JOC Article

Synthesis of Furo[3,4-*c*]furans Using a Rhodium(II)-Catalyzed Cyclization/Diels−Alder Cycloaddition Sequence

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A series of 2-alkynyl 2-diazo-3-oxobutanoates, when treated with a catalytic quantity of rhodium(II) acetate, afforded furo[3,4-*c*]furans in good yield. The reaction proceeds by addition of a rhodium-stablilized carbenoid onto the acetylenic π-bond to give a vinyl carbenoid that subsequently cyclizes onto the neighboring carbonyl group to produce the furan ring. These furo[3,4-*c*]furans react with various dienophiles, furnishing anisole derivatives derived by loss of water from the initially formed Diels−Alder cycloadducts. The Rh(II)-catalyzed cyclization reaction was quite versatile with regard to the nature of the interacting carbonyl group. The methodology was applied to the synthesis of several oxa-polyheterocyclic systems by first generating a 2-alkoxy-substituted furan and then allowing it to undergo a subsequent intramolecular Diels−Alder cycloaddition. Ring opening of the resulting cycloadduct is followed by deprotonation to furnish a rearranged keto lactone. The potential use of this method for the synthesis of the alkaloid strychnine was probed using suitable model diazo compounds. To establish the viability of this approach, the Rh(II)-catalyzed cyclization/cycloaddition sequence of α-diazo amides **64** and **68** were studied. Both compounds underwent the sequential process in good overall yield, leading to novel pentacyclic products. The structural features of the resultant products present numerous opportunities for postcycloaddition manipulations that could be exploited to synthetic advantage.

The chemistry of transition metal carbene complexes has been the subject of intense activity over the past 2 decades.[1−20] Current interest in this area stems from the role of metal carbenes in alkene metathesis,[21] in alkene and alkyne polymerization,[22] in cyclopropanation chemistry,[23] and as intermediates in an impressive array of synthetic methodologies.[24,25] Many transition metal carbene complexes react readily with alkynes to form vinyl carbene complexes.[1−4] The product distribution has been found to vary considerably depending on the metal employed and the nature of the functionality present on the enyne substrate. Of special interest is the intramolecular reaction of carbene complexes with alkynes, which has inspired many variations.[20] Earlier work by our group showed that the rhodium(II)-catalyzed reaction of α-diazo ketones bearing tethered alkyne units represents a powerful method for the construction of a variety of polycyclic skeletons.[26] Exposure of the starting α-diazo ketone to a rhodium(II) catalyst results in cyclization of

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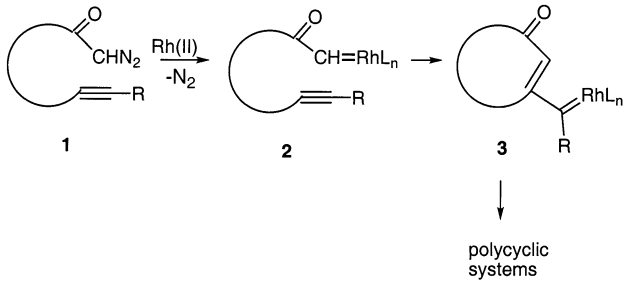
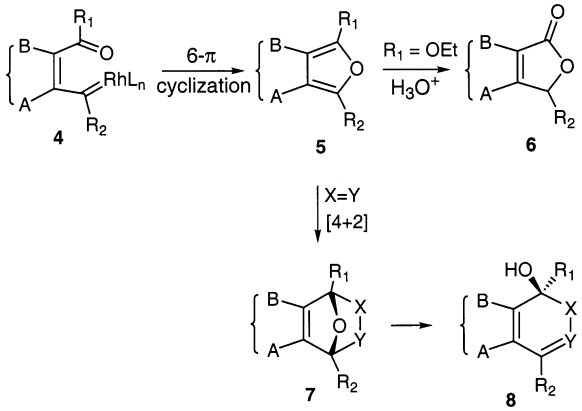
SCHEME 1



SCHEME 2



the α-keto carbenoid to an intermediate in which carbene-like reactivity has been transferred to one of the original alkyne carbon atoms. A neighboring functional group present on the backbone then traps the cyclized intermediate **3** via known carbenoid chemistry to give various products (Scheme 1).[27]

During the course of our studies in this area, we reported on a novel construction of bicyclic furans by coupling a metal carbenoid cyclization onto a tethered alkyne with an electrocyclization reaction (Scheme 2).[28] Transformations of this type are of considerable synthetic utility, since the vast majority of furano-sesquiterpenes are functionalized at the C_3 and C_4 position of the furan ring.[29,30] Use of an ester group (R_1=OEt) also allows for transformation of **5** to the corresponding butenolide system **6**. Formation of five-membered rings by 6π-electrocyclization is a well-precedented process in heterocyclic chemistry.[31−35] Several different synthetic approaches to alkenone carbenes have been developed over the years, producing intermediates that display common trends in their reactivity.[36−42] The utility of this transition metal catalyzed cyclization approach to ring construction would be significantly expanded if the resulting bicyclic furan was to undergo a subsequent [4 + 2]-cycloaddition, since a cyclohexane annulation would then result. Since synthetic methods that combine transformations of different reaction types are extremely useful for organic synthesis, we decided to extend our earlier studies toward more complex ring systems. In this paper, we detail our recent observations dealing with the cyclization/cycloaddition sequence of bicyclic furans derived from the Rh(II)-catalyzed reaction of α-diazo carbonyls tethered to alkynyl groups as a method for the synthesis of polycyclic ring systems.

Results and Discussion

Preparation of the propargyl diazo malonic ester system was straightforward and high-yielding. Silyl propargyl alcohol was acylated with Meldrum's acid and then allowed to react with DCC in the presence of an appropriately substituted alcohol to give the alkynyl ester derivative. Diazo transfer was readily accomplished using *p*-nitrobenzenesulfonyl azide and triethylamine.[43] 2-Diazo malonic ester **9** was efficiently converted to furan **10** in high yield (95%) by treatment with a catalytic amount of rhodium(II) acetate in benzene at 80 °C (Scheme 3). Interestingly, the simpler propargyl ester **11**, which possesses a terminal hydrogen, underwent the cyclization reaction in low yield (19%), producing **12** along with other unidentifiable products. We suspect that some of these products may be formed via a 6-endo cyclization pathway, as had been previously encountered with related keto carbenoids derived from terminal alkynes.[26,27] Exposure of the methoxy silyl substituted furan **10** to TBAF in THF cleanly furnished the desilylated furan **12** in 94% yield. Related cyclizations occurred with both the carbomethoxy and bromo-substituted alkynes **13** and **15**, producing furans **14** and **16** in 73% and 90% yield, respectively. Attempts to induce a [4 + 2]-cycloaddition of the silylated furan **10** with various dienophiles failed to give any cycloadducts, and only starting material was obtained, even after prolonged heating. On the other hand, the sterically less encumbered furan **12** was found to react

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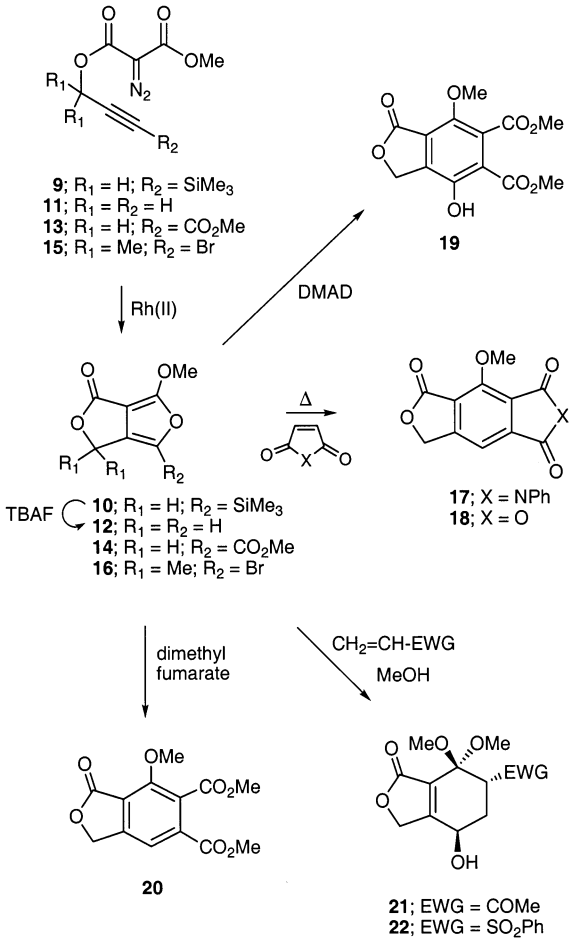
SCHEME 3



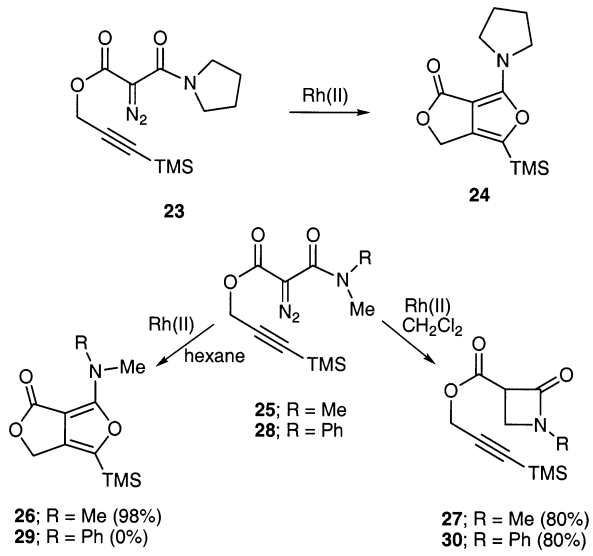
with both *N*-phenylmaleimide and maleic anhydride at 145 °C, furnishing the expected anisole derivatives **17** and **18** in 88% and 65% yield, respectively. The Diels−Alder reaction of **12** also occurred with both dimethyl acetylenedicarboxylate (DMAD) and dimethyl fumarate, giving rise to the anisole derivatives **19** and **20**, which are derived by rearrangement or loss of water from the initially formed cycloadducts.

Furan **12**, however, could not be induced to react with mono-activated dienophiles (e.g. methyl vinyl ketone) under a range of conditions (refluxing xylene, 10 kbar in toluene, trityl perchlorate in CH_2Cl_2, lithium perchlorate in ether, $TiCl_4$ in CH_2Cl_2, etc). Interestingly, the [4 + 2] cycloaddition reaction of **12** with methyl vinyl ketone occurred at 25 °C when nitromethane/methanol was used as the solvent and gave the ring-opened ketal **21** in quantitative yield. An analogous reaction pathway was followed by phenyl vinyl sulfone, which furnished ketal **22** in 89% yield upon treatment with **12** in nitromethane at 25 °C.[44]

The Rh(II)-catalyzed cyclization reaction was quite versatile with regard to the nature of the interacting carbonyl group. Thus, when the cyclization reaction was carried out with the pyrrolidinyl amido system **23**, there was no notable difference in yield (90%) or reaction time

(44) Nitromethane is known to facilitate the Diels−Alder reaction at low temperature with related systems, see: Konopelski, J. P.; Sánchez, A. J. *J. Org. Chem.* **1994**, *59*, 5445.

SCHEME 4



required for cyclization to the pyrrolidino-substituted furo[3,4-*c*]furan **24** (Scheme 4). The success achieved with the Rh(II)-catalyzed cyclization of **23**→**24** was extended to the simpler dimethylamido system **25**. In this case, however, decomposition under standard conditions (Rh_2OAc_4/CH_2Cl_2) afforded a mixture of products from which only a low yield (ca. 2%) of the dimethylamino-substituted furan **26** was obtained. The major product isolated in 80% yield was azetidinone **27**, derived by C−H insertion into one of the amino methyl groups.[45] Interestingly, the product distribution was found to be markedly dependent on the solvent used.[46] Thus, when rhodium(II) acetate [or rhodium(II) octanoate] in hexane was used, a clean transformation was observed and furan **26** was isolated in 98% yield, with no detectable quantities of *β*-lactam **27** being formed. The Rh(II)-catalyzed reaction of the closely related *N*-phenyl-*N*-methyl diazoamide **28** was also examined. In this case only azetidinone **30** (80%) was formed using either of the above sets of conditions. Furan **29** could not be detected in the crude reaction mixtures.

We also discovered that the Rh(II)-catalyzed decomposition of **25** is ligand dependent, thereby suggesting that a metalated species is involved in the product-determining step. Similar observations have been made previously.[47] Changing the catalyst from Rh_2OAc_4 to $Rh_2(pfb)_4$ (pfb = perfluorobutyrate) in CH_2Cl_2 resulted in the exclusive formation of furan **26**. The more electron-withdrawing perfluorobutyrate ligand favors electrocyclization with the tethered alkynyl group, while 1,4-insertion is favored by the more electron-donating acetate ligand. The initially formed rhodium carbenoid derived from the starting diazo compound is highly electron deficient at the carbon center and is further destabilized

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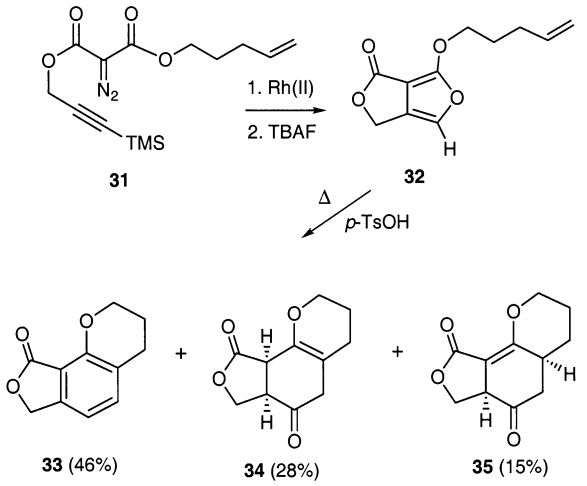
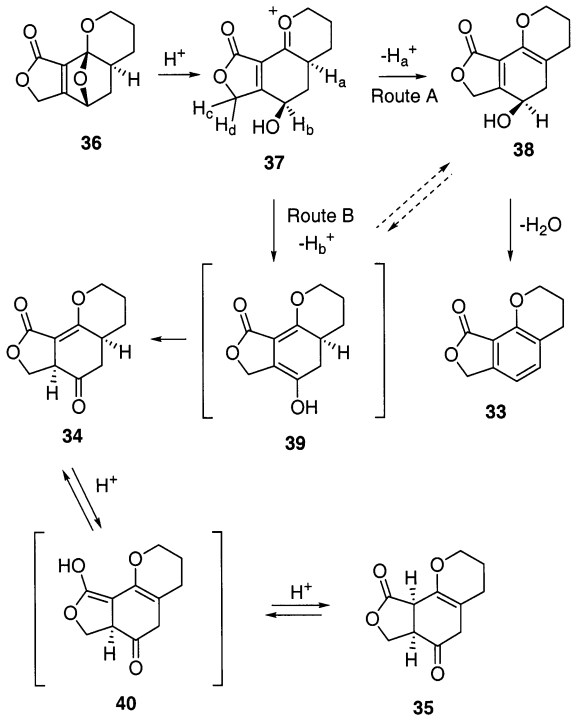
SCHEME 5



by an electron-withdrawing ligand. With this more reactive intermediate, interaction with the acetylenic π-bond is preferred over the entropically more demanding 1,4-insertion pathway. The observed solvent effect can be rationalized in a similar manner. A nonpolar solvent such as hexane apparently facilitates interaction of the rhodium carbenoid with the electron rich acetylenic π-bond thereby favoring furan formation.

To access synthetically more valuable targets, we focused our attention on an intramolecular variation of the Rh(II)-catalyzed cyclization/Diels−Alder cycloaddition sequence. In this regard, we first investigated the IMDAF (intramolecular Diels−Alder of furans) chemistry[48] of furan **32**, which was readily formed by the Rh(II)-catalyzed reaction of **31** followed by protiodesilylation with TBAF (Scheme 5). Thermolysis of a sample of **32** in xylene at 145 °C in the presence of a trace of *p*-TsOH afforded a mixture of three compounds, which were separated by silica gel chromatography and assigned as cyclopenta[*a*]naphthalenones **33** (46%), **34** (28%), and **35** (15%). The relative stereochemistry about the ring juncture for compounds **34** and **35** was established by NOESY NMR experiments. A reasonable mechanism for the formation of the IMDAF products is outlined below (Scheme 6). The initial step proceeds by the expected [4 + 2]-cycloaddition of the furan across the tethered π-bond to give cycloadduct **36**. Following opening of the oxybridge, proton loss (H_a) (route A) is accompanied by a subsequent dehydration of **38** to give the aromatic dihydrobenzopyran **33**. Loss of proton H_b (route B) from the initially formed oxonium ion **37** can compete with route A and furnishes dienol **39**, which rapidly tautomerizes to give **34** (28%). The protonation of enol **39** occurs from the bottom face of this slightly cupped diene, leading to the observed stereoisomer. Once **34** is formed, it is partially equilibrated to **35** (15%) via enol **40**. Again, protonation of the enol (i.e., **40**) occurs from the sterically less crowded α-face.[49] In support of this mechanistic proposal, we noted that heating a pure sample of **34** (or **35**) for 1 h at 80 °C in the presence of *p*-TsOH resulted

SCHEME 6



in an equilibrated mixture of the two cyclopenta[*a*]-naphthalenone isomers (i.e., **34**:**35** = 2:1). This mechanistic description is further complicated, however, by the possibility of a thermally allowed 1,5-H shift that interconverts **38** and **39** and ultimately results in a higher percentage of benzopyran **33** in the equilibrating mixture. Indeed, heating a sample of **34** (or **35**) with *p*-TsOH for several hours at 120 °C in toluene furnished benzopyran **33** as the major product of the mixture.

To further illustrate the viability of the Rh(II)-cyclization/cycloaddition/rearrangement sequence as a strategy for the synthesis of complex polycyclic systems, we studied the Rh(II)-catalyzed behavior of diazo esters **41** and **42**. Synthesis of both these compounds proceeded uneventfully using an analogous procedure to that employed for **31**. Cyclization with Rh_2OAc_4 followed by protiodesilylation afforded furans **43** and **44** in good yield. Thermolysis of **43** at 145 °C in xylene afforded a 1:2-mixture of dihydrobenzofuran **45** and 1,7-dioxa-indacene dione **46** as the two major products in 51% overall yield (Scheme 7). In a similar manner, the related styryl-substituted furo[3,4-*c*]furan **44** was easily prepared by the Rh(II)-catalyzed reaction of diazo malonic ester **42**. Heating a sample of **42** afforded the related indacene dione **47**, but now as the minor component (36%) of the reaction mixture. The major product (63%) corresponded to the dienol-substituted lactone **48**. Both of these products can be rationalized by a mechanism similar to that outlined above. When a phenyl group resides at the bridgehead carbon (i.e., **51**), the deprotonation step is now required to occur from the alternate γ-positions, thereby resulting in the formation of compounds **47** and **48** as shown in Scheme 8. A related pathway seemingly occurs with oxonium ion **50**, producing keto lactone **46** via enol **52** (R = H). An alternative possibility to rationalize the formation of **46** would involve proton loss from the α-position of **50** followed by a rapid 1,5-sigmatropic

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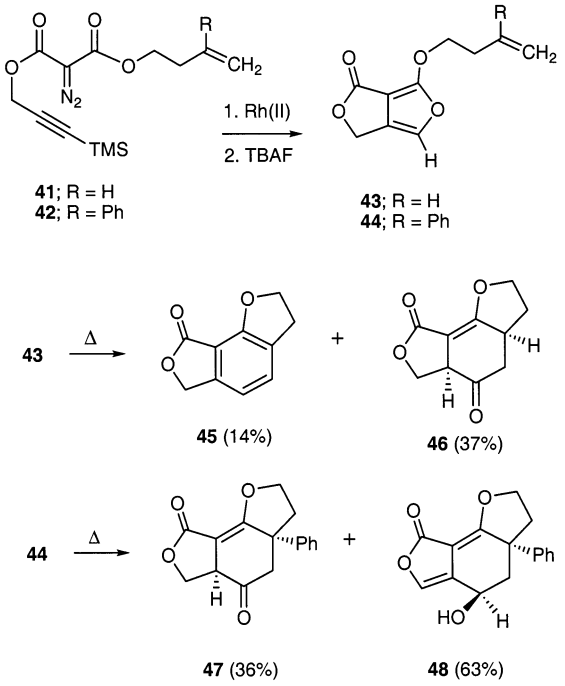
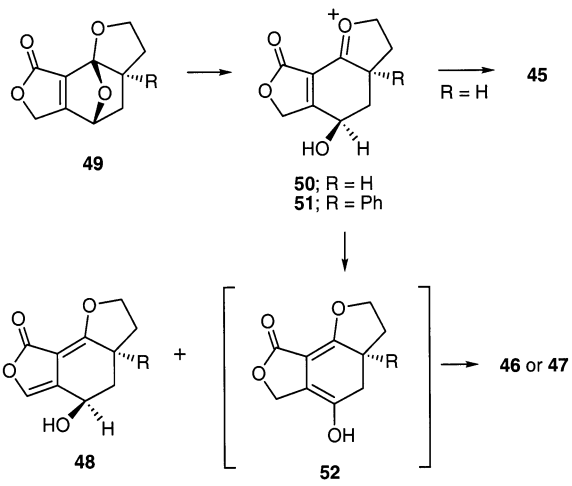
(49) Ab initio MO calculations using the 6-31G* basis set also indicate that the cis-ring juncture present in **35** is preferred over the trans-isomer by 8 kcal/mol.

SCHEME 7



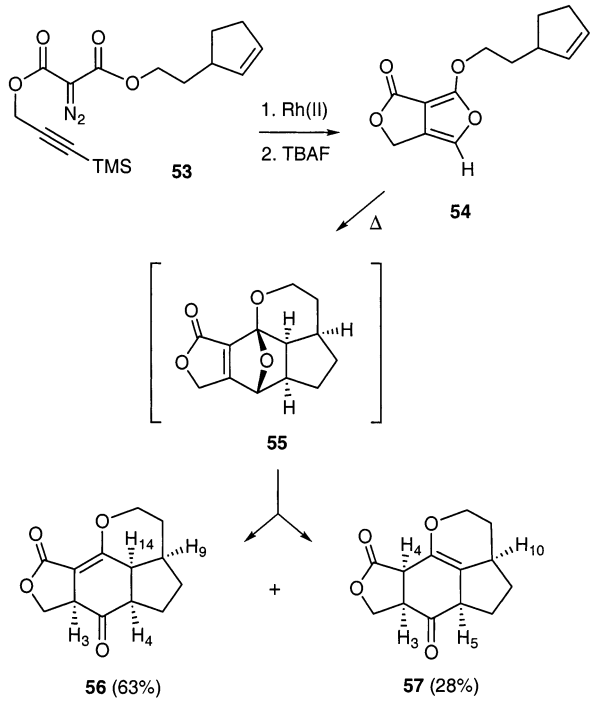
SCHEME 8



hydrogen shift of the initially formed hydroxy-cyclohexadiene to give enol **52** (R = H).

Extension of the carbenoid cyclization/cycloaddition sequence to the related cyclopentenyl diazo ester **53** was also carried out. In this case, diazo ester **53** was converted to furan **54** in 68% overall yield for the two-step sequence. Heating a sample of **54** at 145 °C in xylene afforded a 2:1-mixture of **56** and **57** in 91% yield (Scheme 9). The stereochemical centers in both compounds were assigned on the basis of their NMR spectral data. In **56**, a strong NOE was observed between H_3 and H_4 as well as H_{14}. Additionally, protons H_4 and H_{14} exhibited a strong NOE, as did protons H_9 and H_{14}. An analogous set of NOE enhancements helped to elucidate the stereochemistry of compound **57**. The formation of these products is consistent with a preferred exo-orientation of the tether in the Diels−Alder cycloaddition reaction and is analogous with that reported by others for related furanyl systems possessing short tethers.[50,51] Products resulting

SCHEME 9



from an endo sidearm transition state were neither detected nor isolated. This result is not so surprising since, in these mobile cycloaddition equilibria, the transition state leading to the exo-adduct is sterically less encumbered and the resulting adduct is the thermodynamically most stable isomer. The initially formed Diels−Alder adduct **55** rearranges to the observed products by the same general pathway as that outlined in Scheme 6.

To demonstrate the viability of our sequential process as a practical strategy for the synthesis of complex heterocycles, we have explored the feasibility of this approach in the context of the total synthesis of strychnine (**61**).[52] The key step in our plan involves a sequential cyclization/IMDAF reaction of diazo amide **58** to furnish the rearranged cycloadduct **59** by a process similar to those outlined in Schemes 7−9. Lactone **59** would eventually be transformed into compound **60**, which had previously been converted into strychnine by Kuehne and Xu.[53] Thus, the formation of **60** from diazo amide **58** would constitute a formal synthesis of this challenging alkaloid (Scheme 10).

To establish the viability of this approach, the Rh(II)-catalyzed cyclizations of two model substrates (i.e., **64** and **68**) were examined. Easily prepared *N*-phenyl-*N*-prop-2-ynyl-malonamic acid methyl ester (**62**) was hydrolyzed to the corresponding carboxylic acid **63** which,

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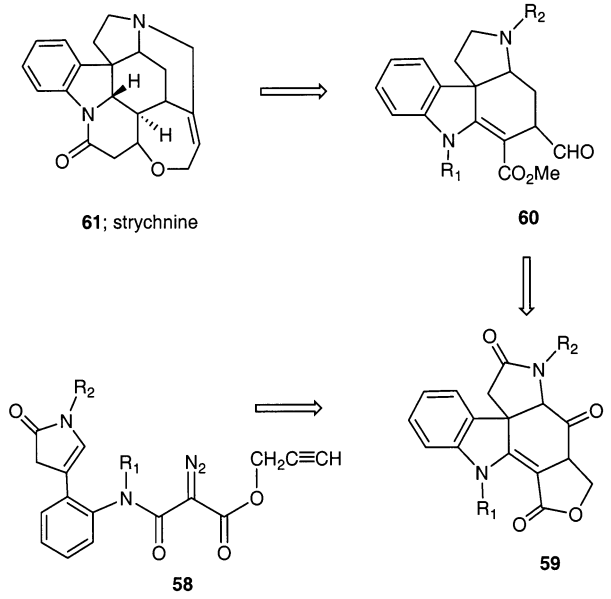
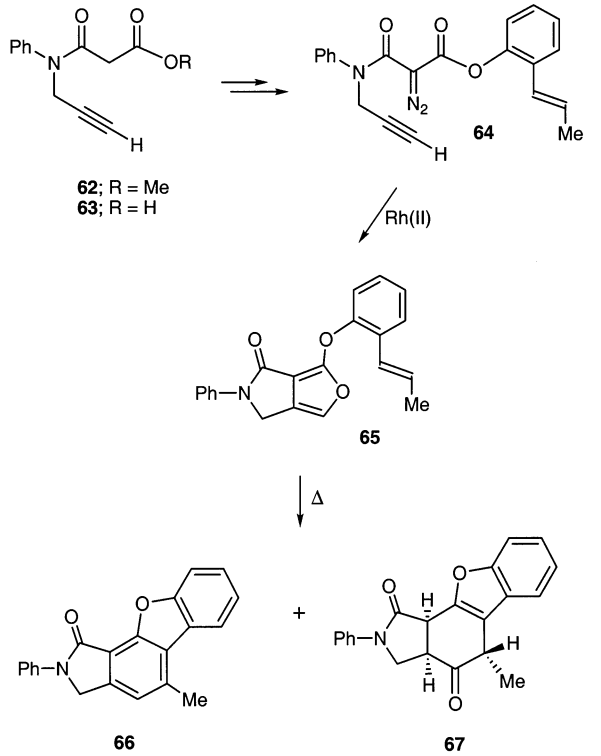
SCHEME 10

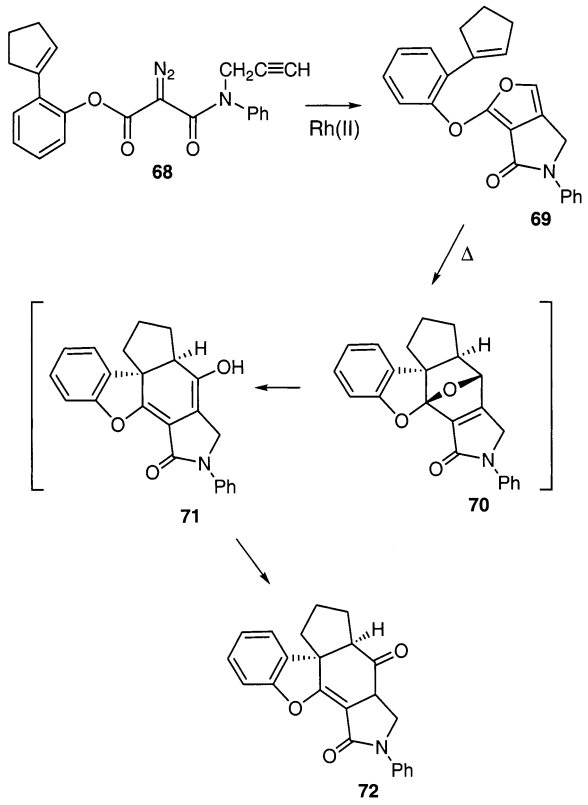


SCHEME 11



in turn, was subjected to a DCC coupling with the appropriate phenol. Diazo transfer to the activated methylene group of the β-amido ester gave the starting α-diazoamides **64** and **68**, which possess the necessary functionalities required for the planned sequence. The rhodium(II)-catalyzed reaction of **64** furnished the expected furan **65** in 81% yield (Scheme 11). An interesting point worth noting is that whereas diazo β-alkoxy esters such as **41** and **42** require the presence of a trimethylsilyl group on the alkyne carbon for efficient cyclization to occur, diazo amido esters **64** and **68** undergo efficient reorganization to 2-alkoxy-substituted furans (i.e., **65** and **69**) without the need to incorporate a silyl substituent

SCHEME 12



at the terminal alkyne carbon. Further heating of **65** at 145 °C in xylene afforded a 1:1-mixture of lactams **66** and **67** in 90% yield, presumably by a mechanism similar to that outlined in Scheme 8.

An analogous cyclization occurred with diazo β-amido ester **68**. Thus, treatment of **68** with a catalytic quantity of rhodium(II) perfluorobutyrate afforded furan **69** in 94% isolated yield. Further heating of this furan at 145 °C furnished the novel pentacyclic product **72** as a single stereoisomer in 68% yield (Scheme 12). The structure and stereochemistry of **72** was confirmed by ^{1}H NMR and NOE experiments. Each of the bond-forming events is assumed to occur by the pathway outlined in Scheme 12.

In conclusion, the Rh(II)-catalyzed cyclization/IMDAF sequence of diazo malonate esters affords structurally elaborated polycyclic products with good to excellent efficiency. The structural features of the resulting products present numerous opportunities for postcycloaddition manipulations that could be exploited to synthetic advantage. Efforts in our laboratory directed toward a formal total synthesis of strychnine using this approach are currently underway and our results will be reported in due course.

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 a 5% ethyl acetate/hexane mixture as the eluent unless specified otherwise. All solids were recrystallized from 3% ethyl acetate/hexane for analytical data.

General Procedure for the Preparation of Diazo Malonic and Malonamic Acid Esters. To a solution containing 42 mmol of the appropriate carboxylic acid in 250 mL of CH_2Cl_2 at 0 °C under argon was added 4.2 mmol of DMAP, 83 mmol of the appropriate alcohol, and 46 mmol of 1,3-dicyclohexylcarbodiimide. The reaction mixture was allowed to stir at room temperature for 3 h. The resulting suspension was filtered, the filtrate concentrated under reduced pressure, and the crude residue was subjected to silica gel chromatography.

To a solution containing 2.1 mmol of the above malonic or malonamic acid ester and 3.1 mmol of 4-nitrobenzenesulfonyl azide[54] in 20 mL of CH_2Cl_2 at 0 °C under argon was added 6.7 mmol of triethylamine. After stirring of the solution for 12 h, the solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography.

2-Diazomalonic Acid Methyl Ester 3-Trimethylsilanylprop-2-ynyl Ester (9). A solution of 4.0 g (28 mmol) of 2,2-dimethyl-1,3-dioxane-4,6-dione and 3.6 g (28 mmol) of 3-(trimethylsilyl)-2-propyn-1-ol[55] in 100 mL of toluene was heated at 110 °C for 4 h. The solvent was removed under reduced pressure to give 6.1 g (100%) of malonic acid mono(3-trimethylsilanyl-prop-2-ynyl) ester as a yellow oil: IR (neat) 2307, 1756, 1723, 1422, 1266, and 849 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 3.50 (s, 2H), 4.78 (s, 2H), and 10.40 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.1, 40.8, 54.3, 93.4, 98.0, 165.9, and 171.3. The acid was used in the next step without further purification.

Esterification of the above compound with methanol furnished malonic acid methyl ester 3-trimethylsilanylprop-2-ynyl ester (94%) as a colorless liquid: IR (neat) 2188, 1762, 1744, 1439, and 1372 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 3.45 (s, 2H), 3.76 (s, 3H), and 4.75 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 41.4, 52.9, 54.0, 93.0, 98.3, 165.8, and 166.6; HRMS calcd for $C_{10}H_{16}O_4Si$ 228.0818, found 228.0816.

Diazo transfer of the above compound gave diazo ester **9** (97%) as a yellow oil: IR (neat) 2140, 1767, 1742, 1700, 1439, and 1327 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 3.85 (s, 3H), and 4.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 52.8, 53.6, 93.0, 98.4, 160.2, and 161.5. Anal. Calcd for $C_{10}H_{14}N_2O_4Si$: C, 47.23; H, 5.55; N, 11.02. Found: C, 47.40; H, 5.47; N, 11.06.

6-Methoxy-4-trimethylsilanyl-3*H*-furo[3,4-c]furan-1-one (10). To a solution of 0.37 g (1.4 mmol) of diazo ester **9** in 15 mL of dry benzene at 80 °C was added 2 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 10 min, then the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.31 g (95%) of **10** as a white solid: mp 35−37 °C; IR (film) 1766, 1621, 1590, 1451, 1316, and 1252 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 4.28 (s, 3H), and 5.12 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.7, 60.9, 65.3, 91.1, 139.6, 142.5, 160.7, and 163.9. Anal. Calcd for $C_{10}H_{14}O_4Si$: C, 53.07; H, 6.24. Found: C, 53.01; H, 6.19.

2-Diazomalonic Acid Methyl Ester Prop-2-ynyl Ester (11). Esterification of malonic acid monomethyl ester[56] with propargyl alcohol afforded malonic acid methyl ester prop-2-ynyl ester (82%) as a light yellow liquid, which was used in the next step without further purification: IR (neat) 2130, 1755, 1739, 1439, 1337, and 1150 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (t, 1H, J = 2.4 Hz), 3.46 (s, 2H), 3.77 (s, 3H), and 4.76 (d, 2H, J = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1, 52.8, 53.0, 75.6, 77.0, 165.8, and 166.6.

Diazo transfer of the above compound furnished diazo ester **11** as a yellow solid: mp 54−56 °C; IR (film) 2143, 1760, 1739, 1700, 1439, and 1328 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.55 (t, 1H, J = 2.4 Hz), 3.86 (s, 3H), and 4.84 (d, 2H, J = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 52.8, 75.8, 75.9, 77.1, 160.2, and 161.3. Anal. Calcd for $C_7H_6N_2O_4$: C, 46.16; H, 3.32; N, 15.38. Found: C, 45.93; H, 3.29; N, 15.38.

6-Methoxy-3*H*-furo[3,4-c]furan-1-one (12). To a solution of 0.5 g (0.26 mmol) of diazo ester **11** in 5 mL of dry benzene at 80 °C was added 0.12 g of $Rh_2(OAc)_4$. The reaction mixture was heated for 10 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.46 g (19%) of **12** as a white solid: mp 88−89 °C; IR (film) 1758, 1756, 1632, 1619, 1443, and 1393 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.31 (s, 3H), 5.16 (d, 2H, J = 1.8 Hz), and 6.70 (t, 1H, J = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 60.9, 64.8, 90.9, 122.2, 131.2, 157.6, and 163.8. Anal. Calcd for $C_7H_6O_4$: C, 54.54; H, 3.93. Found: C, 54.32; H, 3.89.

A sample of furanone **12** was also prepared in 80% yield by treating a 0.84 g (3.7 mmol) sample of furan **10** in 45 mL of THF with a 1.0 M solution of TBAF in THF at 0 °C for 15 min.

2-Diazomalonic Acid 3-Methoxycarbonylprop-2-ynyl Ester Methyl Ester (13). Esterification of malonic acid monomethyl ester with 4-hydroxybut-2-ynoic acid methyl ester[57] gave malonic acid 3-methoxycarbonylprop-2-ynyl ester methyl ester (36%) as a yellow oil: IR (neat) 2250, 1764, 1742, 1719, and 1438 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.46 (s, 2H), 3.77 (s, 3H), 3.80 (s, 3H), and 4.87 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.1, 52.4, 53.0, 53.2, 78.3, 80.5, 153.2, 165.5, and 166.3; HRMS calcd for $C_9H_{10}O_6$ 214.0477, found 214.0476.

Diazo transfer of the above compound afforded diazo ester **13** (24%) as a pale yellow oil: IR (neat) 2250, 2146, 1764, 1742, 1721, and 1438 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.86 (s, 3H), and 4.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.1, 52.9, 53.1, 78.3, 80.6, 153.3, 160.0, and 161.1; HRMS calcd for $C_9H_8N_2O_6$: 240.0382, found 240.0384.

3-Methoxy-4-oxo-4*H*,6*H*-furo[3,4-c]furan-1-carboxylic Acid Methyl Ester (14). To a solution of 0.4 g (1.6 mmol) of diazo ester **13** in 20 mL of dry benzene at 80 °C was added 20 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 5 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.25 g (73%) of **14** as a white solid: mp 156−158 °C; IR (film) 1773, 1708, 1650, 1598, 1443, and 1032 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (s, 3H), 4.39 (s, 3H), and 5.31 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 61.5, 65.6, 94.4, 124.6, 141.9, 157.4, 158.2, and 162.4. Anal. Calcd for $C_9H_8O_6$: C, 50.94; H, 3.80. Found: C, 50.88; H, 3.74.

2-Diazomalonic Acid 3-Bromo-1,1-dimethylprop-2-ynyl Ester Methyl Ester (15). A solution of 2.5 g (15 mmol) of 2,2-dimethyl-1,3-dioxane-4,6-dione and 2.2 g (15 mmol) of 4-bromo-2-methylbut-3-yn-2-ol[58] in 50 mL of toluene was heated at 110 °C for 4 h. The solvent was removed under reduced pressure to give 3.9 g (100%) of malonic acid mono-(3-bromo-1,1-dimethylprop-2-ynyl) ester as a yellow oil, which was used in the next step without further purification: IR (neat) 2209, 1746, 1329, 1252, 1194, and 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 6H), 3.42 (s, 2H), and 10.8 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 41.7, 46.3, 74.8, 80.1, 165.0, and 172.0.

Esterification of the above carboxylic acid with methanol gave 0.57 g (77%) of malonic acid 3-bromo-1,1-dimethylprop-2-ynyl ester methyl ester as a colorless oil, which was used in the next step without further purification: IR (neat) 2211, 1758, 1740, 1438, and 1339 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.68 (s, 6H), 3.36 (s, 2H), and 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.8, 42.2, 45.9, 52.7, 74.2, 80.3, 164.8, and 167.

Diazo transfer in the standard manner gave diazo ester **15** (98%) as a yellow solid: mp 39−40 °C; IR (film) 2207, 2138, 1766, 1740, 1698, and 1337 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.73 (s, 6H), and 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

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29.2, 46.3, 52.7, 74.9, 80.2, 159.1, and 161.8. Anal. Calcd for $C_9H_9BrN_2O_4$: C, 37.39; H, 3.14; N, 9.69. Found: C, 37.47; H, 3.11; N, 9.71.

4-Bromo-6-methoxy-3,3-dimethyl-3*H*-furo[3,4-c]furan-1-one (16). To a solution of 0.1 g (0.35 mmol) of diazo ester **15** in 5 mL of dry benzene at 80 °C was added 2 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for an additional 30 min, and the solvent was removed under reduced pressure to give 90% yield of **16** as a pale yellow oil: IR (C_6D_6) 2361, 1765, and 812 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 1.24 (s, 6H), and 3.68 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 26.4, 60.8, 81.0, 98.1, 118.7, 138.6, 157.5, and 165.3. Anal. Calcd for $C_9H_9BrO_4$: C, 41.54; H, 3.49. Found: C, 41.38; H, 3.51.

8-Methoxy-6-phenyl-3*H*-2-oxa-6-aza-s-indacene-1,5,7-trione (17). A solution of 0.09 g (0.6 mmol) of furan **12** and 0.1 g (0.6 mmol) of *N*-phenylmaleimide in 5 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure, and the residue was recrystallized from EtOAc to give 0.15 g (88%) of **17** as a yellow solid: mp 233−235 °C; IR (KBr) 1767, 1717, 1461, 1378, and 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.49 (s, 3H), 5.38 (s, 2H), 7.41−7.56 (m, 5H), and 7.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.6, 69.3, 112.3, 120.2, 121.7, 127.5, 128.3, 128.9, 131.6, 139.3, 156.0, 157.4, 164.2, 165.5, and 166.8. Anal. Calcd for $C_{17}H_{11}NO_5$: C, 66.01; H, 3.59; N, 4.53. Found: C, 65.97; H, 3.61; N, 4.48.

4-Methoxy-7*H*-benzo[1,2-c;4,5-c′]difuran-1,3,5-trione (18). A solution of 0.13 g (0.9 mmol) of furan **12** and 0.08 g (0.9 mmol) of maleic anhydride in 5 mL of dry xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure and the residue was triturated in ether to give 0.13 g (65%) of **18** as a yellow solid: mp 191−193 °C; IR (KBr) 1848, 1788, 1760, 1610, and 1460 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 4.42 (s, 3H), 5.54 (s, 2H), and 7.93 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 68.9, 74.4, 118.7, 128.1, 144.1, 163.4, 164.5, 165.2, 167.6, and 171.3. Anal. Calcd for $C_{11}H_6O_6$: C, 56.42; H, 2.58. Found: C, 56.26; H, 2.70.

4-Hydroxy-7-methoxy-1-oxo-1,3-dihydroisobenzofuran-5,6-dicarboxylic Acid Dimethyl Ester (19). A solution of 0.1 g (0.7 mmol) of furan **12** and 0.19 g (1.3 mmol) of dimethyl acetylenedicarboxylate in 5 mL of dry xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure and the residue was triturated in ether to give 0.17 g (90%) of **19** as a yellow solid: mp 143−145 °C; IR (Nujol) 1761, 1731, 1684, 1462, 1337, and 1232 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 3.98 (s, 3H), 4.02 (s, 3H), 5.31 (s, 2H), and 10.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 53.9, 64.1, 67.8, 113.8, 124.4, 130.8, 138.1, 147.7, 152.2, 166.4, 167.2, and 168.5. Anal. Calcd for $C_{13}H_{12}O_8$: C, 52.71; H, 4.08. Found: C, 52.44; H, 4.01.

7-Methoxy-1-oxo-1,3-dihydroisobenzofuran-5,6-dicarboxylic Acid Dimethyl Ester (20). A solution of 0.06 g (0.4 mmol) of furan **12** and 0.11 g (0.8 mmol) of dimethyl maleate in 3 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure and the residue was subjected to silica gel chromatography to give 0.08 g (78%) of **20** as a white solid: mp 134−135 °C; IR (film) 1771, 1733, 1458, 1323, 1287, and 1241 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.98 (s, 3H), 4.19 (s, 3H), 5.33 (s, 2H), and 7.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.2, 53.4, 64.3, 69.2, 118.2, 120.6, 130.8, 134.7, 149.7, 156.9, 164.7, 166.7, and 167.1. Anal. Calcd for $C_{13}H_{12}O_7$: C, 55.72; H, 4.32. Found: C, 55.99; H, 4.40.

6-Acetyl-4-hydroxy-7,7-dimethoxy-4,5,6,7-tetrahydro-3*H*-isobenzofuran-1-one (21). A solution of 0.1 g (0.65 mmol) of furan **12**, 0.14 g (2.0 mmol) of methyl vinyl ketone, and 0.03 g (1.0 mmol) of methanol in 5 mL of nitromethane was stirred at 25 °C for 48 h. The solution was concentrated under reduced pressure and the residue was subjected to silica gel chromatography to give 0.17 g (100%) of **21** as a pale yellow oil: IR (neat) 1760, 1710, 1671, 1443, 1362, and 1057 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.16 (ddd, 1H, J = 14.0, 6.8 and 4.0 Hz), 2.30 (s, 3H), 2.36 (ddd, 1H, J = 14.0, 7.2 and 5.6 Hz), 3.34 (s, 3H), 3.35 (s, 3H), 3.44 (dd, 1H, 7.2 and 4.0 Hz), 3.45 (brs, 1H), 4.63 (dd, 1H, J = 6.8 and 5.6 Hz), 4.82 (d, 1H, J = 18.4 and 0.8 Hz), and 5.04 (d, 1H, J = 18.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 32.1, 50.6, 51.2, 52.1, 62.3, 69.9, 98.3, 125.5, 168.7, 171.5, and 207.3. Anal. Calcd for $C_{12}H_{16}O_6$: C, 56.23; H, 6.30. Found: C, 56.15; H, 6.28.

6-Benzenesulfonyl-4-hydroxy-7,7-dimethoxy-4,5,6,7-tetrahydro-3*H*-isobenzofuran-1-one (22). A solution of 0.1 g (0.7 mmol) of furan **12**, 0.33 g (2.0 mmol) of phenyl vinyl sulfone, and 0.03 g (1.0 mmol) of methanol in 5 mL of nitromethane was stirred at 25 °C for 5 days. The solution was concentrated under reduced pressure and the residue was subjected to silica gel chromatography to give 0.2 g (89%) of **12** as a white solid: mp 124−126 °C; IR (neat) 1738, 1457, 1377, 1305, 1131, and 1081 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 2.37 (ddd, 1H, J = 14.0, 8.8 and 4.0 Hz), 2.65 (ddd, 1H, J = 14.0, 5.6 and 5.6 Hz), 2.84 (s, 1H), 2.88 (s, 3H), 3.20 (s, 3H), 4.19 (dd, 1H, J = 5.6 and 4.0 Hz), 4.81 (dd, 1H, J = 18.0 and 0.8 Hz), 4.90 (dd, 1H, J = 8.8 and 5.6 Hz), 4.98 (d, 1H, J = 18.0 Hz), 7.63−7.67 (m, 2H), 7.72−7.76 (m, 1H), and 7.95−7.97 (m, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 32.2, 50.1, 51.4, 62.4, 66.0, 70.0, 98.2, 125.1, 129.8, 130.0, 134.5, 141.7, 169.9, and 170.6. Anal. Calcd for $C_{16}H_{18}O_7S$: C, 54.23; H 5.12. Found: C, 53.97; H, 5.13.

3-Oxo-3-pyrrolidin-1-ylpropionic Acid. To a solution of 2.0 g (14 mmol) of 2,2-dimethyl-1,3-dioxane-4,6-dione in 20 mL of dry CH_2Cl_2 at 0 °C was slowly added 5.5 g (38 mmol) of 1-(trimethylsilyl)pyrrolidine.[59] The reaction mixture was stirred for 48 h and slowly warmed to room temperature, and 20 mL of an aqueous saturated $NaHCO_3$ solution was added. The layers were separated, and the organic layer was extracted with 20 mL portions of aqueous saturated $NaHCO_3$ solution. The aqueous layers were combined, acidified with concentrated HCl, and extracted with $CHCl_3$. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give 1.1 g (50%) of the titled compound, which was used in the next step without further purification: ^1H NMR (400 MHz, $CDCl_3$) δ 1.95−2.07 (m, 4H), 3.33 (s, 2H), 3.46 (t, 2H, J = 8.8 Hz), and 3.55 (t, 2H, J = 8.8 Hz).

2-Diazo-3-oxo-3-pyrrolidin-1-ylpropionic Acid 3-Trimethylsilanyl-prop-2-ynyl Ester (23). Esterification of the above carboxylic acid with 3-(trimethylsilyl)-2-propyn-1-ol gave 3-oxo-3-pyrrolidin-1-yl-propionic acid 3-trimethylsilanylprop-2-ynyl ester (75%) as a yellow solid: mp 52−54 °C; IR (film) 2188, 1752, 1647, 1436, and 1246 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 1.84−2.03 (m, 4H), 3.42−3.53 (m, 4H), 3.45 (s, 2H), and 4.75 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 24.7, 26.4, 42.6, 46.3, 47.4, 53.8, 92.7, 98.7, 163.9, and 166.8. Anal. Calcd for $C_{13}H_{21}NO_3Si$: C, 58.39; H, 7.92; N, 5.24. Found: C, 58.35; H, 7.88; N, 5.24.

Diazo transfer of the above compound gave diazo ester **23** (100%) as a yellow oil: IR (neat) 2186, 2136, 1719, 1625, 1414 and 1287 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.87−1.93 (m, 4H), 3.50−3.55 (m, 4H), and 4.80 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.0, 24.8, 26.2, 47.6, 48.8, 53.4, 92.9, 98.6, 159.3, and 161.3. Anal. Calcd for $C_{13}H_{19}N_3O_3Si$: C, 53.22; H, 6.53; N, 14.32. Found: C, 53.10; H, 6.50; N, 14.21.

6-Pyrrolidin-1-yl-4-trimethylsilanyl-3*H*-furo[3,4-c]-furan-1-one (24). To a solution of 0.08 g (0.3 mmol) of diazo ester **23** in 6 mL of dry benzene at 80 °C was added 2 mg of $Rh_2(OAc)_4$. The reaction mixture was heated at reflux for 30 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.07 g (90%) of **24** as a yellow oil: IR (neat) 1750, 1627, 1461, 1349, and 1148 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 9H), 1.96−2.01 (m, 4H), 3.65−3.71 (m, 4H), and 5.06 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.5, 25.7, 48.5, 64.5, 88.8, 137.0,

(59) Brill, W. K. D.; Nielsen, J.; Caruthers, M. H. *J. Am. Chem. Soc.* **1991**, *113*, 3972.

144.4, 156.5, and 165.2. Anal. Calcd for $C_{13}H_{19}NO_3Si$: C, 58.84; H, 7.22; N, 5.28. Found: C, 58.75; H, 7.04; N, 5.17.

2-Diazo-*N*,*N*-dimethylmalonamic Acid 3-Trimethylsilanylprop-2-ynyl Ester (25). Esterification of *N*,*N*-dimethylmalonamic acid[60] with 3-(trimethylsilyl)-2-propyn-1-ol gave *N*,*N*-dimethylmalonamic acid 3-trimethylsilanylprop-2-ynyl ester (93%) as a pale yellow oil: IR (neat) 2186, 1750, 1657, 1399, 1252, and 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 2.99 (s, 3H), 3.02 (s, 3H), 3.52 (s, 2H), and 4.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 35.7, 38.0, 41.4, 53.7, 92.7, 98.6, 165.7, and 167.0. Anal. Calcd for $C_{11}H_{19}NO_3Si$: C, 54.74; H, 7.93; N, 5.80. Found: C, 54.66; H, 5.77; N, 7.99.

Diazo transfer of the above compound gave diazo ester **25** (100%) as a yellow oil: IR (neat) 2186, 2128, 1717, 1638, and 1295 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9H), 3.01 (s, 6H), and 4.80 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 38.0, 53.4, 92.9, 98.6, 161.4, and 161.5. Anal. Calcd for $C_{11}H_{17}N_3O_3Si$: C, 49.42; H, 6.41; N, 15.72. Found: C, 49.55; H, 6.54; N, 15.62.

6-Dimethylamino-4-trimethylsilanyl-3*H*-furo[3,4-c]furan-1-one (26). To a solution of 0.5 g (1.8 mmol) of diazo ester **30** in 20 mL of dry hexane at 80 °C was added 8 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 3 h and the solvent was removed under reduced pressure to give 0.5 g (98% yield) of **26** as an pale yellow oil: IR (neat) 1743, 1631, 1443, 1250, 1002, and 845 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 9H), 3.23 (s, 6H), and 5.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.6, 38.6, 64.3, 88.7, 136.8, 144.6, 158.7, and 165.3. Anal. Calcd for $C_{11}H_{17}NO_3Si$: C, 55.21; H, 7.17; N, 5.86. Found: C, 55.16; H, 7.24; N, 5.60.

1-Methyl-2-oxoazetidine-3-carboxylic Acid 3-Trimethylsilanylprop-2-ynyl Ester (27). To a solution of 0.12 g (0.43 mmol) of diazo ester **25** in 4 mL of dry CH_2Cl_2 at 50 °C was added 2 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 1 h, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.08 g (80%) of β-lactam **27** as a yellow oil: IR (neat) 2186, 1772, 1740, 1667, 1370, and 1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 2.89 (s, 3H), 3.40 (dd, 1H, 7.2 and 7.2 Hz), 3.58 (dd, 1H, J = 7.2 and 3.6 Hz), 4.10 (dd, 1H, J = 7.2 and 3.6 Hz), 4.72 (d, 1H, J = 18.2 Hz), and 4.84 (d, 1H, J = 18.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 29.2, 44.0, 54.0, 54.5, 92.9, 98.4, 162.0, and 166.9. Anal. Calcd for $C_{11}H_{17}NO_3Si$: C, 55.21; H, 7.17; N, 5.86. Found: C, 55.05; H, 7.04; N, 5.93.

2-Diazo-*N*-methyl-*N*-phenylmalonamic Acid 3-Trimethylsilanylprop-2-ynyl Ester (28). Esterification of *N*-methyl-*N*-phenylmalonamic acid[61] with 3-(trimethylsilyl)-2-propyn-1-ol gave 2-diazo-*N*-methyl-*N*-phenylmalonamic acid 3-trimethylsilanylprop-2-ynyl ester (98%) as a light yellow oil: IR (neat) 2186, 1752, 1669, 1598, 1497, and 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 3.26 (s, 2H), 3.31 (s, 3H), 4.68 (s, 2H), and 7.23−7.44 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 37.6, 41.5, 53.6, 92.6, 98.6, 127.4, 128.5, 130.1, 143.5, 165.7, and 167.0. Anal. Calcd for $C_{16}H_{21}NO_3Si$: C, 63.33; H, 6.98; N, 4.62. Found: C, 63.09; H, 6.97; N, 4.66.

Diazo transfer of the above compound furnished diazo ester **28** (92%) as a yellow solid: mp 57−59 °C; IR (film) 2186, 2128, 1727, 1638, 1596, and 1420 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9H), 3.39 (s, 3H), 4.54 (s, 2H), and 7.20−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.1, 39.0, 53.4, 92.7, 98.4, 125.9, 127.1, 129.5, 143.8, 160.6, and 161.0. Anal. Calcd for $C_{16}H_{19}N_3O_3Si$: C, 58.34; H, 5.81; N, 12.76. Found: C, 58.24; H, 5.78; N, 12.57.

2-Oxo-1-phenylazetidine-3-carboxylic Acid 3-Trimethylsilanylprop-2-ynyl Ester (30). To a solution of 0.2 g (0.65 mmol) of diazo ester **28** in 10 mL of methylene chloride at 80 °C was added 4 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 1.5 h, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.15 g (77%) of **30** as a light yellow oil: IR (film) 1767, 1740, 1602, 1503, 1158, and 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 3.81 (dd, 1H, J = 5.7 and 5.7 Hz), 3.99 (dd, 1H, J = 5.7 and 3.0 Hz), 4.26 (dd, 1H, J = 5.7 and 3.0 Hz), 4.76 (d, 1H, J = 15.9 Hz), 4.87 (d, 1H, J = 15.9 Hz), 7.12−7.18 (m, 1H), and 7.36 (d, 4H, J = 4.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 0.1, 41.6, 53.2, 54.3, 93.2, 98.2, 116.6, 124.7, 129.4, 137.8, 158.3, and 166.2. Anal. Calcd for $C_{16}H_{19}NO_3Si$: C, 63.76; H, 6.35; N, 4.65. Found: C, 63.94; H, 6.37; N, 4.71.

2-Diazomalonic Acid Pent-4-enyl Ester 3-Trimethylsilanylprop-2-ynyl Ester (31). Esterification of malonic acid mono(3-trimethylsilanylprop-2-ynyl) ester with 4-penten-1-ol gave malonic acid pent-4-enyl ester 3-trimethylsilanylprop-2-ynyl) ester (88%) as a colorless liquid: IR (neat) 2187, 1758, 1740, 1642, 1330, and 1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 1.76 (tt, 2H, J = 7.2 and 6.4 Hz), 2.13 (td, 2H, J = 7.6 and 7.2 Hz), 3.43 (s, 2H), 4.17 (t, 2H, J = 6.4 Hz), 4.75 (s, 2H), 4.99−5.08 (m, 2H), and 5.74−5.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 27.8, 30.1, 41.5, 53.9, 65.2, 93.0, 98.3, 115.7, 137.4, 166.0, and 166.3. Anal. Calcd for $C_{14}H_{22}O_4Si$: C, 59.54; H, 7.85. Found: C, 59.78; H, 7.74.

Diazo transfer of the above compound afforded diazo ester **31** (98%) as a yellow oil: IR (neat) 2141, 1764, 1740, 1696, 1642, and 1317 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 1.80 (tt, 2H, J = 6.9 and 6.6 Hz), 2.14 (td, 2H, J = 7.8 and 6.9 Hz), 4.27 (t, 2H, J = 6.6 Hz), 4.84 (s, 2H), 4.98−5.09 (m, 2H), and 5.73−5.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.2, 27.9, 30.1, 53.6, 65.3, 93.0, 98.4, 115.7, 137.3, 160.3, and 161.0. Anal. Calcd for $C_{14}H_{20}N_2O_4Si$: C, 54.52; H, 6.54; N, 9.08. Found: C, 54.63; H, 6.55; N, 9.15.

6-Pent-4-enyloxy-3*H*-furo[3,4-c]furan-1-one (32). To a solution of 1.4 g (4.4 mmol) of diazo ester **31** in 50 mL of dry benzene at 80 °C was added 8 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 1 h, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 1.0 g (83%) of 6-pent-4-enyloxy-4-trimethylsilanyl-3*H*-furo[3,4-*c*]furan-1-one as a light yellow oil: IR (neat) 1766, 1619, 1588, 1373, 1314, and 1252 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.88−1.97 (m, 2H), 2.21−2.28 (m, 2H), 4.64 (t, 2H, J = 6.6 Hz), 5.00−5.11 (m, 2H), 5.14 (s, 2H), and 5.77−5.90 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.7, 28.5, 29.7, 65.3, 73.6, 90.9, 115.8, 137.3, 139.5, 142.6, 160.3, and 164.1; HRMS calcd for $C_{14}H_{20}O_4Si$ 280.1131, found 280.1130.

A solution of 1.0 g (3.6 mmol) of the above furan in 50 mL of THF was cooled in an ice bath. A 1.0 M solution of TBAF in THF (3.9 mmol) was added dropwise to the reaction mixture and the solution was stirred at 0 °C for 20 min. The mixture was poured into 30 mL of a saturated aqueous NH_4Cl solution and extracted with ether. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography to give 0.56 g (76%) of **32** as a yellow oil: IR (neat) 1758, 1627, 1611, 1384, 1307, and 1168 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.89−1.95 (m, 2H), 2.21−2.27 (m, 2H), 4.63 (t, 2H, J = 6.4 Hz), 5.00−5.10 (m, 2H), 5.15 (d, 2H, J = 1.6 Hz), 5.78−5.88 (m, 1H), and 6.69 (t, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 29.7, 64.7, 73.5, 90.6, 115.8, 122.0, 131.1, 137.2, 156.9, and 163.8. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.44; H, 5.81. Found: C, 63.40; H, 5.73.

3,6,7,8-Tetrahydro-2,9-dioxacyclopenta[*a*]naphthalen-1-one (33). A solution of 0.22 g (1.0 mmol) of furan **32** in 8 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography. The first fraction isolated from the column contained 0.09 g (46%) of **33** as a white solid: mp 87−89 °C; IR (film) 1752, 1597, 1490, 1303, and 1072 cm^{-1}; ^1H NMR (400 MHz,

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(61) Manandhar, M. D.; Hussaini, F. A.; Kapil, R. S.; Shoeb, A. *Phytochemistry* **1985**, *24*, 199.

$CDCl_3$) δ 2.05−2.11 (m, 2H), 2.85 (t, 2H, J = 6.4 Hz), 4.40 (t, 2H, J = 5.6 Hz), 5.19 (s, 2H), 6.87 (d, 1H, J = 7.6 Hz), and 7.32 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 24.8, 67.6, 68.9, 112.9, 112.9, 123.0, 136.7, 147.3, 154.4, and 169.6. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.45; H, 5.30. Found: C, 69.33; H, 5.24.

3,3a,6,7,8,9b-Hexahydro-5*H*-2,9-dioxacyclopenta[a]-naphthalene-1,4-dione (34). The second fraction isolated from the silica gel column contained 0.06 g (28%) of **34** as a yellow oil: IR (neat) 1774, 1721, 1301, 1151, and 1046 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90−2.02 (m, 4H), 2.88 (d, 1H, J = 18.6 Hz), 3.01 (d, 1H, J = 18.6 Hz), 3.39 (ddd, 1H, J = 10.0, 6.8 and 2.4 Hz), 3.65 (d, 1H, J = 10.0 Hz), 4.07−4.17 (m, 2H), 4.25 (dd, 1H, J = 9.6 and 6.8 Hz), and 4.91 (dd, 1H, J = 9.6 and 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 25.0, 41.5, 44.1, 47.4, 66.0, 66.8, 104.3, 140.3, 173.2, and 203.9. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.44; H, 5.81. Found: C, 63.22; H, 5.69.

3,3a,5a,6,7,8-Hexahydro-5*H*-2,9-dioxacyclopenta[a]-naphthalene-1,4-dione (35). The third fraction isolated from the column contained 0.03 g (15%) of **35** as a white solid: mp 139−142 °C; IR (film) 1742, 1719, 1642, 1175, and 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48−1.58 (m, 1H), 1.91−2.01 (m, 2H), 2.14−2.22 (m, 1H), 2.26 (dd, 1H, J = 18.4 and 10.8 Hz), 2.71 (dd, 1H, J = 18.4 and 6.0 Hz), 2.98−3.07 (m, 1H), 3.72−3.77 (m, 1H), 4.11−4.17 (m, 1H), and 4.39−4.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 25.8, 34.1, 42.9, 48.2, 65.1, 69.6, 95.3, 163.9, 167.2, and 206.1. Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.44; H, 5.81. Found: C, 63.34; H, 5.77.

2-Diazomalonic Acid But-3-enyl Ester 3-Trimethylsilanylprop-2-ynyl Ester (41). Esterification of malonic acid mono(3-trimethylsilanylprop-2-ynyl) ester with 3-buten-1-ol gave malonic acid but-3-enyl ester 3-trimethylsilanylprop-2-ynyl ester (85%) as a colorless oil: IR (neat) 2186, 1759, 1738, 1638, and 1325 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9H), 2.39−2.44 (m, 2H), 3.43 (s, 2H), 4.21 (t, 2H, J = 7.2 Hz), 4.75 (s, 2H), 5.07−5.15 (m, 2H), and 5.73−5.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 33.0, 41.5, 53.9, 64.8, 93.0, 98.4, 117.8, 133.8, 166.0, and 166.3. Anal. Calcd for $C_{13}H_{20}O_4Si$: C, 58.18; H, 7.51. Found: C, 58.36; H, 7.46.

Diazo transfer of the above compound gave diazo ester **41** (100%) as a yellow oil: IR (neat) 2185, 2140, 1766, 1740, 1700, and 1374 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 2.41−2.48 (m, 2H), 4.30 (t, 2H, J = 6.9), 4.84 (s, 2H), 5.07−5.17 (m, 2H), and 5.72−5.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.2, 33.3, 53.6, 64.8, 93.0, 98.4, 117.9, 133.6, 160.3, and 160.8. Anal. Calcd for $C_{13}H_{18}N_2O_4Si$: C, 53.04; H, 6.16; N, 9.52. Found: C, 52.94; H, 6.10; N, 9.35.

6-But-3-enyloxy-3*H*-furo[3,4-c]furan-1-one (43). To a solution of 0.14 g (0.5 mmol) of diazo ester **41** in 4 mL of dry benzene at 80 °C was added 2 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 30 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.12 g (92%) of 6-but-3-enyloxy-4-trimethylsilanyl-3*H*-furo[3,4-*c*]furan-1-one as a white solid; mp 28−30 °C; IR (film) 1769, 1619, 1588, 1372, 1252, and 843 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9H), 2.57−2.60 (m, 2H), 4.67 (t, 2H, J = 6.3 Hz), 5.11−5.23 (m, 2H), 5.14 (s, 2H), and 5.81−5.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8, 33.6, 65.3, 73.2, 91.0, 118.2, 133.2, 139.6, 142.5, 160.1, and 164.1; HRMS calcd for $C_{13}H_{18}O_4Si$: 266.0974. Found 266.0974.

A solution of 0.12 g (0.5 mmol) of the above furan in 6 mL of THF was cooled in an ice bath. A 1.0 M solution of TBAF in THF (0.5 mmol) was added dropwise to the reaction mixture and the solution was stirred at 0 °C for 15 min. The mixture was poured into 10 mL of an aqueous saturated NH_4Cl solution and extracted with ether. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography to give 0.08 g (95%) of **43** as a clear oil: IR (film) 1762, 1629, 1611, 1308, 1171, and 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.55−2.61 (m, 2H), 4.66 (t, 2H, J = 6.4 Hz), 5.11−5.22 (m, 2H), 5.15 (d, 2H, J = 2.0 Hz), 5.81−5.91 (m, 1H), and 6.70 (t, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.5, 64.7, 73.0, 90.7, 118.2, 122.0, 131.0, 133.1, 156.7, and 163.8. Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19. Found: C, 61.62; H, 5.08.

3,6-Dihydro-2*H*-1,7-dioxa-as-indacen-8-one (45). A solution of 0.22 g (1.1 mmol) of furan **43** in 5 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 13 h. The solution was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography. The first fraction isolated from the column contained 0.03 g (14%) of **45** as a yellow solid: mp 138−139 °C; IR (KBr) 1754, 1482, 1459, 1248, and 982 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.28 (t, 2H, J = 8.8 Hz), 4.83 (t, 2H, J = 8.8 Hz), 5.27 (d, 2H, J = 1.2 Hz), 6.89 (d, 1H, J = 7.2 Hz), and 7.46 (td, 1H, J = 7.2 and 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7, 70.1, 73.8, 108.7, 113.4, 128.9, 131.0, 147.0, 158.3, and 169.3. Anal. Calcd for $C_{10}H_8O_3$: C, 68.16; H, 4.58. Found: C, 68.07; H, 4.49.

2,3,3a,4,5a,6-Hexahydro-1,7-dioxa-as-indacene-5,8-dione (46). The second fraction isolated from the column contained 0.07 g (37%) of **46** as a white solid: mp 98−100 °C; IR (film) 1748, 1713, 1686, 1187, and 945 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74−1.95 (m, 1H), 2.20 (dd, 1H, J = 18.4 and 10.0 Hz), 2.57−2.64 (m, 1H), 2.95 (dd, 1H, J = 18.4 and 7.6 Hz), 3.36−3.46 (m, 1H), 3.67 (ddd, 1H, J = 9.6, 8.0 and 2.4 Hz), 4.39 (dd, 1H, J = 9.6 and 8.0 Hz), 4.46 (ddd, 1H, J = 12.0, 9.2, and 2 Hz), 4.57 (dd, 1H, J = 9.6 and 9.6 Hz), and 4.76 (ddd, 1H, J = 9.2, 9.2 and 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 39.9, 42.0, 46.4, 66.4, 75.5, 89.4, 167.3, 167.4, and 207.1. Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19. Found: C, 61.73; H, 5.10.

2-Diazomalonic Acid 3-Phenylbut-3-enyl Ester 3-Trimethylsilanylprop-2-ynyl Ester (42). Esterification of malonic acid mono(3-trimethylsilanylprop-2-ynyl) ester with 3-phenyl-3-buten-1-ol[62] gave malonic acid 3-phenyl-but-3-enyl ester 3-trimethylsilanylprop-2-ynyl ester (58%) as a pale yellow oil: IR (neat) 2186, 1756, 1740, 1494, and 1326 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 2.86 (dt, 2H, J = 7.2 and 0.9 Hz), 3.37 (s, 2H), 4.26 (t, 2H, J = 7.2 Hz), 4.76 (s, 2H), 5.14 (dd, 1H, J = 0.9 and 0.9 Hz), 5.38 (d, 1H, J = 0.9 Hz), and 7.25−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.2, 34.5, 41.4, 53.9, 64.4, 93.0, 98.4, 114.9, 126.2, 127.9, 128.6, 140.4, 144.1, 165.9, and 166.2. Anal. Calcd for $C_{19}H_{24}O_4Si$: C, 66.25; H, 7.02. Found: C, 65.98; H, 7.10.

Diazo transfer of the above compound gave diazo ester **42** (98%) as a light yellow oil: IR (neat) 2142, 1764, 1738, 1698, and 1322 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 2.91 (t, 2H, J = 6.8 Hz), 4.35 (t, 2H, J = 6.8 Hz), 4.832 (s, 2H), 5.15 (d, 1H, J = 0.8), 5.39 (d, 1H, J = 0.8), and 7.25−7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.1, 34.8, 53.6, 64.5, 93.0, 98.4, 115.1, 126.2, 128.0, 128.7, 140.4, 144.2, 160.3, and 160.7; HRMS calcd for $C_{19}H_{22}N_2O_4Si$ 370.1349, found 370.1348.

6-(3-Phenylbut-3-enyloxy)-3*H*-furo[3,4-c]furan-1-one (44). To a solution of 0.22 g (0.6 mmol) of diazo ester **42** in 8 mL of dry benzene at 80 °C was added 2 mg of $Rh_2(OAc)_4$. The reaction mixture was heated at 80 °C for 30 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.16 g (76%) of 6-(3-phenylbut-3-enyloxy)-4-trimethylsilanyl-3*H*-furo[3,4-*c*]-furan-1-one as a light yellow oil: IR (neat) 1766, 1619, 1588, 1372, 1030, and 845 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.2 (s, 9H), 3.03 (t, 2H, J = 6.6 Hz), 4.74 (t, 2H, J = 6.6 Hz), 5.11 (s, 2H), 5.23 (d, 1H, J = 0.9 Hz), 5.43 (d, 1H, J = 0.9 Hz), and 7.24−7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8, 34.9, 65.2, 72.2, 91.1, 115.2, 126.2, 127.8, 128.6, 139.5, 140.3, 142.5, 143.4, 159.9, and 163.9; HRMS calcd for $C_{19}H_{22}O_4Si$ 342.1287, found 342.1287.

A solution of 1.1 g (3.1 mmol) of the above furan in 50 mL of THF was cooled in an ice bath. A 1.0 M solution of TBAF in THF (3.4 mmol) was added dropwise to the reaction mixture

(62) Maercker, A.; Weber, K. *Justus Liebigs Ann. Chem.* **1972**, 20.

and the solution was stirred at 0 °C for 20 min. The mixture was poured into 30 mL of an aqueous saturated NH_4Cl solution and extracted with ether. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography to give 0.68 g (82%) of **44** as a pale yellow solid: mp 28−30 °C; IR (neat) 1760, 1629, 1611, 1308, 1167, and 1017 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.03 (t, 2H, J = 6.4 Hz), 4.73 (t, 2H, J = 6.4 Hz), 5.12 (d, 2H, J = 1.6 Hz), 5.22 (d, 1H, J = 1.2 Hz), 5.42 (d, 1H, J = 1.2 Hz), 6.66 (t, 1H, J = 1.6 Hz), and 7.26−7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.9, 64.7, 72.2, 90.8, 115.4, 122.0, 126.3, 127.9, 128.6, 131.1, 140.4, 143.4, 156.7, and 163.7. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 70.88; H, 5.14.

3a-Phenyl-2,3,3a,4,5a,6-hexahydro-1,7-dioxa-as-indacene-5,8-dione (47). A solution of 0.09 g (1.1 mmol) of furan **44** in 5 mL of dry xylene was heated at 145 °C in a thick-walled sealed tube for 13 h. The solution was concentrated under reduced pressure and the residue was subjected to silica gel chromatography. The first fraction isolated from the column contained 0.03 g (36%) of **47** as a yellow solid: mp 172−174 °C; IR (film) 1746, 1665, 1449, 1225, 1048, and 942 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.39−2.47 (m, 1H), 2.51−2.55 (m, 1H), 2.67 (d, 1H, J = 18.4 Hz), 3.33 (dd, 1H, J = 9.6 and 8.0 Hz), 3.41 (d, 1H, J = 18.4 Hz), 4.31 (dd, 1H, J = 9.6 and 8.0 Hz), 4.35 (ddd, 1H, J = 11.6, 9.2 and 5.2 Hz), 4.52 (dd, 1H, J = 9.6 and 9.6 Hz), 4.70 (ddd, 1H, J = 9.2, 9.2 and 0.8 Hz), and 7.32−7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.8, 45.9, 51.0, 54.7, 66.6, 73.8, 91.7, 126.2, 128.5, 129.8, 138.5, 167.7, 168.5, and 207.3. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 71.04; H, 5.03.

5-Hydroxy-3a-phenyl-3,3a,4,5-tetrahydro-2*H*-1,7-dioxa-as-indacen-8-one (48). The second fraction isolated from the column contained 0.05 g (63%) of **48** as a yellow solid: mp 84−86 °C; IR (film) 1746, 1665, 1449, 1225, and 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.99 (dd, 1H, J = 11.6 and 11.6 Hz), 2.32 (ddd, 1H, J = 12.4, 12.4 and 8.4 Hz), 2.40 (brs, 1H), 2.48 (dd, 1H, J = 12.4 and 4.8 Hz), 2.79 (dd, 1H, J = 11.6 and 4.8 Hz), 4.18 (ddd, 1H, J = 12.4, 9.2 and 4.8 Hz), 4.24 (ddd, 1H, J = 11.6, 4.8 and 2.4 Hz), 4.65 (dd, 1H, J = 9.2 and 8.8 Hz), 6.65 (d, 1H, J = 2.4 Hz), and 7.24−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5, 46.8, 55.2, 63.0, 74.1, 98.6, 122.3, 126.3, 128.2, 129.4, 132.2, 139.8, 166.0, and 171.5. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22. Found: C, 71.24; H, 5.06.

2-Diazomalonic Acid 2-Cyclopent-2-enyl Ethyl Ester 3-Trimethylsilanylprop-2-ynyl Ester (53). Esterification of malonic acid mono(3-trimethylsilanylprop-2-ynyl) ester with 2-cyclopent-2-enylethanol[63] gave malonic acid 2-cyclopent-2-enylethyl ester 3-trimethylsilanylprop-2-ynyl ester (100%) as a colorless oil: IR (neat) 2187, 1758, 1640, 1251, and 1147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.32−1.48 (m, 1H), 1.54−1.70 (m, 1H), 1.72−1.84 (m, 1H), 2.04−2.13 (m, 1H), 2.22−2.42 (m, 2H), 2.68−2.79 (m, 1H), 3.43 (s, 2H), 4.18−4.23 (m, 2H), 4.75 (s, 2H), 5.64−5.68 (m, 1H), and 5.73−5.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.2, 29.9, 32.1, 34.6, 41.5, 42.4, 53.9, 64.9, 92.9, 98.3, 131.3, 134.1, 166.0, and 166.4. Anal. Calcd for $C_{16}H_{24}O_4Si$: C, 62.30; H, 7.84. Found: C, 62.15; H, 7.82.

Diazo transfer of the above compound gave **53** (94%) as a yellow oil: IR (neat) 2184, 2140, 1764, 1740, and 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.18 (s, 9H), 1.40−1.49 (m, 1H), 1.64−1.72 (m, 1H), 1.77−1.86 (m, 1H), 2.04−2.13 (m, 1H), 2.24−2.41 (m, 2H), 2.71−2.79 (m, 1H), 4.25−4.36 (m, 2H), 4.84 (s, 2H), 5.52−5.68 (m, 1H), and 5.74−5.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.2, 29.8, 32.1, 34.8, 42.5, 53.6, 65.0, 93.0, 98.4, 131.4, 134.1, 160.3, and 161.0; HRMS calcd for $C_{16}H_{22}N_2O_4Si$ 334.1349, found 334.1348.

6-(2-Cyclopent-2-enylethoxy)-3*H*-furo[3,4-c]furan-1-one (54). To a solution of 1.9 g (5.7 mmol) of diazo ester **53** in 50 mL of dry benzene at 80 °C was added 8 mg of $Rh_2(OAc)_4$. The reaction mixture was heated for 25 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 1.7 g (95%) of 6-(2-cyclopent-2-enylethoxy)-4-trimethylsilanyl-3*H*-furo[3,4-*c*]furan-1-one as a colorless oil: IR (neat) 1765, 1619, 1588, 1372, 1313, and 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.23 (s, 9H), 1.45−1.54 (m, 1H), 1.76−1.85 (m, 1H), 1.90−1.99 (m, 1H), 2.07−2.16 (m, 1H), 2.24−2.43 (m, 2H), 2.84−2.92 (m, 1H), 4.63−4.72 (m, 2H), 5.14 (s, 2H), 5.70−5.73 (m, 1H), and 5.75−5.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.7, 29.9, 32.1, 35.2, 42.1, 65.3, 73.4, 90.9, 131.4, 134.1, 139.4, 142.6, 160.3, and 164.1; HRMS calcd for $C_{16}H_{22}O_4Si$: 306.1287, found 306.1288.

A solution of 1.7 g (5.4 mmol) of the above furan in 50 mL of THF was cooled in an ice bath. A 1.0 M solution of TBAF in THF (5.9 mmol) was added dropwise to the reaction mixture and the solution was stirred at 0 °C for 20 min. The mixture was poured into 30 mL of aqueous saturated NH_4Cl and extracted with ether. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography to give 0.91 g (72%) of **54** as a pale yellow oil: IR (neat) 1758, 1626, 1614, 1467, 1384, and 1306 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45−1.53 (m, 1H), 1.76−1.85 (m, 1H), 1.90−1.98 (m, 1H), 2.07−2.15 (m, 1H), 2.24−2.43 (m, 2H), 2.82−2.91 (m, 1H), 4.62−4.71 (m, 2H), 5.15 (d, 2H, J = 2.0 Hz), 5.69−5.72 (m, 1H), 5.75−5.79 (m, 1H), and 6.69 (t, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.9, 32.1, 35.1, 42.1, 64.7, 73.3, 90.6, 121.9, 131.1, 131.4, 134.0, 157.0, and 163.8. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.60; H, 5.92.

3,3a,4,5,5a,6a,7,9a-Octahydro-2*H*-1,8-dioxacyclopenta-[e]acenaphthylene-6,9-dione (56). A solution of 0.22 g (0.9 mmol) of furan **54** in 8 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure and the residue was subjected to silica gel chromatography. The first fraction isolated from the column contained 0.14 g (63%) of **56** as a yellow oil: IR (film) 1775, 1724, 1463,1156, and 1058 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92−1.03 (m, 1H), 1.31−1.41 (m, 1H), 1.70−1.80 (m, 1H), 1.99−2.06 (m, 1H), 2.06−2.13 (m, 1H), 2.30−2.37 (m, 1H), 2.44−2.53 (m, 1H), 3.41−3.46 (m, 1H), 3.60 (ddd, 1H, J = 9.6, 7.2 and 2.8 Hz), 3.88 (ddd, 1H, J = 14.4, 10.8 and 2.0 Hz), 3.96 (ddd, 1H, J = 9.6, 3.6 and 2.4 Hz), 4.26 (dd, 1H, J = 9.2 and 7.2 Hz), 4.38 (ddd, 1H, J = 10.8, 3.6 and 2.4 Hz), and 4.92 (dd, 1H, J = 9.2 and 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 28.6, 32.3, 37.3, 44.5, 47.1, 47.6, 65.0, 66.8, 115.0, 138.7, 172.2, and 202.3. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.51; H, 5.88.

3,3a,4,5,5a,6a,7,9c-Octahydro-2*H*-1,8-dioxacyclopenta-[e]acenaphthylene-6,9-dione (57). The minor fraction isolated from the silica gel column contained 0.06 g (28%) of **57** as a yellow oil: IR (film) 1744, 1719, 1644, 1188, and 1048 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22−1.31 (m, 1H), 1.43−1.53 (m, 1H), 1.73−1.82 (m, 1H), 1.89−1.97 (m, 1H), 2.10−2.27 (m, 2H), 2.47−2.58 (m, 1H), 3.05 (ddd, 1H, J = 10.0, 5.6 and 3.2 Hz), 3.63 (ddd, 1H, J = 10.0, 10.0 and 3.2 Hz), 3.95 (ddd, 1H, J = 9.6, 9.6 and 3.2 Hz), 4.10 (dt, 1H, J = 11.2 and 2.0 Hz), 4.36 (dd, 1H, J = 9.6 and 9.6 Hz), 4.39 (dt, 1H, J = 11.2 and 3.6 Hz), and 4.57 (dd, 1H, J = 9.6 and 9.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 28.2, 32.4, 37.0, 42.6, 46.4, 51.0, 64.3, 66.9, 96.3, 163.6, 167.1, and 203.7; HRMS calcd for $C_{13}H_{14}O_4$ 234.0892, found 234.0890.

2-Diazo-*N*-phenyl-*N*-prop-2-ynylmalonamic Acid 2-Propenylphenyl Ester (64). To a solution of 4.5 g (38 mmol) of malonic acid monomethyl ester in 70 mL of CH_2Cl_2 at 0 °C under an argon atmosphere was added 0.14 g (1.1 mmol) of DMAP, 5.0 g (38 mmol) of *N*-phenyl-*N*-propynylamine, and 8.7 g (42 mmol) of 1,3-dicyclohexylcarbodiimide. The reaction mixture was allowed to stir at room temperature for 24 h. The resulting suspension was filtered, the filtrate concentrated under reduced pressure, and the crude residue was subjected

(63) Irwin, A. J.; Jones, J. B. *J. Am. Chem. Soc.* **1977**, *99*, 1625.

to silica gel chromatography to give 8.2 g (92%) of *N*-phenyl-*N*-prop-2-ynylmalonamic acid methyl ester (**62**) as a yellow liquid: IR (neat) 2120, 1743, 1666, 1595, 1494, and 1397 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (t, 1H, J = 1.8 Hz), 3.22 (s, 2H), 3.67 (s, 3H), 4.52 (d, 2H, J = 1.8 Hz), and 7.31−7.48 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.7, 41.5, 52.5, 72.7, 78.6, 128.5, 129.2, 130.1, 141.1, 165.7, and 167.9; HRMS calcd for $C_{13}H_{13}NO_3$ 231.0895, found 231.0892.

To a solution of 4.1 g (18 mmol) of the above compound in 20 mL of methanol at 0 °C was added a solution of 1.4 g (25 mmol) of potassium hydroxide in 2 mL of methanol. The reaction mixture was allowed to stir for 72 h, concentrated under reduced pressure, taken up in 50 mL of water, and washed with $CHCl_3$. The aqueous layer was acidified with concentrated HCl and extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed under reduced pressure to give 3.9 g (100%) of *N*-phenyl-*N*-prop-2-ynylmalonamic acid (**63**) as a white solid: mp 85−86 °C; IR (film) 2123, 1739, 1661, 1630, 1592, and 1494 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (t, 1H, J = 2.1 Hz), 3.15 (s, 2H), 4.53 (d, 2H, J = 2.1 Hz), 7.27−7.30 (m, 2H), 7.48−7.51 (m, 3H) and 10.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9, 39.1, 73.4, 77.7, 128.0, 129.9, 130.5, 139.6, 168.2, and 169.3. Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.34; H, 5.11; N, 6.45. Found: C, 66.17; H, 5.11; N, 6.32.

Esterification of the above carboxylic acid with 2-propenylphenol gave *N*-phenyl-*N*-prop-2-ynylmalonamic acid 2-propenylphenyl ester (100%), as a 8:1-mixture of trans and cis isomers: IR (neat) 2122, 1763, 1667, 1595, 1493, and 1396 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) trans isomer δ 1.87 (dd, 3H, J = 6.6 and 1.2 Hz), 2.23 (t, 1H, J = 2.4 Hz), 3.47 (s, 2H), 4.56 (d, 2H, J = 2.4 Hz), 6.21 (qd, 1H, J = 15.6 and 6.6 Hz), 6.40 (dd, 1H, J = 15.9 and 1.5 Hz), and 6.97−7.52 (m, 4H); cis isomer δ 1.74 (dd, 3H, J = 6.9 and 1.8 Hz), 2.23 (m, 1H), 3.43 (s, 2H), 4.54 (d, 2H, J = 2.4 Hz), 5.80 (qd, 1H, J = 11.7 and 7.5 Hz), 6.40 (m, 1H), and 6.97−7.52 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) trans isomer δ 19.1, 38.8, 41.6, 72.8, 78.6, 122.5, 124.3, 126.0, 126.4, 126.5, 127.8, 128.6, 129.3, 130.2, 130.6, 141.2, 147.4, 165.3, and 166.0; HRMS calcd for $C_{21}H_{19}NO_3$ 333.1365, found 333.1366.

Diazo transfer of the major *E*-isomer gave **64** in 79% yield: IR (neat) 2127, 1739, 1703, 1642, and 1594 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.86 (d, 3H, J = 4.8 Hz), 2.25 (t, 1H, J = 2.4 Hz), 4.57 (d, 2H, J = 2.4 Hz), 6.09−6.20 (m, 2H), 6.61−6.66 (m, 1H), and 7.10−7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 40.6, 72.8, 78.5, 122.5, 123.9, 126.5, 126.6, 127.2, 127.7, 127.8, 127.9, 128.8, 129.5, 129.5, 141.8, 146.6, 159.8, and 161.1; HRMS calcd for $C_{21}H_{17}N_3O_3$ 359.1270, found 359.1268.

5-Phenyl-3-(2-propenylphenoxy)-5,6-dihydrofuro[3,4-*c*]pyrrol-4-one (65). To a solution of 1.0 g (2.7 mmol) of diazo ester **64** in 50 mL of benzene at 25 °C was added 8 mg of $Rh_2(pfb)_4$. The reaction mixture was stirred for 2 h, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.71 g (81%) of **65** as a clear oil: IR (neat) 1703, 1657, 1593, 1500, and 1376 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.89 (dd, 3H, J = 6.4 and 1.6 Hz), 4.70 (d, 2H, J = 1.6 Hz), 6.30 (qd, 1H, J = 16.0 and 6.4 Hz), 6.73 (dd, 1H, J = 16.0 and 1.6 Hz), 6.88 (t, 1H, J = 1.6 Hz), and 7.09−7.67 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 45.6, 119.3, 119.9, 124.3, 124.4, 124.4, 124.5, 124.8, 125.2, 125.9, 126.9, 128.0, 128.7, 129.2, 140.1, 151.4, 151.8, 160.8; HRMS calcd for $C_{21}H_{17}NO_3$ 331.1208, found 331.1206.

5-Methyl-2-phenyl-2,3-dihydro-10-oxa-2-azacyclopenta[*a*]fluoren-1-one (66). A solution of 0.2 g (0.6 mmol) of **65** in 8 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 15 h. The solution was concentrated under reduced pressure and the residue was subjected to silica gel chromatography. The first fraction isolated from the column contained 0.09 g (47%) of **66** as a yellow solid: mp 247−248 °C; IR (film) 1689, 1595, 1490, 1362, and 1201 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/CD_3OD) δ 2.90 (s, 3H), 4.96 (s, 2H), 7.20−7.24 (m, 2H), 7.31 (s, 1H), 7.40−7.56 (m, 4H), 7.78 (d, 1H, J = 8.1 Hz), 7.89 (d, 1H, J = 8.7 Hz), and 8.05 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$/CD_3OD) δ 20.7, 51.4, 112.6, 115.5, 118.3, 119.7, 122.2, 123.5, 123.7, 124.0, 124.6, 127.3, 129.3, 139.0, 139.5, 140.4, 151.2, 156.8, and 165.9. Anal. Calcd for $C_{21}H_{15}NO_2$: C, 80.48; H, 4.83; N, 4.47. Found: C, 80.26; H, 4.95; N, 4.39.

5-Methyl-2-phenyl-3,3a,5,5a-tetrahydro-2*H*-10-oxa-2-azacyclopenta[a]fluorene-1,4-dione (67). The second fraction isolated from the silica gel column contained 0.08 g (43%) of **67** as a colorless oil: IR (film) 1713, 1702, 1598, 1499, and 1395 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60 (d, 3H, J = 7.2 Hz), 3.66−3.70 (m, 1H), 3.80−3.88 (m, 1H), 3.98−4.08 (m, 1H), 4.54−4.57 (m, 2H), and 7.15−7.62 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 40.5, 40.9, 44.5, 46.9, 112.2, 112.3, 119.3, 120.3, 120.4, 123.1, 125.0, 125.5, 129.1, 138.7, 144.7, 156.3, 168.4, and 207.1. Anal. Calcd for $C_{21}H_{17}NO_3$: C, 76.11; H, 5.17; N, 4.23. Found: C, 76.03; H, 5.22; N, 4.08.

2-Diazo-*N*-phenyl-*N*-prop-2-ynylmalonamic Acid 2-Cyclopent-1-enylphenyl Ester (68). Esterification of *N*-phenyl-*N*-prop-2-ynylmalonamic acid (**63**) with 2-cyclopentenylphenol[64] gave *N*-phenyl-*N*-prop-2-ynylmalonamic acid 2-cyclopent-1-enylphenyl ester (98%) as a yellow oil: IR (neat) 2122, 1764, 1669, 1596, and 1493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85−1.92 (m, 2H), 2.23 (t, 1H, J = 1.8 Hz), 2.39−2.43 (m, 2H), 2.55−2.60 (m, 2H), 3.44 (s, 2H), 4.55 (d, 2H, J = 1.8 Hz), 5.93−5.95 (m, 1H), 7.01−7.03 (m, 1H), and 7.16−7.50 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 33.8, 35.4, 38.9, 41.7, 72.8, 78.6, 123.0, 126.3, 127.8, 128.6, 129.1, 129.3, 130.2, 130.5, 130.8, 138.7, 141.2, 147.8, 165.2, and 166.1; HRMS calcd for $C_{23}H_{21}NO_3$ 359.1521, found 359.1518.

Diazo transfer of the above compound gave diazo ester **68** (71%) as a yellow oil: IR (neat) 2126, 1738, 1702, 1641, 1593, and 1492 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.88−1.96 (m, 2H), 2.24 (t, 1H, J = 1.8 Hz), 2.44−2.49 (m, 2H), 2.50−2.55 (m, 2H), 4.56 (d, 2H, J = 1.8 Hz), 5.87−5.89 (m, 1H), 6.63−6.67 (m, 1H), and 7.10−7.43 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 33.8, 35.4, 40.7, 72.9, 78.6, 123.1, 126.4, 127.3, 127.7, 128.0, 129.1, 129.7, 130.7, 130.8, 138.7, 141.8, 147.0, 159.9, and 161.1; HRMS calcd for $C_{23}H_{19}N_3O_3$ 385.1426, found 385.1424.

3-(2-Cyclopent-1-enylphenoxy)-5-phenyl-5,6-dihydrofuro[3,4-*c*]pyrrol-4-one (69). To a solution of 0.1 g (0.27 mmol) of diazo ester **68** in 8 mL of dry benzene at 25 °C was added 2 mg of $Rh_2(pfb)_4$. The reaction mixture was stirred for 10 min, the solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.09 g (94%) of **69** as a white solid: mp 108−110 °C; IR (film) 1703, 1657, 1593, 1500, and 1376 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.89−1.97 (m, 2H), 2.46−2.51 (m, 2H), 2.73−2.78 (m, 2H), 4.68 (d, 2H, J = 1.2 Hz), 6.29−6.31 (m, 1H), 6.86 (t, 1H, J = 1.2 Hz), 7.09−7.39 (m, 6H), and 7.64−7.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 34.0, 35.4, 45.5, 101.0, 119.6, 119.7, 124.3, 124.7, 125.3, 125.7, 127.9, 129.1, 129.2, 129.4, 131.8, 138.2, 140.1, 151.3, 152.4, and 160.8. Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.28; H, 5.36; N, 3.92. Found: C, 77.14; H, 5.30; N, 3.99.

8-Aza-4-oxa-8-phenyltetracyclo[10.3.0.0^{1,5}.0^{6,10}]pentadec-5(6)-ene-7,11-dione (72). A solution of 0.15 g (0.4 mmol) of furan **69** in 6 mL of xylene was heated at 145 °C in a thick-walled sealed tube for 13 h. The solution was concentrated under reduced pressure, and the residue was subjected to silica gel chromatography to give 0.1 g (68%) of **72** as a yellow oil: IR (film) 1714, 1681, 1597, 1495, and 1389 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.99−2.05 (m, 1H), 2.07−2.15 (m, 2H), 2.17−2.25 (m, 1H), 2.32−2.44 (m, 1H), 2.52−2.61 (m, 1H), 2.91 (dd, 1H, J = 10.0 and 4.8 Hz), 3.92 (dd, 1H, J = 10.0 and 6.0 Hz), 4.00 (t, 1H, J = 10.0 Hz), 4.27 (dd, 1H, J = 10.0 and 6.0 Hz) and 7.06−7.76 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 31.5, 40.8, 41.0, 46.4, 54.1, 58.5, 101.7, 111.4, 119.4, 122.7,

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124.0, 124.6, 129.1, 129.4, 133.1, 139.6, 157.4, 163.5, 163.6, and 209.4. Anal. Calcd for $C_{23}H_{19}NO_3$: C, 77.28; H, 5.36; N, 3.92. Found: C, 77.22; H, 5.25; N, 3.79.

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Supporting Information Available: ^1H 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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