Cross-Metathesis Reaction: Direct Synthesis of Functionalized Allylsilanes

Samir BouzBouz,* Elsa De Lemos, Janine Cossy*

Laboratoire de Chimie Organique associé au CNRS, 10 rue Vauquelin, 75231 Paris Cedex 05, France
Fax: (+ 33)1-40-79-46-60, e-mail: Janine.Cossy@espci.fr

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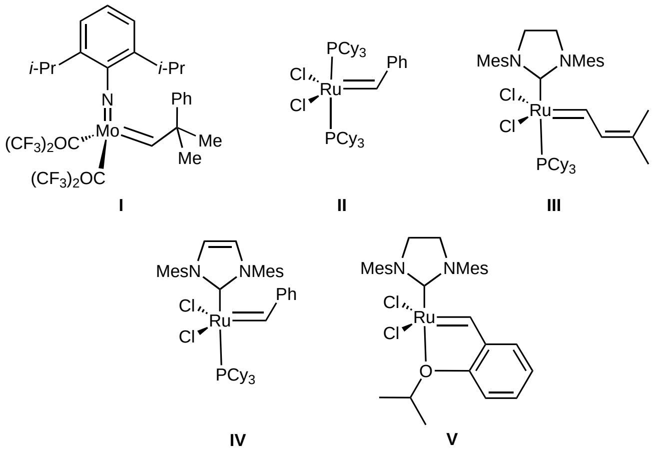
Abstract: Cross-metathesis between α,β-unsaturated carbonyl compounds and allylsilanes with Hoveyda's catalyst leads to functionalized allylsilanes in moderate to good yields and with excellent *E*/*Z* stereoselectivity in favor of the *E*-isomer.

Keywords: allylsilanes; carbenes; cross-metathesis; ruthenium; α,β-unsaturated carbonyl compounds

Allylsilanes are versatile synthetic intermediates.[1] In order to expand their synthetic potential, γ-trialkylsilyl-α,β-unsaturated carbonyl derivatives have been prepared.[2] These compounds react with benzaldehyde in the presence of $ZnBr_2$ to give exclusively the γ-substituted products (*E*-configuration) in high yield.[3] Furthermore, when a fluorine-ion-catalyzed reaction is achieved, α-alkylated compounds are obtained predominantly.[3] Although, the chemospecificity shown by these bifunctional compounds is inherently interesting, a simple and direct preparation from simple starting material is a prerequisite for their use as synthetic intermediates. A practical route to these compounds could involve olefin metathesis utilizing well-defined alkylidene catalysts such as **I**,[4] **II**,[5] **III**,[6] **IV**,[7] or **V**[8] (Scheme 1). However, the formation of olefins with vinylic functionality through cross metathesis (CM) has met with limited success.[9] Furthermore, olefins conjugated with ketones, esters, and amides are not compatible with alkylidene **I** and fail to react with **II** under cross-metathesis conditions.[6] Recently, the highly active ruthenium olefin metathesis catalysts **IV** and **V** were found to efficiently catalyze the cross-metathesis reaction of olefins with activated allylic or homoallylic alcohols and certain derivatives.[10]



Scheme 1. Metal carbenes.

Herein, we report a versatile cross-coupling reaction of α,β-unsaturated esters, ketones, aldehydes, and acids with allyltrimethyl- and allyltriphenylsilane. The reactions were performed at room temperature in methylene chloride (CH_2Cl_2) in the presence of 5 mol % of catalyst **V**. Several unsaturated carbonyl compounds were screened for cross-metathesis with allylsilanes and the results are reported in Table 1.

The reaction of ethyl acrylate with allyltrimethylsilane produced ester **6** in a disappointingly low yield of 40%. However, an excellent *E*/*Z* stereoselectivity of 30/1 was observed. When ethyl vinyl ketone **2** and acrolein **3** were likewise combined with allyltrimethylsilane the corresponding olefins **8** and **10** were obtained in 50% and 37% yield with an *E*/*Z* stereoselectivity greater than 30/1 (Table 1, Entries 3 and 5).

Additionally, we discovered that unsaturated acids, such as acrylic acid **4**, were able to participate in the cross-metathesis reaction with allyltrimethylsilane as compound **12** was obtained in good yield (60%) and with excellent stereoselectivity (Table 1, Entry 7). The low yields of **6**, **8**, and **10** are probably due to the volatility of the cross-metathesis products. To verify this hypothesis, the cross-metathesis reaction of α,β-unsaturated carbonyl compounds was carried out with allyltriphenylsilane. This modification afforded silanes **7**, **9**, **11**, and **13** from substrates **1** – **4** in excellent yields (70% or higher) and with 30/1 *E*/*Z* stereoselectivity (Table 1, Entries 2, 4, 6, and 8).

Hyperconjugative C-Si electron donation from the $-CH_2SiR_3$ substituent of allysilanes enhances olefin nucleophilicity but has little effect on alkylidene stability. Thus, the allylsilanes undergo selective cross-metathesis with π-substituted olefins such ethyl acrylate (**1**),

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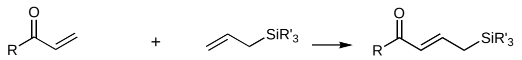
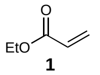
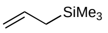
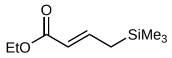
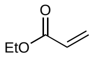
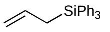
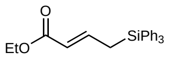
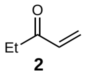
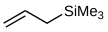
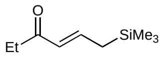
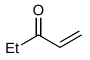
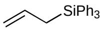
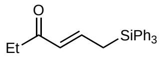
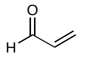
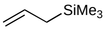
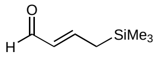
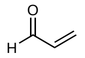
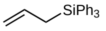
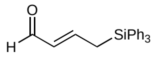
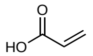
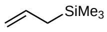
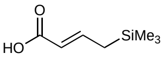
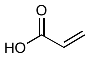
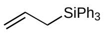
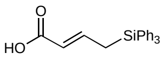
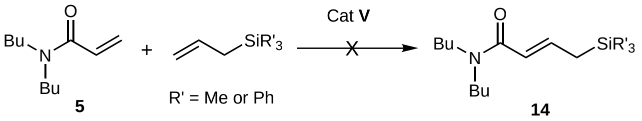
Table 1. Cross-metathesis reaction of α,β-unsaturated carbonyl compounds and allylsilanes.[a]



Entry	α,β-Unsaturated carbonyl compound	Allysilane (R' = Me or Ph)	Product (Yield %, *E*/*Z*)
1	 **1**		 **6** (40%, 30/1)
2	 **1**		 **7** (86%, 30/1)
3	 **2**		 **8** (50%, 30/1)
4	 **2**		 **9** (80%, 30/1)
5	 **3**		 **10** (37%, 30/1)
6	 **3**		 **11** (82%, 30/1)
7	 **4**		 **12** (60%, 30/1)
8	 **4**		 **13** (70%, 30/1)

[a] Reaction with 5 mol % of **V**, at r.t. in CH_2Cl_2.



Scheme 3. Cross-metathesis reaction of α,β-unsaturated amide **5** and allylsilanes.

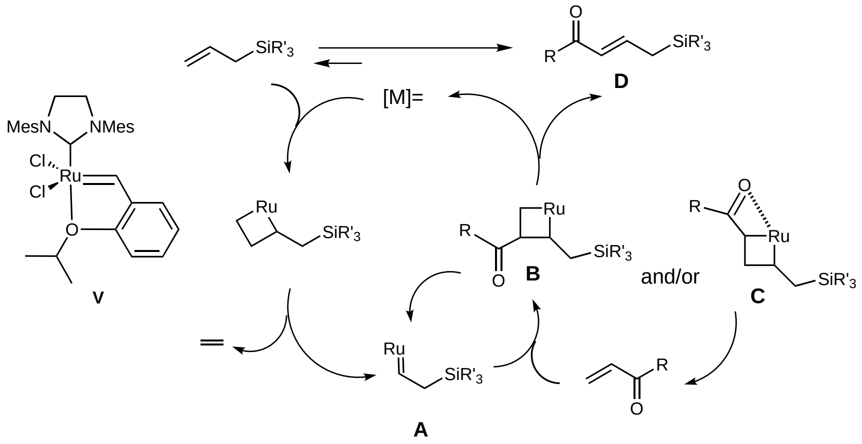
ethyl vinyl ketone (**2**), acrolein (**3**), and acrylic acid (**4**) according to Scheme 2. Complex **A** will be formed and will react with the α,β-unsaturated carbonyl compounds to form complex **B** and/or **C**. Only complex **B** will produce cross-metathesis products of type **D**. In complex **C**, the carbonyl function is chelated to the metal center and the cross-metathesis should not proceed.[11] The degree of chelation will depend on the electron density at the oxygen atom and/or on steric hindrance due to the R group. This hypothesis is in accord with the finding that the α,β-unsaturated amide **5** fails to yield the cross-metathesis product **14** upon treatment with allylsilanes in the presence of catalyst **V** (Scheme 3).

In conclusion, the cross-metathesis reaction of a variety of electron-deficient olefins employing the ruthenium catalyst **V** has been achieved. These results demonstrate the high activity and functional group compatibility of **V** which significantly expands the range of olefins that can participate in the cross-metathesis reaction. The activated allylsilanes obtained through this reaction provide useful synthetic intermediates.

Experimental Section

General Remarks

All the reactions were carried out under an atmosphere of argon. Solvents and reagents were purified beyond reagent grade as follows: diethyl ether was distilled over Na/benzophenone while methylene chloride and pyridine were 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 an ethanolic solution of *p*-anisaldehyde. NMR spectra were acquired on a Bruker spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C, in $CDCl_3$, except for compound **13** in CD_3COCD_3.



Scheme 2. Proposed mechanism.

Preparation of Compound 6

A flame-dried round-bottomed flask was charged with allyltrimethylsilane (0.2 g, 1.75 mmol, 1 equiv.), ethyl acrylate (0.526 g, 5.26 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (55 mg, 0.09 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **6** as a colorless oil; yield: 0.130 g (40%). ^{1}H NMR: $\delta = 7.00$ (dt, $J = 8.8$ and 15.4 Hz, 1H), 5.60 (dt, $J = 1.5$ and 15.4 Hz, 1H), 4.11 (q, $J = 7.3$ Hz, 2H), 1.68 (dd, $J = 1.5$ and 9.2 Hz, 2H), 1.21 (t, $J = 7.3$ Hz, 3H), 0.00 (s, 9H); ^{13}C NMR: $\delta = 166.7$ (s), 147.6 (d), 118.8 (d), 59.6 (t), 24.6 (t), 14.1 (q), –2.0 (3q); MS: $m/z = 186$ (M$^+$, 9), 171 (7), 141 (26), 127 (7), 103 (20), 73 (91), 68 (100); IR (neat): $\nu = 1720$, 1640 cm^{-1}.

Preparation of Compound 7

A flame-dried round-bottomed flask was charged with allyltriphenylsilane (0.2 g, 0.66 mmol, 1 equiv.), ethyl acrylate (0.2 g, 2 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (20.8 mg, 0.03 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **7** as a white solid; yield: 0.213 g (86%); mp 118 – 120 °C. ^{1}H NMR: $\delta = 7.60$ – 7.30 (m, 15H), 7.15 (dt, $J = 8.8$ and 15.4 Hz, 1H), 5.75 (dt, $J = 1.5$ and 15.4 Hz, 1H), 4.13 (q, $J = 7.0$ Hz, 2H), 2.65 (dd, $J = 1.5$ and 8.8 Hz, 2H), 1.21 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR: $\delta = 166.3$ (s), 145.8 (d), 135.5 (6d), 133.3 (3s), 129.8 (3d), 127.9 (6d), 121.0 (d), 59.7 (t), 21.3 (t), 14.2 (q); MS: $m/z = 372$ (M$^+$, 22), 327 (2), 259 (100), 137 (6), 181 (17), 105 (6). IR (KBr): $\nu = 1710$, 1624 cm^{-1}.

Preparation of Compound 8

A flame-dried round-bottomed flask was charged with allyltrimethylsilane (0.2 g, 1.75 mmol, 1 equiv.), ethyl vinyl ketone (0.442 g, 5.26 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (55 mg, 0.09 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **8** as a colorless oil; yield: 0.149 g (50%). ^{1}H NMR: $\delta = 6.91$ (dt, $J = 8.8$ and 15.4 Hz, 1H), 5.92 (dt, $J = 1.5$ and 15.4 Hz, 1H), 2.50 (q, $J = 7.3$ Hz, 2H), 1.70 (dd, $J = 1.1$ and 8.8 Hz, 2H), 1.05 (t, $J = 7.3$ Hz, 3H), 0.00 (s, 9H); ^{13}C NMR: $\delta = 200.4$ (s), 145.8 (d), 128.2 (d), 32.9 (t), 24.9 (t), 8.2 (q), –2.0 (3q); MS: $m/z = 170$ (M$^+$, 10), 155 (40), 141 (22), 113 (5), 73 (100); IR (neat): $\nu = 1670$, 1615 cm^{-1}.

Preparation of Compound 9

A flame-dried round-bottomed flask was charged with allyltrimethylsilane (0.2 g, 0.66 mmol, 1 equiv.), ethyl vinyl ketone (0.526 g, 5.26 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (20.8 mg, 0.03 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **9** as a white solid; yield: 0.189 g (80%); mp 82 – 84 °C. ^{1}H NMR: $\delta = 7.61$ – 7.40 (m, 15H), 7.15 (dt, $J = 8.8$ and 15.4 Hz, 1H), 6.05 (dt, $J = 1.5$ and 15.4 Hz, 1H), 2.65 (dd, $J = 1.1$ and 8.8 Hz, 2H), 2.42 (q, $J = 7.3$ Hz, 2H), 1.07 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR: $\delta = 200.2$ (s), 143.9 (d), 135.5 (6d), 133.3 (3s), 130.1 (d), 129.9 (3d), 128.0 (6d), 33.0 (t), 21.5 (t), 8.2 (q); MS: $m/z = 356$ (M$^+$, 2), 327 (3), 265 (41), 259 (100), 181 (18), 105 (7). IR (KBr): $\nu = 1670$, 1620 cm^{-1}.

Preparation of Compound 10

A flame-dried round-bottomed flask was charged with allyltrimethylsilane (0.2 g, 1.75 mmol, 1 equiv.), acrolein (0.294 g, 5.26 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (55 mg, 0.09 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **10** as a colorless oil; yield: 0.092 g (37%); ^{1}H NMR: $\delta = 9.38$ (d, $J = 8.1$ Hz, 1H), 6.85 (dt, $J = 8.8$ and 15.4 Hz, 1H), 5.92 (ddt, $J = 1.1$, 8.1, and 15.4 Hz, 1H), 1.84 (dd, $J = 1.1$ and 8.8 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR: $\delta = 193.3$ (d), 158.2 (d), 131.4 (d), 26.3 (t), –1.9 (3q); MS: $m/z = 142$ (M$^+$, 18), 127 (24), 111 (6), 99 (13), 73 (100). IR (neat): $\nu = 2980$, 1680, 1640 cm^{-1}.

Preparation of Compound 11

A flame-dried round-bottomed flask was charged with allyltriphenylsilane (0.2 g, 0.66 mmol, 1 equiv.), acrolein (0.112 g, 2 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (20.8 mg, 0.03 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **11** as a white solid; yield: 0.179 g (82%); mp 92 – 94 °C. ^{1}H NMR; $\delta = 9.48$ (d, $J = 7.7$ Hz, 1H), 7.70 – 7.5 (m, 15H), 7.08 (dt, $J = 7.1$ and 15.5 Hz, 1H), 6.15 (ddt, $J = 1.1$, 8.8 and 15.4 Hz, 1H), 2.68 (dd, $J = 1.1$ and 8.8 Hz, 2H); ^{13}C NMR: $\delta = 193.2$ (d), 156.2 (d), 135.4 (6d), 133.1 (d), 132.8 (3s), 130.0 (3d), 128.0 (6d), 22.7 (t). MS: $m/z = 328$ (M$^+$, 1), 259 (100), 237 (27), 181 (17), 155 (6), 130 (8), 105 (7). IR (KBr): $\nu = 1685$, 1630 cm^{-1}.

Preparation of Compound 12

A flame-dried round-bottomed flask was charged with allyltrimethylsilane (0.2 g, 1.75 mmol, 1 equiv.), acrylic acid (0.378 g, 5.26 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (55 mg, 0.09 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **12** as a white solid; yield: 0.166 g (60%); mp

58 – 60 °C. ^{1}H NMR: $\delta = 11.15$ (bs, 1H, OH), 7.15 (dt, $J = 8.8$ and 15.4 Hz, 1H), 5.62 (dt, $J = 1.5$ and 15.4 Hz, 1H), 1.75 (dd, $J = 1.1$ and 8.8 Hz, 2H), 0.00 (s, 9H); ^{13}C NMR: $\delta = 172.1$ (s), 151.2 (d), 118.3 (d), 25.2 (t), –1.9 (3q). MS: $m/z = 158$ (M^+, 0.03), 142 (25), 127 (3), 98 (21), 75 (59), 73 (92), 68 (100); IR (KBr): $\nu = 1680, 1630$ cm^{-1}.

Preparation of Compound 13

A flame-dried round-bottomed flask was charged with allyltriphenylsilane (0.2 g, 0.66 mmol, 1 equiv.), acrylic acid (0.144 g, 2 mmol, 3 equiv.) and CH_2Cl_2 (5 mL). Catalyst **V** (20.8 mg, 0.03 mmol, 0.05 equiv.) was subsequently added as a solid, producing a light green solution which was stirred for 12 h at 25 °C. The mixture was then concentrated under vacuum and the residual dark brown oil was purified by chromatography on silica gel (hexanes/ethyl acetate, 9/1) to afford compound **13** as a white solid; yield: 0.160 g (70%); mp 80 – 82 °C. ^{1}H NMR (CD_3COCD_3): $\delta = 11.15$ (bs, 1H, OH), 7.50 – 7.25 (m, 15H), 7.00 (dt, $J = 8.8$ and 15.4 Hz, 1H), 5.62 (dt, $J = 1.5$ and 15.4 Hz, 1H), 2.68 (dd, $J = 1.1$ and 8.8 Hz, 2H); ^{13}C NMR (CD_3COCD_3): $\delta = 167.5$ (s), 147.3 (d), 136.6 (6d), 134.8 (3s), 131.0 (3d), 129.2 (6d), 122.2 (d), 21.5 (t); MS: $m/z = 344$ (M^+, 2), 267 (83), 259 (100), 223 (32), 199 (33), 181 (17), 105 (6); IR (KBr): $\nu = 1680, 1630$ cm^{-1}.

Acknowledgements

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