DOI: 10.1002/ejoc.200901316

Ring-Rearrangement Metathesis (RRM) Mediated by Ruthenium-Indenylidene Complexes

Hervé Clavier,*[a][‡] Julie Broggi,[a] and Steven P. Nolan*[a]

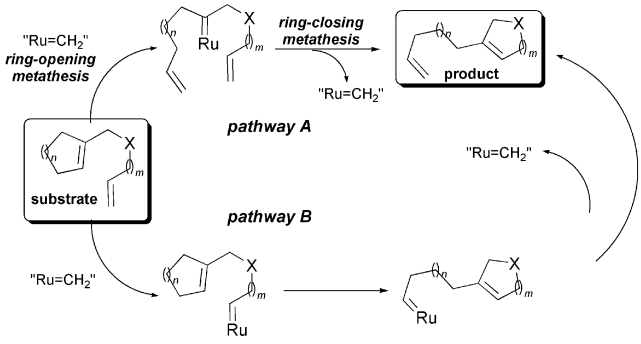
Keywords: Metathesis / Ruthenium / Nitrogen heterocycles / Carbene ligands / Phosphanes / Rearrangment

Several ruthenium-indenylidene complexes bearing N-heterocyclic carbenes (NHCs) and phosphanes have been investigated for the ring rearrangement of cyclic compounds by alkene metathesis. These catalysts were found to promote efficiently such domino reactions, especially sterically hindered NHC-containing complexes. Moreover, indenylidene-type catalysts were compared to benzylidene- and Hoveyda-type analogues. The scope of the reaction highlights the parameters governing the RRM.

Introduction

A fascinating aspect of olefin metathesis is the accessibility to diverse olefin reactivity as a function of substrate architecture and/or reaction conditions using the same metal–carbene pre-catalyst.[1] These metathesis transformations include ring-opening metathesis polymerization (ROMP)[2] ring-closing metathesis[3] (RCM), and cross metathesis[4] (CM) of substrates incorporating either double or triple C–C bonds. Combinations of several metathesis steps are also possible and allow for the straightforward construction of complex scaffolds. Amongst these domino reactions, ring-rearrangement metathesis[5] (RRM) involving ring-opening/ring-closing metathesis steps (Scheme 1) has been successfully applied to the formation of carbo- and heterocycles.[6]

As an attractive alternative to ruthenium-benzylidene pre-catalysts, we[7] and others[8] have focused on the development of indenylidene analogues bearing phosphanes and N-heterocyclic carbenes (NHC) (Figure 1).[9] These complexes were found to be efficient in a wide array of ROMP, RCM, and CM transformations.[7,8] Of note, tricyclohexylphosphane-containing complex **1** and **5** bearing the sterically encumbering NHC SIPr [1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene] appear as most efficient at room temperature, whereas SIMes-indenylidene catalyst **3** [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] is the most capable at higher temperature. In spite of these catalyst development efforts, the breadth of application for ruthenium-indenylidene catalysts remains relatively narrow. We now report the potential of these pre-catalysts in RRM.



Scheme 1. General principle and mechanism of RMM.

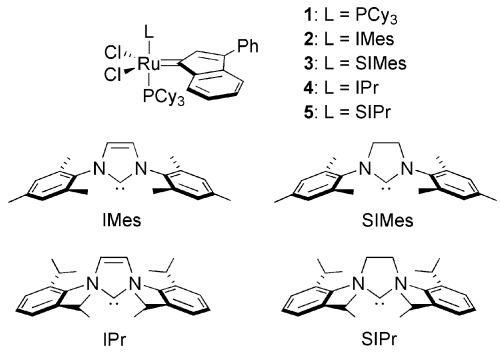


Figure 1. Ruthenium-indenylidene complexes used in this work.

Results and Discussion

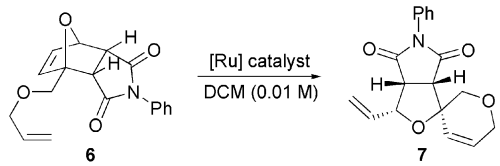
We first compared activity of indenylidene catalysts on the *endo* adduct **6** obtained from Diels–Alder cycloaddition[10] as a benchmark substrate with 1 mol-% ruthenium

[a] EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK
E-mail: snolan@st-andrews.ac.uk
[‡] Present address: Université Aix-Marseille, UMR CNRS 6263 – Institut des Sciences Moléculaires de Marseille, Av. Escadrille Normandie Niemen, 13397 Marseille Cedex 20, France
E-mail: herve.clavier@univ-cezanne.fr

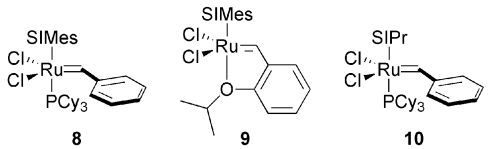
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200901316.

complex using dichloromethane as solvent and low concentration (C = 0.01 M) (Table 1). Complex **1** showed good activity as a 69% conversion was reached after 3 h at room temperature (Entry 1). As expected, saturated NHC-containing catalysts **3** and **5** were found significantly superior to their respective unsaturated counterparts **2** and **4** (Entries 2–8). Complex **3** bearing sterically less demanding SIMes required a slight thermal activation to form the spirocycle **7** (Entries 4 and 5). On the other hand, **5** exhibited remarkable activity and only 15 min were required to achieve the RRM (Entry 8). We then examined the reaction at higher concentration (C = 0.1 M) (Entry 9). Under these conditions, the polymerisation process was more favored and 30% polymer formation was observed. Since it has been observed that **5** could be used in various solvents for RCM,[7e] reactions were carried out in toluene and diethyl ether at 0.1 M. Unfortunately under these conditions, substantial polymerisation was also obtained. The excellent activity of **5** prompted us to decrease the catalyst loading (Entries 10 and 11). However using 0.5 mol-% of **5** required an increase in the reaction time; unfortunately at 0.1 mol-% only traces of **7** were observed after 3 h of reaction.

Table 1. Catalysts comparison on a model substrate.[a]



Entry	Catalyst (loading)	Conditions	NMR conv.
1	**1** (1 mol-%)	25 °C, 3 h	69 %
2	**2** (1 mol-%)	25 °C, 3 h	-[b]
3	**2** (1 mol-%)	40 °C, 3 h	-[b]
4	**3** (1 mol-%)	25 °C, 3 h	< 5 %
5	**3** (1 mol-%)	40 °C, 3 h	48 %
6	**4** (1 mol-%)	25 °C, 3 h	53 %
7	**4** (1 mol-%)	40 °C, 1 h	85 %
8	**5** (1 mol-%)	25 °C, 15 min	97 %
9	**5** (1 mol-%)	25 °C, 30 min[c]	94 %[d]
10	**5** (0.5 mol-%)	25 °C, 30 min	87 %
11	**5** (0.1 mol-%)	25 °C, 3 h	< 5 %
12	**8** (1 mol-%)	25 °C, 3 h	98 %
13	**9** (1 mol-%)	25 °C, 3 h	98 %
14	**10** (1 mol-%)	25 °C, 15 min	99 %

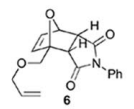
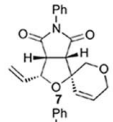
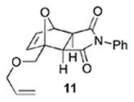
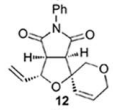
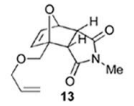
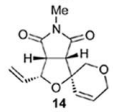
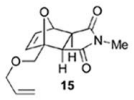
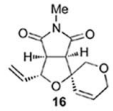
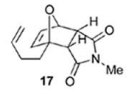
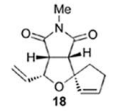
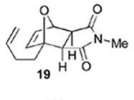
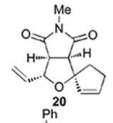
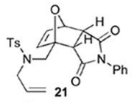
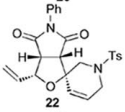
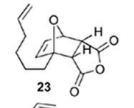
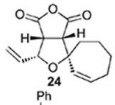
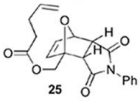
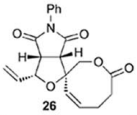
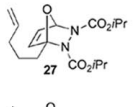
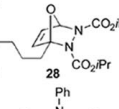
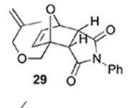
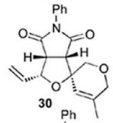
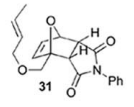
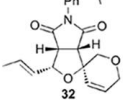
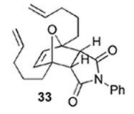
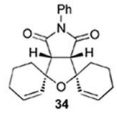
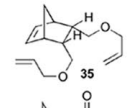
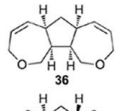
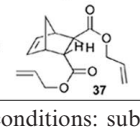
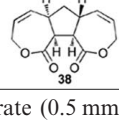


[a] Reaction conditions: substrate (0.5 mmol), [Ru], DCM (50 mL, 0.01 M). [b] Starting material recovered. [c] Reaction was performed at 0.1 M. [d] 30% of polymerisation was obtained.

In addition to examining a variety of NHCs bound to the ruthenium-indenylidene moiety, the benzylidene and 2-isopropoxybenzylidene patterns in the form of the 2nd generation Grubbs[11] and Hoveyda–Grubbs[12] catalysts, respectively **8** and **9**, were examined. Whereas SIMes-containing **3** required a thermal activation at 40 °C (Entries 3 and 4), the benzylidene- and 2-isopropoxybenzylidene-based catalysts **8** and **9** performed well at room temperature, and only 3 h were required to reach complete reaction (Entries 12 and 13). Such activity differences between benzylidene- and indenylidene-ruthenium complexes are in sharp contrast to those previously reported for RCM.[7c] Nevertheless, with the more sterically demanding NHC SIPr, the difference was found insignificant, both catalysts **5** and **10**[13] permitted the complete reaction in 15 min at 25 °C (Entries 8 and 14). Because it has been reported that the 2-isopropoxybenzylidene-based complex bearing SIPr[14] showed slow activation,[15] this complex was not examined.

In light of these preliminary results, we then proceeded to investigate, using 1 mol-% of **5** as the catalyst loading, the scope of RRM reactions involving oxabicyclo[2.2.1]-heptene and norbornene derivatives (Table 2).[10] Whereas the rearrangement of *endo* adducts was found straightforward (Entries 1, 3 and 5), *exo* products were significantly less reactive and required longer reaction time in contrast to data reported in the literature (Entries 2, 4 and 6). Blechert reported identical reaction time for both adducts.[16] This may suggest that the *endo* conformation is more susceptible to RRM in the present system. This also suggests to us that RRM may possibly be use in kinetic resolution. Of note, in this study, the *endo* and *exo* adducts resulting from Diels–Alder cycloaddition were always separable by silica-gel chromatography and consequently we did not attempt any kinetic resolution. Furthermore, the above-mentioned substrates are *endo*; catalytic results with the *exo* adducts can be found in the Supporting Information. Substrate **21** containing a bulkier tosylamine group necessitated prolonged reaction time (Entry 7). Formation of the above-mentioned five- and six-membered rings was easily achieved, however RRM leading to seven-membered ring product **24** required a significant increase in the reaction time with concomitant polymerization (Entry 8). Unfortunately, only traces of the eight-membered ring spirocycle **26** were observed with polymers as major product (Entry 9). Of note, with the *exo* adduct of **25**, reaction occurred more slowly but only lead to polymerization products.[10] In an effort to examine the functional group tolerance of this transformation, the diazabicyclo[2.2.1]hept-5-ene compound **27** was submitted to optimum catalytic conditions (Entry 10). Only dimer **28** was isolated showing that **5** was compatible with such a functionality, but the RRM appears unfavored. The substitution of the exocyclic C=C bond was also of interest. Ψ,Ψ-disubstitution of this architecture leads to a lack of reactivity at room temperature and at 80 °C using catalyst **3**, provides mainly retro Diels–Alder products (Entries 11 and 12). This result highlights the importance of pre-catalysts operating efficiently at low temperature. On the other hand, the RRM transformation of **31** into **32** proceeded smoothly (Entry 13) and the reaction on the *exo* adduct was also found possible.[10] Double cyclization of **33** occurred with thermal activation at 40 °C, but at this temperature the retro Diels–

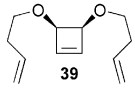
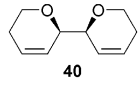
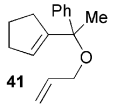
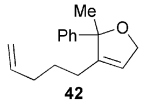
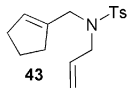
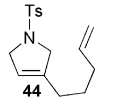
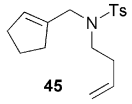
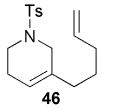
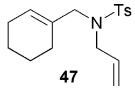
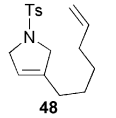
Table 2. RRM of oxabicyclo[2.2.1]heptene and norbornene derivatives.[a]

Entry	Substrate	Product	Yield (Time)
1	 6	 7	94 % (15 min)
2	 11	 12	71 % (5 h)[b]
3	 13	 14	96 % (15 min)
4	 15	 16	74 % (5 h)[b]
5	 17	 18	90 % (15 min)
6	 19	 20	60 % (2 h)[c]
7	 21	 22	69 % (10 h)[b]
8	 23	 24	79 % (1 h)[c]
9	 25	 26	< 5 % (10 h)[c]
10	 27	 28	36 % (10 h)[b]
11	 29	 30	– (24 h)[b]
12			< 5 % (5 h)[d]
13	 31	 32	93 % (3 h)[c]
14	 33	 34	- (10 h)[b]
15			58 % (3 h)[e]
16	 35	 36	73 % (15 min)[c]
17	 37	 38	< 5 % (4 h)[c]

[a] Reaction conditions: substrate (0.5 mmol), **5** (1 mol-%), DCM (50 mL, 0.01 M), 25 °C. [b] Starting material accounts for mass balance. [c] Polymerization product accounts for mass balance. [d] Reaction carried out at 80 °C in toluene using 5 mol-% of **3**; mass balance is decomposition. [e] Reaction performed at 40 °C; mass balance is decomposition.

Alder process was found parasitic and competitive (Entries 14 and 15). At this stage, we cannot explain why **35** provided mostly **36**, while **37** solely lead to polymerization (Entries 16 and 17). This could be due to the *endo*/*exo* conformation of **37** or to the presence of the ester function (amide analogue also gave polymers).[10] Reactions conducted under ethylene atmosphere allowed to slow the polymerization process, but only small quantities of the ring-opened product were isolated under these conditions.[10]

Table 3. Other substrates investigated in RRM.[a]

Entry	Substrate	Product	Yield (Time)
1	 39	 40	96 % (2 h)
2	 41	 42	93 % (15 min)
3	 43	 44	70 % (5 h)[b]
4	 45	 46	95 % (15 min)
5	 47	 48	57 % (30 min)[d]
6	49	50	48 % (*E*/*Z* > 20:1) (10 h)[b]
7	51	52	46 % (*E*/*Z* = 5:1) (10 h)[b]
8	53	54	– (10 h)[b]
9			47 % (5 h)[b,e]
10	55	56	31 % (15 min)[c]
11	57	58	35 % (3 h)[c]
12	59		– (24 h)[b]
13			– (24 h)[b,e]

[a] Reaction conditions: substrate (0.5 mmol), **5** (1 mol-%), DCM (50 mL, 0.01 M), 25 °C. [b] Starting material accounts for mass balance. [c] Polymer accounts for mass balance. [d] Reaction byproducts are an inseparable mixture of dimers of the starting material and of the expected product. [e] Reaction carried out at 80 °C in toluene using 5 mol-% of **3**.

Various other substrates were tested for RRM (Table 3). At room temperature, **5** afforded quantitatively the desired bicyclic product **40**, by opening the strained cyclobutene (Entry 1). RRM of cyclopentene derivatives leading to five- and six-membered rings took place smoothly (Entries 2–4). Nevertheless, in the case of cyclohexene **47**, dimerisation issues were encountered (Entry 5). Attempts to form thermodynamically disfavoured seven-membered ring led to the exclusive dimerisation of the starting materials (Entries 6 and 7). Bicyclic compound **53** did not react at 25 °C and heating to 80 °C using 5 mol-% of SIMes-containing **3** afforded its dimer (Entry 8 and 9), suggesting that the driving force behind the oxabicyclo[2.2.1]heptene RRM is the release of ring strain. More challenging substrates were also studied giving the expected products despite low yields and side polymerization (Entries 10 and 11). Whereas **43** gave, in a straightforward manner, the product **44** (Entry 3), the complete lack of reactivity of its analogue **59** suggests that the reaction may have adopted reaction pathway B of the postulated mechanism where the ruthenium carbene complex reacts first with the exocyclic double bond then with the *endo* double bond (Scheme 1). In spite of the fact that pathway A clearly explains the polymerization process, the second pathway explains the formation of dimeric species as side products. For these reasons the term ring-opening/ring-closing metathesis usually associated with RRM appears an oversimplification of the actual mechanism and only corresponds to the net and formal RRM transformation.

Conclusions

In summary, we have reported the use of ruthenium-indenylidene complexes in RRM. The selection of the sterically demanding NHC SIPr has proven to be beneficial and leads to attractive yields as a function of substrate structure. Thus, some RRM reactions could be carried out in only 15 min using 1 mol-% of catalyst **5**. Moreover, the sterically hindered SIPr allowed to improve the activity of the benzylidene-based catalyst and help close the gap in activity differences between the two types of alkylidene-bearing complexes. Whereas second generation Grubbs and Hoveyda–Grubbs complexes surpass SIMes-containing ruthenium-indenylidene **3**, the catalytic performance of their SIPr counterparts, **10** and **5**, are very similar. We believe the presented reaction scope provides insights into parameters governing the RRM and will facilitate its further development. Ongoing studies aimed at elucidating the reaction mechanism at play in this fascinating reaction sequence are being conducted in our laboratories.

Experimental Section

General Considerations: All reagents were used as received. Dichloromethane (DCM) and toluene were dispensed from a solvent purification system from Innovative Technology. Catalyst syntheses were performed in a MBraun glovebox containing dry argon and less than 1 ppm oxygen. Complexes **1** and **3** were generously provided by Umicore AG and complexes **2**, **4**, **5** and **10** were synthesized according the previously reported procedures.[7a,7e,13] Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded with a Bruker Avance 300 Ultrashield NMR spectrometer. High-Resolution Mass Spectroscopy (HRMS) analyses were performed on a Waters LCT Premier spectrometer. For the synthesis of substrates, see Supporting Information.

General Procedure for Metathesis Reaction: A Schlenk flask, under nitrogen, was charged with the substrate (0.5 mmol) and dry dichloromethane (5–50 mL, c = 0.1–0.01 M) the pre-catalyst (0.005 mmol) was then added. The progress of the reaction was monitored by TLC. The solvent was removed under vacuum and the crude was purified by flash column chromatography to yield the pure product.

(1*S*,3*R*,3a*R*,6a*S*)-5-Phenyl-3-vinyl-2′,3,3a,6′-tetrahydrospiro[furo-[3,4-*c*]pyrrole-1,3′-pyran]-4,6(5*H*,6a*H*)-dione (7): According to the general procedure for metathesis, the title compound was isolated as a colorless oil (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 [t, J(H,H) = 5.5 Hz, 2 H, H^{Ph}], 7.33 [t, J(H,H) = 5.5 Hz, 1 H, H^{Ph}], 7.19 [d, J(H,H) = 5.5 Hz, 2 H, H^{Ph}], 5.99 (m, 2 H, CH=CH and CH=CH_2), 5.77 [d, J(H,H) = 7.7 Hz, 1 H, CH_2=CH], 5.36 [dd, J(H,H) = 12.9 and 0.6 Hz, 1 H, CH=CH], 5.21 [d, J(H,H) = 7.8 Hz, 1 H, CH_2=CH], 4.80 (m, 1 H, CH-O), 4.15–4.02 (m, 2 H, CH_2-O), 3.91 [d, J(H,H) = 9.0 Hz, 1 H, CH_2-C], 3.76 [d, J(H,H) = 9.0 Hz, 1 H, CH_2-C], 3.50 [dd, J(H,H) = 6.8 and 3.5 Hz, 1 H, CH-CO], 3.35 [d, J(H,H) = 6.8 Hz, 1 H, CH-CO] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3 (C), 173.0 (C), 137.4 (CH), 131.5 (C), 130.3 (CH), 129.3 (CH), 128.9 (CH), 128.1 (CH), 126.4 (CH), 117.6 (CH_2), 80.7 (CH), 79.6 (C), 68.3 (CH_2), 65.0 (CH_2), 53.6 (CH), 52.8 (CH) ppm. HRMS (ESI): m/z: calcd. for $C_{18}H_{17}NO_4$ + Na: 334.1055 [M^+ + Na]; found 334.1043.

(1*S*,3*R*,3a*S*,6a*R*)-5-Phenyl-3-vinyl-2′,3,3a,6′-tetrahydrospiro[furo-[3,4-*c*]pyrrole-1,3′-pyran]-4,6(5*H*,6a*H*)-dione (12): According to the general procedure for metathesis, the title compound was isolated as a yellow oil (71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.29 (m, 3 H, H^{Ph}), 7.20–7.17 (m, 2 H, H^{Ph}), 6.00–5.87 (m, 2 H, CH=CH and CH=CH_2), 5.69 [d, J(H,H) = 10.5 Hz, 1 H, CH=CH], 5.42 [dt, J(H,H) = 17.0 and 1.3 Hz, 1 H, CH_2=CH], 5.27 [dt, J(H,H) = 10.5 and 1.1 Hz, 1 H, CH_2=CH], 4.68 [td, J(H,H) = 6.9 and 1.0 Hz, 1 H, CH-O], 4.16 [d, J(H,H) = 2.2 Hz, 2 H, CH-CH_2-O], 3.78 [d, J(H,H) = 10.9 Hz, 1 H, CH-CO], 3.62–3.56 (m, 2 H, C-CH_2-O), 3.51 [d, J(H,H) = 8.1 Hz, 1 H, CH-CO] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.2 (C), 174.1 (C), 133.1 (CH), 132.0 (C), 130.6 (CH), 129.6 (CH), 129.2 (CH), 126.8 (CH), 125.6 (CH), 118.8 (CH_2), 79.6 (CH), 77.9 (C), 70.8 (CH_2), 66.0 (CH_2), 53.5 (CH), 50.2 (CH) ppm. HRMS (ESI): m/z: calcd. for $C_{18}H_{17}NO_4$ + H: 312.1236 [M^+ + H]; found 312.1234.

(1*S*,3*R*,3a*R*,6a*S*)-5-Methyl-3-vinyl-2′,3,3a,6′-tetrahydrospiro[furo-[3,4-*c*]pyrrole-1,3′-pyran]-4,6(5*H*,6a*H*)-dione (14): According to the general procedure for metathesis, the title compound was isolated as a white solid (96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.91–5.89 (m, 2 H, CH=CH and CH=CH_2), 5.76 [dq, J(H,H) = 10.2 and 1.2 Hz, 1 H, CH=CH], 5.35 [d, J(H,H) = 17.2 Hz, 1 H, CH_2=CH], 5.21 [d, J(H,H) = 10.5 Hz, 1 H, CH_2=CH], 4.67 [tt, J(H,H) = 5.1 and 1.4 Hz, 1 H, CH-O], 4.09 [qt, J(H,H) = 17.1 and 2.2 Hz, 2 H, CH-CH_2-O], 3.83 [d, J(H,H) = 12.0 Hz, 1 H, CH-CO], 3.67 [dd, J(H,H) = 12.0 and 1.2 Hz, 1 H, C-CH_2-O], 3.39 [dd, J(H,H) = 8.9 and 4.8 Hz, 1 H, C-CH_2-O], 3.51 [d, J(H,H) = 8.9 Hz, 1 H, CH-CO], 2.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.6 (C), 174.5 (C), 138.0 (CH), 130.5 (CH), 128.5

(CH), 117.9 (CH_2), 80.9 (CH), 79.5 (C), 68.8 (CH_2), 65.3 (CH_2), 54.1 (CH), 52.9 (CH), 25.5 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{13}H_{15}NO_4$ + H: 250.1079 [M^+ + H]; found 250.1073.

(1*S*,3*R*,3a*S*,6a*R*)-5-Methyl-3-vinyl-2′,3,3a,6′-tetrahydrospiro[furo-[3,4-*c*]pyrrole-1,3′-pyran]-4,6(5*H*,6a*H*)-dione (16): According to the general procedure for metathesis, the title compound was isolated as a colorless oil (74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.97 [d, *J*(H,H) = 10.4 Hz, 1 H, C*H*=CH], 5.82 [ddd, *J*(H,H) = 17.0, 10.4 and 6.7 Hz, 1 H, CH_2=CH], 5.57 [d, *J*(H,H) = 10.4 Hz, 1 H, CH_2=CH], 5.35 [d, *J*(H,H) = 17.0 Hz, 1 H, C*H*-O], 5.24 [d, *J*(H,H) = 6.7 Hz, 1 H, C*H*-O], 4.57 [d, *J*(H,H) = 7.1 Hz, 1 H, C*H*-CH_2-O], 4.14 (s, 2 H, CH-CH_2-O), 3.73 [d, *J*(H,H) = 10.9 Hz, 1 H, C-CH_2-O], 3.56 [d, *J*(H,H) = 10.9 Hz, 1 H, C-CH_2-O], 3.44 [t, *J*(H,H) = 7.8 Hz, 1 H, C*H*-CO], 3.35 [d, *J*(H,H) = 7.8 Hz, 1 H, C*H*-CO], 2.91 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.2 (C), 175.1 (C), 133.0 (CH), 130.5 (CH), 125.6 (CH), 119.1 (CH_2), 79.4 (CH), 79.1 (C), 70.7 (CH_2), 65.9 (CH_2), 53.5 (CH), 50.4 (CH), 25.4 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{13}H_{15}NO_4$ + H: 250.1079 [M^+ + H]; found 250.1077.

(1*S*,3′*R*,3a′*R*,6a′*S*)-5′-Methyl-3′-vinyl-3′,3a′-dihydrospiro[cyclopent[2]ene-1,1′-furo[3,4-*c*]pyrrole]-4′,6′(5′*H*,6a′*H*)-dione (18): According to the general procedure for metathesis, the title compound was isolated as a colorless oil (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 [dt, *J*(H,H) = 5.6 and 2.4 Hz, 1 H, C*H*=CH], 5.92 [ddd, *J*(H,H) = 17.2, 10.5 and 5.8 Hz, 1 H, C*H*=CH_2], 5.57 [dt, *J*(H,H) = 5.6 and 2.1 Hz, 1 H, C*H*=CH], 5.35 [d, *J*(H,H) = 17.2 Hz, 1 H, CH_2=CH], 5.20 [d, *J*(H,H) = 10.5 Hz, 1 H, CH_2=CH], 4.50 [t, *J*(H,H) = 5.8 and 1.0 Hz, 1 H, C*H*-O], 3.34 (m, 2 H, CH_2-C-O), 2.93 (s, 3 H, CH_3), 2.49–2.27 (m, 2 H, CH-CH_2-CH_2), 2.10 [ddd, *J*(H,H) = 13.7, 8.1 and 4.6 Hz, 1 H, C*H*-CO], 1.77 [ddd, *J*(H,H) = 13.7, 8.1 and 4.6 Hz, 1 H, C*H*-CO] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.1 (C), 176.1 (C), 137.6 (CH), 136.7 (CH), 134.2 (CH), 117.9 (CH_2), 96.3 (C), 80.3 (CH), 54.3 (CH), 53.1 (CH), 32.7 (CH_2), 31.8 (CH_2), 25.3 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for for $C_{13}H_{15}NO_3$ + H: 234.1130 [M^+ + H]; found 234.1132.

(1*S*,3′*R*,3a′*S*,6a′*R*)-5′-Methyl-3′-vinyl-3′,3a′-dihydrospiro[cyclopent[2]ene-1,1′-furo[3,4-*c*]pyrrole]-4′,6′(5′*H*,6a′*H*)-dione (20): Following the general procedure for metathesis, the title compound was isolated as a colorless oil (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.11 [dt, *J*(H,H) = 5.7 and 2.3 Hz, 1 H, C*H*=CH], 5.84 [ddd, *J*(H,H) = 17.1, 10.4 and 6.8 Hz, 1 H, C*H*=CH_2], 5.62 [dt, *J*(H,H) = 5.7 and 2.3 Hz, 1 H, C*H*=CH], 5.35 [dt, *J*(H,H) = 17.1 and 1.2 Hz, 1 H, CH_2=CH], 5.24 [dt, *J*(H,H) = 10.4 and 1.2 Hz, 1 H, CH_2=CH], 4.48 [t, *J*(H,H) = 7.2 Hz, 1 H, C*H*-O], 3.39 [t, *J*(H,H) = 7.6 Hz, 1 H, CH_2-C-O], 3.16 [d, *J*(H,H) = 7.6 Hz, 1 H, CH_2-C-O], 2.90 (s, 3 H, CH_3), 2.49–2.41 (m, 2 H, CH-CH_2-CH_2), 2.10–2.01 (m, 1 H, C*H*-CO), 1.96–1.88 (m, 1 H, C*H*-CO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.6 (C), 175.1 (C), 137.3 (CH), 132.8 (CH), 130.0 (CH), 118.8 (CH_2), 95.3 (C), 78.7 (CH), 54.8 (CH), 50.2 (CH), 36.9 (CH_2), 31.1 (CH_2), 25.0 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{13}H_{15}NO_3$ + H: 234.1130 [M^+ + H]; found 234.1136.

(1*S*,3*R*,3a*R*,6a*S*)-5-Phenyl-1′-tosyl-3-vinyl-2′,3,3a,6′-tetrahydro-1′*H*-spiro[furo[3,4-*c*]pyrrole-1,3′-pyridine]-4,6(5*H*,6a*H*)-dione (22): Following the general procedure for metathesis, the title compound was isolated as a white solid (69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 [d, *J*(H,H) = 8.2 Hz, 2 H, H^{Ts}], 7.43–7.34 (m, 3 H, H^{Ph}), 7.23–7.19 (m, 4 H, H^{Ph} and H^{Ts}), 5.97–5.86 (m, 1 H, C*H*=CH_2), 5.83–5.79 (m, 1 H, C*H*=CH), 5.68 [d, *J*(H,H) = 10.1 Hz, 1 H, C*H*=CH], 5.33 [d, *J*(H,H) = 17.2 Hz, 1 H, CH_2=CH], 5.20 [d, *J*(H,H) = 10.4 Hz, 1 H, CH_2=CH], 4.78 [t, *J*(H,H) = 5.1 Hz, 1 H, C*H*-O], 3.89–3.83 (m, 1 H, CH_2-NTs), 3.66 [d, *J*(H,H) = 12.4 Hz, 1 H, CH_2-NTs] 3.51 [dd, *J*(H,H) = 9.2 and 5.2 Hz, C*H*-CO], 3.36 [d, *J*(H,H) = 9.2 Hz, 1 H, C*H*-CO], 3.17 [d, *J*(H,H) = 17.2 Hz, 1 H, CH_2-NTs], 3.02 [d, *J*(H,H) = 12.4 Hz, 1 H, CH_2-NTs], 2.32 (s, 3 H, CH_3^{Ts}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3 (C), 173.4 (C), 144.3 (C), 137.6 (CH), 133.5 (C), 131.8 (C), 130.2 (CH), 129.7 (CH), 129.4 (CH), 129.2 (CH), 128.2 (CH), 127.5 (CH), 126.9 (CH), 118.2 (CH_2), 80.1 (CH), 80.7 (C), 54.8 (CH), 53.0 (CH), 48.2 (CH_2), 44.7 (CH_2), 22.0 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{25}H_{24}N_2O_5S$ + Na: 487.1304 [M^+ + Na]; found 487.1296.

(1*S*,3′*R*,3a′*R*,6a′*S*)-3′-Vinyl-3′*H*-spiro[cyclohept[2]ene-1,1′-furo[3,4-*c*]furan]-4′,6′(3a′*H*,6a′*H*)-dione (24): Following the general procedure for metathesis, the title compound was isolated as a colorless oil (79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.97–5.86 (m, 2 H, C*H*=CH_2 and C*H*=CH), 5.53 [dd, *J*(H,H) = 11.6 and 1.1 Hz, 1 H, C*H*=CH], 5.38 [dt, *J*(H,H) = 17.2 and 1.0 Hz, 1 H, CH_2=CH], 5.22 [dt, *J*(H,H) = 11.3 and 1.0 Hz, 1 H, CH_2=CH], 4.67–4.63 (m, 1 H, C*H*-CH=CH_2), 3.56 (s, 2 H, C*H*-CO), 2.23–2.06 (m, 2 H, CH_2), 1.91–1.64 (m, 5 H, CH_2), 1.57–1.50 (m, 1 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8 (C), 168.7 (C), 136.5 (CH), 136.2 (CH), 134.0 (CH), 118.4 (CH_2), 87.7 (C), 80.5 (CH), 59.0 (CH), 53.5 (CH), 31.6 (CH_2), 27.0 (CH_2), 26.3 (CH_2), 23.0 (CH_2) ppm.

(1*S*,4*R*)-Diisopropyl 1-{(*E*)-8-[(1*R*,4*S*)-2,3-Bis(isopropoxycarbonyl)-7-oxa-2,3-diazabicyclo[2.2.1]hept-5-en-1-yl]oct-4-enyl}-7-oxa-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (28): According the general procedure for metathesis, the title compound was isolated as a yellow oil (36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.98 (s br, 2 H, C*H*=CH), 6.11 (s br, 2 H, C*H*=CH), 5.88 [d, *J*(H,H) = 3.1 Hz, 2 H, C*H*-O], 5.34–5.32 (m, 2 H, C*H*=CH), 4.94–4.86 [m, 4 H, C*H*(CH_3)$_2$], 2.49 [t, *J*(H,H) = 7.6 Hz, 4 H, C-CH_2], 1.97–1.93 (m, 4 H, CH-CH_2), 1.60 [quint, *J*(H,H) = 7.1 Hz, 4 H, CH_2-C*H*-CH_2], 1.20 [d, *J*(H,H) = 7.1 Hz, 12 H, CH(CH_3)$_2$], 1.17 [d, *J*(H,H) = 7.1 Hz, 12 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (C), 145.4 (C), 130.6 (CH), 130.1 (CH), 106.8 (CH), 105.4 (CH), 71.8 (CH), 70.4 (CH), 32.2 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 22.4 (CH_3), 22.2 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{32}H_{48}N_4O_{10}$ + Na: 671.3268 [M^+ + Na]; found 671.3260.

(1*S*,3*R*,3a*R*,6a*S*)-5-Phenyl-3-[(*E*)-prop-1-enyl]-2′,3,3a,6′-tetrahydrospiro[furo[3,4-*c*]pyrrole-1,3′-pyran]-4,6(5*H*,6a*H*)-dione (32): According to the general procedure for metathesis, the title compound was isolated as a white solid (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.29 (m, 3 H, H^{Ph}), 7.26–7.14 (m, 2 H, H^{Ph}), 5.93 [dt, *J*(H,H) = 10.2 and 2.3 Hz, 1 H, C-C*H*=CH], 5.84–5.75 (m, 2 H, Me-C*H*=CH and C*H*=CH-C), 5.51 [ddq, *J*(H,H) = 15.2, 6.8 and 1.6 Hz, 1 H, C*H*=CH-Me], 4.61 [t, *J*(H,H) = 5.8 Hz, 1 H, C*H*-O], 4.05 [qt, *J*(H,H) = 9.2 and 2.4 Hz, 2 H, CH-CH_2-O], 3.89 [d, *J*(H,H) = 11.9 Hz, 1 H, C*H*-CO], 3.75 [dd, *J*(H,H) = 11.9 and 0.7 Hz, 1 H, C*H*-CO], 3.43 [dd, *J*(H,H) = 9.2 and 4.9 Hz, 1 H, C-CH_2-O], 3.35 [d, *J*(H,H) = 9.2 Hz, 1 H, C-CH_2-O], 1.67 [dd, *J*(H,H) = 6.5 and 0.8 Hz, 1 H, CH_3] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3 (C), 173.0 (C), 131.5 (C), 130.5 (CH), 130.1 (CH), 129.8 (CH), 129.5 (CH), 129.3 (CH), 128.8 (CH), 128.0 (CH), 126.4 (CH), 80.8 (CH), 79.2 (C), 68.0 (CH_2), 65.0 (CH_2), 53.9 (CH), 53.1 (CH), 17.8 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{19}H_{19}NO_4$ + Na: 348.1212 [M^+ + Na]; found 348.1201.

Dispiro Compound 34: Following the general procedure for metathesis, the title compound was isolated as a white solid (58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.46 (m, 2 H, H^{Ph}), 7.44–7.39 (m, 1 H, H^{Ph}), 7.34–7.30 (m, 2 H, H^{Ph}), 5.99 [dt, *J*(H,H) = 10.2 and 3.6 Hz, 2 H, CH_2-C*H*=CH], 5.66 [dt, *J*(H,H) = 10.2 and 2.0 Hz, 2 H, C-C*H*=CH], 3.51 (s, 2 H, C*H*-CO), 2.13–2.07 (m, 4 H, CH_2), 2.03–1.96 (m, 4 H, CH_2) 1.92–1.81 (m, 4 H, CH_2) ppm. ^{13}C NMR

(75 MHz, $CDCl_3$): δ = 174.0 (C), 131.9 (CH), 131.7 (C), 129.1 (CH), 128.6 (CH), 128.3 (CH), 126.2 (CH), 83.5 (C), 57.2 (CH), 39.1 (CH_2), 24.5 (CH_2), 19.7 (CH_2) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{22}H_{24}NO_3$ + H: 350.1756 [M^+ + H]; found 350.1755.

1,5a,6,6a,9,11,11a,11b-Octahydro-3*H*-oxepino[4′,3′:4,5]cyclopenta-[1,2-*c*]oxepine (36):[6a] Following the general procedure for metathesis, the title compound was isolated as a colorless oil (73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.51 [ddt, *J*(H,H) = 12.3, 4.8 and 2.0 Hz, 2 H, CH-C*H*=CH], 5.34–5.27 (m, 2 H, CH=C*H*-CH_2), 4.20 [ddt, *J*(H,H) = 17.0, 3.5 and 2.0 Hz, 2 H, CH=CH-CH_2-O], 4.20 [dq, *J*(H,H) = 17.0 and 2.4 Hz, 2 H, CH=CH-CH_2-O], 3.81 [dd, *J*(H,H) = 12.2 and 3.7 Hz, 2 H, CH-CH_2-O], 3.48 [dd, *J*(H,H) = 12.9 and 9.3 Hz, 2 H, CH-CH_2-O], 2.78–2.71 (m, 2 H, C*H*-CH_2-C*H*), 2.58–2.50 (m, 2 H, CH_2-C*H*-C*H*-CH_2), 2.15 [dt, *J*(H,H) = 12.2 and 7.3 Hz, 1 H, CH-CH_2-CH], 1.33 [q, *J*(H,H) = 12.2 Hz, 1 H, CH-CH_2-CH] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.9 (CH), 126.4 (CH), 71.2 (CH_2), 69.5 (CH_2), 47.0 (CH), 41.6 (CH_2), 41.4 (CH_2) ppm.

(2*R*,2′*S*)-5,5′,6,6′-Tetrahydro-2*H*,2′*H*-2,2′-bipyran (40):[6a] Following the general procedure for metathesis, the title compound was isolated as a yellow oil (96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.92–5.87 (m, 2 H, C*H*=CH), 5.70–5.65 (m, 2 H, CH=C*H*), 4.09 [d, *J*(H,H) = 1.1 Hz, 2 H, C*H*-O], 4.00 [dd, *J*(H,H) = 11.2 and 5.5 Hz, 2 H, CH_2], 3.62 [dt, *J*(H,H) = 10.6 and 3.8 Hz, 2 H, CH_2], 2.35–2.23 (m, 2 H, CH_2), 1.88–1.81 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 126.51 (CH), 126.49 (CH), 76.2 (CH), 64.1 (CH_2), 25.2 (CH_2) ppm.

2-Methyl-3-(pent-4-enyl)-2-phenyl-2,5-dihydrofuran (42): Following the general procedure for metathesis, the title compound was isolated as a colorless oil (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.22 (m, 4 H, H^{Ph}), 7.19–7.16 (m, 1 H, H^{Ph}), 5.70–5.62 (m, 1 H, C*H*=CH_2), 5.46 [t, *J*(H,H) = 1.7 Hz, 1 H, C*H*=C], 4.90–4.82 (m, 2 H, CH_2=CH), 4.72 (m, 2 H, CH_2-O), 1.98–1.90 (m, 2 H, CH_2), 1.88–1.81 (m, 1 H, CH_2), 1.67–1.64 (m, 1 H, CH_2), 1.60 (s, 3 H, CH_3^{Me}) 1.52–1.39 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.1 (C), 145.3 (C), 138.4 (CH), 128.1 (CH), 127.1 (CH), 125.7 (CH), 118.0 (CH), 114.8 (CH_2), 91.4 (C), 73.9 (CH_2), 33.4 (CH_2), 26.9 (CH_2), 25.7 (CH_2), 24.2 (CH_2) ppm.

3-(Pent-4-enyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (44): Following the general procedure for metathesis, the title compound was isolated as a colorless oil (70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 [d, *J*(H,H) = 8.0 Hz, 2 H, H^{Ar}], 7.33 [d, *J*(H,H) = 8.0 Hz, 2 H, H^{Ar}], 5.81–5.67 (m, 1 H, C*H*=CH_2), 5.28–5.25 (m, 1 H, C*H*=C), 5.00–4.94 (m, 2 H, CH=CH_2), 4.11–4.07 (m, 2 H, CH-CH_2-N), 4.02–3.97 (m, 2 H, C-CH_2-N), 2.43 (s, 3 H, CH_3), 1.98 [q, *J*(H,H) = 7.0 Hz, 4 H, CH_2], 1.47 [quint, *J*(H,H) = 7.6 Hz, 4 H, CH_2] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4 (C), 139.4 (C), 138.0 (CH), 134.2 (C), 129.8 (CH), 127.4 (CH), 118.1 (CH), 115.0 (CH_2), 56.5 (CH_2), 55.1 (CH_2), 33.2 (CH_2), 27.9 (CH_2), 26.3 (CH_2), 21.5 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{16}H_{21}O_2$ + Na: 314.1191 [M^+ + Na]; found 314.1182.

5-(Pent-4-enyl)-1-tosyl-1,2,3,6-tetrahydropyridine (46): Following the general procedure for metathesis, the title compound was isolated as a colorless oil (95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 [d, *J*(H,H) = 8.0 Hz, 2 H, H^{Ar}], 7.25 [d, *J*(H,H) = 8.0 Hz, 2 H, H^{Ar}], 5.76–5.62 (m, 1 H, C*H*=CH_2), 5.37 (s br, 1 H, C*H*=C), 4.94–4.88 (m, 2 H, CH=CH_2), 3.76 [d, *J*(H,H) = 2.0 Hz, 1 H, C-CH_2-N], 3.04 [t, *J*(H,H) = 5.7 Hz, 2 H, CH_2-CH_2-N], 2.36 (s, 3 H, CH_3), 2.13–2.08 (m, 2 H, CH_2), 1.97–1.83 (m, 4 H, CH_2), 1.44–1.34 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.5 (C), 138.3 (CH), 133.8 (C), 133.3 (C), 129.7 (CH), 127.7 (CH), 119.0 (CH), 114.9 (CH_2), 47.2 (CH_2), 42.8 (CH_2), 34.1 (CH_2), 33.3 (CH_2), 26.7 (CH_2), 25.1 (CH_2), 21.6 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{17}H_{23}O_2$ + Na: 328.1335 [M^+ + Na]; found 328.1347.

3-(Hex-5-enyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (48): Following the general procedure for metathesis, the title compound was isolated as a white solid (57%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 [d, *J*(H,H) = 8.2 Hz, 2 H, H^{Ar}], 7.24 [d, *J*(H,H) = 8.2 Hz, 2 H, H^{Ar}], 5.74–5.60 (m, 1 H, C*H*=CH_2), 5.19–5.15 (m, 1 H, C*H*=C), 4.93–4.84 (m, 2 H, CH=CH_2), 4.03–3.98 (m, 2 H, CH-CH_2-N), 3.94–3.90 (m, 2 H, C-CH_2-N), 2.35 (s, 3 H, CH_3), 1.97–1.89 (m, 4 H, CH_2), 1.33–1.20 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4 (C), 139.6 (C), 138.5 (CH), 134.2 (C), 129.8 (CH), 127.4 (CH), 118.0 (CH), 114.6 (CH_2), 56.5 (CH_2), 55.1 (CH_2), 33.4 (CH_2), 28.5 (CH_2), 28.4 (CH_2), 26.6 (CH_2), 21.6 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{17}H_{23}NO_2S$ + Na: 328.1347 [M^+ + Na]; found 328.1341.

***N*,*N*′-(But-2-ene-1,4-diyl)bis[*N*-(cyclohex-3-enylmethyl)-4-methylbenzenesulfonamide] (50):** Following the general procedure for metathesis, the title compound was isolated as a white solid (48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 [d, *J*(H,H) = 8.0 Hz, 4 H, H^{Ts}], 7.22 [d, *J*(H,H) = 8.0 Hz, 4 H, H^{Ts}], 5.62–5.51 (m, 4 H, C*H*=CH^{Cy}), 5.28–5.27 (m, 2 H, C*H*=C*H*), 3.60 [d, *J*(H,H) = 4.7 Hz, 4 H, CH_2-CH-CH_2], 2.86 [d, *J*(H,H) = 7.4 Hz, 4 H, CH_2-CH=CH], 2.35 (s, 3 H, CH_3^{Ts}), 2.03–1.91 (m, 6 H, CH_2), 1.87–1.60 (m, 6 H, CH_2), 1.18–1.04 (m, 2 H, C*H*-CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.3 (C), 136.8 (C), 133.2 (CH), 129.7 (CH), 129.4 (CH), 127.2 (CH), 127.1 (CH), 125.5 (CH), 52.9 (CH_2), 49.7 (CH_2), 32.0 (CH), 29.3 (CH_2), 26.1 (CH_2), 24.5 (CH_2), 21.5 (CH_3) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{32}H_{42}N_2O_4S_2$ + Na: 605.2484 [M^+ + Na]; found 605.2479.

Bis(cyclopentenylmethyl) Oct-4-ene-1,8-dioate (52): According to the general procedure for metathesis, the title compound was isolated as a colorless oil (46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.60–5.57 (m, 2 H, C*H*=C), 5.42–5.39 (m, 2 H, C*H*=C*H*), 4.56 [d, *J*(H,H) = 1.0 Hz, 2 H, CH_2-O], 2.35–2.20 (m, 16 H, CH_2), 1.90–1.85 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.9 (C), 139.1 (C), 129.5 (CH), 129.0 (C), 128.6 (CH), 63.2 (CH_2), 34.2 (CH_2), 32.9 (CH_2), 32.4 (CH_2), 27.9 (CH_2), 23.3 (CH_2) ppm. HRMS (ESI): *m*/*z*: calcd. for $C_{20}H_{28}O_4$ + Na: 355.1885 [M^+ + Na]; found 355.1872.

7,7′-[But-2-ene-1,4-diylbis(oxy)]bis(methylene)bis[4-methyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione] (54): According to the general procedure for metathesis, the title compound was isolated as a white solid (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 [dd, *J*(H,H) = 14.3 and 1.6 Hz, 2 H, OCH_2-C*H*=C*H*-OCH_2], 7.42–7.30 (m, 6 H, H^{Ph}), 7.12–7.07 (m, 4 H, H^{Ph}), 5.55 [dt, *J*(H,H) = 10.0 and 2.0 Hz, 1 H, C*H*=CH], 5.41 [dt, *J*(H,H) = 10.0 and 2.8 Hz, 1 H, C*H*=CH], 4.38–4.25 (m, 4 H, CH_2-O), 3.41 [t, *J*(H,H) = 8.9 Hz, 2 H, CH_2-O], 3.14–3.06 (m, 2 H, C*H*-CH-CO), 2.97 [dd, *J*(H,H) = 10.3 and 8.2 Hz, 2 H, CH-C*H*-CO], 2.52–2.44 (m, 2 H, C*H*-CH-CO), 2.20 [dd, *J*(H,H) = 10.3 and 8.6 Hz, 2 H, CH-C*H*-CO], 1.55 [dd, *J*(H,H) = 6.8 and 1.6 Hz, 4 H, CH_2-O], 0.86 [d, *J*(H,H) = 7.2 Hz, 6 H, CH_3-CH] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.1 (C), 170.4 (C), 138.9 (C), 135.1 (CH), 129.6 (CH), 129.2 (CH), 128.7 (CH), 128.2 (CH), 111.0 (CH), 71.6 (CH_2), 41.7 (CH), 41.2 (CH), 35.6 (CH), 33.4 (CH), 19.6 (CH_3), 15.3 (CH_3) ppm.

2-Tosyl-1,2,3,4,5,6-hexahydrocyclohepta[*c*]pyrrole (56):[6e] According to the general procedure for metathesis, the title compound was isolated as a yellow solid (31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 [d, *J*(H,H) = 8.3 Hz, 2 H, H^{Ar}], 7.25 [d, *J*(H,H) = 8.3 Hz, 2 H, H^{Ar}], 5.76 [dt, *J*(H,H) = 11.3 and 5.5 Hz, 1 H, CH_2-C*H*=CH], 5.45 [d, *J*(H,H) = 11.3 Hz, 1 H, C-C*H*=CH], 4.03 (s, 4 H, CH_2-N),

2.36 (s, 3 H, CH_3), 2.23 [q, J(H,H) = 5.9 Hz, 2 H, CH_2], 2.13 [t, J(H,H) = 5.9 Hz, 2 H, CH_2], 1.70 [quint, J(H,H) = 5.9 Hz, 2 H, CH_2-CH_2-CH_2] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4 (C), 134.8 (CH), 134.3 (C), 134.1 (C), 129.8 (CH), 127.6 (CH), 127.3 (C), 120.5 (CH), 59.8 (CH_2), 58.5 (CH_2), 30.6 (CH_2), 29.5 (CH_2), 23.4 (CH_2), 21.6 (CH_3) ppm.

3-[3-(Prop-1-en-2-yl)hex-5-enyl]-1-tosyl-2,5-dihydro-1*H*-pyrrole (58): Following the general procedure for metathesis, the title compound was isolated as a white solid (35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 [d, J(H,H) = 8.2 Hz, 2 H, H^{Ts}], 7.24 [d, J(H,H) = 8.2 Hz, 2 H, H^{Ts}], 5.63–5.52 (m, 1 H, CH=CH_2), 5.17–5.16 (m, 1 H, CH=C), 4.94–4.90 (m, CH_2=C), 4.88–4.87 (m, 1 H, CH_2=C), 4.68–4.66 (m, 1 H, CH_2=CH), 4.54–4.43 (m, 1 H, CH_2=CH), 4.02–3.99 (m, 2 H, CH_2-NTs), 3.91–3.89 (m, 2 H, CH_2-NTs), 2.35 (s, 3 H, CH_3^{Ts}), 2.00–1.78 (m, 5 H, CH_2-CH_2-CH and CH_2-CH), 1.49 (s, 3 H, CH_3-C=CH_2), 1.40–1.30 (m, 2 H, CH_2-CH_2-CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7 (C), 143.8 (C), 140.0 (C), 137.3 (CH), 134.7 (C), 130.1 (CH), 127.9 (CH), 118.3 (CH), 116.0 (CH_2), 112.6 (CH_2), 56.9 (CH_2), 55.5 (CH_2), 47.0 (CH), 38.5 (CH_2), 30.2 (CH_2), 26.8 (CH_2), 21.9 (CH_3), 18.7 (CH_3) ppm. HRMS (ESI): m/z: calcd. for $C_{20}H_{27}NO_2S$ + H: 346.1841 [M^+ + H]; found 346.1854.

Supporting Information (see also the footnote on the first page of this article): Synthetic procedures, additional catalytic results and compound characterization details.

Acknowledgments

We are grateful to the European Commission (EC) for funding through the FP7 (CP-FP 211468-2-EUMET). We acknowledge Umicore AG for gift of materials and also Mrs. Caroline Horsburgh for HRMS analyses.

[1] For reviews on metathesis, see: a) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140–3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3013–3043; b) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29; c) *Handbook of Metathesis* (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, p. 1204; d) P. H. Deshmukh, S. Blechert, *Dalton Trans.* **2007**, 2479–2491; e) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708–3742.

[2] a) M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565–1604; b) C. Slugovc, *Macromol. Rapid Commun.* **2004**, *25*, 1283–1297.

[3] a) S. K. Chattopadhyay, S. Karmakar, T. Biswas, K. C. Majumdar, H. Rahaman, B. Roy, *Tetrahedron* **2007**, *63*, 3919–3952; b) S. T. Diver, *Coord. Chem. Rev.* **2007**, *251*, 671–701; c) M. Mori, *Adv. Synth. Catal.* **2007**, *349*, 121–135.

[4] S. J. Connon, S. Blechert, *Angew. Chem.* **2003**, *115*, 1944–1968; *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923.

[5] N. Holub, S. Blechert, *Chem. Asian J.* **2007**, *2*, 1064–1082.

[6] For selected references, see: a) W. J. Zuercher, M. Hashimoto, R. H. Grubbs, *J. Am. Chem. Soc.* **1996**, *118*, 6634–6640; b) R. Stragies, S. Blechert, *Synlett* **1998**, 169–171; c) S. N. Osipov, N. M. Kobelíkova, G. T. Shchetnikov, A. F. Kolomiets, C. Bruneau, P. H. Dixneuf, *Synlett* **2001**, 621–622; d) L. C. Usher, M. Estrella-Jimenez, I. Ghiviriga, D. L. Wright, *Angew. Chem. Int. Ed.* **2002**, *41*, 4560–4562; e) T. Kitamura, Y. Kuzuba, Y. Sato, H. Wakamatsu, R. Fujita, M. Mori, *Tetrahedron* **2004**, *60*, 7375–7389; f) J. Holtsclaw, M. Koreeda, *Org. Lett.* **2004**, *6*, 3719–3722; g) C. K. Malik, S. Ghosh, *Org. Lett.* **2007**, *9*, 2537–2540; h) G. Barbe, A. B. Charette, *J. Am. Chem. Soc.* **2008**, *130*, 13873–13874; i) J. A. Herderson, A. J. Phillips, *Angew. Chem. Int. Ed.* **2008**, *47*, 4899–4902.

[7] a) J. Huang, H. J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 2370–2375; b) A. Fürstner, O. R. Thiel, L. Ackermann, H. J. Schanz, S. P. Nolan, *J. Org. Chem.* **2000**, *65*, 2204–2207; c) H. Clavier, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 8029–8036; d) F. Boeda, X. Bantreil, H. Clavier, S. P. Nolan, *Adv. Synth. Catal.* **2008**, *350*, 2959–2966; e) H. Clavier, C. A. Urbina-Blanco, S. P. Nolan, *Organometallics* **2009**, *28*, 2848–2854; f) For use of late transition-metal complexes bearing NHC ligands in catalysis, see: S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612–3676.

[8] a) A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor, R. Mynott, *Chem. Eur. J.* **2001**, *7*, 4811–4820; b) E. A. Shaffer, C. L. Chen, A. M. Beatty, E. J. Valente, H. J. Schanz, *J. Organomet. Chem.* **2007**, *692*, 5221–5233; c) S. Monsaert, R. Drozdzak, V. Dragutan, I. Dragutan, F. Verpoort, *Eur. J. Inorg. Chem.* **2008**, 432–440; d) S. Monsaert, E. De Canck, R. Drozdzak, P. Van Der Voort, F. Verpoort, J. C. Martins, P. M. S. Hendrickx, *Eur. J. Inorg. Chem.* **2009**, 655–665.

[9] For a review on ruthenium-indenylidene complexes, see: F. Boeda, H. Clavier, S. P. Nolan, *Chem. Commun.* **2008**, 2726–2740.

[10] For details see the Supporting Information.

[11] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[12] a) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179; b) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973–9976.

[13] a) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236–3253; b) M. B. Dinger, J. C. Mol, *Adv. Synth. Catal.* **2002**, *344*, 671–677.

[14] F. C. Courchay, J. C. Sworen, K. B. Wagener, *Macromolecules* **2003**, *36*, 8231–8239.

[15] H. Clavier, F. Caijo, E. Borré, D. Rix, F. Boeda, S. P. Nolan, M. Mauduit, *Eur. J. Org. Chem.* **2009**, 4254–4265.

[16] D. Fischer, S. Blechert, *Adv. Synth. Catal.* **2005**, *347*, 1329–1332.

Received: November 17, 2009
Published Online: December 22, 2009

