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Rigid Molecular Racks featuring the 1,10-phenanthroline Ligand especially those Co-functionalised with Redox-active Groups or Other Bidentate Ligands

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Abstract: 6,7-Diazaphencyclone (DAPC), prepared for the first time, exists as a dimer in the solid state but is in thermal equilibrium with the monomer **11** in solution. DAPC is a reactive diene reacting with ring-strained and electron-deficient dienophiles with high stereospecificity. Bridged 1,10-phenanthrolines with different separation distances and ligand, ligand orientations have been prepared and mixed ligand systems are described with diazafluorene and 3,6-di(2-pyridyl)pyridazine ligand components. New diad and triad systems are reported which contain redox-active components linked to ligand centres. The rigid nature of the polyalicyclic molrac framework and the fusion method used to attach the functionality, provides molecules with exact geometric positioning and orientation of chromophores. This makes these systems key molecules for the study of electron-transfer and energy-transfer processes.
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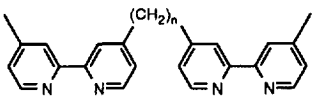
Introduction

The role of bridged ligands in the study of energy transfer and electron-transfer has been well established.[1] The early work involved the linking of the two ligands, or of the ligand and the redox function, by flexible methylene chains, see **1**[2] (Scheme 1). As the field has become more advanced and the need for more sophisticated model systems has been realised, several new types of bridged ligands have been developed.

The role of aromatic spacers, eg **2**,[3] and of acetylene rods, eg **3**,[4] has provided model compounds with fixed distance between the interacting centres within the molecule. However, in this type of molecule, the chromophoric components still retain conformational mobility around the σ-bond joining them to the bridge. More recently, the first conformationally fixed molecular systems have been reported. These fall into two classes: those which are joined by fused aromatics,[5] and those linked by an alicyclic framework such as an adamantane ring, eg **4**.[6] The former act as molecular wires whereby the two ligands are directly conjugated by way of the bridge while the latter offer an insulated bridge where communication between ligands must be through the carbon σ-framework or through space.

This paper is dedicated to the memory of Arthur J. Birch who taught one of us (D.N.B.) early in his research career to appreciate mechanism in the solution of organic structural problems and by the other (R.N.W.) first as an undergraduate teacher at Sydney University and later, as a fellow Professor at the Australian National University.



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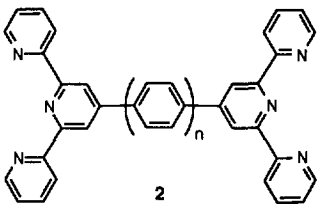

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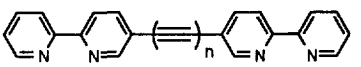

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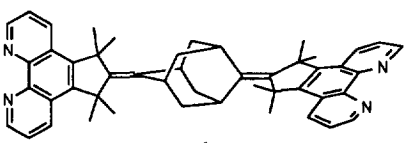


4

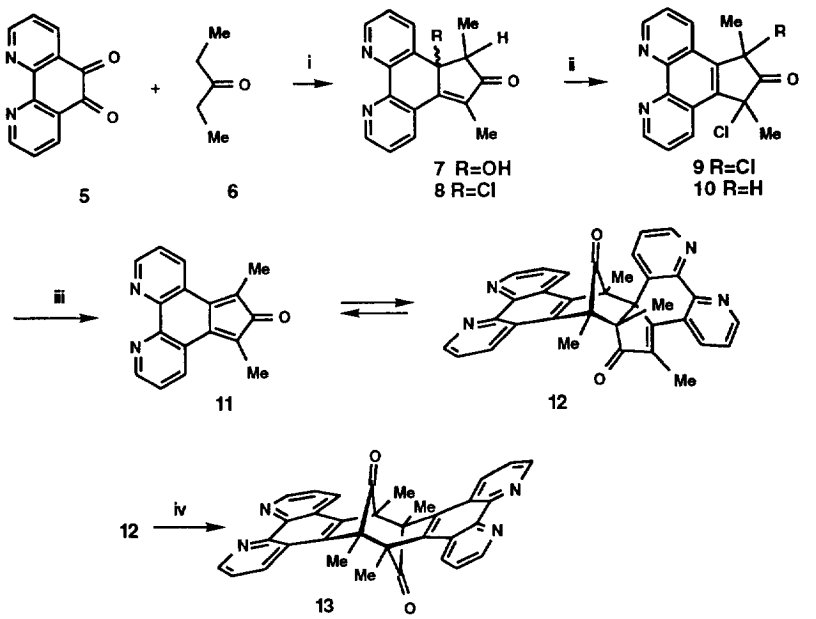
Scheme 1

The molecular racks described herein offer the most sophisticated system yet in the area of bridged ligands. Not only is the bridging group fully carbocyclic and rigid, but such compounds are available in a wide range of sizes and shapes. In addition, the method of fusion used to attach the ligand ensures known stereochemistry and rigid attachment. Another positive feature is the ability to incorporate both electron-donor or electron-acceptor units rigidly to the bridging alicyclic superstructure, as well as different ligating systems. This method offers unprecedented opportunities for the construction of new diads and triad systems, representative examples of which are described herein.

A. Selection and Preparation of a Delivery Agent for 1,10-Phenanthroline.

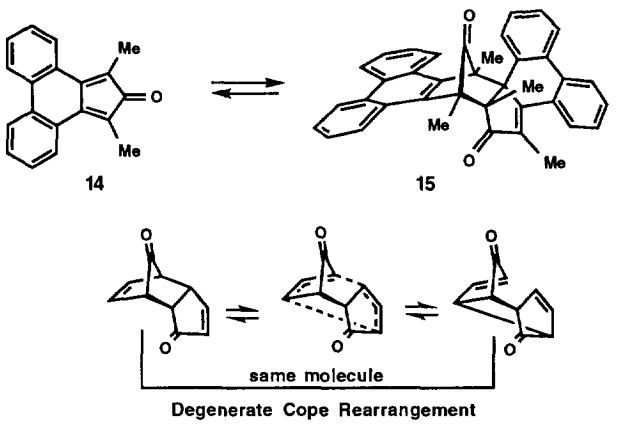
It is well established that cyclopentadienones are highly active Diels-Alder components and can react as either diene or dienophile, eg with themselves to form dimers, or with secondary agents to form mixed cycloadducts.[7] While there is some suggestion that cyclopentadienones are reverse electron-demand dienes, a fact consistent with their colour, they none-the-less react with strongly electron-deficient dienophiles, eg maleic anhydride, with alacrity. Whatever their Diels-Alder persuasion, reaction with ring-strained alkenes is assured.

In seeking a reagent in which to incorporate the 1,10-phenanthroline subunit for delivery to rigid, alicyclic molrac alkenes, we selected the 6,7-diazaphencyclone (DAPC) **11**, a reagent which was unknown at that time. Modelled after the phencyclone counterpart, which had been reported,[8] we based our synthesis on the reaction pathway shown in Scheme 2.



Scheme 2

Reaction of 1,10-phenanthroline-5,6-dione **5** with pentan-3-one **6** under basic conditions produced the cyclopentenone **7** without incident; subsequently this same product has been reported by other workers as an intermediate in the preparation of **4**.[6] The most common method to convert cyclopentenolones to their corresponding cyclopentadienone is by acid-catalysed dehydration in acetic anhydride. However, this was not appropriate in the present case owing to the presence of the basic ring-nitrogen substituents in **7**. Accordingly, the alcohol group in **7** was converted to the related chloride **8** by reaction with thionyl chloride; in some experiments evidence for the formation of **9** and **10** was obtained. This allowed the use of basic conditions to be employed for conversion to the required cyclopentadienone **11**. Indeed treatment of **8** with triethylamine produced a colourless crystalline product considered to be the Diels-Alder dimer **12**.



Scheme 3

A further parallel between diazaphenyclone **11** and its carbocyclic analogue **14** is evident in the properties of their dimers, **12** and **15** respectively. As in the carbocyclic dimer **15**, rapid degenerate Cope rearrangement (Scheme 3) occurs in solution and this is reflected in the ^{1}H NMR spectrum of **12** at room temperature, where the methyl signals have degenerated to a pair of broad resonances. Confirmation of the [4π+2π] structure of dimer **12** was achieved by conducting the ^{1}H NMR spectrum at - 50 °C, shown in Figure 1. It appears the Cope rearrangement is sufficiently slowed at the lower temperature to reveal the expected structure for **12**, characterised by the appearance of four methyl resonances.

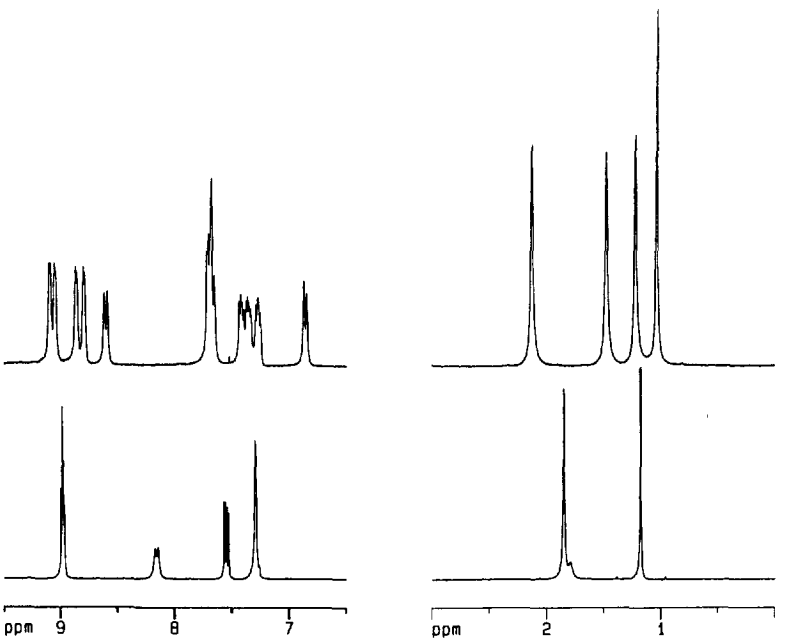
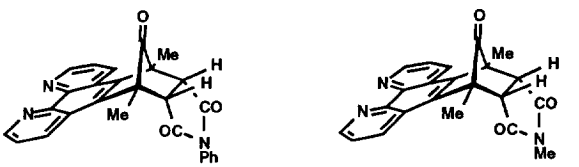


Figure 1: Comparison of ^{1}H NMR spectra of DAPC dimer **12** at i) -50°C, and ii) 30°C.

In many cases involving reactions of DAPC **11**, especially when sluggish dienophiles are involved and high temperatures are used, an insoluble byproduct is often obtained which is considered to be the symmetrical dimer **13**.

Chemical confirmation of the equilibrium between the dimer **12** and monomer **11** was obtained by heating **12** with *N*-phenyl maleimide (NPM) and isolating the 1:1-adduct **16**, m.p. 224 °C. The *endo*-stereochemistry is assigned on the basis of the upfield position of the phenyl ortho protons (δ 5.86) which reflects the strong shielding offered by the proximate 1,10-phenanthroline ring current. *N*-Methyl maleimide (NMM) also formed only a single stereoisomer on reaction with DAPC **11**. This adduct was assigned the *endo*-stereochemistry **17** on account of the high field resonance (δ 2.12) of the *N*-methyl group in the ^{1}H NMR of **17** (Scheme 4).

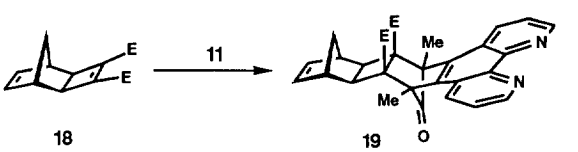


16 17

Scheme 4

B. Reaction of DAPC 11 with Ring-Strained Alkenes

The effectiveness of DAPC **11** as a delivery agent for 1,10-phenanthroline depended on the ability of **11** to react with ring-strained alkenes. In previous studies, we have used the tricyclic bisalkene **18**[9] as a model system for evaluating cycloaddition specificities as it contains a norbornene and a cyclobutene 1,2-diester which are the two main dienophilic end-group alkenes present in molrac spacer alkenes. Reaction of DAPC **11** with **18** produces a single 1:1-adduct by exclusive reaction at the cyclobutene π-bond (Scheme 5).

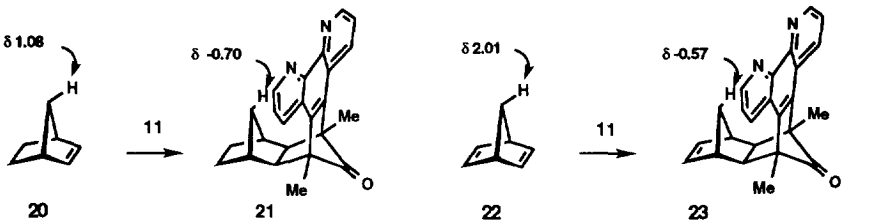


18 19

Scheme 5

Full confirmation of the structure of **19** can be deduced from its ^{1}H NMR spectrum. The site selectivity is confirmed by the presence of the norbornenyl protons at δ 6.11 and the stereochemistry by the significant upfield shift of the ester methyl resonance to δ 3.14. Again the ring-current of the phenanthroline sub-unit plays an important role in deciding stereochemistry and this feature is used repeatedly in this work as a stereochemical probe.

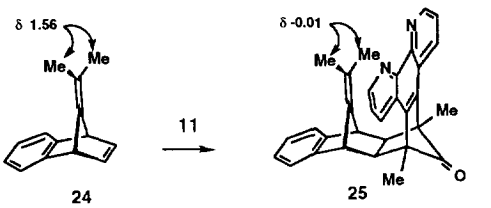
While this result clearly shows the preference for attack at the cyclobutene -1,2-diester π-centre over the norbornene π-centre, the latter is still active towards cycloaddition with DAPC **11**. This is illustrated by the reaction of DAPC **11** with norbornene **20** or norbornadiene **22** which furnish the 1:1-adducts **21** and **23** respectively (Scheme 6). In these cases, stereochemical assignments are supported by ^{1}H NMR where the methylene bridge protons *syn*-related to the phenanthroline ring are dramatically shielded and resonate at δ -0.70 for **21** and δ -0.57 for **23**.



20 21 22 23

Scheme 6

High stereoselectivity is again noted in the reaction of DAPC **11** with the 7-isopropylidene-benzonorbornadiene **24** where *exo,endo*-stereochemistry is observed in the sole adduct **25** (Scheme 7). The upfield chemical shifts for the isopropylidene methyl groups in **25**, relative to the starting material **24**, confirm the assigned stereochemistry which reflects the proximity of the phenanthroline ring to the bridge substituents.



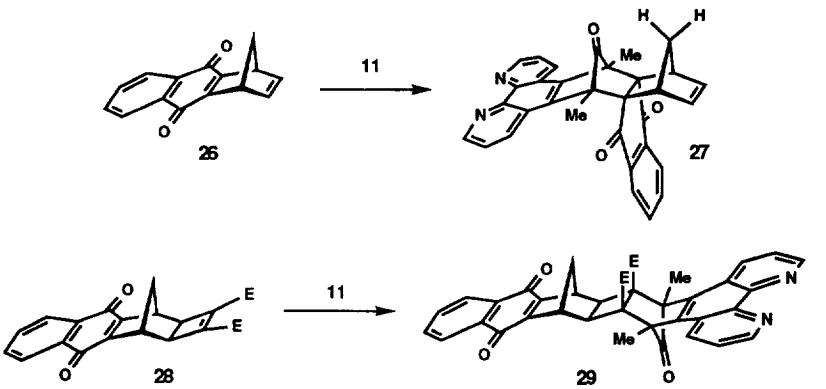
24 25

Scheme 7

C. Preparation of Redox-Containing Ligands

In our quest to prepare phenanthroline ligands which could be used in the study of electron-transfer or energy-transfer, it was necessary to introduce redox-active components into the rigid ligand-containing molracs. In our initial study we elected to approach this task by preparing redox-containing alkenes and attaching the ligand using the DAPC delivery agent.

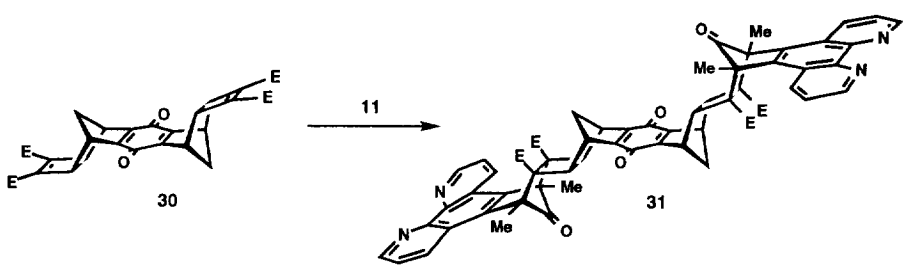
Two approaches were developed for the incorporation of a 1,4-quinone group into the molrac ligand depending on the position to be occupied by the redox-system. In the case where the quinone occupies a terminal position, we investigated direct reaction of DAPC **11** with the known methanoanthraquinone **26**,[10] however, reaction occurred at the quinone π-bond to produce the adduct **27** (Scheme 8). The structure of **27** was supported by the presence of olefinic resonances in the ^{1}H NMR spectrum and the stereochemistry was based on the chemical shift position of the methylene bridge protons which occur at δ 1.60, 2.09. The alternative *exo*-adduct would have the 1,10-phenanthroline ring close to the methylene bridge and be expected to exhibit high-field resonances similar to those present in adducts **21** and **23**.



Scheme 8

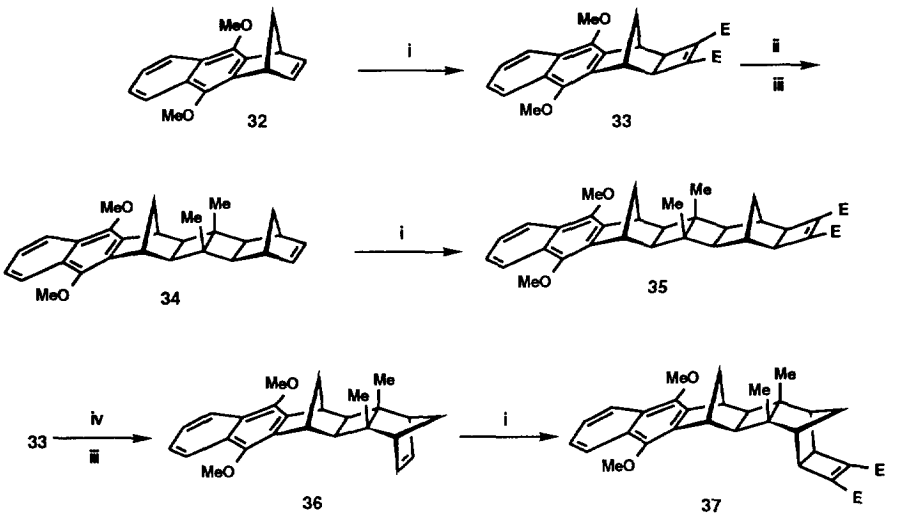
The naphthoquinone group was retained intact when the reaction of DAPC **11** was conducted on the related cyclobutene **28** (Scheme 8). In this case, reaction of DAPC **11** occurs stereospecifically at the more reactive cyclobutene π-bond of **28** to yield adduct **29**. Typically, the ester methyl resonances are shifted to high field (δ 3.20) in **29** which is consistent with the location of the phenanthroline group being adjacent to the ester substituents.

Where the quinone is to be centrally located in the molrac ligand, we have used a preformed molrac bis-alkene containing the 1,4-benzoquinone group and added the 1,10-phenanthroline unit by way of delivery agent DAPC **11**. Thus, reaction of the known *anti*-molrac bis-alkene **30**[11] with excess DAPC **11** produced the bis-adduct **31** (Scheme 9). Stereoselective attack at the cyclobutene π-centre occurred with no evidence for reaction at the central 1,4-benzoquinone. The C_{2v} symmetry of the bis-adduct **31** is reflected in the simplified ^1H NMR spectrum with only six proton resonances being exhibited aside from those of the equivalent 1,10-phenanthroline groups.



Scheme 9

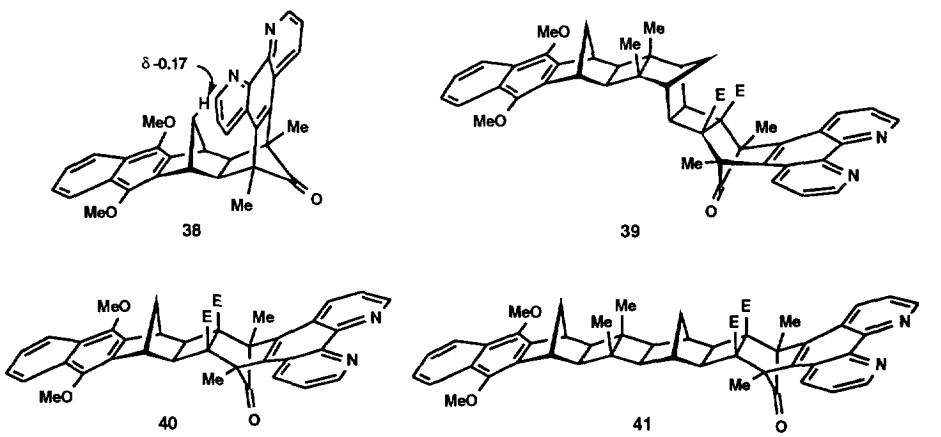
Introduction of the 1,4-dimethoxynaphthalene chromophore was approached using the series of molracs derived from elaboration of the 1,4-dimethoxynaphthonorbornadiene **32** (Scheme 10), using the standard reaction sequences developed and described in our original report on the preparation of binanes.[12]



i) Dimethyl acetylene dicarboxylate, $RuCOH_2(PPh_3)_3$ ii) quadricyclane, heat 150 °C iii) sequential reactions a) LAH; b) MsCl; c) LAH iv) cyclopentadiene in ether overnight

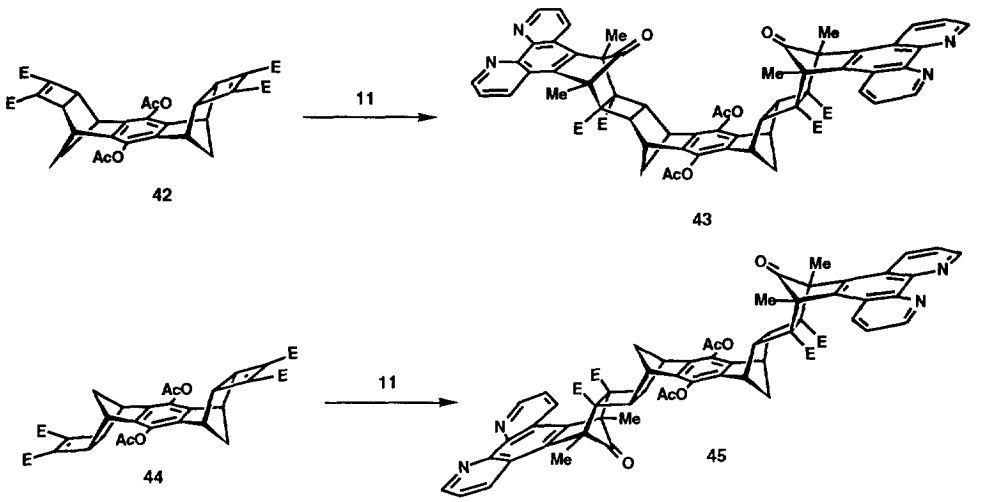
Scheme 10

In the reaction of **32** with DAPC **11**, a single adduct was obtained. The stereochemistry followed by ^1H NMR where the high field shift (δ -0.17) of one of the bridge methylene protons was definitive for the *exo, endo* stereochemistry. In the cases of adducts **39-41** (Scheme 11), cycloaddition was conducted at the cyclobutene-1,2-diester of the appropriate functionalised molrac alkene (**37, 33, 35** respectively). Stereospecific addition was observed on each occasion; the combination of C_s-symmetry and high-field ester methyl resonances confirmed the assigned structures.



Scheme 11

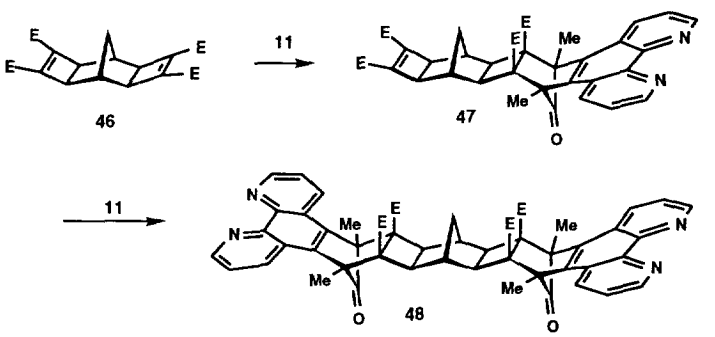
Incorporation of aromaticity (and latent 1,4-benzoquinone or 1,4-dimethoxybenzene) into the central section of the molecular framework is illustrated by reaction of molrac *syn*-bisalkene **42** which contains the 1,4-diacetoxybenzene component (Scheme 12). Here, standard cycloaddition of DAPC **11** provided access to the bis-adduct **43**. Similar transformations were conducted on the *anti*-series to produce **45**. While FGI transformation have not been conducted on **43** or **45**, it should be straightforward to access either 1,4-benzoquinone or 1,4-dimethoxybenzene chromophores in the central ring.



Scheme 12

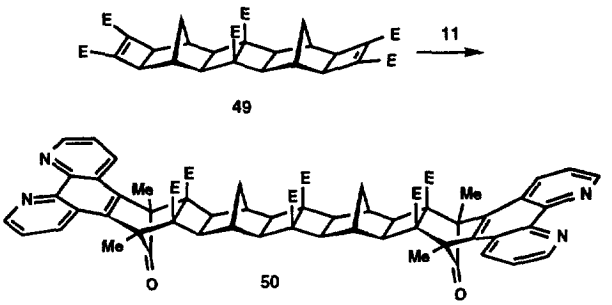
D. Preparation of Rigid Bridged 1,10-phenanthroline ligands

From the above-described cycloaddition reactions of DAPC **11**, it became clear that cyclobutene 1,2-diesters are very much more reactive than 1,4-quinones or norbornenes and that such reactions are highly stereospecific. Thus, we selected molrac bis-alkenes with cyclobutene 1,2-diesters end-groups as substrates from which to produce the required bridging 1,10-phenanthroline bis-ligands. The simplest starting compound of this type, the known tetracyclic bis-alkene **46**,[13] reacted with DAPC **11** to produce the mono-adduct **47** which, on prolonged exposure to **11**, yielded the bis-adduct **48** (Scheme 13). The high field resonance of the ester groups in **47** and **48** confirmed the stereospecificity of these cycloadditions.



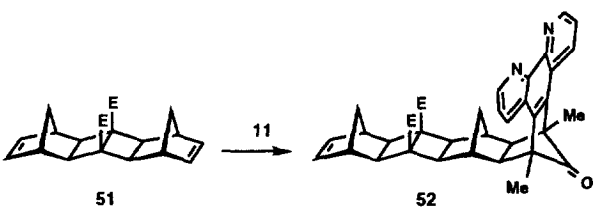
Scheme 13

Similar treatment of the 8σ molrac bisalkene **49**[12] with excess DAPC **11** provided the extended bridged ligand **50**, the structure of which was supported by the usual ^{1}H NMR features (C_{2v}-symmetry; upfield ester resonances) (Scheme 14)



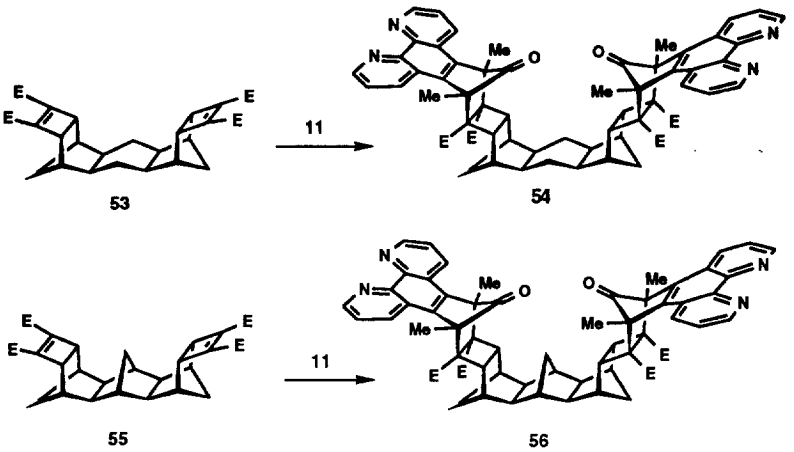
Scheme 14

Attempts to produce bridged 1,10-phenanthroline ligands from norbornene-ended molracs such as the 6σ-bis-alkene **51** were less successful. The reaction of **51** with DAPC **11** was slow and required heating in o-xylene at reflux to initiate reaction and then the only characterised product from this reaction was monoadduct **52** (Scheme 15).



Scheme 15

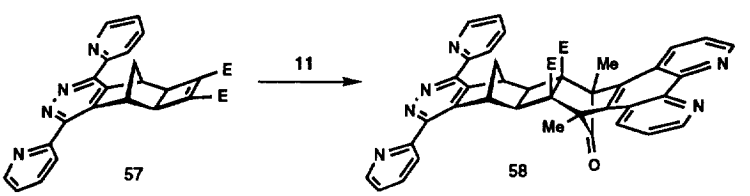
The preparation of U-shaped bridged ligands is illustrated by reactions with U-shaped bis-alkenes **53** and **55** (Scheme 16). Smooth reaction with excess DAPC **11** produced the C_{2v}-symmetric adducts **54** and **56** respectively. The expected stereochemistry for addition to cyclobutene-1,2-diesters applied, and products with inward-facing carbonyl groups were obtained with the 1,10-phenanthroline rings extending outwards. The presence of the methylene bridge in **55** significantly opens the arms of the U-shaped structure compared with the cyclohexane analogue **54** (see modelling section) such that the 1,10-phenanthroline groups are closer to coplanarity.



Scheme 16

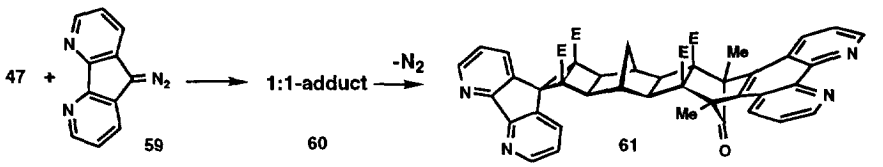
E. Bridged Ligands Containing Two Different Bidentate Ligands.

We have reported elsewhere that the tricyclic bis-alkene **18** reacts with 3,6-di(2'-pyridyl) *s*-tetrazine at the norbornene π-bond to produce a dihydropyridazine (or its bond shift isomer) and that these can be oxidised with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to the fused 2,5-di(2-pyridyl)pyridazine **57**.[14] Reaction of **57** with DAPC **11** yields the adduct **58** where the 1,10-phenanthroline ligand is positioned at one end of the molrac and the 3,6-di(2'-pyridyl)pyridazine ligand at the other (Scheme 17). While this is the only example so far prepared of this type, a range of molrac dpp's suitable for similar derivitisation have been reported in the original paper.[14]



Scheme 17

In a separate study, we reported that spiro-diazafluorenes could be prepared by 1,3-dipolar cycloaddition of 9-diazo-4,5-diazafluorene **59** onto cyclobutenes followed by deazetisation (heat or photochemical).[15] Application of this procedure to cyclobutene-1,2-diester **47** gave bridged bis-ligand **61** by way of the 1:1-cycloadduct **60** (Scheme 18). In this case the cycloaddition was achieved under thermal conditions and the deazetisation step by continued heating at slightly higher temperature. The feature of this combination of ligands and cycloaddition reactions is reflected in the orthogonal orientation of the two ligand centres in the final product.



Scheme 18

F. Molecular modelling

Molecular modelling was conducted on many of the larger molecules, eg **48** (Fig. 2) and **61** (Fig. 3) described herein to obtain a better appreciation of their final shape, in particular the relative orientation of the ligating/redox units.

Several X-ray structures are now available to provide reference points for assessing molecular modelling of the molrac bis-alkenes, eg **51**, its next higher binalogue, and the U-shaped compounds **53** and **55**. While no structures are yet available for any of the DAPC adducts, the 3,6-di(2-pyridyl)pyridazine **57** and a spiro-diazafluorene of the type present in **61** have been reported.[14,15] Modelling was conducted on **38-41** and the interplanar angles for the different 1,10-phenanthroline rings and their separation are summarised in Table 1.

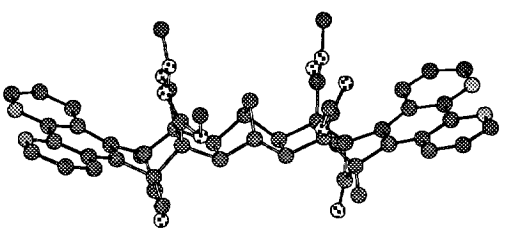


Figure 2: AM1 optimised structure for bridged 1,10-phenanthroline **48**
(Hydrogen atoms omitted from diagrams only for clarification)

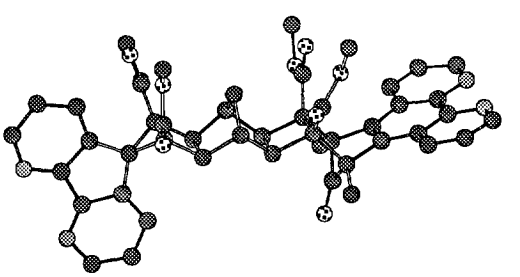
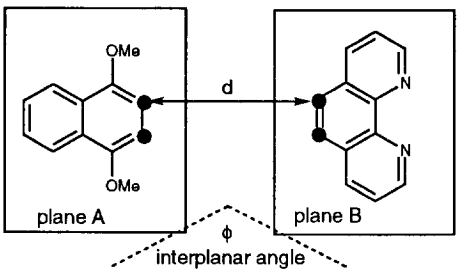


Figure 3: AM1 optimised structure for bridged ligand 61.
(Hydrogen atoms omitted from diagrams only for clarification)

Table 1. Calculated chromophore interplanar angle and separation distances (Å) for redox-containing ligands **38**, **39**, **40** and **41**.



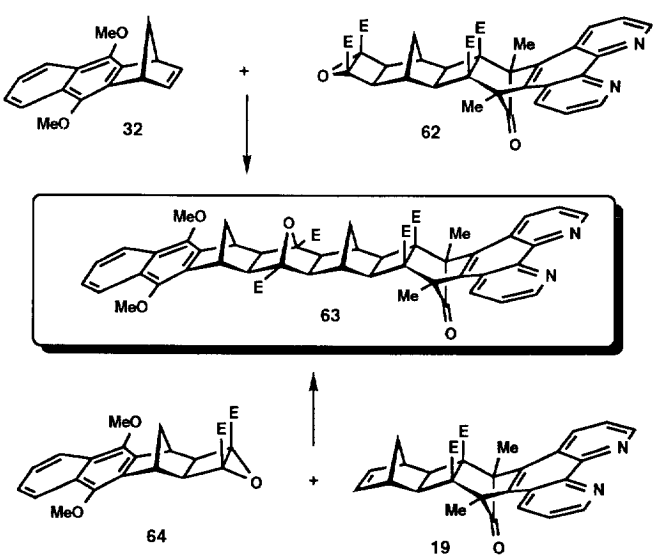
	d	ϕ
38	4.49	137
39	8.33	101
40	6.27	13
41	11.15	34

G. Future Work

Two examples taken from soon-to-be-published work from our laboratory illustrates forcefully some of the future use of molrac 1,10-phenanthrolines containing norbornene or cyclobutene-1,2-diester end-groups. This involved the use of compounds **62** and **19** as building blocks in the epoxycyclobutane-alkene cycloaddition route to polyalicyclic nanostructures.

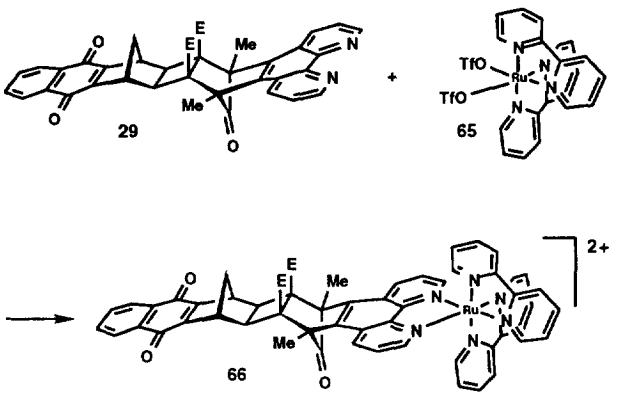
In the first example the 1,10-phenanthroline-functionalised epoxycyclobutene **62** was heated with the 1,4-dimethoxynaphthalene-functionalised norbornene **32** to produce the stereospecifically coupled dual functionalised nanostructure **63** with the redox-active unit at one terminus and the ligand at the other (Scheme 19).

The second example uses the same coupling process to access the identical product **63**. In this variant, the epoxycyclobutane component provides the redox system and the norbornene acts as the delivery agent for the 1,10-phenanthroline. Thus, heating norbornene **19** with epoxycyclobutane **64** yields **63** in good yield. As cyclobutene-1,2-diesters also react with epoxycyclobutanes of type **64** or **62**, so many of the 1,10-phenanthroline-containing alkenes described in this paper can act as building blocks.



Scheme 19

For 1,10-phenanthroline compounds of the type described herein to be useful in the study of metal-centred energy-transfer and electron-transfer studies it was critical that they could be converted to suitable metal complexes. Richard Keene and his group at James Cook University have shown that the redox-active bridged ligand **29** could be converted to the chiral ruthenium complex **66** by treatment with the chiral ruthenium $(bpy)_2$ ditriflate **65** (Scheme 20).[16,17]



Scheme 20

Acknowledgements

This work was funded by the Australian Research Council (grant) and a Central Queensland University Research Grant. R.N.W. thanks the ARC for the award of a Senior Research Fellowship (1992-1996) and A.C.S acknowledges the award of a Central Queensland University Post Graduate Award. Mr Bob Dash is thanked for conducting some of the early work on the preparation of DAPC **11**.

Experimental

Melting points were determined on a GALLENKAMP Melting Point Apparatus and were uncorrected. Microanalyses were performed by either the Australian Microanalytical Service or Central Queensland University. ^1H NMR spectra were recorded using 300 MHz, Bruker AM300. All ^1H NMR spectra were recorded in deuterochloroform solution unless otherwise stated with deuterchloroform as internal standard ($\delta = 7.26$ ppm). The multiplicity of the signals was described as either s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or br (broad). ^{13}C NMR spectra were recorded in deuterochloroform solution using a Bruker AM300 (operating at 75.5 MHz) instrument. Chemical shifts were measured relative to deuterchloroform ($\delta = 77.00$ ppm). Analytical TLC was carried out using Merck (A.T. 5554) silica gel 60 F_{254} precoated on aluminium sheets. Chromatograms were visualised using UV light (254 nm and 365 nm). Preparative radial chromatography was carried out using a Chromatotron Model 7924T (Harrison Research, Palo Alto, California) with Silica gel 60 PF_{254} gipshaltig (Merck Art. 7749) as absorbent. High pressure reactions were carried out using an HOFER High Pressure Apparatus Model HP14 at room temperature. Light

petroleum (PE) refers to the fraction b.p. 65-75 °C. All organic extracts were dried with anhydrous magnesium sulphate.

7,8-diaza-3,3a-dihydro-3a-hydroxy-1,3-dimethylcyclopenta[l]phenanthren-2-one (7)

1,10-phenanthroline-5,6-dione hydrate (**5**) (4.4 g, 19.3 mmol) was added in small portions to potassium carbonate (anhydrous) (4.4 g) and pentan-3-one (3.61 g, 42 mmol) in methanol (110 ml) over a 30 minute period. The mixture was allowed to stir for a further 20 minutes. Water (150 ml) was added and the mixture extracted with ethyl acetate in a continuous extraction apparatus for 18 hours. The organic fraction was filtered, dried ($MgSO_4$) and evaporated to dryness to give an off-white solid which was recrystallised from ethyl acetate/methanol to give **7** as a white solid. Yield 4.23 g, 79%. m.p. 249 °C (dec). ^{1}H NMR δ 1.59 (d; J = 7.2 Hz; 3H), 2.11 (s; 3H), 2.43 (brs; OH) 3.06 (q; J = 7.2 Hz; 1H), 7.37 (dd; J = 7.8, 3.1 Hz; 1H), 7.45 (dd; J = 7.9, 4.8 Hz; 1H), 7.86 (dd; J = 7.8, 1.5 Hz; 1H), 8.07 (dd; J = 7.9, 1.6 Hz; 1H), 8.80 (dd; J = 4.7, 1.5 Hz; 1H), 8.86 (dd; J = 4.7, 1.6 Hz; 1H).

(1α,2β,18α,19α) 10,13-diazanonacyclo[17.14.1.$0^{2,18}$.$0^{6,11}$.$0^{12,17}$.$0^{20,23}$.$0^{21,26}$.$0^{27,32}$] tetraconta-4,6,8,10,12,14,16,20,22,24,26,28,30,32-tetradecaen-3,34-dione (12)

A solution of thionyl chloride (9.5 ml) and pyridine (9.5 ml) was added slowly to a stirred slurry of **7** (3.4 g, 12.2 mmol) in pyridine (25 ml) at room temperature over a period of seven minutes. The suspension quickly dissolved to give a clear brown solution. On completion of the addition, the solution was allowed to stir for a further five minutes before it was cautiously added (dropwise) to an ice slurry (150 ml). The aqueous solution was extracted with chloroform (100 ml + 2 x 50 ml). The organic extracts were washed with 5% HCl solution (2 x 50 ml). The resulting aqueous solution was washed with chloroform (2 x 30 ml) and the organic extracts discarded. The acidic aqueous fraction was basified to pH seven with 10% NaOH solution to precipitate a white solid. The mixture was then extracted with chloroform (3 x 50 ml), the fractions combined, dried ($MgSO_4$), and evaporated to dryness to give a pink solid. The solid was recrystallised from methanol/chloroform to give **12** as a white solid. Yield 1.52 g, 48%; m.p. >350 °C. ^{1}H NMR δ 1.22 (s; 6H), 1.89 (s; 6H), 7.32 (d; J = 2.7 Hz; 4H), 7.58 (dd; J = 8.4, 4.5 Hz; 2H), 8.18 (bd; J = 8.5 Hz; 2H), 9.07 (t; J = 2.7 Hz; 4H). ^{13}C NMR δ 10.8, 122.7, 123.4, 124.7, 133.5, 134.4, 150.2, 151.4, 203.9. Mass spectrum: *m/z* 262 (M^++2, 7%), 261 (19), 260 (M^+, 100%), 245 (5), 232 (39), 231 (91), 218 (7), 217 (24), 205 (8), 204 (9), 190 (5), 176 (8), 164 (4), 115 (16), 102 (24), 88 (24).

(1α,16α,17β,18α,19β,22β,23α,24β) dimethyl 1,16-dimethyl-7,10-diaza-25-oxo-octacyclo [14.8.1.1^{19,22}.$0^{2,15}$.$0^{3,8}$.$0^{9,14}$.$0^{17,24}$.$0^{18,23}$]hexacosa-2,4,6, 8,10,12,14,20-octaen-17,24-dicarboxylate (19)

A solution of bisalkene **18** (270 mg, 0.95 mmol) and DAPC **11** (250 mg, 0.95 mmol) in dichloroethane (10 ml) was heated at reflux for 60 h. The solution was filtered and the filtrate taken to dryness under reduced pressure. The residue was triturated with diethyl ether leaving the residue as the crude adduct. The solid was recrystallised from ethyl acetate to give **19** as a white solid. Yield 295 mg, 57%; m.p. 250-252 °C. ^{1}H NMR δ 1.26 (d; J = 10.0 Hz; 1H), 1.61 (d; J = 10.0 Hz; 1H), 1.99 (s; 2H), 2.04 (s; 6H), 3.14 (s; 6H), 3.23 (s; 2H), 6.11 (s; 2H), 7.62 (dd; J = 8.2, 4.3 Hz; 2H), 8.53 (dd; J = 8.2, 1.5 Hz; 2H), 9.17 (dd; J = 4.3, 1.5 Hz; 2H).^{13}C NMR δ 9.49, 39.07, 43.04, 43.58, 51.24, 59.56, 60.90, 122.59, 125.36, 131.98, 135.71, 137.10,

146.09, 149.68, 169.06, 200.18. Mass spectrum : *m/z* 544 (M^+ absent), 495 (2), 494 (6), 341 (3), 281 (2), 261 (22), 260 (100), 232 (10), 231 (13), 143 (1).

(1α,16α,17α,18β,21β,22α) 1,16-dimethyl-7,10-diaza-heptacyclo[14.6.1.1^{18,21}.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,22}]tricosa-2,4,6,8,10,12,14,-heptaen-23-one (21)

A solution of norbornene **20** (60 mg, 0.64 mmol) and DAPC **11** (167 mg, 0.64 mmol) in chloroform (7 ml) was heated in a pressure bottle at 95 °C for 100 h. The solvent was removed under reduced pressure to leave a pink solid. The solid was recrystallised from methanol/dichloromethane to give **21** as a white solid. Yield 47 mg, 21%; m.p.>340 °C (dec.).^{1}H NMR δ -0.70 (d; *J* = 11 Hz; 1H), 0.10 (d; *J* = 11 Hz; 1H), 1.11 (m; 2H), 1.35 (bd; 2H), 2.03 (s; 6H), 2.12 (s; 2H), 2.17 (s; 2H), 7.66 (dd; *J* = 4.2, 4.2 Hz; 2H), 8.72 (dd; *J* = 4.2, 1.5 Hz; 2H), 9.21 (dd; *J* = 2.1, 1.5 Hz; 2H).

(1α,16α,17α,18β,21β,22α) 1,16-dimethyl-7,10-diaza-heptacyclo[14.6.1.1^{18,21}.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,22}]tricosa-2,4,6,8,10,12,14,19-octaen-23-one (23)

A procedure similar to that used for the preparation of **21** was used to give **23** as a white solid. Yield 43%; m.p. 284 °C (dec.).^{1}H NMR δ -0.57 (d; *J* = 10.0 Hz; 1H), 0.28 (d; *J* = 10.0 Hz; 1H), 2.07 (s; 6H), 2.10 (s; 2H), 2.70 (s; 2H), 6.16 (s; 2H), 7.67 (dd; *J* = 8.2, 4.3 Hz; 2H), 8.72 (dd; *J* = 8.2, 1.5 Hz; 2H), 9.22 (dd; *J* = 4.3, 1.5 Hz; 2H).

(1α,2β,3β,18β,19β,20α) 3,18-dimethyl-27-isopropylidene-9,12-diaza-octacyclo[18.6.1.1^{3,18}.0^{2,19}.0^{4,17}.0^{5,10}.0^{11,16}.0^{21,26}]octacosa-4,6,8,10,12,14,16,21,23,25-decaen-28-one (25)

A procedure similar to that used for the preparation of **21** was used to give **25** as a white solid. Yield 83%; m.p. 273-275 °C (dec.). ^{1}H NMR δ -0.01 (s; 6H), 2.07 (s; 6H), 2.21 (s; 2H), 3.58 (s; 2H), 7.01 (m ; 4H), 7.69 (dd; *J* = 8.3, 4.2 Hz; 2H), 8.85 (d; *J* = 8.4 Hz; 1H), 9.26 (d; *J* = 3.1 Hz; 1H).

(1α,2β,13β,17β,18α,27β,30β) 8,11-diazaheptacyclo[14.8.4.0^{1,18}.0^{3,16}.0^{4,9}.0^{10,15}.0^{20,25}] octacosa-3,5,7,9,11,13,15,20,22,24,28-undecaen-19,26,31-trione (27)

A solution of methanoanthraquinone **26** (100 mg, 0.45 mmol) and DAPC **11** (110 mg, 0.44 mmol) in chloroform (10 ml) was heated in a pressure bottle at 110 °C for 18 h. The solution was filtered and the filtrate taken to dryness under reduced pressure. The residue was triturated with diethyl ether leaving the residue as the crude adduct. The solid was recrystallised from ethyl acetate to give **27** as a brown solid. Yield 135 mg, 62%; m.p. 263 °C (dec.)^{1}H NMR δ 1.66 (d; *J* =11.4 Hz; 1H), 2.14 (d; *J* =11.4 Hz; 1H), 2.24 (s; 3H), 3.68 (s; 2H), 6.24 (s; 2H), 6.90 (dd; *J* = 2.9, 3.3 Hz; 2H), 7.01 (dd; *J* = 2.9, 3.3 Hz; 2H), 7.58 (dd; *J* = 8.5, 4.3 Hz; 2H), 8.42 (dd; *J* = 8.5, 1.6 Hz; 2H), 9.03 (dd; *J* = 4.2, 1.6 Hz; 2H).

(1α,2β,3α,4β,15β,16α,17β,18α) dimethyl 1,18-dimethyl-6,13,33-trioxo-24,27-diaza-deca cyclo[16.14.1.1^{4,15}.0^{2,17}.0^{3,16}.0^{5,14}.0^{7,12}.0^{19,32}.0^{20,25}.0^{26,31}]tetratriaconta-5(14),7(12), 8,10,19,21,23,25,27,29,31-undecaen-2,17-dicarboxylate (29)

A solution of cyclobutene napthoquinone **28** (150 mg, 0.41 mmol) and DAPC **11** (107 mg, 0.41 mmol) in chloroform (5 ml) was heated in a pressure bottle at 120 °C for 6 h. The solvent was removed under reduced pressure to leave a pale solid. The solid was recrystallised from ethyl acetate to give **29** as yellow prisms. Yield

160 mg, 63%; m.p. 308 °C (dec.). ^{1}H NMR δ 1.66 (d; *J* = 10.9 Hz; 1H), 1.91 (s; 6H), 2.10 (d; *J* = 10.9 Hz; 1H), 2.27 (s; 2H), 3.20(s; 6H), 4.01 (s; 2H), 7.38 (dd; *J* = 5.6, 3.3 Hz; 2H), 7.68 (dd; *J* = 8.5, 4.3 Hz; 2H), 7.86 (dd; *J* = 5.6, 3.3 Hz; 2H), 8.83 (dd; *J* = 8.5, 1.6 Hz; 2H), 9.23 (dd; *J* = 4.2, 1.6 Hz; 2H).

(1α,5β,6α,7β,8α,23α,24β,25α,26β,30α,31β,32α,33β,48β,49α,50β) tetramethyl 8,25,33,48-tetramethyl-4,28,53,54-tetraoxo-14,17,39,42-tetraaza-heptadecacyclo[28.20.1.1^{5,26}.1^{8,23}.1^{33,48}.0^{2,29}.0^{4,27}.0^{6,25}.0^{7,24}.0^{9,22}.0^{10,15}.0^{16,21}.0^{31,50}.0^{32,49}.0^{34,47}.0^{35,40}.0^{41,46}]tetra pentaconta-2(29),4(27),9,11,13,15,17,19,21,34,36,38,40,42,44,46-hexadecaen-7,24,32,49-tetracarboxylate (31)

A solution of *anti*-molrac **30** (100 mg, 0.19 mmol) and DAPC **11** (110 mg, 0.42 mmol) in chloroform (5 ml) was heated in a pressure bottle at 95 °C for 100 h. The solvent was removed under reduced pressure to leave a yellow solid. The solid was recrystallised from methanol to give **31** as a yellow solid. Yield 170 mg, 86%; m.p. >350 °C (dec.).^{1}H NMR δ 1.74 (d; *J* = 9.8 Hz; 2H), 2.05-2.10 (m; 14H), 2.17 (s; 4H), 3.23 (s; 12H), 3.90(s; 4H), 7.69 (dd; *J* = 8.2, 4.3 Hz; 4H), 8.56 (dd; *J* = 8.2, 1.5 Hz; 4H), 9.23 (dd; *J* = 4.3, 1.5 Hz; 4H).

(1α,2β,3β,18β,19β,20α) 22,29-dimethoxy-3,18-dimethyl-9,12-diaza-nonacyclo[18.10.1.1^{3,18}.0^{2,19}.0^{4,17}.0^{5,10}.0^{11,16}.0^{21,30}.0^{23,28}]hentricosta-4,6,8, 10,12,14,16,21,23,25, 27,29-dodecaen-32-one (38)

A solution of napthonorbornadiene **32** (101 mg, 0.40 mmol) and DAPC **11** (157 mg, 0.60 mmol) in chloroform (5 ml) was heated in a pressure bottle at 120 °C for 48 h. The solvent was removed under reduced pressure to leave a pale solid. The solid was recrystallised from methanol/dichloromethane to give **38** as a pale solid. Yield 95 mg, 47%; m.p. 267 °C (dec.). ^{1}H NMR δ –0.17 (d; *J* = 10.8 Hz; 1H), 0.69 (d; *J* = 10.8 Hz; 1H), 2.16 (s; 6H), 2.44 (s; 2H), 3.63 (s; 2H), 3.98(s; 6H), 7.46 (dd; *J* = 6.4, 3.3 Hz; 2H), 7.75 (dd; *J* = 8.4, 4.2 Hz; 2H), 8.04 (dd; *J* = 6.4, 3.3 Hz; 2H), 8.86 (dd; *J* = 8.4, 1.6 Hz; 2H), 9.27 (dd; *J* = 4.2, 1.6 Hz; 2H).

(1α,2β,3α,4β,19β,23β,20α,21β,22α,23α,24β,25α,36α,37β,38α) dimethyl 27,34-dimethoxy-4,19,23,38-tetramethyl-40-oxo-10,13-diaza-tridecacyclo [20.16.1.1^{4,19}.1^{25,36}.0^{2,21}. 0^{3,20}. 0^{5,18}.0^{6,11}.0^{12,17}.0^{23,38}.0^{24,37}.0^{26,35}.0^{28,33}]hentetraconta-5,7,9,11,13,15,17,26,28,30, 32,34-dodecaen-3,20-dicarboxylate (39)

A solution of cyclobutene molrac **37** (200 mg, 0.39 mmol) and DAPC **11** (105 mg, 0.40 mmol) in chloroform (10 ml) was heated in a pressure bottle at 120°C for 6 h. The solvent was removed under reduced pressure to leave a pink solid. The solid was recrystallised from chloroform/hexane to give **39** as a white powder. Yield 160 mg, 75%; m.p. 292 °C (dec.). ^{1}H NMR δ 1.11 (s; 6H), 1.52 (d; 1H), 1.75 (d; 1H), 1.76 (d; 1H), 2.27 (d; 1H), 1.96 (s; 6H), 2.22 (s; 2H), 2.31 (s; 2H), 2.73 (s; 2H), 3.10 (s; 6H), 3.60 (s; 2H), 3.94 (s; 6H) 7.46 (dd; *J* = 9.7, 3.3 Hz; 2H), 7.61 (dd; *J* = 8.5, 4.3 Hz; 2H), 8.10 (dd; *J* = 9.7, 3.3 Hz; 2H), 8.48 (dd; *J* = 8.5, 1.6 Hz; 2H), 9.17 (dd; *J* = 4 .3, 1.6 Hz; 2H). ^{13}C NMR δ 9.5, 16.9, 34.7, 44.6, 34.7, 37.5, 40.3, 42.3, 44.7, 46.6, 51.2, 51.7, 59.5, 61.9, 62.6, 122.0, 122.6, 125.0, 125.2, 128.0, 131.8, 135.1, 135.8, 144.1, 146.1, 149.7, 168.9, 200.2.

(1α,2β,3α,4β,15β,16α,17β,18α) dimethyl 6,3-dimethoxy-1,18-dimethyl-33-oxo-24,27-diaza-decacyclo[16.14.1.1^{4,15}.0^{2,17}.0^{3,16}.0^{5,14}.0^{7,12}.0^{19,32}.0^{20,25}.0^{26,31}]tetratriaconta-5,7,9,11, 13,19,21,23,25,27,29,31-dodecaen-2,17-dicarboxylate (40)

A solution of cyclobutene molrac **33** (373 mg, 0.94 mmol) and DAPC **11** (250 mg, 0.94 mmol) in chloroform (7 ml) was heated in a pressure bottle at 95 °C for 60 h. The solvent was removed under reduced pressure to leave a pink solid. The solid was recrystallised from methanol/dichloromethane to give **40** as a white solid. Yield 509 mg, 83%; m.p. 297 °C (dec.). ^{1}H NMR δ 1.81 (d; *J* = 10.9 Hz; 1H), 2.06 (s; 6H), 2.26 (d; *J* = 10.9 Hz; 1H), 2.34 (s; 2H), 3.28 (s; 6H), 4.04 (s; 6H), 4.15 (s; 2H), 7.49 (dd; *J* = 6.4, 3.2 Hz; 2H), 7.67 (dd; *J* = 8.4, 4.3 Hz; 2H), 8.11 (dd; *J* = 6.4, 3.3 Hz; 2H), 8.56 (dd; *J* = 8.5, 1.6 Hz; 2H), 9.21 (dd; *J* = 4.2, 1.6 Hz; 2H). ^{13}C NMR δ 8.48, 40.7, 41.1, 42.5, 50.6, 58.6, 60.4, 60.9, 121.1, 121.7, 124.5, 131.1, 148.9, 124.4, 127.2, 132.4, 134.4, 143.8, 145.3, 168.0, 197.4. Mass spectrum : *m/z* 654 (M^+, absent), 395 (23%), 394 (M^+-260, 97%), 379 (7), 347 (11), 331 (5), 319 (14), 261 (15), 260 (53), 232 (19), 231 (51), 225 (100).

(1α,2β,3α,4β,19β,20α,21β,22α,23β,24α,25β,26α,37α,38β,39α,40β) dimethyl 28,35-dimethoxy-4,19,21,39-tetramethyl-42-oxo-10,13-diaza-tetradecacyclo[20.18.1.1^{4,19}.1^{26,37}. 0^{2,21}.0^{3,20}.0^{5,18}.0^{6,11}.0^{12,17}.0^{23,40}.0^{24,39}.0^{25,38}.0^{27,36}.0^{29,34}] tritetraconta-5,7,9,11,13, 15,17,27,29,31,33,35-dodecaen-3,20-dicarboxylate (41)

A procedure similar to that used for the preparation of **40** was used to give **41** as a white solid. Yield 76%; m.p. 291 °C (dec.). ^{1}H NMR δ 0.97 (s; 6H), 1.65-1.75 and 1.85-1.97 (m; 4H), 2.01 (s; 6H), 1.94 (s; 2H), 2.07 (s; 2H), 2.13 (s; 2H), 2.56 (s; 2H), 3.65, (s; 2H), 3.98 (s; 6H), 7.45 (dd; *J* = 6.4, 3.3 Hz; 2H), 7.65 (dd; *J* = 8.5, 4.3 Hz; 2H), 8.09 (dd; *J* = 6.4, 3.3 Hz; 2H), 8.52 (dd; *J* = 8.5, 1.3 Hz; 2H), 9.21 (br d; *J* = 2.8 Hz; 2H).

(1α,5α,6β,7α,8β,23β,24α,25β,26α,30α,32α,33β,48β,49α,50β) tetramethyl 3,28-diacetoxy-8,23,33,48-tetramethyl-53,54-dioxo-14,17,39,42-tetraaza-heptadecacyclo[28.20.1.1^{5,26}. 1^{8,23}.1^{33,48}.0^{2,29}.0^{4,27}.0^{6,25}.0^{7,24}.0^{9,22}.0^{10,15}.0^{16,21}.0^{31,50}.0^{32,49}.0^{34,47}.0^{35,40}.0^{41,46}]- tetrapentaconta-2,4(27),9,11,13,15,17,19,21,28,34,36,38,40,42,44,46-heptadecaen-7,24, 32,49-tetracarboxylate (43)

A solution of *syn*-bisalkene molrac **42** (200 mg, 0.33 mmol) and DAPC **11** (180 mg, 0.69 mmol) in chloroform (7 ml) was heated in a pressure bottle at 95°C for 100 h. The solvent was removed under reduced pressure to leave a pale solid. The solid was recrystallised from methanol/dichloromethane to give **43** as a white solid. Yield 334 mg, 90%; m.p. >340 °C (dec.).^{1}H NMR δ 1.75 (d; *J* = 9.8 Hz; 2H), 2.04-2.10 (m; 14H), 2.32 (s; 4H), 2.40 (s; 6H), 3.16(s; 12H), 3.68 (s; 4H), 7.66 (dd; *J* = 8.2, 4.3 Hz; 4H), 8.57 (dd; *J* = 8.2, 1.5 Hz; 4H), 9.21 (dd; *J* = 4.3, 1.5 Hz; 4H).

(1α,5β,6α,7β,8α,23α,24β,25α,26β,30α,31β,32α,33β,48β,49α,50β) tetramethyl 3,28-diacetoxy-8,23,33,48-tetramethyl-53,54-dioxo-14,17,39,42-tetraaza-heptadecacyclo[28.20. 1.1^{5,26}.1^{8,23}.1^{33,48}.0^{2,29}.0^{4,27}.0^{6,25}.0^{7,24}.0^{9,22}.0^{10,15}.0^{16,21}.0^{31,50}.0^{32,49}.0^{34,47}.0^{35,40}. 0^{41,46}]tetrapentaconta-2,4(27),9,11,13,15,17,19,21,28,34,36,38,40,42,44,46-heptadecaen-7,24,32,49-tetracarboxylate (45)

A procedure similar to that used for the preparation of **43** was used to give **45** as a white solid. Yield 88%; m.p. 327 °C (dec.).^{1}H NMR δ 1.80 (d; *J* = 9.8 Hz; 2H), 2.07-2.11 (m; 14H), 2.26 (s; 4H), 2.40 (s; 6H), 3.17(s; 12H), 3.69 (s; 4H), 7.66 (dd; *J* = 8.2, 4.3 Hz; 4H), 8.58 (dd; *J* = 8.2, 1.5 Hz; 4H), 9.21 (dd; *J* = 4.3, 1.5 Hz; 4H).

(1α,16α,17β,18α,19β,20α,23α,24β,25α,26β,27α) tetramethyl 1,16-dimethyl-7,10-diaza-27-oxo-nonacyclo[14.10.1.1^{19,24}.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,26}.0^{18,25}.0^{20,23}]octacosa-2,4,6,8,10,12,14,21-octaen-17,21,22,26-tetracarboxylate (47)

A solution of bisalkene **46** (500 mg, 1.3 mmol) and DAPC **11** (370 mg, 1.43 mmol) in chloroform (15 ml) was heated in a pressure bottle at 95 °C for 60 h. ^{1}H NMR analysis revealed mono-adduct **47** and bis-adduct **48** were present in a ratio of approximately 3:1. The solvent was removed and the resulting solid extracted into dichloromethane, filtered and methanol added to the filtrate. Evaporation of the solvent (rotavap) precipitated out most of the bis adduct which was filtered off. The filtrate was evaporated and the resulting solid purified by column chromatography on silica by elution with 10% methanol/dichloromethane to give pure monoadduct **47**. Yield 372 mg, 45%, m.p. 290 °C (dec). ^{1}H NMR δ 1.40 (d; *J* = 12.6 Hz; 1H), 1.85 (d; *J* = 12.6 Hz; 1H), 2.07 (s; 6H), 2.15 (s; 2H), 2.65 (s; 2H), 2.69 (s; 2H), 3.16 (s; 6H), 3.81 (s; 6H), 7.65 (dd; *J* = 8.4, 4.3 Hz; 2H), 8.54 (dd; *J* = 8.5, 1.5 Hz; 2H), 9.20 (dd; *J* = 4.2, 1.5 Hz; 2H).

(1α,2β,3α,4β,19β,20α,21β,22α,23β,24α,25β,40β,41α,42β) tetramethyl 4,19,25,40-tetra methyl-10,13,31,34-tetraaza-43,44-dioxo-tetradecacyclo [20.20.1.1^{4,19}.1^{25,40}.0^{2,21}.0^{3,20}.0^{5,18}. 0^{6,11}.0^{12,17}.0^{23,42}.0^{24,41}.0^{26,39}.0^{27,32}.0^{33,38}]tetratetraconta-5,7,9,11,13,15,17,26, 28,30,32,34,36,38-tetradecaen-3,20,24,41-tetracarboxylate (48)

A solution of bisalkene **46** (500 mg, 1.3 mmol) and DAPC **11** (760 mg, 2.9 mmol) in chloroform (15 ml) was heated in a pressure bottle at 95 °C for 60 h. ^{1}H NMR analysis revealed mono-adduct **47** and bis-adduct **48** were present in a ratio of approximately 1:7. The solvent was removed to give a pink solid which was recrystallised from dichloromethane/methanol to give pure bis-adduct **48** as a white solid. Yield 795 mg, 68%, m.p. 315 °C (dec). ^{1}H NMR δ 1.96 (s; 2H), 2.09 (s; 12H), 2.10 (s; 4H), 3.01 (s; 2H), 3.14 (s; 12H), 7.65 (dd; *J* = 8.4, 4.2 Hz; 4H), 8.54 (dd; *J* = 8.5, 1.6 Hz; 4H), 9.21 (dd; *J* = 4.2, 1.5 Hz; 4H).

(1α,2β,3α,4β,5α,6β,7α,8β,23β,24α,25β,26α,27β,28α,29β,30α,31β,32α,33β,48β,49α,50β) hexamethyl 8,23,33,48-tetramethyl-14,1739,42-tetraaza-53,54-dioxo-heptadecacyclo[28.20. 1.1^{5,26}.1^{8,23}.1^{33,48}.0^{2,29}.0^{3,28}.0^{4,27}.0^{6,25}.0^{7,24}.0^{9,22}.0^{10,15}.0^{16,21}.0^{31,50}.0^{32,49}.0^{34,47}. 0^{35,39}.0^{41,46}]dopentaconta-9,11,13,15,17,19,21,34,36,38,40,42,44,46-tetradecaen-7,24, 32,49-tetracarboxylate (50)

A solution of bis(cyclobutene-1,2-dicarboxylate) **49**[11] (100 mg, 164 μmol) and DAPC **11** (94 mg, 361 μmol) in chloroform (5 ml) was heated in a pressure bottle at 95 °C for 100 h. The solvent was evaporated to give a pink solid which was recrystallised from dichloromethane/methanol to give an off-white solid. The product was purified further by column chromatography on silica by elution with 10% methanol/dichloromethane. Combined fractions were taken to dryness and the residue recrystallised from ethyl acetate/dichloromethane to give **50** as a white solid. Yield 50 mg, 27%, m.p. 290 °C (dec). ^{1}H NMR δ 1.83 (d; *J* = 12.8 Hz; 2H), 2.05 (s; 12H), 2.12 (s; 4H), 2.13 (d; *J* = 12.8 Hz; 2H), 2.35 (s; 4H), 2.56 (s; 4H),

3.10 (s; 12H), 3.76 (s; 6H), 7.64 (dd; J = 8.4, 4.2 Hz; 4H), 8.52 (dd; J = 8.4, 1.5 Hz; 4H), 9.19 (d; J = 4 Hz; 4H). ^{13}C NMR δ 10.26, 30.28, 40.26, 42.12, 51.00, 51.91, 52.08, 56.41, 60.34, 63.07, 123.41, 126.06, 132.85, 135.77, 146.97, 150.57, 169.28, 170.82, 201.1.

(1α,2α,3β,4α,5β,6α,7β,10β,11α,12β,13α,14β,15α,16α) dimethyl 1,16-dimethyl-31-oxo-22,25-diazaundecacyclo[14.14.1.1^{3,14}.1^{7,10}.0^{2,15}.0^{4,13}.0^{5,12}.0^{6,11}.0^{17,30}.0^{18,23}. 0^{24,29}] triconta-8,17,19,21,23,25,27,29-octaen-5,12-dicarboxylate (52)

A solution of 6σ-bisalkene **51** (50 mg, 0.15 mmol) and DAPC **11** (188 mg, 0.72 mmol) in *o*-xylene (5 ml) was heated at reflux for 60 h. The solvent was removed under reduced pressure to leave a pale solid. The solid was purified by column chromatography on silica (G60) by elution with 10% methanol/dichloromethane. The solid was recrystallised from methanol/dichloromethane to give **52** as a white solid. Yield 10 mg, 11%; m.p. ^{1}H NMR δ -0.58 (d; J = 12.3 Hz; 1H), 0.99 (d; J = 9.3 Hz; 1H), 1.03 (d; J = 12.3 Hz; 1H), 1.64 (d; J = 9.3 Hz; 1H), 2.02 (s; 6H), 2.08 (s; 4H), 2.15 (s; 2H), 2.30 (s; 2H), 2.73 (s; 2H), 3.50 (s; 2H), 6.03 (s; 2H), 7.65 (dd; J = 4.2, 4.2 Hz; 2H), 8.67 (dd; J = 4.2, 1.6 Hz; 2H), 9.22 (dd; J = 1.5, 2.1 Hz; 2H).

(1α,2α,4α,5α,6β,7α,8β,23β,24α,25β,26α,27α,29α,30α,31β,32α,33β,48β,49α,50β) tetra methyl-8,23,33,48-tetramethyl-53,54-dioxo-14,17,39,42-tetraaza-octadecacyclo[28.20.1.1^{5,26}.1^{8,23}.1^{35,48}.0^{2,29}.0^{4,27}.0^{6,25}.0^{7,24}.0^{9,22}.0^{10,15}.0^{16,21}.0^{31,50}.0^{32,49}.0^{34,47}.0^{35,40}. 0^{41,47}]tetrapentaconta-9,11,13,15,17,19,21,34,36,38,40,42,44,46-tetradecaen-7,24,32,49-tetracarboxylate (54)

A solution of bisalkene **53** (250 mg, 0.5 mmol) and DAPC **11** (260 mg, 1 mmol) in chloroform (10 ml) was heated in a pressure bottle at 95 °C for 60 h. The solvent was removed to give a pink solid. The material was recrystallised from dichloromethane/methanol to give **54** as a pale pink solid. Yield 318 mg, 63%, m.p. 291 °C (dec). ^{1}H NMR δ 1.28 (d; J = 8 Hz; 2H), 1.60 (s; 4H), 1.80 (d; J = 8 Hz; 2H), 2.12 (s; 12H), 2.18 (s; 2H), 2.52 (s; 4H), 2.67 (s; 4H), 3.13 (s; 12H), 7.64 (dd; J = 8.4, 4.2 Hz; 4H), 8.54 (dd; J = 8.5, 1.5 Hz; 4H), 9.20 (dd; J = 4.2, 1.5 Hz; 4H).

(1α,2β,3β,4α,5β,6α,21α,22β,23α,24β,25β,26α,27β,28β,29α,30β,31α,46α,47β,48α,49β) tetra methyl 6,21,31,46-tetramethyl-53,55-dioxo- 12,15,37,40-tetraaza-octa decacyclo [24.24.1.1^{3,24}.1^{6,21}.1^{28,49}.1^{31,46}.0^{2,25}.0^{4,23}.0^{5,22}.0^{7,20}.0^{8,13}.0^{14,19}.0^{27,50}.0^{29,48}. 0^{30,47}. 0^{32,45}. 0^{33,38}.0^{39,44}]pentapentaconta-7,9,11,13,15,17,19,32,34,36,38,40,42,44-tetradecaen-5,22,30,47-tetracarboxylate (56)

A procedure similar to that used for the preparation of **54** was used to give **56** as a pale pink solid. Yield 834 mg, 83%, m.p. 289 °C (dec). ^{1}H NMR δ 1.28 (d; J = 8 Hz; 2H), 1.60 (s; 4H), 1.64 (s; 2H), 1.80 (d; J = 8 Hz; 2H), 2.12 (s; 12H), 2.18 (s; 2H), 2.52 (s; 4H), 2.67 (s; 4H), 3.13 (s; 12H), 7.64 (dd; J = 8.4, 4.2 Hz; 4H), 8.54 (dd; J = 8.5, 1.5 Hz; 4H), 9.20 (dd; J = 4.2, 1.5 Hz; 4H). ^{13}C NMR δ 10.42, 30.71, 36.86, 39.46, 40.14, 42.83, 51.92, 52.58, 60.47, 62.98, 123.36, 126.10, 132.69, 135.82, 146.90, 150.45, 169.68, 201.69.

(1α,16α,17β,18α,19β,26β,27α,28β) dimethyl 1,16-dimethyl-21,26-di(2'-pyridyl)-29-oxo-7,10,22,23-tetraaza-nonacyclo[14.12.1.1^{19,26}.0^{2,15}.0^{3,8}. 0^{9,14}.0^{18,27}.0^{20,25}] triaconta-2,4,6,8,10,12,14,20,22,24-decaen-17,28-dicarboxylate (58)

A solution of dpp ligand **57**[14] (270 mg, 0.61 mmol) and DAPC **11** (200 mg, 2.1 mmol) in chloroform (10 ml) was heated in a pressure bottle at 95 °C for 50 h. The solvent was removed to give a pink solid which was recrystallised from dichloromethane/methanol to give **58** as a pale pink solid. Yield 346 mg, 85%, m.p. 301 °C (dec). ^{1}H NMR δ 1.73 (d; *J* = 11.3 Hz; 1H), 2.11 (s; 6H), 2.27 (d; *J* =11.3 Hz; 1H), 2.51 (s; 2H), 3.24 (s; 6H), 4.83 (s; 2H), 7.40 (ddd; *J* = 7.5, 4.8, 1.1 Hz; 2H), 7.67 (dd; *J* = 8.5, 4.3 Hz; 2H), 7.92 (ddd; *J* = 7.8, 7.8, 1.8 Hz; 2H), 8.64-8.60 (m; 4H), 8.80 (ddd; *J* = 4.8, 1.8, 0.9 Hz; 2H), 9.22 (dd; *J* = 4.2, 1.6 Hz; 2H). ^{13}C NMR δ 10.05, 40.47, 43.83, 45.40, 52.31, 60.52, 61.42, 123.39, 123.45, 124.49, 126.18, 132.89, 136.25, 137.45, 146.99, 147.98, 149.96, 150.56, 153.30, 156.09, 169.67, 200.25.

spiro-4',5'-diazafluorene-9',22-(1α,16α,17β,18α,19β,20α,21β,23β,24α,25β,26α,27β) tetra methyl 1,16-dimethyl-7,10-diaza-28-oxo-decacyclo[14.11.1.1^{19,25}.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,27}. 0^{18,26}.0^{20,24}.0^{21,23}]nonacosa-2,4,6,8,10,12,14-heptaen-17,21,23,27-tetracarboxylate (61)

A solution of DAPC derivative **47** (112 mg, 0.18 mmol) and 9-diazo-4,5-diazafluorene **59** (41 mg, 0.21 mmol) in toluene (5 ml) was heated at reflux for 14 h. The solvent was removed to leave a yellow residue which was purified by fractional recrystallisation from dichloromethane/methanol to give **61** as a white solid. Yield 62 mg, 44%, m.p. 281 °C (dec), ^{1}H NMR δ 2.10 (s; 6H), 2.12 (d; *J* = 12.8 Hz; 1H), 2.31 (s; 2H), 2.73 (d; *J* = 12.8 Hz; 1H), 2.85 (s; 2H), 2.87 (s; 6H), 3.16 (s; 6H), 3.60 (s; 6H), 7.21 (dd;*J* = 8.1, 4.8 Hz; 1H), 7.43 (dd; *J* = 8.0, 4.8 Hz; 1H), 7.68 (dd; *J* = 8.4, 4.3 Hz; 2H), 7.84 (dd; *J* = 8.1, 1.3 Hz; 1H), 8.03 (bd; *J* = 7.3 Hz; 1H), 8.54 (dd; *J* = 8.5, 1.6 Hz; 2H), 8.71 (dd; *J* = 4.7, 1.3 Hz; 1H), 8.85 (dd; *J* = 4.8, 1.0 Hz; 1H), 9.23 (dd; *J* = 4.2, 1.5 Hz; 2H) .

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