A Tandem Cyclization–Onium Ylide Rearrangement–Cycloaddition Sequence for the Synthesis of Benzo-Substituted Cyclopentenones

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A new annulation sequence leading to benzo-substituted cyclopentenones is effected by treating *o*-alkynyl-substituted α-diazoacetophenones containing tethered heteroatoms with Rh(II) carboxylates. The reaction involves addition of the initially formed keto carbenoid onto the acetylenic π-bond to give a rearranged vinyl carbenoid. Sulfonium ylide formation occurred both intra- and intermolecularly when the reaction was carried out in the presence of a sulfide. In the case where an ether oxygen was present on the backbone of the vinyl carbenoid, the resulting oxonium ylide underwent a [1,2]- or [2,3]-shift to give the rearranged product. These cyclic metallocarbenoids were also found to interact with a neighboring carbonyl or oximino π-bond to produce carbonyl or azomethine ylides. The 1,3-dipoles generated in this manner were trapped with dimethyl acetylenedicarboxylate. The domino transformation was also performed intramolecularly by attaching a trapping agent directly to the carbonyl group. Incorporation of an amido carbonyl on the alkyne side chain was found to dramatically alter the course of the tandem annulation reaction. A novel rearranged cycloadduct was formed in high yield whose structure was elucidated by X-ray crystallography. The mechanism for its formation involves the opening of a transient intermediate oxabicyclo[2.2.1]heptane followed by a Wagner–Meerwein rearrangement.

There has been considerable interest in the synthesis and biological properties of substituted cyclopentenones as a result of the ubiquity of this nucleus in nature.[1–5] The most versatile syntheses of cyclopentenones consist of the initial preparation of acyclic 1,4-dicarbonyl compounds and their subsequent intramolecular base-catalyzed aldol condensation.[6–8] Other successful approaches involve Nazarov type cyclizations[9,10] and the Pauson–Khand $Co_2(CO)_8$-mediated cyclizations of alkynes with olefins.[11–17] However, each of these methods has certain limitations. In this context, recent work by our group[18] as well as Hoye's[19] has shown that the rhodium(II)-catalyzed reaction of α-diazo ketones bearing tethered alkyne units represents a new and useful method for the construction of a variety of substituted cyclopentenones. 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 (Scheme 1). The potential for many other diverse chemical pathways exists through the further chemistry of these vinyl rhodium carbenoids.

The reaction of keto carbenoids with heteroatoms which possess a lone pair of electrons is rapidly gaining prominence as an efficient method for heterocyclic synthesis.[20–28] This process is a mild and high-yielding

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(1) Ellison, R. A. *Synthesis* **1973**, 397.
(2) Bernasconi, S.; Capellini, C.; Sisti, M. *Synth. Commun.* **1978**, *8*, 71.
(3) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 5311.
(4) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. Schore, N. E. *Organic Reactions;* Paquette, L. A., Ed.; Wiley and Sons: New York, 1991; Vol. 40, pp 1–90.
(5) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568.
(6) Miklojczyk, M.; Grzejsczak, S.; Korbacz, K. *Tetrahedron Lett.* **1981**, *22*, 3097. Miklojczyk, M.; Grzejczak, S.; Kyzwa, P. *Tetrahedron Lett.* **1982**, *23*, 2237.
(7) Herman, J. L.; Richmann, J. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 3275.
(8) Bakuzis, P.; Bakuzis, M. L. F. *J. Org. Chem.* **1977**, *42*, 2362.
(9) Denmark, S. E. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 5, pp 751–784.
(10) Santelli-Roovier, C.; Santelli, M. *Synthesis* **1983**, 429.
(11) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. I* **1973**, 977. Pauson, P. L. In *Organometallics in Organic Synthesis. Aspects of a Modern Interdisciplinary Field;* de Meijere, A., tom Dieck, H.; Eds.; Springer: Berlin, 1988; p 233. Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.
(12) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199.
(13) Hoye, T. R.; Suriano, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 1154.
(14) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 2568.
(15) Noyori, R.; Hayakausa, M.; Takaya, H.; Murai, S.; Kobayashi, R.; Sonada, N. *J. Am. Chem. Soc.* **1978**, *100*, 1759.
(16) Oppolzer, W.; Bedoya-Zurita, M.; Surler, Y. *Tetrahedron Lett.* **1988**, *29*, 6433.
(17) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1286.
(18) Padwa, A.; Krumpe, K. E.; Zhi, L. *Tetrahedron Lett.* **1989**, *30*, 2633. 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.; Austin, D.; Xu, S. *J. Org. Chem.* **1992**, *57*, 1330. Padwa, A.; Krumpe, K. E.; Kassir, J. M. *J. Org. Chem.* **1992**, *57*, 4940. Padwa, A.; Kinder, F. R. *J. Org. Chem.* **1993**, *58*, 21. Mueller, P. H.; Kassir, J. M.; Semones, M. A.; Weingarten, M. D.; Padwa, A. *Tetrahedron Lett.* **1993**, *27*, 4285. Padwa, A.; Dean, D. C.; Fairfax, D. J.; Xu, S. L. *J. Org. Chem.* **1993**, *58*, 4646. Padwa, A.; Kassir, J. M.; Semones, M. A.; Weingarten, M. D. *Tetrahedron Lett.* **1993**, *34*, 7853.
(19) 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.
(20) Rapoport, H.; Feldman, P. L.; Moyer, M. P. *J. Org. Chem.* **1985**, *50*, 5223.
(21) Salzmann, T. N.; Ratcliffe, R. W.; Christensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161.

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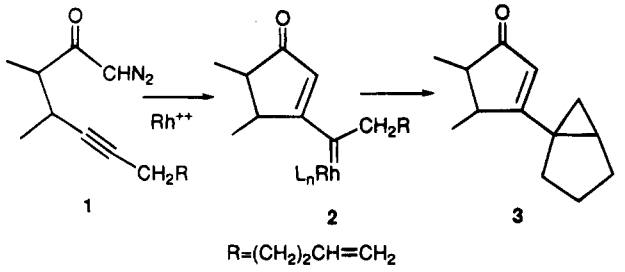
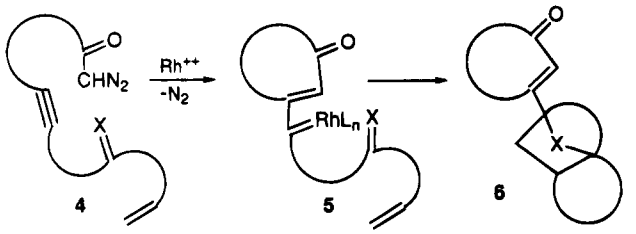
Scheme 1



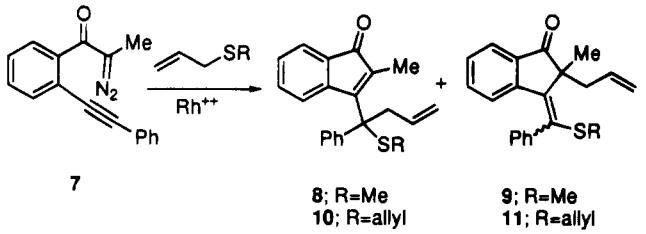
Scheme 2



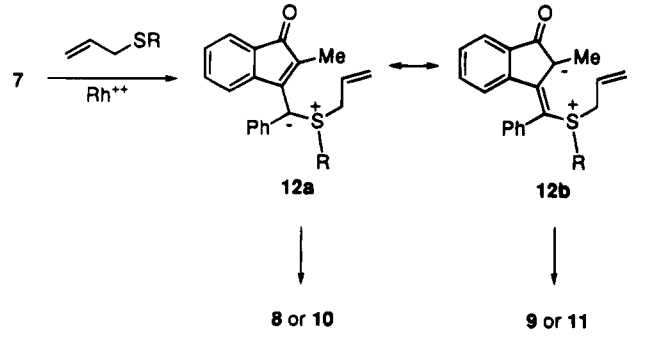
alternative to traditional base-promoted methods of ylide generation. Ylides generated by reaction of carbenoids with heteroatom-containing substrates are transformed into stable compounds by either dipolar cycloaddition, a [1,2]-alkyl shift, or a [2,3]-sigmatropic rearrangement.[28] Previous papers from these laboratories have described a route to polyhetero ring systems which involves the tandem cyclization–cycloaddition reaction of a rhodium carbenoid intermediate with a neighboring hetero π-bond.[29] In an effort to further extend the earlier studies, we envisioned a strategy for the preparation of even more complex cyclopentenones by a merger of our two methodologies. The overall process would lead to a large increase in molecular complexity in a single experimental operation in which three new C–C bonds have been formed (Scheme 2). The novelty of the process lies in the method of ylide generation, which, to our knowledge, is unprecedented. In the present paper we give a full account of our results on the preparation of different heterobicyclic ring systems using the Rh(II)-catalyzed intramolecular tandem ylide–cycloaddition rearrangement sequence.

Results and Discussion

Our studies began with an investigation of the Rh(II)-catalyzed reaction of α-diazo ketone **7** in the presence of allyl methyl sulfide. The reaction of electrophilic carbenes and carbenoids with unsaturated divalent sulfur compounds to give sulfonium ylides, which then undergo a [2,3]-sigmatropic rearrangement, is a well-described process.[30–33] It is believed that the lone pair of the sulfide adds to the electrophilic carbenoid intermediate and subsequent dissociation of the catalyst produces the sulfonium ylide.[30] The symmetry-allowed [2,3]-sigmatropic rearrangement is widely recognized as a facile bond reorganization process, especially for allylic sulfides.[34] In an earlier report, Hoye and Dinsmore[35] demonstrated that acetylenic α-diazo ketones of type **1**, when treated with a Rh(II) catalyst and diallyl sulfide, undergo sequential *alkyne metathesis/ylide formation/sigmatropic rearrangement* to produce α-allylthio cyclic enones. We have found that the reaction of diazo ketone **7** with $Rh_2(OAc)_4$ in CH_2Cl_2 at 25 °C behaves similarly, producing indenone **8** (86%) along with a 1:1 *E/Z* mixture of the isomeric vinyl sulfide **9** in 10% yield. A related reaction occurred using diallyl sulfide resulting in the formation of a 9:1 mixture of **10** and **11**. The possibility that **9** (or



11) was the result of a Cope rearrangement of **8** (or **10**) was excluded by the finding that the thermolysis of **8** (or **10**) did not produce any detectable quantities of **9** (or **11**). The formation of **8** and **10** proceeds in the expected manner by tandem sulfur lone pair insertion and ylide **12a** rearrangement. Presumably, structures **9** and **11** arise *via* a novel antarafacial [3,4]-sigmatropic rearrangement of sulfonium ylide **12b**.



The ease with which the intermolecular *sulfonium ylide generation/[2,3]-rearrangement* sequence occurred

(22) For some recent reviews, see: Mass, G. in *Topics in Current Chemistry;* Marcel Dekker: New York, 1987; Vol. 137, pp 77–188. Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751. Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

(23) Moody, C. J.; Yaylor, R. J. *Tetrahedron Lett.* **1987**, 5351; *J. Chem. Soc., Perkin Trans. 1* **1988**, 1417.

(24) Ibata, T.; Motoyama, T.; Hamaguichi, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2298.

(25) Gillon, A.; Ovadia, D.; Kapon, M.; Bien, S. *Tetrahedron* **1982**, *38*, 1477.

(26) Maier, M. E.; Evertz, K. *Tetrahedron Lett.* **1988**, 1677.

(27) Fang, F. G.; Prato, M.; Kim, G.; Danishefsky, S. J. *Tetrahedron Lett.* **1989**, 3625. Fang, F. G.; Danishefsky, S. J. *Tetrahedron Lett.* **1989**, 2747. Fang, F. G.; Maier, M. E.; Danishefsky, S. J. *J. Org. Chem.* **1990**, *55*, 831. Kim, G.; Chu-Moyer, M. Y.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2003.

(28) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385.

(29) Padwa, A.; Carter, S. P.; Nimmesgern, H.; Stull, P. *J. Am. Chem. Soc.* **1988**, *110*, 2894. Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Org. Chem.* **1988**, *53*, 2875. Padwa, A.; Chinn, R. L.; Hornbuckle, S. F.; Zhi, L. *Tetrahedron Lett.* **1989**, 301. Padwa, A.; Chinn, R. C.; Zhi, L. *Tetrahedron Lett.* **1989**, 1491. Padwa, A.; Hertzog, D. L.; Chinn, R. C. *Tetrahedron Lett.* **1989**, 4077. Padwa, A.; Dean, D. C.; Zhi, L. *J. Am. Chem. Soc.* **1989**, *111*, 6451. Padwa, A.; Dean, D. C.; Krumpe, K. E. *J. Chem. Soc., Chem. Commun.* **1989**, 921. Hertzog, D. L.; Nadler, W. R.; Zhang, Z. J.; Padwa, A. *Tetrahedron Lett.* **1992**, *33*, 5877.

(30) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094.

(31) Kondo, K.; Ojima, I. *J. Chem. Soc., Chem. Commun.* **1972**, 860.

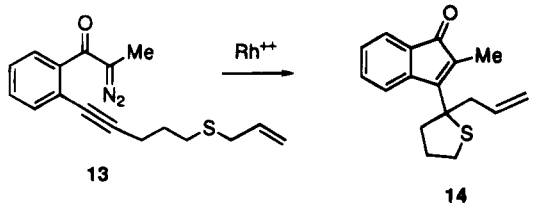
(32) Tamblyn, W. H.; Hoffmann, S. R.; Doyle, M. P. *J. Organomet. Chem.* **1981**, *216*, C64.

(33) Moody, C. J.; Taylor, R. J. *Tetrahedron Lett.* **1988**, *29*, 6005.

(34) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563. Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179. Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75.

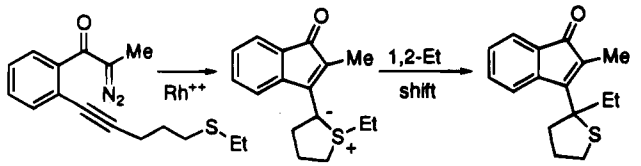
(35) Hoye, T. R.; Dinsmore, C. J. *Tetrahedron Lett.* **1992**, 169.

suggested that a similar process might take place intramolecularly by incorporating the allyl sulfide functionality onto the alkyne unit. The requisite diazo ketone **13** was prepared by first treating methyl 2-iodo benzoate with 5-(allylthio)-1-pentyne under typical Castro–Stephens arylation conditions.[36] The resulting ester was easily converted to diazo ketone **13** by treatment with potassium trimethylsilanolate followed by reaction with methyl chloroformate. The mixed anhydride was then allowed to react with diazoethane. Standard conditions for the rhodium-catalyzed *carbenoid generation / sulfonium ylide formation / [2,3]-sigmatropic shift* protocol consisted of stirring **13** with 3 mg of $Rh_2(OAc)_4$ in CH_2Cl_2 at 25 °C. The sole product isolated in 81% yield corresponded to tetrahydrothiophene **14**.[33]



13 **14**

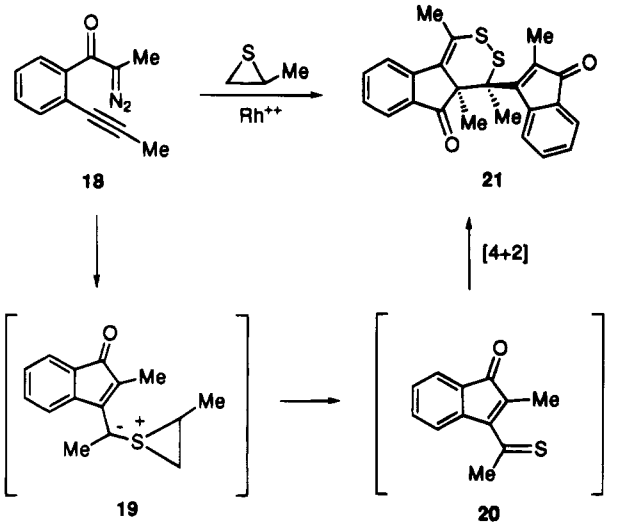
Since [1,2]-shifts of rhodium carbenoid derived cyclic sulfonium ylides are less frequently encountered than [2,3]-sigmatropic shifts,[33] we decided to investigate the Rh(II)-catalyzed behavior of the closely related ethylthio system **15**. The question of importance here was whether the initially formed sulfonium ylide would rearrange by means of a [1,2]-ethyl shift or possibly *via* a 1,2-ring contraction. Treatment of diazo ketone **15** with $Rh_2(OAc)_4$ at 25 °C afforded tetrahydrothiophene **17** in 83% isolated yield. The 1,2-Steven's like rearrangement of sulfonium ylides is generally thought to proceed *via* a radical pair intermediate. The isolation of **17** from ylide **16** is perfectly consistent with this rationale.



15 **16** **17**

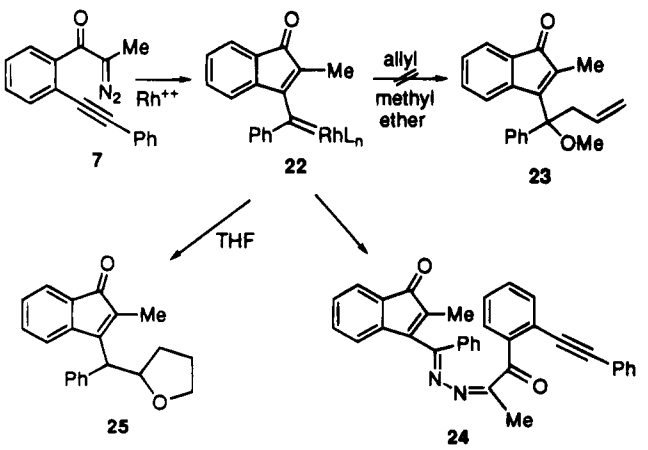
An additional tandem *carbenoid cyclization / sulfonium ylide-rearrangement* sequence which we examined involved the Rh(II)-catalyzed reaction of α-diazo ketone **18** in the presence of propylene sulfide. The only product formed corresponded to the novel cyclic sulfide dimer **21** which was isolated in 97% yield as a crystalline solid. The structure of **21** was assigned on the basis of a detailed NMR analysis and firmly established by an X-ray crystallographic study.[37] Our view of how this unusual product is formed is outlined in Scheme 3. Exposure of the starting α-diazo ketone **18** to the Rh(II) catalyst results in cyclization to the expected vinyl carbenoid. A further reaction with propylene sulfide furnishes ylide **19**, which fragments to thioketone **20**.

Scheme 3



This transformation is closely related to Hata's finding[38] that cyclopropyl sulfonium ylides readily undergo cleavage of both C–S bonds to produce alkenes in high yield. Thioketone **20** undergoes a spontaneous Diels–Alder cycloaddition across the C–S double bond of another molecule to give dimer **21**. It should be noted that simple α,β-unsaturated thioketones, formed from the corresponding ketones by thionation, readily dimerize at ambient temperature to give structures related to **21**.[39–41]

There have been several reports of cyclic oxonium ylide formation by intramolecular rhodium carbenoid addition to an ether oxygen followed by either a [1,2]- or [2,3]-shift.[42–47] However, all of our attempts to generate an oxonium ylide from the *tandem carbenoid cyclization / bimolecular ether lone pair addition* reaction failed. For example, heating a sample of diazo ketone **7** in the presence of a 5 mol excess of allyl methyl ether gave no signs of the product (*i.e.*, **23**) resulting from a [2,3]-sigmatropic rearrangement. Instead, the only compound isolated (75%) corresponded to dimer **24**. It would appear that the initially formed vinyl carbenoid **22** prefers to



7 **22** **23** **25** **24**

(36) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(37) The authors have deposited coordinates for structures **21** and **36** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(38) Hata, Y.; Watanabe, M.; Inoue, S.; Oae, S. *J. Am. Chem. Soc.* **1975**, *97*, 2553.

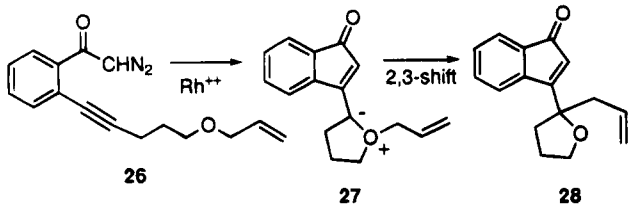
(39) Karakasa, T.; Satsumabayashi, S.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 335. Motoki, S.; Saito, T.; Karakasa, T.; Matsushita, T.; Furono, E. *J. Chem. Soc., Perkin Trans I* **1992**, 2943. Karakasa, T.; Moriyama, S.; Motoki, S. *Chem. Lett.* **1988**, 1029.

(40) Guemas, J. P.; Quiniou, H. *Sulfur Lett.* **1984**, *2*, 121.

(41) Ohno, M.; Sasaki, T. *Yuki Gosei Kagaku Kyokai Shi* **1984**, *42*, 125.

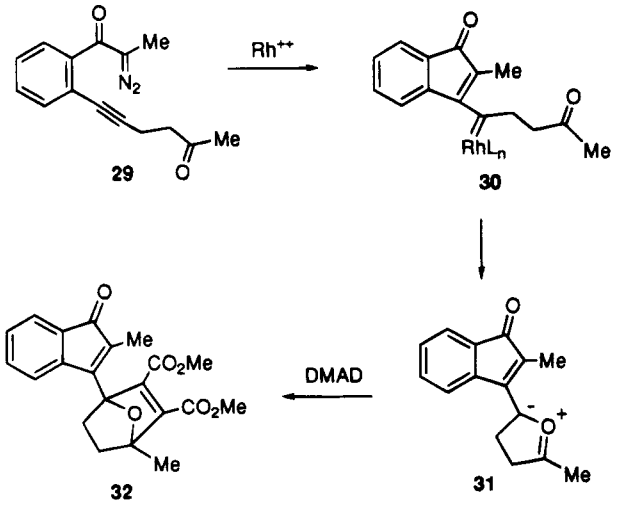
react with another molecule of starting material to give azine **24** rather than interact with the ether oxygen atom lone pair. This result contrasts with that obtained from the related sulfide system (*i.e.*, **8**) which cleanly undergoes *sulfur insertion–[2,3]-sigmatropic rearrangement*. This difference can be attributed to the more polarizable sulfur atom lone pair (soft base) which is more prone to attack the electrophilic carbenoid center. When the Rh-(II)-catalyzed reaction of **7** was carried out using THF as the solvent, the only product formed (73%) corresponded to indenone **25**. This is the consequence of insertion of carbenoid **22** into the activated α-CH bond of the cyclic ether.

In contrast to these results, we have found that the *intramolecular tandem generation/[2,3]-sigmatropic rearrangement* of an oxonium ylide occurs smoothly when diazo ketone **26** is used. The net result of this process corresponds to a formal insertion of the vinyl carbenoid into a C–O bond with concomitant generation of a cyclic ether. Thus, catalytic decomposition of the diazo keto allyl ether **26** in CH_2Cl_2 at 25 °C gave the rearrangement product **28** directly in 81% yield. Clearly, the availabliity of an intramolecular pathway for oxonium ylide formation with diazo ketone **26** accounts for its enhanced reactivity.

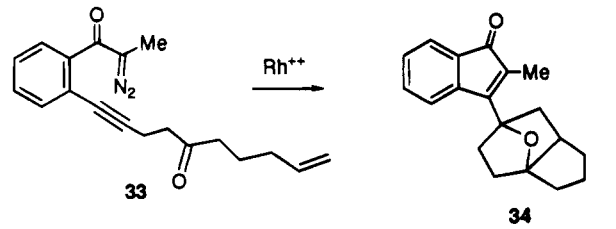


In earlier papers, we have reported on the rhodium-(II)-induced α-diazo ketone cyclization onto a neighboring carbonyl group followed by dipolar cycloaddition of the resulting carbonyl ylide dipole as a method for the formation of oxapolycyclic ring systems.[29] The ease with which α-diazo ketones containing tethered carbonyl groups undergo this tandem cyclization–cycloaddition reaction suggests that a similar sequence could also occur with a vinylogous keto carbenoid. In order to test this possibility, we studied the Rh(II)-catalyzed behavior of diazo ketone **29** which was prepared by treating methyl *o*-iodobenzoate with 5-hexyn-2-one ethylene ketal under typical Castro–Stephens arylation conditions.[36] Hydrolysis of the ketal and conversion of the resulting keto ester to diazo ketone **29** proceeded as required. Treatment of **29** with a catalytic amount of rhodium(II) octanoate at 25 °C in CH_2Cl_2 with 1 equiv of dimethyl acetylenedicarboxylate afforded cycloadduct **32** in 97% yield. This result can easily be accounted for in terms of the intermediacy of vinyl carbenoid **30** which cyclizes onto the oxygen atom of the neighboring carbonyl group to give the resonance-stabilized dipole **31**. Dipolar cycloaddition of **31** across the activated π-bond of DMAD affords cycloadduct **32**.

The above domino transformation can also be performed intramolecularly by attaching the trapping agent directly to the carbonyl group. Thus, diazo ketone **33** was



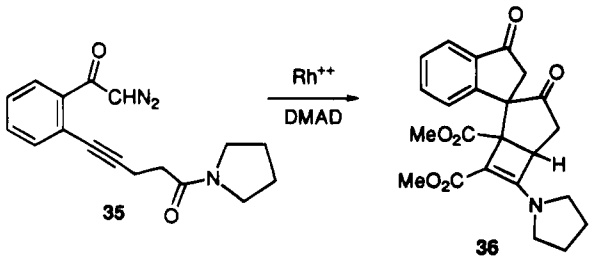
conveniently prepared from methyl 2-(5-hydroxy-1-pentynyl)benzoate, which in turn, was synthesized by the Castro–Stevens reaction[36] of 4-pentyn-1-ol with methyl *o*-iodobenzoate. The domino cyclization sequence proceeded in excellent yield, producing cycloadduct **34**.



In view of the observations described above, it was of interest to explore the effects of another carbonyl derivative on the tandem rhodium(II)-catalyzed cyclization–cycloaddition sequence. Most of the previously examined cases of intramolecular carbonyl ylide formation involved systems in which the remote carbonyl was a keto group.[29] A few cases using amides and esters to trap the rhodium carbenoid were studied,[48–50] but these investigations involved systems where the keto metallocarbenoid and the remote amido or ester functionalities were substituted ortho to each other on a benzene ring. To simultaneously test the electronic and geometric requirements of dipole formation using the tandem annulation approach, we examined the Rh(II)-catalyzed behavior of diazo keto amide **35**. Note that with this system, formation of the carbonyl ylide involves participation of the amido group. Moreover, the tether is a simple dimethylene chain, introducing a conformational "floppiness" not available in the previously studied benzo systems.

Incorporation of the amido carbonyl group on the side chain was found to dramatically alter the course of the tandem annulation reaction. Thus, treatment of diazo keto amide **35** with rhodium(II) octanoate in CH_2Cl_2 at 25 °C in the presence of DMAD gave the rearranged cycloadduct **36** as a 1:1 mixture of diastereomers which

(42) Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060.
(43) Johnson, C. R.; Roskamp, E. J. *J. Am. Chem. Soc.* **1986**, *108*, 6062.
(44) Padwa, A.; Hornbuckle, S. F.; Fryxell, G. E.; Stull, P. D. *J. Org. Chem.* **1989**, *54*, 817.
(45) Thijs, L.; Zwanenburg, B. *Tetrahedron* **1980**, *36*, 2145.
(46) Eberlein, T. H.; West, F. G.; Tester, R. W. *J. Org. Chem.* **1992**, *57*, 3479.
(47) Clark, J. S. *Tetrahedron Lett.* **1992**, *33*, 6193. Clark, J. S.; Krowiak, S. A.; Street, L. J. *Tetrahedron Lett.* **1993**, *34*, 4385.
(48) Padwa, A.; Stull, P. D. *Tetrahedron Lett.* **1987**, 5407.
(49) Taylor, K. G. *Tetrahedron* **1982**, *38*, 159.
(50) Ibata, T.; Toyoda, J.; Sawada, M.; Takai, Y.; Tanaka, T. *Tetrahedron Lett.* **1988**, 317.



could easily be separated and purified in 70% overall yield. The cyclization–cycloaddition reaction to produce **36** is quite remarkable in its facility and mildness of reaction conditions. The structural assignment of **36** is based upon the following characteristic spectral data: the correct molecular weight was obtained from the HRCI mass spectrum; the ^{13}C NMR spectrum indicates four carbonyl groups (163, 173, 202, and 213 ppm); the ^{1}H NMR shows the α-methylene protons adjacent to the phenyl ketone at δ 2.45 and 2.65 (J_{AB} = 17 Hz), the other set of methylene protons at δ 2.49 (d, 1H, J = 17 Hz) and 2.78 (dd, 1H, J = 17 and 10 Hz), a doublet for the methine proton at 3.72 (J = 10 Hz), singlets at 3.05 (3H) and 3.53 (3H) and multiplets centered at 1.95 (4H), 3.75 (2H), 3.95 (2H), and 7.2–7.8 (4H). Furthermore, the structure of **36** was verified by a single-crystal X-ray structure determination.

The mechanism of this unusual reaction has not been unequivocally established, but one reasonable possibility is outlined in Scheme 4. Here it is proposed that the cyclization–cycloaddition sequence produces dipole **38** in the normal manner which cycloadds with DMAD to give **39**. Cycloadduct **39** can then proceed to **36** *via* a series of reactions. The first step involves oxabicyclic ring opening which is driven by the lone pair of electrons on nitrogen, resulting in a Wagner-Meerwein rearrangement to give **40**. This zwitterionic species then undergoes a proton shift to produce **41,** which subsequently reacts *via* a 4π-electrocyclization to generate the final product.[51,52]

As part of our studies in this area, we became interested in determining whether an oximino π-bond would also undergo cyclization with the vinyl carbenoid intermediate to give an azomethine ylide dipole. Earlier work in our laboratory showed that certain diazo-substituted ketones react with imino π-systems to form azomethine ylides when treated with Rh(II)-carboxylates.[53] Toward this end, we examined the Rh(II) catalyzed behavior of diazo keto–oxime **42**. Construction of the requisite oxime was accomplished in 76% yield by treating the corresponding ketone **29** with *O*-methylhydroxylamine hydrochloride and separating the 5:3 mixture of *E*- and *Z*-oximino diazo ketones. In contrast to *N*-alkyl imines, *o*-alkyl-substituted oximes offer the advantage of being geometrically stable at room temperature so that the *E*- and *Z*-isomers can be separated.[54] Subjection of the

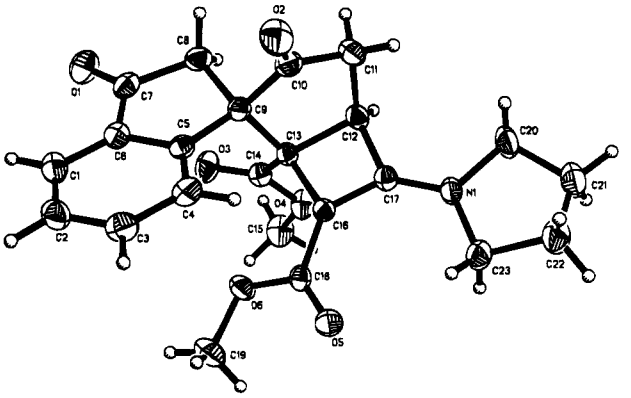
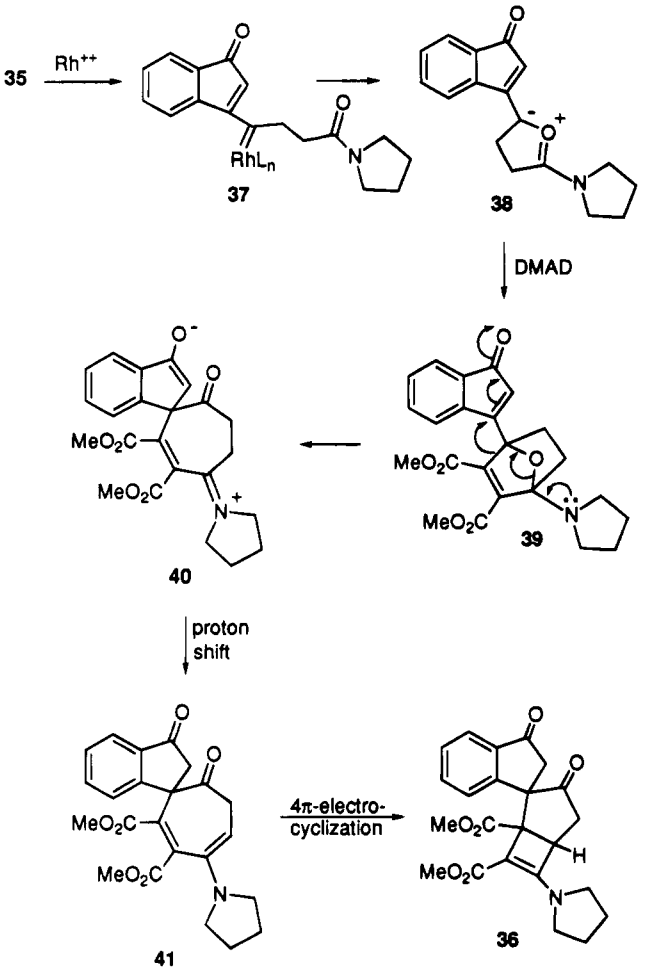


Figure 1. Ortep drawing of 2-(3-oxoindan-1-yl)-3-oxo-6-pyrrolidin-1-yl)bicyclo[3.2.0]hept-6-ene-1,7-dicarboxylic acid dimethyl ester (**36**).

Scheme 4



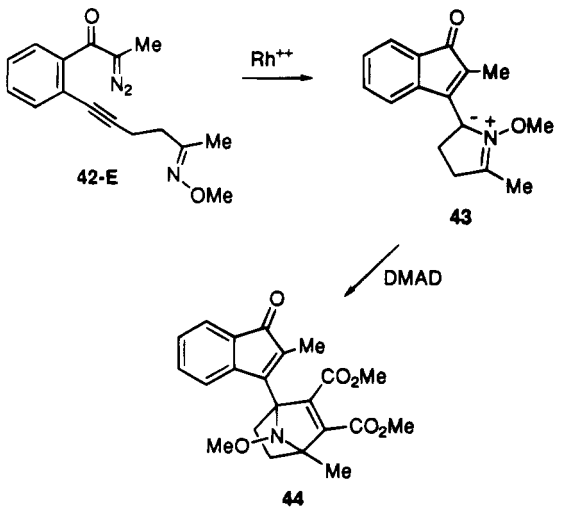
E-oximino isomer **42-E** to a catalytic quantity of $Rh_2(OAc)_4$ in CH_2Cl_2 at 25 °C in the presence of excess of DMAD afforded the bimolecular cycloadduct **44** in 95% yield. The formation of **44** is consistent with the involvement of an azomethine ylide dipole (*i.e.*, **43**) which undergoes bimolecular dipolar cycloaddition with DMAD. In sharp contrast to this result, no characterizable product(s) could be obtained when the isomeric *Z*-oximino diazo derivative **42-Z** was exposed to the same reaction conditions. The difference in behavior of these two systems clearly points out the necessity of having the oximino nitrogen lone pair properly oriented (*i.e.*, *E*-configuration) so as to be able to interact with the vinyl rhodium carbenoid.

(51) Conrotatory 4π-electrocyclization of a *cis,cis*-diene such as **41** should result in a *trans* 4-5 ring junction in **36**.[52] Since the X-ray structure analysis of **36** indicates a *cis* relationship between the H and CO_2Me groups, its formation must either proceed in a stepwise manner from **41** or, alternatively, **36** is formed directly from **40**. Further work is necessary to establish this point.

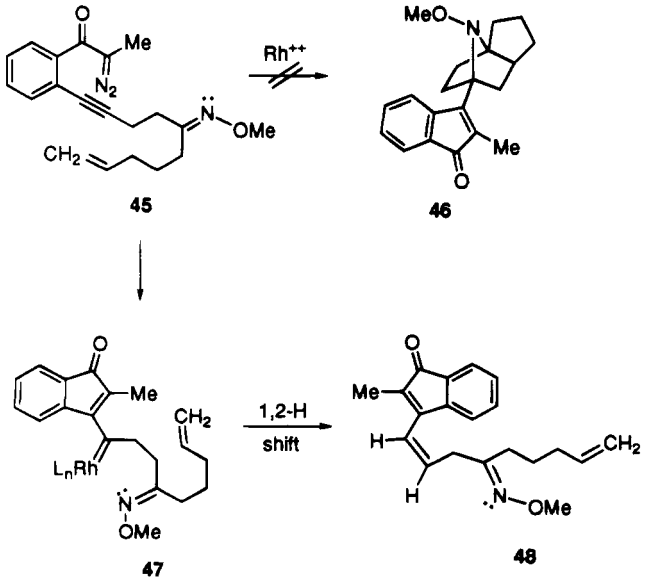
(52) Marrell, E. N. In *Thermal Electrocyclic Reactions;* Academic Press: 1980, New York.

(53) Padwa, A.; Dean, D. C. *J. Org. Chem.* **1990**, *55*, 405.

(54) Curtin, D. Y.; Grubbs, W. J.; McCarty, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 2775.



Intramolecular cyclizations of imino compounds have been of considerable synthetic and mechanistic interest,[55] and our long-standing involvement with the tandem intramolecular cycloaddition reaction of α-diazo carbonyl compounds[29] prompted us to examine the Rh(II)-catalyzed reaction of the *E*-oximino diazo ketone **45**. Treatment of this compound with DMAD in the presence of the Rh(II) catalyst, however, failed to give any sign of the desired cycloadduct **46**. Instead, the only product isolated (86%) corresponded to indenone **48** which is derived from vinyl carbenoid **47** by means of a [1,2]-hydrogen shift.[18,56] With this system, hydrogen migration is faster than interaction of the metallocarbenoid with the lone pair of the nitrogen atom. This result stands in contrast to the facile cyclization observed with the corresponding keto compound (*i.e.*, **33**). One explanation that might account for the difference in behavior between **33** and **45** is that the azomethine dipole is indeed formed from **47**, but the reaction is reversible if the bimolecular trapping is not very efficient.[57] Another possibility is that coordination of the softer oxygen with the rhodium carbenoid center to form the carbonyl ylide dipole is more likely to occur than interaction of the carbenoid with the harder nitrogen atom.[58]



In conclusion, a variety of substituted benzocyclopentenones can be efficiently synthesized by the rhodium-(II)-catalyzed reaction of α-diazo ketones bearing tethered alkyne units. The results obtained in all cases agree with a mechanism which involves addition of the rhodium-stabilized keto carbenoid onto the acetylenic π-bond to give a new rearranged vinyl carbenoid. Several tandem cyclization/onium ylide rearrangements or cycloadditions were studied and found to proceed in exceptionally high yield. The preparation of tricyclic ether **34** illustrates the high synthetic potential of the annulation sequence. The overall process leads to a large increase in molecular complexity in a single experimental operation. The simplicity and availability of the starting materials makes this annulation sequence a powerful method for cyclopentenone construction.

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 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 NEt_3 were added 25 mg of *trans*-bis(triphenylphosphine)palladium(II) chloride and 50 mg of cuprous iodide.[59] 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[60] 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 the mixture was cooled to 0 °C, 5.0 mmol of the 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.

Rhodium(II) Acetate Catalyzed Reaction of 2-Diazo-1-(2-(phenylethynyl)phenyl)propan-1-one (7) with Allyl Methyl Sulfide. A solution containing 100 mg (0.45 mmol) of diazo ketone **7**[18] and 176 mg (2.0 mmol) of allyl methyl sulfide in 20 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 20 min under N_2, and then the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 102 mg (86%) of 2-methyl-3-(1-

(55) Hiemstra, H.; Speckamp, W. N. In *Comprehensive Organic Synthesis;* Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp 1047–1082.

(56) We assume that **48** is formed mainly as the *Z*-isomer from the 1,2-hydrogen shift of **47** since similar findings have been reported with related systems.[18]

(57) We wish to thank one of the reviewers for suggesting this possibility.

(58) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

(59) Sabourin, T. E.; Onopchenko, A. *J. Org. Chem.* **1983**, *48*, 5135.

(60) Laganis, E. D.; Chenard, B. L. *Tetrahedron Lett.* **1984**, 5831.

(methylthio-1-phenylbut-3-enyl)inden-1-one (**8**): IR (neat) 1711, 1598, 1273, and 1190 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.91 (s, 3H), 1.99 (s, 3H), 2.80–2.98 (m, 2H), 4.97 (m, 2H), 5.64 (m, 1H), 7.10 (m, 2H), 7.24 (m, 2H), and 7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.9, 42.5, 55.3, 118.4, 121.7, 123.6, 124.3, 127.5, 127.7, 128.2, 128.4, 132.1, 132.2, 132.6, 139.4, 143.6, 164.7, and 197.4; HRMS calcd for $C_{21}H_{20}OS$ 320.1236, found 320.1234.

The minor product isolated from the column corresponded to a 1:1 *cis*/*trans* mixture of 2-allyl-2-methyl-3-((methylsulfonyl)phenylmethylene)indan-1-one (**9**) (10%): IR (neat) 2915, 1710, 1585, and 1195 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05 (s, 3H) (isomer A), 1.56 (s, 3H) (isomer B), 2.15 (s, 3H) (isomer A), 2.16 (s, 3H) (isomer B), 2.8–3.2 (m, 2H), 4.8–5.1 (m, 2H), 5.6–5.8 (m, 1H), and 7.12–7.60 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.0 (15.4), 22.0 (24.6), 39.8 (42.1), 54.3 (55.0), 117.1 (117.3), 121.3 (121.4), 123.4 (123.5), 126.8, 127.4, 128.4, 129.0, 129.4, 132.1, 133.9, 134.3, 136.0, 138.1, 140.5, and 208.1 (208.4); HRMS calcd for $C_{21}H_{20}OS$ 320.1234, found 320.1231.

Rhodium(II) Acetate Catalyzed Reaction of 2-Diazo-1-(2-phenylethynyl)phenyl)propan-1-one (7) with Allyl Sulfide. A solution containing 100 mg (0.5 mmol) of α-diazo ketone **7** and 168 mg (2.0 mmol) of allyl sulfide was treated with 2 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 20 min, and then the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 120 mg (87%) of 3-(1-(allylthio)-1-phenylbut-3-enyl)-2-methylinden-1-one (**10**) as the major product: IR (neat) 1713, 1436, 1235, 1136, and 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.15 (s, 3H), 3.05 (m, 3H), 3.33 (m, 1H), 4.93 (m, 1H), 5.00 (m, 2H), 5.69 (m, 2H), 6.53 (m, 1H), 6.95 (m, 2H), and 7.20–7.45 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.2, 32.7, 44.3, 59.4, 117.8, 118.4, 121.5,124.8, 126.8, 127.4, 128.3, 130.6, 131.2, 132.7, 133.0, 133.3, 141.0, 145.7, 154.5, and 198.6. Anal. Calcd for $C_{23}H_{22}OS$: C, 79.74; H, 6.40; S, 9.23. Found: C, 79.54; H, 6.43; S, 9.29.

The minor fraction isolated from the column contained 23 mg (11%) of a 1:1 *cis*/*trans* mixture of 2-allyl-3-((allylthio)-phenylmethylene)-2-methylindan-1-one (**11**): IR (neat) 1715, 1430, 1224, and 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 75 MHz) δ 1.56 (s, 3H) (isomer A), 1.84 (s, 3H) (isomer B), 2.6–3.4 (m, 4H), 4.8–5.2 (m, 2H), 5.4–5.6 (m, 1H), 7.0–7.5 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.2 (23.6), 35.0 (35.3), 40.2 (42.1), 54.5 (55.2), 117.1 (117.3), 123.4 (123.5), 124.8, 127.5 (127.7), 128.2 (128.5), 129.2 (129.3), 133.4, 133.9, 134.2 (134.6), 135.5, 136.1, 137.4 (137.6), 138.5, 148.7 (148.9), 154.4, 155.8, and 209.1 (209.6); HRMS calcd for $C_{23}H_{22}OS$ 346.1391, found 346.1395.

Preparation and Rhodium(II)-Catalyzed Reaction of 1-[2-(5-(Allylthio)pent-1-ynyl)-phenyl]-2-diazo-propan-1-one (13). To a solution containing 3.5 g (47.0 mmol) of allyl mercaptan in 35 mL of THF was added 45 mmol of *n*-butyllithium dropwise at −10 °C under N_2. The reaction mixture was stirred at −10 °C for 20 min, and then 6.15 g (45 mmol) of 5-iodo-1-pentyne was added dropwise. After stirring for 5 h at 25 °C, the reaction mixture was washed with a 10% solution of NH_4Cl and then extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated under reduced pressure to give 4.5 g (73%) of 5-(allylthio)-1-pentyne which was used in the next step without purification: IR (neat) 3340, 2950, 1420, and 1110 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.96 (m, 2H), 2.27 (m, 2H), 2.33 (m, 1H), 3.10 (m, 2H), 3.25 (t, 2H, J = 7.5 Hz), 5.10 (m, 2H), and 5.75 (m, 1H).

A mixture containing 4.5 g (32 mmol) of the above acetylene and 6.5 g (25 mmol) of methyl *o*-iodobenzoate was converted under typical Castro–Stephens[36] conditions into 4.85 g (72%) of 2-(5-(allylthio)pent-1-ynyl)benzoic acid methyl ester: IR (neat) 1727, 1433, 1288, and 1251 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.86 (m, 2H), 2.57 (t, 2H, J = 7.5 Hz), 2.65 (t, 2H, J = 7.5 Hz), 3.00 (m, 2H), 3.85 (s, 3H), 5.05 (m, 2H), 5.73 (m, 1H), 7.20–7.46 (m, 3H), and 7.70 (m, 1H).

A 1.0 g (3.6 mmol) sample of the above ester was converted in the normal manner into 0.43 g (41%) of 1-[2-(5-(allylthio)-pent-1-ynyl)phenyl]-2-diazopropan-1-one (**13**): IR (neat) 2071, 1616, 1344, and 990 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.86 (m, 2H), 2.14 (s, 3H), 2.57 (m, 2H), 2.64 (m, 2H), 3.15 (m, 2H), 5.12 (m, 2H), 5.80 (m, 1H), and 7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 18.5, 28.9, 29.5, 34.6, 65.2, 78.2, 93.1, 116.9, 120.9, 126.9, 127.9, 129.7, 132.5, 134.3, 140.5, and 198.3.

A solution containing 150 mg (0.5 mmol) of the above diazo ketone in 20 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 20 min, and then the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 110 mg (82%) of 3-(2-allyltetrahydrothiophene-2-yl)-2-methylinden-1-one (**14**): IR (neat) 1710, 1426, 1373, 1221, and 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H) 2.15 (m, 2H), 2.37 (m, 2H), 2.44 (m, 2H), 2.64 (m, 1H), 2.64 (m, 1H), 5.05 (m, 2H), 5.66 (m, 1H), 7.15 (m, 1H), and 7.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.5, 29.3, 32.2, 39.3, 45.8, 61.2, 118.5, 121.9, 122.6, 127.7, 131.0, 133.1, 133.7, 145.8, 157.5, and 198.7; HRMS calcd for $C_{17}H_{18}OS$ 270.1078, found 270.1077.

Preparation and Rhodium(II)-Catalyzed Reaction of 2-Diazo-1-[2-(5-ethylthio)pent-1-ynyl)phenyl]propan-1-one (15). To a solution containing 2.5 g (40.0 mmol) of ethanethiol in 35 mL of THF was added 36 mmol of *n*-butyllithium dropwise at −10 °C under N_2. The reaction mixture was stirred at −10 °C for 20 min, and then 5.0 g (35.5 mmol) of 5-iodo-1-pentyne was added dropwise. After stirring for 5 h at 25 °C, the reaction mixture was washed with a 10% solution of NH_4Cl and then extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated under reduced pressure to give 3.4 g (68%) of 5-(ethylthio)-1-pentyne, which was used in the next step without purification: IR (neat) 2950, 1426, 1280, and 1127 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, 3H, J = 7.2 Hz), 1.78 (m, 2H), 1.98 (m, 1H), 2.32 (m, 2H), 2.42 (q, 2H, J = 7.2 Hz), and 2.57 (t, 2H, J = 7.2 Hz).

A mixture containing 3.0 g (23.4 mmol) of the above acetylene and 5.2 g (20 mmol) of methyl *o*-iodobenzoate was converted under typical Castro–Stephens[36] arylation conditions into 4.5 g (87%) of 2-(5-(ethylthio)pent-1-ynyl)benzoic acid methyl ester: IR (neat) 2226, 1728, 1427, 1285, and 1247 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15 (t, 3H, J = 7.5 Hz), 1.79 (q, 2H, J = 7.0 Hz), 2.46 (q, 2H, J = 7.5 Hz), 2.50 (t, 2H, J = 7.0 Hz), 2.63 (t, 2H, J = 7.0 Hz), 3.80 (s, 3H), 7.10–7.41 (m, 3H), and 7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.7, 18.8, 25.7, 28.4, 30.4, 51.9, 79.8, 94.6, 124.1, 127.2, 130.0, 134.1, and 166.5.

A 1.5 g (5.7 mmol) sample of the above ester was converted in the normal fashion into 470 mg (41%) of 2-diazo-1-[2-(5-(ethylthio)pent-1-ynyl)phenyl]propan-1-one (**15**): IR (neat) 2073, 1613, 1435, and 1342 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.17 (t, 3H, J = 7.5 Hz), 1.76 (q, 2H, J = 7.0 Hz), 2.05 (s, 3H), 2.47 (m, 4H), 2.58 (t, 2H, J = 7.5 Hz), and 7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.6, 14.7, 18.5, 25.8, 28.3, 30.4, 65.2, 78.1, 93.1, 120.8, 126.9, 127.7, 129.7, 123.4, 140.8, and 198.2.

A solution containing 100 mg (0.5 mmol) of the above diazo ketone in 20 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The reaction mixture stirred at 25 °C for 20 min, and the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 73 mg (83%) of 3-(2-ethyltetrahydrothiophene-2-yl)-2-methylinden-1-one (**17**) whose structure was assigned on the basis of its spectral data: IR (neat) 3032, 2954, 1711, 1325, and 1056 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.80 (t, 3H, J = 7.5 Hz), 1.26 (m, 2H), 1.99 (s, 3H), 2.13 (m, 1H), 2.26 (m, 1H), 2.54 (m, 2H), 2.95 (m, 2H), and 7.20–7.55 (m, 4H); ^{13}C -NMR ($CDCl_3$, 75 MHz) δ 9.5, 10.8, 29.5, 32.0, 34.7, 39.0, 43.5, 62.7, 119.7, 122.7, 127.5,130.0, 131.1, 133.2, 145.9, 157.7, and 198.7; HRMS calcd for $C_{16}H_{18}OS$ 258.1078, found 258.1072.

Rhodium(II) Acetate Catalyzed Reaction of 2-Diazo-1-(2-prop-1-ynylphenyl)propan-1-one (18) with Propylene Sulfide. A solution containing 100 mg (0.5 mmol) of α-diazo ketone **18**[18] and 109 mg (1.5 mmol) of propylene sulfide in 20 mL of CH_2Cl_2 was treated with a catalytic amount of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 20 min, and the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 196 mg (97%) of 1,4,9a-trimethyl-1-(2-methyl-3-oxo-3*H*-inden-1-yl)-1,9a-dihydro-2,3-dithiafluoren-9-one (**21**) whose structure was assigned on the basis of its

spectral properties as well as an X-ray crystal structure analysis;[37] mp 161–162 °C; IR (KBr) 1715, 1710, 1590, and 1464 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.48 (s, 3H), 1.81 (s, 3H), 2.39 (s, 3H), 2.41 (s, 3H), 7.06–7.37 (m, 4H), and 7.51–7.70 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.5, 22.2, 22.6, 28.6, 56.6, 58.0, 121.8, 124.4, 125.4, 125.6, 126.9, 127.9, 130.6, 130.8, 132.7, 132.8, 133.8, 134.7, 137.1, 197.9, and 203.5. Anal. Calcd for $C_{24}H_{20}O_2S_2$: C, 71.27; H, 4.98; S, 15.85. Found: C, 71.15; H, 5.05; S, 15.79.

Dimerization Reaction of (*o*-(2-Phenylethynyl)benzoyl)diazoethane (7) with Rhodium(II) Acetate. A solution containing 100 mg (0.4 mmol) of α-diazo ketone **7** in 20 mL of anhydrous CH_2Cl_2 in the presence of 0.14 g (2.0 mmol) of allyl methyl ether was treated with a catalytic amount of rhodium(II) acetate dimer at 25 °C. The reaction mixture was stirred for 20 min at 25 °C, concentrated under reduced pressure, and subjected to silica gel chromatography. The major fraction contained 147 mg (75%) of 3-({[1-methyl-2-oxo-2-(2-(phenylethynyl)phenyl)ethylidene]hydrazono}-phenylmethyl)inden-1-one (**24**): mp 141–142 °C, IR (neat) 3064, 1713, 1684, 1182, and 935 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.39 (s, 3H), 2.30 (s, 3H), 6.45 (d, 1H, J = 6.9 Hz), 6.95–7.60 (m, 16 H), and 7.83 (d, 2H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 12.3, 87.6, 94.1, 120.8, 121.2, 122.7, 127.5, 133.7, 134.0, 134.4, 141.3, 143.9, 149.8, 155.5, 159.2, 195.7, and 197.6. Anal. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.90; H, 4.91; N, 5.69. Found: C, 82.81; H, 4.88; N, 5.47.

Rhodium(II) Acetate Catalyzed Reaction of 2-Diazo-1-(2-(phenylethynyl)phenyl)propan-1-one (7) with Tetrahydrofuran. A 100 mg (0.5 mmol) sample of α-diazo ketone **7** in 25 mL of anhydrous THF was treated with 3 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 30 min, and then the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 105 mg (73%) of 2-methyl-3-[phenyl(tetrahydrofuran-2-yl)methyl]inden-1-one (**25**). Major diasteromer: IR (neat) 2975, 1711, 1603, 1447, and 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.67 (m, 1H), 1.85 (m, 3H), 2.05 (s, 3H), 3.70–3.95 (m, 2H), 4.17 (m, 1H), 4.77 (m, 1H), 7.10 (m, 4H), and 7.13–7.45 (m 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.4, 25.5, 31.3, 50.5, 68.3, 79.1, 120.9, 122.0, 127.1, 127.7, 128.3, 128.7, 131.0, 133.0, 138.9, 145.8, 156.2, and 198.2; HRMS calcd for $C_{21}H_{20}O_2$ 304.1463, found 304.1459.

Preparation and Rhodium(II)-Catalyzed Reaction of 1-[2-(5-(Allyloxy)pent-1-ynyl)phenyl]-2-diazoethanone (26). To a solution containing 2.0 g (10 mmol) of 4-pentyn-1-ol in 35 mL of THF was added 0.95 g of NaH (60% dispersion). The mixture was stirred under N_2 for 30 min at 0 °C; then 3.67 g (1.2 equiv) of allyl bromide was added dropwise. Stirring was continued overnight at 25 °C, and the mixture was filtered, and the solvent was removed under reduced pressure. The crude residue was distilled at 45 °C (0.5 mm) to give 1.85 g (63%) of 5-(allyloxy)-1–pentyne: IR (neat) 2125, 1450, 1360, 1200, 1010, and 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.80 (q, 2H, J = 6.5 Hz), 1.91 (m, 2H), 2.26 (m, 2H), 3.49 (t, 2H, J = 6.5 Hz), 3.95 (d, 1H, J = 5.7 Hz), 5.12 (d, 1H, J = 10.5 Hz), 5.24 (d, 1H, J = 15.6 Hz), and 5.85 (ddt, 1H, J = 15.6, 10.5 and 5.7 Hz).

To a solution containing 1.2 g (4.6 mmol) of methyl 2-iodobenzoate in 25 mL of dry NEt_3 was added 0.7 g (6.0 mmol) of 5-(allyloxy)-1-pentyne. The solution was stirred at 80 °C under Ar for 20 min before addition of 0.05 g of dichloro bis(triphenylphosphine)palladium(II), 0.05 g of CuI, and 0.1 g of triphenylphosphine. The reaction mixture was heated at reflux for 6 h and was then cooled and filtered and the solvent was removed under pressure. The crude residue was chromatographed on a silica gel column. The major fraction isolated contained 1.0 g (84%) of methyl *o*-(5-(allyloxy)-1-pentynyl)benzoate: IR (neat) 2215, 1725, 1610, 1445, 1370, and 1090 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.87 (q, 2H, J = 6.9 Hz), 2.54 (t, 2H, J = 6.9 Hz), 3.57 (t, 2H, J = 6.9 Hz), 3.86 (s, 3H), 3.91 (d, 2H, J = 5.4 Hz), 5.12 (d, 1H, J = 10.7 Hz), 5.24 (d, 1H, J = 16.0 Hz), 5.87 (ddt, 1H, J = 16.0, 10.7 and 5.4 Hz), and 7.23–7.82 (m, 4H).

A 850 mg (6.5 mmol) sample of the above ester was added to a stirred solution containing 500 mg (3.80 mmol) of potassium trimethylsilanolate in 30 mL of ether at 25 °C under N_2. The reaction mixture was stirred for 3 h, and then 950 mg (10 mmol) of methyl chloroformate was added dropwise. The solution was stirred for an additional 2 h, and the solid that formed was collected by filtration. To the resulting solution was added 20 mmol of diazomethane, and the mixture was stirred for an additional 2 h at 25 °C. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a silica gel column to give 520 mg (60%) of 1-[2-(5-(allyloxy)pent-1-ynyl)phenyl]-2-diazoethanone (**26**): IR (neat) 1630, 1495, 1370, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.87 (q, 2H, J = 6.6 Hz), 2.55 (t, 2H, J = 6.9 Hz), 3.57 (t, 2H, J = 6.6 Hz), 3.95 (d, 2H, J = 5.4 Hz), 5.16 (d, 1H, J = 10.0 Hz), 5.28 (d, 1H, J = 16.2 Hz), 5.90 (ddt, 1H, J = 16.2, 10.0 and 5.4 Hz), 6.28 (s, 1H), and 7.24–7.67 (m, 4H).

A solution containing 200 mg of diazo ketone **26** in 15 mL of dry CH_2Cl_2 was treated with 5 mg of rhodium(II) mandelate. The reaction mixture was stirred at 25 °C for 30 min. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column. The major fraction isolated contained 145 mg (81%) of 3-[allyl(tetrahydrofuran-2-yl)methyl]inden-1-one (**28**): IR (neat) 1715, 1610, 1460, 1200, and 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.90–2.20 (m, 4H), 2.63 (m, 2H), 3.85 (m, 1H), 3.95 (m, 1H), 5.05 (m, 2H), 5.35 (m, 1H), 5.75 (s, 1H), and 7.10–7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.2, 34.0, 42.6, 67.4, 83.9, 117.9, 121.6, 121.7, 128.3, 131.9, 132.3, 132.4, 132.6, 142.5, 168.8 and 196.7; HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1148.

Preparation and Reaction of 2-(5-Oxo-1-hexynyl)-2-diazopropanone (29) with Rhodium(II) Acetate in the Presence of Dimethyl Acetylenedicarboxylate. A mixture containing 19.0 g (72.0 mmol) of methyl 2-iodobenzoate and 10.75 g (76.5 mmol) of 5-hexyn-2-one ethylene ketal[18] in 150 mL of anhydrous NEt_3 was allowed to react under typical Castro–Stephens coupling conditions to give 16.2 g (83%) of methyl 2-[5-(2-methyl-1,3-dioxan-2-yl)-1-butynyl]benzoate: IR (neat) 2950, 1730, 1715, 1431, and 1010 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.36 (s, 3H), 2.02 (t, 2H, J = 9.0 Hz), 2.65 (t, 2H, J = 9.0 Hz), and 3.96 (s, 3H).

A mixture containing 16.2 g (62.2 mmol) of the above ketal, 5.0 g (15.5 mmol) of pyridinium *p*-toluenesulfonic acid, 30 mL of water, and 500 mL of acetone was heated at reflux for 30 h. The mixture was cooled, and the solvent was removed under reduced pressure. The resulting residue was extracted with ether, and the ether layer was washed with a 10% $NaHCO_3$ solution followed by water and then dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by distillation of the residue (160 °C (0.5 mm)) gave 12.4 g (91%) of methyl 2-(5-oxo-1-hexynyl)benzoate: IR (neat) 2240, 1730, 1710, 1500, and 1100 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 2.21 (s, 3H), 2.54–2.90 (m, 4H), 3.95 (s, 3H), 7.20–7.60 (m, 3H), and 7.86–7.98 (m, 1H).

A mixture containing 2.30 g (9.2 mmol) of the above ester was converted into 1.6 g (45%) of 2-(5-oxo-1-hexynyl)-2-diazopropanone (**29**) in the standard fashion: IR (neat) 2234, 2074, 1723, 1615, and 1443 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.91 (s, 3H), 1.96 (s, 3H), 2.40–2.50 (m, 4H), and 7.10–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 29.5, 41.7, 60.0, 65.2, 77.5, 92.4, 120.4, 126.8, 127.8, 129.5, 129.7, 132.3, 199.5, and 205.8.

A solution containing 100 mg (3.8 mmol) of diazo ketone **29** and 500 mg (10.0 mmol) of dimethyl acetylenedicarboxylate in 20 mL of anhydrous CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 15 min, and the solvent was removed under reduced pressure. The crude residue was chromatographed on silica gel to give 137 mg (97%) of 1-methyl-4-(2-methyl-3-oxo-3*H*-inden-1-yl)-7-oxabicyclo[2.2.1]hept-2-ene-2,3 dicarboxylic acid dimethyl ester (**32**): IR (KBr) 1734, 1710, 1609, 1458, and 1084 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.75 (s, 3H), 1.70–1.85 (m, 2H), 1.94 (s, 3H), 2.17 (m, 1H), 2.39 (m, 1H), 3.57 (s, 3H), 3.77 (s, 3H), 7.05 (m, 1H), 7.27 (m, 2H), and 7.39 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.8, 17.4, 32.3, 32.5, 52.1, 52.2, 87.3, 88.3, 122.2, 122.8, 127.6, 130.0, 133.3, 133.7, 144.2, 144.7, 144.8, 148.6, 162.1, 162.9, and 192.7; HRMS calcd for $C_{21}H_{20}O_6$ 368.1259, found 368.1255.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 1-[2-(2-Diazopropionyl)phenyl]dec-9-en-1-yn-5-one (33). A mixture containing 10.0 g (38.2 mmol) of methyl *o*-iodobenzoate and 3.4 g (41 mmol) of 4-pentyn-1-ol was converted under typical Castro–Stephens[36] conditions into 7.6 g (92%) of methyl 2-(5-hydroxy-1-pentynyl)benzoate: IR (neat) 1710, 1230, and 1115 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.80 (m, 2H), 2.50 (t, 2H, J = 7.5 Hz,), 2.20 (s, 3H), 3.82 (t, 2H, J = 7.5 Hz), 3.85 (s, 3H), and 7.20–7.50 (m, 4H).

To a solution containing 4.0 g (18.3 mmol) of the above alcohol in 50 mL of CH_2Cl_2 was added 6.0 g (27.0 mmol) of pyridinium chlorochromate. The reaction mixture was stirred at 25 °C overnight under N_2, filtered over silica gel, and concentrated under reduced pressure. The crude residue was chromatographed on a silica gel column to give 3.8 g (72%) of methyl-2-(-5-oxo-1-pentynyl)benzoate: IR (neat) 2234, 1723, 1438, and 1289 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.64 (m, 4H), 3.74 (s, 3H), 7.14–7.35 (m, 3H), 7.75 (m, 1H), and 9.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.8, 42.1, 51.8, 79.8, 93.1, 123.6, 127.3, 129.9, 131.3, 131.6, 133.8, 166.3, and 200.3.

An ether solution containing 19 mmol of (pent-4-enyl)-magnesium bromide prepared from 2.98 g (20 mmol) of 5-bromo-1-pentene and 0.72 g (30 mmol) of magnesium was added to 3.5 g (16.0 mmol) of the above aldehyde at −78 °C. The reaction mixture was stirred at 25 °C for 5 h under N_2 and then washed with a 10% solution of NH_4Cl. The resulting mixture was extracted with ether, and the ether layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was chromatographed on a silica gel column to give 1.8 g (40%) of methyl 2-(5-hydroxydec-9-en-1-ynyl)-benzoate: IR (neat) 1734, 1566, and 1485 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30–1.65 (m, 5H), 1.94 (m, 2H), 2.53 (m, 2H), 2.66 (m, 2H), 2.90 (s, 1H), 3.77 (s, 3H), 4.90 (m, 2H), 5.68 (m, 1H), 7.15–7.40 (m, 3H), and 7.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.2, 24.8, 33.5, 36.6, 51.9, 70.1, 79.5, 95.4, 114.3, 124.2, 127.0, 129.9, 131.4, 133.9, 138.5, 166.5, and 200.4.

To a solution containing 1.8 g (6.0 mmol) of the above alcohol in 30 mL of CH_2Cl_2 was added 1.7 g (7.8 mmol) of pyridinium chlorochromate. The reaction mixture was stirred at 25 °C for 3 h under N_2 and then filtered over Celite. The solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel to give 1.2 g (71%) of 2-(5-oxodec-9-en-1-ynyl)benzoic acid methyl ester: IR (neat) 2230, 1723, 1450, and 1380 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.64 (q, 2H, J = 7.5 Hz), 2.05 (q, 2H, J = 6.9 Hz), 2.43 (t, 2H, J = 7.5 Hz), 2.50 (m, 4H), 3.85 (s, 3H), 4.95 (m, 2H), 5.72 (m, 1H), 7.20–7.45 (m, 3H), and 7.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 22.4, 32.8, 41.1, 41.5, 51.7, 79.3, 94.0, 114.9, 123.9, 127.1, 129.9, 131.3, 131.6, 137.7, 166.3, and 208.1.

A 1.0 g (3.0 mmol) sample of the above ester was converted in the normal fashion into 0.35 g (41%) of 1-[2-(2-diazopropionyl)phenyl]dec-9-en-1-yn-5-one (**33**): IR (neat) 2080, 1717, 1611, and 1348 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 2H), 1.96 (m, 2H), 2.08 (s, 3H), 2.36 (m, 2H), 2.50 (m, 2H), 4.85 (m, 2H), 5.60 (m, 1H), and 7.24 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 22.9. 32.8, 41.1, 41.6, 65.3, 77.6, 91.4, 115.1, 120.6, 126.8, 127.8, 129.6, 132.4, 137.6, 196.2, and 208.0.

A solution containing 100 mg (0.3 mmol) of diazo ketone **33** in 20 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 15 min, and the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 81 mg (97%) of 2-methyl-3-(10-oxatricyclo[5.2.1.$0^{1,5}$]dec-7-yl)inden-1-one (**34**): IR (neat) 1709, 1610, 1298, and 1010 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.70–1.82 (m, 2H), 1.92 (s, 3H), 2.12–2.25 (m, 3H), 2.30–2.46 (m, 4H), 7.35 (m, 3H), and 7.80 (m,1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 26.5, 29.8, 32.0, 33.5, 35.7, 45.2, 48.0, 86.6, 95.9, 121.9, 122.6, 127.5, 129.3, 130.9, 133.4, 144.7, 155.6, and 198.4; HRMS calcd for $C_{19}H_{20}O_2$ 280.1463, found 280.1465.

Preparation and Rhodium(II) Octanoate Reaction of 5-[2-(2-Diazoacetyl)phenyl]-1-pyrrolidin-1-yl]pent-4-yn-1-one (35). A mixture containing 6.40 g (39 mmol) of 1,1′-carbonyldiimidazole and 3.00 g (31 mmol) of 4-pentynoic acid in 150 mL of THF was allowed to react at 25 °C for 4 h. To this solution was added 4.27 g (60.0 mmol) of pyrrolidine. After the mixture was stirred for 8 h at 25 °C, the solvent was removed under reduced pressure. The resulting residue was extracted with ether, and the ether layer was washed with a 10% $NaHCO_3$ solution followed by water and then dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded 4.5 g (97%) of 1-pyrrolidin-1-ylpent-4-yn-1-one: IR (KBr) 3220, 2963, 1635, and 1442 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.91 (m, 5H), 2.41 (m, 4H) and 3.43 (ddd, 4H, J = 13.3, 6.8, and 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 24.3, 26.0, 33.6, 45.6, 46.5, 68.5, 83.7 and 169.3.

A mixture containing 6.94 g (26.5 mmol) of methyl 2-iodobenzoate and 4.0 g (26.5 mmol) of the above amide in 100 mL of anhydrous NEt_3 was allowed to react under typical Castro–Stephens coupling conditions to give 0.947 g (13%) of 2-(5-oxo-5-pyrrolidin-1-ylpent-1-ynyl)benzoic acid methyl ester: IR (neat) 2952, 2227, 1734, and 1645 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71–1.89 (m, 4H), 2.53 (t, 2H, J = 7.5 Hz), 2.75 (t, 2H, J = 7.5 Hz), 3.35–3.41 (m, 4H), 3.81 (s, 3H), 7.22 (t, 1H, J = 7.5 Hz), 7.33 (t, 1H, J = 7.4 Hz), 7.41 (d, 1H, J = 7.4 Hz), 7.79 (d, 1H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 24.0, 25.7, 33.4, 45.3, 46.2, 51.7, 79.1, 94.4, 123.8, 127.0, 129.8, 131.2, 131.6, 133.8, 166.4, and 169.2.

A mixture containing 1.96 g (6.9 mmol) of the above benzoate was converted into 1.2 g (60%) of 5-[2-(2-diazoacetyl)-phenyl]-1-pyrrolidin-1-yl]pent-4-yn-1-one (**35**) in the standard fashion: IR (neat) 2227, 2103, 1734, and 1642 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.81–1.96 (m, 4H), 2.59 (m, 2H), 2.81 (m, 2H), 3.44 (m, 4H), 6.52 (s 1H), 7.35 (m, 2H), 7.47 (d, 1H, J = 7.4 Hz), and 7.85 (d, 1H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3, 24.3, 25.9, 33.6, 45.6, 46.5, 51.9, 79.3, 94.6, 121.1, 127.2, 127.8, 130.0, 131.4, 134.1, 166.7, and 169.5.

A solution containing 200 mg (0.68 mmol) of the above α-diazo keto amide **35** and 480 mg (3.4 mmol) of dimethyl acetylenedicarboxylate in 50 mL of CH_2Cl_2 was treated with 3 mg of rhodium(II) octanoate. The reaction mixture was stirred at 25 °C for 8 h, and the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 2-(3-oxoindan-1-yl)-3-oxo-6-pyrrolidin-1-yl)bicyclo[3.2.0]hept-6-ene-1,7-dicarboxylic acid dimethyl ester (**36**) as a 1:1 mixture of diastereomers in 70% yield. The two diasteromers were separated by fractional recrystallization. Diastereomer A: mp 228–231 °C; IR (KBr) 1715, 1690, 1611, and 1109 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (m, 4H), 2.48 (d, 1H, J = 18.5), 2.99 (d, 1H, J = 18.5 Hz), 3.12 (dd, 1H, J = 18.5 and J = 10 Hz), 3.31 (s, 3H), 3.45 (m, 2H), 3.51 (s, 3H), 3.68 (d, 1H, J = 18.5 Hz), 3.83 (m, 2H), 3.98 (d, 1H, J = 10 Hz), and 7.2–7.8 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.9, 25.6, 36.8, 41.3, 42.2, 48.3, 50.2, 50.3, 51.7, 57.4, 62.2, 91.0, 122.8, 124.5, 128.6, 134.5, 136.3, 153.0, 157.1, 162.9, 172.8, 204.6, 210.2; HRMS calcd for $C_{23}H_{23}NO_6$ 409.1525, found: 409.1525.

Diastereomer B: mp 187–188 °C; IR (neat) 2923, 1731, 1688, and 1132 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (m, 4H), 2.45 (d, 1H, J = 17 Hz), 2.49 (d, 1H, J = 17 Hz), 2.65 (d, 1H, J = 17 Hz), 2.78 (dd, 1H, J = 17 and J = 10 Hz), 3.05 (s, 3H), 3.53 (s, 3H), 3.72 (d, 1H, J = 10 Hz), 3.75 (m, 2H), 3.95 (m, 2H), and 7.2–7.8 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.0, 25.5, 37.4, 41.3, 42.2, 47.4, 49.6, 50.1, 51.6, 57.8, 60.0, 91.8, 123.1, 127.7, 128.3, 133.1, 138.3, 152.0, 156.3, 163.0, 172.7, 201.7, 212.5; HRMS calcd for $C_{23}H_{23}NO_6$ 409.1525, found 409.1525. The structure of diastereomer B was unequivocally established by a single-crystal X-ray structure determination.[37]

Preparation and Rhodium(II) Acetate Catalyzed Reaction of 6-[2-(2-Diazopropionyl)phenyl]hex-5-yn-2-one *O*-Methyloxime (42). A solution containing 3.0 g (13.0 mmol) of methyl 2-(5-oxo-1-hexynyl)benzoate and 1.3 g (15.5 mmol) of methoxylamine hydrochloride in 30 mL of pyridine was stirred for 5 h at 25 °C under N_2. The solvent was removed under reduced pressure, and the residue was washed with water and then extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was chromatographed on silica gel to give 1.5 g (46%) of (*E*)-methyl 2-(5-(*O*-methylhydroxyimino)-1-hexynyl)benzoate and 0.75 g (30%) of (*Z*)-methyl 2-(5-*O*-methylhydroxyimino-1-hexynyl)benzoate. (*E*)-Isomer: IR (neat) 2228, 1730, 1436, and 1055 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz)

δ 1.85 (s, 3H), 2.45 (t, 2H, J = 7.3 Hz), 2.66 (t, 2H, J = 7.3 Hz), 3.80 (s, 3H), 3.88 (s, 3H), 7.10–7.40 (m, 3H), and 7.67 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 17.1, 34.7, 51.8, 61.0, 94.2, 124.0, 127.2, 129.9, 131.3, 134.0, 155.3, and 166.4. (*Z*)-Isomer: IR (neat) 2943, 2225, 1730, and 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (s, 3H), 2.57 (m, 4H), 3.72 (s, 3H), 3.80 (s, 3H), 7.10–7.45 (m, 3H), and 7.67 (m, 1H).

A 700 mg (0.35 mmol) sample of the above (*E*)-oxime ether was converted into 325 mg (40%) of diazo ketone **42** in the normal fashion: IR (neat) 2078, 1611, 1443, 1348, and 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.85 (s, 3H), 2.05 (brs, 3H), 2.38, (t, 2H, J = 7.8 Hz), 2.57 (t, 2H, J = 7.8 Hz), 3.75 (s, 3H), 7.25 (m, 3H), and 7.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.5, 13.9, 16.8, 34.7, 61.1, 78.1, 92.6, 120.7, 126.9, 127.9, 129.6, 132.5, 155.2, and 198.2.

A solution containing 100 mg (0.4 mmol) of diazo keto oxime **42-E** and 300 mg (1.6 mmol) of dimethyl acetylenedicarboxylate in 20 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 30 min, and the solvent was removed under reduced pressure. The crude residue was chromatographed on a silica gel column to give 109 mg (95%) of 7-methoxy-1-methyl-4-(2-methyl-3-oxo-3*H*-inden-1-yl)-7-azabicyclo[2.2.1]hept-2-ene-2,3 dicarboxylic acid dimethyl ester (**44**): IR (neat) 1730, 1713, 1433, 1261, and 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (s, 3H) 1.50–1.59 (m, 1H), 1.99 (s, 3H), 1.89–2.05 (m, 2H), 2.73 (m, 1H), 3.29 (s, 3H), 3.81 (s, 3H), 7.05–7.45 (m, 3H), and 7.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.9, 14.5, 28.7, 30.3, 52.0, 62.2, 74.3, 74.6, 77.6, 121.8, 123.7, 127.3, 130.0, 133.4, 134.6, 138.8, 144.4, 146.3, 149.6, 162.2, 163.7, and 198.4; HRMS calcd for $C_{22}H_{23}NO_6$ 397.1526 found 397.1527.

A 100 mg (0.35 mmol) sample of the (*Z*)-oxime ether was converted in the normal fashion into 325 mg (40%) of the *Z*-diazo keto oxime **42-Z**: IR (neat) 2075, 1615, 1348, and 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.83 (s, 3H), 2.00 (bs, 3H), 2.47 (m, 4H), 3.75 (s, 3H), 7.21 (m, 3H), and 7.43 (m, 1H). A solution containing 50 mg (0.2 mmol) of this diazo ketone and 150 mg (0.8 mmol) of dimethyl acetylenedicarboxylate in 20 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 30 min, and the solvent was removed under reduced pressure. The crude residue contained many products, and all attempts at separation and characterization failed to give any homogeneous material.

Preparation and Rhodium(II) Acetate Catalyzed Reaction of (*E*)-1-[2-(2-Diazopropionyl)phenyl]dec-9-en-1-yn-5-one O-Methyloxime (45). A solution containing 2.0 g (7.0 mmol) of 2-(5-oxodec-9-en-1-ynyl)-benzoic acid methyl ester and 0.9 g (10.0 mmol) of methoxylamine hydrochloride in 30 mL of pyridine was stirred for 5 h at 25 °C under N_2. The solvent was removed under reduced pressure, and the residue was washed with water and then extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was chromatographed on silica gel to give 1.0 g (65%) of (*E*)-methyl 2-(5-(methoxyiximo)dec-9-en-1-ynyl)benzoate as well as 123 mg (8%) of the (*Z*)-isomer. (*E*)-Isomer: IR (neat) 2228, 1728, 1434, 1249, and 1049 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 2H), 1.92 (m, 2H), 2.17–2.25 (m, 2H), 2.43 (t, 2H, J = 7.0 Hz), 2.51 (t, 2H, J = 7.0 Hz), 2.60 (m, 2H), 3.73 (s, 3H), 3.80 (s, 3H), 4.88 (m, 2H), 5.72 (m, 1H), 7.20–7.45 (m, 3H), and 7.81 (m, 1H). (*Z*)-Isomer: IR (neat) 2222, 1720, 1463, 1249, and 1076 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 2H), 1.92 (m, 2H), 2.17–2.25 (m, 2H), 2.52 (m,4H), 2.61 (m, 2H), 3.70 (s, 3H), 3.78 (s, 3H), 4.73 (m, 2H), 5.71 (m, 1H), 7.15–7.48 (m, 3H), and 7.83 (m, 1H).

A 1.0 g (3.1 mmol) sample of the (*E*)-isomer of the above ester was converted into 417 mg (40%) of α-diazo keto oxime **45** in the normal manner: IR (neat) 2078, 1615, 1346, and 1053 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55 (m, 2H), 2.05 (s, 3H), 2.12 (m, 2H), 2.25 (m, 2H), 2.36 (t, 2H, J = 7.0 Hz), 2.45 (t, 2H, J = 7.0 Hz), 3.71 (s, 3H), 4.98 (m, 2H), 5.40 (m, 1H), and 7.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.0, 24.9, 27.2, 33.0, 33.7, 61.0, 65.1, 77.9, 92.8, 114,9, 120.7, 126.8, 127.9, 129.6, 132.4, 137.1, 158.5, and 198.2.

A solution containing 100 mg (0.29 mmol) of **45** in 20 mL of CH_2Cl_2 was treated with 5 mg of rhodium(II) acetate. The reaction mixture was stirred at 25 °C for 15 min, and the solvent was removed under reduced pressure. The crude residue was chromatographed on silica gel to give 62 mg (86%) of (*Z*)-3-(5-(methoxyimino)-deca-1,9-dienyl)-2-methylinden-1-one (**48**): IR (neat) 1710, 1634, 1456, and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (m, 2H), 1.92 (s, 3H), 2.05, (m, 2H), 2.49 (m, 2H), 3.30 (m, 2H), 3.80 (s, 3H), 4.92 (m, 2H), 5.79 (m, 1H), 6.52 (m, 2H), and 7.10–7.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.3, 33.1, 33.4, 33.6, 61.3, 115.1, 120.0, 122.1, 124.1, 127.9, 130.8, 131.0, 132.9, 133.6, 134.9, 137.8, 149.7, 156.7, and 197.6; HRMS calcd for $C_{20}H_{23}NO_2$ 309.1721, found 309.1719.

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra (75 MHz) for new compounds lacking analyses (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.