Asymmetric Catalysis

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Organocatalytic Activation of Polycyclic Aromatic Compounds for Asymmetric Diels–Alder Reactions**

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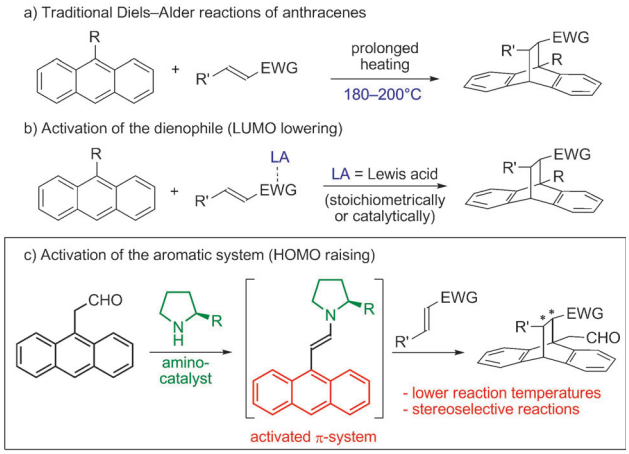
Dedicated to Professor Roald Hoffmann on the occasion of his 75th birthday

The concept of aromaticity has, since its introduction in 1865, played a pivotal role in organic chemistry, governing our fundamental understanding of the structure and reactivity of several classes of important molecules.[1] One such class of important molecules is that of polycyclic aromatic compounds (e.g., naphthalenes, anthracenes, and larger polyaromatic hydrocarbons). These compounds have been found to have broad application in chemical synthesis, biological research, and dye manufacturing.[2] Because of their ability to participate in both thermal and photochemical cycloadditions, anthracenes are the most intriguing subclass of polycyclic aromatic compounds.[3] This unique reactivity has been rationalized by an increase in aromaticity in the outer rings of anthracene during cycloaddition, thereby compensating the unfavorable dearomatization of the central ring. Moreover, according to Clar's empirical rule, the anthracene is assigned with only one aromatic π-sextet, whereas related tricyclic aromatic compounds often have a higher π-sextet/ring ratio and are thus kinetically more stable.[4]

Since the initial disclosure by Diels and Alder in 1931, the thermal [4+2] cycloaddition involving anthracenes has been a subject of intense studies.[5] A central challenge of this pericyclic reaction lies in the high energetic barrier associated with the breakage of aromaticity, which usually requires harsh reaction conditions and prolonged heating (Scheme 1a). The application of an appropriate solvent and/or a Lewis acid may prove useful for reducing the HOMO–LUMO gap of such thermal cycloadditions. Lewis acid catalysts have been shown to activate dienophiles, thus allowing reactions with 9-substituted anthracenes at much lower temperatures (Scheme 1b).[6] In general, the majority of currently available catalytic, rate-enhancing methods focus on the activation of the dienophile (LUMO-lowering principle), whereas the direct activation of the π-system of anthracenes has been much less studied. Recently, great efforts have been made in the development of new HOMO-raising activation modes using aminocatalysts.[7] As such, we envisioned that the polycyclic core of anthracene might be activated using aminocatalysis, if an appropriate molecular handle (such as a formyl group) at a specific position exists. This should allow the central ring of the anthracene subunit to undergo Diels–Alder reactions at low temperatures. More importantly, if proven successful, asymmetric catalytic variants of Diels–Alder reactions of anthracenes could be developed by the employment of chiral aminocatalysts (Scheme 1c). To date, optically active anthracene-derived cycloadducts have been obtained by resolution or auxiliary-based diastereoselective synthesis.[8] The use of anthrone in combination with a chiral catalyst has also been reported.[9] To the best of our knowledge, enantioselective Diels–Alder reactions of anthracenes based on HOMO-raising strategies have never been achieved with good selectivities using small molecule catalysts.[10]



Scheme 1. Diels–Alder reactions of anthracenes: methods of activation.

In order to validate the proposed HOMO-raising activation of polycyclic aromatic compounds by aminocatalysis, the [4+2] cycloaddition of 2-(anthracen-9-yl)acetaldehyde **1a** and nitrostyrene **2a** was studied as the model reaction (Table 1).[11]

Encouragingly, in the presence of catalytic amounts of a sterically bulky amine **3a**[7h,12] and benzoic acid in $CHCl_3$, 40% conversion of 2-(anthracen-9-yl)acetaldehyde **1a** to the corresponding cycloadduct **4a** was achieved at room temperature (Table 1, entry 1). Raising the reaction temperature to 50°C resulted in full conversion of the starting materials, but the enantioselectivity was reduced to 52% *ee* (Table 1,

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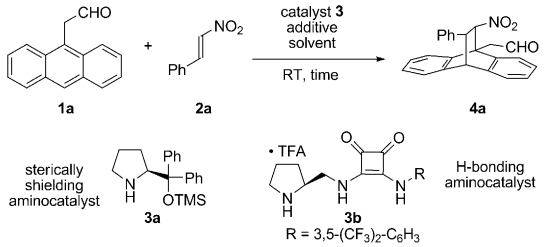
Table 1: Optimization of the aminocatalyzed Diels–Alder reaction of anthracenes.[a]

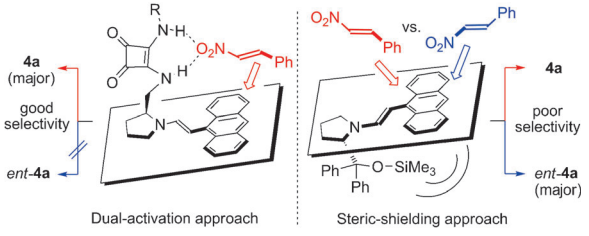


Entry	Catalyst (mol%)	Additive	Solvent	*t* [h]	Conv. [%][b]	*ee* [%][c]
1	**3a** (20)	BA (20 mol%)	$CHCl_3$	16	40	−62
2[d]	**3a** (20)	BA (20 mol%)	$CHCl_3$	16	>99	−52
3[d]	–	BA (20 mol%)	$CHCl_3$	24	0	–
4	**3b** (5)	DEA (1 equiv)	$CHCl_3$	8	>80	98
5[d]	**3b** (5)	DEA (1 equiv)	$CHCl_3$	8	>99	57
6	**3b** (5)	DEA (1 equiv)	PhMe	8	>80	98
7	**3b** (5)	DEA (1 equiv)	CH_2Cl_2	8	>90	98
8	**3b** (5)	DEA (4 equiv)	CH_2Cl_2	6	>99	98
9	**3b** (2)	DEA (2 equiv)	CH_2Cl_2	20	>99	98
10	**3b** (1)	DEA (1 equiv)	CH_2Cl_2	48	>80	98
11[e]	**3b** (2)	DEA (2 equiv)	CH_2Cl_2	20	>99	98

[a] Reactions were performed with **1a** (0.075 mmol) and **2a** (0.05 mmol) in the solvent (0.25 mL). [b] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c] Determined by HPLC analysis on a chiral stationary phase after in situ derivatization. [d] Performed at 50°C. [e] Performed with 0.05 mmol of **1a** and 0.06 mmol of **2a**. BA = benzoic acid. DEA = *N*,*N*-diethylacetamide.

entry 2). Importantly, under identical conditions and in the absence of catalyst **3a**, no reaction occurred (Table 1, entry 3). While this set of experiments provided the proof of concept for the proposed HOMO-raising activation of polyaromatic compounds by aminocatalysis, the stereoselectivity induced by catalyst **3a** in this thermal Diels–Alder reaction was disappointing, as only 62% *ee* was obtained.

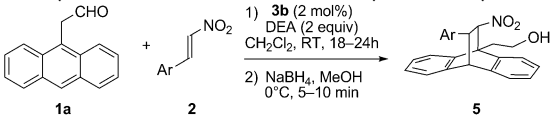
A rationale for the moderate enantioselectivity that was obtained can be found in the symmetrical nature of compound **1a**. Condensation with catalyst **3a** gives a homochiral species, in which one of the anthracene faces is shielded by the steric bulk of the catalyst, while the other remains unshielded for the approach of nitrostyrene (Scheme 2, right). Assuming full facial differentiation, the final enantiomeric distribution will only be determined by the approach of nitrostyrene **2a**, which may react at two enantiotopic faces, leading to **4a** and *ent*-**4a**, respectively. Unfortunately, only moderate control of this approach is offered by **3a**, thus resulting in the poor selectivity observed. Therefore, having a catalyst that provides facial discrimination of both the anthracene and the nitrostyrene is crucial for the success of this asymmetric cycloaddition. As such, we hypothesized that the bifunctional aminocatalyst **3b** may be a qualified candidate for this challenging task (Scheme 2, left).[13] To our delight, by employing **3b** (5 mol%) in the presence of *N*,*N*-diethylacetamide (DEA) as additive at room temperature, product **4a** was formed with more than 80% conversion and 98% *ee* (Table 1, entry 4). For this system, the bifunctional aminocatalyst **3b** serves multiple purposes. The secondary amine should provide activation of the anthracene moiety by the formation of a neighboring enamine species conjugated to the aromatic ring (HOMO-raising activation). At the same time, the squaramide subunit should direct the attack of the dienophile through hydrogen-bonding, thus ensuring good stereoselectivity. After completion of the Diels–Alder reaction, the cycloadduct is liberated by hydrolysis of the enamine, whereas the catalyst enters another cycle. It is noteworthy that elevation of the reaction temperature results in a significant decrease of enantioselectivity (Table 1, entry 5). A brief screening of reaction conditions showed that a larger excess of DEA and the use of CH_2Cl_2 as the solvent accelerates the reaction, although other solvents, such as PhMe, also provided good results. Further reduction of the catalyst loading was also possible, resulting in equally stereoselective formation of the cycloadduct **4a** in the presence of as little as 1 mol% catalyst.[14] However, longer reaction times were required to reach similar levels of conversion (Table 1, entry 10). The use of only 2 mol% of **3b** provided the best trade-off between reaction time and catalyst loading, efficiently promoting and completing the Diels–Alder reaction of anthracene at room temperature within 20 hours.



Scheme 2. Controlling the stereoselectivity: dual activation versus steric shielding.

In order to probe the scope and limitations of the reaction, a range of different nitrostyrenes **2** were evaluated under the optimized conditions (Table 2). To our delight, the reaction proved to be unaffected by the electronic properties of the aryl substituent, as both electron-poor and electron-rich aromatic side chains were tolerated (Table 2, entries 2–7),

Table 2: Asymmetric Diels–Alder reaction: scope of nitrostyrenes.[a]



Entry	**2**	Ar	*t* [h]	**5**	Yield [%][b]	*ee* [%][c]
1	**2a**	Ph	18	**5a**	95	98
2	**2b**	4-Br-C_6H_4	18	**5b**	93	98
3	**2c**	2-Cl-C_6H_4	18	**5c**	90	96
4	**2d**	3-NO_2-C_6H_4	18	**5d**	94	97
5	**2e**	2,6-Cl_2-C_6H_3	24	**5e**	98	92
6	**2f**	4-Me-C_6H_4	48	**5f**	75	93
7[d,e]	**2g**	4-OMe-C_6H_4	48	**5g**	88	97
8[d]	**2h**	2-furyl	24	**5h**	80	97
9	**2i**	3-pyridyl	24	**5i**	69	96

[a] Reactions were performed with **1a** (0.2 mmol) and **2** (0.24 mmol) in CH_2Cl_2 (1 mL). [b] Yield of isolated product over two steps. [c] Determined by HPLC analysis on a chiral stationary phase. [d] 2 equiv of nitroalkene **2** were used. [e] 5 mol% of the catalyst was employed.

thus furnishing products **5a–g** (after in situ reduction)[15] in 75–98% yield and 92–98% *ee*. It should also be mentioned that the substitution pattern of the aryl ring had no influence on the course of the reaction. Furthermore, heteroaryl-substituted nitroalkenes, such as **2h** and **2i**, were also substrates compatible with the developed asymmetric Diels–Alder reaction (Table 2, entries 8 and 9).

The absolute configuration of aldehyde **4b** was unambiguously determined by X-ray crystallographic analysis[16] (Figure 1), and the configurations of the remaining products were assigned by analogy.

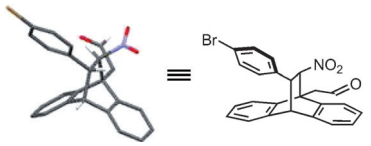
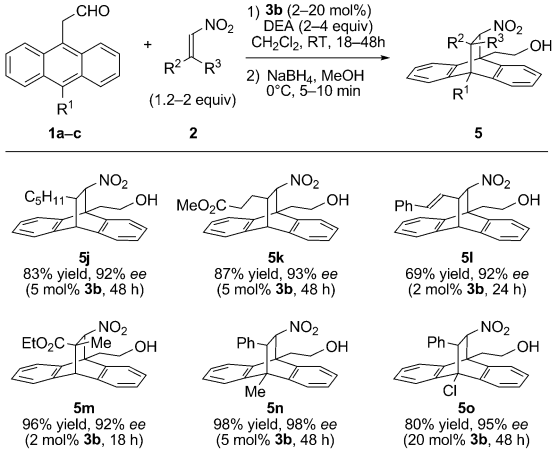


Figure 1. X-ray structure of aldehyde **4b**.

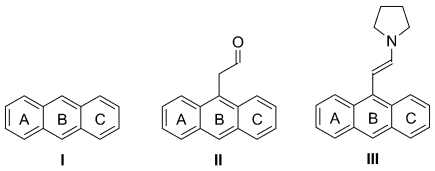
A slight decrease in reactivity was observed when aliphatic nitroalkenes were employed, however, results comparable to those obtained for nitrostyrenes could be achieved by increasing the catalyst loading to 5 mol% (Scheme 3, see **5j** and **5k**). Additionally, it was demonstrated that a nitrodiene reacted selectively with the double bond proximal to the nitro group (**5l**), while an all-carbon quaternary stereocenter may be afforded when a trisubstituted nitroalkene was utilized as dienophile (**5m**). The use of 9,10-disubstituted anthracenes **1b** and **1c** as dienes in this asymmetric [4+2] cycloaddition was also viable, as illustrated by the formation of highly enantioenriched cycloadducts **5n** and **5o**.

The remarkable ability of the aminocatalyst to promote the Diels–Alder reaction of aldehyde-bearing anthracenes at or below room temperature led us to wonder to what extent the formation of the enamine affects the aromaticity and reactivity of the anthracene moiety. DFT calculations (M06-2X/6-31g(d,p))[17] were employed to evaluate these effects.[18] Three structures were modeled: unsubstituted anthracene **I**, the aldehyde **II**, and the enamine-anthracene intermediate **III** (Table 3).



Scheme 3. Asymmetric Diels–Alder reaction: extended scope.

Table 3: Aromaticity data and HOMO and activation energies for **I**, **II**, and **III**.



Structure	NICS(1)$_{zz}$ (A,B,C)	HOMO [eV]
I	−25.3, −34.7, −25.3	−6.7
II	−24.6, −31.6, −24.0	−6,8
III	−24.2, −30.5, −24.1	−5.9

The aromaticity of the anthracenes was assessed using nucleus-independent chemical shifts (NICS).[19] They are a magnetic-based aromaticity index, defined as the negative value of the magnetic shielding, computed at a selected point in the vicinity of the system. NICS(1)$_{zz}$ values were obtained with GIAO-B3LYP/6-31G(d)[20] NMR calculation on M06-2X/6-31+G(d,p)-optimized geometries. Evaluation of the three molecules using NICS(1)$_{zz}$[21] shows that all three molecules have negative values, which indicates that they are all aromatic (Table 3, column 2). The NICS(1)$_{zz}$ data also show that the aromaticity of the central ring decreased when it is substituted with an alkyl group. Comparison of the NICS(1)$_{zz}$ values of the central rings of the two substituted anthracenes (**II** and **III**) shows that the aromaticity is further decreased when a conjugated enamine is present. The NICS(1)$_{zz}$ values of the outer rings in all three systems show little variation. This result suggests that the outer rings are not strongly affected by the substituent on the central ring.[22]

In order to evaluate, how the presence of the aldehyde and, more importantly, the enamine affects the electronic structure of the anthracene moiety, the frontier orbital energy levels of **I**, **II**, and **III** were calculated. The HOMO of **III** is found to be 0.8 eV higher in energy than that of **I** and 0.9 eV higher in energy than **II** (Table 3, column 3). Thus, the HOMO of **III** has a more favorable orbital overlap with the LUMO of the dienophile than **II** or **I**.

In summary, we have disclosed a new activation concept for polycyclic π-systems by using aminocatalysis. This strategy is shown to greatly accelerate the aromaticity breaking process of anthracenes in thermal Diels–Alder reactions. More importantly, a highly asymmetric, catalytic version of the Diels–Alder reaction of anthracenes has been developed using nitroalkenes as dienophiles.[23] The anthracene-derived cycloadducts are obtained in high yields and excellent enantioselectivities by employing a chiral, bifunctional aminocatalyst at remarkably low loadings. Finally, rationalization of this π-activation has been provided on the basis of a series of DFT calculations, which nicely correlate with the experimental results.

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[23] It should be noted that other dienophiles suitable for the Diels–Alder reactions of anthracenes, for example, acrylates and vinyl sulfones, do not react under the present reaction conditions.

