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Hoveyda–Grubbs-Type Precatalysts with Unsymmetrical *N*-Heterocyclic Carbenes as Effective Catalysts in Olefin Metathesis

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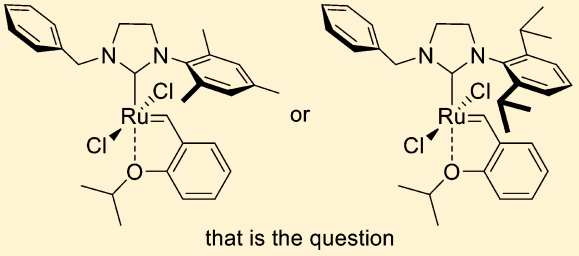
Supporting Information

ABSTRACT: In our search for more-selective olefin metathesis catalysts, a series of Hoveyda–Grubbs-type second-generation complexes bearing unsymmetrical *N*-heterocyclic carbene (NHC) ligands were synthesized and tested in model reactions. It was found that the *N*-benzyl substituent in NHC has a positive influence on the selectivity of the newly obtained catalysts in the self-metathesis reaction of α-olefins. As expected, a typical relationship between activity and selectivity with respect to the *N*-aryl substituent used was observed. Dipp-containing complexes exhibited higher stability at elevated temperature, while Mes-bearing complexes typically gave better yields than their Dipp analogues.



INTRODUCTION

N-Heterocyclic carbenes (NHCs) are of great interest in the chemical community, both in academia and in industry,[1] due to their interesting chemical properties as well as reactivity. Furthermore, their steric and electronic properties can be easily modified by the introduction of various substituents in the *N* or *N*′ position of imidazoliums and imidazoliniums as well as by introduction of substituents on the NHC backbone.[2] Recently, interest in the utilization of NHCs as organocatalysts has grown,[3] with applications including condensation reactions, transesterification, 1,2-addition, or ring-opening reactions; however, the main focus is directed toward their use as ligands in transition metal complexes. In the latter case, complexes bearing unsymmetrical *N*-heterocyclic carbenes (uNHCs) are of key importance.[4]

In recent years, olefin metathesis has been one of the most extensively studied transformations utilized in the formation of carbon–carbon double bonds.[5] The rapid growth of its significance is closely related to the introduction into laboratory practices of second-generation complexes, in which phosphine ligands have been replaced by NHCs. These types of compounds exhibit enhanced stability toward oxygen and moisture, greater functional groups' tolerance, and often also a higher reactivity than their first-generation counterparts. The enormous variety of olefin metathesis catalysts has allowed, inter alia, (a) introduction of metathesis reactions into industrial practice,[6] (b) control of *E*/*Z* selectivity,[7] (c) conversion of biomass into more valuable products,[8] and (d) purification of the products through the utilization of immobilized complexes[9] or those with enlarged mass.[10] Despite these great accomplishments, achieving high selectivity in certain metathesis reactions remains a challenge.

In this context, we[11] and others[12] have relied on the creation of new olefin metathesis ruthenium catalysts bearing uNHCs (Figure 1). Complexes of this type, due to the presence in the proximity of the metal center of substituents of different sizes, might stabilize the key intermediates to affect the selectivity of the reactions.[13] Such ruthenium complexes were successfully utilized in cross-metathesis (CM) reactions to give products

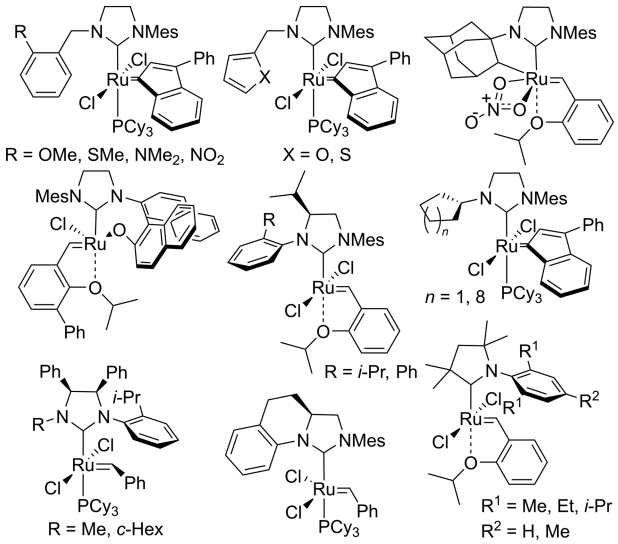


Figure 1. Selected complexes with unsymmetrical *N*-heterocyclic carbenes (uNHCs) and cyclic (alkyl)(amino)carbenes (CAACs).

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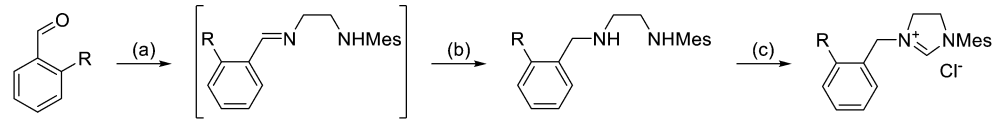
Scheme 1. Synthetic Pathway to the Synthesis of Unsymmetrical NHC Ligands with Mesityl Ligand[a]



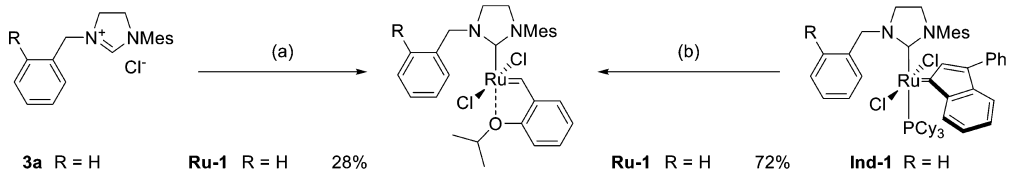
1a R = H
1b R = OMe
1c R = NMe_2

2a R = H 71%
2b R = OMe 60%
2c R = NMe_2 81%
over two steps

3a R = H 76%
3b R = OMe 76%
3c R = NMe_2 81%

[a]Reagents and conditions: (a) *N*-(2,4,6-trimethylphenyl)-1,2-diaminoethane, $HCOOH_{(cat.)}$ (for **1b** and **1c**) or $PTSA_{(cat.)}$ (for **1a**), MeOH, room temperature, 24 h; (b) $NaBH_4$, MeOH, −10 °C to room temperature, 2 h; (c) $(EtO)_3CH$, HCl, 90 °C for 12 h then 105 °C for 2 h.

Scheme 2. Synthesis of Unsymmetrical Hoveyda−Grubbs-Type Complexes Ru-1−Ru-3[a]



3a R = H
3b R = OMe
3c R = NMe_2

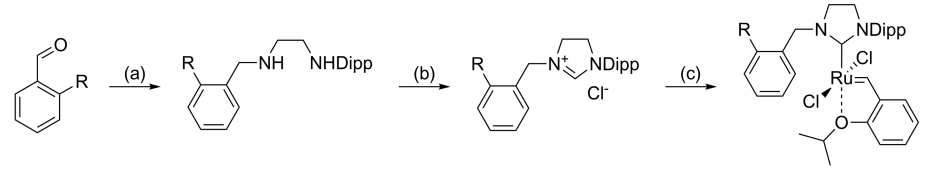
Ru-1 R = H 28%
Ru-2 R = OMe 27%
Ru-3 R = NMe_2 28%

Ru-1 R = H 72%
Ru-2 R = OMe 62%
Ru-3 R = NMe_2 74%

Ind-1 R = H
Ind-2 R = OMe
Ind-3 R = NMe_2

[a]Reagents and conditions: (a) potassium *tert*-amylate, toluene, room temperature, 0.5 h, then **Hov I**, 65 °C; (b) *o*-isopropoxystyrene, CuCl, toluene, 65 °C.

Scheme 3. Synthesis of Unsymmetrical Hoveyda Complexes Ru-4−Ru-8[a]



1a R = H
1b R = OMe
1c R = NMe_2
1d R = CF_3
1e R = NO_2

4a R = H 82%
4b R = OMe 75%
4c R = NMe_2 81%
4d R = CF_3 75%
4e R = NO_2 87%

5a R = H 89%
5b R = OMe 85%
5c R = NMe_2 83%
5d R = CF_3 99%
5e R = NO_2 86%

Ru-4 R = H 77%
Ru-5 R = OMe 56%
Ru-6 R = NMe_2 56%
Ru-7 R = CF_3 54%
Ru-8 R = NO_2 0%

[a]Reagents and conditions: (a) *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene, $MgSO_4$, MeOH, room temperature, then $NaBH_4$, MeOH, −10 °C to room temperature; (b) $(EtO)_3CH$, HCl, 90 °C for 12 h then 105 °C for 2 h; (c) potassium *tert*-amylate, toluene, room temperature, then **Hov I**, 65 °C, 0.5 h.

enriched in *Z*-stereoisomers[7] as well as in diastereoselective ring-rearrangement metathesis (dRRM) to provide predominantly a single diastereoisomer.[11] Furthermore, complexes bearing either uNHC[12f] or cyclic (alkyl)(amino)carbenes (CAACs)[14] were found to be very stable in the presence of ethylene and hence produced better results in ethenolysis reactions. Chiral catalysts containing uNHC ligands allow for conducting asymmetric ring-opening cross-metathesis (AROCM)[12b,c,e] as well as asymmetric ring-closing metathesis (ARCM)[12e] with moderate to excellent enantioselectivity.

Herein we report on the synthesis and evaluation of the catalytic performance of seven new Hoveyda−Grubbs-type metathesis (pre)catalysts bearing *N*-aryl,*N*′-benzyl-substituted uNHCs.

RESULTS AND DISCUSSION

Synthesis of Precatalysts. The synthesis of the Mes-bearing imidazolium ligand precursors was achieved by condensation of *N*-(2,4,6-trimethylphenyl)-1,2-diaminoethane with aldehydes in the presence of a catalytic amount of formic acid (for **1b** and **1c**)[15] or *p*-toluenesulfonic acid (for **1a**).[11a] The resulting diimines were reduced *in situ* to corresponding diamines (**2a−c**), followed by cyclization with triethyl orthoformate to the corresponding NHC precursors (**3a−c**, Scheme 1). The first approach to the synthesis of the Hoveyda−Grubbs-type complexes was based on the direct reaction between *in situ* generated NHC carbenes and **Hov I**. Unfortunately, in all cases, the yield of the desired complexes was low, reaching only about 30% (Scheme 2). Therefore, previously obtained indenylidene-type complexes[11a,15] were subjected to the reaction with *o*-isopropoxystyrene, providing **Ru-1**, **Ru-2**, and **Ru-3** with good yields of 72, 62, and 74%, respectively.

The synthesis of complexes **Ru-4−Ru-7** was easily accomplished in three steps, as shown in Scheme 3. The Hoveyda−Grubbs-type second-generation complexes were obtained in good yields via a standard procedure in which a phosphine ligand was exchanged for the corresponding NHC in **Hov I** catalysts. When a procedure involving transformation of indenylidene-type complexes, **Ind-1−Ind-3**, was applied, compounds with two NHC ligands were obtained. These species are a subject of ongoing study.

X-ray Crystallographic Studies. Single crystals of **Ru-1**, **Ru-2**, **Ru-3**, and **Ru-4** catalysts, suitable for X-ray measure-

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ments, were obtained from a mixture of dichloromethane (DCM)/heptane. To describe differences in conformation between the investigated compounds, we defined a specific torsion angle (T1), Cα−Cβ−Cγ−Nδ (see Figure 2). This angle describes the position of benzyl substituents with respect to the imidazolinium ring.

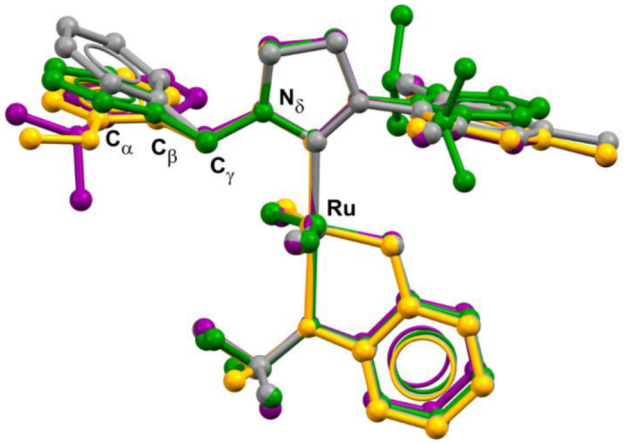


Figure 2. Structural overlay of molecules: **Ru-1** (gray), **Ru-2** (yellow), **Ru-3** (purple), and **Ru-4** (green). Hydrogen atoms have been omitted for clarity.

Depending on the size and position of the modified benzyl moieties, access to the metallic center is open or blocked. The difference between the most blocked substituent (**Ru-3**, T1 = −152.7(2)°) and the most accessible one (**Ru-1**, T1 = −118.4(2)°) is 34.3(2)°.

Thermal Stability Studies. Prior to the test of the activity of newly obtained complexes containing *N*-aryl,*N*′-benzyl-substituted NHC ligands, the thermal stability of these catalysts was examined. For this purpose, each of the ruthenium compounds was dissolved in deuterated toluene under an argon atmosphere and heated for 1 month at 50 °C. Degradation of the reference catalysts, with respect to 1,3,5-trimethoxybenzene utilized as an internal standard, was monitored by ^{1}H NMR spectroscopy.

All new catalysts, as well as the **Hov II**, exhibited high stability under applied conditions (Figure 3), as illustrated by the fact that even the least lasting of them decomposed by only 30% during 1 month (for clarification, the scale covers the range 70−100%). As expected, complexes bearing a mesityl moiety were less stable than their 2,6-diisopropylphenyl analogues. The influence of substituents in the *ortho* position of benzyl moiety varied, depending on the aryl substituent in the imidazolinium ring. When comparing the effects of substituents on the stability of metal complexes for **Ru-1**−**Ru-3**, one can conclude that the more electron-donating the substituent is, the more stable the complex is. In the case of the DIPP series (**Ru-4**−**Ru-7**) this trend was not so obvious, since all complexes exhibited similar stability.

Catalytic Performance Tests: Preliminary Studies. In order to evaluate the influence of structural modifications on the activity of the newly synthesized complexes containing functionalized benzyl substituents on NHCs, the RCM reaction of a model substrate, diethyl diallylmalonate (**6**), was performed (Scheme 4). The results were compared with those of the benchmark **Hov II** complex with the standard SIMes (1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-

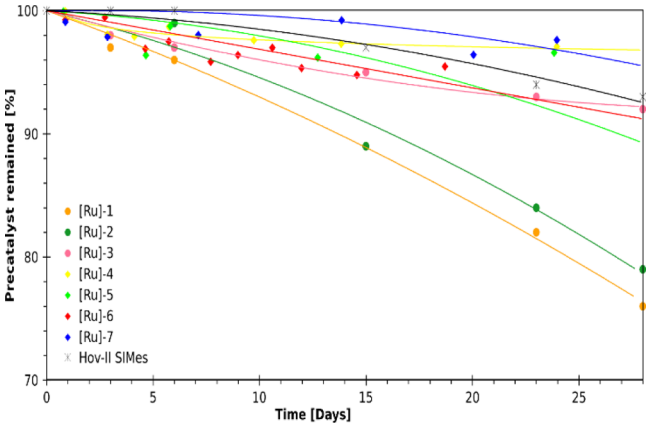
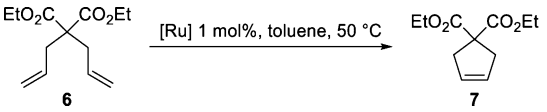


Figure 3. Degradation of precatalysts **Ru-1**−**Ru-7** in toluene-d_8 solution at 50 °C under argon monitored by ^{1}H NMR spectroscopy. Catalyst decomposition was determined based on the signal ratio between ruthenium compounds and internal standard, 1,3,5-trimethoxybenzene. Lines are visual aid only.

Scheme 4. RCM Reaction of Diethyl Diallylmalonate (6)



ylidene) ligand. The structures of all tested complexes are presented in Figure 4.

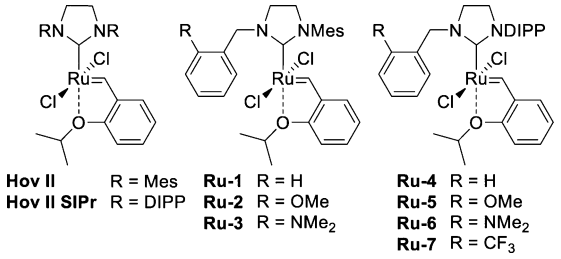


Figure 4. Complexes used in this study.

Model metathesis reaction of **6** was performed in toluene at 50 °C with 0.1 M concentration of substrate in the presence of 1 mol% of the catalyst (Scheme 4).

In this transformation, all *N*-Mes-bearing precatalysts exhibited higher activity than their DIPP analogues (Figure 5). On the other hand, even the best complexes of this series, namely **Ru-2** and **Ru-3**, were slightly worse than their commercially available counterpart, **Hov II**; however, after 10 min they also achieved full conversion. Within each series (for complexes possessing either NMes- or NDIPP-substituted imidazolines), ruthenium complexes containing methoxy (OMe, **Ru-2** and **Ru-5**) and dimethylamino groups (NMe_2, **Ru-3** and **Ru-6**) at the *ortho* position of the *N*′-benzyl substituent gave the best results. This might indicate the impact of the electronic properties of these electron-donating groups on the catalytic activity of new complexes, since, in all cases, their benzyl analogues gave worse results. On the other hand, the **Ru-7**, possessing an electron-withdrawing substituent, CF_3, gave a result very similar to that obtained with **Ru-6**, which may indicate that steric factors are also pivotal in this case.

In the next step, a more demanding substrate, *N*-allyl-4-methyl-*N*-(2-methylallyl)-benzenesulfonamide (**8**), was exam-

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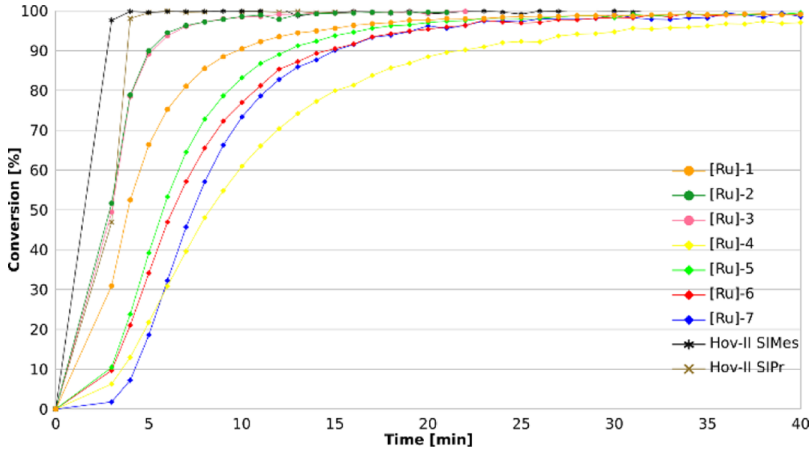
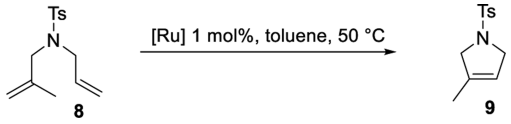


Figure 5. Time/conversion plot for the RCM reaction of diethyl diallylmalonate (**6**).

ined under the conditions previously applied for substrate **6** (toluene, 50 °C, $c_{[8]}$ = 0.1 M, 1 mol% of [Ru], Scheme 5).

Scheme 5. RCM Reaction of *N*-Allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (8)



The results obtained for the more crowded substrate **8** exhibited the same trend that was previously observed for diethyl diallylmalonate (**6**) (Figure 6). Here again, the Hoveyda–Grubbs second-generation catalyst gave the best result; however, complexes **Ru-1**–**Ru-3** containing *N*-benzyl, *N*′-mesityl-substituted NHC ligands were only slightly worse than the benchmark **Hov II**, but again better than their diisopropylphenyl analogues **Ru-4**–**Ru-7**. Within the series, results were also consistent with those obtained previously, which means that the activity of the complexes increased in that order of substituents: OMe > NMe_2 > H. The only exception was **Ru-7**, which was less effective upon reaction of compound **8** with more crowded double bond.

Scope and Limitation Study of uNHC-Bearing Complexes in Metathesis Reactions. Prior to testing the new complexes in the reactions with more demanding substrates, we decided to examine their performance on a wider range of substrates undergoing various types of metathesis reactions (RCM, ene-yne, CM) and compare the results with their commercial analogues **Hov II** and **Hov II SIPr**.

In all cases, the progress of the reaction was monitored by thin-layer chromatography (TLC) until complete consumption of the starting material (or one of the substrates, as in the reaction of allylbenzene (**16**)). In the RCM (Table 1, entries 1 and 2) and ene-yne reactions (Table 1, entry 3), a general trend was observed according to which the complexes in which mesityl was the N-aryl substituent in NHC ligand (**Hov II** and **Ru-1**–**Ru-3**) reached full conversion faster as well as in higher yields than their analogues with a more sterically hindered aromatic "arm" (**Hov II SIPr** and **Ru-4**–**Ru-7**). Moreover, both symmetrical catalysts were found to be the most active complexes in their groups; however, prolonging the reaction time allowed full conversion and high yields also with unsymmetrical Hoveyda-type compounds. The above observation is also true for the CM reaction between allylbenzene (**16**) and *cis*-1,4-diacetoxy-but-2-ene (**17**) (Table 1, entry 4); all complexes allowed the full conversion of the substrate **16** as well as high yield of product **18**. Furthermore, the *E*/*Z* selectivity of the reaction in the majority of cases was close to 7:1, the only clear deviation from the rule being the reaction catalyzed by **Ru-4** (here *E*/*Z* = 3.6:1).

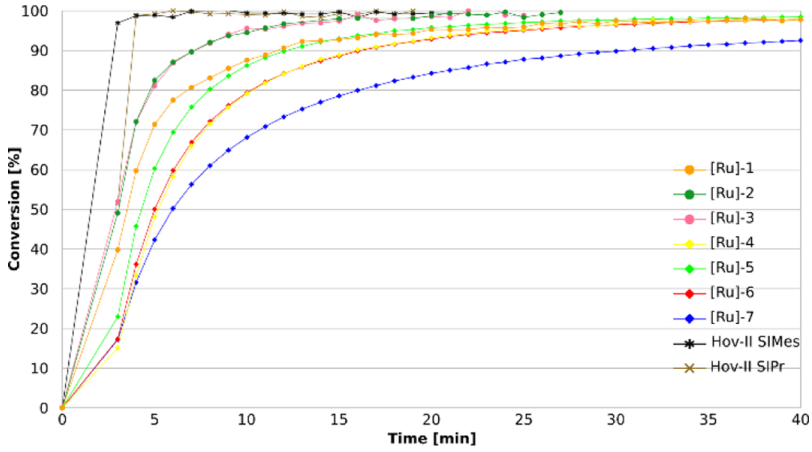


Figure 6. Time/conversion plot for the RCM reaction of *N*-allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (**8**).

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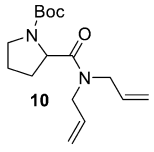
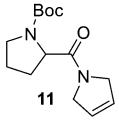
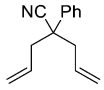
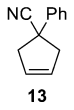
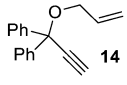
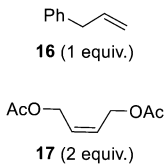
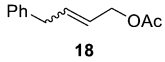
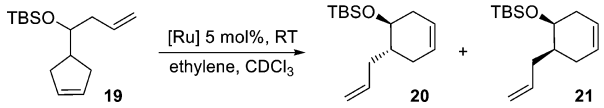
Table 1. Preparative Metathesis Reactions with Different Ru Complexes[a]

Entry	Substrate	Product	Ru-complex	loading [mol%]	Time (h)	Isolated yield [%]
1	 **10**	 **11**	Hov II Ru-1 Ru-2 Ru-3 Hov II SIPr Ru-4 Ru-5 Ru-6 Ru-7	1	0.25 1.25 2 1 0.5 3 3 3 3	97 87 89 92 96 85 94 88 90
2	 **12**	 **13**	Hov II Ru-1 Ru-2 Ru-3 Hov II SIPr Ru-4 Ru-5 Ru-6 Ru-7	0.5	1 1,5 1 1 1 3 3 3 3	95 92 94 96 94 73[b] 87[b] 80[b] 77[b]
3	 **14**	 **15**	Hov II Ru-1 Ru-2 Ru-3 Hov II SIPr Ru-4 Ru-5 Ru-6 Ru-7	2	0.5 2 2 2 1 1.5 1.5 1.5 1.5	95 92 91 92 95 89 91 89 91
4	 **16** (1 equiv.) **17** (2 equiv.)	 **18**	Hov II Ru-1 Ru-2 Ru-3 Hov II SIPr Ru-4 Ru-5 Ru-6 Ru-7	2.5	2 2 2 2 2 2 1.5 1.5 1.5	82 (8:1) 89 (7.1:1) 76 (7.9:1) 93 (6:1) 83 (7.9:1) 74 (3.6:1) 80 (7:1) 81 (8:1) 78 (6.5:1)

[a]Reaction conditions: c = 0.01 M, toluene (dry, degassed), 50 °C, under argon. [b]Determined by ^{1}H NMR

Diastereoselective Ring-Rearrangement Metathesis (dRRM). Owing to Blechert's previous studies on dRRM of cyclopentene **19** (Scheme 6), it is known that Grubbs and

Scheme 6. Diastereoselective Ring Rearrangement Metathesis of Cyclopentene 19



Hoveyda–Grubbs second-generation complexes give better diastereoselectivity than the corresponding first-generation complexes (ratios 2:1 and 1:1, respectively), with an almost quantitative conversion of the substrate.[16] Even better diastereoselectivity (9:1) was obtained with a tetrahydroquinoline-based Grubbs-type precatalyst, but at the expense of conversion.[17] Recently we have shown that also complexes bearing uNHCs as ligands can improve the selectivity toward the *trans* diastereoisomer (up to 4.7:1). As the newly obtained complexes (structures presented in Figure 7) belong to the same class of compounds as catalysts previously tested by us,[11] also in their cases high selectivity toward the *trans* diastereo-

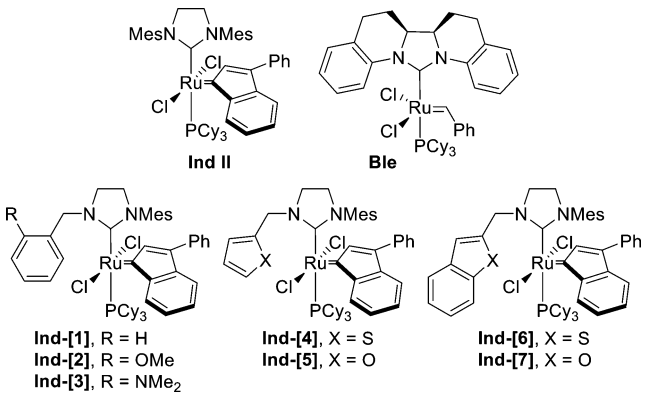


Figure 7. Complexes previously used in dRRM of cyclopentene **19**.

isomer was expected. In this context, their performance in dRRM of **19** was determined and compared with previous results, as well as these obtained with commercial **Hov II SIPr** (Table 2). As expected, when new complexes with uNHCs in which a mesityl was the *N*-aryl substituent (**Ru-1**–**Ru-3**) were utilized, a high selectivity was observed, up to 5:1 for **Ru-1** and 4.9:1 for **Ru-3**. On the other hand, the results obtained for

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Table 2. Results of dRRM of Cyclopentene 19 with Different Ru Complexes[a]

entry	Ru complex	conversion [%][b]	*trans*:*cis* dr[c]
1	**Hov II**	95	2:1
2	**Ru-1**	94	5:1
3	**Ru-2**	96	4.1:1
4	**Ru-3**	98	4.9:1
5	**Hov II SIPr**	99	1:1
6	**Ru-4**	98	1.4:1
7	**Ru-5**	89	1.3:1
8	**Ru-6**	98	1.3:1
9	**Ru-7**	99	1.6:1
10	**Gr II**[17]	95	1:1
11	**Ind II**[15 d]	>95	2:1
12	**Ind-1**[11a d]	>95	3.8:1
13	**Ind-2**[15 d]	>95	4.7:1
14	**Ind-3**[15 d]	>95	4.5:1
15	**Ind-4**[11b d]	95	3.6:1
16	**Ind-5**[11b d]	62	3:1
17	**Ind-6**[11b d]	57	3.4:1
18	**Ind-7**[11b d]	56	3.1:1
19	**Ble**[17 d]	58	9:1

[a]Reaction conditions: *c*[**19**] = 0.02 M, 5 mol% of precatalyst, $CDCl_3$ saturated with ethylene, 22 °C, 10 h. [b]Determined by ^1H NMR. [c]Determined by GC using durene as an internal standard. [d]Structures of complexes are presented in Figure 7.

complexes with SIPr-substituted imidazoline were clearly disappointing. Parent **Hov II SIPr** gave the same result as Grubbs and Hoveyda–Grubbs first-generation complexes, and its unsymmetrical analogues were only slightly better. Still, the most selective Ru complex remained the tetrahydroquinoline-based Grubbs-type precatalyst (*trans*:*cis* dr = 9:1), although at the expense of conversion (58%).

Self-Metathesis of Linear Olefins. Migration of the double bond during the metathesis reaction is one of the most common side reactions which can significantly alter the product distribution and decrease the yield of the desired product. This undesired side process is attributed to ruthenium hydrides like **A**,[18] **B**,[19] and **C** (Figure 8),[20] as well as ruthenium

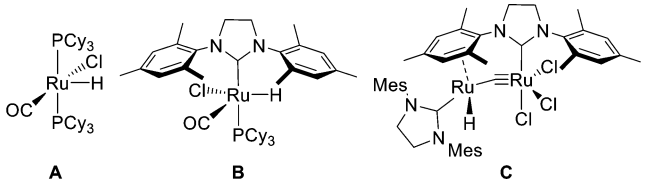


Figure 8. Examples of ruthenium hydrides active in isomerization of double bonds. Cy = cyclohexyl, Mes = mesityl.

nanoparticles,[21] which can be formed as products of decomposition of the metathesis catalysts and can act as isomerization agents. The isomerization of the double bond, and hence the drop in selectivity of the metathesis reaction, is observed mainly in the processes catalyzed by the second-generation complexes. When first-generation catalysts are used, high selectivity is observed; however, high catalyst loading is required to achieve satisfactory yields.[22]

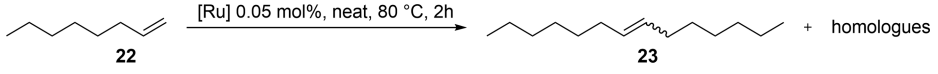
The most commonly used solution to decrease the level of isomerization is addition of quinones[23] or metallic mercury to the reaction mixture.[21] Another possible approach is the utilization of recently developed specialized catalysts bearing uNHCs which do not result in isomerization of the double bond.[12h,i] In the latter case, indenylidene precatalysts bearing uNHC ligands with an *N*-cycloalkyl moiety (see Figure 1) provided the desired product with remarkable 99% selectivity when used at low loading (50 ppm). What's more, this excellent olefin distribution with no isomerization was observed even in the absence of benzoquinone additives and after 24 h of reaction. In this context, we tested our new complexes bearing a substituted benzyl moiety in self-metathesis reaction of 1-octene (**22**) and compared them with their symmetrical analogues **Hov II** and **Hov II SIPr** (Scheme 7, Figure 9).

In the examined reaction, the symmetrical Hoveyda–Grubbs-type complexes were found to be the fastest ones, reaching full conversion after about 5 min. On the other hand, they exhibited the worst selectivity. When **Hov II** was utilized in the reaction, the desired product, tetradec-7-ene (**23**), represented only 25% of the reaction mixture, while the rest was accounted for by its shorter and longer homologues. An even worse result was obtained in the presence of **Hov II SIPr**, when the reaction mixture consisted of side products with an 85% yield. Reactions went in a much cleaner way when unsymmetrical complexes were applied, and at the same time reaction rates were only slightly slower, the full conversion being reached after 30 min for DIPP-containing NHCs and after 90 min for their Mes analogues. In the initial stage of the reaction, mainly the desired product **23** was observed in an amount of about 80% for each of the tested catalysts, and the byproducts appeared more slowly. This process was the slowest for **Ru-2**, for which it was possible to obtain a selectivity of about 80% after 2 h of reaction. Based on the advantages exhibited by the new complexes, in a preparative setup, after the self-CM metathesis reaction reaches its maximum, a commercial isocyanide scavenger, SnatchCat,[24] or a similar fast-acting quenching agent, can be used to cease any further Ru-catalyzed metathesis and isomerization events, allowing product **23** to be obtained in high purity. To confirm the practical applicability of these catalysts, the self-metathesis reaction of 35 mmol (5.59 mL) of 1-octene (**22**) was carried out in the presence of 500 ppm of **Ru-4**. After 10 min, SnatchCat solution (5 equiv) was added and the reaction flask content was distilled to provide 65% of analytically pure tetradec-7-ene (**23**) as a mixture of *E*/*Z* isomers (81:19). Isomerization products were not observed.

CONCLUSIONS

Seven new Hoveyda–Grubbs-type ruthenium complexes bearing unsymmetrical *N*-heterocyclic carbenes were synthesized and fully characterized. Their activity was compared with that of commercially available symmetrical analogues **Hov II** and **Hov II SIPr**. It was found that unsymmetrical catalysts used in typical metathesis reactions like RCM of diethyl diallylmalonate (**6**), *N*-allyl-4-methyl-*N*-(2-methylallyl)-

Scheme 7. Self-Metathesis Reaction of 1-Octene (22) Leading to 7-Tetradecene (23)



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Organometallics XXXX, XXX, XXX–XXX

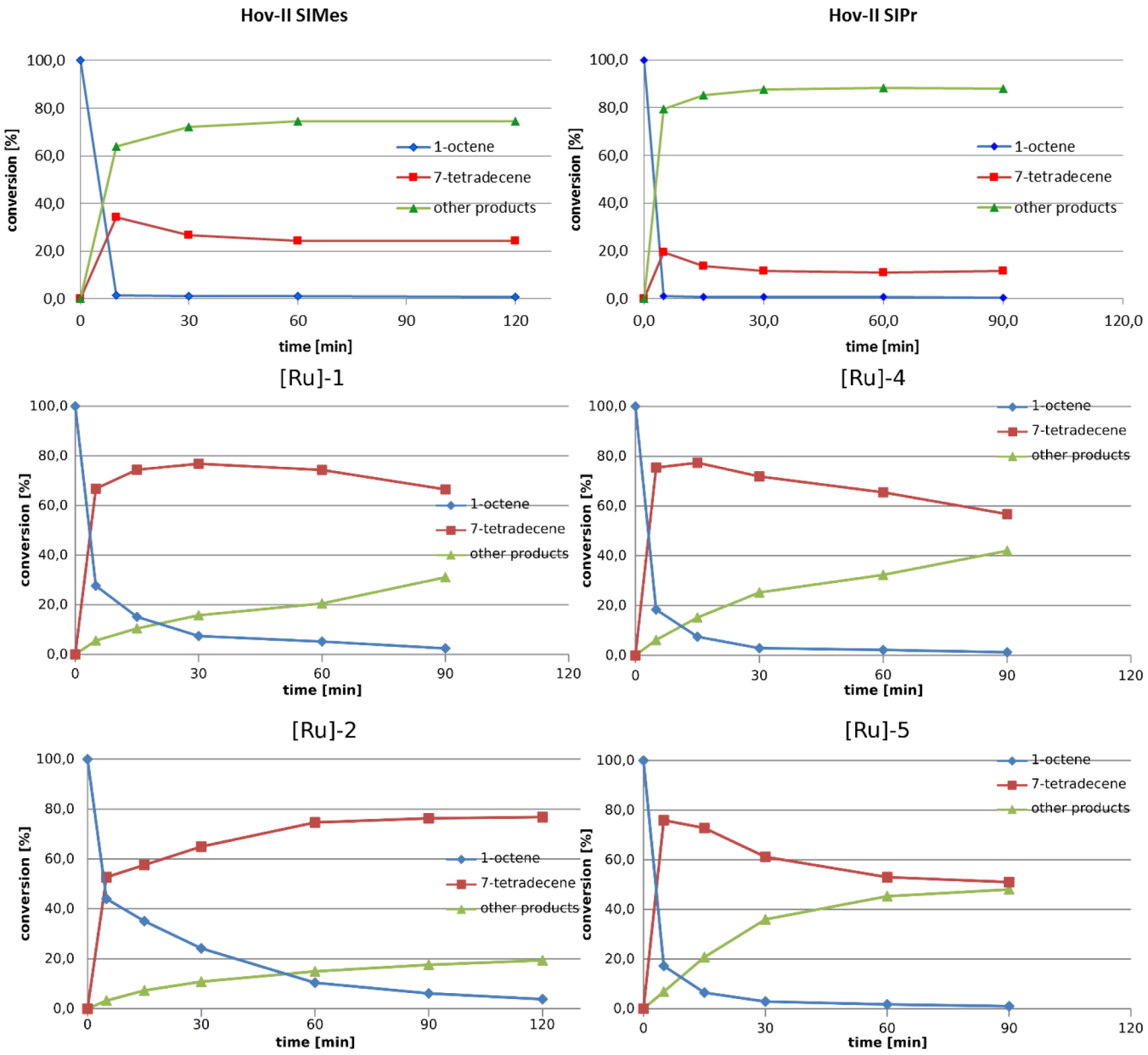

Figure 9. Reaction profiles for self-metathesis reaction of 1-octene (**22**).

benzenesulfonamide (**8**), *tert*-butyl 2-(diallylcarbamoyl)-pyrrolidine-1-carboxylate (**10**), and 2-allyl-2-phenylpent-4-enenitrile (**12**); ene-yne metathesis of (1-(allyloxy)prop-2-yne-1,1-diyl)dibenzene (**14**) or allylbenzene (**16**); and CM of *cis*-1,4-diacetoxy-but-2-ene (**17**) show only a slightly lower activity than the parents **Hov II** and **Hov II SIPr**, which means that this structural modification has a minimal impact on their effectiveness as catalysts. As expected, the differences become more apparent when uNHC-bearing complexes were utilized in reactions of more demanding substrates. In dRRM reaction of cyclopentene (**19**), the new complexes **Ru-1**, **Ru-2**, and **Ru-3** showed a much higher selectivity than **Hov II**, but to our great surprise all SIPr-substituted complexes, including unsymmetrical ones, gave an equimolar mixture of *cis* and *trans* diastereosomers, which means that they cannot be catalysts of choice in this transformation. Even greater differences between catalysts with symmetrical or unsymmetrical NHC ligands were visible in the self-metathesis reaction of 1-octene (**22**). For this transformation, the use of parent Hoveyda–Grubbs complexes (**Hov II** or **Hov II SIPr**) results in the formation of a mixture of byproducts, composed mainly of shorter and longer homologues of **23**. Importantly, the reaction carried out in the presence of unsymmetrical Ru compounds resulted in an almost 80% yield of tetradec-7-ene (**23**), therefore proving the better selectivity of the new catalysts in self-CM of α-olefins. It shall be noted, however, that the Olivier-Bourbigou and Mauduit's catalyst, providing selectivities up to 99%, remains even more advantageous for self-CM of α-olefins.[12i]

EXPERIMENTAL SECTION

General Remarks. All reagents were purchased from Sigma-Aldrich, Strem, TCI, and Alfa Aesar and used without further purification. All reactions involving the synthesis of metal complexes were carried out in oven-dried glassware with magnetic stirring under an argon atmosphere with anhydrous solvents, using standard Schlenk techniques. Toluene and diethyl ether were distilled over potassium, while DMF was distilled over CaH_2 under an atmosphere of argon. To

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test the activity of precatalysts, HPLC-grade solvents (Aldrich) CH_2Cl_2 and toluene were used as received. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization of TLC plates was performed by UV light with $KMnO_4$. Flash chromatography was performed using silica gel 60 (230−400 mesh). NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in ppm and referred to residual solvent peaks at respectively 7.26 and 77.16 ppm for ^1H and ^{13}C in $CDCl_3$, 5.32 and 53.84 ppm for ^1H and ^{13}C in CD_2Cl_2, and 2.50 and 39.52 ppm ^1H and ^{13}C in DMSO-d_6. The following abbreviations are used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Unless otherwise stated, all coupling constants (J) are between protons through three bonds and expressed in Hz. Spectra are reported as follows: chemical shift (δ, ppm), multiplicity, integration, coupling constants (Hz). IR spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer with a diamond ATR accessory. Wavenumbers are given in cm^{-1}. GC analyses were performed using a Clarus 580 chromatograph with durene as an internal standard. Elemental microanalyses were made using a Vario EL III apparatus. Melting points were recorded on an OptiMelt SRS apparatus with a heating rate of 10 °C/min. High-resolution electrospray mass spectra (ESI-HRMS) were recorded on a Quattro LC triple-quadrupole mass spectrometer, calibrated with an internal standard solution of sodium formate or sodium iodide in MeOH.

General Procedure for the Preparation of Diamines. To the solution of an appropriate aldehyde (1.1 equiv) in methanol was added $MgSO_4$ (2 equiv) or a catalytic amount of *p*-toluenesulfonic acid (PTSA, ca. 5−7 mg) or a catalytic amount of HCOOH and *N*-aryl-1,2-diaminoethane (1 equiv). The resulting mixture was stirred for 24 h at room temperature. Then, to the resulting mixture was added MeOH (10−30 mL), and the flask was placed in an ice-cooled bath. After that, $NaBH_4$ (5 equiv) was added portionwise (with 10 min intervals during 30 min) and the mixture was stirred for 2 h at room temperature. The solvent was evaporated, and the crude mixture was washed with saturated $NaHCO_3$(aq) solution until the pH became slightly basic. The product was extracted with EtOAc (3 × 40 mL). Purification of the crude mixture was accomplished by silica gel chromatography (cyclohexane/EtOAc). The fractions containing the desired product were concentrated.

*N^1-(2,4,6-Trimethylphenyl)-N^2-benzyl-1,2-diaminoethane (**2a**).* Following the general procedure, a solution of benzaldehyde (**1a**) (1.79 g, 12.32 mmol) in MeOH (12 mL), PTSA (ca. 5−7 mg), *N*-(2,4,6-trimethylphenyl)-1,2-diaminoethane (2 g, 11.2 mmol), and $NaBH_4$ (1.70 g, 44.8 mmol) were used. Purification by silica gel chromatography (cyclohexane/EtOAc 4:1, followed by cyclohexane/EtOAc, 1:1) yielded **2a** as a yellow oil (2.12 g, 71%).[11a] ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38−7.33 (m, 4H, Ar-H), 7.30−7.27 (m, 1H, Ar-H), 6.83 (s, 2H, Mes-H), 3.86 (s, 2H, Ar-CH_2-N), 3.08−3.06 (m, 2H, N-CH_2-CH_2), 2.88−2.86 (m, 2H, N-CH_2-CH_2) 2.29 (s, 6H, Ar-CH_3), 2.24 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 140.2, 131.2, 129.7, 129.5, 128.6, 128.3, 127.2, 53.9, 49.5, 48.3, 20.7, 18.6 ppm.

*N^1-(2,4,6-Trimethylphenyl)-N^2-(2-methoxybenzyl)-1,2-diaminoethane (**2b**).* Following the general procedure, a solution of 2-methoxybenzaldehyde (**1b**) (2 g, 14.4 mmol) in MeOH (10 mL), formic acid (2 drops), *N*-(2,4,6-trimethylphenyl)-1,2-diaminoethane (2.57 g, 14.4 mmol), and $NaBH_4$ (2.87 g, 72 mmol) were used. Purification by silica gel chromatography (c-Hex/EtOAc 3:1, followed by cHex/EtOAc 1:1) yielded **2b** as a yellow oil (2.65 g, 60%).[15] ^1H NMR (500 MHz, $CDCl_3$): δ = 7.26−7.22 (m, 2H, Ar-H), 6.91 (dt, J_{HH} = 7.4, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 6.87−6.85 (m, 1H, Ar-H), 6.80 (s, 2H, Mes-H), 3.83 (s, 2H, Ar-CH_2-N), 3.82 (s, 3H, O-CH_3), 3.05−3.03 (m, 2H, N-CH_2-CH_2), 2.8−2.6 (m, 2H, N-CH_2-CH_2), 2.26 (s, 6H, Ar-CH_3), 2.22 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.8, 143.9, 131.1, 129.9, 129.7, 129.5, 128.4, 120.5, 110.4, 55.4, 49.2, 48.9, 48.3, 20.7, 18.6 ppm.

*N^1-(2,4,6-Trimethylphenyl)-N^2-(2-(dimethylamino)benzyl)-1,2-diaminoethane (**2c**).* Following the general procedure, a solution of 2-(dimethylamino)benzaldehyde (**1c**) (1 g, 6.7 mmol) in MeOH (10 mL), formic acid (2 drops), *N*-(2,4,6-trimethylphenyl)-1,2-diaminoethane (1.19 g, 6.7 mmol), and $NaBH_4$ (1.43 g, 36 mmol) were used. Purification by silica gel chromatography (c-Hex/EtOAc 3:1, followed by c-Hex/EtOAc 1:1) yielded **2c** as a yellow oil (1.31 g, 63%).[15] ^1H NMR (500 MHz, $CDCl_3$): δ = 7.28 (dd, J_{HH} = 7.4, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.15 (dt, J_{HH} = 7.6, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-H), 7.06−6.93 (m, 2H, Ar-H), 6.74 (s, 2H, Mes-H), 3.83 (s, 2H, Ar-CH_2-N), 2.98−2.95 (m, 2H, N-CH_2-CH_2), 2.77−2.72 (m, 2H, N-CH_2-CH_2), 2.62 (s, 6H, N-Me), 2.19 (s, 6H, Ar-CH_3), 2.15 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.8, 144.0, 134.7, 131.1, 129.7, 129.5, 127.8, 123.4, 119.4, 50.1, 49.7, 48.4, 45.1, 20.7, 18.6 ppm.

*N^1-(2,6-Diisopropylphenyl)-N^2-benzyl-1,2-diaminoethane Dihydrochloride (**4a**).* Following the general procedure, a solution of benzaldehyde (**1a**) (1.59 g, 15 mmol) in MeOH (70 mL), $MgSO_4$ (3.27 g, 27.2 mmol), *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene (3 g, 13.6 mmol), and $NaBH_4$ (2.57 g, 68 mmol) were used. A precipitate of *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene dihydrochloride with HCl/Et_2O instead of column chromatography was used to purified the product. N^1-(2,6-Diisopropylphenyl)-N^2-benzyl-1,2-diaminoethane dichloride (3.45 g, 11.1 mmol, 82%) was obtained as a white powder, mp 215−217 °C (dec). ^1H NMR (400 MHz, CD_3OD): δ = 7.65−7.57 (m, 2H, Ar-H), 7.52−7.44 (m, 4H, Ar-H), 7.43−7.37 (m, 2H, Ar-H), 4.36 (s, 2H, Ar-CH_2-N), 3.77−3.60 (m, 4H, N-CH_2-CH_2), 3.21 (hept, J_{HH} = 6.8 Hz, 2H, Ar-CH), 1.34 (d, J_{HH} = 6.7 Hz, 12H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9, 132.0 131.6, 131.3, 130.9, 130.9, 130.4, 127.2, 52.8, 50.0, 44.3, 29.5, 25.1 ppm. IR (film from CH_2Cl_2): ν = 2969, 2804, 1582, 1459, 1442, 1340, 984, 814, 800, 742, 699, 683, 578, 521 cm^{-1}. Anal. Calcd for $C_{21}H_{32}Cl_2N_2$: C, 65.79; H, 8.53; N, 7.22; Cl, 18.49. Found: C, 65.80; H, 8.53; N, 7.22; Cl, 18.24.. HRMS (ESI): m/z calcd for $C_{21}H_{30}N_2$: $[M+H^+]$ 311.2482, found 311.2469.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-methoxybenzyl)-1,2-diaminoethane (**4b**).* Following the general procedure, a solution of *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene (5 g, 22.7 mmol) in methanol (100 mL), 2-methoxybenzaldehyde (**1a**) (3.47 g, 25 mmol), magnesium sulfate (5.46 g, 45.4 mmol), and sodium borohydride (4.29 g, 114 mmol) were used. Purification by silica gel chromatography yielded **4b** as a yellow oil (5.8 g, 17.03 mmol, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36−7.26 (m, 2H, Ar-H), 7.17−7.11 (m, 2H, Ar-H), 7.10−7.05 (m, 1H, Ar-H), 6.98 (td, J_{HH} = 7.4, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 6.92 (d, J_{HH} = 7.9 Hz, 1H, Ar-H), 3.90 (s, 2H, Ar-CH_2-N), 3.87 (s, 3H, O-CH_3), 3.37 (hept, J_{HH} = 6.8 Hz, 2H, Ar-CH), 3.03 (dd, J_{HH} = 6.7, 4.7 Hz, 2H, N-CH_2-CH_2), 2.90 (dd, J_{HH} = 6.6, 4.6 Hz, 2H, N-CH_2-CH_2), 1.27 (d, J_{HH} = 6.9 Hz, 12H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 143.7, 142.5, 129.7, 128.6, 128.2, 123.6, 120.5, 110.3, 55.3, 51.3, 49.2, 49.0, 27.6, 24.4 ppm. IR (film from CH_2Cl_2): ν = 3356, 2959, 2866, 1588, 1491, 1457, 1362, 1239, 1100, 1050, 1030, 934, 750, 575, 530 cm^{-1}. Anal. Calcd for $C_{22}H_{32}N_2O$: C, 77.60; H, 9.47; N, 8.23. Found: C, 77.54; H, 9.50; N, 8.22. HRMS (ESI): m/z calcd for $C_{22}H_{32}N_2O$: $[M+H^+]$ 341.2587, found 341.2600.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-(dimethylamino)benzyl)-1,2-diaminoethane (**4c**).* Following the general procedure, a solution of *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene (2.43 g, 11 mmol), 2-(*N*,*N*′-dimethylamino)benzaldehyde (1.81 g, 12.1 mmol), magnesium sulfate (2.65 g, 22 mmol), and sodium borohydride (2.09 g, 55.2 mmol) in methanol was used. Purification by silica gel chromatography yielded **4c** as a yellow oil (3.15 g, 8.9 mmol, 81%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J_{HH} = 7.5, $^4J_{HH}$ = 1.6 Hz, 1H, Ar-H), 7.31−7.26 (m, 1H, Ar-H), 7.19−7.06 (m, 5H, Ar-H), 3.98 (s, 2H, Ar-CH_2-N), 3.39 (hept, J_{HH} = 6.8 Hz, 2H, Ar-CH), 3.05 (dd, J_{HH} = 6.6, 4.5 Hz, 2H, N-CH_2-CH_2), 2.93 (dd, J_{HH} = 6.7, 4.4 Hz, 2H, N-CH_2-CH_2), 2.75 (s, 6H, N-CH_3), 1.28 (d, J_{HH} = 6.9 Hz, 12H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 143.8, 142.4, 134.8, 129.5, 127.7, 123.6, 123.6, 123.3, 119.3, 51.4, 50.0, 49.6, 45.1, 27.7, 24.4 ppm. IR (film from CH_2Cl_2): ν = 3356, 2959, 2826, 1491, 1448, 1382, 1310, 1255, 1188, 1154, 1112, 1048, 946, 799, 753, 565 cm^{-1}. Anal. Calcd for $C_{23}H_{35}N_3$: C, 78.14; H, 9.98; N, 11.89. Found: C,

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78.03; H, 9.91; N, 11.82. HRMS (ESI): m/z calcd for $C_{23}H_{35}N_3$: [M+H$^+$] 354.2904, found 354.2910.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-(trifluoromethyl)benzyl)-1,2-diaminoethane (**4d**).* Following the general procedure, a solution of *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene (2 g, 9.08 mmol) in methanol (80 mL), 2-(trifluoromethyl)benzaldehyde (**1d**) (1.77 g, 9.98 mmol), magnesium sulfate (2.19 g, 18.16 mmol), and sodium borohydride (1.72 g, 45.4 mmol) were used. Purification by silica gel chromatography yielded **4d** as a yellow oil (2.57 g, 6.79 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J_{HH} = 7.8 Hz, 1H, Ar-H), 7.69 (d, J_{HH} = 8.5 Hz, 1H, Ar-H), 7.58 (t, J_{HH} = 7.8 Hz, 1H, Ar-H), 7.39 (t, J_{HH} = 7.6 Hz, 1H, Ar-H), 7.15−7.11 (m, 2H, Ar-H), 7.10−7.05 (m, 1H, Ar-H), 4.07 (s, 2H, Ar-$\underline{CH_2}$-N), 3.36 (hept, J_{HH} = 6.8 Hz, 2H, Ar-$\underline{CH}$), 3.04 (dd, J_{HH} = 6.6, 4.0 Hz, 2H, N-$\underline{CH_2}$-CH_2), 2.97 (dd, J_{HH} = 6.6, 4.0 Hz, 2H, N-CH_2-$\underline{CH_2}$), 1.26 (d, J_{HH} = 6.9 Hz, 12H, CH-$\underline{CH_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.6, 142.5, 139.2 (q, $^4J_{CF}$ = 1.5 Hz), 132.0 (q, $^4J_{CF}$ = 1.1 Hz), 130.1, 128.3 (q, $^2J_{CF}$ = 30.1 Hz), 127.0, 126.0 (q, $^3J_{CF}$ = 5.8 Hz), 124.7 (q, $^1J_{CF}$ = 274.0 Hz), 123.7, 123.6, 51.3, 49.8 (q, $^4J_{CF}$ = 2.2 Hz), 49.6, 27.7, 24.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −59.64. IR (film from CH_2Cl_2): ν = 3365, 2961, 2869, 1445, 1311, 1256, 1159, 1115, 1059, 1036, 799, 755, 654 cm^{-1}. Anal. Calcd for $C_{22}H_{29}N_2F_3$: C, 69.82; H, 7.72; N, 7.40; F, 15.06. Found: C, 69.81; H, 7.74; N, 7.38; F, 15.13. HRMS (ESI): m/z calcd for $C_{22}H_{29}N_2F_3$: [M+H$^+$] 379.2356, found 379.2368.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-nitrobenzyl)-1,2-diaminoethane (**4e**).* Following the general procedure, a solution of *N*-(2,6-diisopropylphenyl)-1,2-diaminoethene (2.3 g, 11.5 mmol) in methanol (75 mL), 2-nitrobenzaldehyde (1.74 g, 11.5 mmol), magnesium sulfate (2.4 g, 23 mmol), and sodium borohydride (1.97 g, 52.2 mmol) were used. Purification by silica gel chromatography yielded **4d** as a yellow oil which solidified after standing (3.24 g, 9.1 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (td, J_{HH} = 8.2, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.68 (dd, J_{HH} = 7.7, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 7.61 (td, J_{HH} = 7.5, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.47−7.40 (m, 1H, Ar-H), 7.14−7.01 (m, 3H, Ar-H), 4.13 (s, 2H, Ar-$\underline{CH_2}$-N), 3.30 (hept, J_{HH} = 6.8 Hz, 2H, Ar-$\underline{CH}$), 3.00 (dd, J_{HH} = 6.7, 4.3 Hz, 2H, N-$\underline{CH_2}$-CH_2), 2.91 (dd, J_{HH} = 6.6, 4.3 Hz, 2H, N-CH_2-$\underline{CH_2}$), 1.23 (d, J_{HH} = 6.9 Hz, 12H, CH-$\underline{CH_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.2, 143.5, 142.5, 135.9, 133.3, 131.2, 128.1, 125.0, 123.8, 123.7, 51.4, 50.8, 49.7, 27.7, 24.4 ppm. IR (film from CH_2Cl_2): ν = 3348, 2961, 1527, 1440, 1358, 1312, 1251, 1203, 1107, 1054, 916, 860, 806, 774, 752, 734, 707, 614, 43 cm^{-1}. Anal. Calcd for $C_{21}H_{29}N_3O_2$: C, 70.95; H, 8.22; N, 11.82. Found: C, 70.85; H, 8.21; N, 11.66. HRMS (ESI): m/z calcd for $C_{21}H_{29}N_3O_2$: [M+H$^+$] 356.2333, found 356.2340.

General Procedure for the Preparation of Dihydroimidazolium Salts with Mesityl Substituent. A mixture of diamine (1 equiv), triethyl orthoformate (10 equiv), and HCl in dioxane (4 M, 2.1 equiv) was heated in an open vessel at 90 °C for 12 h and then at 105 °C for 2 h. Next, the reaction mixture was cooled to room temperature, and the solvent was evaporated to one-third of its volume. Again, the mixture was cooled. Subsequent filtration and washing with cold diethyl ether yielded the pure imidazolium salt as a white powder.

*N^1-(2,4,6-Trimethylphenyl)-N^2-benzyl-4,5-dihydro-1H-imidazol-3-ium Chloride (**3a**).* Following the general procedure, from N^1-(2,4,6trimethylphenyl)-N^2-benzyl-1,2-diaminoethane (**2a**) (1.50 g, 5.03 mmol), triethyl orthoformate (8.5 mL), and HCl (4 M solution, 2.64 mL), **3a** was obtained as a white powder (1.26 g, 76%), mp 214−216 °C.[11a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.25 (s, 1H, $\underline{CH}$-Imd), 7.46−7.44 (m, 2H, Ar-H), 7.36−7.32 (m, 3H, Ar-H), 6.84 (s, 2H, Mes-$\underline{H}$), 5.14 (s, 2H, Ar-$\underline{CH_2}$-N), 4.01−4.09 (m, 4H, N-$\underline{CH_2}$-$\underline{CH_2}$), 2.23 (s, 6H, Ar-C$\underline{H_3}$), 2.22 (s, 3H, Ar-C$\underline{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 140.2, 135.1, 133.0, 131.0, 130.8, 129.3, 129.2, 129.1, 52.1, 51.0, 48.1, 21.0, 18.1 ppm.

*N^1-(2,4,6-Trimethylphenyl)-N^2-(2-methoxybenzyl)-4,5-dihydro-1H-imidazol-3-ium Chloride (**3b**).* Following the general procedure, from N^1-(2,4,6-trimethylphenyl)-N^2-(2-methoxybenzyl)-1,2-diaminoethane (**2b**) (1.50 g, 5.03 mmol), triethyl orthoformate (8.5 mL), and HCl (4 M solution, 2.64 mL), **3b** was obtained as white crystals (1.31 g, 76%), decomposes without melting in the range of 223−241 °C.[15] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.62 (s, 1H, $\underline{CH}$-Imd), 7.52 (dd, J_{HH} = 7.4, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-$\underline{H}$), 7.39−7.35 (m, 1H, Ar-$\underline{H}$), 6.97 (dt, J_{HH} = 7.5, $^4J_{HH}$ = 1.1 Hz, 1H, Ar-$\underline{H}$), 6.93 (d, J_{HH} = 8.4 Hz, 1H, Ar-$\underline{H}$), 6.9 (s, 2H, Mes-$\underline{H}$), 5.10 (s, 2H, Ar-$\underline{CH_2}$-N), 4.1 (s, 4H, N-$\underline{CH_2}$-$\underline{CH_2}$), 3.86 (s, 3H, O-$\underline{CH_3}$), 2.27 (s, 9H, Ar-C$\underline{H_3}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.5, 158.0, 140.1, 135.3, 131.8, 131.0, 130.8, 129.9, 121.3, 120.9, 110.8, 55.6, 51.1, 48.3, 48.0, 21.0, 17.9 ppm.

*N^1-(2,4,6-Trimethylphenyl)-N^2-(2-(dimethylamino)benzyl)-4,5-dihydro-1H-imidazol-3-ium Chloride (**3c**).* Following the general procedure, from N^1-(2,4,6-trimethylphenyl)-N^2-(2-dimethylamino)-benzyl)-1,2-diaminoethane (**2c**) (1.2 g, 3.85 mmol), triethyl orthoformate (6.8 mL), and HCl (4 M solution, 2 mL), **3c** was obtained as white crystals (1.1 g, 80%), mp 174−177 °C.[15] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.96 (s, 1H, $\underline{CH}$-Imd), 7.40−7.35 (bs, 1H, Ar-$\underline{H}$), 7.28 (t, J_{HH} = 7.3 Hz, 1H, Ar-$\underline{H}$), 7.14−6.99 (bs, 2H, Ar-$\underline{H}$), 6.83 (s, 2H, Mes-$\underline{H}$), 5.30 (s, 2H, Ar-$\underline{CH_2}$-N), 4.08−3.81 (m, 4H, N-$\underline{CH_2}$-$\underline{CH_2}$), 2.61 (s, 6H, N-$\underline{CH_3}$), 2.22 (s, 6H, Ar-C$\underline{H_3}$), 2.20 (s, 3H, Ar-C$\underline{H_3}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.7, 153.6, 140.2, 135.2, 130.9, 130.8, 130.1, 130.0, 127.3, 124.5, 120.2, 50.9, 48.6, 48.0, 45.5, 21.0, 18.0 ppm.

General Procedure for the Preparation of Dihydroimidazolium Salts with Diisopropylphenyl Substituent. A mixture of diamine (1 equiv), triethyl orthoformate (10 equiv), and ammonium chloride (2 equiv) was heated at 120 °C for 4 h under an argon atmosphere. The reaction mixture was cooled to room temperature, and precipitate was filtered off, washed with Et_2O, and dried in a high vacuum.

*N^1-(2,6-Diisopropylphenyl)-N^2-benzyl-4,5-dihydro-1H-imidazolinium Chloride (**5a**).* Following the general procedure, from N^1-(2,6-diisopropylphenyl)-N^2-benzyl-1,2-diaminoethane (**4a**) (4 g, 12.9 mmol), triethyl orthoformate (19.5 g, 21.9 mL, 129 mmol), and ammonium chloride (1.38 g, 25.8 mmol), **5a** was obtained as a white powder (4.1 g, 11.5 mmol, 89%), mp 254 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.36 (s, 1H, $\underline{CH}$-Imd), 7.53−7.47 (m, 2H, Ar-$\underline{H}$), 7.44−7.34 (m, 4H, Ar-$\underline{H}$), 7.20 (d, J_{HH} = 7.8 Hz, 2H, Ar-$\underline{H}$), 5.30 (s, 2H, Ar-$\underline{CH_2}$-N), 4.19−3.94 (m, 4H, N-$\underline{CH_2}$-$\underline{CH_2}$), 2.81 (hept, J_{HH} = 6.8 Hz, 2H, Ar-$\underline{CH}$), 1.30 (d, J_{HH} = 6.8 Hz, 6H, CH-$\underline{CH_3}$), 1.23 (d, J_{HH} = 6.8 Hz, 6H, CH-$\underline{CH_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 146.4, 133.0, 131.1, 130.0, 129.3, 129.1, 129.1, 124.9, 53.1, 52.2, 47.9, 28.9, 25.1, 24.0 ppm. IR (film from CH_2Cl_2): ν = 2966, 1629, 1459, 1360, 1258, 1234, 1148, 809, 768, 712, 651, 575, 552, 486 cm^{-1}. Anal. Calcd for $C_{22}H_{29}N_2Cl$: C, 74.03; H, 8.19; N, 7.85; Cl, 9.93. Found: C, 74.01; H, 8.16; N, 7.81; Cl, 9.73. HRMS (ESI): m/z calcd for $C_{22}H_{28}N_2$: [M+H$^+$] 321.2325, found 321.2327.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-methoxybenzyl)-4,5-dihydro-1H-imidazolinium Chloride (**5b**).* Following the general procedure, from N^1-(2,6-diisopropylphenyl)-N^2-(2-methoxybenzyl)-1,2-diaminoethane (**4b**) (2.47 g, 7.26 mmol), triethyl orthoformate (11 g, 12.3 mL, 72.6 mmol), and ammonium chloride (0.776 g, 14.5 mmol), **5b** was obtained as a white powder (2.4 g, 6.2 mmol, 85%), mp 255−256 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (s, 1H, $\underline{CH}$-Imd), 7.59 (dd, J_{HH} = 7.4, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-$\underline{H}$), 7.43−7.33 (m, 2H, Ar-$\underline{H}$), 7.20 (d, J_{HH} = 7.8 Hz, 2H, Ar-$\underline{H}$), 6.99 (t, J_{HH} = 7.5 Hz, 1H, Ar-$\underline{H}$), 6.92 (d, J_{HH} = 8.2 Hz, 1H, Ar-$\underline{H}$), 5.20 (s, 2H, Ar-$\underline{CH_2}$-N), 4.26−4.15 (m, 2H, N-$\underline{CH_2}$-CH_2), 4.13−4.04 (m, 2H, N-$\underline{CH_2}$-CH_2), 3.85 (s, 3H, O-$\underline{CH_3}$), 2.86 (hept, J_{HH} = 6.7 Hz, 2H, Ar-$\underline{CH}$), 1.26 (d, J_{HH} = 6.8 Hz, 6H, CH-$\underline{CH_3}$), 1.22 (d, J_{HH} = 6.8 Hz, 6H, CH-$\underline{CH_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 158.1, 146.7, 132.1, 131.1, 131.0, 130.1, 1254.0, 121.5, 121.1, 111.0, 55.9, 53.4, 48.5, 48.0, 28.9, 25.1, 24.3 ppm. IR (film from CH_2Cl_2): ν = 2965, 1629, 1459, 1359, 1258, 1233, 808, 767, 712, 650, 574, 485 cm^{-1}. Anal. Calcd for $C_{23}H_{31}N_2ClO{\cdot}0.5H_2O$: C, 69.77; H, 8.15. Found: C, 69.89; H, 7.98. HRMS (ESI): m/z calcd. for $C_{23}H_{30}N_2O$: [M+H$^+$] 351.2431, found 351.2436.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-(dimethylamino)benzyl)-4,5-dihydro-1H-imidazolinium chloride (**5c**).* Following the general procedure, from N^1-(2,6-Diisopropylphenyl)-N^2-(2-(dimethylamino)-benzyl)-1,2-diaminoethane (**4c**) (1.5 g, 4.24 mmol), triethyl orthoformate (6.42 g, 7.21 mL, 42.4 mmol), and ammonium chloride (0.454 g, 8.49 mmol) **5c** was obtained as a white powder (1.4 g, 3.5

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mmol, 83%), mp 161−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.07 (s, 1H, CH-Imd), 7.49 (dd, J_{HH} = 7.6, $^4J_{HH}$ = 1.6 Hz, 1H, Ar-H), 7.41 (t, J_{HH} = 7.8 Hz, 1H, Ar-H), 7.35 (td, J_{HH} = 7.7, $^4J_{HH}$ = 1.6 Hz, 1H, Ar-H), 7.22 (d, J_{HH} = 7.8 Hz, 2H, Ar-H), 7.19 (d, J_{HH} = 7.9 Hz, 1H, Ar-H), 7.12 (td, J_{HH} = 7.5, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-H), 5.42 (s, 2H, Ar-CH_2-N), 4.09−3.94 (m, 4H, N-CH_2-CH_2), 2.88 (hept, J_{HH} = 6.7 Hz, 2H, Ar-CH), 2.70 (s, 6H, N-CH_3), 1.32 (d, J_{HH} = 6.8 Hz, 6H, CH-CH_3), 1.24 (d, J_{HH} = 6.9 Hz, 6H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 153.6, 146.6, 131.1, 131.1, 130.2, 130.2, 127.6, 125.0, 124.6, 120.2, 53.2, 48.7, 48.1, 45.6, 29.0, 25.2, 24.4 ppm. IR (film from CH_2Cl_2): ν = 3390, 2959, 1641, 1498, 1452, 1263, 1214, 1102, 1055, 946, 818, 750, 475 cm^{-1}. Anal. Calcd for: $C_{24}H_{34}N_3Cl$: C, 72.06; H, 8.57; N, 10.51; Cl, 8.86. Found: C, 71.93; H, 8.54; N, 10.46; Cl, 8.71. HRMS (ESI): m/z calcd for $C_{24}H_{33}N_3$: $[M+H^+]$ 364.2747, found 364.2746.

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-(trifluoromethyl)benzyl)-4,5-dihydro-1H-imidazolinium Chloride (**5d**).* Following the general procedure, from N^1-(2,6-diisopropylphenyl)-N^2-(2-(trifluoromethyl)-benzyl)-1,2-diaminoethane (**4d**) (1.35 g, 3.57 mmol), triethyl orthoformate (5.39 g, 6.06 mL, 35.7 mmol), and ammonium chloride (0.382 g, 7.13 mmol), **5d** was obtained as a white powder (1.5 g, 3.53 mmol, 99%), mp 207−208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.96 (s, 1H, CH-Imd), 7.84 (d, J_{HH} = 7.6 Hz, 1H, Ar-H), 7.64 (d, J_{HH} = 7.8 Hz, 1H, Ar-H), 7.55 (t, J_{HH} = 7.6 Hz, 1H, Ar-H), 7.44 (t, J_{HH} = 7.7 Hz, 1H, Ar-H), 7.33 (t, J_{HH} = 7.8 Hz, 1H, Ar-H), 7.12 (d, J_{HH} = 7.8 Hz, 2H, Ar-H), 5.36 (s, 2H, Ar-CH_2-N), 4.17−3.89 (m, 4H, N-CH_2-CH_2), 2.77 (hept, J_{HH} = 6.5 Hz, 2H, Ar-CH), 1.18 (d, J_{HH} = 6.9 Hz, 6H, CH-CH_3), 1.15 (d, J_{HH} = 6.9 Hz, 6H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 146.3, 133.1, 132.4, 131.1, 131.1, 129.8, 129.5, 128.9 (q, $^2J_{CF}$ = 30.5 Hz), 126.5 (q, $^3J_{CF}$ = 5.6 Hz), 124.8, 124.0 (q, $^1J_{CF}$ = 273.9 Hz), 53.4, 48.6, 48.2, 28.7, 25.0, 23.9 ppm. IR (film from CH_2Cl_2): ν = 2966, 1632, 1459, 1313, 1260, 1235, 1167, 1114, 1058, 1038, 808, 770, 712, 652, 552, 484 cm^{-1}. Anal. Calcd for $C_{23}H_{28}N_2ClF_3{\cdot}0.5\ H_2O$: C, 63.66; H, 6.74. Found: C, 63.54; H, 6.71. HRMS (ESI): m/z calcd for $C_{23}H_{27}N_2F_3$: $[M+H^+]$ 389.2199, found 389.2211

*N^1-(2,6-Diisopropylphenyl)-N^2-(2-nitrobenzyl)-4,5-dihydro-1H-imidazolinium Chloride (**5e**).* Following the general procedure, from N^1-(2,6-diisopropylphenyl)-N^2-(2-nitrobenzyl)-1,2-diaminoethane (**4e**) (1.05 g, 2.95 mmol), triethyl orthoformate (4.47 g, 5.02 mL, 29.5 mmol), and ammonium chloride (0.316 g, 5.91 mmol), **5e** was obtained as a white powder (1.02 g, 2.54 mmol, 86%), mp 236−237 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.44 (s, 1H, CH-Imd), 8.36 (dd, J_{HH} = 7.7, $^4J_{HH}$ = 1.4 Hz, 1H, Ar-H), 8.08 (dd, J_{HH} = 8.2, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.76 (td, J_{HH} = 7.6, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-H), 7.61 (td, J_{HH} = 7.9, $^4J_{HH}$ = 1.4 Hz, 1H, Ar-H), 7.41 (t, J_{HH} = 7.8 Hz, 1H, Ar-H), 5.64 (s, 2H, Ar-CH_2-N), 4.36 (dd, J_{HH} = 12.4, 9.2 Hz, 2H, N-CH_2-CH_2), 4.12 (dd, J_{HH} = 12.5, 9.2 Hz, 2H, N-CH_2-CH_2), 2.86 (hept, J_{HH} = 6.8 Hz, 2H, Ar-CH), 1.27 (d, J_{HH} = 6.8 Hz, 6H, CH-CH_3), 1.23 (d, J_{HH} = 6.8 Hz, 6H, CH-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.6, 148.8, 146.7, 135.1, 134.7, 131.4, 130.8, 129.8, 128.1, 125.4, 125.1, 53.6, 49.1, 49.0, 28.9, 25.2, 24.3 ppm. IR (film from CH_2Cl_2): ν = 2967, 1627, 1527, 1456, 1347, 1259, 1215, 858, 796, 760, 708, 664, 483 cm^{-1}. Anal. Calcd for $C_{22}H_{28}ClN_3O_2$: C, 65.74; H, 7.02; N, 10.45; Cl, 8.82. Found: C, 65.52; H, 6.90; N, 10.42; Cl, 8.87. HRMS (ESI): m/z calcd for $C_{22}H_{27}N_3O_2$: $[M+H^+]$ 366.2176, found 366.2182.

General Procedure 1 for the Preparation of Hoveyda−Grubbs Precatalysts. In an oven-dried Schlenk vessel, the corresponding indenylidene precatalyst (1 equiv) was added at once to the vigorously stirring solution of 1-isopropoxy-2-(prop-1-enyl)-benzene (1.5−2 equiv) in toluene, and the reaction vessel was placed in a preheated (60 °C) oil bath under an atmosphere of argon. Next, CuCl (1.5 equiv) was added in two portions with 5 min interval. The progress of the reaction was monitored by TLC (cyclohexane/ethyl acetate, 4:1). After full consumption of indenylidene precatalyst (ca. 15 min), the reaction mixture was cooled to room temperature, and the solvent was evaporated. Purification by silica gel chromatography (cyclohexane/ethyl acetate 9:1, followed by cyclohexane/ethyl acetate 1:2) and further recrystallization from a DCM/MeOH mixture (1:5) yielded the product as a microcrystalline solid, which was dried *in vacuo*.

General Procedure 2 for the Preparation of Hoveyda−Grubbs Precatalysts. The corresponding imidazonium chloride (1.2 equiv) was dried in preheated Schlenk flask at 60 °C for 2 h under high vacum. After the sample cooled to room temperature, toluene was added under an argon atmosphere to obtain 0.02 M final carbene concentration. To this vigorously stirred suspension was added potassium *tert*-pentoxide (1.7 M in toluene, 1.2 equiv), and the solution was left until it become clear (usually 2 min). The Schlenk flask was placed in a preheated (65 °C) oil bath, and Hoveyda−Grubbs first-generation complex (1 equiv) was added at once. The progress of the reaction was monitored by TLC (cyclohexane/ethyl acetate 4:1). After full consumption of **Hov I** catalyst, the reaction mixture was cooled to room temperature, and the solvent was evaporated. Purification by silica gel chromatography (cyclohexane/ethyl acetate 9:1, followed by cyclohexane/ethyl acetate 1:2) and further recrystallization from a DCM/MeOH mixture (1:5) yielded the product as a microcrystalline solid, which was dried *in vacuo*.

*Synthesis of **Ru-1**.* Following general procedure 1, 1-isopropoxy-2-(prop-1-enyl)benzene (115 mg, 0.651 mmol), **Ind-1** (300 mg, 0.326 mmol), CuCl (50 mg, 0.5 mmol), and toluene (8 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-1** as a khaki-colored microcrystalline powder (140 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.24 (s, 1H, Ru=CH), 7.72 (d, J_{HH} = 6.8 Hz, 2H, Ar-H), 7.53−7.37 (m, 4H, Ar-H), 7.09 (s, 2H, Mes-H), 6.97−6.93 (m, 3H, Ar-H), 5.64 (s, 2H, Ar-CH_2-N), 5.18 (sept, J_{HH} = 6.0 Hz, 1H, O-CH), 3.94−3.89 (m, 2H, N-CH_2-CH_2), 3.66−3.62 (m, 2H, N-CH_2-CH_2), 2.47 (s, 3H, Ar-CH_3), 2.28 (s, 6H, Ar-CH_3), 1.75 (d, J_{HH} = 6.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 291.6, 209.9, 152.6, 144.1, 138.9, 138.2, 137.8, 136.2, 129.7, 129.4, 128.9, 128.4, 123.6, 122.7, 122.6, 112.9, 75.2, 56.1, 52.0, 47.9, 22.0, 21.3, 18.3 ppm. IR (KBr): ν = 2978, 2920, 1588, 1574, 1485, 1452, 1415, 1325, 1294, 1269, 1235, 1109, 1095, 1034, 934, 841, 750, 702 cm^{-1}. Anal. Calcd for $C_{29}H_{34}Cl_2N_2ORu$ (598.57): C, 58.19; H, 5.73; Cl, 11.85; N, 4.68; Found: C, 58.06; H, 5.80; Cl, 11.66; N, 4.48. HRMS (ESI): m/z calcd for $C_{29}H_{34}Cl_2N_2ORu$: $[M-Cl]^+$ 563.1408, found 563.1417.

*Synthesis of **Ru-2**.* Following general procedure 1, 1-isopropoxy-2-(prop-1-enyl)benzene (97.6 mg, 0.522 mmol), **Ind-2** (350 mg, 0.368 mmol), CuCl (55.2 mg, 0.552 mmol), and toluene (10 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-2** as a green microcrystalline powder (144 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.32 (s, 1H, Ru=CH), 7.94 (d, J_{HH} = 8.0 Hz, 1H, Ar-H), 7.53−7.48 (m, 1H, Ar-H), 7.37−7.33 (m, 1H, Ar-H), 7.08−7.05 (m, 3H, Ar-H), 6.97−6.92 (m, 4H, Ar-H), 5.71 (s, 2H, Ar-CH_2-N), 5.18 (sept, 1H, J_{HH} = 6.0, O-CH), 3.92−3.87 (m, 2H, N-CH_2-CH_2), 3.90 (s, 3H), 3.75−3.70 (m, 2H, N-CH_2-CH_2), 2.46 (s, 3H, Ar-CH_3), 2.27 (s, 6H, Ar-CH_3), 1.76(d, J_{HH} = 6.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = C 292.4, 209.1, 157.8, 152.5, 144.1, 138.8, 138.2, 129.6, 129.5, 129.4, 122.6, 122.5, 121.2, 112.9, 110.5, 75.1, 55.5, 51.9, 49.0, 47.9, 22.1, 21.3, 18.3 ppm. IR (KBr): ν = 2927, 1589, 1573, 1493, 1483, 1438, 1412, 1384, 1293, 1268, 1245, 1219, 1161, 1114, 1023, 935, 843, 794, 754 cm^{-1}. Anal. Calcd for $C_{30}H_{36}Cl_2N_2O_2Ru$: C, 57.32; H, 5.77; Cl, 11.28; N, 4.46; Found: C, 57.12; H, 5.80; Cl, 11.07; N, 4.28. HRMS (ESI): m/z calcd for $C_{30}H_{36}Cl_2N_2O_2Ru$: $[M-Cl]^+$ 593.1514, found 593.1504.

*Synthesis of **Ru-3**.* Following general procedure 1, 1-isopropoxy-2-(prop-1-enyl)benzene (84.1 mg, 0.477 mmol), **Ind-3** (230 mg, 0.239 mmol), CuCl (35.8 mg, 0.358 mmol), and toluene (5 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-3** as a deep-green microcrystalline solid (114 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.30 (s, 1H, Ru=CH), 7.90 (d, J_{HH} = 8.0 Hz, 1H), 7.53−7.48 (m, 1H), 7.34−3.30 (m, 1H, Ar-H), 7.20−7.16 (m, 2H, Ar-H), 7.10 (s, 2H, Mes-H), 7.95−6.90 (m, 3H, Ar-H), 5.78 (s, 2H, Ar-CH_2-N), 5.16 (sept, J_{HH} = 6.0 Hz, 1H, O-CH), 3.96−3.91 (m, 2H, N-CH_2-CH_2), 3.69−3.64 (m, 2H, N-CH_2-CH_2), 2.78 (s, 6H), 2.48 (s, 3H, Ar-CH_3), 2.30 (s, 6H, Ar-CH_3), 1.75 (d, J_{HH} = 6.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 291.4, 209.7, 153.2, 152.6, 144.1, 138.9, 138.2, 137.8, 129.9, 129.7, 129.5, 128.4, 123.6, 122.7, 122.6, 119.0, 113.0, 75.0, 52.0, 50.8, 48.0, 45.2, 22.0, 21.4, 18.3

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ppm. IR (KBr): ν = 3027, 2982, 2916, 2835, 1587, 1573, 1488, 1471, 1450, 1380, 1327, 1310, 1291, 1274, 1236, 1214, 1154, 1110, 1094, 934, 763, 753 cm^{-1}. Anal. Calcd for $C_{31}H_{39}Cl_2N_3ORu$: C, 58.03; H, 6.13; Cl, 11.05; N, 6.55. Found: C, 58.04; H, 6.23; Cl, 10.81; N, 6.39. HRMS (ESI): m/z calcd. for $C_{31}H_{39}Cl_2N_3ORu$: $[M\text{-}Cl]^+$ 605.1752, found 605.1743.

Synthesis of ***Ru-4***. Following general procedure 2, N^1-(2,6-diisopropylphenyl)-N^2-benzyl-4,5-dihydro-1*H*-imidazolinium chloride (**5a**) (138 mg, 0.388 mmol), **Hov I** (194 mg, 0.323 mmol), potassium *tert*-pentoxide solution (196 mg, 0,245 mL, 0.388 mmol), and toluene (10 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-4**, as a deep-green microcrystalline solid (159 mg, 0.248 mmol, 77%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 16.21 (s, 1H, Ru=C<u>H</u>), 7.77−7.71 (m, 2H, Ar-<u>H</u>), 7.63 (t, J_{HH} = 7.7 Hz, 1H, Ar-<u>H</u>), 7.55 (ddd, J_{HH} = 8.3, 7.0, $^4J_{HH}$ = 2.0 Hz, 1H, Ar-<u>H</u>), 7.51−7.44 (m, 2H, Ar-<u>H</u>), 7.44−7.36 (m, 3H, Ar-<u>H</u>), 5.64 (s, 2H, Ar-C<u>H</u>$_2$-N), 5.16 (hept, J_{HH} = 6.1 Hz, 1H, O-C<u>H</u>), 3.97−3.86 (m, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.71−3.59 (m, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.16 (hept, J_{HH} = 6.8 Hz, 2H, Ar-C<u>H</u>), 1.73 (d, J_{HH} = 6.2 Hz, 6H), 1.22 (d, J_{HH} = 6.9 Hz, 6H), 0.87 (d, J_{HH} = 6.7 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 290.0, 289.9, 211.2, 153.6, 149.5, 144.2, 138.4, 137.3, 130.6, 130.3, 130.1, 129.6, 129.1, 125.8, 123.3, 122.8, 113.8, 75.9, 56.8, 55.8, 48.2, 28.3, 25.8, 24.0, 22.4 ppm. IR (film from CH_2Cl_2): ν = 2966, 1571, 1441, 1382, 1270, 1218, 1109, 932, 806, 753, 704, 642, 463 cm^{-1}. Anal. Calcd for $C_{32}H_{40}Cl_2N_2ORu$: C, 59.99; H, 6.29; N, 4.37; Cl, 11.07. Found: C, 59.98; H, 6.54; N, 4.41; Cl, 11.03. HRMS (ESI): m/z calcd. for $C_{32}H_{39}N_2OClRu$: $[M + H]^+$ 605.1873, found 605.1859.

Synthesis of ***Ru-5***. Following general procedure 2, N^1-(2,6-diisopropylphenyl)-N^2-(2-methoxybenzyl)-4,5-dihydro-1*H*-imidazolinium chloride (**5b**) (111 mg, 0.286 mmol), **Hov I** (143 mg, 0.239 mmol), potassium *tert*-pentoxide solution (135 mg, 0.168 mL, 0.286 mmol), and toluene (14 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-5** as a green microcrystalline solid (90 mg, 0.134 mmol, 56%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 16.12 (s, 1H, Ru=C<u>H</u>), 8.20 (d, J_{HH} = 7.8 Hz, 1H, Ar-<u>H</u>), 7.81−7.70 (m, 2H, Ar-<u>H</u>), 7.70−7.61 (m, 1H, Ar-<u>H</u>), 7.59−7.48 (m, 2H, Ar-<u>H</u>), 7.43 (dd, J_{HH} = 7.8, $^4J_{HH}$ = 2.3 Hz, 2H, Ar-<u>H</u>), 7.00 (d, J_{HH} = 8.5 Hz, 1H, Ar-<u>H</u>), 6.97−6.86 (m, 2H, Ar-<u>H</u>), 5.83 (s, 2H, Ar-C<u>H</u>$_2$-N), 5.16 (hept, J_{HH} = 6.1 Hz, 1H, O-C<u>H</u>), 4.02−3.92 (m, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.78−3.68 (m, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.20 (hept, J_{HH} = 6.0 Hz, 2H, Ar-C<u>H</u>), 1.71 (d, J_{HH} = 6.2 Hz, 4H), 1.26 (d, J_{HH} = 7.1 Hz, 4H), 0.90 (d, J_{HH} = 6.6 Hz, 4H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 288.8, 209.9, 158.4, 153.1, 149.1, 143.8, 138.1, 131.3, 130.1, 129.8, 125.3, 124.8, 123.0, 122.4, 121.3, 113.4, 111.0, 75.8, 56.0, 55.7, 54.0, 49.9, 48.3, 28.4, 26.0, 24.1, 22.5 ppm. IR (film from CH_2Cl_2): ν = 2964, 1588, 1420, 1291, 1250, 1215, 1114, 1052, 935, 752, 639, 581 cm^{-1}. Anal. Calcd for $C_{33}H_{42}Cl_2N_2O_2Ru$: C, 59.10; H, 6.31; N, 4.18; Cl, 10.57. Found: C, 59.08; H, 6.12; N, 4.15; Cl, 10.39. HRMS (ESI): m/z calcd for $C_{33}H_{41}ClN_2O_2Ru$: $[M + H]^+$ 635.1979, found 635.1977.

Synthesis of ***Ru-6***. Following general procedure 2, N^1-(2,6-diisopropylphenyl)-N^2-(2-(dimethylamino)benzyl)-4,5-dihydro-1*H*-imidazolinium chloride (**5c**) (166 mg, 0.415 mmol), **Hov I** (208 mg, 0.346 mmol), potassium *tert*-pentoxide solution (195 mg, 0.244 mL, 0.415 mmol), and toluene (18 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-6** as a dark-green microcrystalline solid (180 mg, 0.263 mmol, 56%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 16.22 (s, 1H, Ru=C<u>H</u>), 7.86 (dd, J_{HH} = 7.6, $^4J_{HH}$ = 1.7 Hz, 1H, Ar-<u>H</u>), 7.64 (t, J_{HH} = 7.7 Hz, 1H, Ar-<u>H</u>), 7.54 (ddd, J_{HH} = 8.7, 6.5, $^4J_{HH}$ = 2.5 Hz, 1H, Ar-<u>H</u>), 7.43 (s, 1H, Ar-<u>H</u>), 7.41 (s, 1H, Ar-<u>H</u>), 7.37−7.31 (m, 1H, Ar-<u>H</u>), 7.27−7.16 (m, 2H, Ar-<u>H</u>), 6.99 (d, J_{HH} = 8.3 Hz, 1H, Ar-<u>H</u>), 6.96−6.87 (m, 2H, Ar-<u>H</u>), 5.76 (s, 2H, Ar-C<u>H</u>$_2$-N), 5.15 (hept, J_{HH} = 6.1 Hz, 1H, O-C<u>H</u>), 3.94 (dd, J_{HH} = 11.0, 8.3 Hz, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.67 (dd, J_{HH} = 10.9, 8.2 Hz, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.21 (hept, J_{HH} = 6.8 Hz, 2H, Ar-C<u>H</u>), 2.80 (s, 6H), 1.72 (d, J_{HH} = 6.2 Hz, 6H), 1.25 (d, J_{HH} = 6.9 Hz, 6H), 0.90 (d, J_{HH} = 6.7 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 288.5, 288.4, 210.5, 153.9, 153.1, 149.1, 143.8, 138.1, 130.6, 130.2, 130.1, 129.8, 128.83, 125.4, 123.8, 123.0, 122.4, 119.6, 113.5, 75.7, 55.8, 51.7, 48.3, 45.4, 28.6, 25.9, 24.2, 22.5 ppm. IR (film from CH_2Cl_2): ν = 2965, 1589, 1418, 1381, 1268, 1112, 1050, 934, 842, 809, 764, 741, 642, 578 cm^{-1}. Anal. Calcd for $C_{34}H_{45}Cl_2N_3ORu$: C, 59.73; H, 6.63; N, 6.15; Cl, 10.37. Found: C, 59.60; H, 6.53; N, 6.17; Cl, 10.44. HRMS (ESI): m/z calcd for $C_{34}H_{43}N_3ORu$: $[M+2H]^{2+}$ 306.6302, found 306.6291.

Synthesis of ***Ru-7***. Following general procedure 2, N^1-(2,6-Diisopropylphenyl)-N^2-(2-(trifluoromethyl)benzyl)-4,5-dihydro-1*H*-imidazolinium chloride (**5d**) (170 mg, 0.4 mmol), **Hov I** (200 mg, 0.333 mmol), potassium *tert*-pentoxide solution (202 mg, 0.252 mL, 0.4 mmol), and toluene (20 mL) were used. Purification by the general procedure (*vide supra*) yielded the product **Ru-7** as a green microcrystalline solid (128 mg, 0.181 mmol, 54%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 16.12 (s, 1H, Ru = C<u>H</u>), 8.20 (d, J_{HH} = 7.8 Hz, 1H, Ar-<u>H</u>), 7.78 (d, J_{HH} = 7.8 Hz, 1H, Ar-<u>H</u>), 7.73 (t, J_{HH} = 7.7 Hz, 1H, Ar-<u>H</u>), 7.65 (t, J_{HH} = 7.8 Hz, 1H, Ar-<u>H</u>), 7.53 (q, J_{HH} = 8.2 Hz, 2H, Ar-<u>H</u>), 7.44 (d, J_{HH} = 7.8 Hz, 2H, Ar-<u>H</u>), 7.00 (d, J_{HH} = 8.4 Hz, 1H, Ar-<u>H</u>), 6.97−6.86 (m, 2H, Ar-<u>H</u>), 5.83 (s, 2H, Ar-C<u>H</u>$_2$-N), 5.16 (hept, J_{HH} = 6.9 Hz, 1H, O-C<u>H</u>), 4.03−3.92 (m, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.77−3.66 (m, 2H, N-C<u>H</u>$_2$-CH$_2$), 3.20 (hept, J_{HH} = 6.7 Hz, 2H, Ar-C<u>H</u>), 1.71 (d, J_{HH} = 6.2 Hz, 3H), 1.26 (d, J_{HH} = 7.0 Hz, 3H), 0.90 (d, J_{HH} = 6.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 288.4, 212.3, 153.2, 148.9, 143.7, 137.8, 135.6, 132.9, 131.0, 130.3, 130.0, 128.9 (q, $^2J_{CF}$ = 30.3 Hz), 128.5, 126.3 (q, $^3J_{CF}$ = 5.8 Hz), 125.4, 125.1(q, $^1J_{CF}$ = 273.7 Hz), 123.0, 122.5, 113.4, 75.9, 56.0, 52.3 (q, $^4J_{CF}$ = 3.0 Hz), 48.5, 28.5, 25.9, 24.1, 22.4 ppm. IR (film from CH_2Cl_2): ν = 2962, 1590, 1450, 1386, 1310, 1224, 1153, 1113, 1057, 1037, 939, 843, 795, 751, 645, 574 cm^{-1}. Anal. Calcd for $C_{33}H_{39}Cl_2N_2F_3ORu$: C, 55.93; H, 5.55; N, 3.95; Cl, 10.00; F, 8.04. Found: C, 55.85; H, 5.56; N, 3.95; Cl, 9.83; F, 8.20. HRMS (ESI): m/z calcd for $C_{33}H_{37}F_3N_2ORu$: $[M+2H]^{2+}$ 319.1028, found 319.1018.

Synthesis of ***Ru-8***. Following general procedure 2, N^1-(2,6-diisopropylphenyl)-N^2-(2-nitrobenzyl)-4,5-dihydro-1*H*-imidazolinium chloride (**5e**) (120 mg, 0.3 mmol), **Hov I** (150 mg, 0.25 mmol), potassium *tert*-pentoxide solution (151 mg, 0.189 mL, 0.3 mmol), and toluene (18 mL) were used. Product **Ru-8** was not obtained (0 mg, 0%).

Procedure for the Thermal Stability Studies. Solutions of Hoveyda-type precatalysts **Ru-1**-**Ru-7**, **Hov II** (SIMes), and **Hov II′** (SIPr) (12.8 μmol) in toluene (0.6 mL) and a solution of 1,3,5-trimethoxybenzene (internal standard, 12.8 μmol, 2.15 mg) in toluene (0.1 mL) were placed in NMR tubes in the air, and the samples were equilibrated at 50 °C. ^{1}H NMR spectra were measured after appropriate time intervals, and the rate of the precatalyst's decomposition was monitored by the integration of protons of the internal standard at δ = 6.07 (s, 3H) and the characteristic Ru=CH with chemical shifts around 16 ppm.

RCM of Diethyl Diallylmalonate (DEDAM) (6). Stock solution of DEDAM was prepared in the following manner: **6** (140 mg, 0.583 mmol) was weighed into a volumetric flask (5 mL). The flask was then filled with dry, degassed toluene. Next, the flask was closed with a rubber septum and shaken to homogenize the stock solution. This stock solution (600 μL) was introduced to an NMR tube equipped with a septum. The sample was equilibrated at 50 °C in the NMR probe.

Stock solution of precatalyst was prepared in the following manner: precatalyst (3.5 μmol) was weighed into a volumetric flask (1 mL). The flask was then closed with a rubber septum, and dry, degassed toluene (1 mL) was injected. An aliquot of the precatalyst (100 μL, 0.7 μmol) was taken from the stock solution and injected through the septum into a solution of substrate in an NMR tube. Data points were collected over an appropriate period of time, using the Varian array function. The yield of **7** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ = 2.67 (s), with those in the product, δ = 2.98 (s). Yield was calculated according to the following equation: yield (%) = ([P] × 100%)/([P] + [S]).

RCM of *N*-Allyl-4-methyl-*N*-(2-methylallyl)-benzenesulfonamide (8). Stock solutions of substrate **8** and corresponding complexes were prepared analogously to the procedure reported for DEDAM (**6**). Dry, degassed, nondeuterated toluene was used as a solvent, and the reactions were carried out at 50 °C. Data points were

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collected over an appropriate period of time, using the Varian array function. The yield of **9** was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ = 1.70 (s) with those in the product, δ = 1.29 (s). Yield was calculated according to the equation given in the previous section.

General Procedure for Ene-Yne Metathesis of 14. To the substrate **14** (200 mg, 0.805 mmol) in DCM (HPLC grade, 7 mL) was added a solution of precatalyst (2 mol%) in DCM (HPLC grade, 1 mL). The resulting mixture was stirred at 50 °C. Aliquots (25 μL) were taken every 30 min and added to the solution of ethyl vinyl ether in DCM (3 M, 300 μL). The samples were shaken, allowed to stand for 5 min, and then analyzed by GC. After completion of the reaction, the solvent was evaporated, and the crude product was purified via column chromatography (cyclohexane/ethyl acetate 39:1) to yield **15**. ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[25]

General Procedure for RCM of 10. To the substrate **10** (196 mg, 0.666 mmol) in toluene (HPLC grade, 5.6 mL) was added a solution of precatalyst (1 mol%) in toluene (HPLC grade, 1 mL). The resulting mixture was stirred at 50 °C. Aliquots (25 μL) were taken every 30 min and added to the solution of ethyl vinyl ether in toluene (3 M, 300 μL). The samples were shaken, allowed to stand for 5 min, and then analyzed by GC. After completion of the reaction, the solvent was evaporated, and the crude product was purified via column chromatography (cyclohexane/ethyl acetate 1:1) to yield **11** as a brownish oil. ^{1}H NMR spectra are in agreement with those previously reported.[26]

General Procedure for RCM of 12. To the substrate **12** (131 mg, 0.666 mmol) in toluene (HPLC grade, 5.6 mL) was added a solution of the corresponding precatalyst (0.5 mol%) in toluene (HPLC grade, 1 mL). The resulting mixture was stirred at 50 °C. Aliquots (25 μL) were taken every 15 min and added to the solution of ethyl vinyl ether in toluene (3M, 300 μL). The samples were shaken, allowed to stand for 5 min, and then analyzed by GC. After completion of the reaction, the solvent was evaporated, and the crude product was purified via column chromatography (cyclohexane/ethyl acetate 1:1) to yielded **13** as a colorless oil. ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[27]

General Procedure for CM of 16 with 17. To the substrate **16** (100 mg, 0.829 mmol) and *cis*-1,4-diacetoxy-2-butene (**17**) (286 mg, 1.66 mmol) in DCM (HPLC grade, 7 mL) was added a solution of the precatalyst (2.5 mol%) in DCM (HPLC grade, 1 mL). The resulting mixture was stirred at 50 °C for 20 h. Next, the solvent was evaporated, and the crude product was purified via column chromatography (cyclohexane/ethyl acetate 9:1) to yield **18** as a colorless oil. ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[28]

General Procedure for the DRRM Experiments. The substrate **19** (3.53 mg, 0.014 mmol) in $CDCl_3$ (0.1 mL) and durene (0.938 mg, 6.99 μmol) in $CDCl_3$ (0.5 mL) were injected into an NMR tube through the rubber septum under an atmosphere of argon. The tube was then placed inside an ice cooling bath, and the solution was saturated with ethylene. After the solution warmed to room temperature, a solution of precatalyst (5 mol%) in $CDCl_3$ (0.1 mL) was added. After 10 h, the ratio of *E*/*Z* isomers in the products **20**/**21** was measured by GC. ^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[16]

*Self-Metathesis of 1-Octene (**22**).* To a solution of 1-octene (1.5 mL, 9.4 mmol) in tetradecane (0.5 mL, 1.9 mmol) as internal standard, precatalyst (500 ppm) was added. The resulting mixture was stirred at 80 °C under an argon atmosphere. Samples were taken at appropriate time intervals and quenched with SnatchCat solution (35 μmol, 1 mL). Conversion and selectivity were determined by GC measurement.

*Preparative Self-Metathesis of 1-Octene (**22**).* To a solution of 1-octene (5.59 mL, 34.9 mmol) was added **Ru-4** (11.2 mg, 500 ppm). The resulting mixture was stirred for 10 min at 80 °C under an argon atmosphere. SnatchCat solution (87.3 μmol, 2 mL) was then added. The reaction mixture was purified by distillation under reduced pressure using a Kugelrohr apparatus to provide product **23** in 65% yield (purity 99%) as a mixture of *E*/*Z* isomers (81:19 base on GC analysis).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00211.

NMR spectra of diamines, their hydrochlorides (when obtained), NHCs, and Ru complexes; crystallographic data and selected bond lengths and angles of [**Ru**]-**1**, [**Ru**]-**2**, [**Ru**]-**3**, and [**Ru**]-**4**(PDF)

Accession Codes

CCDC 1539095−1539098 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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■ REFERENCES

(1) *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Springer: Dordrecht, 2011; Vol. *32*, pp 1−336.

(2) (a) Gomez-Suarez, A.; Nelson, D. J.; Nolan, S. P. Quantifying and understanding the steric properties of N-heterocyclic carbenes. *Chem. Commun.* **2017**, *53* (18), 2650−2660. (b) Teng, Q.; Huynh, H. V. A unified ligand electronic parameter based on 13C NMR spectroscopy of N-heterocyclic carbene complexes. *Dalton Trans.* **2017**, *46* (3), 614−627.

(3) (a) Marion, N.; Díez-González, S.; Nolan, S. P. N-Heterocyclic Carbenes as Organocatalysts. *Angew. Chem., Int. Ed.* **2007**, *46* (17), 2988−3000. (b) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. Organocatalytic Reactions Enabled by N-Heterocyclic Carbenes. *Chem. Rev.* **2015**, *115* (17), 9307−9387.

(4) (a) Hamad, F. B.; Sun, T.; Xiao, S.; Verpoort, F. Olefin metathesis ruthenium catalysts bearing unsymmetrical heterocyclic carbenes. *Coord. Chem. Rev.* **2013**, *257* (15−16), 2274−2292. (b) Tornatzky, J.; Kannenberg, A.; Blechert, S. New catalysts with unsymmetrical N-heterocyclic carbene ligands. *Dalton Trans.* **2012**, *41* (27), 8215−8225. (c) Song, X.; Ni, Q.; Zhu, C.; Raabe, G.; Enders, D. Asymmetric N-Heterocyclic Carbene Catalyzed Annulation of 2-Alkenylbenzothiazoles with α-Chloro Aldehydes. *Synthesis* **2015**, *47* (03), 421−428. (d) Queval, P.; Jahier, C.; Rouen, M.; Artur, I.; Legeay,

DOI: 10.1021/acs.organomet.7b00211
Organometallics XXXX, XXX, XXX−XXX

J.-C.; Falivene, L.; Toupet, L.; Crévisy, C.; Cavallo, L.; Baslé, O.; Mauduit, M. Multicomponent Synthesis of Unsymmetrical Unsaturated N-Heterocyclic Carbene Precursors and Their Related Transition-Metal Complexes. *Angew. Chem., Int. Ed.* **2013**, *52* (52), 14103−14107.

(5) (a) Grela, K. *Olefin Metathesis: Theory and Practice*; John Wiley & Sons, Inc.: Hoboken, NJ, 2014. (b) Grubbs, R. H.; Wenzel, A. G.; O'Leary, D. J.; Khosravi, E. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2014.

(6) Higman, C. S.; Lummiss, J. A. M.; Fogg, D. E. Olefin Metathesis at the Dawn of Implementation in Pharmaceutical and Specialty-Chemicals Manufacturing. *Angew. Chem., Int. Ed.* **2016**, *55* (11), 3552−3565.

(7) (a) Occhipinti, G.; Hansen, F. R.; Törnroos, K. W.; Jensen, V. R. Simple and Highly Z-Selective Ruthenium-Based Olefin Metathesis Catalyst. *J. Am. Chem. Soc.* **2013**, *135* (9), 3331−3334. (b) Bronner, S. M.; Herbert, M. B.; Patel, P. R.; Marx, V. M.; Grubbs, R. H. Ru-based Z-selective metathesis catalysts with modified cyclometalated carbene ligands. *Chem. Sci.* **2014**, *5* (10), 4091−4098. (c) Nguyen, T. T.; Koh, M. J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. Kinetically controlled E-selective catalytic olefin metathesis. *Science* **2016**, *352* (6285), 569−575.

(8) (a) Nickel, A.; Ung, T.; Mkrtumyan, G.; Uy, J.; Lee, C.; Stoianova, D.; Papazian, J.; Wei, W.-H.; Mallari, A.; Schrodi, Y.; Pederson, R. A Highly Efficient Olefin Metathesis Process for the Synthesis of Terminal Alkenes from Fatty Acid Esters. *Top. Catal.* **2012**, *55* (7−10), 518−523. (b) Ohlmann, D. M.; Tschauder, N.; Stockis, J. P.; Goossen, K.; Dierker, M.; Goossen, L. J. Isomerizing olefin metathesis as a strategy to access defined distributions of unsaturated compounds from fatty acids. *J. Am. Chem. Soc.* **2012**, *134* (33), 13716−13729. (c) Miao, X.; Fischmeister, C.; Dixneuf, P. H.; Bruneau, C.; Dubois, J. L.; Couturier, J. L. Polyamide precursors from renewable 10-undecenenitrile and methyl acrylate via olefin cross-metathesis. *Green Chem.* **2012**, *14* (8), 2179−2183.

(9) Skowerski, K.; Białecki, J.; Czarnocki, S. J.; Żukowska, K.; Grela, K. Effective immobilisation of a metathesis catalyst bearing an ammonium-tagged NHC ligand on various solid supports. *Beilstein J. Org. Chem.* **2016**, *12*, 5−15.

(10) Kajetanowicz, A.; Czaban, J.; Krishnan, G. R.; Malińska, M.; Woźniak, K.; Siddique, H.; Peeva, L. G.; Livingston, A. G.; Grela, K. Batchwise and Continuous Nanofiltration of POSS-Tagged Grubbs−Hoveyda-Type Olefin Metathesis Catalysts. *ChemSusChem* **2013**, *6* (1), 182−192.

(11) (a) Ablialimov, O.; Kędziorek, M.; Malińska, M.; Woźniak, K.; Grela, K. Synthesis, Structure, and Catalytic Activity of New Ruthenium(II) Indenylidene Complexes Bearing Unsymmetrical N-Heterocyclic Carbenes. *Organometallics* **2014**, *33* (9), 2160−2171. (b) Smoleń, M.; Kośnik, W.; Loska, R.; Gajda, R.; Malińska, M.; Wożniak, K.; Grela, K. Synthesis and catalytic activity of ruthenium indenylidene complexes bearing unsymmetrical NHC containing a heteroaromatic moiety. *RSC Adv.* **2016**, *6* (80), 77013−77019.

(12) (a) Paradiso, V.; Bertolasi, V.; Costabile, C.; Grisi, F. Ruthenium olefin metathesis catalysts featuring unsymmetrical N-heterocyclic carbenes. *Dalton Trans.* **2016**, *45* (2), 561−571. (b) Kannenberg, A.; Rost, D.; Eibauer, S.; Tiede, S.; Blechert, S. A Novel Ligand for the Enantioselective Ruthenium-Catalyzed Olefin Metathesis. *Angew. Chem., Int. Ed.* **2011**, *50* (14), 3299−3302. (c) Tiede, S.; Berger, A.; Schlesiger, D.; Rost, D.; Lühl, A.; Blechert, S. Highly Active Chiral Ruthenium-Based Metathesis Catalysts through a Monosubstitution in the N-Heterocyclic Carbene. *Angew. Chem., Int. Ed.* **2010**, *49* (23), 3972−3975. (d) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. Improved Ruthenium Catalysts for Z-Selective Olefin Metathesis. *J. Am. Chem. Soc.* **2012**, *134* (1), 693−699. (e) Van Veldhuizen, J. J.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. Chiral Ru-Based Complexes for Asymmetric Olefin Metathesis: Enhancement of Catalyst Activity through Steric and Electronic Modifications. *J. Am. Chem. Soc.* **2003**, *125* (41), 12502−12508. (f) Thomas, R. M.; Keitz, B. K.; Champagne, T. M.; Grubbs, R. H. Highly Selective Ruthenium Metathesis Catalysts for Ethenolysis. *J. Am. Chem. Soc.* **2011**, *133* (19), 7490−7496. (g) Malinowska, M.; Kozlowska, M.; Hryniewicka, A.; Witkowski, S.; Morzycki, J. W. New indenylidene-type metathesis catalysts bearing unsymmetrical N-heterocyclic ligands with mesityl and nitrobenzyl substituents. *Monatsh. Chem.* **2016**, *147*, 1091−1100. (h) Rouen, M.; Borre, E.; Falivene, L.; Toupet, L.; Berthod, M.; Cavallo, L.; Olivier-Bourbigou, H.; Mauduit, M. Cycloalkyl-based unsymmetrical unsaturated (U2)-NHC ligands: flexibility and dissymmetry in ruthenium-catalysed olefin metathesis. *Dalton Trans.* **2014**, *43* (19), 7044−7049. (i) Rouen, M.; Queval, P.; Borré, E.; Falivene, L.; Poater, A.; Berthod, M.; Hugues, F.; Cavallo, L.; Baslé, O.; Olivier-Bourbigou, H.; Mauduit, M. Selective Metathesis of α-Olefins from Bio-Sourced Fischer−Tropsch Feeds. *ACS Catal.* **2016**, *6* (11), 7970−7976.

(13) (a) Keitz, B. K.; Grubbs, R. H. Probing the Origin of Degenerate Metathesis Selectivity via Characterization and Dynamics of Ruthenacyclobutanes Containing Variable NHCs. *J. Am. Chem. Soc.* **2011**, *133* (40), 16277−16284. (b) Stewart, I. C.; Keitz, B. K.; Kuhn, K. M.; Thomas, R. M.; Grubbs, R. H. Nonproductive Events in Ring-Closing Metathesis Using Ruthenium Catalysts. *J. Am. Chem. Soc.* **2010**, *132* (25), 8534−8535.

(14) (a) Anderson, D. R.; Lavallo, V.; O'Leary, D. J.; Bertrand, G.; Grubbs, R. H. Synthesis and Reactivity of Olefin Metathesis Catalysts Bearing Cyclic (Alkyl) (Amino)Carbenes. *Angew. Chem., Int. Ed.* **2007**, *46* (38), 7262−7265. (b) Gawin, R.; Kozakiewicz, A.; Guńka, P. A.; Dąbrowski, P.; Skowerski, K. Bis(Cyclic Alkyl Amino Carbene) Ruthenium Complexes: A Versatile, Highly Efficient Tool for Olefin Metathesis. *Angew. Chem., Int. Ed.* **2017**, *56* (4), 981−986.

(15) Ablialimov, O.; Kędziorek, M.; Torborg, C.; Malińska, M.; Woźniak, K.; Grela, K. New Ruthenium(II) Indenylidene Complexes Bearing Unsymmetrical N-Heterocyclic Carbenes. *Organometallics* **2012**, *31* (21), 7316−7319.

(16) Böhrsch, V.; Neidhöfer, J.; Blechert, S. Diastereoselective Ring-Rearrangement Metathesis. *Angew. Chem., Int. Ed.* **2006**, *45* (8), 1302−1305.

(17) Vehlow, K.; Gessler, S.; Blechert, S. Deactivation of Ruthenium Olefin Metathesis Catalysts through Intramolecular Carbene−Arene Bond Formation. *Angew. Chem., Int. Ed.* **2007**, *46* (42), 8082−8085.

(18) Yi, C. S.; Lee, D. W. Homogeneous Hydrogenation of Alkenes Catalyzed by the Ruthenium−Hydride Complex (PCy3)2(CO)(Cl)RuH: Spectroscopic Observation of the Ruthenium−Ethyl and Ruthenium−Ethylene−Hydride Intermediate Species. *Organometallics* **1999**, *18* (24), 5152−5156.

(19) (a) Arisawa, M.; Terada, Y.; Takahashi, K.; Nakagawa, M.; Nishida, A. Development of isomerization and cycloisomerization with use of a ruthenium hydride with N-heterocyclic carbene and its application to the synthesis of heterocycles. *J. Org. Chem.* **2006**, *71* (11), 4255−4261. (b) Beach, N. J.; Dharmasena, U. L.; Drouin, S. D.; Fogg, D. E. Improved Syntheses of Versatile Ruthenium Hydrido-carbonyl Catalysts Containing Electron-Rich Ancillary Ligands. *Adv. Synth. Catal.* **2008**, *350* (5), 773−777.

(20) Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. Decomposition of ruthenium olefin metathesis catalysts. *J. Am. Chem. Soc.* **2007**, *129* (25), 7961−7968.

(21) Higman, C. S.; Plais, L.; Fogg, D. E. Isomerization During Olefin Metathesis: An Assessment of Potential Catalyst Culprits. *ChemCatChem* **2013**, *5* (12), 3548−3551.

(22) Jordaan, M.; van Helden, P.; van Sittert, C. G. C. E.; Vosloo, H. C. M. Experimental and DFT investigation of the 1-octene metathesis reaction mechanism with the Grubbs 1 precatalyst. *J. Mol. Catal. A: Chem.* **2006**, *254* (1−2), 145−154.

(23) (a) Hong, S. H.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. Prevention of undesirable isomerization during olefin metathesis. *J. Am. Chem. Soc.* **2005**, *127* (49), 17160−17161. (b) Czaban, J.; Schertzer, B. M.; Grela, K. Low Catalyst Loadings in Self-Metathesis of 1-Dodecene. *Adv. Synth. Catal.* **2013**, *355* (10), 1997−2006.

(24) Szczepaniak, G.; Urbaniak, K.; Wierzbicka, C.; Kosiński, K.; Skowerski, K.; Grela, K. High-Performance Isocyanide Scavengers for Use in Low-Waste Purification of Olefin Metathesis Products. *ChemSusChem* **2015**, *8* (24), 4099−4099.

DOI: 10.1021/acs.organomet.7b00211
Organometallics XXXX, XXX, XXX−XXX

(25) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. Comparative Investigation of Ruthenium-Based Metathesis Catalysts Bearing N-Heterocyclic Carbene (NHC) Ligands. *Chem. - Eur. J.* **2001**, *7* (15), 3236−3253.
(26) Skowerski, K.; Wierzbicka, C.; Szczepaniak, G.; Gulajski, L.; Bieniek, M.; Grela, K. Easily removable olefin metathesis catalysts. *Green Chem.* **2012**, *14* (12), 3264−3268.
(27) Butler, J. D.; Donald, M. B.; Ding, Z.; Fettinger, J. C.; Kurth, M. J. Phenylsulfonyl as a directing group for nitrile oxide cycloadditions and mCPBA epoxidations. *Tetrahedron Lett.* **2009**, *50* (36), 5110−5112.
(28) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. New Approaches to Olefin Cross-Metathesis. *J. Am. Chem. Soc.* **2000**, *122* (1), 58−71.

DOI: 10.1021/acs.organomet.7b00211
Organometallics XXXX, XXX, XXX−XXX