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N-Heterocyclic Carbene and Phosphine Ruthenium Indenylidene Precatalysts: A Comparative Study in Olefin Metathesis

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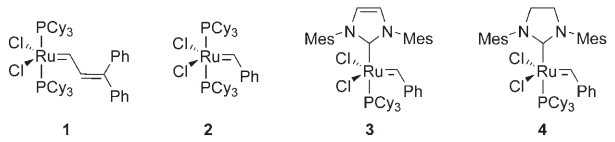
Abstract: Kinetic studies on ring-closing metathesis of unhindered and hindered substrates using phosphine and N-heterocyclic carbene (NHC)-containing ruthenium-indenylidene complexes (first and second generation precatalysts, respectively) have been carried out. These studies reveal an appealing difference, between the phosphine and NHC-containing catalysts, associated with a distinctive rate-determining step in the reaction mechanism. These catalysts have been compared with the benzylidene generation catalysts and their respective representative substrates. Finally, the reaction scope of the two most interesting precatalysts, complexes that contain tricyclohexylphosphine and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (SIMes), has been investigated for the ring-closing and enyne metathesis for a large range of olefins. Owing to their high thermal stability, the SIMes-based indenylidene complexes were more efficient than their benzylidene analogues in the ring-closing metathesis of tetrasubstituted dienes. Importantly, none of the indenylidene precatalysts were found to be the most efficient for all of the substrates, indeed, a complementary complex-to-substrate activity relationship was observed.

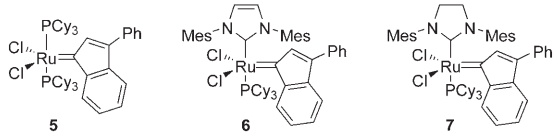
Keywords: indenylidenes · metathesis · N-heterocyclic carbenes · phosphanes · ruthenium

Introduction

Olefin metathesis represents one of the most useful and versatile tools in organic synthesis for the formation of carbon-carbon double bonds. This is owed to the numerous types of metathesis reaction that have been developed, for example, ring-closing metathesis (RCM), enyne metathesis, ring-opening polymerization metathesis, and cross metathesis.[1] The ground-breaking discovery of a well-defined ruthenium-carbene catalyst **1** by Grubbs in 1992[2] generalized their use, the properties of Grubbs' catalyst lead to higher compatibility with functional groups as well as an increased ease of handling.[3] Subsequently, the Grubbs first generation catalyst **2**[4] and a second generation of catalysts, **3**[5] and **4**,[6] containing N-heterocyclic carbene (NHC) ligands[7] were reported between 1995 and 1999. Since then, the Ru-benzylidene class of precatalysts **2**–**4** has been extensively used to develop even more efficient precatalysts such as the "boomerang" complexes of Hoveyda, Blechert and Grela.[8] Nevertheless, a thorough comparison between both catalyst generations in terms of activity and scope has not been reported and the relative usefulness of these generations in numerous applications is a question not yet satisfactorily answered. For example, Blechert[9] reported that phosphine-containing catalysts gave the highest turnover numbers with unhindered substrates, whereas recently, Grubbs[10] found that second generation catalysts performed better in the RCM of diethyldiallyl malonate. Generally, the NHC-containing complexes are considered as superior in terms of activity and stability.[11]



As an alternative to Ru-benzylidene precatalysts, Ru-3-phenylindenylidene complexes[12] such as **5**[13] and its IMes-containing analogue **6**[14] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been recently developed and **5**–**7** are now commercially available. These precatalysts were



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found to be more resistant, to harsh reaction conditions (temperature and functional group tolerance),[15] than their benzylidene counterparts. Nevertheless, their catalytic activities have been scarcely examined, especially the SIMes-containing complex **7** (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) for which no evaluation in catalysis has been reported so far.

Results and Discussion

Kinetic studies and mechanism: Historically, metathesis catalysts have been tested in metathesis transformations such as RCM, without significant optimization of reaction conditions (for instance high temperatures have been generally used). The report of high isolated yields is not satisfactory to determinate catalyst efficiency (this relationship is too often used). Moreover, in numerous instances, such studies do not report reaction conditions, often omitting catalyst loading and reaction time information. Consequently, a comprehensive and useful comparison between metathesis catalysts proves practically difficult or impossible.

To evaluate efficiently the activity of precatalysts **5–7** in RCM, several kinetic studies were carried out. We initiated our study with diethyl diallylmalonate **8** as a model substrate and performed room-temperature reactions with low precatalyst loadings (1 mol %), to slow the rate of RCM reaction to obtain an accurate measurement of conversion (Figure 1). Under these conditions, precatalyst **5** was found

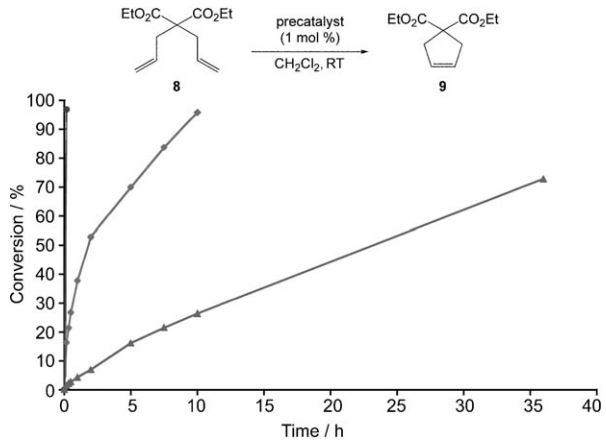


Figure 1. RCM of substrate **8** with precatalyst **5–7** (1 mol %) in CH_2Cl_2 at RT; (●, **5**), (▲, **6**) and (◆, **7**).

to be extremely efficient, only a few minutes were necessary to complete the reaction, whereas **6** and **7** showed slow and moderate reaction kinetics, respectively. Although the activities of **6** and **7** persisted over a few hours at a constant rate, 10 hours were required for **7** to reach a full conversion and a reaction with **6** over 36 hours led to only a 72% conversion.

In an attempt to establish if these catalysts behaved similarly for various substrates, we carried out similar studies with a more hindered substrate, diethyl allymethallylmalonate **10** (Figure 2). The reaction trend observed for substrate **10** with precatalysts **6** and **7** was similar to the trend ob-

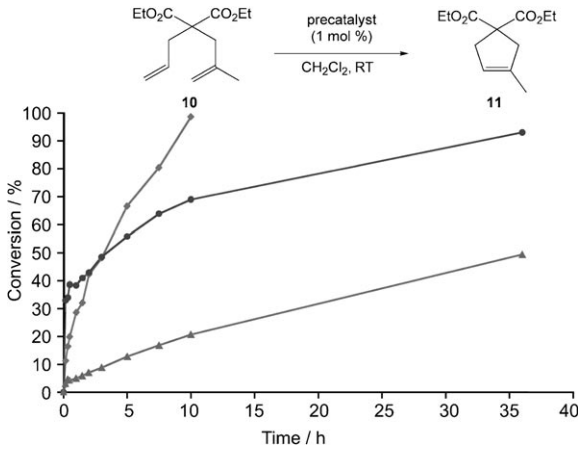


Figure 2. RCM of substrate **10** with precatalyst **5–7** (1 mol %) in CH_2Cl_2 at RT; (●, **5**), (▲, **6**) and (◆, **7**).

served for the previous substrate (diene **8**), a constant reaction rate was observed during the RCM. A 36 hour reaction time led to only ≈50% conversion with **6,** and in 10 hours full conversion was obtained with **7**. Whereas, the phosphine-containing precatalyst **5** led to a significantly different performance. Instead of 10 min for substrate **8**, 10 hours were necessary to complete the RCM for substrate **10**. Interestingly, after a fast initiation, the reaction rate decreased, this indicates a degree of degradation in the active species.

These kinetic studies performed on **8** and its trisubstituted analogue **10** have shown that the efficiency of **5** is closely related to the steric hindrance of the substrate. Whereas, the activities of the NHC-containing complexes were found to be comparable if used with substrates **8** and **10**. These observations suggest different rate-determining steps for each catalyst generation (Figure 3).[16] According to previous mechanistic studies,[17] ruthenium olefin metathesis catalysts involves 14 electron complexes **B** and **E**, which are the active species and their formation represents the rate-determining step of the reaction. The formation of **B**, by dissociation of a phosphine ligand from precatalyst **A**, precedes the olefin coordination and a first metathesis that leads to complex **C**. This activation step (formation of **B**) is not related to the nature of the substrate and corresponds to the limiting step for NHC-containing precatalysts. This explains why, for several substrates, a thermal activation of complexes **6** and **7** is required, whereas **5** reacted faster (vide supra). The formation of the metallacyclobutane **D**, and its conversion to **E** upon the extrusion of RCM product, is directly related to the steric hindrance of the substrate and constitute the limiting step for phosphine-containing precatalysts.

The significant difference in activity between IMes- and SIMes-containing precatalysts is still not clearly explained.

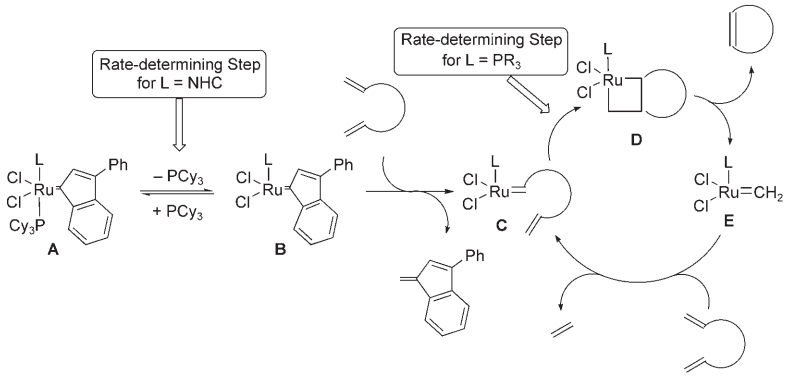


Figure 3. Proposed mechanism and rate-determining steps as a function of ligands.

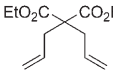
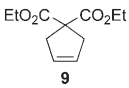
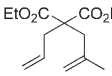
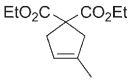
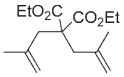
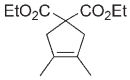
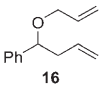
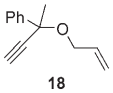
Recently, Jensen and co-workers attributed this gap to both electronic and steric effects but these results should be treated with due consideration, and are still not totally explained.[17d] The specific σ-donor and π-acceptor character of the NHCs are expected to have a large influence on the catalytic activity of the catalysts, in particular on the increased thermal stability of the 14-electron complexes. The steric influence of the ligand (L) in olefin metathesis transformations is still the subject of controversy, but the nonplanarity of the imidazole backbone of SIMes seems to be of major importance.[17d]

Catalyst comparison of representative substrates: Having established a significant difference in the catalytic activity of precatalysts **5**–**7**, we investigated the performance of these complexes on a wider range of substrates. The optimization of the reaction conditions has been considered, to obtain reasonable reaction times (no more than 10 h) depending of the catalyst loading. The reaction progress was monitored by using thin layer chromatography until completion, the product was isolated by using flash chromatography on silica-gel, and consequently characterized by spectroscopy. Notably, the reaction mixture was heated only if after 1 hour no product formation was observed. To establish a true comparison between the performance of **6** and **7**, identical reaction times were used for these precatalysts.

We compared benzylidene and indenylidene-based precatalysts using Grubbs first generation precatalyst **2** and complex **5** (Table 1). For each of the six substrates tested, no noteworthy difference in activity was observed between **2** and **5**. These precatalysts were found to perform the cyclization metathesis transformations of various substrates in a few hours at room temperature by using 2 mol % of precatalyst (Table 1, entries 1, 2, 4–6). Unfortunately, application of precatalysts **2** and **5** was ineffective for tetrasubstituted olefin **12** (entry 3). The considerable steric hindrance of the substrate requires an important thermal activation leading to the degradation of phosphine-containing active species. Both SIMes-containing precatalysts **4** and **7** showed comparable activities. Nevertheless, for the tetrasubstituted diene **12**, IMes and SIMes-containing benzylidene complexes **3** and **4** showed moderate activity (isolated yield, ≈50 %), whereas **7** yielded 85 % of cyclized product **13**. We attribute the improved activity of the indenylidene-based complexes to the higher thermal stability of these precatalysts.[14]

In comparing **6** and **7**, we obtained a better activity for the SIMes-containing precatalyst (**7**) for each of the six substrates. Interestingly, the difference in catalytic activity was found to be slightly lower if thermal activation was necessary (10–20 % for reactions performed at higher temperature instead of 30–40 % at room temperature). For most of these substrates, **5** was found more effective than the SIMes-containing **7**, especially for substrates **16** and **18**, as metatheses could not be carried out at room temperature using **7**. However, precatalyst **7** pro-

Table 1. Precatalysts comparison on model substrates.

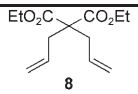
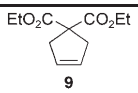
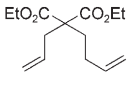
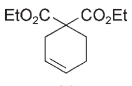
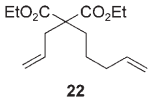
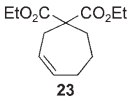
	Substrate	Product	Precatalyst (loading [mol %])[a]	T [°C][b]	t [h]	Isolated yield [%]
1	 **8**	 **9**	**2** (2)	25	0.25	100
			4 (2)	25	5	100
			5 (2)	25	0.25	98
			6 (2)	25	5	64
			7 (2)	25	5	95
2	 **10**	 **11**	**2** (2)	25	6	93
			4 (2)	25	5	96
			5 (2)	25	6	89
			6 (2)	25	5	59
			7 (2)	25	5	99
3	 **12**	 **13**	**2** (5)	80	5	<2
			3 (5)	80	5	47
			4 (5)	80	5	57
			5 (5)	80	5	<2
			6 (5)	80	5	67
			7 (5)	80	5	85
4	 **14**	 **15**	**2** (2)	25	6	87
			4 (2)	25	5	100
			5 (2)	25	6	89
			6 (2)	25	5	56
			7 (2)	25	5	99
5	 **16**	 **17**	**2** (2)	25	2	94
			4 (2)	40	5	95
			5 (2)	25	2	98
			6 (2)	40	5	82
			7 (2)	40	5	94
6	 **18**	 **19**	**2** (2)	25	5	93
			4 (2)	40	5	92
			5 (2)	25	5	89
			6 (2)	40	5	72
			7 (2)	40	5	99

[a] Reaction conditions: CH_2Cl_2, 0.1 M. [b] Reactions at 80 °C were performed in toluene.

duced a very attractive isolated yield of product **13**, which could not be obtained by using **2** and **5**. These observations led us to consider a wider range of substrates to clarify the scope of precatalysts **5** and **7**.

Evaluation of malonate-containing substrates: The study on malonate-based substrates was completed by the examination of the formation of various ring sizes (Table 2). In the case of unhindered dienes **20** and **22**, phosphine-containing **5** was found to be remarkably more active than **7**. Albeit, the ring extension from 5 to 6-membered did not induce a modification of the catalyst activity, the formation of 7-membered rings translated into a substantial increase in the required reaction time for both precatalysts, **5** remaining the more efficient.

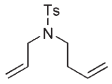
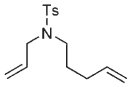
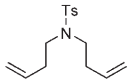
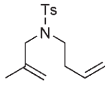
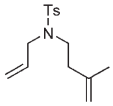
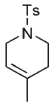
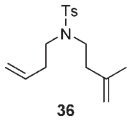
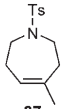
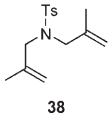
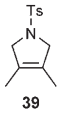
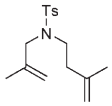
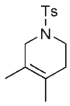
Table 2. Compared activities in RCM on malonate-based substrates.

	Substrate	Product	Precatalyst[a]	*t* [h]	Isolated yield [%]
1	 **8**	 **9**	**5**	0.25	98
			7	5	95
2	 **20**	 **21**	**5**	0.25	100
			7	5	100
3	 **22**	 **23**	**5**	1	93
			7	8	91

[a] Reaction conditions: CH_2Cl_2, 0.1 M, 25 °C, 2 mol % of precatalyst.

Evaluation of tosylamine-containing substrates: As tosylamine-based olefins have been often used as a benchmark for metathesis precatalysts, we closely examined this substrate category (Table 3). In a manner similar to their malonate counterparts, the formation of 7-membered ring products **29** and **31** required longer reaction times than for the smaller rings (Table 3, entries 1–4). The phosphine-containing precatalyst **5** was found to be the most active precatalyst. For trisubstituted olefins **14**, **32**, **34** and **36**, both generations of precatalysts showed comparable activities (Table 3, entries 5–8). For NHC-containing complex **7**, no difference in catalytic performance was observed between application to di- or trisubstituted olefins. For precatalyst **5** the increase in steric hindrance of these di- and trisubstituted olefins requires an increase in reaction time. Despite a 5 % catalyst loading, cyclization of tetrasubstituted olefin **38** by using precatalyst **5** was not observed, even at elevated or moderate temperatures (40 °C; to avoid a quick thermal degradation of the catalytic species, Table 3, entry 9). In contrast, precatalyst **7** was able to catalyze this cyclization at 40 °C and at 80 °C, to produce moderate to quantitative yields. Moreover, by using only 2 mol % of **7**, product **39** was isolated in a respectable yield. Similar results were obtained for the formation of a 6-membered ring in **41** (Table 3, entry 10).

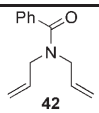
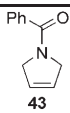
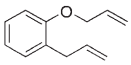
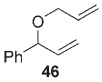
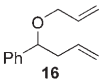
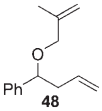
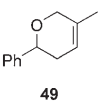
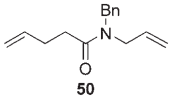
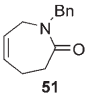
Table 3. Compared activities in RCM on tosylamine-based substrates.

	Substrate	Product	Precatalyst (loading [mol %])[a]	*T* [°C][b]	*t* [h]	Isolated yield [%]
1	 **24**	 **25**	5(2)	25	0.25	97
			7(2)	25	5	97
2	 **26**	 **27**	**5**(2)	25	0.25	99
			7(2)	25	5	100
3	 **28**	 **29**	**5**(2)	25	0.5	98
			7(2)	25	5	95
4	 **30**	 **31**	**5**(2)	25	0.5	100
			7(2)	25	5	98
5	 **14**	 **15**	**5**(2)	25	6	89
			7(2)	25	5	96
6	 **32**	 **33**	**5**(2)	25	6	95
			7(2)	25	6	100
7	 **34**	 **35**	**5**(2)	25	6	93
			7(2)	25	6	98
8	 **36**	 **37**	**5**(2)	25	6	92
			7(2)	25	6	96
9	 **38**	 **39**	**5**(5)	40	5	<2
			5(5)	80	5	<2
			7(5)	40	24	61
			7(2)	80	3	86
			7(5)	80	0.5	99
10	 **40**	 **41**	**5**(5)	80	5	<2
			7(5)	80	0.5	95

[a] Reaction conditions: CH_2Cl_2, 0.1 M. [b] Reactions at 80 °C were performed in toluene.

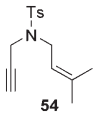
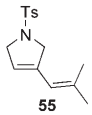
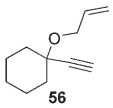
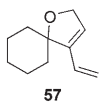
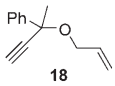
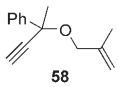
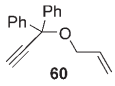
Evaluation of ether and amide-based substrates: Studies on the RCM of ether- and amide-containing olefins are shown in Table 4. Ruthenium indenylidene-based complexes showed a good tolerance for amide-based substrates (Table 4, entry 1). Although **44** does not exhibit steric hindrance, tricyclohexylphosphine-containing **5** was found to be as efficient as precatalyst **7** (Table 4, entry 2). The 5- and 6-

Table 4. Compared activities in RCM on ether and amide-containing substrates.

	Substrate	Product	Precatalyst[a]	T [°C][b]	t [h]	Isolated yield [%]
1	 **42**	 **43**	**5**	25	0.25	96
			7	25	3	98
2	 **44**	 **45**	**5**	25	3	96
			7	25	3	95
3	 **46**	 **47**	**5**	25	2	92
			7	40	5	86
4	 **16**	 **17**	**5**	25	2	98
			7	40	5	94
5	 **48**	 **49**	**5**	40	2	42
			7	40	2	98
6	 **50**	 **51**	**5**	40	3	54
			7	40	3	81

[a] Reaction conditions: CH_2Cl_2, 0.1 M, 2 mol% of precatalyst. [b] Reactions at 80°C were performed in toluene.

Table 5. Precatalysts activities in enyne metathesis.

	Substrate	Product	Precatalyst[a]	T [°C][b]	t [h]	Isolated yield [%]
1	 **52**	 **53**	**5**	25	24	50
			7	80	5	36
2	 **54**	 **55**	**5**	25	24	93
			7	40	5	53
			7	80	0.5	79
3	 **56**	 **57**	**5**	25	3	94
			7	40	2	99
4	 **18**	 **19**	**5**	25	5	89
			7	40	5	99
5	 **58**	 **59**	**5**	80	5	<2
			7	80	5	85
6	 **60**	 **61**	**5**	25	5	94
			7	25	2	99

[a] Reaction conditions: CH_2Cl_2, 0.1 M, 2 mol% of precatalyst. [b] Reaction at 80°C were performed in toluene.

membered ring products **47** and **17** were isolated under identical reaction conditions by using both complexes, but **5** displays a higher efficiency (Table 4, entries 3 and 4). This trend is reversed for the hindered substrate **48** (Table 4, entry 5). NHC-containing **7** exhibited a better activity toward **48** than **16**, showing a special behavior for this category of olefins. The ability of oxygen-containing substrates to coordinate to the ruthenium atom and form stable complexes is well known.[8a–b] We believe that the methyl substituent of **48** destabilizes this formation and subsequently allows for faster cyclization. Finally, the RCM of **50** leading to **51**, a benzodiazepine analogue, was found to be more straightforward by using precatalyst **7** (entry 6).

Evaluation in enyne metathesis: Ring-closing enyne metathesis represents a powerful method for the synthesis of exocyclic 1,3-dienes, which can go on to react further in reactions such as Diels–Alder, to yield complex polycyclic molecules, or Claisen rearrangements.[1a,18] Several substrates for enyne metathesis were tested and the results are reported in the Table 5. For substrate **52**, moderate yields were obtained by using both catalysts, only 50% using 2 mol% of **5** in 24 hours at room temperature, and 36% with **7** in 5 hours at 80°C (Table 5, entry 1). Notably, for this substrate, reactions were performed under an ethylene gas atmosphere, which allowed for higher conversions.[19] Excellent isolated yields of substrate **55** were obtained with both catalysts (Table 5, entry 2), although phosphine-containing **5** was found to be the best.

For the RCM of substrate **56**, the reaction mixture required heating to 40°C using NHC-containing **7** to produce 96% of **57** in only 2 h rather than 3 h for **5** at room temperature (Table 5, entry 3). NHC-containing **7** produced a 99% yield of **57** in only 2 hours, whereas a yield of 94% was achieved by precatalyst **5** in 3 hours (Table 5, entry 3). This example illustrates the very different activities of **5** and **7**. The metathesis transformation for enyne **58** by using **5** does not occur in spite of a reaction time of 5 hours at 40°C, whereas **7** mediated the cyclization and product **59** was isolated in a similar yield (85%) to its unhindered counterpart **19** (Table 5, entries 4 and 5). Interestingly, by using precatalyst **5**, substrates **18** and **60** displayed similar conversion behavior, by using SIMes-containing **7** the difference in activity can be observed (Table 5, entries 4 and 6). To isolate **19** in a reasonable reaction time, thermal activation was required, in contrast to enyne **60**. Seemingly, this enyne category exhibits a particular reactivity in metathesis and further investigations on this class of substrates are currently ongoing in our laboratory.

Conclusion

In summary, we have carried out a comparative study in terms of activity and scope, with, on the one hand, benzylidene and indenylidene-based ruthenium complexes, and on the other phosphine and NHC-containing metathesis catalysts. The kinetic profiles of RCM reactions illustrate that phosphine (first generation) and NHC-containing (second-generation) precatalysts were found to possess two distinct rate-determining steps. As a consequence, the first generation catalysts were found to be more efficient in the meta-

thesis transformations of sterically unhindered substrates. The second generation catalysts showed an excellent activity towards sterically hindered olefins, which do not react if the first catalyst generation is used. Independent of catalyst generation, indenylidene-based precatalysts showed comparable activity when compared against their benzylidene analogues for almost all substrates, and displayed an excellent tolerance toward functional groups. However, for reactions with tetrasubstituted dienes, indenylidene precatalysts showed a better activity. This we attribute to the higher thermal stability of the precatalysts. This study showed how difficult it is to anticipate the activity of precatalysts toward a specific substrate, and highlighted that, unfortunately, any single complex is not omnipotent. Further developments and applications of indenylidene-based ruthenium complexes in application to the metathesis transformation and the substrate class are currently ongoing in our laboratory and will be reported in due course.

Experimental Section

General considerations: All reagents were used as purchased. Dichloromethane (DCM), toluene, dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from a solvent purification system from Innovative Technology. Flash column chromatography was performed on silica-gel 60 (230–400 mesh). ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometer. High Resolution Mass Spectroscopy (HRMS) analyses were performed on a Waters LCT Premier spectrometer or a Waters GCT spectrometer. Complexes **2**, **4**, **5**, **7** and **8** were obtained commercially. The following compounds have been previously described: **3**,[5] **6**,[14] **9**,[20] **10**,[21] **11**,[21] **12**,[21] **13**,[21] **14**,[22] **15**,[20] **16**,[23] **17**,[2b] **19**,[24] **20**,[25] **21**,[26] **22**,[20] **23**,[27] **24**,[22] **25**,[22] **27**,[22] **28**,[20] **29**,[28] **32**,[20] **33**,[29] **36**,[30] **37**,[31] **39**,[28] **40**,[20] **41**,[20] **42**,[32] **44**,[33] **45**,[28] **46**,[34] **47**,[2b] **48**,[34] **49**,[20] **50**,[2b] **51**,[2b] **52**,[35] **53**,[19] **54**,[36] **55**,[24] **59**,[24] **61**.[24]

General procedure for substrates synthesis: To a suspension of sodium hydride, in dry DMF, the starting material in solution, also in dry THF, was added dropwise at 0 °C. 15 min after the end of the gas evolution, the alkylating reagent was added at 0 °C and the resulting mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of water this was followed by the addition of ethyl acetate. The organic layer was washed with a saturated solution of sodium carbonate and brine, separated, dried over magnesium sulfate, filtered, and then concentrated.

(2-(Allyloxy)but-3-yn-2-yl)benzene (***18***): The reagents sodium hydride (11 mmol, 264 mg), 2-phenyl-3-butyn-2-ol (10 mmol, 1.46 g) and allylbromide (11 mmol, 1 mL) were combined by using the general procedure, purification of the crude mixture by silica-gel chromatography (pentane/diethyl ether, 98:2) afforded the title product as a colorless oil (1.71 g, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.66–7.63 (m, 2H; CH^{Ar}), 7.42–7.37 (m, 2H; CH^{Ar}), 7.35–7.31 (m, 1H; CH^{Ar}), 5.97 (ddt, $^3J_{(H,H)}$ = 17.2, 10.3, 5.6 Hz, 1H; CH=CH$_2$), 5.32 (dq, $^3J_{(H,H)}$ = 17.2 Hz, $^4J_{(H,H)}$ = 1.6 Hz, 1H; CH_2=CH), 5.17 (dq, $^3J_{(H,H)}$ = 10.3 Hz, $^4J_{(H,H)}$ = 1.6 Hz, 1H; CH_2=CH), 4.12 (ddq, $^2J_{(H,H)}$ = 12.2 Hz, $^3J_{(H,H)}$ = 5.6 Hz, $^4J_{(H,H)}$ = 1.6 Hz, 1H; CH_2O), 3.70 (ddq, $^2J_{(H,H)}$ = 12.2 Hz, $^3J_{(H,H)}$ = 10.3 Hz, $^4J_{(H,H)}$ = 1.6 Hz, 1H; CH_2O), 2.77 (s, 1H; CHC), 1.80 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 142.6 (C, C^{Ar}), 134.8 (CH, CH=CH$_2$), 128.3 (CH, C^{Ar}), 127.9 (CH, C^{Ar}), 125.9 (CH, C^{Ar}), 116.5 (CH$_2$, CH$_2$=CH), 84.0 (C, CC-O), 77.2 (C, C-O), 75.4 (CH, CHC), 66.2 (CH$_2$, CH$_2$O), 32.9 ppm (CH$_3$, CH$_3$); HRMS (EI): *m/z*: calcd for $C_{13}H_{14}O-H$: 185.0966 [M^+-H]; found: 185.0961.

N,N-*Di(but-3-enyl)-4-methylbenzenesulfonamide* (***30***): The reagents sodium hydride (22 mmol, 528 mg), the *p*-toluenesulfonamide (10 mmol, 1.72 g) and 4-bromobut-1-ene (22 mmol, 2.2 mL) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/ethyl acetate, 8:2) afforded the title product as a colorless oil (1.93 g, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.71 (d, $^3J_{(H,H)}$ = 8.2 Hz, 2H; CH^{Ar}), 7.31 (d, $^3J_{(H,H)}$ = 8.2 Hz, 2H; CH^{Ar}), 5.78–5.68 (m, 2H; CH=CH$_2$), 5.10–5.04 (m, 4H; CH_2=C), 3.23–3.19 (m, 4H; CH_2N), 2.44 (s, 3H; ArCH_3), 2.34–2.27 ppm (m, 4H; CHCH_2CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.1 (C, C^{Ar}), 137.0 (C, C^{Ar}), 134.7 (C, CH=CH$_2$), 129.6 (CH, C^{Ar}), 127.2 (CH, C^{Ar}), 117.1 (CH$_2$, CH$_2$=CH), 47.8 (CH$_2$, CCH$_2$N), 33.2 (CH$_2$, CHCH$_2$), 21.5 ppm (CH$_3$, ArCH_3); HRMS (ESI): *m/z*: calcd for $C_{15}H_{21}NO_2S$+Na: 302.1191 [M^++Na]; found: 302.1179.

N-*(But-3-enyl)-4-methyl*-N-*(2-methylallyl)benzenesulfonamide* (***32***): The reagents sodium hydride, (11 mmol, 264 mg), 4-methyl-*N*-(2-methylallyl)-benzenesulfonamide (10 mmol, 2.25 g) and 4-bromobut-1-ene (11 mmol, 1.1 mL) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/ethyl acetate, 8:2) afforded the title product as a yellow oil (2.06 g, 79 %); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.71 (d, $^3J_{(H,H)}$ = 8.3 Hz, 2H; CH^{Ar}), 7.31 (d, $^3J_{(H,H)}$ = 8.3 Hz, 2H; CH^{Ar}), 5.72–5.62 (m, 1H; CH=CH$_2$), 5.04–5.01 (m, 2H; CH_2=C), 4.92–4.90 (m, 2H; CH_2=CH), 3.72 (s, 2H; CCH_2N), 3.17–3.13 (m, 2H; CH$_2$CH_2N), 2.44 (s, 3H; ArCH_3), 2.27–2.21 (m, 2H; CHCH_2CH$_2$), 1.60 ppm (s, 3H; CH_3C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.2 (C, C^{Ar}), 140.8 (C, C=CH$_2$), 137.1 (C, C^{Ar}), 134.8 (CH, CH=CH$_2$), 129.6 (CH, C^{Ar}), 127.2 (CH, C^{Ar}), 116.8 (CH$_2$, CH$_2$=CH), 114.5 (CH$_2$, CH$_2$=C), 54.6 (CH$_2$, CCH$_2$N), 47.2 (CH$_2$, CH$_2$$CH_2$N), 32.7 (CH$_2$, CH$CH_2$), 21.5 (CH$_3$, ArC$H_3$), 19.8 ppm (CH$_3$, CH$_3$C=CH$_2$); HRMS (ESI): *m/z*: calcd for $C_{15}H_{21}NO_2S$+Na: 302.1191 [M^++Na]; found: 302.1192.

4-Methyl-N,N-*bis(2-methylallyl)benzenesulfonamide* (***38***): The reagents sodium hydride (30 mmol, 720 mg), *p*-toluenesulfonamide (10 mmol, 1.72 g) and 3-chloro-2-methylpropene (30 mmol, 3.3 mL) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/ethyl acetate, 8:2) afforded the title product as a yellow oil (1.81 g, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.70 (d, $^3J_{(H,H)}$ = 8.3 Hz, 2H; CH^{Ar}), 7.28 (d, $^3J_{(H,H)}$ = 8.3 Hz, 2H; CH^{Ar}), 4.85 (s, 2H; CH_2=C), 4.78 (s, 2H; CH_2=C), 3.70 (s, 4H; CH_2N), 2.41 (s, 3H; ArCH_3), 1.60 ppm (s, 6H; CH_3C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.1 (C, C^{Ar}), 140.1 (C, C=CH$_2$), 137.4. (C, C^{Ar}), 129.5 (CH, C^{Ar}), 127.2 (CH, C^{Ar}), 114.5 (CH$_2$, CH$_2$=C), 53.1 (CH$_2$, CH$_2$N), 21.5 (CH$_3$, ArCH$_3$), 20.0 ppm (CH$_3$, CH$_3$C=CH$_2$); HRMS (ESI): *m/z*: calcd for $C_{15}H_{21}NO_2S$+Na: 302.1191 [M^++Na]; found: 302.1194.

4-Methyl-N-*(2-methylallyl)*-N-*(3-methylbut-3-enyl)benzenesulfonamide* (***40***): The reagents sodium hydride (11 mmol, 264 mg), 4-methyl-*N*-(2-methylallyl)benzenesulfonamide (10 mmol, 2.25 g) and 3-methylbut-3-enyl methanesulfonate (12 mmol, 2 g) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/ethyl acetate, 8:2) afforded the title product as a yellow oil (2.49 g, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.72 (d, $^3J_{(H,H)}$ = 8.2 Hz, 2H; CH^{Ar}), 7.31 (d, $^3J_{(H,H)}$ = 8.2 Hz, 2H; CH^{Ar}), 4.95–4.92 (m, 1H; CH_2=C), 4.91–4.89 (m, 1H; CH_2=C), 4.75–4.73 (m, 1H; CH_2=C), 4.64–4.62 (m, 1H; CH_2=C), 3.73 (s, 2H; CCH_2N), 3.22–3.18 (m, 2H; CH$_2$CH_2N), 2.44 (s, 3H; ArCH_3), 2.20–2.16 (m, 2H; CCH_2CH$_2$), 1.74 (s, 3H; CH_3C) 1.68 ppm (s, 3H; CH_3C); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 143.1 (C, C^{Ar}), 142.6 (C, C=CH$_2$), 140.8 (C, C=CH$_2$), 137.2 (C, C^{Ar}), 129.6 (CH, C^{Ar}), 127.2 (CH, C^{Ar}), 114.5 (CH$_2$, CH$_2$=C), 111.8 (CH$_2$, CH$_2$=C), 54.5 (CH$_2$, CCH$_2$N), 46.4 (CH$_2$, CH$_2$$CH_2$N), 36.2 (CH$_2$, C$CH_2CH_2$), 22.4 (CH$_3$, CH$_3$C=CH$_2$), 21.5 (CH$_3$, ArC$H_3$), 19.8 ppm (CH$_3$, CH$_3$C=CH$_2$); HRMS (ESI): *m/z*: calcd for $C_{16}H_{23}NO_2S$+Na: 316.1347 [M^++Na]; found: 316.1332.

1-(Allyloxy)-1-ethynylcyclohexane (***56***): The reagents sodium hydride (11 mmol, 264 mg), 1-ethynylcyclohexanol (10 mmol, 1.24 g) and allylbromide (11 mmol, 1 mL) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/diethyl ether, 98:2) afforded the title product as a colorless oil (1.18 g, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.03–5.94 (m, 1H; CH=CH$_2$), 5.32 (d, $^3J_{(H,H)}$ = 17.2 Hz, 1H; CH_2=CH), 5.16 (d, $^3J_{(H,H)}$ = 9.4 Hz, 1H; CH_2=CH), 4.14 (d, $^3J_{(H,H)}$ = 5.5 Hz, 2H; CH_2O), 2.49 (s, 1H; CHC), 1.94–1.91 (m,

2H; CH_2^{Cy}), 1.71–152 ppm (m, 8H; CH_2^{Cy}); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 135.5 (CH, *C*H=CH$_2$), 116.2 (CH$_2$, *C*H$_2$=CH), 85.2 (C, *C*C-O), 73.7 (C, *C*-O), 73.6 (CH, *C*HC), 64.5 (CH$_2$, *C*H$_2$O), 37.2 (CH$_2$, *C*H$_2^{Cy}$) 25.4 (CH$_2$, *C*H$_2^{Cy}$) 22.7 ppm (CH$_2$, *C*H$_2^{Cy}$); HRMS (EI): *m/z*: calcd for $C_{11}H_{16}O-H$: 163.1123 [*M*+−H]; found: 163.1118.

*(2-(2-Methylallyloxy)but-3-yn-2-yl)benzene (**58**)*: The reagents sodium hydride (11 mmol, 264 mg), 2-phenyl-3-butyn-2-ol (10 mmol, 1.46 g) and 3-chloro-2-methylpropene (11 mmol, 1.2 mL) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/diethyl ether, 98:2) afforded the title product as a colorless oil (1.74 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.67–7.65 (m, 2H; C*H*^{Ar}), 7.42–7.37 (m, 2H; C*H*^{Ar}), 7.35–7.31 (m, 1H; C*H*^{Ar}), 5.07–5.06 (m, 1H; CH_2=C), 4.90–4.98 (m, 1H; CH_2=C), 4.05 (d, $^2J_{(H,H)}$ = 11.9 Hz, 1H; CH_2O), 3.60 (d, $^4J_{(H,H)}$ = 11.9 Hz, 1H; CH_2O), 2.76 (s, 1H; C*H*C), 1.81 (s, 3H; CH_3C=CH$_2$), 1.77 ppm (s, 3H; CH_3C-O); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 142.6 (C, *C*^{Ar}), 142.4 (C, *C*=CH$_2$), 128.3 (CH, *C*^{Ar}), 127.8 (CH, *C*^{Ar}), 125.9 (CH, *C*^{Ar}), 111.4 (CH$_2$, *C*H$_2$=C), 84.0 (C, *C*C-O), 75.9 (C, *C*-O), 75.4 (CH, *C*HC), 68.8 (CH$_2$, *C*H$_2$O), 32.9 (CH$_3$, *C*H$_3$C-O), 19.9 ppm (CH$_3$, *C*H$_3$C=CH$_2$); HRMS (ESI): *m/z*: calcd for $C_{14}H_{16}O$+Na: 223.1099 [*M*$^+$+Na]; found: 223.1101.

*(1-(Allyloxy)prop-2-yne-1,1-diyl)dibenzene (**60**)*: The reagents sodium hydride (11 mmol, 264 mg), 1,1-diphenyl-2-propyn-1-ol (10 mmol, 2.08 g) and allylbromide (11 mmol, 1 mL) by using the general procedure, and purification of the crude mixture by silica-gel chromatography (pentane/diethyl ether, 98:2) afforded the title product as a colorless oil (2.21 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.62 (d, $^3J_{(H,H)}$ = 7.1 Hz, 4H; C*H*^{Ar}), 7.36 (t, $^3J_{(H,H)}$ = 7.1 Hz, 4H; C*H*^{Ar}), 7.38 (t, $^3J_{(H,H)}$ = 7.1 Hz, 2H; C*H*^{Ar}), 6.09–5.99 (m, 1H; C*H*=CH$_2$), 5.41 (d, $^3J_{(H,H)}$ = 16.6 Hz, 1H; CH_2=CH), 5.17 (d, $^3J_{(H,H)}$ = 10.4 Hz, 1H; CH_2=CH), 4.09 (d, $^3J_{(H,H)}$ = 5.2 Hz, 2H; CH_2O), 2.93 ppm (s, 1H; C*H*C); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 143.2 (C, *C*^{Ar}), 134.8 (CH, *C*H=CH$_2$), 128.2 (CH, *C*^{Ar}) 127.7 (CH, *C*^{Ar}), 126.6 (CH, *C*^{Ar}), 116.1 (CH$_2$, *C*H$_2$=CH), 83.3 (C, *C*C-O), 80.1 (C, *C*-O), 77.6 (CH, *C*HC), 66.0 ppm (CH$_2$, *C*H$_2$O); HRMS (ESI): *m/z*: calcd for $C_{18}H_{14}O$+Na: 271.1099 [*M*$^+$+Na]; found: 271.1098.

General procedure for kinetic studies: In a glovebox, a vial was filled with the diene (1 mmol) and dichloromethane (10 mL), then precatalyst **5**–**7** (0.01 mmol) were added. The reaction progress was monitored by ^{1}H NMR spectroscopy by transferring aliquots from the reaction solution by syringe, and by integration of characteristic signals for allylic protons.

General procedure for metathesis reaction: A Schlenk apparatus under argon was filled with the diene (0.5 mmol) and the solvent (5 mL: DCM for reaction at RT and 40°C, toluene for reaction at 80°C), then precatalyst (0.01–0.025 mmol) was added. Progress of the reaction was monitored by TLC. The solvent was removed under vacuum and the crude residue was purified by flash-column chromatography to yield the pure product.

*(Z)-1-Tosyl-2,3,6,7-tetrahydro-1H-azepine (**31**)*: The general procedure yielded after flash chromatography on silica gel (pentane/ethyl acetate, 8:2) the title compound as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.67 (d, $^3J_{(H,H)}$ = 8.2 Hz, 2H; C*H*^{Ar}), 7.32 (d, $^3J_{(H,H)}$ = 8.2 Hz, 2H; C*H*^{Ar}), 5.43–5.41 (m, 1H; C*H*=C), 5.04–5.01 (m, 2H; CH_2=C), 3.40 (s, 2H; CCH_2N), 3.11–3.08 (m, 2H; CH$_2$CH_2N), 2.42 (s, 3H; ArCH_3), 2.19–2.13 (m, 2H; CHCH_2CH$_2$), 1.62 ppm (s, 3H; CH_3C); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 143.5 (C, *C*^{Ar}), 133.3 (C, *C*^{Ar}), 129.9 (C, *C*=CH), 129.6 (CH, *C*^{Ar}), 127.7 (CH, *C*^{Ar}), 119.4 (CH, *C*H=C), 48.2 (CH$_2$, CCH_2N), 42.5 (CH$_2$, CH$_2$CH_2N), 25.1 (CH$_2$, CHCH_2), 21.5 (CH$_3$, ArCH_3), 20.6 ppm (CH$_3$, *C*H$_3$C=CH$_2$); HRMS (ESI): *m/z*: calcd for $C_{13}H_{17}NO_2S$+Na: 274.0878 [*M*$^+$+Na]; found: 274.0878.

*4,5-Dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**41**)*: The general procedure yielded after flash chromatography on silica gel (pentane/ethyl acetate, 8:2) the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.67 (d, $^3J_{(H,H)}$ = 8.1 Hz, 2H; C*H*^{Ar}), 7.31 (d, $^3J_{(H,H)}$ = 8.1 Hz, 2H; C*H*^{Ar}), 3.37 (s, 2H; CCH_2N), 3.11 (t, $^3J_{(H,H)}$ = 5.8 Hz, 2H; CH$_2$CH_2N), 2.42 (s, 3H; ArCH_3), 2.12–2.08 (m, 2H; CCH_2CH$_2$), 1.58 (s, 3H; CH_3C), 1.56 ppm (s, 3H; CH_3C); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 143.4 (C, *C*^{Ar}), 133.1 (C, *C*^{Ar}), 129.6 (CH, *C*^{Ar}) 127.7 (CH, *C*^{Ar}), 124.6 (C, *C*=C), 121.5 (C, *C*=C), 48.9 (CH$_2$, CCH_2N), 43.2 (CH$_2$, CH$_2$CH_2N), 31.1 (CH$_2$, CCH_2CH$_2$), 21.5 (CH$_3$, ArCH_3), 18.4 (CH$_3$, CH_3C=CH$_2$), 16.2 ppm (CH$_3$, CH_3C=CH$_2$); HRMS (ESI): *m/z*: calcd for $C_{14}H_{16}NO_2S$+Na: 288.1034 [*M*$^+$+Na]; found: 288.1026.

*(2,5-Dihydro-1H-pyrrol-1-yl)(phenyl)methanone (**43**)*: The general procedure yielded after flash chromatography on silica gel (pentane/ethyl acetate, 8:2) the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 7.51–7.48 (m, 2H; C*H*^{Ar}), 7.39–7.37 (m, 3H; C*H*^{Ar}), 5.89–5.87 (m, 1H; C*H*=CH), 5.73–5.70 (m, 1H; C*H*=CH), 4.44–4.42 (m, 2H; CH_2N), 4.18–4.17 ppm (m, 2H; CH_2N); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 169.9 (C, *C*O), 136.8 (C, *C*^{Ar}), 129.9 (CH, *C*^{Ar}), 128.4 (CH, *C*^{Ar}), 126.8 (CH, *C*^{Ar}), 125.9 (CH, *C*H=CH), 125.2 (CH, *C*H=CH), 55.8 (CH$_2$, *C*H$_2$N), 53.4 ppm (CH$_2$, *C*H$_2$N); HRMS (ESI): *m/z*: calcd for $C_{11}H_{11}NO$+Na: 196.0738 [*M*$^+$+Na]; found: 196.0737.

*4-Vinyl-1-oxaspiro[4.5]dec-3-ene (**57**)*: The general procedure yielded after flash chromatography on silica gel (pentane/diethyl ether, 98:2) the title compound as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ = 6.19 (dd, $^3J_{(H,H)}$ = 17.8, 11.2 Hz, 1H; C*H*=CH$_2$), 5.83 (s, 1H; C*H*=C), 5.46 (d, $^3J_{(H,H)}$ = 17.8 Hz, 1H; CH_2=CH), 5.15 (d, $^3J_{(H,H)}$ = 11.2 Hz, 1H; CH_2=CH), 4.60 (s, 2H; CH_2O), 2.06–1.64 ppm (m, 10H; CH_2^{Cy}); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C, TMS): δ = 145.1 (C, *C*=CH), 129.1 (CH, *C*H=CH$_2$), 122.7 (CH, *C*H=C), 115.7 (CH$_2$, *C*H$_2$=CH), 88.3 (C, *C*-O), 71.9 (CH$_2$, *C*H$_2$O), 34.7 (CH$_2$, *C*H$_2^{Cy}$), 25.4 (CH$_2$, *C*H$_2^{Cy}$), 22.4 ppm (CH$_2$, *C*H$_2^{Cy}$); HRMS (CI): *m/z*: calcd for $C_{11}H_{16}O$+H: 165.1279 [*M*$^+$+H]; found: 165.1282.

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