products **12** and **13** were obtained with 99 and 98 % selectivity, respectively, whereas when **Hov II** was utilised, the selectivity dropped to 92 % without quinone and to 95 % in the presence of quinone. The same selectivity, 95 %, was observed when **Hov-AQ** was used.

Table 3. Self-metathesis of methyl oleate (**11**) in the presence of ruthenium complexes.[a]

Entry	[Ru]	Time [h]	Conversion [%][b]	Selectivity [%][b]	
				12[c]	**13**[c]
1	**Hov II**	1	55	100	100
2		5	55	93	92
3		24	55	91	92
4	**Hov II** with **Q**[d]	1	52	100	100
5		5	52	97	97
6		24	54	94	95
7	**Hov-BQ**	1	54	100	100
8		5	54	100	100
9		24	54	99	99
10	**Hov-NQ**	1	50	100	100
11		5	51	100	100
12		24	53	98	98
13	**Hov-AQ**	1	55	100	100
14		5	56	100	100
15		24	56	95	95

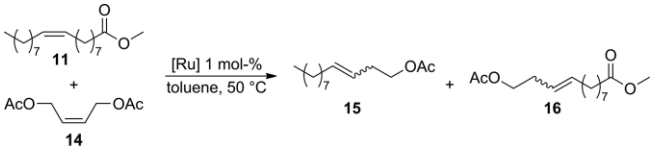
[a] Reaction conditions: 1 mol-% of [Ru], [**11**] = 0.17 M, 0.6 equiv. dodecane (as an internal standard for GC). [b] Calculated as the ratio of the desired product to all products created from the aliphatic or ester part of the substrate **11**. [c] Determined by GC, calculated for a mixture of *E* and *Z* isomers. [d] 2 mol-% of 2-chloro-1,4-benzoquinone was added.

Next, the cross-metathesis reaction of methyl oleate (**11**) with (*Z*)-but-2-ene-1,4-diol diacetate (**14**) was performed (Scheme 7 and Table 4). Isomerisation of the double bond was not observed in this reaction; only the desired products, namely dodec-3-enyl acetate (**15**) and methyl 11-acetoxyundec-9-enoate (**16**), products of the self-metathesis reaction, namely octadec-9-ene (**12**) and dimethyl octadec-9-enedioate (**13**), as well as the two substrates **11** and **14** were detected. In the CM reaction, in which 2 equiv. of (*Z*)-but-2-ene-1,4-diol diacetate (**14**) were utilised, **Hov-AQ** exhibited the highest activity. After 24 h it not only had converted 91 % of methyl oleate (**11**) into the products (Table 4, entry 16), but also the lowest of amounts of self-metathesis byproducts were obtained, namely 14 % of **15** and 12 % of **16**. The other three tested complexes, namely **Hov II**, **Hov-BQ** and **Hov-NQ**, were less effective and after the same reaction time (24 h) the conversions of **11** had only reached 64, 48 and 66 %, respectively (Table 4, entries 4, 8 and 12). Furthermore, the quantities of the desired products in the reaction mixture were lower, being around 80 % for each of the tested catalysts. When 5 equiv. of (*Z*)-but-2-ene-1,4-diol diacetate (**14**) were utilised, the conversion of **11** was lower (40–49 %)



Scheme 6. Self-metathesis of methyl oleate (**11**).

in the presence of all the tested ruthenium compounds (Table 4, entries 5, 9, 13 and 17). This undesired decrease in activity could be related to the decomposition of the complexes used in the presence of a large amount of **14**, because the colour of the reaction mixture changed from green to brown for **Hov II** and **Hov-AQ**; the colour of the solutions containing **Hov-BQ** or **Hov-NQ** did not change because both complexes are intensely coloured. Surprisingly, even in the presence of 5 equiv. of **14**, the self-metathesis byproducts, namely octadec-9-ene (**12**) and dimethyl octadec-9-enedioate (**13**), were still detected in the reaction mixtures (9 % of **15** and 10 % of **16**, regardless of the used catalyst). Utilisation of 2-chloro-1,4-benzoquinone as an additive in the reaction catalysed with **Hov II** did not affect the proportions of cross- and self-metathesis products, but the conversion of **11** was improved (Table 4, entry 3).



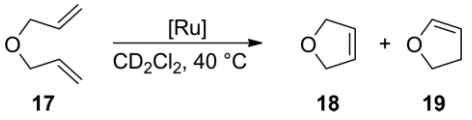
Scheme 7. Cross-metathesis reaction of methyl oleate (**11**) with (*Z*)-but-2-ene-1,4-diol diacetate (**14**).

Table 4. Cross-metathesis reaction of methyl oleate (**11**) with (*Z*)-but-2-ene-1,4-diol diacetate (**14**) in the presence of ruthenium complexes.[a]

Entry	[Ru]	Time [h]	Conversion [%]	Selectivity [%][b]	
				15[c,d]	**16**[c,e]
1	**Hov II**	1	58	78	79
2		5	62	79	79
3		5[f]	75	81	81
4		24	64	79	80
5		24[g]	49	91	90
6	**Hov-BQ**	1	33	81	81
7		5	42	81	82
8		24	48	82	82
9		24[g]	40	91	90
10	**Hov-NQ**	1	66	79	79
11		5	66	79	79
12		24	66	79	79
13		24[g]	48	91	90
14	**Hov-AQ**	1	62	78	77
15		5	86	86	86
16		24	91	86	88
17		24[g]	42	91	90

[a] Reaction conditions: 1 mol-% of [Ru], [**11**] = 0.17 M, 2 equiv. of (*Z*)-but-2-ene-1,4-diol diacetate (**14**), 0.6 equiv. dodecane (as an internal standard for GC). [b] Calculated as the ratio of the cross-metathesis product to the self-metathesis products created in the reaction (homologues were not observed in these reactions). [c] Determined by GC, calculated for a mixture of *E* and *Z* isomers. [d] The second product was **12**. [e] The second product was **13**. [f] 2 mol-% of 2-chloro-1,4-benzoquinone was added. [g] 5 equiv. of (*Z*)-but-2-ene-1,4-diol diacetate (**14**) was used.

Further investigation of the anti-isomerisation properties of the quinone-containing catalysts focused on the ring-closing metathesis of diallyl ether (**17**; Scheme 8). The reaction was performed in an NMR tube utilising the conditions previously applied by Grubbs and co-workers.[47] A high temperature and relatively high catalyst loading were deliberately used to obtain conditions favouring the migration of the double bond. In this process, the initially formed 2,5-dihydrofuran (**18**) undergoes isomerisation of the double bond to form 2,3-dihydrofuran (**19**). This undesired side-reaction has been attributed to the formation of the ruthenium hydride species, created as a product of the decomposition of second-generation ruthenium complexes.



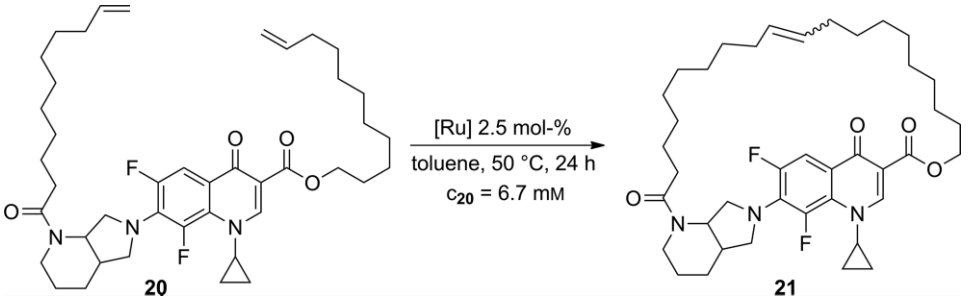
Scheme 8. RCM of diallyl ether (**17**).

Diallyl ether (**17**) easily cyclises and, under the given conditions, was transformed within an hour into products in the presence of the tested catalysts **Hov II**, **Hov-BQ**, **Hov-NQ** and **Hov-AQ**. However, the composition of the reaction mixture varied depending on the complex used. In the reactions with 1 mol-% of the ruthenium complexes, the results were quite similar. In all cases, total conversion was achieved within the first hour and the selectivity was around 100 %. With a prolongation of the reaction time to 24 h, only in the case of **Hov II** was a decrease in selectivity observed, however, this decrease was not pronounced. The situation was more diverse when 5 mol-% of the catalyst were used with the other parameters unchanged. When the commercially available Hoveyda–Grubbs second-generation catalyst was employed, after 1 hour the desired product **18** made up only 26 % of the reaction mixture (Table 5, entry 3). The quinone-containing complexes were found to be more selective towards the desired product **18**, however, in all cases the isomerised product **19** was also detected in the reaction mixture. The highest selectivity was observed in the presence

Table 5. RCM of diallyl ether (**17**) in the presence of ruthenium complexes.[a]

Entry	[Ru]	Loading [%]	Time [h]	Conversion [%][b]	Selectivity [%][b,c,d]
1	**Hov II**	1	1	100	95
2		1	24	100	90
3		5	1	100	26
4		5	24	100	0
5	**Hov II** with **Q**[e]	1	1	100	98
6		1	24	100	98
7		5	1	100	99
8		5	24	100	99
9	**Hov-BQ**	1	1	100	100
10		1	24	100	100
11		5	1	100	45
12		5	24	100	34
13	**Hov-NQ**	1	1	100	100
14		1	24	100	100
15		5	1	100	30
16		5	24	100	21
17	**Hov-AQ**	1	1	100	99
18		1	24	100	99
19		5	1	100	60
20		5	24	100	50

[a] Reaction conditions: 5 mol-% of [Ru], [**17**] = 0.23 M CD_2Cl_2, 40 °C. [b] Calculated as the ratio of the desired product **18** to all the products created in the reaction (**18** + **19**). [c] Determined by ^{1}H NMR spectroscopy. [d] The second product was **19**. [e] 2 equiv. 2,3,5,6-tetrafluoro-1,4-benzoquinone (for 1 equiv. of Hov II) was added.



Scheme 9. RCM of diene **20**.

of **Hov-AQ** (60 %, Table 5, entry 19); **Hov-BQ** was 15 % less selective (i.e., 45 %, Table 5, entry 11), whereas **Hov-NQ** gave results similar to **Hov II** (30 and 26 % selectivity, respectively; Table 5, entries 15 and 3). The situation changed after a prolonged reaction time. When **Hov II** was employed, only 2,3-dihydrofuran (**19**) was observed and not even traces of the desired product **18** were detected in the reaction mixture (Table 5, entry 4). With the quinone-containing catalysts, the selectivity decreased by approximately 10 % (Table 5, entries 12, 16 and 20). When **Hov II** was used in the presence of 2,3,5,6-tetrafluoro-1,4-benzoquinone (**Q**), migration of the double bond was not observed.

Finally, we decided to apply Hoveyda–Grubbs-type complexes in the ring-closing metathesis of diene **20** (Scheme 9), a distant relative of the fluoroquinolone antibacterial agent moxifloxacin.[58] It is known that the use of RCM in the synthesis of macrocyclic compounds not always proceeds smoothly, and dimeric, trimeric and oligomeric byproducts can be present in significant amounts in the reaction mixtures.[59,60] Moreover, because isomerisation of the double bonds can occur during the ring-closing metathesis reaction of **20**, the size of the macrocyclic ring formed may vary from the parental macrocyclic medicament, which can affect the biological properties of the synthesised molecule. The results of the reaction obtained with the quinone-containing catalysts were compared with those obtained when the second-generation Hoveyda–Grubbs catalyst **Hov II** was utilised.

All the ruthenium complexes utilised in the RCM of diene **20** exhibited moderate-to-low effectiveness, however, to the best of our knowledge, this is the first time that olefin **21** has been synthesised in a metathesis reaction (Scheme 9). Although the conversion of **20** was complete and migration of the double bond was not observed, that is, homologues of neither substrate nor product were observed, the use of complexes **Hov-BQ** and **Hov-NQ** (Table 6, entries 2 and 3) led to the synthesis of the desired macrocyclic product **21** in yields of only 10 and 38 %, respectively. When **Hov-AQ** was utilised under the same conditions, the yield of the desired product reached 64 %. Such a low yield of **21** can be attributed to the fact that during the RCM reaction dimeric, trimeric and oligomeric products were also formed. In addition, because **Hov-BQ** and **Hov-NQ** are very stable, it was difficult to bring about their decomposition after the completion of the reaction, either with the standard quenching agent, ethyl vinyl ether, or with the recently discovered isocyanate.[20] This caused additional difficulties in the purification of the desired product, because compound **21**, **Hov-BQ** and **Hov-NQ** exhibit similar polarity. This drawback was not observed in the case of **Hov-AQ** and the isolation of **21** was straightforward. On the other hand, when **Hov II** was utilised in the reaction (Table 6, entry 1), not even traces of the desired product **21** were observed; only substrate **20** and oligomeric products were found in the reaction mixture, even after a prolonged reaction time.

Table 6. RCM of diene **20** in the presence of ruthenium complexes.[a]

Entry	[Ru]	Yield [%][b]
1	**Hov-II**	0[c]
2	**Hov-BQ**	10[d]
3	**Hov-NQ**	38[d]
4	**Hov-AQ**	64[d]

[a] Reaction conditions: 2.5 mol-% of [Ru], [**20**] = 0.0067 M toluene, 50 °C, 24 h. [b] Isolated yields. [c] A complicated mixture of substrate **20** and oligomeric products was observed on the TLC plate. [d] Full conversion was reached, some dimeric and trimeric products were detected.

Conclusions

In this study, three new Hoveyda–Grubbs-type catalysts, **Hov-BQ**, **Hov-NQ**, and **Hov-AQ**, containing a quinone moiety in the benzylidene ligand were synthesised and fully characterised. Their ability to decrease the level of double-bond isomerisation in metathesis reactions was evaluated for model CM reactions with dodec-1-ene (**9**) and methyl oleate (**11**) as well as in model RCM reactions with diallyl ether (**17**) and the precursor (**20**) of an analogue of the fluoroquinolone antibacterial agent moxifloxacin. The results have been compared with the results obtained with second-generation Hoveyda–Grubbs catalyst **Hov II**. All the complexes were also applied in standard metathesis reactions to examine the influence of the quinone moiety on the activity of quinone-containing catalysts in comparison with **Hov II**. It was observed that in all cases **Hov-BQ** and **Hov-NQ** gave higher conversion or selectivity or both in comparison with **Hov II** used either alone or in the presence of quinones added separately to the reaction mixture. **Hov-AQ** usually gave high selectivity but in most cases the conversion was lower than with the other tested complexes, but was found to be the best catalyst for the RCM reaction of **20**. The quinone-containing ruthenium compounds were proved to suppress undesired

double-bond migration, which enabled the synthesis of the desired products in higher yields and purity. However, the system still needs to be improved because after prolonged reaction time some undesired byproducts were observed.

Experimental Section

Unless otherwise noted, all reactions were conducted under argon. Flash column chromatography was carried out by using Merck silica gel 60 (230–400 mesh). NMR (^{1}H, ^{13}C) spectra were recorded with Varian Gemini 400 and 500 spectrometers with samples dissolved in $CDCl_3$. Chemical shifts (δ) are given relative to the residual peak of $CHCl_3$ present in deuteriated solvent (δ = 7.26 ppm). IR spectra were recorded with Perkin–Elmer Spectrum 2000 and 1170 FT-IR spectrometers. ESI-MS were recorded with a Mariner Perseptive Biosystems spectrometer. GC analyses were conducted with a HP 6890 chromatograph with a HP 5 column. Elemental analyses were performed at the Institute of Organic Chemistry, PAS, Warsaw.

4-Isopropoxy-3-(prop-1-en-1-yl)aniline (2): A 250 mL three-necked, round-bottomed flask was charged with ethanol (50 mL). Iron powder (125 mmol, 6.98 g) was added in portions under efficient stirring, followed by a concentrated aqueous solution of HCl (25 mmol, 2.53 g, 2.13 mL), and the suspension was stirred at 65 °C for 2 h. The mixture was cooled to 55–60 °C over a period of 10 min and then 25 % aqueous ammonium chloride solution (20 mL) was added. 5-Nitro-2-isopropoxy-1-prop-1-enylbenzene (**1**;[50] 25 mmol, 5.53 g) was added in portions over a period of 5 min while maintaining the internal temperature at 65–80 °C. When the mixture had thickened, ethanol (75 mL) was added. The reaction mixture was stirred at 55–65 °C for an additional 1.5 h and then cooled to 20 °C. Ethanol (50 mL) and Celite (10 g) were added subsequently. The reaction mixture was filtered through a pad of Celite (1.5 g) with suction. The filter cake was washed with EtOH (50 mL) and the filtrate was concentrated under reduced pressure. Ethyl acetate (60 mL) and saturated $NaHCO_3$ (25 mL) were added to the residue. The biphasic mixture was stirred at 20–25 °C and the organic layer was separated. The organic layer was washed with brine (1 × 25 mL) and dried with sodium sulfate. The solvent was removed under reduced pressure to afford the crude product, which was purified by column chromatography (20 % EtOAc/*c*-hex) to give the desired product (22.4 mmol, 4.27 g, 89 %). The product slowly decomposed during storage (fridge, under argon). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.82 (d, *J* = 2.85 Hz, 1 H), 6.73 (d, *J* = 8.57 Hz, 1 H), 6.55 (dd, *J* = 2.69, 8.57 Hz, 1 H), 6.65 (dd, *J* = 1.68, 15.79 Hz, 1 H), 6.20–6.11 (m, 1 H), 4.30 (sept., *J* = 6.05 Hz, 1 H), 3.80 (br. s, 2 H), 1.88 (dd, *J* = 1.68, 6.55 Hz, 3 H), 1.30 (d, *J* = 6.05 Hz, 6 H) ppm (major isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.29, 139.38, 129.77, 125.86, 117.71, 115.20, 113.38, 72.46, 22.25, 18.85 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3426, 3354, 2974, 2930, 1620, 1492, 1447, 1382, 1255, 1220, 1114, 970, 816, 589 cm^{-1}. MS (EI): *m*/*z* = 191.0 [M]$^+$. $C_{12}H_{17}NO$ (197.27): calcd. C 75.35, H 8.96, N 7.32; found C 75.20, H 8.86, N 7.14.

Procedure for the Synthesis of Ligands 5 and 6: The quinone derivative (3 mmol) was added to a solution of 4-isopropoxy-3-(prop-1-en-1-yl)aniline (**2**; 4.5 mmol, 861 mg) in EtOH (10 mL) at 0 °C. The mixture was warmed to room temperature, stirred for 24 h, and the solvent evaporated. The residue was purified by column chromatography (5–20 % EtOAc/*c*-Hex).

2-Chloro-3-{[4-isopropoxy-3-(prop-1-en-1-yl)phenyl]amino}-5,6-dimethylcyclohexa-2,5-diene-1,4-dione (5): Compound **5** was obtained according to the above procedure with 2,3-dichloro-5,6-dimethyl-1,4-benzoquinone (**3**; 3 mmol, 615 mg). The product was obtained as purple crystals (1.49 mmol, 536 mg, 50 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (s, 1 H), 7.06 (d, *J* = 2.6 Hz, 1 H), 6.85–6.82 (m, 1 H), 6.80–6.77 (m, 1 H), 6.67 (dd, *J* = 1.8, 15.9 Hz, 1 H), 6.22–6.13 (m, 1 H), 4.51 (sept., *J* = 6.0 Hz, 1 H), 2.12 (s, 3 H), 2.06 (s, 3 H), 1.88 (dd, *J* = 1.8, 6.7 Hz, 3 H), 1.36 (d, *J* = 6.0 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.8, 179.6, 178.0, 152.5, 144.1, 141.9, 139.6, 136.6, 130.2, 128.1, 127.0, 125.3, 123.2, 113.8, 109.4, 71.2, 22.2, 18.8, 13.3, 12.2 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3312, 3038, 2976, 1657, 1593, 1503, 1491, 1376, 1298, 1228, 1119, 1110, 968, 955, 831, 719, 427 cm^{-1}. MS (ESI, MeOH): *m*/*z* = 360.1 [M + H]$^+$, 382.1 [M + Na]$^+$, 741.2 [2M + Na]$^+$. $C_{20}H_{22}ClNO_3$ (359.13): calcd. C 66.76, H 6.16, Cl 9.85, N 3.89; found C 66.56, H 6.12, Cl 9.75, N 3.78.

2-Chloro-3-{[4-isopropoxy-3-(prop-1-en-1-yl)phenyl]amino}-naphthalene-1,4-dione (6): Compound **6** was obtained according to the general procedure by with 2,3-dichloro-1,4-naphthoquinone (**4**; 3 mmol, 682 mg). The product was obtained as purple crystals (2.22 mmol, 846 mg, 73 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22–8.17 (m, 2 H), 7.78–7.74 (m, 1 H), 7.70–7.64 (m, 2 H), 7.13 (d, *J* = 2.5 Hz, 1 H), 6.89 (dd, *J* = 3.5, 8.7 Hz, 1 H), 6.84–6.79 (m, 1 H), 6.69 (dd, *J* = 1.4, 15.9 Hz, 1 H), 6.24–6.16 (m, 1 H), 4.53 (sept., *J* = 6.0 Hz, 1 H), 1.89 (dd, *J* = 1.2, 6.5 Hz, 3 H), 1.37 (d, *J* = 6.0 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.1, 177.4, 176.0, 167.1, 152.7, 143.6, 141.7, 134.8, 132.8, 130.9, 129.9, 128.2, 127.8, 127.2, 126.9, 125.2, 123.9, 122.9, 113.7, 71.2, 22.2, 18.8 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3302, 2976, 1671, 1645, 1596, 1570, 1505, 1489, 1289, 1230, 1136, 1120, 1019, 967, 955, 842, 718, 681, 600 cm^{-1}. MS (ESI, MeOH): *m*/*z* = 382.1 [M + H]$^+$, 404.1 [M + Na]$^+$, 785.2 [2M + Na]$^+$. $C_{22}H_{20}ClNO_3$ (381.86): calcd. C 69.20, H 5.28, Cl 9.28, N 3.67; found C 69.21, H 5.36, Cl 9.48, N 3.74.

***N*-[4-Isopropoxy-3-(prop-1-en-1-yl)phenyl]-9,10-dioxo-9,10-dihydroanthracene-2-carboxamide (8):** A solution of 4-isopropoxy-3-(prop-1-en-1-yl)aniline (**2**; 1.9 mmol, 514 mg) in DCM (5 mL) was added, followed by pyridine (2 mL), to a suspension of 9,10-dioxo-9,10-dihydroanthracene-2-carbonyl chloride (**7**; 1.9 mmol, 363 mg) in DCM (5 mL) at 0 °C. The mixture was stirred at room temperature for 24 h and the resulting yellow precipitate was filtered, washed several times with water and dried to give the pure product (1.48 mmol, 630 mg, 78 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 10.52 (s, 1 H), 8.74 (d, *J* = 1.5 Hz, 1 H), 8.42 (dd, *J* = 1.8, 8.2 Hz, 1 H), 8.32 (d, *J* = 8.2 Hz, 1 H), 8.27–8.23 (m, 2 H), 7.98–7.89 (m, 2 H), 7.85 (d, *J* = 2.4 Hz, 1 H), 7.60 (dd, *J* = 2.4, 8.8 Hz, 1 H), 6.99 (d, *J* = 8.8 Hz, 1 H), 6.63 (dd, *J* = 1.6, 16.0 Hz, 1 H), 6.24–6.15 (m, 1 H), 4.55 (sept., *J* = 6.0 Hz, 1 H), 1.86 (dd, *J* = 1.6, 6.5 Hz, 3 H), 1.27 (d, *J* = 6.0 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 182.7, 182.6, 163.9, 151.2, 140.3, 135.2, 133.7, 133.6, 133.5, 132.3, 127. 7, 127.6, 127.4, 127.3, 126.3, 126.2, 126.0, 121.1, 119.1, 115.2, 70.9, 22.4, 19.2 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3278, 3061, 2971, 1677, 1642, 1609, 1592, 1534, 1495, 1414, 1324, 1295, 1271, 1127, 968, 955, 934, 871, 812, 792, 704, 682, 586 cm^{-1}. MS (ESI, MeOH): *m*/*z* = 448.15 [M + Na]$^+$, 873.31 [2M + Na]$^+$, 1298.48 [2M + Na]$^+$. $C_{27}H_{23}NO_4$ (425.16): calcd. C 76.22, H 5.45, N 3.29; found C 76.13, H 5.56, N 3.12.

General Procedure for the Synthesis of the Catalysts: Benzylidene ligand (0.12 mmol), second-generation Grubbs catalyst (Gr II; 0.1 mmol, 84.9 mg) or Ind II (0.1 mmol, 94.9 mg) and CuCl (0.22 mmol, 21.8 mg) were placed in a Schlenk tube under argon and suspended in anhydrous DCM (10 mL). The mixture was heated at 40 °C for 45 min and then cooled to ambient temperature and the solvent evaporated. The mixture was then purified by utilising column chromatography (5–20 % EtOAc/*c*-Hex). The resulting product was concentrated in vacuo, the purple solid was dissolved in a minimal amount of DCM and cold MeOH (10 mL) was added. The resulting precipitate was filtered off, washed with MeOH (5 mL) and dried to afford a purple Ru complex.

Hov-BQ: This compound was obtained according to the general procedure by using 2-chloro-3-{[4-isopropoxy-3-(prop-1-en-1-yl)phenyl]amino}-5,6-dimethylcyclohexa-2,5-diene-1,4-dione (**5**; 0.12 mmol, 43.2 mg) and Gr II. The product was obtained as purple crystals (0.087 mmol, 70.9 mg, 76 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.43 (s, 1 H), 7.38 (s, 1 H), 7.14 (dd, J = 2.7, 8.9 Hz, 1 H), 7.07 (s, 4 H), 6.72 (d, J = 8.8 Hz, 1 H), 6.58 (d, J = 2.5 Hz, 1 H), 4.86 (sept., J = 6.1 Hz, 1 H), 4.17 (s, 4 H), 2.46 (s, 12 H), 2.36 (s, 6 H), 2.13 (s, 3 H), 2.08 (s, 3 H), 1.27 (d, J = 6 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 294.6, 210.5, 182.6, 179.5, 149.7, 144.7, 143.9, 139.0, 136.8, 131.9, 129.4, 116.9, 112.1, 110.8, 75.6, 51.5, 31.6, 26.9, 26.2, 22.6, 21.1, 19.4, 14.1, 13.4, 12.3 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3320, 2918, 1659, 1597, 1485, 1419, 1259, 1220, 1103, 935, 854, 580 cm^{-1}. MS (ESI, $CHCl_3$): m/z = 809.15 $[M]^+$. $C_{39}H_{44}Cl_3N_3O_3Ru$ (810.22): calcd. C 57.82, H 5.47, Cl 13.13, N 5.19; found C 57.87, H 5.67, Cl 13.22, N 4.92.

Hov-NQ: This compound was obtained according to the general procedure by using 2-chloro-3-{[4-isopropoxy-3-(prop-1-en-1-yl)phenyl]amino}naphthalene-1,4-dione (**6**; 0.12 mmol, 45.8 mg) and Gr II. The product was obtained as purple crystals (0.076 mmol, 63.6 mg, 87 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 16.47 (s, 1 H), 8.21 (d, J = 7.1 Hz, 1 H), 8.13 (d, J = 7.8 Hz, 1 H), 7.78 (dt, J = 1.1, 7.6 Hz, 1 H), 7.73–7.68 (m, 2 H), 7.21 (dd, J = 2.6, 8.7 Hz, 1 H), 7.07 (s, 4 H), 6.76 (d, J = 8.9 Hz, 1 H), 6.65 (d, J = 2.4 Hz, 1 H), 4.88 (sept., J = 6.1 Hz, 1 H), 4.18 (s, 4 H), 2.47 (s, 12 H), 2.35 (s, 6 H), 1.28 (d, J = 6.1 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 294.5, 210.5, 180.5, 177.3, 163.6, 149.9, 144.8, 141.2, 139.0, 135.1, 132.4, 129.6, 127.1, 124.4, 117.2, 112.2, 78.7, 78.2, 76.0, 51.5, 21.1, 19.5 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3312, 2920, 1674, 1599, 1571, 1484, 1287, 1261, 1221, 1311, 931, 848, 721, 580 cm^{-1}. MS (ESI, $CHCl_3$): m/z = 831.13 $[M]^+$. $C_{41}H_{42}Cl_3N_3O_3Ru$ (832.22): calcd. C 59.17, H 5.09, Cl 12.78, N 5.05; found C 59.23, H 5.31, N 4.80.

Hov-AQ: This compound was obtained according to the general procedure by using *N*-[4-isopropoxy-3-(prop-1-en-1-yl)phenyl]-9,10-dioxo-9,10-dihydroanthracene-2-carboxamide (**8**; 0.12 mmol, 51.1 mg) and Ind II. The product was obtained as green crystals (0.055 mmol, 48.2 mg, 55 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 16.50 (s, 1 H), 8.71 (d, J = 1.7 Hz, 1 H), 8.46–8.43 (m, 2 H), 8.38–8.33 (m, 2 H), 8.07 (br. s 1 H), 7.90–7.86 (m, 2 H), 7.82 (dd, J = 8.8, 2.6 Hz, 1 H), 7.43 (d, J = 2.6 Hz, 1 H), 7.10 (s, 3 H), 6.86 (d, J = 8.9 Hz, 1 H), 4.89 (sept., J = 6.1 Hz, 1 H), 4.18 (s, 4 H), 2.46 (br. s, 12 H), 1.54 (s, 6 H), 1.25 (d, J = 6.1 Hz, 6 H) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 214.3, 205.1, 192.1, 182.4, 182.3, 163.6, 149.0, 139.8, 139.0, 135.3, 134.5, 134.4, 133.6, 133.4, 133.0, 132.6, 129.2, 127.9, 127.2, 125.0, 121.2, 114.1, 113.0, 75.5, 29.7, 20.9, 20.8, 13.8, 4.2, 0.7 ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 2984, 2960, 2913, 1672, 1588, 1532, 1491, 1448, 1421, 1409, 1335, 1322, 1299, 1254, 1240, 1216, 1136, 1104, 932, 903, 851, 807, 797, 739, 705, 650, 636, 570 cm^{-1}. MS (ESI, MeOH): m/z = 875.18 $[M]^+$. HRMS: calcd. for $C_{46}H_{45}Cl_2N_3O_4Ru$ 875.1831; found 875.1821. $C_{46}H_{45}Cl_2N_3O_4Ru$ (875.85): calcd. C 63.08, H 5.18, Cl 8.09, N 4.80; found C 63.38, H 5.26, Cl 7.99, N 4.96.

Synthesis of (3*S*,4*R*)-4-Allyl-3-{(*R*)-1-[*tert*-butyl(dimethyl)-silyloxy]ethyl}azetidin-2-one: Potassium iodide (105 mmol, 17.4 g) and DMF (400 mL) were placed in a 1 L round-bottomed flask followed by allyl bromide (105 mmol, 12.7 g) and indium powder (70 mmol, 10.5 g). After 1 h, a solution of (2*R*,3*R*)-3-{(1*R*)-1-[*tert*-butyl(dimethyl)silyloxy]ethyl}-4-oxo-2-azetidinyl acetate (35 mmol, 10.1 g) in DMF (100 mL) was added and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with ammonium chloride (250 mL) and extracted with methyl *tert*-butyl ether (3 × 150 mL). The combined organic phases were washed with brine, dried with $MgSO_4$ and the organic phase was concentrated to dryness in vacuo. The residue was purified by column chromatography (5–20 % EtOAc/*c*-hex) to obtain the desired product as a white crystalline solid (8.43 g, 89 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.74–5.86 (m, 2 H), 5.09–5.14 (m, 2 H), 4.16–4.18 (m, 1 H), 3.68 (dd, J = 2.4, 7.6 Hz, 1 H), 2.77 (dt, J = 2.4, 6.6 Hz, 1 H), 2.30–2.5 (m, 2 H), 1.20 (d, J = 6.3 Hz, 3 H), 0.86 (s, 9 H), 0.06 (s, 6 H) ppm.[65]

Synthesis of (3*S*,4*R*)-1,4-Diallyl-3-{(*R*)-1-[*tert*-butyl(dimethyl)-silyloxy]ethyl}azetidin-2-one: (3*S*,4*R*)-4-Allyl-3-{(*R*)-1-[*tert*-butyl(dimethyl)silyloxy]ethyl}azetidin-2-one (3.3 mmol, 0.889 g) was dissolved in DMF (23 mL) in a dried Schlenk tube, followed by sodium hydride (6.6 mmol, 0.264 g, 2 equiv.). After 5 min, allyl bromide (9.9 mmol, 0.857 mL, 3 equiv.) was added dropwise and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with methyl *tert*-butyl ether, washed with brine, dried with $MgSO_4$ and the organic phase concentrated to dryness in vacuo. The residue was purified by column chromatography (5–20 % EtOAc/*c*-hex) to obtain the desired product as a colourless oil (0.776 g, 76 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.82–5.72 (m, 2 H), 5.26–5.09 (m, 4 H), 4.27 (qd, J = 6.2, 4.6 Hz, 1 H), 3.99 (ddt, J = 15.7, 5.5, 1.5 Hz, 1 H), 3.70 (ddd, J = 7.2, 5.1, 1.1 Hz, 1 H), 3.62 (ddq, J = 15.6, 6.9, 1.0 Hz, 1 H), 2.78 (dd, J = 4.4, 2.1 Hz, 1 H), 2.51–2.45 (m, 1 H), 2.33–2.26 (m, 1 H), 1.18 (d, J = 6.3 Hz, 3 H), 0.88 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H) ppm.[66]

Self-Metathesis Reaction of Dodec-1-ene (9): Dodec-1-ene (**9**; 4.5 mmol, 757 mg, 0.999 mL) was added to a dry Schlenk tube, followed by the Ru complex (0.005 equiv., 0.0225 mmol) and the mixture was stirred at 60 °C under vacuum (40 mbar) for 6 h. The reaction mixture was analysed by gas chromatography.

Self-Metathesis Reaction of Methyl Oleate (11):[64] Methyl oleate (**11**; 0.5 mmol, 148 mg) and dodecane (0.3 mmol, 51 mg, internal standard) were dissolved in toluene (3 mL) in a dried Schlenk tube. The Ru complex (**Hov II**, **Hov-NQ**, **Hov-BQ** or **Hov-AQ**; 0.01 equiv., 0.005 mmol) was added and the mixture was stirred at 50 °C. Samples were removed after 1, 5 and 24 h and analysed by gas chromatography.

Cross-Metathesis Reactions of Methyl Oleate (11) with (*Z*)-But-2-ene-1,4-diol Diacetate (14):[67] Methyl oleate (**11**; 0.5 mmol, 148 mg), (*Z*)-but-2-ene-1,4-diol diacetate (**14**; 1 mmol, 172 mg) and tetradecane (internal standard; 0.3 mmol, 51 mg) were dissolved in toluene (3 mL) in a dried Schlenk tube under argon. The Ru complex (**Hov II**, **Hov-NQ**, **Hov-BQ** or **Hov-AQ**; 0.01 equiv., 0.005 mmol) was added and the mixture was stirred at 50 °C. Samples were removed after 1, 5 and 24 h and analysed by gas chromatography.

Ring-Closing Metathesis of Diallyl Ether (12):[47] The Ru complex (**Hov II**, **Hov-NQ**, **Hov-BQ** or **Hov-AQ**; 0.0016 mmol) was dissolved in CD_2Cl_2 (0.7 mL) in a 5 mL vial under argon. Diallyl ether (0.16 mmol, 15.7 mg, 19.6 mL) was added to the solution and the reaction mixture was transferred to an NMR tube fitted with a screw cap. The NMR tube was heated to 40 °C in an oil bath and the reaction was monitored by ^{1}H NMR spectroscopy.

Synthesis of Diene 20: A solution of 1-cyclopropyl-6,8-difluoro-4-oxo-7-(1-undec-10-enoyloctahydropyrrolo[3,4-*b*]pyridin-6-yl)-1,4-dihydroquinoline-3-carboxylic acid[64] (4.99 mmol, 2.77g), *N*,*N*-dimethylaminopyridine (DMAP; 4.99 mmol, 0.61 g) and undec-10-en-1-ol (5.49 mmol, 0.935 g, 1.1 mL) in DCM (15 mL) was cooled with stirring in an ice bath. 1-Ethyl-3-[3-(dimethylamino)propyl]carbodiimide (EDCI; 15 mmol, 2.87 g) dissolved in DCM (5 mL) was added

and the reaction mixture was stirred at 0 °C for 2 h and then overnight at room temperature (TLC monitoring 50 % EtOAc/*c*-hex). The reaction mixture was concentrated to dryness in vacuo and the residue purified by column chromatography (15–50 % EtOAc/*c*-hex). The product was obtained as a white solid (3.02 mmol, 2.14 g, 61 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (s, 0.3 H), 8.47 (s, 0.7 H), 7.89–7.81 (m, 1 H), 5.85–5.75 (m, 2 H), 5.24 (q, *J* = 8.2 Hz, 1 H), 5.01–4.98 (m, 2 H), 4.94–4.90 (m, 2 H), 4.65–4.49 (m, 1 H), 4.29 (t, *J* = 6.9 Hz, 2 H), 4.15–4.05 (m, 0.7 H), 4.03–3.96 (m, 0.3 H), 3.86–3.75 (m, 2 H), 3.60 (t, *J* = 9.1 Hz, 0.7 H), 3.47 (t, *J* = 8.8 Hz, 0.3 H), 3.35 (d, *J* = 8.9 Hz, 1 H), 3.13 (t, *J* = 12.2 Hz, 0.7 H), 2.67 (t, *J* = 12.7 Hz, 0.3 H), 2.51–2.16 (m, 3 H), 2.05–2.00 (m, 4 H), 1.84–1.73 (m, 4 H), 1.66–1.49 (m, 5 H), 1.45–1.26 (m, 21 H), 1.23–1.08 (m, 3 H), 1.05–1.00 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.2, 172.6, 172.1, 165.7, 151.9 (dd, *J* = 246, 7.5 Hz), 149.8, 142.5 (dd, *J* = 250, 7.5 Hz), 139.2, 131.1, 128.1, 120.4 (d, *J* = 7.5 Hz), 114.1 (d, *J* = 7.5 Hz), 109.9, 108.7, 108.5, 65.0, 56.5, 54.4, 50.0, 48.8, 48.3, 41.2, 39.0 (d, *J* = 13.3 Hz), 36.8, 36.1, 35.4, 34.1, 33.8, 33.3, 29.4, 29.4, 29.3, 29.1, 29.0, 28.9, 28.7, 26.0, 25.4, 25.3, 25.2, 25.0, 24.7, 23.8, 9.3 (d, *J* = 7.5 Hz), 8.6 (d, *J* = 7.5 Hz) ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 3076, 2925, 2854, 1730, 1691, 1640, 1618, 1504, 1469, 1322, 1240, 1193, 1173, 1097, 1029, 908, 800, 651 cm^{-1}. MS (ESI, MeOH): *m*/*z* = 730 [M + Na]$^+$. $C_{42}H_{59}F_2N_3O_4$ (707.95): calcd. C 71.26, H 8.40, F 5.37, N 5.94; found C 71.18, H 8.24, F 5.31, N 5.93.

Ring Closing Metathesis of Diene 20: Diene **20** (0.2 mmol, 142 mg) was dissolved in toluene (28 mL) and the reaction mixture was warmed to 50 °C. In a separate vial, complex **Hov II**, **Hov-NQ**, **Hov-BQ** or **Hov-AQ** (0.005 mmol, 0.025 equiv.) was dissolved in toluene (2 mL) and a portion of the solution (0.2 mL) was added to the reaction mixture every 0.5 h. After completion of the reaction (TLC 50 % EtOAc/*c*-hex), the reaction mixture was concentrated to dryness in vacuo and the residue purified by column chromatography (15–50 % EtOAc/*c*-hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.39 (s, 0.3 H), 8.38 (s, 0.7 H), 7.63–7.59 (m, 1 H), 5.33–5.30 (m, 2 H), 4.25–4.21 (m, 1 H), 4.18–4.16 (m, 1 H), 4.02–4.00 (m, 1 H), 3.94–3.90 (m, 1 H), 3.75 (br. s, 1 H), 3.58–3.54 (m, 1 H), 3.45–3.41 (m, 1 H), 3.09 (br. s, 2 H), 2.81 (br. s, 1 H), 2.41–2-38 (m, 2 H), 2.31–2.26 (m, 1 H), 1.88 (s, 4 H), 1.81–1.75 (m, 2 H), 1.67–1.65 (m, 2 H), 1.58–1.55 (m, 4 H), 1.48–1.24 (m, 20 H), 1.16–1.14 (m, 3 H), 1.08–1.5 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.8, 172.7, 171.0, 164.2, 164.0, 150.9, 149.8, 144.1, 142.1, 130.4, 130.2, 129.7, 128.6, 120.3, 109.8, 107.7, 107.5, 64.2, 64.1, 56.5, 50.1, 39.4 (d, *J* = 13.7 Hz), 35.8, 32.7, 32.6, 32.5, 32.4, 32.2, 29.9, 29.7, 29.3, 29.2, 29.1, 29.0, 28.9, 28.7, 28.6, 28.5, 28.4, 28.3, 27.1, 26.8, 26.3, 26.0, 25.3, 25.2, 25.1, 24.1, 9.2 (d, *J* = 2.5 Hz), 8.6 (d, *J* = 7.5 Hz) ppm. IR (CH_2Cl_2 film): $\tilde{\nu}$ = 2924, 2852, 1731, 1691, 1618, 1505, 1469, 1406, 1320, 1238, 1173, 1146, 1097, 1029, 967, 893, 800, 749, 650 cm^{-1}. HRMS (ESI, MeOH): calcd. for $C_{40}H_{55}F_2N_3O_4Na$ 702.4058 [M + Na]$^+$; found 702.4049.

X-ray Diffraction: A four-circle SuperNova diffractometer with a Mo micro-source was used (λ = 0.71073 Å). X-ray data were collected and unit cell refinement and initial data reduction were performed by using the CrysAlisPro software.[61] An analytical numeric absorption correction was performed by using a multi-faceted crystal model based on expressions derived by Clark and Reid.[62] The

Table 7. Crystal data and structure refinement for **Hov-BQ** and **Hov-NQ**.

Compound	**Hov-BQ**	**Hov-NQ**
Chemical formula	$C_{39}H_{44}Cl_3N_3O_3Ru{\cdot}CH_2Cl_2$	$C_{41}H_{42}Cl_3N_3O_3Ru{\cdot}2(CH_2Cl_2)$
M_r	895.12	1002.05
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature [K]	100	100
a [Å]	15.8655(2)	8.6588(2)
b [Å]	8.9003(1)	15.0376(3)
c [Å]	29.2964(4)	17.5307(4)
α [°]	90.0	89.976(2)
β [°]	92.031(1)	77.599(2)
γ [°]	90.0	83.509(2)
V [Å]	4134.29(11)	2214.39(8)
Z	4	2
Radiation type	Mo-K_α	Mo-K_α
μ [mm^{-1}]	0.74	0.82
Crystal size [mm^3]	0.30 × 0.18 × 0.08	0.19 × 0.15 × 0.06
Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	SuperNova, Single source at offset, EOS diffractometer
Absorption correction	Analytical CrysAlisPro, Analytical numeric absorption correction using a multi-faceted crystal model based on expressions derived by Clark and Reid	
T_{min}, T_{max}	0.964, 0.990	0.956, 0.985
No. of measured reflections	127826	70324
No. of independ. reflections	14341	15167
No. of obsd. [$I > 2\sigma(I)$] reflections	12850	12220
R_{int}	0.043	0.056
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.754	0.758
Refinement		
$R[F^2 > 2\sigma(F^2)]$	0.031	0.051
$wR(F^2)$	0.073	0.129
S	1.09	1.12
No. of reflections	14341	15167
No. of parameters	499	544
$\Delta\varrho_{max}$, $\Delta\varrho_{min}$ [e Å^{-3}]	0.95, –0.64	1.43, –1.35

structures were solved with direct methods by using the SHELXS program and refined with SHELXL.[63] Crystal data and details of data collection and structure refinement are summarised in Table 7 and crystal structures are presented in Figure 6 and Figure 7.

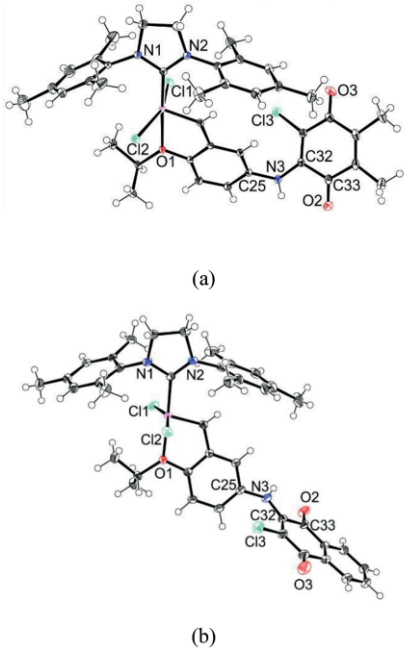


Figure 6. ORTEP drawings of (a) **Hov-BQ** and (b) **Hov-NQ**. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms are shown as open circles. Only selected atoms are labeled. Disordered molecules of DCM have been omitted for clarity.

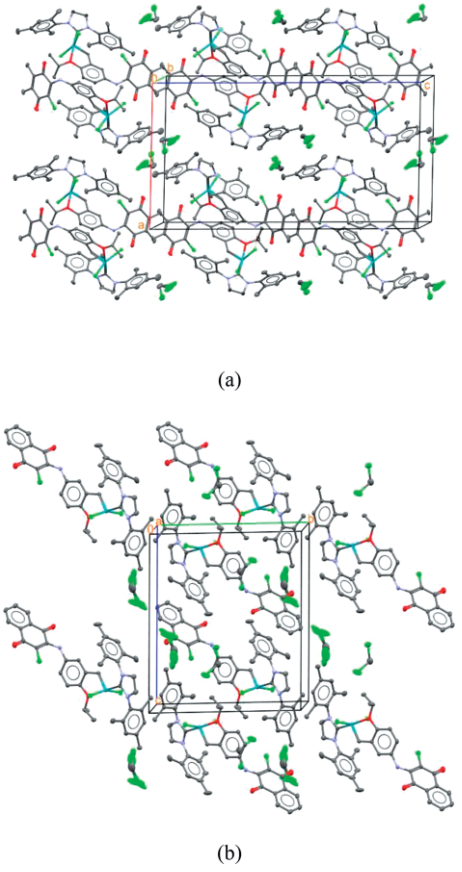


Figure 7. Molecular arrangement in the crystal structures of (a) **Hov-BQ** and (b) **Hov-NQ**. Hydrogen atoms have been omitted for clarity.

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Keywords: Metathesis · Quinones · Ruthenium · Isomerization · Metathesis

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