Intra- and Intermolecular Allene–Alkyne Coupling Reactions by the Use of $Fe(CO)_4(NMe_3)$

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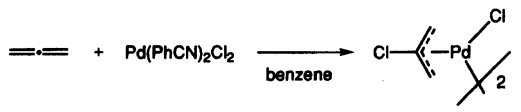
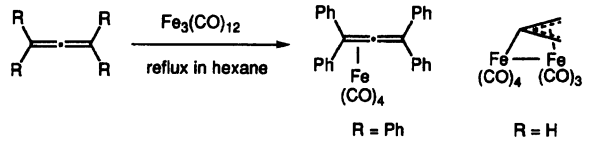
Intramolecular allene–alkyne coupling reactions proceed in the presence of $Fe(CO)_4(NMe_3)$ under photoirradiation conditions to provide various bicyclic dienones through η^3-allyl iron complexes. Various 4-methylene-2-cyclopenten-1-ones could be prepared by intermolecular allene–alkyne coupling reaction under the same reaction conditions.

Allene compounds have been widely employed for the three-carbon synthetic units.[1] For example, various kinds of typical metals have been introduced into allene compounds to provide propargylation reagents for the carbonyl compounds.[2] Reactivity peculiar to allene compounds, but not to alkenes and alkynes, is expected because of their unique structure where two olefins adjoin. Reactions between transition metals and allene compounds were extensively investigated.[3] One of the features of such reactions is facile formation of η^3-allyl complex from allene components. For instance, chloropalladation readily proceeds by bubbling allene gas into the solution of Pd(II) to afford the dimer of η^3-allyl complex (Eq. 1).[4] This reaction was applied to intramolecular oxo- and aminopalladation; (ω-alkoxy)- and (ω-amino)propadienes were converted into cyclic ethers[5] and amines[6] by the use of a catalytic amount of $PdCl_2$.



(1)

The complexations between allenes and various metal carbonyl complexes were also widely investigated. As for the iron carbonyl complex, in the reaction with tetraphenylallene,[7] an η^2-complex was afforded, while with propadiene[8] a unique dinuclear complex was afforded, in which one iron atom is π-bonded to the allyl group and another iron atom is σ-bonded to the center carbon of the allyl ligand and the two iron atoms are linked by a metal–metal bond (η^1,η^3-bridging allyl complex), as shown in Eq. 2.



(2)

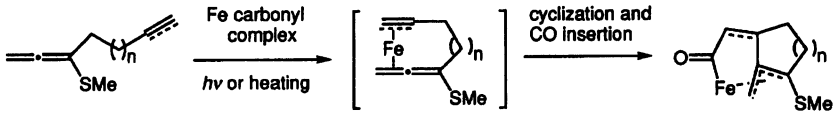
In recent years, some reactions were reported between iron carbonyls and allenes possessing electron-withdrawing groups such as allenic esters and allenic ketones.[9] A thermal reaction of methyl 2-methyl-2,3-butadienoate with $Fe_2(CO)_9$ provided a cyclized and carbonylated trimethylenemethane complex.[9a] Photoirradiation of propadienyl ketones with $Fe(CO)_5$ gave lactones by carbonylation and successive demetallation.[9d]

We have already reported that the introduction of alkylthio group to olefins increases their reactivity in the reactions such as the [2+2] cycloaddition reaction with electron-deficient olefins,[10] the aldol type addition reaction with aldehydes,[11] and the ene reaction with Schiff's bases.[12] On the basis of these facts, we assumed that the introduction of alkylthio group would facilitate the complexation between the allene compound and an iron carbonyl owing to its electron-donating effect.[13] When such a π-complex is generated from a propadienyl sulfide having an olefinic or acetylenic moiety on the end of the side chain, successive intramolecular cyclization reaction and insertion of carbon monoxide would occur to give a cyclic η^3-allyl iron complex, as shown in Scheme 1.

This paper disclosed the full details of the results about both intra- and intermolecular coupling reactions between allenes and olefinic components by the use of iron carbonyls.[14]

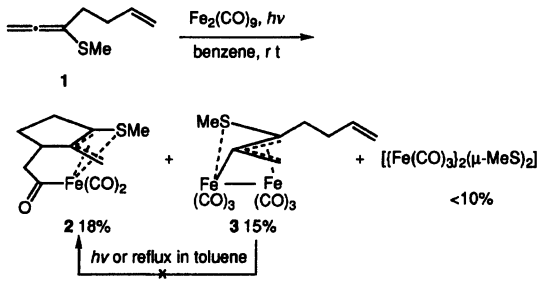
Results and Discussion

Reaction between 1-(ω-Alkenyl)propadienyl



Scheme 1.

Sulfides and Iron Carbonyls. The reaction between propadienyl sulfide possessing a terminal olefin moiety and diiron nonacarbonyl was examined: 1-(3-butenyl)-1,2-propadienyl methyl sulfide (**1**),[15] prepared by alkylation of 1-(methylthio)propadienyllithium with 4-bromo-1-butene, reacted with $Fe_2(CO)_9$ by photoirradiation (Eq. 3). In addition to the formation of a η^1,η^3-bridging allyl dinuclear iron complex **3**[16] and $[\{Fe(CO)_3\}_2(\mu\text{-MeS})_2]$,[17] a cyclic η^3-allyl mononuclear iron complex **2** was obtained in 18% yield, as we expected. Its structure was established by X-ray crystallography, as shown in Fig. 1. In complex **2**, the allene moiety is coordinated to an iron atom as an allyl ligand and the sulfur can also occupy one of the coordination sites of the iron atom. Conversion of the dinuclear complex **3** to the mononuclear **2** was examined by additional photoirradiation or by heating in refluxing toluene, but in vain. These results allow us to infer two distinct pathways for the formation of the complexes **2** and **3**, respectively. We conclude that the dinuclear complex **3** is never an intermediate in the transformation of the propadienyl sulfide **1** to the cyclized product **2**.



(3)

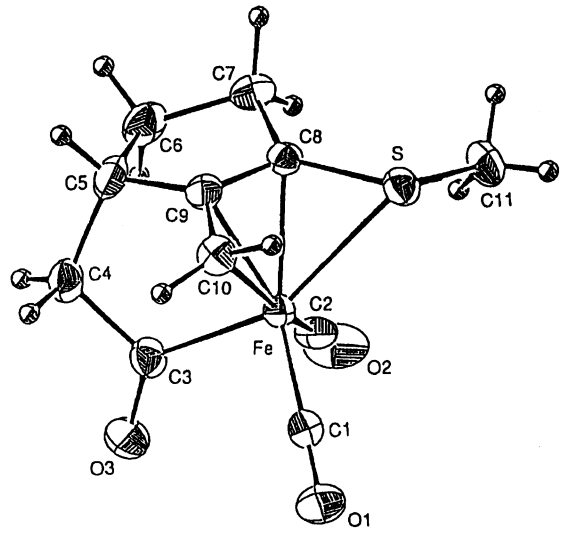
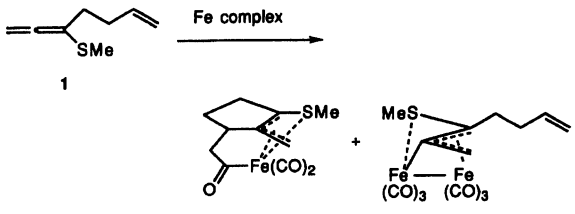


Fig. 1. Molecular structure of **2**.

Accordingly, the complex **2** was thought to be formed by the reaction of the propadienyl sulfide **1** with mononuclear iron carbonyl species generated from $Fe_2(CO)_9$ by photoirradiation. In order to improve the yield of the cyclized complex **2**, the reaction was performed using some mononuclear iron carbonyl complexes (Eq. 4, Table 1). As a result, the mononuclear complex **2** was provided in the best yield of 40% by photoirradiation at room temperature with $Fe(CO)_4(NMe_3)$,[18] which was prepared in situ from $Fe(CO)_5$ and trimethylamine *N*-oxide in THF, along with the dinuclear complex **3** in 15% yield. $Fe(CO)_4(NMe_3)$ was proved to be an appropriate reagent as a source of mononuclear iron carbonyl species. The facile liberation of trimethylamine from $Fe(CO)_4(NMe_3)$ under the mild reaction conditions[18] prevents any side reactions such as an intermolecular reaction or a polymerization of propadienyl sulfide **1** and the formation of dinuclear iron carbonyl species.

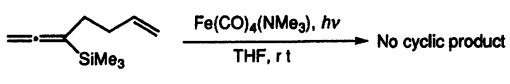
The reaction of a propadienylsilane **4**,[21] a silicon analogue of **1**, was also examined under the same reaction conditions, but it afforded no cyclic product including a cyclized allyl complex like **2** (Eq. 4). This result shows that alkylthio substituent plays a pivotal role in the formation and stabilization of the monocyclic η^3-allyl iron complex **2**.

Table 1. Reaction of **1** with Various Iron Carbonyl Complexes



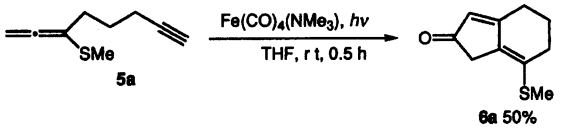
Fe complex	Condition	Solvent	**2**/%	**3**/%
$Fe_2(CO)_9$	100 W $h\nu$	Benzene	18	15
	80 °C	Benzene	23	15
	Ultrasound	Benzene	0	42
$Fe(CO)_5$	400 W $h\nu$	Toluene	21	10
	150 °C	Xylene	10	0
$Fe(CO)_3(bda)$[19]	80 °C	Toluene	<10	<10
$Fe(CO)_4(thf)$[20]	RT	THF	<10	<10
$Fe(CO)_4(NMe_3)$	100 W $h\nu$	THF	40	15

bda=benzylideneacetone.



(4)

Reaction between 1-(ω-Alkynyl)propadienyl Sulfides and $Fe(CO)_4(NMe_3)$. Methyl 1-(4-pentynyl)propadienyl sulfide (**5a**),[15] an acetylenic derivative of **1**, was submitted to the reaction under the same reaction conditions, namely in the presence of $Fe(CO)_4(NMe_3)$ by photoirradiation. In contrast with the reaction of the propadienyl sulfide **1**, the reaction of **5a** with $Fe(CO)_4(NMe_3)$ afforded no monocyclic η^3-allyl iron complex but instead a bicyclic dienone **6a** in the yield of 50%[22] (Eq. 5).



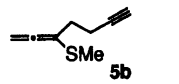
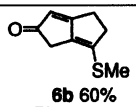
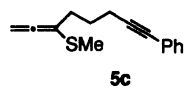
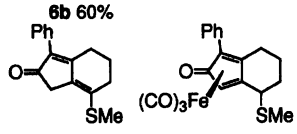
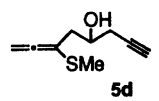
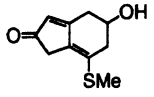
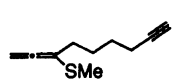
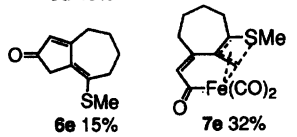
(5)

This intramolecular carbonylative coupling reaction gives the bicyclic skeleton by one-pot reaction. Since the bicyclic product has synthetically useful dienone and vinyl sulfide moieties, the generality of this reaction was investigated (Table 2).

Various 1-(ω-alkynyl)propadienyl sulfides (**5b**—**5e**) were converted into bicyclic [*n*.3.0] dienones (n=3—5) under the same reaction conditions. In the reaction of the propadienyl sulfide **5b**, a dienone **6b** which has the bicyclo[3.3.0] skeleton was afforded in a desirable yield (Entry 1). The propadienyl sulfide **5c** possessing a substituted acetylene moiety on the side chain also reacted to give a bicyclic dienone **6c** in 30% yield, but a (cyclopentadienone)iron complex **7c** was also obtained in 19% yield (Entry 2). A hydroxyl group in the tether of 1, 2-propadienyl sulfide gave no influence on this reaction (Entry 3).

In the reaction of **5e**, a monocyclic η^3-ally iron complex **7e** whose structure was ascertained by X-ray measurements (Fig. 2) was afforded as a major product, along with a bicyclic [5.3.0] decadienone **6e**. The reductive elimination from **7e** easily occurred by heating **7e** in refluxing benzene to give the bicyclic dienone **6e** (Eq. 6).

Table 2. Conversion of 1-(ω-Alkynyl)propadienyl Sulfides to Dienones

Entry	Allenes	Time/h	Products
1		0.5	
2		5	
3		4	
4		3	

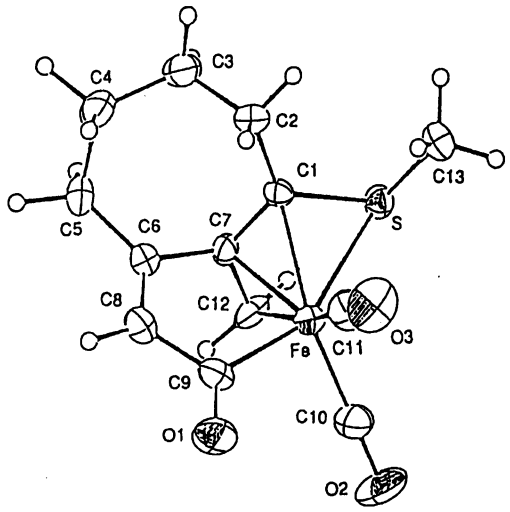
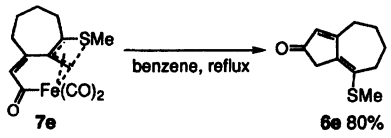
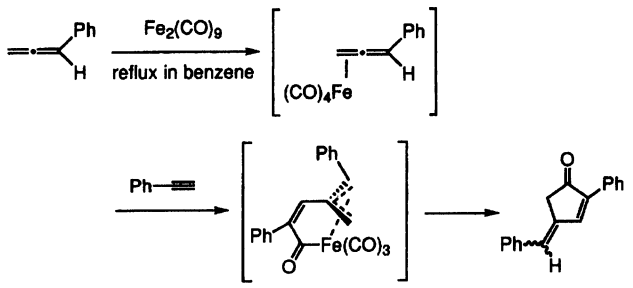


Fig. 2. Molecular structure of **7e**.



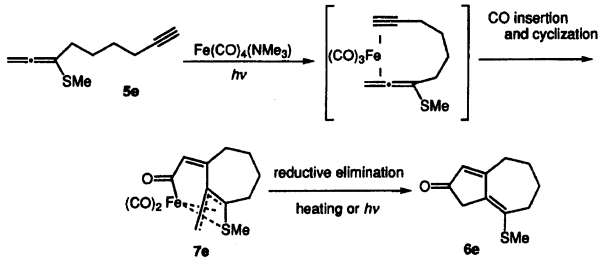
(6)

η^3-Allyl mononuclear iron complex has been a hypothetical intermediate in the intermolecular carbonylative cyclization reaction of allene and acetylene to 4-methylene-2-cyclopenten-1-one, as depicted in Eq. 7.[23]



(7)

The isolation of **7e** and the transformation of **7e** to the dienone **6e** definitely show that the η^3-allyl mononuclear iron complex is really the intermediate, it was stably isolated with the aid of the coordination of sulfur to iron atom (Eq. 8).

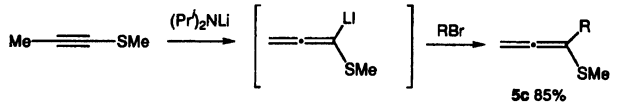


(8)

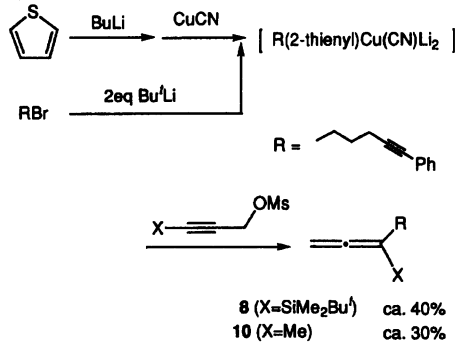
Iron carbonyl complexes have been utilized for intramolecular alkene–alkyne[24] and alkyne–alkyne[25] carbonylative coupling reactions. All these reactions proceed under high pressure of carbon monoxide or by heating over 130 °C. On the contrary, the present intramolecular coupling reaction between alkyne and allene functionality proceeded at ambient temperature under argon atmosphere. These differences of the reaction conditions are attributable to the ready formation of η^3-allyl complex from allene and iron carbonyl complex accompanying the intramolecular cyclization.

Effect of Alkylthio Group in the Allene–Alkyne Coupling Reaction. In order to investigate the indispensability of alkylthio group in the allene–alkyne coupling reaction, various acetylenic allene derivatives **5c**, **8**, **10** possessing methylthio, *t*-butyldimethylsilyl, and methyl group, respectively, were synthesized.

The propadienyl sulfide **5c** was readily prepared by alkylation of 1-methylthiopropadienyl lithium with 5-bromo-1-phenyl-1-pentyne in high yield (Eq. 9). The other allenes **8**, and **10** were prepared by the reaction between propargyl methanesufonates and organocopper reagent which was prepared by the Lipschutz method.[26] But the preparation of the organocopper reagent possessing acetylenic moiety was so difficult that the yield of allene was generally low (Eq. 10).



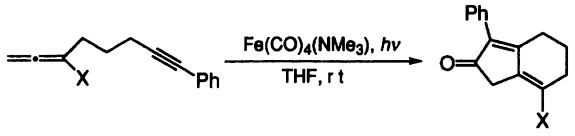
(9)

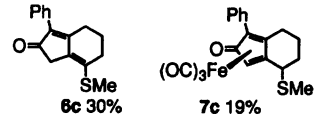
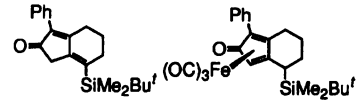
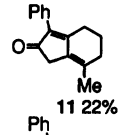
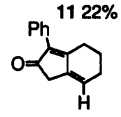


(10)

These allene compounds were submitted to the reaction with $Fe(CO)_4(NMe_3)$ under photoirradiation conditions (Table 3). In the reaction of the propadienyl sulfide **5c**, the carbonylative coupling reaction proceeded in 49% total yield (Entry 1). In the reaction of the allene **8** possessing trialkylsilyl group, which has some electron-donating ability,[27] though inferior to that of alkylthio group,[13] the carbonylative coupling reaction also proceeded in lower yield of 30% including a dienone, **9** (Entry 2). Even the methyl-substituted allene **10** also reacted with $Fe(CO)_4(NMe_3)$ to afford a bicyclic dienone **11**, but in still low yield of 22% (Entry 3).

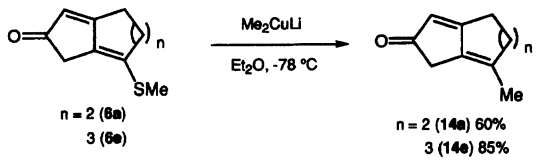
Table 3. Conversion of 1-(ω-Alkynyl)propadiene to Dienone



Entry	X	Time/h	Products
1	SMe (**5c**)	5	 **6c** 30% **7c** 19%
2	$SiMe_2Bu^t$ (**8**)	4	 **9** 28% 2%
3	Me (**10**)	4	 **11** 22%
4	H (**12**)	1	 **13** trace

However, the reaction of the allene **12** possessing a hydrogen on 1-position afforded only a trace amount of a dienone **13**. These results indicate that α,α-disubstituted structure of allene is indispensable to bring allene and acetylenic moieties in close proximity and that the reaction efficiency is improved by introduction of an electron-releasing substituent such as alkylthio group.

Moreover, the vinyl sulfide moiety of the products prepared from propadienyl sulfides is useful for further synthetic transformation.[28] For example, alkylation reaction to the dienones **6a**, and **e** proceeded by employing Me_2CuLi[29] to give methyl-substituted dienones **14a**, and **e**.

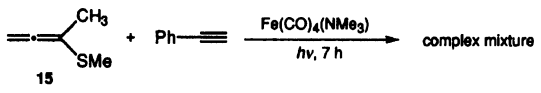


(11)

These findings indicate that introduction of alkylthio group to allene is of advantage not only to promotion of the intramolecular allene–alkyne coupling reaction but also to preparation of allenes possessing acetylenic moiety on their side chain and to the extension of the synthetic utility of the bicyclic products.

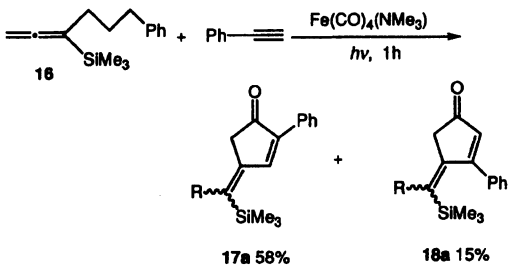
Intermolecular Allene–Alkyne Coupling Reaction by the Use of $Fe(CO)_4(NMe_3)$. $Fe(CO)_4(NMe_3)$ proved to be an efficient reagent for the intramolecular carbonylative allene–alkyne coupling reaction, so it is expected to work as well in intermolecular reactions. When a mixture of a propadienyl sulfide **15** and phenylacetylene was treated with $Fe(CO)_4(NMe_3)$

under photoirradiation conditions, however, the reaction gave a complex mixture and no cyclic product was isolated (Eq. 12). This result implies that propadienyl sulfide is so reactive in the intermolecular reaction that various side reactions like self-coupling and polymerization reactions of propadienyl sulfide proceed prior to the allene–alkyne coupling reaction.



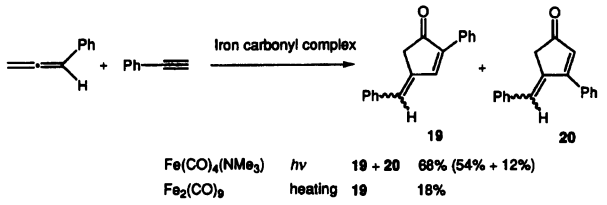
(12)

Next, in place of **15**, a propadienyl silane **16** was submitted to the reaction under the same reaction conditions. As a result, the intermolecular carbonylative coupling reaction proceeded to afford 4-methylene-2-cyclopenten-1-ones **17a**, and **18a** in good yield (Eq. 13).



(13)

The reaction between phenylpropadiene and phenylacetylene also proceeded under the same conditions to give the coupling products **19**, and **20** in 68% in total. Compared with the reaction where $Fe_2(CO)_9$ was employed,[23] the yield is remarkably increased (Eq. 14).



(14)

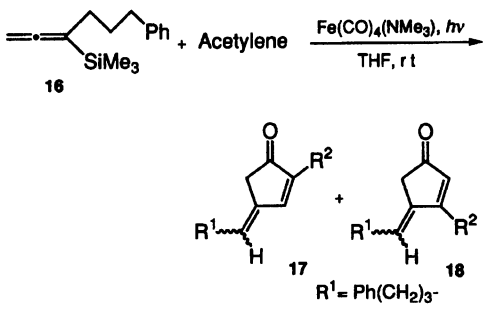
Various acetylenes and propadienylsilane **16** were treated under the same reaction conditions (Table 4). Not only aryl-substituted acetylenes (Entry 1,2) but also alkyl-substituted acetylenes (Entry 3,4) reacted with **16** to provide 4-methylene-2-cyclopenten-1-ones in moderate yield. $Fe(CO)_4(NMe_3)$ was proved to be effective also in the intermolecular coupling reaction of propadienylsilane **16** and acetylenes.

Experimental

General. ^{1}H NMR spectra (500 MHz) and ^{13}C NMR spectra (125 MHz) were measured with a Bruker AM500 spectrometer, using tetramethylsilane as the internal standard. $CDCl_3$ was used as solvent. The IR spectra were recorded with a Horiba FT 300-S spectrophotometer. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-D300 mass spectrometer at an ionization energy of 70 eV. X-Ray diffraction intensities were collected on a Rigaku AFC-5R goniometer with graphite monochromatized Mo $K\alpha$ (λ=0.71069 Å) radiation (Table 5).

Preparative thin-layer chromatography (TLC) was performed on a silica gel (Wakogel B-5F). THF and Et_2O were freshly distilled from sodium diphenylketyl. Benzene was distilled and dried over Molecular Sieves 4A (MS 4A). Fe-

Table 4. Intermolecular Carbonylative Allne–Alkyne Coupling Reaction of **16**



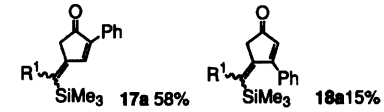
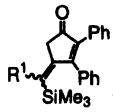
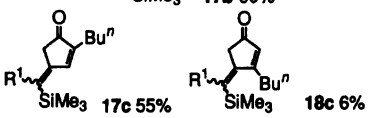
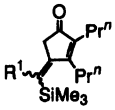
Entry	Acetylene	Time/h	Products
1	Ph—≡	1	 **17a** 58% **18a** 15%
2	Ph—≡—Ph	1	 **17b** 60%
3	Bu^n—≡	8	 **17c** 55% **18c** 6%
4	Pr^n—≡—Pr^n	10	 **17d** 57%

Table 5. Crystallographic Data of **2** and **7e**

	2	**7e**
Color	Orange	Yellow
Crystal shape	Block	Needle
Molecular formula	$C_{11}H_{12}FeO_3S$	$C_{13}H_{14}FeO_3S$
Formula weight	280.12	306.16
Crystal size/mm	0.20×0.10×0.10	0.20×0.10×0.80
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
a/Å	7.93(1)	8.108(3)
b/Å	11.039(4)	19.507(3)
c/Å	13.622(4)	8.606(2)
β/°	98.40(4)	99.63(2)
V/Å^3	1179(1)	1342.0(5)
Z	4	4
D_c/g cm^{-3}	1.577	1.515
μ(Mo $K\alpha$)/cm^{-1}	14.34	12.67
No. of reflections		
Measured	3071	3417
Observed	1930	1701
Variables	145	183
R	0.036	0.053
R_w	0.040	0.056

$(CO)_5$ was reagent grade and was used without further purification. Trimethylamine *N*-oxide was prepared by the sublimation from its dihydrate. All of the operations were carried out under an argon atmosphere.

3-Methylthio-1,2,6-heptatriene (**1**), 3-methylthio-1,2-octadien-7-yne (**5a**) were prepared according to literature methods.[15]

3-Methylthio-1,2-heptadien-6-yne (5b). Compound **5b** was prepared by the reaction between 1-methylthio-1-propyne and 4-bromo-1-butyne according to a literature procedure.[12] Yield 55%. Bp 100 °C/0.1 mmHg (1 mmHg=133.32 Pa) (bulb to bulb distillation). IR (neat) 2119, 1946, 1431 cm^{-1}; ^1H NMR δ=1.95 (1H, t, J=2.4 Hz), 2.13 (3H, s), 2.36—2.39 (4H, m), 5.02 (2H, t, J=2.6 Hz); ^{13}C NMR δ=15.5, 17.6, 32.1, 68.7, 82.0, 83.4, 102.7, 202.3. HRMS Found: m/z 138.0482. Calcd for $C_8H_{10}S$: M, 138.0504.

3-Methylthio-8-phenyl-1,2-octadien-7-yne (5c). Compound **5c** was prepared by the reaction between 1-methylthio-1-propyne and 5-bromo-1-phenyl-1-pentyne according to a literature procedure.[12] Yield 85%. Bp 150 °C/10^{-5} mmHg (bulb to bulb distillation). IR (neat) 2215, 1946, 1489, 756 cm^{-1}; ^1H NMR δ=1.84 (2H, tt, J=7.1, 7.1 Hz), 2.15 (3H, s), 2.34 (2H, tt, J=2.8, 7.1 Hz), 2.46 (2H, t, J=7.1 Hz), 5.01 (2H, t, J=2.8 Hz), 7.14—7.23 (3H, m), 7.38—7.40 (2H, m); ^{13}C NMR δ=15.4, 18.7, 27.1, 32.1, 81.0, 81.3, 89.5, 103.3, 123.9, 127.5, 128.1, 131.5, 202.2. HRMS Found: m/z 228.0977. Calcd for $C_{15}H_{16}S$: M, 228.0973.

6-Methylthio-6,7-octadien-1-yn-4-ol (5d). Compound **5d** was prepared by the reaction between 1-methylthio-1-propyne and 5-bromo-4-(t-butyldimethylsiloxy)-1-trimethylsilyl-1-pentyne according a literature procedure,[12] followed by desilylation in the THF solution of Bu_4NF. Yield 65%. Bp 175 °C/0.1 mmHg (bulb to bulb distillation). IR (neat) 3294, 2107, 1944, 1427 cm^{-1}; ^1H NMR δ=2.03 (1H, t, J=2.7 Hz), 2.13 (3H, s), 2.30 (1H, bs), 2.36—2.48 (4H, m), 3.99 (1H, dd, J=5.7, 5.7 Hz), 5.03 (2H, bs); ^{13}C NMR δ=15.5, 26.3, 39.9, 68.4, 70.5, 80.4, 81.6, 100.5, 203.0. HRMS Found: m/z 168.0612. Calcd for $C_9H_{12}OS$: M, 168.0609.

3-Methylthio-1,2-nonadien-8-yne (5e). Compound **5e** was prepared by the reaction between 1-methylthio-1-propyne and 6-iodo-1-hexyne according a literature method.[12] Yield 88%. Bp 125 °C/0.1 mmHg (bulb to bulb distillation). IR (neat) 2117, 1944, 1431 cm^{-1}; ^1H NMR δ=1.52—1.66 (4H, m), 1.92 (1H, t, J=2.6 Hz), 2.12 (3H, s), 2.14—2.20 (4H, m), 4.96 (2H, t, J=2.8 Hz); ^{13}C NMR δ=15.4, 18.1, 27.1, 27.7, 32.4, 68.3, 81.2, 84.3, 103.7, 202.1. HRMS Found: m/z 166.0804. Calcd for $C_{10}H_{14}S$: M, 166.0817.

8-Phenyl-3-(t-butyldimetylsilyl)-1,2-octadien-7-yne (8). To a THF solution (2 ml) of thiophene (180 mg, 2.14 mmol) was added BuLi (1.38 ml, 1.49 M hexane solution 1 M=1 mol dm^{-3}) at −78 °C. The yellow solution was stirred at 0 °C for 0.5 h, then it was transferred via a cannula into an Et_2O suspension (1 ml) of CuCN (185 mg, 2.05 mmol) at −78 °C. The reaction mixture was next stirred at 0 °C for 5 min. An Et_2O solution of 5-phenyl-4-pentynyllithium was prepared from 1-bromo-5-phenyl-4-pentyne (459 mg, 2.05 mmol) and t-BuLi (2.41 ml, 1.7 M pentane solution) in Et_2O (4 ml) at −78 °C for 1.5 h. To the light tan solution of cuprate was added the Et_2O solution of the above lithium salt at −78 °C, then the mixture was stirred at 0 °C for 5 min. Finally, a THF solution (1 ml) of (3-t-butyldimetylsilyl)-2-propynylmethanesulufonate (568 mg, 2.28 mmol) was injected at −78 °C, then the reaction mixture was warmed to 0 °C over 5 h and quenched by addition of a 90% NH_4Cl–10% NH_4OH aqueous solution. Organic materials were extracted with Et_2O and the combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by TLC to afford the product. Yield ca. 40%. IR (neat) 1923 cm^{-1}; ^1H NMR δ=0.64 (6H, s), 0.90 (9H, s), 1.78 (2H, tt, J=7.0, 7.5 Hz), 2.11 (2H, tt, J=3.5, 7.5 Hz), 2.44 (2H, t, J=7.0 Hz), 4.37 (2H, t, J=3.5 Hz), 7.24—7.28 (3H, m), 7.36—7.38 (2H, m). HRMS Found: m/z 239.1254. Calcd for $C_{20}H_{28}Si-Bu^t$: M−Bu^t, 239.1257.

3-Methyl-8-phenyl-1,2-octadien-7-yne (10). Compound **10** was prepared by the method for the preparation of **8**, except that 2-butynylmethane sulfonate was employed in place of 3-(t-butyldimetylsilyl)-2-propynyl methanesulufonate. Yield ca. 30%. IR (neat) 1959 cm^{-1}; ^1H NMR δ=1.71 (3H, t, J=3.1 Hz), 1.75 (2H, tt, J=7.1, 7.3 Hz), 2.10 (2H, tt, J=3.1, 7.3 Hz), 2.44 (2H, t, J=7.1 Hz), 4.63 (2H, tq, J_t=J_q=3.1 Hz), 7.24—7.29 (3H, m), 7.38 (2H, m); ^{13}C NMR δ=18.8, 18.9, 26.5, 32.5, 74.3, 80.8, 90.0, 97.7, 124.0, 127.5, 128.1, 131.5, 205.1. HRMS Found: m/z 196.1248. Calcd for $C_{15}H_{16}$: M, 195.1253.

8-Phenyl-1,2-octadien-7-yne (12). Compound **12** was prepared by the reaction between 5-bromo-1-phenyl-1-pentyne and propargyl methyl ether by a literature procedure.[30]. IR (neat) 1955, 2229 cm^{-1}; ^1H NMR δ=1.74 (2H, tt, J=7.1, 7.4 Hz), 2.16—2.21 (2H, m), 2.46 (2H, t, J=7.1 Hz), 4.71 (2H, dt, J_d=6.6 Hz, J_t=3.3 Hz), 5.14 (1H, tt, J=6.6, 6.9 Hz), 7.24—7.30 (3H, m), 7.39 (2H, m); ^{13}C NMR δ=18.8, 27.3, 28.0, 75.0, 80.9, 89.2, 89.8, 124.0, 127.5, 128.1, 131.5, 208.6. HRMS Found: m/z 182.1096. Calcd for $C_{14}H_{14}$: M, 182.1103.

A Typical Procedure for the Intramolecular Allene–Alkyne Coupling Reaction Using $Fe(CO)_4(NMe_3)$. Into a Pyrex test tube equipped with an argon-filled balloon, trimethylamine *N*-oxide (225 mg, 3.0 mmol) and THF (4 ml) were charged. Addition of a THF solution (3 ml) of $Fe(CO)_5$ (293 mg, 1.5 mmol) to the suspension at −30 °C gave a red solution of $Fe(CO)_4(NMe_3)$. A THF solution (3 ml) of an allene compound (0.5 mmol) was then added. After external photoirradiation by a 100 W high-pressure mercury lamp at room temperature, the resulting precipitates were removed by filtration through a small pad of silica gel. Purification of the crude products by preparative thin-layer chromatography gave the products.

Spectral data and physical properties of the products are as follows.

The η^3-Allyl Mononuclear Complex 2. Mp 119—121 °C (hexane). IR (KBr disk) 1996, 1934, 1917, 1631, 1454 cm^{-1}; ^1H NMR δ=1.28 (1H, d, J=3.7 Hz), 1.66 (1H, ddd, J=5.8, 8.0, 8.9 Hz), 2.12 (3H, s), 2.39 (1H, d, J=16.3 Hz), 2.58 (1H, ddd, J=9.0, 9.0, 13.8 Hz), 2.84 (1H, d, J=3.7 Hz), 2.89 (1H, dd, J=5.8, 16.3 Hz), 3.00—3.05 (2H, m), 3.20 (1H, ddd, J=8.9, 8.9, 13.8 Hz); ^{13}C NMR δ=17.4, 29.9, 31.3, 39.2, 42.0, 68.3, 94.9, 126.6, 208.7, 215.6, 264.9. Anal. Found: C, 47.29; H, 4.32; S, 11.77%. Calcd for $C_{11}H_{12}O_3SFe$: C, 47.16; H, 4.32; S, 11.45%.

μ-[(1,2,3-η)-(3-Methylthio-2,6-heptadienyl)] bis-

(tricarbonyliron)(*Fe–Fe*) (3). IR (neat) 2065, 2023, 2019, 1990, 1982, 1638, 1421 cm^{-1}; ^1H NMR δ=1.10—1.19 (1H, m), 1.88—1.98 (1H, m), 2.07—2.15 (1H, m), 2.23—2.32 (1H, m), 2.37 (3H, s), 3.47 (1H, s), 4.03 (1H, s), 4.97 (1H, d, J=9.8 Hz), 5.03 (1H, d, J=17.3 Hz), 5.73—6.82 (1H, m). HRMS Found: m/z 419.9032. Calcd for $C_{14}H_{12}O_6SFe$: M, 419.9054.

2-(Methylthio)bicyclo[4.3.0]nona-1,6-dien-8-one (6a). Mp 39 °C (hexane–CH_2Cl_2). IR (neat) 1697, 1571, 1430 cm^{-1}; ^1H NMR δ=1.90 (2H, dt, J_d=J_t=6.2 Hz), 2.33 (3H, s), 2.44 (2H, t, J=6.2 Hz), 2.60 (2H, t, J=6.2 Hz), 2.88 (2H, s), 5.79 (1H, s); ^{13}C NMR δ=13.5, 22.6, 25.5, 27.8, 38.5, 125.3, 131.4, 136.4, 169.9, 204.3. Anal. Found: C, 66.34; H, 6.50; S, 17.97%. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; S, 17.79%.

6-(Methylthio)bicyclo[3.3.0]octa-1,5-dien-3-one (6b). Mp 78—79 °C (hexane–CH_2Cl_2). IR (neat) 1672, 1612, 1568, 1433 cm^{-1}; ^1H NMR δ=2.47 (3H, s), 2.85 (2H, bs), 2.93 (2H, bs), 2.96 (2H, s), 5.69 (1H, s); ^{13}C NMR δ=14.5, 26.3, 36.6, 38.8, 117.0, 137.6, 143.8, 186.6, 207.2. Anal. Found: C, 65.09; H, 6.20; S, 19.63%. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06; S, 19.29%.

2-Methylthio-7-phenylbicyclo[4.3.0]nona-1,6-dien-8-one (6c). Mp 119—120 °C (hexane–CH_2Cl_2). IR (neat) 1684, 1614, 1597, 1444, 698 cm^{-1}; ^1H NMR δ=1.91 (2H, tt, J=6.2, 6.2 Hz), 2.36 (3H, s), 2.51 (2H, t, J=6.2 Hz), 2.76 (2H, t, J=6.2 Hz), 3.06 (2H, s), 7.25—7.40 (5H, m); ^{13}C NMR δ=13.6, 22.8, 25.2, 28.0, 38.6, 127.4, 128.2, 128.9, 130.5, 131.8, 135.2, 136.0, 163.6, 202.0. HRMS Found: m/z 256.0919. Calcd for $C_{16}H_{16}OS$: M, 256.0922.

Tricarbonyl(2-methylthio-7-phenylbicyclo[4.3.0]nona-6,9(1)-dien-8-one)iron (7c). IR (neat) 2071, 2013, 1998, 1712, 1637, 1363 cm^{-1}; ^1H NMR δ=1.80—1.86 (1H, m), 1.93—1.99 (1H, m), 2.12—2.55 (2H, m), 2.20 (3H, s), 2.65 (1H, ddd, J=6.3, 6.3, 17.4 Hz), 2.73 (1H, ddd, J=6.2, 6.2, 17.4 Hz), 3.69 (1H, dd, J=5.5, 5.5 Hz), 4.28 (1H, s), 7.29—7.37 (3H, m), 7.61—7.63 (2H, m). HRMS Found: m/z 396.0116. Calcd for $C_{19}H_{16}O_4SFe$: M, 396.0118.

4-Hydroxy-2-(methylthio)bicyclo[4.3.0]nona-1,6-dien-8-one (6d). Mp 100 °C (hexane–CH_2Cl_2). IR (neat) 3373, 1660, 1614, 1429 cm^{-1}; ^1H NMR δ=1.70 (1H, bs), 2.35 (3H, s), 2.50 (1H, dd, J=6.9, 16.9 Hz), 2.66 (1H, dd, J=8.4, 16.1 Hz), 2.75 (1H, dd, J=4.3, 16.9 Hz), 2.85—2.92 (3H, m), 4.21—4.23 (1H, m), 5.87 (1H, s); ^{13}C NMR δ=13.6, 34.4, 36.6, 38.3, 66.3, 126.9, 131.1, 133.1, 167.6, 204.4. Anal. Found: C, 61.00; H, 6.18; S, 16.11%. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34%.

2-(Methylthio)bicyclo[5.3.0]deca-1,7-dien-9-one (6e). IR (neat) 1678, 1603, 1558, 1421 cm^{-1}; ^1H NMR δ=1.79 (2H, tt, J=6.4, 6.4 Hz), 1.89 (2H, tt, J=6.4, 6.4 Hz), 2.32 (3H, s), 2.64 (2H, t, J=6.4 Hz), 2.74 (2H, t, J=6.4 Hz), 3.02 (2H, s), 5.92 (1H, s); ^{13}C NMR δ=15.0, 23.8, 26.8, 30.5, 30.6, 42.4, 130.5, 133.6, 139.6, 174.0, 204.3. HRMS Found: m/z 194.0760. Calcd for $C_{11}H_{14}OS$: M, 194.0766.

The η^3-Allyl Mononuclear Complex 7e. Decomposed at 120 °C (hexane). IR (neat) 2004, 1996, 1948, 1639, 1623 cm^{-1}; ^1H NMR δ=1.55 (1H, d, J=2.4 Hz), 1.61—1.65 (1H, m), 1.88—1.95 (1H, m), 2.08 (3H, s), 2.16—2.20 (1H, m), 2.24—2.32 (1H, m), 2.53 (1H, ddd, J=5.2, 11.7, 11.7 Hz), 2.77—2.89 (4H, m), 5.36 (1H, s). Anal. Found: C, 50.76; H, 4.61; S, 10.96%. Calcd for $C_{13}H_{14}O_3SFe$: C, 51.00; H, 4.61; S, 10.47%. HRMS Found: m/z 306.0026. Calcd for $C_{13}H_{14}O_3SFe$: M, 306.0013.

2-(*t*-Butyldimethylsilyl)-7-phenylbicyclo[4.3.0]nona-1,6-dien-8-one (9). IR (neat) 1695 cm^{-1}; ^1H NMR δ=0.18 (6H, s), 0.92 (9H, s), 1.75 (2H, tt, J=5.6, 6.3 Hz), 2.37 (2H, t, J=5.6 Hz), 2.79 (2H, t, J=6.3 Hz), 3.13 (2H, s), 7.28—7.30 (1H, bs), 7.37—7.40 (4H, m); ^{13}C NMR δ=−4.7, 18.6, 22.5, 26.5, 27.1, 30.7, 41.3, 127.7, 128.2, 129.1, 131.4, 136.9, 139.9, 143.4, 164.1, 203.8. Anal. Found: C, 77.58; H, 8.68%. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70%.

2-Methyl-7-phenylbicyclo[4.3.0]nona-1,6-dien-8-one (11). IR (neat) 1696 cm^{-1}; ^1H NMR δ=1.81 (2H, tt, J=6.0, 6.4 Hz), 1.87 (3H, s), 2.25 (2H, t, J=6.0 Hz), 2.74 (2H, t, J=6.4 Hz), 3.02 (2H, s), 7.26—7.29 (1H, m), 7.36—7.40 (4H, m); ^{13}C NMR δ=21.1, 22.4, 25.2, 31.1, 37.8, 127.4, 128.2, 129.0, 130.0, 132.0, 135.7, 136.4, 165.7, 203.1. HRMS Found: m/z 224.1159. Calcd for $C_{16}H_{16}O$: M, 224.1202.

Methylation of the Dienones 6a,e by the Use of Me_2CuLi. To a Et_2O solution (5.0 ml) of copper iodide (190.5 mg, 1.00 mmol) was added MeLi (2 mmol, 1.3 M hexane solution) dropwise at −30 °C. To the clear solution of Me_2CuLi was added a Et_2O solution (5 ml) of a dienone **6** (0.5 mmol) at −78 °C. After being stirred at the temperature until no dienone was detected by TLC, the reaction mixture was quenched with sat. NH_4Cl aqueous solution. Inorganic materials were filtered off and organic materials were extracted with Et_2O. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by TLC (hexane/ethyl acetate).

Spectral data and physical properties of the products are as follows.

2-Methylbicyclo[4.3.0]nona-1,6-dien-8-one (14a). IR (neat) 1697, 1670 cm^{-1}; ^1H NMR δ=1.80 (2H, tt, J=6.3, 6.3 Hz), 1.80 (3H, s), 2.18 (2H, t, J=6.3 Hz), 2.60 (2H, t, J=6.3 Hz), 2.85 (2H, s), 5.81 (1H, s); ^{13}C NMR δ=20.9, 22.2, 23.0, 30.8, 37.7, 126.0, 131.2, 136.6, 171.9, 205.4. HRMS Found: m/z 148.0888. Calcd for $C_{10}H_{12}O$: M, 148.0888.

2-Methylbicyclo[5.3.0]deca-1,7-dien-9-one (14e). IR (neat) 1680 cm^{-1}; ^1H NMR δ=1.73 (2H, tt, J=5.9, 5.9 Hz), 1.79 (2H, tt, J=5.9, 5.9 Hz), 1.82 (3H, s), 2.36 (2H, t, J=5.9 Hz), 2.72 (2H, t, J=5.9 Hz), 2.91 (2H, s), 5.89 (1H, s); ^{13}C NMR δ=24.0, 24.1, 26.6, 31.3, 34.7, 41.8, 130.5, 132.5, 140.0, 175.9, 205.2. HRMS Found: m/z 162.1045. Calcd for $C_{11}H_{14}O$: M, 162.1045.

The propadienyl sulfide **15** was prepared according to a literature procedure.[12]

6-Phenyl-3-trimethylsilyl-1,2-heptadiene (16). Compound **16** was obtained by the literature method[21] except that the Grinard reagent was prepared from 3-phenylpropyl bromide. IR (neat) 1927, 1248, 839 cm^{-1}; ^1H NMR δ=0.09 (9H, s), 1.80 (2H, tt, J=7.7, 7.7 Hz), 1.99 (2H, tt, J=3.2, 7.7 Hz), 2.64 (2H, t, J=7.7 Hz), 4.35 (2H, t, J=3.2 Hz), 7.15—7.29 (5H, m); ^{13}C NMR δ=−1.7, 28.2, 30.7, 35.5, 69.1, 94.1, 125.6, 128.2, 128.3, 142.6, 208.3. HRMS Found: m/z 230.1484. Calcd for $C_{15}H_{22}Si$: M, 230.1481.

A Typical Procedure for the Intermolecular Allene–Alkyne Coupling Reaction Using $Fe(CO)_4(NMe_3)$. Into a Pyrex test tube equipped with an argon-filled balloon, trimethylamine *N*-oxide (225 mg, 3.0 mmol) and THF (4 ml) were charged. Addition of a THF solution (3 ml) of $Fe(CO)_5$ (293 mg, 1.5 mmol) to the suspension at −30 °C gave a red solution of $Fe(CO)_4(NMe_3)$. A

THF solution (4 ml) of the propadienyl silane **16** (115.2 mg, 0.50 mmol) and an acetylene compound (1.50 mmol) were added. After external photoirradiation by a 100 W high-pressure mercury lamp at room temperature, the resulting precipitates were removed by filtration through a small pad of silica gel. Purification of the crude products by preparative thin-layer chromatography gave the products.

Spectral data and physical properties of the products are as follows.

2-Phenyl-4-[4-phenyl-1-(trimethylsilyl)butylidene]-2-cyclopenten-1-one (17a). Compound **17a** was obtained as a mixture of *E* and *Z* isomers (1/1), but the assignment of the stereochemistry is unsettled. IR (neat) 1703, 1699, 838, 701 cm^{-1}; ^1H NMR δ=0.20 (9H×0.5, s), 0.28 (9H×0.5, s), 1.69 (2H×0.5, tt, J=7.8, 8.1 Hz), 1.75 (2H×0.5, tt, J=7.8, 8.1 Hz), 2.31 (2H×0.5, t, J=8.1 Hz), 2.48 (2H×0.5, t, J=8.1 Hz), 2.67 (2H×0.5, t, J=7.8 Hz), 2.70 (2H×0.5, t, J=7.8 Hz), 3.12 (2H×0.5, s), 3.19 (2H×0.5, s), 7.17—7.41 (8H, m), 7.76—7.80 (2H, m), 7.99 (1H×0.5, s), 8.16 (1H×0.5, s); ^{13}C NMR δ=−0.2, 0.8, 31.4, 31.7, 33.2, 34.6, 35.8, 36.2, 40.3, 42.5, 125.9, 127.2, 127.4, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 131.5, 131.6, 141.5, 141.7, 141.7, 142.3, 142.5, 143.2, 144.3, 145.4, 148.7, 152.2, 203.0, 204.3. Anal. Found: C, 79.67; H, 7.96%. Calcd for $C_{24}H_{28}OSi$: C, 79.95; H, 7.83%.

3-Phenyl-4-[4-phenyl-1-(trimethylsilyl)butylidene]-2-cyclopenten-1-one (18a). Compound **18a** was obtained as one isomer, but the assignment of the sterochemistry is unsettled. IR (neat) 1701, 1693, 839, 700 cm^{-1}; ^1H NMR δ=0.16 (9H, s), 1.31—1.37 (2H, m), 1.96—1.99 (4H, m), 3.21 (2H, s), 6.14 (1H, s), 6.93 (2H, d, J=7.4 Hz), 7.13 (1H, t, J=7.4 Hz), 7.20 (2H, t, J=7.4 Hz), 7.31—7.33 (2H, m), 7.41—7.43 (3H, m); ^{13}C NMR δ=0.2, 31.8, 33.1, 35.9, 44.1, 125.7, 126.5, 128.1, 128.2, 128.3, 128.4, 135.4, 138.2, 141.9, 142.3, 146.5, 171.8, 204.5. HRMS Found: m/z 360.1903. Calcd for $C_{24}H_{28}OSi$: M, 360.1909.

2,3-Diphenyl-4-[4-phenyl-1-(trimethylsilyl)butylidene]-2-cyclopenten-1-one (17b). Compound **17b** was obtained as a mixture of *E* and *Z* isomers (9/1), but the assignment of the stereochemistry is unsettled. Mp 130—132 °C (hexane–CH_2Cl_2). IR (neat) 1699, 845, 837, 733, 698 cm^{-1}; ^1H NMR δ=−0.29 (9H×0.1, s), 0.18 (9H×0.9, s), 1.31—1.35 (2H, m), 1.89—1.96 (4H, m), 3.35 (2H×0.9, s), 3.36 (2H×0.1, s), 6.94—7.35 (15H, m). Anal. Found: C, 82.23; H, 7.51%. Calcd for $C_{30}H_{32}OSi$: C, 82.52; H, 7.39%.

2-Butyl-4-[4-phenyl-1-(trimethylsilyl)butylidene]-2-cyclopenten-1-one (17c). Compound **17c** was obtained as a mixture of *E* and *Z* isomers (2/1), but the assignment of the stereochemistry is unsettled. IR (neat) 1697, 837 cm^{-1}; ^1H NMR δ=0.13 (9H×0.67, s), 0.20 (9H×0.33, s), 0.90 (3H×0.33, t, J=6.8 Hz), 0.92 (3H×0.67, t, J=6.7 Hz), 1.24—1.37 (2H, m), 1.41—1.49 (2H, m), 1.60—1.70 (2H, m), 2.19—2.27 (2H+2H×0.33, m), 2.34—2.37 (2H×0.67, m), 2.61 (2H×0.33, t, J=7.9 Hz), 2.64 (2H×0.67, t, J=7.5 Hz), 2.90 (2H×0.33, s), 2.97 (2H×0.67, s), 7.13—7.29 (5H, m), 7.51 (1H×0.67, s), 7.58 (1H×0.33, s); ^{13}C NMR δ=−0.2, 0.7, 13.8, 13.8, 22.4, 22.5, 24.5, 29.9, 29.9, 31.2, 31.8, 33.1, 34.3, 35.8, 36.2, 39.1, 41.3, 125.9, 128.3, 128.3, 128.4, 139.6, 141.6, 141.8, 141.9, 143.3, 145.0, 147.1, 147.6, 149.4, 152.7, 205.2, 206.5. Anal. Found: C, 77.67; H, 9.43%. Calcd for $C_{22}H_{32}OSi$: C, 77.39; H, 9.47%.

3-Butyl-4-[4-phenyl-1-(trimethylsilyl)butylidene]-2-cyclopenten-1-one (18c). Compound **18c** was obtained as a mixture of *E* and *Z* isomers (>20/1), but the assignment of the stereochemistry is unsettled. IR (neat) 1697, 837 cm^{-1}; ^1H NMR (major isomer) δ=0.16 (9H, s), 0.91 (3H, t, J=7.4 Hz), 1.27—1.32 (2H, m), 1.49 (2H, tt, J=7.6, 7.6 Hz), 1.62—1.67 (2H, m), 2.43—2.47 (2H, m), 2.50 (2H, t, J=7.6 Hz), 2.64 (2H, t, J=7.4 Hz), 3.02 (2H, s), 6.08 (1H, s), 7.14—7.28 (5H, m); ^{13}C NMR (major isomer) δ=0.3, 13.9, 22.5, 30.6, 31.7, 32.5, 33.3, 36.3, 43.7, 126.0, 128.4, 128.5, 133.4, 141.5, 143.3, 144.1, 175.0, 205.4. HRMS Found: m/z 340.2222. Calcd for $C_{22}H_{32}OSi$: M, 340.2222.

4-[4-Phenyl-1-(trimethylsilyl)butylidene]-2,3-dipropyl-2-cyclopenten-1-one (17d). Compound **17d** was separated into the *E* and *Z* isomer (2/1), respectively, but the assignment of the stereochemistry is unsettled.

The major isomer: IR (neat) 1697, 839 cm^{-1}; ^1H NMR δ=0.15 (9H, s), 0.89 (3H, t, J=7.1 Hz), 0.91 (3H, t, J=7.1 Hz), 1.39—1.46 (4H, tq×2, J_t=J_q=7.1 Hz), 1.65—1.69 (2H, m), 2.19 (2H, t, J=7.8 Hz), 2.38—2.44 (4H, m), 2.64 (2H, t, J=7.4 Hz), 2.97 (2H, s), 7.15—7.28 (5H, m); ^{13}C NMR δ=0.5, 14.3, 14.3, 22.1, 23.1, 25.4, 31.2, 31.4, 33.5, 36.3, 42.8, 126.0, 128.4, 128.4, 140.5, 141.6, 142.2, 145.5, 167.0, 205.5. HRMS Found: m/z 368.2554. Calcd for $C_{24}H_{36}OSi$: M, 368.2535.

The minor isomer: IR (neat) 1697, 839 cm^{-1}; ^1H NMR δ=0.22 (9H, s), 0.91 (3H, t, J=7.4 Hz), 0.96 (3H, t, J=7.4 Hz), 1.38—1.50 (4H, tq×2, J_t=J_q=7.4 Hz), 1.58—1.66 (2H, m), 2.21 (2H, t, J=7.8 Hz), 2.96 (2H, t, J=8.0 Hz), 2.56—2.60 (4H, m), 2.96 (2H, s), 7.12—7.27 (5H, m); ^{13}C NMR δ=1.9, 14.1, 14.3, 21.7, 23.7, 26.1, 31.1, 32.3, 36.0, 36.6, 42.0, 125.9, 128.3, 128.4, 139.0, 141.9, 146.0, 146.7, 168.5, 204.5. HRMS Found: m/z 368.2535. Calcd for $C_{24}H_{36}OSi$: M, 368.2535.

4-Bezylidene-2-phenyl-2-cyclopenten-1-one (19). Compound **19** was obtained as one isomer and its spectral data matched with those in a reference.[23]

4-Bezylidene-3-phenyl-2-cyclopenten-1-one (20). Compound **20** was obtained as a mixture of *E* and *Z* isomers (2/1), but the assignment of the *E* and *Z* isomers is unsettled. IR (neat) 1693, 764, 698 cm^{-1}; ^1H NMR δ=3.09 (2H×0.33, s), 3.45 (2H×0.67, s), 6.31 (1H×0.67, s), 6.40 (1H×0.33, d, J=1.4 Hz), 6.71 (1H×0.67, s), 6.80—7.50 (10H+1H×0.33, m); ^{13}C NMR δ=40.8, 44.4, 127.0, 127.2, 127.6, 127.7, 128.4, 128.7, 128.7, 128.7, 128.8, 129.3, 129.3, 129.8, 131.1, 133.6, 134.7, 134.9, 135.4, 136.2, 136.5, 136.7, 170.0, 173.1, 203.6, 204.2. HRMS Found: m/z 246.1047. Calcd for $C_{18}H_{14}O$: M, 246.1045.

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