Ortho-Functionalization of Aromatic Ketones via Manganation. A Synthesis of Indenols

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Treatment of acetophenone with $PhCH_2Mn(CO)_5$ in refluxing heptane provides (η^2-2-acetylphenyl)tetracarbonylmanganese in high yield. Conversion of the manganese complex to a reactive 16-electron species by oxidative decarboxylation with Me_3N–O in CH_3CN, followed by reaction with an alkyne, directly yielded substituted 1-methyl-1*H*-inden-1-ols in very good yields. The reaction is highly regioselective for terminal, electron-rich, electron-deficient, and 1-(trimethylsilyl)-1-alkynes as well as propargylsilanes. A number of 3-substituted acetophenones and α-tetralone and benzsuberone were ortho-manganated and then subjected to the Me_3N–O induced reaction with alkynes. On the basis of the observed regiochemistry of indenol formation from unsymmetrical alkynes (the large alkyne substituent occupies the 2-position of the indenol), the insertion of the alkyne into the manganese–carbon bond of (η^2-2-acetylphenyl)tetracarbonylmanganese was rationalized as controlled by steric effects, predominantly. Carbethoxyalkynes, the one exception noted to this trend, preferentially react to give indenols with the carbethoxy group in the 2-position, regardless of the other substituent on the alkyne.

Introduction

Electrophilic palladation occurs for a wide variety of substituted aromatic compounds ortho to functional groups such as N=NPh, CH_2NR_2, CH=NR, $NHCOCH_3$, and many others.[2] The resulting palladium complexes can be used in a number of synthetically useful carbon–carbon bond forming reactions.[3,4] Noticeably absent from the list of substrates that undergo ortho-palladation are aromatic ketones. Aryl ketones, however, are known to react with manganese reagents, $RMn(CO)_5$ (R = Me, CH_2Ph), to provide the ortho-manganated derivatives such as **1** in high yields.[4] At the outset of our project, no attempt to use ortho-manganated aromatic ketones for carbon–carbon bond formation had been described in the literature, although a palladium-catalyzed reaction between electron-deficient alkenes and complexes such as **1** was subsequently disclosed by Gommans, Main, and Nicholson.[5] Deuteration and halogenation of the carbon–manganese bond had also been achieved.[6] We describe herein a mild carbon–carbon bond formation ortho to an aromatic ketone providing substituted indenols by the reaction of alkynes with ortho-manganated acetophenones and related complexes.

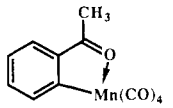

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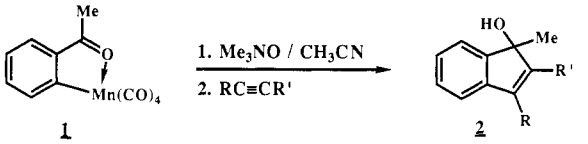
Table I. Synthesis of Indenols from 1 and Alkynes



1 **2**

entry	compd	R	R′	yield, %
1	**2a**	Et	Et	77
2	**2b**	Ph	Ph	60
3	**2c**	H	n-C_4H_9	59
	2d	n-C_4H_9	H	8
4	**2e**	H	c-C_6H_{11}	71
5	**2f**	H	Ph	75
6	**2g**	H	$SiMe_3$	69
7	**2h**	n-C_4H_9	$SiMe_3$	53
8	**2i**	Me	COOEt	75
9	**2j**	Et	COOEt	66
10	**2k**	c-C_6H_{11}	COOEt	55
11	**2l**	H	OEt	60
12	**2m**	OEt	Et	82
13	**2n**	OEt	$SiMe_3$	70
14	**2o**	Me	CH_2SiMe_3	50
15	**2p**	Et	CH_2SiMe_3	31
16	**2q**	Et	$CH_2CH{=}CH_2$	32
	2r	$CH_2CH{=}CH_2$	Et	32

Results

Via a modification of the procedure of Kaesz,[4a] (η^2-2-acetylphenyl)tetracarbonylmanganese (**1**) was prepared in high yield by heating acetophenone with $PhCH_2Mn(CO)_5$[7] in heptane. Thermolysis or photolysis of **1** in the presence of a variety of alkynes failed to induce a clean reaction. However, decarbonylative activation of a yellow solution of **1** was accomplished by brief treatment with anhydrous trimethylamine *N*-oxide[8] (TMANO) in acetonitrile.[9] On addition of alkyne to the resulting reddish-orange solution, a slow reaction occurred over the course of 8–16 h concurrent with a color change to pale yellow-orange resulting in production of the indenols **2** in good yields (Table I).

It can be seen from the results in Table I that the indenol synthesis is very general, proceeding with terminal, internal, electron-rich, and electron-deficient alkynes, and the reaction exhibited a surprising degree of regiochemical

(1) Camille and Henry Dreyfus Foundation Teacher–Scholar, 1986–1991.

(2) Ryabov, A. D. *Synthesis* **1985**, 233.

(3) (a) Holton, R. A.; Sibi, M. K.; Murphy, W. S. *J. Am. Chem. Soc.* **1988**, *110*, 314. (b) Tremont, S. J.; Rahman, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 5759. (c) Ryabov, A. D.; Sakodinskaya, I. K.; Dvoryantsev, S. N.; Eliseev, A. V.; Yatsimirsky, A. K. *Tetrahedron Lett.* **1986**, *27*, 2169. (d) Grigg, R.; Devlin, J. *J. Chem. Soc., Chem. Commun.* **1986**, 631. (e) O'Sullivan, R. D.; Parkins, A. W. *Ibid.* **1984**, 1165. (f) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakrovorty, A. *Ibid.* **1984**, 999.

(4) (a) McKinney, R. J.; Firenstein, G.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2057. (b) Knobler, C. B.; Crawford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2062. (c) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 4, p 788.

(5) Gommans, L. H. P.; Main, L.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1987**, 761.

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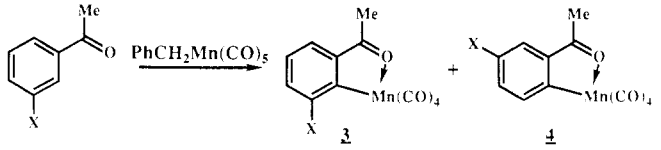
Table II. Ortho-Manganation of Substituted Acetophenones



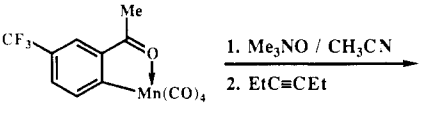
entry	X	compd	ratio 3/4	yield, %
1	F	**3a/4a**	4.54:1.00	85
2	Cl	**3b/4b**	1.05:1.00	86
3	Br	**3c/4c**	1.00:1.44	65
4	Me	**4d**	4 only	77
5	OMe	**3e/4e**	2.07:1.00	94
6	OH			0
7	CF_3	**4f**	4 only	85
8	NO_2			0
9	CN	**4g**	4 only	11

control over the range of alkynes studied. In most cases only one regioisomer could be isolated (traces of the minor isomers were apparent in the crude ^1H NMR spectra of some of the reactions). The reaction seemed to be influenced predominantly by steric effects, with the larger substituent oriented to the 2-position of the indenol ring in most cases. For example, all terminal alkynes reacted to place the non-hydrogen substituent away from the aromatic ring, while trimethylsilylation of the terminal alkyne reversed the regiochemistry (compare entries 3 and 7, 11 and 13). Propargylsilanes also followed a sterically controlled pathway with the CH_2SiMe_3 group also preferring the 2-position of the indenol. The electron-rich ethoxyalkynes gave mechanistically curious results. Ethyl 1-butynyl ether (entry 12) gave a very high yield of 3-ethoxy-2-ethyl-1-methyl-1*H*-inden-1-ol, possibly suggesting that a strong electronic effect might be operating for electron-rich alkynes. However, reaction of 1 with ethyl ethynyl ether gave 2-ethoxy-1-methyl-1*H*-inden-1-ol, completely reversing the regiochemistry relative to the alkoxy substituent, casting doubt on an electronically directed orientation for alkoxyalkynes in the complexes. In fact, ethyl (trimethylsilyl)ethynyl ether (entry 13) reacted in a fashion expected for a sterically biased process by placing the $SiMe_3$ group at the 2-position of the product indenol.

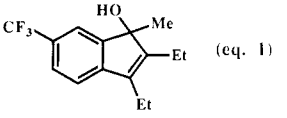
Only one electron-withdrawing substituent was used in this study, and in every case the COOEt group of these acetylenic esters (entries 8–10) was found in the 2-position of the product indenols. Even the somewhat bulky cyclohexyl group of entry 10 in Table I was forced to the 3-position of the indenol, suggesting that steric effects were not controlling the regiochemistry for reaction of electron-deficient alkynes.

Substituted acetophenones were also manganated in order to extend the generality of the indenol synthesis. In 1975 Kaesz described the reaction of *m*-methyl- and *m*-methoxyacetophenone with $CH_3Mn(CO)_5$ and reported that η^2-(2-acetyl-4-methylphenyl)tetracarbonylmanganese and (η^2-2-acetyl-3-methoxyphenyl)tetracarbonylmanganese were the principal isomers formed from each of the substrates.[4a] We have repeated the Kaesz experiments using $PhCH_2Mn(CO)_5$ and extended the observation of regioselective metalation to the additional meta-substituted substrates shown in Table II. The mechanism of cyclomanganation has been probed previously by investigating the products of ortho-manganation of substituted azobenzenes,[10] and the results in Table II, utilizing 3-substituted acetophenones, are consistent with the earlier study. Both a 3-methoxy and 3-fluoro substituent direct the manganation to an ortho position; chlorine gives a 1:1 mixture of ortho- and para-manganation, while bromine begins to favor the product of para-manganation. Our results suggest that manganation is directed adjacent to an electronegative substituent, but only in the absence of steric effects (compare entries 1–3). Steric effects seem to dictate the observed regiochemistry of manganation for the 3-methyl- and 3-(trifluoromethyl)acetophenones (entries 4 and 7). The low isolated yield of product from ortho-manganation of 3-cyanoacetophenone (entry 9) precludes assigning any significance to obtention of only one regioisomer. Both hydroxy and nitro substituents interfered with the reaction. Separation of the regioisomer mixtures of entries 1–3 and 5 of Table II was easily accomplished by silica gel chromatography.

To confirm the generality of the indenol synthesis, manganacycle **4f** was activated with TMANO in acetonitrile and then treated with 3-hexyne (eq 1). Indenol **5**



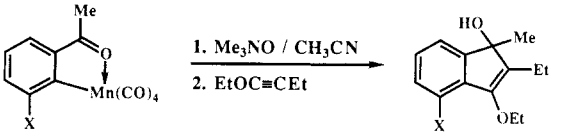
4f



(eq. 1)

5, 58%

was isolated in 58% yield. In a similar fashion, the 6-fluoro- and 6-chloromanganacycles **3a** and **3b** were activated and treated with 2-butynyl ether. Both complexes gave predominantly one indenol isomer, with only traces of a minor isomer apparent in the high-field ^1H NMR spectrum. From the 6-fluoro manganese complex, 4-fluoro-2-ethoxy-1-ethyl-1-methyl-1*H*-inden-1-ol, **6**, was isolated in 71% yield, and 4-chloro-2-ethoxy-1-ethyl-1-methyl-1*H*-inden-1-ol, **7**, was obtained from the corresponding chloro complex in 77% yield (eq 2).



(eq. 2)

3a, X = F

3b, X = Cl

6, X = F, 71%

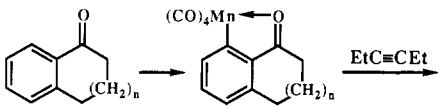
7, X = Cl, 77%

α-Tetralone (**8**) and benzosuberone (**9**) were also subjected to the ortho-manganation–alkynylation reaction sequence. On treatment with $PhCH_2Mn(CO)_5$ in refluxing heptane, α-tetralone was metalated in 92% yield, giving complex **10**, and benzosuberone provided the 7-membered ring homologue **11** in 81% yield. Attempted reaction of **10** with 3-hexyne under the standard conditions gave a complex mixture with no evidence of the desired cyclized product. On the other hand, the benzosuberone derived complex **11** reacted with TMANO followed by 3-hexyne to produce the tetrahydrobenzazulene **12** in 65% yield (eq 3).

Discussion

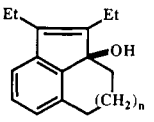
Assignment of regiochemistry to the indenol products was simplest for the alkoxyalkyne reactions. Acid-cata-

(10) Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687.



8, n = 1 10, n = 1, 92%

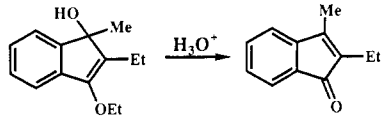
9, n = 2 11, n = 2, 81%



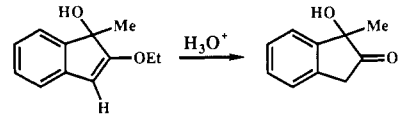
(eq. 3)

12, n = 2, 65%

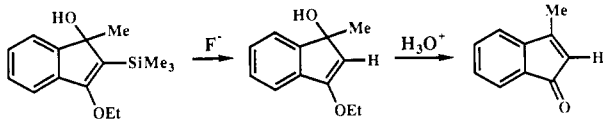
lyzed hydrolysis of indenol **2m** gave the known yellow 2-ethyl-3-methylindenone[11] (**13**) in 59% yield, confirming the relative disposition of the ethoxy and hydroxyl groups in **2m**. In contrast, indenol **2l**, prepared from ethyl ethynyl ether, on hydrolysis formed 1-hydroxy-1-methylindan-2-one (**14**) as a white crystalline solid in 96% yield. A complete reversal of regiochemistry relative to the alkyne alkyl group was noted when the 1-trimethylsilyl derivative of ethyl ethynyl ether was reacted with metallacycle **1**. The silylated indenol **2n** was formed, and it was subjected to fluoride-induced desilylation to give 3-ethoxy-1-methyl-1*H*-inden-1-ol (**15**), the regioisomer of **2l**. In contrast to **2l**, compound **15** underwent acid-catalyzed hydrolysis to give 3-methylinden-1-one **16** in 45% yield. The identity of the products formed on reaction of manganacycles **3a** and **3b** with ethyl 1-butynyl ether was also confirmed by hydrolysis to the corresponding indenones **17** and **18** (67% and 75% yield, respectively).



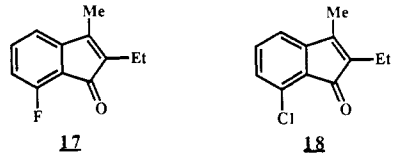
2m 13



2l 14

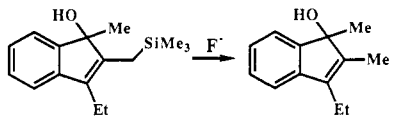


2n 15 16

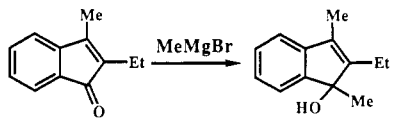


17 18

Next, the propargylsilane derived products **2o** and **2p** were identified. Indenol **2p** reacted with tetra-*n*-butylammonium fluoride in THF and gave a quantitative yield of the desilylated product, 1,2-dimethyl-3-ethyl-1*H*-inden-1-ol, **19**. Confirmation of the vicinal nature of the methyl groups was achieved by comparison of **19** with the reaction product of the known indenone **13** (prepared from **2m** above) with MeMgBr. A clean 1,2-addition product, **20**, was isolated from addition of the Grignard reagent to **13** and must have a 1,3-relationship of the methyl groups. The product from desilylation of indenol **2p** was isomeric with **20**, confirming the assignment of structure **19**. The structure of indenol **2o** was assigned by analogy.

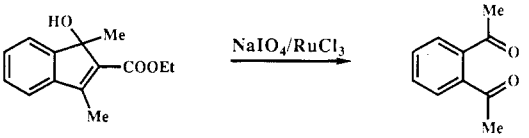


2p 19



13 20

The indenols resulting from reaction with the electron-deficient carboethoxy alkynes were all assigned structures with a 2-carbethoxy group. The hydroxyl proton for all carbethoxy-derived indenols was observed near 3.5 ppm in the ^1H NMR spectrum, in contrast to all other indenols that had hydroxyl absorptions near 1.6–2.1 ppm in the NMR. The downfield shift is consistent with internal hydrogen bonding of the hydroxyl proton to the ester carbonyl group. Further support for internal hydrogen bonding came from infrared data. The carbethoxy indenols showed broad OH stretching frequencies near 3550 cm^{-1} while all other indenols showed a sharp free hydroxyl stretch near 3580 cm^{-1} and a very broad hydrogen bonded OH stretch from 3500 to 3000 cm^{-1}. Infrared data was obtained for carbethoxyindenol **2i** at 1.0, 0.75, 0.40, and 0.10 M in $CHCl_3$, and the position and shape of the OH stretching frequency remained unchanged indicative of intramolecular hydrogen bonding. Finally, chemical degradation confirmed the assignment of regiochemistry to the products of carbethoxyalkyne reactions. Compound **2i** was subjected to diol formation and subsequent cleavage of all 1,2-dioxy functionalities with $NaIO_4/RuCl_3$,[12] which produced 1,2-diacetylbenzene in 30% yield. It is assumed that all carboethoxyalkynes reacted to produce the indenol regioisomer with the carbethoxy group in the 2-position.



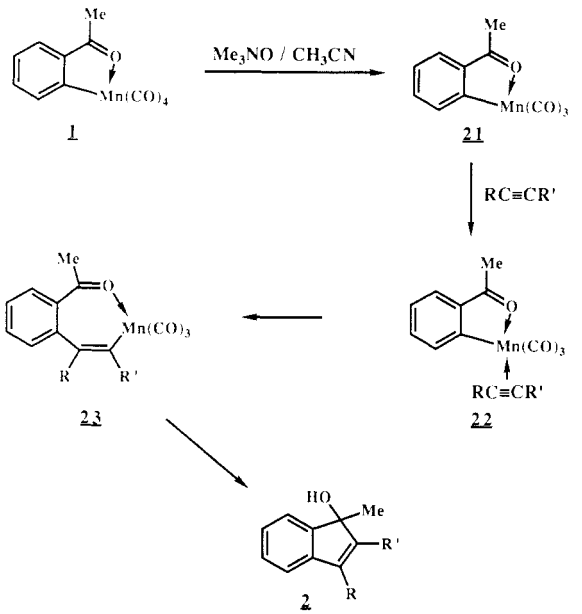
2i

Terminal alkynes reacted with **1** to form the 2-substituted indenols. Only from the 1-hexyne reaction (Table I, entry 3) could a small amount of the 3-substituted regioisomer (**2d**) be isolated. Verification of regiochemistry was obtained by NOE difference spectroscopy on both of the regioisomers obtained from reaction of manganacycle **1** with 1-hexyne. The major isomer, indenol **2c**, on irradiation at H^c showed a 3.6% enhancement of H^b; irradiation at the methyl group absorbance of **2c** enhanced H^a by 8.5%. For the minor isomer, **2d**, irradiation at H^c did not significantly affect H^a or H^b; however, irradiation at the methyl group absorbance of **2d** caused enhancements of both H^a (10%) and H^c (15%). From similarities in the ^1H NMR spectra, all terminal alkynes were presumed to follow the regiochemical orientation established for the 1-hexyne reaction. Reaction of the 1-trimethylsilyl derivatives followed by desilylation provided indenols of

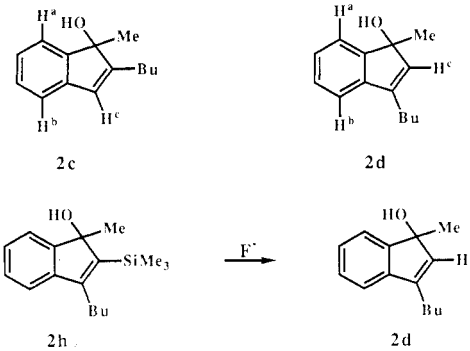
(11) Liebeskind, L. S.; South, M. S. *J. Org. Chem.* **1980**, *45*, 5426.

(12) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

Scheme I

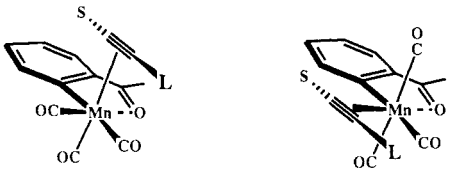


opposite regiochemistry. For example, reaction of manganacycle **1** with 1-hexynyltrimethylsilane produced 3-*n*-butyl-1-methyl-2-(trimethylsilyl)-1*H*-inden-1-ol (**2h**) (Table I, entry 7). Treatment of **2h** with tetra-*n*-butylammonium fluoride gave, in 89% yield, 3-*n*-butyl-1-methyl-1*H*-inden-1-ol (**2d**), the *minor* product formed from **1** and 1-hexyne.

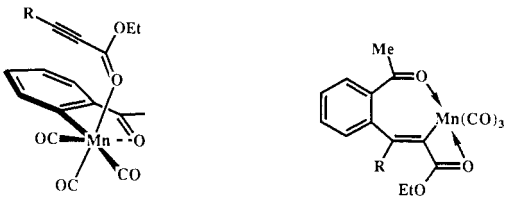


Presumably, the indenol formation occurs as shown in Scheme I. Intermediate **22**, formed by coordination of the alkyne to a coordinatively unsaturated manganese complex (**21**) generated by treatment of the manganacycles with TMANO, could undergo a migratory insertion of the alkyne into the manganese–carbon bond and produce the metallacycle **23**, which would be expected to be very reactive by virtue of its coordinative unsaturation. Collapse of **23** could lead to the observed products. Direct thin-layer chromatographic analysis of the crude reaction mixtures showed the presence of indenol, so it is not clear at the present time if the hydroxyl proton of the product comes from hydrolysis of a manganese–oxygen bond by adventitious moisture or if an alternative radical-decomposition pathway provides the required proton.

The reaction of manganacycles **1**, **3a**, and **3b** with unsymmetrical alkynes proceeded in a remarkably regioselective fashion to produce indenols. A survey of the data presented in Table I suggests that most of the results can be understood by assuming a sterically biased insertion of the alkyne into the manganese–carbon bond (**22** → **23**). Maximum orbital overlap and theoretical arguments[13] suggest that the insertion of the alkyne proceeds via a coplanar alignment of the Mn–carbon bond with the alkyne C≡C bond. Structure **24** depicts the most reasonable geometry for the preinsertion intermediate, since the alternative **25** would possess significant nonbonded interactions between the alkyne substituents and the aromatic ring hydrogen. Of the two possible orientations for the alkyne substituents in **24**, placing the smaller alkyne group over the aromatic ring and the larger alkyne group over the CO ligand (as shown) should minimize steric interactions both in **24** and presumably in the transition state leading to the insertion product **23**.[14] This model nicely accommodates most of the results in Table I by predicting that the larger group of the alkyne should occupy the 2-position of the product indenol.



Reaction of **1** with the electron-deficient alkynyl esters does not appear to respond to steric effects since the COOEt group always occupies the 2-position of the indenol. It is possible that the insertion of the alkynyl esters, in contrast to the other substrates, is directed by an electronic effect manifested by the highly polarized nature of the electron-deficient alkynes. Alternatively, it could be argued that the ester functionality overrides any steric effects and directs the insertion to the observed products by prior coordination of the carbonyl oxygen to the manganese atom as in **26**. An intriguing corollary of this argument is that the ester carbonyl could also function as additional ligand to bring the manganese atom of the insertion product **27** back to coordinative saturation. This latter rationalization does not require the introduction of electronic effects to control the regiochemical outcome of the reaction and therefore is consistent with mechanistic picture emerging from the other alkynes studied, which suggests that polarization of the alkyne does not significantly influence the regiochemistry of the reaction.



Of the three electron-rich ethoxyalkynes used in this study, the outcome of the reaction of ethyl ethynyl ether and ethyl (trimethylsilyl)ethynyl ether is accommodated by the steric-based rationalization depicted in structure **24**. The predominant formation of indenol **2m** from the reaction of **1** with ethyl butynyl ether is, at first glance, an ambiguous result (a trace of the minor regioisomer was apparent in the high-field ^{1}H NMR). However, this result also might be attributable to steric effects. To the limited extent that the conformational free energy difference of substituted cyclohexanes can be used to assay the steric effect of substituents in other processes, it is interesting

(13) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

(14) This argument assumes that the alkyne insertion is not reversible, which would mandate looking at steric effects in intermediate **15** in order to rationalize the observed products.

to note that an ethoxy group has a significantly smaller A value than an ethyl group (0.9 kcal/mol vs 1.8 kcal/mol).[15]

Conclusions

(η^2-2-Acetylphenyl)tetracarbonylmanganese and related ortho-manganated aromatic ketones are converted into indenols in high yield and with excellent regioselectivity upon reaction with alkynes. This chemistry provides an unique means of functionalizing the position on an aromatic ring ortho to a ketone functional group. Extension of this chemistry to other functionalities should be feasible.

Experimental Section

General Considerations. All melting points were performed in open capillary tubes and are uncorrected. Analytical thin-layer chromatography was done with E. Merck silica gel 60F-254 glass backed plates of 0.25 mm thickness, which were visualized with appropriate combinations of UV light, phosphomolybdic acid stain, $KMnO_4$ (5% in water), and vanillin stain. Preparative-scale separations were effected with "flash grade" silica gel available from Aldrich Chemical Co. and by radial chromatography using a Model 7924T Chromatotron purchased from Harrison Research on rotors coated with Merck PF254 silica gel. Methylene chloride was purified for use by distillation over CaH_2 under a N_2 atmosphere. Benzene, tetrahydrofuran, and ether were freshly distilled from sodium and benzophenone. All other solvents were reagent grade quality and used as received.

Starting Materials. All aromatic ketones were purchased from commercial sources. Commercially available alkynes were obtained from Farchan Laboratories. Silylation of terminal alkynes was accomplished according to standard procedures (deprotonation of the alkyne with n-BuLi at −20 °C followed by Me_3SiCl quench), and the propargyl silanes were made by Me_3SiCl quench of propargyl Grignard reagents. Benzylmanganese pentacarbonyl was prepared according to a published procedure.[16]

Synthesis of (η^2-2-Acetylphenyl)tetracarbonylmanganese (1) by Reaction of Acetophenone with Benzylpentacarbonylmanganese. 2-Acetyltetracarbonylmanganese (1) was synthesized according to the procedure of Gommans, Main, and Nicholson,[6] a modification of the original Kaesz method. A solution containing 10 mmol of acetophenone and 2.36 g of benzylpentacarbonylmanganese in 150 mL of heptane was heated under reflux for 30 min. After silica gel flash chromatography with hexane as the eluent, 1.8 g (76%) of 1 was isolated as a yellow solid: mp 114–116 °C; IR ($CHCl_3$) 2080, 1990, 1940, 1580, and 1320 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.62 (s, 3 H), 7.18 (t, J = 7.4 Hz, 1 H), 7.42 (t, J = 7.2 Hz, 1 H), 7.85 (d, J = 7.7 Hz, 1 H), and 8.10 (d, J = 7.4 Hz, 1 H); m/e 286 (M^+), 174, 120, 105 (base), 91, 77, and 55; M_r+ calcd for 285.9674, found 285.9698.

General Procedure for the Reaction of 1 with Acetylenes. A solution containing 0.4–0.6 mmol of manganese complex 1 in 2 mL of anhydrous acetonitrile was treated with a 1-mL solution of anhydrous trimethylamine N-oxide (1.5 equiv) in acetonitrile, and the mixture was stirred for 5 min. At the end of this time, the reddish-orange solution was treated with 2.0 equiv of the appropriate acetylene, and the reaction mixture was allowed to stir at room temperature for 8–16 h over which period the color changed from red to pale orange-yellow. The acetonitrile was removed on a rotary evaporator, and the resulting residue was dissolved in a small quantity of methylene chloride and filtered through a small column of silica to remove polar impurities. The eluate was then concentrated under reduced pressure, and the residue was subjected to radial chromatography with a 3–10% ethyl acetate–hexane mixture as the eluent.

3-Hexyne. Reaction of 1 with 3-hexyne gave a 77% yield of 2,3-diethyl-1-methyl-1H-inden-1-ol (**2a**) as a white solid: mp 78–79 °C (from hexanes); IR ($CHCl_3$) 3570, 2955, 2920, 2860, 1445, 1315, 1095, and 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.17 (t, J = 7.6 Hz, 3 H), 1.18 (t, J = 7.6 Hz, 3 H), 1.52 (s, 3 H), 1.57 (s, 1 H), 2.33 (dq, J = 14.1 and 7.6 Hz, 1 H), 2.41 (dq, J = 14.1 and 7.6 Hz, 1 H), 2.45 (q, J = 7.6 Hz, 2 H), and 7.12–7.42 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.34, 14.74, 17.62, 18.39, 23.38, 82.60, 118.66, 121.27, 125.21, 128.17, 137.68, 142.72, 148.67, and 149.48; m/e 202 (M^+), 173 (base), and 158; M_r+ calcd for 202.1357, found 202.1333. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.07; H, 8.97.

Diphenylacetylene. Reaction of 1 with diphenylacetylene gave a 60% yield of 2,3-diphenyl-1-methyl-1H-inden-1-ol (**2b**) as a white crystalline solid: mp 143–144 °C (from hexanes) (lit.[17] mp 143 °C); IR ($CHCl_3$) 3580, 1705, 1440, 1325, 1170, 1140, 1085, 1075, and 695 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60 (s, 3 H), 2.08 (s, 1 H), 7.2–7.6 (m, 14 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.02, 83.34, 120.83, 121.89, 126.65, 127.32, 127.59, 127.99, 128.53, 129.30, 129.46, 134.70, 134.77, 138.72, 142.18, 146.97, and 149.55; m/e 298 (M^+), 280 (base), 203, and 85; M_r+ calcd for 298.1358, found 298.1373. Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 87.82; H, 6.03.

1-Hexyne. Reaction of 1 with 1-hexyne gave as the major product a 59% yield of 2-butyl-1-methyl-1H-inden-1-ol (**2c**) as a colorless oil. A white crystalline solid melting at 36–38 °C was obtained by crystallization from hexanes: IR (neat) 3510, 3340, 2960, 2920, 2860, 1465, 1455, 1090, and 750 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 0.97 (t, J = 7.3 Hz, 3 H), 1.44 (m, 2 H), 1.46 (s, 3 H), 1.64 (m, 2 H), 2.25 (dddd, J = 24.9, 17.3, 7.6, and 1.8 Hz, 1 H), 2.31 (dddd, J = 24.9, 17.3, 7.6, and 1.8 Hz, 1 H), 6.22 (t, J = 1.8 Hz, 1 H), 7.07–7.14 (m, 2 H), 7.16–7.22 (m, 1 H), and 7.33–7.38 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.04, 22.79, 23.31, 25.50, 29.58, 82.37, 120.33, 121.57, 123.35, 125.04, 128.36, 141.82, 149.64, and 156.47; m/e 202 (M^+), 159, 145 (base), 141, and 115; M_r+ calcd 202.1358, found 202.1371.

The minor product isolated from the reaction (8%) as a colorless oil was identified as 3-butyl-1-methyl-1H-inden-1-ol (**2d**): IR ($CHCl_3$) 3590, 2960, 2925, 2860, 1690 (s), 1680, 1465, and 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 0.96 (t, J = 7.3 Hz, 3 H), 1.25 (s, 1 H), 1.42 (tq, J = 7.4 and 7.3 Hz, 2 H), 1.58 (s, 3 H), 1.63 (m, 2 H), 2.42 (dt, J = 7.6 and 1.5 Hz, 2 H), 5.97 (t, J = 1.5 Hz, 1 H), 7.1–7.3 (m, 3 H), and 7.40 (d, J = 6.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 22.62, 23.91, 26.94, 29.58, 81.04, 119.37, 121.33, 126.27, 128.18, 136.39, 142.53, 143.46, and 150.17; m/e 202 (M^+), 160, 159, 147, 146, 145 (base), 141, 131, 115, and 91; M_r+ calcd 202.1358, found 202.1351.

Confirmation of the regiochemistry for the reaction of terminal alkynes was achieved by NOE difference spectroscopy on **2c** and **2d** with the observed enhancements described in the text of the paper. NOE samples were freeze–pump–thaw degassed and sealed. Data was acquired using 32K of memory with a resolution of 0.19 Hz/data point on a Niclolet NT-360 instrument. The NOE difference spectra were obtained by using the method of Hall and Sanders.[18] Preirradiation times of 10–15 s, resulting in 70–90% reduction of intensity, were used to transfer polarization; data acquisition commenced after a delay of 10 μs. Data acquisition of a subsequent delay allow 7 s for return to equilibrium before repetition of the experiment. The resulting free-induction decays were subjected to exponential multiplication resulting in line broadening of 0.8–1.5 Hz, transformed, and subtracted.

Cyclohexylacetylene. Reaction of 1 with cyclohexylacetylene gave a 71% yield of 2-cyclohexyl-1-methyl-1H-inden-1-ol (**2e**) as a white crystalline solid: mp 123–125 °C (from hexanes); IR ($CHCl_3$) 3600, 2930, 2880, 1470, 1450, 1325, 1115, and 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.2–1.45 (m, 6 H), 1.51 (s, 3 H), 1.69 (s, 1 H), 1.7–1.9 (m, 3 H), 1.92–2.05 (m, 1 H), 2.25–2.4 (m, 1 H), 6.28 (s, 1 H), 7.05–7.25 (m, 3 H), and 7.36 (d, J = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.40, 23.44, 26.23, 26.74, 33.79, 34.20, 35.83, 83.07, 120.45, 121.50, 123.24, 125.17, 128.35, 141.74, 149.37, and 161.44; m/e 228 (M^+), 146 (base), and 145; M_r+ calcd 228.1514, found 228.1510. Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.24; H, 8.84.

Phenylacetylene. Reaction of 1 with phenylacetylene gave a 75% yield of 1-methyl-2-phenyl-1H-inden-1-ol (**2f**) as a white crystalline solid: mp 123–125 °C (from ethyl acetate–hexanes); IR ($CHCl_3$) 3580, 1600, 1490, 1465, 1455, 1325, 1135, 1080, 1040,

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(16) Closson, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.
(17) *Chem. Abstr.* **1954**, *48*, 542*f*.
(18) Hall, L. S.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703.

and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.64 (s, 3 H), 1.96 (s, 1 H), 6.95 (s, 1 H), 7.17–7.5 (m, 7 H), and 7.89 (d, J = 7.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.52, 83.09, 121.43, 121.59, 125.59, 126.26, 126.74, 127.86, 128.49, 128.62, 134.01, 140.51, 151.00, and 151.23; m/e 222 (M^+, base), 207, 178, 144, 116, 101, and 89; M_r+ calcd 222.1045, found 222.1038. Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.38; H, 6.35.

(Trimethylsilyl)acetylene. Reaction of **1** with (trimethylsilyl)acetylene gave a 69% yield of 1-methyl-2-(trimethylsilyl)-1*H*-inden-1-ol (**2g**) as a white crystalline solid: mp 103–105 °C (from hexanes); IR ($CHCl_3$) 3590, 2960, 1320, 1250, 1100, 1085, 1040, 1015, 1000, 840, and 625 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 0.26 (s, 9 H), 1.60 (s, 3 H), 1.65 (br s, 1 H), 6.81 (s, 1 H), 7.14–7.25 (m, 3 H), 7.39 (d, J = 7.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –0.45, 24.96, 86.89, 121.12, 121.50, 126.42, 128.30, 137.84, 141.49, 152.77, and 157.05; m/e 218 (M^+), 202, 185, 128, and 73 (base); M_r+ calcd 218.1127, found 218.1122. Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50, H, 8.31. Found: C, 71.59; H, 8.32.

1-Hexynyltrimethylsilane. Reaction of **1** with 1-hexynyltrimethylsilane gave a 53% yield of 3-butyl-1-methyl-2-(trimethylsilyl)-1*H*-inden-1-ol (**2h**) as a colorless oil: IR ($CHCl_3$) 3580, 2945, 2920, 2855, 1550, 1450, 1310, 1242, 1110, 1088, 1060, and 840 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.30 (s, 9 H), 0.97 (t, J = 7.1 Hz, 3 H), 1.24 (s, 1 H), 1.4–1.6 (m, 4 H), 1.58 (s, 3 H), 2.5–2.6 (m, 2 H), 7.14–7.28 (m, 3 H), and 7.38 (d, J = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 1.04, 13.98, 23.29, 25.07, 28.30, 31.69, 86.56, 119.39, 121.07, 126.29, 127.98, 142.61, 147.62, 152.66, and 152.99; M_r+ calcd for $C_{17}H_{26}OSi$: 274.1753, found 274.1753.

A solution containing 26 mg of **2h** in 10 mL of anhydrous tetrahydrofuran was treated with 0.5 mL of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran, and the mixture was heated at reflux for 4 h. At the end of this time, the reaction mixture was concentrated under reduced pressure, and the residue was subjected to silica gel radial chromatography with a 10% ethyl acetate–hexane mixture as the eluent to give 17 mg (89%) of 3-butyl-1-methyl-1*H*-inden-1-ol (**2d**). This material was identical in all respects with the minor compound isolated from the reaction of **1** with 1-hexyne.

Ethyl 2-Butynoate. Reaction of **1** with ethyl 2-butynoate gave a 75% yield of 2-carbethoxy-1,3-dimethyl-1*H*-inden-1-ol (**2i**) as a colorless oil: IR (neat) 3500 (br), 1690, 1675, 1610, 1375, 1335, 1240, 1205, 1180, 1105, 1090, 1050, and 755 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.39 (t, J = 6.8 Hz, 3 H), 1.67 (s, 3 H), 2.45 (s, 3 H), 3.51 (s, 1 H), 4.34 (m, 2 H), 7.3–7.6 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.62, 14.41, 25.62, 60.29, 81.48, 121.65, 122.05, 128.56, 129.28, 135.27, 141.26, 149.76, 150.78, and 165.64; m/e 232 (M^+), 214, 186, 171 (base), 158, 141, 115, and 84; M_r+ calcd 232.1099, found 232.1106. Confirmation of regiochemistry for the reaction of the carbethoxyalkynes was achieved by conversion of **2i** into 1,2-diacetylbenzene on treatment with $NaIO_4$ and catalytic $RuCl_3$ in CCl_4/acetonitrile/H_2O according to the conditions described in ref 12.

Ethyl 2-Pentynoate. Reaction of **1** with ethyl 2-pentynoate gave a 66% yield of 2-carbethoxy-3-ethyl-1-methyl-1*H*-inden-1-ol (**2j**) as a colorless oil: IR ($CHCl_3$) 3530, 2970, 1665, 1370, 1330, 1255, 1195, 1110, 1100, 1090, and 1045 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.23 (t, J = 7.6 Hz, 3 H), 1.40 (t, J = 1.7 Hz, 3 H), 1.68 (s, 3 H), 2.94 (q, J = 7.6 Hz, 2 H), 3.51 (s, 1 H), 4.26–4.46 (m, 2 H), 7.3–7.46 (m, 3 H), and 7.5–7.55 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 13.21, 14.32, 19.98, 25.75, 60.26, 81.48, 121.68, 122.20, 128.53, 129.18, 134.36, 140.24, 150.12, 156.48, and 165.39; m/e 246 (M^+), 185 (base), 172, 144, 129, and 84; M_r+ 246.1256, found 246.1270.

Ethyl Cyclohexylethynoate. Reaction of **1** with ethyl cyclohexylethynoate gave a 55% yield of 2-carbethoxy-3-cyclohexyl-1-methyl-1*H*-inden-1-ol (**2k**) as a colorless oil: IR (neat) 3560 (br), 3520 (s), 2920, 1695, 1662, 1370, 1328, 1237, and 190 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.3–1.5 (m, 7 H), 1.65 (s, 3 H), 1.7–2.0 (m, 6H), 3.53 (br s, 1 H), 3.6–3.8 (m, 1 H), 4.25–4.50 (m, 2 H), 7.24–7.4 (m, 2 H), 7.51 (d, J = 6.9 Hz, 1 H), and 7.69 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.30, 25.91, 26.15, 26.64, 30.25, 38.33, 60.36, 81.16, 122.33, 124.42, 128.03, 128.64, 134.46, 139.44, 150.57, 158.56, and 165.83; M_r+ calcd for $C_{19}H_{24}O_3$ 300.1725, found 300.1725.

Ethyl Ethynyl Ether. Reaction of **1** with ethyl ethynyl ether gave a 60% yield of 2-ethoxy-1-methyl-1*H*-inden-1-ol (**21**) as a white crystalline solid: mp 92.5–93.5 °C (from hexanes); IR ($CHCl_3$) 3590, 1612, 1467, 1337, 1320, 1170, 1100 (s), and 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.43 (t, J = 7.1 Hz, 3 H), 1.54 (s, 3 H), 2.03 (br s, 1 H), 3.96–4.08 (m, 2 H), 5.38 (s, 1 H), 6.98–7.08 (m, 2 H), 7.13–7.21 (m, 1 H), and 7.27 (d, J = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.34, 23.22, 65.88, 78.51, 96.26, 119.32, 121.36, 123.59, 128.65, 141.42, 143.61, and 168.97; m/e 190 (M^+), 144 (base) and 116; M_r+ calcd 190.0994, found 190.0993. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.71; H, 7.43. Confirmation of this structure was accomplished by hydrolysis to the corresponding hydroxyl ketone.

A solution containing 60 mg of **21** in 20 mL of acetone was treated with 10 mL of water and 2 mL of concentrated hydrochloric acid and stirred for 1 h. At the end of this time, the acetone was removed under reduced pressure, and the aqueous phase was extracted with several portions of methylene chloride. The combined organic extracts were concentrated to give 49 mg (96%) of 1-hydroxyl-1-methylindan-2-one (**14**) as a white crystalline solid: mp 92–93 °C (from hexanes); IR ($CHCl_3$) 3550, 1750, 1145, 1087, 1050, and 948 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.50 (s, 3 H), 3.11 (s, 1 H), 3.58 (AB quartet, J = 22.1 Hz, 2 H), 7.27–7.39 (m, 3 H), and 7.43–7.51 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.68, 39.94, 77.63, 123.92, 124.95, 128.15, 129.01, 134.78, 143.87, and 216.82. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.13; H, 6.22.

Ethyl 1-Butynyl Ether. Reaction of **1** with ethyl 1-butynyl ether gave an 82% yield of 3-ethoxy-2-ethyl-1-methyl-1*H*-inden-1-ol (**2m**) as a white crystalline solid: mp 54–55 °C; IR ($CHCl_3$) 3580, 2970, 1630, 1370, 1328, 1290, 1110, 1090, 1077, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, J = 7.6 Hz, 3 H), 1.39 (t, J = 7.1 Hz, 3 H), 1.53 (s, 3 H), 2.24–2.52 (m, 2 H), 4.14 (q, J = 7.1 Hz, 2 H), 7.1–7.3 (m, 3 H), and 7.35–7.42 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.20, 15.76, 16.66, 23.59, 66.71, 80.19, 118.03, 121.25, 125.87, 127.97, 132.34, 138.50, 148.51, and 150.88. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.20; H, 8.34. A trace of the alternate regioisomer (2-ethoxy-3-ethyl-1-methyl-1*H*-inden-1-ol) was also detected in the ^1H NMR spectrum as determined by a signal at 1.54 ppm corresponding to the C1-quaternary methyl group as well as by a complicated pattern between 4.2 and 4.4 ppm determined to be the C-2 ethoxy methylene. A similar mirroring could also be detected in the ^{13}C NMR spectrum.

Confirmation of the regiochemical assignment for the major isomer was accomplished by hydrolysis to 2-ethyl-3-methylinden-1-one (**13**) previously reported in the literature.[11] A solution containing 86 mg of **2m** in 5 mL of acetone was treated with 5 mL of 10% hydrochloric acid, and the mixture was stirred for 14 h. At the end of this time, the acetone was removed under reduced pressure, and the residue was extracted with methylene chloride. The organic layer was dried over magnesium sulfate, concentrated under reduced pressure, and subjected to silica gel radial chromatography with a 10% ethyl acetate–hexane mixture as the eluent to give 40 mg (59%) of 2-ethyl-3-methylinden-1-one (**13**) as a yellow oil: IR ($CHCl_3$) 2960, 1695, 1625, 1607, 1450, 1382, 995, and 872 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.06 (, J = 7.5 Hz, 3 H), 2.12 (s, 3 H), 2.29 (q, J = 7.5 Hz, 2 H), 7.01 (d, J = 7.1 Hz, 1 H), 7.12–7.20 (m, 1 H), and 7.28–7.40 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.28, 13.61, 16.00, 118.53, 121.46, 128.04, 130.85, 133.19, 136.38, 146.31, and 153.30. The data obtained from this material was identical in all respects with that reported in the literature.

Addition of methylmagnesium bromide to an ethereal solution of **13** produced a 99% yield of 1,3-dimethyl-2-ethyl-1*H*-inden-1-ol (**20**) isolated as a white crystalline solid: mp 118–119 °C; IR ($CHCl_3$) 3580, 2960, 2920, 1463, 1448, 1318, 1102, 1090, and 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.16 (t, J = 6.6 Hz, 3 H), 1.51 (s, 3 H), 1.98 (s, 3 H), 2.27–2.47 (m, 2 H), 7.08–7.18 (m, 2 H), 7.22–7.28 (m, 1 H), and 7.36 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.07, 14.11, 17.67, 23.23, 82.52, 118.26, 121.04, 125.32, 128.22, 131.65, 143.74, 149.08, and 149.24. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.05; H, 8.61.

Ethyl (Trimethylsilyl)ethynyl Ether. Reaction of **1** with ethyl (trimethylsilyl)ethynyl ether gave a 70% yield of 3-ethoxy-1-methyl-2-(trimethylsilyl)-1*H*-inden-1-ol (**2n**) as a colorless oil: IR ($CHCl_3$) 3600, 1562, 1295, 1247, 1075, 850 (s), and 842 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.28 (s, 9 H), 1.41 (t, J = 7.1 Hz,

3 H), 1.59 (s, 3 H), 1.69 (s, 1 H), 4.15 (q, J = 7.1 Hz, 2 H), 7.18–7.25 (m, 3 H), and 7.36–7.42 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.16, 15.60, 25.31, 67.07, 82.82, 119.08, 121.35, 126.81, 127.65, 131.34, 137.19, 153.11, and 164.91; m/e 262 (M^+), 247, 233, 217, 203, 201, 161, 143, 115, 84, and 73; M_r+ calcd for $C_{15}H_{22}O_2Si$ 262.1389, found 262.1389. The regiochemical assignment of this structure was confirmed by desilylation of this material and subsequent hydrolysis of the intermediate to 3-methylinden-1-one (**16**).

A solution containing 117 mg of the above material in 15 mL of anhydrous tetrahydrofuran was treated with 1.0 mL of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran, and the mixture was heated at 60 °C for 90 min. At the end of this time, the reaction mixture was concentrated under reduced pressure, and the residue was subjected to silica gel radial chromatography with a 10% ethyl acetate–hexane mixture as the eluent to give 58 mg (68%) of 3-ethoxy-1-methyl-1*H*-inden-1-ol (**15**) as a colorless oil: IR ($CHCl_3$) 3590, 2990, 1620, 1582, 1375, 1352, 1305, 1138, and 1077 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (t, J = 7.0 Hz, 3 H), 1.60 (s, 3 H), 2.01 (s, 1 H), 3.9–4.05 (m, 2 H), 5.05 (s, 1 H), 7.2–7.28 (m, 3 H), and 7.34–7.40 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.44, 24.82, 65.18, 79.38, 107.26, 118.51, 121.13, 127.21, 128.00, 137.54, 149.35, and 157.49; M_r+ calcd for $C_{12}H_{14}O_2$ 190.0993, found 190.0993. Confirmation of the regiochemical assignment was accomplished by hydrolysis to the corresponding indenone. Via the hydrolysis procedure for ethyl 1-butynyl ether, indenol (**15**) was hydrolyzed over a 90-min period with 5% hydrochloric acid to yield 45% of 3-methylinden-1-one (**16**) as a yellow oil: IR 1712, 1610, 1582, 1385, 1280, and 1192 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.23 (d, J = 1.3 Hz, 3 H), 5.69 (d, J = 1.3 Hz, 1 H), 7.09 (d, J = 7.2 Hz, 1 H), 7.21–7.30 (m, 1 H), and 7.33–7.44 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.07, 119.36, 121.66, 123.72, 129.54, 131.46, 133.11, 145.62, 162,31, and 197.82.

2-Butynyltrimethylsilane. Reaction of **1** with 2-butynyltrimethylsilane gave a 50% yield of 1,3-dimethyl-2-[(trimethylsilyl)methyl]-1*H*-inden-ol (**2o**) as a white crystalline solid: mp 57–58 °C (from hexanes); IR ($CHCl_3$) 3585, 2950, 1320, 1245, 1160, 1075, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9 H), 1.46 (s, 3 H), 1.75 (d, J = 13.8 Hz, 1 H), 1.89 (d, J = 13.8 Hz, 1 H), 1.92 (s, 3 H), 7.03–7.06 (m, 2 H), 7.21–7.3 (m, 1 H), and 7.36 (d, J = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.16, 10.97, 15.17, 23.59, 81.96, 117.61, 120.94, 124.55, 128.29, 128.54, 144.26, 147.29, and 148.69; m/e 246 (M^+), 156 (base), 141, 128, 114, and 73; M_r+ calcd for 246.1440, found 246.1433. Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 71.88; H, 8.87.

Satisfactory analytical data could not be obtained for this compound; however, all spectroscopic data are consistent with the assigned structure.

2-Pentynyltrimethylsilane. Reaction of **1** with 2-pentynyltrimethylsilane gave a 31% yield of 3-ethyl-1-methyl-2-[(trimethylsilyl)methyl]-1*H*-inden-1-ol (**2p**) as a white crystalline solid: mp 64–65 °C (from hexanes); IR ($CHCl_3$) 3575, 2955, 1595, 1460, 1447, 1320, 1240, 1112, 1092, and 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.11 (s, 9 H), 1.14 (t, J = 7.5 Hz, 3 H), 1.40 (s, 1 H), 1.46 (s, 3 H), 1.73 (d, J = 14.0 Hz, 1 H), 1.90 (d, J = 14.0 Hz, 1 H), 2.39 (q, J = 7.5 Hz, 2 H), 7.07–7.15 (m, 2 H), 7.20–7.28 (m, 1 H), and 7.37 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −0.22, 12.22, 14.52, 18.37, 23.15, 81.49, 117.70, 120.70, 123.97, 127.76, 134.00, 142.76, 146.06, and 148.72. Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.70; H, 9.32. Confirmation of the regiochemical assignment was accomplished by desilylation and comparison of the observed product with MeMgBr addition to 2-ethyl-3-methylinden-1-one.

A solution containing 60 mg of the above indenol in 13 mL of anhydrous tetrahydrofuran was treated with 0.5 mL of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran at room temperature, and the mixture was stirred for 10 min. At the end of this time, the reaction mixture was concentrated under reduced pressure, and the residue was subjected to silica gel radial chromatography with a 5% ethyl acetate–hexane mixture as the eluent to give 44 mg (100%) of 1,2-dimethyl-3-ethyl-1*H*-inden-1-ol (**19**) as a white crystalline solid: mp 88–89 °C; IR ($CHCl_3$) 3580, 2960, 2920, 1455 (s), 1448, 1320, 1090, and 1068 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.13 (t, J = 7.6 Hz, 3 H), 1.46 (s, 3 H), 1.88 (s, 3 H), 2.44 (q, J = 7.6 Hz, 2 H), 7.10–7.18 (m, 2 H), 7.21–7.29 (m, 1 H), and 7.38–7.44 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.67, 12.94, 18.25, 22.94, 81.81, 118.48, 121.36, 125.02, 128.15, 136.92, 142.84, 143.26, and 149.47. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.00; H, 8.61. This product was distinctly different from product obtained from MeMgBr addition to the previously reported indenone (**13**).

1-Hepten-4-yne. Reaction of **1** with 1-hepten-4-yne gave a 64% yield of a 1:1 mixture of 2-allyl-3-ethyl-1-methyl-1*H*-inden-1-ol (**2q**) and 3-allyl-2-ethyl-1-methyl-1*H*-inden-1-ol (**2r**) as an oily solid. The mixture of **2q** and **2r** was characterized: IR ($CHCl_3$) 3590, 3080, 3005, 2975, 2935, 2880, 1447, 1373, 1327, 1080, and 918 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.15 and 1.16 (both t, J = 7.6 Hz, 3 H total), 1.47 and 1.50 (both s, 3 H total), 1.65 and 1.66 (both s, 1 H total), 2.27–2.43 (m), and 2.45 (q, J = 7.6, 2 H total for both), 3.03–3.21 (m, 2 H), 4.99–5.17 (m, 2 H), 5.83–5.96 (m, 1 H), 7.1–7.27 (m, 3 H), and 7.33–7.38 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.55, 14.06, 17.26, 18.01, 23.08, 23.14, 28.49, 29.17, 82.02, 82.11, 114.92, 115.50, 118.42, 118.64, 120.76, 120.95, 124.89, 125.04, 127.72 (2 carbons), 132.89, 138.78, 134.64, 136.10, 141.95, 142.21, 143.47, 150.21, 148.81, 149.07. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.98; H, 8.52.

Preparation of (η^2-2-Acetyl-6-fluorophenyl)tetracarbonylmanganese (3a) and (η^2-2-Acetyl-4-fluorophenyl)-tetracarbonylmanganese (4a) by Reaction of 3′-Fluoroacetophenone with Benzylpentacarbonylmanganese. A solution containing 7.89 mmol of 3′-fluoroacetophenone and 2.7 g of benzylpentacarbonylmanganese in 75 mL of heptane was heated under reflux for 3 h. At the end of this time the reaction was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent. The first fraction contained 370 mg (15%) of a gold solid identified at (η^2-2-acetyl-4-fluorophenyl)tetracarbonylmanganese (**4a**) on the basis of its characteristic spectroscopic data; mp 137–139 °C (from hexanes); IR ($CHCl_3$) 2080, 1995, 1950, 1600, 1545, 1415, 1320, and 650 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.62 (s, 3 H), 7.2–7.3 (m, 1 H), 7.55 (dd, J = 8.1 and 2.4 Hz, 1 H), and 8.00 (dd, J = 8.1 and 5.9 Hz, 1 H); m/e 304 (M^+), 220, 192 (base), 138, 123, 95, and 55; M_r+ calcd 303.9580, found 303.9601. Anal. Calcd for $C_{12}H_6FMnO_5$: C, 47.39; H, 1.99. Found: C, 47.48; H, 2.02.

The second fraction contained 1.68 g (70%) of a yellow solid identified as (η^2-2-acetyl-6-fluorophenyl)tetracarbonylmanganese (**3a**): mp 103–105 °C (from hexanes); IR ($CHCl_3$) 2085, 1990, 1950, 1590, 1410, 1320, and 1300 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.64 (s, 3 H), 7.16–7.22 (m, 2 H), 7.68–7.74 (m, 1 H); m/e 304 (M^+), 220, 192 (base), 144, 123, 95, 74, and 55; M_r+ calcd 303.9580, found 303.9599. Anal. Calcd for $C_{12}H_6FMnO_5$: C, 47.39; H, 1.99. Found: C, 47.46; H, 2.04.

Reaction of 3a with Ethyl 1-Butynyl Ether. Complex **3a** was reacted with trimethylamine *N*-oxide and ethyl 1-butynyl ether to give a 71% yield of 4-fluoro-2-ethoxy-1-ethyl-1-methyl-1*H*-inden-1-ol (**6**) as a white solid: mp 57–59 °C; IR ($CHCl_3$) 3595, 2990, 1637, 1470, 1335, 1290, 1270, and 1038 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.19 (t, J = 7.5 Hz, 3 H), 1.36 (t, J = 7.0 Hz, 3 H), 1.48 (s, 3 H), 1.84 (br s, 1 H), 2.20–2.45 (m, 2 H), 4.00 (q, J = 7.0 Hz, 2 H), 6.84–6.94 (m, 1 H), and 7.0–7.18 (m, 2 H); m/e 236 (M^+), 207, 193 (base), 179, 175, and 146; M_r+ calcd 236.1213, Found 136.1214. Confirmation of this regiochemical assignment was accomplished by hydrolysis to the corresponding indenone.

A solution containing 74 mg of **6** in 5 mL of acetone was treated with 5 mL of 10% hydrochloric acid, and the mixture was stirred for 24 h. At the end of this time, the acetone was removed under reduced pressure, and the residue was extracted with methylene chloride. The organic layer was dried over magnesium sulfate, concentrated under reduced pressure, and subjected to silica gel radial chromatography with a 10% ethyl acetate–hexane mixture as the eluent to give 40 mg (67%) of 7-fluoro-2-ethyl-3-methylinden-1-one (**17**) as a yellow crystalline solid: mp 54–56 °C (from hexanes); IR ($CHCl_3$) 1705, 1615, 1600, 1462, 1240, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05 (t, J = 7.6 Hz, 3 H), 2.10 (s, 3 H), 2.27 (q, J = 7.6 Hz, 2 H), 6.75–6.85 (m, 2 H), and 7.25–7.35 (m, 1 H). Anal. Calcd for $C_{12}H_{11}FO$: C, 75.77; H, 5.83. Found: C, 75.70, H; 5.87.

Preparation of (η^2-2-Acetyl-6-chlorophenyl)tetracarbonylmanganese (3b) and (η^2-2-Acetyl-4-chlorophenyl)-tetracarbonylmanganese (4b) by Reaction of 3′-Chloroacetophenone with Benzylpentacarbonylmanganese. A so-

lution containing 5.24 mmol of 3′-chloroacetophenone and 1.8 g of benzylpentacarbonylmanganese in 70 mL of heptane was heated under reflux for 12 h. At the end of this time the reaction was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent. The first fraction contained 700 mg (42%) of a yellowish-orange solid identified as (η^2-2-acetyl-4-chlorophenyl)tetracarbonylmanganese (**4b**) on the basis of its characteristic spectroscopic data: mp 132–134 °C (from hexanes); IR ($CHCl_3$) 2080, 1995, 1940, 1585, and 1312 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.63 (s, 3 H), 7.40 (dd, J = 7.9 and 2.0 Hz, 1 H), 7.82 (d, J = 2.0 Hz, 1 H), and 8.02 (d, J = 7.9 Hz, 1 H); m/e 320 (M^+), 236, 208, 154, 139 (base), 111, 90, 75, and 55; M_r+ calcd 319.9284, found 319.9277. Anal. Calcd for $C_{12}H_6ClMnO_5$: C, 44.96; H, 1.89; Cl, 11.06. Found: C, 45.05; H, 1.98; Cl, 11.00.

The second fraction contained 735 mg (44%) of a yellowish-orange solid identified as (η^2-2-acetyl-6-chlorophenyl)tetracarbonylmanganese (**3b**): mp 105–107 °C (from hexanes); IR ($CHCl_3$) 2080, 1990, 1945, 1590, 1390, and 1315 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.62 (s, 3 H), 7.14 (dd, J = 7.6 and 7.7 Hz, 1 H), 7.54 (dd, J = 7.7 and 0.9 Hz, 1 H), and 7.73 (dd, J = 7.6 and 0.9 Hz, 1 H); m/e 320 (M^+), 236, 208 (base), 154, 139, 111, 90, and 55; M_r+ calcd 319.9284, found 319.9299. Anal. Calcd for $C_{12}H_6ClMnO_5$: C, 44.96; H, 1.89; Cl, 11.06. Found: C, 45.03; H, 1.91; Cl, 10.98.

Reaction of 3b with Ethyl 1-Butynyl Ether. Complex **3b** was reacted with trimethylamine *N*-oxide and ethyl 1-butynyl ether to give a 77% yield of 4-chloro-2-ethoxy-1-ethyl-1-methyl-1*H*-inden-1-ol (**7**) as a white crystalline solid: mp 58–60 °C; IR ($CHCl_3$) 3580, 2990, 1630, 1332, 1270, 1105, and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, J = 7.6 Hz, 3 H), 1.39 (t, J = 7.0 Hz, 3 H), 1.47 (s, 3 H), 1.83 (br s, 1 H), 2.28 (dt, J = 14.8 and 7.6 Hz, 1 H), 2.41 (dt, J = 14.8 and 7.6 Hz, 1 H), 3.99 (q, J = 7.0 Hz, 2 H), 7.02–7.18 (m, 2 H), and 7.24 (d, J = 6.8 Hz, 1 H); m/e 252 (M^+), 234, 223, 209, 191 (base), 143, 128, and 115; M_r+ calcd 252.0917, found 252.0921. Confirmation of this regiochemical assignment was accomplished by hydrolysis to the corresponding indenone.

A solution containing 70 mg of **7** in 5 mL of acetone was treated with 5 mL of 10% hydrochloric acid, and the mixture was stirred for 24 h. At the end of this time, the acetone was removed under reduced pressure, and the residue was extracted with methylene chloride. The organic layer was dried over magnesium sulfate, concentrated under reduced pressure, and subjected to silica gel radial chromatography with a 5% ethyl acetate–hexane mixture as the eluent to give 43 mg (75%) of 7-chloro-2-ethyl-3-melthylinden-1-one (**18**) as a yellow crystalline solid: mp 99–100 °C (from hexanes); IR ($CHCl_3$) 1703, 1590, 1445, and 997 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05 (t, J = 7.6 Hz, 3 H), 2.10 (s, 3 H), 2.29 (q, J = 7.6 Hz, 2 H), 6.92 (d, J = 7.0 Hz, 1 H), 7.06 (d, J = 8.2 Hz, 1 H), and 7.23 (dd, J = 8.2 and 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.15, 13.48, 16.08, 117.14, 125.94, 129.84, 130.08, 133.98, 137.15, 148.54, 151.46, and 194.81. Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.36; Cl, 17.15. Found: C, 69.64; H, 5.38; Cl, 17.24.

Preparation of (η^2-2-Acetyl-6-bromophenyl)tetracarbonylmanganese (3c) and (η^2-2-Acetyl-4-bromophenyl)tetracarbonylmanganese (4c) by Reaction of 3′-Bromoacetophenone with Benzylpentacarbonylmanganese. A solution containing 2.98 mmol of 3′-bromoacetophenone and 0.94 g of benzylpentacarbonylmanganese in 70 mL of heptane was heated under reflux for 12 h. At the end of this time the reaction was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent. The first fraction collected contained 417 mg (38%) of an orange-yellow solid identified as (η^2-2-acetyl-4-bromophenyl)tetracarbonylmanganese (**4c**) on the basis of its characteristic spectroscopic data: mp 129–130.5 °C (from hexanes); IR ($CHCl_3$) 2085, 2000, 1945, 1590, 1400, 1312, and 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.63 (s, 3 H), 7.52 (dd, J = 7.9 and 1.6 Hz, 1 H), 7.97 (d, J = 7.9 Hz, 1 H), and 7.95 (br s, 1 H). Anal. Calcd for $C_{12}H_6BrMnO_5$: C, 39.49; H, 1.66; Br, 21.89. Found: C, 39.55, H, 1.70; Br, 21.82.

The second fraction contained 290 mg (27%) of a yellow solid identified as (η^2-2-acetyl-6-bromophenyl)tetracarbonylmanganese (**3c**): mp 133–135 °C (from hexanes); IR ($CHCl_3$) 2080, 1995, 1950, 1595, 1390, and 1320 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.60 (s, 3 H), 7.06 (dd, J = 7.5 and 7.4 Hz), 7.72 (d, J = 7.5 Hz, 1 H), and 7.78 (d, J = 7.4 Hz, 1 H). Anal. Calcd for $C_{12}H_6BrMnO_5$: C, 39.49; H, 1.66; Br, 21.89. Found: C, 39.52; H, 1.69; Br, 21.80.

Preparation of (η^2-2-Acetyl-4-methylphenyl)tetracarbonylmanganese (4d) by Reaction of 3′-Methylacetophenone with Benzylpentacarbonylmanganese. A solution containing 6.39 mmol of 3′-methylacetophenone and 2.1 g of benzylpentacarbonylmanganese in 75 mL of heptane was heated to reflux for 12 h. At the end of this time, the reaction was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent to give 1.47 g (77%) of an orange solid identified as (η^2-2-acetyl-4-methylphenyl)-tetracarbonylmanganese (**4d**) on the basis of its characteristic spectroscopic data: mp 122–125 °C (from hexanes); IR ($CHCl_3$) 2080, 1985, 1930, 1575, 1525, 1317 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.38 (s, 3 H), 2.61 (s, 3 H), 7.28 (dd, J = 7.5 and 1.3 Hz, 1 H), 7.68 (br s, 1 H), and 7.97 (d, J = 7.5 Hz, 1 H); m/e 300 (M^+), 234, 216, 188 (base), 134, 119, 105, 91, 65, and 55; M_r+ calcd 299.9830, found 299.9838. Anal. Calcd for $C_{13}H_9MnO_5$: C, 52.02; H, 3.02. Found: C, 52.09; H, 3.07.

Preparation of (η^2-2-Acetyl-6-methoxyphenyl)tetracarbonylmanganese (3e) and (η^2-2-Acetyl-4-methoxyphenyl)tetracarbonylmanganese (4e) by Reaction of 3′-Methoxyacetophenone with Benzylpentacarbonylmanganese. A solution containing 6.89 mmol of 3-methoxyacetophenone and 2.3 g of benzylpentacarbonylmanganese in 75 mL of hepatne was heated under reflux for 4 h and 30 min. At the end of this time the reaction was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent. The first fraction collected contained 1.38 g (63%) of a yellowish-solid identified as (η^2-2-acetyl-6-methoxyphenyl)tetracarbonylmanganese (**3e**) on the basis of its characteristic spectroscopic data: mp 121–124 °C (from hexanes); IR ($CHCl_3$) 2080, 1990, 1945, 1590, 1580, 1400, and 1240 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.61 (s, 3 H), 3.87 (s, 3 H), 6.92 (d, J = 7.8 Hz, 1 H), 7.19 (dd, J = 7.8 and 7.6 Hz, 1 H), and 7.52 (d, J = 7.6 Hz, 1 H); m/e 316 (M^+), 266, 232, 204, 174, 150, 135 (base), 107, 92, 77, and 55; M_r+ calcd 315.9780, found 315.9780. Anal. Calcd for $C_{13}H_9MnO_6$: C, 49.39; H, 2.87. Found: C, 49.32; H, 2.88.

The second fraction contained 600 mg (28%) of a yellow solid identified as (η^2-2-acetyl-4-methoxyphenyl)tetracarbonylmanganese (**4e**): mp 110–113 °C (from hexanes); IR ($CHCl_3$) 2080, 1990, 1935, 1580, 1530, and 1330 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.61 (s, 3 H), 3.85 (s, 3 H), 7.14 (dd, J = 8.1 and 2.6 Hz, 1 H), 7.38 (d, J = 2.6 Hz, 1 H), and 7.94 (d, J = 8.1 Hz, 1 H); m/e 316 (M^+), 204, 150, 135 (base), 107, 92, 77, and 55; M_r+ calcd 315.9780, found 315.9772. Anal. Calcd for $C_{13}H_9MnO_6$: C, 49.39; H, 2.87. Found: C, 49.48; H, 2.89.

Preparation of (η^2-2-Acetyl-4-(trifluoromethyl)phenyl)-tetracarbonylmanganese (4f) by Reaction of 3′-(Trifluoromethyl)acetophenone with Benzylpentacarbonylmanganese. A solution containing 5.51 mmol of 3′-(trifluoromethyl)acetophenone and 1.8 g of benzylpentacarbonylmanganese in 75 mL of heptane was heated to reflux for 4 h and 30 min. At the end of this time the reaction mixture was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent to give 1.66 g (85%) of a yellowish-orange solid identified as (η^2-2-acetyl-4-(trifluoromethyl)phenyl)tetracarbonylmanganese (**4f**) on the basis of its characteristic spectroscopic data: mp 128–131 °C (from hexanes); IR ($CHCl_3$) 2090, 1995, 1945, 1605, 1310, 1265, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.70 (s, 3 H), 7.61 (d, J = 7.8 Hz, 1 H), 8.03 (s, 1 H), 8.25 (d, J = 7.8 Hz, 1 H); m/e 354 (M^+), 270, 242 (base), 173, 143, 125, and 55; M_r+ calcd 353.9548, found 353.9610. Anal. Calcd for $C_{13}H_6F_3MnO_5$: C, 44.09; H, 1.71. Found: C, 44.16; H, 1.75.

Reaction of 4f with 3-Hexyne. The above complex was reacted with trimethylamine *N*-oxide and 3-hexyne to give a 58% yield of 2,3-diethyl-1-methyl-7-(trifluoromethyl)-1*H*-inden-1-ol (**5**) as a white crystalline solid: mp 136–138 °C (from ethyl acetate–hexanes); IR ($CHCl_3$) 3590, 2980, 1620, 1330, 1270, 1170, 1125, 1085, 1060, and 840 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15 (t, J = 7.5 Hz, 3 H), 1.17 (t, J = 7.5 Hz, 3 H), 1.50 (s, 3 H), 1.66 (s, 1 H), 2.25–2.55 (m, 2 H), 2.45 (q, J = 7.5 Hz, 2 H), 7.21 (d, J = 7.7 Hz, 1 H), 7.51 (d, J = 7.7 Hz, 1 H), and 7.57 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.11, 14.44, 17.73, 18.30, 23.22, 82.35, 118.07, 118.51, 125.71, 125.75, 127.27 (q, $^1J_{C,F}$ = 32 Hz), 137.18,

146.25, 150.00, and 151.77; m/e 270 (M^+), 241 (base), and 226; M_r+ calcd 270.1232, found 270.1228. Anal. Calcd for $C_{15}H_{17}F_3O$: C, 66.66; H, 6.34. Found: C, 66.74; H, 6.35.

Preparation of (η^2-2-Acetyl-4-cyanophenyl)tetracarbonylmanganese (4g) by Reaction of 3-Acetylbenzonitrile with Benzylpentacarbonylmanganese. A solution containing 2.7 mmol of 3-acetylbenzonitrile and 0.85 g of benzylpentacarbonylmanganese in 50 mL of heptane was heated under reflux for 12 h. At the end of this time the reaction mixture was concentrated, and the residue was subjected to silica gel flash chromatography with hexane as the eluent to give as the only isolable product 88 mg (11%) of (2-acetyl-4-cyanophenyl)tetracarbonylmanganese (**4g**) as an orange solid: mp 109–110 °C (from hexanes); IR ($CHCl_3$) 2230, 2085, 2000, 1950, 1595, and 1310 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.69 (s, 3 H), 7.58 (d, J = 7.6 Hz, 1 H), 8.07 (s, 1 H), and 8.27 (d, J = 7.6 Hz, 1 H). Anal. Calcd for $C_{13}H_6MnNO_5$: C, 50.19; H, 1.94; N, 4.50. Found: C, 50.20; H, 2.02; N, 4.48.

Reaction of α-Tetralone with Benzylpentacarbonylmanganese. A solution containing 6.9 mmol of α-tetralone and 2.37 g of benzylpentacarbonylmanganese in 75 mL of heptane was heated under reflux for 3 h and 45 min. At the end of this time the mixture was concentrated, and the residue was subjected to flash chromatography with hexane as the eluent to give 1.98 g (92%) of [4a,8a-(5,6-dihydro-8(7*H*)-naphthalenone)]tetracarbonylmanganese (**10**) as orange-yellow crystals: mp 96–98 °C (from hexanes); IR ($CHCl_3$) 2080, 1990, 1940, 1592, 1570, 1545, 1423, and 1410 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.10 (tt, J = 6.4 and 6.1 Hz, 2 H), 2.71 (t, J = 6.4 Hz, 2 H), 2.90 (t, J = 6.1 Hz, 2 H), 6.93 (d, J = 7.4 Hz, 1 H), 7.34 (dd, J = 7.4 and 7.3 Hz, 1 H), and 7.91 (d, J = 7.3 Hz, 1 H); m/e 312 (M^+), 258, 228, 200, 146, 131, 118 (base), and 90; M_r+ calcd 311.9830, found 311.9835. Anal. Calcd for $C_{14}H_9MnO_5$: C, 53.87; H, 2.91. Found: C, 53.91; H, 2.95.

Attempted reaction of this material with trimethylamine *N*-oxide and 3-hexyne at room temperature in acetonitrile gave a complex mixture and no evidence of cyclized product.

Reaction of Benzosuberone with Benzylpentacarbonylmanganese. A solution containing 3.9 mmol of benzosuberone and 1.23 g of benzyl(pentacarbonyl)manganese in 75 mL of heptane was heated under reflux for 10 h. At the end of this time the mixture was concentrated, and the residue was subjected to flash chromatography with hexane as the eluent to give 81% of [4a,9a-(benzosuber-9-one)]tetracarbonylmanganese (**11**) as yellow crystals: mp 96–97 °C (from hexanes); IR ($CHCl_3$) 2080, 1990, 1935, 1572, and 1558 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.73–1.85 (m, 2 H), 1.87–2.0 (m, 2 H), 2.89 (t, J = 6.0 Hz, 2 H), 2.96 (t, J = 6.0 Hz, 2 H), 6.95 (d, J = 7.3 Hz, 1 H), 7.30 (dd, J = 7.3 and 7.3 Hz, 1 H), and 7.93 (d, J = 7.5 Hz, 1 H). Anal. Calcd for $C_{15}H_{11}MnO_5$: C, 55.23; H, 3.40. Found: C, 55.22; H, 3.47.

The above complex was reacted with trimethylamine *N*-oxide and 3-hexyne to yield 65% of 1,2-diethyl-9a-hydroxy-6,7,8,9-tetrahydro-9a*H*-benz[*cd*]azulene (**12**) as a white crystalline solid: mp 103–104 °C (from hexanes); IR ($CHCl_3$) 3585, 2960, 2920, 2840, 1595, 1447, 1087, 1067, 1010, and 985 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.08–1.52 (m, 9 H), 1.9–2.12 (m, 2 H), 2.17–2.7 (m, 7 H), 3.20 (m, 1 H), 6.84 (d, J = 7.1 Hz, 1 H), 6.98 (d, J = 7.0 Hz, 1 H), and 7.11 (dd, J = 7.1 and 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.33, 14.95, 17.50, 18.54, 26.75, 28.89, 32.90, 34.46, 85.30, 116.16, 125.63, 127.99, 138.44, 139.57, 142.87, 146.69, and 148.76. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.15; H, 9.17.

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Registry No. **1**, 50831-23-7; **2a**, 117583-04-7; **2b**, 5418-21-3; **2c**, 117583-05-8; **2d**, 117583-06-9; **2e**, 117583-07-0; **2f**, 117583-08-1; **2g**, 117583-09-2; **2h**, 117583-10-5; **2i**, 117583-11-6; **2j**, 117583-12-7; **2k**, 117583-13-8; **2l**, 117583-14-9; **2m**, 117583-15-0; **2n**, 117583-16-1; **2o**, 117583-17-2; **2p**, 117583-18-3; **2q**, 117583-19-4; **2r**, 117583-20-7; **3a**, 117583-32-1; **3b**, 117583-33-2; **3c**, 117583-34-3; **3e**, 55401-25-7; **4a**, 117583-35-4; **4b**, 117583-36-5; **4c**, 117583-37-6; **4d**, 55401-24-6; **4e**, 55401-27-9; **4f**, 117583-38-7; **4g**, 117583-39-8; **5**, 117583-30-9; **6**, 117583-26-3; **7**, 117583-28-5; **8**, 529-34-0; **9**, 826-73-3; **10**, 117583-40-1; **11**, 117583-41-2; **12**, 117583-31-0; **13**, 75421-59-9; **14**, 117583-21-8; **15**, 117583-24-1; **16**, 22303-81-7; **17**, 117583-27-4; **18**, 117583-29-6; **19**, 117583-25-2; **20**, 117583-23-0; EtC≡CEt, 928-49-4; PhC≡CPh, 501-65-5; C_4H_9C≡CH, 693-02-7; *c*-$C_6H_{11}C$≡CH, 931-48-6; PhC≡CH, 536-74-3; Me_3SiC≡CH, 1066-54-2; C_4H_9C≡$CSiMe_3$, 3844-94-8; EtO_2CC≡CMe, 4341-76-8; EtO_2CC≡CEt, 55314-57-3; *c*-$C_6H_{11}C$≡CCO_2Et, 33547-94-3; EtOC≡CH, 927-80-0; EtOC≡CEt, 14272-91-4; EtOC≡$CSiMe_3$, 1000-62-0; Me_3SiCH_2C≡CMe, 18825-29-1; EtC≡CCH_2SiMe_3, 40748-39-8; 3-FC_6H_4COMe, 455-36-7; 3-ClC_6H_4COMe, 99-02-5; 3-BrC_6H_4COMe, 2142-63-4; 3-MeC_6H_4COMe, 585-74-0; 3-$MeOC_6H_4COMe$, 586-37-8; 3-HOC_6H_4COMe, 121-71-1; 3-$F_3CC_6H_4COMe$, 349-76-8; 3-$O_2NC_6H_4COMe$, 121-89-1; 3-NCC_6H_4COMe, 6136-68-1; $PhCH_2Mn(CO)_5$, 14049-86-6; acetophenone, 98-86-2; trimethylamine *N*-oxide, 1184-78-7; 2-ethoxy-3-ethyl-1-methyl-1*H*-inden-1-ol, 117583-22-9; 1-hepten-4-yne, 19781-78-3.

Efficient Preparation of Cis Vicinal Tertiary Diamines from 2-Hydroxy Ketones in Two Steps†,[1]

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Cyclic (C_5 and C_6) cis vicinal tertiary diamines are efficiently prepared by catalytic hydrogenation, Pd(C), of the corresponding N-substituted amino enamines, e.g. **6**. The latter are obtained by *p*-toluenesulfonic acid catalyzed condensation of secondary amines with cyclic 2-hydroxy ketones in refluxing benzene under Dean–Stark conditions or from the N-substituted 2-amino ketones. For example *cis*-1,2-dipyrrolidinocyclohexane has been obtained from adipoin in 69% overall yield, isolated.

Cis vicinal tertiary diamines, a hitherto neglected functionality, are potentially important ligands for Pt^{2+}, Mg^{2+}, Zn^{2+}, and Li^+ as well as catalysts for the reactions of organolithium compounds.[2] However, due to the absence of efficient methods to make them, these interesting

† Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

(1) Abstracted from the Ph.D. Thesis of Howard Rosenzweig, The Ohio State University, 1987.

(2) Langer, A. W. *Trans. N. Y. Acad. Sci. Ser. II* **1965**, *27*, 741.

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