Tetrahedron Vol. 48, No. 36, pp. 7663-7678, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00
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Synthesis of Novel Rigid Norbornylogous Spacers Bearing Heterocyclic Ligands for the Investigation of Long-Range Intramolecular Electron Transfer Involving Metal Centres§

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(*Received in USA 5 May* 1992)

Key Words: pyridazine annulation; pyridine annulation; ruthenium complexes; donor-acceptor systems

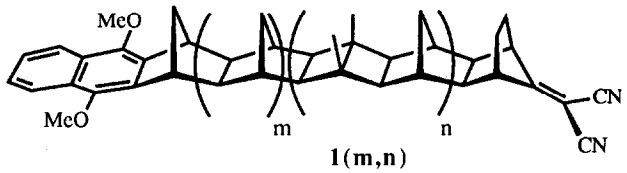
Abstract: *The synthesis of some novel 1,4-dimethoxynaphthalene-bridge-heterocycle systems is described. In these systems, the naphthalene and heterocyclic groups are fused to a rigid bridge consisting of linearly fused norbornyl and bicyclo[2.2.0]hexyl groups. Bridges used herein have relays of 2-, 4-, and 6-bonds long. The heterocycle is either 3,6-di(2'-pyridyl)-pyridazino, or pyrido and was attached to the bridge by annulation methods. The pyridazino systems,* ***2(m,n)****, were synthesized via Diels-Alder reaction of 3,6-di(2'-pyridyl)-1,2,4,5-tetrazine with the alkenes,* ***13*** *and* ***6(m,n)****, and subsequent aromatization of the adducts with DDQ. Pyridine annulation was successfully carried out using two different methods: (i) Boger pyridine annulation of ketones,* ***11****,* ***20b****, and* ***21b****, (with 1,2,4-triazine and pyrrolidine); (ii) Diels-Alder reaction of alkenes* ***13*** *and* ***6(m,n)*** *with 3-thiomethyl-1,2,4-triazine, followed by Raney nickel reductive desulfurization of the aromatized adducts. The synthesis of Ru(II)(2,2'-bipyridyl)$_2$ complexes of the pyridazino systems,* ***9(m,n)*** *and* ***10****, is also described.*

INTRODUCTION

Electron transfer (ET), occurring under both thermal[1-6] and photochemical[7-30] conditions, plays a central role in a multitude of chemical and biological processes. As a consequence, considerable effort from many groups continues to be spent on probing the mechanistic features of long-range ET processes.[1-46] During the past few years, measurements of ET processes between organic donor and acceptor groups have provided valuable insight into the effect of distance, energy, and orientation on ET rates.[1-6,9-30] In this respect, studies on intramolecular ET play a pivotal role because the attachment of donor and acceptor groups to a fairly rigid bridge (spacer) enables the unambiguous delineation of the dependence of ET dynamics on donor-acceptor distance and orientation to be determined. Such systems may be conveniently abbreviated as: donor-bridge-acceptor.

§ Dedicated to Professor Charles W. Rees on the occasion of his 65th birthday.

A variety of hydrocarbon bridges has been used in ET studies, including cyclohexane, decalin, and steroid based systems,[2,3,5,6,10] bicyclo[2.2.2]octane,[25–27] triptycene,[28–30] polyspirocyclobutanes,[31,32] and norbornylogous bridges comprising a mixture of linearly fused norbornyl and bicyclo[2.2.0]hexyl groups, such as **1**.[4,11–21] The norbornylogous bridge systems, synthesized by our group, have proven to be particularly useful in the study of long-range intramolecular ET processes, on account of their total rigidity, symmetry, and their comparative ease of synthesis. The latter advantage has enabled us to synthesize several members of the unique organic donor–acceptor sytems, **1(m,n)**, in which the donor–acceptor separation spans a wide range, from *ca.* 6 Å, for **1(1,0)**, to *ca* 14 Å, for **1(1,2)**.[11–21, 33–36]



1(m,n)

In contrast to the studies so far mentioned in which both donor and acceptor chromophores are organic groups, comparatively fewer ET studies have been carried out on donor–bridge–acceptor systems containing transition metal chromophores.[37–46] Also, in many of these transition metal chromophoric systems that have been studied to date, the majority contain bridges that are not particularly rigid, such as peptides[41] and cyclohexane rings[38] (an important exception is the series of polyspirocyclobutane bridges of Stein *et al*[31,32]). Although such studies have provided important insights into the nature of long-range ET processes involving transition metals, there is still a need for a systematic study in which the bridges in the donor–bridge–acceptor systems are completely rigid and their lengths can be varied over a greater range of values than has hitherto been possible.

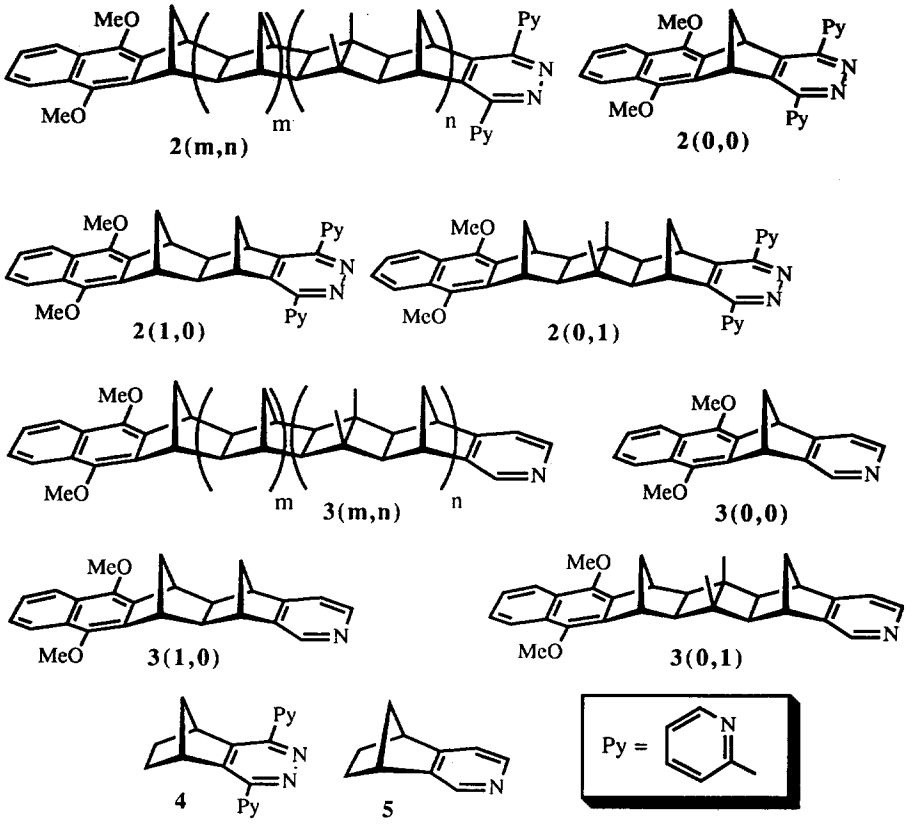
It occurred to us that our norbornylogous bridges offer an ideal opportunity for realizing this need, since all that is required is the ability to fuse a suitable heterocyclic group onto one (or both) of the termini of the norbornylogous bridge. In this paper, we present the preliminary results of our studies into this problem. Specifically, we describe the synthesis of representatives of the pyridazine and pyridine annulated systems, **2(m,n)** and **3(m,n)**, respectively. In these systems synthesized to date, the dimethoxynaphthalene (DMN) and heterocyclic chromophores are separated by bridges with lengths of 2–, 4–, and 6-bonds. For purposes of clarity, these structures are drawn in full in Scheme 1 below, together with the model norbornyl compounds, **4** and **5**, whose synthesis will also be described. We also describe the synthesis of the ruthenium(II) complexes of the DMN—pyridazine systems, **9(m,n)** and **10**. The DMN chromophore was chosen not only from the point of view of synthetic convenience, but also for its ability to act both as a donor and as an acceptor (in the form of the readily accessible naphthoquinone derivative).

RESULTS AND DISCUSSION

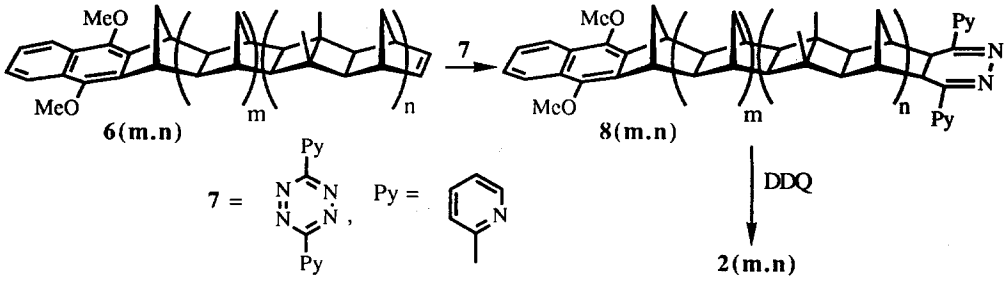
Pyridazine annulation

The synthesis of the pyridazine annulated series of compounds, **2(m,n)**, was readily achieved through Diels–Alder reaction of the known alkenes, **6(m,n)**,[47] with 3,6-di(2'-pyridyl)-1,2,4,5-tetrazine, **7**,[48] in chloroform solvent (Scheme 2). The Diels–Alder reaction proceeded smoothly, with evolution of dinitrogen, to give the pale yellow dihydropyridazine annulated adducts, **8(m,n)**, in quantitative yield. This reaction has ample precedent and has been previously used by our group to annulate several, more simple, norbornyl systems.[49] Dehydrogenation of **8(m,n)** with DDQ gave the desired pyridazinyl systems, **2(m,n)**, in excellent yield. In a similar fashion, the model methanophthalazine, **4**, was synthesized.

Scheme 1

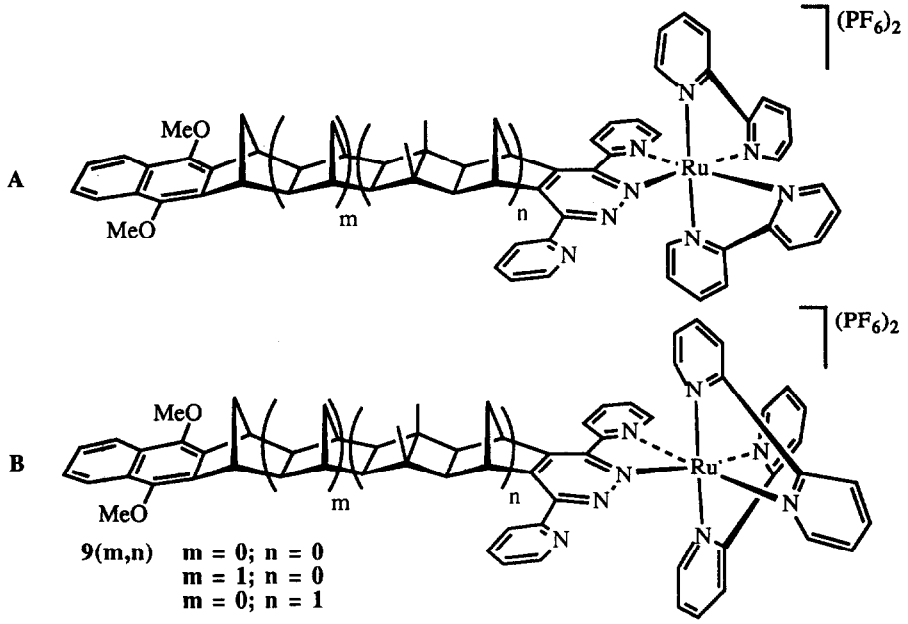


Scheme 2



Ruthenium(II)(bpy)$_2$ complexes of 2(m,n)

The reason for using 3,6–di(2'–pyridyl)–1,2,4,5–tetrazine as the diene in the annulation procedure was to introduce pyridine rings into **2(m,n)** such that one of the pyridine groups could act in conjunction with the pyridazinyl unit as a bidentate ligand for complexation with ruthenium and other transition metals. Treatment of 2–, 4–, and 6–bond pyridazines, **2(m,n)**, with Ru(bpy)$_2$Cl$_2$.2H$_2$O (bpy = 2,2'-bipyridyl) gave high yields of the ruthenium(II) complexes that were isolated and characterized as their bis–PF$_6$ salts, **9(m,n)**. The ruthenium(II) complex, **10**, of the model system, **4**, was prepared in a similar fashion. Bis–ruthenium complexes, through Ru(II) complexation with the remaining free bidentate site in **9(m,n)** and **10** did not occur, even in the presence of excess Ru(bpy)$_2$Cl$_2$.2H$_2$O reagent. The observed absence of bis–complex formation is due to the fact that the sterically large ruthenium centre in the mono–complexes, **9(m,n)** and **10**, blocks further complexation at the adjacent free bidentate site.

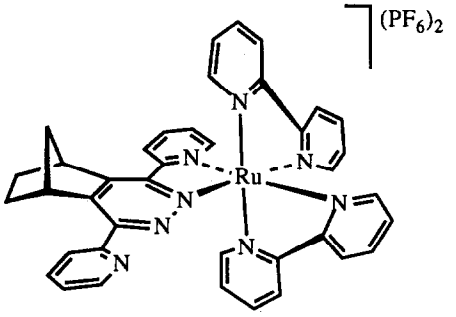


9(m,n) **m = 0; n = 0**
m = 1; n = 0
m = 0; n = 1

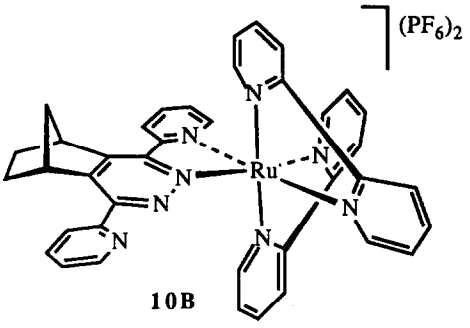
The ^{1}H NMR spectra of the ruthenium complexes revealed them to consist of *ca* 1:1 mixtures of two diastereomers.[50] The essential structural difference between the diastereomers lies in the disposition of the bpy ligands, as shown by **A** and **B** in **9(m,n)** and **10**. Repeated fractional recrystallization of the complexes led to isolation of samples with > 90% diastereomeric enrichment. Unambiguous structural assignment of the diastereomers has yet to be made since all attempts to obtain suitable crystals for X–ray analysis have so far failed. The ^{1}H NMR spectra of the two diastereomers for each system differ slightly in the chemical shifts of the resonances of the two protons in the CH$_2$ bridge of the norbornyl ring that is directly fused to the pyridazine ring. However, correlating these chemical shift differences with the structural differences in **A** and **B** is by no means clearcut.

The methoxy proton resonances showed interesting variations in chemical shift in the series of complexes, **9(m,n)**. For one diastereomer of the 2–bond complex, **9(0,0)**, the methoxy signals occur at δ 4.16 and δ 3.96 ppm, corresponding to a chemical shift difference, $\Delta\delta$, of 0.2 ppm, whereas in the other diasteromer, they have nearly identical chemical shifts, *ie*, δ 4.19 and δ 4.15 ppm ($\Delta\delta$ = 0.04 ppm). The finding that one diastereomer of **9(0,0)** has a larger $\Delta\delta$ value than the other is also observed for the 4–bond and 6–bond complexes, **9(1,0)** and **9(0,1)**, respectively, although the difference is attenuated with increasing

bridge length: $\Delta\delta$ = 0.09 and 0.04 ppm for **9(1,0)** and **9(0,1)**, respectively. These observations are consistent with that diastereomer displaying the larger $\Delta\delta$ value having the structure **9(m,n)B**, since molecular models suggest that the two methoxy groups in this structure experience greater differences in ring current effects resulting from the lower axially disposed pyridine ring than in **9(m,n)A**.[51] The methoxy resonances in both diastereomers of **9(1,0)** are markedly shielded, by *ca* 1 ppm for one diastereomer, and 0.5 ppm for the other diastereomer, compared to those for **9(0,0)** and **9(0,1)**. This could be due to the methoxy groups adopting different conformations, in **9(1,0)**, than in **9(0,0)** and **9(0,1)**. A more satisfactory resolution of these matters must await X–ray structure determinations of these complexes.



10A



10B

The luminescence spectra of the complexes reveal that the lifetimes of the excited states of **9(m,n)** are shorter, compared to that for the model complex, **10**, which lacks the DMN donor group. These results imply that ET is, indeed, occurring from the DMN donor group to the locally excited metal–to–ligand (ruthenium^{3+}–pyridazinyl^{-}) site. The photophysics of this process is being actively investigated.[53]

Pyridine annulation

The synthesis of substituted derivatives of methanoisoquinoline, **5**, (but not the parent compound, **5**, itself) has been described by the Tanida group.[54–56] However, the synthetic route employed by that group consisted of a multistep process starting from the Diels–Alder adduct of cyclopentadiene and glutinic acid and this procedure is unsuitable for the synthesis of the pyridino systems, **3(m,n)**. These systems would be most conveniently synthesized from the olefin precursors, **6(m,n)**,[47] through annulation techniques. Consequently, we investigated the viability of two annulation approaches, which are shown in Scheme 3 for the synthesis of **5** by way of example.

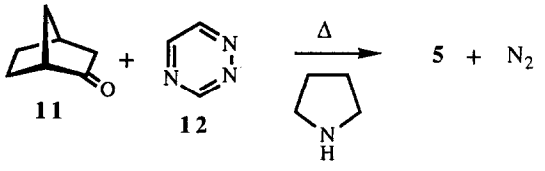
Method A is simply the application of the Boger annulation procedure[57] in which pyridine annulation occurs through Diels–Alder addition of 1,2,4–triazine, **12**, to the *in situ* generated pyrrolidine enamine of norbornanone, **11**. The Boger annulation procedure has not previously been applied to norbornanone systems. Method B involves Diels–Alder reaction between 3–thiomethyl–1,2,4–triazine, **14**, and norbornene, **13**, which should give the thiomethylpyridine annulated adduct, **16**, after dehydrogenation of the initial diene adduct, **15**. Raney nickel desulfurization of **16** should readily give the desired pyridine annulated product.[58] Diels–Alder reactions of simple triazines to electron rich alkenes and alkynes has literature precedent.[59–61] One possible drawback to this method is the competing formation of bis–adduct, **17**, resulting from Diels–Alder reaction of the diene intermediate, **15**, with another molecule of **13**. Indeed, the formation of such bis–adducts from the reaction of **13** with trichloro– and trifluoro–1,2,4–triazine has been reported.[61] Although method B is less direct than method A, and notwithstanding the possible complication of competitive bis–adduct formation, it does have the advantage over the latter method in that the thiomethyltriazine, **14**,[62] is synthetically much more accessible than the parent triazine, **12**.[63]

Reaction of norbornanone, **11**, with 1,2,4–triazine and pyrrolidine in refluxing toluene, in the presence of molecular sieves (Method A), gave the desired methanoisoquinoline, **5**, in 82% yield, as an oil. Reaction of norbornene, **13**, with triazine, **14**, in refluxing xylene for 72 h (Method B) gave a mixture of diene, **15**, (containing a small amount of the aromatized material, **16**), and bis–adduct, **17**, in isolated yields of 40% and 51%, respectively. The structures of the azadiene, **15**, and the bis-adduct , **17**, were assigned on the basis of their spectral data (see experimental). The ^{1}H NMR spectrum of **15** displays two olefinic resonances, each integrating for one proton. These protons are coupled to each other (J = 7.2 Hz) and the more upfield signal (δ 5.0) shows additional weaker coupling (J = 4 Hz) to an allylic proton, resonating at δ 2.66. The *exo* fusion of the azadiene ring to the norbornyl ring, as shown in **15**, is based on the well known strong preference for *exo* addition of dienes to norbornenes.

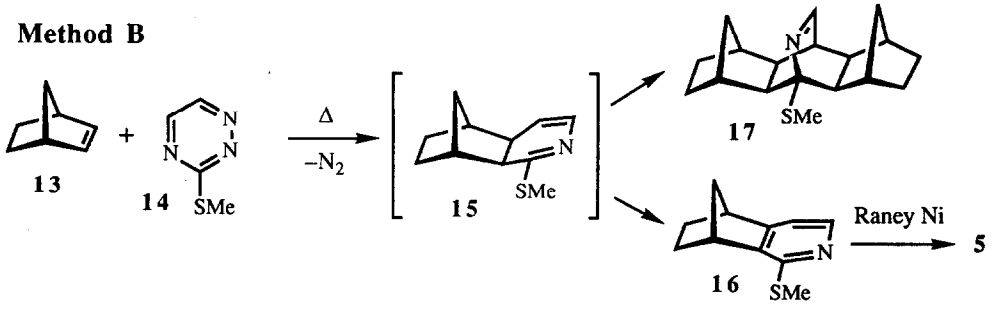
Electron impact ionization mass spectrometry (EIMS) of **17** gives a molecular ion peak at m/z = 287 which, together with the elemental analysis, shows that **17** is consistent with a bis–adduct structure. The ^{1}H NMR and ^{13}C NMR spectra of **17** are strongly suggestive of C_s molecular point group symmetry, and this conclusion is only consistent with the bis–adduct having the structure shown by **17**. This structure results from the expected *exo* attack of diene **15** on the norbornene double bond. Conversely, norbornene approaches the diene, **15**, from the *endo* face of the latter, since the *exo* face of **15** is protected from attack by the CH_2 bridge. As mentioned earlier, formation of bis-adducts, having the same skeletal structure as does **17**, also accompanies Diels–Alder reactions of norbornene with trihalogenated 1,2,4–triazines.[61]

Scheme 3

Method A

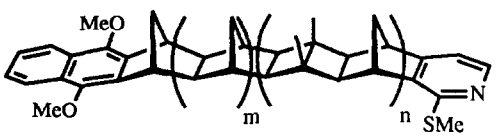


Method B

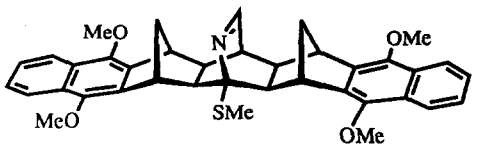


Conversion of **15** into the thiomethylmethanoisoquinoline, **16**, was readily achieved using DDQ. Raney nickel desulfurization of **16** into **5** occurred in 82% yield, making an overall yield of 33% from norbornene. The syntheses of **3(0,0)** and **3(0,1)** were carried out using Method B. Reaction of **6(0,0)** with the thiomethyltriazine, **14**, in refluxing xylene, open to the air, gave the desired aromatized 2–bond compound, **18(0,0)**, directly, together with bis–adduct, **19**, in isolated yields of 36% and 34%, respectively. The structures of these products were secured on the basis of their ^{1}H and ^{13}C NMR spectra (see experimental). Reductive desulfurization of **18(0,0)** gave the annulated pyridine, **3(0,0)**, in 30% overall yield from **6(0,0)**. Interestingly, reaction of the 6–bond olefin, **6(0,1)**, with triazine, **14**, using the same conditions as described

above, gave only adduct **18(0,1)**, in 63% yield, and no bis–adduct. Reductive desulfurization of this material gave the 6–bond pyridine, **3(0,1)**, in 51% overall yield from **6(0,1)**.

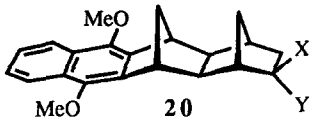


18(m,n)

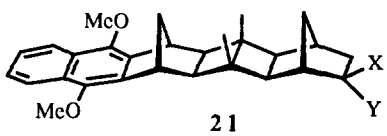


19

Method A was used to synthesize **3(1,0)** and **3(0,1)**. The required ketones, **20b** and **21b**, were obtained through oxidation of the respective alcohols, **20a** and **21a**, using pyridinium chlorochromate. Alcohol, **20a**, was obtained from the acetate, **20c**, which, in turn, was prepared by triflic acid catalyzed rearrangement of the alkene, **22**. The 6–bond alcohol, **21a**, was prepared from the alkene, **6(0,1)**, via hydroboration and subsequent oxidation using alkaline H_2O_2. This procedure has also been used to prepare alcohol, **20a**, from alkene, **6(1,0)**.[65] Annulation of ketones, **20b** and **21b**, gave the corresponding products, **3(1,0)** and **3(0,1)**, in 51% and 74% yields, respectively.



20

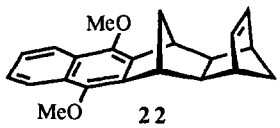


21

a X = OH; Y = H

b X,Y = =O

c X = OAc; Y = H



22

CF_3SO_3H

AcOH, Ac_2O

20c

In summary, Method A gives better yields of annulated pyridines than Method B, but this difference seems to diminish with increasing length of the bridge. Thus, for the 2–bond system the yields of **5** are 82% and 33% from methods A and B, respectively, whereas for the 6–bond system, the yields of **3(0,1)** are 73% and 51%, respectively. Our results to date suggest that Method B constitutes a synthetically viable alternative procedure to Method A, especially if one takes into account the relative ease of synthesis of the respective 1,2,4–triazine reagents used by the two methods. However, competing formation of unwanted bis–adduct using Method B presents a potential problem, although its lack of formation during annulation of **6(0,1)**, to give the 6–bond system, **18(0,1)**, is promising. Whether this holds for annuation of other longer bridged systems remains to be seen. This is under current investigation.

EXPERIMENTAL SECTION

General. Melting points were taken on a Koffler hot—stage and are uncorrected. ^1H NMR spectra were recorded on various machines: at 60 MHz (Varian 360L); at 300 MHz (Brucker AC–300F); at 500 MHz, (Brucker AM–500). ^{13}C NMR spectra were obtained using either the Brucker AC–300F or Brucker AM–500 spectrometers operating at *ca* 75.6 and 126 MHz, respectively. Elemental analyses were carried out by Dr H. Pham, University of New South Wales. EIMS measurements were obtained using an AEI MS12 mass spectrometer operating at 70 eV, with an accelerating voltage of 8000 V, and an ion source temperature of 200 °C. UV/Vis spectra were obtained using a Hitachi U–2000 spectrophotometer.

Synthesis of Phthalazines, 2(0,0), 2(1,0), 2(0,1), and 4.

General procedure.[49] Equimolar amounts of 3,6-di(2'-pyridyl)-1,2,4,5-tetrazine, **7**,[48], and the alkene, **6(m,n)**, or **13**, were reacted together in chloroform solution at 20-60 °C. When the solution turned from purple to yellow and the evolution of nitrogen had ceased (0.5 –1 h), the solvent was removed under reduced pressure and the yellow solid was redissolved in dioxane. DDQ (threefold excess, relative to the amount of alkene used) in the same solvent was added and the mixture stirred at rt. for 2-4 h. The solid was filtered off, washed with chloroform and the filtrate extracted several times with NaOH solution, and then washed with water and brine. The $CHCl_3$ solution was dried (Na_2SO_4), the solvent evaporated under reduced pressure, and the product recrystallized repeatedly from CH_3OH/CH_2Cl_2.

5,6,7,8–Tetrahydro–5,8–methano–1,4–di(2'–pyridyl)–phthalazine, 4. Using the general procedure given above, norbornene (1.2 g, 13 mmol) and **7** (2.13 g, 9 mmol), gave **4** (0.89 g, 74%); mp. 190-192 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.35 (1H, dd, J_1 7.5, J_2 2.3 Hz), 1.59 (1H, d, J 9.4 Hz), 2.10 (1H, t, J 2.05 Hz), 2.12 (1H, t, J 2.05 Hz), 1.78 (1H, t, J 2.0 Hz), 1.82 (1H, t, J 2.0 Hz), 4.48 (2H, t, J 1.9 Hz), 7.33 (2H, ddd, J_1 7.6, J_2 4.8, J_3 1.2 Hz, py), 7.85 (2H, dt, J_1 1.9, J_2 7.8 Hz, py), 8.55 (2H, d, J 8.0 Hz, py), 8.74 (2H, d, J 4.9 Hz, py). Anal. Calcd for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 76.02; H, 5.64; N, 18.58.

5,12–Dihydro – 5,12 -methano–6,11–dimethoxy–1,4–di(2'–pyridyl)–naphtho[2,3–*g*]phthalazine, 2(0,0). Using the general procedure given above, 1,4-Dihydro-9,10-dimethoxy-1,4-methanoanthracene (0.54 g, 2.1 mmol) and **7** (0.47 g, 2.0 mmol), gave **2(0,0)** (0.72 g, 73%); mp. 228 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.62 (1H, d, J 8.82 Hz, C*H*$_2$), 2.85 (1H, d, J 8.82 Hz, C*H*$_2$), 3.69 (6H, s, OC*H*$_3$), 6.23 (2H, t, J 1.58 Hz, bridgehead), 7.39 (2H, m, J 9.69 Hz, naphth), 7.44 (2H, m, J 8.80 Hz, py), 7.90 (2H, td, J_1 7.74, J_2 1.85 Hz, py), 7.96 (2H, m, J 9.68 Hz, naphth), 8.55 (2H, d, J 7.98 Hz, py), 8.93 (2H, d, J 4.80 Hz, py). Anal. Calcd for $C_{29}H_{22}N_4O_2$: C, 75.97; H, 4.84; N, 12.22. Found: C, 76.18; H, 5.10; N, 12.17.

(5α, 5aβ, 6α, 13α, 13aβ, 14α)– 5, 5a, 6, 13, 13a, 14–Hexahydro–5,14:6,13–dimethano–7,12–dimethoxy–1,4–di(2'–pyridyl)–anthraceno[2,3–*g*]phthalazine, 2(1,0). Using the general procedure given above, the olefin, **6(1,0)**, (0.0525 g, 1.65 mmol) and **7** (0.385 g, 1.63 mmol) gave **2(1,0)** (0.59 g, 68%); mp. >250 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.74 (2H, m, J 29.4 Hz, C*H*$_2$), 2.17 (2H, s, C*H*), 2.66 (2H, m, J 31.6 Hz, C*H*$_2$), 3.98 (2H, s, bridgehead), 3.99 (6H, s, OC*H*$_3$), 4.58 (2H, s, bridgehead), 7.36 (4H, m, J 12.4 Hz, py+naphth), 7.86 (2H, td, J_1 7.75, J_2 1.85 Hz, py), 7.98 (2H, m, J 9.7 Hz, naphth), 8.52 (2H, dt, J_1 8.0, J_2 1.1 Hz, py), 8.75 (2H, dm, J_1 4.8, J_2 2.8 Hz, py). Anal. Calcd for $C_{34}H_{28}N_4O_2$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.52; H, 5.59; N, 10.65.

(5α, 5aβ, 5bα, 5cβ, 6α, 13α, 13aβ, 13bα, 13cβ, 14α) – 5, 5a, 5c, 6, 13, 13a, 13c, 14 – Octahydro–5,14:6,13 – dimethano–7,12–dimethoxy–5b, 13b – dimethyl –1,4–di(2'–pyridyl)–anthraceno[2'',3'':3', 4']–cyclobuta[1', 2' : 3, 4]cyclobuta– [1,2–*g*]phthalazine, 2(0,1). Using the general procedure given above, the olefin, **6(0,1)**, (1.165 g, 2.91 mmol) and **7** (0.671 g, 2.84 mmol) gave **2(0,1)** (1.16 g, 66%); mp. >250 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.17 (6H, s, C*H*$_3$), 1.78 (2H, m, J 14.5 Hz, C*H*$_2$), 2.01 (2H, m, J 31.5 Hz, C*H*$_2$), 2.11 (2H, s, C*H*), 2.17 (2H, s, C*H*), 3.76 (2H, s, C*H*), 4.53 (2H, s, C*H*), 3.98 (6H, s, OC*H*$_3$), 7.41 (4H, m, J 23.1 Hz, py+naphth), 7.89 (2H, dt, J_1 7.7, J_2 1.9 Hz, py), 8.06 (2H, m, J 9.7 Hz, naphth), 8.57 (2H, d, J 8.0 Hz, py), 8.81 (2H, dd, J_1 4.9, J_2 2.4 Hz, py). Anal. Calcd for $C_{40}H_{36}N_4O_2$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.14; H, 5.28; N, 8.89.

Synthesis of the ruthenium(II) complexes of 2(0,0), 2(1,0), 2(0,1), and 4.

General procedure. Approximately equimolar quantities of the appropriate ligand, **2(m,n)**, or **4**, and $Ru(bpy)_2Cl_2{\cdot}2H_2O$,[64] were refluxed in methanol overnight. A change of colour from purple to red was observed which indicated completion of reaction. The reaction mixture was then cooled to rt., concentrated under reduced pressure, and filtered to remove any unreacted ligand. The crude complex was taken up in a small amount of methanol and run down a Sephadex LH20 column (2.5 x 120 cm) using methanol as eluant. Only the main deep-red band was collected, other fractions were discarded. The solution was evaporated to dryness under reduced pressure, and the complex was dissolved in water and KPF_6 solution was added dropwise until precipitation was complete. Very fine powder was obtained which could not be isolated by filtration. The suspension was therefore centrifuged; the supernatant (colourless or very faintly coloured) was discarded and the pellet recrystallized from methanol or acetone to yield red crystals of the hexafluorophosphate salt. Isolation of diastereomers was attempted by fractional recrystallization from acetone/methanol mixture.

Preparation of 10. Using the general procedure given above, **4** (0.110 g, 0.37 mmol) and $Ru(bpy)_2Cl_2$ (0.182 g, 0.35 mmol) gave **10** (0.31 g, 88%), as an equimolar mixture of the two diastereomers, **10A** and **10B**. UV/Vis (methanol): MLCT bands: 438nm Ru→bpy, 460nm (sh) Ru→ **4**. Anal. Calcd for $C_{39}H_{32}F_{12}N_8P_2Ru$: C, 46.67; H, 3.21; N, 11.16. Found: C, 46.48; H, 3.10; N, 11.04. Separation of the diastereomers by repeated fractional recrystallization from acetone/methanol led to isolation of pure **10A** (or **10B**) and of an 70% enriched sample of **10B** (or **10A**). ^1H NMR (d_6-acetone, 300 MHz):

10A (or **10B**) (less soluble isomer): δ 1.59 (2H, m, *J* 30 Hz), 1.79 (2H, m, *J* 54 Hz), 2.33 (2H, m, *J* 48.3 Hz), 4.46 (2H, bs, bridgehead), 7.23 (1H, d, *J* 7.95 Hz, arom), 7.39 (3H, m, *J* 25.6 Hz, arom), 7.55 (4H, m, *J* 27.7 Hz, arom), 7.74 (1H, td, J_1 7.7, J_2 1.8 Hz, arom), 7.92 (1H, d, *J* 4.6 Hz, arom), 8.25-8.07 (8H, m, arom), 8.85-8.68 (6H, m, arom).

10B (or **10A**) (more soluble isomer): δ 1.25 (1H, m, *J* 19.5 Hz), 1.39 (1H, m, *J* 21.0 Hz), 1.81 (2H, m, *J* 27.7 Hz), 2.26 (2H, m, *J* 51.0 Hz), 4.53 (2H, dd, J_1 11.5, J_2 5.8 Hz, bridgehead), 7.28 (1H, d, *J* 8.0 Hz, arom), 7.69-7.41 (6H, m, arom), 7.76 (1H, td, J_1 8.0, J_2 1.8 Hz, arom), 7.89 (1H, d, *J* 4.6 Hz, arom), 7.99 (1H, t, *J* 5.6 Hz, arom), 8.25-8.08 (8H, m, arom), 8.91-8.67 (6H, m, arom).

Preparation of 9(0,0). Using the general procedure given above, **2(0,0)** (0.260 g, 0.57 mmol) and $Ru(bpy)_2Cl_2$ (0.239 g, 0.49 mmol) gave **9(0,0)** (0.46 g, 81.6%) as an equimolar mixture of the two diastereomers, **9(0,0)A** and **9(0,0)B**. UV/Vis (methanol): MLCT bands: 438nm Ru→bpy, 469nm (sh) Ru→**2(0,0)**. Anal. Calcd for $C_{49}H_{38}F_{12}N_8O_2P_2Ru$: C, 50.65; H, 3.31; N, 9.64. Found: C, 50.02; H, 3.20; N, 9.16. Separation of the diastereomers by repeated fractional recrystallization from acetone/methanol led to isolation of pure **9(0,0)A** (or **9(0,0)B**) and of an 80% enriched sample of **9(0,0)B** (or **9(0,0)A**). ^1H NMR (d_6-acetone, 300 MHz):

9(0,0)A (or **9(0,0)B**) (less soluble isomer): δ 2.86 (1H, d, *J* 9.1 Hz, CH_2), 3.00 (1H, d, *J* 9.1 Hz, CH_2), 3.96 (3H, s, OCH_3), 4.16 (3H, s, OCH_3), 5.87 (1H, d, *J* 1.6 Hz, bridgehead), 6.39 (1H, d, *J* 1.5 Hz, bridgehead), 7.25 (1H, d, *J* 8.6 Hz, arom), 7.32 (1H, m, *J* 14.4 Hz, arom), 7.65-7.43 (6H, m, arom), 7.86-7.74 (4H, m, arom), 7.93 (1H, td, J_1 8.1, J_2 1.5 Hz, arom), 7.99 (2H, d, *J* 6.3 Hz, arom), 8.04 (1H, d, *J* 5.2 Hz, arom), 8.15 (1H, d, *J* 4.9 Hz, arom), 8.31-8.19 (4H, m, arom), 8.49 (1H, td, J_1 7.2, J_2 1.5 Hz, arom), 8.60 (1H, d, *J* 9.3 Hz, arom), 8.74 (1H, d, *J* 9.4 Hz, arom), 8.84 (2H, t, *J* 7.2 Hz, arom), 8.94 (1H, d, *J* 5.8 Hz, arom), 9.45 (1H, d, *J* 8.6 Hz, arom).

9(0,0)B (or **9(0,0)A**) (more soluble isomer): δ 2.60 (1H, d, *J* 9.2 Hz, CH_2) 2.77 (1H, d, *J* 9.2 Hz, CH_2), 4.15 (3H, s, OCH_3), 4.19 (3H, s, OCH_3), 5.79 (1H, d, *J* 1.5 Hz, bridgehead), 6.31 (1H, d, *J* 1.5 Hz, bridgehead), 7.09 (1H, m, *J* 13.3 Hz, arom), 7.36 (1H, d, *J* 8.0 Hz, arom), 7.70-7.50 (8H, m, arom), 7.82 (2H, td, J_1 6.0, J_2 1.9 Hz, arom), 7.94 (1H, dd, J_1 5.6, J_2 1.5 Hz, arom), 8.28-7.98 (8H, m, arom), 8.33 (1H,

d, *J* 5.6 Hz, arom), 8.45 (1H, td, J_1 7.9, J_2 1.6 Hz, arom), 8.74 (2H, m, *J* 21.7 Hz, arom), 8.82 (1H, d, *J* 8.1 Hz, arom), 8.92 (1H, d, *J* 4.8 Hz, arom), 9.41 (1H, d, *J* 8.1 Hz, arom).

Preparation of 9(1,0). Using the procedure given above, **2(1,0)** (0.176 g, 0.33 mmol) and $Ru(bpy)_2Cl_2 \cdot 2H_20$ (180 g, 0.35 mmol) gave **9(1,0)** (0.33 g, 82%) as an equimolar mixture of the two diastereomers, **9(1,0)A** and **9(1,0)B**. UV/Vis (methanol): MLCT bands: 437nm Ru→bpy, 465nm (sh) Ru→ **2(1,0)**. Anal. Calcd for $C_{54}H_{44}F_{12}N_8O_2P_2Ru$: C, 52.82; H, 3.61; N, 9.12. Found: C, 49.56; H, 3.83; N, 8.48. A satisfactory analysis has not yet been obtained, although spectral data are fully consistent with the proposed structure for **9(1,0)** (*vide infra*). Separation of the diastereomers by repeated fractional recrystallization from acetone/methanol led to isolation of pure **9(1,0)A** (or **9(1,0)B**) and of an 70% enriched sample of **9(1,0)B** (or **9(1,0)A**). ^1H NMR (d_6-acetone, 300 MHz):

9(1,0)A (or **9(1,0)B**) (less soluble isomer): δ 1.82 (1H, d, *J* 12.0 Hz), 2.02 (1H, d, *J* 12.0 Hz), 2.20 (2H, m, *J* 24 Hz), 2.67 (2H, t, *J* 10.5 Hz), 2.79 (2H, d, *J* 10.5 Hz), 3.12 (3H, s, OCH_3), 3.55 (3H, s, OCH_3), 4.52 (1H, s, bridgehead), 4.65 (1H, s, bridgehead), 7.36 (1H, d, *J* 9.0 Hz, arom), 7.70-7.45 (8H, m, arom), 7.80 (2H, m, *J* 18 Hz, arom), 8.07-7.93 (3H, m, arom), 8.27-8.17 (8H, m, arom), 8.64 (1H, d, *J* 9.5 Hz, arom), 8.85-8.70 (4H, m, arom), 9.06 (1H, d, *J* 9.0 Hz, arom).

9(1,0)B (or **9(1,0)A**) (more soluble isomer): δ 1.32 (2H, m,*J* 51 Hz), 1.41 (1H, d, *J* 12.0 Hz), 2.14 (1H, d, *J* 12.0 Hz), 2.64 (2H, t, *J* 12.0 Hz), 2.82 (2H, d, *J* 9.0 Hz), 3.15 (3H, s, OCH_3), 3.67 (3H, s, OCH_3), 4.40 (1H, s), 4.52 (1H, s), 7.19 (1H, d, *J* 10.0 Hz, arom), 7.80-7.46 (11H, m, arom), 7.95 (2H, m, *J* 21 Hz, arom), 8.22 (8H, m, *J* 42 Hz, arom), 8.80 (5H, m, *J* 37.8 Hz, arom), 9.01 (1H, d, *J* 9.5 Hz, arom).

Preparation of 9(0,1). Using the procedure given above, **2(0,1)** (0.235 g, 0.39 mmol) and $Ru(bpy)_2Cl_2$: 0.2025 g, 0.39 mmol gave **9(0,1)** (0.41 g, 79.5%) as an equimolar mixture of the two diastereomers, **9(0,1)A** and **9(0,1)B**. UV/Vis (methanol): MLCT bands: 443nm Ru→bpy, 463nm (sh) Ru→**2(0,1)**. Anal. Calcd for $C_{60}H_{52}F_{12}N_8O_2P_2Ru$: C, 55.09; H, 4.01; N, 8.57. Found: C, 54.86; H, 3.93; N, 8.43. Separation of the diastereomers by repeated fractional recrystallization from acetone/methanol led to isolation of pure **9(0,1)A** (or **9(0,1)B**) and of an 80% enriched sample of **9(0,1)B** (or **9(0,1)A**). ^1H NMR (d_6-acetone, 300 MHz):

9(0,1)A (or **9(0,1)B**) (less soluble isomer): δ 1.19 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.74 (2H, m, *J* 32.2 Hz), 2.13 (2H, d, *J* 9.0 Hz), 2.21 (2H, d, *J* 5.8 Hz), 2.40 (2H, m, *J* 30.2 Hz), 3.83 (2H, d, *J* 4.8 Hz), 3.95 (3H, s, OCH_3), 3.96 (3H, s, OCH_3), 4.52 (1H, s), 4.62 (1H, s), 7.30-7.22 (2H, m, arom), 7.64-7.45 (6H, m, arom), 7.76 (1H, td, J_1 7.8, J_2 1.85 Hz, arom), 7.92 (2H, m, *J* 9.0 Hz, arom), 8.02 (2H, m, *J* 13.6 Hz, arom), 8.08 (1H, dd, J_1 7.8, J_2 1.5 Hz, arom), 8.29-8.15 (7H, m, arom), 8.80 (6H, m, *J* 32.0 Hz, arom), 8.95 (1H, d, *J* 5.8 Hz, arom).

9(0,1)B (or **9(0,1)A**) (more soluble isomer): δ 1.11 (2H, d, *J* 7.2 Hz), 1.18 (3H, s, CH_3), 1.26 (3H, s, CH_3), 1.72 (2H, m, *J* 34.0 Hz), 2.10 (2H, m, *J* 30 Hz), 2.22 (2H, m, *J* 38.2 Hz), 3.79 (2H, d, *J* 4.6 Hz), 3.90 (3H, s, OCH_3), 3.95 (3H, s, OCH_3), 4.56 (1H, s), 4.69 (1H, s), 7.27 (2H, m, *J* 7.7 Hz, arom), 7.80-7.39 (9H, m, arom), 7.98 (2H, m, *J* 27.3 Hz, arom), 8.28-8.13 (7H, m, arom), 8.65 (1H, d, *J* 8.1 Hz), 8.78 (6H, m, *J* 39.0 Hz, arom), 8.97 (1H, d, *J* 7.9 Hz, arom).

4a, 5, 6, 7, 8, 8a–Hexahydro–5, 8–methano–1–thiomethylisoquinoline, 15, and (1α, 4α, 4aβ, 5α, 5aβ, 6α, 9α, 9aβ, 10α, 10aβ)–1, 2, 3, 4, 4a, 5, 5a, 6, 9, 9a, 10, 10a–dodecahydro–5,10–methanimino–1,4:6,9–dimethano–5–thiomethylanthracene, 17. A solution of norbornene, **13**, (5.9 g, 62 mmol) and 3-thiomethyl-1,2,4-triazine, **14**,[62] (8.2 g, 65 mmol) in xylene (6 mL) was flushed with argon and refluxed with stirring for 72 h. The solution was filtered and the crude product was subjected to flash chromatography on silica (3:7 ethyl acetate : light petroleum (60-80 °C) eluent) to give two fractions. The first fraction was distilled (bulb to bulb) at 120 °C / 0.6 mm, yielding the azadiene, **15**, (4.34 g, 40%) as an oil containing a small amount of the aromatic isoquinoline, **16**. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.22 (1H, d, *J* 10.0 Hz), 1.28-1.42 (3H, m), 1.51-1.57 (2H, m), 1.60-1.65 (2H, m), 2.12 (1H, d, *J* 4.0 Hz), 2.28 (3H, s, SCH3), 2.66

(1H, d, *J* 4.0 Hz), 5.00 (1H, dd, J_1 4.0 Hz, J_2 7.2 Hz, H4), 6.43 (1H, d, *J* 7.2 Hz, H3); υ_{max} (neat film, cm^{-1}) 1095, 1570, 2870, 2950, 3040; EIMS: m/z =193 (M, 58%), 125 (M - C_5H_8, 100%).

The second fraction was identified as the bis-adduct, **17**, which was crystallized from ethyl acetate. (4.54 g, 51%); m.p. 137-138 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.64 (2H, d, *J* 10.6 Hz), 1.02 (4H, m), 1.38 (4H, m), 1.62 (2H, m), 1.78 (4H, s), 2.00 (2H, m), 2.12 (3H, s, S*CH*$_3$), 2.59 (2H, m), 2.68 (1H, d, *J* 4.3 Hz, H10), 8.24 (1H, d, *J* 4.3 Hz, *HC*=N). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 11.79 (*S*CH_3), 30.85 (*C*H_2), 31.12 (*C*H_2), 35.12 (*C*H_2), 38.90 (*C*H), 41.28 (*C*H), 41.34 (*C*H), 50.69 (*C*H), 52.07 (*C*H), 74.80 (N-*C*-S), 174.45 (*HC*=N); EIMS: m/z = 287 (M, 77%), 272 (M–CH_3, 86%), 193 (100%). (Found: C, 76.00; H, 9.06; N, 4.82. $C_{18}H_{25}NS$ requires C, 75.21; H, 8.77; N, 4.87%).

5, 6, 7, 8–Tetrahydro–5, 8–methano–1–thiomethyl–isoquinoline, 16. To a solution of the azadiene, **15**, (0.65 g, 3.4 mmol) in dioxane (10 mL) was added with stirring DDQ (1.0 g, 4.4 mmol) and glacial acetic acid (2 drops). The mixture was stirred for 0.5 h and 1,3-cyclohexadiene (0.3 mL) was then added to convert residual DDQ to the hydroquinone. The resulting mixture was then filtered and the filtrate concentrated under reduced pressure and distilled (125 °C / 0.5 mm) to give the methanoisoquinoline, **16**, (0.32 g, 1.7 mmol, 50%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.07 - 1.18 (2H, m), 1.47 (1H, dt, J_1 9.0 Hz, J_2 1.4 Hz), 1.69 (1H, dpent, J_1 9.0 Hz, J_2 2.1 Hz), 1.86 - 1.93 (2H, m), 2.56 (3H, s, SCH_3), 3.31 (1H, d, 1.9 Hz), 3.42 (1H, d, 1.7 Hz), 6.84 (1H, d, 4.9 Hz), 8.19 (1H, d, 4.9 Hz). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 12.41 (*S*CH_3), 25.18 (*C*H_2), 26.30 (*C*H_2), 40.68 (*C*H), 43.60 (*C*H), 48.57 (*C*H_2), 112.74 (*C*H), 140.24 (*C*), 147.23 (*C*H), 150.11 (*C*), 155.96 (*C*). Anal. Calcd for $C_{11}H_{13}NS$: C, 69.06; H, 6.85; N, 7.32. Found: C, 69.01; H, 6.98; N, 7.22.

5, 6, 7, 8–Tetrahydro–5, 8–methano–isoquinoline, 5.

Using method A. To a solution of norcamphor, **13**, (0.50g, 4.5 mmol) and 1,2,4-triazine, **12**,[63] (0.40g, 3.1 mmol) in toluene (5 mL) were added molecular sieves (4A, 2g). The solution was flushed with argon and pyrrolidine (0.25 mL, 0.2 g, 2.7 mmol) was added. The solution was then refluxed with stirring under argon for 22 h. The cooled reaction mixture was filtered and distilled (bulb to bulb at 130 °C/ 2 mm) to give the methanoisoquinoline, **5**, as a hygroscopic oil (0.54 g, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.11 (2H, m), 1.50 (1H, d, *J* 9.0 Hz), 1.69 (1H, d pent, J_1 2 Hz, J_2 9 Hz), 1.89 (2H, m), 3.32 (1H, d, *J* 1.5 Hz), 3.37 (1H, s), 7.06 (1H, d *J* 4.8 Hz, H4), 8.28 (1H, d, *J* 4.8 Hz, H3), 8.32 (1H, s, H1). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 25.95 (*C*H_2), 26.45 (*C*H_2), 41.05 (*C*H), 43.34, (*C*H), 49.10 (*C*H_2), 116.23 (*C*H), 141.02 (*C*H), 143.47 (*C*), 147.34 (*C*H), 156.62 (*C*). HRMS. calc: 145.0891; found: 145.0892. Anal. Calcd for $C_{10}H_{11}N.(H_2O)_{0.15}$: C, 81.20; H, 7.70; N, 9.47. Found: C, 81.26; H, 7.98; N, 9.39.

Using method B. Reductive desulfurization of **16** was carried out according to a modification of the method described by Brown.[58] To a magnetically stirred refluxing solution of the thioether, **16**, (0.80 g, 4.2 mmol) in ethanol (30 mL) and aqueous ammonia (15M, 15 mL) was added the appropriately prepared Raney nickel[58] in ethanol (4 mL of the settled suspension). The solution was refluxed for 90 min after which TLC indicated the reaction was complete. H_2S gas was then passed through the cooled solution for 5 min and the suspension filtered. To the filtrate was added water (100 mL) and the solution was extracted with $CHCl_3$ (3 x 50 mL). The combined organic layers were dried over K_2CO_3, filtered and concentrated under reduced pressure. The residue was distilled (bulb to bulb at 130 °C, 20 mm) to give the methanoisoquinoline, **5**, (0.50 g, 82%), whose ^{1}H and ^{13}C NMR spectra were identical in every respect to those reported above for **5**.

5,12–Dihydro–5,12–methano –6,11– dimethoxy – 1 – thiomethyl – naphtho[2,3–*g*]isoquinoline, 18(0,0), and (6α, 6aβ, 7α, 7aβ, 8α, 15α, 15aβ, 16α, 16aβ, 17α)–6, 6a, 7, 7a, 8, 15, 15a, 16, 16a, 17–Decahydro–7, 16–methanimino–6, 17 : 8, 15–dimethano–5, 9, 14, 18–tetramethoxy–7–thiomethylheptacene, 19. A magnetically stirred solution of the alkene, **6(0,0)**,[66] (2.0 g, 7.9 mmol) and the triazine, **14**, (4.0 g, 31.5

mmol) in xylene (8 mL) was refluxed for 72 h open to the atmosphere. The cooled solution was filtered, and volatiles removed at 120 °C / 0.1 mm. The residue was subjected to column chromatography (silica, $CHCl_3$ eluent) to give a fraction which was recrystallized from ethanol to give the aromatized thiomethylpyridine, **18(0,0)**, (1.0 g, 36%). m.p. 165-166 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.47 (1H, dt, J_1 8.4 Hz, J_2 1.5 Hz, 13 *anti*-H13), 2.53 (1H, dt, J_1 8.4 Hz, J_2 1.6 Hz, *syn*-H13), 2.59 (3H, s, SCH_3), 3.99 (3H, s, OCH_3), 4.17 (3H, s, OCH_3), 4.73 (1H, d, *J* 1.5 Hz, H5), 4.89 (1H, d, *J* 1.4 Hz, H12), 7.09 (1H, d, *J* 4.8 Hz, H4), 7.44 (2H, m, H8, H9), 8.03 (2H, m, H7, H10), 8.19 (1H, d, *J* 4.8 Hz, H3). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 12.70 (S*C*H$_3$), 45.29 (*C*H), 47.87 (*C*H), 62.05 (O*C*H$_3$), 62.87 (O*C*H$_3$), 63.70 (*C*H$_2$), 113.64 (*C*H, py), 121.98 (*C*H, naphth), 122.38 (*C*H, naphth), 125.80 (2*C*H, naphth), 127.92 (*C*, naphth), 128.11 (*C*, naphth), 132.44 (*C*, naphth), 133.59 (*C*, naphth), 142.36 (*C*), 145.67 (*C*), 145.92 (*C*), 147.31 (*C*H, py), 151.10 (*C*), 158.04 (*C*, py). Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.49; H, 5.61; N 4.04.

Further elution with 5% methanol in $CHCl_3$ yielded the bis-adduct, **19**, (0.8 g, 34%) which was recrystallized from ethyl acetate; m.p. 309 - 310 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.39 (2H, d, *J* 10.2 Hz), 2.10 (2H, d, *J* 8.2 Hz), 2.14 (2H, d, *J* 8.2 Hz), 2.36 (2H, d *J* 10.2), 2.46 (3H, s, SCH_3), 3.27 (1H, d, *J* 4.3 Hz, allyl CH), 3.66 (2H, s, bridgehead CH), 3.93 (6H, s, 2 x OCH_3), 4.03 (6H, s, 2 x OCH_3), 4.25 (2H, s, bridgehead CH), 7.41 (4H, m, naphth), 8.01 (4H, m, naphth), 8.68 (1H, d, *J* 4.3 Hz, HC=N). ^{13}C NMR ($CDCl_3$, 75.6 MHz): δ 12.16 (S*C*H$_3$), 41.63 (*C*H), 43.05 (*C*H$_2$), 43.87 (*C*H), 45.57 (*C*H), 49.64 (*C*H), 51.43 (*C*H), 61.68 (O*C*H$_3$), 62.04 (O*C*H$_3$), 74.45 (N-*C*-S), 121.99 (*C*H, naphth), 122.32 (*C*H, naphth), 125.30 (*C*H, naphth), 125.37 (*C*H, naphth), 128.01 (*C*, naphth), 128.12 (*C*, naphth), 135.55 (*C*, naphth), 136.67 (*C*, naphth), 143.36 (*C*, naphth), 143.62 (*C*, naphth), 176.00 (*C*=N). Anal. Calcd for $C_{38}H_{37}NO_4S$: C, 75.60; H, 6.18; N, 2.32. Found: C, 76.00; H, 6.46; N 2.35.

5,12–Dihydro–5,12–methano –6,11– dimethoxynaphtho[2,3–*g*]isoquinoline, 3(0,0).

Using method B. To a magnetically stirred refluxing solution of the methylthiopyridine, **18(0,0)**, (0.90 g, 2.6 mmol) in ethanol (50 mL) and aqueous ammonia (15M, 15 mL) was added Raney nickel in ethanol (approx 2.5 mL settled suspension). The suspension was refluxed for 1 h and the cooled solution was filtered through filter aid, concentrated and the precipitate filtered yielding the pyridine, **3(0,0)**, (0.65 g, 83%); m.p. 129.5-130.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.52 (1H, d, *J* 8.4 Hz, *anti*-H13), 2.56 (1H, d, *J* 8.4 Hz, *syn*-H13), 4.00 (3H, s, OCH_3), 4.02 (3H, s, OCH_3), 4.78 (1H, s, H5), 4.83 (1H, s, H12), 7.32 (1H, d, *J* 4.7 Hz, H4), 7.45 (2H, dd, J_1 3.2 Hz, J_2 6.6 Hz, H8, H9) 8.03 (2H, m, H7, H10), 8.30 (1H, d, *J* 4.7 Hz, H3), 8.57 (1H, s, H1). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 45.53 (*C*H), 47.64 (*C*H), 61.86 (O*C*H$_3$), 61.99 (O*C*H$_3$), 63.52 (*C*H$_2$), 117.38 (*C*H, py), 122.05 (*C*H, naphth), 122.13 (*C*H, naphth), 125.88 (*C*H, naphth), 125.95 (*C*H, naphth), 127.87 (*C*, naphth), 128.08 (*C*, naphth), 133.02 (*C*, naphth), 133.70 (*C*, naphth), 141.77 (*C*H, py), 144.91 (*C*, py), 145.59 (*C*, naphth), 145.85 (*C*, naphth), 147.45 (*C*H, py), 158.45 (*C*, py). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N 4.62. Found: C, 78.90; H, 5.63; N, 4.40.

(5α, 5aβ, 6α, 13α, 13aβ, 14α)– 5, 5a, 6, 13, 13a, 14–Hexahydro–5,14:6,13–dimethano–7,12–dimethoxyanthraceno[2,3–*g*]isoquinoline, 3(1,0).

Using Method A. A solution of the olefin, **22**,[47] (2.6 g, 8.2 mmol) in a 3% solution of acetic anhydride in acetic acid was flushed with argon and trifluoromethanesulfonic acid (2 mL, 23 mmol) was slowly added. The reddish solution was sealed and magnetically stirred for 18 h. The solution was then poured onto ice water (300 mL) and the resulting mixture was extracted with $CHCl_3$ (3 x 100 mL). The combined organic layers were then washed with aqueous ammonia (1 x 20 mL of 15M, followed by 1 x 20 mL of 5M), then brine (1 x 50 mL). The solution was dried over anhyd. Na_2CO_3, filtered and evaporated to dryness, yielding the crude acetate, **20c**, (2.4 g, 77% total) as an oil. This compound was not purified further. ^{1}H NMR ($CDCl_3$, 60 MHz): 2.0 (acetate peak), no olefinic signals; υ_{max} (thin film) 1725 cm^{-1} (C=O).

The crude acetate, **20c**, (2.4 g, 6.3 mmol) was refluxed for 12 h in alcoholic KOH (2M, 150 mL), cooled and poured into ice water (100 mL). This mixture was then extracted with $CHCl_3$ (3 x 50 mL) and the combined organics were washed with saturated aqueous $NaHCO_3$ (50 mL), then brine (50 mL). The solution was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue contained the alcohol, **20a**, (2.1 g, 99% total); υ_{max} (thin film) 3400 cm^{-1} (OH).

The alcohol, **20a**, (0.83 g, 2.5 mmol) in CH_2Cl_2 (10 mL) was added to a stirred suspension of pyridinium chlorochromate in CH_2Cl_2. The mixture was stirred overnight, filtered and purified by flash chromatography on alumina (ethyl acetate eluent) yielding the ketone, **20b**, as an oil (0.74 g, 90%). This product was not purified further. υ_{max} (thin film) 1740 cm^{-1} (C=O).

To a solution of the ketone, **20b**, (0.60g, 1.8 mmol) and 1,2,4-triazine, **12**, (0.165g, 2.0 mmol) in benzene (5 mL) were added molecular sieves (4A, 2g). The solution was flushed with argon and pyrrolidine (0.25 mL, 0.2 g, 2.7 mmol) was added. The solution was then refluxed with stirring under argon for 36 h. The cooled reaction mixture was filtered then loaded directly onto an alumina column (benzene eluent). Chromatography (ethyl acetate) gave an oil (0.2 g) that contained unreacted ketone. Further elution gave a solid which was recrystallized from acetone to give the pyridine, **3(1,0)**, (0.25 g, 51%, yield based on amount of ketone reacted); m.p. 204.5-205.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.65 (1H, d t, J_1 1.3 Hz, J_2 10.8 Hz), 1.72 (1H, d o t, J_1 1.3 Hz, J_2 10.8 Hz), 1.82 (1H, d, J 7.0 Hz), 1.88 (1H, d, J 7.0 Hz), 2.58 (1H, dt, J_1 1.8 Hz, J_2 8.5 Hz), 2.61 (1H, dt, J_1 1.8 Hz, J_2 8.5 Hz), 3.48 (1H, s), 3.53 (1H, s), 3.82 (1H, d, 1.5 Hz), 3.83 (1H, d, 1.5 Hz), 3.97 (6H, br s, 2 x OCH_3), 7.06 (1H, d, J 4.8 Hz, H4), 7.41 (2H, br dd, J_1 3.3 Hz, J_2 6.8 Hz, naphth: H9, H10), 8.03 (2H, m, naphth: H8, H11), 8.23 (1H, d, J 4.8 Hz, H3), 8.32 (1H, s, H1). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 43.53 (*C*H), 43.58 (*C*H_2), 43.64 (*C*H), 44.62 (*C*H), 44.71 (*C*H_2), 46.88 (*C*H), 50.13 (*C*H), 51.00 (*C*H), 61.715 (2 x OCH_3), 115.95 (*C*H, py), 121.93 (*C*H, naphth), 121.99 (*C*H, naphth), 125.15 (2*C*H, naphth), 127.79 (*C*, naphth), 127.83 (*C*, naphth), 136.90 (2*C*, naphth), 140.60 (*C*H, py), 143.51 (*C*, py), 145.86 (2*C*, naphth), 147.33 (*C*H, py), 158.88 (*C*, py). Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27; N, 3.79. Found: C, 81.21; H, 6.50; N, 3.78.

***exo*-2-Hydroxy-(1α, 4α, 4aβ, 4bα, 4cβ, 5α, 12α, 12aβ, 12bα, 12cβ)-1, 2, 3, 4, 4a, 4c, 5, 12, 12a, 12c-decahydro- 1,4 : 5, 12 - dimethano-6, 11-dimethoxy- 4b, 12b-dimethylbenzo[3', 4']cyclobuta-[1', 2' : 3, 4]cyclobut[1, 2 - *b*]anthracene, 21a**. To a magnetically stirred solution of the olefin, **6(0,1)**,[47] (2.0 g, 5.0 mmol) in THF (10 mL), at 0 °C, under argon, was added borane-methyl sulfide complex (3 mL, 2M in THF, 6 mmol). The solution was stirred at 0 °C for 1h, then at 25 °C for 1 h and then finally refluxed for 1 h. After cooling to 0 °C, ethanol (3 mL) was added carefully, followed by aqueous sodium hydroxide (3.1 mL, 2M) and hydrogen peroxide (1 mL, 27.5%). The solution was refluxed for 3 h, cooled and poured into water (50 mL). The resulting suspension was extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with water (10 mL) then brine (10 mL) and dried over $MgSO_4$. The solution was evaporated to dryness and the product precipitated on addition of diethyl ether yielding the *exo*-alcohol, **21a**, (1.77 g, 85%), m.p. (from ether) 163-165 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.92 (3H, s, CH_3), 0.93 (3H, s, CH_3), 1.30 (1H, ddd, J_1 13.2 Hz, J_2 4.0 Hz, J_3 2.0 Hz), 1.41 (1H, br s, OH), 1.50-1.67 (5H, m), 1.80-1.85 (2H, m), 1.95 (1H, d, J 19.4 Hz), 2.10-2.21 (3H, m), 3.63 (1H, br m, H2), 3.65 (2H, s), 3.97 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), 7.44 (2H, m, naphth), 8.07 (2H, m, naphth). ^{13}C NMR ($CDCl_3$, 75.6 MHz): δ 10.19 (*C*H_3), 10.26 (*C*H_3), 31.87, 36.34, 41.16, 42.51, 43.40, 43.79, 44.72, 45.35, 48.08, 51.37, 51.63, 62.53 (OCH_3), 74.47 (*C*H-O), 122.64 (*C*H, naphth), 125.61 (*C*H, naphth), 128.48 (*C*, naphth), 135.90 (*C*, naphth), 144.88 (*C*, naphth); υ_{max} (nujol mull) 3400 cm^{-1} (O-H stretch). Anal. Calcd for $C_{28}H_{32}O_3$: C, 80.73; H 7.74. Found: C, 80.90; H, 7.92.

(1α, 4α, 4aβ, 4bα, 4cβ, 5α, 12α, 12aβ, 12bα, 12cβ)-1, 2, 3, 4, 4a, 4c, 5, 12, 12a, 12c-Decahydro-1,4 : 5, 12 - dimethano - 6, 11 - dimethoxy - 4b, 12b - dimethylbenzo[3' , 4'] cyclobuta [1', 2' : 3, 4] cyclobut[1, 2- *b*]anthracen-2-one, 21b. To a solution of the alcohol, **21a**, (1.47 g, 3.53 mmol) in

dichloromethane (50 mL) was added pyridinium chlorochromate (1.2 g, 5.6 mmol). The solution was stirred for 12 h, then the product isolated by column chromatography on silica gel using dichloromethane. Recrystallization from ethanol yielded the ketone, **21b**, (1.26 g, 85.7%), m.p. (from ethanol) 189-190 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.95 (3H, s, CH_3), 1.01 (3H, s, CH_3), 1.58 (1H, s), 1.69-1.76 (3H, m), 1.94 (2H, dm, J_1 11.2 Hz), 2.12 (1H, dd, J_1 17.8 Hz, J_2 4.9 Hz), 2.18 (1H, d, J 5.7 Hz), 2.23 (1H, d, J 5.7 Hz), 2.24 (2H, s), 2.59 (2H, s), 3.74 (2H, s), 3.96 (3H, s, OCH_3), 3.98 (3H, s, OCH_3), 7.44 (2H, m, naphth: H8, H9), 8.07 (2H, m, naphth: H7, H10). ^{13}C NMR ($CDCl_3$, 75.6 MHz): δ 9.83 (CH_3), 10.50 (CH_3), 34.33, 36.21, 41.17, 41.25, 43.45, 44.21, 45.52, 46.13, 46.41, 50.40, 51.21, 51.34, 62.60 (2 x OCH_3), 122.67 (*C*H, naphth), 122.75 (*C*H, naphth), 125.78 (*C*H, naphth), 128.58 (*C*H, naphth), 135.44 (*C*, naphth), 135.58 (*C*, naphth), 145.00 (*C*, naphth), 216.80 (*C*=O) υ_{max} (nujol mull) 1740 cm^{-1}. Anal. Calcd for $C_{28}H_{30}O_3$: C, 81.13; H, 7.29. Found: C, 81.31; H, 7.54.

(5α, 5aβ, 5bα, 5cβ, 6α, 13α, 13aβ, 13bα, 13cβ, 14α) – 5, 5a, 5c, 6, 13, 13a, 13c, 14 – Octahydro – 5, 14 : 6, 13 – dimethano – 5b, 13b – dimethyl–1–thiomethylanthraceno[2'', 3'' :3', 4']cyclobuta[1', 2' : 3, 4]cyclobuta[1,2–*g*]isoquinoline, 18(0,1). A magnetically stirred solution of the olefin, **6(0,1)**[47] (275 mg, 0.69 mmol) and 3-thiomethyl-1,2,4-triazine (350 mg, 2.8 mmol) in xylene (0.7 mlL was refluxed for 72 h open to the atmosphere. The cooled solution was then filtered and the volatiles removed at 80 °C / 0.1 mm. The residue was then purified by column chromatography (silica, $CHCl_3$ eluent) and recrystallized from ethanol, yielding the thiomethyl pyridine, **18(0,1)** (215 mg, 63%); m.p. 228.5-229.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.05 (3H, s), 1.08 (3H, s), 1.64 (1H, d, J 9.7 Hz), 1.74 (1H, d, J 9.7 Hz), 1.85 (1H, d, J 9.7 Hz), 1.88 (1H, d, J 5.7 Hz), 1.95 (1H, d, J 5.7 Hz), 1.97 (1H, d, J 9.7 Hz), 2.10 (1H, d, J 5.7 Hz), 2.15 (1H, d, J 5.7 Hz), 2.57 (3H, s, SCH_3), 3.30 (1H, s), 3.41 (1H, s), 3.70 (1H, s), 3.72 (1H, s), 3.95 (3H, s, OCH_3), 3.97 (3H, s, OCH_3), 6.86 (1H, d, J 4.9 Hz, H4), 7.43 (2H, m, naphth), 8.06 (2H, m, naphth), 8.20 (1H, d, J 4.9 Hz, H3); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 9.48 (CH_3), 9.81 (CH_3), 12.54 (SCH_3), 40.60 (*C*H), 40.63 (*C*H), 40.97 (*C*H), 42.84 (CH_2), 43.00 (*C*), 43.17 (CH_2), 43.95 (*C*H), 48.47 (*C*H), 49.81 (*C*H), 50.53 (*C*H), 50.61 (*C*H), 61.86 (OCH_3), 61.90 (OCH_3),113.14 (*C*H, py), 121.95 (*C*H), 122.05 (*C*H), 125.00 (*C*H), 127.81 (*C*), 127.86 (*C*),134.91 (*C*), 135.03 (*C*), 140.11 (*C*H), 144.26 (*C*H) 144.39 (*C*), 147.19 (*C*H), 150.16 (*C*), 155.62 (*C*, py); υ_{max} (KBr disk) 773, 966, 980, 1036, 1091, 1193, 1298, 1355, 1404, 1465, 1566, 1588, 1612, 1644, 2839, 2870, 2931, 2977, 3070, 3441 cm^{-1}. Anal. Calcd for $C_{32}H_{33}NO_2S$: C, 77.33; H, 6.63. Found: C, 77.54; H, 6.77.

(5α, 5aβ, 5bα, 5cβ, 6α, 13α, 13aβ, 13bα, 13cβ, 14α) – 5, 5a, 5c, 6, 13, 13a, 13c, 14 – Octahydro – 5, 14 : 6, 13 – dimethano – 5b, 13b – dimethylanthraceno[2'', 3'' :3', 4']cyclobuta[1', 2' : 3, 4]cyclobuta[1,2–*g*]isoquinoline, 3(0,1).

Using method A. To a solution of the ketone, **21b**, (1.0g, 2.42 mmol) and 1,2,4-triazine (0.4 g, 4.94 mmol) in dry toluene (2.4 mL) were added under argon with magnetic stirring, 4A molecular sieves (~2 g). The solution was deoxygenated and pyrrolidine (100 mg, 1.41 mmol) added. The solution was refluxed with stirring for three days after which it was cooled, filtered and the product separated by column chromatography on silica and ethyl acetate eluent. Recrystallization from acetone gave the pyridine, **3(0,1)**, (0.80 g, 74%), m.p. 269-270 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.07 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.66 (1H, d, J 9.6 Hz), 1.75 (1H, d, J 9.6 Hz), 1.89 (2H, t), 1.97 (2H, t), 2.12 (2H, s), 3.33 (1H, s), 3.37 (1H, s), 3.708 (1H, s, H5 or H12), 3.712 (1H, s, H12 or H5), 3.96 (6H, br s, 2 x OCH_3), 7.09 (1H, d, J 4.8 Hz, H4), 7.42 (2H, dd, J_1 3.3 Hz, J_2 6.4 Hz, naphth: H9, H10), 8.06 (2H, m, naphth: H8, H11), 8.31 (1H, d, J 4.8 Hz, H3), 8.35 (1H, s, H1); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 9.43 (CH_3), 9.48 (CH_3), 40.54 (*C*H), 41.26 (*C*H), 42.75 (CH_2), 42.88 (*C*), 42.91 (*C*), 43.62 (*C*H), 43.64 (CH_2), 49.42 (*C*H), 49.95 (*C*H), 50.45 (*C*H), 50.57 (*C*H), 61.79 (2 x OCH_3), 116.56 (*C*, py), 121.92 (*C*H, naphth), 121.96 (*C*H, naphth), 124.97 (*C*H, naphth), 127.79 (*C*, naphth), 134.84 (*C*, naphth), 134.88 (*C*, naphth), 141.18 (*C*H, py), 143.17 (*C*H, py)

144.25 (*C*, naphth), 144.28 (*C*, naphth), 147.30 (*C*H, py), 156.30 (*C*, py). Anal. Calcd for $C_{31}H_{31}NO_2$: C, 82.82; H, 6.95; N, 3.12. Found: C, 83.10; H, 7.23; N, 3.16.

Using Method B. To a magnetically stirred refluxing solution of the thio ether **18(0,1)** (0.80 g, 1.6 mmol) in ethanol (80 mL) and aqueous ammonia (15M, 40 mL) was added Raney nickel in ethanol (*ca* 4 mL of the settled suspension). The suspension was refluxed for 1 h after which time TLC indicated the reaction to be complete. H_2S gas was then passed through the cooled solution for 5 min and the suspension filtered. The cooled solution was concentrated and the precipitate filtered yielding the pyridine, **3(0,1)**, (0.59 g, 81%).

ACKNOWLEDGEMENTS

The support of the Australian Research Council is gratefully acknowledged. One of us (P. J. K.) also acknowledges the award of a Commonwealth Postgraduate Research Award. We thank Dr P. A. Lay for helpful advice on the synthesis on the ruthenium complexes. We also thank Ms H. Stender for the 500 MHz NMR spectra and Dr J. J. Brophy for the EIMS measurements.

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