Model Studies Directed toward the Total Synthesis of (±)-Ribasine. A Tandem Cyclization−Cycloaddition Route Leading to the Core Skeleton

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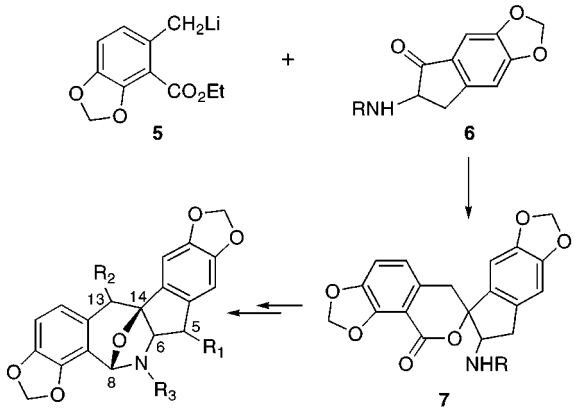
A series of α-diazo-*β*-(*o*-carbomethoxy)-substituted aryl ketones were prepared and employed as model systems for a synthetic approach toward the alkaloid ribasine. Six-membered ring carbonyl ylide dipoles were generated by treating the diazoketones with a rhodium(II) catalyst. The initially formed dipole was trapped using a variety of dipolarophiles including *N*-benzylidene methylamine. The Rh(II)-catalyzed behavior of ethyl 2-diazo-3-(2-formylphenyl)-3-oxo-propionate was also studied to probe the chemoselectivity of the reaction. The major products isolated are derived from bimolecular trapping of the carbonyl ylide dipole, as well as intramolecular C−H insertion of the rhodium carbenoid into the aldehydic hydrogen. Changing the catalyst from Rh(II) trifluoroacetate to Rh(II) acetate caused a significant alteration in product distribution. A study of the tandem cyclization−cycloaddition reaction of an *o*-allyl phenyl substituted diazoketone was also carried out. An unexpected low-temperature intramolecular dipolar cycloaddition of the diazo group across the neighboring *π*-bond first occurred, followed by nitrogen extrusion to give products derived from a 1,3-biradical intermediate. By subjecting the diazoketone to the Rh(II) catalyst at 110 °C, it was possible to prepare the carbonyl ylide derived cycloadduct in high yield. This result provides good precedent for the future implementation of the cycloaddition strategy toward the synthesis of ribasine.

Introduction

Ribasine (**1**), isolated from *Fumariaceae* plants in 1983,[1] is the parent compound of a class of alkaloids that contain an indanobenzazepine in their skeleton and are biogenetically related to the isoquinoline alkaloid family.[2,3] Other members of this class are the hydroxy ribasines himalayamine (**2**)[4] and ribasidine (**3**),[5] and the *N*-demethyl congener norribasine (**4**).[6] Although this family of alkaloids is not known to possess any particular medicinal activity, the presence of the reactive 8,14-epoxy-indano[2,1-*c*][2]benzazepine ring may promote interesting biological responses.[7] Certainly, the structural uniqueness of the skeletal framework makes these compounds attractive targets for synthesis. Rather surprisingly, construction of the ribasine alkaloids has received little attention from synthetic organic chemists.[8] To date, only the Dominguez group[9] has described a successful synthesis of ribasine by a stereocontrolled addition of the 3,4-methylenedioxy-substituted α-lithium-*o*-toluate (**5**) to 2-(9-phenylfluoren-9-yl)-amino-1-indanone (**6**). The resulting lactone **7** was reduced and cyclized to ultimately give ribasine **1** (Scheme 1).[9]

Scheme 1



1; Ribasine, $R_1 = R_2 = H$; $R_3 = Me$
2; Himalayamine, $R_1 = OH$, $R_2 = H$; $R_3 = Me$
3; Ribasidine, $R_1 = H$, $R_2 = OH$; $R_3 = Me$
4; Norribasine, $R_1 = R_2 = R_3 = H$

(1) Boente, J. M.; Castedo, L.; Cuadros, R.; Saá, J. M.; Suau, R.; Perales, A.; Martínez-Ripoll, M.; Fayos, J. *Tetrahedron Lett.* **1983**, *24*, 2029.

(2) Rozwadowska, M. D. *Heterocycles* **1994**, *39*, 903.

(3) Manske, R. H. F. *The Alkaloids*; Academic Press: New York, 1971; Vol. 13, p 166. Ito, S. *Natural Product Chemistry*; Nakanishi, K., Goto, T., Ito, S., Natori, S., Nozoe, S., Eds.; Academic Press: New York, 1975; Vol. 2, pp 310−313.

(4) Allais, D. P.; Guineaudeau, H.; Freyer, A. J.; Shamma, M.; Ganguli, N. C.; Talapatra, B.; Talapatra, S. K. *Tetrahedron Lett.* **1983**, *24*, 2445.

(5) Boente, J. M.; Campello, M. J.; Castedo, L.; Dominguez, D.; Saá, J. M.; Suau, R.; Vidal, M. *Tetrahedron Lett.* **1983**, *24*, 4481.

(6) Allais, D. P.; Guineaudeau, H. *J. Nat. Prod.* **1990**, *53*, 1280.

(7) Substituted phenyl benzazepines have generated considerable interest as medicinal agents for the treatment of psychosis and as specific ligands for serotonin and dopamine receptor subtypes; see: Gentles, R. G.; Middlemiss, D.; Proctor, G. R.; Sneddon, A. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, *6*, 1423. Petterson, I.; Liljefors, T.; Bøgesø, K. *J. Med. Chem.* **1990**, *33*, 2197. McCall, J. M. In *Annual Reports in Medicinal Chemistry*; Academic Press: San Diego, CA, 1990; Vol. 25, pp 1−50.

(8) For some earlier synthetic approaches, see: Paleo, M. R.; Domínguez, D.; Castedo, L. *J. Org. Chem.* **1993**, *58*, 2763. Paleo, M. R.; Domínguez, D.; Castedo, L. *Tetrahedron Lett.* **1993**, *34*, 2369. Allais, D. P.; Guineaudeau, H. *J. Nat. Prod.* **1990**, *53*, 1280. Alonso, R.; Castedo, L.; Domínguez, D. *J. Org. Chem.* **1989**, *54*, 424. Alonso, R.; Castedo, L.; Domínguez, D. *Tetrahedron Lett.* **1986**, *30*, 3539. Ollero, L.; Castedo, L.; Dominguez, D. *Tetrahedron Lett.* **1997**, *32*, 5723.

(9) Ollero, L.; Castedo, L.; Dominguez, D. *Tetrahedron Lett.* **1998**, *39*, 1413.

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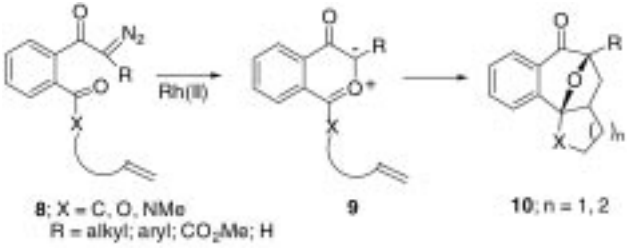
Scheme 2

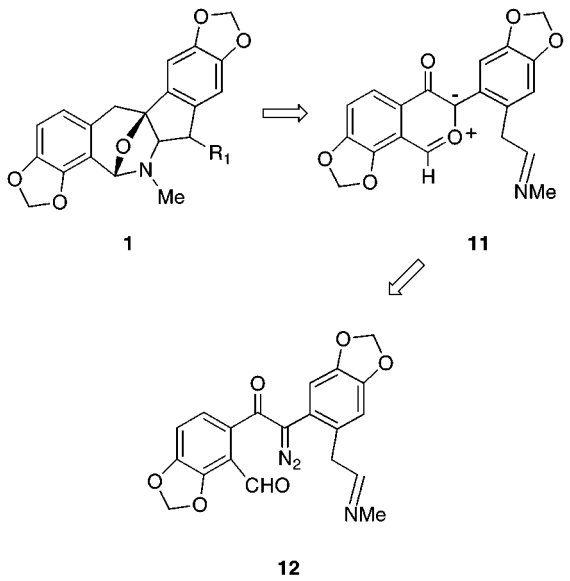


Unlike the above synthesis, which involves formation of the $C_{13}-C_{14}$ bond by nucleophilic addition of an ortho-substituted benzylic anion to a *N*-protected 2-amino-1-indanone, our intention was to construct the indanobenzazepine skeleton in a single step by an intramolecular cycloaddition reaction (vide infra). We have had a long-standing interest in the tandem cyclization−cycloaddition cascade of rhodium carbenoids as a method for the synthesis of natural products.[10,11] Our earlier explorations in this area uncovered efficient intramolecular carbonyl ylide cycloaddition reactions of diazo alkanediones such as **8**.[12] The results arising from this earlier exploratory work stimulated further synthetic investigations in our group that utilized this process as the key *N*-heterocyclic ring building step for the preparation of several different classes of alkaloids.[13] Our previous work also showed that a variety of dipolarophiles could be used to trap the dipole derived from cyclization of the rhodium carbenoid with the neighboring carbonyl group.[14] The high efficiency of the tandem process as exemplified by the transformation **8** → **9** → **10** (Scheme 2) suggested that this method might serve as the basis for a new strategy for the synthesis of ribasine. As depicted in Scheme 3, preparation of ribasine (**1**) based on this design relies on a rhodium(II)-catalyzed cyclization of imino diazo keto aldehyde **12**. We anticipated generating the carbonyl ylide dipole **11** from the Rh(II)-catalyzed reaction of **12**, and we hoped that this intermediate would undergo intramolecular dipolar cycloaddition across the neighboring imine π-bond to produce the indanobenzazepine skeleton found in ribasine. Although the intramolecular cycloaddition reaction to construct a seven-membered ring was precedented,[15] a comparable addition across a C=N double bond had not yet been examined when our synthesis was initiated. The details of our studies include (1) probing the cyclo addition approach described above, (2) uncovering an interesting ligand effect of the metal, and (3) successfully executing a concise transannular cyclization−cycloaddition strategy on a model system are discussed in detail below.

Results and Discussion

The strategy delineated in Scheme 3 for the synthesis of ribasine relies on a tandem cyclization−cycloaddition

Scheme 3



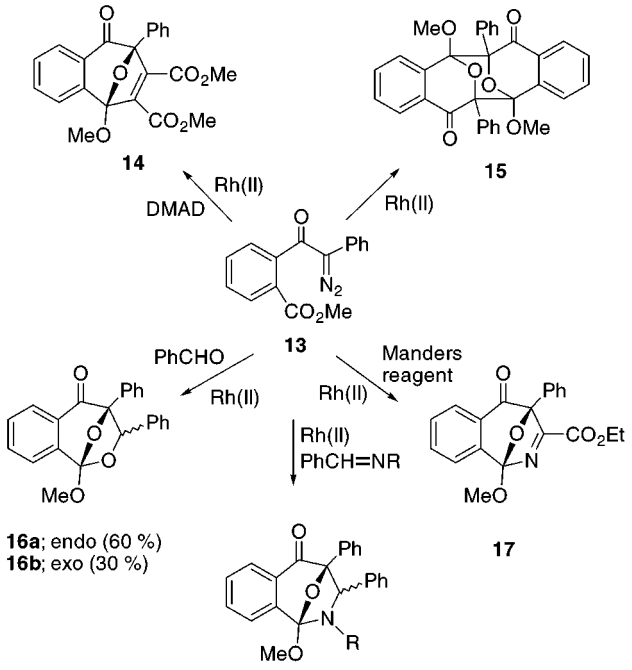
reaction of an appropriately substituted aryl diazoketone (i.e., **12**). To pursue this approach, we decided it was necessary to first probe several issues related to the following questions: (1) Is the rhodium carbenoid derived from an α-diazo-β-aryl ketone comparable in behavior to the more traditionally studied α-diazo-β-ketoester system? (2) What is the propensity for carbonyl ylide dipoles to cycloadd across C=N π-bonds? (3) Do aldehydic groups undergo cyclization with rhodium carbenoids? (4) How does the ligand group on the rhodium catalyst influence the chemoselectivity of dipole formation? This final question is a most important one because the carbonyl and imino groups are equidistant from the carbenoid center generated from diazoketone **12**, and cyclization could result in either a carbonyl or azomethine ylide intermediate.

Our initial foray into this tandem cyclization−cycloaddition chemistry involved substrate **13**, which contained a carbomethoxy group in the ortho-position of the aromatic ring. The tandem cascade was effected by heating a solution of **13** and dimethyl acetylenedicarboxylate with rhodium(II) acetate at 80 °C in toluene. Subsequent chromatography on silica gel afforded the pure cycloadduct **14** in 91% yield. The Rh(II)-catalyzed reaction of **13** in the absence of a trapping agent furnished the 1:1 dimer **15** derived from head-to-tail coupling of the transient carbonyl ylide dipole.

Several types of dipolarophiles were examined so as to establish the scope and generality of the process (Scheme 4). The cycloaddition proceeded readily across the carbonyl group of benzaldehyde affording the expected cycloadduct **16** as a 2:1 mixture of *endo* (**16a**) and *exo* (**16b**) isomers in 90% overall yield. The regiochemistry observed can be readily rationalized in terms of maximum overlap of the dipole HOMO−dipolarophile LUMO, as is generally the case with carbonyl ylide cycloadditions.[16] When Manders reagent[17] was used as the trapping agent, cycloadduct **17** was obtained in 97%

(10) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223.
(11) Padwa, A.; Curtis, E. A.; Sandanayaka, V. P. *J. Org. Chem.* **1997**, *62*, 1317.
(12) Padwa, A.; Carter, S. P.; Nimmesgern, H. *J. Org. Chem.* **1986**, *51*, 1157. Padwa, A.; Carter, S. P.; Nimmesgern, H.; Stull, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 2894.
(13) Padwa, A.; Harring, S. R.; Semones, M. A. *J. Org. Chem.* **1998**, *63*, 44. Padwa, A.; Price, A. T. *J. Org. Chem.* **1998**, *63*, 556. Padwa, A.; Brodney, M. A.; Marino, J. P., Jr.; Sheehan, S. M. *J. Org. Chem.* **1997**, *62*, 78.
(14) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100.
(15) Padwa, A.; Chinn, R. L.; Hornbuckle, S. F.; Zhi, L. *Tetrahedron Lett.* **1989**, *24*, 301. Padwa, A.; Chinn, R. L.; Hornbuckle, S. F.; Zhang, Z. J. *J. Org. Chem.* **1991**, *56*, 3271.
(16) Houk, K. N.; Sims, J.; Duke, R. E.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287.
(17) Mander, L. N.; Sethi, P. *Tetrahedron Lett.* **1983**, 5425.

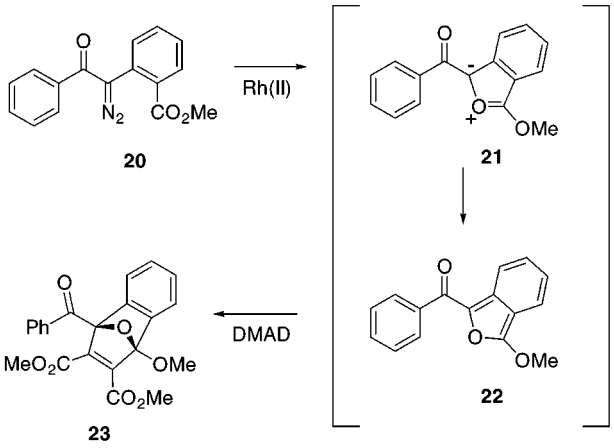
Scheme 4



yield as a single regioisomer, also consistent with FMO theory.[18] Because we were most interested in evaluating the feasibility of cycloaddition of the dipole across a C=N π-bond, we undertook a study of the rhodium(II)-catalyzed reaction of **13** with both *N*-benzylidene benzenesulfonamide and methylamine. In both cases, a mixture of *endo* (major) and *exo* (minor) cycloadducts were obtained. The diastereomers were separated for full characterization, and the *endo* isomer (80%), in the case of cycloadduct **18**, was unequivocally established by an X-ray crystallographic study.[19] The assignment of the stereochemistry of the related cycloadduct **19a** was based on comparison of NMR signals with those of the *endo* isomer **18a**. The results indicate that the *endo* arrangement in the transition state is slightly favored over its *exo* counterpart, perhaps as a consequence of symmetry-controlled HOMO−LUMO interactions.[18,20] The effect of the catalyst on the ratio of stereoisomers was briefly addressed, but the specific catalyst used with this system did not have a pronounced effect on the distribution of isomers. Several aspects of the above chemistry are notable. The tandem cyclization−cycloaddition reactions can be carried out under very mild conditions. This is a clear testimony to the efficiency of the method. In addition, the yields are generally quite high.

Decomposition of the isomeric diazo ketoester **20** also occurred readily in the presence of a catalytic amount of rhodium(II) acetate, producing in this case the five-membered ring dipole **21** (Scheme 5). More than likely,

Scheme 5



this reactive dipole collapses to generate the thermodynamically more stable isobenzofuran **22**. Carrying out the above reaction in the presence of DMAD afforded cycloadduct **23** in 93% yield. It should be noted that all of our attempts to isolate the putative isobenzofuran **22** in the absence of a trapping agent failed to give any characterizable product.

The ease of ring closure as a function of ring size generally increases on going from three- to five-membered rings and then decreases rapidly.[21] This literature observation would tend to suggest that five-membered ring carbonyl ylide formation should occur at a faster rate than six-membered ring formation. Indeed, this was borne out by an examination of the rhodium(II) acetate catalyzed behavior of the dicarbomethoxy-substituted diazoketone **24**. Treatment of **24** with $Rh_2(OAc)_4$ at 110 °C in the presence of DMAD afforded a 4:1-mixture of cycloadducts **27** and **28** in 85% yield. The major product is derived from trapping of the five-membered ring carbonyl ylide **25**, and its structure was unequivocally established by a single-crystal X-ray structure analysis.[19] Interestingly, changing the ligand on the rhodium(II) catalyst caused a significant change in product distribution. Reaction of **24** with $Rh_2(tfa)_4$ and DMAD afforded a 2:1 mixture of the five- and six-membered ring cycloadducts (**27** and **28**) (Scheme 6). Catalysis by rhodium(II) caprolactam ($Rh_2(cap)_4$), however, significantly diminished the yield of the six-membered ring dipole adduct **28** to 5%, and **27** was isolated in 78% yield. Site selectivity in Rh(II)-catalyzed diazocarbonyl reactions are often influenced by the nature of the bridging ligands.[22−24] In the above example, the variation in product distribution presumably reflects both entropic effects and differences in electrophilicity between the various rhodium carbenoids involved in the cyclization−cycloaddition reaction.[23−25]

When rhodium(II) acetate is used as the catalyst, the product distribution encountered amounts to an energy difference of approximately 0.8 kcal/mol at 25 °C. The chemoselectivity encountered is quite similar to that of intramolecular nucleophilic substitution reactions,[21] with

(18) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley-Interscience: New York, 1976.

(19) The authors have deposited coordinates for structures **18a**, **27**, and **35** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(20) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984.

(21) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.

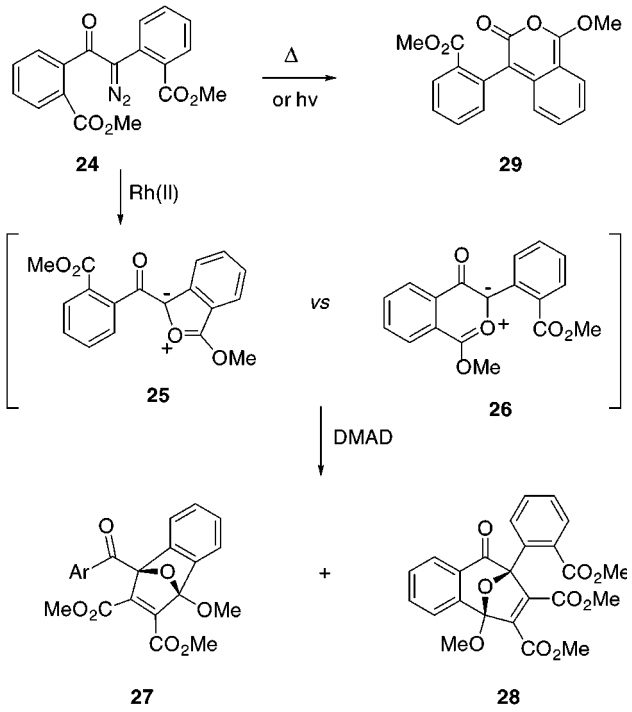
(22) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982; Chapter 7.

(23) Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1797.

(24) Doyle, M. P.; Forbes, D. C.; Protopopova, M. N.; Stanley, S. A.; Vasbinder, M. M.; Xavier, K. R. *J. Org. Chem.* **1997**, *62*, 7210.

(25) Ye, T.; McKervey, A. *Chem. Rev.* **1994**, *94*, 1091.

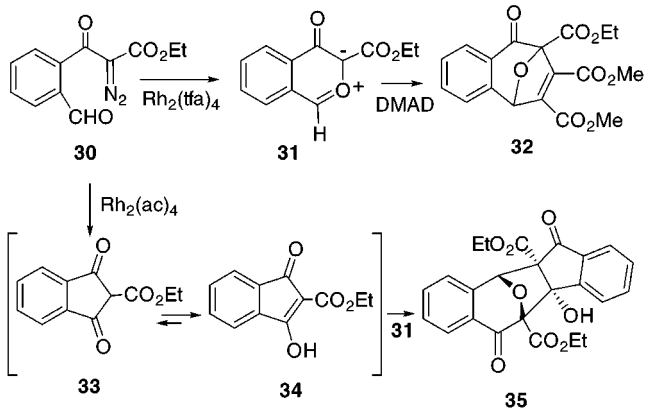
Scheme 6



five-membered ring formation proceeding at the faster rate. This conclusion assumes that the rate of dipolar cycloaddition is approximately the same with both dipoles and that the rate of cyclization to produce the carbonyl ylides would differ. The observed cyclization−cycloaddition profile is clearly related to entropic considerations. The entropy of activation associated with six-membered ring formation is simply more negative than that with the shorter tether. In contrast to the rhodium(II)-catalyzed cycloaddition reaction, heating a sample of **24** in toluene at 110 °C afforded isochromanone **29** in 87% yield. Similar results were obtained upon photolysis of **24** in benzene using a Pyrex filter. The formation of this product can be attributed to an extrusion of nitrogen followed by a Wolff rearrangement of the resulting carbene. The initially formed ketene undergoes a subsequent electrocyclic ring closure to furnish isochromanone **29**.

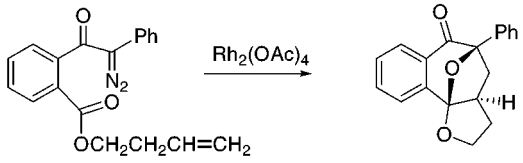
Because an ester carbonyl group in the ortho-position is capable of promoting dipole formation, we decided to explore whether an aldehydic group in the same location would undergo a related reaction. To this end, diazo ketoester **30** was synthesized and subjected to the tandem cyclization−cycloaddition sequence. We were gratified to find that the $Rh_2(tfa)_4$-catalyzed reaction of **30** in the presence of DMAD afforded cycloadduct **32** in 82% yield. This product is derived by trapping of the expected six-membered ring dipole **31** with DMAD (Scheme 7). Most surprisingly, when $Rh_2(OAc)_4$ was used as the catalyst, there were no signs of cycloadduct **32** in the crude reaction mixture. Instead, the only product formed (63%) corresponded to the unusual dimer **35**. The structure of this compound was verified by a single-crystal X-ray analysis.[19] What is so remarkable about this result is the degree of chemoselectivity that can be achieved by simply changing the dirhodium(II) ligand from trifluoracetate to acetate. The more electrophilic ligand on the rhodium metal apparently promotes exclusive dipole formation. We believe that the $Rh_2(OAc)_4$-

Scheme 7



catalyzed reaction produces a mixture of both the six-membered ring dipole **31** as well and as the C−H aldehydic insertion product **33**.[26] Dione **33** exists in rapid equilibrium with its enol tautomer **34**, which in turn undergoes rapid bimolecular cycloaddition with the carbonyl ylide present in solution. Indenone **34** is much more reactive toward dipolar cycloaddition than is DMAD; dimer **35** is the exclusive product formed even when a 3-molar excess of DMAD was present.

Having established the feasibility of the cyclization reaction to occur with an aldehydic group in the ortho-position of the aromatic ring, we next initiated an intramolecular study of the cycloaddition reaction using but-3-enyl diazophenyl benzoate **36**. The internal trapping of a carbonyl ylide dipole with a tethered alkene could prove to be a very effective method for the synthesis of a variety of novel oxypolycyclic ring systems. Diazoketone **36** was easily synthesized starting from benzalphthalide and 3-buten-1-ol. Heating a sample of **36** in toluene at 110 °C in the presence of $Rh_2(OAc)_4$ furnished cycloadduct **37** in 96% yield. In this case, cycloaddition of the dipole readily occurs across the unactivated alkenyl π-bond attached to the ester portion of the molecule. Little difference in the yield of **37** was noted using a variety of ligands on the rhodium(II) metal.

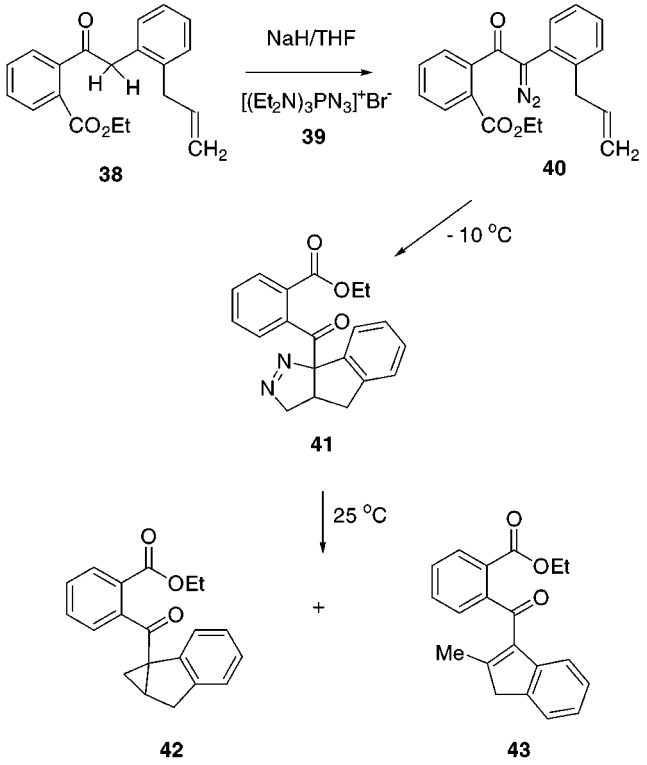


At this point of our studies, we decided to apply the intramolecular cyclization−cycloaddition sequence to the *o*-allyl substituted diazo ketoester **40**. We envisaged that internal cycloaddition of the six-membered ring dipole across the tethered π-bond of this model system would establish the viability of our planned approach toward the indanobenzazepine skeleton of ribasine. Keto ester **38** was treated with azidotris(diethylamino)phosphonium bromide (**39**)[27] at −78 °C and the solution was allowed to warm to −10 °C over a period of several hours. The electrophilic azide salt **39** is an ideal reagent to use for

(26) For a related ligand effect, see: Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669.

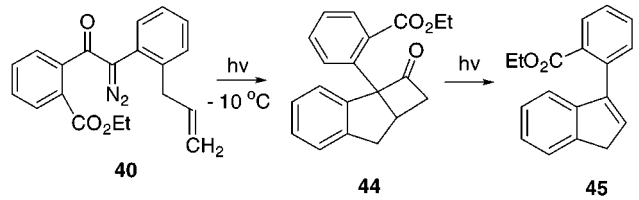
(27) McGuiness, M.; Shechter, H. *Tetrahedron Lett.* **1990**, *31*, 4987.

Scheme 8



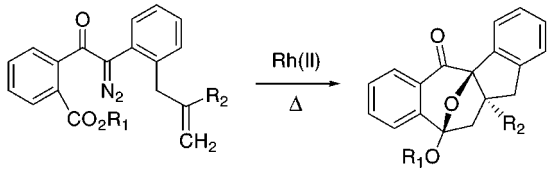
low-temperature diazo transfer reactions because the insoluble byproducts can be easily removed by filtration.[28] We found that formation of the desired diazoketone **40** occurred, but over a period of time, it slowly underwent intramolecular dipolar cycloaddition[29] across the neighboring π-bond at −10 °C to furnish indenopyrazole **41** (Scheme 8). Stirring a sample of **41** in $CHCl_3$ at 25 °C resulted in extrusion of nitrogen and formation of a 1:1 mixture of cyclopropane **42** and indene **43** in 80% overall yield.[30]

In some of the experiments, the diazo transfer−nitrogen extrusion sequence (i.e., **38** → **40** → **42** + **43**) was also accompanied by an additional product (ca. 10%) whose structure was eventually identified as cyclobutanone **44**. This same ketone could be prepared in yields as high as 80% by irradiating a sample of diazo ketoester **40** with a Pyrex filter sleeve. Longer irradiation times led to the formation of indene **45** which results from a Norrish type I induced loss of ketene from cyclobutanone **44**.[31] The formation of cyclobutanone **44** can



be explained in terms of a photochemical (and/or thermal) Wolff rearrangement.[32] The transient ketene that is first formed undergoes a subsequent intramolecular [2 + 2] cycloaddition across the tethered π-bond to furnish the observed product.[33]

The myriad of products encountered in the thermal reaction of diazo ketoester **40** could be significantly suppressed by adding $Rh_2(OAc)_4$ to a hexane solution of **40** and rapidly heating the mixture to 80 °C. In this way, the internal dipolar cycloaddition reaction of the diazo group across the alkenyl π-bond can be minimized. The reaction of **40** under these conditions provides the desired cycloadduct **46** in 65% yield, together with lesser quantities of **42** and **43** (20% total). Various conditions were investigated so as to maximize the yield of **46**. Best results were obtained by heating a sample of **40** in toluene at 110 °C in the presence of $Rh_2(tfa)_4$. With this catalyst system, the ratio of **46** to **43/42** is ≥10:1, and the bicyclic adduct could be isolated in 87% yield. A similar tandem cyclization−cycloaddition sequence was used with the closely related diazoketo diester **47**, which afforded the analogous cycloadduct **48** in 68% yield.



40; $R_1 = C_2H_5$; $R_2 = H$ **46**; $R_1 = C_2H_5$; $R_2 = H$
47; $R_1 = CH_3$; $R_2 = CO_2CH_3$ **48**; $R_1 = CH_3$; $R_2 = CO_2CH_3$

The next task in our projected synthesis of ribasine by this cycloaddition approach would involve using a *N*-methyl imine or its equivalent in place of the methylene π-bond. It seemed reasonable to first evaluate the possibility of using a cyano functionality as the trapping dipolarophile because we had already shown that a carbonyl ylide dipole can cycloadd across a nitrile group in a bimolecular process (i.e., **13** → **17**). Toward this end, cyano ketoester **49** was prepared and treated under the low-temperature diazo transfer conditions previously utilized to prepare **40**. We found, however, that treating **49** with azidotris(diethylamino)phosphonium bromide (**39**) and base gave only the product (i.e., **50**) derived from diazo transfer α to the cyano functionality. When this

compound was allowed to stand at room temperature for 75 min, triazole **53** was obtained in 92% isolated yield. The formation of this compound apparently results by attack of the enol tautomer (i.e., **51**) onto the nitrile functionality followed by a subsequent cyclization at the

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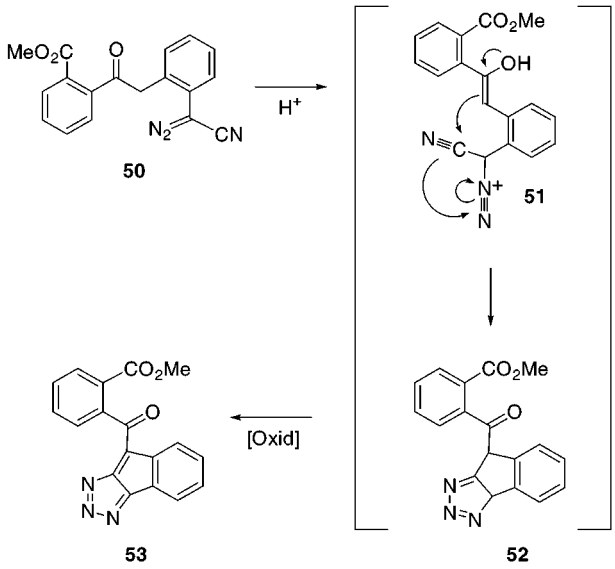
Scheme 9



diazonium site. The product derived from this cyclization (i.e., **52**) undergoes an in situ oxidation to produce the thermodynamically more robust triazole **53** (Scheme 9).

In conclusion, the model studies described in this paper demonstrate that the tandem cyclization−cycloaddition sequence of ortho-substituted diazo ketoesters represents a useful approach toward the synthesis of the oxabicyclo-[3.2.1]octane ring system found in ribasine. In particular, the results obtained with the rhodium(II)-catalyzed reaction of diazo ketoesters **40** and **47** provide good precedent for the future implementation of the strategy toward the synthesis of this alkaloid. Remaining challenges include replacement of the *o*-carboalkoxy functionality with an aldehydic carbonyl group, as well as the incorporation of an imino group at the ortho-position of the second aromatic ring. Further studies along these lines 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 oven-dried glassware under an atmosphere of 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.

6,7-Dicarbomethoxy-5,8-dihydro-5,8-epoxy-5-methoxy-9-oxo-8-phenyl-9*H*-benzocycloheptene (14). The rhodium(II) acetate catalyzed reaction of 0.03 g (0.1 mmol) of α-diazoketone **13**[34] and 0.2 mL of dimethyl acetylenedicarboxylate (DMAD) in 2 mL of toluene at 80 °C for 40 min gave cycloadduct **14** as a white solid (91%): mp 135−136 °C; IR (KBr) 1725, 1649, 1593, 1432, and 1258 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.72 (s, 3H), 3.76 (s, 3H), 7.40−7.58 (m, 6H), 7.71 (d, 2H, J = 7.5 Hz), and 7.99 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 52.6, 52.7, 91.5, 108.8, 122.5, 126.6, 126.7, 128.1, 128.6, 128.9, 129.9, 132.7, 133.3, 142.0, 142.5, 147.3, 161.2, 163.0, and 187.1. Anal. Calcd for $C_{22}H_{18}O_7$: C, 67.01; H, 4.60. Found: C, 66.94; H, 4.63.

5,6,7,12,13,14-Hexahydro-5,12-dimethoxy-7,14-dioxo-6,13-diphenyl-5,13:6,12-diepoxydibenzo[*a*,*f*]cyclodecene (15). The rhodium(II) acetate catalyzed reaction of 0.1 g (0.4 mmol) of α-diazoketone **13** in 50 mL of toluene at 80 °C for 10 min gave the head-to-tail dimer **15** (87% yield) as a white powder: mp 245−246 °C; IR (KBr) 1704, 1597, 1282, and 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, 3H), 6.57 (d, 1H, J = 7.8 Hz), 7.11 (dt, 1H, J = 7.8 and 1.0 Hz), 7.21−7.24 (m, 3H), 7.32 (dt, 1H, J = 7.8 and 1.0 Hz), 7.80−7.82 (m, 2H), and 8.05 (dd, 1H, J = 7.8 and 1.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.7, 85.1, 100.8, 126.7, 126.9, 127.0, 127.4, 127.8, 129.1, 132.2, 133.0, 134.9, 136.8, and 190.4. Anal. Calcd for $C_{32}H_{24}O_6$: C, 76.18; H, 4.79. Found: C, 76.21; H, 4.83.

1-Methoxy-9,10-diphenyl-11,12-dioxa-tricyclo[7.2.1](2,7)-dodeca-2,4,6-trien-8-one (16). The rhodium(II) acetate catalyzed reaction of 39 μL (0.4 mmol) of benzaldehyde and 0.1 g (0.4 mmol) of diazoketone **13** in 3 mL of toluene at 110 °C for 15 min gave a 2:1 mixture of the *endo* (**16a**, 60%) and *exo* (**16b**, 30%) cycloadducts. Silica gel chromatography furnished the *endo* isomer **16a** as a white solid: mp 49−50 °C; IR (neat) 1707, 1604, 1452, 1292, 1220, and 1071 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.21 (s, 1H), 6.87 (d, 2H, J = 7.4 Hz), 7.17−7.26 (m, 3H), 7.38−7.45 (m, 3H), 7.52 (t, 1H, J = 7.4 Hz), 7.58−7.60 (m, 2H), 7.69 (t, 1H, J = 7.7 Hz), 7.80 (d, 1H, J = 7.7 Hz), and 7.95 (d, 1H, J = 7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 49.7, 85.0, 91.2, 117.5, 122.2, 126.3, 127.1, 127.5, 127.9, 128.2, 128.3, 129.0, 129.4, 130.8, 133.7, 133.8, 134.1, 143.5, and 191.0. Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.09; H, 5.09. Found: C, 77.35; H, 5.30.

The second fraction contained the *exo* isomer **16b** as a white crystalline solid: mp 169−170 °C; IR (KBr) 1702, 1601, 1455, 1290, 1228, and 1073 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 3H), 5.14 (s, 1H), 7.09−7.17 (m, 8H), 7.22 (dd, 2H, J = 7.5 and 1.5 Hz), 7.53 (dt, 1H, J = 7.5 and 0.9 Hz), 7.68 (dt, 1H, J = 7.5 and 0.9 Hz), 7.75 (d, 1H, J = 7.5 Hz), and 8.08 (d, 1H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 50.6, 81.2, 90.5, 117.7, 122.8, 127.1, 127.3, 127.5, 128.0, 128.1, 128.4, 129.2, 129.5, 133.1, 134.5, 136.1, 142.1, and 192.0. Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.09; H, 5.06. Found: C, 77.00; H, 5.10.

Ethyl 1-Methoxy-8-oxo-9-phenyl-12-oxa-11-aza-tricyclo[7.2.1](2,7)-dodeca-2,4,6,10-tetraene-10-carboxylate (17). The rhodium(II) acetate catalyzed reaction of 0.2 g (0.5 mmol) of diazoketone **13** with 61 μL (0.6 mmol) of ethyl cyanoformate in 5 mL of toluene at 110 °C for 30 min gave cycloadduct **17** (97%) as a pale yellow oil: IR (neat) 1735, 1718, 1640, 1276, and 1059 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, 3H, J = 7.2 Hz), 3.82 (s, 3H), 4.24 (m, 2H), 7.40−7.59 (m, 5H), 7.67 (dd, 1H, J = 7.5 and 0.9 Hz), 7.83 (dd, 2H, J = 8.1 and 1.5 Hz), and 7.96 (dd, 1H, J = 7.5 and 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 51.4, 62.7, 95.9, 120.9, 123.0, 126.6, 126.9, 127.3, 127.8, 127.9, 128.2, 128.4, 131.1, 140.9, 161.1, 168.8, and 185.2. Anal. Calcd for $C_{20}H_{17}NO_5$: C, 68.36; H, 4.88; N, 3.99. Found: C, 68.19; H, 4.93; N, 3.90.

11-Benzenesulfonyl-1-methoxy-9,10-diphenyl-12-oxa-11-azatricyclo-[7.2.1](2,7)-dodeca-2,4,6-trien-8-one (18). The rhodium(II) acetate catalyzed reaction of 0.15 g (0.5 mmol) of diazoketone **13** and 0.1 g (0.5 mmol) of *N*-benzylidenebenzenesulfonamide in 5 mL of toluene at 110 °C for 30 min gave an 8:1 mixture of *endo* (**18a**) (80%) and *exo* (**18b**) (10%) cycloadducts. Recrystallization of the crude reaction mixture from ether afforded crystals of the *endo* cycloadduct **18a**: mp 178−179 °C; IR (KBr) 1707, 1602, 1220, and 1155 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 3H), 5.04 (s, 1H), 6.59 (d, 2H, J = 7.8 Hz), 6.96 (t, 2H, J = 7.8 Hz), 7.10−7.18 (m, 4H), 7.23 (d, 2H, J = 7.4 Hz), 7.33 (s, 5H), 7.55 (t, 1H, J = 7.8 Hz), 7.76 (t, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), and 7.98 (d, 1H, J = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 70.9, 87.9, 110.9, 122.5, 125.9, 127.2, 127.4, 127.5, 127.7, 127.8, 128.2, 128.4, 128.5, 129.3, 129.6, 130.1, 131.6, 132.1, 134.3, 141.0, 143.7, and 190.2. Anal. Calcd for $C_{29}H_{23}NO_5S$: C, 70.00; H, 4.66; N, 2.81. Found: C, 69.97; H, 4.70; N, 2.72.

Silica gel chromatography of the mother liquor afforded the *exo* cycloadduct **18b** as a white solid: mp 195−196 °C; IR (KBr) 1704, 1600, 1448, and 1171 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.83 (s, 1H), 7.04−7.24 (m, 12H), 7.33 (t, 2H, J = 8.0 Hz), 7.49 (dt, 1H, J = 7.5 and 1.2 Hz), 7.64 (d, 1H, J = 8.0 Hz), 7.73 (dt, 1H, J = 7.5 and 1.2 Hz), 7.78 (d, 1H, J = 7.5 Hz), and 7.99 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.6, 66.4, 90.1, 110.2, 125.2, 127.2, 127.4, 127.5, 127.6, 128.0,

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128.1, 128.4, 128.5, 129.6, 127.7, 132.7, 132.9, 136.1, 142.9, and 192.2. Anal. Calcd for $C_{29}H_{23}NO_5S$: C, 70.00; H, 4.66; N, 2.81. Found: C, 69.89; H, 4.66; N, 2.78.

1-Methoxy-11-methyl-9,10-diphenyl-12-oxa-11-aza-tricyclo[7.2.1](2,7)-dodeca-2,4,6-trien-8-one (19). The rhodium(II) acetate catalyzed reaction of 0.2 g (0.6 mmol) of diazoketone **13** with 150 μL (1.2 mmol) of *N*-benzylidene methyl-amine in 5 mL of toluene at 110 °C for 30 min gave a 2:1 mixture of *endo* (**19a**) (60%) and *exo* (**19b**) (30%) cycloadducts. Silica gel chromatography of the mixture afforded a pure sample of the *endo* isomer **19a** as a colorless oil: IR (neat) 1703, 1599, 1449, and 1263 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.17 (s, 3H), 3.68 (s, 3H), 4.65 (s, 1H), 6.74 (d, 2H, J = 6.9 Hz), 7.18−7.27 (m, 5H), 7.31 (dd, 2H, J = 4.5 and 1.5 Hz), 7.42−7.45 (m, 2H), 7.62 (d, 2H, J = 4.5 Hz), and 8.01 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.7, 49.9, 73.9, 90.3, 110.6, 122.7, 126.1, 127.4, 127.6, 127.8, 128.2, 128.3, 128.4, 130.0, 131.3, 133.2, 133.9, 136.1, 146.0, and 192.4. Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.45; H, 5.61; N, 3.56.

The second fraction isolated from the column contained the *exo* isomer **19b** as a white solid: mp 138−139 °C; IR (KBr) 1699, 1599, 1448, and 1065 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.04 (s, 3H), 3.69 (s, 1H), 3.83 (s, 3H), 7.04−7.10 (m, 7H), 7.23−7.25 (m, 3H), 7.49 (dt, J = 7.1 and 2.0 Hz), 7.63−7.66 (m, 2H), and 8.14 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.7, 49.3, 71.5, 88.1, 110.9, 124.5, 126.7, 126.9, 127.3, 127.5, 127.6, 127.7, 127.8, 128.7, 128.8, 129.4, 133.7, 138.3, 140.9, and 192.1. Anal. Calcd for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77. Found: C, 77.50; H, 5.65; N, 3.72.

Methyl 2-(2-Oxo-2-phenylethyl)benzoate. A procedure similar to that used by McKillop[35] was employed to synthesize 2-(2-oxo-2-phenyl)ethyl benzoic acid. To a solution containing 20 g (120 mmol) of 1-benzoyl acetone, 2.5 g (12 mmol) of 2-bromobenzoic acid, and 0.1 g (0.7 mmol) of cuprous bromide in 20 mL of benzene under nitrogen was added 1.2 g (30 mmol) of NaH (60%) in 10 mL of benzene. The reaction mixture was heated at reflux for 3 h, cooled to 25 °C, and poured into 50 mL of water. The solution was allowed to stand for 15 min and was filtered through a pad of Celite. The filtrate was extracted with ether, and the aqueous layer was acidified to pH 3 with concentrated HCl. The white solid that formed was washed with 10 mL of water, dried, and dissolved in 20 mL of THF.

To a solution of 30 mmol of diazomethane in ether at 0 °C was added the above solution, and the mixture was warmed to 25 °C, stirred overnight, and concentrated under reduced pressure. The resultant residue was recrystallized from ether−hexane to give 0.55 g of methyl 2-(2-oxo-2-phenylethyl) benzoate as a white solid: mp 93−94 °C; IR (KBr) 1710, 1682, 1596, 1267, and 1082 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 3H), 4.73 (s, 2H), 7.24−7.61 (m, 6H), and 8.05−8.08 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.8, 51.8, 127.1, 128.1, 128.5, 129.5, 131.0, 132.3, 132.5, 132.9, 136.8, 137.0, 167.3, and 197.1. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.52; H, 5.57.

Dimethyl 1-Benzoyl-8-methoxy-11-oxa-tricyclo[6.2.1]-(2,7)undeca-2,4,6,9-tetraene-9,10-dicarboxylate (23). A suspension containing 0.01 g (0.5 mmol) of NaH in 2 mL of THF was cooled to −78 °C under N_2 and treated with a solution containing 0.19 g (0.5 mmol) of azidotris(diethylamino)phosphonium bromide[30] and 0.1 g (0.4 mmol) of the above ester in 1 mL of THF. The resulting solution was stirred at −78 °C for 10 min and was allowed to warm to 0 °C over a 2 h period. The solution was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 0.06 g (51%) of α-diazoketone **20** as a labile orange oil which was immediately used in the next step to minimize decomposition: IR (neat) 2070, 1723, 1626, and 1255 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H), 7.31−7.46 (m, 5H), 7.49−7.56 (m, 3H), and 8.02 (d, 1H, J = 7.8 Hz).

The rhodium(II) acetate catalyzed reaction of 0.06 g (0.2 mmol) of α-diazoketone **20** with 32 μL (0.3 mmol) of DMAD in 3 mL of toluene at 110 °C for 40 min gave **23** in 93% yield as a white solid: mp 124−125 °C; IR (KBr) 1726, 1689, 1457, and 1257 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.64 (s, 3H), 3.70 (s, 3H), 3.72 (s, 3H), 7.00−7.11 (m, 2H), 7.35 (t, 2H, J = 7.5 Hz), 7.42−7.55 (m, 3H), and 8.06 (d, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 55.3, 89.2, 115.4, 120.7, 122.3, 126.7, 126.8, 128.4, 130.2, 133.8, 134.4, 143.0, 146.3, 147.8, 155.2, 162.3, 162.8, and 191.3. Anal. Calcd for $C_{22}H_{18}O_7$: C, 67.00; H, 4.60. Found: C, 66.83; H, 4.68.

Dimethyl 1-Methoxy-8-(2-methoxycarbonyl-benzoyl)-11-oxa-tricyclo-[6.2.1](2,7)undeca-2,4,6,9-tetraene-9,10-dicarboxylate (27). To a solution containing 0.06 g (0.9 mmol) of potassium methoxide in 2 mL of dry CH_3CN at 0 °C under N_2 was added a solution of 0.16 g (0.8 mmol) of tosyl azide and 0.2 g (0.7 mmol) of 3-(2-carbomethoxybenzylidene)phthalide[36] in 8 mL of CH_3CN. The mixture was stirred at 25 °C for 3 h, filtered through a pad of Celite with ether, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with a 10% NaOH solution followed by a pH 7 phosphate buffer, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 0.11 g (45%) of methyl 2-[1-diazo-2-oxo-2-(2-carbomethoxyphenyl)-ethyl] benzoate (**24**) as a labile oil which was immediately used in the next step to minimize decomposition: IR (neat) 2093, 1722, 1631, and 1285 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.89 (s, 3H), 3.92 (s, 3H), and 7.23−8.04 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 52.4, 73.1, 127.1, 128.1, 128.5, 129.0, 129.4, 129.6, 130.3, 130.4, 131.1, 132.2, 132.4, 140.3, 166.3, 166.4, and 189.1.

The rhodium(II) acetate catalyzed reaction of 0.05 g (0.2 mmol) of α-diazoketone **24** with 24 μL (0.2 mmol) of DMAD in 2 mL of toluene at 110 °C for 1.5 h followed by removal of the solvent afforded a clear oil which was subjected to silica gel chromatography. The major fraction isolated (68%) corresponded to cycloadduct **27** and was obtained as a white solid: mp 160−161 °C; IR (KBr) 1729, 1654, 1436, and 1290 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.53 (s, 3H), 3.59 (s, 3H), 3.73 (s, 3H), 3.82 (s, 3H), 7.12−7.14 (m, 2H), 7.40−7.43 (m, 1H), 7.49−7.60 (m, 4H), and 7.92 (dd, 1H, J = 7.1 and 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.4, 52.5, 52.7, 55.1, 90.2, 114.5, 120.7, 120.8, 126.7, 126.9, 128.1, 129.4, 130.2, 130.9, 132.3, 137.7, 142.9, 144.0, 147.4, 156.7, 161.9, 162.9, 166.7, and 197.4. Anal. Calcd for $C_{24}H_{20}O_9$: C, 63.70; H, 4.46. Found: C, 63.58; H, 4.39.

The minor fraction isolated from the column contained cycloadduct 6-dicarbomethoxy-5,8-dihydro-5,8-epoxy-5-methoxy-9-oxo-8-(2-carbomethoxyphenyl)-9*H*-benzocycloheptene (**28**) (17%) as a white solid: mp 149−150 °C; IR (neat) 1729, 1653, 1437, and 1254; ^1H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.82 (s, 3H), 3.94 (s, 3H), 4.06 (s, 3H), 7.49−7.77 (m, 4H), 7.91 (m, 1H), and 8.15−8.22 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.6, 52.7, 52.7, 52.8, 88.4, 113.9, 123.2, 123.6, 128.3, 128.9, 129.0, 130.1, 131.0, 132.3, 133.8, 142.0, 142.6, 153.1, 164.7, 164.9, 166.6, and 181.3. Anal. Calcd for $C_{24}H_{20}O_9$: C, 63.70; H, 4.46. Found: C, 63.51; H, 4.42.

Methyl 2-(1-Methoxy-3-oxo-3*H*-isochromen-4-yl)-benzoate (29). Heating a 0.05 g (0.2 mmol) sample of α-diazoketone **24** at 110 °C in toluene for 12 h followed by silica gel chromatography afforded isochromanone **29** (87%) as a pale yellow oil: IR (neat) 1743, 1727, 1647, 1290, and 1256 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 3H), 3.87 (s, 3H), 6.85 (d, 1H, J = 8.1 Hz), 7.26−7.32 (m, 2H), 7.46−7.51 (m, 2H), 7.60 (dt, 1H, J = 7.5 and 1.2 Hz), 8.04 (dd, 1H, J = 7.5 and 1.2 Hz), and 8.24 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.9, 56.5, 96.1, 117.0, 123.0, 125.1, 128.1, 129.8, 130.8, 131.7, 132.2, 132.8, 133.0, 134.9, 140.9, 153.1, 161.0, and 167.0; HRMS calcd for $C_{18}H_{14}O_5$ 310.0841, found 310.0840.

Ethyl 2-Diazo-3-(2-formyl-phenyl)-3-oxo-propionate (30). A solution of LDA was prepared by the addition of 4.0 mL (6.7 mmol) of a 1.6 M solution of *n*-BuLi in hexane to 0.9 mL (6.7

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mmol) of diisopropylamine in 10 mL of THF at 0 °C. This solution was added dropwise to a mixture containing 0.9 g (7.6 mmol) of ethyl diazoacetate and 1.1 g (6.1 mmol) of 2-dimethoxymethylbenzaldehyde[37] in 30 mL of THF at −78 °C. After 2 h of stirring at −78 °C, the solution was transferred to an ice bath and was quenched by the addition of 5 mL of a pH 7 phosphate buffer solution. The reaction mixture was extracted with CH_2Cl_2, and the organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give ethyl 2-diazo-3-(2-dimethoxymethylphenyl)-3-hydroxy-propionate as a yellow oil: IR (neat) 3440, 2097, 1685, 1371, and 1107 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, J = 7.1 Hz), 3.33 (s, 6H), 4.27 (q, 2H, J = 7.1 Hz), 5.44 (s, 1H), 6.23 (s, 1H), 7.34 (dt, 1H, J = 7.5 and 1.2 Hz), 7.41 (dt, 1H, J = 7.5 and 1.2 Hz), 7.56 (d, 1H, J = 7.5 Hz), and 7.65 (d, 1H, J = 7.5 Hz). This compound was used directly in the next step without further purification.

A 3.1 g (12.1 mmol) sample of $BaMnO_4$ was added to a solution of the above ester in 60 mL of CH_2Cl_2, and the mixture was heated at reflux for 44 h. After cooling to room temperature, the mixture was filtered through a plug of Celite and was concentrated under reduced pressure to give ethyl 2-diazo-3-(2-dimethoxymethylphenyl)-3-oxo-propionate as a yellow oil: IR (neat) 2143, 1726, 1693, 1269, and 1108 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 7.2 Hz), 3.27 (s, 6H), 4.15 (q, 2H, J = 7.2 Hz), 5.64 (s, 1H), 7.24 (d, 1H, J = 7.7 Hz), 7.37 (t, 1H, J = 7.7 Hz), 7.44 (dt, 1H, J = 7.7 and 0.9 Hz), and 7.61 (d, 1H, J = 7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 52.5, 61.2, 100.2, 126.4, 126.8, 127.7, 129.5, 135.5, 137.3, 160.5, and 188.4. This compound was used in the next step without further purification.

To a suspension of 14 g of silica gel in 80 mL of CH_2Cl_2 was added 2.8 mL of 10% HCl with vigorous stirring. A solution of the above ester in 20 mL of CH_2Cl_2 was added dropwise to the silica gel suspension, the reaction mixture was stirred at 25 °C for 3 h, and then 0.8 g of solid $NaHCO_3$ was added to the mixture. After 5 min of stirring, the solid phase was separated, and the solution was concentrated under reduced pressure. The resulting residue was subjected to flash silica gel chromatography to give 0.9 g (53% yield) of ethyl 2-diazo-3-(2-formylphenyl)-3-oxo-propionate (**30**) as a yellow solid: mp 58−59 °C; IR (neat) 2147, 1717, 1698, 1320, and 1126 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.13 (t, 3H, J = 7.1 Hz), 4.09 (q, 2H, J = 7.1 Hz), 7.34 (dd, 1H, J = 7.0 and 1.8 Hz), 7.63 (m, 2H), 7.87 (dd, 1H, J = 7.0 and 1.8 Hz), and 9.99 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 61.4, 127.1, 130.2, 131.4, 133.6, 133.7, 139.6, 160.5, 190.8, and 190.9. Anal. Calcd for $C_{12}H_{10}N_2O_4$: C, 58.54; H, 4.09; N, 11.38. Found: C, 58.36; H, 4.15; N, 11.33.

9-Ethyl-10,11-dimethyl-8-oxo-12-oxa-tricyclo[7.2.1](2,7)-dodeca-2,4,6,10-tetraene-9,10,11-tricarboxylate (32). The rhodium(II) trifluoroacetate catalyzed reaction of 0.06 g (0.3 mmol) of α-diazoketone **30** with 38 μL (0.3 mmol) of DMAD in 5 mL of CH_2Cl_2 at 40 °C for 40 min followed by silica gel chromatography afforded cycloadduct **32** (82%) as a white solid: mp 121−122 °C; IR (KBr) 1743, 1723, 1710, 1651, 1602, and 1284 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, 3H, J = 7.1 Hz), 3.77 (s, 3H), 3.86 (s, 3H), 4.37 (m, 2H), 5.92 (s, 1H), 7.30 (dd, 1H, J = 7.2 and 1.2 Hz), 7.49 (m, 2H), and 8.01 (dd, 1H, J = 7.2 and 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 52.8, 52.8, 62.9, 82.9, 96.5, 123.8, 126.7, 129.1, 129.7, 134.0, 141.2, 141.5, 142.9, 160.7, 162.9, 163.1, and 183.2. Anal. Calcd for $C_{18}H_{16}O_8$: C, 60.01; H, 4.48. Found: C, 60.11; H, 4.49.

The same reaction was repeated using rhodium(II) acetate, which furnished 4*b*,5,6,11,11*a*,12-hexahydro-5,11*a*-dicarboethoxy-4*b*-hydroxy-6,12-dioxo-dibenz[*a*,*f*]-azulene (**35**) (63%) as a white solid: mp 188−189 °C; IR (KBr) 3400, 1750, 1721, 1603, and 1277 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (t, 3H, J = 7.2 Hz), 1.22 (t, 3H, J = 7.2 Hz), 4.08 (m, 4H), 5.12 (s, 1H), 5.90 (s, 1H), 7.44−7.61 (m, 4H), 7.74 (d, 1H, J = 7.0 Hz), 7.76 (d, 1H, J = 7.5 Hz), and 8.07 (t, 2H, J = 8.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 13.9, 62.0, 63.0, 74.8, 79.8, 87.5, 93.1, 123.7, 127.0, 127.4, 128.0, 129.3, 129.6, 130.8, 133.3, 134.6, 135.9, 139.7, 151.9, 163.5, 165.8, 185.6, and 193.6. Anal. Calcd for $C_{24}H_{20}O_8$: C, 66.06; H, 4.62. Found: C, 65.91; H, 4.56.

6,7-Dicarbomethoxy-5,8-dihydro-5,8-epoxy-5-methoxy-9-oxo-8-phenyl-9*H*-benzocycloheptene (37). To a solution containing 0.1 g (0.3 mmol) of 60% NaH in 10 mL of ether at 0 °C under N_2 was added 0.2 g (0.3 mmol) of 3-buten-1-ol. The reaction mixture was stirred at 0 °C for 15 min, and the ether was removed under reduced pressure. The resulting salt was suspended in 5 mL of CH_3CN and cooled to 0 °C under N_2. To this suspension was added a mixture of 0.5 g (2.5 mmol) of tosyl azide and 0.5 g (2.2 mmol) of benzalphthalide in 5 mL of CH_3CN. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. An additional 0.5 g (2.5 mmol) of tosyl azide was added, followed by 0.3 g (0.3 mmol) of sodium salt of 3-buten-1-ol in 5 mL of CH_3CN at 0 °C. The reaction mixture was stirred overnight at 25 °C, the solution was filtered through Celite with ether, and the solvent was removed under reduced pressure. The residue was subjected to flash silica gel chromatography to give 0.3 g (42%) of but-3-enyl 2-(2-diazophenylacetyl) benzoate (**36**) as a bright orange oil: IR (neat) 2076, 1720, 1636, 1596, and 1283 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.35−2.42 (m, 2H), 4.29 (t, 2H, J = 6.7 Hz), 5.05 (dd, 1H, J = 9.8 and 1.2 Hz), 5.04 (dd, 1H, J = 17.0 and 1.2 Hz), 5.67−5.80 (m, 1H), 7.21 (t, 1H, J = 7.5 Hz), 7.30−7.60 (m, 7H), and 7.99 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.7, 61.3, 64.6, 117.3, 125.3, 125.5, 126.8, 127.0, 128.6, 128.9, 129.8, 130.6, 132.6, 133.7, 140.5, 165.6, and 189.2. The diazoketone was immediately used in the next step to minimize decomposition.

The rhodium(II) acetate catalyzed reaction of 0.04 g (0.1 mmol) of diazoketone **36** in 25 mL of toluene at 110 °C for 10 min gave the internal cycloadduct **37** in 96% yield as a white solid: mp 141−142 °C; IR (KBr) 1696, 1602, 1444, 1272, 1194, and 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85−1.96 (m, 1H), 2.31 (dd, 1H, J = 12.8 and 4.0 Hz), 2.32−2.44 (m, 1H), 2.71 (dd, 1H, J = 12.8 and 8.7 Hz), 2.75−2.84 (m, 1H), 4.40 (ddd, 1H, J = 15.5, 7.2, and 1.9 Hz), 4.53 (ddd, 1H, J = 15.5, 7.5, and 1.5 Hz), 7.29−7.66 (m, 9H), and 7.96 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.4, 40.5, 48.3, 71.5, 91.0, 113.9, 121.7, 126.1, 127.7, 127.9, 128.7, 130.0, 133.9, 138.8, 144.8, and 195.5. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.07; H, 5.52. Found: C, 78.15; H, 5.56.

3-(2-Allylbenzylidene)phthalide. A procedure similar to that used by Weiss[38] was employed to synthesize 3-(2-bromobenzylidene)phthalide. In a three-necked, 50 mL round-bottom flask equipped with a thermometer and two glass stoppers was placed 2.0 g (13.5 mmol) of phthalic anhydride, 3.4 g (16 mmol) of 2-bromophenyl-acetic acid, and 0.05 g (0.6 mmol) of anhydrous NaOAc. The reaction mixture was heated for 2 h at 220 °C and cooled to room temperature, and the solid was recrystallized from CH_2Cl_2−ether to give 2.2 g (55%) of 3-(2-bromobenzylidene)phthalide as light yellow crystals:[39] mp 153−154 °C; IR (KBr) 1785, 1475, and 1075 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (s, 1H), 7.15 (t, 1H, J = 7.7 Hz), 7.38 (t, 1H, J = 7.7 Hz), 7.58 (t, 1H, J = 7.7 Hz), 7.62 (d, 1H, J = 7.7 Hz), 7.75 (t, 1H, J = 7.7 Hz), 7.86 (d, 1H, J = 7.7 Hz), 7.95 (d, 1H, J = 7.7 Hz), and 8.29 (d, 1H, J = 7.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 104.9, 120.2, 123.4, 124.6, 125.5, 127.7, 129.4, 130.2, 131.8, 132.5, 132.9, 134.6, 140.3, 145.7, and 166.7.

A solution containing 2.0 g (6.6 mmol) of the above phthalide, 2.2 mL (7 mmol) of allyltributyltin, and 0.07 g (0.07 mmol) of tetrakis(triphenylphosphine)palladium(0) in 7 mL of benzene was heated at 100 °C in a sealed tube for 2 h. The mixture was cooled to room temperature, diluted with ether, and poured into a 10% aqueous KF solution. The aqueous mixture was extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to flash silica gel chromatography to give 1.2 g (69%) of 3-(2-allylbenzylidene)phthalide as white needles: mp 89−90 °C; IR (KBr)

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1784, 1770, 1657, 1637, and 1264 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.55 (d, 2H, J = 6.0 Hz), 5.04 (dd, 1H, J = 16.8 and 1.1 Hz), 5.11 (dd, 1H, J = 10.5 and 1.1 Hz), 6.01 (ddt, 1H, J = 16.8, 10.5 and 6.0 Hz), 6.67 (s, 1H), 7.28 (m, 3H), 7.55 (t, 1H, J = 7.5 Hz), 7.70 (d, 1H, J = 7.5 Hz), 7.76 (d, 1H, J = 7.5 Hz), 7.93 (d, 1H, J = 7.5 Hz), and 8.16 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.2, 103.9, 104.9, 116.2, 119.8, 123.5, 125.5, 127.0, 128.6, 129.9, 130.9, 131.5, 134.4, 136.8, 140.6, 144.8, and 167.1. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.21; H, 5.39.

Ethyl 2-[(2-Allylphenyl)acetyl]-benzoate (38). To a solution containing 0.7 g (2.7 mmol) of the above compound in 15 mL of absolute ethanol was added 0.3 mL concentrated sulfuric acid and the mixture was heated at 55 °C for 12 h. The solution was poured into a pH 7 phosphate buffer, extracted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography. The major fraction isolated from the column contained 0.4 g (48%) of **38** as a clear oil: IR (neat) 1715, 1638, 1596, and 1279 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, 3H, J = 7.2 Hz), 3.37 (d, 2H, J = 6.3 Hz), 4.18 (s, 2H), 4.36 (q, 2H, J = 7.2 Hz), 4.94 (dd, 1H, J = 17.1 and 1.5 Hz), 5.03 (dd, 1H, J = 10.4 and 1.5 Hz), 5.90 (ddt, 1H, J = 17.1, 10.4 and 6.3 Hz), 7.19 (m, 5H), 7.48 (m, 2H), and 7.92 (dd, 1H, J = 6.7 and 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 37.4, 46.8, 61.6, 115.8, 126.5, 126.6, 127.4, 128.6, 129.6, 129.8, 130.9, 131.9, 132.4, 136.8, 142.9, 166.5, and 202.8. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.97; H, 6.56.

Ethyl 2-(3*a*,4-Dihydro-3*H*-indeno[1,2-*c*]pyrazole-8*b*-carbonyl)-benzoate (41). A suspension containing 0.08 g (1.9 mmol) of NaH (60%) in 5 mL of THF was washed with hexane, cooled to −78 °C under nitrogen, and treated with a solution containing 0.77 g (2.1 mmol) of azidotris(diethylamino)phosphonium bromide (**39**)[27] and 0.48 g (1.6 mmol) of **38** in 4 mL of THF. The solution was stirred at −78 °C for 10 min and then at −10 °C for 2 h. Removal of the solvent under reduced pressure afforded ethyl 2-[(2-allylphenyl)-diazo-acetyl]-benzoate (**40**) as an orange oil (71%), which was immediately used in the next step to minimize decomposition; IR (neat) 2079, 1716, 1282, and 1084 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36 (t, 3H, J = 7.0 Hz), 3.47 (d, 2H, J = 6.3 Hz), 4.36 (q, 2H, J = 7.0 Hz), 5.06 (d, 1H, J = 17.0 Hz), 5.10 (d, 1H, J = 9.6 Hz), 5.95 (m, 1H), 7.00−7.60 (m, 6H), 7.68 (t, 1H, J = 7.8 Hz), and 7.97 (d, 1H, J = 7.8 Hz).

When a hexane solution of α-diazoketone **40** was allowed to stand at −10 °C for 4 days, it slowly underwent intramolecular 1,3-dipolar cycloaddition to give indenopyrazole **41** (55%) as a white solid: mp 83−84 °C; IR (KBr) 1705, 1654, 1282, and 1081 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 0.76 (t, 3H, J = 7.2 Hz), 2.16 (d, 1H, J = 16.5 Hz), 3.23 (dd, 1H, J = 16.5 and 8.2 Hz), 3.37 (ddd, 1H, J = 9.8, 8.2 and 6.2 Hz), 3.55 (dd, 1H, J = 18.1 and 6.2 Hz), 3.72 (m, 2H), 4.76 (dd, 1H, J = 18.1 and 9.8 Hz), 6.78−6.98 (m, 5H), 7.24 (d, 1H, J = 7.5 Hz), 7.32 (t, 1H, J = 8.0 Hz), and 7.71 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 37.9, 38.7, 61.7, 77.3, 86.0, 117.4, 125.0, 125.7, 127.0, 128.6, 129.2, 120.4, 129.7, 132.9, 138.4, 141.8, 166.0, and 203.2.

Ethyl 2-(6,6*a*-Dihydro-1*H*-cycloprop[*a*]indene-1*a*-carbonyl)-benzoate (42). A solution containing 0.1 g (0.3 mmol) of **41** in 1.0 mL of chloroform was allowed to stand at 25 °C for 2 days. Removal of the solvent under reduced pressure afforded a clear oil, which was subjected to flash silica gel chromatography. Cyclopropane **42** was obtained (40%) as a clear oil: IR (neat) 1717, 1674, 1277, and 1259 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (dd, 1H, J = 5.6 and 4.2 Hz), 1.21 (t, 3H, J = 7.2 Hz), 2.17 (dd, 1H, J = 8.6 and 4.2 Hz), 2.58 (ddd, 1H, J = 8.6, 6.8 and 5.6 Hz), 2.96 (d, 1H, J = 16.9 Hz), 3.35 (dd, 1H, J = 16.9 and 6.8 Hz), 4.21 (m, 2H), 7.04 (m, 5H), 7.44 (dt, 1H, J = 7.5 and 1.1 Hz), 7.51 (dt, 1H, J = 7.5 and 1.1 Hz), and 7.91 (d, 1H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 27.9, 33.3, 34.4, 45.7, 61.5, 104.9, 125.3, 126.1, 126.2, 126.8, 129.1, 129.2, 129.8, 132.1, 142.0, 142.2, 142.6, 165.9, and 204.2. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 77.84; H, 5.88.

Ethyl 2-(2-Methyl-3*H*-indene-1-carbonyl)-benzoate (43). The second fraction isolated from the above chromatographic separation contained indene **43** (40%) as a colorless oil: IR (neat) 1720, 1671, 1596, and 1280 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, 3H, J = 7.1 Hz), 1.86 (s, 3H), 3.51 (s, 2H), 4.04 (q, 2H, J = 7.1 Hz), 7.17 (t, 1H, J = 7.2 Hz), 7.25 (t, 1H, J = 7.2 Hz), 7.37 (d, 1H, J = 7.2 Hz), 7.46 (d, 1H, J = 7.2 Hz), 7.57 (m, 2H), 7.67 (d, 1H, J = 7.2 Hz), and 7.92 (d, 1H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 16.4, 45.1, 61.6, 121.8, 123.0, 124.8, 126.6, 127.4, 129.8, 130.0, 130.1, 130.4, 137.3, 140.7, 143.0, 143.2, 155.9, 166.9, and 194.3; HRMS calcd for $C_{20}H_{18}O_3$ 306.1256, found, 306.1269.

Ethyl 2-(2-Oxo-1,2,7,7*a*-tetrahydrocyclobut[*a*]inden-2*a*-yl)-benzoate (44). In addition to the above two compounds, a small amount (8%) of cyclobutanone **44** was also isolated from the chromatograhic column as a clear oil: IR (neat) 1773, 1715, 1259, and 1072 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, 3H, J = 7.1 Hz), 2.75 (dd, 1H, J = 17.5 and 5.2 Hz), 3.03 (d, 1H, J = 16.5 Hz), 3.38 (ddd, 1H, J = 9.0, 7.0 and 5.2 Hz), 3.52 (dd, 1H, J = 16.5 and 7.0 Hz), 3.56 (dd, 1H, J = 17.5 and 9.0 Hz), 4.23 (m, 2H), 7.10 (dt, 1H, J = 7.5 and 0.9 Hz), 7.30 (m, 6H), and 7.76 (dd, 1H, J = 7.5 and 1.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 37.8, 38.6, 51.1, 61.2, 83.9, 125.8, 126.6, 127.1, 127.4, 128.4, 129.4, 130.0, 131.0, 131.3, 138.7, 141.3, 144.3, 168.7, and 205.1. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.13; H, 5.91.

Cyclobutanone **44** could also be obtained in higher yield by carrying out an irradiation of a solution of 0.09 g (0.3 mmol) of **40** in 200 mL of CH_2Cl_2 at −10 °C with a 450-W Hanovia lamp equipped with a Pyrex glass filter sleeve for 1 h under argon. Removal of the solvent under reduced pressure followed by silica gel chromatography of the residue gave **44** in 80% yield.

Ethyl 2-(1*H*-Inden-3-yl)-benzoate (45). A solution containing 0.06 g (0.2 mmol) of cyclobutanone **44** in 100 mL of CH_2Cl_2 at 25 °C was irradiated with a 450-W Hanovia lamp equipped with a Pyrex glass filter sleeve for 3 h under argon. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography to give the known indene **45**[40] as a clear oil in 78% yield: IR (neat) 1713, 1598, 1288, and 1128 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, 3H, J = 7.0 Hz), 3.52 (d, 2H, J = 1.9 Hz), 3.96 (q, 2H, J = 7.0 Hz), 6.46 (t, 1H, J = 1.9 Hz), 7.07 (m, 1H), 7.20 (m, 2H), 7.50 (m, 4H), and 7.95 (dd, 1H, J = 7.5 and 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 38.1, 60.8, 119.5, 123.7, 124.5, 126.0, 127.5, 130.0, 130.2, 130.6, 130.9, 131.7, 136.4, 143.2, 145.2, 145.5, and 168.0.

4*b*,10-Epoxy-10-ethoxy-4*b*,5,10,11,11a,12-hexahydro-5-oxo-dibenz-[*a*,*g*]azulene (46). A mixture containing 0.1 g diazoketone **40** and 0.02 g of rhodium(II) acetate in 80 mL of hexane was rapidly heated at 80 °C for 30 min. Removal of the solvent followed by silica gel chromatography afforded cycloadduct **46** (65%) together with a 1:1 mixture of **42** and **43** in 20% yield. Repetition of the experiment using rhodium(II) trifluoroacetate in toluene at 110 °C for 30 min gave cycloadduct **46** as a crystalline solid in 87% yield: mp 142−143 °C; IR (neat) 1696, 1600, 1454, 1174, and 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 7.0 Hz), 2.29 (dd, 1H, J = 12.2 and 6.4 Hz), 2.52 (dd, 1H, J = 12.2 and 9.0 Hz), 2.94 (m, 1H), 3.06 (dd, 1H, J = 16.6 and 5.8 Hz), 3.44 (dd, 1H, J = 16.6 and 9.5 Hz), 3.70 (m, 2H), 7.24−7.52 (m, 6H), 7.64 (t, 1H, J = 7.5 Hz), and 8.09 (d, 1H, J = 7.5 Hz);^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 39.1, 43.2, 44.2, 60.6, 98.5, 109.7, 123.5, 124.9, 126.9, 127.0, 127.4, 128.6, 130.1, 130.7, 133.9, 136.5, 145.9, 146.1, and 194.1. Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.53; H, 5.96.

Methyl 2-[2-[2-(2-Methoxycarbonylallyl)phenyl]acetyl]-benzoate. To a solution containing 0.9 g (3 mmol) of 3-(2-bromobenzylidene)phthalide and 1.8 g (4.5 mmol) of 2-(carbomethoxy)allyl tributyltin[41] in 4 mL of toluene was added 0.02 g (0.03 mmol) of bis(tri-*o*-tolylphosphine) palladium(II) chlo-

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ride,[42] and the mixture was heated for 1 h at reflux under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 0.5 g (52%) of 3-[2-(2-methyl-allyl)-benzylidene]-3*H*-isobenzofuranone as a white solid: mp 105−106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.80 (s, 2H), 5.28 (s, 1H), 6.25 (s, 1H), 6.58 (s, 1H), 7.20−7.37 (m, 3H), 7.55 (dt, 1H, J = 7.0 and 1.1 Hz), 7.69−7.77 (m, 2H), 7.93 (d, 1H, J = 7.6 Hz), and 8.18 (d, 1H, J = 7.6 Hz).

To a solution containing 0.5 g (1.5 mmol) of the above compound in 8 mL of methanol was added 0.15 mL of concentrated sulfuric acid, and the mixture was heated at 60 °C for 12 h. The solution was poured into a pH 7 phosphate buffer and extracted with ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to silica gel chromatography to give 0.25 g (48%) of methyl 2-[2-[2-(2-methoxycarbonylallyl)-phenyl]acetyl] benzoate: IR (neat) 1720, 1715, 1640, 1598, and 1280 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62 (s, 2H), 3.73 (s, 3H), 3.88 (s, 3H), 4.15 (s, 2H), 5.22 (s, 1H), 6.18 (s, 1H), 7.13−7.56 (m, 7H), and 7.91 (dd, 1H, J = 7.1 and 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 46.7, 51.8, 52.5, 126.3, 126.5, 126.8, 127.4, 128.2, 129.6, 129.9, 130.3, 131.1, 132.1, 132.6, 137.3, 139.3, 143.0, 166.9, 167.3, and 202.7. Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.56; H, 5.72. Found: C, 71.38; H, 5.66.

11*a*-Carbomethoxy-4*b*,10-epoxy-4*b*,5,10,11,11a,12-hexahydro-10-methoxy-5-oxo-dibenz[*a*,*g*]azulene (48). The above compound was subjected to the diazo transfer conditions using azidotris(diethylamino)phosphonium bromide (**39**) as the diazo transfer agent. No attempts were made to isolate or characterize diazo ketoester **47**. Instead, the crude mixture was subjected to the rhodium(II) acetate thermal conditions, and the crude residue was subjected to silica gel chromatography to give **48** as a white solid (68%): mp 136−137 °C; IR (neat) 1733, 1702, 1600, and 1263 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (d, 1H, J = 12.7 Hz), 3.04 (d, 1H, J = 12.7 Hz), 3.27 (s, 3H), 3.30 (d, 1H, J = 16.5 Hz), 3.38 (s, 3H), 3.71 (d, 1H, J = 16.5 Hz), 7.19−7.46 (m, 6H), 7.60 (t, 1H, J = 7.5 Hz), and 7.97 (t, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.6, 47.4, 52.5, 52.7, 62.0, 100.4, 109.8, 123.6, 124.5, 126.8, 127.1, 127.2, 128.9, 130.4, 131.9, 134.0, 135.9, 144.5, 145.1, 172.8, and 191.4. Anal. Calcd for $C_{21}H_{18}O_5$: C, 71.98; H, 5.18. Found: C, 71.84; H, 5.03.

[2-(3-Oxo-3*H*-isobenzofuran-1-ylidene-methyl)phenyl]-acetonitrile. A solution containing 1.0 g (3.3 mmol) of 3-(2-bromobenzylidene)phthalide, 0.12 g (0.5 mmol) of palladium acetate, 1.26 g (3.8 mmol) of cyanomethyltributyltin,[43] and 0.33 g (1.1 mmol) of tri-*o*-tolylphosphine in 60 mL of toluene under an argon atmosphere was heated at reflux for 12 h. The solvent was removed under reduced pressure, and the residue was filtered and recrystallized from CH_2Cl_2−ether to give 0.6 g (71%) of [2-(3-oxo-3*H*-isobenzofuran-1-ylidene-methyl)phenyl]-acetonitrile: mp 180−181 °C; IR (KBr) 2246, 1785, 1764, 1659, and 982 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 2H), 6.45 (s, 1H), 7.27 (t, 1H, J = 7.5 Hz), 7.34−7.39 (m, 2H), 7.54 (t, 1H, J = 7.5 Hz), 7.78 (d, 1H, J = 7.5 Hz), 7.88 (d, 1H, J = 7.5 Hz), and 8.05 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 101.7, 117.4, 120.2, 123.7, 125.7, 128.1, 128.8, 128.9, 129.3, 130.5, 131.3, 131.4, 134.7, 139.8, 146.2, and 166.6. Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.13; H, 4.26; N, 5.19.

Methyl 2-[2-[2-(Cyanomethyl)phenyl]acetyl]-benzoate (49). To a solution containing 0.4 g (1.5 mmol) of the above compound in 70 mL of methanol was added 5 drops of concentrated sulfuric acid, and the reaction mixture was heated at reflux for 12 h. The solution was poured into a pH 7 phosphate buffer and extracted with ether. The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Recrystallization of the residue gave 0.26 g (58%) of methyl 2-[2-[2-(cyanomethyl)phenyl]acetyl] benzoate: mp 126−127 °C; IR (KBr) 2250, 1715, 1693, 1458, 1287, and 1115 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (s, 2H), 3.83 (s, 3H), 4.15 (s, 2H), 7.11 (d, 1H, J = 6.5 Hz), 7.17−7.28 (m, 3H), 7.39−7.54 (m, 3H), and 7.98 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 47.3, 52.7, 118.0, 126.2, 127.8, 128.3, 129.1, 129.8, 130.0, 130.1, 131.6, 132.1, 132.5, 143.1, 166.6, and 202.2. Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.77. Found: C, 73.54; H, 5.24; N, 4.61.

Methyl 2-(Indeno[1,2,3]triazole-8-carbonyl)-benzoate (53). A suspension containing 0.009 g (0.4 mmol) of NaH in 2 mL of THF was cooled to −78 °C under nitrogen and treated with 0.15 g (0.4 mmol) of azidotris(diethylamino)phosphonium bromide[27] in 2 mL of THF. After the mixture stirred for 10 min, 0.09 g (0.3 mmol) of cyano ester **50** in 2 mL of THF was added, and the reaction mixture was stirred at −78 °C for 10 min and then at −25 °C for 2 h. The crude α-diazo nitrile was filtered through a plug of silica gel using ether as the eluent to give methyl 2-[2-[2-(cyanodiazo-methyl)phenyl]acetyl] benzoate (**50**) as an orange oil: IR (neat) 2244, 2086, 1717, 1623, and 1282 cm^{-1}. This diazo compound rapidly decomposed and was used immediately in the next step without further purification.

A 0.1 g sample of **50** in 8 mL of toluene was stirred at 25 °C for 75 min. The solution was concentrated under reduced pressure, and the residue was recrystallized from CH_2Cl_2−hexane to give **53** (92%) as a yellow solid: mp 184−185 °C; IR (KBr) 1705, 1690, 1299, and 1225 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (s, 3H), 7.64 (dt, 1H, J = 7.8 and 1.4 Hz), 7.69−7.79 (m, 2H), 8.04 (d, 1H, J = 7.8 Hz), 8.15−8.26 (m, 2H), 8.38 (d, 1H, J = 7.8 Hz), and 9.18 (d, 1H, J = 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 113.9, 124.1, 124.3, 127.4, 127.7, 128.9, 129.3, 129.8, 130.6, 133.0, 134.5, 135.6, 139.9, 141.6, 154.6, 166.6, and 196.3. Anal. Calcd for $C_{18}H_{11}N_3O_3$: C, 68.14; H, 3.49; N, 13.24. Found: C, 68.04; H, 3.45; N, 13.02.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for new compounds lacking elemental analyses and ORTEP drawings for structures **18a**, **27**, and **35** (5 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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