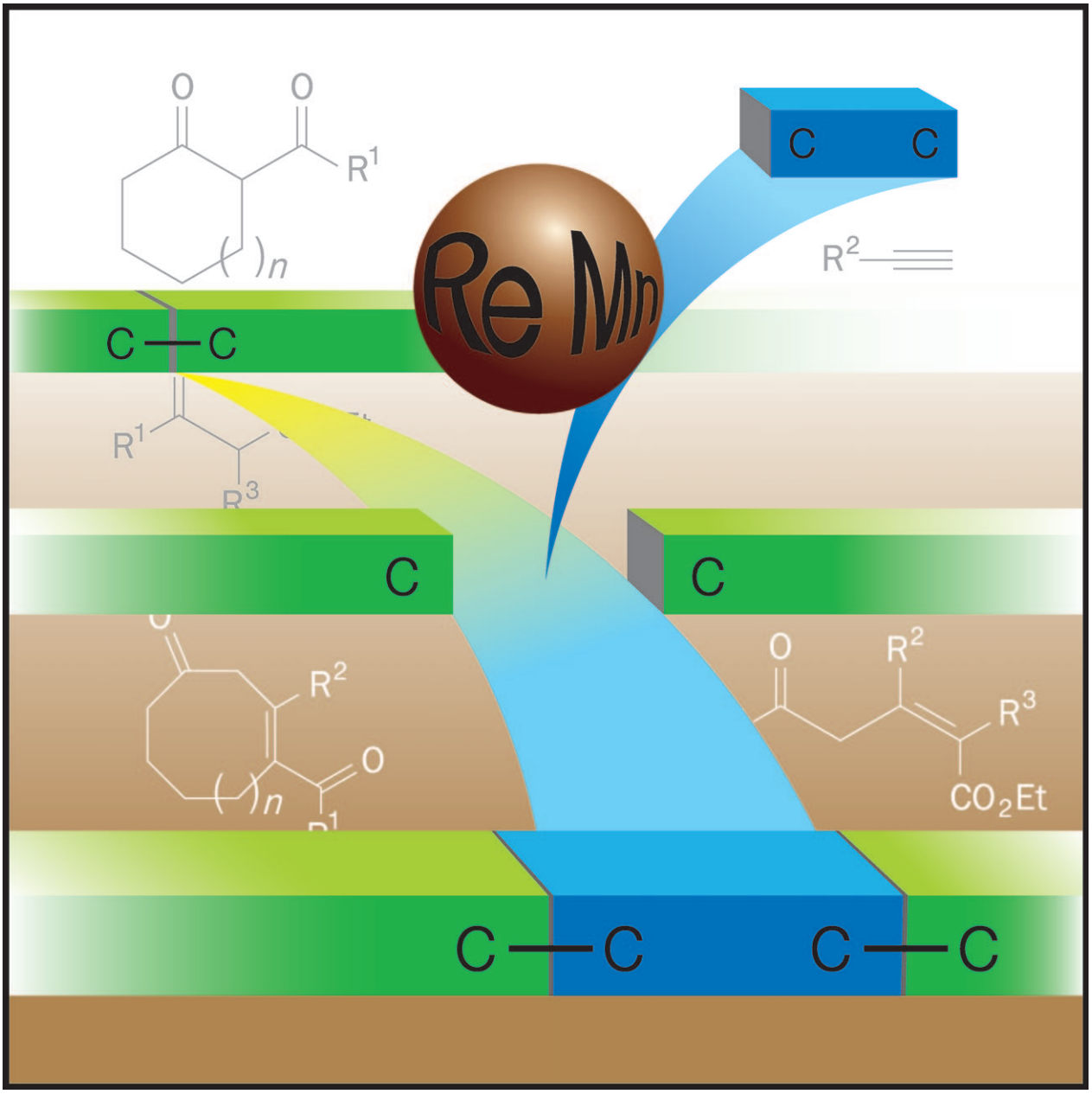
DOI: 10.1002/asia.200900137

VIP

Rhenium- and Manganese-Catalyzed Insertion of Alkynes into a Carbon–Carbon Single Bond of Cyclic and Acyclic 1,3-Dicarbonyl Compounds

Yoichiro Kuninobu,* Atsushi Kawata, Mitsumi Nishi, Salprima Yudha S., Jingjin Chen, and Kazuhiko Takai*[a]



Abstract: Treatment of alkynes with cyclic and acyclic 1,3-dicarbonyl compounds in the presence of a catalytic amount of a rhenium or manganese complex gives ring-expanded and carbon-chain extension products, respectively. In these reactions, alkynes insert into a non-strained carbon–carbon single bond of 1,3-dicarbonyl compounds. The ring-expansion reaction is also promoted by the addition of 4-Å molecular sieves instead of a catalytic amount of an isocyanide.

Keywords: alkynes · C–C activation · insertion · manganese · rhenium

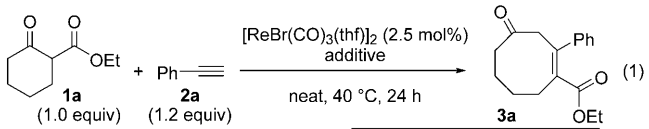
Introduction

The development of new synthetic methods to construct carbon chains has been an essential topic in organic chemistry because of the need to construct complex carbon skeletons present in molecules with a human application. Transformations to synthesize complex organic molecules have generally involved end-to-end reactions to combine two or more molecules together. Another useful method of transformation is the insertion of a molecular unit into a carbon–carbon bond of an existing molecule. Such transformations are direct and powerful ways to construct new carbon skeletons. However, transformations through carbon–carbon bond cleavage are usually difficult.[1] To realize efficient transformations through carbon–carbon bond cleavage, the following types of substrates are typically used: compounds with ring strain, such as three- and four-membered cyclic compounds,[2–4] or in the case of retro-allylation[5] and -arylation reactions, compounds with inherent steric bulkiness.[6] Herein, we report the insertion of alkynes into a carbon–carbon single bond of cyclic and acyclic β-keto esters by using rhenium and manganese catalysts.

Results and Discussion

Ring-Expansion Reactions

Medium-sized cyclic structures are important elements within many natural products and drugs. However, the construction of such structures is not always straightforward. A well-known method to efficiently synthesize medium-sized rings is the olefin metathesis reaction.[7] We have also reported on a rhenium-catalyzed ring-expansion reaction through the insertion of terminal alkynes into a carbon–carbon single bond of cyclic β-keto esters [Eq. (1)],[8] and its application to the regioselective synthesis of multi-substituted aromatic compounds.[9] In this reaction, the addition of isocyanide is important to promote the ring-expansion reaction. Recently, we have found that 4-Å molecular sieves (4 Å-MS) are also effective in promoting the reaction.[10]



(1)

additive	3a
$PhCH_2NC$ (5.0 mol%)	97%
4Å-MS (100 wt% Re-cat.)	98%

As described previously, a rhenium complex, $[ReBr(CO)_3(thf)]_2$, worked well as a catalyst for the ring-expansion reaction. Use of the rhenium catalyst along with a benzyl isocyanide additive provided ring-expanded products for the insertion of aryl, furyl, alkenyl, and alkyl acetylenes in good to excellent yields.[8] Instead of isocyanide, 4 Å-MS proved to be an effective additive to promote the ring-expansion reaction, and the ring-expanded products were obtained in almost the same yields as the previous report (Table 1, entries 1–10).

As a result of transition metals of the fourth row being abundant and cheap compared with those of the fifth and sixth rows, it would be desirable to replace rhenium (higher-row metal) catalysts with manganese (lower-row metal) analogues. Thus, we next examined the catalytic activity of $MnBr(CO)_5$. Reactions between cyclic β-keto ester **1a** and aryl acetylenes **2a–2c** in the presence of a catalytic amount of $MnBr(CO)_5$ at 80 °C for 24 h under solvent-free conditions gave eight-membered-ring products **3a–3c** in excellent

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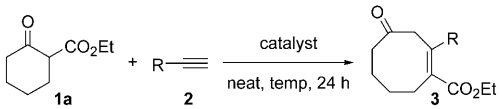
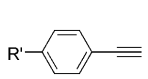
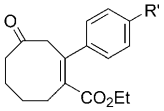
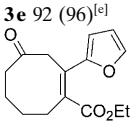
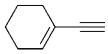
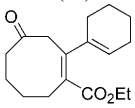
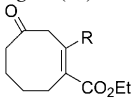
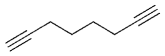
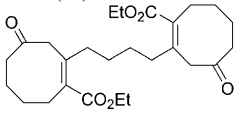
Table 1. Rhenium- or manganese-catalyzed reactions of β-keto ester **1a** with several alkynes **2**.[a]



Entry	Alkyne	Yield [%][b] $[ReBr(CO)_3(thf)]_2$ (2.5 mol%) 4 Å-MS (100 wt% Re-cat.) 40 °C	$MnBr(CO)_5$ (5.0 mol%) 80 °C
1			
	R′ = H **2a**	**3a** 97 (98)	84 (85)
2	MeO **2b**	**3b** 95 (>99)	95 (>99)
3	Me **2c**	**3c** 93 (98)	94 (99)
4	CF_3 **2d**	**3d** 88 (90)[c]	18 (18)[d]
5	Br **2e**	**3e** 92 (96)[e]	8 (8)[e]
6			
	2f	**3f** 74 (87)[f]	23 (27)
7			
	2g	**3g** 99 (99)	99 (>99)
8			
	R = $nC_{10}H_{21}$ **2h**	**3h** 92 (94)[f]	0 (0)
9	$Ph(CH_2)_2$ **2i**	**3i** 93 (95)[f]	22 (23)
10			
	2j	**3j** 95 (98)[g]	0 (0)[h]

[a] **2** (1.2 equiv). [b] Isolated yield. The yield determined by ^1H NMR is reported in parentheses. [c] **2d** (1.5 equiv). [d] **2d** (2.0 equiv). [e] **2e** (1.5 equiv). [f] Toluene, 80 °C. [g] **1a** (2.2 equiv), 80 °C. [h] **1a** (2.0 equiv), toluene was used as a solvent.

yields (Table 1, entries 1–3). On the other hand, aromatic alkynes containing an electron-withdrawing group, **2d** and **2e**, provided the corresponding eight-membered-cyclic compounds, **3d** and **3e**, in low yields (Table 1, entries 4 and 5).

Abstract in Japanese:

レニウムもしくはマンガン触媒存在下、アルキンと環状または鎖状の1,3-ジカルボニル化合物を反応させたところ、環拡大反応および炭素鎖伸長反応が進行した。これらの反応では、1,3-ジカルボニル化合物の歪のない炭素－炭素単結合にアルキンが挿入する。環拡大反応において、触媒量のイソシアニドのかわりにモレキュラーシーブスを添加することによっても、反応が促進されることが分かった。

Although the eight-membered-ring product **3f** was formed in 74% yield by using $[ReBr(CO)_3(thf)]_2$, the yield of **3f** decreased when $MnBr(CO)_5$ was used as a catalyst (Table 1, entry 6). An eight-membered-ring product **3g** was obtained quantitatively by using enyne **3g** (Table 1, entry 7). In contrast with the ring-enlargement reactions of **1a** with conjugated alkynes, those with alkyl acetylenes did not proceed well under the manganese catalysis (Table 1, entries 8–10).

Studies on the scope of the ring-expansion reactions of cyclic 1,3-dicarbonyl compounds are summarized in Table 2. The results indicate that the rhenium and manganese complexes, $[ReBr(CO)_3(thf)]_2$ and $MnBr(CO)_5$, have similar reactivities for 1,3-dicarbonyl compounds. That is, although both catalysts worked well for cyclic β-keto esters, the yields of ring-expanded products decreased when cyclic 1,3-diketones were employed (Table 2). The details of these investigations are described below. A nine-membered β-keto ester **3k** was produced at 40 °C in the presence of a catalytic amount of benzyl isocyanide from a seven-membered cyclic ester **1b** in excellent yield (Table 2, entry 1).[11] Although these reaction conditions were not applicable for the formation of a ten-membered ring from an eight-membered β-keto ester, heating the reaction mixture of a cyclooctanone-2-carboxylic acid ethyl ester (**1c**) and **2a** at 90 °C in the presence of $[ReBr(CO)_3(thf)]_2$ provided a ten-membered cyclic ester **3l** in 50% yield. The yield of the ten-membered cyclic compound **3l** was increased to 78% when benzyl isocyanide was not included in the reaction mixture (Table 2, entry 2). The use of a manganese complex, $MnBr(CO)_5$, as a catalyst, improved the yield of **3l** (Table 2, entry 2). In contrast, the reaction with cyclopentanone-2-carboxylic acid ethyl ester did not afford the expected ring-expansion product, but promoted the insertion of **2a** into a C–H bond of the β-keto ester to give an alkenyl derivative **4a**.[12–14] The reaction of a tetralone-2-carboxylic acid ethyl ester **1d** with **2a** in dichloromethane in the presence of 4-Å molecular sieves gave **3m**, a cyclic compound connected to an aromatic ring, in good yield (Table 2, entry 3). On the other hand, when $MnBr(CO)_5$ was used as a catalyst, **3m′**, which is an olefinic isomer of **3m** was formed (Table 2, entry 3). Next, we examined the ring enlargement of cyclic 1,3-diketones with phenylacetylene (**2a**) in the presence of $[ReBr(CO)_3(thf)]_2$ or $MnBr(CO)_5$. At a higher temperature of 50 °C in 1,2-dichloroethane, rhenium-catalyzed insertion reactions of 1,3-diketones with phenylacetylene (**2a**) proceeded to give eight-, nine-, and ten-membered cyclic compounds **3n–p** in 30–64% yields, respectively (Table 2, entries 4–6). In the case of $MnBr(CO)_5$, the yields of **3n–p** slightly decreased (Table 2, entries 4–6). However, 1,3-cyclohexanedione did not provide the corresponding eight-membered ring product at 50 °C for 24 h, either in 1,2-dichloroethane or in the absence of the solvent.

Modification of Reaction Conditions

The combination of the substrates and catalyst in this reaction is similar to that used in the insertion of terminal al-

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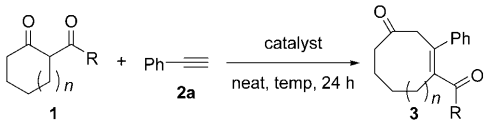
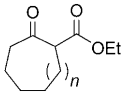
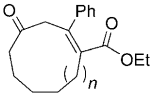
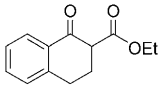
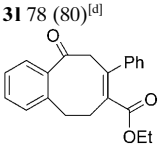
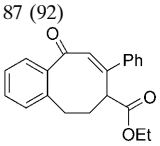
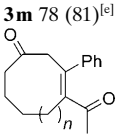
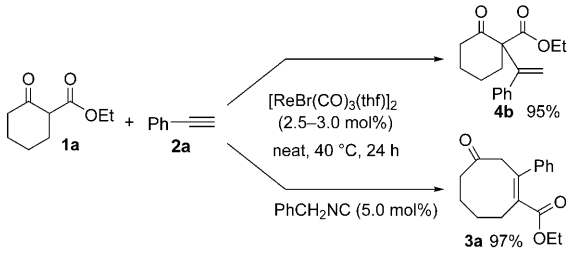
Table 2. Reactions of 1,3-dicarbonyl compounds **1** with phenylacetylene **2a**.[a]



Entry	1,3-Dicarbonyl compound	Yield [%][b] $[ReBr(CO)_3(thf)]_2$ (2.5 mol%) 4 Å-MS (100 wt% Re-cat.) 40 °C	$MnBr(CO)_5$ (5.0 mol%) 80 °C
1			
	$n=1$ **1b**	**3k** 87 (92)[c]	93 (98)
2	$n=2$ **1c**	**3l** 78 (80)[d]	87 (92)
3			
	1d	**3m** 78 (81)[e]	**3m′** 88 (90)[f]
4			
	$n=1$ **1e**	**3n** 61 (62)[g]	23 (25)[h]
5	$n=2$ **1f**	**3o** 64 (67)[g]	39 (49)[i]
6	$n=3$ **1g**	**3p** 30 (34)[g]	23 (27)[i]

[a] **1**: 0.50 mmol; **2a**: 0.60 mmol (1.2 equiv). [b] Isolated yield. The yield determined by ^1H NMR is reported in parentheses. [c] Benzyl isocyanide (5.0 mol%) was added instead of 4 Å-MS. [d] 4 Å-MS was not added. 50 °C. [e] Dichloromethane (1.0 mL) was used as a solvent. [f] 1,2-Dichloroethane was used as a solvent. After the reaction, tetrabutylammonium fluoride (20 mol%) was added and the mixture was stirred at 25 °C for 2 h. [g] 100 °C. [h] **2a** (2.0 equiv), 1,2-dichloroethane was used as a solvent. [i] 1,2-Dichloroethane was used as a solvent.

kynes into a C–H bond of the active methylene moieties of β-keto esters (Scheme 1).[12]

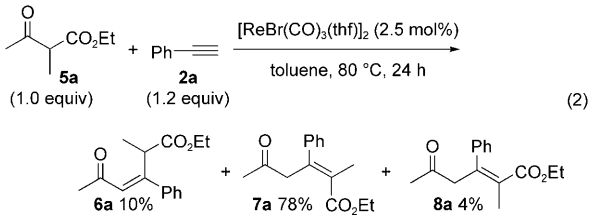


Scheme 1. Insertion of terminal alkynes into a C–H bond of the active methylene moieties of β-keto esters.

To clarify the reason for the difference, several experiments were conducted by using acyclic β-keto ester **5a** (Table 3). When the reaction between β-keto ester **5a** and phenylacetylene (**2a**) was carried out without any additive and solvent at 50 °C, **9** was obtained as a major product (Table 3, entry 1). However, the selectivities of **6a–8a** and **9** changed dramatically when the reactions were conducted in toluene (Table 3, entry 2), in low concentrations (Table 3, entries 3 and 4), at higher temperature (Table 3, entry 5), or by addition of THF or isocyanide (Table 3, entries 6–8).[15] Based on previous work in which the authors report that the dinuclear rhenium complex, $[ReBr(CO)_3(thf)]_2$, is cleaved to a mononuclear rhenium complex $ReBr(CO)_3(thf)_2$ in THF,[16] we are tempted to assume that a dinuclear rhenium species promotes the production of **9**, and that the mixture of **6a–8a** is formed when the mononuclear species is present.

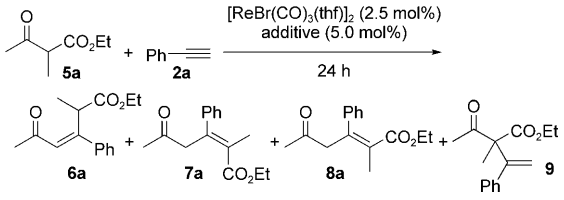
Carbon-Chain Extension Reactions

Treatment of β-keto ester **5a** and phenylacetylene (**2a**) with a catalytic amount of $[ReBr(CO)_3(thf)]_2$ promoted the insertion of an alkyne into a carbon–carbon single bond of the β-keto ester, and afforded a mixture of olefinic isomers, **6a**, **7a**, and **8a**, in 10%, 78%, and 4% yields, respectively [Eq. (2)].[17] This reaction did not proceed with other catalysts such as $RhCl(PPh_3)_3$, $Ir_4(CO)_{12}$, $Pd(OAc)_2/PPh_3$ (1:2), $Ni(cod)_2/PPh_3$ (1:2), $AuCl_3$, or $PtCl_2$.



By the reaction of a β-keto ester with a 2-phenethyl group at the active methylene moiety, **5b**, with phenylacetylene (**2a**) in the presence of the rhenium catalyst and molecular sieves, provided a mixture of δ-keto esters, **6b**, **7b**, and **8b** in 91% yield (**6b**/**7b**/**8b** = 14:84:2; Table 4, entry 1). Although the reason why molecular sieves accelerate the reaction remains unclear, it is notable that this reaction did not proceed when only molecular sieves were used. δ-Keto esters **6c–8c** were formed in moderate yields from a β-keto ester, **5c**, without any substituents at the active methylene moiety (Table 4, entry 2). The addition of a phenyl group at

Table 3. Selectivities between **6a–8a** and **9**.[a]



Entry	Additive	Solvent (conc./M)	Temp [°C]	Yield [%]	
				6a–8a	**9**
1	none	neat	50	33	66
2	none	toluene (2.0)	50	50	46
3	none	toluene (0.50)	50	77	14
4	none	toluene (0.25)	50	85	9
5	none	toluene (0.50)	80	92	<1
6	THF	neat	50	48	48
7[b]	THF	neat	50	65	34
8	2,6-*i*Pr$_2$C$_6$H$_3$NC	neat	50	76	15

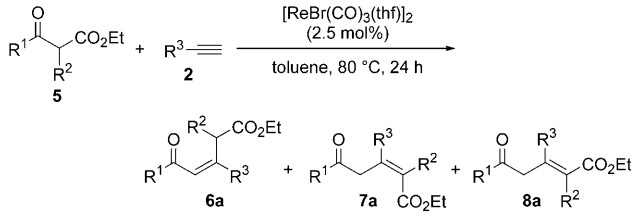
[a] **2a** (1.2 equiv). [b] THF (20 mol%).

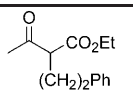
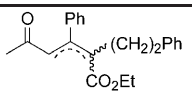
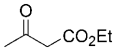
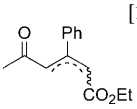
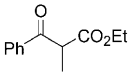
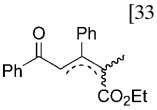
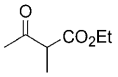
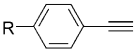
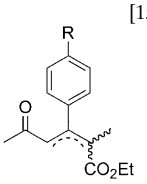
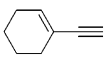
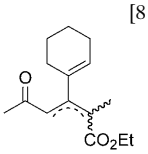
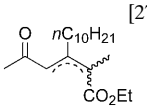
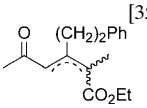
the R^1 position of the β-keto ester, **5d**, decreased the yield of the resulting δ-keto esters (Table 4, entry 3). However, δ-keto esters **6–8** were produced in good to excellent yields by using arylacetylenes with an electron-donating or -withdrawing group at the *para*-position of the phenyl group, **2b**, **2c**, and **2d** (Table 4, entries 4–6). The corresponding δ-keto esters **6h–8h** were obtained from 1-bromo-4-ethynylbenzene (**2e**), without the loss of the bromo group (Table 4, entry 7). Enyne **2f** and alkynes bearing a primary alkyl group, **2g** and **2h**, also afforded mixtures of δ-keto esters **6–8** in good-to-excellent yields (Table 4, entries 8–10). However, 3,3-dimethyl-1-butyne and ethynyltrimethylsilane did not give the corresponding δ-keto esters. A manganese complex, $MnBr(CO)_5$, also promoted the insertion of an alkyne into a carbon–carbon bond of β-keto esters, but the reaction did not stop at this stage. Instead, successive intramolecular cyclization proceeded and 2-pyranone derivatives were formed.[18]

The insertion reaction of an acetylene moiety into a carbon–carbon single bond of β-keto esters proceeds by an intramolecular fashion [Eq. (3)]. By heating a β-keto ester having an acetylene moiety, **10a**, under the reaction conditions shown in [Eq. (3)], insertion of the acetylene moiety into a carbon–carbon bond proceeded and cyclohexene **11a** and methylenecyclohexane **13a** were obtained in 66% and 16% yields, respectively.[19,20] In this reaction, **11a** and **13a** were produced by the insertion of the acetylene moiety into a carbon–carbon or carbon–hydrogen bond of **10a**. The yield and selectivity increased with the addition of 2,6-diisopropylphenyl isocyanide, and cyclohexene **11a** was obtained in 84% yield. Medium- and large-sized cyclic compounds, **11b** and **11c**, were also obtained by using β-keto esters with a longer alkyl chain at the active methylene moieties, **10b** and **10c** [Eq. (3)]. In these reactions, 2-pyranones **12b** and **12c**, which are formed by intramolecular cyclization of **11b** and **11c**, were also produced [Eq. (3)].

Allenes also inserted into a carbon–carbon single bond of 1,3-dicarbonyl compounds. Treatment of 1,3-diketone **14**

Table 4. Reactions between β-keto esters **5** and alkynes **2**.[a]



Entry	β-Keto ester	Alkyne[a]	Yield [%][b] (**6**+**7**+**8**) [**6**:**7**:**8**]	
1[c]				
	5b	**2a**	**6b–8b**	88 (91) [14:84:2]
2[d]		**2a**		
	5c		**6c–8c**	72 (75) [33:67:<1]
3[d]		**2a**		
	5d		**6d–8d**	51 (54) [15:78:7]
4				
	5a			
		R = MeO (**2b**)	**6e–8e**	88 (90) [17:80:3]
5		Me (**2c**)	**6f–8f**	85 (88) [10:89:1]
6[f]		CF_3 (**2d**)	**6g–8g**	90 (93) [9:86:5]
7[f]		Br (**2e**)	**6h–8h**	87 (90) [8:86:6]
8	**5a**			
		2f	**6i–8i**	92 (94) [27:67:6]
9[g]	**5a**	$nC_{10}H_{21}$—		
		2g	**6j–8j**	86 (89) [35:51:14]
10[h]	**5a**	$Ph(CH_2)_2$—		
		2h	**6k–8k**	73 (76) [29:53:18]

[a] **2** (1.2 equiv). [b] Isolated yield. The yield in parentheses (**6**+**7**+**8**) and the ratio [**6**:**7**:**8**] were determined by ^{1}H NMR. The structures of the regioisomers are not determined. [c] 4 Å-MS (100 wt% Re-cat.), 100 °C. [d] 2,6-*i*PrC$_6$H$_3$NC (5.0 mol%), 4 Å-MS (100 wt% Re-cat.). [e] 4 Å-MS (200 wt% Re-cat.), 100 °C. [f] 4 Å-MS (100 wt% Re-cat.). [g] 2,6-*i*PrC$_6$H$_3$NC (5.0 mol%), 4 Å-MS (200 wt% Re-cat.). [h] 4 Å-MS (200 wt% Re-cat.).

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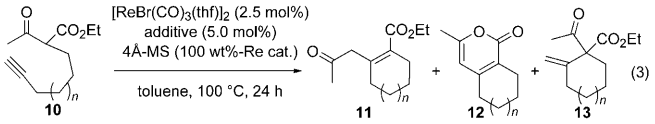
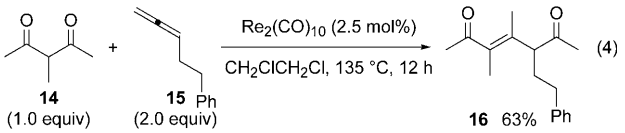


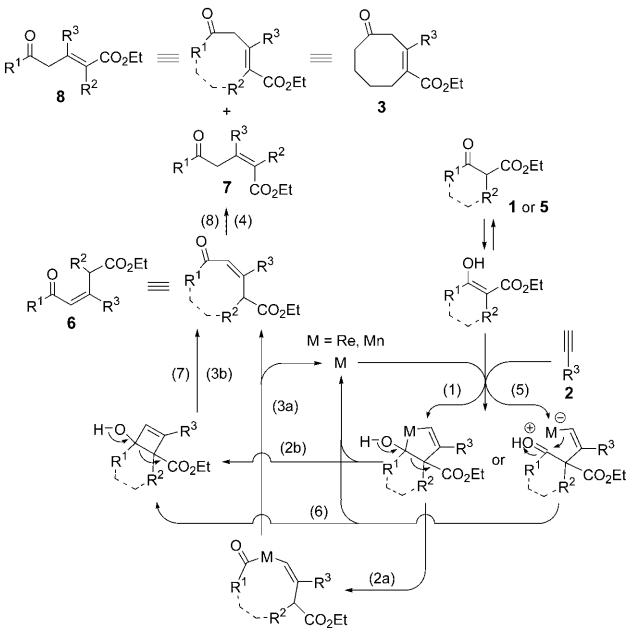
n		additive	11		12		13	
1	**10a**	none	**11a**	66%		<1%	**13a**	16%
1	**10a**	2,6-$iPr_2C_6H_3NC$	**11a**	84%		<1%	**13a**	7%
2	**10b**	2,6-$iPr_2C_6H_3NC$	**11b**	33%	**12b**	43%		<1%
10	**10c**	2,6-$iPr_2C_6H_3NC$	**11c**	12%	**12c**	40%		<1%

with allene **15** in the presence of a catalytic amount of a rhenium complex, $Re_2(CO)_{10}$, produced unsaturated 1,5-diketone **16** in 63% yield [Eq. (4)]. The result for the 1,3-diketones was in sharp contrast to the reactions by using β-keto esters, in which cyclopentene derivatives were formed with the rhenium catalyst.[21] In the case of the reactions between acyclic 1,3-dicarbonyl compounds and alkynes, the products were obtained as a mixture of olefinic isomers.(see [Eq. (2)] and Table 4) From this viewpoint, the reaction in [Eq. (4)] is useful because the allene **15** only produced a single product.



Proposed Mechanism

Although the alkenyl derivative **4b**,[12] which is formed by the insertion of phenylacetylene (**2a**) into a C–H bond of the β-keto esters **1a**, was exposed to similar reaction conditions, the ring expansion and carbon-chain extension reactions did not proceed and the starting material was recovered completely. This result indicates that the ring expansion and chain extension does not occur via alkenyl derivatives. In addition, an increase in reaction time led to a decrease in the yield of δ-keto ester **6** but an increase of the yield of the δ-keto ester **7**. This result indicates that isomerization of **6** proceeded and **7** was formed under the reaction conditions. Isomerization of an olefin moiety may be caused by the thermal stability of the products as compared with the intermediates, which are not isomerized. Our proposed mechanism for the reaction of cyclic and acyclic β-keto esters with terminal alkynes is illustrated in Scheme 2 and is described by the following steps: 1) The formation of a rhenacyclopentene or manganacyclopentene intermediate by the reaction of a rhenium or manganese catalyst, a β-keto ester, and a terminal alkyne.[8] After formation of the rhenacyclopentene or manganacyclopentene intermediate, there are two possible pathways; the difference between them depends on the timing of reductive elimination, outlined as follows: Path A: 2a) Ring opening by a retro-aldol reaction; 3a) reductive elimination; and 4) isomerization; Path B: 2b) Reductive elimination;[22] 3b) ring opening by a retro-aldol reaction; and 4) isomerization of the olefin moiety.[8] In 2007, we reported on rhenium-catalyzed [2+2] cycloaddition reactions of norbornenes with alkynes.[23] A rhenacyclopentene, which is postulated in the first step of the mechanism of this carbon-chain extension reaction, could be generated from $[ReBe(CO)_3(thf)]_2$, norbornene, and an alkyne in the [2+2] cycloaddition reaction. In addition, we observed that the rhenium complex $[ReBe(CO)_3(thf)]_2$ could promote retro-Claisen condensation, a kind of a retro-aldol reaction which is postulated in the cleavage of a carbon–carbon bond.[24] Another possible mechanism is that the reaction proceeds via: 5) The formation of an alkenyl-rhenium or -manganese intermediate;[25] 6) intramolecular nucleophilic cyclization; 7) ring opening by a retro-aldol reaction; and 8) isomerization of the olefin moiety.



Scheme 2. Proposed mechanism for the formation of cyclic and acyclic δ-keto esters.

Conclusions

We have succeeded in the insertion of alkynes into a carbon–carbon single bond of cyclic 1,3-dicarbonyl compounds and acyclic β-keto esters catalyzed by a rhenium complex, $[ReBr(CO)_3(thf)]_2$, or a manganese complex, $MnBr(CO)_5$. As a result, medium-sized cyclic and acyclic keto esters were obtained. These reactions proceed via the formation of a rhenacyclopentene or manganacyclopentene intermediate, carbon–carbon bond cleavage by a retro-aldol reaction, isomerization, and reductive elimination. There have only been a few examples of the insertion of a molecular unit into a non-strained C–C bond. Therefore, we hope that these highly atom-economical transformations will provide a useful concept for synthetic organic chemistry.

Experimental Section

General

All reactions were carried out under an argon atmosphere. Dichloromethane, 1,2-dichloroethane, and toluene were purchased from Kanto Kagaku Co. and were dried and degassed before use. $[ReBr(CO)_3(thf)]_2$ was prepared by heating a THF solution of $ReBr(CO)_5$ at reflux temperature for 16 h. $MnBr(CO)_5$ was prepared by stirring a solution of $Mn_2(CO)_{10}$ and bromine in cyclohexane at room temperature for 7 h. Cycloheptanone-2-carboxylic acid ethyl ester (**1b**),[26] cyclooctanone-2-carboxylic acid ethyl ester (**1c**),[26] ethyl 1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (**1d**),[26] 1-bromo-4-ethynylbenzene (**2e**),[26] ethyl 2-methyl-3-oxo-3-phenylpropionate (**5d**),[26] ethyl 2-acetyloct-7-ynoate (**10**),[27] and 5-phenylpentane-1,2-diene (**15**)[28] were prepared according to the literature method. Other β-keto esters, 1,3-diketone, other alkynes, and benzyl isocyanide were purchased from Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co., and Aldrich Co. and used as received. 4-Å molecular sieves in powder form were purchased from Nacalai Tesque Inc., and used without further activation.

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at $\delta = 0.00$ ppm or the residual solvent peak ($CDCl_3$ at $\delta = 7.26$ ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at $\delta = 77.00$ ppm. IR spectra were recorded on a Nicolet Protégé 460.

General Procedure for the Reaction of Cyclic β-Keto Esters with Terminal Alkynes

A mixture of cyclohexanone-2-carboxylic acid ethyl ester (**1a**, 85.1 mg, 0.500 mmol), phenylacetylene (**2a**, 61.3 mg, 0.600 mmol), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), and benzyl isocyanide (2.9 mg, 0.0250 mmol) was stirred at 40 °C for 24 h under solvent-free conditions. The product was isolated by column chromatography on silica gel to give the eight-membered-ring product **3a** in 97% yield (132 mg, 0.485 mmol).

Ethyl (*Z*)-4-oxo-2-phenyl-1-cyclooctenecarboxylate (3a): IR (neat): $\tilde{\nu} =$ 3026, 2948, 2859, 1700, 1493, 1403, 1389, 1225, 1095, 1030, 944, 918, 869, 767, 702, 639, 550, 520, 452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.82$ (t, $J = 7.2$ Hz, 3H), 1.86–1.95 (m, 4H), 2.56–2.58 (m, 2H), 2.61–2.63 (m, 2H), 3.56 (s, 2H), 3.87 (q, $J = 7.2$ Hz, 2H), 7.14 (d, $J = 7.2$ Hz, 2H), 7.24–7.31 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.3$, 24.4, 27.3, 29.6, 41.9, 50.4, 60.3, 126.7, 127.4, 128.1, 132.6, 140.2, 142.3, 169.9, 210.1 ppm; elemental analysis calcd (%) for $C_{17}H_{20}O_3$: C 74.97, H 7.40; found: C 74.76, H 7.30.

Ethyl (*Z*)-2-(4-methoxyphenyl)-4-oxo-1-cyclooctenecarboxylate (3b): IR (neat): $\tilde{\nu} = 2936$, 2859, 2834, 1701, 1608, 1512, 1464, 1368, 1292, 1249, 1179, 1140, 1108, 1067, 1033, 836, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 7.0$ Hz, 3H), 1.85–1.89 (m, 4H), 2.54–2.61 (m, 4H), 3.54 (s, 2H), 3.78 (s, 3H), 3.92 (q, $J = 7.1$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 7.09 ppm (d, $J = 8.7$ H, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.5$, 24.5, 27.3, 29.9, 41.9, 50.4, 55.1, 60.3, 113.5, 128.1, 132.1, 134.5, 139.5, 159.0, 170.3, 210.3 ppm; elemental analysis calcd (%) for $C_{18}H_{22}O_4$: C 71.50, H 7.33; found: C 71.24, H 7.43.

Ethyl (*Z*)-4-oxo-2-(4-methylphenyl)-1-cyclooctenecarboxylate (3c): IR (neat): $\tilde{\nu} = 3024$, 2936, 2866, 1764, 1721, 1513, 1368, 1239, 1097, 1032, 824, 767, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 7.2$ Hz, 3H), 1.86–1.92 (m, 4H), 2.33 (s, 3H), 2.54–2.63 (m, 4H), 3.55 (s, 2H), 3.90 (q, $J = 7.2$ Hz, 2H), 7.04 (d, $J = 8.1$ Hz, 2H), 7.10 ppm (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.5$, 21.1, 24.6, 27.3, 29.8, 42.0, 50.5, 60.4, 126.7, 128.9, 132.3, 137.3, 139.3, 140.2, 170.3, 210.8 ppm; elemental analysis calcd (%) for $C_{18}H_{22}O_3$: C 75.50, H 7.74; found: C 75.43, H 7.65.

Ethyl (*Z*)-2-[4-(trifluoromethyl)phenyl]-4-oxo-1-cyclooctenecarboxylate (3d): IR (neat): $\tilde{\nu} = 2927$, 2857, 1771, 1733, 1616, 1576, 1540, 1465, 1410, 1371, 1066, 1017, 850, 605 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.2$ Hz, 3H), 1.88–1.93 (m, 4H), 2.60–2.64 (m, 4H), 3.55 (s, 2H), 3.89 (q, $J = 7.2$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 7.58 ppm (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.2$, 24.3, 27.3, 29.5, 42.2, 50.3, 60.6, 123.9 ($J = 271$ Hz), 125.2 ($J = 3.6$ Hz), 127.2, 129.5 ($J = 30.6$ Hz), 133.7, 139.2, 146.1, 169.2, 209.4 ppm; elemental analysis calcd (%) for $C_{18}H_{19}F_3O_3$: C 63.52, H 5.63; found: C 63.40, H 5.61.

Ethyl (*Z*)-2-(4-bromophenyl)-4-oxo-1-cyclooctenecarboxylate (3e): IR (neat): $\tilde{\nu} = 2987$, 2936, 2861, 1701, 1635, 1587, 1486, 1392, 1368, 1239, 1142, 1101, 1070, 1031, 1009, 831, 761, 717, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 7.0$ Hz, 3H), 1.83–1.92 (m, 4H), 2.55–2.60 (m, 4H), 3.51 (s, 2H), 3.90 (q, $J = 7.0$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 7.42 ppm (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.4$, 24.5, 27.2, 29.6, 42.0, 50.2, 60.5, 121.4, 128.5, 131.2, 133.1, 139.0, 141.2, 169.4, 209.6 ppm; elemental analysis calcd (%) for $C_{17}H_{19}BrO_3$: C 58.13, H 5.45; found: C 57.86, H 5.40.

Ethyl (*Z*)-2-(2-furanyl)-4-oxo-1-cyclooctenecarboxylate (3f): IR (neat): $\tilde{\nu} = 3150$, 2937, 2863, 1705, 1635, 1464, 1367, 1318, 1243, 1163, 1131, 1068, 1022, 924, 886, 861, 816, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.25$ (t, $J = 7.2$ Hz, 3H), 1.80–1.90 (m, 4H), 2.51–2.58 (m, 4H), 3.53 (s, 2H), 4.24 (q, $J = 7.2$ Hz, 2H), 6.36–6.40 (m, 2H), 7.33–7.36 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 24.7, 27.5, 30.8, 41.2, 45.0, 60.9, 109.3, 111.4, 124.4, 130.9, 142.7, 152.2, 170.9, 210.2 ppm; HRMS (ESI): m/z: calcd for $C_{15}H_{18}O_4Na$ ($[M+Na]^+$): 285.1103; found: 285.1102.

Ethyl (1*Z*)-1-cyclohexenyl-4-oxo-1-cyclooctenecarboxylate (3g): IR (neat) $\tilde{\nu} = 3024$, 2978, 2932, 2858, 2836, 1704, 1458, 1446, 1367, 1312, 1269, 1221, 1131, 1079, 1031, 920, 764, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.19$ (t, $J = 7.0$ Hz, 3H), 1.47–1.61 (m, 4H), 1.73 (m, 4H), 1.91–1.98 (m, 4H), 2.33–2.34 (m, 2H), 2.42–2.44 (m, 2H), 3.18 (s, 2H), 4.06 (q, $J = 7.1$ Hz, 2H), 5.34 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 21.7, 22.3, 24.5, 25.0, 26.5, 27.4, 29.2, 41.8, 47.0, 60.2, 124.0, 130.4, 140.0, 142.6, 170.4, 210.6 ppm; elemental analysis calcd (%) for $C_{17}H_{24}O_3$: C 73.88, H 8.75; found: C 74.18, H 8.71.

Ethyl (*E*)-2-decyl-4-oxo-1-cyclooctenecarboxylate (3h): IR (neat): $\tilde{\nu} =$ 2926, 2855, 1701, 1458, 1367, 1194, 1078, 1030, 916, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.88$ (t, $J = 7.0$ Hz, 3H), 1.23–1.33 (m, 17H), 1.45 (m, 2H), 1.77 (m, 4H), 2.25–2.30 (m, 2H), 2.42–2.46 (m, 4H), 3.27 (s, 2H), 4.21 ppm (q, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 14.2, 22.6, 24.4, 27.6, 28.0, 29.2, 29.3, 29.4, 29.5 (2C), 29.7, 31.8, 36.0, 42.2, 49.0, 60.3, 129.4, 142.9, 169.2, 210.5 ppm; HRMS (ESI): m/z: calcd for $C_{21}H_{36}O_3Na$ ($[M+Na]^+$): 359.2562; found: 359.2571.

Ethyl (*E*)-4-oxo-2-phenethyl-1-cyclooctenecarboxylate (3i): IR (neat): $\tilde{\nu} = 3061$, 3026, 2933, 2862, 1701, 1647, 1452, 1259, 1080, 1029, 912, 734, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.30$ (t, $J = 7.2$ Hz, 3H), 1.77 (m, 4H), 2.46 (m, 4H), 2.60–2.64 (m, 2H), 2.76–2.81 (m, 2H), 3.30 (s, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 7.16–7.22 (m, 3H), 7.25–7.30 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.2$, 24.2, 27.6, 29.3, 34.2, 38.0, 42.3, 49.4, 60.4, 125.9, 128.2, 128.3, 130.2, 141.2, 142.3, 168.8, 210.2 ppm; HRMS (ESI): m/z: calcd for $C_{19}H_{24}O_3Na$ ($[M+Na]^+$): 323.1623; found: 323.1601.

1-[(*Z*)-2-ethoxycarbonyl-7-oxocyclo-1-octenyl]-4-[(*Z*)-2′-ethoxycarbonyl-7′-oxocyclo-1′-octenyl]butane (3j): IR (neat): $\tilde{\nu} = 2922$, 1700, 1456, 1377, 1165, 1034, 939, 790, 737, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.31$ (t, $J = 7.2$ Hz, 6H), 1.50 (m, 4H), 1.77 (m, 8H), 2.31 (m, 4H), 2.46 (m, 8H), 3.27 (s, 4H), 4.21 ppm (q, $J = 7.2$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$, 24.1, 27.4, 27.8, 29.1, 35.5, 42.0, 48.8, 60.1, 129.4, 142.5, 168.7, 210.1 ppm; HRMS (ESI): m/z: calcd for $C_{26}H_{38}O_6Na$ ($[M+Na]^+$): 469.2566; found: 469.2585.

Ethyl (*Z*)-4-oxo-2-phenylcyclo-1-nonenecarboxylate (3k): IR (neat): $\tilde{\nu} =$ 3056, 2980, 2928, 1707, 1599, 1493, 1445, 1367, 1318, 1173, 1135, 1074, 1033, 794, 766, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J =$ 7.1 Hz, 3H), 1.58–1.70 (m, 4H), 1.78–1.84 (m, 2H), 2.56 (t, $J = 6.5$ Hz, 2H), 2.62 (t, $J = 6.3$ Hz, 2H), 3.52 (s, 2H), 3.87 (q, $J = 7.1$ Hz, 2H), 7.24–7.32 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.5$, 25.1, 25.4, 26.1, 29.2, 42.6, 51.3, 60.3, 127.2, 127.4, 128.1, 134.7, 138.1, 143.1, 169.7, 211.8 ppm; elemental analysis calcd (%) for $C_{18}H_{22}O_3$: C 75.50, H 7.74: found: C 75.72, H 7.92.

Ethyl (*Z*)-4-oxo-2-phenylcyclo-1-decenecarboxylate (3l): IR (nujol): $\tilde{\nu} =$ 3074, 2860, 1715, 1598, 1576, 1467, 1377, 1237, 1241, 1079, 1029, 874, 856, 824, 706, 663, 628, 537 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J =$ 7.2 Hz, 3H), 1.42–1.49 (m, 4H), 1.58–1.61 (m, 2H), 1.77–1.80 (m, 2H), 2.54 (t, $J = 6.0$ Hz, 2H), 2.71 (t, $J = 6.3$ Hz, 2H), 3.55 (s, 2H), 3.90 (q, $J =$

7.2 Hz, 2H), 7.22–7.33 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 21.9, 23.7, 25.0, 25.9, 28.2, 37.8, 50.7, 60.4, 127.3, 127.5, 128.3, 135.6, 138.6, 142.8, 170.2, 212.1 ppm; elemental analysis calcd (%) for $C_{19}H_{24}O_3$: C 75.97, H 8.05; found: C 76.11, H 8.01.

Ethyl (*Z*)-5,6,9,10-tetrahydro-10-oxo-8-phenylbenzo[8]annulene-7-carboxylate (3m): IR (nujol): $\tilde{\nu}$ = 2923, 2853, 1713, 1675, 1597, 1418, 1376, 1266, 1239, 1129, 1095, 1071, 1046, 966, 916, 844, 766, 700, 599, 574 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (t, J = 7.2 Hz, 3H), 3.00 (t, J = 7.5 Hz, 2H), 3.25 (t, J = 7.5 Hz, 2H), 3.70 (q, J = 7.2 Hz, 2H), 3.90 (s, 2H), 6.71–6.76 (m, 2H), 7.17–7.19 (m, 3H), 7.25 (d, J = 8.1 Hz, 1H), 7.29 (t, J = 12.3 Hz, 1H), 7.41–7.48 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.2, 30.1, 33.2, 52.8, 60.3, 126.9, 127.0, 127.4, 127.5, 128.1, 130.1, 131.9, 132.4, 137.6, 138.8, 142.2, 142.5, 169.9, 203.8 ppm; elemental analysis calcd (%) for $C_{21}H_{20}O_3$: C 78.73, H 6.29; found: C 78.48, H 6.24.

Ethyl (*E*)-5,6,7,10-tetrahydro-10-oxo-8-phenylbenzo[8]annulene-7-carboxylate (3m′): IR (nujol): $\tilde{\nu}$ = 2922, 2853, 1712, 1675, 1597, 1418, 1375, 1266, 1239, 1128, 1095, 1071, 1046, 967, 916, 844, 766, 701, 599, 574 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (t, J = 7.2 Hz, 3H), 2.24–2.33 (m, 1H), 2.48–2.56 (m, 1H), 2.96 (dt, J = 13.2, 3.9 Hz, 1H), 3.17 (dt, J = 13.2, 4.8 Hz, 1H), 3.61–3.69 (m, 1H), 3.72–3.80 (m, 1H), 3.85 (dd, J = 12.1, 4.8 Hz, 1H), 6.86 (s, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.32–7.40 (m, 4H), 7.40–7.46 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.82 ppm (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3, 30.0, 33.0, 45.2, 60.7, 126.8, 127.1, 128.5, 128.9, 129.7, 130.1, 132.7, 135.0, 139.4, 139.7, 140.6, 148.5, 172.0, 193.7 ppm; elemental analysis calcd (%) for $C_{21}H_{20}O_3$: C 78.73; H 6.29; found: C 78.53, H 6.25.

4-Acetyl-3-phenyl-3-cyclooctenone (3n): IR (neat): $\tilde{\nu}$ = 3079, 2931, 2860, 1700, 1575, 1492, 1444, 1353, 1325, 1232, 1124, 1076, 969, 771, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70 (s, 3H), 1.84–1.92 (m, 4H), 2.54 (t, J = 5.4 Hz, 2H), 2.60 (t, J = 5.3 Hz, 2H), 3.60 (s, 2H), 7.17–7.19 (m, 2H), 7.29–7.36 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 27.8, 30.2, 30.8, 42.3, 50.5, 127.9, 128.5, 128.7, 138.2, 141.5, 141.7, 206.9, 210.1; elemental analysis calcd (%) for $C_{16}H_{18}O_2$: C 79.31, H 7.49; found: C 79.18, H 7.42.

4-Acetyl-3-phenyl-3-cyclononenone (3o): IR (neat): $\tilde{\nu}$ = 3077, 2922, 2853, 1702, 1448, 1350, 1230, 1151, 1016, 921, 765, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51–1.54 (m, 2H), 1.59–1.65 (m, 2H), 1.70 (s, 3H),1.79–1.85 (m, 2H), 2.59 (t, J = 6.7 Hz, 2H), 2.67 (t, J = 6.4 Hz, 2H), 3.56 (s, 2H), 7.29–7.36 ppm (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 25.2, 25.8, 30.1, 30.7, 42.8, 51.0, 128.2, 128.3, 128.6, 136.7, 142.2, 143.4, 206.9, 211.7;elemental analysis calcd (%)HRMS (ESI): m/z: calcd for $C_{17}H_{20}O_2Na$ ([M + Na]$^+$): 279.1361; found: 279.1367.

4-Acetyl-3-phenyl-3-cyclodecenone (3p): IR (neat): $\tilde{\nu}$ = 3073, 2929, 2860, 1683, 1463, 1353, 1120, 1068, 761, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.43–1.50 (m, 4H), 1.52–1.58 (m, 2H), 1.74 (s, 3H), 1.75–1.80 (m, 2H), 2.53 (t, J = 6.4 Hz, 2H), 2.68 (t, J = 6.3 Hz, 2H), 3.58 (s, 2H), 7.25–7.27 (m, 2H), 7.32–7.34 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4, 24.3, 25.1, 25.8, 28.8, 31.0, 38.8, 50.5, 128.3, 128.4, 128.7, 137.0, 142.0, 144.1, 207.9, 212.4 ppm; HRMS (ESI): m/z: calcd for $C_{18}H_{22}O_2Na$ ([M + Na]$^+$): 293.1518; found: 293.1511.

General Procedure for the Reaction of Acyclic β-Keto Esters with Terminal Alkynes

A mixture of ethyl 2-methylacetoacetate (**5a**, 72.1 mg, 0.500 mmol), phenylacetylene (**2a**, 61.3 mg, 0.600 mmol), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was stirred at 80 °C for 24 h. The product was isolated by column chromatography on silica gel to give the mixture of δ-keto esters **6a**–**8a** in 92% yield (113 mg, 0.460 mmol).

Ethyl (*E*)-2-methyl-5-oxo-3-phenyl-2-hexenoate (7a): IR (neat): $\tilde{\nu}$ = 3057, 2982, 2926, 1717, 1701, 1491, 1356, 1259, 1129, 1027, 776, 704, 532 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3H), 1.83 (s, 3H), 2.17 (s, 3H), 3.87 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 7.16–7.18 (m, 2H), 7.25–7.27 (m, 1H), 7.33–7.36 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 17.2, 29.7, 51.2, 60.4, 127.0, 127.3, 127.4, 127.7, 128.3, 144.7, 168.4, 204.8 ppm; elemental analysis calcd (%) for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 73.12, H 7.53.

Ethyl (*E*)-5-oxo-2-(2-phenylethyl)-3-phenyl-2-hexenoate (7b): IR (neat): $\tilde{\nu}$ = 3062, 3026, 2979, 2927, 1732, 1701, 1599, 1496, 1456, 1356, 1252, 1172, 1026, 911, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.2 Hz, 3H), 2.15 (s, 3H), 2.49 (t, J = 7.8 Hz, 2H), 2.66 (t, J = 7.9 Hz, 2H), 3.81 (s, 2H), 4.24 (q, J = 7.2 Hz, 2H), 6.96–7.33 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 29.8, 33.1, 35.6, 51.5, 60.6, 125.8, 127.1, 127.4, 128.2, 128.4, 128.5, 128.9, 132.4, 141.4, 144.9, 168.4, 204.7 ppm; elemental analysis calcd (%) for $C_{22}H_{24}O_3$: C 78.54, H 7.19; found: C 78.44, H 7.42.

Ethyl (*E*)-5-oxo-3-phenyl-2-hexenoate (7c): IR (neat): $\tilde{\nu}$ = 3060, 2981, 2935, 1707, 1625, 1577, 1447, 1178, 1040, 876, 767, 696, 546 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.2 Hz, 3H), 2.28 (s, 3H), 4.19 (q, J = 7.2 Hz, 2H), 4.22 (s, 2H), 6.31 (s, 1H), 7.35–7.38 (m, 3H), 7.39–7.43 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 29.8, 46.8, 60.1, 119.4, 126.5, 128.7, 129.2, 140.8, 152.1, 166.4, 204.7 ppm; elemental analysis calcd (%) for $C_{14}H_{16}O_3$: C 72.39, H 6.94; found: C 72.26, H 7.10.

Ethyl (*E*)-2-methyl-5-oxo-3,5-diphenyl-2-pentenoate (7d): IR (neat): $\tilde{\nu}$ = 3080, 3060, 2981, 2928, 1732, 1707, 1598, 1492, 1448, 1365, 1332, 1128, 977, 755, 704, 621 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.2 Hz, 3H), 1.88 (s, 3H), 4.12 (q, J = 7.2 Hz, 2H), 4.50 (s, 2H), 7.23–7.48 (m, 8H), 7.94 ppm (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 17.3, 46.6, 60.3, 127.0, 127.1, 127.4, 127.85, 127.92, 128.2, 128.3, 128.4, 132.7, 144.7, 168.4, 196.2; elemental analysis calcd (%) for $C_{20}H_{20}O_3$: C 77.90, H 6.54, found: C 77.91, H 6.66.

Ethyl (*E*)-3-(4-methoxyphenyl)-2-methyl-5-oxo-2-hexenoate (7e): IR (neat): $\tilde{\nu}$ = 2980, 2935, 2907, 2838, 1729, 1606, 1515, 1093, 1029, 838, 770, 602, 542 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3H), 1.86 (s, 3H), 2.16 (s, 3H), 3.80 (s, 3H), 3.86 (s, 2H), 4.20 (q, J = 7.2 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 7.11 ppm (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 17.3, 29.6, 51.4, 55.1, 60.3, 113.6, 128.4, 128.9, 134.7, 144.3, 158.7, 168.6, 205.1 ppm; elemental analysis calcd (%) for $C_{16}H_{20}O_4$: C 69.54, H 7.30; found: C 69.36, H 7.42.

Ethyl (*E*)-3-(4-methylphenyl)-2-methyl-5-oxo-2-hexenoate (7f): IR (neat): $\tilde{\nu}$ = 3022, 2982, 2926, 2871, 1728, 1623, 1512, 1447, 1042, 1021, 826, 769, 548, 519 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3H), 1.84 (s, 3H), 2.16 (s, 3H), 2.34 (s, 3H), 3.86 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 7.16 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 17.3, 21.1, 29.7, 51.4, 60.4, 127.5, 127.6, 129.6, 137.1, 139.6, 144.7, 168.7, 205.0; elemental analysis calcd (%) for $C_{16}H_{20}O_3$: C 73.82, H 7.74; found: C 73.74, H 7.91.

Ethyl (*E*)-3-(4-trifluoromethylphenyl)-2-methyl-5-oxo-2-hexenoate (7g): IR (neat): $\tilde{\nu}$ = 2988, 2926, 1716, 1653, 1616, 1559, 1325, 1259, 1164, 1128, 1068, 1018, 852 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.2 Hz, 3H), 1.82 (s, 3H), 2.19 (s, 3H), 3.89 (s, 2H), 4.23 (q, J = 7.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.62 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 17.1, 29.7, 50.7, 60.6, 123.9 (J = 271 Hz), 125.3 (J = 3.6 Hz), 127.9, 128.7, 129.4 (J = 30.9 Hz), 143.2, 146.4, 168.0, 204.4 ppm; elemental analysis calcd (%) for $C_{16}H_{17}F_3O_3$: C 61.14, H 5.45; found: C 61.13, H 5.47.

Ethyl (*E*)-3-(4-bromophenyl)-2-methyl-5-oxo-2-hexenoate (7h): IR (neat): $\tilde{\nu}$ = 2982, 2931, 1725, 1488, 1259, 1071, 1011, 834, 768, 730, 535 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, J = 7.2 Hz, 3H), 1.82 (s, 3H), 2.17 (s, 3H), 3.85 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 7.48 ppm (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 17.1, 29.7, 50.8, 60.5, 129.0, 129.2, 131.1, 131.4, 141.4, 143.4, 168.1, 204.5 ppm; elemental analysis calcd (%) for $C_{15}H_{17}BrO_3$: C 55.40, H 5.27, found: C 55.46, H 5.16.

Ethyl (*E*)-3-cyclohexenyl-2-methyl-5-oxo-2-hexenoate (7i): IR (neat): $\tilde{\nu}$ = 2982, 2931, 2858, 1725, 1707, 1355, 1265, 1118, 1028, 920, 769, 549 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, JJ = 7.2 Hz, 3H), 1.57–1.60 (m, 2H), 1.63–1.67 (m, 2H), 1.92 (s, 3H), 1.96–1.99 (m, 2H), 2.05–2.08 (m, 2H), 2.17 (s, 3H), 3.61 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 5.46 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 16.7, 21.9, 22.5, 24.8, 26.7, 29.5, 49.0, 60.2, 124.9, 125.7, 139.1, 147.2, 168.8, 205.4 ppm; elemental analysis calcd (%) for $C_{15}H_{22}O_3$: C 71.97, H 8.86; found: C 71.96, H 8.86.

Ethyl (*Z*)-2-methyl-3-(2-oxopropyl)-2-tridecenoate (7j): IR (neat, **6j+7j**): $\tilde{\nu}$ = 2956, 2926, 2855, 1734, 1707, 1616, 1465, 1354, 1098, 862, 768 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.22

(t, $J=7.2$ Hz, 3H), 1.25–1.30 (m, 18H), 1.94 (s, 3H), 2.19 (s, 3H), 3.58 (s, 2H), 4.14 ppm (q, $J=7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, **6j + 7j**): $\delta=13.96$, 14.03, 14.1, 15.0, 22.6, 26.9, 27.7, 29.2, 29.26, 29.32, 29.35, 29.43, 29.46, 29.54, 29.6, 31.77, 31.84, 34.4, 35.9, 41.4, 49.0, 60.1, 60.4, 123.5, 125.3, 145.7, 158.8, 168.5, 173.2, 198.1, 205.7 ppm; elemental analysis calcd (%) for $C_{19}H_{34}O_3$: C 73.50, H 11.04; found: C 73.50, H 11.28.

Ethyl (*E*)-2-methyl-5-oxo-3-(2-phenylethyl)-2-hexenoate (7k): IR (neat): $\tilde{\nu}=3086$, 3062, 2981, 2937, 1721, 1617, 1496, 1454, 1356, 1190, 1103, 1029, 862, 748, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.27$ (t, $J=7.2$ Hz, 3H), 1.89 (s, 3H), 2.18 (s, 3H), 2.48 (t, $J=7.9$ Hz, 2H), 2.69 (t, $J=8.0$ Hz, 2H), 3.58 (s, 2H), 4.14 (q, $J=7.2$ Hz, 2H), 7.16–7.19 (m, 3H), 7.26–7.29 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 15.0, 29.7, 33.0, 37.8, 49.1, 60.3, 124.2, 126.0, 126.1, 128.2, 128.4, 144.2, 168.4, 205.7 ppm; elemental analysis calcd (%) for $C_{17}H_{22}O_3$: C 74.42, H 8.08; found: C 74.32, H 8.21.

Intramolecular Reaction of Ethyl 2-Acetyl-7-octynoate

A mixture of ethyl 2-acetyloct-7-ynoate (**10a**, 105.1 mg, 0.500 mmol), 2,6-diisopropylphenylisocyanide (4.7 mg, 0.0250 mmol), powder 4 Å-MS (10.6 mg, 100 wt% Re-cat.), $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), and toluene (1.0 mL) was heated at 100 °C for 24 h. The product was isolated by column chromatography on silica gel to give compound **11a** in 84% yield (88.3 mg, 0.420 mmol).

Ethyl 2-(2-oxopropyl)-1-cyclohexenecarboxylate (11a): IR (neat): $\tilde{\nu}=$ 2980, 2936, 2862, 1717, 1637, 1356, 1233, 1076, 1052, 764, 684, 589 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.27$ (t, $J=7.2$ Hz, 3H), 1.61–1.65 (m, 4H), 2.14–2.15 (m, 2H), 2.19 (s, 3H), 2.34–2.36 (m, 2H), 3.56 (s, 2H), 4.14 ppm (q, $J=7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 21.96, 21.99, 26.1, 29.6, 33.4, 50.1, 59.9, 127.1, 143.9, 167.9, 205.7 ppm; elemental analysis calcd (%) for $C_{12}H_{18}O_3$: C 68.54, H 8.63; found: C 68.27, H 8.41.

Ethyl 2-(2-oxopropyl)-1-cycloheptenecarboxylate (11b): IR (neat): $\tilde{\nu}=$ 2978, 2940, 2855, 1721, 1640, 1250, 1142, 1092, 1044, 769, 732, 698, 576 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.28$ (t, $J=7.2$ Hz, 3H), 1.50–1.56 (m, 4H), 1.78 (tt, $J=6.0$, 5.4 Hz, 2H), 2.19 (s, 3H), 2.31 (t, $J=$ 5.4 Hz, 2H), 2.53 (t, $J=5.4$ Hz, 2H), 3.60 (s, 2H), 4.16 ppm (q, $J=7.2$ Hz, 2H); ^{13}H NMR (100 MHz, $CDCl_3$): $\delta=14.2$, 24.7, 26.1, 29.6, 29.7, 32.2, 36.8, 51.9, 60.3, 133.9, 148.3, 169.0, 206.1 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{13}H_{20}O_3Na$ ($[M+Na]^+$): 247.1310; found: 247.1321.

Ethyl 2-(2-oxopropyl)-1-cyclopentadecenecarboxylate (11c): IR (neat): $\tilde{\nu}=2977$, 2945, 2855, 1709, 1658, 1343, 1235, 1165, 1090, 1082, 855, 747, 688, 580 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.27$ (t, $J=7.2$ Hz, 3H), 1.28–1.47 (m, 22H), 2.13 (t, $J=8.1$ Hz, 2H), 2.17 (s, 3H), 2.33 (t, $J=$ 8.1 Hz, 2H), 3.52 (s, 2H), 4.15 ppm (q, $J=7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.3$, 25.3, 25.4, 25.9, 26.1, 26.2, 26.6, 26.8, 26.9, 27.4, 27.6, 27.8, 29.4, 29.6, 35.1, 49.3, 60.2, 131.3, 144.1, 169.0, 206.1 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{36}O_3Na$ ($[M+Na]^+$): 359.2562; found: 359.2575.

6,7,8,9-Tetrahydro-3-methylcyclohepta[*c*]pyran-1(5*H*)-one (12b): IR (nujol): $\tilde{\nu}=3028$, 2948, 2857, 1716, 1488, 1279, 1044, 946, 840, 775, 727, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.53$–1.62 (m, 4H), 1.80–1.84 (m, 2H), 2.12 (s, 3H), 2.53 (t, $J=5.4$ Hz, 2H), 2.72 (t, $J=5.4$ Hz, 2H), 5.81 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=19.5$, 25.8, 26.1, 26.3, 32.2, 35.6, 107.7, 124.2, 157.6, 158.0, 164.6; elemental analysis calcd (%) for $C_{11}H_{14}O_2$: C 74.13, H 7.92; found: C 74.08, H 7.98.

6,7,8,9,10,11,12,13,14,15,16,17-Dodecahydro-3-methylcyclopentadeca[*c*]-pyran-1(5*H*)-one (12c): IR (neat): $\tilde{\nu}=3022$, 2940, 2859, 1708, 1655, 1481, 1371, 1270, 1044, 849, 760, 713, 677 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.26$–1.61 (m, 22H), 2.18 (s, 3H), 2.35 (t, $J=8.1$ Hz, 2H), 2.43 (t, $J=$ 8.0 Hz, 2H), 5.80 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=19.5$, 25.2, 25.4, 25.9, 26.0, 26.4, 26.7, 26.79, 26.82, 27.1, 27.3, 27.4, 27.6, 32.6, 106.5, 122.2, 154.1, 157.8, 164.4 ppm; HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{30}O_2Na$ ($[M+Na]^+$): 313.2144; found: 313.2146.

(E)-3,4-Dimethyl-5-phenethyl-3-heptene-2,6-dione (16): A mixture of 3-methyl-2,4-pentanedione (28.5 μL, 0.250 mmol), 5-phenylpentane-1,2-diene (72.1 mg, 0.500 mmol), $Re_2(CO)_{10}$ (4.1 mg, 6.3 μmol), and 1,2-dichloroethane (0.25 mL) was stirred at 135 °C for 12 h. After the solvent was removed in vacuo, the product was isolated by column chromatography on silica gel (hexane/ethyl acetate = 10:1) to give **16** in 63% yield (40.7 mg, 0.158 mmol) as a yellow liquid. IR (nujol): $\tilde{\nu}=3465$, 3025, 2960, 1898, 1719, 1602, 1463, 1378, 1261, 1157, 1094, 962, 916, 733, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.62$ (s, 3H), 1.74–1.78 (m, 1H), 1.81 (s, 3H), 2.07 (s, 3H), 2.19–2.24 (m, 1H), 2.26 (s, 3H), 2.54 (t, $J=7.5$ Hz, 2H), 3.47 (t, $J=7.2$ Hz, 1H), 7.14–7.20 (m, 3H), 7.28–7.29 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=15.3$, 19.7, 29.0, 29.6, 33.1, 38.0, 55.1, 126.0 (2C), 128.35 (2C), 128.41, 134.0, 136.1, 141.3, 205.8, 207.2 ppm; HRMS: *m*/*z*: calcd. for $C_{17}H_{22}O_2Na$ ($[M+Na]^+$): 281.1518, found: 281.1506.

Acknowledgements

Financial support by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18037049) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and for Young Scientists (B) (No. 18750088) from Japan Society for the Promotion of Science. We also thank the Sumitomo Foundation and Meiji Seika Co. for financial support.

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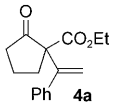

4a

[14] One possible reason that cyclopentanone-2-carboxylic acid ethyl ester did not produce a ring-expansion product is that the retro-aldol reaction (carbon–carbon bond cleavage) of a metalacyclopentene or cyclobutene intermediate might be difficult.
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Received: April 9, 2009
Published online: July 14, 2009

