Rhodium(II)-Catalyzed Carbocyclization Reaction of α-Diazo Carbonyls with Tethered Unsaturation

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o-Alkynyl-substituted α-diazoketones undergo internal cyclization to produce indenone derivatives upon treatment with catalytic quantities of Rh(II)-carboxylates. A variety of structural influences were encountered by varying the nature of the substituent group attached to the diazo center. The cyclization reaction involves addition of a rhodium-stabilized carbenoid onto the acetylenic π-bond to generate a cycloalkenone carbenoid. The cyclized carbenoid was found to undergo both aromatic and aliphatic C−H insertion as well as cyclopropanation across a tethered π-bond. Subjection of diazo phenyl acetic acid 3-phenylprop-2-ynyl ester to Rh(II) catalysis furnished 8-phenyl-1,8-dihydro-2-oxacyclopenta[*a*]indenone in high yield. The formation of this compound involves cyclization of the initially formed carbenoid onto the alkyne to produce a butenolide which then undergoes C−H insertion into the neighboring aromatic system. When a vinyl ether is added, the initially formed rhodium carbenoid intermediate can be intercepted by the electron-rich π-bond prior to cyclization. Different rhodium catalysts were shown to result in significant variation in the product ratios. The competition between bimolecular cyclopropanation, 1,2-hydrogen migration, and internal cyclization was probed using several enol ethers as well as diazoesters which possess different substituent groups on the ester backbone. The specific path followed was found to depend on electronic, steric, and conformational factors.

Over the past two decades, transition metal based methods have gained considerable importance in organic synthesis since they allow simultaneous formation of more than one bond in a single synthetic operation with high selectivity.[1−24] Construction of medium-sized rings through metal intervention has been a particularly fruitful area of investigation. Noteworthy among these are the cyclotrimerization of alkynes to alkenes,[25] the coupling of alkynes with carbene ligands in the Dötz reaction[6,7] and the Pauson−Khand reaction for the formation of cyclopentenones from an alkyne, an alkene, and carbon monoxide.[26] Another emerging area of synthesis is the use of transition metal complexes derived from α-diazo carbonyl compounds to facilitate the construction of various ring systems.[27] The role of α-diazo carbonyl compounds in organic synthesis is well established and in recent years much effort has been devoted to the study of the effect of different transition-metal catalysts on these substrates.[28] In synthetic terms, most of the work has centered on cyclopropanation[29] and C−H insertion reactions[30] of the resulting metallo carbenoids. Much less attention has been paid to the transition metal

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; Mill Valley, CA, 1987.
(2) Mass, G. *Top. Curr. Chem.* **1987**, *137*, 77.
(3) Doyle, M. P. *Acc. Chem. Res.* **1986**, *19*, 348; *Chem. Rev.* **1986**, *86*, 919.
(4) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081.
(5) Deem, M. L. *Synthesis* **1982**, 701; **1972**, 675.
(6) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517.
(7) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5. Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol. 1. McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. Wulff, W. D.; Xu, Y.-C. *Tetrahedron Lett.* **1988**, *29*, 415.
(8) Peterson, G. A.; Kunnig, F.-A.; McCallum, J. S.; Wulff, W. D. *Tetrahedron Lett.* **1987**, *28*, 1381.
(9) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wu, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.
(10) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.
(11) Alt, H. G. *J. Organomet. Chem.* **1985**, *288*, 149.
(12) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055.
(13) Slough, G. A.; Deshong, P. *J. Am. Chem. Soc.* **1988**, *110*, 2575.
(14) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2044.
(15) Bottrill, M.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 292.
(16) Corrigan, P. A.; Dickson, R. S. *Aust. J. Chem.* **1979**, *32*, 2147.
(17) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.
(18) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.
(19) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232.
(20) Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806. Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 5066. Harvey, D. F.; Brown, M. F. *J. Org. Chem.* **1992**, *57*, 5559. Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271.
(21) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Able, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 499.
(22) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.
(23) Casey, C. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1981; p 135.
(24) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587; *Tetrahedron Symposia in Print*; Semmelhack, M. F., Ed. **1986**, *42*, 5741−5887.
(25) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
(26) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.
(27) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385. Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.
(28) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1797.
(29) Doyle, M. P. In *Homogeneous Transition Metal Catalysts in Organic Synthesis*; Moser, W. R., Slocum, D. W., Eds.; ACS Advanced Chemistry Series, No. 230; American Chemical Society: Washington, DC, 1992; Chapter 30.
(30) Taber, D. F. In *Comprehensive Organic Synthesis*; Pattenden, G., Ed.; Pergamon Press: Oxford, 1991; Vol. 3, pp 1045−1062.

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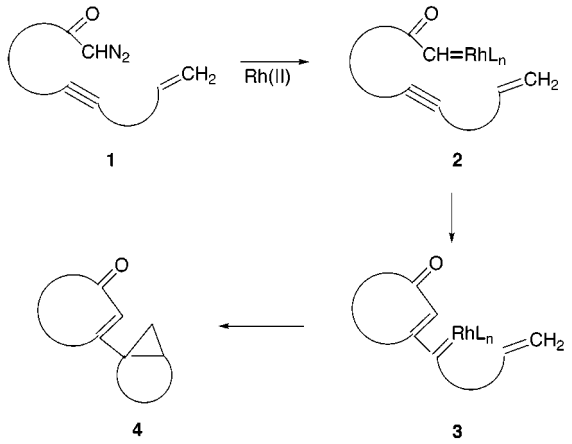
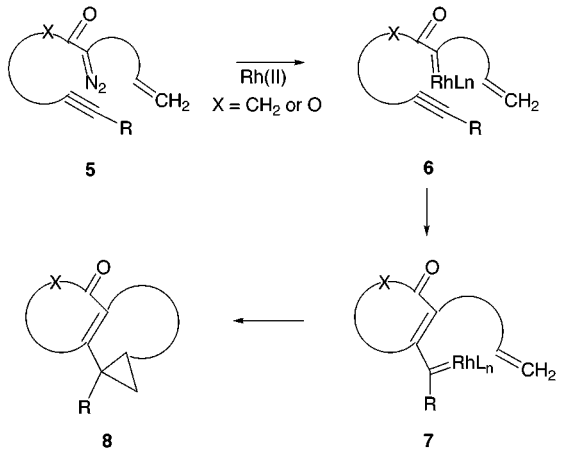
Scheme 1. Type I Internal Cyclization Route



Scheme 2. Type II Internal Cyclization Route



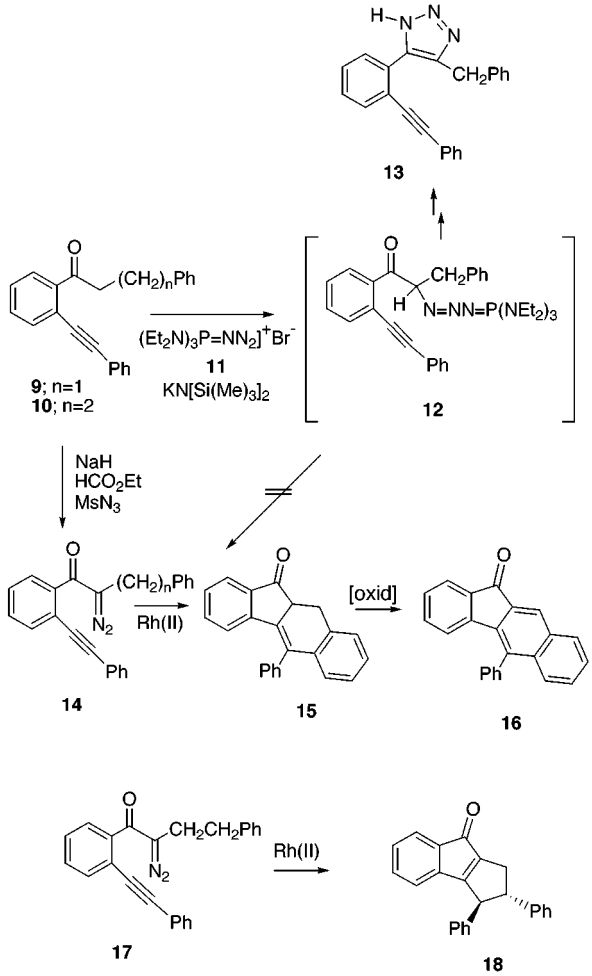
mediated carbocyclization of diazo carbonyls that contain two or more elements of unsaturation.

Several years ago, our group[31] as well as Hoye's[32] described a route for producing cycloalkenone carbenoids which involved the rhodium(II)-catalyzed decomposition of α-diazoalkynyl-substituted ketones (Scheme 1). Such diazo carbonyls are appealing as synthetic intermediates in that they are readily accessible, reasonably robust, and leave functionality in the cyclized product that is useful for further synthetic transformation. The cyclization was interpreted as proceeding by addition of the rhodium carbenoid **2** onto the acetylenic π-bond to give vinyl carbenoid **3**. The vinyl carbenoid complex was subsequently trapped in an intramolecular fashion to give bicyclohexanes such as **4** when an alkene was tethered to the alkynyl group.[31,32] The potential for many other chemical pathways exists with these novel cycloalkenone carbenoids. Two basic structural variations were studied that differed from each other by altering the point of attachment of the functional group to the alkyne center. We refer to these two modes as the type I (Scheme 1) and type II (Scheme 2) internal cyclization routes. In our previous studies with type I molecules, we had observed that the Rh(II)-catalyzed reaction can result in cyclopropanation, C−H insertion, onium ylide formation, and cyclopropenation.[31,33] Since chemical reactivity in intramolecular cyclization processes is easily modified by the choice of substituent group and geometry, we undertook a related study of the chemistry of type II α-diazo carbonyl compounds (Scheme 2). In this paper, we report a full account of our effort with these systems.[34]

Results and Discussion

α-Diazo carbonyl compounds are recognized precursors to carbenoid species when exposed to many transition metal complexes.[27] Intramolecular C−H insertion of the electrophilic rhodium−carbene complex generally leads to the preferential formation of five-membered rings in acyclic, conformationally mobile systems.[30] The specific reaction path followed depends on the nature of the α-diazo carbonyl compound employed and is often governed by steric, conformational factors as well as electronic factors.[27] Our initial efforts with type II molecules focused on the rhodium(II)-catalyzed reaction of α-diazo ketone **14**. This substrate was prepared from ketone **9** as outlined in Scheme 3. The base-catalyzed transfer of a diazo moiety to a methylene group adjacent to one or

Scheme 3



(31) Padwa, A.; Krumpe, K. E.; Zhi, L. *Tetrahedron Lett.* **1989**, 2623. Padwa, A.; Chiacchio, U.; Gareau, Y.; Kassir, J. M.; Krumpe, K. E.; Schoffstall, A. M. *J. Org. Chem.* **1990**, *55*, 414. Padwa, A.; Krumpe, K. E.; Gareau, Y.; Chiacchio, U. *J. Org. Chem.* **1991**, *56*, 2523. Padwa, A.; Krumpe, K. E.; Kassir, J. M. *J. Org. Chem.* **1992**, *57*, 4940. Padwa, A.; Austin, D. J.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 4103. Padwa, A.; Gareau, Y.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 983.

(32) Hoye, T. R.; Dinsmore, C. J.; Johnson, D. S.; Korkowski, P. F. *J. Org. Chem.* **1990**, *55*, 4518. Hoye, T. R.; Dinsmore, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 4343. Hoye, T. R.; Dinsmore, C. J. *Tetrahedron Lett.* **1991**, *32*, 3755. Hoye, T. R.; Dinsmore, C. J. *Tetrahedron Lett.* **1992**, *33*, 169.

(33) Padwa, A.; Kassir, J. M.; Xu, S. L. *J. Org. Chem.* **1997**, *62*, 1642.

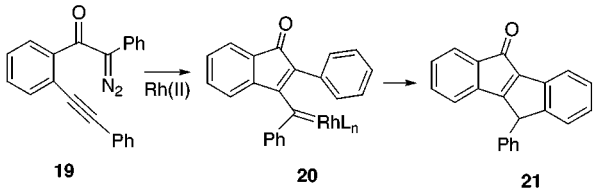
(34) Mueller, P. H.; Kassir, J. M.; Semones, M. A.; Weingarten, M. D.; Padwa, A. *Tetrahedron Lett.* **1993**, *34*, 4285.

more electron-withdrawing groups represents a well-established protocol for α-diazo ketone synthesis.[35−38] The most commonly used reagents for diazo transfer have been tosyl[35] or mesyl azide,[36] though in recent years a number of other azido compounds and methods have been proposed.[37−39] Recently, McGuiness and Shechter reported on the use of azidotris(diethylamino)phosphonium bromide (**11**) as an efficient diazo transfer reagent.[39] This reagent only requires a catalytic amount of base, and the product diazo compounds have been reported to be easily separated from the coproduct, hexaethylphosphorimidic hydrobromide. In our hands, however, the reaction of ketone **9** with phosphonium bromide **11** afforded only triazole **13** in 76% yield. The formation of the triazole ring can be attributed to attack of the initially formed enolate onto the terminal nitrogen of **11** followed by an intramolecular Staudinger reaction[40] and a subsequent 1,3-hydrogen shift.

With simple ketones, the diazo transfer reaction is often facilitated through a prior formylation step and subsequent elimination of the activating formyl group during the course of the actual diazo transfer.[41,42] Consequently, we decided to use this protocol to overcome the diazo transfer difficulty encountered with the Shechter reagent. Treatment of the keto enolate of **9** (or **10**) with ethyl formate produced a dicarbonyl compound that, upon reaction with mesyl azide, afforded the desired diazo ketone **14** in good yield.[41] When **14** was allowed to react with rhodium(II) acetate in benzene, initial cyclization occurred to produce a rhodium carbenoid that underwent subsequent insertion onto the neighboring aromatic ring to ultimately form compound **16** in 75% yield. The structure of **16** was unequivocally established by an X-ray crystal structure analysis. When the reaction was carried out under an atmosphere of argon, it was possible to isolate **15** (60%) in addition to **16**. Compound **15** was readily oxidized to **16** when allowed to stand open to the air. The Rh(II)-catalyzed reaction of the homologous α-diazo ketone **17** was also investigated and was found to give **18** (70%) as the only isolable product. The formation of **18** involves insertion into the benzylic C−H bond, and this is consistent with other Rh(II)-mediated insertions, which generally exhibit a large preference for the generation of five-membered rings.[43]

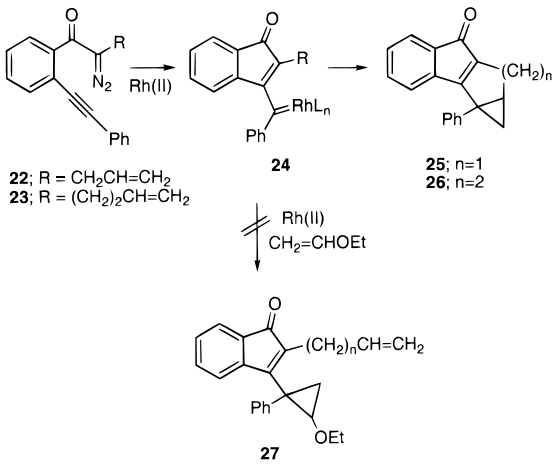
The success achieved by the Rh(II)-catalyzed transformation of diazo ketones **14** and **17** was extended to the simpler diazo phenylethanone derivative **19**. Treatment of this diazo ketone with a catalytic amount of rhodium(II) acetate afforded indenone **21** in 93% yield (Scheme 4). The simplest mechanism to rationalize this result

Scheme 4



19 **20** **21**

Scheme 5



22; R = $CH_2CH{=}CH_2$
23; R = $(CH_2)_2CH{=}CH_2$

24

25; n=1
26; n=2

27

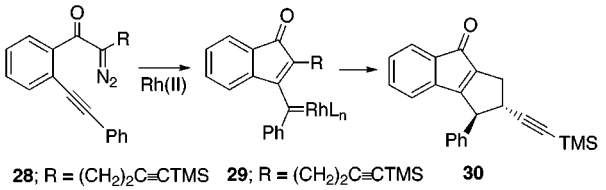
involves addition of the initially formed rhodium-stabilized carbenoid onto the acetylenic π-bond to give vinyl carbenoid **20** which readily undergoes C−H insertion into the aromatic ring. The literature indicates that these aromatic C−H insertions are facile processes which can best be counted for by invoking electrophilic addition of the metal-bound carbene to the adjacent π-bond followed by a 1,2-hydride migration to complete the overall substitution process.[27−30]

As an extension of this methodology, the carbenoid cyclization reaction of α-diazo ketones **22** and **23** was next investigated. In both cases it was possible to isolate the bicycloalkanes derived from intramolecular cyclopropanation[44] (i.e., **25** (67%) and **26** (81%)) (Scheme 5). In our earlier studies, we had found that *o*-alkynyl-substituted α-diazoacetophenone derivatives produce vinyl carbenoids that could be trapped by electron-rich π-bonds (i.e., ethyl vinyl ether) to give indenyl-substituted cyclopropanes in 90% yield.[45] With this in mind, we attempted to bimolecularly trap the cyclized carbenoid intermediate **24**, by carrying out the reaction in the presence of a large excess of ethyl vinyl ether. However, in no case (**22**, **23**) were we able to detect any signs of the bimolecular adduct (e.g., **27**). This observation indicates that, with these systems, bimolecular trapping of the cyclized rhodium carbenoid is significantly slower than either intramolecular cyclopropanation or insertion.

We also attempted to trap the cyclized indenone carbenoid with an acetylenic π-bond. The insertion of alkynes into various transition metal carbon bonds is a well-documented reaction and has been observed in nearly all of the triads of transition metals.[46] Our initial efforts focused on the rhodium(II) carbenoid catalyzed

(35) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 733.
(36) Taber, D. F.; Schuchardt, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5289. Taber, D. F.; Ruckle, R. E.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077.
(37) Baum, J. S.; Shook, D. A.; Davies, H. M. L.; Smith, H. D. *Synth. Commun.* **1987**, *17*, 1709.
(38) Koskinen, A. M. P.; Munoz, L. *J. Chem. Soc., Chem. Commun.* **1990**, 652.
(39) McGuiness, M.; Shechter, H. *Tetrahedron Lett.* **1990**, 4987.
(40) Review: Gololobov, Y. G.; Zhmurova, I. N.; Kasukhim, L. F. *Tetrahedron* **1981**, *37*, 437.
(41) Taber, D. F.; Gleave, D. M.; Herr, R. J.; Moody, K.; Hennessy, M. J. *J. Org. Chem.* **1995**, *60*, 2283. Danheiser, R. L.; Miller, R. F.; Brisbois, R., G.; Park, S. Z. *J. Org. Chem.* **1990**, *55*, 1959. Metcalf, B. W.; Jund, K.; Burkhart, J. P., *Tetrahedron Lett.* **1980**, *21*, 15.
(42) Benati, L.; Nanni, D.; Spagnolo, P. *J. Org. Chem.* **1999**, *64*, 5132 and referenced cited therein.
(43) For leading references, see: Doyle, M. P.; Westrum, L. J.; Wolthuis, W. N. E.; See, M. M.; Boone, W. P.; Bagheri, V.; Pearson, M. M. *J. Am. Chem. Soc.* **1993**, *115*, 958.
(44) For leading references, see: Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424.
(45) Padwa, A.; Austin, D. J.; Chiacchio, U.; Kassir, J. M.; Rescifina, A.; Xu, S. L. *Tetrahedron Lett.* **1991**, *32*, 5923.
(46) For leading references, see: O'Connor, J. M.; Ji, H.; Iranpour, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1586.

Scheme 6



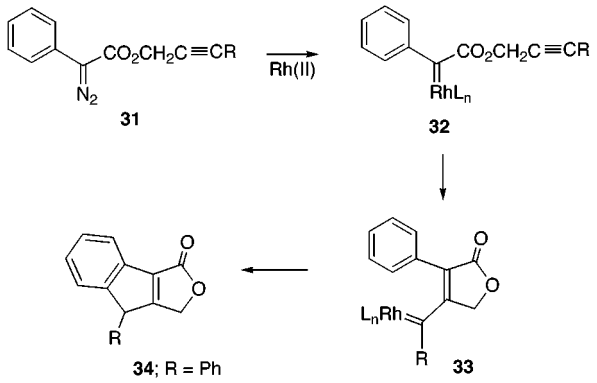
28; R = $(CH_2)_2C{\equiv}CTMS$ **29**; R = $(CH_2)_2C{\equiv}CTMS$ **30**

reaction of α-diazo ketone **28**. We found that treatment of **28** with Rh(II) acetate did not afford the product of internal attack on the acetylenic π-bond. Instead, only indenone **30** was obtained in 83% yield (Scheme 6). Insertion of the rhodium carbenoid into the propargylic C−H bond is clearly preferred over attack at the acetylenic π-bond. This may be related to conformational factors that place the propargylic hydrogens within the reactive environment of the carbenoid center for an easy C−H insertion reaction.

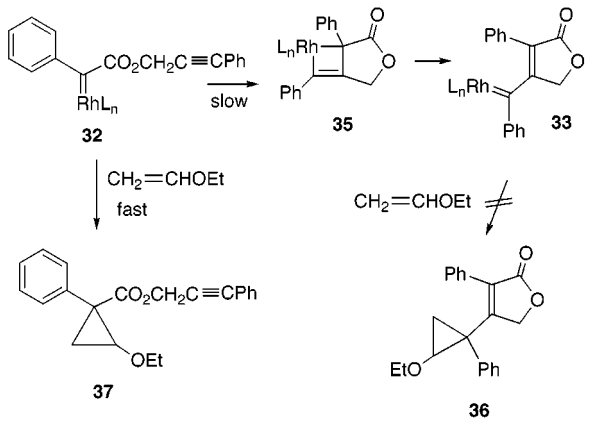
Butenolides are widely distributed in nature, and some of them exhibit interesting biological properties and find applications as insecticides, herbicides, and seed and plant growth regulators.[47] They have also been reported to be useful intermediates in organic synthesis.[48] Because of these reasons, they represent a synthetic target of great interest, and numerous approaches to their preparation have been reported, with many of them relying on palladium chemistry.[49] Our interest in the synthesis of five-membered oxygen heterocycles[50] and the earlier studies we carried out using the Rh(II)-catalyzed reaction of 2-alkynyl 2-diazo-3-oxobutanoates[51] prompted us to examine the possible use of similar chemistry for developing a new and versatile route to functionalized butenolides. To ascertain whether the intramolecular alkyne metathesis reaction of α-diazo carbonyls could be used for a butenolide synthesis, we decided to study the Rh(II)-catalyzed reaction of α-diazo esters of type **31**. These compounds differ from the earlier model systems (i.e., **19**) in that the aryl ketone backbone is now replaced by a propargylic ester tether. Trapping the initially formed rhodium carbenoid with the tethered alkyne group would represent a unique method for the formation of the butenolide ring system. Gratifyingly, we found that when diazo ester **31** (R = Ph) was exposed to a catalytic quantity of rhodium(II) acetate in CH_2Cl_2 at 25 °C, butenolide **34** was obtained in 92% yield. Its formation can be rationalized according to the reaction steps outlined in Scheme 7.

We also carried out experiments designed to trap the cyclized carbenoid intermediate **33** by adding an excess of ethyl vinyl ether to the reaction mixture. On the basis of our earlier results with type I molecules,[31,45] we expected that the reaction would produce the bimolecular adduct derived from **33**. Interestingly, the reaction of **31** with Rh(II) acetate did not furnish the expected bimolecular adduct **36**. Instead, cyclopropyl ester **37** was obtained as the exclusive product in 93% yield (Scheme 8). Its formation is the result of preferential trapping of

Scheme 7



Scheme 8

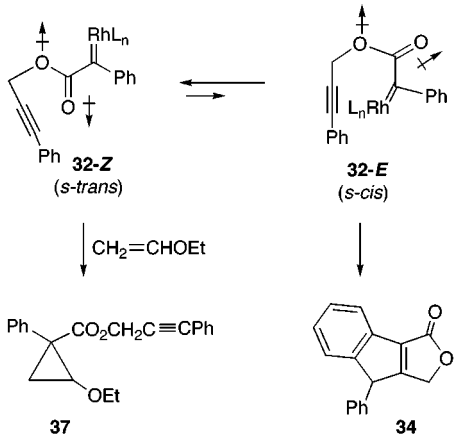


the initially formed carbenoid intermediate **32** prior to the internal cyclization reaction. Apparently, the rate of bimolecular cycloaddition of **32** with the external alkene is faster than intramolecular cyclization to give **33**. The fact that only cyclopropane **37** was obtained is undoubtedly related to conformational factors specific to the ester functionality. The rhodium carbenoid intermediate derived from diazoester **31** exists primarily in the *s-trans* conformation about the ester bond (i.e., **32-*Z***). It is well-known that esters are more stable in this conformation for several reasons, one of which is to minimize steric interactions.[52] It has also been recognized for some time that the *E*-isomers of esters are destabilized by dipole−dipole interactions, and this effect also accounts for a large part of the preference of esters for the *Z*-conformation.[53] In the *Z* or s-trans conformation, intramolecular cyclization of the rhodium carbenoid onto the alkyne π-bond cannot occur. To cyclize, rotation about the ester bond must first take place to furnish the *E* or s-cis conformer, which can then achieve the necessary geometry for internal cyclization and ultimately, butenolide formation (Scheme 9).

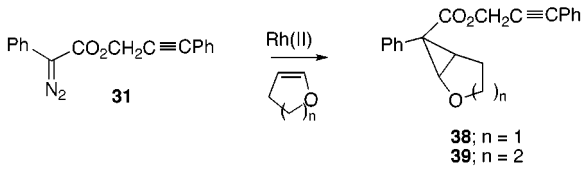
We attempted to determine the conformational energy differences of carbenoids **32-*Z*** and **32-*E*** by molecular mechanics calculations (Gajewski's MMX program[54] with Allinger parameters) using phenylacetic acid 3-phenylprop-2-ynyl as a model system. However, this approach

(47) Pattenden, G. *Fortschr. Chem. Org. Naturst.* **1978**, *35*, 133.
(48) Rao, Y. S. *Chem. Rev.* **1976**, *76*, 6, 625. Nagao, Y.; Dai, W. M.; Ochiai, M.; Shiro, M. *J. Org. Chem.* **1989**, *54*, 5211.
(49) For some leading references, see: Ali, B. E.; Alper, H. *J. Org. Chem.* **1991**, *56*, 5357.
(50) Padwa, A.; Brodney, M. A.; Satake, K.; Straub, C. S. *J. Org. Chem.* **1999**, *64*, 4617.
(51) Kinder, F. R.; Padwa, A. *Tetrahedron Lett.* **1990**, *31*, 6835. Padwa, A.; Kinder, F. R. *J. Org. Chem.* **1993**, *58*, 21.
(52) Dale, J. *Stereochemistry and Conformational Analysis*; Verlag Chemie: New York, 1978; pp 83−85. Testa, B. *Principles of Organic Stereochemistry;* Marcel Dekker: New York, 1979; p 105. Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds;* Wiley-Interscience: New York, 1994; pp 618−621.
(53) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.
(54) PC Model by Serena Software, Bloomington, IN.

Scheme 9



Scheme 10



was terminated after calculations on the propargyl ester indicated no real preference of the two conformers. For these reasons, the structures for the s-trans and s-cis conformers of the propargyl ester were determined using ab initio theory. Both conformers were optimized at the HF/6-31G* level of theory using Gaussian 88. The difference in energy turned out to be 5−8 kcal in favor of the s-trans conformer, similar but somewhat smaller than the values determined for methyl acrylate[55] for which ab initio calculations predicted a difference of 9.5 kcal/mol.[56]

The ease with which α-diazo ester **31** undergoes cyclization to give butenolide **34** as well as cyclopropanation to furnish **37** suggested that this system might serve as a tool for determining the facility with which various enol ethers can undergo reaction with rhodium carbenoids. We examined the bimolecular reaction of **31** with both dihydrofuran and dihydropyran (5 mol excess) as the added enol ether and discovered that, in addition to the expected cyclopropyl esters **38** and **39**, varying amounts of butenolide **34** were also formed (Scheme 10). However, when a 5 mol excess of ethyl vinyl ether was used, only the cyclopropyl adduct **37** was obtained (93%), with no signs of butenolide **34**. The implication of these results is that the rate of cyclopropanation of carbenoid **32** decreases upon changing the trapping agent from ethyl vinyl ether (fastest) to dihydrofuran and then to dihydropyran (slowest).

To decipher the factors which influence the rate of cyclopropanation of this α-diazo ester, we calculated 13 points on the conformational energy surface of ethyl vinyl ether at the 6-31G*/3-21G level of theory.[57] The results of these calculations are summarized in Table 1. The value of the C=C−OC dihedral angle θ was held fixed at the indicated value, and the structure was minimized.

(55) Blom, C. E.; Gunthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267.
(56) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872.
(57) Force field and quantum calculations were carried out using the Spartan package, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92715.

Table 1. Effect of Dihedral Angle on the HOMO of Methyl Vinyl Ether

θ (deg)	HOMO (eV)	θ (deg)	HOMO (eV)
0	−0.339 11	105	−0.355 11
15	−0.339 36	120	−0.349 06
30	−0.340 99	135	−0.342 14
45	−0.343 82	150	−0.336 15
60	−0.347 93	165	−0.332 41
75	−0.353 16	180	−0.331 17
90	−0.356 79		

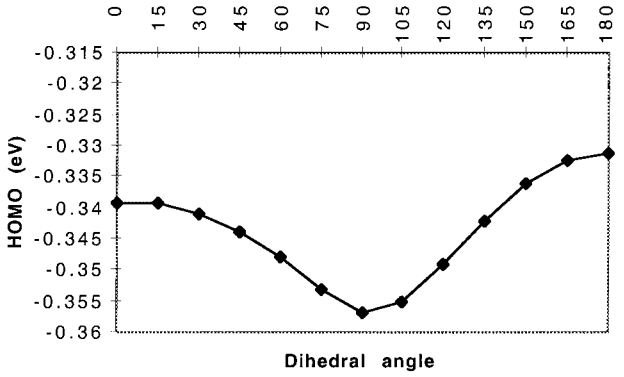


Figure 1. Dihedral angle vs HOMO (eV) for methyl vinyl ether.

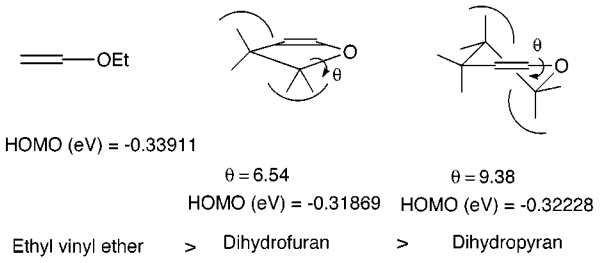
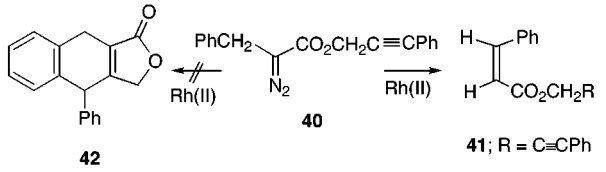


Figure 2. . HOMO and dihedral angle θ.

No other constraints were employed. Variation of the C=C−OC dihedral angle reveals HOMO maxima near 0 and 180° (Figure 1). The overall preference for planarity is expected since such arrangements allow the ethoxy oxygen atom to maximize the effects of conjugation with the adjacent double bond. It is also worthy to note that while the HOMO is higher in energy when $\theta = 180°$ as compared to $\theta = 0°$, the latter conformation is lower in energy by approximately 1.4 kcal/mol. This is probably related to the added stabilization due to hyperconjugation with the C=C π-bond. Although the HOMO does decrease in value when the ethoxy group is not coplanar with respect to the double bond, Figure 1 shows that the effect is negligible when θ is less the 45°. The calculated "flap" angle and HOMO energy level for dihydrofuran and dihydropyran are shown in Figure 2. We found that the HOMOs of these cyclic enol ethers are actually higher in energy than ethyl vinyl ether and consequently interaction with the LUMO of the metallocarbenoid would be expected to be more pronounced. This should result in a rate order of dihydrofuran > dihydropyran > ethyl vinyl ether. However, this predicted reactivity pattern, which is based on electronic factors, is not consistent with the actual experimental data observed. To account for these experimental findings, we assume that steric factors associated with the cyclopropanation play an important role in this reaction. As can be seen from Figure 2, ethyl vinyl ether is the least congested

Scheme 11



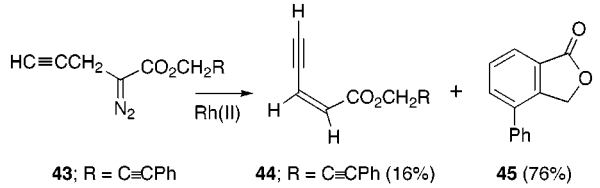
alkene and thus, the reactivity order encountered is perfectly consistent with this steric hindrance rationale.

A number of studies in the literature have shown that, despite their high reactivity, rhodium carbenoid intermediates are often highly chemoselective when two or more reaction pathways are open to them.[58] During the course of our studies with diazoester **31**, we observed that changing the ligand on the rhodium carboxylate significantly altered the product distribution obtained from the reaction of diazoester **31** with a 1.5 mol excess of the cyclic enol ether. Rhodium(II) perfluorobutyrate [Rh_2-(pfb)$_4$] was the most efficient catalyst for producing cyclopropyl esters **38** and **39** (100%), while rhodium(II) acetate was best for forming butenolide **34** (100%). Catalysis by rhodium(II) perfluorobutyramide [Rh_2(pfm)$_4$] afforded a 1:1 mixture of both products. The fact that Rh_2-(pfb)$_4$ led to the exclusive formation of the cyclopropyl esters **38** and **39** is not surprising considering that the ligands on rhodium are known to exert substantial control over the reactivity of the carbenoid.[59] A strongly electron-withdrawing ligand will result in a more reactive carbenoid and lead to cyclopropanation with an electron-rich π-bond. By changing the ligand from perfluorobutyrate to acetate, the reactivity of the carbenoid is attenuated, thereby allowing the intramolecular cyclization and insertion pathway to proceed.

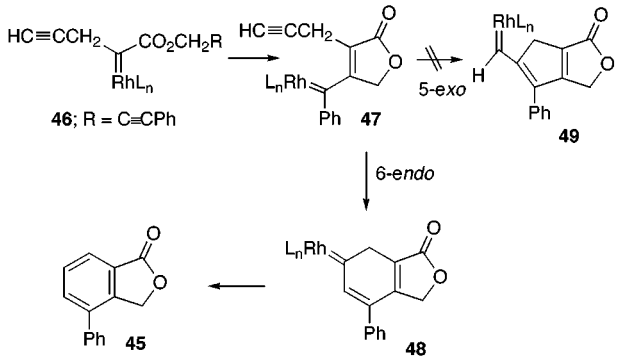
As part of our work in this area, we also decided to probe the competition between the internal cyclization reaction which occurs with a neighboring alkyne versus a 1,2-hydrogen shift that can also take place from the rhodium carbenoid intermediate. These competitive processes were evaluated by preparing α-diazoester **40** and subjecting it to thermolysis in the presence of a rhodium-(II) catalyst. We found that the reaction of **40** with any of the aforementioned rhodium(II) catalysts produced the unsaturated ester **41** as the exclusive product in 92% yield. There was no indication of any of the rearranged butenolide **42** in the crude reaction mixture. Clearly, the 1,2-hydrogen migration route proceeds at a much faster rate than internal cyclization reaction (Scheme 11). With this diazoester, conformational effects play an important role in these competitive reactions. The preferential formation of the thermodynamically less stable *Z*-isomer **41** is consistent with literature observations and can be attributed to steric constraints in the transition state for the 1,2-hydrogen shift.[60]

In our earlier studies with type I diazo ketones (i.e., **1**), a variety of structural influences on the course of the reaction were encountered by varying the nature of the substituent group attached to the alkyne carbon atom.[31]

Scheme 12



Scheme 13



To determine whether type II diazo carbonyls would exhibit a similar dependence, we studied the Rh(II)-catalyzed behavior of diazoester **43**. We expected that this system would also undergo a preferential 1,2-hydrogen shift as was encountered with diazoester **40**. Most surprisingly, the reaction of **43** with Rh_2OAc_4 afforded 4-phenyl-3*H*-isobenzofuranone (**45**) as the major product (76%) together with lesser quantities of the *Z*-pentenynoic acid ester **44** (16%) (Scheme 12). The fact that **43** gave mostly **45** is particularly noteworthy and bears some discussion. This result stands in marked contrast with the exclusive hydrogen shift that occurred with the closely related diazoester **40**. The facility of hydrogen migration with **40** is probably a consequence of the fact that the resulting product (i.e., **41**) possesses a double bond that is in conjugation with both the aromatic ring and the ester carbonyl group. This arrangement is thermodynamically favorable and may well facilitate the rate of the 1,2-hydrogen shift. With diazoester **43**, however, interaction of the alkenyl π-bond with the alkyne would be of lesser importance from a thermodynamic stability viewpoint thereby allowing the internal cyclization reaction of rhodium carbenoid **46** to compete. What is particularly interesting with this system is that only the product derived from 6-endo ring closure (i.e., **47** → **48** → **45**) of the cycloalkenone carbenoid is observed (Scheme 13). No signs of any product derived from the 5-*exo*-*dig* cyclization (i.e., **49**) could be found in the crude reaction mixture. In general, the 5-exo vs 6-endo selectivity in these internal cyclization reactions is derived from a combination of steric interactions between the R group on the alkyne and the catalyst (i.e., **50**) and the ability of the substituent group to stabilize the resulting carbenoid intermediate.[31,32] We suggest that, with diazoester **43**, the preferred 6-endo vs 5-exo selectivity is due to the smaller steric interactions that exist between the hydrogen substituent on the terminal alkyne and the ligand groups on the catalyst (i.e., **50**; R = H) (Scheme 14).

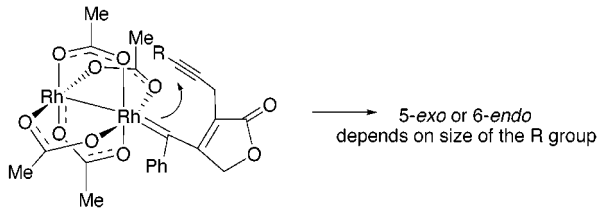
In conclusion, the rhodium(II)-catalyzed reaction of type II α-diazo carbonyl compounds provides a convenient route to a variety of indenones and substituted butenolides. The tandem cyclization−rearrangement sequence proceeds with high chemoselectivity that should prove

(58) Miah, S.; Slawin, M. Z.; Moody, C. J.; Sheehan, S. M.; Marino, J. P., Jr.; Semones, M. A.; Padwa, A. *Tetrahedron* **1996**, *52*, 1996.

(59) Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669.

(60) Doyle, M. P.; High, K. G.; Oon, S. M.; Osborn, A. K. *Tetrahedron Lett.* **1989**, *30*, 3049. Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277.

Scheme 14



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to be useful for further synthetic transformations. We are continuing to explore the scope and mechanistic details of these cyclizations 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 flame-dried glassware under an atmosphere of dry argon. 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. All solids were recrystallized from ethyl acetate/hexane for analytical data.

3-Phenyl-1-(2-phenylethynylphenyl)-1-propanone (9). To a mixture containing 9.4 g (51 mmol) of 2-bromobenzaldehyde and 6.7 g (66 mmol) of phenyl acetylene in 100 mL of triethylamine was added 0.02 g of bis-triphenylphosphine palladium(II) chloride, 0.18 g of cuprous iodide, and 0.01 g of triphenylphosphine. The reaction mixture was heated at reflux under nitrogen for 48 h and filtered to remove the triethylammonium iodide, and the filtrate was concentrated under reduced pressure. The residue was taken up in 100 mL of ether and washed with 5% HCl followed by water. Vacuum distillation of the dark brown oil afforded 8.4 g (80%) of 2-phenylethynylbenzaldehyde[61] as a light yellow oil: bp 123−125 °C (0.15 mm); IR (neat) 2213, 1695, 1266, 1192 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.47 (m, 4H), 7.53−7.67 (m, 4H), 7.96 (m, 1H), 10.68 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 85.0, 96.4, 122.3, 126.8, 127.2, 128.6, 129.1, 131.6, 132.5, 133.2, 133.7, 135.8, 191.5.

To a 100 mL flask containing 0.7 g (27 mmol) of magnesium turnings was added a solution containing 3.6 g (18 mmol) of 2-bromo-1-phenylethane in 50 mL of ether at such a rate so as to produce a mild exotherm. After the addition was complete, the reaction was allowed to stir for 1 h and was then added to a solution containing 2.5 g (12 mmol) of the above aldehyde in 50 mL ether at room temperature. The mixture was poured into 50 mL of a saturated NH_4Cl solution, the phases were separated, and the aqueous layer was extracted with ether. Removal of the solvent under reduced pressure followed by flash silica gel chromatography gave 2.8 g (74%) of 3-phenyl-1-(2-phenylethynylphenyl)-1-propanol as a white solid: mp 87−88 °C; IR (neat) 3370, 3050, 1430, 1210 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.11−2.32 (m, 2H), 2.33 (brs, 1H), 2.80−2.99 (m, 2H), 5.35 (dd,1H, J = 7.7 and 4.7 Hz), 7.21−7.25 (m, 1H), 7.27−7.33 (m, 3H), 7.39−7.42 (m, 4H), 7.49−7.51 (m, 2H), 7.58 (d, 1H, J = 7.7 Hz), 7.62 (d, 1H, J = 7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 39.7, 71.7, 87.2, 94.4, 120.6, 123.1, 125.5, 125.8, 127.2, 128.4, 128.5, 128.5, 128.6, 128.9, 131.6, 132.3, 141.9, 146.6.

A solution containing 2.0 g (6 mmol) of the above alcohol in 30 mL of CH_2Cl_2 was added to a suspension of 3.0 g (14 mmol) of PCC and 3.5 g of Celite in 75 mL of CH_2Cl_2. After the solution was stirred at 25 °C for 4 h, 100 mL of ether was added, and the mixture was filtered through a pad of Florisil. The filter cake was washed with ether, and the combined extracts were concentrated under reduced pressure. Silica gel chromatography of the residue afforded 1.8 g (90%) of **9** as a crystalline solid: mp 54−55 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.15 (t, 2H, J = 7.7 Hz), 3.58 (t, 2H, J = 7.7 Hz), 7.23−7.48 (m, 12H), 7.67 (d, 1H, J = 7.6 Hz), 7.76 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.4, 44.2, 88.6, 95.0, 121.5, 122.8, 126.2, 128.4, 128.5, 128.8, 131.2, 131.6, 133.9, 140.7, 141.3, 201.8. Anal. Calcd for $C_{23}H_{18}O$: C, 88.99; H, 5.85. Found: C, 88.85; H, 5.82.

4-Benzyl-5-(2-phenylethynylphenyl)-1,2,3-triazole (13). A solution containing 0.6 g (0.5 mmol) of ketone **9** in 50 mL of dry THF was cooled to −78 °C. To this solution was added 1.1 mL of a 0.5 M (0.6 mmol) solution of potassium hexamethyl disilazide. The yellow solution of the anion was allowed to stir at −78 °C for 1 h. A solution containing 0.2 mg (0.6 mmol) of azidotris(diethylamino)phosphonium bromide[39] in 15 mL of THF was added dropwise. The solution was allowed to stir at −78 °C for 1 h and was then left to warm to room temperature over an additional 60 min before being poured into 30 mL of 10% NaOH. The phases were separated, and the aqueous portion was extracted with ether. The combined organic extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by silica gel flash chromatography to give 0.1 g (62%) of **13** as a clear oil: IR (neat) 2214, 1601, 1495, 1454, 1002, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.18 (s, 2H), 7.09−7.18 (m, 5H), 7.26−7.40 (m, 8H), 7.64 (d, 1H, J = 7.0 Hz); ^{13}C NMR δ 31.5, 88.2, 93.1, 122.8, 123.1, 126.4, 128.3, 128.4, 128.5, 130.2, 131.5, 132.6, 138.5. Anal. Calcd for $C_{23}H_{17}N_3$: C, 82.35; H, 5.11; N, 12.53. Found: C, 82.28; H, 5.07; N, 12.39.

5-Phenyl-5,10-dihydrobenzo[*b*]fluoren-11-one (15). To a 100 mL flask of 0.3 g of NaH (60% in mineral oil) in 5 mL of ether containing two drops of absolute ethanol was added a solution of 0.7 g (2.4 mmol) of ketone **9**, 1 mL of ethyl formate, and 20 mL of ether. The mixture was stirred at 0 °C for 3 h and at 25 °C for an additional 12 h. A solution of 0.7 g (5.9 mmol) of mesyl azide in 15 mL of ether was added, and the mixture was stirred at room temperature for an additional 2 h. The reaction was quenched with 2 mL of water, and the ether layer was washed with 10% NaOH and extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash silica gel chromatography to give 0.24 g (30%) of 2-diazo-3-phenyl-1-(2-phenylethynylphenyl)propanone (**14**): IR (neat) 2080, 1613, 1450, 1150 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 2H), 7.17−7.43 (m, 10H), 7.56 (m, 4H). This diazo ketone was immediately used in the next step without further purification.

To a 50 mL flask containing 0.1 g (0.3 mmol) of diazo ketone **14** in 25 mL of benzene was added 2 mg of rhodium(II) acetate. The solution was stirred for 12 h at 25 °C. Removal of the solvent under reduced pressure followed by silica gel chromatography of the residue gave 0.07 g (80%) of **15**: IR (neat) 3060, 1710, 1490, 780 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.71 (dd, 1H, J = 5.1, 4.8 Hz), 3.82 (dd, 1H, J = 5.1, 4.8 Hz), 5.07 (t, 1H, J = 5.1 Hz), 6.80−7.45 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 45.6, 120.3, 122.1, 123.8, 126.7, 126.9, 127.3, 128.1, 128.5, 129.1, 129.5, 129.8, 131.1, 131.7, 131.9, 133.2, 136.7, 142.5, 143.9, 196.8. On standing in air, this material was oxidized to a product which was identified as 5-phenylbenzo[*b*]fluoren-11-one (**16**) on the basis of an X-ray structure analysis:[62] ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (m, 1H), 7.22 (m, 3H), 7.45 (m, 4H), 7.60 (m, 3H), 7.73 (m, 1H), 7.93 (m, 1H), 8.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.8, 124.2, 125.2, 126.8, 127.1, 128.0, 128.3, 128.3, 128.4, 128.9, 129.3, 129.7, 130.7, 131.5, 132.5, 133.4, 134.1, 135.3, 136.5, 136.9, 137.4, 154.1, 193.2. Anal. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61. Found: C, 90.03; H, 4.55.

4-Phenyl-1-(2-phenylethynylphenyl)-1-butanone (10). To a 100 mL flask containing 0.8 g (33 mmol) of magnesium

(61) Sakamoto, T.; Kondo, Y.; Miura, N.; Hayashi, K.; Yamanaka, H. *Heterocycles* **1986**, *24*, 2311.

(62) The authors have deposited coordinates for structure **16** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

metal was added a solution of 3.7 g (19 mmol) of 3-bromo-1-phenylpropane in 50 mL of ether at such a rate so as to produce a mild exotherm. After the addition was complete, the reaction was allowed to stir for 1 h at room temperature and was then added to a solution of 2.5 g (12 mmol) of 2-phenylethynylbenzaldehyde in 50 mL of ether at 25 °C. The solution was poured into an ice-cold saturated NH_4Cl solution, the ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Flash silica gel chromatography afforded 3.4 g (86%) of 4-phenyl-1-(2-phenylethynyl)phenyl-1-butanol: IR (neat) 3375, 3061, 2211, 1596, 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.76−1.84 (m, 1H), 1.85−1.91 (m, 1H), 1.91−2.01 (m, 2H), 2.52 (brs, 1H), 2.72 (t, 2H, J = 7.0 Hz), 5.33 (dd, 1H, J = 6.5, 5.0 Hz), 7.20−7.25 (m, 2H), 7.27−7.34 (m, 3H), 7.41−7.46 (m, 3H), 7.57−7.62 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.9, 35.8, 38.0, 72.3, 87.4, 94.4, 120.6, 123.3, 125.5, 125.8, 127.1, 128.3, 128.5, 128.5, 128.5, 128.9, 131.5, 132.3, 142.4, 146.8.

A solution of 2.5 g (7.7 mmol) of the above alcohol in 25 mL of CH_2Cl_2 was added to a stirring suspension containing 3.4 g (16 mmol) of PCC and 4.5 g of Celite in 75 mL of CH_2Cl_2. After the solution was stirred for 4 h, 100 mL of ether was added, and the mixture was filtered through a pad of Florisil. The filter cake was washed with ether, and the combined ether extracts were concentrated under reduced pressure. Silica gel chromatography of the residue afforded 2.0 g (81%) of ketone **10** as a pale yellow oil: IR (neat) 2215, 1690, 1591, 1495, 1219, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.11 (tt, 2H, J = 7.5, 7.3 Hz), 2.71 (t, 2H, J = 7.5 Hz), 3.18 (t, 2H, J = 7.3 Hz), 7.15−7.17 (m, 2H), 7.23−7.39 (m, 5H), 7.41−7.47 (m, 2H), 7.49−7.53 (m, 3H), 7.62−7.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0, 35.3, 41.4, 88.2, 94.6, 121.2, 122.9, 125.9, 128.2, 128.3, 128.3, 128.5, 128.7, 130.9, 131.6, 133.7, 141.4, 141.6, 203.3. Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.22. Found: C, 88.71; H, 6.19.

***trans*-2,3-Dihydro-2,3-diphenylcyclopent[*a*]inden-8(3*H*)-one (18).** To a dry 50 mL flask containing 0.3 g of NaH (60% in mineral oil) was added 5 mL of ether containing two drops of absolute ethanol. The flask was cooled to 0 °C, and a solution of 0.7 g (2 mmol) of ketone **10**, 1 mL of ethyl formate, and 5 mL of ether was added dropwise. The mixture was stirred at 0 °C for 3 h and at 25 °C for an additional 12 h. A solution of 0.7 g (6 mmol) of mesyl azide in 10 mL of ether was added, and the reaction mixture was stirred at room temperature for an additional 2 h. The mixture was quenched by the addition of 2 mL of water, the ether layer was separated and washed with 10% NaOH, and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude diazoketone was purified by flash silica gel chromatography to give 0.3 g (37%) of 2-diazo-4-phenyl-1-(2-phenylethynylphenyl)-1-butanone (**17**) as a pale yellow oil: IR (neat) 2211, 2076, 1654, 1617, 1493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.75−3.85 (m, 2H), 2.80−3.00 (m, 2H), 7.15−7.25 (m, 6H), 7.26−7.38 (m, 5H), 7.40−7.55 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 33.5, 69.4, 86.5, 94.0, 120.4, 122.7, 126.5, 128.3, 128.4, 128.4, 128.5, 128.7, 129.7, 131.0, 131.0, 132.5, 139.8, 140.7, 189.4. This diazo ketone was immediately used in the next step without further purification.

To a 50 mL flask containing 0.16 g (0.46 mmol) of α-diazo ketone **17** in 25 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate. The solution was stirred at 25 °C for 12 h, the solvent was removed, and the residue was subjected to silica gel chromatography to give 0.1 g (70%) of **18** as a yellow solid: mp 172−173 °C; IR (neat) 1690, 1600, 1500, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.94 (d, 2H, J = 8.2 Hz), 4.36 (dt, 1H, J = 8.4, 8.2 Hz), 4.50 (d, 1H, J = 8.4 Hz), 6.57−6.59 (m, 1H), 6.82−6.89 (m, 6H), 7.02−7.06 (m, 4H), 7.13−7.15 (m, 2H), 7.40−7.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.4, 52.6, 54.6, 119.9, 122.4, 126.2, 126.7, 127.7, 128.4, 128.5, 128.8, 132.9, 136.0, 136.5, 139.8, 139.8, 143.4, 171.1, 192.9. Anal. Calcd for $C_{24}H_{18}O$: C, 89.40; H, 5.63. Found: C, 89.27; H, 5.54.

2-Phenyl-1-(2-phenylethynylphenyl)-1-ethanone. To a 100 mL flask containing 0.8 g (33 mmol) of magnesium metal was added 3.1 g (18 mmol) of benzyl bromide in 50 mL of ether at a rate so as to produce a mild exotherm. After the addition was complete, the reaction was allowed to stir for 1 h at room temperature, and the mixture was added to a solution of 2.5 g (12 mmol) of 2-phenylethynylbenzaldehyde in 50 mL ether at 25 °C over a 1.5 h interval. The solution was poured into a saturated NH_4Cl solution, the ether layer was separated, and the aqueous layer was extracted with ether. Removal of the solvent under reduced pressure followed by flash silica gel chromatography of the residue afforded 3.2 g (89%) of 2-phenyl-1-(2-phenylethynyl)phenyl-1-ethanol: IR (neat) 3061, 2207, 1673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.17 (d, 1H, J = 3.4 Hz), 2.89 (dd, 1H, J = 13.8, 9.0 Hz), 3.28 (dd, 1H, J = 13.8, 3.4 Hz), 5.48 (dt, 1H, J = 9.0, 3.4 Hz), 7.24−7.30 (m, 6H), 7.36−7.40 (m, 4H), 7.54−7.61 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.1, 73.3, 87.1, 94.5, 120.3, 123.1, 125.2, 126.5, 127.1, 128.4, 128.7, 129.5, 131.5, 132.1, 138.4, 145.7.

A solution containing 3.0 g (10 mmol) of the above alcohol in 25 mL of CH_2Cl_2 was added to a suspension of 4.3 g (20 mmol) of pyridinium chlorochromate (PCC) and 4.5 g of Celite in 75 mL of CH_2Cl_2. After the solution was stirred for 4 h, ether was added, and the mixture was filtered through a pad of Florisil. The filter cake was washed with ether, and the combined extracts were concentrated under reduced pressure. Silica gel chromatography of the residue afforded 2.1 g (31%) of the titled compound as a clear oil: IR (neat) 3059, 2212, 1686, 1591 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.52 (s, 2H), 7.28−7.45 (m, 10H), 7.54−7.56 (m, 2H), 7.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.6, 88.2, 94.9, 121.2, 122.7, 126.9, 128.3, 128.5, 128.8, 129.7, 131.0, 131.6, 133.7, 134.4, 141.1, 200.8. Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.05; H, 5.35.

10-Phenyl-10*H*-indeno[2,1-*a*]inden-5-one (21). To a 200 mL flask equipped with a stirring bar and nitrogen inlet was added a solution of 1.4 g (4.7 mmol) of the above ketone and 1.9 g (6 mmol) of azidotris(diethylamino)phosphonium bromide (**11**) in 100 mL of dry THF. The reaction mixture was stirred at −78 °C for 20 min, and then 0.2 g of NaH (60% in mineral oil) was added in one portion. After being stirred for 1 h at 25 °C, the reaction mixture was washed with a 10% solution of NH_4Cl and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude diazoketone was purified by flash chromatography to give 0.8 g (53%) of 2-diazo-2-phenyl-1-(2-phenylethynylphenyl)-1-ethanone (**19**) as a labile pale yellow oil that was immediately used in the next step without further purification: IR (neat) 2962, 2217, 2080, 1627 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 6.77−7.07 (m, 8H), 7.16−7.27 (m, 4H), 7.50 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 86.4, 93.6, 120.6, 122.6, 124.9, 125.9, 126.3, 127.4, 128.1, 128.3, 128.7, 129.7, 131.5, 132.0, 141.3, 187.2.

To a 25 mL flask containing 0.1 g (0.3 mmol) of α-diazo ketone **19** in 10 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate. The solution was stirred at 25 °C for 1 h and was concentrated under reduced pressure. Silica gel chromatography of the crude reaction mixture afforded 0.08 g (93%) of **21** as a colorless oil: IR (neat) 3062, 1721, 1598, 1494 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 4.93 (s, 1H), 7.36 (m, 5H), 7.63 (m, 4H) and 7.81 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6) δ 64.2, 124.2, 124.4, 126.3, 127.3, 127.6, 128.0, 128.1, 128.3, 128.8, 129.3, 132.7, 134.1, 137.3, 138.7, 143.8, 144.7, 147.5, 192.7. Anal. Calcd for $C_{22}H_{14}O$: C, 89.76; H, 4.80. Found: C, 89.65; H, 4.73.

1-(2-Phenylethynylphenyl)-4-penten-1-ol. To a mixture containing 0.7 g (30 mmol) of magnesium turnings was added a solution of 4.0 g (30 mmol) of 4-bromo-1-butene in 50 mL of anhydrous ether at a rate sufficient to maintain a mild exotherm. After the addition was complete, the solution was allowed to stir for 2 h and was then added to a solution of 3.8 g (18 mmol) of 2-phenylethynylbenzaldehyde in 50 mL of ether at 0 °C. The solution was stirred at 25 °C for 2 h and was quenched by the addition of a saturated NH_4Cl solution. The ether layer was separated, the aqueous extracts were extracted with ether, and the combined extracts were dried with Na_2SO_4. Concentration under reduced pressure followed by flash

silica gel chromatography afforded 4.1 g (85%) of 1-(2-phenylethynylphenyl)-4-penten-1-ol as a white solid: mp 56−57 °C; IR (neat) 2215, 1642, 1573, 1027 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.89−2.02 (m, 2H), 2.21−2.31 (m, 2H), 4.98 (d, 1H, J = 10.0 Hz), 5.08 (dd, 1H, J = 17.0 and 1.5 Hz), 5.28 (m, 1H), 5.88 (m, 1H), 7.23−7.29 (m, 1H), 7.36−7.39 (m, 4H), 7.51−7.56 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.3, 37.4, 71.7, 87.3, 94.4, 115.0, 120.5, 123.2, 123.5, 127.1, 128.5, 128.8, 128.8, 131.5, 132.2, 138.4, 146.7. Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.92. Found: C, 86.84; H, 6.83.

1-(2-Phenylethynylphenyl)-4-penten-1-one. A solution containing 3.3 g (12 mmol) of the above alcohol in 50 mL of CH_2Cl_2 was added to a suspension containing 5.3 g (24 mmol) of PCC and 6 g of Celite in 150 mL of CH_2Cl_2. After the solution was stirred at room temperature for 4 h, 100 mL of ether was added, and the mixture was filtered through a pad of Florisil. The filter cake was washed with ether, and the combined extracts were concentrated under reduced pressure. Silica gel chromatography afforded 3.3 g (93%) of the titled compound as a pale yellow oil: IR (neat) 1692, 1592, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.52 (dt, 2H, J = 7.4, 7.0 Hz), 3.26 (t, 2H, J = 7.0), 5.03 (dd, 1H, J = 10.0, 1.0 Hz), 5.16 (dd, 1H, J = 17.3, 1.0 Hz), 5.90 (ddt, J = 17.3, 10.0, 7.0 Hz), 7.33−7.44 (m, 5H), 7.53−7.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.4, 41.2, 88.4, 94.7, 115.4, 121.2, 122.9, 128.3, 128.3, 128.5, 128.8, 131.0, 131.6, 133.8, 137.2, 141.1, 202.2. Anal. Calcd for $C_{19}H_{16}O$: C, 87.65; H, 6.20. Found: C, 87.54; H, 6.08.

1*a*,7*c*-Dihydro-7*c*-1*H*-cyclopropa[3,4]cyclopenta[1,2-*a*]-indene-3(2*H*)-one (25). To a dry 50 mL flask of 0.24 g (6.0 mmol) of NaH (60% in mineral oil) was added 5 mL of dry ether containing two drops of absolute ethanol. The flask was cooled to 0 °C, and a solution of 0.5 g (2.0 mmol) of the above ketone, 1 mL of ethyl formate, and 10 mL of dry THF was added dropwise. The mixture was stirred at 0 °C for 1 h and at 25 °C for 12 h. A solution of 0.7 g (6.0 mmol) of mesyl azide in 10 mL ether was added, the reaction was stirred for an additional 2 h, and the mixture was quenched by the addition of 2 mL of water. The ether layer was washed with 10% NaOH, and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude diazoketone was purified by flash silica gel chromatography to give 0.2 g (34%) of 2-diazo-1-(2-phenylethynylphenyl)-3-buten-1-one (**22**) as a pale yellow oil that was immediately used in the next step: IR (neat) 2217, 2082, 1729, 1617, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.25 (brs, 2H), 5.13 (d, 1H, J = 10.0 Hz), 5.22 (d, 1H, J = 17.5 Hz), 5.78−5.91 (m, 1H), 7.34−7.36 (m, 4H), 7.40−7.45 (m, 2H), 7.46−7.51 (m, 2H), 7.55−7.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.4, 69.3, 86.3, 93.0, 118.2, 120.4, 122.7, 127.4, 128.4, 128.7, 128.7, 130.0, 131.7, 132.0, 132.5, 140.6, 188.9.

To a 50 mL flask containing 0.1 g (0.35 mmol) of diazoketone **22** in 25 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate, and the solution was stirred for 12 h at 25 °C. Removal of the solvent followed by silica gel chromatography of the crude reaction mixture gave **25** (57%) as a pale oil: IR (neat) 1702, 1605, 1391, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.00 (dd, 1H, J = 5.2, 4.8 Hz), 2.06 (dd, 1H, J = 8.0, 4.8 Hz), 2.26 (ddd, 1H, J = 8.0, 6.5, 5.2 Hz), 2.66 (d, 1H, J = 18.2 Hz), 2.88 (dd, 1H, J = 18.2, 6.5 Hz), 6.49−6.52 (m, 1H), 7.09−7.12 (m, 2H), 7.28−7.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 28.9, 34.1, 36.1, 104.9, 120.1, 121.8, 127.0, 128.6, 132.5, 136.4, 138.1, 138.9, 139.4, 148.6, 176.0, 192.9. Anal. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.47. Found: C, 88.31; H, 5.29.

1-(2-Phenylethynylphenyl)-5-hexen-1-one. A solution of 2.4 g (16 mmol) of 5-bromo-1-pentene in 50 mL of anhydrous ether was added to 0.5 g (21 mmol) of magnesium turnings. The resulting Grignard reagent was allowed to stir for 2 h and was then added to a solution of 2.1 g (10 mmol) of 2-phenylethynylbenzaldehyde in 50 mL of ether at 0 °C. The solution was stirred at 25 °C for 2 h and then poured into a saturated NH_4Cl solution. The ether layer was separated, and the aqueous portion was extracted with ether. The combined ether extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Flash silica gel chromatography afforded 2.26 g (80%) of 1-(2-phenylethynylphenyl)-5-hexen-1-ol as a pale oil: IR (neat) 1640, 1602, 1573, 1027 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.43−1.58 (m, 1H), 1.60−1.75 (m, 1H), 1.80−1.97 (m, 2H), 2.13 (dd, 2H, J = 7.2, 7.0 Hz), 2.71 (brs, 1H), 4.96 (d, 1H, J = 10.5 Hz), 5.02 (dd, 1H, J = 17.3, 1.5 Hz), 5.28 (dd, 1H, J = 7.4, 5.3 Hz), 5.78−5.87 (m, 1H), 7.26 (t, 1H, J = 7.5 Hz), 7.34−7.41 (m, 4H), 7.53−7.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4, 33.7, 37.9, 72.2, 87.3, 94.3, 114.7, 120.6, 123.2, 125.4, 127.0, 128.5, 128.5, 128.8, 131.5, 132.2, 138.7, 146.8.

A solution containing 1.8 g (6.3 mmol) of the above alcohol in 25 mL of CH_2Cl_2 was added to a stirring suspension of 2.7 g (13 mmol) of PCC and 3 g of Celite in 75 mL of CH_2Cl_2. After the solution was stirred for 4 h, 100 mL of ether was added, and the mixture was filtered through a pad of Florisil. The filter cake was washed with ether, and the combined extracts were concentrated under reduced pressure. Silica gel chromatography of the residue afforded 1.6 g (91%) of 1-(2-phenylethynylphenyl)-5-hexen-1-one as a pale yellow oil: IR (neat) 3064, 2215, 1690, 1642, 1443 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (tt, 2H, J = 7.4, 7.0 Hz), 2.13 (dt, 2H, J = 7.0, 7.0 Hz), 3.13 (t, 2H, J = 7.4 Hz), 4.94 (dd, 1H, J = 10.0, 1.0 Hz), 4.99 (dd, 1H, J = 17.3, 1.0 Hz), 5.78 (ddt, J = 17.3, 10.0, 7.0 Hz), 7.30−7.44 (m, 5H), 7.51−7.67 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 33.0, 41.0, 88.1, 94.2, 115.0, 120.9, 122.6, 127.9, 128.0, 128.2, 128.4, 130.6, 131.3, 133.5, 138.0, 142.0, 203.0. Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.62. Found: C, 87.42; H, 6.65.

1,1*a*,2,3-Tetrahydro-8*c*-cyclopropa[c]fluoren-4(8c*H*)-one (26). A dry 50 mL flask equipped with a stirring bar and nitrogen inlet was charged with 0.3 g (6.3 mmol) of NaH (60% mineral oil) in 5 mL of ether containing two drops of absolute ethanol. To this mixture was added a solution of 0.6 g (2.0 mmol) of the above ketone, 1 mL of ethylformate, and 10 mL of dry THF at 0 °C. The mixture was stirred at 25 °C for 12 h, a solution containing 0.7 g (6.0 mmol) of mesyl azide in 10 mL of ether was added, and the mixture was stirred at 25 °C for an additional 2 h. The solution was quenched with 2 mL of water, the ether layer was washed with 10% NaOH, and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude oil was purified by flash silica gel chromatography to give 0.23 g (37%) of 2-diazo-1-(2-phenylethynylphenyl)-5-hexen-1-one (**23**) as a pale yellow oil that was immediately used in the next step: IR (neat) 3066, 2216, 2073, 1614, 1342 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.25−2.41 (m, 2H), 2.60−2.73 (m, 2H), 4.95 (d, 1H, J = 10.0 Hz), 5.12 (d, 1H, J = 17.5 Hz), 5.78−5.91 (m, 1H), 7.34−7.36 (m, 4H), 7.40−7.45 (m, 2H), 7.46−7.51 (m, 2H), 7.55−7.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 31.4, 69.6, 86.3, 92.9, 116.5, 120.4, 122.8, 127.2, 128.4, 128.4, 128.6, 128.7, 129.9, 131.6, 132.6, 136.2, 189.6.

To a 50 mL flask containing 0.05 g (0.2 mmol) of diazoketone **23** in 25 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate. The solution was stirred for 12 h at 25 °C, the solvent was removed under reduced pressure, and the crude mixture was subjected to silica gel chromatography to give 0.04 g (81%) of **26** as a clear pale oil: IR (neat) 1680, 1600, 1450, 1370 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.42 (dd, 1H, J = 6.2 and 5.4 Hz), 1.68−1.74 (m, 1H), 1.89 (d, 1H, J = 8.4 Hz), 1.91 (d, 2H, J = 8.8 Hz), 2.17−2.29 (m, 1H), 2.59 (d, 1H, J = 12.4 Hz), 5.76 (d, 1H, J = 7.3 Hz), 6.91 (dd, 1H, J = 7.4, 7.3 Hz, 7.00 (dd, 1H, J = 7.4, 7.4 Hz), 7.28−7.38 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5, 18.9, 19.4, 26.2, 28,6, 121.3, 121.4, 127.2, 127.7, 128.5, 128.6, 129.7, 132.3, 132.7, 141.9, 143.6, 196.2. Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.93. Found: C, 88.08; H, 5.76.

6-Trimethylsilyl-1-(2-phenylethynylphenyl)-1-hex-5-yn-one. To a 250 mL flask containing 0.8 g (34 mmol) of magnesium metal was added a solution of 6.0 g (22 mmol) of 5-iodo-1-trimethylsilyl-1-pentyne in 50 mL of ether at such a rate so as to produce a mild exotherm. After the addition was complete, the reaction was allowed to stir for 1 h and was then added to a solution of 4.7 g (23 mmol) of 2-phenylethynylbenzaldehyde in 50 mL ether at 25 °C. The solution was poured into an ice-cold saturated NH_4Cl solution, the ether layer was

separated, and the aqueous layer was extracted with ether. Removal of the solvent gave 4.9 g (63%) of 6-trimethylsilyl-1-(2-phenylethynylphenyl)-1-hex-5-yn-ol, which was used directly in the next step. A solution of this alcohol in 50 mL of CH_2Cl_2 was added to a stirring suspension of 3.4 g (16 mmol) of PCC and 6.0 g of Celite in 75 mL of CH_2Cl_2. After the solution was stirred for 4 h, 100 mL of ether was added, and the mixture was filtered through a pad of Florisil. The filter cake was washed with ether, and the combined ether extracts were concentrated under reduced pressure. Removal of the solvent followed by silica gel chromatography afforded 5.6 g (72%) of the titled compound as a pale yellow oil: IR (neat) 1685, 1250, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9H), 2.05 (q, 2H, J = 7.0 Hz), 2.36 (t, 2H, J = 7.0 Hz), 3.28 (t, 2H, J = 7.0 Hz), 7.34 (m, 5H), 7.48−7.71 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 19.4, 25.1, 40.7, 85.4, 88.3, 94.7, 106.4, 121.4, 122.9, 128.3, 128.5, 128.6, 128.7, 131.0, 131.6, 133.9, 140.9, 202.3. Anal. Calcd for $C_{23}H_{24}OSi$: C, 80.20; H, 7.03. Found: C, 80.34; H, 6.97.

3-Phenyl-2-trimethylsilanylethynyl-2,3-dihydro-1*H*-cyclopenta[*a*]inden-8-one (30). To a 50 mL flask of 0.21 g of NaH (60% in mineral oil) was added 5 mL of ether containing two drops of absolute ethanol. The flask was cooled to 0 °C, and a solution of 0.6 g (1.7 mmol) of the above ketone, 0.4 mL of ethyl formate, and 5 mL of ether was added dropwise. The mixture was stirred at 0 °C for 3 h and at 25 °C for 12 h. A solution of 0.6 g (5.2 mmol) of mesyl azide in 10 mL ether was added, and the reaction mixture was stirred for an additional 2 h. The solution was quenched with 2 mL of water, the ether layer was washed with 10% NaOH, and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4 and were concentrated under reduced pressure. The crude oil that was obtained was purified by flash silica gel chromatography to give 0.2 g (33%) of 2-diazo-6-trimethylsilyl-1-(2-phenylethynylphenyl)-1-hex-5-ynone (**28**) as a pale yellow oil that was immediately used in the next step: IR (neat) 2959, 2174, 2080, 1614, 1350 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 9H), 2.58 (m, 2H), 2.74 (m, 2H), 7.29 (m, 5H), 7.51 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 25.1, 37.5, 69.5, 71.8, 86.2, 94.3, 107.3, 120.5, 122.7, 125.4, 128.4, 128.5, 130.0, 131.5, 132.6, 146.6, 189.2.

To a 25 mL flask containing 0.05 g (0.13 mmol) of α-diazo ketone **28** in 10 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate, and the solution was stirred for 12 h at 25 °C. Removal of the solvent followed by silica gel chromatography of the reaction mixture afforded 0.04 g (83%) of **30**: IR (neat) 3025, 1712, 1421, 1135 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9H), 2.70 (ddd, 1H, J = 16.8, 7.1, 2.1 Hz), 2.93 (dd, 1H, J = 16.8, 8.6 Hz), 3.94 (ddd, 1H, J = 8.6, 7.9, 7.1 Hz), 4.42 (dt, 1H, J = 7.9, 2.1 Hz), 6.57−6.59 (m, 1H), 7.08−7.38 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.3, 32.8, 40.9, 51.6, 89.8, 105.6, 120.0, 122.5, 127.4, 128.2, 128.7, 129.0, 133.0, 136.1, 136.8, 139.5,142.2, 170.4, 192.4; HRMS calcd for $C_{23}H_{22}OSi$ 342.1440, found 342.1455.

Phenylacetic Acid 3-Phenylprop-2-ynyl Ester. To a solution containing 3.3 g (25 mmol) of 3-phenyl-prop-2-yn-1-ol and 3.0 g (22 mmol) of phenylacetic acid in 50 mL of CH_2Cl_2 was added 5.2 g (25 mmol) of dicyclohexylcarbodiimide and 1.2 g (10 mmol) of 4-(dimethylamino)pyridine at 0 °C under N_2. After being stirred for 2 h, the reaction mixture was warmed to 25 °C over a 12 h period. The mixture was filtered through Celite and concentrated under reduced pressure. The residue was taken up in 100 mL of ethyl acetate and was washed with a saturated Na_2CO_3 solution followed by brine. The organic layer was dried over Na_2SO_4 and was concentrated under reduced pressure. The crude ester was purified by flash silica gel chromatography to give 5.1 g (92%) of the titled compound as a clear oil: IR (neat) 2931, 2856, 1744, 1142 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 2H), 4.94 (s, 2H), 7.31−7.35 (m, 8H), 7.44−7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1, 53.2, 82.9, 86.6, 122.2, 127.2, 128.3, 128.7, 128.8, 129.3, 131.9, 133.6, 170.9. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.57; H, 5.64. Found: C, 81.32; H, 5.61.

8-Phenyl-1,8-dihydro-2-oxacyclopenta[*a*]inden-3-one (34). To a 50 mL flask equipped with a stirring bar and nitrogen inlet was added a solution of 0.7 g (2.8 mmol) of the above ester and 1.9 g (6.0 mmol) of azido-*tris*(diethylamino)-phosphonium bromide (**11**) in 10 mL of dry THF. The reaction mixture was stirred at −78 °C for 20 min, and then 0.12 g (3 mmol) of NaH (60% in mineral oil) was added in one portion. After being stirred for 1 h at 0 °C, the reaction mixture was washed with a 10% NH_4Cl solution and the aqueous layer was extracted with ether. The combined ether extracts were dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash silica gel chromatography to give 0.7 g (84%) of diazophenylacetic acid 3-phenylprop-2-ynyl ester (**31**) as a pale yellow oil that was immediately used in the next step: IR (neat) 2931, 2115, 2086, 1702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.09 (s, 2H), 7.17−7.52 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.1, 82.9, 86.7, 122.1, 124.0, 125.6, 126, 128.3, 128.8, 129.0, 131.9, 164.4.

To a 25 mL flask containing 0.13 g (0.5 mmol) of α-diazo ketone **31** in 10 mL of dry CH_2Cl_2 was added 2 mg of rhodium(II) acetate. The solution was stirred at 25 °C for 10 min and was then concentrated under reduced pressure. Silica gel chromatography of the residue afforded 0.11 g (92%) of **34** as a yellow solid: mp 138−139 °C; IR (neat) 2926, 1757, 1452 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.89 (s, 1H), 4.92 (d, 1H, J = 18.8 Hz), 5.10 (d, 1H, J = 18.8 Hz), 7.06 (d, 2H, J = 6.3 Hz), 7.24−7.37 (m, 6H), 7.72 (d, 1H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.0, 69.1, 121.1, 125.1, 127.1, 127.7, 127.8, 127.9, 129.3, 133.9, 136.1, 136.8, 151.5, 167.5, 175.7. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.23; H, 4.87. Found: C, 82.31; H, 4.77.

2-Ethoxy-1-phenylcyclopropanecarboxylic Acid 3-Phenylprop-2-ynyl Ester (37). A solution contaning 0.1 g (0.4 mmol) of α-diazo ester **31** and 0.14 g (2.0 mmol) of ethyl vinyl ether in 30 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate. The mixture was allowed to stir at 25 °C for 30 min and was then concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 0.12 g (93%) of **37** as a clear oil as the only product formed: IR (neat) 2974, 2231, 1716, 1251 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, 1H, J = 6.7 Hz), 1.71 (dd, 1H, J = 5.5, 4.9 Hz), 1.88 (dd, 1H, J = 6.7, 5.5 Hz), 3.56 (q, 2H, J = 6.7 Hz), 4.00 (dd, 1H, J = 6.7, 4.9 Hz), 4.85−4.94 (m, 2H), 7.28−7.51 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.9, 21.1, 35.2, 53.3, 65, 65.6, 80.8, 83.2, 86.2, 122.3, 127.3, 127.9, 128.3, 128.7, 131.5, 131.9, 133.9, 172.3; HRMS calcd for $C_{21}H_{20}O_3$ 320.1412, found 320.1410.

6-Phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylic Acid 3-Phenylprop-2-ynyl Ester (38). A solution contaning 0.1 g (0.4 mmol) of α-diazo ester **31** and 0.14 g (2.0 mmol) of dihydrofuran in 32 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate. The mixture was allowed to stir at 25 °C for 30 min and was concentrated under reduced pressure. Chromatography of the resulting oil on silica gel gave 0.02 g (26%) of butenolide **34** and 0.08 g (65%) of **38**. Cyclopropane **38** exhibited the following spectral properties: IR (neat) 3054, 2897, 1709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (ddd, 1H, J = 11.4, 8.7, 3.7 Hz), 2.18−2.30 (m, 1H), 2.38 (q, 1H, J = 8.7 Hz), 2.70 (t, 1H, J = 5.8 Hz), 3.77 (ddd, 1H, J = 11.4, 8.7, 3.7 Hz), 4.56 (d, 1H, J = 5.8 Hz), 4.79 (s, 2H), 7.24−7.46 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 32.6, 38.1, 53.2, 70.1, 83.2, 86.1, 122.3, 127.6, 128.3, 128.5, 128.7, 131.6, 131.8, 131.9, 170.6. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.21; H, 5.70. Found: C, 79.05; H, 5.66.

7-Phenyl-2-oxabicyclo[4.1.0]heptane-7-carboxylic Acid 3-Phenylprop-2-ynyl Ester (39). A solution contaning 0.1 g (0.4 mmol) of α-diazo ester **31** and 0.15 g (2.0 mmol) of dihydropyran in 30 mL of CH_2Cl_2 was treated with 2 mg of rhodium(II) acetate. The mixture was allowed to stir at 25 °C for 30 min and was concentrated under reduced pressure and analyzed by HPLC. Chromatography of the resulting oil on silica gel gave 0.06 g (69%) of butenolide **34** and 0.03 g (22%) of **39**. Cyclopropane **39** exhibited the following spectral properties: IR (neat) 3025, 2229, 1709 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.22−0.38 (m, 1H), 0.98−1.06 (m, 1H), 1.85−2.07 (m, 2H), 2.21 (t, 1H, J = 7.1 Hz), 3.29 (dt, 1H, J = 11.2, 1.0 Hz), 3.40 (dt, 1H, J = 11.2, 3.3 Hz), 4.26 (d, 1H, J = 7.1 Hz), 4.78

(m, 2H), 7.31−7.46 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 21.1, 25.6, 34.6, 53.2, 62.2, 64.5, 83.3, 86.0, 122.3, 127.2, 128.1, 128.2, 128.6, 131.9, 132.6, 132.9, 148.6, 172.4. Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.48; H, 6.07. Found: C, 79.32; H, 6.05.

3-Oxobutyric Acid 3-Phenylprop-2-ynyl Ester. To a solution containing 3.0 g (23 mmol) of 3-phenylprop-2-yn-1-ol in 10 mL of xylene was added 3.0 mL (23 mmol) of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one under a nitrogen atmosphere. After being heated for 2 h at 140 °C, the reaction was cooled to 25 °C, filtered through Celite, and concentrated under reduced pressure. The crude β-keto ester was purified by flash silica gel chromatography to give 4.5 g (92%) of the titled compound as a clear oil: IR (neat) 3061, 2229, 1745, 1716 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.26 (s, 3H), 3.50 (s, 2H), 4.94 (s, 2H), 7.28−7.31 (m, 3H), 7.41−7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.1, 49.8, 53.6, 82.3, 87.0, 121.9, 128.3, 128.9, 131.9, 166.4, 199.9. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.20; H, 5.60. Found: C, 72.15; H, 5.65.

2-Benzyl-3-oxobutyric Acid 3-Phenylprop-2-ynyl Ester. To a suspension containing 0.1 g (2.4 mmol) of NaH (60% in mineral oil) in 10 mL of THF was added 0.44 g (2.0 mmol) of the above β-keto ester. After being stirred for 30 min at 25 °C, 0.3 mL (2.4 mmol) of benzyl bromide was added. The mixture was stirred for 4 h at 60 °C and then cooled to 25 °C. The solution was poured into an ice-cold saturated NH_4Cl solution, the ether layer was separated, and the aqueous layer was extracted with ether. Removal of the solvent under reduced pressure gave 3.5 g (91%) of the titled compound as a clear oil (5:1 keto/enol): IR (neat) 3431, 3025, 2228, 1745, 1716 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 3H), 2.20 (s, 3H), 3.19 (d, 2H, J = 7.6 Hz), 3.62 (s, 2H), 3.84 (t, 1H, J = 7.6 Hz), 4.84−4.90 (m, 2H), 4.94−4.96 (m, 2H), 7.31−7.48 (m, 20H), 12.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 29.7, 31.5, 34.0, 52.8, 53.7, 61.1, 82.3, 83.1, 86.5, 87, 99.1, 122.0, 126.0, 126.8, 127.9, 128.3, 128.4, 128.7, 128.8, 128.9, 131.9, 137.9, 140.7, 168.5, 172.4, 174.8, 201.8. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.40; H, 5.93. Found: C, 78.33; H, 5.81.

***Z*-3-Phenylacrylic Acid 3-Phenylprop-2-ynyl Ester (41).** To a dry 25 mL flask containing 0.3 g (0.9 mmol) of the above β-keto ester was added 10 mL of CH_2Cl_2 and 0.3 g (1.3 mmol) of *p*-nitrobenzenesulfonyl azide. The flask was cooled to 0 °C, and 0.25 mL (1.7 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene was added dropwise. The mixture was stirred at 0 °C for 10 min and filtered through a pad of silica. The filter cake was washed with ethyl acetate, and the combined extracts were concentrated under reduced pressure. The crude diazoester was purified by flash silica gel chromatography to give 0.2 g (72%) of 2-diazo-3-phenylpropionic acid 3-phenylprop-2-ynyl ester (**40**) as a clear oil that was used in the next step without further purification: IR (neat) 3025, 2229, 2086, 1688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 2H), 5.02 (s, 2H), 7.24−7.32 (m, 8H), 7.44−7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.4, 53.1, 83.1, 86.5, 122.1, 127.2, 128.3, 128.4, 128.8, 128.8, 131.9, 137.0.

To a 25 mL flask containing 0.18 g (0.6 mmol) of α-diazo ester **40** in 10 mL of CH_2Cl_2 was added 2 mg of rhodium(II) acetate. The solution was stirred for 1 h at 25 °C and concentrated under reduced pressure. Silica gel chromatography of the crude residue afforded 0.15 g (92%) of **41** as a clear oil: IR (neat) 3054, 2236, 1723, 1147 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.95 (s, 2H), 6.00 (d, 1H, J = 12.6 Hz), 6.99 (d, 1H, J = 12.6 Hz), 7.29−7.35 (m, 6H), 7.43−7.46 (m, 2H), 7.60−7.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 83.0, 86.5, 118.6, 122.2, 128.1, 128.3, 128.8, 129.3, 129.9, 131.9, 134.5, 144.5, 165.3. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.41; H, 5.38. Found: C, 82.57; H, 5.35.

2-Acetylpent-4-ynoic Acid 3-Phenylprop-2-ynyl Ester. To a suspension containing 0.2 g (4.8 mmol) of NaH (60% in mineral oil) in 20 mL of THF was added 1.0 g (4.6 mmol) of 3-oxobutyric acid 3-phenylprop-2-ynyl ester. After the mixture was stirred for 30 min at 25 °C, 0.7 g (4.7 mmol) of 80% propargyl bromide in toluene was added. The reaction mixture was stirred for 4 h at 60 °C and then cooled to 25 °C. The solution was poured into an ice-cold saturated NH_4Cl solution, the ether layer was separated, and the aqueous layer was extracted with ether. Removal of the solvent under reduced pressure afforded 0.7 g (60%) of 2-acetylpent-4-ynoic acid 3-phenylprop-2-ynyl ester: IR (neat) 3289, 2225, 1745, 1716 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (t, 1H, J = 2.7 Hz), 2.35 (s, 3H), 2.76 (dd, 2H, J = 7.5 and 2.7 Hz), 3.79 (t, 1H, J = 7.5 Hz), 5.00 (s, 2H), 7.28−7.45 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.4, 29.6, 54.0, 58.0, 70.5, 80.1, 82.1, 87.1, 121.8, 128.4, 128.9, 131.9, 167.5, 200.4. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.38; H, 5.44.

4-Phenyl-3*H*-isobenzofuran-1-one (45). To a dry 25 mL flask containing 0.2 g (0.8 mmol) of the above β-keto ester was added 10 mL of CH_2Cl_2 and 0.2 g (0.9 mmol) of *p*-nitrobenzenesulfonyl azide. The flask was placed in an ice bath, and 0.25 mL (1.8 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene was added. The mixture was stirred at 0 °C for 10 min and then filtered through a pad of silica. The filter cake was washed with ethyl acetate, and the combined extracts were concentrated under reduced pressure. The crude diazo ester was purified by flash silica gel chromatography to give 0.14 g (75%) of 2-diazopent-4-ynoic acid 3-phenylprop-2-ynyl ester (**43**) as a clear oil that was used in the next step without further purification: IR (neat) 3289, 2228, 2093, 1688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (t, 1H, J = 2.7 Hz), 3.33 (d, 2H, J = 2.7 Hz), 5.01 (s, 2H), 7.30−7.33 (m, 3H) and 7.44−7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 53.2, 71.6, 77.3, 82.6, 86.6, 122.1, 128.3, 128.8, 131.9, 165.3.

To a 25 mL flask containing 0.13 g (0.55 mmol) of α-diazo ester **43** in 10 mL of benzene at 80 °C was added 2 mg of rhodium(II) acetate. The solution was heated at reflux for 12 h, cooled to 25 °C, and concentrated under reduced pressure. Silica gel chromatography of the crude residue afforded 0.02 g (16%) of *Z*-pent-2-en-4-ynoic acid 3-phenylprop-2-ynyl ester (**44**) and 0.08 g (76%) of 4-phenyl-3*H*-isobenzofuran-1-one[63] (**45**). Compound **44** exhibited the following spectral properties: IR (neat) 3282, 2229, 1730, 1161 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (d, 1H, J = 2.3 Hz), 5.01 (s, 2H), 6.20 (dd, 1H, J = 11.5, 2.5 Hz), 6.29 (d, 1H, J = 11.5 Hz), 7.47−7.26 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.9, 79.4, 82.6, 86.7, 90.0, 122.1, 123.2, 128.3, 128.8, 129.7, 131.8, 163.5; HRMS calcd for $C_{14}H_{10}O_2$ 210.0681, found 210.0679.

4-Phenyl-3*H*-isobenzofuran-1-one (**45**) exhibited the following spectral properties: mp 118−119 °C; IR (neat) 3061, 2923, 1763 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.41 (s, 2H), 7.43−7.53 (m, 5H), 7.63 (t, 1H, J = 7.5 Hz), 7.73 (d, 1H, J = 7.3 Hz) and 7.92 (d, 1H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.7, 124.6, 126.4, 127.7, 128.5, 129.2, 129.8, 133.8, 137.0, 137.6, 144.1, 171.1. Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.97; H, 4.80. Found: C, 79.83; H, 4.78.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for new compounds lacking elemental analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(63) Noguchi, M.; Kakimoto, S.; Kawakami, H. Kajigaeshi, S. *Heterocycles* **1985**, *23*, 1085.