Stereoelectronic Effects on Product Formation from the *E*- and *Z*-Isomers of η^1,η^3-Vinyl Carbene Complexed Intermediates in the Reactions of Fischer Carbene Complexes with Alkynes

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The reactions of 2-dihydropyranyl(methoxy)methylene pentacarbonyl chromium **19** with the series of five acetylenic ketones $CH_3(CH_2)_2C{\equiv}C(O)(p\text{-}X{-}C_6H_4)$ **26** (X = CF_3, Cl, H, OCH_3, NMe_2) gave a mixture of phenol and lactone products. The most electron-rich alkyne (X = NMe_2) gave a greater proportion of the phenol product **27** (81:19), and the most electron-poor alkyne (R = CF_3) gave the lactone **28** as the major product (64:36). Since the lactone product must come from a Z-isomer of a vinyl carbene complexed intermediate and the phenol product must come an E-isomer, this reveals that the stereochemistry of the reactive intermediates involved can be influenced by electronic effects of the substituents on the alkyne. A similar set of experiments with 3-hexyn-2-one **20** and the series of five phenoxy carbene complexes $(CO)_5Cr{=}C(C_5H_6O)O(p\text{-}X{-}C_6H_4)$ **29** (X = CF_3, Cl, H, OCH_3, NMe_2) produced the opposite result, where predominantly the phenol product was produced from the most electron-poor carbene complex (X = CF_3) and for the most electron-rich carbene complex (X = NMe_2) the lactone product was predominant. These results can be explained by a trans effect in the η^1,η^3-vinyl carbene complexed intermediate where the most electron-rich substituent of the β-carbon of this intermediate prefers to be trans to the most electron-poor substituent of the α-carbon. These data are consistent with observation that the complex **19** will react with methyl-2-hexynoate **23** to give only phenol products and with the observation that the diaryl carbene complex $(CO)_5Cr{=}C(p\text{-}Me\text{-}C_6H_4)p\text{-}CF_3C_6H_4$ **7** will react with diphenylacetylene to give the phenol product which results from cyclization onto the more electron-poor aryl substituent by a factor of 3:1. These data are also consistent with and offer an explanation for the fact that under normal conditions the reactions of Fischer carbene complexes with unactivated alkynes give high chemoselectivities for phenol products. Finally the stereoselectivity of lactone formation was examined in the reaction of 1-(2,6-dimethyl-1-cyclohexenyl)(methoxy)methylene pentacarbonyl chromium **32** with 4-phenyl-3-butyn-2-one **33** to give only the lactone product **34** as a single diastereomer. The stereochemistry of **34** was determined to have a trans relationship of the two methyls on the six-membered ring by X-ray diffraction. It is interesting that the same stereochemistry has been previously observed for the reaction of this complex with 1-hexyne, where the cyclohexadienone product is produced form an *E*-isomer of the vinyl carbene complexed intermediate rather than from a *Z*-isomer.

The exact details of the workings of the benzannulation reaction of Fischer carbene complexes with alkynes are still not known despite the fact that the synthetic value of the reaction is well established.[2] The fact that this one reaction can produce such a large and diverse array of organic structures will ensure that it will never cease to amaze and inspire. A substantial amount of information has been collected concerning the scope of substrates permissible for the reaction and the effect of a variety of reaction conditions on the product distribution.[2] This information in conjunction with theoretical studies has identified the η^1,η^3-vinyl carbene complex **2** and η^4-vinyl ketene complex **3** as key intermediates in these reactions and as branchpoints be-

(1) ACS Organic Division Fellow 1995−1996 (John Wiley & Organic Reactions).

(2) For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (b) Wulff, W. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol 12. (c) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol 12. (d) Doyle, M. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol 12. (e) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271.

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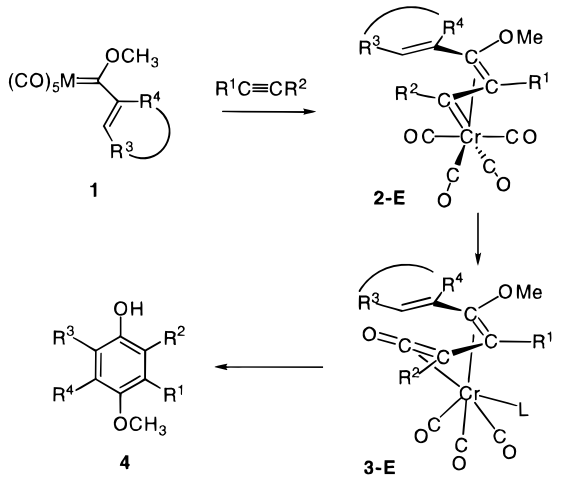
Scheme 1



tween the many and varied products (see Scheme 1).[3] The effect of electronics on the various mechanistic branchpoints that have been proposed to account for the product distribution has not been carefully examined especially between products that are thought to be formed from different stereoisomers of the key reaction intermediates. We report herein the first study that systematically probes the effect of variations of the electronic nature of both the alkyne and the carbene complex on the partition between products that are thought to be derived from the *E*- and *Z*-isomers of the η^1,η^3-vinyl carbene complexed intermediate.

Background

A considerable amount of information is known about the effect of the electronic nature of the carbene complex on the partition between cyclopentadiene (indene from aryl complexes) and phenol products. Both of these products arise from the vinyl carbene intermediate **2-E** and differ by whether CO insertion occurs in the vinyl carbene intermediate (to give phenols via the ketene complex **3**) or whether direct cyclization occurs (to give cyclopentadiene). The general finding that has emerged is that a more electron-poor carbene complex will give a greater proportion of phenol products at the expense of cyclopentadiene (indene) products.[4] The effect of electronics on the regiochemistry of alkyne incorporation has been investigated to some degree, especially with regard to electronic variation of the alkyne.[5] It has been found that in most instances the regioselectivity is determined by the steric differential of the substituents on the alkyne.[5a,6] It is the sterically larger substituent that is incorporated ortho to the phenol function in **4** (R^2). This product results from the vinyl carbene complexed intermediate **2-E** rather than its regioisomer **6-E**. The only known examples where the electronic nature of the alkyne can overcome the steric control in the regiochemistry of these reactions are with alkynyl ketones[5b,c] and with alkynyl stannanes.[5d,e]

The phenol and cyclopentadiene (indene) products must be formed from the *E*-isomers of the vinyl carbene complexed intermediate since cyclization to the unsaturated substituent cannot occur in the *Z*-isomer. However, a number of products can also be formed from the *Z*-vinyl carbene complexed intermediate such as 2-methoxyfurans[7] and bicyclolactones (Scheme 2).[5b,c] There have been no previous studies of the effect of electronics on the partition between products that arise from the *E*-vinyl carbene complexed intermediate and products that arise from the *Z*-vinyl carbene complexed intermediate. The purpose of the present study is to evaluate the effects of the electronic nature of both the carbene complex and the alkyne on the partition between products formed from the *E*- and *Z*-vinyl carbene complexed intermediates. It will be assumed in this work that product distribution is determined at the vinyl carbene intermediate rather than at the vinyl ketene intermediate. The basis of this assumption comes from other work in our laboratory which found that isomers of vinyl carbene complexes can interchange prior to product formation.[9b]

The ideal system for which the stated goal can be probed is one that gives only two products, one of which is known to be derived from the *E*-reaction manifold and the other which is known to be derived from the *Z*-reaction manifold. An example of such a system where the effect of changes of electronics could be unequivocally linked to stereoisomeric vinyl carbene complexed intermediates is the benzannulation of the diaryl carbene complex **7** with diphenylacetylene (Scheme 3). This reaction was originally reported to give the naphthalene **8** in 18% yield.[8] We have repeated this reaction and have confirmed the regiochemical assignment of **8** by an independent synthesis. We have also found that the regioisomer **9** is produced as a minor product along with **8** in 18% total yield as a 1:3 ratio.[9a] It is interesting to see that the major product has the less electron-rich ring incorporated into the naphthol preferentially. This means that the more electron-rich ring on the β-carbon in the vinylcarbene intermediate prefers to be trans to the original carbene carbon, as indicated in intermediate **10.** The source for this preference is not clear but is consistent with the fact that the benzannulation reactions work. That is to say that, unless modified conditions are employed, the reactions tend to produce phenol products that are derived from *E*-vinyl carbene complexed intermediates

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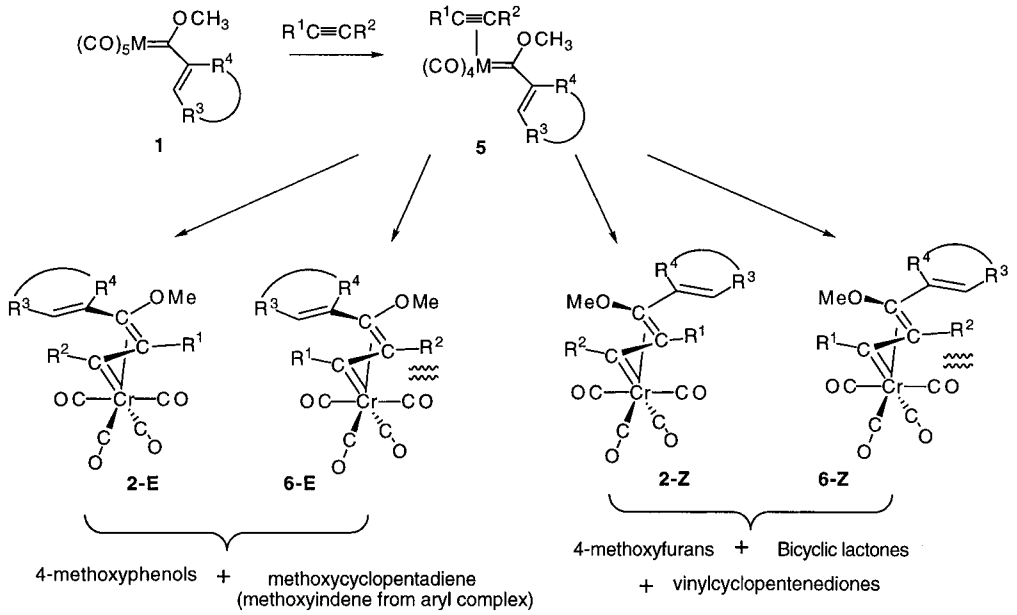
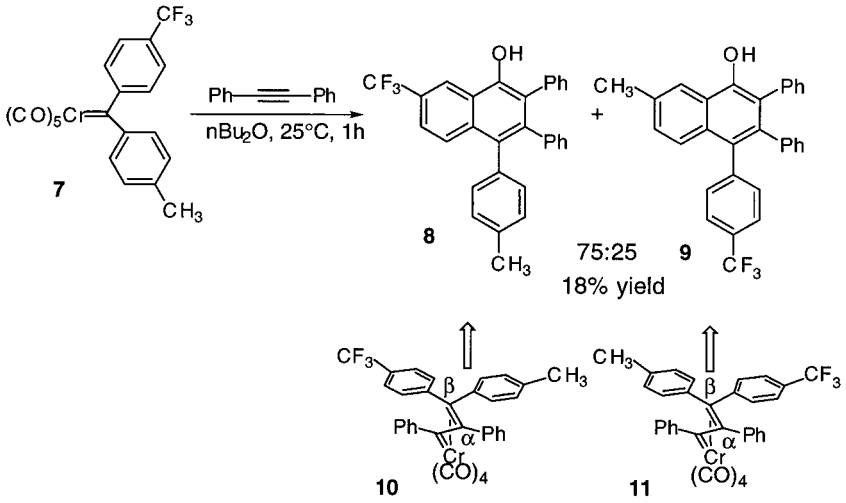
Scheme 2



Scheme 3



in which the methoxyl group is trans to the original carbene carbon (**2-E** in Scheme 2). The low yield for the benzannulation of complex **7** is likely due to competitive decomposition which occurs in the same time period in the absence of alkyne. Thus this system is not expected to be useful for a study in which changes in the electronic nature of the substrates can be correlated with the amount of products produced from the *E*- and *Z*-reaction manifolds.

The electronic effects on the distribution between *E*- and *Z*-derived products could also be potentially studied with reactions that produce both phenol and furan products since it has now been clearly established that the furan products are formed from the *Z*-isomer of the vinyl carbene complexed intermediate.[7] However, the furan products in many cases are sensitive to air oxidation, and this would be a particular problem when the electronics were tuned to the electron-rich side. Another system that could be used are those reactions that produce 2-vinylcyclopentendione products in addition to phenols.[10] These products are thought to be derived from the *Z*-reaction manifold since there is some evidence that links them to furan formation.[11] However, it has not yet been conclusively shown that these compounds are formed from the *Z*-manifold. The system that we have decided to employ in this study is the reaction of vinyl carbene complexes with alkynyl ketones, which we have previously shown gives a mixture of phenols and bicyclic lactones.[5b] The lactones **14** can only arise by a cyclization in which the keto group derived from the alkyne cyclizes to the vinyl substituent present on the carbene complex and thus must arise from the *Z*-reaction manifold (Scheme 4).

The formation of the bicyclic lactone products was most carefully studied in the past with alkynyl ketones, and for the present study we needed to know how much electronic variation could be engineered into the system. Thus, we carried out the reaction of complex **19** with the methyl ester **23** to compare with the published result from the reaction of the same complex with the

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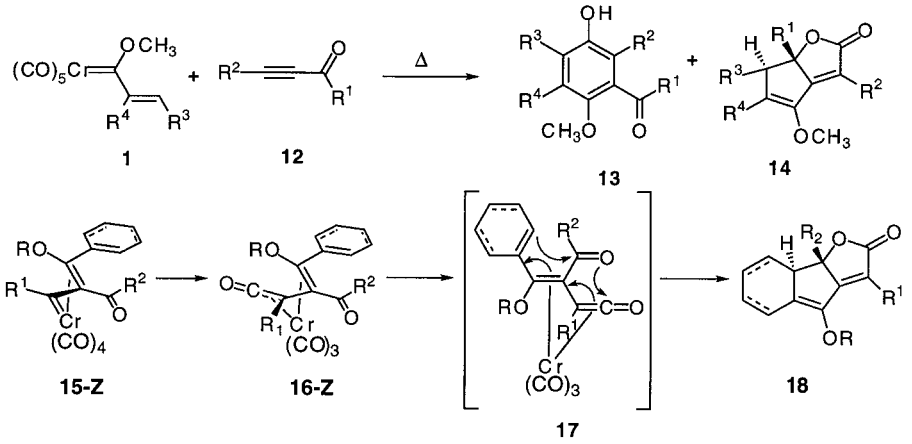
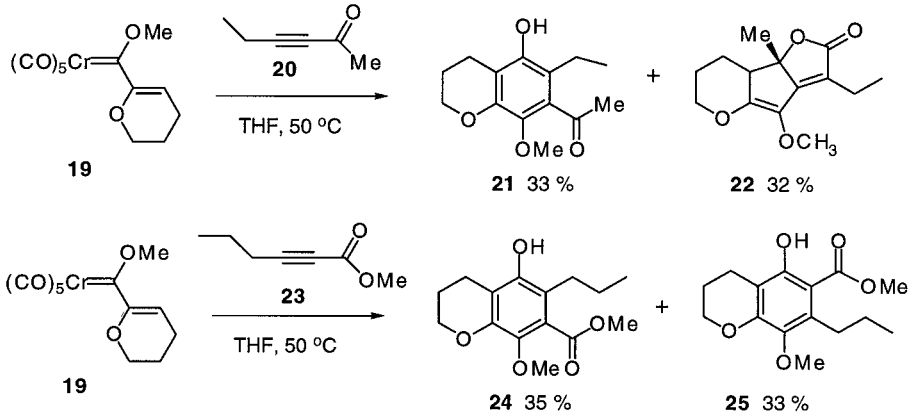
Scheme 4



Scheme 5



alkynyl ketone **20**.[5b] Dramatically different outcomes were observed for these two reactions, as indicated in Scheme 5. The reaction of complex **19** with the alkynyl ketone **20** gives products from both the *E*- and *Z*-manifolds but with only a single regioselectivity. This is in contrast to the reaction with the ester **23**, which gave products with both regioselectivities of alkyne incorporation but only from the *E*-reaction manifold. Thus, since the reaction of the ester **23** only gave phenol products, it appeared that the more electron-poor alkynyl ketones will be required for the present study, although it certainly was not clear at the outset how much the alkynyl ketone could be electronically modified.

Results

A series of aryl alkynyl ketones of the type **26** were prepared in 72−100% yield using the method of Weinreb[12] by the addition of an alkynyllithium to a para-substituted benzamide. The reactions of each of these acetylenic ketones were carried out under identical conditions in THF at 50 °C, and each was repeated at least twice. The results are tabulated in Table 1 and reveal that the ratio of bicyclic lactone products to the phenol products varied by a factor of 8 when the para-substituent is varied from trifluoromethyl to dimethylamino, with the bicyclic lactone **28** being the predominate product with the former and the phenol product **27** being the predominate product with the latter (Scheme 6). The direction of the shift in product distribution toward the bicyclic lactone product with the more electron-poor alkyne is consistent with the difference observed between the alkynyl ketone **20** and the ester **23** (Scheme 5). The mass balance for the two products is not particularly high but is consistent over the range of electronically differentiated alkynyl ketones. The phenol **27** and the bicyclic lactone **28** were the only products that were observed to be mobile on silica gel, and it is suspected that the remainder of the mass balance is due to the formation of high molecular weight materials.

Table 1. Reaction of Complex 19 with Alkyne 26

	X	run	**27**:**28**[a]	% yield[b]	σ_p[c]
26a	CF_3	1	3763	76	0.54
		2	36:64	64	
26b	Cl	1	50:50	46	0.23
		2	52:48	66	
26c	H	1	61:39	63	0.00
		2	61:39	70	
26d	OCH_3	1	74:26[d]	68	−0.27
		2	75:25	68	
26e	NMe_2	1	79:21[d]	72	−0.66
		2	82:18	77	

[a] Ratios determined by integration of the ^{1}H NMR spectrum. [b] Combined yields of isolated products. [c] From Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper Collins, 1987; p 144. [d] Ratio determined from isolated yields of pure products.

The results from the reaction of complex **19** with the series of five substituted alkynes **26** demonstrate that electronic variations of the α-carbon substituent of the

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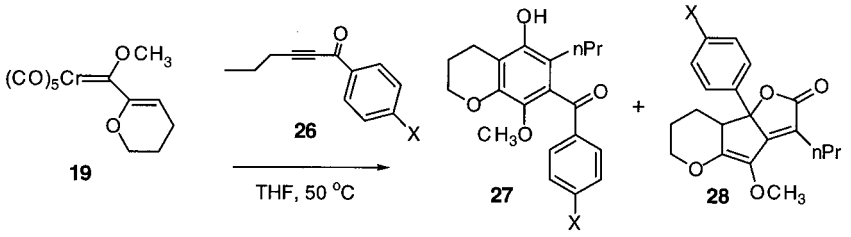
Scheme 6



Scheme 7

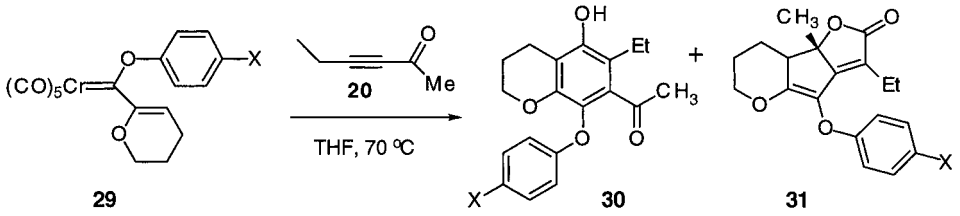


Table 2. Reaction of Complex 29 with Alkyne 20

	X	run	**30**:**31**[a]	% yield[b]	σ_p[c]
29a	CF_3	1	71:29	56	0.54
		2	74:26[d]	67	
		3	68:32[e]	37	
		4	72:28[f]	51	
29b	Cl	1	63:37	60	0.23
		2	67:33	53	
29c	H	1	49:51	63	0.00
29d	OCH_3	1	56:44	49	−0.27
		2	51:49	68	
29e	NMe_2	1	39:61	51	−0.66

[a] Ratios determined by integration of the ^{1}H NMR spectrum. [b] Combined yield of isolated products. [c] From Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper Collins, 1987; p 144. [d] Benzene was used as solvent. [e] Acetonitrile was used as solvent. [f] Methylene chloride was used as solvent.

vinyl carbene complexed intermediate (Scheme 3) can effect the proportion of products that are derived from either the *E*- or *Z*-stereochemistry at the β-carbon of the vinyl carbene complexed intermediate. In an effort to probe the influence of a variation in the electronic nature of a substituent on the β-carbon of the vinyl carbene complexed intermediate on the stereochemistry at the β-carbon of the vinyl carbene complexed intermediate, we prepared a series of phenoxy carbene complexes of the type **29** and examined their reactions with the keto alkyne **20** (Scheme 7). These complexes were prepared from an acetoxy complex via the method of Connor and Fischer.[13] Once isolated as brown-black crystals, these compounds are quite stable, but the yield is highly dependent on the speed and efficiency of the purification. The reactions of the five derivatives with alkyne **20** are summarized in Table 2. There is a change in the product distribution from the trifluoromethyl derivative to the dimethylamino derivative that is similar in magnitude to that seen for the reaction of complex **19** with alkyne **26** except that the change is in the opposite direction. In this case the greatest proportion of the lactone product is found with the *p*-dimethylamino complex and not with the *p*-trifluoromethyl complex. This is not consistent with the outcome of the diaryl complex **7** (Scheme 3), where it is seen that the more electron-rich aryl group is predominately oriented syn to the phenyl group at the α-position. A possible origin of these differences will be discussed below.

The reaction of the trifluoromethyl complex **29a** with alkyne **20** was investigated in THF, benzene, acetonitrile, and methylene chloride, and as can be seen from the first four entries in Table 2, there is very little change in the product distribution over these four solvents. This implies that any buildup of charge is similar along the pathways leading to the *E*- or *Z*-derived products. This also suggests that there is no significant difference in the coordinative saturation of intermediates resulting in phenols or lactones. For example, if formation of the lactone proceeded via an intermediate with an open coordination site, but phenol formation did not, then coordinating solvents would increase the proportion of lactone. Since the product ratio is invariant with solvent, the coordination sphere of the intermediates leading to phenols and lactones must be comparable.

The structure of the lactone product requires that the mechanistic pathway must go through the *Z*-isomer of the vinyl carbene complexed intermediate, but very little is known about other aspects of the mechanism that gives rise to the lactone product.[5b,c] Diastereoselection in lactone formation has not been previously investigated. We decided to probe this with the cyclohexenyl complex **32** containing a chiral center since this complex has previously been shown to react with 1-hexyne to give the cyclohexadienone **35** as the trans-diastereomer in a reaction which must involve an *E*-vinyl carbene complexed intermediate.[16] The reaction of complex **32** with the alkynone **33** gave the lactone product **34** in 62% yield as one diastereomer. The relative stereochemistry of this lactone was determined to be that shown in structure **34** by an X-ray diffraction study.[21] It was

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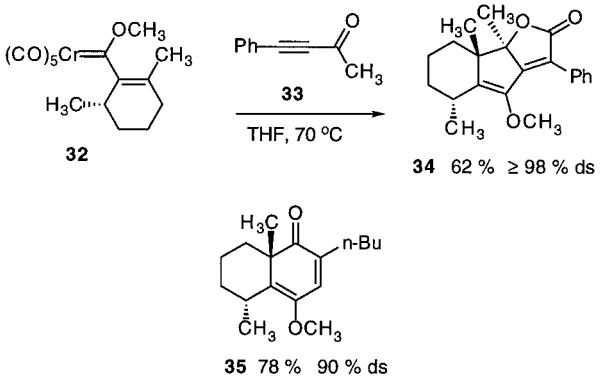
(15) Hayashi, T.; Konishi, M.; Okamoto, Y.; Kaberta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772.

(16) Hsung, R. P.; Wulff, W. D.; Challener, C. A. *Synthesis* **1996**, 773.

(17) Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hydahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

Scheme 8



interesting to find that the relative stereochemistry of the two methyl groups on the six-membered ring is trans for both the cyclohexadienone product **35** and for the lactone **34** despite the fact the lactone is formed from a *Z*-isomer of a vinyl carbene complexed intermediate and the cyclohexadienone from an *E*-isomer. A determination of the source of stereoselection in this reaction will need to await further studies on the mechanism of the lactone-forming reaction.

Discussion

The results outlined above can be explained in terms of a "trans" effect, which is illustrated in Scheme 9. This assumes that the new carbene carbon in the vinyl carbene complexed intermediate **2** is polarized in the same way that the carbene carbon in the starting carbene complex **1** is polarized with a partial negative charge on the carbene carbon and a partial negative charge on the chromium pentacarbonyl fragment. This can be more easily visualized by considering the η^1,η^3-vinyl carbene complexed intermediate **2** as a saturated form of the η^1-vinyl carbene complex **36** by virtue of the coordination of the double bond. Theoretical studies by Hoffmann have shown that the energy difference between **2** and **36** will be quite small.[3a] In any event, the reactions of carbene complexes under most conditions with electronically unperturbed alkynes (R^1, R^2 = alkyl) give phenol products and thus must proceed through the *E*-isomer of **2**. The selectivity for phenol products from the reaction of alkenyl complexes with simple alkynes is usually quite high, with no detectable amounts of side-products. Since this selectivity is much higher than that observed in the formation of phenols **8** and **9** and since the preferred formation of **8** is clearly the result of electronic effects, we attribute the high selectivity for the formation of phenol products from the reaction of alkenyl complexes with alkyl acetylenes to an electronic preference for the methoxyl group at the β-carbon in **2** to be trans to the new carbene carbon in **2**.

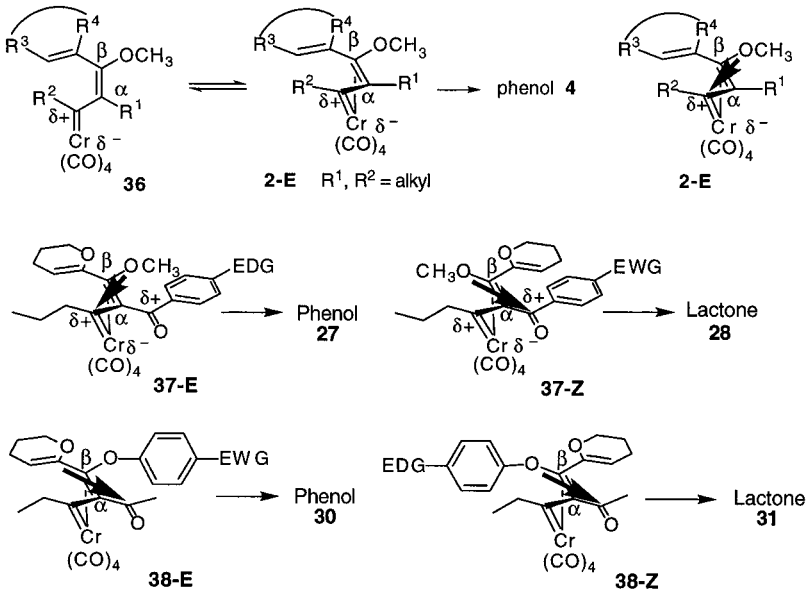
The outcome of the reactions with the aryl-substituted alkynyl ketones **26** can be explained by a competition between the ketone at the α-position in **2** (R^1) and the newly formed carbene carbon in **2** to be trans to the methoxy group in **2**. For alkynes with more electron-withdrawing groups on the alkyne, the ketone will be able to more effectively compete with the carbene carbon and the lactone product will predominate over the phenol product as a result of greater reaction through intermediate **37-Z**. On the other hand, an alkyne with an electron-donating group would be expected to produce a vinyl carbene complexed intermediate in which the ketone group cannot as effectively compete with the carbene complex for the methoxy group in the trans position, and thus a greater proportion of phenol products would be expected via **37-E**, in accord with the observation. Incorporation of para-substituted aryl groups into the carbene complex in place of the methoxyl group would be expected to give the opposite effect assuming that the ketone in the alkyne that was employed had a stronger trans effect than the new carbene carbon. In the case of the alkyne **20**, there would be a stronger trans effect in the intermediate **38-Z** in the case when a more electron-donating group was incorporated into the carbene complex **29**. The crossover to the phenol product with electron-donating groups in this case may be the result of steric interaction between the substituents on the α- and β-carbons of intermediate **38** (Scheme 9).

The source of the "trans effect" observed in these studies is not obvious since π-overlap should be just as good for a cis or a trans ligand. One possibility is that σ-participation plays a role as well. Even if π-overlap is equal for the cis and trans isomers of the vinyl carbene complexed intermediate such as **2**, **37**, or **38**, σ-overlap for the trans isomers would be expected to be larger due to better orbital alignment leading to a lower energy intermediate. This type of σ-overlap in carbon−carbon double bonds is responsible for the larger coupling constants for trans-hydrogens in alkenes[14] and for greater rates for base-induced dehydrobromination of vinyl bromides via an E2-elimination for a trans disposition of the hydrogen and bromide than for the cis disposition.[15]

A Hammett analysis of the data in Tables 1 and 2 was carried out and gave linear plots for both sets of data with a slope of −0.77 for the phenoxyl carbene complexes **29** ($r^2 = 0.88$) and 1.09 for the aryl alkynones **26** ($r^2 = 0.97$). The linearity of the Hammett plots verifies that there is no change in mechanism with the variation of the electronics. Specifically, this shows that varying the electronics does not induce a change in mechanism between one in which vinyl carbene complexed intermediate formation is rate limiting and one in which vinyl ketene complex formation is rate limiting. Additionally, from the slopes one can see that the system is more sensitive to perturbation of the electronics of the ketone than variation of the electronics of the phenoxy group. This may be because in the reaction of the aryl alkynones **26** the aryl ring is directly bonded to the carbonyl in **37**, but the phenyl group in **38** is separated from the carbonyl by the oxygen and the double bond. Finally, it is unexpected that the trans effect of a carbene complex be less than that of a carbonyl. For example, the Diels−Alder reactions of vinyl carbene complexes are greatly accelerated relative to those of α,β-unsaturated carbonyl compounds.[20] This

(18) Tobinaga, S.; Kotani, E. *J. Am. Chem. Soc.* **1972**, *94*, 309.
(19) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132.
(20) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.
(21) Crystals of **34**: space group $Pna2_1$; a = 14.7108(38) Å; b = 10.5970(22) Å; c = 1736.9(6) Å; V = 1736.9(6) Å^3. For addition information, see the Supporting Information.

Scheme 9

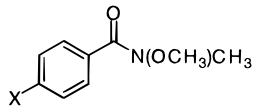


has been attributed to the greater electron-withdrawing effect of the chromium pentacarbonyl group with respect to an oxygen atom. However, the effect of the metal should be quite different in an η^3-vinyl carbene complex than in an η^1-vinyl carbene complex. First, the dihedral angle between the carbon−carbon double bond and the carbon−chromium double bond in the η^3-vinyl carbene complex **2-E** is significantly differenent than 180°, and second, the chromium also can withdraw electron density from the carbon−carbon double bond by direct coordination; this will have a stereoselectonic effect that would be closer to perpendicular to the methoxyl group than trans.

In conclusion, it has been shown that the electronic effects of substituents on a correctly tuned alkyne and on a phenoxy carbene complex can affect the partition between products that arise from *E*- and *Z*-isomers of the reaction intermediates. The effects are reversed for electronic variation on the alkyne versus those on the carbene complex. This can be explained by a "trans effect" in which there is a preference for the most electron-donating group at the β-carbon of the η^1,η^3-vinyl carbene complexed intermediate to be trans to the more electron-withdrawing substituent of the α-carbon of this intermediate. These observations suggest that the reason that the reaction of alkynes with α,β-unsaturated carbene complexes under normal conditions is a highly valuable synthetic method for the preparation of phenols is that there is a preference for the methoxy group to be trans to the new carbene carbon in the η^1,η^3-vinyl carbene complexed intermediate, thus permitting cyclization onto the unsaturated substituent after carbon monoxide insertion. With regard to synthetic utility of the reaction, these results give the first clear picture of how the electronics of the system influence the chemoselectivity of the reaction. This should allow for tuning of the reaction to give the desired product.

Experimental Section

Preparation of Weinreb's Amides 39a−e. These compounds were made by the general procedure of Weinreb.[12] To a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (2.05 g, 21 mmol) in 100 mL of $CHCl_3$ was added 20 mmol of the appropriate para-substituted benzoyl chloride (note: chloroform was washed with water, dried over $MgSO_4$, and distilled before use to remove trace ethanol). The solution was cooled to 0 °C, and 2.1 equiv of pyridine (3.4 mL, 42 mmol) was added slowly. The ice bath was removed, and the solution was stirred for 3 h. The solvent was then removed under reduced pressure, and the residue was dissolved in 1:1 ether/methylene chloride. The organic layer was washed three times with water and once with brine and was dried over $MgSO_4$. The solution was filtered through a plug of Celite, and solvent was removed under reduced pressure. The crude product was then purified by either distillation under reduced pressure or column chromatography.



39a-e

Amide 39a: X = CF_3, 85% yield; ^{1}H NMR ($CDCl_3$) δ 3.38 (s, 3H), 3.54 (s, 3H), 7.69 (d, 2H, J = 8.3 Hz), 7.78 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 33.25, 61.18, 123.7 (quart, J = 271 Hz, CF_3), 124.95, 128.49, 132.2 (d, J = 31.7 Hz, C-CF_3), 137.52, 168.44; IR (neat) 2974 m, 2940 m, 1651 s, 1620 m, 1579 m, 1517 m 1462 m, 1408 m, 1384 s, 1327 s, 1216 m, 1167 s, 1113 s, 1071 s, 1019 s, 982 s, 852 s, 764 m, 702 m; mass spectrum *m*/*z* (rel intensity) 233 M^+ (4), 174 (8), 173 (100), 145 (49), 125 (4), 75 (5), 50 (3). Anal. Calcd for $C_{10}H_{10}F_3NO_2$: C, 51.51; H, 4.32; N, 6.01. Found: C, 51.8; H, 4.37; N, 5.99. Bp = 85 °C at 0.01 mmHg.

Amide 39b: X = Cl, 100% yield; ^{1}H NMR ($CDCl_3$) δ 3.36 (s, 3H), 3.53 (s, 3H), 7.39 (d, 2H, J = 8.5 Hz), 7.67 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 33.19, 60.79, 127.95, 129.57, 132.05, 136.35, 168.26; IR (neat) 2968 m, 2935 m, 1646 s (broad), 1549 s, 1416 s, 1379 s, 1213 m, 1091 s, 1016 s, 980 s, 840 s, 747 s; mass spectrum *m*/*z* (rel intensity) 199 M^+ (4), 141 (32), 139 (100), 111 (27), 75 (15). Anal. Calcd for $C_9H_{10}ClNO_2$: C, 54.20; H, 5.05; N, 7.02. Found: C, 53.99; H, 5.08; N, 7.34. Bp = 80 °C at 0.01 mmHg; R_f = 0.45 (1:1 hexane/ethyl acetate).

Amide 39d: X = OCH_3, 75% yield; ^{1}H NMR ($CDCl_3$) δ 3.36 (s, 3H), 3.56 (s, 3H), 3.85 (s, 3H), 6.92 (d, 2H, J = 8.9 Hz), 7.72 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 33.32, 54.75, 60.30, 112.73, 125.50, 129.99, 161.03, 168.79; IR (neat) 1636

s, 1608 s, 1512 m, 1462 m, 1420 m, 1374 m, 1254 s, 1173 m, 1029 m, 841 m; mass spectrum *m/z* (rel intensity) 195 M^+ (8), 136 (22), 135 (100), 107 (21), 92 (19), 77 (31), 64 (11). Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18. Found: C, 61.10; H, 6.80; N, 7.18.

Amide 39e: X = $N(CH_3)_2$, 68% yield. The product was purified by column chromatography with 2:1 hexane/ethyl acetate as eluent: ^{1}H NMR ($CDCl_3$) δ 3.01 (s, 6H), 3.34 (s, 3H), 3.59 (s, 3H), 6.67 (d, 2H, J = 8.9 Hz), 7.74 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 34.09, 39.94, 60.54, 110.46, 120.19, 130.48, 151.89, 169.75; IR (neat) 2929 w, 1628 m, 1606 s, 1362 s, 1166 m; mass spectrum *m/z* (rel intensity) 208 M^+ (9), 193 (1), 178 (1), 149 (12), 148 (100), 120 (5), 105 (5), 77 (6), 57 (5), 42 (8). Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.47; H, 7.87; N, 13.39. Mp = 37−39 °C.

General Procedure for the Preparation of Alkynones 26a−e. *n*-Butyllithium (8.4 mmol, 3.4 mL of a 2.5 M solution) was added slowly to a solution of 1-pentyne (0.83 mL, 8.4 mmol) in 3 mL of THF at −78 °C. After 30 min, the solution was transferred via cannula to a solution of the Weinreb's amide **39** (7.6 mmol) in 60 mL of THF at −78 °C. After stirring for 1 h at this temperature, the reaction was allowed to warm and was stirred at room temperature for 12 h. At this time the reaction was complete by thin-layer chromatography. The reaction was quenched with water and diluted with ether. The organic layer was washed repeatedly with water until the aqueous layer was no longer basic. The aqueous layer was then neutralized with 1 N HCl and extracted twice with ether. The combined organic layers were washed once with brine, dried over $MgSO_4$, and filtered through a plug of Celite. The solvent was removed under reduced pressure, and the product was purified by column chromatography on silica gel.

Alkyne 26a: X = CF_3, 100% yield. The product was purified by column chromatography with 50:1:1 hexane/methylene chloride/ether as eluent: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3H, J = 7.4 Hz), 1.66 (sext, 2H, J = 7.2 Hz), 2.45 (t, 2H, J = 7.0 Hz), 7.67 (d, 2H, J = 8.2 Hz), 8.18 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.35, 20.97, 21.16, 79.35, 98.00, 125.25 (q, $^1J_{CF}$ = 273 Hz), 125.37 (q, $^3J_{CF}$ = 3.6 Hz), 129.59, 134.75 (q, $^2J_{CF}$ = 33 Hz), 139.29, 176.63; IR (neat) 2969 m, 2939 w, 2878 w, 2239 m, 2203 m, 1653 s, 1583 w, 1509 w, 1462 m, 1411 m, 1326 s, 1262 s, 1173 s, 1133 s, 1066 s, 1016 m, 912 m, 859 m, 766 m, 691; mass spectrum *m/z* (rel intensity) 241 (M + 1)$^+$ 1 (10), 212 (37), 183 (12), 173 (23), 145 (25), 95 (100). Anal. Calcd for $C_{13}H_{11}F_3O$: C, 65.00; H, 4.62. Found: C, 64.68; H, 4.65.

Alkyne 26b: X = Cl, 86% yield. The product was purified by column chromatography with 50:1:1 hexane/methylene chloride/ether as eluent: ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3H, J = 7.4 Hz), 1.65 (sext, 2H, J = 7.2 Hz), 2.43 (t, 2H, J = 7.0 Hz), 7.38 (dd, 2H, J = 8.6, 1.4 Hz), 8.01 (dd, 2H, J = 8.6, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 13.45, 20.98, 21.20, 79.34, 97.06, 128.66, 130.64, 135.15, 140.23, 176.60; IR (neat) 2966 m, 2935 w, 2875 w, 2238 m, 2202 m, 1648 s, 1586 m, 1485 m, 1401 m, 1364 s, 1171 m, 1091 m, 1105 w, 1013 m, 910 m, 845 m, 746 m; mass spectrum *m/z* (rel intensity) 206 M^+ (100), 191 (35), 178 (45), 149 (38), 139 (47), 128 (24), 111 (42), 95 (100), 75 (39). Anal. Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.37. Found: C, 70.19; H, 5.55.

Alkyne 26c: X = H, 87% yield; ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3H, J = 7.4), 1.71 (mult, 2H), 2.47 (t, 2H, J = 7.0 Hz), 7.47 (mult, 2H), 7.59 (t, 1H, J = 6.5 Hz), 8.13 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 13.75, 21.28, 21.52, 79.91, 96.79, 128 0.62, 129.65, 134.02, 137.03, 178.37; IR (neat) 2966 m, 2237 m, 2202 s, 1640 s, 1598 s, 1581 s, 1450 s, 1313 m, 1264 m, 1175 m, 911 m; mass spectrum *m/z* (rel intensity) 173 (12), 172 M^+ (89), 145 (11), 144 (100), 143 (19), 129 (51), 128 (15), 116 (12), 115 (55), 105 (36), 95 (97), 77 (55), 67 (12), 66 (15), 65 (12), 53 (27), 51 (33), 50 (11). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.60; H, 7.08.

Alkyne 26d: X = OCH_3, 97% yield. The product was purified by column chromatography with 40:1:1 hexane/methylene chloride/ether as eluent: ^{1}H NMR ($CDCl_3$) δ 1.09 (t, 3H, J = 7.4 Hz), 1.71 (sext, 2H, J = 7.2 Hz), 2.47 (t, 2H, J = 7.1 Hz), 3.88 (s, 3H), 6.92 (d, 2H, J = 8.8 Hz), 8.08 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.48, 20.98, 21.29, 55.41, 79.62, 95.59, 113.58, 130.15, 131.73, 164.13, 176.78; IR (neat) 2965 w, 2935 w, 2238 w, 2202 m, 1638 m, 1597 s, 1575 m, 1509 m, 1421 w, 1317 w, 1257 s, 1166 m, 1113 w, 1028 m, 911 w, 845 w, 758 m; mass spectrum *m/z* (rel intensity) 202 M^+ (78), 174 (24), 159 (22), 145 (100), 135 (50), 95 (32), 77 (37). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.61; H, 7.11.

Alkyne 26e: X = NMe_2,72% yield. The product was purified by column chromatography with 10:1:1−4:1:1 hexane/methylene chloride/ether as eluent: R_f = 0.15 (10:1:1 hexane/methylene chloride/ether); mp = 70−72 °C; ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3H, J = 7.3 Hz), 1.68 (m, 2H, J = 7.2 Hz), 2.45 (t, 2H, J = 7.0 Hz), 3.08 (s, 6H), 6.67 (d, 2H, 9.0 Hz), 8.02 (d, 2H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 13.53, 21.03, 21.41, 39.91, 79.92, 94.16, 110.37, 125.32, 131.76, 153.85, 176.31; IR (neat) 2963 m, 2933 m, 2874 w, 2236 w, 2199 w, 1620 s, 1599 s, 1580 s, 1383 w, 1233 m, 1189 m, 824 s, 758 s, 690 s cm^{-1}; mass spectrum *m/z* (rel intensity) 216 (15), 215 M^+ (100), 214 (45), 187 (7), 186 (8), 159 (5), 158 (32), 148 (6), 142 (7), 119 (4), 115 (4), 105 (3), 104 (3), 77 (5), 42 (4). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.11; H, 7.96; N, 6.51. Found: C, 78.47; H, 8.02; N, 6.35.

General Procedure for the Benzannulation Reaction of Dihydropyranyl Methoxy Chromium Carbene Complex 19 with Alkynes 26a−e. Dihydropyranyl methoxy chromium carbene complex **19**[17] (200 mg, 0.63 mmol) was added to a round-bottom flask modified with a sidearm and threaded neck containing a stirbar. To the flask was added 5 mL of THF. The alkyne (2 equiv) was then added, followed by the remaining 7.6 mL of THF, resulting in a 0.05 M solution of carbene complex. The threaded Teflon stopper was sealed and the reaction was degassed with three freeze−pump−thaw cycles (i.e., the solution was frozen in liquid nitrogen, evacuated under high vacuum, resealed, and warmed to room temperature). After warming to room temperature the third time, the flask was filled with argon, resealed, and placed in a 50 °C oil bath. The reaction was stirred for 14−15 h, at which time it was cooled to room temperature and analyzed by TLC to ensure that the starting carbene complex was consummed. Ferric chloride−DMF complex[18] (0.32 g) was dissolved in approximately 5 mL of water and added to the reaction. The solution was stirred in air for 30−60 min and then transferred to a separatory funnel and extracted four times with 30 mL portions of ether. The ether layer was then washed twice with brine, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure. To obtain an NMR ratio of phenol/lactone, the excess alkyne had to be removed since it interfered with integration. Thus, a short column was run with 4:1:1 hexane/methylene chloride/ether to separate recovered alkyne from the products. The ratio of products was then determined by ^{1}H NMR spectroscopy. The phenol and lactone were then separated by careful chromatography on silica gel with the same solvent mixture, and the R_f values for each are indicated below for this solvent system unless otherwise specified. Each reaction was run at least twice, and the ratios and yields of products are presented in Table 1.

Phenol 27a: X = CF_3; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, 3H, J = 7.3 Hz), 1.38−1.46 (M, 2H), 2.04−2.08 (m, 2H), 2.28 (t, 2H, J = 7.9 Hz) 2.71 (t, 2H, J = 6.2 Hz), 3.57 (s, 3H), 4.21 (t, 2H, J = 5.0 Hz), 4.77 (br s, 1H), 7.68 (d, 2H, J = 8.2 Hz), 7.94 (d, 2H, J = 8.2); ^{13}C NMR ($CDCl_3$) δ 14.19, 19.59, 21.43, 23.50, 28.95, 61.46, 65.92, 112.43, 115.92, 123.61 (q, $^1J_{CF}$ = 273 Hz), 125.49 (q, $^3J_{CF}$ = 3.6 Hz), 129.69, 131.15, 134.39 (q, $^2J_{CF}$ = 33), 138.61, 140.44, 146.52, 147.93, 196.38; IR (neat) 3473 br m, 2960 m, 2937 m, 2873 w, 1676 m, 1579 m, 1457 m, 1424

m, 1325 s, 1270 m, 1170 m, 1129 s, 1096 m, 1065 m, 1015 m, 982 m, 866 w, 752 w; mass spectrum *m/z* (rel intensity) 394 M^+ (97), 365 (100), 350 (29), 333 (22), 325 (12), 173 (63), 145 (50). $R_f = 0.19$.

Lactone 28a: X = CF_3; ^{1}H NMR (acetone-d_6) δ 0.85 (t, 3H, J = 7.4 Hz), 0.78−0.95 (m, 1H), 1.39−1.62 (m, 2H), 1.65−1.85 (m, 2H), 1.88−1.96 (m, 1H), 2.31 (t, 2H, J = 7.3 Hz), 3.08 (dd, 1H, J = 12.4, 5.7 Hz), 3.65 (td, 1H, J = 11.0, 4.0 Hz), 4.00 (s, 3H), 4.23 (br d, 1H, J = 10.9 Hz), 7.68 (d, 2H, J = 8.4 Hz), 7.75 (d, 2H, J = 8.4 Hz); ^{13}C NMR (acetone-d_6) δ 13.84, 22.47, 23.38, 23.60, 26.44, 47.78, 59.85, 69.92, 89.61, 118.22, 125.08 (q, $^1J_{CF}$ = 272 Hz), 125.96 (q, $^3J_{CF}$ = 3.5 Hz), 128.40, 130.43 (q, $^2J_{CF}$ = 33 Hz), 133.81, 145.46, 147.91, 164.66, 173.73; IR (neat) 2959 m, 2873 w, 1756 s, 1675 w, 1618 s, 1456 m, 1409 m, 1327 s, 1284 m, 1230 m, 1166 m, 1127 m, 1080 m, 1020 m, 980 m, 861 w, 836 w; mass spectrum *m/z* (rel intensity) 395 (17), 394 M^+ (66), 367 (16), 366 (58), 365 (15), 337 (17), 324 (13), 193 (52), 174 (10), 173 (96), 145 (30), 88 (11), 86 (66), 84 (100), 55 (22). $R_f = 0.22$.

Phenol 27b: X = Cl; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3H, J = 7.1 Hz), 1.33−1.42 (m, 2H), 2.04−2.09 (m, 2H), 2.26 (t, 2H, J = 7.1 Hz), 2.65−2.75 (m, 2H), 3.58 (s, 3H), 4.20 (t, 2H, J = 6.3 Hz), 4.85 (br s, 1H), 7.38 (d, 2H, J = 8.4 Hz), 7.78 d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.21, 19.58, 21.46, 23.42, 28.97, 61.45, 65.88, 112.20, 115.91, 128.73, 130.90, 131.44, 136.13, 138.44, 139.76, 146.45, 147.89, 196.17; IR (neat) 3460 br m, 2959 m, 2934 m, 2871 m, 1670 s, 1587 m, 1456 m, 1424 m, 1400 m, 1352 w, 1333 m, 1269 s, 1215 m, 1170 m, 1125 m, 1093 s, 1012 m, 982 m, 868 w, 777 w, 735 m; mass spectrum *m/z* (rel intensity) 360 M^+ (32), 332 (17), 262 (13), 193 (30), 141 (30), 139 (100), 111 (27). $R_f = 0.16$.

Lactone 28b: X = Cl; ^{1}H NMR (acetone-d_6) δ 0.85 (t, 3H, J = 7.4 Hz), 0.7−1.0.0 (m, 1H), 1.4−1.6 (m, 2H), 1.65−1.80 (m, 2H), 1.85−1.95 (m, 1H), 2.30 (t, 2H, J = 7.4 Hz), 3.04 (dd, 1H, J =12.3 Hz, 5.6 Hz), 3.64 (td, 1H, J = 11.0 Hz, 4.5 Hz) 3.97 (s, 3H), 4.22 (br d, 1H, J = 10.5 Hz), 7.40 (d, 2H, J = 8.7 Hz), 7.46 (d, 2H, J = 8.7 Hz); ^{13}C NMR (acetone-d_6) δ 13.84, 22.46, 23.37, 23.57, 26.42, 47.82, 59.81, 69.88, 89.58, 118.03, 129.02, 129.35, 133.75, 134.25, 140.10, 147.85, 164.88, 173.84; IR (neat) 2958 m, 2872 w, 1753 s, 1675 w, 1617 s, 1467 m, 1399 w, 1318 m, 1283 m, 1229 m, 1188 w, 1080 m, 1022 m, 987 m, 941 w, 829 w, 748 m. $R_f = 0.33$.

Phenol 27c: X = H; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3H, J = 7.3 Hz), 1.40−1.46 (m, 2H), 2.02−2.08 (m, 2H), 2.28 (t, 2H, J = 7.9 Hz), 2.68−2.73 (m, 2H), 3.58 (s, 3H), 4.20 (t, 2H, J = 4.8 Hz), 4.66 (br s, 1H), 7.40 (t, 2H, J = 7.6 Hz), 7.52 (t, 1H, J = 7.4 Hz), 7.82 (d, 2H, J = 0.3 Hz); IR (neat) 3463 m, 2959 m, 2936 m, 2869 m, 1664 s, 1580 m, 1456 s, 1423 s, 1333 m, 1290 m, 1270 s, 1125 s, 1095 s, 982 m; ^{13}C NMR ($CDCl_3$) δ 14.22, 19.60, 21.51, 23.39, 29.03, 61.42, 65.87, 111.95, 115.89, 128.37, 129.53, 132.03, 133.32, 137.74 138.48, 146.43, 147.79, 197.42; mass spectrum *m/z* (rel intensity) 326 M^+ (93), 310 (10), 297 (100), 282 (77), 265 (34), 249 (8), 149 (10), 105 (100), 91 (13), 85 (16), 77 (76), 71 (23). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.22; H, 6.83. $R_f = 0.16$.

Lactone 28c: X = H; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, J = 7.5 Hz), 0.8−1.0 (m, 1H), 1.5−1.8 (m, 4H), 1.85−1.9 (m, 1H), 2.35 (t, 2H, J = 7.4 Hz), 2.98 (dd, 1H, J = 12.3, 5.8 Hz), 3.56 (td, 1H, J = 11.5, 3.0 Hz), 3.98 (s, 3H), 4.17 (br d, 1H, J = 12.8 Hz), 7.27−7.33 (m, 3H), 7.41 (d, 2H, J = 7.7 Hz); IR (neat) 2959 s, 2873 m, 1767 s, 1719 s, 1672 m, 1614 s, 1447 m, 1397 w, 1320 m, 1270 s, 1170 m, 1107 m, 1107 s, 1082 s, 1052 m, 978 s; ^{13}C NMR ($CDCl_3$) δ 13.85, 22.49, 23.40, 23.68, 26.44, 47.95, 59.79, 69.83, 90.09, 117.83, 127.61, 128.83, 128.89, 133.84, 141.28, 147.78, 165.31, 174.08; mass spectrum *m/z* (rel intensity) 326 M^+ (5), 310 (12), 299 (8), 281 (14), 228 (22), 199 (20), 114 (12), 105 (100), 77 (47). $R_f = 0.30$.

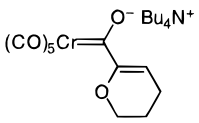
Phenol 27d: X = OCH_3; ^{1}H NMR ($CDCl_3$) δ 0.79 (t, 3H, J = 7.3 Hz), 1.32−1.48 (m, 2H), 1.98−2.07 (m, 2H), 2.25 (t, 2H, J = 7.9 Hz), 2.70 (t, 2H, J = 0.5 Hz), 3.59 (s, 3H), 3.84 (s, 3H), 4.19 (t, 2H, J = 5.1 Hz), 4.95 (s, 1H), 6.88 (d, 2H, J = 8.8 Hz), 7.81 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 14.28, 19.57, 21.53, 23.38, 29.04, 55.41, 61.50, 65.86, 111.84, 113.57, 115.98, 130.90, 131.99, 132.26, 138.30, 146.37, 147.82, 163.75, 195.95; mass spectrum *m/z* (rel intensity) 357 (13), 356 M^+ (59), 355 (18), 328 (21), 327 (100), 325 (14), 313 (13), 312 (47), 311 (10), 296 (16), 295 (24), 281 (8), 156 (8), 142 (7), 135 (39), 107 (10), 92 (12), 77 (23). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.08; H, 6.81. $R_f = 0.10$.

Lactone 28d: X = OCH_3; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3H, J = 7.4 Hz), 0.90−0.99 (m, 1H), 1.5−1.8 (m, 4H), 1.85−1.91 (m, 1H), 2.35 (t, 2H, J = 7.6 Hz), 2.96 (dd, 1H, J = 12.2, 5.7 Hz), 3.58 (td 1H, J = 12.5, 3.9 Hz), 3.79 (s, 3H), 3.97 (s, 3H), 4.17 (d, 1H, J = 10.8 Hz), 6.83 (d, 2H, J = 8.7 Hz), 7.33 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.73, 21.86, 22.80, 22.85, 26.01, 47.30, 55.20, 59.56, 69.05, 89.60, 113.28, 118.05, 128.06, 132.17, 133.25, 146.48, 159.51, 164.34, 174.44; IR (neat) 2959 m, 2872 w, 1749 s, 1673 w, 1617 s, 1511 m, 1462 m, 1252 m, 1180 m, 1080 m, 980 m, 832 m, 731 w. $R_f = 0.23$.

Phenol 27e: X = NMe_2; ^{1}H NMR ($CDCl_3$) δ 0.82 (t, 3H, J = 7.3 Hz); 1.44 (mult, 2H), 2.05 (mult, 2H), 2.3 (mult, 2H), 2.71 (t, 2H, J = 6.5 Hz), 3.05 (s, 6H), 3.62 (s, 3H), 4.21 (t, 2H, J = 5.0 Hz), 4.61 (br s, 1H), 6.62 (d, 2H, J = 9 Hz), 7.73 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 14.56, 19.77, 21.79, 23.61, 29.29, 40.19, 61.73, 66.07, 110.65, 111.30, 115.78, 126.06, 132.18, 133.35, 138.55, 146.64, 147.80, 153.78, 195.06; IR (neat) 3400 br w, 2928 w, 1588 s, 1547 w, 1454 w, 1373 w, 1179 m, 1124 w, 1095 w; mass spectrum *m/z* (rel intensity) 370 (13), 369 M^+ (51), 368 (18), 341 (25), 340 (100), 326 (8), 325 (34), 308 (10), 84 (13). $R_f = 0.13$ (2:1 hexane/ethyl acetate).

Lactone 28e: X = NMe_2; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, J = 7.3 Hz), 1.01 (dq, 1H, J = 12.3, 4.2 Hz), 1.5−1.8 (mult, 5H), 1.85 (mult, 1H), 2.34 (t, 2H, J = 7.5 Hz), 2.95 (s, 6H), 3.59 (dt, 1H, J = 11.1, 3.3 Hz), 3.97 (s, 3H), 4.20 (m, 1H); 6.67 (d, 2H, J = 8.7), 7.27 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.80, 21.90, 22.77, 22.91, 26.10, 40.34, 47.46, 59.61, 69.06, 89.93, 111.50, 117.83, 125.93, 127.70, 133.27, 146.72, 149.92, 164.65, 174.68; IR (neat) 58 m, 1748 s, 1615 s, 1522 m, 1283 m, 1107 m, 1080 m; mass spectrum *m/z* (rel intensity) 55 (14), 84 (10), 104 (10), 121 (9), 148 (100), 149 (13), 354 (79), 355 (20), 369 (76), 370 (21). $R_f = 0.09$.

Preparation of Dihydropyranyl Chromium Tetrabutyl Ammonium Salt 40. The following is a modification of a



40

published procedure.[17] Freshly distilled dihydropyran (2.74 mL, 30 mmol) was dissolved in 4.5 mL of THF and cooled to −78 °C. *tert*-Butyllithium (20 mL, 30 mmol; 1.5 M in pentane) was added slowly over several minutes. The solution became a yellow slurry. After stirring at −78 °C for 15 min, the solution was transferred to an ice bath and stirred an additional 20 min, in which time the solution turned clear yellow. The solution was then transferred via cannula to a slurry of $Cr(CO)_6$ (6.6 g, 30 mmol) in 30 mL of THF at room temperature. The solution was stirred for 2.5 h, at which time the solvent was removed under reduced pressure and the brown oily residue was placed under high vacuum for 1 h, leaving a mustard-colored solid. The solid was dissolved in 20 mL of degassed water and filtered with a Büchner funnel to remove any unreacted $Cr(CO)_6$. Tetrabutylammonium bromide (14.5 g, 45 mmol) was added to the filtrate, which turned opaque yellow immediately. The aqueous filtrate was extracted with methylene chloride in 25 mL portions until the organic layer was only faint yellow. This extraction was performed carefully to avoid emulsions. The organic layer was dried over $MgSO_4$, filtered, and concentrated to approximately 40 mL volume

under reduced pressure. The solution was then placed in the freezer overnight under a static vacuum to crystallize. In some cases, hexane was layered on top of the methylene chloride solution to induce crystallization, 98% yield.

General Synthesis of Aryloxy Carbene Complexes 29. To a solution of 2.0 g (3.7 mmol) of the ammonium salt **40** in 60 mL of methylene chloride was added 300 mL (4.05 mmol) of freshly distilled acetyl bromide at −35 °C. The yellow solution turned deep red immediately upon addition. The solution was stirred for 1 h at −35 °C. The phenol (4.05 mmol) was dissolved in 15 mL of THF and cooled to −78 °C, followed by addition of 4.05 mmol of ^{n}BuLi. The solution was stirred for 15−45 min and was then transferred via cannula to the ammonium salt solution. The reaction mixture was stirred at −35 °C for an additional 2−3 h. The solution was concentrated under reduced pressure to approximately 20 mL, diluted with 40 mL of hexane, and concentrated again to a final volume of about 10 mL. The reaction mixture was not evaporated to dryness because this induced decomposition. The concentrate was loaded on a short column of silica gel and eluted with hexane. A yellow band eluted followed by a deep red-brown band, which corresponded to the carbene complex. The red-brown band was collected and concentrated under reduced pressure and then crystallized at −78 °C under vacuum. The supernatant was removed by pipet, and the crystals were dried under vacuum. The crystalline complexes are quite stable, but the yield is variable and depends on the speed and efficiency with which the carbene complex is purified.

Carbene Complex 29a: X = CF_3, 56% yield; ^{1}H NMR ($CDCl_3$) δ 1.92 (mult, 2H), 2.30 (mult, 2H), 4.26 (t, 2H, J = 4.9 Hz), 5.80 (t, 1H, J = 4.5 Hz), 7.31 (d, 2H, J = 8.3 Hz), 7.45 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 20.96, 21.40, 6.49, 103.16, 126.76, 127.19, 160.95, 161.69, 216.10, 225.50, 333.70 (CF_3 not found); IR (neat) 2062 m, 1939 s, 1323 m, 1169 m, 1129 m, 1063 m cm^{-1}; mass spectrum m/z (rel intensity) 449 (1), 448 M$^+$ (3), 420 (9), 392 (4), 364 (16), 336 (20), 309 (12), 308 (44), 281 (11), 280 (48), 256 (12), 214 (11), 213 (36), 193 (28), 162 (24), 143 (18), 126 (10), 111 (18), 80 (20), 79 (13), 71 (12), 55 (21), 53 (13), 52 (100), 43 (69), 42 (23), 41 (39). Anal. Calcd for $C_{18}H_{11}CrF_3O_7$: C, 48.23; H, 2.47. Found: C, 48.03; H, 2.80. Black crystals; mp = 52−65 °C; R_f = 0.17 (hexane).

Carbene Complex 29b: X = Cl, 34% yield; ^{1}H NMR ($CDCl_3$) δ 1.91 (mult, 2H, J = 5.0 Hz, 5.6 Hz), 2.29 (mult, 2H, J = 5.0 Hz), 4.25 (t, 2H, J = 5.0), 5.77 (t, 1H, J = 4.6 Hz), 7.12 (d, 2H, J = 8.7 Hz), 7.44 (d, 2H, J = 8.7 Hz); ^{13}C NMR (C_6D_6) δ 20.80, 21.36, 66.43, 102.87, 127.91, 130.08, 132.80, 157.43, 161.79, 216.68 (C_{cis-CO}), 225.98 ($C_{trans-CO}$), 334.18 ($C_{carbene}$); IR (neat) 2060 m, 1933 vs, 1587 w, 1483 w, 1205 w, 1164 w, 1141 w, 1094 w, 1085 w, 1057 w, 695 w, 655 m cm^{-1}; mass spectrum m/z (rel intensity) 414 M$^+$ (1), 330 (9), 302 (7), 276 (10), 275 (7), 239 (6), 222 (12), 108 (6), 80 (17), 53 (13), 53 (100), 52 (100). Anal. Calcd for $C_{17}H_{11}CrClO_7$: C, 49.24; H, 2.67. Found: C, 49.21; H, 2.65. Brown crystals; mp = 84−87 °C; R_f = 0.14 (hexane).

Carbene Complex 29c: X = H, 44% yield; ^{1}H NMR ($CDCl_3$) δ 1.90 (mult, 2H), 2.29 (q, 2H, J = 4.9, 6.0 Hz), 4.26 (t, 2H, J = 5.0 Hz), 5.76 (t, 1H, J = 4.5 Hz), 7.18 (d, 2H, J = 7.9 Hz), 7.37 (t, 1H, 7.2, 7.3 Hz), 7.49 (t, 2H, J = 7.8, 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 20.89, 21.45, 66.41, 102.38, 122.25, 126.93, 129.81, 158.85, 161.73, 216.26 (C_{cis-CO}), 225.80($C_{trans-CO}$), 334.02 ($C_{Carbene}$); IR (neat) 2965 w, 2059 s, 1990 m, 1932 br s, 1589 m, 1467 m, 1295 m, 1197 m, 1147 m, 1057 m, 918 m, 896 m cm^{-1}; mass spectrum, m/z (rel intensity) 380 M$^+$ (2), 352 (4), 296 (12), 268 (8), 241 (8), 240 (30), 188 (17), 184 (8), 146 (7), 145 (14), 108 (10), 80 (35), 79 (9), 77 (8), 54 (8), 53 (28), 52 (100), 50 (12). Anal. Calcd for $C_{17}H_{12}CrO_7$: C, 53.70; H, 3.18. Found: C, 53.53; H, 3.24. Brown-black crystals; mp = 57−69 °C; R_f = 0.41 (1:1:15 ether/methylene chloride/hexane).

Carbene Complex 29d: X = OCH_3, 45% yield; ^{1}H NMR ($CDCl_3$) δ 1.91 (mult, 2H), 2.30 (q, 2H, J = 6.2 Hz), 3.85 (s, 3H), 4.26 (t, 2H, J = 5.0 Hz), 5.73 (t, 1H, J = 4.5 Hz), 6.96 (d, 2H, J = 9.1 Hz), 7.09 (d, 2H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ 20.85, 21.45, 55.15, 66.47, 102.50, 115.05, 123.26, 153.09, 158.91, 161.95, 216.95, 226.32, 335.13; IR (neat) 2061 m, 1987 s, 1923 br s, 1504 m, 1464 m, 1197 m, 1176 m, 1102 m, 1034 m, cm^{-1}; mass spectrum, m/z (rel intensity) 410 M$^+$ (2), 382 (5), 326 (14), 298 (8), 271 (8), 270 (31), 220 (43), 218 (12), 214 (7), 175 (7), 109 (8), 108 (43), 81 (13), 80 (74), 54 (11), 53 (19), 52 (100). Anal. Calcd for $C_{18}H_{14}CrO_8$: C, 52.70; H, 3.44. Found C, 52.41 H, 3.41. Black crystals; mp = 101−104 °C; R_f = 0.48 (10:1:1 hexane/methylene chloride/ether).

Carbene Complex 29e: X = NMe_2, 45% yield; ^{1}H NMR ($CDCl_3$) δ 1.91 (mult, 2H), 2.27 (mult, 2H, J = 5.0 Hz), 2.99 (s, 6H), 4.25 (t, 2H, J = 5.0 Hz), 5.69 (t, 1H, J = 4.4 Hz), 6.78 (d, 2H, J = 8.9 Hz), 6.98 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.88, 21.53, 40.80, 66.39, 101.81, 102.61, 112.78, 122.43, 149.55, 150.39, 161.77, 216.44 (C_{cis-CO}), 226.09 ($C_{trans-CO}$), 335.01($C_{carbene}$); IR (neat) 2057 s, 1989 m, 1932 vs, 1509 m, 1209 w, 1147 w cm^{-1}; mass spectrum m/z (rel intensity) 424 (2), 423 M$^+$ (6), 395 (20), 340 (14), 339 (52), 311 (27), 284 (28), 283 (100), 254 (13), 253 (39), 231 (23), 228 (19), 227 (76), 225 (11), 189 (17), 188 (54), 187 (38), 173 (11), 148 (16), 137 (19), 136 (44), 128 (11), 120 (15), 79 (11), 78 (99.5), 77 (27), 65 (13), 58 (11), 57 (24), 56 (24), 55 (15), 53 (13), 52 (96), 51 (25), 50 (21), 43 (55), 42 (12), 41 (21), Anal. Calcd for $C_{19}H_{17}CrNO_7$: C, 53.92; H, 4.05; N, 3.31. Found: C, 53.87; H, 4.07; N, 3.33. Red-brown crystals; mp = 104−107 °C; R_f = 0.31 (1:1:10 ether/methylene chloride/hexane).

General Procedure for the Benzannulation Reaction of Carbene Complexes 29a−e with 3-Hexyn-2-one 20. The carbene complex **29** (150 mg) was placed in a round-bottom flask adapted with a threaded neck and sidearm under argon. Approximately 7 mL of THF was added to give a 0.05 M solution of carbene complex. 3-Hexyne-2-one (1.5 equiv) was added and the flask was sealed with a threaded Teflon stopper. The reaction was degassed by three freeze−pump−thaw cycles, warmed to room temperature, filled with argon, sealed, and placed in a 70 °C oil bath. The reaction was stirred at 70 °C for 24 h, at which time it was checked by TLC to confirm complete reaction. Ferric chloride−DMF[18] (0.36 g) was dissolved in 5 mL of water and added to the reaction mixture. Bubbling occurred upon addition. After stirring for 30 min, the mixture was transferred to a separatory funnel and extracted four times with ether. The ether layer was then washed twice with brine and dried over magnesium sulfate. The solution was filtered through Celite, and the solvent was evaporated leaving a yellow-green oil. Column chromatography with 4:1 hexane/ethyl acetate or 2:1 hexane/ethyl acetate resulted in isolation of the phenol and lactone products. In most cases, the two products were isolated as a mixture and the ratio was determined by ^{1}H NMR. When possible, the products were then separated by running a second column for characterization. Satisfactory elemental analysis could not be obtained for some compounds due to instability.

Phenol 30a: X = CF_3, 40% yield; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3H, J = 7.5 Hz), 1.99 (mult, 2H, J = 5.2 Hz), 2.40 (s, 3H), 2.48 (q, 2H, J = 7.5 Hz), 2.68 (t, 2H, J = 6.5 Hz), 4.01 (t, 2H, J = 5.1 Hz), 4.76 (br s, 1H, O*H*), 6.86 (d, 2H, J = 8.6 Hz), 7.45 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.92, 19.41, 19.97, 21.27, 32.58, 66.05, 112.28, 114.98, 116.88, 123.9 (d, J = 32 Hz, *C*−CF_3), 124.3 (quart, J = 272 Hz, *C*F_3), 126.87 (d, J = 2.5 Hz, *C*−C−CF_3), 130.98, 134.58, 145.86, 149.36, 160.82, 203.46; IR (neat) 3460 m (br), 2970 m, 2938 m, 1697 s, 1615 s, 1596 w, 1513 m, 1477 m, 1439 s, 1358 s, 1327 s, 1267 s, 1228 s, 1171 s, 1126 s, 1108 s, 1066 s, 1048 m, 96 m, 894 w, 839 m 739 w; mass spectrum m/z (rel intensity) 381 (21), 380 M$^+$ (92), 366 (18), 365 (82), 361 (9), 337 (19), 309 (6), 221 (26), 203 (8), 145 (9), 91 (11), 79 (7), 77 (11), 65 (9), 55 (9), 53 (11), 43 (100). R_f = 0.29 (2:1 hexane/ethyl acetate).

Lactone 31a: X = CF_3, 16% yield; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7.5 Hz), 1.62 (s, 3H), 1.79 (mult, 1H), 1.96 (mult,

2H), 2.06 (mult, 2H) 2.16 (mult, 1H), 2.79 (dd, 1H, J = 6.0, 12.1 Hz), 3.90 (td, 1H, J = 3.9, 11.2 Hz), 4.38 (dt, 1H, J = 1.5, 11.0 Hz), 7.04 (d, 2H, J = 8.8 Hz), 7.61 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 13.02, 17.43, 20.54, 22.78, 24.37, 31.56, 45.84, 69.85, 86.79, 115.61, 118.78, 123.76 (quart, J = 232 Hz, CF_3), 124.86 (d, J = 69 Hz, $C-CF_3$), 127.17 (d, J = 4 Hz, $C-C-CF_3$), 153.58, 159.20, 164.26, 173.89; mass spectrum *m/z* (rel intensity) 381 (24), 380 M^+ (100), 361 (11), 353 (15), 352 (72), 337 (19), 324 (10), 323 (23), 310 (11), 309 (33), 219 (16), 191 (43), 149 (17), 91 (11), 55 (11). Waxy solid; R_f = 0.19 (2:1 hexane/ethyl acetate).

Phenol 30b: X = Cl, 38% yield; ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3H, J = 7.5 Hz), 1.99 (mult, 2H), 2.41 (s, 3H), 2.46 (quart, 2H, J = 7.6 Hz), 2.67 (t, 2H, J = 6.5 Hz), 4.04 (t, 2H, J = 5.2 Hz), 4.90 (br s, 1H), 6.77 (d, 2H, J = 8.9 Hz), 7.16 (d, 2H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.91, 19.43, 19.93, 21.29, 32.57, 65.98, 112.28, 116.13, 116.91, 126.53, 129.23, 131.46, 134.57, 145.94, 149.17, 157.06, 203.70; IR (neat) 3460 w (br), 2968 w, 1694 m, 1485 s, 1438 m, 1335 m, 1268 m, 1220 s, 1127 m, 1079 w, 967 w, 828 w; R_f = 0.13 (4:1 hexane/ethyl acetate).

Lactone 31b: X = Cl, 22% yield; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, 3H, J = 7.5 Hz), 1.60 (s, 3H), 1.6−2.2 (m, 6H), 2.74 (dd, 1H, J = 5.7, 11.8 Hz), 3.89 (dt, 1H, J = 4.0, 11.0 Hz), 4.34 (m, 1H, J = 11.0 Hz), 6.89 (d, 2H, J = 8.8 Hz), 7.29 (d, 2H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 13.04, 17.44, 20.55, 22.79, 24.39, 45.84, 69.87, 86.80, 115.62, 188.80, 127.22, 153.56, 159.19, 164.26, 177.70 (2 C not located); IR (neat) 2936 w, 1748 s, 1624 s, 1589 w, 1485 s, 1316 m, 1288 m, 1231 s, 1191 w, 1076 m, 952 m; mass spectrum *m/z* (rel intensity) 348 (15), 347 (10), 346 (42), 320 (11), 318 (32), 289 (11), 275 (11), 219 (13), 191 (63), 149 (18), 111 (11), 91 (12), 91 (12), 81 (12), 77 (12), 55 (17), 53 (13), 43 (100). R_f = 0.09 (4:1 hexane/ethyl acetate).

Phenol 30c: X = H; ^{1}H NMR ($CDCl_3$) δ 1.15 (t, 3H, J = 7.52 Hz), 1.97 (mult, 2H, J = 5.10 Hz), 2.42 (s, 3H), 2.46 (q, 2H, J = 7.50 Hz), 2.5 (t, 2 H), 4.03 (t, 2H, J = 5.10 Hz), 5.07 (br s, 1H), 6.83 (d, 2H, J = 8.36 Hz), 6.95 (t, 1H, J = 7.23 Hz), 7.22 (mult, 2H); ^{13}C NMR ($CDCl_3$) δ 14.95, 19.45, 19.88, 21.31, 32.55, 65.93, 112.35, 114.77, 117.03, 121.62, 129.29, 131.74, 134.57, 146.13, 149.02, 158.40, 204.10; IR (neat) 3455 m (br), 2970 m, 1694 s, 1491 s, 1438 s, 1356 m, 1336 m, 1267 s, 1214 s, 1127 s; mass spectrum *m/z* (rel intensity) 41 (13), 43 (53), 77 (17), 91 (9), 219 (14), 221 (39), 269 (17), 297 (65), 298 (13), 312 (100), 313 (20). Anal. Calcd $C_{19}H_{20}O_4$: C, 73.15; H, 6.45. Found: C, 73.20; H, 7.00. R_f = 0.29 (2:1 hexane/ethyl acetate); 31% yield.

Lactone 31c: X = H; ^{1}H NMR ($CDCl_3$) δ 0.78 (t, 3H, J = 7.50 Hz), 1.62 (s, 3H), 1.6−2.2 (m, 6H), 2.74 (m, 1H), 3.89 (dt, 1H, J = 4.07, 10.68 Hz), 4.38 (mult, 1H), 6.96 (d, 2H, J = 8.12 Hz), 7.06 (t, 1H, J = 7.35 Hz), 7.32 (mult, 2H, J = 8.22 Hz); IR (neat) 2970 w, 1747 s, 1626 s, 1593 w, 1491 m, 1319 w, 1288 m, 1226 m, 1203 w, 1191 w, 1111 w, 1076 m, 1055 w, 1039 w, 952 m. R_f = 0.22 (2:1 hexane/ethyl acetate); 32% yield.

Phenol 30d: X = OCH_3, 27% yield; ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 3H, J = 7.5 Hz), 1.99 (mult, 2H, J = 5.0 Hz), 2.42 (s, 3H), 2.46 (q, 2H, J = 7.5 Hz), 2.68 (t, 2H, J = 6.5 Hz), 3.74 (s, 3H), 4.05 (t, 2H, J = 5.1 Hz), 4.74 (s, 1H, O*H*), 6.74 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 14.96, 19.46, 19.88, 21.33, 32.58, 55.58, 65.95, 112.32, 114.42, 115.49, 116.94, 132.36, 134.66, 146.25, 148.87, 152.61, 154.30, 204.15; IR (neat) 3500 s, 2968 s, 1692 s, 1502 m, 1438 m, 1220 m, 1181 m, 1124 m, 1050 m, 965 m, 892 m, 823 m, 729 m; mass spectrum *m/z* (rel intensity) 344 (4), 343 (21), 342 M^+ (95), 327 (22), 299 (10), 298 (7), 221 (30), 220 (10), 219 (70), 218 (100), 203 (20), 191 (13), 175 (8), 135 (8), 123 (10), 121 (10), 109(9), 108 (8), 91 (11), 79 (7), 77 (16), 65 (8), 43 (48). R_f = 0.23 (2:1 hexane/ethyl acetate).

Lactone 31d: X = OCH_3, 22% yield; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3H, J = 7.5 Hz), 1.60 (s, 3H), 1.67 (mult, 1H), 1.86 (mult, 2H), 1.99 (quart, 2H, J = 7.5 Hz), 2.09 (mult, 1H), 2.72 (quart, 1H, J = 5.7 Hz), 3.77 (s, 3H), 3.86 (dt, 1H, J = 4.0, 11.0 Hz), 4.33 (mult, 1H), 6.85 (d, 2H, J = 6.5 Hz), 6.86 (d, 2H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 13.07, 17.31, 20.68, 22.83, 24.29, 29.62, 45.54, 69.60, 86.77, 114.63, 116.50, 118.34, 127.47, 150.76, 152.04, 155.20, 165.12, 174.15; IR (neat) 2968 w, 2928 w, 2875 w, 1746 s, 1625 m, 1503 s, 1319 w, 1287 w, 1223 m, 1199 w, 1110 w, 1037 w, 951 w; mass spectrum *m/z* (rel intensity) 344 (3), 343 (16), 342 M^+ (73), 327 (4), 314 (28), 313 (14), 285 (7), 243 (9), 219 (16), 192 (12), 191 (87), 190 (8), 175 (8), 149 (22), 147 (8), 135 (30), 124 (42), 123 (11), 121 (13), 109 (8), 93 (11), 92 (10), 91 (16), 81 (18), 79 (8), 77 (21), 67 (8), 65 (11), 55 (19), 53 (16), 43 (100), 41 (19). R_f = 0.18 (2:1 hexane/ethyl acetate).

Phenol 30e: X = NMe_2, 30% yield; ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 3H, J = 7.5 Hz), 1.99 (mult, 2H, J = 5.2 Hz), 2.42 (s, 3H), 2.46 (q, 2H, J = 7.5 Hz), 2.68 (t, 2H, J = 6.6 Hz), 2.85 (s, 6H), 4.06 (t, 2H, J = 5.1 Hz), 4.76 (br s, 1H), 6.67 (d, 2H, J = 9.2 Hz), 6.72 (d, 2H, J = 9.1 Hz); ^{13}C NMR ($CDCl_3$) δ 15.01, 19.51, 19.87, 21.36, 32.62, 41.56, 65.99, 112.12, 114.33, 115.30, 116.68, 132.76, 134.80, 146.16, 146.47, 148.61, 150.82, 203.93; IR (neat) 3452 w (br), 2966 w, 2934 w, 1696 m, 1509 s, 1438 m, 1356 w, 1335 m, 1269 m, 1220 s, 1126 m, 1080 w; R_f = 0.09 (3:1:1 hexane/ether/methylene chloride).

Lactone 31e: X = NMe_2, 31% yield; ^{1}H NMR ($CDCl_3$) δ 0.79 (t, 3H, J = 7.5 Hz), 1.60 (s, 3H), 1.65−2.11 (mult, 6H), 2.71 (dd, 1H, J = 5.7, 11.80 Hz), 2.89 (s, 6H), 3.87 (dt, 1H, J = 4.1, 10.74 Hz), 4.33 (mult, 1H, J = 10.9 Hz), 6.71 (d, 2H, J = 9.0 Hz), 6.84 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.15, 17.36, 20.80, 22.90, 24.33, 41.31, 45.50, 69.57, 86.84, 113.96, 116.41, 118.31, 127.95, 147.00, 148.71, 151.53, 165.50, 174.33; IR (neat) 2936 w, 2932 w, 1745 s, 1624 m, 1510 s, 1319 w, 1287 w, 1227 m, 1110 w, 1075 w, 1056 w, 951 w. R_f = 0.17 (3:1:1 hexane/ether/methylene chloride).

Reaction of Complex 32 with 4-Phenyl-3-butyn-2-one 33. The carbene complex **32**[19] (0.258 g, 0.75 mmol) and alkyne **33** (0.160 mL, 1.13 mmol) in 15 mL of THF were degassed and stirred at 70 °C. When the reaction was complete, chromatography on silcia gel provided tricyclic lactone **34** (130 mg, 0.401 mmol) as a single isomer and an additional fraction (21 mg, ~62% combined) which was greater than 90% **34** by ^{1}H NMR. The contaminant was not identified, but it could conceivably be a second diastereomer of the lactone. The stereochemistry of the lactone was determined by a cyrstal structure, and the details can be found in the Supporting Information. Lactone **34:** mp 183−185 °C; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 3H), 1.14 (qd, 1H, J = 12.5, 3.0 Hz) 1.38 (d, 3H, J = 6.8 Hz), 1.54 (s, 3H), 1.5−1.6 (m, 1H), 1.65−1.85 (m, 4H), 2.50 (sept, 1H, J = 6.8 Hz), 3.40 (s, 3H), 7.31 (t, 1H, J = 7.4 Hz), 7.39 (t, 2H, J = 7.6 Hz), 7.78 (d, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) δ 19.04, 19.69, 21.70, 24.79, 30.38, 32.35, 35.62, 48.48, 59.90, 90.86, 118.86, 128.18, 128.47, 130.31, 147.27, 148.64, 167.70, 173.30; IR (neat) 2994 w, 2957 m, 2930 m, 2870 w, 1745 s, 1630 w, 1587 m, 1447 m, 1371 m, 1275 m, 1217 m, 1163 w, 1125 w, 1077 w, 962 m, 790 m; mass spectrum *m/z* (rel intensity) 324 M^+ (100), 309 (42), 267 (17), 253 (15), 129 (17).

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Supporting Information Available: Crystal structure data for **34** including atomic parameters, anisotropic thermal parameters, bond distances, and bond angles (8 pages). Ordering information is given on any current masthead page.

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