Rearrangement of Alkynyl and Vinyl Carbenoids via the Rhodium(II)-Catalyzed Cyclization Reaction of α-Diazo Ketones

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Abstract: *o*-Alkynyl-substituted α-diazoacetophenones undergo facile cyclization to indenone derivatives upon treatment with catalytic quantities of Rh(II) carboxylates. The cyclization reaction involves addition of a rhodium stabilized α-keto carbenoid onto the neighboring acetylenic π-bond to give a cyclized vinyl carbenoid. When an alkene is tethered to the alkynyl group, the vinyl carbenoid complex undergoes further cyclization to produce a cyclopropenyl-substituted indenone. Different enyl substituents resulted in a significant variation in the behavioral pattern of the reactive cyclopropene ring. The strained cyclopropene ring was intercepted with diphenylisobenzofuran to give Diels–Alder cycloadducts. For alkynyl substituted α-diazo ketones, the resulting vinyl alkynyl carbenoids were found to give products derived from an unusual alkynyl carbenoid rearrangement. The Rh(II)-catalyzed reaction of several *o*-dialkynyl-substituted α-diazoacetophenones which contain a group capable of undergoing reaction with the carbenoid at the terminal position was examined. Products derived from a 1,2-hydrogen shift as well as cyclopropanation of a tethered alkene was obtained in high yield. In addition, the thermal decomposition of a series of aziridinylimines derived from alkynyl-substituted aldehydes led to products derived from a rearranged alkynyl carbene. The initially formed alkynyl carbene at C_1 could be induced to undergo exclusive reaction at the C_3 terminal position.

The chemistry of metal carbene complexes has provided chemists with exceptionally fertile ground for designing and developing new stereoselective bond construction for application to organic synthesis.[1-25] The current activity in this area stems from the role of metal carbenes in alkene metathesis,[26] in cyclopropanation chemistry,[27] and as intermediates in an impressive array of synthetic methodology.[28,29] Due to their lability, metal carbene complexes are often generated in situ from their corresponding precursors prior to use. The reaction of α-diazo ketones with transition metals such as rhodium(II) carboxylates represents a particularly powerful method for generating synthetically useful electrophilic carbene complexes.[30-32] Several years ago we described a route for producing cycloalkenone carbenoids which involved a rhodium(II) catalyzed reaction of α-diazo alkynyl substituted ketones (Scheme I).[33,34] The process proceeds by addition of the rhodium stabilized carbenoid onto the acetylenic π-bond to give a vinyl carbenoid (**2**). We have further demonstrated that the vinyl carbenoid complex can be trapped intramolecularly to give bicyclohexanes **3** in good yield when an alkene is tethered to the alkynyl group. The potential for many other diverse chemical pathways exists through the generation and further reaction of these rhodium carbenoids. For

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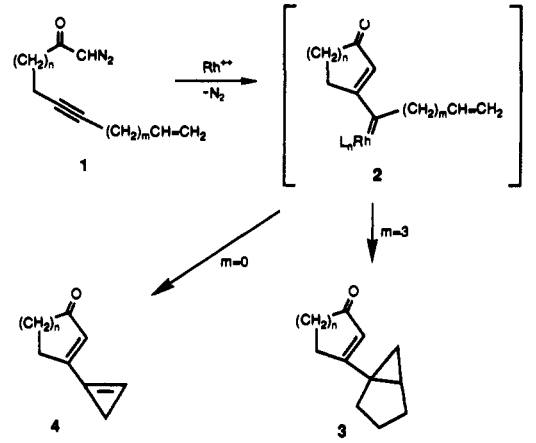
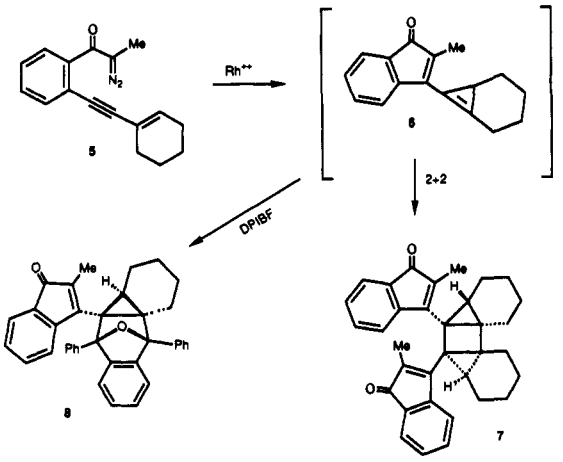
Scheme I



example, connecting the alkene directly to the alkynyl group (i.e., $m = 0$) should result in the formation of cyclopropenes of type **4**. Herein we detail the results of such a study.

Results and Discussion

On the basis of previous studies by ourselves and others,[33,34] it was anticipated that treatment of an α-diazo ketone of type **1** ($m = 0$) with a Rh(II) carboxylate would lead to cyclopropene **4**. This prediction was based on the knowledge that cyclopropenes are readily formed by cyclization of vinyl carbenes or related carbenoids.[35-38] Our initial efforts focused on the rhodium(II) acetate catalyzed reaction of α-diazo ketone **5**. Treatment of **5** with a catalytic quantity of Rh_2OAc_4 in CH_2Cl_2 at 25 °C afforded the 2 + 2 dimer **7**, derived from transient cyclopropene **6** in 73% yield. The structure of dimer **7** was unequivocally established by



X-ray crystal structure analysis; the crystallographic details can be found in Table I and the final ORTEP diagram in Figure 1. Formation of strained cyclopropene **6** as the primary product of the reaction follows from its interception by diphenylisobenzofuran (DPIBF).[39] The *exo*-cyclopropyl adduct **8** was obtained as the exclusive cycloadduct in 84% yield.

Extension of the carbenoid cyclization reaction to α-diazo ketone **9** was next investigated. Compound **9** was prepared by first treating methyl 2-iodobenzoate with 2-methyl-3-buten-1-yne under typical Castro–Stephens arylation conditions.[40] The resulting ester was readily converted to α-diazo ketone **9** by treatment with potassium trimethylsilanolate followed by reaction with methyl chloroformate. The mixed anhydride was then allowed to react with diazoethane. Several rhodium(II) dimers with different electronic influences imparted on the rhodium(II) center by its ligands (i.e., octanoate, mandelate, acetate, trifluoroacetate) were prepared so as to evaluate their catalytic properties. The results obtained indicated very little difference in the yield of the observed product. We did find, however, that the more soluble rhodium(II) mandelate was significantly more reactive than the acetate catalyst. Thus, when **9** was treated with a catalytic quantity of Rh(II) mandelate in CH_2Cl_2 at 25 °C it was possible to obtain cyclopropene **10** in 95% yield. Upon standing in the presence of oxygen, this reactive species underwent ring opening to produce indenone **11**. Cyclopropene **10** was found

Table 1. Experimental Data for the X-ray Diffraction Study of Dimer **7**

formula	$C_{34}H_{32}O_2$
FW	472.63
cryst system	monoclinic
space group	$P21/n$
a, Å	10.054(4)
b, Å	19.164(7)
c, Å	13.476(3)
α, deg	93.46(0)
β, deg	103.47(3)
γ, deg	92.51(0)
V, Å^3	2525(2)
Z	4
D_{calcd}, g/cm^3	1.24
diffractometer	Syntex P2
abs coeff, μ, cm^{-1}	0.8
cryst size	0.38 × 0.45 × 0.50
radiation	Mo Kα with graphite monochrometer
scan speed	2.0–24.0 deg/min in 2θ
data collected	0,0,−15 to 11,21,+15
scan type	coupled θ(crystal) − 2θ(counter)
scan width	(Kα_1 −1.0) to (Kα_2 +1.1)
$2\theta_{min}$, deg	3
$2\theta_{max}$, deg	45
F(000)	1008
unique reflcns {$I > 3\sigma(I)$}	3314
rflcns with $F^2 > 0$	2376
no. of variables	1.75
goodness of fit (S)	1.75
R_f, %	5.9
R_{wf}, %	6.7
$(\Delta/\sigma)_{max}$	0.001
$(\Delta\rho)_{max}$, Å^{-3}	0.4305
$(\Delta\rho)_{min}$, Å^{-3}	−0.3142

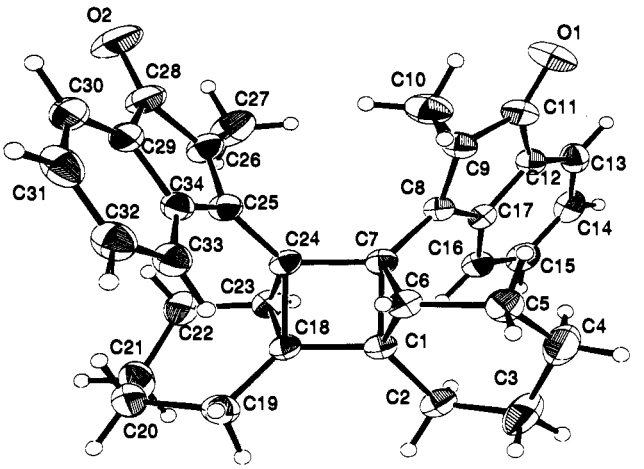


Figure 1.

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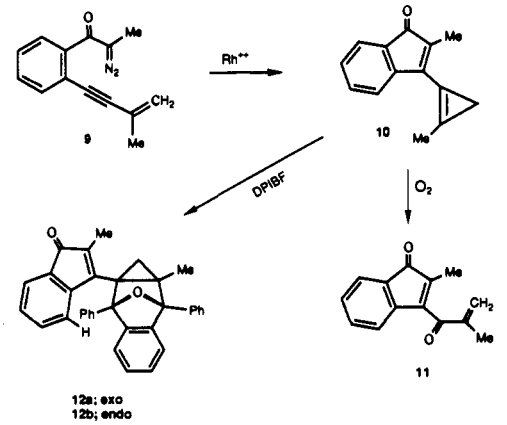

to undergo ready Diels–Alder cycloaddition with DPIBF to afford a 2:1 mixture of exo and endo adducts in 85% overall yield. The exo isomer is readily distinguishable due to shielding of the ortho-aromatic hydrogen (4.47 ppm) by the proximal phenyl ring. The bimolecular [4 + 2] reaction of substituted cyclopropenes is usually subject to a strong steric preference for an exo transition state, because of unfavorable steric interactions with the diene in the endo transition state.[41] Only in instances in which the endo transition state is comparable with or less sterically demanding than the exo transition state have products derived from the endo approach been observed.[41] In these cases the [4 + 2] cycloaddition proceeds at reduced rates and requires the use of pressure for observable reaction to occur.[42]

An additional system which we examined involved the rhodium-(II) catalyzed reaction of the closely related α-diazo ketone **13**. In this case it was not possible to isolate (nor detect) the suspected cyclopropene. Instead, this transient species (i.e., **14**) readily underwent a 2 + 2 dimerization reaction. We initially anticipated that the dimerization of **14** would produce the tricyclo[3.1.0.0^{2,4}]-hexane ring skeleton. This type of dimerization reaction had been studied in some detail by several groups[43–49] and the reaction generally takes the form of a 2 + 2 cycloaddition, releasing a great deal of ring strain.[50] However, we were surprised to find that the 2 + 2 cycloaddition of **14** takes an entirely different course to afford the novel dimer **15** in 54% yield. The structure of **15** was assigned based on a detailed NMR analysis and firmly established by X-ray crystallography study (see Table II, Figure 2). It should be noted that only the exo cycloadduct **16** was isolated when the reaction of **13** was carried out in the presence of DPIBF thereby providing good support for a cyclopropene intermediate. Bimolecular cycloaddition across the double bond in cyclopropene has been found to proceed quite readily since ring strain is reduced by 26 kcal/mol.[51] The transition state energy for the cycloaddition reaction, however, is very sensitive to both steric and electronic factors.[52] FMO theory predicts that

Table II. Experimental Data for the X-ray Diffraction Study of Dimer **5**

formula	$C_{26}H_{20}O_2$
FW	364.44
cryst system	triclinic
space group	$P\bar{1}$
a, Å	8.554(3)
b, Å	9.890(2)
c, Å	12.316(4)
α, deg	93.49(2)
β, deg	103.63(3)
γ, deg	95.48(2)
V, Å^3	1004.20
Z	2
D_{calcd}, g/cm^3	1.21
diffratomter	Syntex P2
abs coeff, μ, cm^{-1}	0.07
cryst size	0.4 × 0.4 × 0.6
radiation	Mo Kα with graphite monochrometer
scan speed	2.0–24.0 deg/min in 2θ
data collected	0,−11,−14 to 10,11,14
scan type	coupled θ(crystal) − 2θ(counter)
scan width	(Kα$_1$ −1.0) to (Kα$_2$ +1.1)
$2\theta_{min}$, deg	3
$2\theta_{max}$, deg	45
F(000)	384.0
unique reflcns {$I > 3\sigma(I)$}	2636
reflcns with F^2 0	1744
no. of variables	253
goodness of fit (S)	2.34
R_f, %	8.25
R_{wf}, %	9.15
$(\Delta/\sigma)_{max}$	0.001
$(\Delta\rho)_{max}$, Å^{-3}	030
$(\Delta\rho)_{min}$, Å^{-3}	−0.32

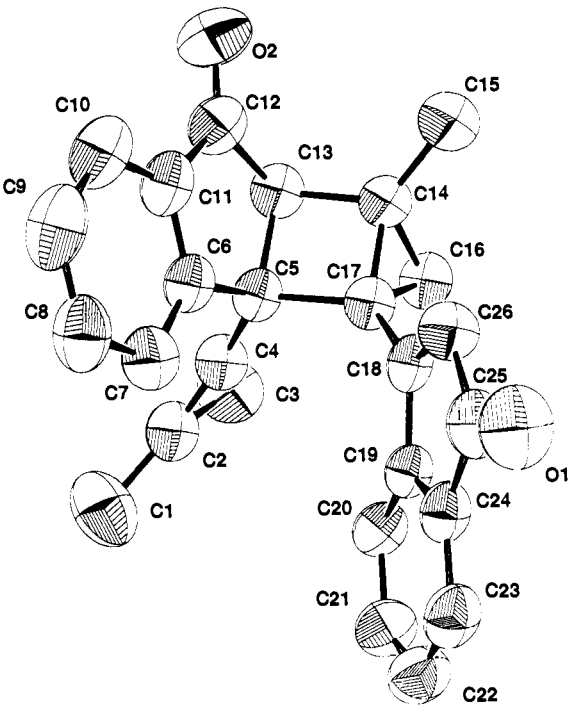

Figure 2.

the preferred 2 + 2 cycloaddition path of **14** will involve reaction of the HOMO of the cyclopropene with the indenone π-bond (larger coefficients) to give the crossed dimer **15**.[53] Introduction

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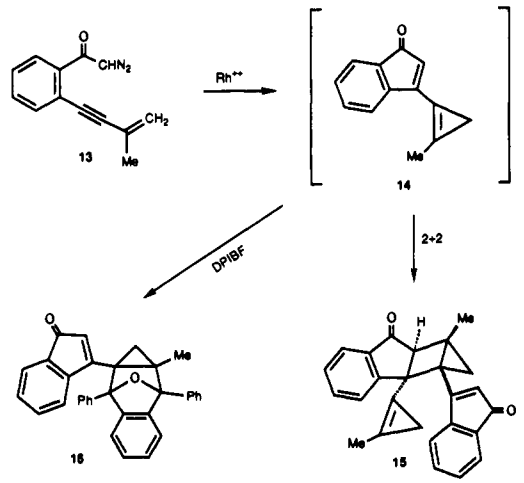
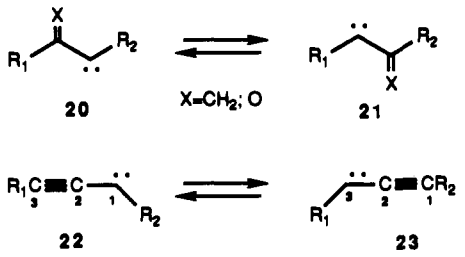
(53) MNDO calculations were performed with the AMPAC program (QCPE 506) using the AM1 Hamiltonian. The calculations show that for indenone **14** the LUMO is located at −1.27 eV and the HOMO at −9.01 eV with coefficients of +0.54 (α), +0.30 (β), −0.35 (γ), and −0.43 (δ) in the HOMO and +0.44 (α), −0.39 (β), −0.17 (γ), and +0.34 (δ) in the LUMO.



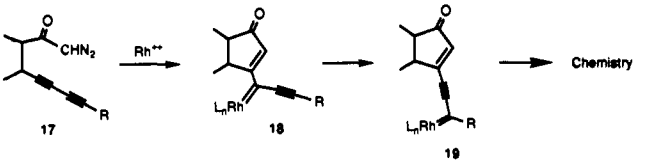
of a substituent group on either the indenone or cyclopropene ring generates steric interactions which retard this mode of cycloaddition.

The ease with which α-diazo ketones **5**, **9**, and **13** undergo Rh(II)-catalyzed cyclization to give cyclopropenyl substituted indenones suggests that a related transformation might occur with the diacetylenic system **17** (vide infra). The wealth of strategically located functionality that could result from the rhodium-catalyzed reaction of **17** motivated us to examine the feasibility of the rearrangement (i.e., **18** ⇌ **19**) by first examining several alkynyl substituted carbenes (i.e., **22** ⇌ **23**). In contrast to the plethora of examples which exist for vinylcarbene–vinylcarbene rearrangements (i.e., X = CH_2; **20** ⇌ **21**),[54-57] the chemistry of ethynyl carbene and closely related species is far less frequently encountered in the literature.[58-63] Ab initio calculations suggest that propargylene (R_1 = R_2 = H) undergoes a degenerate isomerization with a low barrier to rearrangement.[64]



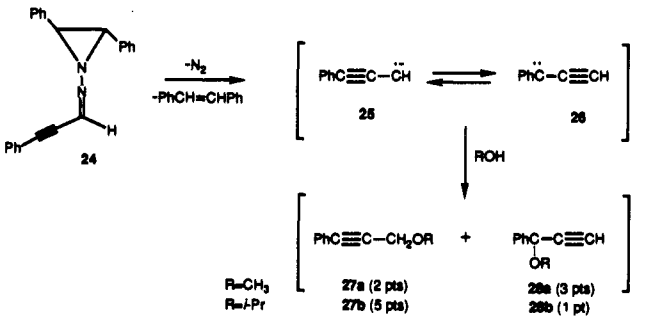
In 1960, Skell and Klebe reported the preparation of propargylene by liquid-phase photolysis of 1-diazo-2-propyne.[58] Propargylene and its methyl and phenyl derivatives, obtained by the photolysis of the appropriate diazopropyne, each showed electron paramagnetic resonance.[58] Triplet propargylene gave

Scheme II



equal reactivity with olefins at C_1 and C_3 whereas singlet propargylene reacted with olefins only at C_1, the position vacated by nitrogen. The predicted equilibrium geometry of the most stable triplet is not linear as was earlier supposed[58] but rather is of C_2 symmetry and is best described in terms of a diradical valence structure.[60] We decided to explore the thermal decomposition of a series of aziridinylimines as a method of generating a variety of ethynyl carbenes. We were particularly interested in determining whether the initially formed carbene at C_1 could be induced to undergo exclusive reaction at the C_3 position since that would provide good support for the suggested sequence of reactions outlined in Scheme II.

Eschenmoser and co-workers[65] have used aziridinylimines as masked diazo compounds; they have an advantage over other diazoalkane precursors, such as tosylhydrazones, in that they are cleaved thermally without the introduction of an external base, and being soluble in organic solvents, they allow homogeneous reactions to occur. Our initial results focused on the thermolysis of aziridinylimine **24**. Heating a sample of **24** in methanol



afforded a 2:3 mixture of ethers **27a** and **28a** in 60% overall yield. The major product **28a** is formed by insertion of the more stable carbene **26** into the solvent OH bond. Interestingly, when the decomposition of **24** was carried out in isopropyl alcohol, the major product **27b** (52%) is that derived from solvent insertion into the initially formed carbene **25**. The difference in relative yields may be attributed to steric influences, the rate for reaction of isopropyl alcohol with **25** being greater than the rate of its reaction with **26**.

Although insertion of unsaturated carbenes into solvent is a common reaction pathway, this process is not always observed, and a number of competing reactions have been reported. These include addition to π-bonds,[66] alkyl group migration,[67] and 1,5-electrocyclization.[52] Since we were interested in exploiting the chemistry of these ethynyl carbenes, we carried out a number of experiments designed to probe the reactivity of these species. Thermolysis of aziridinylimine **29** in benzene proceeded smoothly and afforded benzobicyclo[3.1.0]hexene **31** as the exclusive product in 72% isolated yield. We believe that this reaction proceeds by intramolecular addition of the C_3-rearranged carbene **30** onto the neighboring π-bond. In order to document the 1,5-electrocyclization process, we studied the thermal chemistry of

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(55) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 4739.
(56) Joines, R. C.; Turner, A. B.; Jones, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 7754.
(57) Vanderstouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655.
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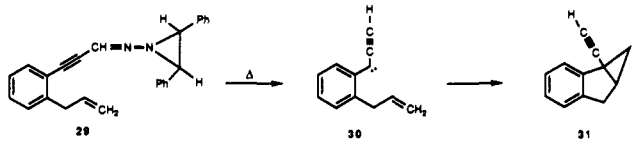
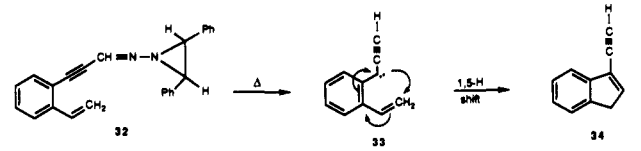
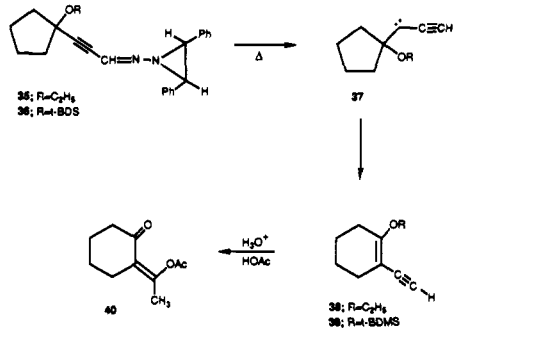
(59) Franck-Neuman, M.; Geoffroy, P.; Miesch, M.; Zaragoza-Dorwald, F. *Tetrahedron Lett.* **1990**, 4121. Hauptmann, H. *Tetrahedron* **1976**, *32*, 1293.
(60) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.
(61) Selvarajan, R.; Boyer, J. H. *J. Org. Chem.* **1971**, *36*, 1679.
(62) Hori, Y.; Noda, K.; Kabayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1969**, 3563.
(63) Freeman, P. K.; Danino, J. C.; Stevenson, B. K.; Clapp, G. E. *J. Org. Chem.* **1990**, *55*, 3867.
(64) Carsky, P.; Spirko, V.; Hess, B. A.; Schaad, L. J. *J. Phys. Chem.* **1990**, *94*, 5493.
(65) Felix, D.; Muller, R. K.; Horn, U.; Jous, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 1276.
(66) Baird, M. S.; Buxton, S. R.; Whitley, J. S. *Tetrahedron Lett.* **1984**, 1509. Al-Dulayymi, J.; Baird, M. S.; Clegg, W. *Tetrahedron Lett.* **1988**, 6149. Petiniot, N.; Anciauz, A. J.; Noels, A. F.; Hubert, A.; Teyssie, P. *Tetrahedron Lett.* **1978**, 1239. Padwa, A.; Blacklock, T. *J. Am. Chem. Soc.* **1984**, *106*, 4446.
(67) Newmann, M. F.; Buchecker, C. *Tetrahedron Lett.* **1973**, 2875.



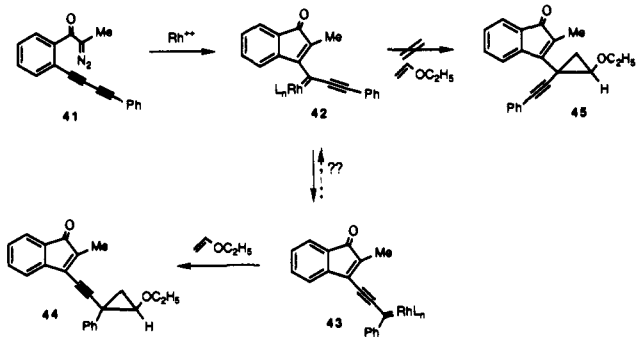
aziridinylimine **32**. The only product that could be isolated (42%) from the thermolysis of **32** in benzene corresponded to indene **34** which was derived from the rearranged carbene **33**.



One of the more frequently encountered reactions of α-alkoxy carbenes involves a 1,2-alkyl shift to give enol ethers.[68] With this in mind, we investigated the thermal behavior of imines **35** and **36** in benzene and found that the resulting rearranged carbene **37** undergoes ring expansion to give the ethynyl substituted enol ethers **38** and **39** in 67% and 54% yield, respectively. Treatment of the *tert*-butyldimethylsilyl enol ether **39** with aqueous acetic acid afforded the acetoxy substituted enone **40** in 54% yield.



Having established the proclivity with which alkynyl substituted carbenes rearrange, we turned our attention to the rhodium(II) catalyzed behavior of several α-diazo ketones possessing a diynyl side chain. An issue critical to the synthetic utility of this reaction is whether the cyclization will occur to give products derived from the fully rearranged carbenoid (i.e., **19**). We therefore prepared α-diazo ketone **41** and investigated its Rh(II)-catalyzed chemistry. Treatment of **41** with a catalytic quantity of rhodium(II) acetate at 25 °C in the presence of ethyl vinyl ether afforded cyclopropane **44** with notable efficiency (90% chemical yield) and selectivity (>95% isomeric purity). No signs of the isomeric cyclopropane **45** could be detected in the crude reaction mixture. The exclusive formation of cyclopropane **44** can be attributed to

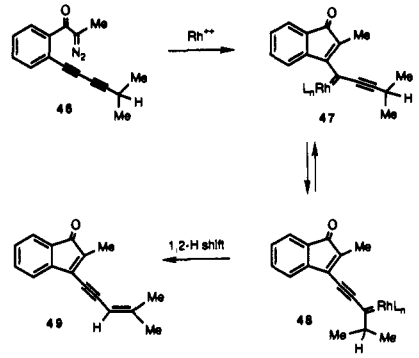


a slower rate of trapping of carbenoid **42** by ethyl vinyl ether, perhaps as a consequence of a more congested transition state.

(68) Robson, J. H.; Shechter, J. *J. Am. Chem. Soc.* **1967**, *89*, 7112.

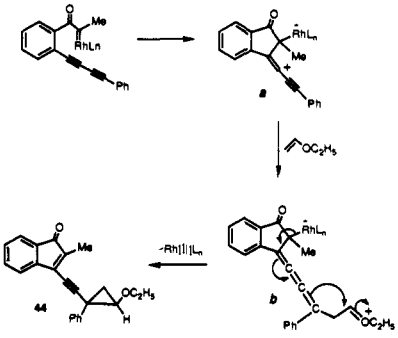
An alternate explanation is that the equilibrium between the two carbenoids lies completely in favor of the more stable phenyl substituted isomer (i.e., **43**).[69] The high chemoselectivity observed in the Rh(II)-catalyzed reaction suggests that the metallocarbenoid complex is more selective than the related thermally derived carbene intermediate (i.e., **24** → **27** + **28**).[70]

Additional studies were carried out which focused on the Rh(II)-catalyzed reaction of *o*-dialkynyl substituted α-diazoacetophenones which contained a group capable of undergoing reaction with the carbenoid at the terminal alkyne position. The 1,2-shift of hydrogen in a singlet carbene to form an alkene formally involves the migration of hydrogen to a vacant π orbital.[71] It is generally assumed that the migrating group carries its electrons into the vacant orbital of the singlet carbene. The ease of migration is related to the ground-state alignment of the vacant π and γ-CH orbitals.[72,73] We assumed that related arguments could be made for the corresponding rhodium carbenoid **48**. Indeed, treatment of **46** with Rh_2OAc_4 gave idenone **49** in 92% yield.[74]



The success achieved by the Rh(II)-catalyzed transformation of **46** was also extended to α-diazo ketone **50**. Our intention here was to generate vinyl carbenoid **52** from the Rh(II)-catalyzed

(69) Other possible variations to explain the formation of **44** are certainly conceivable.[34] For example, the reaction of **41** with Rh(II) acetate could proceed with the formation of an intermediate zwitterion of type ***a***. Stepwise addition of ethyl vinyl ether would then produce ***b***, which upon loss of Rh(II) would give **44**.



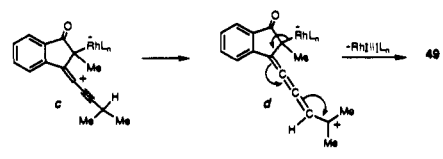
(70) An alternate possibility suggested by one of the reviewers is that trapping of **25** and **26** could be a kinetic result, whereas formation of **44** could be the result of either a steric or an electronic preference.

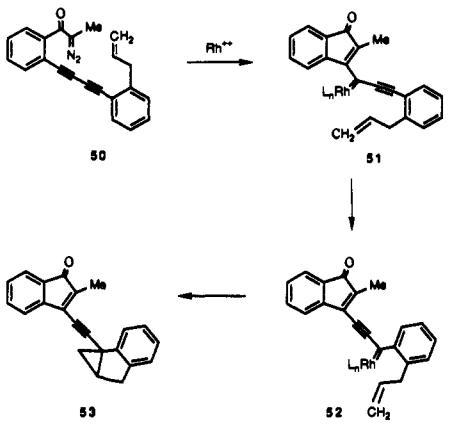
(71) Jones, W. M. In *Rearrangement in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; pp 95–160.

(72) Gaspar, P. P.; Hammond, G. S. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Academic Press: New York, 1975; Vol. 2, pp 207–362.

(73) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385.

(74) An alternate pathway to **49** which avoids a carbenoid intermediate is outlined below. This path proceeds by a 1,2-hydrogen shift from species ***c***. The resulting transient ***d*** loses Rh(II) to give **49**.





reaction and evaluate the intramolecular cyclopropanation reaction. Using standard palladium coupling chemistry, it was possible to synthesize **50** from methyl 2-ethynylbenzoate and 2-(2-propen-1-yl)-2-bromoethynylbenzene. Treatment of **50** with a catalytic quantity of Rh_2OAc_4 at 25 °C in methylene chloride proceeded smoothly to give benzobicyclohexene **53**. Of particular note in this latter example is the high efficiency of the tandem cyclization–rearrangement–cycloaddition sequence leading to the final product in 95% yield.[75]

Our view of how the alkynyl carbenoid rearrangement reaction proceeds is shown in Scheme III. Exposure of the starting α-diazo ketone **17** to a rhodium(II) catalyst results in cyclization of the initially formed α-keto carbenoid **54** to vinyl carbenoid **18** in which carbene-like reactivity has been transferred to one of the original alkyne carbon atoms. A further electrocyclization of **18** with the adjacent alkynyl group produces metallocycle **55**. This transient intermediate rapidly undergoes ring opening to either regenerate **18** or form the rearranged carbenoid **19**. This model is consistent with all the data reported here. It should also be noted that the proposed metallacycle is similar in many respects to a tungstenacyclobutadiene complex isolated by Schrock and co-workers.[76,77]

In summary, the Rh(II)-catalyzed reaction of α-diazo ketones bearing dialkynyl substituted side chains provides a promising new cyclization strategy for generating complex polycyclic ring systems. The tandem cyclization–rearrangement–cycloaddition sequence proceeds with high chemoselectivity, and the cyclized products contain functionality that should prove useful for further synthetic transformations. We are continuing to explore the scope and mechanistic details of these cyclization reactions and will report additional findings at a later date.

Experimental Section

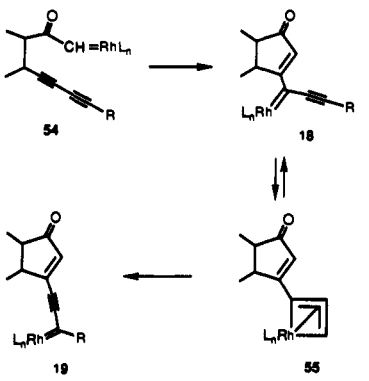
Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven dried glassware under an atmosphere of extra dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate–hexane mixture as the eluent unless specified otherwise.

General Procedure for the Castro–Stephens Arylation Reaction. To a degassed solution containing 5.0 mmol of the appropriate aryl halide and 5.0 mmol of the terminal alkyne in 100 mL of anhydrous triethylamine was added 25 mg of *trans*-bis(triphenylphosphine)palladium(II) chloride and 50 mg of cuprous iodide. The reaction mixture was stirred at 25 °C for 12 h. The resulting slurry was filtered through a pad of Celite. Removal of the solvent under reduced pressure followed by silica gel chromatography using a hexane–ethyl acetate mixture as the eluent afforded the coupled product in good yield.

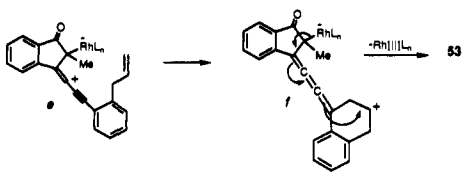
General Procedure for the Preparation of α-Diazo Ketones from the Corresponding Methyl Esters. To a stirred solution containing 5.0 mmol of potassium trimethylsilanolate in 100 mL of anhydrous ether was added, in one portion, 5.0 mmol of the appropriate methyl benzoate derivative. The reaction mixture was heated at reflux for 2 h under a nitrogen atmosphere. After being cooled to 0 °C, 5.0 mmol of methyl chloroformate was added and the resulting mixture was stirred for 2 h at 25 °C. The mixture was filtered through a pad of Celite. The filtrate was concentrated to ca. 20 mL and to this solution was added a 30 mmol excess of an ethereal diazomethane (or diazoethane) solution at 0 °C. The resulting mixture was allowed to stir at 25 °C for 16 h and the excess diazoalkane and ether were removed under reduced pressure. The residue was chromatographed on silica gel using a hexane–ethyl acetate mixture as the eluent to give the appropriate α-diazo ketone, which was used in the next step without further purification.

Preparation and Reaction of (*o*-(2-Cyclohexenyl-1-ethynyl)benzoyl)-diazoethane (5) with Rhodium(II) Acetate. The Castro–Stephens reaction of 4.0 g (7.6 mmol) of methyl 2-iodobenzoate and 2.68 mL (11.4 mmol) of 1-ethynylcyclohexene in 100 mL of anhydrous triethylamine afforded 3.40 g (93%) of methyl 2-(2-cyclohexenyl-1-ethynyl)benzoate: IR (neat) 1733, 1484, 1434, and 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.66–1.75 (m, 4H), 2.13–2.20 (m, 2H), 2.24–2.51 (m, 4H), 3.93 (s, 3H), 6.28 (s, 1H), 7.31 (t, 1H, J = 6.5 Hz), 7.43 (t, 1H, J = 6.5 Hz), 7.52 (d, 1H, J = 6.6 Hz), and 7.91 (d, 1H, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 22.1, 25.6, 28.8, 51.8, 85.5, 96.2, 120.8, 124.0, 127.1, 130.1, 131.3, 131.4, 133.6, 135.7 and 166.5; HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1154.

Scheme III

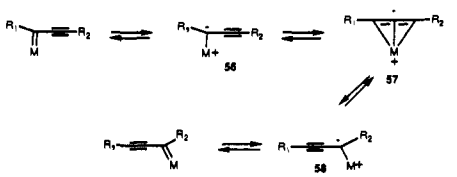


(75) Another route which can accommodate the formation of **53** is shown below. It proceeds in a stepwise manner and involves transients *e* and *f*.

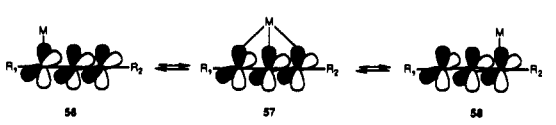


(76) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

(77) There are several alternate ways to represent metallocycle **55**. The alkynyl carbene unit consists of two orthogonal π-systems. The alkynyl carbene complex can be represented in the ionic form **56** which is comparable to an η^1-allyl complex. Binding the metal in an η^3-fashion gives **57** from which the metal can then further migrate to



form η^1-allyl intermediate **58**. With p-orbitals drawn, this can also be represented as shown below. In intermediate **57**, there is considerable bonding between the metal and the middle carbon of the conjugated π-system. Such η^3-coordination is in agreement with the Schrock compound cited as being precedent for **55**.[76]



A solution containing 2.5 g (11.9 mmol) of the above benzoate was converted in the normal fashion to 1.70 g (62%) of (*o*-(2-cyclohexenyl-1-ethynyl)benzoyl)diazoethane (**5**): IR (neat) 2075, 1610, 1445, and 1345 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.52–1.68 (m, 4H), 1.98–2.15 (m, 7H), 6.12 (s, 1H), and 7.24–7.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.6, 21.3, 22.1, 25.6, 28.8, 65.0, 83.6, 94.8, 120.3, 120.8, 127.1, 127.9, 129.7, 131.9, 135.9, and 140.3.

A 200-mg (0.83 mmol) sample of α-diazo ketone **5** in 40 mL of dry dichloromethane was treated with a catalytic amount of rhodium(II) acetate under a nitrogen atmosphere. After the mixture was stirred for 2 h at 25 °C, the solvent was removed under reduced pressure and the residue was subjected to chromatography to give 146 mg (73%) of dimer **7**: mg 186–187 °C; IR ($CHCl_3$) 1708, 1605, 1457, and 940 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.68–0.82 (m, 1H), 0.88–1.02 (m, 1H), 1.05–1.23 (m, 2H), 1.46–1.55 (m, 1H), 1.58 (s, 3H), 1.82–1.96 (m, 1H), 2.15–2.19 (m, 2H), 2.31 (dd, 1H, J = 5.1 and 3.6 Hz), 6.99 (d, 1H, J = 7.2 Hz), 7.15 (t, 1H, J = 7.5 Hz), 7.33 (d, 1H, J = 7.2 Hz), and 7.37 (d, 1H, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.5, 22.0, 22.3, 22.5, 23.3, 36.0, 37.0, 37.5, 120.7, 122.2, 127.9, 131.2, 133.4, 136.6, 146.0, 154.3, and 198.4. Anal. Calcd for $C_{34}H_{32}O_2$: C, 86.41; H, 6.82. Found: C, 86.23; H, 6.88.

Crystals suitable for an X-ray crystallographic structure determination of **7** were grown from a methylene chloride–hexane solution. A single crystal of approximately 0.38 × 0.45 × 0.50 mm was mounted on a quartz fiber such that the longest crystal dimension was parallel to the fiber axis. Unit cell parameters were determined on a Syntex $P2_1$ automated diffractometer using Mo Kα radiation. Twenty four reflections were machine centered and used in the least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were a = 10.054(4) Å, b = 19.164(7) Å, c = 13.476(3) Å, β = 103.47(3)°, V = 2525(2) Å^3, d_{calcd} = 1.24 g cm^{-3}, $F(000)$ = 1008, Z = 4, and space group $P21/n$. Intensity data were collected by using the θ–2θ scan technique with a variable scan rate of 2.0–24.0 deg min^{-1} in 2θ. A scan width of 2.1° was sufficient to collect all of the peak intensity data. Check reflections, monitored after each set of 97 scans, showed no significant change during the course of data collection. Lorentz and polarization corrections were made in the usual manner and no absorption correction was applied. Of the 3657 reflections collected with 3° < 2θ < 45°, 3314 were found to be unique and have $I \geq 3\sigma(I)$. The structure was solved by direct methods using the SHELXTL program. Following anisotropic refinement of the skeleton atoms, the hydrogen atoms were fixed into position and held isotropic. The final discrepancy index and weighted discrepancy index were R = 0.059 and R_w = 0.067, respectively, where $R_w = \sum_\omega^{1/2}(F_o - F_c)/\sum_\omega^{1/2}F$. The final positional and thermal parameters are given in Tables I–V (supplementary material).

A solution containing 200 mg (0.76 mmol) of α-diazo ketone **5** and 0.31 g (1.14 mmol) of diphenylisobenzofuran in 40 mL of dry dichloromethane was treated with a catalytic amount of rhodium(II) acetate under a nitrogen atmosphere. The solution was stirred for 2 h at 25 °C. Removal of the solvent under reduced pressure left an orange oil which was chromatographed to give 0.32 g (84%) of cycloadduct **8** as a yellow solid, mp 116–117 °C; IR ($CHCl_3$) 1708, 1607, 1457, and 986 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.68–0.80 (m, 1H), 1.15–1.37 (m, 3H), 1.58 (s, 3H), 1.65 (td, 1H, J = 14.0 and 5.0 Hz), 1.97–2.13 (m, 2H), 2.92–2.96 (m, 1H), 4.57 (d, 1H, J = 7.2 Hz), 6.76 (t, 1H, J = 7.5 Hz), 6.97 (t, 1H, J = 7.5 Hz), 7.09 (t, 1H, J = 7.5 Hz), 7.25–7.62 (m, 12H), and 7.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.0, 21.3, 21.5, 21.8, 22.2, 26.6, 37.0, 43.9, 88.6, 90.3, 121.3, 121.5, 121.6, 121.6, 125.5, 126.2, 126.2, 127.3, 127.5, 128.2, 128.7, 128.9, 129.4, 130.7, 132.9, 134.4, 135.5, 139.9, 144.6, 148.23, 148.9, 151.9, and 198.7; HRMS calcd for $C_{37}H_{30}O_2$ 506.2246, found 506.2254.

Preparation and Reaction of (*o*-(3-Methylbut-3-en-1-ynyl)benzoyl)-diazoethane (9) with Rhodium(II) Mandelate. The Castro–Stephens reaction of 2.0 g (7.6 mmol) of methyl 2-iodobenzoate and 1.10 mL (11.4 mmol) of 2-methyl-3-buten-1-yne in 50 mL of anhydrous triethylamine afforded 1.45 g (95%) of methyl 2-(3-methylbut-3-en-1-ynyl)benzoate: IR (neat) 1733, 1611, 1434, and 1295 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.02 (s, 3H), 3.93 (s, 3H), 5.33–5.34 (m, 1H), 5.44–5.45 (m, 1H), 7.35–7.56 (m, 3H), and 7.92–7.95 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 51.8, 87.0, 122.3, 123.4, 126.7, 127.6, 130.2, 131.4, 131.7, 133.7, and 166.4. A 2.0-g (10.0 mmol) sample of this compound was converted in the normal fashion to 0.85 g (38%) of (*o*-(3-methylbut-3-en-1-ynyl)-benzoyl)diazoethane (**9**): IR (neat) 2076, 1617, 1443, 1279, and 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.12 (s, 3H), 5.31–5.32 (m, 1H), 5.37 (s, 1H), and 7.37–7.46 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.6, 23.0, 65.3, 85.1, 93.9, 120.2, 122.6, 126.3, 127.1, 128.4, 129.7, 132.1, 140.5, and 189.8.

A solution containing 50 mg (0.2 mmol) of α-diazo ketone **9** in 0.5 mL of chloroform was treated with a catalytic amount of rhodium(II) mandelate. After the mixture was stirred for 10 min, the evolution of nitrogen had ceased and the 300-MHz NMR spectrum indicated the complete disappearance of starting material with the formation of cyclopropene **10** (95%) [($CDCl_3$, 300 MHz) δ 1.41 (s, 2H), 2.09 (s, 3H), 2.53 (s, 3H), 7.16–7.28 (m, 2H), 7.36 (t, 1H, J = 6.5 Hz), and 7.44 (t, 1H, J = 6.5 Hz)]. Cyclopropene **10** could not be isolated due to its rapid decomposition.

A solution containing 200 mg (0.89 mmol) of α-diazo ketone **9** in 20 mL of dichloromethane was treated with a catalytic amount of rhodium-(II) mandelate in the presence of oxygen. After the mixture was stirred at 25 °C for 30 min, the solvent was removed under reduced pressure to leave behind an orange oil. The oil was subjected to silica flash chromatography to give 36 mg (19%) of indenone **11**: IR (neat) 1710, 1684, 1605, 1131, and 936 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.74 (s, 3H), 2.42 (s, 3H), 5.97 (s, 1H), 6.49 (s, 1H), 6.74 (d, 1H, J = 6.0 Hz), 7.12 (t, 1H, J = 7.5 Hz), 7.25 (t, 1H, J = 7.5 Hz), and 7.39 (d, 1H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.6, 26.7, 119.8, 122.5, 128.1, 128.8, 130.1, 133.3, 133.5, 141.8, 145.5, 151.7, 196.9, and 197.4; HRMS calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0839.

A solution containing 200 mg (0.89 mmol) of α-diazo ketone **9** and 0.31 g (1.2 mmol) of diphenylisobenzofuran in 40 mL of dichloromethane was treated with a catalytic amount of rhodium(II) mandelate. The solution was stirred at 25 °C for 2 h. Removal of the solvent under reduced pressure left an orange oil which was chromatographed on silica gel to give 0.32 g (85%) of a 2:1 mixture of the exo and endo cycloadducts **12a** and **12b**: mp 213–214 °C; IR ($CHCl_3$) 1706, 1459, 1158, 895, and 752 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), major exo isomer, δ 0.86 (d, 1H, J = 4.5 Hz), 1.23 (s, 3H), 1.28 (s, 3H), 2.68 (d, 1H, J = 4.5 Hz), 4.47 (d, 1H, J = 7.5 Hz), and 6.75–7.90 (m, 17H); ^1H NMR (300 MHz, $CDCl_3$), minor endo isomer, δ 0.67 (s, 1H), 0.80 (d, 1H, J = 4.8 Hz), 1.28 (s, 3H), 2.61 (d, 1H, J = 4.8 Hz), 6.31 (d, 1H, J = 6.9 Hz), and 6.75–7.90 (m, 17H). Anal. Calcd for $C_{34}H_{26}O_2$: C, 87.53; H, 5.62. Found: C, 87.42; H, 5.64.

Preparation and Reaction of *o*-(3-Methylbut-3-en-1-ynyl)-α-diazoacetophenone (13) with Rhodium(II) Acetate. A 1.5-g (7.5 mmol) sample of methyl 2-(3-methylbut-3-en-1-ynyl)benzoate was converted in the normal fashion into 0.92 g (59%) of *o*-(3-methylbut-3-en-1-ynyl)-α-diazoacetophenone (**13**): IR (neat) 2103, 1617, 1355, and 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.99 (s, 3H), 5.34 (m, 1H), 5.41 (s, 1H), 6.25 (bs, 1H), 7.34–7.50 (m, 3H), and 7.70–7.72 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 56.4, 86.4, 96.2, 120.2, 122.5, 126.0, 127.6, 127.9, 130.5, 133.1, 138.8, and 186.7.

A solution containing 0.51 g (2.4 mmol) of α-diazo ketone **13** in 40 mL of dry dichloromethane was treated with a catalytic amount of rhodium(II) acetate. The solution was stirred at 25 °C for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography to give 0.27 g (54%) of dimer **15** as yellow crystals: mp 117–118 °C; IR ($CHCl_3$) 1707, 1603, and 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, 1H, J = 8.1 Hz), 1.15 (d, 1H, J = 8.1 Hz), 1.30 (d, 1H, J = 4.5 Hz), 1.36 (s, 3H), 2.10 (s, 3H), 2.29 (d, 1H, J = 4.5 Hz), 3.02 (s, 1H), 5.02 (s, 1H), 7.02 (d, 1H, J = 6.0 Hz), 7.22–7.50 (m, 6H), and 7.87 (d, 1H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.6, 11.5, 13.9, 29.9, 30.9, 37.3, 52.3, 58.2, 107.9, 111.0, 120.7, 121.8, 124.3, 124.6, 126.9, 128.6, 129.0, 130.6, 133.3, 134.9, 136.4, 144.7, 155.0, 161.1, 197.4, and 203.1; HRMS calcd for $C_{26}H_{20}O_2$ 364.1463, found 364.1463.

Crystals suitable for an X-ray crystallographic structure determination of dimer **15** were grown from a methylene chloride–hexane solution. A single crystal of approximately 0.40 × 0.40 × 0.60 mm was mounted on a quartz fiber such that the longest crystal dimension was parallel to the fiber axis. Unit cell parameters were determined on a Syntex $P2_1$ automated diffractometer using Mo Kα radiation. Twenty four reflections were machine centered and used in the least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were a = 8.554(3) Å, b = 9.890(2) Å, c = 12.316(4) Å, α = 93.49(2)°, β = 103.63(3)°, γ = 95.48(2)°, V = 1004(1) Å^3, d_{calcd} = 1.21 g cm^{-3}, $F(000)$ = 384.0, Z = 2, and space group $P\bar{1}$. Intensity data were collected by using the ω scan technique with a variable scan rate of 2.0–24.0 deg min^{-1} in 2θ deg min^{-1} in 2θ. A sca width of 2.1° was sufficient to collect all of the peak intensity data. Check reflections, monitored after each set of 97 scans, showed no significant change during the course of data collection. Lorentz and polarization corrections were

made in the usual manner and no absorption correction was applied. Of the 2848 reflections collected with $3° < 2\theta < 45°$, 2636 were found to be unique and have $I \geq 3\sigma(I)$. The structure was solved by direct methods using the SHELXTL program. Following anisotropic refinement of the skeleton atoms, the hydrogen atoms were fixed into position and held isotropic. The final discrepancy index and weighted discrepancy index were $R = 0.0825$ and $R_w = 0.0915$, respectively, where $R_w = \sum_\omega{}^{1/2}(F_o - F_c)/\sum_\omega{}^{1/2}F$. The final positional and thermal parameters are given in Tables VI–X (supplementary material).

A solution containing 0.25 g (1.2 mmol) of α-diazo ketone **13** and 0.48 g (1.8 mmol) of diphenylisobenzofuran in 60 mL of dichloromethane was treated with a catalytic amount of rhodium(II) acetate. The resulting solution was stirred at 25 °C for 2 h. Removal of solvent left an orange oil which was purified by flash silica gel chromatography to give 0.27 g (50%) of cycloadduct **16** as well as 18 mg of dimer **15**. Cycloadduct **16** exhibited the following properties: mp 178–179 °C; IR ($CHCl_3$) 1706, 1603, 1449, 1302, and 984 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.20 (d, 1H, J = 6.0 Hz), 2.73 (d, 1H, J = 6.0 Hz), 4.62 (bs, 1H), 6.67 (s, 1H), 7.15–7.40 (m, 10H), 7.46–7.56 (m, 4H), 7.59–7.62 (m, 2H), and 7.78–7.83 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 24.5, 37.9, 39.1, 90.1, 90.2, 121.6, 121.7, 121.9, 122.0, 126.2, 126.2, 126.4, 127.1, 127.9, 128.1, 128.6, 128.8, 130.7, 133.1, 134.4, 135.6, 145.5, 148.1, 148.4, 161.3, and 197.9. Anal. Calcd for $C_{33}H_{24}O_2$: C, 87.58; H, 5.35. Found: C, 86.78; H, 5.44.

Reaction of Phenylpropynal with *N*-Amino-*trans*-1,2-diphenylaziridine. A mixture containing 150 mg (1.1 mmol) of phenylpropynal and 290 mg (1.4 mmol) of *N*-amino-*trans*-1,2-diphenylaziridine[78] in 10 mL of methylene chloride was stirred at 0 °C for 2 h. The solution was dried over magnesium sulfate and the solvent was removed under pressure. The crude residue was dissolved in 30 mL of benzene and then heated at reflux for 3 h. The solvent was removed under reduced pressure and the resulting residue was purified by silica gel chromatography. The major fraction contained 150 mg (41%) of *N*-((phenylethynyl)methylene)-*trans*-2,3-diphenyl-1-aziridinamine (**24**) as a clear oil: IR (neat) 1590, 1475, 1320, 1160, 1000, 780, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.67 (s, 2H), 6.81 (d, 2H, J = 7.2 Hz), 7.17 (t, 2H, J = 7.2 Hz), and 7.25–7.38 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 53.1, 82.2, 101.2, 120.8, 127.0, 127.6, 127.7, 128.8, 131.4, and 136.7. Anal. Calcd for $C_{23}H_{18}N_2$: C, 85.67; H, 5.65; N, 8.69. Found: C, 85.34; H, 5.74; N, 8.01.

A mixture containing 200 mg (1.5 mmol) of phenylpropynal and 390 mg of *N*-amino-*trans*-1,2-diphenylaziridine (1.9 mmol) in 10 mL of methylene chloride was stirred at 0 °C for 2 h. The solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude residue was dissolved in 30 mL of methanol and the mixture was heated at 80 °C for 3 h. After the solvent was removed, the resulting oil was purified by silica gel chromatography. The first fraction contained 67 mg (31%) of 3-methoxy-3-phenyl-1-propyne[79] (**28a**) as a light yellow oil: IR (neat) 2120, 1500, 1455, 1080, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.64 (d, 1H, J = 2.1 Hz), 3.43 (s, 3H), 5.08 (d, 1H, J = 2.1 Hz), 7.35 (m, 3H), and 7.50 (d, 2H, J = 6.9 Hz). Anal. Calcd for $C_{10}H_{10}O$: C, 82.15; H, 6.90. Found: C, 81.93; H, 6.79. The minor product was identified as 3-methoxy-1-phenyl-1-propyne[74] (**27a**): IR ($CHCl_3$) 1490, 1360, 1095, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.50 (s, 3H), 4.50 (s, 2H), and 7.40 (m, 5H). Anal. Calcd for $C_{10}H_{10}O$: C, 82.15; H, 6.90. Found: C, 82.28; H, 6.64. The same two products were obtained in the same ratio by heating a sample of aziridinamine **24** in methanol for 2 h.

A 200-mg (6.2 mmol) sample of **24** was heated at reflux in 30 mL of 2-isopropanol for 3 h. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography. The first fraction isolated contained 52 mg (18%) of 1-phenyl-3-isopropoxy-1-propyne (**27b**) as a clear oil: IR (neat) 2990, 1490, 1385, 1125, 760, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21 (d, 6H, J = 6.3 Hz), 3.86 (m, 1H), 4.36 (s, 2H), 7.29 (m, 3H), and 7.43 (m, 2H). Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.10. Found: C, 82.59; H, 7.92. The minor product was identified as 3-phenyl-3-isopropoxy-1-propyne (**28b**): IR (neat) 1650, 1450, 1280, 1120, 1050, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (d, 3H, J = 6.0 Hz), 1.23 (d, 3H, J = 6.0 Hz), 2.56 (d, 1H, J = 2.1 Hz), 3.97 (m, 1H), 5.19 (d, 1H, J = 2.1 Hz), 7.32 (m, 3H), and 7.49 (d, 2H, J = 6.9 Hz). Anal. Calcd for $C_{12}H_{14}O$: C, 82.71; H, 8.10. Found: C, 82.65; H, 8.03.

Reaction of 3-(2-Allylphenyl)-2-propynal with *N*-Amino-*trans*-2,3-diphenylaziridine. The Castro–Stephens reaction of 18.0 g (63.7 mmol) of *o*-bromoiodobenzene and 7.44 g (75.7 mmol) of ethynyltrimethylsilane gave 14.2 g (89%) of 1-bromo-2-[(trimethylsilyl)ethynyl]benzene: bp 89–91 °C (2 mm); IR (neat) 1470, 1255, 1030, 850, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.40 (s, 9H), and 7.25–7.80 (m, 4H). To a solution containing 14.2 g (65.4 mmol) of this compound in 400 mL of ether at −78 °C was added 69.1 mL of a 1.7 M solution of *tert*-butyllithium (115 mmol). After the mixture was stirred for 20 min, 20.3 g (167 mmol) of allyl bromide in 70 mL of ether was added over a period of 10 min and the mixture was stirred at 25 °C for an additional 12 h. The solution was quenched with an ammonium chloride solution and then extracted with ether. The combined ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure to give 2-allyl[(trimethylsilyl)ethynyl]benzene in 85% yield which was used directly in the next step without further purification: IR (neat) 1630, 1480, 1250, 870, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9H), 3.55 (d, 2H, J = 6.0 Hz), 4.95 (s, 1H), 5.15 (d, 1H, J = 5.5 Hz), 5.70–6.20 (m, 1H), and 7.10–7.50 (m, 4H).

To a solution containing 12.0 g (56 mmol) of the above compound in 200 mL of a THF–water mixture (10:1) at 0 °C was added dropwise 165 mL of a 1.0 M solution of *tetra*-butylammonium fluoride. The reaction mixture was stirred overnight and poured into a saturated solution of ammonium chloride. After extraction with ether, the combined ether extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure was followed by vacuum distillation to give 4.65 g (58%) of 2-allyl-1-ethynylbenzene: bp 49–50 °C (2 mmHg); IR (neat) 1640, 1450, 925, and 765 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.27 (s, 1H), 3.59 (d, 2H, J = 6.6 Hz), 5.07 (d, 1H, J = 1.5 Hz), 5.11 (d, 1H, J = 1.5 Hz), 5.94–6.07 (m, 1H), 7.15–7.32 (m, 3H), and 7.49 (d, 1H, J = 7.5 Hz).

To a solution containing 1.58 mL of a 1.0 M solution of ethylmagnesium bromide in 10 mL of tetrahydrofuran was added 300 mg (2.1 mmol) of 2-allyl-1-ethynylbenzene in 1 mL of tetrahydrofuran. The mixture was heated at reflux for 30 min and cooled to 0 °C and then 356 mg (3.2 mmol) of 1-morpholinoformaldehyde[80] in 5 mL of ether was added dropwise. The solution was stirred for 45 min at 25 °C and was then acidified with a 3.0 N hydrochloric acid solution followed by extraction with ether. The combined ether extracts were washed with brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 290 mg (83%) of 3-(2-allylphenyl)-2-propynal as a clear oil: IR (neat) 1660, 1260, 985, and 720 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.60 (d, 2H, J = 6.0 Hz), 5.10 (m, 1H), 5.20 (m, 1H), 5.75–6.20 (m, 1H), 7.25–7.70 (m, 4H), and 9.50 (s, 1H). Anal. Calcd for $C_{12}H_{10}O$: C, 84.67; H, 5.93. Found: C, 84.51; H, 6.02.

A mixture containing 290 mg (1.7 mmol) of the above aldehyde and 430 mg (2.0 mmol) of *N*-amino-*trans*-2,3-diphenylaziridine in 15 mL of methylene chloride was stirred at 0 °C for 2 h. The solution was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting oil was dissolved in 25 mL of benzene and was heated at reflux for 3 h. The solvent was removed under reduced pressure and the residue was purified by distillation to give 130 mg (50%) of 1-ethynyl-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**31**): bp 60–65 °C (4 mmHg); IR (neat) 1600, 1475, 765, 725, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.65 (t, 1H, J = 4.8 Hz), 1.61 (m, 1H), 2.19 (s, 1H), 2.33 (dd, 1H, J = 6.9 and 6.6 Hz), 2.93 (d, 1H, J = 17.1 Hz), 3.32 (dd, 1H, J = 17.1 and 6.6 Hz), 7.22 (m, 3H), and 7.53 (d, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.9, 25.7, 26.6, 34.1, 66.2, 84.6, 122.5, 124.9, 125.8, 125.8, 139.9, and 144.5. Anal. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.37; H, 6.48.

Reaction of 1-Ethenyl-2-(2-formylethynyl)benzene with *N*-Amino-*trans*-2,3-diphenylaziridine. The Castro–Stephens reaction of 5.0 g (21.4 mmol) of 2-iodobenzyl alcohol and 4.5 g (32.0 mmol) of tetrahydro-2-(2-propynyloxy)-2*H*-pyran gave 3.50 g (66%) of tetrahydro-2-[3-(2-(hydroxymethyl)phenyl)-2-propynyloxy]-2*H*-pyran as a yellow oil: IR (neat) 2869, 2232, 1202, and 1023 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.53–1.83 (m, 6H), 2.34 (s, 1H), 3.55–3.59 (m, 1H), 3.86–3.90 (m, 1H), 4.53 (s, 2H), 4.81 (d, 2H, J = 3.0 Hz), 4.90 (t, 1H, J = 3.0 Hz), and 7.22–7.47 (m, 4H).

To a flask charged with 3.28 g (15.2 mmol) of pyridinium chlorochromate in 20 mL of methylene chloride was added a solution of 2.5 g

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(10.0 mmol) of the above compound in 5 mL of methylene chloride. The resulting mixture was stirred at 25 °C for 4 h and filtered through a pad of silica gel. Concentration under reduced pressure left an orange oil which was chromatographed on silica gel to give 1.74 g (73%) of tetrahydro-2-[3-(2-formylphenyl)-2-propynyloxy]-2*H*-pyran as a colorless oil: IR (neat) 1690, 1590, 1020, and 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45–1.90 (m, 6H), 3.54–3.58 (m, 1H), 3.84–3.87 (m, 1H), 4.54 (d, 2H, J = 3.0 Hz), 4.88 (t, 1H, J = 3.0 Hz), 7.41–7.55 (m, 3H), 7.90 (d, 1H, J = 9.0 Hz), and 10.51 (s, 1H).

To a flask charged with 5.79 g (16.2 mmol) of methyltriphenylphosphonium bromide in 90 mL of ether was added 9.3 mL (14.9 mmol) of a 1.6 M *n*-BuLi solution. The resulting yellow suspension was stirred at 25 °C for 1 h. To this mixture was added 3.3 g (13.5 mmol) of the above compound in 20 mL of ether. A thick paste was formed which was stirred for an additional 20 min. The reaction was quenched with 10 mL of a 10% NH_4Cl solution, washed with brine, and dried ($MgSO_4$). Removal of solvent under reduced pressure left an orange oil which was chromatographed on silica gel to give 2.6 g (80%) of tetrahydro-2-[3-(2-ethenylphenyl)-2-propynyloxy]-2*H*-pyran as a colorless oil: IR (neat) 1629, 1324, 1183, and 944 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50–1.90 (m, 6H), 3.50–3.60 (m, 1H), 3.84–3.92 (m, 1H), 4.53 (d, 2H, J = 3.0 Hz), 4.91 (t, 1H, J = 3.0 Hz), 5.33 (d, 1H, J = 9.0 Hz), 5.78 (d, 1H, J = 18.0 Hz), 7.14–7.30 (m, 3H), 7.43 (d, 1H, J = 9.0 Hz), and 7.55 (d, 1H, J = 6.0 Hz).

To a solution containing 2.0 g (8.3 mmol) of the above compound in 50 mL of methanol was added 2.0 g of Amberlyst-15. The resulting mixture was stirred at 25 °C for 3 h, filtered through a pad of Celite, and concentrated under reduced pressure. The resulting oil was purified by silica gel chromatography to give 1.20 g (92%) of 1-ethenyl-2-(3-hydroxypropynyl)benzene as a colorless oil: IR (neat) 2865, 2231, 1478, and 1027 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.72 (t, 1H, J = 6.0 Hz), 4.55 (d, 2H, J = 6.0 Hz), 5.35 (d, 1H, J = 12.0 Hz), 5.80 (d, 1H, J = 18.0 Hz), 7.14–7.32 (m, 2H), 7.43 (d, 1H, J = 6.0 Hz), and 7.58 (d, 1H, J = 9.0 Hz).

To a flask charged with 2.0 g (9.5 mmol) of pyridinium chlorochromate in 25 mL of methylene chloride was added a solution of 1.0 g (6.3 mmol) of the above compound in 10 mL of methylene chloride. The resulting mixture was stirred at 25 °C for 2 h and then purified by silica gel chromatography to provide 0.85 g (86%) of 1-ethenyl-2-(2-formylethynyl)-benzene as a pale yellow oil: IR (neat) 1654, 1478, 1010, and 982 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.46 (d, 1H, J = 9.0 Hz), 5.87 (d, 1H, J = 15.0 Hz), 7.18 (dd, 1H, J = 15.0 and 9.0 Hz), 7.29 (t, 1H, J = 7.5 Hz), 7.46 (t, 1H, J = 7.5 Hz), 7.59 (d, 1H, J = 9.0 Hz), 7.62 (d, 1H, J = 9.0 Hz), and 9.47 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 92.3, 92.8, 117.0, 117.5, 124.5, 127.4, 131.0, 133.3, 133.8, 140.7, and 176.1; HRMS calcd for $C_{11}H_8O$ 156.0575, found 156.0574.

To a solution containing 0.40 g (2.6 mmol) of the above aldehyde in 20 mL of methylene chloride at 0 °C was added 0.73 g (3.1 mmol) of *N*-amino-*trans*-2,3-diphenylaziridine. The resulting solution was stirred at 0 °C for 1 h and was then dried over $MgSO_4$. Removal of the solvent left gave a clear oil which was taken up in 40 mL of dry benzene. The solution was heated at reflux for 14 h. Concentration under reduced pressure left an orange oil which was chromatographed on silica gel to give 0.15 g (42%) of 1-ethynyl-1-indene (**34**) as a pale orange oil: IR (neat) 2927, 1459, 1291, and 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.25 (s, 1H), 3.49 (s, 2H), 6.86 (s, 1H), 7.26 (t, 1H, J = 6.0 Hz), 7.35 (t, 1H, J = 6.0 Hz), 7.46 (d, 1H, J = 6.0 Hz), and 7.55 (d, 1H, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.5, 77.8, 80.7, 120.2, 123.6, 125.5, 125.5, 126.5, 139.8, 142.40, and 143.4; HRMS calcd for $C_{11}H_8$ 140.0626, found 140.0622.

An authentic sample of **34** was prepared by the dehydration of 1-ethynyl-1-hydroxyindan: mp 68–69 °C; IR ($CHCl_3$) 2118, 1461, and 1038 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 1H), 2.41–2.50 (m, 1H), 2.54–2.63 (m, 1H), 2.65 (s, 1H), 2.89–2.98 (m, 1H), 3.08–3.18 (m, 1H), 7.24–7.31 (m, 3H), and 7.52–7.55 (m, 1H). Anal. Calcd for $C_{11}H_{10}O$: C, 83.52; H, 6.37. Found: C, 83.60; H, 6.39. To a solution containing 0.5 g (3.2 mmol) of the above hydroxyindan in 50 mL of ether was added 0.4 mL (3.2 mmol) of boron trifluoride etherate. The reaction mixture was heated at reflux for 2 h. Concentration of the mixture under reduced pressure left an orange oil which was chromatographed on silica gel to give 0.39 g (87%) of 1-ethynyl-1-indene (**34**).

Reaction of 3-(1-Ethoxycyclopentyl)-2-propynal with *N*-Amino-*trans*-2,3-diphenylaziridine. To 75 mL of dimethyl sulfoxide was added 9.58 g (240 mmol) of potassium hydroxide and the suspension was stirred at 25 °C for 10 min. To this mixture was added 4.0 g (36 mmol) of 1-ethynylcyclopentanol followed by the addition of 7.91 g (72.6 mmol) of ethyl bromide. After the initial exotherm subsided, the mixture was stirred for 45 min at 25 °C and was quenched with 100 mL of water and extracted with methylene chloride. The combined organic extracts were washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 4.96 g (99%) of 1-ethoxy-1-ethynylcyclopentane: IR (neat) 2105, 1440, 1390, 1205, and 790 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.10 (t, 3H, J = 7.0 Hz), 1.55–2.00 (m, 8H), 2.35 (s, 1H), and 4.50 (q, 2H, J = 7.0 Hz).

To a solution containing 11.1 mL of a 2.0 M ethylmagnesium bromide solution (22 mmol) in 30 mL of tetrahydrofuran was added 2.04 g (14.7 mmol) of the above alkyne in 3 mL of tetrahydrofuran. The mixture was heated at reflux for 30 min and cooled to 0 °C and 2.22 mL (22 mmol) of 1-morpholinoformaldehyde in 15 mL of ether was added dropwise over a 3-min period. The resulting solution was stirred for 45 min at 25 °C and was then acidified with a 3.0 N hydrochloric acid solution. The mixture was extracted with ether and the combined organic extracts were washed with brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 1.74 g (71%) of 3-(1-ethoxycyclopentyl)-2-propynal: IR (neat) 1675, 1450, 1395, 1225, and 1075 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.25 (t, 3H, J = 6.5 Hz), 1.80–2.20 (m, 8H), 3.60 (q, 2H, J = 6.5 Hz), and 9.30 (s, 1H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49. Found: C, 72.08; H, 8.36.

A solution containing 160 mg (0.96 mmol) of the above aldehyde and 220 mg (1.04 mmol) of *N*-amino-*trans*-2,3-diphenylaziridine in 15 mL of methylene chloride was cooled to 0 °C and stirred for 2 h. The mixture was dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure to leave behind a clear oil which was taken up in 30 mL of benzene and heated at reflux for 3 h. Removal of the solvent under reduced pressure left an oil which was purified by silica gel chromatography to give 54 mg (37%) of 1-ethoxy-2-ethynylcyclohexene (**38**): IR (neat) 1630, 1440, 1355, 1220, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.26 (t, 3H, J = 6.9 Hz), 1.50–1.57 (m, 2H), 1.65–1.70 (m, 2H), 2.17 (m, 4H), 3.06 (s, 1H), and 4.01 (q, 2H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.9, 21.6, 21.9, 25.9, 28.3, 63.3, 78.8, 82.5, 96.3, and 159.8. Anal. Calcd for $C_{10}H_{14}O$: C, 79.94; H, 9.40. Found: C, 79.65; H, 9.37.

Reaction of 3-(1-((*tert*-Butyldimethylsilyl)oxy)cyclopentyl)-2-propynal with *N*-Amino-*trans*-2,3-diphenylaziridine. A mixture containing 0.92 g (8.9 mmol) of 1-ethynylcyclopentanol, 2.36 g (21.4 mmol) of imidazole, and 2.51 g (21.4 mmol) of *tert*-butyldimethylsilyl chloride in 16 mL of dimethylformamide was heated at 70 °C for 36 h. The mixture was cooled to room temperature and was diluted with 100 mL of water and extracted with ether. The combined organic extracts were washed with brine and dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 1.54 g (82%) of 1-((*tert*-butyldimethylsilyl)oxy)-1-ethynylcyclopentane: bp 56–59 °C (4 mmHg); IR (neat) 1465, 1250, 1050, 835, and 775 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.15 (s, 6H), 0.85 (s, 9H), 1.80 (m, 8H), and 2.40 (s, 1H).

To a solution containing 5.2 mL of 2.0 M ethylmagnesium bromide (10.4 mmol) in 20 mL of tetrahydrofuran was added 1.54 g (6.86 mmol) of the above alkyne in 2 mL of tetrahydrofuran over a period of 2 min. After being heated at reflux for 30 min, the mixture was cooled to 0 °C and 1.18 g (10.6 mmol) of 1-morpholinoformaldehyde in 10 mL of ether was added over a 3-min period. The solution was allowed to stir at 25 °C for 45 min. At the end of this time, the mixture was acidified with a 3.0 N hydrochloric acid solution and extracted with ether. The combined ether extracts were washed with brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 0.76 g (44%) of 3-(1-((*tert*-butyldimethylsilyl)oxy)cyclopentyl)-2-propynal: bp 91–93 °C (4 mm); IR (neat) 1675, 1260, 1065, 840, and 785 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.20 (s, 6H), 0.90 (s, 9H), 1.80 (m, 8H), and 9.30 (s, 1H).

A solution containing 0.71 g (2.9 mmol) of the above aldehyde and 1.18 g (5.6 mmol) of *N*-amino-*trans*-2,3-diphenylaziridine in 20 mL of methylene chloride was cooled to 0 °C and stirred at this temperature for 2 h. The mixture was dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure to leave behind a clear oil which was taken up in 30 mL of benzene and heated at reflux for 3 h. Removal of the solvent under reduced pressure left a clear oil which was purified by distillation at 60 °C (4 mmHg) to give 0.36 g (55%) of 1-((*tert*-butyldimethylsilyl)oxy)-2-ethynylcyclohexene (**39**): IR (neat) 1640, 1260, 1235, 940, 840, and 790 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 6H), 0.95 (s, 9H), 1.56 (m, 2H), 1.63 (m, 2H), 2.08 (m, 2H), 2.17 (m, 2H), and 2.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –4.4, 17.6, 21.6, 22.2, 25.1, 27.9, 30.2, 78.7, 83.0, 98.1, and 156.6.

A solution containing 130 mg (6.1 mmol) of **39** in 4 mL of acetic acid–water–THF (1:1:3) was stirred at 25 °C for 24 h. The mixture was neutralized with solid sodium bicarbonate and extracted with ether. The combined ether extracts were dried over magnesium sulfate. Removal of the solvent under reduced pressure left an oil which was purified by silica gel chromatography to give 54 mg (54%) of 2-(1-hydroxyethylidene)-cyclohexanone acetate (**40**):[81] IR (neat) 1755, 1690, 1435, 1370, 1180 and 1020 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.65 (quint, 2H, J = 6.0 Hz), 1.80 (m, 2H), 2.11 (s, 3H), 2.13 (s, 3H), and 2.31–2.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 20.1, 22.8, 23.3, 26.0, 41.4, 125.0, 153.1, 167.2, and 201.4; UV (methanol) λ_{max} 240 (ϵ 7300). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.90; H, 7.75. Found: C, 65.74; H, 7.59.

Preparation and Rhodium(II)-Catalyzed Reaction of *o*-[4-Phenylbuta-1,3-diynyl]-2-diazo-1-phenylpropanone (41) with Ethyl Vinyl Ether. To a solution containing 4.0 g (39.0 mmol) phenylacetylene and 39.0 g (120 mmol) of carbon tetrabromide in 100 mL of anhydrous dichloromethane was added 61.0 g (230 mmol) of triphenylphosphine under an argon atmosphere. The reaction mixture was stirred for 30 min at room temperature and then poured into 200 mL of ether. Filtration of the salt followed by evaporation of the solvent afforded 1.80 g (40%) of 2-bromo-1-phenylethyne: IR (neat) 2191, 1520, and 1480 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.30 (m, 2H) and 7.46 (m, 3H).

A solution containing 3.0 g (16.5 mmol) of the above bromide in 8.0 mL of ethanol was added dropwise to a mixture containing 2.24 g (14.0 mmol) of methyl 2-ethynylbenzoate, 3.4 mL of *n*-butylamine, 0.4 g of hydroxylamine hydrochloride, and 0.02 g of cuprous chloride in 35 mL of ethanol. After being stirred at room temperature for 1 h, the reaction mixture was poured into 100 mL of water and extracted with ether. The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure. Chromatography of the residue on silica using benzene as the eluent afforded 1.60 g (45%) of methyl 2-[4-phenylbuta-1,3-diynyl]benzoate: IR (neat) 2197, 1730, 1435, and 1288 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.90 (s, 3H), 7.20–7.60 (m, 6H), and 7.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.2, 74.0, 78.4, 79.7, 83.2, 121.7, 122.5, 128.3, 128.6, 129.2, 130.5, 131.6, 131.7, 132.5, 132.5, 135.1, and 165.9.

To a solution containing 0.60 g (4.5 mmol) of potassium trimethylsilanolate in 50 mL of anhydrous ether was added 1.0 g (3.8 mmol) of the above diacetylenic ester. The reaction mixture was stirred for 5 h at room temperature under a nitrogen atmosphere. After the reaction mixture was cooled to 0 °C, 15 mmol of methyl chloroformate was added and stirring was continued for an additional 4 h at 25 °C. The solution was filtered, an ethereal diazoethane solution (30 mmol) was added, and stirring was continued for 3 h. The excess diazoethane and ether were removed under reduced pressure and the resulting residue was chromatographed on silica gel. The major fraction contained 445 mg (45%) of *o*-[4-phenylbuta-1,3-diynyl]-2-diazo-1-phenylpropanone (**41**): IR (neat) 2076, 1611, 1345, and 997 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (s, 3H), 7.30 (m, 6H), and 7.50 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.0, 65.4, 73.6, 78.1, 79.2, 82.8, 119.1, 121.3, 127.1, 127.2, 128.3, 129.0, 129.3, 129.4, 129.9, 130.0, 132.4, 133.2, 133.7, and 198.4.

To a solution containing 100 mg (0.35 mmol) of α-diazo ketone **41** in 20 mL of ethyl vinyl ether was added a catalytic amount of rhodium(II) acetate dimer. The reaction mixture was stirred at room temperature for 15 min and then the excess ethyl vinyl ether was removed under reduced pressure. The crude residue was chromatographed on silica gel to give 136 mg (90%) of 2-ethoxy-1-[2-methyl-1-oxoindenylethynyl]-1-phenylcyclopropane (**44**): IR (neat) 2970, 1713, 1520, 1430, and 1150 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, 3H, J = 7.0 Hz), 1.28 (m, 1H), 1.88 (dd, 1H, J = 7.0 and 4.0 Hz), 1.98 (s, 3H), 3.35 (m, 1H), 3.57 (m, 1H), 3.72 (dd, 1H, J = 7.0 and 4.0 Hz), 7.08–7.60 (m, 6H), and 7.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.4, 15.0, 24.7, 26.4, 66.2, 66.9, 74.4, 119.8, 121.8, 125.3, 126.4, 126.5, 127.2, 127.6, 127.8, 128.4, 128.8, 130.2, 133.6, 137.4, 138.7, 139.3, 143.7, and 197.8; HRMS calcd for $C_{23}H_{20}O_2$ 328.1463, found 328.1467.

Preparation and Rhodium(II)-Catalyzed Reaction of *o*-[5-Methylhexa-1,3-diynyl]-2-diazo-1-phenylpropanone (46). To a solution containing 3.0 g (18.7 mmol) of methyl 2-ethynylbenzoate and 18.6 g (56 mmol) of carbon tetrabromide in 40 mL of anhydrous dichloromethane was added 30.0 g (106 mmol) of triphenylphosphine under Ar. The reaction mixture was stirred for 20 min at room temperature and was then poured into 200 mL of ether. Filtration and concentration of the solvent under reduced pressure afforded 1.8 g (40%) of methyl 2-[2-bromoethynyl]benzoate: IR (neat) 2200, 1730, and 1253 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.98 (s, 3H) and 7.30–7.95 (m, 4H).

A solution containing 1.5 g (7 mmol) of the above bromide in 8.0 mL of ethanol was added dropwise to a mixture of 0.5 g (5.0 mmol) of 3-methyl-1-butyne, 17.5 mL of ethanol, and 3.4 mL of a *n*-butylamine solution which contained 0.8 g of hydroxylamine hydrochloride and 0.02 g of cuprous chloride. After being stirred at room temperature for 1 h, the reaction mixture was poured into 100 mL of water and extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Chromatography of the residue on silica gel using benzene as the eluent afforded 0.63 g (42%) of methyl 2-[5-methylhexa-1,3-diynyl]benzoate:[82] IR (neat) 2238, 1732, 1485, and 751 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.40 (d, 6H, J = 6.9 Hz), 2.65 (sept, 1H, J = 6.9 Hz), 3.84 (s, 3H), 7.20–7.45 (m, 3H), and 7.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.9, 21.4, 50.7, 52.4, 63.9, 72.9, 78.6, 90.8, 122.2, 128.8, 130.7, 131.8, 133.5, 135.4, and 165.3.

To a solution containing 0.34 g (2.5 mmol) of potassium trimethylsilanolate in 50 mL of anhydrous ether was added 0.5 g (2.2 mmol) of the above compound. The reaction mixture was stirred for 5 h at room temperature under N_2. After the reaction mixture was cooled to 0 °C, 10 mmol of methyl chloroformate was added and stirring was continued for an additional 4 h at 25 °C. The solution was filtered, an ethereal diazoethane solution (20 mmol) was added, and the mixture was stirred for 4 h at 25 °C. The excess diazoethane and ether were removed under reduced pressure and the resulting residue was chromatographed on silica gel to give 225 mg (45%) of *o*-[5-methylhexa-1,3-diynyl]-2-diazo-1-phenylpropanone (**46**); IR (neat) 2228, 2079, 1630, and 1438 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.40 (d, 6H, J = 6.9 Hz), 2.12 (s, 3H), 2.65 (sept, 1H, J = 6.9 Hz), 3.84 (s, 3H), and 7.30–7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.0, 19.9, 21.4, 52.4, 63.9, 72.9, 78.7, 90.8, 122.2, 128.8, 130.7, 131.8, 133.5, 135.4, and 198.5.

To a solution containing 100 mg of **46** in 25 mL of anhydrous methylene chloride was added a catalytic amount of rhodium(II) acetate dimer. The reaction mixture was stirred at room temperature until N_2 evolution had ceased and was then concentrated under reduced pressure. The residue was chromatographed on silica gel to give 98 mg (92%) of 2-methyl-3-[4-methyl-3-penten-1-ynyl]inden-1-one (**49**): IR (neat) 2213, 1715, 1600, and 1464 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.93 (s, 3H), 1.97 (s, 3H), 2.05 (s, 3H), 5.65 (s, 1H), 7.15 (m, 3H), and 7.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.2, 21.4, 25.3, 65.6, 84.7, 105.2, 119.6, 121.7, 128.9, 130.21, 133.3, 137.1, 138.9, 143.6, 152.9, and 197.4; HRMS calcd for $C_{16}H_{14}O$ 222.1044, found 222.1042.

Preparation and Rhodium(II)-Catalyzed Reaction of *o*-(4-[2-(2-Propen-1-yl)phenyl]buta-1,3-diynyl)-2-diazo-1-phenylpropanone (50). To a solution containing 18.0 g (63.6 mmol) of 2-iodobromobenzene, 7.4 g (75.3 mmol) of ethynyltrimethylsilane, and 140 mg of cuprous iodide in 180 mL of anhydrous triethylamine was added 70 mg of bis(triphenylphosphine)palladium(II) chloride under Ar. The reaction mixture was heated at reflux for 12 h, cooled, filtered, and then concentrated under reduced pressure. Distillation of the residue under reduced pressure (bp 89–90 °C (2 mmHg)) afforded 14.1 g (89%) of methyl 1-bromo-2-[(trimethylsilyl)ethynyl]benzene:[83] IR (neat) 2180, 1470, 1255, 1030, 850, and 760 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.40 (s, 9H) and 7.25–7.80 (m, 4H).

To a solution containing 14.1 g (55 mmol) of the above acetylene in 400 mL of anhydrous ether was added 69.0 mL of a 1.7 M solution of *tert*-butyllithium (117 mmol) dropwise at −78 °C. After being stirred for 20 min at −78 °C, a solution containing 20.3 g (167 mmol) of allyl bromide in 70 mL of ether was added dropwise over a period of 10 min. The reaction mixture was stirred at room temperature for 12 h and was then poured into a saturated aqueous solution of ammonium chloride. The solution was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure to give 12.5 g (85%) of 2-(2-propenyl)[(trimethylsilyl)ethynyl]benzene: IR (neat) 2160, 1630, 1250, and 960 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9H), 3.55 (d, 2H, J = 6.0 Hz), 4.95 (d, 1H, J = 1.5 Hz), 5.15 (d, 1H, J = 1.5 Hz), 5.70–6.20 (m, 1H), and 7.10–7.50 (m, 4H).

To a solution containing 12.0 g (67.4 mmol) of the above compound in 200 mL of a 10:1 THF–H_2O mixture was added 165 mL of 1.0 M *tetra*-butylammonium fluoride dropwise at 0 °C. The reaction mixture was stirred at room temperature for 16 h and was then poured into a saturated solution of ammonium chloride. The solution was extracted

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with ether and the combined ether extracts were washed with water and brine, dried over magnesium sulfate, and concentrated under reduced pressure. Distillation of the residue under reduced pressure (bp 49–50 °C (2 mmHg)) afforded 6.16 g (78%) of 2-(2-propen-1-yl)-1-ethynylbenzene: IR (neat) 2120, 1640, and 925 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.28 (s, 1H), 3.61 (d, 2H, J = 6.5 Hz), 5.07 (d, 1H, J = 17.1 Hz), 5.11 (d, 1H, J = 8.5 Hz), 5.94–6.07 (ddt, 1H, J = 17.1, 8.5, and 6.5 Hz), 7.15–7.32 (m, 3H), and 7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.1, 80.7, 81.8, 115.7, 121.2, 125.6, 128.4, 128.5, 132.4, 135.9, and 142.1.

To a solution containing 2.85 g (20.0 mmol) of the above acetylene and 19.9 g (60 mmol) of carbon tetrabromide in 150 mL of anhydrous dichloromethane was added 31.4 g (120 mmol) of triphenylphosphine under Ar. The reaction mixture was stirred for 20 min at room temperature and then poured into 300 mL of ether. Filtration and evaporation of the solvent afforded 2.14 g (65%) of 2-(2-propen-1-yl)-2-bromoethynylbenzene:[84] IR (neat) 2120, 1640, 1450, and 925 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.61 (d, 2H, J = 6.5 Hz), 5.07 (d, 1H, J = 17 Hz), 5.11 (d, 1H, J = 8.4 Hz), 5.94–6.07 (ddt, 1H, J = 17, 8.4, and 6.5 Hz), 7.15–7.32 (m, 3H), and 7.49 (m, 1H).

A 4.0-g (12.0 mmol) sample of the above bromide in 8.5 mL of ethanol was added dropwise to a mixture containing 1.30 g (10 mmol) of methyl 2-ethynylbenzoate in 17.5 mL of ethanol and 4.4 mL of a *n*-butylamine solution which contained 0.4 g of hydroxylamine hydrochloride and 0.02 g of cuprous chloride. After the mixture was stirred at room temperature for 1 h, it was poured into 100 mL of water and extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Chromatography of the residue on silica gel using benzene as the eluent afforded 1.25 g (42%) of methyl 2-[4-(2-(2-propen-1-yl)-phenyl)buta-1,3-diynyl[benzoate:[77] IR (neat) 2213, 1736, 1480, 1080, and 751 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.61 (d, 2H, J = 6.6 Hz), 3.95 (s, 3H), 5.12 (d, 1H, J = 17.2 Hz), 5.14 (d, 1H, J = 8.5 Hz), 6.0 (ddt, 1H, J = 17.2, 8.5 and 6.6 Hz), 7.10–7.57 (m, 6H), 7.65 (d, 1H, J = 7.6 Hz), and 7.98 (d, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.1, 51.7, 72.2, 76.7, 77.1, 77.2, 78.3, 80.0, 81.4, 115.8, 120.7, 121.9, 125.6, 128.1, 128.3, 128.9, 130.0, 131.3, 131.9, 132.7, 134.5, 135.5, 142.9, and 165.3.

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A solution containing 0.53 g (5.0 mmol) of potassium trimethylsilanolate in 50 mL of anhydrous ether was added in one portion to 1.25 g (4.0 mmol) of the above diacetylenic ester. The reaction mixture was stirred for 5 h at room temperature under N_2. After the mixture was cooled to 0 °C, 10.0 mmol of methyl chloroformate was added and stirring was continued for an additional 4 h at 25 °C. The solution was filtered, an ethereal diazoethane solution (30 mmol) was added, and the mixture was stirred at 25 °C for 5 h. The excess diazoethane and ether were removed under reduced pressure and the resulting residue was chromatographed on silica gel to give 800 mg (45%) of *o*-[4-[2-(2-propen-1-yl)phenyl]buta-1,3-diynyl]-2-diazo-1-phenylpropanone (**50**): IR (neat) 2207, 2074, 1612, 1354, and 1432 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.14 (s, 3H), 3.58 (d, 2H, J = 6.5 Hz), 5.09 (d, 1H, J = 17.0 Hz), 5.11 (d, 1H, J = 8.0 Hz), 5.95–6.05 (ddt, 1H, J = 17.0, 8.0 and 6.5 Hz), and 7.10–7.75 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 38.6, 65.4, 77.2, 78.7, 79.7, 81.6, 116.3, 120.9, 126.2, 127.3, 129.3, 129.6, 129.8, 133.2, 133.7, 141.6, 143.6, and 195.3.

To a solution containing 100 mg (0.3 mmol) of **50** in 25 mL of anhydrous methylene chloride was added a catalytic amount of rhodium(II) acetate dimer. The reaction mixture was stirred at room temperature until nitrogen evolution had ceased and was then concentrated under reduced pressure. The residue was chromatographed on silica gel to give 88 mg (95%) of 2-[2-(2-methyl-1-oxoindenyl)ethynyl](1a,6a)-cyclopropylindane (**53**): IR (neat) 2200, 1710, 1589, and 1455 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, 1H, J = 5.1 Hz), 1.77 (dd, 1H, J = 13.0 and 4.5 Hz), 1.93 (s, 3H), 2.50 (m, 1H), 2.95 (d, 1H, J = 17 Hz), 3.37 (dd, 1H, J = 17 and 6.9 Hz), 7.12–7.24 (m, 5H), 7.35 (t, 2H, J = 7.5 Hz), and 7.50 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.4, 26.2, 28.1, 29.4, 34.6, 72.3, 77.1, 111.4, 119.7, 121.8, 122.9, 125.6, 126.5, 128.3, 130.2, 133.5, 137.5, 140.4, 138.6, 143.6, 144.4, and 197.7; HRMS calcd for $C_{22}H_{16}O$ 296.1201, found 296.1206.

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Supplementary Material Available: Tables of final positional and thermal parameters for the X-ray crystal structures of dimers **7** and **15** (10 pages). Ordering information is given on any current masthead page.