Synthesis of Indenones via Palladium-Catalyzed Annulation of Internal Alkynes

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A number of 2,3-disubstituted 1-indenones have been prepared in fair to good yields by treating *o*-iodo- or *o*-bromobenzaldehyde with various internal alkynes in the presence of a palladium catalyst. Synthetically, the methodology provides an especially convenient route to stable hindered indenones containing aryl, silyl, and *tert*-alkyl groups. The reaction is believed to proceed through a palladium-(IV) intermediate, and the regiochemistry of the reaction is controlled sterically.

Introduction

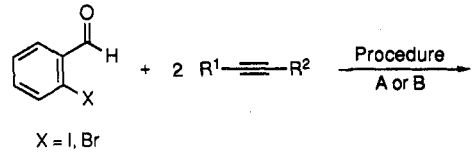
Indenones are useful intermediates in the synthesis of a variety of molecules, including the *C*-nor-*D*-homosteroid ring system,[1] photochromic indenone oxides,[2] 2,4- and 3,4-disubstituted 1-naphthols,[3] gibberellins,[4] indanones,[5] and indenes.[6] Indenones themselves have also been used as alcoholic fermentation activators,[7] fungicides,[8] and potential estrogen binding receptors.[9] Among the most recent synthetic targets have been the hindered fungicidally active 2-cyano-3-alkyl-1-indenones[8] and various 2,3-diaryl-1-indenones.[3,9-11]

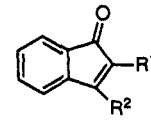
Although traditional indenone syntheses have largely relied upon Friedel–Crafts-type cyclizations and the addition of Grignard reagents to 2-substituted indandiones, a number of organometallic approaches utilizing alkynes have been reported over the last few years. These approaches tend to be stoichiometric in the metal and/or use carbon monoxide to form the carbonyl group of the indenone. Many different metal complexes have been employed, including nickel,[12] rhodium,[13] iron,[14] manganese,[15] and palladium.[10-12]

Heck first reported the palladium-catalyzed formation of 2,3-diphenyl-1-indenone from *o*-iodobenzaldehyde and diphenylacetylene as a single example in 1989.[10] A stoichiometric approach to 2,3-disubstituted 1-indenones from (*o*-formylaryl)mercury and -palladium complexes and internal alkynes has also been recently reported.[11] Because of our own current interest in this type of annulation process,[16-19] we have explored the scope and limitations of this chemistry and wish now to report improved reaction conditions for the palladium-catalyzed synthesis of a wide variety of 2,3-disubstituted indenones.

Results and Discussion

We have developed two general procedures for the annulation of internal alkynes by *o*-iodo- or *o*-bromobenzaldehyde, the use of which depends on the alkyne undergoing annulation: procedure A, 5 mol % $Pd(OAc)_2$, 4 equiv of NaOAc, 1 equiv of *n*-Bu_4NCl, 10 mL of DMF at 100 °C; procedure B, 5 mol % $Pd(OAc)_2$, 1 or 4 equiv of Na_2CO_3, 1 equiv of *n*-Bu_4NCl, 10 mL of *N*,*N*-dimethylacetamide (DMA) at 100 °C (eq 1). Our results using





(1)

these procedures are summarized in Table I. Procedure A works well for diarylalkynes (entries 1, 2, and 12) and provides an 84% isolated yield of 2,3-diphenyl-1-indenone, a 26% improvement in yield over the previously reported procedure.[10] Procedure B seems to be a more general procedure for a variety of alkynes containing aryl, silyl, and *tert*-alkyl groups (entries 3–11). Either *o*-iodo or *o*-bromobenzaldehyde can be employed successfully in the

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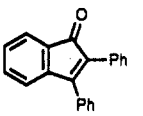
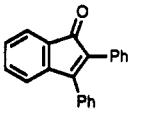
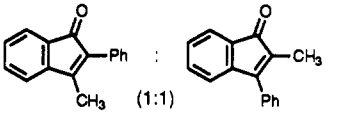
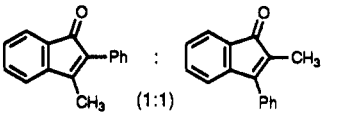
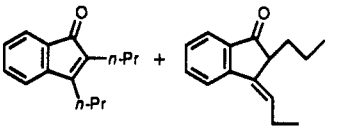
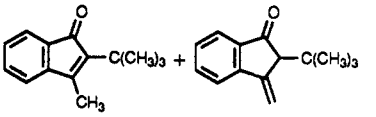
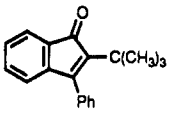
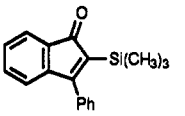
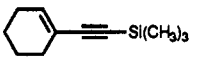
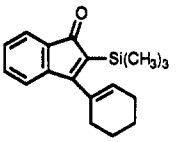
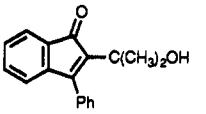
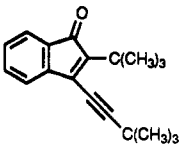
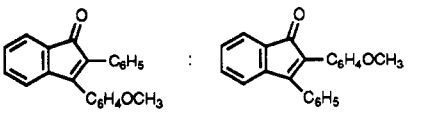
Table I. Synthesis of Indenones from o-Halobenzaldehydes and Internal Alkynes (eq 1)

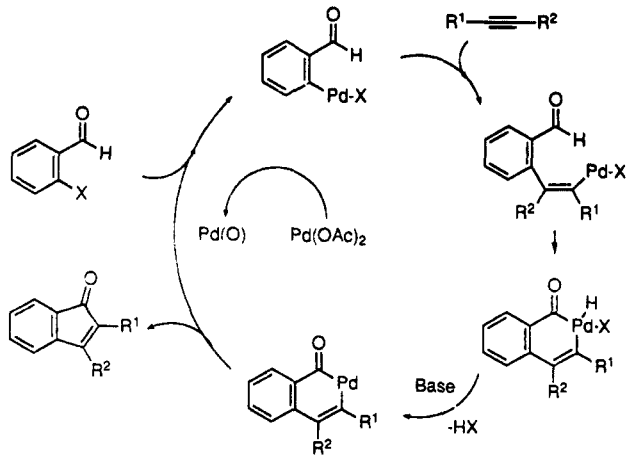
entry	halide (X)	alkyne	procedure[a]	time (h)	product(s)[b]	yield[c] (%)
1	I	Ph—≡—Ph	A	13		84
2	Br	Ph—≡—Ph	A	36		82
3	I	Ph—≡—CH_3	B	1.5	 (1:1)	62
4	Br	Ph—≡—CH_3	B	1	 (1:1)	56
5	I	*n*-Pr—≡—*n*-Pr	B	3		52 + 56[d]
6	I	CH_3—≡—$C(CH_3)_3$	B	10		26 + 26
7	I	Ph—≡—$C(CH_3)_3$	B	24		81
8	I	Ph—≡—$Si(CH_3)_3$	B	17		42[e]
9	I		B	30		49[e,f]
10	I	Ph—≡—$C(CH_3)_2OH$	B	24		58
11	I	$(CH_3)_3C$—≡—≡—$C(CH_3)_3$	B	24		58
12	I	*p*-$CH_3OC_6H_4$—≡—C_6H_5	A	24	 (1:1)	82

[a] See the text and Experimental Section for the detailed procedures. [b] A colon (:) indicates that the products were inseparable and a plus (+) indicates that they were separated. [c] Yields refer to isolated compounds purified by chromatography. [d] The second compound is tentatively assigned based on a crude ^1H NMR spectrum, and its yield is based on GC measurements. [e] One equiv of base used. [f] Temperature is 80 °C.

annulation process, although the iodide generally provides slightly higher indenone yields and fewer side products. Although the majority of reactions have been run on a 0.5 mmol scale, increasing the scale to 5.0 mmol for the transformation depicted in entry 10 of Table I resulted in an almost identical yield (55% versus 58%).

Isomerization of the product is a problem with certain indenones. Isomerization to β,γ-enones is observed with some indenones bearing a primary alkyl group in the 3-position (entries 5 and 6). The β,γ-enones are relatively unstable, and this type of isomerization is known to occur under a variety of conditions during the synthesis of

Scheme I

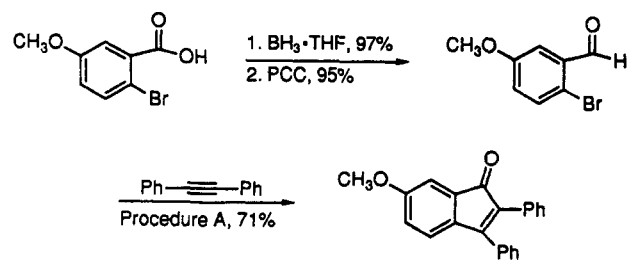


indenones.[2,7,9] The ease of isomerization has been attributed to indenone antiaromaticity, and a number of different mechanisms have been postulated for the isomerization depending on the reaction conditions. The rate of isomerization was dependent on the indenone being formed. 2-Phenyl-3-methyl-1-indenone isomerized at such a slow rate that the resultant β,γ-enone showed up only after a few days, whereas 2,3-di-*n*-propyl-1-indenone and 2-*tert*-butyl-3-methyl-1-indenone rapidly isomerized to a mixture within minutes. The latter indenone, possessing a bulky group in the 2-position, isomerized more extensively, possibly due to a relief in strain (entry 6).

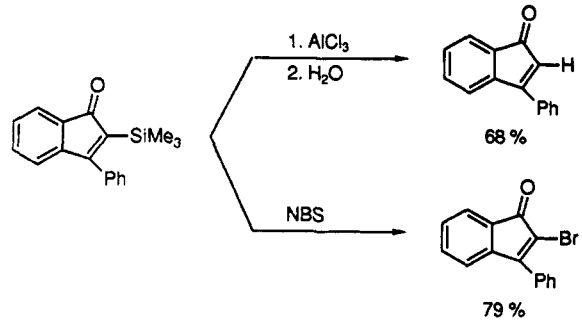
This annulation process is highly regioselective for alkynes containing tertiary alkyl, trimethylsilyl, or other hindered groups, with the major isomer having the more sterically demanding group in the 2-position of the indenone (entries 6–11). Less hindered alkynes, such as 1-phenyl-1-propyne, tend to produce a 1:1 mixture of regioisomers (entries 3 and 4). Electronic effects through aromatic rings appear to be minimal (entry 12). The regiochemistry was established for the products of entries 3,[12] 6,[12] and 12[20] by comparison with known compounds and was determined by subsequent desilylation for the silyl derivatives (see below). On the basis of these results, the regiochemistry shown was assumed for the products of entries 7, 10, and 11. The reported ^{1}H NMR spectrum for 3-phenyl-1-indenone was inconsistent with the spectrum obtained after desilylation of the product of entry 8.[21] The reported position for the 2-proton was at a chemical shift greater than 7.1 ppm. The proton shift observed for the compound described here was at 6.0 ppm, in agreement with those of other known indenones.[1,12,22]

We believe that this annulation process proceeds as shown in Scheme I: (1) reduction of $Pd(OAc)_2$ to the actual catalyst Pd(0), (2) oxidative addition of the aryl halide to Pd(0), (3) arylpalladium coordination to the alkyne and then insertion of the alkyne to form a vinylpalladium intermediate, (4) a second oxidative insertion into the aldehyde C–H bond to form a palladium(IV) intermediate, (5) elimination of HX by base, and (6) regeneration of the Pd(0) catalyst by reductive elimination to the indenone. A similar mechanism involving oxidative addition of an aldehyde to an organopalladium(II) intermediate has been proposed for the palladium-catalyzed reactions of *o*-bromobenzaldehyde with methyl acrylate.[23] Another possible mechanism involves addition of the C–Pd bond of the vinylpalladium intermediate across the C=O bond of the aldehyde to produce a palladium(II) alkoxide, followed by β-hydride elimination. However, there does not appear to be any precedent for either of these steps.

Scheme II



Scheme III



Although the synthetic applications of this process are somewhat limited in scope due to isomerization and a lack of regiochemical control, this chemistry proves to be very convenient and useful for the synthesis of some indenones that are difficult to obtain by traditional methods.[1] For example, 2,3-diphenyl-6-methoxy-1-indenone was readily prepared regioselectively in 65% overall yield from commercially available 2-bromo-5-methoxybenzoic acid, employing our alkyne annulation as the key step (Scheme II). This compound has previously been prepared as a potential estrogen binding receptor from 3-methoxybenzoic acid in 23% overall yield as a 16:1 mixture of regioisomers via cyclodehydration.[24]

The silyl-substituted indenones are also synthetically useful, as the silyl moiety can be removed or readily converted to other functional groups. For example, 3-phenyl-2-(trimethylsilyl)-1-indenone was easily converted to 3-phenyl-1-indenone in the presence of aluminum chloride, followed by water, or brominated to produce 2-bromo-3-phenyl-1-indenone using NBS (Scheme III).

In conclusion, a useful synthesis of 2,3-disubstituted 1-indenones has been developed using the palladium-catalyzed annulation of internal alkynes by *o*-iodo- or *o*-bromobenzaldehyde. The procedure utilizes readily available starting materials. The reactions proceed under relatively mild conditions and give fair to good indenone yields. Although the reaction is somewhat limited in scope synthetically, it is particularly suited for the synthesis of hindered alkyl, aryl, or silyl 2,3-disubstituted-1-indenones and allows the regiochemistry of the aryl ring of the indenone to be readily controlled, alleviating a problem

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frequently encountered during traditional Friedel–Crafts-type cyclizations and 2-substituted indandione chemistry.[1,8,9,20]

Experimental Section

General. All ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively. Thin-layer chromatography (TLC) was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) or basic $KMnO_4$ solution [3 g of $KMnO_4$ + 20 g of K_2CO_3 + 5 mL of NaOH (5%) + 300 mL of H_2O]. All melting points are uncorrected.

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of Na_2CO_3, NaOAc, and $AlCl_3$ were purchased from Fischer-Scientific. All palladium compounds were donated by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. 2-Bromobenzaldehyde, 2-iodobenzyl alcohol, 4-iodoanisole, phenylacetylene, 1-phenyl-2-(trimethylsilyl)acetylene, 1-(1-cyclohexenyl)-2-(trimethylsilyl)acetylene, 2-chloro-2-methylpropane, borane–THF, CuI, NBS, and PCC were obtained from Aldrich Chemical Co., Inc. 1-Phenyl-1-propyne, 4,4-dimethyl-2-pentyne, and 4-octyne were purchased from Farchan Scientific Co. Diphenylacetylene was purchased from Eastman Kodak Co. 2-Bromo-5-methoxybenzoic acid was purchased from Lancaster Synthesis, Inc. The following starting materials were prepared.

2-Iodobenzaldehyde. 2-Iodobenzyl alcohol (11.5 g, 0.05 mol) and PCC (31.5 g, 0.15 mol) were vigorously stirred in 200 mL of CH_2Cl_2 at rt for 24 h. The reaction mixture was filtered through Celite, washed with 5 × 150-mL portions of 5% HCl, and dried over $MgSO_4$. The organic phase was evaporated under reduced pressure to yield a brown solid. EtOAc was added to the solid, and the solution was filtered through silica gel to yield 93% of the desired compound with spectral properties identical to those previously reported.[25]

2-Bromo-5-methoxybenzaldehyde. To 2-bromo-5-methoxybenzoic acid (0.5 g, 2.17 mmol) in THF (1 mL) purged with N_2 and cooled to 0 °C was added borane–THF (2.85 mmol) over a period of 10 min. After 5 h, the reaction was quenched with 1.3 mL of a 1:1 THF/H_2O mixture, and the aqueous phase was saturated with 0.55 g of K_2CO_3. The mixture was extracted with 3 × 10 mL of ether and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield 0.46 g (97%) of 2-bromo-5-methoxybenzyl alcohol as a clear liquid: ^1H NMR ($CDCl_3$) δ 2.03 (s, 1 H, OH), 3.80 (s, 3 H, CH_3), 4.71 (s, 2 H, CH_2), 6.71 (dd, J = 3, 8.7 Hz, 1 H, aryl), 7.06 (d, J = 3 Hz, 1 H, aryl), 7.41 (d, J = 8.7 Hz, 1 H, aryl). This alcohol (0.46 g, 2.13 mmol) and PCC (1.34 g, 6.23 mmol) were stirred at rt for 10 h in 8.5 mL of CH_2Cl_2. The reaction mixture was diluted with 40 mL of ether and filtered through Celite. The organic phase was concentrated by evaporation of the solvent at reduced pressure to yield a brown solid. EtOAc was added to the solid, and the solution was filtered through silica gel to yield 0.43 g (95%) of the desired compound as a white solid (mp 75–76 °C): ^1H NMR ($CDCl_3$) δ 3.76 (s, 3 H, CH_3), 6.95 (dd, J = 3, 8.7 Hz, 1 H, aryl), 7.33 (d, J = 3 Hz, 1 H, aryl), 7.44 (d, J = 8.7 Hz, 1 H, aryl), 10.22 (s, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 55.7, 112.6, 117.9, 123.0, 133.8, 134.5, 159.2, 191.8; IR ($CHCl_3$) 1699 (C=O) cm^{-1}; mass spectrum m/z 213.96330 (calcd for $C_8H_7O_2Br$, 213.96294).

***tert*-Butylphenylacetylene.**[26] $AlCl_3$ (0.114 g, 0.086 mmol) was placed in 25 mL of CH_2Cl_2 under N_2 at −78 °C. 1-Phenyl-2-(trimethylsilyl)acetylene (1.5 g, 8.6 mmol) and 2-chloro-2-methyl-1-propane (1.59 g, 17.24 mmol) in 25 mL of CH_2Cl_2 were added dropwise. The reaction was complete in 4.25 h. The reaction mixture was quenched with water and extracted with ether and the extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure, and vacuum distillation (104 °C/24 mmHg) afforded 0.89 g (65%) of a clear liquid whose spectral data were identical with previous reports.[27]

4-Methoxydiphenylacetylene.[28] 4-Iodoanisole (2.34 g, 10 mmol), phenylacetylene (1.02 g, 10 mmol), CuI (17.3 mg, 0.09 mmol), $PdCl_2(PPh_3)_2$ (6.7 mg, 0.0095 mmol), $PdCl_2(CH_3CN)_2$ (11.7 mg, 0.045 mmol), and diethylamine (60 mL) were stirred for 3 d at rt. The reaction mixture was diluted with 100 mL of ether, extracted with 5 × 50-mL of saturated NH_4Cl, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was chromatographed using 15:1 hexane/EtOAc to give 1.45 g of the desired compound with spectral properties identical to those previously reported.[29]

General Procedure for the Palladium-Catalyzed Formation of 2,3-Disubstituted Indenones. $Pd(OAc)_2$ (6 mg, 0.027 mmol), the base (2.0 mmol unless otherwise noted), n-Bu_4NCl (150 mg, 0.54 mmol, Lancaster), the aldehyde (0.5 mmol), and the alkyne (1 mmol) were placed in a 4-dram vial which was heated in an oil bath at 100 °C for the necessary period of time. The reaction was monitored by TLC (15:1 hexane/EtOAc) to establish completion. The reaction mixture was cooled, diluted with 30 mL of ether, washed with 2 × 45-mL portions of saturated NH_4Cl, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure (may have contained a small amount of solvent), and the product was isolated by chromatography on a silica gel column. The following compounds were prepared by the above procedure.

2,3-Diphenyl-1-indenone (Entries 1 and 2, Table I). The reaction mixture was chromatographed using 2:1 hexane/CH_2Cl_2 to afford the desired compound with spectral properties identical to those previously reported.[10]

2-Methyl-3-phenyl-1-indenone and 2-Phenyl-3-methyl-1-indenone (Entries 3 and 4, Table I). The reaction mixture was chromatographed using 15:1 hexane/EtOAc to yield a 1:1 mixture of phenylmethylindenones with spectral properties identical to those previously reported.[12]

2,3-Di-*n*-propyl-1-indenone (Entry 5, Table I). The reaction mixture was chromatographed using 25:1 hexane/EtOAc to yield a yellow oil: ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3 H, CH_3), 1.03 (t, J = 7.5 Hz, 3 H, CH_3), 1.49 (sextet, J = 7.5 Hz, 2 H, CH_2), 1.64 (sextet, J = 7.5 Hz, 2 H, CH_2), 2.23 (t, J = 7.5 Hz, 2 H, CH_2), 2.51 (t, J = 7.5 Hz, 2 H, CH_2), 7.02 (d, J = 7.2 Hz, 1 H, aryl), 7.13 (t, J = 6.9 Hz, 1 H, aryl), 7.2–7.4 (m, 2 H, aryl); ^{13}C NMR ($CDCl_3$) δ 14.2, 14.5, 21.2, 22.5, 24.8, 28.2, 118.9, 121.8, 127.8, 131.1, 133.1, 134.7, 145.8, 157.6, 198.5; IR (neat) 1703 (C=O) cm^{-1}; mass spectrum m/z 214.13555 (calcd for $C_{15}H_{18}O$, 214.13577).

2-*n*-Propyl-3-propylidene-1-indanone (Entry 5, Table I). The structure of this apparently unstable compound was tentatively assigned based on the ^1H NMR spectrum of the crude product mixture. It possessed an R_f slightly lower than that of the indenone and partially decomposed to a red, very low R_f material during chromatography.[9] The isolated compound was contaminated with a small amount of the corresponding indanone, and the yield is based on GC measurements.

2-*tert*-Butyl-3-methyl-1-indenone (Entry 6, Table I). The reaction mixture was chromatographed using 25:1 hexane/EtOAc to yield the desired compound with spectral properties identical to those previously reported.[12]

2-*tert*-Butyl-3-methylidene-1-indanone (entry 6, Table I): ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H, CH_3), 2.82 (s, 1 H, CH), 5.28 (s, 1 H, vinyl), 5.87 (d, J = 1.2 Hz, 1 H, vinyl), 7.40 (t, J = 7.8 Hz, 1 H, aryl), 7.60 (t, J = 7.2 Hz, 1 H, aryl), 7.72 (m, 2 H, aryl); ^{13}C NMR ($CDCl_3$) δ 28.1, 35.2, 61.1, 109.7, 120.5, 122.9, 128.9, 134.6, 137.3, 143.3, 149.9, 205.2; IR ($CHCl_3$) 1710 (C=O) cm^{-1}; mass spectrum m/z 200.12004 (calcd for $C_{14}H_{16}O$, 200.12012).

2-*tert*-Butyl-3-phenyl-1-indenone (Entry 7, Table I). The reaction mixture was chromatographed using 15:1 hexane/EtOAc to yield a yellow solid (mp 114–116 °C, from n-hexane): ^1H NMR ($CDCl_3$) δ 1.16 (s, 9 H, CH_3), 6.47 (d, J = 7.2 Hz, 1 H, aryl), 7.0–7.6 (m, 8 H, aryl); ^{13}C NMR ($CDCl_3$) δ 30.6, 33.6, 120.3, 121.7, 127.8, 128.03, 128.08, 128.1, 129.8, 133.3, 135.3, 141.4, 147.6, 153.9, 198.4; IR ($CHCl_3$) 1699 (C=O) cm^{-1}; mass spectrum m/z 262.13617 (calcd for $C_{19}H_{18}O$, 262.13577).

3-Phenyl-2-(trimethylsilyl)-1-indenone (Entry 8, Table I). The reaction mixture was chromatographed using 15:1

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hexane/EtOAc to yield an orange oil: ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H, CH_3), 6.87 (d, J = 6.6 Hz, 1 H, aryl), 7.2–7.6 (m, 8 H, aryl); ^{13}C NMR ($CDCl_3$) δ –0.15, 120.7, 122.1, 127.5, 128.3, 129.00, 129.04, 132.2, 132.9, 134.6, 134.8, 147.1, 170.6, 201.6; IR ($CHCl_3$) 1697 (C=O) cm^{-1}; mass spectrum m/z 278.11264 (calcd for $C_{18}H_{18}OSi$, 278.11269).

3-(1-Cyclohexenyl)-2-(trimethylsilyl)-1-indenone (Entry 9, Table I). The reaction mixture was chromatographed using 25:1 hexane/EtOAc to yield a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9 H, CH_3), 1.75 (m, 4 H, CH_2), 2.2 (m, 4 H, CH_2), 5.78 (m, 1 H, vinyl), 7.02 (d, J = 7.2 Hz, 1 H, aryl), 7.20 (dt, J = 0.9, 6.9 Hz, 1 H, aryl), 7.31 (dt, J = 1.2, 6.6 Hz, 1 H, aryl), 7.40 (d, J = 6.9 Hz, 1 H, aryl); ^{13}C NMR ($CDCl_3$) δ –0.05, 21.8, 22.3, 24.9, 28.1, 120.2, 121.8, 126.6, 128.7, 132.2, 132.5, 132.8, 133.3, 146.6, 173.7, 202.2; IR (neat) 1697 (C=O) cm^{-1}; mass spectrum m/z 282.14372 (calcd for $C_{18}H_{22}OSi$, 282.14399).

2-(1-Hydroxy-1-methylethyl)-3-phenyl-1-indenone (Entry 10, Table I). The reaction mixture was chromatographed using 4:1 hexane/EtOAc to yield an orange-yellow solid (mp 103–104 °C, from n-hexane): ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 6 H, CH_3), 4.00 (s, 1 H, OH), 6.64 (d, J = 6.9 Hz, 1 H, aryl), 7.1–7.6 (m, 8 H, aryl); ^{13}C NMR ($CDCl_3$) δ 30.5, 71.1, 121.2, 122.4, 127.3, 128.5, 128.5, 128.6, 129.7, 133.5, 133.9, 138.3, 146.7, 153.9, 199.6; IR ($CHCl_3$) 3500 (OH), 1697 (C=O) cm^{-1}; mass spectrum m/z 264.11453 (calcd for $C_{18}H_{16}O_2$, 264.11503). This reaction gave a 55% isolated yield when run on a 5.0 mmol scale.

2-*tert*-Butyl-3-(*tert*-butylethynyl)-1-indenone (Entry 11, Table I). The reaction mixture was chromatographed using 25:1 hexane/EtOAc to yield an orange solid (mp 95–97 °C, from ethanol): ^{1}H NMR ($CDCl_3$) δ 1.37 (s, 9 H, CH_3), 1.40 (s, 9 H, CH_3), 7.1–7.4 (m, 4 H, aryl); ^{13}C NMR ($CDCl_3$) δ 29.0, 29.6, 30.4, 33.9, 74.1, 118.2, 119.5, 121.2, 128.3, 130.0, 133.4, 135.9, 144.0, 145.8, 197.9; IR ($CHCl_3$) 1697 (C=O) cm^{-1}; mass spectrum m/z 266.16671 (calcd for $C_{19}H_{22}O$, 266.16707).

2-(*p*-Methoxyphenyl)-3-phenyl-1-indenone and 3-(*p*-Methoxyphenyl)-2-phenyl-1-indenone (Entry 12, Table I). The reaction mixture was chromatographed using 4:1 hexane/EtOAc to yield a 1:1 mixture of indenones with spectral properties identical to those previously reported.[20]

2,3-Diphenyl-6-methoxy-1-indenone. This compound was isolated in 71% yield after 30 h from the reaction of 2-bromo-5-methoxybenzaldehyde with diphenylacetylene using procedure A. The reaction mixture was chromatographed using 2:1 hexane/CH_2Cl_2 to yield the desired compound with spectral properties identical to those previously reported.[24]

3-Phenyl-1-indenone. 3-Phenyl-2-(trimethylsilyl)-1-indenone (44 mg, 0.158 mmol) and $AlCl_3$ (23 mg, 0.172 mmol) were stirred in 5 mL of CH_2Cl_2 (dried over 4-Å sieves) at 0 °C under N_2, and the temperature was raised to rt after 3.5 h. After 6 h, water was added and the reaction mixture was extracted with ether. The ether solution was dried over $MgSO_4$ and concentrated. The residue was chromatographed using 15:1 hexane/EtOAc to yield 68% of the desired compound as an orange-yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.01 (s, 1 H, vinyl), 7.26–7.7 (m, 9 H, aryl); ^{13}C NMR ($CDCl_3$) δ 121.5, 122.6, 122.9, 127.3, 128.9, 129.2, 130.4, 132.3, 132.8, 133.0, 143.9, 162.7, 197.0; IR ($CHCl_3$) 1699 (C=O) cm^{-1}; mass spectrum m/z 206.07270 (calcd for $C_{15}H_{10}O$, 206.07317).

2-Bromo-3-phenyl-1-indenone. 3-Phenyl-2-(trimethylsilyl)-1-indenone (61 mg, 0.219 mmol) and NBS (78 mg, 0.44 mmol) were refluxed in 5.5 mL of CH_2Cl_2 (dried over 4-Å sieves) for 52 h. The reaction mixture was concentrated, ether was added to the mixture, and the residual solid was decanted. The solvent was removed under reduced pressure, and the residue was chromatographed using 15:1 hexane/EtOAc to yield 48.9 mg (79%) of the desired compound as an orange solid (mp 112–113 °C, from n-hexane): ^{1}H NMR ($CDCl_3$) δ 7.1–7.7 (m, 9 H, aryl); ^{13}C NMR ($CDCl_3$) δ 117.9, 121.2, 123.6, 128.1, 128.6, 128.8, 129.8, 130.2, 131.0, 133.7, 144.4, 156.7, 189.7; IR ($CHCl_3$) 1717 (C=O) cm^{-1}; mass spectrum m/z 283.98348 (calcd for $C_{15}H_9OBr^{79}$, 283.98368).

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for all new indenones (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.