Oxidative Transformation of *tert*-Cyclobutanols by Palladium Catalysis under Oxygen Atmosphere

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Palladium(II)-catalyzed oxidative reaction of *tert*-cyclobutanols involving the cleavage of a C−C bond via β-carbon elimination under atmospheric pressure of oxygen is described. An alkylpalladium intermediate produced by β-carbon elimination from a Pd(II) alcoholate gives a variety of products, depending on the substituents on the cyclobutane ring, in which reactions such as dehydrogenative ring opening, ring expansion and ring contraction are involved. For some substrates, the addition of a catalytic amount of ethyl acrylate dramatically accelerates the reaction. In all cases, the dehydrogenative products are obtained and the Pd(II)-hydride species produced at the final stage can be converted again to active Pd(II) species by molecular oxygen.

Introduction

The transformation of small ring compounds permits the development of synthetic strategy to various useful compounds in organic synthesis because of the unique reactivity provided by the ring strain.[1] Especially, transition metal catalyzed reactions utilizing the cleavage of a C−C bond in small ring compounds[2a,c] have been developed in recent years, as well as the unstrained C−C bond cleavage reactions,[2] and various kinds of soluble late transition metals such as Ru,[3−5] Co,[6] Rh,[7−15] Ir,[16] Ni,[17,18] Pd[19−22] and Pt,[23] and Zn[24] have been used for their reactions. Among several types of a selective C−C bond cleavage reaction, the catalytic β-dealkylation from late transition metal alkyl complexes involving cyclobutane or cyclopropane group is a class of the most interesting processes to construct an M−C bond for successive reaction affording useful organic compounds.[5,7c,12,14,15,20c−h] On the other hand, catalytic reactions involving β-alkyl elimination from the late transition metal alcoholates[25] have also been developed for the past few years, although their examples are still limited.[26−28] For example, Tamaru and co-workers demonstrated that β-carbon elimination via a π-allylpalladium alcoholate intermediate generated

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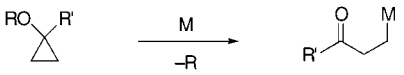
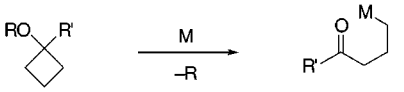
from vinyl cyclic carbonate gave unsaturated aldehydes and ketones.[26] Kondo, Mitsudo, and co-workers reported the ruthenium-catalyzed β-allyl elimination of *tert*-homoallyl alcohols.[27] Quite recently, the ring opening reactions of *tert*-cyclopropanols were studied by two groups independently.[28]

As a versatile strategy for the synthesis of ketones using small ring compounds, a metal homoenolate is well-established.[29] The formation of a stable β-metallo ketone (metal homoenolate) can be accomplished by the reaction of siloxycyclopropanes with metal salts such as Ti, Hg, Pt, Zn, Sn, etc. (eq 1), and further transformations of it are possible to create a new C−C bond.[29] In addition, catalytic reactions involving β-metallo ketone were also reported.[22a−f,23b,28,29h]



(1)

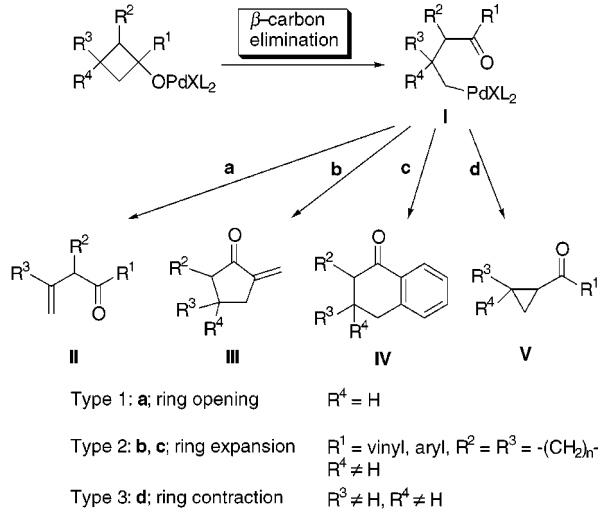
The formation of γ-metallo ketones from cyclobutanols is an analogous process (eq 2), and this process may become a new synthetic methodology.



(2)

In the course of our studies on the aerobic oxidation of alcohols by palladium catalysis,[30] we found the novel transformation of *tert*-cyclobutanols to a variety of organic compounds via an organopalladium intermediate **I** generated by β-carbon elimination from an initially produced palladium(II) alcoholate (Scheme 1).[31,32] Thus, the fate of **I** leading to dehydrogenated products (**II**−**V**) largely depends on the type of substituents on the cyclobutane ring as shown in Scheme 1 and can be exemplified with three types of reaction mode. When R^4 = H, the dehydrogenative ring opening reaction proceeds to afford unsaturated ketones (type 1, path **a**). Type 2 reactions include the oxidative ring expansion to five- or six-membered cyclic ketones (path **b** or **c**). Type 3 reactions represent the oxidative ring contraction en route to a cyclopropane ring (path **d**). In our preliminary communication,[31a] we partly demonstrated the former two types of reactions, and recently we found that the oxidative ring contracting reaction of *tert*-cyclobutanols proceeded to give cyclopropane derivatives. In this paper, we describe the details of the type 3 reaction as well as type 1 and 2 reactions in these oxidative transformations of *tert*-cyclobutanols in the presence of a palladium catalyst under atmospheric pressure of oxygen.

Scheme 1



Results and Discussion

Dehydrogenative Ring Opening Reaction (Type 1). A Pd(II)-promoted or -catalyzed rearrangement of

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(31) (a) For palladium(II)-catalyzed oxidative ring cleavage of *tert*-cyclobutanols, see: Nishimura, T.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 2645. (b) For palladium(0)-catalyzed arylation of *tert*-cyclobutanols, see: Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 11010.

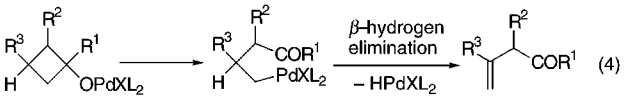
(32) For a recent review of the metal-mediated oxidation of *tert*-alcohols, see: Wietzerbin, K.; Bernadou, J.; Meunier, B. *Eur. J. Inorg. Chem.* **2000**, 1391.

1-alkenyl or 1-alkynyl cyclobutanols to cyclopentanones is a well-established method, and it has been applied to the synthesis of a variety of natural products.[33] This reaction is promoted by the initial complexation of palladium with alkenic or alkynic bond prior to migration of a β-carbon in a cyclobutanol, in which usually a secondary carbon atom can migrate more easily than a primary one (eq 3).

(3)

In our initial communication,[31a] we reported that the different bond-cleavage reaction proceeds via β-carbon elimination to give a primary alkylpalladium intermediate as shown in Scheme 1.

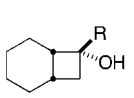
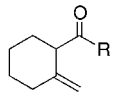
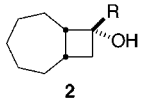
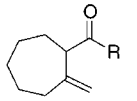
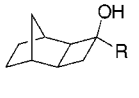
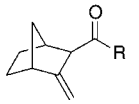
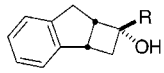
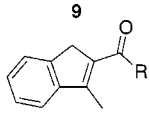
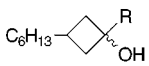
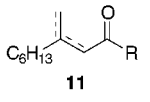
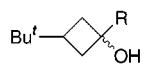
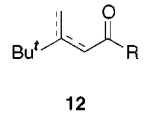
First, the oxidative reaction of *tert*-cyclobutanols, in which an alkylpalladium intermediate produced has β-hydrogen available to be eliminated as shown in eq 4, was carried out in the presence of $Pd(OAc)_2$, pyridine, ethyl acrylate, and MS3A at 80 °C under atmospheric pressure of oxygen. In this type of reaction, a selective C−C bond cleavage occurred to give β,γ- or α,β-unsaturated ketones (Table 1).



(4)

The presence of ethyl acrylate was essential for the efficient transformation, except for vinyl-substituted cyclobutanols **1a** and **2a** (entries 1 and 4).[34] It should be noted that the reaction of butyl-substituted cyclobutanols **1c**−**6c** could also smoothly proceed to give the corresponding ketones in good yields. These results indicate that the precoordination of palladium with the π-bond is not required prior to C−C bond cleavage, compared with the palladium(II)-mediated cyclobutane rearrangement. The formation of a palladium(II) alcoholate is a crucial step, and actually, *tert*-butyldimethylsilylated-**1b** did not give any products. Bicyclic or tricyclic compounds (**1**−**3**) yielded *exo*-methylene products (β,γ-unsaturated ketones), while **4**[35] and monocyclic ones (**5** and **6**) produced β,γ- and/or α,β-unsaturated ketones. In the cases of **4** and **5** a Pd(II)-H species produced by the β-hydrogen elimination might cause isomerization of an initially formed β,γ-unsaturated ketones to α,β-enones. On the other hand, in the case of **6** having a bulkier *tert*-butyl group, the isomerization of the product was suppressed to some extent (entries 13 and 14).

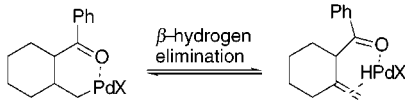
Table 1. Palladium(II)-Catalyzed Oxidative Ring Cleavage Reaction of Cyclobutanols[a]

entry	substrate	R	time (h)	product and isolated yield (%)
1[b]		**a**: vinyl	20	 56
2		**b**: Ph	16	97
3		**c**: Bu	38	71
	1			**7**
4[b]		**a**: vinyl	23	 52
5		**b**: Ph	21	93
6		**c**: Bu	16	77
	2			**8**
7		**b**: Ph	17	 91
8		**c**: Bu	24	80
	3			**9**
9		**b**: Ph	22	 81
10		**c**: Bu	26	41
	4			**10**
11		**b**: Ph	48	 60[c]
12		**c**: Bu	48	62[d]
	5			**11**
13		**b**: Ph	48	 76[e]
14		**c**: Bu	48	69[f]
	6			**12**

[a] Reaction conditions: alcohol (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), pyridine(1.0 mmol), ethyl acrylate (0.2 mmol), MS3A (50 mg), toluene (5 mL), 80 °C, O_2. [b] Without ethyl acrylate. [c] $\beta,\gamma/\alpha,\beta$ = 5/95. [d] $\beta,\gamma/\alpha,\beta$ = 34/66. [e] $\beta,\gamma/\alpha,\beta$ = 56/44. [f] $\beta,\gamma/\alpha,\beta$ = 71/29.

To know the role of ethyl acrylate, we examined the reaction of **1b** in the presence or absence of other acrylate analogues (Table 2).

Substituents in an alkenic part of the acrylate decreased the reaction rate. Next, we investigated a time course of the conversion of **1b** to the product **7b** (Figure 1). The time profile of the reaction of **1b** in the presence of ethyl acrylate showed a fine curve. On the other hand, the reaction without ethyl acrylate was considerably slow after ca. 0.5 h. When ethyl acrylate was added to the reaction mixture after 1 h the reaction was accelerated again. These observations suggest that the step of the β-hydrogen elimination from an alkylpalladium intermediate produced by β-carbon elimination might be reversible and ethyl acrylate may expel an intramolecular coordination of palladium with carbonyl oxygen to promote the reaction (eq 5).[36]



(5)

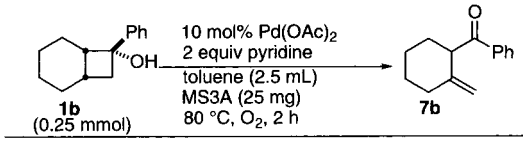
The presence of oxygen was another crucial factor for the reaction efficiency. When the reaction of **1b** was

(33) For recent works on the palladium-catalyzed ring expansion of cyclobutanols and cyclobutenols, see: (a) Clark, G. R.; Thiensathit, S. *Tetrahedron Lett.* **1985**, *26*, 2503. (b) Liebeskind, L. S.; Mitchell, D.; Foster, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 7908. (c) Demuth, M.; Pandey, B.; Wietfeld, B.; Said, H.; Viader, J. *Helv. Chim. Acta* **1988**, *71*, 1392. (d) de Almeida Barbosa, L.-C.; Mann, J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 177. (e) Mitchell, D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 291. (f) Nemoto, H.; Nagamochi, M.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2329. (g) Nemoto, H.; Nagamochi, M.; Ishibashi, H.; Fukumoto, K. *J. Org. Chem.* **1994**, *59*, 74. (h) Nemoto, H.; Shiraki, M.; Fukumoto, K. *Synlett* **1994**, 599. (i) Vo, N. H.; Snider, B. B. *J. Org. Chem.* **1994**, *59*, 5419. (j) Nemoto, H.; Miyata, J.; Fukumoto, K. *Tetrahedron* **1996**, *52*, 10363. (k) Nemoto, H.; Yoshida, M.; Fukumoto, K. *J. Org. Chem.* **1997**, *62*, 6450. (l) Nemoto, H.; Miyata, J.; Yoshida, M.; Raku, N.; Fukumoto, K. *J. Org. Chem.* **1997**, *62*, 7850. (m) Kočovský, P.; Dunn, V.; Gogoll, A.; Langer, V. *J. Org. Chem.* **1999**, *64*, 101. (n) Yoshida, M.; Memoto, H.; Ihara, M. *Tetrahedron Lett.* **1999**, *40*, 8583. (o) Miyata, J.; Nemoto, H.; Ihara, M. *J. Org. Chem.* **2000**, *65*, 504. (p) Hegedus, L. S.; Ranslow, P. B. *Synthesis* **2000**, 953. (q) Yoshida, M.; Sugimoto, K.; Ihara, M. *Tetrahedron Lett.* **2000**, *41*, 5089.

(34) The addition of ethyl acrylate did not show a significant difference in the yield of the products.

(35) In our preliminary communication (ref 31a), the structures of **4b** and **10b** were described incorrectly. The correct structures should be as those described here (Table 1, entry 9).

Table 2. Effect of Additives



1b (0.25 mmol) **7b**

entry	additive (0.1 mmol)	conversion (%)[a]
1	—	21
2	CO_2Et	60
3	CO_2Et	33
4	EtO_2C CO_2Et	19
5	CO_2Et EtO_2C	8

[a] Determined by GLC.

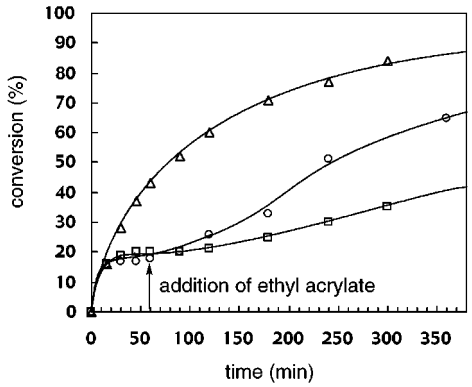


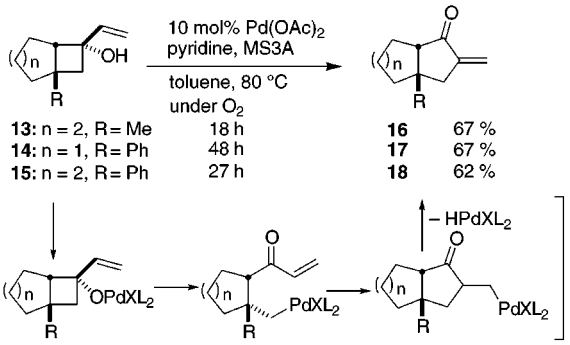
Figure 1. Time profile of the reaction of *tert*-cyclobutanol **1b**: the reaction in the presence of ethyl acrylate (0.1 mmol) (△), in the absence of ethyl acrylate (□), and in the presence of ethyl acrylate (0.1 mmol) after 1 h (○).

carried out under nitrogen atmosphere, the conversion of **1b** to **7b** was only 10% after 16 h.[37] We postulated that a Pd(II)-H species produced by β-hydrogen elimination from an alkylpalladium intermediate at the final stage can react with molecular oxygen to give the Pd(II)-OOH species, and this reactive species subsequently undergoes ligand exchange with a *tert*-cyclobutanol to reproduce the Pd(II) alcoholate and H_2O_2 as described in the oxidation of primary and secondary alcohols under similar reaction conditions.[30b] In fact, the formation of H_2O_2 was detected by the qualitative test of an aqueous layer extracted from the reaction mixture of **1b** (after 6 h in the absence of MS3A) with KI containing starch aqueous solution.

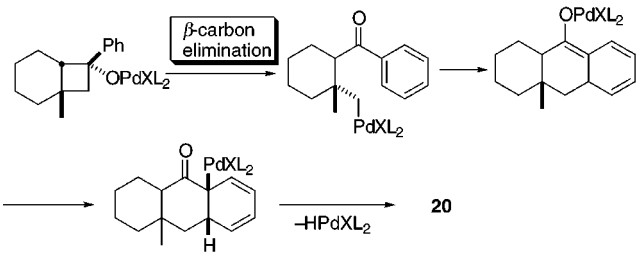
Oxidative Ring Expansion Reaction (Type 2). The reaction could be applied to vinyl-substituted bicyclic cyclobutanols **13**−**15** having an angular substituent, which blocks β-hydrogen elimination from the produced alkylpalladium species (Scheme 2).

In the reaction of these substrates cyclopentanones were obtained. These results show that an alkylpalladium intermediate undergoes cyclization in 5-*exo* mode and subsequent β-hydrogen elimination to give a cyclopentanone.[38] On the other hand, in the case of substrate

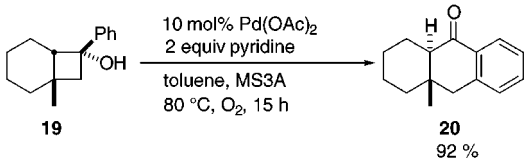
Scheme 2



Scheme 3



19 bearing a phenyl group instead of a vinyl group, the ketone **20**[39] was obtained in high yield (eq 6).



19 **20** 92 % (6)

The stereochemistry of **20** was confirmed by X-ray crystallographic analysis, indicating that its ring juncture was isomerized at some stage during the reaction (Figure S1, Supporting Information).[40] In this reaction, the addition of ethyl acrylate did not affect both the reaction rate and the yield of the product.

The formation of **20** can be explained by assuming the reaction sequence shown in Scheme 3. An alkylpalladium intermediate produced by β-carbon elimination undergoes an intramolecular cyclization with the phenyl ring to give a *cis*-organopalladium complex via a palladium enolate. Successive β-hydrogen *syn*-elimination affords the product **20**. In this case, β-hydrogen elimination step might be irreversible mainly as a result of the aromaticity of the product, and thus the addition of ethyl acrylate did not affect the reaction, compared with the reaction giving unsaturated ketones (vide supra). Next, we examined the behavior of cyclobutanols having either an electron-withdrawing or electron-donating substituent on the phenyl ring, the results of which are summarized in Table 3.[41]

4-Chlorophenyl-substituted cyclobutanol **21** yielded **26** in high yield (entry 2), although the reaction was slower than that of the 4-methoxy-substituted one (entry 4).[42] Interestingly, cyclobutanols **22** and **24** having a substitu-

(36) Similar effect using diphenylacetylene was observed in the rhodium-catalyzed C−C bond activation of cyclobutanones (ref 7d).

(37) The formation of a palladium black was immediately observed.

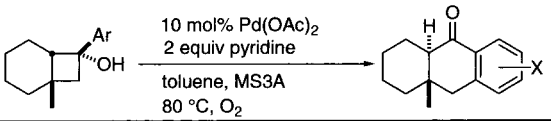
(38) For these substrates, the effect of the addition of ethyl acrylate was not observed.

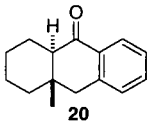
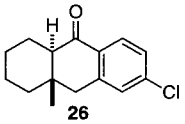
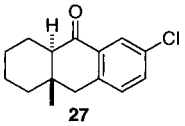
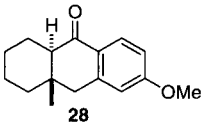
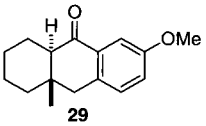
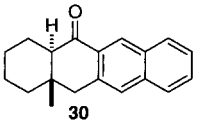
(39) Thompson, H. W.; Long, D. J. *J. Org. Chem.* **1988**, *53*, 4201.

(40) A small amount (<5%) of *cis*-isomer was detected by ^{1}H NMR spectra of the crude reaction mixture.

(41) The stereochemistry of these products in Table 3 was confirmed by ^{1}H NMR.

Table 3. Palladium(II)-Catalyzed Oxidative Ring Expansion Reaction of Cyclobutanols[a]

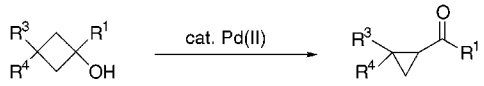


entry	Ar	time (h)	product and isolated yield (%)
1	C_6H_5 **19**	15	 **20** 92
2	4-ClC_6H_4 **21**	42	 **26** 93
3	3-ClC_6H_4 **22**	42	 **27** 85
4	4-$MeOC_6H_4$ **23**	15	 **28** 83
5	3-$MeOC_6H_4$ **24**	15	 **29** 85
6	2-naphthyl **25**	23	 **30** 81

[a] Reaction conditions: alcohol (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), pyridine (1.0 mmol), MS3A (50 mg), toluene (5 mL), 80 °C, O_2.

ent at the 3-position on the aromatic ring afforded 7-chloro- (**27**) and 7-methoxyhexahydroanthrathenone (**29**) selectively and respectively, probably as a result of the steric reason in the alkylpalladium species produced from Pd(II) alcoholate (entries 3 and 5). 2-Naphthyl-substituted cyclobutanol **25** also gave the ketone **30** selectively (entry 6). We also attempted the oxidation of other cyclobutanols having a variety of substituents, such as 3,5-bis(trifluoromethyl)phenyl, 2-methylphenyl, 2-methoxyphenyl, 2-pyridyl, 3-pyridyl, and 2-furyl, but all reactions failed.[43]

Oxidative Ring Contracting Reaction (Type 3). When the same procedure as described above was applied to 1,3,3-trisubstituted cyclobutanols in order to obtain the corresponding cyclohexanone derivatives (vide supra), the unexpected ring contracting reaction took place to afford cyclopropane derivatives (eq 7).

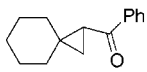
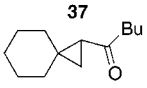
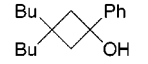
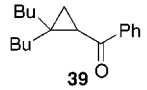
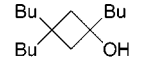
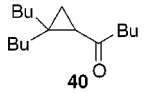
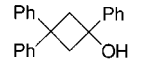
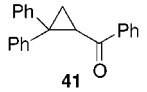
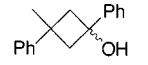
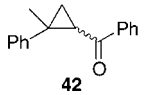


(7)

Thus, 2-phenylspiro[3.5]nonan-2-ol (**31**) afforded phenyl spiro[2.5]oct-1-yl ketone (**37**) almost quantitatively (Table 4, entry 1).

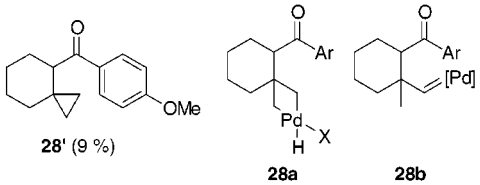
The reaction was accelerated by the addition of a catalytic amount of ethyl acrylate (entry 2). 1,3,3-Trisubstituted cyclobutanols **32**−**34** having a phenyl group or a butyl group at the α-position of a hydroxyl group afforded the corresponding cyclopropanes **38**−**40** in high yields (entries 3−5). The reaction of cyclobutanols **35** and **36** bearing a phenyl group at the 3-position was sluggish, and a longer reaction time was required. In these reactions, the addition of ethyl acrylate was quite effective to obtain cyclopropanes **41**[44] and **42**[45] in sufficient yields (entries 6−10). *tert*-Cyclobutanol **43** derived from α-pinene gave a cyclopropane derivative as well (eq 8).

Table 4. Palladium(II)-Catalyzed Oxidative Ring Contracting Reaction of *tert*-Cyclobutanols[a]

entry	substrate	ethyl acrylate (mmol)	time (h)	product and isolated yield (%)
1	 **31**	–	15	 **37** 98
2		0.1	8	98
3	 **32**	0.1	22	 **38** 95
4	 **33**	0.1	21	 **39** 94
5	 **34**	0.1	24	 **40** 83
6	 **35**	–	72	 **41** 47 (59)[b]
7		0.2	72	65 (85)[b]
8	 **36**[c]	–	48	 **42** 30 (48)[b,c]
9		0.2	48	69 (72)[b,c]
10		0.5	48	81[c]

[a] Reaction conditions: alcohol (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), pyridine (1.0 mmol), ethyl acrylate (0–0.5 mmol), MS3A (50 mg), toluene (5 mL), 80 °C, O_2. [b] The value in parentheses is the conversion of the alcohol (%). [c] cis/trans = 1/1.

(42) In the reaction of **23**, cyclopropane **28′** was also isolated in 9% yield, which might be formed via a Pd(IV) intermediate **28a** or Pd-carbene complex **28b** produced by α-elimination.

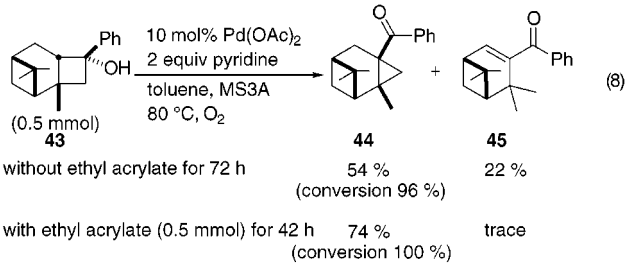


For reviews of organopalladium(IV) chemistry, see: (a) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83. (b) Canty, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 9, pp 225−290.

(43) 3,5-Bis(trifluoromethyl)phenyl- or 2-pyridyl-substituted cyclobutanol did not afford any products, while the oxidation of 2-furyl, 2-methylphenyl, 2-methoxyphenyl or 3-pyridyl one was sluggish and resulted in the formation of many unidentified products.

(44) A small amount of byproducts (ca. 5%) was also obtained, which might be formed by the intermolecular reaction of an alkylpalladium intermediate with ethyl acrylate.

(45) Each of the *cis*- and *trans*-isomers of **42** could be isolated and each stereochemistry was confirmed by the observation of the NOE spectra (methine proton and methyl proton, see Experimental Section).



In the absence of ethyl acrylate both the ring contracted compound **44** and the ring opening product **45** were obtained, while in the presence of ethyl acrylate, **44** was produced selectively. The relationship between the product yields and the reaction time was investigated in the absence of ethyl acrylate (Figure 2). Figure 2 shows that both compounds were produced competitively, showing that **45** was not derived from **44**.

A plausible reaction pathway for the formation of cyclopropanes is shown in Scheme 4 (ligands have been omitted for clarity).[46] The first step is the β-carbon elimination from an initially produced palladium(II) alcoholate to give an alkylpalladium(II) species **A**. Next, a palladium enolate from the enol form of **A** is produced, which may be in equilibrium with a palladacycle **B**. A reductive elimination of a Pd(0) from the species **B** affords the product cyclopropane.[47,48] Similarly to the type 1 reaction, we propose that a divalent palladium species such as a XPd(II)-OOH generated from XPdH and O_2 works as an active species and reproduces a palladium-(II) alcoholate and H_2O_2 by the reaction with an alcohol in this cyclopropane formation. Actually, the generation of H_2O_2 was detected by a simple KI/starch test in the case of **31** (after 6 h in the absence of MS3A). Under the present reaction conditions, the reoxidation of a Pd(0) species to a Pd(II) species may take place by in situ formed acetic acid and O_2.[49] In fact, when the oxidation of **31** was carried out using $Pd_2(dba)_3$·$CHCl_3$ (10 mol % Pd) as a catalyst in the presence of 20 mol % acetic acid under oxygen, 48% conversion of **31** to the compound **37** was observed after 2 h (nearly the same value obtained in the reaction using $Pd(OAc)_2$), while the conversion of **31** was only 9% without acetic acid.[50] The present oxidative conditions favor the formation of AcOPdH in

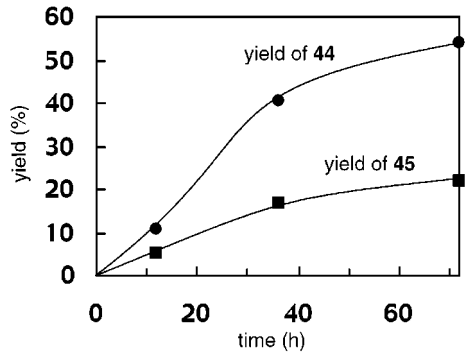
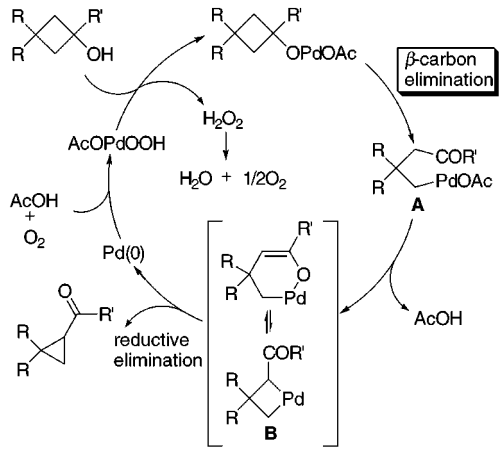


Figure 2. Time profile of the reaction of **43**.

Scheme 4. Plausible Reaction Pathway



equilibrium because of the stabilization effect of pyridine for Pd(II)-H and Pd(II)-OOH species and also the facile formation of AcOPdOOH with O_2 (eq 9).[51]

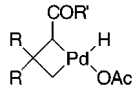
$$\text{AcOH} + \text{Pd(0)} \rightleftharpoons \text{AcOPdH} \xrightarrow{O_2} \text{AcOPdOOH} \qquad (9)$$

The formation of **44** and **45** can be explained by assuming the reaction sequence shown in Scheme 5. An alkylpalladium intermediate **C**, produced by β-carbon elimination, is converted into a palladacyclobutane **E** via the formation of a palladium enolate **D**. Cyclopropane **44** can be produced by reductive elimination of Pd(0) from the intermediate **E**, while β-hydrogen elimination from **E** giving the species **F** followed by successive reductive elimination results in the formation of the product **45**. The addition of ethyl acrylate probably increases the rate of reductive elimination step as a π-acid in this ring contraction.

(46) The formation of acetylcyclopropane from a γ-palladaketone intermediate was reported, see: Ogoshi, S.; Morimoto, T.; Nishio, K.; Ohe, K.; Murai, S. *J. Org. Chem.* **1993**, *58*, 9.

(47) For recent studies on catalytic cyclopropanation via reductive elimination from palladacyclobutane, see: Satake, A.; Nakata, T. *J. Am. Chem. Soc.* **1998**, *120*, 10391 and references therein.

(48) We may also assume an alternative pathway for this ring contracting reaction via a Pd(IV) species (**B′**) considering from the formation of cyclopropane **28′** obtained as a byproduct in the reaction of **23** (ref 42), although details are not yet known.



B'

For recent example of Pd-catalyzed domino-reaction of bromodienynes producing a cyclopropane ring under *C−H activation*, see: Schweizer, S.; Song, Z.-Z.; Meyer, F. E.; Parsons, P. J.; de Meijere, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1452. For the study of γ-elimination from a dialkylplatinum complex affording a platinacyclobutane, see: Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948.

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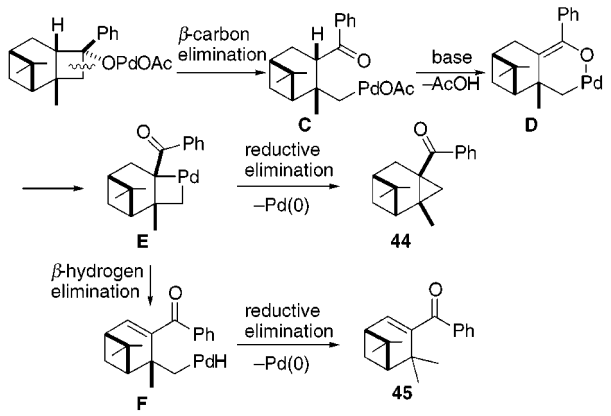
(50) A 97% conversion of **31** in the presence of 10 mol % $Pd_2(dba)_3$·$CHCl_3$ was observed after 23 h, in which an induction period (ca. 2 h) was observed, whereas $Pd(OAc)_2$ did not show any induction period. This induction period shows two possible pathways for the oxidation of Pd(0) to Pd(II). For a recent example of direct oxidation of Pd(0) with oxygen, see ref 51c. For examples of oxidative addition of an alcoholic O−H bond to Pd(0) to produce a hydridopalladium(II) alcoholate, see: (a) Braga, D.; Sabatino, P.; Di Bugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *334*, C46. (b) Di Bugno, C.; Pasquali, M.; Leoni, P.; Sabatino, P.; Braga, D. *Inorg. Chem.* **1989**, *28*, 1390.

(51) (a) Igersheim, F.; Mimoun, H. *Nouv. J. Chim.* **1980**, *4*, 711. (b) Hosokawa, T.; Murahashi, S.-I. *Acc. Chem. Res.* **1990**, *23*, 49. (c) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1636.

Scheme 5. Plausible Reaction Pathway



Conclusions

Several transformations of *tert*-cyclobutanols to afford oxidative products by palladium(II) catalysis using atmospheric pressure of oxygen as a sole reoxidant are described. β-Carbon elimination from a Pd(II) alcoholate proceeds to give an alkylpalladium intermediate, which shows an interesting reactivity to afford several types of products. Although more detailed studies are required to solve the question of mechanism for some steps including β-carbon elimination, these results demonstrate the interesting possibility and utility of palladium catalysis using β-carbon elimination in organic synthesis.

Experimental Section

General Methods. ^{1}H NMR spectra were obtained in $CDCl_3$ at 270 or 400 MHz with Me_4Si as an internal standard. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sxt, sextet; m, multiplet. ^{13}C NMR spectra were obtained at 67.8 or 100 MHz. Melting points are uncorrected. GLC yields were determined using bibenzyl or biphenyl as an internal standard. Elemental analysis was done at the Microanalytical Center of Kyoto University.

Materials. $Pd(OAc)_2$ was purchased from Wako Pure Chemical Ind. Ltd. and used without further purification. $Pd_2(dba)_3{\cdot}CHCl_3$[52] (dba = dibenzylideneacetone) was synthesized by the literature method. Pyridine was purchased and used without further purification. Solvents were dried and distilled by known methods. MS3A (powder) was commercially available from Nacalai Tesque, which was activated by calcination (by a gas burner) just before use. Cyclobutanols were prepared from the corresponding cyclobutanones and Grignard reagent or alkyllithium. Cyclobutanones were prepared by the reduction of α,α-dichlorocyclobutanones synthesized by the reported procedure[53] in the presence of Zn powder and AcOH.[54]

7-Vinylbicyclo[4.2.0]octan-7-ol (1a). Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.11−1.80 (m, 9H), 2.00−2.18 (m, 3H), 2.22−2.32 (m, 1H), 5.08 (dd, J = 10.7, 1.4 Hz, 1H), 5.29 (dd, J = 17.3, 1.4 Hz, 1H), 6.19 (dd, J = 17.3, 10.7 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.6, 21.8, 22.7, 23.5, 25.9, 37.0, 42.5, 73.2, 111.1, 143.4. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.64; H, 10.57.

7-Phenylbicyclo[4.2.0]octan-7-ol (1b). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14−1.26 (m, 1H), 1.42−1.60 (m, 5H), 1.68−1.94 (m, 3H), 1.96−2.06 (m, 1H), 2.29 (dd, J = 11.2, 10.6 Hz, 1H), 2.49 (ddd, J = 11.2, 7.8, 4.4 Hz, 1H), 2.69 (ddd, J = 16.8, 8.3, 4.4 Hz, 1H), 7.25−7.31 (m, 1H), 7.34−7.40 (m, 2H), 7.51−7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 22.1, 22.8, 24.1, 26.2, 37.9, 43.1, 75.3, 125.7, 127.3, 128.4, 146.7. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.84; H, 8.94.

7-Butylbicyclo[4.2.0]octan-7-ol (1c). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 6.8 Hz, 3H), 1.01−1.13 (m, 1H), 1.25−1.70 (m, 14H), 1.86−2.01(m, 3H), 2.12 (ddd, J = 17.6, 8.3, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.8, 22.7, 23.2, 24.2, 26.0, 26.1, 37.3, 39.6, 42.3, 73.3. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.79; H, 12.25.

8-Vinylbicyclo[5.2.0]nonan-8-ol (2a). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98−1.28 (m, 3H), 1.39 (q, J = 11.7 Hz, 1H), 1.55−1.89 (m, 7H), 1.94−2.03 (m, 1H), 2.10−2.21 (m, 1H), 2.33−2.41 (m, 2H), 5.01 (dd, J = 10.7, 1.0 Hz, 1H), 5.21 (dd, J = 17.1, 1.0 Hz, 1H), 6.11 (dd, J = 17.1, 10.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 28.9, 29.7, 30.9, 32.0, 34.2, 40.9, 49.5, 72.1, 110.0, 144.5. Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.73; H, 10.79.

8-Phenylbicyclo[5.2.0]nonan-8-ol (2b). Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.98−1.35 (m, 3H), 1.50−2.04 (m, 9H), 2.18−2.34 (m, 1H), 2.68−2.80 (m, 2H), 7.21−7.28 (m, 1H), 7.31−7.39 (m, 2H), 7.45−7.50 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 25.3, 29.2, 29.6, 32.1, 32.1, 34.1, 41.4, 50.4, 74.1, 124.7, 126.9, 128.4, 148.1. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.00; H, 9.47.

8-Butylbicyclo[5.2.0]nonan-8-ol (2c). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 0.95−1.40 (m, 8H), 1.44−1.66 (m, 7H), 1.72−1.87 (m, 3H), 1.93−2.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.2, 25.1, 25.5, 28.9, 30.0, 31.1, 32.0, 34.4, 41.3, 41.5, 49.5, 72.1. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.38; H, 12.13.

3-Phenyl-*exo*-tricyclo[4.2.1.0^{2,5}]nonan-3-ol (3b). White solid; mp 66.5−66.9 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.00−1.15 (m, 2H), 1.34 (d, J = 10.3 Hz, 1H), 1.50−1.58 (m, 2H), 1.88 (s, OH, 1H), 2.00 (dd, J = 13.1, 5.8 Hz, 1H), 2.07−2.19 (m, 1H), 2.16 (br s, 1H), 2.27 (d, J = 10.3 Hz, 1H), 2.35 (br s, 1H), 2.45 (d, J = 5.8 Hz, 1H), 2.55 (ddd, J = 13.1, 8.3, 2.2 Hz, 1H), 7.20−7.27 (m, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.53 (dd, J = 7.6, 1.7 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.2, 28.3, 34.1, 34.5, 35.5, 38.9, 40.1, 55.0, 74.8, 124.0, 126.6, 128.3, 149.4. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.00; H, 8.63.

3-Butyl-*exo*-tricyclo[4.2.1.0^{2,5}]nonan-3-ol (3c). White solid; mp 38.3−38.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 0.97−1.09 (m, 2H), 1.20−1.40 (m, 5H), 1.40−1.60 (m, 6H), 1.85−1.92 (m, 1H), 1.95−2.07 (m, 3H), 2.04 (br s, 1H), 2.19 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.1, 24.9, 28.1, 28.4, 33.7, 33.8, 35.2, 37.8, 38.8, 43.2, 52.7, 73.9. Anal. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41. Found: C, 80.07; H, 11.34.

2,3-Benzo-6-phenylbicyclo[3.2.0]hept-2-en-7-ol (4b). White solid; mp 55.0−55.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, OH, 1H), 2.24 (ddd, J = 13.2, 3.9, 1.0 Hz, 1H), 3.13 (dd, J = 17.1, 9.3 Hz, 1H), 3.21 (ddd, J = 13.2, 8.3, 1.5 Hz, 1H), 3.46−3.57 (m, 2H), 3.73 (td, J = 8.3, 3.9 Hz, 1H), 7.18−7.33 (m, 5H), 7.35−7.42 (m, 2H), 7.50−7.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.6, 39.0, 45.5, 49.1, 75.9, 124.5, 124.7, 124.9, 126.9, 127.0, 128.4, 145.0, 147.5. Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.27; H, 6.75.

2,3-Benzo-6-butylbicyclo[3.2.0]hept-2-en-7-ol (4c). White solid; mp 37.6−38.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H), 1.30−1.41 (m, 4H), 1.47 (br s, OH, 1H), 1.58−1.68 (m, 2H), 1.80 (dd, J = 12.7, 4.9 Hz, 1H), 2.63 (ddd, J = 12.7, 8.5, 1.7 Hz, 1H), 2.99−3.08 (m, 2H), 3.25−3.35 (m, 1H), 3.47−3.54 (m, 1H), 7.12−7.18 (m, 3H), 7.24−7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.1, 25.3, 32.2, 38.6, 42.2, 44.2, 47.3, 74.3, 124.2, 124.9, 126.5, 126.7, 145.0, 148.0. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.02; H, 9.24.

3-Hexyl-1-phenylcyclobutanol (5b, *cis*/*trans* = 67/33). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz), 1.15−1.35 (m), 1.41 (q, J = 6.8 Hz, 1H, *trans*-isomer), 1.50 (q, J = 6.8 Hz, 1H, *cis*-isomer), 1.75−1.90 (m, 1H, *cis*-isomer), 1.92−2.05 (m, 2H, *cis*-isomer), 2.05−2.18 (m, 2H, *trans*-isomer), 2.40−2.47 (m, 2H, *trans*-isomer), 2.54−2.68 (m, 1H,

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trans-isomer), 2.69−2.75 (m, 2H, *cis*-isomer), 7.22−7.40 (m), 7.51−7.55 (m). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.60; H, 10.70.

1-Butyl-3-hexylcyclobutanol (5c, *cis*/*trans* = 67/33). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz), 0.93 (t, J = 6.8 Hz), 1.15−1.44 (m), 1.47−1.75 (m), 2.03−2.10 (m, 2H, *trans*-isomer), 2.16−2.24 (m, 2H, *cis*-isomer), 2.35 (sept, J = 7.8 Hz). Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.48; H, 13.25.

3-*tert*-Butyl-1-phenylcyclobutanol (6b, *cis*/*trans* = 65/35). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 9H, *trans*-isomer), 0.86 (s, 9H, *cis*-isomer), 1.65−1.75 (m, 1H, *cis*-isomer), 1.89 (br s, OH, 1H, *trans*-isomer), 1.96 (br s, OH, 1H, *cis*-isomer), 2.08−2.16 (m, 2H, *cis*-isomer), 2.16−2.30 (m, 4H, *trans*-isomer), 2.45−2.52 (m, 2H, *cis*-isomer), 2.56−2.66 (m, 1H, *trans*-isomer), 7.22−7.41 (m), 7.54−7.59 (m). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.06; H, 10.03.

1-Butyl-3-*tert*-butylcyclobutanol (6c, *cis*/*trans* = 86/14). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (s, 9H, *trans*-isomer), 0.86 (s, 9H, *cis*-isomer), 1.20−1.82 (m), 1.94−2.00 (m, 2H, *cis*-isomer), 2.35−2.45 (m, 1H, *trans*-isomer). Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.36; H, 13.27.

1-Methyl-7-vinylbicyclo[4.2.0]octan-7-ol (13). Colorless oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.14−1.70 (m, 8H), 1.87 (d, J = 12.6 Hz, 1H), 1.89−1.97 (m, 1H), 1.98 (d, J = 12.6 Hz, 1H), 2.03 (br dd, J = 7.4, 3.1 Hz, 1H), 4.98 (dd, J = 10.6, 1.4 Hz, 1H), 5.14 (dd, J = 17.3, 1.4 Hz, 1H), 5.99 (dd, J = 17.3, 10.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.2, 21.2, 22.6, 28.4, 31.7, 36.0, 47.3, 47.9, 75.7, 110.8, 145.6. Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.39; H, 10.77.

1-Phenyl-6-vinylbicyclo[3.2.0]heptan-6-ol (14). White solid; mp 51.4−52.2 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.53 (td, J = 12.4, 6.9 Hz, 1H), 1.63 (s, OH, 1H), 1.70−2.15 (m, 5H), 2.18 (d, J = 12.8 Hz, 1H), 2.71 (dd, J = 12.8, 2.9 Hz, 1H), 2.94 (br dd, J = 8.0, 2.9 Hz, 1H), 4.87 (dd, J = 10.7, 1.1 Hz, 1H), 5.06 (dd, J = 17.3, 1.1 Hz, 1H), 5.94 (dd, J = 17.3, 10.7 Hz, 1H), 7.14−7.34 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 27.5, 27.5, 44.4, 45.2, 46.2, 54.4, 69.8, 109.7, 125.4, 125.8, 128.2, 145.2, 148.5. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.79; H, 8.63.

1-Phenyl-7-vinylbicyclo[4.2.0]octan-7-ol (15). White solid; mp 55.7−56.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13−1.30 (m, 1H), 1.45−1.53 (m, 1H), 1.66 (s, OH, 1H), 1.67−1.85 (m, 3H), 1.87 (br d, J = 11.7 Hz, 2H), 2.34 (td, J = 13.2, 3.4 Hz, 1H), 2.37 (d, J = 12.2 Hz, 1H), 2.41 (d, J = 12.2 Hz, 1H), 2.69 (br d, J = 6.8 Hz, 1H), 4.96 (d, J = 10.8 Hz, 1H), 5.13 (d, J = 17.1 Hz, 1H), 5.90 (dd, J = 17.1, 10.8 Hz, 1H), 7.14−7.20 (m, 3H), 7.27−7.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 21.5, 23.0, 38.6, 40.4, 45.2, 48.4, 76.6, 111.1, 125.2, 125.8, 128.0, 144.9, 152.3. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.41; H, 9.06.

1-Methyl-7-phenylbicyclo[4.2.0]octan-7-ol (19). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.21−1.32 (m, 1H), 1.48−1.77 (m, 5H), 1.75 (s, OH, 1H), 1.82−1.91 (m, 1H), 1.96−2.06 (m, 1H), 2.15 (d, J = 12.0 Hz, 1H), 2.29 (d, J = 12.0 Hz, 1H), 2.38 (br dd, J = 7.8, 2.4 Hz, 1H), 7.21−7.25 (m, 1H), 7.30−7.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 22.8, 28.3, 31.6, 35.9, 48.1, 48.7, 76.7, 124.8, 126.9, 128.4, 148.4. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.25; H, 9.24.

7-(4-Chlorophenyl)-1-methylbicyclo[4.2.0]octan-7-ol (21). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.19−1.32 (m, 1H), 1.46−1.75 (m, 6H), 1.78−1.86 (m, 1H), 1.93−2.04 (m, 1H), 2.14 (d, J = 12.2 Hz, 1H), 2.26 (d, J = 12.2 Hz, 1H), 2.32 (br dd, J = 7.8, 2.9 Hz, 1H), 7.28−7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.3, 22.8, 28.3, 31.6, 35.9, 48.2, 48.8, 76.6, 126.4, 128.4, 132.6, 146.8. Anal. Calcd for $C_{15}H_{19}ClO$: C, 71.85; H, 7.64. Found: C, 71.86; H, 7.87.

7-(3-Chlorophenyl)-1-methylbicyclo[4.2.0]octan-7-ol (22). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.20−1.32 (m, 1H), 1.50−1.72 (m, 5H), 1.76 (br s, OH, 1H), 1.78−1.86 (m, 1H), 1.94−2.03 (m, 1H), 2.13 (d, J = 12.2 Hz, 1H), 2.26 (d, J = 12.2 Hz, 1H), 2.33 (br dd, J = 7.3, 2.9 Hz, 1H), 7.18−7.28 (m, 3H), 7.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.3, 22.8, 28.3, 31.7, 35.9, 48.3, 48.9, 76.7, 123.0, 125.3, 126.9, 129.7, 134.3, 150.3. Anal. Calcd for $C_{15}H_{19}ClO$: C, 71.85; H, 7.64. Found: C, 72.12; H, 7.59.

7-(4-Methoxyphenyl)-1-methylbicyclo[4.2.0]octan-7-ol (23). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.20−1.34 (m, 1H), 1.46−1.75 (m, 6H), 1.82−1.90 (m, 1H), 1.93−2.04 (m, 1H), 2.14 (d, J = 12.2 Hz, 1H), 2.26 (d, J = 12.2 Hz, 1H), 2.35 (br dd, J = 7.8, 2.4 Hz, 1H), 3.80 (s, 3H), 6.78 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.4, 22.8, 28.4, 31.5, 35.9, 48.1, 48.7, 55.3, 76.6, 113.7, 126.1, 141.0, 158.5. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.78; H, 9.16.

7-(3-Methoxyphenyl)-1-methylbicyclo[4.2.0]octan-7-ol (24). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.20−1.33 (m, 1H), 1.50−1.75 (m, 6H), 1.85−1.90 (m, 1H), 1.95−2.05 (m, 1H), 2.14 (d, J = 12.2 Hz, 1H), 2.29 (d, J = 12.2 Hz, 1H), 2.36 (br dd, J = 7.8, 2.4 Hz, 1H), 3.82 (s, 3H), 6.78 (dd, J = 8.1, 2.4 Hz, 1H), 6.93−6.99 (m, 2H), 7.27 (dd, J = 8.1, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 22.9, 28.3, 31.5, 35.9, 48.1, 48.7, 55.2, 76.7, 110.9, 112.1, 117.2, 129.4, 150.2, 159.7. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.92; H, 8.95.

1-Methyl-7-(2-naphthyl)bicyclo[4.2.0]octan-7-ol (25). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 3H), 1.23−1.38 (m, 1H), 1.50−1.80 (m, 5H), 1.83 (br s, OH, 1H), 1.88−1.97 (m, 1H), 1.99−2.10 (m, 1H), 2.23 (d, J = 12.2 Hz, 1H), 2.40 (d, J = 12.2 Hz, 1H), 2.49 (br dd, J = 7.8, 2.4 Hz, 1H), 7.40−7.50 (m, 2H), 7.53 (dd, J = 8.8, 2.0 Hz, 1H), 7.76−7.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 22.8, 28.4, 31.7, 36.0, 48.0, 48.6, 77.1, 122.8, 123.9, 125.8, 126.1, 127.5, 128.1, 128.3, 132.4, 133.1, 145.5. Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.45; H, 8.35.

2-Phenylspiro[3.5]nonan-2-ol (31). White solid; mp 101.7−102.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32−1.74 (m, 10H), 1.84 (br s, OH, 1H), 2.17 (d, J = 13.7 Hz, 2H), 2.40 (d, J = 13.7 Hz, 2H), 7.23−7.28 (m, 1H), 7.33−7.38 (m, 2H), 7.42−7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 23.1, 25.9, 31.4, 38.6, 39.2, 47.1, 73.0, 125.1, 127.0, 128.4, 147.8. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.01; H, 9.11.

2-Butylspiro[3.5]nonan-2-ol (32). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 1.25−1.43 (m, 13H), 1.50−1.57 (m, 4H), 1.73 (d, J = 13.2 Hz, 2H), 1.86 (d, J = 13.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.8, 23.0, 23.1, 25.3, 25.8, 30.5, 38.8, 40.2, 43.2, 46.5, 71.4. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.77; H, 12.59.

3,3-Dibutyl-1-phenylcyclobutanol (33). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 7.3 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H), 1.05−1.40 (m, 10H), 1.63−1.70 (m, 2H), 1.75 (br s, OH, 1H), 2.16 (d, J = 13.7 Hz, 2H), 2.39 (d, J = 13.7 Hz, 2H), 7.23−7.28 (m, 1H), 7.34−7.39 (m, 2H), 7.42−7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 23.2, 23.4, 26.2, 26.3, 32.9, 38.0, 38.6, 46.7, 72.9, 125.1, 127.0, 128.4, 147.9. Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.74; H, 10.92.

1,3,3-Tributylcyclobutanol (34). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 1.05−1.36 (m, 14H), 1.47−1.57 (m, 5H), 1.73 (d, J = 13.2 Hz, 2H), 1.83 (d, J = 13.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.2, 23.0, 23.4, 25.3, 26.1, 26.4, 32.2, 38.5, 39.5, 43.3, 46.1, 71.3. Anal. Calcd for $C_{16}H_{32}O$: C, 79.93; H, 13.41. Found: C, 79.65; H, 13.38.

1,3,3-Triphenylcyclobutanol (35). White solid; mp 130.7−131.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, OH, 1H), 3.32 (dm, J = 8.5 Hz, 2H), 3.47 (dm, J = 8.5 Hz, 2H), 7.05−7.10 (m, 1H), 7.14−7.39 (m, 12H), 7.45−7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.0, 49.9, 73.4, 125.0, 125.6, 125.7, 126.1, 126.4, 127.2, 128.3, 128.3, 128.5, 146.0, 149.3, 149.5. Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 84.74; H, 6.77.

3-Methyl-1,3-diphenylcyclobutanol (36, *cis* and *trans* mixture). White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s), 1.69 (br s, OH), 1.72 (s), 2.96 (d, J = 12.7 Hz), 2.86−3.03 (m), 7.10−7.44 (m), 7.54−7.58 (m). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.39; H, 7.65.

2,8,8-Trimethyl-4-phenyltricyclo[5.1.1.0^{2,5}]nonan-4-ol (43). The stereochemistry of **43** was confirmed by the observa-

tion of the NOE spectra (methyl protons; δ 0.92, 1.15, 1.28 ppm and methine proton; δ 2.71 ppm). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 1.15 (s, 3H), 1.28 (s, 3H), 1.64 (br s, OH, 1H), 1.71 (dd, J = 6.3, 4.9 Hz, 1H), 1.88−2.01 (m, 2H), 2.05 (d, J = 10.7 Hz, 1H), 2.24 (dddd, J = 10.7, 6.3, 6.3, 2.0 Hz, 1H), 2.31 (ddd, J = 13.7, 2.9, 2.4 Hz, 1H), 2.41 (dd, J = 13.7, 1.7 Hz, 1H), 2.53 (d, J = 13.7 Hz, 1H), 2.71 (br d, J = 10.7 Hz, 1H), 7.24−7.29 (m, 1H), 7.37 (t, J = 7.3 Hz, 2H), 7.49 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 24.0, 27.2, 27.5, 28.6, 34.9, 39.8, 41.0, 45.3, 46.7, 50.2, 71.3, 125.1, 127.0, 128.5, 149.8. Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.43. Found: C, 84.54; H, 9.69.

Typical Procedure for Palladium(II)-Catalyzed Transformation of *tert*-Cyclobutanols under Oxygen Atmosphere. To a mixture of $Pd(OAc)_2$ (0.05 mmol) and toluene (3 mL) in a 10-mL two-necked flask fitted with an O_2 balloon were added pyridine (1.0 mmol) and MS3A (powder, 50 mg) activated by calcination. After oxygen was introduced into the vessel and the mixture was stirred at 80 °C for 5 min, alcohol (0.5 mmol) in toluene (2 mL) was added. In some cases, ethyl acrylate (0.1−0.5 mmol) was added before the addition of alcohol. The mixture was stirred at 80 °C under O_2 until the reaction had reached completion by monitoring with TLC analysis. The reaction mixture was cooled to room temperature and then filtered through a pad of Florisil. The filtrate was concentrated under vacuum to give a yellow oil that was subjected to column chromatography on SiO_2 with EtOAc−hexane (2/98) as eluents.

2-Methylene-1-cyclohexyl Vinyl Ketone (7a). Colorless oil; IR (neat) 2935, 2858, 1698 (C=O), 1678, 1645, 1612, 1447, 1400, 979, 962, 898 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.43−1.80 (m, 5H), 1.92−2.04 (m, 1H), 2.18 (dd, J = 5.9, 5.9 Hz, 2H), 3.35 (dd, J = 6.7, 4.3 Hz, 1H), 4.63 (d, J = 1.1 Hz, 1H), 4.87 (d, J = 1.1 Hz, 1H), 5.69 (dd, J = 10.4, 1.7 Hz, 1H), 6.28 (dd, J = 17.5, 1.7 Hz, 1H), 6.58 (dd, J = 17.5, 10.4 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.7 (t), 28.1 (t), 28.9 (t), 35.0 (t), 54.7 (d), 110.4 (t), 127.7 (t), 134.7 (d), 147.5 (s), 200.8 (s). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.70; H, 9.56.

2-Methylene-1-cyclohexyl Phenyl Ketone (7b). Colorless oil; IR (neat) 2934, 2857, 1685 (C=O), 1644, 1597, 1447, 1360, 1247, 1199, 953, 894, 752, 692 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.45−2.03 (m, 6H), 2.15−2.33 (m, 1H), 2.42 (ddd, J = 12.6, 4.2, 4.2 Hz, 1H), 3.99 (br dd, J = 8.7, 4.2 Hz, 1H), 4.44 (s, 1H), 4.80 (s, 1H), 7.40−7.55 (m, 3H), 7.92−7.97 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 24.6 (t), 28.3 (t), 30.1 (t), 35.9 (t), 51.5 (d), 109.9 (t), 128.5 (d), 132.8 (d), 137.1 (s), 148.8 (s), 201.8 (s). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.23; H, 8.15.

Butyl 2-Methylene-1-cyclohexyl Ketone (7c). Colorless oil; IR (neat) 2934, 2859, 1712 (C=O), 1644, 1447, 1051, 893 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 1H), 1.30 (sxt, J = 7.4 Hz, 2H), 1.42−1.72 (m, 9H), 1.96−2.06 (m, 1H), 2.08−2.21 (m, 2H), 2.46 (dt, J = 16.6, 7.4 Hz, 1H), 2.49 (dt, J = 16.6, 7.4 Hz, 1H), 3.18 (t, J = 5.1 Hz, 1H), 4.66 (s, 1H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (q), 22.4 (t), 23.4 (t), 25.9 (t), 28.0 (t), 28.8 (t), 34.6 (t), 40.8 (t), 56.4 (d), 110.2 (t), 147.9 (s), 211.9 (s). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.06; H, 11.36.

2-Methylene-1-cycloheptyl Vinyl Ketone (8a). Colorless oil; IR (neat) 2927, 2854, 1697 (C=O), 1677, 1635, 1447, 1399, 983, 962, 893 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22−1.40 (m, 3H), 1.62−1.92 (m, 5H), 2.17 (ddd, J = 13.6, 9.8, 3.9 Hz, 1H), 2.34 (ddd, J = 13.6, 12.8, 3.9 Hz, 1H), 3.51 (dd, J = 10.5, 5.1 Hz, 1H), 4.80 (s, 1H), 4.97 (s, 1H), 5.69 (dd, J = 10.7, 1.5 Hz, 1H), 6.26 (dd, J = 17.6, 1.5 Hz, 1H), 6.48 (dd, J = 17.6, 10.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9 (t), 29.0 (t), 29.5 (t), 30.2 (t), 34.9 (t), 56.8 (d), 115.3 (t), 127.7 (t), 134.9 (d), 148.8 (s), 200.1 (s). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.25; H, 9.84.

2-Methylene-1-cycloheptyl Phenyl Ketone (8b). Colorless oil; IR (neat) 2926, 2853, 1681 (C=O), 1447, 1210, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35−1.55 (m, 3H), 1.70−2.05 (m, 5H), 2.37 (ddd, J = 14.0, 9.8, 4.4 Hz, 1H), 2.46 (dt, J = 14.0, 4.9 Hz, 1H), 4.15 (dd, J = 10.7, 4.9 Hz, 1H), 4.72 (s, 1H), 4.89 (s, 1H), 7.41−7.47 (m, 2H), 7.50−7.56 (m, 1H), 7.90−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5 (t), 28.7 (t), 29.6 (t), 30.8 (t), 35.4 (t), 52.7 (d), 114.6 (t), 128.5 (d), 132.6 (d), 136.8 (s), 149.5 (s), 201.2 (s). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.90; H, 8.52.

Butyl 2-Methylene-1-cycloheptyl Ketone (8c). Colorless oil; IR (neat) 2927, 2855, 1711 (C=O), 1635, 1451, 894 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.18−1.38 (m, 4H), 1.52 (qui, J = 7.3 Hz, 2H), 1.65−1.90 (m, 6H), 2.11 (td, J = 10.3, 3.4 Hz, 1H), 2.24−2.34 (m, 1H), 2.40 (dt, J = 17.1, 7.3 Hz, 1H), 2.55 (dt, J = 17.1, 7.3 Hz, 1H), 3.32 (dd, J = 10.3, 5.4 Hz, 1H), 4.82 (s, 1H), 4.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (q), 22.3 (t), 26.0 (t), 26.6 (t), 28.9 (t), 29.9 (t), 30.7 (t), 34.5 (t), 40.5 (t), 59.2 (d), 114.8 (t), 149.4 (s), 211.3 (s). Anal. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41. Found: C, 80.11; H, 11.61.

3-Methylenebicyclo[2.2.1]hept-*exo*-2-yl Phenyl Ketone (9b). Colorless oil; IR (neat) 2961, 2923, 2871, 1683 (C=O), 1655, 1448, 1337, 1237, 1206, 876, 766, 694 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.31 (dm, J = 9.9 Hz, 1H), 1.42−1.50 (m, 2H), 1.68−1.77 (m, 2H), 1.85 (dm, J = 9.9 Hz, 1H), 2.65 (s, 1H), 2.79 (s, 1H), 3.89 (d, J = 1.9 Hz, 1H), 4.50 (d, J = 2.1 Hz, 1H), 5.02 (d, J = 2.1 Hz, 1H), 7.43−7.60 (m, 3H), 7.96−8.01 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.7 (t), 29.6 (t), 37.1 (t), 41.7 (d), 45.5 (d), 55.1 (d), 105.5 (t), 128.6 (d), 128.8 (d), 132.8 (d), 137.6 (s), 153.5 (s), 199.1 (s). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.11; H, 7.69.

Butyl 3-Methylenebicyclo[2.2.1]hept-*exo*-2-yl Ketone (9c). Colorless oil; IR (neat) 2959, 2872, 1712 (C=O), 1655, 1454, 883 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3H), 1.22−1.38 (m, 5H), 1.52−1.72 (m, 5H), 2.51 (t, J = 7.3 Hz, 2H), 2.57 (br s, 1H), 2.73 (br s, 1H), 3.02 (br d, J = 2.0 Hz, 1H), 4.71 (d, J = 1.7 Hz, 1H), 5.02 (d, J = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (q), 22.4 (t), 26.0 (t), 28.4 (t), 30.0 (t), 37.2 (t), 40.8 (d), 42.0 (t), 45.3 (d), 60.8 (d), 104.8 (t), 153.4 (s), 209.7 (s). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.49; H, 10.65.

3-Methylinden-2-yl Phenyl Ketone (10b). Colorless oil; IR (neat) 1633 (C=O), 1597, 1577, 1446, 1382, 1353, 1261, 935, 915, 762, 724, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (t, J = 2.4 Hz, 3H), 3.83 (q, J = 2.4 Hz, 2H), 7.33−7.57 (m, 7H), 7.76 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4 (q), 40.2 (t), 121.1 (d), 123.9 (d), 126.7 (d), 127.5 (d), 128.4 (d), 128.7 (d), 132.0 (d), 138.8 (s), 140.1 (s), 143.5 (s), 145.4 (s), 147.9 (s), 195.4 (s). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.94; H, 5.95.

Butyl 3-Methylinden-2-yl Ketone (10c). White solid; mp 57.0−57.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H), 1.32−1.48 (m, 2H), 1.62−1.74 (m, 2H), 2.55 (t, J = 2.3 Hz, 3H), 2.73 (t, J = 7.3 Hz, 2H), 3.69 (q, J = 2.3 Hz, 2H), 7.34−7.40 (m, 2H), 7.46−7.54 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.0 (q), 14.0 (q), 22.5 (t), 26.2 (t), 39.0 (t), 41.9 (t), 121.5 (d), 124.0 (d), 126.8 (d), 127.9 (d), 137.4 (s), 143.0 (s), 145.6 (s), 149.8 (s), 199.5 (s). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.53; H, 8.52.

(*E*)-3-Methyl-1-phenyl-2-nonen-1-one (11b). Colorless oil; IR (neat) 2956, 2929, 2857, 1661 (C=O), 1611, 1448, 1239, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 3H), 1.25−1.40 (m, 6H), 1.50−1.60 (m, 2H), 2.19 (d, J = 1.5 Hz, 3H), 2.25 (t, J = 7.3 Hz, 2H), 6.73 (q, J = 1.5 Hz, 1H), 7.41−7.55 (m, 3H), 7.89−7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (q), 19.8 (q), 22.6 (t), 27.6 (t), 29.0 (t), 31.7 (t), 41.6 (t), 120.5 (d), 128.2 (d), 128.4 (d), 132.2 (d), 139.5 (s), 160.6 (s), 191.8 (s). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.51; H, 9.80.

2-Hexyl-1-octen-4-one and (*E*)-7-Methyl-6-tridecen-5-one (11c, $\beta,\gamma/\alpha,\beta$ = 34/66). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85−0.94 (m), 1.22−1.64 (m), 2.02 (t, J = 7.3 Hz, 2H, β,γ), 2.11 (t, J = 7.8 Hz, 2H, α,β), 2.12 (s, 3H, α,β), 2.41 (t, J = 7.8 Hz, 2H, α,β), 2.45 (t, J = 7.3 Hz, 2H, β,γ), 3.10 (s, 2H, β,γ), 4.83 (s, 1H, β,γ), 4.93 (s, 1H, β,γ), 6.05 (s, 1H, α,β). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.88; H, 12.73.

3-*tert*-Butyl-1-phenyl-3-buten-1-one and (*E*)-3,4,4-Trimethyl-1-phenyl-2-penten-1-one (12b, $\beta,\gamma/\alpha,\beta$ = 56/44).

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 9H; β,γ), 1.20 (s, 9H; α,β), 2.16 (d, J = 1.0 Hz, 3H; α,β), 3.70 (s, 2H; β,γ), 4.67 (s, 1H; β,γ), 5.08 (s, 1H; β,γ), 6.76 (d, J = 1.0 Hz, 1H; α,β), 7.40−7.56 (m), 7.83−8.03 (m). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.84; H, 9.21.

2-*tert*-Butyl-1-octen-4-one and (*E*)-2,3,3-Trimethyl-3-nonen-5-one (12c, $\beta,\gamma/\alpha,\beta$= 71/29). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H; β,γ), 0.91 (t, J = 7.3 Hz, 3H; α,β), 1.06 (s, 9H; β,γ), 1.11 (s, 9H; α,β), 1.24−1.38 (m), 1.50−1.64 (m), 2.12 (d, J = 1.0 Hz, 3H; α,β), 2.44 (t, J = 7.3 Hz, 2H; α,β), 2.47 (t, J = 7.3 Hz, 2H; β,γ), 3.13 (s, 2H; β,γ), 4.72 (s, 1H; β,γ), 5.07 (s, 1H; β,γ), 6.12 (s, 1H; α,β). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.31; H, 12.36.

1-Methyl-8-methylenebicyclo[4.3.0]nonan-7-one (16). Colorless oil; IR (neat) 2929, 2860, 1727 (C=O), 1643, 1641, 1448, 1057, 949, 934 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02−1.27 (m, 2H), 1.19 (s, 3H), 1.32−1.58 (m, 5H), 1.95−2.02 (m, 2H), 2.33 (dt, J = 16.1, 3.1 Hz, 1H), 2.45 (dt, J = 16.1, 1.6 Hz, 1H), 5.30−5.33 (m, 1H), 6.05−6.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2 (t), 21.6 (t), 22.6 (t), 25.2 (q), 34.6 (t), 35.8 (s), 43.0 (t), 55.8 (d), 117.9 (t), 144.4 (s), 207.3 (s). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.25; H, 9.96.

7-Methylene-1-phenylbicyclo[3.3.0]octan-6-one (17). Colorless oil; IR (neat) 2955, 2909, 2875, 1723 (C=O), 1642, 1497, 1446, 1273, 1088, 938, 761, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56−1.74 (m, 3H), 1.97−2.24 (m, 3H), 2.85 (dt, J = 16.6, 2.9 Hz, 1H), 3.01 (br dd, J = 10.0, 2.7 Hz, 1H), 3.10 (dt, J = 16.6, 2.0 Hz, 1H), 5.36−5.39 (m, 1H), 6.06−6.11 (m, 1H), 7.21−7.28 (m, 3H), 7.31−7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4 (t), 29.1 (t), 40.4 (t), 41.5 (t), 53.2 (s), 58.0 (d), 118.9 (t), 125.7 (d), 126.3 (d), 128.5 (d), 144.2 (s), 147.5 (s), 209.5 (s). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.14; H, 7.68.

8-Methylene-1-phenylbicyclo[4.3.0]heptan-7-one (18). Colorless oil; IR (neat) 2934, 2857, 1727 (C=O), 1644, 1046, 933, 764, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03−1.19 (m, 2H), 1.35−1.54 (m, 3H), 1.67−1.76 (m, 1H), 2.05−2.12 (m, 1H), 2.27−2.34 (m, 1H), 2.57 (dt, J = 16.6, 3.2 Hz, 1H), 2.82 (dt, J = 16.6, 1.5 Hz, 1H), 2.88 (dt, J = 5.4, 2.7 Hz, 1H), 5.35−5.38 (m, 1H), 6.13−6.16 (m, 1H), 7.22−7.27 (m, 2H), 7.34−7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (t), 21.8 (t), 22.3 (t), 35.4 (t), 43.9 (s), 44.9 (t), 52.9 (d), 118.2 (t), 126.2 (d), 128.6 (d), 143.5 (s), 146.0 (s), 206.2 (s). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.70; H, 8.02.

***trans*-1,2,3,4,4a,9a-Hexahydro-4a-methyl-9(10*H*)-anthracenone (20).** White solid; mp 71.7−72.2 °C; IR (KBr) 2928, 2863, 1687 (C=O), 1600, 1455, 1446, 1319, 1275, 1212, 749 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3H), 1.22−1.65 (m, 6H), 1.85−1.94 (m, 1H), 2.05−2.15 (m, 1H), 2.37 (dd, J = 11.7, 3.4 Hz, 1H), 2.72 (d, J = 16.4 Hz, 1H), 2.98 (d, J = 16.4 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.27 (dd, J = 7.8, 7.8 Hz, 1H), 7.45 (ddd, J = 7.8, 7.8, 1.0 Hz, 1H), 7.98 (dd, J = 7.8, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3 (q), 21.2 (t), 21.3 (t), 25.8 (t), 37.6 (s), 41.1 (t), 46.3 (t), 55.0 (d), 126.4 (d), 126.7 (d), 129.3 (d), 132.6 (s), 133.3 (d), 141.8 (s), 199.8 (s). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.88; H, 8.56.

Data for **20** (a colorless crystal, grown in pentane at −10 °C) was collected on a Rigaku AFC7R diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. Crystal data for **20** are as follows: monoclinic, space group $P2_{1/n}$ (#14); a = 9.099(5), b = 6.640(6), c = 20.065(4) Å; V = 1205(1) Å^3; β = 96.16(3)°; Z = 4; D_{calcd} = 1.181 g cm^{-3}; μ(Mo Kα) = 0.72 cm^{-1}; total of 2941 reflections within 2θ = 55°. The final R value was 0.051 (R_w = 0.055). The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares techniques. All atoms were refined anisotropically.

The stereochemistry of **26**−**30** was confirmed by that of **20** and almost the same chemical shift of the angular methyl proton (δ 0.85 ppm).

***trans*-6-Chloro-1,2,3,4,4a,9a-hexahydro-4a-methyl-9(10*H*)-anthracenone (26).** White solid; mp 105.0−106.2 °C; IR (KBr) 2936, 1690 (C=O), 1595, 1280, 873, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3H), 1.20−1.66 (m, 6H), 1.88−1.96 (m, 1H), 2.06−2.14 (m, 1H), 2.36 (dd, J = 11.5, 3.7 Hz, 1H), 2.68 (d, J = 16.6 Hz, 1H), 2.95 (d, J = 16.6 Hz, 1H), 7.20 (s, 1H), 7.25 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2 (q), 21.0 (t), 21.2 (t), 25.7 (t), 37.6 (s), 41.0 (t), 46.0 (t), 54.9 (d), 126.9 (d), 128.4 (d), 129.1 (d), 130.9 (s), 139.4 (s), 143.4 (s), 198.7 (s). Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89. Found: C, 72.16; H, 6.93.

***trans*-7-Chloro-1,2,3,4,4a,9a-hexahydro-4a-methyl-9(10*H*)-anthracenone (27).** White solid; mp 123.5−123.7 °C; IR (KBr) 2922, 2854, 1683 (C=O), 1592, 1473, 1446, 1409, 1250, 822, 690 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (s, 3H), 1.22−1.68 (m, 6H), 1.87−1.95 (m, 1H), 2.07−2.14 (m, 1H), 2.36 (dd, J = 11.5, 3.7 Hz, 1H), 2.70 (d, J = 16.4 Hz, 1H), 2.92 (d, J = 16.4 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.41 (dd, J = 7.8, 2.5 Hz, 1H), 7.94 (d, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2 (q), 21.1 (t), 21.2 (t), 25.7 (t), 37.6 (s), 41.0 (t), 45.7 (t), 54.9 (d), 126.5 (d), 130.9 (d), 132.6 (s), 133.1 (d), 133.8 (s), 140.0 (s), 198.5 (s). Anal. Calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89. Found: C, 72.30; H, 6.90.

***trans*-1,2,3,4,4a,9a-Hexahydro-6-methoxy-4a-methyl-9(10*H*)-anthracenone (28).** White solid; mp 84.7−85.0 °C; IR (KBr) 2928, 1677 (C=O), 1600, 1445, 1329, 1278, 1253, 1105, 1094, 1028 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (s, 3H), 1.20−1.62 (m, 6H), 1.82−1.93 (m, 1H), 2.07−2.15 (m, 1H), 2.31 (dd, J = 11.5, 3.7 Hz, 1H), 2.65 (d, J = 16.1 Hz, 1H), 2.93 (d, J = 16.1 Hz, 1H), 3.84 (s, 3H), 6.65 (d, J = 2.4 Hz, 1H), 6.79 (dd, J = 8.8, 2.4 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2 (q), 21.2 (t), 21.3 (t), 25.9 (t), 37.5 (s), 41.1 (t), 46.7 (t), 54.8 (d), 55.3 (q), 112.5 (d), 113.3 (d), 126.2 (s), 129.1 (d), 144.2 (s), 163.5 (s), 198.4 (s). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.51; H, 8.18.

4-Methoxyphenyl Spiro[2.5]oct-4-yl Ketone (28′). Colorless oil; IR (neat) 2950, 1669 (C=O), 1600, 1250, 1209, 1173 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15−0.28 (m, 3H), 0.40−0.46 (m, 1H), 1.38−1.96 (m, 8H), 3.26 (dd, J = 7.6, 4.2 Hz, 1H), 3.86 (s, 3H), 6.92 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.5 (t), 12.1 (t), 20.7 (s), 24.1 (t), 25.3 (t), 28.6 (t), 35.8 (t), 48.4 (d), 55.4 (q), 113.6 (d), 130.5 (d), 130.8 (s), 163.2 (s), 201.0 (s). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.65; H, 8.34.

***trans*-1,2,3,4,4a,9a-Hexahydro-7-methoxy-4a-methyl-9(10*H*)-anthracenone (29).** White solid; mp 86.0−86.3 °C; IR (KBr) 2919, 2838, 1674 (C=O), 1612, 1498, 1431, 1294, 1271, 1234, 1035, 816, 741 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (s, 3H), 1.21−1.68 (m, 6H), 1.87−1.95 (m, 1H), 2.06−2.15 (m, 1H), 2.35 (dd, J = 11.7, 3.4 Hz, 1H), 2.66 (d, J = 16.1 Hz, 1H), 2.91 (d, J = 16.1 Hz, 1H), 3.83 (s, 3H), 7.04 (dd, J = 8.3, 2.9 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 7.48 (d, J = 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.2 (q), 21.2 (t), 21.3 (t), 25.8 (t), 37.8 (s), 41.1 (t), 45.6 (t), 54.9 (d), 55.4 (q), 109.0 (d), 121.3 (d), 130.4 (d), 133.3 (s), 134.2 (s), 158.2 (s), 199.7 (s). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.53; H, 8.29.

***trans*-1,2,3,4,4a,12a-Hexahydro-4a-methyl-12(5*H*)-naphthacenone (30).** White solid; mp 195.2−196.2 °C; IR (KBr) 2936, 2859, 1678 (C=O), 1625, 1592, 1445, 1197, 925, 760, 478 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3H), 1.23−1.36 (m, 1H), 1.39−1.69 (m, 5H), 1.87−1.97 (m, 1H), 2.14−2.23 (m, 1H), 2.42 (dd, J = 11.7, 3.4 Hz, 1H), 2.89 (d, J = 16.1 Hz, 1H), 3.08 (d, J = 16.1 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.62 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 8.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4 (q), 21.3 (t), 25.8 (t), 37.3 (s), 41.1 (t), 46.5 (t), 55.6 (d), 125.8 (d), 127.0 (d), 127.4 (d), 128.0 (d), 128.2 (d), 129.9 (d), 130.6 (s), 131.6 (s), 136.0 (s), 137.1 (s), 199.9 (s). Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.15; H, 7.63.

Phenyl Spiro[2.5]oct-1-yl Ketone (37). Colorless oil; IR (neat) 2924, 2851, 1666 (C=O), 1448, 1397, 1218, 984, 719, 689 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (dd, J = 7.3, 3.9 Hz, 1H), 1.13−1.24 (m, 1H), 1.39−1.68 (m, 10H), 2.50 (dd, J = 7.3, 5.4 Hz, 1H), 7.43−7.56 (m, 3H), 7.98−8.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (t), 25.8 (t), 26.0 (t), 26.1 (t), 28.3 (t), 32.0 (d), 35.4 (s), 37.8 (t), 128.0 (d), 128.4 (d), 132.3 (d), 139.0 (s), 198.1 (s). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.37; H, 8.77.

Butyl Spiro[2.5]oct-1-yl Ketone (38). Colorless oil; IR (neat) 2926, 2853, 1694 (C═O), 1445, 1399, 1072 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (dd, J = 7.3, 3.9 Hz, 1H), 0.92 (t, J = 7.3 Hz, 3H), 1.16−1.25 (m, 1H), 1.25 (dd, J = 5.9, 3.9 Hz, 1H), 1.27−1.63 (m, 13H), 1.80 (dd, J = 7.3, 5.9 Hz, 1H), 2.48−2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (q), 21.7 (t), 22.5 (t), 26.0 (t), 26.1 (t), 26.2 (t), 26.5 (t), 28.0 (t), 34.4 (d), 34.5 (s), 37.8 (t), 44.5 (t), 208.8 (s). Anal. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41. Found: C, 80.64; H, 11.66.

2,2-Dibutylcyclopropyl Phenyl Ketone (39). Colorless oil; IR (neat) 2957, 2929, 2871, 1668 (C═O), 1449, 1397, 1217, 693 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (t, J = 7.3 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H), 0.95−1.08 (m, 2H), 1.12−1.72 (m, 12H), 2.48 (dd, J = 7.3, 5.4 Hz, 1H). 7.40−7.55 (m, 3H), 7.93−8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (q), 14.1 (q), 21.8 (t), 22.8 (t), 23.0 (t), 28.0 (t), 28.7 (t), 29.1 (t), 31.9 (d), 36.2 (s), 37.3 (t), 128.0 (d), 128.4 (d), 132.3 (d), 139.2 (s), 198.4 (s). Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.71; H, 10.31.

Butyl 2,2-Dibutylcyclopropyl Ketone (40). Colorless oil.; IR (neat) 2957, 2930, 2861, 1697 (C═O), 1466, 1398, 1069 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (dd, J = 7.3, 3.9 Hz, 1H), 0.86 (t, J = 7.3 Hz, 3H), 0.91 (t, J = 7.3 Hz, 6H), 1.04−1.15 (m, 1H), 1.22 (dd, J = 5.9, 3.9 Hz, 1H), 1.24−1.42 (m, 13H), 1.58 (qui, J = 7.3 Hz, 2H), 1.79 (dd, J = 7.3, 5.9 Hz, 1H), 2.53 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (q), 14.1 (q), 21.9 (t), 22.4 (t), 22.9 (t), 22.9 (t), 26.4 (t), 27.4 (t), 28.7 (t), 29.3 (t), 34.3 (d), 35.1 (s), 37.2 (t), 44.6 (t), 208.9 (s). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.78; H, 12.96.

Phenyl 2,2-Diphenylcyclopropyl Ketone (41). White solid; mp 128.7−129.2 °C; IR (KBr) 1668 (C═O), 1497, 1450, 1383, 1221, 1036, 1012, 740, 719, 698, 690 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (dd, J = 7.8, 4.4 Hz, 1H), 2.56 (dd, J = 6.2, 4.4 Hz, 1H), 3.51 (dd, J = 7.8, 6.2 Hz, 1H), 7.12−7.34 (m, 10H), 7.43−7.49 (m, 2H), 7.52−7.58 (m, 1H), 7.98−8.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (t), 33.7 (d), 43.8 (s), 126.6 (d), 127.0 (d), 127.2 (d), 128.1 (d), 128.3 (d), 128.6 (d), 128.6 (d), 130.2 (d), 132.8 (d), 138.7 (s), 139.2 (s), 145.2 (s), 195.5 (s). Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.52; H, 6.03.

***cis*-2-Methyl-2-phenylcyclopropyl Phenyl Ketone (42).** The stereochemistry of *cis*-**42** was confirmed by the observation of different NOE spectra (methine proton; δ 2.91 ppm and methyl proton; δ 1.65 ppm). Colorless oil; IR (neat) 1673 (C═O), 1598, 1448, 1385, 1239, 1215, 1066, 991, 763, 715, 670, 690, cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (dd, J = 7.6, 4,2 Hz, 1H), 1.65 (s, 3H), 2.21 (dd, J = 5.6, 4.2 Hz, 1H), 2.91 (dd, J = 7.6, 5.6 Hz, 1H), 7.10−7.20 (m, 5H), 7.42−7.48 (m, 2H), 7.51−7.56 (m, 1H), 7.91−7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6 (t), 28.6 (q), 33.6 (d), 36.5 (s), 126.7 (d), 128.0 (d), 128.1 (d), 128.5 (d), 128.9 (d), 132.4 (d), 138.8 (s), 140.8 (s), 196.2 (s). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.36; H, 6.78.

***trans*-2-Methyl-2-phenylcyclopropyl Phenyl Ketone (42).** The stereochemistry of *trans*-**42** was confirmed by the observation of different NOE spectra (methine proton; δ 2.91 ppm and methylene proton; δ 1.61 ppm). Colorless oil; IR (neat) 1669 (C═O), 1598, 1448, 1386, 1221, 977, 766, 739, 715, 699, 690 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 3H), 1.61 (dd, J = 7.8, 4.6 Hz, 1H), 1.88 (dd, J = 6.4, 4.6 Hz, 1H), 2.91 (dd, J = 7.8, 6.4 Hz, 1H), 7.25−7.29 (m, 1H), 7.36−7.40 (m, 4H), 7.44−7.49 (m, 2H), 7.53−7.58 (m, 1H), 7.97−8.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7 (q), 20.9 (t), 33.6 (s), 34.1 (d), 126.5 (d), 126.6 (d), 128.1 (d), 128.6 (d), 128.7 (d), 132.7 (d), 138.7 (s), 145.8 (s), 197.5 (s). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.13; H, 6.80.

2,7,7-Trimethyltricyclo[4.1.1.0^{2,4}]oct-4-yl Phenyl Ketone (44). The stereochemistry of **44** was confirmed by the observation of different NOE spectra (methyl proton; δ 1.18, 1.29 and 1.32 ppm). White solid; mp 53.4−55.2 °C; IR (KBr) 2896, 1670 (C═O), 1595, 1455, 1385, 1360, 1265, 1230, 1215, 1020, 985, 920, 684, 616 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (d, J = 4.9 Hz, 1H), 1.16 (d, J = 8.8 Hz, 1H), 1.18 (s, 3H), 1.29 (s, 3H), 1.32 (s, 3H), 1.62 (d, J = 4.9 Hz, 1H), 1.79 (ddd, J = 8.3, 5.4, 2.9 Hz, 1H), 1.93 (t, J = 5.4 Hz, 1H), 2.09 (dd, J = 14.2, 2.9 Hz, 1H), 2.12−2.18 (m, 2H), 7.40−7.52 (m, 3H), 7.92−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8 (q), 22.7 (q), 26.6 (t), 27.2 (q), 27.2 (t), 28.6 (s), 29.6 (s), 32.0 (t), 40.6 (s), 41.8 (d), 46.5 (d), 128.2 (d), 128.9 (d), 132.0 (d), 138.1 (s), 202.3 (s). Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.87; H, 8.91.

4,4,6,6-Tetramethylbicyclo[3.1.1]hept-2-en-3-yl Phenyl Ketone (45). Colorless oil; IR (neat) 2944, 1644 (C═O), 1597, 1263, 872, 726, 699 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 1.34 (s, 3H), 1.38 (s, 3H), 1.41 (s, 3H), 1.52 (d, J = 9.3 Hz, 1H), 1.85 (t, J = 6.0 Hz, 1H), 2.36 (dd, J = 12.0, 6.0 Hz, 1H), 2.37−2.44 (m, 1H), 6.95 (d, J = 6.0 Hz, 1H), 7.35−7.50 (m, 3H), 7.56−7.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1 (q), 25.2 (q), 27.4 (q), 29.4 (q), 30.5 (t), 41.0 (s), 41.7 (s), 43.4 (d), 56.0 (d), 127.9 (d), 128.9 (d), 131.0 (d), 140.7 (s), 142.1 (s), 154.4 (d), 198.0 (s). Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.02; H, 8.68.

Supporting Information Available: Crystallographic data including ORTEP drawing of compound **20** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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