Ruthenium- and Platinum-Catalyzed Sequential Reactions: Selective Synthesis of Fused Polycyclic Compounds from Propargylic Alcohols and Alkenes

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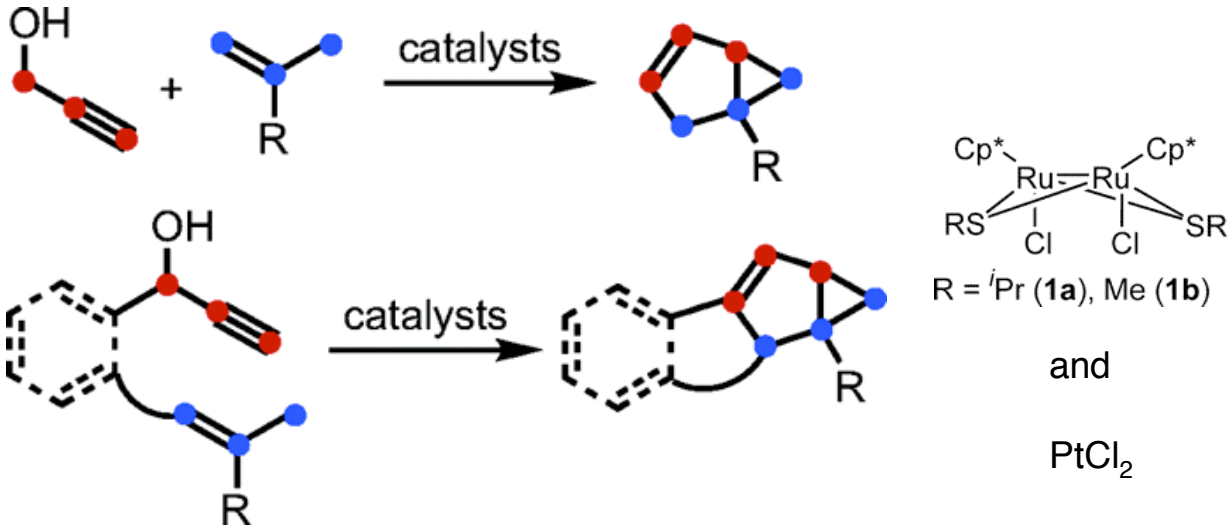
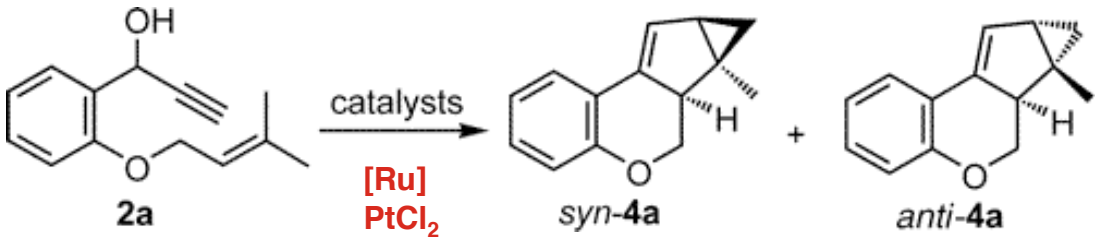
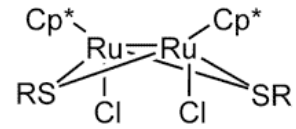


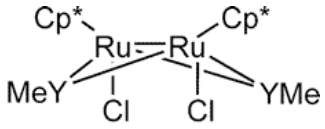
Introduction

- Bimetallic system, different catalytic cycle, same medium.
- No successive addition of reagents. No change in temperature or atmosphere on the way.





R = ^{i}Pr (**1a**), Me (**1b**)

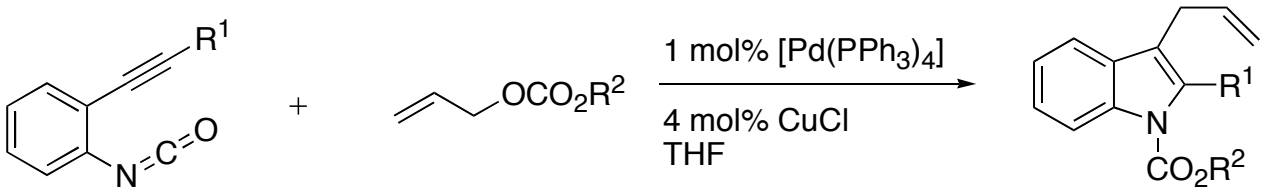


Y = Se (**1c**), Te (**1d**)

•Bimetallic system, different catalytic cycle, same medium.

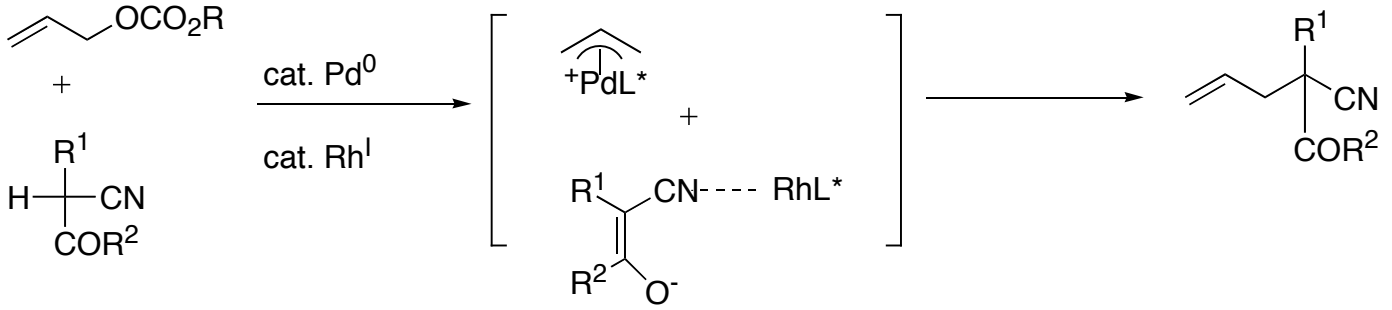
Catalysts activating different functional groups.

Pd^0-Cu^I synthesis of indoles from isocyanates:



Yamamoto et al, *ACIEE*, **2002**, *41*, 3230.

Asymmetric Tsuji-Trost:

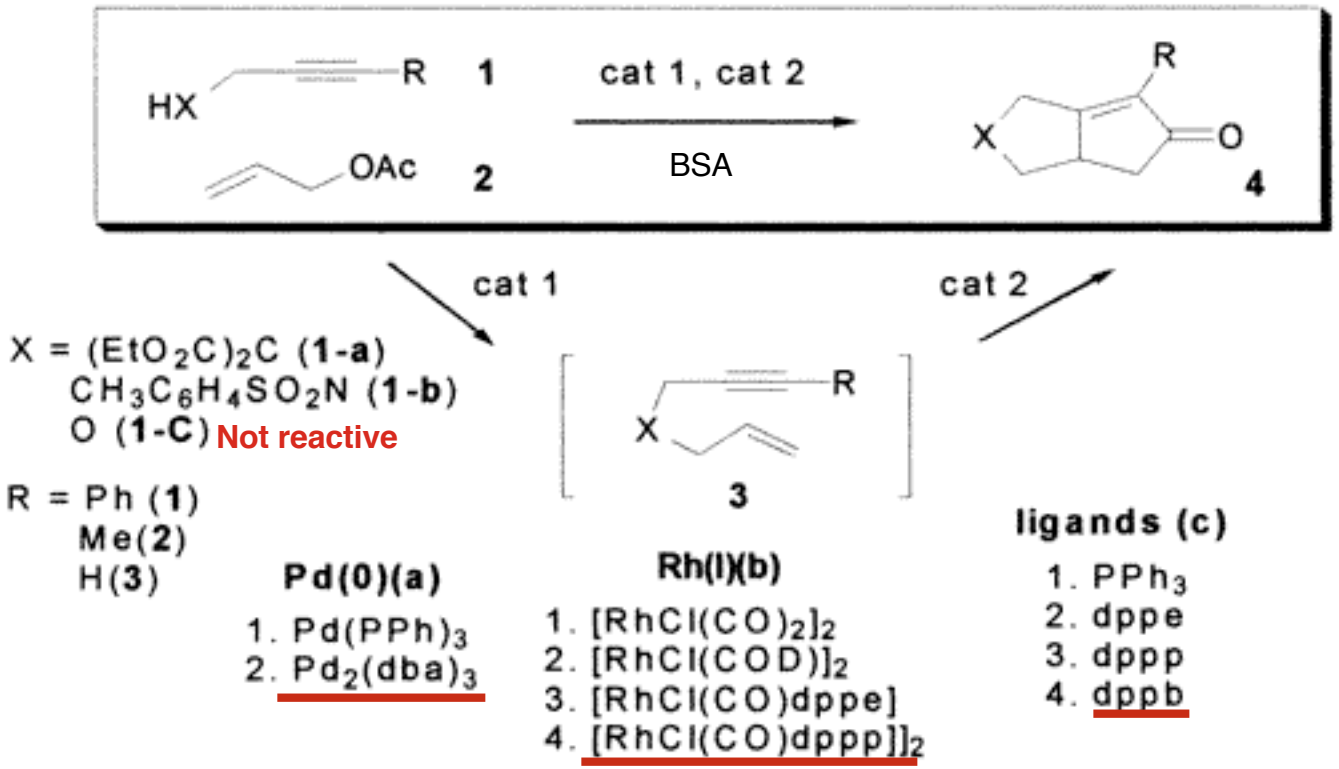


Ito et al, *JACS*, **1996**, *118*, 3309.

•Bimetallic system, different catalytic cycle, same medium.

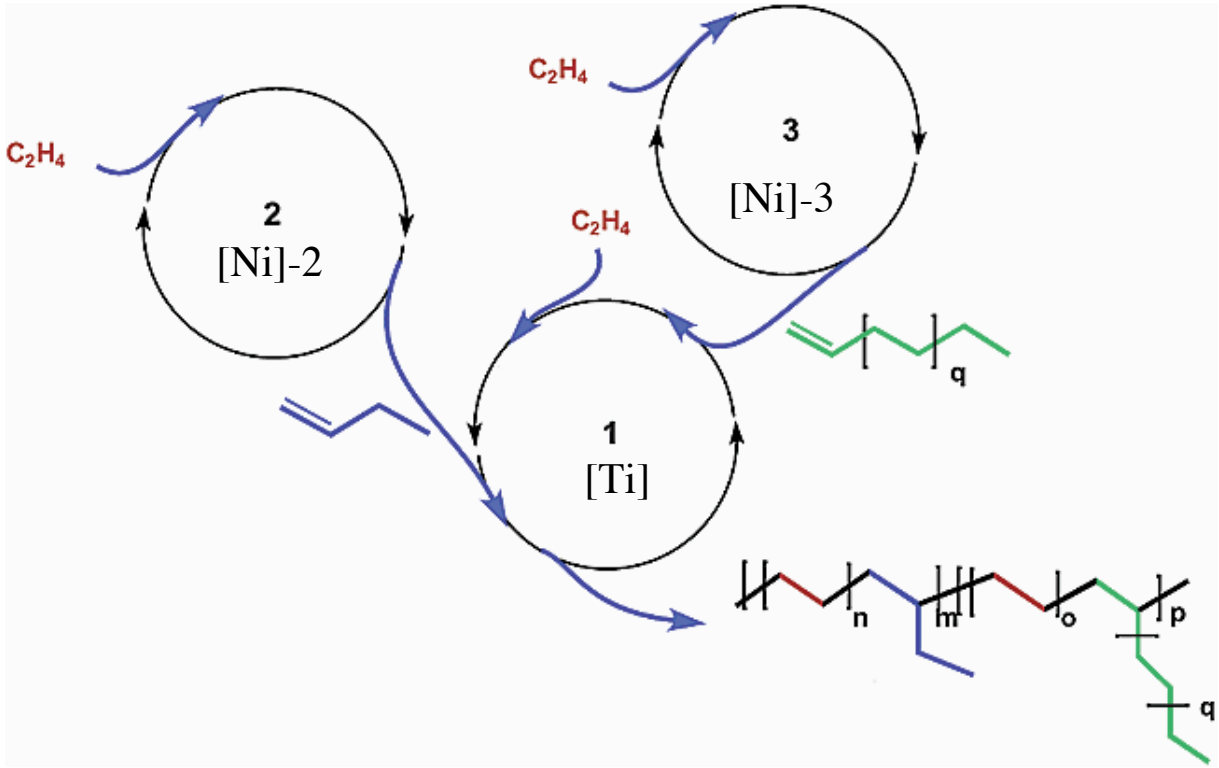
Catalysts activating intermediates sequentially.

Pd^0-Rh^I synthesis of bicyclopentenones:



Jeong et al, *JACS*, **2000**, *122*, 10220

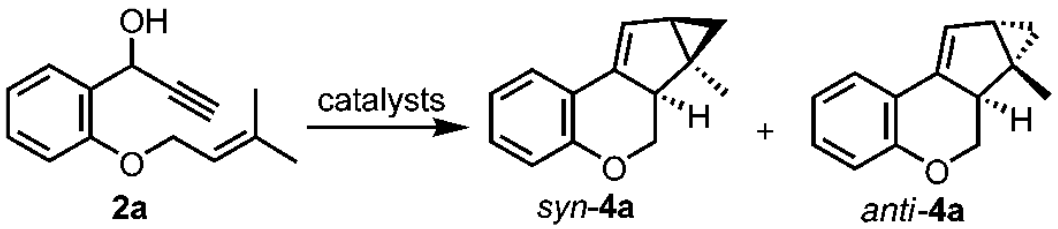
Triple Tandem catalysts mix synthesis of polyethylenes:



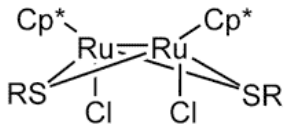
Bazan et al, *JACS*, **2002**, *124*, 15280.

Results and Discussion

Table 1. Reaction of Propargylic Alcohol (**2a**) in the Presence of Chalcogenolate-Bridged Diruthenium Complex (**1**) and Other Catalyst[a]



run	catalysts (mol %)	yield of **4a** (%)[b]
1	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and $PtCl_2$ (10)	**4a**, 75 (83)[c,d]



R = ^{i}Pr (**1a**), Me (**1b**)

Best conditions: $ClCH_2CH_2Cl$, NH_4BF_4 (10 mol%), 60 °C, 24h.

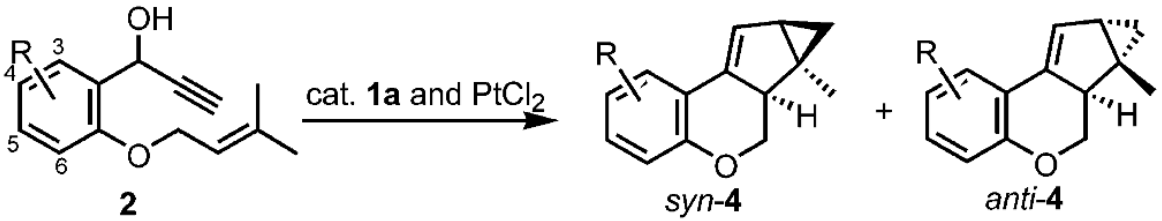
$PtCl_4$, $PdCl_2$, $AuCl_3$ and $[Rh(OAc)_2]_2$ not effective.

Selenolate-bridged diruthenium complex afforded moderate yield, but the Tellurolate one provided low yield.

Uemura, Nishibayashi et al, *JACS*, **2004**, *ASAP*.

Scope and limitation:

Table 2. Reaction of Various Propargylic Alcohols (**2**) in the Presence of [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*Cl] (**1a**) and $PtCl_2$[a]

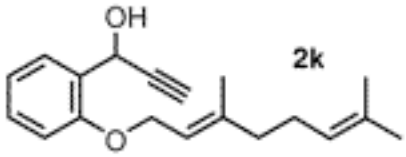
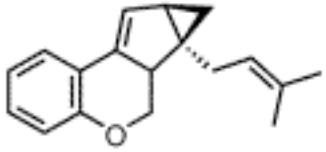
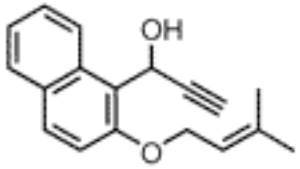
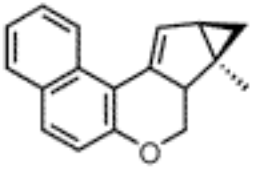
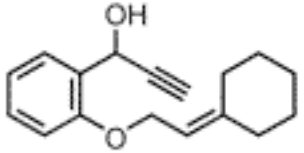
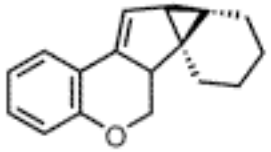
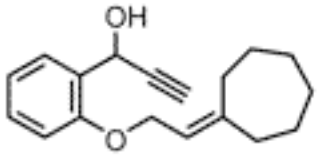
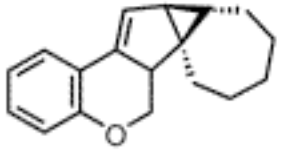


2 *syn*-**4** *anti*-**4**

run	propargylic alcohol	yield of **4** (%)[b]	ratio of isomers[c] (*syn*-**4**:*anti*-**4**)
1	**2a**, R = H	**4a**, 75	92:8
2	**2b**, R = 4-Me	**4b**, 76	91:9
3	**2c**, R = 4-OMe	**4c**, 66	92:8
4	**2d**, R = 4-Cl	**4d**, 65	94:6
5	**2e**, R = 4-Br	**4e**, 69	93:7
6	**2f**, R = 4-NO_2	**4f**, 70	95:5
7	**2g**, R = 6-Me	**4g**, 83	92:8
8	**2h**, R = 6-OMe	**4h**, 81	92:8
9	**2i**, R = 4-Cl, 6-Cl	**4i**, 38	98:2
10	**2j**, R = 4-Br, 6-Br	**4j**, 39	93:7

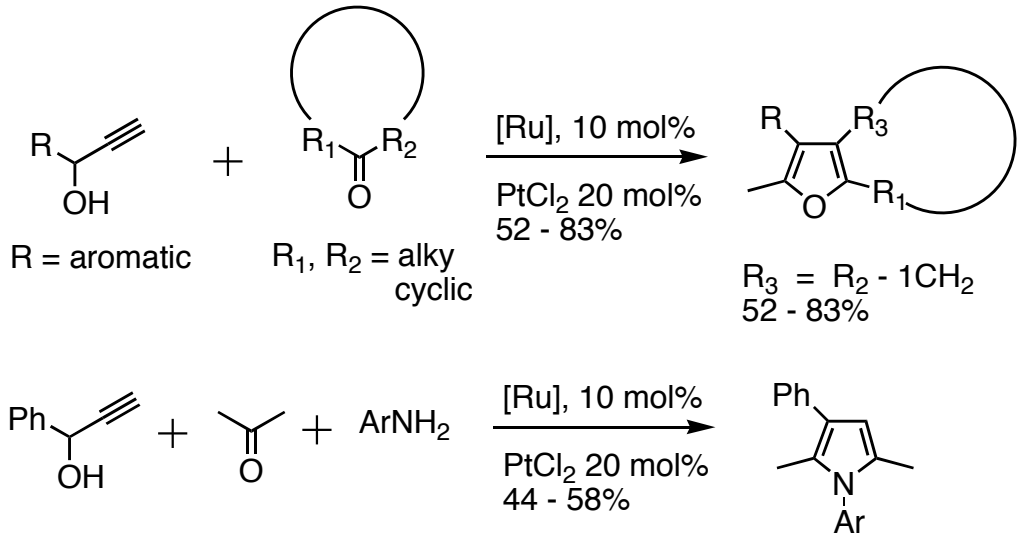
Uemura, Nishibayashi et al, *JACS*, **2004**, *ASAP*.

Scope and limitation:

run	propargylic alcohol	polycyclic compound (*syn*-**4**)	yield of **4** (%)[b]	ratio of isomers[c] (*syn*-**4** : *anti*-**4**)
1	 **2k**		86 (**4k**)	77 : 23
2	 **2l**		68 (**4l**)	62 : 38
3	 **2m**		90 (**4m**)	>95 : <5
4	 **2n**		89 (**4n**)	>95 : <5

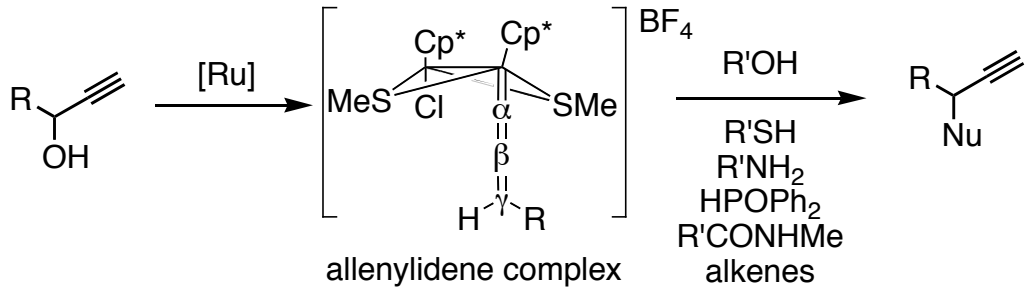
Uemura, Nishibayashi et al, *JACS*, **2004**, *ASAP*.

[Ru]/$PtCl_2$ system and the synthesis of furans and pyrrols:

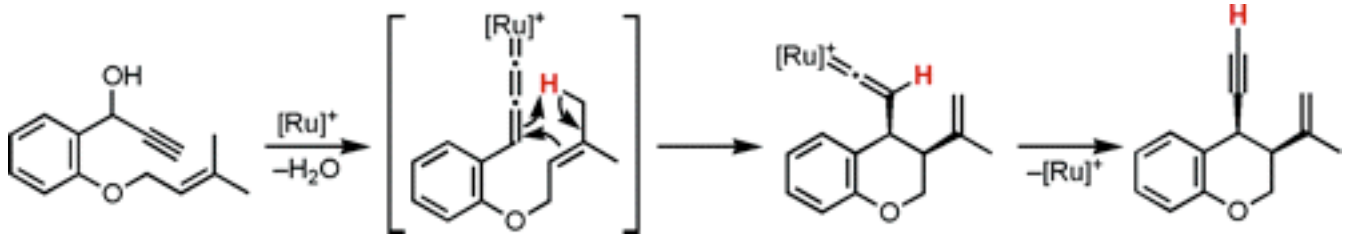


Hidai, Uemura et al, *ACIEE*, **2003**, *42,* 2681.

So, the mechanism



Hidai et al, *JACS*, **2000**, *122,*11019.
Hidai, Uemura et al, *JACS*, **2003**, *125,*6060.
Hidai, Uemura et al, *JACS*, **2002**, *124,*15172.



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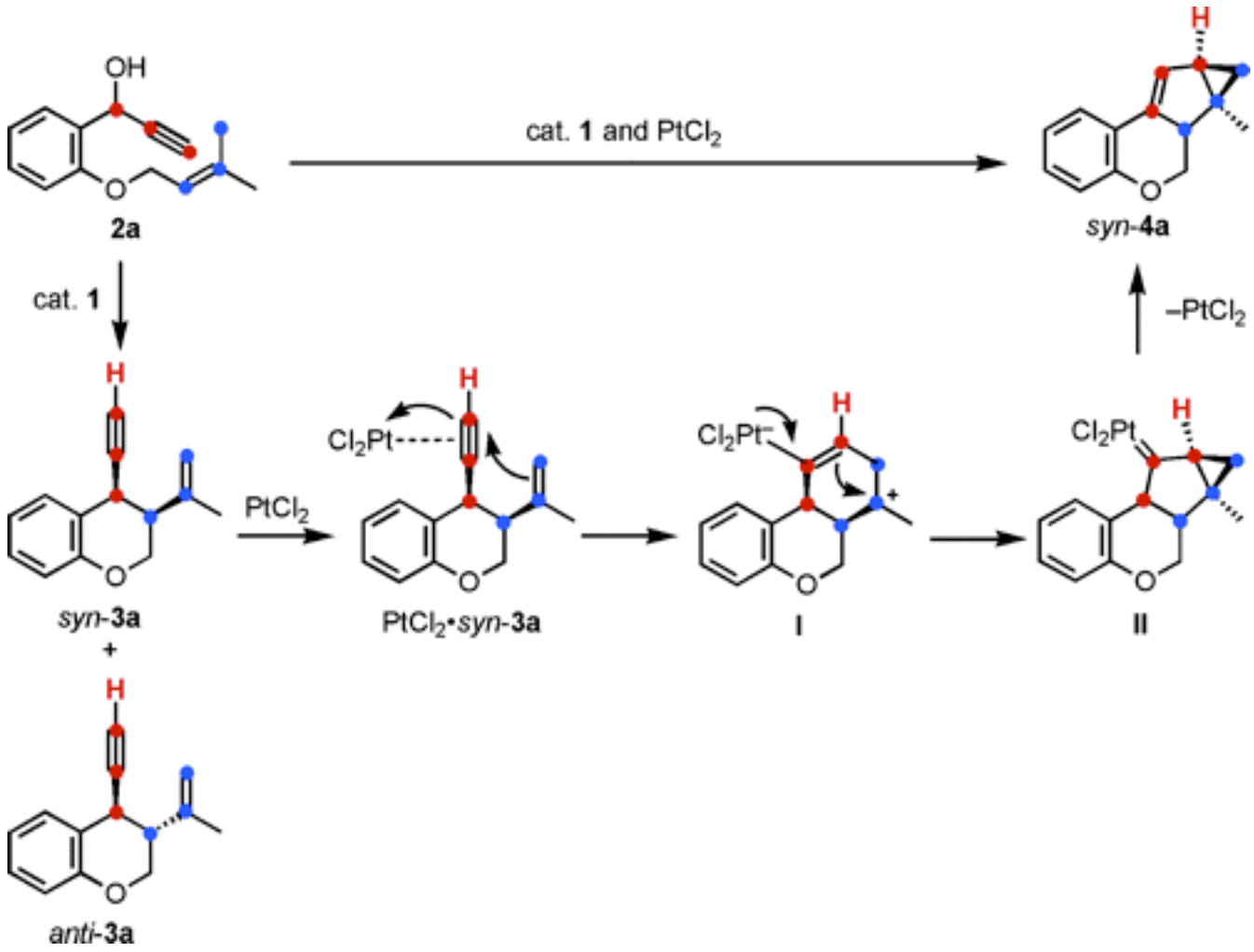

Conclusion

- Fused polycyclic compounds made through a bimetallic catalytic system in a sequential $[Ru]^{I}$ promoted propargylic alcohol substitution, followed by a $PtCl_2$ cycloisomerisation.
- Catalysts operating in the same conditions. Simple experiment set up.
- Moderate to excellent yields, good diastereoselectivity.
- Broadening of the scope of the sequence is necessary.
- Application in natural products synthesis was not mentioned.