Studies on the Synthesis of Richardianidin-1 via the Tautomer-Arrested Annulation of Fischer Carbene Complexes

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Abstract: A strategy for the synthesis of richardianidin-1 is evaluated which has as its key step the tautomer-arrested annulation of chromium–carbene complexes. Both inter- and intramolecular variations of the strategy are examined. The intramolecular reaction involves the tethering of the alkyne to the oxygen stabilizing substituent of the carbene carbon. The outcome of the intramolecular tautomer-arrested annulation was found to be highly dependent on the nature of the tether and the on the type of substituent on the alkyne. The product distribution from these reactions included the desired hydrindenone resulting from tautomer-arrested annulation, a naphthalenedione, and a spirocyclohexadienone. The latter two products result from CO insertion prior to cyclization. The optimal tether length for the tautomer-arrested product is four atoms between the alkyne and the carbene carbon. The yields for the intramolecular reaction dropped significantly for a substituent on the alkyne terminus that was larger than a methyl group and this was not suitable for a synthesis of richardianidin-1. Initial studies on the intermolecular tautomer-arrested annulation focused on the regioselectivity of alkyne incorporation. The reaction with isopropyl(methyl)acetylene gives a single regioisomer and reveals that the tautomer-arrested annulation is more regioselective than the normal benzannulation. Furthermore, the intermolecular reaction is more tolerant of larger substituents on the terminus of the alkyne. As a result of the studies on the intermolecular tautomer-arrested annulation a suitable alkyne was found that introduces all of the carbons present in the six-membered lactone of richardianidin-1.

Key words: richardianidin-1, chromium–carbene complexes, annulation, carbon monoxide insertion, cyclization

The rather rare 6,7-seco-6,11-cyclolabdane skeleton is present in richardianidin-1 (**1**) and richardianidin-2 (**2**), which were isolated from the leaves of a toxic plant that grows in the mountainous regions of western and southern Saudi Arabia.[1] This plant, *Cluytia richardiana L.*, is one of several species of *Cluytia* which are widely used in folk medicine. Several other related labdane-type diterpenes have been isolated from this plant and, of these, richardianidin-1 (**1**) and richardianidin-2 (**2**), along with saudin, have the highest hypoglycemic activity both in vitro and in vivo and support the historical use of this plant.[2] A synthetic study on route to the richardianidins has been published in which the strategy was demonstrated in the construction of the BCD ring system in **3** as shown in Figure 1.[3] We report here our strategy for the synthesis of richardianidins and the initial evaluation of the strategy,

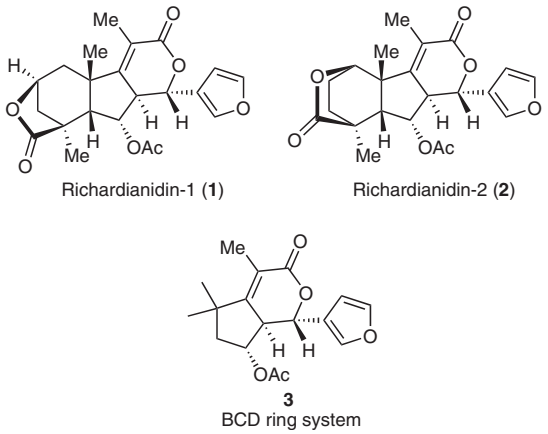

Figure 1

which focuses on a unique organometallic approach to the AB ring system.

The retrosynthetic analysis of richardianidin-1 (**1**) is shown in Scheme 1. The butyrolactone ring is unmasked as the homoallylic alcohol **4** which in turn is envisioned to arise from a 2,3-Wittig rearrangement from the stannylmethyl ether **5**.[4] The stannyl ether **5** in turn should be accessible from the stereoselective reduction and alkylation of the hydrindenone **6**, the key intermediate in our strategy. The assembly of hydrindenone **6** is envisioned to proceed from the extension of an untested synthetic methodology, the tautomer-arrested annulation that has previously been developed in our laboratories.[5] This reaction involves the formation of hydrindenones from the reaction of alkynes with 2,6-disubstituted 4-hydroxyphenylcarbene complexes of the type **9**. The implementation of this method could potentially be realized in either an intermolecular or intramolecular venue. A first-order analysis of the retrosynthesis would lead to the conclusion that the intramolecular version is the more attractive since only a single regioisomer of the hydrindenone would be possible. The intermolecular approach has the potential of producing either the desired regioisomer **6** or the undesired regioisomer **10**. We present here an evaluation of both intermolecular and intramolecular approaches of the tautomer-arrested annulation to the synthesis of richardianidin-1 (**1**) within the context of the strategy presented in Scheme 1.

The reaction of Fischer carbene complexes with alkynes is one of the most useful methods for the synthesis of substituted phenols.[6] This is illustrated in the reaction of the 2-methoxyphenylcarbene complex **11** with alkyl-substi-

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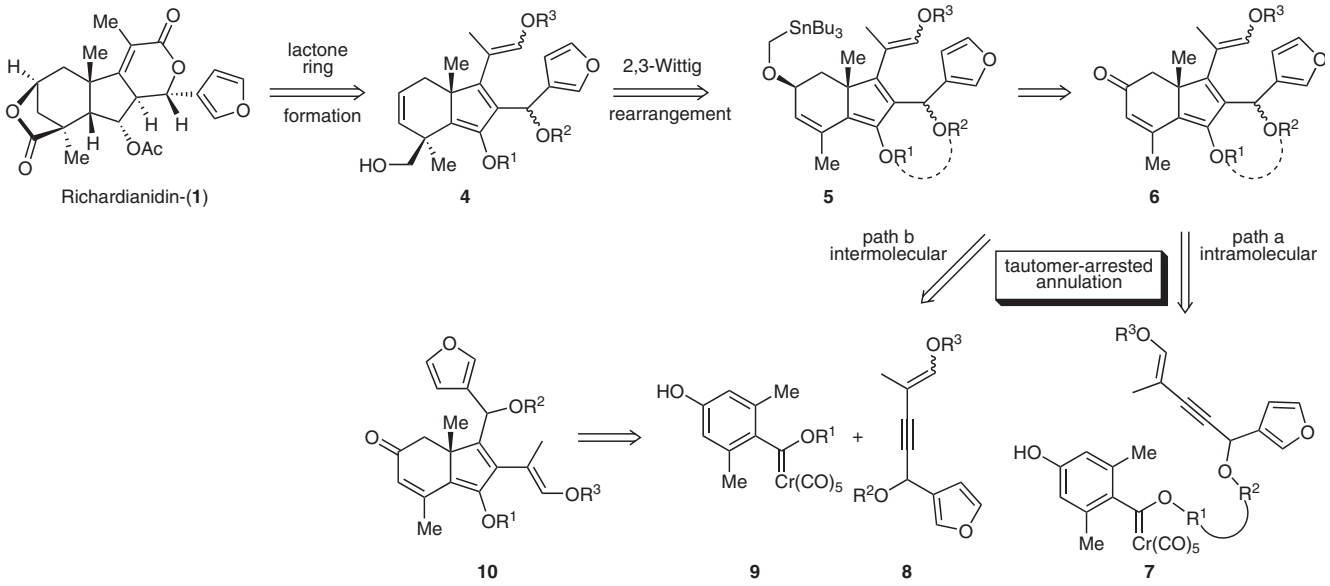


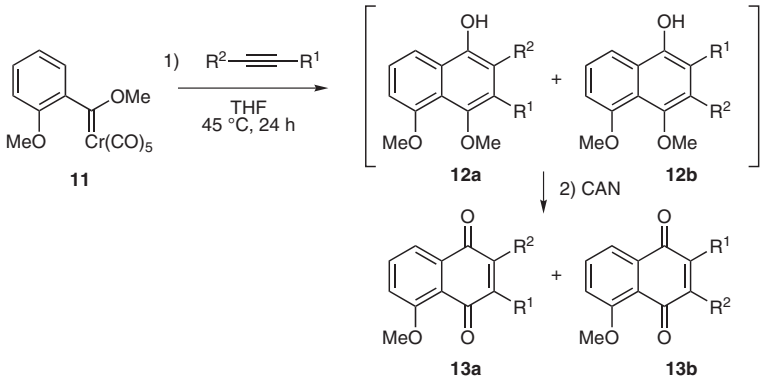
Scheme 1

tuted acetylenes (Scheme 2, Table 1).[7] The primary products of this benzannulation are 4-methoxynaphthols and in the case of unsymmetrical acetylenes the two possible regioisomeric products are the naphthols **12a** and **12b**. For ease of determining the regioselectivity, the naphthols **12a** and **12b** were converted into the corresponding quinones **13a** and **13b**. The regioselectivity is largely controlled by the steric bulk of the two different acetylene substituents with the larger substituent becoming incorporated into the position adjacent to the phenol function.[7,8] Internal alkynes generally give mixtures of the two regioisomers, whereas, terminal alkynes generally give greater than 100:1 selectivity. The reaction of Fischer carbene complexes of chromium with alkynes generally gives the benzannulated products, but one of the more common of the many side products are indenes, which are mechanistically related to the phenol products but differ in that the final CO insertion does not occur. This is illustrated in the reaction of complex **11** with hex-3-yne, which gives, after oxidative workup, mixtures of the quinone **14** and the five-membered annulated products **15** and **16**.[9] The ratio of six- to five-membered annulated products is dependent on a variety of factors including concentration, temperature, and the nature of the solvent as illustrated by the data in Equation 1 and Table 2. In general, the six-membered ring product is favored by high concentration, nonpolar solvents, and lower reaction temperatures.

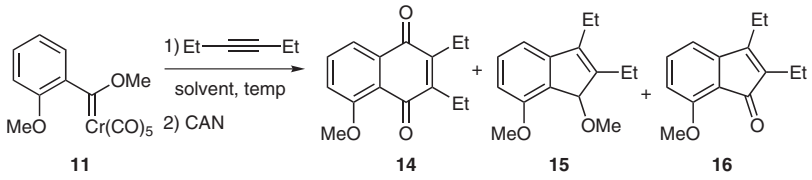
Table 1 Reaction **of 11** with Alkyl-Substituted Acetylenes

R^1	R^2	Yield (%)	Ratio **13a/13b**
Me	Pr	64	2.9:1.0
H	Pr	74	>111:1
Me	*i*-Pr	61	4.8:1.0

The five-membered ring annulated product is the generally the only product of the reaction of alkynes with 2,6-disubstituted phenylcarbene complexes.[10] As an example, the reaction of the 2,6-dimethylphenyl complex **17** with hex-3-yne gives the indenes **18a** and **18b** as a mixture of metal-coordinated and metal-free forms (Equation 2). Note that the tautomer-arrested annulation requires a



Scheme 2



Equation 1

Table 2 Effect of Various Conditions on the Ratio of **15** to **16**

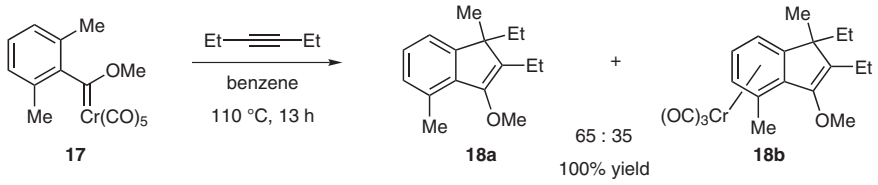
Solvent	Temp (°C)	Concn (M)	Yield (%)		Ratio **15/16**
			14	**15** + **16**	
THF	110	0.005	trace	75	87:13
benzene	110	0.005	<1	71	4:96
benzene	110	0.5	29	43	14:86
benzene	45	0.5	77	7	29:71
THF	45	0.5	61	23	78:22

much higher temperature than the normal benzannulation (Equation 1, Table 2) and possible reasons for this will be presented in the conclusion to this work. The formation of the aromatic ring in the indene product results from a 1,5-sigmatropic rearrangement of a methyl group from an intermediate of the type **21** which in turn results from the cyclization of the carbene-complexed intermediate **20** that results from insertion of the alkyne into the metal–carbene double bond in carbene complex **19** (Scheme 3). We reasoned that if the carbene complex had a hydroxy group in the *para*-position as in complex **19**, then it might be possible to intercept the 1,5-shift of the methyl group by a tautomerization of intermediate **21** to give the hydrinden-5-one **22** rather than the inden-6-ol **23**. This, in fact, proved to be possible and the degree to which this was successful was dependent on the nature of the alkyne substituents. The reaction of complex **19** with diphenylacetylene gave a 1:1 mixture of **22** and **23** and hex-3-yne gave exclusively the hydrindenone product **22** in 75% yield (Table 3).[5] The corresponding *tert*-butyldimethylsilyl-protected complex **24** has no recourse but to give the indene product **25** and this was isolated in 64% yield. It was thus the success of this tautomer-arrested annulation that led to the consideration of the retrosynthetic analysis for richardianidin-1 presented in Scheme 1.

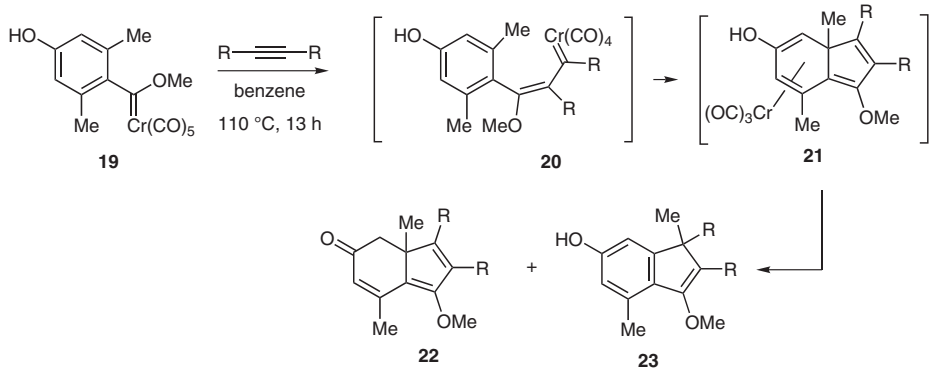
Table 3 Reaction of Complex 19 with Acetylenes

R	Yield (%) **22** + **23**	Ratio **22/23**
Ph	88	49:51
Et	75	100:0

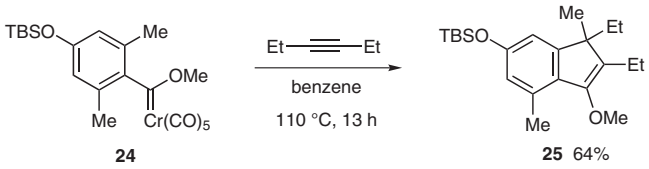
For the reasons discussed above and summarized in Scheme 1, the strategy involving the intramolecular tautomer-arrested annulation was experimental broached first since it would not be complicated by the possibility



Equation 2



Scheme 3



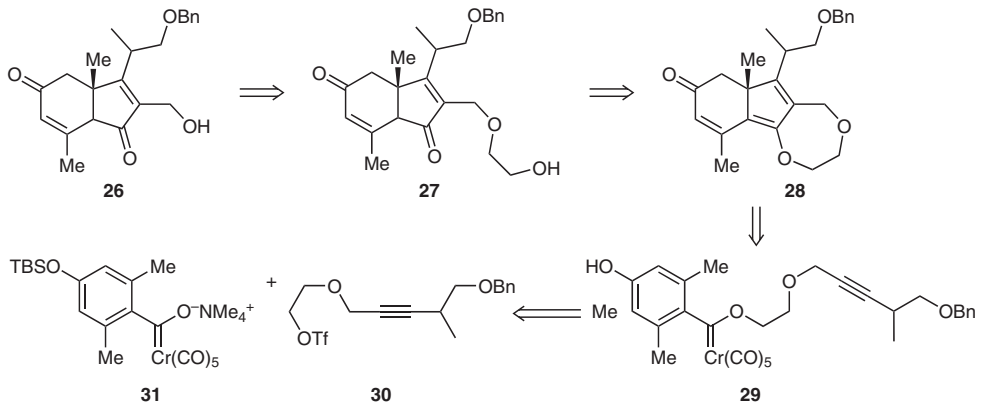
24 25 64%

Equation 3

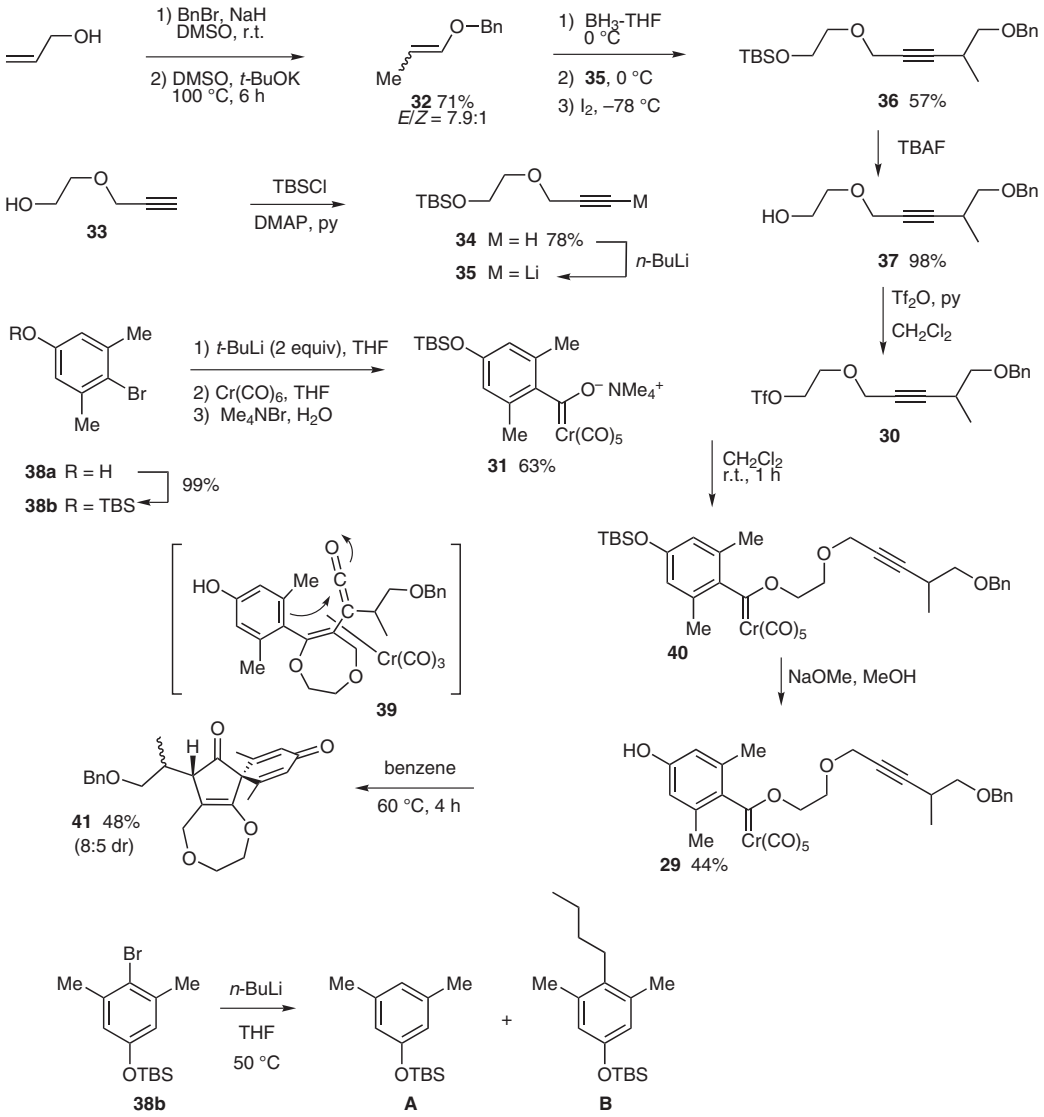
of the formation of regioisomers. In addition, rather than initially undertaking the likely time-consuming development of a synthesis of the highly functionalized carbene complex **7** (Scheme 1), the synthesis of the much simpler analogue **29** was targeted (Scheme 4). This particular complex with a 2-alkoxyethyl tether was chosen since Semmelhack had previously demonstrated that an ethylenedioxy tether can be successfully employed as a removable tether in the intramolecular benzannulation of Fischer carbene complexes with alkynes in the total synthesis of deoxyfrenolicin.[11] The tether will be introduced via alkylation of the ammonium acylate **31** with the triflate **30**. The alkyne portion of this triflate will contain all five carbons of the lactone ring in richardianidin-1 but not the furyl substituent. The intramolecular tautomer-arrested annulation of complex **29** would be expected to produce the hydrindenone **28** from which the tether can be liberated by hydrolysis of the enol ether to give **27** and then subsequent cleavage of the 2-hydroxyethyl ether to give **26**.

The preparation and intramolecular annulation of complex **29** is outlined in Scheme 5. The key step in the synthesis of the alkyne tether involves the iodine-induced coupling of a secondary alkyl group and an alkyne mediated by an in situ generated borate to generate the alkyne **36**.[12] This coupling is set up by the hydroboration of the enol ether **32**, subsequent addition of the lithium acetylide **35** and then addition of iodine. The lithium acetylide **35** in turn is generated from the 2-hydroxyethyl propargyl ether **33**, which was prepared according to the procedure of Semmelhack for closely related compounds.[11c] The coupling of the alkyne fragment to the carbene complex was affected by conversion of the alcohol **37** into the triflate **30** and then without purification, using it to alkylate the tetramethylammonium acylate **31**. This produced a red solution of the carbene complex **40** which was not purified but rather directly desilylated with sodium methoxide in methanol to give the 4-hydroxy-2,6-dimethylphenylcarbene complex **29** in 44% yield in three steps from **37**. The thermolysis of carbene complex **29** did not produce the expected hydrindenone **28**, but rather, the spirocyclic diketone **41**. This type of product has been seen before in the intermolecular tautomer-arrested annulation.[5] The normal tautomer-arrested product **22** (Scheme 3) is replaced by a diketone of the type **41** if the reaction solvent is acetonitrile instead of benzene. The formation of **41** in the present work represents the first time that this product has been seen in a reaction carried out in benzene. The formation of this product is thought to result from a spirocyclization of the vinylketene intermediate **39** onto the *para*-position of a phenol. The vinylketene complex **39** presumably results from a CO insertion in a vinylcarbene-complexed intermediate similar to **20** in Scheme 3.

The failure of the intramolecular cyclization of the carbene complex **29** to give a hydrindenone product prompted a more fundamental examination of the intramolecular tautomer-arrested annulation. The series of carbene complexes **42a–c** have identically functionalized alkyne tethers and differ only by the number of methylene units separating the alkyne and the carbene complex. Thus, they were designed to probe the effect of the size of the newly formed oxacyclic ring on the yield of the tautomer-arrested product as well as on the entire product distribution. These complexes were prepared in 56–86% yields utilizing a procedure similar to that developed for the complex **29** (Scheme 5) and involves the alkylation of the metal acylate **31** with an alkynyl triflate derived from the appropriate alkynol. The results of the thermolysis of complexes **42a–c** are presented in Scheme 6 and clearly show that the hydrindenone product is favored when a six-membered oxacyclic product is formed giving a 64% yield of **43b** upon thermolysis at 60 °C in benzene at 0.005 M. With the exception of a tentatively identified trace product from the thermolysis of complex **42b**, none of the reactions in Scheme 6 gave a spirocyclic diketone product



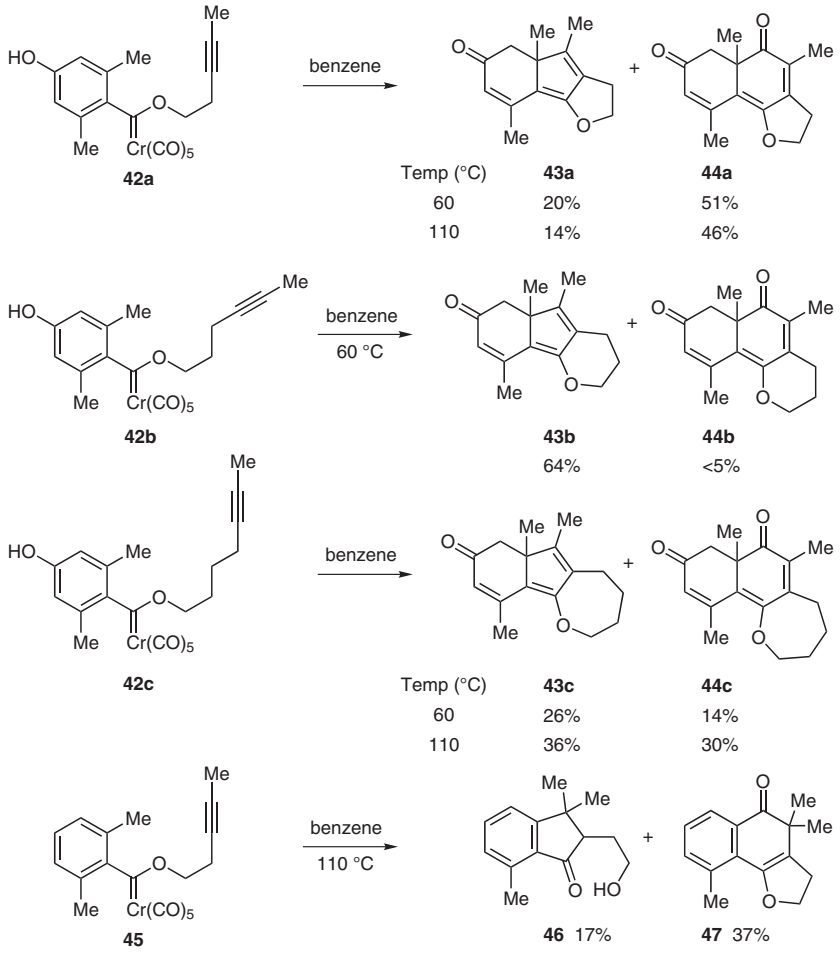
Scheme 4



Scheme 5

similar to that seen in the thermolysis of complex **29** (Scheme 5). In contrast, these reactions produced the cyclohexadienone-annulated products **44** either as a side product or, in some cases, as the major product of the reaction. These products presumably arose from the cyclization of a vinylketene-complexed intermediate of the type **39** (Scheme 5) where closure occurs ipso to the methyl group. There is not a great temperature effect on the product distribution for **42a** but for **42c**, an increase in mass balance was observed at higher temperature along with a slight shift towards the CO inserted product **44c**. Finally, as a control, the cyclization of the complex **45** gives a similar product distribution as that of the complex **42a** indicating that the presence of the *para*-hydroxy group on the phenyl ring of the carbene complex does not greatly affect the outcome.

In an effort to properly calibrate the effect of a 2-(propargyloxy)ethoxy tether in the carbene complex, the complex **48** was prepared and its thermolysis investigated. This reaction produced the three products **49**–**51** in proportions that were somewhat dependent on the temperature, concentration, and the mode of addition. The results show that the total mass balance and the proportion of the hydrindenone product **49** increase with lower concentration. In addition, the proportion of the hydrindenone product increases at higher temperature. However, the addition of the carbene complex **48** slowly via syringe pump does not result in a significant change compared to the addition of the carbene complex all at once to a 0.005 M solution. As a point of comparison, all of the reactions in Scheme 6 were performed at 0.005 M and thus the cyclization of **48** gives roughly the same yields of the hydrindenone and cyclohexadienone products as its methylene analogue **42c** in Scheme 6. Thus, the presence of the 'extra' oxygen in the tether of complex **48** does not seem to have a detrimental effect on the yield of the tautomer-arrested product. Small amounts of the spirocyclic product **51** are observed in the cyclizations of **48**, but no spirocyclic product could be detected in the crude ^{1}H NMR spectrum of the thermolysis

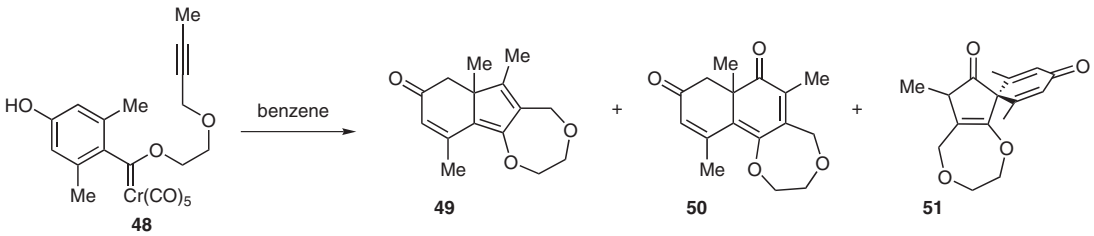


Scheme 6

of complex **42c** (Scheme 6). The results of these studies (Schemes 6 and 7, Table 4) clearly show optimal hydrindenone formation is to be expected when a six-membered oxacycle is formed in the tautomer-arrested reaction.

In considering a redesign of the removal tether, the acetal carbene complex **55f** provides a very attractive second generation target. The complex should be preparable via the direct alkylation with the chloromethyl ether **56f**, its cyclization produces the six-membered oxygen heterocycle in **53f**, and subsequent to hydrindenone formation, the linker for the tethered alkyne could be liberated in a single step (Scheme 8). Hydrolysis of the enol ether in **53f** would leave a hemiacetal that would further hydrolyze to the oxo alcohol **52f**, which in turn could serve as an attractive advanced intermediate in the synthesis of richardianidin-1. Fischer carbene complexes that have the oxygen heteroatom stabilizing substituent incorporated into a methoxymethyl ether (MOM) group are known[13] and do not differ significantly in stability from simple alkoxy-stabilized complexes and can be handled without special precautions and can be chromatographically purified on silica gel. However, alkynes that are tethered through the oxygen-stabilizing substituent via an acetal linkage have not been previously reported.

The preparation of the acetal tethered carbene complexes **54** required access to the chloromethyl propargyl ethers **56**. As indicated in Scheme 9 and Table 5, these were synthesized from the analogous propargyl alcohol and chlo-

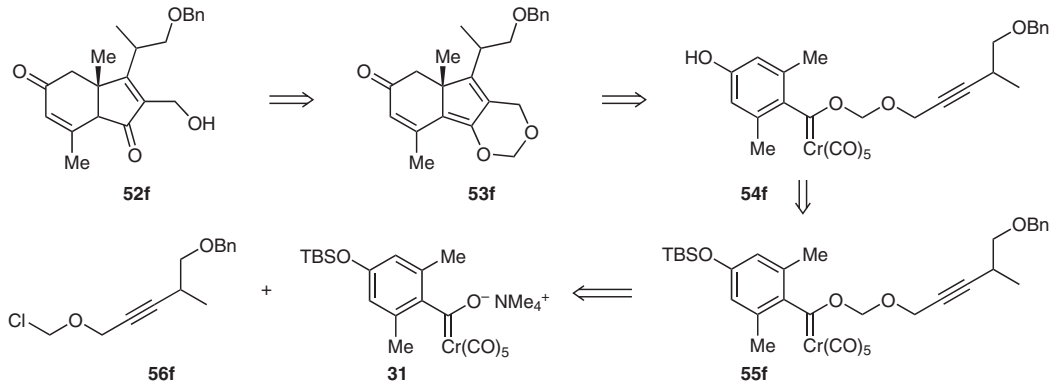


Scheme 7

Table 4 Hydrindenone Formation

Concn (M)	Temp (°C)	Yield (%)			Ratio **49**/(**50** + **51**)	Total Yield (%)
		49	**50**	**51**		
0.05	60	15	5	21	0.58	41
0.05	110	20	8	13	0.95	41
0.005	60	27	15	16	0.87	58
0.005	110	38	18	6	1.58	62
spa[a]	80	35	15	12	1.30	61
spa[b]	110	39	19	4	1.70	62

[a] Syringe pump addition of **48** (0.27 mmol) in benzene (20 mL) to refluxing benzene (25 mL) over 4 h.
[b] Syringe pump addition of **48** (0.38 mmol) in toluene (10 mL) to refluxing toluene (50 mL) over 1.25 h.



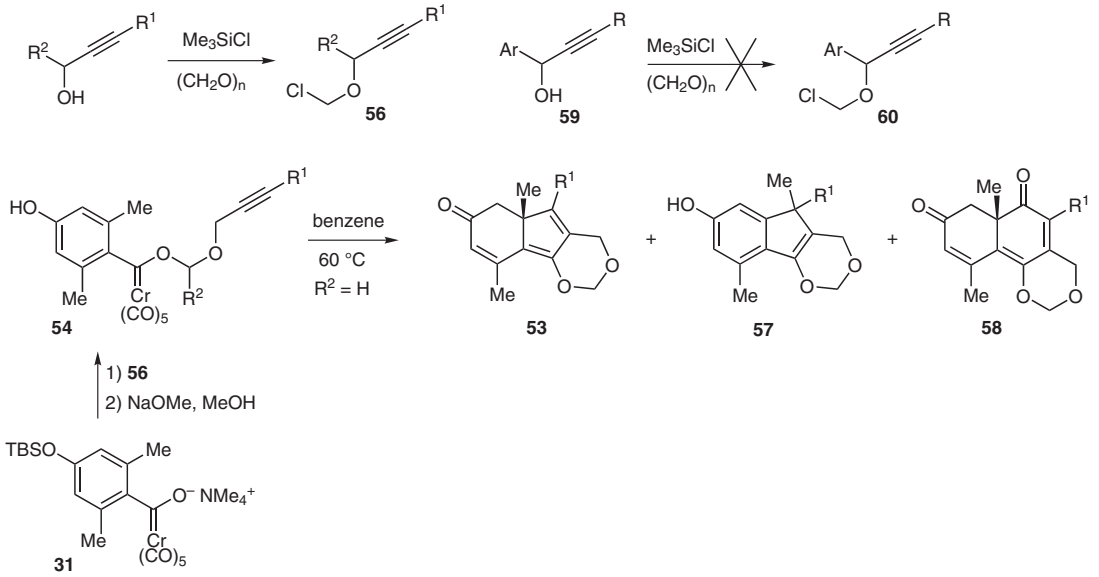
Scheme 8

rotrimethylsilane and paraformaldehyde according to the procedure reported by Shipov, Savostyanova, and Baukov.[14] The chloromethyl ethers **56** were not purified, but directly reacted with a slight deficiency of the ammonium acylate salt **31** to give 68–98% yields of the carbene complex **55** which is the *tert*-butyldimethylsilyl-protected form of **54**. The deprotection of complex **55** to give **54** was accomplished with sodium methoxide in methanol in 37–54% yield. No attempt was made to optimize this deprotection by screening other nucleophiles. It was pleasing to find that the thermolysis of complex **54a** (R^1 = Me, R^2 = H) gave the hydrindenone **53** in 51% yield, consistent with the finding that the carbene complex **42b** (Scheme 6), which gives a six-membered oxygen heterocycle in the intramolecular tautomer-arrested annulation, gave the highest yield of hydrindenone product of all the complexes in Scheme 6. However, it was quickly found that the outcome of the reaction was very sensitive to the nature of the substituent on the alkyne in complex **54**. When the substituent R^1 is changed from methyl to ethyl, the yield of **53** drops to 9% and when it is isopropyl, the only product that could be identified from the crude reaction mixture was the cyclohexadienone **58** in 16% yield.

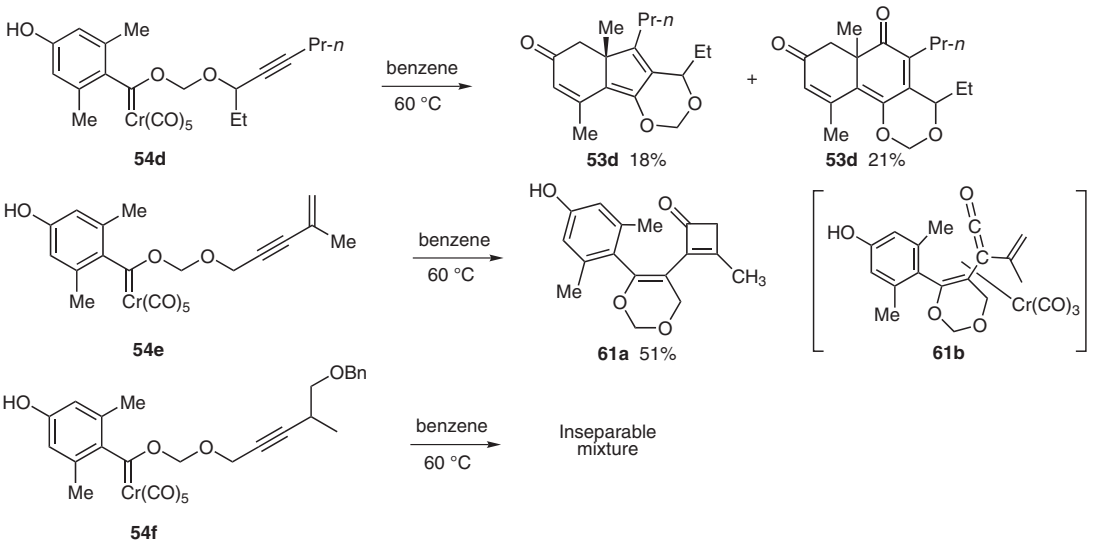
The reaction of the α-substituted propargyl ether tethered complex **54d** also resulted in a disappointingly low yield of the hydrindenone product **53d** (Scheme 10). The product distribution for thermolysis of this complex is similar to that seen for the complex **54b** in Scheme 9, indicating that the α-propargyl substituent does not have a large impact on the reaction. The reaction manifold for the thermolysis of complex **54e** is diverted from any of the products seen to this point, and instead, this reaction produced a 58% yield of the cyclobutenone **61a**. This outcome can most rationally be ascribed to an electrocyclic ring closure of the vinylketene complexed intermediate **61b**. The failure to be able to incorporate a vinyl group on the acetylene will necessitate a slight revamping to the retrosynthesis outlined in Scheme 1. To this end, the complex **54f** was prepared and its thermolysis was carried out, however, a complicate mixture of compounds was produced which resisted attempts at their separation and further analysis was discontinued.

Table 5 Yield of Compounds 53, 57, and 58

53, **57**, **58**	R^1	Yield (%)		
		53	**57**	**58**
a	Me	51	trace	
b	Et	9		25
c	*i*-Pr			16

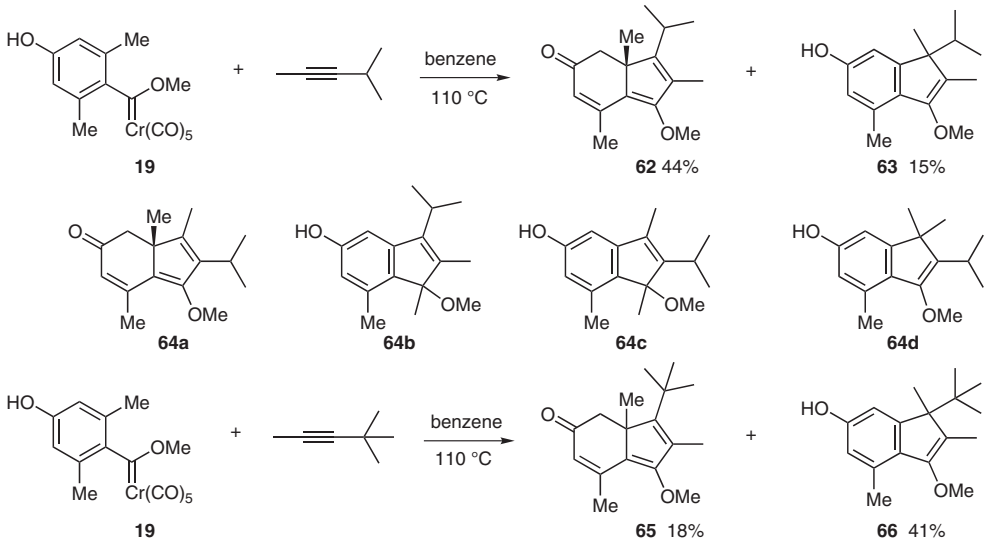


Scheme 9



Scheme 10

Given the less than encouraging results from the above studies aimed at probing the efficacy of an approach to the synthesis of richardianidin-1 featuring an intramolecular tautomer-arrested annulation as the key step, the alternative intermolecular variation outlined in Scheme 1 was next considered. The regioselectivity of the tautomer-arrested annulation has not been extensively investigated,[5] and thus, we initially set out to determine the degree of the regioselectivity for an alkyne where the determinant is the simple steric difference between and isopropyl group and a methyl group.[7,8] Note that for the benzannulation reaction outlined in Scheme 2, the regioselectivity with isopropyl(methyl)acetylene was found to be 4.8:1 in favor of the phenol **12a** over **12b**. The reaction of complex **19** with the same alkyne gave a 3:1 mixture of isomers, however, after careful analysis, it was determined that these two isomeric products were not the result of a different regioselectivity of alkyne incorporation (Scheme 11). The products were assigned as hydrindenone **62** and the indene **63** which have both incorporated the alkyne with the same regiochemistry. In some runs, there was a trace of a third compound, which was also found to be isomeric with **62** and **63**. This compound was isolated with **62** and was obtained in a 14:1 ratio. The ^{1}H and ^{13}C NMR spectrum of an enriched sample of this minor component allowed the structures **64a** to **64d** to be ruled out as possibilities. The spectral data was consistent with a product that did not result from cyclization onto the aryl ring. It is not clear why the tautomer-arrested reaction of complex **19** occurs with much higher regioselectivity than the reaction of complex **11** with the same acetylene (Scheme 2), but the result is clearly important in terms of providing a regioselective route to richardianidin-1 via an intermolecular tautomer-arrested annulation as outlined in Scheme 1. Based on this

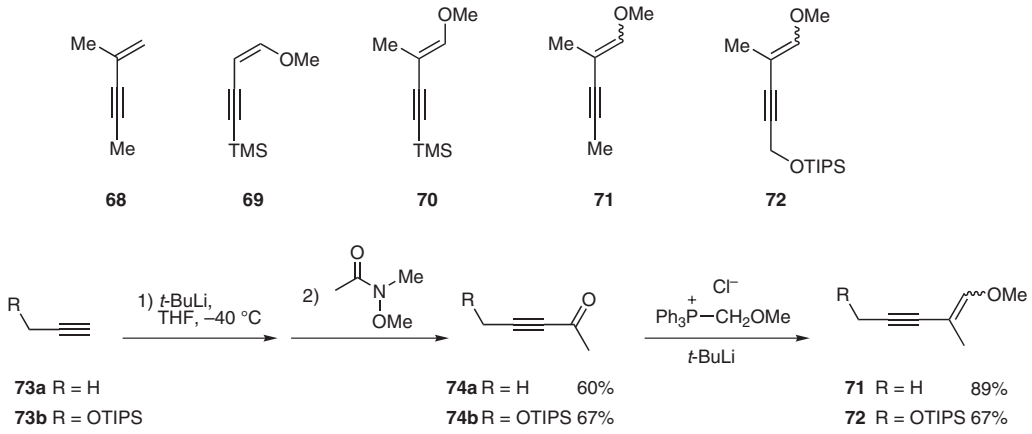


Scheme 11

result, it would thus be expected that the reaction of complex **19** with *tert*-butyl(methyl)acetylene would also be highly regioselective and this in fact found to be the case although the reaction gave a smaller proportion of the tautomer-arrested product **65** relative to the methyl-migrated product **66**.

The finding that isopropyl(methyl)acetylene gave a single regioisomer of the tautomer-arrested product with carbene complex **19**, then prompted an examination of the set of enynes in Scheme 12 each of which has all five of the carbons present in the lactone ring of richardianidin-1. The enyne **68** is commercially available and enyne **69** is prepared by the silylation of the commercially available (*Z*)-1-methoxybut-1-en-3-yne.[15] The enyne **70** is made by the methylation of **69** in a procedure that is a slight modification of that originally reported by Zweifel.[15] In a quite unexpected process, the treatment of **69** with *n*-butyllithium in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine results in metalation on the propargylic carbon which is β to the oxygen and then the resulting vinyllithium undergoes isomerization about the double bond to form a chelated vinyllithium that upon reaction with methyl iodide gives the enyne **70** as a single diastereomer in 49% yield after distillation. The enynes **71** and **72** were made in a two-step process that is outlined in Scheme 12. The terminal acetylenes **73** were converted into the pentynones **74** by reaction of the corresponding lithium acetylide with the Weinreb amide of acetic acid. Subsequent Wittig reaction with (methoxymethylene)phosphorane gave the enynes **71** and **72** in good yields and as a nearly equal mixture of isomers in each case.

The reaction of the commercially available enyne **68** with carbene complex **19** produced a very complicated reaction mixture of a number of products and it was suspected that among them were oligomers or polymers of the enyne. Based on the outcome of the intramolecular reaction of complex **54e** (Scheme 10), a cyclobutenone product of the type **61a** may also be among the many products produced in the reaction of enyne **68** with complex **19**. The reaction of the enyne (*Z*)-**69** is a much cleaner reaction with the major silica gel mobile component identified as the desired tautomer-arrested product **75** which was isolated in

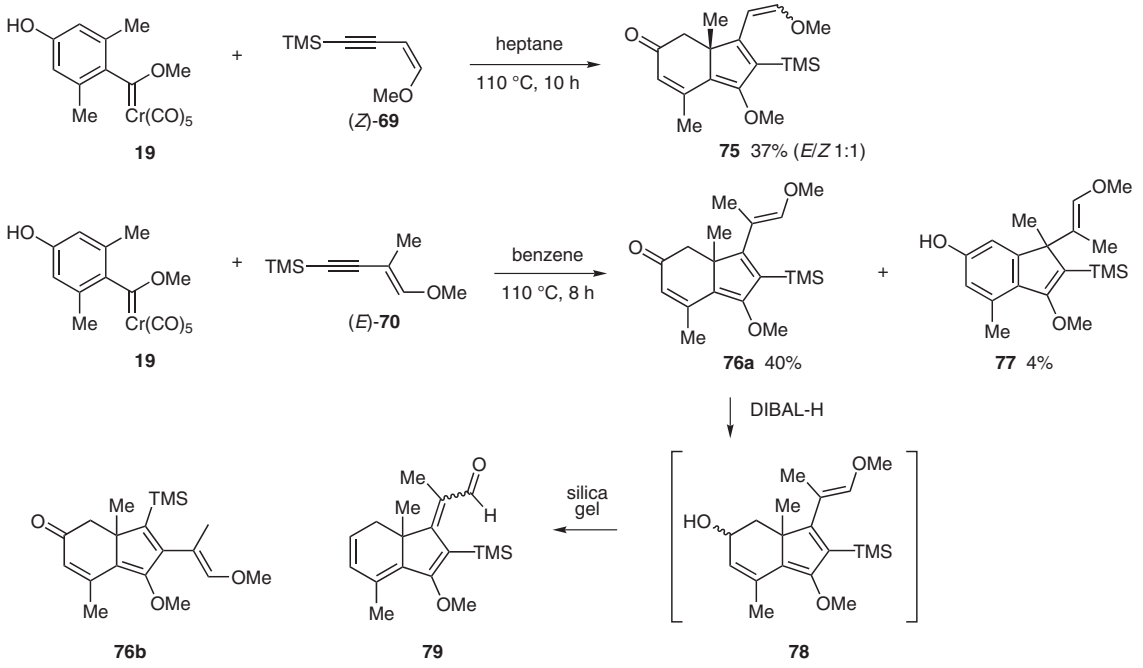


Scheme 12

37% yield as a 1:1 mixture of *E*- and *Z*-isomers (Scheme 13). The hydrindenone **75** was isolated as a single regioisomer, which is a little surprising given the steric differential between the two substituents of the alkyne. However, it is likely in this case that the enol ether is electronically affecting the regioselectivity. Although sterics are usually the predominant factor in controlling the regiochemistry of alkyne incorporation, it has been observed that electron-withdrawing groups will prefer to be incorporated α to the methoxy group and electron-donating groups will prefer to incorporated β to the methoxy group.[16] The reaction of enyne (*E*)-**70** also gave a single regioisomer **76a** in 40% yield along with a small amount of the aromatized product **77**. An assignment of the regiochemistry of these reactions was made possible when **76a** was reduced with diisobutylaluminum hydride to give a 4:1 mixture of isomers of **78** in 72–80% yield. This alcohol was not stable to silica gel or magnesium sulfate and underwent ready hydrolysis to give the bright yellow aldehyde **79**. The regioisomeric hydrindenone **76b** cannot undergo hydrolysis to give this unsaturated aldehyde. This regiochemical assignment of **76a** was confirmed by an X-ray diffraction analysis.

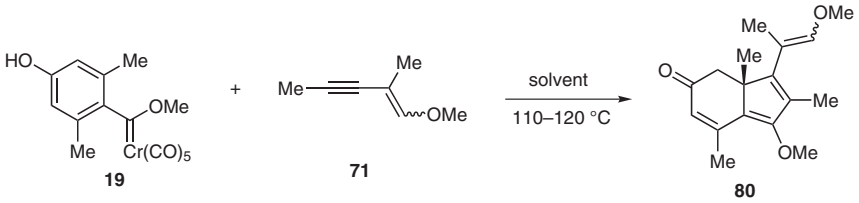
The fact that the enynes (*Z*)-**69** and (*E*)-**70** did not give any of the cyclobutenone product of the type **61a** (Scheme 10) and that they both give a single regioisomer of the tautomer-arrested products **75** and **76a** was quite encouraging for a continued investigation of the intermolecular strategy for the synthesis of richardianidin-1 outlined in Scheme 1. The next phase of the study involved the optimization of the tautomer-arrested reaction of carbene complex **19** with the enyne **71** was utilized as a 1:1 mixture of isomers (Table 6). The isomers of **71** could be separated with some care and were reacted individually. The reaction of the pure *E*-isomer of **71** in benzene gives the product **80** with a 96:4 mixture of *E*- to *Z*-isomers. Increased amounts of the *Z*-isomer was found in other solvents. The reaction of (*Z*)-**71** gives predominantly (*Z*)-**80** in similar yields. The optimal conditions for this reaction are those in Table 6, entry 3 which involves reaction in benzene at 0.05 M in **19** at 110–120 °C. The yield of **80** was similar in toluene, but dropped significantly in heptane and in polar solvents such as tetrahydrofuran and acetonitrile. Syringe pump addition of **71** over two hours did not improve the yield of the reaction (entries 9 and 10) neither did raising the temperature to 145 °C (entries 3 and 8). The maximum yield of hydrindenone **80** under the optimum conditions for the reaction of carbene complex **19** and enyne **71** was 60% (entry 3).

In an effort to further optimize the tautomer arrested annulation with the enyne **71** the (dimethylamino)carbene complex **83** was synthesized. It is well known that aminocarbene complex have a much higher tendency to give non-CO inserted products in the normal benzannulation, but this has yet to be tested in the tautomer-arrested annulation.[17] It was curious to find that there was no reaction between the carbene complex **24** and dimethylamine; most aryl complexes will react within minutes at room temperature. The lack of reactivity of **24** is presumably due to the steric hindrance presented by the 2,6-dimethyl-substituted arene ring. The only way complex **82** could be prepared was to first react complex **24** with ammonia to give the primary amino complex **81** in 88% yield and then to exhaustively methylate with methyl iodide under phase transfer catalysis to give the desired dimethylamino complex **82** in 75% yield (Scheme 14). Finally, the *para*-hydroxy group is liberated by treatment of **82** with hydrogen fluoride–pyridine to give **83** in 50% yield.



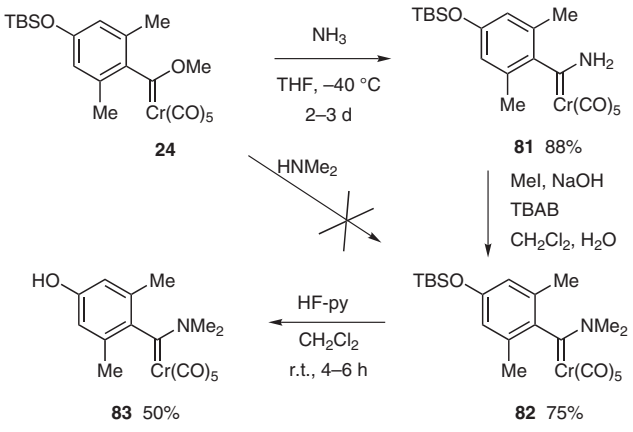
Scheme 13

Table 6 Optimization of the Reaction of Carbene Complex **19** with Alkyne **71**[a]



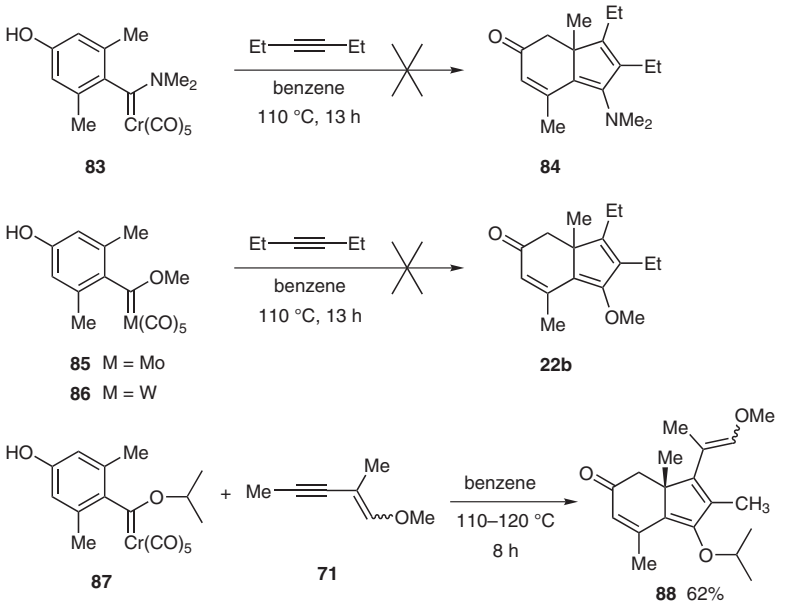
Entry	Solvent	Concn (M)	Time (h)	Yield (%) of **80**	Recovery (%) of **19**
1	benzene	0.5	8	47	–
2	benzene	0.1	8	52	–
3	benzene	0.05	8	60	–
4	benzene	0.01	8	30	28
5	benzene	0.005	8	30	43
6	benzene	0.05	2	41	20
7	benzene	0.05	4	43	12
8	benzene	0.05	4	55[b]	7
9	toluene	0.05	8	51	<5
10	toluene	0.05	8	50[c]	–
11	heptane	0.05	8	28	15
12	$Cl(CH_2)_2Cl$	0.05	8	30	17
13	DME	0.05	8	22	10
14	THF	0.05	8	<20	–
15	MeCN	0.05	8	–	–

[a] Reactions with **71** (2 equiv).
[b] Reaction at 145 °C.
[c] Syringe addition of **71** over 2 h.



Scheme 14

The reaction of the amino complex **83** with hex-3-yne failed to give any of the hydrindenone product **84** Scheme 15). Most of the carbene complex was recovered after reaction in tetrahydrofuran at 110 °C. Aminocarbene complexes are usually less reactive than their methoxy analogues and thus the reaction of amino complex **83** with diphenylacetylene was investigated in diglyme (not shown). Reaction with diphenylacetylene at 140 °C for 10 hours gave no detectable products and the recovery of the carbene complex and raising the temperature to 180 °C for a few hours resulted in >90% conversion of the carbene complex, however, no silica gel mobile products were formed. The benzannulations of aryl tungsten and aryl molybdenum carbene complexes are also known to give fewer CO insertion products than their chromium counterparts.[18] The tautomer-arrested annulation has not been previously examined with tungsten or molybdenum complexes. Complex **85** and **86** were prepared in a manner similar to its chromium analogue **19**. When the reactions of the complexes **85** and **86** with hex-3-yne was carried out in benzene at 110 °C no evidence for the formation of **22b** could be obtained. The carbene complexes were largely consumed in each case but, as was the case with the amino complex **83**, there were no products produced that were mobile on silica gel. Finally, isopropoxy-

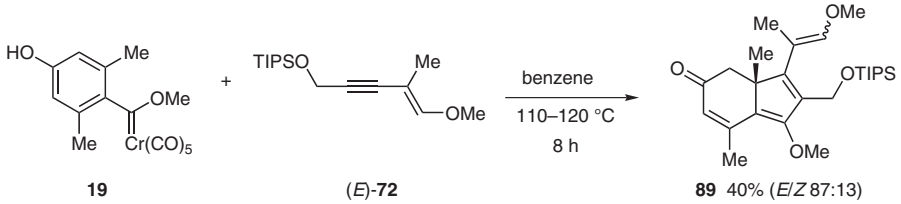


Scheme 15

carbene complexes have been shown in some instances to give higher yields than methoxy complexes in the benzannulation reaction.[19] Therefore, the isopropoxy complex **87** was prepared and its reaction with enyne **71** was carried out under the optimized conditions developed for the methoxy analogue **19** (Table 6). The hydrindenone **88** was isolated in 62% yield, which is not significantly greater than the methoxy complex **19**.

Finally, the reaction of the enyne **72** was investigated. This enyne has a triisopropylsilyl-protected oxygenated carbon substituent on the acetylene, which will allow for eventual introduction of the 2-furyl substituent at the nascent C6 carbon of the lactone ring of richardianidin-1. The reaction of carbene complex **19** with enyne (*E*)-**72** under the optimized conditions for enyne **71** (Table 6) gave the hydrindenone **89** in 40% yield (Scheme 16). While optimization studies may increase the yield of this reaction, the preparation of **89** via the tautomer-arrested annulation allows for the rapidly assembly of an advanced intermediate in the synthesis of richardianidin-1. Aside, from the final introduction of the furan unit, the intermediate **89** has all the carbons but one present in the core structure of richardianidin-1 and with an oxygen present on all the carbons that are oxygenated in the natural product. Access to **89** is very straightforward since the starting enyne (*E*)-**72** is prepared in three steps from propargyl alcohol and the carbene complex **19** is prepared in four steps from 4-bromo-3,5-dimethylphenol.

A summary of the important pieces of information gained during the course of this study on the inter- and intramolecular tautomer-arrested annulation will be presented in the context of a mechanistic accounting of the various products and competing pathways (Scheme 17). The formation of the tautomer-arrested product **94** begins with the loss of a carbon monoxide ligand on the starting carbene complex **90** to form the unsaturated 16-electron complex **91**. In the normal benzannulation reaction this is the rate-limiting step of the reaction, although it is considered unlikely to be the case for the tautomer-arrested annulation since the thermal requirement is ~50 °C higher than that for the benzannulation reaction and since it would not be expected that the energy barrier for the CO dissociation from **90** would significantly depend on the presence of the two methyl groups on the arene ring. In fact, if anything, the energy barrier for CO dissociation from **90** would be expected to be lowered to relieve steric interactions. At the present time, no kinetic studies have been carried out for the tautomer-arrested annulation reaction to confirm these expectations. The next step would be the coupling of **91** with the alkyne to give the η^1,η^3-vinylcarbene-complexed intermediate **92** where a carbon–carbon bond is formed between the original carbene carbon

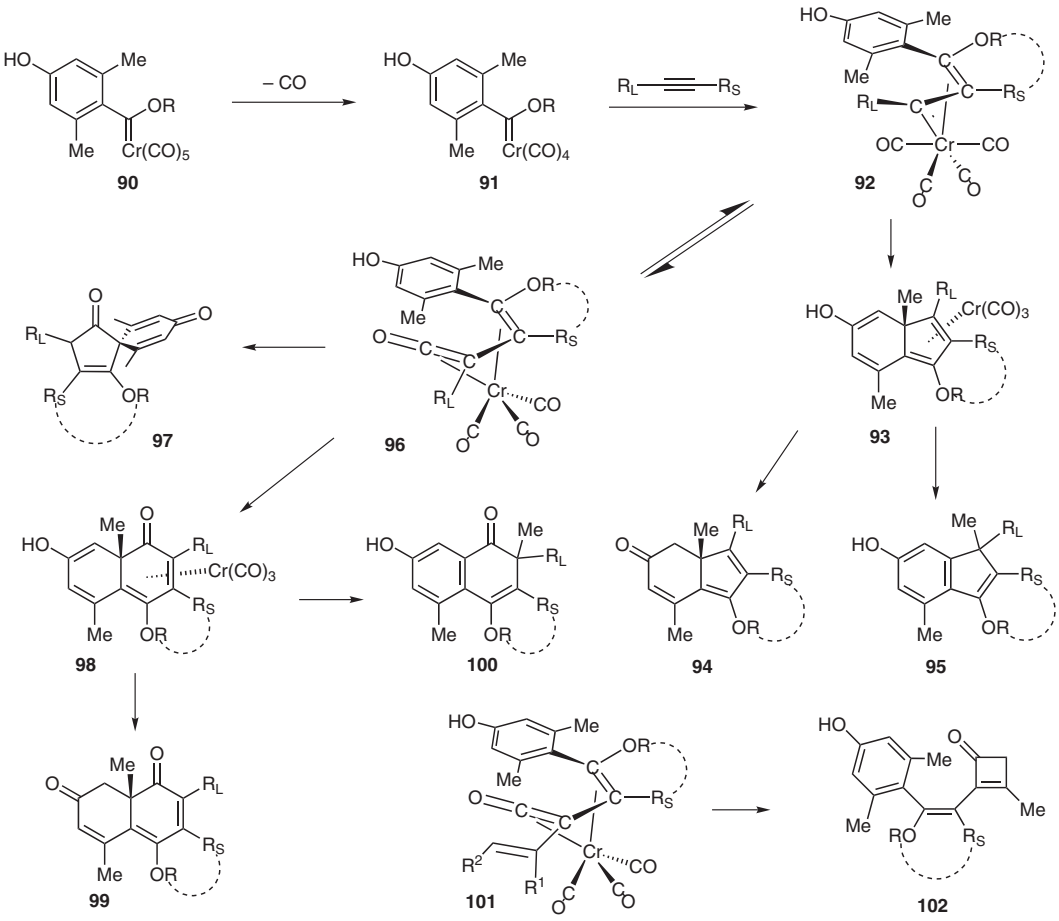


Scheme 16

and the carbon of the alkyne bearing the smallest substituent. An electrocyclic ring closure then generates the indenyl derivative **93** from which there is a competition between a tautomerization to give hydrindenone **94** and a 1,5-sigmatropic shift of methyl restoring the aromaticity of the arene and giving the hydroxyindene **95**.

The spirocyclic cyclohexadienone **97** represents a rare outcome of the tautomer-arrested and previously had only been observed in intermolecular reactions in acetonitrile solvent. This product results from a CO insertion in the η^1,η^3-vinylcarbene-complexed intermediate **92** to give the η^4-vinylketene complex **96**, which is presumably on the pathway to **97** but also the branch point between **97** and the tetralone derivatives **99** and **100**. The fact that it had only been observed before in acetonitrile suggests that the solvent will affected a ligand displacement on complex **96** to give the metal-free vinylketene which then cyclizes via an electrophilic addition to the ipso aromatic carbon rather than an electrocyclic ring closure to give a tetralone derivative. This selectivity for closure could be the result of combined electronic and steric effects. It is not clear why the intramolecular annulation of complex **29** produces the spirocyclic product **41** (Schemes 5 and 7). This is likely related to the oxygen atom in the tether since none of the complexes in Scheme 6 give this product. It must also be related to the position of the oxygen in the tether since the complexes in Schemes 9 and 10 do not give the spirocyclic product. Could it be that the oxygens in the tether of complex **29** serve to affect a ligand displacement in the vinylketene complex **96** rendering a vinylketene in which there is no metal coordinated to the four carbons of the vinyl ketene?

For most of the intramolecular annulations described in this work the two most common products are the hydrindenone **94** and the naphthalenedione **99**. For the normal benzannulation (Scheme 2), the CO insertion to give a vinylketene complex and cyclization to a phenol occur at temperatures of 45–60 °C. The tautomer-arrested annulation of complexes of the type **90** require temperatures in excess of 110 °C to achieve similar rates. Three possible explanations for this are: (1) the CO insertion in the vinyl carbene complexed intermediate **92** is reversible and that the electrocyclic ring closure of the vinylketene complex **96** is slowed by the presence of the methyl groups on the arene ring, or (2) the rate of CO insertion in the vinylcarbene-complexed intermediate **92** is depressed as a result of the presence of the methyl groups which may be possible if coordination of the chromium to one of the double bonds of the chromium occurs concurrent with CO insertion, or (3) the rate of addition of the alkyne to the unsaturated intermediate **91** is slowed by the presence of the methyl groups. A differentiation between these possibili-



Scheme 17

ties will have to await further mechanistic studies. In any event, the branch point between the hydrindenone product **94** and the naphthalenedione product **99** is the vinylcarbene complexed intermediate **92**. Clearly, for the intramolecular reactions examined in this work (Schemes 6 and 9) the partition between these two products is a function of size of the newly formed heterocyclic ring with the greatest proportion of the hydrindenone product when a six-membered ring is formed. Increased amounts of the naphthalenedione product were observed when five- or seven-membered heterocyclic rings are formed (Scheme 6). This correlation of the product distribution with the size of the heterocyclic ring that is formed may be a function of the strain that this newly formed ring introduces into the product. The idea that ring strain is a controlling factor is this product distribution is consistent with the observation that naphthalenedione products have not yet been observed from an inter-molecular tautomer-arrested annulation. The observation that the distribution between products **53** and **58** is a function of the size of the substituent R^1 on the end of the tethered alkyne in complex **54** could be accounted for by the effect that this change in substitution would be expected to have on the relative rates of cyclization of vinylcarbene-complexed intermediate **92** versus vinylketene complex **96**. In the cyclization of the vinylcarbene complex **92**, the substituent R_L comes a lot closer to one of the methyl groups on the arene ring than in the cyclization of the vinylketene complex **96**. Finally, the reaction of an enyne with an alkyl substituent on the double bond leads to the formation of the cyclobutanone **61a** (Scheme 10), whereas, enynes that have an oxygen substituent on the double bond do not (Schemes 13 and 15 and Table 6). A reasonable explanation of these results is that when substituent R^2 in **101** (Scheme 17) is an ether oxygen, then the vinylketene complex would be expected to be stabilized as a vinylogous ester relative to the cyclobutanone in which the oxygen is no longer conjugated to the carbon–oxygen double bond.

All experiments were performed under an argon atmosphere. Benzene, THF, and Et_2O were distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride under nitrogen. Isopropanol was distilled from $NaBH_4$ onto 4 Å MS. Other reagents were purified by simple distillation or by passing through a pad of activated silica gel. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 (300 MHz ^1H, 75.5 MHz ^{13}C) or Bruker Avance (400 MHz ^1H, 100 MHz ^{13}C) spectrometer in $CDCl_3$ using residual $CHCl_3$ (7.25 ppm ^1H, 77.25 ppm ^{13}C) as an internal reference unless otherwise stated. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. Components were visualized by illumination with long-wave ultraviolet light, exposure to iodine vapor, or by staining with one of the following reagents (followed by heating): *p*-anisaldehyde (or vanillin) in ethanol/sulfuric acid; 7% phosphomolybdic acid in ethanol; 0.04 M ammonium molybdate in 10% sulfuric acid. Solvents for extraction and chromatography were reagent grade and used as received. Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh).

Benzyl Prop-1-enyl Ether (32)

Allyl benzyl ether was prepared by adding allyl alcohol (13.6 mL, 200 mmol) in DMSO (20 mL) to a slurry of NaH (60 wt%, 8.4 g, 210 mmol), which had been washed with hexanes (2 ×) under N_2, and DMSO (60 mL) at 0 °C over 30 min. After H_2 evolution ceased, benzyl bromide (24.4 mL, 205 mmol) was added quickly and the mixture was stirred overnight. The solids were filtered off and upon heating allyl benzyl ether co-distilled with DMSO into a clean flask at ambient pressure. To this was added *t*-BuOK (2 g) and the mixture was heated at 100 °C for 6 h. The mixture was cooled and poured into hexanes and the DMSO was extracted with several portions of H_2O (1 L total). Drying ($MgSO_4$), concentration, and Kugelrohr distillation gave enol ether **32** as a colorless oil; yield: 21.09 g (71%); ratio *E*/*Z* 7.9:1; R_f = 0.33 (hexanes).

IR (neat): 1669 s, 1454 m, 1357 m, 1126 s, 1094 s, 1075 s, 733 m, 697 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = (isomer A) 1.64 (dd, *J* = 6.8, 1.3 Hz, 3 H), 4.42–4.47 (m, 1 H), 4.80 (s, 2 H), 6.02 (dq, *J* = 1.4, 7.8 Hz, 1 H), 7.28–7.36 (m, 5 H, mixture with B).

^1H NMR ($CDCl_3$): δ = (isomer B) 1.58 (dd, *J* = 6.7, 1.3 Hz, 3 H), 4.70 (s, 2 H), 4.83–4.91 (m, 1 H), 6.30 (br d, *J* = 12.4 Hz, 1 H), 7.28–7.36 (m, 5 H, mixture with A).

3-[2-(*tert*-Butyldimethylsiloxy)ethoxy]prop-1-yne (34)

2-(Prop-2-ynyloxy)ethanol (**33**) was prepared by a procedure developed by Semmelhack for closely related compounds.[11c] In CH_2Cl_2 (100 mL) were combined **33** (7.7 g, 76.9 mmol), TBSCl (13.91 g, 92.3 mmol), pyridine (8.7 mL, 107 mmol), and DMAP (940 mg, 0.77 mmol). After stirring overnight, the solvent was removed and the residue mixed with pentane (100 mL). The solids were filtered off on a Celite pad and washed with additional pentane. The pentane was washed sat. NH_4Cl (2 × 50 mL), dried ($MgSO_4$), and concentrated. Kugelrohr distillation at 65 °C/0.7 mbar gave **34** as a colorless oil; yield: 12.842 g (78%); R_f = 0.58 (Et_2O–CH_2Cl_2–hexanes, 1:1:20).

IR (neat): 2117 w, 1256 m, 1106 s, 837 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.09 (s, 6 H, Si-*t*-BuMe_2), 0.91 (s, 9 H, Si-*t*-BuMe_2), 2.42 (t, *J* = 2.1 Hz, 1 H, C≡C-H), 3.61 (t, *J* = 5.2 Hz, 2 H, OCH_2CH_2O), 3.79 (t, *J* = 5.2 Hz, 2 H, OCH_2CH_2O), 4.20 (d, *J* = 2.3 Hz, 2 H, C≡CCH_2O).

5-Benzyloxy-1-[2-(*tert*-butyldimethylsiloxy)ethoxy]-4-methylpent-2-yne (36)

To THF (25 mL) at 0 °C under N_2 was added **32** (4.41 g, 29.8 mmol) followed by 1.0 M BH_3 in THF (9.9 mL, 9.92 mmol). The mixture was stirred at 0 °C for 20 min and at r.t. for 10 min, the clear colorless soln was then cooled to 0 °C and a soln of **35** [formed by treatment of alkyne **34** (2.13 g, 9.92 mmol) with 1.6 M *n*-BuLi (6.2 mL, 9.92 mmol) in THF (20 mL) at 0 °C under argon for 30 min] was transferred via cannula with additional THF (5 mL). After 5 min, the colorless soln was cooled to –78 °C, and I_2 (2.52 g, 9.92 mmol) in Et_2O (50 mL) was added dropwise to give a dark red soln in which a precipitate eventually formed. After stirring for 1 h, the orange slurry was brought to r.t. and the mixture was washed with 3 M KOH [2 × 20 mL, spiked with sat. $Na_2S_2O_3$ soln (1 mL)]. The aqueous layers were back-extracted with Et_2O (20 mL). The combined pale yellow organic layers were treated with 3 M NaOH (3.3 mL) and 30 wt% H_2O_2 (1.3 mL) for 20 min (slightly exothermic reaction). The reaction was washed with $NaHCO_3$ and brine, dried, and concentrated. Chromatography (silica gel, Et_2O–CH_2Cl_2–hexanes, 1:1:30) gave **36** as a clear colorless oil; yield: 1.98 g (57%).

IR (neat): 2954 s, 2930 s, 2885 m, 2857 s, 2244 w, 1254 m, 1099 vs, 827 s, 778 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.08 (s, 6 H), 0.91 (s, 9 H), 1.22 (d, *J* = 7.0 Hz, 3 H), 2.79 (m, 1 H), 3.36 (dd, *J* = 8.8, 7.8 Hz, 1 H), 3.53 (dd,

J = 9.0, 6.1 Hz, 1 H), 3.57 (t, J = 5.3 Hz, 2 H), 3.77 (t, J = 5.2 Hz, 2 H), 4.18 (d, J = 1.8 Hz, 2 H), 4.54 (d, J = 2.8 Hz, 2 H), 7.25–7.33 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –5.31, 17.68, 18.31, 25.88, 26.70, 58.84, 62.57, 70.94, 72.91, 73.86, 76.87, 88.34, 127.50, 128.27, 138.13 (1 aryl carbon not located).

5-Benzyloxy-1-[2-hydroxyethoxy]-4-methylpent-2-yne (37)

A soln of **36** (1.98 g, 5.47 mmol) dissolved in THF (30 mL) under N_2 at r.t. was treated with 1.0 M TBAF THF (7.4 mL, 7.4 mmol) for 5 h. The mixture was poured into brine overlaid with Et_2O, dried ($MgSO_4$), and concentrated. Chromatography (silica gel, 40% EtOAc–hexanes) gave **37** as a clear oil; yield: 1.32 g (98%); R_f = 0.38 (40% EtOAc–hexanes).

IR (neat): 3425 br m, 2933 s, 2861 s, 2237 w, 1454 m, 1356 m, 1099 s, 1076 s, 739 s, 699 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.21 (d, J = 6.8 Hz, 3 H), 1.97 (br s, 1 H), 2.78 (br q, J = 6.8 Hz, 1 H), 3.36 (dd, J = 7.3, 1.7 Hz, 1 H), 3.50 (dd, J = 6.4, 2.6 Hz, 1 H), 3.60 (t, J = 4.5 Hz, 2 H), 3.73 (br s, 2 H), 4.17 (d, J = 1.8 Hz, 2 H), 4.53 (d, J = 1.2 Hz, 2 H), 7.25–7.30 (m, 5 H).

2-Bromo-5-(*tert*-butyldimethylsiloxy)-1,3-dimethylbenzene (38b)

To TBSCl (8.55 g, 56.7 mmol) was added 4-bromo-3,5-dimethylphenol (**38a**; 10.87 g, 54 mmol) followed by CH_2Cl_2 (60 mL). To this slurry was added Et_3N (9.9 mL, 70 mmol) with dissolution of the phenol occurring within 5 min. After stirring at r.t. for 12 h, the solvent was removed and the residue mixed with hexanes. Filtration through Celite to remove solids, evaporative removal of volatiles, and Kugelrohr distillation (120–130 °C/5.3 mbar) gave **38b** as a colorless oil at r.t., white solid at 0 °C; yield: 16.93 g (99%); R_f = 0.62 (hexanes).

IR (neat): 1466 m, 1323 m, 1169 m, 841 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 6 H, Si-t-BuMe_2), 0.95 (s, 9 H, Si-t-BuMe_2), 2.33 (s, 6 H, aryl CH_3), 6.56 (s, 2 H, aryl H).

^{13}C NMR ($CDCl_3$): δ = –4.4, 18.2, 23.9, 25.7, 119.0, 119.9, 139.0, 154.1.

MS: m/z (%) = 316 [M$^+$, ^{81}Br] (21), 314 [M$^+$, ^{79}Br] (21), 260 (^{81}Br, 32), 258 (^{79}Br, 32), 259 (^{81}Br, 100), 257 (^{79}Br, 100), 178 (82), 177 (52), 163 (31), 139 (^{81}Br, 18), 137 (^{79}Br, 18), 73 (17).

Anal. Calcd for $C_{14}H_{23}BrOSi$: C, 53.33; H, 7.35. Found: C, 53.61; H, 7.28.

1-(*tert*-Butyldimethylsiloxy)-3,5-dimethylbenzene (A) and 2-Butyl-5-(*tert*-butyldimethylsiloxy)-1,3-dimethylbenzene (B)

To a soln of bromide **38b** (496 mg, 1.6 mmol) in THF (2 mL) at –50 °C was added 1.6 M n-BuLi in hexanes (1.2 mL, 1.9 mmol). An aliquot removed after 30 min was quenched with sat. NH_4Cl soln and examined by GC. Three peaks were observed, corresponding to reduced product **A** (64%), starting material **38b** (5%) and butyl-substituted product **B** (31%). After an additional hour, the ratio between **A** and **B** had changed: **A** (30%), starting material (5%), and **B** (64%). Through workup and chromatography with hexanes, it was possible to isolate by shaving fractions a small amount of **B** for MS analysis.

1-(*tert*-Butyldimethylsiloxy)-3,5-dimethylbenzene (A)

^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 6 H, Si-t-BuMe_2), 0.97 (s, 9 H, Si-t-BuMe_2), 2.24 (s, 6 H, aryl CH_3), 6.45 (s, 2 H, aryl m-H), 6.58 (s, 1 H, aryl H).

2-Butyl-5-(*tert*-butyldimethylsiloxy)-1,3-dimethylbenzene (B)

^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 6 H, Si-t-BuMe_2), 0.95–0.98 (m, 12 H, Si-t-BuMe_2 and -$CH_2CH_2CH_2CH_3$), 1.38–1.43 (m, 4 H, -$CH_2CH_2CH_2CH_3$), 2.25 (s, 6 H, aryl H), 2.51 (br t, 2 H, -$CH_2CH_2CH_2CH_3$), 6.49 (s, 2 H, aryl H).

MS: m/z (%) = 292 [M$^+$] (26), 277 (17), 249 (49), 235 [M – n-Bu] (100), 193 (24), 179 (37).

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl](oxido)methylene}pentacarbonylchromium(0) Tetramethylammonium Salt (31)

To bromide **38b** (3.70 g, 11.7 mmol) in THF (20 mL) at –40 °C under argon was added dropwise over 7 min 1.7 M t-BuLi in pentane (14.5 mL, 24.7 mmol). The temperature rose to –30 °C and a yellow color developed. After 20 min, precipitation occurred and the mixture was stirred at 0 °C for 30 min. The soln was transferred via cannula into $Cr(CO)_6$ (2.99 g, 13.6 mmol) in THF (10 mL) at 0 °C. After warming to r.t., the dark brown soln was stirred 2–3 h, and the THF was removed. Note: the concentrated lithium acylate can decompose exothermically in air, so caution is required in handling. To the residue was added N_2-purged H_2O (bubbled through for 30 min) and the material was filtered through Celite under an N_2 blanket. The filtrate was transferred to a separatory funnel, and shaken quickly with N_2-purged hexanes, discarding the hexanes. The aqueous layer was treated with Me_4NBr or Me_4NCl portionwise until no precipitation was observed. The yellow slurry was filtered onto a Celite pad under an inverted N_2 umbrella and washed with H_2O and hexanes. The receiver flask was changed and the yellow solid washed through with purged CH_2Cl_2. Drying ($MgSO_4$), trituration with hexanes or benzene, and solvent removal gave a yellow to gold-green solid; yield: 3.90 g (63%).

^{1}H NMR (acetone-d_6, broadened): δ = 0.15 (s, 6 H), 0.96 (s, 9 H), 2.13 (s, 6 H), 3.39 (s, 12 H), 6.32 (s, 2 H).

{[2-(5-Benzyloxy-4-methylpent-2-yloxy)ethoxy][4-hydroxy-2,6-dimethylphenyl]methylene}pentacarbonylchromium(0) (29)

A soln of alkynol **37** (299.1 mg, 1.20 mmol) in CH_2Cl_2 (10 mL) at 0 °C under N_2 was treated sequentially with pyridine (125 μL, 1.6 mmol) and Tf_2O (243 μL, 1.44 mmol). The mixture was stirred for 1.5 h and then poured into brine. The layers were separated and the organic layer added directly to a soln of ammonium salt **31** (700 mg, 1.32 mmol) in CH_2Cl_2 (5 mL) under N_2 at r.t. After 45 min, the orange soln of complex **40** was washed with brine and the CH_2Cl_2 removed in vacuo. Et_2O (20 mL) was added followed by 25 wt% NaOMe in MeOH (4 mL). The mixture was stirred under argon until TLC showed complete desilylation. Chromatography (20% EtOAc–hexanes) gave complex **29**; yield: 300 mg (44%).

5-Benzyloxy-4-methyl-1-[2-(triflyloxy)ethoxy]pent-2-yne (30)

R_f = 0.55 (Et_2O–CH_2Cl_2–hexanes, 1:1:4).

IR (neat): 2244 w, 1413 s, 1245 s, 1207 s, 1147 s, 1126 s, 1105 s, 931 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.22 (d, J = 6.8 Hz, 3 H), 2.80 (br q, J = 6.7 Hz, 1 H), 3.38 (dd, J = 8.8, 7.3 Hz, 1 H), 3.50 (dd, J = 8.9, 6.5 Hz, 1 H), 3.81 (t, J = 4.4 Hz, 2 H), 4.21 (d, J = 1.7 Hz, 2 H), 4.54 (s, 2 H), 4.60 (t, J = 4.4 Hz, 2 H), 7.26–7.34 (m, 5 H).

{[2-(5-Benzyloxy-4-methylpent-2-yloxy)ethoxy][4-hydroxy-2,6-dimethylphenyl]methylene}pentacarbonylchromium(0) (29)

Red oil; R_f = 0.24 (20% EtOAc–hexanes).

IR (neat): 3301 br w, 2977 m, 2062 s, 1988 s, 1935 vs, 1314 m, 1255 m, 1173 m, 1136 s, 1116 s, 661 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.21 (d, J = 7.0 Hz, 3 H), 2.11 (s, 6 H), 2.76–2.80 (m, 1 H), 3.36 (m, 2 H), 3.94 (br s, 2 H), 4.17 (br s, 2 H), 4.23 (d, J = 1.4 Hz, 2 H), 4.54 (s, 2 H), 4.8–5.0 (br s, 1 H), 6.47 (s, 2 H), 7.25–7.33 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 17.51, 19.40, 26.64, 59.03, 66.98, 72.97, 73.79, 76.12, 77.16, 89.31, 114.89, 127.68, 127.81, 128.33, 128.65, 137.79, 143.66, 155.34, 216.12, 224.57, 364.54.

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl](methoxy)methylene}pentacarbonylchromium(0) (24)

The lithium acylate can be prepared as described above in the preparation of the ammonium acylate **31**. The lithium acylate was dissolved in CH_2Cl_2 and treated with methyl fluorosulfonate (1.3 equiv) for 30 min to 1 h. The soln was poured into Et_2O and brine and separated. Back extraction of the aqueous layer with Et_2O and washing of the combined organic layers with brine was performed, followed by drying ($MgSO_4$), and solvent removal. Chromatography on silica gel (5% Et_2O–hexanes) gave **24**; yield: 57%; orange needles from hexane, discolors at 66 °C; mp 86–87 °C; R_f = 0.30 (hexanes).

IR ($CHCl_3$): 2064 w, 1948 vs cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 6 H), 0.99 (s, 9 H), 2.09 (s, 6 H), 3.98 (br s, 3 H), 6.50 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –3.95, 18.64, 19.83, 26.08, 65.08, 120.12, 128.61, 144.49, 155.69, 216.84, 224.99, 366.19.

MS: *m*/*z* (%) = 470 [M$^+$] (1), 442 (3), 414 (13), 386 (5), 358 (13), 330 (100), 300 (32), 247 (13), 126 (22).

Anal. Calcd for $C_{21}H_{26}CrO_7Si$: C, 53.61; H, 5.57. Found: C, 53.74, H, 5.63.

Pentacarbonyl[(4-hydroxy-2,6-dimethylphenyl)(methoxy)methylene]chromium(0) (19)

Desilylation of the purified 4-siloxy complex **24** was performed (*vide infra*) to give the 4-hydroxy complex **19** in 91% yield. However, the 4-hydroxy complex may be obtained most conveniently without chromatographic isolation of the silylated complex **24**. In this case, the crude 4-siloxy complex (preceding preparation) was dissolved in Et_2O (ca. 30 mL) under argon (for 10 mmol scale) and treated with 25% wt% NaOMe in MeOH (5 mL) until TLC (20% EtOAc–hexanes) showed no further starting material, ca. 30 min to 1 h. The slurry was poured into Et_2O and brine and the layers separated. The Et_2O was washed with additional brine and set aside. The colored aqueous layer (dark brown to green) was neutralized with 10% HCl and extracted with Et_2O (1 ×). After washing this layer with brine, the combined extracts were dried, the solvents were removed, and the residue was chromatographed (silica gel, 20% EtOAc–hexanes) to give **19** in 72–83% yield.

Cyclization of Complex 29 in Benzene

A soln of complex **29** (118 mg, 0.21 mmol) in benzene (0.01 M, 20.6 mL) was added to a single-necked flask that had the 14/20 joint replaced with a threaded high-vacuum Teflon stopcock. The soln was deoxygenated (freeze–pump–thaw, 2 cycles) and then backfilled with 1 atm argon at r.t. and the flask sealed. The flask was placed in an oil bath at 60 °C for 4 h. Benzene was removed in vacuo and the residue chromatographed (silica gel, 40% EtOAc–hexanes). Several fast eluting bands were not collected/characterized; these were minor products by TLC and crude NMR. Two bands were yellow and possibly contained small amounts of the diastereomeric hydrindenone products. The major uncolored band was collected and found to contain the two diastereomeric spiroketones **41** as a colorless oil; yield: 38.1 mg (48%); 8:5 ratio. The spectra were collected on the mixture of isomers; R_f = 0.30 (40% EtOAc–hexanes).

IR (neat): 1754 m, 1670 m, 1658 s, 1629 m, 1617 m, 1384 m, 1291 m, 1092 m, 750 m cm^{-1}.

^{1}H NMR (C_6D_6): δ = 0.81 (d, *J* = 7.1 Hz, 3 H, major), 0.96 (d, *J* = 7.1 Hz, 3 H, minor), 1.520 (s, 3 H, major), 1.522 (s, 3 H, minor), 1.53 (s, 3 H, minor), 1.64 (s, 3 H, major), 1.98–2.01 (m, 1 H, major), 2.40–2.44 (m, 1 H, minor), 3.16–3.19 (m), 3.27–3.37 (m), 3.45 (s), 3.48 (dd, *J* = 8.9, 6.4 Hz), 3.57–3.67 (m), 3.79 (t, *J* = 8.6 Hz), 3.86 (d, *J* = 15.6 Hz), 3.95–3.98 (m), 4.02 (d, *J* = 15.5 Hz), 4.20–4.23 (m), 4.28 (d, *J* = 12.3 Hz), 4.39 (d, *J* = 12 Hz), 4.43 (d, *J* = 12 Hz).

MS: *m*/*z* (%) = 408 M$^+$ (12), 317 (19), 149 (9), 91 (100), 83 (27), 73 (17).

Pentacarbonyl[(4-hydroxy-2,6-dimethylphenyl)(pent-3-ynyloxy)methylene]chromium(0) (42a); Typical Procedure

To a slurry of the adduct of Tf_2O (1.85 mL, 11 mmol) and pyridine (1.05 mL, 13 mmol) in CH_2Cl_2 (20 mL) at 0 °C under N_2 was added commercially available pent-3-yn-1-ol to give a pink suspension. This was stirred for 1 h, then washed with brine. After drying ($MgSO_4$) and solvent removal, the residue was dissolved in CH_2Cl_2 (~20 mL) and ammonium salt **31** (1.5 g, 2.83 mmol) was added. After stirring for 1 h, the red soln was washed with brine, dried ($MgSO_4$), and the solvent removed. To the resultant red oil was added sequentially anhyd Et_2O (20 mL) and 25 wt% NaOMe in MeOH (4 mL) under argon. The reaction was stirred for 1 h at r.t. when TLC indicated completion and then was poured into brine and additional Et_2O (20 mL). The layers were separated without shaking, and the aqueous layer treated with 10% HCl (20 mL). This was re-extracted with Et_2O (40 mL), then washed with brine. The combined organic extracts were dried ($MgSO_4$), concentrated, and chromatographed (silica gel, 20% EtOAc–hexanes). In this manner, complex **42a** was obtained as a dark red oil; yield: 990.3 mg (86%). No crystallization could be induced upon cooling in hexanes to –78 °C. This complex failed to give satisfactory MS. Additionally, because it was impossible to thoroughly remove all traces of solvent by high vacuum without observing product decomposition, no attempts at obtaining combustion analysis data were made; R_f = 0.48 (tails) (20% EtOAc–hexanes).

IR (neat): 3374 br w, 2063 vs, 1928 vs, 1255 m, 1168 m, 1131 s, 682 m, 653 m, 617 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.74 (s, 3 H), 2.10 (s, 6 H), 2.76 (s, 2 H), 4.02 (s, 2 H), 6.51 (s, 2 H) (line broadened, hydroxy not observed).

^{13}C NMR ($CDCl_3$): δ = 3.23, 19.36, 19.79, 73.66, 76.15, 78.66, 114.94, 128.68, 144.08, 154.89, 216.27, 224.56, 363.87.

Pentacarbonyl[(hex-4-ynyloxy)(4-hydroxy-2,6-dimethylphenyl)methylene]chromium(0) (42b)

The triflic ester of hex-4-yn-1-ol was prepared from hex-4-yn-1-ol (1.01 g, 11.3 mmol) by the general procedure and purified by bulb-to-bulb distillation at 60 °C. The alkynyl triflate (652 mg, 2.83 mmol) was then reacted with ammonium salt **31** (1.00 g, 1.88 mmol) according to the general procedure. Purification of the product as for **42a** gave two fractions of complex **42b**; one containing pure material as a red oil (493.0 mg, 62%) and another consisting of slightly impure material (149 mg, ~18%); R_f = 0.32 (20% EtOAc–hexanes).

IR (neat): 3386 br m, 2062 vs, 1927 vs, 1253 s, 1168 s, 1132 s, 663 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.75 (br s, 3 H), 2.13 (br s, 8 H), 2.46 (br s, 2 H), 4.10 (br s, 2 H), 5.0–5.5 (br s, 1 H), 6.50 (s, 2 H) (line broadened).

^{13}C NMR ($CDCl_3$): δ = 3.31, 14.69, 15.20, 19.35, 28.29, 66.00, 76.74, 114.85, 128.47, 144.20, 155.13, 214.44, 224.49, 364.22.

MS: *m*/*z* (%) = 366 [M$^+$ – 2 CO] (1), 338 [M$^+$ – 3 CO] (0.5), 310 [M$^+$ – 4 CO] (1), 282 [M$^+$ –5 CO] (5), 230 [M$^+$ –Cr(CO)$_5$] (6), 83 (100) (molecular ion not observed).

Pentacarbonyl[(hept-5-ynyloxy)(4-hydroxy-2,6-dimethylphenyl)methylene]chromium(0) (42c)
This complex was prepared from hept-5-yn-1-ol (407 mg, 3.63 mmol) and ammonium salt **31** (1.5 g, 2.83 mmol) according to the general procedure. Purification in the same manner gave complex **42c** as an orange-red oil; yield: 694 mg (56%); R_f = 0.45 (20% EtOAc–hexanes).

IR (neat): 3398 br w, 2062 s, 1988 s, 1958 s, 1309 m, 1254 m, 1166 m, 1133 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.73 (br m, 2 H), 1.77 (s, 3 H), 2.04 (br s, 2 H), 2.11 (br s, 6 H), 2.24 (br s, 2 H), 4.05 (br s, 2 H), 5.27 (s, 1 H), 6.52 (br s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 3.24, 18.17, 19.30, 25.11, 28.20, 53.37, 78.19, 114.90, 128.40, 144.15, 154.80, 216.36, 224.42, 363.39 (1 alkynyl carbon not located).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 42a; Typical Procedure
A soln of complex **42a** (112.6 mg, 0.28 mmol) in benzene (0.005 M, 55.2 mL) was added to a single-necked flask that had the 14/20 joint replaced with a threaded high-vacuum Teflon stopcock. The soln was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 2 cycles), backfilled with 1 atm argon at r.t.. The flask was sealed placed in an oil bath at 60 °C for 1.5 h. After opening to air and filtration through Celite, the mixture was stripped of volatiles. Chromatographic purification (silica gel, 40% EtOAc–hexanes) gave two compounds: hydrindenone **43a** (12.2 mg, 20%), and cyclohexadienone **44a** (34.6 mg, 51%). When the reaction was carried out at 110 °C and 0.005 M the products were **43a** (14%) and **44a** (46%).

Indeno[1,2-*b*]furan-6-one 43a
Yellow solid; R_f = 0.16 (20% EtOAc–hexanes).

IR ($CHCl_3$): 2975 w, 2855 w, 1666 m, 1639 s, 1596 s, 1335 w, 1119 w, 1085w cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.16 (s, 3 H), 1.88 (s, 3 H), 2.08 (d, *J* = 14.8 Hz, 1 H), 2.16 (s, 3 H), 2.45 (d, *J* = 14.8 Hz, 1 H), 2.72–2.75 (m, 2 H), 4.87–4.93 (m, 2 H), 5.59 (s, 1 H).

MS: *m*/*z* (%) = 216 [M^+] (100), 201 (62), 173 (84), 145 (12), 115 (11), 91 (10).

HRMS: *m*/*z* [M^+] calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1144.

Naphtho[1,2-*b*]furan-5,7-dione 44a
Yellow solid, discolors at 140 °C; mp 159–165 °C; R_f = 0.22 (40% EtOAc–hexanes).

IR ($CHCl_3$): 1653 vs, 1594 m, 1569 w, 1337 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.23 (s, 3 H), 1.98 (s, 3 H), 2.28 (d, *J* = 16.9 Hz, 1 H), 2.30 (s, 3 H), 2.86 (d, *J* = 16.9 Hz, 1 H), 3.00–3.05 (m, 2 H), 4.47 (apparent quartet, *J* = 8.2 Hz, 1 H), 4.56 (dt, *J* = 8.7, 6.1 Hz, 1 H), 5.78 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.42, 23.32, 27.81, 28.50, 44.53, 47.58, 70.57, 115.02, 125.15, 129.21, 148.35, 152.07, 152.18, 197.26, 202.52.

MS: *m*/*z* (%) = 244 [M^+] (100), 229 (65), 201 (97), 188 (17), 185 (18), 173 (29), 115 (15), 91 (22), 83 (71).

HRMS: *m*/*z* [M^+] calcd for $C_{15}H_{16}O_3$: 244.1099; found: 244.1092.

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 42b
The thermolysis of complex **42b** (297.8 mg, 0.71 mmol) was carried out according to the typical procedure at 60 °C for 6.5 h and 0.05 M in **42b**. Purification of the mixture gave **43b** (104.4 mg, 64%) and a compound tentatively identified as a spiroketone (7.0 mg, 4%, related in structure to **41**). Subsequent reactions gave spiroketone and cyclohexadienone products in the same fractions off the column, typically in less than 5% combined yield. The assignments for the spiroketone and cyclohexadienone **44b** are made only on the bases of the following discernible chemical shifts in the mixtures: spiroketone: quartet at 3.15 (1 H), singlets at 6.22 and 6.28 (1 H each), and at 1.82 and 1.89 (3 H each); cyclohexadienone **44b**: doublet at 2.87 (1 H, large *J*), singlets at 5.80 (1 H), 2.29 (3 H), and 1.90 (3 H).

Indeno[1,2-*b*]pyran-7(2*H*)-one 43b
Bright yellow solid; mp 150 °C; R_f = 0.25 (20% EtOAc–hexanes).

IR ($CHCl_3$): 1630 m, 1561 s, 1343 m, 1145 m, 1094 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.08 (s, 3 H), 1.84 (s, 3 H), 1.89 (d, *J* = 14.9 Hz, 1 H), 1.91–1.94 (m, 2 H), 2.21 (d, *J* = 1 Hz, 3 H), 2.44 (d, *J* = 14.9 Hz, 1 H), 2.47–2.50 (m, 2 H), 4.18 (t, *J* = 5.2 Hz, 2 H), 5.57 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 10.08, 20.61, 20.77, 22.29, 22.70, 46.58, 51.00, 67.97, 118.95, 119.47, 128.20, 150.83, 154.25, 155.21, 199.24.

MS: *m*/*z* (%) = 230 [M^+] (100), 215 (56), 187 (56), 159 (40), 131 (12).

HRMS: *m*/*z* [M^+] calcd for $C_{15}H_{18}O_2$: 230.1308; found: 230.1311.

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 42c
Thermolysis of complex **42c** (149 mg, 0.34 mmol) was carried out according to the typical procedure at 60 °C for 12 h. Purification by chromatography (silica gel, 20% EtOAc–hexanes) gave **43c** (21.8 mg) contaminated with benzene(tricarbonyl)chromium (26% after repurification) and **44c** (13.1 mg, 14%). When the reaction was carried out at 110 °C and 0.005 M the reaction gave **43c** (35.7 mg, 36%) and **44c** (33.4 mg, 30%) and no spiro compound was observed in the crude ^1H NMR.

Indeno[1,2-*b*]oxepin-8-one 43c
Yellow solid; R_f = 0.33 (20% EtOAc–hexanes).

IR ($CHCl_3$): 2929 m, 2855 m, 1629 vs, 1572 s, 1462 m, 1379 m, 1369 m, 1348 s, 1305 m, 1142 m, 1100 m, 902 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.07 (s, 3 H), 1.69–1.78 (m, 2 H), 1.84 (s, 3 H), 1.91 (d, *J* = 15 Hz, 1 H), 1.94–1.99 (m, 2 H), 2.23 (d, *J* = 0.8 Hz, 3 H), 2.42–2.48 (m, 3 H), 3.97–4.01 (m, 1 H), 4.08–4.13 (m, 1 H), 5.63 (s, 1 H).

^{13}C NMR (CDCl3): δ = 12.45, 22.55, 24.45, 26.99, 27.46, 33.03, 47.71, 52.53, 72.64, 120.16, 123.92, 135.02, 148.28, 150.73, 157.91, 195.58.

MS: *m*/*z* (%) = 244 [M^+] (100), 229 (17), 201 (21), 187 (33), 173 (12), 159 (30), 145 (11), 131 (13), 115 (17).

HRMS: *m*/*z* [M^+] calcd for $C_{16}H_{20}O_2$: 244.1463; found: 244.1463.

Naphtho[1,2-*b*]oxepin-7,9-dione 44c
Yellow solid; mp 112–3 °C; R_f = 0.22 (20% EtOAc–hexanes).

IR ($CHCl_3$): 2931 w, 1657 vs, 1621 m, 1570 w, 1363 w, 1339 w, 1105 w cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.23 (s, 3 H), 1.84–1.99 (m, 4 H), 2.01 (s, 3 H), 2.32 (d, *J* = 16.9 Hz, 1 H), 2.35 (d, *J* = 1 Hz, 3 H), 2.59–2.63 (m, 1 H), 2.77–2.82 (m, 1 H), 2.91 (d, *J* = 17 Hz, 1 H), 3.64–3.69 (m, 1 H), 4.23–4.26 (m, 1 H), 5.89 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.60, 24.35, 25.99, 27.36, 29.74, 29.90, 44.51, 48.49, 75.27, 128.61, 128.91, 131.32, 151.66, 152.30, 154.10, 197.20, 202.81.

MS: *m*/*z* (%) = 272 [M^+] (100), 257 (42), 244 (11), 229 (49), 201 (21), 187 (32), 159 (22), 149 (44), 123 (33), 115 (23), 105 (15).

HRMS: *m*/*z* [M$^+$] calcd for $C_{17}H_{20}O_3$: 272.1412; found: 272.1413.

Pentacarbonyl[(2,6-dimethylphenyl)(pent-3-ynyloxy)methylene]chromium(0) (45)
Pentacarbonyl[(2,6-dimethylphenyl)(oxido)methylene]chromium(0) Tetramethylammonium Salt

A soln of 2-bromo-*m*-xylene (1.33 mL, 10 mmol) in Et_2O (10 mL) was treated with 1.7 M *t*-BuLi in pentane (12.4 mL, 21 mmol) at –78 °C for 30 min, then warmed to r.t. for 30 min. The yellow soln was transferred via cannula into a slurry of $Cr(CO)_6$ (2.42 g, 11 mmol) in Et_2O (20 mL) at 0 °C, then warmed to r.t. for 1 h. The solvent was then removed in vacuo to leave a brown oil residue, which was taken up in H_2O and filtered through Celite to remove undissolved solids. The aqueous layer was then shaken with hexanes (2 ×, discarded), and treated with solid Me_4NBr until precipitation of the yellow salt was no longer observed. After standing for 5 min, the salt was filtered onto a pad of Celite and washed with H_2O and hexanes. The collection flask was changed and the solids washed through with CH_2Cl_2. After drying ($MgSO_4$), the solvent was removed to leave pentacarbonyl[(2,6-dimethylphenyl)(oxido)methylene]chromium (0) tetramethylammonium salt as a yellow crystalline solid; yield: 3.36 g (84%); pure by NMR assay.

^{1}H NMR (acetone-d_6): δ = 2.17 (s, 6 H), 3.36 (s, 12 H), 6.79 (s, 3 H).

Pentacarbonyl[(2,6-dimethylphenyl)(pent-3-ynyloxy)methylene]chromium(0) (45)

In CH_2Cl_2 (20 mL) at 0 °C under N_2 were combined Tf_2O (1.0 mL, 6.0 mmol) and pyridine (526 μL, 6.5 mmol). After 5 min, pent-3-yn-1-ol (553 μL) was added and the slurry stirred at 0 °C for 20 min. To this was added the above ammonium salt (2.0 g, 5.0 mmol) and stirring was continued for 30 min. The red soln was poured into Et_2O and washed with brine and $NaHCO_3$. After drying, the organic layer was stripped and the residue taken up in hexanes. Again it was filtered through Celite and concentrated. Chromatography (Et_2O–CH_2Cl_2–hexanes, 1:1:20) gave complex **45** as a red oil; yield: 1.467 g (75%); contains a small amount of alkynol impurity by NMR. This material could be crystallized ($CHCl_3$–hexanes) at –78 °C to give an orange solid; mp 75–76 °C; R_f = 0.41 (Et_2O–CH_2Cl_2–hexanes, 1:1:20).

IR ($CHCl_3$): 2064 vs, 1991 s, 1932 vs, 1142 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.74 (t, *J* = 2.5 Hz, 3 H), 2.15 (s, 6 H), 2.72–2.84 (br s, 2 H), 3.94–4.08 (br s, 2 H), 7.0–7.13 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 3.32, 19.33, 19.87, 73.54, 77.71, 102.57, 126.42, 128.10, 128.33, 150.24, 216.27, 224.47, 362.50.

MS: *m*/*z* (%) = 364 [M$^+$ – CO] (2), 336 [M$^+$ – 2 CO] (7), 308 [M$^+$ – 3 CO] (2), 280 [M$^+$ – 4 CO] (16), 252 [M$^+$ – 5 CO] (43), 213 (11), 185 (28), 84 (100), 52 (64) (molecular ion not observed).

HRMS: *m*/*z* [M – CO]$^+$ calcd for $C_{18}H_{16}CrO_5$: 364.0403; found: 364.0395.

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 45

A deoxygenated soln of **45** (180.0 mg, 0.46 mmol) in benzene (0.005 M, 90 mL) was heated under argon at 110 °C for 16 h. A metalloid species (perhaps a tricarbonyl complex of **47**) co-elutes with the product and persists after stirring in air overnight. Thus, the solvent was removed, the residue dissolved in THF (30 mL) and treated with $FeCl_3$–DMF (1.75 g, 3.2 mmol) at r.t. for 30 min. The soln was washed with H_2O and brine and then dried ($MgSO_4$). Chromatography (5% to 20% EtOAc–hexanes) gave naphthalenone **47** (39.0 mg, 37%) and indanone **46** (18.8 mg). The latter compound was repurified by preparative TLC (20% EtOAc–hexanes) to give **46** (16.6 mg, 17%). If the reaction was stopped before complete conversion and chromatographed under the same solvent conditions, an orange band and a purple band could be eluted off the column. The purple band was somewhat air-sensitive and decomposed to the orange band before solvent could be removed. Upon dissolution in benzene and heating at 110 °C, this material proceeded mainly to naphthalenone **47**. The orange band could be separated into two components. The orange band also proceeded to product upon resubmission to reaction conditions.

Naphtho[1,2-*b*]furan-5(4*H*)-one 47

Yellow solid; R_f = 0.40 (10% EtOAc–hexanes).

IR (neat): 1672 vs, 1589 s, 1082 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 6 H), 2.56 (s, 3 H), 2.75 (t, *J* = 9.4 Hz, 2 H), 4.46 (t, *J* = 9.4 Hz, 2 H), 7.16 (t, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 6.9 Hz, 1 H), 7.86 (d, *J* = 7.7 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 21.65, 24.82, 29.37, 44.56, 69.32, 118.49, 126.14, 127.27, 129.68, 130.13, 133.61, 137.35, 147.00, 204.14.

MS: *m*/*z* (%) = 228 [M$^+$] (19), 213 (100), 185 (15), 170 (5).

HRMS: *m*/*z* [M$^+$] calcd for $C_{15}H_{16}O_2$: 228.1150; found: 228.1145.

Indan-1-one 46

IR ($CHCl_3$): 3400 br s, 2963 m, 1702 vs, 1594 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.11 (s, 3 H), 1.44 (s, 3 H), 1.79–1.91 (m, 2 H), 2.50 (dd, *J* = 9.4, 4.2 Hz, 1 H), 2.59 (s, 3 H), 3.75–3.83 (m, 1 H), 3.93–3.98 (m, 1 H), 7.10 (d, *J* = 7.4 Hz, 1 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 18.46, 26.79, 27.90, 28.52, 41.64, 60.29, 62.71, 120.55, 129.37, 131.48, 134.50, 138.82, 163.62, 209.85.

{[2-(But-2-ynyloxy)ethoxy](4-hydroxy-2,6-dimethylphenyl)methylene}pentacarbonylchromium(0) (48)

2-(But-2-ynyloxy)ethanol was prepared by a procedure developed by Semmelhack for closely related compounds.[11c] A mixture of 2-(but-2-ynyloxy)ethanol (1.01 g, 8.89 mmol) and pyridine (935 μL, 11.6 mmol) in CH_2Cl_2 (20 mL) at 0 °C was treated with Tf_2O (1.65 mL, 9.8 mmol) to give an exothermic reaction with precipitation occurring. After several hours stirring at 0 °C, the reaction was washed with H_2O and brine, and concentrated to give a dark brown oil, 1.65 g crude weight. From this was removed alkynyl triflate (1.34 g, 5.5 mmol), which was dissolved in CH_2Cl_2 (10 mL) at r.t.. To this was added ammonium salt **31** (1.5 g, 2.83 mmol) neat; an immediate red coloration developed. The alkylation reaction was stirred for 40 min, then washed with brine, dried, and solvent removed. Et_2O (20 mL) was added to the residue followed by 25 wt% NaOMe in MeOH (4 mL), and the whole was stirred at r.t. for 1 h. Extractive workup as usual followed by chromatography (20% EtOAc–hexanes) gave complex **48** as a red oil; yield: 982 mg (79%). No crystallization could be induced upon cooling in hexanes to –78 °C. This complex failed to give satisfactory MS. Additionally, because it was impossible to thoroughly remove all traces of solvent by high vacuum without observing product decomposition, no attempts at obtaining combustion analysis were made; R_f = 0.25 (20% EtOAc–hexanes).

IR (neat): 3383 br w, 2063 m, 1932 vs cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.85 (t, *J* = 2.1 Hz, 3 H), 2.12 (s, 6 H), 3.90–4.02 (br s, 2 H), 4.1–4.25 (br m, 4 H), 4.68–4.85 (br s, 1 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 3.53, 19.45, 59.20, 67.08, 74.40, 77.21, 83.24, 114.92, 128.87, 143.81, 155.11, 216.35, 224.59, 364.46.

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 48 at 60 °C and 0.05 M; Typical Procedure

A soln of complex **48** (125.9 mg, 0.29 mmol) in benzene (0.05 M, 5.7 mL) was added to a 25-mL single-necked flask that had the 14/20 joint replaced with a threaded high-vacuum Teflon stopcock.

The mixture was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles) and back-flushed with 1 atm of argon at r.t.. The flask was sealed and placed in an oil bath and heated at 60 °C for 13 h to give a dark brown mixture. Solvent was removed and the residue dissolved in Et_2O. Filtration through Celite gave a clear yellow filtrate. After chromatography (40% EtOAc–hexanes), **49** (10.8 mg, 15%), **50** (4.0 mg, 5%), and **51** (16.2 mg, 21%) were recovered. Reactions performed under different conditions were chromatographed differently.

Indeno[1,2-*e*][1,4]dioxepin-8(5*H*)-one 49

Yellow solid; R_f = 0.49 (40% EtOAc–hexanes).

IR (neat): 2958 w, 1652 m, 1633 vs, 1569 vs, 1407 w, 1154 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.10 (s, 3 H), 1.88 (s, 3 H), 1.96 (d, *J* = 15 Hz, 1 H), 2.24 (s, 3 H), 2.49 (d, *J* = 15 Hz, 1 H), 3.97–4.14 (m, 4 H), 4.35 (d, *J* = 14.2 Hz, 1 H), 4.46 (d, *J* = 14.2 Hz, 1 H), 5.68 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 10.31, 20.74, 22.54, 46.31, 52.57, 65.88, 73.60, 73.66, 122.40, 125.85, 135.47, 150.30, 154.33, 158.30, 199.11.

MS: *m*/*z* (%) = 246 [M^+] (100), 231 (12), 203 (8), 187 (35), 174 (12), 159 (35), 131 (14), 115 (13), 91 (20), 83 (63).

HRMS: *m*/*z* [M^+] calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1256.

Naphtho[1,2-*e*][1,4]dioxepin-7,9-dione 50

Yellow solid; R_f = 0.30 (40% EtOAc–hexanes).

IR ($CHCl_3$): 2859 m, 1720 m, 1667 vs, 1625 s, 1573 m, 1363 m, 1342 m, 1127 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.25 (s, 3 H), 2.07 (s, 3 H), 2.32 (d, *J* = 17 Hz, 1 H), 2.35 (d, *J* = 1 Hz, 3 H), 2.91 (d, *J* = 17 Hz, 1 H), 3.92–3.98 (m, 3 H), 4.10–4.33 (m, 1 H), 4.53 (d, *J* = 13 Hz, 1 H), 4.66 (d, *J* = 13 Hz, 1 H), 5.91 (s, 1 H).

MS: *m*/*z* (%) = 274 [M^+] (12), 259 (6), 231 (4), 187 (10), 159 (6), 149 (6), 91 (8), 83 (100).

HRMS: *m*/*z* [M^+] calcd for $C_{16}H_{18}O_4$: 274.1205; found: 274.1206.

Spiro[cyclohexa-2,5-diene-1,8′-cyclopenta[*e*][1,4]dioxepin]-4,7′(6′*H*)-dione 51

White solid; mp 124 °C (dec.); R_f = 0.15 (40% EtOAc–hexanes).

IR (neat): 1756 m, 1660 s, 1629 m, 1287 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.31 (d, *J* = 7.3 Hz, 3 H), 1.86 (d, *J* = 1 Hz, 3 H), 1.90 (s, 3 H), 3.24 (q, *J* = 7.2 Hz, 1 H), 3.87–3.90 (m, 2 H), 4.17 (t, *J* = 3.6 Hz, 2 H), 4.37 (d, *J* = 4.6 Hz, 2 H), 6.23 (d, *J* = 1.2 Hz, 1 H), 6.27 (d, *J* = 1.3 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.73, 20.05, 20.86, 50.49, 67.96, 71.39, 71.99, 74.86, 116.95, 129.51, 130.18, 150.21, 152.49, 152.93, 186.14, 209.78.

MS: *m*/*z* (%) = 274 [M^+[(33), 259 (16), 247 (96), 231 (29), 187 (31), 149 (100).

HRMS: *m*/*z* [M^+] calcd for $C_{16}H_{18}O_4$: 274.1205; found: 274.1205.

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 48 at 60 °C and 0.005 M

A deoxygenated soln of complex **48** (131.8 mg, 0.30 mmol) in benzene (0.005 M, 57 mL) was thermolyzed according to the general procedure at 60 °C for 13 h. Chromatography (40% EtOAc–hexanes) gave two bands. (Note: The CO- and non-CO inserted products elute so similarly that they were collected in one fraction and yields were determined by NMR integration of the vinylic proton α to the enone carbonyl.) In this manner, enones **49** and **50** (31.9 mg) were obtained, comprised of **49** (27%) and **50** (15%), as well as **51** (13.4 mg, 16%). Analytical samples of enones **49** and **50** were obtained by combining material from several reactions followed by careful chromatography (20% EtOAc–hexanes).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 48 in Benzene at Reflux

A 100-mL 2-necked round-bottomed flask was fitted with a condenser and septum inlet and flushed with N_2. A N_2 bubbler protected the condenser top. To this was added anhyd, degassed benzene (25 mL) (distilled directly from benzophenone ketyl) and the solvent brought to reflux in a 100 °C oil bath. The carbene complex **48** (119.3 mg, 0.27 mmol) was weighed into a separate flask which was evacuated and flushed with argon. Benzene (20 mL) was added and the orange soln drawn back up into the syringe. The carbene complex was added through the septum dropwise via syringe pump (6.5 mL/hour) to the refluxing soln. When the addition was complete, the reaction was heated an additional hour, then cooled and filtered. Concentration and chromatography gave combined **49** and **50** (34.1 mg; ratio **49/50** 2.4:1, 35% and 15% respectively) followed by **51** (8.7 mg, 12%).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 48 at 110 °C and 0.05 M

This reaction, in which complex **48** (117.9 mg, 0.27 mmol) was thermolyzed according to the typical procedure at 110 °C in benzene (0.05 M, 5.3 mL) for 30 min, gave **49** (20%), **50** (8%), and **51** (13%).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 48 at 110 °C and 0.005 M

A soln of complex **48** (100.1 mg, 0.23 mmol) was thermolyzed according to the typical procedure in benzene (0.005 M, 46 mL) for 20 h. The usual workup and purification resulted in isolation of **49** (21.1 mg, 38%), **50** (11.1 mg, 18%), and **51** (4.0 mg, 6%).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 48 in Toluene at Reflux

In a 100-mL sidearm flask with N_2-protected condenser was placed toluene (50 mL) and N_2 was bubbled through a submerged needle inserted through the sidearm for 30 min. The flask was immersed in a hot oil bath and brought to reflux. The carbene complex **48** (166.1 mg, 0.38 mmol) was taken up in purged toluene (10 mL) under argon and added dropwise (1 drop/3–4 s) over 75 min. TLC indicated complete reaction. After cooling, the mixture was filtered through Celite to give a bright yellow soln. Chromatography (40% EtOAc–hexanes) gave **49** (36.0 mg, 39%), **50** (19.8 mg, 19%), and **51** (3.7 mg, 4%).

{[(But-2-ynyloxy)methoxy](4-hydroxy-2,6-dimethylphenyl)methylene}pentacarbonylchromium(0) (54a); Typical Procedures: But-2-ynyl Chloromethyl Ether (56a)

But-2-yn-1-ol (175 mg, 2.50 mmol) was added dropwise to a suspension of paraformaldehyde (75.0 mg, 2.50 mmol) in TMSCl (1.25 mL, 10.0 mmol) at r.t.. The mixture was stirred at r.t. until the paraformaldehyde had been consumed. The clear soln was evaporated under reduced pressure to remove the excess TMSCl to afford but-2-ynyl chloromethyl ether (**56a**). The purity of the chloromethyl ether was checked by ^1H NMR, and then used without further purification.

^1H NMR ($CDCl_3$): δ = 1.82 (t, *J* = 2.2 Hz, 3 H), 4.29 (q, *J* = 2.2 Hz, 2 H), 5.54 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 54.98, 56.60, 72.48, 80.05, 84.30.

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl](but-2-ynyloxy)methoxy]methylene}pentacarbonylchromium(0) (55a)

The freshly prepared chloromethyl ether **56a** (2.50 mmol) in CH_2Cl_2 (5 mL) was added drop wise to a soln of ammonium salt **31** (recrystallized from CH_2Cl_2) (1.08 g, 2.00 mmol) in CH_2Cl_2 (20

mL) at r.t.. The resulting red soln was stirred at r.t. for 15 min under argon, and then passed through a short silica gel column (3 × 10 cm) to give the TBS-protected carbene complex **55a** as a red oil; yield: 980 mg (91%); R_f = 0.60 (hexane–Et_2O, 9:1).

IR (neat): 2957 m, 2932 m, 2860 m, 2230 vw, 2064 s, 1991 s, 1941 vs, 1601 m, 1471 w, 1315 m, 1157 s, 1060 m, 841 s, 656 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.18 (s, 6 H), 0.95 (s, 9 H), 1.84 (s, 3 H), 2.09 (s, 6 H), 4.52 (s, 2 H), 5.25 (s, 2 H), 6.47 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.46, 12.36, 13.50, 19.52, 25.58, 57.69, 72.70, 90.73, 97.14, 119.54, 128.15, 144.85, 155.24, 216.26, 224.65, 365.35.

MS: *m*/*z* (%) = 510 [M^+ – CO] (0.09), 398 [M^+ – 5 CO] (18), 369 (23), 368 (63), 275 (57), 263 (24), 163 (16), 125 (25), 105 (16), 75 (35), 73 (73), 53 (55), 52 (100).

{[(But-2-ynyloxy)methoxy](4-hydroxy-2,6-dimethylphenyl)methylene}pentacarbonylchromium(0) (54a)

The TBS-protected carbene complex **55a** (2.14 g, 3.97 mmol) was dissolved in anhyd Et_2O (20 mL), and then treated with NaOMe in MeOH (2 equiv). The mixture was stirred under argon at r.t. until TLC showed complete desilylation. The mixture was then quenched with H_2O, and extracted with Et_2O (2 × 10 mL). The combined organic layer was washed with brine (1 × 10 mL), dried ($MgSO_4$), concentrated, and chromatographed to afford the carbene complex with free hydroxy group **54a** as a red oil; yield: 995 mg, (59%). In most cases the carbene complex was characterized as the TBS derivative **55**. The *p*-phenol complex **54** was typically generated and utilized in the next step directly although it could be stored for periods of a day or so without decomposition; R_f = 0.20 (hexane–EtOAc, 2:1).

IR (neat): 3397 br w, 2965 w, 2933 w, 2231 w, 2068 s, 1917 vs, 1609 s, 1456 m, 1309 m, 1236 m, 1152 m, 897 m, 791 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.84 (s, 3 H), 2.11 (s, 6 H), 4.52 (s, 2 H), 4.84 (s, 1 H), 5.26 (s, 2 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 3.56, 19.47, 57.80, 72.60, 85.07, 97.08, 114.96, 128.74, 144.32, 155.17, 216.24, 224.56, 365.39.

MS: *m*/*z* (%) = 424 [M^+] (0.07), 159 (31), 149 (63), 122 (35), 119 (33), 115 (22), 108 (15), 107 (47), 104 (17), 91 (47), 82 (16), 80 (34), 79 (25), 77 (47), 69 (24), 65 (17), 54 (18), 53 (55), 52 (100), 50 (16).

Pentacarbonyl{(4-hydroxy-2,6-dimethylphenyl)[(pent-2-ynyloxy)methoxy]methylene}chromium(0) (54b)

Chloromethyl Pent-2-ynyl Ether (56b)

The chloromethyl ether **56b** was prepared from pent-2-yn-1-ol (210 mg, 2.50 mmol) according to the typical procedure.

^1H NMR ($CDCl_3$): δ = 1.09–1.16 (m, 3 H), 2.19–2.24 (m, 2 H), 4.35 (t, *J* = 2.2 Hz, 2 H), 5.58 (s, 2 H).

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl][(pent-2-ynyloxy)methoxy]methylene}pentacarbonylchromium(0) (55b)

The carbene complex **55b** was prepared from the salt **31** (1.08 g, 2.00 mmol) and chloromethyl ether **56b** (2.50 mmol) as red oil; yield: 1.07 g (97%); R_f = 0.25 (hexane–CH_2Cl_2, 9:1).

IR (neat): 2959 m, 2934 m, 2861 w, 2064 s, 1991 s, 1937 s, 1601 m, 1473 w, 1315 m, 1157 s, 1069 m, 841 s, 655 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.18 (s, 6 H), 0.96 (s, 9 H), 1.12 (t, *J* = 7.7 Hz, 3 H), 2.10 (s, 6 H), 2.17 (qt, *J* = 7.7, 2.2 Hz, 2 H), 4.55 (t, *J* = 2.2 Hz, 2 H), 5.26 (br s, 2 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.44, 12.39, 13.52, 18.16, 19.53, 25.60, 57.71, 72.74, 90.76, 97.19, 119.56, 128.17, 144.91, 155.26, 216.28, 224.66, 365.40.

MS: *m*/*z* (%) = 552 [M^+] (0.02), 412 (25), 410 (16), 383 (26), 382 (79), 380 (23), 301 (20), 263 (22), 179 (30), 126 (17), 107 (16), 80 (31), 75 (33), 73 (68), 67 (16), 52 (100).

Pentacarbonyl{(4-hydroxy-2,6-dimethylphenyl)[(pent-2-ynyloxy)methoxy]methylene}chromium(0) (54b)

The carbene complex **55b** (1.05 g, 1.90 mmol) was desilylated according to the above procedure to give phenol carbene complex **54b** as a red oil; yield: 384 mg (46%); R_f = 0.24 (hexane–Et_2O, 4:1).

IR (neat): 3407 br w, 2982 w, 2938 w, 2232 vw, 2064 s, 1937 vs, 1607 m, 1308 m, 1238 m, 1152 m, 1069 m, 891 m, 654 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.12 (t, *J* = 7.4 Hz, 3 H), 2.11 (s, 6 H), 2.20 (qt, *J* = 7.4, 2.2 Hz, 2 H), 4.55 (t, *J* = 2.2 Hz, 2 H), 5.28 (br s, 2 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 12.37, 13.49, 19.50, 57.73, 72.67, 90.81, 97.01, 114.96, 128.69, 144.22, 155.22, 216.24, 224.56, 365.31.

MS: *m*/z (%) = 438 [M^+] (0.03), 410 (0.05), 216 (15), 188 (16), 187 (55), 149 (100), 137 (17), 121 (27), 115 (16), 108 (33), 91 (37), 80 (42), 79 (18), 77 (35), 74 920), 67 (22), 65 (17), 59 (24), 55 (19), 54 (22), 52 (69), 51 (23).

Pentacarbonyl{(4-hydroxy-2,6-dimethylphenyl)[(4-methylpent-2-ynyloxy)methoxy]methylene}chromium(0) (54c)

Chloromethyl 4-Methylpent-2-ynyl Ether (56c)

The chloromethyl ether **56c** was prepared from 4-methylpent-2-yn-1-ol (392 mg, 4.00 mmol) according to the typical procedure.

^1H NMR ($CDCl_3$): δ = 1.17 (d, *J* = 7.1 Hz, 6 H), 2.56–2.59 (m, 1 H), 4.35 (d, *J* = 2.2 Hz, 2 H), 5.57 (s, 2 H).

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl][(4-methylpent-2-ynyloxy)methoxy]methylene}pentacarbonylchromium(0) (55c)

The carbene complex **55c** was prepared from the salt **31** (1.61 g, 3.00 mmol) and chloromethyl ether **56c** as red oil; yield: 1.16 g (68%); R_f = 0.40 (hexane–Et_2O, 4:1).

IR (neat): 2936 m, 2250 w, 2086 s, 1935 vs, 1601 m, 1474 w, 1315 m, 1156 s, 910 s, 841 s, 656 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.18 (s, 6 H), 0.96 (s, 9 H), 1.14 (d, *J* = 6.9 Hz, 6 H), 2.10 (s, 6 H), 2.55 (m, 1 H), 4.55 (d, *J* = 2.2 Hz, 2 H), 5.25 (br s, 2 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.47, 18.14, 19.51, 19.56, 20.39, 22.39, 22.73, 25.57, 65.56, 93.45, 97.36, 119.43, 119.63, 127.87, 128.30, 144.88, 155.20, 216.32, 224.63, 364.69.

MS *m*/*z* (%) = 538 [M^+ – CO] (0.03), 426 [M^+ – 5 CO] (32), 397 (31), 396 (100), 358 (19), 357 (79), 351 (21), 329 (25), 303 (36), 301 (39), 263 (57), 229 (18), 219 (18), 215 (17), 191 (15), 179 (40), 163 (22), 126 (21), 125 (20), 108 (19), 103 (18), 102 (21), 91 (19), 82 (34), 81 (38), 79 (52), 75 (40), 74 (30), 73 (91), 72 (77), 57 (19), 52 (68).

Pentacarbonyl{(4-hydroxy-2,6-dimethylphenyl)[(4-methylpent-2-ynyloxy)methoxy]methylene}chromium(0) (54c)

The carbene complex **55c** (467 mg, 0.825 mmol) was desilylated according to the typical procedure to give of phenol carbene complex **54c** as a red oil; yield: 206 mg (55%); R_f = 0.15 (hexane–CH_2Cl_2, 1:1).

IR (neat): 3402 br m, 2976 m, 2936 w, 2257 vw, 2068 s, 1927 vs, 1608 m, 1590 m, 1454 m, 1308 m, 1237 m, 1150 s, 1070 s, 898 s, 709 s cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.13 (d, *J* = 6.9 Hz, 6 H), 2.11 (s, 6 H), 2.56 (sept, *J* = 6.9 Hz, 1 H), 3.76 (br s, 1 H), 4.55 (d, *J* = 1.9 Hz, 2 H), 5.25 (s, 2 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 19.52, 20.48, 22.62, 57.64, 72.49, 94.85, 96.95, 114.93, 128.69, 144.30, 155.18, 216.24, 224.56, 365.33.

MS *m*/*z* (%) = 452 [M$^+$] (0.03), 312 [M$^+$ – 5 CO] (2), 187 (30), 180 (15), 149 (100), 121 (30), 91 (15), 90 (18), 80 (27), 79 (19), 77 (31), 53 (16), 52 (42).

Pentacarbonyl{[(1-ethylhex-2-ynyloxy)methoxy](4-hydroxy-2,6-dimethylphenyl)methylene}chromium(0) (54d)
Chloromethyl 1-Ethylhex-2-ynyl Ether (56d)
The chloromethyl ether **56d** was prepared from oct-4-yn-3-ol (315 mg, 2.50 mmol) according to the typical procedure.

^{1}H NMR ($CDCl_3$): δ = 0.97 (t, *J* = 7.4 Hz, 3 H), 0.98 (t, *J* = 7.1 Hz, 3 H), 1.52 (m, 2 H), 1.72 (m, 2 H), 2.19 (td, *J* = 7.2, 1.9, 2 H Hz), 4.46 (t, *J* = 6.3 Hz, 1 H), 5.56 (d, *J* = 5.4 Hz, 1 H), 5.72 (d, *J* = 5.4 Hz, 1 H).

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl][(2-ethylhex-2-ynyloxy)methoxy]methylene}pentacarbonylchromium(0) (55d)
The carbene complex **55d** was prepared from the salt **31** (1.05 g, 1.95 mmol) and chloromethyl ether **56d** as a red oil; yield: 1.16 g (100%); R_f = 0.13 (hexane).

IR (neat): 2963 m, 2936 m, 2886 w, 2237 vw, 2084 s, 1940 vs, 1601 m, 1471 m, 1315 m, 1253 m, 1155 s, 1064 m, 912 m, 841 s, 655 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 6 H), 0.94 (t, *J* = 7.4 Hz, 3 H), 0.96 (s, 9 H), 1.03 (t, *J* = 7.5 Hz, 3 H), 1.49 (q, *J* = 7.5 Hz, 2 H), 1.80 (m, 2 H), 2.10 (s, 6 H), 2.16 (td, *J* = 6.8, 1.9 Hz, 2 H), 4.67 (t, *J* = 6.4 Hz, 1 H), 5.20 (br s, 1 H), 5.43 (br s, 1 H), 6.47 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.48, 9.43, 13.36, 18.14, 19.44, 19.54, 20.58, 21.92, 25.58, 29.08, 71.06, 88.59, 97.67, 119.46, 119.62, 127.90, 128.24, 145.00, 155.21, 216.33, 224.63, 364.34.

MS *m*/*z* (%) = 594 [M$^+$] (0.03), 454 [M$^+$ – 5 CO] (19), 425 (18), 424 (47), 423 (37), 422 (91), 420 (25), 385 (15), 373 (15), 372 (24), 371 (22), 358 (20), 357 (33), 356 (39), 343 (16), 330 (20), 329 (53), 327 (25), 315 (23), 271 (17), 263 (63), 257 (33), 243 (17), 191 (23), 165 (16), 163 (18), 128 (19), 125 (18), 115 (19), 75 (36), 74 (24), 73 (100), 72 (64), 59 (18), 57 (36), 56 (28), 55 (24), 52 (47), 51 (25).

Pentacarbonyl{[(1-ethylhex-2-ynyloxy)methoxy](4-hydroxy-2,6-dimethylphenyl)methylene}chromium(0) (54d)
The carbene complex **55d** (951 mg, 1.60 mmol) was desilylated according to the typical procedure to give phenol carbene complex **54d** as a red oil; yield: 309 mg (40%); R_f = 0.25 (hexane–Et_2O, 4:1).

IR (neat): 3400 br w, 2970 w, 2933 w, 2881 w, 2237 vw, 2064 s, 1943 vs, 1149 m, 904 m, 654 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.93 (t, *J* = 7.4 Hz, 3 H), 1.03 (t, *J* = 7.4 Hz, 3 H), 1.49 (q, *J* = 7.1 Hz, 2 H), 1.80 (m, 2 H), 2.12 (s, 6 H), 2.17 (t, *J* = 7.1 Hz, 2 H), 4.67 (br s, 1 H), 5.28 (br s, 1 H), 5.44 (br, 1 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 9.43, 13.37, 19.44, 19.55, 20.58, 21.90, 29.07, 71.15, 88.72, 97.54, 114.88, 115.02, 128.46, 128.82, 144.40, 155.12, 216.31, 224.56, 364.30.

MS *m*/*z* (%) = 480 [M$^+$] (0.03), 318 (32), 290 (15), 289 (77), 275 (16), 261 (22), 25), 247 (43), 245 (47), 231 (25), 220 (17), 219 (17), 218 (19), 217 (100), 203 (40), 189 (39) 187 (20), 175 (42), 161 (27), 159 (15), 149 (65), 147 (22), 145 (16), 13 (20), 128 (18), 122 (31), 121 (31), 119 (19), 115 (24), 109 (18), 108 (49), 107 939), 105 (30), 97 (24), 95 (15), 94 (18), 93 (26), 91 (58), 81 (37), 80 (76), 79 (69), 78 (19), 77 (69), 69 (23), 67 (54), 65 (25), 57 (35), 55 (46), 53 (38), 52 (98).

Pentacarbonyl{(4-hydroxy-2,6-dimethylphenyl)[(4-methylpent-4-en-2-ynyloxy)methoxy]methylene}chromium(0) (54e)
Chloromethyl 4-Methylpent-4-en-2-ynyl Ether (56e)
The chloromethyl ether **56e** was prepared from 4-methylpent-4-en-2-yn-1-ol (384 mg, 4.00 mmol) according to the typical procedure.

^{1}H NMR ($CDCl_3$): δ = 1.87 (s, 3 H), 4.48 (s, 2 H), 5.26 (s, 1 H), 5.32 (s, 1 H), 5.57 (s, 2 H).

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl][(4-methylpent-4-en-2-ynyloxy)methoxy]methylene}pentacarbonylchromium(0) (55e)
The carbene complex **55e** was prepared from the salt **31** (1.34 g, 2.50 mmol) and chloromethyl ether **56e** as a red oil; yield: 919 mg (65%); R_f = 0.24 (hexane–CH_2Cl_2, 9:1).

IR (neat): 2957 w, 2932 w, 2220 vw, 2064 s, 1940 s, 1601 w, 1315 w, 1155 w, 841 m, 653 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 6 H), 0.96 (s, 9 H), 1.86 (s, 3 H), 2.10 (s, 6 H), 4.69 (s, 2 H), 5.27–5.30 (4 H), 6.48 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = –4.44, 18.15, 19.54, 23.07, 25.59, 57.63, 81.24, 89.47, 97.03, 119.58, 123.29, 125.72, 128.19, 155.30, 216.25, 224.64, 365.59.

MS *m*/*z* (%) = 564 [M$^+$] (0.08), 263 (17), 262 (25), 221 (23), 220 (40), 207 (46), 191 (16), 179 (94), 177 (12), 163 (16), 149 (14), 107 (62), 105 (27), 86 (64), 84 (98), 80 (100), 77 (16), 75 (100), 73 (47), 59 (55), 57 (16), 51 (100), 49 (94), 45 (27).

Pentacarbonyl& lcub;(4-hydroxy-2,6-dimethylphenyl)[(4-methylpent-4-en-2-ynyloxy)methoxy]methylene}chromium(0) (54e)
The carbene complex **55e** (722 mg, 1.28 mmol) was desilylated according to the typical procedure to give phenol carbene complex **54e** as a red oil; yield: 287 mg (50%); R_f = 0.21 (hexane–Et_2O, 2:1).

IR (neat): 3384 br w, 2959 w, 2928 w, 2228 vw, 2064 sm 1940 vs, 1609 m, 1456 m, 1307 m, 1236 m, 1150 m, 1064 m, 897 m, 653 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.86 (s, 3 H), 2.12 (s, 6 H), 4.69 (s, 2 H), 5.05 (br s, 4 H), 6.47 (s, 2 H).

^{13}C NMR ($CDCl_3$) δ = 19.53, 23.09, 57.66, 81.19, 89.48, 96.84, 114.97, 123.37, 125.69, 128.75, 144.27, 155.18, 216.23, 224.56, 365.52.

MS *m*/*z* (%) = 394 [M$^+$ – 2 CO] (0.2), 228 (12), 213 (15), 187 (10), 185 (16), 149 (100), 121 (16), 115 (12), 108 (11), 91 (29), 80 (16), 79 (30), 78 (14), 77 (52), 53 (15), 52 (23), 51 (15).

{[(5-Benzyloxy-4-methylpent-2-ynyloxy)methoxy](4-hydroxy-2,6-dimethylphenyl)methylene}pentacarbonylchromium(0) (54f)
5-Benzyloxy-4-methylpent-2-ynyl Chloromethyl Ether (56f)
The chloromethyl ether **56f** was prepared from 4-(benzyloxy)methyl)pent-2-yn-1-ol (334 mg, 1.64 mmol) according to the typical procedure.

^{1}H NMR ($CDCl_3$): δ = 1.19 (d, *J* = 6.9 Hz, 3 H), 2.77 (m, 1 H), 3.37 (dd, 1 H), 3.49 (dd, 1 H), 4.36 (d, *J* = 2.2 Hz, 2 H), 4.54 (s, 2 H), 5.56 (s, 2 H), 7.32 (m, 5 H).

{[(5-Benzyloxy-4-methylpent-2-ynyloxy)methoxy][4-(*tert*-butyldimethylsiloxy)-2,6-dimethylphenyl]methylene}pentacarbonylchromium(0) (55f)
The carbene complex **55f** was prepared from the salt **31** (700 mg, 1.30 mmol) and chloromethyl ether **56f** as red oil; yield: 748 mg (86%); R_f = 0.45 (hexane–EtOAc, 9:1).

^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 6 H), 0.96 (s, 9 H), 1.18 (d, *J* = 7.1 Hz, 3 H), 2.08 (s, 6 H), 2.77 (m, 1 H), 3.36 (dd, 1 H), 3.47 (dd, 1 H),

4.51 (s, 2 H), 4.56 (d, *J* = 2.2 Hz, 2 H), 5.24 (br s, 2 H), 6.47 (s, 2 H), 7.27–7.35 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = –4.44, 17.45, 18.15, 19.54, 25.59, 26.83, 57.56, 73.02, 73.60, 74.30, 91.03, 97.00, 119.55, 127.57, 127.65, 128.17, 128.35, 138.05, 144.91, 155.27, 216.26, 224.64, 365.58.

IR (neat): 2959 w, 2933 w, 2862 w, 2243 w, 2064 s, 1943 vs, 1601 m, 1471 w, 1316 m, 1156 m, 841 m, 655s cm^{-1}.

{[(5-Benzyloxy-4-methylpent-2-ynyloxy)methoxy](4-hydroxy-2,6-dimethylphenyl)methylene}pentacarbonylchromium(0) (54f)

The carbene complex **55f** (560 mg, 0.832 mmol) was desilylated according to the typical procedure to give phenol carbene complex **54f** as a red oil; yield: 175 mg (36%).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 54a; Typical Procedure

A 100-mL single-necked flask which had its 14/20 joint replaced with a threaded Teflon high-vacuum stop-cock was flushed with N_2 for 10 min before it was charged with the carbene complex **54a** (155 mg, 0.365 mmol) and benzene (0.1 M, 36.5 mL). The mixture was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles), back-filled with 1 atm of argon at r.t., sealed and heated at 60 °C for 4 h. The mixture was cooled to r.t., and then diluted with Et_2O. After stirring at r.t. for 2 h in air, the soln was passed through Celite, concentrated, and then purified by chromatography (silica gel, hexane–EtOAc, 2:1) to afford the cyclized product **53a** as a yellow solid ; yield: 44.5 mg (51%); R_f = 0.20 (hexane–EtOAc, 2:1).

IR (neat): 2958 w, 2920 w, 1642 s, 1575s, 1443 w, 1424 w, 1180 m, 1072 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 3 H), 1.79 (s, 3 H), 1.88 (d, *J* = 14.8 Hz, 1 H), 2.17 (s, 3 H), 2.43 (d, *J* = 14.8 Hz, 1 H), 4.69 (s, 2 H), 5.16 (s, 2 H), 5.61 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 10.16, 20.50, 22.55, 46.28, 51.47, 65.28, 92.16, 120.14, 120.80, 125.38, 150.03, 150.30, 152.07, 198.81.

MS *m*/*z* (%) = 233 (48), 232 [M$^+$] (94), 203 (17), 202 (96), 187 (75), 174 (85), 159 (100), 131 (51), 115 (21), 91 (27), 51 (15).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 54b

A soln of carbene complex **54b** (134 mg, 0.307 mmol) in benzene (30.7 mL) was heated according to the typical procedure to give **53b** (7.0 mg, 9%) and **58b** (21.0 mg, 25%) after purification.

Indeno[1,2-*d*][1,3]dioxin-7(4*H*)-one 53b

R_f = 0.25 (hexanes–EtOAc, 2:1).

IR (neat): 2924 m, 1635 s, 1578 s, 1456 m, 1180 m, 1074 m, 918 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.07 (t, *J* = 7.7 Hz, 3 H), 1.10 (s, 3 H), 1.95 (d, *J* = 14.8 Hz, 1 H), 2.19 (s, 3 H), 2.22–2.32 (m, 2 H), 2.42 (d, *J* = 14.8 Hz, 1 H), 4.76 (s, 2 H), 5.18 (s, 2 H), 5.65 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 13.09, 19.30, 20.65, 22.57, 46.54, 51.76, 65.50, 91.98, 119.72, 120.84, 125.53, 150.15, 150.36, 157.90. 198.86.

MS *m*/*z* (%) = 246 [M$^+$] (55), 216 (30), 188 (100), 187 (73), 160 (28), 159 (38), 131 (27), 91 (15).

Naphtho[1,2-*d*][1,3]dioxin-6,8-dione 58b

R_f = 0.11 (hexanes–EtOAc, 2:1).

IR (neat): 2971 w, 1659 s, 1626 m, 1363 w, 1251 m, 1184 m, 1076 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.98 (t, *J* = 7.4 Hz, 3 H), 1.19 (s, 3 H), 2.10–2.20 (m, 1 H), 2.26 (d, *J* = 16.8 Hz, 1 H), 2.30 (s, 3 H), 2.35–2.44 (m, 1 H), 2.85 (d, *J* = 16.8 Hz, 1 H), 4.81 (q, *J* = 16.5 Hz, 2 H), 5.09 (d, *J* = 5.7 Hz, 1 H), 5.24 (d, *J* = 5.7 Hz, 1 H), 5.84 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.12, 17.83, 24.79, 26.96, 44.07, 48.57, 65.18, 90.63, 122.56, 127.60, 135.37, 136.66, 145.81, 151.81, 196.97, 200.84.

MS *m*/*z* (%) = 274 [M$^+$] (38), 259 (15), 231 (26), 230 (21), 229 (100), 216 (38), 215 (27), 202 (17), 201 (56), 188 (27), 159 (23), 93 (19), 91 (17), 77 (20), 65 (15).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 54c

A soln of carbene complex **54c** (206 mg, 0.456 mmol) in benzene (45.6 mL) was heated according to the typical procedure to give **58c** (20.3 mg, 16%) as a yellow solid after purification; R_f = 0.22 (hexanes–Et_2O, 1:1).

IR (neat): 2926 m, 1661 s, 1615 m, 1383 m, 1251 m, 1186 m, 1074 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 3 H), 1.16 (d, *J* = 6.8 Hz, 3 H), 1.27 (d, *J* = 6.8 Hz, 3 H), 2.27 (d, *J* = 17.0 Hz, 1 H), 2.31 (s, 3 H), 2.58 (m, 1 H), 2.81 (d, *J* = 17.0 Hz, 1 H), 4.72 (d, *J* = 16.8 Hz, 1 H), 4.95 (d, *J* = 16.8 Hz, 1 H), 5.07 (d, *J* = 5.5 Hz, 1 H), 5.23 (d, *J* = 5.5 Hz, 1 H), 5.86 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 18.68, 21.22, 24.91, 25.90, 27.36, 29.70, 43.46, 65.47, 90.41, 121.93, 127.72, 135.65, 138.60, 146.16, 151.40, 197.20, 201.32.

MS *m*/*z* (%) = 289 (16), 288 [M$^+$] (57), 273 (18), 259 (20), 258 (86), 245 (52), 244 (100), 243 (26), 231 (26), 216 (33), 215 (40), 203 (17), 201 (24), 189 (18), 188 (24), 187 (43), 176 (19), 173 (24), 159 (26), 145 (20), 131 (15), 115 (20), 91 (23), 77 (30), 51 (16).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 54d

A soln of carbene complex **54d** (120 mg, 0.250 mmol) in benzene (25.0 mL) was heated according to the typical procedure to give **53d** (13.1 mg, 18%) and **58d** (16.8 mg, 21%) after purification.

Indeno[1,2-*d*][1,3]dioxin-7(4*H*)-one 53d

Yellow solid; R_f = 0.30 (hexanes–Et_2O, 1:1).

IR (neat): 2963 m, 1657 m, 1632 s, 1568 s, 1557 m, 1425 w, 1182 w, 1065 m, 922 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.95 (t, *J* = 7.4 Hz, 3 H), 1.01 (t, *J* = 7.4 Hz, 3 H), 1.09 (s, 3 H), 1.12–1.40 (m, 2 H), 1.50–1.62 (m, 1 H), 1.81–1.88 (m, 2 H), 1.93 (d, *J* = 14.7 Hz, 1 H), 2.10–2.26 (m, 1 H), 2.19 (s, 3 H), 2.53 (d, *J* = 14.7 Hz, 1 H), 4.70 (t, *J* = 6.1 Hz, 1 H), 5.09 (d, *J* = 5.8 Hz, 1 H), 5.25 (d, *J* = 5.8 Hz, 1 H), 5.63 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 9.33, 14.69, 20.68, 22.51, 22.76, 25.69, 28.83, 46.77, 51.77, 76.13, 88.87, 119.58, 120.72, 129.67, 150.42, 150.90, 157.34, 198.89.

MS *m*/*z* (%) = 288 [M$^+$] (34), 258 (46), 243 (21), 229 (25), 217 (16), 216 (96), 215 (100), 201 (39), 188 (39), 187 (67), 173 (23), 171 (15), 159 (31), 145 (20), 143 (17), 141 (20), 129 (26), 128 (51), 115 (32), 105 (21), 93 (18), 91 (39), 77 (26), 65 (19), 57 (15), 55 (18), 53 (17).

Naphtho[1,2-*d*][1,3]dioxin-6,8-dione 58d

Yellow solid; R_f = 0.27 (hexanes–Et_2O, 2:1).

IR (neat): 2967 m, 2930 w, 2874 w, 1771 w, 1663 s, 1620 w, 1361 w, 1076, 1012 w cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.97 (t, *J* = 7.5 Hz, 3 H), 1.04 (t, *J* = 7.4 Hz, 3 H), 1.16 (s, 3 H), 1.33–1.40 (m, 1 H), 1.45–1.49 (m, 1 H), 1.82–1.88 (m, 2 H), 2.10–2.16 (m, 1 H), 2.28 (dd, *J* = 16.7, 1.1 Hz, 1 H), 2.31 (s, 3 H), 2.37–2.39 (m, 1 H), 2.82 (dd, *J* = 16.7, 1.1 Hz, 1 H),

4.94 (dd, J = 7.1, 4.0 Hz, 1 H), 4.97 (d, J = 5.8 Hz, 1 H), 5.21 (d, J = 5.8 Hz, 1 H), 5.86 (t, J = 1.1 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 9.12, 14.54, 21.90, 24.81, 26.49, 28.14, 28.61, 43.79, 48.42, 74.79, 88.10, 121.12, 127.34, 135.42, 141.05, 148.85, 151.33, 197.06, 202.44.

MS m/z (%) = 316 [M$^+$] (17), 286 (39), 271 (100), 257 (22), 243 (63), 173 (43), 215 (55), 201 (25), 187 (39), 159 (24), 149 (29), 129 (16), 128 (37), 115 (24), 107 (23), 93 (20), 92 (38), 91 (45), 79 (27), 77 (19), 76 (35), 67 (27), 64 (15), 57 (19), 55 (26), 53 (20).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 54e

A soln of carbene complex **54e** (184 mg, 0.408 mmol) in benzene (40.8 mL) was heated according to the typical procedure to give **61** (59.1 mg, 51%) as a light yellow solid after purification; R_f = 0.31 (hexanes–Et_2O, 1:1).

IR (neat): 3400 br, 2924 m, 2857 w, 1754 s, 1611 m, 1318 m, 1194 s, 1157 m, 1017 m, 904 w, 736 w cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.56 (s, 3 H), 2.20 (s, 6 H), 2.96 (s, 2 H), 4.61 (s, 2 H), 5.15 (s, 2 H), 5.40 (s, 1 H), 6.50 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 16.49, 19.75, 51.67, 64.53, 90.38, 105.44, 114.53, 126.31, 139.23, 140.96, 150.59, 156.03, 168.65, 188.81.

MS m/z (%) = 286 [M$^+$] (20), 241 (59), 213 (58), 185 (23), 149 (100), 121 (28), 91 (33), 77 (27).

Intramolecular Tautomer-Arrested Annulation of Carbene Complex 54f

A soln of carbene complex **54f** (87.0 mg, 0.156 mmol) in benzene (15.6 mL) was heated according to the typical procedure to give unstable cyclized product, which was decomposed during isolation.

Intermolecular Reaction of Carbene Complex 19 with Isopropyl(methyl)acetylene; Typical Procedure

A 25-mL single-necked flask which had its 14/20 joint replaced with a threaded Teflon high-vacuum stop-cock was flushed with N_2 for 10 min before it was charged with the carbene complex **19** (173 mg, 0.486), isopropyl(methyl)acetylene (79.5 mg, 0.97 mmol), and benzene (9.72 mL). The mixture was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles), back-filled with 1 atm of argon at r.t., sealed and heated at 110 °C for 8 h. The mixture was cooled to r.t., and then diluted with Et_2O. After stirring at r.t. for 2 h in air, the soln was passed through Celite, concentrated, and then purified by chromatography (silica gel, hexanes–Et_2O, 2:1) to give compound **62** (52.1 mg, 44%) and compound **63** (17.9 mg, 15%).

Inden-5-one 62

R_f = 0.24 (hexane–Et_2O, 2:1).

IR (neat): 2963 m, 2932 w, 1655 s, 1626 m, 1570 s, 1445 w, 1318 m, 1119 w cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.06 (s, 3 H), 1.12 (d, J = 7.1 Hz, 3 H), 1.20 (d, J = 7.2 Hz, 3 H), 1.88 (d, J = 15.1 Hz, 1 H), 1.93 (s, 3 H), 2.21 (s, 3 H), 2.55 (d, J = 15.0 Hz, 1 H), 2.62 (sept, J = 7.1 Hz, 1 H), 3.72 (s, 3 H), 5.67 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 10.76, 20.29, 21.31, 21.70, 21.79, 27.04, 46.34, 52.35, 60.73, 122.69, 128.07, 131.82, 149.44, 159.89, 163.19, 199.55.

MS m/z (%) = 247 (54), 246 [M$^+$] (100), 245 (22), 244 (44), 231 (57), 204 (37), 203 (89), 201 (35), 189 (38), 188 (15), 187 (17), 176 (15), 175 (63), 173 (22), 171 (17), 161 (26), 160 (18), 159 (17), 145 (22), 115 (15), 91 (21), 77 (16).

Inden-6-ol 63

R_f = 0.37 (hexane–Et_2O, 2:1).

IR (neat): 3386 br, 2983 s, 2932 m, 2874 w, 1644 w, 1609 m, 1468 m, 1360 m, 1306 m, 1145 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.54 (d, J = 6.6 Hz, 3 H), 0.94 (d, J = 6.6 Hz, 3 H), 1.16 (s, 3 H), 1.79 (s, 3 H), 1.89 (m, 1 H), 2.44 (s, 3 H), 3.72 (s, 3 H), 4.81 (s, 1 H), 6.43 (s, 1 H), 6.64 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 8.72, 17.32, 17.91, 21.86, 33.83, 51.92, 60.14, 60.20, 108.46, 115.24, 129.86, 130.04, 130.66, 151.65, 152.96, 153.37.

MS m/z (%) = 247 (31), 246 [M$^+$] (95), 231 (61), 204 (29), 203 (100), 189 (26), 175 (38), 171 (17), 161 (25), 149 (32), 91 (18).

In one instance the reaction of complex **19** (reaction temperature varied between 90 and 110 °C) with isopropyl(methyl)acetylene gave inden-5-one **62** that was pure. In other reactions at 110 °C the inden-5-one **62** co-eluted with another compound which has remained unidentified. The ratio of **62** to unknown is typically about 14:1. GC-MS of the mixture reveals that the unknown is an isomer of **62**.

MS: m/z (%) = 247 (57), 246 [M$^+$] (100), 231 (49), 204 (20), 203 (19), 189 (17), 175 (30), 161 (17).

In an effort to obtain ^{13}C NMR data for the unknown compound the reaction was repeated on carbene complex **19** (1.174 g, 3.30 mmol) to give phenol **63** (414 mg, 51%) and of a mixture of **62** and the unknown (14:1, 233 mg, 29%). The ^{13}C NMR spectrum of this mixture revealed a peak at δ = 170.2 and 232.6 for the unknown but no other peaks in between. This rules out the regioisomeric **64a** as a structure for the unknown (Scheme 11). Indenes of the type **64b** and **64c** (Scheme 11) with a methoxy group at a sp^3-carbon adjacent to the benzene ring would be expected to have the methoxy group show an absorption between δ = 3.0 and 3.5 ppm in the ^{1}H NMR.[9] The lack of any absorption in the ^{1}H NMR in this region would allow us to eliminate structures **64b** and **64c** as possibilities. While there is a methoxy at δ = 3.84 that would be in the range expected for the methoxy in structure **64d** (Scheme 11), the lack of two different aromatic protons in the region of δ = 6–7 ppm can be used to rule out structure **64d**. There is a singlet 2 H absorption (relative to the methoxy at δ = 3.84 ppm) at δ = 6.52 ppm that suggests that cyclization to the aryl group has not occurred and that the aryl ring is still symmetrical. The two aryl protons in **63** are at δ = 6.43 and 6.64 ppm and it would not be expected that the two aryl protons in the closely related compound **64d** would have identical shifts. This conclusion is also supported by the pattern of the aryl carbons in the ^{13}C NMR spectrum. Compound **63** has three carbons between δ = 129–131 ppm and three carbons between δ = 151–153 ppm. In the ^{13}C NMR spectrum of the mixture of **62** and the unknown, there could be at most three carbons in these two ranges. There does appear to be carbons from the unknown at δ = 170.2, 157.6, 152.6, 137.5, 124.5 ppm. Although the structure of the unknown could not be determined, the spectral data that was obtained on the mixture are not consistent with structures **64a–d** in Scheme 11 and thus with any cyclized structure resulting from the incorporation of the alkyne with the opposite regiochemistry observed for **62**.

Intermolecular Reaction of Carbene Complex 19 with *tert*-Butyl(methyl)acetylene

A soln containing carbene complex **19** (142 mg, 0.40 mmol) and *tert*-butyl(methyl)acetylene (77.0 mg, 0.8 mmol) in benzene (8 mL) was reacted at 110 °C for 8 h according to the typical procedure. The mixture was cooled to r.t., and then diluted with Et_2O. After stirring at r.t. for 2 h in air, the soln was passed through Celite, concentrated, and then purified by chromatography (silica gel, hexane–Et_2O, 2:1) to give compound **65** (18.6 mg, 18%) and compound **66** (42.8 mg, 41%).

Inden-5-one 65

R_f = 0.21 (hexane–Et_2O, 2:1).

IR (neat): 2961 m, 1655 s, 1622 s, 1570 m, 1547 m, 1447 m, 1395 m, 1329 m, 1124 m cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.24 (s, 3 H), 1.28 (s, 9 H), 1.99 (s, 3 H), 2.07 (d, *J* = 15.3 Hz, 1 H), 2.22 (s, 3 H), 2.98 (d, *J* = 15.3 Hz, 1 H), 3.69 (s, 3 H), 5.72 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.40, 20.48, 22.70, 30.83, 35.96, 47.26, 53.88, 60.83, 122.84, 129.05, 133.40, 149.13, 159.45, 164.43, 199.83.

MS *m*/*z* (%) = 261 (47), 260 [M^+] (100), 245 (18), 204 (53), 203 (20), 189 (69), 175 (17), 161 (22).

Inden-6-ol 66
White solid; R_f = 0.38 (hexane–Et_2O, 2:1).

IR (neat): 3387 br m, 2961 s, 1635 m, 1597 m, 1359 s, 1302 m, 1251 m, 1155 m, 1136 m, 1708 m, 1007 m, 860 w cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.90 (s, 9 H), 1.18 (s, 3 H), 1.90 (s, 3 H), 2.44 (s, 3 H), 3.72 (s, 3 H), 4.69 (br s, 1 H), 6.42 (s, 1 H), 6.71 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.72, 17.72, 17.86, 27.22, 35.81, 54.76, 59.87, 110.13, 115.13, 129.43, 130.54, 130.79, 152.37, 152.78, 154.85.

MS *m*/*z* (%) = 260 [M^+] (5), 204 (17), 203 (100), 188 (9), 145 (5).

5-(Triisopropylsiloxy)pent-3-yn-2-one (74b); Typical Procedure
A soln of 3-(triisopropylsiloxy)prop-1-yne (**73b**; 5.4 g, 25.5 mmol) in THF (120 mL) was cooled at –40 °C. A soln of 1.7 M *n*-BuLi in pentane (16.5 mL, 28 mmol) was added slowly. After 1 h at –40 °C, *N*-methoxy-*N*-methylacetamide (2.88 g, 28 mmol) was added. The mixture was warmed up to r.t. slowly and stirred for a further 1 h. After addition of H_2O (50 mL), the organic layer was extracted with Et_2O (3 × 25 mL). The combined organic layers were dried ($MgSO_4$). The product was purified by column chromatography (silica gel, hexanes–Et_2O, 9:1) to give **74b** as a light yellow liquid; yield: 67%; R_f = 0.55 (hexanes–Et_2O, 9:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (m, 21 H), 2.36 (s, 3 H), 4.56 (s, 2 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 11.85, 17.80, 32.50, 51.73, 84.04, 90.25, 184.19.

MS (EI): *m*/*z* (%) = 211 (84), 169 (71), 141 (100), 125 (51), 111 (37), 99 (14), 87 (12), 75 (23), 61 (29), 43 (26).

1-Methoxy-2-methylpent-1-en-3-yne (71); Typical Procedure
Into a round–bottomed flask containing Et_2O (250 mL) was introduced Ph_3PCH_2OMeCl (36.7 g, 107 mmol). The soln was cooled to –78 °C under a blanket of argon and 1.7 M *t*-BuLi in pentane (63 mL, 107 mmol) was added slowly. The red mixture was stirred at –78 °C for 0.5 h. Then ketone **74a** (7.95 g, 97 mmol) was added and the mixture was stirred for a further 2 h. Before warming to r.t., H_2O (60 mL) was added. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and the amount of Et_2O was reduced to ~10 mL. Hexanes (50 mL) was added to the soln to remove much of the phosphine oxide. After filtration and evaporation, the mixture was purified by column chromatography (silica gel, gradient of pentane–Et_2O from 100:0 to 95:5) to separate the *Z*- and *E*-isomers. The isomeric ratio varies from 60:40 to 50:50 and the combined yield is typically 65%.

(*E*)-1-Methoxy-2-methylpent-1-en-3-yne [(*E*)-71]
Colorless liquid; R_f = 0.65 (hexanes–Et_2O, 95:5).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.70 (s, 3 H), 1.93 (s, 3 H), 3.64 (s, 3 H), 6.31 (br s, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 4.15, 14.03, 59.85, 79.55, 82.30, 97.44, 151.70.

(*Z*)-1-Methoxy-2-methylpent-1-en-3-yne [(*Z*)-71]
Light yellow liquid; R_f = 0.52 (hexanes–Et_2O, 95:5).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.64 (s, 3 H), 1.98 (s, 3 H), 3.64 (s, 3 H), 6.10 (br s, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 4.46, 13.93, 59.93, 76.53, 89.73, 95.24, 150.79.

1-Methoxy-2-methyl-5-(triisopropylsiloxy)pent-1-en-3-yne (72)
This compound was prepared from the ketone **74b** according to the typical procedure. Purification gave **72**; yield: 67%; ratio *E*/*Z* 50:50. A gradient of hexanes–Et_2O from 100:0 to 95:5 was used to separate the *Z*- and *E*-isomers.

(*E*)-1-Methoxy-2-methyl-5-(triisopropylsiloxy)pent-1-en-3-yne [(*E*)-72]
Light yellow liquid; R_f = 0.60 (hexanes–Et_2O, 95:5).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 (m, 21 H), 1.71 (d, *J* = 1.5 Hz, 3 H), 3.68 (s, 3 H), 4.50 (s, 2 H), 6.37 (d, *J* = 1.5 Hz, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 12.53, 17.86, 22.64, 31.58, 52.46, 60.06, 85.20, 96.65, 152.90.

(*Z*)-1-Methoxy-2-methyl-5-(triisopropylsiloxy)pent-1-en-3-yne [(*Z*)-72]
Light yellow liquid; R_f = 0.50 (hexanes–Et_2O, 95:5).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (m, 21 H), 1.70 (s, 3 H), 3.69 (s, 3 H), 4.58 (s, 2 H), 6.17 (s broad, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 12.04, 17.95, 22.65, 31.59, 52.65, 60.11, 81.81, 92.19, 151.84.

Intermolecular Reaction of Carbene Complex 19 with 1-Methoxy-4-(trimethylsilyl)but-1-en-3-yne (69)
A 25-mL single-necked flask which had its 14/20 joint replaced with a threaded Teflon high-vacuum stop-cock was flushed with N_2 for 10 min before it was charged with the carbene complex **19** (247 mg, 0.69 mmol), (*Z*)-enyne (*Z*)-**69**[15] (321 mg, 2.1 mmol) and heptane (0.5 M, 1.4 mL). The mixture was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles), back-filled with 1 atm of argon at r.t., sealed and heated at 110 °C for 10 h. The reaction was diluted with Et_2O and stirred in air overnight. After filtration and concentration, the residue was column chromatographed (silica gel, 20% EtOAc–hexanes). The first band collected was rechromatographed (Et_2O–CH_2Cl_2–hexanes, 1:1:10 and then with 1:1:4) to give (*E*)-**75** (40.0 mg, 18%). The second band contained (*Z*)-**75** (41.5 mg, 19%), which isomerized slowly upon standing to the *E* compound.

(*Z*)-75
Yellow oil.

^1H NMR ($CDCl_3$): δ = 0.29 (s, 9 H), 1.19 (s, 3 H), 1.97 (d, *J* = 15.6 Hz, 1 H), 2.26 (d, *J* = 0.9 Hz, 3 H), 3.09 (d, *J* = 15.7 Hz, 1 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 5.18 (d, *J* = 7.5 Hz, 1 H), 5.73 (br s, 1 H), 5.95 (d, *J* = 7.3 Hz, 1 H).

MS *m*/*z* (%) = 318 [M^+] (69), 303 (23), 288 (8), 260 (6), 245 (9), 89 (18), 73 (100).

(*E*)-75
Yellow oil; R_f = 0.31 (20% EtOAc–hexanes).

^1H NMR ($CDCl_3$): δ = 0.33 (s, 9 H), 1.22 (s, 3 H), 2.19 (d, *J* = 15.4 Hz, 1 H), 2.27 (s, 3 H), 2.60 (d, *J* = 15.4 Hz, 1 H), 3.67 (s, 3 H), 3.69 (s, 3 H), 5.66 (s, 1 H), 5.94 (d, *J* = 13 Hz, 1 H), 6.84 (d, *J* = 13 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.53, 20.36, 25.90, 48.73, 53.81, 57.24, 62.06, 102.82, 122.42, 130.91, 135.58, 149.78, 150.79, 164.58, 167.65, 199.11.

MS *m*/*z* (%) = 318 [M$^+$] (62), 303 (23), 288 (7), 275 (11), 260 (8), 245 (9), 115 (9), 83 (32), 73 (100).

(*E*)-1-Methoxy-2-methyl-4-(trimethylsilyl)but-1-en-3-yne [(*E*)-70]

This was prepared by a modification of a procedure original published by Zweifel.[15] To a soln of (*Z*)-1-methoxy-4-(trimethylsilyl)but-1-en-3-yne (**69**; 8.21 g, 53.2 mmol) and TMEDA (8.0 mL, 53.2 mmol) in THF (120 mL) at –78 °C was added 2.5 M *n*-BuLi in hexanes (21.3 mL, 53.2 mmol) over 15 min. The pale yellow soln was stirred at –78 °C for 2 h. MeI (6.6 mL, 106.4 mmol) was added all at once and the mixture was stirred at –78 °C for a further 2 h and then overnight at 0 °C. After quenching with H_2O at 0 °C, the mixture was poured into pentane, washed with H_2O and brine, dried ($MgSO_4$), and concentrated via distillation at ambient pressure under N_2. Distillation at 2.4–2.7 mbar into an ice-cooled receiver gave two fractions: (1) bp 45–54 °C, pure (*E*)-**70** (4.42 g, 49%) and (2) bp 52–74 °C, slightly impure (*E*)-**70** (1.20 g, contains about 10% (*Z*)-**69**). (*E*)-**70** was obtained as a colorless, musty-smelling liquid, slowly oxidized with molybdate; R_f = 0.20 (pentane).

IR (neat): 2959 s, 2935 m, 2229 m, 2144 s, 2113 m, 1641 s, 1250 s, 1227 s, 1139 s, 871 s, 841 s, 760 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 9 H), 1.68 (d, *J* = 1.4 Hz, 3 H), 3.65 (s, 3 H), 6.45 (q, *J* = 1.4 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.14, 13.62, 60.06, 90.58, 106.23, 154.03.

Alkyne (*E*)-**70** was photolyzed in benzene in a Rayonet reactor to give a sample of (*Z*)-**70**.

^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 9 H), 1.93 (s, 3 H), 3.69 (s, 3 H), 6.17 (s, 1 H).

Intermolecular Reaction of Carbene Complex 19 with Zweifel's Enyne (*E*)-70

An 8-mL heavy-walled tube that was topped with a threaded Teflon high-vacuum stop-cock was flushed with N_2 for 10 min before it was charged with the carbene complex **19** (106 mg, 0.30 mmol), (*E*)-**70** (100 mg, 0.59 mmol), and benzene (0.5 M, 0.60 mL). The mixture was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles), back-filled with 1 atm of argon at r.t., sealed and heated at 110 °C for 8 h. Purification by chromatography (silica gel, Et_2O–CH_2Cl_2–hexanes, 1:1:4) gave a mixture of **76a** and isomeric aromatized indanol **77**; combined yield: 44.1 mg (44%); ratio 9:1.

Inden-6-ol 77

Pale yellow oil; R_f = 0.46 (20% EtOAc–hexanes).

IR (neat): 3396 br w, 2954 m, 2933 m, 1603 m, 1554 m, 1285 m, 1247 m, 1221 m, 1125 s, 862 m, 836 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.23 (s, 9 H), 1.06 (s, 3 H), 1.34 (s, 3 H), 2.48 (s, 3 H), 3.64 (s, 3 H), 3.72 (s, 3 H), 4.63 (br s, 1 H), 6.09 (s, 1 H), 6.46 (m, 2 H).

Inden-5-one 76a

Yellow oil at r.t., can be crystallized ($CHCl_3$–hexanes, 0 °C); R_f = 0.42 (20% EtOAc–hexanes).

IR ($CHCl_3$): 2957 m, 1657 s, 1586 vs, 1443 m, 1268 m, 1248 s, 1227 s, 1160 m, 1131 s, 1103 m cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 9 H), 1.09 (s, 3 H), 1.74 (d, *J* = 1 Hz, 3 H), 2.08 (d, *J* = 15.3 Hz, 1 H), 2.26 (s, 3 H), 2.63 (d, *J* = 15 Hz, 1 H), 3.65 (s, 3 H), 3.71 (s, 3 H), 5.70 (s, 1 H), 5.81 (br s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 0.85, 14.29, 20.59, 23.55, 47.17, 55.47, 59.74, 61.57, 111.29, 123.02, 129.93, 137.48, 145.97, 149.98, 163.27, 173.84, 199.42.

MS *m*/*z* (%) = 332 [M$^+$] (49), 317 (10), 302 (8), 259 (6), 213 (10), 89 (16), 73 (100).

HRMS: *m*/*z* [M$^+$] calcd for $C_{19}H_{28}O_3Si$: 332.1808; found: 332.1850.

The regiochemistry of the inden-5-one **76a** from the reaction of carbene complex **19** and enyne (*E*)-**70** was assigned based on the fact that reduction of **76a** with DIBAL-H at 0 °C gave a 4:1 mixture of the alcohols **78** which when treated with silica gel underwent hydrolysis and dehydration to give an a bright yellow oil that was assigned the structure of aldehyde **79**. The other possible regioisomer **76b** could not undergo hydrolysis and dehydration to give **79**. Spectra data for major isomer of **79** is given; R_f = 0.64 (20% EtOAc–hexanes).

IR ($CHCl_3$): 2957 m, 1652 vs, 1495 s, 1336 m, 1249 m, 845 s cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 9 H), 0.99 (s, 3 H), 1.91 (s, 3 H), 2.10 (s, 3 H), 2.18 (d, *J* = 17 Hz, 1 H), 2.80 (dd, *J* = 17, 5.7 Hz, 1 H), 3.88 (s, 3 H), 5.96–6.01 (m, 2 H), 9.71 (s, 1 H).

Finally the structure of **76a** was confirmed by X-ray diffraction analysis.

Intermolecular Reaction of Carbene Complex 19 with 1-Methoxy-2-methylpent-1-en-3-yne [(*E*)-71]; Typical Procedure

The chromium carbene complex **19** (142 mg, 0.4 mmol), (*E*)-1-methoxy-2-methylpent-1-en-3-yne [(*E*)-**71**; 88 mg, 0.8 mmol), and benzene (0.05 M, 8 mL) were placed in a flame-dried, single-necked flask that had been modified by replacement of the 14/20 joint with a 10-mm threaded high-vacuum stopcock. The mixture was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles). Then the flask was backfilled with 1 atm of argon at r.t., sealed with the stopcock and heated at 110 °C for 8 h. After removal of solvent, the crude mixture was purified (silica gel, hexanes–CH_2Cl_2–Et_2O, 4:1:1) to give **80**; yield: 60%; ratio *E*/*Z* 96:4. Increased amounts of the *Z*-isomer can be found in reactions in different solvents. The reaction of (*Z*)-**71** gives predominately (*Z*)-**80** in similar yields.

(*E*)-Inden-5-one (*E*)-80

R_f = 0.36 (hexanes–CH_2Cl_2–Et_2O, 4:1:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 3 H), 1.75 (d, *J* = 1.5 Hz, 3 H), 1.93 (s, 3 H), 2.04 (d, *J* = 15.3 Hz, 1 H), 2.23 (d, *J* = 1.2 Hz, 3 H), 2.70 (d, *J* = 15.3 Hz, 1 H), 3.64 (s, 3 H), 3.76 (s, 3 H), 5.69 (s, 1 H), 5.95 (br s, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 11.67, 14.11, 20.57, 23.48, 47.26, 52.81, 59.86, 60.68, 108.89, 122.65, 128.92, 133.72, 147.02, 149.54, 156.74, 158.76, 198.35.

MS (EI): *m*/*z* (%) = 274 (50), 259 (13), 243 (6), 227 (9), 211 (3), 199 (10), 171 (11), 129 (14), 115 (14), 91 (14), 84 (100), 47 (18).

HRMS: *m*/*z* [M$^+$] calcd for $C_{17}H_{22}O_3$: 274.1575; found: 274.1569.

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.23; H, 8.22.

(*Z*)-Inden-5-one (*Z*)-80

R_f = 0.35 (hexanes–CH_2Cl_2–Et_2O, 4:1:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 3 H), 1.71 (s, 3 H), 1.86 (s, 3 H), 2.14 (d, *J* = 15 Hz, 1 H), 2.64 (d, *J* = 15 Hz, 1 H), 2.27 (s, 3 H), 3.55 (s, 3 H), 3.83 (s, 3 H), 5.74 (s, 1 H), 6.02 (br s, 1 H).

Intermolecular Reaction of Carbene Complex 87 with (*E*)-1-Methoxy-2-methylpent-1-en-3-yne [(*E*)-71]

The chromium carbene complex **87** (142 mg, 0.37 mmol), (*E*)-**71** (88 mg, 0.8 mmol) were reacted according to the typical procedure to give (*E*)-**88**; yield: 62% ratio *E*/*Z* >98%:

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (s, 3 H), 1.28 (d, *J* = 8 Hz, 6 H), 1.74 (s, 3 H), 1.91 (s, 3 H), 2.00 (d, *J* = 15.3 Hz, 1 H), 2.23 (d, *J* = 1.2 Hz, 3 H), 2.66 (d, *J* = 15.3 Hz, 1 H), 3.63 (s, 3 H), 4.37 (sept, *J* = 6.3 Hz, 1 H), 5.68 (s, 1 H), 5.88 (br s, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 12.13, 14.01, 20.92, 22.44, 23.21, 42.28, 52.88, 59.72, 74.69, 108.65, 122.65, 129.77, 133.71, 147.02, 146.95, 150.65, 156.95, 157.31, 199.44.

Intermolecular Reaction of Carbene Complex 19 with (*E*)-1-Methoxy-2-methyl-5-(triisopropylsiloxy)pent-1-en-3-yne [(*E*)-72]

The chromium carbene complex **19** (82 mg, 0.23 mmol), (*E*)-1-methoxy-2-methyl-5-(triisopropylsiloxy)pent-1-en-3-yne [(*E*)-**72**; 130 mg, 0.46 mmol] were reacted according to the typical procedure to give (*E*)-**89** and (*Z*)-**89**; yield: 40%; ratio *E*/*Z* 87:13.

(*E*)-Inden-5-one (*E*)-89

R_f = 0.34 (hexanes–CH_2Cl_2–Et_2O, 4:1:1).

IR (neat): 2944 m, 2867 m, 1657 m, 1612 m, 1462 w, 1229 m, 1136 s, 1059 w, 881 w, 681 m cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 24 H), 1.75 (s, 3 H), 2.09 (d, *J* = 15.1 Hz, 1 H), 2.25 (s, 3 H), 2.68 (d, *J* = 15.1 Hz, 1 H), 3.64 (s, 3 H), 3.87 (s, 3 H), 4.37 (d, *J* = 11.2 Hz, 1 H), 4.52 (d, *J* = 11.2 Hz, 1 H), 5.70 (s, 1 H), 6.04 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 12.11, 13.86, 18.08, 20.57 23.20, 47.22, 52.71, 59.64, 59.81, 61.12, 108.45, 122.79, 128.98, 135.76, 147.67, 150.36, 159.31, 160.10, 199.33.

MS *m*/*z* (%) = 447 (28), 446 [M$^+$] (74), 388 (55), 345 (28), 273 (24), 241 (57), 226 (43), 75 (100), 59 (87).

(*Z*)-Inden-5-one (*Z*)-89

R_f = 0.32 (hexanes–CH_2Cl_2–Et_2O, 4:1:1).

IR (neat): 2944 m, 2867 m, 1657 m, 1613 m, 1462 m, 1140 s, 1062 m, 884 m, 681 m cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (m, 21 H), 1.07 (s, 3 H), 1.70 (s, 3 H), 2.13 (d, *J* = 15.0 Hz, 1 H), 2.24 (s, 3 H), 2.58 (d, *J* = 15.0 Hz, 1 H), 3.47 (s, 3 H), 3.94 (s, 3 H), 4.36 (d, *J* = 3.2 Hz, 2 H), 5.69 (s, 1 H), 5.97 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 11.99, 18.00, 18.56, 20.68, 22.68, 47.78, 52.23, 57.74, 59.40, 60.14, 107.01, 122.46, 128.61, 136.90, 145.37, 150.90, 156.28, 159.16, 199.96.

MS *m*/*z* (%) = 447 (18), 446 [M$^+$] (52), 388 (37), 241 (47), 199 (38), 145 (46), 115 (63), 75 (100), 59 (87);

{Amino[4-(*tert*-butyldimethylsiloxy)-2,6-dimethylphenyl]methylene}pentacarbonylchromium(0) (81)

To a 100-mL round–bottomed flask equipped with a dry ice condenser was added chromium carbene complex **24** (1.88 g, 4 mmol) and THF (40 mL). The mixture was cooled at –40 °C and ammonia gas was introduced via a cannula. The reaction was followed by TLC and stirred at –40 °C for 2–3 d. After warming up at r.t. and evaporation of the solvent, the product was purified by column chromatography (silica gel, hexanes–Et_2O, 80:20) to give **81** as a yellow solid; yield: 1.60 g (88%); mp 120 °C (dec.); R_f = 0.20 (hexanes–Et_2O, 80:20).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 6 H), 0.96 (s, 9 H), 2.14 (s, 6 H), 6.48 (s, 2 H), 8.45 (br s, 1 H), 9.24 (br s, 1 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = –4.28, 14.26, 19.71, 25.71, 119.36, 128.75, 145.48, 154.34, 216.76, 216.59 (C_{carb} not located).

MS (EI): *m*/*z* (%) = 399 [M$^+$ – 2 CO] (1), 343 [M$^+$ – 4 CO] (1), 315 [M$^+$ – 5 CO] (21), 263 (17), 204 (100), 188 (14), 179 (27), 130 (64), 121 (14), 115 (12), 105 (23), 75 (64), 41 (43).

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{26}CrNO_6Si$: 456.0935; found: 456.0942.

Anal. Calcd for $C_{20}H_{25}CrNO_6Si$: C, 52.74; H, 5.53; N, 3.08. Found: C, 52.72; H, 5.54; N, 3.15.

{[4-(*tert*-Butyldimethylsiloxy)-2,6-dimethylphenyl](dimethylamino)methylene}pentacarbonylchromium(0) (82)

In a 10-mL round-bottomed flask was placed TBAB (0.1 g, 0.32 mmol), NaOH (1.05 g, 25.6 mmol) and amino carbene complex **81** (1.46 g, 3.2 mmol). CH_2Cl_2 (2 mL), H_2O (1 mL), and MeI (0.6 mL, 9.6 mmol) were then added. The mixture was followed by TLC and stirred for 5–6 h at r.t.. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 1 mL). The combined organic phases were dried ($MgSO_4$) and the solvent evaporated. The product was purified by column chromatography (silica gel, hexanes–Et_2O, 50:50) to give **82** as a yellow solid; yield: 1.16 g (75%); mp 120 °C (dec.); R_f = 0.52 (hexanes–Et_2O, 50:50).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 6 H), 0.95 (s, 9 H), 1.99 (s, 6 H), 3.04 (s, 3 H), 4.00 (s, 3 H), 6.49 (s, 2 H).

^{13}C NMR (300 MHz, $CDCl_3$): δ = –4.32, 18.31, 19.48, 25.76, 44.47, 48.37, 119.67, 127.08, 145.28, 153.71, 216.69, 222.97 (C_{carb} not located).

MS (EI): *m*/*z* (%) = 455 (2), 427 (4), 399 (9), 371 (8), 343 (99), 300 (36), 276 (17), 204 (23), 244 (11), 204 (10), 162 (10), 143 (10), 126 (56), 95 (35), 73 (47), 52 (100).

HRMS: *m*/*z* [M$^+$] calcd for $C_{22}H_{29}CrNO_6Si$: 483.1169; found: 483.1191.

Anal. Calcd for $C_{22}H_{29}CrNO_6Si$: C, 54.64; H, 6.04; N, 2.90. Found: C, 54.83; H, 5.98; N, 2.96.

Pentacarbonyl[(dimethylamino)(4-hydroxy-2,6-dimethylphenyl)methylene]chromium(0) (83)

The dimethylamino carbene complex **82** (0.92 g, 1.9 mmol) was dissolved in THF (25 mL). HF–pyridine complex (3.2 mL) was added at r.t. over 4–6 h until no starting material was observed by TLC. Sat. Na_2CO_3 (10 mL) was added slowly. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The organic layers were combined and dried ($MgSO_4$). After evaporation, purification of the product by column chromatography (silica gel, hexanes–Et_2O, 50:50) gave **83** as a yellow solid; yield: 0.35 g (50%); mp 150 °C (dec.); R_f = 0.26 (hexanes–Et_2O 50:50).

^{1}H NMR (300 MHz, acetone-d_6): δ = 0.86 (s, 6 H), 1.98 (s, 3 H), 2.90 (s, 3 H), 5.34 (s, 2 H), 7.40 (br s, 1 H).

^{13}C NMR (300 MHz, acetone-d_6): δ = 19.55, 44.89, 51.14, 115.38, 128.16, 144.62, 156.40, 206.55, 217.69 (C_{carb} not located).

MS (EI): *m*/*z* (%) = 271 (4), 257 (1), 243 (22), 229 (12), 200 (19), 175 (17), 162 (31), 147 (80), 135 (58), 121 (100), 115 (27), 103 (25), 95 (45), 91 (76), 77 (27), 52 (78), 44 (89).

Anal. Calcd for $C_{16}H_{15}CrNO_6$: C, 52.04; H, 4.09; N, 3.79. Found: C, 52.31; H, 4.22; N, 3.75.

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