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Generation of β-Carbonyl Radicals from Cyclopropanol Derivatives by the Oxidation with Manganese(III) 2-Pyridinecarboxylate and Their Reactions with Electron-Rich and -Deficient Olefins

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Various β-carbonyl radicals are generated oxidatively from cyclopropanol derivatives by the use of manganese(III) 2-pyridinecarboxylate (Mn(pic)$_3$). These β-carbonyl radicals react with electron-rich olefins such as conjugated silyl enol ethers, a ketene thioacetal, a ketene dithioacetal, and a vinyl ether intermolecularly to give crossed-addition products in good yield. Furthermore, the combined use of Mn(pic)$_3$ and tributylhydridotin makes it possible to carry out the 1 : 1 addition reaction of these β-carbonyl radicals with electron-deficient olefins such as acrylonitrile, acrylaldehyde, methyl acrylate, methyl vinyl ketone, and *N*,*N*-dimethylacrylamide, and the corresponding products are obtained in moderate to good yield.

Recently, oxidative generation of radical species using metal oxidants has attracted much attention as a useful method for carbon-carbon bond formations.$^{1)}$ Most of these researches have been concerned with the generation of α-carbonyl radicals from enol derivatives or active methylene compounds using Mn$^{\text{III}}$ or Ce$^{\text{IV}}$ compounds as one-electron oxidants.$^{2,3)}$

In contrast with α-carbonyl radicals, the studies of their homologs, β-carbonyl radicals, have been much more limited and especially their applications as a synthetic tool have been scarce. Cyclopropanols are known as homologs of enol compounds,$^{4)}$ from which β-carbonyl radicals can be generated by oxidation. However, oxidative generation of β-carbonyl radicals from cyclopropanol derivatives has not been explored extensively.$^{5-10)}$ Especially thus generated β-carbonyl radicals have been scarcely utilized for carbon–carbon bond formation.$^{7-10)}$ In the intermolecular reactions, Fe$^{\text{III}}$ or Cu$^{\text{II}}$ compounds are employed as oxidants and electron-deficient olefins such as acrylonitrile or ethyl acrylate are used as radical acceptors. However, the yield of crossed-addition products are not sufficiently high, and the generality of these methods is not explored in detail.

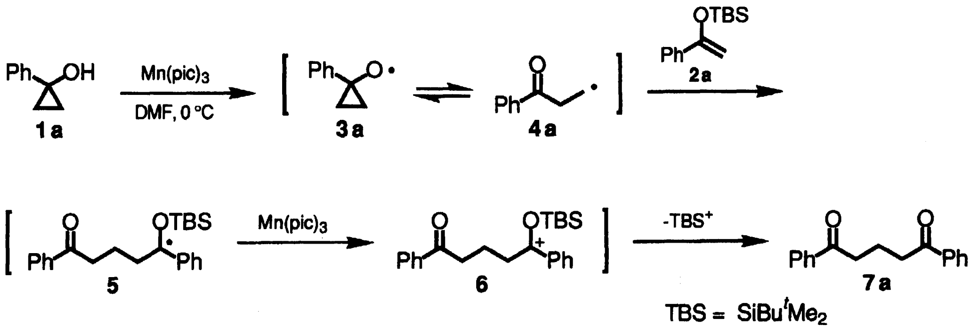
Previously, our laboratory reported that α-keto radicals are generated from β-keto carboxylic acids by the use of manganese(III) 2-pyridinecarboxylate (Mn(pic)$_3$) as an oxidant, which react intermolecularly with electron-rich olefins.$^{11)}$ This oxidant can also be employed in the generation of cation radicals from silyl ethers of *aci*-nitroalkanes.$^{12)}$ This mild oxidant was further applied to the generation of β-carbonyl radicals from cyclopropanol derivatives. In fact, these radicals thus generated were found to add to electron-rich olefins to give crossed-addition products in good yield.$^{13)}$ In this paper, we would like to disclose full account of the generation and the reactions of β-carbonyl radicals including the addition reactions to various electron-rich and -deficient olefins.

We first examined the reaction of 1-phenylcyclopropanol (**1a**) with α-(t-butyldimethylsiloxy)styrene (**2a**) as a representative electron-rich olefin using Mn(pic)$_3$. It was thought that a β-keto radical **4a** generated oxidatively from the cyclopropanol **1a** via an alkoxyl radical **3a** would react with the electron-rich olefin **2a** to give a radical intermediate **5**, which would be further oxidized to a cation **6** by Mn(pic)$_3$ affording the 1,5-diketone **7a** eventually (Scheme 1).

When **1a** and 1.5 mole equivalents of **2a** were added to 2.4 mole equivalents of Mn(pic)$_3$ in DMF, the reaction proceeded smoothly (0°C, 0.5 h) yielding the product **7a** in high yield (89%) without accompanying a self-coupling product of **1a** or **2a**. The reaction was also examined by employing other oxidants such as Mn$_3$O(OAc)$_7$, Fe(NO$_3$)$_3$, and CuCl$_2$, however, much inferior results were observed in these cases. Treatment of **1a** with Mn(pic)$_3$ in the absence of the olefin **2a** afforded propiophenone and 1,6-diphenyl-1,6-hexanedione, the self-coupling product of the β-keto radical **4a**, in ca. 30 and 50% yield, respectively. When the silyl enol ether **2a** was treated with Mn(pic)$_3$ in the absence of the cyclopropanol for 3 h at 0°C, the self-coupling product of **2a** was not detected and **2a** was recovered. These results indicate that the β-keto radical **4a**, which is oxidatively generated from the cyclopropanol **1a**, is actually the reactive species in this reaction.

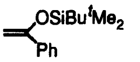
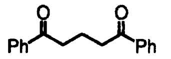
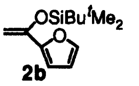
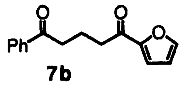
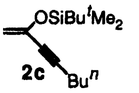
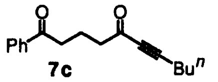
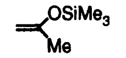
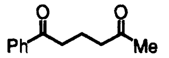
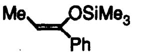
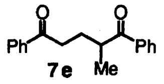
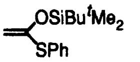
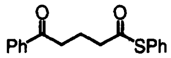
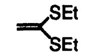
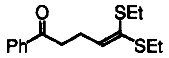
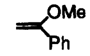
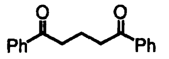
The cyclopropanol **1a** was further reacted with various electron-rich olefins in the presence of Mn(pic)$_3$. As shown in Table 1, conjugated silyl enol ethers **2b** and **2c** gave the corresponding products in high yield (Entries 2 and 3). A nonconjugated silyl enol ether **2d** gave a product **7d** in poorer yield than the conjugated ones **2a**—**c** (Entry 4), and the introduction of a substituent on the β-carbon of a silyl enol ether also lowered the product yield considerably (Entry 5). In addition to silyl enol ethers, electron-rich olefins such as a ketene thioacetal **2f** and a vinyl ether **2h** gave the adducts in good yield (Entries 6 and 8). When a ketene dithioacetal **2g** was employed, an olefin **7g** was obtained (Entry 7).

In addition to 1-phenylcyclopropanol (**1a**), various cyclopropanol derivatives were found to react with **2a**



Scheme 1.

Table 1. The Reactions of 1-Phenylcyclopropanol (**1a**) with Various Electron-Rich Olefins[a)]

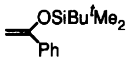
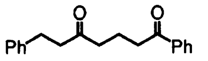
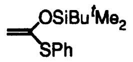
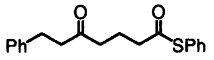
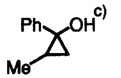
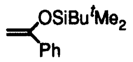
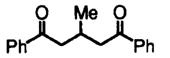
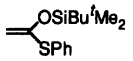
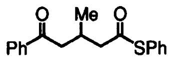
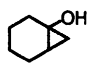
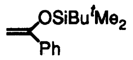
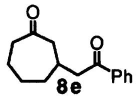
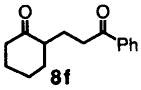
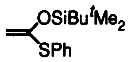
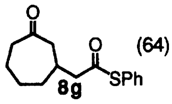
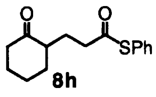
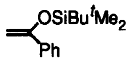
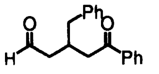
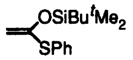
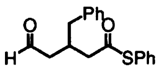
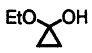
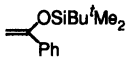
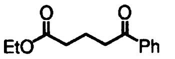
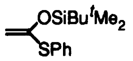
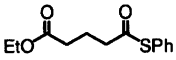
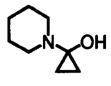
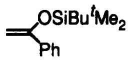
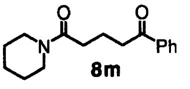
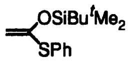
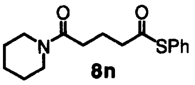
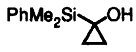
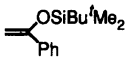
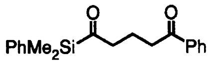
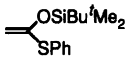
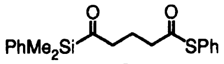
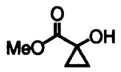
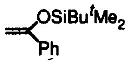
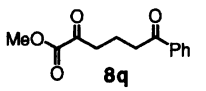
Entry	Olefin	Amount of reagent/mole ratio[b)] Mn(pic)$_3$	 Olefin	Product	Yield/%[b)]
1	 **2a**	2.4	1.5	 **7a**	89
2	 **2b**	2.4	1.5	 **7b**	80
3	 **2c**	2.4	1.5	 **7c**	88
4	 **2d**	2.6	3.1	 **7d**	14
5	 **2e**	2.9	1.7	 **7e**	41
6	 **2f**	2.5	2.6	 **7f**	66
7	 **2g**	2.4	2.1	 **7g**	71
8	 **2h**	2.4	1.5	 **7a**	72

a) Reaction conditions: DMF, 0°C, 0.5—5 h. b) Based on **1a**.

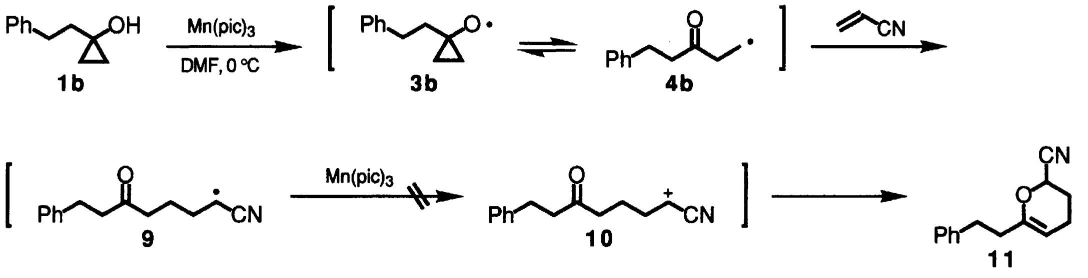
and **2f**, and the results were listed in Table 2. A 1-alkylcyclopropanol **1b** reacted with the olefins **2a** and **2f**, giving the corresponding adducts in moderate to good yield (Entries 1 and 2). In cases of 2-substituted cyclopropanols **1c**, **1d**, and **1e**, the cyclopropyl group cleaved to generate secondary radicals preferentially (Entries 3—8). Especially notable is the fact that the reaction of bicyclo[4.1.0]heptan-1-ol (**1d**) afforded the ring-expanded seven-membered adducts **8e** and **8g** as major products (Entries 5 and 6).[14)] In addition, a 1-unsubstituted cyclopropanol **1e**, a cyclopropanone hemiacetal **1f**, 1-piperidinocyclopropanol (**1g**), and 1-(dimethylphenylsilyl)cyclopropanol (**1h**) could be employed as a β-formyl, a β-ethoxycarbonyl, a β-piperidinocarbonyl, and a β-(dimethylphenylsilyl)carbonyl radical sources respectively. The corresponding aldehydes, esters, amides, and acylsilanes were obtained in moderate to high yield (Entries 7—14). Although the yield was not high, a 1-(methoxycarbonyl)cyclopropanol **1i** also reacted with the olefin **2a** and an α-keto ester **8q** was prepared (Entry 15).

Thus, various β-carbonyl radicals are generated oxidatively from cyclopropanol derivatives using Mn(pic)$_3$ as an oxidant, and react with electron-rich olefins to give 1 : 1 addition products in good yield without using large excess of the radical trapping reagents. As β-carbonyl

Table 2. The Reactions of Various Cyclopropanols with Representative Electron-Rich Olefins$^{a)}$

Entry	Cyclopropanol	Olefin	Amount of reagent/mole ratio$^{b)}$		Product (Yield/%$^{b)}$)
			Mn(pic)$_3$	Olefin	
1	 **1b**	 **2a**	2.4	1.5	 (80) **8a**
2		 **2f**	2.4	2.7	 (59) **8b**
3	 **1c**	 **2a**	2.4	1.3	 (78) **8c**
4		 **2f**	2.7	2.3	 (66) **8d**
5	 **1d**	 **2a**	2.4	1.5	 (77) **8e**  (5) **8f**
6		 **2f**	2.4	2.4	 (64) **8g**  (10) **8h**
7	 **1e**	 **2a**	2.0	3.4	 (78) **8i**
8		 **2f**	2.0	3.4	 (33) **8j**
9	 **1f**	 **2a**	2.4	1.5	 (85) **8k**
10		 **2f**	2.0	1.5	 (63) **8l**
11	 **1g**	 **2a**	2.5	3.7	 (65) **8m**
12		 **2f**	2.4	3.6	 (46) **8n**
13	 **1h**	 **2a**	2.5	3.0	 (60) **8o**
14		 **2f**	2.4	3.1	 (61) **8p**
15	 **1i**	 **2a**	2.4	1.5	 (29) **8q**

a) Reaction conditions: DMF, 0°C, 0.5—5.5 h. b) Based on **1**. c) *c*-2-Methyl-*r*-1-hydroxy form. d) *cis*-Form.



Scheme 2.

radicals are considered to also work as nucleophilic radicals, the reaction was examined with electron-deficient olefins.

The reaction of the 1-alkylcyclopropanol **1b** with 4.7 mole equivalents of acrylonitrile was tried using 2.4 mole equivalents of Mn(pic)$_3$ under the same reaction conditions as described for the reaction with electron-rich olefins (DMF, 0°C, 2 h), but a 1 : 1 crossed-addition product, such as **11**, was not obtained and unidentified polymerized products were generated (Scheme 2).

The formation of the polymer mixture is probably explained as follows. In an intermediate radical adduct **9**, the electron-withdrawing substituent (cyano group) on the radical carbon makes the oxidation to a cation **10** difficult, and the radical **9** further adds to another acrylonitrile successively to give the polymerized mixture. To prevent such a side reaction, the above reaction was investigated in the presence of various trapping reagents of the radical intermediate **9**.

The use of *t*-butyl isocyanide[15] and 2,6-di-*t*-butyl-4-methylphenol ("BHT") gave no 1 : 1 crossed-addition product. When CuCl$_2$,[16] carbon tetrabromide, and diphenyl diselenide[17] were employed, the β-keto radical **4b** initially formed was directly trapped by these reagents, and 1-chloro-5-phenyl-3-pentanone (19%) and 5-phenyl-1-penten-3-one (33%) (in the case of CuCl$_2$), 5-phenyl-1-penten-3-one (74%) (in the case of CBr$_4$), and 1-phenyl-5-phenylseleno-3-pentanone (76%) (in the case of diphenyl diselenide) were obtained, respectively.

The desired 1 : 1 addition product, 6-oxo-8-phenyloctanenitrile (**12c**), was obtained in 16 and 34% yield respectively, when 1,4-cyclohexadiene or triphenylmethane was employed. Furthermore, when hydridotriphenyltin was used, 36% yield of the adduct **12c** was obtained, and the use of dibutyldihydridotin gave only 5% yield of **12c** with 43% of recovered **1b** and 39% of 1-phenyl-3-pentanone which was produced by direct hydrogen abstraction of the β-keto radical from dibutyldihydridotin. In the case of using tributylhydridotin, the yield of **12c** increased up to 52%. In contrast to the cases of reactions with electron-rich olefins, the use of small excess of acrylonitrile resulted in decrease of yield of the addition product and considerable amounts of the ketone derived by hydrogen abstraction of the β-keto radical **4b** from tributylhydridotin were obtained.

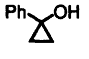
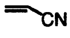
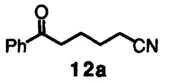
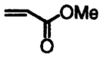
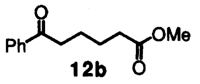
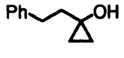
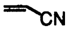
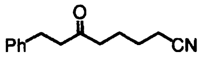
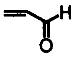
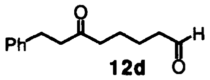
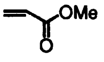
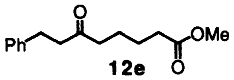
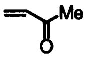
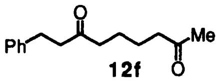
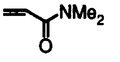
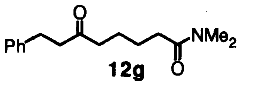
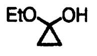
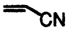
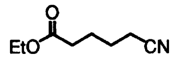
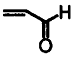
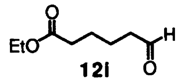
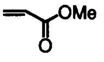
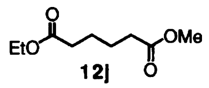
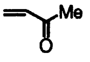
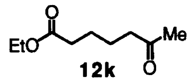
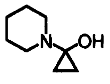
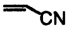
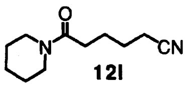
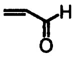
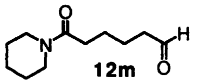
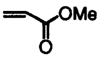
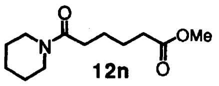
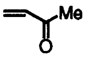
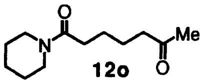
As tributylhydridotin proved to be able to coexist with Mn(pic)$_3$ and to work as an efficient radical-trapping reagent, the reaction of several cyclopropanols with electron-deficient olefins was investigated using Mn(pic)$_3$ and tributylhydridotin. As shown in Table 3, acrylonitrile reveals to be a good β-carbonyl radical acceptor in the cases of reactions with the cyclopropanone hemiacetal **1f** or 1-piperidinocyclopropanol (**1g**), and addition products were obtained in good yield (Entries 8 and 12). Acrylaldehyde, methyl acrylate, methyl vinyl ketone, and *N*,*N*-dimethylacrylamide could also be employed as a radical acceptor to give the corresponding adducts in moderate yield. However, in these cases, small amounts of by-products such as unidentified polymerized products or hydrogen-abstraction products of β-carbonyl radicals were obtained. In the cases of the reactions of the 1-alkylcyclopropanol **1b** with acrylaldehyde (Entry 4) and methyl vinyl ketone (Entry 6), the use of tributylhydridotin gave the polymer mixture and the 1 : 1 adducts **12d** and **12f** could not be obtained, but in these cases dibutyldihydridotin served as an efficient hydrogen donor to give the 1 : 1 addition products in moderate yield.

As exemplified above, the use of Mn(pic)$_3$ for the generation of β-carbonyl radicals enables their utilization as both nucleophilic and electrophilic radicals. These radicals add to both electron-rich and -deficient olefins by the selection of trapping method of intermediate addition radicals, and various kinds of synthetically useful 1,5- and 1,6-dicarbonyl compounds or their equivalents can be synthesized.

Experimental

General. All melting points are uncorrected. IR spectra were measured with a Horiba FT-300S spectrometer. ^{1}H NMR spectra were recorded at 500 MHz on a Bruker AM500 spectrometer with CHCl$_3$ (δ=7.24) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-D300 or a JEOL JMS-SX102A mass spectrometer operating at 70 eV. Preparative TLC was carried out on silica gel (Wakogel B-5F). DMF was dried over P$_2$O$_5$, distilled at reduced pressure, and dried over MS 4A. Mn(pic)$_3$ was prepared according to a literature.[18] Electron-rich olefins **2a**—**f** were prepared by the method of a literature.[19] α-Methoxystyrene (**2h**) was prepared according to a literature.[20] A ketene dithioacetal **2g** was prepared by the method of Kaya and Beller.[21] Electron-deficient olefins were purified by distillation. Bu$^n_3$SnH and

Table 3. The Reactions of Various Cyclopropanols with Various Electron-Deficient Olefins[a]

Entry	Cyclopropanol	Olefin	Amount of reagent/mole ratio[b]			Product (Yield/%[b])	
			Mn(pic)$_3$	Bu$^n{}_3$SnH	Olefin		
1	 **1a**		1.5	1.5	5.7	 **12a**	(47)[c]
2			1.5	1.5	10.2	 **12b**	(57)
3	 **1b**		1.4	1.4	10.3	 **12c**	(52)[c]
4			1.5	1.3[d]	13.0	 **12d**	(46)
5			1.4	2.1	10.0	 **12e**	(60)
6			1.5	0.8[d]	4.8	 **12f**	(43)
7			1.7	1.8	5.9	 **12g**	(27)
8	 **1f**		1.4	1.5	6.1	 **12h**	(72)
9			1.5	1.6	4.3	 **12i**	(47)
10			1.6	1.9	4.1	 **12j**	(44)
11			1.5	1.4	2.8	 **12k**	(51)
12	 **1g**		1.6	1.7	6.5	 **12l**	(75)
13			1.4	1.7	6.7	 **12m**	(48)
14			1.5	1.5	3.8	 **12n**	(49)
15			1.4	1.6	10.9	 **12o**	(52)

a) Reaction conditions: DMF, 0°C, 1—2 h. b) Based on **1**. c) 13% (Entry 1) and 34% (Entry 3) of **1** was recovered, respectively. In these cases, further addition of Mn(pic)$_3$ and Bu$^n{}_3$SnH to the reaction mixtures resulted in the increase of the product yield (62% for Entry 1 and 70% for Entry 3). d) Bu$^n{}_2$SnH$_2$ was used.

Ph_3SnH were commercially available and purified by distillation. $Bu^n{}_2SnH_2$ was prepared according to a literature.[22]

Cyclopropanols: Cyclopropanols **1a**—**e** were prepared by desilylation of the corresponding trimethylsiloxy derivatives by K_2CO_3 in methanol, and purified by preparative TLC (hexane/ethyl acetate). These trimethylsiloxy derivatives were prepared by the method of Ito et al.[6b] Cyclopropanols **1f**,[23] **1g**,[24] and **1i**[25] were prepared according to literatures. A cyclopropanol **1h** was prepared by the method of Cunico and Kuan.[26]

1-Phenylcyclopropanol (1a): Colorless oil; IR (CH_2Cl_2) 3579 and 1456 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=1.03$ (2H, dd, $J=7.4$ and 5.2 Hz), 1.25 (2H, dd, $J=7.4$ and 5.2 Hz), 2.44 (1H, br), 7.19—7.23 (1H, m), and 7.28—7.34 (4H, m). Found: *m/z* 134.0719. Calcd for $C_9H_{10}O$: M, 134.0732.

1-Phenethylcyclopropanol (1b): Colorless oil; IR (CH_2Cl_2) 3589 and 1454 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.45$ (2H, dd, $J=6.6$ and 5.3 Hz), 0.75 (2H, dd, $J=6.6$ and 5.3 Hz), 1.85—1.88 (1H+2H, br+m), 2.83—2.86 (2H, m), 7.16—7.21 (3H, m), and 7.26—7.29 (2H, m). Found: *m/z* 162.1046. Calcd for $C_{11}H_{14}O$: M, 162.1045.

***c*-2-Methyl-1-phenyl-*r*-1-cyclopropanol (1c):** Colorless oil; IR (CH_2Cl_2) 3575 and 1450 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.81$ (1H, qdd, $J=6.1$, 4.7, and 1.5 Hz), 1.19—1.29 (2H, m), 1.31 (3H, d, $J=6.1$ Hz), 2.23 (1H, br), 7.18—7.21 (1H, m), 7.25—7.27 (2H, m), and 7.30—7.33 (2H, m). Found: *m/z* 148.0902. Calcd for $C_{10}H_{12}O$: M, 148.0889.

Bicyclo[4.1.0]heptan-1-ol (1d): Colorless oil; IR (CH_2Cl_2) 3583, 1468, and 1450 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.30$ (1H, dd, $J=5.7$ and 5.5 Hz), 0.81 (1H, ddd, $J=10.6$, 5.5, and 1.4 Hz), 0.99—1.07 (1H, m), 1.10—1.15 (1H, m), 1.19—1.24 (2H, m), 1.31—1.37 (1H, m), 1.46—1.52 (1H, m), 1.83—1.89 (1H+1H, br+m), 1.95—2.01 (1H, m), and 2.11—2.16 (1H, m). Found: *m/z* 112.0886. Calcd for $C_7H_{12}O$: M, 112.0889.

***cis*-2-Benzylcyclopropanol (1e):** Colorless oil; IR (CH_2Cl_2) 3593 and 1452 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.38$ (1H, ddd, $J=6.3$, 6.2, and 3.1 Hz), 0.79 (1H, ddd, $J=9.3$, 6.3, and 6.2 Hz), 0.98—1.05 (1H, m), 1.68 (1H, br), 2.79 (1H, dd, $J=15.2$ and 7.3 Hz), 2.86 (1H, dd, $J=15.2$ and 7.3 Hz), 3.61 (1H, ddd, $J=6.4$, 6.3, and 3.1 Hz), 7.17—7.21 (1H, m), and 7.29—7.30 (4H, m). Found: *m/z* 148.0896. Calcd for $C_{10}H_{12}O$: M, 148.0889.

1-(Dimethylphenylsilyl)cyclopropanol (1h): Colorless oil; IR (CH_2Cl_2) 3585 and 1442 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.29$ (6H, s), 0.50 (2H, dd, $J=7.0$ and 5.1 Hz), 0.69 (2H, dd, $J=7.0$ and 5.1 Hz), 1.37 (1H, br), 7.35—7.40 (3H, m), and 7.59—7.61 (2H, m). Found: *m/z* 192.0949. Calcd for $C_{11}H_{16}OSi$: M, 192.0971.

General Procedure for the Reaction of Cyclopropanols and Electron-Rich Olefins. To $Mn(pic)_3$ (0.13—0.18 g, 0.30—0.44 mmol) was added a DMF (1.0 cm^3) solution of **1** (0.15 mmol) and **2** (0.20—0.56 mmol) with stirring at 0°C under an argon atmosphere. After being stirred for 0.5—5.5 h, phosphate buffer (pH 7) was added and the resulting mixture was filtered through Celite. Organic materials were extracted with ether, and the combined extracts were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane/ethyl acetate) to afford the desired product **7** or **8**.

1,5-Diphenyl-1,5-pentanedione (7a): Colorless crystals (from petroleum ether/ether); mp 65—66°C; IR (CH_2Cl_2) 1684 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=2.19$ (2H, quintet, $J=6.9$ Hz), 3.10 (4H, t, $J=6.9$ Hz), 7.42—7.45 (4H, m), 7.52—7.55 (2H, m), and 7.95—7.97 (4H, m). Found: C, 81.07; H, 6.43%. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39%. Found: *m/z* 252.1157. Calcd for $C_{17}H_{16}O_2$: M, 252.1151.

1-(2-Furyl)-5-phenyl-1,5-pentanedione (7b): Colorless crystals (from petroleum ether/ether); mp 55—57°C; IR (CH_2Cl_2) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=2.16$ (2H, quintet, $J=7.0$ Hz), 2.95 (2H, t, $J=7.0$ Hz), 3.08 (2H, t, $J=7.0$ Hz), 6.50 (1H, dd, $J=3.5$ and 1.8 Hz), 7.19 (1H, d, $J=3.5$ Hz), 7.42—7.45 (2H, m), 7.52—7.55 (2H, m), and 7.94—7.96 (2H, m). Found: C, 74.16; H, 5.86%. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82%. Found: *m/z* 242.0918. Calcd for $C_{15}H_{14}O_3$: M, 242.0943.

1-Phenyl-6-undecyne-1,5-dione (7c): Colorless oil; IR (CH_2Cl_2) 2212, 1684, and 1672 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.88$ (3H, t, $J=7.3$ Hz), 1.35—1.43 (2H, m), 1.49—1.55 (2H, m), 2.07 (2H, quintet, $J=7.1$ Hz), 2.32 (2H, t, $J=7.1$ Hz), 2.65 (2H, t, $J=7.1$ Hz), 3.00 (2H, t, $J=7.1$ Hz), 7.41—7.44 (1H, m), 7.51—7.54 (2H, m), and 7.92—7.94 (2H, m). Found: *m/z* 256.1476. Calcd for $C_{17}H_{20}O_2$: M, 256.1464.

1-Phenyl-1,5-hexanedione (7d): Colorless crystals (from petroleum ether/ether); mp 66—67°C; IR (CH_2Cl_2) 1714 and 1685 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=2.00$ (2H, quintet, $J=7.0$ Hz), 2.13 (3H, s), 2.55 (2H, t, $J=7.0$ Hz), 3.00 (2H, t, $J=7.0$ Hz), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.93—7.95 (2H, m). Found: C, 75.56; H, 7.34%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. Found: *m/z* 190.0981. Calcd for $C_{12}H_{14}O_2$: M, 190.0994.

2-Methyl-1,5-diphenyl-1,5-pentanedione (7e): Colorless oil; IR(CH_2Cl_2) 1684 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=1.24$ (3H, d, $J=7.0$ Hz), 1.88—1.95 (1H, m), 2.23—2.30 (1H, m), 2.89 (1H, ddd, $J=17.1$, 8.1, and 6.4 Hz), 3.08 (1H, ddd, $J=17.1$, 8.1, and 6.4 Hz), 3.64 (1H, sextet, $J=7.0$ Hz), 7.40—7.46 (4H, m), 7.51—7.55 (2H, m), 7.90—7.92 (2H, m), and 7.97—7.98 (2H, m). Found: *m/z* 266.1302. Calcd for $C_{18}H_{18}O_2$: M, 266.1307.

***S*-Phenyl 5-Oxo-5-phenylpentanethioate (7f):** Colorless crystals (from petroleum ether/ether); mp 68—69°C; IR (CH_2Cl_2) 1701 and 1685 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=2.14$ (2H, quintet, $J=7.1$ Hz), 2.79 (2H, t, $J=7.1$ Hz), 3.07 (2H, t, $J=7.1$ Hz), 7.39 (5H, s), 7.43—7.46 (2H, m), 7.53—7.56 (1H, m), and 7.93—7.95 (2H, m). Found: C, 71.98; H, 5.74; S, 11.31%. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67; S, 11.28%.

5,5-Bis(ethylthio)-1-phenyl-4-penten-1-one (7g): Colorless oil; IR (CH_2Cl_2) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=1.19$ (6H, t, $J=7.3$ Hz), 2.68 (2H, q, $J=7.3$ Hz), 2.74+2.77 (2H+2H, q+q, $J=7.3$ and 7.3 Hz), 3.04 (2H, t, $J=7.3$ Hz), 6.17 (1H, t, $J=7.3$ Hz), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.93—7.95 (2H, m). Found: C, 64.17; H, 7.10; S, 22.98%. Calcd for $C_{15}H_{20}OS_2$: C, 64.24; H, 7.19; S, 22.87%. Found: *m/z* 280.0959. Calcd for $C_{15}H_{20}OS_2$: M, 280.0957.

1,7-Diphenyl-1,5-heptanedione (8a): Colorless crystals (from petroleum ether/ether); mp 52—53°C; IR (CH_2Cl_2) 1712 and 1685 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=1.99$ (2H, quintet, $J=7.0$ Hz), 2.50 (2H, t, $J=7.0$ Hz), 2.72 (2H, t, $J=7.6$ Hz), 2.89 (2H, t, $J=7.6$ Hz), 2.95 (2H, t, $J=7.0$ Hz), 7.14—7.16 (3H, m), 7.23—7.26 (2H, m), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.92—7.93 (2H, m). Found: C, 81.69; H, 7.26%. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%. Found: *m/z* 280.1443. Calcd for $C_{19}H_{20}O_2$: M, 280.1464.

***S*-Phenyl 5-Oxo-7-phenylheptanethioate (8b):** Colorless crystals (from petroleum ether/ether); mp 67—68°C; IR (CH_2Cl_2) 1716 and 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.95 (2H, quintet, J=7.1 Hz), 2.47 (2H, t, J=7.1 Hz), 2.65 (2H, t, J=7.1 Hz), 2.71 (2H, t, J=7.6 Hz), 2.88 (2H, t, J=7.6 Hz), 7.15—7.19 (3H, m), 7.24—7.28 (2H, m), and 7.39 (5H, s). Found: C, 72.93; H, 6.28; S, 10.61%. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; S, 10.26%.

3-Methyl-1,5-diphenyl-1,5-pentanedione (8c): Colorless oil; IR (CH_2Cl_2) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.07 (3H, d, J=6.3 Hz), 2.80—2.88 (3H, m), 3.16 (2H, dd, J=14.0 and 5.1 Hz), 7.43—7.46 (4H, m), 7.52—7.56 (2H, m), and 7.97—8.00 (4H, m). Found: m/z 266.1282. Calcd for $C_{18}H_{18}O_2$: M, 266.1307.

***S*-Phenyl 3-Methyl-5-oxo-5-phenylpentanethioate (8d):** Colorless oil; IR (CH_2Cl_2) 1701 and 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, d, J=6.6 Hz), 2.64—2.70 (1H, m, J=12.4 and 5.7 Hz), 2.73—2.81 (2H, m), 2.86 (1H, dd, J=16.5 and 7.3 Hz), 3.14 (1H, dd, J=16.5 and 5.7 Hz), 7.39 (5H, s), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.93—7.95 (2H, m). Found: C, 72.67; H, 6.20; S, 10.59%. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08; S, 10.75%.

3-(Benzoylmethyl)cycloheptanone (8e): Colorless crystals (from petroleum ether/ether); mp 53—54°C; IR (CH_2Cl_2) 1697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32—1.39 (1H, m), 1.48—1.63 (2H, m), 1.84—1.91 (3H, m), 2.42—2.60 (5H, m), 2.93 (2H, d, J=6.6 Hz), 7.42—7.46 (2H, m), 7.53—7.56 (1H, m), and 7.90—7.93 (2H, m). Found: C, 78.34; H, 7.99%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%. Found: m/z 230.1319. Calcd for $C_{15}H_{18}O_2$: M, 230.1307.

2-(2-Benzoylethyl)cyclohexanone (8f): Colorless oil; IR (CH_2Cl_2) 1705 and 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.40—1.49 (1H, m), 1.64—1.72 (3H, m), 1.83—1.89 (1H, m), 2.01—2.16 (3H, m), 2.25—2.32 (1H, m), 2.36—2.45 (2H, m), 2.95 (1H, ddd, J=16.9, 8.4, and 6.3 Hz), 3.11 (1H, ddd, J=16.9, 8.4, and 6.3 Hz), 7.42—7.45 (2H, m), 7.51—7.54 (1H, m), and 7.95—7.97 (2H, m). Found: m/z 230.1309. Calcd for $C_{15}H_{18}O_2$: M, 230.1307.

***S*-Phenyl 2-(3-Oxocycloheptyl)ethanethioate (8g):** Colorless oil; IR (CH_2Cl_2) 1703 and 1697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.32—1.40 (1H, m), 1.42—1.51 (1H, m), 1.53—1.62 (1H, m), 1.84—1.94 (3H, m), 2.32—2.39 (1H, m), 2.42—2.50 (3H, m), 2.55 (1H, ddd, J=14.5, 2.9, and 1.5 Hz), 2.62 (2H, d, J=6.9 Hz), and 7.39 (5H, s). Found: C, 68.37; H, 6.89; S, 12.46%. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92; S, 12.22%. Found: m/z 262.1039. Calcd for $C_{15}H_{18}O_2S$: M, 262.1028.

***S*-Phenyl 3-(2-Oxocyclohexyl)propanethioate (8h):** Colorless oil; IR (CH_2Cl_2) 1707 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.33—1.41 (1H, m), 1.57—1.75 (3H, m), 1.80—1.88 (1H, m), 2.02—2.13 (3H, m), 2.25—2.32 (1H, m), 2.36—2.42 (2H, m), 2.66—2.79 (2H, m), and 7.38 (5H, s). Found: m/z 153.0918. Calcd for $C_9H_{13}O_2$: M−SPh, 153.0916.

5-Oxo-3-benzyl-5-phenylpentanal (8i): Colorless oil; IR (CH_2Cl_2) 1722 and 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.52 (2H, dd, J=6.0 and 1.7 Hz), 2.69 (1H, dd, J=13.5 and 6.9 Hz), 2.75 (1H, dd, J=13.5 and 6.9 Hz), 2.91—3.05 (3H, m), 7.17—7.22 (3H, m), 7.26—7.29 (2H, m), 7.41—7.44 (2H, m), 7.52—7.55 (1H, m), 7.86—7.87 (2H, m), and 9.70 (1H, t, J=1.7 Hz). Found: m/z 266.1328. Calcd for $C_{18}H_{18}O_2$: M, 266.1307.

***S*-Phenyl 3-Benzyl-5-oxopentanethioate (8j):** Colorless oil; IR (CH_2Cl_2) 1722 and 1701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.47 (1H, ddd, J=17.5, 6.4, and 1.5 Hz), 2.55 (1H, ddd, J=17.5, 6.4, and 1.5 Hz), 2.64—2.77 (4H, m), 2.83 (1H, septet, J=6.7 Hz), 7.16—7.18 (2H, m), 7.20—7.23 (1H, m), 7.28—7.31 (2H, m), 7.36—7.41 (5H, m), and 9.67 (1H, t, J=1.5 Hz). Found: m/z 189.0927. Calcd for $C_{12}H_{13}O_2$: M−SPh, 189.0916.

Ethyl 5-Oxo-5-phenylvalerate (8k): Colorless oil; IR (CH_2Cl_2) 1730 and 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, t, J=7.1 Hz), 2.05 (2H, quintet, J=7.2 Hz), 2.41 (2H, t, J=7.2 Hz), 3.03 (2H, t, J=7.2 Hz), 4.11 (2H, q, J=7.1 Hz), 7.42—7.45 (2H, m), 7.52—7.55 (1H, m), and 7.93—7.95 (2H, m). Found: m/z 220.1072. Calcd for $C_{13}H_{16}O_3$: M, 220.1100.

Ethyl 4-[(Phenylthio)carbonyl]butyrate (8l): Colorless oil; IR (CH_2Cl_2) 1730 and 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, t, J=7.1 Hz), 2.01 (2H, quintet, J=7.3 Hz), 2.38 (2H, t, J=7.3 Hz), 2.72 (2H, t, J=7.3 Hz), 4.12 (2H, q, J=7.1 Hz), and 7.39 (5H, s). Found: C, 61.73; H, 6.39; S, 12.66%. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39; S, 12.71%.

1-(5-Oxo-5-phenylvaleryl)piperidine (8m): Colorless oil; IR (CH_2Cl_2) 1685 and 1631 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.45—1.52 (4H, m), 1.56—1.60 (2H, m), 2.03 (2H, quintet, J=7.0 Hz), 2.39 (2H, t, J=7.0 Hz), 3.05 (2H, t, J=7.0 Hz), 3.36 (2H, t, J=5.6 Hz), 3.50 (2H, t, J=5.6 Hz), 7.39—7.42 (2H, m), 7.48—7.52 (1H, m), and 7.92—7.94 (2H, m). Found: m/z 259.1583. Calcd for $C_{16}H_{21}NO_2$: M, 259.1573.

***S*-Phenyl 5-Oxo-5-piperidinopentanethioate (8n):** Colorless crystals (from petroleum ether/ether); mp 74—75°C; IR (CH_2Cl_2) 1703 and 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.48—1.54 (4H, m), 1.58—1.63 (2H, m), 2.01 (2H, quintet, J=7.2 Hz), 2.38 (2H, t, J=7.2 Hz), 2.75 (2H, t, J=7.2 Hz), 3.35 (2H, t, J=5.5 Hz), 3.52 (2H, t, J=5.5 Hz), and 7.38 (5H, s). Found: C, 66.05; H, 7.24; N, 5.09; S, 11.07%. Calcd for $C_{16}H_{21}NO_2S$: C, 65.81; H, 7.26; N, 4.80; S, 10.98%.

1-(Dimethylphenylsilyl)-5-phenyl-1,5-pentanedione (8o): Colorless oil; IR (CH_2Cl_2) 1685 and 1641 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.48 (6H, s), 1.89 (2H, quintet, J=7.0 Hz), 2.69 (2H, t, J=7.0 Hz), 2.85 (2H, t, J=7.0 Hz), 7.33—7.37 (3H, m), 7.40—7.43 (2H, m), 7.50—7.54 (3H, m), and 7.87—7.89 (2H, m). Found: m/z 310.1364. Calcd for $C_{19}H_{22}O_2Si$: M, 310.1390.

***S*-Phenyl 5-(Dimethylphenylsilyl)-5-oxopentanethioate (8p):** Colorless oil; IR (CH_2Cl_2) 1703 and 1643 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.47 (6H, s), 1.85 (2H, quintet, J=7.1 Hz), 2.56 (2H, t, J=7.1 Hz), 2.65 (2H, t, J=7.1 Hz), 7.33—7.40 (8H, m), and 7.51—7.53 (2H, m). Found: C, 66.74; H, 6.55; S, 9.69%. Calcd for $C_{19}H_{22}O_2SSi$: C, 66.62; H, 6.47; S, 9.36%.

Methyl 2,6-Dioxo-6-phenylhexanoate (8q): Colorless oil; IR (CH_2Cl_2) 1732 and 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.08 (2H, quintet, J=7.0 Hz), 2.98 (2H, t, J=7.0 Hz), 3.04 (2H, t, J=7.0 Hz), 3.85 (3H, s), 7.43—7.46 (2H, m), 7.53—7.56 (1H, m), and 7.92—7.94 (2H, m). Found: m/z 234.0887. Calcd for $C_{13}H_{14}O_4$: M, 234.0892.

General Procedure for the Reaction of Cyclopropanols and Electron-Deficient Olefins. To Mn(pic)$_3$ (89—185 mg, 0.21—0.44 mmol) was added a DMF (0.25 cm^3) mixture of tin hydride (0.12—0.51 mmol), followed by a DMF (0.75 cm^3) solution of **1** (0.15 mmol) and olefins (0.42—1.95 mmol) with stirring at 0°C under an argon atmosphere. After being stirred for 1—2 h, phosphate buffer (pH 7) was added and the resulting mixture was filtered through Celite. Organic materials were extracted with ether, and the combined extracts were washed with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane/ethyl acetate) to afford the desired product **12**.

6-Oxo-6-phenylhexanenitrile (12a): Colorless crystals (from petroleum ether/ether); mp 69—70°C; IR (CH_2Cl_2) 2249 and 1685 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=$ 1.72—1.78 (2H, m), 1.87—1.93 (2H, m), 2.39 (2H, t, J=7.1 Hz), 3.03 (2H, t, J=6.9 Hz), 7.44—7.47 (2H, m), 7.54—7.57 (1H, m), and 7.92—7.94 (2H, m). Found: C, 77.16; H, 6.94; N, 7.48%. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%. Found: m/z 187.1004. Calcd for $C_{12}H_{13}NO$: M, 187.0998.

Methyl 6-Oxo-6-phenylhexanoate (12b): Colorless oil; IR (CH_2Cl_2) 1734 and 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.68—1.80 (4H, m), 2.36 (2H, t, J=7.2 Hz), 2.98 (2H, t, J=7.1 Hz), 3.65 (3H, s), 7.42—7.46 (2H, m), 7.52—7.55 (1H, m), and 7.92—7.94 (2H, m). Found: m/z 220.1099. Calcd for $C_{13}H_{16}O_3$: M, 220.1100.

6-Oxo-8-phenyloctanenitrile (12c): Colorless oil; IR (CH_2Cl_2) 2249 and 1714 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=$ 1.56—1.62 (2H, m), 1.66—1.71 (2H, m), 2.29 (2H, t, $J=$ 7.0 Hz), 2.41 (2H, t, J=6.9 Hz), 2.72 (2H, t, J=7.5 Hz), 2.88 (2H, t, J=7.5 Hz), 7.15—7.19 (3H, m), and 7.25—7.28 (2H, m). Found: m/z 215.1307. Calcd for $C_{14}H_{17}NO$: M, 215.1311.

6-Oxo-8-phenyloctanal (12d): Colorless oil; IR (CH_2Cl_2) 1718 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.56—1.59 (4H, m), 2.37—2.43 (4H, m), 2.71 (2H, t, J=7.6 Hz), 2.88 (2H, t, J=7.6 Hz), 7.15—7.19 (3H, m), 7.24—7.27 (2H, m), and 9.73 (1H, t, J=1.6 Hz). Found: m/z 234.1275. Calcd for $C_{14}H_{18}O_3$: M, 234.1256.

Methyl 6-Oxo-8-phenyloctanoate (12e): Colorless oil; IR (CH_2Cl_2) 1734 and 1714 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.56—1.59 (4H, m), 2.27—2.29 (2H, m), 2.37—2.39 (2H, m), 2.70 (2H, t, J=7.6 Hz), 2.87 (2H, t, J=7.6 Hz), 3.64 (3H, s), 7.15—7.21 (3H, m), and 7.25—7.28 (2H, m). Found: m/z 248.1438. Calcd for $C_{15}H_{20}O_3$: M, 248.1413.

9-Phenyl-2,7-nonanedione (12f): Colorless oil; IR (CH_2Cl_2) 1712 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.49—1.54 (4H, m), 2.10 (3H, s), 2.37+2.39 (2H+2H, t+t, J=6.9 and 6.8 Hz), 2.70 (2H, t, J=7.6 Hz), 2.87 (2H, t, J=7.6 Hz), 7.14—7.18 (3H, m), and 7.24—7.27 (2H, m). Found: m/z 232.1457. Calcd for $C_{15}H_{20}O_2$: M, 232.1464.

***N*,*N*-Dimethyl-6-oxo-8-phenyloctanamide (12g):** Colorless oil; IR (CH_2Cl_2) 1712 and 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.57—1.60 (4H, m), 2.25—2.29 (2H, m), 2.38—2.42 (2H, m), 2.70 (2H, t, J=7.6 Hz), 2.86 (2H, t, J=7.6 Hz), 2.91 (3H, s), 2.96 (3H, s), 7.14—7.17 (3H, m), and 7.23—7.26 (2H, m). Found: m/z 261.1703. Calcd for $C_{16}H_{23}NO_2$: M, 261.1730.

Ethyl 5-Cyanovalerate (12h): Colorless oil; IR (CH_2Cl_2) 2249 and 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.24 (3H, t, J=7.2 Hz), 1.66—1.72 (2H, m), 1.74—1.79 (2H, m), 2.33+2.35 (2H+2H, t+t, J=7.1 and 7.0 Hz), and 4.11 (2H, q, J=7.2 Hz). Found: m/z 155.0964. Calcd for $C_8H_{13}NO_2$: M, 155.0947.

Ethyl 6-Oxohexanoate (12i): Colorless oil; IR (CH_2Cl_2) 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.23 (3H, t, J=7.1 Hz), 1.63—1.66 (4H, m), 2.29—2.32 (2H, m), 2.43—2.46 (2H, m), 4.11 (2H, q, J=7.1 Hz), and 9.75 (1H, t, J=1.7 Hz). Found: m/z 158.0958. Calcd for $C_8H_{14}O_3$: M, 158.0943.

Ethyl Methyl Adipate (12j): Colorless oil; IR (CH_2Cl_2) 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (3H, t, J=7.2 Hz), 1.62—1.65 (4H, m), 2.27—2.32 (4H, m), 3.64 (3H, s), and 4.10 (2H, q, J=7.2 Hz). Found: m/z 188.1066. Calcd for $C_9H_{16}O_4$: M, 188.1049.

Ethyl 6-Oxoheptanoate (12k): Colorless oil; IR (CH_2Cl_2) 1726 and 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (3H, t, J=7.2 Hz), 1.55—1.59 (4H, m), 2.09 (3H, s), 2.26 (2H, t, J=7.0 Hz), 2.41 (2H, t, J=6.8 Hz), and 4.08 (2H, q, J=7.2 Hz). Found: m/z 172.1098. Calcd for $C_9H_{16}O_3$: M, 172.1100.

1-(5-Cyanovaleryl)piperidine (12l): Colorless oil; IR (CH_2Cl_2) 2248 and 1626 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=$ 1.49—1.56 (4H, m), 1.60—1.64 (2H, m), 1.68—1.80 (4H, m), 2.33+2.35 (2H+2H, t+t, J=7.1 and 7.1 Hz), 3.36 (2H, dd, J=5.6 and 5.6 Hz), and 3.52 (2H, dd, J=5.6 and 5.6 Hz). Found: m/z 194.1415. Calcd for $C_{11}H_{18}N_2O$: M, 194.1420.

1-(6-Oxohexanoyl)piperidine (12m): Colorless oil; IR (CH_2Cl_2) 1718 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50—1.67 (10H, m), 2.31—2.34 (2H, m), 2.47—2.50 (2H, m), 3.37 (2H, dd, J=5.6 and 5.6 Hz), 3.53 (2H, dd, J=5.6 and 5.6 Hz), and 9.76 (1H, t, J=1.5 Hz). Found: m/z 197.1412. Calcd for $C_{11}H_{19}NO_2$: M, 197.1417.

Methyl 6-Oxo-6-piperidinohexanoate (12n): Colorless oil; IR (CH_2Cl_2) 1734 and 1633 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.48—1.56 (4H, m), 1.59—1.66 (6H, m), 2.29—2.34 (4H, m), 3.36 (2H, dd, J=5.5 and 5.5 Hz), 3.51 (2H, dd, J=5.5 and 5.5 Hz), and 3.64 (3H, s). Found: m/z 227.1512. Calcd for $C_{12}H_{21}NO_3$: M, 227.1522.

1-(6-Oxoheptanoyl)piperidine (12o): Colorless oil; IR (CH_2Cl_2) 1712 and 1633 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=$ 1.48—1.55 (4H, m), 1.58—1.64 (6H, m), 2.11 (3H, s), 2.28—2.31 (2H, m), 2.43—2.46 (2H, m), 3.36 (2H, dd, J=5.6 and 5.6 Hz), and 3.51 (2H, dd, J=5.6 and 5.6 Hz). Found: m/z 211.1588. Calcd for $C_{12}H_{21}NO_2$: M, 211.1573.

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