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Convenient Preparative Method of α,β-Disubstituted Cyclopentenone by Zirconium Promoted Intermolecular Coupling of an Alkyne, EtMgBr (or Ethylene) and CO

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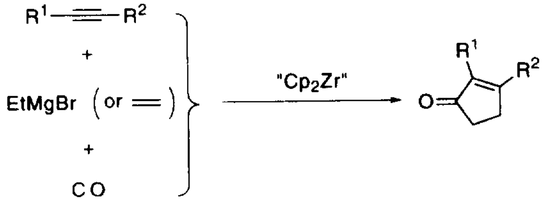
Abstract: Treatment of Cp_2ZrCl_2 with 2 equiv of EtMgBr in THF, followed by addition of an internal alkyne and subsequent treatment with CO/I_2 gave α,β-disubstituted cyclopentenone in good to high yields. When a conjugated enyne was used as an alkyne component, α-alkenyl cyclopentenone was selectively formed in 80-89% yields. In the case of 4,6-decadiyne, α-alkynylcyclopentenone was formed in 88% yield. Bridged alkynes such as 1,4-dihexynylbenzene afforded α,α'-bridged cyclopentenone compounds in good yields. © 1997 Elsevier Science Ltd.

INTRODUCTION

Cyclopentenone compounds have been widely used for organic synthesis as starting materials or intermediates. Preparation of cyclopentenone compounds from three components such as an alkyne, CO and an alkene is most attractive. One of the most extensively studied procedures for *inter*molecular coupling reaction of the three components is the Pauson-Khand reaction using $Co_2(CO)_8$.[2] However, this method for the preparation of α,β-disubstituted cyclopentenones entails some crucial problems. The use of gaseous ethylene requires an autoclave, and internal alkynes gives relatively low yields of cyclopentenones.[2] In this paper we describe a convenient preparative method for α,β-disubstituted cyclopentenones from three components, alkynes, CO and EtMgBr (or ethylene) using zirconocene compounds under atmospheric pressure (eq.1). α-Alkyl, aryl, silyl, alkenyl, alkynyl, as well as α,α'-bridged cyclopentenones were readily prepared by this method.



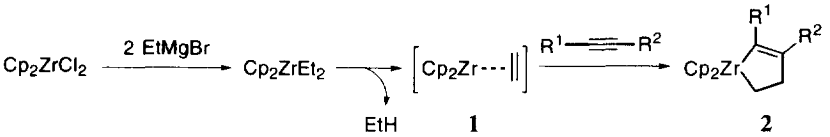
(1)

RESULTS AND DISCUSSION

α,β-Alkyl, aryl, silyl-substituted cyclopentenones:

Zirconocene or titanocene-mediated *intra*molecular cyclization reactions of enynes followed by CO insertion giving bicyclic cyclopentenones have been reported.[3] However, for the *inter*molecular coupling reaction of ethylene, alkyne and CO only a few examples have been reported *via* some phosphine-stabilized zirconocene-ethylene complexes or zirconocene-alkyne complexes.[4]

Recently we have reported that Cp_2ZrEt_2, which is easily prepared from Cp_2ZrCl_2 and 2 equiv of EtMgBr, is converted into a zirconocene-ethylene complex **1**.[5] The zirconocene-ethylene complex **1** thus prepared *in situ* reacted with one equiv of alkynes to give zirconacyclopentenes **2** in high yields without phosphine ligands (eq. 2).[6] Very recently we have reported an alternative route to the zirconacyclopentenes **2** using Cp_2ZrBu_2, ethylene gas and an alkyne (eq. 3).[7] In order to prepare α,β-disubstituted cyclopentenones **3**, we used both of these two methods. Treatment of zirconacyclopentenes **2** formed *in situ* with CO under a slightly positive pressure at -78°C smoothly produced cyclopentenones **3** after 3h (eq. 4).[6]



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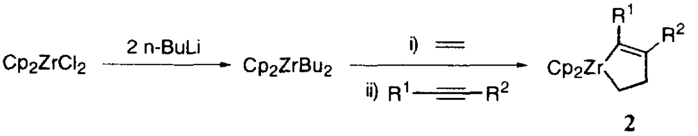

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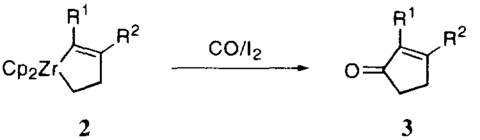


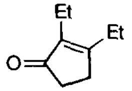
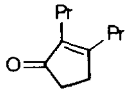
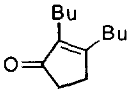
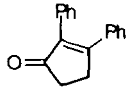
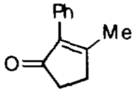
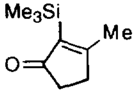
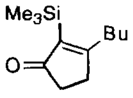
(4)

Results are listed in Table 1. α,β-Disubstituted cyclopentenones with alkyl, aryl and silyl substituents were all obtained in good to high yields. Cyclopentenones were formed in similar yields when EtMgBr (eq. 2) or ethylene gas (eq. 3) was employed as the alkene component. Although the use of EtMgBr afforded a small amount of zirconacyclopentadienes as by-products in the preparation of zirconacyclopentenes.[7] α,β-disubstituted cyclopentenones were obtained as pure compounds after separation. In some cases the combination of Cp_2ZrCl_2 and 2 equiv of EtMgBr (procedure 1) gave better yields than the combination of Cp_2ZrCl_2 with 2 equiv of n-BuLi (procedure 3) which was the best combination for preparation of unsymmetrical zirconacyclopentadienes.[7b] This might be due to the effect of the magnesium salt which is *in situ formed*, or due to the inhibition of CO insertion by an excess of ethylene, but it is not clear yet. It should be pointed out that in order to obtain the desired cyclopentenones, work-up of the CO-insertion reaction mixture with I_2 is necessary. Normal quenching with 3N HCl gives a mixture of the cyclopentenone and its corresponding alcohol.

α-Alkynyl or alkenyl disubstituted cyclopentenones:

Reactions of conjugated diynes with a zirconocene-ethylene complex gave zirconacyclopentenes **4** with alkynyl substituents at the α-position with very high regioselectivities (Scheme 1).[8] Conjugated enynes **5** were obtained in high yields after hydrolysis of zirconacyclopentenes **4**. When zirconacyclopentenes **4** were treated with CO at -78°C, α-alkynyl substituted cyclopentenones **6** were obtained in good yields. It is noteworthy that zirconacyclopentenes thus prepared using diynes did not react with the second diynes even in the presence of an excess of diynes except in the case of 1,4-bis(trimethylsilyl)-1,3-butadiyne.[9] This is in contrast to the usual alkynes such as 4-octyne and diphenyl acetylene which gave the corresponding zirconacyclopentadienes.[6,7]

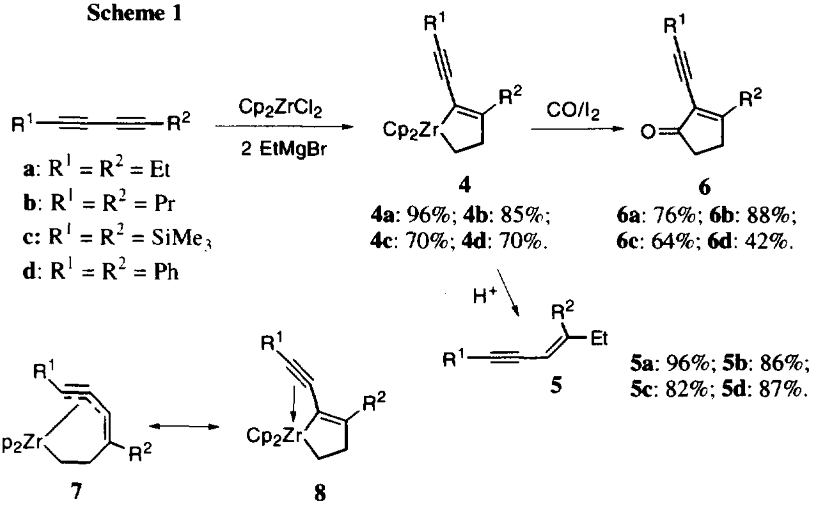
Table 1. Preparation of α,β-Disubstituted Cyclopentenones from Zirconacyclopentenes[a]

Cyclopentenones		Procedure 1/%[b]	Procedure 2/%[c]	Procedure 3/%[d]
	3a	89 (71)	71	70
	3b	80 (58)	52	70
	3c	96 (74)	88	76
	3d	64 (48)	65	68
	3e	98 (64)	85	65
	3f	44	57 (40)	23
	3g	24	52 (36)	-

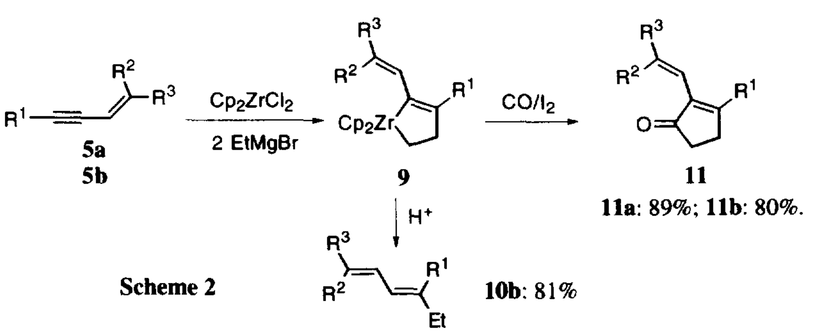
[a] GC yields. Isolated yields are given in parentheses. [b]Procedure 1: Cp_2ZrCl_2 + 2 eq of EtMgBr ; [c]Procedure 2: Cp_2ZrCl_2 + 2 eq of EtMgBr + ethylene gas; [d]Procedure 3: Cp_2ZrCl_2 + 2 eq of BuLi + ethylene gas.

NMR study of the zirconacyclopentenes **4** revealed that two alkynyl carbons in the α-position showed very characteristic chemical shifts. The ^{13}C NMR spectra of these zirconacyclopentenes showed that one of the alkynyl carbon signals appeared at about 140 ppm, e.g. 144.20 (**4a**), 143.12 (**4b**). The other alkynyl carbon appeared in the normal region of *sp*-carbon, e.g. 88.19 (**4a**), and 87.53 (**4b**). These low-field shifts are probably due to the strong interaction with the Cp_2Zr moiety. Similar downfield shifts were reported when 1,4-bis(trimethylsilyl)-1,3-butadiyne or 1,4-bis(*tert*-butyl)-1,3-butadiyne was complexed with zirconocene forming cyclocumulenes.[9] Strong interaction of a triple bond in the α-position of zirconacyclopentenes with the Cp_2Zr moiety prevented the zirconacyclopentene from reacting with the second diyne. This interaction of a triple bond in the α-position also contributes to the high regioselectivity. Although the real structure of **4** is not clear yet since we could not obtain good crystals suitable for X-ray analysis, contributions of **7** and **8** in addition to **4** should be considered.

Scheme 1



When a conjugated enyne **5** was used as the alkyne component, similar regioselective coupling to give a zirconacylopentene **9** was observed (Scheme 2). Alkenyl substituents were in the α-position of zirconacyclopentenes. Hydrolysis of these zirconacyclopentenes derived from conjugated enynes gave dienes **10** in good yields. Treatment of the zirconacyclopentenes with CO/I_2 afforded the corresponding α-alkenyl substituted cyclopentenones **11**. It is also interesting that only the triple bond in a conjugated enyne **5** couples with an ethylene molecule on zirconocene forming a zirconacyclopentene **9**. Coupling reaction between the double bond in a conjugated enyne **5** and an ethylene molecule on zirconocene was not observed. Dimerization of conjugated enynes **5** forming the corresponding zirconacyclopentadienes was not detected either.

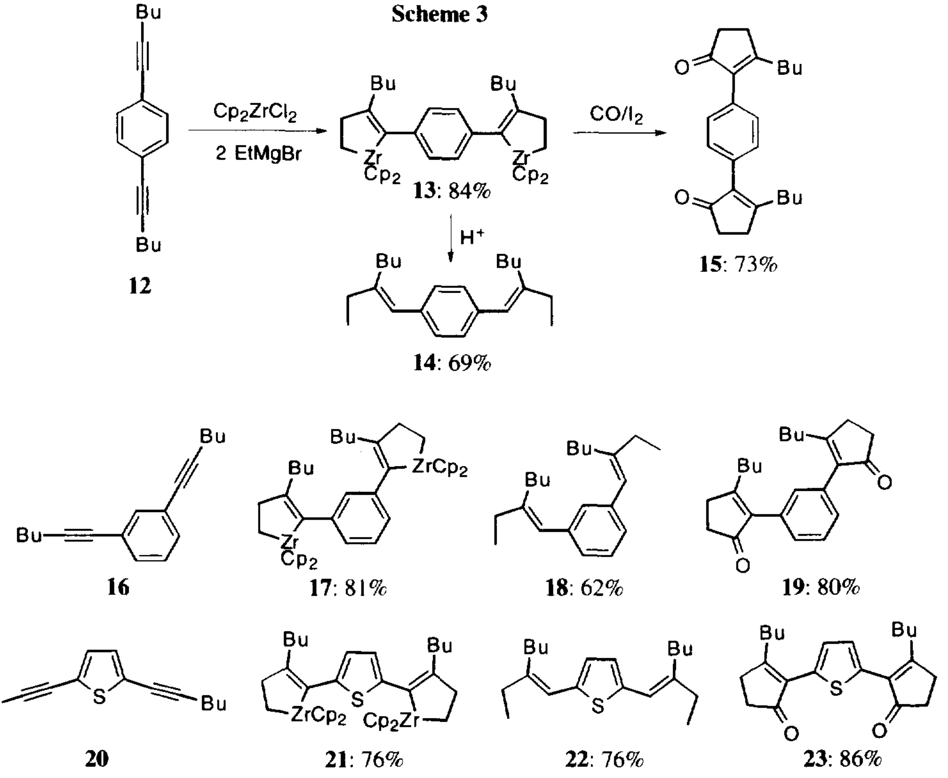


Scheme 2

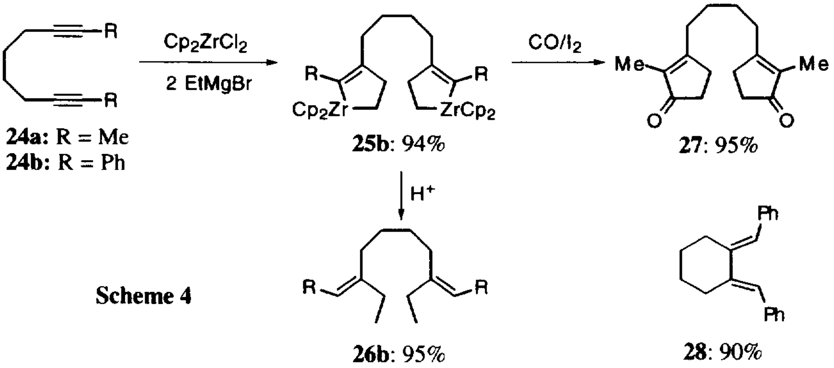
Bridged cyclopentenones:

α,α'-Bridged cyclopentenones are difficult to prepare from cyclopentenones, since the substitution reaction method at the α-carbon of cyclopentenones is limited.[10] In this sense bridged zirconacyclopentenes are very attractive for the preparation of α,α'-bridged cyclopentenones *via* the CO insertion reaction described above. However, formation of bridged zirconacyclopentenes has not been reported. One major reason is that the alkyne-alkyne coupling reaction is usually much faster than the intermolecular alkyne-alkene coupling on reduced zirconocene compounds.[11,12] When aromatic ring-bridged diynes **12**, **16**, **20** were used, α,α'-bridged zirconacyclopentenes **13**, **17**, **21** with aryl moieties at the α-positions were formed in high yields. Their NMR spectra showed the selective formation of bridged zirconacyclopentenes. Hydrolysis of **13**, **17**, **21** afforded the corresponding products **14**, **18**, **22** in 69%, 62%, and 76% yields, respectively, as single products. No formation of isomers was observed. This is consistent with the regiochemistry usually observed in the coupling reaction of aryl-substituted alkynes on zirconocene. These zirconacyclopentenes were converted *via* the CO insertion reaction into α,α'-bridged cyclopentenones **15**, **19**, **23** in 73%, 80%, and 86% yields, respectively.

Scheme 3

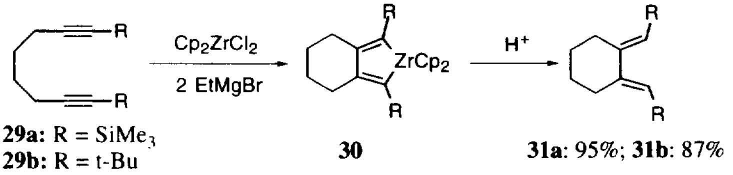


In the case of $(CH_2)_n$ bridged diynes, reaction products were dependent on the nature of substituents at the non-conjugated diynes.[13] When methyl-substituted diyne **24a** was used (Scheme 4), the corresponding zirconacyclopentene was formed as a mixture of three regioisomers in a ratio of 5:3:1 which were transformed into a mixture of three bridged cyclopentenones **27** in a similar ratio of 5:3:1 after the CO insertion reaction. In the case of phenyl substituted diyne **24b**, a bridged zirconacyclopentene **25b** was selectively formed in 94% NMR yield (Scheme 4). Hydrolysis of **25b** afforded **26b** in 95% yield as a single product. Unfortunately, however, treatment of zirconacyclopentene **25b** with CO gas resulted in the formation of *intra*molecularly bicyclized zirconacyclopentadiene which gave **28**[14] in 90% yield after hydrolysis. No formation of a bridged cyclopentenone from **25b** was observed.



Scheme 4

It is interesting that when silylated non-conjugated diyne **29a** or tert-butyl-substituted non-conjugated diyne **29b** was used, reaction with zirconocene-ethylene complex **1** gave only *intra*molecularly bicyclized zirconacyclopentadienes **30**, which produced **31a** (95 % yield)[15] and **31b** (87% yield), respectively, after hydrolysis. In these cases, zirconocene-ethylene complex **1** behaves similarly to the zirconocene-butene complex which is well known for dimerization or cyclization of alkynes.[11,14] Carbon monoxide does not insert into zirconacyclopentadienes under normal reaction conditions.



(5)

CONCLUSION

A convenient procedure for the preparation of α,β-disubstituted cyclopentenones *via inter*molecular coupling of three components, ethylene, alkyne and CO, has been developed using zirconocene-ethylene complex **1**. α-Alkyl, aryl, silyl, alkenyl, alkynyl, as well as α,α'-bridged cyclopentenones were readily prepared by this procedure.

EXPERIMENTAL

General. Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions were run under a slightly positive pressure of dry N_2. THF was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc. Ethylmagnesium bromide (THF solution) and butyllithium (hexane solution) were purchased from Kanto Chemicals Co. Ltd. ^{1}H-NMR (270 MHz) and ^{13}C-NMR (67.5 MHz) spectra were recorded on a JEOL EX270 NMR spectrometer, infrared spectra on a Shimadzu FTIR-4200 spectrometer. GLC analysis was performed on a gas chromatograph equipped with a flame ionization detector using a capillary column (CBP1-M25-025). GLC yields were determined using suitable hydrocarbons as internal standards.

A Representative Procedure for the Preparation of Cyclopentenones 3 via Zirconacyclopentenes 2: Synthesis of 2, 3-Diethylcyclopenten-1-one (3a). Procedure 1[6]: A 50mL Schlenk tube under dried nitrogen was charged with Cp_2ZrCl_2 (1.54g, 6 mmol) and THF (30 mL). To this solution was added ethylmagnesium bromide (0.92 M THF solution, 12 mmol) at -78 °C. After stirring for 1 h, 3-hexyne (411 mg, 5 mmol) was added and the reaction mixture was stirred at room temperature for 1h. The reaction mixture was cooled to -78 °C and carbon monoxide was slowly bubbled into the solution for 3 h with stirring. The reaction mixture was quenched with iodine (2.3 g, 9 mmol). The above reaction mixture was quenched with 3N HCl and extracted with ether (3 x 70 mL). The extract was washed with water, $Na_2S_2O_3$, $NaHCO_3$, brine and dried over $MgSO_4$. The solvent was evaporated *in vacuo* . Distillation or flash chromatograph provided the product **3a**, GC yield 89%, isolated yield 71% (0.49g). Procedure 2: The reaction was carried out in a similar manner to Procedure 1. After addition of EtMgBr, the mixture was stirred at -78°C for 1h under nitrogen. Then ethylene gas was introduced for 1h. The reaction mixture was gradually warmed to room temperature. To this solution was added 3-hexyne. The resulting mixture was stirred for 1h at room temperature under a slightly positive pressure of ethylene gas. CO insertion reaction was carried out in a same way as described in Procedure 1. The product **3a** was obtained in 71% GC yield. Procedure 3[7]: The reaction was carried out in a similar way to Procedure 2 using 2eq. of n-BuLi (12 mmol, 1.7 M, 7.1 mL) instead of EtMgBr. The product **3a** was obtained in 70% GC yield. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, J = 8 Hz, 3H), 1.16 (t, J = 8 Hz, 3H), 2.19 (q, J = 8 Hz, 2H), 2.33-2.37 (m, 2H), 2.47 (q, J = 8 Hz, 2H), 2.51-2.54 (m, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 12.13, 13.35, 16.26, 24.17, 28.57, 34.30, 141.20, 174.91, 209.88. IR (neat): 2998, 2936, 2876, 1698, 1642 cm^{-1}. HRMS calcd for $C_9H_{14}O$ 138.1045, found 138.1042.

α-Alkynyl and α-alkenyl cyclopentenones **6** and **11** were prepared by Procedure 1 as described above. Compounds **5** or **10** were isolated after hydrolysis of the reaction mixture containing zirconacyclopentenes **4** or **9** with 3N HCl.

2, 3-Dipropylcyclopenten-1-one (3b). Procedure 1: GC yield 80%, isolated yield 58%; Procedure 2: GC yield 52%; Procedure 3: GC yield 70%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 8 Hz, 3H), 0.98 (t, J = 8 Hz, 3H), 1.36-1.44 (m, 2H), 1.52-1.63 (m, 2H), 2.12-2.17 (m, 2H), 2.31-2.43 (m, 4H), 2.45-2.53 (m, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.57, 13.57, 20.29, 21.31, 24.55, 28.36, 32.60, 33.64, 139.77, 173.24, 209.07. IR (neat): 2961, 2934, 2872, 1699, 1640 cm^{-1}. HRMS calcd for $C_{11}H_{18}O$ 166.1358, found 166.1359.

2, 3-Dibutylcyclopenten-1-one (3c). Procedure 1: GC yield 96%, isolated yield 74%; Procedure 2: GC yield 88%; Procedure 3: GC yield 76%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J = 7 Hz, 3H), 0.95 (t, J = 7 Hz, 3H), 1.27-1.45 (m, 6H), 1.48-1.60 (m, 2H), 2.16 (t, J = 7 Hz, 2H), 2.31-2.52 (m, 6H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.94, 13.94, 22.84, 22.91, 22.91, 29.09, 29.79, 30.91, 31.00, 34.27, 140.41, 174.14, 209.90. IR (neat): 2957, 2932, 2863, 1698, 1640 cm^{-1}. HRMS calcd for $C_{13}H_{22}O$ 194.1671, found 194.1679.

2, 3-Diphenylcyclopenten-1-one (3d). Procedure 1: GC yield 64%, isolated yield 48%; Procedure 2: GC yield 65%; Procedure 3: GC yield 68%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 2.58-2.61 (m, 2H), 2.92-2.95 (m, 2H), 7.16-7.31 (m, 10H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 29.42, 34.68, 127.67, 127.96, 128.32, 129.36, 129.70, 131.31, 135.60, 139.64, 167.94, 207.22. IR (neat): 3083, 3056, 3032, 2972, 2924, 1694, 1352, 1159, 762, 698 cm^{-1}. HRMS calcd for $C_{17}H_{14}O$ 234.1045, found 234.1041.

2-Phenyl-3-methylcyclopenten-1-one (3e). Procedure 1: GC yield 98%, isolated yield 64%; Procedure 2: GC yield 85%; Procedure 3: GC yield 65%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 2.14 (s, 3H), 2.49-2.53 (m, 2H), 2.60-2.63 (m, 2H), 7.26-7.42 (m, 5H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 18.29, 31.75, 34.81, 127.53, 128.19, 129.09, 131.84, 140.21, 171.96, 207.54. IR (neat): 3082, 3056, 3034, 3022, 2912, 1693, 1638, 1379, 1134, 764, 702 cm^{-1}. HRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0891.

2-Trimethylsilyl-3-methylcyclopenten-1-one (3f). Procedure 1: GC yield 44%; Procedure 2: GC yield 57%, isolated yield 40%; Procedure 3: GC yield 23%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.22 (s, 9H), 2.18 (s, 3H), 2.31-2.35 (m, 2H), 2.55-2.59 (m, 2H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ -0.50, 20.32, 35.62, 35.97, 139.48, 185.44, 214.16. IR (neat): 2955, 2910, 1690, 1593, 1259, 814 cm^{-1}. HRMS calcd for $C_9H_{16}OSi$ 168.0970, found 168.0972.

2-Trimethylsilyl-3-butylcyclopenten-1-one (3g). Procedure 1: GC yield 24%; Procedure 2: GC yield 52%, isolated yield 36%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.92 (s, 9H), 1.65 (t, *J* = 7 Hz, 3H), 1.35-1.40 (m, 2H), 1.43-1.55 (m, 2H), 2.30-2.34 (m, 2H), 2.52 (t, *J* = 8 Hz, 2H), 2.57-2.60 (m, 2H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ -0.38, 13.93, 22.93, 30.82, 32.78, 33.84, 35.81, 139.24, 189.72, 214.35. IR (neat): 2977, 2951, 2930, 2910, 1692, 1588, 1261, 814 cm^{-1}. HRMS calcd for $C_{12}H_{22}OSi$ 210.1440, found 210.1439.

1,1-Bis(η^5-cyclopentadienyl)-2-(1-butynyl)-3-ethyl-zirconacyclopent-2-ene (4a). Yield 96% (by ^{1}H-NMR) . ^{1}H-NMR (C$_6$D$_6$, Me$_4$Si) δ 1.16 (t, *J* = 7 Hz, 3H), 1.28 (t, *J* = 7 Hz, 3H), 1.78 (t, *J* = 6 Hz, 2H), 2.33 (q, *J* = 7 Hz, 2H), 2.71 (q, *J* = 7 Hz, 2H), 3.66 (t, *J* = 6 Hz, 2H), 5.32 (s, 10H). ^{13}C-NMR (C$_6$D$_6$, Me$_4$Si) δ 12.92, 17.48, 21.29, 27.96, 28.66, 55.79, 88.19, 105.95, 144.20, 157.84, 166.90.

1,1-Bis(η^5-cyclopentadienyl)-2-(1-pentynyl)-3-propyl-zirconacyclopent-2-ene (4b). Yield 85% (by ^{1}H-NMR). ^{1}H-NMR (C$_6$D$_6$, Me$_4$Si) δ 0.93 (t, *J* = 7 Hz, 3H), 1.03 (t, *J* = 7 Hz, 3H), 1.6-1.7 (m, 4H), 1.81 (t, *J* = 6 Hz, 2H), 2.32 (t, *J* = 7 Hz, 2H), 2.70 (t, *J* = 7 Hz, 2H), 3.66 (m, 2H) , 5.33 (s, 10H). ^{13}C-NMR (C$_6$D$_6$, Me$_4$Si) δ 13.98, 14.12, 21.29, 21.87, 28.61, 34.32, 37.21, 55.97, 87.53, 105.98, 143.12, 155.13, 167.15.

1,1-Bis(η^5-cyclopentadienyl)-2-(2-trimethylsilyl-ethynyl)-3-trimethylsilyl-zirconacyclopent-2-ene (4c). Yield 70% (by ^{1}H-NMR). ^{1}H-NMR (C$_6$D$_6$, Me$_4$Si) δ 0.24 (s, 9H), 0.35 (s, 9H), 2.00 (t, *J* = 5.7 Hz, 2H), 3.82 (t, *J* = 5.7 Hz, 2H), 5.34 (s, 10H). ^{13}C-NMR (C$_6$D$_6$, Me$_4$Si) δ -1.42 1.26, 36.98, 58.02, 106.04, 107.43, 156.35, 162.30, 185.96.

1,1-Bis(η^5-cyclopentadienyl)-2-(2-phenyl-ethynyl)-3-phenyl-zirconacyclopent-2-ene (4d). Yield 70% (by ^{1}H-NMR). ^{1}H-NMR (C$_6$D$_6$, Me$_4$Si) δ 1.89 (t, *J* = 6 Hz, 2H), 4.13 (t, *J* = 6 Hz, 2H), 5.47 (s, 10H), 7.2-7.8 (m, 10H). ^{13}C-NMR (C_6D_6, Me_4Si) δ 31.83, 52.44, 93.73, 106.44, 127.27, 127.85, 128.32, 129.51, 129.77, 131. 40, 132.83, 136.90, 140.22, 161.67, 168.95.

3-Ethyl-3-octen-5-yne (5a). Yield 96%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 1.01 (t, *J* = 7 Hz, 3H), 1.02 (t, *J* = 7 Hz, 3H), 1.16 (t, *J* = 7 Hz, 3H), 2.07 (q, *J* = 7 Hz, 2H), 2.2-2.4 (m, 4H), 5.20 (s, 1H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 12.35, 12.54, 13.35, 25.75, 26.19, 28.39, 77.73, 93.85, 103.34, 157.41. HRMS calcd for $C_{10}H_{16}$ 136.1252, found 136.1274.

(Z)-4-Ethyl-4-decen-6-yne (5b). Yield 86%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, *J* = 7 Hz, 3H), 1.01 (t, *J* = 7 Hz, 6H), 1.4 - 1.6 (m, 4H), 2.07 (q, *J* = 7 Hz, 2H), 2.28 (t, *J* = 7 Hz, 2H), 2.31 (m, 2H), 5.26 (s, 1H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 12.36, 13.55, 14.09, 21.29, 21.65, 22.59, 28.79, 35.13, 78.63, 92.31, 104.11, 155.90. HRMS calcd for $C_{12}H_{20}$ 164.1565, found 164.1540.

(Z)-1,4-Bis(trimethylsilyl)-3-hexen-1-yne (5c). Yield 82%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.19 (s, 9H), 0.24 (s, 9H), 1.00 (t, *J* = 7 Hz, 3H), 2.19 (dq, *J* = 7, 2 Hz, 2H), 6.03 (br, 1H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ -1.00, -0.10, 14.20, 30.82, 97.62, 105.67, 118.14, 161.28. HRMS calcd for $C_{12}H_{24}Si_2$ 224.1417, found 224.1415.

(Z)-1,4-Diphenyl-3-hexen-1-yne (5d). Yield 87%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 1.06 (t, *J* = 8 Hz, 3H), 2.56 (dq, *J* = 8, 1 Hz, 2H), 5.79 (t, *J* = 1 Hz, 1H), 7.2 - 7.7 (m, 10H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.12, 31.95, 88.66, 91.34, 105.01, 127.90, 127.71, 127.78, 127.87, 128.05, 128.17, 131.25, 139.64, 155.02. HRMS calcd for $C_{18}H_{16}$ 232.1252, found 232.1249.

2-Butynyl-3-ethyl-cyclopenten-1-one (6a). GC yield 76%, isolated yield 35%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 1.16-1.24 (m, 6H), 2.40-2.48 (m, 4H), 2.58-2.67 (m, 4H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 11.37, 13.41, 13.88, 25.85, 29.07, 34.47, 70.09, 100.51, 125.53, 183.58, 206.57. HRMS calcd for $C_{11}H_{14}O$ 162.1044. found 162.1018.

2-Pentynyl-3-propyl-cyclopenten-1-one (6b). GC yield 88%, isolated yield 52%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.99 (t, *J* = 8 Hz, 3H) , 1.03 (t, *J* = 7 Hz, 3H), 1.57-1.68 (m, 4H), 2.39-2.48 (m, 4H), 2.55-2.63 (m, 4H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.50, 14.09, 20.63, 21.73, 22.16, 29.63, 34.56, 34.72, 71.14, 99.05, 126.40, 182.17, 206.47. HRMS calcd for $C_{13}H_{18}O$ 190.1357, found 190.1353.

2-Trimethylsilylethynyl-3-trimethylsilylcyclopenten-1-one (6c). Colorless crystals (from hexane), GC yield 64%, isolated yield 44%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.20 (s, 9H), 0.27 (s, 9H), 2.35-2.39 (m, 2H), 2.69-2.72 (m, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ -2.46, -0.30, 31.20, 34.41, 97.49, 103.60, 136.63, 186.09, 206.71. HRMS calcd for $C_{13}H_{22}OSi_2$ 250.1208. found 250.1214.

2-Phenylethynyl-3-phenylcyclopenten-1-one (6d). Yellow crystals (from hexane-methylene chloride), isolated yield 42%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 2.61-2.65 (m, 2H), 3.08-3.12 (m, 2H), 7.31-7.37 (m, 3H), 7.46-7.59 (m, 5H), 8.20-8.13 (m, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 28.61, 34.19, 82.22, 99.70, 128.89, 127.82, 128.21, 128.40, 128.61, 128.79, 131.40, 131.78, 134.59, 170.51, 205.60. HRMS calcd for $C_{19}H_{14}O$ 258.1044. found 258.1042.

Isolation of diene 10b: GC yield 81%, isolated yield 72%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J = 7 Hz, 6H), 1.03 (t, J = 7 Hz, 6H), 1.36-1.50 (m, 4H), 2.04-2.17 (m, 8H), 6.03 (s, 2H). ^{13}C- NMR ($CDCl_3$, Me_4Si) δ 13.01, 14.29, 22.02, 30.48, 32.71, 119.77, 142.30. HRMS calcd for $C_{14}H_{26}$ 194.2033. found 194.2027.

Isolation of 11a: GC yield 89%, isolated yield 67%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.94 (t, J = 8 Hz, 3H), 1.08 (t, J = 8 Hz, 3H), 1.13 (t, J = 8 Hz, 3H), 1.93 (q, J = 8 Hz, 2H), 2.18 (qd, J = 8 Hz, 2 Hz, 2H), 2.41 (q, J = 8 HZ, 2H), 2.40-2.43 (m, 2H), 2.54-2.60 (m, 2H), 5.51 (s, 1H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 11.39, 12.51, 12.69, 25.05, 28.43, 28.57, 34.61, 112.31, 138.11, 150.19, 176.28, 208.68.

Isolation of 11b: GC yield 80%, isolated yield 58%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.81 (t, J = 7 Hz, 3H), 0.94 (t, J = 7 Hz, 3H), 1.08 (t, J = 7 Hz, 3H), 1.30-1.43 (m, 2H), 1.50-1.64 (m, 2H), 1.85-1.91 (m, 2H), 2.12-2.21 (m, 2H), 2.32-2.44 (m, 4H), 2.54-2.56 (m, 2H), 5.54 (s, 1H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 12.68, 14.20, 20.89, 20.41, 28.90, 29.00, 33.88, 34.22, 34.61, 113.01, 138.91, 148.92, 175.08, 208.81. HRMS calcd for $C_{15}H_{24}O$ 220.1826. found 220.1848.

A Representative Procedure for the Preparation of α,α'-Bridged Cyclopentenones 15, 19, 23, 27: Basically, this procedure is the same as that described in Procedure 1. To a mixture of Cp_2ZrCl_2 (2.4 mmol,.0.702 g) and 2 equiv of EtMgBr (4.8 mmol, 1.0 M, 4.8 mL) in 10 ml of THF at -78°C was added alkynyl compound **12**, **16**, **20**, **24** or **29** (1.0 mmol). The following steps are exactly the same as in Procedure 1.

Observation of 13 : Yield 84% (by ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.90 (t, J = 7 Hz, 6H), 1.34 (tq, J = 7 Hz, 4H), 1.51-1.62 (m, 4H), 2.53-2.59 (m, 8H), 2.66-2.69 (m, 4H), 6.01 (s, 10H), 7.29 (s, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.85, 22.79, 29.11, 29.87, 31.55, 34.73, 129.00, 131.25, 140.02, 176.24, 207.92.

Observation of 17: Yield 81% (by ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.84 (t, J = 7 Hz, 6H), 1.24-1.32 (m, 4H), 1.37 (t, J = 7 Hz. 4H), 1.48-1.54 (m, 4H), 1.91 (t, J = 8 Hz, 4H), 2.64 (t, J = 7 Hz, 4H), 5.95 (s, 10H), 6.76 (s, 4H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 14.31, 23.11, 30.86, 31.22, 35.89, 41.32, 111.63, 125.74, 144.57, 144.66, 185.38.

Observation of 21: Yield 76% (by ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.94 (t, J = 7 Hz, 6H), 1.34 (t, J = 7 Hz, 4H), 1.38-1.46 (m, 4H), 1.50-1.58 (m, 4H), 2.25 (t, J = 8 Hz, 4H), 2.67 (t, J = 7 Hz, 4H), 6.03 (s, 10H), 6.10 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.43, 23.38, 31.59, 32.24, 36.14, 40.92, 111.88, 119.37, 147.72, 149.13, 172.99.

Isolation of 15: Yield 73%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.90 (J = 7 Hz, 6H), 1.34 (qt, J = 7 Hz, 4H), 1.51-1.62 (m, 4H), 2.53-2.59 (m, 8H), 2.66-2.69 (m, 4H), 7.29 (s, 4H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 13.85, 22.79, 29.11, 19.87, 31.55, 34.73, 129.00, 131.25, 140.02, 176.24, 207.92. HRMS calcd for $C_{24}H_{30}O_2$ 350.2246, found 350.2246.

Isolation of 19: Yield 80%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.89 (t, *J* = 7 Hz, 6H), 1.35 (qt, *J* = 7 Hz, 4H), 1.50-1.61 (m, 4H), 2.51-2.55 (m, 4H), 2.58 (t, *J* = 8 Hz, 4H), 2.65-2.69 (m, 4H), 7.14-7.15 (m, 1H), 7.19-7.29 (m, 2H), 7.41-7.46 (m, 1H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 13.84, 22.77, 29.13, 29.85, 31.54, 34.72, 128.16, 128.34, 130.06, 131.89, 140.14, 176.12, 207.80. HRMS calcd for $C_{24}H_{30}O_2$ 350.2246, found 350.2249.

Isolation of 23: Yield 86%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.97 (t, *J* = 7 Hz, 6H), 1.45 (qt, *J* = 7 Hz, 4H), 1.58-1.69 (m, 4H), 2.44-2.56 (m, 4H), 2.67-2.71 (m, 4H), 2.76 (t, *J* = 8 Hz, 4H), 7.43 (s, 2H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 13.89, 23.02, 29.56, 29.87, 32.43, 34.56, 126.86, 132.67, 132.88, 174.64, 206.74.

Isolation of 14: Yield 69% . ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.89 (t, *J* = 7 Hz, 6H), 1.10 (t, *J* = 7 Hz, 6H), 1.32 (qt, *J* = 7 Hz, 4H), 1.41-1.52 (m, 4H), 2.18 (q, *J* = 7 Hz, 4H), 2.26 (t, *J* = 8 Hz, 4H), 6.22 (s, 2H), 7.15 (s, 4H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 12.92, 13.96, 22.95, 30.17, 30.60, 30.66, 123.57, 128.34, 136.26, 145.08. HRMS calcd for $C_{22}H_{34}$ 298.2661, found 298.2664.

Isolation of 18: Yield 62%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.87 (t, *J* = 7 Hz, 6H), 1.10 (t, *J* = 7 Hz, 6H), 1.30 (qt, *J* = 7 Hz, 4H), 1.39-1.50 (m, 4H), 2.14-2.27 (m, 8H), 6.24 (s, 2H), 7.01-7.04 (m, 3H), 7.19-7.26 (m, 1H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 12.90, 13.96, 22.86, 29.94, 30.94, 30.55, 123.84, 126.13, 127.69, 129.16, 138.49, 145.10. HRMS calcd for $C_{22}H_{34}$ 298.2661, found 298.2654.

Isolation of 22: Yield 76%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 0.95 (t, *J* = 7 Hz, 6H), 1.09 (t, *J* = 8 Hz, 6H), 1.36-1.56 (m, 8H), 2.18 (q, *J* = 7 Hz, 4H), 2.40 (t, *J* = 8 Hz, 4H), 6.29 (s, 2H), 6.74 (s, 2H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 12.94, 14.07, 23.25, 30.35, 31.03, 32.13, 117.23, 125.91, 139.85, 143.99. HRMS calcd for $C_{20}H_{32}S$ 304.2225, found 304.2230.

Observation 25b: NMR yield 94%. ^{1}H-NMR (C$_6$D$_6$, Me$_4$Si) δ 1.20-1.35 (m, 8H), 2.50-2.65 (m, 8H), 6.04 (s, 20H), 6.75-7.30 (m, 10H). ^{13}C-NMR (C$_6$D$_6$, Me$_4$Si) δ 29.15, 31.00, 36.39, 41.67, 111.89, 127.69, 128.05, 128.41, 144.54, 150.46, 184.49.

Isolation of 26b: GC yield 95%, isolated yield 70%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ 1.10 (t, *J* = 8 Hz, 6H), 1.43-1.46 (m, 4H), 2.15-2.25 (m, 8H), 6.25 (s, 2H), 7.15-7.30 (m, 10H). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ 12.85, 28.50, 29.94, 30.71, 123.79, 125.80, 128.05, 128.62, 138.70, 145.05.

Isolation of 27: A mixture of 3 isomers in 5:3:1. Isolated yield 64%. ^{1}H-NMR (CDCl$_3$, Me$_4$Si) δ (for the mixture) 1.33-1.6 (m), 1.67-1.70 (m), 2.05 (s), 2.07 (s), 2.17- 2.30 (m), 2.35-2.50 (m). ^{13}C-NMR (CDCl$_3$, Me$_4$Si) δ for the major isomer: 8.04, 17.29, 22.75, 22.82, 27.12, 28.28, 30.98, 31.05, 34.10, 34.30, 136.12, 140.07, 170.71, 173.83, 209.75, 210.35; for the middle isomer: 17.29, 22.75, 29.92, 31.54, 34.30, 140.32, 170.71, 209.86; for the minor isomer: 8.07, 22.82, 28.19, 30.95, 34.12, 136.39, 172.95, 210.16. HRMS calcd for $C_{16}H_{22}O_2$ 246.1619, found 246.1609.

Isolation of 28[14]: GC yield 90%, isolated yield 76%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 1.62-1.66 (m, 4H), 2.60-2.64 (m, 4H), 6.63 (s, 2H), 7.21-7.35 (m, 10H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 26.29, 29.97, 124.15, 126.34, 128.07, 129.47, 138.00, 144.47.

Isolation of 31a[15]: GC yield 95%, isolated yield 62%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 0.11 (s, 18H), 1.60-1.65 (m, 4H), 2.33-2.36 (m, 4H), 5.47 (s, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 0.22, 26.74, 34.70, 122.03, 161.66.

Isolation of 31b: GC yield 87%, isolated yield 71%. ^{1}H-NMR ($CDCl_3$, Me_4Si) δ 1.11 (s, 18H), 1.58-1.61 (m, 4H), 2.32-2.38 (m, 4H), 5.29 (s, 2H). ^{13}C-NMR ($CDCl_3$, Me_4Si) δ 26.77, 30.31, 31.39, 31.73, 132.85, 143.66. HRMS calcd for $C_{16}H_{28}$ 220.2190, found 220.2194.

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