Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 4525–4531

TETRAHEDRON

Cross-metathesis reaction of vinyl sulfones and sulfoxides

Anna Michrowska, Michał Bieniek, Mikhail Kim, Rafał Klajn and Karol Grela*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 4452, P.O.B. 58, PL01-224 Warsaw, Poland

Received 27 January 2003; revised 31 March 2003; accepted 29 April 2003

Abstract—Cross-metathesis reactions of α,β-unsaturated sulfones and sulfoxides in the presence of molybdenum and ruthenium pre-catalysts were tested. A selective metahesis reaction was achieved between functionalized terminal olefins and vinyl sulfones by using the 'second generation' ruthenium catalysts **1c–h** while the highly active Schrock catalyst **1b** was found to be functional group incompatible with vinyl sulfones. The cross-metathesis products were isolated in good yields with an excellent (*E*)-selectivity. Both the molybdenum and ruthenium-based complexes were, however, incompatible with α,β- and β,γ-unsaturated sulfoxides. © 2003 Published by Elsevier Science Ltd.

---

1. Introduction

Sulphur chemistry has been a standard part of synthetic organic chemistry for more than one century. A variety of versatile sulfur-containing synthons is known today, and among those, α,β-unsaturated sulfones have attracted special attention as they can be transformed into versatile synthetic intermediates. These compounds serve efficiently as, e.g. Michael acceptors and as 2π partners in cycloaddition reactions. In addition, the easy further transformations of sulfur group via elimination or either reductive or alkylative desulfonylation render further advantages of these compounds in synthesis.[1]

In our preliminary communication[2] we have described a simple (*E*)-selective method of preparation of substituted unsaturated sulfones based on olefin cross-metathesis (CM) of phenyl vinyl sulfone catalyzed by the 'second generation' Grubbs' carbene[3] **1c**.

Several sulfur-containing alkenes have been applied as substrates in metathesis reactions. The 'first generation' ruthenium pre-catalysts,[4] such as **1a** are known to be of low or no reactivity toward the RCM of α,φ-dienes containing sulfide and disulfide moieties, whereas Schrock molybdenum complex[5] **1b** was found to be more compatible with these substrates.[6a] More recently, a study has been published to show that the 'second generation' Nolan-type pre-catalyst[7] **1e** acts in such transformation extremely well, and can be successfully employed in metathesis of sulfides, disulfides, and dithianes and even in the self-cross metathesis reaction of thiols.[6b]

The compatibility of remote sulfone function with ruthenium and molybdenum-based metathesis catalysts is well established.[8] The cross-metathesis of allyl sulfone has been reported by Grubbs.[9] Recently, Yao has published a very elegant method for the preparation of cyclic sulfones by RCM or enyne metathesis of various diallyl and homoallyl sulfones.[10] Also preparation of unsaturated sultams and sultones from α,φ-unsaturated sulfonamides[11] and sulfonates[12] has been described (Scheme 1).

Although, after publication of our preliminary communication,[2] some examples of metathesis of conjugated sulfones have been reported,[13] applications of such substrates in metathesis remain rare. Similarly, according to our best knowledge the cross metathesis reaction of vinyl sulfoxides has not yet been reported.

In order to fill these empty places in the electron deficient alkenes-metathesis catalysts 'compatibility matrix' we decided to screen the catalytic activity of selected molybdenum and ruthenium carbenes **1a–h** with representative α,β-unsaturated sulfur-contained compounds.

2. Results and discussion

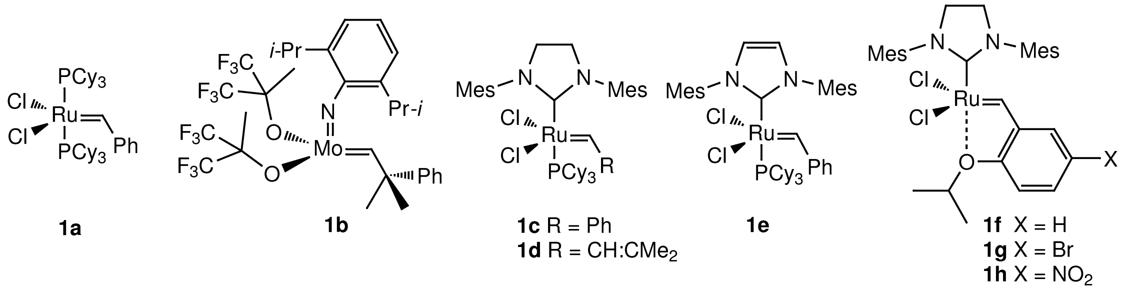
We used the previously optimised[2] cross-metathesis of olefin **2a** and phenyl vinyl sulfone **3a** as a model transformation (Table 1) in this investigation. The 'first-generation' Grubbs' alkylidene[4] **1a** did not promote cross-metathesis with α,β-unsaturated sulfone and under these conditions only the product of alkene self-metathesis **5a** was observed (entry a). More interestingly, the very reactive

---

Keywords: carbene complex; olefin metathesis; sulfone; ruthenium; homogenous catalysis.

* Corresponding author. Tel.: +48-22-632-32-21; fax: +48-22-632-66-81; e-mail: grela@icho.edu.pl

0040–4020/03/$ - see front matter © 2003 Published by Elsevier Science Ltd.
doi:10.1016/S0040-4020(03)00682-3



Scheme 1. The catalysts for olefin metathesis.

Schrock molybdenum catalyst[5] **1b** was the most probably completely poisoned by **3a**, as neither product **4a** nor 'homodimer' **5a** were formed after 15 h of the reaction (entry b). Although molybdenum alkylidene **1b** effects CM reactions of some α,β-unsaturated substrates (e.g. acrylonitrile),[14] our observation suggest that vinyl sulfones constitute a class of substrates which are not functional group compatible with this very sensitive catalyst.

All 'second-generation' NHC-ruthenium complexes, in contrast, effect the formation of corresponding product **4a** (entries c–g).[15] With these pre-catalysts we also observed the formation of small amounts of 'homodimer' **5a** which decreased significantly after prolongated stirring. As it can be seen from Table 1, all NHC-containing complexes gave similarly high yields (≥80%), although in respect to the reaction selectivity (cross- versus homometathesis) and over-all conversion the Nolan-type pre-catalyst[7] **1e** and the phosphine-free carbene[16] **1h** were found to be superior to the other catalysts tested (entries d and g). In line with the previous observation[2] the CM of **1a** and phenyl vinyl sulfone was in all cases highly stereoselective, as the (*E*)-**4a** was the only isomer detected by GC and NMR.

Having identified ruthenium complexes **1c**–**g** as effective catalysts for this transformation, we decided to extend this investigation to a more diverse set of substituted and sterically demanded substrates. The results compiled in Table 2 illustrate the scope and synthetic utility of sulfone cross-metathesis. Thus substrates bearing various functionality, including O–H (entries b, c, g) and C–H acids (entry f) can be easily converted to corresponding α,β-unsaturated sulfones in good yields. In all reported cases the (*E*)-isomer was the only sulfone product detected by GC or NMR. Dimerisation products **5a**–**d**,**f** of the terminal olefin were observed only in minute amounts. It is well established that Hoveyda-type catalysts display higher reactivity towards a broad range of electron-deficient substrates.[13b,16,17] Indeed, the highly active carbene **1h**, recently introduced by our group,[16] proved to be the catalyst of choice for this transformation.

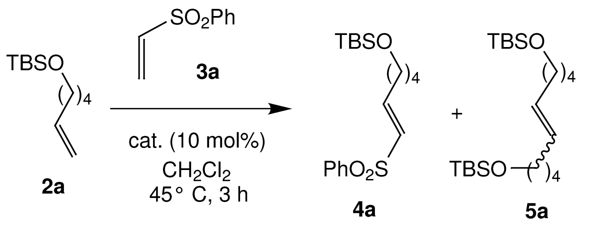
More sterically crowded substrates such as **2h**–**i** gave somewhat lower yields. It has been claimed that ruthenium carbene complex **1c**, bearing a 'saturated' NHC ligand, shows higher reactivity then its 'unsaturated' congener, **1e**.[3] In the light of these observations we were surprised to find that in this particular case **1c** was clearly inferior not only to **1h** but also to Nolan catalyst **1e**.

The commercially available divinyl sulfone **3b** can be also used in the CM with terminal alkenes. In this case we considered that metathesis can occur at one or both C=C bonds of **3b**. Fortunately, when divinyl sulfone **3b** was used in excess (**3b**/olefin 2:1 molar ratio), the very clean and selective formation of only 'monosubstituted' products (*E*)-**4j**–**l** was observed. Attempts to prepare divinyl sulfone functionalized at both sides, such as the compound **6k**, were less rewarding, and even under forcing conditions (**2k**/**3b** 4:1) the monosubstituted **4k** was the predominant sulfone-product formed (Fig. 1).

Unfortunately, geminal disubstituted olefins (**2m**–**o**) failed to react with **3a** even when the most active ruthenium complex **1e** was used. Similarly, α-substituted-α,β-unsaturated sulfones (**3c**–**d**) were unreactive in the model reaction with **2a**, suggesting that the cross-metathesis of α,β-unsaturated sulfones is very sensitive to steric hindrance (Fig. 2).

We next examined the cross-metathesis of vinyl sulfoxides. To our surprise the commercially available phenyl vinyl sulfoxide **3e** failed to react with model alkene **2a**, and the starting materials were recovered after the reaction almost quantitatively. Both the molybdenum (**1b**) and ruthenium-based catalysts (**1c**) were tested and neither product **7a** nor 'homodimer' **5a** were observed (Scheme 2). One example of application of sulfoxide in metathesis has recently been

Table 1. Cross-metathesis between olefins **2a**–**l** (1 equiv.) and sulfones **2a**,**b** (2 equiv.)

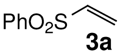
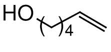
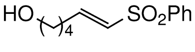
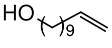
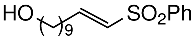
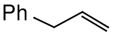
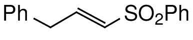
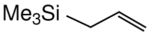
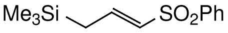
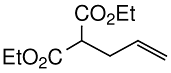
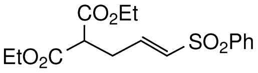
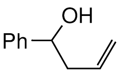
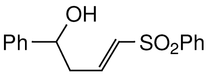
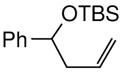
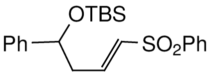
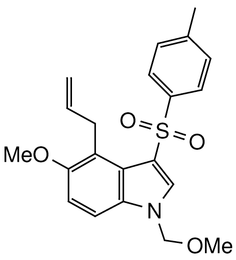
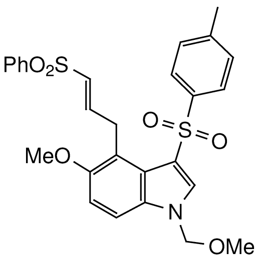
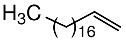
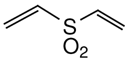
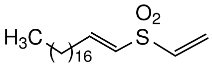
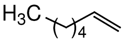
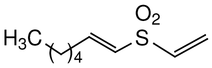
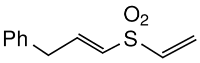


Entry	Catalyst	GC Yield (%)[a]	
a	**1a**	0	82 (85)
b	**1b**	0	0
c	**1c**	92 (>99)	8 (<1)
d	**1e**	98 (>99)	2 (<1)
e	**1f**	87 (91)	13 (9)
f	**1g**	80 (89)	16 (11)
g[b]	**1h**	95 (>99)	5 (<1)

[a] GC yield after 3 h of reaction. In parentheses are the GC yields after 15 h of reaction.

[b] GC yield after 1 h of reaction.

Table 2. Screening of the catalysts **1a–h**

Entry	Olefin **2a–l**	Sulphone **3a**,**b**	Product **4a–l**	Cat. 1	Yield (%)[a]
a	**2a**	 **3a**	**4a**	**1c** **1h**	85 90[b]
b		**3a**		**1c**	(81)[c]
c		**3a**		**1h**	96
d[d]		**3a**		**1c** **1h**	68 86
e[e]		**3a**		**1c** **1h**	26 33
f		**3a**		**1c**	74
g		**3a**		**1g**	71
h		**3a**		**1c** **1e** **1g** **1h**	(55)[c] 53 30 48
i		**3a**		**1c** **1e** **1g** **1h**	(33)[c] 44 (54)[c] 41 53
j				**1c**	59
k		**3b**		**1c**	42
l	**2d**	**3b**		**1c**	84

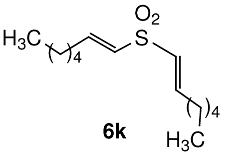
[a] Isolated yields of analytically pure compounds. All reactions were carried out with 5 mol% of **1c–h** in refluxing CH_2Cl_2 for 3–24 h, unless stated otherwise.

[b] Reaction with 2.5 mol% of **1h**, 25°C.

[c] Reaction with 10 mol% of **1c–e**, reflux.

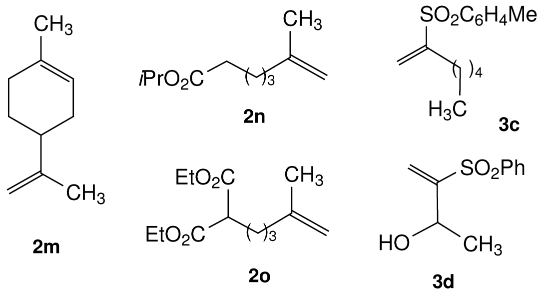
[d] Reaction with 5 mol% of **1c** or **1h**, 25°C. Yield determined by GC.

[e] Reaction of 3 equiv. of olefin **2e** with 1 equiv. of sulphone **3a**.



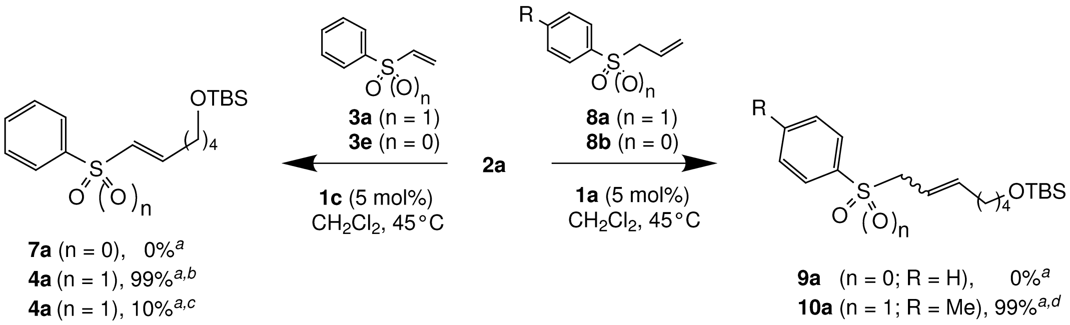
6k

Figure 1.



2m **2n** **2o** **3c** **3d**

Figure 2.



Scheme 2. Cross metathesis of vinyl and allyl sulfoxides. (a) Reaction of **2b** (1 equiv.) with vinyl sulfone **3a** or sulfoxide **3e** (2 equiv.) and allyl sulfone **8a** or sulfoxide **8b** (2 equiv.) in refluxing CH_2Cl_2, 15 h. Yields based on GC. (b) With 10 mol% of **1c**. (c) DMSO (50 equiv. relative to **1c**) was added. (d) (*E*)/(*Z*)=84:16 (GC). Isolated yield.

described.[18] The RCM reaction of a substituted vinyl sulfoxide and **1a** was the key step cyclisation in route to (±)-securinine, a member of the Securinega family of alkaloids. It is notable that this transformation was achieved by the stoichiometric amount of the complex **1a**, while the use of **1a** in catalytic amounts was ineffective.[18] To the best of our knowledge, except this single example, the metathesis of unsaturated sulfoxides has not been reported in the literature.[19] Therefore, we decided to study in more detail the behaviour of sulfoxide function in olefin metathesis. To do so, we compared CM reactions of a β,γ-unsaturated sulfones[9] and sulfoxides. We have found that in contrast to allyl sulfone **8a**, allyl sulfoxide **8b** has failed to react with the model alkene **2a** (Scheme 2). Georg has recently demonstrated the ability of dimethylsulfoxide (DMSO) to sequester traces of ruthenium.[20] In our control experiment DMSO (50 equiv. relative to **1c**) almost completely inhibited the cross-metathesis between olefin **2a** and sulfone **3a** (Scheme 2). Therefore, we suppose that the observed lack of reactivity with sulfoxide bearing alkenes is due to the poisoning of catalyst by ligation of metal by a sulfoxide function.[21]

3. Conclusion

In conclusion, we have demonstrated that vinyl sulfones readily participate in the CM reaction with terminal olefins, leading to synthetically useful β-functionalized α,β-unsaturated sulfones with an excellent (*E*)-selectivity under mild conditions. The robust, ‘second generation’ ruthenium complexes **1c–h** gave the highest yields, while the highly active Schrock catalyst **1b** was found to be functional group incompatible with vinyl sulfones. Both the molybdenum and ruthenium-based complexes were, however, incompatible with α,β- and β,γ-unsaturated sulfoxides.

4. Experimental

4.1. General

Unless otherwise noted, all reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH_2Cl_2 (CaH_2), Et_2O ($LiAlH_4$). Flash column chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker AVANCE 500, Varian Gemini 200 and 400 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: Perkin–Elmer Spectrum 2000 FT-IR. MS (EI, LSIMS): AMD 604 Intectra GmbH. MS (ESI): Mariner Perseptive Biosystems, Inc. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. All commercially available substrates were used as received. All other chemicals or reagents were prepared according to literature procedures: **2g–h**,[22a] **2i**,[22b] **2n–o**,[22c] **3c**,[22d] **3d**.[22e]

4.2. Hoveyda-type carbene (1g)

4.2.1. 2-Isopropoxy-5-bromostyrene. To a suspension of NaH (60% in oil, 687 mg, 17.2 mmol) in DMF (15 mL) a solution of 2-hydroxy-5-bromobenzaldehyde (2.527 g, 12.5 mmol) in DMF (15 mL) was added dropwise at rt. After 30 min of stirring 2-iodopropane (2 mL, 19.0 mmol) was added. After stirring at rt for 24 h, DMF was removed under vacuum and the residue was poured into water (50 mL) and extracted with *t*-BuOMe (4×25 mL). The combined organic extracts were washed with brine, dried (Mg_2SO_4) and concentrated in vacuo. The crude product (3.0 g) was used directly in the next step.

To a stirred suspension of $Ph_3P{=}CH_2$ (6.8 g, 16.25 mmol, 2.4 mmol/g) in THF (50 mL) a solution of crude 2-isopropoxy-5-bromobenzaldehyde (3.0 g) in THF (10 mL) was added at −78°C. The reaction mixture was allowed to warm to rt and was stirred at rt for 1 h before diluted with *t*-BuOMe (100 mL). The insoluble material was filtered off and the crude product was passed through a short column of silica, concentrated to dryness and distilled in vacuo to give **5** (2.03 g, 67% over two steps) as a colourless oil. Bp 70°C/0.2 Torr. [Found: C, 54.82; H, 5.41. $C_{11}H_{13}BrO$ requires C, 54.79; H, 5.43%] ν(film) 3087, 1624, 1479, 1244, 1125 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.34 (6H, d, *J*=6.0 Hz, $CH(CH_3)_2$), 4.49 (1H, sept, *J*=6.0 Hz, $CH(CH_3)_2$), 5.27 (1H, dd, *J*=1.3, 11.3 Hz, $=CH$), 5.71 (1H, dd, *J*=1.3, 17.8 Hz, $CH=$), 6.75 (1H, d, *J*=8.8 Hz, $CH=$), 6.98 (1H, dd, *J*=17.8, 11.3 Hz, Ar*H*), 7.28 (1H, dd, *J*=2.5, 8.8 Hz, Ar*H*), 7.57 (1H, d, *J*=2.5 Hz, Ar*H*); δ_C (50 MHz, $CDCl_3$) 22.0, 71.26, 113.0, 115.2, 115.9, 129.2, 130.0, 130.8, 131.1, 154.2; *m*/*z* (EI) 242 (30, M^+), 200 (67), 172 (3), 118 (14), 102 (3), 91 (61), 89 (13), 65 (11), 63 (10), 43 (13).

4.2.2. Hoveyda-type carbene (1g). Carbene complex **1c** (90 mg, 0.106 mmol), CuCl (14 mg, 0.138 mmol) and CH_2Cl_2 (5 mL) were placed in a Schlenk flask equipped with a condenser. A solution of 2-isopropoxy-5-bromostyrene (30 mg, 0.127 mmol) in CH_2Cl_2 (2 mL) was then added at rt and the resulted solution was stirred at 45°C for 1 h. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated in vacuo and the resulted material was purified by column chromatography on silica. Elution with 1:1 *c*-hexane/CH_2Cl_2 removed a green band from the column. Removal of solvent, washing with a minimal amount of cold *n*-pentane and drying under vacuum afforded **1g** (77 mg, 93%) as a bright green microcrystalline solid. δ_H (500 MHz, $CDCl_3$) 1.25 (6H, d, *J*=6.1 Hz, $CH(CH_3)_2$), 2.41 (6H, s, $C_6H_2(CH_3)$), 2.47 (12H, s, $C_6H_2(CH_3)_2$), 4.17 (4H, s, CH_2CH_2), 4.84 (1H, sept, *J*=6.1 Hz, $CH(CH_3)_2$), 6.67 (1H, d, *J*=8.7 Hz, Ar*H*), 6.67 (1H, d, *J*=8.7 Hz, Ar*H*), 7.04 (1H, d, *J*=2.4 Hz, Ar*H*), 7.08 (4H, s, $C_6H_2(CH_3)_3$), 7.59 (1H, dd, *J*=2.4, 8.7 Hz, Ar*H*), 16.35 (1H, br. s, Ru=C*H*); δ_C (125 MHz, $CDCl_3$) 21.2, 25.9, 30.2, 51.5, 75.7, 114.3, 115.1, 124.8, 129.4, 129.6, 130.9, 138.8, 139.0, 146.4, 151.0, 212.0, 284.7; *m/z* (ESI) 706 MH^+; HRMS (ESI): MH^+, found 706.0437. $C_{31}H^{81}_{37}Br^{35}Cl_2N_2O^{102}Ru$ requires 706.0489.

4.3. General procedure for cross-metathesis of α,β-unsaturated sulfones

To a mixture of **2** (0.25 mmol) and vinyl sulfone **3** (0.50 mmol) in CH_2Cl_2 (15 mL) was added a solution of catalyst **1** (2.5–10 mol%) in CH_2Cl_2 (5 mL). The resulting mixture was stirred at 45°C for 2–16 h. The solvent was removed under reduced pressure. The crude product **4** was purified by flash chromatography with *c*-hexane/EtOAc mixtures.

4.3.1. *tert*-Butyl(dimethyl){[(*E*)-6-(phenylsulfonyl)-5-hexenyl]oxy}silane (4a). Colourless oil (90%). ν (film) 2952, 2931, 2858, 1321, 1148, 1088, 836, 777, 753, 688, 596, 553 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.03 (6H, s, $Si(CH_3)_2$), 0.88 (9H, s, $C(CH_3)_3$), 1.46–1.60 (4H, m, CH^2), 2.20–2.35 (2H, m, CH_2), 3.53–3.62 (2H, m, CH_2O), 6.32 (1H, dt, *J*=15.1, 1.5 Hz, $CH{=}CHSO_2Ph$), 7.00 (1H, dt, *J*=15.1, 6.8 Hz, $CH{=}CHSO_2Ph$), 7.47–7.93 (5H, m, C_6H_5); δ_C (50 MHz, $CDCl_3$) −5.37, 18.26, 24.04, 25.90, 31.22, 32.00, 62.50, 127.50, 127.65, 129.18, 130.43, 133.16, 140.72, 147.00; *m/z* (EI) 299 (16), 298 (22), 297 (100), 199 (10), 135 (50), 125 (5), 81 (5), 79 (5), 77 (4), 75 (13), 73 (8); HRMS (LSIMS): MH^+, found 335.1768. $C_{18}H_{31}O_3SSi$ requires 355.1763.

4.3.2. (*E*)-6-(Phenylsulfonyl)-5-hexen-1-ol (4b). Colourless oil (81%). ν (film) 3377, 2935, 2863, 1447, 1306, 1145, 1086, 754, 688, 595, 553 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.35–1.63 (4H, m, CH_2), 2.21–2.36 (2H, m, CH_2), 3.64 (2H, t, *J*=6.3 Hz, CH_2O), 6.34 (1H, dt, *J*=15.1, 1.7 Hz, $CH{=}CHSO_2Ph$), 7.00 (1H, dt, *J*=15.1, 6.8 Hz, $CH{=}CHSO_2Ph$), 7.48–7.92 (5H, m, C_6H_5); δ_C (50 MHz, $CDCl_3$) 23.90, 25.60, 31.18, 31.90, 32.16, 32.20, 62.26, 62.86, 127.54, 127.66, 129.23, 130.34, 130.63, 133.24, 140.63, 146.68; *m/z* (EI) 169 (22), 143 (42), 125 (76), 98 (75), 80 (100), 79 (40), 78 (35), 77 (64), 53 (24), 51 (35), 41 (35); HRMS (LSIMS): MH^+, found 241.0913. $C_{12}H_{17}O_3S$ requires 241.0898.

4.3.3. (*E*)-11-(Phenylsulfonyl)-10-undecen-1-ol (4c). Colourless oil (81%). [Found: C, 65.35; H, 8.20; S, 10.27. $C_{17}H_{22}NO_3S$) requires C, 65.77; H, 8.44; S, 10.33%]; ν (film) 3370, 2928, 2855, 1447, 1318, 1306, 1289, 1147, 1086, 753, 688, 595 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.24–1.35, 1.41–1.49, 1.51–1.58 (15H, 3m, CH_2), 2.23 (2H, m, CH_2), 3.62 (2H, t, *J*=6.6 Hz, CH_2O), 6.32 (1H, dt, *J*=15.1, 1.5 Hz, $CH{=}CHSO_2Ph$), 6.98 (1H, dt, *J*=15.1, 6.9 Hz, $CH{=}CHSO_2Ph$), 7.51–7.92 (5H, m, C_6H_5); δ_C (125 MHz, $CDCl_3$) 25.57; 27.43, 28.83, 29.02, 29.17, 29.23, 31.34, 32.60, 62.76, 127.40, 129.12, 130.23, 133.11, 140.67, 147.22; *m/z* (ESI) 333 ($[M+Na]^+$); HRMS (ESI) $[M+Na]^+$, found 333.1515. $C_{17}H_{26}O_3SNa$ requires 333.1495.

4.3.4. Trimethyl-[(*E*)-3-(phenylsulfonyl)-2-propenyl]-silane (4d). Colourless oil (33%); ν (film) 2956, 2898, 1614, 1447, 1318, 1306, 1291, 1251, 1147, 1086, 856, 754, 689, 596 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.02 (9H, s, $(CH_3)_3Si$), 1.76 (2H, dd, *J*=1.5, 9.0 Hz, CH_2Si), 6.13 (1H, dt, *J*=14.9, 1.2 Hz, $CH{=}CHSO_2Ph$), 7.03 (1H, dt, *J*=14.9, 9.0 Hz, $CH{=}CHSO_2Ph$), 7.49–7.88 (5H, m, C_6H_5); δ_C (125 MHz, $CDCl_3$) −1.87, 24.36, 127.26, 127.62, 129.10, 132.85, 141.69, 146.43; *m/z* (EI) 256 (2, M^+), 237 (10), 199 (3), 147 (45), 125 (11), 115 (23), 91 (8), 77 (100), 59 (11), 51 (8); *m/z* (ESI) 277 ($[M+Na]^+$); HRMS (ESI) $[M+Na]^+$, found 277.0696. $C_{12}H_{18}O_2SSiNa$ requires 277.0689.

4.3.5. Diethyl 2-[(*E*)-3-(phenylsulfonyl)-2-propenyl]-malonate (4f). Colourless oil (74%); ν (film) 2984, 2938, 1731, 1447, 1321, 1308, 1148, 1087, 821, 596 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.23 (6H, t, *J*=7.1 Hz, CH_3CH_2), 2.80 (2H, td, *J*=7.4, 1.2 Hz, $H_2CH{=}CH$), 3.48 (1H, t, *J*=7.4 Hz, $CH(CO_2Et)_2$), 4.21 (4H, q, *J*=7.1 Hz, CH_3CH_2), 6.15 (1H, dt, *J*=15.8, 7.0 Hz, $CH{=}CHSO_2Ph$), 6.48 (1H, dt, *J*=15.8, 1.2 Hz, $CH{=}CHSO_2Ph$), 7.14–7.78 (5H, m, C_6H_5); δ_C (50 MHz, $CDCl_3$) 14.11, 32.22, 52.03, 61.46, 76.65, 77.34, 77.46, 125.61, 126.18, 127.37, 128.50, 132.80, 137.06, 168.90; *m/z* (EI) 276 (23), 202 (36), 157 (16), 130 (16), 129 (100), 128 (31), 117 (34), 115 (20), 91 (11); HRMS (LSIMS) MH^+, found 341.1040. $C_{16}H_{21}O_6S$ requires 341.1059.

4.3.6. (*E*)-1-Phenyl-4-(phenylsulfonyl)-3-buten-1-ol (4g). Colourless oil (71%); ν (film) 3487, 3062, 1448, 1307, 1147, 1086, 747, 702, 688, 595, 559 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 2.39–2.73 (2H, m, $CH_2CH{=}CH$), 4.61–4.92 (1H, m, $CH(OH)Ph$), 6.36 (1H, dt, *J*=15.1, 1.4 Hz, $CH{=}CHSO_2$-Ph), 7.00 (1H, dt, *J*=15.1, 7.3 Hz, $CH{=}CHSO_2Ph$), 7.21–7.43, 7.46–7.70, 7.77–7.94 (10H, 3m, C_6H_5); δ_C (50 MHz, $CDCl_3$) 40.75, 42.67, 72.63, 73.20, 73.30, 125.60, 125.72, 127.56, 127.76, 127.88, 128.05, 128.38, 128.66, 129.19, 129.32, 129.90, 132.67, 133.25, 133.63, 138.40, 139.50, 140.38, 142.83, 143.80, 143.86; *m/z* (EI) 182 (13), 168 (19), 144 (26), 129 (27), 125 (100), 107 (23), 97 (11), 79 (17), 78 (11), 77 (67), 51 (26); HRMS (LSIMS) $[M+Na]^+$, found 311.0715. $C_{16}H_{16}O_3SNa$ requires 311.0718.

4.3.7. *tert*-Butyl(dimethyl){(*E*)-1-phenyl-4-(phenylsulfonyl)-3-butenyl]oxy}silane (4h). Colourless oil (55%); ν (film) 2955, 2930, 2857, 1320, 1258, 1147, 1087, 836, 778, 595 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.16 (6H, s, $(CH_3)_2Si$), 1.00 (9H, s, $C(CH_3)_3$), 2.68–2.80 (2H, m, $CH_2CH{=}CH$), 4.97 (1H, t, J=5.5 Hz, CH(OTBS)Ph), 6.44 (1H, dt, J=15.1, 1.3 Hz, $H{=}CHSO_2Ph$), 7.10 (1H, dt, J=15.1, 7.4 Hz, $CH{=}CHSO_2Ph$), 7.32–7.83, 7.94–8.03 (10H, 2m, C_6H_5); δ_C (50 MHz, $CDCl_3$) −5.06, −4.74, 18.08, 25.73, 42.70, 73.37, 125.58, 127.48, 127.65, 128.29, 132.58, 133.17, 140.60, 143.20, 143.61; *m/z* (EI) 345 (57), 239 (65), 221 (100), 199 (37), 149 (85), 135 (41), 125 (25), 82 (34), 73 (54), 55 (26), 41 (20); HRMS (LSIMS) $[M+Na]^+$, found 425.1597. $C_{22}H_{30}O_3SiSNa$ requires 425.1583.

4.3.8. (*E*)-5-Methoxy-1-(methoxymethyl)-3[(4-methylphenyl)sulfonyl]-*H*-indol-4-yl-1-propenyl phenyl sulfone (4i). Colourless crystals, mp 140–141°C (54%). [Found: C, 61.46; H, 5.35; N, 2.76. $C_{17}H_{27}NO_6S_2$ requires C, 61.70; H, 5.18; N, 2.66%]; ν (KBr) 3532, 3119, 2926, 2852, 1627, 1514, 1286, 1143, 1085, 1027, 798, 676, 593 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 2.43 (3H, s, $C_6H_4CH_3$), 3.32 (3H, s, CH_3O), 3.58 (3H, s, CH_3O), 3.96 (2H, dd, J=5.8, 1.5 Hz, $CH_2CH{=}CH$), 5.46 (2H, s, CH_2OMe), 5.74 (1H, dt, J=15.0, 1.5 Hz, $CH{=}CHSO_2Ph$), 6.54 (1H, dt, J=15.0, 5.8 Hz, $CH{=}CHSO_2Ph$), 6.92 (1H, d, J=9 Hz, ArH), 7.25–7.32 (2H, m, ArH), 7.39–7.56 (4H, m, ArH), 7.66–7.77 (4H, AA′XX′, $C_6H_4CH_3$), 8.08 (1H, s, ArH); δ_C (125 MHz, $CDCl_3$) 21.64, 29.67, 56.24, 56.40, 78.59, 109.58, 110.64, 115.42, 116.63, 124.42, 126.54, 127.20, 128.90, 129.13, 130.06, 132.75, 137.44, 139.50, 141.30, 144.35, 145.76, 154.20; *m/z* (EI) 525 (5, M^+), 494 (6), 384 (52), 370 (37), 366 (10), 349 (12), 306 (16), 229 (47), 214 (20), 198 (31), 184 (16), 169 (17), 105 (38), 77 (19).

4.3.9. (*E*)-1-Nonadecenyl vinyl sulfone (4j). Colourless waxy solid (59%). [Found: C, 70.55; H, 11.21; S, 8.78. $C_{21}H_{40}O_2NS$ requires C, 70.73; H, 11.31; S, 8.99%]; ν (film) 2918, 2849, 1629, 1472, 1305, 1125, 967, 730 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.87 (3H, t, J=6.9 Hz, CH_3), 1.18–1.36 (28H, m, CH_2), 1.46 (2H, q, J=7.3 Hz, CH_2), 2.26 (2H, tdd, J=7.0, 6.8, 1.5 Hz, CH_2), 6.04 (1H, d, J=9.8 Hz, $CH{=}CH$), 6.22 (1H, dt, J=15.2, 1.5 Hz, $CH{=}CH$), 6.38 (1H, d, J=16.6 Hz, $CH{=}CH$), 6.58 (1H, dd, J=16.6, 9.8 Hz, $CH{=}CH$), 6.94 (1H, dt, J=15.2, 6.8 Hz, $CH{=}CH$); δ_C (100 MHz, $CDCl_3$) 14.10, 22.67, 27.53, 29.02, 29.27, 29.34, 29.44, 29.57, 29.61, 29.64, 29.67, 31.66, 31.90, 128.29, 128.47, 137.75, 149.58; *m/z* (EI) 357 (1, M^+), 339 (14), 321 (5), 313 (1), 290 (3), 264 (2), 123 (30), 109 (55), 95 (85), 81 (100); HRMS (LSIMS) $[M+Na]^+$, found 379.2650. $C_{21}H_{40}O_2NaS$ requires 379.2641.

4.3.10. (*E*)-1-Heptenyl vinyl sulfone (4k). Colourless oil (42%); ν (film) 3055, 2961, 2859, 1627, 1462, 1316, 1261, 1129, 1016, 818, 799 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.90 (3H, t, J=7.0 Hz, CH_3), 1.26–1.37 (4H, m, CH_2), 1.48 (2H, q, J=7.4 Hz, CH_2), 2.27 (2H, tdd, J=6.9, 6.8, 1.6 Hz, CH_2), 6.06 (1H, d, J=9.8 Hz, $CH{=}CH$), 6.23 (1H, dt, J=15.1, 1.6 Hz, $CH{=}CH$), 6.39 (1H, d, J=16.6 Hz, $CH{=}CH$), 6.58 (1H, dd, J=9.8, 16.6 Hz, $CH{=}CH$), 6.95 (1H, dt, J=15.1, 6.8 Hz, $CH{=}CH$); δ_C (100 MHz, $CDCl_3$) 13.86, 22.30, 27.19, 31.14, 31.60, 128.29, 128.48, 137.72, 149.60; *m/z* (EI) 189 (1, MH^+), 145 (4), 133 (6), 119 (33), 96 (18), 93 (14), 81 (70), 75 (13), 67 (54), 55 (100); HRMS (LSIMS) $[M+Na]^+$, found 211.0774. $C_9H_{16}O_2NaS$ requires 211.0763.

4.3.11. (*E*)-3-Phenyl-1-propenyl vinyl sulfone (4l). Colourless oil (84%); ν (film) 3057, 2921, 1630, 1496, 1384, 1315, 1127, 976, 792 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.59 (2H, dd, J=6.4, 1.7 Hz, $PhCH_2$), 6.05 (1H, d, J=9.9 Hz, $CH{=}CH$), 6.16 (1H, dt, J=15.1, 1.7 Hz, $CH{=}CH$), 6.37 (1H, d, J=16.5 Hz, $CH{=}CH$), 6.56 (1H, dd, J=16.5, 9.9 Hz, $CH{=}CH$), 7.11 (1H, dt, J=15.1, 6.4 Hz, $CH{=}CH$), 7.14–7.18, 7.24–7.37 (5H, 2m, C_6H_5); δ_C (100 MHz, $CDCl_3$) 37.74, 127.13, 128.72, 128.84, 128.83, 128.89, 129.73, 136.01, 137.44, 147.66; *m/z* (EI) 208 (11, M^+), 163 (3), 142 (5), 128 (2), 117 (100), 103 (2), 91 (34), 89 (7), 77 (6), 65 (13); HRMS (EI) M^+, found 208.0556. $C_{11}H_{12}O_2S$ requires 208.0558.

4.3.12. *tert*-Butyl-dimethyl-[7-(toluene-4-sulfonyl)-hept-5-enyloxy]-silane (10a). Colourless oil (99%; (*E*)/(*Z*) 84:16). [Found: C, 62.61; H, 8.86; S, 8.26. $C_{20}H_{34}O_3SSi$ requires C, 62.78; H, 8.79; S, 8.14%]; ν (film) 2930, 2858, 1598, 1472, 1320, 1302, 1255, 1143, 1089, 836, 776 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.04 (6H, s, $Si(CH_3)_3$), 0.88 (9H, s, $C(CH_3)_3$), 1.29–1.37 (2H, m, CH_2), 1.39–1.46 (2H, m, CH_2), 2.02 (2H, m, $CH_2CH{=}$), 2.44 (3H, s, CH_3), 3.56 (2H, t, J=6.3 Hz, CH_2OTBS), 3.72 (2H, d, J=7.2 Hz, CH_2SO_2), 5.36–5.44 (1H, m, $CH{=}CH$), 5.47–5.55 (1H, m, $CH{=}CH$), 7.31–7.35 (2H, m, ArH), 7.71–7.76 (2H, m, ArH) (isomer (*E*)); δ_C (125 MHz, $CDCl_3$) −5.33, 18.30, 21.56, 24.95, 25.92, 27.01, 32.23, 60.18, 62.77, 116.25, 128.52, 129.58, 135.55, 141.34, 144.44 (isomer (*E*)); *m/z* (EI) 325 (11), 231 (30), 227 (6), 215 (9), 213 (100), 155 (5), 149 (77), 139 (11), 95 (25), 91 (11), 73 (6); HRMS (LSIMS) MH^+, found 383.1059. $C_{20}H_{35}O_3SSi$ requires 383.2078.

4.3.13. Di[(*E*)-1-heptenyl] sulfone (6k). To a mixture of 1-heptene **2k** (353 mg, 3.6 mmol, 4 equiv.) and divinyl sulfone **3b** (106 mg, 0.9 mmol, 1 equiv.) in CH_2Cl_2 (25 mL) was added a solution of catalyst **1c** (38 mg, 5 mol%) in CH_2Cl_2 (5 mL). The resulting mixture was stirred at 45°C for 16 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (5% EtOAc/*c*-hexane) to give the monosubstituted product **4k** (106 mg, 60%) and the title compound **6k** (35 mg, 14%) as a colourless oils. **6k**: ν (film) 3047, 2957, 2931, 2860, 1634, 1467, 1319, 1293, 1131, 984, 830, 608 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.90 (6H, t, J=6.8 Hz, CH_3), 1.26–1.37 (8H, m, CH_2), 1.42–1.51 (4H, m, CH_2), 2.20–2.28 (4H, m, CH_2), 6.21 (2H, dt, J=15.1, 1.5 Hz, $CH{=}CHSO_2$), 6.88 (1H, dt, J=15.1, 6.8 Hz, $CH{=}CHSO_2$); δ_C (125 MHz, $CDCl_3$) 13.87, 22.33, 27.29, 31.18, 31.51, 129.53, 147.79; *m/z* (ESI) 259 (1, MH^+), 215 (9), 203 (14), 187 (2), 163 (35), 95 (40), 91 (15), 81 (51), 67 (41); HRMS (ESI) $[M+Na]^+$, found 281.1551. $C_{14}H_{26}O_2NaS$ requires 281.1546.

4.4. Homo cross-metathesis of 2a

4.4.1. 1,10-Bis-(*tert*-butyl-dimethylsilanyloxy)-dec-5-ene (5a). To a mixture of **2a** (171 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) a solution of catalyst **1a** (30 mg, 5 mol%) in CH_2Cl_2 (2 mL) was added. The resulting mixture was stirred at 45°C for 16 h. The solvent was removed under reduced pressure and the product was purified by flash chromatography (*c*-hexane) to give the title compound **5a** (148 mg, 92%) as a colourless oil ((*E*)/(*Z*) 85:15). [Found: C, 65.52; H, 11.96. $C_{22}H_{48}O_2Si_2$ requires C, 65.93; H, 12.07%]; ν(film) 2930, 2858, 1472, 1388, 1255, 1103, 1006, 836, 774 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 0.07 (12H, s, $Si(CH_3)_3$), 0.92 (18H, s, $C(CH_3)_3$), 1.37–1.45 (4H, m, CH_2), 1.50–1.58 (4H, m, CH_2), 1.97–2.05 (4H, m, CH_2), 3.60–3.66 (4H, m, CH_2-OTBS), 5.40–5.45 (2H, m, $CH{=}CH$) (isomer (*E*)); δ_C (125 MHz, $CDCl_3$) −5.27, 1.01, 18.37, 25.82, 25.99, 32.46, 63.16, 130.35 (isomer (*E*)); *m/z* (IE) 343 (2), 234 (2), 233 (8), 219 (1), 189 (12), 147 (60), 137 (10), 95 (100), 89 (11), 81 (99), 75 (65), 69 (18), 67 (44), 59 (12); HRMS (ESI) $[M+Na]^+$, found 423.3107. $C_{22}H_{48}O_2NaSi_2$ requires 423.3085.

Acknowledgements

This work was supported by the State Committee of Scientific Research (Grant No. 4 T09A 136 22). K. G. wishes to thank the Alexander von Humboldt foundation for books and equipment donation.

References

1. For reviews, see: (a) Procter, D. J. *J. Chem. Soc. Perkin Trans. 1* **1999**, 641–667. (b) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951–6984. (c) In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappaport, Z., Stirling, C., Eds.; Wiley: New York, 1988. For representative recent applications, see e.g.: (d) Mauleón, P.; Alonso, I.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2001**, *40*, 1291–1293. (e) Bentley, P. A.; Bickley, J. F.; Roberts, S. M.; Steiner, A. *Tetrahedron Lett.* **2001**, *42*, 3741–3743. (f) Lusinchi, M.; Stanbury, T. V.; Zard, S. Z. *Chem. Commun.* **2002**, 1532–1533. (g) Fahrat, S.; Marek, I. *Angew. Chem. Int. Ed.* **2002**, *41*, 1410–1412. (h) Teyssot, M. L.; Fayolle, M.; Philouze, C.; Dupuy, C. *Eur. J. Org. Chem.* **2002**, 54–62.
2. Grela, K.; Bieniek, M. *Tetrahedron Lett.* **2001**, *42*, 6425–6428.
3. (a) Morgan, J. P.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 3153–3155. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956. (c) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906.
4. (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041. (b) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503–5511. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110.
5. (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886. (b) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899–6907.
6. (a) Shon, Y.-S. S.; Lee, T. R. *Tetrahedron Lett.* **1997**, *38*, 1283–1286. (b) Spagnol, G.; Heck, M.-P.; Nolan, S. P.; Mioskowski, C. *Org. Lett.* **2002**, *4*, 1767–1770.
7. (a) Huang, J.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678. (b) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247–2250. (c) Ackermann, L.; Fürstner, A.; Weskamp, T.; Kohl, F. J.; Herrmann, W. A. *Tetrahedron Lett.* **1999**, *40*, 4787–4790.
8. For example: (a) Paquette, L. A.; Leit, S. M. *J. Am. Chem. Soc.* **1999**, *121*, 8926–8927. (b) Paquette, L. A.; Fabris, F.; Tae, J.; Gallucci, J. C.; Hofferberth, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 3391–3398. (c) Fürstner, A.; Gastner, T.; Weintritt, H. *J. Org. Chem.* **1999**, *64*, 2361–2366. (d) Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95–98.
9. (a) Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751–1753. (b) Blackwell, H. E.; O'Leary, D. J.; Chatterjee, A. K.; Washenfelder, R. A.; Bussmann, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 58–71.
10. Yao, Q. *Org. Lett.* **2002**, *4*, 427–430.
11. (a) Hanson, P. R.; Probst, D. A.; Robinson, R. E.; Yau, M. *Tetrahedron Lett.* **1999**, *40*, 4761–4764. (b) Wanner, J.; Harned, A. M.; Probst, D. A.; Poon, K. W. C.; Klein, T. A.; Snelgrove, K. A.; Hanson, P. R. *Tetrahedron Lett.* **2002**, *43*, 917–921.
12. Karsch, S.; Metz, P. *Synlett* **2002**, 2019–2022.
13. (a) Basu, K.; Cabral, J. A.; Paquette, L. A. *Tetrahedron Lett.* **2002**, *43*, 5453–5456. (b) Randl, S.; Connon, S. J.; Blechert, S. *Chem. Commun.* **2001**, 1796–1797.
14. Crowe, W. E.; Goldberg, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 5162–5163.
15. It should be noted, however, that the structurally very similar complex **1d** was found to be not reactive in cross-metathesis of vinyl sulfones: Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783–3784.
16. Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 4038–4040.
17. (a) Randl, S.; Gessler, S.; Wakamatsu, H.; Blechert, S. *Synlett* **2001**, 430–432. (b) Imhof, S.; Randl, S.; Blechert, S. *Chem. Commun.* **2001**, 1692–1693. (c) Grela, K.; Kim, K. M. *Eur. J. Org. Chem.* **2003**, 963–966.
18. Liras, S.; Davoren, J. E.; Bordner, *J. Org. Lett.* **2001**, *3*, 703–706.
19. For the metathesis of enantiopure η^4-(1-sulfinyldiene)-iron(0) tricarbonyl complexes (protected vinyl sulfoxides), see: Paley, R. S.; Estroff, L. A.; Gauguet, J.-M.; Hunt, D. K.; Newlin, R. C. *Org. Lett.* **2000**, *2*, 365–368.
20. (a) Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411–1413. For recent application, see: Stymiest, J. L.; Mitchell, B. F.; Wong, S.; Vederas, J. C. *Org. Lett.* **2003**, *5*, 47–49.
21. A referee suggested that the inability of vinyl sulfoxides to participate in the CM reaction can be also explained by a red-ox catalyst degradation, as it is known that sulfoxides can oxidise Fisher-type carbenes, cf: Wienand, A.; Reissig, H. U. *Organometallics* **1990**, *9*, 3133–3142, We gratefully acknowledge a referee for pointing out this possibility.
22. (a) Makosza, M.; Nieczypor, P.; Grela, K. *Tetrahedron* **1998**, *54*, 10827–10836. (b) Makosza, M.; Stalewski, J.; Wojciechowski, K.; Danikiewicz, W. *Tetrahedron* **1997**, *53*, 193–214. (c) Prowotorow, I.; Wicha, J.; Mikami, K. *Synthesis* **2001**, 145–149. (d) Sas, W. *Chem. Commun.* **1984**, 862–863. (e) Weichert, A.; Hoffmann, H. M. R. *J. Org. Chem.* **1991**, *56*, 4098–4112.