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The Preparation and Evaluation of Electron Poor Benzylidene Fischer Carbene Complexes: Studies Toward the Total Synthesis of (+)-Olivin

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Abstract—The continued exploration into the fate of the benzannulation reaction is put forth using the electronic nature of substituents on the aryl ring of benzylidene Fischer carbene complexes as a handle to predict, using σ-*para* values as a guide, the outcome of the reaction based on the accepted mechanism. The design of this work focuses on evaluation of the synthetic utility of the benzannulation reaction and the means by which this reaction may be improved to be a better synthetic tool in the preparation of complex natural products as this is illustrated in our ongoing total synthesis of (+)-olivin which uses the benzannulation reaction as the key convergent synthetic step. To accomplish these tasks, the preparation of several electron poor benzylidene Fischer carbene complexes was carried out and their reaction with simple alkyne substrates studied. While much is known about the preparation of electron rich benzylidene Fischer carbene complexes, little is known about the preparation of their electron poor counterparts. Thus efforts toward developing useful preparative methods of these elusive targets has also been studied. While the use of both carbon and oxygen based aryl substituents has been explored, to date the preparation of benzylidene carbene complexes containing oxygen based aryl substituents has been exploited to a greater degree since these systems carry more immediate synthetic importance. This is so because the skeletal core of many of the natural products that have been targeted with the benzannulation reaction including (+)-olivin contain a highly oxygenated polycyclic aromatic core. The enhancement in efficiency of the benzannulation reaction using this synthetic methodology is demonstrated by the successful completion of the convergent synthetic step in the total synthesis of (+)-olivin.

Introduction

Since its discovery in 1975, the benzannulation reaction has been the subject of a great deal of methodological and mechanistic study.[1] Additionally, the benzannulation reaction has been demonstrated to have significant utility as a tool for the total synthesis of a variety of natural products.[1] However, the full synthetic potential of the benzannulation reaction has been not yet realized because of the inherent inefficiency and unpredictability which have plagued the benzannulation reaction to this point. Most of this unpredictability has been associated with aryl (or benzylidene) complexes rather than with alkenyl complexes which tend to give cleaner reaction mixtures over a broader range of substrates and reaction conditions.[2] Therefore, the greatest impact on enhancing the synthetic utility of the benzannulation reaction would result from improved predictability in the reactions of aryl or benzylidene complexes. This is especially the case since a majority of the applications in natural product synthesis have involved the benzannulation of aryl complexes to give polyoxygenated naphthalene and anthracenes.[1]

The chemoselectivity of the product distribution as a function of the substitution pattern of the carbene complex is illustrated by the data in Table 1.[3] While it is clear (entry a, Table 1) that the reactions of simple aryl Fischer carbene complex with simple alkynes may give good yields of the desired phenol product, the complexity of the reaction mixture quickly increases and/or the overall reaction efficiency decreases as the substitution pattern on the aryl ring is varied. The data in entries b–f demonstrate quite clearly this loss of yield and reaction efficiency with both THF and benzene as solvent. It is interesting to note that all of these examples have the common characteristic of containing oxygen substituents that can be electron donating by resonance. The general trend that can be seen from these and a substantial amount of other data in the literature[1,2a,3] is that more electron rich carbene complexes will tend to give rise to a more complex reaction profile.

The currently accepted mechanism for the formation of phenol products and for the origin of many of the side-products observed from the benzannulation reaction is shown in Scheme 1.[2–12] The first branchpoint occurs with the coupling of the alkyne and the carbene carbon to give the

Keywords: Fischer carbene complexes; benzannulation reaction; σ-*para*; (+)-olivin.

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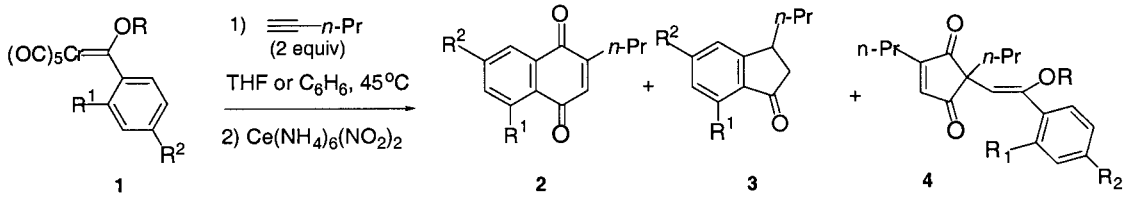
Table 1. The benzannulation of benzylidene complexes **1a**–**1f** (R=Me) with 1-pentyne (all reactions were run at 0.5 M in carbene complex; N indicates that product was not detected in the 500 MHz ^{1}H NMR spectrum of the crude reaction mixture; Tr indicates that a trace was observed but the amount was not determined)

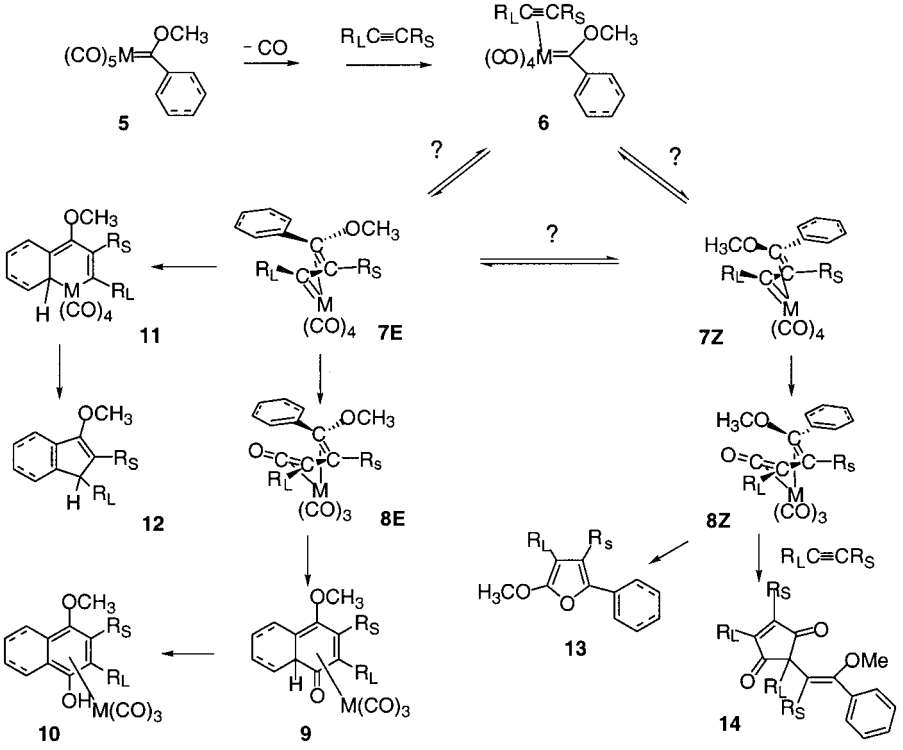


1 **2** **3** **4**

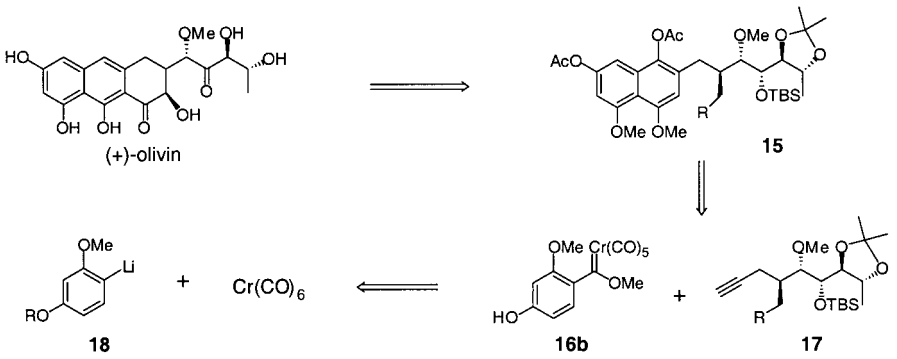
Entry	Complex	R^1	R^2	Solvent	Yield **2** (%)	Yield **3** (%)	Yield **4** (%)
a	**1a**	H	H	THF	73	N	N
b	**1b**	H	OCH_3	THF	36	40	N
c	**1c**	OCH_3	H	Benzene	60	N	Tr
d	**1d**	H	OAc	THF	61	N	N
e	**1e**	OCH_3	OCH_3	Benzene	47	14	10
f	**1f**	OCH_3	OAc	Benzene	51	10	26

diastereomeric η^1, η^3-vinyl carbene complexed intermediates **7*E*** and **7*Z***. Recent evidence shows that these intermediates are in equilibrium but it is not known if they isomerize by alkyne de-insertion to intermediate **6** or by some other mechanism.[8] The *Z*-isomer of **7** has been shown to be the origin of the furan product **13**[6,13] and the cyclopentenedione product **14**.[14] From the intermediate **7*Z***, the furan product is usually predominate in THF solution and the cyclopentenedione is predominate in benzene solution.[2b,3] The second branch-point in phenol formation is intermediate **7*E***. It is the *E*-isomer of the η^1, η^3-vinyl carbene complexed intermediate **7** that, after CO insertion to the η^4-vinyl ketene complex **8*E***, has the proper geometry to cyclize to give the phenol product **10**. The major side-product of the benzannulation reaction that is observed from the E-manifold is the indene product **12**. Given the scores of other side-products have been observed from the reaction of alkynes with Fischer carbene complexes under various conditions it is thus surprising that this reaction is as reliable as it is for the synthesis of phenols. Significant progress toward improving the utility of the benzannulation reaction could be achieved if the side-products shown in Scheme 1 could be eliminated from the reaction of aryl complexes.

It is known from previous studies that the partition between the *E* and *Z*-isomers of the vinyl carbene complexed intermediate **7** is a function of the relative electron density of the two substituents of the starting carbene complex.[7] The more electron releasing substituent will preferentially be oriented trans to the carbon bearing the substituent R_L of the alkyne. This explains why for most simple complexes that intermediate **7*E*** is preferentially formed as a result of the



Scheme 1.



Scheme 2.

directing effect of the methoxyl group and why the benzannulation reaction produces good to excellent yields of phenol products for simple Fischer carbene complexes. If the combined electron releasing ability of the substituents of the carbene carbon is too great then this is also detrimental to phenol formation since, in this case, CO insertion in **7*E*** is disfavored relative to direct cyclization and the formation of indene products.[15a,b] These studies of the effect of electronics on product distributions suggest that proper electronic tuning of the carbene complex could potentially lead to improved chemoselectivity for phenol formation. However, of the hundreds of benzannulation reactions that have been reported to date, only a handful have involved aryl complexes with electron withdrawing substituents on the aryl group. The two main reasons for this are discussed below.

One primary reason for the paucity of examples of the benzannulation of aryl carbene complexes bearing electron-withdrawing groups is that all of the natural products whose syntheses have been pursued with the benzannulation as a key step in the retrosynthesis have contained oxygenated aromatic subunits. Depending on the degree of oxygenation and the substitution pattern, oxygenated aryl carbene complexes can be unpredictable and inefficient in the benzannulation reaction. The ongoing total synthesis of (+)-olivin in our laboratories is the perfect embodiment of the difficulties encountered when attempting to apply the benzannulation as the convergent step toward the synthesis of a complex natural product (Scheme 2). The main skeletal feature of olivin is a highly oxygenated anthracenone system which under our current approach would be largely assembled in a single convergent step using the benzannulation reaction as the source of a highly oxygenated naphthalene system which, upon further elaboration, would lead to the desired anthracenone. Our current retrosynthetic approach to olivin relies on the preparation of acylphenol **15** from the benzannulation of carbene complex **16** with a highly functionalized alkyne of the type **17** (Scheme 2). Our current synthesis of the necessary alkyne **17** requires 15 steps and can be achieved in 6% overall yield.[16] The required carbene complex can be prepared in seven steps and is achieved in 20% overall yield.[3] Under this approach then not only is the benzannulation a highly convergent step of the synthesis, but it is also important because of the value of alkyne **17** which contains 4 of the 5 stereocenters present in the final target.

Table 2. Substituent σ-*para* values

Substituent	σ-*para*
OCH_3	−0.27
H	0.00
Br	0.23
OAc	0.31
CHO	0.42
$CO(C_6H_5)$	0.46
$CO(CH_3)$	0.50
OTf	0.53
CF_3	0.54

A second major reason that the benzannulation reaction of aryl complexes bearing electron-withdrawing groups has been so sparsely examined is that they are difficult to prepare by existing methods. The Fischer method for the synthesis of group 6 carbene complexes involving the addition of an organolithium to the metal hexacarbonyl is almost exclusively the method that is used in the preparation of aryl complexes.[15c] While this method, which necessitates the generation of aryl lithiums, is compatible with aryllithiums of the type **18** bearing ether oxygen substituents, it is not compatible with a variety of arenes bearing electron-withdrawing groups.

Given the difficulties encountered in the benzannulation of 2,4-dioxygenated aryl complexes for the synthesis of olivin and other natural products in our laboratories (Table 1), we therefore have embarked on an investigation into the fate of the benzannulation reaction of electron poor aryl Fischer carbene complexes and the results of these studies are reported herein. As a part of this investigation we were necessarily required to develop new methods for the generation of electron poor carbene complexes and these results will also be described in this work. Finally, in conjunction with the first systematic study of the benzannulation of a series of aryl carbene complexes with electron withdrawing substituents on the aryl group, the first systematic study of the effect of the size of the oxygen heteroatom stabilizing substituent is reported for a series of methoxy and *iso*-propoxy carbene complexes.

Results and Discussion

To begin our investigation, we analyzed the σ-*para* values of several possible substituents and decided on several candidates which we felt would be useful for our study

Table 3. Benzannulation of complex **19** with 1-pentyne (unless otherwise specified, all reactions were run with 2 equiv. of 1-pentyne in benzene at 80°C and at 0.1 M in carbene complex; N means that this product was not detected in the ^{1}H NMR of the crude reaction mixture; Quinone **2** and indanone **3** are numbered after the methoxy carbene complex from which they are derived)

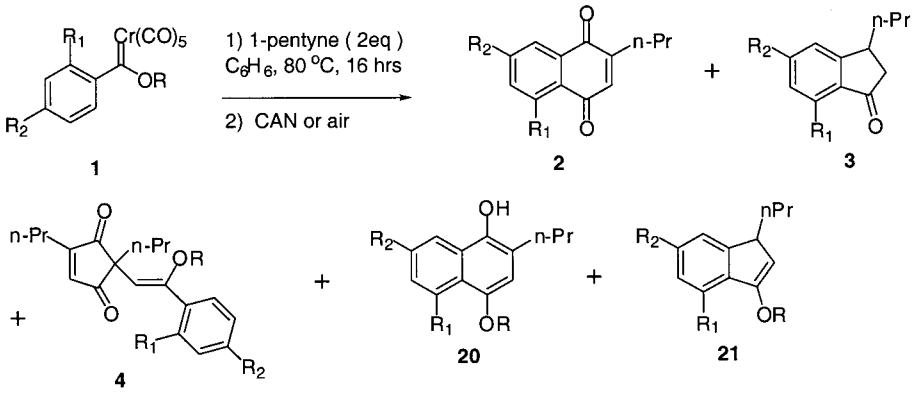
Entry	Carbene complex	R	R_1	R_2	Workup	2/20[a]	3/21[b]	4
1	**1b**	Me	H	OMe	CAN	36[c]	40	N
2	**1g**	*i*-Pr	H	OMe	CAN	29[c]	59	N
3	**1a**	Me	H	H	Air	76	1	7.5
4	**1a**	Me	H	H	CAN	78	1	7.5
5	**1a**	Me	H	H	CAN	82[d]	N	11
6	**1h**	*i*-Pr	H	H	Air	90	≤1	<5
7	**1h**	*i*-Pr	H	H	CAN	90	≤1	<5
8	**1l**	Me	H	Br	Air	72	N	5
9	**1i**	Me	H	Br	CAN	75	N	5
10	**1j**	*i*-Pr	H	Br	Air	90	N	<5
11	**1j**	*i*-Pr	H	Br	CAN	91	N	<5
12	**1d**	Me	H	OAc	Air	60	N	N
13	**1k**	*i*-Pr	H	OAc	Air	60	N	N
14	**1l**	Me	H	$COCH_3$	CAN	63	N	N
15	**1m**	Me	H	CF_3	Air	96	N	<2
16	**1m**	Me	H	CF_3	CAN	95	N	<2
17	**1n**	*i*-Pr	H	CF_3	Air	98	N	<1
18	**1n**	*i*-Pr	H	CF_3	CAN	98	N	<1
19	**1c**	Me	OMe	H	CAN	60[c]	N	Tr[e]
20	**1o**	Me	CF_3	H	CAN	64	N	N
21	**1p**	*i*-Pr	CF_3	H	CAN	60	N	N
22	**1q**	Me	Me	H	Air	65[f]	N	3[g]
23	**1q**	Me	Me	H	CAN	66	N	3[g]
24	**1q**	Me	Me	H	CAN	78[d]	4	N
25	**1r**	*i*-Pr	Me	H	Air	67[h]	N	N
26	**1r**	*i*-Pr	Me	H	CAN	66	N	N
27	**1s**	Me	*i*-Pr	H	CAN	49	11	N

[a] **20** results from removal of the $Cr(CO)_3$ moiety by stirring in air, and **2** results from CAN oxidation of the crude reaction mixture.
[b] **21** results from air workup, and **3** results from CAN oxidative workup.
[c] Reaction performed at 0.5 M and 45°C. Reaction of **1b** and **1c** from ref. 3.
[d] Reaction performed at 0.005 M.
[e] Trace of furan product **13** observed.
[f] A 62% yield of phenol and 3% yield of quinone isolated.
[g] Tentatively identified as furan **13q**.
[h] 48% yield phenol and 19% yield quinone isolated.

(Table 2).[17] Our hypothesis based on the previous electronic studies discussed above, if correct, would predict that as the *para* substituent is changed from methoxyl (σ-*para*=−0.27) down the list to trifluoromethyl (σ-*para*=0.54), the equilibrium between η^1,η^3-vinylcarbene intermediates **7E** and **7*Z*** should be shifted farther to the **7*E*** and, in addition, the energy barrier for CO insertion in **7*E*** should be lowered, thus producing an increased relative yield of phenol product. The reaction of a number of complexes with two equivalents of 1-pentyne was examined in benzene (0.1 M in carbene complex) at 80°C and the results are presented in Table 3.

Considering first only those complexes bearing a methoxyl group as the heteroatom stabilizing group (R=Me), an analysis of the data in Table 3 reveals that there is a correlation between the yield of the phenol product and the σ-*para* value of substituent on the carbene complex, however, the correlation is that of a step function and not a linear correlation. The *p*-methoxyl complex **1b** gives a low yield of phenol (36%, entry 1) and the *p*-trifluoromethyl complex gives the highest yield (96%, entry 12) and the *p*-bromo, *p*-acetoxy, *p*-acetyl and the unsubstituted complexes give between 60 and 78% yield (entries 3, 8, 11 and 19). In many of the cases both an oxidative and non-oxidative workup were employed and it was found that the yields of isolated phenols and quinones were within experimental error in each case. The high yield of phenol product from the reaction of the *p*-trifluoromethylphenyl complex **1m** is consistent with the electronic considerations discussed in Scheme 1 and is an important experimental result. The benzannulation of *para*,[18] *meta*[19] and *ortho*-trifluoromethylphenyl[20] carbene complexes have each been reported only once and in each case have been reported to give lower yields than the unsubstituted complex **1a**. The yield of benzannulation product from the *para*-substituted complex was reported on the unstable chromium tricarbonyl complex and thus this yield may not reflect the real effect of the *p*-trifluoromethyl group on the reaction.[18] The only report of a bromo-substituted aryl chromium carbene complex was of a *para*-substituted complex with an aryl alkyne and the yield for this reaction was the same as for the unsubstituted complex as is observed in this work for the reaction **1i** with 1-pentyne.[21]

As anticipated by the analysis outlined in Scheme 1, the amounts of side-products in general do decrease with more electron-poor substituted complexes. For example, the methoxyl substituted complex **1b** gives a 40% yield of the indenone **3b** (entry 1), the unsubstituted complex **1a** gives only a 1% yield of the indenone **3a** along with 7.5% yield of the cyclopentenedione **4a** (entry 4) and the trifluoromethyl complex **1m** gives less than 2% yield of **4m** (entry 16). However, the mechanism shown in Scheme 1 cannot



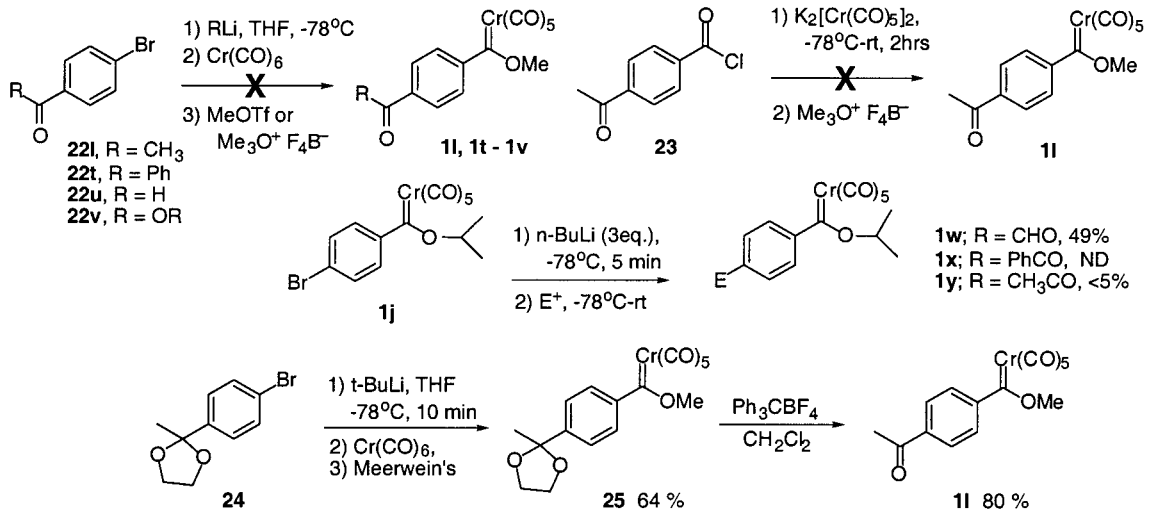
Scheme 3.

account for all of the products in each of the reactions since the mass balance is not uniformly high for all substrates. It is known that one of the many other possible side-process that occurs during the benzannulation reaction is the oligiomerization of the alkyne.[22] This could occur via multiple insertion of alkyne into the vinyl ketene complex **8*Z*** or the insertion of alkynes into the vinyl carbene complexed intermediate **7*E*** or **7*Z***. That this is occurring to some extent is suggested by the data in entries 4 and 5. The total mass balance of the reaction of complex **1a** with 1-pentyne increases from 86.5 to 93% when the concentration is lowered from 0.1 to 0.005 M which should favor the intramolecular processes leading to the products shown in Scheme 1 over intermolecular reactions with the alkyne. A similar effect is seen with complex **1g** (entries 23 and 24) (Scheme 3).

The correlation between the electronic nature of the substituent on the carbene complex and the efficiency of phenol formation does not hold up when the substituent is moved from the *para* to the *ortho* position. It has been shown in our previous studies that the reaction of several electron rich *ortho* substituted aryl carbene complexes with 1-pentyne resulted in slightly depressed yields from the parent phenyl carbene complex.[3] Interestingly, the data in Table 3 reveal that the yields are depressed for all *ortho* substituted complexes examined regardless of their electronic nature. The *ortho*-methoxyl, *ortho*-methyl and *ortho*-trifluoromethyl substituted complexes all give yields of phenol product between 60 and 66%. The suppression of the phenol product by an *ortho* substituent in fact has steric origins as indicated by the reaction of the *o-iso*-propyl complex **1s** which gives a reduced yield relative to the *o*-methyl complex **1q** (entries 4, 23 and 27). This becomes significant when, in a total synthesis application, a highly functionalized aryl carbene complex is required containing an *ortho* substituent. This can be offset to some degree by lowering the concentration ((entries 23 and 24), however, this does not work for an *o*-methoxyl group.[3]

The data in Table 3 also reveal for the first time that the size of the oxygen heteroatom stabilizing substituent on the carbene complex can have a significant effect on the yield of phenol product. The yield of phenol increases to 90% or above for most *para*-substituted complexes in which the methoxyl group on the carbene carbon is replaced by an *iso*-propoxy group. This effect is overridden by the negative *ortho* effect and no difference is seen for the reaction of the *ortho*-trifluoromethyl and *ortho*-methyl complexes (entries 20–26). Previously, very little information was available concerning the effect of size of the oxygen-stabilizing group on the carbene carbon and the yield of phenol product. There are two reports[23] on the benzannulation of a Fischer carbene complexes (both alkenyl) where a larger alkoxy group leads to no change or decreased yields in phenol products and two reports[24] (one on an alkenyl complex and one on an aryl complex) where increased yields of phenol product are observed with larger alkoxy groups. The data in Table 3 clearly show that for the *p*-substituted aryl complexes with 1-pentyne, that *iso*-propoxy groups are superior to methoxy groups in providing the high efficiencies for phenol product. The yields of phenol product for the *p*-bromo and unsubstituted phenyl complexes are increased from 78 to 90% (entries 4 and 6) and from 75 to 91% (entries 9 and 11) yield, respectively, upon changing from methoxyl to *iso*-propoxy complexes. Curiously, this effect is not seen for the *para* oxygen substituted complex (**1b** vs. **1g** and **1d** vs. **1k**). The effect of replacement of the methoxyl group with an *iso*-propoxyl group on the partition between vinyl carbene complexed intermediates **7*E*** and **7*Z*** is likely to be electronic rather than steric. The increase in steric bulk of the alkoxy group should favor **7*Z*** and not **7*E*** with a resulting increase in furan or cyclopentenedione product. However, the increased electron donating ability of an *iso*-propoxy group would be expected to electronically favor **7*E*** for reasons discussed in Scheme 1,[7] and thus to an increase of the yield of phenol product as observed for the data in Table 3. This could explain the reason that the yield of phenol from the *ortho* methoxy complex **1b** does not increase when the methoxyl group on the carbene carbon is replaced by *iso*-propoxy. In this case, the electron donating effect of the *para* methoxyl can dominate the increased electronic releasing ability of *iso*-propoxy over methoxy. The lack of an effect of an *iso*-propoxy group on the *para* acetoxy complex is not understood at this time (entries 12 and 13).

The reaction of the *para*-acetyl substituted complex **1l** with 1-pentyne (Table 3, entry 14) is the first example of the benzannulation of an aryl carbene complex that bears a carbonyl functional group.[25] The synthesis of this complex was not achieved by the standard Fischer method and



Scheme 4.

deserves special comment. Since aldehyde, ketone and ester functional groups are not compatible with organolithiums, the preparation of carbene complexes **1l**, **1t**–**1v** via the Fischer method from the aryl bromides **22l**, **22t**–**22v** was not attempted (Scheme 4). We therefore attempted several direct and indirect methods for preparing these complexes which are summarized in Scheme 4.

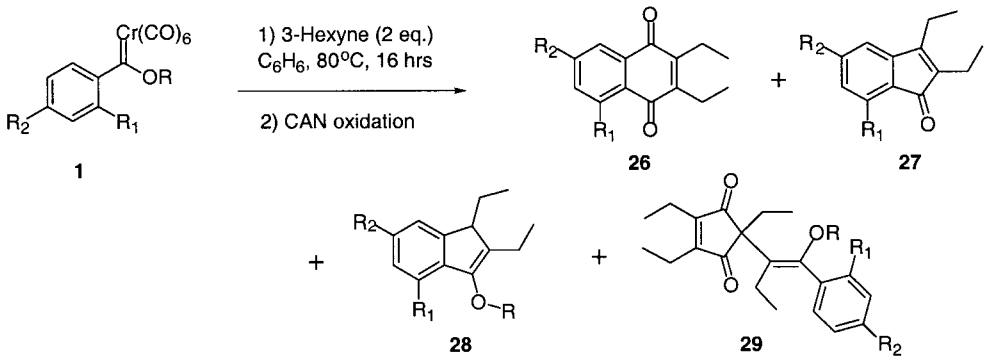
A modified Semmelheck/Hegedus procedure[26] applying dipotassium chromium pentacarbonyl to acyl chloride **23** was also attempted, but failed to give any desired carbene complex. We were able to achieve moderate success for the formation of the *p*-formylphenyl(isopropoxy) carbene complex **1w** by developing a lithium halogen exchange procedure on the *p*-bromophenyl carbene complex **1i**. The idea for this approach is that creating enough steric hindrance around the carbene complex would inhibit decomposition by attack from the alkyl lithium.[27] Quenching the anion derived from **1i** with DMF gave the desired carbene complex **1w** in 49% yield. This result, while quite promising, was not indicative of how other electrophiles[28] would behave. Attempted quenching of this anion with benzoyl chloride did give some **1x**, but as a mixture with several other inseparable products. The anion was also quenched with acetyl chloride in an attempt to prepare carbene complex **1y**; however, this method proved to yield only minimal amounts of the desired carbene complex. Unfortunately, the aldehyde containing complex **1w** is not robust enough to be used in the benzannulation reaction, as reaction with 1-pentyne under the standard conditions did not produce any identifiable products.

Success in preparing the *p*-acetylphenyl carbene complex **1l** was finally realized by the preparation of **25** by the standard Fischer method from halide **24** in 64% yield, followed by cleavage of the ethylene acetal by trityl tetrafluoroborate[29] giving the desired carbene complex **1l** in 80% yield. The deprotection of an acetal in the presence of a Fischer carbene complex cannot be achieved by many of the commonly used methods and has only been achieved on one other occasion.[30] The benzannulation of this novel carbene complex with 1-pentyne followed by CAN oxidation (Entry 14, Table 3) gave quinone **2l** in 63% yield. While this yield does not perfectly fit our prediction based on the

Table 4. Benzannulation of complex **1** with 3-hexyne (unless otherwise specified, all reactions were run with 2 equiv. of 3-hexyne in benzene at 80°C and at 0.1 M in carbene complex; oxidative workup with CAN was employed; all yields are after isolation by silica gel chromatography; N means that this product was not detected in the ^{1}H NMR of the crude reaction mixture)

Entry	Carbene complex	R	R_1	R_2	26	27	28	29
1	**1b**	Me	H	OMe	93[a]	D	D	N
2	**1a**	Me	H	H	96.5[b]	<0.7[c]	<0.7[c]	N
3	**1h**	*i*-Pr	H	H	97	<0.5	N	<1
4	**1i**	Me	H	Br	93	<1	N	<2
5	**1j**	*i*-Pr	H	Br	98	N	N	N
6	**1m**	Me	H	CF_3	96	N	N	N
7	**1n**	*i*-Pr	H	CF_3	99	N	N	N
8	**1c**	Me	OMe	H	77[d]	5	2	N
9	**1o**	Me	CF_3	H	74	N	N	N
10	**1p**	*i*-Pr	CF_3	H	36	20	26	N
11	**1q**	Me	Me	H	58	N	N	N
12	**1r**	*i*-Pr	Me	H	59	6	N	N

[a] Reaction in THF at 45°C and 0.5 M in **1b**, Ref. 3.
[b] Reference 2b.
[c] Combined yield of **27** and **28** is <0.7%.
[d] Reaction at 45°C and 0.5 M in **1c**, Ref. 3.



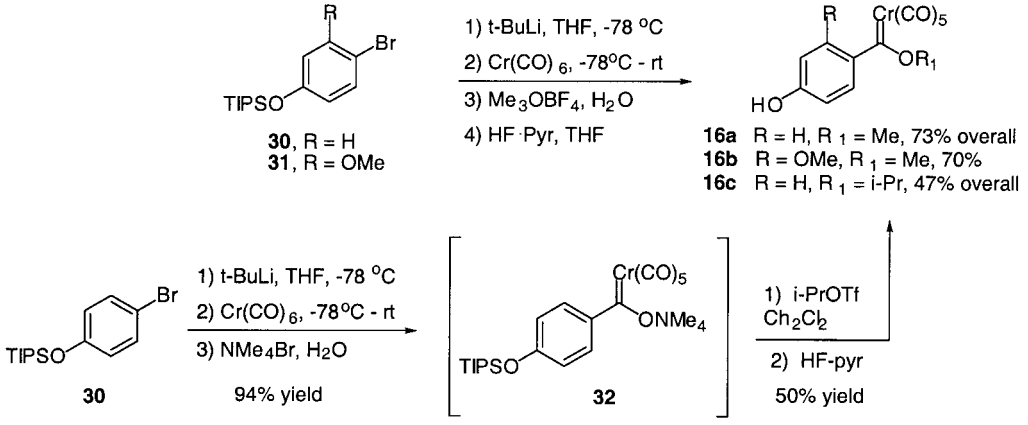
Scheme 5.

σ-*para* value of acetyl (in comparison with CF_3) it does represent a significant advance in Fischer carbene chemistry in that it demonstrates that very electron deficient aryl alkoxy carbene complexes can be prepared and benzannulated to give phenols in reasonable yield.[25]

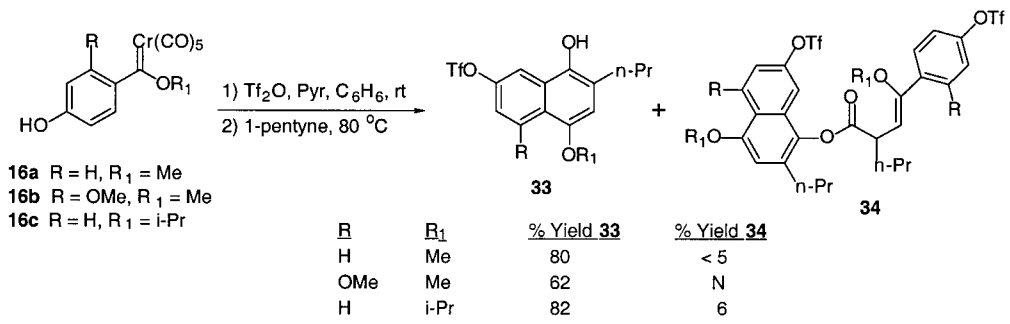
A similar set of carbene complexes were also subjected to reaction, under similar conditions, with 3-hexyne given that substantial differences in the benzannulation of internal and terminal alkynes have been observed previously.[1–3] The results of these reactions are summarized in Table 4 and in general the same trends are seen with the *para*-substituted complexes with the only difference being that the starting point for the electron rich *p*-methoxyl complex **1b** is much higher (93%, entry 1). In the case of the *para*-trifluoromethyl methoxy carbene complex (entry 6, Table 4), the yield of phenol derived product is once again very high (96%). Also, in the case of all of the *iso*-propoxy stabilized *para*-substituted carbene complexes (entries 3 5, and 7), all of the yields are nearly quantitative. These results with *para*-substituted systems clearly demonstrate that if sufficiently electron poor carbene complexes can be prepared, then their application to the benzannulation can produce predictable, high yielding, and efficient reactions (Scheme 5).

As was seen with the reaction with 1-pentyne, an *ortho* substituent on the aryl carbene complex leads to depressed yields and the electron withdrawing *ortho*-trifluoromethyl group has little effect in improving the reaction. Again, the electronic nature of the *ortho*-substituent had little effect with the methyl, methoxy and trifluoromethyl groups given between 58 and 77% yield with no correlation with the electron nature of the group. However, switching to the isopropoxy carbene complex (entry 10) in this case produced an unexpected result with the trifluoromethyl substituent. The overall mass balance went up, but the formation of five membered ring products also went from essentially zero to a 1.3:1 ratio in favor of the unwanted 5 membered ring products. This may be the result of the increased steric requirements of the isopropoxy; however, as yet, we have no supporting evidence for this being the origin of such a drastic change in product distribution.

While very interesting from an academic perspective, the above results do not demonstrate what advantages that could be realized in an actual synthetic application. To achieve this goal, we choose to examine the key benzannulation step in the synthesis of (+)-olivin outlined in Scheme 2 and this required that more synthetically interesting substituted aryl carbene complexes had to be prepared. For this task, the starting point chosen was the preparation of the *para*-hydroxyphenyl carbene complexes **16a** and **16b** (Scheme 6). Our previous preparation of **16a** starting from 4-(*o*-*tert*-butyldimethylsiloxy)bromobenzene under similar conditions was accomplished in 43% overall yield.[3] However, changing to the tri-isopropylsilyl analog **30**, we were able to prepare the same compound in 73% overall yield. In a similar manner, the 4-hydroxy-2-methoxyphenyl carbene complex **16b** could be prepared in an improved



Scheme 6.



R	R_1	% Yield **33**	% Yield **34**
H	Me	80	< 5
OMe	Me	62	N
H	i-Pr	82	6

Scheme 7.

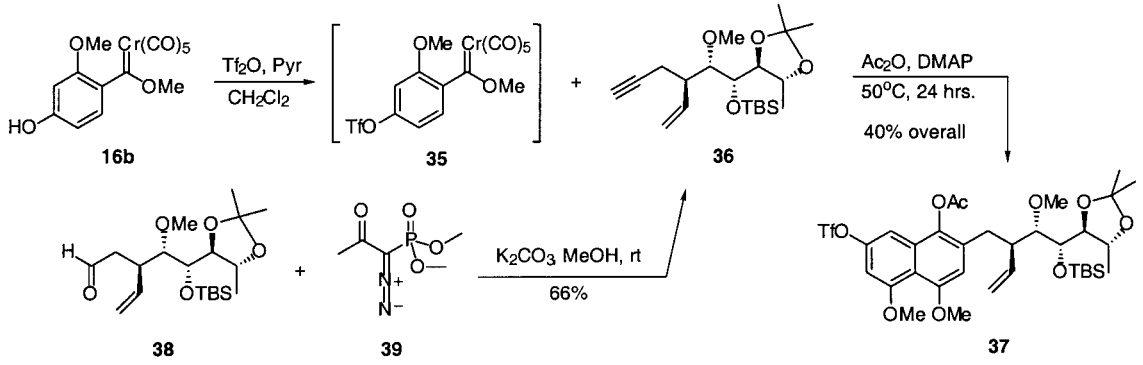
yield of 70% yield from **31**.[3] The isopropoxy derivative **16c** can be prepared in 47% overall yield via tetramethylammonium salt **32**.[31]

Benzannulation of these substrates (Scheme 7) produced desired phenol **33** and compound **34** as the only observable products. These benzannulation reactions were carried out as a one-pot sequence of in situ triflation followed immediately by benzannulation with 1-pentyne. This was done so because the resulting 4-triflatophenyl carbene complexes were found to be quite sensitive to air oxidation, thus the one-pot option was the most efficient and simple solution.[32] When the *para* substituent is a triflato group the results (80% overall yield of phenol from complex **16a**; >90% average yield per step) reveal what appears to be a strong inductive effect. The yield of phenol formation is much higher than that observed for the *para* acetoxy complex **1d** (Table 3, 11) and comparable to that of the *para* trifluoromethyl complex **1m** (Table 3, entry 15). When this same 2-step procedure is applied to the dioxygenated carbene complex **16b**, again the results are quite pleasing. In our previous studies (Table 1, entries e and f) benzannulation reactions of this type produced only moderate yield of phenol and a complex product mixture. In this case however, the overall yield was 62% (79% average yield for each of 2 steps) which compares favorably to the 33% overall yield which results from the previously known similar 2 step sequence.[3] Thus, this result shows that even with highly oxygenated carbene complexes, if the substrate is made sufficiently electron poor, good yields for the benzannulation reaction can result. Compound **34** is thought to result from a pyridine assisted trapping of ketene intermediate **8*E*** (Scheme 1) by phenoxide ion of the naphthol product **33**. Since this byproduct is actually formed from the desired product and its intermediate precursor, it is thought that this product is produced as a function of concentration and reaction temperature, and thus could be eliminated by the optimization of these variables.

Finally, the convergent step of our synthesis of (+)-olivin was studied using this new methodology. Aldehyde **38** (Scheme 8) was prepared in 10 steps according to a synthesis that we have previously reported in the literature.[16] The aldehyde **38** was converted to enyne **36** in 66% unoptimized yield by one-pot one carbon homologation reaction that produces the alkyne function directly upon with dimethyl-1-diazo-2-oxopropylphosphonate **39**.[33,34] Alkyne **36** was then submitted to conditions similar to those previously used in our (+)-olivin studies (Scheme 8).[16] This three step, one-pot reaction with of carbene complex **16b** with alkyne **36** and in situ trapping of the phenol with acetic anhydride to give acetylated phenol **37** occurred in 40% overall yield (74% average yield).

Conclusions

While the benzannulation has great potential as a synthetic tool due to the inherent structural features which are present in the phenol product produced, we believe that it has not yet been fully exploited because of certain inconsistencies in the performance of the reaction itself and difficulties in the preparation of carbene complexes with the diversity necessary to tackle many synthetic problems. This work has provided a demonstration that predictability and high efficiency can be the norm of the benzannulation reaction. It has also demonstrated that functional constraints imposed by retrosyntheses for certain complex natural products can



Scheme 8.

be accommodated in aryl Fischer carbene complexes without loss of the overall reaction efficiency if the groups can be sufficiently electronically deactivated. This work, while the continuation of a long standing theme in the study of Fischer chromium carbene complex reactivity, has shown that electron withdrawing groups in the *para* position of aryl carbene complexes increase the chemoselectivity for phenol formation, and has shown that the presence of substituents in the *ortho* position are detrimental to phenol formation regardless of the electronic nature of the *ortho* substituent and finally, has shown that larger alkyl groups on the oxygen heteroatom stabilizing substituent of the carbene carbon give rise to increased yields of the desired phenol product.

Experimental

General information

The atmosphere under which synthetic reagents were combined was argon. Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. Prior to use, tetrahydrofuran and diethyl ether were distilled from Na/benzophenone ketyl, and methylene chloride and benzene were distilled from Na. Triflic anhydride was prepared by distillation from triflic acid and P_2O_5, redistilled under Ar, and stored under Ar in a sealed Kontes flask with screw top. Isopropyl triflate was freshly prepared by stirring *i*-PrOH and triflic anhydride with pyridine in CH_2Cl_2 at 0°C for 1 h, worked up by washing 2×distilled H_2O, drying over $MgSO_4$, and concentrating in vacuo. Ceric ammonium nitrate was prepared as a 0.5 M stock solution in 0.1 M HNO_3. Carbene complexes **1a**,[35] **1d**,[3] **1i**[35] and **1q**[3] were prepared according to their literature procedures using methyl triflate as alkylating agent. All other reagents obtained from commercial suppliers were used as received. Flash chromatography was carried out according to Still[36] using 230–240 mesh silica gel. Routine ^{1}H NMR spectra were recorded on Bruker 400 and 500 MHz spectrometers with tetramethylsilane (δ 0.0) as an internal reference. Routine ^{13}C NMR spectra were recorded on Bruker 100 and 125 MHz spectrometers with the central peak of the $CDCl_3$ triplet (δ=77.0) as an internal reference. Infrared spectra were recorded on a Nicolet 20SXB FTIR spectrometer. Low-resolution and high-resolution mass spectra were recorded at the University of Illinois Urbana—Champagne department of chemistry mass spectrometry laboratory. Elemental Analyses were performed by Galbraith Inc., Knoxville, TN.

General procedure for the preparation of methoxybenzylidene Fischer chromium carbene complexes (Procedure I)

To a flame dried round bottom flask, under Ar, was added 1 equiv. of an aryl halide (I or Br) in the volume of THF or ethyl ether necessary to make the concentration of aryl halide 0.2–0.5 M. The solution was cooled to −78°C, and 2 equiv. of *t*-butyl lithium or 1 equiv. of *n*-butyl lithium were added dropwise. The resulting solution was stirred at −78°C for 10–15 min, at which time $Cr(CO)_6$ was added all at once as a solid. Stirring at −78°C was continued for 5–10 min and the reaction was allowed to warm to room temperature and stir for 3–4 h. The resulting dark yellow-orange carbene lithium acylate solution was concentrated in vacuo on a rotary evaporator, and allowed to stand under high vacuum (0.1–0.2 mmHg) for 1–1.5 h. At this time, the acylate was dissolved in a minimum of distilled water and filtered over a Buchner funnel. The acylate solution was diluted with a few mL of CH_2Cl_2 then treated portionwise with solid trimethyloxonium tetrafluoroborate under vigorous stirring until pH 2.0 had been achieved. At this point, the dark red biphasal solution was stirred for 30 min at room temperature. The reaction was then worked up by pouring into a separatory funnel containing saturated $NaHCO_3$ and hexanes. The aqueous layer was extracted 1–2 additional times with hexanes (until all of the red color was removed from the aqueous layer), the organics were washed 2 times with saturated NaCl solution, and dried over $MgSO_4$. The dried solution was filtered through a fritted funnel dry packed with Celite 545. After removal of the solvent in vacuo, the product was obtained by silica gel chromatography, and recrystallized from hexanes where possible.

Pentacarbonyl (methoxy)*p*-trifluoromethylbenzylidene chromium (0) 1m.[35] Carbene complex **1m** was prepared according to Procedure I in 73% recrystallized yield. Compound **1m** was obtained as a cranberry red needles; mp=100–101°C. R_f=0.20 (hexane). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 4.67 (s, 3H); 7.25 (bd, 2H, J=7.8 Hz); 7.65 (d, 2H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 67.4, 122.4, 123.5 (q, CF_3, J=275 Hz), 125.4, 131.2 (q, CF_3–*C*, J=25 Hz), 156.2, 215.6, 223.7, 350.5. IR (nujol, cm^{-1}) 2065 (m), 1927 (m), 1281 (mw), 1123 (mw), 1066 (mw), 829 (mw), 721 (w), 709 (m). MS (EI) *m*/*z* (% rel. intensity): 379.9 M$^+$ (8); 351.9 (15); 314 (27); 295.9 (13); 267.9 (28); 240 (100); 224.9 (14); 196.9 (61); 173 (7); 153 (10); 126 (13); 107 (30); 79.9 (11). HRMS (EI) calcd for $C_{14}H_7F_3CrO_6$ 379.959983, found 379.960080. Anal. calcd for $C_{14}H_7F_3CrO_6$: C, 44.23; H, 1.85. Found: C, 44.29; H, 1.86.

Pentacarbonyl (methoxy)*o*-trifluoromethylbenzylidene chromium (0) 1o.[35] Carbene complex **1o** was prepared according to Procedure I in 59% recrystallized yield. Compound **1o** was obtained as strawberry red crystals; mp=54–55°C. R_f=0.27 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.54 (bs, 3H); 7.12 (bs, 1H); 7.44 (t, 1H, J=8 Hz); 7.63 (m, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2). δ 67.7, 120.4, 122.1, 124.2 (q, –*C*F_3, J=263 Hz); 127.0, 127.1, 128.9, 132.4, 216.1, 224.6, 351.9. IR (nujol, cm^{-1}): 2065 (m), 1927 (m), 1281 (mw), 1123 (mw), 1066 (mw), 829 (mw), 721 (w), 709 (m). MS (EI) *m*/*z* (% rel. intensity): 380.1 (20, M$^+$); 352.1 (22); 321.0 (63); 293.1 (46); 268.1 (17); 240.1 (16); 205.1 (46); 185.1 (100); 155.1 (46); 136.1 (25); 107.1 (5). HRMS (FAB) calcd for $C_{14}H_7F_3CrO_6$ 379.959983, found 379.960080. Anal. calcd for $C_{14}H_7F_3CrO_6$: C, 44.23; H, 1.85. Found: C, 44.55; H, 2.07.

Pentacarbonyl (methoxy)*o*-isopropylbenzylidene chromium (0) 1s. Carbene complex **1s** was prepared according to Procedure I in 66% yield. Compound **1s** was obtained as red prisms after recrystallization from pentane/Et_2O (50/1); mp=dec. 102–105°C. R_f=0.22 (hexane). ^{1}H NMR

(500 MHz, $CDCl_3$): δ 1.25 (d, 6H, J=6.0 Hz); 2.55 (bd, 1H, J=6.5 Hz); 4.34 (bs, 3H); 6.82 (bs, 1H); 7.26–7.30 (m, 3H).). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.1 (–$CH(CH_3)_2$), 30.5, 66.1, 120.4, 125.9, 126.0, 128.6 (2×Ar), 137.9, 215.9, 224.2, 360.4. IR (thin film, cm^{-1}): 3064 (w), 2967 (s), 2873 (m), 2062 (vs), 2020 (w), 1960 (vs), 1932 (m), 1596 (w), 1479 (m), 1440 (s), 1252 (s), 1138 (s), 928 (s), 759 (s); MS (EI) m/z (% rel. intensity): 354 M^+ (3), 326 (7), 298 (41), 267 (40), 242 (26), 211 (66), 179 (100), 163 (32), 147 (41), 131 (81), 119 (27), 105 (35), 91 (27), 59 (57). Anal. calcd for $C_{16}H_{14}CrO_6$: C, 54.24; H, 3.98. Found: C, 54.35; H, 3.99.

General procedure for the preparation of isopropoxybenzylidene Fischer chromium carbene complexes (Procedure II)

To a flame dried round bottom flask, under Ar, was added 1 equiv. of an aryl halide (Br or I) in the volume of THF or ethyl ether necessary to make the concentration of aryl halide 0.2–0.5 M. The solution was cooled to −78°C, and 2 equiv. of *t*-butyl lithium or 1 equiv. of *n*-butyl lithium were added dropwise. The resulting solution was stirred at −78°C for 10–15 min, at which time $Cr(CO)_6$ was added all at once as a solid. Stirring at −78°C was continued for 5–10 min and the reaction was allowed to warm to room temperature and stir for 3–4 h. The resulting dark yellow–orange carbene lithium acylate solution was concentrated in vacuo on a rotary evaporator, and allowed to stand under high vacuum (0.1–0.2 mmHg) for 1–1.5 h. At this time, the acylate was dissolved in a minimum volume of distilled water and filtered over a Buchner funnel containing 1.5 equiv. of tetramethylammonium bromide dissolved in a few mL's of distilled water. Upon filtration, the vacuum adapted Erlenmeyer flask was shaken for 1–2 min and allowed to stand at room temperature for 30–45 min. At this time, the crude, crystalline, bright yellow–orange carbene ammonium salt was collected by suction filtration over a Buchner funnel. This crude salt was then dissolved in CH_2Cl_2 and dried over $MgSO_4$. The methylene chloride solution was then filtered through a fritted funnel dry packed with Celite 545, and the solvent removed in vacuo. After pumping under high vacuum (0.1–0.2 mmHg) for 1–2 h, the crude acylate was dissolved in dry CH_2Cl_2. To the resulting solution was added 2–3 equiv. of isopropyltriflate as a concentrated solution in methylene chloride, the reaction was stirred at room temperature for 30–45 min. The reaction was then worked up by pouring into a separatory funnel containing saturated $NaHCO_3$ and hexanes. The aqueous layer was extracted 1–2 additional times with hexanes (until all of the red color was removed from the aqueous layer), the organics were washed 2 times with saturated NaCl solution, and dried over $MgSO_4$. The dried solution was filtered through a fritted funnel dry packed with Celite 545. After removal of the solvent in vacuo, the product was obtained by silica gel chromatography, and recrystallized from hexanes where possible.

Pentacarbonyl (isopropoxy)*p*-methoxybenzylidene chromium (0) 1g. Carbene complex **1g** was prepared according to Procedure I in 41% yield. Compound **1g** was obtained as red solid. mp=82–83°C. R_f=0.10 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 1.62 (d, 6H, J=6.0 Hz); 3.88 (s, 3H); 5.98 (bh, 1H, J=6.0 Hz); 6.90 (d, 2H, J=9.0 Hz); 7.67 (d, 2H, J=8.5 Hz). IR (nujol, cm^{-1}): 2890 (w), 2056 (vs), 1960 (vs), 1598 (ms), 1231 (ms), 1163 (ms), 1095 (m). MS (EI) m/z (% rel. intensity): 370 M^+ (4), 342 (11), 314 (21), 298 (9), 286 (10), 258 (30), 230 (100), 188 (30), 172 (30), 159 (85), 135 (50), 91 (21), 77 (30), 63 (25). Anal. calcd for $C_{16}H_{14}CrO_7$: C, 51.90; H, 3.81. Found: C, 51.66; H, 3.91.

Pentacarbonyl (isopropoxy)benzylidene chromium (0) 1h. Carbene complex **1h** was prepared according to Procedure II in 45% recrystallized yield. Compound **1h** was obtained as a bright red solid; mp 45–46°C. R_f=0.36 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 1.7 (d, 6H, J=6.5 Hz); 5.7 (m, 1H); 7.2–7.5 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.8, 85.9, 122.6, 128.3, 129.9, 153.9, 216.4, 224.5, 345.3. IR (nujol, cm^{-1}): 2061 (s), 1924 (s), 1246 (w), 1079 (w), 653 (m). MS (EI) m/z (% rel. intensity): 312 M^+-CO (3); 284 (11); 256 (3); 230 (1); 228 (18); 200 (90); 178 (20); 158 (41); 157 (30); 129 (75); 118 (22); 105 (30); 86 (62); 84 (100). Anal. calcd for $C_{15}H_{12}CrO_6$: C, 52.82; H, 3.55. Found: C, 52.71; H, 3.65.

Pentacarbonyl (isopropoxy)*p*-bromobenzylidene chromium (0) 1j. Carbene complex **1j** was prepared according to Procedure II in 42% recrystallized yield. Compound **1j** was obtained as dark purple crystals; mp=92–93°C. R_f=0.28 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 1.58 (d, 6H, J=6 Hz); 5.72 (bs, 1H); 7.11 (bd, 2H, J=8 Hz); 7.53 (d, 2H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.6, 86.1, 124.5, 131.4 (2 overlapping Ar), 152.3, 216.1, 224.0, 343.3. IR (Nujol): 2060 (s), 1950 (s), 1377 (s), 1232 (m). MS (EI) m/z (% rel. intensity): 420 M^+ (12, ^{81}Br), 418 (12, ^{79}Br), 391 (50, ^{81}Br), 364 (85, ^{81}Br), 338 (81), 306 (100), 280 (65), 236 (50), 183 (65), 127 (27). HRMS (FAB) calcd for $C_{15}H_{11}{}^{79}BrCrO_6$ 417.914409, found 417.914400. Anal. calcd for $C_{15}H_{14}BrCrO_6$: C, 42.98; H, 2.65. Found: C, 43.14; H, 2.72.

Pentacarbonyl (isopropoxy)*p*-acetoxybenzylidene chromium (0) 1k. Carbene complex **1k** was prepared according to Procedure I in 41% yield. Compound **1k** was obtained as red solid. mp=dec. 80–83°C. ^1H NMR (500 MHz, $CDCl_3$): δ 2.32 (s, 3H); 4.79 (s, 3H); 7.16 (d, 2H, J=8.0 Hz); 7.45 (d, 2H, J=8.0 Hz). MS (EI) m/z (% rel. intensity): 398 M^+ (6), 370 (40), 342 (60), 314 (25), 286 (49), 258 (100), 216 (20), 187 (7), 121 (4); HRMS (EI) calcd for $C_{17}H_{14}CrO_8$ m/z 398.009327, found. 398.004500. Anal. calcd for $C_{17}H_{14}CrO_8$: C, 51.40; H, 3.30. Found: C, 51.51; H, 3.64.

Pentacarbonyl (isopropoxy) *p*-trifluoromethylbenzylidene chromium (0) 1n. Carbene complex **1n** was prepared according to Procedure II in 43% recrystallized yield. Compound **1n** was obtained as a dark violet needles; mp=66–68°C. R_f=0.29 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, 6H, J=6.0 Hz); 5.64 (bs, 1H); 7.19 (bd, 2H, J=8 Hz); 7.67 (d, 2H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$). δ 22.6, 86.4, 121.8, 123.7 (q, –CF_3, J=275 Hz); 125.4, 130.7, 156.2, 215.8, 223.9, 345.1. IR (nujol, cm^{-1}). IR (Nujol): 2063 (s), 1951 (s), 1377 (s), 1312 (m), 1242 (m). MS (EI) m/z (% rel. intensity): 408 M^+ (22); 380 (60); 352 (100); 328.1 (84); 296 (61); 268 (74); 226 (42); 186 (40); 167 (84); 127 (63); 107 (73); 89

(21). HRMS (FAB) calcd for $C_{16}H_{11}F_3CrO_6$ 407.991283, found 407.991200.

Pentacarbonyl (isopropoxy)*o*-trifluoromethylbenzylidene chromium (0) 1p. Carbene complex **1p** was prepared according to Procedure I in 54% yield. Compound **1p** was obtained as red solid; mp=57–58°C. R_f=0.30 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55 (bs, 6H, $-CHC\mathit{H}_3)_2$); 4.5–6.0 (bs, 1H, $-C\mathit{H}(CH_3)_2$); 7.09 (bs, 1H); 7.41 (t, 1H, J=8 Hz); 7.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.7 ($-CH(\mathit{C}H_3)_2$), 87.8, 120.6, 123.1, 124.2 (q, $-\mathit{C}F_3$, J=275 Hz), 127.0, 128.3, 132.0, 216.1, 224.4, 346.3 (one aryl C not located). IR (nujol, cm^{-1}): 2066 (s), 1950 (s), 1377 (s), 1310 (m), 1238 (s). MS (EI) m/z (% rel. intensity): 408 M^+ (21), 380 (20), 352 (25), 321 (75), 293 (57), 265 (22), 249 (28), 231 (26), 191 (62), 171 (100), 155 (88), 127 (72), 79 (18); HRMS (FAB) calcd for $C_{16}H_{11}F_3CrO_6$ m/z 407.99128, found. 407.99133. Anal. calcd for $C_{16}H_{11}F_3CrO_6$: C, 47.07; H, 2.72. Found: C, 47.16; H, 2.81.

Pentacarbonyl (isopropoxy)*o*-methylbenzylidene chromium (0) 1r. Carbene complex **1r** was prepared according to Procedure II in 62% yield. Compound **1r** was obtained as bright orange solid; mp=64.5–66°C. R_f=0.40 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.52 (bs, 6H, $-CHC\mathit{H}_3)_2$), 2.15 (s, 3H), 4.65 (bs, 1H, $-C\mathit{H}(CH_3)_2$); 6.86 (bs, 1H), 7.17–7.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.8, 22.4 ($-CH(\mathit{C}H_3)_2$), 84.0, 120.3, 125.6, 127.9, 130.5, 135.4, 216.1, 224.6, 360.0 (one aryl C not located). IR (nujol, cm^{-1}): 3064w, 2987s, 2935m, 2060vs, 1950vs, 1596w, 1452m, 1376s, 1264vs, 1175vs, 1072vs, 914vs, 893s, 745vs, 766s.

Procedure for the preparation of carbene complex 1l. Compound **24** was formed by ketalization of *p*-bromophenyl methyl ketone (13.8 mmoles) by refluxing for 12 h in 25 mL of benzene with excess ethylene glycol and 4–5 mol% *p*-toluenesulfonic acid in a 50 mL round bottom flask attached to a Dean–Stark trap.[37] The reaction was washed with 2×10 mL sat. $NaHCO_3$, 2×10 mL brine, and dried over Na_2SO_4. The crude product was recrystallized from pet. ether to give 2.7 g (83%) of the ketalized aryl halide as a colorless solid. Spectral data of compound **24**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.62 (s, 3H); 3.75 (m, 2H); 4.03 (m, 2H); 7.35 (d, 2H, J=8 Hz); 7.46 (d, 2H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.5, 64.5, 108.4, 121.9, 127.2, 131.3, 142.4. IR (thin film, cm^{-1}): 3413 (bm), 2983 (m), 2947 (w), 2892 (ms), 1481 (w), 1392 (s), 1370 (m), 1221 (s), 1196 (s), 1144 (m), 1092 (s), 1030 (s), 1009 (m), 941 (m), 869 (ms), 831 (s); MS (EI) m/z (% rel. intensity): 229 (100, M^+–15, ^{81}Br), 227 (100, M^+–15, ^{79}Br), 211 (7, ^{81}Br), 183 (51, ^{81}Br), 155 (15, ^{81}Br), 133 (8), 103 (13), 87 (38), 76 (14), 63 (5). HRMS (FAB) calcd for $C_{10}H_{11}O_2{}^{79}Br$ m/z 241.99424, found 241.99337. Anal. calcd for $C_{10}H_{11}O_2Br$: C, 49.41; H, 4.56. Found: C, 49.42; H, 4.68. This material was then converted to carbene complex **25** by procedure I to yield the desired carbene complex in 64% yield after chromatography as a dark red solid. Spectral data for **25**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (s, 3H); 3.76 (m, 2H); 4.04 (m, 2H); 4.73 (s, 3H); 7.30 (d, 2H, J=8.0 Hz); 7.52 (d, 2H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.3, 64.6, 67.2, 108.5, 123.5, 125.1, 145.8, 153.2, 216.1, 224.0, 350.3. IR (thin film, cm^{-1}): 2991 (m), 2959 (m), 2889 (m), 2060 (s), 1945 (s), 1750 (w), 1620 (w), 1452 (m), 1227 (s), 1040 (s), 984 (s), 873 (s). MS (EI) m/z (% rel. intensity): 399 (M^++1, 6), 370 (13), 351 (21), 315 (34), 286 (26), 251 (7), 237 (3), 223 (100), 207 (20), 193 (5), 179 (19), 121 (3), 103 (2), 87 (47), 73 (5); HRMS (FAB) calcd for $C_{17}H_{14}CrO_8$ m/z 398.00930, found 398.14110. Anal. calcd for $C_{17}H_{14}CrO_8$: C, 51.27; H, 3.54. Found: C, 51.72; H, 3.85.

Pentacarbonyl (methoxy)*p*-acetoylbenzylidene chromium (0) 1l. To a flame dried round bottom flask under Ar was added **25** (0.25 mmoles) in 6 mL CH_2Cl_2. To this solution was added 2.0 equiv. of Ph_3CBF_4.[29] The reaction was stirred at room temperature for 5–10 min. The crude reaction was poured into 20 mL H_2O. The aqueous layer was extracted with 1×10 mL CH_2Cl_2, and the organics dried over $MgSO_4$. Purification by silica gel chromatography (2×16 cm, 4/1/1 hex/CH_2Cl_2/Et_2O) gave 70.5 mg (80%) of the title compound as a dark red oil. Spectral data for **1l**: R_f=0.36 (4/1/1 hex/CH_2Cl_2/Et_2O). ^{1}H NMR (CD_2Cl_2) δ 1.59 (d, 6H, J=4.0 Hz), 2.29 (s, 3H), 5.79 (bs, 1H), 7.15 (d, 2H, J=8.6 Hz), 7.37 (d, 2H, J=8.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.6, 67.2, 122.1, 128.4, 129.8, 137.2, 197.0, 215.7, 223.8, 351.0. IR (thin film, cm^{-1}): 2958 (w), 2900 (w), 2064 (s), 1950 (s), 1688 (s), 1452 (m), 1265 (s), 1221 (s), 1143 (m), 984 (m). This carbene complex is too unstable for further characterization.

Procedure for the preparation of pentacarbonyl (isopropoxy)*p*-formylbenzylidene chromium (0) 1w. To a flame dried round bottom flask was added 2.0 mmoles **1j** in 30 mL Et_2O. The solution was cooled to −78°C and 3 equiv. *n*-BuLi was added dropwise slowly over 1–2 min. The resulting solution was stirred for 5 min at which time 4 equiv. DMF was added. The reaction was allowed to warm to room temperature over ~30 min. The crude reaction was filtered over a fritted funnel through silica gel, and purified by silica gel chromatography (3×12 cm; 20% EtOAc/hexanes) to give 360 mg (49%) of the desired carbene complex as a dark red oil. Spectral data for **1w**: R_f=0.6 (20% EtOAc/hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58 (d, 6H, J=7 Hz); 5.65 (bs, 1H); 7.18 (d, 2H, J=7.8 Hz); 7.92 (d, 2H, J=7.8 Hz); 10.03 (s, 1H).

General procedure for the benzannulation of carbene complexes 1 with 1-pentyne (Procedure III)

To a 25 mL flame dried Kontes flask equipped with a Teflon screw top was added 0.5 mmoles of carbene complex in 5 mL C_6H_6. To this solution was added 2.0 equiv. of 1-pentyne. The system was degassed by running 3 cycles of freeze–pump–thaw. After the third cycle, the flask was back-filled with Ar, and sealed. The reaction was then heated with stirring to 75–80°C for 16 h. At this point, the reaction was split in half and worked-up using two methods.

Method A: The crude reaction mixture was diluted with ether and washed with 3×10 mL of brine. The aqueous layer was then back extracted 1×10 mL ether. The organic layer was then dried over $MgSO_4$. The solution was filtered through a fritted funnel dry packed with Celite 545 and the products were collected by silica gel chromatography (usually 2×15–20 cm, 5% EtOAc/Hexanes).

Method B: The crude reaction mixture was diluted with ether and treated with 2–3 mL of the above described CAN solution. The biphasal reaction was stirred for 2–3 h at room temperature. At this point, the reaction was poured into a 125 mL separatory funnel and diluted with ether. 15 mL of sat. $NaHCO_3$ was then added to the separatory funnel to quench the CAN solution, and separated with out shaking to avoid emulsion. The ether layer was washed 1×10 mL sat. $NaHCO_3$. The aqueous layer was then back extracted 2×10 mL ether. The combined organics were then washed 1×15 mL brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the products were collected by silica gel chromatography (usually 2×15–20 cm, 5% EtOAc/Hexanes).

Benzannulation of carbene complex 1a with 1-pentyne. The benzannulation of **1a** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 41 mg (76%) of the desired phenol product **20a** as a colorless solid, and 7.5% of **4a** based on crude NMR data. Spectral data for **20a** was identical to that found in the literature.[38] ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, J=7.3 Hz); 1.71 (sextet, 2H, J=7.5 Hz); 2.70 (t, 2H, J=7.7 Hz); 3.93 (s, 3H); 4.70 (bs, 1H), 6.54 (s, 1H), 7.41 (t, 1H, J=7.2 Hz); 7.45 (t, 1H, J=7.1 Hz); 8.03 (d, 1H, J=8.3 Hz); 8.12 (d, 1H, J=8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 23.4, 32.5, 55.7, 106, 120, 121, 122, 124, 125.6, 125.8, 126, 142, 149. IR (nujol, cm^{-1}) 3400 (bs, –OH), 2950 (ms), 1680 (m), 1590 (m), 1461 (s), 1383 (s), 1270 (m), 1231 (m), 1190 (w), 1167 (w), 1125 (s), 1100 (s), 764 (S). Spectral data for **4a** was identical to that found in the literature:[24] R_f=0.18 (5% EtOAc/hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, 3H, J=7.3 Hz); 1.03 (t, 3H, J=7.5 Hz); 1.21 (sextet, 2H, J=7.5 Hz); 1.68 (sextet, 2H, J=7.5 Hz); 1.82 (t, 2H, J=8 Hz); 2.50 (t, 2H, J=8 Hz); 3.17 (s, 3H); 4.99 (s, 1H); 6.93 (s, 1H); 7.31 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 14.3, 17.8, 20.4, 27.6, 37.2, 55.0, 56.9, 111.2, 127.1, 128.3, 128.7, 133.7, 142.0, 156.4, 164.2, 205.8, 206.0.

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 39 mg (78%) of the desired quinone product **2a** as a yellow solid, and 7.5% of **4a** based on crude NMR data. Spectral data for **2a** was identical to that previously shown in the literature.[38] R_f=0.29 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, J=7.35 Hz); 1.62 (q, 2H, J=7.4 Hz); 2.55 (t, 2H, J=7.7 Hz); 6.78 (s, 1H); 7.72 (m, 2H); 8.05 (m, 1H); 8.09 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.2, 31.5, 125.5, 126.1, 132.0, 132.2, 133.7, 134.0, 151.6, 185.6.

Benzannulation of carbene complex 1d with 1-pentyne. The benzannulation of **1d** (0.4 mmoles) with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×13 cm, 7/1/1–4/1/1 hexanes/CH_2Cl_2/Et_2O) gave 34 mg (60%) of a yellow oil that was identified as phenol **20d**. Phenol **20d** was characterized by oxidation with CAN (Method B from Procedure III) which gave quinone **20d** that was found have spectral data identical to that reported in the literature for this compound.[3]

Benzannulation of carbene complex 1g with 1-pentyne. The benzannulation of **1g** (0.48 mmoles) with 1-pentyne following Procedure III, Method B and isolation by silica gel chromatography (2×18 cm, 5% EtOAc/Hexanes) gave 34 mg (29%) of a yellow solid that was identified as quinone **2b**, and 60 mg (59%) of a second yellow solid that was identified as indanone **3b**. Spectral data for **2b** and **3b** were identical to that found in the literature.[3]

Benzannulation of carbene complex 1h with 1-pentyne. The benzannulation of **1h** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 55 mg (90%) of the desired phenol product **20h** as a colorless solid, and <5% of **4h** based on crude NMR data. Spectral data for **20h**: mp=110–111°C And R_f=0.27 (10% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, J=7.3 Hz); 1.41 (d, 6H, J=6 Hz); 1.71 (sextet, 2H, J=7.5 Hz); 2.70 (t, 2H, J=7.7 Hz); 4.61 (h, 1H, J=6 Hz); 4.73 (bs, 1H), 6.65 (s, 1H), 7.42 (t, 1H, J=7.8 Hz); 7.46 (t, 1H, J=7.4 Hz); 8.05 (d, 1H, J=8.4 Hz); 8.18 (d, 1H, J=8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 22.2 (–CH(CH_3)$_2$), 23.4, 32.4, 71.2, 110.3, 120.7, 121.3, 122.4, 124.6, 125.6, 125.8, 126.2, 141.8, 147.0. IR (nujol, cm^{-1}) 3200 (bs, –OH), 2750 (ms), 1620 (m), 1590 (m). MS (EI) m/z (% rel. intensity): 244.2 M^+ (90); 230.1 (6); 202.1 (100); 173.1 (72); 159.1 (3); 145.1 (5); 128.1 (5); 115.1 (8); 105.1 (11); 77 (3). HRMS (EI) calcd for $C_{16}H_{20}O_2$ 244.146330, found 244.145785. Anal. calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.36; H, 8.18. Spectral data for **4h**: R_f=0.28 (5% EtOAc/hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, 3H, J=7.3 Hz); 1.03 (t, 3H, J=7.5 Hz); 1.21 (sextet, 2H, J=7.5 Hz); 1.41 (d, 6H, J=6 Hz); 1.68 (sextet, 2H, J=7.5 Hz); 1.82 (t, 2H, J=8 Hz); 2.50 (t, 2H, J=8 Hz); 4.58 (h, 1H, J=6 Hz); 4.99 (s, 1H); 6.93 (s, 1H); 7.31 (m, 5H).

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 45 mg (90%) of a yellow solid that was identified as the quinone **2a**, and <5% of **4h** based on crude NMR data. Spectral data for **2a** was identical to that previously shown in the literature:[24] R_f=0.29 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, J=7.35 Hz); 1.62 (q, 2H, J=7.4 Hz); 2.55 (t, 2H, J=7.7 Hz); 6.78 (s, 1H); 7.72 (m, 1H); 8.05 (m, 1H); 8.09 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.2, 31.5, 125, 126, 132, 132.2, 133, 134, 151, 185.

Benzannulation of carbene complex 1i with 1-pentyne. The benzannulation of **1i** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×20 cm, 5% EtOAc/Hexanes) gave 53 mg (72%) of the desired phenol product **20i** as a colorless solid, and <5% of **4i** based on crude NMR data. Spectral data for **20i**: mp=114–115°C; R_f=0.16 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, J=7.3 Hz); 1.70 (s, 2H, J=7.5 Hz); 2.69 (t, 2H, J=7.5 Hz); 3.93 (s, 3H); 4.64 (s, 1H, –O*H*); 6.56 (s, 1H); 7.48 (d, 1H, J=8.8 Hz); 8.02 (d, 1H, J=8.8 Hz); 8.26 (d, 1H, J_{meta}=1.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 23.3, 32.5, 55.7, 106.4, 120.5, 122.5, 123.4, 123.7, 123.8, 126.9, 128.1, 140.9, 149.6. IR (nujol, cm^{-1}) 3300 (bs, –OH), MS (EI) m/z (% rel. intensity): 296 (100, M^+, ^{81}Br), 294 (100, M^+, ^{79}Br), 281 (41,

^{81}Br), 265 (57, ^{79}Br), 251 (10, ^{79}Br), 237 (15, ^{79}Br), 223 (6), 199 (4), 183 (19, ^{79}Br), 172 (5), 158 (19), 143 (8), 128 (21), 115 (42), 89 (5), 75 (15), 63 (8). HRMS (EI) calcd for $C_{14}H_{15}{}^{79}BrO_2$ *m/z* 294.025541, found 294.024733. Anal. calcd for $C_{14}H_{15}{}^{79}BrO_2$: C, 56.97; H, 5.12. Found: C, 57.26; H, 5.26. Spectral data for **4i**: R_f=0.15 (5% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, 3H, *J*=7.4 Hz); 1.02 (t, 3H, *J*=7.4 Hz); 1.22 (sextet, 2H, *J*=7.5 Hz); 1.68 (sextet, 2H, *J*=7.5 Hz); 1.81 (t, 2H, *J*=7.5 Hz); 2.49 (t, 2H, *J*=7.5 Hz); 3.17 (s, 3H); 4.99 (s, 1H); 6.92 (s, 1H); 7.20 (d, 2H, *J*=8 Hz); 7.44 (d, 2H, *J*=8 Hz).

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 52 mg (75%) of the desired quinone product **2i** as an orange solid, and <5% of **4i** based on crude NMR data. Spectral data for **2i**: mp=66–67°, R_f=0.30 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, *J*=7.4 Hz); 1.61 (sextet, 2H, *J*=7.4 Hz); 2.54 (t, 2H, *J*=7.5 Hz); 6.79 (t, 1H, *J*=1.3 Hz); 7.85 (dd, 1H, J_{ortho}=8.25, J_{meta}=2.0 Hz); 7.92 (d, 1H, *J*=8.24 Hz); 8.21 (d, 1H, J_{meta}=1.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.2, 31.5, 127.7, 129.0, 129.5, 130.6, 133.3, 134.8, 136.6, 151.6, 184.1, 184.3. IR (nujol, cm^{-1}) 2700 (m), 1670 (s), 1621 (ms), 1584 (mw). MS (EI) *m/z* (% rel. intensity): 280 (100, M^+, ^{81}Br), 278 (100, M^+, ^{79}Br), 252 (23, ^{81}Br), 237 (25), 199 (11), 184 (26), 143 (16), 128 (42), 75 (30). HRMS (EI) calcd for $C_{13}H_{11}{}^{79}BrO_2$ 277.994241, found 277.993114. Anal. calcd for $C_{13}H_{11}BrO_2$: C, 55.33; H, 3.97. Found: C, 55.28; H, 4.08.

Benzannulation of carbene complex 1j with 1-pentyne. The benzannulation of **1j** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 73 mg (90%) of the desired phenol product **20j** as a colorless solid, and <5% of **4j** based on crude NMR data. Spectral data for **20j**: mp=117–118°C; R_f=0.18 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, 3H, *J*=7.4 Hz); 1.40 (d, 6H, –CH(C*H*$_3$)$_2$, *J*=6 Hz); 1.70 (sextet, 2H, *J*=7.4 Hz); 2.68 (t, 2H, *J*=7.7 Hz); 4.61 (h, 1H, –C*H*(CH$_3$)$_2$, *J*=6 Hz); 4.65 (s, 1H, –O*H*); 6.63 (s, 1H), 7.46 (d, 1H, *J*=8.9 Hz); 8.03 (d, 1H, *J*=8.9 Hz); 8.25 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 22.1 (–CH(*C*H$_3$)$_2$), 23.3, 32.4, 71.3, 110.3, 120.3, 122.5, 123.7, 124.3, 124.7, 126.9, 128.0, 140.9, 147.6. IR (nujol, cm^{-1}) 3250 (bs, –OH), 2700 (m), 1620 (m), 1592 (m). MS (EI) *m/z* (% rel. intensity): 324 (10, M^+, ^{81}Br), 322 (10, M^+, ^{79}Br), 282 (100, ^{81}Br), 251 (56, ^{79}Br), 225 (5), 202 (50), 173 (46), 144 (14), 129 (15), 115 (32), 77 (10). HRMS (EI) calcd for $C_{16}H_{19}{}^{79}BrO_2$ 322.056841, found 322.055971. Anal. calcd for $C_{16}H_{19}BrO_2$: C, 59.45; H, 5.92. Found: C, 59.55; H, 6.01. Spectral data for **4j**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=7.5 Hz); 1.03 (t, 3H, *J*=7.5 Hz); 1.42 (d, 6H, *J*=6 Hz); 1.24 (sextet, 2H, *J*=7.5 Hz); 1.68 (sextet, 2H, *J*=7.5 Hz); 1.82 (t, 2H, *J*=7.5 Hz); 2.49 (t, 2H, *J*=7.5 Hz); 4.64 (h, 1H, *J*=6 Hz); 6.64 (s, 1H); 6.90 (s, 1H); 7.13 (d, 2H, *J*=8 Hz); 7.49 (d, 2H, *J*=8 Hz).

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 63 mg (91%) of an orange solid that was identified as the quinone **2i**, and <5% of **4j** based on crude NMR data. Spectral data for the quinone product was found to be identical to the quinone obtained above from the reaction of complex **1i** with 1-pentyne.

Benzannulation of carbene complex 1k with 1-pentyne. The benzannulation of **1k** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×16 cm, 10% EtOAc/Hexanes) gave 93 mg (62%) of the desired phenol product **20k** as a colorless solid. Phenol **20k** was characterized by oxidation with CAN (Method B of Procedure III) to give quinone **2k** which was found to have spectral data identical to that reported in the literature for this compound.[3] Spectral data for **20k**: R_f=0.18 (10% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, 3H, *J*=7.6 Hz); 1.40 (d, 6H, –CH(C*H*$_3$)$_2$, *J*=6 Hz); 1.65 (sextet, 2H, *J*=7.6 Hz); 2.34 (s, 3H); 2.68 (t, 2H, *J*=7.6 Hz); 4.62 (h, 1H, –C*H*(CH$_3$)$_2$, *J*=6 Hz); 6.61 (s, 1H), 7.13 (dd, 1H, J_1=9, J_2=2.2 Hz); 7.77 (d, 1H, *J*=2.4 Hz); 8.18 (d, 1H, *J*=9.2 Hz).

Benzannulation of carbene complex 1l with 1-pentyne. The benzannulation of **1l** (0.48 mmoles) with 1-pentyne following Procedure III, Method B and isolation by silica gel chromatography (2×18 cm, 5% EtOAc/Hexanes) gave 31 mg (63% based recovered ester) of the desired quinone product **2l** as a yellow solid, and recovered 14% of air oxidized carbene complex. Spectral data for **2l**: R_f=0.17 (10% EtOAc/Hex.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, 3H, *J*=7.5 Hz); 1.64 (sextet, 2H, *J*=7.5 Hz); 2.59 (t, 2H, *J*=7.5 Hz); 2.72 (s, 3H); 6.86 (s, 1H); 8.16 (d, 1H, *J*=8 Hz); 8.30 (dd, 1H, J_{ortho}=8, J_{meta}=3.5 Hz); 8.62 (d, 1H, *J*=3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 21.2, 27.0, 31.6, 126.6, 126.7, 132.5, 132.6, 134.6, 135.0, 140.7, 152.3, 184.4, 184.5, 196.7. IR (thin film, cm^{-1}): 2950 (m), 2930 (m), 2869 (m), 1967 (m), 1887 (m), 1680 (s), 1662 (s), 1627 (m), 1603 (m), 1368 (s), 1265 (s), 1248 (m), 1191 (m), 1111 (m), 1060 (w), 828 (w). MS (EI) *m/z* (% rel. intensity): 243 (M^++1, 75), 224 (100), 215 (16), 201 (20), 185 (7), 171 (16), 159 (8), 147 (30), 128 (15), 115 (22), 97 (10), 71 (18); HRMS (EI) calcd for $C_{15}H_{14}O_3$ *m/z* 242.09429, found 242.094702. Anal. calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.33; H, 5.92.

Benzannulation of carbene complex 1m with 1-pentyne. The benzannulation of **1m** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×20 cm, 5% EtOAc/Hexanes) gave 68 mg (96%) of the desired phenol product **20m** as a colorless solid, and <2% of **4m** based on crude NMR data. Spectral data for **20m**: mp=95–96°C; R_f=0.30 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, 3H, *J*=7.3 Hz); 1.72 (sextet, 2H, *J*=7.4 Hz); 2.71 (t, 2H, *J*=7.7 Hz); 3.96 (s, 3H); 4.80 (s, 1H, –O*H*); 6.67 (s, 1H); 7.59 (dd, 1H, J_{ortho}=7.25 Hz, J_{meta}=1.5 Hz); 8.26 (d, 1H, *J*=8.0 Hz); 8.44 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 23.3, 32.5, 55.8, 108.1, 119.4, 120.3, 122.3, 123.0, 124.5 (q, –*C*F$_3$, *J*=272 Hz), 124.6, 126.6, 127.6 (q, –*C*CF$_3$, *J*=32 Hz), 142.3, 149.3. IR (nujol, cm^{-1}) 3300 (bs, –OH), 2700 (m), 1620 (m), 1576 (m). MS (EI) *m/z* (% rel. intensity): 284.1 M^+ (100), 269.1 (31), 255.1 (60), 241.1 (10), 227.1 (16), 212.1 (6), 173 (11), 145 (4), 115.1, (11), 93.1 (1), 75 (3). HRMS (EI) calcd for $C_{15}H_{15}F_3O_2$ 284.102415, found 284.101820. Anal. calcd for $C_{15}H_{15}F_3O_2$: C, 63.37; H, 5.32. Found: C, 63.21; H, 5.40.

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hexanes) gave 64 mg (95%) of the desired quinone product **2m** as an orange solid, and <2% of **4m** based on crude NMR data. Spectral data for **2m**: mp=49–50°C, R_f=0.10 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (t, 3H, J=7.3 Hz); 1.64 (sextet, 2H, J=7.5 Hz); 2.59 (t, 2H, J=7.3 Hz); 6.87 (d, 1H, J=1.3 Hz); 7.97 (dd, 1H, J_{ortho}=8.0 Hz, J_{meta}=1.0 Hz); 8.19 (d, 1H, J=8.0 Hz); 8.31 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.2, 31.5, 123.1 (q, $-CF_3$, J=273 Hz), 123.8, 126.8, 130.0, 132.6, 134.1, 134.9, 135.2 (q, $-CCF_3$, J=34 Hz), 152.3, 183.8, 183.9. IR (nujol, cm^{-1}) 2700 (m), 1674 (s), 1615 (w). MS (EI) *m/z* (% rel. intensity): 268 M^+ (100), 253 (31), 225 (36), 197 (14), 173 (22), 144 (31), 115 (20), 94 (5), 75 (16). HRMS (EI) calcd for $C_{14}H_{11}F_3O_2$ 268.071114, found 268.070663. Anal. calcd for $C_{14}H_{11}F_3O_2$: C, 62.69; H, 4.13. Found: C, 62.72; H, 4.19.

Benzannulation of carbene complex 1n with 1-pentyne. The benzannulation of **1n** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×20 cm, 5% EtOAc/Hexanes) gave 76 mg (98%) of the desired phenol product **20n** as a colorless solid, and <1% of **4n** based on crude NMR data. Spectral data for **20n**: mp=100–101°C; R_f=0.30 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (t, 3H, J=7.3 Hz); 1.41 (d, 6H, $-CH(CH_3)_2$, J=6 Hz); 1.70 (sextet, 2H, J=7.5 Hz); 2.69 (t, 2H, J=7.7 Hz); 4.63 (h, 1H, $-CH(CH_3)_2$, J=6 Hz); 4.81 (s, 1H, $-OH$); 6.75 (s, 1H); 7.57 (d, 1H, J=8.7 Hz); 8.27 (d, 1H, J=8.7 Hz); 8.43 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 22.1 ($-CH(CH_3)_2$), 23.2, 32.4, 71.5, 112.2, 119.4, 120.2, 122.5, 123.4, 124.6 (q, $-CF_3$, J=272 Hz), 124.7, 127.4, 127.5 (q, $-CCF_3$, J=32 Hz), 142.5, 147.3. IR (nujol, cm^{-1}) 3350 (bs, –OH), 2730 (m), 1615 (mw), 1518(m). MS (EI) *m/z* (% rel. intensity): 312.2 M^+ (37), 293.2 (5), 270.1 (100), 241.1 (78), 213.1 (6), 173 (11), 145 (5), 115.1 (6), 75 (2). HRMS (EI) calcd for $C_{17}H_{19}F_3O_2$ 312.133715, found 312.133386. Anal. calcd for $C_{17}H_{19}F_3O_2$: C, 65.37; H, 6.13. Found: C, 65.06; H, 6.18.

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hexanes) gave 66 mg (98%) of an orange solid that was identified as the quinone **2m**, and <1% of **4n** based on crude NMR data. The spectral data for the quinone product was found to be identical to the quinone obtained above from the reaction of complex **1m** with 1-pentyne.

Benzannulation of carbene complex 1o with 1-pentyne. The benzannulation of **1o** with 1-pentyne following Procedure III, Method B and isolation by silica gel chromatography (1×22 cm, 10% EtOAc/Hexanes) gave 43 mg (64%) of the desired quinone product **2o** as an yellow solid. Spectral data for **2o**: mp=74–75°C, R_f=0.40 (10% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, 3H, J=7 Hz); 1.63 (sextet, 2H, J=7 Hz); 2.55 (t, 2H, J=7 Hz); 6.83 (t, 1H, J=1 Hz); 7.83 (t, 1H, J=7 Hz); 8.10 (d, 1H, J=8 Hz); 8.39 (d, 1H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.1, 31.0, 122.9 (q, $-CF_3$, J=275 Hz), 128.8 (q, $-CCF_3$, J=38 Hz), 130.6, 130.7, 132.2, 133.0, 134.6, 136.4, 149.8, 182.9, 184.0. IR (nujol, cm^{-1}) 2700 (m), 1674 (s), 1615 (w). MS (EI) *m/z* (% rel. intensity): 268 (M^+, 45), 253 (6), 240 (1), 225 (15), 199 (9), 177 (100), 144 (13), 128 (5), 113 (72), 89 (4), 78 (48); HRMS (EI) calcd for $C_{14}H_{11}F_3O_2$ *m/z* 268.07111, found 268.071769. Anal. calcd for $C_{14}H_{11}F_3O_2$: C, 62.69; H, 4.13. Found: C, 62.63; H, 4.22.

Benzannulation of carbene complex 1p with 1-pentyne. The benzannulation of **1p** with 1-pentyne following Procedure III, Method B and isolation by silica gel chromatography (1×22 cm, 10% EtOAc/Hexanes) gave 47 mg (60%) of a yellow solid that was identified as the quinone **2o**. The spectral data for the quinone product was found to be identical to the quinone obtained above from the reaction of complex **1o** with 1-pentyne.

Benzannulation of carbene complex 1q with 1-pentyne. The benzannulation of **1q** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hexanes) gave 33 mg (62%) of the desired phenol product **20q** as a colorless solid, along with 1.6 mg (3%) of quinone **2q**, and <3% of **4q** based on crude NMR data. Phenol **20q** was characterized by oxidation with CAN (Method B of Procedure III) to give the corresponding quinone **2q** which had spectral data identical to that reported for this compound.[3] Spectral data for **20q**: R_f=0.33 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, 3H, J=7.5 Hz); 1.70 (sextet, 2H, J=7 Hz); 2.68 (t, 2H, J=6.75 Hz); 2.86 (s, 3H); 3.86 (s, 3H); 4.72 (s, 1H, $-OH$); 6.58 (s, 1H); 7.16 (d, 1H, J=8 Hz); 7.31 (t, 1H, J=7.5 Hz); 7.94 (d, 1H, J=8.5 Hz).

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hex) to give 36 mg (66%) of an orange solid that was identified as the quinone **2q**, and <3% of **4q** based on crude NMR data. The spectral data for the quinone product was found to be identical to the quinone obtained above from the reaction phenol **20q** with CAN.

Benzannulation of carbene complex 1r with 1-pentyne. The benzannulation of **1r** with 1-pentyne following Procedure III, Method A and isolation by silica gel chromatography (1.5×28 cm, 5% EtOAc/Hexanes) gave 31 mg (48%) of the desired phenol product **20r** as a colorless solid, along with 10 mg (19%) of quinone **2r**, and <3% of **4r** based on crude NMR data. Phenol **20r** was characterized by oxidation with CAN (Method B of Procedure III) to give the corresponding quinone **2q** which had spectral data identical to that reported for this compound.[3] Spectral data for **20r**: R_f=0.25 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, 3H, J=7.5 Hz); 1.45 (d, 6H, $-CH(CH_3)_2$, J=6 Hz); 1.72 (sextet, 2H, J=7.75 Hz); 2.69 (t, 2H, J=7.5 Hz); 2.89 (s, 3H), 4.66 (h, 1H, $-CH(CH_3)_2$, J=6 Hz); 4.84 (s, 1H, $-OH$); 6.67 (s, 1H); 7.60 (d, 1H, J=8 Hz); 7.42 (t, 1H, J=8.4 Hz); 7.88 (d, 1H, 8).

Reaction following Procedure III, Method B and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hex) to give 35 mg (66%) of an orange solid that was identified as the quinone **2q**, and <3% of **4q** based on crude NMR data. The spectral data for the quinone product was found to be identical to that of the quinone obtained above from the reaction phenol **20q** with CAN.

Benzannulation of carbene complex 1s with 1-pentyne. The benzannulation of **1s** (0.48 mmoles) with 1-pentyne following Procedure III, Method B and isolation by silica gel chromatography (2×18 cm, 5% EtOAc/Hexanes) gave 59 mg (49%) of the desired quinone product **2s** as a yellow oil, and 12 mg (11%) of indanone **3s** as a yellow oil. Spectral data for **2s**: R_f=0.50 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, 3H, J=7.5 Hz); 1.27 (d, 6H, J=7.0 Hz); 1.61 (sextet, 2H, J=7.5 Hz); 2.51 (t, 2H, J=7.0 Hz); 4.39 (h, 1H, J=6.5 Hz); 6.69 (s, 1H); 7.64 (t, 1H, J=8.0 Hz); 7.73 (dd, 1H, J_1=8.0, J_2=1.0 Hz); 8.02 (dd, 1H, J_1=8.0, J_2=1.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.1, 23.5 (–CH(CH_3)$_2$), 28.5, 30.9, 125.2, 128.7, 132.1, 133.0, 133.9, 137.1, 149.1, 151.9, 185.7, 187.6. IR (neat, cm^{-1}): 3050 (w), 2966 (s), 2932 (s), 2873 (s), 1650 (s), 1631 (s), 1585 (s), 1464 (s), 1383 (s), 1315 (s), 1260 (s), 1238 (s), 1064 (ms), 978 (m), 913 (m), 782 (s);). MS (EI) m/z (% rel. intensity): 242 M^+ (100), 227 (40), 215 (30), 199 (35), 185 (40), 171 (19), 152 (17), 141 (14), 128 (17), 115 (22), 89 (6), 77 (6), 63 (5);); HRMS (EI) calcd for $C_{16}H_{18}O_2$ m/z 242.13068, found 242.131306. Anal. calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.77; H, 7.45. Spectral data for **3s**: R_f=0.45 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (t, 3H, J=7.2 Hz); 1.23 (d, 3H, J=6.5 Hz); 1.24 (d, 3H, J=6.5 Hz); 1.41 (m, 3H); 1.88 (m, 1H); 2.34 (dd, 1H, J_1=19, J_2=3.5 Hz); 2.81 (dd, 1H, J_1=19, J_2=7.5 Hz); 3.27 (m, 1H); 4.18 (h, 1H, J=6.5 Hz); 7.29 (m, 2H); 7.51 (t, 1H, J=8.0 Hz).). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 20.8, 23.0, 23.2, 27.1, 37.2, 38.6, 43.9, 122.8, 123.9, 132.7, 150.1, 160.1, 207.2; 9 MS (EI) m/z (% rel. intensity): 216 M^+ (100), 201 (80), 188 (33), 134 (42), 159 (15), 146 (28), 131 (37), 115 (34), 103 (6), 91 (18), 77 (18).

General procedure for the benzannulation of carbene complexes 1 with 3-hexyne (Procedure IV)

To a 25 mL flame dried Kontes flask equipped with a Teflon screw top was added 0.5 mmoles of carbene complex in 5 mL C_6H_6. To this solution was added 2.0 equiv. of 3-hexyne. The system was degassed by running 3 cycles of freeze–pump–thaw. After the third cycle, the flask was back-filled with Ar, and sealed. The reaction was then heated with stirring to 75–80°C for 16 h. At this time, the reaction was cooled to room temperature, and the crude reaction mixture was diluted with ether and treated with 2–3 mL of the above described CAN solution. The biphasal reaction was stirred for 2–3 h at room temperature. At this point, the reaction was poured into a 125 mL sep funnel and diluted with ether. 15 mL of sat. $NaHCO_3$ was then added to the sep funnel to quench the CAN solution, and separated with out shaking to avoid emulsion. The ether layer was washed 1×10 mL sat. $NaHCO_3$. The aqueous layer was then back extracted 2×10 mL ether. The combined organics were then washed 1×15 mL brine and dried over $MgSO_4$. The solvent was removed in vacuo, and the products were collected by silica gel chromatography (usually 2×15–20 cm, 5% EtOAc/Hexanes).

Benzannulation of carbene complex 1h with 3-hexyne. The benzannulation of **1h** with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×17 cm, 5% EtOAc/Hexanes) gave 55 mg (90%) of the desired quinone product **26a** as an orange solid, and <1% of **29h** based on crude NMR data. Spectral data for **26a** was identical to that found in the literature from the reaction of **1a**.[24] mp=72–72°C; R_f=0.27 (10% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.16 (t, 6H, J=7.5 Hz); 2.66 (q, 4H, J=7.5 Hz); 7.67–7.72 (m, 2H); 8.06–8.09 (m, 2H).

Benzannulation of carbene complex 1i with 3-hexyne. The benzannulation of **1i** with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hexanes) gave 136 mg (93%) of the desired quinone product **26i** as an orange solid, and <2% of **29i** based on crude NMR data. Spectral data for **26i**: mp=97–98°C; R_f=0.45 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (t, 6H, J=7.5 Hz); 2.64 (q, 4H, J=7.5 Hz); 7.80 (dd, 1H, J_{ortho}=8.3 Hz, J_{meta}=2.0 Hz); 7.92 (d, 1H, J=8.2 Hz); 8.18 (d, 1H, J=2.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9 (overlapping –CH_2CH_3), 20.1, 20.2, 128.0, 128.7, 129.2, 130.8, 133.3, 136.2, 148.0, 148.3, 183.8, 184.2. IR (nujol, cm^{-1}) 2700 (m), 1670 (s), 1630 (ms), 1575 (m). MS (EI) m/z (% rel. intensity): 294 (100, M^+, ^{81}Br), 292 (100, M^+, ^{79}Br), 277 (30, ^{79}Br), 264 (5), 251 (16, ^{81}Br), 237 (7, ^{81}Br), 213 (3), 198 (76), 181 (8), 170 (15), 152 (12), 141 (20, ^{79}Br), 128 (25), 115 (14), 86 (5), 75 (32), 63 (10). HRMS (EI) calcd for $C_{14}H_{13}{}^{79}BrO_2$ 292.009891, found 292.008601. Anal. calcd for $C_{14}H_{13}BrO_2$: C, 57.36; H, 4.47. Found: C, 57.64; H, 4.70.

Benzannulation of carbene complex 1j with 3-hexyne. The benzannulation of **1j** with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×16 cm, 5% EtOAc/Hexanes) gave 143 mg (98%) of the desired quinone product **26i** as an orange solid. No other products were observed for this reaction.

Benzannulation of carbene complex 1m with 3-hexyne. The benzannulation of **1m** with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×13 cm, 5% EtOAc/Hexanes) gave 135 mg (96%) of the desired quinone product **26m** as a yellow solid. No other products were observed for this reaction. Spectral data for **26m**: mp=57–59°C; R_f=0.39 (5% EtOAc/Hex.) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.17 (t, 6H, J=7.5 Hz); 2.69 (q, 2H, J=7.5 Hz); 2.70 (q, 2H, J=7.5 Hz); 7.92 (d, 1H, J=8.0 Hz); 8.21 (d, 1H, J=8.0 Hz); 8.36 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 13.9, 20.2, 20.3, 123.2 (q, –CF_3, J=272 Hz); 123.5, 127.0, 129.6, 132.5, 134.3, 134.9 (q, –CCF_3, J=33 Hz); 148.5, 148.6, 183.6, 183.9. IR (nujol, cm^{-1}) 2700 (m), 1666 (s), 1611 (ms), 1583 (m). MS (EI) m/z (% rel. intensity): 282.1 M^+ (100), 267.1 (54), 239.1 (46), 225.1 (15), 201 (17), 172 (17), 144 (29), 128.1 (17), 115.1 (13), 94 (5), 75 (20). HRMS (EI) calcd for $C_{15}H_{13}F_3O_2$ 282.086765, found 282.087535. Anal. calcd for $C_{15}H_{13}F_3O_2$: C, 63.83; H, 4.64. Found: C, 63.72; H, 4.78.

Benzannulation of carbene complex 1n with 3-hexyne. The benzannulation of **1n** with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×13 cm, 5% EtOAc/Hexanes) gave 139 mg (99%) of the desired quinone product **26m** as an orange solid. No other products were observed for this reaction.

Benzannulation of carbene complex 1o with 3-hexyne. The benzannulation of **1o** (0.4 mmoles) with 3-hexyne

following Procedure IV and isolation by silica gel chromatography (2×13 cm, 5% EtOAc/Hexanes) gave 84 mg (74%) of the desired quinone product **26o** as a bright yellow solid. Spectral data for **26o**: R_f=0.25 (5% EtOAc/hex). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 (m, 6H); 2.65 (m, 4H); 7.79 (t, 1H, J=7.5 Hz); 8.08 (d, 1H, J=8 Hz); 8.37 (d, 1H, J=8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.4 (2×CH_3); 19.9, 20.6, 121.5 (q, $-CF_3$, J=275 Hz); 130.6, 131.3, 132.7, 134.4, 141.8, 146.9, 150.0, 157.8, 183.4 (2×CO). IR (thin film, cm^{-1}): 3108 (s), 2981 (s), 2942 (m), 2850 (m), 1672 (s), 1656 (s), 1622 (s), 1587 (s), 1420 (m), 1350 (s), 1314 (s), 1279 (s), 1255 (s), 1225 (m), 1165 (s), 1139 (s), 1103 (s), 1084 (m), 1059 (m), 807 (m); MS (EI) *m/z* (% rel. intensity): 282 M^+(60), 263 (34), 247 (100), 219 (53), 205 (12), 172 (25), 157 (6), 144 (34), 125 (13), 94 (6), 75 (15); HRMS (EI) calcd for $C_{15}H_{13}F_3O_2$ *m/z* 282.086765, found 282.086650. Anal. calcd for $C_{15}H_{13}F_3O_2$: C, 63.83; H, 4.64. Found: C, 63.63; H, 4.70.

Benzannulation of carbene complex 1p with 3-hexyne. The benzannulation of **1p** (0.4 mmoles) with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×13 cm, 2.5% EtOAc/Pentane) gave 40.4 mg (36%) of the desired quinone product **26o** as a bright yellow solid, 20.7 mg (20%) of indenone **27o** as a bright yellow solid, and 31 mg (26%) of indene **28p** as a colorless oil. Spectral data for **26o** was identical to that shown above. Spectral data for **27o**: R_f=0.28 (2.5% EtOAc/pent). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.09 (t, 3H, J=7.5 Hz); 1.23 (t, 3H, J=7.5 Hz); 2.30 (q, 2H, J=7.5 Hz); 2.58 (q, 2H, J=7.5 Hz); 7.23 (d, 1H, J=7 Hz); 7.39–7.44 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.3, 13.8, 16.1, 19.2, 121.5, 122.4 (q, $-CF_3$, J=275 Hz); 124.5, 128.1, 132.6, 133.2, 136.1, 147.3, 157.3, 194.2. Spectral data for **28p**: R_f=0.37 (2.5% EtOAc/pent). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.50 (t, 3H, J=7.5 Hz); 1.15 (t, 3H, J=7.5 Hz); 1.28 (d, 3H, J=5 Hz); 1.30 (d, 3H, J=5 Hz); 1.88 (m, 1H); 2.09 (m, 1H); 2.20 (sextet, 1H, J=7 Hz); 2.71 (sextet, 1H, J=7 Hz); 3.42 (t, 1H, J=4.5 Hz), 4.53 (h, 1H, J=5 Hz); 7.19 (t, 1H, J=8 Hz); 7.45 (d, 1H, J=7 Hz); 7.53 (d, 1H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 8.1, 13.1, 19.3, 21.7, 21.9, 22.2, 46.3, 121.2, 123.7, 124.2 (q, $-CF_3$, J=275 Hz); 124.3, 125.3, 133.8, 134.5, 146.8, 149.1.

Benzannulation of carbene complex 1q with 3-hexyne. The benzannulation of **1q** (0.5 mmoles) with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×20 cm, 2.5% EtOAc/Pentane) gave 66 mg (58%) of the desired quinone product **26q** as a bright yellow solid. Spectral data for **26q** was identical to that reported in the literature for this compound.[3]

Benzannulation of carbene complex 1r with 3-hexyne. The benzannulation of **1r** (0.5 mmoles) with 3-hexyne following Procedure IV and isolation by silica gel chromatography (2×20 cm, 2.5% EtOAc/Pentane) gave 68 mg (59%) of the desired quinone product **26q** as a bright yellow solid, and 6 mg (6%) of indenone **27q** as a yellow oil. Spectral data for **26q** and **27q** were identical to that reported for these compounds.[3]

Improved preparation of 16a (Procedure V)

Preparation of 4-bromophenyl-triisopropylsilyl ether 30. To a 100 mL flame dried round bottom flask under Ar was added 264 mg (6.6 mmoles) NaH (60% dispersion in mineral oil). The mineral oil was removed by washing 3×5 mL hexanes. The flask was kept under Ar and 20 mL of dry THF was added. The stirring suspension was cooled to 0°C, and 1.04 g (6.0 mmoles) of *p*-bromophenol was added dropwise slowly over 5–10 min as a solution in 15 mL THF. The reaction was then allowed to stir at 0°C for 30 min then warmed to room temperature and stirred for 1 h. At this time, 1.39 g (7.2 mmoles) of TIPSCl was added all at once to the reaction, and stirring was continued for 3.5 h. The reaction was then poured onto 50 mL brine and 50 mL of ethyl ether in a sep funnel. The organic layer was washed 2×50 mL distilled H_2O, 1×50 mL brine, and dried over $MgSO_4$. The solvent was removed in vacuo, followed by silica gel chromatography (3×20 cm, eluant: hexanes) to give 1.91 g (97%) of **30** as a colorless oil. Spectral data for **30**: R_f=0.7 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (d, 18H, $-CH(CH_3)_2$, J=7.2 Hz); 1.22 (h, 3H, $-CH(CH_3)_2$, J=7.8 Hz); 6.75 (d, 2H, J=8.7 Hz); 7.30 (d, 2H, J=8.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.6, 17.9, 113.2, 121.7, 132.2, 155.3. IR (neat, cm^{-1}): 2945 (s), 2927 (s), 2891 (m), 2867 (s), 1585 (s), 1488 (s), 1463 (m), 1384 (w), 1275 (s), 1164 (m), 1094 (m), 1070 (m), 1006 (m), 909 (s), 883 (s), 827 (s), 781 (s). MS (EI) *m/z* (% rel. intensity): 330 (26, M^+, ^{81}Br), 328 (26, M^+, ^{79}Br), 285 (100, ^{79}Br), 259 (56, ^{81}Br), 243 (16, ^{79}Br), 231 (80), 217 (60, ^{81}Br), 201 (32, ^{81}Br), 178 (12), 150 (24), 135 (34), 122 (25), 91 (10), 75 (19). HRMS (EI) calcd for $C_{15}H_{25}{}^{79}BrOSi$ *m/z* 328.085805, found 328.085264. Anal. calcd for $C_{15}H_{25}BrOSi$: C, 54.70; H, 7.65. Found: C, 55.08; H, 7.54.

Conversion of 30 to Complex 16a. To 25 mL flame dried round bottom flask under Ar was added 658 mg (2.0 mmoles) of **30** in 20 mL of dry THF. The solution was cooled to −78°C, and 2.38 mL (4 mmoles, 2 equiv.) of 1.68 M *tert*-butyllithium was added dropwise over 2–3 min. The reaction was stirred at −78°C for 15–20 min, at which time, 484 mg (2.2 mmoles, 1.1 equiv.) of solid $Cr(CO)_6$ was added all at once. After stirring an additional 15 min at −78°C, the reaction was warmed to room temperature over 1 h and stirred at that temperature for 3 additional hours. The resulting lithium acylate was concentrated on a rotary evaporator, then pumped under high vacuum (0.1–0.2 mmHg) for 1–1.5 h. to remove all THF. The crude acylate was then dissolved in a minimum of distilled H_2O, diluted with 2–3 mL CH_2Cl_2, and treated portionwise with small amounts of Meerwein's salt, until the biphasal reaction has reached a pH of 2–3. After stirring at room temperature for 30 min, the reaction was diluted with 20 mL hexanes, and poured into 20 mL $NaHCO_3$ (sat.) and 20 mL hexanes. The aqueous layer was extracted 2×15 mL of hexane or until all the dark red carbene color had been removed. The combined organics were then washed 1×25 mL brine, and dried over $MgSO_4$. The dried solution was then filtered over a fritted funnel dry packed with Celite 545, and the solvent removed in vacuo. After pumping the crude product under high vacuum for 30 min, the carbene complex was dissolved in 15 mL of dry THF in a flame dried 100 mL round bottom flask, and cooled to 0°C. To this solution was added, dropwise slowly, 0.5 mL HF·Pyridine. The reaction was checked by TLC after 2 min (25% EtOAc/Hex) and showed almost complete

removal of the TIPS group (R_f ~0.7 for TIPS protected carbene complex and R_f ~0.25 for deprotected). After stirring the reaction for an additional 10 min at room temperature, ~25 mL of sat. $NaHCO_3$ was added dropwise via an addition funnel to quench the reaction. The reaction was then vigorously stirred for ~15 min after complete addition. The reaction was then poured into 15 mL hexanes. The organic layer was washed 1×15 mL sat. $NaHCO_3$. The combined aqueous washes were then back extracted 2×20 mL hexanes or until all of the red carbene color had been removed. The combined organics were then washed 1×25 mL brine, and dried over $MgSO_4$. The solvent was removed in vacuo, and the product isolated by silica gel chromatography (3×20 cm, 25% EtOAc hexanes) to give 481 mg (73%) of the desired carbene complex **16a** as a dark red solid. Spectral data was identical to that reported in the literature.[3]

Improved preparation of 16b

Preparation of 4-bromo-3-methoxyphenyltriisopropylsilyl ether 31. Following the same procedure as for the preparation of **30**, **31** was prepared in 92% yield (after chromatography) from 4-bromo-3-methoxyphenol which was prepared according to Ref. 3. Spectral data for **31**: R_f=0.7 (hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, 18H, $-CH(CH_3)_2$, J=7.5 Hz); 1.26 (h, 3H, $-CH(CH_3)_2$, J=7.8 Hz); 3.85 (s, 3H), 6.38 (dd, 1H, J_{ortho}=9.0 Hz, J_{meta}=2.5 Hz); 6.46 (d, 1H, J=2.5 Hz) 7.31 (d, 1H, J=8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.7, 17.9, 56.1, 102.6, 104.9, 113.0, 133.0, 156.5, 156.7. IR (neat, cm^{-1}): 2957 (s), 2944 (s), 2892 (m), 2867 (s), 1587 (s), 1580 (s), 1487 (s), 1461 (s), 1447 (s), 1403 (s), 1302 (s), 1206 (s), 1171 (s), 1120 (m), 900 (s). MS (EI) *m/z* (% rel. intensity): 360 (42, M^+, ^{81}Br), 358 (42, M^+, ^{79}Br), 317 (100, ^{81}Br), 289 (53, ^{81}Br), 273 (15, ^{79}Br), 259 (65, ^{79}Br), 247 (40, ^{81}Br), 221 (22), 193 (23), 180 (35), 166 (37), 151 (27), 130 (66), 111 (18), 97 (32), 85 (38), 71 (55). HRMS (EI) calcd for $C_{16}H_{27}{}^{79}BrO_2Si$, *m/z* 358.096370, found 358.096384.

Conversion of 31 to 16b. Following Procedure V, the desired carbene complex was prepared from **31** in 73.5% combined yield of non-chelated and chelated carbene complex **16b** (chelate: 234 mg (25.5%); nonchelate 480 mg (48%)). Spectral data for both the chelated and non-chelated forms of **16b** was identical to that previously reported in Ref. 3.

Preparation of 16c. Following Procedure V starting with 4 mmoles of **30**, after the lithium acylate had been pumped on high vacuum for 1 h, the crude product was dissolved in a minimum of distilled H_2O, and filtered through a Buchner funnel into a few mL of distilled H_2O containing 1.1 equiv. of NMe_4Br. The Erlenmeyer flask was shaken for 1–2 min then allowed to stand at room temperature for 30 min. The crude orange–yellow ammonium salt was collected by suction filtration over a Buchner funnel. The crude solid was then dissolved in CH_2Cl_2 and dried over $MgSO_4$. The methylene chloride solution was the filtered through a fritted funnel dry packed with Celite 545, and the solvent removed in vacuo. After pumping under high vacuum (0.1–0.2 mmHg) for 1–2 h, the crude acylate was dissolved in dry CH_2Cl_2. To the resulting solution was added 2–3 equiv. of isopropyltriflate as a concentrated solution in methylene chloride, the reaction was stirred at room temperature for 30–45 min. The reaction was then worked up by pouring into a separatory funnel containing saturated $NaHCO_3$ and hexanes. The aqueous layer was extracted 1–2 additional times with hexanes (until all of the red color was removed from the aqueous layer), the organics were washed 2 times with saturated NaCl solution, and dried over $MgSO_4$. The dried solution was filtered through a fritted funnel dry packed with Celite 545. After removal of the solvent in vacuo, 670 mg (47%) of the desired product **16c** was obtained after silica gel chromatography as a dark red solid. Spectral data for **16c**: R_f=0.08 (25/5/1 hexanes/CH_2Cl_2/Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, 6H, J=6.0 Hz); 5.70 (bs, 1H); 6.42 (bs, 1H, –OH); 7.14 (d, 2H, J=8 Hz); 7.46 (d, 2H, J=8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.7, 85.6, 114.7, 129.0, 146.7, 159.0, 216.8, 224.0, 336.5. IR (thin film, cm^{-1}): 3341 (bs, OH), 2984 (w), 2950 (w), 2057 (s), 1950 (s), 1602 (m), 1210 (m), 920 (m). Anal. calcd for $C_{15}H_{12}CrO_7$: C, 50.57; H, 3.40. Found: C, 50.68; H, 3.56.

In situ preparation and benzannulation of pentacarbonyl 4-triflato-benzylidenemethoxy chromium (0) with 1-pentyne (Procedure VI)

To a 25 mL flame dried Kontes flask equipped with a Teflon screw top was added 0.5 mmoles of carbene complex **16a**, and 1.0 mmoles of pyridine in 5 mL dry benzene. The flask was submitted to 3 cycles of freeze–pump–thaw to remove all volatiles. At this time, 1.05 equiv. of Tf_2O was added all at once. The reaction immediately darkened to a blackish-red was analyzed by TLC (25% EtOAc/Hex) after 1 min to show that almost complete conversion to the *p*-triflato-benzylidene had occurred. After stirring the reaction for 5 additional minutes, 1.0 mmoles of 1-pentyne was added. The reaction was again degassed by 3 cycles of FPT, and the reaction was sealed under Ar and stirred at 75–80°C for 16 h. After cooling to room temperature, the reaction was diluted with 15 mL ethyl ether, poured onto 15 mL brine in a sep funnel, and washed 2 more times with brine and dried over $MgSO_4$. The solvent was removed in vacuo and the reaction purified by silica gel chromatography (2×20 cm, 25/5/1 hexanes/CH_2Cl_2/Et_2O) to give 146 mg (80%) of the desired phenol **33a** as an off white solid, and <5% of **34a** based on crude NMR data (See compound **34c**). Spectral data for **33a**: mp=55–56°C; R_f=0.17 (25/5/1 hexanes/CH_2Cl_2/Et_2O) ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (t, 3H, J=8.0 Hz); 1.72 (sextet, 2H, J=7.5 Hz); 2.70 (t, 2H, J=8.0 Hz); 3.96 (s, 3H); 4.75 (s, 1H, –OH); 6.62 (s, 1H), 7.29 (dd, 1H, J_{ortho}=9.0 Hz, J_{meta}=2.0 Hz); 8.02 (d, 1H, J=2.0 Hz); 8.24 (d, 1H, J=9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 23.2, 32.5, 55.8, 107.2, 113.6, 118.1, 118.5 (q, $-CF_3$, J=325 Hz), 123.3, 123.9, 124.9, 126.1, 141.7, 147.7, 149.4. IR (nujol, cm^{-1}) 3300 (bs, –OH), 1620 (m), 1603 (m), 1588 (mw), 1250 (m), 1212 (m), 1115 (w), 1100 (ms), 879 (m), 834 (m), 814 (mw), 718 (m). MS (EI) *m/z* (% rel. intensity): 364.1 M^+ (89), 335 (7), 321 (2), 253 (2), 132.1 (45), 203.1 (100), 188.1 (4), 174.1 (16), 159.1 (5), 145.1 (10), 115.1 (10), 69 (25). HRMS (EI) calcd for $C_{15}H_{15}F_3SO_5$ 364.059230, found 364.058110. Anal. calcd for $C_{15}H_{15}F_3SO_5$: C, 49.45; H, 4.15. Found: C, 49.49; H, 4.24.

In situ preparation and benzannulation of pentacarbonyl 4-triflato-2-methoxybenzylidenemethoxy chromium (0) with 1-pentyne. Following Procedure VI starting with 0.65 mmoles of carbene complex, the benzannulation of **16b** was carried out, and gave 78 mg (62% yield) of the desired phenol **33b** as the only observable product. Spectral data for **33b**: R_f=0.08 (25/5/1 hexanes/CH_2Cl_2/Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, 3H, J=7.0 Hz); 1.69 (sextet, 2H, J=7 Hz); 2.66 (t, 2H, J=7 Hz); 3.90 (s, 3H); 3.97 (s, 3H); 4.86 (2, 1H, –OH); 6.65 (d, 1H, J=3 Hz); 6.69 (s, 1H); 7.67 (d, 1H, J=3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 23.0, 32.2, 56.5, 57.4, 99.4, 105.9, 110.7, 116.1, 118.5 (q, –CF_3, J=310 Hz), 124.0, 127.5, 142.2, 147.3, 150.9, 158.8. IR (nujol, cm^{-1}) MS (EI) *m/z* (% rel. intensity): 394 (M+, 40), 335 (8), 321 (2), 253 (1), 231 (48), 203 (100), 188 (4), 174 (17), 159 (5), 145 (11), 115 (12), 69 (25); HRMS (EI) calcd for $C_{15}H_{15}O_5F_3S$ *m/z* 364.059230, found 364.058110. Anal. calcd for $C_{16}H_{17}F_3SO_6$: C, 48.70; H, 4.34. Found: C, 48.60; H, 4.45.

In situ preparation and benzannulation of pentacarbonyl 4-triflato-benzylideneisopropoxy chromium (0) with 1-pentyne. Following Procedure VI, the desired phenol product **33c** was obtained in 82% yield as a colorless solid, and the ketene trapped product **34c** was isolated in 6% yield as a colorless oil. Spectral data for **33c**: MP=50–51°C, R_f=0.14 (5% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.02 (t, 3H, J=7.5 Hz); 1.41 (d, 6H, –CH(CH_3)$_2$, J=6.0 Hz); 1.71 (sextet, 2H, J=7.5 Hz); 2.69 (t, 2H, J=7.5 Hz); 4.63 (h, 1H, J=6 Hz); 4.72 (s, 1H, –OH); 6.69 (s, 1H); 7.27 (dd, 1H, J_{ortho}=9.5 Hz, J_{meta}=2.5 Hz); 8.01 (d, 1H, J=3 Hz) 8.25 (d, 1H, J=9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.9, 22.1 (–CH(CH_3)$_2$), 23.2, 32.5, 71.3, 110.8, 113.5, 118.1, 118.5, (q, –CF_3, J=312 Hz), 123.3, 125.2, 125.4, 126.2, 141.7, 147.6, 147.7. IR (nujol, cm^{-1}) 3210 (bs), 1700 (w), 1680 (w), 1670 (w), 1459 (s), 1380 (s), 1195 (m), 1144 (ms), 1101 (m). MS (EI) *m/z* (% rel. intensity): 392 (M$^+$, 25), 350 (77), 321 (9), 267 (3), 217 (80), 189 (100), 160 (25), 147 (4), 131 (14), 115 (7), 103 (5), 77 (4), 64 (7); HRMS (EI) calcd For $C_{17}H_{19}F_3SO_5$ *m/z* 392.090531, found, 392.090467. Spectral data for **34c**: R_f=0.31 (5% EtOAc/Hex.). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, 3H, J=7.5 Hz); 1.05 (t, 3H, J=7 Hz); 1.28 (d, 6h, J=7 Hz); 1.45 (d, 6h, J=6 Hz); 1.56 (m, 2H); 1.65 (m, 2H); 1.78 (m,1H); 2.05 (m, 1H); 2.58 (bt, 2H, J=8 Hz); 4.03 (h, 1H, J=6 Hz); 4.15 (m, 1H); 4.74 (h, 1H, J=8 Hz); 5.44 (d, 1H, J=10 Hz); 6.73 (s, 1H); 7.28 (m, 3H); 7.53 (d, 1H, J=3 Hz); 7.59 (d, 2H, J=9 Hz); 8.31 (d, 1H, J=9 Hz).

Preparation of enyne 36. To 10 mL flame dried round bottom flask under Ar, was added 565 mg (1.46 mmoles) of aldehyde **38**[16] in 20 mL of dry MeOH. Added 2.0 equiv. of K_2CO_3 followed by 1.2 equiv. of dimethyl-1-diazo-2-oxopropylphosphonate **39**[33,34] as a solution in 5 mL of MeOH. The reaction was stirred for 9 h at room temperature. The crude reaction was filtered over Celite 545, and purified by silica gel chromatography (2×22 cm, 20/1/1 hexanes/CH_2Cl_2/Et_2O) to give 367 mg (66%) of the desired enyne **36**. Spectral data for **36**: R_f=0.18 (20/1/1 hexanes/CH_2Cl_2/Et_2O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.10 (s, 3H); 0.12 (s, 3H); 0.91 (s, 9H); 1.33 (d, 3H, J=7.6 Hz); 1.37 (s, 3H); 1.40 (s, 3H); 1.97 (t, 1H, J=3.3 Hz); 2.44–2.57 (m, 3H); 3.29 (m, 1H); 3.47 (s, 3H); 3.73 (t, 1H, J=8.4 Hz); 3.89 (m, 1H); 4.11 (p, 1H, J=7.9 Hz); 5.11–5.17 (m, 2H); 5.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ −3.80, −3.61, 18.3, 20.4 (-SiC(CH_3)$_3$), 26.1, 27.3, 27.6, 44.6, 60.3, 69.6, 73.7, 75.1, 82.5, 82.8, 83.0, 108.4, 116.4, 138.7. IR (neat, cm^{-1}): 3313 (m), 2982 (s), 2954 (s), 2931 (s), 2887 (s), 2857 (s), 2100 (w), 1473 (m), 1463 (m), 1378 (s), 1369 (s), 1252 (s), 1093 (s), 918 (m), 836 (s), 775 (s). MS (CI) *m/z* (% rel. intensity): 383 (4, M$^+$+1), 370.2 (2), 367.4 (100), 355.4 (2), 349.4 (3), 338.4 (2). HRMS (CI) calcd For $C_{21}H_{38}SiO_4$ 382.253864, found 382.252600.

Benzannulation of enyne 36 with pentacarbonyl (2-methoxy-4-triflatobenzylidene)methoxy chromium (0). To a 50 mL flask equipped with a high vacuum threaded teflon stopcock was added a stirring bar and 179 mg (0.5 mmol) of carbene complex **16b** in 3.5 mL of CH_2Cl_2. After addition of 2.2 equiv. of pyridine, the solution was deoxygenated by the freeze–thaw method (3 cycles) and then backfilled with argon at room temperature. Triflic anhydride (1.05 equiv., 0.525 mmol, 88 μL) was added and the resulting solution was stirred for 5 min. Enyne **36** (1.05 equiv., 0.525 mmol, 200 mg) was added and the solution was then deoxygenated by the freeze–thaw method (2 cycles). The flask was back-filled with argon at room temperature and then sealed and heated at 45°C for 24 h. Upon cooling to room temperature, 2.0 equiv. of acetic anhydride (1.0 mmol, 95 μL) was added and the reaction mixture was stirred for an additional 12 h at room temperature. The reaction was quenched by addition of 10 mL of H_2O. The organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. The product was purified by silica gel chromatography with 10% ethyl acetate in hexane as eluent to give 150 mg (40% yield) of the desired acetylated phenol **37** (a colorless oil) as the only observable product. Spectral data for **37**: R_f=0.14 (10% EtOAc/Hex). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.11 (s, 3H); 0.13 (s, 3H); 0.93 (s, 9H); 1.33 (d, 3H, J=6.0 Hz); 1.37 (s, 3H); 1.40 (s, 3H); 2.47 (m, 4H); 2.68 (m, 1H); 3.09 (dd, 1H, J_1=13, J_2=3 Hz); 3.20 (t, 1H, J=5.5 Hz); 3.48 (s, 3H); 3.72 (t, 1H, J=6.5 Hz); 3.92–3.97 (m, 7H); 4.14 (p, 1H, J=6.5 Hz); 4.74 (d, 1H, J=17 Hz); 4.90 (d, 1H, J=12 Hz); 5.68 (m, 1H); 6.65 (d, 1H, J=2 Hz); 6.69 (s, 1H); 7.11 (d, 1H, J=2 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ −3.80, −3.61, 18.3, 20.3 (-SiC(CH_3)$_3$), 20.6, 26.2 (–OC(CH_3)$_3$), 27.3, 27.5, 47.1, 56.7, 60.9, 73.5, 74.5, 83.0, 84.7, 99.5, 104.9, 108.2, 110.3, 116.0, 116.8, 119.0 (q, –CF_3, J=325 Hz), 130.0, 132, 138.0, 138.9, 148.2, 154.7, 159.6, 169.5. IR (neat, cm^{-1}): 3077 (w), 2955 (s), 2933 (s), 2904 (s), 2857 (s), 2752 (w), 1767 (s), 1630 (s), 1610 (m), 1587 (s), 1513 (w), 1456 (s), 1424 (s), 1370 (s), 1244 (s), 1199 (s), 1130 (s), 1107 (s), 1023 (s), 958 (s), 910 (s), 862 (s), 837 (s), 776 (m), 731 (s). MS (EI) *m/z* (% rel. intensity): 750.4 (9, M$^+$), 708.4 (15), 634.3 (29), 603.3 (47), 561.3 (20), 503.3 (10), 471.3 (15), 448.2 (32), 417.2 (80), 356.2 (89), 339.2 (4), 287.3 (10), 232.2 (25), 197.2 (32), 171.2 (20), 145.2 (24), 115.2 (100), 73.1 (97). HRMS (EI) calcd For $C_{34}H_{49}O_{11}F_3SSi$ *m/z* 750.271698; found 750.270804.

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