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Synthesis and Diels–Alder reactions of 9-(4-benzyloxazolin-2-yl) anthracene

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Abstract—The synthesis of 9-(4-benzyloxazolin-2-yl)anthracene is described employing a new approach for the cyclisation of β-hydroxy amides to oxazolines. Thermal Diels–Alder reactions with *N*-methyl maleimide were found to be considerably slower than those previously observed. Essentially no diastereoselectivity was observed in these reactions as the benzyl stereodirecting group is remote from the reactive site. Minor rate enhancements were noticeable in the presence of some added Lewis acids, but with no diastereoselection.

1. Introduction

Chiral auxiliaries now form part of the routine set of tools available to the synthetic chemist and can be used in a great variety of stereoselective transformations.[1] As part of an ongoing research programme we have been developing chiral anthracene derived auxiliaries such as the methyl ether **1** (Fig. 1) that make use of a highly diastereoselective Diels–Alder reaction with alkenes in the addition step.[2–5]

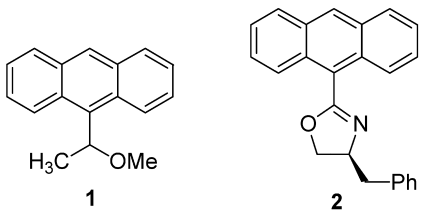

Figure 1.

Although the synthesis of ether **1** in enantiomerically pure form is relatively straightforward, this still requires use of catalytic asymmetric reduction to introduce the chirality. In contrast, more classical auxiliaries, such as Evans' oxazolidinone, employ stereogenic elements installed directly from the chiral pool. We have been working towards the goal of introducing stereogenic elements from the chiral pool directly into the anthracene framework. This work details our approach to the synthesis and evaluation of Diels–Alder reactions of 9-(4-benzyloxazolin-2-yl)-anthracene **2** (Fig. 1). This target was chosen since oxazolines can easily be prepared from naturally occurring α-amino acids and have been successfully employed in many asymmetric transformations.[6]

2. Results and discussion

2.1. Synthesis of oxazoline 2

Synthesis of the target oxazoline **2** started from commercially available anthracene 9-carboxylic acid **3**. Heating in an excess of thionyl chloride gave the acid chloride **4** in excellent yield (98%), followed by treatment with (*S*)-phenylalaninol[7] to give the key β-hydroxy amide **5**. Cyclisation of this amide to the oxazoline proved to be troublesome. Classical reaction with thionyl chloride[8] surprisingly returned starting material, as did direct treatment with the more reactive $TiCl_4$. Use of triethylorthoformate as a dehydrating agent also returned starting material (Scheme 1).

However, using diethylaminosulfur trifluoride (DAST) the reaction was more successful.[9] Addition of 1.1 equiv. of DAST at low temperature gave the desired oxazoline **2** cleanly. Although this reagent gave the desired product, its high cost is prohibitive of performing this reaction on a larger scale. Research from this group has recently reported a titanium catalysed phosphorylation procedure[10] that could be used to prepare the phosphate **6** which could then be induced to cyclise upon treatment with a suitable base. However, using the standard conditions for this reaction only the chloride **7** was obtained in excellent isolated yield. This is surprising, since in the phosphorylation of all primary alcohols previously studied, no trace of the corresponding chloride was ever observed. In any event, reaction of the chloride **7** with *t*-BuOK led to deprotonation

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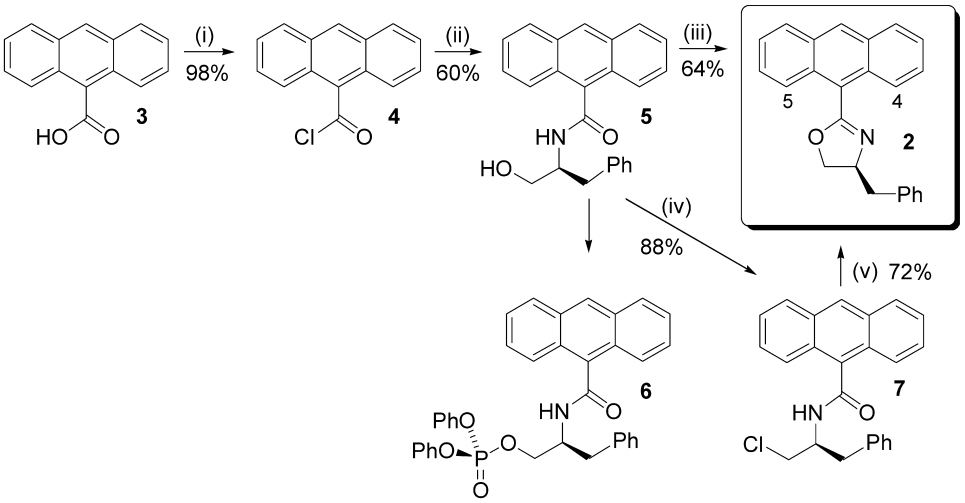


Scheme 1. Reagents and conditions: (i) $SOCl_2$ (excess), △; (ii) (*S*)-phenylalaninol, Et_3N, THF, 0 °C; (iii) DAST, CH_2Cl_2, −78 °C; (iv) 5 mol. % $TiCl_4$, $(PhO)_2P(O)Cl$, Et_3N, CH_2Cl_2, rt; (v) *t*-BuOK, THF.

of the N–H proton of the amide and subsequent ring closure to give the target oxazoline **2**. Although this route comprises two steps, the overall yield of 63% is comparable to that of the DAST reaction, but at a fraction of the cost of the reagents. Efforts are ongoing to further elaborate this method as an effective alternative route for the synthesis of oxazolines.

It is interesting to note that if the oxazoline **2** was left for prolonged periods of time during the crystallization process, the dimer **8** was formed (Fig. 2). Attempts to replicate this using photochemical dimerisation in acetonitrile returned starting material. Thermal dimerisation by heating at reflux in toluene returned starting material even after 5 days, although changing solvent to dichloromethane gave a small quantity of dimer (15%). The dimer could be cleaved back to the anthracene adduct by heating at reflux in toluene for 24 h.

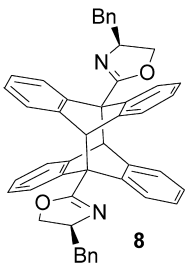


Figure 2.

The ^{1}H NMR spectrum of the oxazoline **2** is interesting compared to the methyl ether **1**. Many 9-substituted anthracenes suffer from restricted rotation around the C-9 bond due to steric interactions with the proximal *peri* hydrogen atoms (H-4 and H-5). For the ether **1** this manifests itself as broad signals for the *peri* protons at δ 8.71 ppm leading to a rotational barrier of approximately 12.2 kcal mol^{-1} at 281 K.[4] However the H-4 and H-5 protons of the oxazoline **2** appear as sharp signals in the aromatic region of the ^{1}H NMR spectrum implying free rotation about the C-9 bond. This is a consequence of a change in hybridisation from sp^3 to sp^2 adjacent to C-9 leading to a reduction of allylic strain. This was confirmed by calculation of the rotational barrier of oxazoline **2** using molecular modeling[11] giving an estimated energy barrier to rotation of 3.43 kcal mol^{-1}. Such a small value would permit free rotation at room temperature. The minimum energy conformer was found to be that with the oxazoline lying perpendicular to the anthracene ring system (Fig. 3).

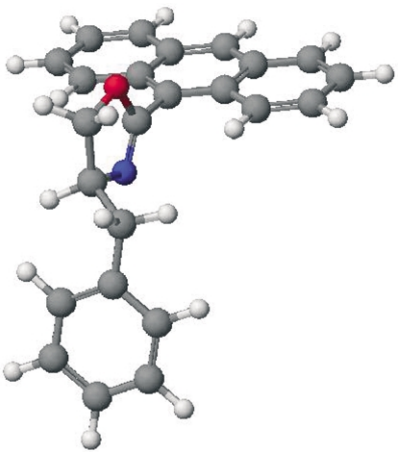
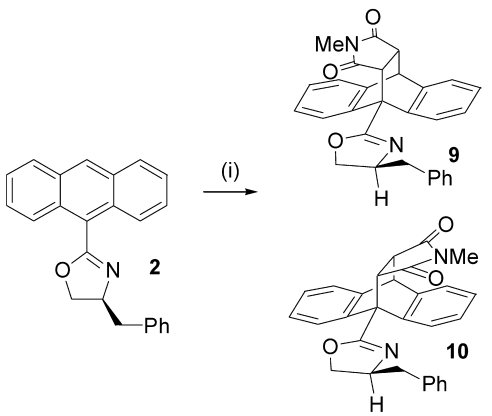


Figure 3. Minimum energy conformer of oxazoline **2**.

2.2. Thermal Diels–Alder reactions

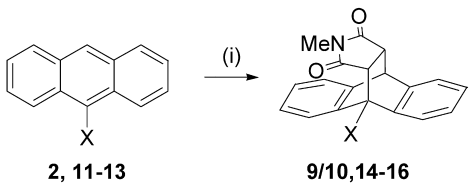
Trial Diels–Alder reactions were performed by heating oxazoline **2** in toluene at reflux for 2 h with maleic anhydride and *N*-methylmaleimide. Surprisingly, no reaction was observed with maleic anhydride, however some product (73%) was observed with *N*-methyl maleimide giving the addition adduct as a 50:50 mixture of diastereoisomers **9** and **10** as observed from the signals in the ^{1}H NMR spectrum (Scheme 2). Partial separation of these two diastereoisomers allowed the relative assignment of a number of signals in the ^{1}H and ^{13}C NMR spectrum, although absolute assignment was not possible.

The yield observed in this reaction is significantly lower



Scheme 2. Reagents and conditions: (i) *N*-methyl maleimide, $C_6H_5CH_3$, △, 2 h.

when compared to the ether **1** (73% for **2** vs 96% for **1** under otherwise identical reaction conditions). This was attributed to the electron withdrawing nature of the oxazoline group and to confirm this, the Diels–Alder reaction with *N*-methyl maleimide was performed with a series of electron rich and poor 9-substituted anthracene derivatives (Scheme 3, Table 1). These results predictably indicate that electron withdrawing groups do retard the rate of the Diels–Alder reaction and that the oxazoline, as suspected, is a good electron withdrawing group.



Scheme 3. Reagents and conditions: (i) *N*-methyl maleimide, $C_6H_5CH_3$, △, 2 h.

Table 1. Diels–Alder additions of anthracene derivatives **2**, **11**–**13** with *N*-methyl maleimide in toluene at reflux for 2 h

Starting material	X	Product	Conversion (%)[a]
11	Me	**14**	98
12	H	**15**	81
13	Br	**16**	82
2	2-Oxazolinyl	**9/10**	73

[a] Calculated from the ratio of integrals of the signals corresponding to starting material and addition product in the ^{1}H NMR spectrum.

The absence of diastereoselectivity observed in this reaction is in retrospect perhaps not so surprising. Using a rationale based upon kinetic arguments,[12,13] the approach of a dienophile will occur where electrostatic interactions can be minimized. The minimum energy conformation of the oxazoline is likely to have the oxazoline ring orientated orthogonally to the anthracene ring system to minimize *peri* interactions, a premise supported by the modeling studies discussed earlier. However in this conformation, the stereogenic centre of the oxazoline ring is located remote from the reactive centre, resulting in no interaction with the carbonyl group of the dienophile on either face of the anthracene ring and hence no discrimination (Fig. 4). Invoking a rationale based upon thermodynamic stability of the diastereoisomeric products, the predicted heats of formation of **9** and **10** are −8.66 and −8.50 kcal mol^{-1}, respectively, leading to a calculated K_{eq} of 1.23 at 110 °C.[14] This equates to a 55:45 ratio of diastereisomers which is in good agreement with the observed selectivity.

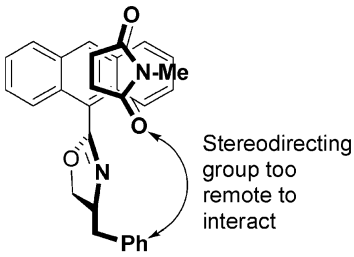


Figure 4.

2.3. Diels–Alder reactions in the presence of Lewis acidic metal triflates

Lewis acids, especially metal triflates, have been used to successfully catalyse the room temperature Diels–Alder reaction of anthracene derivatives with dienophiles.[15] Oxazolines have also been shown to act as efficient templates for cation co-ordination. Thus, oxazoline **2** was treated with *N*-methyl maleimide at room temperature in the presence of the metal triflates $Mg(OTf)_2$, $Cu(OTf)_2$, $Y(OTf)_3$ and $Sc(OTf)_3$. Unfortunately, essentially no rate enhancement was observed, with any improvement in the diastereomeric ratio. The latter is not surprising since addition of a Lewis acid is unlikely to bring the benzyl stereodirecting group into closer proximity to the reactive site.

3. Conclusions

Synthesis of 9-(4-benzyloxazolin-2-yl) anthracene has been achieved and a new synthetic route to such compounds disclosed. All attempted stereoselective Diels–Alder reactions proved to be unsuccessful resulting from poor reaction rates and no selectivity. However this work does indicate the need for an electron-rich auxiliary to increase reaction rates, in addition to ensuring the close proximity of the stereodirecting group to the reaction centre for high selectivity.

4. Experimental

4.1. General

THF and toluene were freshly dried over sodium, while CH_2Cl_2 was dried over lithium aluminium hydride. Anhydrous DMSO was obtained by distillation in vacuuo. Glassware was flame dried and cooled under vacuum before use and all reactions were carried out under nitrogen unless otherwise stated. TLC was carried out using Merck aluminium TLC sheets (silica gel 60 F_{254}). Visualisation of the TLC plates was carried out using a UV lamp or by dipping in $KMnO_4$ then exposure by heating. Flash column

chromatography was carried out with Fluorochem Limited Silica Gel 40-63u 60A. Melting points were measured on a Gallenkamp apparatus and are uncorrected. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC-250 or a Bruker Avance 300 spectrometer or AMX-400 spectrometer or JEOL 500 MHz spectrometer. Residual proton signals from the deuteriated solvents were used as references [chloroform (^{1}H, 7.25 ppm; ^{13}C, 77 ppm) and DMSO (^{1}H, 2.50 ppm; ^{13}C, 39.7 ppm)]. Coupling constants were measured in Hz. All infrared spectra were recorded on Perkin–Elmer Spectrum RX/FT-IR system with a Dura-Sampl*IR* II ATR accessory. Optical rotations were recorded on a Perkin–Elmer 241 automatic polarimeter at 589 nm (Na D line) with a path length of 1 dm with concentrations quoted in gm 100 mL^{-1}. Mass spectra were recorded on a Micromass Autospec M spectrometer.

4.1.1. 9-Anthranoyl chloride 4.[16] 9-Anthracene carboxylic acid **3** (0.455 g, 2.05 mmol) and thionyl chloride (3.5 cm^3) were stirred at reflux for 3 h under nitrogen, then allowed to cool to room temperature. The excess thionyl chloride was removed under reduced pressure, the residue washed with diethyl ether (2×2 cm^3), and the diethyl ether evaporated to afford a dull yellow solid of 9-anthranoyl chloride **4** (0.489 g, 98%) that required no further purification, mp 94–96 °C (lit.[15] 96–97 °C); δ_H (300 MHz; $CDCl_3$) 8.62 (1H, s, 10H), 8.14 (2H, d, *J*=8.7 Hz, ArC*H*), 8.08 (2H, d, *J*=8.4 Hz, ArC*H*), 7.67 (2H, dd, *J*=8.7, 6.6 Hz, ArCH), 7.56 (2H, dd, *J*=8.4, 6.6 Hz, ArCH). Spectroscopic data was in agreement to that in the literature.

4.1.2. Anthracene-9-carboxylic acid (1-benzyl-2*S*-hydroxy-ethyl)-amide 5. 9-Anthranoyl chloride **4** (1.73 g, 7.17 mmol) was dissolved in THF (30 cm^3) in the presence of triethylamine (2.60 cm^3, 18.68 mmol). A solution of (*S*)-3-phenyl-2-amino-1-propanol (1.09 g, 7.19 mmol) in THF (35 cm^3) was then added dropwise to the reaction mixture at 0 °C. The reaction was stirred at 0 °C for 1 h, warmed to room temperature followed by filtration. The solvent was removed to afford a yellow solid, which was dissolved in CH_2Cl_2 (20 cm^3), washed with water (3×10 cm^3), and the organic phase dried over Na_2SO_4. The solvent was removed to obtain a yellow solid of the hydroxyl-amide **5** (1.54 g, 60%) that was used without purification in subsequent steps. A sample was purified for analytical purposes by two recrystallizations from EtOAc/petrol) giving the title compound as yellow needles, mp 190–194 °C (EtOAc/petrol); $[\alpha]_D$=+13.3 (*c* 1, $CHCl_3$); (Found: C, 80.95; H, 5.97; N, 3.87. $C_{24}H_{21}NO_2$ requires C, 81.10; H, 5.96; N, 3.94%); ν_{max} (film)/cm^{-1} 1634, 1519, 1455; δ_H [300 MHz; $(CD_3)_2SO$] 8.65 (1H, d, *J*=9.0 Hz, ArC*H*), 8.59 (1H, s, 10H), 8.11–8.03 (3H, m, ArC*H*), 7.57–7.35 (8H, m, ArC*H*), 7.22 (1H, dd, *J*=8.3, 6.7 Hz, ArC*H*), 7.02 (1H, d, *J*=8.7 Hz, N*H*), 5.07 (1H, t, *J*=5.6 Hz, O*H*), 4.65 (1H, m, C*H*), 3.56 (1H, ddd, *J*=11.6, 10.5, 5.6 Hz, C*H*HOH), 3.59 (1H, ddd, *J*=11.6, 10.5, 5.6 Hz, C*H*HOH), 3.11 (1H, dd, *J*=13.7, 4.0 Hz, PhC*H*H), 2.63 (1H, dd, *J*=13.7, 11.0 Hz, PhC*H*H); δ_C [75 MHz; $(CD_3)_2SO$] 168.0 (*C*=O), 139.7 (Ar*C*), 134.1 (Ar*C*), 131.0 (Ar*C*), 130.9 (Ar*C*H), 129.7 (Ar*C*H), 128.6 (Ar*C*H), 128.3 (Ar*C*H), 127.5 (Ar*C*H), 127.1 (Ar*C*H), 126.6 (Ar*C*H), 126.4 (2×Ar*C*H), 126.2 (Ar*C*H), 126.0 (Ar*C*H), 125.8 (Ar*C*H), 64.4 (CH_2OH), 53.5 (*C*HNH), 37.0 (PhCH_2); *m*/*z* (EI^+) 355.1576 (33%, $C_{24}H_{21}NO_2$ requires 355.1572), 221 (31), 205 (100, $C_{15}H_9O^+$), 177 (38), 151 (5), 91 (6).

4.1.3. 9-(4*S*-Benzyloxazolin-2-yl)anthracene 2 (DAST method). The hydroxy-amide **5** (2.534 g, 7.140 mmol) was dissolved in dry CH_2Cl_2 (140 cm^3) and then cooled to −78 °C. DAST (2 cm^3, 16.33 mmol) was added to the cooled mixture and stirred for 2 h at −78 °C. The resulting solution was quenched with NH_4OH (25 cm^3, 10% by vol.) and the reaction mixture warmed to room temperature. EtOAc (20 cm^3) was added, followed by $NaHCO_3$ (25 cm^3) and the organic layer separated. The aqueous layer was extracted with EtOAc (2×20 cm^3) and the combined organic layers washed with brine (25 cm^3) and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford a dull yellow solid (2.348 g). The crude material was purified using column chromatography (EtOAc/petrol 10:90) to afford the title compound **2** as a thick yellow oil (1.532 g, 64%); $[\alpha]_D$=−12.7 (*c* 1, $CHCl_3$); (Found: C, 85.80; H, 5.44; N, 4.18. $C_{24}H_{19}NO$ requires C, 85.43; H, 5.68; N, 4.15%); ν_{max} (film)/cm^{-1} 3056, 3028, 1659; δ_H (300 MHz; $CDCl_3$) 8.56 (1H, s, 10H), 8.04–7.97 (4H, m, ArC*H*), 7.53–7.43 (4H, m, ArC*H*), 7.38–7.29 (5H, m, ArC*H*), 5.04 (1H, dtd, *J*=9.6, 7.8, 4.9 Hz, C*H*), 4.66 (1H, dd, *J*=8.6, 7.8 Hz, CH*H*O), 4.48 (1H, dd, *J*=8.6, 9.6 Hz, C*H*HO), 3.46 (1H, dd, *J*=13.8, 4.9 Hz, PhC*H*H), 3.21 (1H, dd, *J*=13.8, 7.8 Hz, PhC*H*H); δ_C (75 MHz; $CDCl_3$) 163.8 (*C*=N), 138.0, (Ar*C*), 131.4 (Ar*C*H), 130.5 (Ar*C*H), 130.2 (Ar*C*H), 129.9 (Ar*C*H), 129.1 (Ar*C*H), 128.9 (Ar*C*H), 127.1 (Ar*C*H), 125.8 (Ar*C*H), 123.1 (Ar*C*), 72.0 (*C*H_2O), 69.0 (*C*HN), 42.1 (PhCH_2); *m*/*z* (EI^+) 337.1461 (35%, $C_{24}H_{19}NO$ requires 337.1467), 246 (100, M^+-C_7H_7), 218 (21), 203 (52), 191 (8), 177 (12), 91 (11).

4.1.4. Anthracene-9-carboxylic acid (1*S*-benzyl-2-chloro-ethyl)-amide 7. $TiCl_4$ (0.01 cm^3, 0.07 mmol, 2 mol %) was dissolved in THF (5 cm^3) and the hydroxyl amide (1.18 gm, 3.33 mmol) was added as a solution in THF (15 cm^3) via a dropping funnel followed by Et_3N (0.71 cm^3, 5.00 mmol), THF (5 cm^3), diphenylphosphorochloridate (1.04 cm^3, 5.00 mmol) and THF (10 cm^3). The resulting mixture was stirred at room temperature for 1 h before quenching with water (15 cm^3). The organic layer was extracted with CH_2Cl_2 and the combined organic layers dried over Na_2SO_4 and filtered. Removal solvent afforded the crude material (1.72 gm, 2.93 mmol, 88% yield) that was used without purification in subsequent steps. A sample was purified for analytical purposes by column chromatography (10% EtOAc/petrol) followed by recrystallization from toluene to give white crystals, mp 198–203 °C (toluene); $[\alpha]_D$=−14 (*c* 0.5, $CHCl_3$); ν_{max} (ATR)/cm^{-1} 1673, 1488, 1424; δ_H (250 MHz; $CDCl_3$) 8.51 (1H, s, ArC*H*), 8.32 (1H, d, *J*=8.4 Hz, ArC*H*), 8.08–7.95 (3H, m, ArC*H*), 7.61–7.30 (9H, m, ArC*H*), 6.27 (1H, d, *J*=7.9 Hz, N*H*), 5.14 (1H, m, C*H*), 4.09 (1H, dd, *J*=11.5, 4.2 Hz, CH*H*Cl), 3.82 (1H, dd, *J*=11.5, 3.5 Hz, C*H*HCl), 3.21–3.10 (2H, m, PhCH_2); δ_C (100 MHz; $CDCl_3$) 172.3 (*C*O), 131.4 (Ar*C*), 130.6 (Ar*C*), 129.7 (Ar*C*H), 129.4 (Ar*C*H), 129.1 (Ar*C*H), 128.9 (Ar*C*H), 128.4 (Ar*C*H), 127.7 (Ar*C*H), 127.5 (Ar*C*H), 127.2 (2×Ar*C*H), 125.9 (Ar*C*H), 125.6 (Ar*C*H), 125.3 (Ar*C*H), 51.8 (*C*H), 47.7 (*C*H_2Cl), 38.3 (*C*H_2Ph); *m*/*z* (ES) 374.1314 (42% $C_{24}H_{21}NOCl$ requires 374.1312), 205 (100); (EI^+) 374 (32), 373 (22), 307 (21), 289 (12), 222 (87), 205 (44), 177 (13), 154 (100), 136 (74).

4.1.5. 9-(4*S*-Benzyloxazolin-2-yl)anthracene 2 (from 7). Potassium *t*-butoxide (1.2 gm, 10.66 mmol) was added as a solid to a stirred solution of chloride **7** (3.12 gm, 5.31 mmol) in THF (20 cm^3). The reaction mixture was stirred for 1 h at room temperature, filtered through short pad of silica, eluting with EtOAc (5 cm^3). Removal of solvent gave the title compound **2** (1.28 g, 3.80 mmol, 72%).

4.1.6. 9-(4*S*-Benzyloxazolin-2-yl)-10-hydro-9,10-ethanoanthracene-11*R*,12*R*-dicarbonyl *N*-methylamide 9 and 9-(4*S*-benzyloxazolin-2-yl)-10-hydro-9,10-ethanoanthracene-11*S*,12*S*-dicarbonyl *N*-methylamide 10. 9-(4-Benzyloxazolin-2-yl)anthracene **2** (0.500 g, 1.48 mmol) was dissolved in dry toluene (10 cm^3), the resulting solution heated to 90–95 °C and *N*-methylmaleimide (0.442 g, 3.98 mmol) added. This was left at this temperature for 4 and 1/2 h, then cooled to room temperature, and the solvent was removed under reduced pressure to afford a pale yellow solid of the two diastereisomers **9** and **10** (50/50 by ^{1}H NMR spectroscopy). This mixture was purified using column chromatography (EtOAc/petrol, 30:70) to give a 60/40 mixture of two diastereoisomers (0.279 g, 42%) as a yellow solid; ν_{max} (ATR)/cm^{-1} 1776, 1697, 1456, 1433, mp 101–104 °C; $[\alpha]_D$=−8.0 (*c* 0.5, $CHCl_3$); δ_H (300 MHz; $CDCl_3$) Diastereoisomer A, 8.28 (1H, d, *J*=7.3 Hz, ArC*H*), 7.32–7.26 (4H, m, ArC*H*), 7.23–7.02 (7H, m, ArC*H*), 6.84 (1H, d, *J*=7.3 Hz, ArC*H*), 4.81 (1H, m, C*H*), 4.68 (1H, m, C*H*), 4.47 (1H, m, CH*H*O), 4.26 (1H, m, CH*H*O), 3.76 (1H, d, *J*=8.6 Hz, C*H*), 3.32 (1H, dd, *J*=13.8, 5.0 Hz, C*H*), 3.21–3.15 (1H, m, PhC*H*H), 2.99–2.91 (1H, m, PhC*H*H), 2.40 (3H, s, CH_3); Diastereoisomer B, 8.22 (1H, d, *J*=7.1 Hz, ArC*H*), 7.32–7.26 (4H, m, ArC*H*), 7.23–7.02 (7H, m, ArC*H*), 6.95 (1H, d, *J*=7.2 Hz, ArC*H*), 4.81 (1H, m, C*H*), 4.68 (1H, m, C*H*), 4.47 (1H, m, CH*H*O), 4.26 (1H, m, CH*H*O), 3.82 (1H, d, *J*=8.6 Hz, C*H*), 3.41 (1H, dd, *J*=13.7, 5.5 Hz, C*H*), 3.21–3.15 (1H, m, PhC*H*H), 2.99–2.91 (1H, m, PhC*H*H), 2.42 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 176.9 (*C*=O), 175.9 (*C*=O), 141.2 (*C*=N), 138.6, 138.0, 137.2, 130.1 (Ar*C*H), 129.8 (Ar*C*H), 129.1 (Ar*C*H), 127.6 (Ar*C*H), 127.5 (Ar*C*H), 127.1 (Ar*C*H), 127.0 (Ar*C*H), 126.1 (Ar*C*H), 125.1 (Ar*C*H), 124.3 (Ar*C*H), 123.7 (Ar*C*H), 71.7 (Diastereomer A, *C*H_2O), 71.3 (Diastereomer B, *C*H_2O), 69.1, 68.7, 51.3, 49.4, 49.1, 47.7, 46.4, 42.4, 42.2, 24.7 (N*C*H_3); *m*/*z* (ES) 449.1881 (100%, $C_{29}H_{25}N_2O_3$ requires 449.1865).

4.1.7. 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarbonyl *N*-methylamide 15.[17] Anthracene **12** (0.178 g, 1.00 mmol) was dissolved in toluene (10 cm^3), the resulting solution heated to 90–95 °C, and *N*-methylmaleimide (0.111 g, 1.00 mmol) was added in one portion. The reaction mixture was stirred at 90–95 °C for 2 h, cooled to room temperature and the solvent was removed under reduced pressure to afford the title product **15** as a grey solid, which was recrystallized from toluene (0.169 g, 59%), mp 278–279 °C (lit.[17] 262–264 °C); δ_H (300 MHz; $CDCl_3$) 7.40 (2H, m, ArC*H*), 7.27 (2H, m, ArC*H*), 7.20–7.12 (4H, m, ArC*H*), 4.80 (2H, s, ArC*H*), 3.22 (2H, s, COC*H*), 2.52 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 177.3 (*C*=O), 141.8 (Ar*C*), 138.9 (Ar*C*), 127.4 (Ar*C*H), 127.1 (Ar*C*H), 125.3 (Ar*C*H), 125.7 (Ar*C*H), 47.4 (*C*H), 45.9 (*C*H), 24.7 (*C*H_3). Spectroscopic data was in agreement to that in the literature.

4.1.8. 9,10-Dihydro-9-bromo-9,10-ethanoanthracene-11,12-dicarbonyl *N*-methylamide 16. *N*-Methylmaleimide (0.611 g, 5.51 mmol) was added in one portion as a solid at 90–95 °C to a stirred solution of 9-bromoanthracene **13** (0.500 g, 1.95 mmol) in toluene (12 cm^3). The resulting mixture was left stirring for further 7 h at 90–95 °C, cooled to room temperature and the solvent removed under reduced pressure to give the target compound, which was recrystallized from toluene to afford a white solid of the title compound **16** (0.554 g, 77%), mp 228–232 °C; (Found: C, 62.0; H, 3.8; N, 3.8; Br, 21.9. $C_{19}H_{14}BrNO_2$ requires C, 62.0; H, 3.8; N, 3.80; Br, 21.70%); ν_{max} (ATR)/cm^{-1} 1776, 1690, 1456, 1426; δ_H (300 MHz; $CDCl_3$) 7.82 (1H, m, ArC*H*), 7.63 (1H, m, ArC*H*), 7.32 (1H, m, ArC*H*), 7.25–7.12 (5H, m, ArC*H*), 4.74 (1H, d, *J*=3.3 Hz, C*H*), 3.37 (1H, d, *J*=8.6 Hz, COC*H*CHCO), 3.25 (1H, dd, *J*=8.6, 3.3 Hz, COC*H*CH), 2.48 (3H, s, NCH_3); δ_C (100 MHz; $CDCl_3$) 175.3 (*C*=O), 173.4 (*C*=O), 141.0 (Ar*C*), 140.0 (Ar*C*), 138.1 (Ar*C*), 136.6 (Ar*C*), 128.0 (Ar*C*H), 127.9 (Ar*C*H), 127.5 (Ar*C*H), 127.1 (Ar*C*H), 125.8 (Ar*C*H), 125.3 (Ar*C*H), 124.5 (Ar*C*H), 123.5 (Ar*C*H), 64.6 (*C*Br), 53.4 (*C*H), 49.0 (*C*H), 45.1 (*C*H), 24.5 (N*C*H_3); *m*/*z* (ES) 390.0117 (100%, M^++Na; $C_{19}H_{14}NO_2Na^{79}Br$ requires 390.0106); *m*/*z* (EI^+) 370 (6%), 369 [14, M^+ (^{81}Br)], 367 [21, M^+ (^{79}Br)], 259 (15), 258 (97, $C_{14}H_8{}^{81}Br^+$), 256 (100, $C_{14}H_8{}^{79}Br^+$), 202 (11), 177 (13), 176 (16), 101 (8).

4.1.9. 9,10-Dihydro-9-methyl-9,10-ethanoanthracene 11,12-dicarbonyl *N*-methylamide 14.[18] 9-Methylanthracene **11** (0.192 g, 1.00 mmol) was dissolved in toluene (10 cm^3) then the resulting solution was heated to 90–95 °C and *N*-methylmaleimide (0.111 g, 1.00 mmol) was added in one portion as a solid. The reaction mixture was stirred at 90–95 °C for 2 h, cooled to room temperature and finally the solvent was removed under reduced pressure to afford the title product **14** as a white solid in 98% conversion as calculated from the ^{1}H NMR spectrum, which was recrystallized from toluene (0.247 g, 82%), mp 146–150 °C (lit.[18] 267–168 °C);† δ_H (300 MHz; $CDCl_3$) 7.44–7.39 (2H, m, ArC*H*), 7.30–7.11 (6H, m, ArC*H*), 4.78 (1H, d, *J*=3.3 Hz, COCHC*H*), 3.28 (1H, dd, *J*=3.3, 8.4 Hz, COC*H*CH), 2.86 (1H, d, *J*=8.4 Hz, COC*H*CHCO), 2.53 (3H, s, NCH_3), 2.31 (3H, s, CH_3); δ_C (75 MHz; $CDCl_3$) 177.2 (*C*=O), 176.6 (*C*=O), 144.9 (Ar*C*), 142.2 (Ar*C*), 141.4 (Ar*C*), 139.0 (Ar*C*), 127.3 (Ar*C*H), 127.1 (Ar*C*H), 126.9 (2×Ar*C*H), 125.2 (Ar*C*H), 124.2 (Ar*C*H), 122.5 (Ar*C*H), 122.4 (Ar*C*H), 51.0 (*C*H), 48.9 (*C*H), 45.9 (*C*H), 45.4 (*C*), 24.7 (N*C*H_3), 15.7 (*C*H_3).

4.1.10. 9-(3-Benzyloxazolinoyl)anthracene dimer 8. The title compound was obtained as a yellow solid on leaving a toluene solution of oxazoline **2** to slowly evaporate over the period of several weeks, mp 219–221 °C; $[\alpha]_D$=−6.0 (*c* 1, $CHCl_3$); ν_{max} (film)/cm^{-1} 1651, 1476, 1454; δ_H (250 MHz; $CDCl_3$) 7.46–7.29 (11H, m, ArC*H*), 7.06 (4H, m, ArC*H*), 6.75 (5H, m, ArC*H*), 6.61 (4H, m, ArC*H*), 5.98 (2H, t, *J*=3.5 Hz, PhC*H*), 4.87 (2H, m, C*H*), 4.46 (2H, t, *J*=9.0 Hz, CH*H*O), 4.26 (2H, dd, *J*=9.0, 7.6 Hz, 2×C*H*HOH), 3.25 (4H, m, PhCH_2); δ_C (100 MHz; $CDCl_3$) 169.3 (*C*=N), 142.6 (Ar*C*), 142.1 (Ar*C*), 142.0 (Ar*C*), 141.9 (Ar*C*H),

† The reported melting point for this compound is as stated but probably refers to 167–168 °C. No other spectroscopic data is reported for this compound.

137.1 (Ar*C*H), 130.3 (Ar*C*H), 128.6 (Ar*C*H), 128.1 (Ar*C*H), 127.9 (Ar*C*H), 126.8 (Ar*C*H), 126.2 (Ar*C*H), 125.9 (Ar*C*H), 125.6 (Ar*C*H), 125.5 (Ar*C*H), 125.4 (Ar*C*H), 71.6 (*C*H_2O), 66.7 (N*C*H), 59.8 (Ph*C*), 55.8 (Ph*C*H), 41.3 (Ph*C*H_2); *m/z* (ES^+) 675.2988 (7% $C_{48}H_{39}N_2O_2$ requires 675.3012); (FAB^+) 675 (12%, MH^+), 613 (19), 461 (20), 460 (71), 443 (13), 392 (27), 391 (100), 354 (14), 339 (27), 338 (96), 337 (41).

4.2. General procedure for metal triflate-catalysed Diels–Alder reaction

9-(3-Benzyloxazolinoyl)anthracene **2** (0.100 g, 0.297 mmol) was dissolved in CH_2Cl_2 and *N*-methylmaleimide (0.033 g, 0.297 mmol) was added as a solid followed by the addition of metal triflate (0.0003 mmol, 10 mol %) in CH_2Cl_2. The reaction mixture was stirred overnight at room temperature, brine (5 cm^3) added and the organic layer separated and dried over Na_2SO_4. The solution was filtered and the solvent removed to give crude material that was analyzed by ^1H NMR spectroscopy.

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References and notes

1. Jones, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1–21.
2. Jones, S.; Atherton, J. C. C. *Tetrahedron: Asymmetry* **2001**, *12*, 1117–1119.
3. Atherton, J. C. C.; Jones, S. *Tetrahedron Lett.* **2001**, *42*, 8239–8241.
4. Atherton, J. C. C.; Jones, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2166–2173.
5. Atherton, J. C. C.; Jones, S. *Tetrahedron Lett.* **2002**, *43*, 9097–9100.
6. Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297–2360.
7. Kostyanovsky, R.; Giella, I.; Markov, V.; Samojlova, Z. *Tetrahedron* **1974**, *30*, 39–45.
8. Frump, J. A. *Chem. Rev.* **1971**, *71*, 483–505.
9. Phillips, A. J.; Uto, Y.; Wipf, P.; Reno, M. J.; Williams, D. R. *Org. Lett.* **2000**, *2*, 1165–1168.
10. Jones, S.; Selitsianos, D. *Org. Lett.* **2002**, *4*, 3671–3673.
11. Performed using Quantum CAChe 5.04, Fujitsu Ltd. Calculations carried out by generating an optimised map about the dihedral angle at 15° intervals, minimising using PM3 methods.
12. Sanyal, A.; Snyder, J. K. *Org. Lett.* **2000**, *2*, 2527–2530.
13. Corbett, M. S.; Liu, X.; Sanyal, A.; Snyder, J. K. *Tetrahedron Lett.* **2003**, *44*, 931–935.
14. Performed using Quantum CAChe 5.04, Fujitsu Ltd. Heats of formation calculated using PM3 parameters.
15. Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147–14155.
16. Benniston, A. C.; Harriman, A.; Lynch, V. M. *Tetrahedron Lett.* **1994**, *35*, 1473–1476.
17. Rigaudy, J.; Baranne-Lafont, J.; Defoin, A.; Cuong, N. K. *Tetrahedron* **1978**, *34*, 73–82.
18. Schummann, E. L.; Roberts, E. M.; Claxton, G. P. US 3123618, 1964..