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Cyclisation reactions of *N*-cinnamoyl-9-aminoanthracenes†

Frank D. King,* Abil Aliev, Stephen Caddick and Derek Tocher

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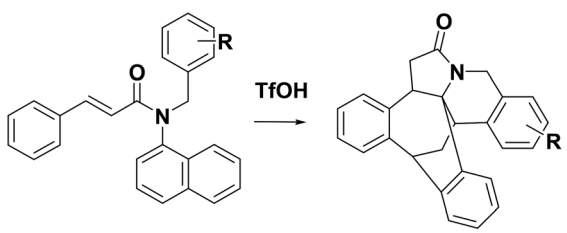
N-Cinnamoyl-9-aminoanthracenes cyclise with PPA or triflic acid to form novel 2-azahexacyclo-[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-ones. In contrast, both *N*-cinnamoyl-*N*-methyl-9-(2-aminomethyl)anthracene and *N*-cinnamoyl-9-(2-aminoethyl)anthracene undergo an intramolecular Diels–Alder cycloaddition.

Introduction

An amine and one or more aryl groups are key structural features of many modulators of G-protein coupled receptors. We are therefore interested in approaches to the synthesis of structures which have a unique special disposition of these functional groups to identify more potent and selective modulators. We have recently reported that the triflic acid-mediated cyclisation of *N*-cinnamoyl-anilines[1] and *N*-cinnamoyl-naphthylamines[2] give novel azacycles. For example, *N*-benzyl-*N*-cinnamoyl-1-naphthylamines **1** cyclise to give the polycyclics **2** (Scheme 1).[2]

In this paper, we report the results obtained from an investigation into the cyclisation of *N*-cinnamoyl-9-aminoanthracenes and homologues. Anthracenes have a very reactive central ring. For example, 9-amidoanthracenes are known to act as dienes in Diels–Alder cycloadditions[3] and nitration in HCl gives the 9-nitro-10-chloro addition product.[4] Therefore, by analogy with the cinnamoyl-naphthylamines, we anticipated that we would get novel products from either Diels–Alder or carbocation addition to the central ring.



1 **2**

Scheme 1 TfOH-mediated cyclisation of *N*-benzyl-*N*-cinnamoyl-1-aminonaphthalenes.

Department of Chemistry, University College London, 20 Gordon Street, London, UK. E-mail: fd.king@btinternet.com

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Results and discussion

The *N*-cinnamoyl-9-aminoanthracenes **3a**, **3e**, **3g**, **3i**, **3k** and **3m** were prepared from 9-aminoanthracene[4] and the appropriate cinnamoyl chloride with *N*,*N*-dimethylaniline as base. The required products formed as precipitates, which were collected and dried. Further product could be obtained from the mother liquors by column chromatography. The *N*-substituted analogues **3b–d** and **3f**, **3h**, **3j**, **3l** and **3n** were readily prepared by N-alkylation with the appropriate iodide or bromide with KO*t*-Bu as base.

The NH-amides **3a**, **3e**, **3g**, **3i**, **3k** and **3m** were found to be very insoluble in a wide range of solvents. However, recrystallisation was possible from DMSO–water. Considering the structure of these amides, the NMR of **3a** at room temperature showed a symmetry about the anthracene, with no evidence of rotamers in DMSO-d_6. In contrast, despite its low solubility in $CDCl_3$, two sets of peaks were observed in $CDCl_3$ solution with the ratio of 3 : 2. Exchange cross-peaks were observed in NOESY spectra, confirming that the observed two sets of peaks are due to two rotamers. The largest chemical shift difference was observed for the COC**H**=C proton resonating at 6.95 ppm in the major rotamer and at 5.91 ppm in the minor rotamer. Therefore, we concluded that the structure of the major rotamer has the expected *syn* relationship of the amide carbonyl[5] (Fig. 1A), with the amide plane orthogonal to the plane of the anthracene. This conformation would minimise the steric interactions between the amide carbonyl and COC**H**=C proton, and the 1,8 protons of the anthracene. The upfield shift of the COC**H**=C proton in the minor conformer is due to the ring current effect[6] and suggests that this proton is placed above the anthracene ring, in agreement with structure B in Fig. 1. Ring current effects are relatively strong and are felt at rela-

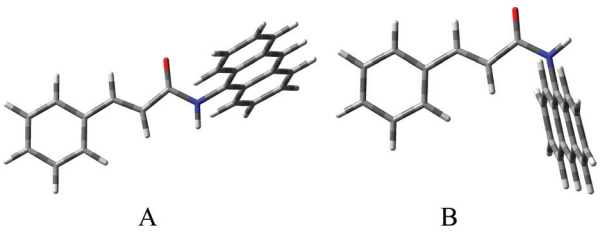
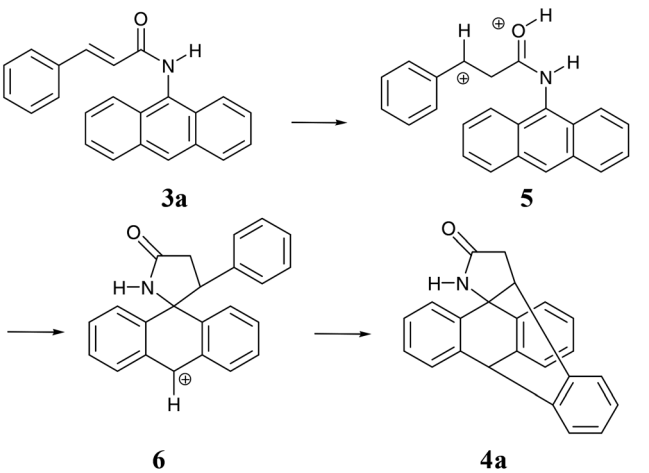


Fig. 1 DFT-optimised geometries of two rotamers of **3a**.

tively long distances of >4 Å.[6] Therefore, the change in chemical shift of the *ortho*-Ph protons from 7.65 ppm in the major rotamer to 7.08 ppm in the minor rotamer is also in agreement with structures A (major) and B (minor) shown in Fig. 1. The NMR spectra of the *N*-alkyl derivatives **3b–d** showed symmetry similar to that in **3a**, but with a large upfield shift of the COC**H**=C cinnamoyl proton to δ 5.82–5.87 ppm in **3b–d**. As discussed above for rotamer **3a–B**, this is consistent with a shielding ring current effect when the proton is placed above the aromatic ring.[6] For the *N*-benzyl **3d**, NOEs were observed between the COC**H**=C proton and the 1,8 protons of the anthracene, and the COCH=C**H** proton and the *ortho* protons of the cinnamoyl phenyl. No NOE was observed with the benzylic CH_2, which itself showed NOE's with the 1,8-protons of the anthracene and the *ortho* protons of the benzyl phenyl. Thus, we believe that the structure of the *N*-alkyl derivatives also have the amide group orthogonal to the plane of the anthracene, but with the anthracene *anti* to the carbonyl and the alkyl group *syn*. This would place the COC**H**=C proton over the top of the anthracenyl central ring (Fig. 1B). The conformation of the amide in rotamer B would be that required for a cyclo-addition reaction.

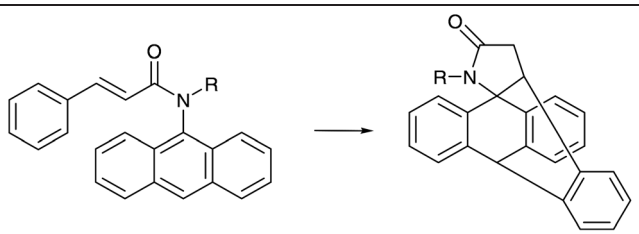
The results from the acid-mediated cyclisation reactions are shown in Table 1. From TLC, the initial reaction of **3a** with TfOH (10 equiv.) in $CHCl_3$ (Table 1, entry 1) gave a trace of a less polar product, which under UV light showed as a bright blue fluorescent spot, and a more polar product that was weak when viewed under UV light, but reacted strongly with $KMnO_4$. On purification by column chromatography on SiO_2, the small amount of the less polar product could not be obtained in pure form. However, the more polar major product (69% yield) was found to be the 9,10 addition product **4a** (Scheme 2).

The structure was assigned by ^1H and ^{13}C NMR. In particular, in the ^1H NMR spectrum, there were four aliphatic protons, three mutually coupled doublet of doublets and a singlet at δ 4.96, and twelve aromatic protons. In the ^{13}C NMR spectrum, four aliphatic C signals were observed, a CH_2, two CH and a C, consistent with the proposed structure, which was further verified using two- and three-bond ^1H–^{13}C correlations in the HMBC spectrum.



Scheme 2 Proposed mechanism of formation of **4a**.

Table 1 Acid-mediated cyclisation of *N*-cinnamoyl-9-aminoanthracenes **3a–d**



Entry	Amide	R	Solvent	Acid[a]	Temp. (°C)	Time (h)	Product	R	Yield (%)
1	**3a**	H	$CHCl_3$	TfOH	65	3	**4a**	H	69
2	**3a**	H	—	PPA	120	2	**4a**	H	78
3	**3a**	H	—	CSA	120	5	**4a**	H	0
4	**3a**	H	PhCl	$AlCl_3$	25	24	**4a**	H	0
5	**3b**	Me	$CHCl_3$	TfOH	65	2	**4b**	Me	92
6	**3b**	Me	—	PPA	120	2	**4b**	Me	89
7	**3c**	Et	—	PPA	120	2	**4c**	Et	90
8	**3d**	$PhCH_2$	—	PPA	120	2	**4d**	$PhCH_2$	88

[a] TfOH: triflic acid; PPA: polyphosphoric acid; CSA: (+)10-camphorsulfonic acid.

Other acids were investigated and PPA was found to give a superior yield of **4a** (78% yield). However, neither (+)10-camphorsulfonic acid nor $AlCl_3$ gave any **4a**. The former gave recovered starting material and the latter a black insoluble material. By analogy with the reaction with *N*-benzyl-*N*-cinnamoyl-1-amino-naphthalenes,[2] we believe that the acid doubly protonates the cinnamoyl group to form a benzylic carbocation, which adds to the 9 position to form a spiro intermediate, with the carbocation now located at the 10 position, close to the phenyl group, which facilitates ring closure (Scheme 2).

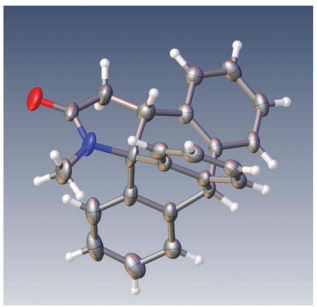
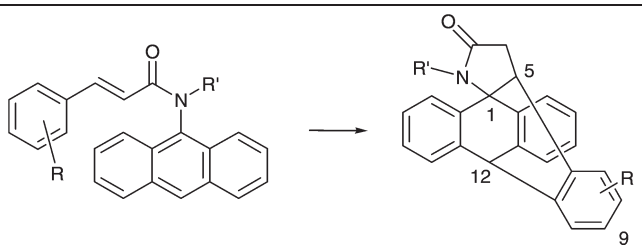


Fig. 2 Structure of **4b** as determined by X-ray structure crystallography. ORTEP diagram (50% probability ellipsoids) showing the crystallographic atom numbering scheme. Cambridge Crystallographic Data Centre deposition number CCDC 958857.

The *N*-methyl **3b** gave excellent yields of the 9,10 addition product **4b** with both TfOH (92% yield) and PPA (89% yield). The NMR of **4b** was similar to that of **4a** and the structure was confirmed by X-ray crystallographic analysis (Fig. 2). With PPA, both the *N*-ethyl **3c** and *N*-benzyl **3d** also gave excellent yields of 9,10 addition products **4c** and **4d** (both 90% yield). The presence of the *N*-alkyl group appears to inhibit the formation of the less polar by-product seen with **4a**.

The effect of substituents in the cinnamoyl group was investigated and the results are summarised in Table 2. *N*-Benzyl derivatives were also investigated because, on reduction to the amine, the benzyl group should be readily removable by catalytic hydrogenation.[7] The results for **3a** and **3d** are included for comparison. With PPA, the 4-methyl derivatives **3e** and **3f** (Table 2, entries 2 and 3) gave excellent yields of the 9,10 addition products **4e** and **4f** respectively. However, the reaction of the 4-chloro **3g** (entry 5) gave considerable amounts of a black insoluble material and only a modest yield of the 9,10 addition product **4g** was obtained (36% yield). With TfOH (entry 6), less insoluble material was formed, however **4f** was still only obtained in a moderate yield. In both cases, considerably more of the less polar by-product was obtained (20% yield in both cases), which was found to be the product **7** derived from cyclisation onto the 1 position of the anthracene.

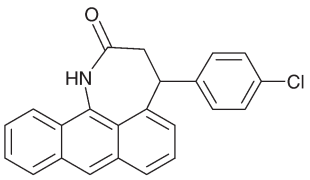
Table 2 Acid-mediated cyclisation of *N*-cinnamoyl-9-aminoanthracenes **3e–n**



4a, e-i- **4a, e-i**

Entry	Amide	R	R′	Acid[a]	Temp. (°C)	Time (h)	Product	R	Yield (%)
1	**3a**	H	H	PPA	120	2	**4a**	H	78
2	**3d**	H	CH_2Ph	PPA	120	2	**4d**	H	90
3	**3e**	4-Me	H	PPA	120	2	**4e**	9-Me	84
4	**3f**	4-Me	CH_2Ph	PPA	120	2	**4f**	9-Me	88
5	**3g**	4-Cl	H	PPA	120	2	**4g**	9-Cl	36
6	**3g**	4-Cl	H	TfOH	65	4	**4g**	9-Cl	44
7	**3h**	4-Cl	CH_2Ph	PPA	120	8	**4h**	9-Cl	45
8	**3h**	4-Cl	CH_2Ph	TfOH	65	4	**4h**	9-Cl	70
9	**3i**	4-CF_3	H	PPA	120	8	**4i**	9-CF_3	0
10	**3j**	4-CF_3	CH_2Ph	PPA	120	8	**4j**	9-CF_3	0
11	**3j**	4-CF_3	CH_2Ph	TfOH	65	8	**4j**	9-CF_3	0
12	**3j**	4-CF_3	CH_2Ph	TfOH	135	8	**4j**	9-CF_3	0
13	**3k**	4-OMe	H	PPA	120	1	**4k**	9-OMe	31
14	**3k**	4-OMe	H	TfOH	65	0.25	**4k**	9-OMe	46
15	**3k**	4-OMe	H	TfOH	25	1	**4k**	9-OMe	58
16	**3l**	4-OMe	CH_2Ph	TfOH	25	1	**4l**	9-OMe	77
17	**3l**	4-OMe	CH_2Ph	CSA	135	8	**4l**	9-OMe	0
18	**3m**	3-Me	H	PPA	120	2	**4m**	8-Me	73
19	**3n**	3-Me	CH_2Ph	PPA	120	2	**4n**	8-Me	87

[a] TfOH: triflic acid; PPA: polyphosphoric acid; CSA: (+)10-camphorsulfonic acid.



7

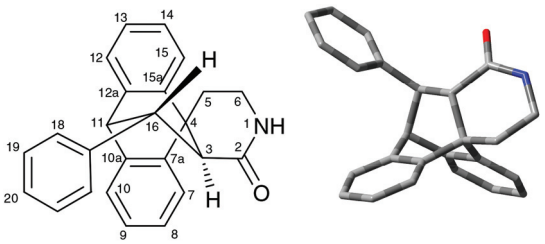
We believe that the electron withdrawing nature of the chlorine reduces the rate of the final carbocation cyclisation **6** → **4a** (Scheme 2). This result is also consistent with the formation of the spiro carbocation **6** being reversible, in equilibrium with the carbocation **5**. This could then undergo the alternative, less favoured cyclisation to give **7**, analogous to that previously observed with the *N*-cinnamoyl-naphthylamines.[2] N-alkylation would be expected to inhibit this reaction due to a steric interaction with the 8-proton of the anthracene. In agreement with this, cyclisation of the *N*-benzyl derivative **3h** with TfOH gave a good yield of product **4h** (entry 8), better than with PPA (entry 7), with little formation of the *N*-benzyl analogue of **7**.

With the much more electron withdrawing CF_3 substituent (entries 9–12), no cyclisation was observed and starting material was recovered. With the 4-methoxy compound **3k**, only moderate yields of **4k** were obtained with both PPA (entry 13) and TfOH (entry 14) under the normal heated conditions. However, with TfOH at room temperature, **3k** rapidly reacted to give a slightly better yield of **4k** (entry 15). Similarly the *N*-benzyl derivative **3l** rapidly cyclised with TfOH at room temperature to give a good yield of **4l** (entry 16). For both **3m** (entry 17) and **3n** (entry 18), only single regioisomers, **4m** and **4n** respectively, were formed in good yields. NMR analysis showed that they were the products derived from cyclisation onto the less sterically hindered 6-position, *para* to the methyl. This result was surprising, as in a previous study on the TfOH-mediate iminium ion cyclisation onto a *meta*-methyl substituted phenyl, a mixture of isomers derived from cyclisation onto both the *ortho* and *para* positions was obtained.[8] Similar electrophilic reactions, such as nitration, of *meta*-xylene give mixtures of products.[9] However, on examination of molecular models, it appears that the product derived from cyclisation onto the *ortho* position of the *meta*-substituted phenyl would have a severe steric clash between the 10-methyl group and the 12-CH proton.

The cyclisation reaction to form the polycyclics could theoretically be reversible. If the reaction were reversible, heating the polycyclics with TfOH in benzene should re-form the initial carbocation **5** (Scheme 2), which would be trapped by the solvent to form the 3,3-diphenylpropionamide.[10] However, on heating the polycyclics **4a** and **4d** with TfOH in benzene at reflux for 18 h, no reaction was observed and starting material was recovered in both cases. Thus it would appear that the cyclisation reaction is essentially irreversible.

The investigation of homologated cinnamamides was then undertaken to see if 6- and 7-membered spiro compounds could be formed. The aminoethyl analogue **8** was prepared in a 68% yield by a one-pot procedure *via* alane reduction of 9-(2-nitrovinyl)anthracene,[11] followed by acylation with cinnamoyl chloride. Previously, the use of LAH had been reported, but no yield of the amine was quoted.[12] Reaction of **8** with TfOH gave no identifiable products. However, with PPA the product obtained was the Diels–Alder adduct **9** (96% yield). The same product was obtained in similar yield simply by heating **8** in chlorobenzene. However, the reaction in chlorobenzene was slower (4 h *vs.* 30 min). In both cases, the expected *trans* stereochemistry was obtained.[15] The NMR assignments for **9** are included in Table 3. The NMR spectrum in the aliphatic region clearly showed a $-CH_2-CH_2-$ and a separate –CH–CH–CH– arrangement. In the carbon spectrum there was also an aliphatic, tetra-substituted C at δ 44.83, a mono-substituted phenyl and two 1,2-disubstituted phenyls. The bicyclo[2.2.2]-octane unit, formed by carbons 15a, 12a, 11, 10a, 7a, 4, 3 and

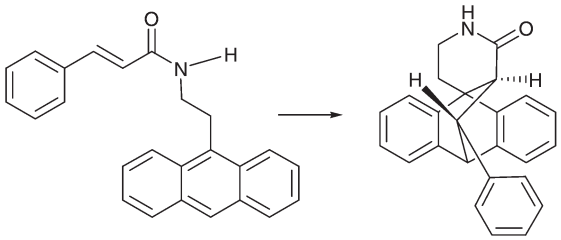
Table 3 ^{1}H and ^{13}C NMR assignments for (±)**9**. The optimised geometry (below) and calculated *J* couplings (in brackets) are also shown



Proton	δ/ppm	Coupled protons	*J*/Hz
3	2.66	3,16	6.3 (5.1)
5a	2.88	5a,5e	−14.1 (−13.2)
5e	3.12	5a,6a	11.7 (11.2)
6e	3.72	5a,6e	7.9 (7.7)
16	3.85	5e,6a	6.1 (5.7)
6e	4.09	5e,6e	1.9 (0.9)
11	4.20	6a,6e	−12.4 (−11.6)
NH	5.84	11,16	2.3 (2.4)
18	6.76	12,13	7.3 (6.5)
12	7.04	12,14	1.4 (0.9)
13	7.08	13,14	7.3 (6.6)
8	7.12	13,15	1.2 (0.8)
9	7.13	14,15	7.6 (6.7)
20	7.13		
19	7.14		
14	7.22		
15	7.31		
10	7.33		
7	7.40		

Carbon	δ/ppm	Carbon	δ/ppm
5-CH_2	23.89	14-CH	126.06
6-CH_2	39.25	20-CH	126.47
3-CH	54.14	9-CH	126.52
4-C	44.83	12-CH	126.62
16-CH	48.51	18-CH	128.04
11-CH	51.82	19-CH	128.23
15-CH	119.79	7a-C	140.23
7-CH	122.04	12a-C	141.59
10-CH	124.02	17-C	144.29
8-CH	125.79	15a-C	145.98
13-CH	125.92	10a-C	146.31
		2-C=O	172.81

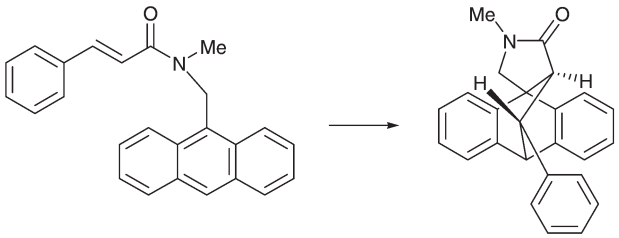
16, is a rigid structure and the coupling between the 3-H and 16-H of 6.3 Hz is consistent with a *trans* orientation. There is also a strong NOE observed between the signals for the 3-H and the 18-H protons, consistent with them being *cis*.



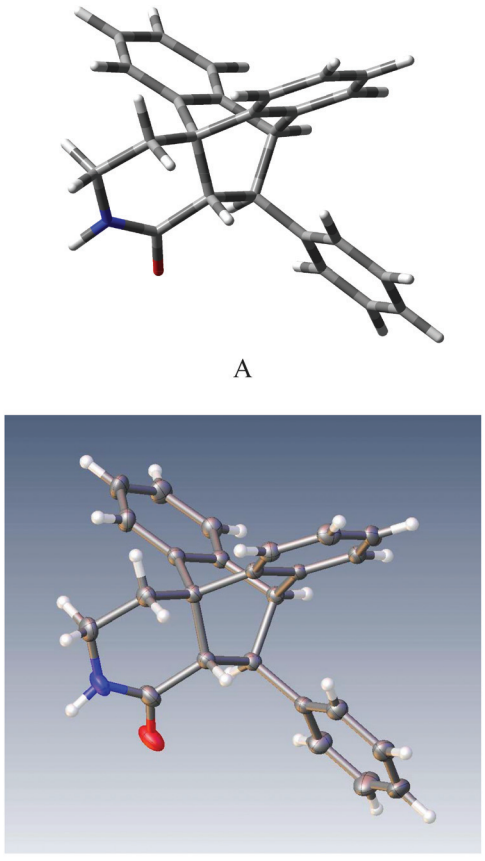
8 (±)**9**

Based upon the NMR studies and using a DFT geometry optimisation, the solution phase structure of **9** (A) is shown in Fig. 3 together with the ORTEP (50% probability ellipsoids) diagram (B) from the X-ray crystal structure analysis.

The anthracenylmethyl homologue **10**, prepared from the commercially available amine, gave no identifiable product with either TfOH or PPA, although the starting material rapidly disappeared. We believe that the anthracenylmethyl group is rapidly cleaved due to the high stability of the 9-anthracenylmethyl carbocation.[13] Indeed, 9-anthracenylmethyl has been used as an acid-cleavable protecting group for phenols.[14] However, on heating in chlorobenzene, **10** gave an excellent yield of the Diels–Alder product **11**. The structure of **11** was assigned by NMR spectral comparison with **9**.



10 (±)**11**



A B

Fig. 3 Solution phase structure of (19*S*,20*R*) **9** from NMR studies (A) and (B), an ORTEP diagram of (19*R*,20*S*) **9** (50% probability ellipsoids) from X-ray structure crystallography. Cambridge Crystallographic Data Centre deposition number CCDC 984577.

Summary and conclusion

We have shown that both *N*-cinnamoyl-9-aminomethyl- and *N*-cinnamoyl-9-aminoethyl-anthracenes give Diels–Alder cycloaddition products on heating. However, *N*-cinnamoyl-9-aminoanthracenes cyclise with either PPA or TfOH to give the novel polycyclic 2-azahexa-cyclo[10.6.6.$0^{1,5}$.$0^{6,11}$.$0^{13,18}$.$0^{19,24}$]-tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-ones in moderate to good yields. We believe that protonation of the cinnamoyl group forms a benzylic carbocation, which adds to the 9-position of the anthracene to give a doubly benzylic-stabilised carbocation at the 10 position. This then undergoes an electrophilic ring closure onto the phenyl of the cinnamoyl group. The cyclisation reaction is facilitated by electron donating groups on the phenyl ring. In most cases, for NH cinnamamides, a small amount of by-product is formed *via* cyclisation onto the 1-position of the anthracene. N-alkylation inhibits this side reaction. Only with a mildly electron withdrawing group on the cinnamoyl moiety is this by-product formed in sufficient quantity to be isolated, purified and characterised. However, no cyclisation is observed with strongly electron withdrawing substituents. We believe that the 9-aminoanthracenes do not undergo the Diels–Alder cycloadditions because the resultant spiro-azetidinones would be too strained to be thermo-dynamically favoured.

Experimental

All reagents were commercially available, unless otherwise specified, and used without purification. The chloroform used was stabilized with amylene. Petroleum ether was the 40–60 °C fraction. Infrared spectra were run neat on a Perkin Elmer 100 FT IR spectrometer. Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer DRX500 or Avance III 600 equipped with *z*-gradient facilities. ^{1}H and ^{13}C chemical shifts are given relative to TMS. Unless otherwise specified,

spectra were recorded at 25 °C. NMR *J*-couplings were predicted using calculations based on density functional theory (DFT), as described in detail previously.[16] Geometry optimisations were carried using M06-2X/6-31+G(d) level of theory. Mass spectra were run on a Thermo Mat900XP. Melting points were determined on a Sanyo-Gallenkamp capillary melting point apparatus and are uncorrected.

General procedure for the synthesis of *N*-cinnamoyl-9-aminoanthracenes

A suspension of the appropriate acid (2.5 g, 15 mmol), oxalyl chloride (1.4 mL, 16 mmol) and DMF (2 drops) in DCM (50 mL) was stirred at ambient temperatures until evolution of CO_2 had ceased (about 2 h). $CHCl_3$ (50 mL) was added and the solvent removed by rotary evaporation. The residue was dissolved in EtOAc (20 mL) and added to a stirred solution of 9-aminoanthracene[4] (2.9 g, 15 mmol) and *N*,*N*-diethylaniline (2.5 mL, 20 mmol) in EtOAc (100 mL), then heated to 60 °C for 1 h. On cooling to 0 °C, the solid product was collected, washed with EtOAc (2 × 20 mL) and dried. The product was used for reactions without further purification, although a small amount was recrystallised from DMSO–EtOH for characterization purposes. Additional product was obtained by washing the EtOAc mother liquors with 1 M HCl (2 × 50 mL), water (2 × 50 mL), 1 M NaOH (1 × 50 mL), brine (50 ML), drying ($MgSO_4$), concentration *in vacuo* and purification by flash column chromatography on SiO_2, the product eluting with DCM to 2% MeOH–DCM, depending upon the polarity. Quoted yields are that of the combined quantities.

***N*-Cinnamoyl-9-aminoanthracene 3a.** Isolated as a yellow solid (78% yield); mp >310 °C; ^{1}H NMR (600 MHz, $CDCl_3$), Rotamer **A**: δ 6.95 (1H, d, J = 15.6 Hz, COC*H*), 7.44 (1H, m, *p*-Ph), 7.45 (2H, m, *m*-Ph), 7.49 (2H, m, H-3,6), 7.54 (2H, m, H-2,7), 7.65 (2H, m, *o*-Ph), 7.91 (1H, d, J = 15.6 Hz, COCHC*H*), 8.04 (2H, d, J = 8.0 Hz, H-4,5), 8.09 (2H, d, J = 8.1 Hz, H-1,8), 8.48 (1H, s, H-10); Rotamer **B**: δ 5.91 (1H, d, J = 15.5 Hz, COC*H*), 7.08 (2H, m, *o*-Ph), 7.14 (2H, m, *m*-Ph), 7.20 (1H, m, *p*-Ph), 7.53 (2H, m, H-3,6), 7.58 (2H, m, H-2,7), 7.86 (1H, d, J = 15.5 Hz, COCHC*H*), 8.10 (2H, d, J = 8.6 Hz, H-4,5), 8.22 (2H, d, J = 8.7 Hz, H-1,8), 8.58 (1H, s, H-10); ^{1}H NMR (600 MHz, DMSO-d_6) 7.23 (1H, d, J = 15.9 Hz), 7.45 (1H, t, J = 7.5 Hz), 7.50 (2H, t, J = 7.5 Hz), 7.53–7.59 (4H, m), 7.69 (1H, d, J = 15.9 Hz), 7.73 (2H, d, J = 7.2 Hz), 8.08 (2H, m), 8.15 (2H, m), 8.63 (1H, s), 10.55 (1H, s); ^{13}C NMR (150.1 MHz, DMSO-d_6) δ = 121.6 (CH), 124.0 (CH), 125.6 (CH), 125.9 (CH), 126.1 (CH), 127.9 (CH), 127.9 (C), 128.5 (CH), 129.1 (CH), 129.5 (C), 129.9 (CH), 131.3 (C), 134.9 (C), 140.4 (CH), 165.2 (C); FTIR (solid) ν = 3253, 1652, 1623, 1502, 1338, 1205, 963, 729, 695, 676 cm^{-1}; MS (EI) m/z (%) 323 (M^+, 69), 193 (100), 131 (31); HMRS (EI): m/z calcd for $C_{23}H_{17}NO$ [M^+] 323.1310, found 323.1306.

***N*-(4-Methylcinnamoyl)-9-aminoanthracene 3e.** Isolated as a yellow solid (82% yield); mp >310 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.36 (3H, s), 7.15 (1H, d, J = 15.6 Hz), 7.29 (2H, d, J = 7.8 Hz), 7.52–7.57 (4H, m), 7.60 (2H, d, J = 8.4 Hz), 7.63 (1H, d, J = 15.6 Hz), 8.03–8.06 (2H, m), 8.12–8.15 (2H, m), 8.61 (1H, s), 10.49 (1H, s); ^{13}C NMR (150.1 MHz, DMSO-d_6) δ 21.1 (CH_3), 120.5 (CH), 123.9 (CH), 125.6 (CH), 125.9 (CH), 126.0 (CH), 126.8 (CH), 127.8 (CH), 127.9 (C), 128.4 (CH), 129.6 (CH), 129.7 (CH), 131.3 (C), 132.1 (C), 133.8 (C), 134.6 (CH), 139.7 (C), 140.4 (CH), 165.3 (C); FTIR (solid) ν = 3245, 1649, 1613, 1499, 1333, 1191, 975, 815, 731 cm^{-1}; MS (EI) m/z (%) 337 (M^+, 57), 193 (94), 145 (60), 86 (69), 85 (100); HMRS (EI): m/z calcd for $C_{24}H_{19}NO$ [M^+] 337.1467, found 337.1460.

***N*-(4-Chlorocinnamoyl)-9-aminoanthracene 3g.** Isolated as a yellow solid (84% yield); mp >310 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.21 (1H, d, J = 15.8 Hz), 7.53–7.70 (7H, m), 7.67 (1H, d, J = 15.8 Hz), 7.76 (2H, d, J = 8.3 Hz), 8.05–8.08 (2H, m), 8.13–8.16 (2H, m), 8.63 (1H, s), 10.51 (1H, s); ^{13}C NMR (150.1 MHz, DMSO-d_6) δ 122.4 (CH), 123.9 (CH), 125.6 (CH), 126.0 (CH), 126.1 (CH), 127.9 (C), 128.5 (CH), 129.1 (CH), 129.4 (C), 129.6 (CH), 131.3 (C), 133.8 (C), 134.3 (C), 139.0 (CH), 164.9 (C); FTIR (solid) ν = 3244, 1650, 1615, 1504, 1206, 1093, 973, 822, 730 cm^{-1}; MS (EI) m/z (%) 359 (M^+, 10), 357 (M^+, 31), 193 (100), 165 (47); HMRS (EI): m/z calcd for $C_{23}H_{16}ClNO$ [M^+] 357.0924, found 357.0934.

***N*-(4-Trifluoromethylcinnamoyl)-9-aminoanthracene 3i.** Isolated as a yellow solid (75% yield); mp 296 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.30 (1H, d, J = −15.9 Hz), 7.50–7.58 (4H, m), 7.71 (1H, d, J = 15.9 Hz), 7.82 (2H, d, J = 8.1 Hz), 7.93 (2H, d, J = 8.0 Hz), 8.02 (2H, d, J = 7.7 Hz), 8.13 (2H, dd, J = 1.8, 8.1 Hz), 8.61 (1H, s), 10.89 (1H, s); ^{13}C NMR (150.1 MHz, DMSO-d_6) δ 124.0 (CH), 124.1 (CH), 124.5 (C, q, J = 272 Hz), 124.6 (C), 124.7 (CH), 126.1 (CH), 126.3 (CH), 126.7 (CH), 128.2 (C), 128.8 (CH), 128.9 (CH), 129.4 (CH), 129.9 (C, q, J = 32 Hz), 131.6 (C), 139.2 (CH), 139.3 (C), 165.3 (C); F NMR (376.4 MHz, DMSO-d_6) δ = −61.15; FTIR (solid) ν = 3245, 1653, 1614, 1504, 1324, 1169, 1116, 1067, 835, 734 cm^{-1}; MS (EI) m/z (%) 391 (M^+, 92), 199 (32), 193 (100; HMRS (EI): m/z calcd for $C_{24}H_{16}F_3NO$ [M^+] 391.1184, found 391.1195.

***N*-(4-Methoxycinnamoyl)-9-aminoanthracene 3k.** Isolated as a yellow solid (95% yield); mp >310 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 3.80 (3H, s), 7.01–7.07 (3H, m), 7.50–7.56 (4H, m), 7.59 (1H, d, J = 15.8 Hz), 7.67 (2H, d, J = 8.3 Hz), 8.02 (2H, d, J = 8.2 Hz), 8.13 (2H, m), 8.61 (1H, s), 10.50 (1H, s); ^{13}C NMR (150.1 MHz, DMSO-d_6) δ 55.3 (CH_3), 114.5 (CH), 118.8 (CH), 123.8 (CH), 125.6 (CH), 125.9 (CH), 126.2 (CH), 127.2 (C), 127.9 (C), 128.5 (CH), 129.4 (C), 129.6 (CH), 131.3 (C), 140.4 (CH), 160.7 (C), 165.7 (C); FTIR (solid) ν = 3266, 1646, 1601, 1512, 1254, 1176, 1036, 973, 830, 731 cm^{-1}; MS [EI] m/z (%) 353 (M^+, 64), 193 (96), 161 (91), 84 (100), 71 (88); HMRS (EI): m/z calcd for $C_{24}H_{19}NO_2$ [M^+] 353.1416, found 353.1410.

***N*-(3-Methylcinnamoyl)-9-aminoanthracene 3m.** Isolated as a yellow solid (89% yield); mp >310 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.38 (s, 3H), 6.98 (1H, d, J = 6.9 Hz), 7.20–7.57 (7H, m), 8.06 (2H, d, J = 8.9 Hz), 8.14 (2H, d, J = 7.0 Hz), 8.28 (1H, d, J = 8.8 Hz); 8.62 (1H, s), 10.51 (1H, s); ^{13}C NMR (150.1 MHz, DMSO-d_6) δ 21.0 (CH_3), 121.5 (CH) 124.0 (CH), 125.1 (CH), 125.6 (CH), 125.9 (CH), 126.1 (CH), 127.9 (C), 128.4 (CH), 128.5 (CH), 129.0 (CH), 129.5 (C); 129.9 (C); 130.6 (CH), 131.3 (C); 134.8 (C); 138.3 (C); 140.4 (CH), 165.2 (C); FTIR (solid) ν = 3250, 1650, 1614, 1504, 1018, 972, 952, 758, 729 cm^{-1}; MS (EI) m/z (%) 337 (M^+, 17), 193 (58), 145 (32), 86 (62), 84 (100%);

HMRS (EI): *m*/*z* calcd for $C_{24}H_{19}NO$ [M^+], 337.1467, found 337.1471.

General procedure for the synthesis of *N*-alkyl-*N*-cinnamoyl-9-aminoanthracenes

The appropriate *N*-cinnamoyl-9-aminoanthracene (5.0 mmol), alkyl iodide or benzyl bromide (0.60 mL, 5.0 mmol) and KBu^tO (0.55 g, 5.0 mmol) in THF (100 mL) were stirred and heated under reflux for 2 h. On cooling, the THF was removed by rotary evaporation and the residue partitioned between H_2O (50 mL) and EtOAc (100 mL). The EtOAc was separated, washed with brine (50 mL) and dried ($MgSO_4$). Removal of the solvent gave the crude product, which was purified by column chromatography on SiO_2, the product eluting with 1 : 1 DCM–petrol to DCM depending upon the polarity of the product.

***N*-Methyl-*N*-cinnamoyl-9-aminoanthracene 3b.** Product isolated from the SiO_2 column by elution with DCM + 5% Et_2O as a yellow solid (83% yield); mp 56–58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (3H, s), 5.87 (1H, d, J = 15.5 Hz), 7.00 (2H, d, J = 7.8 Hz), 7.09 (2H, t, J = 7.3 Hz), 7.11–7.15 (1H, m), 7.50–7.59 (4H, m), 7.76 (1H, d, J = 15.5 Hz), 7.97 (2H, d, J = 8.7 Hz), 8.10 (2H, d, J = 8.3 Hz), 8.56 (1H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 37.0 (CH_3), 118.1 (CH), 122.9 (CH), 126.0 (CH), 127.6 (CH), 127.9 (CH), 128.5 (CH), 128.9 (CH), 128.9 (C), 129.5 (CH), 132.0 (C), 134.5 (C), 135.0 (C), 142.7 (CH), 167.8 (C); FTIR (solid) ν = 1650, 1611, 1373, 1351, 1213, 1084, 762, 735 cm^{-1}; MS (EI) *m*/*z* (%) 337 (M^+, 20), 207 (38), 144 (100), 131 (41); HMRS (EI): *m*/*z* calcd for $C_{24}H_{19}NO$ [M^+] 337.1467, found 337.1456.

***N*-Ethyl-*N*-cinnamoyl-9-aminoanthracene 3c.** Product isolated from the SiO_2 column by elution with DCM + 5% Et_2O as a grey solid (78% yield); mp 141–142 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (3H, t, J = 7.2 Hz), 4.12 (2H, q, J = 7.2 Hz), 5.83 (1H, d, J = 15.5 Hz), 6.98 (2H, d, J = 7.8 Hz), 7.08 (2H, t, J = 7.3 Hz), 7.10–7.15 (1H, m), 7.50–7.57 (4H, m), 7.76 (1H, d, J = 15.5 Hz), 7.97 (2H, d, J = 8.7 Hz), 8.10–8.13 (1H, m), 8.07–8.11 (1H, m), 8.56 (1H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.8 (CH_3), 45.5 (CH_2), 118.6 (CH), 123.5 (CH), 125.9 (CH), 127.4 (CH), 127.8 (CH), 127.9 (CH), 128.5 (CH), 128.8 (CH), 129.4 (CH), 129.7 (C), 132.0 (C), 133.4 (C), 135.1 (C), 142.6 (CH), 167.4 (C); FTIR (solid) ν = 1649, 1613, 1393, 1341, 1241, 977, 886, 845, 764, 740 cm^{-1}; MS (EI) *m*/*z* (%) 351 (M^+, 11), 158 (100), 131 (31), 84 (43; HMRS (EI): *m*/*z* calcd for $C_{25}H_{21}NO$ [M^+] 351.1623, found 351.1618.

***N*-Benzyl-*N*-cinnamoyl-9-aminoanthracene 3d.** Product isolated from the SiO_2 column by elution with DCM as a grey solid (75% yield); mp 138–140 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.20 (2H, s), 5.82 (1H, d, J = 15.6 Hz), 6.98 (2H, d, J = 7.8 Hz), 7.05–7.18 (8H, m), 7.34 (2H, dd, J = 7.8, 8.4 Hz), 7.46 (2H, t, J = 7.2 Hz), 7.67 (2H, d, J = 8.4 Hz), 7.81 (1H, d, J = 15.6 Hz), 8.05 (2H, d, J = 8.4 Hz), 8.55 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 54.0 (CH_2), 118.3 (CH), 123.5 (CH), 125.8 (CH), 127.1 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 128.7 (CH), 129.5 (C), 129.6 (CH), 130.5 (CH), 131.9 (C), 133.2 (C), 135.0 (C), 137.1 (C), 143.2 (CH), 167.6 (C); FTIR (solid) ν = 1643, 1602, 1389, 1338, 1220, 997, 959, 740 cm^{-1}; MS [EI] *m*/*z* (%) 413 (M^+, 3,), 322 (22), 220 (100), 131 (34), 91 (54); HMRS (EI): *m*/*z* calcd for $C_{30}H_{23}NO$ [M^+] 413.1779, found 413.1761.

***N*-Benzyl-*N*-(4-methylcinnamoyl)-9-aminoanthracene 3f.** Product isolated from the SiO_2 column by elution with DCM as a pale yellow solid (87% yield); mp 222–223 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.18 (3H, s), 5.19 (2H, s), 5.75 (1H, d, J = 15.6 Hz), 6.88 (4H, s), 7.06–7.12 (4H, m), 7.13–7.17 (1H, m), 7.33 (2H, t, J = 7.5 Hz), 7.45 (2H, t, J = 7.2 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.77 (1H, d, J = 15.6 Hz), 8.05 (2H, d, J = 8.4 Hz), 8.53 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 21.4 (CH_3), 53.9 (CH_2), 117.3 (CH), 123.6 (CH), 125.8 (CH), 127.0 (CH), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.2 (CH), 128.6 (CH), 129.2 (CH), 129.5 (C), 130.5 (CH), 131.9 (C), 132.3 (C), 133.3 (C), 137.2 (C), 139.9 (C), 143.2 (CH), 167.8 (C); FTIR (solid) ν = 1648, 1614, 1604, 1381, 1331, 1221, 1207, 815, 740, 700 cm^{-1}; MS [EI] *m*/*z* (%) 427 (M^+, 37), 283 (32), 234 (100), 145 (76), 91 (58); HMRS (EI): *m*/*z* calcd for $C_{24}H_{19}NO$ [M^+] 427.1936, found 427.1930.

***N*-Benzyl-*N*-(4-chlorocinnamoyl)-9-aminoanthracene 3h.** Product isolated from the SiO_2 column by elution with 3 : 1 DCM–petrol as a pale yellow solid (82% yield); mp 210–211 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.18 (2H, s), 5.77 (1H, d, J = 15.5 Hz), 6.88 (2H, d, J = 8.6 Hz), 7.13–7.16 (3H, m), 7.16–7.19 (1H, m), 7.31–7.38 (2H, m), 7.42–7.49 (2H, m), 7.64 (2H, d, J = 8.8 Hz), 7.73 (1H, d, J = 15.5 Hz), 8.05 (2H, d, J = 8.3 Hz), 8.70 (1H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 54.0 (CH_2), 118.9 (CH), 123.4 (CH), 125.8 (CH), 127.1 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.4 (C), 130.4 (CH), 131.9 (C), 133.0 (C), 133.5 (C), 135.3 (C), 137.0 (C), 141.7 (CH), 167.2 (C); FTIR (solid) ν = 1648, 1614, 1381, 1213, 984, 822, 739, 701 cm^{-1}; MS [EI] *m*/*z* (%) 447 (M^+, 12), 356 (12), 283 (15), 254 (50), 91 (100); HMRS (EI): *m*/*z* calcd for $C_{30}H_{22}ClNO$ [M^+] 447.1390, found 447.1391.

***N*-Benzyl-*N*-(4-trifluoromethylcinnamoyl)-9-aminoanthracene 3j.** Product isolated from the SiO_2 column by elution with 3 : 1 DCM–petrol as a white solid (73% yield); mp 164–165 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (2H, s), 5.88 (1H, d, J = 15.5 Hz), 6.98–7.21 (6H, m), 7.30–7.42 (4H, m), 7.45 (2H, t, J = 7.6 Hz), 7.65 (2H, d, J = 8.8 Hz), 7.80 (1H, d, J = 15.5 Hz), 8.06 (2H, d, J = 8.5 Hz), 8.56 (1H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 54.0 (CH_2), 120.9 (CH), 123.3 (CH), 123.8 (C, q, J = 270 Hz), 125.4 (CH, q, J = 3.8 Hz), 125.8 (CH), 127.2 (CH), 127.8 (CH), 127.9 (CH), 128.2 (CH), 128.7 (CH), 129.4 (CH), 130.4 (CH), 131.0 (C, q, J = 32 Hz), 131.9 (C), 132.8 (C), 136.8 (C), 138.4 (C), 141.3 (C), 141.4 (CH), 167.0 (C); FTIR (solid) ν = 1652, 1619, 1320, 1217, 1165, 1126, 1067, 833, 738, 702 cm^{-1}; MS [EI] *m*/*z* (%) 481 (M^+, 75), 390 (76), 288 (95), 193 (33), 91 (96%), 84 (100); HMRS (EI): *m*/*z* calcd for $C_{24}H_{19}NO$ [M^+] 481.1654, found 481.1649.

***N*-Benzyl-*N*-(4-methoxycinnamoyl)-9-aminoanthracene 3l.** Product isolated from the SiO_2 column by elution with DCM + 5% Et_2O as a white solid (86% yield); mp 202–203 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (3H, s), 5.19 (2H, s), 5.68 (1H, d, J = 15.4 Hz), 6.59 (2H, d, J = 8.7 Hz), 6.92 (2H, d, J = 8.7 Hz), 7.07–7.20 (4H, m), 7.31–7.35 (2H, m), 7.43–7.50 (2H, m), 7.66 (2H, d, J = 8.8 Hz), 7.75 (1H, d, J = 15.4 Hz), 8.04 (2H, d,

J = 8.5 Hz), 8.53 (1H, s); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 53.9 (CH_2), 55.3 (CH_3), 113.9 (CH), 116.0 (CH), 123.6 (CH), 125.7 (CH), 126.9 (CH), 127.6 (CH), 127.8 (C), 127.9 (CH), 128.2 (CH), 128.6 (CH), 129.4 (CH), 129.5 (C), 130.4 (CH), 131.9 (C), 133.4 (C), 137.2 (C), 142.8 (C), 142.8 (CH), 160.8 (C), 167.8 (C); FTIR (solid) ν = 1647, 1616, 1594, 1509, 1257, 1214, 1167, 827, 738, 698 cm^{-1}; MS [EI] m/z (%) 443 (M^+, 13), 283 (18), 250 (80), 161 (100), 91 (37); HMRS (EI): calcd for $C_{24}H_{19}NO$ [M^+] 443.1885, found 443.1878.

***N*-Benzyl-*N*-3-methyl-cinnamoyl-9-anthracene 3n.** Product isolated from the SiO_2 column by elution with 3 : 1 DCM–petrol as a pale grey solid (90% yield); mp 127–128 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.12 (3H, s), 5.19 (2H, s), 5.79 (1H, d, J = 15.6 Hz), 6.76 (1H, d, J = 6.6 H), 6.80 (1H, s), 6.92–6.98 (2H, m), 7.06–7.12 (4H, m), 7.13–7.18 (1H, m), 7.34 (2H, dd, J = 6.6, 7.8 Hz), 7.46 (2H, t, J = 7.5 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.77 (1H, d, J = 15.6 Hz), 8.05 (2H, d, J = 8.4 Hz), 8.54 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 21.2 (CH_3), 54.0 (CH_2), 118.1 (CH), 123.6 (CH), 124.9 (CH), 125.8 (CH), 127.1 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.5 (C), 130.4 (CH), 130.5 (CH), 131.9 (C), 133.2 (C), 134.9 (C), 137.1 (C), 138.2 (C), 143.5 (CH), 167.7 (C); FTIR (solid) ν = 1645, 1612, 1387, 1336, 1239, 961, 891, 849, 790, 740 702 cm^{-1}; MS [EI] m/z (%) 427 (M^+, 82), 336 (28), 283 (28), 234 (100), 145 (21), 86 (35), 84 (57); HMRS (EI): calcd for $C_{24}H_{19}NO$ [M^+] 427.1936, found 427.1930.

General procedure for the PPA-mediated cyclisation

A suspension of the *N*-cinnamoyl-9-aminoanthracene (1.0 mmol) in $CHCl_3$ (5 mL) and PPA (5 g) was heated to 120 °C (block temperature), distilling off the $CHCl_3$. After heating for 2 h, the reaction mixture was cooled and partitioned between ice/water (50 g) and DCM (100 mL). The organic layer was separated, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by column chromatography on SiO_2.

General procedure for the TfOH-mediated cyclisation

Triflic acid (1 mL, 10 mmol) was added to a stirred solution of the amide (2.0 mmol) in $CHCl_3$ (20 mL) and the reaction mixture was heated under gentle reflux until no starting material was present by TLC. The reaction mixture was cooled to room temperature, water (20 mL) was added and the mixture basified with an excess of solid K_2CO_3 until CO_2 evolution ceased. The product was extracted into EtOAc (3 × 50 mL), dried ($MgSO_4$), concentrated *in vacuo* and the product purified by column chromatography on SiO_2.

2-Azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4a. (a) With PPA. Following the general procedure, reaction of **3a** (0.32 g) with PPA and elution of the SiO_2 column with DCM + 5% Et_2O gave the title compound **4a** (0.25 g, 78% yield) as a buff solid; mp 234–236 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (H-4, dd, J = 12.9, 16.0 Hz), 2.95 (H-4, dd, J = 7.6, 16.0 Hz), 3.75 (H-5, dd, J = 7.6, 12.9 Hz), 4.94 (H-12, s), 6.88 (H-7, m), 6.88 (NH, brs), 7.11 (H-8, m), 7.13 (H-9, m), 7.21 (H-22, dt, J = 1.4, 2.3 Hz); 7.24 (H-21, dt, J = 1.4, 7.4 Hz), 7.25 (H-15, dt, J = 1.3, 7.4 Hz), 7.29 (H-16, dt, J = 1.4, 7.4 Hz), 7.36 (H-10, m), 7.37 (H-14, m), 7.46 (H-23, dd, J = 1.4, 7.2 Hz), 7.47 (H-20, dd, J = 1.4, 7.4 Hz), 7.51 (H-17, dd, J = 1.4, 7.5 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 35.8 (C-13), 48.2 (C-5), 55.3 (C-12), 66.2 (C-1), 119.9 (C-17), 124.3 (C-20), 125.0 (C-10), 126.8 (C-23), 127.0 (C-21), 127.4 (C-9), 127.4 (C-16), 127.6 (C-8), 127.7 (C-15), 127.8 (C-14), 128.2 (C-22), 129.7 (C-7), 134.6 (C-6), 136.4 (C-13), 139.4 (C-11), 139.5 (C-19), 141.8 (C-18), 144.5 (C-24), 178.0 (C-3); FTIR (solid) ν = 1696, 747, 722, 613, 477 cm^{-1}; MS [EI] m/z (%) 323 (M^+, 100), 294 (20), 280 (41), 265 (27); HMRS (EI): m/z calcd for $C_{23}H_{17}NO$ [M^+] 323.1310, found 323.1319.

(b) With TfOH. Following the general procedure, reaction of **3a** (0.32 g) and purification as above gave the title product **4a** (0.22 g, 69% yield).

(±)2-Methyl-2-azahexa-cyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4b. Following the general procedure, reaction of **3b** (0.34 g) with PPA and elution of the SiO_2 column with DCM + 5% Et_2O gave the title compound **4b** (0.31 g, 89% yield) as a white solid; mp 240–242 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (1H, dd, J = 13.1, 15.7 Hz), 3.00 (1H, dd, J = 7.7, 15.7 Hz), 3.23 (3H, s), 3.57 (1H, dd, J = 7.7, 13.1 Hz), 4.99 (1H, s), 6.86–6.89 (1H, m), 7.00–7.02 (1H, m), 7.08–7.11 (2H, m), 7.20–7.23 (2H, m), 7.27 (1H, dt, J = 1.4, 7.4 Hz), 7.29–7.34 (2H, m), 7.37–7.41 (2H, m), 7.48 (1H, dd, J = 1.1, 7.3 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 29.7 (CH_3), 35.3 (CH_2), 46.8 (CH), 55.2 (CH), 71.3 (C), 121.8 (CH), 125.1 (CH), 125.2 (CH), 126.7 (CH), 126.9 (CH), 127.3 (CH), 127.3, (CH), 127.4 (CH), 127.6 (CH), 127.6 (CH), 128.2 (CH), 129.8 (CH), 133.6 (C), 134.6 (C), 139.5 (C), 139.8 (C), 141.1 (C), 144.7 (C), 176.4 (C); (solid) ν = 1691, 1367, 757, 747, cm^{-1}; MS [EI] m/z (%) 337 (M^+, 100), 265 (33); HMRS (EI): m/z calcd for $C_{24}H_{19}NO$ [M^+] 337.1467, found 337.1471.

(±)2-Ethyl-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4c. Following the general procedure, **3c** (0.36 g) was reacted with PPA and elution of the SiO_2 column with DCM + 5% Et_2O gave the title compound **4c** (0.33 g, 90% yield) as a white solid; mp 204–205 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73 (3H, t, J = 7.1 Hz), 2.36 (1H, dd, J = 12.8, 16.0 Hz), 3.00 (1H, dd, J = 7.8, 16.0 Hz), 3.09 (1H, dq, J = 7.1, 14.4 Hz), 3.57 (1H, dd, J = 7.8, 12.8 Hz), 3.93 (1H, dq, J = 7.1, 14.4 Hz), 4.93 (1H, s), 6.86–6.89 (1H, m), 7.07–7.13 (3H, m), 7.18–7.22 (2H, m), 7.28 (1H, dt, J = 1.2, 7.4 Hz), 7.30–7.35 (2H, m), 7.36–7.40 (1H, m), 7.48 (1H, dd, J = 1.2, 7.4 Hz), 7.56 (1H, dd, J = 0.8, 7.3 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 14.6 (CH_3), 35.9 (CH_2), 39.6 (CH_2), 46.9 (CH), 55.2 (CH), 73.0 (C), 121.6 (CH), 125.1 (CH), 125.5 (CH), 126.7 (CH), 126.8 (CH), 127.3 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 128.1 (CH), 129.9 (CH), 134.7 (C), 139.6 (C), 140.9 (C), 144.3 (C), 177.4 (C); FTIR (solid) ν = 1682, 1393, 1346, 1315, 753, 743, 732 cm^{-1}; MS [EI] m/z (%) 351 (M^+, 100), 265 (34); m/z calcd for $C_{25}H_{21}NO$ [M^+] 351.1623, found 351.1619.

(±)2-Benzyl-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4d. Following the general procedure, **3d** (0.41 g) was reacted with PPA and elution of the SiO_2 column with 2 : 1 DCM–petroleum

ether gave the title compound **4d** (0.36 g, 88% yield) as a white solid; mp 230–231 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.46 (1H, dd, J = 13.2, 16.2 Hz), 3.16 (1H, dd, J = 7.8, 16.2 Hz), 3.71 (1H, dd, J = 7.8, 13.2 Hz), 4.06 (1H, d, J = 16.2 Hz), 4.94 (1H, s), 5.39 (1H, d, J = 16.2 Hz), 6.90–6.95 (2H, m), 7.07 (1H, d, J = 7.8 Hz), 7.09–7.17 (4H, m), 7.23–7.28 (2H, m), 7.32–7.37 (2H, m), 7.40–7.45 (4H, m), 7.48 (2H, d, J = 7.2 Hz); ^{13}C NMR (150.1 MHz, $CDCl_3$) δ 34.3 (CH_2), 46.7 (CH), 48.1 (CH_2), 55.2 (CH), 73.7 (C), 122.8 (CH), 125.4 (CH), 125.5 (CH), 126.4 (CH), 127.0 (CH), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.6 (CH), 127.7 (CH), 127.7 (CH), 128.3 (CH), 128.8 (CH), 130.0 (CH), 134.6 (C), 134.7 (C), 138.5 (C), 139.6 (C), 139.7 (C), 140.3 (C), 144.7 (C), 177.9 (C); FTIR (solid) ν = 1689, 1357, 754, 745, 712 cm^{-1}; MS [EI] m/z (%) 413 (M^+, 100), 322 (19), 280 (45), 265 (55), 91 (42); m/z calcd for $C_{30}H_{23}NO$ [M^+] 413.1779, found 413.1780.

(±)9-Methyl-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4e. Following the general procedure, **3e** (0.34 g) was reacted with PPA and elution of the SiO_2 column with DCM gave the title compound **4e** (0.28 g, 82% yield) as a light brown solid; mp >310 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.41 (1H, dd, J = 12.9, 16.0 Hz), 2.92 (1H, dd, J = 7.6, 16.0 Hz), 3.70 (1H, dd, J = 7.6, 12.9 Hz), 4.88 (1H, s), 6.68 (1H, s), 6.76 (1H, d, J = 7.8 Hz), 6.92 (1H, d, J = 7.8 Hz), 7.16–7.29 (5H, m), 7.37 (1H, dd, J = 1.4, 7.5 Hz), 7.42–7.46 (2H, m), 7.49 (1H, d, J = 7.4 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 21.0 (CH_3), 35.8 (CH_2), 47.9 (CH), 55.3 (CH), 66.2 (C), 119.8 (CH), 124.2 (CH), 124.9 (CH), 126.6 (CH), 126.9 (CH), 127.3 (CH), 127.5 (CH), 128.1 (CH), 128.2 (CH), 128.5 (CH), 129.5 (CH), 131.4 (C), 136.4 (C), 137.1 (C), 139.0 (C), 141.8 (C), 144.6 (C), 177.6 (C); FTIR (solid) ν = 1694, 1346, 818, 763, 731, cm^{-1}; MS [EI] m/z (%) 337 (M^+, 100), 294 (28), 279 (22), 86 (29), 84 (47); m/z calcd for $C_{24}H_{19}NO$ [M^+] 337.1467, found 337.1467.

(±)2-Benzyl-9-methyl-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]-tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4f. Following the general procedure, **3f** (0.43 g) was reacted with PPA and elution of the SiO_2 column with DCM gave the title compound **4f** as a white solid (0.38 g, 88% yield); mp 288–289 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (3H, s), 2.42 (1H, dd J = 12.6, 16.2 Hz), 3.13 (1H, dd, J = 7.8, 16.2 Hz), 3.66 (1H, dd, J = 7.8, 12.6 Hz), 4.04 (1H, d, J = 15.6 Hz), 4.89 (1H, s), 5.37 (1H, d, J = 15.6 Hz), 6.91 (1H, d, J = 7.8 Hz), 6.89–6.94 (2H, m), 7.06 (1H, d, J = 7.2 Hz), 7.12–7.17 (3H, m), 7.23–7.27 (2H, m), 7.34 (1H, t, J = 7.2 Hz), 7.39–7.43 (4H, m), 7.46 (2H, d, J = 7.2 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 21.1 (CH_3), 35.8 (CH_2), 46.4 (CH), 48.1 (CH_2), 55.3 (CH), 73.7 (C), 122.8 (CH), 125.3 (CH), 125.5 (CH), 126.3 (CH), 127.0 (CH), 127.1 (CH), 127.2 (CH), 127.4 (CH), 127.7 (CH), 128.3 (CH), 128.3 (CH), 128.3 (CH), 128.8 (CH), 129.9 (CH), 131.5 (C), 134.6 (C), 137.1 (C), 138.6 (C), 139.4 (C), 139.6 (C), 140.3 (C), 144.7 (C), 178.0 (C); FTIR (solid) ν = 1688, 1392, 1353, 810, 762, 749, 735, 709 cm^{-1}; MS [EI] m/z (%) 427 (M^+, 100), 336 (15), 294 (21), 279 (27); HMRS (EI): m/z calcd for $C_{24}H_{19}NO$ [M^+] 427.1936, found 427.1939.

(±)9-Chloro-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4g and 4-phenyl-3,4-dihydro-1*H*-1-azacyclohept[de]anthracen-2-one 7. Following the general procedure, **3g** (0.36 g) was reacted with PPA and elution of the SiO_2 column with 2 : 1 DCM–petroleum ether gave the title compound **7** (0.06 g, 16% yield) as an orange solid; mp >310 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.31–3.41 (2H, m), 4.91–4.95 (1H, m), 7.06 (2H, d, J = 8.4 Hz), 7.22 (2H, d, J = 8.4 Hz), 7.25–7.30 (1H, m), 7.39 (1H, t, J = 7.8 Hz), 7.53–7.59 (2H, m), 7.99 (1H, d, J = 8.4 Hz), 8.03 (2H, d, J = 8.8 Hz), 8.10 (1H, d, J = 8.8 Hz), 8.36 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 41.7 (CH_2), 47.7 (CH), 121.3 (CH), 122.4 (C), 123.8 (C), 124.9 (CH), 125.7 (CH), 126.2 (CH), 127.2 (CH), 128.2 (C), 128.7 (CH), 128.9 (CH), 129.2 (CH), 129.5 (CH), 129.7 (CH), 131.6 (C), 132.7 (C), 133.4 (C), 172.6 (C); MS [EI] m/z (%) 359 (M^+, 35), 357 (M^+, 100), 314 (85), 204 (23), 111 (24); m/z calcd for $C_{23}H_{16}ClNO$ [M^+] 357.0924, found 357.0925. Further elution with DCM gave the title compound **4g** (0.13 g, 36% yield) as a light brown solid; mp >310 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (1H, dd, J = 12.9, 14.5 Hz), 2.91 (1H, dd, J = 7.6, 14.5 Hz), 3.68 (1H, dd, J = 7.6, 12.9 Hz), 4.89 (1H, s), 6.75–6.82 (2H, m), 7.08 (1H, dm, J = 6.4 Hz), 7.2–7.34 (4H, m), 7.35–7.39 (2H, m), 7.42–7.53 (3H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 35.6 (CH_2), 47.8 (CH), 54.9 (CH), 65.9 (C), 119.9 (CH), 124.3 (CH), 125.1 (CH), 126.8 (CH), 127.3 (CH), 127.6 (CH), 127.7 (CH), 127.7 (CH), 128.3 (CH), 131.1 (CH), 132.7 (C), 133.0 (C), 136.2 (C), 138.8 (C), 140.9 (C), 141.6 (C), 143.8 (C), 177.1 (C); FTIR (solid) ν = 1702, 1346, 841, 815, 759, 748, 722 cm^{-1}; MS [EI] m/z (%) 359 (M^+, 35), 357 (M^+, 100), 314 (34), 299 (14), 279 (13), 165 (20), 84 (25); m/z calcd for $C_{23}H_{16}ClNO$ [M^+] 357.0924, found 357.0926.

(±)2-Benzyl-9-chloro-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]-tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4h. Following the general procedure, **3h** (0.45 g) was reacted with PPA and elution of the SiO_2 column with DCM gave the title compound **4h** (0.2 g, 45% yield) as a white solid; mp 308–309 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (1H, dd, J = 13.2, 16.2 Hz), 3.12 (1H, dd, J = 7.8, 16.2 Hz), 3.64 (1H, dd, J = 7.8, 13.2 Hz), 4.03 (1H, d, J = 15.6 Hz), 4.89 (1H, s), 5.37 (1H, d, J = 15.6 Hz), 6.85 (1H, d, J = 8.4 Hz), 6.93 (1H, dt, J = 0.6, 7.5 Hz), 7.06 (1H, d, J = 7.8 Hz), 7.09 (1H, dd, J = 2.4, 8.4 Hz), 7.12–7.15 (1H, m), 7.17 (1H, dt, J = 0.6, 7.5 Hz), 7.26–7.30 (2H, m), 7.32–7.36 (2H, m), 7.39–7.47 (6H, m); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 35.7 (CH_2), 46.3 (CH), 48.1 (CH_2), 54.8 (CH), 73.5 (C), 122.9 (CH), 126.5 (CH), 127.3 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.5 (CH), 127.6 (CH), 127.7 (CH), 128.4 (CH), 128.8 (CH), 131.5 (CH), 132.6 (C), 133.1 (C), 134.4 (C), 138.4 (C), 140.1 (C), 141.2 (C), 143.9 (C), 177.6 (C); FTIR (solid) ν = 1693, 1475, 1394, 1356, 852, 812, 751, 716 cm^{-1}; MS [EI] m/z (%) 449 (M^+, 35), 447 (M^+, 100), 356 (15), 314 (26), 299 (17), 279 (17); m/z calcd for $C_{30}H_{22}ClNO$ [M^+] 447.1390, found 447.1379.

(±)9-Methoxy-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4k. Following the general procedure, **3k** (0.35 g) was reacted with PPA and elution of the SiO_2 column with DCM gave the title compound **4k** as a light grey solid (0.11 g, 31% yield); mp >310 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.40 (1H, dd, J = 13.2, 16.2 Hz), 2.91 (1H, dd, J = 7.8, 16.2 Hz), 3.67 (1H, dd, J = 7.8, 13.2 Hz),

3.78 (3H, s), 6.65 (1H, dd, J = 3.0, 8.4 Hz), 6.75 (1H, brs), 6.79 (1H, d, J = 8.4 Hz), 6.93 (1H, d, J = 3.0 Hz), 7.19–7.27 (3H, m), 7.29 (1H, t, J = 6.9 Hz), 7.36 (1H, d, J = 6.6 Hz), 7.45 (2H, m), 7.50 (1H, d, J = 7.8 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 36.0 (CH_2), 47.7 (CH), 55.4 (CH), 55.4 (CH_3), 66.2 (C), 112.2 (CH), 113.8 (CH), 119.9 (CH), 124.3 (CH), 125.0 (CH), 126.5 (C), 126.8 (CH), 127.0 (CH), 127.5 (CH), 127.6 (CH), 128.1 (CH), 130.8 (C), 136.5 (C), 139.2 (C), 140.4 (C), 141.8 (C), 144.2 (C), 158.5 (C), 177.7 (C); FTIR (solid) ν = 1700, 1661, 1350, 1257, 981, 801, 731 cm^{-1}; MS [EI] m/z (%) 353 (M^+, 100), 310 (16), 86 (20), 84 (30); HMRS (EI): m/z calcd for $C_{24}H_{19}NO_2$ [M^+] 353.1416, found 353.1419.

(±)2-Benzyl-9-methoxy-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]-tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4l. Following the general procedure, **3l** (0.44 g) was reacted with TfOH, but with stirring at room temperature for 1 h and elution of the SiO_2 column with DCM gave the title compound **4l** as a white solid (0.34 g 77% yield); mp 268–269 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.40 (1H, dd, J = 12.6, 16.2 Hz), 3.11 (1H, dd, J = 7.8, 16.2 Hz), 3.63 (1H, dd, J = 7.8, 12.6 Hz), 3.77 (3H, s), 4.04 (1H, d, J = 15.6 Hz), 4.87 (1H, s), 5.37 (1H, d, J = 15.6 Hz), 6.65 (1H, dd, J = 3.0, 8.4 Hz), 6.83 (1H, d, J = 8.4 Hz), 6.89 (1H, d, J = 3.0 Hz), 6.91 (1H, dt, J = 1.2, 7.8 Hz), 7.06 (1H, d, J = 7.2 Hz), 7.11–7.17 (2H, m), 7.23–7.27 (2H, m), 7.34 (1H, t, J = 7.2 Hz), 7.39–7.44 (4H, m), 7.46 (2H, d, J = 7.2 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 36.0 (CH_2), 46.2 (CH), 48.1 (CH_2), 55.4 (CH), 55.4 (CH_3), 73.8 (C), 112.3 (CH), 113.6 (CH), 122.8 (CH), 125.4 (CH), 125.5 (CH), 126.4 (CH), 126.5 (C), 127.0 (CH), 127.2 (CH), 127.2 (CH), 127.4 (CH), 127.7 (CH), 128.3 (CH), 131.1 (CH), 134.6 (C), 138.5 (C), 139.2 (C), 140.3 (C), 140.7 (C), 144.3 (C), 158.4 (C), 178.0 (C); FTIR (solid) ν = 1688, 1501, 1351, 1244, 1034, 842, 762, 732, 712 cm^{-1}; MS [EI] m/z (%) 443 (M^+, 100), 352 (15), 310 (21), 295 (16), 91 (21); HMRS (EI): calcd for $C_{24}H_{19}NO$ [M^+] 443.1885, found 443.1890.

(±)8-Methyl-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4m. Following the general procedure, **3m** (0.34 g) was reacted with PPA and elution of the SiO_2 column with DCM gave the title compound **4m** (0.25 g, 73% yield) as a light brown solid; mp 304–306 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (3H, s), 2.44 (1H, dd, J = 12.9, 16.0 Hz), 2.94 (1H, dd, J = 7.6, 16.0 Hz), 3.71 (1H, dd, J = 7.6, 12.9 Hz), 4.91 (1H, s), 6.69 (1H, s), 6.95 (1H, d, J = 7.6 Hz), 7.17–7.30 (6H, m), 7.35 (1H, d, J = 7.1 Hz), 7.44 (1H, d, J = 7.2 Hz), 7.45–7.50 (2H, m), 7.53 (1H, d, J = 7.4 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 21.0 (CH_3), 35.9 (CH_2), 48.2 (CH), 55.0 (CH), 66.4 (C), 119.9 (CH), 124.3 (CH), 124.8 (CH), 126.6 (CH), 126.8 (CH), 127.3 (CH), 127.5 (CH), 127.6 (CH), 128.0 (CH), 128.1 (CH), 130.3 (CH), 134.3 (C), 136.5 (C), 136.5 (C), 137.3 (C), 139.7 (C), 141.8 (C). 144.7 (C), 178.1 (C); FTIR (solid) ν = 3180, 1697, 1343, 812, 736 cm^{-1}; MS [EI] m/z (%) 337 (M^+, 100), 294 (30), 279 (25), 86 (18), 84 (29); m/z calcd for $C_{24}H_{19}NO$ [M^+] 337.1467, found 337.1452.

(±)2-Benzyl-8-methyl-2-azahexacyclo[10.6.6.0^{1,5}.0^{6,11}.0^{13,18}.0^{19,24}]-tetracosa-6(11),7,9,13,15,17,19(24),20,22-nonaen-3-one 4n. Following the general procedure, **3n** (0.43 g) was reacted with PPA and elution of the SiO_2 column with DCM gave the title compound **4n** (0.37 g, 87% yield) as a pale yellow solid; mp 156–158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.23 (3H, s), 2.49 (1H, dd, J = 12.6, 16.2 Hz), 3.18 (1H, dd, J = 7.8, 16.2 H), 3.70 (1H, dd, J = 7.8, 12.6 Hz), 4.08 (1H, d, J = 16.2 Hz), 4.95 (1H, s), 5.41 (1H, d, J = 16.2 Hz), 6.76 (1H, s), 6.90–6.97 (2H, m), 7.10 (1H, d, J = 7.2 Hz), 7.14–7.19 (2H, m), 7.24–7.30 (3H, m), 7.37 (1H, t, J = 7.2 Hz), 7.40–7.48 (4H, m), 7.50 (2H, d, J = 7.2 Hz); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 21.3 (CH_3), 36.0 (CH_2), 46.8 (CH), 48.3 (CH_2), 54.7 (CH), 73.9 (C), 123.6 (CH), 126.3 (CH), 126.9 (CH), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 128.8 (CH), 130.9 (CH), 134.4 (C), 134.6 (C), 136.9 (C), 137.4 (C), 138.6 (C), 139.8 (C), 140.3 (C), 145.0 (C), 178.2 (C); FTIR (solid) ν = 1698, 1454, 1346, 1320, 744, 710 cm^{-1}; MS [EI] m/z (%) 427 (M^+, 100), 336 (20), 294 (23), 279 (24), 86 (58), 84 (89); m/z calcd for $C_{31}H_{25}NO$ [M^+] 427.1936, found 427.1931.

***N*-(Anthracen-9-yl-ethyl)-3-phenylacryl-amide 8.** To a stirred solution of LAH (5 mL of a 2 M solution) in dry THF (30 mL) under Ar at −78 °C was added, in one portion, $AlCl_3$ 0.5 g, 3.7 mmol) and the solution warmed to 0 °C over 10 min. On re-cooling to −78 °C, 9-(2-nitrovinyl)anthracene (1.3 g, 5.2 mmol)[11] was added in one portion and the reaction mixture allowed to warm to room temperature, then heated to 40 °C for 30 min. On cooling to 0 °C, 50 mL of THF was added, followed by careful addition of 2 M NaOH (3 mL). After stirring for 30 min, Et_3N (0.7 mL, 5 mmol) and cinnamoyl chloride (0.8 g 4.8 mmol) were added, and the reaction stirred at room temperature for 1 h. The reaction mixture was filtered through celite and the collected solids washed with DCM (3 × 50 mL). The combined organics were concentrated by rotary evaporation and the residue re-dissolved in 9 : 1 Et_2O–DCM. This solution was then washed with 2 M HCl (30 mL), H_2O (3 × 30 mL) and 1 M NaOH (30 mL) and dried ($MgSO_4$), Filtration and removal of the solvent by rotary evaporation gave an oil which, on trituration with ether gave the title compound (0.8 g) as pale yellow solid. Purification of the concentrated mother liquors by column chromatography on SiO_2, eluting with 3 : 1 DCM/petrol–DCM gave a further 0.45 g of product, total yield 1.25 g, (68% yield); mp 189–190 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.83 (2H, m), 3.96 (2H, 7.3 Hz), 5.79 (1H, brs), 6.25 (1H, d, J = 15.6 Hz), 7.25 (1H, s), 7.32–7.38 (2H, m), 7.43–7.49 (3H, m), 7.53 (2H, ddd, J = 1.2, 6.4, 7.7 Hz), 7.62 (1H, d, J = 15.6 Hz), 8.02 (2H, d, J = 8.4 Hz), 3.70 (2H, d, J = 8.9 Hz), 8.39 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 27.8 (CH_2), 40.9 (CH_2), 120.6 (CH), 124.4 (CH), 125.2 (CH), 126.2 (CH), 126.7 (CH), 127.9 (CH), 128.9 (CH), 129.3 (CH), 129.8 (CH), 130.3 (C), 131.0 (C), 131.7 (C), 134.9 (C), 141.2 (CH), 166.5 (C); FTIR (solid) ν = 3302, 1651, 1613, 1535, 1329, 1215, 1120, 969, 873, 834, 727, 714, 658 cm^{-1}; MS [EI] m/z (%) 351 (M^+, 8), 204 (41), 191 (100), 189 (48), 131 (85), 103 (53), 69 (51); m/z calcd for $C_{25}H_{21}NO$ [M^+] 351.1623, found 351.1620.

(19*S*,20*R*)(19*R*,20*S*)-20-Phenyl-17-azapentacyclo[6.-6-.6.-0^{1,19}.0^{2,7}.0^{9,14}]icosa-2,4,6,9(14),10,12-hexaen-18-one 9. Following the general procedure for the PPA cyclisation, 9 (0.70 g, 2 mmol) was heated for 30 min at 130 °C (heating block temperature). The product was purified by column chromatography

on SiO_2, eluting with 5% EtOAc–DCM, isolated as a cream solid from ether trituration (0.67 g, 96% yield); mp 159–160 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.77 (3H, s), 5.80 (2H, s), 6.88 (1H, d, J = 15.6 Hz), 7.32–7.40 (3H, m), 7.50 (2H, t, J = 7.5 Hz), 7.52–7.59 (4H, m), 7.86 (1H, d, J = 15.6 Hz), 8.05 (2H, d, J = 8.4 Hz), 8.37 (2H, d, J = 8.4 Hz), 8.50 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 33.2 (CH_3), 41.9 (CH_2), 117.8 (CH), 124.3 (CH), 125.3 (CH), 126.9 (CH), 127.8 (C), 128.0 (CH), 128.5 (CH), 128.9 (CH), 129.4 (CH), 129.8 (CH), 131.5 (C), 135.4 (C), 143.2 (C), 143.2 (CH), 166.7 (C); FTIR (solid) ν = 1647, 1593, 1408, 1242, 1115, 990, 885, 760, 733, 701, 518 cm^{-1}; MS [EI] m/z (%) 351 (M^+, 64), 204 (100), 191 (83), 189 (29), 131 (47), 103 (19); m/z calcd for $C_{25}H_{21}NO$ [M^+] 351.1623, found 351.1627.

***N*-(Anthracen-9-yl-methyl)-*N*-methyl-3-phenylacryl-amide 10.** To a stirred solution of *N*-anthracen-9-yl-methyl-methylamine (1.0 g, 4.6 mmol) and Et_3N (0.7 mL, 5 mmol) in DCM (50 mL) was added cinnamoyl chloride (0.77 g, 4.6 mmol) in DCM (20 mL) and stirred at room temperature for 1 h. Water (20 mL) was added and the solid collected, washed with water (20 mL), Et_2O (2 × 50 mL) and dried (1.5 g, 92% yield). A small sample was recrystallised from EtOAc–petroleum ether as a white solid, mp 211–212 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.77 (3H, s), 5.80 (2H, s), 6.88 (1H, d, J = 15.6 Hz), 7.32–7.40 (3H, m), 7.50 (2H, t, J = 7.5 Hz), 7.52–7.59 (4H, m), 7.86 (1H, d, J = 15.6 Hz), 8.05 (2H, d, J = 8.4 Hz), 8.37 (2H, d, J = 8.4 Hz), 8.50 (1H, s); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 33.2 (CH_3), 41.9 (CH_2), 117.8 (CH), 124.3 (CH), 125.3 (CH), 126.9 (CH), 127.8 (C), 128.0 (CH), 128.5 (CH), 128.9 (CH), 129.4 (CH), 129.8 (CH), 131.5 (C), 135.4 (C), 143.2 (C), 143.2 (CH), 166.7 (C); FTIR (solid) ν = 1686, 1398, 776, 765, 755, 731, 704, 591 cm^{-1}; MS [EI] m/z (%) 351 (M^+, 100), 220 (58), 191 (49); MS [EI] m/z (%) 351 (M^+, 100), 220 (19), 191 (17), 179 (26); m/z calcd for $C_{25}H_{21}NO$ [M^+] 351.1623, found 351.1611.

(±)16-Methyl-19-phenyl-16-azapentacyclo[6.6.5.0^{1,18}.0^{2,7}.0^{9,14}]-nonadeca-2,4,6,9(14),10,12-hexaen-17-one 11. A solution of **10** (0.35 g, 1 mmol) in chlorobenzene (10 mL) was heated under gentle reflux for 2 h. The reaction mixture was cooled and the product purified by column chromatography on silica, initially eluting with 3 : 1 petroleum ether–DCM to remove the chlorobenzene, then with DCM to give 0.30 g of (±)16-methyl-19-phenyl-16-azapentacyclo[6.6.5.0^{1,18}.0^{2,7}.0^{9,14}]nonadeca-2,4,6,9-(14),10,12-hexaen-17-one **11** as a white solid (86% yield), crystallised from Et_2O–petroleum ether, mp 211–212 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.70 (1H, dd, J = 0.9, 7.6 Hz), 3.03 (3H, d, J = 0.9 Hz), 3.31 (1H, dd, J = 1.7, 766 Hz), 4.31 (1H, d, J = 10.5 Hz), 4.34 (1H, d, J = 10.5 Hz), 4.88 (1H, d, J = 1.7 Hz), 7.11 (2H, d, J = 7.2 Hz), 7.14–7.23 (6H, m), 7.25–7.27 (1H, m), 7.31–7.36 (2H, m); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 30.41 (CH_3), 45.1 (CH), 48.8 (CH_2), 50.4 (CH), 51.1 (CH), 119.3 (CH), 121.7 (CH), 123.2 (CH), 126.1 (CH), 126.2 (CH), 126.3 (CH), 126.6 (CH), 126.8 (CH), 127.1 (CH), 127.7 (CH), 128.5 (CH), 138.4 (C), 140.8 (C), 143.6 (C), 143.8 (C), 146.7 (C), 173.6 (C); FTIR (solid) ν = 1686, 1398, 776, 765, 755, 731, 704, 591 cm^{-1}; MS [EI] m/z (%) 351 (M^+, 100), 220 (58), 191 (49); m/z calcd for $C_{25}H_{21}NO$ [M^+] 351.1623, found 351.1620.

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