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DOTTADs – readily made novel metal ligands with multivariant functionality

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The interaction of Hantzsch pyridinecarboxylic acids with dialkylformamides and $POCl_3$, followed by treatment with NH_4OH yields 1,8-dioxo-1,2,7,8-tetrahydro-2,7,10-triazaanthracenes (DOTTADs), which have great potential as useful ligands for Group I and II metals and some transition metals. The corresponding Hantszch esters similarly give DOTTADs or their bis-imines by way of isolable intermediates, which are then treated with an amine RNH_2. DOTTAD-imines are also available from DOTTADs with amines and this reaction is also effective with 1,8-diamino-3,6-dioxaoctane to give macrocyclic analogues, as well as with chiral amines. DOTTAD-imines can be reduced with diethylsilane and Wilkinson's catalyst to the corresponding amines, which can also be formed from DOTTADs by reductive amination with amines and $Na(AcO)_3BH$. Mono-aldols of DOTTADs are easily formed by treatment of DOTTADs with acetone.

Introduction

Heterocyclic ligands such as imidazole, pyridine, 2,2′-bipyridyl and 1,10-phenanthroline have played a formative role in the development of co-ordination chemistry. Many thousands of complexes and complex ions containing these and other ligands have been prepared and characterised.[1] In this paper[2] we describe a general multi-purpose synthesis of a new class of heterocyclic ligands which we refer to as DOTTADs from the name of the parent system, 1,8-*di*oxo-1,2,7,8-*t*etrahydro-2,7,10-*t*riaza*a*nthracene-4,5-*di*carbaldehydes.

Some years ago we described[3] a new cyclisation whereby *ortho*-methylarenecarboxylic acids (*e.g.* **1**) in which the methyl group was "activated", underwent diformylation at the methyl group with a Vilsmeier reagent followed by intramolecular acylation at the introduced nitrogen and subsequent *N*-demethylation to generate a fused pyridone-aldehyde (**2**, Scheme 1).

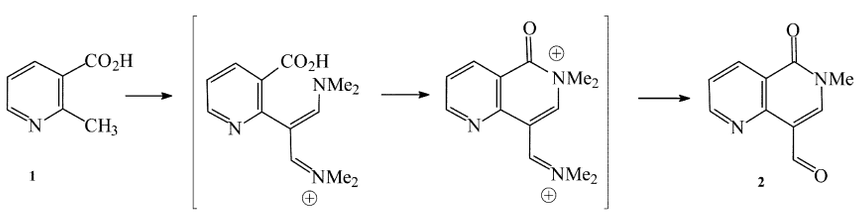
This reaction proved quite general, the activation being effected by a conjugated nitro-group, a pyridine nitrogen or even an α-carboxylic acid group. In this present work we show that the reaction is a highly efficient and versatile route to useful ligands with novel potential. We have focused in particular on the formylation of readily available Hantzsch pyridinecarboxylic acids and esters. The formylation results in bis-cyclisations to generate a number of novel compounds which are potent ligands for Group I and II metals and some transition metals.

Results and discussion

Reactions of 2,6-dimethylpyridine-3,5-dicarboxylic acid

In the first experiments the most simple Hantzsch acid was investigated: 2,6-dimethylpyridine-3,5-dicarboxylic acid **4** was reacted with different Vilsmeier reagents, preformed from the corresponding dialkylformamides using $POCl_3$ as a solvent. After 12 hours heating at 80 °C (when the starting dicarboxylic acid **4** was consumed as judged by ^{1}H-NMR) the volatile materials were removed and the residue was treated with ice–water. The expected 2,7-dialkyl-DOTTADs (**5**) were precipitated by basification with ammonium hydroxide (Scheme 2). The use of ammonium hydroxide rather than, for example, sodium hydroxide, is important to avoid metal salt complexation and thus water solubilisation of the product. These first results indicated that an excess of formamide is essential for good yields (*cf.* Entries 1–3), while bulky groups such as R = isopropyl in the formamide inhibited the reaction (Table 1).

In the next series of experiments, some examples in which the dialkylformamides were replaced by a cyclic formamide, such as *N*-formylpyrrolidine, were examined. The formylation step proceeded normally, while the subsequent cyclisation was followed by ring-opening to give DOTTADs **6** and **7** bearing an ω-chloroalkyl function on the introduced ring nitrogens (Table 1, Entries 7–8; Scheme 3).



Scheme 1

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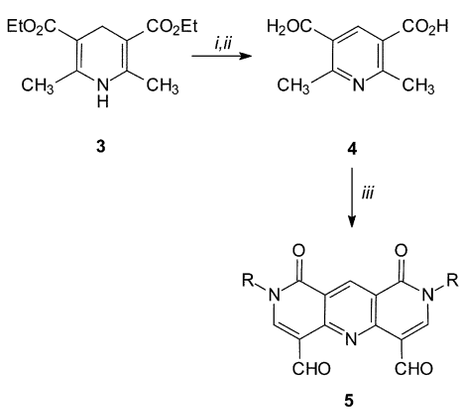
Table 1 Formation of DOTTADs **5** from Hantszch acids **4**

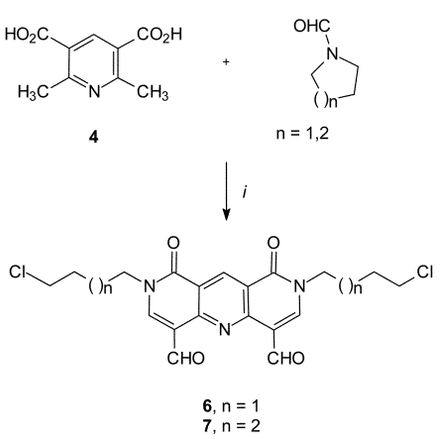
Entry	Product	Formamide (mol excess)	Reaction time/hours	Crude yield (%)
1	**5a** R = Me	4.2	12	46
2	**5a** R = Me	5	12	80
3	**5a** R = Me	6	12	88
4	**5b** R = Et	4.2	12	46
5	**5c** R = $–CH_2CH=CH_2$	6	12	76
6	**5d** R = i-Pr	4.2	12	0
7	**6** R = $–(CH_2)_4Cl$	6	12	66
8	**7** R = $–(CH_2)_5Cl$	6	12	100

Table 2 Formation of DOTTAD and DOTTAD-imines by action of amines on intermediate **9**

Entry	R =	Product	Reaction time	Yield (%)	Mp/°C
1	H	**10**	1 h	90	>300
2	H	**11**	1 min	100	>300
3	Me–	**13a**	1 min	73	247–8
4	Et–	**13b**	1 min	62	280
5	^nBu –	**13c**	1 min	54	119–20
6	$–CH_2=CHCH_2$	**12d**	1 min	80	235
7	$–CH_2=CHCH_2$	**13d**	2 h	65	182
8	$–CH_2Ph$	**13e**	1 min	73	199
9	$–CH_2$-(4-MeOPh)	**13f**	1 min	77	214–5
10	$–CH(CH_3)Ph$	**13g**	48 h	62	183–4
11	$–CH_2CH_2OH$	**13h**	1 min	52	>292
12	PhNH–	**13i**	48 h	0	—
13	$–COCF_3$	**13j**	48 h	0	—
14	$–CH_2CO_2Et$	**13k**	48 h	0	—
15	4-MeOPh–	**13m**	6 h	0	—



Scheme 2 *Reagents and conditions*: i. dilute HNO_3; ii. NaOH, EtOH, H_2O; iii. $POCl_3$, R_2NCHO, 80 °C; then NH_4OH.



Scheme 3 *Reagents and conditions*: i. $POCl_3$, 80 °C.

Reactions of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (8)

Given the proposed mechanism of the above reactions, we next examined formylation of the diethyl ester **8** instead of the free acid **4**. We presumed that the cyclisation of the acid-derived intermediates proceeded by way of their acid chlorides and that the corresponding esters would thus be less easily cyclised, perhaps allowing the intermediate iminium salts to be isolated (as a PF_6^- salt). Subsequent addition of different amines in this stage could then yield the same products as above or allow preparation of otherwise inaccessible products.

The diester **8** was added to a dimethylformamide–$POCl_3$ mixture and the progress of the reaction was monitored by ^{1}H-NMR spectroscopy. After two days at 80 °C no starting material was observed. The spectrum of the crude sample corresponded to the salt **9**, which was isolated quantitatively as its hexafluorophosphate **11**. Addition of ammonium hydroxide to the stable aqueous solution of **9** gave the parent DOTTAD, the highly insoluble dialdehyde **10**, isolated in good yield (Scheme 4).

On stirring the solution of **9** with a large excess of different primary amines, precipitation of a DOTTAD was observed (Table 2). However, these DOTTADs were generally isolated as the corresponding diimines **13** of the dialdehydes **12** (except for one case, Entry 6). Interestingly, the same type of DOTTAD-diimine was formed from 2-aminoethanol (Entry 10) and phenylhydrazine (Entry 11). However the reaction did not proceed with weakly basic amines such as anilines, trifluoroacetamide, and glycine ethyl ester (entries 12–14). Chiral products, such as DOTTAD-imine **13g** were easily made in this way.

In order to achieve further simplification in the DOTTAD synthesis the dihydropyridine ester **3** was subjected to the above described conditions. After 2 days heating with an excess of Vilsmeier reagent in $POCl_3$ as a solvent the usual work-up again gave the diimines of the DOTTADs **13d** (42%) and **13e** (77%) respectively. The oxidation of the dihydropyridine was no doubt achieved by the iminium salt acting as a hydride abstractor.

The reactivity of the DOTTAD-dialdehydes

We have also studied some simple chemical transformations of these new heterocycles in order to establish their usefulness in the synthesis of multidentate ligands or even macrocycles

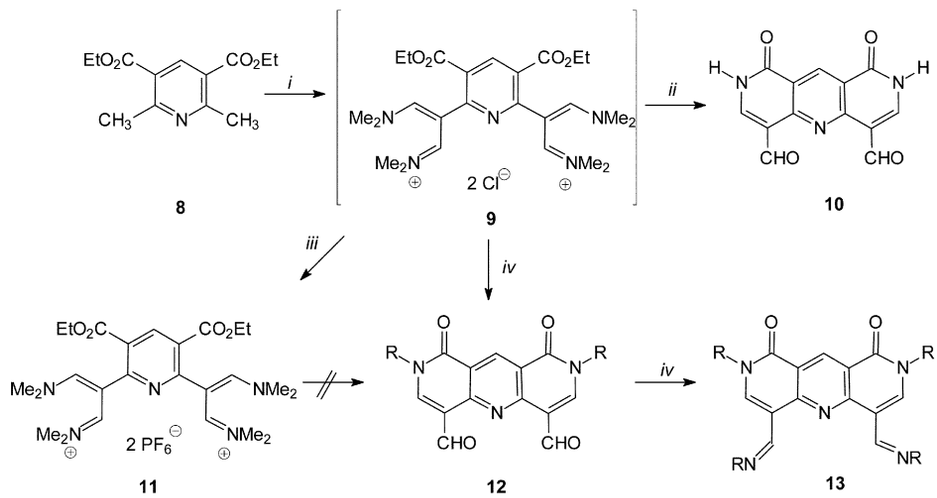
Table 3 Formation of DOTTAD-imines **14** from DOTTAD-aldehydes **5** and **6**

Entry	Starting material	Product	Amine excess (mol %)	Yield (%)
1	**5a** R = Me	**14a** R′ = Ph	240	58
2	**6** R= $(CH_2)_4Cl$	**14b** R′ = Ph	10	85
3	**6** R = $(CH_2)_4Cl$	**14c** R′ = 4-MeO–Ph	10	95
4	**6** R = $(CH_2)_4Cl$	**14d** R′ = 3-NO_2–Ph	10	80
5	**6** R = $(CH_2)_4Cl$	**14e** R′ = (*S*)-Ph–$CH(CH_3)$	10	93
6	**5c** R = CH_2=CH–CH_2–	**14f** R′ = Ph	10	70
7	**5c** R = CH_2=CH–CH_2–	**14g** R′ = 4-MeOPh	10	75

Table 4 Formation of DOTTAD-amines **15**

Entry	Starting material	Product	Method[a]	Yield (%)
1	**14f** R = CH_2=CH–CH_2–; R^1 = 4-MeO–Ph–	**15a**	A	54
2	**14c** R= –$(CH_2)_4Cl$; R^1 = 4-MeO–Ph–	**15b**	A	92
3	**6** R= –$(CH_2)_4Cl$,	**15c** R^1 = Ph–	B	81
4	**6** R = –$(CH_2)_4Cl$,	**15d** R^1 = 3-NO_2-Ph–	B	82
5	**6** R = –$(CH_2)_4Cl$	**15e** R^1 = –$CH(CH_3)CH(OH)$–Ph	B	78
6	**5c** R = CH_2=CH–CH_2–	**15f** R^1 = –$CH(CH_3)CH(OH)$–Ph	B	69

[a] Method A: Wilkinson's catalyst; Et_2SiH_2; CH_2Cl_2; rt; Method B: R_1NH_2, $NaBH(OAc)_3$, DCE, rt.



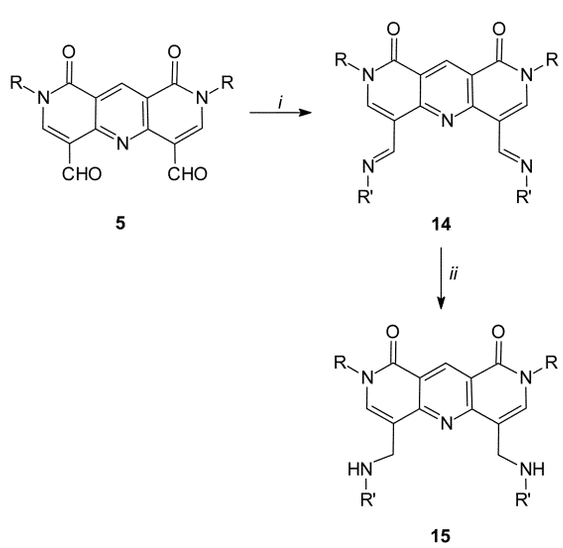
Scheme 4 *Reagents and conditions*: i. DMF, $POCl_3$, 48 h; ii. NH_4OH; iii. NH_4PF_6; iv. RNH_2.

which, in theory, could be easily constructed around the symmetric bifunctionality.

Reaction with anilines and reduction of the C–N double bond

As can be expected from the reactions outlined in Scheme 4, these quite insoluble aldehydes reacted readily with anilines in refluxing ethyl acetate, giving rise to the formation of the corresponding anils **14**. In the case of the less soluble aldehyde **5a** a huge excess of aniline was necessary to achieve this condensation (Scheme 5, Table 3).

The reduction of these imines proved to be a much more difficult task. Many methods were tried, but so far, only two of them were successful. Complex mixtures of products were formed using, for example, H_2–PtO_2, $NaBH_4$, $LiAlH_4$ and $Zn(BH_4)_2$, under different conditions. No reaction occurred using indium or *n*-Bu_4NBH_4 as a reducing agent. The two successful methods were: (A) transfer hydrogenation catalysed by rhodium(I) catalyst under the very mild conditions developed by Ojima *et al*.[4] Thus, in dichloromethane at room temperature using diethylsilane as a hydrogen donor in the presence of freshly prepared Wilkinson's catalyst, the reduction took place within a few hours (Scheme 5, Table 4). DOTTADs bearing an allylic side-chain led to the formation of a lower yield of product, probably caused by the interactions of the Rh(I) catalyst with the allylic function; (B) The one-step reductive amination

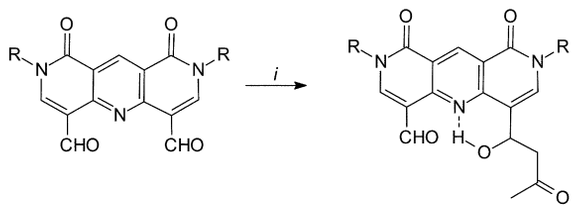


Scheme 5 *Reagents and conditions*: i. R′NH_2, EtOAc; ii. Wilkinson's catalyst, Et_2SiH_2.

of the DOTTAD dialdehydes using sodium triacetoxyborohydride as a reducing agent. In these two ways, various homochiral 'DOTTAD-amines' **15**, have been prepared (Table 4).

Aldol- type condensation with acetone

The reaction of pure DOTTADs with pure, dry acetone at room temperature easily gave the corresponding mono-aldol adducts **16a**,**b** quantitatively, but so far attempts to make the bis-aldol adduct have failed. The reaction did not proceed in the presence of any base or acid contaminants (Scheme 6).

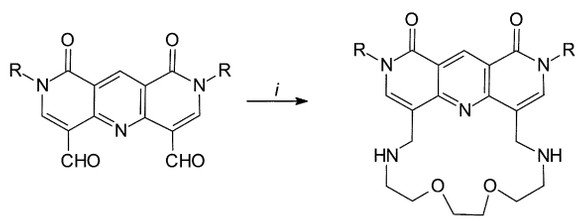


5c, R = $CH_2CH{=}CH_2$ **16a**, R = $CH_2CH{=}CH_2$
6, R = $(CH_2)_4Cl$ **16b**, R = $(CH_2)_4Cl$

Scheme 6 *Reagents and conditions*: i. dry acetone, rt.

Synthesis of macrocyclic products

Using the above described imine ⟶ amine transformation, two macrocyclic products **17a** and **17b** have been synthesised under high dilution conditions by the condensation of DOTTADs **5c** and **6** with 1,8-diamino-3,6-dioxaoctane (Scheme 7).



5c, R = $CH_2CH{=}CH_2$ **17a**, R = $CH_2CH{=}CH_2$
6, R = $(CH_2)_4Cl$ **17b**, R = $(CH_2)_4Cl$

Scheme 7 *Reagents and conditions*: i.$H_2NCH_2CH_2OCH_2CH_2OCH_2$-$CH_2NH_2$, CH_2Cl_2, high dilution.

It is evident that these interesting systems have considerable potential as useful ligands and thus also for metal-catalysed reactions, particularly for homochiral catalysis. This aspect is now under investigation as a continuation of this work.

Experimental

Mps were determined on a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed on a Perkin-Elmer 240C or Carlo Erba 1106 Elemental Analyser. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR or Unicam research series FTIR spectrophotometer using sodium chloride plates. ^{1}H NMR spectra were acquired on a JEOL GSX 270 FT NMR at 270 MHz. Coupling constants are given in Hz and all chemical shifts are relative to an internal standard of tetramethylsilane. ^{13}C NMR spectra were obtained on a JEOL GFX 270 FT NMR (68 MHz) spectrometer. Low resolution electron impact mass spectra were obtained on a Trio 2000 VG. High resolution spectra were obtained on a VG ZAB-E spectrometer (E.P.S.R.C. Mass Spectrometry Service Centre, Swansea). Thin layer chromatography was performed on Merck silica gel $60F_{254}$. All solvents were purified according to standard procedures. The 1,8-diamino-3,6-dioxaoctane was prepared from triethylene glycol by the method of Bradshaw *et al.*,[5] and pyridines **3** and **4** were prepared by the method of Böcker.[6]

Synthesis of 1,8-dioxo-1,2,7,8-tetrahydro-2,7,10-triaza-anthracene-4,5-dicarbaldehydes (DOTTADs) and their imines

Route A: From 2-methylpyridine-3-carboxylic acids – general procedure. Phosphoryl chloride (9.3 mL) was added dropwise to the *N*-formyldialkylamine (60 mmol) with good stirring and external cooling by ice (the first few mL being added very slowly with a vigorous reaction ensuing). To this solution was added in one portion the 2,6-dimethylpyridine-3,5-dicarboxylic acid **4** (1.95 g, 10 mmol) and after one minute stirring the mixture was heated in an oil bath at 80–85 °C for 12 hours, soon becoming red in colour. Most of the excess of $POCl_3$ was removed *in vacuo* and then ice–water added followed by concentrated ammonium hydroxide until basic. Stirring slowly caused precipitation of a tan coloured solid. After ½ h stirring, the precipitate was filtered off, washed well with water, recrystallised and dried *in vacuo*. Yields are collected in Table 1 and other properties recorded below:

*1,8-Dioxo-2,7-dimethyl-1,2,7,8-tetrahydro-2,7,10-triaza-anthracene-4,5-dicarbaldehyde (**5a**).* Pale brown crystals, mp >310 °C (from AcOH) (Found: C, 60.4; H, 3.7; N, 14.2. $C_{15}H_{11}N_3O_4$ requires C, 60.61; H, 3.73; N, 14.14%); ν_{max} KBr/cm^{-1} 1681, 1622, 1600, 1577, 1550, 1459, 1359, 1303, 1240, 1058, 950; δ_H (270 MHz, DMSO-d_6): 10.67 (s, 2H, CHO), 9.22 (s, 1H, 9-H), 8.51 (s, 2H, H-3 and H-6), 1.89 (s, 6H, 2 × Me); δ_C (68 MHz, DMSO-d_6): 187.6, 161.4, 153.7, 146.1, 137.5, 117.8, 112.7, 39.1; *m*/*z* (electrospray): 298 (M + 1, 72%), 284 (5), 278 (4), 207 (12).

*1,8-Dioxo-2,7-diethyl-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4,5-dicarbaldehyde (**5b**).* Pale yellow crystals, mp 282 °C (from AcOH) (Found: C, 62.9; H, 4.8; N, 13.0. $C_{17}H_{15}N_3O_4$ requires C, 62.76; H, 4.65; N, 12.92%); ν_{max} KBr/cm^{-1} 1690, 1662, 1599, 1471, 1370, 1315; δ_H (270 MHz, DMSO-d_6, 120 °C): 10.63 (s, 2H, CHO), 9.19 (s, 1H, 9-H), 8.48 (s, 2H, H-3 and H-6), 4.14 (q, 4H, *J* 7.3 Hz, CH_2), 1.38 (t, 6H, 2 × Me); δ_C (DMSO-d_6, 120 °C): 187.3, 160.6, 153.4, 144.8, 137.5, 117.9, 113.0, 44.3, 13.9; *m*/*z* (electrospray): 326 (M + 1, 55), 312 (7), 297 (11), 217 (8).

*1,8-Dioxo-2,7-diallyl-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4,5-dicarbaldehyde (**5c**).* Pale yellow crystals, mp 235 °C (from $CHCl_3$) (Found: C, 65.4; H, 4.3; N, 12.1. $C_{19}H_{15}N_3O_4$ requires C, 65.32; H, 4.33; N, 12.03%); ν_{max} KBr/cm^{-1} 1710, 1685, 1598, 1573, 1467, 1367, 1314, 1274, 935, 811; δ_H (270 MHz, DMSO-d_6, 50 °C): 10.83 (s, 2H, CHO), 9.58 (s, 1H, 9-H), 8.35 (s, 2H, H-3 and H-6), 6.09–5.95 (m, 2H, allyl), 5.41–5.34 (m, 4H, allyl), 4.75–4.73 (m, 4H, allyl); δ_C (68 MHz, CDCl3, 50 °C): 187.3, 161.0, 154.2, 143.0, 139.7, 131.0, 120.0, 118.9, 113.8, 51.2; *m*/*z* (CI): 350 (M + 1, base peak), 336 (2), 322 (12), 301 (7), 287 (3), 159 (6), 85 (55), 57 (57).

*2,7-Bis(4-chlorobutyl)-1,8-dioxo-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4,5-dicarbaldehyde (**6**).* White crystals, mp 216 °C (from AcOH) (Found: C, 56.1; H, 4.7; N, 9.3. $C_{21}H_{21}N_3Cl_2O_4$ requires C, 56.01; H, 4.70; N, 9.33%); ν_{max} KBr/cm^{-1} 3035, 2952, 2875, 1664, 1600, 1469, 1369, 1313, 1278, 1199, 1066, 944, 811, 615; δ_H (270 MHz, DMSO-d_6): 10.73 (s, 2H, CHO), 9.30 (s, 1H, 9H), 8.56 (s, 2H, H-3 and H-6), 4.19 (t, 4H, *J* 6.6 Hz, CH_2), 3.66 (t, 4H, *J* 6 Hz, CH_2), 1.97–1.91 (m, 8H, CH_2); δ_C (68 MHz, DMSO-d6): 187.2, 160.8, 153.4, 144.7, 137.6, 117.9, 113.1, 48.0, 44.1, 28.7, 25.7; *m*/*z* (EI): 450 (M^+, 13), 414 (8), 352 (5), 285 (8), 257 (17), 127 (35), 97 (base peak).

*2,7-Bis(4-chloropentyl)-1,8-dioxo-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4,5-dicarbaldehyde (**7**).* Pale pink crystals, mp 182 °C (from AcOH) (Found: C, 56.3; H, 5.2; N, 8.7. $C_{23}H_{25}N_3Cl_2O_4$ requires C, 57.75; H, 5.27; N, 8.78%); ν_{max} KBr/cm^{-1} 3150, 3095, 2950, 2870, 1664, 1601, 1470, 1401, 1371, 1312, 1278, 1155, 811; δ_H (270 MHz, DMSO-d_6, 80 °C): 10.67 (s, 2H, CHO), 9.16 (s, 1H, 9H), 8.62 (s, 2H, H-3 and H-6), 4.12 (t, 4H, *J* 7.3 Hz, CH_2), 3.64 (t, 4H, *J* 6.6 Hz, CH_2), 1.82–1.70 (m, 8H, CH_2), 1.49–1.41 (m, 4H, CH_2); δ_C (68 MHz, DMSO-d_6, 80 °C): 187.6, 160.9, 153.5, 145.2, 137.8, 118.0, 112.9, 48.8, 44.8, 31.2, 27.5, 23.1; *m*/*z* (electrospray): 479 (M + 1, 48), 441 (8), 373 (13), 326 (11), 122 (38), 85 (base peak).

Route B: from the esters of 2-methylpyridine-3-carboxylic acids (3) – general procedure. Phosphoryl chloride (9.3 mL) was added dropwise to dry dimethylformamide (4.38 g, 4.64 mL,

60 mmol) with vigorous stirring and external cooling by ice as above. To this solution was added in one portion, diethyl 2,6-dimethylpyridine-3,5-dicarboxylate **3** (2.51 g, 10 mmol) and after one minute stirring the mixture was heated in an oil bath at 80–85 °C for two days. Most of the excess of $POCl_3$ was removed *in vacuo* and then ice–water added followed by concentrated ammonium hydroxide, NH_4PF_6 or the appropriate amine. Stirring precipitated a tan coloured solid. After ½ h stirring the precipitate was filtered off, washed well with water, recrystallised and dried *in vacuo* to give products as pale yellow–brown crystals. Yields are collected in Table 2 and other properties recorded below:

*1,8-Dioxo-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4,5-dicarbaldehyde (**10**)*. Pale brown crystals. Mp >300 °C; ν_{max} KBr/cm^{-1} 3035, 2944, 2842, 1664, 1602, 1554, 1494, 1415, 1280, 1211, 1089; δ_H (270 MHz, DMSO-d_6, 80 °C): 10.63 (s, 2H, CHO), 9.88 (s, NH), 9.06 (s, 1H, H-9), 8.20 (s, 2H, H-3 and H-6); δ_C (68 MHz, DMSO-d_6, 80 °C): 187.4, 160.5, 153.6, 141.5, 136.9, 118.4, 112.9; *m*/*z* (electrospray): 270 (M + 1, 100), 251 (8), 236 (13), 214 (12), 163 (55); *m*/*z* (CI): 269 (M$^+$, 5), 256 (7), 241 (10), 231 (28), 226 (18), 220 (68), 141 (39), 69 (34), 60 (100) (Found: 269.0427; $C_{13}H_7N_3O_4$ requires 269.0436).

*Hexafluorophosphate Salt **11***. Pale brown crystals. Mp <300 °C (Found: C, 39.1; H, 5.2; N, 9.1. $C_{25}H_{39}N_5O_4P_2F_{12}$ requires C, 39.33; H, 5.15; N, 9.17%); ν_{max} KBr/cm^{-1} 1724, 1600, 1420, 1403, 1294, 1256; δ_H (270 MHz, DMSO-d_6, 80 °C): 9.20 (s, 1H, H-4), 8.06 (s, 4H, CH=), 4.45 (q, 4H, *J* 7.3 Hz, CH_2), 3.53 (s, 12H, CH_3), 2.90 (s, 12H, CH_3), 1.45 (t, 6H, *J* 7.3 Hz, CH_3); δ_C (68 MHz, DMSO-d_6, 80 °C): 164.3, 163.2, 154.1, 140.4, 127.7, 101.8, 60.1, 48.3, 13.8.

*1,8-Dioxo-2,7-dimethyl-4,5-bis(methyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13a**)*. Soft, pale yellow needles, mp 247–248 °C (from acetonitrile); ν_{max} KBr/cm^{-1} 1671, 1641, 1608, 1586, 1454, 1353, 1328, 1286, 809; δ_H (270 MHz, $CDCl_3$): 9.55 (s, 1H, H-9), 9.06 (s, 2H, CH=N), 8.23 (s, 2H, H-3 and H-6), 3.68 (s, 6H, NMe), 3.58 (s, 6H, NMe); δ_C (68 MHz, $CDCl_3$): 161.6, 156.2, 153.3, 138.6, 138.2, 118.6, 112.9, 47.9, 36.8; *m*/*z* (CI): 324 (M + 1, 30), 311 (20), 299 (15), 285 (8), 272 (2), 85 (32), 60 (base peak) (Found: 323.1394; $C_{17}H_{17}N_5O_2$ requires 323.1382).

*1,8-Dioxo-2,7-diethyl-4,5-bis(ethyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13b**)*. Yellow crystals, mp 280 °C (from acetonitrile); ν_{max} KBr/cm^{-1} 1684, 1641, 1606, 1581, 1465, 1367, 1327, 1285, 1248, 810; δ_H (270 MHz, $CDCl_3$): 9.66 (s, 1H, H-9), 9.14 (s, 2H, CH=N), 8.32 (s, 2H, H-3 and H-6), 4.17 (q, 4H, *J* 7.3 Hz, CH_2), 3.74 (q, 4H, *J* 7.2 Hz, CH_2), 1.49–1.35 (m, 12H, CH_3); δ_C (68 MHz, $CDCl_3$): 161.4, 154.5, 153.8, 139.5, 137.8, 119.3, 113.6, 55.9, 45.1, 16.3, 14.5; *m*/*z* (CI): 380 (M + 1,base peak), 366 (2), 353 (20), 341 (2), 325 (3) (Found: 379.1999; $C_{21}H_{25}N_5O_2$ requires 379.2008).

*1,8-Dioxo-2,7-dibutyl-4,5-bis(butyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13c**)*. Pale yellow crystals, mp 119–120 °C (from acetonitrile); ν_{max} KBr/cm^{-1} 2956, 2931, 2885, 1680, 1641, 1611, 1582, 1464, 1364, 1334, 1278, 813; δ_H (270 MHz, DMSO-d_6): 9.17 (s, 1H, H-9), 8.96 (s, 2H, CH=N), 8.31 (s, 2H, H-3 and H-6), 4.05 (t, 4H, *J* 6.9 Hz, CH_2), 3.61 (t, 4H, CH_2), 1.73–1.60 (m, 8H, CH_2), 0.96–0.91 (m, 12H, CH_3); δ_C (68 MHz, DMSO-d_6, 40 °C): 160.7, 154.2, 153.1, 138.5, 137.6, 118.2, 112.2, 60.4, 48.4, 32.2, 30.5, 19.7, 19.2, 13.5, 13.4; *m*/*z* (electrospray): 492 (M + 1, 18), 434 (6), 376 (9), 85 (base peak) (Found: 491.3269; $C_{29}H_{41}N_5O_2$ requires 491.3260).

*1,8-Dioxo-2,7-diallyl-4,5-bis(allyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13d**)*. Pale yellow crystals, mp 182 °C (from acetonitrile); ν_{max} KBr/cm^{-1} 3075, 3058, 2981, 2923, 2883, 1700, 1673, 1643, 1602, 1581, 1465, 1361, 1319, 1269, 1220, 923, 809; δ_H (270 MHz, DMSO-d_6, 100 °C): 9.29 (s, 1H, H-9), 9.07 (s, 2H, CH=N), 8.35 (s, 2H, H-3 and H-6), 6.13–5.98 (m, 4H, allyl), 5.31–5.13 (m, 4H, allyl), 4.75–4.71(m, 4H, allyl), 4.29–4.27 (m, 4H, allyl); δ_C (68 MHz, DMSO-d_6, 100 °C): 158.6, 153.4, 151.3, 136.5, 135.9, 134.7, 131.0, 116.3, 113.9, 110.3, 60.7, 48.3; *m*/*z* (EI): 427 (M$^+$, 17), 386 (100), 347 (20), 331 (12), 319 (5), 281 (5), 56 (12) (Found: 427.2003; $C_{25}H_{25}N_5O_2$ requires 427.2008).

*1,8-Dioxo-2,7-dibenzyl-4,5-bis(benzyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13e**)*. Yellow crystals, mp 199 °C (from acetonitrile); Found: C, 78.3; H, 5.2; N, 11.0. $C_{41}H_{33}N_5O_2$ requires C, 78.45; H, 5.30; N, 11.16%); ν_{max} KBr/cm^{-1} 3054, 3035, 2953, 1672, 1642, 1600, 1581, 1466, 1432, 1364, 1346, 1325, 1255; δ_H (270 MHz, DMSO-d_6, 90 °C): 9.37 (s, 1H, H-9), 9.11 (s, 2H, CH=N), 8.45 (s, 2H, H-3 and H-6), 7.33–7.20 (m, 20H, Ph), 5.32 (s, 4H, CH_2N=), 4.81 (s, 4H, CH_2N–); δ_C (68 MHz, DMSO-d_6, 90 °C): 160.7, 155.1, 153.2, 139.1, 138.4, 137.9, 136.3, 128.3, 128.2, 127.8, 127.6, 127.3, 126.3 (overlapping signals), 118.4, 112.6, 63.5, 51.0; *m*/*z* (electrospray): 628 (M$^+$, 2), 539 (74), 450 (5), 225 (22), 91 (base peak).

*1,8-Dioxo-2,7-bis(4-methoxybenzyl)-4,5-bis[(4-methoxybenzyl)iminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13f**)*. Yellow crystals, mp 214–215 °C (from acetonitrile) (Found: C, 72.1; H, 5.3; N, 9.4. $C_{45}H_{41}N_5O_6$ requires C, 72.27; H, 5.53; N, 9.36%); ν_{max} KBr/cm^{-1} 3035, 2998, 2960, 2935, 2834, 1676, 1639, 1608, 1582, 1511, 1462, 1301, 1251, 1175, 1029, 823; δ_H (270 MHz, DMSO-d_6, 70 °C): 9.31 (s, 1H, H-9), 9.03 (s, 2H, CH=N), 8.51 (s, 2H, H-3 and H-6), 7.33 (d, 4H, *J* 8.6 Hz, Ar), 7.26 (d, 4H, *J* 8.6 Hz, Ar), 6.90 (d, 8H, *J* 8.6 Hz), 5.24 (s, 4H, CH_2N=), 4.75 (s, 4H, CH_2N–), 3.71 (s, 9H, OCH_3); δ_C (68 MHz, DMSO-d_6, 70 °C): 160.8, 158.8, 154.8, 153.2, 138.3, 138.0, 131.1, 129.1, 129.0, 128.7, 128.4, 118.4, 113.9, 113.6, 112.6, 63.0, 54.9, 54.8, 50.4; *m*/*z* (electrospray): 748 (M$^+$, 4), 629 (50), 121 (base peak).

*(S,S,S,S)-1,8-Dioxo-2,7-bis(1-phenylethyl)-4,5-bis-[(1-phenylethyl)iminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13g**)*. Pale brown crystals, mp 183–184 °C; $[\alpha]_D^{23}$ = +28 (*c* 0.2 in $CHCl_3$); ν_{max} KBr/cm^{-1} 3552, 3473, 3413, 2965, 1673, 1637, 1616, 1600, 1573, 1450, 1367, 1230, 698; δ_H (270 MHz, DMSO-d_6): 9.26 (s, 1H, H-9), 9.01 (s, 2H, CH=N), 8.23 (s, 2H, H-3 and H-6), 7.40–7.19 (m, 20 H, Ph), 6.17 (q, 2H, *J* 7.3 Hz, CH), 4.63 (q, 2H, *J* 6.6 Hz, CH), 1.72 (d, 6H, *J* 7.3 Hz, CH_3), 1.45 (d, 6H, *J* 6.6 Hz, CH_3); δ_C (68 MHz, DMSO-d_6): 160.8, 153.3, 153.1, 144.9, 140.0, 138.5, 135.1, 128.1–125.9 (overlapping 10 C), 118.7, 112.7, 68.1, 53.9, 24.6, 18.7; *m*/*z* (EI): 683 (M$^+$, 39), 578 (base peak), 474 (29), 370 (24), 266 (64), 105 (99) (Found: 683.3257; $C_{45}H_{41}N_5O_2$ requires 683.3260).

*1,8-Dioxo-2,7-bis(2-hydroxyethyl)-4,5-bis(2-hydroxyethyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (**13h**)*. Orange crystals, mp >300 °C (from acetonitrile) (Found: C, 59.0; H, 5.7; N, 15.9. $C_{21}H_{25}N_5O_6$ requires C, 58.86; H, 5.69; N, 15.80%); ν_{max} KBr/cm^{-1} 3392, 2927, 2863, 1668, 1635, 1604, 1580, 1466, 1355, 1335, 1060; δ_H (270 MHz, DMSO-d_6, 100 °C): 9.23 (s, 1H, H-9), 9.05 (s, 2H, CH=N), 8.40 (s, 2H, H-3 and H-6), 4.98 (t, 4H, *J* 5.5 Hz, CH_2), 4.65 (t, 4H, *J* 5.5 Hz, CH_2), 4.13 (t, 4H, *J* 5.5 Hz, CH_2), 3.92 (t, 4H, *J* 5.5 Hz, CH_2); δ_C (68 MHz, DMSO-d_6, 100 °C): 161.0, 155.5, 153.4, 140.2, 137.7, 118.2, 111.4, 63.6, 60.9, 58.6, 51.6; *m*/z (electrospray): 444 (M + 1, 6), 401 (38), 79 (base peak).

Formation of bis-imines from dialdehydes – general procedure:

The corresponding DOTTAD (1 mmol) was suspended in ethyl acetate (10 mL) and an amine (2.2 mmol) was added. The reaction mixture was stirred under reflux for 4–24 hours. The yellow precipitate formed was filtered off, washed and dried to yield a bright yellow solid. Yields are collected in Table 3 and other properties recorded below:

2,7-Dimethyl-1,8-dioxo-4,5-bis[phenyliminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14a). Yellow crystals, mp 236 °C (from ethyl acetate) (Found: C, 72.4; H, 4.8; N, 15.5. $C_{27}H_{21}N_5O_2$ requires C, 72.47; H, 4.73; N, 15.65%); ν_{max} KBr/cm^{-1} 2925, 2852, 1678, 1630, 1606, 1584, 1462, 1353, 1315,

1281, 762, 690; δ_H (270 MHz, $CDCl_3$): 9.50 (s, 1H, H-9), 9.26 (s, 2H, C*H*=N), 8.39 (s, 2H, H-3 and H-6), 7.42–7.35 (m, 4H, Ar–H), 7.27–7.20 (m, 6H, Ar), 3.65 (s, 6H, NMe); δ_C (68 MHz, $CDCl_3$): 161.8, 154.1, 153.7, 151.6, 139.8, 139.2, 129.2, 126.2, 121.5, 119.2, 113.3, 37.5; *m*/*z* (electrospray): 450 (M + 3, 5), 373 (base peak), 359 (6), 312 (13), 298 (79), 284 (7).

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis(phenyliminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14b). Yellow crystals, mp 161–162 °C (from ethyl acetate) (Found: C, 66.2; H, 5.2; N, 11.7; $C_{33}H_{31}Cl_2N_5O_2$ requires C, 66.00; H, 5.20; N, 11.66%); ν_{max} KBr/cm^{-1} 3054, 2927, 2863, 1691, 1626, 1602, 1585, 1463, 1349, 761; δ_H (270 MHz, $CDCl_3$): 9.53 (s, 1H, H-9), 9.30 (s, 2H, CH=N), 8.37 (s, 2H, H-3 and H-6), 7.42–7.37 (m, 4H, Ar–H), 7.24–7.28 (m, 6H, Ar–H), 4.10 (t, 4H, *J* 7.3 Hz, CH_2), 3.50 (t, 4H, *J* 5.9 Hz, CH_2), 2.04–1.86 (m, 8H, CH_2); δ_C (68 MHz, $CDCl_3$): 161.3, 154.1, 153.9, 151.7, 139.2, 129.2, 126.2, 121.0, 119.1, 113.5, 49.1, 44.1, 29.4, 26.7; *m*/*z* (electrospray): 601 (M + 1, 5), 555 (13), 525 (78), 464 (28), 450 (base peak), 425 (15), 350 (18), 144 (29).

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis[(4-methoxyphenyl)-iminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14c). Pale yellow crystals, mp 189 °C (from ethyl acetate) (Found: C, 63.7; H, 5.2; N, 10.7. $C_{35}H_{35}Cl_2N_5O_4$ requires C, 63.64; H, 5.34; N, 10.60%); ν_{max} KBr/cm^{-1} 2925, 2852, 1680, 1624, 1607, 1586, 1506, 1465, 1345, 1249; δ_H (270 MHz, DMSO-d_6): 9.41 (s, 3H, H-9, H-3 and H-6), 8.65 (s, 2H, CH=N), 7.32 (d, 4H, *J* 8.5 Hz, Ar–H), 7.04 (d, 4H, *J* 8.5 Hz, Ar–H), 4.25 (t, 4H, *J* 7.0 Hz, CH_2), 3.90 (s, 6H, OMe), 3.77 (t, 4H, *J* 6.3 Hz, CH_2), 2.06–1.92 (m, 8H, CH_2); δ_C (68 MHz, DMSO-d_6): 160.4, 157.5, 153.0, 152.0, 144.7, 138.9, 121.3, 118.2, 114.2, 112.5, 54.9, 47.7, 44.0, 28.7, 25.6; *m*/*z* (electrospray): 587 (4), 555 (base peak), 524 (4), 510 (4), 474 (9), 466 (14), 450 (60), 361 (5), 265 (6), 187 (28).

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis[(3-nitrophenyl)imino-methyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14d). Pale yellow crystals, mp 201 °C (from acetone) (Found: C, 57.7; H, 4.4; N, 14.0. $C_{33}H_{29}Cl_2N_7O_6$ requires C, 57.40; H, 4.23; N, 14.20%); ν_{max} Nujol/cm^{-1} 1693, 1627, 1602, 1585, 1349; δ_H (270 MHz, $CDCl_3$): 9.44 (s, 2H, CH=N), 9.28 (s, 1H, H-9), 8.82 (s, 2H, H-3 and H-6), 7.96–7.93 (m, 4H, Ar–H), 7.66 (d, 2H, *J* 7.9 Hz, Ar–H), 7.53 (t, 2H, *J* 8.2 Hz, Ar–H), 4.21 (t, 4H, *J* 7.3 Hz, CH_2), 3.71 (t, 4H, *J* 5.9 Hz, CH_2), 1.95–1.85 (m, 8H, CH_2); δ_C (68 MHz, DMSO-d6): 161.3, 159.8, 150.1, 145.4, 140.8, 138.1, 133.6, 129.8, 119.9, 118.3, 113.1, 109.7, 107.0, 48.5, 44.8, 29.1, 26.0; *m*/*z* (electrospray): 688 (M^+ − 2, 10), 675 (8), 620 (5), 574 (5), 496 (16), 464 (66), 450 (base peak), 236 (41).

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis[(1-phenylethyl)imino-methyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14e). Pale yellow crystals, mp 172 °C (from acetonitrile); $[\alpha]_D^{23}$ = + 46 (*c* 0.35 in $CHCl_3$) (Found: C, 67.4; H, 6.0; N, 10.6. $C_{37}H_{39}Cl_2N_5O_2$ requires C, 67.68; H, 5.99; N, 10.66%); ν_{max} KBr/cm^{-1} 3552, 3478, 3415, 1678, 1637, 1617, 1579, 1359; δ_H (270 MHz, $CDCl_3$): 9.58 (s, 2H, CH=N), 9.15 (s, 1H, H-9), 8.30 (s, 2H, H-3 and H-6), 7.51–7.24 (m, 10H, Ph), 4.73–4.66 (m, 2H, CH), 4.11–4.03 (m, 4H, CH_2), 3.61–3.56 (m, 4H, CH_2), 2.15–1.83 (m, 8H, CH_2), 1.68 (d, 6H, *J* 6.5 Hz, CH_3); δ_C (68 MHz, $CDCl_3$): 161.5, 153.6, 144.8, 139.5, 137.9, 128.5, 126.8, 125.6, 119.1, 113.5, 69.5, 48.9, 44.1, 29.5, 26.7, 24.5.

2,7-Diallyl-1,8-dioxo-4,5-bis[phenyliminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14f). Yellow crystals, mp 237–238 °C (from ethyl acetate); ν_{max} KBr/cm^{-1} 1677, 1625, 1604, 1580, 1463, 1353; δ_H (270 MHz, $CDCl_3$): 9.61 (s, 1H, H-9), 9.34 (s, 2H, CH=N), 8.44 (s, 2H, H-3 and H-6), 7.41–7.36 (m, 4H, Ph), 7.27–7.22 (m, 6H, Ph), 6.07–5.97 (m, 2H, allyl), 5.38–5.32 (m, 2H, allyl), 4.72–4.70 (m, 4H, allyl); δ_C (68 MHz, $CDCl_3$): 161.4, 154.4, 154.1, 151.9, 139.5, 138.8, 131.7, 129.2, 126.1, 121.1, 119.7, 119.4, 113.8, 51.5; *m*/*z* (EI): 499 (M^+, 9), 422 (100); *m*/*z* (CI): 500 (M + 1, 4), 437 (3), 287 (5), 263 (6), 257 (7), 235 (15), 201 (18), 94 (base peak), 57 (80) (Found: 499.2024; $C_{31}H_{25}N_5O_2$ requires 499.2008).

2,7-Diallyl-1,8-dioxo-4,5-bis[(4-methoxyphenyl)iminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (14g). Yellow crystals, mp 220 °C (from ethyl acetate) (Found: C, 70.6; H, 5.3; N, 12.4. $C_{33}H_{29}N_5O_4$ requires C, 70.83; H, 5.22; N, 12.51%); ν_{max} KBr/cm^{-1} 3037, 2929, 1678, 1625, 1612, 1592, 1578, 1504, 1464, 1334, 1246, 1199, 812; δ_H (270 MHz, $CDCl_3$): 9.58 (s, 1H, H-9), 9.35 (s, 2H, CH=N), 8.44 (s, 2H, H-3 and H-6), 7.28 (d, 4H, *J* 8.6 Hz, Ar), 6.92 (d, 4H, *J* 8.6 Hz, Ar), 6.11–5.97 (m, 2H, allyl), 5.35 (m, 4H, allyl), 4.74 (m, 4H, allyl), 3.91 (s, 6H, MeO); δ_C (68 MHz, $CDCl_3$): 160.9, 158.0, 153.6, 151.54, 144.5, 139.3, 137.9, 131.4, 122.0, 119.2, 118.9, 114.1, 113.5, 55.1, 51.1; *m*/*z* (electrospray): 560 (M + 1, 3), 524 (11), 510 (17), 455 (36), 350 (28), 243 (27), 144 (base peak).

Reduction of imines by catalytic hydrosilylation

General procedure: The appropriate imine (0.5 mmol) was dissolved in dry dichloromethane (5 ml) and diethylsilane (0.15 mL, 1.1 mmol) was added. The reaction mixture was deoxygenated with nitrogen for ½ h then Wilkinson's catalyst (15–20 mg) was added. The reaction mixture was stirred overnight under nitrogen. The reaction mixture was diluted with dichloromethane (10 mL) washed with water and brine, dried over magnesium sulfate and evaporated. The residue was recrystallised from acetone to give the product. Yields are collected in Table 4 and other properties recorded below:

2,7-Diallyl-1,8-dioxo-4,5-bis[(4-methoxyphenyl)amino-methyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (15a). Yellow crystals, mp 180–181 °C (from ethyl acetate); ν_{max} KBr/cm^{-1} 3548, 3473, 3413, 3650, 1660, 1631, 1579, 1513, 1463, 1249, 815; δ_H (270 MHz, $CDCl_3$): 9.69 (s, 1H, H-9), 7.39 (s, 2H, H-3 and H-6), 6.73 (d, 4H, *J* 9.2 Hz, Ar), 6.60 (d, 4H, *J* 9.2 Hz, Ar), 5.94–5.88 (m, 2H, allyl), 5.27–5.22 (m, 4H, allyl), 4.62–4.60 (m, 4H, allyl), 4.49 (s, 4H, CH_2NH), 3.72 (s, 6H, OMe); δ_C (68 MHz, $CDCl_3$): 161.4, 154.8, 152.6, 142.0, 139.7, 136.1, 132.2, 120.3, 118.7, 115.0, 114.4, 55.7, 50.5, 44.1, 29.7; *m*/*z* (EI): 563 (M^+, 27), 468 (28), 440 (100), 425 (12), 399 (65), 346 (20), 320 (44), 278 (27), 108 (28) (Found: 563.2505; $C_{33}H_{33}N_5O_4$ requires 563.2532).

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis[(4-methoxyphenyl)-aminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (15b). Yellow crystals, mp 155–156 °C (from ethyl acetate); ν_{max} KBr/cm^{-1} 3343, 2952, 2925, 2854, 1659, 1629, 1578, 1514, 1466, 1249; δ_H (270 MHz, $CDCl_3$): 9.67 (s, 1H, H-9), 7.38 (s, 2H, H-3 and H-6), 7.50 (d, 4H, *J* 8.6 Hz, Ar), 6.60 (d, 4H, *J* 8.6 Hz, Ar), 4.52 (s, 4H, CH_2NH), 4.02 (t, 4H, *J* 6.9 Hz, CH_2), 3.72 (s, 6H, OMe), 3.54 (t, 4H, *J* 5.3 Hz, CH_2), 1.93–1.74 (m, 8H, CH_2); δ_C (68 MHz, $CDCl_3$): 161.6, 154.7, 152.6, 141.9, 139.5, 136.2, 120.2, 115.0, 114.9 (overlapping signals), 55.7, 48.3, 44.3, 44.0, 29.3, 26.6; *m*/*z* (electrospray): 664 (M^+, 24), 541 (20), 401 (8), 293 (10), 257 (54), 124 (base peak), 79 (99) (Found: 663.2357; $C_{35}H_{39}Cl_2N_5O_4$ requires 663.2379).

Reductive amination of DOTTADs

General procedure: The corresponding DOTTAD (0.5 mmol) and aniline (1.1 mmol) was dissolved in dichloroethane (30 mL) under nitrogen atmosphere. At room temperature sodium triacetoxyborohydride (0.34 g, 1.6 mmol) was added and the reaction mixture was stirred until all the starting material was consumed (monitored by TLC). The dichloroethane was removed *in vacuo* and the residue was taken up in chloroform, extracted with water and brine, dried over magnesium sulfate and evaporated. The product was obtained by trituration with acetone. Yields are collected in Table 4 and other properties recorded below:

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis(phenylaminomethyl)-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (15c). Yellow crystals, mp 206 °C (from ethyl acetate); ν_{max} KBr/cm^{-1} 3399, 2937, 2854, 1656, 1631, 1602, 1579, 1498, 1461, 1313, 1278, 744; δ_H (270 MHz, DMSO-d$_6$): 9.26 (s, 1H, H-9), 7.84 (s, 2H, H-3 and H-6), 7.06–7.00 (m, 4H. Ph), 6.64–6.49 (m, 6H, Ph), 5.80–5.74 (m, 2H, NH), 4.46 (d, 2H, *J* 6 Hz, CH_2), 3.98 (t, 4H, *J* 6 Hz, CH_2), 3.61 (t, 4H, *J* 6 Hz, CH_2), 1.76–1.65 (m, 8H, CH_2); δ_C (68 MHz, CDCl3): 161.1, 154.2, 147.6, 138.7, 135.9, 128.8, 119.6, 117.2, 114.4, 112.9, 47.7, 43.9, 42.0, 28.8, 26.0; *m*/*z* (EI): 604 (M + 3, 0.23), 578 (0.4), 552 (0.5), 510 (21), 370 (48), 92 (100); (Found: 601.2011; $C_{33}H_{33}N_5O_2$ requires 601.2011).

2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis[(3-nitrophenyl)-aminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (15d). Yellow crystals, mp 154–155 °C (from ethyl acetate); ν_{max} KBr/cm^{-1} 3544, 3471, 3411, 1660, 1629, 1585, 1527, 1463, 1346; δ_H (270 MHz, DMSO-d$_6$): 9.25 (s, 1H, H-9), 7.87 (s, 2H, H-3 and H-6), 7.39 (s, 2H, Ar–H), 7.28–7.24 (m, 2H, Ar–H), 7.00 (d, 2H, *J* 7.3 Hz, ArH), 6.53 (br s, 2H, ArH), 4.48 (d, 4H, *J* 5.3 Hz, CH_2NH), 4.00 (t, 4H, *J* 7.3 Hz, CH_2), 3.60 (t, 4H, *J* 6.3 Hz, CH_2), 1.97–1.66 (m, 8H, CH_2); δ_C (68 MHz, $CDCl_3$): 161.3, 154.6, 148.4, 145.6, 139.1, 136.0, 131.7, 129.4, 116.1, 114.2, 109.4, 108.9, 47.8, 44.4, 42.1, 29.1, 27.2; *m*/*z* (EI): 693 (M$^+$, 0.055), 578 (0.38), 138 (100), 92 (99), 65 (84) (Found: 693.1900; $C_{33}H_{33}Cl_2N_7O_6$ requires 693.1869).

[*S,R,S,R*]-2,7-Bis(4-chlorobutyl)-1,8-dioxo-4,5-bis[(2′-hydroxy-1′-methyl-2′-phenylethyl)aminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (15e). Yellow crystals, mp 152 °C (from ethyl acetate) (Found: C, 65.4; H, 6.3; N, 9.6; $C_{39}H_{45}Cl_2N_5O_4$ requires C, 65.18; H, 6.31; N, 9.74%); ν_{max} KBr/cm^{-1} 3421, 3284, 2952, 2875, 1668, 1631, 1579, 1461, 701; δ_H (270 MHz, DMSO-d$_6$): 9.60 (s, 1H, H-9), 8.13 (s, 2H, H-3 and H-6), 7.45 (d, 2H, *J* 7.3 Hz, Ar–H), 7.38–7.25 (m, 6H, Ar–H), 5.45 (br s, 2H), 4.71 (d, 2H, *J* 6 Hz, C*H*OH), 4.48–4.36 (m, 4H, 2 × CH + CH_2), 4.18 (d, 2H, *J* 14.5 Hz, CH_2NH), 4.12 (t, 2H, *J* 6.3 Hz, CH_2), 3.88 (d, 2H, *J* 14.5 Hz, CH_2NH), 3.00 (t, 2H, *J* 6.3 Hz, CH_2), 2.91 (br s, 2H, CH_2), 2.23–2.19 (br m, 8H, CH_2), 1.38 (d, 6H, *J* 5.9 Hz, 2 × Me); δ_C (68 MHz, DMSO-d$_6$): 161.5, 154.2, 143.4, 137.8, 128.2, 127.9, 127.0, 126.7, 126.5, 119.3, 114.8, 76.1, 47.8, 45.4, 44.0, 31.1, 29.6, 26.6, 15.6.

[*S,R,S,R*]-2,7-Diallyl-1,8-dioxo-4,5-bis[(2′-hydroxy-1′-methyl-2′-phenylethyl)aminomethyl]-1,2,7,8-tetrahydro-2,7,10-triazaanthracene (15f). Yellow crystals, mp 176 °C (from ethyl acetate) (Found: C, 72.1; H, 6.3; N, 11.3. $C_{37}H_{39}N_5O_4$ requires C, 71.94; H, 6.36; N, 11.34%); ν_{max} KBr/cm^{-1} 3411, 3288, 3060, 2973, 2933, 2636, 1670, 1629, 1581, 1463, 1355, 701; δ_H (270 MHz, DMSO-d$_6$): 9.71 (s, 1H, H-9), 7.36 (s, 2H, H-3 and H-6), 7.26–7.18 (m, 10H, Ph-H), 6.05–5.93 (m, 2H, allyl-H), 5.36–5.27 (m, 4H, allyl-H), 4.85 (d, 2H, *J* 4.0 Hz, C*H*OH), 4.67–4.61 (m, 4H), 4.12 (q, 2H, *J* 7 Hz, C*H*Me), 4.08 (d, 2H, *J* 13.2 Hz, CH_2N), 3.93 (d, 2H, *J* 13.2 Hz, CH_2N), 0.90 (d, 6H, *J* 6.6 Hz, CH_3); δ_C (68 MHz, DMSO-d$_6$): 161.6, 154.2, 143.4, 138.8, 135.2, 129.7, 127.9, 126.7, 126.5, 116.6, 114.5, 110.4, 75.8, 51.5, 45.7, 31.4, 15.7.

Reactions with acetone

General procedure: a sample of dry, pure, recrystallised DOTTAD **5c** or **6** was stirred with a large excess of dry, redistilled acetone overnight. Removal of the solvent *in vacuo* give the pure, crystalline product in 100% yield.

2,7-Diallyl-5-(1-hydroxy-3-oxobutyl)-1,8-dioxo-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4-carbaldehyde (16a). White crystals, mp 96–97 °C (from acetone); ν_{max} KBr/cm^{-1} 3497, 3211, 1705, 1665, 1622, 1559, 1472, 1211; δ_H (270 MHz, $CDCl_3$): 11.74 (s, 1H, OH), 9.53 (s, 2H, H-9 and C*H*O), 7.83 (s, 2H, H-3 and H-6), 6.04–5.94 (m, 2H, allyl), 5.38–5.27 (m, 4H, allyl), 4.64–4.62 (m, 4H, allyl), 4.49 (t, 1H, *J* 5.3 Hz, C*H*–OH), 2.77 (d, 2H, *J* 4.7 Hz, CH_2CO), 2.20 (s, 3H, CH_3); δ_C (68 MHz, $CDCl_3$): 207.5, 187.9, 160.0, 148.5, 142.7, 131.3, 119.7, 108.2, 105.1, 50.9, 47.8, 29.4, 28.0; *m*/*z* (CI): 408 (M^{+1}, 93) (Found: 407.1486; $C_{22}H_{21}N_3O_5$ requires 407.1481).

2,7-Bis(4-chlorobutyl)-5-(1-hydroxy-3-oxo-butyl)-1,8-dioxo-1,2,7,8-tetrahydro-2,7,10-triazaanthracene-4-carbaldehyde (16b). White crystals, mp 104 °C (from acetone) (Found: C, 55.95; H, 5.1; N, 8.5; $C_{23}H_{25}Cl_2N_3O_5$ requires C, 55.88; H, 5.10; N, 8.50%); ν_{max} KBr/cm^{-1} 3556, 3490, 3216, 1706, 1668, 1625, 1565, 1475, 1288, 1205, 781; δ_H (270 MHz, DMSO-d$_6$): 11.60 (s, 1H, OH), 9.53 (s, 2H, H-9 and C*H*O), 8.54 (s, 2H, H-3 and H-6), 4.34 (t, 1H, *J* 6.3 Hz, C*H*OH), 4.05–3.91 (m, 4H, CH_2), 3.68 (t, 4H, *J* 6.3 Hz, CH_2), 2.53 (d, 2H, *J* 5.9 Hz, CH_2CO), 2.35 (s, 3H, CH_3), 1.84–1.68 (m, 8H, CH_2); δ_C (68 MHz, DMSO-d$_6$): 206.4 (*C*OMe), 189.3 (CHO), 160.6, 159.9, 156.6, 151.1, 149.0, 148.6, 142.3, 125.3, 122.2, 107.5, 104.0, 48.2 (2 × CH_2), 47.8, 44.8 (2 × CH_2), 29.7, 28.9 (2 × CH_2), 27.6, 26.1 (2 × C H$_2$); *m*/*z* (electrospray): 308 (M$^+$, 27), 464 (46), 450 (base peak), 240 (21), 163 (28).

Synthesis of macrocycles 17a and 17b

General procedure: a solution of DOTTAD **5c** or **6** (2.5 mmol) in dry dichloromethane (200 mL) was added dropwise simultaneously with a solution of 1,8-diamino-3,6-dioxaoctane (0.44 g, 3 mmol) in dichloromethane (200 mL) into a reaction vessel containing dichloromethane (400 mL). The reaction mixture was refluxed for 8 h when the solvent was removed *in vacuo* and the residue recrystallised from acetonitrile.

Compound 17a. Yield: 51%; yellow crystals, mp 167 °C; ν_{max} KBr/cm^{-1} 2861, 1677, 1639, 1606, 1579, 1463, 1359, 1326, 1116, 809; δ_H (270 MHz, DMSO-d$_6$): 9.44 (s, 1H, H-9), 9.25 (s, 2H, C*H*=N), 7.36 (s, 2H, H-3 and H-6), 6.27–6.08 (m, 2H, allyl-H), 5.46–5.41 (m, 4H, allyl-H), 4.90–4.88 (m, 4H, allyl-H), 3.95–3.90 (m, 4H), 3.87–3.82 (m, 4H), 3.74 (br s, 4H); δ_C (68 MHz, DMSO-d$_6$): 161.5, 159.3, 154.3, 139.6, 137.0, 131.8, 119.4, 115.2, 71.1–70.3 (4 × C overlapping signals), 61.0, 59.3, 51.1; *m*/*z* (EI): 461 (M$^+$, 38), 432 (17), 416 (23), 403 (13), 388 (35), 373 (80), 359 (70), 344 (base peak), 322 (37), 318 (73), 57 (85) (Found: 461.2042; $C_{25}H_{27}N_5O_4$ requires 461.2063).

Compound 17b. Yield: 45%; yellow crystals, mp 165–167 °C; ν_{max} KBr/cm^{-1} 2952, 2854, 1670, 1637, 1617, 1579, 1463, 1349, 1278, 1091; δ_H (270 MHz, $CDCl_3$): 9.66 (s, 1H, H-9), 9.23 (s, 2H), 8.06 (s, 2H), 4.10 (t, 4H, *J* 7.3 Hz), 3.90–3.86 (m, 4H), 3.79–3.74 (m, 4H), 3.62–3.57 (m, 8H), 2.01–1.85 (m, 8H); δ_C (68 MHz, $CDCl_3$): 161.7, 159.2, 139.4, 137.1, 119.3, 115.1, 48.8, 44.1, 29.5, 26.7; *m*/*z* (EI): 561 (M$^+$, 60), 549 (12), 532 (22), 518 (28), 473 (27), 446 (26), 421 (59), 231 (38), 87 (47), 63 (base peak) (Found: 561.1949; $C_{27}H_{33}N_5O_4Cl_2$ requires 561.1909).

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