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$Ru_3(CO)_{12}$-Catalyzed Cyclocarbonylation of 1,6-Enynes to Bicyclo[3.3.0]octenones

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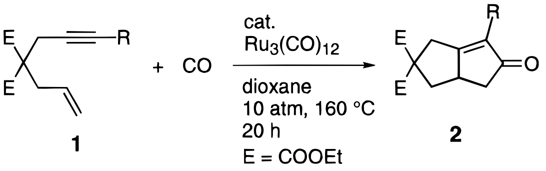
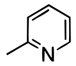
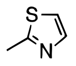
The intramolecular Pauson−Khand reaction[1] is presently regarded as one of the most potent methods for the construction of bicyclo[3.3.0]octenones. While stoichiometric amounts of $Co_2(CO)_8$ were originally and generally used as the CO source,[1] several other metal carbonyl complexes such as $Fe(CO)_4$(acetone),[2] $W(CO)_5$(THF),[3] $W(CO)_5F^-$,[4] $Cr(CO)_5F^-$,[4] $Cp_2Mo_2(CO)_4$,[5] and $Mo(CO)_6$[6] have also been found to serve as a CO source in place of $Co_2(CO)_8$ for this reaction. In addition, a number of other different systems, such as Cp_2TiCl_2/CO,[7] Cp_2ZrCl_2/CO,[8] Cp_2TiCl_2/RNC,[7] $Ni(COD)_2$/PhNC,[9] $Cp_2Ti(PMe_3)_2/R_3SiCN$,[10] and $Ni(COD)_2/{}^iPr_3SiCN$[11] have been shown to be effective for the conversion of 1,6-enynes to bicyclo[3.3.0]octenone derivatives. In contrast to extensive studies of stoichiometric systems, only a few examples dealing with catalytic version of the intramolecular Pauson−Khand reaction have appeared.[12−15] Jeong and co-workers reported that a catalytic reaction was attained in the case of $Co_2(CO)_8/P(OPh)_3$ (3−5 mol %/10−20 mol %) at 120 °C in an atmosphere of CO (4−5 atm).[12] Other cobalt-catalyzed systems, such as (indenyl)Co(COD) and $Co(acac)_2/NaBH_4$,[13] have also been reported, and Livinghouse reported a photochemical promotion using 10 mol % of $Co_2(CO)_8$ at 50−55 °C and 1 atm of CO pressure.[14] Quite recently, Buchwald reported that the treatment of enynes with a catalytic amount of $Cp_2Ti(CO)_2$ (5−20 mol %) in an atomosphere of CO (18 psig) gives rise to cyclopentenones.[15] On the other hand, it has been known for many years that a variety of metal carbonyl complexes catalyze a variety of carbonylation reactions.[16] It is, therefore, surprising that reports of the Pauson−Khand type reaction with CO in the presence of late transition metal complexes as the catalyst, other than cobalt, has not yet appeared. In this paper, we wish to report the first use of a ruthenium complex for a Pauson−Khand type reaction of enynes.[17] The new reaction appears to be catalytic in nature.

Scheme 1



1a:	R = $SiMe_3$	**2a:**	90%
1b:	R = Ph	**2b:**	66%
1c:	R = 	**2c:**	80%
1d:	R = 	**2d:**	62%
1e:	R = Me	**2e:**	86%
1f:	R = COOEt	**2f:**	0%
1g:	R = H	**2g:**	47%

We initially examined the reaction of a trimethylsilyl-substituted enyne **1a**, because the silyl group can be converted into other functional groups in a variety of ways.[18] The reaction of **1a** (1 mmol) under 20 atm of CO at 160 °C in toluene in the presence of $Ru_3(CO)_{12}$ (0.02 mmol) for 20 h results in complete consumption of **1a** to give the 2-(trimethylsilyl)bicyclo[3.3.0]octenone derivative **2a**[19] in 72% isolated yield, based on **1a**. When the reaction was run at 140 °C, the yield decreased to a 61% yield and 31% of **1a** was recovered. At 100 °C, no reaction observable occurred. The reaction is not as sensitive to CO pressure (20 atm 72% yield, 10 atm 70%, 5 atm 63%). Among the solvents examined (toluene 72%, cyclohexane 72%, $ClCH_2CH_2Cl$ 54%, CH_3OH 22%), dioxane (90% yield) or CH_3CN (86%) were the solvents of choice, when the reaction was run at 160 °C under 10 atm of CO for 20 h. This reaction represents the first use of $Ru_3(CO)_{12}$ as a catalyst for the cyclocarbonylation of enynes to cyclopentenones.

The reaction of phenyl-substituted enyne **1b** gave **2b** in 66% yield. Replacement of the phenyl group with a

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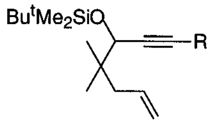
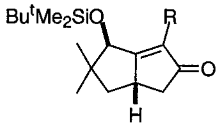
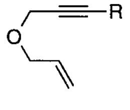
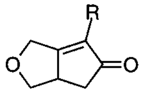
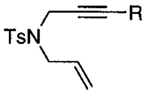
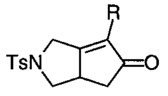
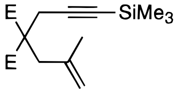
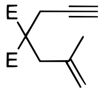
Table 1. Catalytic Cyclocarbonylation of 1,6-Enynes[a]

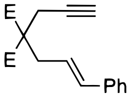
run	enyne	product [b]
		
1	**3a:** R = SiMe$_3$	**4a** 65% (10:0)
2	**3b:** R = Ph	**4b** 44% (26:1)
3	**3c:** R = Me	**4c** 69% (2.4:1)
4	**3c**	**4c** 81% (1.5:1) [c]
		
5	**5a:** R = SiMe$_3$	**6a** 92%
6	**5b:** R = Ph	**6b** 57%
		
7	**7a:** R = SiMe$_3$	**8a** 95%
8	**7b:** R = SiMe$_2$(CH=CH$_2$)	**8b** 89%

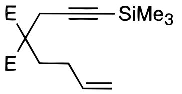
[a] Reaction conditions: enyne (1 mmol), Ru$_3$(CO)$_{12}$ (0.02 mmol), dioxane (5 mL), CO (10 atm), 160 °C for 20 h. [b] Yields refer to chromatographically purified samples. Values in parentheses are the ratio of cis:trans isomers and were determined by GC analysis. [c] For a reaction at 140 °C.

2-pyridyl group, as in **1c**, led to higher yields. Although the Co$_2$(CO)$_8$-promoted Pauson–Khand reaction is known to tolerate a wide range of functionalities, no studies of reactions of enynes bearing a pyridyl group have appeared, to our knowledge. The methyl-substituted enyne **1e** is also a reactive substrate and gave **2e** in 86% yield. The electron-deficient alkyne **1f** was, as anticipated, a poor substrate.[20] However, successful carbonylation of **1d** provides an alternative method for the preparation of bicyclo[3.3.0]octenone having a formyl or ester group at the 2-position.[21] The reaction of terminal alkyne **1g** gave **2g** in 47% yield, although **1g** was completely consumed. A decrease in reaction temperatures, shorter reaction times, and changing solvents failed to improve the yield of **2g**. The scope of the reaction with respect to the alkene is limited. This catalytic system lacks the ability to cyclocarbonylate 1,6-enynes containing substituted olefins and an 1,7-enyne, such as those shown below.









Some results for 1,6-enynes are shown in Table 1. The reaction of silyl-substituted enyne **3a** gave exclusively *cis*-**4a**, with no detectable *trans* isomer (run 1). Magnus[22] observed a diastereomeric ratio of 26:1 of *cis*-**4a**:*trans*-**4a** for the Co$_2$(CO)$_8$-promoted cyclization of **3a** and Pearson[2b] observed a 13:1 ratio for a Fe(CO)$_5$-promoted reaction. The reaction of phenyl-substituted enyne **3b** gave **4b** in moderate yield with a high diastereosiomeric ratio (run 2). When the reaction of **3c** was run at 140 °C, an improved yield was obtained (run 4).[23] The reaction of an enyne having an oxygen atom in the tether **5a** afforded 2-(trimethylsilyl)-7-oxabicylo[3.3.0]oct-1-en-3-one (**6a**) with significant efficiency (run 5). The reaction of *N*-ally-*N*-propargyl amides **7a** and **7b** gave the corresponding 7-azabicyclo[3.3.0]octenones **8a** and **8b** in nearly quantitative yield (runs 7 and 8). Introduction of a vinyl group into the silyl group had no effect on the yield (run 8).

While the exact course of this transformation is unclear, we propose that the reaction proceeds via a mechanism similar to the iron carbonyl promoted reaction.[2b] Thus, the reductive cyclization of an enyne yields a metallacycle. The subsequent insertion of CO and reductive elimination produce the cyclopentenone.

In summary, we report the development of a Ru$_3$(CO)$_{12}$-catalyzed process for the transformation of 1,6-enynes to bicyclic cyclopentenones. The present reaction represents the first catalytic Pauson–Khand type reaction using a ruthenium complex as a catalyst. This transformation shows a high level of functional group compatibility, and the catalyst is commercially available and easily handled.

Experimental Section

Typical Procedure. A 50-mL stainless autoclave was charged with diethyl 1-(trimethylsilyl)-6-hepten-1-yne-5,5-dicarboxylate (**1a**) (1 mmol, 310 mg), dioxane (5 mL), and Ru$_3$(CO)$_{12}$ (0.02 mmol, 13 mg). The system was flushed with 10 atm of CO three times. Finally it was pressurized to 10 atm and immersed in an oil bath at 160 °C. After 20 h had elapsed, the autoclave was removed from the oil bath and allowed to cool for 1 h. The CO was then released. The contents were transferred to a round-bottomed flask with CH$_2$Cl$_2$ and the volatiles removed in vacuo. The residue was subjected to column chromatography on silica gel (eluent; hexane/Et$_2$O = 2/1) to give 3,3a,4,5-tetrahydro-5-oxo-6-(trimethylsilyl)-2,2(1*H*)-pentalenedicarboxylic acid diethyl ester (**2a**) (334 mg, 90% yield) as a white solid.

3,3a,4,5-Tetrahydro-5-oxo-6-(trimethylsilyl)-2,2(1*H*)-pentalenedicarboxylic Acid Diethyl Ester (2a). White solid; mp 66–68 °C; R_f 0.22 (hexane/ether = 2/1); ^{1}H NMR (CDCl$_3$) δ 0.19 (s, 9H), 1.25 (t, J = 7.3 Hz, 3H), 1.28 (t, J = 7.3 Hz, 3H), 1.66 (t, J = 12 Hz, 1H), 2.06 (dd, J = 4.1 Hz, J = 18 Hz, 1H), 2.57 (dd, J = 6.5 Hz, J = 18 Hz, 1H), 2.78 (dd, J = 7.6 Hz, J = 12 Hz, 1H), 2.95–3.09 (m, 1H), 3.22 (d, J = 19 Hz, 1H), 3.32 (d, J = 19 Hz, 1H), 4.20 (q, J = 7.3 Hz, 2H), 4.24 (q, J = 7.3 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ −1.3, 14.0, 36.2, 38.5, 42.9, 46.5, 60.8, 61.9, 62.0, 136.6, 171.0, 171.6, 192.4, 213.2; IR (KBr) 1728, 1695, 1615 cm^{-1}; MS, *m/z* (relative intensity, %) 338 (M$^+$, 23), 323 (18), 75 (100). Anal. Calcd for C$_{17}$H$_{26}$O$_5$Si: C, 60.33; H, 7.74. Found: C, 60.24; H, 7.63.

3,3a,4,5-Tetrahydro-5-oxo-6-phenyl-2,2(1*H*)-pentalenedicarboxylic Acid Diethyl Ester (2b). Colorless oil; R_f 0.17 (hexane/ether = 2/1); ^{1}H NMR (CDCl$_3$) δ 1.23 (t, J = 6.8 Hz, 3H), 1.31 (t, J = 6.8 Hz, 3H), 1.77 (t, J = 12 Hz, 1H), 2.31 (dd, J = 3.2 Hz, J = 18 Hz, 1H), 2.82 (dd, J = 6.5 Hz, J = 18 Hz, 1H), 2.83 (dd, J = 7.6 Hz, J = 12 Hz, 1H), 3.07-3.23 (m, 1H), 3.29 (d, J = 19 Hz, 1H), 3.65 (d, J = 19 Hz, 1H), 4.17 (dq, J = 1.9 Hz, J = 6.8 Hz, 2H), 4.28 (q, J = 6.8 Hz, 2H), 7.27-7.58 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 13.9, 14.0, 35.9, 38.7, 42.6, 42.8, 61.3, 61.9, 62.2, 128.2, 128.4, 130.9, 135.5, 170.7, 171.6, 178.9, 207.1; IR (neat) 1726, 1651 cm^{-1}; MS, *m/z* (relative intensity, %) 342

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(20) One of limitations of Pauson–Khand reaction had been that electron-deficient alkynes are poor substrates. However, some successes in this area have recently appeared. Krafft, M. E.; Romero, R. H.; Scott, I. L. *J. Org. Chem.* **1992**, *57*, 5277. Hoye, T. R.; Suriano, J. A. *J. Org. Chem.* **1993**, *58*, 1659.

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(23) For Co$_2$(CO)$_8$-mediated reaction, the ratio was 3:1.[22]

(M^+, 24), 268 (81), 195 (100). Anal. Calcd for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.03; H, 6.48.

3,3a,4,5-Tetrahydro-5-oxo-6-(2-pyridyl)-2,2(1*H*)-pentalenedicarboxylic Acid Diethyl Ester (2c). White solid; mp 76−78 °C (hexane/ether); R_f 0.19 (hexane/ether = 1/1); ^{1}H NMR (CDCl$_3$) δ 1.24 (t, J = 7.0 Hz, 3H, CH$_3$), 1.30 (t, J = 7.0 Hz, 3H), 1.74 (t, J = 13 Hz, 1H), 2.32 (dd, J = 3.5 Hz, J = 18 Hz, 1H), 2.85 (dd, J = 6.8 Hz, J = 18 Hz, 1H), 2.88 (dd, J = 7.0 Hz, J = 13 Hz, 1H), 3.13-3.28 (m, 1H), 3.78 (s, 2H), 4.19 (q, J = 7.0 Hz, 2H), 4.26 (dq, J = 1.9 Hz, J = 7.0 Hz, 2H), 7.19 (dd, J = 1.9 Hz, J = 4.9 Hz, 1H), 7.70 (dt, J = 1.9 Hz, J = 7.8 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 8.64 (d, J = 4.9 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 14.0, 14.1, 37.5, 38.7, 42.9, 43.4, 61.3, 61.9, 62.0, 122.5, 122.9, 133.6, 136.2, 149.5, 150.9, 171.0, 171.6, 185.7, 206.7; IR (KBr) 1730, 1699, 1649 cm^{-1}; MS, *m/z* (relative intensity, %) 343 (M^+, 30), 270 (100). Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.17; H, 6.16; N, 4.07.

3,3a,4,5-Tetrahydro-5-oxo-6-(2-thiazolyl)-2,2(1*H*)-pentalenedicarboxylic Acid Diethyl Ester (2d). White solid; mp 79−81 °C (hexane/ether); R_f 0.10 (hexane/ether = 2/1); ^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 7.0 Hz, 3H), 1.30 (t, J = 7.3 Hz, 3H), 1.82 (t, J = 12 Hz, 1H), 2.33 (dd, J = 3.5 Hz, J = 18 Hz, 1H), 2.87 (dd, J = 6.2 Hz, J = 18 Hz, 1H), 2.90 (dd, J = 7.3 Hz, J = 12 Hz, 1H), 3.19-3.36 (m, 1H), 3.80 (t, J = 22 Hz, 2H), 4.21 (dq, J = 0.81 Hz, J = 7.0 Hz, 2H), 4.27 (q, J = 7.3 Hz, 2H), 7.41 (d, J = 3.2 Hz, 1H), 7.95 (d, J = 3.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.9, 14.0, 37.1, 38.7, 41.7, 43.9, 61.4, 62.0, 62.1, 119.6, 129.0, 142.9, 157.1, 170.6, 171.4, 183.4, 205.0; IR (KBr) 1731, 1702, 1658 cm^{-1}; MS, *m/z* (relative intensity, %) 349 (M^+, 37), 276 (100). Anal. Calcd for $C_{17}H_{19}NO_5S$: C,58.44; H, 5.48; N, 4.01. Found: C, 58.45; H, 5.39; N, 4.04.

3,3a,4,5-Tetrahydro-5-oxo-6-methyl-2,2(1*H*)-pentalenedicarboxylic Acid Diethyl Ester (2e). Colorless oil; R_f 0.11 (hexane/ether = 2/1); ^{1}H NMR (CDCl$_3$) δ 1.25 (t, J = 7.3 Hz, 3H), 1.27 (t, J = 7.3 Hz, 3H), 1.63 (t, J = 13 Hz, 1H), 1.70 (bs, 3H), 2.07 (dd, J = 3.3 Hz, J = 18 Hz, 1H), 2.63 (dd, J = 6.3 Hz, J = 18 Hz, 1H), 2.77 (dd, J = 5.3 Hz, J = 13 Hz, 1H), 2.89-3.03 (m, 1H), 3.14 (d, J = 19 Hz, 1H), 3.23 (d, J = 19 Hz, 1H), 4.19 (q, J = 7.3 Hz, 2H), 4.23 (q, J = 7.3 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 8.4, 13.9, 33.9, 39.1, 41.3, 42.6, 60.9, 61.8, 61.9, 132.8, 170.9, 171.5, 177.7, 209.3; IR (neat) 1723, 1672 cm^{-1}; MS, *m/z* (relative intensity, %) 280 (M^+, 12), 206 (43), 133 (100); exact mass calcd for $C_{15}H_{20}O_5$ 280.1311, found 280.1311.

3,3a,4,5-Tetrahydro-5-oxo-2,2(1*H*)-pentalenedicarboxylic Acid Diethyl Ester (2g). Colorless oil; R_f 0.17 (hexane/ether = 1/1); ^{1}H NMR (CDCl$_3$) δ 1.24 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H), 1.72 (t, J = 13 Hz, 1H), 2.11 (dd, J = 3.5 Hz, J = 18 Hz, 1H), 2.62 (dd, J = 6.2 Hz, J = 18 Hz, 1H), 2.78 (dd, J = 7.8 Hz, J = 13 Hz, 1H), 3.02−3.17 (m, 1H), 3.23 (d, J = 19 Hz, 1H), 3.34 (d, J = 19 Hz, 1H), 4.19 (q, J = 7.0 Hz, 2H), 4.23 (q, J = 7.0 Hz, 2H), 5.92 (d, J = 1.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.9, 35.1, 38.8, 42.1, 45.0, 60.7, 61.9, 62.1, 125.5, 170.7, 171.4, 185.5, 209.5; IR (neat) 1733, 1638 cm^{-1}; MS, *m/z* (relative intensity, %) 266 (M^+, 15), 119 (100). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.21; H, 6.96.

***cis*-5,5-Dimethyl-4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-4,5,6,6a-tetrahydro-3-(trimethylsilyl)-2(1*H*)-pentalenone (4a).** Colorless oil; R_f 0.31 (hexane/ether = 10/1); ^{1}H NMR (CDCl$_3$) δ 0.02 (s, 3H), 0.11 (s, 3H), 0.22 (s, 9H), 0.76 (s, 3H), 0.88 (s, 3H), 1.05 (dd, J = 5.9 Hz, J = 12 Hz, 1H), 1.13 (s, 3H), 1.98 (dd, J = 4.0 Hz, J = 18 Hz, 1H), 2.02 (t, J = 12 Hz, 1H), 2.67 (dd, J = 6.9 Hz, J = 18 Hz, 1H), 3.33−3.43 (m, 1H), 4.16 (s, 1H); ^{13}C NMR (CDCl$_3$) δ −4.7, −4.1, −0.9, 18.2, 24.1, 25.7, 28.5, 42.1, 42.2, 44.1, 46.1, 77.4, 135.9, 195.0, 215.7; IR (neat) 1699, 1621 cm^{-1}; MS, *m/z* (relative intensity, %) 352 (M^+, 3), 73 (100). Anal. Calcd for $C_{19}H_{36}O_2Si_2$: C, 64.71; H, 10.29. Found: C 64.78; H 10.13.

5,5-Dimethyl-4-[[1,1-dimethylethyl)dimethylsilyl]oxy]-3-phenyl-4,5,6,6a-tetrahydro-2(1*H*)-pentalenone (4b). GC analysis of the crude reaction mixture showed that a mixture of *cis*-**4b** and *trans*-**4b** was produced in a ratio of 26:1. Both isomers can be separated easily by column chromatography on silica gel (hexane/ether = 5/1). ***cis*-4b**: White solid; mp 79−80 °C (hexane/ether); R_f 0.29 (hexane/ether = 5/1); ^{1}H NMR (CDCl$_3$) δ −0.18, −0.07 (s, 3H), 0.83 (s, 9H), 0.93 (s, 3H), 1.17 (s, 3H), 1.21 (dd, J = 6.8 Hz, J = 13 Hz, 1H), 2.13 (dd, J = 1.4 Hz, J = 13 Hz, 1H), 2.20 (dd, J = 3.2 Hz, J = 18 Hz, 1H), 2.90 (dd, J = 7.0 Hz, J = 18 Hz, 1H), 3.37-3.47 (m, 1H), 4.35 (s, 1H), 7.29−7.41 (m, 5H); ^{13}C NMR (CDCl$_3$) δ −5.0, −4.7, 18.1, 24.1, 25.7, 29.1, 39.1, 42.9, 44.9, 45.4, 76.4, 127.9, 128.2, 128.4, 131.6, 135.4, 182.5, 209.2; IR (KBr) 1712, 1670 cm^{-1}; MS, *m/z* (relative intensity, %) 356 (M^+, 2), 300 (46), 299 (84), 73 (100). Anal. Calcd for $C_{22}H_{32}O_2Si$: C, 74.11; H, 9.05. Found: C, 74.09; H, 9.03. ***trans*-4b**: White solid; mp 99−101 °C (hexane/ether); R_f 0.10 (hexane/ether = 5/1); ^{1}H NMR (CDCl$_3$) δ −0.55 (s, 3H, SiMe$_2$), −0.03 (s, 3H), 0.73 (s, 9H), 1.02 (s, 3H), 1.20 (s, 3H), 1.41 (dd, J = 5.4 Hz, J = 13 Hz, 1H), 2.07 (dd, J = 2.7 Hz, J = 13 Hz, 1H), 2.16 (dd, J = 3.5 Hz, J = 18 Hz, 1H), 2.81 (dd, J = 7.0 Hz, J = 18 Hz, 1H), 2.94−3.05 (m, 1H), 4.66 (s,1H), 7.19−7.35 (m, 5H); ^{13}C NMR (CDCl$_3$) δ −5.1, −5.0, 18.1, 25.0, 26.0, 28.5, 35.2, 43.0, 43.8, 44.1, 80.5, 127.4, 127.8, 129.9, 131.4, 136.7, 181.2, 208.6; IR (KBr) 1713, 1673, 1602 cm^{-1}; MS, *m/z* (relative intensity, %) 356 (M^+, 0.2), 300 (34), 299 (72), 73 (100). Anal. Calcd for $C_{22}H_{32}O_2Si$: C, 74.11; H,9.05. Found: C, 74.04; H, 9.04.

4-[[1,1-Dimethylethyl)dimethylsilyl]oxy]-4,5,6,6a-tetrahydro-3,5,5-trimethyl-2(1*H*)-pentalenone (4c). GC analysis of the grude reaction mixture showed that a mixture of *cis*-**4c** and *trans*-**4c** was produced in a ratio of 2.4:1. Both isomers can be separated easily by column chromatography on silica gel (hexane/ether = 7/1). ***cis*-4c**: Colorless oil; R_f 0.26 (hexane/ether = 7/1); ^{1}H NMR (CDCl$_3$) δ 0.01 (s, 3H), 0.10 (s, 3H), 0.80 (s, 3H, CH$_3$), 0.88 (s, 9H), 1.03 (dd, J = 7.0 Hz, J = 13 Hz, 1H), 1.12 (s, 3H), 1.75 (d, J = 2.4 Hz, 3H), 1.99 (dd, J = 3.0 Hz, J = 18 Hz, 1H), 2.00 (dd, J = 2.4 Hz, J = 13 Hz, 1H), 2.71 (dd, J = 6.8 Hz, J = 18 Hz, 1H), 3.16-3.32 (m, 1H), 4.09 (s, 1H); ^{13}C NMR (CDCl$_3$) δ −4.9, −4.7, 8.9, 18.1, 24.0, 25.7, 29.0, 39.3, 43.0, 44.0, 45.1, 76.2, 131.9, 180.8, 211.7; IR (neat) 1712, 1678 cm^{-1}; MS, *m/z* (relative intensity, %) 294 (M^+, 1), 237 (24), 75 (100). Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27. Found: C, 69.22; H, 10.26. ***trans*-4c**: Colorless oil; R_f 0.14 (hexane/ether = 7/1); ^{1}H NMR (CDCl$_3$) δ 0.12 (s, 6H), 0.83 (s, 3H), 0.95 (s, 9H), 1.15 (s, 3H), 1.24 (dd, J = 4.9 Hz, J = 13 Hz, 1H), 1.82 (t, J = 2.2 Hz), 1.94 (dd, J = 3.2 Hz, J = 13 Hz, 1H), 1.96 (dd, J = 3.2 Hz, J = 18 Hz, 1H), 2.63 (dd, J = 6.8 Hz, J = 18 Hz, 1H), 2.72-2.87 (m, 1H), 4.57 (s, 1H); ^{13}C NMR (CDCl$_3$) δ −4.6, −4.5, 7.8, 18.0, 24.6, 25.9, 28.8, 35.2, 43.4, 43.7, 43.8, 80.4, 132.2, 180.1, 210.9; IR (neat) 1711, 1673 cm^{-1}; MS, *m/z* (relative intensity, %) 279 (M^+ − 15, 1), 73 (100). Anal. Calcd for $C_{17}H_{30}O_2Si$: C, 69.33; H, 10.27. Found: C, 69.19; H, 10.32.

3a,4-Dihydro-6-(trimethylsilyl)-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6a). Colorless oil; R_f 0.17 (hexane/ether = 2/1); ^{1}H NMR (CDCl$_3$) δ 0.18 (s, 9H), 2.09 (dd, J = 3.8 Hz, J = 18 Hz, 1H), 2.60 (dd, J = 5.1 Hz, J = 18 Hz, 1H), 3.20-3.25 (m, 2H, 3-H), 4.30 (t, J = 14 Hz, 1H), 4.47 (d, J = 16 Hz, 1H, 1-H), 4.65 (d, J = 16 Hz, 1H, 1-H); ^{13}C NMR (CDCl$_3$) δ −1.6, 40.2, 47.0, 66.1, 71.4, 136.1, 191.2, 212.7; IR (neat) 1705, 1622 cm^{-1}; MS, *m/z* (relative intensity, %) 196 (M^+, 4), 181 (30), 75 (100); exact mass calcd for $C_{10}H_{16}O_2Si$ 196.0920, found 196.0913.

3a,4-Dihydro-6-phenyl-1*H*-cyclopenta[*c*]furan-5(3*H*)-one (6b). Colorless oil; R_f 0.21 (hexane/ether = 1/1); ^{1}H NMR (CDCl$_3$) δ 2.34 (dd, J = 3.5 Hz, J = 18 Hz, 1H), 2.85 (dd, J = 6.2 Hz, J = 18 Hz, 1H), 3.20−3.39 (m, 2H), 4.38 (t, J = 7.0 Hz, 1H), 4.59 (d, J = 16 Hz, 1H), 4.94 (d, J = 16 Hz, 1H), 7.35−7.55 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 40.1, 43.1, 66.1, 71.2, 127.9, 128.4, 130.5, 134.4, 177.3, 206.7; IR (neat) 1709, 1656, 1601 cm^{-1}; MS, *m/z* (relative intensity, %) 200 (M^+, 34), 142 (100), 115 (88); exact mass calcd for $C_{13}H_{12}O_2$ 200.0837, found 200.0846.

2,3,3a,4-Tetrahydro-2-[(4-methylphenyl)sulfonyl]-6-(trimethylsilyl)cyclopenta[*c*]pyrrol-5(1*H*)-one (8a). White solid; mp 95−96 °C (hexane/ether); R_f 0.30 (hexane/ether = 1/2); ^{1}H NMR (CDCl$_3$) δ 0.11 (s, 9H), 1.97 (dd, J = 3.9 Hz, J = 17 Hz, 1H), 2.39 (s, 3H), 2.49 (dd, J = 6.8 Hz, J = 17 Hz, 1H), 2.56 (dd, J = 1.4 Hz, J = 11 Hz, 1H), 2.92−3.08 (m, 1H), 3.95 (t, J = 11 Hz, 1H), 3.98 (d, J = 17 Hz, 1H), 4.26 (d, J = 17 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ −1.7, 21.4, 40.5, 45.2, 48.1, 52.0, 127.2, 129.8, 133.4, 137.8, 143.9, 185.3, 211.2; IR (KBr) 1696, 1632, 1601 cm^{-1}; MS, *m/z* (relative intensity, %) 349 (M^+, 6), 334 (34), 73 (100). Anal. Calcd for $C_{17}H_{23}NO_3SSi$: C, 58.42; H, 6.63; N, 4.01. Found: C, 58.12; H, 6.69; N, 4.03.

2,3,3a,4-Tetrahydro-2-[(4-methylphenyl)sulfonyl]-6-(dimethylethenylsilyl)cyclopenta[*c*]pyrrol-5(1*H*)-one (8b). White solid; mp 53−55 °C (hexane/ether); R_f 0.16 (hexane/ether = 1/1); ^{1}H NMR (CDCl$_3$) δ 0.21 (s, 3H), 0.23 (s, 3H), 1.99 (dd, J = 4.1 Hz, J = 18 Hz, 1H), 2.43 (s, 3H), 2.53 (dd, J = 6.5 Hz, J = 18 Hz, 1H), 2.56 (dd, J = 1.6 Hz, J = 9.7 Hz, 1H), 2.96-3.12

(m, 1H), 3.97 (t, $J = 9.7$ Hz, 1H), 4.01 (d, $J = 18$ Hz, 1H), 4.24 (d, $J = 18$ Hz, 1H), 5.69 (dd, $J = 4.3$ Hz, $J = 19$ Hz, 1H), 6.02 (dd, $J = 4.3$ Hz, $J = 15$ Hz, 1H), 6.15 (dd, $J = 15$ Hz, $J = 19$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.8, −3.5, 21.5, 40.5, 45.4, 48.3, 52.1, 127.4, 129.9, 133.5, 133.7, 136.0, 136.5, 144.0, 186.2, 211.1; IR (KBr) 1698, 1630 cm^{-1}; MS, 361 (M^+, 0.3), 206 (82), 178 (59), 59 (100). Anal. Calcd for $C_{18}H_{23}NO_3SSi$: C, 59.80; H, 6.41; N, 3.87. Found: C, 59.76; H, 6.32; N, 3.82.

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