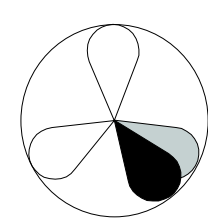


HIGHLY SELECTIVE CROSS-METATHESIS WITH VINYL SULFONES AND SULFOXIDES USING THE “SECOND GENERATION” RUTHENIUM CATALYSTS

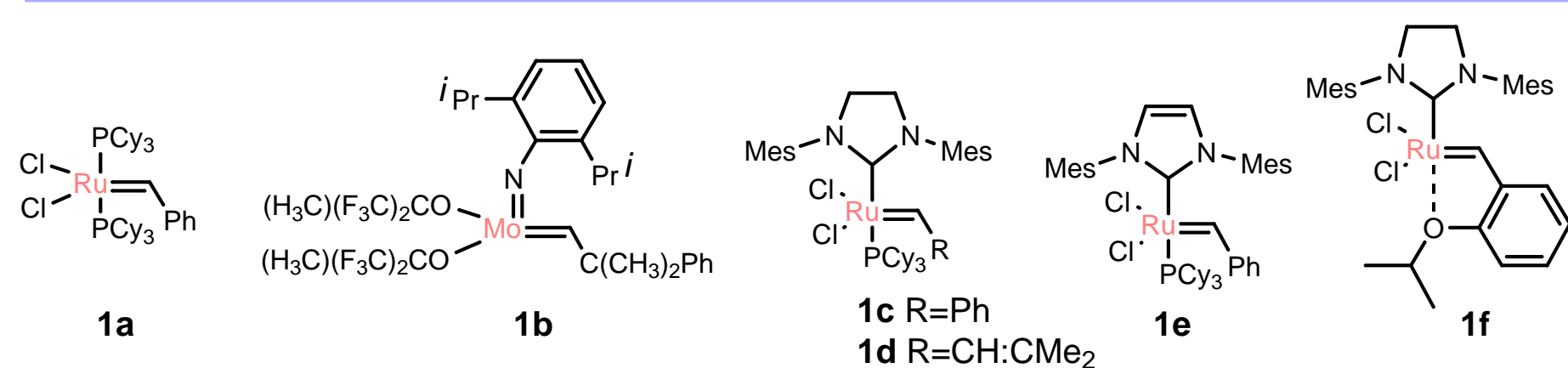
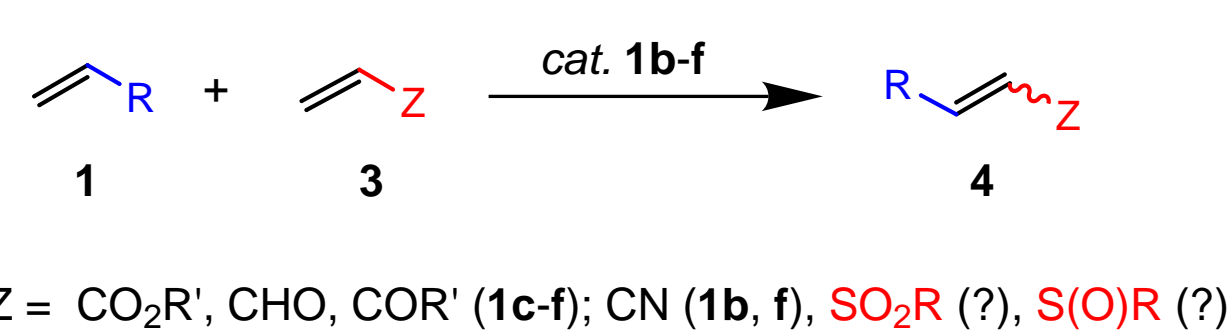


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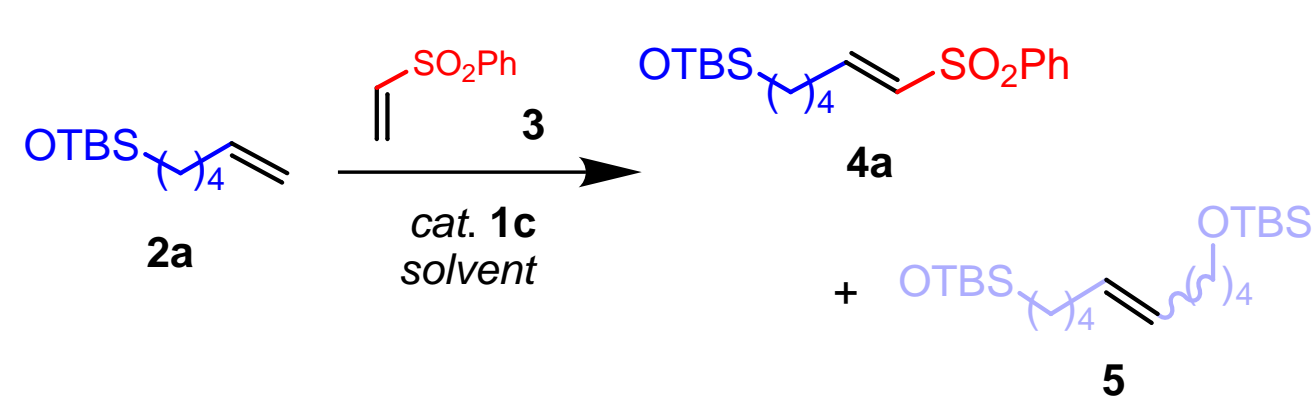
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Grubbs *et al.* have shown recently that the “second generation” catalyst **1d**, which contains 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand, readily promotes the cross metathesis reaction of terminal olefins with α,β -unsaturated aldehydes, ketones and esters. The authors have noted, however, that other electron deficient substrates, such as *vinyl sulfones* and *acrylonitriles* are not reactive in cross-metathesis using **1d**.¹



Substituted α,β -unsaturated sulfones are generally well accepted as useful intermediates in organic synthesis. Thus, vinyl sulfones serve efficiently, *e.g.* as Michael acceptors and as 2π partners in cycloaddition reactions. In addition, the stability and easy further transformations of the sulfonyl group *via* elimination or either reductive or alkylative desulfonylation render further advantages of vinyl sulfones as intermediates in total synthesis.²

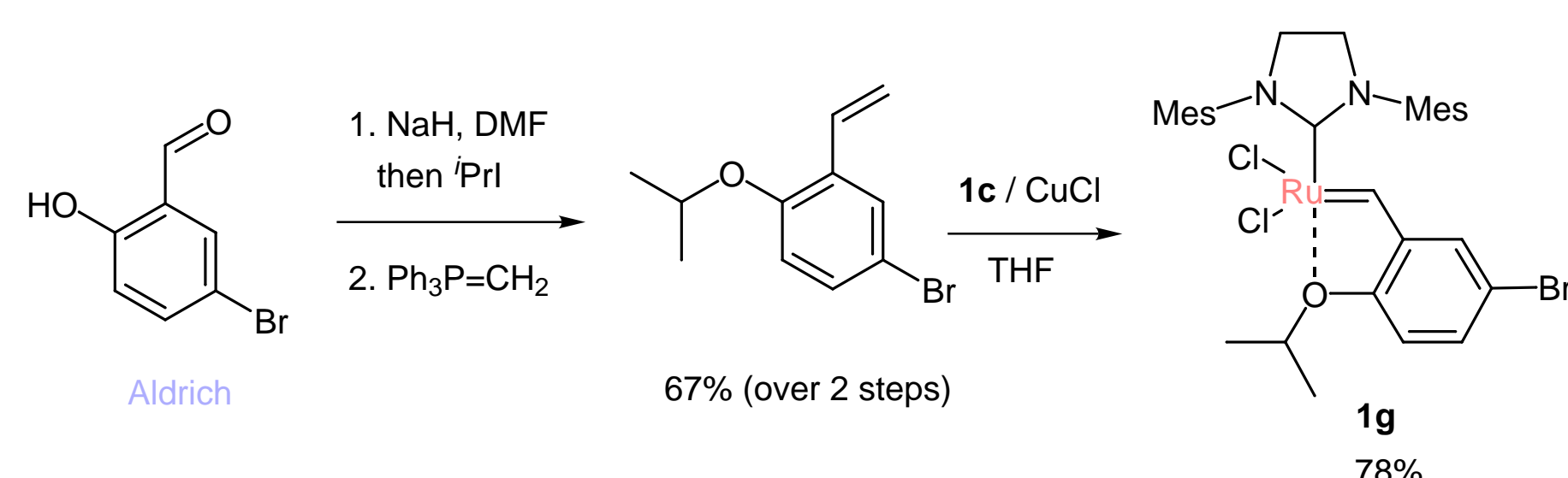
Therefore, we decided to investigate the cross metathesis of the readily available phenyl vinyl sulphone and phenyl vinyl sulfoxide with terminal olefins. In this communication, we report the single-step synthesis of functionalized α,β -unsaturated sulfones **4** *via* highly selective cross-metathesis reaction catalyzed by the “second generation” ruthenium alkylidenes **1c** and **1g**.³



Ratio (mol.) 2a : 3 : 1c	Conditions	Yield (%) ^{a)} 4a 5
1 2 0.10	PhMe; 50 °C	86 5
1 2 0.10	Et ₂ O; reflux	80 (90) 20 (10)
1 2 0.10	CH ₂ Cl ₂ ; reflux	92 (>99) 8 (<1)
1 3 0.05	CH ₂ Cl ₂ ; reflux	82 0
1 1 0.05	CH ₂ Cl ₂ ; reflux	57 17
1 0 0.05	CH ₂ Cl ₂ ; reflux	(0) (>95)

^{a)} Yields based on GC after 3 h of the reaction. Data in parentheses are the GC yields after 15 h of reaction.

Test reactions between olefin **2a** and phenyl vinyl sulfone **3** were performed under argon, at 45 °C in dichloromethane. The “classical” Grubbs’ alkylidene **1a** **did not react** under these conditions. However, in the case of NHC-ruthenium complex **1c** corresponding product **4a** **was formed** after 15h in quantitative yield (99%) and with excellent stereoselectivity as the (*E*)-isomer was the only product detected by GC and NMR.

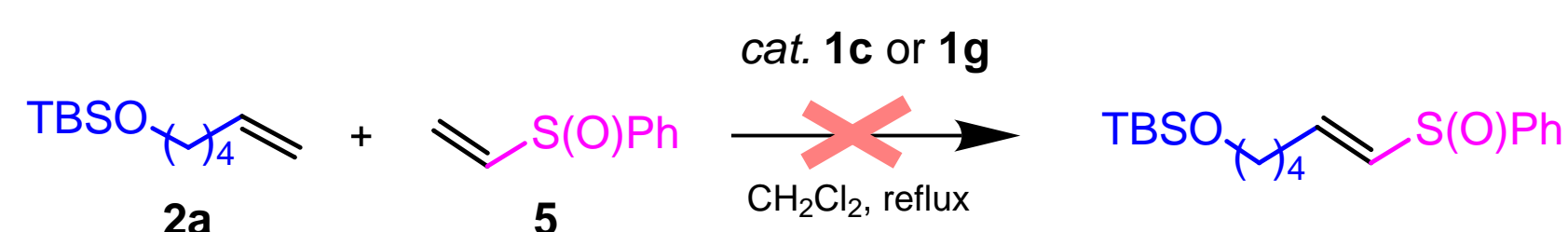


Under such conditions the reaction of terminal alkenes **2a-g** with sulfone **3** proceeds smoothly to give the corresponding products **4a-e** in moderate to good yields. In all reported cases the (*E*)-alkene was the only isomer detected by GC/MS and NMR. Dimerisation products of the terminal olefin were observed only as traces. Unprotected alcohol (**2b**) and highly C-H acidic malonic ester (**2c**) were converted in good yields. Somewhat lower yields gave more sterically crowded substrates such as **2e** and **2g**.

Entry	Olefin 2	Product 4	Cat. 1	Yield (%) ^{a)}
a			1c	85 ^{b)}
b			1c	81 ^{c)}
c			1c	74
d			1c	76 ^{d)}
e			1c	55 ^{c)}
f			1g	71
g			1c 1g	33 ^{c)} 41

^{a)} Isolated yields of analytically pure compounds. All reactions were carried out with 5 mol.% of **1c** or **1g** in refluxing CH₂Cl₂ for 3–24h, unless stated otherwise; ^{b)} TBS = *tert*-butyldimethylsilyl; ^{c)} with 10 mol.% of **1c**; ^{d)} GC-yield

Our attention then turned to the cross-metathesis reaction of vinyl sulfoxides. To our surprise, the commercially available phenyl vinyl sulfoxide (**5**) **failed to react**, as the starting materials **2a** and **5** were recovered after the reaction almost quantitatively. Georg has demonstrated the ability of dimethylsulfoxide (DMSO) to sequester traces of ruthenium.⁴ In the control experiment DMSO (50 eq. relative to **1c**) almost completely inhibited the cross-metathesis between olefin **2a** and sulphone **3**. In this context it is germane to note that Liras has recently reported a successful RCM of vinyl sulfoxide with the **stoichiometric** amount of **1a**.⁵



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¹Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783–3784.

²(a) Procter, D. J. *J. Chem. Soc. Perkin Trans. 1* **1999**, 641–667; (b) Simpkins, N. S. *Tetrahedron* **1990**, *46*, 6951–6984.

³For some preliminary results, see: Grela, K.; Bieniek, M.; *Tetrahedron Lett.* **2001**, *42*, 6425–6428.

⁴Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett.* **2001**, *3*, 1411–1413

⁵Liras, S.; Davoren, J. E.; Bordner, J. *Org. Lett.* **2001**, *3*, 703–706.