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$W(CO)_5$(L)-promoted cyclization of 1-iodo-1-alkynes via iodovinylidene tungsten complexes

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Abstract

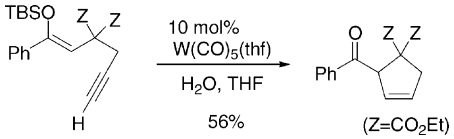
Iodovinylidene tungsten complexes are generated from 1-iodo-1-alkynes and $W(CO)_5$(thf), and are employed for two types of synthetically useful reaction, that is, 6π-electrocyclization for *o*-(iodoethynyl)styrenes, and endo-selective cyclization for ω-iodoacetylenic silyl enol ethers and 1-iodo-5-en-1-yne.

Keywords: Iodovinylidene tungsten complex; 1-Iodo-1-alkynes; π-Electrocyclization; Endo-selective cyclization; Trimethylsilylvinylidene rhodium complexes

1. Introduction

Free vinylidene, one of the unsaturated carbenes, is a highly unstable tautomer of alkyne [1]. When stabilized by coordination to a transition metal, however, they have become increasingly important as a synthetic intermediate due to their unique reactivities in organic and organometallic chemistry. The most pertinent and common route to generate vinylidene complexes involved the rearrangement of terminal alkynes with an appropriate transition metal by either direct 1,2-hydrogen migration over the carbon–carbon triple bond or oxidative addition of the carbon–hydrogen bond to the metal center and subsequent 1,3-hydrogen migration to the alkynyl ligand. For a review on vinylidene complexes, see [2]. Whereas several useful reactions utilizing the vinylidene complexes generated from terminal alkynes have been developed over the past decade (for the recent synthetic use of vinylidene complexes, see [3]), generation and reactions of vinylidene complexes derived from alkynes possessing a labile substituent at the terminus involving 1,2-migration of that substituent have hardly been studied. For examples of migration of trialkylsilyl group, alkylthio group, iodo group and other iodinated vinylidene complexes, see [4–6].

We have previously reported several synthetic reactions using vinylidene complexes of group 6 metals derived from terminal alkynes, that is, $W(CO)_5$(thf)-catalyzed endo-selective cyclization of ω-acetylenic silyl enol ethers (Eq. (1)) [7], and 6π-electrocyclization of *o*-ethynylstyrenes (Eq. (2)) [8] and *o*-ethynylphenylketones [9].



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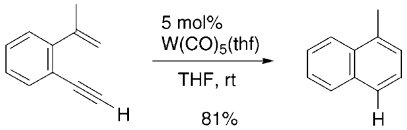

(2)

However, it is not possible, by these procedures, to introduce a substituent onto the olefinic part derived from terminal alkynes. For example, although 6π-electrocyclization of *o*-ethynylstyrenes can give 1-substituted or 1,2-disubstituted naphthalenes with wide generality, it is not possible to introduce a substituent at the 4-position by this protocol. Therefore, the development of a method allowing us to manipulate this position effectively is highly desirable. We then decided to examine the generation and reactions of vinylidene complexes from alkynes possessing a labile substituent at the terminus, expecting that cyclizations similar to those described above could be achieved along with

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introduction of a substituent onto the olefinic part of the products. In this paper is described a full account of the work directed towards this purpose, that is, generation of novel iodovinylidene tungsten complexes from 1-iodo-1-alkynes and $W(CO)_5$(thf), and their use for the preparation of synthetically useful carbocyclic compounds [10].

2. Experimental

2.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500, a JEOL AL-400, a JEOL LA-400 using $CHCl_3$ (^{1}H, δ (ppm): 7.24) and $CDCl_3$ (^{13}C, δ (ppm): 77.0) as internal standards. Mass spectra were recorded on a JEOL JMS-700. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Photochemical reactions were performed with an USHIO INC. super high-pressure mercury lamp (250 W). Flash column chromatography was conducted on silica-gel (Kanto 60 N) and preparative thin-layer chromatography (PTLC) was carried out on silica-gel (Wako gel B-5F).

2.2. Materials

THF was freshly distilled from sodium benzophenone ketyl, and all other solvents were distilled according to the usual procedures and stored over molecular sieves. $W(CO)_6$ was purchased from Soekawa Chemical Co., Ltd and used without further purification. All operations were performed under an argon atmosphere. The corresponding *o*-ethynylstyrenes [3(1),8] and ω-acetylenic silyl enol ethers [7,11a] were prepared according to the literature.

2.2.1. 1-[1-(p-Tolyl)ethenyl]-2-[(trimethylsilyl)-ethynyl]benzene (**1a**)

To a THF (16 ml) solution of 1-bromo-2-(trimethylsilylethynyl)benzene [8] (2.0 g, 8 mmol) was added a 1.45 M pentane solution of *t*-butyllithium (11 ml, 16 mmol) at −78 °C. After 2 h, a solution of Weinreb's amide (1.6 g, 8 mmol) in THF (4 ml), which was prepared by the reaction of *p*-toluoyl chloride and *N*,*O*-dimethylhydroxylamine, was added at −78 °C, and the mixture was further stirred for 1 h at this temperature. The reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate = 20:1) to give 1-*p*-toluoyl-2-[(trimethylsilyl)ethynyl]benzene (1.9 g, 6.3 mmol) in 79% yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.08 (9H, s), 2.40 (3H, s), 7.22 (2H, d, J = 8.2 Hz), 7.38–7.46 (3H, m), 7.48–7.52 (1H, m), 7.68 (2H, d, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −0.6, 21.7, 100.6, 102.5, 121.4, 128.2, 128.5, 128.9, 129.9, 130.3, 132.7, 134.8, 142.5, 143.9, 196.8; IR (neat): 2960, 2160, 1670, 1250, 870 cm^{-1}. Anal. found: C 78.17; H 6.83%. Calc for $C_{19}H_{20}OSi$: C 78.03; H 6.89%.

To a THF (10 ml) solution of methyltriphenylphosphonium bromide (3.6 g, 10 mmol) was added a 1.60 M hexane solution of *n*-butyllithium (6.3 ml, 10 mmol) at 0 °C. After 1 h, a solution of 1-*p*-toluoyl-2-[(trimethylsilyl)ethynyl]-benzene (1.5 g, 5.2 mmol) in THF (5 ml) was added and the mixture was further stirred for 2 h. The reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane). Yield: 99%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.00 (9H, s), 2.32 (3H, s), 5.29 (1H, d, J = 1.2 Hz), 5.67 (1H, d, J = 1.2 Hz), 7.07 (2H, d, J = 8.2 Hz), 7.14 (2H, d, J = 7.9 Hz), 7.21–7.32 (3H, m), 7.50 (1H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −0.3, 21.1, 98.6, 103.9, 115.2, 122.4, 127.1, 127.2, 128.4, 128.8, 130.0, 133.0, 137.1, 138.3, 144.9, 148.7; IR (neat): 2970, 2170, 1250, 870, 850 cm^{-1}. Anal. found: C 82.95; H 7.72%. Calc for $C_{20}H_{22}Si$: C 82.70; H 7.63%.

2.2.2. 1-(p-Tolyl)-4-trimethylsilylnaphthalene (**2a**)

To a cyclohexane (0.4 ml) solution of $[RhCl(cot)_2]_2$ (8.8 mg, 12 μmol) was added triisopropylphosphine (14 μl, 73 μmol) at room temperature. After 30 min, a solution of **1a** (35.2 mg, 0.12 mmol) in cyclohexane (0.2 ml) was added at room temperature and the mixture was further stirred under reflux for 11 h. The reaction mixture was filtered through a short pad of Florisil, and the filtrate was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane). Yield: 90%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.48 (9H, s), 2.44 (3H, s), 7.29 (2H, d, J = 7.7 Hz), 7.33–7.44 (4H, m), 7.46–7.53 (1H, m), 7.72 (1H, d, J = 7.0 Hz), 7.96 (1H, d, J = 8.0 Hz), 8.14 (1H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 0.3, 21.2, 125.3, 125.4, 126.1, 127.2, 128.4, 128.9, 129.9, 131.7, 132.8, 136.9, 137.3, 137.4, 137.9, 141.7; IR (neat): 3040, 2960, 1505, 1260, 830 cm^{-1}. Anal. found: C 82.41; H 7.73%. Calc for $C_{20}H_{22}Si$: C 82.70; H 7.63%.

2.2.3. General procedure for synthesis of o-(iodoethynyl)styrenes (**4a**, **4b**, **4e**–**4h**)

To the morpholine–iodine complex [12] formed from morpholine (16.5 mmol) and iodine (4.8 mmol) in benzene (7 ml) was added a benzene (3 ml) solution of an *o*-ethynylstyrene (3.3 mmol). The reaction mixture was heated at 40–50 °C for 2 h. After the mixture was cooled to room temperature, the reaction was quenched with saturated $Na_2S_2O_3$. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography.

*2.2.3.1. 1-(Iodoethynyl)-2-(1-methylethenyl)benzene (**4a**).* Yield: 89%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.15 (3H, s), 5.10–5.14 (1H, m), 5.19–5.23 (1H, m), 7.16–7.29 (3H, m), 7.41–7.44 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 8.8, 23.3, 93.5, 116.1, 120.9, 126.6, 127.8, 128.7, 133.7, 144.4, 146.8; IR (neat): 3060, 2980, 2910, 1480, 1440, 755 cm^{-1}. Anal. found: C 49.29; H 3.20%. Calc for $C_{11}H_9I$: C 49.28; H 3.38%.

*2.2.3.2. 1-(Iodoethynyl)-2-[1-(p-tolyl)ethenyl]benzene (**4b**).* Yield: 83%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.33 (3H, s), 5.31 (1H, d, $J = 1.2$ Hz), 5.67 (1H, d, $J = 1.2$ Hz), 7.07–7.17 (4H, m), 7.22–7.32 (3H, m), 7.43–7.45 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 9.8, 21.1, 93.3, 115.7, 122.5, 127.1, 127.2, 128.5, 128.8, 129.7, 133.3, 137.2, 138.2, 145.5, 148.3; IR (neat): 3025, 1610, 1510, 905, 830, 760 cm^{-1}. Anal. found: C 59.15; H 3.95%. Calc for $C_{17}H_{13}I$: C 59.32; H 3.81%.

*2.2.3.3. 1-Ethenyl-2-(iodoethynyl)benzene (**4e**).* Yield: 58%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.35 (1H, dd, $J = 0.8$, 11.0 Hz), 5.80 (1H, dd, $J = 0.8$, 17.5 Hz), 7.11–7.22 (2H, m), 7.25–7.32 (1H, m), 7.38–7.44 (1H, m), 7.52–7.59 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 10.2, 92.5, 116.0, 122.0, 124.5, 127.3, 128.9, 133.3, 134.5, 140.0; IR (neat): 3060, 1620, 1475, 990, 920, 770, 755 cm^{-1}. Anal. found: C 47.00; H 2.58%. Calc for $C_{10}H_7I$: C 47.27; H 2.78%.

*2.2.3.4. 1-(Iodoethynyl)-2-[1-(p-tolyl)prop-1-enyl]benzene (**4f**).* Yield: 85% as a 1:1 mixture of regioisomers, ^{1}H NMR ($CDCl_3$, 400 MHz) (*E*, *Z* mixture) δ (ppm): 1.64 (1.5H, d, $J = 7.0$ Hz), 1.88 (1.5H, d, $J = 7.2$ Hz), 2.30 (1.5H, s), 2.34 (1.5H, s), 5.97 (0.5H, q, $J = 7.1$ Hz), 6.19 (0.5H, q, $J = 7.0$ Hz), 7.02–7.08 (3H, m), 7.10–7.39 (4.5H, m), 7.46–7.50 (0.5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) (*E*, *Z* mixture) δ (ppm): 8.1, 9.0, 15.6, 15.7, 21.0, 21.2, 93.3, 93.7, 122.2, 123.5, 124.8, 126.4, 126.6, 126.7, 127.3, 128.5, 128.5, 128.6, 128.8, 129.7, 129.8, 130.2, 133.1, 133.5, 136.2, 136.2, 136.8, 139.4, 140.4, 140.9, 143.8, 147.6; IR (neat): 3020, 2910, 1510, 810, 760 cm^{-1}. Anal. found: C 60.27; H 4.42%. Calc for $C_{18}H_{15}I$: C 60.35; H 4.22%.

*2.2.3.5. 1-Iodoethynyl-2-(1-methylpropenyl)benzene (**4g**).* Yield: 85% as a 3:1 mixture of regioisomers. The geometry was not determined. ^{1}H NMR ($CDCl_3$, 400 MHz) (*E*, *Z* mixture) δ (ppm): 1.42 (0.75H, dq, $J = 1.6$, 7.1 Hz), 1.77 (2.25H, d, $J = 6.6$ Hz), 1.98 (0.75H, t, $J = 1.5$ Hz), 2.01 (2.25H, s), 5.53–5.66 (1H, m), 7.05–7.30 (3H, m), 7.37–7.46 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) (*E*, *Z* mixture) δ (ppm): 7.3, 8.2, 14.2, 14.8, 17.0, 24.8, 93.3 93.9, 121.0, 122.0, 123.0, 125.6, 126.0, 126.2, 128.1, 128.5, 128.6, 128.7, 133.2, 133.5, 135.7, 135.7, 145.8, 149.1; IR (neat): 2980, 2910, 1475, 1440, 760 cm^{-1}. Anal. found: C 51.04; H 4.00%. Calc for $C_{12}H_{11}I$: C 51.09; H 3.93%.

*2.2.3.6. 1-(Iodoethynyl)-2-(1-methylethenyl)cyclohex-1-ene (**4h**).* Yield: 83%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.52–1.64 (4H, m), 1.89 (3H, s), 2.10–2.23 (4H, m), 4.96 (2H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 6.0, 21.9, 22.17, 22.24, 29.3, 30.6, 95.7, 113.8, 115.1, 145.6, 148.6; IR (neat): 2930, 2870, 1440, 900 cm^{-1}. Anal. found: C 48.28; H 4.89%. Calc for $C_{11}H_{13}I$: C 48.55; H 4.82%.

*2.2.4. 1-[1-(t-Butyldimethylsiloxy)ethenyl]-2-(iodoethynyl)benzene (**4c**)*

Iodination of 1-[1-(*t*-butyldimethylsiloxy)ethenyl]-2-(trimethylsilylethynyl)benzene [10] was carried out according to the same procedure as that of the synthesis of ω-iodoacetylenic silyl enol ether described in Section 2.2.7. Yield: 64%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.13 (6H, s), 0.93 (9H, s), 4.65 (1H, d, $J = 1.5$ Hz), 4.93 (1H, d, $J = 1.5$ Hz), 7.18–7.30 (2H, m), 7.41–7.50 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −4.7, 9.8, 18.3, 25.8, 93.6, 96.4, 120.8, 127.5, 127.7, 128.4, 134.2, 141.6, 154.8; IR (neat): 2920, 2860, 1625, 1470, 1310, 1260, 830 cm^{-1}. Anal. found: C 49.91; H 5.42%. Calc for $C_{16}H_{21}IOSi$: C 50.00; H 5.51%.

*2.2.5. Methyl 2-[2-(iodoethynyl)phenyl]propenoate (**4d**)*

Iodination of methyl 2-[2-(trimethylsilylethynyl)phenyl]-propenoate [10] was carried out according to the same procedure as that of the synthesis of ω-iodoacetylenic silyl enol ether described in Section 2.2.7. Yield: 81%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.78 (3H, s), 5.81 (1H, s), 6.44 (1H, s), 7.20–7.50 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 10.4, 52.4, 92.8, 122.6, 127.9, 128.6, 128.8, 129.0, 132.8, 140.8, 141.0, 167.0; IR (neat): 2960, 1710 cm^{-1}. Anal. found: C 46.40; H 2.62%. Calc for $C_{12}H_9IO_2$: C 46.18; H 2.91%.

*2.2.6. General procedure for 6π-electrocyclization of 1-iodo-1-alkynes (**5a**–**5d**, **5f**–**5h**)*

A 0.1 M THF solution of $W(CO)_5$(thf) was prepared by irradiation of a slurry of $W(CO)_6$ (176 mg, 0.5 mmol) in freshly distilled THF (5.0 ml) for 2 h. An yellow solution (2.0 ml in the case of a stoichiometric amount of the catalyst or 0.2–0.4 ml in the case of a catalytic amount of the catalyst) of $W(CO)_5$(thf) was added to an *o*-(iodoethynyl)styrene (0.2 mmol) at room temperature. The solution was stirred at room temperature until the starting material disappeared, and then the resulting solution was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography.

*2.2.6.1. 1-Iodo-4-methylnaphthalene (**5a**).* Yield: 95%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.65 (3H, s), 7.02 (1H, d, $J = 7.5$ Hz), 7.51–7.59 (2H, m), 7.89–7.95 (1H, m), 7.96 (1H, d, $J = 7.5$ Hz), 8.07–8.13 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.3, 97.0, 124.7, 126.6, 127.3, 127.8, 132.8, 133.5, 134.1, 135.5, 137.1; IR (neat): 3060,

2940, 1380, 895, 820, 755 cm^{-1}. Anal. found: C 49.26; H 3.50%. Calc for $C_{11}H_9I$: C 49.28; H 3.38%.

*2.2.6.2. 1-Iodo-4-(p-tolyl)naphthalene (**5b**).* Yield: 93%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.44 (3H, s), 7.10 (1H, d, $J = 7.5$ Hz), 7.26–7.37 (4H, m), 7.43 (1H, t, $J = 7.7$ Hz), 7.56 (1H, t, $J = 7.6$ Hz), 7.83 (1H, d, $J = 8.2$ Hz), 8.11 (1H, d, $J = 7.5$ Hz), 8.16 (1H, d, $J = 8.7$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm): 21.2, 98.8, 126.7, 126.9, 127.5, 127.9, 129.1, 129.8, 132.5, 132.6, 134.4, 136.9, 137.0, 137.3, 141.4; IR (neat): 2915, 1380, 960, 815, 760 cm^{-1}. Anal. found: C 59.61; H 3.92%. Calc for $C_{17}H_{13}I$: C 59.32; H 3.81%.

*2.2.6.3. 1-(t-Butyldimethylsiloxy)-4-iodonaphthalene (**5c**).* Yield: 83%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.27 (6H, s), 1.07 (9H, s), 6.62 (1H, d, $J = 8.0$ Hz), 7.44–7.58 (2H, m), 7.88 (1H, d, $J = 8.0$ Hz), 7.99 (1H, d, $J = 8.0$ Hz), 8.14 (1H, d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −4.3, 18.4, 25.8, 88.9, 114.1, 123.1, 125.9, 127.9, 129.1, 131.9, 135.3, 137.0, 152.7; IR (neat): 2920, 2860, 1260, 840, 760 cm^{-1}. Anal. found: C 50.19; H 5.70%. Calc for $C_{16}H_{21}IOSi$: C 50.00; H 5.51%.

*2.2.6.4. Methyl 4-iodonaphthalene-1-carboxylate (**5d**).* Yield: 84%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.98 (3H, s), 7.56–7.67 (2H, m), 7.79 (1H, d, $J = 7.7$ Hz), 8.13 (1H, d, $J = 7.7$ Hz), 8.13–8.20 (1H, m), 8.81–8.88 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 52.3, 106.6, 126.4, 128.0, 128.0, 128.5, 130.3, 131.7, 132.9, 134.5, 136.5, 167.6; IR (neat): 2950, 1720, 1510, 1250, 1410 cm^{-1}. Anal. found: C 46.15; H 2.70%. Calc for $C_{12}H_9IO_2$: C 46.18; H 2.91%.

*2.2.6.5. 4-Iodo-2-methyl-1-p-tolylnaphthalene (**5f**).* Yield: 42%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.18 (3H, s), 2.45 (3H, s), 7.11 (2H, d, $J = 8.0$ Hz), 7.30 (2H, d, $J = 7.7$ Hz), 7.30–7.38 (2H, m), 7.43–7.50 (1H, m), 8.05 (1H, s), 8.07 (1H, d, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 20.3, 21.3, 98.5, 126.4, 126.5, 126.9, 129.2, 129.8, 132.0, 132.7, 133.8, 134.7, 135.9, 136.9, 139.4, 139.9; IR (neat): 2920, 1520, 1370, 820, 760 cm^{-1}. Anal. found: C 60.05; H 4.15%. Calc for $C_{18}H_{15}I$: C 60.35; H 4.20%.

*2.2.6.6. 4-Iodo-1,2-dimethylnaphthalene (**5g**).* Yield: 20%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.42 (3H, s), 2.55 (3H, s), 7.43–7.56 (2H, m), 7.92 (1H, s), 7.91–7.97 (1H, m), 8.00–8.07 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.7, 20.3, 96.7, 124.2, 126.2, 126.5, 132.5, 132.6, 132.8, 133.6, 134.7, 140.2; IR (neat): 3080, 2910, 2320, 1560, 1510, 875, 745 cm^{-1}. Anal. found: C 51.28; H 3.82%. Calc for $C_{12}H_{11}I$: C 51.09; H 3.93%.

*2.2.6.7. 5-Iodo-8-methyl-1, 2, 3, 4-tetrahydronaphthalene (**5h**).* Yield: 67%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.70–1.82 (4H, m), 2.15 (3H, s), 2.52–2.71 (4H, m), 6.69 (1H, d, $J = 8.0$ Hz), 7.57 (1H, d, $J = 8.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.4, 23.0, 23.7, 27.6, 36.6, 100.3, 128.8, 136.0, 136.8, 138.1, 138.9; IR (neat): 2920, 2870, 1445, 800 cm^{-1}. Anal. found: C 48.49; H 4.76%. Calc for $C_{11}H_{13}I$: C 48.55; H 4.82%.

*2.2.7. General procedure for synthesis of ω-iodoacetylenic silyl enol ethers (**7a–7i**)*

To a DMF (10 ml) solution of an ω-acetylenic silyl enol ether (0.8 mmol) [13] was added *N*-iodosuccinimide (250 mg, 1.1 mmol) and $AgNO_3$ (189 mg, 1.1 mmol) at 0 °C. The reaction vessel was wrapped by aluminum foil to avoid light and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with sat. $Na_2S_2O_3$. The aqueous layer was extracted with hexane three times and the combined extracts were washed with brine, and dried over $MgSO_4$. The solvent was evaporated, and the crude product was purified by silica-gel column chromatography.

*2.2.7.1. Diethyl (Z)-2-[2-(t-butyldimethylsiloxy)-2-phenylethenyl]-2-(3-iodoprop-2-ynyl)malonate (**7a**).* Yield: 91%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): −0.18 (6H, s), 0.87 (9H, s), 1.24 (6H, t, $J = 7.1$ Hz), 3.32 (2H, s), 4.15–4.27 (4H, m), 5.44 (1H, s), 7.25–7.37 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −4.4, −3.3, 14.1, 18.3, 25.9, 27.2, 56.3, 61.7, 90.1, 106.5, 127.8, 127.9, 128.3, 139.7, 152.9, 169.1; IR (neat): 2930, 1740 1650, 1070 cm^{-1}. Anal. found: C 51.70; H 6.10%. Calc for $C_{24}H_{33}IO_5Si$: C 51.80; H 5.98%.

*2.2.7.2. 1-(tert-Butyldimethylsiloxy)-3-(3-iodoprop-2-ynyl)-2-methylcyclohexene (**7b**).* Yield: 92%, ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.10 (6H, s), 0.92 (9H, s), 1.50–1.75 (4H, m), 1.56 (3H, s), 1.95–2.04 (2H, m), 2.16–2.25 (1H, m), 2.33 (1H, dd, $J = 8.9, 16.9$ Hz), 2.53 (1H, dd, $J = 3.6, 16.9$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.9, −3.9, −3.8, 14.2, 18.2, 20.4, 25.1, 25.8, 27.7, 30.5, 38.8, 93.8, 113.1, 145.4; IR (neat): 2929, 2857, 1676, 1256, 1175 cm^{-1}. Anal. found: C 49.06; H 7.13%. Calc for $C_{16}H_{27}IOSi$: C 49.23; H 6.97%.

*2.2.7.3. 1-(t-Butyldimethylsiloxy)-3-(3-iodo-1-methylprop-2-ynyl)-2-methylcyclohexene (**7c**).* Yield: 84% (a 1:1 mixture of diastereomers), ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.075 (1.5H, s), 0.084 (1.5H, s), 0.12 (1.5H, s), 0.13 (1.5H, s), 0.927 (4.5H, s), 0.931 (4.5H, s), 0.97 (1.5H, d, $J = 7.3$ Hz), 1.16 (1.5H, d, $J = 7.3$ Hz), 1.30–1.61 (2.0H, m), 1.51 (1.5H, s), 1.59 (1.5H, s), 1.65–1.88 (2.0H, m), 1.89–2.12 (2.5H, m), 2.31–2.41 (0.5H, m), 2.93–3.08 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −7.2, −6.8, −4.0, −3.72, −3.71, 13.8, 14.0, 15.0, 18.15, 18.18, 18.8, 21.8, 21.9, 24.0, 24.2, 25.84, 25.87, 29.7, 30.76, 30.78, 30.8, 43.3, 44.5, 97.4, 99.2, 112.0, 113.2, 146.1, 146.7; IR (neat): 2931, 2858, 1673, 1255, 1176 cm^{-1}. Anal. found: C 50.45; H 7.27%. Calc for $C_{17}H_{29}IOSi$: C 50.49; H 7.23%.

*2.2.7.4. 1-(tert-Butyldimethylsiloxy)-3-(3-iodoprop-2-ynyl)-5-isopropenyl-2-methylcyclohexene (**7d**).* Yield: 59%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.10 (6H, s), 0.92 (9H, s), 1.44–1.53 (1H, m), 1.57 (3H, s), 1.73 (3H, s), 1.88–2.09 (3H, m), 2.22–2.41 (3H, m), 2.54–2.65 (1H, m) 4.70–4.76 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.7, −3.8, −3.7, 14.7, 18.2, 20.9, 24.9, 25.8, 31.3, 35.6, 37.0, 39.1, 94.2, 109.1, 112.6, 144.5, 148.8; IR (neat): 3082, 2928, 2857, 1681, 1615, 1177 cm^{-1}; HRMS found: *m/z* 430.1174. Calc for $C_{19}H_{31}IOSi$: M, 430.1189.

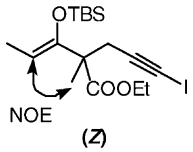
*2.2.7.5. 1-(t-Butyldimethylsiloxy)-3-(1-n-butyl-3-iodoprop-2-ynyl)-2-methylcyclohexene (**7e**).* Yield: 69% (a 1:1 mixture of diastereomers), ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.11 (3H, s), 0.14 (3H, s), 0.80–1.00 (3H, m), 0.93 (4.5H, s), 0.94 (4.5H, s), 1.15–1.89 (8H, m), 1.58 (3H, s), 1.72 (3H, s), 1.92–2.16 (2.5H, m), 2.27–2.44 (1H, m), 2.72–2.88 (1.5H, m), 4.69 (1H, s), 4.72(1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −6.1, −5.3, −3.65, −3.59, −3.52, 14.1, 15.0, 15.3, 18.29, 18.31, 20.9, 21.1, 22.56, 22.62, 25.9, 26.0, 28.8, 30.1, 30.4, 30.6, 31.5, 33.7, 35.1, 35.2, 36.5, 37.68, 37.72, 38.6, 42.4, 42.8, 97.5, 98.5, 108.8, 109.0, 111.6, 112.1, 144.9, 145.2, 148.6, 148.9; IR (neat): 3082, 2956, 2930, 1678, 1177 cm^{-1}. Anal. found: C 56.73; H 8.24%. Calc for $C_{23}H_{39}IOSi$: C 56.78; H 8.08%.

*2.2.7.6. Ethyl 1-(3-iodoprop-2-ynyl)-2-(t-butyldimethylsiloxy)cyclohex-2-ene-1-carboxylate (**7f**).* Yield: 88%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.12 (3H, s), 0.14 (3H, s), 0.86 (9H, s), 1.22 (3H, t, J = 7.3 Hz), 1.54–1.71 (2H, m), 1.88–2.12 (4H, m), 2.80 (1H, d, J = 16.7 Hz), 2.87 (1H, d, J = 16.9 Hz), 4.05–4.18 (2H, m), 4.87 (1H, t, J = 4.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −5.6, −4.8, −4.7, 14.2, 18.0, 19.1, 23.8, 25.6, 27.7, 32.1, 50.7, 60.9, 91.8, 104.2, 148.6, 174.2; IR (neat): 2930, 1730, 1670, 1230, 830 cm^{-1}. Anal. found: C 47.92; H 6.46%. Calc for $C_{18}H_{29}IO_3Si$: C 48.21; H 6.52%.

*2.2.7.7. Ethyl 1-(3-iodoprop-2-ynyl)-2-(t-butyldimethylsiloxy)cyclooct-2-ene-1-carboxylate (**7g**).* Yield: 99%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.14 (3H, s), 0.15 (3H, s), 0.85 (9H, s), 1.24 (3H, t, J = 7.1 Hz), 1.34–1.46 (1H, m), 1.46–1.80 (4H, m), 1.84–2.00 (2H, m), 2.00–2.15 (1H, m), 2.30–2.46 (2H, m), 2.84 (1H, d, J = 16.9 Hz), 2.89 (1H, d, J = 17.2 Hz), 4.02–4.21 (2H, m), 4.75 (1H, t, J = 9.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −5.6, −4.7, −4.6, 14.1, 18.1, 22.9, 23.1, 25.4, 25.7, 27.1, 29.4, 33.6, 56.2, 60.7, 91.8, 105.4,150.8, 173.6; IR (neat): 2930, 1730, 1220, 840 cm^{-1}. Anal. found: C 50.36; H 7.21%. Calc for $C_{20}H_{33}IO_3Si$: C 50.42; H 6.98%.

*2.2.7.8. Ethyl 2-[1-(t-butyldimethylsiloxy)ethenyl]-5-iodo-2-methylpent-4-ynoate (**7h**).* Yield: 74%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.15 (3H, s), 0.16 (3H, s), 0.87 (9H, s), 1.22 (3H, t, J = 7.1 Hz), 1.39 (3H, s), 2.82 (2H, s), 4.04–4.18 (2H, m), 4.14 (1H, d, J = 2.4 Hz), 4.18 (1H, d, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −5.1, −5.0, −5.0, 14.1, 18.0, 20.8, 25.5, 28.4, 51.9, 61.0, 88.9, 91.0, 158.5, 173.5; IR (neat): 2930, 1730, 1630, 1260, 1110, 830 cm^{-1}. Anal. found: C 45.55; H 6.42%. Calc for $C_{16}H_{27}IO_3Si$: C 45.50; H 6.44%.

*2.2.7.9. Ethyl (Z)-3-(t-butyldimethylsiloxy)-2-(3-iodoprop-2-ynyl)-2-methylpent-3-enoate (**7i**).* The geometry of the minor isomer was assigned as *Z* on the basis of the measurement of differential NOE spectra.



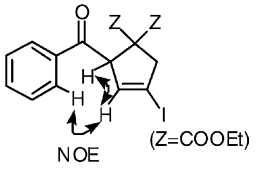
(*Z*)

Yield: 99% as a 3:2 mixture of *E* and *Z* isomers, ^{1}H NMR ($CDCl_3$, 500 MHz) (*E*) δ (ppm): 0.12 (3H, s), 0.14 (3H, s), 0.90 (9H, s), 1.22 (3H, t, J = 7.1 Hz), 1.36 (3H, s), 1.56 (3H, d, J = 6.8 Hz), 2.79 (2H, s), 4.11 (2H, q, J = 7.1 Hz), 4.63 (1H, q, J = 6.8 Hz); (*Z*) δ (ppm): 0.14 (3H, s), 0.15 (3H, s), 0.89 (9H, s), 1.24 (3H, t, J = 7.1 Hz), 1.42 (3H, s), 1.45 (3H, d, J = 7.5 Hz), 2.80 (2H, s), 4.14 (2H, q, J = 7.1 Hz), 4.62 (1H, q, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) (*E*, *Z* mixture) δ (ppm): −5.1, −5.1, −4.4, −4.7, −3.29, −3.34, 11.1, 11.7, 14.1, 14.2, 18.3, 18.9, 21.8, 21.9, 25.8, 26.1, 28.8, 29.6, 50.9, 52.0, 60.9, 61.0, 91.26, 91.29, 101.26, 101.30, 150.5, 150.6, 174.1, 174.3; IR (neat): 2930, 1735, 845 cm^{-1}. Anal. found: C 46.86; H 6.82%. Calc for $C_{17}H_{29}IO_3Si$: C 46.79; H 6.70%.

*2.2.8. General procedure for endo-selective cyclization of 1-iodo-1-alkynes (**8a**–**8i**)*

A 0.1 M THF solution of $W(CO)_5$(thf) was prepared by irradiation of a slurry of $W(CO)_6$ (176 mg, 0.5 mmol) in freshly distilled THF (5.0 ml) for 2 h. An yellow solution of $W(CO)_5$(thf) (0.2 ml) was added to a solution of an ω-iodoacetylenic silyl enol ether (0.2 mmol) in THF (4.0 ml) and 3–15 molar amounts of H_2O at room temperature. The mixture was stirred at room temperature until the starting material disappeared, and then the resulting mixture was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography deactivated with 10% H_2O at 0 °C (hexane:ethyl acetate = 20:1–5:1) or preparative thin-layer chromatography (hexane:ethyl acetate = 5:1).

*2.2.8.1. Diethyl 2-benzoyl-4-iodocyclopent-3-ene-1,1-dicarboxylate (**8a**).* The position of iodine atom was confirmed on the basis of the measurement of differential NOE spectra.



Yield: 65%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.02 (3H, t, J = 7.1 Hz), 1.25 (3H, t, J = 7.1 Hz), 3.10 (1H, dd, J = 1.3, 17.3 Hz), 3.83 (1H, dt, J = 2.7, 17.3 Hz), 3.95–4.10 (2H, m), 4.16–4.30 (2H, m), 5.34 (1H, t, J = 2.8 Hz), 5.99–6.02 (1H, m), 7.45–7.50 (2H, m), 7.58–7.61 (1H, m), 7.98–8.02 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 13.7, 13.9, 50.2, 60.3, 61.7, 62.5, 63.6, 93.3, 128.7, 128.8, 133.7, 135.8, 136.0, 168.2, 170.3, 196.2; IR (neat): 2990, 1740, 1680, 1260 cm^{-1}. Anal. found: C 49.07; H 4.56%. Calc for $C_{18}H_{19}IO_5$: C 48.89; H 4.33%.

*2.2.8.2. 8-Iodo-6-methylbicyclo[4.3.0]non-7-en-5-one (**8b**).* The stereochemistry of this compound was determined by Bu_3SnH reduction to give the deiodinated compound, which is identical with 1-methylbicyclo[3.3.0]oct-2-en-8-one. For the recent examples of nucleophilic endo-selective cyclization onto alkynes, see [11a]. Yield: 66%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.22 (3H, s), 1.55–1.58 (1H, m), 1.78–1.86 (3H, m), 2.23–2.30 (1H, m), 2.34–2.45 (3H, m), 2.80–2.87 (1H, m), 6.01 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 21.3, 23.7, 27.3, 38.3, 48.1, 49.4, 61.9, 93.8, 144.1, 213.7; IR (neat): 2927, 1705, 1604, 1450, 1120 cm^{-1}; HRMS found: m/z 277.0082. Calc for $C_{10}H_{14}IO$: M+H, 277.0089.

*2.2.8.3. 8-Iodo-6,9-dimethylbicyclo[4.3.0]non-7-en-5-one (**8c**).* The stereochemistry of the ring junction was assigned as *cis* on the basis of the measurement of differential NOE spectra. Yield: 79% as a 1:1 mixture of stereoisomers concerning the methyl group at C-9, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.03 (1.5H, d, J = 7.4 Hz), 1.07 (1.5H, d, J = 7.0 Hz), 1.24 (1.5H, s), 1.29 (1.5H, s), 1.41–1.50 (0.5H, m), 1.68–1.84 (2.5H, m), 1.86–1.98 (1.5H, m), 1.98–2.04 (0.5H, m), 2.18–2.43 (1.5H, m), 2.45–2.51 (0.5H, m), 2.55 (0.5H, dquint, J = 2.4, 7.4 Hz), 3.05 (0.5H, dquint, J = 2.4, 7.4 Hz), 6.06 (0.5H, d, J = 2.3 Hz), 6.15 (0.5H, d, J = 2.3 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 15.6, 20.3, 21.6, 22.6, 22.7, 23.6, 24.7, 25.0, 38.2, 38.3, 49.0, 50.2, 50.7, 54.4, 61.4, 61.9, 104.3, 104.5, 142.6, 143.4, 213.6, 214.5; IR (neat): 2927, 1705, 1601, 1454 cm^{-1}. Anal. found: C 45.32; H 5.06%. Calc for $C_{11}H_{15}IO$: C 45.54; H 5.21%.

*2.2.8.4. 8-Iodo-3-isopropenyl-6-methylbicyclo[4.3.0]nona-7-en-5-one (**8d**).* The stereochemistry of this compound was determined by Bu_3SnH reduction to give the deiodinated compound, which is identical with 3-isopropenyl-6-methylbicyclo[4.3.0]non-7-en-5-one. For the recent examples of nucleophilic endo-selective cyclization onto alkynes, see [11a]. Yield: 59%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.25 (3H, s), 1.73 (3H, s), 1.77–1.84 (2H, m), 2.28–2.41 (2H, m), 2.43–2.56 (3H, m), 2.71–2.83 (1H, m), 4.69 (1H, s), 4.79 (1H, s), 6.06 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 20.8, 23.6, 30.7, 39.3, 43.3, 46.6, 48.9, 60.8, 93.6, 110.4, 144.4, 146.9, 214.0; IR (neat): 2925, 1703, 1448 cm^{-1}. Anal. found: C 49.62; H 5.55%. Calc for $C_{13}H_{17}IO$: C 49.38; H 5.42%.

*2.2.8.5. 9-(n-Butyl)-8-iodo-6-methylbicyclo[4.3.0]non-7-en-5-one (**8e**).* Yield: 74% as a 1:1 mixture of *cis* and *trans* isomers, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 0.93 (1.5H, t, J = 7.0 Hz), 0.94 (1.5H, t, J = 7.1 Hz), 1.17 (1.5H, s), 1.24–1.46 (6H, m), 1.28 (1.5H, s), 1.62–1.88 (2H, m), 1.74 (1.5H, s), 1.76 (1.5H, s), 2.20–2.32 (1.5H, m), 2.40–2.61 (2.5H. m), 2.62–2.70 (0.5H, m), 2.86–2.92 (0.5H, m), 4.59 (0.5H, s), 4.73 (0.5H, s), 4.80 (0.5H, t, J = 1.3 Hz), 4.84–4.86 (0.5H, m), 5.99 (0.5H, d, J = 2.3 Hz), 6.07 (0.5H, d, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.0, 20.6, 20.8, 21.6, 22.8, 22.9, 24.9, 25.9, 28.0, 29.2, 30.2, 31.0, 33.3, 39.1, 39.3, 43.0, 43.5, 44.9, 49.4, 52.6, 56.1, 60.8, 61.6, 103.6, 104.7, 110.1, 111.4, 142.9, 143.5, 146.7, 147.2, 212.9, 213.8; IR (neat): 3083, 2957, 2927, 1703, 1455 cm^{-1}. Anal. found: C 54.73; H 6.98%. Calc for $C_{17}H_{25}IO$: C 54.85; H 6.77%.

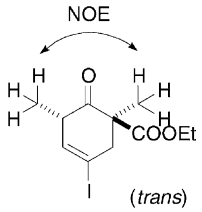
*2.2.8.6. Ethyl 3-iodo-9-oxobicyclo[3.3.1]non-2-ene-5-carboxylate (**8f**).* Yield: 70%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.26 (3H, t, J = 7.1 Hz), 1.67–1.77 (1H, m), 1.80–2.10 (4H, m), 2.34 (1H, ddt, J = 1.4, 4.8, 14.2 Hz), 2.86–2.92 (1H, m), 2.90 (1H, d, J = 18.4 Hz), 3.76 (1H, d, J = 18.4 Hz), 4.20 (2H, q, J = 7.1 Hz), 6.80–6.14 (1H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.1, 17.5, 32.8, 38.8, 51.1, 51.6, 60.9, 61.7, 94.9, 136.5, 170.3, 206.9; IR (neat): 2940, 1740, 1450, 1220 cm^{-1}. Anal. found: C 43.14; H 4.63%. Calc for $C_{12}H_{15}IO_3$: C 43.13; H 4.52%.

*2.2.8.7. Ethyl 9-iodo-11-oxobicyclo[5.3.1]undec-8-ene-1-carboxylate (**8g**).* Yield: 73%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.15–1.31 (1H, m), 1.25 (3H, t, J = 7.1 Hz), 1.50–1.65 (4H, m), 1.58–1.75 (1H, m), 1.81–1.91 (2H, m), 2.04–2.20 (2H, m), 2.75 (1H, d, J = 17.9 Hz), 2.96–3.03 (1H, m), 3.46 (1H, dt, J = 3.0, 17.8 Hz), 4.18 (2H, q, J = 7.1 Hz), 6.21 (1H, t, J = 3.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.0, 22.2, 22.4, 26.6, 31.9, 33.8, 49.2, 51.6, 61.3, 61.8, 91.6, 138.6, 171.5, 210.2; IR (neat): 2920, 1740, 1710, 1215 cm^{-1}. Anal. found: C 46.31; H 5.34%. Calc for $C_{14}H_{19}IO_3$: C 46.42; H 5.29%.

*2.2.8.8. Ethyl 3-iodo-1-methyl-6-oxocyclohex-3-ene-1-carboxylate (**8h**).* Yield: 43%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.25 (3H, t, J = 7.1 Hz), 1.30 (3H, s), 2.68 (1H, dq, J = 2.5, 17.5 Hz), 2.84–2.91 (1H, m), 3.13 (1H, ddd, J = 2.5, 3.9, 21.6 Hz), 3.40 (1H, d, J = 17.5 Hz), 4.16–4.21 (2H, m), 6.24 (1H, dt, J = 2.5, 3.8 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.0, 19.2, 42.3, 49.3, 57.7, 61.8, 91.1, 134.2, 171.5, 202.9; IR (neat): 2900, 1730, 1720, 1230 cm^{-1}. Anal. found: C 38.99; H 4.52%. Calc for $C_{10}H_{13}IO_3$: C 38.98; H 4.25%.

*2.2.8.9. Ethyl 3-iodo-1,5-dimethyl-6-oxocyclohex-3-ene-1-carboxylate (**8i**).* The starting material **7i** was a 3:2 mixture of *E*, *Z* isomers. The product **8i** was obtained as a 1:2 mixture of *cis* and *trans* isomers. The stereochemistry of

the *trans* isomer was assigned as *trans* on the basis of the measurement of differential NOE spectra.



Yield: 64%, ^{1}H NMR ($CDCl_3$, 500 MHz) (*trans*) δ (ppm): 1.13 (3H, d, J = 7.0 Hz), 1.23 (3H, t, J = 7.1 Hz), 1.28 (3H, s), 2.63 (1H, dt, J = 2.8, 17.7 Hz), 3.15–3.23 (1H, m), 3.41 (1H, d, J = 17.4 Hz), 4.10–4.26 (2H, m), 6.14 (1H, t, J = 3.0 Hz); (*cis*) δ (ppm): 1.19 (3H, d, J = 7.5 Hz), 1.25 (3H, t, J = 7.0 Hz), 1.42 (3H, s), 2.70 (1H, dt, J = 1.9, 17.4 Hz), 2.97–3.06 (1H, m), 3.43 (1H, d, J = 18.6 Hz), 4.10–4.26 (2H, m), 6.18–6.21 (1H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) (*trans*) δ (ppm): 14.0, 14.8, 19.5, 45.5, 49.8, 57.8, 61.8, 91.2, 140.6, 171.9, 204.5; (*cis*) δ (ppm): 14.1, 16.7, 20.2, 45.7, 48.8, 57.4, 61.7, 90.7, 139.8, 171.0, 206.5; IR (neat): 2990, 2930, 1720, 1230 cm^{-1}. Anal. found: C 41.02; H 4.77%. Calc for $C_{11}H_{15}IO_3$: C 41.01; H 4.69%.

2.2.9. General procedure for air oxidation (**9g**, **9i**)

The cyclized products (0.15 mmol) were kept in an open vessel without solvent. The mixture gradually changed from colorless oil to red oil. After 1 week, the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate = 8:1) to give α,β-unsaturated diketones.

*2.2.9.1. Ethyl 9,11-dioxobicyclo[5.3.1]undec-7-ene-1-carboxylate (**9g**).* Yield: 76%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 0.99–1.11 (1H, m), 1.29 (3H, t, J = 7.1 Hz), 1.39–1.50 (1H, m), 1.55–1.71 (2H, m), 1.79–2.02 (3H, m), 2.04–2.14 (1H, m), 2.48 (1H, dd, J = 14.2, 8.0 Hz), 2.78 (1H, dd, J = 18.2, 1.6 Hz), 2.85–2.93 (1H, m), 3.34 (1H, d, J = 18.1 Hz), 4.25 (2H, q, J = 7.0 Hz), 6.31 (1H, t, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.1, 27.0, 27.9, 28.0, 31.3, 40.2, 45.5, 60.1, 61.7, 133.1, 158.2, 170.2, 194.9, 200.9; IR (neat): 2940, 1740, 1690, 1250, 1215 cm^{-1}. Anal. found: C 67.27; H 7.36%. Calc for $C_{14}H_{18}O_4$: C 67.18; H 7.25%.

*2.2.9.2. Ethyl 1,3-dimethyl-2,5-dioxocyclohex-3-ene-1-carboxylate (**9i**).* Yield: 82%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.19 (3H, t, J = 7.1 Hz), 1.46 (3H, s), 2.01 (3H, d, J = 1.5 Hz), 2.63 (1H, d, J = 16.7 Hz), 3.30 (1H, dd, J = 1.2, 16.7 Hz), 4.06–4.20 (2H, m), 6.50–6.52 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.9, 16.9, 20.4, 47.2, 56.2, 62.2, 137.5, 150.4, 170.9, 194.8, 196.0; IR (neat): 2990, 1730, 1680, 1250 cm^{-1}. Anal. found: C 62.55; H 6.71%. Calc for $C_{11}H_{14}O_4$: C 62.85; H 6.71%.

2.2.10. Ethyl 1-(3-iodoprop-2-ynyl)-2-methylenecyclohexane-1-carboxylate (**10a**)

To a THF (20 ml) solution of methyltriphenylphosphonium bromide (1.8 g, 5 mmol) was added a 1.69 M hexane solution of *n*-butyllithium (3.0 ml, 5 mmol) at 0 °C. After 1 h, a solution of ethyl 1-(prop-2-ynyl)cychexan-2-one-1-carboxylate [7a] (560 mg, 2.7 mmol) in THF (5 ml) was added at –78 °C and the mixture was warmed slowly to room temperature. The reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane) to give ethyl 2-methylene-1-(prop-2-ynyl)cyclohexane-1-carboxylate **10b** (289 mg, 1.4 mmol) in 52% yield as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.24 (3H, t, J = 7.1 Hz), 1.30–1.50 (2H, m), 1.54–1.73 (3H, m), 2.00 (1H, t, J = 2.7 Hz), 2.03–2.14 (1H, m), 2.21–2.35 (2H, m), 2.33 (1H, dd, J = 2.7, 16.8 Hz), 2.69 (1H, dd, J = 2.7, 16.6 Hz), 4.17 (2H, dq, J = 1.2, 7.2 Hz), 4.80 (1H, s), 4.90 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.2, 22.9, 26.8, 27.8, 34.6, 35.0, 52.4, 60.9, 71.1, 80.4, 109.2, 148.3, 173.6; IR (neat): 3300, 2940, 1730, 1645, 1200 cm^{-1}. Anal. found: C 75.40; H 8.78%. Calc for $C_{13}H_{18}O_2$: C 75.69; H 8.80%. Iodination of **10b** was carried out according to the same procedure as that of the synthesis of ω-iodoacetylenic silyl enol ether. Yield: 91%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.25 (3H, t, J = 7.2 Hz), 1.30–1.46 (2H, m), 1.56–1.72 (3H, m), 2.04–2.14 (1H, m), 2.21–2.34 (2H, m), 2.70 (1H, d, J = 16.7 Hz), 2.85 (1H, d, J = 16.7 Hz), 4.11–4.25 (2H, m), 4.78 (1H, s), 4.9 (1H, s); ^{13}C NMR ($CDCl_3$, 100MHz) δ (ppm): –4.0, 14.3, 23.0, 27.8, 29.2, 34.6, 35.2, 52.7, 60.9, 90.5, 109.3, 148.2, 173.5; IR (neat): 2940, 1730, 1645, 1200 cm^{-1}. Anal. found: C 47.21; H 5.30%. Calc for $C_{13}H_{17}IO_2$: C 47.00; H 5.16%.

2.2.11. Diethyl 2-(3-iodoprop-2-ynyl)-2-(1-phenylethenyl)-malonate (**10c**)

Iodination of diethyl 2-(1-phenylethenyl)-2-(prop-2-ynyl) malonate was carried out according to the same procedure as that of the synthesis of ω-iodoacetylenic silyl enol ether. Yield: 82%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.19 (6H, t, J = 7.1 Hz), 3.06 (2H, s), 4.10–4.25 (4H, m), 5.39 (1H, s), 5.56 (1H, s), 7.18–7.35 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.4, 13.9, 28.3, 61.9, 63.1, 90.1, 120.3, 127.6, 127.9, 128.3, 140.4, 145.1, 169.0; IR (neat): 2990, 1730, 1625, 1200, 1060, 700 cm^{-1}. Anal. found: C 51.02; H 4.75%. Calc for $C_{18}H_{19}IO_4$: C 50.72; H 4.49%.

*2.2.11.1. Ethyl bicyclo[4.4.0]deca-1,3-diene-6-carboxylate (**11a**).* A freshly prepared yellow solution of $W(CO)_5$(thf) (0.65 ml) was added to a solution of **10a** (22 mg, 0.065 mmol) in THF (5.85 ml) at room temperature. After the mixture was stirred at room temperature for 11 h, the resulting

mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate = 5:1). Yield: 51%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.26 (3H, t, J = 7.1 Hz), 1.28–1.40 (3H, m), 1.58–1.70 (1H, m), 1.76–1.83 (1H, m), 2.21–2.42 (3H, m), 2.60 (1H, dd, J = 2.1, 17.5 Hz), 3.13 (1H, d, J = 17.5 Hz), 4.09–4.25 (2H, m), 5.53 (1H, dd, J = 2.2, 5.8 Hz), 6.45 (1H, dd, J = 3.1, 5.7 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.2, 23.0, 25.8, 32.3, 38.6, 49.0, 49.0, 61.0, 89.5, 121.2, 134.2, 139.1, 174.7; IR (neat): 2930, 1720, 1645, 1195, 825 cm^{-1}. Anal. found: C 46.90; H 5.24%. Calc for $C_{13}H_{17}IO_2$: C 47.00; H 5.16%.

*2.2.11.2. Diethyl 5-iodo-2-phenylcyclohexa-2,4-diene-1,1-dicarboxylate (**11c**).* Cyclization was carried out according to the same procedure as that of the synthesis of **11a**. Yield: 14%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.08 (6H, t, J = 7.1 Hz), 3.43 (2H, s), 3.95–4.20 (4H, m), 5.92 (1H, d, J = 5.8 Hz), 6.73 (1H, d, J = 5.8 Hz), 7.17–7.32 (3H, m), 7.32–7.48 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.7, 44.6, 61.4, 62.0, 91.8, 125.5, 127.4, 127.6, 128.0, 134.8, 136.3, 139.5, 170.1; IR (neat): 2980, 1730, 1625, 1240, 1060, 700 cm^{-1}. Anal. found: C 50.56; H 4.57%. Calc for $C_{18}H_{19}IO_4$: C 50.72; H 4.49%.

*2.2.12. Diethyl 2-(prop-2-enyl)-2-(3-iodoprop-2-ynyl)-malonate (**12**)*

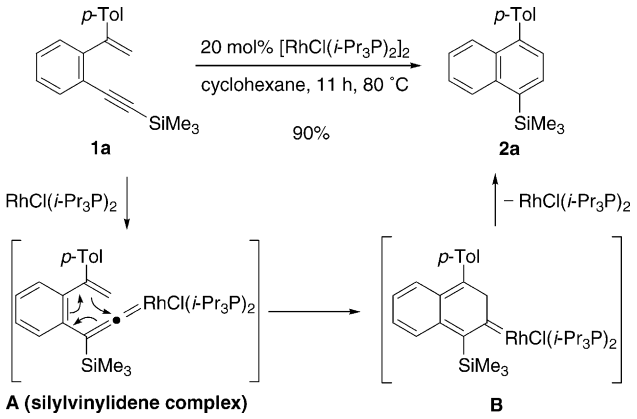
Iodination of diethyl 2-allyl-2-(prop-2-ynyl)malonate was carried out according to the same procedure as that of the synthesis of ω-iodoacetylenic silyl enol ether. Yield: 83%, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.23 (6H, t, J = 7.1 Hz), 2.76 (2H, d, J = 7.5 Hz), 2.93 (2H, s), 4.18 (4H, q, J = 7.1 Hz), 5.07–5.20 (2H, m), 5.53–5.66 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): −3.2, 14.1, 24.9, 36.6, 56.8, 61.7, 89.0, 119.9, 131.7, 169.6; IR (neat): 2980, 1730, 1640, 1220, 1190 cm^{-1}. Anal, found: C 42.94; H 4.89%. Calc for $C_{13}H_{17}IO_4$: C 42.87; H 4.71%.

*2.2.13. Diethyl 2-iodo-3-oxobicyclo[3.3.0]oct-1-ene-7,7-dicarboxylate (**13**)*

A freshly prepared yellow solution of $W(CO)_5$(thf) (4.4 ml) was added to a solution of **12** (84 mg, 0.22 mmol) in THF (1 ml) at room temperature. After the mixture was stirred at room temperature for 3 h, the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate = 3:1). Yield: 33%, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.16–1.32 (6H, m), 1.77 (1H, t, J = 12.7 Hz), 2.23 (1H, dd, J = 2.2, 17.9 Hz), 2.76–2.88 (2H, m), 3.10 (1H, d, J = 19.6 Hz), 3.08–3.32 (1H, m), 3.35 (1H, d, J = 19.5 Hz), 4.11–4.23 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 14.0, 14.0, 37.2, 39.1, 40.0, 46.4, 59.8, 62.1, 62.3, 94.6, 170.3, 171.1, 188.4, 203.2; IR (neat): 2980, 1730, 1635, 1250, 1180, 1060 cm^{-1}. Anal. found: C 43.16; H 4.49%. Calc for $C_{14}H_{17}IO_5$: C 42.87; H 4.37%.

3. Results and discussion

In the first place, we chose trimethylsilyl group as a labile substituent based on the seminal work by Werner and Schneider [4e]. They reported that the trimethylsilylvinylidene rhodium complex was obtained by the reaction of bis(trimethylsilyl)acetylene and $[RhCl(i\text{-}Pr_3P)_2]_2$ at −20 °C with 1,2-migration of the trimethylsilyl substituent. We then decided to examine the 6π-electrocyclization of *o*-(trimethylsilylethynyl)styrenes with the expectation that trimethylsilyl-substituted naphthalenes would be obtained through the trimethylsilylvinylidene rhodium complexes. When a cyclohexane solution of 1-[1-(*p*-tolyl)ethenyl]-2-[(trimethylsilyl)ethynyl]benzene **1a** was treated with 20 mol% amount of $[RhCl(i\text{-}Pr_3P)_2]_2$ prepared in situ from $[RhCl(cot)_2]_2$ and i-Pr_3P in cyclohexane, it was completely consumed at 80 °C within 11 h to afford 1-(*p*-tolyl)-4-trimethylsilylnaphthalene **2a**, the desired product, in 90% yield. The position of the trimethylsilyl group was confirmed by the presence of two doublets at δ (ppm): 7.37 and 7.72 (J = 7.0 Hz), corresponding to the C2 and C3 protons, respectively. A proposed mechanism of this reaction using $[RhCl(i\text{-}Pr_3P)_2]_2$ is shown in Scheme 1.



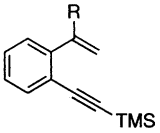
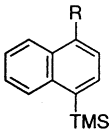
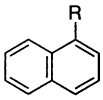
Scheme 1.

Treatment of **1a** with $[RhCl(i\text{-}Pr_3P)_2]_2$ would give an alkyne–$RhCl(i\text{-}Pr_3P)_2$ π-complex, which gradually isomerizes to the silylvinylidene rhodium complex **A** with 1,2-migration of the trimethylsilyl group; then 6π-electrocyclization occurs giving the carbene intermediate **B**, which affords the silyl-substituted naphthalene by 1,2-hydrogen migration with regeneration of $RhCl(i\text{-}Pr_3P)_2$.[1] No reaction occurred when other transition metal complexes such as $RhCl(Ph_3P)_3$, $[IrCl(i\text{-}Pr_3P)_2]_2$, $CpMn(CO)_2$(thf), and $W(CO)_5$(thf) were employed.

Generality of this reaction was examined using $[RhCl(i\text{-}Pr_3P)_2]_2$, however, other *o*-(trimethylsilylethynyl)styrenes (Table 1, **1b** and **1c**) gave rather low yield of the desired products (Table 1, **2b** and **2c**) and the proto-desilylated

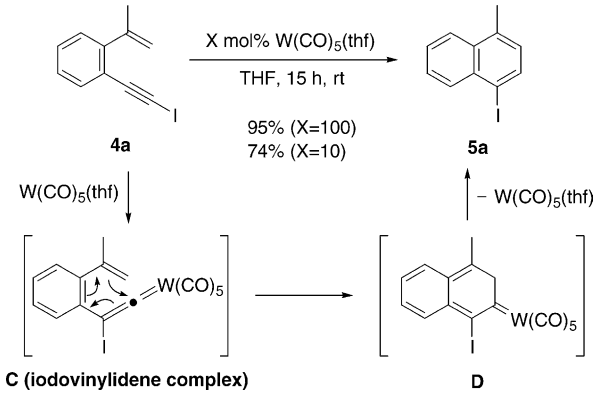
[1] It is known that $[RhCl(i\text{-}Pr_3P)_2]_n$ is a dimer in the solid state but a monomer in solution.

Table 1
Synthesis of TMS-substituted naphthalene derivatives

Substrate	Product (%)	
		
1a R=*p*-Tol	**2a** 90	**3a** 0
1b R=Me	**2b** 29	**3b** 29
1c R=OTBS	**2c** 14	**3c** 14

naphthalene derivatives were obtained to considerable amounts in these cases (Table 1, **3b** and **3c**). While this research was under investigation in our laboratory, a paper describing a $[RhCl(CO)_2]_2$-catalyzed cyclization of 1-trimethylsilyl-1-alkynes **1c** via silylvinylidene rhodium complex has appeared, see [14].

As the utilization of the silylated vinylidene complex formation from 1-trimethylsilyl-1-alkynes for a synthetic purpose has resulted in a partial success, we next examined the possibility of utilizing halogenated vinylidene complex formation from 1-halo-1-alkynes. To our knowledge, only one example has been reported for the preparation of iodovinylidene complexes from 1-iodo-1-alkynes using $CpMn(CO)_2(thf)$, and no synthetic utility has been reported for such complexes [6a]. We then decided to examine the reaction of *o*-(haloethynyl)styrenes with various transition metal complexes. When a stoichiometric amount of $CpMn(CO)_2(thf)$ prepared in situ from $CpMn(CO)_3$ was added to a pentane/ether solution of 1-(iodoethynyl)-2-[1-(*p*-tolyl)ethenyl]benzene **4b** possessing an iodo group at the alkyne terminus, low yield of 1-iodo-4-(*p*-tolyl)naphthalene **5b** was obtained along with a complex mixture of unidentified products. However, when 1-(iodoethynyl)-2-(1-methylethenyl)benzene **4a** was treated with a stoichiometric amount of $W(CO)_5(thf)$, it was completely consumed at room temperature within 4 h and 1-iodo-4-methylnaphthalene **5a** was obtained in 95% yield. This reaction could be carried out successfully even with only 10 mol% amount of $W(CO)_5(thf)$ to give the same product in 74% yield. The position of the iodine atom is confirmed by the presence of two doublets at δ (ppm): 7.02 and 7.96 ($J = 7.5$ Hz), corresponding to the C2 and C3 protons, respectively. A control experiment was run at room temperature using HI instead of $W(CO)_5(thf)$, however, only the starting material was recovered. o-Alkynylstyrenes cyclized in the presence of HI at 50 °C to yield 3-iodoindene derivatives, see [15]. To get information on the reaction mechanism, we monitored the reaction of **4a** with $W(CO)_5(thf\text{-}d_8)$ by ^1H NMR in THF-d_8. During the course of the reaction, only the starting material and the cyclized product were observed and none of the possible intermediates could be detected. Furthermore, when **4a** deuterated at both positions of the alkene terminus was treated with



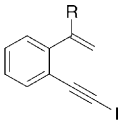
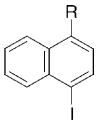
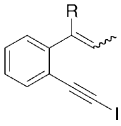
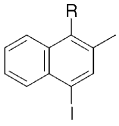
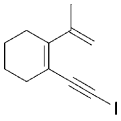
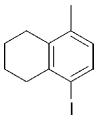
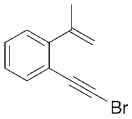
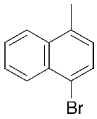
Scheme 2.

$W(CO)_5(thf)$, two doublets corresponding to the C2 and C3 protons completely disappeared in ^1H NMR spectra of the product **5a**. Therefore, the reaction is thought to proceed as follows: treatment of **4a** with $W(CO)_5(thf)$ would give an alkyne–$W(CO)_5$ π-complex, which gradually isomerizes to the iodovinylidene tungsten complex **C** through 1,2-migration of the iodine atom; then 6π-electrocyclization occurs forming the carbene intermediate **D**, which affords the iodo-substituted naphthalene by 1,2-hydrogen migration with regeneration of $W(CO)_5(thf)$ (Scheme 2).

The scope of the reaction is summarized in Table 2. Not only iodo-substituted aromatic enynes **4a**–**4g** but also a non-aromatic dienyne derivative **4h** was cyclized to afford the corresponding iodo-substituted naphthalene and benzene derivatives. However, the reaction of the vinyl derivative **4e** proceeded sluggishly to yield a small amount of the proto-deiodinated compound, naphthalene. Therefore, the α-substituent on the olefinic part would favor the conformation in which the olefinic double bond faces the actylenic part due to steric repulsion between it and the latter. This tendency is the same as we have already reported in the 6π-electrocyclization of *o*-ethynylstyrenes using $W(CO)_5(thf)$ [8]. In this reaction, use of a stoichiometric amount of $W(CO)_5(thf)$ generally gave the product in good yield, while the yield of the catalytic reaction varied depending on the structure and the substituents of the substrate. The difference of reactivity between α-siloxy derivative **4c** and α-methoxycarbonyl derivative **4d** suggests that this cyclization proceeds smoothly when the electron density at the β-position of the olefin is high.[2] When 1-(bromoethynyl)-2-(1-methylethenyl)benzene **4i** possessing a bromo group at the alkyne terminus was treated with a stoichiometric amount of $W(CO)_5(thf)$, the reaction proceeded sluggishly resulting in a complex mixture of products.

[2] The reaction time necessary for consumption of the starting material under the stoichiometric conditions: 1 h for **4c** and 2 h for **4d**. The reaction of **4d** with 20 mol% amount of $W(CO)_5(thf)$ gave a substantial amount of polymerization products judging from the presence of broadening peaks in the ^1H NMR spectrum of the crude product.

Table 2
Synthesis of halo-substituted naphthalene derivatives

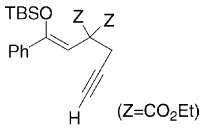
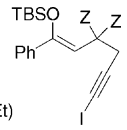
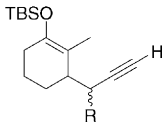
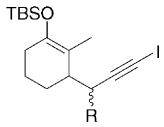
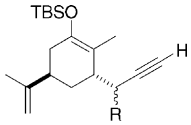
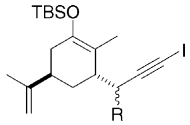
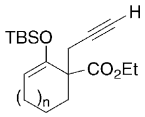
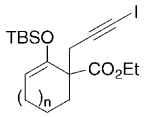
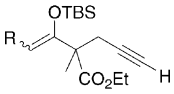
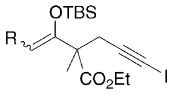
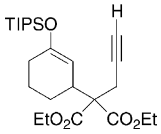
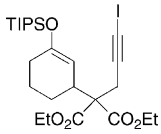
Substrate	Product	Yield (%)	
		Amount of $W(CO)_5$(thf) (mol%)	
		100	10–20
			
4a R = Me	**5a**	95	74[a]
4b R = *p*-Tol	**5b**	93	81[a]
4c R = OTBS	**5c**	83	81[b]
4d R = CO_2Me	**5d**	84	26[b]
4e R = H	**5e**	0	–
			
4f R = *p*-Tol[c]	**5f**	42	32[b]
4g R = Me[d]	**5g**	20	–
			
4h	**5h**	67	34[b]
			
4i	**5i**	0	–

[a] $W(CO)_5$(thf) used was 10 mol%.
[b] $W(CO)_5$(thf) used was 20 mol%.
[c] 1:1 mixture of *E* and *Z* isomers.
[d] 3:1 mixture of *E* and *Z* isomers.

We next studied intramolecular nucleophilic attack of a silyl enol ether onto the carbene carbon of the iodovinylidene tungsten complex. For the recent examples of nucleophilic endo-selective cyclization onto alkynes, see [11]. Required substrates, ω-iodoacetylenic silyl enol ethers, were easily prepared by treatment of ω-acetylenic silyl enol ethers with *N*-iodosuccinimide in the presence of $AgNO_3$ in DMF at 0 °C in good yield without formation of the hydrolyzed product of the starting material [16]. The results with various ω-acetylenic silyl enol ethers were summarized in Table 3. As these ω-iodoacetylenic silyl enol ethers were not very stable, they were usually kept in a refrigerator.

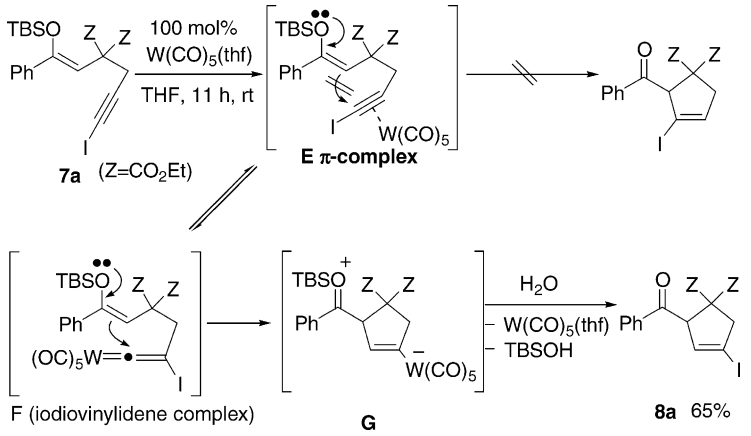
When an ω-iodoacetylenic silyl enol ether **7a** was treated with a stoichiometric amount of $W(CO)_5$(thf) in the presence of 300 mol% amounts of H_2O, the reaction proceeded smoothly at room temperature to give an iodo-substituted cyclopentene derivative **8a** in 65% yield. The position of iodine atom, confirmed by an NOE experiment, supports that this reaction also proceeds through the iodovinylidene tungsten complex **F** (Scheme 3).

Table 3
Iodination of ω-acetylenic silyl enol ethers using *N*-iodosuccinimide and $AgNO_3$

Substrate	Product	Yield (%)
		
6a	**7a**	91
		
6b R = H	**7b** R = H	92
6c R = Me[a]	**7c** R = Me[a]	84
		
6d R = H	**7d** R = H	69
6e R = *n*-Bu[a]	**7e** R = *n*-Bu[a]	59
		
6f *n* = 1	**7f** *n* = 1	88
6g *n* = 3	**7g** *n* = 3	99
		
6h R = H	**7h** R = H	74
6i R = Me[b]	**7i** R = Me[b]	99
		
		77

[a] 1:1 mixture of stereoisomers.
[b] 3:2 mixture of *E* and *Z* isomers.

The reaction is thought to proceed as follows: treatment of **7a** with $W(CO)_5$(thf) would first give an alkyne–$W(CO)_5$ π-complex **E**, which is isomerized to the iodovinylidene tungsten complex **F**; then nucleophilic attack of the silyl enol ether onto the carbene carbon of the iodovinylidene tungsten complex occurs to give the vinyl metallic species **G**, which is protonated by H_2O to give the corresponding iodo-substituted β,γ-unsaturated ketone **8a**. We have previously proposed that when the same type of reaction for terminal alkynes was carried out, the cyclization took place either through the alkyne–$W(CO)_5$ π-complex (like **E**) or through the vinylidene complex (like **F**) on the basis of deuterium experiments [7a]. In contrast, it is noted that this reaction for the ω-iodoacetylenic silyl enol ether occurs through the iodovinylidene complex **F** only. It is likely that the presence of the iodo group would make the cyclization through the



Scheme 3.

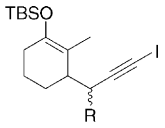
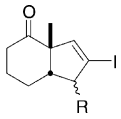
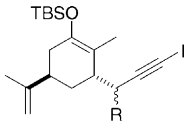
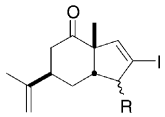
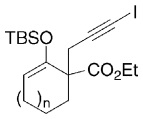
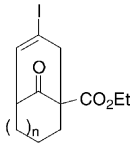
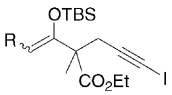
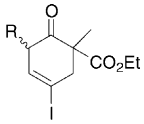
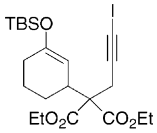
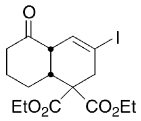
alkyne–$W(CO)_5$ π-complex **E** difficult due to steric repulsion between the iodo group and the silyl enol ether moiety.

Generality of the reaction employing representative substrates is summarized in Table 4. Reaction of 1-iodo-6-siloxy-5-en-1-yne derivatives (**7b**–**7e**) with $W(CO)_5$(thf) proceeded readily at room temperature to give the 5-endo cyclized products (**8b**–**8e**) in good yield without formation of the alternative iodine positional isomers. Furthermore, 1-iodo-5-siloxy-5-en-1-yne derivatives (**7f**–**7i**) gave the corresponding 6-endo cyclized products (**8f**–**8i**) in good yield. However, 1-iodo-7-siloxy-6-en-1-yne derivative **7j** with $W(CO)_5$(thf) proceeded sluggishly and the 6-endo cyclized product **8j** was not obtained. Although one would expect that the reaction should proceed with only a catalytic amount of $W(CO)_5$(thf), in fact, only a poor yield of the product along with the hydrolyzed product of the starting material was obtained under several catalytic conditions examined.

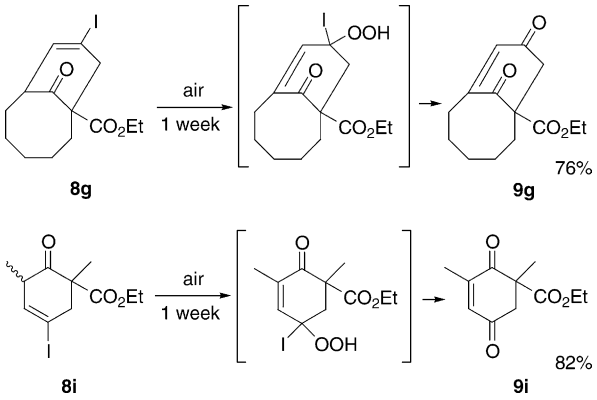
We also found that these cyclized products were gradually oxidized by air to provide α,β-unsaturated diketones in good yield. For example, when the bicyclic compound **8g** was kept in an open vessel without solvent for 1 week at room temperature, the diketone derivative **9g** was obtained in 76% yield. Under similar conditions the monocyclic compound **8i** was also transformed into the corresponding product **9i** in 82% yield. We assume that this reaction proceeds through allylic oxidation by molecular oxygen to give an α,β-unsaturated γ-peroxy ketone as the initial product, which is converted to the enedione [17]. It is noteworthy that the iodo-substituted products are easily oxidized by molecular oxygen, while the corresponding hydrogen-substituted products are air-stable for a longer period of time (Scheme 4).

We next applied this annulation through iodovinylidene tungsten complexes to 1-iodo-5-en-1-yne derivatives having an exo methylene as the nucleophilic moiety. When a cyclic 1-iodo-5-en-1-yne derivative **10a** was treated with a stoichiometric amount of $W(CO)_5$(thf), the reaction proceeded smoothly at room temperature to give the 6-endo cyclized product **11a** in 51% yield (Eq. (3)). This is a unique character of the iodovinylidene tungsten complex because the

Table 4
Cyclization of ω-iodoacetylenic silyl enol ethers using a stoichiometric amount of $W(CO)_5$(thf)

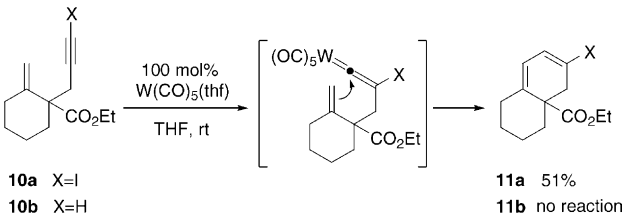
Substrate	Product	Yield (%)
		
7b R = H	**8b** R = H	66
7c R = Me[a]	**8c** R = Me[a]	79
		
7d R = H	**8d** R = H	59
7e R = *n*-Bu[a]	**8e** R = *n*-Bu[a]	74
		
7f *n* = 1	**8h** *n* = 1	70
7g *n* = 3	**8i** *n* = 3	73
		
7h R = H	**8h** R = H	46
7i R = Me[b]	**8i** R = Me[c]	64
		
7j	**8j**	0

[a] 1:1 mixture of stereoisomers.
[b] 3:2 mixture of *E* and *Z* isomers.
[c] 1:2 mixture of stereoisomers.

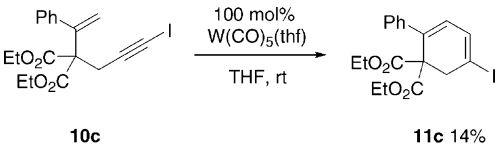


Scheme 4.

reaction of the corresponding 5-en-1-yne derivative **10b** under the same conditions resulted in recovery of the starting material. This big difference of reactivity is probably due to the higher electrophilicity of the carbene carbon of the iodovinylidene complex compared to that of the corresponding hydrogen-substituted vinylidene complex because of the inductive effect of iodine atom. The reaction of an acyclic 1-iodo-5-en-1-yne derivative **10c** proceeded sluggishly and rather low yield of the desired product was obtained.

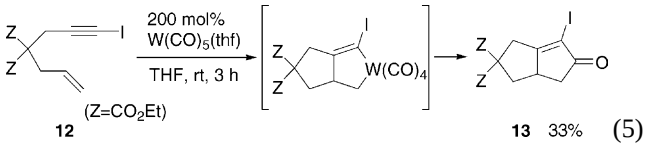


(3)



(4)

In the course of our investigation of ω-iodo enyne derivative with $W(CO)_5$(thf), we found that treatment of acyclic 1-iodo-6-en-1-yne **12** with $W(CO)_5$(thf) gave the iodo-substituted bicyclo[3.3.0]octenone derivative **13**, a Pauson–Khand type product, in 33% yield (Eq. (5)). Although the Pauson–Khand reactions have been examined using a variety of substrates, 1-iodo-1-alkynes have not been employed as the alkyne partner so far. For a review on Pauson–Khand reaction, example of Pauson–Khand reaction using $W(CO)_5$(thf), and example of Pauson–Khand reaction of 1-chloro-1-alkynes using $Co_2(CO)_8$, see [18–20]. Therefore this reaction is a rare example of such reaction.



(5)

4. Conclusion

An efficient cyclization of 1-iodo-1-alkynes was accomplished through iodovinylidene tungsten complex using $W(CO)_5$(thf). The iodine is retained in the products of these reactions, making them very versatile substrates for further coupling reactions.

Acknowledgements

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