ELSEVIER

Journal of Organometallic Chemistry 624 (2001) 327–332

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Cross-metathesis reaction. Generation of highly functionalized olefins from unsaturated alcohols

Janine Cossy [a,*], Samir BouzBouz [a], Amir H. Hoveyda [b]

[a] *Laboratoire de Chimie Organique associé au CNRS, 10 Rue Vauquelin, 75231 Paris Cedex 05, France*
[b] *Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467, USA*

Received 14 November 2000; accepted 6 December 2000

Dedicated to Professor J. Normant on the occasion of his 65th birthday

Abstract

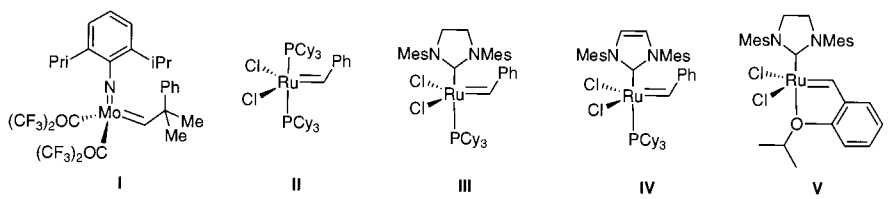
A cross-metathesis reaction was achieved between acid- and base-sensitive functionalized olefins and electron-deficient olefins or allylsilane by using the recyclable ruthenium catalyst **V** at room temperature. The cross-metathesis products are isolated in moderate to good yield. Ratios of *E* and *Z* cross-metathesis products depend upon substituents on the electron-deficient coupling partner. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cross-metathesis; Alcohols; Electron-deficient olefins; Allylsilane; Ruthenium

1. Introduction

During recent years, olefin metathesis has gained a position of increasing significance [1]. This method of carbon–carbon double bond formation has been stimulated by the development of new catalysts such as $(CF_3)_2Me(CO)_2(ArN)–Mo{=}CH(t\,Bu)$ (**I**) [2] and $P(Cy_3)_2Cl_2Ru{=}CHPh$ (**II**) [3]. The ruthenium carbene $(PCy_3)_2Cl_2Ru{=}CHPh$ (**II**) developed by Grubbs et al. constitutes a highly efficient metathesis pre-catalyst tolerating most functional groups. This catalyst has evolved into a versatile and reliable tool for advanced organic synthesis. As a consequence, many investigations have been reported which aim at expanding its application profile and fine-tuning of its reactivity and specificity. In this context, catalysts **III** [4], **IV** [5] and **V** [6] have been synthetized (Scheme 1).

The generation of olefins with vinylic functionality through the use of the cross-metathesis reaction has met with limited success. For example, acrylonitrile participates in cross-metathesis reactions with a variety of terminal olefins by using molybdenum catalyst **I** [7], but enones and enoic esters are not functionally compatible with **I** and fail to react with **II** [7]. On the contrary, catalyst **III** was found to catalyze the cross-metathesis reaction of 1,1-geminally disubstituted olefins and a recent publication from Grubbs et al. features the cross-metathesis of olefins with π-conjumgated compounds with moderate stereoselectivity [8]. More recently, good stereoselectivities were obtained

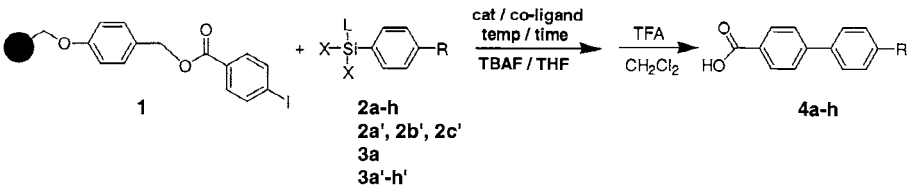


I II III IV V

Scheme 1. Ruthenium catalysts.

* Corresponding author. Tel.: +33-1-40794429; fax: +33-1-40794660.
E-mail address: janine.cossy@espci.fr (J. Cossy).

PII: S0022-328X(00)00932-3



	R =	*p*-Bu	*p*-MeO	H	*p*-Me	*o*-Me	*m*-Me	*p*-F	*p*-CF_3
L = ethyl	X = Cl	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
	X = F	**2a'**	**2b'**					**2g'**	
L = cyclohexyl	X = Cl	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**
	X = F	**3a'**	**3b'**	**3c'**	**3d'**	**3e'**	**3f'**	**3g'**	**3h'**

Scheme 2.

when catalyst **III** was prepared in situ in the presence of ethereal HCl [9]. However, acid sensitive protecting groups can be cleaved under these acidic conditions, posing a limitation in the use of catalyst **III**.

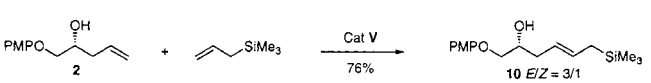
2. Results and discussion

Here, we would like to disclose our results concerning the cross-metathesis between α,β-unsaturated aldehydes, esters, allylsilane (olefins **B**) and functionalized unsaturated alcohols (**A**) in the presence of catalyst **V** which produces compounds of type 7 and/or homodimers of type **C**.

All cross-metathesis reactions were performed under argon, at room temperature in methylene chloride, in the presence of 2.5 mol% of catalyst **V**, one equivalent of olefin **A** and three equivalents of various electron-deficient olefins **B** (Scheme 2). Under these conditions, acrolein participates in cross-metathesis with terminal olefin **1** to generate the disubstituted unsaturated aldehyde **7a** in good yield (80%) and with excellent stereoselectivity as the (*E*)-stereomer was the only product detected by NMR spectroscopy and GC/MS (Table 1, entry a). This positive result led us to examine the cross-metathesis reaction of various olefins with various electron-deficient olefins such as alkyl acrylates and acrylonitrile. Excellent yields (> 70%) and (*E*)-stereoselectivities were attained when the reaction was conducted with different terminal olefins of type **A** and acrolein or alkyl acrylate as the cross-metathesis products were the only detectable compounds (Table 1, entries b, c, g, i, j). A considerably lower coupling yield was obtained when acrylonitrile was used instead of acrolein. When olefin **2** and acrylonitrile were treated with catalyst **V**, the cross-coupling product **7d** and the homodimer **8** were formed in 20% and 49% yield, respectively. Interestingly, the cross-metathesis product **7d** was obtained as the (*Z*)-stereomer and the homodimer **8** was formed as a mixture of *E*/*Z* stereomers in a ratio of 4/1. This high *Z* selectivity observed in acrylonitrile cross-metathesis is intriguing since related cross-metathesis reactions with acrolein and alkyl acrylates proceed with a high degree of *E* selectivity. This *Z* selectivity must be kinetically controlled (as the *E* compound is more stable) and is probably related to either the small size or to the electron-withdrawing properties of the cyano substituent.

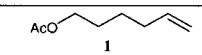
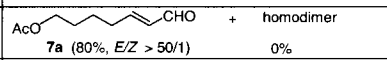
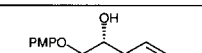
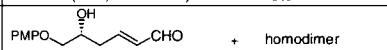
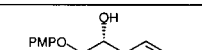
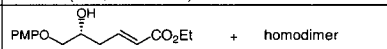
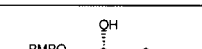
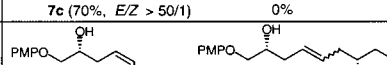
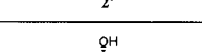
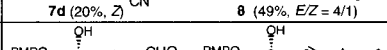
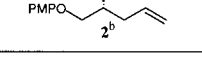
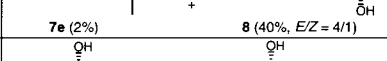
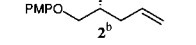
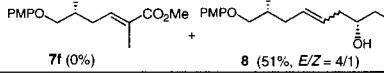
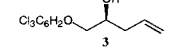
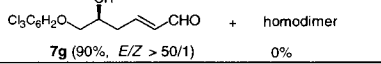
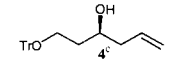
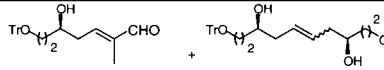
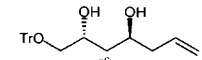
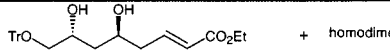
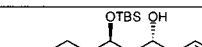
The presence of a methyl group on the electron deficient olefin, amplifies the formation of homodimers of type **C** (yield > 20%) and, only traces of cross-metathesis compounds of type **7** were detected by NMR and GC/MS (2%). Furthermore, the conversion was not complete (50–70%) (Table 1, entries e, f, h). It is worth noting that when compound **6** and methyl 2-methacrylate were treated with catalyst **V**, no coupling product was observed and **6** was recovered quantitatively, suggesting that under these conditions the cross-mehathesis reaction is very sensitive to steric hinderance.

From a preparative point of view, the cross-metathesis with allyltrimethylsilane is interesting as functionalized allylsilane adducts could be used for nucleophilic addition to electrophilic centers. The reaction of compound **2** with allyltrimethylsilane (0.9 equivalents) in the presence of catalyst **V** led to the cross-coupling products **10***E*/**10***Z* in a ratio of 3/1 (yield 76%) (Scheme 3).



Scheme 3. Cross-metathesis with allyltrimethylsilane.

Table 1
Cross-metathesis between **A** and electron-deficient olefins at 25°C [a]

entry	A	Electron-deficient olefin (3 equiv.) R' = H or Me	Conversion of **A** (h)	7 (yield, *E/Z*) + C (yield, *E/Z*)
a	 **1**		100% (24)	 **7a** (80%, *E/Z* > 50/1) + homodimer 0%
b	 **2**[b]		100% (36)	 **7b** (75%, *E/Z* > 50/1) + homodimer 0%
c	 **2**[b]		100% (36)	 **7c** (70%, *E/Z* > 50/1) + homodimer 0%
d	 **2**[b]		80% (36)	 **7d** (20%, *Z*) + **8** (49%, *E/Z* = 4/1)
e	 **2**[b]		50% (36)	 **7e** (2%) + **8** (40%, *E/Z* = 4/1)
f	 **2**[b]		50% (36)	 **7f** (0%) + **8** (51%, *E/Z* = 4/1)
g	 **3**		100% (36)	 **7g** (90%, *E/Z* > 50/1) + homodimer 0%
h	 **4**[c]		70% (36)	 **7h** (2%, *E/Z* > 30/1) + **9** (25%, *E/Z* = 4/1)
i	 **5**[c]		100% (36)	 **7i** (80%, *E/Z* > 50/1) + homodimer 0%
j	 **6**[d]		100% (36)	 **7j** (75%, *E/Z* > 50/1) + homodimer 0%
k	 **6**[d]		0% (48)	no reaction

a) Reaction with 2.5 mol% of **V**; b) PMP: *p*-methoxyphenyl; c) Tr: trityl; d) TBDPS: *tert*-butyldiphenylsilyl.

3. Conclusion

The use of catalyst **V**, which is not air sensitive, demonstrates the applicability of cross-metathesis for the synthesis of unsymmetrical functionalized disubstituted olefins with good stereoselectivity under mild conditions.

A variety of functional groups can be tolerated including non-protected alcohols and acid- or base-sensitive groups. The cross-metathesis reaction with catalyst **V** can replace advantageously the Wittig or Wittig–Horner reactions when base-sensitive substrates are present. Application of this reaction to the synthesis of biologically active compounds is currently under investigation and will be reported in due course.

4. Experimental

4.1. General considerations

All reactions were carried out under an atmosphere of argon. Methylene chloride was dried by distillation over CaH_2. Flash chromatography: Merck silica gel 60 (230–400 mesh), plates eluting with the solvents indicated, visualized by a 254 nm UV lamp, and stained with ethanolic solution of *p*-anisaldehyde. Nuclear magnetic resonnance spectra were acquired in $CDCl_3$, on a Bruker spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C. Optical rotations were obtained on a Perkin Elmer 241 mc polarimeter (Na d line) using a microcell with a 1-dm path length. Concentrations are reported in g/100 ml.

4.2. Preparation of compound **7a**

A flame-dried round-bottomed flask was charged with 5-acetoxy-1-hexene (**1**) (0.1 g, 0.7 mmol, one equivalent), acrolein (0.118 g, 2.10 mmol, three equivalents) and dichloromethane (3 ml). Catalyst **V** (11 mg, 0.0175 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 24 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 9/1) affords compound **7a** as a colorless oil (95.7 mg, 80%). ^{1}H-NMR δ: 9.50 (d, $J = 8.2$Hz, 1H), 6.91 (dt, $J = 7.0$ and 15.5 Hz, 1H), 6.11 (ddt, $J = 1.5$, 8.1 and 15.5 Hz, 1H), 4.05 (m, 2H), 2.38 (m, 2H), 2.05 (s, 3H), 1.70–1.50 (m, 4H). ^{13}C-NMR δ: 193.8 (d), 170.9 (s), 157.6 (d), 133.1 (d), 63.7 (t), 32.0 (t), 27.9 (t), 24.1(t), 20.8 (q).

4.3. Preparation of compound **7b**

A flame-dried round-bottomed flask was charged with olefin **2** (0.5 g, 2.4 mmol, one equivalent), acrolein (0.4 g, 7.2 mmol, three equivalents) and dichloromethane (10 ml). Catalyst **V** (38 mg, 0.06 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 7/3) affords compound **7b** as a colorless oil (0.425 g, 75%). $[\alpha]_D^{22} = +5.3$ (c 0.97, $CHCl_3$). ^{1}H-NMR δ: 9.48 (d, $J = 8.2$ Hz, 1H), 6.91 (dt, $J = 7.1$ and 15.5 Hz, 1H), 6.80 (m, 4H), 6.11 (ddt, $J = 1.5$, 8.1 and 15.5 Hz, 1H), 4.15 (m, 1H), 3.90 (m, 2H), 3.76 (s, 3H), 3.45 (bs, 1H, OH), 2.52 (m, 2H). ^{13}C-NMR δ: 194.1 (d), 154.3 (d), 154.0 (s), 152.3 (s), 134.6 (d), 115.5 (2d, Ar), 114.6 (2d, Ar), 72.1 (t), 68.6 (d), 55.5 (q), 36.5 (t). MS m/z 236 ([M$^+$], 53), 218 (2), 166 (13), 137 (6), 124 (100), 109 (45).

4.4. Preparation of compound **7c**

A flame-dried round-bottomed flask was charged with olefin **2** (0.20 g, 0.96 mmol, one equivalent), ethyl acrylate (0.29 g, 2.88 mmol, three equivalents) and dichloromethane (5 ml). Catalyst **V** (15 mg, 0.024 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 7/3) affords compound **7c** as a yellow oil (0.188 g, 70%). $[\alpha]_D^{22} = -9.9$ (c 3, $CHCl_3$). ^{1}H-NMR δ: 7.01 (dt, $J = 7.3$, 15.5 Hz, 1H), 6.80 (m, 4H), 5.92 (dt, $J = 1.5$, 15.8 Hz, 1H), 4.15 (q, $J = 7.0$ Hz, 2H), 4.10 (m, 1H), 3.90 (m, 2H), 3.75 (s, 3H), 2.70 (bs, 1H, OH), 2.52 (m, 2H), 1.28 (t, $J = 7.0$ Hz, 3H). ^{13}C-NMR δ: 166.1 (s), 154.1 (s), 152.4 (s), 144.0 (d), 123.9 (d), 115.5 (2d, Ar), 114.6 (2d, Ar), 72.0 (t), 68.8 (d), 60.2 (t), 55.5 (q), 36.0 (t), 14.1 (q). MS m/z 280 ([M$^+$], 46), 217 (2), 166 (3), 149 (2), 137 (3), 124 (100), 109 (28).

4.5. Preparation of compounds **7d** and **8**

A flame-dried round-bottomed flask was charged with olefin **2** (0.10 g, 0.48 mmol, one equivalent), acrylonitrile (0.08 g, 1.44 mmol, three equivalents) and dichloromethane (3 ml). Catalyst **V** (7.50 mg, 0.012 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 1/1) affords of mixture compounds **7d** (22.4 mg, 20%) and **8** (91.3 mg, 49%). For **7d**: ^{1}H-NMR δ: 6.75 (m, 4H), 6.62 (dt, $J = 7.3$ and 11.0 Hz, 1H), 5.39 (d, $J = 11.0$, 13 Hz, 1H), 4.15 (m, 1H), 3.90 (m, 2H), 3.72 (s, 3H), 2.71 (m, 2H), 2.50 (bs, 1H, OH). ^{13}C-NMR δ: 154.2 (s), 152.2 (s), 150.5(d), 115.7 (s, CN), 115.5 (2d, Ar), 114.6 (2d, Ar), 101.6 (d), 72.1 (t), 68.7 (d), 55.5 (q), 35.4 (t). MS m/z 233 ([M$^+$], 49), 166 (4), 149 (4), 137 (3), 124 (100), 109 (41). For **8**: ^{1}H-NMR minor isomer Z δ: 6.80 (m, 8H), 5.67 (t, $J = 4.8$ Hz, 2H, CH=CH), 4.00 (m, 2H), 3.90–3.71 (m, 4H), 3.73 (s, 6H), 2.45 (bs, 2H, 2OH), 2.40–2.34 (m, 4H); major isomer E δ: 6.80 (m, 8H), 5.63 (t, J 3.7 Hz, 2H, CH=CH E), 4.00 (m, 2H), 3.90–3.71 (m, 4H), 3.73 (s, 6H), 2.45 (bs, 2H, 2OH), 2.40–2.34 (m, 4H). ^{13}C-NMR minor isomer Z δ: 154.1 (2s), 152.6 (2s), 127.6 (2d), 115.4 (4d, Ar), 114.6 (4d, Ar), 72.0 (2t), 69.5 (2d), 55.5 (2q), 31.0 (2t); major isomer E δ:153.9 (2s), 152.6 (2s), 128.9 (2d), 115.5 (4d, Ar), 114.5 (4d, Ar), 72.1 (2t), 69.4 (2d), 55.5 (2q), 36.6 (2t). HRMS [Cl$^+$] Calc. for $C_{22}H_{28}0_6$ 388.1886. Found 388.1885.

4.6. Preparation of compounds **7e** and **8**

A flame-dried round-bottomed flask was charged with olefin **2** (0.10 g, 0.48 mmol, one equivalent), methacrolein (0.1 g, 1.44 mmol, three equivalents) and dichioromethane (3 ml). Catalyst **V** (7.50 mg, 0.012 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 1/1) affords compounds **7e** (traces) and **8** (74.5 mg, 40%).

4.7. Preparation of compounds *7f* and *8*

A flame-dried round-bottomed flask was charged with olefin **2** (0.10 g, 0.48 mmol, one equivalent), methyl methacrylate (0.144 g, 1.44 mmol, three equivalents) and dichloromethane (3 ml). Catalyst **V** (7.5 mg, 0.012 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 1/1) affords only compound **8** (95.1 mg, 51%).

4.8. Preparation of compound *7g*

A flame-dried round-bottomed flask was charged with olefin **3** (0.10 g, 0.355 mmol, one equivalent), acrolein (0.06 g, 1.06 mmol, three equivalents) and dichloromethane (3 ml). Catalyst **V** (7.50 mg, 0.012 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 7/3) affords compound **7g** as a yellow solid (98.9 mg, 90%), m.p. 112–110°C. $[\alpha]_D^{22} = +126$ (c 4.4, $CHCl_3$). H-NMR δ: 9.58 (d, J 8.2 Hz, 1H), 7.47 (s, 1H), 7.27 (s, 1H), 6.97 (dt, $J = 7.1$ and 15.4 Hz, 1H), 6.26 (ddt, $J = 1.5$, 8.1 and 15.5 Hz, 1H), 4.25 (m, 1H), 4.10–3.92 (m, 2H), 2.70 (m, 2H), 1.75 (bs, 1H, OH). ^{13}C-NMR δ: 193.5 (d), 152.7 (s), 152.6 (d), 135.1 (d), 131.3 (s), 130.9 (d), 125.0 (s), 122.1 (s), 115.2 (d), 73.0 (t), 68.3 (d), 36.2 (t). MS m/z 309 ([M^+], 11), 240 (7), 209 (13), 196 (100), 181(8), 167 (10), 145 (7), 95 (11), 70 (19).

4.9. Preparation of compounds *7h* and *9*

A flame-dried round-bottomed flask was charged with olefin **4** (0.30 g, 0.83 mmol, one equivalent), methacrolein (0.176 g, 2.55 mmol, three equivalents) and dichloromethane (3 ml). Catalyst **V** (13 mg, 0.02 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 1/1) affords a mixture compounds **7h** (traces) and **9** (144.1 mg, 25%). For **9**: ^{1}H-NMR minor isomer Z δ: (m, 30H), 5.58 (t, $J =$ 4.8 Hz, 2H, CH=CH), 3.75 (m, 2H), 3.41–3.10 (m, 6H), 2.15 (m, 4H), 1.70 (m, 4H); major isomer E δ: (m, 30H), 5.49 (t, $J = 4$ Hz, 2H, CH=CH), 3.75 (m, 2H), 3.41–3.10 (m, 6H), 2.15 (m, 4H), 1.70 (m, 4H). ^{13}C-NMR δ: 143.7 (6s), 129.3 (2d), 128.4 (12d, Ar), 127.9 (12d, Ar), 126.9 (6d, Ar), 87.1 (2s), 70.4 (2d), 62.2 (2t), 40.5 (2t), 36.1 (2t).

4.10. Preparation of compound *7i*

A flame-dried round-bottomed flask was charged with olefin **5** (16.5 mg, 0.04 mmol, one equivalent), ethyl acrylate (12.8 mg, 0.127 mmol, three equivalents) and dichioromethane (1 ml). Catalyst **V** (0.62 mg, 1×10^{-5} mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 6/4) affords compound **7i** as a colorless oil (15.7 mg, 80%). $[\alpha]_D^{22} = +2.5$ (c 1.4, $CHCl_3$).^{1}H-NMR δ: 6.95 (dt, $J = 7.3$ and 15.8 Hz, 1H), 5.88 (dt, $J =$ 1.5 and 15.5 Hz, 1H), 4.15 (q, $J = 7.0$ and 7.3 Hz, 2H), 4.10–3.95 (m, 2H), 3.15 (m, 2H), 2.65 (bs, 1H, OH), 2.55 (bs, 1H, OH), 2.35 (m, 2H), 1.65 (m, 2H), 1.28 (t, $J = 7.0$, 7.3 Hz, 3H). ^{13}C-NMR δ: 166.1 (s), 144.7 (d), 143.5 (3s), 128.4 (6d, Ar), 127.8 (6d, Ar), 127.0 (3d, Ar), 123.8 (d), 86.7 (s), 68.2 (d), 67.4 (d), 67.3 (t), 60.1(t), 40.1(t), 38.5 (t), 14.1(q). HRMS (FAB + –NBA + Na) Calc. for $C_{29}H_{32}O_5Na$ [M + Na] 483.2147. Found 483.2138.

4.11. Preparation of compound *7j*

A flame-dried round-bottomed flask was charged with olefin **6** (70 mg, 0.126 mmol, one equivalent), methyl acrylate (32.5 mg, 0.378 mmol, three equivalents) and dichloromethane (1.5 ml). Catalyst **V** (2 mg, 3×10^{-5} mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 7/3) affords compound **7j** as a colorless oil (54.1 mg, 70%). $[\alpha]_D^{22} = +11$ (c 1.25, $CHCl_3$).^{1}H-NMR δ: 7.60–7.30 (m, 10 H), 7.07 (dt, $J = 7.3$ and 15.8 Hz, 1H), 5.89 (d, $J = 15.8$ Hz, 1H), 3.85–3.68 (m, 3H), 3.73 (s, 3H), 3.58 (bs, 1H, OH), 3.48 (m, 1H), 2.40 (m, 1H), 2.15 (m, 1H), 1.86 (m, 1H), 1.09 (s, 9H), 1.01 (d, $J = 7.3$, 3H), 0.95 (d, $J = 7.0$, 3H), 0.91 (d, $J = 7.0$, 3H), 0.82 (s, 9H), 0.03 (s, 3H), −0.90 (s, 3H). ^{13}C-NMR δ :166.9 (s), 152.9 (d), 135.5 (d), 133.5 (2s), 129.5 (4d, Ar), 127.5 (4d, Ar), 120.4 (2d, Ar), 79.9(d), 74.5 (d), 66.2 (t), 51.2 (q), 40.6 (d), 39.9 (d), 34.2 (d), 26.7 (3q), 25.9 (3q), 19.1 (s), 17.9 (s), 15.6 (q), 13.2 (q), 11.9 (q), −4.0 (q), −4.5 (q). HRMS [Cl^+] Calc. for $C_{35}H_{57}O_5Si_2$, [M + 1] 613.3745. Found 613.3743.

4.12. Preparation of compound **10**

A flame-dried round-bottomed flask was charged with olefin **2** (0.20 g, 0.96 mmol, one equivalent), allyltrimethylsilane (0.098 g, 0.86 mmol, 0.9 equivalents) and dichloromethane (6 ml). Catalyst **V** (15 mg, 0.024 mmol, 0.025 equivalents) was subsequently added as a solid, producing a light green solution which was stirred for 36 h at ambient temperature. The mixture was then concentrated in vacuo to a dark brown oil. Purification of this residue by silica gel chromatography (hexanes/ethyl acetate: 8/2) affords compound **10** as a colorless oil (214.8 mg, 76%). ^{1}H-NMR δ: 6.80 (m, 4H), 5.56 (m, 1H), 5.35 (m, 1H), 4.10–3.80 (m, 3H), 3.75 (s, 3H), 2.34 (m, 3H), 1.48 (m, 2H), 0.01 (s, 9H). ^{13}C-NMR minor isomer *Z* δ: 154.0 (s), 152.7 (s), 128.9 (d), 121.5 (d), 115.4 (2d, Ar), 114.5 (2d, Ar), 72.2 (t), 70.0(d), *55.5* (q), 30.9 (t), 18.6 (t), −1.9 (3q); major isomer *E* δ: 153.9 (s), 152.6 (s), 130.5 (d), 123.0 (d), 115.4 (2d, Ar), 114.5 (2d, Ar), 72.1 (t), 69.8 (d), 55.5 (q), 36.8 (t), 22.8 (t), −2.0 (3q). MS *m*/*z* 294 ([M$^+$], 32), 196 (16), 181(18), 166 (3), 150 (5), 124 (100), 109 (16), 73 (47).

Acknowledgements

J.C. is grateful to Eli-Lilly for financial support and A.H.H. is grateful to the US National Science Foundation (CHE-9905806) for financial support. S.B. thanks the CNRS for a grant.

References

[1] For recent reviews on olefin metathesis, see: (a) R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413. (b) A. Fürstner, Top. Catal. 4 (1997) 285. (c) M. Schuster, S. Blechert, Angew. Chem. Int. Ed. Engl. 36 (1997) 2036. (d) A. Fürstner, Top. Organomet. Chem. 1 (1998) 37. (e) A. Fürstner, Angew. Chem. Int. Ed. Engl. 39 (2000) 3013. (f) A. Fürstuer (Ed.), Alkene Metathesis in Organic Synthesis, Springer, Berlin, 1998.

[2] (a) R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. Dimare, M. O'Reagan, J. Am. Chem. Soc. 112 (1990) 3875. (b) G.C. Bazan, E. Khosravi, R.R. Schrock, W.J. Reast, V.C. Gibson, M. O'Reagan, J.K. Thomas, W.M. Davis, J. Am. Chem. Soc. 112 (1990) 8378. (c) G.C. Bazan, J.H. Oskam, H.N. Cho, L.Y. Park, R.R. Schrock, J. Am. Chem. Soc. 113 (1991) 6899.

[3] (a) P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, Angew. Chem. Int. Ed. Engl. 34 (1995) 2039. (b) P. Schwab, R.R. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.

[4] (a) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674. (b) M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, Tetrahedron Lett. 40 (1999) 2247.

[5] L. Ackermann, A. Fürstner, T. Weskamp, F.J. Kohl, W.A. Herrmann, Tetrahedron Lett. 40 (1999) 4787.

[6] (a) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, Jr., A.H. Hoveyda, J. Am. Chem. Soc. 121 (1999) 791. (b) S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, J. Am. Chem. Soc. 122 (2000) 8168.

[7] (a) W.E. Crowe, D.R. Goldberg, J. Am. Chem. Soc. 117 (1995) 5162. (b) O. Brümmer, A. Rückert, S. Blechert, Chem. Eur. J. 3 (1997) 441.

[8] A.K. Chatterjee, J.R. Morgan, M. Scholl, R.H. Grubbs, J. Am. Chem. Soc. 122 (2000) 3783.

[9] J.P. Morgan, R.H. Grubbs, Org. Lett. 2 (2000) 3153.