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Asymmetric control in Diels–Alder cycloadditions of chiral 9-aminoanthracenes by relay of stereochemical information

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Abstract—Two approaches to the synthesis of chiral 9-amino anthracenes are described. The first, by nucleophilic addition of organolithium reagents to imines promoted by $BF_3{\cdot}OEt_2$, unexpectedly provided stable aminoboranes as products. The second approach, using palladium catalysed cross coupling, was more successful for primary amines, and the key 9-(α-methylbenzylamino)anthracene subjected to cycloadditions with *N*-methyl maleimide and maleic anhydride. Excellent reactivity was achieved with good levels of diastereoselectivity, through a favourable combination of electrostatic and hydrogen bonding effects. Trial studies of the retro Diels–Alder reaction of these cycloadducts were also performed.

1. Introduction

The introduction of stereocontrol elements into reagents to allow subsequent stereoselective transformations is still one of the most powerful methods for introducing new stereogenic centres into target substrates, despite intense competition from catalytic methods. We have previously demonstrated that excellent levels of diastereoselectivity are observed in the Diels–Alder reaction of 9-(methoxyethyl)-anthracene **1** (Fig. 1) with dienophiles, such as maleic anhydride, maleimides and *p*-benzoquinone.[1]

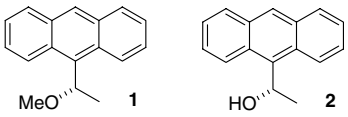

Figure 1. Chiral 9-substituted anthracenes.

Research from this group and others has also demonstrated that these and similar compounds can function as chiral auxiliaries.[1b,2] The two key issues in using these compounds as auxiliaries is obtaining high diastereoselectivities in the cycloaddition step, coupled with the ease of synthesis of the chiral anthracene. Although parent ether **1** has always given exceptionally high diastereoselectivity, its asymmetric synthesis requires a key crystallisation to enhance levels of enantioselectivity. Thus, we recently began a programme aimed at investigating the stereocontrol element and have prepared oxazolines, in which the stereogenic centre is too far from the reaction centre to control the selectivity of the cycloaddition,[3] and oxazolidines,[4] whereby suitable choice of nitrogen protecting groups can lead to a change in the sense of diastereoselection. Earlier we had noted that 9-(1-hydroxyethyl)-anthracene **2** led to an enhanced reaction rate and a different sense of diastereoselection, presumably through hydrogen bonding effects.[5] We thus envisioned that 9-amino anthracenes could participate in hydrogen bonding and lead to increased reactivity of the diene through the interaction of the lone pair with the aromatic system.[6]

2. Results and discussion

2.1. Synthesis of *rac*-9-(*N*-α-methylbenzylamino)anthracene 10

There are a number of existing ways to construct the target molecule, however, we initially chose to access racemic material in order to assess the viability of the reaction by a four-step synthetic route via key imine **6**. Thus, nitration of anthracene using concd HNO_3/HCl in glacial acetic acid[7] afforded a pale yellow precipitate of 9-nitro-10-chloro-9,10-dihydroanthracene **3** that was converted to

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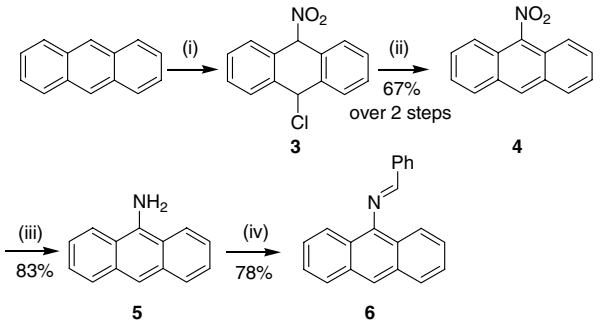
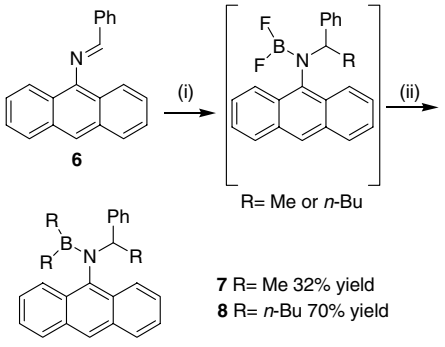
9-nitroanthracene **4** after treatment with aqueous NaOH. This was reduced with a suspension of $SnCl_2$ in concd HCl to give a yellow precipitate of the desired 9-aminoanthracene **5**,[8] which was condensed with benzaldehyde in toluene to afford target compound **6** as an orange solid in 78% yield (Scheme 1).



Scheme 1. Reagents and conditions: (i) concd HNO_3/HCl, <30 °C; (ii) NaOH (10%), 60–70 °C; (iii) $SnCl_2$/concd HCl, glacial HOAc, 70–80 °C; (iv) PhCHO, toluene, reflux.

In an initial attempt to add a methyl group across the C=N bond, methylmagnesium bromide and methyl lithium were added to imine **6** leading to the recovery of the starting material. In order to increase the reactivity, $BF_3{\cdot}OEt_2$ was added prior to the addition of methyl lithium at −78 °C. The resulting mixture was stirred for 21 h at room temperature giving complete conversion to a single component, which unexpectedly contained three methyl groups clearly visible in the ^{1}H NMR spectrum. Surprisingly, two of these methyl groups could not be detected by ^{13}C NMR spectroscopy. Similar results were obtained when using *n*-BuLi, giving complete conversion to a single component containing extra two butyl groups from the ^{1}H NMR spectrum, with two methylene signals missing from the ^{13}C NMR spectrum. A ^{13}C NMR experiment at 400 MHz revealed the two extra methyl and methylene groups as broad signals with very low intensity, suggesting the interaction with a proximal boron atom through quadrupole relaxation. This implied that the compounds obtained were anthrylaminodialkylboranes **7** and **8** formed by nucleophilic attack on the intermediate aminoborane complex, which was supported by ^{11}B NMR spectroscopy and high resolution mass spectroscopy (Scheme 2). This class of compounds has previously been prepared by ther-

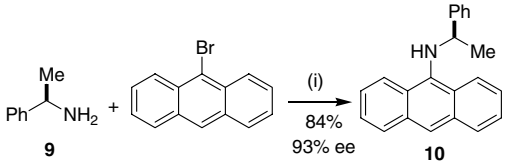


Scheme 2. Reagents and conditions: (i) MeLi or *n*-BuLi, toluene, −78 °C, $BF_3{\cdot}OEt_2$, 24 h; (ii) aq $NaHCO_3$, rt.

mal decomposition of aminoboranes in sealed tubes under high vacuum,[9] by the reaction of metalloborohydrides and ammonium halides,[10] and by the reaction of N-disubstituted aminodichloroboranes with an excess of Grignard reagents.[11] However, this remains the first example of anthrylaminoboranes prepared to date.

2.2. Preparation of (*R*)-9-(*N*-α-methylbenzylamino)anthracene 10

Since preparation via organometallic addition appeared to be unviable, transition metal-catalysed formation of the key carbon–nitrogen bond was considered as an alternative strategy.[12] This had the added advantage of using commercial, enantiomerically pure chiral amines, negating a resolution or asymmetric synthesis step in our route. A cross-coupling reaction of (*R*)-α-methylbenzylamine **9** with 9-bromoanthracene was carried out using $Pd(OAc)_2$ (4.8 mol % Pd) and (−)-BINAP (16 mol %) as a catalyst system to form 9-*N*-α-methylbenzylaminoanthracene **10** in 100% conversion within 21 h and 84% yield with 93% ee. The enantiomeric excess of the product was slightly lower than the precursor primary amine **9** (98% ee), the partial racemisation in such reactions being previously noted by Buchwald et al.[13] (Scheme 3).

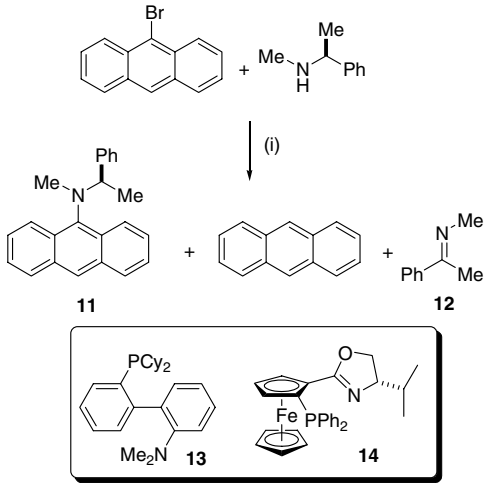


Scheme 3. Reagents and conditions: (i) 4.8% $Pd(OAc)_2$, 16% (−)-BINAP, *t*-BuONa, toluene, 90–95 °C.

2.3. Preparation of (*R*)-9-(*N*-methyl-α-methylbenzylamino)anthracene

Since our previous studies have shown that the proximity of the stereodirecting group has important consequences on the level of diastereoselectivity observed, analogues bearing alkyl groups at the nitrogen centre were also considered. Attempts to prepare the *N*-methyl analogue by a similar palladium catalysed cross coupling with (*R*)-*N*-methyl-α-methylbenzylamine using $Pd(OAc)_2$/(−)-BINAP as a catalyst combination in the presence of *t*-BuONa with toluene as the solvent led to recovery of the starting materials. This reaction was repeated using a variety of mono- and bidentate phosphine ligands [$Pd_2(dba)_3$/P(*o*-tolyl)$_3$, $Pd(OAc)_2$/(−)-BINAP, $Pd_2(dba)_3$/(−)-BINAP, $Pd_2(dba)_3$/dppe, $Pd_2(dba)_3$/(*o*-tolyl)$_3$P, $Pd(Ph_3)_4$/PPh_3], with starting materials being recovered in all cases. However, a combination of $Pd_2(dba)_3$ and Buchwald's phosphine ligand **13**[14] produced 20% conversion of the starting materials to the target amino anthracene **11**. Surprisingly, unlike the ligands previously used, ligand **13** gave rise to both imine **12** and anthracene via a β-hydride elimination pathway (Scheme 4). The ^{1}H NMR data of the crude material also revealed that imine **12** was formed as the *E*-isomer.[15]

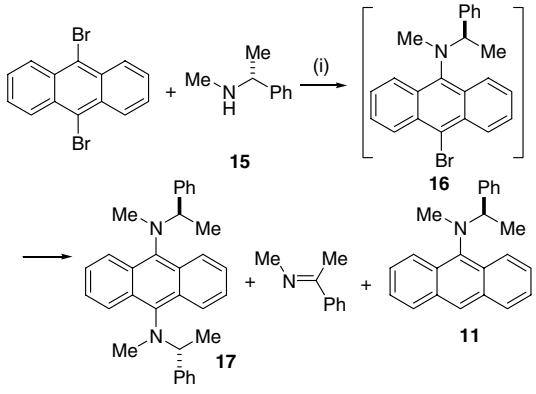
Since this aminophosphine ligand appeared to give promising results, other related phosphine–nitrogen containing



Scheme 4. Reagents and conditions: (i) 6% $Pd_2(dba)_3$/6% **13** or **14**, *t*-BuONa, toluene, 80–85 °C.

ligands were considered. Thus, oxazolinylphosphine ligand **14** was prepared via a three-step sequence following a literature procedure[16] and used with $Pd_2(dba)_3$ to give target aminoanthracene **11** in ca. 20% conversion, but with no formation of anthracene or imine as a side product. Although not pursued, optimisation of this class of ferrocenyl ligands may be useful in the development of catalyst systems that do not result in the decomposition of valuable starting materials by β-hydride elimination.

Since β-hydride elimination tends to be exasperated by electron rich aryl halides, it was thought that the electronic density around the anthracene ring may be reduced by having another withdrawing group, such as a bromine atom, attached to C10 of the anthracene ring.[17] Theoretically, this could lead to the formation of 9,10-diaminoanthracene **17**. When the cross-coupling reaction of 9,10-dibromoanthracene and secondary amine **14** was carried out using $Pd_2(dba)_3$/ligand **13** in the presence of NaO*t*-Bu using toluene as a solvent, aminoanthracene **11** was formed (17% conversion). No formation of 9,10-di-(*N*-methyl-α-methylbenzylamino)anthracene **17** was observed which could be attributed to the fact that intermediate **16** is electron-rich with β-hydride elimination taking place to form amine **11** along with the imine (Scheme 5). Once again, the ^1H NMR data of the crude material also revealed that the imine was formed as the *E*-isomer.

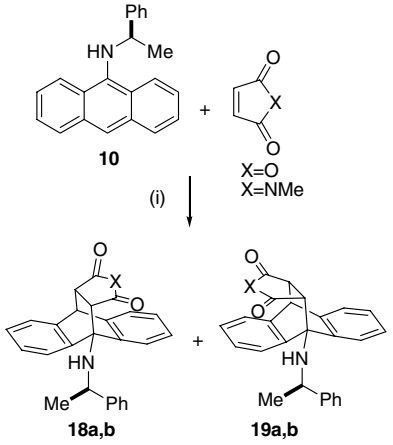


Scheme 5. Reagents and conditions: (i) 4% $Pd_2(dba)_3$/8% **13**, *t*-BuONa, toluene, 85 °C.

Although compound **11** was made in 16% yield, it was impractical to carry out any further transformations with such a low yield. Attempts to improve the yield by employing a deptrotonation/alkylation strategy with compound **10** failed, as did use of alternative alkylation reagents such as benzyl bromide. In view of this, only auxiliary **10** was taken forward for evaluation.[18]

2.4. Diels–Alder cycloaddition of (*R*)-9-(*N*-α-methylbenzylamino) anthracene 10 with *N*-methylmaleimide and maleic anhydride

As the reactivity and diastereoselectivity of methyl ether **1** in Diels–Alder cycloadditions with *N*-methylmaleimide have been previously reported,[1b] this was used as a benchmark for evaluating the chiral anthracene prepared. Amine **10** was reacted with 1 equiv of *N*-methylmaleimide and maleic anhydride for 2 h at 80–85 °C, in each case, producing a mixture of two diastereoisomers in excellent conversion and good selectivity (Scheme 6, Table 1).



Scheme 6. Reagents and conditions: (i) toluene, 80–85 °C, 2 h.

Table 1. Reactions of amine **10** with maleic anhydride and *N*-methyl maleimides

	Conversion[a] (%)	Diastereomeric ratio[a]	Yield (major isomer)[b]
X = NMe	100	**18a**:**19a** = 92:8	89%
X = O	100	**18b**:**19b** = 91:9	Not determined

[a] Calculated from the integrals of appropriate signals in the ^1H NMR spectrum.
[b] Based on isolated product.

The reactivity of this amine was found to be higher than the reactivity of ether **1** and neither temperature nor reaction time had an effect on the diastereoselectivity. In each case, scalemic mixtures of **18a**, **19a** and **18b**, **19b** (76:24 and 86:14, respectively) obtained after partial diastereomeric enhancement by recrystallisation were stirred for 2 h in toluene at 80–85 °C. No change in the diastereomeric ratio was observed indicating that these reactions were

irreversible and hence kinetically controlled. In the case of the maleimide reaction, effective recrystallisation allowed the identity of the major diastereoisomer **18a** to be determined by single crystal X-ray diffraction.[19] Although separation was more difficult and not preparatively useful, repeated crystallisation of the maleic anhydride adducts allowed isolation of the major and minor isomers, the identity of which was again confirmed by single crystal X-ray diffraction (Figs. 2–4).

It should be noted that the stereochemical outcome is opposite to that which has previously been reported.[6] In earlier work, the absolute sense of diastereroselection was confirmed by conversion of the anhydride cycloadduct into a lactone, whose absolute configuration was known. The stereochemistry was then assigned by comparison of the specific rotation with that in the literature, however this was not conducted in the same solvent, which may have led to the discrepancy reported.[20]

The origin of the stereoselectivity is very unlikely to result from the direct interaction of the stereogenic centre with the dienophile, since this group is located too far away from the approaching dienophile, essentially occupying space beneath the anthracene ring system, exemplified by the single crystal X-ray structure (Figs. 5 and 6).

However, the reaction can be rationalised via a relay of stereochemical information from the fixed stereogenic centre via the stereochemically labile amine atom. The dienophile approaches from the least hindered face of aminoanthracene **10** opposite to the α-methylbenzyl group (models **A**

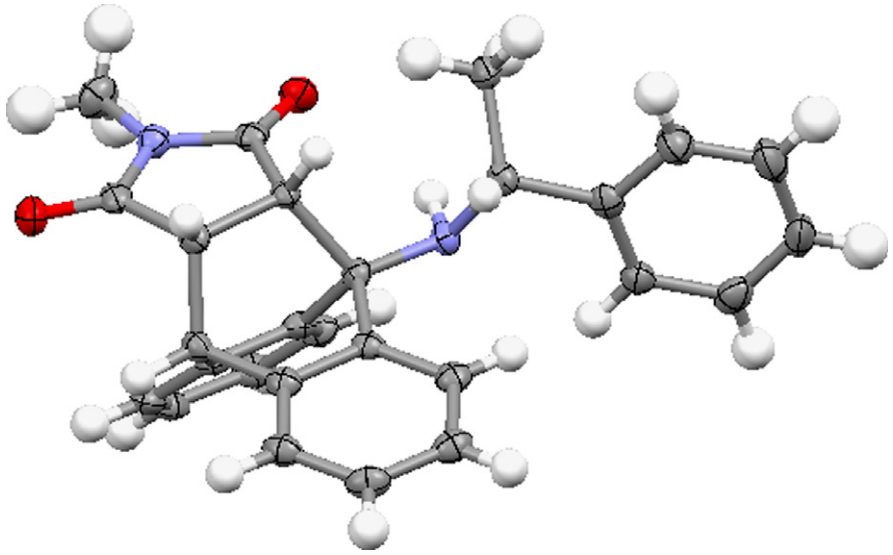


Figure 2. Crystal structure of (3a*S*,9a*S*)-3a,4,9,9a-tetrahydro-4-[(*R*)-α-methylbenzylamino]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3-(2*H*)-dione **18a**. Thermal ellipsoids shown at 50% probability.

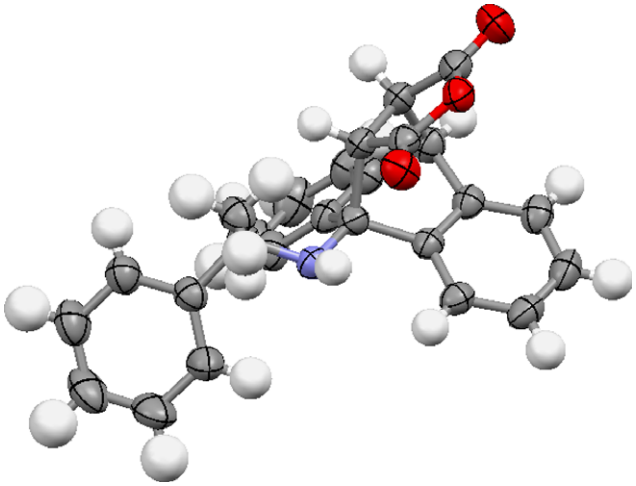


Figure 3. Crystal structure of (11*S*,15*S*)-9,10,11,15-tetrahydro-9-[(*R*)-α-methylbenzylamino]-9,10[3′,4′]-furanoanthracene-12,14-dione **18b**. Thermal ellipsoids shown at 50% probability.

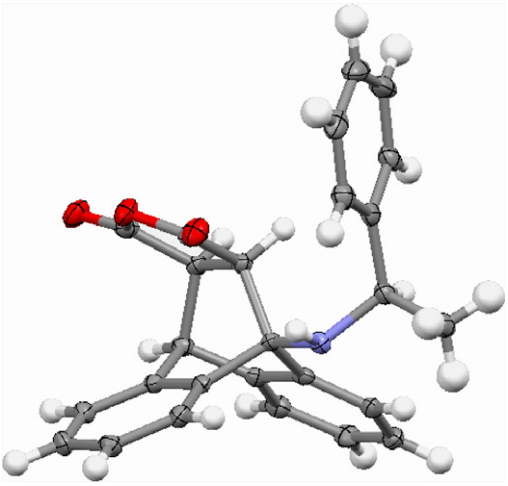


Figure 4. Crystal structure of (11*R*,15*R*)-9,10,11,15-tetrahydro-9-[(*R*)-α-methylbenzylamino]-9,10[3′,4′]-furanoanthracene-12,14-dione **19b**. Thermal ellipsoids shown at 50% probability.

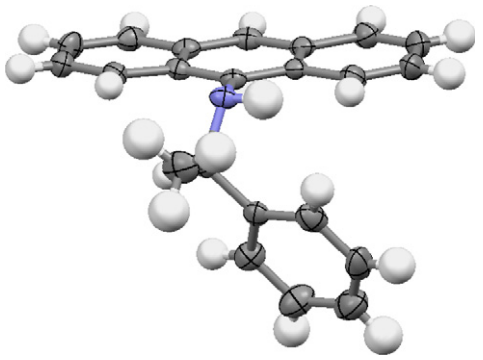


Figure 5. Crystal structure of 9-[(*R*)-α-methylbenzylamino]anthracene **10**. Thermal ellipsoids shown at 50% probability.

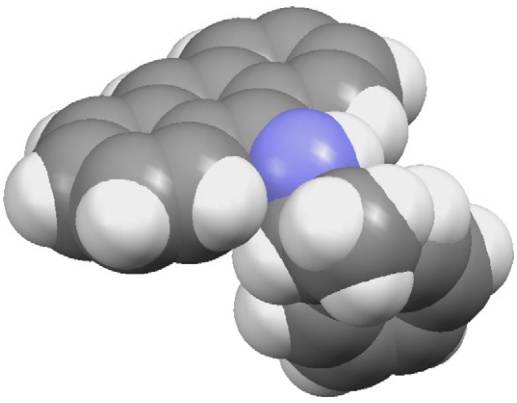


Figure 6. Space-filling representation of the crystal structure of 9-[(*R*)-α-methylbenzylamino]anthracene **10**.

and **B**) (Fig. 7). The diastereoselection can then be explained by the dienophile approaching the anthracene ring with the carbonyl oxygen orientated towards the hydrogen of the amino group, thus forming a hydrogen bond, and additionally avoiding possible electrostatic repulsion with the nitrogen lone pair (model **A**). This leads to the formation of isomers **18a** and **18b** as the major diastereoisomers. The minor diastereoisomers **19a** and **19b** are formed when the dienophile attacks the anthracene ring with the carbonyl oxygen orientated towards the nitrogen lone pair (model **B**).

Given the relatively small size difference between the lone pair and the hydrogen atom, this example highlights the importance of a combination of electrostatic repulsion and attractive hydrogen bonding in establishing high levels of stereoselection. This is further exemplified by the Diels–Alder reactions that have been reported with *N*-methyl analogue **11**. Here there is no hydrogen bond, instead relying on repulsive effects from the lone pair and methyl group, resulting in a very poor diastereoselectivity (1.2:1).[2]

2.5. Retro Diels–Alder reaction of adduct 18a

Attempts at a retro Diels–Alder reaction were carried out on adduct **18a** under basic and acidic conditions. This reaction was first conducted under basic conditions using a number of strong bases (NaH, LDA and *t*-BuLi) in an attempt to deprotonate the amino group, thus increasing the electron density and effecting an efficient retro Diels–Alder reaction.[21] However, all these bases returned unreacted starting material, indicating that the amine proton might be too sterically hindered to be removed. Promoting the retro Diels–Alder reaction by simply heating at reflux was thought to be hopeless, as amine **10** showed high reactivity in the competing forward Diels–Alder reaction. Therefore, adduct **18a** was refluxed in toluene in the presence of trifluoroacetic acid in order to trap any amine **10** that may form from a retro Diels–Alder reaction as an ammonium salt, leading to an electron-deficient anthracene derivative, which would in turn slow the forward Diels–Alder reaction and allow the isolation of the *N*-methylmaleimide and ammonium salt of the auxiliary which could be recovered.

However, the product of this reaction anthrone **20** was formed after elimination of the stereodirecting group and partial cleavage of the *N*-methylsuccinamide unit. This probably results from protonation of the carbonyl group leading to cleavage of the bond between C10 and C11. Hydrolysis of the resulting iminium ion **21** by water would give anthrone **20** (Scheme 7).

In an attempt to confirm this, a ^{1}H NMR experiment involving heating adduct **18a** at 90 °C in deuterated toluene in the presence of trifluoroacetic acid was carried out. After 3 h, the formation of anthrone **20** along with (*R*)-α-methylbenzyl ammonium trifluoroacetate was seen in the ^{1}H NMR spectrum. This finding supports the proposed mechanism, with the water coming from the deuterated chloroform.

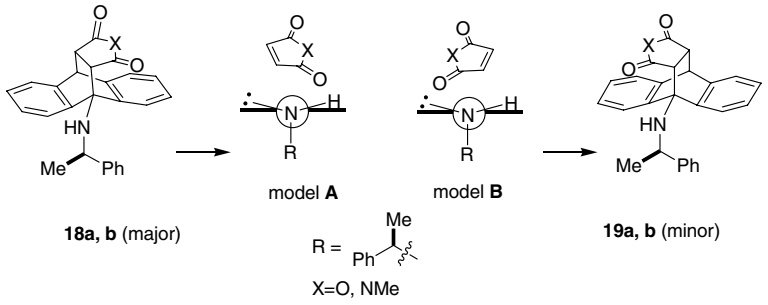
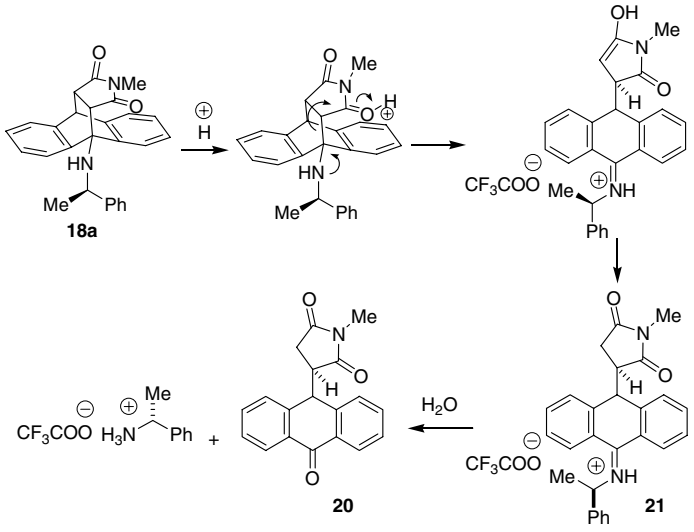


Figure 7. Possible models to explain the diastereoselection.



Scheme 7. Possible mechanism for the formation of anthrone **20**.

3. Conclusion

We have shown that 9-anthryl amines can be readily prepared via palladium catalysed coupling reactions, and in doing so we have discovered new routes for preparing anthryl aminoboranes and new ligands for the N-arylation reaction that appear to inhibit competitive β-hydride elimination. The 9-anthryl amine produced displayed excellent reactivity and very good diastereoselectivity in trial Diels–Alder reactions, the reaction being controlled by a through space relay from the adjacent fixed stereodirecting group. Our results on the sense of diastereoselection contradict those previously reported by Snyder, although this is probably due to an error made in comparison of specific rotations with known compounds. The main issue with the methodology is the problem encountered in performing the retro Diels–Alder reaction required for use as an effective auxiliary.

4. Experimental

4.1. Materials

The solvents utilised were dried as appropriate, unless otherwise stated. THF, toluene and ether were dried over sodium, whereas CH_2Cl_2 was dried over calcium hydride. Glassware was flame-dried and dried under vacuum before use. TLC was carried out using Fluorochem Limited Silica Gel 40–63u 60A. Visualisation of the TLC plates was achieved by employing UV lamps at 254 nm and 356 nm or $KMnO_4$ and then heating.

4.2. Instrumentation

Melting points were measured on a Gallenkamp apparatus and are uncorrected. Specific rotations were performed on an Optical Activity LTD. AA-10 automatic polarimeter at 589 nm (Na D-line) and measured at 20 °C unless otherwise stated. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. All infrared spectra were recorded on a Perkin–Elmer Spectrum RX/FT-IR system with a DuraSampl*IR* II ATR accessory. 250 MHz and 300 MHz ^{1}H NMR were carried out on a AC-250 or Avance 300 instrument, respectively, supported by an Aspect 200 or Aspect 300 data system. ^{13}C NMR (100 MHz) was carried out on a Bruker AMX-400 spectrometer. Residual proton signals from the deuterated solvents were used as references [chloroform (^{1}H 7.25 ppm, ^{13}C 77 ppm)]. Coupling constants were measured in Hz. Mass spectra were recorded on a Micromass Autospec M spectrometer. Elemental microanalysis was performed using a Perkin–Elmer 2400 CHNS/0 Series II elemental analyser.

Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Single crystals of compounds **10**, **18a**, **18b** and **19b** were grown by liquid diffusion from dichloromethane/petroleum ether (40–60 °C), mounted in inert oil and transferred to the cold gas stream of the diffractometer.

4.3. Preparation of 9-nitroanthracene 4[7]

Concentrated nitric acid (4 cm^3) was added dropwise to a suspension of anthracene (10.0 g, 56.0 mmol) in glacial acetic acid (40 cm^3) maintaining the temperature below 30 °C. This was stirred vigorously for 1 h to form a clear solution. A mixture of concentrated HCl (50 cm^3) and glacial acetic acid (50 cm^3) was added slowly resulting in a pale yellow precipitate of 9-nitro-10-chloro-9,10-dihydroanthracene **3**. This was filtered, washed with glacial acetic acid (3×25 cm^3) and thoroughly with water until the washings were neutral. The resulting yellow solid was treated with a warm solution (60–70 °C) of 10% NaOH (200 cm^3), filtered, washed with warm water until the washings were neutral, air-dried and recrystallised from glacial acetic acid affording a fluffy yellow solid (8.31 g, 67% yield), mp 153–157 °C (acetic acid) (lit.[7] 148–149 °C acetic acid); δ_H (250 MHz; $CDCl_3$) 8.59 (1H, s, ArC*H*), 8.03 (2H, d, *J* 7.6, ArC*H*), 7.92 (2H, d, *J* 7.6, ArC*H*), 7.68–7.52 (4H, m, ArC*H*); δ_C (62.5 MHz; $CDCl_3$) 130.7 (Ar*C*NO$_2$), 130.4

(2 × ArC), 128.9 (2 × ArC), 128.4 (Ar-C), 126.2 (2 × ArC), 122.6 (2 × ArC), 121.3 (4 × ArC). NMR data were in accordance with the literature.[22]

4.4. Preparation of 9-aminoanthracene 5[8]

A suspension of 9-nitroanthracene **4** (7.24 g, 32.5 mmol) in glacial acetic acid (145 cm^3) was heated to 70–80 °C for 1.5 h. To the resulting clear solution was added a slurry of $SnCl_2$ (31.0 g, 163.2 mmol) in concentrated HCl (110 cm^3) via a dropping funnel. The resulting yellow precipitate was stirred at 80 °C for a further 30 min, cooled to room temperature, filtered, washed with concentrated HCl (3 × 10 cm^3), treated with a solution of 5% NaOH for approximately 15 min with manual stirring from time to time, filtered, washed thoroughly with water until the washings were neutral and vacuum-dried at 50 °C for 6 h to afford a yellow powder (5.18 g, 83% yield). No further purification was required, mp 165–170 °C (lit.[8] 153–154 °C, benzene); δ_H (250 MHz; $CDCl_3$) 7.90 (4H, m, ArCH), 7.85 (1H, s, ArCH), 7.43 (4H, m, ArCH), 4.85 (2H, br s, NH_2); δ_C (62.5 MHz; $CDCl_3$) 129.0 (2 × ArC), 125.2 (4 × ArC), 123.8 (2 × ArC), 121.1 (2 × ArC), 116.3 (4 × ArC). NMR data were in accordance with the literature.[8]

4.5. Preparation of 9-*N*-anthrylbenzylidene 6

A mixture of benzaldehyde (4 cm^3, 39.5 mmol) and 9-aminoanthracene **5** (3.85 g, 20.0 mmol) in toluene (40 cm^3) was refluxed for 24 h. The reaction mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure to give a yellow-brown solid. The crude product was purified by column chromatography (5% EtOAc/petroleum ether 40–60 °C) to afford the target compound as an orange solid (4.36 g, 78% yield), mp 138–142 °C; (Found: C, 89.8; H, 5.4; N, 4.9. $C_{21}H_{15}N$ requires C, 89.7; H, 5.4; N, 5.0); ν_{max} (ATR)/cm^{-1} 1630; δ_H (250 MHz; $CDCl_3$) 8.52 (1H, s, PhCH=N), 8.35 (1H, s, ArCH), 8.13–8.07 (2H, m, ArCH), 8.05–7.95 (4H, m, ArCH), 7.64–7.53 (3H, m, ArCH), 7.53–7.60 (4H, m, ArCH); δ_C (62.5 MHz; $CDCl_3$) 165.3 (C=N), 146.0 (ArC), 135.9 (Ar-C), 132.0 (2 × ArCH), 131.9 (2 × ArC), 129.0 (2 × ArCH), 128.2 (2 × ArCH), 125.5 (2 × ArCH), 124.9 (2 × ArCH), 124.0 (2 × ArCH), 122.2 (2 × ArCH), 122.0 (2 × ArC); *m*/*z* (ES^+) 282.1281 (100%, $C_{21}H_{16}N$ requires 282.1283); (EI^+) 282 (28), 281 (100), 280 (36), 204 (16), 203 (12), 178 (25), 177 (22), 176 (24), 151 (15), 140 (14), 126 (6), 103 (8).

4.6. Preparation of *rac*-*N*-(9-anthryl)-α-methylbenzylamino-*N*-dimethylborane 7

9-*N*-Anthrylbenzylidene **6** (0.70 g, 2.50 mmol) was dissolved in dry toluene (30 cm^3), cooled to −20 °C and $BF_3{\cdot}OEt_2$ (0.7 cm^3, 5.60 mmol) was then added. The reaction mixture was stirred for 5 min at −20 °C, cooled to −78 °C and MeLi (7 cm^3, 9.80 mmol) was added dropwise. The resulting mixture was stirred for 6 h, allowed to warm to room temperature and stirred for a further 12 h. The reaction was quenched with satd aq $NaHCO_3$ (20 cm^3), the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 cm^3). The organic phases were combined, washed with brine (2 × 30 cm^3), dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (100% petroleum ether 40–60 °C) to give the title compound as a yellow thick oil (0.27 g, 32% yield), ν_{max} ATR/cm^{-1} 1670; δ_H (250 MHz; $CDCl_3$) 8.29 (1H, s, ArCH), 8.22–8.16 (1H, m, ArCH), 8.03–7.94 (1H, m, ArCH), 7.79 (1H, d, *J* 8.6, ArCH), 7.49–7.40 (2H, m, ArCH), 7.25–7.14 (2H, m, ArCH), 6.96 (1H, m, ArCH), 6.89–6.80 (3H, m, ArCH), 6.67–6.64 (2H, m, ArCH), 5.60 (1H, q, *J* 7.3, NCHCH$_3$), 1.39 (3H, d, *J* 7.3, CHCH$_3$), 0.75 (3H, s, BCH$_3$), −0.65 (3H, s, BCH$_3$); δ_C (100 MHz; $CDCl_3$) 142.5 (ArC), 138.2 (ArC), 131.7 (ArC), 131.6 (ArC), 130.4 (ArC), 130.0 (ArC), 128.6 (2 × ArCH), 128.4 (ArCH), 127.5 (2 × ArCH), 127.4 (ArCH), 126.8 (ArCH), 125.6 (ArCH), 125.1 (ArCH), 125.0 (2 × ArCH), 124.8 (ArCH), 124.5 (ArCH), 123.9 (ArCH), 60.5 (CH), 21.7 (CH$_3$), 6.8 (br s, BCH$_3$), 5.8 (br s, BCH$_3$); δ_B (128.4 MHz; $CDCl_3$) 48.1 (br s, NBMe$_2$); *m*/*z* (EI^+) 338 (12%), 337.2008 (46, $C_{24}H_{24}{}^{11}BN$ requires 337.2002); 336 (10), 233 (46), 232 (100), 231 (50), 218 (22), 217 (78), 216 (34), 105 (65).

4.7. Preparation of *rac*-*N*-(9-anthryl)-α-butylbenzylamino-*N*-dibutylborane 8

9-*N*-Anthrylbenzylidene **6** (0.20 g, 0.71 mmol) was dissolved in dry toluene (10 cm^3), cooled to −20 °C and $BF_3{\cdot}OEt_2$ (0.2 cm^3, 1.64 mmol) was added. The reaction mixture was stirred for 5 min at −20 °C, cooled to −78 °C and *n*-BuLi (1.2 cm^3, 3.00 mmol) was added dropwise. The resulting mixture was stirred for 6 h, allowed to warm to room temperature and left stirring for a further 12 h. The reaction was quenched with satd aq $NaHCO_3$ (10 cm^3). The organic layer was separated and the aqueous layer extracted with EtOAc (3 × 10 cm^3). The organic phases were combined, washed with brine (2 × 20 cm^3), dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified by column chromatography (100% petroleum ether 40–60 °C) to give the title compound as a yellow thick oil (0.23 g, 70% yield), ν_{max} ATR/cm^{-1} 1520; δ_H (250 MHz; $CDCl_3$) 8.32–8.27 (2H, m, ArCH), 8.02–7.98 (1H, m, ArCH), 7.74 (1H, d, *J* 8.4, ArCH), 7.49–7.43 (2H, m, ArCH), 7.28 (1H, d, *J* 8.4, ArCH), 7.14 (1H, app. t, *J* 8.4, ArCH), 6.86–6.80 (2H, m, ArCH), 6.70 (2H, app. t, *J* 8.4, ArCH), 6.40 (2H, d, *J* 7.0, ArCH), 5.37 (1H, dd, *J* 11.5, 4.4, CH), 2.15 (1H, m, CHH), 1.91–1.59 (5H, m, 2 × CH$_2$ and CHH), 1.55–1.49 (2H, m, CH$_2$), 1.35–0.93 [8H, m, 4 × CH$_2$], 0.91–0.74 [6H, m, 3 × CH$_2$], 0.48 (3H, t, *J* 7.2, CH$_3$), 0.19 (2H, dd, *J* 9.3, 6.9, BCH$_2$); δ_C (100 MHz; $CDCl_3$) 139.6 (ArC), 138.3 (ArC), 131.6 (ArC), 131.4 (ArC), 130.4 (ArC), 130.3 (ArC), 129.6 (2 × ArCH), 128.3 (ArCH), 127.2 (ArCH), 127.0 (2 × ArCH), 126.6 (ArCH), 125.7 (ArCH), 125.2 (ArCH), 125.1 (ArCH), 124.9 (ArCH), 124.8 (ArCH), 124.5 (ArCH), 124.4 (ArCH), 123.8 (ArCH), 66.0 (CH), 36.4 (CH$_2$), 31.9 (CH$_2$), 29.7 (CH$_2$), 29.4 (CH$_2$), 28.4 (CH$_2$), 28.0 (CH$_2$), 26.8 (CH$_2$), 25.8 (CH$_2$), 22.5 (CH$_2$), 20.7 (br s, BCH$_2$), 18.8 (br s, BCH$_2$), 14.3 (CH$_3$), 14.0 (CH$_3$), 13.8 (CH$_3$); δ_B (128.4 MHz; $CDCl_3$) 49.2 [br s, NB(*n*-Bu)$_2$]; *m*/*z* (EI^+) 464 (16%), 463.3420 (47, $C_{33}H_{42}{}^{11}BN$ requires 463.3410); 462 (13), 407 (12), 406 (16), 317 (44), 316 (82), 315 (26), 260 (67), 259 (74), 204 (42), 203 (64), 147 (68), 91 (100).

4.8. Preparation of (*R*)-9-(*N*-α-methylbenzylamino)anthracene 10[23]

A mixture of (−)-BINAP (0.01 g, 0.016 mmol, 16 mol %) and $Pd(OAc)_2$ (0.0012 g, 0.0048 mmol, 4.8 mol %) was stirred in dry toluene (2 cm^3) for 5 min at room temperature. 9-Bromoanthracene (0.51 g, 2.00 mmol), (*R*)-α-methylbenzylamine (0.4 cm^3, 3.00 mmol), NaO*t*-Bu (0.27 g, 2.80 mmol) and dry toluene (2 cm^3) were added. The reaction mixture was stirred for 21 h at 90–95 °C and cooled to room temperature. The reaction was then diluted with diethyl ether (10 cm^3), filtered though Celite, concentrated and dried in vacuo. The crude product was purified by column chromatography (10% EtOAc/petroleum ether 40–60 °C) to afford 0.50 g (84% yield) of the dried product, mp 134–136 °C; $[\alpha]_D$ +198 (*c* 0.5, $CHCl_3$); ν_{max} (ATR)/cm^{-1} 1556, 1411, 1354; δ_H (250 MHz; $CDCl_3$) 8.16–8.12 (2H, m, ArC*H*), 8.13 (1H, s, ArC*H*), 7.98–7.94 (2H, m, ArC*H*), 7.46–7.23 (9H, m, ArC*H*), 4.73 (1H, q, *J* 6.7, C*H*), 4.24 (1H, br s, N*H*), 1.57 (3H, d, *J* 6.7, CH_3); δ_C (62.5 MHz; $CDCl_3$) 144.9 (Ar*C*), 140.3 (Ar*C*), 132.2 (2 × Ar*C*), 128.8 (2 × Ar*C*H), 128.6 (2 × Ar*C*H), 127.1 (Ar*C*H), 126.2 (2 × Ar*C*H), 126.0 (Ar*C*), 125.1 (2 × Ar*C*H), 124.6 (2 × Ar*C*H), 123.3 (Ar*C*H), 121.5 (Ar*C*H), 60.3 (*C*H), 23.1 (CH_3); *m*/*z* (ES^+) 298.1602 (100%, $C_{22}H_{20}N$ requires 298.1596); *m*/*z* (EI^+) 298 (12), 297 (45), 204 (9), 193 (100), 192 (60), 177 (9), 165 (52), 151 (6), 139 (6), 105 (59), 91 (9).

4.9. Preparation of (*R*)-(+)-α-methylbenzyl formamide[24]

(*R*)-(+)-α-Methylbenzylamine (1.0 cm^3, 7.83 mmol) was dissolved in THF (15 cm^3) at 50 °C in the presence of Amberlyst (ca. 0.05 g) as a catalyst. Ethylformate (4.8 cm^3, 59.5 mmol) was added to the reaction mixture and then heated at reflux for 21 h. This was allowed to cool to room temperature, diethyl ether (15 cm^3) added, the catalyst filtered and the solvent removed in vacuo. (*R*)-(+)-α-Methylbenzylformamide was obtained as an oily residue, which did not require purification (1.15 g, 99% yield), $[\alpha]_D = +168.6$ (*c* 1, $CHCl_3$), [lit.[24] +171.5 (*c* 6.07, $CHCl_3$)]; δ_H (300 MHz; $CDCl_3$) 8.06 (1H, s, C*H*O), 7.26–7.22 (5H, m, ArC*H*), 6.32–5.80 (1H, br s, N*H*), 5.12 (0.8H, quintet, *J* 7.2, C*H* major rotamer), 4.63 (0.2H, quintet, *J* 7.2, C*H* minor rotamer), 1.49 (0.6H, d, *J* 7.2, CH_3 minor rotamer), 1.45 (2.4H, d, *J* 7.2, CH_3 major rotamer); δ_C (125 MHz; $CDCl_3$) 164.1 (*C*HO minor rotamer), 160.3 (*C*HO, major rotamer), 142.8 (Ar*C*, minor rotamer), 142.6 (Ar*C*, major rotamer), 128.8 (Ar*C*H, minor rotamer), 128.6 (Ar*C*H, major rotamer), 127.7 (Ar*C*H, minor rotamer), 127.4, 126.0 (Ar*C*H, major rotamer), 125.7 (Ar*C*H, minor rotamer), 51.6 (*C*H, minor rotamer), 47.5 (*C*H, major rotamer), 23.5 (CH_3, minor rotamer), 21.7 (CH_3, major rotamer). NMR data were in accordance with the literature.[24]

4.10. Preparation of (*R*)-(+)-*N*-methyl-α-methylbenzylamine[24]

(*R*)-(+)-α-Methylbenzylformamide (1.10 g, 7.38 mmol) was dissolved in THF (4 cm^3), and then added dropwise to a suspension of $LiAlH_4$ (1.00 g, 26.3 mmol) in THF (12 cm^3) at 65 °C. The reaction mixture was refluxed for 5 h, and then allowed to stir overnight at room temperature. The excess of $LiAlH_4$ was destroyed with water (10 cm^3), followed by adding diethyl ether (15 cm^3), after which the reaction mixture was filtered through Celite. The organic layer was separated, dried over Na_2SO_4, filtered and the solvent removed to afford an oil which was dried in vacuo to give *N*-methyl-α-methylbenzylamine (0.61 g, 61% yield). No further purification was required, $[\alpha]_D = +77.7$ (*c* 1, $CHCl_3$) [lit.[24] +78.3 (*c* 2.18, $CHCl_3$)]; δ_H (300 MHz; $CDCl_3$) 7.27–7.17 (5H, m, ArC*H*), 3.57 (1H, q, *J* 6.1, C*H*), 2.24 (3H, s, NCH_3), 1.37 (3H, d, *J* 6.1, CH_3); δ_C (125 MHz; $CDCl_3$) 145.4 (Ar*C*), 128.4 (2 × Ar*C*H), 126.9 (Ar*C*H), 126.6 (2 × Ar*C*H), 60.2 (*C*H), 34.5 (NCH_3), 22.8 (CH_3). NMR data were in accordance with the literature.[24]

4.11. Preparation of 9-[*N*-methyl-*N*-(*R*)-α-methylbenzylamino]anthracene 11[23]

A mixture of $Pd_2(dba)_3$ (0.06 g, 0.06 mmol, Pd 6 mol %) and (*S*)-2-[(*S*)-2-(diphenylphosphino)ferrocenyl]-4-(1-methylethyl)oxazoline **14** (0.03 g, 0.06 mmol, 6 mol %) in dry toluene (3 cm^3) was stirred for 5 min at room temperature. 9-Bromoanthracene (0.51 g, 2.00 mmol), *N*-methyl-*N*-α-methylbenzylamine (0.41 g, 3.00 mmol), NaO*t*-Bu (0.27 g, 2.80 mmol) and dry toluene (3 cm^3) were added and the reaction mixture was refluxed for 24 h. The reaction was allowed to cool to room temperature, after which diethyl ether (10 cm^3) was added, and the diluted mixture passed through a short plug of Celite. The solvent was removed under reduced pressure to give the crude material (25% conversion). This material was purified by column chromatography (neat petroleum ether 40–60 °C) to afford a yellow solid of the title compound (0.10 g, 16% yield), mp 120–121 °C; $[\alpha]_D = +70$ (*c* 1, $CHCl_3$); ν_{max} (ATR/cm^{-1}) 2920, 1672, 1590, 1492, 1450; δ_H (250 MHz; $CDCl_3$) 9.00 (1H, d, *J* 8.6, ArC*H*), 8.40 (1H, s, ArC*H*), 8.30 (1H, app. d, *J* 9.5, ArC*H*), 8.12–8.05 (2H, m, ArC*H*), 7.77–7.73 (2H, m, ArC*H*), 7.67–7.58 (1H, m, ArC*H*), 7.58–7.47 (5H, m, ArC*H*), 7.41–7.35 (1H, m, ArC*H*), 5.03 (1H, q, *J* 6.7, C*H*CH_3), 3.04 (3H, s, NCH_3), 1.09 (3H, d, *J* 6.7, CH_3CH); δ_C (62.5 MHz; $CDCl_3$) 146.4 (Ar*C*), 143.6 (Ar*C*), 132.9 (Ar*C*), 132.6 (Ar*C*), 132.5 (Ar*C*), 131.4 (Ar*C*), 129.7 (Ar*C*H), 128.6 (Ar*C*H), 128.5 (Ar*C*H), 127.7 (2 × Ar*C*H), 127.2 (2 × Ar*C*H), 125.6 (2 × Ar*C*H), 125.4 (Ar*C*H), 125.3 (Ar*C*H), 125.0 (Ar*C*H), 124.8 (Ar*C*H), 124.6 (Ar*C*H), 64.2 (*C*H), 41.6 (NCH_3), 22.7 (CH_3); *m*/*z* (EI^+) 311.1661 (22%, $C_{23}H_{21}N$ requires 311.1674), 268 (100), 267 (25), 265 (17), 208 (36), 206 (43), 191 (32), 180 (34), 178 (32), 152 (34), 105 (45).

4.12. Preparation of 9-[*N*-methyl-*N*-(*R*)-α-methylbenzylamino]anthracene 11 (from 9,10-dibromoanthracene)

A mixture of $Pd_2(dba)_3$ (0.04 g, 0.04 mmol, Pd 4 mol %) and 2,2′-dimethylaminodicyclohexylphosphinobiphenyl **13** (0.03 g, 0.08 mmol, 8 mol %) in toluene (4 cm^3) was stirred for approximately 5 min at room temperature, and 9,10-dibromoanthracene (0.17 g, 0.50 mmol), *N*-methyl-*N*-α-methylbenzylamine (0.20 g, 1.50 mmol), NaO*t*-Bu (0.13 g, 1.40 mmol) and toluene (2 cm^3) were added and the reaction mixture was stirred for 52 h at 85–90 °C. The reaction

was allowed to cool to room temperature. Diethyl ether (10 cm^3) was added and the diluted mixture passed through a short pad of Celite. The solvent was removed under reduced pressure to afford the crude material (0.21 g, 17% conversion). Spectroscopic data were as described previously.

4.13. Preparation of (3a*S*,9a*S*)-3a,4,9,9a-tetrahydro-4-[(*R*)-α-methylbenzylamino]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3-(2*H*)-dione 18a[23]

9-(*N*-α-Methylbenzylamino)anthracene **10** (0.08 g, 0.27 mmol) was dissolved in dry toluene (10 cm^3). The resulting solution was heated to 80–85 °C. *N*-Methylmaleimide (0.03 g, 0.27 mmol) was added as a solid and the reaction mixture was stirred for 2 h. The resulting mixture was allowed to cool to room temperature, and the solvent removed under reduced pressure to afford the title cycloaddition adduct (0.10 g, 89% yield) as two diastereoisomers in the ratio of 92:8. A sample was purified by diffusion recrystallisation using CH_2Cl_2/petroleum ether 40–60 °C to afford the target cycloadduct as a white solid, mp 158–160 °C (CH_2Cl_2/petroleum ether 40–60 °C); $[\alpha]_D = +50$ (*c* 0.5, $CHCl_3$); ν_{max} (ATR)/cm^{-1} 1691; δ_H (250 MHz; $CDCl_3$) 7.68–7.65 (2H, m, ArC*H*), 7.50–7.41 (3H, m, ArC*H*), 7.33–7.27 (2H, m, ArC*H*), 7.25–7.17 (2H, m, ArC*H*), 7.12–7.01 (3H, m, ArC*H*), 6.86 (1H, app. td, *J* 7.6, 1.3, ArC*H*), 4.64 (1H, d, *J* 3.1, C*H*), 4.48–4.59 (1H, m, CH_3C*H*), 3.58 (1H, d, *J* 8.2, COC*H*), 3.37 (1H, dd, *J* 8.2, 3.1, CHC*H*CH), 3.14 (1H, br d, *J* 6.4, N*H*), 2.52 (3H, s, NCH_3), 1.78 (3H, d, *J* 6.7, CH_3); δ_C (62.5 MHz; $CDCl_3$) 176.9 (*C*O), 176.7 (*C*O), 149.1 (Ar*C*), 142.1 (Ar*C*), 141.8 (Ar*C*), 141.7 (Ar*C*), 137.3 (Ar*C*), 128.6 (2 × Ar*C*H), 127.0 (Ar*C*H), 126.5 (2 × Ar*C*H), 126.4 (2 × Ar*C*H), 126.3 (Ar*C*H), 126.2 (Ar*C*H), 124.8 (Ar*C*H), 124.7 (Ar*C*H), 123.7 (Ar*C*H), 121.1 (Ar*C*H), 66.4 (*C*), 53.6 (*C*H), 47.8 (*C*H), 46.3 (*C*H), 45.7 (*C*H), 27.9 (*C*H_3), 24.2 (*C*H_3); *m*/*z* (EI^+) 409.1904 (1%, $C_{27}H_{25}N_2O_2$ requires 409.1916), 408 (1), 297 (64), 280 (4), 243 (2), 204 (6), 194 (15), 193 (100), 178 (8), 165 (45).

Selected ^{1}H NMR signals for the minor diastereoisomer **19a** (3a*R*,9a*R*)-3a,4,9,9a-tetrahydro-4-[(*R*)-α-methylbenzylamino]-2-methyl-4,9-[1′,2′]benzeno-1*H*-benzo[*f*]isoindole-1,3-(2*H*)-dione δ_H (250 MHz; $CDCl_3$) 4.63 (1H, d, *J* 7.0, C*H*), 3.18 (1H, dd, *J* 8.6, 3.1, C*H*), 2.34 (3H, s, NCH_3).

4.14. Preparation of (11*S*,15*S*)-9,10,11,15-tetrahydro-9-[(*R*)-α-methylbenzylamino]-9,10[3′,4′]-furanoanthracene-12,14-dione 18b

Maleic anhydride (0.10 g, 1.01 mmol) was added as a solid to a stirred solution of 9-α-methylbenzylaminoanthracene **10** (0.30 g, 1.01 mmol) in toluene (4 cm^3) at 80–85 °C. The reaction mixture was stirred for 2 h, cooled to room temperature, and the solvent was evaporated to give a yellow solid of the title compound (0.40 g, 100%) as a mixture of diastereoisomers in the ratio of 91:9. The major diastereoisomer **18b** was purified by recrystallisation from petroleum ether (40–60)/EtOAc, followed by a second recrystallisation from petroleum ether (40–60)/CH_2Cl_2, mp 178–183 °C; (Found: C, 78.74; H, 5.16; N, 3.41. $C_{26}H_{21}NO_3$ requires C, 78.97; H, 5.35; N, 3.54.); $[\alpha]_D = +26$ (*c* 1, $CHCl_3$); ν_{max} (ATR/cm^{-1}) 1777; δ_H (500 MHz; $CDCl_3$) 7.70–7.60 (2H, m, ArC*H*), 7.59–7.51 (2H, m, ArC*H*), 7.49–7.18 (6H, m, ArC*H*), 7.15–7.09 (2H, m, ArC*H*), 6.95–6.82 (1H, m, ArC*H*), 4.74 (1H, d, *J* 3.1, C*H*), 4.52 (1H, app. q, *J* 6.3, NC*H*CH_3), 3.92 (1H, d, *J* 9.9 C*H*), 3.71 (1H, dd, *J* 9.9, 3.1, C*H*), 3.08 (1H, br s, N*H*), 1.79 (3H, d, *J* 6.3, CHCH_3); δ_C (100 MHz; $CDCl_3$) 170.5 (*C*O), 170.0 (*C*O), 148.4 (Ar*C*), 141.5 (Ar*C*), 141.3 (Ar*C*), 141.1 (Ar*C*), 136.7 (Ar*C*), 128.7 (2 × Ar*C*H), 127.7 (Ar*C*H), 127.5 (Ar*C*H), 126.6 (Ar*C*H), 126.5 (2 × Ar*C*H), 126.2 (2 × Ar*C*H), 125.2 (Ar*C*H), 124.7 (Ar*C*H), 123.8 (Ar*C*H), 121.3 (Ar*C*H), 66.3 (*C*), 53.5 (*C*H), 48.5 (*C*H), 47.7 (*C*H), 45.4 (*C*H), 27.7 (*C*H_3); *m*/*z* (ES^+) 414 (10%), 396.1587 (75, MH^+. $C_{26}H_{22}NO_3$ requires 396.1600), 292 (100).

Selected ^{1}H NMR signals for the minor diastereoisomer **19a** (11*R*,15*R*)-9,10,11,15-tetrahydro-9-[(*R*)-α-methylbenzylamino]-9,10[3′,4′]-furanoanthracene-12,14-dione **18b** δ_H (500 MHz; $CDCl_3$) 4.70 (1H, s, C*H*), 4.68–4.62 (1H, m, C*H*), 3.70 (1H, d, *J* 10.1, C*H*), 3.52 (1H, dd, *J* 10.1, 2.8, C*H*), 1.79 (3H, d, *J* 5.7, CH_3).

4.15. Preparation of 1-methyl-(3*R*)-(10-oxo-9,10-dihydroanthracen-9-yl)pyrrolidine-2,5-dione 114[21]

The major maleimide diastereoisomer **18a** (0.50 g, 1.23 mmol) was dissolved in dry toluene (10 cm^3). Trifluoroacetic acid (0.5 cm^3, 7.00 mmol) was added and the resulting mixture was stirred at reflux for 4 h, cooled to room temperature and the solvent removed under reduced pressure. The crude was purified by column chromatography (5% MeOH/CH_2Cl_2) to give a yellow solid (0.26 g, 69% yield) of the title compound, mp 85–88 °C [(lit. rac)[21] 122–122.5 °C]; $[\alpha]_D = +125$ (*c* 0.08, $CHCl_3$); ν_{max} (ATR)/cm^{-1} 1694, 1663, 1598; δ_H (500 MHz; $CDCl_3$) 8.32–8.28 (2H, m, ArC*H*), 7.66–7.62 (1H, m, ArC*H*), 7.61–7.59 (1H, m, ArC*H*), 7.53–7.47 (3H, m, ArC*H*), 7.35–7.38 (1H, m, ArC*H*), 5.16 (1H, d, *J* 2.9, C*H*), 3.48–3.43 (1H, m, COC*H*), 2.87 (3H, s, NCH_3), 2.21 (1H, dd, *J* 18.5, 9.2, COC*H*), 1.87 (1H, dd, *J* 18.5, 4.9, COC*H*); δ_C (125 MHz; $CDCl_3$) 183.8 (*C*O), 178.0 (*C*O), 175.0 (*C*O), 142.4 (Ar*C*), 138.2 (Ar*C*), 133.8 (Ar*C*H), 133.4 (Ar*C*), 133.2 (Ar*C*H), 132.4 (Ar*C*), 128.6 (Ar*C*H), 128.0 (Ar*C*H), 127.9 (2 × Ar*C*H), 127.8 (2 × Ar*C*H), 50.1 (*C*H), 41.6 (*C*H), 28.9 (*C*H_2), 24.8 (*C*H_3); *m*/*z* (EI^+) 306.1122 (17%, $C_{19}H_{16}NO_3$ requires 306.1130), 305 (17), 236 (22), 221 (16), 205 (13), 194 (19), 193 (100), 178 (7), 165 (25). NMR data were in accordance with the literature.[21]

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