The University of Osaka
Institutional Knowledge Archive

Title	THE STUDY ON THE RHODIUM- AND RUTHENIUM-CATALYZED REACTIONS WITH HYDROSILANES AND CARBON MONOXIDE
Author(s)	福本, 能也
Citation	大阪大学, 1995, 博士論文
Version Type	VoR
URL	https://doi.org/10.11501/3100633
rights	
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

https://ir.library.osaka-u.ac.jp/

The University of Osaka

THE STUDY ON THE RHODIUM- AND RUTHENIUM-CATALYZED REACTIONS WITH HYDROSILANES AND CARBON MONOXIDE

YOSHIYA FUKUMOTO

OSAKA UNIVERSITY

1995

THE STUDY ON THE RHODIUM- AND RUTHENIUM-CATALYZED REACTIONS WITH HYDROSILANES AND CARBON MONOXIDE

（ヒドロシランと一酸化炭素を用いたロジウム
およびルテニウム触媒反応に関する研究）

YOSHIYA FUKUMOTO

OSAKA UNIVERSITY

1995

Preface

The studies presented in this thesis have been carried out under the direction of Professor Shinji Murai at the Department of Applied Chemistry, Faculty of Engineering, Osaka University. The thesis is concerned with the rhodium- and ruthenium-catalyzed reactions with hydrosilanes and carbon monoxide.

I would like to express my deepest gratitude to Professor Shinji Murai for his guidance, insight, encouragement, and inspiration throughout my career as a graduate student.

I would like to acknowledge Dr. Naoto Chatani for his helpful suggestions and stimulating discussions.

I would like to thank for Professor Yoshikane Kawasaki, Dr. Kouichi Ohe, and Dr. Fumitoshi Kakiuchi for their useful advice and continuing encouragement.

I would like to thank Mr. Tomohide Ida and Mr. Shinshi Yamaguchi for his contribution to this work.

The lab atmosphere was greatly enhanced by the friendships with Dr. Shin-ichi Ikeda, Mr. Yasuteru Kajikawa, Mr. Hideo Tokuhisa, Mr. Masa-aki Shinohara, Mr. Takahide Fukuyama and many others.

Finally, I would like to express my thanks to my parents for their perpetual support.

Department of Applied Chemistry
Faculty of Engineering
Osaka University
Suita, Osaka 565
Japan
January 1995

Yoshiya Fukumoto

List of Publications

The contents of this thesis are composed of the following papers.

(1) Rhodium-Catalyzed Ring-Opening Silylformylation of Epoxides Leading to β-Siloxy Aldehydes

Y. Fukumoto, N. Chatani, and S. Murai

J. Org. Chem. **58**, 4187-4188 (1993).

(2) Ruthenium-Catalyzed Reaction of 1,6-Diynes with Hydrosilanes and Carbon Monoxide: A Third Way of Incorporating CO

N. Chatani, Y. Fukumoto, T. Ida, and S. Murai

J. Am. Chem. Soc. **115**, 11614-11615 (1993).

(3) Ring-Opening Silylformylation of Oxetanes Catalyzed by $[RhCl(CO)_2]_2$-Amine

Y. Fukumoto, S. Yamaguchi, N. Chatani, and S. Murai

J. Organomet. Chem. in press.

(4) Ruthenium-Catalyzed Reaction of 1,6-Diynes with H_2O/CO

Y. Fukumoto, T. Ida, C. M. Crudden, N. Chatani, and S. Murai

In preparation.

Contents

General Introduction

The carbon monoxide (CO) incorporation reaction into organic compounds is one of the most important reactions in organic syntheses.[1] The CO incorporation reaction catalyzed by transition-metals has been the subject of numerous studies since the early 1940s. Syntheses of various types of organic compounds—both carbonyl compounds and *non*-carbonyl compounds—have been achieved by transition-metal catalyzed reactions in high yields and with high selectivities. A number of important industrial processes, such as Oxo prosess and Monsanto process, are also known and careful studies of such processes have provided the basis for much of the present mechanistic understanding.

The catalytic reactions using a reagent combination of a hydrosilane and CO ($HSiR_3/CO$) have been developed. In 1977, Murai has discovered that $Co_2(CO)_8$-catalyzed reaction of olefins with $HSiR_3/CO$ affording to enol silyl ethers,[2] subsquently the catalytic system has been extended the reaction of various oxygen-containing compounds.[3] The $Co_2(CO)_8$-catalyzed reactions of oxygen-containing compounds with $HSiR_3/CO$ can be classified into four types of transformation as follows: (1) silylformylation of cyclic ethers[4] and aldehydes,[5] (2) 1,2-bis(siloxy)vinylation of THF,[5] (3) siloxymethylenation of aldehydes,[6] esters,[7] cyclobutanones,[8] and THF,[9] and (4) siloxymethylation of cyclic ethers,[10] glicosyl acetates,[11] benzylic esters,[12] cyclic orthoesters,[13] acetals,[14] and aromatic aldehydes.[15] Sisak has reported that reductive coupling of CO leading to C_2 compounds is catalyzed by $Co_2(CO)_8$/amines (or phosphines) with $HSiR_3/CO$.[16] Applicability to a wide range of oxygen-containing compounds and diversity of the products are features of the $Co_2(CO)_8$-catalyzed reaction with $HSiR_3/CO$. Even after 20 years of continuous development by our group it is clear that $HSiR_3/CO$ chemistry has not yet reached its full potential. Indeed, novel transformations with $HSiR_3/CO$ has still been discovered by the use of transition-metal complexes other than $Co_2(CO)_8$ in these few years. Matsuda and Ojima have reported independently that Rh-complexes are effective catalysts for the silylformylation of alkynes.[17] $[RhCl(CO)_2]_2$ catalyzed the reaction of nitrogen-containing compounds such as enamines,[18] *N*,*N*-acetals,[19] and *N*,*O*-acetals[19] with $HSiR_3/CO$. No CO incorporation products have been obtained when the substrates mentioned above reacted in the $HSiR_3/CO/Co_2(CO)_8$ system. Wright has reported that the silylformylation of aldehydes to the corresponding α-siloxyaldehydes was catalyzed by

$[RhCl(COD)]_2$,[20] which was more effectively than by $Co_2(CO)_8$.[5] Ir-catalyzed reaction of olefines with $HSiR_3$/CO gave enol silyl ethers of acylsilanes.[21] Finally, Hidai has reported that $PdCl_2(PPh_3)_2$-$Co_2(CO)_8$ bimetallic system is effective for the reaction of iodoarenes with $HSiR_3$/CO giving to 1,2-diaryl-1,2-disiloxyethane in the presence of Et_3N.[22] The versatility and increasing sophistication of the $HSiR_3$/CO/transition-metal reaction system as a synthetic tool will undoubtly lead to its further development in organic syntheses.

The prime objective of this research was to develop new catalytic reactions using transition-metal catalysts (Rh and Ru) with hydrosilanes and carbon monoxide. This thesis consists of the following two chapters.

Chapter 1 deals with the rhodium-catalyzed ring-opening silylformylation of cyclic ethers yielding to ω-siloxy aldehydes. The addition of amines as an additive was crucial for incorporating CO into the cyclic ethers.

Chapter 2 deals with the ruthenium-catalyzed reaction of 1,6-diynes with hydrosilanes and carbon monoxide. This reaction afforded catechol derivatives which are incorporated two molecules of carbon monoxide successively into 1,6-diynes. In this reaction system, the use of H_2O instead of hydrosilanes also transformed 1,6-diynes into the similar catechol derivatives. And a new way of incorporating carbon monoxide via an oxycarbyne complex will be also described.

References

(1) For leading reviews of carbonylation, see: (a) Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*; Wiley Interscience: New York, 1975; Vol. 2. (b) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: Berlin, 1980. (c) Thatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 101-223. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, 1987. (e) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (f) Thompson, D. J. In *Comprehensive Organic Snthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon Press; Oxford, 1991; Vol. 3, pp 1015-1043.

(2) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174.

(3) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(4) Seki, Y.; Murai, S.; Yamamoto, Y.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 789.

(5) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393.

(6) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 119.

(7) (a) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370. (b) Chatani, N.; Fujii, S.; Yamasaki, Y.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1986**, *108*, 7361.

(8) Chatani, N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 430.

(9) Murai, T.; Kato, T.; Murai, S.; Hatayama, Y.; Sonoda, N. *Tetrahedron Lett.* **1985**, *26*, 2683.

(10) (a) Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N. *Organometallics* **1983**, *2*, 1883. (b) Murai, T.; Kato, T.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 6093. (c) Murai, T.; Furuta, K.; Kato, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1986**, *302*, 249. (d) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938.

(11) Chatani, N.; Ikeda, T.; Sano, T.; Sonoda, N.; Kurosawa, H; Kawasaki, Y.; Murai, S. *J. Org. Chem.* **1988**, *53*, 3387.

(12) Chatani, N.; Sano, T.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Org. Chem.* **1990**, *55*, 5923.

(13) Chatani, N.; Kajikawa, Y.; Nishimura, H.; Murai, S. *Organometallics* **1991**, *10*, 21.

(14) Chatani, N.; Kido, Y.; Nakayama, Y.; Fujii, S.; Kajikawa, Y.; Murai, S. submitted for publication.

(15) Chatani, N.; Tokuhisa, H., Kokubu, I.; Fujii, S.; Murai, S. submitted for publication.

(16) Sisak, A.; Angyalossy, Z. Abstracts of *7th International Symposium on Homogeneous Catalysis*, France, Lyon, 1990, P160.

(17) (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi,Y.; *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (c) Doyle, M.

P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11. (d) Zhou, J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1591.

(18) Ikeda, S.; Chatani, N.; Kajikawa, Y.; Ohe, K.; Murai, S. *J.Org. Chem.* **1992**, *57*, 2.

(19) Ikeda, S.; Chatani, N.; Murai, S. *Organometallics* **1992**, *11*, 3494.

(20) Wright, M. E.; Cohren, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059.

(21) Chatni, N.; Ikeda, S.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* **1992**, *114*, 9710.

(22) Misumi, Y.; Ishii, Y.; Hidai, M. *Chem. Lett.* **1994**, 685.

Chapter 1

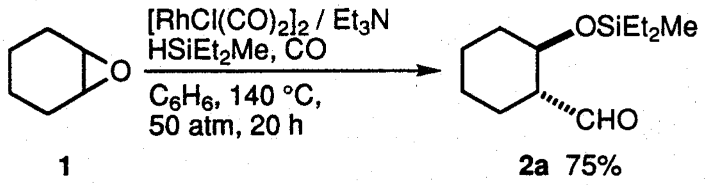
The Rhodium-Catalyzed Ring-Opening Silylformylation of Cyclic Ethers

1-1 Introduction

The carbonylative ring opening of cyclic ethers has been of long-standing interest not only because of its synthetic potential but also because of the related interests in homogeneous catalysis.[1] Ring-opening esterifications,[2] carboxylations,[3] amino-carbonylations,[4] and formylations[5] of cyclic ethers of varing efficiencies success have been reported. In 1977, Murai and co-workers reported that the $Co_2(CO)_8$-catalyzed reaction of cyclic ethers with a hydrosilane and carbon monoxide resulted in ring-opening silylformylation[6] yielding to ω-siloxy aldehydes.[7] In this reaction, however, the desire to prevent the product aldehydes from undergoing further reactions such as formylations,[6e, 8] hydrosilylations,[9] and dehydrogenative silylations[10] required us to use excess amounts of the starting cyclic ethers. In this chapter, it is described that the use of Rh-amine catalysts enables the conversion of cyclic ethers to ω-siloxy aldehydes without causing further reactions of the product aldehydes.

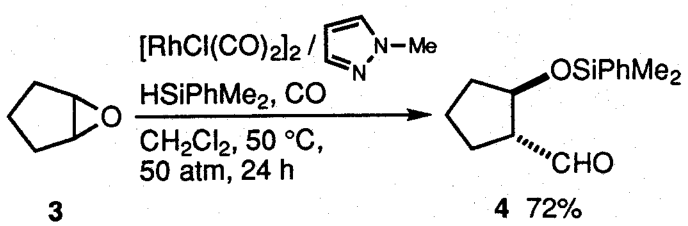
1-2 The Rhodium-Catalyzed Ring-Opening Silylformylation of Oxiranes Leading to β-Siloxyaldehydes

Early in this study, the reaction of cyclohexene oxide (**1**) (2.5 mmol) was carried out with $HSiEt_2Me$ (7.5 mmol) and CO (50 atm initial pressure at 25 °C) in the presence of $[RhCl(CO)_2]_2$ (0.1 mmol) in C_6H_6 (5 mL) at 100 °C for 20 h. Only cyclohexanol silyl ether was obtained in 21% yield without the formation of any carbonylation products. An examination of the effects of various additives to this reaction revealed that Et_3N (1 mmol) promotes ring-opening silylformylation. Thus, *trans*-2-(diethylmethylsiloxy)cyclohexanecarbaldehyde (**2a**) was obtained in 75% yield (eq 1). The ring-opening of **1** occurred predominantly in a *trans* manner. To our surprise, the addition of Et_3N did not give a similar results with other oxiranes, including cyclopentene oxide (**3**), 1-butene oxide, and styrene oxide. For example the reaction of **3** gave the corresponding formylation product in only 8% yield.



(1)

The prudent choice of both an additive and a hydrosilane is crucial to the effective silylformylation of **3**. Among additives examined, 1-methylpyrazole[11] was found to be the additive of choice. Other such as PPh_3, Et_3N, TMEDA, morpholine, pyridine, pyrrole, and DBU were not effective. The optimized conditions for the reaction of **3** are as follows: **3** (2.5 mmol) is treated with $HSiPhMe_2$ (3 mmol) and CO (50 atm, initial pressure at 25 °C) in the presence of $[RhCl(CO)_2]_2$ (0.05 mmol) and 1-methylpyrazole (1 mmol) in CH_2Cl_2 (5 mL) at 50 °C for 24 h to give *trans*-2-(dimethylphenylsiloxy)cyclopentanecarbaldehyde (**4**) in 72% yield (eq 2). While $RhCl(PPh_3)_3$ was not effective, $[RhCl(1,5\text{-hexadiene})]_2$ (72%), $[RhCl(COD)]_2$ (72%), $Rh(CO)_2(acac)$ (70%), and $Rh_6(CO)_6$ (20%) exhibited catalytic activity when used in combination with 1-methylpyrazole.

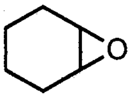
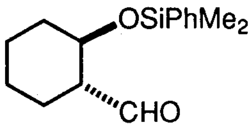
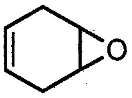
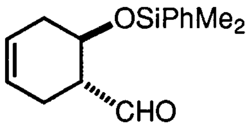
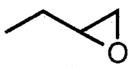
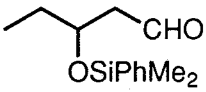
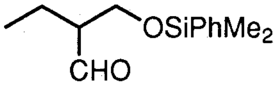
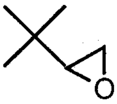
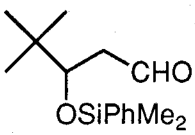
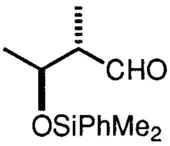
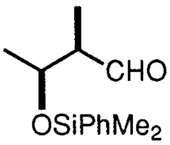


(2)

The results of the reaction conditions on several oxiranes are summarized in Table 1. The reaction of **1** afforded **2b** in 82% yield (entry 1). An olefin remained intact under these reaction conditions (entry 2). The reaction of cycloheptene oxide gave a silylformylation product in 15% yield, along with a 42% yield of 1-(dimethylphenylsiloxy)cycloheptene (not shown in Table I).[12] The ring opening of 1-butene oxide (**7**) occurred preferentially at the primary carbon to give a 77 : 23 mixture of 3-(dimethylphenylsiloxy)pentanal (**8a**) and 2-[(dimethylphenylsiloxy)methyl]butanal (**8b**) in a combined yield of 60% (entry 3). An oxirane having a bulky substituent (**9**) underwent completely regioselective silylformylation (entry 4). The stereospecificity of the ring opening is demonstrated in acyclic systems by entries 5 and 6.

Althrough the mechanistic details of the present reaction have not been understood, the plausible one can be made on the basis of the knowledge of the $HSiR_3/CO/Co_2(CO)_8$ catalytic reaction. The

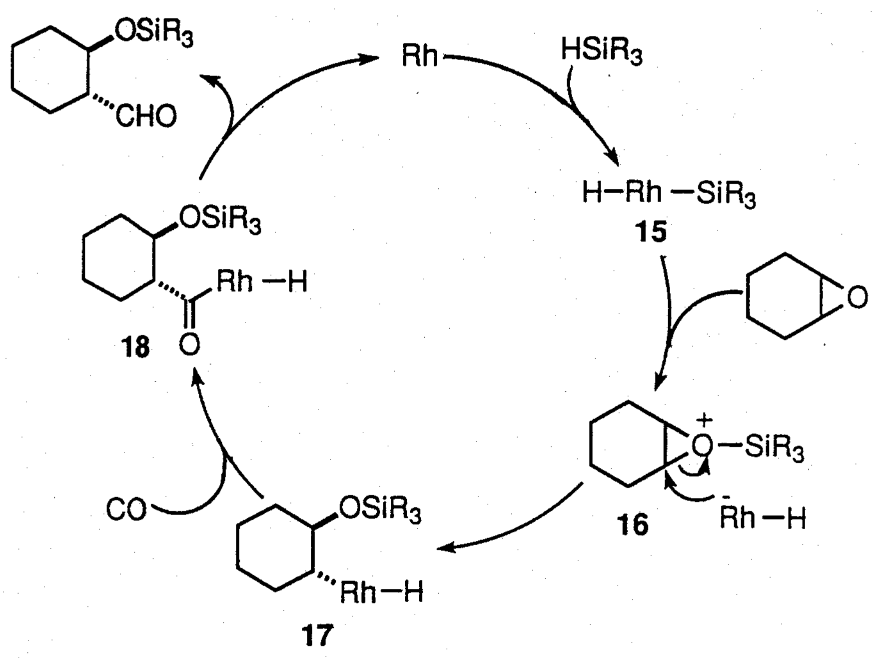
Table 1. Rhodium-Catalyzed Ring-Opening Silylformylation of Oxiranes with $HSiPhMe_2$ and CO[a]

entry	oxirane	product	yield, %[b]
1	 **1**	 **2b**	82
2	 **5**	 **6**	66
3[c]	 **7**	 **8a**  **8b**	60 (77 : 23)[d]
4[c]	 **9**	 **10**	65
5[c]	 **11**	 **12**	70
6[c]	 **13**	 **14**	55

[a] Reaction conditions: oxirane (2.5 mmol), $HSiPhMe_2$ (3 mmol), $[RhCl(CO)_2]_2$ (0.05 mmol), 1-methylpyrazole (1 mmol), CO (50 atm), CH_2Cl_2 (5 mL) at 50 °C for 24 h. [b] GC yields based on the oxirane. [c] 1-Methylpyrazole (2 mmol) was used. [d] The ratio of regioisomers was determined by the integration of their formyl proton resonances in ^1H NMR.

mechanism is shown in Scheme I.

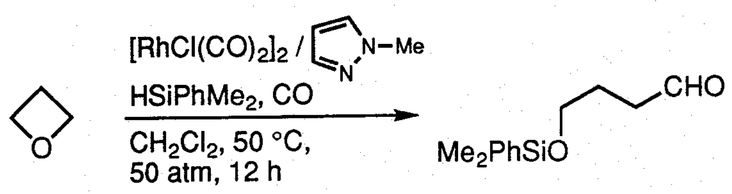
Scheme I



The key catalyst species in the present reaction would be a silyl rhodium hydride **15**. The reaction of **15** with the substrate **1** obtaines a silyloxonium ion **16** and Rh^--H, followed by the nucleophilic attack on **1** to give the alkyl rhodium complex **17**. After CO insersion to form acyl rhodium complex **18**, reductive elimination would be produced β-siloxy aldehyde **2**. Oxidative addition of $HSiR_3$ to Rh complex reproduces the key catalyst species **15**. The role of the additive amines is not clear. It is considered that three types of complexes are formed by the reaction of silyl metal hydride complexes and amines.[13] The two ionic complexes ($[R'_3SiNR_3]^+[MH]^-$: **I**, $[HNR_3]^+[MSiR'_3]^-$: **II**) are obtained by cleavage of Si-M or H-M monds, respectively. The last complex is $M(H)(SiR'_3)(NR_3)$ (**III**) which is formed by coordination of amines on the complexes. The addition of almost amines to the reaction mixture resulted in depositing solids. However, only when 1-methylpyrazole was added, the reaction mixture remained clear. It is likely that type **III** is formed when 1-methylpyrazole was added, and is the catalytic species in the present reaction.

1-3 The Rhodium-Catalyzed Ring-Opening Silylformylation of Oxetanes Leading to γ-Siloxyaldehydes

The reaction of oxetane with $HSiR_3$/CO catalyzed by $[RhCl(CO)_2]_2$-amine was attempted since oxetane has more basic oxygen atom than ethylene oxide[14] and its strain energy is similar to that of ethylene oxide.[15] Concequently, the corresponding γ-siloxy aldehydes were obtained by the ring-opening silylformylation of oxetanes (eq 3).



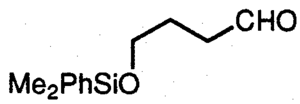
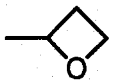
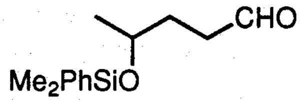
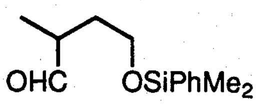
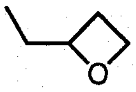
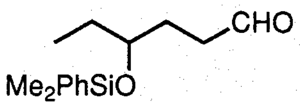
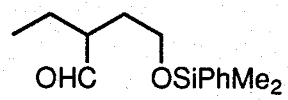
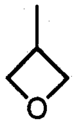
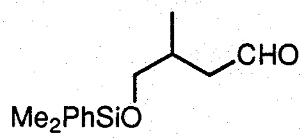
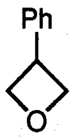
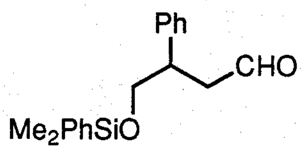
(3)

19 **20** 81%

The results are summarized in Table 2. To begin with, the reaction of oxetane (**19**) under the same reaction conditions as in the reaction of oxiranes was examined. Thus, the reaction of **19** (2.5 mmol) with dimethylphenylsilane (3 mmol) and carbon monoxide (50 atm, initial pressure at room temperature) in the presence of $[RhCl(CO)_2]_2$ (0.05 mmol) and 1-methylpyrazole (1 mmol) in CH_2Cl_2 (5 ml) at 50 °C for 12 h gave 4-(dimethylphenylsiloxy)butanal (**20**) in 81% yield (entry 1). The use of toluene as the solvent afforded **2** in 83% yield (entry 2). Although Et_2O (71%) gave a comparable yield, CH_3CN (17%) and hexane (2%) were not suitable solvent for silylformylation of **19** (entries 3-5). Some other amines were moderatetly effective for the silylformylation of **19** (Et_3N: 63%, TMEDA: 10%, DBU: 3%, pyridine: 17%), but 1-methylimidazole was not effective as the additive. These results showed that 1-methylpyrazole is additive of choice. When the reactants and the catalyst were mixed without addition of amines, oxetane was immediately and completely consumed in minutes at room temperature even before the reaction vessel was pressurized to 50 atm of carbon monoxide. The products were 1-(dimethylphenylsiloxy)propane (40%) and 3-(dimethylphenylsiloxy)propene (17%). Trialkylsilanes such as triethylsilane ($HSiEt_3$) and diethylmethylsilane ($HSiEt_2Me$) and ethoxydimethylsilane ($HSiMe_2(OEt)$) were unreactive in the present silylformylation, the starting oxetane being recovered intact.

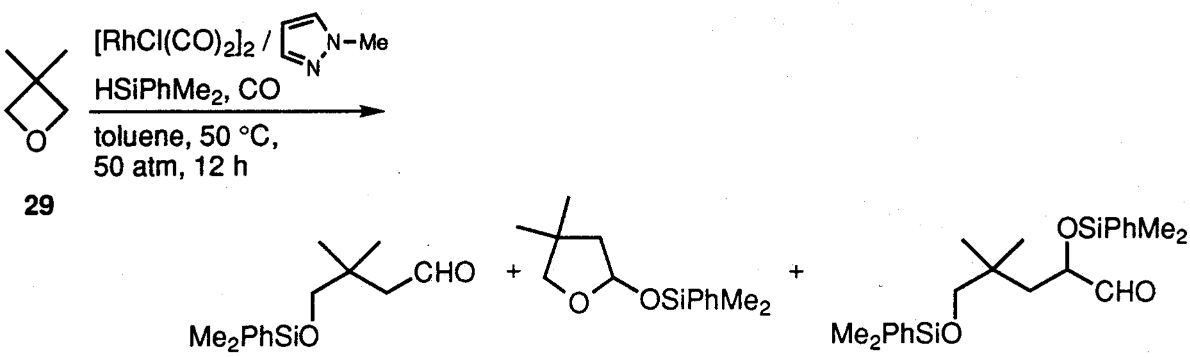
High regioselectivity was observed in the reaction of 2-methyloxetane (**21**). The ring opening of **21** occurred regioselectively at the primary carbon atom to give a 95 : 5 mixture of 4-(dimethylphenylsiloxy)pentanal (**22a**) and 4-(dimethylphenylsiloxy)-2-methylbutanal (**22b**) (entry

Table 2. Rhodium-Catalyzed Ring-Opening Silylformylation of Oxetanes with $HSiPhMe_2$ and CO[a]

entry	oxetane	solvent	product	yield, %[b]
1 2	 **19**	CH_2Cl_2 toluene	 **20**	81 83
3	 **21**	toluene	 +  **22a** **22b**	62 (95 : 5)[c]
4	 **23**	toluene	 +  **24a** **24b**	64 (95 : 5)[c]
5	 **25**	toluene	 **6**	80
6	 **27**	toluene	 **28**	42[d]

[a] Reaction conditions: oxetane (2.5 mmol), $HSiPhMe_2$ (3.0 mmol), $[RhCl(CO)_2]_2$ (0.05 mmol), 1-methylpyrazole (1 mmol), CO (50 atm), and solvent (5 mL) at 50 °C for 12 h. [b] GC yields. [c] The ratio of regioisomers was determined by the integration of their formyl proton resonances in ^{1}H NMR. [d] 24 h.

3). The reaction of 2-ethyloxetane (**23**) gave the same result (entry 4). The regioselectivity of the ring-opening of **21** or **23** is higher than that in the case of 1,2-epoxybutane (entry 3, Table 1). The reaction of 3-methyloxetane (**25**) underwent ring-opening silylformylation effectively to give the corresponding γ-siloxy aldehyde **26** in 80% yield (entry 5). In the reaction of 3-phenyloxetane (**27**), an aldehyde **28** was formed in 42% yield and 40% of the starting oxetane **27** was remained even after 24 h (entry 6). The reaction of 3,3-dimethyloxetane (**29**) afforded three products, 4-(dimethylphenylsiloxy)-3,3-dimethylbutanal (**30**), 2-(dimethylphenylsiloxy)-4,4-dimethyl-oxolane (**31**), and 2,5-bis(dimethylphenylsiloxy)-4,4-dimethylpentanal (**32**) which is the product of further silylformylation of **30**[6e, 7, 16] (eq 4). No reaction took place when tetrahydrofuran was treated under the present reaction conditions.



29

30 42% **31** 3% **32** 17% (4)

1-4 Experimental Section

General. Boiling points were uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-EX270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are recorded as follows: chemical shift in ppm (δ), mutiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a HITACHI 270-50 spectrometer; absorptions are reported in reciprocal centimeters (cm^{-1}). Mass spectra (MS) were obtained on a Shimadzu GCMS-QP 1000 with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were performed by Elemental Analyses Section of Osaka University. Analytical GLC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Medium-pressure liquid chromatography (MPLC) was performed using 30-mm x 300-mm silica-gel column (YAMAZEN YFLC Gel 7024) with a YAMAZEN FFLC-540 pumping system.

Materials. Dichloromethane and toluene were distilled from CaH_2. Carbon monoxide was purchased from Neriki gas CO. and used as received. $[RhCl(CO)_2]_2$ was purchased from Aldrich Chemical Co. and used without further purification. Cyclohexene oxide (**1**), cyclopentene oxide (**3**), 1,2-epoxybutane (**7**), *cis*-2,3-epoxybutane (**11**), *trans*-2,3-epoxybutane (**13**), trimethylene oxide (**19**) and 3,3-dimethyloxetane (**29**) were purchased from Aldrich Chemical Co. and distilled from CaH_2. Dimethylphenylsilane was purchased from Shin-etsu Chemical Co. and distilled from CaH_2. 1-Methylpyrazole was purchased from Tokyo Kasei Kogyo Co. and distilled from NaOH. 1,4-Cyclohexadiene monoepoxide (**5**) and 3,3-dimethyl-1-butene oxide (**9**) were prepared by the oxydation of the corresponding olefins using *m*-chloroperbenzoic acid. 2-Methyloxetane (**21**),[17] 2-ethyloxetane (**23**),[18] 3-methyloxetane (**25**),[19] and 3-phenyloxetane (**27**)[20] were prepared according to described methods.

General Procedure. In a carbon monoxide purged glass vessel containing $[RhCl(CO)_2]_2$ (19.5 mg, 0.05 mmol) were placed $HSiPhMe_2$ (0.46 mL, 3 mmol), 1-methylpyrazole (85 mL, 1 mmol), cyclic ether (2.5 mmol), and solvent (5 mL) in this order and the glass vessel was placed in a 50-mL stainless steel autoclave. The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated in an oil bath at 50 °C for 12 h. The solvent was removed under reduced pressure. Column chromatography on Florisil (100-200 mesh) of the residue (hexane : AcOEt = 20 : 1) gave a crude product aldehyde, which was purified by MPLC (hexane : AcOEt = 50 : 1) to obtain an analytical pure sample. For GC yield, an appropriate hydrocarbon ($C_{15}H_{32}$ or $C_{16}H_{34}$) calibrated against purified products were added before the catalytic reaction. The ratio of the regioisomers was determined by the integration of their formyl proton resonances for ^1H NMR spectra of the reaction mixture.

***trans*-2-(Diethylmethylsiloxy)cyclohexanecarbaldehyde (2a).** A colorless oil. ^1H NMR ($CDCl_3$): δ 0.05 (s, 3H, $SiCH_3$), 0.55 (q, J = 7.3 Hz, 4H, $SiCH_2$), 0.91 (t, J = 7.3 Hz, 6H, $SiCCH_3$), 1.19-1.39 (c, 4H, CH_2), 1.67-1.93 (c, 4H, CH_2), 2.21-2.32 (m, 1H, C*H*CHO), 3.80 (td, J = 4.1, 9.7 Hz, 1H, CHOSi), 9.74 (d, J = 2.7 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -4.20 ($SiCH_3$), 6.71 ($SiCH_2$), 6.99 ($SiCCH_3$), 24.10, 24.16, 24.90, 35.38 (CH_2), 57.84 (CHCHO), 70.98 (CHOSi), 205.02 (CHO). IR (neat): 2948 s, 2884 s, 2712 w, 1732 s, 1454 m, 1418 m, 1366 m, 1254 s, 1102 s, 1014 s, 966 m, 870 s, 816 s, 766 s, 695 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 213 (2, M^+ - CH_3), 200 (10), 199 (63, M^+ - C_2H_5), 171 (11), 169 (31), 131 (10), 103 (19), 101 (13), 93 (12), 91 (19), 89 (98), 79 (11), 75 (14), 73 (34), 67 (11), 61 (100). Anal. Calcd for $C_{12}H_{24}O_2Si$: C,63.10; H, 10.59. Found: C, 63.21; H, 10.73.

***trans*-2-(Dimethylphenylsiloxy)cyclohexanecarbaldehyde (2b).** A colorless oil. ^1H NMR ($CDCl_3$): δ 0.38 (s, 3H, $SiCH_3$), 0.39 (s, 3H, $SiCH_3$), 1.10-1.88 (c, 8H, CH_2), 2.28-2.39 (m, 1H, C*H*CHO), 3.83 (td, J = 4.3, 9.9 Hz, 1H, CHOSi), 7.37-7.58 (m, 5H, Ph), 9.65 (d, J =

3.0 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.16, -0.97 ($SiCH_3$), 24.01, 24.07, 24.87, 35.03 (CH_2), 57.73 (*C*HCHO), 71.19 (CHOSi), 127.84, 129.67, 133.43, 137.81 (Ph), 204.85 (CHO). IR (neat): 3064 m, 3016 m, 2944 s, 2864 s, 2720 m, 1730 s, 1594 w, 1454 s, 1432 s, 1366 s, 1254 s, 1092 s, 942 s, 878 s, 830 s, 786 s, 700 s, 644 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 247 (33, M^+ - CH_3), 217 (10), 185 (70), 169 (38), 155 (13), 151 (11), 138 (13), 137 (100), 136 (12), 135 (85), 121 (20), 107 (12), 105 (16), 91 (19), 81, (10), 77 (21), 75 (45), 67 (12), 53 (11). HRMS Calcd for $C_{15}H_{22}O_2Si$ (M^+): 262.1389, Found: 262.1373.

***trans*-2-(Dimethylphenylsiloxy)cyclopentanecarbaldehyde (4).** A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.40 (s 6H, $SiCH_3$), 1.50-1.97 (c, 6H, CH_2), 2.73-2.83 (m, 1H, C*H*CHO), 4.32 (q, *J* = 5.5 Hz, 1H, CHOSi), 7.35-7.60 (m, 5H, Ph), 9.55 (d, *J* = 1.9 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.42, -1.33 ($SiCH_3$), 22.67, 24.10, 35.53 (CH_2), 60.74 (*C*HCHO), 74.28 (CHOSi), 127.88, 129.75, 133.47, 137.63 (Ph), 202.66 (CHO). IR (neat): 2964 s, 2888 s, 2720 w, 1728 s, 1466 m, 1418 m, 1378 m, 1254 s, 1100s, 1054 s, 1010 s, 852 s, 800 s, 764 s, 688 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 247 (1, M^+ - H), 233 (24, M^+ - CH_3), 191 (35), 171 (40), 155 (43), 137 (75), 136 (14), 135 (100), 121 (19), 117 (14), 107 (16), 105 (17), 67 (15), 59 (13), 53 (10). HRMS Calcd for $C_{14}H_{19}O_2Si$ (M^+ - H): 247.1154, Found: 247.1125.

***trans*-2-(Dimethylphenylsiloxy)-4-cyclohexenecarbaldehyde (6).** A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.40 (s, 6H, $SiCH_3$), 2.05-2.31 (c, 4H, CH_2), 2.57-2.67 (m, 1H, C*H*CHO), 4.12 (ddd, *J* = 5.5, 8.2, 9.6 Hz, 1H, CHOSi), 5.49-5.66 (m 2H, =CH), 7.35-7.60 (m, 5H, Ph), 9.71 (d, *J* = 2.7 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.33, -1.10 ($SiCH_3$), 24.53, 34.45 (CH_2), 53.36 (*C*HCHO), 68.40 (CHOSi), 124.35, 124.48 (=CH), 133.43, 127.90, 129.81, 137.46 (Ph), 204.40 (CHO). IR (neat): 3036 m, 2964 m, 2916 m, 2848 m, 2724 w, 1730 s, 1658 w, 1594 w, 1432 s, 1364 m, 1254 s, 1212 s, 1194 s, 1000 m, 934 m, 870 s, 832 s, 786 s, 740 s, 700 s, 666 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 245 (17, M^+ - CH_3), 191 (24), 183 (35), 167 (24), 138 (13), 137 (100), 135 (60), 129 (30), 121 (13), 117 (17), 115 (21), 108 (12), 107 (19), 105 (14), 91 (34), 80 (16), 79 (43), 78 (15), 77 (38), 75 (31), 59 (11), 53 (15), 51 (17). HRMS Calcd for $C_{15}H_{19}O_2Si$ (M^+ - H): 259.1254, Found: 259.1142.

3-(Dimethylphenylsiloxy)pentanal (8a). A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.40 (s, 6H, $SiCH_3$), 0.87 (t, *J* = 7.4 Hz, 3H, CH_3), 1.53 (quint, *J* = 7.4 Hz, 2H, CH_2), 2.48 (dd, *J* = 7.4, 2.3 Hz, 1H, C*H*$_2$CHO), 2.50 (dd, *J* = 7.4, 2.3 Hz, 1H, C*H*$_2$CHO), 4.14 (quint, *J* = 7.4 Hz, 1H, CHOSi), 7.37-7.60 (m, 5H, Ph), 9.71 (t, J = 2.3 Hz 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.28, -1.20 ($SiCH_3$), 9.57 (CH_3), 30.41 (CH_2), 50.37 (CH_2CHO), 69.53 (CHOSi), 127.87, 129.72, 133.46, 137.66 (Ph), 202.10 (CHO). IR (neat): 3060 w, 2968 s, 2732 w, 1728 s, 1594 w, 1466 m, 1432 m, 1378 m, 1254 s, 1116 s, 1044 s, 830 s, 786 s, 740 s, 702 s cm^{-1}. MS: m/z (relative intensity, %) 221 (27, M^+ - CH_3), 164 (16), 163 (100), 159 (70), 143 (16), 137 (36), 136 (13), 135 (96), 121 (59), 115 (12), 107 (11), 105 (14), 103 (41), 101 (31), 91 (13), 77 (13), 75 (19), 59 (14). HRMS Calcd for $C_{13}H_{19}O_2Si$ (M^+ - H): 235.1154, Found: 235.1173.

2-[(Dimethylphenylsiloxy)methyl]butanal (8b). A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.37 (s, 6H, $SiCH_3$), 0.90 (t, J = 7.3 Hz, 3H, CH_3), 1.42-1.77 (m, 2H, CH_2), 2.31-2.38 (m, 1H, *C*HCHO), 3.81 (dd, J = 6.2, 10.3 Hz, 1H, CH_2OSi), 3.82 (dd, J = 6.2, 10.3 Hz, 1H, CH_2OSi), 7.37-7.56 (m, 5H, Ph), 9.67 (d, J = 2.4 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -2.04 ($SiCH_3$), 11.36 (CH_3), 18.56 (CH_2), 55.59 (*C*HCHO), 61.26 (CH_2OSi), 127.90, 129.75, 133,41, 137.23 (Ph) 204.66 (CHO). IR (neat): 3064 m, 2968 s, 2880 m, 2728 w, 1732 s, 1594 w, 1466 m, 1432 m, 1384 m, 1254 s, 1118 s, 1050 m, 830 s, 788 s, 740 s, 700 s, 642 w cm^{-1}. MS: m/z (relative intensity, %) 221 (15, M^+ - CH_3), 191 (12), 159 (55), 143 (29), 138 (12), 137 (100), 135 (50), 131 (16), 121 (27), 117 (14), 113 (14), 105 (11), 91 (18), 77 (10), 75 (23) cm^{-1}. HRMS Calcd for $C_{12}H_{17}O_2Si$ (M^+ - CH_3): 221.0998, Found: 221.0992.

4,4-Dimethyl-3-(dimethylphenylsiloxy)pentanal (10). A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.37 (s, 3H, $SiCH_3$), 0.39 (s, 3H, $SiCH_3$), 0.85 (s, 9H, $(CH_3)_3C$), 2.43-2.60 (m, 2H, *C*H_2CHO), 3.93 (dd, J = 4.9, 6.5 Hz, 1H, CHOSi), 7.36-7.59 (m, 5H, Ph), 9.65 (t, J = 2.2 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -0.99 ($SiCH_3$), 25.90 ($(CH_3)_3C$), 35.44 ($C(CH_3)_3$), 47.56 (CH_2CHO), 75.50 (CHOSi), 127.74, 129.52, 133.51, 137.94 (Ph), 202.37 (CHO). IR (neat): 3064 m, 2972 s, 2728 m, 1728 s, 1594 m, 1484 s, 1432 s, 1398 s, 1366 s, 1252 s, 1216 m, 1188 m, 1092 s, 1024 s, 992 s, 830 s, 784 s, 740 s, 700 s, 642 m cm^{-1}. MS: m/z (relative intensity, %) 249 (17, M^+ - CH_3), 207 (12), 187 (16), 163 (42), 137 (22), 136 (14), 135 (100), 121 (23), 107 (10), 103 (11), 101 (25), 75 (11), 57 (15). HRMS Calcd for $C_{14}H_{21}O_2Si$ (M^+ - CH_3): 249.1311, Found: 249.1317.

(*2S,*3S**)-4-(Dimethylphenyksiloxy)-3-methylbutanal (12).** A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.39 (s, 6H, $SiCH_3$), 1.03 (d, J = 6.8 Hz, 3H, *C*H_3CHCHO), 1.17 (d, J = 6.3 Hz, 3H, *C*H_3CHOSi), 2.38 (ddq, J = 2.4, 6.3, 6.8 Hz, 1H, *C*HCHO), 4.04 (quint, J = 6.3 Hz, 1H, CHOSi), 7.35-7.60 (m, 5H, Ph), 9.69 (d, J = 2.4 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.28, -1.16 ($SiCH_3$), 10.41 (CH_3CHCHO), 21.46 (CH_3CHOSi), 53.50 (*C*HCHO), 69.83 (CHOSi), 127.85, 129.70, 133.43, 137.63 (Ph), 204.95 (CHO). IR (neat): 3068 w, 2976 m, 2888 m, 2724 w, 1730 s, 1594 w, 1456 m, 1432 m, 1380 m, 1254 s, 1116 s, 1068 s, 1038 s, 986 m, 956 m, 828 s, 786 s, 740 s, 700 s, 642 w cm^{-1}. MS: m/z (relative intensity, %) 221 (21, M^+- CH_3), 177 (35), 159 (59), 143 (24), 137 (56), 136 (15), 135 (100), 121 (34), 117 (34), 115 (24), 107 (14), 105 (19), 99 (27), 91 (15), 77 (13), 75 (48), 61 (15), 59 (13), 55 (10). HRMS Calcd for $C_{13}H_{20}O_2Si$ (M^+): 236.1233, Found: 236.1224.

***(2R*,3S*)*-4-(Dimethylphenylsiloxy)-3-methylbutanal (14).** A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 3H $SiCH_3$), 0.38 (s, 3H $SiCH_3$), 1.06 (d, J = 7.1 Hz, 3H, CH_3CHCHO), 1.16 (d, J = 6.2 Hz, 3H, CH_3CHOSi), 2.37 (ddq, J = 1.2, 4.3, 7.1 Hz, 1H, C*H*CHO), 4.24 (dq, J = 4.2, 6.2 Hz, 1H, CHOSi), 7.35-7.61 (m, 5H, Ph), 9.70 (d, J = 1.2 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.23, -1.14 ($SiCH_3$), 8.39 (CH_3CHCHO), 21.12 (CH_3CHOSi), 53.32 (*C*HCHO), 68.47(CHOSi), 127.85, 129.70, 133.44, 137.75 (Ph), 204.98 (CHO). IR (neat): 3076 m, 2980 s, 2884 m, 2628 m, 2720 m, 1730 s, 1594 w, 1454 m, 1432 s, 1380 s, 1254 s, 1116 s, 1038 s, 958 s, 894 m, 830 s, 786 s, 740 s, 700 s, 644 m cm^{-1}. MS: m/z (relative intensity, %) 221 (20, M^+ - CH_3), 177 (36), 159 (59), 143 (23), 137 (57), 136 (15), 135 (100), 121 (34), 117 (33), 115 (21), 107 (14), 105 (18), 99 (25), 91 (16), 77 (12), 75 (48), 61 (14), 59 (13). HRMS Calcd for $C_{13}H_{19}O_2Si$ (M^+ - H): 235.1154, Found: 235.1190.

4-(Dimethylphenylsiloxy)butanal (20). A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiCH_3$), 1.86 (quint, J = 6.5 Hz, 2H, CH_2), 2.48 (dt, J = 1.6, 6.5 Hz, 2H, CH_2CHO), 3.63 (t, J = 6.5 Hz, 2H, CH_2OSi), 7.38-7.58 (m, 5H, Ph), 9.75 (t, J = 1.6 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -2.01 ($SiCH_3$), 25.16 (CH_2), 40.61 (CH_2CHO), 61.87 (CH_2OSi), 127.87, 129.67, 133.39, 137.56 (Ph), 202.37 (CHO). IR (neat): 3142 w, 3066 w, 3008 w, 2952 m, 2904 m, 2818 m, 2730 w, 1722 s, 1604 w, 1478 w, 1429 m, 1411 m, 1391 m, 1250 s, 1180 w, 1110 s, 1087 s, 1013 m, 944 m, 832 s, 783 s, 737 s, 697 m, 632 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 221 (1, M^+ - H), 207 (14, M^+ - CH_3), 145 (38), 138 (13), 137 (100), 135 (31), 131 (23), 129 (20), 121 (11), 105 (12), 99 (19), 91 (20), 77 (32), 75 (21), 61 (12). HRMS Calcd for $C_{12}H_{18}O_2Si$ (M^+): 222.1076, Found: 222.1059.

4-(Dimethylphenylsiloxy)pentanal (22a). The reaction mixture consisted of two regioisomers, **22a** and **22b** (95 : 5), the ratio of which was determined by the integration of their formyl proton resonances in the ^{1}H NMR spectrum of the reaction mixture (δ 9.68 **22a**, 9.62 **22b**). Purification by MPLC gave pure **22a** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 6H, $SiCH_3$), 1.12 (d, *J* = 5.9 Hz, 3H, CH_3), 1.74-1.78 (m, 2H, CH_2), 2.42 (dt, *J* = 1.6, 7.3 Hz, 2H, CH_2CHO), 3.85 (sext, *J* = 5.9 Hz, 1H, CHOSi), 7.37-7.59 (m, 5H, Ph), 9.68 (t, *J* = 1.6 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.31, -1.27 ($SiCH_3$), 23.56 (CH_3), 31.52 (CH_2) 40.16 (CH_2CHO), 67.89 (CHOSi), 127.82, 129.61, 133.46, 137.93 (Ph), 202.60 (CHO). IR (neat): 3072 m, 3052 m, 2958 s, 2868 m, 2728 m, 2302 m, 1726 s, 1429 m, 1394 m, 1249 s, 1138 s, 1114 s, 1036 s, 965 m, 824 s, 781 s, 736 m, 699 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 235 (1, M^+ - H), 221 (4, M^+ - CH_3), 159 (37), 143 (12), 138 (12), 137 (100), 136 (10), 135 (66), 105 (12), 91 (11), 77 (24), 75 (42). HRMS Calcd for $C_{13}H_{20}O_2Si$ (M^+): 236.1233, Found: 236.1218.

4-(Dimethylphenylsiloxy)hexanal (24a). The reaction mixture consisted of two regioisomers, **24a** and **24b** (95 : 5), the ratio of which was determined by the integration of their formyl proton resonances in the ^{1}H NMR spectrum of the reaction mixture (δ 9.67 **24a**, 9.61 **24b**). Purification by MPLC gave pure **24a** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.39 (s, 6H, $SiCH_3$), 0.84 (t, *J* = 7.5 Hz, 3H, CH_3), 1.38-1.51 (m, 2H, CH_2), 1.61-1.87 (m, 2H, CH_2), 2.41 (dt, *J* = 1.6, 5.4 Hz, 2H, CH_2CHO), 3.58-3.71 (m, 1H, CH_2OSi), 7.37-7.59 (m, 5H, Ph), 9.67 (t, *J* = 1.6 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.20 ($SiCH_3$), 9.65 (CH_3), 28.47 (CH_2), 29.76 (CH_2), 39.91 (CH_2CHO), 72.96 (CHOSi), 127.82, 129.61, 133.46, 138.04 (Ph), 202.60 (CHO). IR (neat): 3056 m, 3018 m, 2956 s, 2926 s, 2878 s, 2831 m, 2718 m, 1725 s, 1591 w, 1462 m, 1429 s, 1411 m, 1383 m, 1251 s, 1112 s, 1057 s, 1010 s, 825 s, 780 s, 736 s, 697 s, 636 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 235 (22, M^+ - CH_3), 173 (28), 137 (75), 136 (16), 135 (100), 105 (11), 91 (11), 77 (19), 75 (48). HRMS Calcd for $C_{14}H_{22}O_2Si$ (M^+): 250.1389, Found: 250.1407.

4-(Dimethylphenylsiloxy)-3-methylbutanal (26). A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 6H, $SiCH_3$), 0.91 (d, *J* = 6.5 Hz, 3H, CH_3), 2.14-2.36 (c, 2H, *C*H and CH_2CHO), 2.44-2.58 (m, 1H, CH_2CHO), 3.34 (dd, *J* = 7.6, 10.0 Hz, 1H, CH_2OSi), 3.53 (dd, *J* = 4.9, 10.0 Hz, 1H, CH_2OSi), 7.28-7.60 (m, 5H, Ph), 9.74 (t, *J* = 2.2 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -2.08, -2.05 ($SiCH_3$),16.59 (CH_3), 31.18 (CH), 48.12 (CH_2CHO), 67.46 (CH_2OSi), 127.84, 129.61, 133.37, 137.52 (Ph), 202.53 (CHO). IR (neat): 3072 m, 3020 w, 2960 s, 2886 m, 2720 m, 1724 s, 1592 w, 1459 m, 1428 m, 1390 m, 1251 s, 1112 s, 1086 s, 1040 m, 827 s, 784 s, 738 s, 698 s, 639 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 221 (14, M^+ - CH_3), 159 (40), 145 (17), 143 (13), 138 (13), 137 (100), 136 (10), 135 (70), 121 (16), 113 (14), 105 (15), 91 (19), 77 (26), 75 (41). HRMS Calcd for $C_{13}H_{20}O_2Si$ (M^+): 236.1232, Found: 236.1236.

4-(Dimethylphenylsiloxy)-3-phenylbutanal (28). A colorless oil. ^1H NMR ($CDCl_3$): δ 0.31 (s, 6H, $SiCH_3$), 2.68 (ddd, J = 2.2, 7.3, 16.5 Hz, 1H, CH_2CHO), 2.93 (ddd, J = 2.2, 7.3, 16.5 Hz, 1H, CH_2CHO), 3.34-3.66 (m, 1H, CH), 3.60 (dd, J = 8.4, 10.0 Hz, 1H, CH_2OSi), 3.75 (dd, J = 5.1, 10.0 Hz, 1H, CH_2OSi), 7.15-7.52 (c, 10H, Ph), 9.72 (t, J = 2.2 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -2.15 ($SiCH_3$), 42.70 (CH), 46.56 (CH_2CHO), 67.28 (CH_2OSi), 126.99, 127.76, 127.87, 128.57, 129.70, 133.39, 137.25, 140.77 (Ph), 201.72 (CHO). IR (neat): 3184 w, 3030 s, 2956 m, 2904 m, 2864 m, 2726 m, 1775 m, 1725 s, 1605 m, 1554 m, 1495 m, 1454 m, 1428 s, 1416 m, 1321 m, 1249 s, 1112 s, 1089 s, 957 m, 828 s, 784 s, 762 s, 737 s, 696 s, 640 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 298 (1, M^+), 283 (1, M^+ - CH_3), 268 (21), 254 (18), 221 (15), 190 (17), 165 (60), 163 (14), 137 (17), 136 (17), 135 (100), 121 (11), 91 (10). HRMS Calcd for $C_{18}H_{22}O_2Si$ (M^+): 298.1389, Found: 298.1389.

4-(Dimethylphenylsiloxy)-3,3-dimethylbutanal (30). A colorless oil. ^1H NMR ($CDCl_3$): δ 0.35 (s, 6H, $SiCH_3$), 1.01 (s, 6H, CH_3), 2.27 (d, J = 3.0 Hz, 2H, CH_2CHO), 3.34 (s, 2H, CH_2OSi), 7.37-7.57 (m, 5H, Ph), 9.82 (t, J = 3.0 Hz 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -2.06 ($SiCH_3$), 24.58 (CH_3), 36.12 (C), 52.78 (CH_2CHO), 71.59 (CH_2OSi), 127.85, 129.63, 133.41, 137.61 (Ph), 203.25 (CHO). IR (neat): 3056 w, 2952 m, 2886 m, 1722 s, 1475 w, 1448 w, 1428 s, 1398 m, 1250 s, 1087 s, 852 s, 828 s, 782 s, 735 m, 697 s cm^{-1}. MS: m/z (relative intensity, %) 249 (1, M^+ - H), 235 (16, M^+ - CH_3), 206 (15), 173 (28), 165 (19), 163 (29), 137 (46), 135 (100), 121 (29), 107 (10), 105 (15), 103 (10), 91 (17), 77 (13), 75 (31), 70 (19), 59 (11). HRMS Calcd for $C_{14}H_{22}O_2Si$ (M^+): 250.1389, Found: 250.1375.

2-(Dimethylphenylsiloxy)-4,4-dimethyloxolane (31). A colorless oil. ^1H NMR ($CDCl_3$): δ 0.41 (s, 3H, $SiCH_3$), 0.43 (s, 3H, $SiCH_3$), 1.04 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.69 (dd, J = 3.0, 13.0 Hz, 1H, CH_2), 1.89 (dd, J = 5.4, 13.0 Hz, 1H, CH_2), 3.47 (d, J = 8.1 Hz, 1H, CH_2O), 3.69 (d, J = 8.1 Hz, 1H, CH_2O), 5.54 (dd, J = 3.0, 5.4 Hz, 1H, CHOSi), 7.36-7.62 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ -1.29, -0.82 ($SiCH_3$), 26.20, 27.82 (CH_3), 38.98

(C), 49.97 (CH_2), 79.21 (CH_2O), 100.25 (CHOSi), 127.75, 129.47, 133,50, 137.99 (Ph). IR (neat): 3052 w, 2960 s, 2866 m, 2698 w, 2320 w, 1428 m, 1367 m, 1318 m, 1240 s, 1152 s, 1113 s, 1091 s, 1017 s, 912 m, 822 s, 783 s, 725 m, 696 m, 632 w cm^{-1}. MS: m/z (relative intensity, %) 250 (9, M^+), 249 (18, M^+ - H), 236 (11), 235 (57, M^+ - CH_3), 205 (15), 191 (10), 173 (13), 172 (10), 165 (37), 163 (47), 157 (12), 138 (11), 137 (85), 136 (12), 135 (84), 121 (25), 107 (11), 105 (16), 104 (10), 103 (100), 91 (16), 77 (17), 75 (34), 70 (60), 55 (50). HRMS Calcd for $C_{14}H_{22}O_2Si$ (M^+): 250.1389, Found: 250.1371.

2,5-Bis(dimethylphenylsiloxy)-4,4-dimethylpentanal (32). A colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.32 (s, 6H, $SiCH_3$), 0.41 (s, 6H, $SiCH_3$), 0.83 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.49 (dd, J = 7.6, 14.5 Hz, 1H, CH_2), 1.69 (dd, J = 4.6, 14.5 Hz, 1H, CH_2), 3.23 (s, 2H, CH_2OSi), 4.11 (ddd, J = 1.6, 4.6, 7.6 Hz, 1H, CHOSi), 7.35-7.55 (m, 10H, Ph), 9.42 (d, J = 1.6 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ -1.96, -1.92, -1.31, -1.22 ($SiCH_3$), 24.32, 25.02 (CH_3), 35.04 (C), 40.15 (CH_2), 71.61 (CH_2OSi), 76.52 (CHOSi), 127.76, 127.91, 129.49, 129.90, 133.42, 133.57, 136.80, 138.01 (Ph), 202.62 (CHO). IR (neat): 2954 s, 1733 s, 1591 m, 1474 s, 1420 m, 1252 s, 1085 s, 823 s, 781s , 727 s, 697 s, 639 m cm^{-1}. MS: m/z (relative intensity, %) 399 (3, M^+ - CH_3), 385 (14), 315 (16), 234 (10), 233 (43), 219 (21), 206 (19), 178 (41), 165 (18), 163 (19), 137 (30), 136 (15), 135 (100), 104 (15), 75 (20). HRMS Calcd for $C_{23}H_{34}O_3Si_2$ (M^+): 414.2046, Found: 414.2051.

1-5 References and Notes

(1) For leading reviews of carbonylation, see: (a) Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*; Wiley Interscience: New York, 1975; Vol. 2. (b) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: New York, 1980. (c) Tkatchenko, I. In *Comprehensive Organometallic Chemistry;* Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Eds; Pergamon Press: Oxford, 1982; Vol. 8, pp 101-223. (d) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Didect Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (e) Thompson, D. J. In *Comprehensive Organic Snthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon Press; Oxford, 1991; Vol. 3, pp 1015-1043.

(2) (a) Eisenmann, J.; Yamartino, R. L.; Howard, J. F. *J. Org. Chem.* **1961**, *26*, 2102. (b)

Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1460. (c) McClure, J. D. *J. Org. Chem.* **1967**, *32*, 3888. (d) Takegami, Y.; Watanabe, Y.; Mitsudo, T.; Masada, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 202.

(3) McRae, W. A.; Eisenmann, J. L. U. S. Patent 3024275, **1962**; *Chem. Abstr.* **1962**, *57*, 2077.

(4) Tsuji, Y.; Kobayashi, M.; Okuda, F.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1253.

(5) (a) Yokokawa, C.; Watanabe, Y.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 677. (b) Takegami, Y.; Yokokawa, C.; Watanabe, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 935. (c) Roos, L.; Goetz, R. W.; Orchin, M. *J. Org. Chem.* **1965**, *30*, 3023. (d) Rosenthal, A.; Kan, G. *Tetrahedron Lett.* **1967**, 477.

(6) The catalytic silylformylation of acetylenes and aldehydes by a hydrosilane and carbon monoxide has been recently reported. (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Ojima, I.; Ingallina, P.; Donovan, R. J. Clos, N. *Organometallics* **1991**, *10*, 38. (c) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, *12*, 11. (d) Zhou, J. Q.; Alper, H. *Organometallics* **1994**, *13*, 1591. (e) Wright, M. E.; Cohren, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2059.

(7) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 789.

(8) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393.

(9) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z. Eds.; John Wiley & Sons: New York, 1989; Part 2, pp 1479-1526.

(10) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 199.

(11) (a) Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A.; Ruiz, N.; Schlünken, C.; Valero, C.; Werner, H. *Inorg. Chem.* **1992**, *31*, 5580. (b) García, M. P.; Esteruelas, M. A.; Martín, M.; Oro, L. A. *J. Organomet. Chem.*, **1994**, *47*, 151.

(12) In the case of cyclooctene oxide, 1-siloxycyclooctene was the sole product, in 45% yield.

(13) (a) Jetz, W.; Simons, P. B.; Thompson, J. J. A.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 2217. (b) Aylett, B. J.; Campbell. J. M. *J. Chem. Soc., (A)* **1969**, 1920. (c) Arnulf,

P.; Hagen, P.; Claudia, R.; Higgins, R.; Russo, P. J. *Inorg. Chem.* **1971**, *10*, 1657.

(14) Eigenmann, H. K.; Goldman, D. M.; Benson, S. W. *J. Phys. Chem.* **1973**, *77*, 1687.

(15) Pell, A. S.; Pilcher, G. *Trans. Faraday Soc.* **1965**, *61*, 71.

(16) Gradysz and co-workers reported that oxetanes were transformed to 2-siloxyoxolanes (similar to **31**) and γ-siloxy aldehydes (similar to **30**) on the stoichiometric reaction of oxetanes with $(CO)_5MnSiMe_3$ and $(CO)_5MnH$. See: Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

(17) Sondheimer, F.; Woodward, R. B. *J. Am. Chem. Soc.* **1953**, 75, 5438.

(18) Clarke, M. J.; Holbrook, K. A. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 890.

(19) Searles, S. Jr.; Pollart, K. A.; Lutz, E. F. *J. Am. Chem. Soc.* **1957**, *79*, 948.

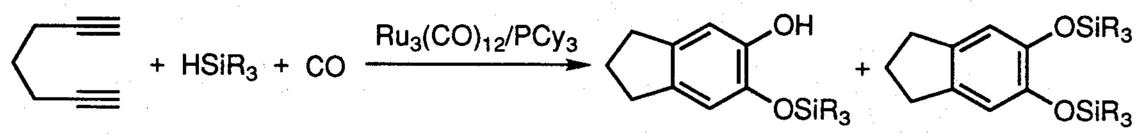
(20) Picard, P.; Leelercq, D.; Bats, J. -P.; Moulines, J. *Synthesis* **1981**, 550.

Chapter 2

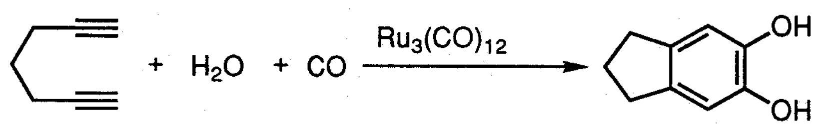
The Ruthenium-Catalyzed Reactions of 1,6-Diynes with Carbon Monoxide

2-1 Introduction

Transition-metal-catalyzed CO incorporation reaction has been a powerful tool for preparation of a variety of carbonyl compounds or *non*-carbonyl compounds.[1] The $HSiR_3$/CO/transition-metal reaction is a useful reaction to introduce a silyl group and CO into organic molecules. Although a number of functional groups were transformed in this reaction system, only a few examples[2] have been reported that two functionalities in one molecule were allowed to react with $HSiR_3$/CO simultaneously. Firstly, this chapter describes that a new ruthenium-catalyzed reaction of 1,6-diynes with $HSiR_3$ and CO leading to catechol derivatives (eq 1). It is well-known that cyclization of diynes[3] with one molecule of CO gives cyclopentadienone derivatives or their dimers in the presence of Co,[4a] Rh,[4b] Fe,[4c, d] or Pd.[4e-g] The present reaction exhibits a new mode of successive incorporation of two molecules of CO.[5] In this chapter, it is also described that the use of H_2O instead of hydrosilanes also enables to similar transformation (eq 2).

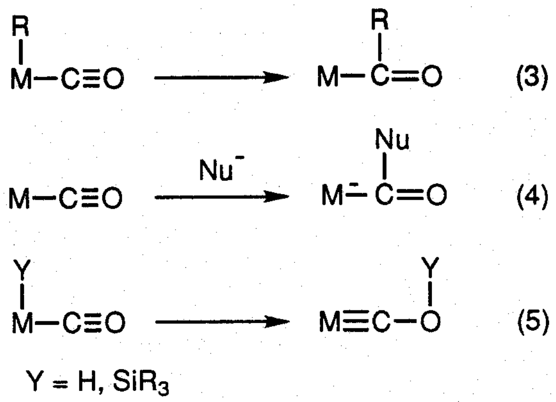


(1)



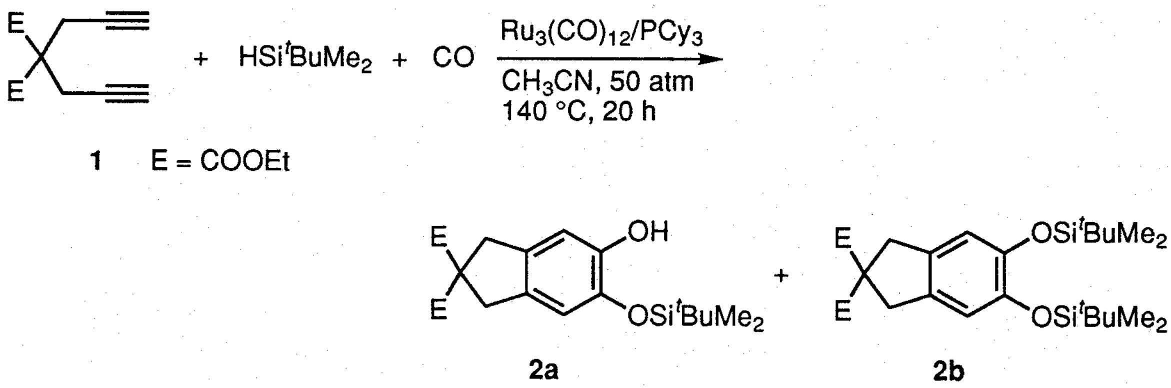
(2)

All catalytic CO incorporation processes involve either of two distinct mechanisms as the key step: (1) migration of an R group from a metal to the coordinated CO (eq 3) or (2) nucleophilic attack on the coordinated CO by an external nucleophile (eq 4).[6] In this chapter, it is discussed that the catalytic cycle of the present reaction involves a third way of incorporating CO via an oxycarbyne complex (eq 5).



2-2 The Ruthenium-Catalyzed Reaction of 1,6-Diynes with Hydrosilanes and Carbon Monoxide

The ruthenium carbonyl/phosphine-catalyzed reaction of 1,6-diyne **1** with HSi^tBuMe_2 and CO gave two catechol derivatives, 5-(*tert*-butyldimethylsiloxy)-1,3-dihydro-6-hydroxy-2*H*-indene-2,2-dicarboxylic acid diethyl ester (**2a**) and 5,6-bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (**2b**), or in certain cases afforded only one of these. Selected results are given in Table 1. Obviously, **2a** is the primary product and it gives **2b** by further silylation. Although, as shown in Table 2, other trialkylsilanes reacted similarly, HSi^tBuMe_2 was used throught this work because of product stability.



(6)

Table 1. $Ru_3(CO)_{12}$-Catalyzed Reaction of **1** with HSi^tBuMe_2 and CO^a

entry	**1** mmol	HSi^tBuMe_2 mmol	solvent	product[b] **2a**, %	**2b**,%
1	1	3	dioxane	52	0
2	1	3	toluene	34	0
3	1	3	CH_3CN	40	31
4	1	6	CH_3CN	0	74
5[c]	1	6	CH_3CN	0	60

[a] Reaction conditions: $Ru_3(CO)_{12}$ (0.02 mmol), PCy_3 (0.06 mmol), CO (50 atm), solvent (10 mL) at 140 °C for 20 h. [b] Isolated yields. [c] No tricyclohexylphosphine was added.

Table 2. $Ru_3(CO)_{12}$-Catalyzed Reaction of **1** with $HSiR_3$ and CO^a

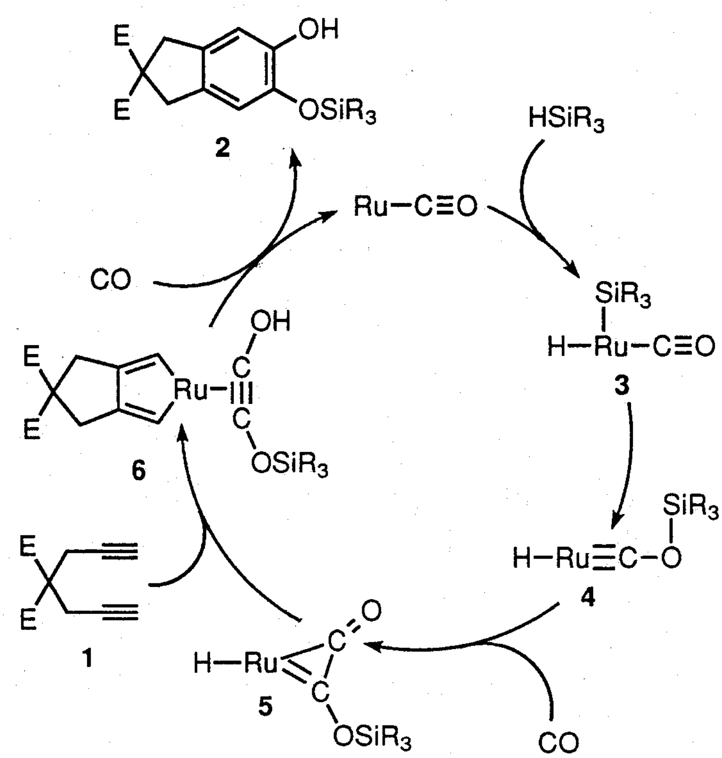
entry	$HSiR_3$	yield of **2**, %[b]
1	HSi^tBuMe_2	74, **2b**
2	$HSiEt_2Me$	71, **2c**
3	$HSiEt_3$	70, **2d**
4	$HSiPhMe_2$	55, **2e**
5	$HSi(OEt)Me_2$	25, **2f**

[a] Reaction conditions: **1** (1 mmol), $HSiR_3$ (6 mmol), $Ru_3(CO)_{12}$ (0.02 mmol), PCy_3 (0.06 mmol), CO (50 atm) in CH_3CN (10 mL) at 140 °C for 20 h. [b] Isolated yields.

A rationale for the formation of **2a** is shown in Scheme I. Firstly, oxidative addition of $HSiR_3$ to ruthenium complex produces a complex (**3**). The key catalyst species in the present reaction, siloxycarbyne-ruthenium complex (**4**), is formed by 1,3-shift of silyl group from the ruthenium atom to oxygen atom of CO ligand. The carbyne complex **4** is coupled with another CO to give siloxyhydroxyacetylene-ruthenium complex (**6**) via η^2-ketenylcomplex (**5**). Finally, the reaction of siloxyhydroxyacetylene ligand with a diyne **1** gives a monosilylated product **2a**.

Many precedents in stoichiometric reactions strongly suggest that the steps from a carbyne complex **4** to the product **2** are quite reasonable. A carbyne[7]/CO coupling (similar to steps from **4** to an oxyacetylene complex via **5**) has been well studied for tungsten.[8] Complexes bis(siloxy)acetylene Nb,[9a,b] Ta,[9a,b] V,[9c] and Mn[9d] complexes similar to **6** (but without a diyne moiety) are known. The strongest support for the Scheme I comes from a stoichiometric reaction

Scheme I

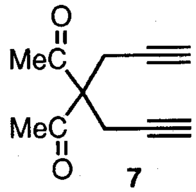
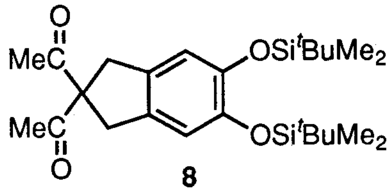
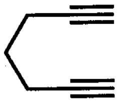
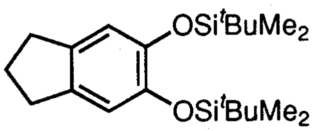
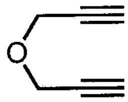
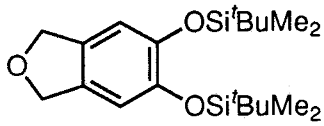
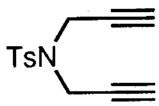
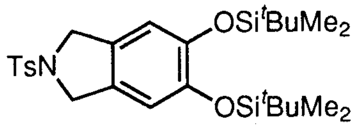
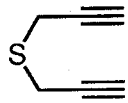
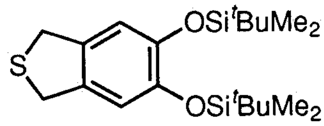
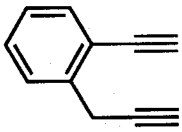
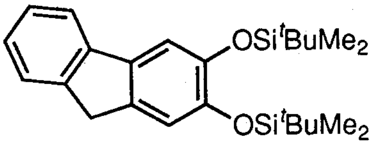
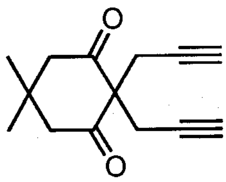
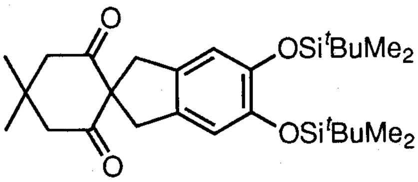
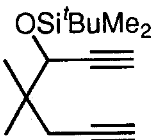
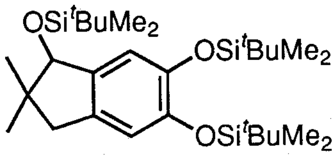


reported by Katz of methylcarbyne complexes $(CO)_4BrM\equiv CCH_3$ (M = Cr and W) with diyne to give a similar product.[10] All of these precedents suggest the intervention of a siloxy(or hydroxy[11])carbyne complex **4** in the present catalytic reaction (eq 6). Nicholas proposed, without experimental support, that a 1,3-hydrogen shift from a metal to the oxygen atom of the CO ligand in metal carbonyls might be an important step in homogeneous transition-metal-catalyzed CO reduction.[12] It is believed that the catalytic cycle outlined in Scheme I is reasonable, and it represents the first example of the oxycarbyne-based catalytic cycle.[13]

The catalytic reaction provides a useful synthetic method for fused ring catechol derivatives. For synthetic purposes, the reaction conditions of entry 4 in Table 1 are adopted since they gave only one relatively air- and moisture-stable disilylated catechol in higher yields. The representative results are shown in Table 3, and these indicate the potential utility of the present catalytic reaction.[14]

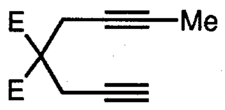
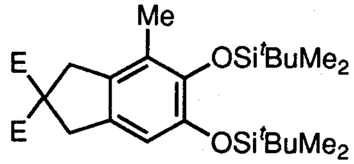
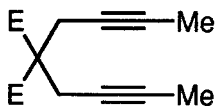
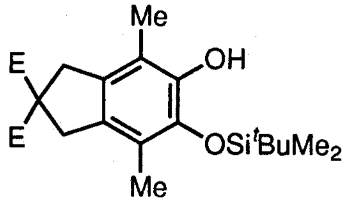
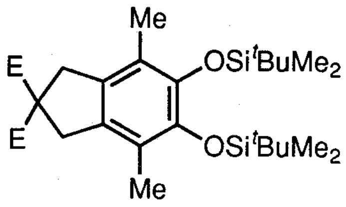
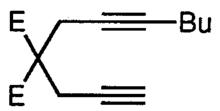
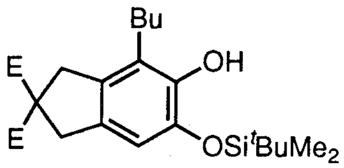
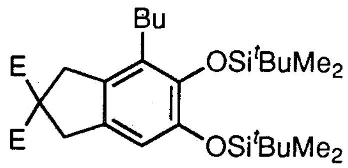
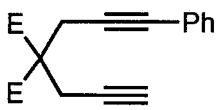
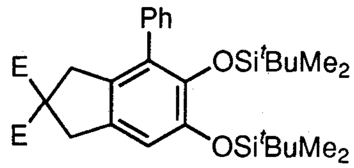
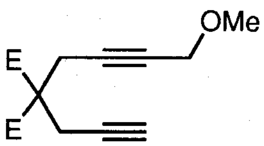
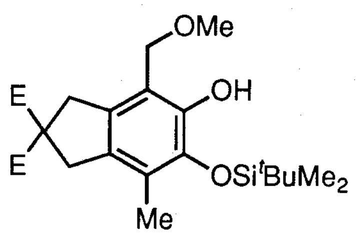
Functional groups such as ester, ketone, ether, amide, sulfide, and aromatic ring were compatible in the present reaction. The yields were not affected by the presence of methyl groups attached to the terminal acetylenic carbons (entries 9 and 10). A dimethyl substituted diyne **25** reacted

Table 3. $Ru_3(CO)_{12}$-Catalyzed Reaction of Diynes with HSi^tBuMe_2 and CO Leading to Catechols[a]

entry	diyne	product	yield, %[b]
1	 **7**	 **8**	71
2	 **9**	 **10**	45
3	 **11**	 **12**	40
4	 **13**	 **14**	45
5	 **15**	 **16**	43
6	 **17**	 **18**	60
7	 **19**	 **20**	50
8	 **21**	 **22**	71

[a] Reaction conditions: diyne (1 mmol), HSi^tBuMe_2 (6 mmol), CO (50 atm), $Ru_3(CO)_{12}$ (0.02 mmol), PCy_3 (0.06 mmol), CH_3CN (10 mL) at 140 °C for 20 h. The group E stands for COOEt. [b] Isolated yields based on the diyne.

(continued)

entry	diyne	product	yield, %
9	 **23**	 **24**	62
10	 **25**	 **26a**	6
		 **26b**	53
11[c]	 **27**	 **28a**	17
		 **28b**	32
12[c]	 **29**	 **30**	50
13	 **31**	 **32**	60

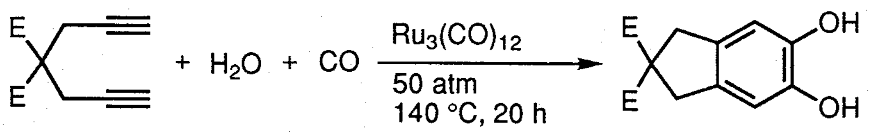
[c] $Ru_3(CO)_{12}$ (0.06 mmol) was added.

reacted similarly but gave a monosilylated catechol **26a** as a byproduct even when a prolonged time was used (entry 10). The reaction of diynes having butyl or phenyl groups on the terminal acetylenic carbon requiered more catalyst (6 mmol%, 3 times as usual) to consume the starting diyne for 20 h. The formation of a fused six-membered ring was not observed from a 1,7-diyne system.

2-3 The Ruthenium-Catalyzed Reaction of 1,6-Diynes with H_2O and Carbon Monoxide

Numerous studies have been reported for the water-gas shift reaction (WGSR) which is produce H_2, and byporuct CO_2, from H_2O and CO.[15] This equilibrium process is catalyzed by many soluble transition-metal complexes. Via the WGSR, various H_2/CO ratios of synthesis gas can be adjusted. Many mechanisms for catalysis of the WGSR have been proposed, which vary depending on the catalyst systems and reaction conditions.

In section 2-2, the ruthenium-catalyzed reaction of 1,6-diynes with $HSiR_3$/CO leading to catechol derivatives was described. This reaction is the first example of succesive two molecules of CO into diynes catalytically. This reaction was extended to the reaction with H_2 in place of $HSiR_3$ because of the similarity in reactivity between H_2 and $HSiR_3$ toward transition-metal catalyzed reactions, i.e., hydrogenation and hydrosilylation of olefins. Althrough occationally the desired catechol was obtained, the reproducibility of the reaction was very poor. After the study in detail, it was found that the presence of a trace amount of H_2O in the system caused the reaction. In this section, the ruthenium-catalyzed reaction of 1,6-diynes with H_2O and CO leading to catechol derivatives (eq 7).



(7)

1 E = COOEt **33**

Diyne **1** was reacted with H_2O and CO (50 atm) in the presence of $Ru_3(CO)_{12}$ at 140 °C for 20 h. The effect of the amount of H_2O used, CO pressure, and the reaction temperature on the yield of the product catechol **33** are shown in Table 4. The use of 2 equiv of H_2O to **1** yielded in 51% but about 10% of starting diyne was recovered (entry 1). When 3 equiv of H_2O was added, **1** was consumed completely and catechol **33** was obtained in 71% (entry 2). The use of 4 equiv gave the best result (entry 3). A decrease in CO pressure to 30 atm and a lowing the reaction temperature to 120 °C decreased in the yield of **33** (entries 5 and 6).

Table 4. $Ru_3(CO)_{12}$-Catalyzed Reaction of **1** with H_2O and CO Leading to **33**.[a]

entry	H_2O, mmol	CO, atm	temp., °C	yield, %[b]
1	6	50	140	51
2	9	50	140	71
3	12	50	140	79
4	56 (1 mL)	50	140	70
5	12	30	140	61
6	12	50	120	24 (68)[c]

[a] Reaction conditions: **1** (3 mmol), $Ru_3(CO)_{12}$ (0.06 mmol), CH_3CN (15 mL).[b] Isolated yield. [c] 48 h.

As can be seen in Table 5, CH_3CN, Dioxane, THF, and acetone as asolvent were good solvents for formation of **33**. The use of MeOH, CH_2Cl_2, and toluene as a solvent gave a lower yield, H_2O is not a good solvent.

Table 5. $Ru_3(CO)_{12}$-Catalyzed Reaction of **1** with H_2O and CO Leading to **33**.[a]

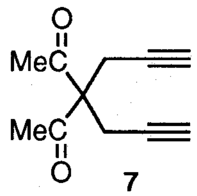
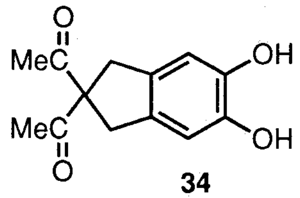
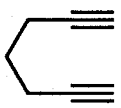
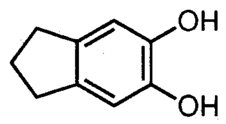
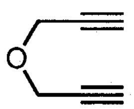
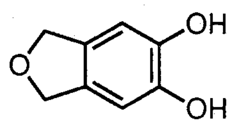
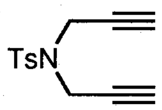
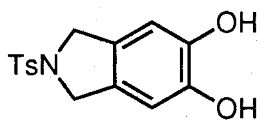
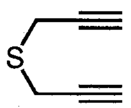
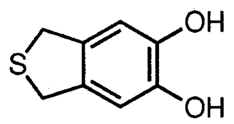
entry	catalyst	solvent	yield, %
1	$Ru_3(CO)_{12}$	CH_3CN	79
2		dioxane	83
3		THF	81
4		acetone	77
5		CH_3OH	51
6		CH_2Cl_2	46
7		toluene	38
8		H_2O	18
9	$Fe_3(CO)_{12}$	dioxane	n.r.
10	$Os_3(CO)_{12}$	dioxane	n.r.

[a] Reaction conditions: **1** (1 mmol), H_2O (4 mmol), CO (50 atm), $Ru_3(CO)_{12}$ (0.02 mmol), solvent (5 mL) at 140 °C for 20 h. [b] Isolated yields based on the diyne.

In table 6 summarized the reaction of various diynes. As the similar to the reaction of diynes with $HSiR_3/CO$, the functionarities such as ester, ketone, oxygen, amide, sulfur, and aromatic ring are compatible in the present reaction. Methyl groups attached to terminal acetylenic carbon did not affected to the product yields. The reaction of diynes having butyl, phenyl, ethoxycarbonyl, or 2-methyl-1-propenyl groups on the terminal acetylenic carbon required more catalyst (6 mmol%, 3 times as usual) to consume the starting diyne for 20 h.

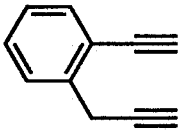
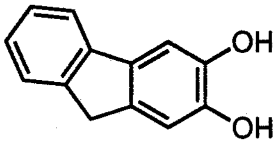
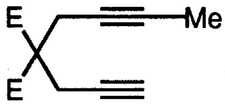
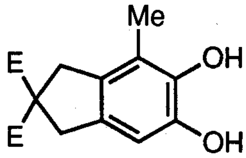
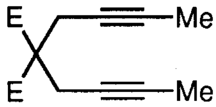
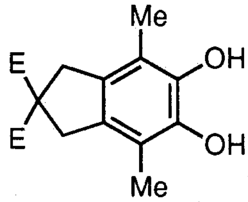
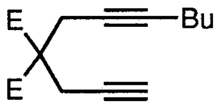
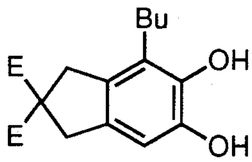
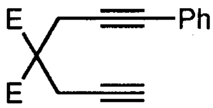
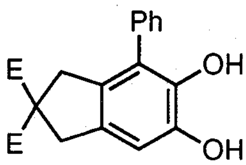
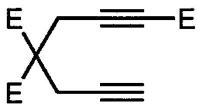
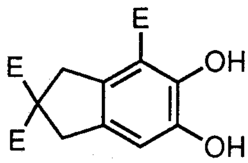
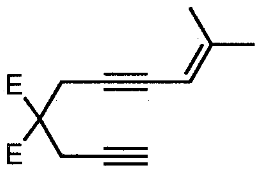
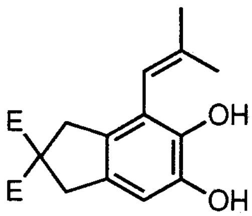
It is well-known that the reaction of acetylene with H_2O and CO in the presence of $Ru_3(CO)_{12}$ give not catechol but hydroquinone.[16] However, in the present reaction, no hydroquinone derivatives were obtained.

Table 6. $Ru_3(CO)_{12}$-Catalyzed Reaction of Diynes with H_2O and CO Leading to Catechols[a]

entry	diyne	product	yield, %[b]
1	 **7**	 **34**	77
2	 **9**	 **35**	62
3	 **11**	 **36**	62
4	 **13**	 **37**	70
5	 **15**	 **38**	58

[a] Reaction conditions: diyne (1 mmol), H_2O (4 mmol), CO (50 atm), $Ru_3(CO)_{12}$ (0.02 mmol), dioxane (5 mL) at 140 °C for 20 h. The group E stands for COOEt. [b] Isolated yields based on the diyne.

(continued)

entry	diyne	product	yield, %[b]
6	 **17**	 **39**	77
7	 **23**	 **40**	82
8	 **25**	 **41**	82
9[c]	 **27**	 **42**	60
10[c]	 **29**	 **43**	60
11[c]	 **44**	 **45**	62
12[c]	 **46**	 **47**	66

[c] $Ru_3(CO)_{12}$ (6 mmol) was added.

2-4 Experimental Section

General. Boiling points were uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL GSX-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are recorded as follows: chemical shift in ppm (δ), mutiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a HITACHI 270-50 spectrometer; absorptions are reported in reciprocal centimeters (cm^{-1}). Mass spectra (MS) were obtained on a Shimadzu GCMS-QP 1000 with ionization voltages of 70 eV. Elemental Analyses and high resolution mass spectra (HRMS) were performed by Elemental Analyses Section of Osaka University. Analytical GC was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector.

General Procedures. In a 50-mL stainless steel autoclave were placed a diyne (1 mmol), HSi^tBuMe_2 (1.0 mL, 6 mmol), $Ru_3(CO)_{12}$ (12.6 mg, 0.02 mmol), PCy_3 (16.8 mg, 0.06 mmol), CH_3CN (10 mL). The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated in an oil bath at 140 °C for 20 h. The autoclave was cooled and depressured. The solvent was removed *in vacuo*, and the disilylated product was isolated by column chromatography on silica-gel. The monosilylated cathecols **2a**, **26a**, and **28a**, and catechols **33-42**, **44**, **46** were isolated by column chromatography on silica-gel which is deactivated by 6 wt% of water.

Materials. CH_3CN was distilled from CaH_2. Carbon monoxide was purchased from Neriki gas Co. and used as received. $Ru_3(CO)_{12}$ was purchased from Aldrich Chemical Co. and used after recrystallization from hexane. *tert*-Butyldimethylsilane was purchased from Aldrich Chemical Co. and distilled from CaH_2. 1,6-Heptadiyne was purchased from Tokyo Kasei Kogyo Co. and distilled from CaH_2.

Preparation of 4,4-Di(ethoxycarbonyl)-1,6-heptadiyne (1). Na (3.634 g, 158 mmol) was added to dry EtOH (70 mL) by portions and the mixture was stirred until Na was disappeared. Diethyl malonate (9.706 g, 60 mmol) was added dropwise over 15 min. The mixture was stirred for 30 min. Propargyl bromide (21.609 g, 158 mmol) was added over 1 h and then the mixture was warmed at 70 °C for 5 h. After cooling the reaction mixture, the volatiles were removed *in vacuo*. Water (100 mL) was added to the residue. The aqueous layer was extracted with Et_2O (50 mL x 4) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated and **1** (10.621 g, 75%) was obtained by distillation under reduced pressure (92-93 °C/3 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.23 (t, J = 7.0 Hz, 6H, CH_3), 2.02 (t, J = 2.4 Hz, 1H, CH), 2.99 (d, J = 2.4 Hz, 4H, CCH_2), 4.23 (q, J = 7.0 Hz, 4H, OCH_2).

Preparation of 4,4-Di(1-oxoethyl)-1,6-heptadine (7). Na (3.400 g, 148 mmol) was added to dry EtOH (70 mL) by portions and the mixture was stirred until Na was disappeared. Pentan-2,4-dione (6.823 g, 55 mmol) was added dropwise over 15 min. The mixture was stirred for 30 min. Propargyl bromide (21.713 g, 183 mmol) was added over 1 h. The mixture was warmed at 70 °C for 5 h. After cooling the reaction mixture, the volatiles were removed *in vacuo*. Water (100 mL) was added to the residue. The aqueous layer was extracted with Et_2O (50 mL x 4) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated and **7** (6.785 g, 70%) was obtained by distillation under reduced pressure (69-71 °C/2 mmHg). ^{1}H NMR ($CDCl_3$): δ 2.02 (t, J = 2.7 Hz, 2H, CH), 2.18 (s, 6H, CH_3), 2.99 (d, J = 2.7 Hz, 4H, CH_2).

Preparation of Dipropargyl Ether (11).[17] To a suspension of NaH (1.009 g, 25.2 mmol) in THF (20 mL) at -78 °C, was added propargyl alcohol (1.223 g, 21.8 mmol) in THF (6 mL) dropwise over 10 min. The mixture was stirred for 30 min at -78 °C, and then for 20 min at 0 °C. The mixture was cooled again at -78 °C and propargyl bromide (2.678 g, 22.5 mmol) in THF (14 mL) was added over 5 min. The mixture was warmed to room temperature and allowed to stand overnight. After quenching by water (20 mL), the aqueous layer was extracted with Et_2O (20 mL x 3) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo*, **11** (1.410 g, 69%) was isolated by distillation under reduced pressure (51-54 °C/60 mmHg). ^{1}H NMR ($CDCl_3$): δ 2.45 (t, J = 2.4 Hz, 2H, CH), 4.26 (d, J = 2.4 Hz, 4H, CH_2).

Preparation of *N*,*N*-Dipropargyl-*p*-toluenesulfonamide (13) and *N*-Propargyl-*p*-toluenesulfonamide (13').[18] A mixture of *p*-toluenesulfonamide (25.604 g, 149.5 mmol), K_2CO_3 (21.006 g, 152.0 mmol), and propargyl bromide (9.817 g, 82.5 mmol) in CH_3CN (100 mL) was warmed at 60 °C for 20 h. The precipitate was filtered and the filtrate was evaporated. **13** (6.897 g, 68%) and **13'** (3.021 g, 17%) were isolated by column chromatography on silica-gel. **13**: A white solid. R_f 0.31 (hexane/AcOEt = 5/1). ^{1}H NMR ($CDCl_3$): δ 2.15 (t, J = 2.3 Hz, 2H, CH), 2.43 (s, 3H, CH_3), 4.16 (d, J = 2.3 Hz, 4H, CH_2), 7.32 (d, J = 9.4 Hz, 2H, Ph), 7.77 (d, J = 9.4 Hz, 2H, Ph). **13'**: A white solid. R_f 0.16 (hexane/AcOEt = 2/1). ^{1}H NMR

($CDCl_3$): δ 2.15 (t, J = 2.3 Hz, 2H, CH), 2.43 (s, 3H, CH_3), 3.83 (dd, J = 2.3, 5.9 Hz, 2H, CH_2), 4.60 (br, 1H, NH), 7.33 (d, J = 9.4 Hz, 2H, Ph), 7.77 (d, J = 9.4 Hz, 2H, Ph).

Preparation of Dipropargyl Sulfide (15).[19] To a solusion of propargyl bromide (20.784 g, 174.7 mmol) in MeOH (20 mL), was added NaS•$9H_2O$ (20.555 g, 85.6 mmol) in MeOH (20 mL) dropwise over 1 h. The mixute was stirred for 4 h. The volatiles were removed *in vacuo* and the residue was extracted with Et_2O (100 mL x 3). After drying over $MgSO_4$ and filtration, the solvent was evaporated. **15** (4.439 g, 47%) was obtained by distillation under reduced pressure (63-65 °C/20 mmHg). ^1H NMR ($CDCl_3$): δ 2.26 (t, J = 2.4 Hz, 2H, CH), 3.43 (d, J = 2.4 Hz, 4H, CH_2).

Preparation of 1-Ethynyl-2-(2-propynyl)benzene (17). (i) Preparation of 2-bromobenzyl iodide.[20] To a solusion of PBr_3 (4.35 mL, 46 mmol) in benzene (4.6 mL) at 0 °C, was added pyridine (2.52 mL, 31 mmol) in benzene (2.9 mL) dropwise over 5 min. The mixture was stirred for 20 min. 2-Iodobenzyl alcohol (30.010 g, 128 mmol) was added by three portions at -10 °C (in an ice-salt bath). The mixture was allowed to stand for 2 days at room temperature, and then was refluxed for 2 h. After cooling to room temperature, 5% HCl (40 mL) and $CHCl_3$ (60 mL) were added. The organic layer was washed quickly with 5% NaOH (50 mL x 2) and water (50 mL x 2). After drying over $MgSO_4$, evaporation of the solvent afforded 2-bromobenzyl iodide (33.360 g, 88%). ^1H NMR ($CDCl_3$): δ 4.60 (s, 2H, CH_2), 6.98 (dt, J = 1.6, 7.6 Hz, 1H, CH), 7.31 (t, J = 7.6 Hz, 1H, CH), 3.43 (dd, J = 1.6, 7.8 Hz, 1H, CH), 7.85 (d, J = 7.8 Hz, 1H, CH).

(ii) Preparation of 2-(3-trimethylsilyl-2-propynyl)iodobenzene.[21] To a suspension of magnesium (1.100 g, 45.2 mmol) in THF (3 mL), was added six drops of ethyl bromide. After starting the reaction, THF (7 mL) was added to the mixture. Ethyl bromide (4.577 g, 42.0 mmol) in THF (10 mL) was added dropwise over 30 min. The solution was warmed at 40 °C for 30 min. After cooling to room temperature, trimethylsilylacetylene (4.116 g, 41.9 mmol) was added dropwise over 30 min. The mixture was stirred over 30 min. THF (10 mL) was added to the mixture and the resulting THF solution (1.45 M) was added to a suspension of CuBr•Me_2S (0.411 g, 2.00 mmol) in THF (5 mL) by cannula. The mixture was stirred over 30 min. 2-Bromobenzyliodide (12.172 g, 41.0 mmol) in THF (8 mL) was added to the suspension. The mixture was refluxed over 3 days. The mixture was cooled and poured onto saturated NH_4Cl (50 mL). The mixture was stirred for 30 min. The aqueous layer was extracted with Et_2O (200 mL x 3). The combined organic layers were washed with water (100mL x 2) and dried over $MgSO_4$. The solvent was removed *in vacuo* and 2-(3-trimethylsilyl-2-propynyl)iodobenzene (6.419 g, 50%) was isolated by distillation under reduced pressure (128-130 °C/2 mmHg). ^1H NMR ($CDCl_3$): δ 0.25 (s, 9H, $SiCH_3$), 3.67 (s, 2H, CH_2), 6.95 (t, J = 7.4 Hz, 1H, CH), 7.36 (t, J = 7.4 Hz, 1H, CH), 3.43 (d, J = 8.0 Hz, 1H, CH), 7.85 (d, J = 8.0 Hz, 1H, CH).

(iii) Preparation of 1-ethynyl-2-(2-propynyl)benzene (**17**).[22] A solution of 2-(3-trimethylsilyl-2-propynyl)iodobenzene (6.419 g, 20.0 mmol), trimethylsilylacetylene (2.376 g, 24.2 mmol), $PdCl_2(PPh_3)_2$ (0.277g, 0.39 mmol), and CuI (0.040 g, 0.21 mmol) in pyperidine (70 mL) was stirred at room temperature for 10 h. The mixture was filtered with Celite and the volatiles were removed *in vacuo*. To the residue were added KF (92.370 g, 40.8 mmol), H_2O (1.45 mL, 80.6 mmol), and DMF (40 mL). The mixture was stirred for 5 h at room temperature and then poured onto 3N HCl (100 mL). The mixture was extracted with hexane (150 mL x 3). The organic layer was washed with 3N HCl (100 mL x 2), saturated $NaHCO_3$ (100 mL), water (100 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo*, **17** (0.959 g, 38%) was isolated by distillation under reduced pressure (73-75 °C/5 mmHg). ^1H NMR ($CDCl_3$): δ 2.22 (t, J = 2.7 Hz, 1H, ≡CH), 3.33 (s, 1H, ArC≡CH), 3.80 (d, J = 2.7 Hz, 2H, CH_2), 7.23-7.62 (c, 4 H, Ar).

Preparation of 5,5-Dimethyl-1,3-dioxo-2,2-di(2-propynyl)cyclohexane (19).[23] A solution of propargyl bromide (16.410 g, 137.9 mmol), dimedone (9.034 g, 64.4 mmol), and K_2CO_3 (18.703 g, 135.3 mmol) in acetone (180 mL) was refluxed for 20 h. After cooling to room temperature, the white precipitate was filtered and washed with acetone (20 mL). The volatiles were removed *in vacuo*. The residue was dissolved in Et_2O (20 mL) and the solution was stored in the refrigerator for 3 days. The white precipitate **19** (6.495 g, 47%) was filtered and dried *in vacuo*. ^1H NMR ($CDCl_3$): δ 1.06 (s, 6H, CH_3), 2.07 (d, J = 2.7 Hz, 2H, CH), 2.67 (d, J = 2.7 Hz, 4H, CH_2), 2.69 (s, 4H, CH_2CO).

Preparation of 4,4-Dimethyl-3-*tert*-buthyldimethylsiloxy-1,6-heptadiyne (21). (i) Preparation of dicyclohexyl-2-methyl-1-propenylamine.[24] To a round-bottomed flask equipped with a Dean-Stark apparatus, were placed isobutyraldehyde (72.305 g, 1.00 mol), dicyclohexylamine (181.430 g, 1.00 mol), *p*-toluenesulfonic acid (1.080 g), and benzene (200 mL). The mixture was heated at 100 °C. After 5 days the mixture was cooled and the volatiles were removed *in vacuo*. Dicyclohexyl-2-methyl-1-propenylamine (111.720 g, 47%) was obtained by distillation under reduced pressure (101-104 ° C/1 mmHg). Dicyclohexyl-2-methy-1-propenylamine was used immediately since it is labile in air.

(ii) Preparation of 2,2-Dimethyl-4-pentynal.[25] A mixture of dicyclo-hexyl-2-methyl-1-propenylamine (43.227 g, 180 mmol) and propargyl bromide (29.927 g, 250 mmol) in CH_3CN (50 mL) was warmed at 45 °C for 36 h. The volatlies were removed *in vacuo* and then 10 % KOH (240 mL) was added to the residue. the mixture was stirred vigorously at room temperature for 2.5 h. The aqueous layer was extracted with Et_2O (10 mL x 3). The combined organic layers were washed with saturated NaCl (10 mL x 4) and dried over Na_2SO_4. 2,2-Dimethyl-4-pentynal (9.182 g, 46%) was obtained by distillation (132-134 °C). ^1H NMR ($CDCl_3$): δ 1.17 (s, 6H, CH_3), 2.02 (t, J = 2.4 Hz, 1H, CH), 2.34 (d, J = 2.4 Hz, 2H, CH_2), 9.53 (s, 1H, CHO).

(iii) Preparation of 4,4-dimethyl-1,6-heptadiyn-3-ol.[26] To ethynyl magnesium bromide (200 mL in THF, 100 mmol), was added 2,2-dimethylpentynal (9.182 g, 83.4 mmol) in THF (50 mL) dropwise over 30 min. The mixture was allowed to stand for 2.5 h at room temperature. After quenching by water (100 mL), 12N HCl (10 mL) was added to the mixture. The aqueous layer was extracted with Et_2O (10 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$ (10 mL x 3) and dried over $MgSO_4$. After filtration and evaporation of the solvent, 4,4-dimethyl-1,6-heptadiyn-3-ol (7.350 g, 65%) was gained by distillation under reduced pressure (95-97 °C/30 mmHg). ^1H NMR ($CDCl_3$): δ 1.08 (s, 3H, CH3), 1.10 (s, 3H, CH_3), 2.02 (t, J = 2.7 Hz, 1H, ≡CH), 2.03 (br, 1H, OH), 2.23 (dd, J = 2.7, 16.7 Hz, 1H, CH_2), 2.40 (d, J = 2.7, 16.7 Hz, 1H, CH_2), 2.48 (d, J = 2.2 Hz, 1H, ≡CH), 4.28 (d, J = 2.2 Hz, 1H, CH).

(iv) Preparation of 4,4-dimethyl-3-tert-buthyldimethylsiloxy-1,6-heptadiyne (**21**).[27] To a mixture of 4,4-dimethyl-1,6-heptadiyn-3-ol (3.420 g, 25.1 mmol) and triethylamine (3.5 mL, 25.1 mmol) in CH_2Cl_2 (20 mL), was added $^tBuMe_2SiOTf$ (5.8 mL, 25.3 mmol) dropwise over 5 min. The mixture was stirred for 24 h at room temperature. Water (50 mL) was added. The aqueous layer was extracted with Et_2O (10 mL x 3), and the combined organic layers were washed with saturared $NaHCO_3$ (50 mL x 2). After drying over $MgSO_4$, **21** (5.948 g, 95%) was isolated by distillation under reduced pressure (70-72 °C/6 mmHg). ^1H NMR ($CDCl_3$): δ 0.12 (s, 3H, $SiCH_3$), 0.16 (s, 3H, $SiCH_3$), 0.90 (s, 9H, $SiC(CH_3)_3$), 1.04 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.98 (t, J = 2.7 Hz, 1H, ≡CH), 2.19 (dd, J = 2.7, 16.5 Hz, 1H, CH_2), 2.28 (dd, J = 2.7, 16.5 Hz, 1H, CH_2), 2.37 (d, J = 2.2 Hz, 1H, ≡CH), 4.21 (d, J = 2.2 Hz, 1H, CH).

Preparation of 4,4-Di(ethoxycarbonyl)-1,6-octadiyne (23). (i) Preparation of ethyl 2-(2-ethoxycarbonyl)-4-pentynate. Na (11.495 g, 0.5 mol) was added to dry EtOH (400 mL) by portions and the mixture was allowed to stand until Na was dissolved. Diethyl malonate (80.085 g, 0.5 mol) in EtOH (100 mL) was added dropwise over 1 h and then the mixture was stirred for 1 h. Propargyl bromide (59.485 g, 0.5 mol) in EtOH (100 mL) was added dropwise over 1 h. After stirring for 12 h, the volatiles were removed *in vacuo*. To the residue were added Et_2O (200 mL) and water (100 mL). The aqueous layer was extracted with Et_2O (100 mL x 2) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo*, ethyl 2-(2-ethoxycarbonyl)-4-pentynate (30.811 g, 32%) was isolated by distillation under reduced pressure using a 20 cm-Hempel column (98-99 °C/12 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.28 (t, J = 7.2 Hz, 6H, CH_3), 2.01 (t, J = 2.7 Hz, 1H, CH), 2.78 (dd, J = 2.7 Hz, 7.6 Hz, 2H, CH_2), 3.56 (t, J = 7.6 Hz, 1H, CH), 4.23 (q, J = 7.2 Hz, 2H, CH_2O), 4.30 (q, J = 7.2 Hz, 2H, CH_2O).

(ii) Preparation of 1-bromo-2-butyne.[28] To a solusion of 2-butyne-1-ol (14.370g, 210 mol) and pyridine (0.43 mL, 0.053 mmol) in Et_2O (110 mL), was added PBr_3 (8.2 mL, 86 mmol) in Et_2O (25 mL) dropwise over 1 h. The mixture was refluxed for 2 h. After cooling to room temperature, the mixture was poured onto ice (*ca.* 150 g). The organic layer was washed with saturated $NaHCO_3$ (100 mL x 2) and dried over $MgSO_4$. The solvent was removed *in vacuo*, and 1-bromo-2-butyne (15.143 g, 54%) was obtained by distillation under reduced pressure (52-53 °C/50 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.88 (t, J = 2.4 Hz, 3H, CH_3), 3.90 (q, J = 2.4 Hz, 2H, CH_2).

(iii) Preparation of 4,4-di(ethoxycarbonyl)-1,6-octadiyne (**23**). Na (0.700 g, 30.4 mmol) was added to dry EtOH (25 mL) by portions and the mixture was stirred until Na was dissloved. Ethyl 2-(2-ethoxycarbonyl)-4-pentynate (3.970 g, 20.0 mmol) was added over 10 min. The mixture was stirred for 1 h. 1-Bromo-2-butyne (4.594 g, 34.5 mmol) was added dropwise over 10 min and the mixture was stirred for 12 h. The volatiles were removed *in vacuo*. Water (25 mL) was added to the mixture. The aqueous layer was extracted with Et_2O (50 mL x 2) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo*, **23** (2.841g, 57%) was isolated by distillation under reduced pressure (114-116 °C/2 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 6H, CH_3), 1.75 (t, J = 2.6 Hz, 3H, CCH_3), 2.01 (t, J = 2.7 Hz, 1H, CH), 2.92

(q, J = 2.6 Hz, 2H, CH_2), 2.97 (d, J = 2.7 Hz, 2H, CH_2), 4.22 (q, J = 7.1 Hz, 4H, OCH_2)

Preparation of 5,5-Di(ethoxycarbonyl)-2,7-nonadiyne (25). Na (0.926 g, 40.3 mmol) was added to dry EtOH (20 mL) by portions and the mixture was stirred until Na was disappeared. Diethylmalonate (2.593 g, 16.2 mmol) was added dropwise over 10 min and the mixture was allowed to stand for 1 h. 1-Bromo-2-butyne (6.368 g, 47.9 mmol) was added dropwise over 10 min. After stirring for 12 h, the volatiles were removed *in vacuo* . Et_2O (50 mL) and water (50 mL) were added to the residue. The aqueous layer was extracted with Et_2O (50 mL x 2) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo* and **25** (2.538 g, 60%) was isolated by distillation under reduced pressure (115-117 °C/2 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 7.1 Hz, 6H, CH_3), 1.74 (t, J = 2.6 Hz, 6H, CCH_3), 2.90 (q, J = 2.6 Hz, CH_2), 4.21 (q, J = 7.1 Hz, 4H, OCH_2).

Preparation of 4,4-Di(ethoxycarbonyl)-1,6-undecadiyne (27). (i) Preparation of 2-heptyn-1ol.[29] To a solusion of 1-hexyne (7.46 mL, 65 mmol) in Et_2O (270 mL) at -78 °C, (in a dry ace-acetone bath), was added *n*-BuLi (44 mL, 71 mmol, 1.6 M in hexane) dropwise over 10 min. After 10 min, the mixture was warmed to 0 °C and kept for 30 min. The mixture was cooled again to -78 °C, the suspension of dry paraformaldehyde (3.000 g, 100 mmol) in Et_2O (10 mL) was added via cannula. The mixture was warmed to 0 °C and allowed to stand for 1 h. After quenching by water (200 mL), the aqueous layer was extracted with Et_2O (150 mL x 3). The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, 2-heptyn-1-ol (6.186 g, 85%) was obtained by distillation under reduced pressure. ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, J = 7.4 Hz, CH_3), 1.29-1.62 (c, 5H, $CH_3CH_2CH_2$ and OH), 2.22 (m, 2H, CH_2CH_2C), 4.25 (m, 2H, CH_2OH).

(ii) Preparation of 1-bromo-2-heptyne. 2-Heptyn-1-ol was treated by the same procedure described in the preparation of 1-bromo-2-butyne to give 1-Bromo-2-heptyne (66 °C/17 mmHg, 93%) . ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, J = 7.1 Hz, CH_3), 1.25-1.61 (c, 4H, $CH_3CH_2CH_2$), 2.25 (m, 2H, CH_2CH_2C), 3.93 (t, J = 2.2 Hz, 2H, CH_2Br).

(iii) Preparation of 4,4-di(ethoxycarbonyl)-1,6-undecadiyne (**27**).[30] To a suspension of NaH (1.5 g, 37.5 mol) in THF (90 mL) and DMF (30 mL) at 0 °C, was added ethyl 2-(2-ethoxy-carbonyl)-4-pentynate (4.797g, 24.2 mmol) dropwise. The mixture was stirred for 1 h. 1-Bromo-2-heptyne (5.800 g, 32.4 mol) in THF (10 mL) was added dropwise. The mixture was stirred for 40 min. The reaction was quenched by water (5 mL). Et_2O (20 mL) and hexane (20 mL) were then added and the mixture was stirred for 30 min. The organic layer was washed with water (50 mL x 2). The combined aqueous layers were extracted with a 1 : 1 mixture of Et_2O and hexane (200 mL x 8). After drying over $MgSO_4$ and filtration, the volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica-gel deactivated with 6% water. **27** (6.755 g, 95%) was obtained after evaporation of required fractions. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.23 (t, J = 7.1 Hz, 6H, CH_3), 1.41-1.26 (c, 4H, CH_2), 2.00 (t, J = 2.7 Hz, 1H, C≡CH), 2.12 (m, 2H, C≡CH_2CH_2), 2.96 (c, 4H, CCH_2), 4.21 (q, J = 7.1 Hz, OCH_2).

Preparation of 4,4-Di(ethoxycarbonyl)-1-phenyl-1,6-heptadiyne (25). (i) Preparation of 3-bromo-1-phenyl-1-butyne. 3-Bromo-1-phenyl-1-butyne was prepared from phenylacetylene according to the precedent procedure for 1-bromo-2-heptyne. 3-Bromo-1-phenyl-1-butyne: bp 115 °C/5 mmHg, 70%. ^{1}H NMR ($CDCl_3$): δ 4.17 (s, 2H, CH_2), 7.30-7.46 (c, 5H, Ph). 1-Phenyl-1-propyn-3-ol: ^{1}H NMR ($CDCl_3$): δ 2.01 (br, 1H, OH), 4.49 (s, 2H, CH_2), 7.29-7.45 (c, 5H, Ph).

(ii) Preparation of 4,4-di(ethoxycarbonyl)-1-phenyl-1,6-heptadiyne (**25**). To a suspension of NaH (1.7 g, 42.5 mol) in THF (100 mL) and DMF (33 mL) at 0 °C, was added ethyl 2-(2-ethoxycarbonyl)-4-pentynate (5.290 g, 26.7 mmol) dropwise. The mixture was stirred for 1 h. 3-Bromo-1-phenyl-1-propyne (5.260 g, 26.7 mmol) in THF (10 mL) was added dropwise and the resulting mixture was stirred for 40 min. The reaction was quenched by water (5 mL). Et_2O (20 mL) and hexane (20 mL) were then added and the mixture was stirred for 30 min. The organic layer was washed with water (50 mL x 2), and the combined aqueous layers were extracted with a 1 : 1 mixture of Et_2O and hexane (200 mL x 8). After drying over $MgSO_4$ and filtration, the volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica-gel deactivated with 6% water. **27** (7.560 g, 91%) was obtained after evapolation of required fractions. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, J = 7.1 Hz, 6H, CH_3), 2.04 (t, J = 2.6 Hz, 1H, C≡CH), 3.05 (d J = 2.6 Hz, 2H, CH_2C≡CH), 3.21 (s, 2H, CH_2≡CPh), 4.25 (q, J = 7.1 Hz, 4H, OCH_2), 7.28-7.37 (c, 5H, Ph).

Preparation of 5,5-Di(ethoxycarbonyl)-1-(methoxymethyl)-2,7-heptadiyne (29). (i) Preparation of 2-butyn-1,4-diol monomethyl ether.[31] To a solusion of NaOH (23.990 g, 1.00 mol) and 2-butyn-1,4-diol (40.144 g, 0.466 mol) in water (100 mL), was added Me_2SO_4 (31.017 g, 0.246 mol) dropwise over 2 h. The mixture was warmed to 80 °C and kept for 2 h. The mixture was concentrated to 50 mL and the product was extracted with Et_2O (100 mL x 5). The Et_2O solution was washed with saturated NH_4Cl (150 mL x 2) and dried over $MgSO_4$. 2-Butyn-1,4-diol monomethyl ether (8.477 g, 18%) was isolated by distillation under reduced pressure (74-75 °C/5 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.91 (br, 1H, OH), 3.38 (s, 3H, CH_3), 4.13 (t, J = 1.9 Hz, 2H, CH_2), 4.31 (t, J = 1.9 Hz, 2H, CH_2).

(ii) Preparation of 1-bromo-4-methoxy-2-butyne. 2-Butyn-1,4-diol monomethyl ether was treated by the same procedure described in the preparation of 1-bromo-2-butyne to give 1-bromo-4-methoxy-2-butyne (51-53 °C/5 mmHg, 70%). ^{1}H NMR ($CDCl_3$): δ 3.38 (s, 3H, CH_3), 3.95 (t, J = 1.9 Hz, 2H, CH_2), 4.15 (t, J = 1.9 Hz, 2H, CH_2).

(iii) Preparation of 5,5-di(ethoxycarbonyl)-1-(methoxymethyl)-2,7-heptadiyne. To a suspension of NaH (1.440 g, 36.0 mol) in THF (100 mL) and DMF (35 mL) at 0 °C, was added ethyl 2-(2-ethoxycarbonyl)4-pentynate (5.986g, 30.2 mmol) dropwise. The mixture was stirred for 1 h. 1-Bromo-4-methoxy-2-butyne (7.433 g, 45.7 mol) in THF (25 mL) was added dropwise to the mixtrure and the resulting mixture was stirred 1 h. The volatiles were removed *in vacuo,* and to the residue were added Et_2O (100 mL) and hexane (100 mL). The aqueous layer was extracted with Et_2O (100 mL x 3). The combined organic layers were washed with water (50 mL x 2) and dryied over $MgSO_4$. After the filtration, the solvents were removed *in vacuo* and **29** (5.876 g, 69%) was obtained by distillation under reduced pressure (120-122 °C/1 mmHg). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 6H, CH_3), 2.02 (t, J = 2.7 Hz, 1H, CH), 2.98 (d, J = 2.7 Hz, 2H, $CH_2{\equiv}CH$), 3.04 (t, J = 2.7 Hz, 1H, $CH_2{\equiv}C$), 3.34 (s, 3H, OCH_3), 4.05 (t, J = 2.7 Hz, 2H, CH_2OCH_3), 4.22 (q, J = 7.1 Hz, OCH_2).

Preparation of 1,4,4-Tri(ethoxycarbonyl)-1,6-heptadiyne (44). (i) Preparation of 3-ethoxycarboyl-2-propyn-1-ol. 3-Ethoxycarboyl-2-propyn-1-ol tetrahydropyranyl ether was treated by the same procedure described in the preparation of 1-bromo-2-butyne, followed by deprotection to give 3-ethoxycarboyl-2-propyn-1-ol (80 °C/1 mmHg, 80%). ^{1}H NMR ($CDCl_3$): δ 1.32 (t, J = 7.3 Hz, 3H, CH_3), 1.89 (t, J = 6.5 Hz, 1H, OH), 4.25 (q, J = 7.3 Hz, 2H, OCH_2), 4.40 (d, J = 6.5 Hz, 2H, CH_2).

(ii) Preparation of 1-bromo-3-ethoxycarbony-2-propyne.[32] To a solusion of PPh_3 (31.860 g, 122 mmol) in CH_2Cl_2 (700 mL) was added Br_2 (19.401 g, 122 mmol) in CH_2Cl_2 (300 mL) by two portions. After stirring for 10 min, Et_3N (16.107 g, 122 mmol) was added. 3-Ethoxycarboyl-2-propyn-1-ol (12.974 g, 101 mmol) in CH_2Cl_2 (300 mL) was added over 15 min. After quenching by water (500 mL), The organic layer was washed with saturated $NaHCO_3$ (500 mL), water (500 mL), and saturated NaCl (500 mL). The volatiles were removed *in vacuo*, PPh_3O was filtered off and washed with hexane (20 mL). Evaporation of hexane gained 1-bromo-3-ethoxycarbony-2-propyne (19.351 g, 79%). ^1H NMR ($CDCl_3$): δ 1.25 (t, J = 7.0 Hz, 3H, CH_3), 3.90 (s, 1H, CH_2), 4.18 (q, J = 7.0 Hz, 4H, OCH_2).

(iii) Preparation of 1,4,4-tri(ethoxycarbonyl)-1,6-heptadiyne (**44**).[33] To a suspension of NaH (1.301 g, 33.0 mol) in THF (100 mL) and DMF (50 mL), was added ethyl 2-(ethoxycarbonyl)-4-pentynate (4.950, 25.0 mmol) in THF (30 mL) and DMF (10 mL) dropwise over 30 min. The mixture was stirred for 1 h. The mixture was transfered by cannula into a round-bottomed flask containing a suspension of $CeCl_3$ (13.320 g, 54.0 mmol) in THF (50 mL) at 0°C. The mixture was stirred for 30 min at 0°C and then for 30 min at room temperature. The mixture was cooled again at 0 °C and 1-bromo-3-ethoxycarbonyl-2- propyne (5.203 g, 27.1 mmol) in THF (10 mL) and DMF (20 mL) was added to the mixture over 30 min. The mixture was allowed to stand overnight. Water (200 mL), Et_2O (100 mL), and hexane (100 mL) were added. The organic layer was washed with water (100 mL), and the combined aqueous layers were extracted with Et_2O (100 mL x 3). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed *in vacuo*. **44** (3.752 g, 40%) was obtained by column chromatography on silica-gel. δ 1.26 (c, 9H, CH_3), 2.01 (t, J = 2.7 Hz, 1H, ≡CH), 3.03 (t, J = 2.7 Hz, 2H, CH_2≡C), 3.23 (s, 2H, CH_2≡CC), 4.22 (c, 6H, OCH_2).

Preparation of 4,4-Di(ethoxycarbonyl)-9-methyl-8-decen-1,6-diyne (46). (i) Preparaiton of 5-methyl-4-hexen-2-yn-1-ol.[34] To a suspension of 1-bromo-2-methyl-1-propene (10.01 g, 74.1 mmol), $PdCl_2(PPh_3)_2$ (0.519 g, 0.37 mmol), and CuI (0.070 g, 0.37 mmol) in Et_2NH (100 mL), was added 2-Propyn-1-ol (5.603 g, 100.0 mmol) in Et_2NH (50 mL) dropwise to the mixture over 30 min. The mixture was stirred for 1 h at room temperature and then for 1 h at 60 °C. Brine (100 mL) and Et_2O (100 mL) were added to the mixture. The aqueous layer was extracted with Et_2O (50 mL x 2). The combined organic layers were dried over $MgSO_4$. 5-methyl-4-hexen-2-yn-1-ol (6.552 g, 60%) was obtained by clumn chromatography on silica-gel.

1H NMR ($CDCl_3$): δ 1.81 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 4.42 (s, 2H, CH_2), 5.28 (s, 1H, CH).

(ii) Preparation of 1-bromo-5-methyl-4-hexen-2-yne.[35] A mixture of CBr_4 (2.830 g, 15.0 mmol), PPh_3 (4.251 g, 16.0 mmol), and 5-methyl-4-hexyn-2-yn-1-ol (1.320 g, 12.0 mmol) in Et_2O (30 mL) was stirred over 1 h. The mixture was filtered and the filtrate was washed with Et_2O (100 mL). After evaporation, 1-bromo-5-methyl-4-hexen-2-yne (1.882 g, 97%) was obtained by column chromatography on silica-gel.

(iii) Preparation of 4,4-di(ethoxycarbonyl)-9-methyl-8-decen-1,6-diyne (**46**). To a suspension of NaH (0.175 g, 4.40 mol) in THF (10 mL) and DMF (5 mL) at 0 °C, was added ethyl 2-(ethoxycarbonyl)- 4-pentynate (0.792g, 4.00 mmol) dropwise. The mixture was stirred for 30 min. 1-Bromo-5-methyl-4-hexen-2-yne (0.692 g, 4.00 mmol) in THF (10 mL) and DMF (2.5 mL) was added dropwise. The mixture was stirred for 3 h and then refluxed overnight. After cooling and quenching by saturated NaCl (50 mL), Et_2O (50 mL) was added and the aqueous layer was extracted with Et_2O (30 mL x 2). After drying over $MgSO_4$ and filtration, the volatiles were removed *in vacuo* and **46** (1.083 g, 93%) was obtained by column chromatography on silica-gel. ^{1}H NMR ($CDCl_3$): δ 1.25 (t, J = 6.9 Hz, 6H, CH_3), 1.76 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.01 (t, J = 2.7 Hz, 2H, ≡CH), 2.98 (d, J = 2.7 Hz, 2H, CH_2), 3.12 (s, 2H, CH_2), 4.21 (q, J = 6.9 Hz, 4H, OCH_2), 5.18 (s, 1H, CH).

Preparation of 4,4-Di(ethoxycarbonyl)-8,8-dimethyl-1,6-nonadiyne. (i) Preparation of 1-bromo-4,4-dimethyl-2-pentyne. 3,3-Dimethyl-1-butyne was treated by the same procedure described in the preparation of 1-bromo-2-heptyne, to give 1-bromo-4,4-dimethyl-2-pentyne (71-73 °C/26 mmHg, 71%). ^{1}H NMR ($CDCl_3$): δ 1.21 (s, 9H, CH_3), 3.93 (s, 2H, CH_2). 4,4-Dimethyl-2-pentyn-1-ol; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H, CH_3), 1.73 (br, 1H, OH), 4.25 (s, 2H, CH_2).

(ii) Preparation of 4,4-di(ethoxycarbonyl)-8,8-dimethyl-1,6-nonadiyne. To a suspension of NaH (1.700 g, 42.5 mol) in THF (100 mL) and DMF (33 mL) at 0 °C, was added 4,4-di(ethoxycarbonyl)- 1-butyne (5.445g, 27.7 mmol) dropwise and the mixture was stirred for 1 h. 1-Bromo-4,4-dimethyl-2-pentyne (4.851 g, 27.7 mmol) in THF (10 mL) was added dropwise. The mixture was stirred for 40 min. After quenching by water (5 mL), were added Et_2O (20 mL) and hexane (20 mL). The mixture was stirred for 30 min. The organic layer was washed with water (50 mL x 2), and the combined aqueous layers were extracted with a 1 : 1 mixture of Et_2O and hexane (200 mL x 8). After drying over $MgSO_4$ and filtration, the volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica-gel deactivated with 6% water. 4,4-Di(ethoxycarbonyl)-8,8-dimethyl-1,6-nonadiyne (5.413 g, 67%) was obtained after evaporation of reauired fractions. ^{1}H NMR ($CDCl_3$): δ 1.16 (s, 9H, $C(CH_3)_3$), 1.26 (t, J = 7.1 Hz, 6H, CH_3), 2.00 (t, J = 2.7 Hz, 1H, C≡CH), 2.91 (s, 2H, $CH_2C≡C(CH_3)_3$), 2.94 (d, J = 2.7 Hz, 2H, CH_2≡CH), 4.20 (q, J = 7.1 Hz, 4H, OCH_2).

Preparation of 1-(Trimethylsilyl)-4,4-di(ethoxycarbonyl)-1,6-heptadiyne. (i) Preparation of 1-bromo-3-(trimethylsilyl)-2-propyne. 2-Propyn-1-ol was treated by the same procedure described in the preparation of 1-bromo-2-heptyne, to give 1-bromo-3-(trimethylsilyl)-2-propyne (74-76 °C/29 mmHg, 50%). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 9H, $SiCH_3$), 3.91 (s, 2H, CH_2). 3-(trimethylsilyl)-2-propyn-1-ol; ^{1}H NMR ($CDCl_3$): δ 0.17 (s, 9H, $SiCH_3$), 1.66 (s, 1H, OH), 4.26 (s, 2H, CH_2).

(ii) Preparation of 1-(trimethylsilyl)-4,4-di(ethoxycarbonyl)-1,6-heptadiyne.[36] To a suspension of NaH (1.920 g, 48.0 mol) in THF (50 mL) and DMF (15 mL) at 0 °C, was added ethyl 2- (ethoxycarbonyl)-4-pentynate (7.890 g, 40.0 mmol) in THF (50 mL) and DMF (15 mL) dropwise over 1 h. The mixture was stirred for 15 min. 1-Bromo-3-(trimethylsilyl)-2-propyne (9.162 g, 48.0 mmol) in THF (50 mL) and DMF (15 mL) was added dropwise over 1 h and the resulting mixture was stirred for 3 h. The volatiles were removed *in vacuo* and to the residue were added Et_2O (100 mL) and water (100 mL). The aqueous layer was extracted with Et_2O (50 mL x 2). After drying over $MgSO_4$ and filtration, the volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica-gel deactivated with 6% water. 1-(Trimethylsilyl)-4,4-di(ethoxycarbonyl)-1,6-heptadiyne (2.891 g, 34%) was obtained after evaporation of required fractions. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H, $SiCH_3$), 1.26 (t, J = 7.1 Hz, 6H, CH_3), 2.01 (t, J = 2.7 Hz, 1H, CH), 2.96 (d, J = 2.7 Hz, 2H, CH_2), 2.99 (s, 2H, CH_2), 4.22 (q, J = 7.1 Hz, 4H, OCH_2).

5-(*tert*-Butyldimethylsiloxy)-1,3-dihydro-6-hydroxy-2*H*-indene-2,2-dicarboxylic acid diethyl ester (2a). A colorless oil; R_f 0.28 (hexane/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 6H, $SiCH_3$), 0.99 (s, 9H, $SiCCH_3$), 1.24 (t, J = 7.0 Hz, 6H, CH_3), 3.46 (s 2H, CH_2), 3.48 (s, 2H, CH_2), 4.19 (q, J = 7.0 Hz, 4H, CH_2O), 5.26 (s, 1H, OH), 6.62 (s, 1H, Ar), 6.75

(s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.34 ($SiCH_3$), 14.00 (CH_3), 18.16 (SiCCH_3), 25.72 (SiCCH_3), 40.16, 40.21 (CH_2), 60.77 (C), 61.59 (CH_2O), 110.34, 113.34, 130.89, 133.14, 141.48, 146.43 (Ar), 171.72 (C=O). IR (neat): 3548 s, 2944 s, 2864 s, 1942 w, 1738 s, 1624 m, 1602 m, 1506 s, 1472 m, 1392 m, 1366 m, 1332 s, 1248 s, 1186 s, 1158 s, 1090 m, 1008 m, 902 s, 838 s, 784 s, 698 w, 670 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 408 (5, M^+), 352 (24), 351 (100, M^+ - ^{t}Bu), 335 (16), 205 (19), 204 (30), 203 (23), 75 (36), 73 (20). Anal. Calcd for $C_{21}H_{32}O_6Si$: C,61.74; H, 7.89. Found: C, 61.55; H, 7.99.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (2b). A white solid; mp 61-62 °C. R_f 0.21 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$): δ 0.17 (s, 12H, $SiCH_3$), 0.97 (s, 18H, $SiCCH_3$), 1.24 (t, J = 7.0 Hz, 6H, CH_3), 3.46 (s 4H, CH_2), 4.19 (q, J = 7.0 Hz, 4H, CH_2O), 6.62 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.08 ($SiCH_3$), 14.02 (CH_3), 18.42 (SiCCH_3), 25.97 (SiCCH_3), 40.21 (CH_2), 60.96 (C), 61.57 (CH_2O), 116.42, 132.50, 145.97 (Ar), 171.80 (C=O). IR (KBr): 2944 s, 2868 s, 1728 s, 1616 w, 1586 w, 1506 s, 1470 s, 1444 s, 1420 m, 1366 s, 1340 s, 1252 s, 1186 m, 1096 s, 1052 m, 1006 m, 928 s, 904 s, 838 s, 780 s, 708 m, 668 m, 604 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 522 (3, M^+), 278 (10), 277 (48), 204 (10), 203 (10), 115 (13), 73 (100). Anal. Calcd for $C_{27}H_{46}O_6Si_2$: C,62.03; H, 8.87. Found: C, 61.93; H, 9.01.

5,6-Bis(diethylmethylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (2c). A colorless liquid. R_f 0.28 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$): δ 0.17 (s, 6H, $SiCH_3$), 0.70 (q, J = 7.8 Hz, 8H, $SiCH_2$), 0.97 (t, J = 7.8 Hz, 12H, $SiCH_2CH_3$), 1.24 (t, J = 7.3 Hz, 6H, CH_3), 3.46 (s, 4H, CH_2), 4.19 (q, J = 7.3 Hz, 4H, CH_2O), 6.61 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.11 ($SiCH_3$), 6.65 ($SiCH_2$), 6.76 ($SiCH_2CH_3$), 14.00 (CH_3), 40.22 (CH_2), 60.86 (C), 61.57 (CH_2O), 116.10, 132.63, 145.82 (Ar), 171.84 (C=O). IR (neat): 2958 s, 2880 s, 2738 s, 2320 w, 1734 s, 1612 w, 1586 w, 1541 w, 1502 s, 1458 m, 1419 m, 1336 s, 1238 s, 1180 m, 1095 m, 1066 m, 1002 m, 967 m, 919 m, 848 m, 799 m, 687 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 495 (12, M^+ + 1), 494 (32, M^+), 291 (24), 245 (10), 218 (11), 217 (11), 101 (13), 73 (100). Anal. Calcd for $C_{25}H_{42}O_6Si_2$: C,60.69; H, 8.56. Found: C, 60.57; H, 8.73.

5,6-Bis(triethylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (2d).

A colorless liquid. R_f 0.26 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$): δ 0.72 (q, J = 7.9 Hz, 12H, $SiCH_2$), 0.97 (t, J = 7.9 Hz, 18H, $SiCH_2CH_3$), 1.24 (t, J = 7.0 Hz, 6H, CH_3), 3.46 (s 4H, CH_2), 4.19 (q, J = 7.0 Hz, 4H, CH_2O), 6.61 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 5.70 ($SiCH_2CH_3$), 6.67 ($SiCH_2$), 14.00 (CH_3), 40.24 (CH_2), 60.90 (C), 61.55 (CH_2O), 115.85, 132.45, 145.93 (Ar), 171.84 (C=O). IR (neat): 2962 s, 2880 s, 2740 w, 2336 w, 1733 s, 1614 m, 1582 m, 1500 s, 1460 s, 1418 s, 1365 m, 1334 s, 1271 s, 1241 s, 1183 s, 1093 s, 1068 s, 1003 s, 973 s, 918 s, 849 s, 720 s cm^{-1}. MS (70 eV): m/z (relative intensity, %) 523 (14, M^+ + 1), 522 (36, M^+), 305 (31), 232 (11), 231 (11), 115 (47), 87 (100), 59 (81). HRMS Calcd for $C_{27}H_{46}O_6Si_2$ (M^+): 522.2833, Found 522.2822.

5,6-Bis(dimethylphenylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (2e). A colorless liquid. R_f 0.20 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.44 (s, 12H, $SiCH_3$), 1.22 (t, J = 7.0 Hz, 6H, CH_3), 3.39 (s 4H, CH_2), 4.17 (q, J = 7.0 Hz, 4H, CH_2O), 6.55 (s, 2H, Ar), 7.33-7.63 (c, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ -1.04 ($SiCH_3$), 13.98 (CH_3), 40.15 (CH_2), 60.72 (C), 61.57 (CH_2O), 116.17, 127.82, 129.69, 132.87, 133.48, 137.66, 145.39 (Ar), 171.77 (C=O). IR (neat): 3054 m, 2964 m, 2910 m, 2358 s, 1733 s, 1615 m, 1591 m, 1560 w, 1502 s, 1429 m, 1366 m, 1335 s, 1240 s, 1182 s, 1116 s, 1095 s, 1065 m, 1007 w, 933 s, 872 s, 830 s, 788 s 734 m, 699 s, 648 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 564 (17, M^+ + 2), 563 (45, M^+ + 1), 562 (100, M^+), 489 (21), 488 (26), 136 (13), 135 (88). HRMS Calcd for $C_{31}H_{38}O_6Si_2$ (M^+): 562.2207, Found 562.2195.

5,6-Bis(ethoxyldimethylsiloxy)-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (2f). A colorless liquid. R_f 0.19 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.23 (s, 12H, $SiCH_3$), 1.23 (t, J = 6.8 Hz, 6H, $SiOCH_2CH_3$), 1.25 (t, J = 7.3 Hz, 6H, CH_3), 3.48 (s 4H, CH_2), 3.82 (q, J = 6.8 Hz, 4H, $SiOCH_2CH_3$), 4.19 (q, J = 7.3 Hz, 4H, CH_2O), 6.76 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -2.60 ($SiCH_3$), 13.98 (CH_3), 18.22 ($SiOCH_2CH_3$), 40.16 (CH_2), 58.38 ($SiOCH_2CH_3$), 60.79 (C), 61.58 (CH_2O), 116.08, 133.19, 144.55 (Ar), 171.75 (C=O). IR (neat): 2962 s, 2880 s, 2740 w, 2336 w, 1733 s, 1614 m, 1582 m, 1500 s, 1460 s, 1418 s, 1365 m, 1334 s, 1271 s, 1241 s, 1183 s, 1093 s, 1068 s, 1003 s, 973 s, 918 s, 849 s, 720 s cm^{-1}. MS (70 eV): m/z (relative intensity, %) 500 (14, M^+ + 2), 499 (37, M^+ + 1), 498 (100, M^+), 426 (11), 425 (31), 424 (37), 277 (14), 276 (19), 231 (11), 205 (11), 204 (17), 203 (23), 133 (15), 103 (66), 77 (11), 75 (93), 59 (45). HRMS Calcd for $C_{23}H_{38}O_8Si_2$ (M^+): 498.2106, Found 498.2099.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-2,2'-2*H*-indenylidenebisethan-one (8). A white solid; mp 99-100 °C. R_f 0.25 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.17 (s, 12H, $SiCH_3$), 0.97 (s, 18H, $SiCCH_3$), 2.15 (s, 6H, CH_3), 3.38 (s, 4H, CH_2), 6.64 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.09 ($SiCH_3$), 18.43 (Si*C*CH_3), 25.94 (SiCCH_3), 26.55 (CH_3), 37.40 (CH_2), 75.08 (C), 116.67, 132.19, 146.22 (Ar), 205.29 (C=O). IR (KBr): 2940 s, 2864 m, 1720 s, 1700 s, 1616 w, 1508 s, 1476 m, 1420 m, 1394 m, 1338 s, 1310 m, 1254 s, 1206 s, 1174 m, 1104 s, 1008 w, 936s, 864 s, 838 s, 782 s, 710 w, 656 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 462 (1, M^+), 361 (13), 231 (12), 73 (100). HRMS Calcd for $C_{25}H_{42}O_4Si_2$ (M^+): 462.2602, Found 462.2609.

5,6-Bis(*tert*-butyldimethylsiloxy)-2,3-dihydro-1*H*-indene (10). A white solid; mp 62-63 °C. R_f 0.31 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 12H, $SiCH_3$), 0.98 (s, 18H, $SiCCH_3$), 2.03 (quint, J = 7.3 Hz, 2H, CH_2), 2.78 (t, J = 7.3 Hz, 4H, CH_2Ar), 6.67 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.08 ($SiCH_3$), 18.45 (Si*C*CH_3), 25.83 (CH_2), 26.01 (SiCCH_3), 32.58 (CH_2Ar), 116.65, 136.55, 145.06 (Ar). IR (KBr): 2940 s, 2860 s, 1618 w, 1580 m, 1496 s, 1476 s, 1448 m, 1418 m, 1392 m, 1364 m, 1328 s, 1290 m, 1252 s, 1202 s, 1160 s, 1088 s, 1006 m, 926 s, 902 s, 878 s, 840 s, 782 s, 688 m, 668 m, 600 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 378 (6, M^+), 321 (13), 206 (14), 205 (67), 115 (20), 75 (12), 74 (21), 73 (100). Anal. Calcd for $C_{21}H_{38}O_2Si_2$: C,66.60; H, 10.11. Found: C, 66.47; H, 10.25.

5,6-Bis(*tert*-butyldimethylsiloxy)-1*H*, 3*H*-isobenzofuran (12). A colorless oil; R_f 0.23 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 12H, $SiCH_3$), 0.98 (s, 18H, $SiCCH_3$), 4.99 (s, 4H, CH_2), 6.68 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.09 ($SiCH_3$), 18.46 (Si*C*CH_3), 25.97 (SiCCH_3), 73.49 (CH_2), 113.27, 131.55, 146.42 (Ar). IR (neat): 3048 w, 2956 s, 2864 s, 2716 w, 1772 w, 1692 w, 1624 m, 1588 m, 1502 s, 1466 s, 1426s , 1392 m, 1364 s, 1324 s, 1256 s, 120 6s, 1172 s, 1102 s, 1050 s, 1006 m, 934 s, 840 s, 782 s, 710 m, 672 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 380 (1, M^+), 324 (11), 207 (13), 73 (100). HRMS Calcd for $C_{20}H_{36}O_3Si_2$ (M^+): 380.2211, Found 380.2216.

5,6-Bis(*tert*-butyldimethylsiloxy)-2-(4-methylbenzenesulfonyl)-1*H*, 3*H*-isoindole (14). A white solid; mp 153-154 °C. R_f 0.37 (hexane/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 12H, $SiCH_3$), 0.95 (s, 12H, $SiCCH_3$), 2.41 (s, 3H, CH_3), 4.49 (s, 4H,

CH_2), 6.59 (s, 2H, Ar), 7.29 (d, J = 8.1 Hz, 2H, Ar), 7.66 (d, J = 8.1 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.12 ($SiCH_3$), 18.39 ($SiCCH_3$), 21.46 (CH_2), 25.86 ($SiCCH_3$), 53.47 (CH_2), 114.73, 127.58, 128.59, 129.72, 133.98, 143.48, 146.84 (Ar). IR (KBr): 2940 s, 2864 s, 1620 w, 1602 w, 1512 s, 1472 m, 1432 m, 1394 w, 1346 s. 1324 m, 1296 m, 1256 m, 1224 m, 1164 s, 1100 s, 1060 m, 1006 w, 930 s, 840 s, 780 s, 708 m, 664 s, 606 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 533 (M^+, 3), 478 (12), 476 (62), 360 (20), 179 (13), 73 (100). Anal. Calcd for $C_{27}H_{43}O_4SSi_2$: C, 60.74; H, 8.12; N, 2.62; S, 6.01. Found: C, 60.50; H, 8.19; N, 2.64; S, 6.05.

5,6-Bis(*tert*-butyldimethylsiloxy)-1*H*, 3*H*-isobenzothiophene (16). A white solid; mp 92-93 °C. R_f 0.28 (hexane/EtOAc = 40/1). ^1H NMR ($CDCl_3$): δ 0.19 (s, 12H, $SiCH_3$), 0.98 (s, 18H, $SiCCH_3$), 4.14 (s, 4H, CH_2), 6.68 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.10 ($SiCH_3$), 18.48 ($SiCCH_3$), 25.97 ($SiCCH_3$), 37.83 (CH_2), 116.48, 132.69, 145.80 (Ar). IR (KBr): 2932 s, 2894 s, 2858 s, 1613 m, 1580 w, 1503 s, 1474 s, 1442 m, 1404 s, 1360 m, 1322 s, 1279 w, 1249 s, 1231 s, 1200 s, 1161 m, 1094 s, 1003 m, 921 s, 903 s, 843 s, 785 s, 728 w, 676 m, 683 m, 652 w, 611 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 396 (2, M^+), 339 (12), 223 (23), 73 (100). Anal. Calcd for $C_{20}H_{36}O_2SSi_2$: C, 60.55; H, 9.15. Found: C, 60.41; H, 9.27.

2,3-Bis(*tert*-butyldimethylsiloxy)-9*H*-fluorene (18). A white solid; mp 77-78 °C. R_f 0.57 (hexane/EtOAc = 100/1). ^1H NMR ($CDCl_3$): δ 0.23 (s, 6H, $SiCH_3$), 0.24 (s, 6H, $SiCH_3$), 1.01 (s, 9H, $SiCCH_3$), 1.02 (s, 9H, $SiCCH_3$), 3.77 (s, 2H, CH_2), 7.00 (s, 1H, Ar), 7.21 (dt, J = 1.1, 7.4 Hz, 1H, Ar), 7.22 (s, 1H, Ar), 7.32 (t, J = 7.4 Hz, 1H, Ar), 7.47 (d, J = 7.4 Hz, 1H, Ar), 7.51 (d, J = 7.4 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.02 ($SiCH_3$ x 2), 18.53 ($SiCCH_3$ x 2), 26.00, 26.04 ($SiCCH_3$), 36.46 (CH_2), 112.17, 117.56, 118.89, 124.76, 125.46, 126.56, 135.15, 136.35, 141.96, 143.45, 146.25, 146.45 (Ar). IR (KBr): 3040 w, 2932 s, 2860 s, 1616 m, 1572 m, 1492 s, 1474 s, 1458 s, 1420 m, 1350 s, 1310 s, 1286 s, 1248 s, 1204 s, 1168 s, 1124 m, 990 m, 908 s, 838 s, 778 s, 722 m, 690 m, 670 m, 638 w, 614 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 426 (7, M^+), 73 (100). Anal. Calcd for $C_{25}H_{38}O_2Si_2$: C, 70.36; H, 8.98. Found: C, 70.31; H, 9.13.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-2*H*-indene-2-spiro-1'-(4,4-dimethyl)-cyclohexen-2,6-dione (20). A white solid; mp 135-136 °C. R_f 0.16 (hexane/EtOAc = 10/1). ^1H NMR ($CDCl_3$): δ 0.16 (s, 12H, $SiCH_3$), 1.01 (s, 18H, $SiCCH_3$), 1.02 (s, 6H, CH_3), 2.68 (s, 4H, CH_2CO), 3.34 (s, 4H, CH_2), 6.59 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.10 ($SiCH_3$), 18.42 (Si*C*CH_3), 25.97 (SiC*C*H_3), 28.39 (C(*C*H_3)$_2$), 30.50 (*C*(CH_3)$_2$), 38.26 (*C*H_2CO), 51.50 (CH_2), 71.88 (C), 116.30, 131.81, 146.15 (Ar), 206.47 (C=O). IR (KBr): 2934 s, 2894 m, 2858 s, 2326 w, 1728 s, 1694 s, 1609 w, 1503 s, 1473 m, 1418 m, 1389 w, 1361 m, 1335 s, 1296 m, 1251 s, 1202 s, 1168 m, 1130 w, 1098 m, 1022 w, 1003 w, 930 s, 876 s, 857 s, 834 s, 774 s, 691 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 502 (4, M^+), 445 (13), 73 (100). Anal. Calcd for $C_{28}H_{46}O_4Si_2$: C, 66.88; H, 9.22. Found: C, 66.88; H, 9.43.

2,2-Dimethyl-1,5,6-tris(*tert*-butyldimethylsiloxy)-2,3-dihydro-1*H*-indene (22). A pale yellow oil; R_f 0.14 (hexane). ^{1}H NMR ($CDCl_3$): δ 0.13 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.17 (s, 3H, $SiCH_3$), 0.18 (s, 3H, $SiCH_3$), 0.19 (s, 3H, $SiCH_3$), 0.89 (s, 3H, CH_3), 0.95 (s, 9H, $SiCCH_3$), 0.97 (s, 1H, $SiCCH_3$), 0.98 (s, 9H, $SiCCH_3$), 1.13 (s, 3H, CH_3), 2.51 (s, 2H, CH_2), 4.61 (s, 1H, CH), 6.68 (s, 1H, Ar), 6.60 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.24, -4.09, -4.04 ($SiCH_3$), 18.17, 18.40, 18.47 (Si*C*CH_3), 21.84 (CH_3), 25.95 (SiC*C*H_3), 26.68 (CH_3), 44.41, 45.91 (CH_2 or C), 83.24 (CHOSi), 116.59, 117.20, 133.63, 138.24, 145.27, 145.96 (Ar). IR (neat): 3044 w, 2960 s, 2864 s, 2716 w, 1734 w, 1616 m, 1584 m, 1498 s, 1476 s, 1446 s, 1420 s, 1392 m, 1364 s, 1336 s, 1302 s, 1256 s, 1218 s, 1174 s, 1146 s, 1114 s, 1076 m, 1006 m, 930 s, 874 s, 780 s, 718 m, 674 m, 610 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 537 (6, M^+), 406 (17), 405 (46), 350 (11), 349 (35), 233 (15), 73 (100). Anal. Calcd for $C_{29}H_{56}O_3Si_3$: C, 64.86; H, 10.51. Found: C, 65.15; H, 10.75.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-4-methyl-2*H*-indene-2,2-dicarboxylic acid diethyl ester (24). A white solid; mp 73-74 °C. R_f 0.21 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 6H, $SiCH_3$), 0.18 (s, 6H, $SiCH_3$), 0.95 (s, 9H, $SiCCH_3$), 1.01 (s, 9H, $SiCCH_3$), 1.25 (t, J = 7.0 Hz, 6H, CH_3), 2.09 (s, 3H, CH_3), 3.41 (s 2H, CH_2), 3.48 (s 2H, CH_2), 4.19 (q, J = 7.0 Hz, 4H, CH_2O), 6.50 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -3.62, -3.53 ($SiCH_3$), 14.02 (CH_3), 14.28 (CH_3), 18.54, 18.69 (Si*C*CH_3), 26.19, 26.23 (SiC*C*H_3), 39.55, 40.45 (CH_2), 60.22 (C), 61.57 (CH_2O), 113.55, 125.73, 131.53, 132.28, 143.56, 146.36 (Ar), 171.98 (C=O). IR (KBr): 2944 s, 2868 s, 1744 s, 1602 w, 1478 s, 1440 s, 1394 m, 1350 s, 1252 s, 1184 s, 1100 s, 1056 s, 1008 m, 918 s, 842 s, 780 s, 746 w, 672 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 536 (3, M^+), 479 (12), 291 (38), 73 (100). Anal. Calcd for $C_{28}H_{48}O_6Si_2$: C,62.64; H, 9.01. Found: C, 62.34; H, 9.07.

5-(*tert*-Butyldimethylsiloxy)-1,3-dihydro-4,7-dimethyl-6-hydroxy-2*H*-indene-2,2-dicarboxylic acid diethyl ester (26a). A white solid; mp 50-51 °C. R_f 0.28 (hexane/EtOAc = 20/1). ^1H NMR ($CDCl_3$): δ 0.18 (s, 6H, $SiCH_3$), 1.05 (s, 9H, $SiCCH_3$), 1.26 (t, J = 7.0 Hz, 6H, CH_3), 2.07 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.43 (s, 2H, CH_2), 3.48 (s, 2H, CH_2), 4.20 (q, J = 7.0 Hz, 4H, CH_2O), 5.06 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ -3.89, ($SiCH_3$), 12.32 (CH_3), 13.91, 14.03 (CH_3), 18.54 (Si*C*CH_3), 25.89 (SiC*C*H_3), 39.47, 39.60 (CH_2), 59.51 (C), 61.61 (CH_2O), 116.88, 120.93, 129.82, 132.07, 139.46, 144.72 (Ar), 172.04 (C=O). IR (KBr): 3488 m, 2936 m, 2860 m, 1726 s, 1462 m, 1364 m, 1326 m, 1278 s, 1248 s, 1216 s, 1188 s, 1156 m, 1088 m, 928 m, 888 m, 828 m, 778 m, 728 w, 688 w, 656 w, 600 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 436 (1, M^+), 379 (20), 378 (66), 306 (16), 305 (59), 304 (100), 277 (17), 276 (17), 275 (10), 259 (12), 233 (11), 232 (34), 231 (55), 217 (17). Anal. Calcd for $C_{23}H_{36}O_6Si$: C,63.27; H, 8.31. Found: C, 63.37; H, 8.40.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-4,7-dimethyl-2*H*-indene-2,2-dicarboxylic acid diethyl ester (26b). A white solid; mp 112-113 °C. R_f 0.19 (hexane/EtOAc = 20/1). ^1H NMR ($CDCl_3$): δ 0.06 (s, 12H, $SiCH_3$), 1.02 (s, 18H, $SiCCH_3$), 1.25 (t, J = 7.0 Hz, 6H, CH_3), 2.06 (s, 6H, CH_3), 3.44 (s, 4H, CH_2), 4.20 (q, J = 7.0 Hz, 4H, CH_2O). ^{13}C NMR ($CDCl_3$): δ -3.53 ($SiCH_3$), 14.02 (CH_3), 14.31 (CH_3), 18.68 (Si*C*CH_3), 26.50 (SiC*C*H_3), 39.75 (CH_2), 59.51 (C), 61.58 (CH_2O), 122.81, 131.69, 144.28 (Ar), 172.15 (C=O). IR (KBr): 2944 s, 2868 s, 1730 s, 1468 s, 1392 m, 1350 s, 1248 s, 1178 s, 1084 s, 1058 s, 1030 m, 1008 m, 940 m, 906 s, 834 s, 780 s, 706 w, 670 m, 600 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 550 (2, M^+), 305 (31), 73 (100). Anal. Calcd for $C_{29}H_{50}O_6Si_2$: C,63.23; H, 9.15. Found: C, 63.16; H, 9.26.

6-(*tert*-Butyldimethylsiloxy)-1,3-dihydro-4-butyl-6-hydroxy-2*H*-indene-2,2-dicarboxylic acid diethyl ether (28a). A colorless liquid. R_f 0.26 (hexane/EtOAc = 20/1). ^1H NMR ($CDCl_3$): δ 0.25 (s, 6H, $SiCH_3$), 0.93 (t, J = 7.0 Hz, 3H, CH_3), 1.00 (s, 9H, $SiCCH_3$), 1.25 (t, J = 7.0 Hz, 6H, CH_3), 1.27-1.55 (c, 4H, CH_2), 2.57 (t, J = 7.6 Hz, 2H, CH_2CH_2Ar), 3.46 (s, 4H, CH_2 x 2), 4.20 (q, J = 7.0 Hz, 4H, CH_2), 5.44 (s, 1H, OH), 6.50 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -4.33 ($SiCH_3$), 14.02 (CH_3), 18.15 (Si*C*CH_3), 22.88 (CH_2), 25.73 (SiC*C*H_3), 27.44, 31.32, 38.91, 40.34 (CH_2), 60.41 (C), 61.60 (CH_2), 110.60, 124.65, 129.72, 132.08, 141.35, 144.12 (Ar), 171.84 (C=O). IR (neat): 3536 m, 2934 s, 2860 s, 2056 w, 1735 s, 1618 m, 1561 w, 1476 s, 1389 s, 1333 s, 1250 s, 1182 s, 1155 s, 1085 s, 1005 m, 965 m, 886 s, 835 s, 781 s, 669 s cm^{-1}. MS (70 eV): m/z (relative intensity, %) 450 (13), 449 (45, M^+ - CH_3), 407 (22), 392 (15), 376 (15), 350 (33), 348 (14), 334 (17), 333 (29), 319 (25), 318 (73), 277 (16), 276 (84), 243 (21), 217 (24), 203 (28), 202 (26), 201 (31), 145 (12), 129 (20), 128 (12), 115 (13), 75 (36), 73 (100), 59 (33), 57 (17), 55 (11). HRMS Calcd for $C_{25}H_{40}O_6Si$ (M^+): 464.2594, Found 464.2583.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-4-butyl-2*H*-indene-2,2-di-carbylic acid diethyl ether (28b). A white solid; mp 47-48 °C. R_f 0.26 (hexane/EtOAc = 20/1). ^1H NMR ($CDCl_3$): δ 0.10 (s, 6H, $SiCH_3$), 0.18 (s, 6H, $SiCH_3$), 0.89 (t, J = 7.0 Hz, 3H, CH_3), 0.92 (s, 9H, $SiCCH_3$), 1.00 (s, 9H, $SiCCH_3$), 1.24 (t, J = 7.1 Hz, 6H, CH_3), 1.25-1.55 (c, 4H, CH_2), 2.51 (t, J = 7.6 Hz, 2H, CH_2CH_2Ar), 3.44 (s, 2H, CH_2), 3.46 (s, 2H, CH_2), 4.29 (q, J = 7.1 Hz, 4H, CH_2), 6.50 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -3.56, -3.52 ($SiCH_3$), 14.01, 14.13 (CH_3), 18.47, 18.81 ($SiCCH_3$), 22.72 (CH_3), 26.17, 26.28 ($SiCCH_3$), 28.26, 31.49, 39.22, 40.34 (CH_2), 60.56 (C), 61.54 (CH_2), 113.85, 130.94, 131.87, 131.89, 143.22, 146.37 (Ar), 171.93 (C=O). IR (KBr): 2928 s, 2864 s, 1736 s, 1602 m, 1468 s, 1392 m, 1344 s, 1236 s, 1182 s, 1154 s, 1088 s, 1006 m, 962 m, 904 m, 836 s, 778 s, 670 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 578 (2, M^+), 521 (10), 333 (31), 73 (100). Anal. Calcd for $C_{31}H_{54}O_6Si_2$: C, 64.32; H, 9.40. Found: C, 64.32; H, 9.49.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-4-phenyl-2*H*-indene-2-spiro-2,2-dicarboxylic acid diethyl ether (30). A white solid; mp 101-102 °C. R_f 0.28 (hexane/EtOAc = 20/1). ^1H NMR ($CDCl_3$): δ -0.26 (s, 6H, $SiCH_3$), 0.24 (s, 6H, $SiCH_3$), 0.70 (s, 9H, $SiCCH_3$), 0.98 (s, 9H, $SiCCH_3$), 1.21 (t, J = 7.0 Hz, 6H, CH_3), 3.34 (s, 2H, CH_2), 3.52 (s, 2H, CH_2), 4.25 (q, J = 7.0 Hz, 2H, CH_2), 4.26 (q, J = 7.0 Hz, 2H, CH_2), 6.67 (s, 1H, Ar), 7.22-7.39 (c, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ -3.96, -3.52 ($SiCH_3$), 13.98 (CH_3), 18.15, 18.87 ($SiCCH_3$), 25.95, 26.33 ($SiCCH_3$), 40.24, 40.52 (CH_2), 60.52 (C), 61.53 (CH_2), 115.42, 126.69, 127.80, 130.73, 131.41, 131.81, 132.29, 137.63, 142.81, 146.99 (Ar), 171.78 (C=O). IR (KBr): 2940 s, 2864 m, 1730 s, 1596 m, 1460 s, 1440 s, 1390 m, 1348 s, 1270 s, 1248 s, 1190 m, 1146 s, 1094 m, 1070 m, 1050 m, 1004 w, 960 m, 892 m, 834 s, 776 s, 698 m, 672 m, 610 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 598 (1, M^+), 541 (20), 354 (12), 353 (40), 73 (100). Anal. Calcd for $C_{33}H_{50}O_6Si_2$: C, 66.18; H, 8.42. Found: C, 66.16; H, 8.44.

5,6-Bis(*tert*-butyldimethylsiloxy)-1,3-dihydro-4-methoxymethyl-2*H*-indene-2, 2-dicarboxylic acid diethyl ether (32). A white solid; mp 51-52 ° C. R_f 0.29 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 6H, $SiCH_3$), 0.18 (s, 6H, $SiCH_3$), 0.94 (s, 9H, $SiCCH_3$), 1.02 (s, 9H, $SiCCH_3$), 1.24 (t, *J* = 7.0 Hz, 6H, CH_3), 3.28 (s, 3H, OCH_3), 3.46(s, 2H, CH_2), 3.54 (s, 2H, CH_2), 4.43 (s, 2H, OCH_2), 6.62 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ -3.92, -3.61 ($SiCH_3$), 13.98 (CH_3), 18.49, 1873 ($SiCCH_3$), 26.17, 26.22 ($SiCCH_3$), 39.19, 40.13 (CH_2), 57.56(OCH_3), 60.54 (C), 61.51 (CH_2), 67.15 (OCH_2), 115.92, 125.55, 132.53, 133.64, 143.83, 146.31 (Ar), 171.86 (C=O). IR (KBr): 2956 s, 2938 s, 2860 s, 1732 s, 1604 w, 1471 s, 1380 m, 1343 s, 1251 s, 1182 s, 1154 s, 1092 s, 1040 s, 1004 m, 916 s, 841 s, 778 s, 678 w, 606 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 480 (18), 363 (23), 291 (33), 217 (11), 73 (100). HRMS Calcd for $C_{29}H_{50}O_7Si_2$ (M^+): 566.3095, Found 566.3092.

5,6-Dihydroxy-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (33). A white solid; mp 123-124 °C. R_f 0.21 (hexane/EtOAc = 3/2). ^{1}H NMR ($CDCl_3$): δ 1.25 (t, *J* = 7.2 Hz, 6H, CH_3), 3.45 (s, 4H, CH_2), 4.20 (q, *J* = 7.2 Hz, 4 H, CH_2), 5.38 (s, 2H, OH), 6.67 (s, 2H, Ar). ^{13}C NMR ($CDCl_3$): δ 13.96 (CH_3), 40.07 (CH_2), 60.99 (C), 61.93 (CH_2O), 110.95, 131.70, 143.02 (Ar), 172.13 (C=O). IR (KBr): 3492 m, 3392 s, 2996 m, 1720 s, 1618 m, 1516 s, 1466 s, 1370 m, 1316 s, 1270 s, 1208 s, 1148 m, 1068 m, 872 m, 852 m, 816 w, 744 w, 692 w, 658 w, 630 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 294 (36, M^+), 221 (41), 220 (100), 193 (27), 192 (17), 175 (22), 148 (33), 148 (73), 131 (14), 130 (18), 102 (23), 101 (16), 91 (11), 51 (10). Anal. Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16. Found: C, 61.25; H, 6.23.

5,6-Dihydroxy-1,3-dihydro-2,2'-2*H*-indelidenebisethanone (34). A white solid; mp 151-152 °C. R_f 0.20 (CH_2Cl_2/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, CH_3), 3.38 (s, 4H, CH_2), 5.19 (s, 2H, OH), 6.70 (s, 2H, Ar). ^{13}C NMR (acetone-d_6): δ 26.53 (CH_3), 37.87 (CH_2), 75.24 (C), 111.78, 131.84, 145.21 (Ar), 205.69 (C=O). IR (KBr): 3422 s, 3042 w, 2932 m, 2870 m, 1688 s, 1613 s, 1516 s, 1467 s, 1431 m, 1357 s, 1321 s. 1283 s, 1183 s, 1144 s, 1087 m, 1074 m, 1038 w, 960 m, 940 w, 860 s, 744 w, 718 w, 644 m, 621 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 234 (6, M^+), 192 (17), 191 (100). HRMS Calcd for $C_{13}H_{14}O_4$ (M^+): 234.0892, Found: 234.0888.

5,6-Dihydroxy-1,3-dihydro-2*H*-indene (35). A white solid; mp 108-109 °C. R_f 0.31 (CH_2Cl_2/EtOAc = 10/1). ^{1}H NMR (acetone-d_6): δ 2.00 (quint, *J* = 7.1 Hz, 2H, CH_2), 2.72 (t, *J* =

7.1 Hz, 4H, CH_2Ar), 6.68 (s, 2H, Ar),7.49 (s, 2H, OH). ^{13}C NMR (acetone-d_6): δ 26.16 (CH_2), 32.70 (CH_2Ar), 114.48, 135.18, 144.04 (Ar). IR (KBr): 3312 s, 2960 s, 2864 s, 2716 w, 1734 w, 1616 m, 1584 m, 1498 s, 1476 s, 1446 s, 1420 s, 1392 m, 1364 s, 1336 s, 1302 s, 1256 s, 1218 s, 1174 s, 1146 s, 1114 s, 1076 m, 1006 m, 930 s, 874 s, 780 s, 718 m, 674 m, 610 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 151 (13, M^+ + 1), 150 (100), 149 (54), 133 (39), 132 (27), 131 (49), 104 (32), 103 (39), 91 (12), 77 (29), 65 (11), 55 (11), 51 (44). HRMS Calcd for $C_9H_{10}O_2$ (M^+): 305.0722, Found 305.0722.

5,6-Dihydroxy-1*H*-3*H*-isobenzofuran (36). A white solid; mp 215 °C (decompose). R_f 0.27 (hexane/THF = 3/1). ^{1}H NMR (acetone-d_6): δ 4.87 (s, 4H, CH_2), 6.74 (s, 2H, Ar), 7.92 (s, 2H, OH). ^{13}C NMR (acetone-d_6): δ 73.65 (CH_2), 108.29, 130.89, 145.55 (Ar). IR (KBr): 3360 s, 3252 s, 2880 w, 1618 w, 1520 m, 1474 m, 1370 m, 1340 s, 1298 s, 1188 m, 1156 m, 1094 w, 1038 w, 1006 m, 880 m, 858 m, 782 m, 708 w, 660 w, 612 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 152 (65, M^+), 151 (63), 124 (10), 123 (100), 77 (35), 67 (11), 66 (11), 65 (10), 55 (15), 53 (15), 51 (35). Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.95; H, 5.27.

5,6-Dihydroxy-2-(4-methylbenzenesulfonyl)-1*H*-3*H*-isoindole (37). A white solid; mp 190 °C (decompose). R_f 0.17 (hexane/EtOAc = 3/1). ^{1}H NMR (acetone-d_6): δ 2.39 (s, 3H, CH_3), 4.44 (s, 4H, CH_2), 6.69 (s, 2H, Ar), 7.41 (d, J = 8.1 Hz, 2H, Ar), 7.76 (d, J = 8.1 Hz, 2H, Ar), 8.02 (s, 2H, OH). ^{13}C NMR (acetone-d_6): δ 21.30 (CH_3), 54.28 (CH_2), 109.90, 127.81, 128.45, 130.61, 134.85, 144.41, 145.96, (Ar), 172.04 (C=O). IR (KBr): 3388 m, 2864 w, 1624 w, 1600 w, 1518 m, 1474 m, 1330 s, 1308 s, 1284 s, 1148 s, 1090 s, 1062 m, 880 m, 858 m, 832 w, 814 w, 750 w, 708 w, 668 s, 608 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 305 (10, M^+), 150 (40), 149 (100), 139 (13), 41 (39), 65 (18). Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 63.27; H, 8.31. Found: C, 63.37; H, 8.40.

5,6-Dihydroxy-1*H*-3*H*-isobenzothiophene (38). A pale yellow solid; mp 123 °C (decompose). R_f 0.27 (hexane/THF = 3/1). ^{1}H NMR (acetone-d_6): δ 4.08 (s, 4H, CH_2), 6.73 (s, 2H, Ar), 7.84 (s, 2H, OH). ^{13}C NMR (acetone-d_6): δ 37.91 (CH_2), 111.58, 132.16, 145.07 (Ar). IR (KBr): 3268 m, 2868 s, 1730 s, 1468 s, 1392 m, 1350 s, 1248 s, 1178 s, 1084 s, 1058 s, 1030 m, 1008 m, 940 m, 906 s, 834 s, 780 s, 706 w, 670 m, 600 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 170 (13, M^+ + 2), 169 (50, M^+ + 1), 168 (100, M^+), 167 (63), 151 (18), 150

(10), 121 (11), 77 (13), 61 (11), 60 (12), 55 (13), 51 (12). HRMS Calcd for $C_8H_8O_2S$ (M^+): 168.0245, Found 168.0246.

2,3-Dihydroxy-9*H*-fluorene (39). A white solid; mp 176-177 °C. R_f 0.28 (hexane/AcOEt = 3/2). ^1H NMR (acetone-d_6): δ 3.73 (s, 2H, CH_2), 7.05 (s, 1H, Ar), 7.16 (t, J = 8.1 Hz, 1H, Ar), 7.28 (t, J = 8.1 Hz, 1H, Ar), 7.31 (s, 1H, Ar), 7.46 (d, J = 8.1 Hz, 1H, Ar), 7.63 (d, J = 8.1 Hz, 1H, Ar), 7.91 (s, 1H, OH), 7.97 (s, 1H, OH). ^{13}C NMR (acetone-d_6): δ 36.83 (CH_2), 107.32, 112.66, 119.39, 125.47, 125.88, 127.32, 134.51, 135.94, 143.15, 144.08, 145.40, 145.83 (Ar). IR (KBr): 3268 s, 3070 s, 3048 s, 2958 m, 1941 w, 1893 w, 1788 w, 1711 w, 1616 m, 1585 m, 1488 s, 1448 s, 1408 s, 1395 s, 1346 s, 1309 s, 1285 s, 1251 s, 1209 s, 1185 s, 1161 s, 1116 m, 1093 m, 1021 m, 975 m, 948 m, 919 m, 878 m, 863 m, 839 m, 808 m, 759 s, 723 s, 640 m, 608 m cm^{-1}. MS (70 eV): m/z (relative intensity, %) 199 (19, M^+ + 1), 198 (100, M^+), 197 (20, M^+ - 1), 181 (13), 180 (21), 152 (28), 151 (12), 76 (17). HRMS Calcd for $C_{13}H_{10}O_2$ (M^+): 198.0680, Found 198.0703.

5,6-Dihydroxy-4-methyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (40). A white solid; mp 155-156 °C. R_f 0.23 (hexane/EtOAc = 3/2). ^1H NMR ($CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 6H, CH_3), 2.13 (s, 3H, CH_3), 3.43 (s, 2H, CH_2), 3.45 (s, 2H, CH_2), 4.21 (q, J = 7.1 Hz, 4H, OCH_2), 5.17 (s, 1H, OH), 5.42 (s, 1H, OH), 6.51 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 12.52, 14.28 (CH_3), 39.69, 40.95 (CH_2), 60.77 (C), 61.96 (OCH_2), 108.74, 120.58, 130.45, 131.26, 143.19, 144.71 (Ar), 172.24 (C=O). IR (KBr): 3521 s, 3376 m, 2988 m, 2916 w, 1748 s, 1720 s, 1626 w, 1510 m, 1474 s, 1372 m, 1290 s, 1192 s, 1160 s, 1070 s, 1034 m, 1014 m, 990 m, 896 w, 846 m, 724 w, 658 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 308 (41, M^+), 235 (48), 234 (100), 207 (23), 206 (14), 189 (18), 162 (28), 161 (68), 144 (13), 116 (13), 115 (22), 77 (10). Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.03; H, 6.50.

5,6-Dihydroxy-4,7-dimethyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (41). A white solid; mp 196-197 °C. R_f 0.32 (hexane/EtOAc = 3/2). ^1H NMR (CD_3CN): δ 1.22 (t, J = 7.1 Hz, 6H, CH_3), 2.08 (s, 6H, $ArCH_3$), 3.40 (s, 4H, CH_2), 4.17 (q, J = 7.1 Hz, 4H, OCH_2), 6.09 (s, 2H, OH). ^{13}C NMR (CD_3CN): δ 12.54 (CH_3), 14.18 ($ArCH_3$), 39.75 (CH_2), 60.12 (C), 62.36 (OCH_2), 117.36, 130.87, 142.72 (Ar), 172.67 (C=O). IR (KBr): 3512 s, 3384 m, 2988 w, 1750 w, 1720 s, 1628 w, 1514 w, 1476 w, 1374 w, 1292 s, 1268 s, 1196 m, 1164 m, 1074 m, 1036 m, 1016 w, 992 w, 898 w, 846 m, 728 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 323 (10, M^+ + 1), 322 (47, M^+), 249 (46), 248 (100), 221 (19), 220 (11), 203 (14), 176 (24), 175 (62), 115 (10). HRMS Calcd for $C_{17}H_{22}O_6$ (M^+): 322.1316, Found 322.1438.

4-Butyl-5,6-dihydroxy-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (42). A colorless liquid; R_f 0.28 (hexane/EtOAc = 3/2). ^{1}H NMR (acetone-d_6): δ 0.93 (t, *J* = 7.2 Hz, 3H, CH_3), 1.22 (t, *J* = 7.2 Hz, 6H, CH_3), 1.33 (sext, *J* = 7.2 Hz, 2H, CH_2), 1.54 (quint, *J* = 7.2 Hz, 2H, CH_2), 2.59 (t, *J* = 7.2 Hz, 2H, $ArCH_2$), 3.40 (s, 2H, CH_2), 3.43 (s, 2H, CH_2), 4.16 (q, *J* = 7.2 Hz, 4H, OCH_2), 6.57 (s, 1H, Ar), 6.80 (s, 1H, OH), 8.20 (s, 1H, OH). ^{13}C NMR (acetone-d_6): δ 14.27 (CH_3), 23.37 (CH_3), 27.81 (CH_2), 32.17 ($ArCH_2$), 39.43, 40.83 (CH_2), 60.07 (C), 61.93 (OCH_2), 108.97, 125.59, 130.57, 130.93, 143.01, 144.62 (Ar), 172.17 (C=O). IR (neat): 3300 m, 3188 m, 3056 m, 2932s , 1730 s, 1452 s, 1368 s, 1250 s, 1092 m, 1022 m, 930 w, 858 m, 752 m, 664 w, 608 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 351 (17, M^+ + 1), 350 (45, M^+), 278 (15), 277 (59), 276 (100), 249 (16), 162 (12), 161 (34). HRMS Calcd for $C_{19}H_{26}O_6$ (M^+): 350.1730, Found 350.1751.

4-Phenyl-5,6-dihydroxy-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (43). A white solid; mp 168-170 °C. R_f 0.27 (hexane/EtOAc = 3/2). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, *J* = 7.2 Hz, 6H, CH_3), 3.31 (s, 2H, CH_2), 3.52 (s, 2H, CH_2), 4.15 (q, *J* = 7.2 Hz, 4H, OCH_2), 5.17 (s, 1H, OH), 5.73 (s, 1H, OH), 6.73 (s, 1H, Ar), 7.25-7.49 (c, 5H, Ph). ^{13}C NMR (acetone-d_6): δ 14.17 (CH_3), 40.33, 40.73 (CH_2), 61.07 (C), 61.83 (OCH_2), 108.57, 110.51, 125.99, 127.54, 128.79, 130.47, 131.13, 137.60, 142.11, 145.22 (Ar), 171.87 (C=O). IR (KBr): 3344 s, 3066 m, 2988 s , 2900 s, 1972 w, 1909 w, 1823 w, 1730 s, 1628 s, 1601 s, 1576 m, 1466 s, 1365 s, 1326 s, 1241 s, 1089 m, 1065 s, 1008 s, 931 m, 897 s, 762 s, 700 s, 674 s, 642 s cm^{-1}. MS (70 eV): m/z (relative intensity, %) 370 (62, M^+), 296 (100), 269 (18), 268 (12), 251 (15), 224 (31), 223 (36), 221 (10), 205 (15), 178 (13), 165 (12). HRMS Calcd for $C_{21}H_{22}O_6$ (M^+): 370.1417, Found 370.1417.

5,6-Dihydroxy-1,3-dihydro-2*H*-indene-2,2,4-tricarboxylic acid triethyl ester (45). A white solid; mp 109-110 °C. R_f 0.27 (hexane/EtOAc = 3/1). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, *J* = 7.1 Hz, 6H, CH_3), 1.44 (t, *J* = 7.1 Hz, 3H, CH_3), 3.48 (s, 2H, CH_2), 3.78 (s, 2H, CH_2), 4.22 (q, *J* = 7.1 Hz, 4H, OCH_2), 4.44 (q, *J* = 7.1 Hz, 2H, OCH_2), 5.72 (s, 1H, OH), 6.93 (s, 1H, Ar), 11.29 (s, 1H, OH). ^{13}C NMR (acetone-d_6): δ 14.04 (CH_3), 14.27 (CH_3), 39.90, 42.30 (CH_2), 59.87 (C), 61.76, 61.84 (OCH_2), 109.27, 115.18, 131.09, 131.56, 144.44, 148.84 (Ar), 170.92 171.84 (C=O). IR (KBr): 3560 m, 3504 m, 3200 m, 2966 m, 1756 m, 1724 s, 1672 s, 1600 m, 1478 m, 1404 w, 1374 m, 1338 m, 1302 w, 1274 s, 1240 s, 1206 s, 1192 s, 1164s, 1078 s, 1052 m, 1018 s, 864 w, 798 w cm^{-1}. MS (70 eV): m/z (relative intensity, %) 366 (26, M^+), 320 (85), 247 (33), 246 (100), 174 (14), 173 (13), 145 (11), 89 (10). HRMS Calcd for $C_{18}H_{22}O_8$ (M^+): 366.1314, Found 366.1312.

4-(2-Methyl-1-propenyl)-5,6-dihydroxy-1,3-dihydro-2*H*-indene-2,2-dicarboxylic acid diethyl ester (47). A white solid; mp 126-128 °C (decompose). R_f 0.23 (hexane/EtOAc = 3/2). ^{1}H NMR (acetone-d_6): δ 1.30 (t, *J* = 7.1 Hz, 6H, CH_3), 1.67 (d, *J* = 1.0 Hz, 3H, =CCH_3), 1.97 (d, *J* = 1.0 Hz, 3H, =CCH_3), 3.37 (s, 2H, CH_2), 3.52 (s, 2H, CH_2), 4.25 (q, *J* = 7.1 Hz, 4H, OCH_3), 6.11 (s, 1H, OH), 7.01 (s, 1H, Ar), 7.80 (s, 1H, OH). ^{13}C NMR (acetone-d_6): δ 14.28 (CH_3), 20.03, 25.56 (=CCH_3), 40.28, 40.85 (CH_2), 60.94 (C), 61.93 (OCH_2), 101.91, 119.61, 122.63, 130.73, 130.82, 138.14, 142.16, 145.04 (Ar), 172.75 (C=O). IR (KBr): 3344 s, 3066 m, 2988 s , 2900 s, 1972 w, 1909 w, 1823 w, 1730 s, 1628 s, 1601 s, 1576 m, 1466 s, 1365 s, 1326 s, 1241 s, 1089 m, 1065 s, 1008 s, 931 m, 897 s, 762 s, 700 s, 674 s, 642 s cm^{-1}. MS (70 eV): m/z (relative intensity, %) 349 (14, M^+ + 1), 348 (64, M^+), 275 (52), 274 (100), 247 (21), 229 (17), 202 (15), 201 (27), 200 (14), 199 (17), 185 (16), 183 (15), 155 (10), 128 (11), 115 (12), 60 (15), 58 (13), 56 (14). HRMS Calcd for $C_{19}H_{24}O_6$ (M^+): 348.1573, Found 348.1554.

2-5 References and Notes

(1) (a) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: Berlin, 1980. (b) Thatchenko, I. In *Comprehensive Organometallic Chemistry*; (c) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, pp 101-223. (d) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991. (e) Thompson, D. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon Press; Oxford, 1991; Vol. 3, pp 1015-1043.

(2) (a) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am . Chem. Soc.* **1990**, *112*, 6120. (b) Seki, Y.;

Kawamoto, K.; Chatani, N.; Hidaka, A.; Sonoda, N.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Organomet. Chem.* **1991**, *403*, 73. (c) Matsuda, I.; Sakakibara, J.; Nagashima, H. *Tetrahedron Lett.* **1991**, *32*, 7431. (d) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580.

(3) For a review on transition-metal-mediated cyclization, see: Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

(4) (a) Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023. (b) Müller, E.; Thomas, R.; Zountsas, G. *Liebigs Ann. Chem.* **1972**, *758*, 16. (c) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 202. (d) Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**,*11*, 4096. (e) Chiusoli, G. P.; Costa, M.; Gerbella, M.; Salerno, G. *Gazz. Chim. Ital.* **1985**, *115*, 697. (f) Bocelli, G.; Chiusoli, G. P.; Costa, M.; Fambri, L. *J. Chem. Soc., Chem. Commun.* **1987**, 1182. (g) Dickson, R. S.; Mok, C.; Connor, G. *Aust. J. Chem.* **1977**, *30*, 2143.

(5) For a review on so-called "double carbonylation", see: Collin, J. *Bull. Soc. Chim. Fr.* **1988**, *6*, 976. See also ref 1.

(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Fink, R. G. *Principles and Application of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, 1987.

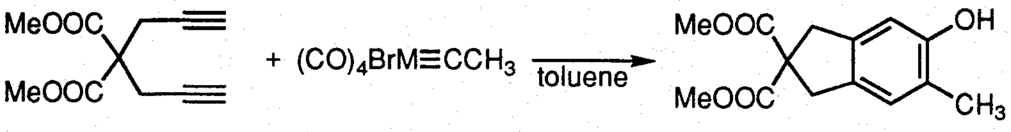
(7) For reviews on carbyne complexes, see: (a) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (b) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51. (c) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227.

(8) (a) Fischer, E. O.; Friedrich, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 327. (b) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766. (c) Howard, J. A. K.; Jeffery, J. C.; Laurie, J. C. V.; Moore, I.; Stone, F. G. A.; Stinger, A. *Inorg. Chim. Acta* **1985**, *100*, 23. (d) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474. (e) Mayr, A.; McDermott, G. A.; Dorries, A. M.; van Engen, D. *Organometallics* **1987**, *6*, 1503. (f) Mayr, A.; Bastos, C. M.; Chang, R. T.; Haberman, J. X.; Robinson, K. S.; Belle-Oudry, D. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 747. (g) Mayr, A.; Bastos, C. M.; Daubenspeck, N.; McDermott, G. A. *Chem. Ber.* **1992**, *125*, 1583.

(9) (a) Bianconi, P. A.; Vrtis, R. N.; Rao, C. P.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968. (b) Vrtis, R. N.; Liu, S.; Rao, C. P.; Bott, S. G.; Lippard, S.

J. *Organometallics* **1991**, *10*, 275. (c) Protasiewicz; J. D. Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 6564. (d) Handwerker, H.; Beruda, H.; Kleine, M.; Zybill, C. *Organometallics* **1992**, *11*, 3542.

(10) Sivavec, T. M.; Katz, T. J. *Tetrahedron Lett.* **1985**, *26*, 2159.



M = W, Cr

(11) Whether SiR_3 or H migrates is not clear at the present time. A topologically similar intramoleculer 1,3-hydrogen shift has been observed in alkynylcobalt complexes. Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697.

(12) Nicholas, K. M. *Organometallics* **1982**, *1*, 1713.

(13)Carbyne complexes have been postulated as a catalytic key species in metathesis of acetylenes. See refs 7b, 7c.

(14) A large number of natural products, in particular antitumor agents, possess catechol or *o*-quinone as a subunit. Tisler, M. *Adv. Heterocycl. Chem.* **1989**, *45*, 37.

(15) For reviews on the WGSR, see: (a) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31. (b) Laine, R. M.; Crawford, E. J. *J. Mol. Cat.* **1988**, *44*, 357. (c) Ford, P. C.; Rokicki, A. *Adv. Organomet Chem.* **1988**, *28*, 139.

(16) Pino, P.; Braca, G.; Sbrana, G.; Cuccuru, A. *Chem. and Ind.* **1968**, 1732.

(17) Scheller, A.; Winter, W.; Müller, E. *Liebigs Ann. Chem.* **1976**, 1448.

(18) Ozaki, S.; Matsushita, H.; Ohmori, H.; *J. Chem. Soc., Perkin Trans. 1* **1993**, 2339.

(19) Skattebøl, L.; Boulette, B.; Solomon, S. *J. Org. Chem.* **1968**, *33*, 548.

(20) Sindelar, K.; Metsova, J.; Protiva, M. *Collect. Czeck. Chem. Commun.* **1972**, *37*, 1734.

(21) Rossi, R.; Carpita, A.; Lippolis, V.; Benetti, M. *Gazz. Chim. Ital.* **1990**, *120*, 783.

(22) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(23) Grigg, R.; Scott, R.; Stevenson, P. J. *Chem. Soc.,Perkin Trans. 1* **1988**, 1357.

(24) Opitz, G.; Mildenberger, H. *Justus Liebigs Ann. Chem.* **1961**, *650*, 122.

(25) Stevens, R. V.; Chiristensen, C. G.; Edmonson, W. L.; Kaplan ,M.; Reid, E. B.; Wentlamd, M. P. *J. Am. Chem. Soc.* **1971**, *93*, 6629.

(26) Skattebøl, L.; Jones, E. R. H.; Writing, M. *Org. Synth., Collect. Vol. 4*, 792.

(27) Murata, S.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 767.

(28) Miller, R. B.; *Synth. Commun.* **1972**, *2*, 267.

(29) Corey, E. J.; Albright, J. O. *J. Org. Chem.* **1983**, *48*, 2114.

(30) Brillon, D. *Synth. Commun.* **1986**, *16*, 291.

(31) Ichikizaki, I.; Yao, C. C.; Fujita, Y.; Hasebe, Y. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 80.

(32) Taschener, M. J.; Rosen, T.; Heathcock, C. H. Org. *Synth. Collect. Vol. 7*, 226.

(33) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964.

(34) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

(35) Axelrod, E. H.; Milne, G. M.; van Tamelene, E. E. *J. Am. Chem. Soc.* **1970**, *92*, 2139.

(36) Jung, M. E.; Hagenah, J, A. *J. Org. Chem.* **1987**, *52*, 1889.

Conclusion

In this thesis, new catalytic carbon monoxide incorporating reactions using the effective transition-metal complexes (Rh and Ru) with hydrosilanes and carbon monoxide have been studied. The results mentioned in each chapter of this thesis are summarized as follows.

In Chapter 1, it has been described that rhodium complexes catalyze the reacton of oxiranes and oxetanes with a hydrosilane and carbon monoxide resulting to the ring-opening silylformylation, which yields the corresponding β- and γ-siloxy aldehydes. Rh complexes are more effective catalysts than $Co_2(CO)_8$. The addition of amines as an additive was crucial for this reaction. Especially, 1-methylpyrazole was the most effective amine examined. The ring-opening of oxiranes was predominantly occurred in *trans* manner. The stereospecific ring-opening was demonstrated in *cis*- and *trans*-2-butene oxide. As contrasted with oxiranes, ring-opening silylformylation of oxetanes is a rare example of ring-opening carbonylation of oxetanes.

In Chapter 2, it is found that ruthenium complexes catalyzed reaction of 1,6-diynes with hydrosilanes and carbon monoxide yielding to catechol derivatives. This reaction is the first example of successive incorporation of two molecules of carbon monoxide into diynes and is also the first catalytic reaction involving the intermediary of an oxycarbyne complex as the key catalytic species. It has been also described that the use of H_2O instead of hydrosilanes enables similar transformation. The present way of activation/bond formation of carbon monoxide will open up new fields for carbonylation. Experiments designed to detect, trap, and isolate siloxy(or hydroxy)carbyne complexes are underway.

These new catalytic reactions with hydrosilanes and carbon monoxide would contribute to the development of a part of homogeneous catalyzed reactions.