Introduction of Benzo[*h*]quinoline and 1,10-Phenanthroline Subunits by Friedländer Methodology

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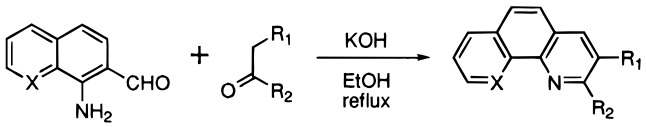
Received December 5, 1995[⊗]

An improved preparation of 8-amino-7-quinolinecarbaldehyde has been developed. The methyl group of 7-methyl-8-nitroquinoline may be oxidized to an aldehyde by treatment first with dimethylformamide dimethyl acetal followed by sodium periodate. Reduction with iron provides the amino aldehyde. An analogous sequence affords 1-amino-2-naphthalenecarbaldehyde. Friedländer condensation of the quinoline derivative with a series of acetylaromatics provides the corresponding 2-aryl-1,10-phenanthrolines. Condensation of either amino aldehyde with 1,3-diacetylbenzene or 2,6-diacetylpyridine provides the expected Friedländer product. Similar chemistry is described for reactions of the amino aldehydes with 1,4-diacetylbenzene, 4,4′-diacetylbiphenyl, 1,5-diacetylanthracene, 1,2,3,4,5,6,7,8-octahydroacridine-1,8-dione, and tetracyclo-[6.3.0.0.^{4,11}0^{5,9}]undecane-2,7-dione (TCU-2,7-dione).

Introduction

Along with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) is one of the more important available chelating ligands. The incorporation of substituents onto the parent nucleus, especially at the 2-position, has been shown to have a profound influence on the properties of the resulting metal complexes. Sauvage and co-workers have developed a synthesis of 2,9-diaryl-1,10-phenanthrolines *via* dilithiation of the parent system.[1] These derivatives, in turn, have been used to prepare a family of topologically interesting catenanes and oriented diporphyrins.[2] The Cu(I) chemistry of a variety of 2,9-disubstituted 1,10-phenanthrolines has been examined.[3] These complexes take advantage of the stabilizing effect of the 2,9-substituents which effectively prohibit the planarization of the complex which would occur upon oxidation to the Cu(II) species. Methodology has been developed for the extensive functionalization of 2,9-dimethyl-1,10-phenanthroline[4] and the subsequent incorporation of these functionalized species into macrocyclic systems.[5] A variety of other 2-substituted phenanthrolines have been examined including several which incorporate crown ethers and thus allow for the formation of dinuclear complexes involving alkali metals.[6]

The Friedländer condensation is an extremely useful and versatile method for the direct construction of a pyridine ring.[7] The condensation of an aromatic *o*-aminoaldehyde with an enolizable ketone proceeds directly with the loss of two molecules of water. By varying the nature of the aromatic ring, a variety of annulated pyridines can be prepared. To use this approach for the



1a X = N
b X = CH

2a X = N
b X = CH

incorporation of the 1,10-phenanthroline nucleus, the prerequisite amino aldehyde would be 8-amino-7-quinolinecarbaldehyde (**1a**). We have recently reported the six-step synthesis of this material from 8-hydroxyquinoline.[8] Although this method allows for the preparation of gram quantities of **1a**, the overall sequence was somewhat tedious. A more efficient route to this amino aldehyde has been developed which is more general in scope and allows for the preparation of the analogous naphthalene derivative **1b**. This paper will describe the syntheses of these amino aldehydes and their subsequent use in the preparation of a variety of derivatives of 1,10-phenanthroline and benzo[*h*]quinoline.

Results and Discussion

Our improved synthesis of **1a** (Scheme 1) begins with 7-methylquinoline (**3a**) which is commercially available and also can be readily prepared by the Skraup reaction of *o*-toluidine with glycerol.[9] Straightforward nitration produces **4a** in excellent yield. The 7-methyl group can then be functionalized by condensation with *N*,*N*-dimethylformamide dimethyl acetal (DMFDMA) to provide the corresponding (*N*,*N*-dimethylamino)alkene **5a**. Oxidation of the aminoalkene is accomplished with sodium

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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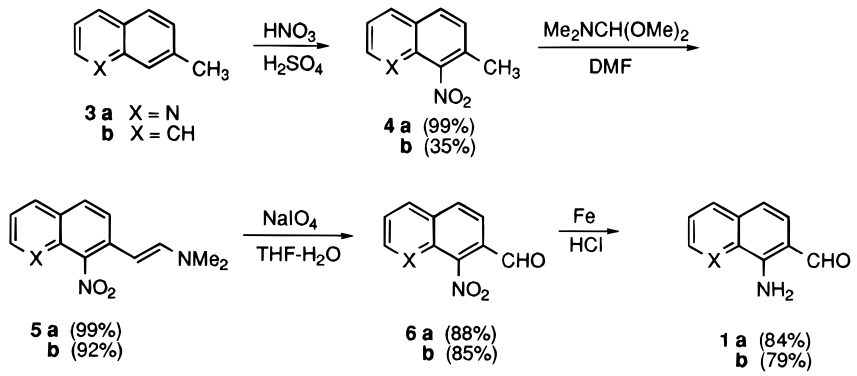
S0022-3263(95)02164-5 CCC: $12.00

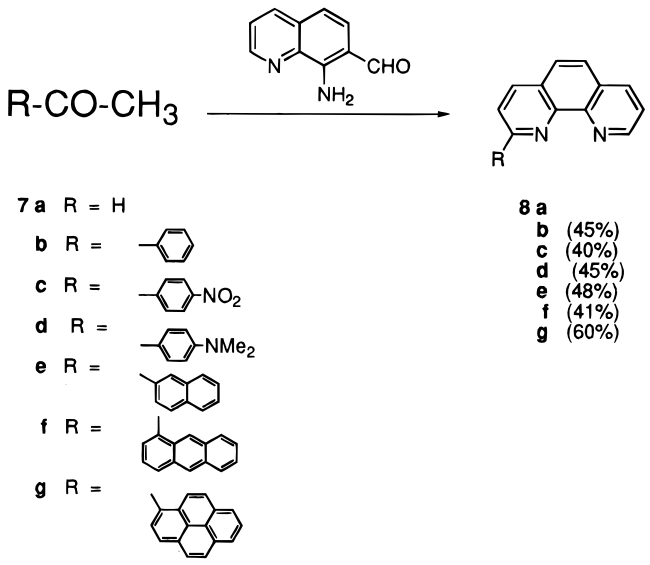
Scheme 1



periodate to provide the *o*-nitro aldehyde **6a** in good yield.[10] Reduction to the analogous amino compound is carried out with powdered iron. Due to moderate reactivity of the amino aldehyde, we normally store the nitro aldehyde and reduce it to amino aldehyde in portions as needed. The shelf life of **1a** is about 1−2 months. Like other *o*-amino aldehydes, self-condensation is believed to account for the major loss of this material.

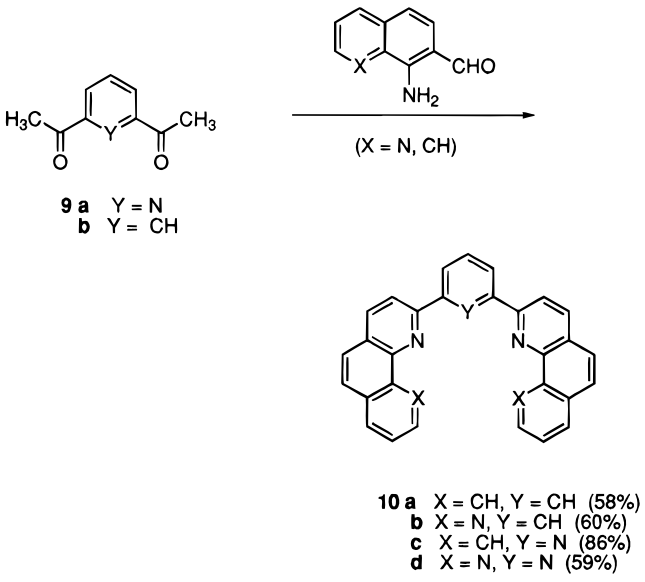
The same synthetic sequence also works well for the preparation of the analogous 1-amino-2-naphthalenecarbaldehyde (**1b**). Friedländer condensation of this material leads to the corresponding benzo[*h*]quinolines **2b**. Efforts are underway to extend this synthetic approach to other related systems, especially diamino dialdehydes.

Our initial objective in 1,10-phenanthroline synthesis was the series of 2-aryl derivatives **8b**−**g**. Molecular modeling studies as well as work with the analogous 6-phenyl-2,2′-bipyridine[11] indicate that in complexes such as $[Ru(bpy)_2(\mathbf{8b})]^{2+}$ the phenyl substituent exists in a π-stacked conformation with a pyridine of one of the auxilliary bpy ligands. The series **8b**−**g** would help to



investigate this π-stacking effect. The condensation of **1a** with acetyl aromatics **7b**−**g** provides the corresponding 2-aryl-1,10-phenanthrolines in yields of 40−60%. These materials could be readily characterized by their ^{1}H NMR spectra. Although it was not always possible to completely resolve and assign all the proton resonances, certain features were characteristic and diagnostic. The lowest field peak was always H_9, showing a doublet with a characteristically small coupling constant (*ca.* 4.6 Hz). Integration of this proton versus the remaining aromatic resonances would provide a proton inventory and a good assessment of product homogeneity. Typically, H_5 and H_6 showed an AB quartet.

In our earlier report we described the condensation of **1a** with 1,2-cycloalkanediones to provide 3,3′-polymethylene-bridged derivatives of 2,2′-bi-1,10-phenanthroline.[8] Other diketones will condense in a similar 2:1 fashion, and thus, 1,3-diacetylbenzene or 2,6-diacetylpyridine provide cavity-shaped molecules **10b,d**. When these same diketones are condensed with the naphthalene aminoaldehyde **1b**, the analogous benzo[h]quinolines **10a,c** are prepared.



Diketone **11** may be considered as a bridged derivative of **9a**. Although it condenses with **1b** to provide the highly congested terpyridine derivative **12**, the analogous condensation with **1a** was unsuccessful.

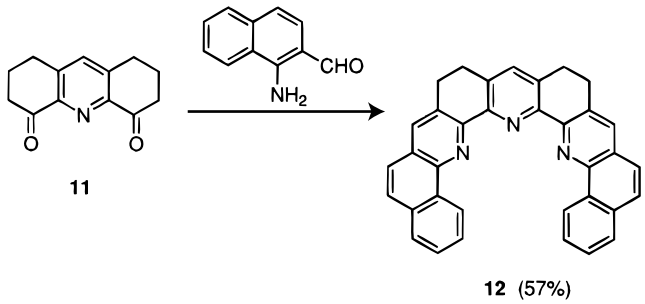


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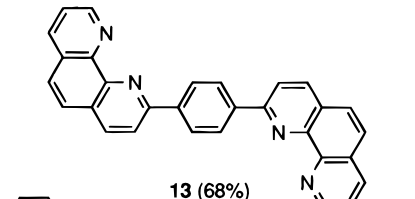
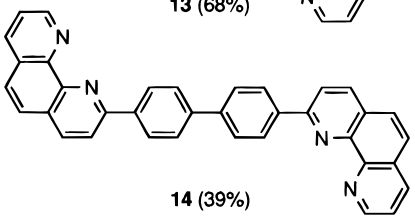
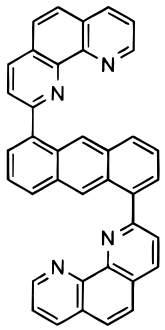
Chart 1



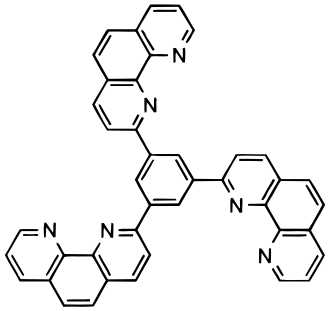
13 (68%)



14 (39%)



15 (85%)

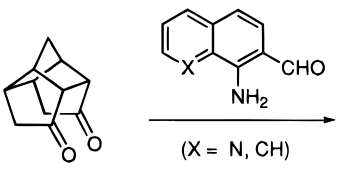


16 (65%)

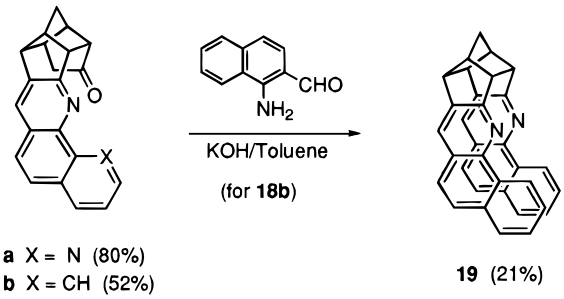
The condensation of 1,4-diacetylbenzene with **1a** provides the corresponding 1,4-di(1,10-phenanthrolin-2-yl)-benzene (**13**) in good yield (Chart 1). Similarly, 4,4′-diacetylbiphenyl provides the homologated biphenyl-bridged system **14**. The 1,5-diacetylation of anthracene can be accomplished in a straightforward fashion,[12] and the subsequent condensation of this material with **1a** provides the corresponding 1,5-di(1,10-phenanthrolin-2-yl)anthracene (**15**). These three systems provide an interesting series of ligands wherein the orientation between metals bound at the two 1,10-phenanthroline sites will be controlled by the bridging group. This group will also strongly influence any electronic communication between the metal centers through the π-framework.

One example of a triple condensation has been explored. Treatment of 1,3,5-triacetylbenzene with 3 equiv of **1a** provides the propeller-shaped molecule **16** wherein the three bidentate chelating sites might interact in a cooperative fashion above or below the plane of the central benzene ring.

In earlier work we have demonstrated the utility of tetracyclo[6.3.0.0^{4,11}.0^{5,9}]unde-cane-2,7-dione (**17**) in the construction of rigid orthocyclophanes *via* Friedländer methodology.[13] We observed that condensation of this



17



18 a X = N (80%)
b X = CH (52%)

19 (21%)

diketone normally proceeded in a stepwise fashion since the initially formed monoketone exists as its hydrate due to stabilization of this species through intramolecular H-bonding. Thus, the reaction of **17** with either **1a** or **1b** leads exclusively to the monocondensed species **18a,b**. The second condensation with **1b** proceeds to form **19** in a satisfactory manner; however, the analogous reaction with **1a** has thus far been unsuccessful.

Our interest in molecules such as **19** stems from the well defined cavity which is produced by the two layered benzo[*h*]quinoline rings. Two features of this cavity are noteworthy: its potential intercalation of a planar aromatic guest and electronic interaction between the benzo-[*h*]quinolines.

In our earlier report on benzo[*g*]quinolines, we were unable to detect any host−guest interaction with arylalkylamines in which the amino group would H-bond across the two nitrogens of the cage compound and the pendant phenyl ring would intercalate between the terminal benzo rings.[14] The cleft presented by **19** appeared to offer a more favorable site for such binding in that the hydrophobic cavity is located closer to the H-binding sites. The addition of small amounts of benzylamine did not cause appreciable changes in the benzo[*h*]quinoline ^{1}H NMR resonances, indicating that binding was still unfavorable. A molecular mechanics evaluation of the geometry of **19** indicated that, for the terminal benzo rings, the outermost carbons were about 7.5 Å apart while the ring juncture carbons were separated by only about 5.5 Å providing a mean interplanar distance of about 6.5 Å which is apparently still too close for intercalation.[15] The optimized geometry for **19** further indicated that the two benzo[*h*]quinoline rings were splayed apart rather than parallel and the bay regions of these rings are canted slightly toward one another, making the cleft between them more accessible from the non-bay region side.

For the analogous benzo[*g*]quinoline we observed that the two aromatic rings interacted to form an exciplex resulting in strong fluoresence quenching. Cage compound **19**, on the other hand, did not evidence such quenching and concentration dependent studies with a simple model, 2,3-cyclopentenobenzo[*h*]quinoline, showed no evidence for exciplex formation.

Future studies will focus on the metal binding properties of these new ligands.

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Experimental Section

Nuclear magnetic resonance spectra were obtained on a General Electric QE-300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Melting points were measured with a capillary melting point apparatus and are not corrected. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ.

p-(*N*,*N*-Dimethylamino)acetophenone,[16] 1-acetylanthracene,[17] 1-acetylpyrene,[18] 1,2,3,4,5,6,7,8-octahydroacridine-1,8-dione,[19] tetracyclo[6.3.0.0.^{4,11}0^{5,9}]undecane-2,7-dione (TCU-2,7-dione),[20] 4,4′-diacetylbiphenyl,[21] and 1,5-diacetylanthracene[12] were prepared according to published procedures. Other ketones and diketones were commercially available.

7-[*β-trans*-(*N*,*N*-dimethylamino)ethenyl]-8-nitroquinoline (5a). A solution of 7-methyl-8-nitroquinoline (10.0 g, 78.1 mmol) and DMFDMA (8.4 g, 70 mmol) in DMF (5 mL) was heated at 140 °C under Ar for 16 h. The solution was concentrated under reduced pressure, and the residue was washed with hexane (2 x 10 mL) to afford 12.8 g (99%) of **5a**: mp 181−183 °C; ^{1}H NMR ($CDCl_3$) δ 8.83 (dd, 1H, J = 4.3 Hz), 8.02 (dd, 1H, J = 8.1 Hz), 7.61 (q, 2H, J = 8.9 Hz, J = 16.2 Hz), 7.29 (d 1H, J = 3.2 Hz), 7.09 (d, 1H, J = 13.8 Hz), 5.05 (d, 1H, J = 13.4 Hz), 2.92 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 151.8, 145.0, 142.5, 141.2, 135.4, 132.8, 128.7, 124.7, 122.0, 120.2, 88.2, 40.8. Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.20; H, 5.35; N, 17.28. Found: C, 64.08; H, 5.43; N, 17.22.

8-Nitro-7-quinolinecarbaldehyde (6a). A solution of **5a** (15.1 g, 62.5 mmol) and sodium periodate (39.9 g, 187 mmol) was stirred in 50% aqueous THF (700 mL) at 25 °C for 2 h. The insolubles were removed by filtration and washed with EtOAc (200 mL). The organic layer was washed with saturated $NaHCO_3$ solution (2 × 200 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified by elution through a SiO_2 column (70 g), eluting with CH_2Cl_2/hexanes (1:1), to provide 11.0 g (88%) of **6a**: mp 174−75 °C (lit.[22] mp 172−74 °C); ^{1}H NMR ($CDCl_3$) δ 10.23 (s, 1H), 9.12 (d, 1H, J = 2.7 Hz), 8.32 (dd, 1H, J = 7.0 Hz), 8.11 (q, 2H), 7.69 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 189.6, 154.1, 145.9, 137.7, 136.4, 131.6, 131.2, 126.7, 125.2, 124.7.

8-Amino-7-quinolinecarbaldehyde (1a). A mixture of **6a** (1.29 g, 6.39 mmol), iron powder (2.64 g, 47.6 mmol), concd HCl (2 drops), and a mixture of EtOH, HOAc and H_2O (2:2:1, 65 mL) was refluxed for 15 min and then stirred at 25 °C for 25 min. The solution was filtered, diluted with water (100 mL), and extracted with EtOAc (3 × 100 mL). The organic layer was washed with saturated $NaHCO_3$ (2 × 100 mL) and H_2O (2 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (10 g), eluting with CH_2Cl_2, to afford 0.92 g (84%) of **1a**: mp 81−86 °C (lit.[8] mp 85−86 °C); ^{1}H NMR ($CDCl_3$) δ 9.96 (s, 1H), 8.76 (d, 1H, J = 4.0 Hz), 8.02 (d, 1H, J = 7.4 Hz), 7.40−8.20 (b, 2H), 7.50 (m, 2H), 6.99 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 192.8, 148.8, 147.3, 138.2, 135.5, 130.9, 130.0, 129.9, 124.0, 113.0.

1-Nitro-2-methylnaphthalene (4b). A solution of 2-methylnaphthalene (20 g, 0.14 mol) in HOAc (38 mL) was cooled to 5 °C, and concd HNO_3 (10.5 g) was added dropwise. After addition, the solution was stirred at 25 °C for 16 h. The resulting precipitate was filtered, washed with cold H_2O (50 mL), and recrystallized from MeOH to yield 9.25 g (35%) of **4b**: mp 74−76 °C (lit.[23] mp 80−81 °C); ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 2H, J = 8.0 Hz), 7.71 (d, 1H, J = 8.2 Hz), 7.46−7.58 (m, 2H), 7.30 (d, 1H, J = 8.2 Hz), 2.46 (s, 3H).

2-[*β-trans*-(*N*,*N*-dimethylamino)ethenyl]-1-nitronaphthalene (5b). A solution of **4b** (4.26 g, 23.0 mmol) and DMFDMA (4.11 g, 34.5 mmol) in DMF (40 mL) was heated at 140 °C under Ar for 6 h and then stirred at 25 °C for 26 h. The solution was concentrated under reduced pressure, and the residue was washed with hexane (2 × 25 mL) to afford 5.12 g (92%) of **5b**: mp 98−100 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (t, 2H, J = 9.3 Hz), 7.50 (m, 3H), 7.36 (t, 1H, J = 7.8 Hz), 7.02 (d, 1H, J = 13.4 Hz), 5.13 (d, 1H, J = 13.4 Hz), 2.90 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 144.4, 142.6, 130.3, 130.2, 130.1, 128.5, 128.0, 126.0, 125.1, 120.8, 89.3, 40.9. Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.42; H, 5.78; N, 11.57. Found: C, 69.00; H, 5.47; N, 11.25.

1-Nitro-2-naphthalenecarbaldehyde (6b). Following the procedure described for **6a**, **5b** (5.12 g, 21.1 mmol) and sodium periodate (13.6 g, 63.4 mmol) provided 3.62 g (85%) of **6b**: mp 99−100 °C (lit.[22] mp 100−101 °C); ^{1}H NMR ($CDCl_3$) δ 10.2 (s, 1H), 8.12 (d, 1H, J = 8.5 Hz), 7.92−8.02 (m, 3H), 7.35−7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 186.9, 150.1, 136.6, 131.5, 130.2, 129.7, 128.4, 123.9, 123.6, 123.0, 122.8.

1-Amino-2-naphthalenecarbaldehyde (1b). Following the procedure described for **1a**, **6b** (0.15 g, 0.75 mmol) and iron powder (0.31 g, 5.6 mmol) provided a material which was purified by elution through an Al_2O_3 column (75 g), eluting with CH_2Cl_2/hexanes (3:2), to yield 0.10 g (77%) of **1b**: mp 97−100 °C; ^{1}H NMR ($CDCl_3$) δ 9.96 (s, 1H), 7.92 (d, 1H, J = 8.4 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.30−7.70 (broad s, 2H), 7.60 (t, 1H, J = 7.6 Hz), 7.46−7.52 (m, 2H) 7.13 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 193.6, 149.1, 136.8, 129.8, 129.7, 128.7, 125.5, 122.6, 122.0, 116.2, 112.4. Anal. Calcd for $C_{11}H_9NO$-0.25 H_2O: C, 75.21; H, 5.41; N, 7.98. Found: C, 75.10; H, 5.25; N, 7.81.

2-Phenyl-1,10-phenanthroline (8b). To a mixture of **1a** (0.25 g, 1.45 mmol) and acetophenone (0.17 g, 1.45 mmol) in absolute EtOH (15 mL) under Ar was added saturated ethanolic KOH (0.5 mL) dropwise, and the mixture was refluxed for 15 h. After cooling, water was added and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave a crude material which was purified by chromatography on Al_2O_3 (15 g), eluting with CH_2Cl_2. Recrystallization from ethyl acetate/hexane (1:2) provided 0.16 g (45%) of **8b** as a white solid: mp 119−122 °C (lit.[1b] mp 141−44 °C); ^{1}H NMR ($CDCl_3$) δ 9.30 (d, 1H, J = 4.3 Hz), 8.40 (d, 2H, J = 8.7 Hz), 8.36 (d, 1H, J = 7.2 Hz), 8.32 (d, 1H, J = 6.8 Hz), 8.14 (d, 1H), 7.82 (AB quartet, 2H), 7.68 (t, 1H), 7.68 (q, 2H), 7.52 (t, 1H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 157.2, 150.3, 145.8, 146.2, 139.4, 136.6, 135.8, 129.1, 128.8, 128.6, 127.9, 127.6, 126.1, 126.0, 122.7, 120.5.

2-(*p*-Nitrophenyl)-1,10-phenanthroline (8c). To a mixture of **1a** (0.17 g, 1.0 mmol) and *p*-nitroacetophenone (0.17 g, 1.0 mmol) in absolute EtOH (5 mL) under Ar was added saturated ethanolic KOH (0.5 mL), and the mixture was refluxed for 4 h. After cooling, the solvent was evaporated. The residue was purified by chromatography on Al_2O_3 (15 g), eluting with $CHCl_3$. Recrystallization from ethyl acetate/hexanes (1:2) provided 0.093 g (40%) of **8c** as a yellow solid: mp > 210 °C; ^{1}H NMR ($CDCl_3$) δ 9.29 (d, 1H, J = 2.8 Hz), 8.55 (d, 2H, J = 8.7 Hz), 8.41 (d, 1H, J = 8.1 Hz), 8.39 (d, 2H), 8.33 (d, 1H, J = 8.1 Hz), 8.18 (d, 1H), 7.87 (AB quartet, 2H), 7.73 (q, 1H), 2.00 (H_2O); ^{13}C NMR ($CDCl_3$) δ 154.7, 150.6, 148.3, 146.1, 145.4, 137.3, 137.0, 136.3, 129.2, 128.7, 128.2, 127.4, 126.2, 123.9, 123.2, 120.7. Anal. Calcd for $C_{18}H_{11}N_3O_2$-0.5 H_2O: C, 69.69; H, 3.87; N, 13.55. Found: C, 70.37; H, 3.86; N, 13.14.

2-[*p*-(Dimethylamino)phenyl]-1,10-phenanthroline (8d). To a mixture of **1a** (0.17 g, 1.0 mmol) and *p*-(dimethylamino)-acetophenone (0.16 g, 1.0 mmol) in absolute EtOH (5 mL) under Ar was added saturated ethanolic KOH (0.5 mL), and the mixture was refluxed for 36 h. After cooling, the solvent was evaporated. The residue was purified by chromatography on Al_2O_3 (15 g), eluting with CH_2Cl_2/hexanes (2:1), to give 0.14

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g (45%) of **8d** as a yellow solid: mp 201−204 °C; ^{1}H NMR ($CDCl_3$) δ 9.22 (dd, 1H, J = 4.32 Hz), 8.32 (d, 2H, J = 8.9 Hz), 8.22 (overlapping m, 2H), 8.04 (d, 1H, J = 8.5 Hz), 7.72 (AB quartet, 2H), 7.61 (dd, 1H), 6.85 (d, 2H), 3.05 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 169.8, 158.2, 152.2, 149.9, 146.8, 146.6, 137.3, 136.2, 134.6, 133.7, 133.6, 130.0, 128.5, 127.3, 126.0, 124.2, 120.1, 112.6, 40.3. Anal. Calcd for $C_{20}H_{17}N_3$-0.25 H_2O: C, 79.07; H, 5.76; N, 13.83. Found: C, 79.53, H, 5.65, N, 13.38.

2-(*β*-Naphthyl)-1,10-phenanthroline (8e). To a mixture of **1a** (0.17 g, 1.0 mmol) and 2-acetylnaphthalene (0.17 g, 1.0 mmol) in EtOH (7 mL) under Ar was added saturated ethanolic KOH (0.5 mL), and the mixture was refluxed for 18 h. After cooling, water was added and the mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed with water and dried ($MgSO_4$). Evaporation of the solvent gave a crude material which was recrystallized from CH_2Cl_2/cyclohexane to provide 0.14 g (48%) of **8e** as a yellow solid: mp 157−159 °C; ^{1}H NMR ($CDCl_3$) δ 9.38 (d, 1H, J = 3.3 Hz), 8.95 (s, 1H), 8.59 (d, 1H, J = 8.6 Hz), 8.40−8.30 (overlapping m, 3H), 8.09 (m, 1H), 8.03 (d, 1H), 7.91(m, 1H), 7.86 (AB quartet, 2H), 7.72 (q, 1H), 7.53 (overlapping m, 2H); ^{13}C NMR ($CDCl_3$) δ 157.4, 150.1, 145.9, 145.8, 136.8, 136.7, 136.5, 133.9, 133.5, 132.1, 129.1, 129.0, 128.5, 127.6, 127.5, 126.7, 126.5, 126.2, 125,8, 125.4, 122.9, 120.9. Anal. Calcd for $C_{22}H_{14}N_2$: C, 86.27; H, 4.58; N, 9.15. Found: C, 86.00; H, 4.65; N, 9.55.

2-(1′-Anthracenyl)-1,10-phenanthroline (8f). To a mixture of **1a** (0.17 g, 1.0 mmol) and 1-acetylanthracene (0.22 g, 1.0 mmol) in absolute EtOH (7 mL) under Ar was added saturated ethanolic KOH solution (0.5 mL) dropwise, and the mixture was refluxed for 36 h. After cooling, the solvent was evaporated and the crude product was purified by chromatography on Al_2O_3 (20 g), eluting with CH_2Cl_2, to give 0.14 g (41%) of **8f**: mp 113−117 °C; ^{1}H NMR ($CDCl_3$) δ 9.21 (d, 1H, J = 4.1 Hz), 8.68 (s, 1H), 8.52 (s, 1H), 8.42 (d, 1H, J = 8.2 Hz), 8.31 (d, 1H, J = 8.0 Hz), 8.13 (d, 1H), 8.04 (d, 2H), 7.92 (AB quartet, 2H), 7.88 (m, 2H), 7.62 (q, 1H), 7.59 (m, 1H), 7.42 (overlapping m, 2H), 1.56 (H_2O); ^{13}C NMR ($CDCl_3$) δ 150.5, 146.5, 139.0, 136.0, 135.9, 132.2, 132.0, 131.4, 130.0, 129.8, 129.3, 129.0, 128.9, 128.7, 128.0, 127.9, 127.6, 126.6, 126.5, 126.3, 125.5, 125.2, 125.1, 124.9, 124.7, 122.9. Anal. Calcd for $C_{26}H_{16}N_2$-0.5 H_2O: C, 85.48; H, 4.66; N, 7.67. Found: C, 86.01; H, 4.41; N, 7.36.

2-(1′-Pyrenyl)-1,10-phenanthroline (8g). To a mixture of **1a** (0.37 g, 0.15 mmol) and 1-acetylpyrene (0.26 g, 0.15 mmol) in EtOH (8 mL) under Ar was added saturated ethanolic KOH (0.5 mL), and the mixture was refluxed for 24 h. After cooling, the solvent was evaporated. Purification by chromatography on Al_2O_3 (15 g), eluting with $CHCl_3$, provided 0.45 g (60%) of **8g**: mp 190−193 °C; ^{1}H NMR ($CDCl_3$) δ 9.22 (d, 1H, J = 2.9 Hz), 8.38 (m, 3H), 8.25 (m, 3H), 8.13 (m, 3H), 8.05 (m, 3H), 7.80 (q, 2H), 7.64 (q, 1H), 1.56 (H_2O); ^{13}C NMR ($CDCl_3$) δ 114.4, 115.8, 122.6, 124.8, 124.9, 125.4, 125.7, 125.8, 125.9, 126.0, 126.1, 126.2, 126.3, 126.4, 127.2, 127.5, 128.2, 129.0, 130.2, 130.7, 131.2, 133.2, 134.6, 135.9, 138.8, 140.4, 144.8, 147.8. Anal. Calcd for $C_{28}H_{16}N_2$-0.5 H_2O: C, 86.38; H, 4.37; N, 6.81. Found: C, 86.42; H, 4.14; N, 6.81.

1,3-Di(benzo[*h*]quinolin-2-yl)benzene (10a). To a solution of 1,3-diacetylbenzene (0.15 g, 0.93 mmol) and **1b** (0.32 g, 1.85 mmol) in absolute EtOH (25 mL) was added saturated ethanolic KOH (1 mL). The solution was refluxed under Ar for 31 h. The mixture was cooled and filtered to yield 0.23 g (58%) of **10a**: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.62 (d, 2H, J = 8.1 Hz), 9.37 (s, 1H), 8.46 (d, 2H, J = 7.6 Hz), 8.31 (d, 2H, J = 8.3 Hz), 8.18 (d, 2H, J = 8.4 Hz), 7.94 (d, 2H, J = 7.7 Hz), 7.78 (overlapping m, 9H), 1.58 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 155.4, 146.3, 140.3, 136.6, 134.0, 131.4, 129.3, 128.3, 128.2, 127.8, 127.5, 126.9, 126.6, 125.3, 125.1, 124.8, 119.0. Anal. Calcd for $C_{32}H_{20}N_2$-3.25 H_2O: C, 86.20; H, 4.83; N, 6.29. Found: C, 86.30; H, 4.46; N, 6.13.

1,3-Di(1,10-phenanthrolin-2-yl)benzene (10b). To a solution of 1,3-diacetylbenzene (0.16 g, 0.99 mmol) and **1a** (0.34 g, 1.98 mmol) in absolute EtOH (50 mL) was added saturated ethanolic KOH (2 mL). The solution was refluxed under Ar for 17 h. After cooling, filtration yielded crude material which was chromatographed on SiO_2 (40 g), eluting first with CH_2Cl_2 to separate the unreacted amino aldehyde and then with CH_2Cl_2/EtOH (9:1), to give 0.24 g (60%) of **10b**: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.24 (d, 2H, J = 4.0 Hz), 9.15 (s, 1H), 8.54 (d, 2H, J = 8.0 Hz), 8.34 (m, 4H), 8.26 (d, 2H, J = 8.0 Hz), 7.81 (AB quartet, 2H), 7.76 (m, 3H), 7.64 (dd, 2H), 2.48 (broad s, H_2O); ^{13}C NMR ($CDCl_3$) δ 157.5, 150.3, 146.4, 146.0, 140.1, 136.8, 136.2, 129.5, 129.3, 129.1, 127.7, 127.0, 126.5, 126.2, 122.9, 121.1. Anal. Calcd for $C_{30}H_{18}N_4$-0.5 H_2O: C, 81.26; H, 4.18; N, 12.64. Found: C, 80.97; H, 4.13; N, 12.29.

2,6-Di(benzo[*h*]quinolin-2-yl)pyridine (10c). To a solution of 2,6-diacetylpyridine (0.20 g, 1.16 mmol) and **1b** (0.40 g, 2.34 mmol) in absolute EtOH (50 mL) was added saturated ethanolic KOH (2 mL). The solution was refluxed under Ar for 18 h, cooled, and filtered to yield 0.43 g (86%) of **10c**: mp > 300 °C; ^{1}H NMR (nitrobenzene-d_5 at 100 °C) δ 9.58 (d, 2H, J = 8.1 Hz), 9.06 (m, 4H), 8.42 (d, 2H, J = 7.9 Hz), 8.24 (t, 1H), 7.95 (d, 2H, J = 7.8 Hz), 7.80 (m, 8H); ^{13}C NMR could not be obtained due to poor solubility. Anal. Calcd for $C_{31}H_{19}N_3$: C, 85.91; H, 4.39; N, 9.70. Found: C, 86.21; H, 4.43; N, 9.62.

2,6-Di(1,10-phenanthrolin-2-yl)pyridine (10d). To a solution of 2,6-diacetylpyridine (0.20 g, 1.16 mmol) and **1a** (0.40 g, 2.34 mmol) in absolute EtOH (50 mL) was added saturated ethanolic KOH (2 mL). The solution was refluxed under Ar for 24 h, cooled, and poured into H_2O (100 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent yielded a residue which was recrystallized from CH_2Cl_2 to give 0.30 g (59%) of **10d**: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.27 (d, 2H, J = 4.3 Hz), 9.08 (m, 4H), 8.40 (d, 2H, J = 8.3 Hz), 8.26 (d, 2H, J = 8.1 Hz), 8.16 (t, 1H), 7.82 (AB quartet, 4H), 7.66 (dd, 2H), 1.95 (s, H_2O); ^{13}C NMR ($CDCl_3$) δ 156.4, 155.3, 150.5, 147.0, 146.0, 138.1, 136.8, 136.1, 129.0, 128.8, 126.7, 126.5, 123.3, 122.9, 121.0. Anal. Calcd for $C_{29}H_{17}N_5$-0.25 H_2O: C, 79.18; H, 3.98; N, 15.93. Found: C, 79.26; H, 3.79; N, 15.75.

3,4,6,7-Tetrahydrobis(2,3-benzo[*h*]quinolino)[*c*,*l*]acridine (12). A mixture of 1,2,3,4,5,6,7,8-octahydroacridine-2,8-dione (**11**, 0.06 g, 0.28 mmol) and **1b** (0.10 g, 0.58 mmol) in absolute EtOH (10 mL) containing 1 pellet of KOH was refluxed under Ar for 5 h. The product precipitated and was filtered to yield 0.07 g of **12**. The filtrate was evaporated, and the residue was chromatographed on SiO_2 (10 g), eluting with CH_2Cl_2/EtOAc (4:1) and then CH_2Cl_2/EtOH, to give an additional 0.01 g (57% combined yield) of **12**: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.93 (d, 2H), 7.96 (s, 2H), 7.89 (m, 4H), 7.79 (d, 2H), 7.73 (m, 2H), 7.62 (d, 2H), 7.56 (s, 1H), 3.22 (m, 4H), 3.17 (m, 4H), 2.38 (broad s, H_2O). ^{13}C NMR could not be obtained due to poor solubility. Anal. Calcd for $C_{35}H_{23}N_3$·2.0H_2O: C, 80.61; H, 4.46; N, 7.83. Found: C, 80.12; H, 4.46; N, 7.83.

1,4-Di(1,10-phenanthrolin-2-yl)benzene (13). A mixture of **1a** (0.12 g, 0.71 mmol), 1,4-diacetylbenzene (0.06 g, 0.35 mmol), and saturated ethanolic KOH (0.25 mL) in absolute ethanol (5 mL) was heated at 50 °C for 3 h and then at 90 °C for 18 h. The solvent was evaporated, and the residue was purified by chromatography on Al_2O_3, eluting with EtOAc/CH_2Cl_2 (2:3), to provide 0.10 g (68%) of **13**: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.28 (dd, 2 H, J = 4.4, 1.5 Hz), 8.56 (s, 4 H), 8.37 (d, 2 H, J = 8.4 Hz), 8.29 (dd, 2 H, J = 8.1, 1.5 Hz), 8.24 (d, 2 H, J = 8.4 Hz), 7.83 (AB quartet, 4 H), 7.67 (dd, 2 H, J = 8.1, 4.4 Hz), 1.56 (H_2O); ^{13}C NMR could not be obtained due to poor solubility. Anal. Calcd for $C_{30}H_{18}N_4$-0.75 H_2O: C, 80.44; H, 4.36, N, 12.51. Found: C, 80.37, H, 4.12, N, 12.51.

4,4′-Di(1,10-phenanthrolin-2-yl)biphenyl (14). To a mixture of **1a** (0.17 g, 1.0 mmol) and 4,4′-diacetylbiphenyl (0.12 g, 1.0 mmol) in absolute EtOH (35 mL) under Ar was added saturated ethanolic KOH (0.5 mL), and the mixture was refluxed for 23 h. After cooling, the mixture was stored at 0 °C overnight. The precipitate was collected and washed several times with EtOH to provide 0.20 g (39%) of **14** as a brown solid: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.27 (d, 2H, J = 3.1 Hz), 8.50 (d, 4H, J = 8.1 Hz), 8.37 (d, 2H, J = 8.3 Hz), 8.28 (d, 2H, J = 7.5 Hz), 8.20 (d, 2H), 7.91 (d, 4H), 7.82 (AB quartet, 4H), 7.66 (q, 2H); ^{13}C NMR ($CDCl_3$) δ 157.0, 155.6, 150.3, 146.1, 141.4, 138.6, 136.7, 136.0, 131.0, 129.0, 128.3, 127.4, 126.3, 123.2, 122.8, 120.4.

1,5-Di(1,10-phenanthrolin-2-yl)anthracene (15). To a mixture of **1a** (0.16 g, 0.92 mmol) and 1,5-diacetylanthracene (0.12 g, 0.46 mmol) in absolute EtOH (7 mL) under Ar was added saturated ethanolic KOH (0.5 mL), and the mixture was refluxed for 36 h. After cooling, the mixture was stirred at 0 °C overnight. The precipitate was collected and washed several times with EtOH to provide 0.22 g (88%) of **15** as a brown solid: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.15 (d, 2H, J = 3.0 Hz), 8.71 (s, 2H), 8.37 (d, 2H, J = 8.2 Hz), 8.21 (d, 2H), 7.98 (d, 2H), 7.85 (overlapping m, 8H), 7.57 (m, 2H), 7.45 (m, 2H); ^{13}C NMR could not be obtained due to poor solubility. Anal. Calcd for $C_{38}H_{22}N_4 \cdot 2.0H_2O$: C, 80.00; H, 4.56; N, 9.82. Found: C, 79.63; H, 3.99; N, 9.84.

1,3,5-Tri(1,10-phenanthrolin-2-yl)benzene (16). A mixture of **1a** (0.24 g, 1.4 mmol), 1,3,5-triacetylbenzene (0.08 g, 0.40 mmol), and KOH (0.16 g, 3.2 mmol) in 100 mL of EtOH was heated at reflux under Ar for 24 h. The reaction mixture was evaporated, and the residue was crystallized from EtOAc/MeOH to provide 0.18 g (65%) of **16** as a yellow solid: mp 245−8 °C; ^{1}H NMR (DMSO-d_6) δ 9.30 (s, 3H), 9.15 (d, 3H, J = 4.3 Hz), 8.70 (AB quartet, 6H), 8.53 (d, 3H, J = 8.0 Hz), 8.04 (AB quartet, 6H), 7.80 (dd, 3H, J = 4.3, 8.3 Hz); ^{13}C NMR (DMSO-d_6) δ 156.0, 150.0, 145.6, 145.4, 140.6, 137.5, 136.2, 128.9, 127.8, 127.7, 126.7, 126.4, 123.3, 121.1. Anal. Calcd for $C_{42}H_{24}N_6 \cdot 2.0H_2O$: C, 77.77; H, 4.32; N, 12.96. Found: C, 76.28; H, 4.18; N, 13.02.

7,6-(2′,3′-[1,10]Phenanthrolino)tetracyclo[6.3.0.0.^{4,11}0^{5,9}]-undecan-2-one (18a). A stirred mixture of **1a** (0.25 g, 1.40 mmol) and TCU-2,7-dione (**17**, 0.24 g, 1.35 mmol) in absolute EtOH (15 mL) was combined with saturated ethanolic KOH (1 mL) and refluxed for 17 h. After cooling and evaporation of the solvent, the residue was chromatographed on Al_2O_3 (30 g), eluting with hexane/EtOAc (1:1) to separate starting material and then with $CHCl_3$, to provide 0.35 g (80%) of **18a**: mp > 275 °C dec; ^{1}H NMR ($CDCl_3$) δ 9.11 (d, 1H), 8.14 (d, 1H), 7.81 (s, 1H), 7.66 (m, 2H), 7.50 (m, 1H), 3.80 (d, 1H), 3.42 (broad s, 2H), 2.97 (broad s, 1H), 2.82 (m, 2H), 2.74 (broad s, 1H), 2.07 (m, 2H), 1.57 (d, 1H); ^{13}C NMR ($CDCl_3$) δ 217.9, 170.1, 150.6, 146.6, 145.6, 141.1, 136.2, 131.1, 128.8, 128.0, 126.9, 126.4, 122.9, 58.1, 57.8, 54.6, 51.0, 48.2, 40.9, 35.9. Anal. Calcd for $C_{21}H_{14}N_{20}$-1.0 H_2O: C, 76.83, H, 4.88; N, 8.54. Found: C, 76.78; H, 5.16; N, 8.25.

7,6-(2′,3′-Benzo[*h*]quinolino)tetracyclo[6.3.0.0.^{4,11}0^{5,9}]-undecan-2-one (18b). To a stirred mixture of **1b** (0.25 g, 1.46 mmol) and TCU-2,7-dione (**17**, 0.24 g, 1.35 mmol) in absolute EtOH (15 mL) was added 1 pellet of KOH. The mixture was refluxed under Ar for 3 h and cooled, and the precipitate was collected to yield 0.22 g (52%) of **18b**: mp 265−267 °C; ^{1}H NMR ($CDCl_3$) δ 9.29 (d, 1H, J = 8.6 Hz), 7.86 (d, 1H, J = 7.3 Hz), 7.78 (s, 1H), 7.75 (d, 1H, J = 8.8 Hz), 7.63 (overlapping dd, 2H), 7.58 (d, 1H, J = 8.8 Hz), 3.67 (dd, 1H), 3.46 (broad s, 1H), 3.44 (m, 1H), 3.02 (broad s, 1H), 2.86 (m, 2H), 2.12 (d, 1H, J = 6.9 Hz), 2.06 (s, 2H), 1.57 (d, 1H, J = 18.8 Hz); ^{13}C NMR ($CDCl_3$) δ 218.5, 170.0, 145.5, 138.8, 133.3, 131.5, 130.5, 127.6, 127.4, 127.1, 126.6, 125.3, 124.9, 124.7, 57.6, 53.9, 50.6 47.6, 42.3, 40.5, 35.3, 35.5. Anal. Calcd for $C_{22}H_{15}NO \cdot 0.33H_2O$: C, 83.81; H, 4.97; N, 4.44. Found: C, 83.81; H, 5.44; N, 4.40.

2,3;7,6-Bis(2′,3′-benzo[*h*]quinolino)tetracyclo-[6.3.0.0.^{4,11}0^{5,9}]undecane (19). A mixture of **18b** (0.25 g, 0.80 mmol) and **1b** (0.16 g, 0.90 mmol) in freshly distilled toluene (20 mL) containing saturated ethanolic KOH (1 mL) was refluxed for 15 h under Ar using a Dean−Stark water separator. The solvent was evaporated, and the residue was chromatographed on Al_2O_3 (40 g), eluting with EtOAc/hexanes (3:2), to provide 0.075 g (21%) of **19**: mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.12 (d, 2H, J = 9.6 Hz), 7.64 (d, 2H, J = 8.3 Hz), 7.55−7.42 (overlaping m, 6H), 7.53 (s, 2H), 7.32 (d, 2H, J = 8.8 Hz), 3.93 (broad s, 2H), 3.66 (d, 4H, J = 19.5 Hz), 3.10 (broad s, H_2O), 2.26 (q, 2H); ^{13}C NMR ($CDCl_3$) δ 168.9, 148.4, 144.4, 140.3, 133.0, 132.9, 131.2, 129.4, 127.2, 127.1, 126.3, 125.1, 124.4, 60.7, 53.2, 49.2, 35.6. Anal. Calcd for $C_{33}H_{22}N_2 \cdot 0.50H_2O$: C, 87.03, H, 5.05; N, 6.15. Found: C, 86.71; H, 4.80; N, 5.92.

Acknowledgment. We would like to thank the Robert A. Welch Foundation, the National Science Foundation (CHE-9224686), and the Texas Higher Education Coordinating Board for financial support of this work. E.C.R. thanks the NIH for a National Service award.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **14** (2 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.

JO952164H