I-12a (R^4 = troc): NMR (300 MHz, $CDCl_3$) δ 1.46 (two s, 18 H), 1.64 (m, 2 H), 2.15 (m, 1 H), 2.72 (t, 1 H, J = 12 Hz), 2.96 (m, 1 H), 3.1 (m, 1 H), 3.25 (d + m, 1 H), 4.2 (m, 1 H), 4.7 (s, 2 H), 5.1 (m + br s, 5 H), 5.7 (br s, 1 H), 6.35 (s, 1 H), 6.83 (s, 1 H), 7.4 (m, 10 H); IR (neat) 3320 with shoulder 3400, 1725, 1665 cm^{-1}; MS (CI with isobutane) m/e 808 (M + 1), 806, 752, 750, 708, 706.

II-12a (R^4 = troc): NMR (300 MHz, $CDCl_3$) δ 1.2 (s, 9 H), 1.4 (s, 9 H), 1.9 (m, 2 H), 2.2 (m, 1 H), 2.63 (t, 1 H, J = 11 Hz), 2.9 (m, 1 H), 3.23 (m, 1 H), 3.4 (m, 1 H), 4.2 (m, 1 H), 4.7 (dd, 1 H, J = 12 Hz), 4.8 (s, 1 H), 5.2 (m, 5 H), 5.4 (m, 1 H), 6.5 (s, 1 H), 7.4 (m, 10 H); IR (film) 3320 with shoulder 3400, 1730, 1660 cm^{-1}; MS (CI with isobutane) m/e 809, 808 (MH), 806, 752.

1-[1-(*tert*-Butoxycarbonyl)-3-[(trichloroethoxycarbonyl)amino]propyl]-3-[(*tert*-butoxycarbonyl)amino]-6,7-bis(benzyloxy)tetrahydroquinoline-2-thione (29c). A solution of 323 mg (0.4 mmol) of **12a** (R^4 = troc) and 162 mg (0.4 mmol) of Lawesson's reagent in 15 mL of benzene was refluxed overnight under nitrogen. The reaction mixture was passed through a silica gel column with hexanes-ethyl acetate (3:1) as the eluent to provide 210 mg (64%) of product **29c**. A number of unidentified compounds, resulting from decomposition of **12a** (R^4 = troc), were also observed. **29c**: NMR (300 MHz, $CDCl_3$) δ 1.45 (3s, 18 H), 2.5 (m, 2 H), 2.8 (m, 1 H), 3.0 (m, 1 H), 3.2 (m, 2 H), 3.35 (m, 1 H), 4.2 (m, 1 H), 4.7 (two s, 2 H), 5.2 (m, 6 H), 6.2 and 6.4 (two s, 1 H), 6.42 and 6.85 (two s, 1 H), 7.4 (m, 10 H); IR (neat) 3340, broad 1710 with shoulders 1730 and 1690 cm^{-1}; MS (CI with isobutane) m/e 826, 824 (M + 1), 822, 768, 766.

5-[*N*-(*tert*-Butoxycarbonyl)amino]-2,3-dihydro-8,9-bis(benzyloxy)-1*H*-pyrimido[1,2-*a*]quinoline-1-carboxylic Acid *tert*-Butyl Ester (5a). To 823 mg (1 mmol) of **29c** in 50 mL of THF was added with vigorous stirring 1.5 g of zinc powder followed by addition of 10 mL 1 M KH_2PO_4, and the course of the reaction was followed by TLC analysis. After 2 h, 50 mL of THF, 1.5 g of Zn powder, and 10 mL of 1 M KH_2PO_4 were added, and the reaction was continued for 2 h more. The product was extracted with ethyl acetate, washed with water and brine, dried over anhydrous $MgSO_4$, and filtered. The ethyl acetate was evaporated under reduced pressure. The residue was dissolved in 25 mL of ethanol and treated with mercuric acetate under reflux for 2 h. The ethanol was removed under reduced pressure, and the crude reaction mixture was chromatographed on a silica gel column with CH_2Cl_2-EtOH (9:1) as the eluent to give 440 mg (90%) of **5a**: mp 152-154 °C; NMR (300 MHz, $CDCl_3$) δ 1.4 (s, 9 H), 1.53 (s, 9 H), 2.0 (m, 1 H), 2.3 (dm, 1 H), 3.4 (dd, 1 H, J = 12 Hz), 3.63 (dm, 1 H), 4.6 (m, 1 H), 5.15 (dd, 2 H), 6.5 (s, 1 H), 6.9 (s, 1 H), 7.4 (m, 11 H), 7.8 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.604, 27.469, 27.877, 39.321, 55.602, 71.197, 71.515, 79.777, 82.382, 98.566, 113.311, 114.798, 126.834, 126.964, 127.400, 127.594, 128.054, 128.143, 130.741, 136.371, 136.589, 143.036, 143.988, 148.311, 152.547, 169.615. Anal. Calcd for $C_{36}H_{41}N_3O_6$: C, 70.70; H, 6.71; N, 6.87; Found: C, 70.74; H, 6.70; N, 6.71.

Acknowledgment. We gratefully acknowledge the National Institutes of Health for support of this research. We also sincerely appreciate helpful suggestions made by Dr. Daniel Reno regarding the use of the thioamide to promote cyclizations. Frequent discussions related to the pseudomonal siderophores with Prof. Thammaiah Viswanatha were especially helpful.

Lewis Acid Catalyzed Reactions of α,β-Unsaturated *N,N*-Dimethylhydrazones with 1,4-Benzoquinone. Formation of Indoles by a Novel Oxidative Rearrangement

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The Diels-Alder reaction of quinones and (*E*)-3-arylpropenal *N,N*-dimethylhydrazones only proceeds with 1,4-naphthoquinone as the dienophile. The addition of Lewis acids leads to the formation of *trans*-2,3-dihydrobenzofurans in a highly regioselective [3 + 2] process. When [*o*-(acylamino)phenyl]propenal *N,N*-dimethylhydrazones **4** and **5** were allowed to react with 1,4-benzoquinone and boron trifluoride, an unprecedented oxidative rearrangement took place yielding indole-3-carboxaldehyde *N,N*-dimethylhydrazones **7** and **8**, respectively.

The ability of α,β-unsaturated hydrazones to react with electrophilic reagents at C-3[1] has been successfully exploited in their utilization as 1-azadienes[2,3] in Diels-Alder cycloaddition reactions with electron-deficient dienophiles.[4] In an effort to apply this annulation strategy as a key step in the synthesis of polycyclic marine alkaloids,[5,6] the cy-

(1) Severin, T.; Wanninger, G.; Lerche, H. *Chem. Ber.* **1984**, *117*, 2875 and references cited therein.

(2) For recent reviews on the Diels-Alder reaction of 1-azadienes, see: (a) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: Orlando, FL, 1987. (b) Kametani, T.; Hibino, S. *Adv. Heterocycl. Chem.* **1987**, *42*, 246.

(3) For recent examples of the synthetic use of 1-azadienes, see: (a) Barluenga, J.; Joglar, J.; González, F. J.; Gotor, V.; Fustero, S. *J. Org. Chem.* **1988**, *53*, 5960. (b) Boger, D. L.; Wysocki, R. J., Jr. *J. Org. Chem.* **1989**, *54*, 714. (c) Boger, D. L.; Kasper, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 1517. (d) Teng, M.; Fowler, F. W. *Tetrahedron Lett.* **1989**, *30*, 2481.

(4) For the cycloaddition chemistry of α,β-unsaturated *N,N*-dimethylhydrazones, see: (a) Ghosez, L.; Serckx-Poncin, B.; Rivera, M.; Bayard, P.; Sainte, F.; Demoulin, A.; Hesbain-Frisque, A. M.; Mockel, A.; Munoz, L.; Bernard-Henriet, C. *Lett. Heterocycl. Chem.* **1985**, *8*, 69. (b) Walder, A. *Helv. Chim. Acta* **1988**, *71*, 486. (c) Walder, A. *Helv. Chim. Acta* **1988**, *71*, 493. (d) Chigr, M.; Fillion, H.; Rougny, A. *Tetrahedron Lett.* **1988**, *29*, 5913. (e) Dolle, R. E.; Armstrong, W. P.; Shaw, A. N.; Novelli, R. *Tetrahedron Lett.* **1988**, *29*, 6349. (f) Potts, K. T.; Walsh, E. B.; Bhattacharjee, D. *J. Org. Chem.* **1987**, *52*, 2285. (g) For the attempts to construct the C ring of the tetracyclic ergot alkaloids by this chemistry, see: Hegedus, S. S.; Sestrick, M. R.; Michaelson, E. T.; Harrington, P. J. *J. Org. Chem.* **1989**, *54*, 4141.

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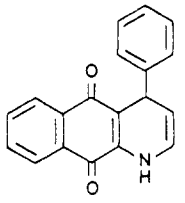
cloaddition reaction of substituted cinnamyl *N,N*-dimethylhydrazones with 1,4-benzoquinones was examined (Scheme I). Such a process would provide a route to 4-arylquinolines, a class of compounds not readily available by the Skraup quinoline synthesis.[7-9]

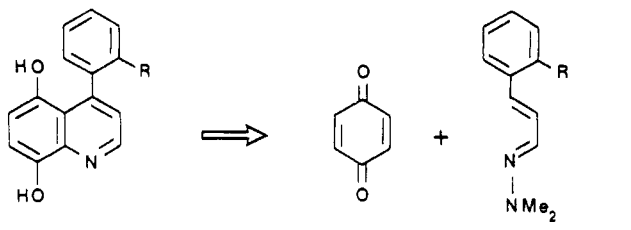
However, no [4 + 2] cycloaddition reaction was ever observed when solutions of hydrazones **1–5** with benzoquinone or a number of substituted derivatives, such as 2-chloro-, 2,6-dibromo-,[10] 2-(phenylthio)-,[11] and 2-(phenylsulfinyl)-1,4-benzoquinone,[11] were heated. Slow decomposition of the hydrazones leading to quinoline and reduction of the quinone was observed under forcing conditions.[12] Limited success was obtained in the reaction of naphthoquinone and unsubstituted hydrazone **1** leading to dihydro-1-azaanthraquinone **6** in 28% yield. Quinone **6** arises from a Diels–Alder reaction followed by dimethylamine elimination and isomerization of the double bond.[4d] In contrast, attempted cycloaddition of naphthoquinone with substituted hydrazones **2–5** failed, yielding intractable mixtures of products.



6

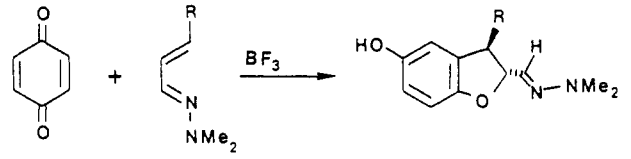
In an attempt to increase the reactivity of the dienophiles, the effect of Lewis acid catalysts was examined. Although it was evident that coordination of the Lewis acid with the basic dienes could take place,[13] an equilibrium with the Lewis acid–quinone adduct was expected to trigger the desired cycloaddition.[14] Herein, we report on the unusual reactions of α,β-unsaturated *N,N*-dimethylhydrazones with 1,4-benzoquinone in the presence of Lewis acids.

Scheme I



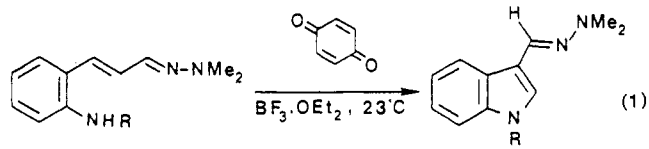
1 R = H
2 R = NO_2
3 R = NH_2
4 R = NHCOPh
5 R = NHCOMe

Table I



entry	R	product	yield, %	trans–cis
1	Ph (1)	**12**	71	5:1
2	*o*-$MeOC_6H_4$ (11)	**13**	64	3:1
3	Me (14)	**15**	39	>20:1

Readily available hydrazone **4** reacts with benzoquinone in dichloromethane solution at 23 °C after addition of 1 equiv of $BF_3{\cdot}OEt_2$, to give rearranged indole **7** in 52% yield as the only detectable cyclized product, together with hydroquinone (isolated in 62% yield) (eq 1). Structural



(1)

4 R = COPh
5 R = COMe

7 R = COPh
8 R = COMe
9 R = H

assignment of **7** was based on its ^1H NMR spectrum and was further confirmed by its quantitative cleavage with anhydrous KOH[15] into known indole **9**, identical with a sample prepared from commercially available 3-formylindole.[16] Unprotected aniline **3** gave a quantitative yield of quinoline under similar reaction conditions, while cyclization of acetanilide **5** gave **8** in 32% yield. The reaction between **4** or **5** and benzoquinone was also promoted by a variety of Lewis acids (i.e., $TiCl_4$, $SnCl_4$, $ZnCl_2$, and TMSOTf) and, more remarkably, by treatment with 2,3-dichloro-5,6-dicyanoquinone in dichloromethane (42 and 32% of **7** and **8**, respectively) in the absence of Lewis acids. Many other electrophiles were tried in order to increase the efficiency of this unexpected oxidative rearrangement. However, most reactions resulted in decomposition of the starting materials, whereas treatment with I_2 in acetonitrile gave indoles **7** and **8** in very low yield. On the other hand,

(5) See, inter alia: (a) Amphimedine: Schmitz, F. J.; Agarwal, S. K.; Gunasekera, S. P.; Schmidt, P. G.; Schoolery, J. N. *J. Am. Chem. Soc.* **1983**, *105*, 4835. (b) Segolines: Rudi, A.: Benayahu, Y.; Goldberg, I.; Kashman, Y. *Tetrahedron Lett.* **1988**, *29*, 3861. (c) Cystodytins: Kobayashi, J.; Cheng, J.; Wälchi, M. R.; Nakamura, H.; Hirata, Y.; Sasaki, Y.; Ohizumi, Y. *J. Org. Chem.* **1988**, *53*, 1800. (d) 2-Bromoleptoclinidinone: de Guzman, F. S.; Schmitz, F. J. *Tetrahedron Lett.* **1989**, *30*, 1069.

(6) For synthetic work in this area; see: Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 4051. Kubo, A.; Nakahara, S. *Heterocycles* **1988**, *27*, 2095. Labarca, C. V.; MacKenzie, A. R.; Moody, C. J.; Rees, C. W.; Vaquero, J. J. *J. Chem. Soc., Perkin Trans 1* **1987**, 927. Thompson, C. M.; Docter, S. *Tetrahedron Lett.* **1988**, *29*, 5213. Prager, R. H.; Tsopelas, C. *Heterocycles* **1989**, *29*, 847. Subramanyam, C.; Noguchi, M.; Weinreb, S. M. *J. Org. Chem.* **1989**, *54*, 5580. Ciufonili, M. A.; Byrne, N. E. *Tetrahedron Lett.* **1989**, *30*, 5559.

(7) (a) Jones, G., Ed. Quinolines. In *The Chemistry of Heterocyclic Compounds*; John Wiley: Chichester, 1982; Vol. 32 (parts 1 and 2). (b) Manske, R. H. F.; Kulka, M. *Org. React. (N.Y.)* **1973**, *7*, 59.

(8) Eisch, J. J.; Dluzniewski, T. *J. Org. Chem.* **1989**, *54*, 1269.

(9) A low yield of 4-phenylquinoline was obtained by the condensation of β-chloropropiophenone and aniline: Kenner, J.; Statham, F. S. *J. Chem. Soc.* **1935**, 299. For a related reaction in the synthesis of 4-phenyl-1,10-phenanthrolines, see: Case, F. H. *J. Org. Chem.* **1951**, *16*, 1541.

(10) Perumal, P. J.; Bahtt, M. V. *Synthesis* **1979**, 205.

(11) Brimble, M. A.; Brimble, M. T.; Gibson, J. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 179.

(12) Variable amounts of readily oxidized 2-(dimethylamino)hydroquinone (Wunderer, H. *Arch. Pharm. (Weinheim, Ger.)* **1973**, *306*, 438) were isolated in the reactions of 1,4-benzoquinone: ^1H NMR ($CDCl_3$, 200 MHz) δ 6.62 (dd, *J* = 10.0, 2.4 Hz, 1 H), 6.49 (d, *J* = 10.0 Hz, 1 H), 5.58 (d, *J* = 2.4 Hz, 1 H), 3.14 (s, 6 H); LRMS *m/z* 153 (M^+, 78), 138 (43), 111 (100).

(13) Addition of 1 equiv of $BF_3{\cdot}OEt_2$ to a deuteriochloroform solution of **1** induced downfield shifts on the ^1H NMR signals of H-1 and H-3 (1.41 and 1.21 ppm, respectively). No decomposition was observed after 2 days at 30 °C.

(14) For the Diels–Alder reaction of 2-aza-1,3-dienes with electron-rich dienophiles under Lewis acid catalysis, see: Cheng, Y.-S.; Ho, E.; Mariano, P. S.; Ammon, H. L. *J. Org. Chem.* **1985**, *50*, 5678.

(15) Gassman, P. G.; Hodgson, P. K. G.; Balchunis, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 1275.

(16) Wiley, R. H.; Irick, G. *J. Org. Chem.* **1959**, *24*, 1925.

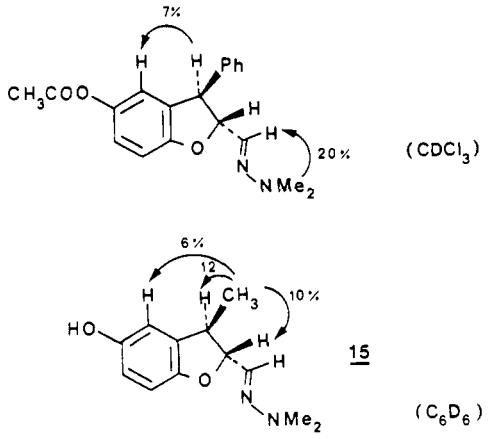
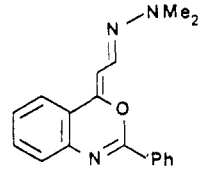


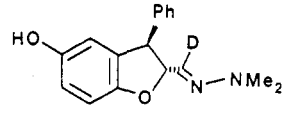
Figure 1. ^{1}H NOEDIFF enhancements (300 MHz, 30 °C).

reaction of **4** with *t*-BuOCl (THF, 23 °C, 1 h) led to yellow-orange benz-3,1-oxazine **10** in 47% yield, resulting from an electrophile-promoted cyclization.[17]



10

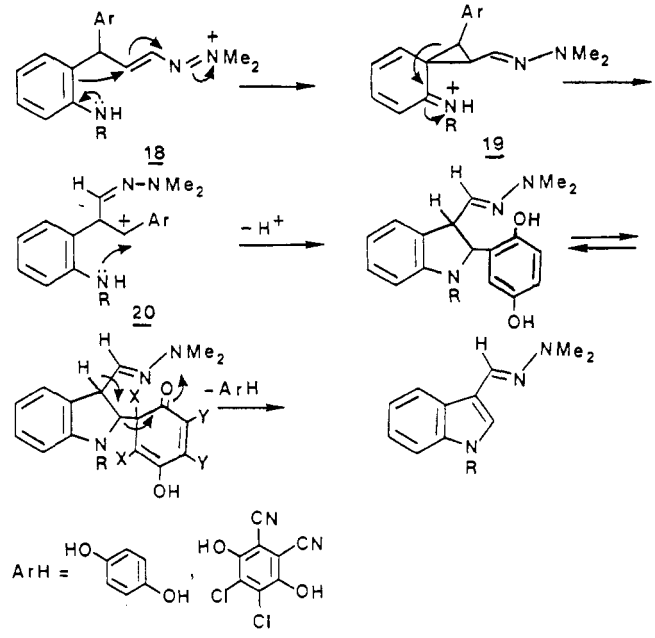
N,N-Dimethylhydrazones lacking a nucleophilic function in the ortho position of the aryl ring were found to behave differently. Thus, reaction of cinnamyl hydrazones **1** and **11** with benzoquinone and BF_3·OEt_2 in dichloromethane at 23 °C gave 5-hydroxy-2,3-dihydrobenzofuran derivatives **12** and **13**, respectively (Table I). The structure elucidation of the [3 + 2] cycloadducts was facilitated by the synthesis of the deuterio derivative **16**, starting from the hydrazone of 1-deuterio-3-phenylpropenal.[18] The reaction is not limited to cinnamyl hydrazones since crotonaldehyde *N,N*-dimethylhydrazone (**14**),[1] known to cycloadd quinones under thermal conditions,[4d] gave regio- and stereoselectively **15**, albeit in lower yield. The stereo- and regiochemistry of the dihydrobenzofurans were conclusively demonstrated by means of nuclear Overhauser effect difference spectroscopy (Figure 1).



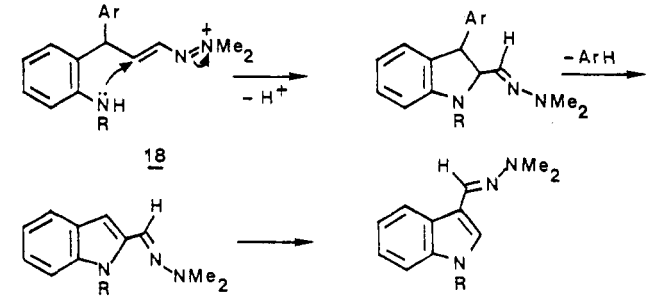
16

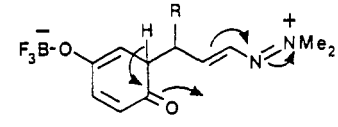
The formation of dihydrobenzofurans **12**, **13**, and **15** may take place by ring closure of intermediate **17**,[19] resulting from a Michael-type attack of the C-3 nucleophilic terminus of the *N,N*-dimethylhydrazone on the quinone–Lewis acid adduct. Thus, in accordance with our expectations, the Lewis acid promotes the attack of the nucleophilic aza-1,3-diene yielding intermediate **17**, although the ring closure does not result in the formation of the desired [4 + 2] cycloadduct. On the other hand, the *o*-acylamino function can promote the formation of spiro intermediate **19**,[21] which could evolve by carbon–carbon bond cleavage to give the benzylic carbocation **20**. Cyclization and hydroquinone elimination,[20] via a retro-Michael-type reaction, should furnish the 3-substituted indole (Scheme II).

Scheme II



Scheme III





17

An alternate reaction pathway could be conceived in which intermediate **18** undergoes a favorable *5-exo-trigonal* cyclization to give a 2-substituted indole, after hydroquinone elimination. Lewis acid catalyzed rearrangement could then afford the 3-substituted indoles (Scheme III).

Although seemingly unlikely, this migration has a precedent in the finding that the reaction of 2,3-butanedione

(17) For a review of heterocyclization reactions, see: Ellis, G. P. Synthesis of Fused Heterocycles. In *The Chemistry of Heterocyclic Compounds*; John Wiley: Chichester, 1987; Vol. 47.

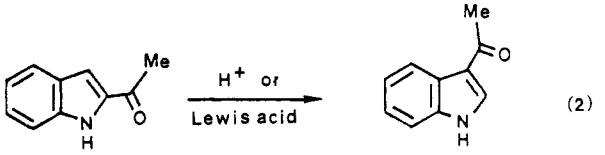
(18) Pinhas, A. R.; Samuelson, A. G.; Risemberg, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. X. *J. Am. Chem. Soc.* **1981**, *103*, 1668.

(19) For related cyclizations, see: Engler, T. A.; Combrink, K. D.; Ray, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 7931. Engler, T. A.; Combrink, K. D.; Takusagawa, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1573 and references cited therein.

(20) For the involvement of 1,4-benzoquinone–substrate adducts as intermediates in oxidative processes, see: Bhattacharya, A.; DiMichele, L. M.; Dolling, U.-H.; Douglas, A. W.; Grabowski, E. J. J. *J. Am. Chem. Soc.* **1988**, *110*, 3318. Bhattacharya, A.; DiMichele, L. M.; Dolling, U.-H.; Grabowski, E. J. J.; Grenda, V. J. *J. Org. Chem.* **1989**, *54*, 6118. I thank a referee for suggesting these references.

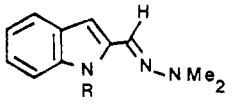
(21) A related intermediate is involved in the abnormal aromatic Claisen rearrangement. See: Schmid, E.; Fráter, G.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 1525. Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1.

phenylhydrazone with polyphosphoric acid at 100 °C yields 3-acetylindole, instead of the expected 2-derivative. Treatment of 2-acetylindole with protic or Lewis acids effects a clean rearrangement into 3-acetylindole (eq 2).[22]



(2)

In an effort to distinguish between the two mechanistic proposals, 2-formylindole *N,N*-dimethylhydrazone (**21**) was prepared from 2-formylindole.[23] Dimethylhydrazone **21** displayed a characteristic high-field doublet at 6.43 ppm, in DMSO-d_6 for the H-3 hydrogen coupled with the NH hydrogen with a ^4J of 2.0 Hz. Benzoylation was effected with benzoyl chloride and 4-(*N,N*-dimethylamino)pyridine in refluxing tetrahydrofuran, to give **22** as a yellow oil.



21 R = H

22 R = COPh

When **22** was exposed to $BF_3{\cdot}OEt_2$ in deuteriochloroform solution for 24 h at 23 °C, only the expected low-field shifts, resulting from coordination of the Lewis acid with the hydrazone, were observed in the ^1H NMR spectrum. Neutralization of the reaction mixture gives unchanged **22** in quantitative yield. Not surprisingly, similar treatment of unprotected **21** with $BF_3{\cdot}OEt_2$ led to decomposed material. The observed stability of **22** in the presence of Lewis acids rules out its intermediacy in the rearrangement and supports the reaction pathway shown in Scheme II.

The reaction of cinnamyl hydrazones with acetylenic substrates under Lewis acid catalysis was also briefly examined. The reaction of hydrazone **1** and methyl propiolate in dichloromethane or deuteriochloroform at 23 °C in the presence of 1 equiv of $BF_3{\cdot}OEt_2$ for 14 h yielded cinnamonitrile in 81% yield, while a thermal reaction in benzene or acetonitrile, in the absence of Lewis acids, gave recovered starting material.[24]

In summary, a new pathway for indole ring formation by a novel oxidative rearrangement of *o*-(acylamino)-cinnamyl *N,N*-dimethylhydrazones has been uncovered. Furthermore, the reaction of α,β-unsaturated *N,N*-dimethylhydrazones with benzoquinone in the presence of Lewis acid catalysts leads to 2,3-dihydrobenzofurans in a highly regioselective manner.

Experimental Section

^1H NMR spectra were recorded on a Bruker AM 200 (200 MHz), an IBM 270 (270 MHz), or a Varian XL-300 (300 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a Bruker AM 200 (50 MHz) spectrometer with the solvent [$CDCl_3$ or $(CD_3)_2SO$] as internal standard. Carbon multiplicities were determined by DEPT. IR spectra were obtained on a Perkin-Elmer 681 spectrophotometer. Low-resolution mass spectra (LRMS) were obtained on a VG-12-250 spectrometer. Elemental analyses were performed at the Instituto de Química Orgánica (CSIC).

Dichloromethane was freshly distilled from calcium hydride. Tetrahydrofuran and diethyl ether were freshly distilled over sodium benzophenone ketyl under argon. All reactions were carried out under an argon atmosphere.

Melting points were determined with a Reichert Kofler apparatus and are uncorrected. Boiling points refer to Kugelrohr distillation temperature. Thin-layer chromatographic analyses (TLC) were performed on aluminum sheets precoated with silica gel $60F_{254}$ (0.2 mm) (Merck). Flash column chromatography was performed with Macherey Nagel 230–400-mesh silica gel.

(*E*)-3-Phenylpropenal *N,N*-dimethylhydrazone (**1**)[4b] and (*E*)-2-butenal *N,N*-dimethylhydrazone[1] were prepared according to literature methods.

(*E*)-3-(2-Nitrophenyl)propenal *N,N*-Dimethylhydrazone (2). A solution of (*E*)-3-(2-nitrophenyl)propenal (4.73 g, 26.70 mmol) and *N,N*-dimethylhydrazine (2.10 mL, 27.63 mmol) in benzene (100 mL) was heated to reflux in a Dean–Stark apparatus for 4 h. The solvent was evaporated, to give **2** as a red solid (5.80 g, 99%): mp 37–38 °C (hexanes); IR (KBr) 1605, 1550, 1520, 1345, 1070, 1045, 955, 940 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.89 (dd, J = 8.2, 1.3 Hz, 1 H), 7.69 (dd, J = 8.0, 1.2 Hz, 1 H), 7.52 (td, J = 7.6, 1.3 Hz, 1 H), 7.31 (td, J = 8.2, 1.2 Hz, 1 H), 7.13–6.93 (m, 3 H), 2.99 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.67 (s), 133.01 (d), 132.78 (d), 132.60 (d), 127.14 (d), 124.57 (d), 124.00 (d), 42.38 (t, 2×) (one quaternary carbon overlaps); LRMS m/z 219 (M^+, 16.8), 129 (16.0), 115 (26.0). Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98; N, 19.17. Found: C, 60.18; H, 5.86; N, 19.36.

(*E*)-3-(2-Aminophenyl)propenal *N,N*-Dimethylhydrazone (3). A mixture of hydrazone **2** (1.15 g, 5.25 mmol) and $FeSO_4{\cdot}7H_2O$ (14.0 g, 50.4 mmol) was heated to 80 °C in a mixture of methanol (40 mL), ammonium hydroxide (25% solution, 15 mL), and water (10 mL). After 3 h, the mixture was cooled to room temperature, diluted with water, and extracted with ethyl acetate. The organic extract was washed with water and dried (Na_2SO_4). The solvent was evaporated, to give **3** as a pale yellow solid (930 mg, 94%): mp 82–83 °C (cyclohexane); IR (KBr) 3420, 3350, 3240, 1640, 1495, 1460, 1030, 965, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.34 (dd, J = 7.8, 1.6 Hz, 1 H), 7.17 (d, J = 8.6 Hz, 1 H), 7.07 (td, J = 7.6, 1.5 Hz, 1 H), 6.60 (dd, J = 15.7, 8.7 Hz, 1 H), 6.77 (td, J = 7.7, 1.1 Hz, 1 H), 6.67 (overlapping d, J = 15.8 Hz, 1 H), 6.68 (overlapping dd, J = 7.9, 1.1 Hz, 1 H), 3.77 (br, 2 H), 2.93 (s, 6 H); ^{13}C NMR ($CDCl_3$, 68 MHz), δ 143.70, 135.41, 128.71, 128.30, 126.98, 126.86, 123.52, 119.02, 116.28, 42.60 (2×); LRMS m/z 189 (M^+, 23.2), 130 (100), 117 (19.9). Anal. Calcd for $C_{11}H_{15}N_3$: C, 69.81; H, 7.99. Found: C, 70.04; H, 8.04.

(*E*)-3-[2-(Benzoylamino)phenyl]propenal *N,N*-Dimethylhydrazone (4). A mixture of (*E*)-3-[2-(benzoylamino)-phenyl]propenal[25] (2.00 g, 7.96 mmol) and *N,N*-dimethylhydrazine (530 mg, 8.82 mmol) in benzene (30 mL) was heated to reflux in a Dean–Stark apparatus for 2 h. After cooling to room temperature, the white crystals were filtered and washed with benzene, to give **4** as a white crystalline solid (2.00 g; 86%): mp 184–185 °C (benzene); IR (KBr) 3260, 1650, 1525, 1485, 1310, 1100, 960, 750, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.93–7.90 (m, 2 H), 7.84–7.81 (m, 2 H), 7.58–7.48 (m, 4 H), 7.32–7.27 (m, 1 H), 7.23–7.19 (m, 1 H), 7.10 (d, J = 8.8 Hz, 1 H), 6.91 (dd, J = 15.7, 8.9 Hz, 1 H), 6.68 (d, J = 15.7 Hz, 1 H), 2.94 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.85, 134.60, 134.20, 134.09, 131.79, 131.03, 130.78, 128.68 (2×), 127.20 (2×), 126.09, 125.93, 125.10, 124.78, 42.57 (2×); LRMS m/z 293 (M^+, 23), 234 (14.6), 130 (15.7), 105 (100). Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.32. Found: C, 73.34; H, 6.40; N, 14.43.

(*E*)-3-(2-Acetamidophenyl)propenal *N,N*-Dimethylhydrazone (5). To a suspension of hydrazone **3** (400 mg, 2.1 mmol) in a solution of NaOH (190 mg, 4.7 mmol) in water (40 mL) cooled to 0 °C was added acetic anhydride (1.7 mL, 21 mmol). The resulting mixture was stirred at 23 °C for 1 h. The solid was filtered and washed with water, to give **5** as a white solid (480 mg, 98%): mp 147–148 °C (1:1 EtOAc–hexanes); IR (KBr) 3290, 1655, 1585, 1040, 955, 755 cm^{-1}; ^1H NMR (Me_2SO-d_6, 270 MHz) δ 9.52 (br s, 1 H), 7.65 (dd, J = 7.4, 2.0 Hz, 1 H), 7.36 (dd, J = 7.7, 1.6 Hz, 1 H), 7.22–7.13 (m, 3 H), 6.91–6.75 (m, 2 H), 2.87 (s, 6 H), 2.07 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.06, 134.47,

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133.96, 133.94, 129.64, 127.56, 125.73, 125.67, 125.53, 125.21, 42.56, 23.64. Anal. Calcd for $C_{13}H_{17}N_3O$: C, 67.50; H, 7.41. Found: C, 67.40; H, 7.44.

(*E*)-3-(2-Methoxyphenyl)propenal *N*,*N*-Dimethylhydrazone (11). A mixture of (*E*)-3-(2-methoxyphenyl)propenal (1.00 g, 6.17 mmol) and *N*,*N*-dimethylhydrazine (0.57 mL, 7.50 mmol) was heated to reflux in benzene (10 mL) for 1 h. After cooling to room temperature, the mixture was partitioned between dichloromethane and water. The organic layer was dried (Na_2SO_4) and evaporated, to give **11** as a yellow oil (1.22 g, 97%): bp 160–165 °C (1 mmHg); IR (neat) 3000, 2960, 2860, 2840, 2790, 1615, 1600, 1580, 1555, 1490, 1465, 1440, 1360, 1290, 1240, 1130, 1100, 1080, 975, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54 (dd, J = 7.7, 1.6 Hz, 1 H), 7.31–7.22 (m, 2 H), 7.04–7.02 (m, 2 H), 6.97 (dt, J = 7.6, 1.0 Hz, 1 H), 6.91 (dd, J = 8.2, 0.7 Hz, 1 H), 3.90 (s, 3 H), 2.96 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 156.46, 139.39, 128.32, 127.89, 126.62, 126.14, 120.64, 110.78, 55.31, 42.66 (2×) (one carbon signal overlaps); LRMS m/z 204 (M^+, 100), 189 (5.5), 173 (80.5). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.55; H, 8.20; N, 13.93.

(*E*)-[1-^{2}H]-3-Phenylpropenal *N*,*N*-Dimethylhydrazone. This compound was prepared as reported for **1**: pale yellow oil; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.43–7.21 (m, 5 H), 6.94 (d, J = 16.0 Hz, 1 H), 6.61 (d, J = 16.0 Hz, 1 H), 2.92 (s, 6 H); LRMS m/z 175 (M^+, 100), 160 (10), 131 (36), 116 (29.9).

4-Phenyl-1,4-dihydro-1-azaanthracene-9,10-dione (6). A solution of naphthoquinone (1.00 g, 6.32 mmol) and hydrazone **1** (730 mg, 4.20 mmol) was heated to reflux in acetonitrile (30 mL). After 6 days, the solvent was evaporated and the residue was chromatographed (15:1 hexanes–EtOAc) to give **6** as a purple solid (340 mg, 28%): mp 185–187 °C (2:1 EtOAc–hexanes); IR (KBr) 3370, 1725, 1625, 1570, 1545, 1360, 1340, 1255, 760, 740, 725, 700 cm^{-1}; ^1H NMR (Me_2SO-d_6, 200 MHz) δ 9.23 (d, J = 4.3 Hz, 1 H), 8.00–7.70 (m, 4 H), 7.30–7.10 (m, 4 H), 6.33 (dd, J = 7.7, 4.6 Hz, 1 H), 5.04 (dd, J = 7.6, 4.9 Hz, 1 H), 4.77 (d, J = 4.9 Hz, 1 H); ^{13}C NMR (Me_2SO-d_6, 50 MHz) δ 181.57, 180.30, 147.28, 140.06, 134.76, 132.55, 130.19, 128.86, 128.31, 127.60, 126.16, 125.67, 125.34, 123.57, 112.16, 107.82, 36.85; LRMS m/z 287 (M^+, 30.7), 256 (3.1), 210 (100). Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.65; H, 4.73; N, 4.92.

***N*-Benzoylindole-3-carboxaldehyde *N*,*N*-Dimethylhydrazone (7).** To a solution of 1,4-benzoquinone (210 mg, 1.94 mmol) and hydrazone **4** (570 mg, 1.94 mmol) in dichloromethane (15 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (0.24 mL, 1.95 mmol). After being stirred at 23 °C for 24 h, the mixture was partitioned between 10% aqueous $NaHCO_3$ and ethyl acetate. The organic solvent was evaporated and the residue chromatographed (3:1 hexanes–EtOAc), to give **7** as a pale yellow solid (295 mg, 52%): mp 143–144 °C (hexanes); TLC (4:1 hexanes–EtOAc) R_f 0.27; IR (KBr) 1680, 1535, 1455, 1450, 1380, 1335, 1320, 1225, 870, 740, 690, 650 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.41–8.34 (m, 2 H), 7.76–7.71 (m, 2 H), 7.64–7.44 (m, 3 H), 7.42–7.35 (m, 2 H), 7.39 (s, 1 H), 7.33 (s, 1 H), 2.97 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 168.13, 136.13, 134.53, 131.59, 128.87 (2×), 128.41 (2×), 128.24, 126.73, 125.32, 125.16, 124.08, 122.46, 119.89, 115.98, 42.54 (2×). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.29; H, 5.70; N, 14.78.

***N*-Acetylindole-3-carboxaldehyde *N*,*N*-Dimethylhydrazone (8).** A procedure analogous to the one above gave **8** as a pale yellow solid: mp 118–119 °C (3:1 hexanes–Et_2O); ^1H NMR ($CDCl_3$, 200 MHz) δ 8.43 (br d, J = 7.3 Hz, 1 H), 8.27 (dd, J = 6.1, 1.7 Hz, 1 H), 7.47 (s, 1 H), 7.44 (s, 1 H), 7.42–7.28 (m, 2 H), 3.00 (s, 6 H), 2.63 (s, 3 H). Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.09; H, 6.59. Found: C, 68.39; H, 6.38.

Indole-3-carboxaldehyde *N*,*N*-Dimethylhydrazone (9). To a solution of indole **7** (40 mg, 0.14 mmol) in diethyl ether (5 mL) at 23 °C were added KOt-Bu (80 mg, 0.71 mmol) and water (0.05 mL, 0.28 mmol). After being stirred at this temperature for 17 h, the mixture was diluted with diethyl ether and washed with water. The organic extract was dried ($MgSO_4$) and evaporated, to give **9** as a pale yellow solid: mp 101–102 °C (1:1 benzene–hexane) (lit.[15] mp 102 °C); TLC (3:1 hexanes–EtOAc) R_f 0.04; IR (KBr) 3250, 1635, 1525, 1440, 1240, 1020, 1010, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.33–8.30 (m, 1 H), 8.18 (br, 1 H), 7.68 (s, 1 H), 7.36–7.14 (m, 4 H), 2.93 (s, 6 H); ^1H NMR (Me_2SO-d_6, 300 MHz) δ 11.16 (br, 1 H), 8.20 (d, J = 7.8 Hz, 1 H), 7.68 (s, 1 H), 7.50 (d, J = 2.4 Hz, 1 H; collapses to s on irradiation at δ 11.16), 7.40 (d, J = 8.3 Hz, 1 H), 7.15 (m, 1 H), 7.07 (m, 1 H), 2.82 (s, 6 H); ^{13}C NMR (Me_2SO-d_6, 50 MHz) δ 136.84, 132.28, 125.99, 124.48, 121.87, 121.72, 119.41, 113.59, 113.37, 43.15 (2×); LRMS m/z 187 (M^+, 100), 172 (8.2), 145 (16.6).

(*Z*)-4-(Formylmethylene)-2-phenyl-4*H*-benz-3,1-oxazine *N*,*N*-Dimethylhydrazone (10). To a suspension of hydrazone **4** (425 mg, 1.45 mmol) in tetrahydrofuran (10 mL) cooled to 0 °C was added *t*-BuOCl (0.180 mL, 1.59 mmol). The mixture turned yellow. After being stirred for 1 h at 23 °C, the mixture was partitioned between water and dichloromethane. The organic layer was washed with water and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (5:1 hexanes–EtOAc), to give **10** as a bright orange solid (198 mg, 47%): mp 103–105 °C; IR (KBr) 2920, 2850, 1640, 1615, 1570, 1460, 1280, 1255, 1240, 1115, 1035, 1020, 810, 750, 680 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 8.13–8.10 (m, 2 H), 7.54 (br d, J = 7.9 Hz, 1 H; collapses to br s on irradiation at δ 6.12), 7.52–7.40 (m, 5 H), 7.29–7.25 (m, 2 H), 7.20–7.13 (m, 1 H), 6.12 (d, J = 9.2 Hz, 1 H), 2.97 (s, 6 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 154.45, 145.44, 138.91, 131.71, 131.49, 130.05, 129.35, 128.51, 127.71, 127.61, 126.62, 121.67, 121.58, 101.32, 42.74; LRMS m/z 291 (M^+, 100), 262 (18.2), 247 (51.4), 246 (32.9), 221 (38.1), 218 (28.1), 105 (56.3). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.48; H, 5.68; N, 14.03.

***trans*-2,3-Dihydro-5-hydroxy-3-phenylbenzofuran-2-carboxaldehyde *N*,*N*-Dimethylhydrazone (12).** To a solution of 1,4-benzoquinone (1.00 g, 9.25 mmol) and $BF_3{\cdot}OEt_2$ (1.15 mL, 9.35 mmol) in dichloromethane (20 mL) was added hydrazone **1** (1.60 g, 9.18 mmol). After being stirred at 23 °C for 20 h, the mixture was partitioned between 10% aqueous $NaHCO_2$ and evaporated. The residue was chromatographed (5:1 hexanes–EtOAc), to give **12** as a viscous oil (1.85 g, 71%) (decomposes on standing at room temperature): IR (neat) 3420–3240 (br), 1600, 1495, 1470, 1195, 960, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37–7.18 (m, 5 H), 6.69 (d, J = 8.5 Hz, 1 H), 6.65 (d, J = 6.0 Hz, 1 H), 6.60 (ddd, J = 8.5, 2.5, 0.8 Hz, 1 H), 6.45 (dd, J = 2.5, 0.9 Hz, 1 H), 5.58 (br, 1 H), 5.11 (dd, J = 7.9, 6.0 Hz, 1 H), 4.63 (d, J = 7.9 Hz, 1 H), 2.82 (s, 6 H) [the minor cis isomer showed a singlet signal at δ 2.51 (s, 6 H)]; ^{13}C NMR ($CDCl_3$, 50 MHz) 152.74 (s), 150.33 (s), 141.07 (s), 131.90 (s), 131.30 (d), 128.60 (d, 2×), 128.11 (d, 2×), 127.10 (d), 115.13 (d), 112.52 (d), 109 (d), 90.90 (d), 53.22 (d), 48.18 (t, 2×); LMRS m/z 282 (M^+, 4.6), 223 (100), 210 (13.2). Acetylation gave ***trans*-5-(acetyloxy)-2,3-dihydro-3-phenylbenzofuran-2-carboxaldehyde *N*,*N*-dimethylhydrazone.** To a mixture of **12** (95 mg, 0.34 mmol) in dichloromethane were added pyridine (270 mg, 3.41 mmol) and acetic anhydride (170 mg, 1.67 mmol). After being stirred at 23 °C for 20 h, the mixture was treated with methanol (5 mL). After 1.5 h of additional stirring, the mixture was partitioned between dichloromethane and water. The organic layer was washed with water and 1 M HCl, dried (Na_2SO_4), and evaporated. The residue was chromatographed (4:1 hexanes–EtOAc), to give the acetate as a viscous oil (73 mg, 67%): IR (neat) 3060, 3015, 2950, 2880, 2790, 1760, 1600, 1480, 1370, 1215–1180, 1125, 1050, 1015, 960, 825, 755, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.21 (m, 5 H), 6.69–6.84 (m, 2 H), 6.71 (dd, J = 2.0, 0.9 Hz, 1 H), 6.63 (d, J = 5.9 Hz, 1 H), 5.19 (dd, J = 8.0, 5.9 Hz, 1 H), 4.74 (d, J = 8.0 Hz, 1 H), 2.85 (s, 6 H), 2.21 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.86 (s), 156.90 (s), 144.54 (s), 141.12 (s), 131.53 (s), 130.01 (d), 128.74 (d, 2×), 128.25 (d, 2×), 127.14 (d), 121.39 (d), 118.63 (d), 109.69 (d), 91.86 (d), 52.83 (d), 42.43 (t, 2×), 20.93 (t); LMRS m/z (M^+, 3.4), 265 (33.6), 223 (45.4). Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.22; N, 8.64. Found: C, 70.41; H, 6.33; N, 8.31.

Procedures analogous to those above were employed for the preparation of **13**, **15**, and **16**.

***trans*-2,3-Dihydro-5-hydroxy-3-phenyl-2-deuteriobenzofuran-2-carboxaldehyde *N*,*N*-dimethylhydrazone (16)**: viscous oil (decomposes on standing at room temperature); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30–7.23 (m, 5 H), 6.71 (d, J = 8.5 Hz, 1 H), 6.62 (d, J = 8.5, 2.7, 0.8 Hz, 1 H), 6.45 (dd, J = 2.6, 0.7 Hz, 1 H), 5.58 (br, 1 H), 5.11 (d, J = 8.0 Hz, 1 H), 4.62 (d, J = 8.0 Hz, 1 H), 2.82 (s, 6 H); LRMS m/z 283 (M^+, 5.7), 224 (100), 210 (13).

2,3-Dihydro-5-hydroxy-3-(2-methoxyphenyl)benzofuran-2-carboxaldehyde *N*,*N*-dimethylhydrazone (3:1 trans–cis)

(13): pale yellow-white solid: IR (KBr) 3450–3300, 1600, 1590, 1495, 1465, 1250, 1200 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.25–7.09 (m, 1 H, trans + cis), 6.93–6.51 (m, 7 H trans + 6 H cis), 5.94 (d, J = 7.5 Hz, 1 H, cis), 5.45 (dd, J = 9.2, 7.4 Hz, cis), 5.19 (d, J = 9.3 Hz, 1 H, cis), 5.09 (t, J = 6.8 Hz, 1 H, trans), 5.01 (d, J = 7.3 Hz, 1 H, trans), 4.47 (br, 1 H, cis), 4.40 (br, 1 H, trans), 3.79 (s, 3 H, trans), 3.78 (s, 3 H, cis), 2.83 (s, 6 H, trans), 2.51 (s, 6 H, cis); ^{13}C NMR ($CDCl_3$, 50 MHz) trans δ 156.95, 152.83, 150.32, 133.58, 130.62, 129.15, 128.30, 127.94, 120.63, 114.73, 112.47, 110.43, 109.37, 89.91, 55.11, 46.69, 42.32 (2×), cis δ 156.77, 153.39, 150.41, 133.37, 129.68, 128.79, 128.06, 127.07, 120.12, 115.12, 113.03, 109.87, 109.47, 85.40, 55.03, 44.79, 42.13 (2×); LMRS m/z 312 (M^+, 1.6), 253 (100), 221 (11). Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 68.91; H, 6.44; N, 8.59.

***trans*-2,3-Dihydro-5-hydroxy-3-methylbenzofuran-2-carboxaldehyde *N,N*-dimethylhydrazone (15)**: white solid; mp 98–100 °C (3:1 hexanes–benzene); IR (KBr) 3170 (br), 1600, 1495, 1470, 1200, 965, 805 cm^{-1}; ^1H NMR (C_6D_6, 300 MHz) δ 6.68 (d, J = 8.4 Hz, 1 H), 6.47 (d, J = 6.2 Hz, 1 H), 6.40 (dd, J = 2.7, 1.1 Hz, 1 H; collapses to d on irradiation at δ 3.29), 6.32 (ddd, J = 8.4, 2.7, 0.8 Hz, 1 H; collapses to dd on irradiation at δ 3.29), 4.92 (dd, J = 8.3, 6.1 Hz, 1 H), 3.99 (br, 1 H), 3.29 (br quintet, J = 7 Hz, 1 H), 2.43 (s, 6 H), 1.10 (d, J = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.70, 149.93, 133.31, 132.41, 114.31, 111.22, 109.52, 90.93, 42.56, 41.71, 17.53; LMRS m/z 220 (M^+, 2.0), 161 (19.5), 110 (100). Anal. Calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32. Found: C, 65.36; H, 7.12.

Indole-2-carboxaldehyde. This indole was prepared by modification of known procedures from 2-(ethoxycarbonyl)-indole.[23a] (i) **2-(Hydroxymethyl)indole.** To a solution of 2-(ethoxycarbonyl)indole (1.70 g, 8.98 mmol) in tetrahydrofuran (5 mL) cooled to −80 °C was added diisobutylaluminum hydride (12.0 mL, 1.5 M solution in toluene, 18.0 mmol). After being stirred at −80 °C for 1 h, the solution was warmed up to 23 °C and stirred at this temperature for 1 h. The mixture was carefully poured into 0.2% HCl and extracted with ethyl acetate. The organic layer was washed with a concentrated solution of sodium chloride and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed, to give a white solid (1.228 g, 93%): mp 75–76 °C (2:1 hexanes–benzene) (lit.[23a] mp 75 °C). (ii) **Indole-2-carboxaldehyde.** The above alcohol (1.10 g, 7.74 mmol) was dissolved in dichloromethane at 23 °C and treated with pyridinium dichromate (4.28 g, 11.38 mmol) in small portions over 45 min. After 1 h, the mixture was filtered through Celite. The filtrate was washed with water, 1 M HCl, and water and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed (8:1 hexanes–EtOAc), to give the aldehyde as a white crystalline solid (458 mg, 42%): mp 139–140 °C (5:1 hexanes–benzene) (lit.[23b] mp 139–141 °C); ^1H NMR ($CDCl_3$, 300 MHz) δ 9.59 (s, 1 H), 9.10 (br, 1 H), 7.75 (dd, J = 8.1, 0.9 Hz, 1 H), 7.47–7.37 (m, 2 H), 7.28 (dd, J = 2.1, 0.9 Hz, 1 H), 7.21–7.16 (m, 1 H).

Indole-2-carboxaldehyde *N,N*-Dimethylhydrazone (21). A solution of indole-2-carboxaldehyde (450 mg, 3.10 mmol), *N,N*-dimethylhydrazine (380 mg, 63 mmol), and *p*-toluenesulfonic acid monohydrate (29 mg, 0.15 mmol) was heated to reflux in benzene (5 mL) for 30 min. After being cooled to room temperature, the mixture was diluted with ethyl acetate and washed with 5% aqueous $NaHCO_3$. The organic layer was washed with water and dried (Na_2SO_4). The solvent was evaporated, to give **21** as a white solid (552 mg, 95%): mp 105–106 °C (10:1 hexanes–benzene); TLC (3:1 hexanes–EtOAc) R_f 0.32; IR (KBr) 3250, 1620, 1585, 1580, 1520, 1460, 1455, 1420, 1340, 1295, 1055, 750, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.77 (br, 1 H), 7.57 (d, J = 7.8 Hz, 1 H), 7.33 (d, J = 7.9 Hz, 1 H), 7.30 (s, 1 H), 7.17 (t, J = 7.8 Hz, 1 H), 7.07 (t, J = 7.8 Hz, 1 H), 6.47 (s, 1 H), 2.99 (s, 6 H); ^1H NMR (Me_2SO-d_6, 300 MHz) δ 10.93 (br, 1 H), 7.44 (d, J = 7.8 Hz, 1 H), 7.34 (s, 1 H), 7.33 (d, J = 7.8 Hz, 1 H), 7.03 (m, 1 H), 6.92 (m, 1 H), 6.43 (d, J = 2.0 Hz, 1 H; on irradiation at δ 10.93 collapses to s), 2.92 (s, 6 H); ^{13}C NMR (Me_2SO-d_6, 50 MHz) δ 136.74, 136.24, 128.21, 125.26, 121.36, 119.67, 118.82, 111.16, 100.86, 42.50 (2×). Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.65; H, 6.85; N, 22.67.

***N*-Benzoylindole-2-carboxaldehyde *N,N*-Dimethylhydrazone (22).** A mixture of indole **21** (300 mg, 1.60 mmol), (*N,N*-dimethylamino)pyridine (200 mg, 1.64 mmol), and benzoyl chloride (0.190 mL, 1.64 mmol) in tetrahydrofuran (25 mL) was heated to reflux for 24 h. After being cooled to room temperature, the mixture was diluted with diethyl ether and washed with water. The organic extract was washed with water, dried ($MgSO_4$), and evaporated. Chromatography (6:1 hexanes–EtOAc) gave **22** as a viscous yellow oil (333 mg, 71%; several other fractions contained slightly impure **22**): TLC (4:1 hexanes–EtOAc) R_f 0.35; IR (neat) 3060, 2960, 2860, 2800, 1690, 1605, 1585, 1560, 1475, 1450, 1380, 1330–1300, 1220, 1140, 1050, 870, 750, 700, 635 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.69–7.66 (m, 2 H), 7.60–7.54 (m, 2 H), 7.50–7.42 (m, 3 H), 7.23–7.13 (m, 2 H), 6.94 (s, 1 H), 6.91 (s, 1 H), 2.72 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.82, 137.93, 137.43, 135.88, 132.50, 129.68, 129.41 (2×), 128.38 (2×), 123.87, 123.61, 122.87, 120.39, 113.87, 105.81, 42.13 (2×). Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.23; H, 6.10; N, 14.39.

(*E*)-3-Phenylpropenenitrile. To a solution of hydrazone **1** (600 mg, 3.44 mmol) and methyl propynoate (440 mg, 5.23 mmol) in dichloromethane (10 mL) at 0 °C was added BF_3·OEt_2 (0.430 mL, 3.50 mmol). The resulting solution was stirred at 23 °C for 19 h. The mixture was partitioned between dichloromethane and 5% aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and evaporated and the residue chromatographed (20:1 hexanes–EtOAc), to give the nitrile as an oil (362 mg, 81%): IR (neat) 2220, 1625, 1450, 970, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.41 (br s, 5 H), 7.36 (d, J = 16.7 Hz, 1 H), 5.85 (d, J = 16.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.33 (d), 133.33 (s), 131.02 (d), 128.98 (d), 127.19 (d), 117.99 (s), 96.15 (d); LRMS m/z 129 (M^+, 100), 115 (12).

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Registry No. **1**, 15023-38-8; **2**, 127280-03-9; **3**, 127280-04-0; **4**, 127280-05-1; **5**, 127280-06-2; **6**, 127280-08-4; **8**, 92487-30-4; **9**, 92487-36-0; **10**, 127280-09-5; **11**, 127280-10-8; *trans*-**12**, 127280-11-9; *cis*-**12**, 127280-12-0; *trans*-**13**, 127280-13-1; *cis*-**13**, 127280-14-2; **15**, 127280-15-3; **16**, 127280-16-4; **21**, 127280-17-5; **22**, 127280-18-6; naphthoquinone, 130-15-4; 1,4-benzoquinone, 106-51-4; quinoline, 91-22-5; (*E*)-3-(2-nitrophenyl)propenal, 66894-06-2; (*E*)-3-[2-(benzoylamino)phenyl]propenal, 127280-19-7; (*E*)-3-(2-methoxyphenyl)propenal, 60125-24-8; (*E*)-[1-^{2}H]-3-phenylpropenal *N,N*-dimethylhydrazone, 127280-20-0; *trans*-5-(acetoxy)-2,3-dihydro-3-phenylbenzofuran-2-carbonaldehyde *N,N*-dimethylhydrazone, 127280-21-1; 2-(ethoxycarbonyl)indole, 3770-50-1; indole-2-carboxaldehyde, 19005-93-7; 2-(hydroxymethyl)indole, 24621-70-3; (*E*)-3-phenylpropenenitrile, 1885-38-7; methyl propynoate, 922-67-8; (*E*)-2-butenal *N,N*-dimethylhydrazone, 119045-69-1.