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Direct Preparation of Differentially Protected Hydroquinone-Chromium(tricarbonyl) Complexes from the Benzannulation Reaction of Fischer Carbene Complexes

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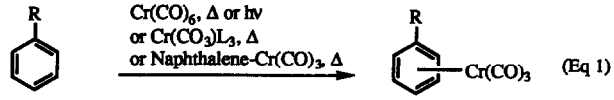
Abstract: Methods for the preparation of differentially protected hydroquinone-chromium(tricarbonyl) complexes directly from alkenyl Fischer carbene complexes and alkynes are described. The benzannulation reaction of methoxy carbene complexes with alkynes produces hydroquinone chromium tricarbonyl complexes as their mono-methyl ethers which may be protected at the free aryl hydroxyl with either sequential or concurrent reaction with a variety of electrophiles, including silyl chlorides and triflates, acyl and alkyl halides, and anhydrides. The yields obtained for the arene complexes equal or exceed the yields for the phenol or quinone products isolated from the same benzannulation reactions in which the chromium tricarbonyl group has been oxidatively liberated from the arene. Differentially protected complexes can also be obtained directly from the reaction of β-silyl-alkenyl complexes with alkynes. These methods are not applicable to the preparation of differentially protected naphthohydroquinone chromium tricarbonyl complexes from the reaction of aryl carbene complexes with alkynes.

Introduction

Since the initial report of the synthesis of benzene-chromium(tricarbonyl) from (bis)benzene-chromium by Fischer and Ofele,[3] a variety of synthetic approaches to this frequently studied class of compounds have been developed. In addition to the simple thermolysis of $Cr(CO)_6$ in the presence of the arene reported independently by three groups in 1958,[4] methods for obtaining these complexes using milder conditions and shorter reaction times have been discovered.[5] (Equation 1) These milder methods include 1) the more facile thermolysis of $Cr(CO)_6$ in the presence of donating solvents such as THF or piperidine, 2) the photolysis of $Cr(CO)_6$ at ambient temperature, 3) the facile thermolysis of $Cr(CO)_3L_3$, where L is a poorer pi-acceptor such as pyridine, picoline, acetonitrile, or ammonia, or 4) the transfer of the $Cr(CO)_3$ fragment from another, less

stable arene complex, such as naphthalene-Cr(CO)3. Common to all of these methods is the basic approach of attaching a metal fragment to an arene ring necessarily obtained by some other synthetic means prior to arene-Cr(CO)3 complex formation.[6]

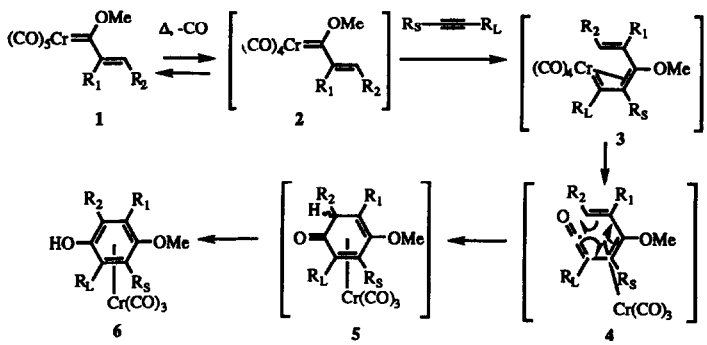


(Eq 1)

These reactions are believed to share a common mechanism for the formation of arene-Cr(CO)3 complexes.[5] Thermal or photolytic dissociation of one of the ligands of the initial chromium species generates a reactive unsaturated metal center which attacks the free arene, forming an η^2-arene-Cr(CO)3L2 complex. This newly-formed chromium species becomes an η^6-arene-Cr(CO)3 complex after intramolecular displacement of the remaining two ligands by the arene ring. A limitation common to these approaches is the difficulty in obtaining selective complexation of a particular arene ring in substrates with multiple, electronically similar arene rings.

A fundamentally different synthetic route to arene-Cr(CO)3 complexes is known.[7] This approach begins with a chromium (0) organometallic species, an α,β-unsaturated Fischer carbene complex **1**, which reacts with alkynes under mild conditions to give arene-Cr(CO)3 complexes. Initially reported by Dotz in 1975,[8] this reaction assembles the arene in the coordination sphere of the chromium atom. A mechanism for this transformation is shown in Scheme 1.[9] After initial loss of CO either by mild heating or photolysis at reduced temperature, reaction with a molecule of alkyne yields a new α,β-unsaturated carbene **3**. This non-heteroatom stabilized complex can undergo CO insertion, generating **4**, a vinyl ketene coordinated to a Cr(CO)3 fragment. Electrocyclic ring closure followed by tautomerization generates **6**, a hydroquinone monomethyl ether Cr(CO)3 complex.

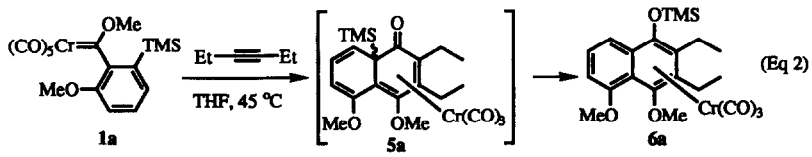
Scheme 1



Despite the fact that the benzannulation products are arene-Cr(CO)3 complexes, isolated yields of these complexes have almost always been significantly lower than the yields of the benzannulation products obtained after oxidative removal of the metal fragment. This is true for the reactions of both alkenyl and aryl carbene complexes which generate chromium tricarbonyl complexes of mono-methyl ether hydroquinones and naphthohydroquinones, respectively. With very few exceptions, mono-methyl ether hydroquinones and naphthohydroquinones are very labile ligands for chromium tricarbonyl fragments. Aryl carbene complexes yield naphthalene Cr(CO)3 complexes, which are known to readily lose their metal fragments by slipping from η^6 to η^4 metal coordination,[10] regaining the aromaticity of the ring adjacent to the complexed ring and making

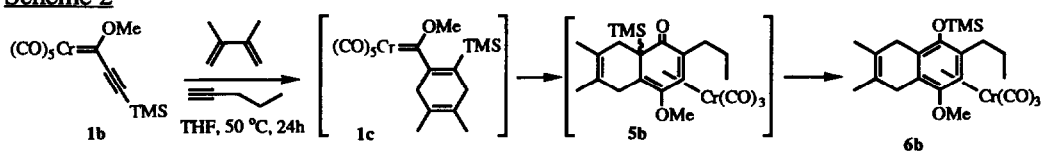
the chromium fragment easily dislodged by coordinating ligands or by oxidation. Alkenyl carbene complexes yield simple mono-methyl ether hydroquinone-Cr(CO)3 complexes, which exhibit the sensitivity to oxidative decomplexation characteristic of phenolic-Cr(CO)3 complexes.[11] Because of the lability of the metal fragment, purification of the benzannulation-generated Cr(CO)3 complexes leads to significant losses. Even flash column chromatography under inert atmosphere at -20 °C, followed by recrystallization typically gives yields of arene-Cr(CO)3 complexes which are less than half of the yields for the purified free arenes available from the same benzannulation reaction followed by an oxidative workup either by air or by an added external oxidant.

The production of more stable arene Cr(CO)3 complexes by protecting the free hydroxyl of phenol complexes as esters has been known since 1959,[11] when Nicolls and Whiting described the conversion of the unstable Cr(CO)3 complex of phenol to the stable acetate derivative. We sought to test the possibility of obtaining more stable arene complexes from the benzannulation reaction by protecting the generated hydroxy group as a trimethylsilyl (TMS) ether. Since the migratory ability of the TMS group had been previously established to be greater than that of hydrogen,[12] we attempted to substitute the TMS group for the proton which migrates in the final tautomerization of **5** to **6** (Scheme 1). Our initial effort at this approach made use of the aryl complex **1a**.[13] As is shown in Equation 2, the desired arene complex **6a** was not found in the product mixture.



In contrast to this early result, we later found that the benzannulation of the alkenyl complex **1c** gave a clean conversion to the desired arene complex **6b**[14] (Scheme 2). As we had hoped, this protected complex was much more stable than the benzannulation products of simple alkenyl complexes in which the hydroxyl was unprotected. The silylated arene complex **6b** was an air-stable crystalline solid. However, it could only be purified by recrystallization since it proved to be unstable to silica gel. The difference in the results from **1a** and **1c** has not been thoroughly explored. It seems probable from the complexity of the reaction mixtures obtained from benzannulations with **1a** that intermediates like **5a** are only one of many formed. In contrast, the reaction of **1c** presumably cleanly generates the intermediate **5b**.

Scheme 2

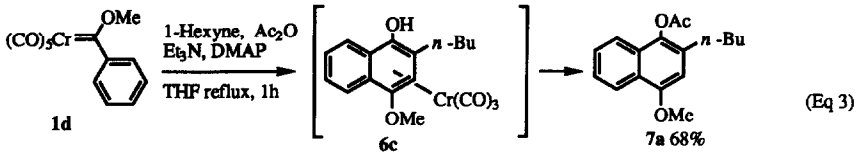


We recently communicated the benzannulation of alkenyl Fisher carbene complexes followed by intramolecular addition of nucleophiles to the generated arene-Cr(CO)3 complexes.[2] As a part of the development of that synthetic method, we have found ways to obtain air- and silica-gel stable, bis-protected hydroquinone-Cr(CO)3 complexes in yields that equal or, in many cases, exceed the yields of the free arenes

obtained by oxidation of crude benzannulation mixtures. Herein we report a full account of our work directed at obtaining stable arene complexes directly from the benzannulation reaction.

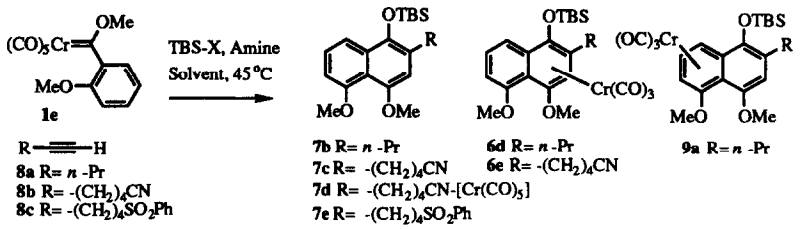
Results with Aryl Carbene Complexes

In the historical development of the benzannulation reaction the early focus was primarily on reactions of aryl carbene complexes with alkynes. There are no reports in the literature of successful attempts to protect the phenol function in the 4-alkoxy-1-naphthyl chromium tricarbonyl complexes (such as **6c** in Eq 3) while at the same time retaining the metal complexation. In addition to failed attempts to generate silyl-protected arene complexes from **1a**, attempts to *ex post facto* O-alkylate the metal-complexed benzannulation products from aryl carbene complexes such as **1d**, which were known to give good yields of annulation products, led to loss of the metal fragment. An example in the literature from the work of Yamashita and Toy[15] is shown in



(Eq 3)

equation 3 and although they were not attempting explicitly to isolate the complexed arene, the benzannulation was carried out in the presence of reagents for acetylation, but only the free protected arene **7a** was isolated, reflecting the lability of the Cr(CO)3 fragment of the benzanulation products derived from aryl complexes. This and several other related unpublished examples from our laboratory are consistent with the difficulty encountered in the attempts at silylation of the naphthol chromium tricarbonyl complexes which are summarized in Table I.



R—≡—H
8a R= *n* -Pr
8b R= -$(CH_2)_4$CN
8c R= -$(CH_2)_4SO_2Ph$

7b R= *n* -Pr
7c R= -$(CH_2)_4$CN
7d R= -$(CH_2)_4$CN-[$Cr(CO)_5$]
7e R= -$(CH_2)_4SO_2Ph$

6d R= *n* -Pr
6e R= -$(CH_2)_4$CN

9a R= *n* -Pr

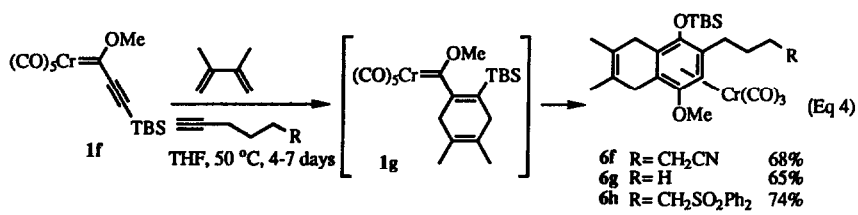
Table 1 Benzannulation/Silylation with Aryl Complex 1e

Entry	Solvent	TBS-X	Amine	Alkyne	Product (Yield)
1	Heptane	OTf	2,6-Lutidene	**8b**	**7c** (22) + **7d**(?) (tr)
2	CH_2Cl_2	OTf	2,6-Lutidene	**8b**	**7c** (22) + **7d**(?) (tr)
3	Heptane	Cl	Et_3N	**8c**	**7e** (not determined)
4	THF	Cl	Et_3N	**8a**	**7b** (not determined)
5	Heptane	Cl	Et_3N	**8a**	**6d** + **9a** (34)
6	CH_2Cl_2	OTf	2,6-Lutidene	**8a**	**7b** (86), **6d** + **9a** (tr)

Our initial target was **6e**, since we wanted to explore sequential benzannulation/intramolecular nucleophilic substitution reactions.[2] Unfortunately, we were unable to obtain arene complexes with a tethered carbanion stabilizing group. Inclusion of a nitrile in the alkyne in reactions in non-coordinating solvents gives low yields of the protected uncomplexed naphthalene **7c** along with a small amount of material containing a chromium pentacarbonyl fragment which has been tentatively identified as the nitrile coordinated derivative **7d**. Alkyne **8c**, containing a tethered phenyl sulphone, reacts with carbene complex **1e** in heptane to give only the silylated benzannulation product **7e** with no detectable amount of an organometallic complex. Use of the non-coordinating solvent heptane and an alkyne with no heteroatoms (Table 1, entry 5) leads to modest and variable yields of arene complexes which are generally mixtures of **6d** and **9a**. A similar mixture of **6d** and **9a** is obtained by sequential annulation/silylation for complex **1e** in heptane (see Experimental section). Even 1-pentyne **8a** fails to yield arene complexes in the mildly coordinating solvent THF.

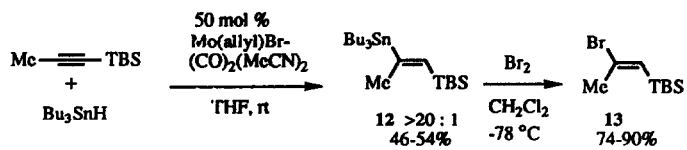
Stable Arene Complexes via Silyl Migration in Alkenyl Complexes

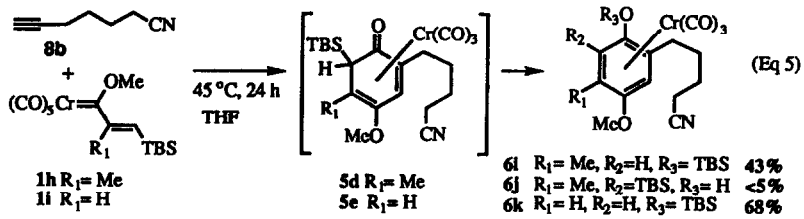
Our initial efforts at obtaining complexes which would be suitable substrates for intramolecular nucleophilic addition directly from benzannulation reactions made use of the silyl migration methodology. Although previous work had shown the TMS group able to migrate[14] (Scheme 2), we did not know if the more bulky *tert*-butyldimethylsilyl (TBS) group necessary for complexes with the desired stability would also migrate effectively. Analogous to previous work, the TBS-ethynyl complex **1f**, excess 2,3-dimethylbutadiene, and a slight excess of 6-heptynylnitrile **8b** were heated at 50 ° C in THF for six days (Equation 4). As indicated, this route gave direct access to the air- and silica gel-stable complexes **6f-h**. The sequential Diels-Alder generation of **1g** followed by benzannulation is slower than the TMS analogue shown in Scheme 2 presumably because of the adverse steric interaction between the TBS substituent of **1f** and the approaching diene.



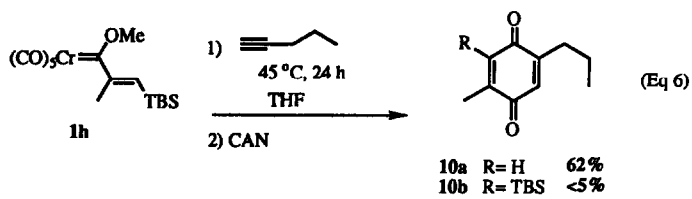
We were also interested in extending the silyl migration strategy to β-TBS alkenyl carbene complexes not derived from Diels-Alder reactions of alkynyl carbene complexes. The first of this type of carbene complex which we sought to make was complex **1h** (Eq 5). We hoped to have access to complex **6i**, another substrate for intramolecular nucleophilic attack, from the benzannulation reaction of **1h**. Complex **1h** was made using the standard Fischer method (see Experimental Section) by condensing the corresponding vinyllithium reagent with chromium hexacarbonyl. The required vinyllithium was obtained from bromide **13** which was made accessible by the regioselective hydrostannylation[30] shown in Scheme 3.

Scheme 3





Heating **1h** in the presence of alkyne **8b** in THF gives the desired complex **6i**, but only in moderate yield (Eq 5). Unlike the silyl carbene complexes **1c** and **1g** obtained from Diels-Alder reactions, complex **1h** contains both a silyl substituent and proton in position to migrate during the aromatization of the complexed cyclohexadienone **5d**. Competetive rates of migration would lead to a mixture of the stable silyl-protected complex **6i** and the unstable unprotected complex **6j**. This possibility was explored by treating the crude annulation mixture from **1h** and 1-pentyne with oxidant (Eq 6). After treatment with excess ceric ammonium nitrate (CAN), the only quinone obtained was **10a**, demonstrating the TBS group as the predominant migratory species. The reason for the lower yield of **6i** versus **10a** was not further explored because of our discovery of the much easier route to the desired arene complexes discussed in the next section. As indicated in Equation 5, another member of this class of β-TBS vinyl carbene complexes, **1i**, annulates efficiently, giving arene complex **6k** in good yield. This result is interesting, since **1i** serves as an annulation equivalent for the parent vinyl complex which failed to give significant amounts of benzannulation products.[16b,17] A more complete study of the reactivity of complex **1i** will be the subject of a separate report.[17]



Sequential Benzannulation/Protection of Alkenyl Complexes

Hoping to increase synthetic efficiency and flexibility, we considered the possibility of obtaining protected arene-Cr(CO)3 complexes from simple alkenyl carbenes. Our initial attempt is shown in Table 4, entry 2. Acetic anhydride and triethylamine were added to a mixture of cyclohexenyl carbene complex **1m** and alkyne **8b** in THF. After heating, aqueous workup, and chromatography on silica gel, an encouraging 31% yield of arene complex **6w** was obtained. This result showed that the decreased lability of the metal fragment of hydroquinone versus naphthohydroquinone chromium tricarbonyl complexes would allow their direct synthesis from simple alkenyl complexes, generating first the complexed hydroquinone mono-methyl ethers followed by protection of the free phenolic function with an electrophile. Also significant for the prospects of sequential benzannulation/ nucleophilic addition was the fact that the pendant nitrile did not dislodge the metal fragment.

Since Fischer carbene complexes are known to react with amines,[18] we decided to investigate benzannulations under standard conditions followed by addition of electrophile and an amine base. As the results summarized in Table 2 show, this method is effective. The isolated yields of the arene complexes compare favorably to the yields of arenes available from the benzannulation followed by oxidative removal of

the metal. The reaction proved to be general for the carbene complexes examined. Complex **1j** was intially prepared to see if an α-TMS vinyl carbene complex would yield cyclopentadienones as has been observed for the β-TMS vinyl carbene complex.[19] No detectable amounts of cyclopentadienones were observed for the three reactions of **1j** shown in Table 2. Good yields of the normal benzannulation products could be isolated indicating that complex **1j** can function similarly to **1i** as a benzannulation synthon for the parent vinyl carbene complex. In addition, since the TMS-aryl carbon bond can be cleaved to yield oxygenated products,[20] **1j** also functions as a synthon for α-alkoxy carbene complexes which give low yields of annulation products.[13] The yield from the reaction of the *trans* -propenyl complex **1k** indicated in entry 4 in Table 2 is surprisingly low and this most likely this has to do with difficulty in protecting the hindered 2,6-disubstituted phenol function in the benzannulation product. This is reflected in the fact that only for the reactions of complex **1k** was the use of TBS triflate necessary to silylate the intermediate hydroquinone mono-methyl ether complex. In general, internal as well as terminal alkynes gave reasonable yields of the desired arene complexes which, as shown in Table 2, entry 8, gives ready access to hexasubstituted aryl complexes.

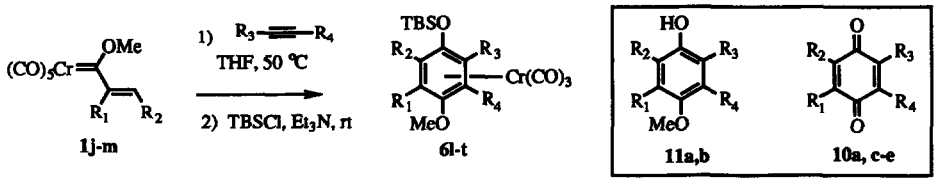


Table 2 Sequential Benzannulation/Silylation

Entry	Carbene Complex	R1	R2	R3	R4	Arene Complex	Free Arene
1	**1j**	TMS	H	Et	Et	**6l** (38)	**11a** (33)
2	**1j**	TMS	H	*n* -Pr	H	**6m** (60)	**10c** (76)
3	**1j**	TMS	H	-$(CH_2)_4$CN	H	**6n** (52)	
4	**1k**	H	Me[a]	-$(CH_2)_4$CN	H	**6o** (22)	**10d** (57)
5	**1l**	Me	H	Et	Et	**6p** (59)	
6	**1l**	Me	H	*n* -Pr	H	**6q** (65)	**10a** (51)[b]
7	**1l**	Me	H	-$(CH_2)_4$CN	H	**6i** (67)	**10e** (76)
8	**1m**	-$(CH_2)_4$-		Et	Et	**6r** (65)	
9	**1m**	-$(CH_2)_4$-		*n* -Pr	H	**6s** (65)	**11b** (61)[b]
10	**1m**	-$(CH_2)_4$-		-$(CH_2)_4$CN	H	**6t** (65)	

[a] TBSOTf/Et_3N used for this reaction. [b] Ref. 16a.

Solvent effects[21] appear to be minimal for this reaction sequence. For example the *iso* -propenyl carbene complex **1l** annulated with 1-pentyne followed by silylation with TBSCl/Et_3N, gives arene complex **6q** in 57 % yield in heptane and 40 % in acetonitrile (See Table 2, entry 6). We were surprised to find that even the highly-coordinating acetonitrile can be used as solvent without drastically reducing the efficiency of the reaction. Reactions in methylene chloride give yields similar to those run in THF. Because reactions in heptane become heterogeneous, THF and methylene chloride are the solvents of choice for these reactions.

Compared to the multistep synthesis of carbene **1i** (Scheme 3), this sequential benzannulation/protection sequence using readily available alkenyl carbene complexes is simple and straightforward. Experimentally all that is required is thorough deoxygenation of the reaction mixture by the freeze-thaw method before the benzannulation and immediately after addition of the silylating agent and amine.

Concurrent Benzannulation/Protection of Alkenyl Complexes

Our successful efforts to find an even more efficient method for obtaining the differentially-protected hydroquinone complexes from carbene complexes is summarized in Table 3. Eliminating the need for the second deoxygenation of the reaction mixture after addition of the electrophile and amine, an alkenyl carbene complex, alkyne, silylating agent and amine are heated together in deoxygenated solvent under argon for 18 to 24 hours, leading to the direct formation of the protected complexes. Initially we tried using the non-nucleophilic amine 2,6-lutidene with TBS-chloride, but TLC analysis of crude reaction mixtures showed that this combination of reagents failed to silylate the intermediate hydroquinone complexes. Triethylamine and TBS-chloride, though effective in giving silylated complexes, gave reduced yields of arene complexes compared to the yields obtained for sequential benzannulation/silylation with the same substrates (Table 3, entry 1 versus Table 2, entry 2). We attributed this to the partial decomposition of the starting alkenyl carbene complexes by Et_3N. This was not necessarily expected given the results of Yamashita and Toy[15] (Eq 3) where an aryl complex in the presence of Et_3N gives useful annulation yields. The less nucleophilic diisopropylethyl amine (Hunigs' base) with TBSCl or TBSOTf failed to give improved results (Table 3, entry 2 vs. Table 2, entry 2; and Table 3, entry 6 vs. Table 2, entry 6).

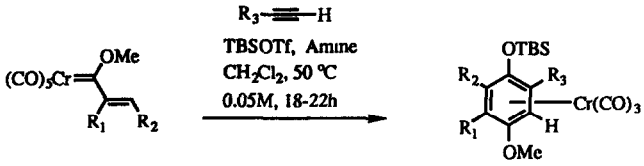


Table 3 **Concurrent Benzannulation/Silylation**

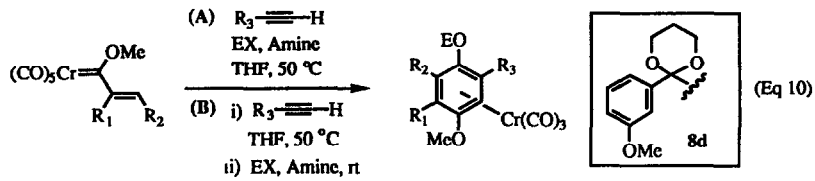
Entry	R1	R2	R3	Amine	Solvent	Complex	Free Arene
1	TMS	H	*n*-Pr	Et_3N[a]	THF	**6m** (44)	**10c** (76)
2	TMS	H	*n*-Pr	$Et(i\text{-}Pr)_2N$[a]	THF	**6m** (37)	**10c** (76)
3	TMS	H	*n*-Pr	2, 6-Lutidine	CH_2Cl_2	**6m** (79)	**10c** (76)
4	H	Me	$-(CH_2)_4CN$	2, 6-Lutidine	CH_2Cl_2	**6o** (73)	**10d** (57)
5	H	Me	*n*-Pr	2, 6-Lutidine	CH_2Cl_2	**6u** (74)	**10f** (75)[b]
6	Me	H	*n*-Pr	$Et(i\text{-}Pr)_2N$	THF	**6q** (55)	**10a** (51)[b]
7	Me	H	*n*-Pr	2, 6-Lutidine	THF	**6q** (73)	**10a** (51)[b]
8	Me	H	*n*-Pr	2, 6-Lutidine	CH_2Cl_2	**6q** (77)	**10a** (51)[b]
9	Me	H	$-(CH_2)_4CN$	2, 6-Lutidine	CH_2Cl_2	**6i** (73)	**10e** (76)
10	$-(CH_2)_4-$		$-(CH_2)_4CN$	2, 6-Lutidine	CH_2Cl_2	**6t** (72)	

[a] TBSCl used in this reaction. [b]Ref. 16a.

The best reagent combination for the concurrent benzannulation/silylation method of arene complex formation is a silyl triflate and 2,6-lutidene in methylene chloride. Although THF can be used as solvent with these reagents without reduction of yield, polymerization of the solvent from heating in the presence of the silyl triflate occurs (Table 3, entry 7). Entries 3, 4, 5, 8, 9, and 10 all use the optimum reaction conditions with methylene chloride as solvent. In all cases there is improvement in the isolated yields of arene complexes compared to the sequential method, with dramatic improvement in the cases of the a-TMS vinyl carbene complex **1j** (Table 3, entry 3 vs. Table 2, entry 2) and the *trans* -propenyl carbene complex **1k** (Table 3,

entries 4 and 5, vs. Table 2, entry 4). In addition, the efficiency of the concurrent benzannulation/silylation method is demonstrated by the fact that the isolated yields of arene complexes obtained either equal or exceed the yields of free arenes obtained after oxidative workup of benzannulation reactions using the same carbene complexes and alkynes.

The results summarized in Table 4 show some of the range of arene complexes available by the methods discussed above. The triisopropylsilyl (TIPS) group can be introduced effectively through use of the silyl triflate, while for the methoxyethoxymethyl (MEM) group the chloride is sufficiently active. The TIPS group can be introduced using 2,6-lutidene, but Hunigs' base is necessary for alkylation with MEMCl. Acetates are available in reasonable yield by sequential benzannulation/acetylation (Table 4, entries 3 & 4), but attempts to protect the benzannulation products as pivalates or trichloroacetates yielded protected complexes which were sensitive to decomplexation on silica gel and which were readily cleaved at -78 °C by LDA in THF. In contrast to those complexes, the triflate protected complex **6bb** is robust, opening the possibility of exploring palladium or copper catalyzed coupling reactions with this type of arene complex.[34]



(Eq 10)

Table 4

Entry	R1	R2	R3	EX	Base	Method	Yield	
1	-(CH2)4-		-(CH2)4SPh	TIPSOTf	2, 6-Lutidine	A	**6v**	(65)
2	-(CH2)4-		-(CH2)4CN	Ac2O	Et3N	B	**6w**	(31)
3	-(CH2)4-		-(CH2)4CN	AcBr	Et(*i*-Pr)2N	A	**6w**	(55)
4	-(CH2)4-		*n*-Pr	AcBr	Et(*i*-Pr)2N	A	**6x**	(64)
5	-(CH2)4-		*n*-Pr	MEMCl	Et(*i*-Pr)2N	B	**6y**	(68)
6	-(CH2)4-		**8d**	MEMCl	Et(*i*-Pr)2N	B[a]	**6z**	(65)
7	-(CH2)4-		-(CH2)4CN	TIPSOTf	2, 6-Lutidine	B[a]	**6aa**	(72)
8	Me	H	-(CH2)4CN	Tf2O	2, 6-Lutidine	A[a]	**6bb**	(47)

[a] CH_2Cl_2 solvent

Entries 1 and 6 of Table 4 show one of the advantages of the benzannulation approach to Cr(CO)3-complexed arenes; the metal fragment remains exclusively coordinated to the newly formed arene ring. It would not be expected that any of the methods for complexing a Cr(CO)3 fragment to an existing arene shown in Equation 1 would yield complexes such as **6v** or **6z** selectively. The reaction of **8d** is also noteworthy in that prior to this study it was not known if the benzannulation reaction would proceed with alkynes posessing the propargylic acetal function. Unprotected propargylic alcohols are known to give reduced annulation yields[22] as are ketoalkynes.[23] Since an important application of arene-Cr(CO)3 complexes involves stereoselective reactions of benzylic aldehydes and ketones[24], we were pleased to see that this functionality could be carried through the benzannulation reaction. Extension of the benzannulation/protection methodology to prepare arene complexes diasteroselectively is currently under investigation.

Conclusion

Methods for the efficient generation of air- and silica-stable differentially protected hydroquinone chromium tricarbonyl complexes from alkenyl Fischer carbene complexes have been developed. Protection of the benzannulation products is accomplished either by intramolecular silyl-migration or by reaction of the intermediate hydroquinone mono-methyl ether chromium tricarbonyl complexes with a variety of electrophiles. Concurrent benzannulation/protection has been found to be the most efficient means of preparing the desired arene-$Cr(CO)_3$ complexes.

Experimental Section

NMR spectra were recorded at 500 MHz (Chicago-built) for ^1H NMR and 75 MHz (GE-QE 300) for ^{13}C NMR. FTIR spectra were obtained with a Nicolet 20 SXB instrument. Melting points are uncorrected. THF was distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. All reactions were performed in flame dried glassware which had been evacuated and backfilled with argon. Unless otherwise specified R_f values were determined with ternary solvent mixtures of diethyl ether, dichloromethane, and hexanes (v/v/v). All column chromatography was performed with medium pressure on EM Science 330 - 400 mesh silica gel. Alkynes which are oils at room temperature were purified immediately prior to use by distillation or gravity filtration through a short plug of neutral alumina. Preparations of alkynes **8b**,[29] **8c**,[26] 1-thiophenyl-5-hexyne,[26] and carbene complexes **1e**,[31] **1k**,[27] and **1m**[21] are published.

Carbene Complex (1f) Prepared analogously to **1b**[32] from TBS-acetylene[25] in 72% yield. (dark red oil which solidifies when kept at -20 °C, R_f= 0.50, hexanes) ^1H NMR ($CDCl_3$) δ 0.28 (s, 6H), 1.05 (s, 9H), 4.35 (s, 3H); ^{13}C NMR ($CDCl_3$) δ -5.2, 16.7, 26.0, 66.0, 105.0, 153.4, 216.0, 225.6, 318.3; IR (neat film) 2064m, 1954vs, 1880m cm^{-1}; mass spectrum m/e (relative intensity) 374(M^+, 30), 318(40), 290(10), 262(95), 234(98), 204(80), 178(100); calcd for $C_{15}H_{18}CrO_6Si$ m/e 374.0278, found 374.0310.

Carbene complex (1h). Prepared analogously to the isopropenyl tungsten complex[27] from **13** in 54% yield. (red oil, R_f= 0.22, hexanes) ^1H NMR ($CDCl_3$) δ 0.18 (s, 6H), 0.95 (s, 9H), 1.90 (s, 3H), 4.41 (br s, 3H), 5.10 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.6, 17.2, 17.5, 26.3, 64.9, 119.8, 164.6, 216.3, 223.9, 355.7; IR (neat film) 2063s, 1987sh, 1929vs, 1242m cm^{-1}; mass spectrum m/e (relative intensity) 390(M^+, 30), 362(20), 334(10), 306(30), 278(70), 250(100), 235(10), 221(5), 208(12), 194(100), 179(80); calcd for $C_{16}H_{22}CrO_6Si$ m/e 309.0591, found 390.0715.

Carbene complex (1j) Prepared analogously to the tungsten complex[28] from 1-bromo-1-trimethylsilylethylene in 79% yield. (red oil, R_f= 0.67, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.21 (s, 9H), 4.49 (s, 3H), 5.42 (s, 1H), 5.55 (s, 1H), ^{13}C NMR ($CDCl_3$) δ -0.72, 65.6, 121.4, 170.2, 216.4, 223.9, 358.6; IR (neat film) 2061s, 1985sh, 1926vs, 1228m cm^{-1}; mass spectrum m/e (relative intensity) 334(M^+, 10), 306(12), 250(25), 222(35), 194(65), 164(100); calcd for $C_{12}H_{14}CrO_6Si$ m/e 333.9965, found 333.9965.

Carbene complex (1l)[33] Prepared analogously to the isopropenyl tungsten complex[27] except that the intermediate lithium acylate was converted to the Me_4N^+ salt. The crude lithium acylate, obtained after evaporation of solvent, was dissolved in the minimum of water, filtered through Celite, and stirred with a slight excess of NMe_4Br. The resulting yellow solid was collected by filtration and dried under vacuum to give the orange Me_4N^+ salt (76-80%) which can be stored for months at -20 °C under argon without decomposition. Complex **1l** was obtained by adding 1.5 eq MeOTf to a stirred CH_2Cl_2 solution of the Me_4N^+ salt at 0 °C, then rt 1h, followed by normal aqueous workup to give **1l** in 72 % yield. Because **1l** as a purified neat oil decomposes readily, we have found it best to use **1l** immediately after chromatographic purification (hexanes), with final removal of solvent performed under high vaccuum at 0 °C in a tared reaction flask. The spectral data for this compound matches that reported in the literature.[33]

General Procedure for the Generation of Arene-Chromium Tricarbonyl Complexes by Sequential Benzannulation/Protection of Fischer Carbene Complexes. (Procedure A) The carbene complex (typically 0.5-5.0 mmol, 1.0 eq) and alkyne (1.5-2.0 eq) are dissolved in sufficient solvent required for a 0.05 M solution in carbene in a pear-shaped flask modified as previously described[9] and fitted with a small stir bar. The reaction mixture is degassed by the freeze-pump-thaw method (three or four cycles), blanketed with argon, and heated at 50 °C (unless otherwise indicated) until the carbene complex is consumed. After cooling the reaction vessel to rt, the stopcock is replaced with a rubber septum under positive argon pressure. The electrophile and amine are added separately and quickly as solids or neat liquids under an argon stream. The septum is replaced immediately with the threaded stopcock and the reaction mixture is again degassed (three cycles). After stirring at rt for 6-12 h the reaction mixture is diluted with ether, washed once with water, twice with dilute HCl, once with brine, and dried over $MgSO_4$. Following filtration and removal of volatiles at reduced pressure, the arene complexes, **6**, are purified by flash chromatography on silica gel.

General Procedure for the Generation of Arene-Chromium Tricarbonyl Complexes by Concurrent Benzannulation/Protection of Fischer Carbene Complexes. (Procedure B) As in Procedure A, the carbene complex is placed a modified flask[9], the stopcock is replaced with a rubber septum, and the flask is evacuated and backfilled with argon. One half of the volume of anhydrous methylene chloride required for a 0.05 M solution in carbene complex, 1.5 equivalents of alkyne, 2.5 equivalents of anhydrous amine, 1.5 equivalents of electrophile, and the remaining solvent are added by syringe. Under a stream of argon, the septum is replaced quickly with the threaded stopcock, the solution degassed using the freeze-pump-thaw method (three cycles), and the flask backfilled with argon. After being heated in an oil bath at 50 °C (unless otherwise indicated) until the carbene complex is consumed (12-24 h), workup and purification are as Procedure A.

Arene complexes 6d and 9a (Procedure B) Complex **1e** (0.0938 g, 0.274 mmol), 1-pentyne (0.054 ml, 0.549 mmol), TBSCl (0.070 g, 0.466 mmol), and Et_3N (0.076 ml, 0.549 mmol) were heated at 48 °C for 20h, yielding **6d** and **9a** (0.046g, 0.093 mmol, 34%) as an orange solid. (Procedure A) Carbene complex **1e** (0.961 g, 0.281 mmol) and 1-pentyne (0.042 ml, 0.421 mol) were heated in 0.8 ml heptane at 50 °C for 16h resulting in a yellow solution with a brown precipitate. TBS-triflate (0.10 ml, 0.421 mmol) and lutidene (0.10 ml, 0.703 mmol) were added. After 8h stiring at rt, normal workup and chromatography (1:1:6) gave an approx. 1:1 mixture of **6d** and **9a**. (R_f= 0.37, 1:1:4) ^{1}H NMR ($CDCl_3$) **(6d)** δ 0.497 (s, 3H), 0.503 (s, 3H), 1.05 (t, 3H, J=7.2 Hz), 1.11 (s, 9H), 1.60 - 1.71 (m, 2H), 2.25 - 2.32 (m, 1H), 2.84 - 2.91 (m, 1H), 3.86 (s, 3H), 3.98 (s, 3H), 4.95 (s, 1H), 6.63 (d, 1H, J= 7.3 Hz), 7.35 - 7.38 (m, 2H) ; **(9a)** δ 0.20 (s, 3H), 0.28 (s, 3H), 0.94 (t, 3H, J= 7.2 Hz), 1.11 (s, 9H), 1.55 - 1.62 (m, 2H), 2.42 -2.48, (m, 1H), 2.76 - 2.83 (m, 1H), 3.89 (s, 3H), 3.93 (s, 3H), 5.03 (d, 1H, J= 6.7 Hz), 5.63 (t, 1H, J=6.8 Hz), 5.98 (d, 1H, J= 6.8 Hz), 6.45 (s, 1H); **(6d) + (9a)** IR (neat film) 1953s, 1870s, 1599w, 1464w, 1388m, 1255m, 1068m cm^{-1}; **(6d) + (9a)** mass spectrum m/e (relative intensity) 496(M^+, 10), 440(5), 412(40), 360(100), 345(5), 303(15).

Arene complex (6f) Carbene complex **1f** (0.388 g, 1.037 mmol) and **8b** (0.166 g, 1.55 mmol) were combined in a mixture of 10 ml THF and 3.5 ml 2,3-dimethylbutadiene, degassed (four cycles), and heated at 50 °C under argon for six days. Concentration and chromatography (1:1:6) gave 0.376 g (0.702 mmol, 68%) of **6f**. (yellow needles (pentane), mp= 104 - 107 °C, R_f= 0.22, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 3H), 0.40 (s, 3H), 1.02 (s, 9H), 1.65 - 1.83 (m, 4H), 1.77 (s, 3H), 1.80 (s, 3H), 2.30 - 2.38 (m, 1H), 2.40 (br s, 2H), 2.68 - 2.75 (m, 1H), 3.05 - 3.34 (m, 4H), 3.72 (s, 3H), 4.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -3.2, -2.3, 17.0, 18.3, 18.4, 18.6, 25.0, 25.8, 29.3, 29.5, 30.7, 32.4, 55.8, 73.8, 96.7, 102.2, 103.7, 119.2, 121.3, 121.9, 125.8, 136.2, 234.7; IR (neat film) 2250w, 1945s, 1861vs, cm^{-1}; mass spectrum m/e (relative intensity) 535(M^+, 8), 451(60), 39 (40), 342(45); calcd for $C_{27}H_{37}CrNO_5Si$: C, 60.54, H , 6.96, N, 2.61, found C, 60.70, H, 7.10, N, 2.41.

Arene complex (6g) (Prepared analogously to **1f**, seven day reaction time) (yellow solid, mp = 108 - 110 °C, R_f= 0.58, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 3H), 0.42 (s, 3H), 1.03 (br s, 12H), 1.60 - 1.68(m, 2H), 1.78 (s, 3H), 1.81 (s, 3H), 2.21 - 2.28 (m, 1H), 2.65 - 2.72 (m, 1H), 3.08- 3.35 (m, 4H), 3.72 (s, 3H), 4.94 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -3.2, -2.1, 14.0, 18.4, 18.5, 18.8, 23.9, 26.0, 30.9, 32.3, 32.6,

55.9, 74.1, 96.6, 103.4, 103.7, 121.5, 122.0, 125.9, 136.3, 235.0; IR (neat film) 1949s, 1866s, 1462m, 1355m, 1257m, 1132m cm^{-1}; mass spectrum m/e (relative intensity) 496(M^+, 10), 440(5), 412(100), 360(30), calcd for $C_{25}H_{36}CrO_5Si$ m/e 496.1737, found 496.1784.

Arene complex (6h) (Prepared analogously to **1f**, four day reaction time) (yellow solid, mp = 136.5 - 138.0 °C, R_f= 0.23, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.28 (s, 3H), 0.34 (s, 3H), 0.94 (s, 9H), 1.65 - 1.85 (m, 4H), 1.73 (s, 3H), 1.75 (s, 3H), 2.24 (dt, 1H, J= 13.8, 7.0 Hz), 2.61 (dt, 1H, J=13.8, 7.0 Hz), 3.07 - 3.13 (m, 5 H), 3.20 - 3.30 (m, 1H), 3.67 (s, 3H), 4.87 (s, 1H), 7.56 (t, 2H, J= 7.7 Hz), 7.65 (t, 1H, J=7.3 Hz), 7.87 (d, 2H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$) δ -3.1, -2.1, 18.4, 18.5, 18.7, 22.4, 25.9, 28.9, 29.8, 30.8, 32.5, 55.8, 56.0, 73.8, 96.8, 102.0, 103.6, 121.4, 122.0, 125.9, 127.9, 129.3, 133.8, 136.2, 138.9, 234.7; IR (neat film) 1946s, 1860s, 1463m, 1355w, 1306w, 1257w, 1150m, 1133w cm^{-1}; mass spectrum m/e (relative intensity) 650(M^+, 10), 566(45), 514(100), 457(100), 372(20), 331(20), 317(75); calcd for $C_{32}H_{47}CrO_7SSi$: C, 59.06, H, 6.50, found C, 58.67, H, 6.14.

Arene complex (6i) (Procedure B) (yellow solid, mp= 95.5 - 98.5 °C, R_f= 0.21, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.31 (s, 3H), 0.37 (s, 3H), 0.97 (s, 9H), 1.67 - 1.78 (m, 4H), 2.14 (s, 3H), 2.20 - 2.24 (m, 1H), 2.39 (t, 2H, J= 6.0 Hz), 2.70 - 2.74 (m, 1H), 3.69 (s, 3H), 5.13 (s, 1H), 5.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.4, 15.8, 17.0, 18.0, 25.1, 25.3, 29.6, 29.7, 56.5, 79.3, 86.3, 97.8, 100.3, 119.3, 131.4, 134.4, 234.7 ; IR (neat film) 2248w, 1952s, 1868s, 1484m, 1371m, 1224m, 1019m cm^{-1}; mass spectrum m/e (relative intensity) 469(M^+, 5), 400(15), 385(45), 370(8), 333(15), 276(100), 248(15); calcd for $C_{22}H_{31}CrNO_5Si$: C, 56.27, H , 6.65, N, 2.98, found C, 56.14, H, 6.33, N, 2.91.

Arene complex (6l) (Procedure A) (yellow solid, mp= 116.5 - 118.0 °C, R_f= 0.59, 1:1:10) ^1H NMR ($CDCl_3$) δ 0.33 (s, 3H), 0.36 (s, 3H), 0.40 (s, 9H), 1.00 (s, 9H), 1.27 (t, 3H, J = 7.5 Hz), 1.33 (t, 3H, J = 7.5 Hz), 2.45 - 2.57 (m, 2H), 2.63 -2.71 (m, 1H), 2.76 - 2.84 (m, 1H), 3.72 (s, 3H), 5.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.1, -0.05, 15.2, 16.5, 18.1, 20.6, 21.0, 25.5, 64.5, 86.7, 92.9, 108.3, 110.1, 132.3, 140.7, 234.6; IR (neat film) 1943s, 1866s, 1514m, 1470m, 1419m, 1340m, 1254s cm^{-1}; mass spectrum m/e (relative intensity) 502(M^+, 10), 446(10), 418(100), 366(15), 346(30), 294(10), 237(10), 207(10), 14 (15), 126(25); calcd for $C_{23}H_{38}CrO_5Si_2$: C, 54.95, H 7.62, found C, 54.87, H, 7.65.

Arene complex (6m) (Procedure B) (yellow solid, mp= 77 - 79 °C, R_f= 0.55, 1:1:10) ^1H NMR ($CDCl_3$) δ 0.32 (s, 12 H), 0.33 (s, 3H), 0.97 (s, 9H), 1.05, (t, 3H, J = 7.2 Hz), 1.56 - 1.62 (m, 1H), 1.63 - 1.73 (m, 1H), 2.14 - 2.20 (m, 1H), 2.83 - 2.89 (m, 1H), 3.77 (s, 3H), 4.95 (s, 1H), 5.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.8, -4.0, -0.7, 14.1, 18.0, 23.8, 25.4, 33.2, 55.6, 75.9, 85.9, 91.3, 107.0, 128.3, 143.2, 235.0; IR (neat film) 1953s, 1871s, 1466s, 1343m, 1253s, 1203s, 1000m cm^{-1}; mass spectrum m/e (relative intensity) 488(M^+, 10), 432(5), 404(100), 352(15).

Arene complex (6n) (Procedure A) (yellow solid, mp = 114-115 °C, R_f = 0.27, 1:1:4)^1H NMR ($CDCl_3$) δ 0.32 (s, 9H), 0.333 (s, 3H), 0.336 (s, 3H), 0.97 (s, 9H), 1.75 - 1.90 (m, 4H), 2.24 - 2.30 (m, 1H), 2.42 (dd, 2H, J = 6.0, 4.7 Hz), 2.88 - 2.93 (m, 1H), 3.71 (s, 3H), 4.93 (s, 1H), 5.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.8, -4.1, -0.8, 17.1, 18.0, 25.2, 25.4, 29.3, 30.4, 55.7, 75.6, 86.2, 91.0, 105.5, 119.3, 128.2, 143.0, 234.7; IR (neat film) 2247w, 1951s, 1869s, 1464m, 1256m, 1208m, 1004m cm^{-1}; mass spectrum m/e (relative intensity) 527(M^+, 8), 443(100), 391(10), 334(65).

Arene complex (6o) (Procedure B, 65 °C) (fine yellow needles [ether / pentane], mp= 76.5 -78.0 °C, R_f= 0.29, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.357 (s, 3H), 0.362 (s, 3H), 1.01 (s, 9H), 1.73 - 1.89 (m, 4H), 2.24 (s, 3H), 2.31- 2.39 (m, 1H), 2.42 (t, 2H, J= 5.9 Hz), 2.77-2.83 (m, 1H), 3.67 (s, 3H), 4.943 (s, 1H), 4.945 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -2.9, -2.6, 17.1, 17.8, 18.6, 25.1, 25.8, 28.8, 29.9, 55.7, 78.0, 78.8, 102.1, 106.0, 119.2, 126.4, 139.2, 234.4; IR (neat film) 2247w, 1955s, 1862s, 1546m, 1465s, 1264m, 1050m cm^{-1}; mass spectrum m/e (relative intensity) 469(M^+, 10), 385(70), 370(10), 328(20), 276(40) ; calcd for $C_{22}H_{31}CrNO_5Si$: C, 56.27, H, 6.65, N, 2.98, found C, 56.35, H, 6.82, N, 2.92.

Arene complex (6p) (Procedure A) (yellow solid, mp= 60 - 62 °C, R_f= 0.44, 1:1:10) ^1H NMR ($CDCl_3$) δ 0.31 (s, 3H), 0.41 (s, 3H), 1.00 (s, 9H), 1.21 (t, 3H, J= 7.4 Hz), 1.28 (t, 3H, J= 7.4 Hz), 2.23 (s, 3H),

2.38 - 2.44 (m, 1H), 2.49 - 2.58(m, 2H), 2.70 - 2.80 (m, 1H), 3.68 (s, 3H), 4.78 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.0, 15.2, 16.4, 16.8, 18.1, 20.0, 21.6, 25.4, 65.8, 80.6, 102.8, 104.3, 113.1, 131.5, 136.4, 234.6; IR (neat film) 1952s, 1870s, 1451w, 1363w, 1258w, 1233w, 1125w, 1004w cm^{-1}; mass spectrum m/e (relative intensity) 444(M^+, 10), 388(5), 360(100), 308(15), 251(15), 126(10).

Arene complex (6q) (Procedure B) (yellow solid, mp= 76.5-78.0 °C, R_f= 0.58, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.30 (s, 3H), 0.38 (s, 3H), 0.99 (s, 9H), 1.02 (t, 3H, J= 7.0 Hz), 1.55 - 1.65 (m, 2H), 2.13 - 2.18 (m, 1H), 2.15 (s, 3H), 2.65 - 2.70 (m, 1H), 3.70 (s, 3H), 5.13 (s, 1H), 5.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.4, -4.3, 14.0, 15.9, 18.0, 24.2, 25.4, 32.4, 56.5, 79.6, 86.5, 97.6, 101.8, 131.5, 134.6, 235.0; IR (neat film) 1952s, 1865s, 1482w, 1370w, 1233w, 1210w, 1019w cm^{-1}; mass spectrum m/e (relative intensity) 430(M^+, 20), 374(15), 346(100), 294(20), 261(10), 237(25), 207(15), 126(45); calcd for $C_{20}H_{30}CrO_5Si$: C, 55.80, H , 7.02 , found C, 55.44, H, 7.27.

Arene complex (6r) (Procedure A) (yellow prisms [pentane], mp= 84.5 - 86.5 °C , R_f= 0.58, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.35 (s, 3H), 0.37 (s, 3H), 1.02 (s, 9H), 1.24 (t, 3H, J= 7.5 Hz), 1.25 (t, 3H, J= 7.3 Hz), 1.60 - 1.68 (m, 1H), 1.75 - 1.86 (m, 2H), 1.92 - 1.97 (m, 1H), 2.45 - 2.54 (m, 4H), 2.59 - 2.64 (m, 1H), 2.68 - 2.76 (m, 2H), 2.79 - 2.88 (m, 1H), 3.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ -2.2, -2.1, 15.5, 17.3, 19.9, 21.0, 21.6, 21.8, 23.8, 25.7, 26.1, 29.7, 65.0, 98.9, 104.3, 106.0, 110.6, 132.5, 134.1, 235.3; IR (neat film) 1948s, 1859s, 1399w, 1342w cm^{-1}; mass spectrum m/e (relative intensity) 484(M^+, 20), 428(20), 400(100), 348(25); calcd for $C_{24}H_{36}CrO_6Si$: C, 59.48 , H , 7.49 , found C, 59.17, H, 7.52 .

Arene complex (6s) (Procedure A) (yellow solid, mp= 106 - 108 °C , R_f= 0.55, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.39 (s, 6H), 1.00 (s, 9H), 1.03 (t, 3H, J= 7.3 Hz), 1.58 - 1.66 (m, 3H), 1.68 - 1.82 (m, 2H), 1.93- 1.98 (m, 1H), 2.17 - 2.23 (m, 1H), 2.47 - 2.53 (m, 1H), 2.66 - 2.81 (m, 4H), 3.69 (s, 3H), 4.88 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -3.4, -1.9, 14.0, 18.7, 21.1, 21.9, 23.7, 24.0, 25.1, 25.9, 32.4, 55.3, 73.9, 98.7, 103.8, 106.1, 125.6, 137.3, 235.2; IR (neat film) 1948vs, 1859vs, 1456m, 1430m, 1374w, 1336m, 1247m cm^{-1}; mass spectrum m/e (relative intensity) 470(M^+, 10), 414(10), 386(100), 334(55), 277(65).

Arene complex (6t) (Procedure B) (yellow needles [ether], mp= 119- 120°C , R_f= 0.30, 1:1:4) ^1H NMR ($CDCl_3$) δ 0.37 (s, 3H), 0.39 (s, 3H), 1.01 (s, 9H), 1.49 - 1.65 (m, 1H), 1.69 - 1.82 (m, 6H), 1.91 - 1.98 (m, 1H), 2.28- 2.32 (m, 1H), 2.41 (t, 2H, J= 7.0 Hz), 2.49 - 2.54 (m, 1H), 2.69 - 2.80 (m, 4H), 3.71 (s, 3H), 4.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -3.3, -2.0, 17.1, 18.6, 21.0, 21.7, 23.6, 25.0, 25.1, 25.8, 29.5, 29.6, 55.8, 73.4, 98.8, 102.5, 106.1, 119.2, 125.5, 137.2, 234.9; IR (neat film) 2247vw, 1946s, 1857s, 1457m, 1429m, 1259m, 1091m cm^{-1}; mass spectrum m/e (relative intensity) 509(M^+, 10), 425(45), 41 (10), 373(15), 316(100), 288(10); calcd for $C_{25}H_{35}CrNO_5Si$: C, 58.92, H, 6.92, N, 2.75, found C, 58.77, H, 7.00, N, 2.53.

Arene complex (6u) (Procedure B, 60 °C) (yellow-orange solid, mp= 101-103 °C, R_f= 0.48, 1:1:4); ^1H NMR ($CDCl_3$) δ 0.36 (s, 3H), 0.37 (s, 3H), 1.00 (s, 9H), 1.04 (t, 3H, J= 7.3 Hz), 1.55- 1.70 (m, 2H), 2.23 (s, 3H), 2.74 (m, 2H), 3.66 (s, 3H), 4.94 (d, 1H, J = 2.7 Hz), 4.96 (d, 1H, J= 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ -2.9, -2.6, 14.0, 17.9, 18.7, 23.4, 25.9, 32.7, 55.6, 78.3, 78.8, 102.3, 107.4, 126.5, 139.3, 234.7 ; IR (neat film) 1953s, 1860s, 1465m, 1254s cm^{-1}; mass spectrum m/e (relative intensity) 430(M^+, 25), 374(15), 346(100), 294(20), 261(15), 237(20), 207(18), 126(50); calcd for $C_{20}H_{30}CrO_5Si$: C, 55.43, H, 6.81, found C, 55.79, H, 7.02.

Arene complex (6v) (Procedure A) (yellow needles [pentane], mp= 89.5 - 90.5 °C , R_f= 0.32, 1:1:6) ^1H NMR ($CDCl_3$) δ 1.13 (d, 18 H, J= 7.1 Hz), 1.21 - 1.38 (m, 3H), 1.58 - 1.66 (2H), 1.80 - 1.95 (m, 6H), 2.55 (t, 2H, J= 8.0 Hz), 2.58 - 2.65 (m, 2H), 2.70 - 2.80 (m, 1H), 2.90 - 3.09 (m, 3H), 3.65 (s, 3H), 5.10 (s, 1H) ,7.17 (t, 1H, J=7.2 Hz), 7.27 (t, 2H, J=7.5 Hz), 7.33 (d, 2H, J= 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 14.3, 17.2, 21.3, 21.6, 22.9, 25.6, 28.4, 29.2, 29.3, 33.3, 56.2, 75.6, 100.3, 100.8, 103.2, 125.8, 128.8, 128.9,132.3, 134.2, 136.4, 235.1; IR (neat film) 1944s, 1861s, 1453m, 1427m, 1337m, 1228m, 1090m, 1069w cm^{-1}; mass spectrum m/e (relative intensity) 634(M^+, 10), 550(50), 498(100), 455(65), 440(15), 388(15), 346(60); calcd for $C_{33}H_{46}CrO_5SSi$: C, 62.43, H, 7.30, found C, 62.51, H, 7.49

Arene complex (6w) (Procedure A) (yellow needles [EtOAc/hexanes], mp= 114 - 116 °C (dec.), R_f= 0.10, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.60 - 1.95 (m, 8H), 2.27 (s, 3H), 2.32 - 2.42 (m, 4H), 2.48 - 2.52 (m, 1H), 2.58 - 2.65 (m, 2H), 2.75 (br d, 1H, J= 16.7 Hz), 3.69 (s, 3H), 4.95 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.8, 20.3, 20.9, 21.0, 22.6, 23.8. 25.1, 28.7, 29.5, 56.0, 72.7, 98.2, 103.6, 106.9, 119.2, 121.4, 138.7, 169.9, 233.2; IR (neat film) 2250w, 1954s, 1867vs, 1762s, 1457m, 1435m, 1371m, 1190s, 1100m, 1069m cm^{-1}; mass spectrum m/e (relative intensity) 437(M^+, 10), 381(15), 353(100), 311(80), 301(90), 286(65), 271(30); calcd for $C_{21}H_{23}CrNO_6$: C, 57.66, H, 5.30, N, 3.20, found C, 57.90, H, 5.13, N, 2.87.

Arene complex (6x) (Procedure A) (yellow prisms [ether], mp = 136 - 138 °C, R_f= 0.37, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.02 (t, 3H, J=7.4 Hz), 1.52 - 1.60 (m, 2H), 1.61 - 1.69 (m, 1H), 1.79 - 1.90 (m, 3H), 2.27 - 2.36 (m, 1H), 2.29 (s, 3H), 2.40 - 2.51 (m, 2H), 2.62 - 2.68 (m, 2H), 2.79 (dt, 1H, J=16.8, 5.4 Hz), 3.71 (s, 3H), 4.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 20.2, 20.9, 21.1, 22.6, 23.2, 23.8, 32.3, 55.9, 73.1, 97.9, 104.9, 106.9, 121.5, 138.7, 169.8, 233.3; IR (neat film) 1954vs, 1869vs, 1765s, 1456m, 1434m, 1370m, 1334m, 1190vs, 1100m cm^{-1}; mass spectrum m/e (relative intensity) 398(M^+, 10), 346(10), 314(100), 286(10), 271(12), 262(5), 243(8), 220(35), 191(15).

Arene complex (6y) (Procedure B) (yellow oil, R_f= 0.55, 50% EtOAc/hexanes) ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3H, J = 7.4 Hz), 1.60 - 1.80 (m, 5H), 1.89 - 1.96 (m, 1H), 2.31- 2.38 (m, 1H), 2.51 (dt, 1H, J= 16.9, 5.0 Hz), 2.68 - 2.75 (m, 2H), 2.78 - 2.85 (m, 2H), 3.41 (s, 3H), 3.61 (t, 2H, J= 4.7 Hz), 3.73 (s, 3H), 3.89 - 3.91 (m, 2H), 4.83 (s, 1H), 4.89 (d, 1H, J= 5.4 Hz), 4.98 (d, 1H, J=5.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 21.1, 21.5, 23.3, 23.8, 24.2, 32.7, 55.7, 59.0, 69.2, 71.5, 72.6, 97.1, 102.8, 107.6, 108.9, 128.1, 139.0, 234.1; IR (neat film) 1948s, 1862vs, 1457m, 1435m, 1239w, 1167w, 1100m cm^{-1}; mass spectrum m/e (relative intensity) 444(M^+, 8), 360(40), 308(45), 233(10), 219(45), 191(30), 177(8).

Arene complex (6z) (Procedure B) (orange foam, R_f= 0.42, 1:1 EA/Hex) ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 1H, J= 13.3 Hz), 1.44- 1.51 (m, 1H), 1.60 - 1.75 (m, 2H), 1.85 -1.91 (m, 1H), 2.33- 2.47 (m, 2H), 2.62- 2.88 (m, 3H), 3.43 (s, 3H), 3.64 (t, 2H, J= 4.9 Hz), 3.72 (s, 3H), 3.82 (s, 3H), 3.83 - 3.89 (m, 2H), 3.95 - 4.11 (m, 4H), 4.92(d, 1H, J= 5.2 Hz), 5.19 (d, 1H, J= 5.2 Hz), 5.33 (s, 1H), 6.84 (d, 1H, J= 8.1 Hz), 7.14 (d, 1H, J= 7.4 Hz), 7.15 (s, 1H), 7.29 (t, 1H, J= 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.6, 23.5, 23.8, 24.3, 55.0, 55.6, 58.9, 61.4, 61.7, 68.9, 69.2, 71.5, 97.3, 98.3, 105.9, 109.1, 113.0, 113.3, 113.7, 119.8, 125.3, 129.4, 138.2, 139.8, 159.7, 234.2; IR (neat film) 1952s, 1875s, 1863s, 1459w, 1433w, 1333w, 1254w, 1137m cm^{-1}; mass spectrum m/e (relative intensity) 594 (M^+, 3), 510(3), 480(8), 458(25), 430(5), 369(10), 341(5), 312(35), 296(10), 281(5), 265(5), 193(100), 135(60); calcd for $C_{29}H_{34}CrO_{10}$ m/e 594.1557, found 594.1529.

Arene complex (6aa) (Procedure B) (fine yellow needles [ether / pentane], mp= 135.0- 136.0 °C , R_f= 0.28, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 18 H, J = 6.8 Hz), 1.22 - 1.30 (m, 3H), 1.55 - 1.68 (m, 1H), 1.78 -1.98 (m, 7H), 2.44 - 2.51 (m, 2H), 2.57 - 2.67 (m, 4H), 2.73 - 2.78 (m, 1H), 2.92 (dt, 1H, J = 16.4, 5.4 Hz), 3.67 (s, 3H), 5.11 (s, 1H) ; ^{13}C NMR ($CDCl_3$) δ 14.4, 17.1, 18.03, 18.06, 21.3, 21.6, 23.0, 25.61, 25.65, 28.3, 29.0, 56.3, 75.5, 99.4, 101.1, 103.1, 119.3, 132.4, 134.2, 235.0; IR (neat film) 2248w, 1943vs, 1901m, 1862vs, 1453m, 1422m cm^{-1}; mass spectrum m/e (relative intensity) 551(M^+, 22), 467(100), 415(45), 372(85), 340(15) ; calcd for $C_{28}H_{41}CrNO_5Si$: C, 60.96, H, 7.49, N, 2.54, found C, 60.62, H, 7.53, N, 2.23.

Arene complex (6bb) (Procedure A) (yellow needles [EtOAc/Hex], mp= 73-4 °C, R_f= 0.10, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 4H), 2.16 (s, 3H), 2.38 - 2.45 (m, 2H), 2.48 - 2.52 (m, 1H), 2.60- 2.69 (m, 1H), 3.72 (s, 3H), 5.07 (s, 1H), 5.71 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.4, 16.7, 24.9, 29.1, 29.3, 56.4, 73.5, 89.7, 94.9, 103.8, 118.0 (q, J= 320 Hz), 119.1, 121.5, 139.1, 231.1; IR (neat film) 2249w, 1968s, 1891s, 1219m cm^{-1}; mass spectrum m/e (relative intensity) 487(M^+, 8), 431(90), 403(100), 388(30) 375 (40); calcd for $C_{17}H_{16}CrF_3O_7NS$: C, 41.90 , H, 3.31, N, 2.87, found C, 41.77, H, 3.24 , N, 2.62.

Naphthalene (7b) (Procedure B) A mixture of 0.251 g (0.760 mmol) of complex **1e**, 0.15 ml (1.52 mmol) of 1-pentyne, 0.18 ml (1.62 mmol) of 2,6-lutidene, and 0.26 ml (1.14 mmol) of TBSOTf in 15 ml of CH_2Cl_2 heated at 45 °C for 18h gave 0.235 g (0.652 mmol, 86%) of **7b** as a pale amber oil contaminated with a trace

(^{1}HNMR) of an approx. 1:1 mixture of **6d** and **9a** after normal workup and chromatography (1:1:6). (R_f= 0.37, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 6H), 0.96 (t, 3H, J= 7.3 Hz), 1.11 (s, 9H), 1.65 (sextet, 2H, J= 7.6 Hz), 2.70 (t, 2H, J= 7.8 Hz), 3.92 (s, 3H), 3.96 (s, 3H), 6.66 (s, 1H), 6.78 (d, 1H, J= 7.7 Hz), 7.29 (t, 1H, J=8.1 Hz), 7.62 (d, 1H, J= 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ -3.2, 14.0, 18.6, 23.4, 26.1, 32.8, 56.3, 57.2, 105.5, 109.4, 116.0, 117.0, 125.1,127.8, 131.3, 141.9, 151.2, 156.7; IR (neat film) 1600s, 1509w, 1463m, 1388s, 1262s, 1130m, 1074s cm^{-1}; mass spectrum m/e (relative intensity) 360(M^+, 100), 345(15), 303(40), 272(10), 260(30), 245(15); calcd for $C_{21}H_{32}O_3Si$ m/e 360.2121, found 360.2140 .

Naphthalene (7c) (Procedure B) A mixture of 0.822 g (2.40 mmol) of complex **1e**, 0.386 g (3.60 mmol) of **8b**, 0.60 ml (4.3 mmol) of Et_3N, and 0.616g (4.08 mmol) of TBSCl in 10 ml of heptane were heated at 45 °C for 18h gave 0.209 g (0.526 mmol, 22%) of **7c** as an amber oil after normal workup and chromatography (20% EtOAc/Hex). (R_f= 0.29, 1:1:4)^{1}H NMR ($CDCl_3$) δ 0.15 (s, 6H), 1.11 (s, 9H), 1.7-1.8 (m, 4H), 2.45 (t, 2H, J= 7.0 Hz), 2.79 (t, 2H, J= 7.2 Hz), 3.92 (s, 3H), 3.96 (s, 3H), 6.58 (s, 1H), 6.81 (d, 1H, J= 7.8 Hz), 7.31 (t, 1H, J= 8.1 Hz), 7.61 (d, 1H, J= 8.1 Hz). A similar result was obtained using TBSOTf, 2,6-lutidine, and CH_2Cl_2.

Preparation of Alkyne 8d Condensation of lithium triisopropylsilyl acetylide with *m* - anisaldehyde, followed by Jones oxidation,[25] and ketal formation (1,3-propanediol, p-TsOH (cat.), toluene reflux, Dean-Stark trap, 18h) gave the silylketal **14** as colorless needles [MeOH] in 75% yield. (mp= 42.0 - 43.5 °C, R_f= 0.58, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.14 (s, 21 H), 1.47 (br d, 1H, J= 13.3 Hz), 2.15 - 2.28 (m, 1H), 3.82 (s, 3H), 4.06 (dd, 2H, J= 12.6, 5.0 Hz), 4.52 (dt, 2H, J= 12.3, 2.1 Hz), 6.87 (dd, 1H, J= 8.0, 2.0 Hz), 7.25(t, 1H, J= 7.9 Hz), 7.30 (t, 1H, J= 2.0 Hz), 7.33 (d, 1H, J= 7.8 Hz); Anal calc'd for $C_{22}H_{34}O_3Si$, C, 70.54, H, 9.15, found C, 70.93, H, 9.37. Removal of the TIPS group from **14** with TBAF yielded **8d** in 92% yield. (amber oil, R_f= 0.48, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.49 (d, 1H, J= 13.3 Hz), 2.18 - 2.25 (m, 1H), 2.84 (s, 1H), 3.83(s, 3H), 4.09 (dd, 2H, J=, 11.2, 5.0 Hz), 4.47(t, 2H, J= 8.0 Hz), 6.88 (d, 1H, J=, 7.4 Hz), 7.26- 7.31 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 25.0, 55.3, 62.8, 76.7, 79.2, 95.0, 110.6, 115.1, 117.8, 129.2, 142.3, 159.4; IR (neat film) 3280m, 2108w, 1608m, 1589w, 1489m, 1430m, 1300m, 1270s, 1218m, 1108s cm^{-1}; mass spectrum m/e (relative intensity) 218(M^+, 85), 187(10), 160(100), 145(10), 132(25), 117(10).

Benzoquinone (10c) A solution of complex **1j** (0.1558 g, 0.4898 mmol) and 1-pentyne (0.097 ml, 0.98 mmol) in 1.0 ml heptane was deoxygenated by the freeze-pump-thaw method (three cycles) , blanketed with argon, and heated at 45 - 50 ° C for 24 h. After cooling to rt and dilution with ether, the mixture was vigorously stirred with 7.0 ml of 0.5 M CAN solution for 30 min. After standard workup, chromatography (1:1:10) yielded 0.0828 g (0.373 mmol, 76%) of **10c** as an orange solid. (mp= 45 - 8 °C , R_f= 0.49, 1:1:10) ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 9H), 0.94 (t, 3H, J = 7.4 Hz), 1.51 (sext., 2H, J = 7.5 Hz), 2.33 (t, 2H, J = 7.7 Hz), 6.48 (s, 1H), 6.79 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -1.8, 13.8, 21.0, 30.7, 133.8, 143.6, 148.9, 151.7, 187.0, 191.2; IR (neat film) 1652sh, 1643s, 1621m, 1334m, 1253m, 1224m cm^{-1}; mass spectrum m/e (relative intensity) 222(M^+, 20), 207(95), 194(20), 179(80), 165(25), 93(100).

Benzoquinone(10d) (Prepared analogously to **10c**) (orange solid, mp = 60.0- 62.0 °C , R_f = 0.13, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.63-1.72 (m, 4H), 2.02 (d, 3H, J= 1.2 Hz), 2.37 (t, 2H, J= 6.8 Hz), 2.44 (t, 2H, J= 7.2 Hz), 6.46 (d, 1H, J= 1.1 Hz), 6.51 (d, 1H, J= 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 15.9, 16.8, 24.9, 26.8, 28.3, 119.2, 132.6, 133.1, 145.8, 148.1, 187.4, 187.6; IR (neat film) 2246w, 1655s, 1652s, 1614s, 1296s cm^{-1}; mass spectrum m/e (relative intensity) 203(M^+, 100), 186(100), 103,(100), 149(25), 137(50).

Benzoquinone(10e) (Prepared analogously to **10c**) (orange needles (pentane) mp= 54.5-56.0 °C , R_f= 0.17, 1:1:4) ^{1}H NMR ($CDCl_3$) δ 1.66- 1.75 (m, 4H), 2.04 (d, 3H, J= 1.5 Hz), 2.39 (t, 2H, J= 6.8 Hz), 2.45 (t, 2H, J= 7.5 Hz), 6.54 (s, 1H), 6.58 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 15.4, 16.8, 24.9, 26.8, 27.8, 119.2, 132.7, 133.4, 145.6, 148.1, 187.4, 187.8; IR (neat film) 2246w, 1656s, 1650s cm^{-1}; mass spectrum m/e (relative intensity) 203(M^+, 50), 163(100), 149(15), 135(20), 121(15); calcd for $C_{12}H_{13}NO_2$: C, 70.92, H, 6.45, N, 6.89, found C, 70.75, H, 6.54, N, 6.56.

Phenol [11a] Complex **1j** (0.216 g, 0.647 mmol) and 0.110 ml (0.080 g, 0.970 mmol) were dissolved in 12 ml THF, deoxygenated (three cycles), and heated under argon for 26 h. After cooling to rt, the reaction mixture was stirred open to air for 24 h. The crude mixture was filtered through Celite and concentrated. The proton spectrum showed the desired phenol to be the major product. Chromatography with 1:1:20 yielded 0.0537 g (0.213 mmol, 33%) of **11a** as an amber oil. (R_f= 0.39, 1:1:10) ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9H), 1.20 (t, 3H, J = 7.6 Hz), 1.22 (t, 3H, J = 7.7 Hz), 2.67 (q, 2H, J= 7.4 Hz), 2.69 (q, 2H, J =7.4 Hz), 3.72 (s, 3H), 5.01 (s, 1H), 6.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.00, 14.2, 15.7, 19.8, 19.9, 62.7, 118.8, 130.3, 131.5, 135.9, 149.9, 157.6; IR (neat film) 3397 br s, 1442m, 1384s, 1320m, 1250m, 1218m cm^{-1}; mass spectrum m/e (relative intensity) 252(M^+, 100), 237(20), 219(15), 207(75), 191(10), 163(15).

2-[(E)-1- *Tert*-butyldimethylsilyl]propenyltri-*n*-butylstannane (12) The desired vinylstannane was obtained in 46-54% yield by catalytic hydrostannation[30] of 1-t-butyldimethylsilyl-1-propyne.[25] (clear, colorless oil. R_f= 0.68, hexanes) ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 6H), 0.80-1.00 (m, 24 H), 1.28-1.37(m, 6H), 1.48-1.54 (m, 6H), 2.06 (s, 3H), 5.82 (s, 1H); IR (neat film) 2955s, 2927s, 2854s, 1464m, 1557w, 1376w, 1249m cm^{-1}.

(E)-1- *Tert*-butyldimethylsilyl-2-bromopropene (13) Neat bromine (0.63ml, 1.95 g, 12.18 mol) was added to **12** (5.40 g, 12.18 mmol) stirred in 50 ml CH_2Cl_2 and 15 ml CCl_4 at -78 °C. Concentration and chromatography (hexanes) gave **13** (1.39 g, 5.92 mmol, 49%) as a clear, colorless oil. (R_f= 0.53, hexanes) ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 6H), 0.91 (s, 9H), 2.38 (s, 3H), 5.95 (s, 1H); ^{13}C NMR ($CDCl_3$) δ -4.6, 17.2, 26.2, 29.5,.130.2, 133.9; IR (neat film) 1606m, 1464w, 1251m, 1055w cm^{-1}; mass spectrum m/e (relative intensity) 235(M^+, 100), 233(79), 179(100), 177(90), 135(9), 121(28).

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