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Synthesis of Linear (*Z*)-α,β-Unsaturated Esters by Catalytic Cross-Metathesis. The Influence of Acetonitrile

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Abstract

Kinetically-controlled catalytic cross-metathesis reactions that generate (Z)-α,β-unsaturated esters selectively are disclosed. A key finding is that the presence of acetonitrile obviates the need for using excess amounts of a more valuable terminal alkene substrates. On the basis of X-ray structure and spectroscopic investigations a rationale for the positive impact of acetonitrile is provided. Transformations leading to various E,Z-dienoates are highly Z-selective as well. Utility is highlighted by application to stereoselective synthesis of the C1–C12 fragment of biologically active natural product (−)-laulimalide.

Keywords

alkenes; catalysis; enoates; cross-metathesis; dienoates; synthesis; molybdenum

*C*onspicuously absent from the list of available kinetically-controlled stereoselective olefin metathesis reactions[1,2] are cross-metathesis (CM) processes that can deliver linear (*Z*)-α,β-unsaturated esters.[3,4,5] Such transformations would offer a valuable disconnection that may be complementary to Wittig-type[6] or alkyne partial hydrogenation reactions.[7] A case in point is a possible stereoselective route to the C1–C12 segment of (−)-laulimalide, a naturally occurring microtubule stabilizing agent (Scheme 1a).[8] *Z*-Enoate **i** could accordingly be synthesized through two *Z*-selective CM steps (**ii**→**i** and **v**→**iv**). Small-ring

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lactones are accessible through ring-closing metathesis (RCM), but because of carbonyl coordination to the metal center, these processes are at times inefficient and demand elevated temperatures and relatively high catalyst loadings (e.g., 20 mol %).[9] In such instances a Lewis acidic additive can enhance efficiency[10] but not always.[11]

Development of a *Z*-selective enoate CM requires that the following problems are resolved (Scheme 1b): 1) The carbonyl unit of a carboxylic ester-substituted alkylidene might coordinate to the metal center to reduce reaction rates. 2) High efficiency might demand larger amounts of a structurally complex alkenyl compound. For example, excess of the more valuable α-alkenes **ii** or **v** might be required for high efficiency (Scheme 1a). 3) Electronic factors do not favor formation of productive metallacyclobutanes. Unlike macrocyclic RCM reactions,[12] where geometric constraints oppose the mismatched electronic factors (see **I**, Scheme 1b), in CM formation of electronically (and sterically) favored intermediates **II**–**III** would lead to nonproductive metallacyclobutanes (vs. **IV**–**V**, Scheme 1b). The active complex must therefore be sufficiently long living for productive CM that occurs subsequent to nonproductive cycles.

We began by probing the ability of a number of complexes to promote CM between 1-decene (3.0 equiv.) and acrylate **1a** (Table 1). With **Ru-1**[13] formation of ***Z*-2a** was fully *Z*-selective but inefficient (Table 1, entry 1) and with **Ru-2**[5e] none of the expected product was formed (entry 2). Reaction with bis-alkoxide **Mo-1** proceeded only to 35% conversion after 4 hours and was mildly *E*-selective (31:69 *Z*:*E*). There was 90% conversion to the 1,2-disubstituted enoate with monoaryloxide pyrrolide (MAP) complex **Mo-2a**[14] but the *E* isomer was again formed preferentially (6:94 *Z*:*E*, entry 4) probably due to facile post-metathesis isomerization. The latter scenario is consistent with the findings in entries 5 and 6: for CM with **Mo-2b**, which carries a more sizeable aryloxide group, conversion was lower (62% vs. 90% with **Mo-2a**) but **2a** was obtained with 92:8 *Z*:*E* selectivity. With the more active pentafluorophenylimido **Mo-3**, there was 96% conversion after four hours but a nearly equal mixture of *Z* and *E*-**2a** was generated (58:42).

Our goal then became to find conditions that would deliver high efficiency and *Z* selectivity simultaneously. What made the task particularly challenging was that enhanced efficiency would have to be achieved without excess amounts of the (non-enoate) terminal alkene. In light of the possibility of *Z*-to-*E* interconversion and because **Mo-3** was similarly efficient but delivered a more favorable *Z*:*E* ratio than **Mo-2a** (cf. entries 4 and 6, Table 1) we reasoned that the CM process with the former complex might be substantially improved under a different set of conditions. Accordingly, the studies summarized in Table 2 were carried out. Under mild vacuum (100 torr) and with the same initial 1-decene:acrylate ratio as before (3:1), there was 79% conversion to **2a** after five minutes and stereoselectivity improved to 79:21 *Z*:*E* (62% yield; entry 1). However, the *Z* selectivity was diminished within 30 minutes (53:47 *Z*:*E*; entry 2), further supporting the post-metathesis isomerization scenario. Selectivity was considerably higher (>98%) with lesser amounts of 1-decene but efficiency was poor (≤30% conv., entries 3–4) and extended times did not improvement matters.

To gain more information as to whether internal carbonyl chelation hampers reactivity, spectroscopic analysis of the reaction between **Mo-2b** with **1b** was performed (Scheme 2). An alkylidene proton resonance appeared in one hour at δ 11.47 ppm, which probably belongs to the *anti* isomer **Mo-4** (J_{CH} = 160 Hz).[15] We were also able to secure the X-ray structure of a closely related *anti*-alkylidene **Mo-5**; the Mo–O bond length (2.33 Å) suggests Mo-carbonyl association. The alkylidene C–H resonance for **Mo-5** appears at δ 10.46 ppm (J_{CH} = 182 Hz), suggesting the major isomer in the initial process to be *anti*.

We surmised that internal chelation might be weakened or entirely inhibited if an external Lewis base, which would likely be more readily displaced by an alkene substrate, were to be coordinated to the Mo center. Turnover frequency could be diminished, but turnover number could increase if olefin binding and displacement of the external Lewis base were to become more competitive. Further, the Lewis base-chelated 16-electron methylidene species would be less prone to decomposition and less able to promote post-metathesis isomerization.[16] Diminished reactivity could then translate to superior chemoselectivity. As pointed out previously regarding CM involving **Mo-1**,[17] an alkyl-substituted alkylidene might react faster with an electron deficient acrylate and vice versa. Nonetheless, the challenge here was to identify a Lewis basic additive that would coordinate readily with a Mo MAP complex and yet could be displaced by an olefin.

Mindful of observations regarding increased enantioselectivity of reactions with chiral Mo diolates in tetrahydrofuran (vs. benzene),[18] we investigated the CM of 1-decene and **1a** in the same solvent. Efficiency and *Z* selectivity was notably higher (**2a** in 70% yield and 90:10 *Z*:*E*; entry 1, Table 3) and more so in a less concentrated solution (93:7; entry 2). Still, after 30 minutes olefin isomerization became problematic (69:31 *Z*:*E*; entry 3).

We then examined the impact of acetonitrile,[19] envisioning that this mildly Lewis basic[20] but less sterically demanding (vs. thf) additive might coordinate to the Mo complex, disrupting internal chelation. This would allow the acetonitrile-bound *syn* alkylidene, the precursor to a productive metallacyclobutane (cf. **IV**, Scheme 1b), to be formed (alkene substrate may displace the MeCN). With acetonitrile as the solvent the model CM remained highly *Z*-selective (>98% *Z*) but efficiency decreased substantially (14% conv., 60 min; Table 3, entry 4). In a more concentrated solution (entry 5) **2a** was formed in 67% yield and 91% *Z* selectivity; there was no significant change in efficiency or stereochemical purity with an equal mixture of the two substrates (entry 6). With a 1:2 ratio of 1-decene:**1a** (entry 7, Table 3), *Z*-**2a** was isolated in 71% yield and 94:6 *Z*:*E* selectivity (22 °C, 1 h).

The method has appreciable range (Scheme 3). With a 1:2 ratio of the α-olefin:**1a**, *Z*-enoates **2b-h** were isolated in up to 71% yield and >98% *Z* selectivity. Reactions with aryl olefins were hampered by stilbene formation, but those of sterically hindered vinylcyclohexane afforded **2g** in 64% yield and 94:6 *Z*:*E* ratio. Transformations with 1,3-dienes were less efficient but highly stereoselective (cf. *Z*,*E*-**2h**).[21]

Spectroscopic studies support acetonitrile–Mo coordination.[22] With more MeCN the alkylidene proton singlet moves downfield (Figure 1), consistent with previous observations.[23] The broader signal, and the absence of separate resonances for the free and

acetonitrile-containing species at different temperatures, implies rapidly reversible complex formation (Figure 1; in neat acetonitrile; cf. Table 3). An additional resonance was detected at ~δ 10.7 ppm when the ^{1}H NMR spectrum of the sample containing 0.5 equivalents of Me^{13}CN was recorded at −60 to −80 °C; we attribute this to the acetonitrile-free complex, which was not simultaneously present when 5.0 equivalents of the additive was present.[23]

E,*Z*-Dienoates may be prepared through catalytic CM as well (Scheme 4), allowing access to either stereoisomer of an α,β,γ,δ-unsaturated ester. Either a *t*-butyl or a phenyl ester may be accessed, as indicated by synthesis of *E*,*Z*-**4a** and *E*,*Z*-**5a**. Although products were obtained in similar yield and *Z* selectivity in this case, use of *t*-butyl dienoate often led to better outcomes.[21] Here, adamantylimido **Mo-6** is optimal. For example, **5a** was generated with 87:13 *Z*:*E* selectivity with **Mo-3**. There was <2% conversion to the desired product with **Ru-1**,**2** and **Mo-1** (cf. Table 1). Two additional points are noteworthy: (1) Because the dienoate carbonyl group can no longer associate intramolecularly with the Mo center, addition of thf or MeCN only led to lower reaction rates. (2) Excess amounts of the terminal alkene are needed as otherwise formation of the less reactive[24] alkenyl-substituted Mo alkylidene species leads to lower efficiency.

To complete the study, we examined the feasibility of the aforementioned application regarding synthesis of laulimalide (Scheme 5). CM between alkene **6**[9b] and **1a** (2.0 equiv.) performed in a 10:1 MeCN:PhCN[25] mixture afforded **7** with 91:9 *Z*:*E* selectivity. Ester hydrolysis/silyl ether removal and lactone formation occurred upon treatment with 10 mol % *p*-toluenesulfonic acid, affording **8** in 74% overall yield. Conversion to homoallyl ether **9**[10b] was followed by a second CM, delivering diene **10**, formerly utilized in a former synthesis of laulimalide,[9b] in 63% yield and 94:6 *Z*:*E* selectivity.

Further mechanistic investigations and applications to the development of other kinetically controlled stereoselective olefin metathesis reactions are in progress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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[15]. The value of J_{CH} coupling for a *syn* alkylidene proton is typically 120–130 Hz whereas those corresponding to the corresponding *anti* isomers are ~140 Hz. See: Schrock RR, Hoveyda AH. Angew. Chem. Int. Ed. 2003; 42:4592–4633. and references therein.

[16]. It is unlikely that the alkylidene derived from 1-decene reacts with the kinetically formed *Z*-enoate to cause stereoisomerization; the corresponding all-*syn* trisubstituted metallacyclobutane intermediate would probably be energetically disfavored due to steric repulsion. For related discussions, see: Ref. [4f].

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[21]. The comparatively lower yield of *Z*-**2h** might be partly the result of CM at the internal *E*-alkene. However, the corresponding byproduct could not be isolated due to the formation of several other inseparable byproducts.

[22]. See the Supporting Information for details.

[23]. a) Schrock RR. Chem. Rev. 2002; 102:145–179. [PubMed: 11782131] b) Halbert S, Copeéret C, Raynaud C, Eisenstein O. J. Am. Chem. Soc. 2016; 138:2261–2272. Ref. [15]. *Syn* and *anti* alkylidene resonances are known to shift downfield upon binding of a base to the metal to give a five-coordinate complex. For a detailed study and explanation of chemical shifts in NMR spectra of d^0 alkylidene complexes, see: and references therein. [PubMed: 26787258]

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[25]. Screening studies indicate that use of this solvent mixture (vs. pure MeCN) leads to higher yields of the desired products due to lower amounts of terminal alkene homocoupling byproducts formed; for example, in pure MeCN, *Z*-lactone **9** and enoate **10** were formed in 41% overall and 50% yield, respectively (vs. 74% overall and 63% yield). The reason for this effect is not clear at the present time. Use of benzonitrile as solvent is not practical due to its high boiling point (191 °C).

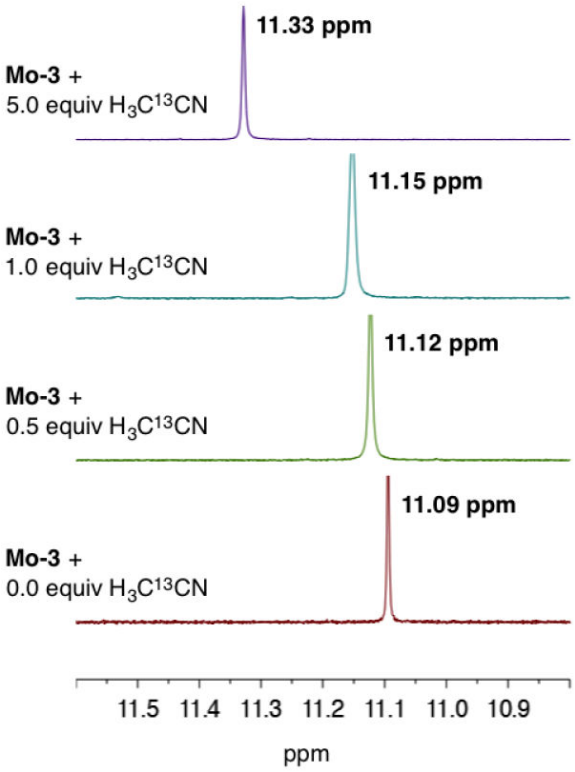
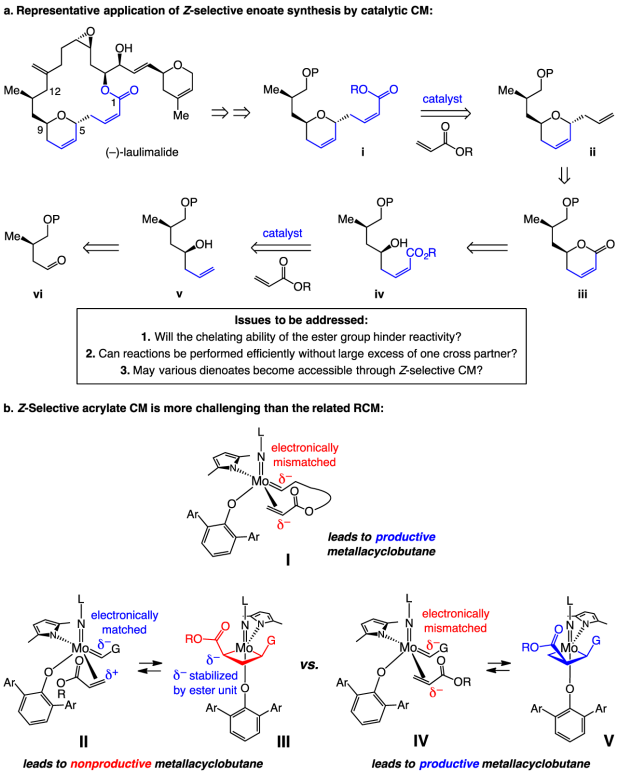


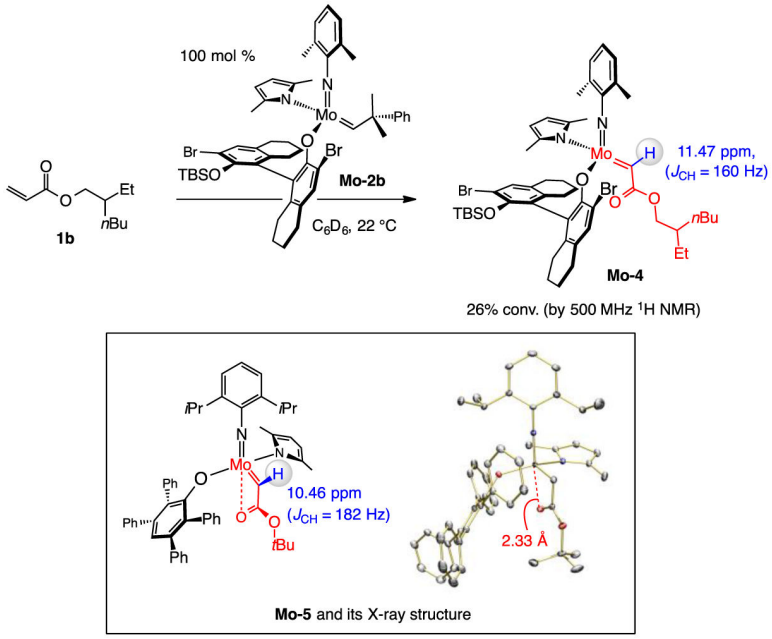
Figure 1.

Spectroscopic analysis indicating rapid and reversible formation of an acetonitrile complex derived from **Mo-3** (600 MHz ^{1}H NMR, 22 °C, C_6D_6; see the Supporting Information for details).



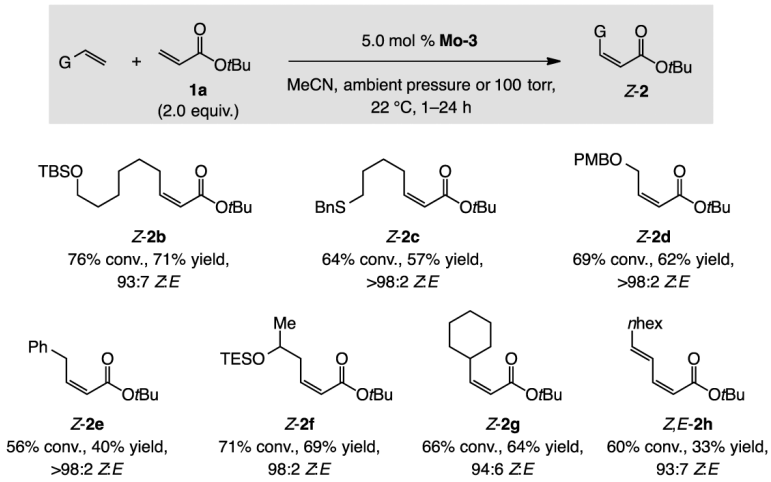
Scheme 1.

The principal objectives of the study and the challenges involved.



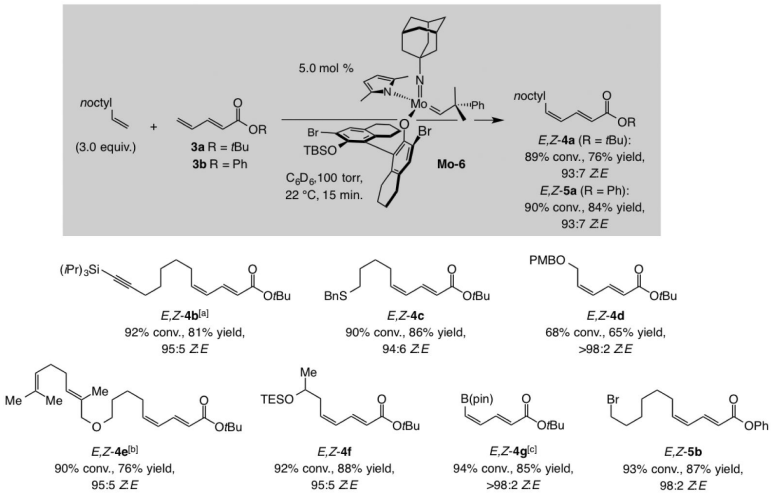
Scheme 2.

Preparation and structural analysis of two ester-substituted Mo alkylidene complexes.



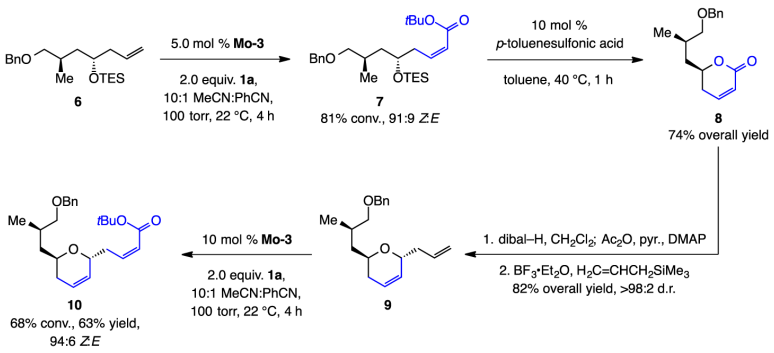
Scheme 3.

(*Z*)-α,β-Unsaturated esters obtained through catalytic cross-metathesis. Reactions performed at 100 torr for 1 h (**2b**–**c**), at 100 torr for 4 h (**2d**–**f**) and at ambient pressure for 24 h (**2g**–**h**). See the Supporting Information for details.



Scheme 4.

(*E,Z*)-Dienoates obtained through catalytic *Z*-selective cross-metathesis. [a] Overall yield after removal of the silyl group. [b] 1.5 equiv. 1-decene used. [c] Reaction time = 24 h. See the Supporting Information for details.

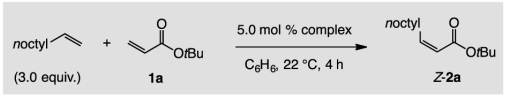


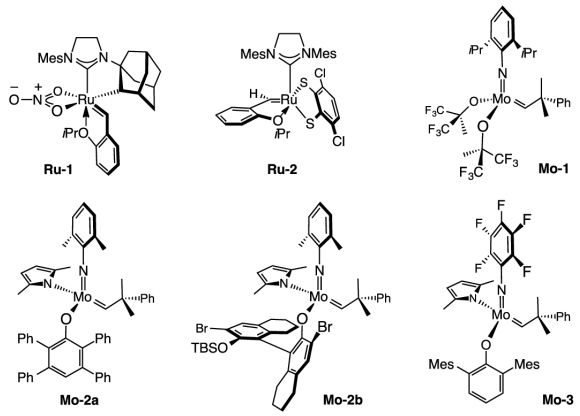
Scheme 5.

Application to stereoselective synthesis of the C1–C12 segment of laulimalide.

Table 1

Examination of various complexes for CM of 1-decene and acrylate **1a**.[a]





Entry	Complex	Conv. [%][b]	Yield [%][c]	*Z*:*E*[b]
1	**Ru-1**	27	ND	>98:2
2	**Ru-2**	<2	NA	NA
3	**Mo-1**	35	31	31:69
4	**Mo-2a**	90	90	6:94
5	**Mo-2b**	62	55	92:8
6	**Mo-3**	96	83	58:42

See the Supporting Information for details. Abbreviations: Mes, 2,4,6-$(Me)_3C_6H_2$; ND, not determined; NA, not applicable.

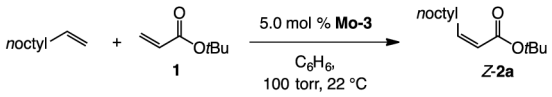
[a]Performed at ambient pressure (entries 1–2) or under 100 torr vacuum (entries 3–6).

[b]Determined by analysis of ^{1}H NMR spectra of unpurified mixtures; conv. (±2%) with dmf as the internal standard.

[c]Yields of isolated and purified products (±5%).

Table 2

Influence of time and substrate ratios on the CM leading to *Z*-**2a**.[a]



Entry	*t* [min]	Decene:1a	Conv. [%][b]	Yield [%][c]	*Z*:*E*[b]
1	5	3:1	79	62	79:21
2	30	3:1	82	56	53:47
3	5	1:1	30	ND	>98:2
4	5	1:3	20	ND	>98:2

See the Supporting Information for details. Abbreviation: ND, not determined.

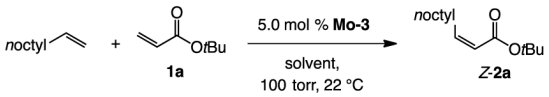
[a] Performed under N_2 atm.

[b] Determined by analysis of ^1H NMR spectra of unpurified mixtures (±2%).

[c] Yields of isolated and purified products (±5%).

Table 3

Effect of coordinating solvents on the CM leading to *Z*-**2a**.[a]



Entry	Solvent	Mo-3 [M]	*t* [min]	Decene:1a	Conv. [%][b]	Yield [%][c]	*Z*:*E*[b]
1	thf	0.1	5	3:1	79	70	90:10
2	thf	0.025	5	3:1	71	53	93:7
3	thf	0.025	30	3:1	90	64	69:31
4	MeCN	0.025	60	3:1	14	ND	>98:2
5	MeCN	0.1	60	2:1	88	67	91:9
6	**MeCN**	**0.1**	**60**	**1:1**	**79**	**69**	**91:9**
7	**MeCN**	**0.1**	**60**	**1:2**	**75**	**71**	**94:6**

See the Supporting Information for details. Abbreviation: ND, not determined.

[a]Performed under N_2 atm.

[b]Determined by analysis of ^{1}H NMR spectra of unpurified mixtures (±2%).

[c]Yields of isolated and purified products (±5%).