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Synthetic studies related to diketopyrrolopyrrole (DPP) pigments. Part 3: Syntheses of tri- and tetra-aryl DPPs☆

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Abstract—Novel synthetic methodologies leading towards 2,3,5-triaryl- and 2,3,5,6-tetraaryl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-diones (tri- and tetra-aryl-DPPs) and their derivatives have been investigated. Direct arylation of 3,6-diphenyl-DPP was possible using 1-fluoro-2,4-dinitrobenzene. Acylation of ethyl 2-aryl-4,5-dihydro-5-oxopyrrole-3-carboxylates with *N*-arylbenzimidoyl chlorides in the presence of a strong base gives the novel 2,3,6-triaryl-DPPs together with the corresponding uncyclised enamines. A new and simple method for the synthesis of ethyl 1,2-diaryl-4,5-dihydro-5-oxopyrrole-3-carboxylates has led to an alternative route to triaryl-DPPs via reaction with benzonitrile under basic conditions, and combination of this with the benzimidoyl chloride methodology has enabled the synthesis of variously substituted 2,3,5,6-tetraphenyl-DPPs.

1. Introduction

The synthesis of derivatives of the 3,6-diphenyl-2*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione **1** (diketopyrrolopyrrole or DPP) ring system may be accomplished by several different routes, for example, reaction of dialkyl succinates or of alkyl 4,5-dihydro-5-oxo-2-phenylpyrrole-3-carboxylates (e.g., **2a**) with aromatic nitriles in the presence of a strong base such as sodium *t*-amyloxide.[1,2] Those DPPs in which both nitrogen atoms are unsubstituted (e.g., **1**) find commercial application as red pigments, not only because of their colour strength and brightness, but also because of their very low solubility in most common solvents. The low solubility results in part from the solid-state arrangement of molecules in parallel sheets, with strong intermolecular hydrogen-bonding between adjacent molecules, and the colour derives not only from the fundamental chromophore but also from π–π stacking:[3] for example, a DPP derivative such as **1** (R = Ph), which is red in the solid state, is yellow (and fluorescent) in very dilute solution in DMSO.

Similarly *N*,*N*′-disubstitution, which removes the possibility of intermolecular hydrogen bonding, not only increases the solubility but also changes the perceived colour of the solid. Dialkylation at the two nitrogens[4,5] is possible (Scheme 1), and these dialkyl derivatives **3** are fluorescent and relatively soluble in organic solvents. Direct arylation of DPPs has not until now been recorded, although *N*,*N*′-diaryl-DPPs **4** may be obtained in certain cases from the corresponding furo[3,4-*c*]furans **5** by reaction with aniline derivatives,[6] by the cyclisation of bis-anilides **6**[7] or by oxidation of a tetrahydro-DPP precursor **7**[4] with DDQ (Scheme 1). The isomeric *N*,*N*′-diarylpyrrolo[3,2-*b*]pyrroles **8** are known, and can be synthesised from arylacetic esters using bis-imidoyl chlorides as electrophiles.[8] The bis-*N*-arylimidoyl chlorides **9** react with 2 equiv of ester anions, to give the bis-imines **10a** or bis-enamines **10b**, which are cyclised to the *N*,*N*′-diaryl-pyrrolopyrroles **8**. In particular, unsymmetrical derivatives can be made via the corresponding unsymmetrical bis-imidoyl chlorides.[9] All of these methods should be adaptable to provide routes to unsymmetrically diarylated DPPs. Mono-*N*-arylated DPPs, in which the other nitrogen is unsubstituted, constitute a class of DPP derivatives which are hitherto uninvestigated. Mono-*N*-aryl-DPPs might be expected to have properties intermediate between those of the di-*NH*- and the di-*N*-aryl-DPPs, to the extent that they retain the potential to exhibit intermolecular hydrogen bonding, perhaps to form dimers in the solid state. In Part

☆ Part 2, see Ref. 10.

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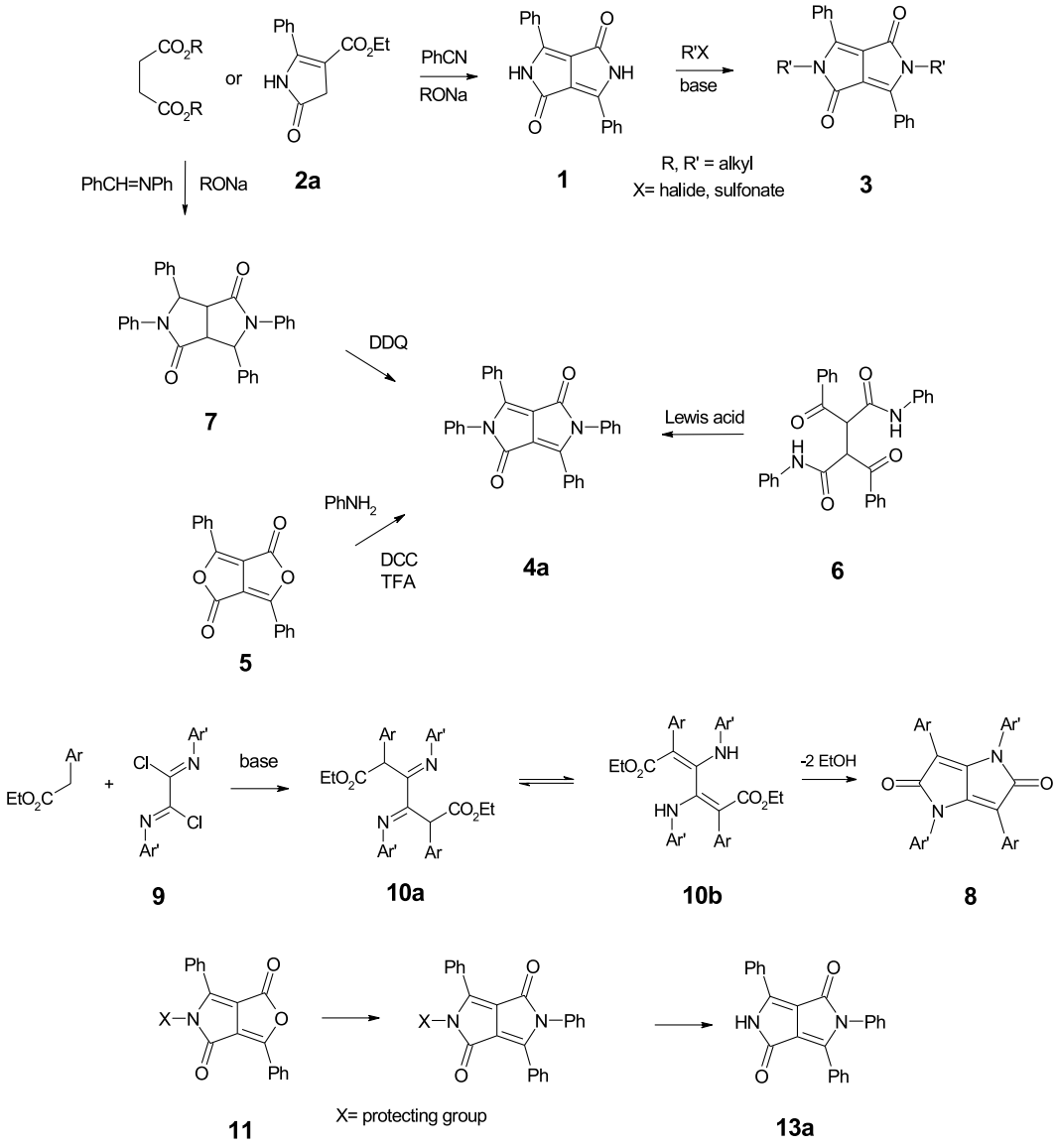


Scheme 1.

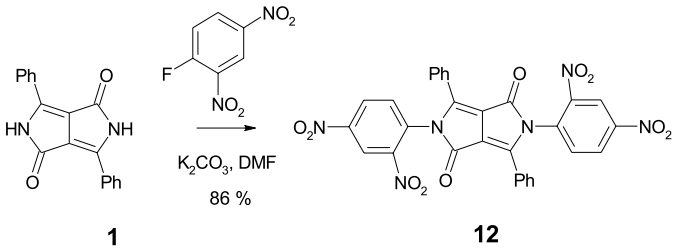
2[10] we have described what is potentially an indirect route to such compounds, although the ring-opening/ring-closure sequence which converts the furopyrrolediones **11** into DPPs requires that the nitrogen of the former be substituted,[10] and *N*-protection and deprotection would represent additional steps in such a synthesis (Scheme 1).

2. Results and discussion

2.1. Direct arylation of 3,6-diphenyl-DPP

In contrast to alkylation, direct *N*-arylation of amides is not readily accomplished without using highly electron-deficient aryl electrophiles such as 1-fluoro-2,4-dinitrobenzene. It was found that diphenyl-DPP **1** reacted with 1-fluoro-2,4-dinitrobenzene and potassium carbonate in DMF at room temperature to give the *N*,*N*′-bis-(2,4-dinitrophenyl)-DPP **12** as an orange crystalline solid in high yield (Scheme 2). It is noteworthy that this reaction typically requires reaction times of several days, and this time cannot be reduced by heating as this causes significant decomposition. The structure of compound **12** was confirmed by X-ray crystallography, which shows that the molecule crystallises with two molecules of DMF (Fig. 1). Despite the simplicity and high yields of this reaction, the four nitro groups strongly quench the fluorescence properties, rendering these compounds unsuitable for any fluorescence-based application.

In agreement with earlier observations by workers within Ciba,[11] no reaction was observed at all between compound **1** and less electrophilic arylating agents—even 1-fluoro-4-nitrobenzene. Similarly, treatment of both DPPs **1** and **13a** (see below) with iodobenzene and either copper[12,13] or palladium[14,15] catalysts under a variety of conditions and solvents gave none of the *N*-arylated products; only starting materials were recovered, presumably because of the insolubility of these substrates.



Scheme 2.

2.2. Mono-*N*-aryl-DPPs

Mono-*N*-aryl-DPPs, in which the other nitrogen is unsubstituted, have not hitherto been reported. The present paper describes two methods for the synthesis of triaryl-DPPs, the combination of which enables the synthesis of tetraaryl-DPPs in which all four aryl groups can vary independently of one another.

2.2.1. *N*-arylbenzimidoyl chlorides as electrophiles. The tetrahydro-DPPs referred to above are obtained when a Schiff base replaces the nitrile in a standard DPP synthesis. For example, the use of *N*-benzylideneaniline, PhCH=NPh, leads to compound **7**. If on the other hand the nitrile is replaced by an *N*-arylbenzimidoyl chloride, ArC(Cl)=NAr′, the mono-*N*-arylated DPP may be obtained directly. These *N*-arylbenzimidoyl chlorides, for example, **14a**–**d**, are most conveniently obtained from the corresponding benzanilides and thionyl chloride or phosphorus pentachloride.

Reaction of the ester **2a** with a strong base (sodium hydride or sodium hexamethyldisilazide) and *N*-phenylbenzimidoyl chloride **14a** in tetrahydrofuran gave a mixture of two products. The insoluble orange compound was identified by NMR and mass spectrometry as the DPP derivative **13a**, whereas work-up of the reaction solution yielded a beige compound, identified as the enamine **15a**. The corresponding reactions of compound **2a** and of its *p*-chloro-analogue **2b** with a range of *N*-arylbenzimidoyl chlorides **14a**–**d** led to a series of mono-*N*-aryl-DPPs **13a**–**d** and enamines **15a**–**d**.

Treatment of the 2,3,6-triaryl-DPPs **13a**–**d** with methyl *p*-toluenesulfonate and potassium carbonate in DMF gave the corresponding *N*-methyl analogues **16a**–**d**; likewise, treatment with benzyl bromide under the same conditions gave the *N*-benzyl derivatives **17a**–**d**. Due to the breakdown of any hydrogen bonding ability, these *N*-alkyl compounds are markedly more soluble than the *N*-unsubstituted precursors, and similarly are highly coloured and fluorescent. The triaryl derivatives **13b**,**d** also reacted with 1-fluoro-2,4-dinitrobenzene to give novel tetra-aryl-DPPs **18b**,**d**. These reactions were significantly faster than that of the unsubstituted analogue, with high yields generated after relatively short periods of time. These compounds are summarised in Table 1 and Scheme 3.

It was demonstrated in Part 2[10] that the 4-acyl derivatives of the esters **2a**,**b**, which exist substantially as the enol tautomers, underwent thermal cyclisation, either in a high-boiling solvent or in a microwave reactor, to give furo[3,4-*c*]pyrrolediones, even if the preferred geometry of the enol was *Z*. The enamines **15a**–**d**, however, were resistant to thermal cyclisation under analogous conditions: it therefore seems a reasonable hypothesis that these enamines have the *Z*-configuration. This assignment is supported, as in the enol series, by the anomalously low chemical shift ($\delta_H \sim 3.2$) of

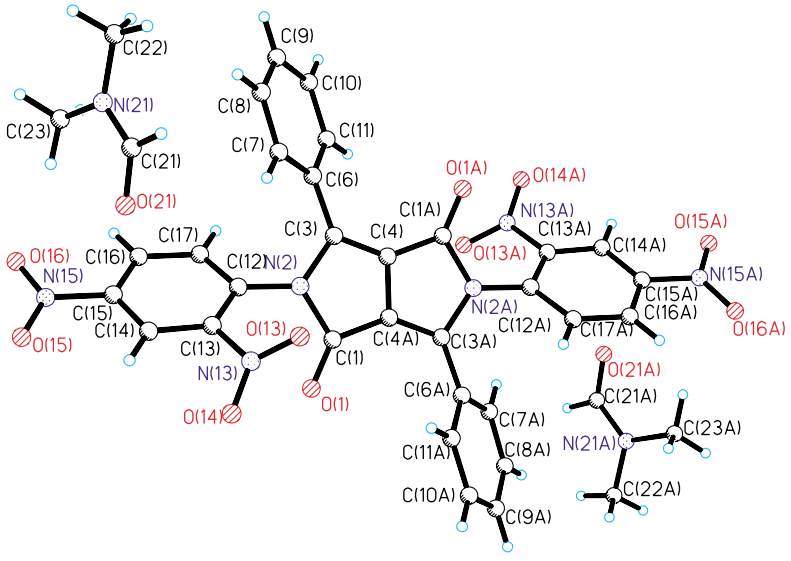
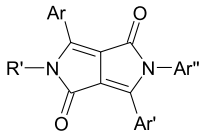


Figure 1. X-ray structure of compound **12**. Selected bond lengths (Å): C(1)–N(2), 1.439(3); N(2)–C(3), 1.413(3); C(3)–C(4), 1.371(4); C(1)–C(4A), 1.449(4); N(2)–C(12), 1.404(3); C(3)–C(6), 1.447(4); C(4)–C(4A), 1.404(5). Selected interbond angles (°): C(1)–N(2)–C(3), 111.6(2); C(1)–N(2)–C(12), 121.4(2); N(2)–C(3)–C(4), 106.1(2); C(3)–C(4)–C(1A), 140.5(2); C(4)–C(4A)–C(1), 109.0(3). Selected torsion angles (°): C(1)–N(2)–C(12)–C(13), 50.6(3); N(2)–C(3)–C(6)–C(7), 43.2(4).

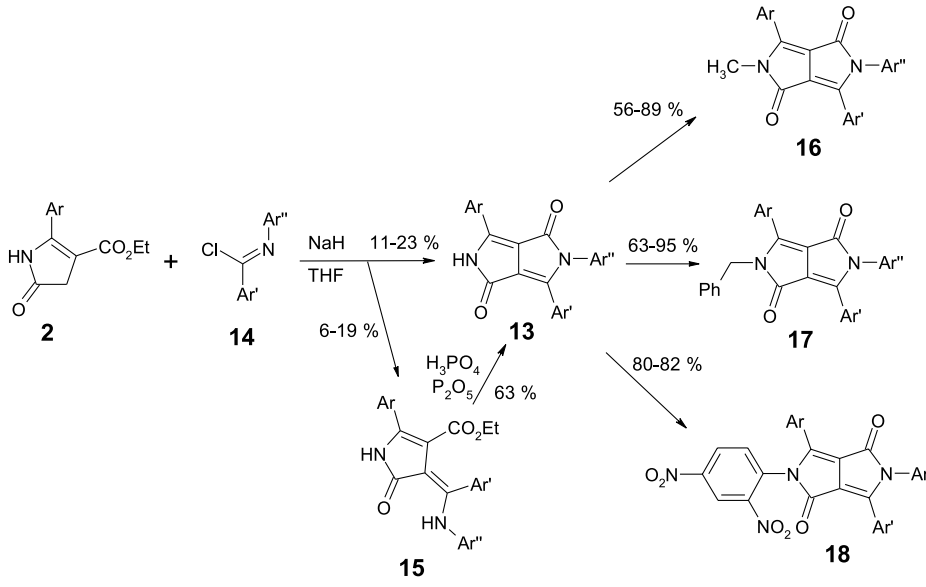
Table 1. Various DPP derivatives synthesised



Compound number	R′	Ar	Ar′	Ar″	λ_{max} abs	Log ε	Solvent	λ_{max} em	Quantum yield (%)
12	*o*/*p*-$(NO_2)_2C_6H_3$	Ph	Ph	*o*/*p*-$(NO_2)_2C_6H_3$	470	4.33	DMSO	516	2
13a	H	Ph	Ph	Ph	498	4.23	DMSO	520	44
					470	4.21			
13b	H	Ph	Ph	*p*-$MeOC_6H_4$	500	4.20	DMSO	521	3
					472	4.17			
13c	H	Ph	Ph	*p*-$F_3CC_6H_4$	493	4.19	DMSO	519	43
					467	4.17			
13d	H	*p*-ClC_6H_4	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	511	4.46	DMSO	532	9
					481	4.43			
16a	CH_3	Ph	Ph	Ph	468	4.11	DCM	521	43
16b	CH_3	Ph	Ph	*p*-$MeOC_6H_4$	471	4.19	DCM	522	23
16c	CH_3	Ph	Ph	*p*-$F_3CC_6H_4$	470	4.11	DCM	520	48
16d	CH_3	*p*-ClC_6H_4	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	487	4.18	DCM	533	15
17a	CH_2Ph	Ph	Ph	Ph	468	4.11	DCM	519	42
17b	CH_2Ph	Ph	Ph	*p*-$MeOC_6H_4$	470	4.27	DCM	522	27
17c	CH_2Ph	Ph	Ph	*p*-$F_3CC_6H_4$	468	4.12	DCM	518	43
17d	CH_2Ph	*p*-ClC_6H_4	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	488	4.28	DCM	532	5
18b	*o*/*p*-$(NO_2)_2C_6H_3$	Ph	Ph	*p*-$MeOC_6H_4$	470	4.26	DMSO	515	0
18d	*o*/*p*-$(NO_2)_2C_6H_3$	*p*-ClC_6H_4	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	483	4.43	DMSO	513	0
4a	Ph	Ph	Ph	Ph	488	4.27	*o*-$Cl_2C_6H_4$	524	29
4b	Ph	Ph	Ph	*p*-$MeOC_6H_4$	490	4.24	*o*-$Cl_2C_6H_4$	520	12
4c	Ph	Ph	Ph	*p*-$F_3CC_6H_4$	486	4.29	*o*-$Cl_2C_6H_4$	520	32

the ester methylene protons, and was confirmed unambiguously for **15b**,**d** by X-ray crystallography (see Figs. 4 and 5). It seems also reasonable to suggest that the reaction of the esters **2a**,**b** with the imidoyl chlorides **14a–d** gives initially both *E* and *Z*-enamines, that the former undergo spontaneous cyclisation to the DPPs **13a–d** and that the enamines undergo *Z*→*E* transformation much less easily than the corresponding enols. Cyclisation of the enamines **15a–d** was, however, promoted by treatment with polyphosphoric acid.

These triaryl-DPPs **13a–d** appear amorphous to the naked eye when crystallisation is attempted from most solvents; however, in the case of the *N*-*p*-methoxyphenyl-DPP **13b**,



13-18: a) Ar = Ar′ = Ar″ = Ph
b) Ar = Ar′ = Ph, Ar″ = *p*-$MeOC_6H_4$
c) Ar = Ar′ = Ph, Ar″ = *p*-$CF_3C_6H_4$
d) Ar = *p*-ClC_6H_4, Ar′ = *p*-BrC_6H_4, Ar″ = *p*-$MeOC_6H_4$

Scheme 3.

crystals suitable for X-ray analysis were obtained from acetic acid. These did not contain dimers, but showed hydrogen bonding between the amidic moiety of the DPP and the carboxyl group of acetic acid (Fig. 2). The compound was efflorescent, however, solvent being lost from the surface molecules during the drying process in vacuo, so that the analytical sample contained a non-stoichiometric proportion of acetic acid. The crystal structure of the *N*-methyl analogue **16b** could also be solved (Fig. 3). Similarly, when the enamine **15d** was crystallised from acetic acid, the crystal structure showed hydrogen bonding between the amide and acetic acid (Fig. 4). However, when the enamine **15b** was crystallised from ethanol, the crystal structure showed that there was hydrogen bonding between two molecules resulting in a dimeric structure (Fig. 5). The crystal structures of both these enamines showed the geometry of the enamine double bond to be *Z*, that is, with hydrogen bonding of the enamine N–H to the ring carbonyl oxygen.

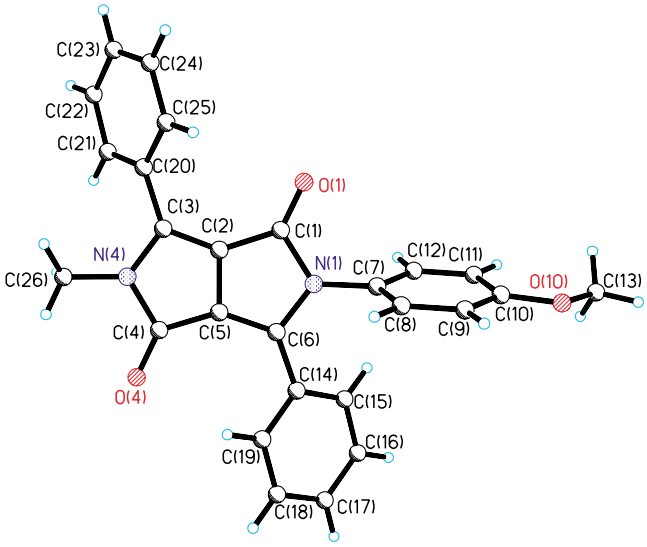


Figure 3. X-ray structure of compound **16b**. Selected bond lengths (Å): C(1)–C(2), 1.4522(17); C(1)–O(1), 1.2169(16); C(1)–N(1), 1.4360(16); C(2)–C(3), 1.3782(17); C(2)–C(5), 1.4248(18); C(3)–C(20), 1.4653(18); C(3)–N(4), 1.3917(16); N(4)–C(26), 1.4564(15). Selected interbond angles (°): C(1)–C(2)–C(3), 141.28(12); C(1)–N(1)–C(6), 111.24(10); C(1)–C(2)–C(5), 108.60(11); C(3)–N(4)–C(26), 127.55(10). Selected torsion angles (°): C(1)–N(1)–C(7)–C(12), −86.42(16); C(2)–C(3)–C(20)–C(25), −31.1(2); C(5)–C(6)–C(14)–C(19), −33.7(2).

2.2.2. Syntheses from *N*-arylpyrrolinones. All the previous reactions in our DPP-related investigations have started with pyrrolinones **2a**,**b**, and access to the *N*-aryl analogues of these would in principle enable the synthesis of tetra-aryl-DPP derivatives. According to Caballero and co-workers,[16] enamines analogous to **19** undergo reaction with glyoxal, at room temperature in methanol, to give cyclised pyrrolin-5-ones. Accordingly, the enamine **19** was prepared by condensation of ethyl benzoylacetate with aniline (Scheme 4), and X-ray crystallography showed this to have the *Z*-configuration (Fig. 6). However, in our hands no reaction at all was observed between **19** and glyoxal or glyoxal trimeric hydrate in various solvents and temperatures, but the enamine **19** reacted successfully with oxalyl chloride in ether, as reported in the literature, to give the known pyrroledione **20**.[17] Reaction of the enamine **19** with chloroacetyl chloride did not, however, give a pyrrolinone; only one of the chlorines was displaced and the product had spectroscopic properties consistent with its formulation as **21** (or its *Z*-isomer). Despite the fact[18] that *N*-alkyl analogues of **21** are cyclised in base to pyrrol-4-ones, attempts to effect the cyclisation of **21** to **22**, either thermally or in the presence of acid or base, were unsuccessful.

The corresponding oxygen analogue of the required pyrrolinones, ethyl 5-oxo-2-phenyl-4,5-dihydrofuran-3-carboxylate **23**, is known in the literature, and is synthesised by cyclisation of the acid **24** formed by alkylating ethyl benzoylacetate with bromoacetic acid.[27] This furanone **23** reacted with aniline to give a crystalline solid, whose structure was determined by X-ray crystallography (Fig. 7) to be the ring-opened amide, ethyl 2-benzoyl-*N*-phenylsuccinamate **25**. In Part 2,[10] we reported that reaction of aniline with 3,6-diphenylfuro[3,4-*c*]pyrrole-1,4-dione gave a

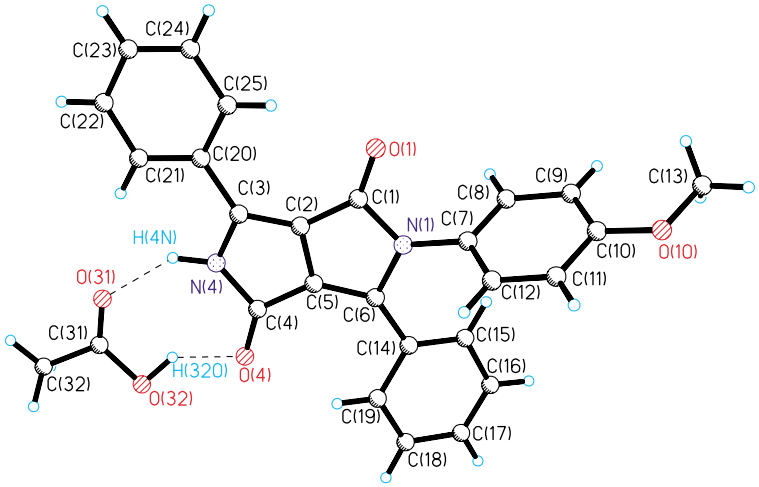


Figure 2. X-ray structure of compound **13b**. Selected bond lengths (Å): C(1)–C(2), 1.454(18); C(1)–O(1), 1.237(16); C(1)–N(1), 1.440(17); C(2)–C(3), 1.364(16); C(2)–C(5), 1.399(16); C(3)–C(20), 1.457(18); C(3)–N(4), 1.325(18); N(4)–O(31), 2.849(14); O(4)–O(32), 2.585(14); C(31)–O(31), 1.171(19); C(31)–O(32), 1.308(19). Selected interbond angles (°): C(1)–C(2)–C(3), 142.8(16); C(1)–N(1)–C(6), 111.9(12); C(1)–C(2)–C(5), 106.7(12). Selected torsion angles (°): C(1)–N(1)–C(7)–C(8), −75.2(16); C(2)–C(3)–C(20)–C(21), −179.6(15); C(5)–C(6)–C(14)–C(15), 149.6(16).

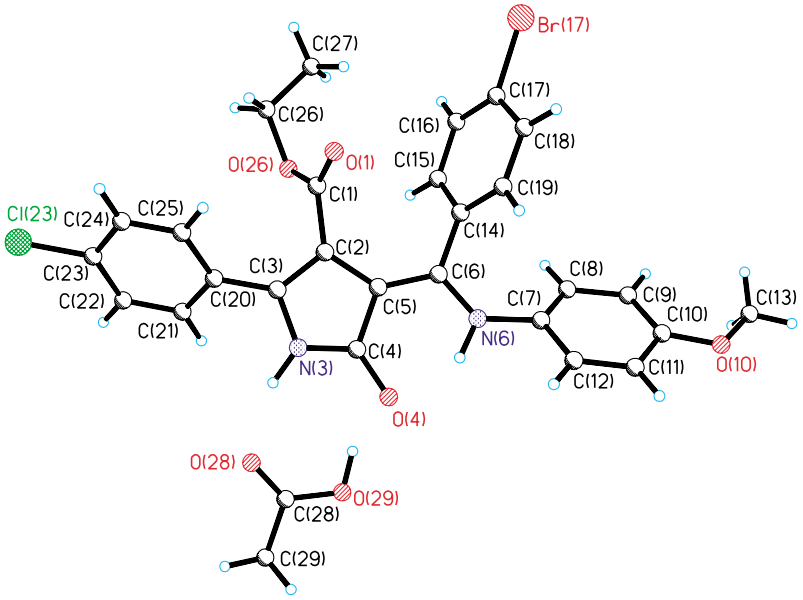


Figure 4. X-ray structure of compound **15d**. Selected bond lengths (Å): C(2)–C(3), 1.373(17); C(2)–C(5), 1.435(17); C(5)–C(6), 1.392(18); C(6)–N(6), 1.332(16); N(6)–O(4), 2.670(14); N(3)–O(28), 2.813(14); O(4)–O(29), 2.571(12). Selected interbond angles (°): N(3)–C(3)–C(2), 108.0(11); C(2)–C(5)–C(6), 134.5(11); C(5)–C(6)–N(6), 119.2(12); C(6)–N(6)–C(7), 132.3(11). Selected torsion angles (°): C(2)–C(3)–C(20)–C(21), 140.5(13); O(4)–C(4)–C(5)–C(6), 3(2); O(1)–C(1)–C(2)–C(3), 121.8(14); C(5)–C(6)–C(14)–C(15), −47.9(18); C(6)–N(6)–C(7)–C(8), −41(2).

ring-opened and decarboxylated product, indicating that attack of aniline takes place at the alkene carbon. This is in contrast to the product reported here, which clearly indicates aniline attack at the lactone carbonyl. It was found that treatment of this acyclic amide with acid promoted cyclisation to the corresponding ethyl 4,5-dihydro-5-oxo-1,2-diphenylpyrrole-3-carboxylate **26a**, and in fact treatment of furanone **23** with aniline in acetic acid gives the *N*-phenylpyrrolinone **26a** directly (Scheme 5). The structure of this compound was confirmed by X-ray crystallography (Fig. 8), which indicates clearly the presence of a localised C(2)–C(3) double bond and a C(3)–C(4) single bond in the ring system. The furanone **23** was also reacted with *p*-anisidine and *p*-aminobenzotrifluoride to give two further pyrrolinones **26b**,**c**.

Like the *N*-unsubstituted pyrrolinones **2a**,**b**, the novel *N*-phenylpyrrolinone **26a** may be readily *C*-acylated by

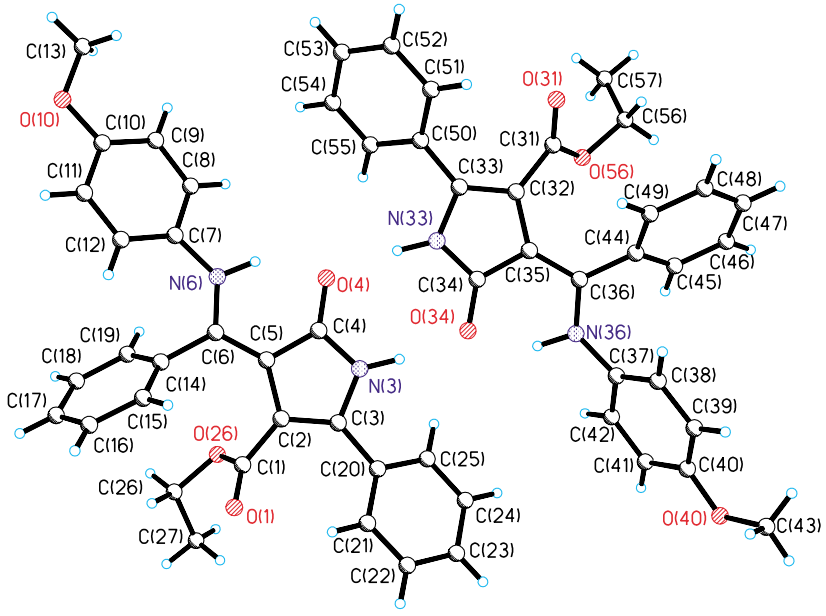
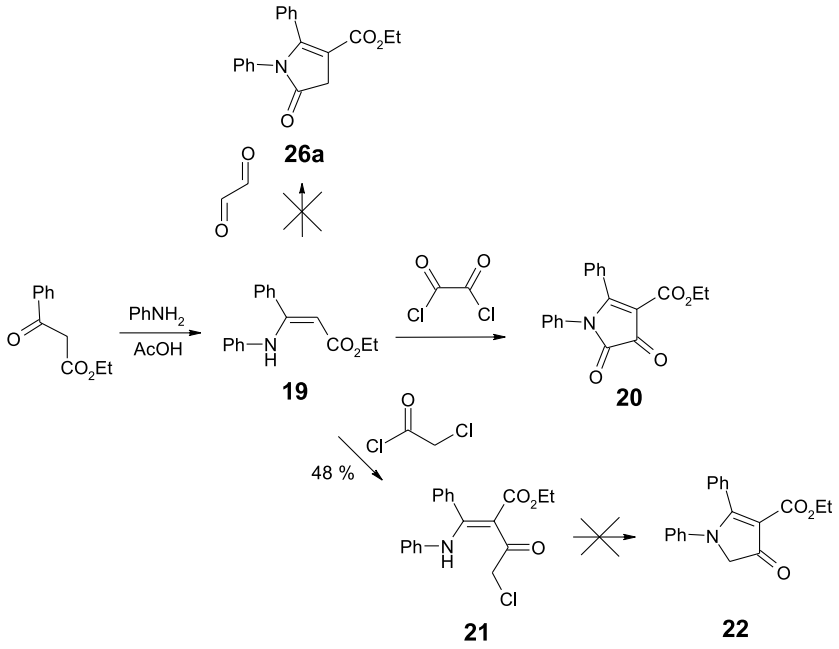


Figure 5. X-ray structure of compound **15b**. Selected bond lengths (Å): C(2)–C(3), 1.376(4); C(2)–C(5), 1.460(4); C(5)–C(6), 1.399(4); C(6)–N(6), 1.350(3); N(3)–O(34), 2.808(3); N(6)–O(4), 2.654(3). Selected interbond angles (°): N(3)–C(3)–C(2), 108.0(2); C(2)–C(5)–C(6), 132.2(2); C(5)–C(6)–N(6), 116.9(2); C(6)–N(6)–C(7), 132.2(2). Selected torsion angles (°): C(2)–C(3)–C(20)–C(21), −41.9(5); O(4)–C(4)–C(5)–C(6), −0.1(5); O(1)–C(1)–C(2)–C(3), 60.6(4); C(5)–C(6)–C(14)–C(15), 57.0(4); C(6)–N(6)–C(7)–C(8), −160.9(3).



Scheme 4.

treatment with benzoyl chloride and lithium hexamethyldisilazide to give the acylated product **27**, which presumably adopts the same *Z*-enol configuration as in the *N*-unsubstituted series (methylene chemical shift of ~3.5 ppm). This acylated compound may then be cyclised to the corresponding furopyrrole **28** by heating to around 200 °C in a microwave reactor. This furopyrrole has been synthesised previously, albeit in very low yield, by Langhals and co-workers[6] using a different method: this new method represents a far more efficient synthetic route to the same compound, which in turn can be converted into the tetraphenyl-DPP **4** (Scheme 6). This overall strategy for tetra-aryl DPP synthesis constitutes a versatile method, in which all four aryl groups can be selected independently from one another. Similarly to the furopyrroles reported in Part 2, in the absence of any carbodiimide coupling reagent the furopyrrole **27** undergoes attack of aniline at the alkenyl carbon, giving the decarboxylated product **29**.

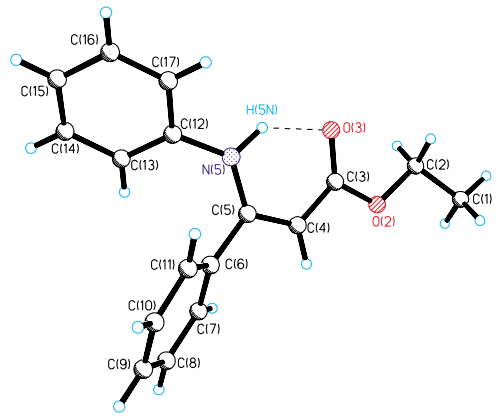


Figure 6. X-ray structure of compound **19**.

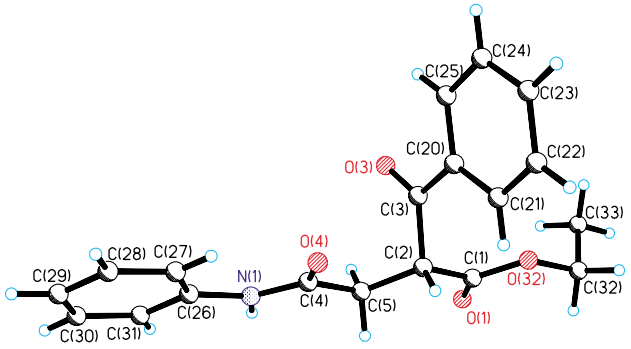


Figure 7. X-ray structure of compound **25**. Selected bond lengths (Å): C(1)–C(2), 1.5249(17); C(2)–C(3), 1.5481(17); C(3)–O(3), 1.2180(15).

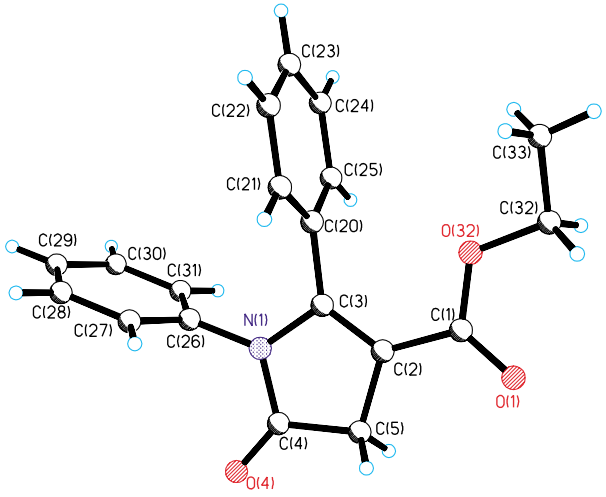
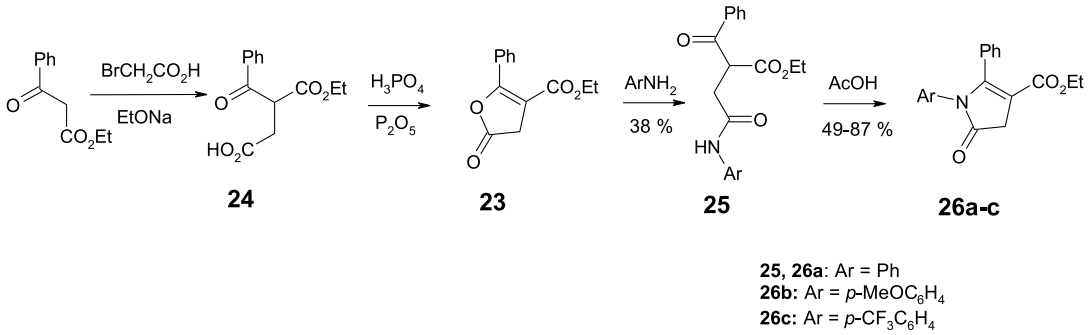


Figure 8. X-ray structure of compound **26a**. Selected bond lengths (Å): C(1)–C(2), 1.459(2); C(2)–C(3), 1.348(2); N(1)–C(3), 1.414(2); N(1)–C(4), 1.387(2); C(4)–C(5), 1.508(2); C(2)–C(5), 1.506(2). Selected interbond angles (°): C(3)–C(2)–C(5), 109.30(14); N(1)–C(4)–C(5), 107.02(14); C(4)–C(5)–C(2), 103.16(13); C(4)–N(1)–C(3), 110.64(13); N(1)–C(3)–C(2), 109.88(14). Selected torsion angles (°): C(3)–N(1)–C(26)–C(27), −95.7(2); C(2)–C(3)–C(20)–C(21), −94.8(2); C(5)–C(2)–C(1)–O(1), −4.5(2).



Scheme 5.

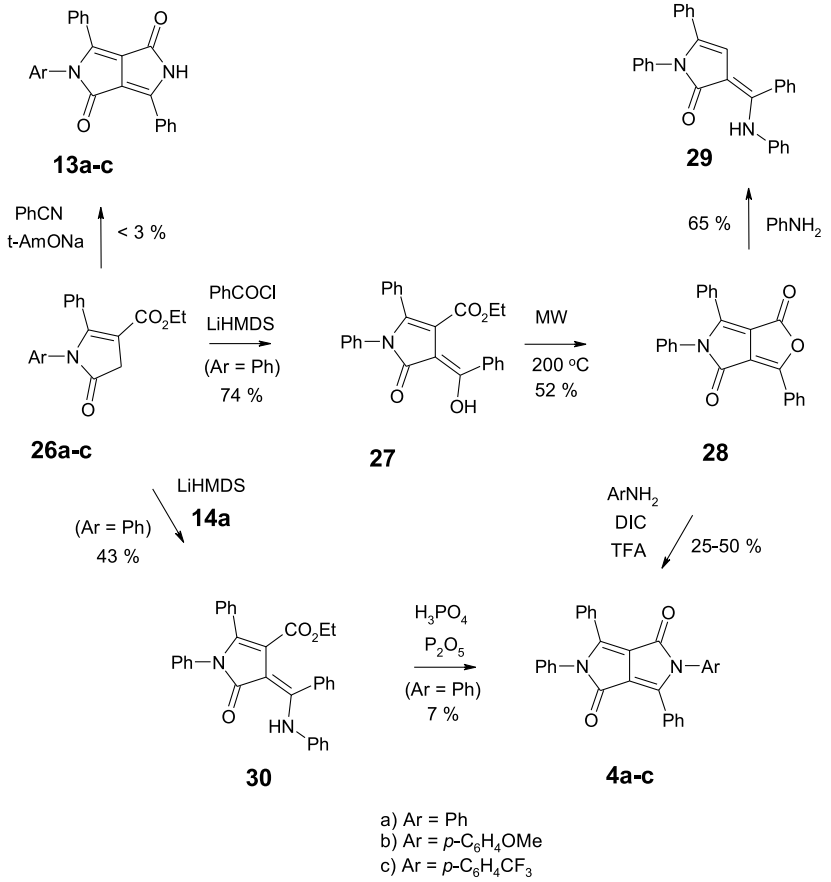
In the standard synthesis of DPPs, either a dialkyl succinate or the pyrrolinone **2a** is reacted with an aromatic nitrile and a strong base such as sodium *t*-amyloxide. Similarly, the *N*-phenylpyrrolinone **26a** when treated with benzonitrile and heated with sodium *t*-amyloxide in *t*-amyl alcohol, gave the triphenyl-DPP **13a**, albeit in low yield. This same method using *N*-arylpyrrolinones **26b**,**c** gave the triaryl-DPPs **13b**,**c**, identical with those obtained as in Section 2.2.1. Although product **13b** could be identified by TLC, yields were so low that the product could not be isolated.

2.3. Reaction of *N*-arylpyrrolinones with imidoyl chlorides to give tetraaryl-DPPs

Similarly to the reaction of pyrrolinones **2a**,**b**, the *N*-phenylpyrrolinone **26a** reacts with *N*-phenylbenzimidoyl chloride and sodium hexamethyldisilazide to give the uncyclised enamine **30**. Unlike the reactions of the pyrrolinone **2a**,**b**, however, no DPP was detected in this reaction mixture and cyclisation of **30** could not be promoted by treatment with base or by heating (either conventionally or by microwave irradiation). However, cyclisation to the tetraphenyl-DPP **4** did occur by heating in the presence of polyphosphoric acid (Scheme 6).

3. Spectroscopic properties of these compounds

A variety of both symmetrical and unsymmetrical *N*-substituted DPPs have been synthesized in the present work. Analysis of the visible absorption spectra of these compounds gives some interesting results. A comparison



Scheme 6.

of compounds **13a–d** reveals that substitution of the *N*-phenyl ring with either an electron-donating methoxy substituent or electron-withdrawing trifluoromethyl substituent does little to change either the absorption wavelength maximum or the extinction coefficient, values differing by only 2–6 nm from those of the unsubstituted **13a** (498 and 470 nm). This is in contrast to values reported in Part 2 of this series, where it was reported that substitution on the *C*-aryl ring resulted in shifts of up to 30 nm. This clearly implies that the *N*-phenyl rings are not nearly as conjugated to the chromophore as the *C*-aryl rings, their substitution affecting absorption wavelengths only marginally. This is repeated in compounds **16a–d**, **17a–d** and **18b**,**d**, again showing that the strongly electron-withdrawing 2,4-dinitrophenyl group does little to change the absorption maxima. Additionally, the fluorescence emission maxima change only marginally upon *N*-aryl substitution, although quantum yields decrease markedly upon the introduction of electron-donating (*p*-OMe) or highly electron-withdrawing groups [*o*,*p*-$(NO_2)_2$].

4. Conclusion

We have reported herein various methods for the synthesis of both symmetrical and unsymmetrical *N*-arylated DPPs. *N*-arylbenzimidoyl chlorides have been used as electrophiles in a two-step, one-pot synthesis of novel triaryl-DPPs. *N*-arylpyrrolinones have been produced via the corresponding furanones, thus providing new routes to *N*-aryl- and *N*,*N*′-diaryl-DPPs, via the corresponding furopyrrole and enamine intermediates. Using these methods it is now possible for the first time to synthesise DPPs with a diverse range of *N*- and *C*-aryl substituents.

5. Experimental

5.1. General

Melting points in excess of 300 °C were recorded using differential scanning calorimetry (DSC). FT-IR spectra of solids were recorded for Nujol mulls, and those of liquids were recorded for thin films; frequencies are expressed in cm^{-1}. Unless otherwise indicated, UV–visible spectra were recorded (wavelengths expressed in nm) for solutions in dichloromethane, and ^1H and ^{13}C NMR spectra were obtained at 300 and 75.4 MHz, respectively, for solutions in $CDCl_3$ (or, where indicated, DMSO-d_6). Chemical shifts (δ) are expressed relative to $SiMe_4$ ($\delta_H=\delta_C=0$) and coupling constants (J) in Hz. ^{13}C assignments were supported, where necessary, using the PENDANT sequence. Mass spectra and accurate mass measurements were obtained using electron impact (EI) ionisation at 70 eV, or electrospray ionization (ESI) with a Micromass LCT instrument. The microwave reactor was a CEM Discover™ model, with a circular single mode cavity design and a maximum operating power of 300 W; the samples were contained in sealed glass tubes, whereby the pressure was allowed to increase to a maximum of 2.07 MPa (300 psi). 'Ether' refers to diethyl ether and 'petrol' to the fraction of bp 40–60 °C. Ethyl 4,5-dihydro-5-oxo-2-phenylpyrrole-3-carboxylate **2a**[2] and its *p*-chlorophenyl analogue **2b**[10] were prepared as previously described. Fluorescence quantum yields were measured relative to perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt[19] (compounds **12**, **4a–c**), with quantum yield 1.0 or *N*,*N*′-bis(butylpentyl)-3,4,9,10-perylenebis(dicarboximide)[20] (compounds **13a–d**, **16a–d**, **17a–d**, **18b**,**d**), assumed quantum yield of 100%.

5.1.1. 2,5-Bis-(2,4-dinitrophenyl)-DPP 12. DPP **1** (200 mg, 0.69 mmol) was stirred with potassium carbonate (383 mg, 2.77 mmol) and 1-fluoro-2,4-dinitrobenzene (517 mg, 349 μl, 2.77 mmol) in DMF (20 cm^3) for 4 days at room temperature. Water was added, and the precipitate filtered off and washed with water. Recrystallisation from DMF gave the DPP **12** as an orange solid (369 mg, 86%), mp 373–376 °C. (Found: C, 56.35; H, 3.65; N, 14.6. $C_{36}H_{30}N_8O_{12}$ (+2 DMF) requires C, 56.4; H, 3.9; N, 14.6%). υ_{max} 1710 (C=O), 1670 (DMF C=O), 1530 and 1350 (NO_2). δ_H (DMSO-d_6) 7.32–7.64 (10H, m, Ph), 7.80 and 7.88 (2×1H, d, $J=8.6$ Hz, 6-Ar-H), 8.51 and 8.60 (2×1H, dd, $J=8.6$, 2.6 Hz, 5-Ar-H), 8.84 and 8.90 (2×1H, d, $J=2.6$ Hz, 3-Ar-H).

5.1.2. *N*-Phenylbenzimidoyl chloride 14a. Benzanilide (1.0 g, 5.08 mmol) and thionyl chloride (8.19 g, 5.0 cm^3) were stirred at 65 °C for 2 h, and the excess of thionyl chloride was then removed by distillation. The crude product was then heated with hexane, filtered, and the filtrate evaporated, to give the imidoyl chloride, mp 38–39 °C (lit.[21]: 38–40 °C), in almost quantitative yield. δ_H 6.91–6.96 (2H, m), 7.09–7.15 (1H, m), 7.25–7.50 (5H, m), and 8.05–8.11 (2H, m). The imidoyl chloride was used in subsequent reactions without further purification.

5.1.3. *N*-(*p*-Methoxyphenyl)benzimidoyl chloride 14b. This was similarly obtained from *N*-(*p*-methoxyphenyl)-benzamide[22] (1.0 g, 4.4 mmol) and thionyl chloride (8.15 g, 5.0 cm^3), and had mp 58–60 °C (lit.,[23] 58.5–59.5 °C) δ_H 3.84 (3H, s, OCH_3), 6.95 and 7.08 (each 2H, AA′BB′, *p*-$MeOC_6H_4$), 7.43–7.57 (3H, m, *m*- and *p*-Ph-H), and 8.14–8.18 (2H, m, *o*-Ph-H).

5.1.4. *N*-(*p*-Trifluoromethylphenyl)benzimidoyl chloride 14c. This was similarly obtained from *N*-(*p*-trifluoromethylphenyl)benzamide, mp 207–210 °C (from ethanol; lit.,[24] 205–206 °C) (2.0 g, 7.55 mmol), phosphorus pentachoride (1.57 g, 7.55 mmol) and thionyl chloride (20 cm^3), mp 100–103 °C (known,[25] but no lit. mp recorded). δ_H 7.08 (2H, half of AA′BB′, Ar-H), 7.46–7.62 (3H, m, Ph-*m*/*p*-H), 7.67 (2H, half of AA′BB′, Ar-H) and 8.19 (2H, m, Ph-*o*-H).

5.1.5. *N*-(*p*-Methoxyphenyl)-*p*-bromobenzimidoyl chloride 14d. This was similarly obtained from *N*-(*p*-methoxyphenyl)-*p*-bromobenzamide[26] (2.0 g, 6.54 mmol) and thionyl chloride (10 cm^3) and was used without further purification, mp 104–107 °C. υ_{max} 1735 (C=N). δ_H 3.77 (3H, s, CH_3), 6.88 and 7.01 (each 2H, AA′BB′, *p*-$MeOC_6H_4$), 7.53 and 7.95 (each 2H, AA′BB′, *p*-BrC_6H_4). δ_C 157.9 (quat), 141.0 [C(Cl)=N],[†] 140.2 (quat), 135.1 (quat), 132.0 (2×CH), 131.2 (2×CH), 127.1 (quat), 123.0 (2×CH), 114.5 (2×CH) and 55.8 (CH_3).

[†] Provisional assignment.

5.1.6. 2,3,6-Triphenyl-DPP 13a. (a) The pyrrolinone ester **2a** (1.0 g, 4.33 mmol) was added to sodium hydride (866 mg, 21.7 mmol) in THF (50 cm^3), and the mixture was stirred at room temperature for 30 min. To this was added the imidoyl chloride **14a** (0.93 g, 4.33 mmol), the mixture stirred at room temperature overnight, then acidified (HCl) and the orange precipitate filtered off, to give 2,3,6-triphenyl-DPP **13a** (362 mg, 23%).

(b) The *N*-phenylpyrrolinone ester **26a** (see below) (663 mg, 2.16 mmol) and benzonitrile (446 mg, 440 μl, 4.3 mmol) were added successively to a solution of sodium *t*-amyloxide [from sodium (150 mg, 6.5 mmol) and *t*-amyl alcohol (4.0 cm^3)], and the mixture heated to reflux for 6 h. The mixture was then cooled, acidified (HCl), and extracted with dichloromethane. The organic extracts were then dried and the solvent evaporated. Precipitation from methanol followed by filtration gave the triphenyl-DPP as a bright orange solid (18 mg, 3%).

(c) The enamine **15a** (200 mg, 0.549 mmol) was mixed with polyphosphoric acid (5.0 cm^3), and the mixture heated to 120 °C for 1 h. Water was added and the precipitate filtered and washed with ethanol, to give the pyrrolopyrrole (111 mg, 63%), mp 389 °C. (Found: C, 79.0; H, 4.3; N, 7.7. $C_{24}H_{16}N_2O_2$ requires C, 79.1; H, 4.4; N, 7.7%). υ_{max} 3160 (NH), 1670 (C=O), 1610; δ_H (DMSO-d_6) 7.29–7.33 (2H, m, Ar-H), 7.38–7.54 (6H, m, Ar-H), 7.57–7.67 (5H, m, Ar-H), 8.49–8.53 (2H, m, Ar-H), 11.54 (1H, s, NH). *m/z* (ESI −ve): 364 (30%, $M^{+\cdot}$) and 363 [100%, $(M-H)^+$].

5.1.7. 2-(*p*-Methoxyphenyl)-3,6-diphenyl-DPP 13b. NaHMDS (67 cm^3 of 1 M THF solution, 67 mmol) and the pyrrolinone ester **2a** (4.83 g, 20.9 mmol) in THF (200 cm^3) were stirred at room temperature for 30 min. The solid imidoyl chloride **14b** (5.13 g, 20.9 mmol) was then added, and the mixture stirred at room temperature overnight, then acidified (HCl) and the orange precipitate filtered off, to give **13b** as an orange solid (1.42 g, 18%), mp 368 °C (from *o*-$Cl_2C_6H_4$). [Found: C, 73.6; H, 4.0; N, 6.65. $C_{25}H_{18}N_2O_3$ (4:1 ratio with *o*-$C_6H_4Cl_2$) requires C, 73.8; H, 4.4; N, 6.5%.] $\upsilon_{max.}$3150 (NH), 1680 (C=O), 1620 (C=C). δ_H (DMSO-d_6) 3.85 (3H, s, OCH_3), 7.01 and 7.21 (each 2H, AA′BB′, C_6H_4), 7.36–7.45 (3H, m, Ar-H), 7.57–7.63 (5H, m, Ar-H), 8.49–8.54 (2H, m, Ar-H) and 11.52 (1H, s, NH). *m/z* (ESI −ve): 394 (30%, $M^{+\cdot}$) and 393 [100%, $(M-H)^+$].

5.1.8. 3,6-Diphenyl-2-(*p*-trifluoromethylphenyl)-DPP 13c. To sodium hydride (1.69 g, 70.5 mmol) was added THF (300 cm^3), followed by the pyrrolinone **2a** (4.07 g, 17.6 mmol), and the mixture was stirred at room temperature for 30 min. To this was added the imidoyl chloride **14c** (5.0 g, 17.6 mmol), and the mixture stirred at room temperature for 1 week. The mixture was then acidified (HCl) and the precipitate filtered off, to give the triaryl-DPP **13c** as an orange solid (854 mg, 11%), mp 377 °C. (Found: C, 69.6; H, 3.8; N, 6.3. $C_{25}H_{15}F_3N_2O_2$ requires C, 69.4; H, 3.5; N, 6.5%). δ_H (DMSO-d_6) 7.36–7.64 (10H, m, Ar-H), 7.78–7.84 (2H, m, Ar-H) 8.46–8.51 (2H, m, Ar-H) and 11.56 (1H, s, NH). *m/z* (ESI −ve): 432 (28%, $M^{+\cdot}$) and 431 [100%, $(M-H)^+$].

5.1.9. 3-*p*-Bromophenyl-6-*p*-chlorophenyl-2-*p*-methoxyphenyl-DPP 13d. To sodium hydride (0.79 g, 19.75 mmol) was added THF (200 cm^3), followed by the pyrrolinone ester **2b** (1.64 g, 6.17 mmol), and the mixture was stirred at room temperature for 30 min. To this was added the imidoyl chloride **14d** (2.00 g, 6.17 mmol), and the mixture stirred at room temperature for 48 h. The mixture was then acidified (HCl) and the precipitate filtered, to give the triaryl-DPP **13d** as an orange solid (452 mg, 15%), mp 372 °C. (Found: C, 59.2; H, 3.1; N, 5.6. $C_{25}H_{16}BrClN_2O_3$ requires C, 59.1; H, 3.2; N, 5.5%). δ_H (DMSO-d_6) 3.59 (3H, s, OCH_3), 6.80 and 6.99 (each 2H, AA′BB′, Ar-H), 7.28 and 7.42 (each 2H, AA′BB′, Ar-H), 7.49 and 8.30 (each 2H, AA′BB′, Ar-H) and 11.33 (1H, s, NH). *m/z* (EI): 506/508/510 (27/100/74%, $M^{+\cdot}$) and 288/290 (71/63%).

5.1.10. Ethyl 2-phenyl-4-[1-phenyl-1-(phenylamino)-methylidene]-4,5-dihydro-5-oxopyrrole-3-carboxylate 15a. The filtrate from **13a** [procedure (a) above] was concentrated in vacuo, and gave the uncyclised enamine **15a** (177 mg, 10%), mp 263 °C (from ethanol). (Found: C, 76.4; H, 5.6; N, 6.8. $C_{26}H_{22}N_2O_3$ requires C, 76.1; H, 5.4; N, 6.8%.). υ_{max} 3000–3200 (lactam NH), 2720 (H-bonded enamine NH), 1700 (ester C=O), 1650 (lactam C=O), 1620 (C=C) and 1550 (NH bend). δ_H (DMSO-d_6): 0.81 (3H, t, $J=7.2$ Hz, OCH_2CH_3), 3.22 (2H, q, $J=7.2$ Hz, OCH_2CH_3), 6.76–6.91 (2H, m, Ar-H), 6.98–7.04 (1H, m, Ar-H), 7.11–7.19 (2H, m, Ar-H), 7.25–7.48 (10H, m, Ar-H), and 11.00 and 12.10 (each 1H, s, NH; exchangeable with D_2O). *m/z* (EI): 410 (100%, $M^{+\cdot}$), 365 [$(M-EtOH)^{+\cdot}$: possibly the triphenyl-DPP **13a**], 180 $(PhC{=}NHPh)^+$ and 91 (C_6H_5N).

5.1.11. Ethyl 2-phenyl-4-[1-phenyl-1-(*p*-methoxyphenylamino)methylidene]-4,5-dihydro-5-oxopyrrole-3-carboxylate 15b. The filtrate from the above preparation of **13b** was cooled with ice, and the precipitated uncyclised enamine **15b** filtered off, to give an orange solid (0.78 g, 9%), mp 244.5–248 °C (from ethanol). (Found: C, 73.3; H, 5.4; N, 6.4. $C_{27}H_{24}N_2O_4$ requires C, 73.6; H, 5.5; N, 6.4%). δ_H (DMSO-d_6) 0.71 (3H, t, $J=7.2$ Hz, OCH_2CH_3), 3.12 (2H, q, OCH_2CH_3), 3.58 (3H, s, OCH_3), 6.61–6.73 (4H, m, Ar-H), 7.17–7.38 (8H, m, Ar-H), 7.48–7.54 (2H, m, Ar-H), 10.77 (1H, s, NH) and 11.92 (1H, s, NH).

5.1.12. Ethyl 2-phenyl-4-[1-phenyl-1-(*p*-trifluoromethylphenylamino)methylidene]-4,5-dihydro-5-oxopyrrole-3-carboxylate 15c. The filtrate from the above preparation of **13c** was cooled with ice, and the precipitated uncyclised enamine **15c** filtered off, to give a beige solid (541 mg, 6%), mp 264.5–265.5 °C (from ethanol). (Found: C, 67.5; H, 4.1; N, 5.7. $C_{27}H_{21}F_3N_2O_3$ requires C, 67.8; H, 4.4; N, 5.85%). δ_H (DMSO-d_6) 0.79 (3H, t, $J=7.2$ Hz, CH_2CH_3), 3.22 (2H, q, $J=7.2$ Hz, OCH_2), 6.86–6.94 (2H, m, Ar-H), 7.31–7.54 (12H, m, Ar-H), 10.94 (1H, s, NH) and 11.84 (1H, s, NH).

5.1.13. Ethyl 4-[1-*p*-bromophenyl-1-(*p*-methoxyphenylamino)methylidene]-2-chlorophenyl-4,5-dihydro-5-oxopyrrole-3-carboxylate 15d. The filtrate from the above preparation of **13d** was cooled with ice, and the precipitated uncyclised enamine **15d** filtered off, to give a beige solid (660 mg, 19%), mp 265–266 °C (from AcOH). (Found: C, 56.8; H, 4.0; N, 4.85. $C_{27}H_{22}BrClN_2O_4$ (+AcOH) requires

C, 56.7; H, 4.3; N, 4.6%). υ_{max} 3120 (NH), 1710 (ester C=O), 1630 (lactam C=O). δ_H (DMSO-d_6) 0.84 (3H, t, J=7.2 Hz, CH_2CH_3), 2.10 (3H, s, AcOH), 3.31 (2H, q, J=7.2 Hz, OCH_2) 3.67 (3H, s, OMe), 6.76 and 6.84 (each 2H, AA′BB′, p-$MeOC_6H_4$), 7.44 (4H, s, Ar), 7.22 and 7.57 (each 2H, AA′BB′, Ar), 10.93 (1H, s, NH) and 11.92 (1H, s, NH). δ_C 14.0 (CH_3), 55.7 (OCH_3), 60.2 (OCH_2), 102.6 (quat), 107.3 (quat), 114.5 (2×CH), 125.9 (2×CH), 127.7 (2×CH), 128.8 (4×CH), 129.8 (2×CH), 131.1 (2×quat), 132.1 (2×quat), 132.4 (quat), 133.4 (quat), 157.1 (quat), 157.4 (quat), 165.6 and 168.8 (2×CO).

5.1.14. 5-Methyl-2,3,6-triphenyl-DPP 16a. The triphenyl-DPP **13a** (500 mg, 1.37 mmol) was stirred with methyl p-toluenesulfonate (383 mg, 2.06 mmol), potassium carbonate (380 mg, 2.75 mmol) and DMF (40 cm^3) overnight. Water was added, and the organic component extracted with DCM. The solvent was evaporated and washing with water then methanol gave the DPP **16a** as an orange solid (290 mg, 56%), mp 267–269 °C. (Found: C, 79.4; H, 5.0; N, 7.3. $C_{25}H_{18}N_2O_2$ requires C, 79.35; H, 4.8; N, 7.4%). δ_H 3.42 (3H, s, NCH_3), 7.15–7.20 (2H, m, Ar) 7.28–7.41 (6H, m, Ar), 7.51–7.56 (3H, m, Ar), 7.62–7.68 (2H, m, Ar), 7.91–7.95 (2H, m, Ar). m/z (ESI +ve): 402 [28%, $(M+Na+1)^+$], 401 [100%, $(M+Na)^+$] and 379 [14%, $(M+1)^+$].

5.1.15. 2-(p-Methoxyphenyl)-5-methyl-3,6-diphenyl-DPP 16b. The triaryl-DPP **13b** (1.23 g, 3.12 mmol), methyl p-toluenesulfonate (1.13 g, 6.08 mmol) and potassium carbonate (0.841 g, 6.08 mmol) were heated to 120 °C in DMF (40 cm^3) for 2 h. The mixture was cooled to room temperature, water was added and the organic component extracted with DCM. Evaporation of the solvent and recrystallisation from toluene gave the methylated compound **16b** (0.99 g, 80%), mp 252–254 °C. (Found: C, 76.15; H, 4.9; N, 6.9. $C_{26}H_{20}N_2O_3$ requires C, 76.45; H, 4.9; N, 6.9%). δ_H 3.53 (3H, s, NCH_3), 3.93 (3H, s, OCH_3), 7.00 and 7.21 (each 2H, AA′BB′, p-$MeOC_6H_4$), 7.41–7.50 (3H, m, Ar-H), 7.61–7.67 (3H, m, Ar-H), 7.77–7.82 (2H, m, Ar-H), and 8.02–8.07 (2H, m, Ar-H). δ_C 30.0 (NCH_3), 55.9 (OCH_3), 114.7 (2×CH), 128.1 (2×C quat), 128.2 (2×quat), 128.7 (2×CH), 129.0 (2×quat), 129.2 (2×CH), 129.4 (2×CH), 129.6 (2×CH), 130.1 (2×CH), 131.4 (CH), 131.8 (CH), 147.6 (quat), 149.2 (quat), 159.3 and 162.6 (2×C=O)[‡] and 163.2 (quat). m/z (ESI +ve): 447 [10%, $(M+K+H)^+$], 446 (27%, M+K), 431 [100%, $(M+Na)^+$] and 409 [35%, $(M+1)^+$].

5.1.16. 5-Methyl-3,6-diphenyl-2-p-trifluoromethylphenyl-DPP 16c. A mixture of the DPP **13c** (200 mg, 0.463 mmol), methyl p-toluenesulfonate (129 mg, 0.695 mmol), potassium carbonate (128 mg, 0.93 mmol) and DMF (10 cm^3) was stirred at room temperature overnight, added to water and extracted with DCM. Evaporation of the solvents followed by washing with water then methanol gave the pyrrolopyrrole **16c** as an orange solid (184 mg, 89%), mp 237.5–238.5 °C. (Found: C, 69.9; H, 3.7; N, 6.1. $C_{26}H_{17}F_3N_2O_2$ requires C, 69.95; H, 3.8; N, 6.3%). δ_H 7.94–7.87 (2H, m, Ph-H), 7.67–7.51 (7H, m, Ph-H), 7.45–7.27 (5H, m, Ar-H) and 3.42 (3H, s, N–CH_3).

[‡] Provisional assignment.

5.1.17. 3-p-Bromophenyl-6-p-chlorophenyl-2-p-methoxyphenyl-5-methyl-DPP 16d. A mixture of DPP **13d** (100 mg, 0.2 mmol), methyl p-toluenesulfonate (75.1 mg, 0.404 mmol), potassium carbonate (70 mg, 0.51 mmol) and DMF (10 cm^3) was heated to 100 °C for 3 h, cooled to room temperature, added to water and extracted with DCM. Evaporation of the solvents followed by washing with water then methanol gave the pyrrolopyrrole **16d** as a red-orange solid (81 mg, 79%), mp 262–264 °C. (Found: C, 59.5; H, 3.3; N, 5.3. $C_{25}H_{16}BrClN_2O_3$ requires C, 59.1; H, 3.3; N, 5.5%). υ_{max} 1670 (C=O) and 1610; δ_H 3.31 (3H, s, NCH_3), 3.75 (3H, s, OCH_3), 6.83 and 7.01 (each 2H, AA′BB′, NC_6H_4OMe), 7.37 and 7.47 (each 2H, AA′BB′, p-Ar), 7.41 and 7.80 (each 2H, AA′BB′, p-Ar). δ_C 30.1 (NCH_3) 55.9 (OCH_3) 114.9 (2×C, Ar-H), 126.2 (2×C, quat), 126.4 (quat), 126.8 (quat), 128.5 (2×C, quat), 129.3 (2×C, Ar), 129.6 (2×C, Ar), 130.9 (2×C, Ar) 131.4 (2×C, Ar), 132.1 (2×C, Ar), 138.1 (quat), 146.6 (quat), 148.1 (quat), 159.6 (2×C, quat) and 162.9 (quat). m/z (EI): 520/522/524 (27/100/78%, M^+) and 288/290 (60/61%).

5.1.18. 5-Benzyl-2,3,6-triphenyl-DPP 17a. The triphenyl-DPP **13a** (500 mg, 1.37 mmol) was stirred with benzyl bromide (352 mg, 245 µl, 2.06 mmol), potassium carbonate (380 mg, 2.75 mmol) and DMF (40 cm^3) overnight. Water was added, and the organic component extracted with DCM. The solvent was evaporated and washing with water and then methanol gave the pyrrolopyrrole **17a** as an orange solid (548 mg, 93%), mp 262–264 °C. (Found: C, 81.9; H, 4.8; N, 6.2. $C_{31}H_{22}N_2O_2$ requires C, 81.9; H, 5.0; N, 6.2%). υ_{max} 1680 (CO), 1590; δ_H 5.05 (2H, s, $PhCH_2N$), 7.16–7.24 (4H, m, Ar-H), 7.27–7.50 (12H, m, Ar-H), 7.66–7.70 (2H, m, Ar-H) and 7.74–7.79 (2H, m, Ar-H). δ_C 46.1 (CH_2), 127.1 (2×CH), 127.8 (CH), 128.0 (2×quat), 128.1 (quat), 128.2 (2×CH), 128.3 (CH), 128.7 (2×CH), 129.2 (4×CH), 129.4 (2×CH), 129.5 (2×CH), 130.2 (2×CH), 131.6 (CH), 131.9 (CH), 136.1 (quat), 137.8 (quat), 147.9 (quat), 149.7 (quat), 162.3 and 163.3 (2×CO).

5.1.19. 5-Benzyl-2-p-methoxyphenyl-3,6-diphenyl-DPP 17b. The triaryl-DPP **13b** (100 mg, 0.254 mmol), benzyl bromide (118 mg, 83 µl, 0.66 mmol) and potassium carbonate (100 mg, 0.71 mmol) were heated to 120 °C in DMF (10 cm^3) for 2 h. The mixture was cooled to room temperature, water was added and the organic component extracted with DCM. Evaporation of the solvent from the dried extract gave the benzylated compound **17b** (108 mg, 88%), mp 263–264 °C (from AcOH). [Found: C, 76.2; H, 4.8; N, 5.6. $C_{32}H_{24}N_2O_3$ (3:2 ratio with AcOH) requires C, 76.3; H, 5.1; N, 5.3%]. δ_H 2.10 (3H, s, AcOH), 3.74 (3H, s, OCH_3), 4.97 (2H, s, NCH_2), 6.82 and 7.04 (each 2H, AA′BB′, p-$MeOC_6H_4$), 7.11–7.41 (6H, m, Ar-H), and 7.61–7.71 (4H, m, Ar-H). δ_C 46.1 (CH_2), 55.9 (OCH_3), 114.8 (CH), 127.0 (CH), 127.8 (CH), 128.0 (quat), 128.1 (2×quat), 128.7 (CH), 129.2 (2×CH), 129.4 (CH), 129.5 (CH), 130.2 (CH), 131.5 (CH), 131.8 (CH), 137.8 (quat), 148.0 (quat), 149.4 (quat), 159.4 (2×C=O),[‡] 162.6 (quat) and 163.3 (quat). m/z (ESI +ve): 508 [34%, $(M+Na+1)^+$], 507 [100, $(M+Na)^+$] and 485 [8, $(M+1)^+$].

5.1.20. 5-Benzyl-3,6-diphenyl-2-(p-trifluoromethylphenyl)-DPP 17c. A mixture of the triaryl-DPP **13c** (200 mg, 0.46 mmol), benzyl bromide (119 mg, 83 µl, 0.695 mmol),

potassium carbonate (128 mg, 0.93 mmol) and DMF (10 cm^3) was stirred at room temperature overnight, added to water and extracted with DCM. Evaporation of the solvents followed by washing with methanol gave the pyrrolopyrrole **17c** as an orange solid (151 mg, 63%), mp 254.5–256.5 °C (from toluene). (Found: C, 73.3; H, 3.8; N, 5.2. $C_{32}H_{21}F_3N_2O_2$ requires C, 73.6; H, 4.05; N, 5.4%). δ_H 5.05 (2H, s, PhCH_2N), 7.17–7.22 (2H, m, Ar-H), 7.27–7.54 (11H, m, Ar-H), 7.60–7.67 (4H, m, Ar-H) and 7.71–7.76 (2H, m, Ar-H).

5.1.21. 5-Benzyl-3-*p*-bromophenyl-6-*p*-chlorophenyl-2-*p*-methoxyphenyl-DPP 17d. A mixture of the triaryl-DPP **13d** (2.0 g, 3.95 mmol), benzyl bromide (1.0 g, 0.7 cm^3, 5.92 mmol), K_2CO_3 (1.1 g, 7.9 mmol) and DMF (50 cm^3) was stirred at room temperature overnight, added to water and extracted with DCM. Evaporation of the solvents followed by washing with methanol gave the pyrrolopyrrole **17d** as a red-orange solid (2.25 g, 95%), mp 215–217 °C. (Found: C, 64.6; H, 3.4; N, 4.6. $C_{32}H_{22}BrClN_2O_3$ requires C, 64.3; H, 3.7; N, 4.7%). δ_H 3.76 (3H, s, NCH_3), 4.95 (2H, s, PhCH_2N), 6.85 and 7.04 (4H, AA′BB′, Ar-H), 7.10–7.16 (2H, m, *o*-Ph), 7.21–7.28 (3H, m, *m*/*p*-Ph), 7.15 and 7.33 (4H, AA′BB′, Ar-H) and 7.39 and 7.64 (4H, AA′BB′, Ar-H).

5.1.22. 2-(*p*-Methoxyphenyl)-5-(2,4-dinitrophenyl)-3,6-diphenyl-DPP 18b. The triaryl-DPP **13b** (100 mg, 0.25 mmol), 1-fluoro-2,4-dinitrobenzene (94 mg, 0.51 mmol) and potassium carbonate (70 mg, 51 mmol) were stirred in DMF (20 cm^3) at room temperature for 5 h. Water was then added, and the orange precipitate filtered. Recrystallisation from DMF gave the pyrrolopyrrole **18b** as an orange crystalline solid (117 mg, 82%), mp 293–295 °C. (Found: C, 66.2; H, 3.2; N, 10.1. $C_{31}H_{20}N_4O_7$ requires C, 66.4; H, 3.6; N, 10.0%). υ_{max} 1690 (C=O), 1600; δ_H (DMSO-d_6) 3.60 (3H, s, OCH_3), 7.10 and 7.40 (each 2H, AA′BB′, *p*-MeOC_6H_4), 7.50–7.80 [11H, m, Ph+Ar-H(6)], 8.60 [1H, dd, J=8.6 l, 2.6 Hz, Ar-H(5)] and 8.90 [1H, d, J=2.6 Hz, Ar-H(3)]. δ_C 55.7 (CH_3), 107.5 (quat), 112.3 (quat), 114.7 (2×CH), 121.6 (CH), 126.6 (quat), 127.1 (quat), 127.9 (quat), 128.7 (3×CH), 128.8 (2×CH), 129.3 (CH), 129.4 (2×CH), 129.9 (4×CH), 132.2 (CH), 132.3 (CH), 133.9 (quat), 144.5 (quat), 145.8 (quat), 146.7 (quat), 150.1 (quat), 159.3 (quat), 159.7 and 161.7 (2×CO).†

5.1.23. 3-(*p*-Bromophenyl)-6-(*p*-chlorophenyl)-5-(2,4-dinitrophenyl)-2-(*p*-methoxyphenyl)-DPP 18d. The triaryl-DPP **13d** (300 mg, 0.59 mmol), 1-fluoro-2,4-dinitrobenzene (220 mg, 1.18 mmol) and potassium carbonate (245 mg, 1.77 mmol) were stirred in DMF (40 cm^3) at room temperature for 5 h. This was acidified (HCl), and the organic component extracted with DCM. Evaporation of the solvent and recrystallisation from acetic acid gave the pyrrolopyrrole **18d** as an orange-red crystalline solid (320 mg, 80%), mp 290–293 °C. (Found: C, 55.2; H, 2.6; N, 8.4. $C_{31}H_{18}BrClN_4O_7$ requires C, 55.3; H, 2.7; N, 8.3%). δ_H (DMSO-d_6) 3.60 (3H, s, OCH_3), 6.82 and 7.04 (each 2H, AA′BB′, Ar-H) 7.35 and 7.43 (each 2H, AA′BB′, Ar-H), 7.43 [2H, d, J=8.7 Hz, Ar-H(6)], 7.24 and 7.46 (each 2H, AA′BB′, Ar-H) 8.37 [1H, dd, J=2.6, 8.7 Hz, Ar-H(5)] and 8.69 [1H, d, J=2.6 Hz, Ar-H(3)].

5.1.24. Ethyl 2-(1-phenyl-1-aminophenylmethylidene)-3-oxo-4-chlorobutanoate 21. Chloroacetyl chloride (220 mg, 2.0 mmol) was added dropwise to a solution of the enamine **19** (240 mg, 0.9 mmol) in ether (5 cm^3) at −50 °C. The reaction mixture was stirred at −45 to −35 °C for 2 h, then at room temperature for a further 2 h. Evaporation of the solvent and column chromatography (silica gel, eluent: 1:6 ethyl acetate/hexane) gave the enamine as a white crystalline solid (133 mg, 48%), mp 122.5–123.5 °C (from ethanol). (Found: C, 66.4; H, 5.05; N, 4.0. $C_{19}H_{18}ClNO_3$ requires C, 66.4; H, 5.3; N, 4.1%). ν_{max} 1545, 1600, 1690 (CO_2Et or C=O), 3165 (NH) δ_H 0.67 (3H, t, J=7.2 Hz, CH_3), 3.70 (2H, q, J=7.2 Hz, OCH_2), 4.64 (2H, s, CH_2), 6.70–6.76 (2H, m, *o*-N-Ph), 7.01–7.15 (3H, m, *m*/*p*-Ph-H), 7.22–7.17 (2H, m, *o*-Ph-H) and 7.25–7.38 (3H, m, *m*/*p*-Ph-H). δ_C 13.7 (CH_3), 48.9 (CH_2Cl), 60.9 (OCH_2), 125.0 (2×CH), 126.3 (CH), 128.7 (2×CH), 128.8 (2×CH), 129.2 (2×CH), 130.1 (CH), 134.8 (quat), 138.1 (quat), 166.7 (CO_2) and 190.5 (CO). *m*/*z* (ESI +ve): 366/368 [100%, $(M+Na)^+$], 330 [95%, $(M-Cl+Na)^+$] and 308 [75%, $(M-Cl)^+$].

5.1.25. Ethyl 2-benzoyl-*N*-phenylsuccinamate 25. A solution of the furanone **23**[27] (100 mg, 0.43 mmol) and aniline (51 mg, 50 μl, 0.55 mmol) in toluene (2.0 cm^3) was heated to 120 °C (using microwave irradiation) for 10 min. The solution was then cooled, and the solvent evaporated. Recrystallisation from ethanol gave the amide **25** as a colourless crystalline solid (53 mg, 38%), mp 106–106.5 °C. (Found: C, 69.9; H, 5.6; N, 4.3. $C_{19}H_{19}NO_4$ requires C, 70.1; H, 5.9; N, 4.3%). υ_{max} 1670 (amide CO), 1685 (ketone CO), 1735 (ester CO) and 3340 (NH). δ_H 1.16 (3H, t, J=7.2 Hz, $COCH_2CH_3$), 3.09 (2H, d, J=6.9 Hz, $CHCH_2CONH$), 4.15 (2H, q, J=7.2 Hz, CH_2CH_3), 5.06 (1H, t, J=6.9 Hz, $COCHCO_2Et$), 7.05–7.13 (1H, m, Ar-H), 7.26–7.33 (2H, m, Ar-H), 7.43–7.53 (4H, m, Ar-H), 7.57–7.64 (1H, m, Ar-H) and 8.05–8.10 (2H, m, Ar-H). δ_C 14.3 (CH_3), 36.7 (CH_2), 50.3 (CH), 62.4 (OCH_2), 120.2 (2×CH), 124.8 (CH), 129.2 (2×CH), 129.4 (2×CH), 129.5 (2×CH), 134.2 (CH), 136.1 (quat), 138.0 (quat), 168.7 and 169.6 (2×CO) and 195.2 (ketone CO).

5.1.26. Ethyl 4,5-dihydro-5-oxo-1,2-diphenylpyrrole-3-carboxylate 26a. Aniline (2.65 g, 2.59 cm^3, 28.5 mmol) was added to a solution of the furanone **23** (6.0 g, 25.9 mmol) and acetic acid (100 cm^3), and the solution heated to reflux for 3 h. The solution was then cooled, diluted with water and extracted with ether. The organic extracts were dried and concentrated. Column chromatography (silica gel, eluent: DCM) gave the pyrrolinone **26a** as a colourless solid (6.9 g, 87%), mp 129–130 °C. (Found: C, 74.1; H, 5.6; N, 4.5. $C_{19}H_{17}NO_3$ requires C, 74.25; H, 5.6; N, 4.6%). υ_{max} 1725 (ester C=O), 1690 (amide C=O), 1590 (C=C). δ_H 1.11 (3H, t, J=6.9 Hz, OCH_2CH_3), 3.67 (2H, s, CH_2), 4.08 (2H, q, J=6.9 Hz, OCH_2CH_3), 6.93–6.98 (2H, m, *o*-Ph-N) and 7.15–7.32 (8H, m, Ar-H). δ_C 14.5 (CH_3), 38.0 (CH_2), 60.5 (OCH_2), 128.0 (4×CH), 128.1 (CH), 129.3 (2×CH), 129.8 (CH), 130.0 (2×CH), 134.6 (2×quat), 154.8 (NC=C), 163.6 (amide CO) and 175.5 (ester CO).

5.1.27. Ethyl 4,5-dihydro-1-(*p*-methoxyphenyl)-5-oxo-2-phenylpyrrole-3-carboxylate 26b. This was prepared similarly to **26a** from *p*-anisidine (5.83 g, 47.40 mmol),

furanone **23** (10.00 g, 43.10 mmol) and acetic acid (150 cm^3). Recrystallisation from diethyl ether gave the pyrrolinone **26b** as a colourless solid (7.4 g, 49%), mp 149.5–151.5 °C. (Found: C, 70.9; H, 5.7; N, 4.0. $C_{20}H_{19}NO_4$ requires C, 71.2; H, 5.7; N, 4.15%). δ_H 1.10 (3H, t, J=7.2 Hz, CH_3), 3.64 (2H, s, CH_2), 3.73 (3H, s, OCH_3), 4.07 (2H, q, J=7.2 Hz, OCH_2), 6.75 and 6.88 (each 2H, AA′BB′, p-$MeOC_6H_4$) and 7.31–7.16 (5H, m, Ph).

5.1.28. Ethyl 4,5-dihydro-5-oxo-2-phenyl-1-(*p*-trifluoromethylphenyl)pyrrole-3-carboxylate 26c. This was prepared similarly to **26a** from p-aminobenzotrifluoride (7.63 g, 47.40 mmol), furanone **23** (10.00 g, 43.10 mmol) and acetic acid (150 cm^3). Recrystallisation from a mixture of ether and hexane gave the pyrrolinone **26c** as a light beige solid, mp 131–132 °C. (Found: C, 64.05; H, 4.0; N, 3.6. $C_{20}H_{16}F_3NO_3$ requires C, 64.0; H, 4.3; N, 3.7%). δ_H 1.12 (3H, t, J=7.2 Hz, CH_3), 3.69 (2H, s, CH_2), 4.09 (2H, q, J=7.2 Hz, OCH_2), 7.16–7.22 (2H, m, o-Ph), 7.25–7.38 (3H, m, m/p-Ph), and 7.07 and 7.49 (each 2H, AA′BB′, p-$F_3CC_6H_4$).

5.1.29. Ethyl 4-benzoyl-4,5-dihydro-5-oxo-1,2-diphenylpyrrole-3-carboxylate 27. A solution of the pyrrolinone ester **26a** (1.76 g, 5.74 mmol) in tetrahydrofuran (100 cm^3) was cooled to −78 °C, and a 1.0 M solution of lithium hexamethyldisilazide (17.2 cm^3, 17.2 mmol) in THF was added. After 5 min, benzoyl chloride (0.97 g, 0.79 cm^3, 6.89 mmol) was added, and the solution stirred for 30 min. Methanol was added, and the solution warmed to room temperature. The mixture was acidified (HCl) and extracted with ether. The ether extracts were concentrated, and chromatography (silica gel, eluent DCM) gave the enol **27** as a yellow solid (1.74 g, 74%), mp 137–139 °C. (Found: C, 75.8; H, 4.9; N, 3.3. $C_{26}H_{21}NO_4$ requires C, 75.9; H, 5.1; N, 3.4%). υ_{max} 1720 (ester C=O), 1650 (sh), 1625; δ_H 0.65 (3H, t, J=7.2 Hz, CH_3), 3.54 (2H, q, J=7.2 Hz, CH_2) 7.07–7.14 (2H, m, Ar), 7.19–7.34 (8H, m, Ar), 7.44–7.54 (3H, m, Ar) and 7.68–7.75 (2H, m, Ar). δ_C 13.6 (CH_3), 61.0 (OCH_2), 103.2 (*C*–CON), 108.8 (*C*–CO_2), 127.8 (2×CH), 127.9 (CH), 128.1 (2×CH), 128.8 (2×CH), 129.4 (2×CH), 129.5 (quat), 130.5 (CH), 131.0 (2×CH), 131.9 (CH), 134.5 (quat), 136.0 (quat), 140.1 (quat), 164.5 (COH), 168.9 (CO_2) and 176.15 (CON).

5.1.30. 3,5,6-Triphenyl-1*H*-furo[3,4-*c*]pyrrole-1,4(5*H*)-dione 28. The benzoylpyrrolinone ester **27** (74 mg) was irradiated with microwave radiation (at 300 W) without solvent, heating to 200 °C for 10 min. The crude product was then allowed to cool, methanol was added and the solid filtered off and washed with methanol. This gave the furopyrrole as an orange solid (34 mg, 52%), mp 230–232 °C (lit.[6] 230–232 °C). δ_H 7.20–7.61 (13H, m, Ar-H) and 8.42–8.48 (2H, m, Ar-H).

5.1.31. 1,2-Diphenyl-4-[1-phenyl-1-(phenylamino)-methylidene]-4,5-dihydropyrrol-5-one 29. The furopyrrole **28** (50 mg, 0.14 mmol), aniline (14 mg, 14 µl, 0.15 mmol) and toluene (2.0 cm^3) were heated to 120 °C for 10 min under microwave irradiation. The mixture was cooled, and evaporation of the solvent and recrystallisation from ethanol gave the pyrrolinone as an orange solid (37 mg, 65%), mp 212.5–214.5 °C. (Found: C, 83.7; H, 5.4; N, 6.8. $C_{29}H_{22}N_2O$ requires C, 84.0; H, 5.35; N, 6.8%). υ_{max} 1630 (C=O), 1590 (C=C or NH bending). δ_H 5.94–5.97 (1H, s, C=C–CH), 6.69–6.75 (2H, m, o-N-Ph-H), 6.91–7.01 (1H, m, p-N-Ph-H), 7.03–7.18 (7H, m, Ph-H), 7.19–7.30 (3H, m, Ph-H), 7.32–7.40 (2H, m, Ph-H), 7.40–7.47 (5H, m, Ph-H), and 11.88 (1H, s, NH). δ_C 104.3 (CH), 104.9 (OC*C*=CN), 122.7 (2×CH), 124.3 (CH), 126.9 (CH), 127.5 (CH), 127.6 (2×CH), 128.5 (2×CH), 129.1 (4×CH), 129.2 (2×CH), 129.7 (4×CH), 130.2 (CH), 132.7 (quat), 133.5 (2×quat), 134.2 (quat), 136.5 (quat), 153.8 (quat) and 168.7 (CO).

5.1.32. Ethyl 1,2-diphenyl-4-[1-phenyl-1-(phenylamino)-methylidene]-4,5-dihydro-5-oxopyrrole-3-carboxylate 30. A solution of the pyrrolinone **26a** (200 mg, 0.862 mmol) in THF (20 cm^3) was cooled to −78 °C, and sodium hydride (62 mg, 2.59 mmol) was added, followed by the imidoyl chloride **13a** (557 mg, 2.59 mmol). The solution was left to warm to room temperature overnight, then acidified (HCl). The organic component was extracted with DCM and the extract evaporated. Recrystallisation from ethanol gave the enamine **30** as a yellow solid (180 mg, 43%), mp 237–239 °C. (Found: C, 78.9; H, 5.7; N, 5.8. $C_{32}H_{26}N_2O_3$ requires C, 79.0; H, 5.4; N, 5.8%). υ_{max} 1715 (ester C=O), 1625 (lactam C=O), 1590 (C=C or NH bend). δ_H, 0.81 (3H, t, J=7.2 Hz, CH_3), 3.35 (2H, q, J=7.2 Hz, OCH_2), 6.75–6.69 (2H, m, Ar-H), 7.02–6.96 (2H, m, Ar-H), 7.44–7.05 (16H, m, Ar-H) and 12.22 (1H, s, NH). δ_C 14.1 (CH_3), 60.9 (CH_2), 105.3 (quat), 112.4 (quat), 118.9 (quat), 121.8 (quat), 123.8 (2×CH), 125.1 (CH), 127.5 (CH), 128.0 (2×CH), 128.1 (3×CH), 128.6 (CH), 129.0 (2×CH), 129.1 (2×CH), 129.2 (2×CH), 129.7 (2×CH), 130.4 (2×CH), 134.0 (quat), 136.2 (quat), 139.1 (2×quat), 157.8 (CO) and 177.4 (CO).

5.1.33. 2,3,5,6-Tetraphenyl-DPP 4a. (a) A solution of the furopyrrole **28** (100 mg, 0.274 mmol), aniline (38 mg, 37 µl, 0.411 mmol), *N*,*N*′-diisopropylcarbodiimide (69 mg, 85 µl, 0.548 mmol) trifluoroacetic acid (one drop) and DCM (5 cm^3) was stirred at room temperature for 14 days. Filtration of the formed precipitate, followed by washing with methanol and DCM gave the pyrrolopyrrole **4a** as an orange solid (30 mg, 25%); no mp was observed by DSC up to 400 °C (lit.[6] >360 °C).

(b) The enamine **30** (50 mg, 0.114 mmol) was mixed with polyphosphoric acid (2.0 cm^3) and the mixture heated to 175 °C for 5 min. Water was added, and the precipitate filtered and washed with methanol, to give the pyrrolopyrrole (3 mg, 7%). m/z (EI TOF): 441 [37%, $(M+1)^+$], 440 (100%, M^+), 439 [43%, $(M-1)^+$], 364 [57%, $(M-Ph)^+$] and 180 (59%, PhC–NPh). An accurate NMR spectrum could not be obtained due to very low solubility.

5.1.34. 2-*p*-Methoxyphenyl-3,5,6-triphenyl-DPP 4b. A solution of the triphenyl-furopyrrole **28** (100 mg, 0.27 mmol), p-anisidine (67 mg, 0.55 mmol), *N*,*N*′-diisopropylcarbodiimide (69 mg, 85 µl, 0.55 mmol), DMAP (67 mg, 0.55 mmol), HOBT (74 mg, 0.55 mmol) and DCM (10 cm^3) was stirred at room temperature for 24 h. The formed precipitate was filtered and washed with DCM, methanol and acetone, to give the tetraaryl-DPP as an orange solid (63 mg, 48%), mp 374–376 °C (from o-$Cl_2C_6H_4$). [Found: C, 78.0; H, 4.4; N, 5.55. $C_{31}H_{22}N_2O_3$

(6:1 ratio with o-$Cl_2C_6H_4$) requires C, 77.6; H, 4.6; N, 5.7%]. m/z (ES +ve): 494 [12%, $(M+Na+1)^+$], 493 [100%, $(M+Na)^+$] and 471 [5%, $(M+1)^+$]. An accurate NMR spectrum could not be obtained due to very low solubility.

5.1.35. 3,5,6-Triphenyl-2-*p*-trifluoromethylphenyl-DPP 4c. A solution of the furopyrrole **28** (100 mg, 0.27 mmol), *p*-aminobenzotrifluoride (88 mg, 69 μl, 0.55 mmol), *N*,*N*′-diisopropylcarbodiimide (69 mg, 85 μl, 0.55 mmol), dimethylaminopyridine (67 mg, 0.55 mmol) and *N*-hydroxybenzotriazole (74 mg, 0.55 mmol) in DCM (10.0 cm^3) was stirred for 2 weeks at room temperature. The precipitate was filtered and washed with further DCM and hot ethanol, to give the tetraaryl-DPP as an orange solid (70 mg, 50%), mp 363–364.5 °C. (Found: C, 71.7; H, 3.5; N, 5.0. $C_{31}H_{19}F_3N_2O_2$ (4:1 ratio with o-$Cl_2C_6H_4$) requires C, 71.6; H, 3.7; N, 5.1%). m/z (ESI +ve): 532 [12%, $(M+Na+1)^+$] and 531 [100%, $(M+Na)^+$]. An accurate NMR spectrum could not be obtained due to very low solubility.

6. X-ray crystallography

The intensity data for compounds **15b** and **15d** were recorded at 93 K using a Rigaku MM007/Mercury diffractometer (rotating anode, confocal optics Mo-Kα radiation), and for **12** and **19** at 125 K using a Bruker SMART diffractometer (sealed tube graphite-monochromated Mo Kα radiation). In **12**, two molecules of DMF were included in the lattice, in **15b** two crystallographically independent molecules were present in the asymmetric unit and in **15d** an acetic acid molecule and disordered water in two locations were present in the asymmetric unit. All data were corrected for Lorentz, polarisation and absorption effects (multiple equivalent reflection method). Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL). All N–H hydrogen atoms in compounds **15b** and **19** were refined isotropically subject to a distance constraint (N–H=0.98 Å). In **15d**, due to the poorer data quality the N–H was refined in an idealised position at a fixed distance of 0.98 Å and with a riding isotropic thermal parameter. All remaining hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries.

CCDC-276105-276112 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB21EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk).

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