Diels–Alder reaction of benzylidene(cyano)methyl-1,3-benzoxa/thiazoles as stable 1-azabuta-1,3-dienes

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Diels–Alder reactions of benzylidene(cyano)methyl-1,3-benzothiazoles **2** and -1,3-benzoxazoles **3** as 1-azabuta-1,3-dienes are described. The dienes **2**, **3**, featuring stabilized imine moieties in the form of heteroaromatic rings, react with both electron-deficient and electron-rich dienophiles **7–9** to give corresponding cycloadducts **10–15** regioselectively. Cycloadditions of the intramolecular systems **18c**, **d** and **19c**, **d** proceed smoothly *via* an *exo*-transition state, stereoselectively affording polycyclic compounds **20c**, **d** and **21c**, **d** in good to excellent yields. X-Ray crystallographic studies of compounds **12e**, **13a** and **14b** are also reported.

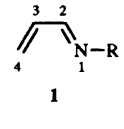
Introduction

A six-membered, nitrogen-containing ring system (piperidine ring) is a common partial structure of biologically active compounds. One of the most direct approaches to the system is obviously a nitrogen-containing hetero-Diels–Alder reaction.[1] However, Diels–Alder reaction of 1-azabuta-1,3-dienes, simple α,β-unsaturated imines **1a**, has been difficult due to the low reactivity of these substrates as dienes, side-reactions and instability arising from the imine moiety.[1a] To solve these problems, various 1-azabuta-1,3-dienes carrying modified substituents at the 1-position have been developed during the last decade. In particular, 1-acyl **1b**,[2] 1-sulfonyl **1c**,[3] 1-dimethylamino **1d**,[4] and 1-phenyl **1e**[5] derivatives are noteworthy. While amides **1b, c** tend to react with electron-rich dienophiles (inverse-type Diels–Alder reaction), the hydrazine **1d** reacts with electron-deficient dienophiles (normal-type Diels–Alder reaction), and the anil **1e** underwent Diels–Alder reaction with both of them. Although it was reported that introduction of an electron-withdrawing group into the 2-position of compounds **1b, c, e** causes a remarkable rise in their reactivity to above that of the parent 1-azadienes,[2d,e,3b,d,5a,c] introduction of the electron-withdrawing group into the 3-position of the dienes has rarely been investigated.[3d] Moreover, to our knowledge, no conscious effort has been made to study the stability of the imine moiety of 1-azabutadiene. We recently reported another type of 1-azabuta-1,3-diene, benzylidene-(cyano)methyl-1,3-benzoxa/thiazoles (**2** and **3**), in which the imine moieties are stabilized by their constituting heteroaromatic rings.[6] It was also reported that dienes **2** and **3** have adequate reactivity arising from the electron-withdrawing cyano group, and undergo Diels–Alder reaction with both electron-rich and electron-deficient dienophiles to give the corresponding cycloadducts.[6] Furthermore, the cycloaddition is efficiently applicable to the intramolecular system.[6] We present here a full account of this work.

Results and discussion

Intermolecular Diels–Alder reaction of benzylidene(cyano)-methyl-1,3-benzothiazoles 2 and benzylidene(cyano)methyl-1,3-benzoxazoles 3

As shown in Scheme 1, the starting dienes **2a–e** and **3a–e**, stable crystalline materials, were readily prepared by condensation of (1,3-benzothiazol-2-yl)acetonitrile **4** and (1,3-benzoxazol-2-yl)acetonitrile **5** with benzaldehydes **6** bearing various groups at the *para* position.[7] With the starting dienes **2** and **3** in hand, dienophiles **7–9** possessing three typical electronic requirements were selected for the reactions with dienes **2** and **3**. In other words, *N*-methylmaleimide **7**, anethole **8**, and 3,4-dihydro-2*H*-pyran **9** can be classified into olefins having electron-withdrawing conjugate-type Z, simple conjugate-type C, and electron-donating heteroatom-type X substituents, respectively.[8]



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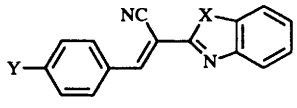


a; R = alkyl group
b; R = COR′
c; R = SO_2Ar
d; R = NMe_2
e; R = Ph

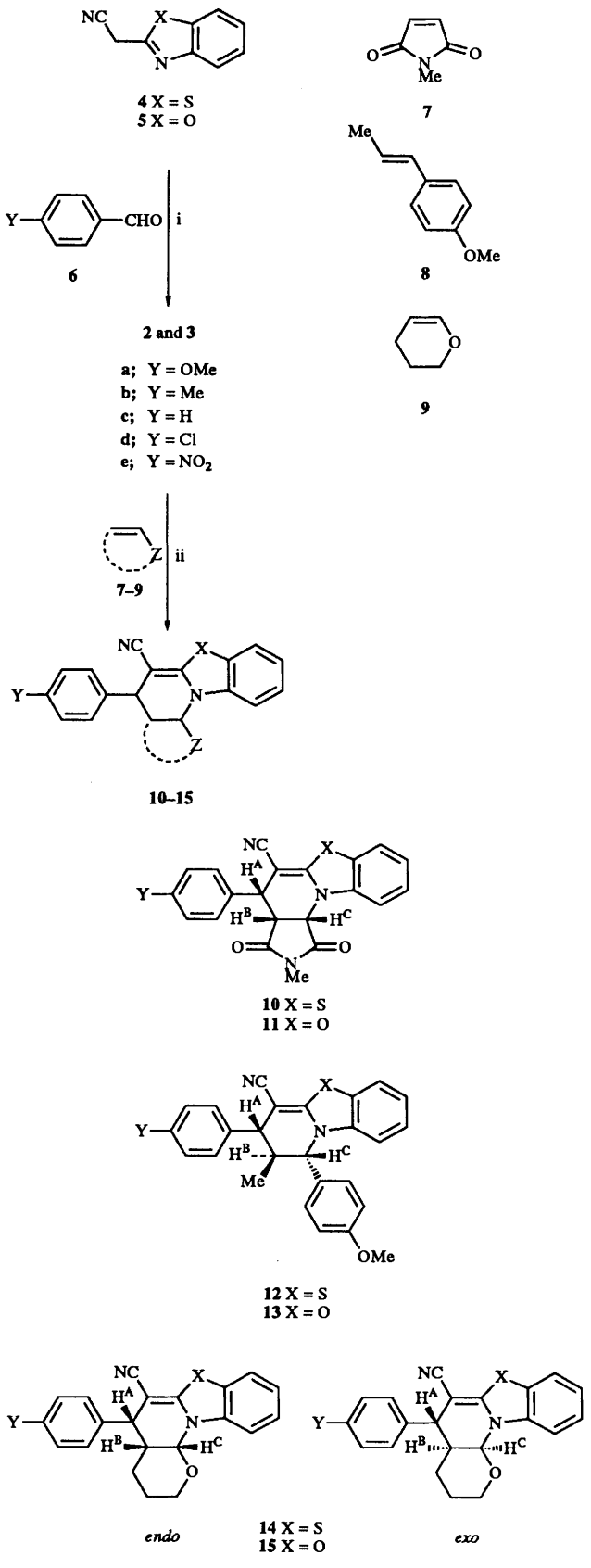
2 X = S (Y is defined in **3** X = O Tables 1–3)

Table 1 Diels–Alder reaction of the dienes **2**, **3** with *N*-methylmaleimide **7**[a]

Run	Diene	Time (*t*/h)	Product (Y)	Yield (%)	J_{AB} (Hz)	J_{BC} (Hz)
1	**2a**	72	**10a** (OMe)	33	7.3	7.9
2	**2b**	30	**10b** (Me)	32	6.9	8.3
3	**2c**	66	**10c** (H)	52	6.9	7.9
4	**2d**	18	**10d** (Cl)	86	7.6	7.9
5	**2e**	60	**10e** (NO_2)	85	7.6	7.9
6	**3a**	66	**11a** (OMe)	14	6.9	8.3
7	**3b**	42	**11b** (Me)	21	7.0	8.3
8	**3c**	48	**11c** (H)	18	7.8	7.8
9	**3d**	42	**11d** (Cl)	25	7.2	7.9
10	**3e**	12	**11e** (NO_2)	71	7.3	8.6

[a] All the reactions were carried out using 8 mol equiv. of dienophile **7** at 120 °C.

First, Diels–Alder reaction of the dienes **2a–e** and **3a–e** with imide **7** was examined (Table 1). Thus, mixtures of the dienes (**2a–e** and **3a–e**, 1 mol equiv.) and imide **7** (7.5 mol equiv.) were heated at 120 °C to give the corresponding *endo*-cycloadducts **10a–e** and **11a–e**. The *endo*-selectivities were probably due to secondary orbital interactions. Table 1 shows that



Scheme 1 *Reagents*: i, **6**, Et_3N, EtOH; ii, **7–9**

benzothiazole-derived dienes **2a–e** give higher yields than those (**3**) from benzoxazole. Surprisingly, compounds **2d, e** and **3e** having an electron-deficient group (Cl or NO_2) tend to be more reactive with highly electron-deficient dienophile **7** than are dienes **2a** and **3a** bearing an electron-donating group (OMe) (runs 1,6 *vs.* runs 4,5,10).† The stereochemistry of compounds **10** and **11** was assigned based on the coupling constants (J_{AB} and J_{BC}) in their ^1H NMR spectra, and confirmed by nuclear overhauser effect (NOE) experiments of compound **10c** (Fig. 1).

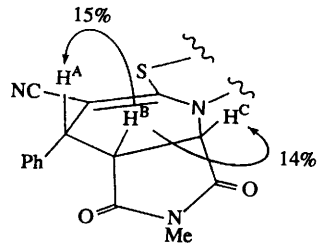


Fig. 1 NOEs of compound **10c**

Table 2 Diels–Alder reaction of the dienes **2, 3** with anethole **8** [a]

Run	Diene	Time (t/h)	Product (Y)	Yield (%)	J_{AB} (Hz)	J_{BC} (Hz)
1	**2a**	36	**12a** (OMe)	42	5.2	5.2
2	**2b**	12	**12b** (Me)	57	5.8	5.5
3	**2c**	24	**12c** (H)	77	4.9	4.9
4	**2d**	6	**12d** (Cl)	76	4.0	4.0
5	**2e**	12	**12e** (NO_2)	75	2.7	2.9
6	**3a**	78	**13a** (OMe)	45	10.3	10.0
7	**3b**	72	**13b** (Me)	63	10.3	10.3
8	**3c**	18	**13c** (H)	69	10.1	10.1
9	**3d**	12	**13d** (Cl)	79	10.0	10.0
10	**3e**	12	**13e** (NO_2)	63	9.9	9.6

[a] All the reactions were carried out using 2 mol equiv. of dienophile **8** at 120 °C.

Next, Diels–Alder reactions of dienes **2** and **3** with anethole **8** were investigated. Heating of the dienes (**2** and **3**, 1 mol equiv.) with anethole **8** (2 mol equiv.) at 120 °C caused a Diels–Alder reaction to occur, and gave the corresponding cycloadducts **12** and **13**, and the results are summarized in Table 2. The regiochemistry of the cycloadducts **12** and **13** was opposite to that of the product from the related reaction of 1-acetyl-2-cyano-4-phenyl-1-azabuta-1,3-diene with β-methylstyrene,[2e] and was similar to that of the product from the related reaction of 4-ethoxycarbonyl-1-phenylsulfonyl-1-azabuta-1,3-diene with diene **3b**.[3d] In the ^1H NMR spectra, the coupling constants (J_{AB} and J_{BC}) of products **13a–e** were observed in the range 9.9–10.3 Hz and 9.6–10.3 Hz, respectively, which indicated that their H_A, H_B and H_C have 1,2-axial–axial relationships. These facts clearly show that cycloadducts **13a–e** have *endo*-stereochemistry. However, it was difficult to establish the *endo*- or *exo*-stereochemistry of cycloadducts **12a–e** from their ^1H NMR spectra; since the spectra showed smaller J_{AB}-values (2.7–5.2 Hz), there is a tendency for adducts **12** having a more powerful electron-withdrawing group to exhibit a smaller coupling constant. To solve this stereochemical ambiguity, single-crystal structure analyses of compound **12e** having the smallest coupling constant, and of compound **13a** having the largest one, were performed. The crystal structures revealed that both adducts have *endo*-stereochemistry and the same chair-like conformations (Figs. 2, 3). The stereochemistries of the other products **12a–d** were tentatively assigned as *endo* by comparison of their ^1H NMR spectra with

† This curious tendency was also observed in Diels–Alder reactions of methyl acrylate with other 1-azabuta-1,3-dienes.[5c]

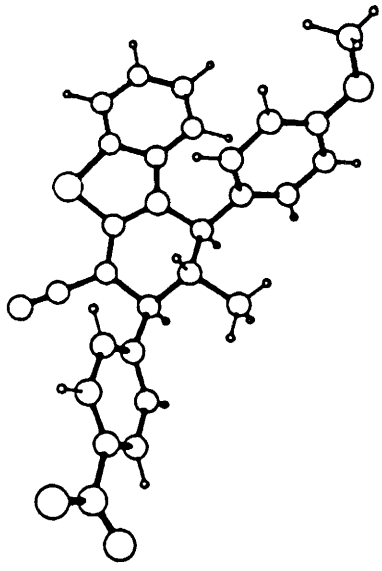


Fig. 2 X-ray molecular structure of compound **12e**

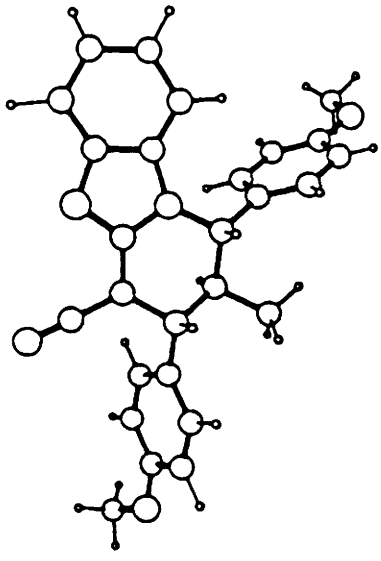


Fig. 3 X-ray molecular structure of compound **13a**

those of compound **12e**. The *endo*-selectivities of the reactions of dienes **2** and **3** with anethole **8** may also arise from secondary orbital interactions.

Normally, coupling constants of 1,2-diaxial protons are observed in the range 8–10 Hz in their ^{1}H NMR spectra. In our cases, both J_{AB} and J_{BC} of adducts **12** appear in the range 2.7–5.2 Hz, although the protons occupy axial positions in the crystalline state. One possibility is that adducts **12** might have a different conformation in solution from that in the crystalline state. Indeed, NOE experiments on compound **12e** showed NOE enhancements between H_A and H_B, and between H_C and H_B as illustrated in Fig. 4. Since 1,2-diaxial protons should have no NOE enhancements, the above NOEs may support the assumption concerning the conformational differences of adducts **12**. In sharp contrast, the ^{1}H NMR spectrum of compound **13a** showed NOEs between H_A and H_C, which indicate that H_A and H_C have a 1,3-diaxial relationship.

Finally, reactions of dienes **2** and **3** with dihydropyran **9** were examined; they require higher temperatures than those with dienophiles **7** or **8**. Thus, the dienes (**2** and **3**, 1 mol equiv.) were heated in an excess of compound **9** at 190 °C in a sealed tube to give cycloadducts **14** and **15** as mixtures of diastereoisomers,

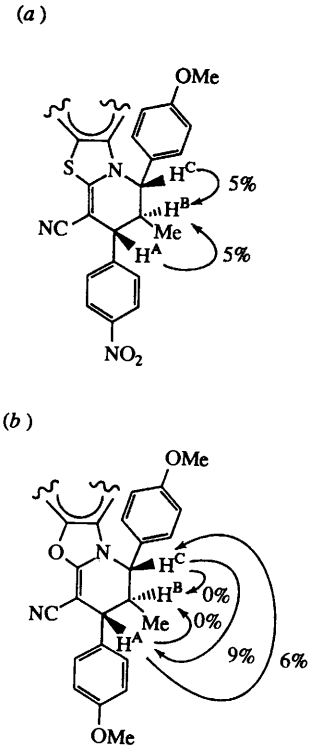


Fig. 4 NOEs of (a) compound **12e** and (b) compound **13a**

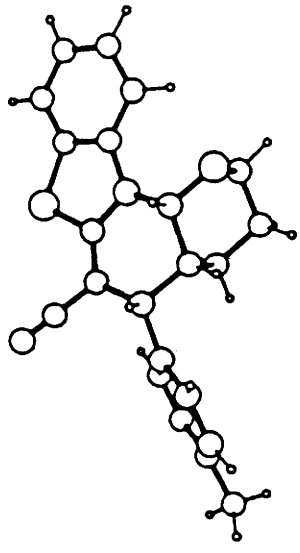


Fig. 5 X-ray molecular structure of compound *endo*-**14b**

respectively (Table 3). In their ^{1}H NMR spectra, the products having smaller coupling constants (J_{AB}) were assigned as *endo*-products. These stereochemical assignments were confirmed by crystal-structure determination of product *endo*-**14b** (Fig. 5).

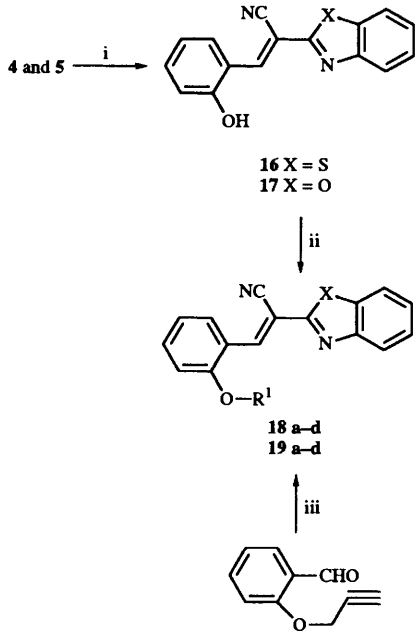
Intramolecular Diels–Alder reaction of 2-(2-allyloxybenzylidene)(cyano)methyl-1,3-benzazoles

With the results of the intermolecular Diels–Alder reactions of dienes **2** with **3** in hand, we turned our attention to the application of this reaction to an intramolecular version. As shown in Scheme 2, substrates for the intramolecular cycloaddition were prepared. Condensation of heterocycles **4** and **5** with salicylaldehyde followed by alkylation of resulting diene alcohols **16** and **17** with allyl bromides gave the substrates **18a, c, d** and **19a, c, d** having olefin moieties as intramolecular dienophiles. During the preparation of compound **19d**, the

Table 3 Diels–Alder reaction of the dienes **2**, **3** with 3,4-dihydro-2*H*-pyran **9**[a]

Run	Diene	Time (*t*/h)	Product (Y)	Yield (%)	*endo*:*exo*	*endo*-**14**, **15** J_{AB} (Hz)	*exo*-**14**, **15** J_{AB} (Hz)
1	**2a**	24	**14a** (OMe)	34	1:1	5.6	11.2
2	**2b**	36	**14b** (Me)	49	1:1.5	5.1	11.2
3	**2c**	12	**14c** (H)	39	1.3:1	5.5	11.0
4	**2d**	24	**14d** (Cl)	41	1:1.2	5.6	11.0
5	**2e**	6	**14e** (NO_2)	46	1:1.6	5.8	11.2
6	**3a**	84	**15a** (OMe)	30	2:1	4.6	6.9
7	**3b**	66	**15b** (Me)	49	6:1	4.6	6.6
8	**3c**	42	**15c** (H)	56	1.3:1	4.6	6.6
9	**3d**	30	**15d** (Cl)	31	4.2:1	5.9	6.9
10	**3e**	18	**15e** (NO_2)	30	1:2	4.9	6.6

[a] All the reactions were carried out at 190 °C using dienophile **9** as the solvent in a sealed tube.



Scheme 2 *Reagents and conditions*: i, salicylaldehyde, Et_3N, EtOH, **16** (97%), **17** (94%); ii, allyl bromide for **18a** and **19a**, (*E*)-but-2-enyl bromide for **18c** and **19c** or cinnamyl bromide for **18d** and **19d**, K_2CO_3, acetone, reflux; **18a** (62%), **18c** (59%), **18d** (46%), **19a** (60%), **19c** (46%), **19d** (35%); iii, **4** or **5**, Et_3N, EtOH; **18b** (66%), **19b** (68%)

intramolecular cycloadduct **21d** was also produced, in 21% yield, due to the high reactivity of substrate **19d**. Substrates **18b** and **19b** with acetylene moieties as dienophiles were prepared by condensation of 2-propargyloxybenzaldehyde with heterocycles **4** and **5**.

With eight types of substrates in hand, the intramolecular Diels–Alder reaction was next examined in refluxing *o*-dichlorobenzene (Table 4). Heating of substrates **18a** and **19a** bearing ethylene moieties gave *cis*-fused cycloadducts **20a** and **21a** *via* *endo*-transition state A‡ in 19% and 21% yield, respectively, accompanied by coumarins **22** and **23** as by-products arising from Claisen rearrangement followed by lactonization (runs 1,5) (Fig. 6, Scheme 3). The stereochemistry of the products **20a** and **21a** was tentatively assigned by the coupling constants (J_{AB}) in their ^1H NMR spectra, and confirmed by NOE experiments on compound **20a** (Fig. 7). Reactivities of acetylenes **18b** and **19b** were extremely low, and

‡ The term *exo* refers to the orientation of the dienophile-to-aryl-connecting side-chain rather than to the orientation of the phenyl or methyl group.[9]

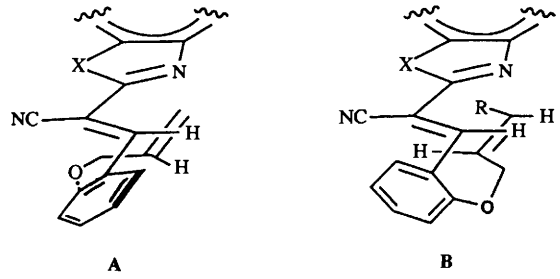
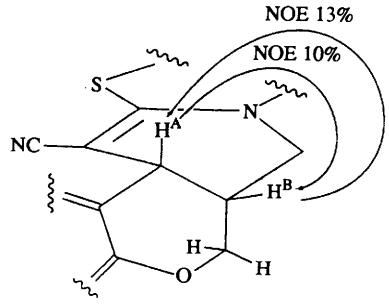


Fig. 6



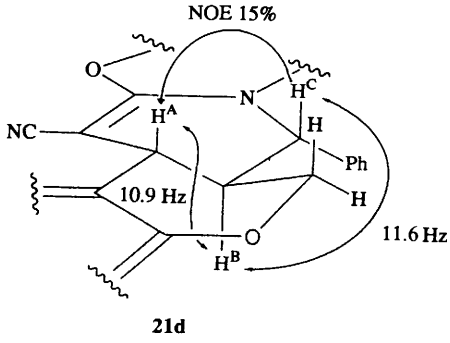
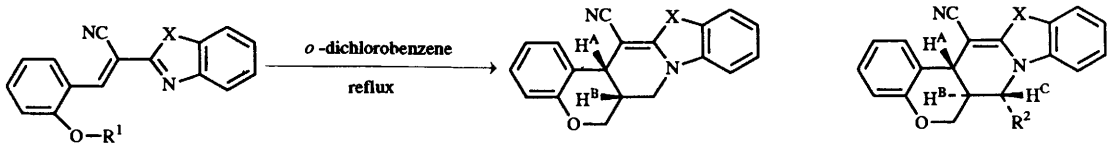


Fig. 7 NOEs for compounds **20a**, **21d**

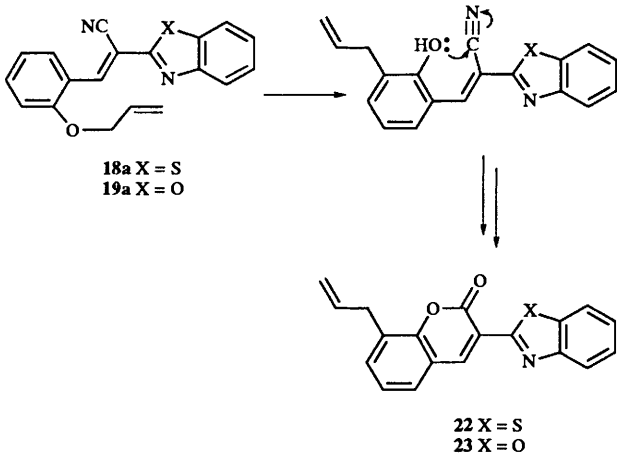
none of the cycloadducts was obtained (runs 2,6). However, successful intramolecular cycloadditions were achieved by employing substrates **18c, d** and **19c, d** having electron-rich olefin moieties. Thus, intramolecular cycloaddition of the substrates took place smoothly to afford adducts **20c, d** and **21c, d** in *trans*-fused forms exclusively, arising from *exo*-transition states **B**,‡ in good to excellent yields (runs 3,4,7,8) (Fig. 6). The

Table 4 Intramolecular cycloaddition of compounds **18a–d** and **19a–d**

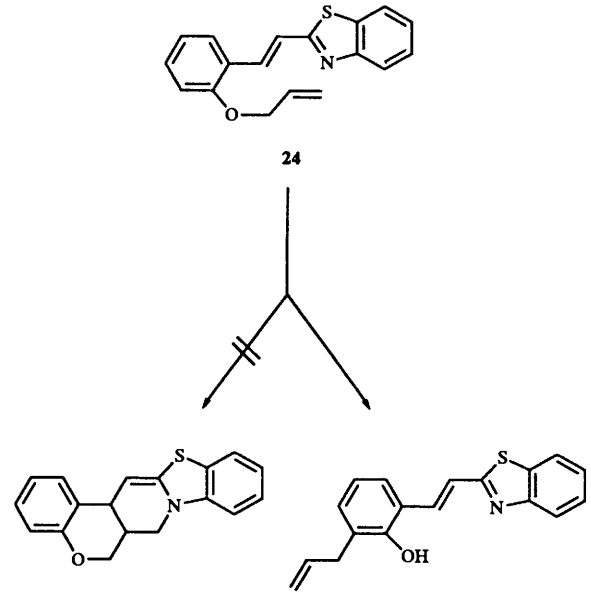


18a–d and 19a–d **20a and 21a** **20c, d and 21c, d**

Run	Starting substrate	Reaction time	Cycloadduct	Yield (%)	J_{AB}/Hz
1	**18a** X = S, R^1 = $CH_2CH{=}CH_2$	3 h	**20a**	19	5.0
2	**18b** X = S, R^1 = $CH_2C{\equiv}CH$	50 h			
3	**18c** X = S, R^1 = (*E*)-$CH_2CH{=}CHMe$	40 min	**20c** R^2 = Me	62	11.2
4	**18d** X = S, R^1 = (*E*)-$CH_2CH{=}CHPh$	20 min	**20d** R^2 = Ph	90	10.9
5	**19a** X = O, R^1 = $CH_2CH{=}CH_2$	3 h	**21a**	21	4.6
6	**19b** X = O, R^1 = $CH_2C{\equiv}CH$	50 h			
7	**19c** X = O, R^1 = (*E*)-$CH_2CH{=}CHMe$	30 min	**21c** R^2 = Me	72	10.9
8	**19d** X = O, R^1 = (*E*)-$CH_2CH{=}CHPh$	30 min	**21d** R^2 = Ph	94	10.9



Scheme 3



Scheme 4

stereostructure of the cycloadducts was assigned based on axial–axial coupling constants in their ^{1}H NMR spectra (J_{AB}, J_{BC} both 10–11 Hz)[9] and on NOE difference experiments of adduct **21d** (Fig. 7).

These results deserve some comment concerning the novel aspects of this intramolecular cycloaddition. A substrate having an acetylene moiety exhibits lower reactivity than that carrying an ethylene moiety (runs 1,5 *vs.* runs 2,6).§ This fact seems to be due to the lower highest occupied molecular orbital (HOMO) of the acetylene moiety than that of the ethylene moiety.[8c] Moreover, cycloaddition of the congener **24** of **18a** did not take place without the electron-withdrawing cyano group, and gave only Claisen rearrangement product **25** (Scheme 4). These results suggest that the present intramolecular cycloaddition may be classified as an inverse-type Diels–Alder reaction. Accordingly, the substrates **18c, d** and **19c, d** having electron-donating groups (methyl or phenyl) in the olefin moieties possess good reactivity, and the reactions gave higher yields within a shorter reaction time (runs 3,4,7,8). Although the high *exo*-selectivities of the reactions of compounds **18d** and **19d** may arise from secondary orbital interactions, the cause(s) of the stereoselectivity of the reactions of substrates **18a, c** and **19a, c** remain(s) unknown.

As stated, we have developed a novel hetero-Diels–Alder reaction of benzylidene(cyano)methylazoles as stable 1-azabuta-1,3-dienes. This methodology may facilitate access to various N-heterocycles of biological interest.

§ In contrast to these facts, it was reported that heating of the **1d**-congener of azadienes **18b** and **19b** causes a normal-type intramolecular Diels–Alder reaction to give corresponding cycloadducts, while that of the **1d**-congener of azadienes **18a** and **19a** did not.[4e]

Experimental

General

All mps were determined with a Yanagimoto MP-21 melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 270–30, and a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured with a JEOL-PMX60$_{SI}$ (60 MHz), JEOL JNM-EX270 (270 MHz), or a JEOL JNM-EX400 (400 MHz) spectrometer. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using tetramethylsilane (δ = 0) and/or residual chloroform (δ = 7.25) as internal standard. *J* Values are given in Hz. Mass spectra were taken with a JEOL JMS-DX302 mass spectrometer. Unless otherwise noted, all experiments were

carried out under an atmosphere of dry argon and in anhydrous solvents. For TLC analyses, Merck precoated TLC plates (silica gel 60 F254, 0.25 mm, Art 5715) were used. The known compounds **2a–d** and **4** were prepared according to reported methods.[7]

(1,3-Benzoxazol-2-yl)acetonitrile 5
A mixture of 2-aminophenol (1.30 g, 12 mmol), malononitrile (2.40 g, 36 mmol), and acetic acid (2 cm^3) in EtOH (30 cm^3) was heated at reflux for 24 h. After cooling, the mixture was concentrated under reduced pressure, and the residue was diluted with $CHCl_3$. The mixture was filtered, and the filtrate was washed successively with saturated aq. $NaHCO_3$ and water. The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting crystalline residue was recrystallized from hexane–Et_2O (1 : 5) to give title compound **5** (0.540 g, 30%) as crystals, mp 70–72 °C (Found: C, 68.2; H, 3.5; N, 17.6. Calc. for $C_9H_6N_2O$: C, 68.35; H, 3.8; N, 17.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2268 (CN); δ_H(400 MHz; $CDCl_3$) 4.11 (2 H, s, CH_2), 7.35–7.41 (2 H, m, ArH), 7.54–7.56 (1 H, m, ArH), 7.73–7.75 (1 H, m, ArH); *m/z* 158 (M^+, 100%), 130 (5), 103 (14) and 64 (19).

(*E*)-2-(1,3-Benzothiazol-2-yl)-3-(4-nitrophenyl)acrylonitrile 2e
To a stirred solution of compound **4** (3.50 g, 20 mmol) and 4-nitrobenzaldehyde **6e** (3.00 g, 20 mmol) in EtOH (30 cm^3) was added 5 drops of triethylamine at room temp. After 3 h, the yellow crystals which had precipitated out were collected by filtration and washed with EtOH to give title compound **2e** (3.90 g, 71%). An analytical sample was obtained by recrystallization from EtOH–tetrahydrofuran (THF), mp 178–181 °C (Found: C, 62.6; H, 2.65; N, 13.8. Calc. for $C_{16}H_9N_3O_2S$: C, 62.55; H, 2.9; N, 13.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2230 (CN); δ_H(60 MHz; $CDCl_3$) 7.23–8.43 (9 H, m, ArH, =CH); *m/z* 307 (M^+, 71%), 306 (100) and 260 (55).

(*E*)-2-(1,3-Benzoxazol-2-yl)-3-(4-methoxyphenyl)acrylonitrile 3a
This compound (282 mg, 89%) was prepared from substrates **5** (158 mg, 1.0 mmol) and **6a** (204 mg, 1.5 mmol), triethylamine (2 drops), and EtOH (2 cm^3) in the same manner as for the preparation of analogue **2e**, mp 175–177 °C (from EtOH) (Found: C, 73.9; H, 4.1; N, 10.15. Calc. for $C_{17}H_{12}N_2O_2$: C, 73.9; H, 4.4; N, 10.15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2225 (CN); δ_H(400 MHz; $CDCl_3$) 3.89 (3 H, s, OMe), 7.01 (2 H, d, *J* 8.9, ArH), 7.37 (2 H, m, ArH), 7.56 (1 H, m, ArH), 7.77 (1 H, m, ArH), 8.05 (2 H, d, *J* 8.9, ArH) and 8.22 (1 H, s, =CH); *m/z* 276 (M^+, 52%), 275 (100), 250 (10) and 232 (22).

(*E*)-2-(1,3-Benzoxazol-2-yl)-3-(*p*-tolyl)acrylonitrile 3b
This compound (780 mg, 76%) was prepared from substrates **5** (690 mg, 3.9 mmol) and **6b** (780 mg, 6.5 mmol), triethylamine (5 drops), and EtOH (14 cm^3) in the same manner as for the preparation of analogue **2e**, mp 191–193 °C (from MeOH) (Found: C, 78.3; H, 4.35; N, 10.75. Calc. for $C_{17}H_{12}N_2O$: C, 78.45; H, 4.65; N, 10.75%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2225 (CN); δ_H(60 MHz; $CDCl_3$) 2.41 (3 H, s, Me), 7.21–7.93 (8 H, m, ArH) and 8.20 (1 H, s, =CH); *m/z* 259 (M^+, 100%), 234 (7) and 216 (3).

(*E*)-2-(1,3-Benzoxazol-2-yl)-3-phenylacrylonitrile 3c
This compound (329 mg, 87%) was prepared from substrates **5** (237 mg, 1.5 mmol) and **6c** (159 mg, 1.5 mmol), triethylamine (3 drops), and EtOH (3 cm^3) in the same manner as for the preparation of analogue **2e**, mp 138–140 °C (from EtOH) (Found: C, 78.0; H, 3.95; N, 11.4. Calc. for $C_{16}H_{10}N_2O$: C, 78.0; H, 4.1; N, 11.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2232 (CN); δ_H(60 MHz; $CDCl_3$) 7.26–8.16 (9 H, m, ArH) and 8.30 (1 H, s, =CH); *m/z* 245 (M^+, 100%), 220 (6) and 140 (3).

(*E*)-2-(1,3-Benzoxazol-2-yl)-3-(4-chlorophenyl)acrylonitrile 3d
This compound (471 mg, 78%) was prepared from substrates **5** (340 mg, 2.0 mmol) and **6d** (450 mg, 3.2 mmol), triethylamine (7 drops), and EtOH (7 cm^3) in the same manner as for the preparation of analogue **2e**, mp 149–151 °C (from EtOH) (Found: C, 68.5; H, 2.9; N, 10.0. Calc. for $C_{16}H_9ClN_2O$: C, 68.5; H, 3.2; N, 10.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2223 (CN); δ_H(60 MHz; $CDCl_3$) 7.07–8.07 (8 H, m, ArH) and 8.26 (1 H, s, =CH); *m/z* 282 (M^+, 25%), 281 (44), 280 (M^+, 73), 279 (100) and 254 (5).

(*E*)-2-(1,3-Benzoxazol-2-yl)-3-(4-nitrophenyl)acrylonitrile 3e
This compound (1.36 g, 90%) was prepared from substrates **5** (960 mg, 5.5 mmol) and **6e** (1.36 mg, 9.0 mmol), triethylamine (5 drops), and EtOH (10 cm^3) in the same manner as for the preparation of analogue **2e**, mp 218–222 °C (from AcOEt) (Found: C, 65.9; H, 2.9; N, 14.4. Calc. for $C_{16}H_9N_3O_3$: C, 66.0; H, 3.1; N, 14.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2225 (CN); δ_H(60 MHz; $CDCl_3$) 7.2–8.8 (9 H, m, ArH, =CH); *m/z* 290 (M^+, 100%), 244 (100) and 216 (21).

General procedure for the intermolecular Diels–Alder reaction of compounds 2 and 3 (Tables 1–3)
A mixture of a diene **2** or **3** and a dienophile **7**, **8** or **9** (**7**, 8 mol equiv.; **8**, 2 mol equiv.; **9**, as a solvent) was heated. After cooling, the mixture was concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel and/or crystallization. The reaction temperature, the reaction time, and the yield are listed in Tables 2–4.

(3a*R,4*R**,11a*S**)-4-(4-Methoxyphenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,11a-hexahydropyrrolo[3′,4′:5,6]pyrido[2,1-*b*]benzothiazole-5-carbonitrile 10a (Table 1, run 1).** This compound (226 mg) was prepared from diene **2a** (500 mg, 1.7 mmol) and imide **7** (1.52 g, 14 mmol), mp 250–253 °C (Found: C, 65.25; H, 4.3; N, 10.3. Calc. for $C_{22}H_{17}N_3O_3S$: C, 65.5; H, 4.25; N, 10.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190 (CN) and 1723 (CO); δ_H[270 MHz; $(CD_3)_2SO$] 2.22 (3 H, s, NMe), 3.67 (1 H, dd, *J* 7.3 and 7.9, NCHC*H*CHAr), 3.70 (3 H, s, OMe), 4.20 (1 H, d, *J* 7.3, NCHCHC*H*Ph), 5.64 (1 H, d, *J* 7.9, NC*H*CHCHPh), 6.81 (2 H, d, *J* 8.6, ArH), 6.89 (2 H, d, *J* 8.6, ArH), 7.4–7.2 (3 H, m, ArH) and 7.74 (1 H, d, *J* 7.6, ArH); *m/z* 403 (M^+, 100%), 388 (27), 372 (12) and 291 (34).

(3a*R,4*R**,11a*S**)-2-Methyl-1,3-dioxo-4-(*p*-tolyl)-1,2,3,3a,4,11a-hexahydropyrrolo[3′,4′:5,6]pyrido[2,1-*b*]benzothiazole-5-carbonitrile 10b (Table 1, run 2).** This compound (237 mg) was prepared from diene **2b** (500 mg, 1.9 mmol) and imide **7** (1.69 g, 14 mmol), mp 250–253 °C (from $CHCl_3$) (Found: C, 68.2; H, 4.4; N, 10.8. Calc. for $C_{22}H_{17}N_3O_2S$: C, 68.2; H, 4.4; N, 10.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190 (CN) and 1722 (CO); δ_H[270 MHz; $(CD_3)_2SO$] 2.20 (3 H, s, CMe), 2.23 (3 H, s, NMe), 3.66 (1 H, dd, *J* 6.9 and 8.3, NCHC*H*CHAr), 4.20 (1 H, d, *J* 6.9, NCHCHC*H*Ph), 5.47 (1 H, d, *J* 8.3, NC*H*CHCHPh), 6.84 (2 H, d, *J* 8.3, ArH), 7.05 (2 H, d, *J* 8.3, ArH), 7.1–7.5 (3 H, m, ArH) and 7.73 (1 H, d, *J* 7.9, ArH); *m/z* 403 (M^+, 100%), 388 (27), 372 (12) and 291 (34).

(3a*R,4*R**,11a*S**)-2-Methyl-1,3-dioxo-4-phenyl-1,2,3,3a,4,11a-hexahydropyrrolo[3′,4′:5,6]pyrido[2,1-*b*]benzothiazole-5-carbonitrile 10c (Table 1, run 3).** This compound (370 mg) was prepared from diene **2c** (500 mg, 1.9 mmol) and imide **7** (1.70 g, 15 mmol), mp > 300 °C (from acetone) (Found: C, 67.45; H, 3.95; N, 11.2. Calc. for $C_{21}H_{15}N_3O_2S$: C, 67.55; H, 4.05; N, 11.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN) and 1726 (CO); δ_H[270 MHz; $(CD_3)_2SO$] 2.15 (3 H, s, Me), 3.71 (1 H, dd, *J* 6.9 and 7.9, NCHC*H*CHAr), 4.27 (1 H, d, *J* 6.9, NCHCHC*H*Ph, spin saturation at δ 3.71, NOE, 15%), 5.66 (1 H, d, *J* 7.9, NC*H*CHCHPh, spin saturation at δ 3.71, NOE, 14%), 6.96–7.00 (2 H, m, ArH), 7.18–7.38 (6 H, m, ArH) and

7.75 (1 H, d, *J* 8.8, ArH); *m/z* 373 (M^+, 100%), 296 (26), 261 (34) and 211 (18).

(3a*R,4*R**,11a*S**)-4-(4-Chlorophenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzothiazole-5-carbonitrile 10d (Table 1, run 4).** This compound (588 mg) was prepared from diene **2d** (500 mg, 1.7 mmol) and imide **7** (1.50 g, 14 mmol), mp 291–294 °C (from acetone) (Found: C, 61.9; H, 3.45; N, 10.2. Calc. for $C_{21}H_{14}ClN_3O_2S$: C, 61.85; H, 3.45; N, 10.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN) and 1717 (CO); δ_H[270 MHz; $(CD_3)_2SO$] 2.20 (3 H, s, NMe), 3.70 (1 H, dd, *J* 7.6 and 7.9, NCHC*H*CHAr), 4.31 (1 H, d, *J* 7.6, NCHCHC*H*Ph), 5.67 (1 H, d, *J* 7.9, NC*H*CHCHPh), 7.00 (2 H, d, *J* 8.6, ArH), 7.1–7.5 (5 H, m, ArH) and 7.74 (1 H, d, *J* 7.6, ArH); *m/z* 407 (M^+, 100%), 372 (17), 321 (11), 295 (38) and 211 (25).

(3a*R,4*R**,11a*S**)-2-Methyl-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzothiazole-5-carbonitrile 10e (Table 1, run 5).** This compound (570 mg) was prepared from diene **2e** (500 mg, 1.6 mmol) and imide **7** (1.80 g, 16 mmol), mp 291–294 °C (from acetone) (Found: C, 60.25; H, 3.2; N, 13.2. Calc. for $C_{21}H_{14}N_4O_4S$: C, 60.3; H, 3.35; N, 13.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN) and 1727 (CO); δ_H[270 MHz; $(CD_3)_2SO$] 2.20 (3 H, s, Me), 3.78 (1 H, dd, *J* 7.6 and 7.9, NCHC*H*CHPh), 4.54 (1 H, d, *J* 7.6, NCHCHC*H*Ph), 5.73 (1 H, *J* 7.9, NC*H*CHCHPh), 7.2–7.4 (5 H, m, ArH), 7.78 (1 H, d, *J* 7.9, ArH) and 8.14 (2 H, d, *J* 8.6, ArH); *m/z* 418 (M^+, 100%), 371 (29) and 296 (29).

(3a*R,4*R**,11a*S**)-4-(4-Methoxyphenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzoxazole-5-carbonitrile 11a (Table 1, run 6).** This compound (78 mg) was prepared from diene **3a** (400 mg, 1.45 mmol) and imide **7** (1.45 g, 13 mmol), mp 202–205 °C (acetone) (Found: C, 68.0; H, 4.25; N, 10.7. Calc. for $C_{22}H_{17}N_3O_4$: C, 68.2; H, 4.4; N, 10.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2198 (CN) and 1723 (CO); δ_H[270 MHz; $(CD_3)_2SO$] 2.30 (3 H, s, NMe), 3.60 (1 H, dd, *J* 6.9 and 8.3, NCHC*H*CHAr), 3.70 (3 H, s, OMe), 4.22 (1 H, d, *J* 6.9, NCHCHC*H*Ph), 5.47 (1 H, d, *J* 8.3, NC*H*CHCHPh), 6.76 (2 H, d, *J* 8.6, ArH), 6.91 (2 H, d, *J* 8.6, ArH), 7.1–7.4 (3 H, m, ArH) and 7.47 (1 H, d, *J* 7.6, ArH); *m/z* 387 (M^+, 100%), 372 (46), 356 (12) and 275 (63).

(3a*R,4*R**,11a*S**)-2-Methyl-1,3-dioxo-4-(*p*-tolyl)-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzoxazole-5-carbonitrile 11b (Table 1, run 7).** This compound (120 mg) was prepared from diene **3b** (400 mg, 1.5 mmol) and imide **7** (1.37 g, 12 mmol), mp 273–276 °C (from AcOEt) (Found: C, 71.1; H, 4.4; N, 11.3. Calc. for $C_{22}H_{17}N_3O_3$: C, 71.15; H, 4.6; N, 10.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190 (CN) and 1723 (CO); δ_H[400 MHz; $(CD_3)_2SO$] 2.21 (3 H, s, CMe), 2.23 (3 H, s, NMe), 3.64 (1 H, dd, *J* 7.0 and 8.3, NCHC*H*CHAr), 4.27 (1 H, d, *J* 7.0, NCHCHC*H*Ar), 5.51 (1 H, d, *J* 8.3, NC*H*CHCHAr), 6.89 (2 H, d, *J* 8.2, ArH), 7.03 (2 H, d, *J* 8.2, ArH), 7.1–7.4 (3 H, m, ArH) and 7.54 (1 H, d, *J* 7.9, ArH); *m/z* 371 (M^+, 100%), 356 (60), 280 (14) and 259 (71).

(3a*R,4*R**,11a*S**)-2-Methyl-1,3-dioxo-4-phenyl-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzoxazole-5-carbonitrile 11c (Table 1, run 8).** This compound (78 mg) was prepared from diene **3c** (300 mg, 1.2 mmol) and imide **7** (1.08 g, 10 mmol), mp 282–285 °C (from acetone) (Found: C, 70.45; H, 4.15; N, 11.7. Calc. for $C_{21}H_{15}N_3O_3$: C, 70.6; H, 4.2; N, 11.75%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2196 (CN) and 1725 (CO); δ_H[400 MHz; $(CD_3)_2SO$] 2.28 (3 H, s, NMe), 3.75 (1 H, t, *J* 7.8, NCHC*H*CHAr), 4.41 (1 H, d, *J* 7.8, NCHCHC*H*Ar), 5.61 (1 H, d, *J* 7.8, NC*H*CHCHAr), 7.05–7.15 (2 H, m, ArH), 7.25–7.45 (6 H, m, ArH) and 7.63 (1 H, d, *J* 7.6, ArH); *m/z* 357 (M^+, 100%), 300 (6), 280 (17), 245 (63) and 195 (19).

(3a*R,4*R**,11a*S**)-4-(4-Chlorophenyl)-2-methyl-1,3-dioxo-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzoxazole-5-carbonitrile 11d (Table 1, run 9).** This compound (139 mg) was prepared from diene **3d** (400 mg, 1.4 mmol) and imide **7** (1.27 g, 11 mmol), mp 274–277 °C (Found: C, 64.3; H, 3.45; N, 10.6. Calc. for $C_{21}H_{14}ClN_3O_3$: C, 64.4; H, 3.6; N, 10.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190 (CN), 1723 (CO) and 1674; δ_H[270 MHz; $(CD_3)_2SO$] 2.28 (3 H, s, NMe), 3.67 (1 H, dd, *J* 7.2 and 7.9, NCHC*H*CHAr), 4.37 (1 H, d, *J* 7.2, NCHCHC*H*Ar), 5.52 (1 H, d, *J* 7.9, NC*H*CHCHAr), 7.05 (2 H, d, *J* 8.6, ArH), 7.2–7.4 (5 H, m, ArH) and 7.51 (1 H, d, *J* 7.9, ArH); *m/z* 393 (M^+, 37%), 392 (42), 391 (M^+, 100%), 356 (34), 279 (65) and 195 (23).

(3a*R,4*R**,11a*S**)-2-Methyl-4-(4-nitrophenyl)-1,3-dioxo-1,2,3,3a,4,11a-hexahydropyrrolo[3',4':5,6]pyrido[2,1-*b*]benzoxazole-5-carbonitrile 11e (Table 1, run 10).** This compound (491 mg) was prepared from diene **3e** (500 mg, 1.7 mmol) and imide **7** (1.53 g, 14 mmol), mp 288–290 °C (from aq. MeOH) (Found: M^+, 404.0958. $C_{21}H_{14}N_4O_5$ requires M, 402.0964); $\nu_{max}(CHCl_3)/cm^{-1}$ 2202 (CN) and 1727 (C=O); δ_H(270 MHz; $CDCl_3$) 2.10 (3 H, s, Me), 3.60 (1 H, dd, *J* 7.3 and 8.6, NCHC*H*CHAr), 4.38 (1 H, d, *J* 7.3, NCHCHC*H*Ar), 4.87 (1 H, d, *J* 8.6, NC*H*CHCHAr), 7.1–7.4 (6 H, m, ArH) and 8.05 (2 H, d, *J* 8.6, ArH); *m/z* 402 (M^+, 100%), 355 (60), 290 (35) and 280 (25).

(1*R,2*R**,3*S**)-1,3-Bis-(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzothiazole-4-carbonitrile 12a (Table 2, run 1).** This compound (949 mg) was prepared from diene **2a** (1.00 g, 3.4 mmol) and anethole **8** (1.00 g, 6.75 mmol), mp 209–211 °C (from hexane–$CHCl_3$) (Found: C, 73.5; H, 5.35; N, 6.35. Calc. for $C_{27}H_{24}N_2O_2S$: C, 73.6; H, 5.5; N, 6.35%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2184 (CN); δ_H(400 MHz; $CDCl_3$) 1.08 (3 H, d, *J* 7.0, *Me*CH), 2.62 (1 H, tq, *J* 5.2 and 7.0, NCHC*H*CHAr), 3.48 (1 H, d, *J* 5.2, NCHCHC*H*Ar), 3.70 (6 H, s, OMe × 2), 4.84 (1 H, d, *J* 5.2, NC*H*CHCHAr), 6.37 (1 H, m, ArH), 6.61 (2 H, m, ArH), 6.79 (2 H, d, *J* 8.5, ArH), 6.95 (2 H, d, *J* 8.6, ArH), 6.99 (2 H, m, ArH) and 7.39 (1 H, m, ArH); *m/z* 440 (M^+).

(1*R,2*R**,3*S**)-1-(4-Methoxyphenyl)-2-methyl-3-(*p*-tolyl)-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzothiazole-4-carbonitrile 12b (Table 2, run 2).** This compound (870 mg) was prepared from diene **2b** (1.02 mg, 3.6 mmol) and anethole **8** (1.10 g, 6.75 mmol), mp 211–212 °C (from hexane–$CHCl_3$) (Found: C, 76.35; H, 5.55; N, 6.6. Calc. for $C_{27}H_{24}N_2OS$: C, 76.4; H, 5.65; N, 6.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2182 (CN); δ_H(400 MHz; $CDCl_3$) 1.06 (3 H, d, *J* 7.0, *Me*CH), 2.12 (3 H, s, Me), 2.61 (1 H, br tq, *J* 5.7 and 7.0, NCHC*H*CHAr), 3.49 (1 H, d, *J* 5.8, NCHCHC*H*Ar), 3.69 (3 H, s, OMe), 4.82 (1 H, d, *J* 5.8, NC*H*CHCHAr), 6.35 (1 H, m, ArH), 6.60 (2 H, d, *J* 8.9, ArH), 6.80 (2 H, d, *J* 8.9, ArH), 6.85–7.05, (6 H, m, ArH) and 7.37 (1 H, m, ArH); *m/z* 424 (M^+, 43), 275 (7) and 148 (100).

(1*R,2*R**,3*S**)-1-(4-Methoxyphenyl)-2-methyl-3-phenyl-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzothiazole-4-carbonitrile 12c (Table 2, run 3).** This compound (1.11 g) was prepared from diene **2c** (920 mg, 3.5 mmol) and anethole **8** (1.04 g, 7.0 mmol), mp 216–218 °C (from benzene) (Found: C, 76.0; H, 5.25; N, 6.8. Calc. for $C_{26}H_{22}N_2OS$: C, 76.1; H, 5.4; N, 6.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2182 (CN); δ_H(400 MHz; $CDCl_3$) 1.13 (3 H, d, *J* 7.0, *Me*CH), 2.72 (1 H, tq, *J* 4.9 and 7.0, NCHC*H*CHAr), 3.54 (1 H, d, *J* 4.9, NCHCHC*H*Ar), 3.68 (3 H, s, OMe), 4.87 (1 H, d, *J* 4.9, NC*H*CHCHAr), 6.39 (1 H, m, ArH), 6.57 (2 H, d, *J* 8.9, ArH), 6.67 (2 H, d, *J* 8.9, ArH), 6.95–7.10 (7 H, m, ArH) and 7.39 (1 H, m, ArH); *m/z* 410 (M^+, 10%), 261 (14) and 148 (100).

(1*R,2*R**,3*S**)-3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzothiazole-4-carbonitrile 12d (Table 2, run 4).** This compound (2.28 g) was prepared from diene **2d** (1.04 g, 6.0 mmol) and anethole **8** (1.68 g, 10.9 mmol), mp 131–134 °C (from hexane–$CHCl_3$) (Found: C, 70.4; H, 5.0; N, 6.05. Calc. for $C_{26}H_{21}ClN_2OS$: C, 70.2; H, 4.8; N, 6.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2182 (CN); δ_H(400 MHz; $CDCl_3$) 1.17 (3 H, d, *J* 7.0, *Me*CH), 2.75 (1 H, tq, *J* 4.0 and 7.0, NCHC*H*CHAr), 3.53 (1 H, d, *J* 4.0, NCHCHC*H*Ar), 3.69 (3 H, s, OMe), 4.93 (1 H, d, *J* 4.0, NC*H*CHCHAr), 6.45 (1 H, m,

ArH), 6.55 (2 H, d, *J* 8.7, ArH), 6.67 (2 H, d, *J* 8.7, ArH), 6.9–7.19 (6 H, m, ArH) and 7.43 (1 H, m, ArH); *m/z* 440 (M^+).

(1*R,2*R**,3*S**)-1-(4-Methoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzothiazole-4-carbonitrile 12e (Table 2, run 5).** This compound (120 mg) was prepared from diene **2e** (100 mg, 0.32 mmol) and anethole **8** (100 mg, 0.64 mmol), mp 216–218 °C (from EtOH) (Found: C, 68.5; H, 4.45; N, 9.2. Calc. for $C_{26}H_{21}N_3O_3S$: C, 68.55; H, 4.65; N, 9.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2182 (CN); δ_H(400 MHz; $CDCl_3$) 1.30 (3 H, d, *J* 7.1, *Me*CH), 2.93 (1 H, m, NCHC*H*CHAr, spin saturation at δ 3.67, NOE, 5%; spin saturation at δ 5.03, NOE, 5%), 3.60 (3 H, s, OMe), 3.67 (1 H, d, *J* 2.7, NCHCHC*H*Ar), 5.03 (1 H, d, *J* 2.9, NC*H*CHCHAr), 6.45 (2 H, d, *J* 8.8, ArH), 6.54 (1 H, m, ArH), 6.60 (2 H, d, *J* 8.8, ArH), 7.11 (4 H, m, ArH), 7.48 (1 H, m, ArH) and 7.84 (2 H, d, *J* 8.8, ArH); *m/z* 455 (M^+, 24%) and 148 (100).

(1*R,2*R**,3*S**)-1,3-Bis-(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzoxazole-4-carbonitrile 13a (Table 2, run 6).** This compound (340 mg) was prepared from diene **3a** (500 g, 1.8 mmol) and anethole **8** (496 mg, 3.6 mmol), mp 230–231.5 °C (from EtOH) (Found: C, 76.65; H, 5.6; N, 6.65. Calc. for $C_{27}H_{24}N_2O_3$: C, 76.4; H, 5.7; N, 6.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190 (CN); δ_H(400 MHz; $CDCl_3$) 0.66 (3 H, d, *J* 6.6, *Me*CH), 2.12 (1 H, m, NCHC*H*CHAr), 3.48 (1 H, d, *J* 10.3, NCHCHC*H*Ar, spin saturation at δ 4.50, NOE, 9%), 3.79 (3 H, s, OMe), 3.85 (3 H, s, OMe), 4.50 (1 H, d, *J* 10.0, NC*H*CHCHAr, spin saturation at δ 3.48, NOE, 6%), 5.56 (1 H, d, *J* 7.9, ArH), 6.74 (1 H, t, *J* 7.8, ArH), 6.85–7.0 (5 H, m, ArH) 7.14 (1 H, d, *J* 7.8, ArH) and 7.2–7.3 (4 H, m, ArH); *m/z* 424 (M^+, 25%), 275 (12) and 148 (100).

(1*R,2*R**,3*S**)-1-(4-Methoxyphenyl)-2-methyl-3-(*p*-tolyl)-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzoxazole-4-carbonitrile 13b (Table 2, run 7).** This compound (295 mg) was prepared from diene **3b** (300 g, 1.15 mmol) and anethole **8** (340 mg, 2.3 mmol), mp 221–223 °C (from MeOH) (Found: C, 79.25; H, 5.8; N, 6.8. Calc. for $C_{27}H_{24}N_2O_2$: C, 79.4; H, 5.9; N, 6.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190 (CN); δ_H(400 MHz; $CDCl_3$) 0.66 (3 H, d, *J* 6.6, *Me*CH), 2.14 (1 H, m, NCHC*H*CHAr), 2.32 (3 H, s, Me), 3.48 (1 H, d, *J* 10.3, NCHCHC*H*Ar), 3.84 (3 H, s, OMe), 4.49 (1 H, d, *J* 10.3, NC*H*CHCHAr), 5.55 (1 H, dd, *J* 0.7 and 7.8, ArH), 6.74 (1 H, dt, *J* 1.2 and 8.1, ArH), 6.89 (1 H, dt, *J* 1.2 and 8.1, ArH), 6.93 (2 H, d, *J* 8.8, ArH), 7.1–7.2 (5 H, m, ArH) and 7.24 (2 H, d, *J* 7.8, ArH); *m/z* 408 (M^+, 16%), 259 (11) and 148 (100).

(1*R,2*R**,3*S**)-1-(4-Methoxyphenyl)-2-methyl-3-phenyl-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzoxazole-4-carbonitrile 13c (Table 2, run 8).** This compound (1.09 g) was prepared from diene **3c** (984 mg, 4.0 mmol) and anethole **8** (1.19 g, 8.0 mmol), mp 234–236 °C (from hexane–CH_2Cl_2) (Found: C, 79.05; H, 5.5; N, 7.1. Calc. for $C_{26}H_{22}N_2O_2$: C, 79.15; H, 5.6; N, 7.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN); δ_H(400 MHz; $CDCl_3$) 0.67 (3 H, d, *J* 6.7, *Me*CH), 2.18 (1 H, m, NCHC*H*CHAr), 3.53 (1 H, d, *J* 10.1, NCHCHC*H*Ar), 3.85 (3 H, s, OMe), 4.51 (1 H, d, *J* 10.1, NC*H*CHCHAr), 5.56 (1 H, d, *J* 7.3, ArH), 6.75 (1 H, dt, *J* 1.2 and 7.9, ArH), 6.87–6.97 (3 H, m, ArH), 7.15 (1 H, d, *J* 7.9, ArH) and 7.23–7.37 (7 H, m, ArH); *m/z* 394 (M^+, 19%), 245 (7) and 148 (100).

(1*R,2*R**,3*S**)-3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-2-methyl-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzoxazole-4-carbonitrile 13d (Table 2, run 9).** This compound (442 mg) was prepared from diene **3d** (365 g, 1.3 mmol) and anethole **8** (385 mg, 2.6 mmol), mp 241–243 °C (from hexane–$CHCl_3$) (Found: C, 72.8; H, 4.75; N, 6.5. Calc. for $C_{26}H_{21}ClN_2O_2$: C, 72.8; H, 4.95; N, 6.55%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN); δ_H(400 MHz; $CDCl_3$) 0.68 (3 H, d, *J* 6.6, *Me*CH), 2.13 (1 H, m, NCHC*H*CHAr), 3.53 (1 H, d, *J* 10.0, NCHCHC*H*Ar), 3.85 (3 H, s, OMe), 4.52 (1 H, d, *J* 10.0, NC*H*CHCHAr), 5.58 (1 H, d, *J* 7.3, ArH), 6.76 (1 H, dt, *J* 1.0 and 7.8, ArH), 6.9–6.95 (3 H, m, ArH) and 7.15–7.35 (7 H, m, ArH); *m/z* 428 (M^+, 17%), 279 (5) and 148 (100).

(1*R,2*R**,3*S**)-1-(4-Methoxyphenyl)-2-methyl-3-(4-nitrophenyl)-2,3-dihydro-1*H*-pyrido[2,1-*b*]benzoxazole-4-carbonitrile 13e (Table 2, run 10).** This compound (220 mg) was prepared from diene **3e** (200 mg, 0.69 mmol) and anethole **8** (204 mg, 1.4 mmol), mp 251–254 °C (from AcOEt) (Found: C, 72.8; H, 4.7; N, 6.5. Calc. for $C_{26}H_{21}ClN_2O_2$: C, 72.8; H, 4.9; N, 6.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2200 (CN); δ_H(270 MHz; $CDCl_3$) 0.73 (3 H, d, *J* 6.6, *Me*CH), 2.22 (1 H, m, NCHC*H*CHAr), 3.71 (1 H, d, *J* 9.9, NCHCHC*H*Ar), 3.84 (3 H, s, OMe), 4.58 (1 H, d, *J* 9.6, NC*H*CHCHAr), 5.64 (1 H, d, *J* 7.9, ArH), 6.79 (1 H, dt, *J* 1.0 and 7.6, ArH), 6.9–7.0 (3 H, m, ArH), 7.15–7.3 (3 H, m, ArH), 7.48 (2 H, d, *J* 8.9, ArH) and 8.21 (2 H, d, *J* 8.9, ArH); *m/z* 439 (M^+, 7%), 290 (3), 244 (3) and 148 (100).

(4a*R,5*R**,12a*R**)-5-(4-Methoxyphenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzothiazole-6-carbonitrile *endo*-14a and its (5*S**)-isomer *exo*-14a (Table 3, run 1).** Compounds *endo*-**14a** (109 mg) and *exo*-**14a** (110 mg) were prepared from diene **2a** (500 mg, 1.7 mmol) and dihydropyran **9** (5 cm^3, 55 mmol). Compound *endo*-**14a**: mp 223–225 °C (from EtOH) (Found: C, 70.1, H, 5.25; N, 7.4. Calc. for $C_{22}H_{20}N_2O_2S$: C, 70.2; H, 5.35; N, 7.45%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2186 (CN); δ_H(270 MHz; $CDCl_3$) 1.02 (1 H, br s, CH_2), 1.24 (1 H, br s, CH_2), 1.80 (2 H, m, CH_2), 2.37 (1 H, m, NCHC*H*CHAr), 3.56 (2 H, m, OCH_2), 3.79 (3 H, s, OMe), 3.86 (1 H, d, *J* 5.6, NCHCHC*H*Ar), 5.54 (1 H, br d, *J* 4.6, NC*H*CHCHAr), 6.84 (2 H, d, *J* 8.9, ArH), 7.0–7.2 (1 H, m, ArH), 7.2–7.3 (4 H, m, ArH) and 7.34 (1 H, d, *J* 7.9, ArH); *m/z* 376 (M^+, 47%), 292 (100), 291 (98), 277 (6), 266 (21) and 248 (13). Compound *exo*-**14a**: mp 277 °C (from acetone) (Found: C, 70.2; H, 5.2; N, 7.45%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN); δ_H(400 MHz; $CDCl_3$) 1.45 (1 H, br d, *J* 13.7, CH_2), 1.71 (2 H, m, CH_2), 1.90 (1 H, m, CH_2), 2.09 (1 H, m, NCHC*H*CHAr), 3.76 (1 H, dt, *J* 2.7 and 11.7, OC*H*H), 3.80 (3 H, s, OMe), 3.88 (1 H, d, *J* 11.2, NCHCHC*H*Ar), 4.11 (1 H, br d, *J* 11.7, OCH*H*), 5.27 (1 H, d, *J* 2.7, NC*H*CHCHAr), 6.90 (2 H, d, *J* 8.8, ArH), 6.99 (1 H, d, *J* 8.1, ArH), 7.06 (1 H, dt, *J* 0.7 and 7.6, ArH), 7.17 (2 H, d, *J* 8.8, ArH), 7.23 (1 H, d, *J* 7.6, ArH) and 7.35 (1 H, d, *J* 7.6, ArH); *m/z* 376 (M^+, 52%), 292 (93), 291 (100), 277 (7), 266 (20) and 248 (10).

(4a*R,5*R**,12a*R**)-5-(*p*-Tolyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzothiazole-6-carbonitrile *endo*-14b and its (5*S**)-isomer *exo*-14b (Table 3, run 2).** Compounds *endo*-**14b** (130 mg) and *exo*-**14b** (189 mg) were prepared from diene **2b** (500 mg, 1.8 mmol) and dihydropyran **9** (5 cm^3, 55 mmol). Compound *endo*-**14b**: mp 228–231 °C (from acetone) (Found: C, 73.35; H, 5.5; N, 7.8. Calc. for $C_{22}H_{20}N_2OS$: C, 73.3; H, 5.6; N, 7.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2186; δ_H(400 MHz; $CDCl_3$) 1.07 (1 H, br s, CH_2), 1.29 (1 H, br s, CH_2), 1.65 (1 H, m, CH_2), 1.78 (1 H, m, CH_2), 2.28 (1 H, m, NCHC*H*CHAr), 2.33 (3 H, s, Me), 3.51 (1 H, ddd, *J* 3.7, 7.6 and 11.1, OC*H*H), 3.63 (1 H, ddd, *J* 3.9, 6.1 and 11.1, OCH*H*), 3.91 (1 H, d, *J* 5.1, NCHCHC*H*Ar), 5.57 (1 H, d, *J* 3.2, NC*H*CHCHAr) and 7.05–7.40 (8 H, m, ArH); *m/z* 360 (M^+, 38%), 275 (100) and 261 (7). Compound *exo*-**14b**: mp 267–271 °C (from AcOEt) (Found: C, 73.35; H, 5.45; N, 7.75%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2186 (CN); δ_H(400 MHz; $CDCl_3$) 1.44 (1 H, br d, *J* 13.9, CH_2), 1.70 (2 H, m, CH_2), 1.92 (1 H, m, CH_2), 2.11 (1 H, m, NCHC*H*CHAr), 2.34 (3 H, s, Me), 3.76 (1 H, dt, *J* 2.7 and 11.5, OC*H*H), 3.89 (1 H, d, *J* 11.2, NCHCHC*H*Ar), 4.11 (1 H, br d, *J* 11.5, OCH*H*), 5.27 (1 H, d, *J* 2.7, NC*H*CHCHAr) and 6.9–7.4 (8 H, m, ArH); *m/z* 360 (M^+, 42%), 275 (100), 261 (7) and 250 (11).

(4a*R,5*R**,12a*R**)-5-Phenyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzothiazole-6-carbonitrile *endo*-14c and its (5*S**)-isomer *exo*-14c (Table 3, run 3).**

Compounds *endo*-**14c** (145 mg) and *exo*-**14c** (115 mg) were prepared from diene **2c** (500 mg, 1.9 mmol) and dihydropyran **9** (5 cm^3, 55 mmol). Compound *endo*-**14c**: mp 265–267 °C (from acetone) (Found: C, 72.9; H, 5.1; N, 8.1. Calc. for $C_{21}H_{18}N_2OS$: C, 72.8; H, 5.25; N, 8.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2200 (CN); δ_H(400 MHz; $CDCl_3$) 1.01 (1 H, br s, CH_2), 1.28 (1 H, br s, CH_2), 1.71 (1 H, m, CH_2), 1.81 (1 H, m, CH_2), 2.32 (1 H, m, NCHC*H*CHAr), 3.53 (1 H, m, OC*H*H), 3.63 (1 H, ddd, *J* 3.7, 6.4 and 11.0, OCH*H*), 3.94 (1 H, d, *J* 5.5, NCHCHC*H*Ar), 5.57 (1 H, br d, *J* 2.7, NC*H*CHCHAr), 7.08 (1 H, m, ArH) and 7.15–7.40 (8 H, m, ArH); *m/z* 346 (M^+, 33%), 261 (100) and 235 (10). Compound *exo*-**14c**: mp 256–259 °C (from acetone) (Found: C, 72.6; H, 5.1; N, 8.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2180 (CN); δ_H(400 MHz; $CDCl_3$) 1.46 (1 H, br d, *J* 13.7, CH_2), 1.70 (2 H, m, CH_2), 1.91 (1 H, m, CH_2), 2.13 (1 H, m, NCHC*H*CHAr), 3.76 (1 H, dt, *J* 2.4 and 11.3, OC*H*H), 3.93 (1 H, d, *J* 11.0, NCHCHC*H*Ar), 4.10 (1 H, br d, *J* 11.3, OCH*H*), 5.28 (1 H, d, *J* 2.8, NC*H*CHCHAr), 7.01 (1 H, d, *J* 7.9, ArH), 7.07 (1 H, t, *J* 7.6, ArH) and 7.20–7.40 (7 H, m, ArH); *m/z* 346 (M^+, 36%), 261 (100) and 236 (10).

(4a*R,5*R**,12a*R**)-5-(4-Chlorophenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzothiazole-6-carbonitrile *endo*-14d and its (5*S**)-isomer *exo*-14d (Table 3, run 4).** Compounds *endo*-**14d** (121 mg) and *exo*-**14d** (140 mg) were prepared from diene **2d** (500 mg, 1.7 mmol) and dihydropyran **9** (5 cm^3, 55 mmol). Compound *endo*-**14d**: mp 222–225 °C (from CH_2Cl_2) (Found: C, 66.05; H, 4.3; N, 7.35. Calc. for $C_{21}H_{17}ClN_2OS$: C, 66.2; H, 4.5; N, 7.35%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2184; δ_H(270 MHz; $CDCl_3$) 0.96 (1 H, br s, CH_2), 1.28 (1 H, br s, CH_2), 1.6–1.9 (2 H, m, CH_2), 2.32 (1 H, m, NCHC*H*CHAr), 3.5–3.6 (2 H, m, OCH_2), 3.88 (1 H, d, *J* 5.6, NCHCHC*H*Ar), 5.52 (1 H, d, *J* 3.6, NC*H*CHCHAr), 7.05–7.3 (7 H, m, ArH) and 7.36 (1 H, d, *J* 7.9, ArH); *m/z* 382 (M^+, 21%), 380 (M^+, 51) and 295 (100). Compound *exo*-**14d**: mp > 300 °C (from THF) (Found: C, 66.1; H, 4.3; N, 7.35%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2188 (CN); δ_H(400 MHz; $CDCl_3$) 1.48 (1 H, br d, *J* 13.9, CH_2), 1.65–1.8 (2 H, m, CH_2), 1.85–2.0 (1 H, m, CH_2), 2.05–2.15 (1 H, m, NCHC*H*CHAr), 3.77 (1 H, dt, *J* 2.4 and 11.5, OC*H*H), 3.93 (1 H, d, *J* 11.0, NCHCHC*H*Ar), 4.13 (1 H, br d, *J* 11.5, OCH*H*), 5.28 (1 H, d, *J* 2.7, NC*H*CHCHAr), 7.00 (1 H, d, *J* 8.1, ArH), 7.08 (1 H, dt, *J* 1.0 and 7.8, ArH), 7.15–7.3 (4 H, m, ArH) and 7.3–7.4 (2 H, m, ArH); *m/z* 382 (M^+, 20%), 380 (M^+, 42) and 295 (100).

(4a*R,5*R**,12a*R**)-5-(4-Nitrophenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzothiazole-6-carbonitrile *endo*-14e and its (5*S**)-isomer *exo*-14e (Table 3, run 5).** Compounds *endo*-**14e** (180 mg) and *exo*-**14e** (115 mg) were prepared from diene **2e** (500 mg, 1.9 mmol) and dihydropyran **9** (5 cm^3, 55 mmol). Compound *endo*-**14e**: mp 259–262 °C (from AcOEt) (Found: C, 64.45; H, 4.2; N, 10.7. Calc. for $C_{21}H_{17}N_3O_3S$: C, 64.45; H, 4.4; N, 10.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2184; δ_H(400 MHz; $CDCl_3$) 0.85 (1 H, br s, CH_2), 1.27 (1 H, br s, CH_2), 1.79 (1 H, m, CH_2), 1.90 (1 H, m, CH_2), 2.43 (1 H, m, NCHC*H*CHAr), 3.56–3.7 (2 H, m, OCH_2), 4.02 (1 H, d, *J* 5.8, NCHCHC*H*Ar), 5.53 (1 H, d, *J* 2.8, NC*H*CHCHAr), 7.13 (1 H, dt, *J* 0.9 and 7.6, ArH), 7.20 (1 H, br d, *J* 7.9, ArH), 7.29 (1 H, td, *J* 0.9 and 7.6, ArH), 7.42 (1 H, d, *J* 7.6, ArH), 7.54 (2 H, d, *J* 8.9, ArH), 8.19 (2 H, d, *J* 8.9, ArH); *m/z* 391 (M^+, 100%), 306 (40), 260 (19) and 211 (6). Compound *exo*-**14e**: mp > 300 °C (from acetone) (Found: C, 64.5; H, 4.2; N, 10.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2186 (CN); δ_H(400 MHz; $CDCl_3$) 1.52 (1 H, br d, *J* 13.9, CH_2), 1.63 (1 H, br d, *J* 13.9, CH_2), 1.79 (1 H, tt, *J* 4.4 and 14.2, CH_2), 1.85–2.0 (1 H, m, CH_2), 2.15–2.2 (1 H, m, NCHC*H*CHAr), 3.80 (1 H, dt, *J* 2.4 and 11.5, OC*H*H), 4.11 (1 H, d, *J* 11.2, NCHCHC*H*Ar), 4.17 (1 H, br d, *J* 11.5, OCH*H*), 5.31 (1 H, d, *J* 2.4, NC*H*CHCHAr), 7.02 (1 H, d, *J* 8.1, ArH), 7.12 (1 H, dt, *J* 1.0 and 7.8, ArH), 7.28 (1 H, dt, *J* 1.0 and 7.8, ArH), 7.40 (1 H, d, *J* 8.1, ArH), 7.47 (2 H, d, *J* 8.8, ArH), 8.25 (2 H, d, *J* 8.8, ArH); *m/z* 391 (M^+, 78%), 306 (34), 260 (25), 211 (17) and 84 (100).

(4a*R,5*R**,12a*R**)-5-(4-Methoxyphenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzoxazole-6-carbonitrile *endo*-15a and its (5*S**)-isomer *exo*-15a (Table 3, run 6).** Compounds *endo*-**15a** (130 mg) and *exo*-**15a** (65 mg) were prepared from diene **3a** (500 mg, 1.8 mmol) and dihydropyran **9** (5 cm^3, 54 mmol). Compound *endo*-**15a**: mp 275–277 °C (from acetone) (Found: C, 73.25; H, 5.5; N, 7.75. Calc. for $C_{22}H_{20}N_2O_3$: C, 73.3; H, 5.6; N, 7.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192; δ_H(270 MHz; $CDCl_3$) 1.4–1.6 (4 H, m, CH_2), 2.17 (1 H, m, NCHC*H*CHAr), 3.45 (1 H, m, OC*H*H), 3.75 (1 H, br d, *J* 12.9, OCH*H*), 3.81 (3 H, s, OMe), 4.16 (1 H, d, *J* 4.6, NCHCHC*H*Ar), 5.72 (1 H, d, *J* 3.6, NC*H*CHCHAr), 6.9 (2 H, br d, *J* 6.9, ArH), 7.06 (1 H, dt, *J* 1.3 and 8.9, ArH), 7.13 (1 H, dt, *J* 1.3 and 7.6, ArH) and 7.2–7.3 (4 H, m, ArH); *m/z* 360 (M^+, 30%), 275 (100), 250 (7) and 232 (5). Compound *exo*-**15a**: mp 215–217 °C (from EtOH) (Found: C, 73.15; H, 5.5; N, 7.75%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN); δ_H(270 MHz; C_6D_6) 1.0–1.3 (4 H, m, CH_2), 1.53 (1 H, m, NCHC*H*CHAr), 3.1–3.35 (2 H, m, OCH_2), 3.37 (3 H, s, OMe), 3.53 (1 H, d, *J* 6.9, NCHCHC*H*Ar), 4.80 (1 H, br d, *J* 3.3, NC*H*CHCHAr), 6.6–6.8 (4 H, m, ArH), 6.97 (2 H, br d, *J* 8.6, ArH) and 7.45 (2 H, br s, ArH); *m/z* 360 (M^+, 34%), 275 (100), 250 (7) and 232 (6).

(4a*R,5*R**,12a*R**)-5-(*p*-Tolyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzoxazole-6-carbonitrile *endo*-15b and its (5*S**)-isomer *exo*-15b (Table 3, run 7).** Compounds *endo*-**15b** (239 mg) and *exo*-**15b** (42 mg) were prepared from diene **3b** (430 mg, 1.65 mmol) and dihydropyran **9** (5 cm^3, 54 mmol). Compound *endo*-**15b**: mp 202–204 °C (from AcOEt) (Found: C, 76.7; H, 5.7; N, 8.15. Calc. for $C_{22}H_{20}N_2O_2$: C, 76.7; H, 5.85; N, 8.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2190; δ_H(270 MHz; $CDCl_3$) 1.3–1.7 (4 H, m, CH_2), 2.19 (1 H, m, NCHC*H*CHAr), 2.35 (3 H, s, Me), 3.3–3.5 (1 H, m, OC*H*H), 3.77 (1 H, br d, *J* 12.5, OCH*H*), 4.18 (1 H, d, *J* 4.6, NCHCHC*H*Ar), 5.73 (1 H, d, *J* 3.6, NC*H*CHCHAr) and 7.0–7.3 (8 H, m, ArH); *m/z* 344 (M^+, 34%), 259 (100), 234 (4) and 195 (3). Compound *exo*-**15b**: mp 212–213 °C (from AcOEt) (Found: C, 76.6; H, 5.7; N, 8.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN); δ_H(270 MHz; C_6D_6) 0.9–1.1 (4 H, m, CH_2), 1.5–1.6 (1 H, m, NCHC*H*CHAr), 2.13 (3 H, s, Me), 3.1–3.2 (2 H, m, OCH_2), 3.49 (1 H, d, *J* 6.6, NCHCHC*H*Ar), 4.73 (1 H, br d, *J* 3.3, NC*H*CHCHAr) and 6.6–7.6 (8 H, m, ArH); *m/z* 344 (M^+, 32%), 259 (100), 234 (4) and 195 (2).

(4a*R,5*R**,12a*R**)-5-phenyl-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3′,2′:5,6]pyrido[2,1-*b*]benzoxazole-6-carbonitrile *endo*-15c and its (5*S**)-isomer *exo*-15c (Table 3, run 8).** Compounds *endo*-**15c** (160 mg) and *exo*-**15c** (120 mg) were prepared from diene **3c** (370 mg, 1.5 mmol) and dihydropyran **9** (5 cm^3, 54 mmol). Compound *endo*-**15c**: mp 256–257 °C (from AcOEt) (Found: C, 76.2; H, 5.3; N, 8.5. Calc. for $C_{21}H_{18}N_2O_2$: C, 76.35; H, 5.5; N, 8.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN); δ_H(270 MHz; $CDCl_3$) 1.3–1.7 (4 H, m, CH_2), 2.2–2.3 (1 H, m, NCHC*H*CHAr), 3.4–3.5 (1 H, m, OC*H*H), 3.7–3.8 (1 H, m, OCH*H*), 4.21 (1 H, d, *J* 4.6, NCHCHC*H*Ar), 5.73 (1 H, d, *J* 3.6, NC*H*CHCHAr) and 7.0–7.7 (9 H, m, ArH); *m/z* 330 (M^+, 33%), 245 (100) and 220 (4). Compound *exo*-**15c**: mp 194–195 °C (from Et_2O) (Found: C, 76.1; H, 5.3; N, 8.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN); δ_H(270 MHz; $CDCl_3$) 0.9–1.3 (4 H, m, CH_2), 1.52 (1 H, m, NCHC*H*CHAr), 3.15 (2 H, br s, OCH_2), 3.49 (1 H, d, *J* 6.6, NCHCHC*H*Ar), 4.72 (1 H, d, *J* 3.3, NC*H*CHCHAr), 6.6–6.8 (3 H, m, ArH) and 7.0–7.2 (6 H, m, ArH); δ_H(270 MHz; C_6D_6) 0.4–0.8 (4 H, m, CH_2), 1.10 (1 H, m, NCHC*H*CHAr), 2.66 (2 H, br t, *J* 4.8, OCH_2), 3.01 (1 H, d, *J* 6.6, NCHCHC*H*Ar), 4.24 (1 H, d, *J* 3.3, NC*H*CHCHAr), 6.1–6.3 (4 H, m, ArH) and 6.5–6.8 (5 H, m, ArH); *m/z* 330 (M^+, 38%), 245 (100) and 220 (5).

(4a*R,5*R**,12a*R**)-5-(4-Chlorophenyl)-3,4,4a,12a-tetrahydro-2*H*,5*H*-pyrano[3',2':5,6]pyrido[2,1-*b*]benzoxazole-6-carbonitrile *endo*-15d and its (5*S**)-isomer *exo*-15d (Table 3, run 9).** Compounds *endo*-**15d** (130 mg) and *exo*-**15d** (31 mg) were prepared from diene **3d** (400 mg, 1.4 mmol) and dihydropyran **9** (5 cm^3, 54 mmol). Compound *endo*-**15d**: mp 272–273 °C (from acetone) (Found: C, 69.1; H, 4.5; N, 7.75. Calc. for $C_{21}H_{17}ClN_2O_2$: C, 69.15; H, 4.7; N, 7.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN); δ_H(270 MHz; $CDCl_3$) 1.25–1.65 (4 H, m, CH_2), 2.1–2.25 (1 H, m, NCHC*H*CHAr), 3.4–3.5 (1 H, m, OC*H*H), 3.7–3.8 (1 H, m, OCH*H*), 4.19 (1 H, d, *J* 5.9, NCHCHC*H*Ar), 5.73 (1 H, d, *J* 3.6, NC*H*CHCHAr) and 7.0–7.4 (8 H, m, ArH); *m/z* 366 (M^+, 14%), 364 (M^+, 40), 279 (100) and 254 (6). Compound *exo*-**15d**: mp 242–244 °C (from acetone) (Found: C, 68.9; H, 4.55; N, 7.6%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN); δ_H(270 MHz; C_6D_6) 1.0–1.2 (4 H, m, CH_2), 1.4–1.5 (1 H, m, NCHC*H*CHAr), 3.1–3.2 (2 H, m, OCH_2), 3.37 (1 H, d, *J* 6.9, NCHCHC*H*Ar), 4.67 (1 H, d, *J* 3.3, NC*H*CHCHAr), 6.6–6.8 (6 H, m, ArH), 7.05–7.15 (2 H, m, ArH); *m/z* 366 (M^+, 19%), 364 (M^+, 51), 279 (100) and 254 (6).

(4a*R,5*R**,12a*R**)-5-(4-Nitrophenyl)-3,4,4a,12-tetrahydro-2*H*,5*H*-pyrano[3',2':5,6]pyrido[2,1-b]benzoxazole-6-carbonitrile *endo*-15e and its (5*S**)-isomer *exo*-15e (Table 3, run 10).** Compounds *endo*-**15e** (65 mg) and *exo*-**15e** (129 mg) were prepared from diene **3e** (500 mg, 1.7 mmol) and dihydropyran **9** (5 cm^3, 54 mmol). Compound *endo*-**15e**: mp 295–297 °C (from EtOH–acetone) (Found: C, 67.2; H, 4.4; N, 11.0. Calc. for $C_{21}H_{17}N_3O_4$: C, 67.2; H, 4.55; N, 11.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2192 (CN); δ_H(270 MHz; $CDCl_3$) 1.2–1.6 (4 H, m, CH_2), 2.1–2.25 (1 H, m, NCHC*H*CHAr), 3.45–3.55 (1 H, m, OC*H*H), 3.75–3.85 (1 H, m, OCH*H*), 4.34 (1 H, d, *J* 4.9, NCHCHC*H*Ar), 5.75 (1 H, d, *J* 3.6, NC*H*CHCHAr), 7.05–7.2 (4 H, m, ArH), 7.52 (2 H, br d, *J* 9.2, ArH) and 8.24 (2 H, br d, *J* 9.2, ArH); *m/z* 375 (M^+, 45%), 290 (17), 244 (14), 216 (5) and 84 (100). Compound *exo*-**15e**: mp 277–280 °C (from acetone) (Found: C, 67.2; H, 4.4; N, 11.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2194 (CN); δ_H (270 MHz; C_6D_6) 0.9–1.2 (4 H, m, CH_2), 1.3–1.45 (1 H, m, NCHC*H*CHAr), 3.1–3.3 (2 H, m, OCH_2), 3.36 (1 H, d, *J* 6.6, NCHCHC*H*Ar), 3.61 (1 H, d, *J* 3.3, NC*H*CHCHAr), 6.6–6.8 (6 H, m, ArH) and 7.80 (2 H, br d, *J* 8.6, ArH); *m/z* 375 (M^+, 43%), 290 (15), 244 (11), 216 (4) and 84 (100).

(*E*)-2-(Benzothiazol-2-yl)-3-(2-hydroxyphenyl)acrylonitrile 16. This compound (9.13 g) was prepared from the nitrile **4** (5.95 g, 34 mmol), salicylaldehyde (4.89 g, 40 mmol), triethylamine (9 drops), and EtOH (30 cm^3) by the same manner as for the preparation of compound **2e**, mp 192–195 °C (from $CHCl_3$) (Found: C, 69.05; H, 3.5; N, 10.05. Calc. for $C_{16}H_{10}N_2OS$: C, 69.05; H, 3.6; N, 10.05%); ν_{max}(Nujol)/cm^{-1} 1670 (C=C); δ_H[270 MHz; $(CD_3)_2SO$] 7.2–8.2 (8 H, m, ArH), 8.73 (1 H, br s, =CH) and 9.11 (1 H, br, OH); *m/z* 278 (M^+, 49%), 261 (100), 252 (5) and 223 (5).

(*E*)-2-(Benzoxazol-2-yl)-3-(2-hydroxyphenyl)acrylonitrile 17. This compound (490 mg) was prepared from nitrile **5** (322 mg, 2.0 mmol), salicylaldehyde (249 mg, 2.0 mmol), triethylamine (one drop), and EtOH (10 cm^3) in the same manner as for the preparation of compound **2e**, mp 193–194 °C (from $CHCl_3$) (Found: C, 73.3; H, 3.7; N, 10.7. Calc. for $C_{16}H_{10}N_2O_2$: C, 73.3; H, 3.85; N, 10.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2222 (CN) and 1658 (C=C); δ_H(270 MHz; $CDCl_3$) 7.1–7.8 (8 H, m, ArH), 8.80 (1 H, br s, =CH) and 9.6–10.7 (1 H, br, OH); *m/z* 262 (M^+, 51%), 245 (100) and 236 (3).

(*E*)-3-(2-Allyloxyphenyl)-2-(benzothiazol-2-yl)acrylonitrile 18a. A mixture of the phenol **16** (2.09 g, 7.5 mmol), allyl bromide (1.31 g, 11 mmol), and K_2CO_3 (1.04 g, 7.5 mmol) in dry acetone (30 cm^3) was heated at reflux for 8 h. After cooling, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was diluted with AcOEt, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The crystalline residue was recrystallized from acetone to give title compound **18a** (1.47 g, 62%), mp 96–99 °C (Found: C, 71.6; H, 4.2; N, 8.75. Calc. for $C_{19}H_{14}N_2OS$: C, 71.7; H, 4.4; N, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2226 (CN); δ_H(270 MHz; $CDCl_3$) 4.62 (2 H, br s, OCH_2), 5.34 (1 H, dd, *J* 1.3 and 10.6, CH=C*H*H), 5.45 (1 H, dd, *J* 1.3 and 17.2, CH=CH*H*), 6.06 (1 H, m, C*H*=CH_2), 6.91 (1 H, d, *J* 8.2, ArH), 7.04 (1 H, t, *J* 7.6, ArH), 7.35–7.75 (3 H, m, ArH), 7.84 (1 H, d, *J* 7.9, ArH), 8.06 (1 H, d, *J* 8.3, ArH), 8.30 (1 H, d, *J* 7.9, ArH) and 8.60 [1 H, s, C(CN)=CH]; *m/z* 318 (M^+, 13%), 277 (11), 261 (100) and 248 (14).

(*E*)-2-(Benzothiazol-2-yl)-3-{2-[(*E*)-but-2-enyloxy]phenyl}-acrylonitrile 18c. This compound (392 mg, 59%) was prepared from the phenol **16** (556 mg, 2.0 mmol), (*E*)-but-2-enyl bromide (405 mg, 3.0 mmol), K_2CO_3 (278 mg, 2.0 mmol) and acetone (8 cm^3) in the same manner as for the preparation of compound **18a**, mp 102–104 °C (from Et_2O) (Found: C, 72.2; H, 4.7; N, 8.4. Calc. for $C_{20}H_{16}N_2OS$: C, 72.25; H, 4.85; N, 8.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2224 (CN); δ_H(270 MHz; $CDCl_3$) 1.78 (3 H, dd, *J* 1.0 and 6.3, Me), 4.59 (2 H, d, *J* 5.6, OCH_2), 5.65–6.0 (2 H, m, C*H*=C*H*Me), 6.96 (1 H, d, *J* 8.6, ArH), 7.07 (1 H, t, *J* 7.6, ArH), 7.4–7.55 (3 H, m, ArH), 7.88 (1 H, d, *J* 7.3, ArH), 8.09 (1 H, d, *J* 8.3, ArH), 8.31 (1 H, dd, *J* 1.3 and 7.9, ArH) and 8.63 [1 H, s, C(CN)=CH]; *m/z* 332 (M^+, 16%), 315 (11), 277 (19), 261 (100), 248 (14) and 197 (15).

(*E*)-2-(Benzothiazol-2-yl)-3-{2-[(*E*)-cinnamoyloxy]phenyl}-acrylonitrile 18d. This compound (331 mg, 46%) was prepared from compound **16** (556 mg, 2.0 mmol), cinnamyl bromide (591 mg, 3.0 mmol), K_2CO_3 (278 mg, 2.0 mmol) and acetone (8 cm^3) in the same manner as for the preparation of compound **18a**, mp 118–121 °C (from Et_2O) (Found: C, 76.0; H, 4.55; N, 7.0. Calc. for $C_{25}H_{18}N_2OS$: C, 76.1; H, 4.6; N, 7.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2224 (CN); δ_H(270 MHz; $CDCl_3$) 4.52 (2 H, dd, *J* 1.3 and 5.6, OCH_2), 6.45 (1 H, td, *J* 5.6 and 15.8, PhCH=C*H*), 6.80 (1 H, td, *J* 1.3 and 15.8, PhC*H*=CH), 7.0–7.5 (11 H, m, ArH), 7.95 (1 H, d, *J* 7.6, ArH), 8.08 (1 H, d, *J* 7.9, ArH), 8.60 [1 H, s, C(CN)=CH]; *m/z* 394 (M^+, 100%), 377 (15), 301 (23), 290 (43) and 259 (39).

(*E*)-3-(2-Allyloxyphenyl)-2-(benzoxazol-2-yl)acrylonitrile 19a. This compound (306 mg, 60%) was prepared from the phenol **17** (446 mg, 1.7 mmol), allyl bromide (315 mg, 2.6 mmol), K_2CO_3 (253 mg, 1.7 mmol) and acetone (8 cm^3) in the same manner as for the preparation of compound **18a**, mp 103–104 °C (from acetone) (Found: C, 75.6; H, 4.8; N, 9.4. Calc. for $C_{19}H_{14}N_2O_2$: C, 75.5; H, 4.7; N, 9.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2230 (CN); δ_H(270 MHz; $CDCl_3$) 4.70 (2 H, td, *J* 1.5 and 5.3, OCH_2), 5.36 (1 H, qd, *J* 1.5 and 10.6, CH=C*H*H), 5.46 (1 H, qd, *J* 1.5 and 17.2, CH=CH*H*), 6.11 (1 H, tdd, *J* 5.6, 10.6 and 17.2, C*H*=CH_2), 6.97 (1 H, d, *J* 8.3, ArH), 7.09 (1 H, t, *J* 7.6, ArH), 7.4–7.8 (5 H, m, ArH), 8.36 (1 H, dd, *J* 1.3 and 7.9, ArH) and 8.81 [1 H, s, C(CN)=CH]; *m/z* 302 (M^+, 10%), 285 (10), 261 (10), 245 (100) and 233 (11).

(*E*)-2-(Benzoxazol-2-yl)-3-{2-[(*E*)-but-2-enyloxy]phenyl}-acrylonitrile 19c. This compound (1.59 g, 46%) was prepared from the phenol **17** (2.88 g, 11 mmol), (*E*)-but-2-enyl bromide (2.22 g, 16.5 mmol), K_2CO_3 (1.52 g, 11 mmol) and acetone (30 cm^3) in the same manner as for the preparation of compound **18a**, mp 127–128 °C (from acetone) (Found: C, 75.6; H, 5.2; N, 8.75. Calc. for $C_{20}H_{16}N_2O_2$: C, 75.9; H, 5.1; N, 8.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2230 (CN); δ_H(270 MHz; $CDCl_3$) 1.78 (3 H, d, *J* 6.3, Me), 4.62 (2 H, d, *J* 4.6, OCH_2), 5.65–6.0 (2 H, m, C*H*=C*H*Me), 6.98 (1 H, d, *J* 8.3, ArH), 7.07 (1 H, t, *J* 7.6, ArH), 7.35–7.85 (5 H, m, ArH), 8.36 (1 H, d, *J* 7.6, ArH) and 8.79 [1 H, s, C(CN)=CH]; *m/z* 316 (M^+, 25%), 299 (25), 261 (26) and 245 (100).

(*E*)-2-(Benzoxazol-2-yl)-3-{2-[(*E*)-cinnamyloxy]phenyl}acrylonitrile 19d. A crude mixture was obtained from the phenol **17** (2.88 g, 11 mmol), cinnamyl bromide (4.33 g, 22 mmol), K_2CO_3

(1.52 g, 11 mmol) and acetone (30 cm^3) in the same manner as for the preparation of compound **18a**. The mixture was subjected to column chromatography on silica gel with hexane–AcOEt (5:2) to give title compound **19d** (1.45 g, 35%) and the pentacycle **21d** (873 mg, 21%). Compound **19d**: mp 146–148 °C (from acetone) (Found: C, 79.3; H, 4.9; N, 7.4. Calc. for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.8; N, 7.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2241 (CN); δ_H(270 MHz; $CDCl_3$) 4.86 (2 H, dd, *J* 1.7 and 5.6, OCH_2), 6.48 (1 H, td, *J* 5.6 and 15.8, PhCH=C*H*), 6.77 (1 H, td, *J* 1.7 and 15.8, PhC*H*=CH), 7.04 (1 H, d, *J* 8.6, ArH), 7.10 (1 H, t, *J* 7.6, ArH), 7.2–7.6 (9 H, m, ArH), 7.75–7.85 (1 H, m, ArH), 8.38 (1 H, dd, *J* 1.7 and 7.9, ArH) and 8.85 [1 H, s, C(CN)=CH]; *m/z* 378 (M^+, 33%), 361 (3), 261 (9), 245 (8) and 117 (100). Physical and spectral data of compound **21d** are given below.

(*E*)-2-(Benzothiazol-2-yl)-3-[2-(prop-2-ynyloxy)phenyl]acrylonitrile 18b. This compound (441 mg, 66%) was prepared from nitrile **4** (336 mg, 2.1 mmol), 2-(prop-2-ynyloxy)benzaldehyde (367 mg, 2.1 mmol), triethylamine (one drop) and EtOH (10 cm^3) in the same manner as for the preparation of compound **2e**, mp 103–104 °C (from EtOH) (Found: C, 72.2; H, 4.0; N, 8.95. Calc. for $C_{19}H_{12}N_2OS$: C, 72.1; H, 3.8; N, 8.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2226 (CN); δ_H(270 MHz; $CDCl_3$) 2.58 (1 H, t, *J* 2.6, CCH), 4.84 (2 H, d, *J* 2.6, OCH_2), 7.12 (1 H, d, *J* 8.3, ArH), 7.13 (1 H, t, *J* 7.9, ArH), 7.35–7.55 (3 H, m, ArH), 7.88 (1 H, br d, *J* 7.9, ArH), 8.09 (1 H, d, *J* 8.3, ArH), 8.34 (1 H, d, *J* 7.9, ArH) and 8.60 [1 H, s, C(CN)=CH]; *m/z* 316 (M^+, 6%), 277 (9), 261 (100), 248 (14) and 223 (4).

(*E*)-2-(Benzoxazol-2-yl)-3-[2-(prop-2-ynyloxy)phenyl]acrylonitrile 19b. This compound (1.04 g, 68%) was prepared from nitrile **5** (800 mg, 5.1 mmol), 2-(prop-2-ynyloxy)benzaldehyde (810 mg, 5.1 mmol), triethylamine (one drop) and EtOH (30 cm^3) in the same manner as for the preparation of compound **2e**, mp 170–172 °C (from EtOH) (Found: C, 75.95; H, 4.2; N, 9.4. Calc. for $C_{19}H_{12}N_2O_2$: C, 76.0; H, 4.0; N, 9.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2230 (CN); δ_H(270 MHz; $CDCl_3$) 2.58 (1 H, t, *J* 2.3, CCH), 4.87 (2 H, d, *J* 2.3, OCH_2), 7.1–7.2 (2 H, m, ArH), 7.35–7.65 (4 H, m, ArH), 7.75–7.85 (1 H, m, ArH), 8.38 (1 H, dd, *J* 1.2 and 8.1, ArH) and 8.76 [1 H, s, C(CN)=CH]; *m/z* 300 (M^+, 9%), 261 (7), 245 (100), 233 (6) and 207 (3).

General procedure for the intramolecular Diels–Alder reaction of ethers 18, 19 (Table 4)

A 0.1–0.2 mol dm^{-3} solution of a substrate (**18** or **19**) in *o*-dichlorobenzene was heated at reflux. After cooling, the solution was concentrated under reduced pressure to give a crude product (**20** or **21**), which was purified by column chromatography on silica gel. The reaction time and the yield are shown in Table 4.

(6a*R,14a*R**)-6a,14a-Dihydro-6*H*,7*H*-[1]benzopyrano[4′,3′:4,5]pyrido[2,1-*b*]benzothiazole-14-carbonitrile 20a and 8-allyl-3-(benzothiazol-2-yl)coumarin 22 (Table 4, run 1).** A crude mixture was obtained from compound **18a** (600 mg, 1.9 mmol) in *o*-dichlorobenzene (20 cm^3). The mixture was subjected to column chromatography on silica gel with hexane–AcOEt (5: 2) to give title products **20a** (188 mg, 19%) and **22** (64 mg, 10%). Compound **20a**: mp 224–226 °C (from $CHCl_3$–AcOEt) (Found: C, 71.8; H, 4.5; N, 8.95. Calc. for $C_{19}H_{14}N_2OS$: C, 71.7; H, 4.4; N, 8.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2178 (CN); δ_H(270 MHz; C_6D_6) 0.9–1.15 (1 H, m, spin saturation at δ 3.06, NOE, 10%, NCHC*H*CHAr), 2.41 (1 H, dd, *J* 5.0 and 12.5, NC*H*HCHCHAr), 2.47 (1 H, dd, *J* 9.2 and 12.5, NCH*H*CHCHAr), 3.06 (1 H, d, *J* 5.0, spin saturation at δ 1.03, NOE, 13%, $NCH_2CHCHAr$), 3.20 (1 H, dd, *J* 3.6 and 11.2, OC*H*H), 3.25 (1 H, dd, *J* 2.6 and 11.2, OCH*H*), 5.61 (1 H, d, *J* 8.3, ArH), 6.25–6.35 (1 H, m, ArH), 6.4–6.7 (6 H, m, ArH) and 7.64 (1 H, d, *J* 7.6, spin saturation at δ 3.06, NOE, 3%, ArH); *m/z* 318 (M^+, 100%) 301 (5), 287 (7), 278 (13) and 174 (52).

Compound **22**: mp 182–184 °C (from EtOH–$CHCl_3$) (Found: M^+, 319.0666. $C_{19}H_{13}NO_2S$ requires M, 319.0667); $\nu_{max}(CHCl_3)/cm^{-1}$ 1728 and 1713 (CO); δ_H(270 MHz; $CDCl_3$) 3.74 (2 H, d, *J* 6.6, $CH_2CH=CH_2$), 5.05–5.25 (2 H, m, $CH_2CH=CH_2$), 5.95–6.15 (1 H, m, $CH_2CH=CH_2$), 7.3–7.6 (5 H, m, ArH), 7.99 (1 H, d, *J* 7.9, ArH), 8.10 (1 H, d, *J* 7.9, ArH), 9.08 (1 H, s, CH=C–C=O); *m/z* 319 (M^+, 100%) 303 (12), 290 (20), 262 (8) and 236 (4).

(6a*R,7*S**,14a*S**)-7-Methyl-6a,14a-dihydro-6*H*,7*H*-[1]benzopyrano[4′,3′:4,5]pyrido[2,1-*b*]benzothiazole-14-carbonitrile 20c (Table 4, run 3).** This compound (310 mg) was prepared from compound **18c** (500 mg, 1.5 mmol) in *o*-dichlorobenzene (8 cm^3), mp 258–259 °C (from $CHCl_3$–AcOEt) (Found: C, 72.1; H, 4.9; N, 8.5. Calc. for $C_{20}H_{16}N_2OS$: C, 72.25; H, 4.85; N, 8.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2172 (CN); δ_H(270 MHz; $CDCl_3$) 1.54 (3 H, d, *J* 5.9, *Me*CH), 2.24 (1 H, dq, *J* 3.2 and 11.2, NCHC*H*CHAr), 3.60 (1 H, d, *J* 11.2, NCHCHC*H*Ar), 3.92 (1 H, t, *J* 11.2, OC*H*H), 3.99 (1 H, qd, *J* 5.9 and 11.2, NC*H*CHCHAr), 4.43 (1 H, dd, *J* 3.2 and 11.2, OCH*H*), 6.87–7.28 (6 H, m, ArH), 7.44 (1 H, d, *J* 7.9, ArH) and 7.78 (1 H, d, *J* 7.8, ArH); *m/z* 332 (M^+, 100%), 317 (20), 287 (18) and 261 (21).

(6a*R,7*R**,14a*S**)-7-Phenyl-6a,14a-dihydro-6*H*,7*H*-[1]benzopyrano[4′,3′:4,5]pyrido[2,1-*b*]benzothiazole-14-carbonitrile 20d (Table 4, run 4).** This compound (99 mg) was prepared from compound **18d** (110 mg, 0.28 mmol) in *o*-dichlorobenzene (2 cm^3), mp 227–228 °C (from AcOEt) (Found: C, 76.15; H, 4.7; N, 7.2. Calc. for $C_{25}H_{18}N_2OS$: C, 76.1; H, 4.6; N, 7.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2181 (CN); δ_H(270 MHz; $CDCl_3$) 2.55 (1 H, dq, *J* 3.3 and 10.9, NCHC*H*CHAr), 3.89 (1 H, d, *J* 10.9, NCHCHC*H*Ar), 3.92 (1 H, t, *J* 10.9, OC*H*H), 4.43 (1 H, dd, *J* 3.3 and 10.9, OCH*H*), 4.80 (1 H, d, *J* 10.9, NC*H*CHCHAr), 6.24 (1 H, d, *J* 7.6, ArH), 6.80–7.37 (11 H, m, ArH) and 7.89 (1 H, d, *J* 7.9, ArH); *m/z* 394 (M^+, 65%), 301 (4) and 117 (100).

(6a*R,14a*R**)-6a,14a-Dihydro-6*H*,7*H*-[1]benzopyrano[4′,3′:4,5]pyrido[2,1-*b*]benzoxazole-14-carbonitrile 21a and 8-allyl-3-(benzoxazol-2-yl)coumarin 23 (Table 4, run 5).** A crude mixture was obtained from compound **19a** (500 mg, 1.7 mmol) in *o*-dichlorobenzene (15 cm^3). The mixture was subjected to column chromatography on silica gel with hexane–AcOEt (5:2) as eluent to give title compounds **21a** (98 mg, 21%) and **23** (63 mg, 11%). Compound **21a**: mp 252–253 °C (from $CHCl_3$–AcOEt) (Found: C, 75.3; H, 4.7; N, 9.3. Calc. for $C_{19}H_{14}N_2O_2$: C, 75.5; H, 4.5; N, 9.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2177 (CN); δ_H(270 MHz; $CHCl_3$) 2.5–2.6 (1 H, m, NCHC*H*CHAr), 3.86 (1 H, dd, *J* 9.9 and 12.5, NC*H*HCHCHAr), 4.02 (1 H, dd, *J* 5.3 and 12.5, NCH*H*CHCHAr), 4.10 (1 H, d, *J* 4.6, NCH_2-CHC*H*Ar), 4.30 (1 H, dd, *J* 3.9 and 11.8, OC*H*H), 4.40 (1 H, dd, *J* 2.6 and 11.8, OCH*H*), 6.75–7.2 (7 H, m, ArH), 6.4–6.7 (6 H, m, ArH) and 7.67 (1 H, d, *J* 7.9, ArH); *m/z* 304 (M^+, 5%), 277 (11), 201 (18), 185 (90) and 93 (100).

Compound **23**: mp 143–145 °C (from EtOH–$CHCl_3$) (Found: M^+, 303.0891. $C_{19}H_{13}NO_3$ requires M, 303.0894); ν_{max}(KBr)/cm^{-1} 1752 and 1733 (CO); δ_H(270 MHz; $CDCl_3$) 3.70 (2 H, d, *J* 6.6, $CH_2CH=CH_2$), 5.16 (1 H, dd, *J* 1.7 and 9.2, $CH_2CH=CHH$), 5.21 (1 H, *J* 1.7 and 13.3, $CH_2CH=CHH$), 6.02 (1 H, m, $CH_2CH=CH_2$), 6.9–7.9 (7 H, m, ArH) and 8.87 (1 H, s, CH=C–C=O); *m/z* 303 (M^+, 100%), 274 (23), 258 (6), 246 (6) and 220 (4).

(6a*R,7*S**,14a*R**)-7-Methyl-6a,14a-dihydro-6*H*,7*H*-[1]benzopyrano[4′,3′:4,5]pyrido[2,1-*b*]benzoxazole-14-carbonitrile 21c (Table 4, run 7).** This compound (220 mg) was prepared from compound **19c** (308 mg, 0.97 mmol) in *o*-dichlorobenzene (5 cm^3), mp 234–235 °C (from $CHCl_3$–EtOH) (Found: C, 75.6; H, 5.2; N, 8.9. Calc. for $C_{20}H_{16}N_2O_2$: C, 75.9; H, 5.1; N, 8.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2178 (CN); δ_H(270 MHz; $CDCl_3$) 1.70 (3 H, d, *J* 5.9, Me), 2.22 (1 H, dq, *J* 3.3 and 10.6, NCHC*H*CHAr), 3.78 (1 H, d, *J* 10.9, NCHCHC*H*Ar), 3.92 (1 H, t, *J* 10.9, OC*H*H), 3.97 (1 H, m, NC*H*CHCHAr), 4.43 (1 H, dd, *J* 3.3 and 10.9, OCH*H*), 6.88 (1 H, d, *J* 8.3, ArH), 6.94–7.29

(6 H, m, ArH) and 7.91 (1 H, d, *J* 7.9, ArH); *m/z* 316 (M^+, 100%), 299 (21), 271 (26) and 245 (20).

(6a*R,7*R**,14a*S**)-7-Phenyl-6a,14a-dihydro-6*H*,7*H*-[1]benzopyrano[4',3':4,5]pyrido[2,1-*b*]benzoxazole-14-carbonitrile 21d (Table 4, run 8).** This compound (245 mg) was prepared from compound **19d** (260 mg, 0.69 mmol) in *o*-dichlorobenzene (5 cm^3), mp 240–241 °C (from acetone) (Found: C, 79.3; H, 4.95; N, 7.55. Calc. for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.8; N, 7.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2189 (CN); δ_H(270 MHz; $CDCl_3$) 2.60 (1 H, m, NCHC*H*CHAr), 3.91 (2 H, m, OCH_2), 4.07 (1 H, d, *J* 10.9, NCHCHC*H*Ar, spin saturation at δ 4.74, NOE, 15%), 4.74 (1 H, d, *J* 11.6, NC*H*CHCHAr), 5.66 (1 H, d, *J* 7.9, ArH), 6.77–7.58 (11 H, m, ArH) and 8.04 (1 H, d, *J* 7.9, ArH); *m/z* 378 (M^+, 81%), 361 (8), 261 (10) and 117 (100).

X-Ray structure analysis of compound 12e

Crystal data. $C_{26}H_{21}N_3O_3S$, M = 455.54, *T* = 291 K. Monoclinic, *a* = 26.961(2), *b* = 9.685(1), *c* = 9.610(1) Å, β = 116.34(1)°, *V* = 2248.7(4) $Å^3$ (by least-squares refinement on diffractometer angles for 23 automatically centred reflections, λ = 1.5418 Å), space group $P2_1/a$, *Z* = 4, D_x = 1.345 g cm^{-3}. Yellow prisms. Crystal dimensions: 0.35 × 0.35 × 0.35 mm^3, μ(Cu-Kα) = 1.527 mm^{-1}.

Data collection and processing. Rigaku AFC5 four-circle diffractometer, $\omega/2\theta$ scan, $0 < 2\theta < 120°$, graphite-monochromated Cu-Kα radiation; 3345 unique reflections measured giving 2785 with $F_o \geqslant 2.667\ \sigma(F_o)$. No absorption corrections were applied.

Structure analysis. The structure was solved by direct methods using MULTAN 80[10] and refined by the block-diagonal matrix least-squares method. The final *R*-value was 0.058 (R_w = 0.061). Weighting scheme $w = 1/(F_o)$. Residual electron density max. 0.40, min. −0.40 e $Å^{-3}$.

X-Ray structure analysis of compound 13a

Crystal data. $C_{27}H_{24}N_2O_3$, M = 424.50, *T* = 291 K. Orthorhombic, *a* = 9.634(1), *b* = 10.922(1), *c* = 21.209(2) Å, *V* = 2231.6(3) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 1.5418 Å) in the range of 2θ = 30–60°, space group $Pna2_1$, *Z* = 4, D_x = 1.263 g cm^{-3}. Colourless prisms. Crystal dimensions: 0.40 × 0.40 × 0.40 mm^3, μ(Cu-Kα) = 0.674 mm^{-1}.

Data collection and processing. Rigaku AFC5 four-circle diffractometer, $\omega/2\theta$ scan, $0 < 2\theta < 120°$, scan speed, automode, graphite-monochromated Cu-Kα radiation; 1714 unique reflections measured giving 1567 with $F_o \geqslant 2.667\ \sigma(F_o)$. No absorption correction was applied.

Structure analysis. The structure was solved by direct methods using SIR 85[11] and refined by the block-diagonal matrix least-squares method. The final *R*-value was 0.053 (R_w = 0.070). Weighting scheme $w = 1/(F_o)$. Residual electron density max. 0.50, min. −0.40 e $Å^{-3}$.

X-Ray structure analysis of compound *endo*-14b

Crystal data. $C_{20}H_{20}N_2OS$, M = 304.35, *T* = 291 K. Monoclinic, *a* = 16.158(1), *b* = 11.302(1), *c* = 10.979(1) Å, β = 116.14(1)°, *V* = 1799.8(2) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 1.5418 Å), space group $P2_1/a$, *Z* = 4, D_x = 1.330 g cm^{-3}. Colourless prisms. Crystal dimensions: 0.35 × 0.35 × 0.25 mm^3, μ(Cu-Kα) = 1.652 mm^{-1}.

Data collection and processing. Rigaku AFC5 four-circle diffractometer, $\omega/2\theta$ scan, $0 < 2\theta < 120°$, scan speed, automode, graphite-monochromated Cu-Kα radiation; 2672 unique reflections measured giving 2394 with $F_o \geqslant 2.667\ \sigma(F_o)$. No absorption correction applied.

Structure analysis. The structure was solved by direct methods using MULTAN 80[10] and refined by the block-diagonal matrix least-squares method. The final *R*-value was 0.053 (R_w = 0.074). Weighting scheme $w = 1/(F_o)$. Residual electron density max. 0.46, min. −0.35 e $Å^{-3}$.¶

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¶ *Supplementary data:* see Instructions for Authors, January issue. Tables of atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

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