Olefin metathesis reactions of sulfur-containing alkenes and dienes

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Dedicated to Professor Siegfried Blechert on the occasion of his 65th birthday

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Abstract

The olefin metathesis reaction of sulfur-containing olefins is a challenging transformation. However, these molecules are valuable in organic synthesis. In this article the reactivity of sulfides, sulfones and sulfoxides in olefin metathesis reactions is discussed.

Keywords: Olefin metathesis, ruthenium, sulfur, fluorinated aromatic hydrocarbons

Introduction

Since 1995, when the first well-defined ruthenium carbene complexes such as **1a** were introduced by Grubbs (Figure 1), olefin metathesis has become a routine process in the manipulation of C-C double bonds.[1] Further improvements of ruthenium pre-catalysts structure,[2] namely the exchange of the one phosphine ligand with an *N*-heterocyclic carbene, leads to the so-called 'second generation' complexes **1b** and **1c**.[3] Subsequently, a second generation phosphine free ruthenium complex[4a] was independently synthesized by Blechert and Hoveyda **1d**.[4] Afterwards, highly active counterparts of complex **1d** were synthesized by Blechert **1e** (activated *via* steric interactions)[5a] and Grela **1f** (activated *via* electronic interactions).[5b,c] Nowadays, olefin metathesis has emerged as a versatile and powerful tool for target oriented organic synthesis as well as in material science.[1] Ruthenium-based pre-catalysts display a high functional group tolerance and satisfactory to excellent air and thermodynamic stability (Figure 1). However, further research aimed at developing of new catalysts of improved stability and/or activity is of vital importance. Besides evolutionary improvements of the catalyst structure, research aimed at finding some new reaction conditions that allow more optimal use of known catalysts can be considered as a complementary approach.[6] Cross-metathesis (CM),[7] ring closing metathesis (RCM),[1] enyne metathesis and their combinations are commonly used reactions to form C-C double bonds of highly sophisticated molecules.[1]

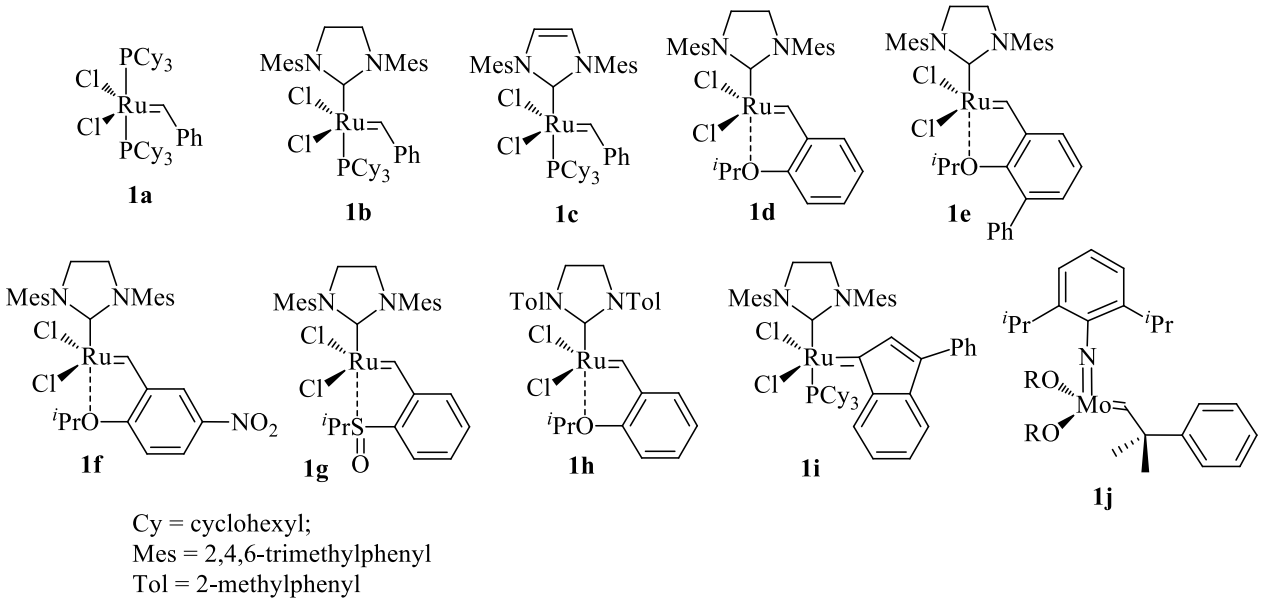
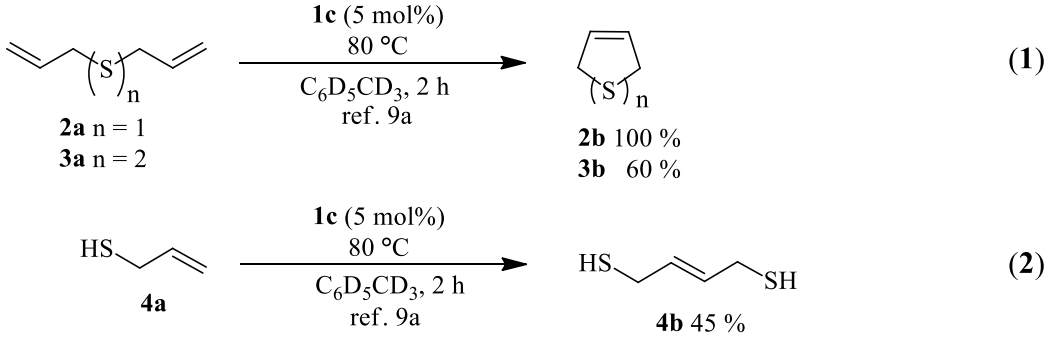


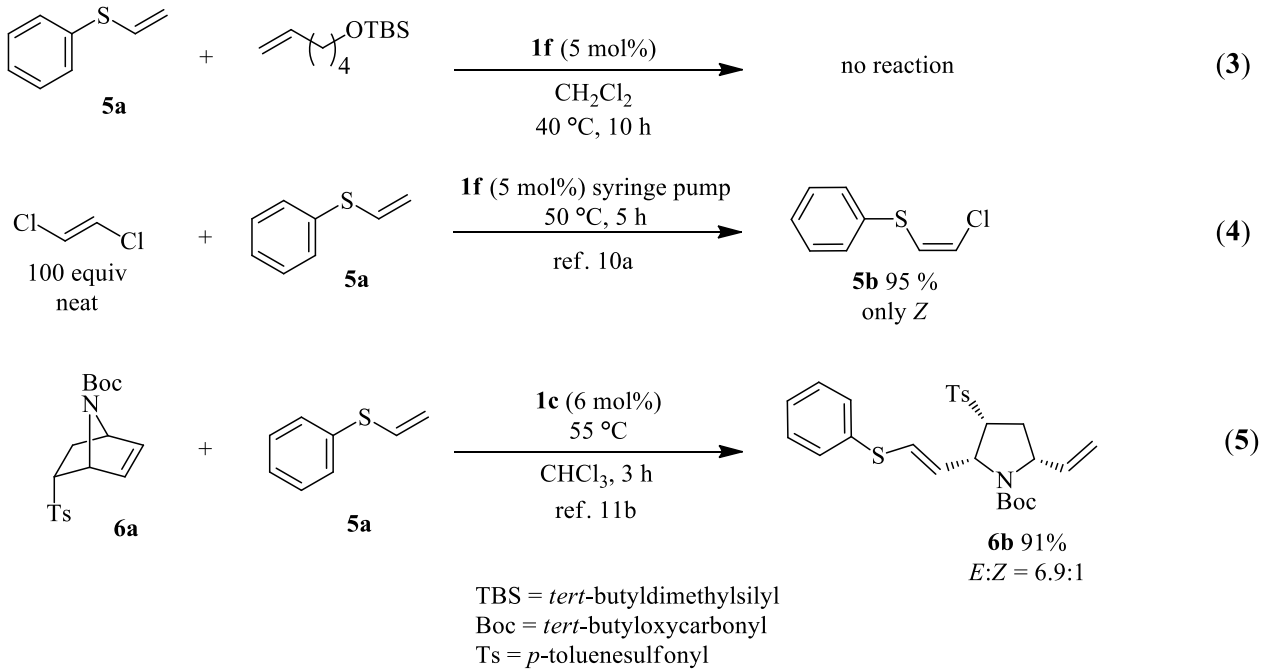
Figure 1. Olefin metathesis ruthenium and molybdenium based (pre)catalysis.

Results and Discussion

Sulfides and thiols. Several sulfur-containing alkenes have been applied as substrates in olefin metathesis reactions. The 'first generation' ruthenium pre-catalysts, such as **1a** are known to be poorly or not reactive in the RCM of α,ω-dienes containing sulfide and disulfide moieties,[8a-c] whereas Schrock's molybdenum complex **1j** was found to be more compatible with these substrates.[8d-f] Later, Nolan and Mioskowski *et al*., have published an elegant study to show that the 'second generation' pre-catalyst **1c** acts in such transformations extremely well, and can be successfully employed in RCM and CM of allyl substituted sulfides **2a** (equation 1), disulfides **3a** (equation 1), and dithianes, and even in the self-cross metathesis reaction of thiols **4a** (equation 2).[9a] Allyl sulfides participate in olefin metathesis reaction catalyzed by ruthenium based complexes, and thus have found applications in the site selective modification of proteins *via* CM reactions performed in water.[9b]

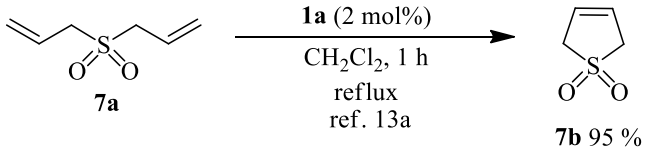


On the other hand, vinyl sulfides are electron rich alkenes that usually do not participate in olefin metathesis reactions due to the formation of Fischer type carbenes.[1a] We tested the CM reaction of phenyl vinyl sulfide **5a** with our standard CM reaction partner (5-hexenyl *tert*-butyldimethylsilyl ether) in the presence of the very active ruthenium catalyst **1f**. Despite many attempts, we found that this reaction indeed does not proceed (equation 3). This result was quite surprising, because we had observed previously that vinyl sulfides participate in CM reactions with vinyl halides (equation 4). CM of **5a** performed in neat (*E*)-1,2-dichloroethene catalyzed by 5 mol% of the highly active complex **1f** lead to the desired sulfide **5b** with excellent (*Z*)-diastereocontrol (equation 4).[10] It is worth to mention that the use of (*Z*)-1,2-dichloroethene, instead of the (*E*) isomer, causes a drop in selectivity and isolated yield.[10a] The reaction works perfectly well when the catalyst is added portion-wise *via* a syringe pump over 5 h (95% isolated yield of **5b**). Recently vinyl sulfides were used in ring-opening/cross-metathesis sequence[10] (equation 5). In this reaction the ring strain of 7-azanorbornene derivative **6a** is a driving force for the reaction with **5a**, which proceeds in very high yield (equation 5).[11] Ring-opening/cross-metathesis reaction and ring rearrangement metathesis have been intensely studied in the Blechert laboratories.[1e] An excellent review, presenting many outstanding target-oriented syntheses in this area, was recently published by Blechert *et al*.[12] These results show that while vinyl sulfides can actually participate in some CM reactions, their use is rather limited.



The sulfone moiety is an important functionality in organic synthesis. Sulfones are useful substrates in many reactions, such as the Julia-Kocienski olefination and Ramberg–Bäcklund reactions.[13a] Moreover, sulfones are present in some bioactive compounds, for instance vinyl sulfones are well-known covalent inhibitors of Falcipain-2,[14] and were reported to inactivate the

enzyme by irreversible addition to the thiol group of an active cysteine site to the electrophilic vinyl sulfone moiety. The CM reaction can be a reasonable method for the synthesis of sulfone-containing alkenes, completing other approaches known in classical organic synthesis.



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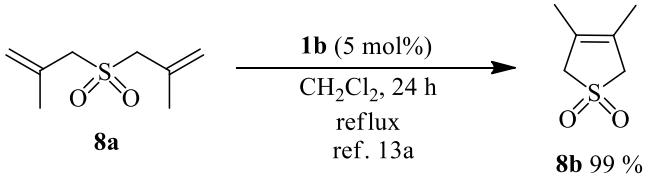

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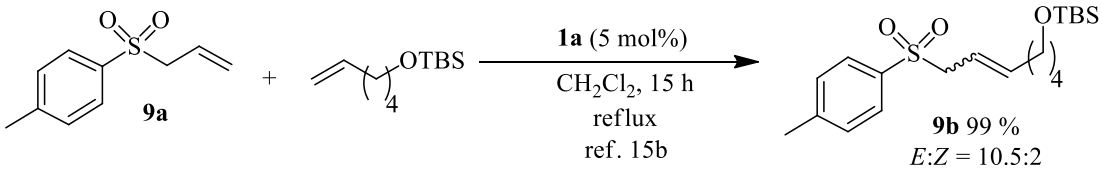

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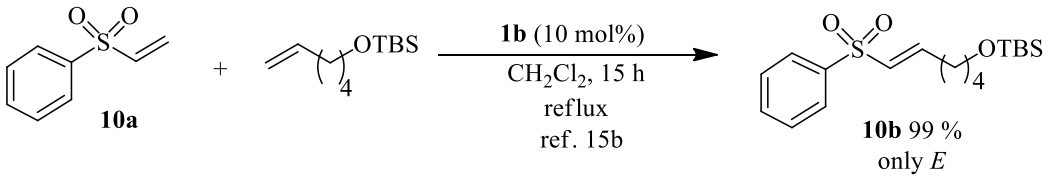


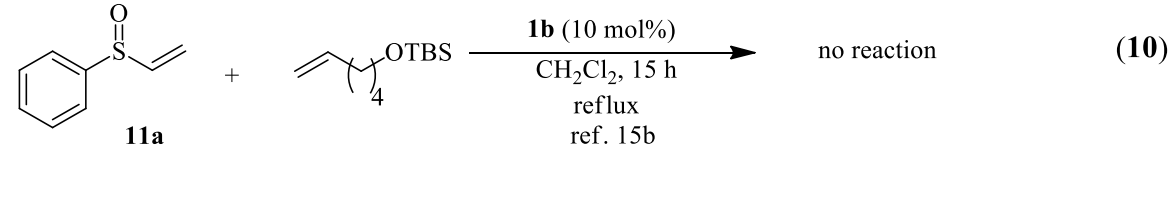
(**9**)

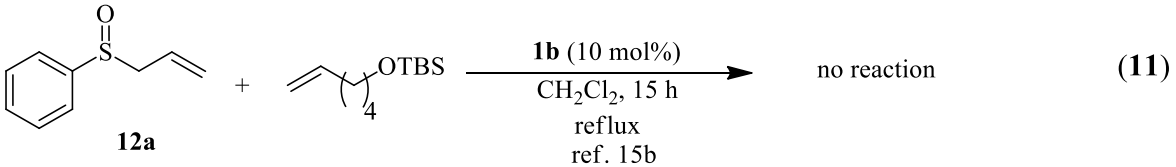
The compatibility of remote sulfone moiety with ruthenium and molybdenum-based metathesis catalysts is well established.[13,15] The first CM of allyl sulfones catalyzed by ruthenium complexes has been reported by Grubbs.[13b,c] Recently, Yao has published a very elegant method for the preparation of cyclic sulfones by RCM or enyne metathesis of various diallyl **7a** and **8a** (equations 6 and 7) and homoallyl sulfones.[13a] Yao also presented preparation of α,ω-unsaturated sultams and sultones from unsaturated sulfonamides and sulfonates.[13a] On the other hand, we previously described that CM of vinyl sulfones is more challenging comparing to allyl sulfones but still possible using commercially available 'second generation' ruthenium complexes (equations 8 and 9).[15] Vinyl sulfones are electron poor olefin that are type III alkenes in CM reactions.[7a] The CM of vinyl sulfones have been than applied in a number of syntheses of natural and biologically active compounds.[14]

Sulfoxides are important intermediates in organic synthesis, especially if containing an asymmetric sulfur atom. To the best of our knowledge, only a few examples of the application of unsaturated sulfoxides in olefin metathesis reactions have been described.[16] Liras *et al.* published an example, where the RCM reaction of a substituted vinyl sulfoxide with a stoichiometric amount of catalyst **1a** was employed as the key cyclisation step *en route* to (±)-securinine, an

important member of the Securinega family of alkaloids.[16a] Bates *et al.* recently successfully employed RCM of allyl sulfoxide derivatives catalyzed by **1b** (10 mol%) in the synthesis of thiazocine-2-acetic acid derivatives.[16b] Colbert *et al.* showed an example of CM reaction of a molecule containing a chiral sulfoxide moiety (asymmetric 5-pentene-sulfinyl derivative) in the synthesis of a α-tocopherol derivative. This transformation was forced by use of 20 mol% of the very active complex **1h** (using microwave irradiation heating), but only 50% of the desired product was obtained.[16c] Previously, we had studied CM reactions of vinyl and allyl sulfoxides and found that these compounds were inactive in olefin metathesis using 'classical' reaction conditions.[15] While CM of allyl and vinyl sulfones is generally straightforward (equations 8 and 9), we found that when vinyl **11a** and allyl sulfoxide **12a** were used in the same model reaction only starting material was recovered (equations 10 and 11). Inability of sulfoxides to participate in the CM reaction was initially explained by redox catalyst degradation, as it is known that Fisher-type carbenes can be oxidized by sulfoxides.[17] Moreover, the sulfoxide moiety could also form stable chelates with ruthenium, thus 'arresting' the active propagating species and slowing down the productive metathesis process.[18] Interestingly, Szadkowska *et al*. reported that the sulfoxide moiety can be actually present in the ruthenium complex **1g**, without destroying its catalytic activity in olefin metathesis.[19] Having in mind this divergence in the literature, we decided to reinvestigate selected representative CM and RCM reactions of vinyl and allyl sulfoxides.

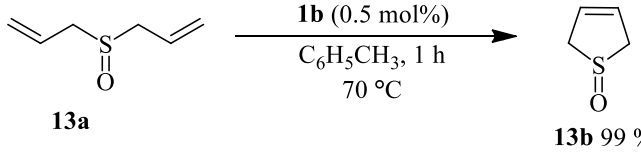
Comparison between vinyl sulfone **10a** and sulfoxide **11a** shows that under identical reaction conditions the first was quantitatively converted into the corresponding sulfone **10b**, while in the latter case only the starting material was recovered.[15b] Similarly, in our model CM reaction, promoted by the 'first generation' complex **1a**, allyl sulfone **9a** was transformed into the desired product **9b** (equation 8). In contrast, allyl sulfoxide **12a** was practically inert, even when the more active 'second generation' pre-catalyst **1b** was used (equation 11).



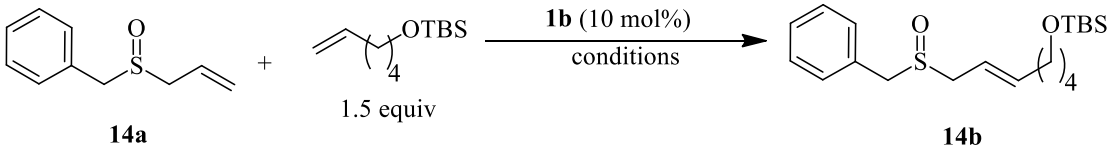


To our surprise diallyl sulfoxide **13a** was quantitatively transformed into desired product **13b** in the RCM reaction using only 0.5 mol% of **1b** (equation 12) under otherwise the same conditions as used in the previous reaction (equation 11). Having such solid evidence that the sulfoxide group is indeed compatible with ruthenium catalysts, we returned to the CM of allyl sulfoxides that failed previously (equation 13). In a hope to 'force' this reaction, we tested a

number of conditions (elevated temperature, concentration, solvents etc),[6] to find that even addition of a Lewis acid (10 mol% of triphenyl borate) was rather ineffective (TON = 1).[18] Next, we decided to use fluorinated aromatic hydrocarbons (FAH), the highly activating solvents which were independently developed in Blechert's and Grela's groups.[20] It has been proven that FAH solvents can increase the efficiency of the 'second generation' ruthenium catalysts in many olefin metathesis reactions.[20] Unfortunately, in the present model reaction of allyl sulfoxide carried out in C_6F_6 and catalyzed by 10 mol% of **1b** only 31 % of desired product was isolated (TON = 3) under these conditions. The vinyl sulfoxide **11a** was again completely inert (equation 10), even in the highly-promoting reaction conditions using aromatic fluorinated solvents.[20]



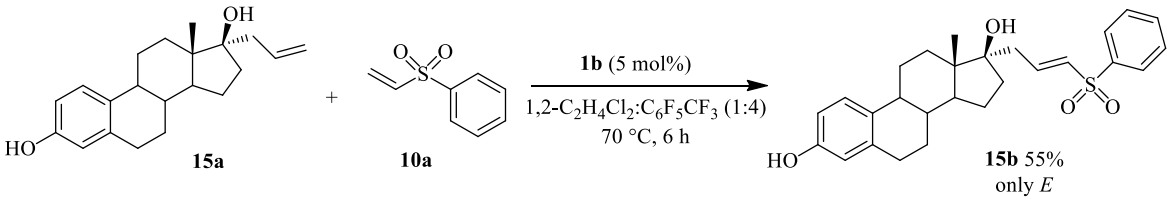
13a **13b** 99 % (**12**)



14a 1.5 equiv **14b** only *E* (**13**)

conditions	isolated yield
$C_6H_5CH_3$, 70 °C, 6 h	9 %
$C_6H_5CH_3$, 70 °C, 6 h 10 mol% of $(PhO)_3B$	12 %
C_6F_6, 70 °C, 6 h	31 %

The present results force us to conclude that while the sulfoxide moiety is in general compatible with ruthenium catalysts, and the RCM of allylic sulfoxides is actually very easy, the related CM reactions of allyl and vinyl sulfoxides are either very difficult or impossible. This is in distinct contrast with the analogous reactions of vinyl and allyl sulfones, which are generally quite straightforward. This difference between sulfones and sulfoxides was also clearly apparent in reactions conducted with more advanced substrates, such as compound **15a** studied by us in our current project devoted to steroid side-chain modifications *via* CM (equation 14). While the reaction of **10a** with **15a** gave the expected product **15b** in a satisfactory isolated yield (55% of (*E*) isomer exclusively), the analogous CM reaction between **15a** and allyl sulfoxide **14a** gave a complicated reaction mixture.



(14)

Conclusions

In conclusion: the differences in reactivity of olefins containing sulfur atom on different oxidation states are presented.[21] The most challenging transformations are cross-metathesis reactions with allyl and vinyl sulfoxides. We confirmed our recent observation that vinyl sulfoxides are unreactive, while allyl sulfoxides can react, but in general are very poor partners in CM reaction. In contrast, the RCM of dienes containing the sulfoxide group, as well as RCM and CM reactions of unsaturated sulfones, are straightforward.

Experimental Section

General. All reactions were carried out under argon atmosphere in pre-dried glassware using Schlenk techniques. The solvents: octafluorotoluene (FluoroChem), hexafluorobenzene (FluoroChem), toluene (Fluka), dichloromethane (Merck) and 1,2-dichloroethane (Aldrich) were dried by distillation over CaH_2 under argon and stored under argon atmosphere. Commercially available ruthenium pre-catalysts were obtained from Sigma Aldrich **1a**, **1b**, **1d** or Apeiron Catalysts **1f** (www.apeiron-catalysts.com) and used as received. Analytical thin layer chromatography (TLC) was accomplished using Merck TLC aluminum sheets (silica gel 60 F_{254}). Flash column chromatography was carried out on Merck silica gel (230-400 mesh). NMR spectra were recorded with Bruker (500 MHz) or Varian (200 or 400 MHz) machines in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) are in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). MS (ESI) spectra were recorded on Mariner Perseptive Biosystems, Inc. MS (TOF MS FD) spectra were recorded on Waters GCT Premier. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with Diamond ATR accessory. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw.

2,5-Dihydrothiophene *S*-oxide (13b). Compound **13a**, (130 mg, 1 mmol) was dissolved in toluene (5 mL) under argon atmosphere. To the solution, pre-catalyst **1b** (0.5 mol%, 4 mg, 0.005 mmol) was added in one portion and resulting mixture was heated at 70 °C during 1 h. Reaction was controlled by TLC. When full consumption of substrate was observed, mixture was concentrated *in vacuo* and purified by flash chromatography (EtOAc; R_f = 0.1) to afford

analytically pure product (101 mg, 99% yield, oil). IR (film) 3430, 1640, 1396, 1331, 1133, 1015, 894, 696, 647 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): 3.65 (AB, J_{AB} = 16.6, 4H), 5.98 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): 60.1 (CH_2), 125.3 (CH). HRMS (ESI^+): *m/z* calcd for ($C_4H_6SONa^+$): 125.0037,found: 125.0033. Anal. Calcd for C_4H_6SO: C, 47.03; H, 5.92; S, 31.39. Found: C, 46.92; H, 6.05; S, 31.89.

***tert*-Butyldimethyl-(7-benzylsulfinylhept-5-enyloxy)silane (14b).** Sulfoxide **14a** (126.2 mg, 0.7 mmol) and 5-hexenyl-*tert*-butyldimethylsilyl-ether (1.5 equiv, 225.2 mg, 1.05 mmol) were placed in a Schlenk tube and dissolved in hexafluorobenzene (4 mL) under argon atmosphere. Then catalyst **1b** was added in one portion (60 mg, 10 mol%), and the reaction mixture was heated at 70 °C for 6 h. The reaction was controlled by TLC. Then solvent was evaporated and the crude product was purified by flash chromatography (*c*-hexane:EtOAc = 3:1; R_f = 0.2) affording the desired product **14b** (80 mg, 31%, brownish oil). IR (film): 3377, 2936, 1770, 1382, 1246, 1055 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 0.04 (s, 6H), 0.89 (s, 9H), 1.40-1.60 (m, 4H), 2.14 (q, *J* = 7.1, 2H), 3.25 (ABX, J_{AB} = 13.2, J_{AX} = 7.4, 1H), 3.38 (ABX, J_{AB} = 13.2, J_{AX} = 7.4, 1H), 3.61 (t, *J* = 6.4, 2H), 3.96 (AB, J_{AB} = 13.0, 2H), 5.53 (dt, *J* = 15.4, 7.4, 1H), 5.80 (dt, *J* = 15.4, 6.7, 1H), 7.28-7.39 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.3 (CH_3), 18.3 (C), 25.3 (CH_2), 25.9 (CH_3), 32.2 (CH_2), 32.5 (CH_2), 53.6 (CH_2), 56.6 (CH_2), 62.9 (CH_2), 115.4 (CH), 117.1 (CH), 128.3 (CH), 128.9 (CH), 129.4 (C), 130.0 (CH). HRMS (ESI^+): *m/z* calcd for ($C_{20}H_{34}SO_2SiNa^+$): 389.1947; found: 389.1969.

Preparation of 17-(3-benzenesulfonyl-allyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (15b). To a solution of 17α-(2'-propen-l'-yl)estra-1,3,5(10)-trien-3,17β-dio1 **15a** (125 mg, 0.40 mmol) and phenyl vinyl sulfone (3 equiv., 202 mg, 1.20 mmol) in the mixture of 1,2-dichloromethane (1 mL) and octafluorotoluene (4 mL), **1b** was added in one portion (19 mg, 0.02 mmol, 5 mol%). The resulting mixture was refluxed for 6 h in argon atmosphere. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (*c*-hexane/EtOAc, 3:1, R_f = 0.2) to obtain analytically pure product **15b** (99.5 mg, 0.22 mmol, 55%), exclusively as a *E* isomer (colorless crystals, m.p. = 105 °C). IR (KBr): 3437, 2928, 1622, 1499, 1447, 1356, 1305, 1285, 1251, 1144, 1084, 1022, 968, 910, 788, 733, 687, 596, 548 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): 0.92 (s, 3H), 1.70 – 1.20 (m, 7H), 1.99 – 1.80 (m, 3H), 2.15 – 2.04 (m, 2H), 2.24 – 2.34 (m, 1H), 2.48 (dd, *J* = 14.5, 5.5, 1H), 2.56 (dd, *J* = 14.5, 5.5, 1H), 2.86 – 2.76 (m, 2H), 6.44 (d, *J* = 15.2, 1H), 6.56 (s, 1H), 6.62 (d, *J* = 8.2, 1H), 7.12 (d, *J* = 8.4, 1H), 7.06 (dd, *J* = 14.5, 6.3, 1H), 7.64 – 7.50 (m, 3H), 7.88 (d, *J* = 7.4, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.1 (CH_3), 23.4 (CH_2), 26.2 (CH_2), 27.3 (CH_2), 29.5 (CH_2), 31.7 (CH_2), 35.6 (CH_2), 39.3 (CH_2), 39.6 (CH), 43.7 (CH), 46.8 (C), 49.7 (CH), 83.1 (C), 112.7 (CH), 115.2 (CH), 126.4 (CH), 127.6 (CH), 129.2 (CH), 132.2 (C), 132.7 (CH), 133.2 (CH), 138.1 (C), 140.6 (C), 144.7 (CH), 153.4 (C). HRMS (TOF MS FD^+) *m/z* calcd for $C_{27}H_{32}O_4S$: 452.2021, found: 452.2030.

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2. Precisely, the common Ru-based olefin metathesis catalysts should be called pre-catalysts: “Compounds that are well-characterized, and that under some conditions will catalyze the metathesis of olefins, but that have not been proven to be essentially identical to the active species for the metathesis reaction, are not well-defined catalysts. They are catalyst precursors, or (pre)catalysts.” Schrock. R. R. *J. Mol. Catal. A: Chem.* **2004**, *213*, 21.
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