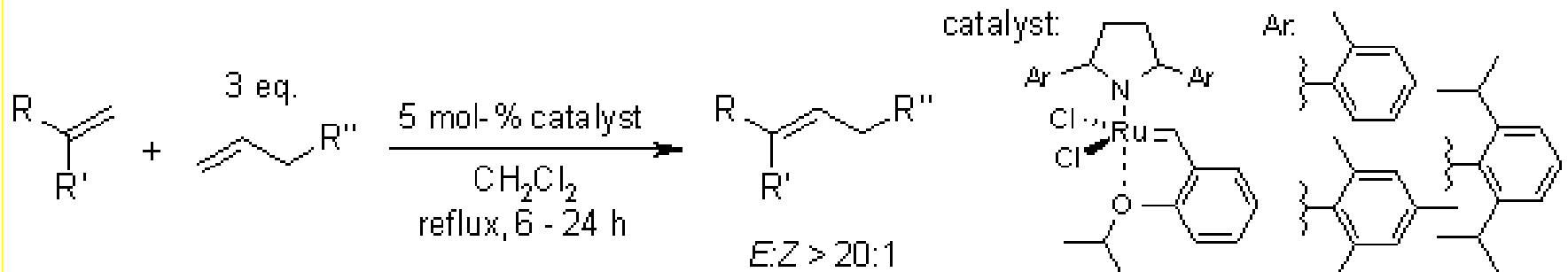
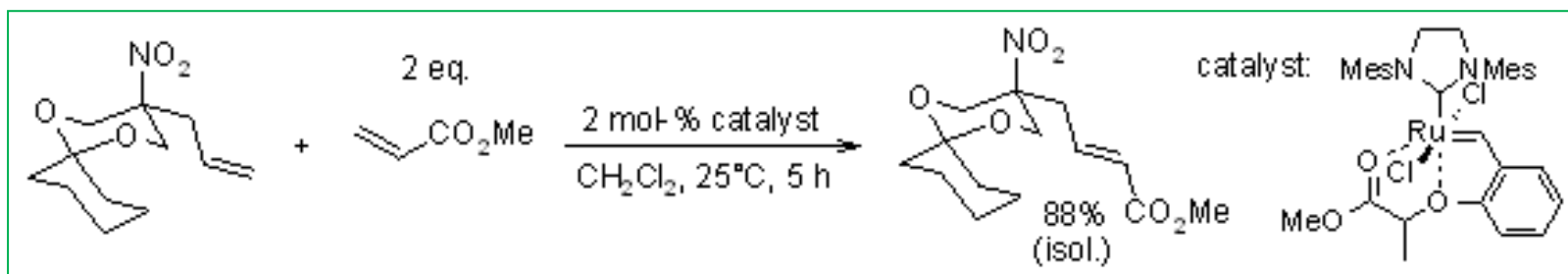
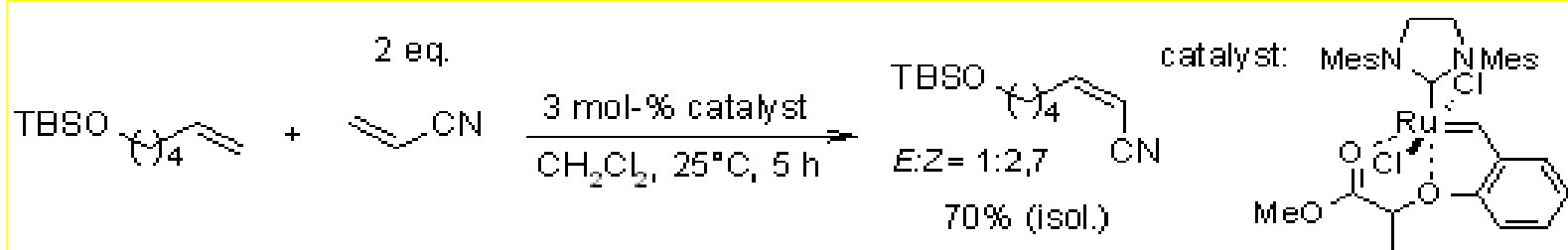


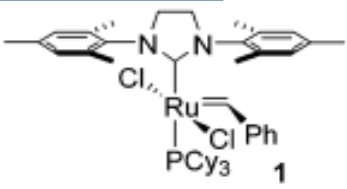
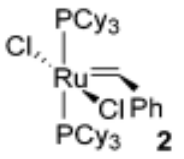
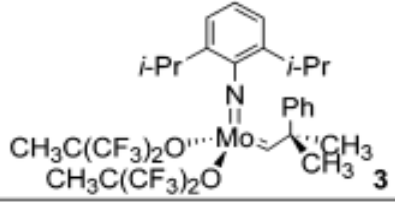
## Αντιδράσεις Cross Metathesis.

Αντιδράσεις Cross Metathesis παρεμποδισμένων αλκενίων (Org. Lett. 2008, 10, 441).



Αντιδράσεις cross-metathesis με **2-πλάσιες ποσότητες** ακρυλικών πρώτων υλών (J. Am. Chem. Soc. 2006, 128, 13652).



Olefin type			
<b>Type I (fast homodimerization)</b>	terminal olefins, <sup>6</sup> 1° allylic alcohols, esters, <sup>6h,20</sup> allyl boronate esters, <sup>6f</sup> allyl halides, <sup>6f,6i</sup> styrenes (no large ortho substit.), <sup>6c,d,f,i</sup> allyl phosphonates, <sup>6d</sup> allyl silanes, <sup>25</sup> allyl phosphine oxides, <sup>6h</sup> allyl sulfides, <sup>6h</sup> protected allyl amines <sup>6h</sup>	terminal olefins, <sup>8</sup> allyl silanes, <sup>14,18,19</sup> 1° allylic alcohols, ethers, esters, <sup>8,19,21</sup> allyl boronate esters, <sup>10f</sup> allyl halides <sup>17</sup>	terminal olefins, <sup>11a,b,12,14</sup> allyl silanes <sup>11b</sup>
<b>Type II (slow homodimerization)</b>	styrenes (large ortho substit.), <sup>6d,f</sup> acrylates, <sup>6b,i</sup> acrylamides, <sup>6c</sup> acrylic acid, <sup>6c</sup> acrolein, <sup>6b,24</sup> vinyl ketones, <sup>6b</sup> unprotected 3° allylic alcohols, <sup>6f,h</sup> vinyl epoxides, <sup>6b</sup> 2° allylic alcohols, perfluorinated alkane olefins <sup>6b,23</sup>	styrene, <sup>16</sup> 2° allylic alcohols, vinyl dioxolanes, <sup>8</sup> vinyl boronates <sup>8</sup>	styrene, <sup>11a,11b</sup> allyl stannanes <sup>15</sup>
<b>Type III (no homodimerization)</b>	1,1-disubstituted olefins, <sup>6a,g</sup> non-bulky trisub. olefins, <sup>6a,g</sup> vinyl phosphonates, <sup>6d</sup> phenyl vinyl sulfone, <sup>22</sup> 4° allylic carbons (all alkyl substituents), 3° allylic alcohols (protected)	vinyl siloxanes <sup>16</sup>	3° allyl amines, <sup>14</sup> acrylonitrile <sup>12</sup>
<b>Type IV (spectators to CM)</b>	vinyl nitro olefins, trisubstituted allyl alcohols (protected)	1,1-disubstituted olefins, <sup>8</sup> disub. α,β-unsaturated carbonyls, 4° allylic carbon-containing olefins, <sup>8</sup> perfluorinated alkane olefins, <sup>8</sup> 3° allyl amines (protected) <sup>14</sup>	1,1-disubstituted olefins <sup>11a</sup>

olefin reactivity ↑

- Type I - Rapid homodimerization, homodimers consumable
- Type II - Slow homodimerization, homodimers sparingly consumable
- Type III - No homodimerization
- Type IV - Olefins inert to CM, but do not deactivate catalyst (Spectator)

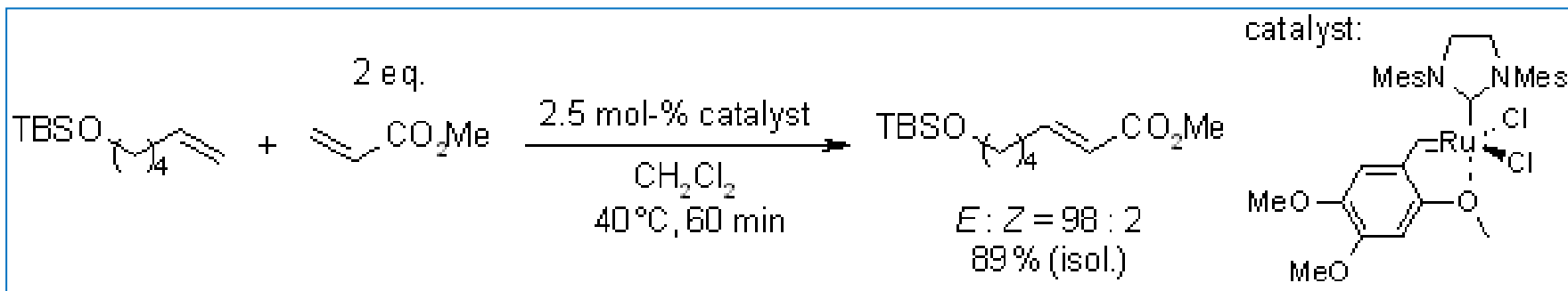
Reaction between two olefins of Type I = *Statistical CM*

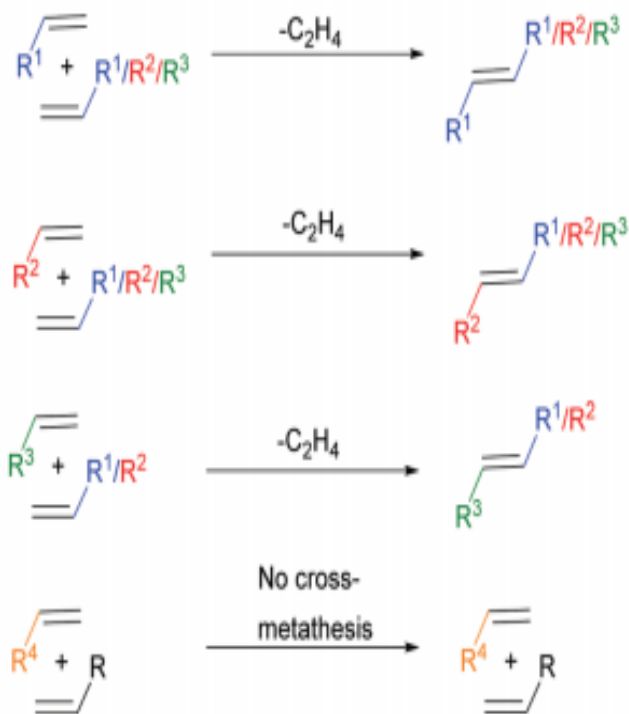
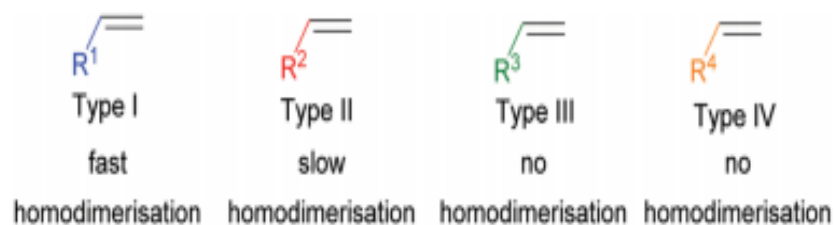
Reaction between two olefins of same type (non-Type I) = *Non-selective CM*

Reaction between olefins of two different types = *Selective CM*

**Figure 2.** Olefin categorization and rules for selectivity.

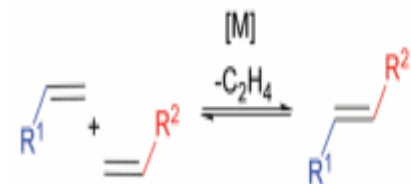
Αντίδραση cross-metathesis με 2-πλάσια ποσότητα ακρυλικού μεθυλεστέρα  
(Eur. J. Org. Chem. 2003, 963)



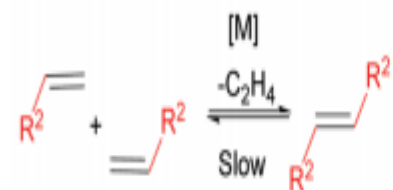


Scheme 2 Alkene categorisation into type I, type II, type III or type IV.

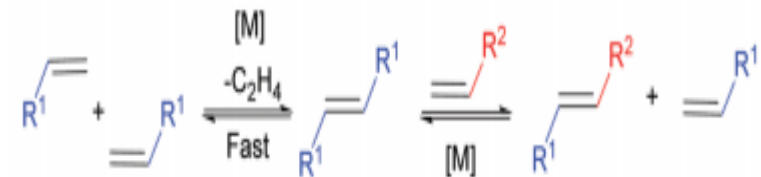
Scenario 1: Type I reacting with Type II



Scenario 2: Type II reacting with Type II

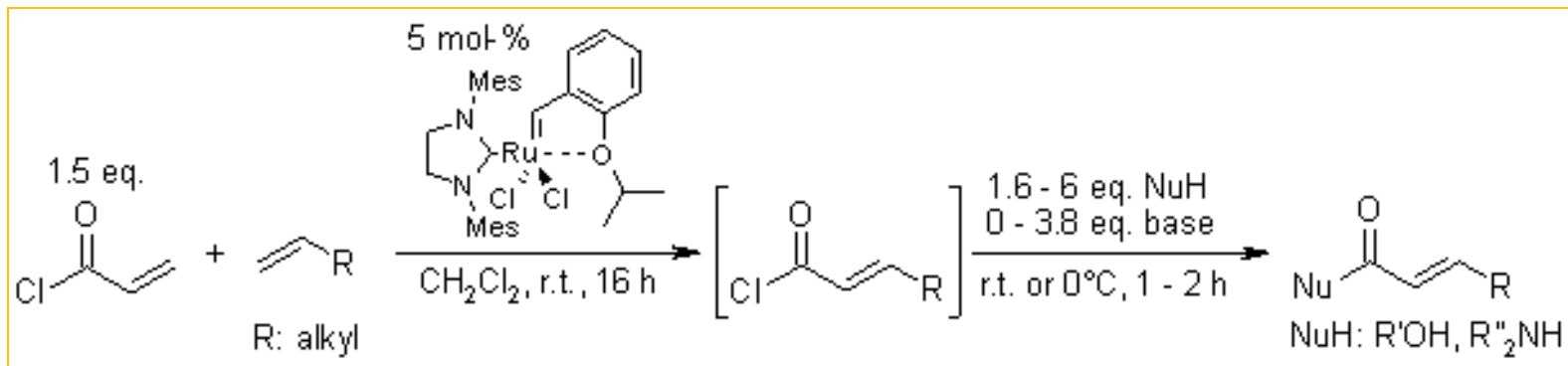


Scenario 3: Type I reacting with Type I

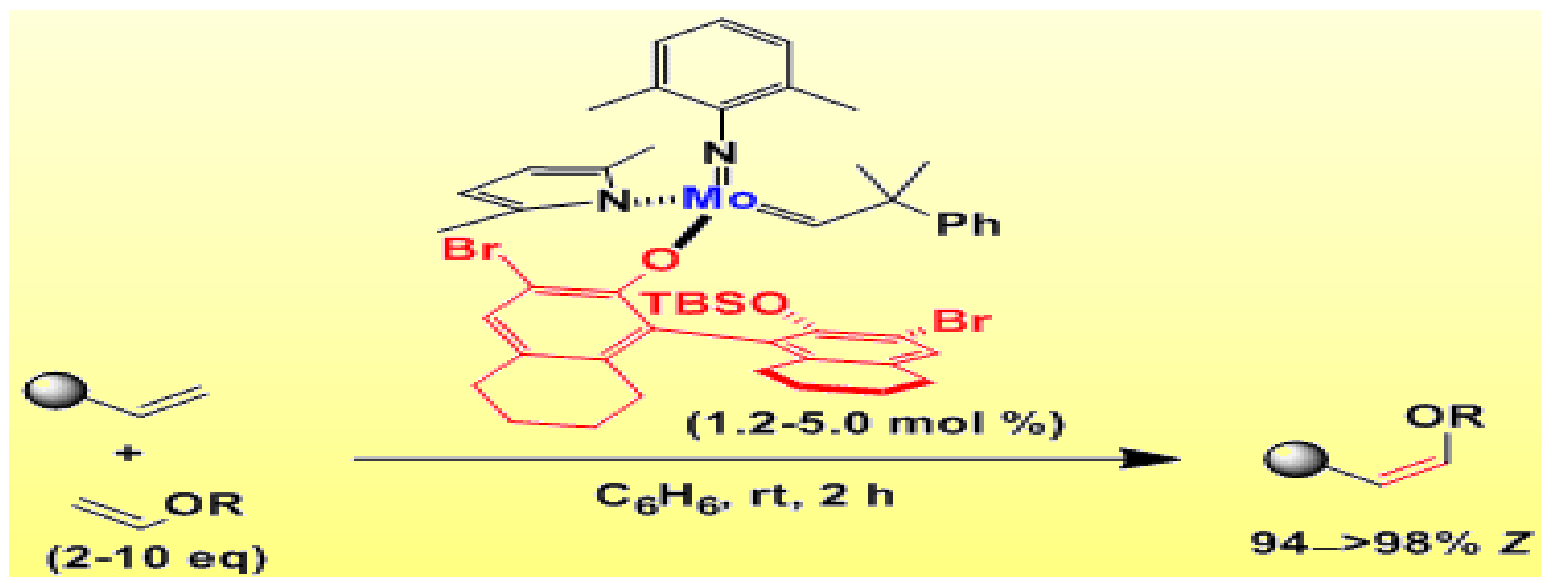


Scheme 3 Selective cross metathesis reaction between a type I alkene and a type II alkene.

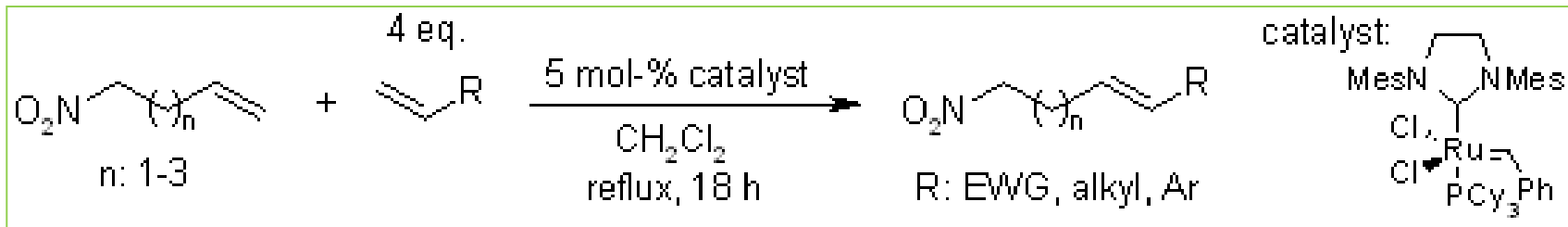
Σύνθεση «one-pot» (με μια πειραματική διαδικασία) α,β-ακορέστων καρβονυλικών παραγώγων αρχίζοντας με αντίδραση cross-metathesis ακρυλοϋλοχλωριδίου με αλκένια (Org. Lett. 2009, 11, 5446)



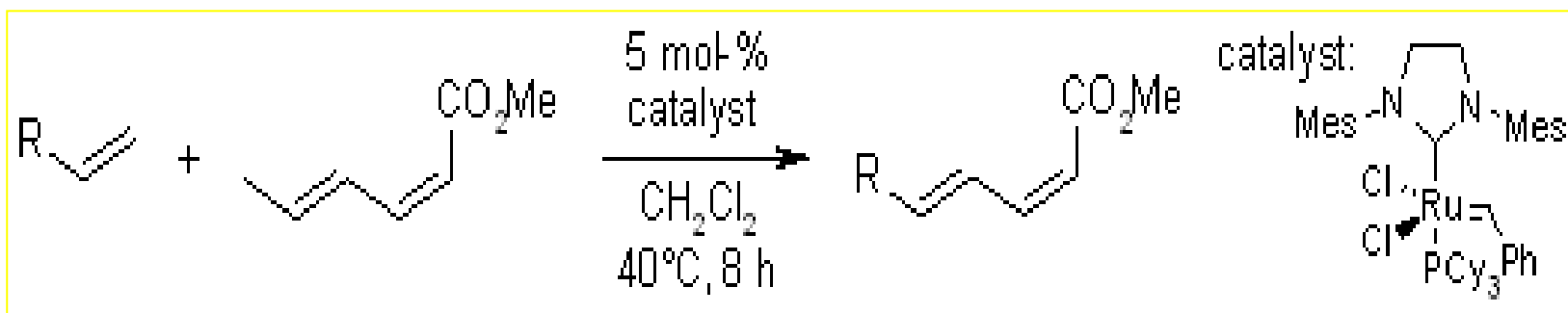
Cross metathesis με καταλύτη εκλεκτικό για τη λήψη Z-προϊόντος (Nature 2011, 471, 461).



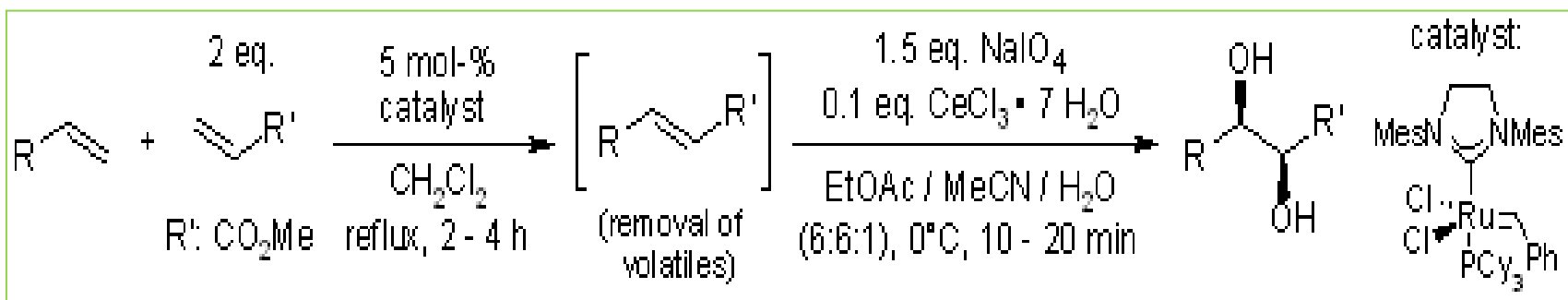
## Σύνθεση νιτροαλκενίων με αντίδραση cross-metathesis (Org. Lett. 2007, 9, 2613).



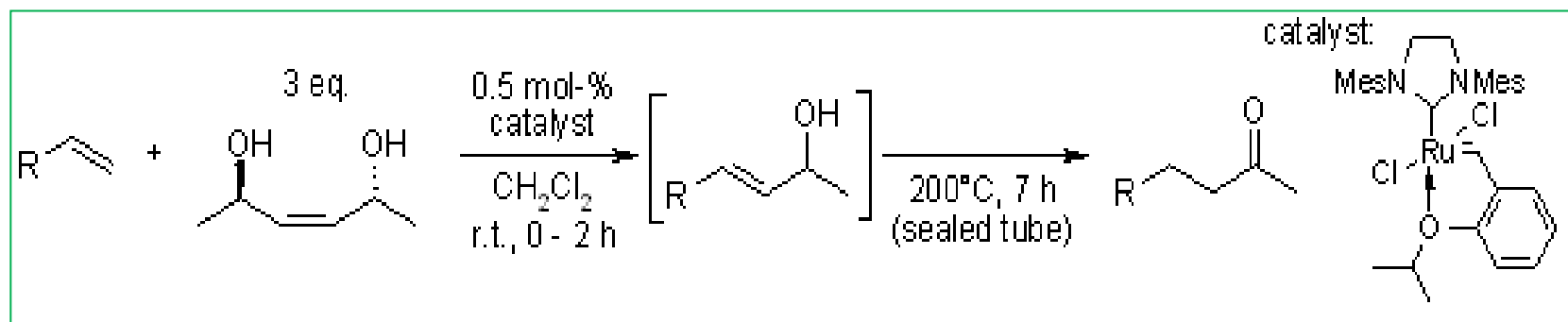
## Εκλεκτικός σχηματισμός (2Z,4E-διενίων) μέσω αντίδρασης cross-metathesis ενίου-διενίου (Org. Lett. 2007, 9, 5)



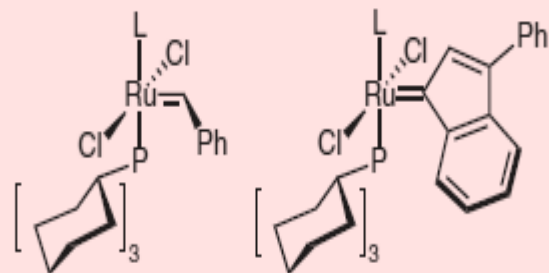
Συνεχόμενη (**tandem**) αντίδραση cross-metathesis/οξείδωσης (Org. Lett. 2006, 8, 4759).



Σύνθεση αλειφατικών κετονών μέσω **tandem** αντίδρασης cross-metathesis/αλλυλικής ισομερείωσης (Org. Lett. 2006, 8, 2603).

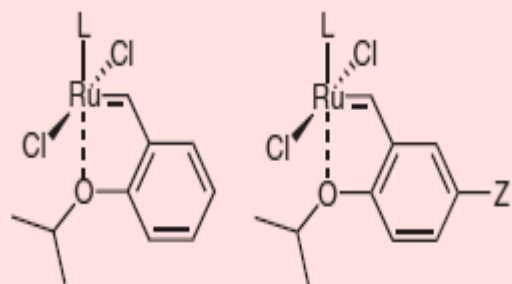


Σύνθεση **one-pot** πυρρολίων μέσω αντίδρασης cross-metathesis αλλυλαμινών με α,β-ακόρεστες καρβονυλικές ενώσεις (Synlett 2011, 124).



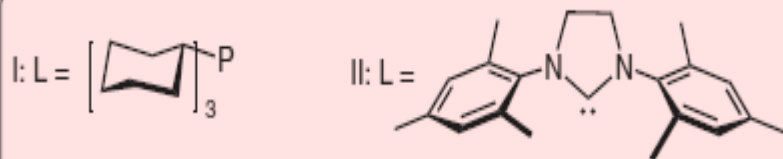
Gru-I, Gru-II

Ind-I, Ind-II



Hov-I, Hov-II

Gre-II, Z = NO<sub>2</sub>



I ⇨ I-generation  
II ⇨ II-generation

(SIMes)

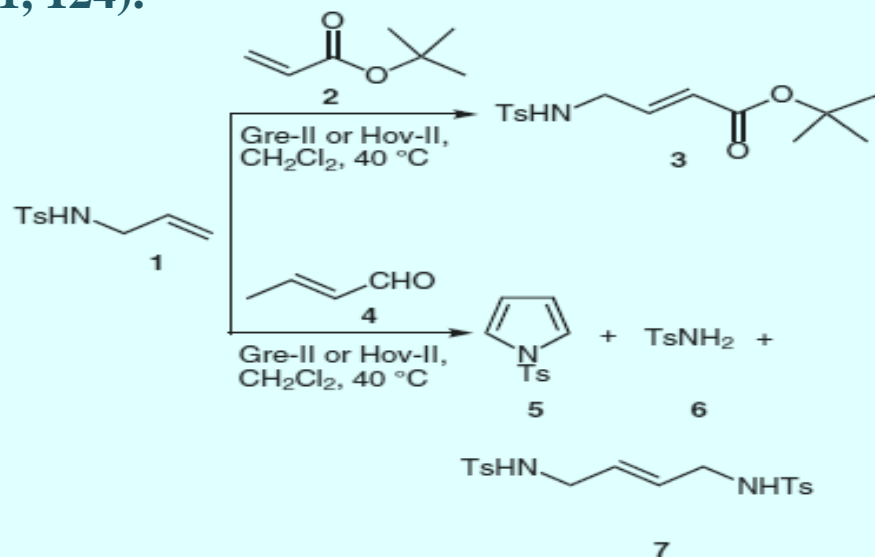
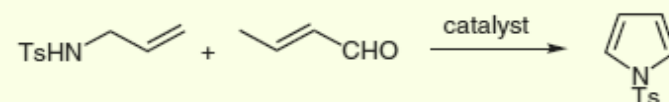


Table 1 Catalyst Screening for Cross Metathesis

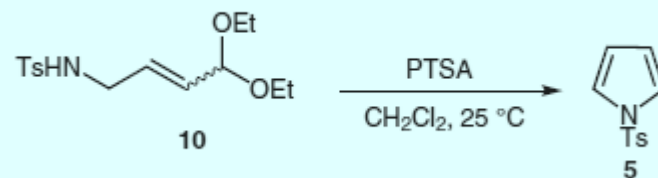
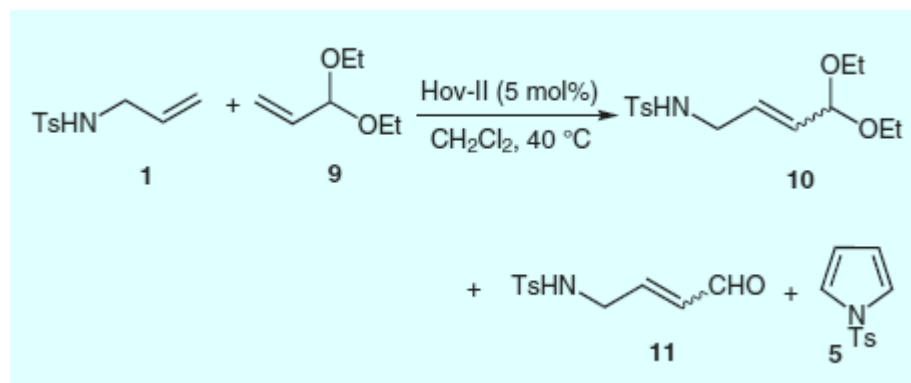
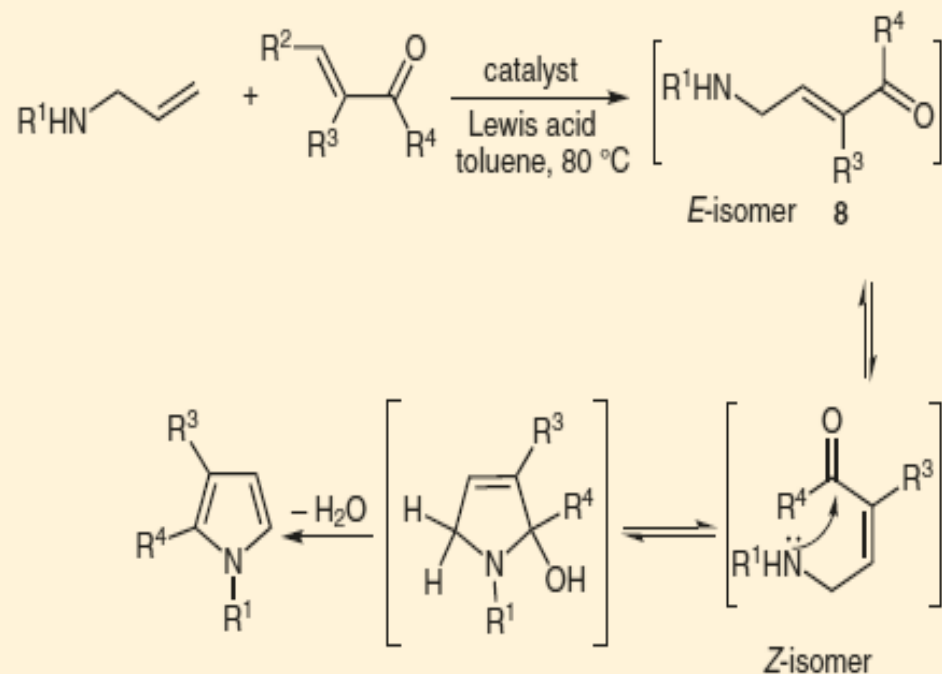


Catalyst	Catalyst (mol%)	Time (h)	Isolated yield (%)	
			CH <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>	Toluene <sup>b</sup>
Gru-I	10	48	–	5
Gru-II	10	48	5	8
Ind-I	10	48	–	6
Ind-II	10	48	–	16
Gre-II	5	36	32	35
Hov-II	5	36	60	60

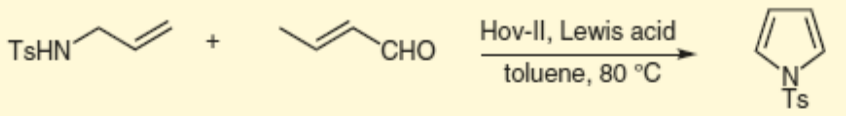
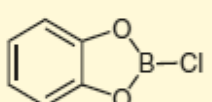
<sup>a</sup> Reaction temperature 40 °C.

<sup>b</sup> Reaction temperature 80 °C.





**Table 2** Screening of Lewis Acids for the Cross Metathesis<sup>a</sup>

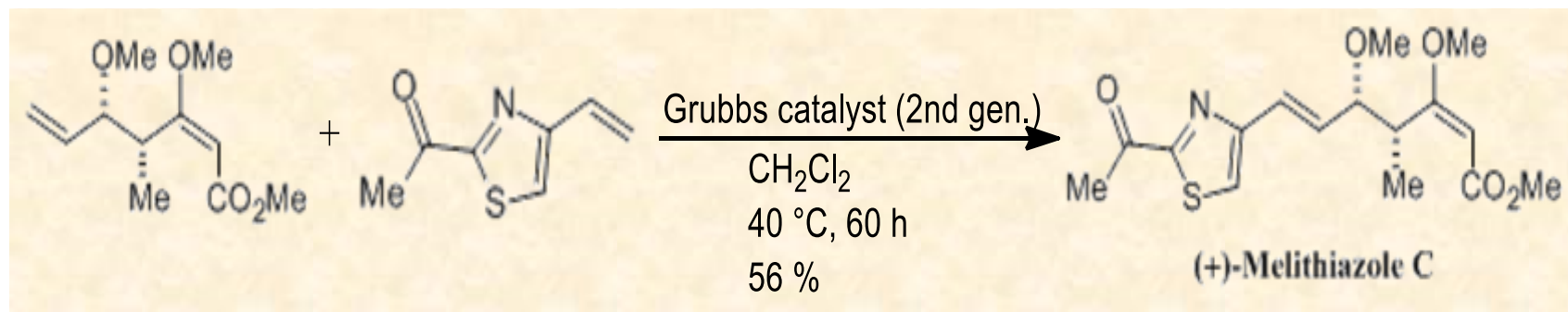
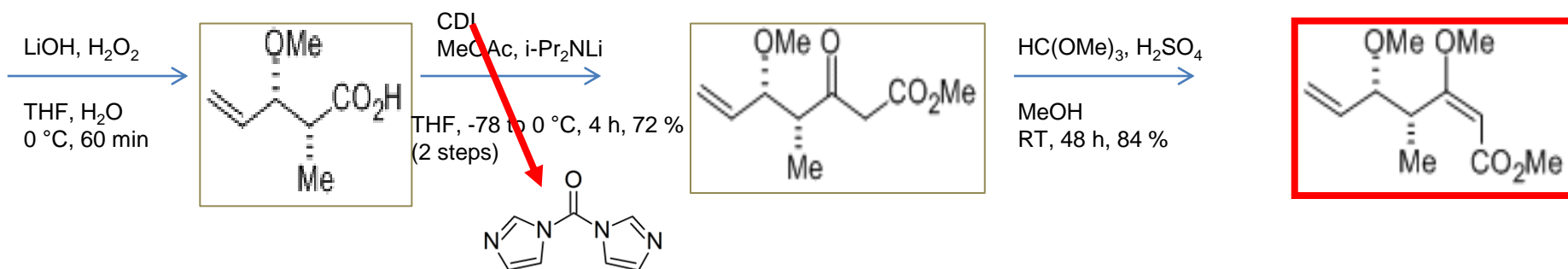
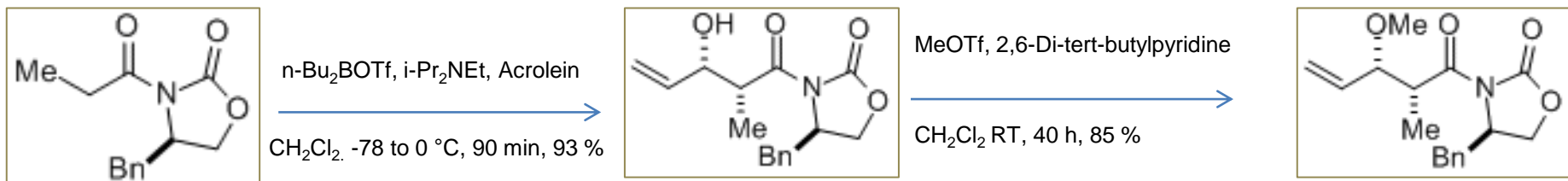
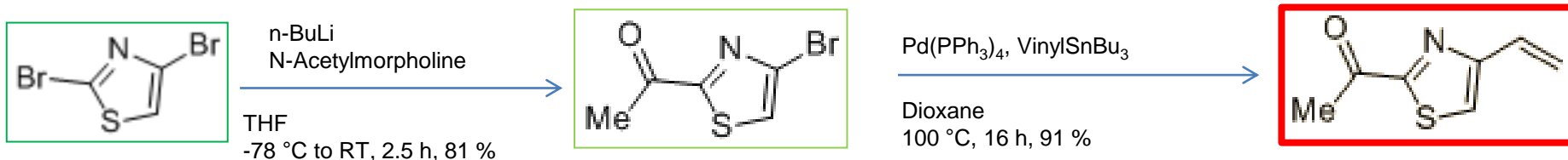
Lewis acid	Acid amount (mol%)	Time (min)	Yield (%) <sup>b</sup>
			
LiCl	100	120	5 <sup>c</sup>
AlCl <sub>3</sub>	100	120	5 <sup>c</sup>
Ti(O <i>i</i> -Pr) <sub>4</sub>	100	120	20 <sup>c</sup>
Zn(OTf) <sub>2</sub>	100	60	60
RuCl <sub>3</sub> · <i>n</i> H <sub>2</sub> O	100	45	60
	100	90	60
PhBCl <sub>2</sub>	100	90	70
B(OPh) <sub>3</sub>	100	30	93
B(OPh) <sub>3</sub>	50	30	93
B(OPh) <sub>3</sub>	20	30	92
B(OPh) <sub>3</sub>	10	30	92

<sup>a</sup> Reaction conditions: *N*-tosyl allylamine (0.47 mmol), crotonaldehyde (2.3 mmol), Lewis acid, Hov-II (5 mol%), toluene (5 mL).

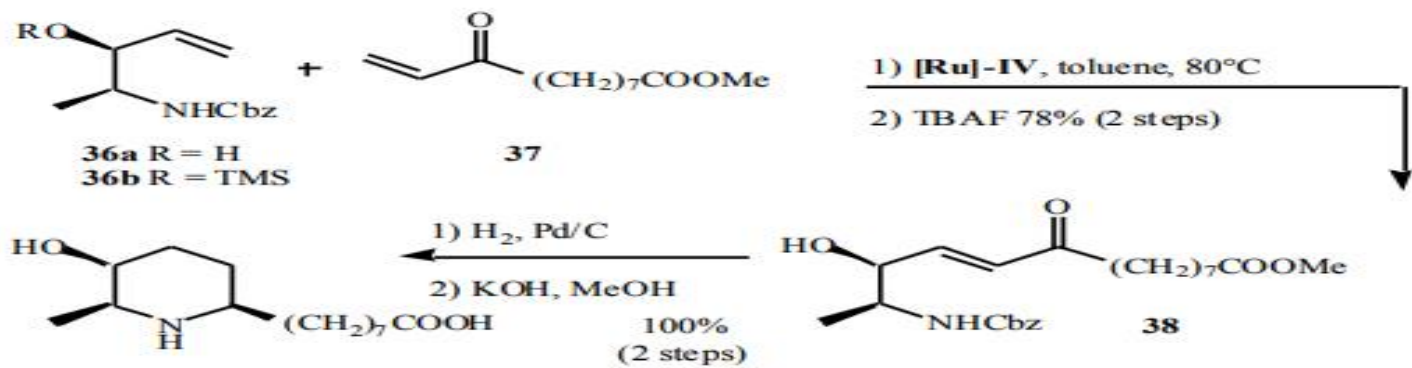
<sup>b</sup> Isolated yields.

<sup>c</sup> Catalyst decomposed.

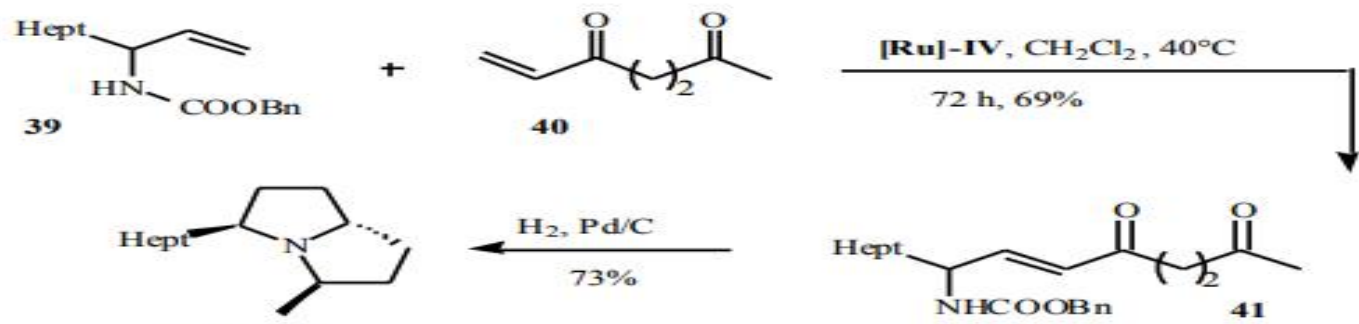
# Ολική σύνθεση του αντιβιοτικού **μυξοβακτηρίου μελιθειαζολίου C** μέσω εκλεκτικής *E*-αντίδρασης cross-metathesis (Org. Lett. 2007, 9, 3425).



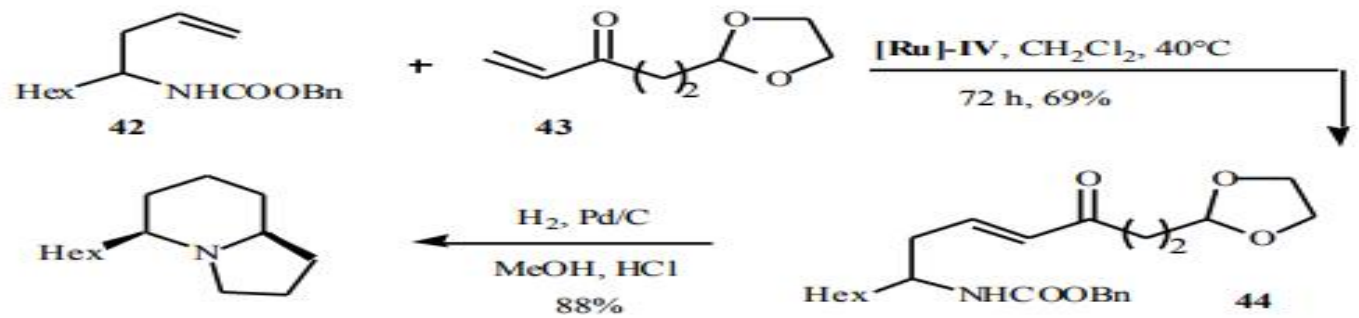
Syntheses of piperidine and pyrrolidine alkaloids with a CM/reductive cyclization sequence



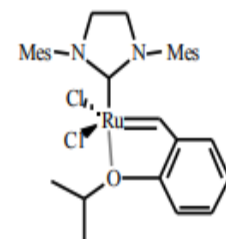
(+)-Carpamic acid



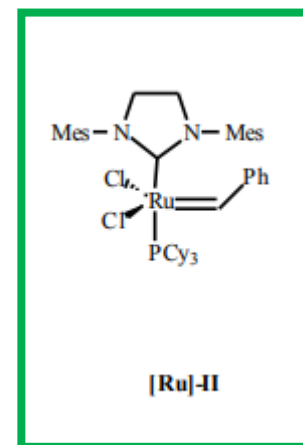
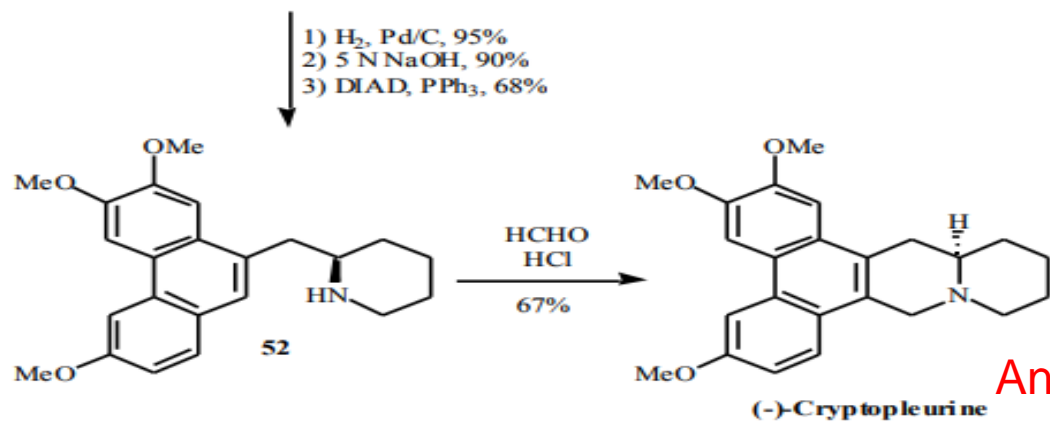
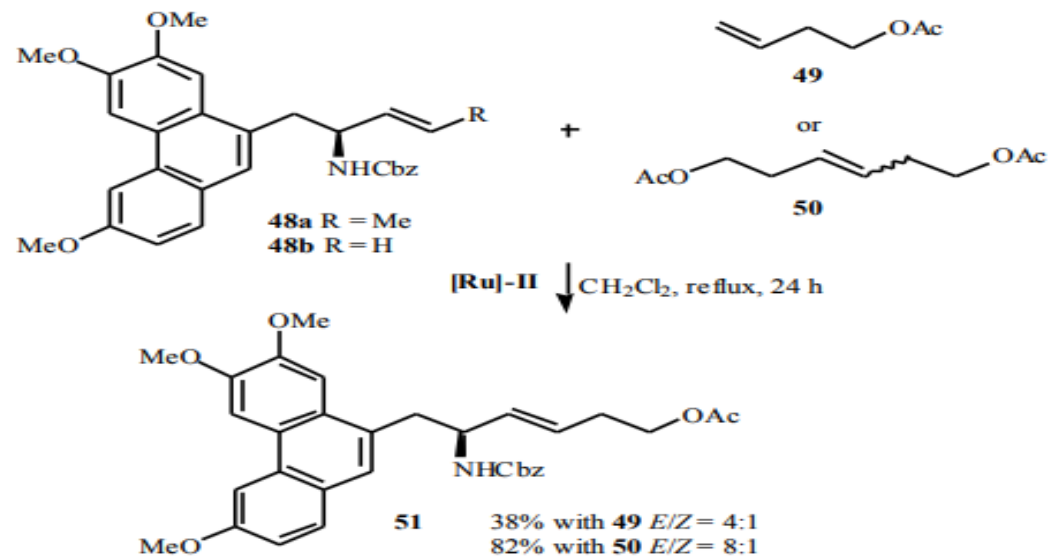
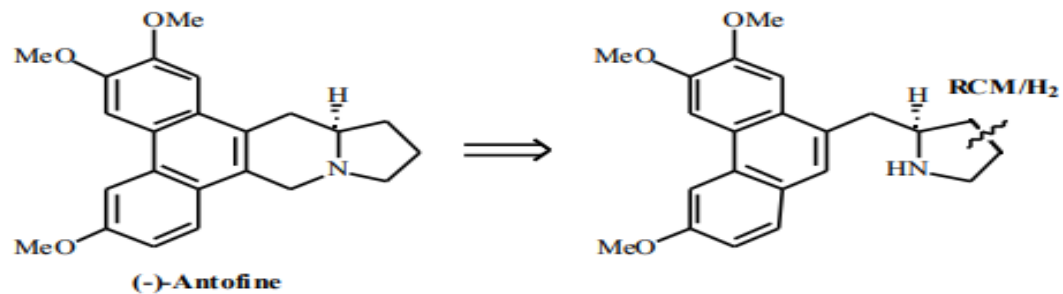
Xenovenine



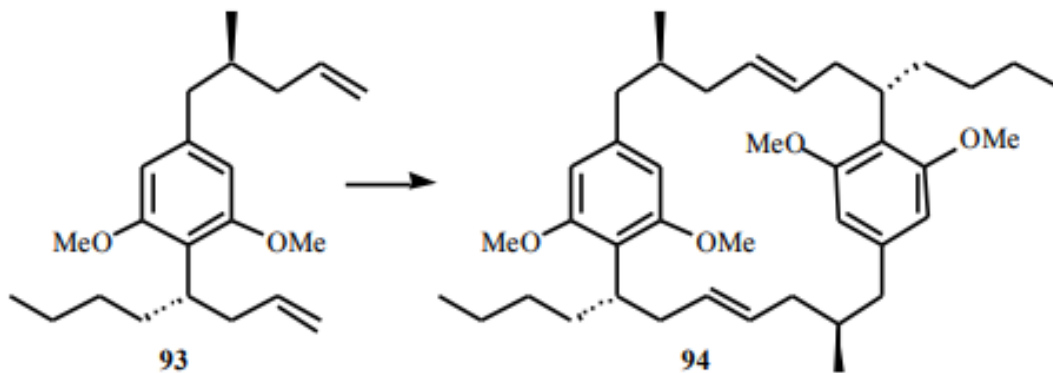
Indolizidine 209D



[Ru]-IV



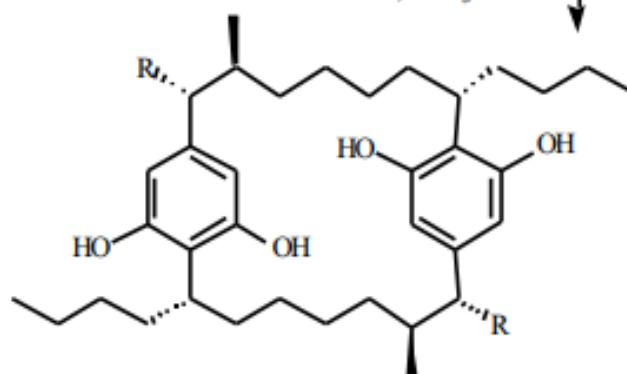
Anti-cancer activity



**[Ru]-I**, CH<sub>2</sub>Cl<sub>2</sub>, 20°C, 75 h  
**[Ru]-II**, benzene, 40°C, 27 h  
**[Mo]**, benzene, 20°C, 2 h

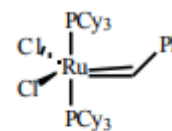
61%  
 58%  
 72%  
*E,E* only

1) H<sub>2</sub>, Pd/C  
 2) BBr<sub>3</sub>  
 84%  
 (2 steps)

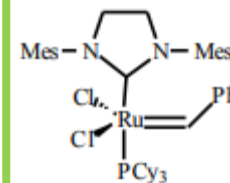


(-)-Cyclindrocyclophane F R = H  
 (-)-Cyclindrocyclophane A R = OH

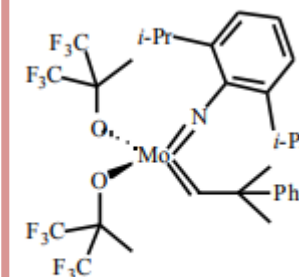
Synthesis of (-)-cyclindrocyclophanes A and F.



**[Ru]-I**



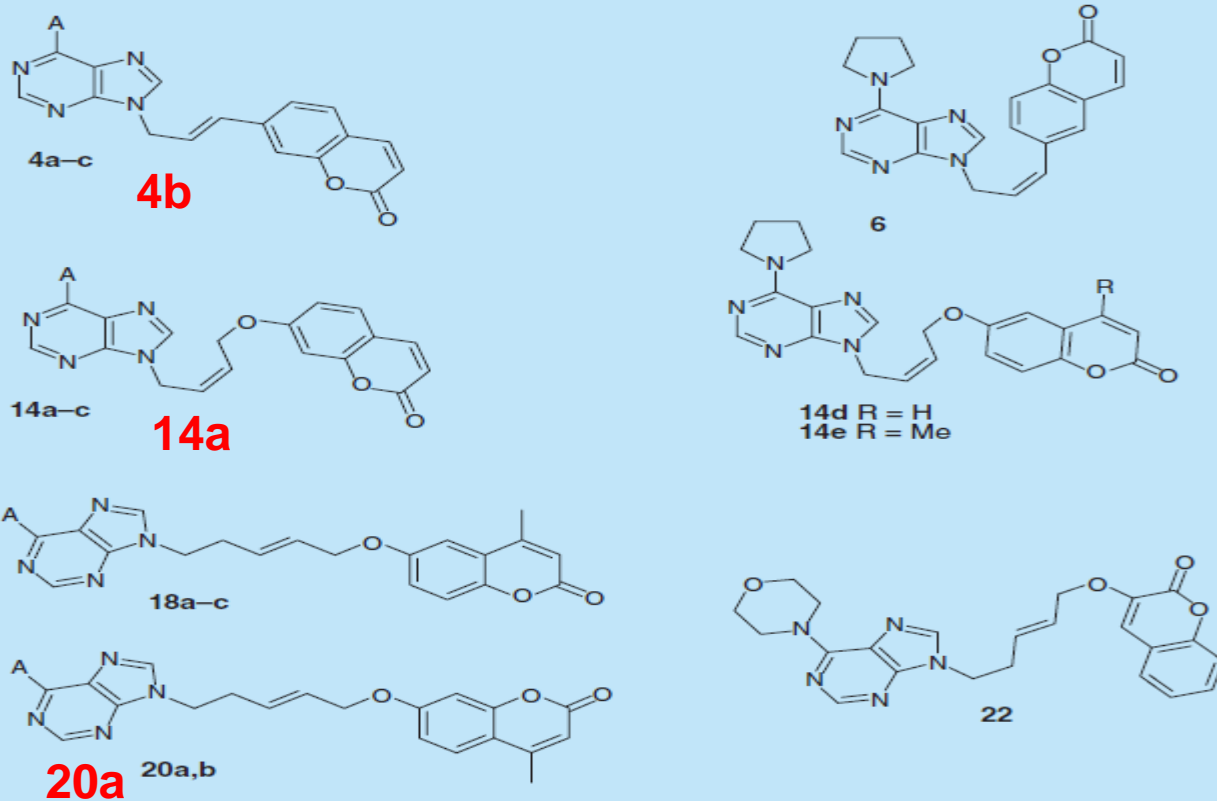
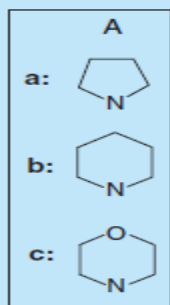
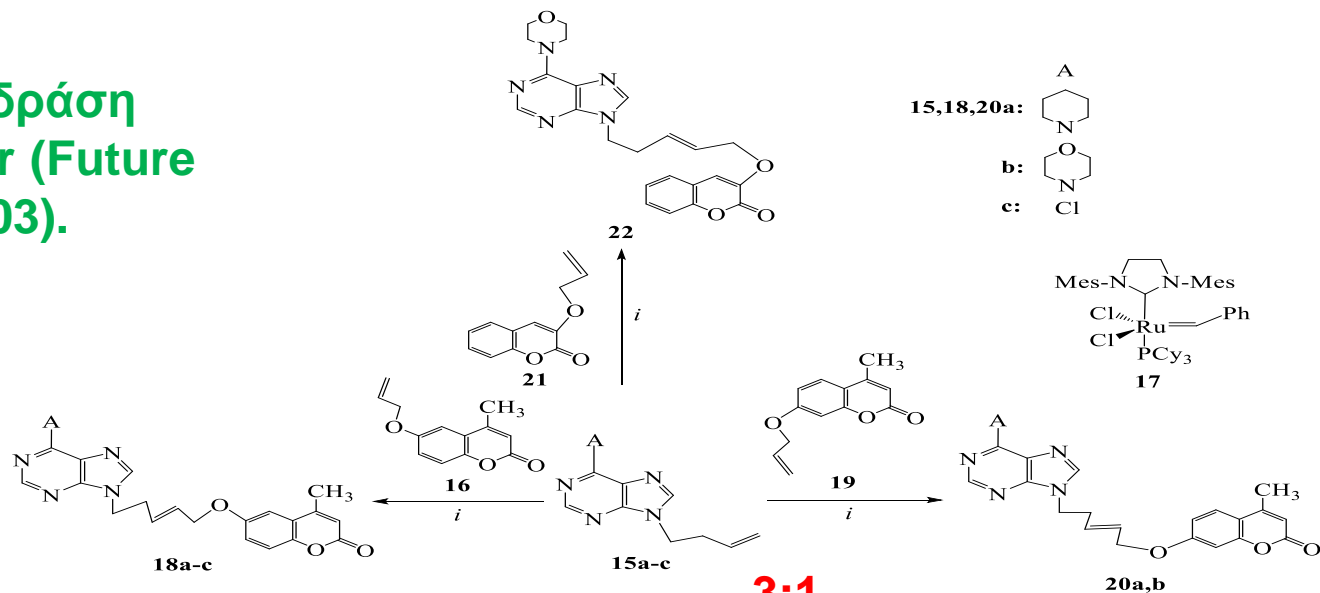
**[Ru]-II**



**[Mo]**

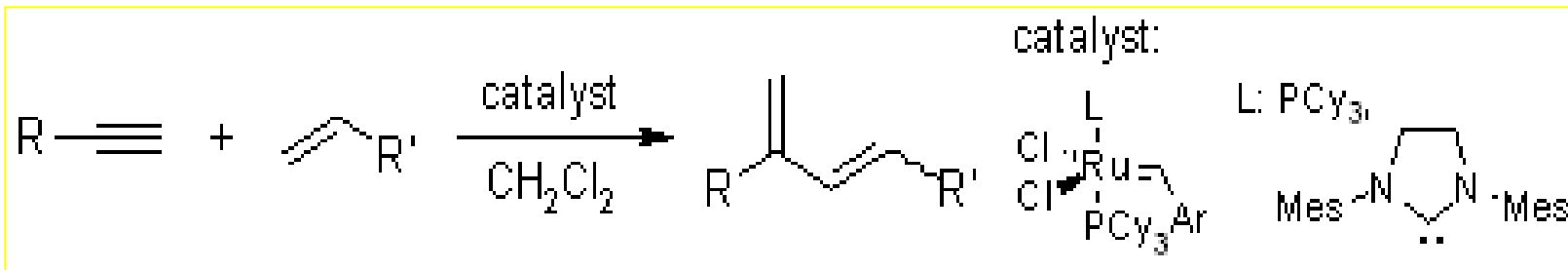
blue-green algae *Cylindrocapsa licheniforme*

Υβριδικές ενώσεις με δράση  
εναντίον της Alzheimer (Future  
Med. Chem. 2015, 7, 103).



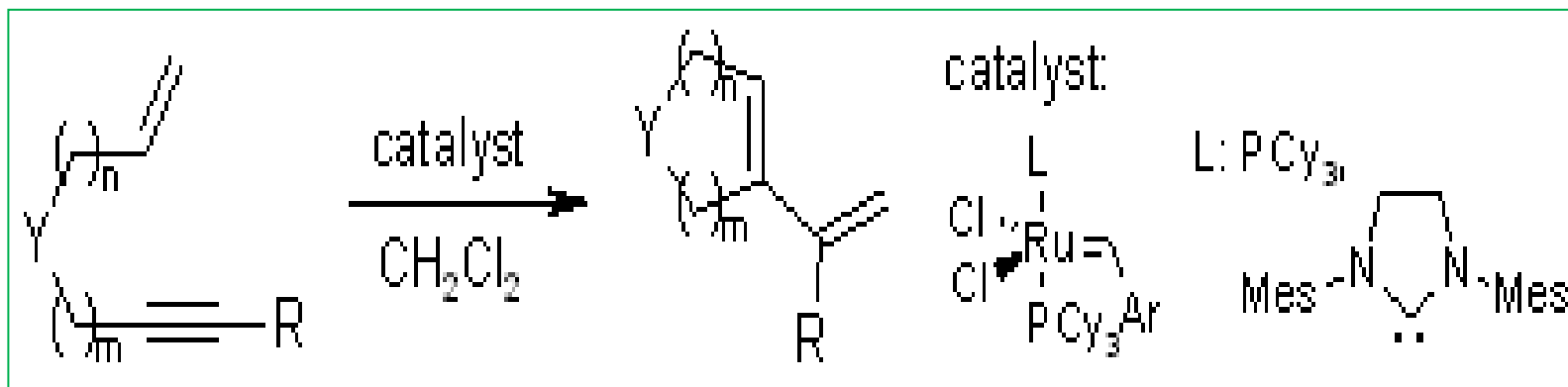
## Αντιδράσεις μετάθεσης ενυνίων (Enyne Metathesis).

Αντίδραση μετάθεσης μεταξύ ενός αλκενίου και ενός αλκυνίου που οδηγεί στη σύνθεση 1,3-διενίων (J. Chem. Rev. 2004, 104, 1317).



Η ενδομοριακή διαδικασία χαρακτηρίζεται σαν **μετάθεση ενυνίου με κλείσιμο δακτυλίου (RCEYM, Ring Closing Enyne Metathesis)**.

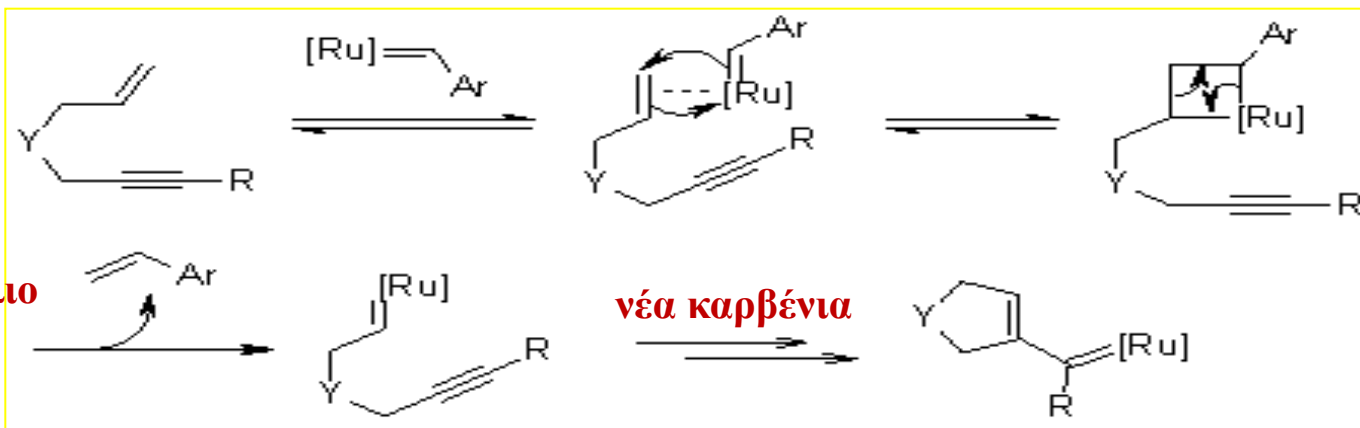
Οι αντιδράσεις αυτές γίνονται σε αραιώση για την αποφυγή σχηματισμού προϊόντων cross-metathesis.



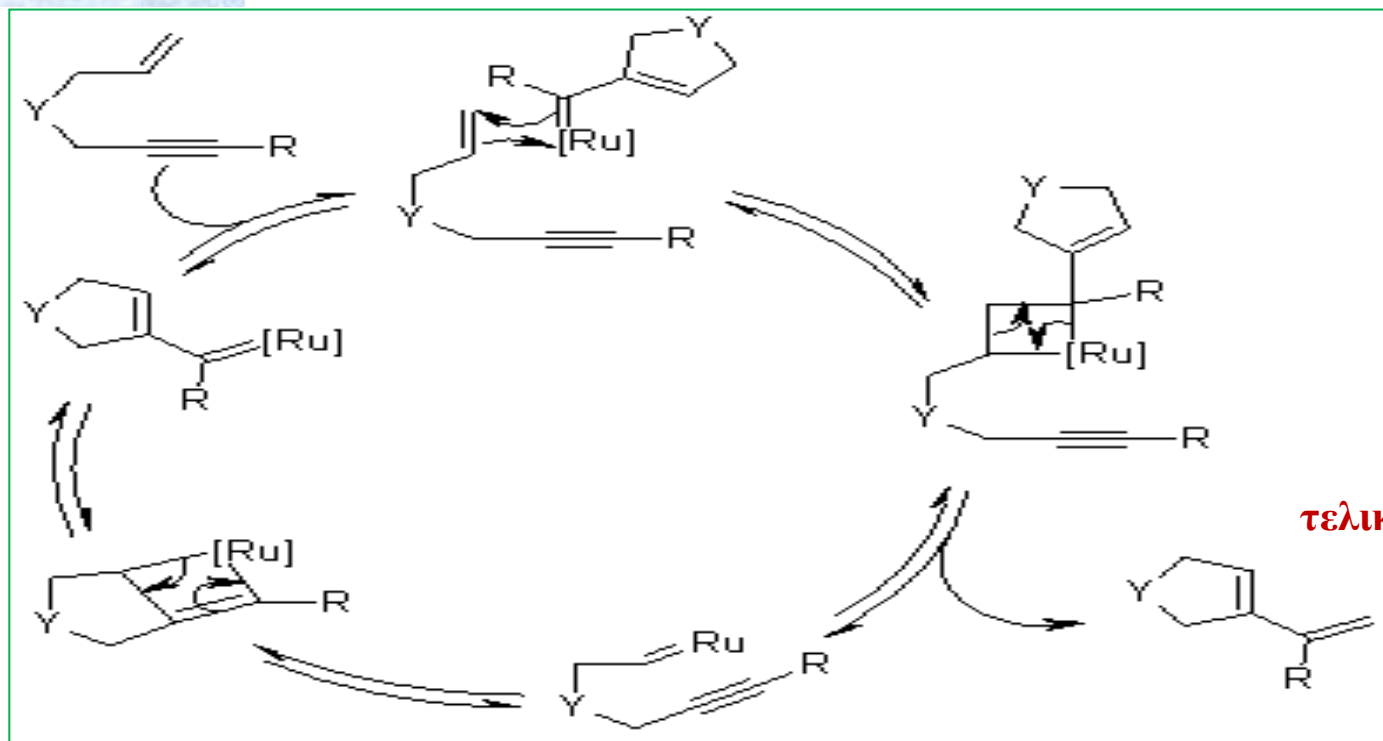
# Μηχανισμός αντίδρασης:

## Έναρξη

στυρόλιο

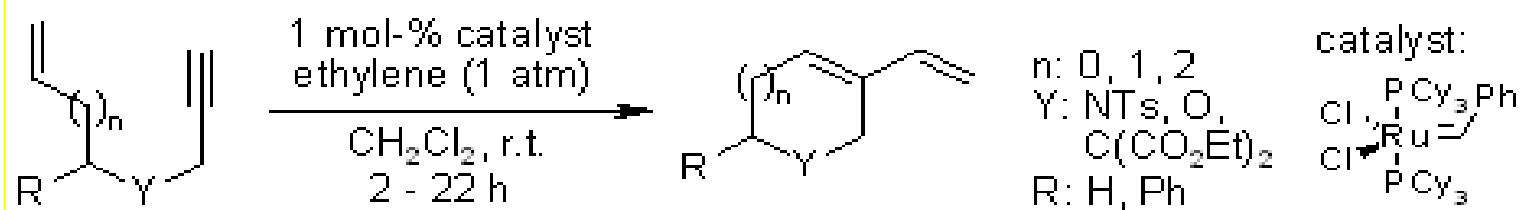


## Καταλυτικός κύκλος

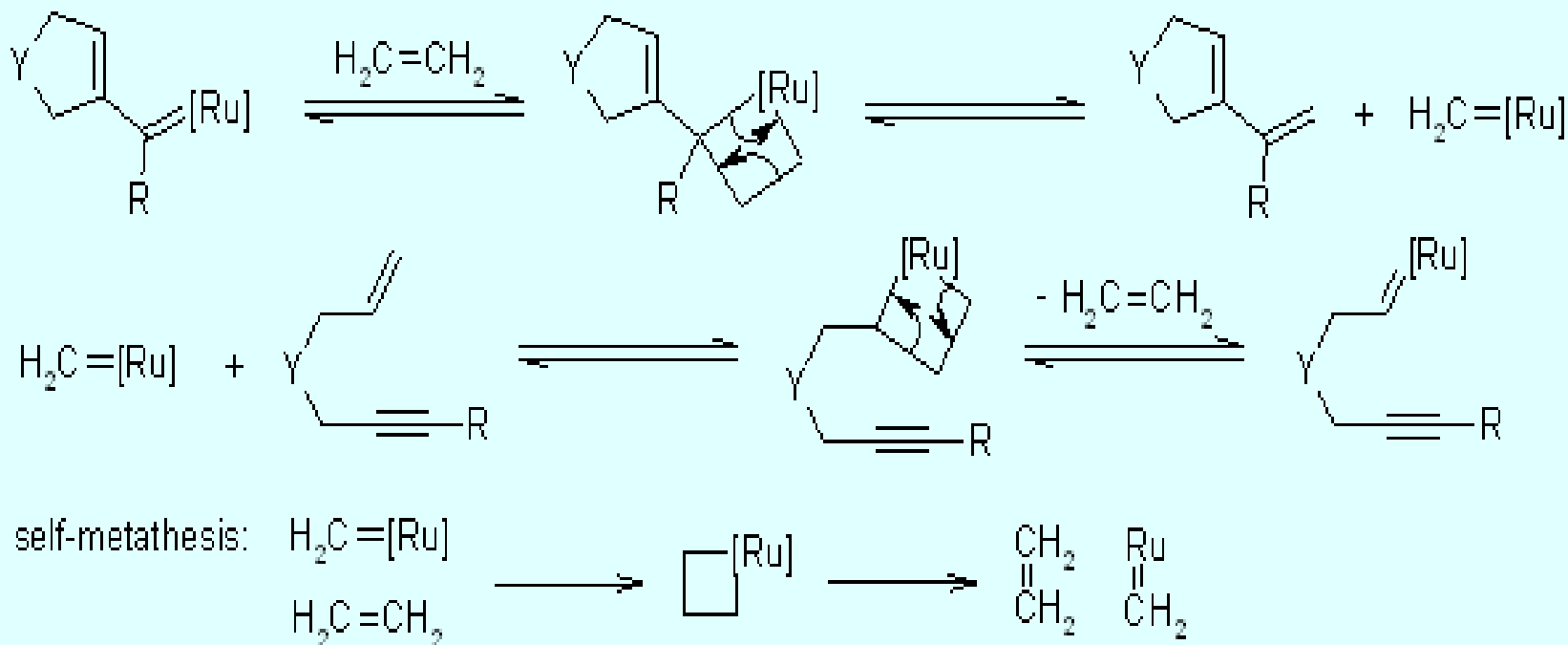




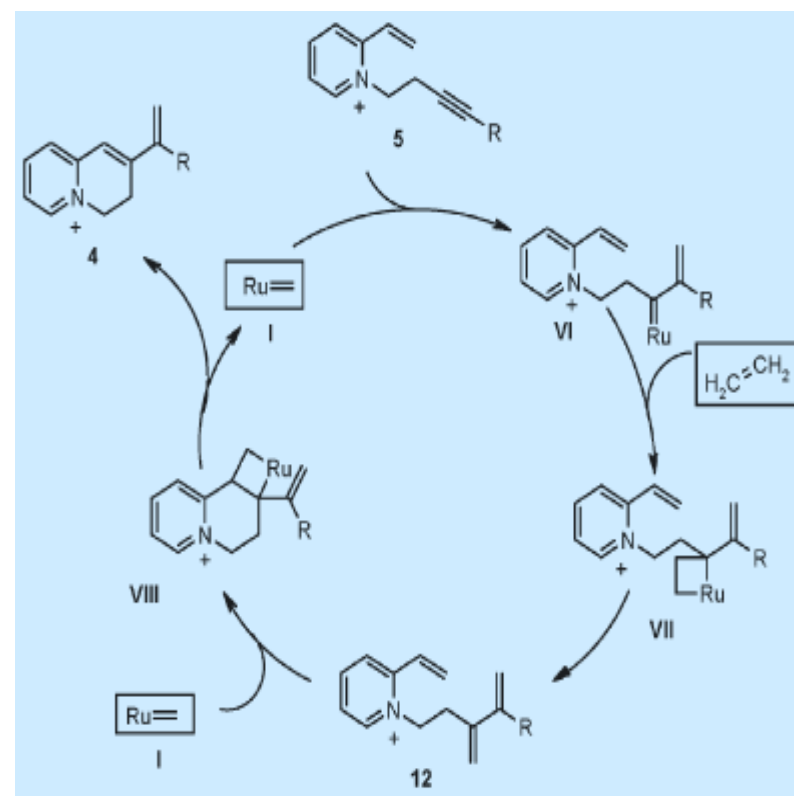
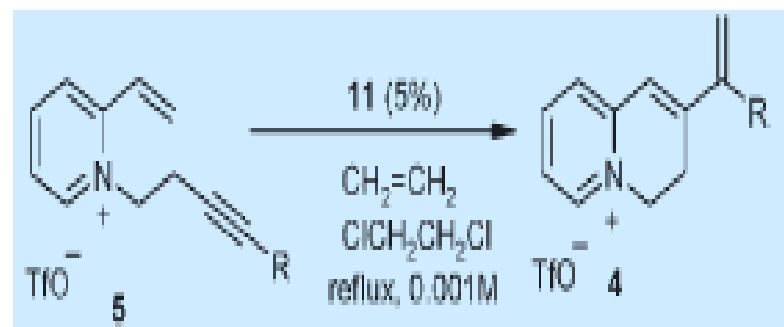
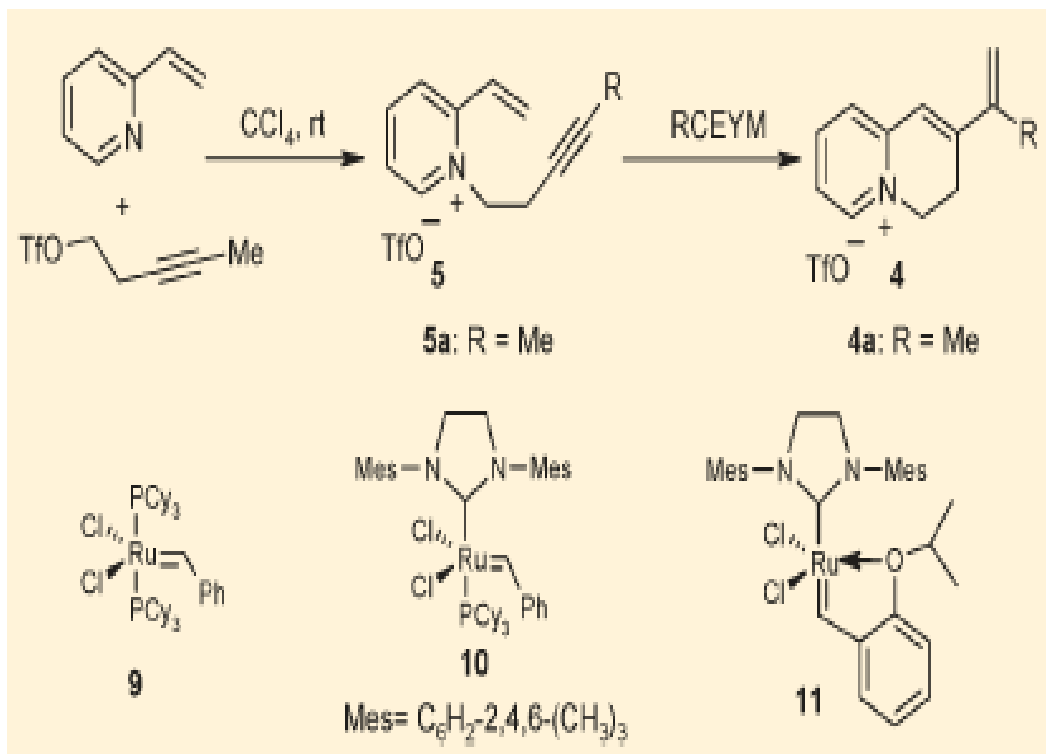
Με τη χρήση παράλληλα **αιθυλενίου**, για την αναγέννηση του καταλύτη, μπορούν να χρησιμοποιηθούν και λιγότερο δραστικοί καταλύτες (J. Org. Chem. 1998, 63, 608).



Με τη βοήθεια του αιθυλενίου αυξάνεται η συγκέντρωση του δραστικού καταλύτη. Η αντίδραση μετάθεσης του αιθυλενίου με το δραστικό βινυλοκαρβένιο δεν επηρεάζει την πορεία της αντίδρασης του ενυνίου.



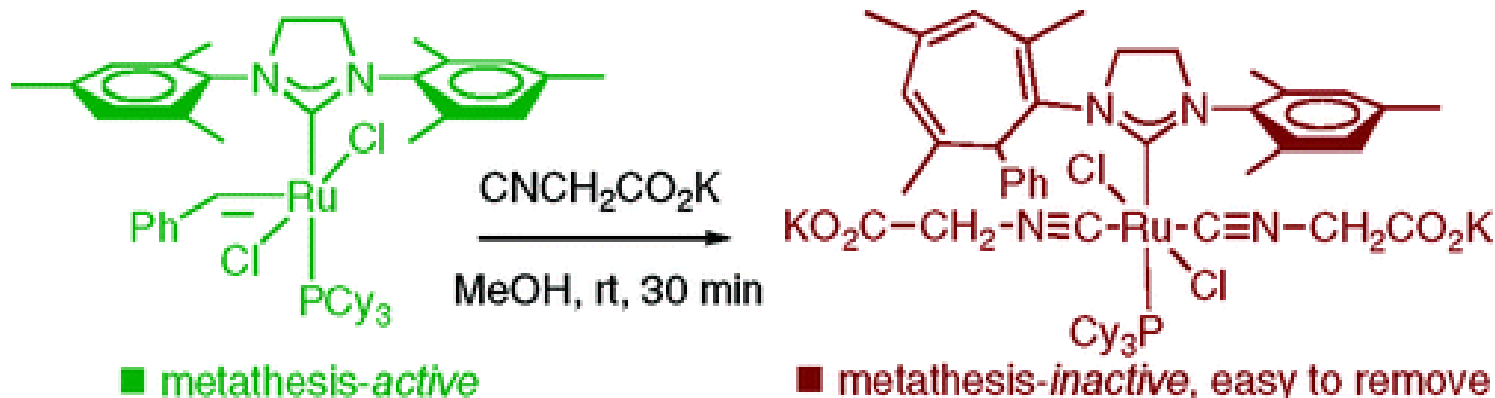
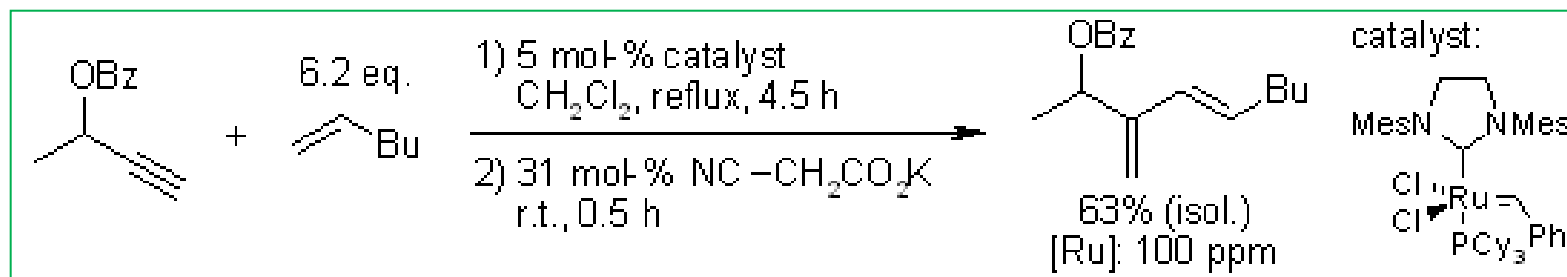
# Μετάθεση ενυνίου παρουσία του καταλύτη Hoveyda-Grubbs και αιθυλενίου σε ετεροαρωτικά κατιόντα (J. Chem. Soc. 2006, 2690).



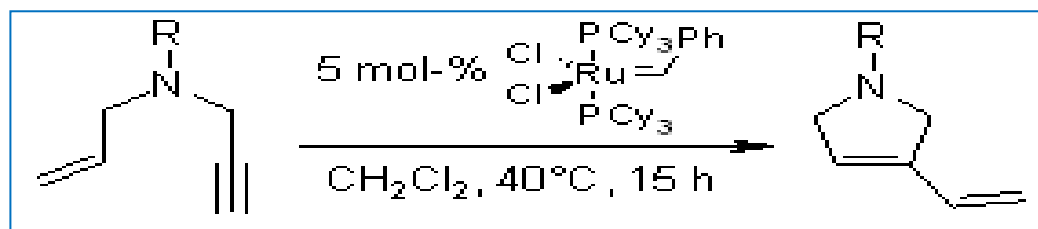
Scheme 3 Mechanism for the metathesis of enynes **5**.



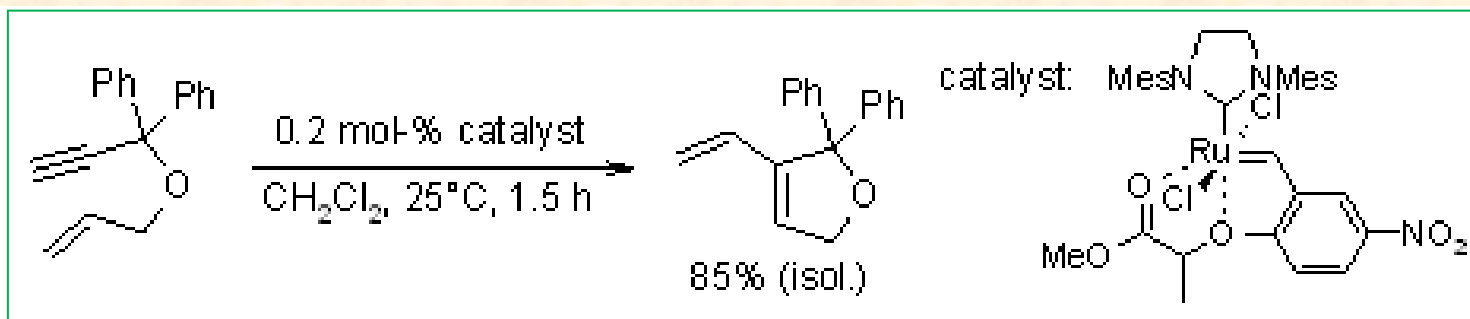
Χρησιμοποίηση  $\text{NCCH}_2\text{COOK}$  για την απομάκρυνση του καταλύτη μετά το τέλος της αντίδρασης ενυνίου (Org. Lett. 2007, 9, 1203).



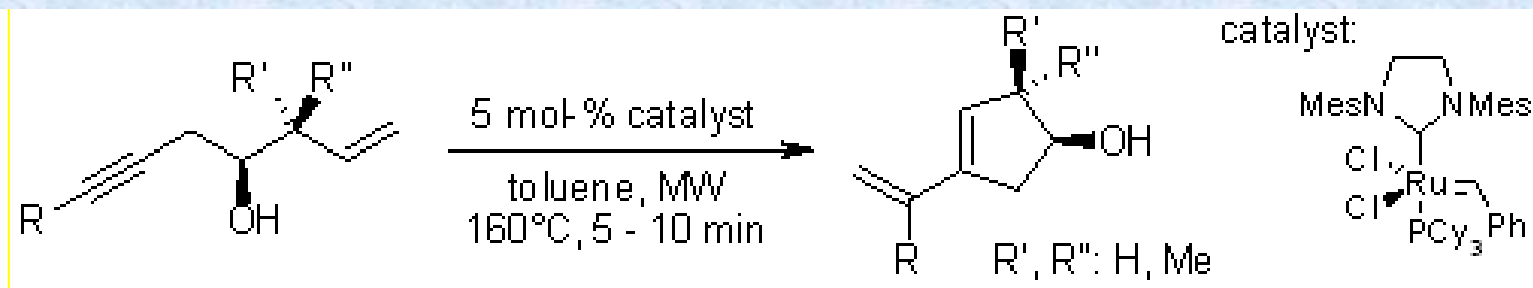
Σύνθεση **πυρρολινικών παραγώγων** μέσω αντίδρασης RCEYM (Org. Lett. 2007, 9, 769).



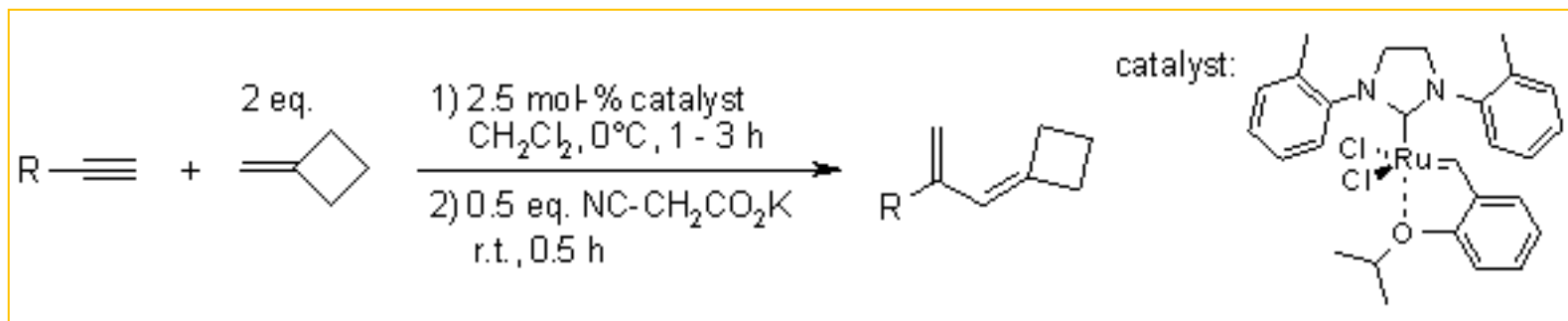
Αντίδραση μετάθεσης ενυνίου με τον καταλύτη του τύπου Hoveyda-Grubbs (J. Am. Chem. Soc. 2006, 128, 13652).

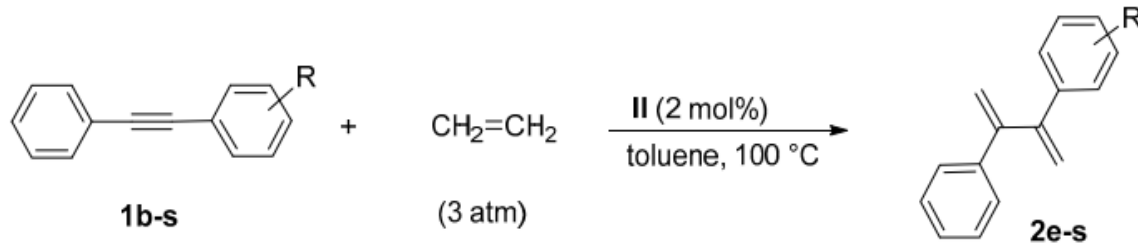


Σύνθεση βινυλοκυκλοπεντενολών μέσω αντίδρασης μετάθεσης ενυνίου (J. Org. Chem. 2007, 72, 1822)

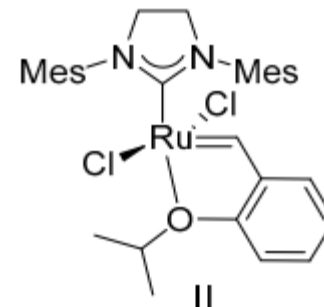


Αντίδραση ενυνίου αλκενίου με τάση με αλκύνιο (Org. Lett. 2008, 10, 492).



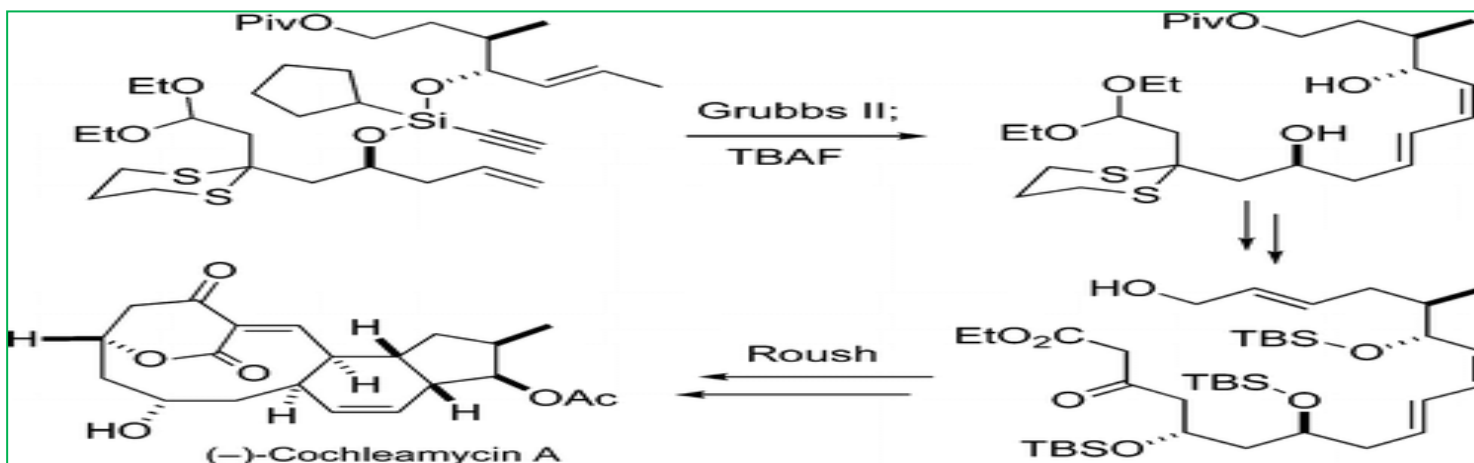
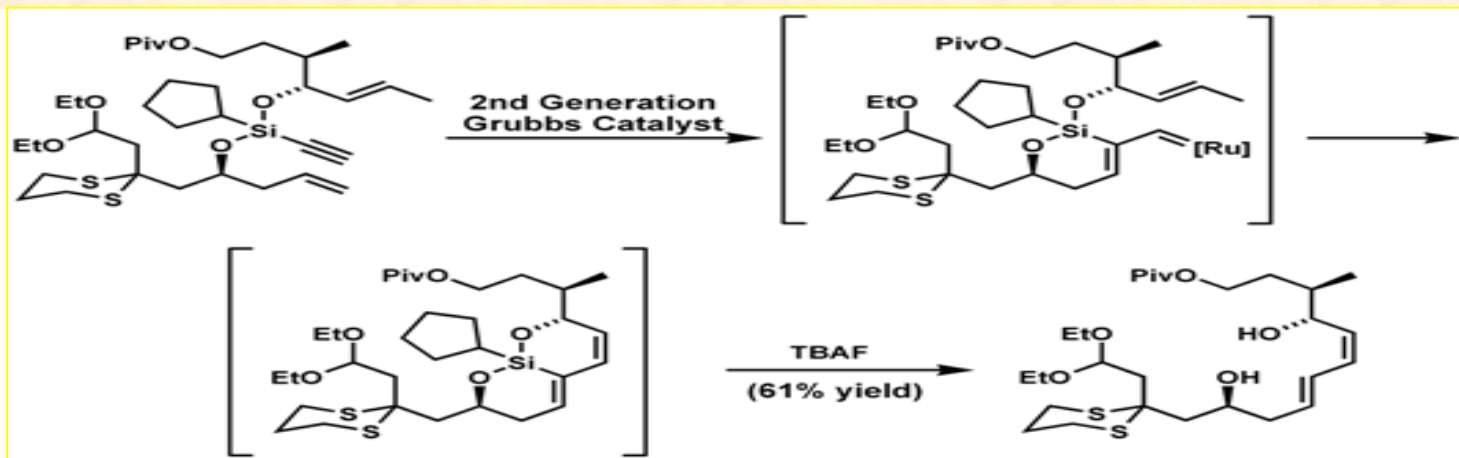


Scheme 2. Ene-yne cross-metathesis of unsymmetrical diarylacetylenes.

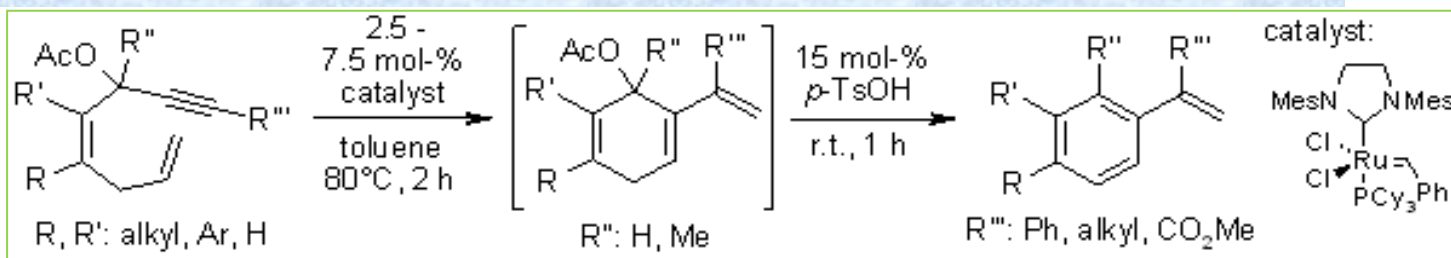
Table 2. Ene-yne cross-metathesis of unsymmetrical diarylacetylenes with ethylene <sup>a</sup>.

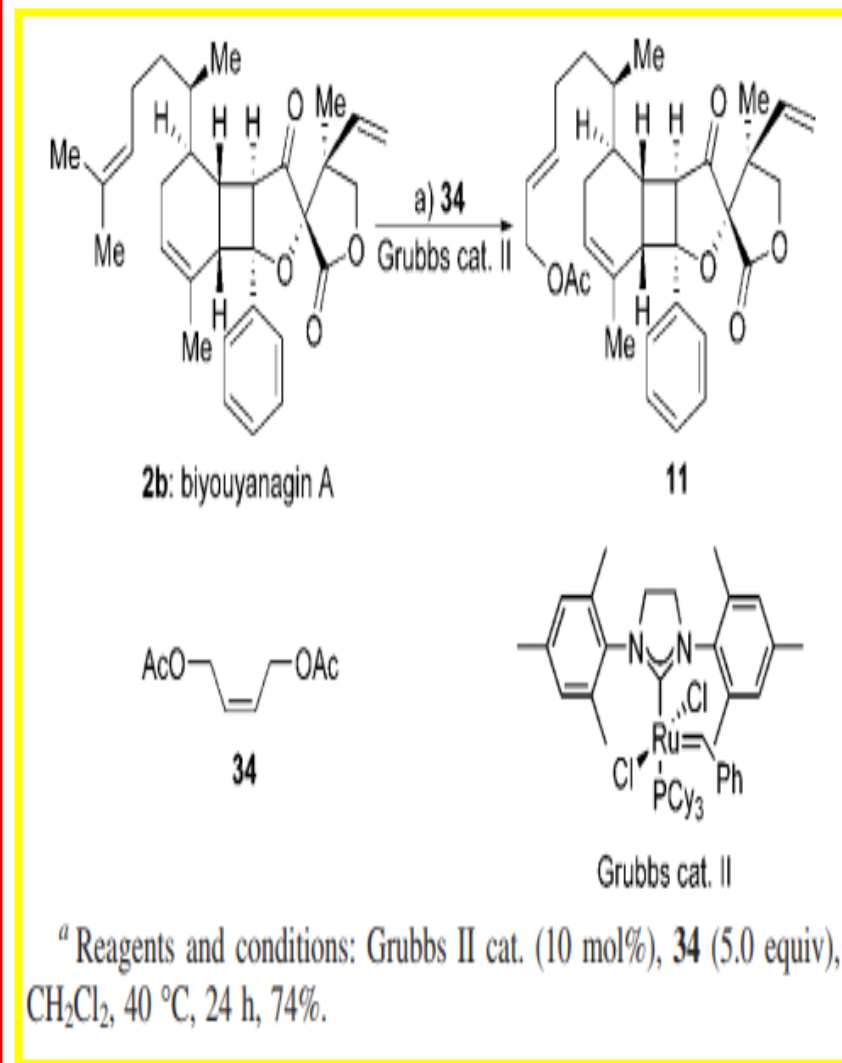
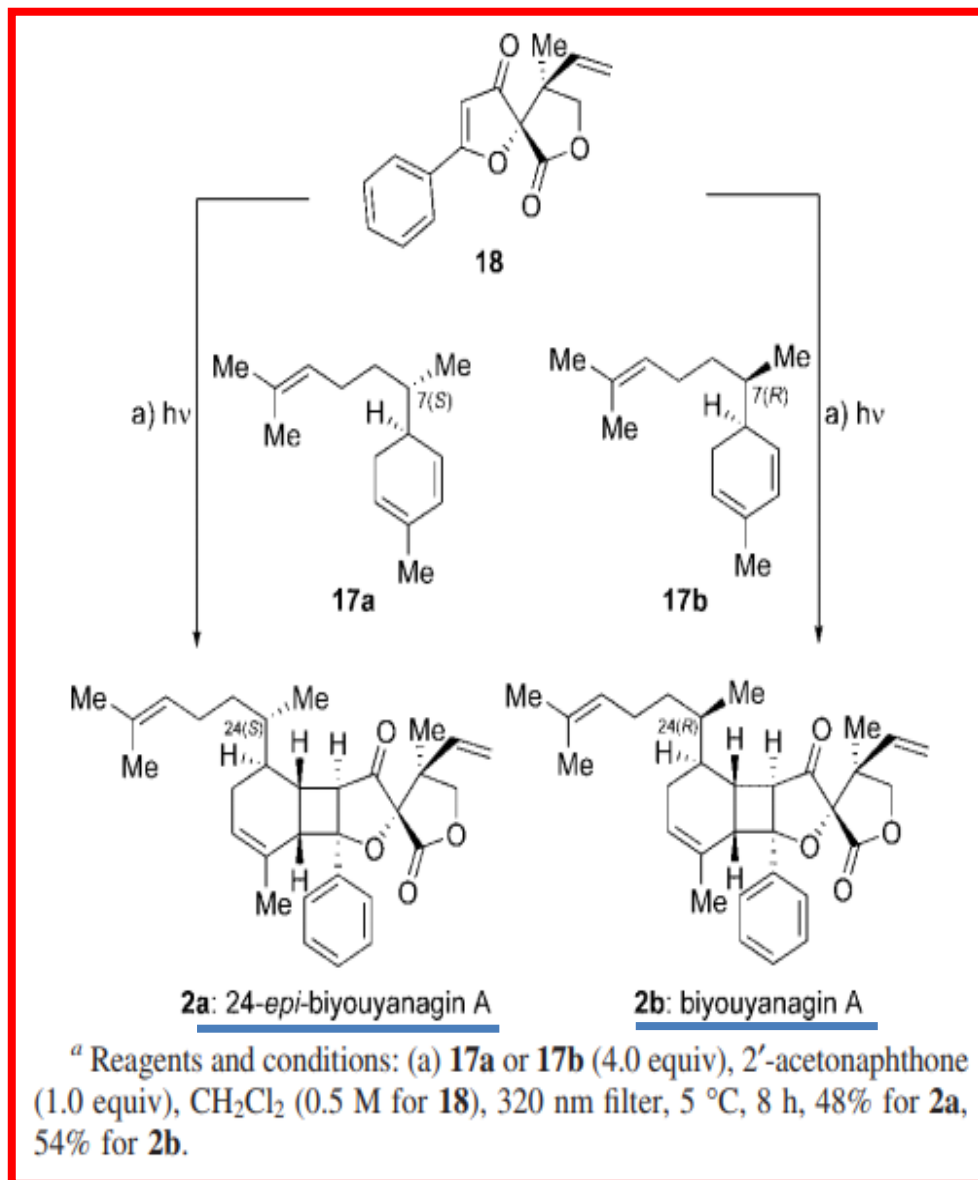
Entry	Substrate	<i>t</i> (h)	Conversion (%) <sup>b</sup>	Product	Yield (%) <sup>c</sup>
1	<b>1b</b>	24	100	<b>2b</b>	91
2	<b>1c</b>	17	100	<b>2c</b>	98
3	<b>1d</b>	17	100	<b>2d</b>	99
4	<b>1e</b>	17	100	<b>2e</b>	91
5	<b>1f</b>	17	100	<b>2f</b>	99
6	<b>1g</b>	24	100	<b>2g</b>	97

Χρησιμοποίηση ακολουθίας αντιδράσεων εννίου/RCM για την ολική σύνθεση της (-)-κοχλιαμκίνης A (Org. Lett. 2009, 11, 2916).



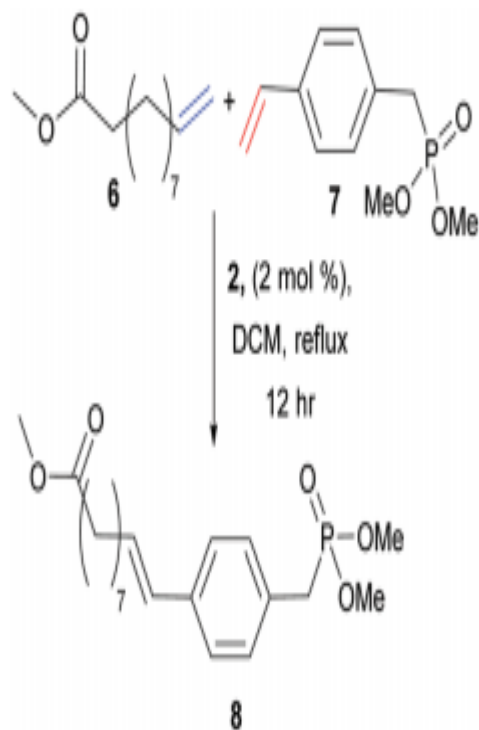
Σύνθεση **στυρολίων** μέσω αντίδρασης RCEYM (Org. Lett. 2008, 10, 2777).



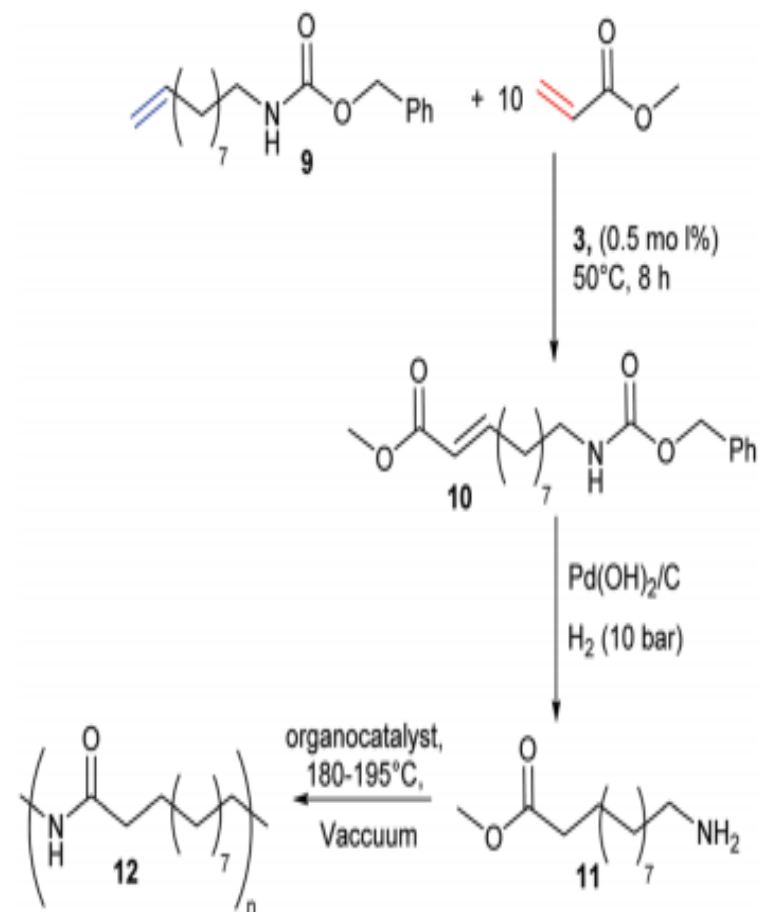


Anti-HIV-1 Activity





**Scheme 4** Vegetable oil-based thermosets generated from the cationic copolymerisation of divinyl benzene, styrene, soybean oil and 8, which was generated from the olefin cross metathesis of methyl 10-undecanoate, 6, with styrene phosphonate, 7.



**Scheme 5** Renewable polyamide synthesis via sequential olefin cross metathesis and hydrogenation.