Chapter 2:

Cross Metathesis of Functionalized Olefins by an N-Heterocyclic Carbene Containing Ruthenium Catalyst

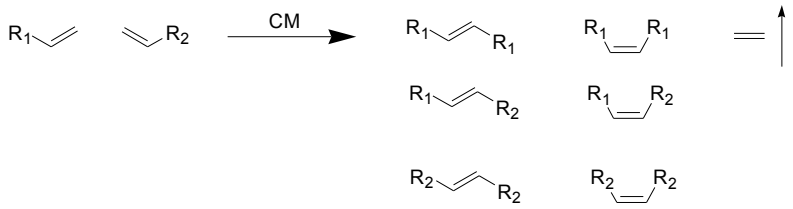
Abstract

Cross metathesis (CM) has been an under-investigated area due to the lack of catalysts' activity and selectivity compared to other olefin metathesis process. Over the past few years, controlling product selectivity has been the key issue on CM. With the development of a highly active and functional group tolerant catalyst **1** bearing an N-heterocyclic carbene, substrate scope has been greatly expanded, opening a mild route to many valuable reagents by CM. Also, the product selectivity has been greatly improved, often yielding one product exclusively. In this chapter, new substrate scopes, mainly α,β-unsaturated carbonyl compounds and efforts to control the product selectivity by catalyst **1** are described.

Background

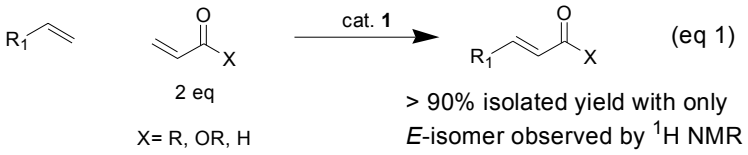
Cross metathesis (CM) is an the intermolecular coupling of two olefins forming a new internal olefin.[1] CM has advantages over other metal-catalyzed coupling reactions such as high catalyst stability and ready availability or accessibility (easy synthesis) of the reagents, olefins. Also, many times the reactions are run at room temperature or slightly elevated temperature (40 ^{o}C) with relatively short reaction time (less than 12 hours). Since the development of well-defined catalysts, $Cl_2(PCy_3)_2Ru$=CHPh (**2**)[2] and $((CF_3)_2MeCO)_2$(ArN)-Mo=CH(*t*-Bu) (**3**),[3] the use of CM has begun to increase along with the increase in the catalysts' functional group tolerance, especially with catalyst **2** which showed high functional group tolerance even with moisture and air, but decreased activity compared to **3**.

However, CM reactions have a limitation that other transition metals do not suffer from. For example, Suzuki reaction catalyzed by Pd(0) promotes exclusive coupling between aryl halides with its organoboronic acids or esters.[4] Also the olefin-forming Suzuki reaction between vinyl halides and organoboronic acids or esters exclusively produces only one new internal olefin with the same olefin geometry of the vinyl halides. However, due to the similar reactivity of two olefins and the thermodynamic control of olefin metathesis process, typical CM produces six different products, a statistical mixture of cross-coupled product, and two homo-coupled products with each having two stereoisomers, *cis* and *trans* isomers (Scheme 1). Out of these six possible CM products, only one of them is typically desired. For example, use of a 1: 1 ratio of two reagents produces only 50% of the desired CM product with mixture of *cis* and *trans* isomers. To achieve higher than 90% yield of the desired product, an impractical ratio at least 10 : 1 of two reagents are required. Even so, the yield is again eroded by the mixture of stereoisomers although many times, the reversible thermodynamic control of olefin metathesis gives moderate to high *E* / *Z* ratios.



Scheme 1. Possible mixture of prodcuts obtained by CM

A breakthrough in CM came with the development of highly active and functional group tolerant catalyst **1** from our group.[5] The new catalyst made CM more useful by improving the E / Z ratio to 10: 1 from 4 : 1, and expanding the substrate scope to include olefins which were unreactive with the previous catalysts, **2** and **3**. Most importantly, catalyst **1** was able to react with different rates depending on the electronics and sterics of the two olefins. Therefore, CM between two olefins with different reactivities allowed the selective CM. The first examples of the selective CM reactions between terminal olefins and acrylein, acrylates and vinyl ketones were demonstrated by Dr. Chatterjee in our lab (eq 1).[6]



(eq 1)

This chapter further expands the substrates scope accessible by catalyst **1**.[7] Also, some new strategies to increase the product selectivity and new reactions are demonstrated here. From the results of CM reactions from the literature reports and our group, as well as data presented in this chapter, we devised a general model based on the categorization of olefin reactivity which can be used to predict both selective and non-selective cross metathesis reactions.[8]

Although the various possible alkylidene intermediates and the numerous primary and secondary metathesis pathways involved in a cross metathesis reaction complicate the attempts to fully understand and predict the CM outcome, we can empirically categorize or rank olefins with different reactivity based on their ability to homodimerize. However, instead of simply looking at the absolute rates of homodimerization, we looked at the relative homodimerization rates to other olefins and describe olefins on a gradient scale of their propensity to undergo homodimerization, and more importantly, the

subsequent reactivity of their homodimers. This analysis leads to a general model that comprises four distinct olefin Types which can be used to predict both selective and non-selective CM reactions (Figure 1).

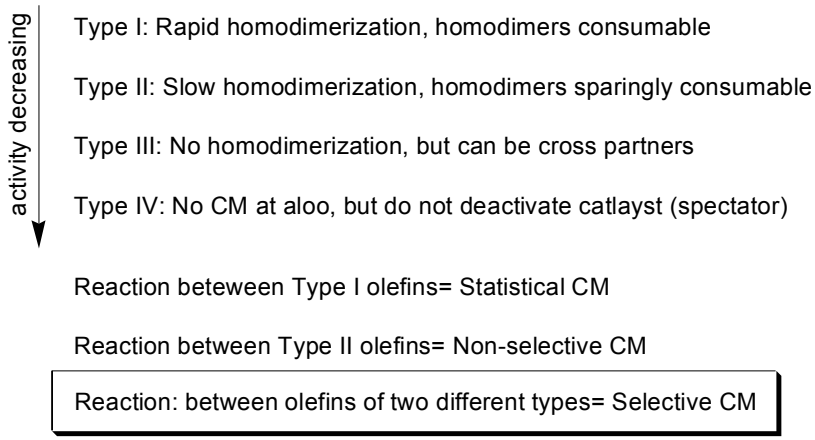


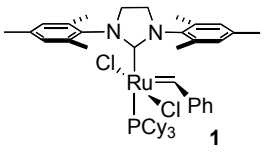
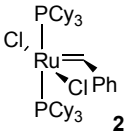
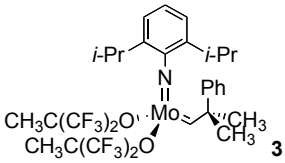
Figure 1. Categorization of olefins and rules for selective CM

Type I olefins are categorized as those able to undergo a rapid homodimerization, and whose homodimers can participate in further CM. Type II olefins homodimerize slowly, and unlike Type I olefins, their homodimers can only be sparingly consumed in subsequent metathesis reactions. Type III olefins are essentially unable to be homodimerized by the catalyst, but are still able to undergo CM with Type I and Type II olefins. Type IV olefins are not able to participate in CM with a particular catalyst, but do not inhibit catalyst activity toward other olefins. Outside these categories are olefins that deactivate the catalyst. In general, a reactivity gradient exists from most active Type (Type I olefin) to least active Type (Type IV), with sterically unhindered, electron-rich olefins categorized as Type I and increasingly sterically hindered and/or electron-deficient olefins falling into Types II through IV.

To achieve selective CM reaction, two olefins with different types should be coupled. For example, CM between terminal olefins (Type I) and methyl acrylate (Type II) by catalyst **1** gives the desired CM product with 95% isolated yield.[6] On the other hand, reactions between the same type of olefins result in either statistical CM (for Type I olefins) or non-selective CM (for Type II olefins). The main difference between statistical and non-selective CM is that the CM products of Type I olefins can be

re-equilibrated to give statistical mixtures, but the CM products of Type II olefins can hardly undergo further metathesis reactions. In addition, the conversion of more challenging Type II olefins tends to be lower than Type I. Table 1 shows categorization of various olefins reported in the literature for three most used catalysts.

Table 1. Olefin Categories for Selective Cross Metathesis

Olefin type	 1	 2	 3
Type I (fast homodimerization)	terminal olefins, 1° allylic alcohols, esters, allyl boronate esters, allyl halides, styrenes (no large ortho substit.), allyl phosphonates, allyl silanes, phosphine oxides, sulfides, protected amines	terminal olefins, allyl silanes, 1° allylic alcohols, ethers, esters, allyl boronate esters, allyl halides	terminal olefins, allyl silanes
Type II (slow homodimerization)	styrenes (large ortho substit.), acrylate, acrylamides, acrylic acids, acrolein, vinyl ketones, unprotected 3° allylic alcohols, vinyl epoxides, 2° allylic alcohols, perfluorinated alkane olefins	styrene, 2° allylic alcohols, vinyl dioxolanes, vinyl boronates	styrene, allyl stannanes
Type III (no homodimerization)	1,1-disubstituted olefins, non-bulky trisub. olefins, vinyl phosphonates, phenyl vinyl sulfone, 4° allylic carbons (all alkyl substituents), 3° allylic alcohols (protected)	vinyl siloxanes	tertiary allyl amines, acrylonitrile
Type IV (spectators to CM)	vinyl nitro olefins, trisubstituted allylic alcohols (protected)	1,1-disubstituted olefins, disub. α,β-unsaturated carbonyls, 4° allylic carbon containing olefins, perfluorinated alkane olefins, 3° allylamines (protected)	1,1-disubstituted olefins

Part I. Cross Metathesis of Functionalized Olefins

Introduction

Over the past few years, olefin metathesis has become a useful reaction in organic,[9] polymer[10] and bioorganic chemistry.[11] Among olefin metathesis reactions, ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) have received the most attention. However, cross metathesis (CM) is also of increasing utility in new C=C bond formation under mild conditions.[12] The synthesis of trisubstituted[14] and functionalized alkenes[6] by cross-metathesis has become possible due to the development of the more active and the more stable catalyst **1**, containing the 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligand,[5] Catalyst **1** not only has activity comparable to early transition metal catalysts, but also retains functional group tolerance comparable to catalyst **2**.[2]

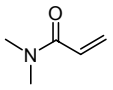
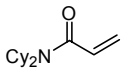
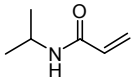
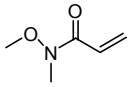
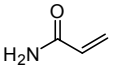
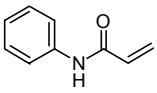
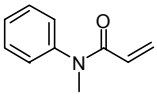
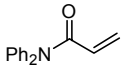
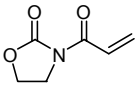
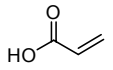
The efficient preparation of α,β-unsaturated amides remains as one of underdeveloped areas of organic synthesis. Current approaches to acrylic amides include Wittig and aldol chemistry which requires strong bases. Therefore milder methodology by CM would be valuable. This section describes a versatile cross-coupling reaction of various α,β-unsaturated amides with terminal olefins and styrene, and shows that CM efficiency is affected by the substituents on the amide nitrogen.

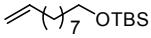
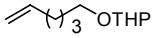
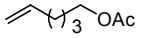
Results and Discussion

Several acrylic amides (Type II olefin) were screened for CM with terminal olefins (Type I olefin) (Table 2). Initially, dimethyl acrylamide with 1.25 equivalents of terminal olefin **I** (entry 1a) was tried and a disappointingly low yield of 39% of CM product was obtained. However, with higher catalyst loading, (9 mol % of catalyst **1**) and 1.5 equivalents of terminal olefin, the yield was improved to 83% (entry 1b). Other substrates showed good to excellent yields ranging from 77% to 100% with excellent diastereoselectivity (*E*: *Z* > 25: 1). Particularly valuable is the compatibility with Weinreb amides[14] (entry 4) and oxazolidinone imides (entry 9).[15] These functional groups are used widely in organic synthesis and CM now provides synthons for further manipulations. In particular, oxazolidinone imides are widely used

in asymmetric reactions[16] such as Michael additions,[17] aldol,[18] and Diels-Alder reactions.[19] Surprisingly, acrylic acid shown to be an excellent cross partner with terminal olefins (entry 10) even though acids are known to accelerate the catalyst decomposition.[20] Another valuable cross partner, styrene (Type I olefin), was examined for CM with acrylic amides. The yields with styrene are lower but show a similar trend in yields (ranging from 25% to 87%) to CM with terminal olefins (Table 2).

Table 2. CM of acrylamides with terminal olefins[a] and stryene[b]

entry	acrylamide	terminal olefin	isolated yield of CM with terminal olefin(*E*/*Z*) [%]	isolated yield of CM with styrene [%][c]
1a		I	**4:** 39 (25:1)	**5:** 25
1b[d]		I	**4:** 83 (25:1)	
2		I	**6:** 77	**7:** 57
3		II	**8:** 80	**9:** 62
4		II	**10:** 89 (60:1)	**11:** 66
5		III	**12:** 89	**13:** 69
6		II	**14:** 90	**15:** 69
7		II	**16** 97 (28:1)	**17:** 83
8		II	**18:** 100 (40:1)	**19:** 87
9		I	**20:** 87 (60:1)	**21:** 40[e]
10		II	**22:** 100	**23:** 63

I:  **II**:  **III**: 

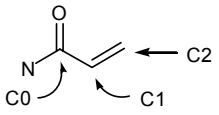
[a] Reactions with 5 mol% catalyst **1** and 1.25 eq terminal olefin in 0.2 M CH_2Cl_2 at 40 °C for 12 hours. [b] Reaction with 5 mol% catalyst **1** and 1.9 eq styrene in 0.2 M CH_2Cl_2 at 40 °C for 12 hours. [c] Only E-isomers observed by ^{1}H NMR. [d] Reaction with 9 mol% catalyst **3** and 1.5 eq terminal olefin. [e] Yield determined by ^{1}H NMR.

A certain trend on the nature of nitrogen substituents seemed to govern the yield of CM. Electron-donating substituents, such as alkyl groups, on the amide nitrogen resulted in lower yields of cross products, whereas electron-withdrawing substituents resulted in higher yields. These observations led us to suggest that the amide carbonyl group might be chelated to the metal center, (Scheme 2, **A** or **B**) thus decreasing catalyst turnover. The degree of chelation would depend on the electron density on the amide oxygen. Ab initio calculations (HF 6-31G**) of several amides showed a distinct inverse relationship between the calculated electron density on the carbonyl oxygen of the amides and the observed CM yields. (Table 3)

Table 3. Electron Density Calculation[a]

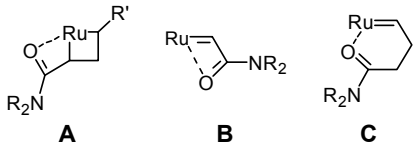
atom(NPA)	Me_2N	iPrNH	NH_2	HNPh	MeNPh	Ph_2N
N	-.572	-.754	-.929	-.748	-.579	-.582
C0	.829	.830	.815	.831	.831	.835
C1	-.370	-.375	-.370	-.376	-.365	-.368
C2	-.305	-.304	-.309	-.306	-.314	-.311
O	-.741	-.735	-.725	-.725	-.730	-.707
Yield[b]:	25%	62%	69%	69%	83%	87%

[a] Calculation was done by Spartan using Hartree-Fock 6.31G ** method.
[b] Yields of CM with 1.9 eq styrene.



Chelation effects in olefin metathesis have been seen occasionally. Schrock isolated a metallocyclobutane moiety possessing a 4-membered chelate from the reactions between Mo and W based catalysts and acrylates and acrylic amides.[21] The new species were catalytically inactive suggesting strong chelation. Although ruthenium-based catalysts are much less oxophilic than the early transition metal catalysts, and the more electron rich catalyst **1** is even less prone to chelation than **2**,[22] chelation to form stable 5- and 6-membered rings with both catalysts **1** and **2** has been previously observed or proposed.[23] Although no direct evidence for catalyst deactivation by chelation of carbonyl oxygen to the Ru metal center was known, more electron rich carbonyl containing acrylic amides might have a higher propensity for chelation. In addition, dicyclohexyl acrylamide (Table 2, entry 2) gave higher a yield in

CM than dimethyl acrylamide (entry 1), despite the similar electronic properties. Perhaps unfavorable steric interactions between bulky dicyclohexyl group and bulky imidazolylidene ligand decreased carbonyl chelation, and increased catalyst turnover.



A **B** **C**

Scheme 2. Proposed chelation

Kinetic studies were performed in order to obtain detailed information about the CM reactions with terminal olefins. As expected, the more electron rich amides reacted more slowly than the electron poor amides. Most notably, when dimethyl acrylamide was the CM partner, only 33% of the terminal olefin participated in either CM or dimerization after 1 hour. In contrast, when diphenyl acrylamide was used, 93% of the terminal olefin participated in metathesis reactions in the same period of time. This strongly supports our speculation that chelation effect of electron-rich amides slows down the metathesis activity by lowering catalytic turnover.

Further kinetic study of the homodimerization of four terminal olefins provides support for the proposed catalyst inhibition by chelation (Figure 2). Of the four olefins, the non-functionalized terminal olefin **I** dimerized fastest followed by substrates **IV**, **V**, and **VI**, respectively. The fact that the rate of dimerization decreases as the electron density on the carbonyls increases (**IV** < **V** < **VI**), supports the six-membered chelate intermediate (Scheme 2 **C**). In all cases, the metathesis reaction was slow enough for a new alkylidene to be observed by ^{1}H NMR (18.5 ppm in CD_2Cl_2) at the beginning of the reaction. A second new alkylidene peak at 18.6 ppm, assigned as the chelated alkylidene, was detected in significant amounts during the dimerization of olefin **VI**. This observation strongly supports the deactivation of the catalyst by chelation of the electron-rich carbonyl group.

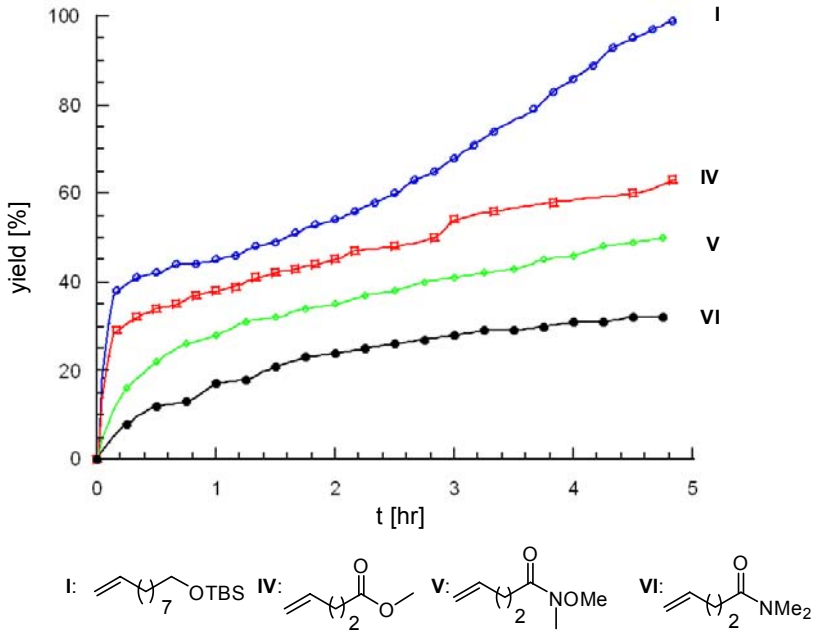
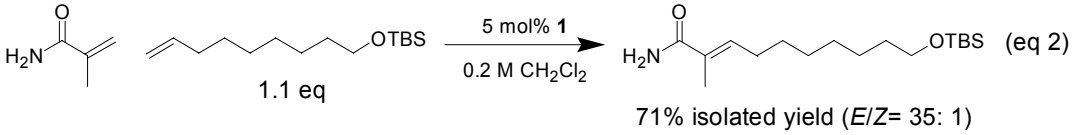


Figure 2. Kinetic studies of various terminal olefins by ^{1}H NMR

Synthesis of trisubstituted acrylamides further extended the application of CM reactions. Methacrylic amide underwent successful CM of terminal olefin **I** with a good yield and an excellent stereoselectivity to produce a trisubstituted acrylic amide (eq 2). This is a typical example of CM between Type I and III olefin (methacrylamide).

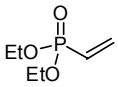
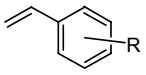
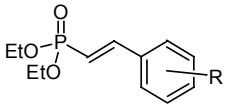
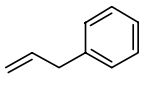
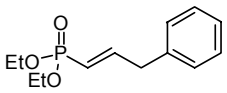
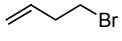
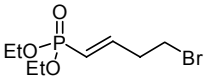


Vinylphosphonates are important synthetic intermediates[24] and have been investigated as biologically active compounds.[25] Vinylphosphonates[26] have been used as intermediates in stereoselective synthesis of trisubstituted olefins[27] and in heterocycle synthesis.[28] The synthesis of vinylphosphonates has also been widely examined and a variety of non-catalytic approaches have been described in the literature.[29] Recent metal-catalyzed methods include palladium catalyzed cross-coupling[30] and Heck coupling of aryldiazonium salts with vinyl phosphonates,[31] but are limited by the requirement of highly reactive functional groups in the substrates. Therefore, a more mild, general and stereoselective method

for the synthesis of vinyl phosphonates using commercially available starting materials would be valuable, and may provide an additional degree of orthogonality to the previously reported syntheses.

Firstly, the participation of a variety of styrenes in the CM reaction with another Type II olefin, vinyl phosphonate was investigated. These results indicate a variety of styrenes were converted to (*E*)-cinnamyl phosphonates in excellent yield (Table 4). Notably, 4-bromostryene crossed product (**26**) was obtained in an excellent yield which can be further functionalized by conventional Pd(0) couplings. Sterically challenging substrates like 2,4-dimethly styrene also gave good yield (compound **27**). However, substrate with bulky and electron withdrawing group at *ortho* position gave a poor result (compound **30**). In general, the CM method tolerates electronic and some steric constraints in the styrene partner and allows for CM between two electron-deficient olefins. Also, 4-bromobutene and allyl benzene were shown to be good substrates of CM with diethyl vinyl phosphonate (compound **31** and **32**).

Table 4. Cross metathesis of diethyl vinyl phosphonate

substrate	cross partner(1.5 eq)	product[b]	isolated yield [%]
			**24:** 97 R = H **25:** 97 R = 4-OMe **26:** 93 R = 4-Br **27:** 77 R = 2,4-$(CH_3)_2$ **28:** 73 R= 4- OAc **29:** 68 R= 4- NO_2 **30:** 34 R= 2-Cl
			**31:** 90
			**32:** 82

[a] 5 mol% catalyst **1** at 40 °C in 0.2 M CH_2Cl_2 for 12 hours [b] Only *E* isomer observed by ^1H NMR

Conclusion

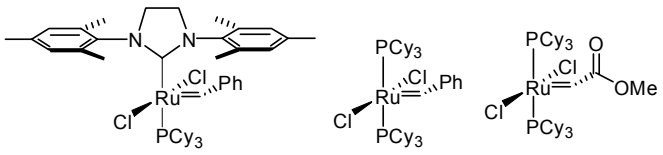
In summary, α,β-unsaturated amides are excellent cross metathesis partners with terminal olefins and styrene. This method allows for an efficient one-step formation of functionalized α,β-unsaturated

amides under mild conditions. More electron rich amides give lower yields due to lower metathesis activity resulting from carbonyl chelation to the Ru center. However, higher catalyst loading compensates for the chelation effect. Also, vinyl phosphonate was a good CM partner with Type I olefins.

Part II. Cross Metathesis of Enoic Carbenes

Introduction

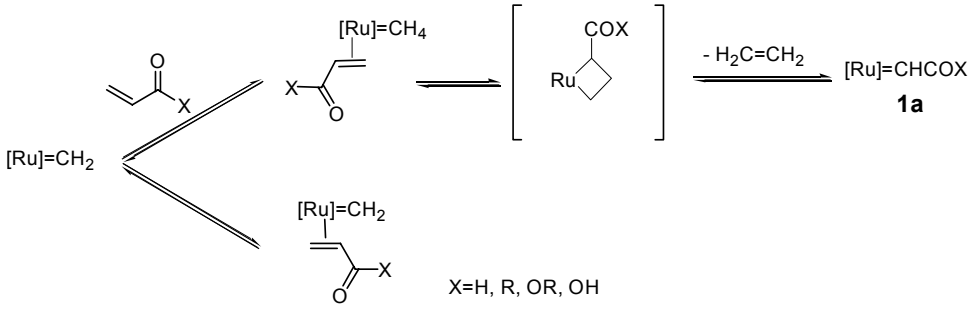
Olefin metathesis has become a valuable reaction in organic synthesis, as has been demonstrated by its frequent use as the key bond constructions for total syntheses of many natural products.[10] With the recent discovery of highly active catalyst **1**,[6] trisubstituted alkenes and functionalized alkenes have been synthesized efficiently by cross metathesis (CM), further expanding the substrate scope for this reaction.[7, 14] With these successes in hand, unprecedented metathesis reactions were explored. There have been no previous reports of the dimerization of α,β-unsaturated carbonyl compounds by a metathesis mechanism. Molybdenum and tungsten-based catalysts form metallocyclobutane with acrylates, but the newly formed intermediates are inactive due to carbonyl oxygen chelation.[21] Our group reported the synthesis of enoic carbene **2a** by a non-metathesis route and showed that **2a** was extremely reactive to be the first carbene to ring-open cyclohexene although the reaction was stoichiometric in **2a**.[32] Due to non-trivial synthesis, lack of stability, and the absence of catalytic turnover, enoic carbene **2a** has not been investigated further.



1 **2** **2a**

Previous reports on the mechanism of cross metathesis reactions between terminal olefins and α,β-unsaturated carbonyl compounds state that catalyst **1** reacts preferentially with terminal olefins to form an alkylidene which crosses onto α,β-unsaturated carbonyl compounds to form methylidene and CM product.[7, 33] At that time, the formation of the unstable enoic carbene **1a** was believed to be less likely. However it was recently discovered that the electron rich catalyst **1** was, in fact, able to react with

α,β-unsaturated carbonyl compounds directly to form enoic carbene **1a** effectively under certain conditions. Herein, we report the first efficient generation of enoic carbenes **1a** in situ with catalyst **1** (Scheme 3), and successful catalytic CM and ring-opening reactions of previously inactive metathesis substrates.



Scheme 3. Direct generation of enoic carbene

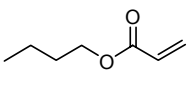
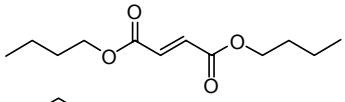
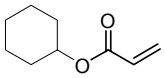
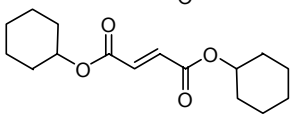
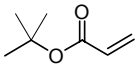
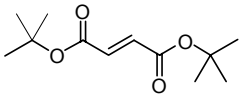
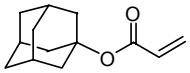
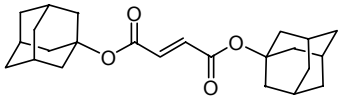
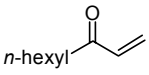
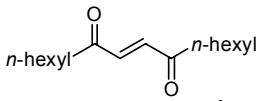
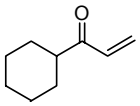
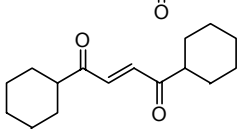
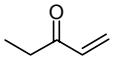
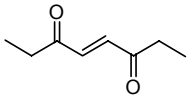
Results and Discussion

The formation of enoic carbene **1a** was initially discovered in the dimerization of acrylates to form fumarates. Initial attempts to dimerize *n*-butyl acrylate at 0.2 M in refluxing CH_2Cl_2 only gave 44% of the desired product of *E*-isomer, and the balance as starting material. GC analysis showed the reaction was completed in less than two hours and no carbene peak including the parent benzylidene or methylidene was observed by ^1H NMR after two hours. This suggests enoic carbene **5** is still unstable, with a much shorter lifetime than other alkylidene or benzylidene. To our delight, an attempt to increase the rate by doubling the concentration to 0.4 M resulted in 87% yield of dimer (Table 5, entry 1). Other solvents like $CHCl_3$, CCl_4, C_6H_6, and THF were tried, but they all produced much poorer results than CH_2Cl_2. Normally, olefin metathesis catalysts are not extremely sensitive to solvents conditions except for coordinating solvents like THF or protic solvent, so the dramatic observed solvent effect is unprecedented. It is speculated that enoic carbene **5** is the most stable in CH_2Cl_2 among other solvents. Various acrylates with different sizes, even the tertiary acrylates were effectively dimerized by this

procedure (Table 5, entry 1-4). However, the dimerization of phenyl acrylate was unsuccessful, implying the enoic carbenes might have a subtle electronic effect.

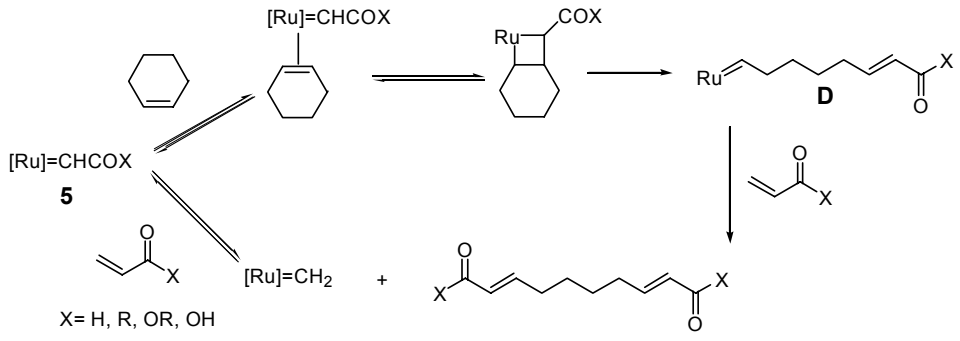
Interestingly, vinyl ketones behaved quite differently from acrylates. Dimerization of hexyl vinyl ketone at 0.4 M gave only 29% of the desired product, and increasing concentration further decreased the yield (less than 5% at 0.6 M by ^{1}H NMR). However, decreasing the concentration increased the yield and an optimized yield was obtained at 0.05 M (Table 5, entry 5-7). Following the reactions by ^{1}H NMR revealed that at 0.05 M, the rate of formation of enoic carbene from vinyl ketones was at least five times faster than that of acrylates. Therefore, a high concentration is required for acrylates to speed up the reactions whereas at that condition, much higher concentration of unstable enoic carbene leads to bimolecular decomposition.[32] Again, similar to the phenyl acrylate case, phenyl vinyl ketone dimerized with low conversion. It is still unknown why the phenyl functionality suppress the dimerization of α,β-unsaturated carbonyl compounds.

Table 5. Dimerization of α,β-unsaturated carbonyl compounds[a]

entry	substrate	product [b]	isolated yield [%]
1			87
2			75
3			94
4			80
5			77
6			95
7			94[c]

[a] 5 mol% catalyst **1** at 0.4 M for acrylates and 0.05 M for vinyl ketones in refluxing CH_2Cl_2 for 3 hrs.
[b] Only the *E* isomer was obtained. [c] Yield was determined by ^1H NMR.

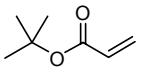
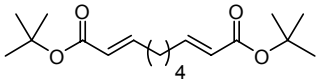
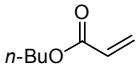
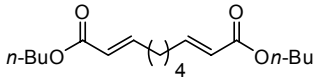
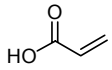
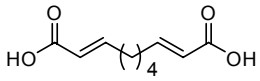
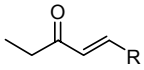
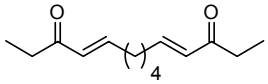
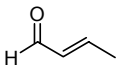
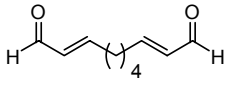
GC analysis showed dimethyl maleate (*Z* isomer) isomerized to dimethyl fumarate (*E* isomer) very slowly when compared to normal internal *cis* olefins.[13] This observation again reflects the unfavorable formation of enoic carbenes compared to alkylidenes. Also, only the *E* isomer was obtained even at early conversion in dimerization reactions, suggesting that the *E* isomer is the kinetic as well as thermodynamic product in these CM reactions.



Scheme 4. Ring-opening of cyclohexene with enoic carbene

Applications of the enoic carbenes to various metathesis reactions beyond simple dimerization are shown in Table 6. Cyclohexene is unique compared to other cycloalkenes because it is not polymerized by ROMP due to the equilibrium exclusively favoring ring-closure. An interesting observation was made when catalyst **2a** unlike catalysts **1**-**3**, could ring-open thermodynamically stable cyclohexene.[32] However, this reaction was stoichiometric in catalyst **2a** because the product of one turnover is an alkylidene which was unreactive towards cyclohexene or acrylates. However, now that enoic carbene **1a** could be generated in situ by catalyst **1**, ring opening of cyclohexene could be achieved in a catalytic fashion (Scheme 4) yielding linear C-10 chains doubly capped with α,β-unsaturated carbonyl compounds (Table 6, entries 1-6). We believe that the reversed ring-closure for intermediate alkylidene **D** is greatly slowed down because it would produce the unstable enoic carbene from more stable alkylidene. Therefore the CM with another molecule of acrylate becomes relatively favored. An excess of cyclohexene (3 equiv.) was used to minimize the dimerization of α,β-unsaturated carbonyl compounds since ring-opening reaction competes with dimerization whose products hardly undergo secondary metathesis reactions. For ethyl vinyl ketone, a relatively fast dimerization became a problem resulting in a lower yield of the ring-opening product. To slow down the undesired dimerization, 2-hexen-4-one was used instead and gave a higher yield for the desired product and less dimer (Table 6, entry 4).

Table 6. Ring-opening cross metathesis reactions of cyclohexene[a]

entry	carbene precusor	cross-partner	product[b]	isolated yield [%]	
1				88	
2				56	
3				94	
4				57 72	R= H R= Me
6				43	

[a] 5 mol% catalyst **1** with 3 eq. of cyclohexene at 0.1 - 0.3 M in refluxing CH_2Cl_2 for 3 hrs. [b] Only the *E* isomer was observed by ^1H NMR.

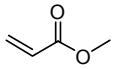
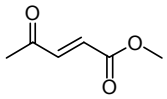
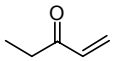
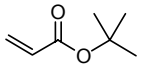
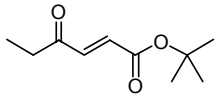
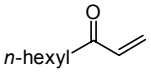
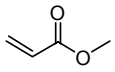
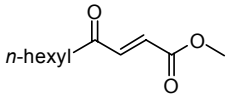
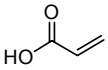
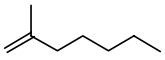
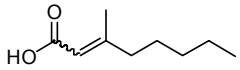
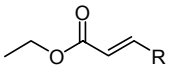
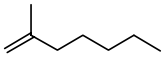
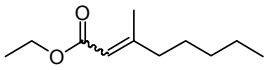
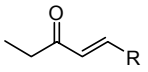
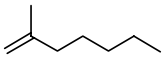
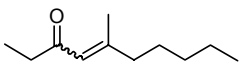
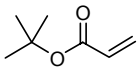
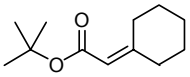
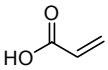
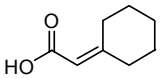
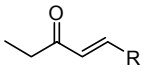
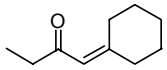
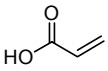
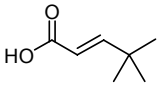
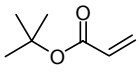
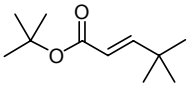
Utilizing enoic carbenes to general CM seems challenging as Type II olefins react slowly with catalyst **1** and their dimers do not undergo further CM reaction. CM between acrylates and vinyl ketones were attempted and only up to 41% of the cross-coupled products were obtained (Table 7, entry 1- 3). Therefore attempts to couple two Type II olefins only result in non-selective CM. Excess of acrylates (2 equiv.) was added to slow down the otherwise faster dimerization of vinyl ketones.

Cross metathesis reactions between α,β-unsaturated carbonyl compounds (Type II) and α-methyl disubstituted olefin (Type III) are more promising because of their different reactivity. Since catalyst **1** reacted preferentially with more reactive Type II olefins to form enoic carbene **1a**, excess of α-methyl disubstituted olefin can be used without resulting in dimerization. Although the formation of **1a** is thermodynamically less favorable, it seems kinetically preferred over reacting with bulky disubstituted alkenes.[14] However, increasing the stoichiometry of the disubstituted olefins produced CM products with good yields. For example, with 2 equiv of α-methyl disubstituted olefin, a 5: 4 mixture of acrylate dimer and the cross product yield was obtained, whereas up to 83% yield of the cross product was achieved by using 4 equiv of α-methyl disubstituted olefin with an *E* to *Z* ratio of 2: 1 (Table 7, entries 4- 6). The rest

was a trace amount of acrylate dimer and the remaining unreacted starting material which can be recovered. Not surprisingly, less sterically hindered methylenecyclohexane proved to be a better cross partner producing up to 99% of the CM products with 2 equiv. of the *gem*-disubstituted olefin.

Compared to terminal α,β-unsaturated carbonyl compounds, β-methyl-disubstituted α,β-unsaturated carbonyl compounds improved the CM yields by 2-40% because the rate of dimerization was suppressed by the methyl group, thereby increasing the relative rate for CM reaction. (Entries 5, 6 and 9). This strategy is particularly useful in the reactions where dimer was substantial side-product. Another example of Type III olefin is 3,3-dimethyl-1-butene which was also a good cross partner (Entries 10 and 11). Since the reagent is relatively cheap and low boiling, it was used as a solvent.

Table 7. Cross metathesis of enoic carbenes[a]

entry	carbene precusor	cross-partner	product	isolated yield [%]	
1				41[b, c]	
2				41[b, c]	
3				33[b, c]	
4				83[e, f]	
5				55[d, e] 83[d, e]	R= H R= Me
6				26[d, e] 68[d, e]	R= H R= Me
7				75[f]	
8				83[f]	
9				57[f] 99[f]	R= H R= Me
10				73[b, g]	
11				73[b, g]	

[a] 5 mol% catalyst at 0.1 - 0.3 M in refluxing CH_2Cl_2 for 3 hrs. [b] Only the *E* isomer was observed by ^1H NMR. [c] 2 eq of acrylates used. [d] 4 eq 2-methyl 1-heptene used. [e] *E* / *Z* = 2.0 determined by 1H NOE NMR. [f] 2 eq of methylenecyclohexene used. [g] 3,3-dimethyl-1-butene was used as a solvent.

Conclusion

We have demonstrated that the highly active catalyst **1** reacts with α,β-unsaturated carbonyl compounds directly to form enoic carbene **1a**, whose activity is dependent on solvent and concentration. It illustrates that the electron rich catalyst **1** sufficiently stabilizes the electron deficient enoic carbene **1a**.

With the in situ generation of enoic carbenes, dimerization, CM with Type III olefins, and catalytic ring-opening of cyclohexene are now attainable.

Acknowledgement: I would like to thank the NIH for generous support of this research, and Dr. C. W. Lee, Dr. A. K. Chatterjee, Dr. M. Scholl, Dr. J. P. Morgan, Daniel P. Sanders, Prof. F. D. Toste, Christie Morrill and Dr. S. D. Goldberg for helpful discussions.

Experimental Section

General Experimental Section. NMR spectra were recorded on Varian-300 NMR. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to internal solvent. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), and multiplet (m). The reported ^{1}H NMR data refer to the major olefin isomer unless stated otherwise. The reported ^{13}C NMR data include all peaks observed and no peak assignments were made. High-resolution mass spectra (EI) were provided by the UCLA Mass Spectrometry Facility (University of California, Los Angeles).

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. All other chemicals were purchased from the Aldrich, Strem, or Nova Biochem Chemical Companies, and used as delivered unless noted otherwise. CH_2Cl_2 was purified by passage through a solvent column prior to use.

General procedure for Part I:

To a flask charged with α,β-unsaturated olefin (1.0 eq) in CH_2Cl_2, catalyst **1** (0.05 eq) in CH_2Cl_2 was added by cannulation followed by addition of either terminal olefin (1.25 eq) or styrene (1.5 to 1.9 eq) via syringe. The flask was fitted with a reflux condenser and was refluxed under argon for 12 hours. The

reaction was monitored by TLC. After the solvent was evaporated, the product was purified directly by a silica gel chromatography.

Compound 4. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 2= ethyl acetate: hexane. A viscous oil (R_f= 0.45 in 1: 1= EA: Hx) was obtained (26 mg, 39% yield 1.0 mg of *cis* compound separated) ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.85 (1H, dt, *J*= 7.0, 17.0 Hz), 6.20 (1H, d, *J*= 17.0 Hz), 3.58 (2H, t, *J*= 6.7 Hz), 3.00 (6H, s), 2.18 (2H, dt, *J*= 6.7, 6.7 Hz), 1.42 (4H, m), 1.30 (8H, m) 0.82 (9H, s), 0.0 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 167.0, 146.5, 120.4, 63.5, 33.1, 33.8, 30.0, 29.6, 29.4, 29.0, 26.5, 26.1, 18.7, -4.99. HRMS (EI) calcd.for $C_{19}H_{39}NO_2Si$: 341.2750. Found: 341.2747.

Compound 5. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 2: 1= EA: Hx. A solid was obtained (R_f= 0.30 in 2: 1= EA/Hx, 8.3 mg, 25% yield). Characterization by: Gill, G. etc. *J. Chem. Soc. Perkin Trans.1* **1994**, 369-378.

Compound 6. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 10=EA: Hx. A viscous oil was obtained (R_f= 0.30 in 1: 10= EA: Hx, 75.6 mg, 77% yield) ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.70 (1H, dt, *J*= 7.0, 17.0 Hz), 6.16 (1H, d, *J*= 17.0 Hz), 3.58 (2H, t, *J*= 6.7 Hz), 3.00 (6H, s), 2.18 (2H, dt, *J*= 6.7, 6.7 Hz), 1.42 (4H, m), 1.30 (8H, m) 0.82 (9H, s), 0.0 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 116.7, 144.5, 123.4, 63.6, 33.2, 33.8, 32.1, 30.7, 29.8, 29.7, 29.5, 28.8, 26.8, 26.5, 26.3, 26.1, 25.8, 18.7, -4.9. HRMS (EI) calcd. for $C_{29}H_{55}NO_2Si$: 477.4002. Found: 477.4018.

Compound 7. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1:10= EA: Hx. Solid was obtained (R_f= 0.30 in 1: 10= EA: Hx, 20 mg, 57% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.76 (1H, d, *J*= 17.0 Hz), 7.50 (2H, m), 7.35 (3H, m), 6.84 (1H, d, *J*= 17.0 Hz), 3.56 (2H, broad), 2.15 (2H, broad), 1.80 (6H, broad), 1.65 (6H, broad), 1.20 (6H, broad). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.4, 140.9, 136.0, 128.9, 127.8, 121.2, 56.1, 30.7, 26.9, 25.8. HRMS (EI) calcd. for $C_{21}H_{29}NO$: 311.2249. Found: 311.2254.

Compound 8. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 1= EA: Hx. Viscous oil was obtained (R_f= 0.30 in 1: 1= EA: Hx, 41.9 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.80 (1H, dt, *J*= 7.0, 17 Hz), 5.70 (1H, d, *J*= 17.0 Hz), 5.2 (1H, broad), 4.56 (1H, t, *J*= 4.0 Hz), 4.10 (1H, m), 3.82 (1H, m), 3.72 (1H, m), 3.46 (1H, m), 3.38 (1H, m), 2.20 (2H, dt, *J*= 6.7, 6.7 Hz), 1.45-1.80 (10H, m), 1.18 (6H, d, *J*= 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.3, 144.1, 124.3, 99.1, 67.5, 62.6, 41.5, 32.1, 31.1, 29.6, 25.8, 25.3, 23.1, 20.0. HRMS (EI) calcd for $C_{15}H_{27}NO_3$: 269.1991. Found: 269.1997.

Compound 9. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 1= EA: Hx. Solid was obtained (R_f= 0.40 in 1: 1= EA: Hx, 24.0 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.60 (1H, d, *J*= 17.0 Hz), 7.48 (2H, m), 7.38 (3H, m), 6.26 (1H, d, *J*= 17.0 Hz), 5.40 (1H, broad), 1.19 (6H, d, *J*= 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.2, 140.7, 135.1, 129.2, 127.7, 121.3, 41.8, 23.5, 22.9. HRMS (EI) calcd. for $C_{12}H_{15}NO$: 189.1154. Found: 189.1152.

Compound 10. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 2= EA: Hx. Viscous oil was obtained (R_f= 0.30 in 1: 2= EA: Hx, 64.1 mg, 89% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 6.90 (1H, dt, *J*= 7.0, 17 Hz), 6.30 (1H, d, *J*= 17.0 Hz), 4.50 (1H, t, *J*= 4.0 Hz), 3.82 (1H, m), 3.72(1H, m), 3.61 (3H, s) 3.46 (1H, m), 3.38 (1H, m), 3.17 (1H, s), 2.20 (2H, dt, *J*= 6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 167.0, 147.6, 119.0, 99.0, 67.4, 62.5, 61.9, 32.6, 31.0, 29.6, 25.8, 25.4, 20.0. HRMS (EI) calcd. for $C_{14}H_{25}NO_4$: 271.1784. Found: 271.1791.

Compound 11. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 2= EA: Hx. Viscous oil was obtained (R_f= 0.35 in 1: 2= EA: Hx, 25.2 mg, 66% yield). Characterization by: Solladie. G. etc.*J. Org. Chem.* **1999**, *64*, 2309-2314.

Compound 12. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 2: 1= EA: Hx. Solid was obtained (R_f= 0.30 in 3: 1= EA: Hx, 72 mg, 89% yield). ^{1}H

NMR (300 MHz, $CDCl_3$, ppm): δ 6.78 (1H, dt, *J*= 7.3, 17.0 Hz), 6.22 (2H, broad) 5.83 (1H, d, *J*= 17.0 Hz), 4.01 (2H, t, *J*= 7.0 Hz), 2.20 (2H, m), 2.00 (3H, s), 1.60 (2H, m), 1.50 (2H, m), ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.4, 168.4, 145.5, 123.6, 64.4, 31.8, 28.4, 24.9, 21.4. HRMS (EI) calcd. for $C_9H_{15}NO_3$: 185.1052. Found: 185.1061.

Compound 13. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 4: 1= EA: Hx. Solid was obtained (R_f= 0.35 in 4: 1= EA: Hx, 20.3 mg, 69% yield). Characterization by: Moriarty, R.M. etc. *J. Org. Chem.* **1993**, *58*, 2478-2482.

Compound 14. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 3= EA: Hx. Solid was obtained (R_f= 0.35 in 1: 3= EA: Hx, 55.4 mg, 90% yield). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.58 (2H, d, *J*= 11 Hz), 7.25 (2H, m), 7.10 (1H, t, *J*= 11 Hz) 6.95 (1H, dt, *J*= 7.3, 17 Hz), 5.93 (1H, d, *J*= 17.0 Hz), 4.58 (1H, t, *J*= 4.0 Hz), 3.82 (1H, m), 3.72(1H, m), 3.61 (3H, s) 3.46 (1H, m), 3.38 (1H,m), 3.17 (1H, s), 2.22 (2H, dt, *J*= 6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.3, 147.9, 140.6, 130.9, 126.3, 126.1, 122.0, 101.2, 69.4, 64.6, 34.1, 33.1, 31.6, 27.8, 27.2, 22.1. HRMS (EI) calcd.for $C_{18}H_{25}NO_3$: 303.1834. Found: 303.1840.

Compound 15. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 3= EA: Hx. Solid was obtained (R_f= 0.35 in 1: 3= EA: Hx, 30.5 mg, 69% yield). Characterization by: Wang, T. etc. *Synthesis* **1997**, 87-90.

Compound 16. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 2= EA: Hx. Viscous oil was obtained (R_f= 0.30 in 1: 2= EA: Hx, 62.0 mg, 97% yield). ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.40 (3H, m), 7.16 (2H, d, *J*= 11.0 Hz) 6.83 (1H, dt, *J*= 7.3, 17 Hz), 5.70 (1H, d, *J*= 17.0 Hz), 4.52 (1H, t, *J*= 4.0 Hz), 3.80 (1H, m), 3.62 (1H, m), 3.44 (1H, m), 3.38 (1H,m), 3.35 (3H, s), 2.06 (2H, dt, *J*= 6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.3, 145.8, 143.9, 129.7, 127.6, 127.5, 121.7, 98.9, 67.4, 62.5, 37.7, 32.3, 31.0, 29.5, 25.8, 25.4, 19.9 HRMS (EI) calcd. for $C_{19}H_{27}NO_3$: 317.1991. Found: 317.1996.

Compound 17. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 3= EA: Hx. Solid was obtained (R_f= 0.30 in 1: 3= EA: Hx, 43.2 mg, 83% yield). Characterization by: Froeyen, P. etc. *Synth. Commun.* **1995**, *25*, 959-968.

Compound 18. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 5= EA: Hx. Viscous was obtained (R_f= 0.35 in 1: 3= EA: Hx, 76.7 mg, 100% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.35 (6H, m), 7.23 (8H, m), 7.00 (1H, dt, *J*= 7.3, 17 Hz), 5.82 (1H, d, *J*= 17.0 Hz), 4.56 (1H, t, *J*= 4.0 Hz), 3.80 (1H, m), 3.62 (1H, m), 3.44 (1H, m), 3.38 (1H,m), 2.18 (2H, dt, *J*= 6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.3, 147.1, 143.0, 129.4, 127.6, 126.8, 122.9, 99.0, 67.4, 62.5, 32.5, 31.1, 29.6, 25.8, 25.4, 20.0 HRMS (EI) calcd. for $C_{24}H_{29}NO_3$: 379.2147. Found: 379.2144.

Compound 19. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 1= toluene: methylene chloride. Solid was obtained (R_f= 0.30 in 1: 1= toluene: methylene chloride, 52.3 mg, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.81 (2H, 2, *J*= 16 Hz), 7.23-7.42 (10H, m), 6.50 (1H, d, *J*= 16 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 166.3, 142.9, 135.3, 123.0, 129.5, 129.0, 128.2, 127.1, 120.0. HRMS (EI) calcd. for $C_{21}H_{17}NO$: 299.1310. Found: 299.1301.

Compound 20. See **General Procedure.** The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 3= EA: Hx. Viscous oil was obtained (R_f= 0.40 in 1: 5= EA: Hx, 66.4 mg, 87% yield). ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 7.24(1H, d, *J*= 17 Hz), 7.17 (1H, dt, *J*= 6.7, 17 Hz), 4.41 (2H, t, *J*= 12 Hz), 4.08 (2H, t, *J*= 12 Hz), 3.57 (2H, t, *J*= 11 Hz), 2.25 (2H, m), 1.50 (4H, m), 1.25 (8H, m), 0.84 (9H, s), 0.00 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.6, 154.8, 152.1, 120.2, 63.6, 62.4, 43.1, 33.2, 33.1, 29.8, 29.7, 29.5, 28.4, 26.4, 26.1, 18.8, -4.85. HRMS (EI) calcd. for $C_{20}H_{37}NO_4Si$: 383.2492. Found: 383.2496.

Compound 22. See **General Procedure**. The product was purified directly on a silica gel column (1x15 cm), eluting with 1: 2= EA: Hx. Viscous oil was obtained (R_f= 0.25 in 1: 2= EA: Hx, 46 mg, 100% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 11.2 (1H, broad), 7.07 (1H, dt, *J*= 7.7, 17.3 Hz), 5.82 (1H, d, *J*=

17.3 Hz), 4.58 (1H, t, *J*= 4.0 Hz), 3.82 (1H, m), 3.72 (1H, m), 3.46 (1H, m), 3.38 (1H, m), 3.17 (1H, s), 2.24 (2H, dt *J*= 6.7, 6.7 Hz), 1.45-1.80 (10H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.9, 151.9, 121.1, 99.0, 67.4, 62.6, 32.4, 31.0, 29.5, 25.8, 25.0, 19.9. HRMS (EI) calcd. for $C_{12}H_{20}O_4$: 228.1362. Found: 228.1369.

Compound 23. To a stirred solution of catalyst **1** in CH_2Cl_2,, (1.0 mL), styrene (42 *u*l, 0.39 mmol) and arylic acid (14 *u*l, 0.20 mmol) was added by syringe. The flask was fitted with a condenser and refluxed under argon for 18 hours. The reaction was quenched by evaporating the solvent and purified directly on a silica gel column (1x15 cm), eluting with 1: 2= EA: Hx. Viscous oil was obtained (R_f= 0.30 in 1: 2= EA: Hx, 19.0 mg, 63% yield). Characterization by: Kim, T. etc. *J. Chem. Soc. Perkin Trans.1* **1995**, 2257.

Compound in eq 2. To a flask charged with methacrylamide (17.2 mg, 0.20 mmol), TBS protected 9-decen-1-ol (65 mg, 0.24 mmol) and 1 (8.5mg, 0.01 mmol, 5 mol%), solvent of 1 ml CH_2Cl_2 was added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The reaction mixture was then reduced in volume to 0.5 ml and purified directly on a silica gel column (2x10 cm), eluting with 2: 1= hexane: ethyl acetate. Clear oil was obtained (46.6 mg, 71% yield, >20: 1 = *E*: *Z*). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.39 (1H, t, *J*= 7.5 Hz), 5.87 (2H, br), 3.55 (2H, *J*= 6.6 Hz), 2.10 (2H, m), 1.80 (3H, s), 1.2- 1.48 (12H, m), 0.86 (9H, s), 0.00 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 171.7, 138.2, 129.9, 63.6, 33.2, 29.8, 29.7, 29.7, 29.1, 28.8, 26.3, 26.1, 18.7, 13.1, -4.8. R_f = 0.35 (1: 1=hexane: ethyl acetate); HRMS (EI) calcd for $C_{18}H_{37}NO_2Si$ 327.2594, found 327.2594.

Compound 24. See **General Procedure.** The product was purified directly on a silica gel column, eluting with 2: 1= ethyl acetate: hexane and yielded 45.3 mg of the product in 97% (R_f= 0.3 in EA: Hx= 2: 1, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.2-7.4 (6H, m), 6.10 (1H, t, *J*=17.4 Hz), 4.00 (4H, dq, *J*= 0.9, 8.1Hz), 1.22 (6H, t, *J*= 4.2 Hz)

Compound 25. See **General Procedure.** The product was purified directly on a silica gel column, eluting with 1: 4=hexane: ethyl acetate and yielded 51.2 mg of the product in 97% (R_f= 0.5 in EA, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.50 (1H, dd, *J*= 17.4, 22.8 Hz), 7.44 (2H, d, *J*= 8.7 Hz), 6.89

(2H, d, *J*=8.7 Hz), 6.06 (1H, t, *J*= 17.7 Hz), 4.12(4H, dq, *J*= 0.9, 8.1 Hz), 3.81 (3H, s), 1.32(6H, t, *J*= 7.2 Hz).

Compound 26. See **General Procedure.** The product was purified directly on a silica gel column, eluting with ethyl acetate and yielded 40.5 mg of the product in 77% (R_f = 0.4 in EA, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.39 (2H, d, *J*= 6.6 Hz), 7.37 (1H, dd, *J*= 18.6, 22.8 Hz), 7.20 (2H, d, *J*= 6.6Hz), 6.12 (1H, t, *J*= 17.4 Hz), 4.00 (4H, dq, *J*= 1.2, 8.1Hz), 1.22 (6H, t, *J*=4.2 Hz).

Compound 27. See **General Procedure.** The product was purified directly on a silica gel column, eluting with ethyl acetate and yielded 42.4 mg of the product in 73% (R_f = 0.3 in EA, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.73 (1H, dd, *J*= 17.4, 22.8 Hz), 7.43 (1H, d, *J*= 8.7 Hz), 7.00 (2H, m), 6.11 (1H, t, *J*= 17.4 Hz), 4.10 (6H, dq, *J*= 0.6, 7.2 Hz), 2.37 (3H, s), 2.30 (3H, s), 1.22 (6H, t, *J*= 4.2 Hz).

Compound 28. See **General Procedure.** The product was purified directly on a silica gel column, eluting with ethyl acetate and yielded 37.8 mg of the product in 68% (R_f = 0.4 in EA, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.5 (3H, m), 7.10 (2H, d, *J*= 6.0 Hz), 6.18 (1H, t, *J*= 17.4 Hz), 4.10 (4H, dq, *J*= 1.5, 7.2 Hz), 2.27 (3H, s), 1.32 (6H, t, *J*= 6.9 Hz).

Compound 29. See **General Procedure.** The product was purified directly on a silica gel column, eluting with ethyl acetate and yielded 18.0 mg of the product in 34% (R_f = 0.4 in EA, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.22 (2H, d, *J*= 6.0 Hz), 7.4-7.6 (4H, m), 6.40 (1H, t, *J*= 17.4 Hz), 4.10 (4H, dq, *J*= 1.5, 7.2 Hz), 1.32 (6H, t, *J*= 6.9 Hz).

Compound 31. See **General Procedure.** The product was purified directly on a silica gel column, eluting with ethyl acetate and yielded 44.4 mg of the product in 90% (R_f = 0.3 in EA, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.30 (5H, m), 6.90 (1H, m), 6.60 (1H, t, *J*= 18.6 Hz), 4.05 (4H, dq, *J*= 1.5, 6.9 Hz), 3.55(2H, d, *J*=5.7 Hz), 1.30 (6H, t, *J*= 6.9 Hz).

Compound 32. See **General Procedure.** The product was purified directly on a silica gel column, eluting with ethyl acetate and yielded 14.0 mg of the product in 82% (R_f = 0.3 in EA, clear oil). ^{1}H NMR

(300 MHz, $CDCl_3$, ppm): δ 6.70 (1H, m), 5.75 (1H, t, *J*= 17.4 Hz), 4.10 (4H, dq, *J*= 1.5, 6.9 Hz), 3.43(2H, t, *J*= 6.9 Hz), 2.78 (2H, m), 1.33 (6H, m).

General Procedure for Part II: To a flask charged with catalyst **1** (0.05 equiv in 0.05 to 0.4 M CH_2Cl_2), α,β-unsaturated carbonyl compounds, or disubstituted olefins were added via syringe. The flask was fitted with a condenser and refluxed under argon for 3 to 5 hours. The reaction was monitored by TLC. After the solvent was evaporated, the product was purified directly on a silica gel column.

Compound in Table 5, entry 1. See **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 40 *u*l of *n*-butyl acrylate gave 22.7 mg of the dimer in 87% yield (R_f = 0.3 in 1: 10 = EA: Hx, white solid). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.83 (2H, s), 4.19 (4H, t, *J* = 6.6 Hz), 1.65 (4H, m), 1.38 (4H, m), 0.93 (6H, q, *J* = 7.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 165.2, 133.8, 65.5, 30.9, 19.5, 14.0. HRMS (EI) calcd for $C_{12}H_{20}O_4$ 228.1362, found 228.1373.

Compound in Table 5, entry 2. See **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 50.6 mg of cyclohexyl acrylate gave 34.7 mg of the dimer (R_f = 0.5 in 1: 10 = EA: Hx, white solid). Characterization by: Kansui, H.; Hiraoka, S.; Kunieda, T.; *J. Am.Chem. Soc.* **1996,** *118*, 5346.

Compound in Table 5, entry 3 see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 30 *u*l of *t*-butyl acrylate gave 21.9 mg of the dimer (R_f = 0.5 in 1: 10 = EA: Hx, clear oil). Characterization by: Charlton, J. L.; Maddaford, S. *Can. J. Chem*. **1993**, *71*, 827.

Compound in Table 5, entry 4. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 40.0 mg of admantyl acrylate gave 37.3 mg of the dimer (R_f = 0.4 in 1: 10 = EA: Hx, white solid). Characterization by: Matsumoto, A.; Otsu, T. *Chem. Lett.* **1991**, *8*, 1361.

Compound in Table 5, entry 5. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 14.0 mg of hexyl vinyl ketone gave 9.7 mg of the dimer (R_f = 0.4 in 1: 10 = EA: Hx, white solid). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.65 (2H, s) 2.62 (4H, t, *J* = 8.0 Hz), 1.59 (4H, m), 1.27(12H, m), 0.863(6H, t, *J* = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 200.9, 136.4, 42.0, 31.9, 29.1, 24.1, 22.8, 14.4. HRMS (EI) calcd for $C_{16}H_{28}O_2$ 252.2089, found 252.2090.

Compound in Table 5, entry 6. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 20 = ethyl acetate: hexane. 13.8 mg of cyclohexyl vinyl ketone gave 11.8 mg of the dimer (R_f = 0.4 in 1: 10 = EA: Hx, white solid). Characterization by: House, H.O. et al. *J. Org .Chem*. **1971**, *36*, 3429.

Compound in Table 5, entry 7. To a flask charged with catalyst **1** (0.05 equiv in 0.05 CD_2Cl_2), 20 *u*l of ethyl vinyl ketone was added via syringe. After 3 hours, the crude solution was put into a NMR tube. The conversion was determined by integration ratio between 6.8 ppm and 6.4 ppm. Characterization by Bach, J.; Berenguer, R.; Garcia, J.; Lopez, M.; Manzanal, J.; Vilarrasa, J. *Tetrahedron* **1998**. *54*, 14947.

Compound in Table 6, entry 1. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 28.0 mg of the product was obtained (R_f = 0.4 in 1: 10 = EA: Hx, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.80 (2H, dt, *J* = 15.6, 6.9 Hz), 5.70 (2H, d, *J* = 15.9 Hz), 2.14 (4H, m), 1.44 (22H, m). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 166.2, 147.6, 123.4, 80.3, 32.1, 28.5, 27.9. HRMS (EI) calcd for $C_{18}H_{30}O_4$ 310.2144, found 310.2151.

Compound in Table 6, entry 2. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 18.3 mg of the product was obtained (R_f = 0.3 in 1: 10 = EA: Hx, clear oil). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.89 (2H, dt, *J*= 7.0, 16.8 Hz), 5.82 (2H, d, *J*= 16.8 Hz), 4.13 (4H, t, *J*= 6.6 Hz), 2.20 (4H, m), 1.62 (4H, m), 1.48 (4H, m),1.37 (4H, m), 0.94 (6H, q, *J*= 7.4 Hz).

Compound in Table 6, entry 3. see **General Procedure**. The product was purified directly by filtering and washed with dichloromethane. 29.1 mg of the product was obtained (white solid). ^{1}H NMR (300 MHz, THF-d_8, ppm): δ 10.64 (2H, s), 6.80 (2H, dt, *J* = 15.6, 6.3 Hz), 5.75 (2H, d, *J* = 15.6 Hz), 2.20 (4H, m), 1.50 (4H, m). ^{13}C NMR (75 MHz,THF-d_8, ppm): δ 168.3, 149.9, 123.9, 33.8, 29.8. HRMS (EI) calcd for $C_{10}H_{14}O_4$ 198.0893, found 198.0896.

Compound in Table 6, entry 4. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 4 = ethyl acetate: hexane. 15.4 mg of the product was obtained (R_f = 0.3 in 1: 3 = EA: Hx, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.80 (2H, dt, *J* = 15.6, 6.9 Hz), 6.05 (2H, d, *J* = 15.6 Hz), 2.52 (4H, q, *J* = 7.5 Hz), 2.19 (4H, m), 1.47 (4H, m), 1.06 (6H, t, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 201.1, 146.4, 130.5, 39.7, 32.5, 28.0, 8.5. HRMS (EI) calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1622.

Compound in Table 6, entry 5. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 2 = ethyl acetate: hexane. 7.4 mg of the product was obtained in 41% yield. (R_f = 0.3 in 1: 2 = EA: Hx, clear oil).^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.49 (2H, d, *J* = 7.8 Hz), 6.81 (2H, dt, *J* = 15.6, 6.9 Hz), 6.10 (2H, ddt, *J* = 15.6, 7.8, 1.5 Hz), 2.35 (4H, m), 1.47 (4H, m).

Compound Table 7, entry 1. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 3 = ethyl acetate: hexane. 25.0 mg of the product was obtained (R_f = 0.3 in 1: 3 = EA: Hx, white solid). Characterization by: Verhe,R. et al. *J. Org. Chem.* **1977**, *42*, 1256.

Compound Table 7, entry 2. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 15.0 mg of the product was obtained (R_f = 0.4 in 1: 10 = EA: Hx, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.94 (1H, d, *J* = 16.2 Hz), 6.57 (1H, d, *J* = 15.9 Hz), 2.63 (2H, q, *J* = 7.2 Hz), 1.49 (9H, s), 1.10 (3H, t, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 200.5, 164.9, 138.6, 132.8, 82.2, 34.9, 28.3, 8.0 HRMS (EI) calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1103.

Compound Table 7, entry 3. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 10 = ethyl acetate: hexane. 6.5 mg of the product was obtained (R_f = 0.3 in 1: 10 = EA: Hx, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.05 (1H, d, *J* = 15.9 Hz), 6.55 (1H, d, *J* = 16.2 Hz), 3.80 (3H, s), 2.61 (2H, t, *J* = 7.2 Hz), 1.27 (8H, br), 0.86 (3H, t, *J* = 6.3 Hz).

Compound Table 7, entry 4. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 29.7 mg of the product was obtained (R_f = 0.4 in 1: 10 = EA: Hx, clear oil). *E* / *Z* ratio was confirmed by ^{1}H NOE. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.62 (1H, s), 4.12 (2H, m), [2.58 (2H, t, *J* = 7.5 Hz), 1.84 (3H, s) for *cis*], [2.11 (3H, s), 2.00 (2H, *J* = 7.5 Hz), for *trans*] 1.50 (2H, m), 1.30 (6H, m), 0.86 (3H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ [167.0, 160.5, 115.6, 59.7, 41.2, 31.7, 27.4, 22.8, 19.1, 14.7, 14.4. for *trans*], [166.5, 160.9, 116.1, 59.7, 33.7, 32.3, 28.2, 25.5, 22.9, 14.7, 14.3. for *cis*]. HRMS (EI) calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1460.

Compound Table 7, entry 5. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 5 = ethyl acetate: hexane. 26.5 mg of the product was obtained (R_f = 0.3 in 1: 5 = EA: Hx, white solid). *E* / *Z* ratio was confirmed by ^{1}H NOE. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.67 (1H, s), [2.60 (2H, t, *J* = 7.5 Hz), 1.90 (3H, s) for *cis*], [2.14 (3H, s), 2.10 (2H, *J* = 7.0 Hz), for *trans*] 1.50 (2H, m), 1.30 (6H, m), 0.87 (3H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ [172.6, 163.8, 115.2, 41.5, 31.7, 27.4, 22.8, 19.4, 14.4. for *trans*], [172.6, 163.8, 115.7, 33.8, 32.2, 28.2, 25.9, 19.4, 14.4. for *cis*]. HRMS (EI) calcd for $C_9H_{16}O_2$ 156.1150, found 156.1145.

Compound Table 7, entry 6. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15=ethyl acetate: hexane. 22.0 mg of the product was obtained (R_f = 0.4 in 1: 10 = EA: Hx, white solid). *E* / *Z* ratio was confirmed by ^{1}H NOE. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.02 (1H, s), [2.54 (2H, t, *J* = 7.5 Hz), 1.83 (3H, s) for *cis*], [2.10 (3H, s), 2.08 (2H, *J* = 7.0 Hz), for *trans*], 2.40 (2H, *J* = 5.4 Hz), 1.50 (2H, m), 1.30 (6H, m), 1.00 (3H, *J* = 6.6 Hz), 0.87 (3H, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ [201.8, 158.7, 123.0, 41.5, 37.7, 31.8, 27.5, 22.8, 19.6, 14.4, 8.5. for

trans], [201.2, 159.4, 123.5, 37.7, 34.1, 32.3, 28.3, 25.8, 22.9, 14.4, 8.5. for *cis*]. HRMS (EI) calcd for $C_{10}H_{20}O$ 168.1514, found168.1513.

Compound Table 7, entry 7. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 30 = ethyl acetate: hexane. 30.6 mg of the product was obtained (R_f = 0.35 in 1: 30 = EA: Hx, clear oil). Characterization by: Inoue, S.; Sato, Y. *J. Org. Chem.* **1991**, *56*, 347.

Compound Table 7, entry 8. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 3 = ethyl acetate: hexane. 23.8 mg of the product was obtained (R_f = 0.35 in 1: 3 = EA: Hx, white solid). Characterization by: Brittelli, D. R. *J. Org.Chem.* **1981**, *46*, 2514.

Compound Table 7, entry 9. see **General Procedure**. The product was purified directly on a silica gel column, eluting with 1: 15 = ethyl acetate: hexane. 29.3 mg of the product was obtained (R_f = 0.40 in 1: 10 = EA: Hx, clear oil). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.94 (1H, s), 2.77 (2H, s), 2.39 (2H, t, *J* = 7.2 Hz), 2.13 (2H, t, *J* = 5.1 Hz), 1.56 (6H, m) 1.03 (3H, t, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 202.4, 161.7, 120.9, 38.4, 37.8, 30.3, 29.2, 28.3, 26.6, 8.5. HRMS (EI) calcd for $C_{10}H_{16}O$ 152.1201, found 152.1203.

Compound in Table 7, Entry 10. To flask charged with **1** (12.4 mg, 0.015 mmol, 5.0 mol%), acrylic acid (20 *u*l, 0.29 mmol) and 2,2-dimethyl 3-butene (1 ml, 7.75 mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The product was purified directly on a silica gel column, eluting with 1: 2 = ethyl acetate: hexane. 20.2 mg of the product was obtained (73%, R_f = 0.30 in 1: 2 = EA: Hx, white solid). Spectra match those of a previously characterized product, see: Freeman, F.; Kappso, J. C. *J. Org. Chem.* **1986**, *51*, 1654.

Compound in Table 7, Entry 11. To flask charged with **1** (8.5 mg, 0.01 mmol, 5.0 mol%), *t*-butyl acrylate (30 *u*l, 0.21 mmol) and 2,2-dimethyl 3-butene (1 ml, 7.75 mmol) were added via syringe. The flask was fitted with a condenser and refluxed under nitrogen for 12 hours. The product was purified directly on a silica gel column, eluting with 1: 30 = ethyl acetate: hexane. 27.5 mg of the product was

obtained (73%, R_f = 0.40 in 1: 20 = EA: Hx, white solid). Spectra match those of a previously characterized product, see: Inoue, S.; Sato, Y. *J. Org. Chem.* **1991**, *56*, 347.

Reference:

1. For recent reviews, see: a) Schuster, M.; Blechert, S. *Angew. Chem*. **1997**, *109*, 2124; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2067; b) Blechert, S. *Pure Appl. Chem.* **1999**, *71*, 1393; c) Connon, S. J.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **2003**, *41*, 3171.
2. Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.
3. a) Schrock, R. R.; Murdzek, J. S.; Bazan, G, C.; Robibins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875, b) Bazan, G. C. ; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899, c) Feldman, J.; Schrock, R. R. *Prog. Inorg, Chem.* **1991**, *39*, 1.
4. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
5. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.
6. Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783.
7. This portion of work is published, see: a) Choi, T.-L.; Chatterjee, A. K. Grubbs R. H. *Angew. Chem.* **2001***, 113*, 1317; *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1277. b) Chatterjee, A. K.; Choi, T.-L.; Grubbs R. H. *Synlett* **2001**, 1034; c) Choi, T.-L.; Lee. C. W.; Chatterjee, A. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 10417.
8. Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.
9. For recent reviews on organic applications, see: a) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446; b) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413; c) Armstrong, S. K. *J. Chem. Soc. Perkin Trans. 1* **1998**, 371; d) Furstner, A. *Angew. Chem., Int. Ed. Engl* **2000**, *39*, 3013.
10. For recent reviews on ROMP, see: a) Novak, B. M.; Risse, W.; Grubbs, R. H. *Adv. Polym. Sci.*

1992, *102*, 47; b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, CA, **1997**; c) Grubbs, R. H.; Khosravi, E. *Material Science and Technology*, **1999**, *20*, 65; d) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.

11. a) Fraser, C.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7248; b) Mortell, K. H.; Weatherman, R. V.; Kiessling, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 2297; c) Huwe, C. M.; Woltering, T. J.; Jiricek,J; Weitz-Schmidt, G.; Wong, C. H. *Bioorg. Med. Chem.* **1999**, *7*, 773; d) Maynard, H. D.; Okada, S.;Grubbs, R. H. *J. Am. Chem. Soc.* in press.
12. 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.
13. Chatterjee, A. K.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 1751.
14. Nahm, S; Weinreb, S. M *Tetrahedron Lett.* **1981**, *22*, 3815.
15. Gage, J. R.; Evans, D. A. *Org. Synth.* **1990**, *68*, 83.
16. For a recent review, see: Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325.
17. Evans, D. A.; Willis, M. C.; Johnston, J. N. *Org. Lett.* **1999**, *1*, 865.
18. a) Evans, D. A.; Bartroli,J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127; b) Evans, D. A; Ennis, M. D.; Mathre, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1737.
19. Evans, D. A.; Miller, S. J.; Lectka, T.; von Matt P., *J. Am. Chem. Soc.* **1999**, *121*, 7559.
20. For detailed study, see: Morgan, J. P. *Ph. D. Thesis, Caltech*, **2003**.
21. Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260.
22. Smulik, J. A.; Diver, S. T. *Org. Lett.* **2000**, *2*, 2271.
23. a) Furstner, A.; Langemann, K. *J. Am. Chem. Soc.* **1997**, *119*, 9130; b) Ghosh, A. K.; Cappiello, J.; Shin,.D. *Tetrahedron Lett.* **1998**, *39*, 4651; c) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791; d) Coalter, J. N.; Bollinger, J. C.;. Huffman, J. C.; Werner-Zwanziger, U.; Caulton, K. G.; E. Davidson, R.; Gerard, H.; Clot, E.;

Eisenstein, O. *New J. Chem.* **2000**, *24*, 9; e) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.;Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

24. For a review see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.
25. a) Stowasser, B.; Budt, K.-H.; Jian-Qi, L.; Peyman, A.; Ruppert, D. *Tetrahedron Lett.* **1992**, *33*, 6625. b) Hirschmann, R.; Smith, A. B.; Taylor, C. M.; Benkovic, P. A.; Taylor, S. D.; Yager, K. M.; Sprengeler, P. A.; Benkovic, S. J. *Science* **1994**, *265*, 234. c) Wester, R. T.; Chambers, R. J.; Green, M. D.; Murphy, W. R. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2005.
26. A wide variety of reactions have been performed on vinylphosphonate alkenes: Conjugate additions: a) Afarinkia, K.; Binch, H. M.; De Pascale, E. D. *Synlett* **2000**, *12*, 1769. b) Afarinkia, K.; Binch, H. M.; Forristal, I. *Synlett* **2000**, *12*, 1771. c) Cuprate additions: Li, N.-S.; Yu, S.; Kabalka, G. W. *Organometallics* **1999**, *18*, 1811. d) Aminohydroxylation: Thomas, A. A.; Sharpless, K. B. *J. Org. Chem.* **1999**, *64*, 8379. e) Cycloadditions: Ruder, S. M.; Ding, M. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1771. f) McClure, C. K.; Hansen, K. B.; Herzog, K. J.; Link, J. S.; Arnold, F. P. *Phosphorus Sulfur* **1996**, *109-110*, 333. g) Hydroboration: Pergament, I.; Srebnik, M. *Org. Lett.* **2001**, *3*, 217. h) Asymmetric hydrogenation: Burk, M. J.; Stammers, T. A.; Straub, J. A. *Org. Lett.* **1999**, *1*, 387. i) Ozonolysis: Gil, J. M.; Hah, J. H.; Park, K. Y.; Oh, D. Y. *Synth. Commun.* **2000**, *30*, 789. j) Oxime ether synthesis: Shen, Y.; Jiang, G.-F. *Synthesis* **2000**, 502.
27. a) Shen, Y.; Jiang, G.-F. *Synthesis* **2000**, 99. b) Tago, K.; Kogen, H. *Org. Lett.* **2000**, *2*, 1975.
28. a) Kouno, R.; Okauchi, T.; Nakamura, M.; Ichikawa, J.; Minami, T. *J. Org. Chem.* **1998**, *63*, 6239. b) Kouno, R.; Tsubota, T.; Okauchi, T.; Minami, T. *J. Org. Chem.* **2000**, *65*, 4326.
29. a) Probst, M. F.; Modro, A. M.; Modro, T. A. *Can. J. Chem.* **1997**, *75*, 1131.b) Gil, J. M.; Oh, D. Y. *J. Org. Chem.* **1999**, *64*, 2950. c) Zhong, P.; Huang, X.; Xiong, Z. X. *Synlett* **1999**, 721. d) Otaka, A.; Mitsuyama, E.; Watanabe, H.; Tamamura, H.; Fujii, N. *J. Chem. Soc., Chem. Commun.* **2000**, 1081. e) Braga, A. L.; Alves, E. F.; Silveira, C. C.; de Andrade, L. L.

Tetrahedron Lett. **2000**, *41*, 161. f) Jang, W. B.; Oh, D. Y.; Lee, C.-W. *Tetrahedron Lett.* **2000**, *41*, 5103.

30. a) Holt, D. A.; Erb, J. M. *Tetrahedron Lett.* **1989**, *30*, 5393. b) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571. c) Kazankova, M. A.; Trostyanskaya, I. G.; Lutsenko, S. V.; Beletskaya, I. P. *Tetrahedron Lett.* **1999**, *40*, 569. d) Okauchi, T.; Yano, T.; Fukamachi, T.; Ichikawa, J.; Minami, T. *Tetrahedron Lett.* **1999**, *40*, 5337. e) Zhong, P.; Xiong, Z. X.; Huang, X. *Synth. Commun.* **2000**, *30*, 273. f) Han, L.-B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407.
31. Brunner, H.; de Courcy, N. L.; Genet, J.-P. *Synlett* **2000**, 201.
32. Ulman, M.; Belderrain, T. R.; Grubbs, R. H. *Tetrahedron Lett.* **2000**, *41*, 4689.
33. Choi, T.-L.; Grubbs, R. H. *Chem. Comm.* **2001**, 2648.