An Approach to Lysergic Acid Utilizing an Intramolecular Isomünchnone Cycloaddition Pathway

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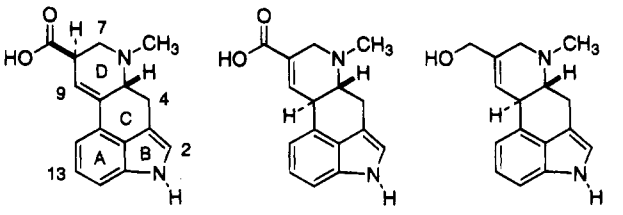
A series of alkenyl- and alkynyl-substituted diazo imides were prepared to demonstrate that the intramolecular cycloaddition across a transient isomünchnone dipole was a viable approach to the quinoline ring system (rings C and D) of the ergot alkaloids. The diazo imides were synthesized by N-malonylacylation of the appropriate amide followed by exposure to standard diazo transfer conditions. The carbenoid intermediate derived by treatment of the diazo imide with rhodium(II) acetate undergoes ready cyclization onto the neighboring amide carbonyl oxygen to generate an isomünchnone intermediate. Subsequent 1,3-dipolar cycloaddition across the pendant olefin affords the cycloadduct in high yield. The stereochemical assignment of several of the cycloadducts was deduced by X-ray crystallography. The stereochemical outcome of the reaction is the consequence of an *endo* cycloaddition of the neighboring π-bond across the transient isomünchnone dipole. Exposure of the olefinic cycloadduct to boron trifluoride etherate resulted in exclusive carbon–oxygen bond cleavage producing a transient *N*-acyliminium ion which undergoes rapid proton loss to afford an enamide derivative. In contrast, exposure of the acetylenic cycloadduct to boron trifluoride etherate resulted in exclusive carbon–nitrogen bond cleavage. The resulting oxonium ion underwent reduction with triethylsilane, producing a dihydrofuran derivative. In the absence of a reducing agent, the alkyne cycloadduct underwent a retro Diels–Alder reaction to give a substituted furan derivative in high yield. The Rh(II) acetate catalyzed reaction of the appropriate diazo imide precursor to lysergic acid resulted in a mixture of the desired dipolar cycloadduct as well as a C–H insertion product. Switching to rhodium(II) perfluorobutyrate as the catalyst significantly enhanced the cycloadditon pathway. The inability to carry out a double-bond isomerization thwarted our efforts to synthesize lysergic acid.

The dried sclerotial bodies of the filamentous ergot fungus *Claviceps purpurea,* found on the infected seed heads of rye, have proven to be a rich source of alkaloids possessing a wide spectrum of interesting and potent biological activity.[1–3] As early as the 17th century, members of this family of alkaloids had been implicated in outbreaks of the deadly epidemic known as Saint Anthony's Fire, caused by ingesting bread made from the flour of wet, infested rye grain.[1–3] Since that time, several biologically active members of the ergot family have found useful application in the treatment of hypertension, migraine, prolactin-dependent disorders, and postpartum hemorrhage.[1] The hallucinatory properties[4] of lysergic acid diethylamide (LSD) were extensively exploited by the hippie culture in the 1960s. The pioneering investigations of Stoll dealing with the isolation and characterization of the active components of the ergot alkaloids showed that lysergic acid (**1**) was a central figure.[2,3] All of the natural derivatives isolated to date have been shown to contain amides of lysergic acid in which the amide portion is a small peptide or a simple alkyl amide. Other members of the ergot alkaloid family that have been isolated and fully characterized include paspalic acid[5] (**2**) which can be readily converted to lysergic acid upon alkaline hydrolysis,[6] as well as elymoclavine (**3**),[7] a key intermediate in the biosynthetic pathway to ergot alkaloids.[8]



1; lysergic acid **2**; paspalic acid **3**; elymoclavine

As a result of lysergic acid's role as a key member of the ergot alkaloid family, it has garnered a rich synthetic history. To date, there have been eight independent syntheses,[9–16] the first by Kornfeld and Woodward[9] in

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

(1) Berde, C.; Schild, H. O., Eds. *Ergot Alkaloids and Related Compounds*; Springer-Verlag: Berlin, 1978.
(2) Stoll, H.; Hofmann, A. *The Alkaloids*; Academic Press: New York, 1965; Vol. III.
(3) Stoll, H.; Hoffmann, A. In *The Chemistry of Alkaloids*; Pelletier, S. W., Ed.; Van Nostrand: New York, 1971.
(4) Stoll, H. *Schweiz. Arch. Neurol. Psychiatr.* **1947**, *60*, 279.
(5) Kobel, H.; Schreier, E.; Rutschmann, J. *Helv. Chim. Acta* **1964**, *47*, 1057.
(6) Troxler, F. *Helv. Chim. Acta* **1968**, *51*, 1372.
(7) Ninomiya, I.; Hashimoto, C.; Kiguichi, T. *Heterocycles* **1984**, *22*, 1035.
(8) Floss, H. G. *Tetrahedron* **1976**, *32*, 873.
(9) Kornfeld, E. C.; Fornefeld, E. J.; Kline, G. B.; Mann, M. J.; Jones, G. G.; Woodward, R. B. *J. Am. Chem Soc.* **1954**, *76*, 5256. Kornfeld, E. C.; Fornefeld, E. J.; Kline, G. B.; Mann, M. J.; Morrison, D. E.; Jones, R. G.; Woodward, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 3087.
(10) Julia, M.; Le Goffic, F.; Igolen, J.; Baillarge, M. *Tetrahedron Lett.* **1969**, 1569.
(11) Ramage, R.; Armstrong, V. W.; Coulton, S. *Tetrahedron Lett.* **1976**, 4311. Ramage, R.; Armstrong, V. W.; Coulton, S. *Tetrahedron Suppl.* **1981**, *37*, 157.
(12) Oppolzer, W.; Francotte, E.; Battig, K. *Helv. Chim. Acta* **1981**, *64*, 478.
(13) Kiguichi, T.; Hashimoto, C.; Naito, T.; Ninomya, I. *Heterocycles* **1982**, *19*, 2279.
(14) Rebek, J., Jr.; Tai, D. F. *Tetrahedron Lett.* **1983**, *24*, 859. Rebek, J., Jr.; Tai, D. F.; Shue, Y. K. *J. Am. Chem. Soc.* **1984**, *106*, 1813.
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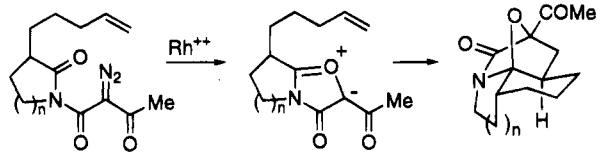
0022-3263/95/1960-2704$09.00/0

1954 and the last being completed in 1994 by Vollhardt.[16] The strategy utilized in these approaches has generally been divided into two classes, each defined by the choice of starting material (*i.e.* indole or indoline derivatives). Only the Oppolzer group[12] has successfully achieved a synthesis of lysergic acid starting from the indole nucleus. The high reactivity of the indole ring and the potential for indole–naphthalene tautomerization[9] implied that a synthetic approach to lysergic acid using an indoline derivative would be more advantageous and less fraught with obstacles than an approach starting with an indole system.

Earlier reports from our laboratories and others have demonstrated that monocyclic and fused-bicyclic piperidines may be synthesized by the 3 + 2 cycloaddition reaction of mesoionic isomünchnones with various π-bonds.[17–19] We were able to show that the dipolar cycloaddition of isomünchnones with alkenes also occurred intramolecularly and that the overall reaction represents an efficient way to synthesize complex polyheterocyclic ring systems.[20] The complexity of the resultant cycloadducts was significantly increased by generating isomünchnones where the peripheral substituents were part of a cyclic system containing a tethered alkene (*i.e.* **4**→**6**).[21,22]



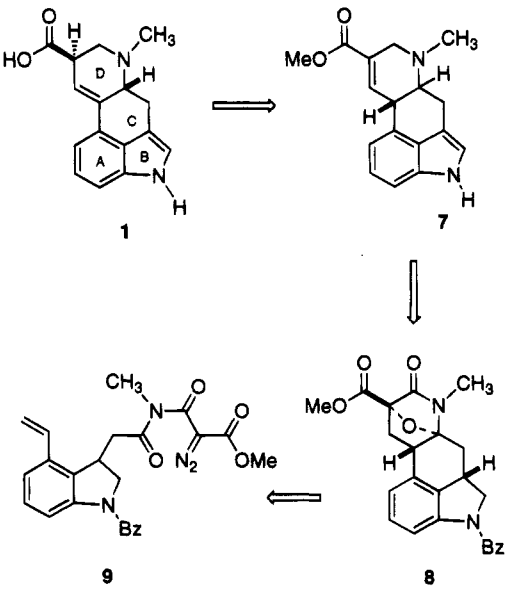
As an extension of our work with isomünchnone cycloadditions, we planned to use this method as the key step in a total synthesis of lysergic acid. Detailed in this paper are our efforts toward this goal.

Our retrosynthetic analysis of lysergic acid (Scheme 1) suggests that the quinoline skeleton (rings C and D) could be constructed by chemical manipulation of the aza–oxo ketal within cycloadduct **8**. Conversion of cycloadduct **8** to the methyl ester of paspalic acid (**7**), which has already been shown to undergo isomerization to lysergic acid under alkaline conditions,[6] would constitute a novel strategic route to lysergic acid and other members of the ergot alkaloids. Cycloadduct **8** could, in principle, be constructed in a single step utilizing an intramolecular 1,3-dipolar cycloaddition of an appropriately functionalized isomünchnone (*i.e.* **9**).

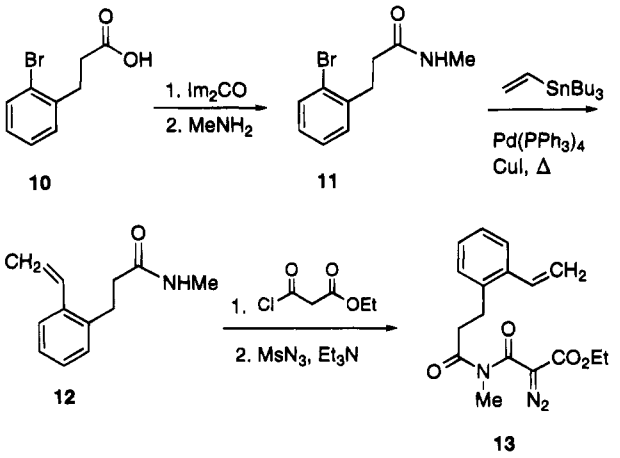
Results and Discussion

Our initial goal was to demonstrate that intramolecular dipolar cycloaddition of an isomünchnone across a

Scheme 1



pendent olefin or alkyne would provide the quinoline ring skeleton (rings C and D) observed in lysergic acid and other ergot alkaloids. Toward this end, diazo imide **13** was synthesized as a model system as it contains the appropriately positioned olefin. Treatment of 3-(2-bromophenyl)propanoic acid (**10**)[23] with 1,1′-carbonyldiimidazole[21] followed by quenching of the acyl imidazolide with 40% aqueous methylamine afforded the *N*-methyl-substituted amide **11** in 93% yield. Subjection of **11** to a



palladium(0)-catalyzed Stille coupling with vinyltributyltin[24] produced amide **12** which contained the appropriately positioned double bond for cycloaddition. N-Malonylacylation[21] followed by standard diazo transfer methodology[25] gave the prerequisite diazo imide **13**. In a related fashion, *N*-methyl-3-(2-iodophenyl)propanamide[23] (**14**) was prepared and was used for the introduction of an alkyne tether. Treatment of aryl iodide **14** with (trimethylsilyl)acetylene under modified Castro–Stevens[26,27] conditions gave, after basic methanolysis of

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(17) Padwa, A.; Hertzog, D. L.; Chinn, R. L. *Tetrahedron Lett.* **1989**, *30*, 4077. Doyle, M. P.; Pieters, R. J.; Tauton, J.; Pho, H. Q.; Padwa, A.; Hertzog, D. L.; Precedo, L. *J. Org. Chem.* **1991**, *56*, 820.

(18) For some alternate methods to generate isomünchnones, see: Hamaguchi, M. *J. Chem. Soc., Chem. Commun.* **1978**, 247. Hamaguchi, M.; Ibata, T. *J. Chem. Soc., Chem. Commun.* **1980**, 230. Potts, K. T.; Marshall, J. L. *J. Org. Chem.* **1979**, *44*, 626. Haddadin, M. J.; Tannus, H. T. *Heterocycles*, **1984**, *22*, 773. Moore, D. R.; Mathias, L. J. *J. Org. Chem.* **1987**, *52*, 1599. Hamaguchi, M.; Ibata, T. *Tetrahedron Lett.* **1974**, 4475.

(19) Padwa, A.; Hertzog, D. L. *Tetrahedron* **1993**, *49*, 2589.

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(23) Ciufolini, M. A.; Browne, M. E. *Tetrahedron Lett.* **1987**, *28*, 171.

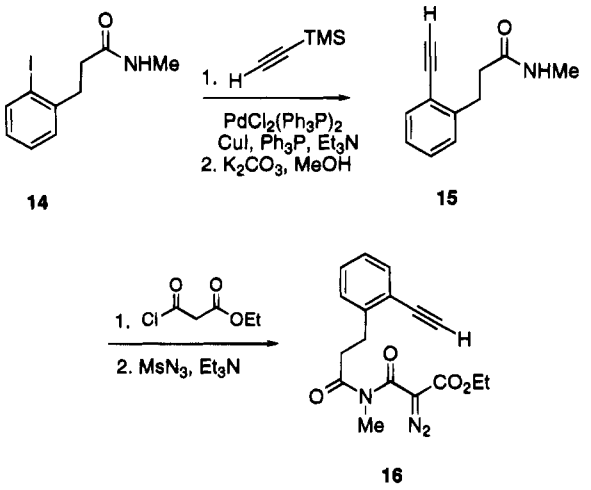
(24) McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422.

(25) Taber, D. F.; Ruckle, R. E., Jr.; Hennesy, M. J. *J. Org. Chem.* **1986**, *51*, 1663. Regitz, M.; Hocker, J.; Leidhergener, A. *Organic Syntheses*; John Wiley: New York, 1973; Collect. Vol. 5, pp 179–183.

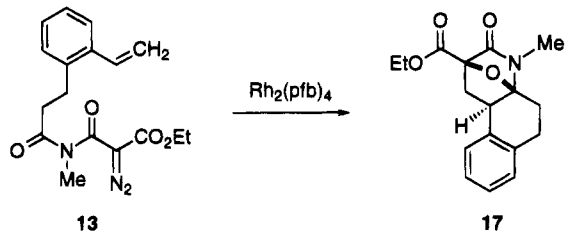
(26) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 2163.

(27) Austin, W. B.; Bilow, N.; Keleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

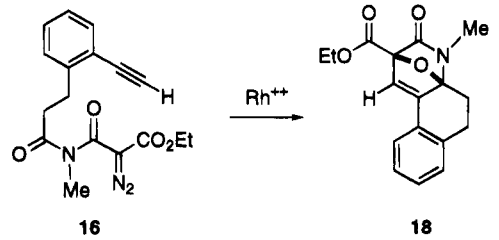
the trimethylsilyl group, the tethered alkyne species **15**. Following the standard procedures described above, diazo imide **16** was synthesized in good overall yield.



Treatment of diazo imide **13** with a catalytic amount of rhodium(II) perfluorobutyrate in CH_2Cl_2 at 25 °C afforded cycloadduct **17** in 75% yield. The stereochem-

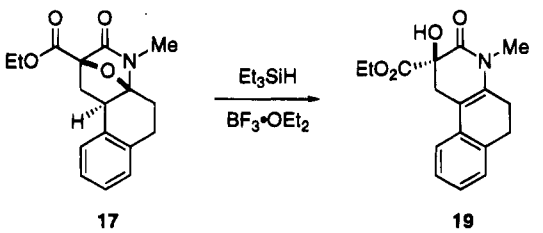


istry of the cycloadduct was based on its spectral properties and comparison to an analogous cycloadduct whose structure had been deduced by X-ray crystallography.[21] Formation of cycloadduct **17** is the consequence of *endo* cycloaddition with regard to the dipole which is in full accord with the lowest energy transition state. In the case of the alkyne-tethered diazo imide **16**, dipolar cycloaddition occurred on exposure of **16** to a catalytic quantity of rhodium(II) perfluorobutyrate in refluxing methylene chloride. The unsaturated cycloadduct **18** was



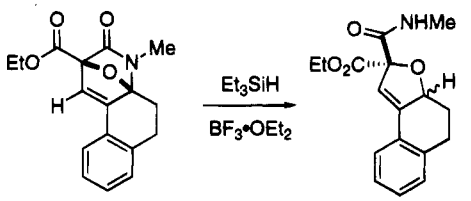
isolated in 80% yield, and its assignment was based on the appearance of the vinylic proton singlet at 6.95 ppm in the ^{1}H-NMR spectrum. The isolation of **18** is somewhat surprising in view of the earlier results of Ibata[28] and Maier[29] who showed that the inter- or intramolecular cycloadducts of isomünchnones with acetylenic dipolarophiles readily extrude alkyl or aryl isocyanates (RNCO) via a retro Diels–Alder reaction providing substituted furans in high yield. In this case, the extrusion of methyl isocyanate from the isomünchnone cycloadduct is slow enough to permit its isolation.

Given the success in forming complex polyheterocyclic systems from the intramolecular isomünchnone cycloaddition reaction, it seemed to us that selective modification of the cycloadduct skeleton would allow application of the method toward the ergot alkaloid family. In particular, reductive cleavage of the oxy bridge of the isomünchnone cycloadducts would provide ring systems containing both piperidine and quinoline skeletons so frequently found in the ergot family. In earlier reports, both Maier[29] and Meyers[30] have demonstrated that it is possible to selectively reduce N,O-ketals. Maier utilized hydride donors such as Et_3SiH in the presence of Lewis acids.[31] The Meyers group showed that AlH_3 is a viable reducing agent for the reductive ring opening of bicyclic lactams.[30] Our attempts to selectively reduce cycloadduct **17** with Et_3SiH and BF_3•OEt_2 failed. Rather than forming the desired reduction product, we isolated enamide **19** as the exclusive product. The lone pair of electrons on the amide nitrogen undoubtedly assists in opening the oxy bridge generating a transient *N*-acyliminium ion. Unfortunately, proton loss from this transient species affords enamide **19** prior to reduction by Et_3SiH. Attempts to use a more powerful hydride donor such as AlH_3 or Et_2SiH_2 also failed, and once again, only enamide **19** was isolated. Other attempts at reducing the N,O-ketal with a variety of reducing agents only resulted in intractable tar.

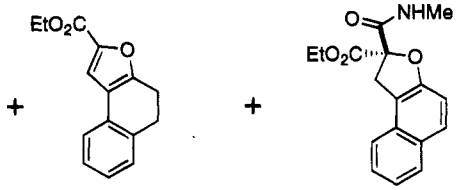


With the hope that we might be able to avoid the undesired proton elimination from the acyliminium ion, we examined the reaction of the alkynyl cycloadduct **18** with Et_3SiH and BF_3•OEt_2. When **18** was treated under these conditions, a 1:1 diastereomeric mixture of 2,5-dihydrofuran **20** (50%), the trisubstituted furan derivative **21** (25%), and a small amount of **22** (5%) were isolated after column chromatography. The structure of one of the diastereomers of **20** was unequivocally established by a single-crystal X-ray analysis.[32] Structure **20** is presumed to arise via a formal C–N bond cleavage which produces the corresponding oxonium ion, that in turn is reduced under the reaction conditions. A Lewis acid catalyzed retro Diels–Alder reaction[17] is responsible for the formation of furan **21**. Support for this suggestion comes from the BF_3•OEt_2-catalyzed reaction of **18** which afforded **21** in quantitative yield. Naphthalene **22** is the consequence of proton loss from the initially formed oxonium ion followed by a series of 1,3-H shifts. The difference in directionality of ring opening of cycloadduct **17** *vs* **18** is arguably a manifestation of the heteroatom

(28) Ibata, T.; Hamaguchi, M.; Kiyohara, H. *Chem. Lett.* **1975**, 21. Hamaguchi, M.; Ibata, T. *Chem. Lett.* **1975**, 499.
(29) Maier, M. E.; Schöffling, B. *Chem. Ber.* **1989**, *122*, 1081. Maier, M. E.; Evertz, K. *Tetrahedron Lett.* **1988**, 1677.
(30) Burgess, L. E.; Meyers, A. I. *J. Org. Chem.* **1992**, *57*, 1656.
(31) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.
(32) The authors have deposited coordinates for structures **20a** and **31** with the Cambridge Data Centre. The coordinates can be obtained from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambrigde, CB2 1EZ, U.K.



18 20

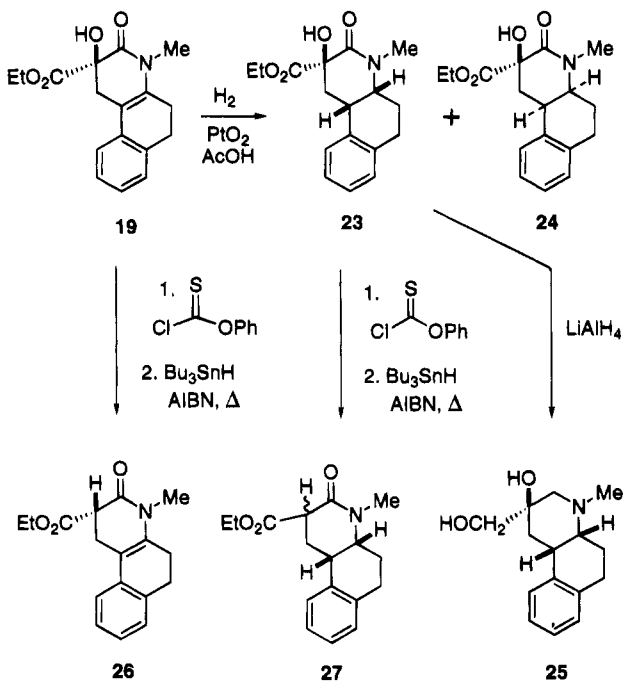


21 22

lone pair alignment with the bonds that are being broken. The added olefinic unit present in cycloadduct **18** ostensibly causes the amide lone pair to be out of alignment with the C–O bond, which is generally the bond that is ruptured. An alternative explanation is that a much more stable carbocation is formed by C–N bond scission from cycloadduct **18** since the positive charge is now stabilized by allylic delocalization. Whatever the reason, it is clear that cycloadduct **18** provides reduction products that are unsuitable for conversion to the functionality present in ring D of lysergic acid. Consequently, our attention was redirected to the possible utilization of enamide **19** for further chemical manipulation.

Attempts at reducing enamide **19** under standard enamine reducing conditions[33] only resulted in the recovery of starting material. The use of catalytic hydrogenation to reduce the double bond was more fruitful. Subjecting **19** to hydrogenation (50 psi) over Adam's catalyst using acetic acid as the solvent[34] afforded a 4:1 mixture of lactams **23** and **24** in 71% isolated yield. Unfortunately, all attempts to dehydrate either lactam **23** or **24** under a wide variety of dehydrating conditions[35–37] failed to produce the desired alkene. We suspect that the presence of two strongly electron withdrawing groups on the hydroxyl bearing carbon atom makes the elimination extremely difficult to carry out. It was possible, however, to fully reduce **23** to diol **25** in quantitative yield.

Lactam **19** contains the proper functionality needed for the construction of the C–D rings present in the ergot alkaloid family except that it is overfunctionalized. Before attempting the preparation of the cycloadduct needed for the lysergic acid synthesis (*vide infra*), we decided to examine the deoxygenation of **19** with the



19 23 24

26 27 25

ultimate intention of isomerizing the double bond in the resulting lactam **26**.[38] A modification[39] of the original Barton–McCombie[40] deoxygenation reaction was found to be the method of choice. Treatment of **19** with NaH and phenyl chlorothionoformate gave the stable, easily handled phenyl thiocarbonate derivative. Heating this ester in toluene at 75 °C with slow addition of a solution of 2,2′-azobis(isobutyronitrile) (AIBN) and tributyltin hydride afforded the deoxygenated lactam **26** in 83% isolated yield. A similar set of conditions was used to reduce **23** to the corresponding lactam **27**, which was isolated as a 1:1 mixture of diastereomers in high yield.

The retrosynthesis of lysergic acid as summarized in Scheme 1 requires the synthesis of diazo imide **9**. This was accomplished in eight steps (Scheme 2) starting from the known tricyclic olefin **28**.[41] Ozonolysis of **28** followed by reductive workup with $NaBH_4$ gave the expected diol in 95% yield.[42] Selective oxidation of the benzylic alcohol with MnO_2[43] followed by Wittig olefination provided the 4-vinyl-2,3-dihydroindoline derivative **29**. Conversion of the primary alcohol to *N*-methylamide **30** was accomplished in three steps. Thus, oxidation of **29** with Jones reagent[44] gave the expected carboxylic acid which was treated with 1,1′-carbonyldiimidazole followed by reaction with 40% aqueous methylamine to produce amide **30** in 80% overall yield. N-Malonylacylation using methyl malonyl chloride afforded the corresponding *N*-methylimide (98%), which was readily converted to the prerequisite diazo imide **9** (100%) using standard diazo transfer conditions.

The Rh(II)-catalyzed decomposition of diazo imides results first in the formation of a rhodium carbenoid,

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(37) Williams, D. R.; Coleman, P. J.; Henry, S. S. *J. Am. Chem. Soc.* **1993**, *115*, 11654.

(38) Martinez, S. J.; Joule, J. A. *Tetrahedron* **1978**, *34*, 3027. Beeken, P.; Fowler, F. W. *J. Org. Chem.* **1980**, *45*, 1336. Mueller, R. H.; Thompson, M. E.; DiPardo, R. M. *J. Org. Chem.* **1984**, *49*, 2217.

(39) Robins, M. J.; Wilson, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 932.

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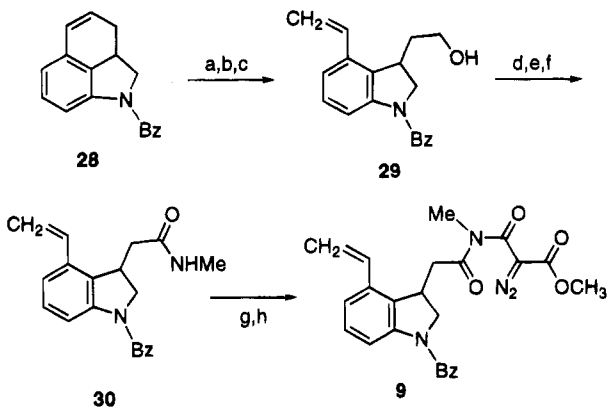
(43) Giersch, W.; Ohloff, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 401.

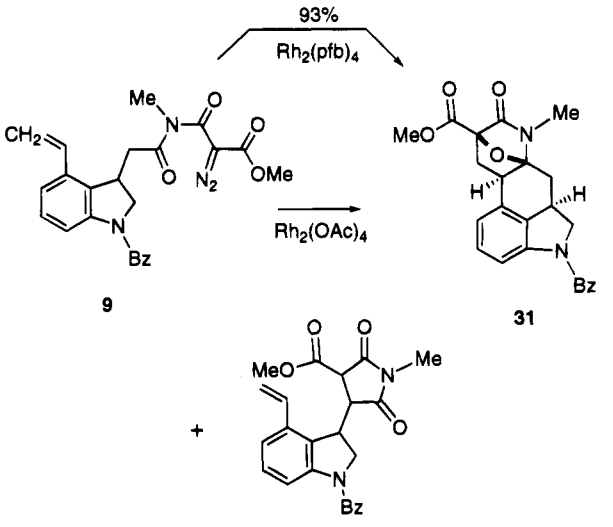
(44) Bowden, K.; Heilborn, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39.

Scheme 2



[a] Reagents: (a) O_3; $NaBH_4$; (b) MnO_2; (c) $Ph_3P{=}CH_2$; (d) H_2CrO_4; (e) Im_2CO; (f) $MeNH_2$; (g) $ClCOCH_2CO_2Me$; (h) MsN_3; NEt_3.

which then cyclizes onto the neighboring amide carbonyl oxygen to generate the intermediate isomünchnone dipole.[22] Our initial experiments with diazo imide **9** involved using rhodium(II) acetate as the catalyst. This bimolecular D_{4h}-symmetric compound with four bridging acetates has one vacant coordination site per metal atom, which weakly binds Lewis basic ligands.[45] The reaction of **9** with this catalyst led to a mixture of the desired isomünchnone cycloadduct **31** (67%) (X-ray determination)[32] as well as the C−H insertion product **32** (33%).[17] Recent studies of regioselectivity,[46] enantioselectivity,[47] and chemoselectivity[48] in rhodium-mediated reactions have shown that an impressive degree of control can be exerted by the ligand groups on rhodium.[45] Site selectivity not only depends on the type of ligand used but is also governed by steric,[49-52] conformational,[53] and electronic factors.[54-58] The question of chemoselectivity of rhodium carbenoids has been addressed by the preparation of diazo carbonyl compounds containing two different reaction sites and studying the competition between the two carbenoid processes.[45] These studies have revealed some dramatic ligand effects; for example, carboxamide and perfluoro carboxylate ligands in rhodium(II) catalysts can effectively control chemoselectivity in competitive carbenoid transformations of diazo carbonyl compounds.



Indeed, we found that the reaction of **9** using rhodium(II) perfluorobutyrate as the catalyst significantly enhanced the amount of cycloadduct **31**. In fact, with this catalyst no sign of the C−H insertion product was detected and cycloadduct **31** was isolated as the exclusive product in 93% yield. The *tandem cyclization−cycloaddition sequence* also occurred under milder conditions when rhodium(II) perfluorobutyrate was used as the catalyst. This is probably related to the fact that metal carbene reactions catalyzed by dirhodium(II) carboxylates are electrophilic in character, resembling those of a metal-stabilized carbocation.[59] Increased electron withdrawal by the ligand from the metal increases the electronegativity of the carbene center, causing the loss of nitrogen to take place at a faster rate as well as promoting cyclization onto the basic amide carbonyl site.

The conversion of cycloadduct **31** to methyl paspalate was undertaken by treating **31** with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at 0 °C, which furnished the expected tetrasubstituted enamide **33** in quantitative yield. The Barton−McCombie reaction[39,40] of **33** using the phenyl thiocarbonate derivative with tributyltin hydride gave the expected deoxygenated amido ester **34** as a 2:1 mixture of diastereomers. Unfortunately, all of our attempts using a variety of bases failed to isomerize the double bond. A successful route to paspalic acid or lysergic acid from **34** will require an alternate method for isomerizing the double bond.

In conclusion, while we were ultimately thwarted at the last stages by an uncooperative double-bond isomer-

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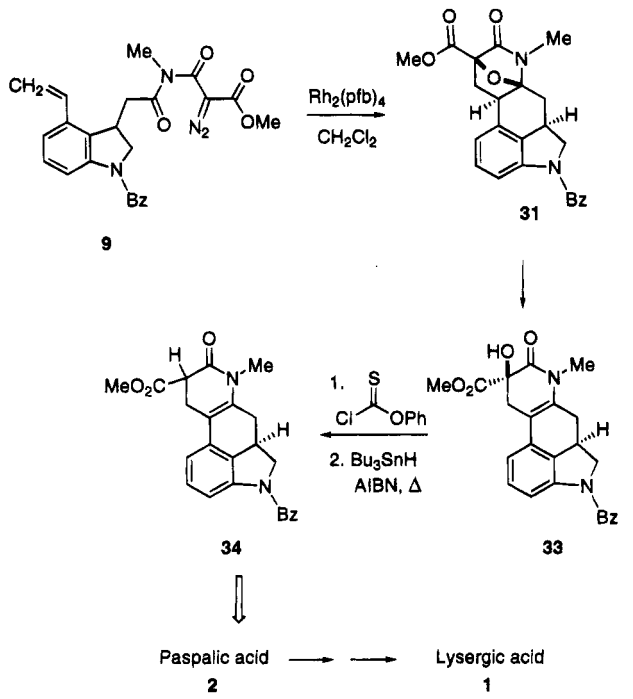

ization, there is no doubt that the intramolecular isomünchnone cycloaddition reaction has shown its potential for the synthesis of complex polyheterocyclic ring systems. In one operation, it was possible to create the CD ring system of the quinoline skeleton present in the ergot alkaloid family. Further studies dealing with the conversion of **34** into lysergic acid as well as application of the isomünchnone cycloaddition method to the synthesis of other alkaloids is currently being explored.

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. Reaction mixtures were purified by silica gel chromatography using a hexane–ethyl acetate mixture as eluent.

General Procedure for the Synthesis of Diazo Imides. A solution containing 5.0 mmol of the appropriate amide and 10.0 mmol of ethyl malonyl chloride[21] in 15 mL of anhydrous benzene was heated at reflux for 1 h. After being cooled to 23 °C, the reaction mixture was diluted with ether and washed with 10% aqueous NaOH and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on a silica gel column. A variation of the procedure described by Taber and co-workers[25] was used to prepare the diazo imide system. To a solution containing 2 mmol of the appropriate keto lactam and 2.2 mmol of mesyl azide in 5 mL of acetonitrile or CH_2Cl_2 was added 4.0 mmol of NEt_3 under N_2 at 23 °C. After the solution was stirred for 3 h, the solvent was removed under reduced pressure and the residue was subjected to flash chromatography on a silica gel column.

Preparation and Rhodium(II)-Catalyzed Reaction of 2-Diazo-*N*-methyl-*N*-[3-(2-vinylphenyl)propionyl]-malonamic Acid Ethyl Ester (13). To a solution of 3.01 g (13.15 mmol) of 3-(2-bromophenyl)propanoic acid[23] in 120 mL of CH_2Cl_2 was added 2.56 g (15.78 mmol) of 1,1'-carbonyldiimidazole, and the solution was stirred for 2 h. This solution was poured into an excess of 40% aqueous methylamine at 0 °C, and the mixture was stirred for 10 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated under reduced pressure, and the crude residue was subjected to flash silica gel chromatography using a 5% hexane–ethyl acetate mixture as eluent to give 2.96 g of 3-(2-bromophenyl)-*N*-methylpropionamide (**11**) as a white crystalline solid (93%): mp 59–60 °C; IR (neat) 1646, 1556, 1025, and 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (t, 2H, J = 7.5 Hz), 2.71 (d, 3H, J = 7.5 Hz), 3.02 (t, 2H, J = 7.5 Hz), 5.83 (bs, 1H), 7.00 (m, 1H), 7.18 (m, 2H), and 7.46 (d, 1H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 32.1, 36.3, 124.3, 127.5, 127.9, 130.5, 132.7, 140.1, and 172.4.

To a flask charged with 2.0 g (8.26 mmol) of the above amide in 25 mL of toluene were added 191 mg (0.165 mmol) of palladium tetrakis(triphenylphosphine) and 2.89 g (9.08 mmol) of vinyltributyltin, and the solution was heated at reflux for 24 h. The solution was cooled to 23 °C and diluted with CH_2Cl_2. The organic layer was extracted with a saturated aqueous KF solution and brine and dried over Na_2SO_4. The organic extracts were filtered and concentrated under reduced pressure and subjected to flash silica gel chromatography using a 6% hexane–ethyl acetate mixture as the eluent to give 1.45 g of *N*-methyl-3-(2-vinylphenyl)propionamide (**12**) as a clear oil (90%): IR (neat) 1647, 913, and 772 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (t, 2H, J = 8.4 Hz), 2.68 (d, 3H, J = 4.8 Hz), 2.96 (t, 2H, J = 8.4 Hz), 5.24 (d, 1H, J = 11.1 Hz), 5.58 (d, 1H, J = 18.6 Hz), 6.13 (bs, 1H), 6.94 (dd, 1H, J = 18.6 and 11.1 Hz), 7.12 (m, 3H), and 7.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 29.1, 37.5, 115.8, 125.8, 126.6, 127.9, 129.3, 134.2, 136.3, 138.2, and 172.8.

N-Malonylacylation was carried out on the above amide in the normal manner to give *N*-[3-(2-vinylphenyl)propionyl]-*N*-methylmalonamic acid ethyl ester as a clear oil (89%): IR (neat) 1739, 1695, and 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7.2 Hz), 2.80 (t, 2H, J = 7.2 Hz), 3.01 (t, 2H, J = 7.2 Hz), 3.17 (s, 3H), 3.82 (s, 2H), 4.18 (q, 2H, J = 7.2 Hz), 5.30 (d, 1H, J = 11.1 Hz), 5.64 (d, 1H, J = 17.1 Hz), 6.95 (dd, 1H, J = 17.1 and 11.1 Hz), 7.18 (m, 3H), and 7.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 28.0, 31.1, 38.2, 46.3, 61.2, 116.3, 126.0, 126.9, 128.0, 129.5, 134.1, 136.5, 137.5, 167.3, 168.6, and 174.8.

The above compound was subjected to standard diazo transfer conditions to give 2-diazo-*N*-[3-(2-vinylphenyl)propionyl]-*N*-methylmalonamic acid ethyl ester (**13**) as a yellow oil (94%): IR (neat) 2136, 1716, 1652, 1326, and 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, 3H, J = 7.2 Hz), 2.78 (t, 2H, J = 7.5 Hz), 3.03 (t, 2H, J = 7.5 Hz), 3.23 (s, 3H), 4.24 (q, 2H, J = 7.2 Hz), 5.29 (d, 1H, J = 11.1 Hz), 5.63 (d, 1H, 17.1 Hz), 6.97 (dd, 1H, J = 17.1 and 11.1 Hz), 7.18 (m, 3H), and 7.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 28.5, 33.3, 37.3, 61.8, 116.0, 125.9, 126.7, 127.9, 129.5, 134.2, 136.5, 137.9, 160.3, 166.3, and 174.5.

To a flask charged with 7.2 g (21.9 mmol) of the above diazo imide in 50 mL of CH_2Cl_2 at 23 °C was treated with 35 mg of rhodium(II) perfluorobutyrate and stirred for 24 h. The reaction mixture was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 4.9 g of 2,4a-epoxy-4-methyl-3-oxo-1,2,3,4,4a,5,6,-10b-octahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**17**) as a crystalline solid (75%); mp 130–131 °C; IR (neat) 1750, 1724, 1402, and 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, 2H, J = 7.0 Hz), 2.17 (dd, 1H, J = 12.5 and 4.5 Hz), 2.23 (dd, 1H, J = 12.5 and 5.5 Hz), 2.43 (ddd, 1H, J = 13.3, 5.5, and 2.5 Hz), 2.76 (dd, 1H, J = 12.5 and 9 Hz), 2.82 (s, 3H), 2.90 (ddd, 1H, J = 16.3, 6.0, and 2.5 Hz), 3.21 (m, 1H), 3.31 (dd, 1H, J = 9 and 4.5 Hz), 4.31 (m, 2H), 7.04 (d, 1H, J = 7.5 Hz), and 7.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 24.3, 24.8, 25.3, 38.2, 43.7, 62.1, 86.0, 96.3, 126.5, 126.9, 128.6, 129.0, 133.8, 137.6, 165.5, and 171.0. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.37; N, 4.65. Found: C, 67.89; H, 6.45, N; 4.57.

Preparation of 2-Hydroxy-4-methyl-3-oxo-1,2,3,4,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic Acid Ethyl Ester (19). To a solution of 4.30 g (14.3 mmol) of cycloadduct **17** in 120 mL of CH_2Cl_2 at 0 °C was added 2.43 g (17.1 mmol) of $BF_3{\cdot}Et_2O$. This solution was allowed to warm to 23 °C and was stirred for 24 h. The reaction was quenched with 10 mL of MeOH, and the mixture was extracted with water and brine and dried over Na_2SO_4. The organic extract was filtered and

concentrated under reduced pressure to give 4.1 g of 2-hydroxy-4-methyl-3-oxo-1,2,3,4,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**19**) as a pale yellow solid (95%): mp 115–116 °C; IR (neat) 3420, 2932, 1737, 1670, 1491, and 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, 3H, J = 7.0 Hz), 2.41 (m, 2H), 2.64 (d, 1H, J = 15.5 Hz), 2.77 (t, 2H, J = 7.0 Hz), 3.15 (s, 3H), 3.29 (d, 1H, J = 15.5 Hz), 4.06 (q, 2H, J = 7.0 Hz), 4.46 (s, 1H), 7.01 (d, 2H, J = 4.0 Hz), 7.07 (d, 1H, J = 8.0 Hz), and 7.12 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 23.5, 28.2, 29.6, 31.0, 61.9, 73.9, 111.4, 121.7, 126.2, 126.9, 127.0, 132.5, 133.8, 135.4, 168.5, and 169.9. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.37; N, 4.65. Found: C, 67.70; H, 6.39; N, 4.55.

Free Radical Deoxygenation of 2-Hydroxy-4-methyl-3-oxo-1,2,3,4,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic Acid Ethyl Ester (19). To solution of 203 mg (0.67 mmol) of enamide **19** in 5 mL of THF was added 78 mg (2.02 mmol) of NaH (60% dispersion in mineral oil), and the solution was stirred at 23 °C for 0.5 h. To this mixture was added 0.19 mL (1.35 mmol) of phenyl chlorothionocarbonate dropwise, and the mixture was stirred for 5 h. The reaction was quenched with aqueous NH_4Cl, and the solution was extracted with ether. The extracts were washed with brine, dried over Na_2SO_4, and filtered. The solution was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography using a 5% hexane–ethyl acetate mixture as the eluent to give 155 mg of 4-methyl-3-oxo-2-((phenoxythiocarbonyl)oxy)-1,2,3,4,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester as a yellow oil (53%): IR (neat) 1744, 1687, 1646, 1487, and 731 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (t, 3H, J = 7.2 Hz), 2.52 (m, 2H), 2.88 (t, 2H, J = 7.8 Hz), 3.24 (s, 3H), 3.45 (d, 1H, J = 16.1 Hz), 3.72 (d, 1H, J = 16.1 Hz), 4.20 (m, 2H), 7.09 (t, 4H, J = 6.3 Hz), 7.19 (m, 1H), 7.25 (m, 2H), and 7.37 (t, 2H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 23.7, 28.2, 29.7, 30.2, 62.5, 83.9, 109.2, 121.5, 121.7, 126.2, 126.7, 127.0, 127.1, 129.5, 132.4, 133.6, 136.3, 153.3, 162.7, 166.1, and 191.6.

To a solution of 133 mg (0.30 mmol) of the above phenyl thiocarbonate in 5 mL of toluene were added 50 mg (0.30 mmol) of AIBN and 0.41 mL (1.52 mmol) of tributyltin hydride. This mixture was heated for 1.5 h at 75 °C. The reaction was then cooled to 23 °C, and the mixture was concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography using a 5% hexane–ethyl acetate mixture as the eluent to give 71 mg (83%) of 4-methyl-3-oxo-1,2,3,4,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**26**) as a clear oil: IR (neat) 1736, 1673, 1394, and 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 6.9 Hz), 2.48 (t, 2H, J = 8.1 Hz), 2.84 (m, 3H), 3.08 (m, 1H), 3.16 (s, 3H), 3.60 (dd, 1H, J = 9.6 and 6.3 Hz), 4.22 (m, 2H), 7.11 (m, 3H), and 7.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 23.7, 24.3, 28.3, 28.8, 47.9, 61.4, 112.0, 121.2, 125.8, 126.8, 127.0, 132.2, 134.4, 136.2, 166.2, and 169.7; HRMS calcd for $C_{17}H_{19}NO_3$ 285.1364, found 285.1376.

Catalytic Hydrogenation of 2-Hydroxy-4-methyl-3-oxo-1,2,3,4,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic Acid Ethyl Ester (19). To a solution of 2.4 g (7.9 mmol) of **19** in 80 mL of acetic acid was added 220 mg (0.9 mmol) of platinum oxide; the mixture was then hydrogenated at 50 psi for 5 h. The mixture was then filtered through a Celite plug and washed with EtOAc. The filtrate was concentrated under reduced pressure and subjected to flash silica gel chromatography using a 4% hexane–ethyl acetate mixture as the eluent to give 1.9 g (71%) of 2-hydroxy-4-methyl-3-oxo-1,2,3,4,4a,5,6,-10b-octahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**23** and **24**) as a 4:1 mixture of diastereomers. The major diastereomer was obtained through recrystallization using acetone/hexane: mp 145–146 °C; IR (neat) 1748, 1639, 1242, and 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, 3H, J = 7.2 Hz), 1.98 (m, 1H), 2.10 (dd, 1H, J = 14.2 and 3.0 Hz), 2.24 (m, 1H), 2.55 (m, 1H), 2.80–3.01 (m, 2H), 3.05 (s, 3H), 3.59 (m, 2H), 4.09 (s, 1H), 4.23 (m, 2H), 7.10 (t, 1H, J = 5 Hz), 7.15 (m, 2H), and 7.23 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 23.0, 28.6, 33.3, 34.0, 38.6, 59.6, 62.5, 74.7, 126.4, 126.7, 128.7, 129.2, 134.6, 137.1, 167.1, and 172.2. Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.29; H, 6.99; N, 4.62. Found: C, 67.20; H, 7.02; N, 4.62.

Free Radical Deoxygenation of 2-Hydroxy-4-methyl-3-oxo-1,2,3,4,4a,5,6,10b-octahydrobenzo[*f*]quinoline-2-carboxylic Acid Ethyl Ester (23). To a solution of 120 mg (0.39 mmol) of **23** in 5 mL of THF was added 47 mg (1.19 mmol) of NaH (60% dispersion in mineral oil), and the solution was stirred at 23 °C for 0.5 h. To this mixture was added 0.11 mL (0.79 mmol) of phenyl chlorothionocarbonate dropwise, and the solution was stirred for 5 h at 23 °C. The reaction was quenched with aqueous NH_4Cl, and the solution was diluted with ether. The organic layer was washed with brine and dried over Na_2SO_4. The organic extracts were concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography using a 5% hexane–ethyl acetate mixture as the eluent to give 137 mg of 4-methyl-3-oxo-2-(phenoxythiocarbonyl)oxy)-1,2,3,4,4a,5,6,10b-octahydrobenzo-[*f*]quinoline-2-carboxylic acid ethyl ester as a light yellow solid (79%): mp 138–139 °C; IR (neat) 2932, 1763, 1734, 1664, 1487, and 1280 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, 3H, J = 6.9 Hz), 1.97 (m, 1H), 2.25 (m, 1H), 2.87 (m, 3H), 3.08 (s, 3H), 3.61 (m, 3H), 4.26 (m, 2H), 7.10 (m, 3H), 7.16 (d, 3H, J = 7.8 Hz), 7.29 (t, 1H, J = 7.2 Hz), and 7.43 (t, 2H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 23.1, 28.4, 32.9, 33.9, 34.9, 59.5, 62.6, 85.3, 121.9, 126.6, 126.8, 126.9, 128.8, 129.2, 129.6, 134.9, 136.3, 153.1, 161.8, 165.9, and 191.4.

To a solution of 140 mg (0.32 mmol) of the above phenyl thiocarbonate in 5 mL of toluene were added 52 mg (0.32 mmol) of AIBN and 0.43 mL (1.59 mmol) of tributyltin hydride. This mixture was heated for 1.5 h at 75 °C. The reaction was cooled to 23 °C and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography using a 5% hexane–ethyl acetate mixture as the eluent to give 90 mg (98%) of 4-methyl-3-oxo-1,2,3,4,4a,5,6,10b-octahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**27**) as a 1:1 inseparable mixture of diastereomers: IR (neat) 2939, 1732, and 1643 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.33 (t, 3H, J = 7.2 Hz), 1.92 (m, 1H), 2.14–2.43 (m, 3H), 2.78–2.99 (m, 2H), 3.05 (s, 3H), 3.19–3.68 (m, 3H), 4.21 (m, 2H), and 7.15 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 14.2, 23.9, 28.0, 28.6, 31.1, 32.0, 33.8, 34.1, 34.5, 36.8, 47.5, 49.6, 59.0, 59.3, 61.2, 61.4, 126.3, 126.4, 126.6, 126.8, 128.7, 128.8, 128.9, 129.1, 134.8, 135.1, ,136.9, 137.2, 165.4, 165.5, 170.5, and 171.1; HRMS calcd for $C_{17}H_{21}NO_3$ 287.1521, found 287.1528.

Preparation and Rhodium(II)-Catalyzed Reaction of 2-Diazo-*N*-methyl-*N*-[3-(2-ethynylphenyl)propionyl]-malonamic Acid Ethyl Ester (16). To a solution of 4.0 g (14.5 mmol) of 3-(2-iodophenyl)propanoic acid[23] in 120 mL of CH_2Cl_2 was added 2.8 g (17.4 mmol) of 1,1'-carbonyldiimidazole, and the solution was stirred for 2 h. This solution was then poured into an excess of 40% aqueous methylamine at 0 °C, and the mixture was stirred for 10 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were concentrated under reduced pressure, and the crude residue was subjected to flash silica gel chromatography to give 3.45 g of 3-(2-iodophenyl)-*N*-methylpropionamide (**14**) as a white crystalline solid (83%): mp 72–72 °C; IR (neat) 2929, 1644, and 1560 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.42 (t, 2H, J = 7.5 Hz), 2.75 (d, 3H, J = 6.6 Hz), 3.03 (t, 2H, J = 7.5 Hz), 5.50 (bs, 1H), 6.86 (m, 1H), 7.22 (d, 2H, J = 4.5 Hz), and 7.77 (d, 1H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 36.7, 100.2, 128.1, 128.5, 129.7, 139.4, 143.3, and 172.1.

To a solution of 3.0 g (10.4 mmol) of the above amide in 40 mL of a 3:1 mixture of Et_3N/toluene were added 2.93 g (20.8 mmol) of (trimethylsilyl)acetylene, 146 mg (0.21 mmol) of *trans*-bis(triphenylphosphine)palladium(II) chloride, 198 mg (1.03 mmol) of CuI, and 210 mg (0.79 mmol) of triphenylphosphine. The mixture was heated at 120 °C for 2 h. After being cooled to 23 °C, the reaction mixture was filtered through a pad of Celite topped with Florisil, and the residue was washed with ether. The resulting filtrate was concentrated under reduced pressure, and the crude (trimethylsilyl)phenylacetylene derivative was used without further purification. The crude residue was taken up in 50 mL of MeOH, and 10 g (72.4

mmol) of K_2CO_3 was added. This mixture was stirred at 23 °C for 24 h and then filtered through a pad of Celite. The methanolic solution was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 1.87 g of 3-(2-ethynylphenyl)-*N*-methylpropionamide (**15**) as a red crystalline solid (96%): mp 77–78 °C; IR (neat) 3212, 1633, and 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.46 (t, 2H, J = 7.5 Hz), 2.69 (d, 3H, J = 4.8 Hz), 3.06 (t, 2H, J = 7.5 Hz), 3.22 (s, 1H), 5.91 (bs, 1H), 7.07–7.23 (m, 3H), and 7.40 (d, 1H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 30.4, 36.9, 81.2, 81.9, 121.3, 126.2, 128.8, 129.0, 132.9, 143.4, and 172.7.

N-Malonylacylation was carried out on the above amide in the normal manner to give *N*-[3-(2-ethynylphenyl)propionyl]-*N*-methylmalonamic acid ethyl ester as a clear oil (90%): IR (neat) 1740, 1694, and 1094 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 6.9 Hz), 2.91 (t, 2H, J = 7.2 Hz), 3.11 (t, 2H, J = 7.2 Hz), 3.20 (s, 3H), 3.25 (s, 1H), 3.82 (s, 2H), 4.17 (q, 2H, J = 6.9 Hz), 7.14–7.29 (m, 3H), and 7.46 (d, 1H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 29.4, 31.2, 37.6, 46.4, 61.2, 81.4, 81.8, 121.5, 126.4, 129.1, 133.0, 142.8, 167.3, 168.6, and 174.8.

The above compound was subjected to standard diazo transfer conditions to give 2-diazo-*N*-[3-(2-ethynylphenyl)-propionyl]-*N*-methylmalonamic acid ethyl ester (**16**) as a yellow oil (85%): IR (neat) 2137, 1714, 1652, and 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, 3H, J = 7.2 Hz), 2.88 (t, 2H, J = 7.2 Hz), 3.01 (t, 2H, J = 7.2 Hz), 3.08 (s, 3H), 3.25 (s, 1H), 4.20 (q, 2H, J = 7.2 Hz), 7.13 (m, 1H), 7.21 (m, 2H), and 7.41 (d, 1H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 29.8, 33.2, 36.6, 61.7, 72.1, 81.4, 81.8, 121.4, 126.2, 129.0, 132.9, 143.1, 160.3, 166.2, and 174.4.

A flask charged with 3.85 g (12.30 mmol) of the above diazo imide in 50 mL of CH_2Cl_2 at 23 °C was treated with 25 mg of rhodium(II) perfluorobutyrate, and this mixture was heated at reflux for 8 h. The reaction mixture was concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 1.4 g of 2,4a-epoxy-4-methyl-3-oxo-2,3,4,4a,5,6-hexahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**18**) as a clear oil (80%): IR (neat) 1755, 1728, 1204, 908 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.37 (t, 3H, J = 7.2 Hz), 2.56 (m, 2H), 2.72 (s, 3H), 3.06 (m, 2H), 4.40 (m, 2H), 6.95 (s, 1H), and 7.23 (m, 3H), and 7.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 24.3, 26.3, 28.7, 62.5, 91.0, 98.1, 122.7, 125.8, 127.3, 127.8, 128.9, 129.6, 135.6, 149.8, 164.2, and 173.9.

A solution of 97 mg (0.32 mmol) of the above cycloadduct was heated in toluene at reflux for 1 h. The reaction mixture was concentrated under reduced pressure to give 4,5-dihydronaptho[2,1-*b*]furan-2-carboxylic acid ethyl ester (**21**) as a pale yellow crystalline solid (100%): mp 58–59 °C; IR (neat) 1719, 1534, 1157, and 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.39 (t, 3H, J = 6.9 Hz), 2.98 (t, 2H, J = 7.5 Hz), 3.10 (t, 2H, J = 7.5 Hz), 4.37 (q, 2H, J = 6.9 Hz), 7.18 (m, 3H), 7.31 (d, 1H, J = 7.2 Hz), and 7.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 22.0, 28.8, 60.8, 113.9, 120.7, 122.5, 126.7, 126.9, 128.2, 129.6, 133.0, 143.9, 157.1, and 158.8. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.35; H, 5.83. Found: C, 74.10; H, 5.76.

To a flask containing 450 mg (1.50 mmol) of cycloadduct **18** in 15 mL of CH_2Cl_2 were added 1.75 g (15.0 mmol) of triethylsilane and 1.07 g (7.51 mmol) of $BF_3{\cdot}Et_2O$, and this mixture was stirred at 23 °C for 6 h. The reaction was quenched with 10 mL of MeOH, and the solution was extracted with water and brine. The organic extracts were concentrated under reduced pressure, and the crude residue was subjected to flash silica gel chromatography. The major product obtained (50%) was a readily separable 1:1 diastereomeric mixture of 2-(methylcarbamoyl)-2,3a,4,5-tetrahydronaptho[2,1-*b*]furan-2-carboxylic acid ethyl ester (**20a** and **20b**). Diastereomer **20a**: mp 125–126 °C; IR (neat) 1740, 1674, 1525, 1235, and 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, 3H, J = 6.9 Hz), 1.80 (m, 1H), 2.49 (m, 1H), 2.83 (d, 3H, J = 4.8 Hz), 2.95 (m, 2H), 4.26 (q, 2H, 6.9 Hz), 5.13 (ddd, 1H, J = 12, 9.7, and 2.1 Hz), 6.23 (d, 1H, J = 2.1 Hz), 6.81 (brs, 1H), 7.12–7.24 (m, 3H), and 7.54 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 26.0, 28.1, 31.1, 62.1, 85.3, 94.0, 116.3, 125.9, 126.6, 128.4, 128.7, 129.0, 136.5, 141.7, 168.5, and 168.8. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.75; H, 5.69; N, 4.65. Found: C, 67.55; H, 6.39, N; 4.62.

Diastereomer **20b**: IR (neat) 1739, 1667, 1075, and 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 6.9 Hz), 1.82 (m, 1H), 2.40 (m, 1H), 2.83 (d, 3H, J = 5.1 Hz), 2.92 (m, 2H), 4.22 (q, 2H, J = 6.9 Hz), 5.05 (m, 1H), 6.23 (s, 1H), 6.88 (brs, 1H), 7.09–7.23 (m, 3H), and 7.49 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.01, 25.9, 28.0, 31.1, 62.1, 85.6, 94.5, 116.0, 125.9, 126.5, 128.5, 128..6, 129.0, 136.4, 141.6, 168.6, and 168.9; HRMS calcd for $C_{17}H_{19}NO_4$ 301.1314, found 301.1304.

The second product isolated from the column (5%) was assigned as 2-(methylcarbamoyl)-1,2-dihydronaphtho[2,1-*b*]-furan-2-carboxylic acid ethyl ester (**22**) as a pale yellow solid: mp 104–105 °C; IR (neat) 1746, 1677, 1244, and 787 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 3H, J = 6.9 Hz), 2.85 (d, 3H, J = 5.1 Hz), 3.96 (d, 1H, J = 16.5 Hz), 4.25 (d, 1H, J = 16.5 Hz), 4.29 (q, 2H, J = 6.9 Hz), 6.86 (bs, 1H), 7.17 (d, 1H, J = 8.7 Hz), 7.35 (t, 1H, J = 7.5 Hz), 7.49 (t, 1H, J = 7.5 Hz), 7.60 (d, 1H, J = 8.1 Hz), 7.71 (d, 1H, J = 8.7 Hz), and 7.80 (d, 1H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 26.2, 36.1, 62.8, 90.3, 111.4, 117.1, 123.0, 123.9, 127.2, 128.6, 129.5, 129.9, 130.2, 154.2, 167.7, and 169.1; HRMS calcd for $C_{17}H_{17}NO_4$ 299.1157, found 299.1151.

The third product isolated (25%) was identified as 4,5-dihydronaptho[2,1-*b*]furan-2-carboxylic acid ethyl ester (**21**).

Preparation of 2-(Hydroxymethyl)-4-methyl-1,2,3,4,-4a,5,6,10b-octahydrobenzo[*f*]quinolin-1-ol (25). To a solution of 101 mg (0.34 mmol) of 2-hydroxy-4-methyl-3-oxo-1,2,3,4,4a,5,6,10b-octahydrobenzo[*f*]quinoline-2-carboxylic acid ethyl ester (**23**) in 8 mL of a 1:1 mixture of ether/THF was added 3.37 mL (3.4 mmol) of a 1.0 M solution of $LiAlH_4$ in 10 mL of ether. The mixture was stirred at 55 °C for 48 h, the reaction was quenched with a 10% KOH solution, and the aluminum salts were filtered through a fritted funnel. The filtrate was taken up in 20 mL of water and was extracted with ether. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure to provide 81 mg (97%) of 2-(hydroxymethyl)-4-methyl-1,2,3,4,4a,5,6,10b-octahydrobenzo[*f*]quinolin-1-ol (**25**) as a clear oil: IR (neat) 3410, 2941, 1461, and 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.39 (t, 2H, J = 13.2 Hz), 1.77 (m, 2H), 2.50 (s, 3H), 2.54 (m, 2H), 2.71–2.83 (m, 1H), 2.90–2.98 (m, 1H), 3.09 (m, 1H), 3.29 (m, 1H), 3.34 (d, 1H, J = 11.1 Hz), 3.54 (d, 1H, J = 11.1 Hz), and 7.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 29.1, 35.5, 37.3, 42.5, 54.5, 59.2, 68.2, 70.9, 125,8, 125.9, 128.6, 128.8, 135.3, and 140.2; HRMS calcd for $C_{15}H_{21}NO_2$ 247.1572, found 247.1579.

Preparation and Rhodium(II)-Catalyzed Cycloaddition of N-[2-(1-Benzoyl-4-vinyl-2,3-dihydro-1*H*-indol-3-yl)acetyl]-2-diazo-*N*-methylmalonamic Acid Ethyl Ester (9). A solution of 1.07 g (4.09 mmol) of 1-benzoyl-1,2,2a,3-tetrahydrobenz[*cd*]indole[41] (**28**) in 100 mL of a 1:1 mixture of CH_2Cl_2/MeOH at −78 °C was saturated with ozone until the blue color persisted. After the mixture was purged with oxygen, 0.31 g (8.19 mmol) of $NaBH_4$ was added and the mixture was slowly warmed to 23 °C. The mixture was concentrated under reduced pressure and diluted with CH_2Cl_2. The organic layer was washed with 10% aqueous HCl, aqueous NH_4Cl, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography gave 1.19 g of [3-(2-hydroxyethyl)-4-(hydroxymethyl)-2,3-dihydroindol-1-yl]phenylmethanone as a white solid (98%): mp 50-51 °C; IR (neat) 2881, 1627, 1588, and 1059 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70–2.00 (m, 2H), 2.10 (brs, 1H), 2.59 (t, 1H, J = 5.2 Hz), 3.50–3.72 (m, 3H), 3.88 (brs, 1H), 4.09 (dd, 1H, J = 11.0 and 8.3 Hz), 4.69 (m, 2H), 7.20–6.97 (brm, 2H), 7.35–7.60 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5, 36.9, 56.3, 59.8, 61.9, 116.3, 124.0, 127.2, 127.8, 128.7, 130.6, 134.4, 136.4, 137.1, 142.1, and 169.3.

To a solution of 1.18 g (3.97 mmol) of the above 2,3-dihydroindolediol in 25 mL of CH_2Cl_2 at 23 °C was added 5.0 g (57.5 mmol) of MnO_2. After being stirred for 7 h, the mixture was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography afforded 0.87 g (87%) of 1-benzoyl-3-(2-hydroxyethyl)-2,3-dihydro-1*H*-indole-

4-carboxaldehyde as a white solid: mp 124–125 °C; IR (neat) 1696, 1642, 1600, and 1385 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.65–1.95 (m, 4H), 3.64 (m, 2H), 4.00 (m, 1H), 4.18 (dd, 1H, J = 11.0 and 8.3 Hz), 7.30–7.70 (m, 8H), and 10.1 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.5, 37.5, 56.9, 60.2, 122.7, 127.2, 128.4, 128.7, 130.7, 131.9, 136.2, 137.9, 143.6, 169.5, and 192.5.

To a suspension of 3.12 g (8.74 mmol) of methyltriphenylphosphonium bromide in 100 mL of a 4:1 mixture of THF/DMF at 0 °C was added 3.6 mL of a 2.5 M solution of n-BuLi in hexanes. After being stirred for 0.5 h at 0 °C, a solution of 0.86 g (2.91 mmol) of the above 2,3-dihydroindoline-4-carboxaldehyde in 20 mL of DMF was added and the mixture was slowly warmed to 23 °C. The reaction was quenched by the addition of an aqueous NH_4Cl solution. The mixture was diluted with EtOAc and washed with aqueous NH_4Cl and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography provided 0.81 g (95%) of [3-(2-hydroxyethyl)-4-vinyl-2,3-dihydroindol-1-yl]phenylmethanone (**29**) as a viscous syrup: IR (neat) 2884, 1638, and 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.60–1.98 (m, 2H), 2.11 (m, 1H), 3.45–3.75 (m, 3H), 3.69 (brs, 1H), 4.07 (dd, 1H, J = 16.0 and 8.0 Hz), 6.79 (dd, 1H, J = 17.5 and 11.0 Hz), 7.00–7.30 (brm, 2H), 7.35–7.60 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 37.1, 56.0, 60.1, 77.4, 115.8, 120.5, 127.2, 128.6, 130.5, 132.9, 133.9, 134.3, 136.6, 142.2, and 169.2.

To a solution of 0.81 g (2.76 mmol) of the above primary alcohol in 50 mL of acetone at 0 °C were added 1.0 g of Celite and 2.1 mL of a 2.67 M solution of Jones reagent. After 0.5 h of stirring at 0 °C, the reaction was quenched with the addition of 10 mL of *i*-PrOH and the solids were filtered through a pad of Celite topped with Florasil. The solids were washed with EtOAc, and the filtrate was concentrated under reduced pressure. The residue was dissolved in 25 mL of CH_2Cl_2, and 0.38 g (2.31 mmol) of 1,1′-carbonyldiimidazole was added. After being stirred at 23 °C for 0.5 h, the mixture was poured into an excess of 40% aqueous $MeNH_2$. This mixture was stirred at 23 °C for 2 h. This biphasic solution was diluted with CH_2Cl_2 and washed with 10% aqueous HCl and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography afforded 0.41 g (47%) of 2-(1-benzoyl-4-vinyl-2,3-dihydro-1*H*-indol-3-yl)-*N*-methylacetamide (**30**) as an oil: IR (neat) 1640, 1576, and 1387 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05–2.48 (m, 2H), 2.73 and 2.72 (d, 3H), 3.88 (m, 2H), 4.19 (dd, 1H, J = 11.5 and 8.3 Hz), 5.36 (d, 1H, J = 11.1 Hz), 5.48 (brs, 1H), 5.78 (d, 1H, J = 17.7), 6.77 (dd, 1H, J = 17.5 and 11.0 Hz), 7.10–7.20 (m, 3H), 7.62–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1, 35.6, 40.2, 56.5, 116.2, 117.0, 120.7, 126.9, 128.1, 128.4, 128.6, 130.4, 132.7, 133.9, 136.5, 142.2, 169.4, and 171.2.

N-Malonylacylation was carried out on the above amide in the normal manner to give *N*-[2-(1-benzoyl-4-vinyl-2,3-dihydro-1*H*-indol-3-yl)acetyl]-*N*-methylmalonamic acid methyl ester as a solid (95%): mp 64–65 °C; IR (neat) 1744, 1696, and 1343 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.83 (AB of ABX, 2H, J = 17.8, 11.5 and 1.0 Hz), 3.17 (s, 3H), 3.61 (brs, 3H), 3.33–3.95 (m, 4H), 4.30 (dd, 1H, J = 11.6 and 8.4 Hz), 5. 39 (d, 1H, J = 11.1 Hz), 5.79 (d, 1H, J = 17.6 Hz), 6.70 (dd, 1H, J = 17.5 and 11.0 Hz), 7.22 (brs, 1H), 7.40–7.63 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.2, 34.9, 41.7, 45.9, 52.3, 56.7, 116.5, 116.8, 120.8, 127.3, 128.6, 130.5, 132.6, 133.9, 136.5, 142.7, 167.5, 168.3, 169.0, and 174.0.

The above compound was subjected to the standard diazo transfer conditions to give *N*-[2-(1-benzoyl-4-vinyl-2,3-dihydro-1*H*-indol-3-yl)acetyl-2-diazo-*N*-methylmalonamic acid methyl ester (**9**) as a yellow solid (98%): mp 146–147 °C; IR (neat) 2140, 1723, 1642, and 1335 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.78 (m, 2H), 3.11 (s, 3H), 3.63 (brs, 3H), 3.93 (m, 2H), 4.23 (dd, 1H, J = 11.6 and 8.4 Hz), 5.38 (d, 1H, J = 11.1 Hz), 5.79 (d, 1H, J = 17.5 Hz), 6.75 (dd, 1H, J = 17.5 and 11.0 Hz), 7.20 (brs, 2H), 7.44 (m, 4H), 7.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.2, 35.4, 40.3, 52.4, 56.3, 72.0, 77.3, 116.5, 120.8, 127.3, 128.5, 130.3, 132.1, 132.7, 133.8, 136.7, 142.7, 160.5, 166.2, 169.2, and 173.5.

To a solution of 1.51 g (3.38 mmol) of the above diazo imide in 50 mL of anhydrous CH_2Cl_2 at 23 °C was added 2 mg (0.02 mmol) of rhodium(II) perfluorobutyrate. After being stirred at 23 °C for 2 h, the mixture was concentrated under reduced pressure. The solid residue was purified by flash silica gel chromatography to give 1.31 g (93%) of 4-benzoyl-7a,9-epoxy-7-methyl-8-oxo-5,5a,6,7,8,9,10,10a-octahydroindolo[4,3-*fg*]quinoline-9-carboxylic acid ethyl ester (**31**) as a white solid: mp 245–247 °C; IR (neat) 1758, 1725, 1646, and 1131 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.96 (dd, 1H, J = 14.9 and 12.5 Hz), 2.53 (AB of ABX, 2H, J = 13.8, 8.5 and 5.4 Hz), 2.88 (m, 4H), 3.06 (t, 1H, J = 6.7 Hz), 3.50 (m, 1H), 3.79 (m, 1H), 3.86 (s, 3H), 4.45 (brs, 1H), 6.80 (brs, 1H), 7.35–7.62 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.5, 32.3, 32.9, 44.2, 53.1, 77.2, 86.5, 99.2, 121.1, 127.1, 127.2, 127.5, 128.1, 128.7, 130.7, 165.6, 168.9, and 170.2. Anal. Calcd for $C_{24}H_{22}N_2O_5$: C, 68.87; H, 5.30; N, 6.70. Found: C, 68.75; H, 5.25; N, 6.53.

The Rh(II)-catalyzed reaction of **9** was also carried out using Rh_2OAc_4 as the catalyst. To a solution of 112 mg (0.23 mmol) of diazo imide **9** in 2 mL of anhydrous benzene at 23 °C was added 5 mg (0.006 mmol) of rhodium(II) acetate. After being stirred at 50 °C for 12 h, the mixture was concentrated under reduced pressure. The resultant residue was subjected to flash silica gel chromatography to give cycloadduct **31** (67%) as well as 29 mg (33%) of 4-(1-benzoyl-4-vinyl-2,3-dihydro-1*H*-indol-3-yl)-1-methyl-2,5-dioxopyrrolidine-3-carboxylic acid ethyl ester (**32**) as a pale yellow oil: IR (neat) 1785, 1740, 1707, 1648, and 791 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 3H), 3.21 (m, 1H), 3.47 (m, 1H), 3.72 (s, 3H), 4.11 (m, 2H), 4.28 (t, 1H, J = 8.7 Hz), 5.28 (d, 1H, J = 10.8 Hz), 5.64 (d, 1H, J = 17.1 Hz), 6.62 (dd, 1H, J = 17.1 and 10.8 Hz), 7.16 (brs, 2H), and 7.46–7.56 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 29.6, 37.5, 48.3, 49.1, 53.4, 116.8, 120.9, 127.2, 128.2, 128.6, 129.3, 130.8, 133.3, 135.1, 135.9, 143.3, 148.5, 167.5, 168.6, 170.7, and 175.9; HRMS calcd for $C_{24}H_{22}N_2O_5$ 418.1528, found 418.1516.

Preparation and Free Radical Deoxygenation of 4-Benzoyl-9-hydroxy-7-methyl-8-oxo-4,5,5a,6,7,8,9,10-octahydroindolo[4,3-*fg*]quinoline-9-carboxylic Acid Ethyl Ester (33). To a solution of 0.75 g (1.79 mmol) of cycloadduct **31** in 5 mL of CH_2Cl_2 at 0 °C was added 0.51 g (3.58 mmol) of $BF_3{\cdot}Et_2O$. This reaction mixture was warmed to 23 °C and was stirred for 8 h. The reaction was quenched with an aqueous $NaHCO_3$ solution and diluted with CH_2Cl_2. The organic layer was further washed with aqueous $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash silica gel chromatography to give 0.74 g (98%) of enamide **33** as a white solid: mp 230–231 °C; IR (neat) 3417, 2954, 1742, 1578, and 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (td, 1H, J = 15.2 and 4.2 Hz), 2.72 (dd, 1H, J = 15.7 and 4.2 Hz), 2.80 (brm, 1H), 3.22 (s, 3H), 3.33 (d, 1H, J = 15.9 Hz), 3.55 (m, 1H), 3.67 (s, 3H), 3.81 (t, 2H, J = 10.8 Hz), 4.38 (brs, 1H), 6.79 (brs, 1H), 7.48–7.62 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.5, 29.8, 30.5, 53.1, 57.5, 73.7, 111.7, 111.8, 116.7, 127.2, 127.3, 128.8, 131.2, 131.3, 135.0, 135.1, 139.9, 168.7, 169.9, and 170.0. Anal. Calcd for $C_{24}H_{22}N_2O_5$: C, 68.87; H, 5.30; N, 6.70. Found: C, 68.87; H, 5.30; N, 6.59.

To a solution of 100 mg (0.23 mmol) of enamide **33** in 5 mL of DMF was added 28 mg (0.69 mmol) of NaH (60% dispersion in mineral oil), and the solution was stirred at 23 °C for 1 h. To this mixture was added 96 mL (0.69 mmol) of phenyl chlorothionocarbonate dropwise, and the mixture was stirred for 5 h and the reaction was then quenched with an aqueous NH_4Cl solution. The organic layer was extracted with ether, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure, and the residue was subjected to flash silica gel chromatography to give 26 mg (20%) of 4-benzoyl-7-methyl-8-oxo-9-((phenoxythiocarbonyl)-oxy)-4,5,5a,6,7,8,9,10-octahydroindolo[4,3-*fg*]quinoline-9-carboxylic acid methyl ester as a yellow oil: IR (neat) 2875, 1749, 1687, 1644, and 786 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.63 (m, 1H), 2.40 (m, 1H), 2.87 (m, 1H), 3.26 (s, 3H), 3.46 (m, 1H), 3.66 (m, 1H), 3.76 (s, 3H), 3.81–3.89 (m, 2H), 6.78 (m, 1H), 7.11 (d, 2H, J = 7.8 Hz), 7.28 (m, 2H), 7.37–7.51 (m, 5H), and 7.58 (d, 3H, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 28.9, 29.8, 30.1, 53.2, 65.8, 83.3, 109.3, 120.9, 121.7, 121.8,

126.7, 127.3, 128.6, 128.8, 129.5, 130.7, 136.0, 136.2, 140.5, 153.3, 162.7, 166.4, 168.8, and 191.6.

To a solution of 26 mg (0.045 mmol) of the above thiocarbonate in 2 mL of benzene were added 60 mL (0.22 mmol) of tributyl tin hydride and 7.4 mg (0.045 mmol) of AIBN. The mixture was heated to 95 °C for 8 h, cooled to 23 °C, and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography to give 2 mg (19%) of 4-benzoyl-7-methyl-4,5,5a,6,7,8,9,10-octahydroindolo[4,3-*fg*]-quinoline-9-carboxylic acid methyl ester (**34**) as a yellow oil: IR (neat) 2918, 1741, 1670, 1647, and 1393 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (m, 1H), 2.81 (m, 2H), 3.08 (m, 1H), 3.18 (s, 0.66 H), 3.20 (s, 0.33 H), 3.63 (m, 2H), 3.71 (s, 0.33 H), 3.80 (s, 0.66 H), 3.82 (m, 1H), 4.06 (t, 1H, J = 6.6 Hz), 6.79 (bs, 1H), 7.48 (m, 4H), and 7.56 (m, 3H); HRMS calcd for $C_{24}H_{22}N_2O_4$ 402.1579, found 402.1578.

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Supplementary Material Available: Copies of ^{13}C NMR spectra (75 MHz) of compounds lacking analyses (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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