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Gold(I)-Catalyzed Cyclizations of 1,6-Enynes: Alkoxycyclizations and *exo*/*endo* Skeletal Rearrangements

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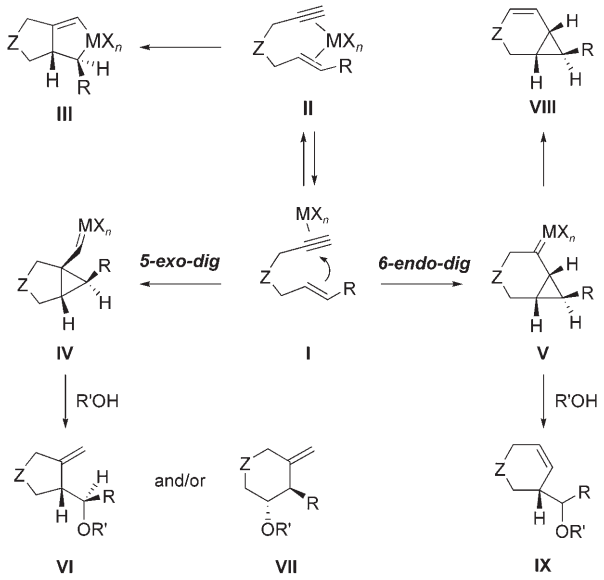
Abstract: Gold(I) complexes are the most active catalysts for alkoxy- or hydroxycyclization and for skeletal rearrangement reactions of 1,6-enynes. Intramolecular alkoxycyclizations also proceed efficiently in the presence of gold(I) catalysts. The first examples of the skeletal rearrangement of enynes by the endocyclic cyclization pathway are also documented. Iron(III) is also able to catalyze *exo* and *endo* skeletal rearrangements of 1,6-enynes, although the scope of this transformation is more limited. The gold(I)-catalyzed endocyclic cyclization proceeds by a mechanism different from those followed in the presence of Pd^{II}, Hg^{II}, or Rh^{I} catalysts.

Keywords: alkynes · cyclization · gold · iron · rearrangement

Introduction

Reactions of 1,6-enynes catalyzed by electrophilic transition-metal complexes or salts proceed through two general pathways, depending on whether the metal coordinates selectively to the alkyne (as in **I**) or to both the alkyne and the alkene (as in **II**) (Scheme 1).[1–3] In the second case, an oxidative cyclometalation could then form **III**, which should usually evolve by β-hydrogen elimination to give Alder-ene type products.[2,4–6] Cyclopropyl metal carbenes **IV** or **V** are formed from **I** by *exo-dig* or *endo-dig* processes, respectively.[2,7] Reactions of **IV** with alcohols or water give products of alkoxy- or hydroxycyclization **VI** and/or **VII**.[2,8] Intermediates **V** can undergo α-CH insertion and elimination to form **VIII**,[3b,9,10] whereas reactions with alcohols afford **IX**.[3a]

In the absence of nucleophiles, enynes undergo skeletal rearrangement to form dienes **X** (*single cleavage*) and/or **XI** (*double cleavage*) (Scheme 2).[1,5,11,12] Cyclobutenes **XII** have been proposed as intermediates for the formation of dienes **X**.[12,13] Interestingly, cyclobutenes of type **XIII** have also been isolated in certain reactions catalyzed by Pd^{II},[13] Au^{I},[14] and Pt^{II}.[15]



Scheme 1. Mechanisms for the *endo*- and *exo*-alkoxycyclization of enynes.

By using cationic gold(I) complexes $[Au(L)(S)]^+ X^-$ as catalysts we uncovered the first examples of the *6-endo-dig*

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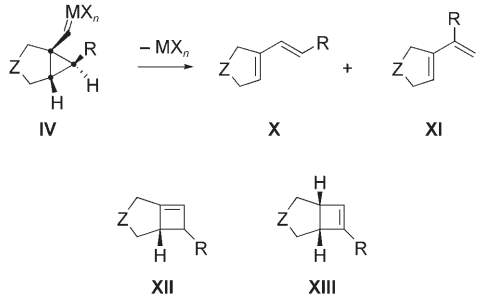


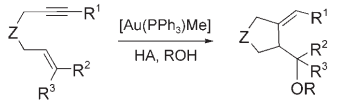
Scheme 2. *exo*-Skeletal rearrangement and formal [2+2] cycloaddition products.

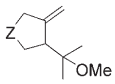
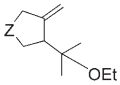
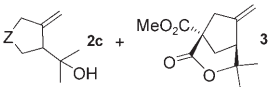
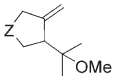
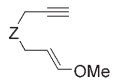
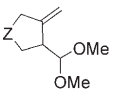
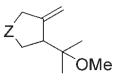
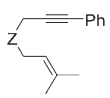
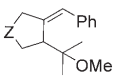
skeletal rearrangement of 1,6-enynes,[16] a type of reaction of enynes that, somewhat surprisingly, had not been reported before with other transition-metal catalysts. Gold(I) complexes are also excellent catalysts for the cyclization of a variety of enynes.[14,17] Here we report the results of an in-depth study of the cyclization of 1,6-enynes with different gold(I) complexes, resulting variously in alkoxy- or hydroxycyclization or in skeletal rearrangement. We have also found that Fe^{III} catalyzes the skeletal rearrangement, and in one case gives *6-endo-dig* skeletal rearrangement products, although the scope of this transformation is more limited. In the accompanying paper in this issue we analyze the mechanism and stereoselectivity observed in the double cyclopropanation reaction catalyzed by gold(I).[18]

Results and Discussion

$[Au^{I}(PPh_3)(S)]^+$-catalyzed intermolecular alkoxy- and hydroxycyclization: Alkoxycyclization was observed when enynes were allowed to react in alcohols ROH as solvent in the presence of a catalyst formed in situ from $[Au(PPh_3)Me]$ and a protic acid such as HBF_4, phosphotungstic acid trihydrate, or trifluoroacetic acid (TFA) (Table 1). Under these conditions the complex $[Au(PPh_3)(ROH)]^+$ is presumably generated. No cyclizations were observed with the protic acids in the absence of Au^I. Addition of PPh_3 or diphosphanes (dppe, dppe, dppf) (3 mol%) resulted in unreactive gold(I) complexes, but the reaction could be carried out in the presence of bulky and electron-rich PCy_3 (Table 1, entry 6). Hydroxycyclization of **1** in aqueous acetone gave a 1:1 mixture of alcohol **2c** and bicyclic lactone **3** (Table 1, entry 5). The cyclization of enol ether **6** could be carried out in the presence of only 1 mol% of catalyst (Table 1, entries 7 and 8). The reactions in the presence of gold(I) usually proceeded at room temperature, although the cyclization

Table 1. Alkoxy- or hydroxycyclization of enynes on treatment with $[Au(PPh_3)Me]$ (3 mol%) and protic acid (6 mol%).



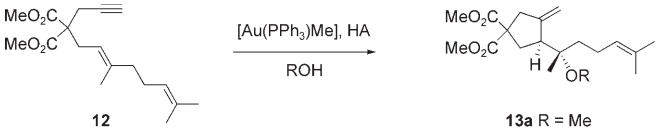
Entry	Enyne	ROH	HA	t [h]	Product (yield [%])
1	 **1**, Z = $C(CO_2Me)_2$	MeOH	HBF_4	4	 **2a** (97)
2	**1**	MeOH	TFA	3	**2a** (82)
3	**1**	MeOH	$H_3PW_{12}O_{40}$[a]	4	**2a** (96)
4	**1**	EtOH	TFA	24	 **2b** (75)
5	**1**	H_2O/acetone	TFA	24	 (100, 1:1)
6[b]	 **4**, Z = $C(SO_2Ph)_2$	MeOH	HBF_4	12	 **5** (85)
7	 **6**, Z = $C(CO_2Me)_2$	MeOH	TFA	0.5	 **7** (95)
8[c]	**6**	MeOH	$H_3PW_{12}O_{40}$[a]	2	**7** (96)
9[d]	 **8**, Z = NTs	MeOH	$H_3PW_{12}O_{40}$[b]	17	 **9**(85)
10[d]	 **10**, Z = $C(SO_2Ph)_2$	MeOH	$H_3PW_{12}O_{40}$[b]	17	 **11** (96)

[a] The trihydrate was used. [b] PCy_3 (3 mol%) was also added. [c] 1 mol% $[Au(PPh_3)Me]$ and 2 mol% protic acid. [d] Reaction was carried out under reflux.

of the less reactive substrates **8** and **10** had to be performed at reflux in methanol (Table 1, entries 9 and 10). In all cases the alkoxycyclizations proceeded more readily in the presence of gold(I) than in the presence of platinum(II) catalysts.[2]

As previously observed for Pt^{II}-catalyzed alkoxy- and hydroxycyclizations,[2] the Au^{I}-catalyzed process is stereospecific. Treatment of **12** in MeOH, EtOH, or aqueous acetone thus gave **13a–c** as single diastereomers (Table 2). These reactions were carried out at room temperature over 4–7 h in the presence of 3 mol% catalyst and provided adducts **13a–c** in satisfactory yields. However, the hydroxycyclization of **12** also afforded products of skeletal rearrangement and biscyclopropanation.[18]

Table 2. Alkoxy- or hydroxycyclization of enynes **12** in the presence of [Au(PPh$_3$)Me] and protic acid.



12

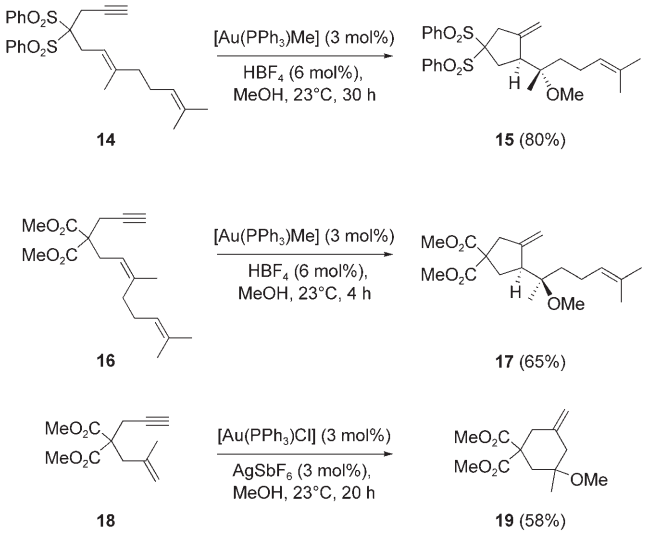
13a R = Me
13b R = Et
13c R = H

Entry	[Au(PPh$_3$)Me] [mol%]	HA ([mol%])	ROH	T [°C]	t [h]	Product (yield [%])
1	5	HBF_4 (25)	MeOH	65	0.5	**13a** (78)
2	5	TFA (25)	MeOH	23	4	**13a** (96)
3	3	TFA (6)	MeOH	23	4	**13a** (82)
4	3	HBF_4 (6)	MeOH	23	4	**13a** (82)
5	3	$H_3PW_{12}O_{40}$[a]	MeOH	23	7	**13a** (67)
6	3	TFA (6)	EtOH	23	4	**13b** (79)
7	3	TFA (6)	H_2O/acetone	23	4	**13c** (63)[b]

[a] The trihydrate was used. [b] The skeletal rearrangement product and a tetracyclic derivative were also obtained in 22% and 15% yields, respectively.[18]

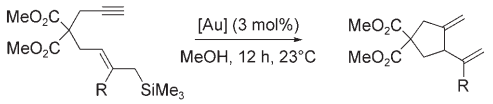
The corresponding treatment of bissulfone **14** proceeded more slowly to give **15** (Scheme 3), which can be attributed to the strongly electron-withdrawing effect of the sulfone groups. Enyne **16**, the *Z* diastereomer of **12**, reacted in MeOH to give ether **17**, the diastereomer of **13a**, exclusively. On the other hand, the regioselectivity in the C–C bond formation (the formation of products of type **VI** or **VII**; Scheme 1) is dictated by the substituents at the alkene, the Au^{I}-catalyzed reaction of enyne **18** in methanol thus giving the six-membered derivative **19**. In this case, the best results were achieved with a catalyst formed in situ from [Au(PPh$_3$)Cl] and $AgSbF_6$.

The allylsilane **20** reacted in the presence of cationic gold(I) complexes to give the diene **21**[19] (Table 3, entries 1 and 2). In the case of the more reactive substrate **22**, the cyclization could also be carried out in the presence of the neutral complex [Au(PPh$_3$)Cl], although the reaction had to be performed in MeOH at reflux (Table 3, entry 5). With a catalyst formed from [Au(PPh$_3$)Cl] by chloride abstraction with $AgSbF_6$, the cyclization of **20** could be carried out at room temperature (Table 3, entry 3). Desilylation assisted by attack of MeOH presumably takes place on an intermediate of type **IV** (Scheme 1).[19b]



Scheme 3. Regioselective and/or stereospecific methoxycyclizations of **14**, **16**, and **18**.

Table 3. Au^{I}-catalyzed intramolecular reactions between allylsilane and alkyne functional units.



20 R = H
22 R = Me

21 R = H
23 R = Me

Entry	Allylsilane	[Au] ([mol%])	HA (mol%) ([mol%])	Product (yield [%])
1	**20**	[Au(PPh$_3$)Me] (3)	TFA (6)	**21** (93)
2	**20**	[Au(PPh$_3$)Me] (3)	$H_3PW_{12}O_{40}$[a]	**21** (82)
3	**20**	[Au(PPh$_3$)Cl] (5)/$AgSbF_6$ (5)	-	**21** (94)
4	**22**	[Au(PPh$_3$)Me] (3)	HBF_4 (6)	**23** (97)
5[b]	**22**	[Au(PPh$_3$)Cl] (5)	-	**23** (97)

[a] The trihydrate was used. [b] The reaction was carried out at 65 °C.

Although, in general, the cationic catalysts generated in situ from [Au(PPh$_3$)Me] and protic acid (6 mol%) proved to be satisfactory for the cyclization of enynes, we sought to develop alternative conditions that could allow the reactions to be performed under neutral conditions. We reasoned that highly active Au^{I} catalysts should be formed by chloride abstraction from [Au(L)Cl] complexes bearing bulky phosphanes as ligands.[14] In particular, we focused on the bulky, biphenyl-based phosphanes developed by Buchwald in the context of palladium-catalyzed C–C and C–X bond-formation reactions.[20,21] The gold(I) complexes **24a–d** were thus readily prepared by the known procedure for the synthesis of [Au(PPh$_3$)Cl] (Figure 1),[22] whilst the cationic complexes **24e** and **25** were prepared by chloride abstraction from the corresponding neutral complexes with $AgSbF_6$ in acetoni-

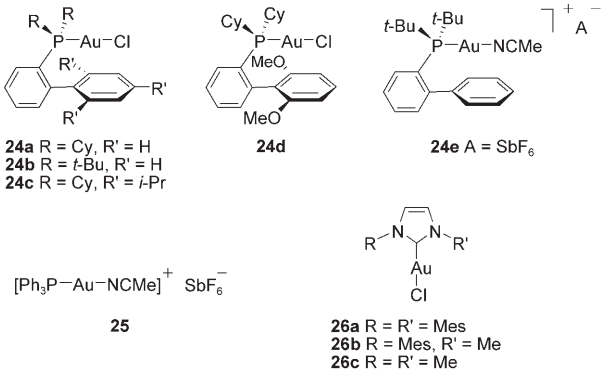


Figure 1. Au^{I} complexes with bulky phosphane or *N*-heterocyclic ligands.

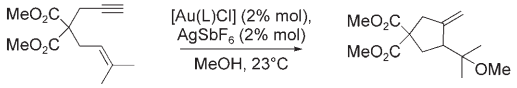
trile.[12] The Au^{I} complexes **26a–c**, with *N*-heterocyclic donor ligands,[23] were also tested as catalysts for the methoxycyclization of enyne **1** (Table 2). Complex **26a** and other related complexes have been independently prepared by Nolan et al.[24]

The reaction of **1** in MeOH proceeded inefficiently in the presence of catalysts generated from AuCl or [Au(Me$_2$S)Cl] and AgSbF$_6$ (Table 4, entries 1–2).[25,26] However, complexes [Au(L)Cl]—where L = PPh$_3$, PCy$_3$, P(C$_6$F$_5$)$_3$, or AsPh$_3$—gave **2a** in similar yields in 3–5 h (Table 4, entries 3–6). Treatment of **1** with [Au(L)Cl] complexes containing the bulkier phosphanes P(*o*-Tol)$_3$ or P(1-Napth)$_3$ resulted in slower reactions (Table 4, entries 7 and 8). Remarkably, use of the complexes **24a–e** provided **2a** in 15–30 min at room temperature (Table 4, entries 9–13), whilst cyclization with Au^{I} complexes **26a–c**, containing *N*-heterocyclic donor ligands, was not as efficient (Table 4, entries 14–16).

Cyclization of enyne **27** to give **28** proceeded more satisfactorily in the presence of catalyst **24c** (Table 5, entry 9), although reaction times were in all cases longer than those require to cyclize enyne **1** (Table 4), which bears a more reactive trisubstituted alkene. Similarly, enyne **29** reacted with MeOH in the presence of catalysts **24e** or **25** to give **30** in excellent yield (Scheme 4). In contrast, the nitro derivative **31** failed to provide any methoxycyclized derivative under the same conditions. After long reaction times (72 h, 23 °C), ketone **32** was obtained in moderate yield (15–22 %) as a result of the Au^{I}-catalyzed hydration of the alkyne by the traces of water contained in the methanol.[27] Interestingly, the double bond migration products **31′** and **32′** were also detected in the crude reaction mixtures. Addition of 4 Å molecular sieves inhibited the hydration of the alkyne.

[Au^{I}PPh$_3$)(S)]$^+$-catalyzed intramolecular alkoxycyclization: The corresponding treatment of substrate **33**, containing a propargylic alcohol, resulted in intramolecular attack of the hydroxy group on the cyclopropyl gold carbene intermediate to afford ether **34** quantitatively (Scheme 5). Similarly, sub-

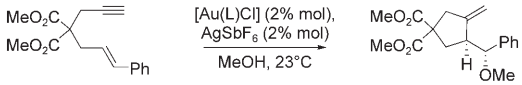
Table 4. Au^{I}-catalyzed methoxycyclization of enyne **1**.



Entry	Complex	Time [h]	Conversion [%][a]	Yield of **2a** [%]
1	AuCl	24	32	10
2	[Au(SMe$_2$)Cl]	24	<2	<2
3	[Au(PPh$_3$)Cl]	3	>98	84
4	[Au(PCy$_3$)Cl]	3.5	>98	77
5	[Au{P(C$_6$F$_5$)$_3$}Cl]	5	>98	77
6	[Au(AsPh$_3$)Cl]	4	>98	78
7	[Au{P(*o*-Tol)$_3$}Cl]	24	>98	90
8	[Au{P(1-Naph)$_3$}Cl]	12	>98	76
9	**24a**	0.5	>98	97
10	**24b**	0.25	>98	90
11	**24c**	0.25	>98	92
12	**24d**	0.25	>98	89
13	**24e**	0.25	>98	91
14	**26a**	1.5	>98	71
15	**26b**	5	>98	87
16	**26c**	24	>98	34

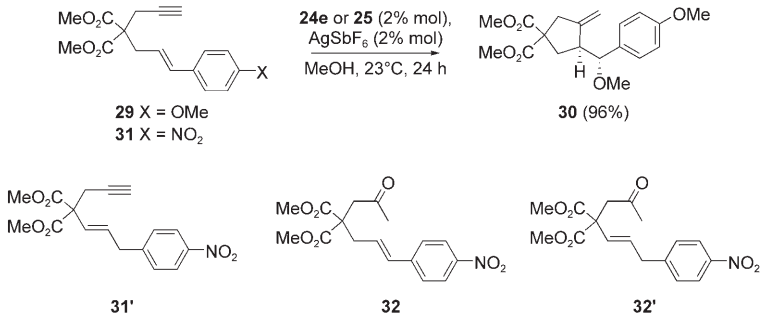
[a] Conversions were determined by GC.

Table 5. Au^{I}-catalyzed methoxycyclization of enyne **27**.

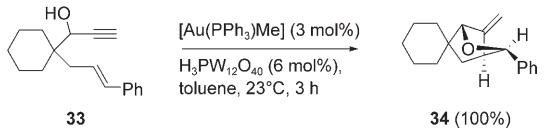


Entry	Complex	*t* [h]	Conversion [%][a]	Yield [%]
1	AuCl	48	50	35
2	[Au(Me$_2$S)Cl]	48	21	5
3	[Au(Ph$_3$P)Cl]	18	93	70
4	[Au(Cy$_3$P)Cl]	18	>98	83
5	[Au{(C$_6$F$_5$)$_3$P}Cl]	48	66	44
6	[Au(Ph^{3}As)Cl]	48	68	48
7	[Au{(*o*-Tol)$_3$P}Cl]	30	>98	79
8	**24a**	18	>98	68
9	**24c**	18	>98	94
10	**26a**	20	>98	76
11	**26b**	24	73	51
12	**26c**	48	84	48

[a] Levels of conversion were determined by GC.



Scheme 4. Methoxycyclization of cinnamyl derivatives **29** and **31**.



33 34 (100%)

Scheme 5. Intramolecular alkoxycyclization of enyne **33**.

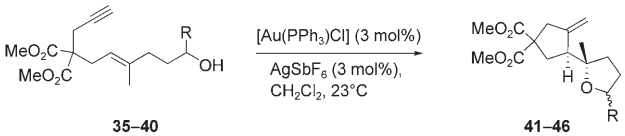
strates **35**–**40**, containing hydroxy groups in their alkene chains, underwent intramolecular cyclizations to give **41**–**46** (Table 6). These cyclizations took place within 5–30 min at room temperature in the presence of a catalyst formed from [Au(PPh_3)Cl] and $AgSbF_6$. In contrast, when $PtCl_2$ was used as catalyst, the reaction had to be performed at 80 °C for 3 h (Table 6, entry 6). Cyclization of enynes **36**–**40** gave 1:1 mixtures of diastereomers, epimeric at C-5 of the tetrahydrofuran ring. In the case of substrate **40**, containing two hydroxy groups, exclusive formation of tetrahydrofurans **46a**/**46b** was observed as the result of the opening of the cyclopropyl gold carbene intermediate by the less hindered secondary hydroxy moiety (Table 6, entry 7).

Skeletal rearrangement: On application of catalysts formed in situ from [Au(PPh_3)Cl]/AgX (X = BF_4 or SbF_6), the enynes underwent skeletal rearrangement (Scheme 2). The rearrangements of enynes **1**, **16**, **18**, and **47**–**50** proceeded readily at room temperature in CH_2Cl_2 and were completed in less than 1 h, giving the corresponding 1,3-dienes (Table 7). The reaction did not take place in solvents such as MeCN or toluene, and no reaction was observed with [Au(PPh_3)Cl] alone. In addition, the reaction was not catalyzed by Ag^I salts. The reaction could also be performed in the presence of $AuCl_3$ or AuCl (Table 7, Entries 5 and 6), although it was very slow in the latter case. The rearrangement was stereospecific, as shown in the reactions of enynes **50** and **16**, each with a *Z* configuration at the alkene, which gave *Z*-dienes **55** and **57**, respectively (Table 7, entries 8 and 10). In the case of substrate **50**, the allylic alcohol did not interfere in the rearrangement.

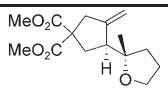
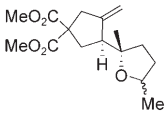
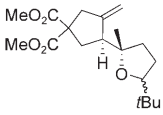
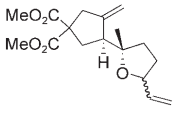
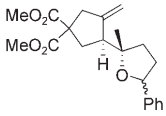
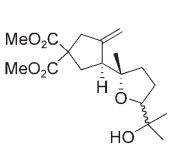
Surprisingly, in contrast with **1** (entry 1, Table 7), enyne **58** gave **59** as the major 1,3-diene, along with the *exo*-skeletal rearrangement product **60** (Scheme 6). Diene **59** is the product of an endocyclic skeletal rearrangement (see below). Trost had reported the reaction of **58** to give **59** catalyzed by [$Pd(OAc)_2$]/bis(2-methoxyphenylphosphane)propane.[28] However, the involvement of a palladium hydride in this reaction was proposed and the cyclization takes place through an intramolecular insertion of an alkenylpalladium complex.[28–30] It is interesting to note that products with this structure have also been obtained by the ring-closing metathesis of enynes catalyzed by a second-generation ruthenium Grubbs catalyst[31] and, more recently, in the cycloisomerization of enynes with Rh^I, which proceeds via vinylidene intermediates.[32,33] Enyne **27** gave a mixture of *endo* (**61**) and *exo* (**62**) skeletal rearrangement products (Scheme 6). The reaction behavior of substrates **29** and **31** was studied to determine the effect of substituents at the alkene. As expected, **29** reacted more rapidly than **31**, containing an electron-withdrawing *para*-nitrophenyl substituent. Monitoring of the reactions by ^1H NMR in CD_2Cl_2 at 5 °C showed pseudo-first order behavior, with k(**29**)/k(**31**) = 2.6. The *exo*/*endo* ratio depended on the electronic effects of substituents at the alkene: cinnamyl (**27**) and *p*-nitrocinnamyl (**31**) derivatives thus afforded 1:1.1–1.9 ratios of *endo*/*exo* products, whereas the *exo* pathway was more clearly favored in the reaction of *p*-methoxycinnamyl derivative **29** (1:5.5–7 ratios).

Enynes with NTs as tethers were particularly prone to un-

Table 6. Intramolecular alkoxycyclization of enynes **35**–**40**.

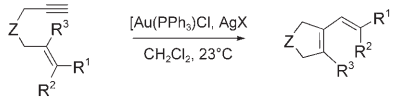


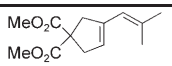
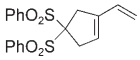
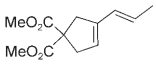
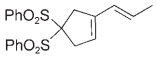
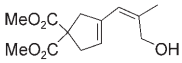
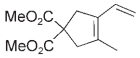
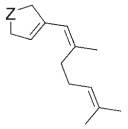
35–40 41–46

Entry	Enyne	*t* [min]	Product(s) (yield [%])
1	**35**, R = H	45	 **41** (76)
2	**36**, R = Me	15	 **42a**/**42b** (1:1, 60)
3	**37**, R = *t*Bu	30	 **43a**/**43b** (1:1, 85)
4	**38**, R = CH=CH$_2$	30	 **44a**/**44b** (1:1, 82)
5	**39**, R = Ph	5	 **45a**/**45b** (1:1, 80)
6[a]	**39**	180	**45a**/**45b** (1:1, 82)
7	**40**, R = C(OH)Me$_2$	10	 **46a**/**46b** (1:1, 77)

[a] Reaction carried out with $PtCl_2$ (3 mol%) in toluene at 80 °C.

Table 7. *exo*-Skeletal rearrangement of enynes in the presence of [Au(PPh$_3$)Cl] (2 mol %) and AgX (2 mol %).



Entry	Enyne	AgX	*t* [min]	Product (yield [%])
1	**1**, Z = C(CO$_2$Me)$_2$, R^1 = R^2 = Me, R^3 = H	AgSbF$_6$	25	 **51** (91)[a]
2[b]	**1**	–	5	**51** (98)
3	**47**, Z = C(SO$_2$Ph)$_2$, R^1 = R^2 = R^3 = H	AgSbF$_6$	5	 **52** (100)
4	**48**,[c] Z = C(CO$_2$Me)$_2$, R^1 = Me, R^2 = R^3 = H	AgBF$_4$	10	 **53**[c] (96)
5[d]	**48**	–	5	**53**[c] (70)
6[e]	**48**	–	840	**53**[c] (81)
7	**49**,[b] Z = C(SO$_2$Ph)$_2$, R^1 = Me, R^2 = R^3 = H	AgBF$_4$	15	 **54**[b] (100)
8	**50**, Z = C(CO$_2$Me)$_2$, R^1 = Me, R^2 = CH$_2$OH, R^3 = H	AgSbF$_6$	5	 **55** (67)
9	**18**, Z = C(CO$_2$Me)$_2$, R^1 = R^2 = H, R^3 = Me	AgBF$_4$	5	 **56** (76)
10[f]	**16**, Z = C(CO$_2$Me)$_2$, R^1 = Me, R^2 = (CH$_2$)$_2$CH=CMe$_2$, R^3 = H	AgSbF$_6$	60	 **57** (47)

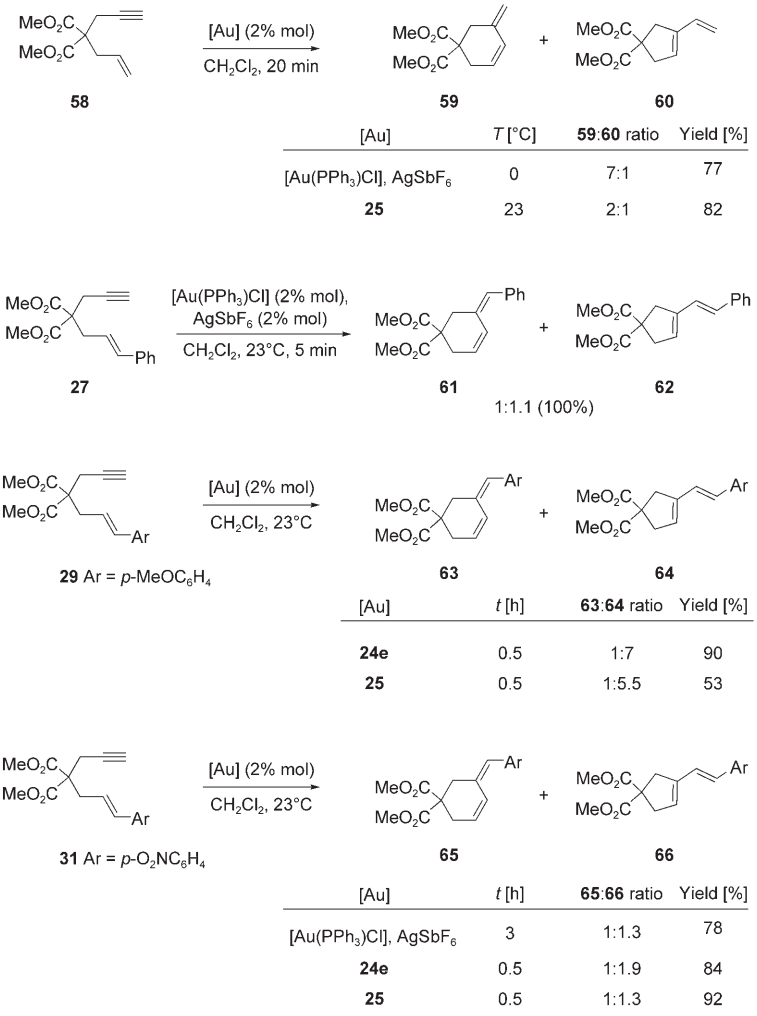
[a] Isomerization product **87** was also obtained as a minor product (see Table 8, entry 1). [b] The reaction was carried out in the presence of catalyst **24e** (2 mol %). [c] *E*/*Z* 4:1. [d] The reaction was carried out in the presence of AuCl$_3$ (5 mol %). [e] The reaction was carried out in the presence of AuCl (10 mol %). [f] The reaction was performed at −4 °C.

dergo the *endo*-skeletal rearrangement (Scheme 7). The *N*-propargyl-*N*-allyl toluene-4-sulfonylamine **67** thus gave a >10:1 mixture of *endo* (**68**) and *exo* (**69**) rearranged products, whereas the more highly substituted **8** exclusively afforded **70**. Diene **70** was also formed as a minor product (12–19 % yield) in the skeletal rearrangement of enyne **8** in the presence of 5 mol % PtCl$_2$ (toluene, reflux) or 5 mol % PtCl$_4$ (toluene, 23 °C). In platinum-catalyzed reactions of **8**, Alder–ene cycloisomerization was the major pathway.[2a,b] Enynes **71a**,**b** also underwent *endo* rearrangement to yield **72a**,**b** as the major products. In these cases the bicyclo-[4.1.0]heptenes **74a**,**b** were also obtained as byproducts, whilst similar bicyclic derivatives were also obtained in the cyclizations of **75** and **84**. On the other hand, **79** and **82** rearranged quite cleanly to give the *endo* products **80** and **83**, respectively. The formation of bicyclo[4.1.0]heptenes and *endo* skeletal rearrangement products in some of these cyclizations strongly suggests that a common intermediate **V** (Scheme 1) is involved for both processes.

Interestingly, the *exo*/*endo* selectivity may be different in the methoxycyclization and the skeletal rearrangement of enynes. Thus, substrate **8** underwent skeletal rearrangement by an *endo* pathway in the presence of [Au(PPh$_3$)]$^+$ (Scheme 8), whilst in MeOH the reaction proceeded exocyclically (Table 1, entry 9). The opposite was the case with enyne **18**, which rearranged exocyclically (Table 7, entry 9) but reacted by the *endo* pathway with respect to the alkene in MeOH (Scheme 3).

We also decided to compare these results with those of reactions catalyzed by harder Lewis acids. Thus, after investigation of a variety of Lewis acids, we found that FeCl$_3$ itself was also able to catalyze skeletal rearrangements of enynes (Table 8). This is in contrast with the cyclization of certain enynes promoted by stoichiometric amounts of FeCl$_3$, which resulted in cyclization with concomitant addition of chloride to the triple bond.[34] On the other hand, treatment of enyne **1** with the Fe^0 complex [Fe(CO)$_4$(acetone)] had been reported to give Alder–ene cycloisomerization.[35] The reactions had to be carried out with 5 mol % catalyst in toluene at 80–90 °C and were more limited in scope than those catalyzed by Au^I. The *exo*-skeletal rearrangement was the most favored process for enynes with Z = C(CO$_2$Me)$_2$ or C(SO$_2$Ph)$_2$ (Table 8, entries 1–6). However, enyne **8** gave **70**, the *endo* rearrangement derivative, as the major product (Table 8, entry 7), although the *exo* rearrangement diene **89** was also formed in the Fe^{III}-catalyzed process. In the cyclization of **1**, in addition to **51**, a second diene **87** was also formed as the result of the isomerization of the endocyclic double bond of **51** (Table 8, entry 1). Diene **87** has also been observed as a minor product in reactions of **1** catalyzed by Au^I complexes.

Mechanistic insights into the skeletal rearrangement of enynes catalyzed by Au^I complexes: Since metal carbenes have been proposed as intermediates in enyne cyclization reactions,[1d,2,16] and as, on the other hand, products of *endo* cyclization had been observed in cyclization of enynes catalyzed by Grubbs carbenes,[31] we wished to examine the possible involvement of alkene metathesis in the skeletal rearrangement of enynes. For that purpose, experiments involving mixtures of two different enynes were carried out to determine whether any cross-over was occurring in the presence of Au^I catalysts.

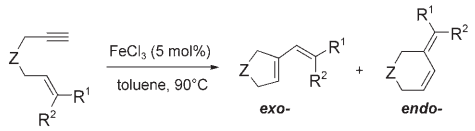


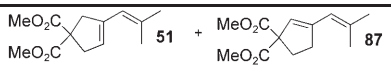
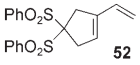
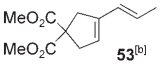
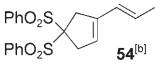
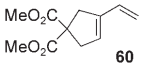
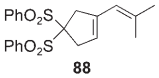
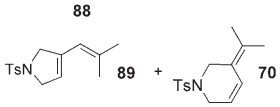
Scheme 6. *endo*-Skeletal rearrangements of enynes with malonate as the tether.

In the event, treatment of a 1:1 mixture of **58** and **8** with Au^I gave a mixture of **59** and **60** (arising from **58**), together with **70**, which is derived from **8** (Scheme 8a). Similar treatment of a 1:1 mixture of enynes **1** and **47** afforded only those products expected from fully intramolecular processes (Scheme 8b).

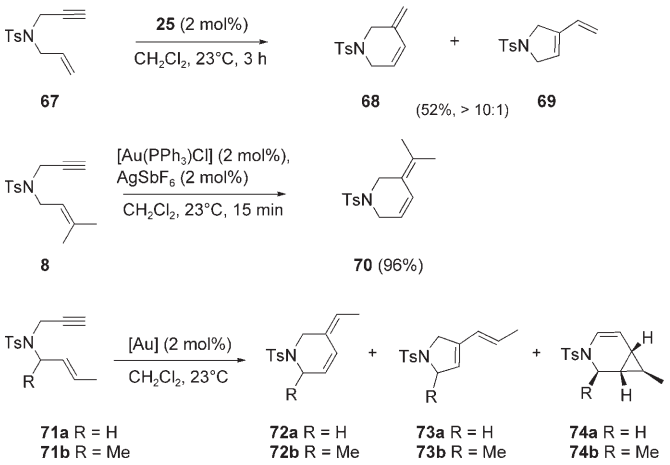
With regards to the formation of *endo* rearrangement products, we found that treatment of enyne **18** with $Hg(OTf)_2$ (2 mol%)[7] as catalyst surprisingly afforded diene **90** (Scheme 9), in contrast with findings from the Au^I-catalyzed reaction of **18** described above (Table 7, entry 9). Treatment of $[D_1]$-**18** with $Hg(OTf)_2$ gave $[D_1]$-**90**, which demonstrates that there is no skeletal rearrangement in this transformation. On the other hand, $[D_1]$-**18** reacted in the presence of a Au^I catalyst to give $[D_1]$-**56**, the product of a single *exo* rearrangement, whilst enyne $[D_1]$-**75** gave a mixture of *endo* products $[D_1]$-**76** and $[D_1]$-**78**.

Table 8. Skeletal rearrangement of enynes in the presence of $FeCl_3$ in toluene at 90°C.

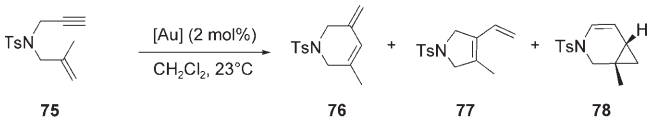


Entry	Enyne	*t* [h]	Product(s) (yield [%], ratio])	
1	**1**, Z = $C(CO_2Me)_2$, $R^1 = R^2 = Me$	12	 **51** + **87**	(88, 0.8:1)
2	**47**, Z = $C(SO_2Ph)_2$, $R^1 = R^2 = H$	12	 **52**	(84)
3	**48**,[b] Z = $C(CO_2Me)_2$, $R^1 = Me$, $R^2 = R^3 = H$	12	 **53**[b]	(79)
4	**49**,[b] Z = $C(SO_2Ph)_2$, $R^1 = Me$, $R^2 = H$	15	 **54**[b]	(85)
5	**58**, Z = $C(CO_2Me)_2$, $R^1 = R^2 = H$	17	 **60**	(98)[a]
6	**4**, Z = $C(SO_2Ph)_2$, $R^1 = R^2 = Me$	12	 **88**	(36)
7[c]	**8**, Z = NTs, $R^1 = R^2 = Me$	17	 **89** + **70**	(63, 0.4:1)

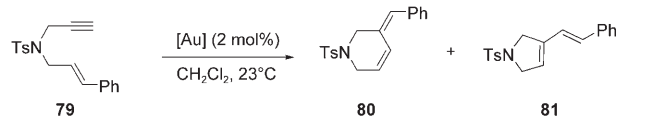
[a] Based on 84% conversion. [b] *E*/*Z* 4:1. [c] The reaction was performed at 80°C.



Enzyme	[Au]	*t* [min]	**72**:**73**:**74** ratio	Yield [%]
71a	$[Au(PPh_3)Cl]$, $AgSbF_6$	5	5:0:1	91
71a	**24e**	30	4:1:0	31
71a	**25**	30	4:1:0	30
71b	$[Au(PPh_3)Cl]$, $AgSbF_6$	10	15:14:1	99

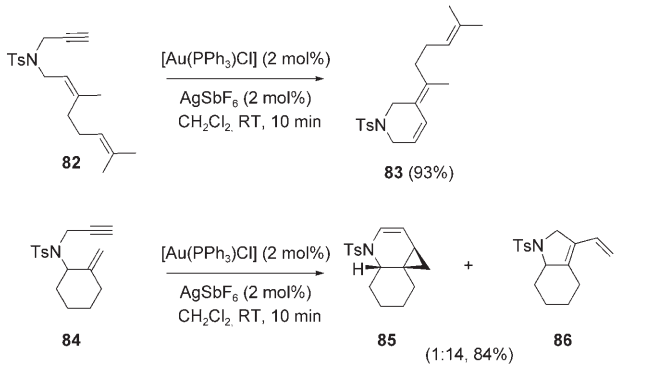


[Au]	*t* [min]	**76**:**77**:**78** ratio	Yield [%]
$[Au(PPh_3)Cl]$, $AgSbF_6$	5	1:0:2.4	93
24e	120	1.8:1:4.8	80

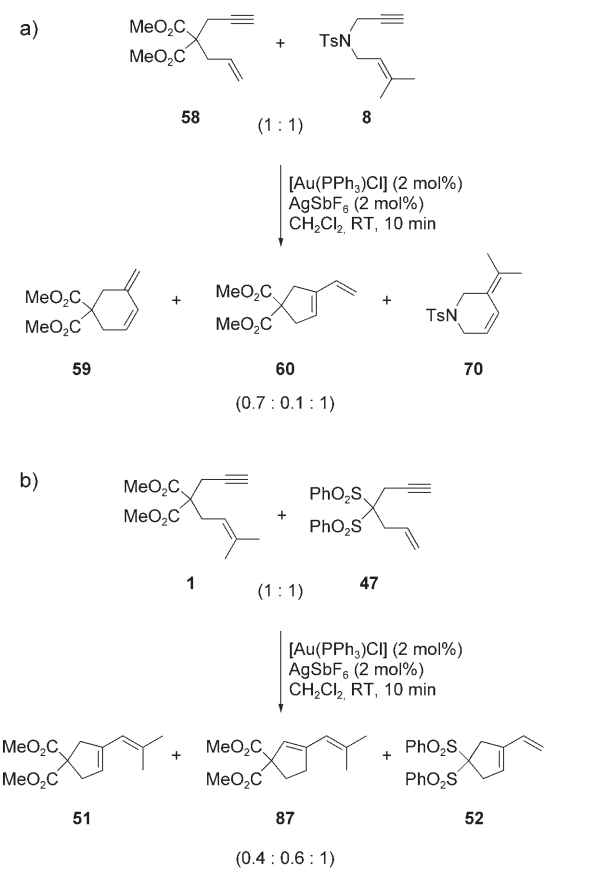


[Au]	*t* [min]	**80**:**81** ratio	Yield [%]
$[Au(PPh_3)Cl]$, $AgSbF_6$	5	1:0	100
24e	120	7.3:1	87
25	120	8.3:1	61[a]

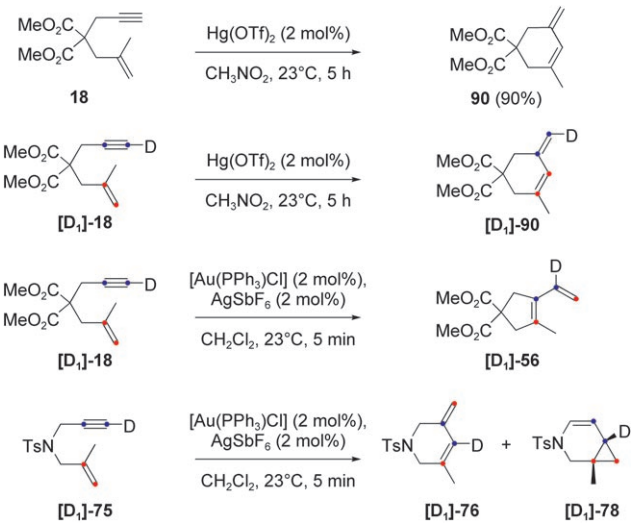
[a] Conversion = 76%



Scheme 7. *endo*-Skeletal rearrangement of enynes with TsN- as the tether.

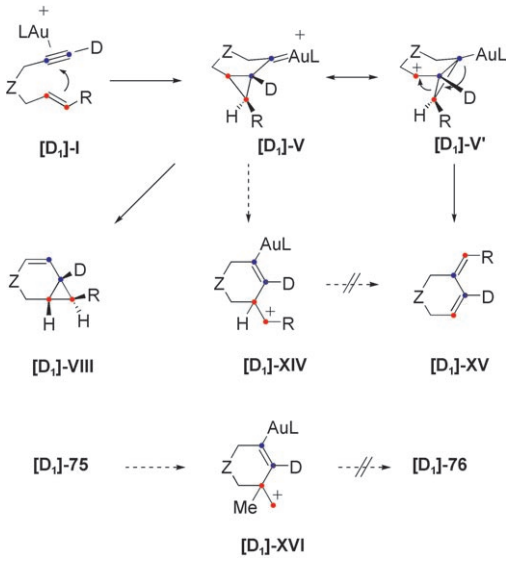


Scheme 8. Experiments aimed at determining cross-metathesis between different enynes.



Scheme 9. Hg^{II}- and Au^{I}-catalyzed cyclization and experiments with deuterated substrates in the *exo*- and *endo*-skeletal rearrangement.

The formation of the same type of skeleton, but with different deuteration patterns, in the reactions of **18** and **75** indicates that two different mechanisms are operating. For the *endo* rearrangement, the formation of D_1-**76** from D_1-**75** can be explained by evolution of intermediate **V** (Scheme 10).

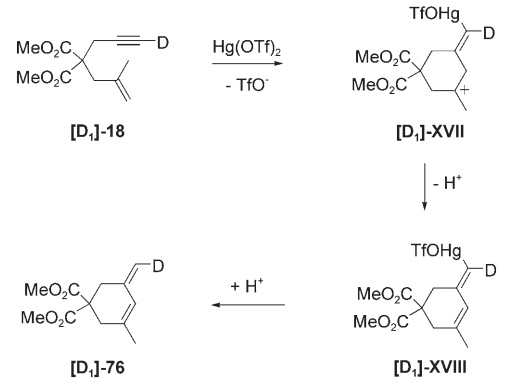


Scheme 10. Proposed mechanism for the *endo*-skeletal rearrangement with Au^{I}.

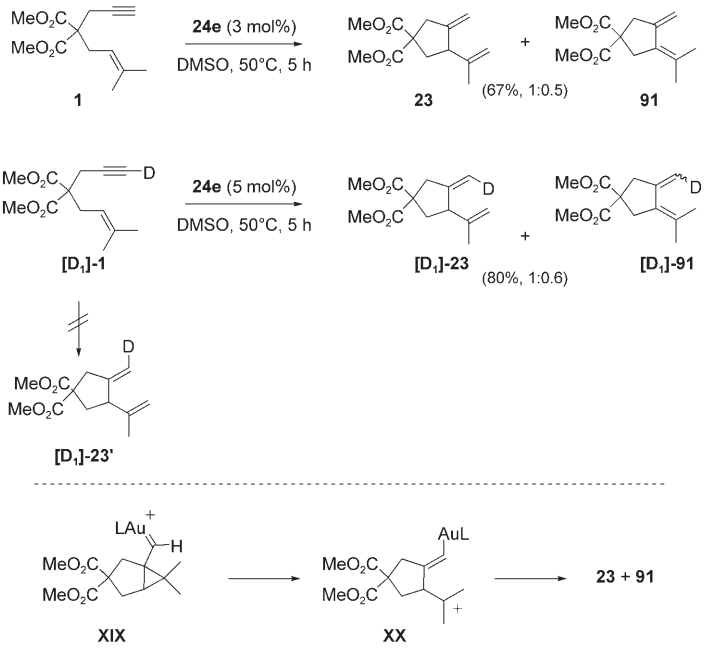
Opening of cyclopropane **V** to form **XIV**, followed by proton loss and final cleavage of the M–C bond, could also be conceived as a possible mechanism for the formation of products **XV**. However, this mechanism can be excluded because an intermediate like **XVI** would be formed from **75**, which would not explain the formation of **76**. In addition, involvement of a metal vinylidene as an intermediate[32] is excluded by the observed deuteration pattern and by the fact that the cyclization also proceeded with enynes containing a methyl substituent at C-2 of the alkene, which would not be able to undergo the required β-hydride elimination.

To interpret the different reactivity of **18** with Hg^{II}, we propose the involvement of intermediate **XVII**, which would undergo proton loss to give **XVIII**, followed by proto-demercuration (Scheme 11). A similar mechanism has recently been proposed independently by Mikami et al.[36] and by Yamamoto et al. for the Pd^{0}-catalyzed *endo*-cyclization of enynes.[37]

Importantly, cation $[Au(PPh_3)]^{+}$, which is isolobal to H^{+},[38] cannot coordinate to the alkene and the alkyne simultaneously and, in consequence, the Alder-ene cycloisomerization does not compete and the cyclizations proceed exclusively through complexes of type **I** (Scheme 1). However, when the reaction of enyne **1** was attempted in DMSO as the solvent at 50 °C in the presence of the highly reactive Au^{I} complex **24e**, a mixture of dienes **23** and **91** was obtained (Scheme 12).



Scheme 11. Proposed mechanism for the Hg^{II}-catalyzed cycloisomerization.



Scheme 12. Formation of dienes **23** and **91** from **1** with **24e** as catalyst in DMSO.

Diene **23** is the product of formal Alder–ene type cycloisomerization of **1**. However, treatment of $[D_1]$-**1** with **24e** (3 mol%) in DMSO at 50 °C afforded dienes $[D_1]$-**23** and $[D_1]$-**91** with a deuteration pattern that excluded the participation of Alder-ene type cycloisomerization in this transformation, as this would have resulted in the formation of $[D_1]$-**23′**.[2b] This result, and the formation of **91**, can be satisfactorily explained by ring-opening of intermediate **XIX** to carbocation **XX**, followed by proton loss.

Conclusion

Gold(I) complexes are the most active catalysts for the alkoxy-/hydroxycyclization and skeletal rearrangement of enynes. In particular, gold(I) catalysts generated by chloride abstraction with a silver salt or cationic complexes such as **24e** and **25** are, by far, more active as catalysts than the Pt^{II} salts or complexes used for alkoxycyclization, hydroxycyclization, and skeletal rearrangement reactions.[2] Gold(I) complexes are selective alkynophilic catalysts, promoting reactions through the exclusive coordination of the metal complex to the alkyne of the enyne. With these catalysts, the first examples of skeletal rearrangement of enynes by the

endocyclic cyclization pathway have been documented. This endocyclic cyclization proceeds by a mechanism different from those followed in the presence of Pd^{II}, Hg^{II}, or Rh^{I} catalysts.

Experimental Section

Unless otherwise stated, all reactions were carried out under Ar under anhydrous conditions. Chromatography purifications were carried out with flash grade silica gel (SDS Chromatogel 60 ACC, 40–60 μm).

The following compounds have been described: a) Starting enynes: **1**,[39] **4**,[2a,b] **6**,[2c] **7**,[40] **8**,[41] **10**,[2a,b] **12**,[2a,b] **16**,[42] **18**,[13a] **20**,[19] **22**,[19] **27**,[52] **47**,[43] **48**,[44] **49**,[4a] **58**,[44] **67**,[45] **72a**,[46] **71b**,[47] **75**,[2a,b] **79**,[8] and **84**;[48] b) carbo- and heterocycles: **2a**,[2a,b] **5**,[2a,b] **9**,[8] **11**,[2a,b] **13a**,[2a,b] **17**,[2a,b] **19**,[2a,b] **21**,[49] **23**,[50] **51**,[51] **52**,[10a] **53**,[52] **54**,[2a,b] **56**,[44] **59**,[29] **60**,[52] **62**,[52] **68**,[10b] **69**,[10b] **73a**,[53] **76**,[54] **77**,[55] **78**,[10] **79**,[8] **81**,[53] **89**,[53] **90**,[53] and **91**.[56]

Synthesis of new enynes

(*E*)-1,1-Bis(phenylsulfonyl)-4,8-dimethylnona-3,7-diene: Bis(phenylsulfonyl)methane (500 mg, 1.68 mmol) was added at 0 °C to a suspension of NaH (68 mg, 1.68 mmol, 60 % in mineral oil) in DMF (15 mL). After 20 min, geranyl bromide (365 mg, 1.68 mmol) was added, and the resulting mixture was stirred at 23 °C for 12 h. After extractive workup (Et_2O/10 % HCl) and chromatography (2:1 hexane/EtOAc), the title compound was obtained (552 mg, 76 %) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98–7.97 (m, 2H), 7.96–7.94 (m, 2H), 7.72–7.67 (m, 2H), 7.61–7.55 (m, 4H), 5.08–5.01 (m, 2H), 4.42 (t, J = 6.1 Hz, 1H), 3.10 (m, 2H), 2.01–1.86 (m, 4H), 1.68 (d, J = 1.2 Hz, 3H), 1.59 (s, 3H), 1.47 (d, J = 1.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.69, 138.19, 134.49, 131.75, 129.64, 129.03, 123.78, 118.03, 84.35, 39.44, 26.27, 25.67, 24.62, 17.71, 16.13 ppm; HMRS-FAB: *m/z* calcd for $C_{23}H_{29}O_4S_2$: 433.1507; found 433.1499 $[M+1]^+$; elemental analysis (%) calcd for $C_{23}H_{28}O_4S_2$: C 63.86, H 6.52; found: C 63.79, H 6.18.

(*E*)-4,4-Bis(phenylsulfonyl)-7,11-dimethyldodeca-6,10-dien-1-yne (14): (*E*)-1,1-Bis(phenylsulfonyl)-4,8-dimethylnona-3,7-diene (500 mg, 1.15 mmol) was added at 0 °C to a suspension of NaH (55 mg, 1.38 mmol, 60 % mineral oil) in DMF (15 mL). After 20 min, propargyl bromide (138 mg, 1.15 mmol) was added, and the resulting mixture was stirred at 23 °C for 12 h. After extractive workup (Et_2O/10 % HCl) and chromatography (hexane/EtOAc 4:1), **14** (245 mg, 45 %) was obtained as a pale yellow solid: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16–8.14 (m, 2H), 8.13–8.11 (m, 2H), 7.73–7.68 (m, 2H), 7.59–7.55 (m, 4H), 5.42 (t, J = 6.5 Hz, 1H), 5.12–5.10 (m, 1H), 3.18 (d, J = 2.8 Hz, 2H), 3.04 (d, J = 6.5 Hz, 2H), 2.16–2.02 (m, 5H), 1.69 (s, 3H), 1.62 (s, 3H), 1.58 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.44, 136.48, 134.64, 131.52, 128.45, 123.91, 114.87, 89.27, 76.11, 73.99, 39.88, 27.69, 26.18, 25.68, 20.36, 17.74, 16.59 (one carbon signal overlaps) ppm; HMRS-CI: *m/z* calcd for $C_{26}H_{31}O_4S_2$: 471.1664; found 471.1675 $[M+1]^+$.

Dimethyl 2-(*p*-methoxycinnamyl)-2-propargylmalonate (29): A solution of dimethyl 2-propargylmalonate (0.22 mL, 1.44 mmol) in DMF (5 mL) was added at 0 °C to a suspension of NaH (63.0 mg, 1.57 mmol, 60 % in mineral oil) in DMF (3 mL). After 20 min, a solution of *p*-methoxycinnamyl bromide (597 mg, 2.60 mmol) in DMF (10 mL) was added and the resulting mixture was stirred at 23 °C for 18 h. After extractive workup (Et_2O/10 % HCl) and chromatography (hexane/EtOAc 10:1), **29** (398 mg, 87 %) was obtained as a white, waxy solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.46 (d, J = 15.7 Hz, 1H), 5.85 (q, J = 15.5, 7.7 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 6H), 2.94 (d, J = 7.7 Hz, 2H), 2.84 (d, J = 2.7 Hz, 2H), 2.05 (t, J = 2.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.20, 159.14, 134.05, 129.78, 127.42, 120.68, 113.89, 71.52, 71.51, 57.26, 55.26, 52.78, 35.85, 22.80 ppm; HRMS-ESI: *m/z* calcd for $C_{18}H_{20}O_5Na$: 339.1208; found 339.1199 $[M+Na]^+$.

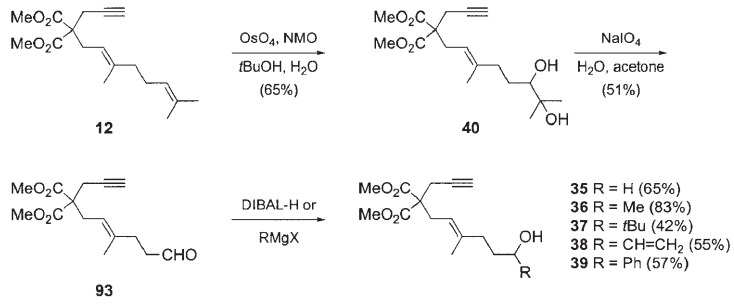
Dimethyl 2-(*p*-nitrocinnamyl)-2-propargylmalonate (31): A solution of dimethyl 2-propargylmalonate (561 mg, 2.64 mmol) in DMF (10 mL) was added at 0 °C to a suspension of NaH (133.2 mg, 3.33 mmol, 60 % in mineral oil) in DMF (5 mL). After 20 min, a solution of *p*-nitrocinnamyl bromide (798 mg, 3.13 mmol) in DMF (15 mL) was added and the resulting mixture was stirred at 23 °C for 16 h. After extractive workup (Et_2O/10 % HCl), chromatography (hexane/EtOAc 10:1), and recrystallization from hexane, **31** was obtained (704 mg, 81 %) as yellow crystals, m.p. 73–75 °C: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.87 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 15.7 Hz, 1H), 6.24 (q, J = 7.7, 15.6 Hz, 1H), 3.77 (s, 6H), 3.01 (d, J = 6. 7 Hz, 2H), 2.85 (d, J = 2.7 Hz, 2H), 2.08 (t, J = 2. 7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$; DEPT, HMQC, and HMBC): δ = 168.89, 146.90, 143.23, 132.57, 128.67, 126.78, 123.94, 71.93, 71.92, 57.00, 52.94, 36.08, 23.18 ppm; IR (KBr): $\tilde{\nu}$ = 1731 cm^{-1}; HRMS-ESI: *m/z* calcd for $C_{17}H_{17}NO_6Na$: 354.0954; found 354.0965 $[M+Na]^+$.

1-(1-Cinnamylcyclohexyl)prop-2-yn-1-ol (33): Propargylmagnesium bromide (0.5 M in THF, 11.39 mL, 5.69 mmol) was added at −40 °C to a solution of 1-*trans*-cinnamylcyclohexanecarbaldehyde[57] (1.00 g, 4.38 mmol) in THF (10 mL), and the mixture was stirred for 2 h at this temperature and for 1 h at 23 °C. After extractive workup (Et_2O) and chromatography (hexane/EtOAc 10:1), **33** was obtained as a colorless oil (643 mg, 58 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 5H), 6.53 (d, J = 16.0 Hz, 1H), 6.35 (q, J = 7.3 Hz, 1H), 4.35 (dd, J = 6.7, 2.0 Hz, 1H), 2.57 (d, J = 2.2 Hz, 1H), 2.52 (dq, J = 8.1, 2.2 Hz, 2H), 2.00 (d, J = 6.7 Hz, 1H), 1.65–1.51 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 137.52 (C), 132.69 (CH), 128.46 (CH), 127.55 (CH), 127.51 (CH), 127.01 (CH), 126.81 (CH), 126.02 (CH), 83.34 (CH), 74.82 (C), 68.55 (CH), 41.48 (C), 35.97 (CH_2), 31.18 (CH_2), 30.10 (CH_2) 26.00 (CH_2), 21.37 (CH_2), 21.27 (CH_2) ppm; HRMS-CI: *m/z* calcd for $C_{18}H_{23}O$: 253.1592; found 253.1583 $[M+1]^+$.

Dimethyl 2-(3-methyl-2-buten-4-ol)-2-(prop-2-ynyl)malonate (50): 2-Methyl-2-vinyloxirane (0.57 mL, 5.87 mmol) and dimethyl propargylmalonate (0.89 mL, 5.87 mmol) were added at 23 °C to a suspension of $[Pd_2(dba)_3{\cdot}dba]$ (337 mg, 0.59 mmol) and Ph_3P (154 mg, 0.59 mmol) in CH_3CN. The mixture was stirred at this temperature for 16 h. Then CH_3CN was evaporated (without heating) and the mixture was diluted with CH_2Cl_2 and filtered through Celite. After chromatography (hexane/EtOAc 10:1 to 3:1), **50** was obtained as a yellow oil and as a *E*/*Z* isomer mixture (1.20 g, 81 %): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.22 (tdd, J = 7.7, 2.8, 1.2 Hz, 1H; *E* isomer), 5.07 (td, J = 8.1, 1.2 Hz, 1H; *Z* isomer), 4.1 (brs, 2H; *Z* isomer), 3.99 (s, 2H; *E* isomer), 3.75 (s, 6H; *Z* isomer), 3.74 (s, 6H; *E* isomer), 2.89 (dm, J = 7.7 Hz, 2H; *E* isomer), 2.83 (d, J = 2.8 Hz, 2H; *E* isomer, 2H; *Z* isomer), 2.78 (d, J = 2.8 Hz, 2H; *Z* isomer), 2.06 (t, J = 2.8 Hz, 2H), 2.05 (s, 1H; *E* isomer), 1.81 (m, 3H; *Z* isomer), 1.70 (s, 3H; *E* isomer) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 170.3 (2 C; *E* isomer, *Z* isomer), 140.0 (C; *Z* isomer), 139.9 (C; *E* isomer), 120.4 (CH; *Z* isomer), 117.9 (CH; *E* isomer), 88.0 (CH; *E* isomer), 81.9 (CH; *Z* isomer), 78.9 (2 C; *E* isomer, *Z* isomer), 72.0 (C; *Z* isomer), 71.4 (C; *E* isomer), 68.4 (CH_2; *E* isomer), 61.2 (CH_2; *Z* isomer), 56.9 (2 C; *E* isomer, *Z* isomer), 52.9 (CH_3; *Z* isomer), 52.8 (CH_3; *E* isomer), 30.3 (CH_2; *Z* isomer), 30.2 (CH_2; *E* isomer), 22.6 (CH_3; *E* isomer), 21.7 (CH_3; *Z* isomer) ppm; HRMS-EI: *m/z* calcd for $C_{13}H_{18}O_5$: 254.1154; found 254.1158.

***N*-((2*Z*)-3,7-Dimethyl-octa-2,6-dienyl)-*N*-(prop-2-ynyl)toluene-4-sulfonamide (82)**: A solution of *N*-(prop-2-ynyl)toluene-4-sulfonamide (1.00 g, 4.79 mmol) in DMF (10 mL) was added at 0 °C to a suspension of NaH (60 % in mineral oil, 192 mg, 4.79 mmol) in DMF (5 mL), followed by neryl bromide (1.04 g, 4.79 mmol). The mixture was stirred for 17 h at 23 °C and was then quenched with H_2O. After extractive workup (Et_2O/HCl 10 %) and chromatography (hexane/EtOAc 30:1), **82** (1.03 g, 62 %) was obtained as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 5.12–5.02 (m, 2H), 4.05 (d, J = 2.4 Hz, 2H), 3.79 (d, J = 7.3 Hz, 2H), 2.42 (s, 3H), 2.06 (m, 4H), 1.97 (t, J = 2.6 Hz, 1H), 1.72 (d, J = 1.2 Hz, 3H), 1.66 (s, 3H), 1.57 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 143.32 (C), 142.30 (C), 136.21 (C), 132.07 (C), 129.35 (CH), 127.77 (CH), 123.62 (CH), 118.76 (CH), 77.07 (CH), 73.37 (C), 43.63 (CH_2), 35.39 (CH_2), 31.75 (CH_2), 26.47 (CH_2), 25.65 (CH_3), 23.42 (CH_3), 21.49 (CH_3), 17.62 (CH_3) ppm; HRMS-EI: *m/z* calcd for $C_{20}H_{27}NO_2S$: 345.1762; found 345.1751.

Synthesis of alcohols 35–40



Dimethyl 2-((*E*)-6,7-dihydroxy-3,7-dimethyloct-2-enyl)-2-(prop-2-ynyl)-malonate (40): A solution of OsO_4 (4% wt. in water, 3.3 mL, 0.55 mmol) was added to a solution of *N*-methylmorpholine *N*-oxide (1.623 g, 12 mmol) in *tert*-butyl alcohol (10 mL) and water (10 mL). Dienyne **12** (3.342 g, 10.92 mmol), dissolved in *tert*-butyl alcohol (20 mL) and water (10 mL), was added at 23 °C to the former solution. After stirring for 6 h, the mixture was extracted with CH_2Cl_2, washed with a saturated aqueous solution of $NaHSO_3$ and with saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was evaporated and the residue mixture was chromatographed (hexane/EtOAc 1:1) to give **40** (2.397 g, 65%) as a pale brown oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.05–4.97 (m, 1H), 3.74 (s, 6H), 3.30 (dd, J = 10.4, 2.0 Hz, 1H), 2.83–2.76 (m, 4H), 2.30–2.03 (m, 2H), 2.01 (t, 2.6 Hz, 1H), 1.66 (s, 3H), 1.65–1.52 (m, 2H), 1.47–1.33 (m, 2H), 1.20 (s, 3H), 1.16 (s, 3H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$): δ = 170.46 (C), 170.45 (C), 140.14 (C), 117.75 (CH), 79.08 (C), 77.72 (CH), 72.94 (C), 71.31 (CH), 57.10 (C), 52.74 (2×CH_3), 36.92 (CH_2), 30.63 (CH_2), 29.36 (CH_2), 26.29 (CH_3), 23.33 (CH_3), 22.61 (CH_2), 16.03 (CH_3) ppm; HRMS-ESI: *m/z* calcd for $C_{18}H_{28}O_6Na$: 363.1784; found 363.1785 $[M+Na]^+$.

Dimethyl 2-((*E*)-3-methyl-6-oxohex-2-enyl)-2-(prop-2-ynyl)malonate (93): A solution of $NaIO_4$ (330 mg, 1.54 mmol) in water (2.5 mL) was added to a solution of **40** (240 mg, 0.706 mmol) in acetone (10 mL). The mixture was stirred for 2 h and then filtered through Celite. It was then partitioned between CH_2Cl_2 and water and, after extractive workup and chromatography (hexane/EtOAc 5:1), aldehyde **93** (101 mg, 51%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.73 (t, J = 1.8 Hz, 1H), 5.01–4.93 (m, J = 7.7, 2.3 Hz, 1H), 3.72 (s, 6H), 2.81–2.73 (two overlapping d, J = 7.6, 2.7 Hz, 4H), 2.54–2.46 (m, 2H), 2.32 (t, J = 7.4 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H), 1.66 (s, 3H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$): δ = 201.96 (CH), 170.27 (2 C), 138.48 (C), 118.19 (CH), 79.04 (C), 71.33 (CH), 57.00 (C), 52.73 (2×CH_3), 42.08 (CH_2), 32.02 (CH_2), 30.58 (CH_2), 22.59 (CH_2), 16.29 (CH_3) ppm; HRMS-ESI: calcd for $C_{15}H_{20}O_5Na$: 303.1208; found 303.1198 $[M+Na]^+$.

Dimethyl 2-((*E*)-6-hydroxy-3-methylhex-2-enyl)-2-(prop-2-ynyl)malonate (35): Dimethyl 2-((*E*)-3-methyl-6-oxohex-2-enyl)-2-(prop-2-ynyl)malonate (**93**, 99 mg, 0.353 mmol) was dissolved in THF (4 mL) at 0 °C. DIBAL-H solution in CH_2Cl_2 was added (0.350 mL, 0.350 mmol) and the mixture was stirred for 45 min at 0 °C. After that time, the reaction was quenched with a saturated aqueous sodium/potassium tartrate solution (2 mL) and EtOAc (2 mL). This was stirred for 1 h, and the reaction mixture was then extracted with CH_2Cl_2, washed with saturated aqueous NaCl solution, and dried over $MgSO_4$. Flash chromatography (hexane/EtOAc 2:1) yielded **35** (64 mg, 65% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.97 (t, J = 7.7 Hz, 1H), 3.73 (s, 6H), 3.60 (t, J = 6.4 Hz, 2H), 2.81–2.76 (two overlapping d, J = 7.8, 2.8 Hz, 4H), 2.07 (t, J = 7.5 Hz, 2H), 2.00 (t, J = 2.5 Hz, 1H), 1.72–1.60 (overlapping s and m, 5H) ppm; ^{13}C NMR, DEPT (100 MHz, $CDCl_3$): δ = 170.44 (2 C), 140.09 (C), 117.45 (CH), 79.15 (C), 71.28 (CH), 62.44 (CH_2), 57.14 (C), 52.71 (2×CH_3), 36.20 (CH_2), 30.66 (2×CH_2), 22.62 (CH_2), 16.07 (CH_3) ppm; HRMS-ESI: *m/z* calcd for $C_{15}H_{23}O_5$: 283.1545; found 283.1549.

Dimethyl 2-((*E*)-6-hydroxy-3-methylhept-2-enyl)-2-(prop-2-ynyl)malonate (36): A solution of methylmagnesium bromide in hexane (3.0 M, 0.156 mL, 0.467 mmol) was added at −45 °C to a solution of aldehyde **93** (131 mg, 0.467 mmol) in THF (5 mL). The solution was warmed up to 23 °C and after 2 h was quenched with a saturated aqueous solution of NH_4Cl, washed with saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed (hexane/EtOAc 3:2) to yield **36** (115 mg, 83%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.97 (tq, J = 7.7, 1.2 Hz, 1H), 3.71 (overlapping s and m, 7H), 2.80–2.73 (m, 4H), 2.15–2.00 (m, 2H), 2.00 (t, J = 2.7 Hz, 1H), 1.64 (s, 3H), 1.55–1.45 (m, 2H), 1.18 (d, J = 6.3 Hz, 3H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$): δ = 171.09 (2 C), 141.04 (C), 117.87 (CH), 79.79 (C), 71.92 (CH), 68.34 (CH), 57.76 (C), 53.34 (2×CH_3), 37.91 (CH_2), 36.90 (CH_2), 31.26 (CH_2), 24.11 (CH_3), 23.22 (CH_2), 16.77 (CH_3) ppm; HRMS-ESI: *m/z* calcd for $C_{16}H_{25}O_5$: 297.1702; found 297.1703; elemental analysis (%) calcd for $C_{16}H_{24}O_5$: C 64.84, H 8.16; found: C 64.78, H 8.07.

Dimethyl 2-((*E*)-6-hydroxy-3,7,7-trimethyloct-2-enyl)-2-(prop-2-ynyl)malonate (37): A solution of *tert*-butylmagnesium chloride in hexanes (1.0 M, 0.350 mL, 0.35 mmol) was added at 0 °C to a solution of aldehyde **93** (98 mg, 0.35 mmol) in THF (4 mL). The solution was stirred for 30 min at 0 °C and the cooling bath was then removed so that the solution could reach 23 °C. The reaction was quenched with a saturated aqueous solution of NH_4Cl, washed with saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed (hexane/EtOAc 5:1) to give **37** (50 mg, 42%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.98 (tq, J = 7.7, 1.26 Hz, 1H), 3.73 (s, 6H), 3.15 (br d, J = 10.4 Hz, 1H), 2.82–2.76 [overlapping dd (J = 7.8, 3.2 Hz, 2H) and dd (J = 2.7, 1.3 Hz, 2H)], 2.26–2.17 (m, 1H), 2.11–2.02 (m, 1H), 2.00 (t, J = 2.7 Hz, 1H), 1.65 (s, 3H), 1.67–1.60 (overlapping s and m, 4H), 1.45 (br s, 1H), 1.37–1.26 (m, 1H), 0.89 (s, 9H) ppm; ^{13}C NMR, DEPT (100 MHz, $CDCl_3$): δ = 170.49 (C), 170.45 (C), 140.54 (C), 117.48 (CH), 79.21 (CH), 79.08 (C), 71.25 (CH), 57.19 (C), 52.72 (CH_3), 52.70 (CH_3), 37.32 (CH_2), 34.91 (C), 30.68 (CH_2), 29.29 (CH_2), 25.70 (3×CH_3), 22.62 (CH_2), 16.08 (CH_3) ppm; HRMS-ESI: *m/z* calcd for $C_{19}H_{31}O_5$: 339.2171; found 339.2170.

Dimethyl 2-((*E*)-6-hydroxy-3-methylocta-2,7-dienyl)-2-(prop-2-ynyl)malonate (38): A solution of vinylmagnesium bromide in THF (1.0 M, 0.156 mL, 0.467 mmol) was added at −0 °C to a solution of aldehyde **93** (146 mg, 0.521 mmol) in THF (5 mL). The solution was warmed up to 23 °C and after 1 h was quenched with a aqueous solution of NH_4Cl (pH 8), washed with saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed (hexane/EtOAc 4:1) to yield **38** (89 mg, 55%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.86 (ddd, J = 17.2, 10.4, 6.2 Hz, 1H), 5.22 (dt, J = 17.2, 1.4 Hz, 1H), 5.11 (dt, J = 10.4, 1.3 Hz, 1H), 4.97 (dt, J = 7.7, 1.2 Hz, 1H), 4.06 (q, J = 6.4 Hz, 1H), 3.73 (s, 6H), 2.82–2.76 (two overlapping d, J = 7.8, 2.7 Hz, 4H), 2.15–2.01 (m, J = 7.0 Hz, 2H), 2.00 (t, J = 2.6 Hz, 1H), 1.66 (s, 3H), 1.65–1.57 (m, 3H) ppm; ^{13}C NMR, DEPT (100 MHz, $CDCl_3$): δ = 170.43 (2 C), 141.06 (CH), 140.11 (C), 117.45 (CH), 114.73 (CH_2), 79.17 (C), 72.69 (CH), 71.26 (CH), 57.14 (C), 52.70 (2×CH_3), 35.72 (CH_2), 35.08 (CH_2), 30.66 (CH_2), 22.61 (CH_2), 16.18 (CH_3) ppm; HRMS-ESI: *m/z* calcd for $C_{17}H_{24}O_5Na$: 331.1521; found 331.1530 $[M+Na]^+$.

Dimethyl 2-((*E*)-6-hydroxy-3-methyl-6-phenylhex-2-enyl)-2-(prop-2-ynyl)malonate (39): A solution of phenylmagnesium bromide in hexane (1.0 M, 0.156 mL, 0.467 mmol) was added at 0 °C to a solution of aldehyde **93** (98 mg, 0.350 mmol) in THF (5 mL). This mixture was stirred for 30 min, the cooling bath was removed, and the mixture was stirred for an additional 30 min, quenched with saturated aqueous NH_4Cl, washed with saturated aqueous NaCl solution, and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed (hexane/EtOAc 3:1) to yield **39** (72 mg, 57% yield) as a colorless oil. ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 7.31–7.17 (m, 5H), 4.90 (dt, J = 7.7, 1.1 Hz, 1H), 4.56 (dd, J = 7.7, 5.3 Hz, 1H), 3.66 (s, 6H), 2.75–2.69 (two overlapping d, J = 7.9, 2.6 Hz, 4H), 2.12–1.95 (m, 2H), 1.93 (t, J = 2.6 Hz, 1H), 1.86–1.65 (m, 3H), 1.59 (s, 3H) ppm; ^{13}C NMR, DEPT (100 MHz, $CDCl_3$): δ = 170.44 (C), 170.43 (C), 144.71 (C), 140.01 (C), 128.47 (2×CH), 127.54 (CH), 125.87 (2×CH), 117.53 (CH), 79.17 (C), 74.02 (CH), 71.28 (CH), 57.14 (C), 52.72 (CH_3), 52.71 (CH_3), 37.09 (CH_2), 36.21 (CH_2), 30.67 (CH_2), 22.62 (CH_2), 16.19 (CH_3) ppm; HRMS-ESI: m/z calcd for $C_{21}H_{26}O_5Na$: 381.1678; found 381.1672 $[M+Na]^+$.

Synthesis of [Au(L)Cl] complexes: These complexes were prepared by the literature procedure for the synthesis of $[Au(PPh_3)Cl]$:[22] sodium tetrachloroaurate(III) dihydrate or tetrachloroauric acid (1 mmol) was dissolved in water, and the orange solution was cooled in ice. 2,2′-Thiodiethanol (3 mmol) was slowly added (ca. 45 min) to this solution with stirring. A solution of the phosphine ligand (1 mmol) in EtOH was added dropwise to give a white solid. The solid was filtered off, washed with MeOH, and dried in vacuo.

[Au(PCy$_3$)Cl]: Yield 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03–1.93 (m, 9H), 1.89–1.85 (m, 6H), 1.75–1.72 (m, 3H), 1.52–1.41 (m, 6H), 1.35–1.21 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.28 (d, $^1J_{^{13}C,^{31}P}$ = 31 Hz), 30.75, 26.96 (d, $^2J_{^{13}C,^{31}P}$ = 12.2 Hz), 25.80 (d, $^3J_{^{13}C,^{31}P}$ = 1.5 Hz) ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 57.12 ppm; HRMS-ESI (from MeCN solution) m/z calcd for $C_{20}H_{36}AuNP$: 518.2251; found 518.2241 $[M+MeCN-Cl]^+$.

[Au{P(C$_6$F$_5$)$_3$}Cl]: Yield 82% ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 57.08 ppm; HRMS-FAB: m/z calcd for $C_{18}F_{15}AuP$: 728.9164; found 728.9169.

[Au{P(*o*-Tol)$_3$}Cl]: Yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (tt, J = 7.5, 1.5 Hz, 3H), 7.35 (m, 3H), 7.19 (t, J = 7.7 Hz, 3H), 6.92 (ddd, J = 13.3, 7.8, 1.1 Hz, 3H), 2.67 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0 (d, $^2J_{^{13}C,^{31}P}$ = 12 Hz), 133.49 (d, $^3J_{^{13}C,^{31}P}$ = 9.6 Hz), 132.42 (d, $^3J_{^{13}C,^{31}P}$ = 9.1 Hz), 131.97 (d, $^4J_{^{13}C,^{31}P}$ = 2.6 Hz), 126.69 (d, $^2J_{^{13}C,^{31}P}$ = 10.5 Hz), 125.00 (d, $^1J_{^{13}C,^{31}P}$ = 61.3 Hz), 23.31 (d, $^3J_{^{13}C,^{31}P}$ = 11.3 Hz) ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 11.50 ppm; HRMS-ESI (from MeCN solution) m/z calcd for $C_{23}H_{24}AuNP$: 542.1312; found 542.1318 $[M+MeCN-Cl]^+$.

[Au(AsPh$_3$)Cl]: Yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 15H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.23, 131.44, 131.05, 129.62 ppm; HRMS-ESI (from MeCN solution) m/z calcd for $C_{20}H_{18}AuNAs$: 544.0321; found 544.0306 $[M+MeCN-Cl]^+$.

[Au{P(1-Naph)$_3$}Cl]: This compound was prepared by the described procedure.[58] Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 8.5 Hz, 3H), 8.09 (d, J = 8.0 Hz, 3H), 8.00 (d, J = 8.2 Hz, 3H), 7.61 (dd, J = 7.9, 7.1 Hz, 3H), 7.51 (dd, J = 8.1, 7.5 Hz, 3H), 7.33 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.04 (d, $^3J_{^{13}C,^{31}P}$ = 8.1 Hz), 134.14 (d, $^3J_{^{13}C,^{31}P}$ = 8.1 Hz), 133.94 (d, $^2J_{^{13}C,^{31}P}$ = 11.8 Hz), 133.51, 129.26 (d, $^4J_{^{13}C,^{31}P}$ = 1.3 Hz), 127.79, 126.97, 126.50 (d, $^2J_{^{13}C,^{31}P}$ = 14.4 Hz), 125.13 (d, $^2J_{^{13}C,^{31}P}$ = 12.0 Hz), 122.53 (d, $^1J_{^{13}C,^{31}P}$ = 62.7 Hz) ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 9.59 ppm: HRMS-ESI (from MeCN solution) m/z calcd for $C_{32}H_{24}AuNP$: 650.1312; found 650.1335 $[M+MeCN-Cl]^+$.

Complex 24a: Yield 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.71 (m, 1H), 7.57–7.44 (m, 5H), 7.33–7.28 (m, 1H), 7.18 (d, J = Hz, 3H), 2.08–1.94 (m, 4H) 1.83–1.74 (m, 4H), 1.68–1.43 (m, 6H) 1.33–1.18 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.09, 134.29, 132.48 (d, $^3J_{^{13}C,^{31}P}$ = 7.4 Hz), 130.71, 129.24, 128.64, 128.35, 127.43 (d, $^3J_{^{13}C,^{31}P}$ = 8.4 Hz), 124.43, 36.58 (d, $^1J_{^{13}C,^{31}P}$ = 33.3 Hz), 31.16 (d, $^3J_{^{13}C,^{31}P}$ = 4.5 Hz), 29.42, 26.54 (d, $^2J_{^{13}C,^{31}P}$ = 10 Hz), 24.43 (d, $^2J_{^{13}C,^{31}P}$ = 14 Hz), 25.58 ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 47.15 ppm; HRMS-ESI(from MeCN solution) m/z calcd for $C_{26}H_{34}AuNP$: 588.2094; found 588.2075 $[M+MeCN-Cl]^+$.

Complex 24b: Yield 43%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (td, J = 7.7, 1.7 Hz, 1H), 7.51 (m, 5H), 7.31 (m, 1H), 7.13 (dd, J = 8.0. 1.0 Hz, 2H), 1.41 (d, J = 15.6, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.16 (d, $^2J_{^{13}C,^{31}P}$ = 13.5 Hz), 142.10 (d, $^3J_{^{13}C,^{31}P}$ = 6.3 Hz), 133.46 (d, $^4J_{^{13}C,^{31}P}$ = 3.0 Hz), 133.22 (d, $^3J_{^{13}C,^{31}P}$ = 7.5 Hz), 129.19, 128.67, 128.22, 126.67 (d, $^3J_{^{13}C,^{31}P}$ = 6.8), 126.06 (d, $^1J_{^{13}C,^{31}P}$ = 45.3 Hz), 37.75 (d, $^1J_{^{13}C,^{31}P}$ = 25.7 Hz), 30.84 (d, $^2J_{^{13}C,^{31}P}$ = 6.7 Hz) ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 63.11 ppm; HRMS-ESI (from MeCN solution) m/z calcd for $C_{22}H_{30}AuNP$: 536.1781; found 536.1779 $[M+MeCN-Cl]^+$.

Complex 24c: Yield 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.55 (m, 1H), 7.47–7.45 (m, 2H), 7.23 (m, 1H), 7.05 (s, 2H), 2.95 (hept, J = 7.0 Hz, 1H), 2.21 (hept, J = 6.7 Hz, 2H), 2.05–2.01 (m, 4H), 1.83–1.71 (m, 6H), 1.67–1.61 (m, 2H), 1.53–1.42 (m, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 1.23–1.13 (m, 7H), 0.92 (s, 3H), 0.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.06, 145.48, 133.82 (d, $^3J_{^{13}C,^{31}P}$ = 8.1 Hz), 132.04 (d, $^1J_{^{13}C,^{31}P}$ = 3.2 Hz), 130.35 (d, $^1J_{^{13}C,^{31}P}$ = 1.8 Hz), 127.08 (d, $^1J_{^{13}C,^{31}P}$ = 7.1 Hz), 121.70, 37.23 (d, $^1J_{^{13}C,^{31}P}$ = 33.5 Hz), 34.30, 30.93, 30.81, 27.01 (d, $^1J_{^{13}C,^{31}P}$ = 13.5 Hz), 26.69 (d, $^1J_{^{13}C,^{31}P}$ = 12.9 Hz), 24.36, 23.12 ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 38.48 ppm; HRMS-ESI: m/z calcd for $C_{33}H_{49}AuPNa$: 731.2823; found 731.2789 $[M+Na]^+$.

Complex 24d: Yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.42 (m, 4H), 7.23–7.20 (m, 1H), 6.66 (d, J = 8.4 Hz, 2H), 3.70 (s, 6H), 2.18–2.13 (m, 2H), 1.98–1.93 (m, 2H), 1.83–1.64 (m, 8H), 1.48–1.36 (m, 4H), 1.33–1.15 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.44, 152.44 (d, $^1J_{^{13}C,^{31}P}$ = 7.9 Hz), 151.08 (d, $^1J_{^{13}C,^{31}P}$ = 3.9 Hz), 150.19 (d, $^1J_{^{13}C,^{31}P}$ = 2.4 Hz), 149.25, 146.27 (d, $^1J_{^{13}C,^{31}P}$ = 3.3 Hz), 146.16 (d, $^1J_{^{13}C,^{31}P}$ = 2.9 Hz), 123.60, 74.54, 55.58 (d, $^1J_{^{13}C,^{31}P}$ = 34.20 Hz), 49.52 (d, $^1J_{^{13}C,^{31}P}$ = 3.8 Hz), 48.45, 45.94 (d, $^1J_{^{13}C,^{31}P}$ = 12.8 Hz), 45.80 (d, $^1J_{^{13}C,^{31}P}$ = 14.3 Hz), 44.94 (d, $^1J_{^{13}C,^{31}P}$ = 1.6 Hz) ppm; ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 41.79 ppm; HRMS-ESI (from MeCN solution) m/z calcd for $C_{28}H_{38}AuPNO_2$: 648.2306; found 648.2286 $[M+MeCN-Cl]^+$.

Synthesis of cationic gold complexes 24e and 25: A mixture of [Au(L)Cl] complex (0.5 mmol) and $AgSbF_6$ (0.5 mmol) was suspended in MeCN (4 mL). The reaction mixture was stirred at 23°C for 12 h, the solvent was evaporated, and the crude product was dissolved in MeCN (1 mL). The mixture was then filtered through a pad of Celite, and the solvent was evaporated under reduced pressure to give the cationic complexes as white solids.

Complex 24e: Yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (m, 1H), 7.65–7.50 (m, 5H), 7.35–7.30 (m, 1H), 7.20 (m, 2H), 2.42 (s, 3H), 1.42 (d, $J_{^1H,^{31}P}$) = 16.3 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.00 (d, $J_{^{13}C,^{31}P}$ = 11.7 Hz), 142.36 (d, $J_{^{13}C,^{31}P}$ = 7.20 Hz), 133.22 (d, $J_{^{13}C,^{31}P}$ = 7.6 Hz), 133.04 (d, $J_{^{13}C,^{31}P}$ = 3.8 Hz), 131.43 (d, $J_{^{13}C,^{31}P}$ = 2.4 Hz), 129.44, 129.20, 127.99, 127.56 (d, $J_{^{13}C,^{31}P}$ = 7.8 Hz), 123.72 (d, $J_{^{13}C,^{31}P}$ = 53.2 Hz), 118.97, 38.00 (d, $J_{^{13}C,^{31}P}$ = 27.2 Hz), 30.77, 2.20 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 60.29 ppm; HRMS-ESI m/z calcd for $C_{22}H_{30}AuNP$: 536.1781; found 536.1791 $[M-SbF_6]^+$.

Complex 25: Yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.46 (m, 15H), 2.49 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.11 (d, $J_{^{13}C,^{31}P}$ = 13.2 Hz), 132.89 (d, $J_{^{13}C,^{31}P}$ = 2.9 Hz), 129.78 (d, $J_{^{13}C,^{31}P}$ = 12.44 Hz), 126.38 (d, $J_{^{13}C,^{31}P}$ = 66.55 Hz), 2.64 (one carbon signal was not observed) ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 32.36 ppm; HRMS-ESI m/z calcd for $C_{20}H_{18}AuNP$: 500.0842; found 500.0829 $[M-SbF_6]^+$.

***N*-Methyl-*N*′-(2,4,6-trimethylphenyl)imidazolium iodide**:[59] MeI (1.91 g, 13.5 mmol) was added dropwise to a solution of 1-(2,4,6-trimethyl)imidazole[60] (500 mg, 2.7 mmol) in THF (2 mL). The mixture was heated at reflux while the white product precipitated. After 48 h, the reaction mixture was filtered to give a white solid (1.98 mmol, 73%). The solid was used without any further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.86 (t, J = 1.8 Hz, 1H), 7.18 (t, J = 1.8 Hz, 1H), 6.99 (s, 2H), 4.36 (s, 3H), 2.33 (s, 3H), 2.08 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.39, 137.66, 134.25, 130.46, 129.85, 124.69, 123.07, 37.96, 21.06, 17.91 ppm; HRMS-EI: m/z calcd for $C_{13}H_{15}N_2I$: 327.0358; found 327.0359 $[M-1]^+$.

General procedure for the synthesis of NHC Au^I complexes 26a–c:[61] Ag_2O (0.5 mmol) was added to a solution of the imidazolium ligand (1 mmol)[62] in CH_2Cl_2. The suspension became clear after stirring for 3 h at 23°C. A solution of $[Au(Me_2S)Cl]$ (1 mmol) in CH_2Cl_2 was added dropwise, the reaction mixture was stirred for another 4 h, the solution was filtered through Celite, and the solvent was partially evaporated. Addition of hexane resulted in the precipitation of the NHC Au^I complex.

Complex 26a: Yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 (s, 2H), 6.97 (brs, 4H), 2.33 (s, 6H), 2.09 (s, 12H) ppm; ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 139.79, 134.68, 129.49, 122.12, 21.13, 17.75 (one signal is missing) ppm; HRMS-FAB: *m/z* calcd for $C_{21}H_{26}AuN_2Cl$: 537.1372; found 537.1361 $[M+H]^+$. This complex has been also described by Nolan et al.[24]

Complex 26b: Yield 60%. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.14 (d, J = 2.0 Hz, 1H), 6.95 (brs, 2H), 6.88 (d, J = 2.0 Hz, 1H), 3.95 (s, 3H), 2.32 (s, 3H), 2.00 (s 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.69, 139.71, 134.80, 134.69, 129.45, 122.18, 121.69, 38.37, 21.12, 17.85 ppm; HRMS-ESI: *m/z* calcd for $C_{13}H_{18}AuN_2Cl$: 433.0746; found 433.0739 $[M+H]^+$.

Complex 26c: ^1H NMR (400 MHz, $CDCl_3$): δ = 6.92 (brs, 2H), 3.82 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.32, 121.72, 38.19 ppm; HRMS-ESI (from MeCN solution) *m/z* calcd for $C_7H_{11}AuN_3$: 334.0619; found 334.0623 $[M+MeCN-Cl]^+$.

General procedures for Au^I-catalyzed intermolecular alkoxycyclization: The protic acid (6 mol%) was added to a mixture of the enyne (0.2–0.5 mmol) and gold(I) catalyst [Au(PPh$_3$)Me] (3 mol%) in the stated solvent (3–5 mL of MeOH, EtOH, or aqueous acetone) and the mixtures were stirred under the conditions stated in Tables 1 and 2 and Scheme 3. The resulting mixture was filtered through Celite, the solvent was evaporated, and the residue was chromatographed (hexane/EtOAc) to give the corresponding carbo- or heterocycle. Alternatively, complex [Au(L)Cl] and a Ag^I salt or the corresponding cationic Au^I complex were used as the catalyst (Tables 4 and 5 and Scheme 4). Routinely, synthetic grade MeOH or EtOH (>99.8% purity) were used as solvents, without further drying.

General procedure for Au^I-catalyzed intramolecular alkoxycyclization or skeletal rearrangement of enynes: The enyne (0.10–0.50 mmol) in CH_2Cl_2 (1 mL) was added to a mixture of [Au(PPh$_3$)Cl] (2 mol%) and silver(I) salt (2 mol%) (or the corresponding cationic Au^I complex) in CH_2Cl_2 (2 mL) and the mixture was stirred for the time and at the temperature indicated in Schemes 5–7 and Tables 6 and 7. The resulting mixture was filtered through SiO_2 and the solvent was evaporated to give the corresponding product.

General procedure for Fe^{III}-catalyzed skeletal rearrangement of enynes: The same procedure was followed but with $FeCl_3$ (5 mol%) as catalyst in toluene at 80–90°C (Table 8).

Dimethyl 3-(1-ethoxy-1-methylethyl)-4-methylenecyclopentane-1,1-dicarboxylate (2b): Colorless oil: ^1H NMR (300 MHz, $CDCl_3$): δ = 4.97 (brd, J = 8.9 Hz, 2H), 3.70 (s, 3H), 3.69 (s, 3H), 3.37 (m, 2H), 2.92–2.78 (m, 3H), 2.51 (ddd, J = 13.3, 8.1, 1.6 Hz, 1H), 2.00 (dd, J = 13.3, 9.3 Hz, 1H), 1.16 (s, 3H), 1.10 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.01, 171.90, 148.34, 110.33, 76.41, 58.54, 56.19, 52.63, 49.47, 43.39, 36.01, 23.23, 22.59, 15.84 ppm; EI-HMRS calcd for $C_{15}H_{23}O_4$: 283.1545; found 283.1544 $[M-1]^+$.

Bicyclic lactone 3: Colorless oil: ^1H NMR (500 MHz, $CDCl_3$): δ = 5.17 (dd, J = 2.0, 1.9 Hz, 1H), 5.14 (dd, J = 3.1, 2.6 Hz, 1H), 3.82 (s, 3H), 2.98 (dt, J = 17.9, 2.5 Hz, 1H), 2.77 (dd, J = 17.9, 1.5 Hz, 1H), 2.67 (d, J = 5.0 Hz, 1H), 2.62 (dd, J = 12.3, 1.8 Hz, 1H), 2.04 (dd, J = 12.3, 5.1 Hz, 1H), 1.53 (s, 3H), 1.41 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.45, 170.40, 144.73, 112.20, 84.91, 56.41, 52.71, 50.81, 37.89, 33.39, 27.84, 27.51 ppm; EI-HMRS calcd for $C_{12}H_{16}O_4$: 224.1048; found 224.1038. The structure was confirmed by COSY, NOESY, HMBC, and HMQC experiments.

(3*R)-Dimethyl 3-[(1*R**)-1-ethoxy-1,5-dimethyl-4-hexenyl]-4-methylenecyclopentane-1,1-dicarboxylate (13b)**: Colorless oil: ^1H NMR (300 MHz, $CDCl_3$): δ = 5.10 (m, 1H), 5.00 (s, 1H), 4.89 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.35 (m, 2H), 2.96–2.82 (m, 4H), 2.77–2.50 (m, 1H), 2.15 (ddd, J = 14.5, 8.9, 7.9 Hz, 1H), 2.09–1.95 (m, 2H), 1.66 (s, 2H), 1.60 (s, 2H), 1.12 (t, J = 6.9 Hz, 3H), 1.02 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.13, 171.96, 148.65, 131.28, 124.63, 110.40, 78.03, 58.58, 56.01, 52.62, 48.25, 43.76, 35.68, 35.25, 25.66, 22.32, 19.96, 17.58, 15.73 ppm; EI-HRMS calcd for $C_{20}H_{32}O_5$: 352.2250; found 352.2251.

Carbocycle 13c: ^1H NMR (300 MHz, $CDCl_3$): δ = 5.05 (brs, 2H), 4.92 (s, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 2.84 (m, 2H), 2.66 (tq, J = 8.0, 2.0 Hz, 1H), 2.55 (m, 2H), 2.13–1.95 (m, 2H), 1.64 (s, 3H), 1.58 (s, 3H), 1.47 (td, J = 8.9, 1.6 Hz, 2H), 1.16 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.91, 148.45, 134.23, 131.95, 129.29, 74.71, 58.65, 52.71, 51.51, 43.67, 38.68, 35.42, 25.69, 24.65, 22.45, 17.66 ppm; HMRS-CI: *m/z* calcd for $C_{18}H_{27}O_5$: 323.1858; found 323.1860 $[M-1]^+$.

3-(1-Methoxy-1,5-dimethyl-4-hexenyl)-4-methylene-1,1-bis(phenylsulfonyl)cyclopentane (15): White solid: ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07–8.01 (m, 4H), 7.72–7.66 (m, 2H), 7.60–7.53 (m, 4H), 5.10 (m, 1H), 4.97 (s, 1H), 4.92 (s, 1H), 3.48 (dq, J = 17.0, 2.8 Hz, 1H), 3.08 (s, 3H), 2.72 (m, 4H), 1.95 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.56 (m, 2H), 1.04 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.21, 135.98, 134.57, 134.39, 131.61, 131.04, 124.11, 110.98, 91.89, 76.57, 48.89, 48.72, 40.84, 34.91, 32.80, 25.63, 21.69, 19.01, 17.61 ppm; HRMS-CI *m/z* calcd for $C_{27}H_{34}O_4S_2$: 485.1820; found 485.1797 $[M-OH]^+$.

Dimethyl 3-[methoxy(4-methoxyphenyl)methyl]-4-methylenecyclopentane-1,1-dicarboxylate (30): Colorless oil: ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.18 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.90 (brs, 1H), 4.46 (brs, 1H), 4.08 (d, J = 6.3 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.67 (s, 3H), 3.16 (s, 3H), 2.99–2.93 (m, J = 16.0, 2.4 Hz, 1H), 2.90–2.84 (m, 2H), 2.48 (dd, J = 13.5, 8.0 Hz, 1H), 2.30 (dd, J = 13.5 Hz, 8.9 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz; DEPT): δ = 172.11, 172.08, 159.11, 148.36, 132.62, 128.47, 113.60, 108.69, 85.36, 58.59, 56.88, 55.22, 52.65, 49.29, 42.06, 35.76 ppm; HRMS-ESI: *m/z* calcd for $C_{19}H_{24}O_6Na$: 371.1471; found 371.1456 $[M+Na]^+$.

Dimethyl 2-((*E*)-3-(4-nitrophenyl)allyl)-2-(2-oxopropyl)malonate (32): Yellow solid: ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.14 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.45 (d, J = 15.8 Hz, 1H), 6.28 (q, J = 15.6, 7.7 Hz, 1H), 3.74 (s, 6H), 3.14 (s, 2H), 2.97 (d, J = 7.6 Hz, 2H), 2.12 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz; DEPT): δ = 204.89, 170.54, 147.10, 143.20, 132.06, 129.94, 126.75, 124.01, 55.27, 52.93, 46.13, 37.28, 30.27 ppm; IR (KBr): $\tilde{\nu}$ = 1740, 1709 cm^{-1}; HRMS-ESI: *m/z* calcd for $C_{17}H_{19}NO_7Na$: 372.1059; found 372.1061 $[M+Na]^+$. The structure of **32** was confirmed by COSY, NOESY, HMQC, and HMBC experiments. Isomer **32′** was also obtained as a byproduct (ca. 5:1 **32**/**32′** ratio) that could not be separated from **32**: ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.18 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 11.8 Hz, 1H), 5.71, (dt, J = 11.8, 7.4 Hz, 1H), 3.69 (s, 6H), 3.11 (s, 2H), 3.08 (d, J = 7.6 Hz, 2H), 2.03 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.89, 170.54, 147.10, 143.20, 132.06, 129.94, 126.75, 124.01, 55.27, 52.93, 46.13, 37.28, 30.27 ppm. Recovered enyne **31** was also contaminated with **31′** (ca. 5:1 **31**/**31′** ratio): ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.19 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 11.9 Hz, 1H), 5.68 (dt, J = 11.8, 7.5 Hz, 1H), 3.70 (s, 6H), 3.09 (d, J = 7.5 Hz, 2H), 2.81 (d, J = 2.6 Hz, 2H), 1.85 (t, J = 2.7 Hz, 1H).

Tricycle 34: Yellow oil: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.30 (m, 5H), 5.00 (s, 1H), 4.76 (s, 1H), 4.71 (s, 1H), 4.04 (s, 1H), 2.53 (d, J = 4.05 Hz, 1H), 1.69–1.31 (m, 12H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 149.36 (C), 142.74 (C), 127.81 (CH), 127.09 (CH), 125.94 (CH), 102.88 (CH_2), 83.07 (CH), 82.74 (CH), 48.79 (CH), 43.11 (C), 41.71 (CH_2), 35.78 (CH_2), 33.02 (CH_2), 26.02 (CH_2), 23.23 (CH_2), 22.25 (CH_2) ppm; HRMS-EI: *m/z* calcd for $C_{18}H_{22}O$: 254.1671; found 254.1663. The structure of **34** was confirmed by COSY, NOESY, HMBC, and HMQC experiments.

Dimethyl 4-methylene-3-(2-methyltetrahydrofuran-2-yl)cyclopentane-1,1-dicarboxylate (41): Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.02 (q, J = 2.0 Hz, 2H), 3.84–3.74 (m, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 2.93–2.80 (m, 3H), 2.62 (dd, J = 13.2, 8.6 Hz, 1H), 2.01–1.52 (m, 4H), 1.13 (s, 3H) ppm; ^{13}C NMR, DEPT (75 MHz, $CDCl_3$): δ = 171.92 (2 C), 148.29 (C), 110.34 (CH_2), 84.99 (C), 67.23 (CH_2), 58.48 (C), 52.67 (CH_3), 52.63 (CH_3), 50.53 (CH), 43.29 (CH_2), 36.82 (CH_2), 34.90 (CH_2), 26.02 (CH_2), 23.87 (CH_3) ppm; HRMS-ESI: *m/z* calcd for $C_{15}H_{22}O_5Na$: 305.1365; found 305.1361 $[M+Na]^+$. The structure of **41** was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 3-(2,5-dimethyltetrahydrofuran-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (42a/42b): Colorless oil. ^1H NMR (500 MHz, $CDCl_3$): 5.06 (m, 1H (major)), 5.01 (m, 3H (2H minor, 1H major)), 4.09–4.00 (m, 2H (both)), 3.71 (s, 3H), 3.701 (s, 6H), 3.699 (s, 3H), 2.93–2.83 (m, 5H (2H major, 3H minor)), 2.78 (ddq, J = 9.7, 8.2, 1.9 Hz, 1H (major)), 2.69–2.59 (m, 2H (1H major, 1H minor)), 2.04–1.83 (m, 6H (3H major, 3H minor), 1.74 (ddd, J = 12.0, 7.7, 2.4 Hz, 1H (minor)), 1.63 (dt, J = 12.4, 8.2 Hz, 1H (major)), 1.59–1.50 (m, J = 10.5, 9.4, 7.8 Hz, 1H

(minor)), 1.45 (ddt, J = 12.1, 9.6, 7.9 Hz, 1H (major)), overlapping 1.20 (d, J = 5.0 Hz, 3H minor) and 1.19 (d, J = 5.0 Hz, 3H major), 1.15 (s, 6H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$): δ = 171.99 (2 C), 171.94 (2 C), 148.44 (C), 148.09 (C), 110.59 (CH_2), 110.42 (CH_2), 85.26 (C), 85.07 (C), 75.62 (CH), 73.67 (CH), 58.56 (C), 58.50 (C), 52.71 (2×CH_3), 52.67 (2×CH_3), 50.75 (2×CH), 43.50 (CH_2), 43.47 (CH_2), 36.90 (CH_2), 36.84 (CH_2), 35.96 (CH_2), 34.99 (CH_2), 33.82 (CH_2), 33.75 (CH_2), 25.62 (CH_3), 24.35 (CH_3), 22.08 (CH_3), 21.03 (CH_3) ppm; HRMS-ESI: m/z calcd for $C_{16}H_{25}O_5Na$: 319.1545; found 319.1536 $[M+Na]^+$. The structures of **42a/42b** were confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 3-(5-*tert*-butyl-2-methyltetrahydrofuran-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (43a/43b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.02–5.04 (q, J = 2.02 Hz, 2H), 4.99–5.01 (m, J = 1.1 Hz, 1H), 4.93–4.95 (m, J = 1.1 Hz, 1H), 3.721 (s, 3H), 3.717 (s, 3H), 3.713 (s, 3H), 3.711 (s, 3H), 3.55–3.62 (m, 2H), 2.74–2.96 (m, 6H), 2.63–2.71 (ddd, J = 1.9, 8.5, 13.4 Hz, 1H), 2.56–2.63 (m, 1H), 2.04–2.11 (dd, J = 9.1, 13.4 Hz, 1H), 1.88–1.95 (dd, J = 9.7, 13.4 Hz, 1H), 1.60–1.85 (overlapping m, 8H), 1.127 (s, 3H), 1.101 (s, 3H), 0.86 (s, 9H), 0.85 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.09, 172.00, 171.99, 171.97, 148.57, 148.52, 110.56, 110.01, 87.93, 85.27, 84.51, 83.97, 58.58, 58.55, 52.66, 52.64 (2 C), 52.59, 51.14, 50.73, 43.56, 43.37, 36.83, 36.14 (2 C), 35.20, 33.58, 33.07, 26.42(2 C), 25.94 (3 C), 25.83, 25.81 (3 C), 25.41 ppm; HRMS-EI: m/z calcd for $C_{19}H_{31}O_5$: 339.2171; found 339.2171.

Dimethyl 3-(2-methyl-5-vinyltetrahydrofuran-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (44a/44b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (dtd, J = 17.0, 10.2, 6.8 Hz, 2H), 5.22 (dddd, J = 17.1, 9.3, 1.6, 1.2 Hz, 2H), 5.10–5.00 (overlapping m, 6H), 4.36 (m, J = 6.8 Hz, 2H), 3.720 (s, 6H), 3.717 (s, 6H), 2.97–2.80 (overlapping m, 6H), 2.73–2.60 (overlapping m, 2H), 2.15–1.85 (overlapping m, 6H), 1.82–1.60 (overlapping m, 4H), 1.19 (s, 3H), 1.18 (s, 3H) ppm; ^{13}C NMR, DEPT (100 MHz, $CDCl_3$): δ = 171.91 (4 C), 148.33 (C), 148.11 (C), 140.15 (CH), 139.10 (CH), 115.16 (2×CH_2), 110.55 (CH_2), 110.52 (CH_2), 85.81 (C), 85.44 (C), 80.75 (CH), 78.92 (CH), 58.52 (2 C), 52.69 (2×CH_3), 52.65 (2×CH_3), 50.84 (CH), 50.74 (CH), 43.44 (CH_2), 43.41 (CH_2), 36.93 (CH_2), 36.80 (CH_2), 35.43 (CH_2), 35.24 (CH_2), 32.64 (CH_2), 32.49 (CH_2), 25.29 (CH_3), 23.84 (CH_3) ppm; HRMS-ESI: m/z calcd for $C_{17}H_{24}O_5Na$: 331.1521; found 331.1508 $[M+Na]^+$. The structures of **44a/44b** were confirmed by COSY, NOESY, HMBC, and HMQC experiments.

Dimethyl 3-(2-methyl-5-phenyltetrahydrofuran-2-yl)-4-methylenecyclopentane-1,1-dicarboxylate (45a/45b): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.28 (m, 8H; both isomers), 7.26–7.21 (m, 2H; both isomers), 5.12–5.07 (m, 2H; major isomer), 5.06–5.02 (m, 2H; minor isomer), 4.98–4.91 (m, 2H; both isomers), 3.74 (s, 3H; minor isomer), 3.730 (s, 3H; major isomer), 3.727 (s, 3H; minor isomer), 3.71 (s, 3H; major isomer), 3.04–2.87 (m, 6H; both isomers), 2.83–2.75 (ddd, J = 13.4, 8.3, 2.1 Hz, 1H (minor isomer)), 2.70 (ddd,, J = 13.4, 8.3, 1.0 Hz, 1H; major isomer), 2.39–2.26 (m, 2H; both isomers), 2.18–1.78 (m, 8H; both isomers), 1.32 (s, 3H; major isomer), 1.29 (s, 3H; minor isomer) ppm; ^{13}C NMR, DEPT (100 MHz, $CDCl_3$): δ = 171.99 (2 C), 171.92 (2 C), 148.39 (C), 148.27 (C), 143.41 (C), 142.72 (C), 128.29 (2×CH), 128.23 (2×CH), 127.16 (CH), 127.14 (CH), 125.91 (2×CH), 125.76 (2×CH), 110.76 (CH_2), 110.49 (CH_2), 86.05 (C), 85.32 (C), 81.57 (CH), 79.24 (CH), 58.58 (C), 58.56 (C), 52.73 (2×CH_3), 52.67 (2×CH_3), 51.12 (CH), 50.87 (CH), 43.53 (CH_2), 43.47 (CH_2), 37.00 (CH_2), 36.60 (CH_2), 36.20 (CH_2), 35.95 (CH_2), 35.32 (CH_2), 35.03 (CH_2), 25.36 (CH_3), 23.15 (CH_3) ppm; HRMS-EI: m/z calcd for $C_{21}H_{26}O_5$: 358.1780; found 358.1773. The structures of **45a/45b** were confirmed by COSY, NOESY, HMQC, and HMBC experiments.

Dimethyl 3-[5-(2-hydroxypropan-2-yl)-4-methylene-2-methyltetrahydrofuran-2-yl]cyclopentane-1,1-dicarboxylate (46a/46b): Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.06 (m, 2H), 5.02 (m, 1H), 4.94 (m, 1H), 3.78–3.71 (overlapping m, 2H), 3.73 (s, 6H), 3.72 (s, 3H), 3.71 (s, 3H), 2.98–2.74 (m overlapping qt, J = 15.0, 2.4 Hz and qt, J = 8.3, 1.6 Hz, 6H), 2.70 (ddd, J = 13.1, 8.7, 1.5 Hz, 1H), 2.61 (dd, J = 13.0, 8.3 Hz, 1H), 2.10 (dd, J = 13.3, 8.3 Hz, 2H), 1.97–1.66 (m, 10H), 1.23 (s, 3H), 1.19 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 1.10 (s, 3H), 1.09 (s, 3H) ppm; ^{13}C NMR, DEPT (125 MHz, $CDCl_3$): δ = 172.35 (C), 171.99 (C), 171.95 (2 C), 149.01 (C), 148.34 (C), 110.86 (CH_2), 110.72 (CH_2), 86.56 (CH), 85.47 (C), 84.86 (C), 83.94 (CH), 71.33 (C), 70.32 (C), 58.67 (C), 58.56 (C), 52.88 (2×CH_3), 52.77 (2×CH_3), 50.89 (CH), 50.87 (CH), 43.53 (CH_2), 43.48 (CH_2), 36.80 (CH_2), 36.12 (CH_2), 35.38 (CH_2), 35.25 (CH_2), 27.73 (CH_3), 27.64 (CH_3), 26.14 (CH_2), 25.67 (CH_2), 25.43 (CH_3), 24.76 (CH_3), 24.04 (CH_3), 22.71 (CH_3) ppm; HRMS-ESI: m/z calcd for $C_{18}H_{28}O_6Na$: 363.1784; found 363.1780 $[M+Na]^+$. The structures of **46a/46b** were confirmed by COSY, NOESY, HMBC, and HMQC experiments.

Dimethyl 3-((*Z*)-3-hydroxy-2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (55): Yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85 (brs, 1H), 5.44 (brs, 1H), 4.25 (s, 2H), 3.73 (s, 6H), 3.14 (brs, 2H), 3.05 (s, 2H), 1.88 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.44, 140.02, 137.80, 126.79, 123.29, 62.38, 59.37, 52.90, 43.10, 40.39, 22.19 ppm; HRMS-EI: m/z calcd for $C_{13}H_{17}O_5$: 253.1076; found 253.1070 $[M-1]^+$.

Dimethyl 3-((*Z*)-2,6-dimethylhepta-1,5-dienyl)cyclopent-3-ene-1,1-dicarboxylate (57): Pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.73 (s, 1H), 5.38 (s, 1H), 5.12 (tsext, J = 8.7, 1.4 Hz, 1H), 3.73 (s, 6H), 3.16 (d, J = 1.8 Hz, 2H), 3.03 (s, 2H), 2.20 (m, 2H), 2.13 (m, 2H), 1.77 (s, 3H), 1.68 (d, J = 1.0 Hz, 3H), 1.60 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 172.59 (C), 139.42 (C), 138.48 (C), 131.82 (C), 124.58 (CH), 123.92 (CH), 121.04 (CH), 59.37 (C), 52.79 (CH_3), 43.13 (CH_2), 40.23 (CH_2), 33.37 (CH_2), 27.05 (CH_2), 25.67 (CH_3), 24.66 (CH_3), 17.63 (CH_3). HMRS-ESI: m/z calcd for $C_{18}H_{26}O_4$: 306.1831; found 306.1824. The structure of **57** was confirmed by a NOESY experiment.

Dimethyl (*E*)-5-benzylidenecyclohex-3-ene-1,1-dicarboxylate (61): Yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.19 (m, 5H), 6.60 (d, J = 10.1 Hz, 1H), 6.34 (brs, 1H), 5.87 (m, 1H), 3.73 (s, 6H), 2.95 (d, J = 1.4 Hz, 2H), 2.76 (dd, J = 4.2, 2.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.35, 137.08, 131.15, 129.17, 128.11, 128.02, 127.59, 126.67, 125.08, 52.76, 52.71, 37.69, 31.90 ppm; HRMS-ESI: m/z calcd for $C_{17}H_{18}O_4Na$: 286.1205; found 309.1092 $[M+Na]^+$.

Dimethyl 3-((*E*)-4-methoxystyryl)cyclopent-3-ene-1,1-dicarboxylate (64): Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.17 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 12.0 Hz, 1H), 6.14 (d, J = 12.0 Hz, 1H), 5.63 (brs, 1H), 3.81 (s, 3H), 3.70 (s, 6H), 3.02 (brs, 2H), 2.86 (brs, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.32, 158.77, 138.42, 130.19, 130.08, 128.41, 124.82, 133.35, 59.34, 55.41, 52.92, 42.13, 40.31 ppm; HRMS-ESI: m/z calcd for $C_{18}H_{20}O_5$: 339.1208; found 339.1222. The structure of **64** was confirmed by HMQC, HMBC, COSY, and NOESY experiments.

Dimethyl 5-((*Z*)-4-methoxybenzylidene)cyclohex-3-ene-1,1-dicarboxylate (63): Colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.17 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.6 (d, J = 10.1 Hz, 1H), 6.28 (brs, 1H), 5.86–5.81 (m, 1H), 3.76 (s, 3H), 3.72 (6H), 2.94 (brd, J = 1.4 Hz, 2H), 2.76–2.75 (brm, 2H) ppm; HRMS-ESI: m/z calcd for $C_{18}H_{20}O_5$: 339.1208; found 339.1222. The structure of **63** was confirmed by HMQC, HMBC, COSY, and NOESY experiments.

Dimethyl 3-((*E*)-4-nitrostyryl)cyclopent-3-ene-1,1-dicarboxylate (66): Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.16 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 15.7 Hz, 1H), 6.47 (d, J = 16.1 Hz, 1H), 5.86 (brs, 1H), 3.77 (s, 6H), 3.27 (brs, 2H), 3.19 (brs, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 172.05, 146.81, 146.21, 143.63, 139.21, 131.09, 130.79, 127.71, 126.75, 58.4, 53.02, 41.19, 39,39 ppm; HRMS-ESI: m/z calcd for $C_{17}H_{17}NO_6Na$: 354.0954; found 354.0955 $[M+Na]^+$. The structure of **66** was confirmed by HMQC, HMBC, COSY, and NOESY experiments.

Dimethyl 5-((*Z*)-4-nitrobenzylidene)cyclohex-3-ene-1,1-dicarboxylate (65): Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 6.54 (d, J = 10.1 Hz, 1H), 6.35 (brs, 1H), 6.03–5.98 (m, J = 10.1 Hz, 1H), 3.74 (s, 6H), 2.99 (d, J = 1.5 Hz, 2H), 2.81–2.80 (brm, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.94, 145.96, 134.95, 130.68, 129.68, 125.26, 124.21, 123.63, 53.91, 52.94, 37.73, 31.72 (one signal is missing due to overlapping) ppm; HRMS-ESI: m/z calcd for $C_{17}H_{17}NO_6Na$: 354.0954; found 354.0955 $[M+Na]^+$. The structure of **65** was confirmed by HMQC, HMBC, COSY, and NOESY experiments.

3-(Prop-2-ylidene)-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine (70): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.37 (dt, J = 10.3, 2.1 Hz, 1H), 5.55 (dt, J = 10.3, 3.5 Hz, 1H), 3.93 (s, 2H), 3.80 (s, 2H), 2.45 (s, 3H), 1.80 (s, 3H), 1.71 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 143.26 (C), 134.19 (C), 129.84 (C), 129.69 (C), 129.26 (CH), 127.63 (CH), 124.43 (CH), 120.84 (CH), 44.98 (CH_2), 44.96 (CH_2), 21.43 (CH_3), 20.23 (CH_3), 19.55 (CH_3) ppm; HMRS-EI: m/z calcd for $C_{15}H_{19}NO_2S$: 277.1136; found 277.1145. The structure of **71** was confirmed by COSY, NOESY, HMBC, and HMQC experiments.

3-Ethylidene-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine (72a): Viscous, yellow oil: Isomer mixture, E/Z 4:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (dd, J = 8.3, 3.0 Hz, 2H; minor isomer), 7.67 (d, J = 8.3 Hz, 2H; major isomer), 7.32 (dd, J = 8.5, 4.0 Hz, 2H; minor), 7.28 (d, J = 8.3 Hz, 2H; major), 6.30 (dt, J = 10.1, 3.4 Hz, 1H), 5.60 (m, 1H), 5.29 (q, J = 7.6 Hz, 1H), 3.70 (t, J = 2.4 Hz, 2H), 3.65 (t, J = 1.2 Hz, 2H), 2.32 (s, 3H; minor), 2.33 (s, 3H; major), 1.63 (d, J = 7.2 Hz, 3H; minor), 1.59 (d, J = 7.3 Hz, 3H; major) ppm; ^{13}C NMR (125 MHz, $CDCl_3$; DEPT; major isomer): δ = 143.49 (C), 137.14 (C), 133.77 (C), 129.54 (CH), 127.86 (CH), 123.60 (CH), 122.87 (CH), 122.72 (CH), 49.67 (CH_2), 45.72 (CH_2), 21.53 (CH_3), 12.45 (CH_3) ppm; HRMS-EI: m/z calcd for $C_{14}H_{17}NO_2S$: 263.0980; found 263.0984. The structure of **73a** was confirmed by COSY, HMBC, HMQC, and NOESY experiments (major E isomer).

7-Methyl-3-(toluene-4-sulfonyl)-3-azabicyclo[4.1.0]hept-4-ene (74a): Isomer mixture, 10:1; white solid: mp 96–98 °C (major isomer); colorless oil (minor isomer); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.2 Hz, 2H; minor isomer), 7.67 (d, J = 8.2 Hz, 2H; minor), 7.63 (d, J = 8.3 Hz, 2H; major isomer), 7.30 (d, J = 7.9 Hz, 2H; major), 6.63 (d, J = 8.5 Hz, 1H; minor), 6.28 (d, J = 8.1 Hz, 1H; major), 5.40 (dd, J = 8.1, 5.4 Hz, 1H; major), 5.03 (dd, J = 7.5, 4.2 Hz, 1H; minor), 4.08 (d, J = 2.5 Hz, 1H; minor), 3.88 (d, J = 11.5 Hz, 1H), 3.35 (dd, J 12.0, 5.6 Hz, 1H; minor), 2.94 (dd, J = 11.5, 3.0 Hz, 1H; major), 2.43 (s, 3H; minor), 2.42 (s, 3H; major), 1.23–1.20 (m, 1H; major), 0.96 (d, J = 6.1 Hz, 3H; major), 0.85–0.82 (m, 1H), 0.74 (d, J = 5.6 Hz, 3H; minor), 0.72–0.68 (m, 1H; major) ppm; ^{13}C NMR (125 MHz, $CDCl_3$; DEPT; major isomer): δ = 143.59 (C), 134.88 (C), 129.70 (CH), 127.21 (CH), 120.74 (CH), 111.85 (CH), 40.73 (CH_2), 26.39 (CH), 21.72 (CH), 21.55 (CH_3), 17.44 (CH_3), 15.46 (CH) ppm; HRMS-EI: m/z calcd for $C_{14}H_{17}NO_2S$: 263.0980; found 263.0992.

3-Ethylidene-6-methyl-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine (72b) and 2-methyl-4-propenyl-1-(toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole (73b): Compound **72b**: Orange solid: mp 65–67 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.18 (dd, J = 10.2, 0.8 Hz, 1H), 5.56 (s, 1H), 5.30 (q, J = 7.0 Hz, 1H), 4.47 (quint, J = 6.5 Hz, 1H), 4.23 (d, J = 15.6 Hz, 1H), 3.88 (dt, J = 15.8, 2.0 Hz, 1H), 2.41 (s, 3H), 1.56 (dd, J = 7.1, 2.0 Hz, 3H), 1.34 (d, J = 6.8 Hz, 3H) ppm. Compound **73b**: vitreous solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 6.07 (d, J = 15.9 Hz, 1H), 5.56 (m, 1H), 5.35 (br s, 1H), 4.51 (quint, J = 5.8 Hz, 1H), 4.30 (ddd, J = 13.6, 4.7, 1.7 Hz, 1H), 4.14 (m, 1H), 2.44 (s, 3H), 1.78 (d, J = 6.8 Hz, 3H), 1.44 (d, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$; DEPT): δ = 143.33 (C), 142.82 (C), 137.26 (C), 135.37 (C), 134.87 (C), 129.73 (CH; *endo*), 129.48 (CH; *exo*), 128.98 (CH; *endo*), 127.48 (CH; *endo*), 127.43 (CH; *exo*), 126.43 (CH; *exo*), 126.65 (CH; *exo*), 122.52 (CH; *exo*), 121.62 (CH; *exo*), 63.14 (CH; *exo*), 54.42 (CH_2; *exo*), 50.63 (CH; *endo*), 44.91 (CH_2; *exo*), 22.86 (CH_3; *exo*), 21.52 (CH_3), 21.48 (CH_3), 19.96 (CH_3; *endo*), 18.39 (CH_3; *exo*), 12.19 (CH_3; *endo*) ppm; HRMS-EI: m/z calcd for $C_{15}H_{19}NO_2S$ (mixture of): 277.1136; found 277.1133. The structures of **73b**/**74b** were confirmed by COSY, HMBC, HMQC, and NOESY experiments.

2,7-Dimethyl-3-(toluene-4-sulfonyl)-3-azabicyclo[4.1.0]hept-4-ene (74b): White solid: mp 167–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.07 (dm, J = 7.7 Hz, 1H), 5.50 (dd, J = 7.8, 5.6 Hz, 1H), 4.27 (q, J = 6.4 Hz, 1H), 2.42 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H), 1.07 (ddd, J = 8.4, 5.0, 1.4 Hz, 1H), 0.83 (m, 1H), 0.79 (d, J = 6.0 Hz, 3H), 0.00 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 143.16 (C), 136.33 (C), 129.52 (CH), 126.67 (CH), 117.41 (CH), 114.83 (CH), 46.21 (CH), 36.12 (CH), 22.22 (CH), 21.45 (CH_3), 20.44 (CH_3), 17.20 (CH_3), 15.29 (CH) ppm; HRMS-EI: m/z calcd for $C_{15}H_{19}NO_2S$: 277.1136; found 277.1144. The structure of **75b** was confirmed by COSY, HMBC, HMQC, and NOESY experiments and by selective NOE experiments (irradiation on signals at 4.27 and 0.00 ppm).

3-((*E*)-Benzylidene)-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine (80): White solid: mp 57–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.3 Hz, 2H), 7.38–7.25 (m, 5H), 7.11 (d, J = 6.7 Hz, 2H), 6.54 (dt, J = 10.1, 2.4 Hz, 1H), 6.37 (s, 1H), 5.78 (dtd, J = 10.1, 3.4, 1.6 Hz, 1H), 4.01 (d, J = 1.2 Hz, 2H), 3.95 (t, J = 3.2 Hz, 2H), 2.44 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 135.89 (C), 134.31 (C), 129.48 (C), 129.00 (CH), 128.87 (C), 128.10 (CH), 127.74 (CH), 127.09 (CH), 127.02 (CH), 126.00 (CH), 124.08 (CH), 49.78 (CH_2), 45.85 (CH_2), 21.43 (CH_3) ppm; HRMS-EI calcd for $C_{19}H_{19}NO_2S$: 325.1136; found 325.1136. The structure of **80** was confirmed by COSY, HMBC, HMQC, and NOESY experiments.

3-(1,5-Dimethylhex-4-enylidene)-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridine (83): Viscous, colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.33 (dt, J = 10.3, 2.2 Hz, 1H), 5.54 (dt, J = 10.3, 3.7 Hz, 1H), 5.10 (tq, J = 5.7, 1.4 Hz, 1H), 3.87 (q, J = 1.2 Hz, 2H), 3.74 (td, J = 2.9, 0.5 Hz, 2H), 2.40 (s, 3H), 2.16–2.04 (m, 4H), 1.69 (d, J = 0.6 Hz, 3H), 1.67 (d, J = 1.0 Hz, 3H), 1.60 (dd, J = 1.40, 0.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 143.27 (C), 134.05 (C), 133.85 (C), 132.33 (C), 129.29 (CH), 127.66 (CH), 124.68 (CH), 123.46 (CH), 122.69 (C), 121.27 (CH), 45.07 (CH_2), 44.78 (CH_2), 34.44 (CH_2), 26.52 (CH_2), 25.68 (CH_3), 21.44 (CH_3), 17.75 (CH_3), 17.56 (CH_3) ppm; HRMS-EI: m/z calcd for $C_{20}H_{27}NO_2S$: 345.1762; found 345.1769.

(1a*R,4a*S**,8*R**)-4-(Toluene-4-sulfonyl)-1,1a,4,4a,5,6,7,8-octahydrocyclopropa[*d*]quinoline (85)**: White solid: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.11 (d, J = 7.7 Hz, 1H), 5.50 (dd, J = 7.6, 5.4 Hz, 1H), 3.91 (dd, J = 11.2, 4.1 Hz, 1H), 2.41 (s, 3H), 1.83 (m, 1H), 1.78 (qd, J = 13.7, 3.78 Hz, 2H), 1.55 (m, 1H), 1.44 (m, 1H), 1.42 (sext.t, J = 13.2, 3.2 Hz, 1H), 1.22 (qt, J = 12.9, 3.5 Hz, 1H), 0.90 (t, J = 3.9 Hz, 1H), 0.92–0.85 (m, 1H), 0.33 (dd, J = 8.2, 4.2 Hz, 1H), −0.18 (t, J = 4.1 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$; DEPT): δ = 143.14 (C), 136.30 (C), 129.61 (CH), 126.60 (CH), 117.35 (CH), 115.08 (CH), 52.73 (CH), 36.36 (CH_2), 33.86 (C), 30.80 (CH_2), 25.40 (CH_2), 24.31 (CH_2), 21.51 (CH_2), 21.10 (CH), 15.32 (CH_3); EI-MS (m/z): 303.2 $[M]^+$; HRMS-EI: m/z calcd for $C_{17}H_{21}NO_2S$: 303.1293; found 303.1290; elemental analysis (%) calcd for $C_{17}H_{21}NO_2S$: C 67.29, H 6.98, N 4.62, S 10.57; found: C 66.97, H 7.82, N 4.52, S 10.77. The structure of **85** was confirmed by COSY and NOESY experiments.

1-(Toluene-4-sulfonyl)-2-vinyl-2,4,5,6,7,7a-hexahydro-1*H*-indole (86): Colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 6.43 (dd, J = 17.6, 10.9 Hz, 1H), 5.10 (d, J = 10.9 Hz, 1H) 4.95 (d, J = 17.4 Hz, 1H), 4.27 (dd, J = 12.5, 4.3 Hz, 1H), 4.12 (d, J = 14.9 Hz, 1H), 4.07 (m, 1H), 2.65 (d, J = 15.6 Hz, 1H), 2.52 (m, 1H), 2.42 (s, 3H), 1.80 (m, 3H), 1.39 (m, 2H), 1.22 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 143.32 (C), 138.61 (C), 129.73 (CH), 127.52 (CH), 125.21 (C), 115.08 (CH_2), 68.05 (CH), 54.74 (CH_2), 36.32 (CH_2), 26.08 (CH_2), 25.63 (CH_2), 23.99 (CH_2), 21.51 (CH_3) (two carbon signals overlap) ppm; EI-MS (m/z): 302.1 $[M-1]^+$.

Dimethyl 3-(2-methylprop-1-enyl)-cyclopent-2-ene-1,1-dicarboxylate (87): Colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.73 (m, 1H), 5.52 (m, 1H), 3.65 (s, 6H), 2.58 (td, J = 6.5, 1.9 Hz, 2H), 2.40 (m, 2H), 1.77 (d, J = 0.9 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$; DEPT): δ = 172.02 (2 C), 146.13 (C), 138.04 (C), 124.86 (CH), 120.69 (CH), 65.98 (C), 52.66 (CH_3), 52.72 (CH_3), 34.78 (CH_2), 32.14 (CH_2), 27.42 (CH_3), 20.51 (CH_3).

3-(2-Methyl-1-propenyl)-1,1-bis(phenylsulfonyl)cyclopent-3-ene (88): Pale orange solid: mp 139–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.3 Hz, 4H), 7.69 (tt, J = 6.9, 1.2 Hz, 2H), 7.55 (t, J = 6.8 Hz, 4H), 5.39 (s, 1H), 5.02 (s, 1H), 3.47 (s, 2H), 3.36 (s, 2H), 1.71 (s, 3H), 1.57 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 138.21 (C), 137.49 (C), 136.93 (C), 134.51 (CH), 130.82 (CH), 128.73 (CH), 122.73 (CH), 118.97 (CH), 91.44 (C), 41.30 (CH_2), 38.54 (CH_2), 27.05 (CH_3),

19.80 (CH_3) ppm; HRMS-CI *m/z* calcd for $C_{21}H_{22}O_4S_2$: 403.1045; found 403.1045 $[M+1]^+$.

3-(2-Methyl-1-propenyl)-1,1-bis(phenylsulfonyl)cyclopent-3-ene (89): Pale orange solid: mp 139–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.3 Hz, 4H), 7.69 (tt, J = 6.9, 1.2 Hz, 2H), 7.55 (t, J = 6.8 Hz, 4H), 5.39 (s, 1H), 5.02 (s, 1H), 3.47 (s, 2H), 3.36 (s, 2H), 1.71 (s, 3H), 1,57 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 138.21 (C), 137.49 (C), 136.93 (C), 134.51 (CH), 130.82 (CH), 128.73 (CH), 122.73 (CH), 118.97 (CH), 91.44 (C), 41.30 (CH_2), 38.54 (CH_2), 27.05 (CH_3), 19.80 (CH_3) ppm; HRMS-CI *m/z* calcd for $C_{21}H_{22}O_4S_2$: 403.1045; found 403.1045 $[M+1]^+$.

Dimethyl 3-methyl-5-methylenecyclohex-3-ene-1,1-dicarboxylate (91): Yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (s, 1H), 4.78 (s, 2H), 3.69 (s, 6H), 2.80 (s, 2H), 2.57 (s, 2H), 1.79 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$; DEPT): δ = 171.38 (C), 139.30 (C), 135.48 (C), 124.38 (CH), 111.05 (CH_2), 54.42 (C), 52.71 (CH_3), 35.64 (CH_2), 35.48 (CH_2), 23.34 (CH_3) ppm; HRMS-EI: *m/z* calcd for $C_{12}H_{16}O_4$: 224.1049; found 224.1048. The corresponding reaction of deuterated enyne [D_1]-**18** gave [D_1]-**91a** (Scheme 9), in which the signal at 4.78 ppm (1H) was not observed.

[Au(PPh$_3$)Cl]/AgSbF$_6$-catalyzed cyclization of [D$_1$]-75 (Scheme 9): Cyclization of the deuterated enyne [D_1]-**75** gave [D_1]-**76** and [D_1]-**78**. In [D_1]-**76** the olefinic hydrogen at 5.89 ppm was not observed [^{1}H NMR (300 MHz, $CDCl_3$) for **76**: δ = 7.68 (d, J = 7.7 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 5.89 (s, 1H), 4.81 (d, J = 8.7 Hz, 2H), 3.77 (s, 2H), 3.59 (s, 2H), 2.43 (s, 3H), 1.73 (s, 3H)]. In [D_1]-**78** the signal at 0.92 ppm (1H) was not observed [^{1}H NMR (300 MHz, $CDCl_3$): for **78**: δ = 7.65 (d, J = 84 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.28 (d, J = 7.9 Hz, 1H), 5.40 (dd, J = 7.9, 5.6 Hz, 1H), 3.84 (d, J = 11.3 Hz, 1H), 2.72 (dd, J = 11.3, 0.7 Hz, 1H), 2.42 8 s, 3H), 1.11 (s, 3H), 0.92 (m, 1H), 0.63 (ddd, J = 8.1, 4.4, 1.2 Hz, 1H), 0.56 (t, J = 4.4 Hz, 1H)].

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[1] Reviews: a) G. C. Lloyd-Jones, *Org. Biomol. Chem.* **2003**, *1*, 215–236; b) C. Aubert, O. Buisine, M. Malacria, *Chem. Rev.* **2002**, *102*, 813–834; c) S. T. Diver, A. Giessert, *J. Chem. Res.* **2004**, *104*, 1317–1382; d) A. M. Echavarren, M. Méndez, M. P. Muñoz, C. Nevado, B. Martín-Matute, C. Nieto-Oberhuber, D. J. Cárdenas, *Pure Appl. Chem.* **2004**, *76*, 453–463; e) A. M. Echavarren, C. Nevado, *Chem. Soc. Rev.* **2004**, *33*, 431–436; f) L. Añorbe, G. Domínguez, J. Pérez-Castells, *Chem. Eur. J.* **2004**, *10*, 4938–4943; g) C. Bruneau, *Angew. Chem.* **2005**, *117*, 2380–2386; *Angew. Chem. Int. Ed.* **2005**, *44*, 2328–2334.

[2] a) M. Méndez, M. P. Muñoz, A. M. Echavarren, *J. Am. Chem. Soc.* **2000**, *122*, 11549–11550; b) M. Méndez, M. P. Muñoz, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2001**, *123*, 10511–10520; c) M. P. Muñoz, M. Méndez, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Synthesis* **2003**, 2898–2902; d) M. P. Muñoz, J. Adrio, J. C. Carretero, A. M. Echavarren, *Organometallics* **2005**, *24*, 1293–1300.

[3] a) C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2003**, *9*, 2627–2635; b) C. Nevado, C. Ferrer, A. M. Echavarren, *Org. Lett.* **2004**, *6*, 3191–3194.

[4] a) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **2000**, *122*, 714–715; b) P. Cao, B. Wang, X. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 6490–6491.

[5] a) N. Chatani, T. Morimoto, T. Muto, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 6049–6050; b) N. Chatani, N. Furukawa, H. Sakurai, S. Murai, *Organometallics* **1996**, *15*, 901–903; c) N. Chatani, H. Inoue, T. Ikeda, S. Murai, *J. Org. Chem.* **2000**, *65*, 4913–4918.

[6] a) E. Soriano, P. Ballesteros, J. Marco-Contelles, *J. Org. Chem.* **2004**, *69*, 8018–8023; b) R.-X. He, M. Li, X.-Y. Li, *J. Mol. Struct.* **2005**, *717*, 21–32.

[7] Hydroxycyclization catalyzed by mercuric triflate: M. Nishizawa, V. K. Yadav, M. Skwarczynski, H. Takao, H. Imagawa, T. Sugihara, *Org. Lett.* **2003**, *5*, 1609–1611.

[8] C. Nevado, L. Charruault, V. Michelet, C. Nieto-Oberhuber, M. P. Muñoz, M. Méndez, M.-N. Rager, J.-P. Genêt, A. M. Echavarren, *Eur. J. Org. Chem.* **2003**, 706–713.

[9] J. Blum, H. Berr-Kraft, Y. Badrieh, *J. Org. Chem.* **1995**, *60*, 5567–5569.

[10] a) A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* **2000**, *122*, 6785–6786; b) A. Fürstner, F. Stelzer, H. Szillat, *J. Am. Chem. Soc.* **2001**, *123*, 11863–11869.

[11] S. Oi, I. Tsukamoto, S. Miyano, Y. Inoue, *Organometallics* **2001**, *20*, 3704–3709.

[12] C. Nieto-Oberhuber, S. López, M. P. Muñoz, D. J. Cárdenas, E. Buñuel, C. Nevado, A. M. Echavarren, *Angew. Chem.* **2005**, *117*, 6302–6304; *Angew. Chem. Int. Ed.* **2005**, *44*, 6146–6148.

[13] a) B. M. Trost, G. J. Tanoury, *J. Am. Chem. Soc.* **1988**, *110*, 1636–1638; b) B. M. Trost, M. K. Trost, *Tetrahedron Lett.* **1991**, *32*, 3647–3650; c) B. M. Trost, M. Yanai, K. Hoogsteed, *J. Am. Chem. Soc.* **1993**, *115*, 5294–5295; d) N. Chatani, H. Inoue, T. Kotsuma, S. Murai, *J. Am. Chem. Soc.* **2002**, *124*, 10294–10295; e) F. Marion, J. Coulomb, C. Courillon, L. Fensterbank, M. Malacria, *Org. Lett.* **2004**, *6*, 1509–1511; f) G. B. Bajracharya, I. Nakamura, Y. Yamamoto, *J. Org. Chem.* **2005**, *70*, 892–897.

[14] C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179.

[15] A. Fürstner, P. W. Davies, T. Gress, *J. Am. Chem. Soc.* **2005**, *127*, 8244–8245.

[16] C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2004**, *116*, 2456–2460; *Angew. Chem. Int. Ed.* **2004**, *43*, 2402–2406.

[17] Cyclization of 1,5-enynes with Au^I catalysts: a) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* **2004**, *126*, 8654–8655; b) M. R. Luzung, J. P. Markham, F. D. Toste, *J. Am. Chem. Soc.* **2004**, *126*, 10858–10859; c) L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2004**, *126*, 11806–11807; d) L. Zhang, S. A. Kozmin, *J. Am. Chem. Soc.* **2005**, *127*, 6962–6963; e) cyclization of 1,4-enynes with Au^I catalysts: X. Shi, D. J. Gorin, F. D. Toste, *J. Am. Chem. Soc.* **2005**, *127*, 5802–5803.

[18] C. Nieto-Oberhuber, S. López, M. P. Muñoz, E. Jiménez-Núñez, E. Buñuel, D. J. Cárdenas, A. M. Echavarren, *Chem. Eur. J.* **2006**, *12*, 1694–1702.

[19] a) C. Fernández-Rivas, M. Méndez, A. M. Echavarren, *J. Am. Chem. Soc.* **2000**, *122*, 1221–1222; b) C. Fernández-Rivas, M. Méndez, C. Nieto-Oberhuber, A. M. Echavarren, *J. Org. Chem.* **2002**, *67*, 5197–5201.

[20] E. R. Strieter, D. G. Blackmond, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 13978–13980.

[21] a) S. D. Walker, T. E. Border, J. R. Martinelli, S. L. Buchwald, *Angew. Chem.* **2004**, *116*, 1907–1912; *Angew. Chem. Int. Ed.* **2004**, *43*, 1871–1876; b) S. Kaye, J. M. Fox, F. A. Hicks, S. L. Buchwald, *Adv. Synth. Catal.* **2001**, *343*, 789–794.

[22] Preparation of [Au(PPh$_3$)Cl]: A. K. Al-Sa′ady, C. A. McAuliffe, R. V. Parish, J. A. Sandeank, *Inorg. Synth.* **1985**, *23*, 191–194.

[23] a) B. Bovio, A. Burini, B. R. Pietroni, *J. Organomet. Chem.* **1993**, *452*, 287–291; b) X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, *Organometallics* **2004**, *23*, 755–764, and references therein; c) S. Singh, S. S. Kumar, V. Jancik, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* **2005**, 3057–3062.

[24] P. de Fremont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 2411–2418.

[25] a) M. Preisenberger, A. Schier, H. Schmidbaur, *J. Chem. Soc. Dalton Trans.* **1999**, 1645–1650; b) K. A. Porter, A. Schier, H. Schmidbaur, *Organometallics* **2003**, *22*, 4922–4927.

[26] Hydroarylation of alkynes catalyzed by [Au(PPh_3)Cl] and silver salts: M. T. Reetz, K. Sommer, *Eur. J. Org. Chem.* **2003**, 3485–3496.
[27] Hydration of enynes catalyzed by Au^I: a) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem.* **1998**, *110*, 1475–1478; *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418; b) E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, *Angew. Chem.* **1998**, *110*, 4745–4747; *Angew. Chem. Int. Ed.* **2002**, *41*, 4563–4565.
[28] B. M. Trost, J. Dumas, *Tetrahedron Lett.* **1993**, *34*, 19–22.
[29] B. M. Trost, L. Zhi, K. Imi, *Tetrahedron Lett.* **1994**, *35*, 1361–1364.
[30] For other examples of palladium-catalyzed *endo*-cyclizations proceeding by intramolecular insertion; see: S. Brown, S. Clarkson, R. Grigg, V. Sridharan, *Tetrahedron Lett.* **1993**, *34*, 157–160.
[31] a) T. *34*, Kitamura, Y. Sato, M. Mori, *Adv. Synth. Catal.* **2002**, 344, 678–693; b) M. Mori, *J. Mol. Catal. A* **2004**, *213*, 73–79.
[32] H. Kim, C. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 10180–10181.
[33] An earlier example of cyclization of enynes with Wilkinson's catalyst [Rh(PPh_3)$_3$Cl] can now be mechanistically reinterpreted as taken place via vinylidenes (Cf. ref. [32]): R. Grigg, P. Stevenson, T. Worakun, *Tetrahedron* **1988**, *44*, 4967–4972.
[34] S. Yamazaki, K. Yamada, K. Yamamoto, *Org. Biomol. Chem.* **2004**, *2*, 257–264.
[35] A. J. Pearson, R. A. Dubbert, *Organometallics* **1994**, *13*, 1656–1661.
[36] K. Mikami, M. Hatano, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5767–5769.
[37] Y. Yamamoto, S. Kuwabara, Y. Ando, H. Nagata, H. Nishiyama, K. Itoh, *J. Org. Chem.* **2004**, *69*, 6697–6705.
[38] a) R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725–739; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711–724; b) K. P. Hall, D. M. P. Mingos, *Prog. Inorg. Chem.* **1984**, *32*, 237–325.
[39] B. M. Trost, R. Braslau, *Tetrahedron Lett.* **1988**, *29*, 1231–1234.
[40] S.-I. Ikeda, H. Miyashita, M. Taniguchi, H. Kondo, M. Okano, Y. Sato, K. Odashima, *J. Am. Chem. Soc.* **2002**, *124*, 12060–12061.
[41] T. Kataoka, H. Yoshimatsu, Y. Noda, T. Sato, H. Shimizu, M. Hori, *J. Chem. Soc. Perkin Trans. 1* **1987**, 121–129.
[42] B. M. Trost, M. Lautens, C. Chan, D. J. Jebaratnam, T. Mueller, *J. Am. Chem. Soc.* **1991**, *113*, 636–644.
[43] B. M. Trost, K. Burgess, *J. Chem. Soc. Chem. Commun.* **1985**, 1084–1086.
[44] B. M. Trost, G. J. Tanoury, *J. Am. Chem. Soc.* **1987**, *109*, 4753–4755.
[45] N. Jeong, Y. K. Chung, B. Y. Lee, S. H. Lee, S. E. Yoo, *Synlett* **1991**, 204–206.
[46] M. E. Krafft, L. V. R. Bonaga, J. A. Wright, C. Hirosawa, *J. Org. Chem.* **2002**, *67*, 1233–1246.
[47] B. L. Pagenkopf, D. B. Belanger, D. J. R. O'Mahony, T. Livinghouse, *Synthesis* **2000**, 1009–1019.
[48] M. Ishizaki, K. Iwahara, Y. Niimi, H. Satoh, O. Hoshino, *Tetrahedron* **2001**, *57*, 2729–2738.
[49] W. Oppolzer, A. Fürstner, *Helv. Chim. Acta* **1993**, *76*, 2329–2337.
[50] A. M. Castaño, M. Ruano, A. M. Echavarren, *Tetrahedron Lett.* **1996**, *37*, 6591–6594.
[51] T. R. Hoye, J. A. Suriano, *Organometallics* **1992**, *11*, 2044–2050.
[52] Diethyl ester: Ref. [5a].
[53] H.-Y. Lee, H. Y. Kim, H. Tae, B. G. Kim, J. Lee, *Org. Lett.* **2003**, *5*, 3439–3442.
[54] C.-W. Lee, K. S. Oh, K. S. Kim, K. H. Ahn, *Org. Lett.* **2000**, *2*, 1213–1216.
[55] S.-K. Kang, B.-S. Ko, D. M. Lee, *Tetrahedron Lett.* **2002**, *43*, 6693–6696.
[56] B. M. Trost, D. C. Lee, F. Rise, *Tetrahedron Lett.* **1989**, *30*, 651–654.
[57] M. Kimura, Y. Horino, R. Mukai, S. Tanaka, Y. Tamaru, *J. Am. Chem. Soc.* **2001**, *123*, 10401–10402.
[58] T. E. Müller, J. C. Green, D. M. P. Mingos, C. M. McPartlin, C. Whittingham, D. J. Williams, T. M. Woodroffe, *J. Organomet. Chem.* **1998**, *551*, 313–330.
[59] V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr, W. A. Herrmann, *Angew. Chem.* **2000**, *112*, 1672–1674; *Angew. Chem. Int. Ed.* **2000**, *39*, 1602–1604.
[60] M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, *J. Organomet. Chem.* **1999**, *572*, 239–247.
[61] a) H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975; b) H. M. J. Wang, C. Y. L. Chen I. J. B. Lin, *Organometallics* **1999**, *18*, 1216–1223.
[62] Synthesis of *N*,*N*′-dimethylimidazolium iodide: C. G. Overberger, J. C. Salamone, S. Yaroslavsky, *J. Org. Chem.* **1965**, *30*, 3580.

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