Halogen-Dependent Coupling Reaction of Alkynes with (Z)-3-Halopropenoates Catalyzed by Nickel

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Abstract: Ni-catalyzed coupling reaction of alkynes with (Z)-3-halopropenoates depended on the halogen of halopropenoates. The reaction with (Z)-3-bromopropenoate afforded cyclopentadienes and the reaction with (Z)-3-iodopropenoates gave pyrones. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

The formation of useful compounds from commercially available, simple starting materials is an important task of organic chemistry. One such example is cyclopentadienes that have wide application as ligands in transition metal chemistry.[1] Recently, we reported that the coupling reaction of two alkynes and (Z)-3-iodopropenoate through zirconacyclopentadiene intermediates afforded pentasubstituted cyclopentadienes.[2] A critical limitation of our procedure is the use of a stoichiometric amount of zirconocene dichloride for each molecule of the formed cyclopentadiene. In order to develop a more economical procedure we investigated nickel-catalyzed[3] coupling reaction of alkynes and halopropenoates, giving pentasubstituted cyclopentadiene derivatives. During the course of our study, we found that the outcome of this nickel-catalyzed coupling reaction substantially depends on the halogen of halopropenoates. In this paper we report halogen-dependent catalytic reaction of alkynes with halopropenoates (Scheme 1), where (Z)-3-bromopropenoate afforded cyclopentadienes and (Z)-3-iodopropenoate gave pyrones.

Scheme 1
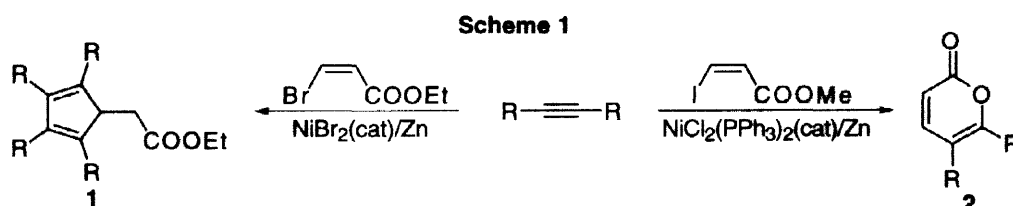
Results and discussion

Formation of cyclopentadienes. The most efficient method for the preparation of cyclopentadienes would be a catalytic coupling of alkynes. Trimerization of alkynes to cyclopentadienes in the presence of Pd[4] and Ni[5] catalysts is well known. However, this process is hampered by the fact that the trimerization proceeds only with internal alkynes to give hexasubstituted cyclopentadienes, whereas it is desirable to gain access to penta- or less substituted ones.

On the other hand, we found here that the reaction of (Z)-3-bromopropenoate with alkynes in the presence of cat.NiBr$_2$/Zn at 50 °C afforded a convenient procedure for the preparation of pentasubstituted cyclopentadienes. Cyclopentadienes were obtained usually as a mixture of three isomers of **1** in 1:1:1 ratio (Scheme 2). At low conversions (up to 20-30%) the symmetrical isomer **1** was the only product. This observation indicates that the isomerization was caused by the Ni^0 species after the coupling reaction at prolonged reaction time. It is noteworthy that the isomerization of the double bond did not proceed outside of the ring and the formation of exocyclic olefins was not detected. The nature of the solvent was very important as well. The reaction gave satisfactory yields only in MeCN. When other solvents such as THF or DMF were used, the reaction either did not proceed (THF) or low yields of products **1** were obtained (<20% for 3-hexyne in DMF). The results of the reaction of different alkynes with ethyl (Z)-3-bromopropenoate are summarized in Table 1.
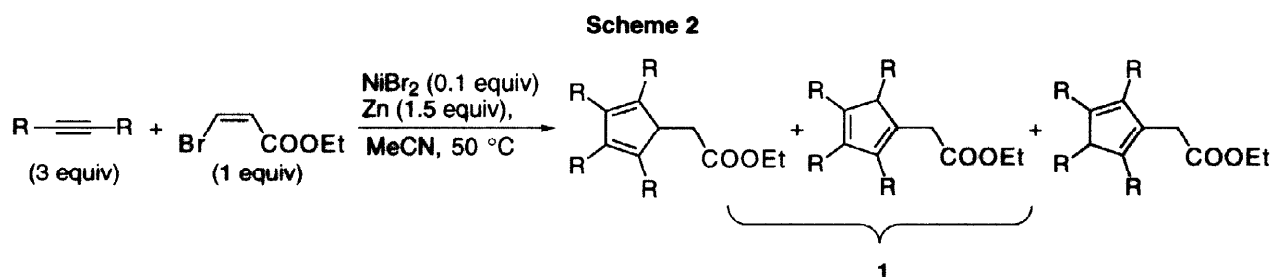
Scheme 2

Table 1. Formation of pentasubstituted cyclopentadienes.

Entry	Alkyne	t (h)	Product[a]		Yield (%)[b]
1	Et—≡—Et	24		(1a)	99 (74)
2	Pr—≡—Pr	24		(1b)	90 (56)
3	Ph—≡—Ph	24		(1c)	- (44)
4	Ph—≡—Me	24		(1d)	86 (55)[c]
5		48		(1e)	- (35)

[a] Mixture of positional isomers. Only a symmetrical isomer is shown. [b] GC combined yields of positional isomers of double bonds. Isolated yields are given in parentheses. [c] Mixture of regioisoimers

The reaction proceeded smoothly with alkyl substituted alkynes (entries 1 and 2) to give high yields of the corresponding cyclopentadienes **1a** and **1b**. Diphenylacetylene (entry 3) gave a relatively low yield of cyclopentadiene **1c**. On the other hand, 1-phenyl-1-propyne (entry 4) gave cyclopentadiene derivatives **1d** in a reasonable yield; however, in this case a complex mixture of both the double bond isomers and regioisomers was formed. The reaction of 3,9-dodecadiyne (entry 5) gave the corresponding tetrahydroindene derivative **1e** in 35% yield.

As far as the nickel catalyst was concerned, several nickel salts and complexes were tested and the results are summarized in Table 2. $NiBr_2$ gave the highest yield of cyclopentadienes **1a**. Nickel phosphine complexes could be also used, but the yields of **1a** were substantially lower. Surprisingly, also $NiCl_2 \cdot 6H_2O$ could be used as a catalyst, but only a moderate yield of cyclopentadiene **1a** was obtained.

**Table 2.** Ni-complex catalyzed of formation of **1a**.

Entry	Catalyst	t (h)	Yield (%)[a]
1	$NiBr_2$	24	99
2	$NiCl_2(PPh_3)_2$	24	67
3	$NiCl_2(dppb)$[b]	24	68
4	$NiCl_2 \cdot 6H_2O$	48	53

[a] GC yields. [b] Dppb - bis(diphenylphosphino)butane.

Formation of 2-pyrones. In order to improve the cyclopentadiene formation described above, we used methyl (Z)-3-iodopropenoate instead of ethyl (Z)-3-bromopropenoate. Unexpectedly, we obtained 2-pyranone as shown in Scheme 3. In comparison with the cyclopentadiene formation, the preparation of pyrones has been studied more extensively. Thus, pyrones can be prepared, for example, by Ni-catalyzed co-cycloaddition of alkynes with carbon dioxide,[5b-c,6] by Rh-catalyzed carbonylation of cyclopropenylester and ketones,[7] by Pd-catalyzed carbonylative cross-coupling of halocyclobutenones with vinylstannanes,[9] and Pd-catalyzed annulation of 3-halo or 3-alkoxypropenoates with alkynes.[9] All these methods were used to prepare highly substituted pyrones.

For our Ni-catalyzed coupling of (Z)-3-iodopropenoate with alkynes which gave 5,6-substituted pyrones, the following conditions were important: i) to use Ni-phosphine complexes as the catalyst, ii) to conduct the reaction at approximately 20 °C, and iii) to use methyl 3-iodopropenoate (Scheme 3).
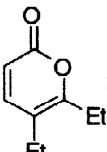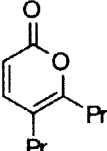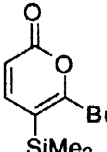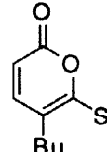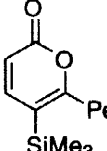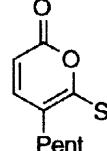
Scheme 3
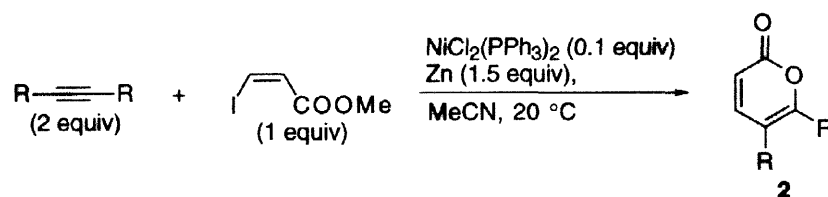
Generally, the formation of pyrones proceeded surprisingly fast and the reaction was usually finished within 1 hour. In comparison with the cyclopentadiene formation, the formation of pyrones was limited only to internal alkynes substituted with alkyl and alkyl-trialkylsilyl groups. The results are summarized in Table 3. The reaction with dialkyl substituted alkynes (entry 1 and 2) proceeded uneventfully and gave good yields of the corresponding pyrones **2a** and **2b**. The best catalyst was $NiCl_2(PPh_3)_2$; other Ni-phosphine complexes catalyzed the reaction as well but the yields of products were considerably lower. Suprisingly, a combination of

$NiCl_2\cdot6H_2O$ and $P(o\text{-tolyl})_3$ as the catalyst gave 70% yield of **2a**. The reaction with trimethylsilyl substituted alkynes (entry 3 and 4) afforded the corresponding pyrones as a mixture of positional regioisomers **2c** and **2d**, and **2e** and **2f**. Moreover, to achieve good yields it was necessary to add zinc chloride[10] (0.2 equiv.) into the reaction mixture. In the absence of zinc chloride the yields were always lower than 50%. Interestingly, in the presence of zinc chloride the ratio of regioisomers (**2c:2d**; **2e:2f**) was 3:1, whereas in its absence the ratio was 5.9:1. It is noteworthy that the regioselectivity in the Ni-catalyzed reaction with trimethylsilylsubstituted alkynes was opposite to that reported for the Pd-catalyzed reaction.[9] It is also important to note that the reactions carried out with ethyl (Z)-3-iodopropenoate gave considerably lower yields of pyrones (≤35%). Formation of a homo-coupled prodcut of iodopropenoate was not observed.

Table 3. Formation of pyrones.

Entry	Alkyne	Product	Yield (%)[a]
1	Et——≡——Et	**2a**	71 (50)
2	Pr——≡——Pr	**2b**	65 (53)
3	Bu——≡——SiMe₃[b]	**2c** **2d**	59 (50)[c]
4	Pent——≡——SiMe₃[b]	**2e** **2f**	60 (52)[c]

[a] NMR yields. Isolated yields are given in parentheses. [b] 0.2 equiv. of $ZnCl_2$ were added to the reaction mixture. [c] **2c:2d** and **2e:2f** =3:1.

To assign the proper structure of the regioisomers, the major product **2c** was desilylated with tetrabutylammonium fluoride in THF to give compound **3a** (71%) whose spectral characteristics were in agreement with the published data.[11a] The same procedure was also carried out with compound **2e** which, after desilylation under the identical conditions, afforded compound **3b** in 90% yield (Scheme 4). 6-Pentylpyranone (**3b**) is found in a number of plants[12] and also functions as an ant pheromone.[13]

Scheme 4

Bu₄NF, THF

R = Bu (**2c**), Pent (**2e**)   R = Bu (**3a**), Pent (**3b**)
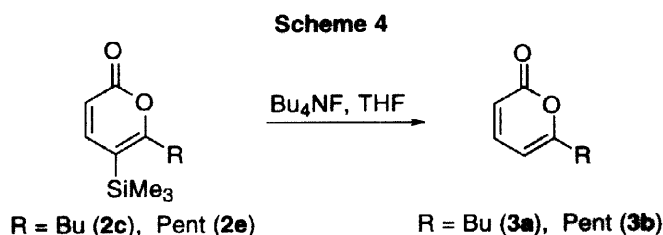
Reaction mechanism. It is evident from the experimental results that these two classes of compounds, cyclopentadienes and pyrones, must be formed by two distinct reaction mechanisms. We assume that this is attributed to the different reaction rates of bromo- and iodopropenoate with Ni^0 formed by the reduction of Ni^{II} by metallic zinc. On the basis of the above-mentioned results we propose the following two reaction mechanisms for the formation of cyclopentadienes (Scheme 5) and pyrones (Scheme 6).

Scheme 5
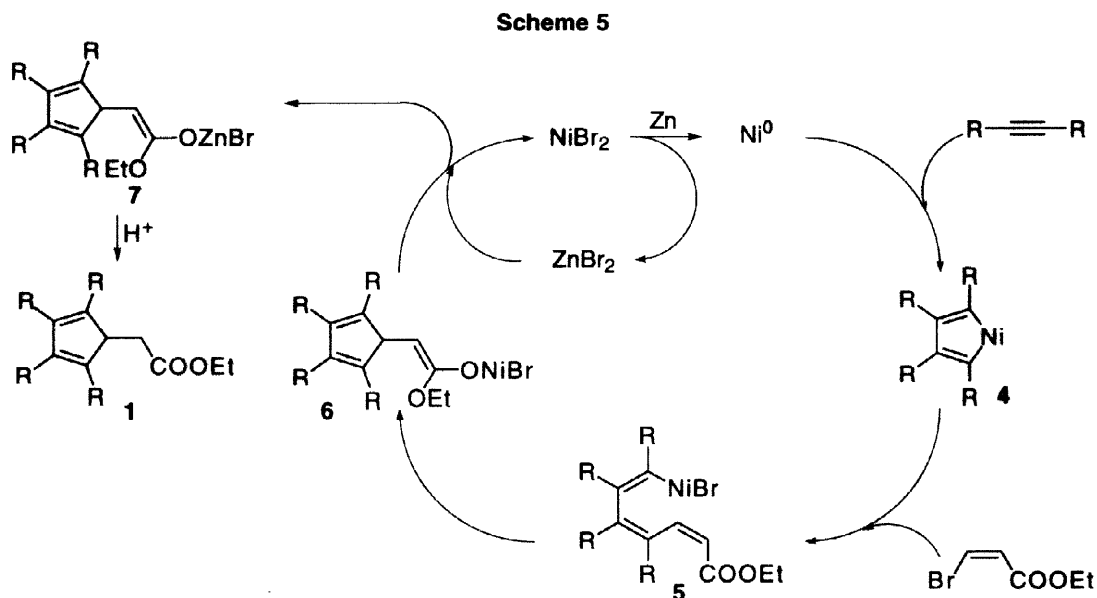
The formation of cyclopentadienes is initiated by the reduction of nickel bromide with zinc to a Ni^0 species that reacts with two alkynes to form nickelacyclopentadiene **4**. Then one Ni-C bond of nickelacyclopentadiene reacts by cross-coupling with ethyl (Z)-3-bromopropenoate to form intermediate **5**. Intermediate **5** then undergoes intramolecular Michael reaction to afford nickel enolate **6** that undergoes metal exchange with zinc bromide to zinc enolate **7** and nickel bromide that enters the catalytic cycle again. Upon quenching the enolate **7** gives cyclopentadiene derivative **1**.
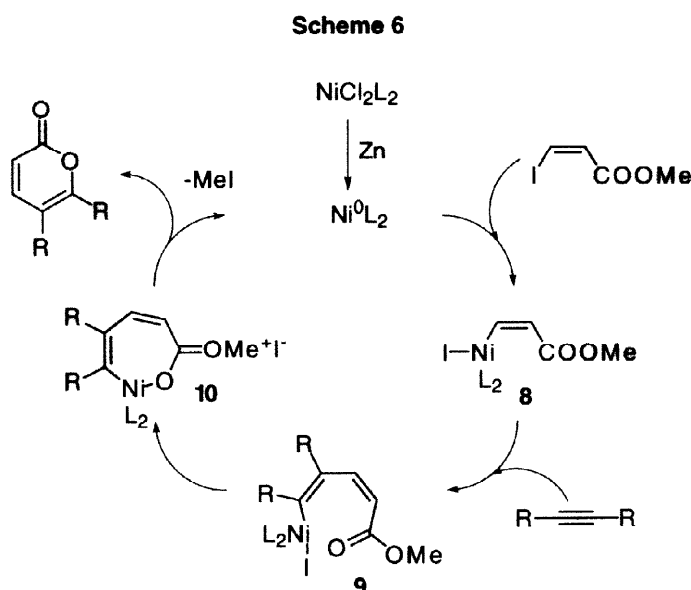
Scheme 6

We assume that the reaction mechanism of the Ni-catalyzed formation of pyrones is similar to that of the Pd-catalyzed reaction (Scheme 6).[9] In the first step is formed the Ni^0 species by reduction of $NiCl_2(PPh_3)_2$ with zinc powder. However, the greater reactivity of the C-I bond of iodopropenoate in comparison with the C-Br bond of bromopropenoate enables it to be oxidatively added to Ni^0 to form vinyl nickel compound **8**. Vinylnickel **8** compound then adds to an alkyne forming **9**. The nickel in **9** intramolecularly attacks the carbonyl group to form an oxonium salt **10**. Finally, the reductive elimination affords an oxonium salt, which decomposes to alkyl halide and pyrone, and Ni^0 which enters the catalytic cycle again.

This reaction mechanism suggests that only a stoichiometric amount of Zn should be sufficient for the reduction of nickel chloride; however, experimental data showed that for the succesful course of the reaction it is necessary to use an excess of Zn. This indicates that the last step of the whole process might be more complicated and it is reasonable to assume that Ni^0 reacts with an alkyl halide formed from the oxonium salt to form the Ni^{II} species that has to be reduced by zinc.

An alternative reaction mechanism for the formation of cyclopentadienes that involves oxidative addition of ethyl (Z)-3-bromopropenoate to Ni^0 and insertion of alkynes to the Ni-C bond should be considered.[3] However, the use of ethyl (Z)-3-iodopropenoate resulted in low yields of cyclopentadienes (~10%) and the use of $PdCl_2$ instead $NiBr_2$ did not give any cyclopentadiene product. This indicates that in this instance the alternative mechanism is not likely.

Conclusion

Simple variation of a halide substituent (Br or I) in the starting material and the reaction conditions profoundly changes the reaction pattern of the Ni-catalyzed reaction of (Z)-3-halopropenoate with alkynes to give selectively cyclopentadienes or pyrones. The former reaction is the first example of the catalytic formation of pentasusbtituted cyclopentadienes in one step from alkynes. The latter reaction is a new, convenient and shorter method for the preparation of 5,6-disubstituted 2-pyrones from alkynes, compared with the methods used so far.[11] This method was applied to the synthesis of naturally occurring 6-pentyl-2-pyrone in a two-step synthesis from the starting materials.

Experimental Part

All reactions were carried out under nitrogen. Tetrahydrofuran was dried over sodium and benzophenone. 3-Hexyne, 4-octyne were purchased from Aldrich Inc. 3,9-Dodecadiyne, 1-phenyl-1-propyne, and ethyl propynoate were purchased from TCI Co.Ltd. Zinc powder was obtained from Kato Chemical Co. Ltd. and was used without further treatment. Ethyl (Z)-3-bromopropenoate, ethyl (Z)-3-iodopropenoate, methyl (Z)-3-iodopropenoate,[14] and $NiX_2(L)_2$ complexes[15] were prepared according to the previously published procedure.

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded for $CDCl_3$ or C_6D_6 (containing 1% TMS) solutions at 25 °C on Bruker ARX NMR spectrometer. IR spectra were recorded on Shimadzu FTIR-4200 spectrometer. GC analysis was performed on Shimadzu GC-14A equipped with a fused silica capillary column Shimadzu CBP1-M25-O25 and Shimadzu C-R6A-Chromatopac integrator. Mesitylene was used as an internal standard.

Typical experimental procedure: Formation of cyclopentadienes 1a. A stirred mixture of $NiBr_2$ (22 mg, 0.1 mmol), ethyl (Z)-3-bromopropenoate (179 mg, 1 mmol), 3-hexyne (246 mg, 3 mmol), and Zn powder (98 mg, 1.5 mmol) in acetonitrile (5 mL) was heated at 50 °C for 24 h. The reaction mixture was

quenched with 3 N HCl and extracted with hexane. Combined organic fractions were washed with sat. solution of $NaHCO_3$, dried (Na_2SO_4), and concentrated *in vacuo*. Column chromatography on silica gel (19/1 hexane/Et_2O) afforded 195 mg (74%) of the 1:1:1 mixture of three isomers **1a** as a colorless liquid. In its ^{13}C NMR spectrum, the COOR group of the mixture clearly showed three characteristic signals at 172.74 ppm assigned for the symmetrical isomer, and at 171.91 and 172.04 ppm assigned for unsymmetrical isomers. The other carbons such as CH of the cyclopentadiene ring and CH_2COOR group also showed three peaks each at 47.37 (symmetrical), 51.07 and 52.04 ppm (unsymmetrical), and 34.24 (symmetrical), 31.69 and 32.58 ppm (unsymmetrical), respectively, with 1:1:1 intensities. Ethyl 2-(2',3',4',5'-tetraethyl-1'-cyclopentadienyl)ethanoate: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.00 (t, J = 7.6 Hz, 6H), 1.03 (t, J = 7.5 Hz, 6H), 1.22 (t, J = 7.1 Hz, 3H), 2.07-2.16 (m, 2H), 2.21 (q, J = 7.5 Hz, 4H), 2.38 (d, J = 6.4 Hz, 2H), 2.36-2.45 (m, 2H), 3.26 (t, J = 6.4 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.11 (2C), 15.36 (2C), 18.54 (2C), 19.35 (2C), 34.24, 47.37, 60.13, 140.88 (2C), 142.34 (2C), 172.74; IR (neat) v 1737 cm^{-1}; HRMS calcd. for $C_{17}H_{28}O_2$ 264.2087; found 264.2084.

Formation of cyclopentadienes 1b. Column chromatography on silica gel (19/1 hexane/Et_2O) afforded 195 mg (74%) of the 1:1:1 mixture of three isomers **1b** as a colorless liquid. Ethyl 2-(1',2',3',4'-tetra-*n*-propyl-5'-cyclopentadienyl)ethanoate: ^1H NMR (C_6D_6, Me_4Si) δ 0.90 (t, J = 7.3 Hz, 6H), 0.92 (t, J = 7.3 Hz, 6H), 1.02 (t, J = 7.2 Hz, 3H), 1.3-1.6 (m, 8H), 2.15-2.25 (m, 2H), 2.35-2.45 (m, 6H), 2.35 (d, J = 6.3 Hz, 2H), 3.37 (t, J = 6.3 Hz, 1H), 3.97 (q, J = 7.2 Hz, 2H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.29, 14.43 (2C), 14.56 (2C), 24.04 (2C), 24.24 (2C), 28.23 (2C), 29.12 (2C), 34.82, 48.43, 60.07, 140.20 (2C), 141.92 (2C), 172.04; IR (neat) v 1738 cm^{-1}; HRMS calcd. for $C_{21}H_{36}O_2$ 320.2713; found 320.2703.

Formation of cyclopentadienes 1c. Column chromatography on silica gel (9/1 hexane/Et_2O) gave 320 mg (70%) of 1:1:1 mixture of three isomers **1c** as a white solid. Ethyl 2-(2',3',4',5'-tetraphenyl-1'-cyclopentadienyl)ethanoate: ^1H NMR ($CDCl_3$, Me_4Si,) δ 1.01 (t, J = 7.1 Hz, 3H), 2.55 (d, J = 6.1 Hz, 2H), 3.76 (q, J = 7.2 Hz, 2H), 4.60 (t, J = 6.2 Hz, 1H), 7.01-7.23 (m, 20H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.95, 35.26, 51.80, 60.23, 126.58 (2C), 126.61 (2C), 127.64 (4C), 127.97 (4C), 129.28 (4C), 130.11 (4C), 135.54 (2C), 136.03 (2C), 143.71 (2C), 145.01 (2C), 171.72; IR (neat) v 1738 cm^{-1}; Anal. Calcd. for $C_{33}H_{28}O_2$: C, 86.81; H, 6.18. Found C: 86.90; H, 6.33.

Formation of cyclopentadienes 1d. Column chromatography on silica gel (9/1 hexane/Et_2O) afforded 320 mg (70%) of a mixture positional isomers and regioisomers **1d** as a white solid. Ethyl 2-(2',4'-diphenyl-3',5'-dimethyl-1'-cyclopentadienyl)ethanoate: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.16 (t, J = 7.1 Hz, 3H), 1.91 (d, J = 1.3 Hz, 3H), 1.93 (s, 3H), 2.31 (dd, J = 15, 7.9 Hz, 1H), 2.50 (dd, J = 15, 5.3 Hz, 1H), 3.85-3.91 (m, 1H), 3.92-4.08 (m, 2H), 7.1-7.4 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.97, 13.61, 14.13, 34.87, 51.93, 60.31, 126.03, 126.68, 128.06, 128.20, 128.80, 129.93, 136.35, 136.42, 137.46, 141.20, 141.42, 143.16, 172.54; HRMS calcd. for $C_{23}H_{24}O_2$ 332.1775; found 332.1773.

Formation of cyclopentadienes 1e. Column chromatography on silica gel (9/1 hexane/Et_2O) afforded 92 mg (35%) of a mixture positional isomers **1e** as a colorless liquid. Ethyl 2-(1',3'-diethyl-1*H*-4',5',6',7'-tetrahydroinden-2'-yl)ethanoate: ^1H NMR (C_6D_6, Me_4Si) δ 1.00 (t, J = 7.1 Hz, 3H), 1.04 (t, J = 7.3 Hz, 6H), 1.45-1.50 (m, 4H), 2.1-2.2 (m, 2 H), 2.25-2.30 (m, 4H), 2.34 (d, J = 6.6 Hz, 2H), 2.35-2.40 (m, 2H), 3.40-3.45 (m, 1H), 3.99 (q, J = 7.1 Hz, 2H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.30, 14.76 (2C), 19.73 (2C), 24.14

(2C), 24.20 (2C), 34.28, 48.58, 60.07, 135.89 (2C), 141.23 (2C), 172.36; HRMS calcd. for $C_{17}H_{26}O_2$ 262.1931; found 262.1927.

Formation of pyrones. Typical experimental procedure: A mixture of methyl (Z)-3-iodopropenoate (212 mg, 1 mmol), alkyne (2 mmol), $NiCl_2(PPh_3)_2$ (64 mg, 0.1 mmol), and Zn powder (98 mg, 1.5 mmol) in MeCN (5 mL) was stirred at 20 °C for 1 h under nitrogen. The reaction mixture was quenched with 3N HCl and extracted with hexane. Combined organic fractions were dried ($MgSO_4$) and concentrated *in vacuo*. Column chromatography on silica gel gave the desired products.

2H-5,6-Diethylpyranone (2a). Column chromatography on silica gel (3/1 hexane/EtOAc) provided 76 mg (50%) of the title compound as a colorless liquid: R_f(3/1 hexane/EtOAc) = 0.4; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.12 (t, J = 7.6 Hz, 3H), 1.24 (t, J = 7.5 Hz, 3H), 2.34 (q, J = 7.6 Hz, 2H), 2.53 (q, J = 7.5 Hz, 2H), 6.16 (d, J = 9.4 Hz, 1H), 7.21 (d, J = 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.07, 14.68, 22.37, 24.02, 113.46, 115.90, 146.76, 162.50, 162.90; IR (neat) 3024, 1726, 1639, 1554, 1101, 1057, 825 cm^{-1}; HRMS calcd for $C_9H_{12}O_2$ 152.0837; found 152.0840.

2H-5,6-Di-n-propylpyranone (2b). Column chromatography on silica gel (4/1 hexane/EtOAc) afforded 95 mg (53%) of the title compound as a colorless liquid: R_f(4/1 hexane/EtOAc) = 0.5; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.5 Hz, 3H), 1.45-1.57 (m, 2H), 1.65-1.77 (m, 2H), 2.28 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.5 Hz, 2H), 6.14 (d, J = 9.4 Hz, 1H), 7.18 (d, J = 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.47, 13.61, 20.88, 23.19, 31.03, 32.47, 113.22, 114.98, 146.95, 161.71, 162.85; IR (neat) 2963, 1728, 1637, 1553, 1107, 1068, 916, 828 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_2$ 180.1149; found 180.1146.

2H-5-(Trimethylsilyl)-6-butylpyranone (2c) and 2H-6-(trimethylsilyl)-5-butylpyranone (2d). Column chromatography on silica gel (85/15 hexane/EtOAc) gave 90 mg (40%) of **2c** as a yellow liquid and 24 mg (10%) of **2d** as a colorless liquid. **2c**: R_f(85/15 hexane/EtOAc) = 0.56; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.24 (s, 9H), 0.90 (t, J = 7.3 Hz, 3H), 1.30-1.42 (m, 2H), 1.60-1.70 (m, 2H), 2.45-2.53 (m, 2H), 6.11 (d, J = 9.4 Hz, 1H), 7.24 (d, J = 9.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -0.36 (3C), 13.75, 22.54, 30.17, 34.60, 108.89, 112.69, 148.27, 162.77, 170.93; IR (neat) 2959, 1736, 1599, 1531, 1253, 1149, 1100, 842 cm^{-1}; HRMS calcd for $C_{12}H_{20}O_2Si$ 224.0123; found 224.1234. **2d**: R_f(85/15 hexane/EtOAc) = 0.47; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.35 (s, 9H), 0.95 (t, J = 7.2 Hz, 3H), 1.30-1.50 (m, 4H), 2.30-2.40 (m, 2H), 6.25 (d, J = 9.6 Hz, 1H), 7.14 (d, J = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.13 (3C), 13.90, 22.50, 29.85, 33.11, 116.39, 128.00, 144.74, 163.54, 167.91.

2H-5-(Trimethylsilyl)-6-pentylpyranone (2e) and 2H-6-(trimethylsilyl)-5-pentylpyranone (2f). Column chromatography on silica gel (85/15 hexane/EtOAc) provided 95 mg (40%) of **2e** as a yellow liquid and 28 mg (12%) of **2f** as a colorless liquid. **2e**: R_f(85/15 hexane/EtOAc) = 0.56; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.22. (s, 9H), 0.85 (t, J = 7.0 Hz, 3H), 1.20-1.35 (m, 4H), 1.60-1.70 (m, 2H), 2.43-2.50 (m, 2H), 6.10 (d, J = 9.3 Hz, 1H), 7.23 (d, J = 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -0.39 (3C), 13.82, 22.31, 27.80, 31.56, 34.83, 108.86, 112.67, 148.23, 162.71, 170.92; IR (neat) 2959, 1740, 1599, 1532, 1148, 1101, 843 cm^{-1}; HRMS calcd for $C_{13}H_{22}O_2Si$ 238.1388; found 238.1382. **2f**: R_f(85/15 hexane/EtOAc) = 0.47; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.30 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H), 1.25-1.35 (m, 4H); 1.40-1.50 (m,

2H), 2.08-2.12 (m, 2H), 6.22 (d, J = 9.6 Hz, 1H), 7.10 (d, J = 9.6 Hz, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ -1.16 (3C), 13.89, 22.43, 30.07, 30.64, 31.53, 116.35, 128.00, 144.70, 163.49, 167.87.

2H-6-Butylpyranone (3a). To a solution of 2H-5-(trimethylsilyl)-6-butylpyranone **2c** (56 mg, 0.25 mmol) in THF (2 mL) was added 1M solution of TBAF (1 mL, 1 mmol) at 0 °C. After 1 h the reaction mixture was diluted with water (10 mL) and extracted with Et$_2$O. Combined organic fractions were dried (MgSO$_4$) and concentrated *in vacuo*. Column chromatography on silica gel (3/1 hexane/Et$_2$O) afforded 27 mg (71%) of the title compound as a colorless liquid: R$_f$(3/1 hexane/Et$_2$O) = 0.5; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.93 (t, J = 7.3 Hz, 3H), 1.30-1.40 (m, 2H), 1.60-1.70 (m, 2H), 2.49 (t, J = 7.6 Hz, 2H), 5.98 (d, J = 6.6 Hz, 1H), 6.15 d, J = 9.3 Hz, 1H), 7.26 (dd, J = 9.3, 6.6 Hz, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 13.63, 22.02, 28.88, 33.46, 102.54, 113.01, 143.68, 162.88, 166.74; IR (neat) 2932, 1730, 1635, 1560, 1080, 802 cm^{-1}. The spectral data were in agreement with the published data.[11a]

2H-6-Pentylpyranone (3b). To a solution of 2H-5-(trimethylsilyl)-6-pentylpyranone **2d** (119 mg, 0.5 mmol) in THF (3 mL) was added 1M solution of TBAF (2 mL, 2 mmol) at 0 °C. After 1 h the reaction mixture was diluted with water (10 mL) and extracted with Et$_2$O. Combined organic fractions were dried (MgSO$_4$) and concentrated *in vacuo*. Column chromatography on silica gel (3/1 hexane/Et$_2$O) afforded 75 mg (90%) of the title compound as a colorless liquid: R$_f$(3/1 hexane/Et$_2$O) = 0.24; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 0.90 (t, J = 7.0 Hz, 3H), 1.30-1.40 (m, 4H), 1.6-1.7 (m, 2H), 2.48 (t, J = 7.6 Hz, 2H), 5.98 (d, J = 6.6 Hz, 1H), 6.15 (d, J = 9.3 Hz, 1H), 7.26 (dd, J = 9.3, 6.6 Hz, 1H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 13.83, 22.25, 26.52, 31.07, 33.75, 102.55, 113.02, 143.68, 162.90, 166.76; IR (neat) 2967, 1742, 1636, 1561, 1084, 800 cm^{-1}. The spectral data were in agreement with the published data.[12c]

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