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The rhodium-catalyzed Pauson–Khand reaction

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Dedicated to Professor Jean Normant on the occasion of his 65th birthday

Abstract

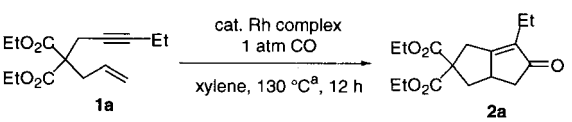
A rhodium carbonyl complex, $[RhCl(CO)_2]_2$, serves as a catalyst of the intra- and inter-molecular Pauson–Khand reaction. By the use of the rhodium catalyst, cyclopentenone derivatives are prepared from various 1,6- and 1,7-enynes under 1 atm of CO. Furthermore, this rhodium-catalyzed reaction is accelerated by reducing partial pressure of CO to less than 1 atm. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pauson–Khand reaction; Rhodium; Catalytic reaction; Cyclopentenone

1. Introduction

Cocyclization of alkene, alkyne, and CO mediated by transition metal complexes, known as the Pauson–Khand reaction, is now regarded as one of the useful methods to prepare cyclopentenone derivatives [1]. The first example of this reaction was reported in 1973, using a stoichiometric amount of $Co_2(CO)_8$ [2], and later carbonyl complexes of iron, tungsten, chromium, and molybdenum were also found to promote the Pauson–Khand reaction [3–6]. Because bicyclo skeletons can be constructed in one step, the intramolecular Pauson–Khand reaction has been often utilized as the key step of total synthesis of natural products [7–9]. In 1990 the first example of the catalytic Pauson–Khand reaction was reported using $Co_2(CO)_8$ under high pressure of CO [10a]. Following this discovery, some reports dealing with catalytic intramolecular Pauson–Khand reactions have appeared, in which cobalt, titanium, and ruthenium complexes serve as catalysts [10–12]. Most of these reactions were, however, conducted under medium or high pressure of CO. Only $Co_2(CO)_8$ with high-intensity visible light system [10b], highly purified $Co_2(CO)_8$ [10c], cobalt complex generated in situ from alkynecobalt complex and triethylsilane [10d], and titanocene complexes [11] could serve as catalysts under 1 atm of CO. During our study on the rhodium-catalyzed Pauson–Khand reaction, three types of the catalytic Pauson–Khand reactions under an atmospheric pressure of CO were reported, such as phosphane sulfide/$Co_2(CO)_8$ system [13], (*S*)-BINAP/$Co_2(CO)_8$-catalyzed asymmetric reaction [14], and (*S*)-tolBINAP-/$[Ir(cod)Cl]_2$-catalyzed asymmetric reaction [15]. Recently we found that $[RhCl(CO)_2]_2$ serves as a catalyst of the intramolecular Pauson–Khand reaction under 1 atm of CO [16a], and after our

Table 1
The Pauson–Khand reaction by using some rhodium complexes



1a 2a

Entry	Catalyst (mol%)	Yield (%)
1	2 $[RhCl(CO)_2]_2$	90
2	2 $[RhCl(cod)]_2$	84
3	1 $Rh_4(CO)_{12}$	18 [b]
4	4 $Rh(CO)_2(acac)$	22 [b]
5	2 $[RhCl(CO)_2]_2$ + 4 PPh_3	20 [b]

[a] The oil bath temperature.
[b] The starting material was recovered.

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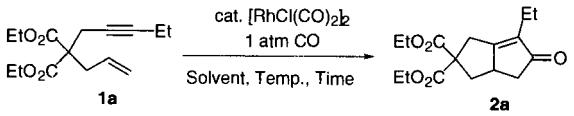
PII: S0022-328X(00)00835-4

Table 2
Solvent effect on the $[RhCl(CO)_2]_2$-catalyzed intramolecular Pauson–Khand reaction of **1a**



Entry	Temp. (°C) [a]	Catalyst (mol%)	Solvent	Time (h)	Yield (%)
1	130	1	Xylene	12	60
2	130	1	*N*,*N*-Dimethyl acetamide	12	20 [b]
3	130	1	Chlorobenzene	12	88
4	130	1	Dibutyl ether	12	91
5	110	1	Dibutyl ether	42	83
6	130	0.5	Dibutyl ether	40	82

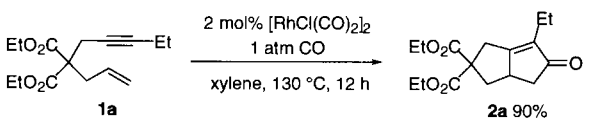
[a] The oil bath temperature.
[b] The starting material was recovered.

report, Jeong et al. reported that *trans*-$[RhCl(CO)(dppp)]_2$ and (*S*)-BINAP/$[RhCl(CO)_2]_2$ can also catalyze the Pauson–Khand reaction under 1 atm of CO [16b]. In this paper, we would like to report the details of the $[RhCl(CO)_2]_2$-catalyzed Pauson–Khand reaction.

2. Results and discussion

2.1. The $[RhCl(CO)_2]_2$-catalyzed reaction under atmospheric CO pressure

When a xylene solution of the 1,6-enyne **1a**, prepared from diethyl allylmalonate and 2-pentynyl methanesulfonate, and 2 mol% of $[RhCl(CO)_2]_2$ were heated at 130°C under 1 atm of CO, cyclocarbonylated product **2a** was obtained in 90% yield without recovery of the **1a** (Eq. (1)). Thus, the reaction is catalytic in rhodium and the first example of the rhodium-catalyzed intramolecular Pauson–Khand reaction.



(1)

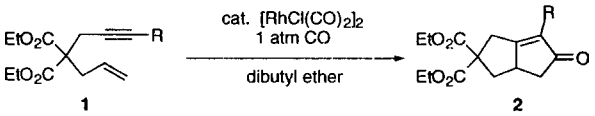
Then we examined the reaction by using some rhodium complexes as shown in Table 1. By the use of $[RhCl(CO)_2]_2$ and $[RhCl(cod)]_2$ as a catalyst, the bicyclic enone **2a** was obtained in high yield (entries 1 and 2). On the other hand, the reaction with a rhodium(0) carbonyl complex gave many products to afford **2a** in low yield (entry 3). By using an acetylacetonato rhodium(I) dicarbonyl complex or the addition of a triphenyl phosphine to $[RhCl(CO)_2]_2$, the reaction proceeded slowly and **1a** was recovered (entry 4 and 5). Because $[RhCl(cod)]_2$ is known to be readily converted to $[RhCl(CO)_2]_2$ under CO atmosphere [17], $[RhCl(CO)_2]_2$ was chosen as the catalyst in the following experiments (Table 1).

The optimization of the solvent is summarized in Table 2. The use of *N*,*N*-dimethylacetamide as the solvent gave a complex mixture with a little recovery of the enyne (entry 1). In the case of xylene, the reaction proceeded slowly and the enyne was recovered even after 12 h (entry 2). On the other hand, the reaction in chlorobenzene (entry 3) or in dibutyl ether (entry 4) at 130°C permitted an efficient conversion of the enyne **1a** to the cyclopentenone **2a** with 1 mol% of the catalyst, and dibutyl ether was chosen as the solvent in the following experiments. Though longer reaction time was needed, **2a** was also obtained in good yield even at 110°C (entry 5). The reaction could be conducted by employing only 0.5 mol% of the rhodium complex without a significant loss of the yield (entry 6).

2.2. Investigation of the generality of the intramolecular reaction

Various 1,6-enynes were converted to cyclopentenones by using the rhodium complex as described in Table 3. Enynes **1a** and **1b** having an alkyl- or phenyl-substituted alkyne moiety reacted to afford the α-substituted cyclopentenones **2a** and **2b** in high yield (entries 1 and 2). Enyne **1c** having a terminal alkynyl moiety was converted to cyclopentenone **2c** in 55% yield by heating at 150°C with the complete consumption of **1c** (entry 3). Murai et al. reported that **1c** isomerizes to diethyl-3-ethenyl-3-cyclopentene-1,1-dicarboxylate (**3**) by the catalytic use of $[RhCl(CO)_2]_2$ [18], while under our reaction conditions **3** was formed only in 9% yield. As another by-product, a trace amount of intermolecular cyclized product **4** was also obtained. Thus, the enyne having terminal alkyne moiety **1c** is not so suitable for the rhodium-catalyzed Pauson–Khand reaction. This drawback was overcome by employing

Table 3
Cyclopentenones from 1,6-enynes



1 2

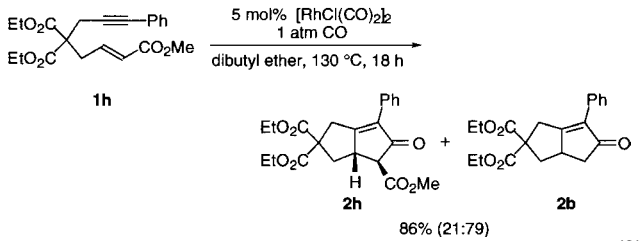
Entry		R	Cat. (mol%)	Temp. (°C) [a]	Time (h)		Yield (%)
1	**1a**	Et	1	130	12	**2a**	91
2	**1b**	Ph	1	130	16	**2b**	94
3	**1c**	H	1	150	2	**2c**	55
4	**1d**	$SiMe_3$	5	150	18	**2d**	76 [b]

[a] The oil bath temperature.
[b] The desilylated product (**2c**) was included (41%).

trimethylsilyl-substituted alkyne **1d**, which was converted to α-silyl cyclopentenone **2d** and the desilylated product **2c** in 76% total yield (entry 4). Though the mechanism of the desilylation is not clear, it was found that the desilylated product **2c** was formed by heating the α-silyl cyclopentenone **2d** in the presence of the rhodium complex (Fig. 1).

Next, the cyclization of 1,6-enynes **1e**, **1f**, and **1g** having a methyl group at the alkenyl moiety were examined and the results are summarized in Table 4. Enyne **1e** possessing a methyl group at the internal alkenyl carbon gave **2e** in 71% yield with a skeletal reorganization product **5a** in about 15% yield with a trace amount of **5b** (entry 1) [18]. Enynes **1f** and **1g** having a methyl group at the terminal alkenyl carbon gave products **2f** and **2g** stereospecifically (entries 2 and 3) [19] Fig. 2.

It was reported that electron-deficient alkenes are not suitable for the $Co_2(CO)_8$ mediated Pauson–Khand reaction, which gives dienes instead of cyclopentenones [20]. There are only few successful reports of the Pauson–Khand reaction of such enynes having an electron-withdrawing group on the alkenyl moiety. Only the enynes having an α-substituted enone moiety is known to be utilized for the $Co_2(CO)_8$ mediated intramolecular Pauson–Khand reaction, because β-hydrogen elimination can not occur [21]. 1,6-Enyne having a sulfinyl group is utilized for the $Co_2(CO)_8$ mediated reaction [22]. Though $Co_2(CO)_8$ mediated intermolecular Pauson–Khand reaction of electron-deficient alkenes is known to proceed by using NMO at low temperature [23], and a stoichiometric amount of $W(CO)_5$(thf) also promotes the intramolecular Pauson–Khand reaction of such enynes having electron-deficient alkene [24], in these examples, the yield of cyclopentenones are not sufficiently high and the catalytic reaction has never been reported. Nonetheless the reaction of α,β-unsaturated ester **1h** was found to proceed smoothly with the rhodium catalyst and carbocyclized products **2b** and **2h** were obtained in high total yield (Eq. (2)), in which the demethoxycarbonylated product **2b** was the major product. In the early stage of the reaction, however, only **2h** was produced. Thus, with the progress of the reaction, **2b** was generated, and the demethoxycarbonylation of **2h** was found to occur just by heating **2h** without the rhodium catalyst.



(2)

Electron-deficient alkynes have also rarely been employed in the Pauson–Khand reaction [25]. In particular, there has been no report on the catalytic Pauson–Khand reaction concerning such enynes as **1i** and **1j** having an electron-withdrawing group on the alkynyl moiety. In the present rhodium catalyzed reaction, however, cyclopentenone annulation proceeded smoothly as shown in Eqs. (3) and (4). Moreover, these enynes **1i** and **1j** exhibited high reactivity and the reaction was completed within 1 and 3 h, respectively.

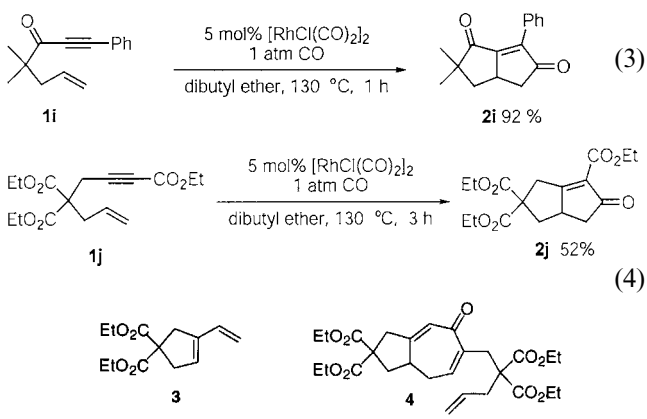
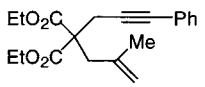
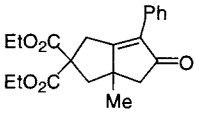
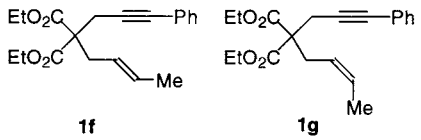
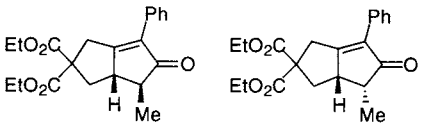


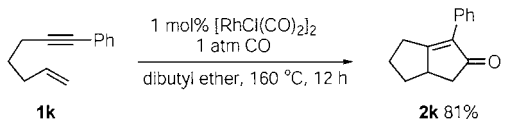
Fig. 1. By-products from enyne **1c**.

Table 4
Cyclization of enynes having a disubstituted alkenyl moiety [a]

Entry		Cat. mol%	Time h	Products	Yield
1	 **1e**	5	15	 **2e**	71 %
	 **1f** **1g**			 **2f** **2g**	
2	91 : 9	1	6	95 : 5	96 %
3	29 : 71	1	12	31 : 69	90 %

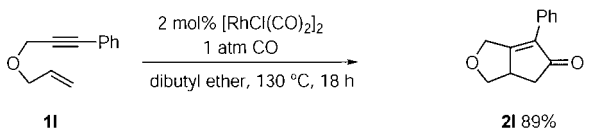
[a] The reaction was conducted in dibutyl ether at 160°C under 1 atm of CO.

The enynes examined so far have *gem*-disubstituents on the trimethylene tether. As shown in Eq. (5), enyne **1k** without *gem*-substituents on the tether also cyclized smoothly to give bicyclic enone **2k** in high yield.

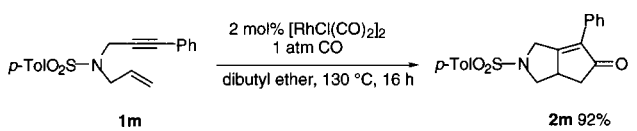


1k **2k** 81% (5)

Furthermore, enynes **1l** and **1m** containing hetero atoms on the tether of the enynes were converted to bicyclic heterocycles **2l** and **2m** in 89% and 92% yield, respectively (Eqs. (6) and (7)).

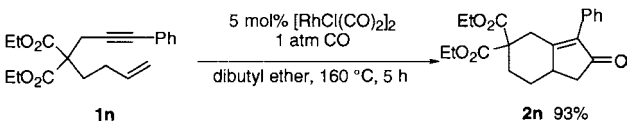


1l **2l** 89% (6)



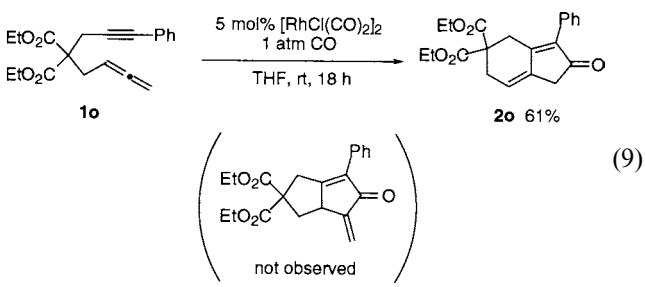
1m **2m** 92% (7)

This rhodium-catalyzed reaction could be applied to the construction of not only bicyclo[3.3.0] skeleton but also bicyclo[4.3.0] skeleton; that is, 1,7-enyne **1n** was converted to **2n** in high yield (Eq. (8)).



1n **2n** 93% (8)

The cyclopentenone annulation of allenyne **1o** also proceeded successfully. The allene **1o** has high reactivity and the reaction proceeded at room temperature to yield only bicyclo[4.3.0] skeleton selectively, without forming bicyclo[3.3.0] skeleton (Eq. (9)). This makes a good contrast to the reaction with a stoichiometric amount of molybdenum carbonyl complex, in which bicyclo[3.3.0] skeleton is constructed by the *cyclo*-carbonylation with the inner double bond of the terminal allene moiety [26].



1o **2o** 61% (9)

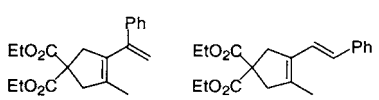
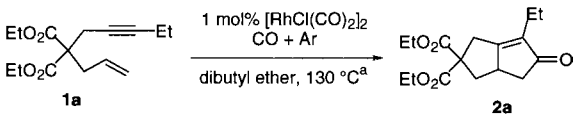

5a **5b**

Fig. 2. By products from enyne **1e**.

Table 5
The effect of the CO pressure

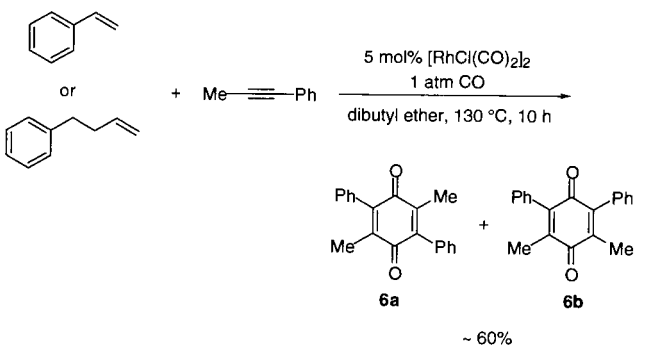


Entry	Pressure (atm)		Time (h)	Yield (%)
	CO	Ar		
1	3	0	36	70 [b]
2	1	0	18	91
3	0.2	0.8	5	90
4	0.1	0.9	2	92
5	0.05	0.95	3	85

[a] The oil bath temperature.
[b] The starting material **1a** was recovered in 24%.

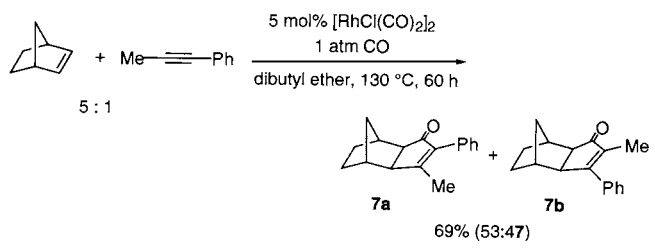
2.3. Rhodium-catalyzed intermolecular Pauson–Khand reaction under 1 atm of CO

This rhodium catalyst was next applied to the intermoleculer Pauson–Khand reaction. First using styrene or 1-phenyl-3-butene as alkenes, the reaction with 1-phenylpropyne were examined, however, quinones **6a** and **6b** were obtained without forming the Pauson–Khand products (Eq. (10))



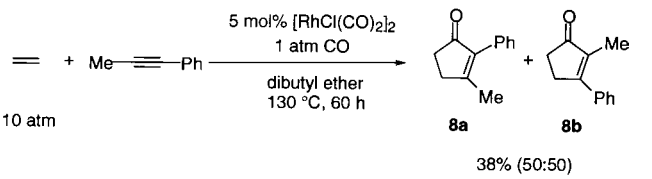
(10)

These results suggested that the use of more reactive alkene is essential for the intermolecular reaction. In fact, by the combination of norbornene and 1-phenylpropyne, cyclic enone **7** was obtained in 69% yield as a mixture of regioisomers (Eq. (11)).



(11)

Ethylene can be also utilized in the intermolecular reaction. Under 10 atm of ethylene and 1 atm of CO, cyclopentenones **5a** and **5b** were obtained in 38% total yield (Eq. (12)).



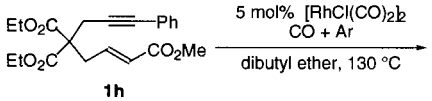
(12)

2.4. Rhodium-catalyzed Pauson–Khand reaction under low partial pressure of CO

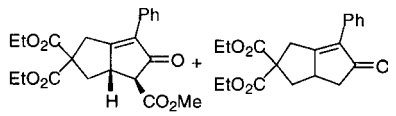
As mentioned, $[RhCl(CO)_2]_2$ is found to catalyze the Pauson–Khand reaction under an atmospheric pressure of CO, however, the reaction has to be carried out at rather high temperature of 130–160°C. Because most of the catalytic Pauson–Khand reactions were conducted under elevated CO pressure [10d–h,12], the catalytic reaction of **1a** was examined under 3 atm of CO with the expectation to facilitate the reaction. Even after 36 h, however, 24% of **1a** was recovered and the desired product **2a** was obtained in 70% yield. This finding prompted us to examine the cyclization under lower pressure of CO, and the reaction was performed under a mixture of CO and Ar at 1 atm (Table 5).

When a mixture of **1a** and 1 mol% of $[RhCl(CO)_2]_2$ in dibutyl ether was heated to 130°C under 0.2 atm of CO and 0.8 atm of Ar atmosphere, **1a** was consumed within 5 h, giving **2a** in 90% yield. Furthermore, under 0.1 atm of CO and 0.9 atm of Ar, the cyclization was completed within 2 h. Under 0.05 atm of CO and 0.95 atm of Ar, however, it took 3 h to complete the reaction and the yield of **2a** was slightly decreased. Accordingly, the subsequent experiments were carried out in an apparatus equipping a plastic balloon containing 0.1 atm of CO and 0.9 atm of Ar. Similar influence of the pressure of CO was also observed in the titanium-catalyzed Pauson–Khand reaction, where the cyclization of enynes having a 1,2-disubstituted alkenyl moiety proceeds faster under reduced pressure of CO [1,2a].

The advantage of low pressure of CO was observed clearly in the reaction of the enyne **1b** having an electron-deficient alkene moiety. As mentioned above, the demethoxycarbonylation of the initially formed keto ester **2h** occurred thermally in the carbocyclization of **1h** and the demethoxycarbonyl compound **2b** was obtained as the major product, whereas **2h** was obtained in 59% yield with 31% yield of **2b** under 0.1 atm CO due to the short reaction time (Eq. (13)).



1h

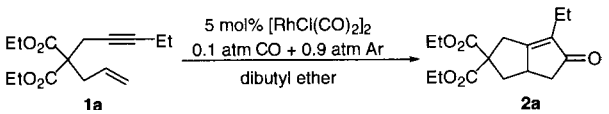


(13)

	2h	2b
CO 0.1 atm + Ar 0.9 atm, 4 h	59 %	31 %
CO 1 atm, 18 h	19 %	68 %

Since the reaction was accelerated by reducing pressure of CO, the cyclization was examined at lower temperature, and the results are summarized in Table 6. The product **2a** was obtained in high yield at 100 and 80°C (entries 1 and 2), while reaction did not finish at 60°C even after 72 h and the starting material **1a** was recovered, because the catalyst was decomposed during such a long reaction time (entry 3). It was noted that the concentration of **1a** is crucial to accelerate the reaction. By changing the concentration of **1a** from 0.1 to 1 M, the reaction finished even at 60°C in 24 h to give **2a** in 91% yield (entry 4).

Table 6
The investigation of reaction temperature under 0.1 atm of CO

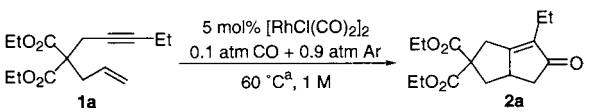


1a 2a

Entry	Temp. (°) [a]	Conc. (M)	Time (h)	Yield (%)
1	100	0.1	9	95
2	80	0.1	18	94
3	60	0.1	72	62 [b]
4	60	1	24	91

[a] The oil bath temperature.
[b] The starting material was recovered.

Table 7
Solvent effect on the $[RhCl(CO)_2]_2$-catalyzed Pauson–Khand reaction under 0.1 atm of CO



1a 2a

Solvent	Time (h)	Yield (%)
Dibutyl ether	24	91
THF	24	82
DME	12	85
Toluene	12	90

[a] The oil bath temperature.

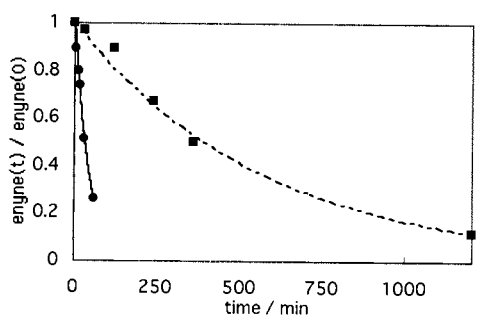
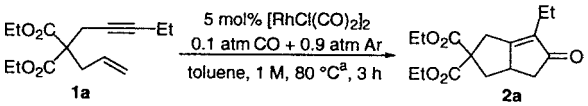


Fig. 3. The effect of CO pressure.

Table 8
The surface area and yield of **2a**



1a 2a

Entry	Scale (mmol)	The area of surface (cm^2)	Yield (%)
1	1	7.1	68 [b]
2	1	9.6	69 [b]
3	1	25	90
4	10	196	96

[a] The oil bath temperature.
[b] The starting material **1a** was recovered.

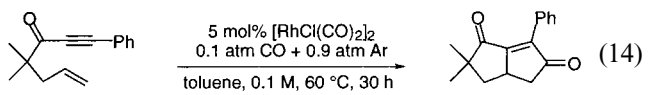
So far dibutyl ether was employed as a solvent because the reaction had to be performed at 130°C under 1 atm of CO atmosphere. As the reaction proceeded at lower temperature by reducing the pressure of CO, the reaction was examined in various solvents. As shown in Table 7, toluene was found to be suitable for this transformation.

Under the optimized conditions, at 80°C under 0.1 atm of CO with 1 M concentration of the enyne **1a**, the pressure effect of CO to the reaction rate was studied by chasing the rate of the consumption of **1a** by gas chromatography. Fig. 1 shows the relationship between the reaction time and the amount of the starting material **1a**. The half-life period of **1a** is 31 minutes under 0.1 atm of CO, while it is 385 minutes under atmospheric pressure of CO. Thus the effect of pressure of CO is clearly emerged on the reaction rate. (Fig. 3)

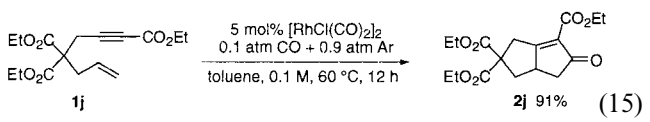
Under such conditions, however, the consumption of dissolved CO is so fast that, without enough surface area of the reaction mixture, the rhodium catalyst is decomposed and the reaction stops. As shown in Table 8, in the case of the reaction using 1 mmol of **1a**, because the surface area of 7 to 10 cm^2 was not large enough, the reaction stopped and the starting material was recovered besides the product (entries 1 and 2), while the reaction was completed and **2a** was obtained in high yield with the surface area of 25 cm^2 (entry 3). When 10 mmol of **1a** was used, the surface area of 196 cm^2 was enough for the reaction (entry 4).

Under these optimized conditions, **1a** having ethyl-substituted alkynyl moiety was converted to **2a** within 3 h at 80°C in 90% yield as summarized in Table 9. The cyclization of the trimethylsilylated alkyne **1d** proceeds at 100°C and yielded the α-silyl enone **2d** and the desilylated enone **2c** in 84% total yield (**2d**:**2c** = 65:35). Then the reactions of 1,6-enynes **1e**, **1f**, and **1g** having a methyl group on the alkenyl moiety were investigated. While the cyclization of **1e** possessing a methyl group at internal alkenyl carbon afforded **2e** in rather low yield (entry 3), enynes **1f** and **1g** with a methyl group at the terminal alkenyl carbon gives cyclopentenones **2f** and **2g** in high yield in a stereospecific manner concerning the stereochemistry of the alkene moiety (entry 4). The 1,7-enyne **1n** afforded **2n** in low yield in 1 M concentration, perhaps due to the intermolecular reaction. Accordingly, the reaction was conducted in 0.1 M solution and the enone with bicyclo[4.3.0] skeleton was obtained in 89% yield, though the temperature of 130°C was needed (entry 5).

The enynes **1i** and **1j**, possessing an electron-deficient alkynyl moiety exhibited high reactivity and even in the 0.1 M solution of the enyne, the carbocyclization proceeds at 60°C under a mixture of CO and Ar (1:9) in the presence of 5 mol% of $[RhCl(CO)_2]_2$ and the dienones **2i** and **2j** were obtained in 91% yield (Eqs. (14) and (15)).

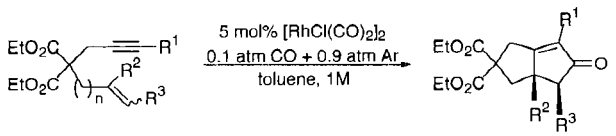


(14)



(15)

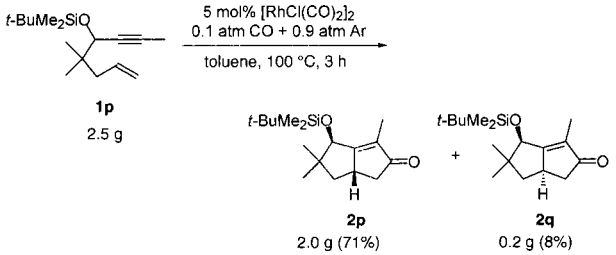
Table 9
Cyclization of various enynes under 0.1 atm of CO



Entry	R^1	R^2	R^3	n		Temp. (°C) [a]	Time (h)		Yield (%)
1	Et	H	H	1	**1a**	80	3	2a	90
2	$SiMe_3$	H	H	1	**1d**	100	24	2d	84 [b]
3 [c]	Ph	Me	H	1	**1e**	100	16	2e	69
4	Ph	H	Me	1	**1f**,**1g** [d]	80	18	2f,2g [e]	93
5 [f]	Ph	H	H	2	**1n**	130	24	2n	89

[a] The oil bath temperature.
[b] The desilylated product (**2c**) was included.
[c] The reaction was conducted under 0.05 atm of CO.
[d] *trans* (**1f**):*cis* (**1g**) = 77:23.
[e] *trans* (**2f**):*cis* (**2g**) = 78:22.
[f] The reaction was conducted in 0.1 M solution of dibutyl ether.

Finally, by this rhodium-catalyzed reaction, bicyclic enone **2p** and **2q**, which are the key intermediates for the total synthesis of *dl*-coliorin, were synthesized from enyne **1p** (Eq. (16)). Magnus reported that **2p** can be derived from **1p** by the classical Pauson–Kiland reaction with a stoichiometric amount of $Co_2(CO)_8$ under atmospheric pressure of CO [9]. However, by using a catalytic amount of $[RhCl(CO)_2]_2$, the carbocyclization of **1p** proceeded smoothly under 0.1 atm of CO and **2p** and **2q** were obtained in 9:1 ratio in 79% total yield in 2.2 g scale.



(16)

3. Conclusions

1,6-and 1,7-enynes having various substituents at alkenyl or alkynyl moiety are converted to cyclopentenone derivatives in high yield by the use of a catalytic amount of $[RhCl(CO)_2]_2$. Even 1,6-enynes having electron-withdrawing group at alkenyl or alkynyl moiety, which are not suitable for the other Pauson–Khand reaction using other complexes, can be converted to enones by the rhodium-catalyzed reaction. Not only enynes, but 1,6-allenyne cyclizes smoothly and bicy-

clo[4.3.0] skeleton is constructed selectively. Furthermore, using norbornene or ethylene, the intermoleculer reaction with 1-phenyl-1-propyne also proceeds.

This $[RhCl(CO)_2]_2$ catalyzed reaction can be conducted under 1 atm of CO. Moreover, by reducing partial pressure of CO, the reaction is accelerated and the reaction proceeds at lower temperature under 0.1 atm of CO.

4. Experimental

^{1}H-NMR (500 MHz) spectra in $CDCl_3$ were recorded on Bruker AM500 and Bruker DRX500 spectrometers using $CHCl_3$ as an internal standard ($\delta = 7.24$). ^{13}C-NMR (125 MHz) spectra in $CDCl_3$ were measured with Bruker AM500 and Bruker DRX500 spectrometers using $CDCl_3$ as an internal standard ($\delta = 77.0$). IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-SX102A mass spectrometer. Elemental analyses were carried out at The Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Dibutyl ether, toluene, and tetrahydrofuran (THF) were freshly distilled from lithium aluminum hydride before use. Xylene was distilled from CaH_2, and dried over Molecular Sieves 4Å. Chlorobenzene was distilled from CaH_2, and stored under argon. Dichloromethane was distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieves 4Å. Silica gel column chromatography was carried out with Merck Art 7734 and Kanto 60N. Preparative TLC was performed on silica gel (Wakogel B-SF). Tetracarbonyl dichloro dirhodium ($[RhCl(CO)_2]_2$) was prepared by the literature procedure [27].

4.1. Preparation of substrates **1a–1p**

4.1.1. Diethyl 8-nonen-3-yne-6,6-dicarboxylate (**1a**) [12b]

In a dry flask under argon, a dichloromethane solution (90 ml) of 2-pentyn-1-ol (10.0 g, 119 mmol) and triethylamine (20.0 ml, 143 mmol) were combined. To this mixture a dichloromethane solution (8 ml) of methanesulfonyl chloride (15.0 g, 131 mmol) was added at -78°C and stirred at room temperature (r.t.) for 30 min. The reaction was quenched with water and organic materials were extracted with chloroform. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give 2-pentynyl methanesulfonate. In a separate dry flask under argon, to a suspension of sodium hydride (3.15 g, 131 mmol) in THF (300 ml) was added diethyl allylmalonate (20.0 ml, 101 mmol) at 0°C. The reaction mixture was allowed to stir at r.t. for 1 h and a THF solution (10 ml) of 2-pentynyl methanesulfonate synthesized above was added at 0°C. After stirring at r.t. over night, the reaction mixture was quenched with phosphate buffer (pH 7) and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and purification by flash column chromatography and vacuum distillation (97°C/0.9 mmHg) afforded the title compound **1a** (22.5 g, 84.5 mmol; 84% yield). Colorless oil; IR (neat) 2981, 1736, 1288, 1215, 1192 cm^{-1}; ^{1}H-NMR $\delta = 1.06$ (t, $J = 7.6$ Hz, 3H), 1.22 (t, $J = 6.9$ Hz, 6H), 2.10 (tq, $J_t = 2.4$ Hz, $J_q = 7.6$ Hz, 2H), 2.71 (t, $J = 2.4$ Hz, 2H), 2.76 (d, $J = 7.5$ Hz, 2H), 4.17 (q, $J = 6.9$ Hz, 4H), 5.07–5.15 (m, 2H), 5.61 (ddt, $J_d = 10.1$, 17.5 Hz, $J_t = 7.6$ Hz, 1H); ^{13}C-NMR $\delta =$ 12.3, 14.1, 14.1, 22.9, 36.4, 57.0, 61.4, 73.7, 84.9, 119.4, 132.1, 170.0.

4.1.2. Diethyl 1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (**1b**) [28]

This compound was prepared from 3-phenyl-2-propyn-1-ol and diethyl allylmalonate following the same procedure used for the synthesis of **1a**. Colorless oil; IR (neat) 2981, 1738, 1734, 1215, 1192 cm^{-1}; ^{1}H-NMR $\delta = 1.24$ (t, $J = 7.1$ Hz, 6H), 2.85 (d, $J = 7.5$ Hz, 2H), 2.99 (s, 2H), 4.18–4.24 (m, 4H), 5.11–5.21 (m, 2H), 5.67 (ddt, $J_d = 9.8$, 17.4 Hz, $J_t = 7.5$ Hz, 1H), 7.25–7.37 (m, SH); ^{13}C-NMR $\delta = 14.1$, 23.5, 36.6, 57.0, 61.6, 83.5, 84.4, 119.7, 123.3, 127.9, 128.2, 131.6, 131.9, 169.8.

4.1.3. Diethyl 6-hepten-1-yne-4,4-dicarboxylate (**1c**) [10c]

In a dry flask under argon, to a suspension of sodium hydride (660 mg, 27.5 mmol) in THF (80 ml) was added diethyl allylmalonate (4.15 ml, 21.0 mmol) at 0°C. The reaction mixture was allowed to stir at r.t. for 30 min and 3-bromopentyne (2.25 ml, 25.3 mmol) was added at 0°C. After stirring at r.t. overnight, the reaction mixture was quenched with phosphate buffer (pH 7) and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the purification by flash column chromatography afforded the title compound **1c** (3.74 g, 15.7 mmol; 75% yield). Colorless oil; IR (neat) 1736, 1288, 1217, 1192 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (t, $J = 7.1$ Hz, 6H), 1.99 (t, $J = 2.7$ Hz, 1H), 2.76 (d, $J = 2.7$ Hz, 2H), 2.78 (d, $J = 7.6$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 4H), 5.10 (dd, $J = 1.5$, 10.0 Hz, 1H), 5.16 (dd, $J = 1.5$, 16.8 Hz, 1H), 5.60 (ddt, $J_d = 10.0$, 16.8 Hz, $J_t = 7.6$ Hz, 1H); ^{13}C-NMR $\delta = 14.0$, 22.5, 36.3, 56.6, 61.6, 71.4, 78.9, 119.8, 131.7, 169.7.

4.1.4. Diethyl 1-(trimethylsilyl)-6-hepten-1-yne-4,4-dicarboxylate (**1d**) [29]

This compound was prepared from 3-trimethylsilyl-2-propyn-1-ol and diethyl allylmalonate following the same procedure used for the synthesis of **1a**. Colorless oil; IR (neat) 1741, 1738, 1215, 845 cm^{-1}; ^{1}H-NMR $\delta = 0.10$ (s, 9H), 1.23 (t, $J = 7.1$ Hz, 6H), 2.76 (d, $J = 7.5$ Hz, 2H), 2.78 (s, 2H), 4.12–4.22 (m, 4H), 5.08–5.17 (m, 2H), 5.61(ddt, $J_d = 9.9$, 16.9 Hz, $J_t =$ 16.9 Hz, 1H); ^{13}C-NMR $\delta = -0.1$, 14.1, 23.9, 36.4, 56.8, 61.5, 88.1, 101.4, 119.6, 132.0, 169.7.

4.1.5. Diethyl 6-methyl-1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (**1e**)

This compound was prepared from 1-bromo-2-methyl-2-propene and diethyl 3-phenyl-2-propynylmalonate [30] following the same procedure used for the synthesis of **1c**. Colorless oil; IR (neat) 2981, 1736, 1205, 1184 cm^{-1}; ^{1}H-NMR $\delta = 1.25$ (t, $J = 7.1$ Hz, 6H), 1.69 (s, 3H), 2.88 (s, 2H), 3.03 (s, 2H), 4.14–4.26 (m, 4H), 4.88–4.91 (m, 2H), 7.25–7.36 (m, SH); ^{13}C-NMR $\delta = 14.0$, 23.3, 23.5, 39.6, 56.7, 61.6, 83.7, 84.8, 116.2, 123.3, 127.9, 128.2, 131.6, 140.1, 170.3; Anal. Found: C, 73.18; H, 7.43. Calc. for $C_{20}H_{24}Q_4$: C, 73.15; H, 7.37%.

4.1.6. Diethyl 1-phenyl-6-octen-1-yne-4,4-dicarboxylate

This compound was prepared from 1-bromo-2-butene (*trans-cis* mixture) and 3-phenyl-2-propynylmalonate [30] following the same procedure used for the synthesis of **1c** as a mixture of *trans*-diethyl-1-phenyl-6-octen-1-yne-4,4-dicarboxylate (**1f**) and *cis*-diethyl-1-phenyl-6-octen-1-yne-4,4-dicarboxylate (**1g**) (**1f**:**1g** = 77:23). Purification with HPLC afforded a *trans*-major mixture (**1f**:**1g** = 91:9) and a *cis*-major mixture (**1f**:**1g** = 29:71).

4.1.7. trans-Diethyl 1-phenyl-6-octen-1-yne-4,4-dicarboxylate (**1f**) [11a]

Colorless oil; IR (neat) 2983, 1738, 1734, 1207, 1188 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (t, $J = 7.1$ Hz, 6H), 1.64 (d, $J = 6.4$ Hz, 3H), 2.77 (d, $J = 7.4$ Hz, 2H), 2.97 (s, 2H), 4.19 (q, $J = 7.1$ Hz, 4H), 5.24–5.30 (m, 1H), 5.60 (dq, $J_d = 13.1$ Hz, $J_q = 6.4$ Hz, 1H), 7.24–7.35 (m, SH); ^{13}C-NMR $\delta = 14.1$, 18.0, 23.4, 35.4, 57.3, 61.5, 83.3, 84.7, 123.4, 124.2, 127.9, 128.2, 130.4, 131.6, 170.0.

4.1.8. cis-Diethyl 1-phenyl-6-octen-1-yne-4,4-dicarboxylate (**1g**) [11a]

Colorless oil; IR (neat) 1736, 1207, 1188 cm^{-1}; ^{1}H-NMR $\delta = 1.24$ (t, $J = 7.1$ Hz, 6H), 1.67 (dd, $J = 1.1$, 6.9 Hz, 3H), 2.88 (d, $J = 7.8$ Hz, 2H), 2.98 (s, 2H), 4.15–4.26 (m, 4H), 5.20–5.25 (m, 1H), 5.62–5.68 (m, 1H), 7.24–7.26 (m, 3H), 7.33–7.35 (m, 2H); ^{13}C-NMR $\delta =$ 14.1, 23.4, 29.6, 35.5, 57.2, 61.5, 83.3, 84.8, 123.3, 123.4, 127.9, 128.2, 128.8, 131.6, 170.1.

4.1.9. 4,4-Diethyl-7-methyl-1-phenyl-6-hepten-1-yne-4,4,7-tricarboxylate (**1k**)

This compound was prepared from methyl-4-bromo-2-propenoate and diethyl-3-phenyl-2-propynylmalonate [30] following the same procedure used for the synthesis of **1c**. Colorless oil; IR (neat) 1734, 1277, 1294, 1174 cm^{-1}; ^{1}H-NMR $\delta = 1.25$ (t, $J = 7.1$ Hz, 6H), 2.98 (dd, $J = 1.2$, 7.8 Hz, 2H), 3.00 (s, 2H), 3.69 (s, 3H), 4.17–4.27 (m, 4H), 5.95 (d, $J = 15.5$ Hz, 1H), 6.82 (dt, $J_d = 15.5$ Hz, $J_t = 7.8$ Hz, 1H), 7.24–7.27 (m, 3H), 7.32–7.35 (m, 2H); ^{13}C-NMR $\delta = 14.1$, 24.0, 35.1, 51.5, 56.8, 61.9, 83.7, 84.0, 123.0, 125.1, 128.1, 128.2, 131.6, 142.4, 166.2, 169.3; Anal. Found: C, 67.73; H, 6.48. Calc. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50%.

4.1.10. 4,4-Dimethyl-1-phenyl-6-hepten-1-yne-3-one (**1i**)

In a dry flask under argon, to a THF solution (150 ml) of phenylacetylene (4.32 g, 42.3 mmol) was added butyllithium (1.6 M solution of hexane, 24.0 ml, 38.4 mmol) at 0°C. Then a THF solution (20 ml) of 2,2-dimethyl-4-pentenal [31] was added at 0°C. The mixture was allowed to stir at r.t. over night. The reaction was quenched with phosphate buffer (pH 7) and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the purification by flash column chromatography afforded 4,4-dimethyl-1-phenyl-6-hepten-1-yn-3-ol (5.44 g, 25.4 mmol; 73% yield). In a dry flask under argon, to a dichloromethane solution (260 ml) of 4,4-dimethyl-1-phenyl-6-hepten-1-yn-3-ol (5.44 g, 25.4 mmol) was added pyridinium dichromate (14.4 g, 38.3 mmol). The reaction mixture was stirred at r.t. for 48 h and filtered through Celite. The filtrate was concentrated in vacuo and purification by flash column chromatography gave the title compound **1i** (4.45 g, 21.0 mmol; 83% yield). Pale yellow oil; IR (neat) 2972, 2199, 1664, 1059, 1053, 758, 689 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (s, 6H), 2.41 (d, $J = 7.4$ Hz, 2H), 5.06–5.10 (m, 2H), 5.73 (ddt, $J_d =$ 10.1, 16.9 Hz, $J_t = 7.4$ Hz, 1H), 7.35–7.38 (m, 2H), 7.42–7.44 (m, 1H), 7.55–7.57 (m, 2H); ^{13}C-NMR $\delta =$ 23.7, 43.7, 48.2, 86.2, 92.2, 118.3, 120.3, 128.6, 130.6, 132.9, 133.6, 193.4; Anal. Found: C, 84.74; H, 7.64. Calc. for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

4.1.11. Triethyl 6-hepten-1-yne-1,4,4-tricarboxylate (**1j**) [18]

This compound was prepared by the literature procedure [18]. Colorless oil; IR (neat) 1738, 1734, 1722, 1714, 1255, 1215 cm^{-1}; ^{1}H-NMR $\delta = 1.24$ (t, $J = 7.1$ Hz, 6H), 1.26 (t, $J = 7.1$ Hz, 3H), 2.78 (d, $J = 7.5$ Hz, 2H), 2.91 (s, 2H), 4.15–4.22 (m, 6H), 5.13 (d, $J = 10.1$ Hz, 1H), 5.19 (dd, $J = 1.4$, 17.0 Hz, 1H), 5.55–5.63 (m, 1H); ^{13}C-NMR $\delta = 14.0$, 14.0, 22.8, 36.7, 56.3, 61.9, 61.9, 75.6, 83.3, 120.3, 131.3, 153.3, 169.2.

4.1.12. 1-Phenyl-6-hepten-1-yne (**1k**) [29]

This compound was prepared by the literature procedure [29]. Colorless oil; IR (neat) 1491, 914, 756, 692 cm^{-1}; ^{1}H-NMR $\delta = 1.69$ (tt, $J = 7.2$, 7.2 Hz, 2H), 2.21 (dt, $J_d = 7.2$ Hz, $J_t = 7.2$ Hz, 2H), 2.41 (t, $J = 7.2$ Hz, 2H), 4.99 (d, $J = 11.5$ Hz, 1H), 5.06 (dd, $J = 1.4$, 17.1 Hz, 1H), 5.78–5.85 (m, 1H), 7.24–7.27 (m, 3H), 7.37–7.39 (m, 2H); ^{13}C-NMR $\delta = 18.8$, 27.9, 32.8, 80.8, 89.9, 115.2, 124.0, 127.5, 128.2, 131.5, 137.9.

4.1.13. Allyl 3-phenyl-2-propynyl ether (**1l**) [3]

This compound was prepared by the literature procedure [3]. Colorless oil; IR (neat) 1088, 1084, 1074, 758, 690 cm^{-1}; ^{1}H-NMR $\delta = 4.12$ (ddd, $J = 1.3$, 1.3, 5.8 Hz, 2H), 4.37 (s, 2H), 5.22 (ddt, $J_d = 1.4$, 10.4 Hz, $J_t = 1.4$ Hz, 1H), 5.33 (ddt, $J_d = 1.5$, 17.2 Hz, $J_t = 1.5$ Hz, 1H), 5.90–5.98 (m, 1H), 7.27–7.32 (m, 3H), 7.41–7.45 (m, 2H); ^{13}C-NMR $\delta = 57.9$,70.7, 85.0, 86.3, 117.9, 122.7, 128.3, 128.4, 131.8, 134.1.

4.1.14. N-Allyl-N-(3-phenyl-2propynyl)-4-methylphenylsulfonamide (**1m**) [10j]

In a dry flask under argon, a diethyl ether solution (5 ml) of allylamine (4 ml, 53.2 mmol) and a diethyl ether solution (5 ml) of 3-bromo-1-phenyl-1-propyne (1.00 g, 5.13 mmol) were combined at 0°C. Then the reaction mixture was stirred for 5 min at 0°C and 1 h at r.t.. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and purification by flash column chromatography afforded *N*-allyl-*N*-(3-phenyl-2-propynyl)amine (0.756 g, 4.41 mmol; 86% yield). To the mixture of *N*-allyl-*N*-(3-phenyl-2-propynyl)amine (724 mg, 4.23 mmol), triethylamine (0.9 ml) and dichloromethane (5 ml) was added a dichloromethane solution of *p*-toluenesulfonyl chloride (967 mg, 5.07 mmol) at 0°C. The mixture was stirred for 5 min at 0°C and 30 min at r.t. The reaction was quenched with phosphate buffer (pH 7) and organic materials were extracted with chloroform. The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and purification by column chromatography followed by recrystallization from hexane–AcOEt gave the title compound **1m** (1.2 g, 3.7 mmol; 87%). Colorless crystals; mp 74°C (hexane–AcOEt) (lit., 73.5–75.2°C); IR(KBr) 1352, 1325, 1163, 1158,768 cm^{-1}; ^{1}H-NMR $\delta = 2.31$ (s, 3H), 3.87 (d, $J = 6.5$ Hz, 2H), 4.29 (s, 2H), 5.25 (dd, $J = 1.7$, 10.1 Hz, 1H), 5.31 (dd, $J = 1.3$, 17.1 Hz, 1H), 5.78 (ddt, $J_d =$ 10.1, 17.1 Hz, $J_t = 6.5$ Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 2H), 7.20–7.28 (m, 5H), 7.75 (d, $J = 8.2$ Hz, 2H); ^{13}C-NMR $\delta = 21.4$, 36.7, 49.3, 81.7, 85.7, 119.9, 122.2, 127.8, 128.1, 128.4, 129.5, 131.5, 132.1, 136.0, 143.5.

4.1.15. Diethyl 1-phenyl-7-octen-1-yne-4,4-dicarboxylate (**1n**)

This compound was prepared from 1-bromo-3-butene and diethyl 3-phenyl-2-propynylmalonate [30] heating to reflux for 24 h following the same procedure used for the synthesis of **1c**. Colorless oil; IR (neat) 2981, 1738, 1732, 1207, 1190 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (t, $J = 7.0$ Hz, 6H), 1.98–2.02 (m, 2H), 2.16–2.19 (m, 2H), 3.12 (s, 2H), 4.14–4.23 (m, 4H), 4.95 (dd, $J = 1.5$, 10.2 Hz, 1H), 5.03 (dd, $J = 1.5$, 17.1 Hz, 1H), 5.78 (ddt, $J_d = 10.2$, 17.1 Hz, $J_t = 6.7$ Hz, 1H), 7.22–7.25 (m, 3H), 7.30–7.33 (m, 2H); ^{13}C-NMR $\delta = 14.0$, 23.7, 28.4, 56.9, 61.5, 83.3, 84.4, 115.1, 123.3, 127.9, 128.2, 131.6, 137.5, 170.3; Anal. Found: C, 73.11; H, 7.40. Calc. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37%.

4.1.16. Diethyl 1-phenyl-6,7-octadien-1-yne-4,4-dicarboxylate (**1o**)

This compound was prepared from 1-bromo-2,3-butadiene [32] and diethyl 3-phenyl-2-propynylmalonate [30] following the same procedure used for the synthesis of **1c**. Colorless oil; IR (neat) 1734, 1284, 1205, 1188 cm^{-1}; ^{1}H-NMR $\delta = 1.25$ (t, $J = 7.1$ Hz, 6H), 2.82 (dt, $J_d = 8.0$ Hz, $J_t = 2.4$ Hz, 2H), 3.05 (s, 2H), 4.18–4.24 (m, 4H), 4.67 (dt, $J_d = 6.7$ Hz, $J_t = 2.4$ Hz, 2H), 5.00 (tt, $J = 6.7$, 8.0 Hz, 1H), 7.24–7.27 (m, 3H), 7.33–7.36 (m, 2H); ^{13}C-NMR $\delta = 14.1$, 23.5, 31.8, 57.4, 61.6, 74.7, 83.5, 84.0, 84.3, 123.3, 127.9, 128.2, 131.6, 169.7, 210.2; HRMS Found m/z 326.1518. Calc. for $C_{20}H_{22}O_4$: M, 326.1518.

4.1.17. 4-tert-butyldimethylsiloxy-5,5-dimethyl-7-octen-2-yne (**1p**) [9]

This compound was prepared by the literature procedure [9]. Colorless oil; IR (neat) 2958, 2929, 2858, 1473, 1250, 1078, 856, 837, 775 cm^{-1}; ^{1}H-NMR $\delta = 0.06$ (s, 3H), 0.11 (s, 3H), 0.87 (s, 3H), 0.88 (s, 3H), 0.88 (s, 9H), 1.82 (d, $J = 2.1$ Hz, 3H), 2.04 (dd, $J = 7.6$, 13.5 Hz, 1H), 2.09 (dd, $J = 7.5$, 13.5 H, 1H), 3.96 (dd, $J = 2.1$, 4.2 Hz, 1H), 4.98–5.02 (m, 2H), 5.80 (m, 1H); ^{13}C-NMR $\delta = -5.2$, -4.3, 3.4, 18.2, 22.6, 22.7, 25.9, 39.2, 42.6, 70.9, 79.4, 81.2, 116.9, 135.6.

4.2. The general procedure for the Rh-catalyzed intramolecular Pauson–Khand reaction under 1 atm CO

To a dibutyl ether (4 ml) solution of $[RhCl(CO)_2]_2$ (3.9 mg, 0.01 mmol) was added a dibutyl ether (6 ml) solution of diethyl 6-nonen-3-yn-6,6-dicarboxylate (**1a**, 266.7 mg, 1.00 mmol) under an atmospheric pressure of CO and the mixture was heated at 130°C (the oil bath temperature) for 18 h. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 4:1, three times) to afford diethyl 8-ethyl-7-oxobicyclo[3.3.0]oct-1-(8)-ene-3,3-dicarboxylate (**2a**, 268.7 mg; 91% yield).

4.3. The Rh-catalyzed carbocyclization of norbornene and 1-phenylpropyne.

In a pressure-resistant glass tube, a dibutyl ether (0.7 ml) solution of $[RhCl(CO)_2]_2$ (4.2 mg, 0.0108 mmol), a dibutyl ether (0.7 ml) solution of 1-phenylpropyne (25.0 mg, 0.215 mmol), and a dibutyl ether (0.75 ml) solution of norbornene were combined with flowing argon. The atmosphere was replaced with 1 atm of CO and the tube was sealed. The reaction mixture was heated for 60 h at 130°C (the oil bath temperature). After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 7:1) to afford a mixture of (3a*R**,4*S**,7*R**, 7a*S**)-3-methyl-2-phenyl-3a,4,5,6,7,7a-tetrahydro-4,7-methano-inda-2-en-1-one (**7a**) and (3a*R**,4*S**, 7*R**,7a*S**)-2-methyl-2-phenyl-3a,4,5,6,7,7a-tetrahydro-4,7-methano-inda-2-en-1-one (**7b**). (**7a**:**7b** = 53:47, 35.6 mg; 69% total yield).

4.4. The Rh-catalyzed carbocyclization of ethylene and 1-phenylpropyne.

In a pressure-resistant glass tube, a dibutyl ether (1.5 ml) solution of $[RhCl(CO)_2]_2$ (6.5 mg, 0.0167 mmol) and a dibutyl ether (1.85 ml) solution of 1-phenylpropyne were combined with flowing argon. The atmosphere was replaced with 1 atm of CO and 10 atm of ethylene was introduced. The reaction mixture was heated for 60 h at 130°C (the oil bath temperature). After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane:ethyl acetate = 5:1, three times) to afford 3-methyl-2-phenyl-2-cyclopentenone (**8a**, 11.3 mg; 19%) and 2-methyl-3-phenyl-2-cyclopentenone (**8b**, 11.1 mg; 19%).

4.5. The general procedure for the Rh-catalyzed intramolecular Pauson–Khand reaction under 0.1 atm CO and 0.9 atm argon.

Carbon monoxide (10 atm) was introduced to an autoclave (100 ml) and transferred to a plastic balloon. Then 90 atm of argon was introduced to the autoclave and transferred to the balloon. The atmosphere of a three-necked flask (2 1) equipped with a mechanical stirrer bar was replaced with the mixed gas (CO:Ar = 1:9) in the balloon. In this flask, a toluene (5 ml) solution of $[RhCl(CO)_2]_2$ (192.9 mg, 0.496 mmol) and a toluene (5 ml) solution of 4-*tert*-butyldimethylsiloxy-5,5-dimethyl-7-octen-2-yne (**1p**, 2.51 g, 9.94 mmol) were combined. The mixture was heated at 100°C (the oil bath temperature) for 3 h with vigorous stirring by a mechanical stirrer (500 rpm). After evaporation of the solvent, the crude products were purified by column chromatography (silica gel, hexane:ethyl acetate = 100:1) to afford (5*R**,8*S**)-8-*tert*-butyldimethylsiloxy-2,7,7-trimethylbicyclo[3.3.0]oct-2(1)en-3-one (**2p**, 1.97 g; 71% yield) and (5*R**,8*R**)-8-dimethyl-(1,1-dimethylethyl)siloxy-2,7,7-trimethylbicyclo[3.3.0]oct-1-en-3-one (**2q**, 0.21 g; 8% yield).

4.6. The spectral data and the physical properties of the products

4.6.1. Diethyl 8-ethyl-7-oxobicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2a**) [12b]

Colorless oil; IR (neat) 1732, 1713, 1707, 1668, 1261 cm^{-1}; ^{1}H-NMR $\delta = 1.03$ (t, $J = 7.6$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.26 (t, $J = 7.0$ Hz, 3H), 1.62 (dd, $J = 12.6$, 12.6 Hz, 1H), 2.05 (dd, $J = 3.1$, 17.9 Hz, 1H), 2.10–2.16 (m, 1H), 2.19–2.27 (m, 1H), 2.60 (dd, $J =$ 6.3, 17.9 Hz, 1H), 2.76 (dd, $J = 7.4$, 12.6 Hz, 1H), 2.90–2.98 (m, 1H), 3.21(s, 2H), 4.18 (q, $J = 7.0$ Hz, 2H), 4.22 (q, $J = 7.0$ Hz, 2H); ^{13}C-NMR $\delta = 12.5$, 14.0, 14.0, 17.1, 34.1, 39.1, 41.5, 42.8, 61.1, 61.9, 62.0, 138.5, 171.0, 171.6, 177.1, 209.1.

4.6.2. Diethyl 7-oxo-8-phenyl-bicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2b**) [12a]

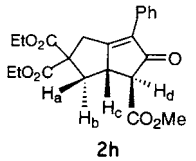
Colorless crystals; mp 90–91°C (hexane); IR (KBr) 1730, 1705, 1273, 1254 cm^{-1}; ^{1}H-NMR $\delta = 1.20$ (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.74 (dd, $J = 12.7$, 12.7 Hz, 1H), 2.28 (dd, $J = 3.4$, 17.8 Hz, 1H), 2.78–2.83 (m, 2H), 3.07–3.16 (m, 1H), 3.27 (d, $J = 19.2$ Hz, 1H), 3.62 (d, $J = 19.2$ Hz, 1H), 4.10–4.20 (m, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 7.31 (dd, $J = 7.5$, 7.5 Hz, 1H), 7.39 (dd, $J = 7.5$, 7.5 Hz, 2H), 7.54 (d, $J = 7.5$ Hz, 2H); ^{13}C-NMR $\delta = 13.9$, 14.0, 35.8, 38.7, 42.6, 42.8, 61.3, 61.9, 62.1, 128.1, 128.4, 130.9, 135.4, 170.7, 171.5, 178.9, 207.1.

4.6.3. Diethyl 7-oxobicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2e**) [12a]

Colorless oil; IR (neat) 2980, 1734, 1635, 1254 cm^{-1}; ^{1}H-NMR $\delta = 1.27$–1.21 (m, 6H), 1.71 (dd, $J = 12.8$, 12.8 Hz, 1H), 2.10 (dd, $J = 3.2$, 17.9 Hz, 1H), 2.60 (dd, $J = 6.4$, 17.9 Hz, 1H), 2.77 (dd, $J = 7.7$, 12.8 Hz, 1H), 3.04–3.12 (m, 1H), 3.22 (d, $J = 19.0$ Hz, 1H), 3.32 (d, $J = 19.0$ Hz, 1H), 4.16–4.24 (m, 4H), 5.90 (s, 1H); ^{13}C-NMR $\delta = 14.0$, 35.1, 38.9, 42.1, 45.0, 60.8, 62.0, 62.1, 125.5, 170.7, 171.4, 185.5, 209.5.

4.6.4. Diethyl 7-oxo-8-trimethylsilyibicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2d**) [12a]

Colorless crystals; mp 64–65°C (hexane–Et_2O) (lit., 66–68°C); IR (KBr) 1726, 1697, 1259, 1240, 1188 cm^{-1}; ^{1}H-NMR $\delta = 0.18$ (s, 9H), 1.23 (t, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.65 (dd, $J = 12.7$, 12.7 Hz, 1H), 2.04 (dd, $J = 4.0$, 17.5 Hz, 1H), 2.55 (dd, $J = 6.7$, 17.5 Hz, 1H), 2.76 (dd, $J = 7.7$, 12.7 Hz, 1H), 2.95–3.04 (m, 1H), 3.21 (d, $J = 19.0$ Hz, 1H), 3.30 (d,



2h

Fig. 4.

$J = 19.0$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 4.20–4.25 (m, 2H); ^{13}C-NMR $\delta = -1.3$, 14.0, 36.2, 38.5, 42.9, 46.5, 60.8, 61.9, 62.0, 136.6, 171.0, 171.6, 192.4, 213.2.

4.6.5. Diethyl 5-methyl-7-oxo-8-phenylbicyclo-[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2e**)

Colorless oil; IR (neat) 2979, 1732, 1711, 1257 cm^{-1}; ^{1}H-NMR $\delta = 1.13$ (t, $J = 7.1$ Hz, 3H), 1.20 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 2.27 (d, $J = 13.7$ Hz, 1H), 2.52 (s, 1H), 2.55 (s, 1H), 2.60 (d, $J = 13.7$ Hz, 1H), 3.24 (d, $J = 18.3$ Hz, 1H), 3.77 (d, $J = 18.3$ Hz, 1H), 4.05 (dq, $J_d = 10.8$ Hz, $J_q = 7.1$ Hz, 1H), 4.11 (dq, $J_d = 10.8$ Hz, $J_q = 7.1$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 7.28–7.50 (m, 5H); ^{13}C-NMR $\delta = 13.8$, 14.0, 26.9, 34.6, 44.2, 47.8, 52.4, 60.7, 62.0, 62.2, 128.1, 128.3, 128.7, 130.8, 134.2, 171.2, 171.8, 182.0, 206.9; Anal. Found: C, 70.57; H, 6.84. Calc. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79%.

4.6.6. (5R*,6R*)-diethyl 6-methyl-7-oxo-8-phenylbicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2f**) [11a]

Colorless oil; IR (neat) 1732, 1707, 1267, 1255 cm^{-1}; ^{1}H-NMR $\delta = 1.21$ (t, $J = 7.0$ Hz, 3H), 1.28 (d, $J = 7.3$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.79 (dd, $J = 12.5$, 12.5 Hz, 1H), 2.28 (dq, $J_d = 3.4$ Hz, $J_q = 7.3$ Hz, 1H), 2.73–2.78 (m, 1H), 2.84 (dd, $J = 7.6$, 12.5 Hz, 1H), 3.27 (d, $J = 19.2$ Hz, 1H), 3.61 (d, $J = 19.2$ Hz, 1H), 4.13 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 4.17 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 4.26 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 4.28 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 7.29–7.57 (m, 5H); ^{13}C-NMR $\delta = 13.8$, 14.0, 14.0, 35.9, 38.2, 49.7, 51.6, 61.4, 61.9, 62.2, 128.1, 128.3, 128.4, 131.1, 134.6, 170.8, 171.6, 176.2, 209.0.

4.6.7. (5R*,6S*)-diethyl 6-methyl-7-oxo-8-phenylbicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate (**2g**) [11a]

Colorless oil; IR (neat) 1732, 1703, 1271, 1254 cm^{-1}; ^{1}H-NMR $\delta = 1.14$ (d, $J = 7.4$ Hz, 3H), 1.22 (d, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.88 (dd, $J = 13.0$, 13.0 Hz, 1H), 2.56 (dd, $J = 7.6$, 12.4 Hz, 1H), 2.76 (dq, $J_d = 7.5$ Hz, $J_q = 7.5$ Hz, 1H), 3.21–3.27 (m, 1H), 3.25 (dd, $J = 1.5$, 19.9 Hz, 1H), 3.65 (d, $J = 20.1$ Hz, 1H), 4.13–4.19 (m, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 7.30 (tt, $J = 1.2$, 7.4 Hz, 1H), 7.38 (dd, $J = 7.5$, 7.5 Hz, 2H), 7.55 (dd, $J = 1.3$, 7.5 Hz, 2H); ^{13}C-NMR $\delta = 13.5$, 14.0, 14.0, 33.6, 36.0, 43.8, 47.1, 60.8, 62.0, 62.1, 128.1, 128.4, 131.2, 133.3, 170.8, 171.6, 177.7, 210.4.

4.6.8. (5R*,6R*)-3,3-Diethyl-6-methyl-8-phenyl-7-oxobicyclo[3.3.0]oct-1(8)-ene-3,3,6-tricarboxylate (**2h**)

Colorless oil; IR (neat) 1730, 1714, 1271 cm^{-1}; ^{1}H-NMR $\delta = 1.20$ (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.86 (dd, $J = 12.7$, 12.7 Hz, 1H), 2.87 (dd, $J = 7.7$, 12.9 Hz, 1H), 3.26–3.30 (m, 2H), 3.50–3.57 (m, 1H), 3.68 (d, $J = 19.3$ Hz, 1H), 3.79 (s, 3H), 4.10–4.20 (m, 2H), 4.22–4.32 (m, 2H), 7.32 (t, $J = 7.4$ Hz, 1H), 7.39 (dd, $J = 7.5$, 7.5 Hz, 2H), 7.53 (dd, $J = 1.1$, 7.4 Hz, 2H), 7.55 (dd, $J = 1.3$, 7.5 Hz, 2H); ^{13}C-NMR $\delta = 13.9$, 14.0, 35.8, 37.7, 46.6, 52.6, 59.8, 61.1, 62.1, 62.3, 128.4, 128.5, 128.6, 130.3, 133.6, 169.2, 170.5, 171.1, 177.7, 200.2; Anal. Found: C, 65.73; H, 5.96. Calc. for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04%. The relative stereochemistry was determined by NOESY spectrum in which NOEs between H_a and H_c, H_b and H_d were observed while NOEs between H_c and H_d, H_b and H_d were not observed (Fig. 4).

4.6.9. 3,3-Dimethyl-8-phenylbicyclo[3.3.0]oct-1(8)-ene-2,7-dione (**2i**)

Yellow oil; IR (neat) 2964, 1743, 1712, 1045,758, 692 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (s, 6H), 2.43 (d, $J = 7.4$ Hz, 2H), 5.06–5.10 (m, 2H), 5.73 (ddt, $J_d = 10.1$, 16.9 Hz, $J_t = 7.4$ Hz, 1H), 7.35–7.38 (m, 2H), 7.42–7.44 (m, 1H), 7.55–7.57 (m, 2H); ^{13}C-NMR $\delta = 23.7$, 43.7, 48.2, 86.2, 92.2, 118.3, 120.3, 128.6, 130.6, 132.9, 133.6, 193.4; HRMS Found m/z 240.1171. Calc. for $C_{17}H_{22}O_7$: M, 240.1150.

4.6.10. Triethyl 7-oxobicyclo[3.3.0]oct-1(8)-ene-3,3,8-tricarboxylate (**2j**)

This compound was purified via flush column chromatography with neutral silica gel (E. Merck). Pale yellow oil; IR (neat) 1747, 1738, 1732, 1275, 1254, 1230 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (t, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.31 (t, $J = 7.1$ Hz, 3H), 1.76 (dd, $J = 12.8$, 12.8 Hz, 1H), 2.22 (dd, $J = 3.9$, 17.8 Hz, 1H), 2.73 (dd, $J = 6.7$, 17.8 Hz, 1H), 3.08–3.14 (m, 1H), 3.58 (d, $J = 21.2$ Hz, 1H), 3.59 (d, $J = 21.5$ Hz, 1H), 4.15–4.30 (m, 6H); ^{13}C-NMR $\delta = 14.0$ (probably overlapped), 14.3, 37.0, 38.4, 42.7, 43.6, 60.7, 60.8, 62.1, 62.3, 127.7, 161.7, 170.3, 171.1, 194.4, 202.3; HRMS Found m/z 338.1366. Calc. for $C_{17}H_{22}O_7$: M, 338.1366.

4.6.11. 2-Phenyl-bicyclo[3.3.0]oct-1-en-3-one (**2k**) [29]

Colorless crystals; mp 59°C (hexane–Et_2O) (lit., 62–63°C); IR (KBr) 1691, 1628, 1134 cm^{-1}; ^{1}H-NMR $\delta = 1.07$–1.15 (m, 1H), 2.04–2.11 (m, 2H), 2.18–2.26 (m, 2H), 2.63 (ddd, $J = 8.3$, 8.3, 19.1 Hz, 1H), 2.79 (dd, $J = 6.7$, 17.8 Hz, 1H), 2.84–2.91 (m, 2H), 7.28 (t, $J = 7.4$ Hz, 1H), 7.37 (dd, $J = 7.6$, 7.6 Hz, 2H), 7.57 (dd, $J = 1.3$, 7.9 Hz, 2H); ^{13}C-NMR $\delta = 25.9$, 27.2, 30.9, 42.9, 44.6, 127.6, 128.2, 128.2, 131.7, 134.4, 185.3, 208.6.

*4.6.12. 2-Phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one (**2l**) [12a]*

Colorless oil; IR (neat) 1707, 1026 cm^{-1}; ^{1}H-NMR $\delta = 2.32$ (dd, $J = 3.5$, 17.6 Hz, 1H), 2.83 (ddd, $J = 0.4$, 6.3, 17.6 Hz, 1H), 3.22 (dd, $J = 7.8$, 11.2 Hz, 1H), 3.26–3.35 (m, 1H), 4.35 (dd, $J = 7.7$, 7.7 Hz, 1H), 4.57 (d, $J = 16.3$ Hz, 1H), 4.92 (d, $J = 16.3$ Hz, 1H), 7.31–7.34 (m, 1H), 7.37–7.41 (m, 2H), 7.50 (dd, $J = 1.4$, 7.9 Hz, 2H); ^{13}C-NMR $\delta = 40.3$, 43.3, 66.3, 71.3, 128.0, 128.6, 128.6, 130.5, 134.7, 177.4, 206.8.

*4.6.13. 7-(4-Methylphenylsulfonyl)-2-phenyl-7-azabicyclo[3.3.0]oct-1-en-3-one (**2m**) [10b,10j]*

Colorless crystals; mp 139–142°C (hexane–Et_2O) (lit., 120°C [10b], 165.2–166.5°C [10j]); IR (KBr) 1705, 1348, 1168, 1157 cm^{-1}; ^{1}H-NMR $\delta = 2.23$ (dd, $J = 3.7$, 17.8 Hz, 1H), 2.38 (s, 3H), 2.59 (dd, $J = 9.4$, 10.9 Hz, 1H), 2.77 (dd, $J = 6.5$, 17.8 Hz, 1H), 3.14–3.22 (m, 1H), 4.03–4.08 (m, 2H), 4.61 (d, $J = 16.9$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.33–7.44 (m, SH), 7.69 (d, $J = 8.2$ Hz, 2H); ^{13}C-NMR $\delta = 21.5$, 40.7, 41.8, 48.3, 52.0, 127.4, 128.2, 128.7, 128.9, 129.9, 130.0, 133.8, 136.1, 144.0, 171.8, 205.4.

*4.6.14. Diethyl 8-oxo-9-phenylbicyclo[4.3.0]non-1(9)-ene-3,3-dicarboxylate (**2n**)*

Colorless crystals; mp 104°C (hexane); IR (KBr) 1730, 1687, 1259, 1244, 1198 cm^{-1}; ^{1}H-NMR $\delta = 0.97$ (t, $J = 7.0$ Hz, 3H), 1.20 (t, $J = 7.0$ Hz, 3H), 1.38–1.47 (m, 1H), 1.92–1.98 (m, 1H), 2.11 (d, $J = 16.8$ Hz, 1H), 2.17–2.22 (m, 1H), 2.50 (ddd, $J = 3.4$, 5.5, 13.7 Hz, 1H), 2.66–2.77 (m, 3H), 3.67 (dd, $J = 2.1$, 13.7 Hz, 1H), 3.91 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 4.03 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 4.14 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 4.17 (dq, $J_d = 10.7$ Hz, $J_q = 7.0$ Hz, 1H), 7.28–7.32 (m, 3H), 7.37–7.40 (m, 2H); ^{13}C-NMR $\delta = 13.6$, 13.9, 30.3, 30.7, 33.4, 39.0, 41.5, 56.2, 61.4, 61.9, 127.8, 128.3, 129.0, 130.9, 139.9, 170.0, 171.1, 171.4, 205.9; Anal. Found: C, 70.76; H, 6.88. Calc. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79%.

*4.6.15. Diethyl 8-oxo-9-phenylbicyclo[4.3.0]non-1(9),5-diene-3,3-dicarboxylate (**2o**)*

This compound was so unstable that the yield was determined by NMR with anthracene as an internal standard. Colorless oil; IR (neat) 1734, 1695, 1252 cm^{-1}; ^{1}H-NMR $\delta = 1.18$ (t, $J = 7.1$ Hz, 6H), 2.93 (d, $J = 4.4$ Hz, 2H), 3.04 (s, 2H), 3.31 (s, 2H), 4.10–4.20 (m, 4H), 5.95 (t, $J = 4.3$ Hz, 1H), 7.30–7.34 (m, 1H), 7.39–7.44 (m, 4H); ^{13}C-NMR $\delta = 13.9$, 31.0, 31.3, 38.5, 54.5, 61.9, 121.8, 128.1, 128.4, 128.9, 130.8, 134.9, 139.0, 160.3, 170.2, 202.9; HRMS Found m/z 354.1473. Calc. for $C_{21}H_{22}O_5$:M, 354.1467.

4.6.16. (5R,8S*)-8-tert-Butyldimethylsiloxy-2,7,7-trimethylbicyclo[3.3.0]oct-1-en-3-one (**2p**) [9]*

Brown oil; IR (neat) 2954, 2929, 1712, 1678, 1090, 1068, 858, 837, 775 cm^{-1}; ^{1}H-NMR $\delta = 0.00$ (s, 3H), 0.09 (s, 3H), 0.79 (s, 9H), 0.86 (s, 3H), 1.02 (dd, $J = 7.1$, 12.9 Hz, 1H), 1.10 (s, 3H), 1.74 (d, $J = 2.3$ Hz, 3H), 1.97 (dd, $J = 3.0$, 18.0 Hz, 1H), 1.99 (dd, $J = 11.0$, 12.9 Hz, 1H), 2.69 (dd, $J = 6.6$, 18.0 Hz, 1H), 3.18–3.25 (brs, 1H), 4.05–4.08 (brs, 1H); ^{13}C-NMR $\delta = -4.9$, -4.6, 8.8, 18.2, 24.0, 25.7 (probably 2 carbons overlapped), 29.0, 39.3, 43.1, 44.0, 45.2, 76.2, 132.0, 180.7, 211.6.

4.6.17. (5R,8R*)-8-tert-Butydimethylsiloxy-2,7,7-trimethylbicyclo[3.3.0]oct-1-en-3-one (**2q**) [9]*

Brown oil; IR (neat) 2956, 2931, 2860, 1713, 1672, 1134, 837, 775 cm^{-1}; ^{1}H-NMR $\delta = 0.11$ (s, 6H), 0.82 (s, 3H), 0.94 (s, 9H), 1.14 (s, 3H), 1.23 (dd, $J = 8.3$, 13.2 Hz, 1H), 1.81 (dd, $J = 1.8$, 1.8 Hz, 3H), 1.93 (dd, 10.0, 13.2 Hz, 1H), 1.95 (dd, $J = 3.0$, 17.9 Hz, 1H), 2.62 (dd, $J = 6.7$, 17.0, 1H), 2.74–2.83 (brs, 1H), 4.52–4.56 (brs, 1H); ^{13}C-NMR $\delta = -4.6$, -4.5, 7.8, 18.0, 24.5, 25.9 (probably 2 carbons overlapped), 28.8, 35.2, 43.3, 43.7, 43.9, 80.4, 132.2, 179.9, 210.7.

*4.6.18. Diethyl 8-(2,2-bis(ethoxycarbonyl)-4-pentenyl)-7-oxobicyclo[5.3.0]deca-5,8-diene-3,3-dicarboxylate (**4**)*

Colorless oil; IR(neat) 1732, 1290, 1254, 1190 cm^{-1}; ^{1}H-NMR $\delta = 1.18$–1.25 (m, 12H), 1.91 (dd, $J = 10.9$, 12.9 Hz, 1H), 2.29–2.37 (m, 2H), 2.44 (dd, $J = 7.0$, 14.3 Hz, 1H), 2.52 (dd, $J = 7.6$, 14.3 Hz, 1H), 2.60 (d, $J = 13.8$ Hz, 1H), 2.61–2.65 (m, 1H), 2.90–2.99 (m, 1H), 3.16 (dt, $J_d = 18.8$ Hz, $J_t = 2.3$ Hz, 1H), 3.23 (d, $J = 18.8$ Hz, 1H), 3.30 (d, $J = 13.9$ Hz, 1H), 4.03–4.23 (m, 8H), 5.04 (d, $J = 15.5$ Hz, 1H), 5.04 (d, $J = 11.7$ Hz, 1H), 5.66–5.75 (m, 1H), 6.06 (d, $J = 2.2$ Hz, 1H), 6.51 (dd, $J = 4.4$, 8.2 Hz, 1H); ^{13}C-NMR $\delta = 13.9$, 14.0 (probably 2 carbons overlapped), 32.2, 35.7, 37.6, 40.8, 41.4, 42.3, 58.0, 58.5, 61.0, 61.1, 61.9 (probably overlapped), 118.7, 126.0, 132.9, 139.4, 140.2, 162.8, 170.7, 170.8, 170.8, 170.9, 190.1; HRMS Found m/z 504.2361. Calc. for $C_{27}H_{36}O_9$: M, 504.2359.

*4.6.19. Diethyl 4-methyl-3-(1-phenylethenyl)-3-cyclopentene-1,1-dicarboxylate (**5a**)*

After removal of **5b** by HPLC, **5a** was isolated in a pure form. Colorless oil; IR(neat) 1732, 1254, 1184, 1070 cm^{-1}; ^{1}H-NMR $\delta = 1.23$ (t, $J = 7.1$ Hz, 6H), 1.52 (s, 3H), 3.07 (brs, 2H), 3.10 (dd, $J = 1.8$, 3.7Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 4H), 5.09 (d, $J = 1.5$ Hz, 1H), 5.41 (d, $J = 1.6$ Hz, 1H), 7.22–7.30 (m, 5H); ^{13}C-NMR $\delta = 14.0$, 14.9, 44.5, 46.4, 57.4, 61.5, 114.8, 127.0, 127.5, 128.2, 132.6, 134.2, 140.4, 144.9, 172.2; HRMS Found m/z 328.1688. Calc. for $C_{20}H_{24}O_4$: M, 328.1675.

*4.6.20. 2,5-Dimethyl-3,6-diphenylyclohexa-2,5-diene-1,4-dione (**6a**), 2,6-Dimethyl-3,5-diphenylcyclohexa-2,5-diene-1,4-dione (**6b**)*

These compounds were obtained as a mixture (**6a**:**6b** = ca. 2:1). Yellow solid; IR (neat) 1652, 1644, 1693, 1492, 1442, 1375, 1294 cm^{-1}; **6a**: ^{1}H-NMR δ = 1.97 (s, 6H), 7.16–7.21 (m, 4H), 7.35–7.46 (m, 6H); ^{13}C-NMR $\delta = 14.1$, 128.1, 128.4, 129.4, 133.4, 141.3, 143.8, 187.3. **6b**: ^{1}H-NMR $\delta = 2.02$ (s, 6H), 7.16–7.21 (m, 4H), 7.35–7.46 (m, 6H); ^{13}C-NMR $\delta = 14.1$, 128.0, 128.4, 129.6, 133.2, 141.4, 143.5, 185.8, 188.9.

4.6.21. (3aR,4S*,7R*,7aS*)-3-methyl-2-phenyl-3a,4,5,6,7,7a-tetrahydro-4,7-methano-ind-2-en-1-one (**7a**) [33]; (3aR*,4S*,7R*,7aS)-2-methyl-3-phenyl-3a,4,5,6,7,7a-tetrahydro-4,7-methano-ind-2-en-1-one (**7b**)*

These compounds were obtained as a mixture (**7a**:**7b** = 53:47). Colorless oil; IR (neat) 2952, 2931, 1693, 698 cm^{-1}; ^{1}H-NMR $\delta = 0.91$ (ddd, $J = 1.2$, 1.2, 10.5 Hz, 1H × 0.47), 0.98–1.04 (m, 1H), 1.11 (ddd, $J = 1.6$, 1.6, 10.5 Hz, 1H × 0.53), 1.27–1.38 (m, 2H), 1.58–1.64 (m, 1H + 1H × 0.47), 1.68–1.75 (m, 1H × 0.53), 1.89 (m, 3H × 0.47), 2.01(brs, 1H × 0.47), 2.12 (s, 3H × 0.53), 2.31 (d, $J = 5.2$ Hz, 1H × 0.53), 2.32 (d, $J = 4.8$ Hz, 1H × 0.47), 2.35 (d, $J = 4.1$ Hz, 1H × 0.53), 2.46 (brs, 1 × 0.47H), 2.48 (d, $J = 3.8$ Hz, 1H × 0.53), 2.58 (d, $J = 5.2$ Hz, 1H × 0.53), 3.04 (d, $J = 4.8$ Hz, 1H × 0.47), 7.24–7.27 (m, 2H × 0.53), 7.28–7.30 (m, 1H × 0.53), 7.36–7.40 (m, 1H + 1H × 0.53), 7.41–7.47 (m, 4H × 0.47); ^{13}C-NMR $\delta = 9.7$, 16.7, 28.6, 28.8, 28.9, 29.2, 31.4, 31.4, 37.6, 38.0, 39.1 (probably overlapped), 50.8, 52.8, 53.5, 54.0, 127.5, 127.9, 128.2, 128.5, 129.0, 129.1, 131.9, 135.9, 139.5, 143.3, 168.5, 172.2, 208.4, 210.8; HRMS Found m/z 238.1344. Calc. for $C_{17}H_{18}O$: M, 238.1357. The relative stereochemistry of major isomer (**7a**) was determined by the NOESY spectrum in which NOEs between H_a and H_c, H_b and H_d, H_c and H_d were observed, while NOEs between H_c and H_e were not observed. The relative stereochemistry of minor isomer (**7b**) was also determined by the NOESY spectrum in which NOEs between H_f and H_g, H_g and H_h were observed, while NOEs between H_g and H_i were not observed (Fig. 5).

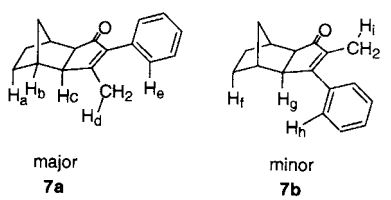


Fig. 5.

*4.6.22. 3-Methyl-2-phenyl-2-cyclopenten-1-one (**8a**) [34]*

Colorless oil; IR (neat) 1718, 1697, 1379, 1134 cm^{-1}; ^{1}H-NMR $\delta = 2.16$ (s, 3H), 2.53 (d, $J = 4.7$ Hz, 2H), 2.65 (d, $J = 4.4$ Hz, 2H), 7.26–7.31 (m, 3H), 7.39 (dd, $J = 7.6$, 7.6 Hz, 2H); ^{13}C-NMR $\delta = 9.9$, 29.3, 34.0, 127.5, 128.6, 129.4, 136.5, 136.6, 166.5, 209.7.

*4.6.23. 2-Methyl-3-phenyl-2-cyclopenten-1-one (**8b**) [35]*

Colorless oil; IR (neat) 1699, 1346 cm^{-1}; ^{1}H-NMR $\delta = 1.94$ (t, $J = 2.0$ Hz, 3H), 2.51–2.53 (m, 2H), 2.89–2.91 (m, 2H), 7.38–7.46 (m, 3H), 7.50 (d, $J = 7.0$ Hz, 2H); ^{13}C-NMR $\delta = 18.3$, 31.8, 34.8, 127.6, 128.2, 129.1, 131.9, 140.4, 171.6, 207.5.

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