Syntheses and electronic structures of benzannelated isoquinolinones and their photoinduced cycloaddition reactions with electron deficient alkenes †

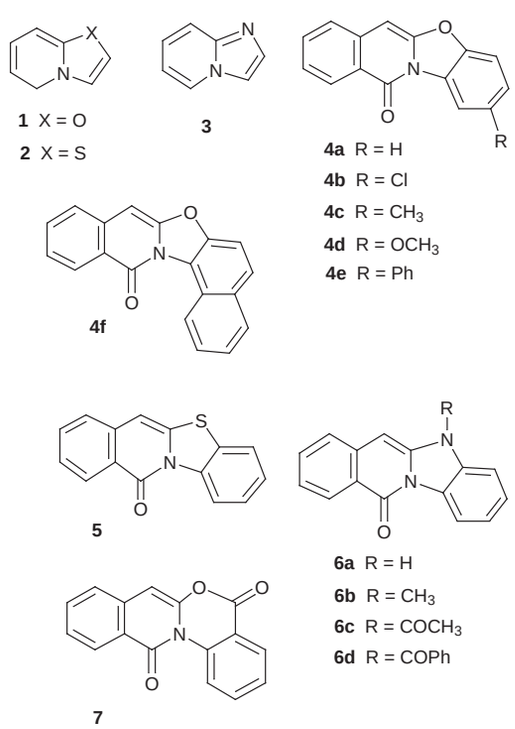
Ke-Qing Ling,[a] Xian-Yang Chen,[a] Hoong-Kun Fun,[b] Xiao-Ying Huang[c] and Jian-Hua Xu*[a]

[a] *Department of Chemistry, Nanjing University, Nanjing 210093, China*
[b] *X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800, USM, Penang, Malaysia*
[c] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

Received (in Cambridge) 27th July 1998, Accepted 20th October 1998

Benzoxazolo[3,2-*b*]isoquinolin-11-ones **4**, benzothiazolo[3,2-*b*]isoquinolin-11-one **5**, benzimidazo[1,2-*b*]isoquinolin-11-ones **6** and isoquino[2,3-*a*][3,1]benzoxazine-5,12-dione **7** were synthesized by the reaction of homophthalic anhydride with the corresponding *o*-substituted anilines. Reaction mechanisms were investigated by isolation of the intermediate products under controlled reaction conditions. Electronic structures of **4a** and **5** were investigated by *ab initio* calculations. Photoinduced [2+2] cycloaddition reactions of **4a** and **5** with electron deficient alkenes (acrylonitrile, methyl acrylate, dimethyl fumarate and dimethyl maleate) gave cyclobutane products (**36**, **37** and **39**–**47** respectively). The regioselectivity in these photocycloadditions was examined by FMO interaction considerations. The mechanism of the cycloadditions was investigated by fluorescence quenching and triplet quenching experiments, solvent effect on the reaction and calculation of free energy change for electron transfer (SET) between the excited states of **4a** (and **5**) and the alkenes.

Derivatives of *5H*-oxazolo[3,2-*a*]pyridine **1**, *5H*-thiazolo[3,2-*a*]-pyridine **2** and imidazo[1,2-*a*]pyridine **3** are of current research interest due to their biological activities and potential medical applications.[1] However, their dibenzo derivatives have not been much investigated except in a few isolated examples.[2,3] Their dibenzo derivatives such as **4**–**6** are also benzannelated isoquinolines. Considering the widespread occurrence in nature and the diverse biological activities of many isoquinoline derivatives,[4] these dibenzo derivatives of **1**–**3** are interesting in view of the search for new compounds with potential medical applications. In relation to our interest in the syntheses and photochemistry of isoquinoline derivatives with elaborate structures,[5] we report here the syntheses and electronic structure studies of benzoxazolo[3,2-*b*]isoquinolin-11-ones **4**, benzothiazolo[3,2-*b*]isoquinolin-11-one **5**, benzimidazo[1,2-*b*]isoquinolin-11-ones **6** and isoquino[2,3-*a*][3,1]benzoxazine-5,12-dione **7** and their photoinduced cycloaddition reactions with alkenes.



Results and discussion

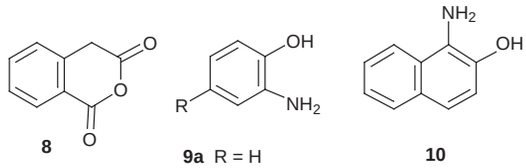
Syntheses of compounds 4–7

Compounds **4**, **5**, **6a** and **7** were synthesized by the reactions of homophthalic anhydride (α-carboxy-*o*-toluic acid cyclic anhydride; isochromane-1,3-dione) **8** with *o*-aminophenols **9**, 2-amino-1-naphthol **10**, *o*-aminothiophenol **11**, *o*-phenylenediamine **12** and 2-aminobenzoic acid **13** respectively.

Although the synthetic potential of the reactions of homophthalic anhydride with different nucleophiles such as amines and imines, and with dienophiles in Diels–Alder reactions for the syntheses of heterocycles[6] and polycyclic compounds[7] has long been recognized and explored, reaction mechanisms involved in these reactions have not been well clarified in many cases. In our syntheses of compounds **4**–**7**, we have also investigated the reaction mechanisms by carefully controlling the reaction conditions to examine the intermediate products in different stages of the syntheses.

Compounds **4a**–**4e** were prepared in one pot reactions by

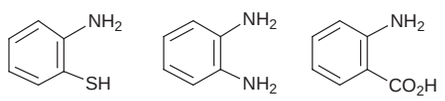
† The atomic charges and geometrical parameters for compounds **4a** and **5** are available as supplementary data (SUPPL. NO. 57451, pp. 3) from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors).



8

9a R = H
9b R = Cl
9c R = CH_3
9d R = OCH_3
9e R = Ph

10

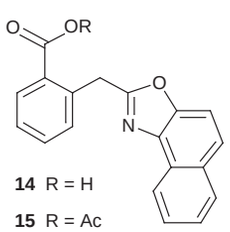


11 **12** **13**

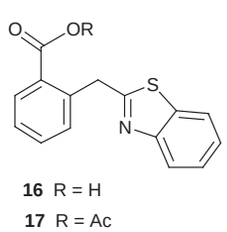
Table 1 Syntheses of compounds **4**–**7** by the reaction of homophthalic anhydride **8** with the *o*-substituted aromatic amines $ArNH_2$ **9**–**13**

$ArNH_2$	Reaction conditions[a]	Reaction time/h	Product and yield (%)[b]
9a	A	4	**4a** (72)
9b	A	6	**4b** (71)
9c	A	4	**4c** (70)
9d	A	2	**4d** (72)
9e	A	8	**4e** (62)
10	B	4 and then 0.5[a]	**4f** (37)
11	C	4 and then 0.5[a]	**5** (79)
12	A	4	**6a** (90)
13	D	8 and then 0.5[a]	**7** (73)

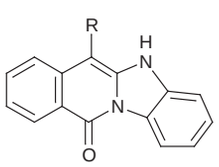
[a] For reaction conditions A, B, C and D, see Experimental section. [b] Yield of isolated pure product based on consumed homophthalic anhydride.



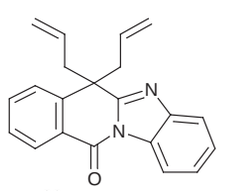
14 R = H
15 R = Ac



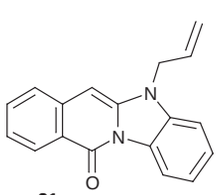
16 R = H
17 R = Ac



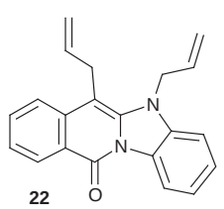
18 R = $COCH_3$
19 R = COPh



20



21



22

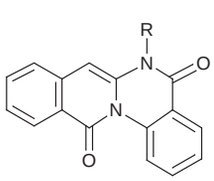
refluxing homophthalic anhydride **8** with the corresponding *o*-aminophenols **9a**–**9e** respectively in acetic acid. The reaction conditions and the yields are listed in Table 1.

On the other hand, refluxing homophthalic anhydride **8** with 1-amino-2-naphthol **10** similarly in acetic acid afforded the α-(naphth[1,2-*d*]oxazol-2-yl)-*o*-toluic acid **14** (39% yield) which could not be further cyclized to **4f** on prolonged refluxing in acetic acid. However, refluxing **14** in acetic anhydride for half an hour gave **4f** in 98% yield.

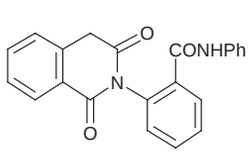
Compound **5** was prepared as **4f**. Refluxing **8** with *o*-aminothiophenol **11** in acetic acid for 4 h gave the α-(benzothiazol-2-yl)-*o*-toluic acid **16** (80% yield), which was then heated at reflux temperature in acetic anhydride to afford **5** in 99% yield (Table 1).

Compound **6a** was synthesized as **4a**–**4e** by refluxing **8** with *o*-phenylenediamine **12** in acetic acid (Table 1). *N*-Methylation of **6a** was accomplished by first treating **6a** with sodium methoxide in THF–MeOH at room temperature and then refluxing the reaction mixture with added methyl iodide. This gave **6b** in 79% yield. Acylation of **6a** was carried out with acetic anhydride and benzoyl chloride respectively. It turned out that these reactions gave predominantly the *C*-acylation products. Therefore, refluxing **6a** in acetic anhydride afforded the *C*-acylation product **18** in 76% yield and the *N*-acylation product **6c** in 16% yield. Also, refluxing **6a** and benzoyl chloride in pyridine led to the formation of **19** in 71% yield and **6d** in 18% yield, while refluxing **6a** directly in benzoyl chloride gave only the *C*-acylation product **19** (86% yield). Allylation of **6a** was conducted under two sets of reaction conditions. Deprotonation of **6a** by sodium methoxide in THF–methanol at room temperature followed by reaction with allyl chloride at reflux temperature gave the doubly *C*-allylated product **20** in 86% yield. In another approach, compound **6a** was allylated under phase transfer catalysis (PTC) conditions at room temperature by stirring a mixture of **6a**, allyl chloride, sodium hydroxide and a catalytic amount of TEBA in THF–water. This also gave **20** in 80% yield. No *N*-allylation product was found in these reactions. Since alkylation of **6a** tends to take place at the nitrogen atom to lead to *N*-alkylation as shown above in the methylation of **6a**, it is speculated that the *C*-allylation of **6a** is probably the result of two sequential Cope rearrangements of the primary *N*-allylated products **21** and **22**. However, no attempt has been made to examine this possibility at this stage.

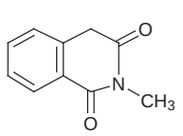
The isoquino[2,3*a*][3,1]benzoxazine-5,12-dione **7** was prepared in one pot by first refluxing **8** and 2-aminobenzoic acid **13** in acetic acid and then, after removing the acetic acid by distillation, further refluxing the residue in added acetic anhydride (Table 1). Two ways to convert **7** into its *N*-analogue **23** were attempted without success. Treating **7** with aniline in acetic acid at room temperature gave *N*-phenyl-2-homophthalimidobenzamide **24**, which on prolonged refluxing in acetic acid or acetic anhydride, or on heating at 250 °C could not be cyclized to give **23**. Heating a solution of **7** in aqueous methylamine to boiling to remove water and then melting the solid residue resulted in the formation of *N*-methylhomophthalimide **25** which is obviously derived from the intermediate **26**.



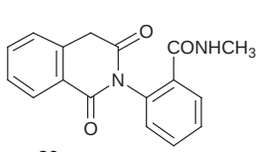
23



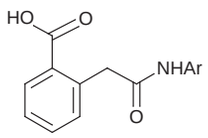
24



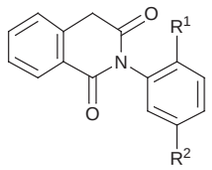
25



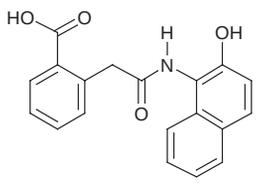
26



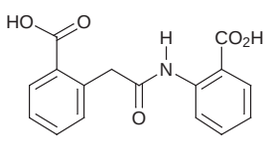
27



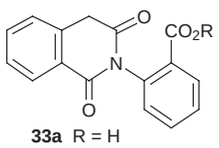
28a-e R^1 = OH,
R^2 = H, Cl, CH_3,OCH_3, Ph
29 R^1 = SH, R^2 = H
30 R^1 = NH_2, R^2 = H



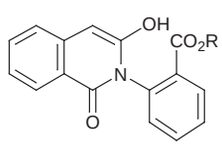
31



32



33a R = H
33b R = Ac



34a R = H
34b R = Ac

Reaction mechanisms in the syntheses

Nucleophilic attack on homophthalic anhydride **8** by neutral nucleophiles such as methanol, primary and secondary (aromatic) amines always takes place at C^3 which is the site of the least electron density in **8**.[8] Therefore, reactions of **8** with substituted anilines afford the corresponding *N*-aryl-homophthalimide in high yield with the *α*-(*N*-arylamino-carbonyl)-*o*-toluic acid **27** as intermediate products.[9] However, in the reactions of **8** with the *ortho*-substituted anilines **9**–**12**, several control experiments to examine the reaction mechanisms showed that homophthalimides **28**–**30** were not the intermediates leading to **4a**–**4e**, **5** and **6a**. In the case of reaction of **8** with **10**, for example, control of the experimental conditions permits us to isolate intermediate products in different stages of the reaction. Warming **8** with **10** in acetic acid at 40 °C afforded the amide **31** in 96% yield, which, when subjected to reflux in acetic acid, underwent intramolecular cyclization by nucleophilic attack of the phenolic hydroxy group toward the aliphatic amide carbonyl group to afford the naphthoxazole **14** rather than by the attack of the amide nitrogen toward the the less electrophilic aromatic carboxylic carbonyl group to form the homophthalimide intermediate like **28**. Converting **14** to **4f** could not be achieved by further refluxing in acetic acid since the naphthoxazole nitrogen is not nucleophilic enough to attack the carboxylic carbonyl group. In this case, warming **14** in acetic anhydride at 40 °C converted **14** into the anhydride **15** which has a carbonyl group with increased electrophilicity and a better leaving group (OAc^-) than **14** (OH^-). Cyclization of **15** in the same pot without separation proceeded smoothly to give the final product **4f** almost quantitatively.

In the synthesis of **5**, the benzothiazole **16** was obtained as mentioned above. Converting **16** into the anhydride **17** by warming in acetic anhydride followed by nucleophilic attack of the thiazole nitrogen to the carbonyl group yielded **5**.

In the reactions of homophthalic acid[2a] and homophthalimide[2b] with *o*-phenylenediamine, α-(benzimidazol-2-yl)-*o*-toluic acid have been observed to be formed and was proposed as the intermediate *en route* to **6a**.

The reaction of **8** with 2-aminobenzoic acid **13** to afford **7** followed a different pathway. In this case, the 2-homophthalimidobenzoic acid **33a** is the intermediate product. In a control experiment, warming a mixture of **8** and 2-aminobenzoic acid in acetic acid gave the amide **32** in 75% yield. Refluxing **32** in acetic acid gave the homophthalimide **33a** (65% yield), which could not be cyclized to **7** either by further refluxing in acetic acid or by melting at 250 °C. However, **33a** could be smoothly cyclized to **7** simply by treating with acetic anhydride at reflux temperature. These observations indicate that it is the nucleophilic attack of the enolic hydroxy group to the carboxylic carbonyl (as shown in **34a**) instead of the nucleophilic attack of the carboxylic hydroxy group to the 3-carbonyl (as shown in **33a**) that is responsible for the cyclization of **33a** to **7**. The electrophilicity of the carboxylic carbonyl group in **33a** was significantly enhanced by acylation to form **33b**, which subsequently underwent cyclization to give **7** *via* the enolic intermediate **34b**.

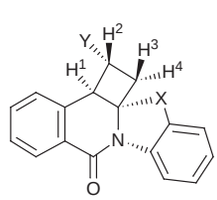
Molecular structures of compounds 4a and 5

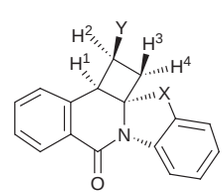
In combination with the syntheses, electronic structures of compounds **4a** and **5** as representative examples of **4**–**6** were investigated by *ab initio* calculations. The geometric optimization was carried out at HF/3-21G* level, and using Schlegel's algorithm.[10] Atomic charges were obtained from the Mulliken population analysis of the HF/3-21G* wave function. All calculations were performed using the GAUSSIAN-94 program package[11] at an SGI station. It was shown that the carbon atoms bearing the heaviest negative charges are C^6 (designated as C^8 in Fig. 1) in **4a** (−0.367) and C^{4a} (designated as C^5 in Fig. 1) in **5** (−0.372) respectively, whereas the C^6 (designated as C^8 in Fig. 1) in **5** is also heavily negatively charged (−0.327). The energy and the atomic coefficients of the HOMO and LUMO of **4a** and **5** are depicted in Fig. 1. The atomic charges and the geometrical parameters for **4a** and **5** are available as supplementary materials if needed.†

Photoinduced cycloaddition reactions of compounds 4a and 5 with electron deficient alkenes

In line with the electronic structure studies, photocycloaddition reactions of compounds **4a** and **5** with alkenes were investigated. Irradiation of a benzene solution of **4a** and acrylonitrile **35** with light of wavelength longer than 334 nm resulted in the formation of cycloadducts **36** and **37** in a total yield of 95% as a pair of stereoisomers inseparable by silica gel column chromatography. ^{1}H NMR measurement of the product mixture showed that the ratio of **36**:**37** is 2.1:1. Stepwise crystallization of the product mixture from ethyl acetate gave pure samples of **36** and **37**. The structure of **37** was determined by crystallographic analysis and is shown in Fig. 2. The regiochemistry and stereochemistry of product **36** are determined by analysis of its spectral data, especially the ^{1}H NMR data and comparison of them with those of **37**.

Photolysis of **4a** with methyl acrylate **38** in benzene under the





36 X = O, Y = CN
39 X = O, Y = CO_2CH_3
41 X = S, Y = CN
43 X = S, Y = CO_2CH_3

37 X = O, Y = CN
40 X = O, Y = CO_2CH_3
42 X = S, Y = CN
44 X = S, Y = CO_2CH_3

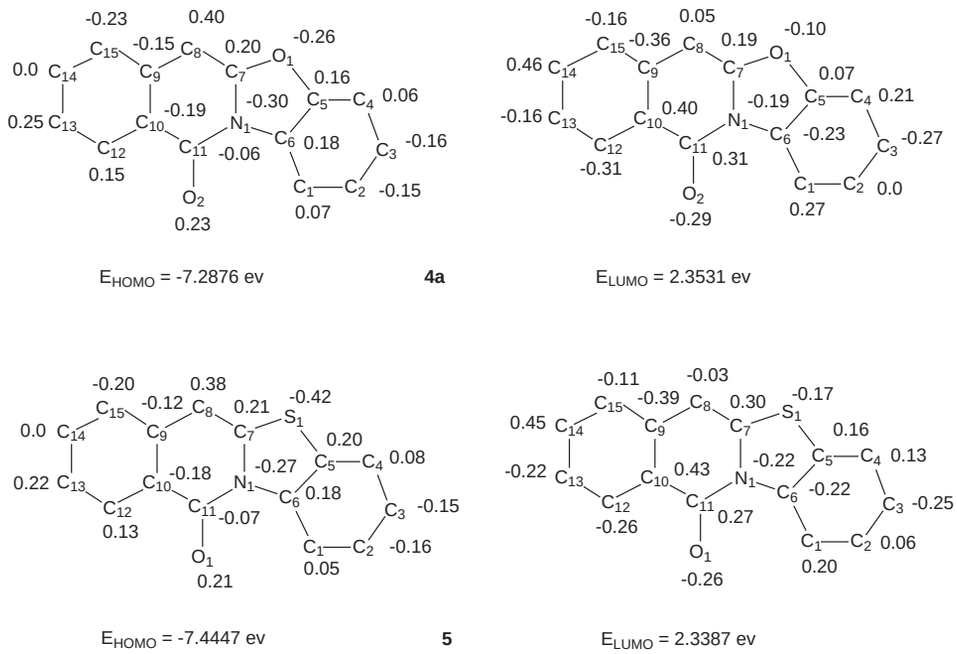


Fig. 1 Energy and atomic coefficient of the FMOs of **4a** and **5**.

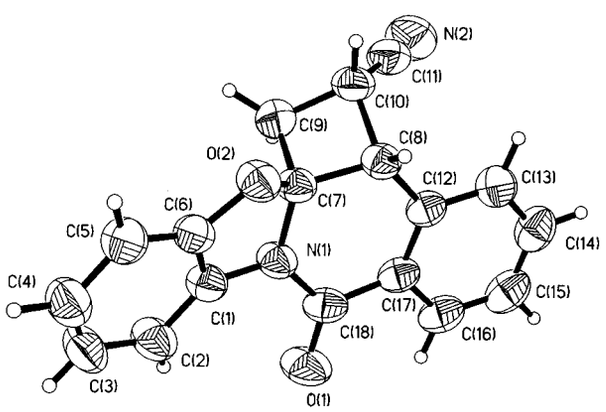


Fig. 2 ORTEP drawing of compound **37**.

Table 2 Photoinduced cycloaddition reactions of compounds **4a** and **5** with electron deficient alkenes **35**, **38**, **F** and **M**[a]

Substrates	Irrad. time/h	Products and yield (%)[b]	Product ratio[c]
4a 35	10	(**36** + **37**) (95)	2.1 : 1 (**36** : **37**)
4a 38	15	(**39** + **40**) (92)	2.1 : 1 (**39** : **40**)
5 35	4	(**41** + **42**) (96)	1.8 : 1 (**41** : **42**)
5 38	6	(**43** + **44**) (93)	2.3 : 1 (**43** : **44**)
5 F	60	(**45** + **46** + **47**) (71), **48** (2)	2 : 2 : 1 (**45** : **46** : **47**)
5 M	60	(**45** + **46** + **47**) (71), **48** (2)	3 : 3 : 2 (**45** : **46** : **47**)

[a] Solvent: benzene; irradiation wavelength: $\lambda > 334$ nm for **35** and **38**, $\lambda > 400$ nm for **F** and **M**. [b] Isolated yield based on consumed **4a** or **5**. [c] Determined by ^{1}H NMR (500 MHz) measurement of the product mixture.

same conditions afforded cycloadducts **39** and **40** in a ratio of 2.1 : 1 in 92% total yield.

Similar photolysis of **5** with acrylonitrile in benzene furnished **41** and **42**, while irradiation of **5** with methyl acrylate in benzene gave **43** and **44** (Table 2).

It is found, however, that photocycloadditions of **4a** and **5** with the alkenes **35** and **38** could not proceed well in polar solvents such as acetonitrile, and on prolonged irradiation in acetonitrile, **4a** and **5** were gradually consumed with only a trace amount of cycloadducts formed. It is also noted that under the same conditions as mentioned above, **4a** and **5** could not take part in photocycloadditions with electron rich alkenes such as cyclohexene and styrene, either in benzene or in acetonitrile.

The regioselectivity in these cycloadditions was examined by frontier molecular orbital (FMO) interaction considerations. In photochemical reactions, the FMO interactions to be considered are the HOMO–HOMO and LUMO–LUMO interactions of the two reactants respectively. The energy gap between the HOMOs of **4a** and **35** is 3.63 eV, while that between the LUMOs of **4a** and **35** is 2.37 eV. Similarly, the energy gaps between the HOMOs and LUMOs of **5** and **35** are 3.48 eV and 2.36 eV respectively. Therefore, in both cases, LUMO–LUMO interactions are stronger than the HOMO–HOMO interactions and should play a more important role in deciding the regioselectivity of the cycloadditions. The calculated FMO energies and the atomic coefficients for C^{5a} and C^6 in the FMOs of **4a** and **5** are shown in Fig. 3. In photocycloadditions of **5** with **35**, in the HOMO–HOMO interaction (Fig. 3), since the atomic coefficients at C^2 and C^3 of **35** are of similar value,[12] this interaction is not as important in deciding the regioselectivity as the LUMO–LUMO interaction, in which the interactions of C^2 (**35**) with C^6 (**5**) (designated as C^8 in Fig. 1) and of C^3 (**35**) with C^{5a} (**5**) (designated as C^7 in Fig. 1) both lead to maximum orbital overlap and resulted in an unambiguous regioselectivity in the cycloaddition reactions. This regiospecificity predicted by the LUMO–LUMO interaction is actually found in products **41** and **42**. An analysis of FMO interactions in the cycloaddition of **4a** with **35** gave a similar result to that for **5**. In this case, although the calculated atomic coefficients at C^{5a} and C^6 (designated as C^7 and C^8 in Fig. 1 respectively) in the LUMO of **4a** are of the same sign, consideration of maximum positive overlap still slightly favors the regioselectivity found in products **36** and **37**.

The facts that photocycloaddition reactions of **4a** and **5** with **35** and **38** take place in benzene but not in acetonitrile and that **4a** and **5** are not able to undergo cycloadditions with electron rich alkenes imply that electron transfer interactions between the reactants may play some roles in the reactions. To further test this point, photoinduced reactions of **5** with dimethyl fumarate (**F**) and dimethyl maleate (**M**) were investigated. In each case, irradiation of **5** with either **F** or **M** in a benzene solution resulted in the formation of three stereoisomeric cyclobutane products **45**, **46**, and **47**, along with a small amount of adduct **48** (2%). The structure of **45** was determined by crystallographic analysis as shown in Fig. 4.

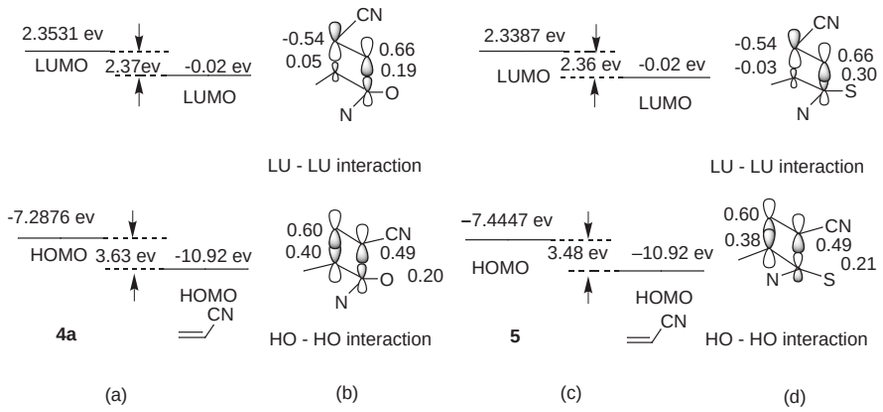


Fig. 3 (a) and (c) FMO energy levels of **4a**, **5** and acrylonitrile; (b) and (d) FMO interactions.

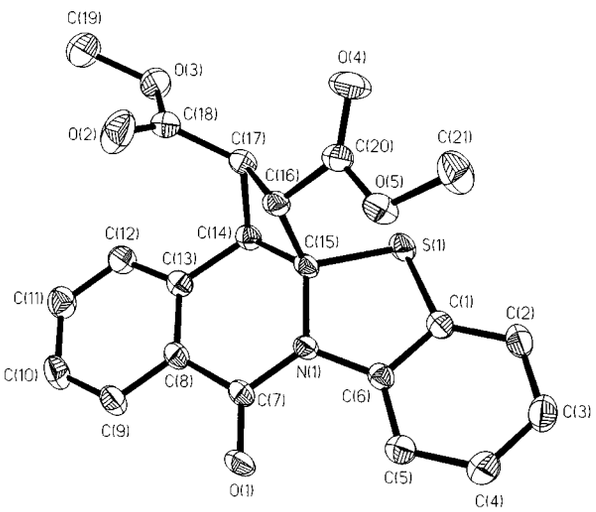
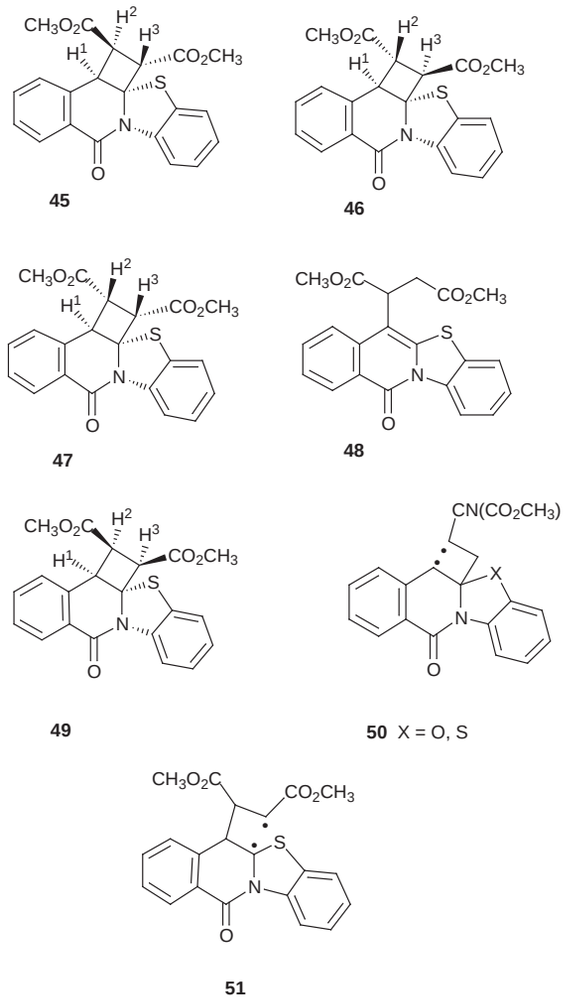


Fig. 4 ORTEP drawing of compound **45**.



The stereochemistry in **46** and **47** are temporarily assigned by the analyses of their ^{1}H NMR data, especially by comparison of the chemical shifts and coupling constants of the aliphatic hydrogens in the cyclobutane moieties with each other and with those of **45**, **36**, **37** and **39**–**44**. Therefore, in **46** and **47**, the H^2s are both in the shielding area of the isoquinoline benzene ring and resonate at higher fields than in **45** (δ 3.881). Similar results are also observed in products **36**, **37** and **39**–**44** where the H^2s in the *exo*-adducts (**36**, **39**, **41** and **43**) always resonate at higher fields than in the corresponding *endo*-adducts (**37**, **40**, **42** and **44**) (see Experimental section). However, since H^2 in **46** is also in the deshielding area of the β-CO_2CH_3, its chemical shift (δ 3.605) is at lower field than the H^2 in **47** (δ 3.290) which is not deshielded by the carbonyl of either α- or β-CO_2CH_3. Also, in **46**, the all-*trans* arrangement of the three aliphatic protons (H^1, H^2 and H^3) is manifested by the rather small coupling constants between them (7.5 and 8 Hz respectively), while in **47**, the *J* values are 10 Hz for the two *cis*-protons (H^2, H^3) and 6 Hz for the two *trans*-protons (H^1, H^2). Of the four possible stereoisomeric products of the cycloadditions, only the *endo*,*cis* product **49** is absent, which has the most serious steric hindrance between the two CO_2CH_3 groups and between the CO_2CH_3 groups and the isoquinoline framework. The product ratios **45**:**46**:**47** are roughly 2:2:1 and 3:3:2 for the photocycloadditions of **5** with **F** and **M** respectively (Table 2), the two *trans*-isomers are formed in substantially larger amounts than the *exo*-*cis*-isomer **47**, in which the two CO_2CH_3 groups have large steric hindrance. Isomerization of the alkenes (**F**→**M** and **M**→**F**) was also found in these reactions. It should be noted that under the conditions used for the photolyses, the incident light ($\lambda > 400$ nm) is entirely absorbed by **5**, and a control experiment showed that neither **F** nor **M** undergoes isomerization when irradiated in benzene solution under conditions as mentioned above in the absence of **5**. These results can be best explained by the intermediacy of triplet diradical species such as **51**, in which intersystem crossing to a singlet diradical (accompanied by single bond rotation) followed by radical combination afforded **45**–**47**, while intramolecular hydrogen transfer yielded **48**, and β-bond cleavage resulted in the isomerization of the alkenes.

Fluorescence quenching experiments were carried out for **4a** and **5** with **35**, **38** and **M** as quenchers respectively in benzene and in acetonitrile solutions, and the quenching rate constants were calculated by Stern–Volmer treatment of the data. The fluorescence lifetime τ_S of **4a** and **5** for the calculation are listed in Table 3. Acrylonitrile and methyl acrylate were found to be inefficient quenchers of the fluorescence of **4a** and **5**, while

Table 3 Excited state properties and electrochemical data for compounds **4a** and **5**

Compound	Solvent	τ_S/ns	E(D/D$^{\bullet+}$)/V[a]	E_S/kcal mol^{-1}	E_T/kcal mol^{-1}
4a	MeCN	2.45	1.23	75.9	
4a	C_6H_6	2.00		75.9	
4a	EtOH[b]				65.7
5	MeCN	0.314	1.11	73.3	
5	C_6H_6	0.317		73.3	
5	EtOH[b]				63.7

[a] *Vs*. SCE. [b] In glassy state at 77 K.

Table 4 Fluorescence quenching data and free energy changes for electron transfer of the excited states of **4a** and **5** with electron deficient alkenes[a]

Substrate	Quencher	Solvent	k_q/M^{-1} s^{-1}	ΔG_{ET}^S/kcal mol^{-1}	ΔG_{ET}^T/kcal mol^{-1}
4a	**35**	MeCN	~5×10^7	1.7	12.4
4a	**38**	MeCN	~6×10^7	2.6	13.3
4a	**F**	MeCN		−22.4	−12.2
4a	**M**	MeCN	5.39×10^9	−19.4	−9.2
4a	**35**	C_6H_6	~4×10^7	11.8	22.5
4a	**38**	C_6H_6	~5×10^7	12.7	23.4
4a	**F**	C_6H_6		−12.3	−2.1
4a	**M**	C_6H_6	4.10×10^9	−9.3	0.9
5	**35**	MeCN	~2×10^8	1.7	11.2
5	**38**	MeCN	~2×10^8	2.6	12.1
5	**F**	MeCN		−22.6	−13.0
5	**M**	MeCN	6.58×10^9	−19.6	−10.0
5	**35**	C_6H_6	~1×10^8	11.8	21.4
5	**38**	C_6H_6	~1×10^8	12.7	22.3
5	**F**	C_6H_6		−12.4	−2.8
5	**M**	C_6H_6	5.88×10^9	−9.4	0.2

[a] The excitation wavelengths (λ_{ex}) for **4a** and **5** are both 360 nm, the emission wavelengths (λ_{em}) of maximum intensity for **4a** in MeCN and in benzene are both 417 nm, whereas the λ_{em} for **5** is 435 nm in MeCN and 432 nm in benzene respectively. The half wave reduction potentials E(A/A$^{\bullet-}$) for **35** and **38** in MeCN are −2.44 V [13] and −2.40 V [14] (*vs*. Ag/Ag$^+$) respectively and the E(A/A$^{\bullet-}$) values (*vs*. SCE) are obtained by adding 0.3 V to the corresponding E(A/A$^{\bullet-}$) (Ag/Ag$^+$),[14] the E(A/A$^{\bullet-}$)s (*vs*. SCE) for **F** and **M** are −1.15 V and −1.28 V respectively.[15]

dimethyl maleate quenches the fluorescence of **4a** and **5** efficiently. The k_q values are listed in Table 4 together with the calculated free energy change for electron transfer (ΔG_{ET}) between the excited state of the heterocycles (**4a** and **5**) and the alkenes. The oxidation potentials of **4a** and **5** were measured by cyclic voltammetry in acetonitrile solutions *vs*. SCE and are listed in Table 3. The energy of the singlet (S_1) and triplet (T_1) state were determined from the corresponding 0–0 band in their fluorescence and phosphorescence spectra. The ΔG_{ET} values were calculated by Weller equations [eqn. (1) and (2)];[16] where

$$\text{In benzene} \quad \Delta G_{ET} = 23.06[E(D/D^{\bullet+}) - E(A/A^{\bullet-}) + 0.38] - \Delta E^* \quad (1)$$

$$\text{In acetonitrile} \quad \Delta G_{ET} = 23.06[E(D/D^{\bullet+}) - E(A/A^{\bullet-}) - 0.06] - \Delta E^* \quad (2)$$

E(D/D$^{\bullet+}$) and E(A/A$^{\bullet-}$) are the half wave oxidation potential of the donor and the half wave reduction potential of the acceptor respectively, while ΔE^* is the excited state energy. The k_q values for **35** and **38** are far smaller than the diffusion controlled rate constant in benzene (1×10^{10} M^{-1} s^{-1} [17]) and in acetonitrile (2×10^{10} M^{-1}s^{-1} [17]), and are in accord with the large positive ΔG_{ET} values listed in Table 4. At the same time, the k_q values for **M** are close to the diffusion controlled rate constant in the solvents, again consistent with the negative ΔG_{ET} values. These correlations of k_q with the acceptor ability of the alkenes and with the values of ΔG_{ET} indicate the SET nature of the quenching process. In these fluorescence quenching studies, long wavelength exciplex emission was not observed even at high alkene concentrations. Therefore, a triplet exciplex of **4a** or **5** with the alkene, which is supposed to be the precursor of the triplet diradical, could be formed by fast intersystem crossing (ISC) of ^{1}**4a*** (or ^{1}**5***) to ^{3}**4a*** (or ^{3}**5***) followed by quenching of ^{3}**4a*** (or ^{3}**5***) by the alkene, and (or) by intersystem crossing of the nonfluorescent singlet exciplex of **4a** (or **5)** with the alkene. The triplet exciplex in turn gave the triplet diradical intermediate **50** or **51**. This conclusion was also supported by the triplet quenching experiments with *trans*-stilbene ($E_S \sim 90$ kcal mol^{-1}, $E_T = 50$ kcal mol^{-1} [18]) as a triplet quencher. For example, photocycloaddition of **5** (2×10^{-2} mol dm^{-3}) with acrylonitrile in benzene on irradiation with light of wavelength longer than 400 nm was found to be almost completely quenched by added *trans*-stilbene at a concentration of 8×10^{-2} mol dm^{-3}. Similarly, the photocycloaddition reaction of **4a** (1×10^{-2} mol dm^{-3}) with acrylonitrile under the same conditions was also nearly completely quenched by 5×10^{-2} mol dm^{-3} of *trans*-stilbene. Since there is no competitive light absorption by the quencher under the experimental conditions, these observations are in good agreement with the predominant involvement of the triplet state of **4a** and **5** as well as the triplet exciplex of **4a** and **5** with the alkenes in the photocycloaddition reactions.

In summary, benzannelated isoquinolinones **4**, **5**, **6a** and **7** have been synthesized from homophthalic anhydride and the corresponding *o*-substituted anilines. Reaction mechanisms in these syntheses were clarified by isolation of the intermediate products in different stages of the reactions, *i.e.* the formations of **4**, **5**, and **6a** involved the azole intermediates such as **14** and **16**, whereas in the formation of **7**, homophthalimide **33a** was the intermediate. Electronic structures (atomic charge in ground state molecules, MO energy and atomic coefficients in the FMOs) of **4a** and **5** were calculated by *ab initio* methods. Photoinduced cycloaddition reactions of **4a** and **5** with electron deficient alkenes afforded cyclobutane products and resulted in the Schenck isomerization of the alkenes. Fluorescence quenching and triplet quenching studies, as well as estimation of ΔG_{ET} values showed that the cycloaddition reactions involved SET interactions between the heterocyclic substrates (**4a** and **5**) and the alkenes, and proceeded *via* triplet diradical intermediates.

Experimental

Melting points were measured on a YANACO microscopic melting point apparatus and are uncorrected. ^{1}H NMR spectcra were recorded on a JEOL PMX-60 SI spectrometer at 60 MHz or on a Bruker AC-500 spectrometer at 500 MHz with $SiMe_4$ as internal standard and $CDCl_3$ as solvent unless otherwise stated. J Values are given in Hz. IR spectra were taken with a Shimadzu IR 408 or a Nicolet 5DX FT-IR spectrometer in KBr pellets. Mass spectra were recorded with a VG ZAB-HSS spectrometer. Elemental analyses were obtained using a Perkin-Elmer 240 C analyser. Fluorescence spectra and fluorescence quenching data were obtained on a Perken-Elmer LS 50B spectrofluorimeter. Phosphorescence spectra were recorded on a Hitachi MPF-4 spectrofluorimeter in glassy ethanol at 77 K. Fluorescence lifetime was determined on a Horiba NAES-1100 single photon counting instrument. Cyclic voltammetric measurements were done on a Model 370 Electrochemistry System (EG & G PAR Co.).

Acetonitrile (CP grade) was first refluxed with phosphorus pentaoxide and distilled, then refluxed with anhydrous potassium carbonate and redistilled. Benzene (AR grade) was dried with sodium and distilled before use. Other reagents were CP or AR grade and were used as received without further purification.

Preparations of compounds 4–7

The methods and the results are listed in Table 1.

Method A. A mixture of homophthalic anhydride **8** (20 mmol) and the corresponding substituted *o*-aminophenols **9** (20 mmol) in HOAc (20 ml) was refluxed for the time indicated in Table 1. After cooling to room temperature, the solid product was collected by filtration. The mother liquor was concentrated to afford a further crop of product. The combined crude product was recrystallized with activated charcoal as decolorant to give the pure product.

Method B. A mixture of **8** (20 mmol) and **10** (20 mmol) in HOAc (20 ml) was refluxed for 4 h. Acetic anhydride (5 ml) was then added and the mixture was further refluxed for 0.5 h. The work-up was the same as in method A.

Method C. A mixture of **8** (4.00 g, 24.7 mmol) and **11** (3.50 g, 28 mmol) in HOAc (20 ml) was refluxed for 4 h. After cooling, the solid product **16** (5.31 g, 80% yield) was collected by filtration. A suspension of **16** (4.93 g, 18.3 mmol) in Ac_2O (5 ml) was refluxed until the white solid disappeared (0.5 h). After cooling, the yellow crystals were filtered off to give pure product **5** (4.54 g, 99% yield). The overall yield for **5** starting from **8** is 79%.

Method D. A mixture of **8** (8.10 g, 50 mmol) and **13** (7.0 g, 50 mmol) in HOAc (100 ml) was refluxed for 8 h. The acetic acid was removed by distillation and acetic anhydride (20 ml) was added to the residue. The mixture was then refluxed for 0.5 h. Work up as in Method A gave **7** (9.60 g, 73% yield).

11H-[1,3]Benzoxazolo[3,2-b]isoquinolin-11-one ***4a***. Yellow needles, mp 204–206 °C (sublimes) (from HOAc); ν_{max}/cm^{-1} 3098, 3050, 1684, 1641, 1600, 1481, 1462, 1223, 743, 694; δ_H (60 MHz) 6.73 (1H, s, Ar-CH=C), 7.2–7.7 (6H, m, ArH), 8.3–8.7 (2H, m, ArH); *m*/*z* (%) 235 (M^+, 100), 207 (8.7), 178 (11.5), 149 (11.3), 132 (4.4), 119 (21) (Found: C, 76.57; H, 3.73; N, 5.96. $C_{15}H_9NO_2$ requires C, 76.59; H, 3.86; N, 5.96%).

2-Chloro-11H-[1,3]benzoxazolo[3,2-b]isoquinolin-11-one ***4b***. Light yellow plates, mp 211–212.5 °C (sublimes) (from HOAc); ν_{max}/cm^{-1} 3080, 3005, 1680, 1636, 1608, 1538, 1464, 1382, 1056, 1038, 1012, 806, 778, 684, 672; δ_H (60 MHz, $CDCl_3$–DMSO-d_6) 6.53 (1H, s, Ar-CH=C), 7.4–7.9 (5H, m, ArH), 8.3–8.7 (2H, m, ArH); *m*/*z* (%) 271 (M+2, 33.4), 269 (M^+, 100), 206 (14.1), 178 (19.6), 127 (19.8), 126 (8.0), 121 (38) (Found: C, 66.86; H, 2.97; N, 5.17. $C_{15}H_8ClNO_2$ requires C, 66.81; H, 2.99; N, 5.19%).

2-Methyl-11H-[1,3]benzoxazolo[3,2-b]isoquinolin-11-one ***4c***. Light yellow needles, mp 195–196.5 °C (sublimes) (from HOAc); ν_{max}/cm^{-1} 3065, 3020, 2998, 2894, 1680, 1634, 1605, 1538, 1484, 1468, 1441, 1384, 1182, 1060, 814, 770, 684; δ_H (60 MHz) 2.47 (3H, s, CH_3), 6.38 (1H, s, Ar-CH=C), 7.1–7.7 (5H, m, ArH), 8.3–8.6 (2H, m, ArH); *m*/*z* (%) 249 (M^+, 100), 221 (7.8), 192 (9.0), 165 (6.2) (Found: C, 77.17; H, 4.56; N, 5.64. $C_{16}H_{11}NO_2$ requires C, 77.10; H, 4.45; N, 5.62%).

2-Methoxy-11H-[1,3]benzoxazolo[3,2-b]isoquinolin-11-one ***4d***. Light yellow needles, mp 155–157 °C (from ethyl acetate); ν_{max}/cm^{-1} 3050, 3020, 2998, 2800, 1674, 1641, 1606, 1581, 1568, 1484, 1384, 1268, 1196, 1054, 792, 780, 684; δ_H (60 MHz) 3.87 (3H, s, CH_3), 6.30 (1H, s, Ar-CH=C), 6.7–7.7 (5H, m, ArH), 8.0–8.5 (2H, m, ArH); *m*/*z* (%) 265 (M^+, 100), 250 (17.7), 222 (26.0), 194 (7.4) (Found: C, 72.47; H, 4.12; N, 5.17. $C_{16}H_{11}NO_3$ requires C, 72.44; H, 4.18; N, 5.28%).

2-Phenyl-11H-[1,3]benzoxazolo[3,2-b]isoquinolin-11-one ***4e***. Yellow prisms, mp 239–240 °C (from HOAc–THF); ν_{max}/cm^{-1} 3060, 1682, 1636, 1598, 1538, 1461, 1382, 1222, 1118, 1008, 761, 684; δ_H (60 MHz, DMSO-d_6) 6.63 (1H, s, Ar-CH=C), 7.3–8.7 (12H, m, ArH); *m*/*z* (%) 311 (M^+, 100), 254 (15.2), 155 (6.4) (Found: C, 81.21; H, 4.35; N, 4.48. $C_{21}H_{13}NO_2$ requires C, 81.01; H, 4.21; N, 4.50%).

13H-Naphth[1′2′:4,5][1,3]oxazolo[3,2-b]isoquinolin-13-one ***4f***. Yellow needles, mp 217–218 °C (sublimes) (from ethyl acetate–THF); ν_{max}/cm^{-1} 3080, 3020, 1674, 1638, 1612, 1600, 1538, 1478, 1282, 1030, 798, 744, 686; δ_H (500 MHz, DMSO-d_6) 6.813 (1H, s, Ar-CH=C), 7.454 (1H, s, ArH), 7.561 (1H, t, *J* 8, ArH), 7.689 (1H, t, *J* 8, ArH), 7.737 (2H, d, ArH), 7.825 (1H, d, *J* 9, ArH), 8.073 (1H, d, *J* 8, ArH), 8.093 (1H, d, *J* 9, ArH), 8.418 (1H, d, *J* 8, ArH), 9.933 (1H, d, *J* 9, ArH); *m*/*z* (%) 285 (M^+, 100), 257 (23.3), 228 (20.2), 202 (6.3), 114 (8.1) (Found: C, 79.98; H, 3.87; N, 4.98. $C_{19}H_{11}NO_2$ requires C, 79.99; H, 3.89; N, 4.91%).

11H-[1,3]Benzothiazolo[3,2-b]isoquinolin-11-one ***5***. Yellow needles, mp 186–186.5 °C (from HOAc); ν_{max}/cm^{-1} 3100, 3035, 1668, 1608, 1598, 1541, 1474, 1450, 1164, 800, 750, 686; δ_H (60 MHz) 6.71 (1H, s, Ar-CH=C), 7.1–7.8 (6H, m, ArH), 8.4–8.6 (1H, m, ArH), 9.0–9.3 (1H, m, ArH); *m*/*z* (%) 251 (M^+, 100), 223 (20.3), 190 (1.8), 149 (2.4), 104 (8.7) (Found: C, 71.52; H, 3.55; N, 5.52. $C_{15}H_9NOS$ requires C, 71.69; H, 3.61; N, 5.57%).

11H-Benzimidazo[1,2-b]isoquinolin-11-one ***6a***. Bright yellow plates, mp >320 °C (decomp.) (from HOAc) (lit.,[2a] 324–326 °C); ν_{max}/cm^{-1} 3100 (broad), 1670, 1630, 1568, 1482, 1344, 1284, 1156, 778, 736; δ_H (60 MHz, DMSO-d_6) 6.35 (1H, s, Ar-CH=C), 7.0–7.7 (6H, m, ArH), 8.31 (1H, d, *J* 8, ArH), 8.67 (1H, d, *J* 8, ArH); *m*/*z* (%) 234 (M^+, 100), 205 (23.0), 177 (3.7), 151 (5.1), 103 (6.1) (Found: C, 76.86; H, 4.40; N, 11.95. $C_{15}H_{10}N_2O$ requires C, 76.91; H, 4.30; N, 11.96%).

5H,12H-Isoquino[2,3-a][3,1]benzoxazine-5,12-dione ***7***. Yellow needles, mp 220–221 °C (from HOAc); ν_{max}/cm^{-1} 3100, 3035, 1760, 1668, 1628, 1450, 1382, 1248, 1078, 746, 678; δ_H (60 MHz) 6.34 (1H, s, Ar-CH=C), 7.3–8.6 (7H, m, ArH), 9.30 (1H, d, *J* 8, ArH); *m*/*z* (%) 264 (M+1, 100), 263 (M^+, 22.5), 236 (68.6), 208 (14.0), 180 (8.3), 146 (4.1), 118 (4.4) (Found: C, 73.14; H, 3.46; N, 5.50. $C_{16}H_9NO_3$ requires C, 73.00; H, 3.45; N, 5.32%).

Methylation of 6a. To a solution prepared by dissolving sodium (0.690 g, 30 mmol) in methanol (10 ml) and THF (30 ml) was added **6a** (3.51 g, 15 mmol). The mixture was refluxed until **6a** was completely dissolved. An excess amount of MeI was added to the resulting red solution and the mixture was refluxed until the red color of the solution faded. To this mixture were repeatedly added, with refluxing, small portions of sodium methoxide in methanol and MeI until the solution remained colorless under alkaline conditions. The solution was then neutralized with acetic acid to pH = 7. The solvents were removed by distillation and the residue extracted with benzene. The benzene solution was decolorized with charcoal and concentrated to give **6b** (2.95 g, 79%).

5-Methyl-11H-benzimidazo[1,2-b]isoquinolin-11-one ***6b***. Bright yellow needles, mp 234–236 °C (from toluene) (lit.,[2b] 227 °C); ν_{max}/cm^{-1} 1663, 1622, 1602, 1586, 1538, 1478, 1338, 774, 741; δ_H (500 MHz, DMSO-d_6) 3.678 (1H, s, CH_3), 6.414 (1H, s, Ar-CH=C), 7.218–7.278 (2H, m, ArH), 7.419–7.481 (2H, m, ArH), 7.606–7.646 (2H, m, ArH), 8.286 (1H, d, *J* 8, ArH), 8.629 (1H, d, *J* 8, ArH); *m*/*z* (%) 248 (M^+, 100), 233 (52.0), 205 (12.9), 177 (4.1), 124 (7.9) (Found: C, 77.43; H, 5.06; N, 11.28. $C_{16}H_{12}N_2O$ requires C, 77.40; H, 4.87; N, 11.28%).

Acylation of 6a: method 1. A mixture of **6a** (5.00 g, 21.4 mmol) and acetic anhydride (10 ml) was refluxed for 3 h. After cooling, the solid products were collected by filtration and extracted with THF at room temperature. The THF extract was concentrated and allowed to crystallize to afford **6c** (950 mg, 16%). The residue undissolved in THF was recrystallized in pyridine to give **18** (4.50 g, 76%).

5-Acetyl-11H-benzimidazo[1,2-b]isoquinolin-11-one ***6c***. Pale yellow needles, mp 225–227 °C (sublimes) (from THF); ν_{max}/cm^{-1} 3098, 3020, 2960, 1690, 1653, 1616, 1584, 1541, 1476, 1394, 1368, 1321, 1168, 1144, 1080, 748, 691; δ_H (500 MHz,

DMSO-d_6) 2.841(1H, s, CH_3), 7.445–7.510 (4H, m, Ar-CH=C and ArH), 7.762 (1H, t, *J* 8, ArH), 7.853 (1H, d, *J* 8, ArH), 8.074 (1H, d, *J* 7.5, ArH), 8.345 (1H, d, *J* 8, ArH), 8.812 (1H, *d, J* 7.5, ArH); *m/z* (%) 276 (M^+, 21.1), 234 (100), 205 (8.9), 84 (19.3) (Found: C, 73.76; H, 4.50; N, 10.07. $C_{17}H_{12}N_2O_2$ requires C, 73.90; H, 4.38; N, 10.14%).

6-Acetyl-11H-benzimidazo[1,2-b]isoquinolin-11-one ***18***. Pale yellow needles, mp 294–296 °C (decomp.) (from pyridine); ν_{max}/cm^{-1} 3180, 1680, 1600, 1540, 1480, 1361, 1300, 1144, 1122, 762, 759, 700; δ_H (500 MHz, DMSO-d_6) 2.733 (1H, s, CH_3), 7.398–7.501 (3H, m, ArH), 7.762–7.793 (2H, m, ArH), 8.187 (1H, d, *J* 7.5, ArH), 8.422 (1H, d, *J* 8, ArH), 8.615 (1H, d, *J* 7.5, ArH), 12.891 (1H, br s, NH); *m/z* (%) 276 (M^+, 100), 261 (81.3), 233 (40.8), 205 (36.5), 177 (6.0), 151 (6.3) (Found: C, 73.67; H, 4.48; N, 9.99. $C_{17}H_{12}N_2O_2$ requires C, 73.90; H, 4.38; N, 10.14%).

Acylation of 6a: method 2. To a mixture of **6a** (3.51 g, 15 mmol) and pyridine (50 ml) was added with stirring an excess amount of benzoyl chloride. The mixture was refluxed until **6a** was totally dissolved and then poured into water. The solid products were collected by filtration and were subjected to stepwise crystallization in THF to give **6d** (900 mg, 18%) and **19** (3.60 g, 71%).

In another approach, a mixture of **6a** (1.00 g, 4.27 mmol) and PhCOCl (5 ml) was refluxed for 2 h. After cooling to room temperature, the crystals were filtered out and recrystallized from THF to afford **19** (1.25 g, 86%).

5-Benzoyl-11H-benzimidazo[1,2-b]isoquinolin-11-one ***6d***. Golden needles, mp 282–284 °C (decomp.) (from THF); ν_{max}/cm^{-1} 3060, 1706, 1668, 1640, 1608, 1598, 1480, 1380, 1278, 1238, 956, 758, 740, 728; δ_H (500 MHz, DMSO-d_6) 6.570 (1H, d, *J* 8, Ar-CH=C), 7.261–7.751 (11H, m, ArH), 8.509 (1H, d, *J* 8, ArH), 8.841 (1H, d, *J* 8, ArH); *m/z* (%) 338 (M^+, 3.7), 337 (M − 1, 6.1), 308 (5.5), 279 (3.6), 105 (100) (Found: C, 78.10; H, 4.07; N, 8.12. $C_{22}H_{14}N_2O_2$ requires C, 78.09; H, 4.17; N, 8.28%).

6-Benzoyl-11H-benzimidazo[1,2-b]isoquinolin-11-one ***19***. Bright yellow needles, mp 308–310 °C (decomp.) (from THF); ν_{max}/cm^{-1} 3290, 3060, 1680, 1608, 1580, 1540, 1480, 1450, 1321, 1150, 1080, 762, 746, 700; δ_H (500 MHz, DMSO-d_6) 7.085–7.698 (11H, m, ArH), 8.354 (1H, d, *J* 6, ArH), 8.650 (1H, d, *J* 6, ArH), 12.688 (1H, br s, NH); *m/z* (%) 338 (M^+, 100), 309 (4.0), 281 (4.6), 276 (9.0), 261 (19.3), 251 (10.5), 233 (16.3), 205 (14.0), 105 (7.3) (Found: C, 77.95; H, 4.28; N, 8.10. $C_{22}H_{14}N_2O_2$ requires C, 78.09; H, 4.17; N, 8.28%).

Allylation of 6a. To a solution of **6a** (468 mg, 2 mmol) and NaOMe (4 mmol) in MeOH–THF (10 ml, 1 : 1, v/v) was added an excess amount of allyl chloride. The solution was treated in a similar manner as in the methylation of **6a** described above. At the end of the reaction, the solvents were evaporated and the residue extracted with benzene. The benzene solution was passed through a short silica gel column and the column was washed with a small amount of benzene. The combined benzene solution was dried and the solvent was evaporated *in vacuo* to afford the oily product **20** (540 mg, 86%), which solidified on standing.

In another approach, to a mixture composed of **6a** (468 mg, 2 mmol) in THF (10 ml), aqueous NaOH (10%, 6 ml) and a catalytic amount of TEBA was added with stirring at room temperature an excess amount of allyl chloride. The mixture was continuously stirred until the red color faded. The reaction mixture was extracted with benzene and the extracts were treated as above to afford **20** (500 mg, 80%).

6,6-Diallyl-11H-benzimidazo[1,2-b]isoquinolin-11-one ***20***. Colorless prisms from petroleum ether (bp 60–90 °C)–ethyl acetate, mp 87–89 °C; ν_{max}/cm^{-1} 3090, 2990, 2910, 1730, 1660, 1640, 1600, 1538, 1478, 1446, 1368, 1352, 920, 752, 738, 700; δ_H (500 MHz) 2.994 (2H, dd, *J* 7, 13, 2 × 1/2 -CH_2-), 3.398 (2H, dd, *J* 7, 13, 2 × 1/2 -CH_2-), 4.693 (2H, d, *J* 10, 2 × 1/2 =CH_2), 4.787 (2H, d, *J* 17, 2 × 1/2 =CH_2), 5.116 (2H, ddt, *J* 10, 17, 7, 2 × =CH–C), 7.426–7.474 (2H, m, ArH), 7.552 (1H, t, *J* 7.5, ArH), 7.679 (1H, d, *J* 8, ArH), 7.801 (1H, t, *J* 8, ArH), 7.852 (1H, d, *J* 7.5, ArH), 8.421 (1H, d, *J* 7.5, ArH), 8.463 (1H, d, *J* 8, ArH); *m/z* (%) 314 (M^+, 9.8), 274 (20.4), 273 (100), 272 (18.4), 271 (35.1), 245 (13.2) (Found: C, 80.15; H, 5.63; N, 8.99. $C_{21}H_{18}N_2O$ requires C, 80.23; H, 5.77; N, 8.91%).

Isolations of the intermediate products in the syntheses. The reaction conditions are described in the text and the physical and spectral data for the intermediate products are as follows.

α-(Naphth[1,2-d]oxazol-2-yl)-o-toluic acid ***14***. Colorless needles from petroleum ether (bp 60–90 °C)–ethyl acetate, mp 178–180 °C; ν_{max}/cm^{-1} 3000 (broad), 2750, 2600, 1712, 1600, 1580, 1564, 1482, 1380, 1248, 1234, 1138, 802, 744; δ_H (60 MHz, DMSO-d_6) 4.89 (2H, s, CH_2), 7.2–8.6 (10H, m, ArH); *m/z* (%) 303 (M^+, 42.7), 285 (100), 257 (28.9), 228 (16.0), 114 (14.7), 89 (12.3) (Found: C, 75.21; H, 4.29; N, 4.79. $C_{19}H_{13}NO_3$ requires C, 75.24; H, 4.32; N, 4.62%).

α-([1,3]Benzothiazol-2-yl)-o-toluic acid ***16***. Colorless needles, mp 197–198.5 °C (sublimes) (from HOAc); ν_{max}/cm^{-1} 3050, 2860, 2750, 2580, 2460, 1698, 1600, 1514, 1454, 1436, 1316, 1298, 1254, 1238, 780, 760; δ_H (60 MHz, DMSO-d_6) 4.89 (2H, s, CH_2), 7.1–8.3 (8H, m, ArH), 12.85 (1H, br s, OH); *m/z* (%) 269 (M^+, 30.1), 252 (18.8), 251 (100), 224 (20.3), 223 (44.5), 222 (16.7), 149 (11.4) (Found: C, 66.62; H, 4.00; N, 5.13. $C_{15}H_{11}NO_2S$ requires C, 66.89; H, 4.12; N, 5.20%).

N-Phenyl-2-homophthalimidobenzamide ***24***.‡ Colorless needles, mp 200.5–201.5 °C (from acetone); ν_{max}/cm^{-1} 3280, 3120, 3050, 2900, 1706, 1662, 1600, 1530, 1486, 1438, 1372, 1316, 1260, 1244, 760, 738, 696; δ_H (60 MHz, DMSO-d_6) 4.21 (2H, s, CH_2), 6.8–8.3 (13H, m, ArH), 9.95 (1H, br s, NH); *m/z* (%) 263 (M − NPh, 93.9), 235 (66.5), 207 (100), 179 (36.6), 89 (49.2) (Found: C, 74.12; H, 4.57; N, 7.85. $C_{22}H_{16}N_2O_3$ requires C, 74.15; H, 4.53; N, 7.86%).

α-[N-(2-Hydroxynaphthalenyl)aminocarbonyl]-o-toluic acid ***31***. Colorless needles, mp 224–225 °C (decomp.) (from HOAc); ν_{max}/cm^{-1} 3250 (broad), 3050, 2620, 1690, 1621, 1538, 1520, 1438, 1278, 818, 750, 744; δ_H (60 MHz, DMSO-d_6) 4.30 (2H, s, CH_2), 7.0–8.1 (10H, m, ArH), 9.71 (1H, br s, NH); *m/z* (%) 321 (M^+, 1.5), 303 (29.7), 285 (51.0), 257 (14.0), 228 (7.4), 159 (100), 130 (52.4), 118 (53.7), 90 (64.6) (Found: C, 71.02; H, 6.55; N, 4.33. $C_{19}H_{15}NO_4$ requires C, 71.02; H, 6.63; N, 4.36%).

2-[2-(2-Carboxyphenyl)acetamido]benzoic acid ***32***. Colorless needles, mp 188–189 °C (from HOAc); ν_{max}/cm^{-1} 3380, 3320, 3000 (broad), 2620, 2500, 1674 (broad), 1600, 1584, 1520, 1444, 1300, 1260, 762, 736; δ_H (60 MHz, DMSO-d_6) 4.12 (2H, s, CH_2), 6.9–7.7 (5H, m, ArH), 7.8–8.1 (2H, m, ArH), 8.92 (1H, d, *J* 8, ArH), 10.92 (1H, br s, OH); *m/z* (%) 299 (M^+, 0.5), 281 (3.9), 263 (6.6), 207 (6.0), 137 (55.9), 119 (79.9), 118 (85.7), 92 (51.9), 90 (100) (Found: C, 64.34; H, 4.44; N, 4.75. $C_{16}H_{13}NO_5$ requires C, 64.21; H, 4.38; N, 4.68%).

2-Homophthalimidobenzoic acid ***33a***.§ Light yellow prisms, mp 228.5–229.5 °C (decomp.) (from HOAc); ν_{max}/cm^{-1} 3050, 2930, 2630, 2580, 2520, 1718, 1670 (broad), 1600, 1489, 1460, 1305, 1269, 1242, 752, 745; δ_H (60 MHz, DMSO-d_6) 4.15 (2H, s, CH_2), 7.1–8.3 (8H, m, ArH); *m/z* (%) 281 (M^+, 16.3), 263 (80.1), 237 (23.5), 236 (64.2), 235 (47.9), 209 (15.2), 208 (28.1), 207 (48.3), 179 (14.9), 118 (71.8), 90 (100), 89 (70.9) (Found: C, 68.44; H, 3.96; N, 5.00. $C_{16}H_{11}NO_4$ requires C, 68.32; H, 3.94; N, 4.98%).

‡ IUPAC name: *N*-phenyl-2-[1,3-dioxo-3,4-dihydroisoquinolin-2(1*H*)-yl]benzamide.

§ IUPAC name: 2-[1,3-dioxo-3,4-dihydroisoquinolin-2(1*H*)-yl]benzoic acid.

Photoinduced cycloaddition reactions of 4a and 5 with electron deficient alkenes

General procedures for the preparative photolyses. A solution of **4a** or **5** (3 mmol) and an excess amount of alkene (2 ml for **35** and **38**; 1.73 g for **F** and **M**) in benzene (60 ml) was placed in three glass tubes (20 ml each) and purged with dry argon for 30 min. The solutions were then irradiated with a 500 W medium pressure mercury lamp through a cutoff light filter (aqueous sodium nitrate for $\lambda > 334$ nm and aqueous sodium nitrite for $\lambda > 400$ nm) at room temperature under continuous argon purging. At the end of the reaction (TLC monitoring), the solvent was removed *in vacuo* and the residue was separated by flash chromatography on a silica gel column with petroleum ether (bp 60–90 °C)–ethyl acetate as eluents to afford the cycloadducts as a mixture of stereoisomers, which was subjected to ^{1}H NMR (500 MHz) measurement for determination of the product ratio. The reaction time, the total yield and the product ratio are listed in Table 2. The pure samples of the isomers were obtained by using the procedures described as follows.

Irradiation of 4a with acrylonitrile (35). The mixture of **36** and **37** was subjected to stepwise crystallization from ethyl acetate to give pure samples of the two isomers.

(1S,2aR,13bS*)-1,2,9,13b-Tetrahydro-9-oxo-[1,3]benzoxazolo[3,2-b]cyclobuta[c]isoquinoline-1-carbonitrile* ***36***. Colorless prisms, mp 256–257 °C; ν_{max}/cm^{-1} 3030, 2995, 2220, 1655, 1595, 1477, 1399, 1300, 1270, 1229, 900, 750, 685; δ_H (500 MHz, DMSO-d_6) 2.822 (1H, dt, *J* 13, 4, 1/2H^{3}H^4), 3.154 (1H, dd, *J* 10, 13, 1/2H^{3}H^4), 3.417 (1H, ddd, *J* 3, 4, 10, H^2), 4.737 (1H, br, H^1), 7.058 (1H, t, *J* 7.5, ArH), 7.149 (2H, d, ArH), 7.550 (1H, t, *J* 7.5, ArH), 7.613 (1H, d, *J* 7.5, ArH), 7.278 (1H, t, *J* 7.5, ArH), 7.800 (1H, d, *J* 7.5, ArH), 8.117 (1H, d, *J* 7.5, ArH); *m*/*z* (%) 288 (M$^+$, 1.0), 273 (1.6), 235 (100), 207 (7.0), 179 (6.7), 178 (9.7), 156 (8.1), 152 (6.7), 133 (5.6) (Found: C, 74.88; H, 4.00; N, 9.55. $C_{18}H_{12}N_2O_2$ requires C, 74.99; H, 4.20; N, 9.72%).

(1R,2aR,13bS*)-1,2,9,13b-Tetrahydro-9-oxo-[1,3]benzoxazolo[3,2-b]cyclobuta[c]isoquinoline-1-carbonitrile* ***37***. Colorless needles, mp 221–222 °C; ν_{max}/cm^{-1} 3020, 2900, 2210, 1661, 1592, 1475, 1385, 1282, 1225, 755, 691; δ_H (500 MHz) 2.855 (1H, t, *J* 12, 1/2 H^{3}H^4), 3.004 (1H, ddd, *J* 5, 7, 12, 1/2 H^{3}H^4), 3.903 (1H, ddd, *J* 7, 9, 12, H^2), 4.471 (1H, dd, *J* 5, 9, H^1), 6.925 (1H, d, *J* 8, ArH), 7.028 (1H, t, *J* 7.5, ArH), 7.081 (1H, t, *J* 7.5, ArH), 7.436 (1H, d, *J* 8, ArH), 7.545 (1H, t, *J* 7.5, ArH), 7.694 (1H, t, *J* 7.5, ArH), 7.939 (1H, d, *J* 7.5, ArH), 8.347 (1H, d, *J* 8, ArH); *m*/*z* (%) 288 (M$^+$, 3.7), 273 (11.7), 235 (100), 207 (5.0), 179 (5.3), 178 (6.8), 169 (6.5), 156 (8.3), 152 (5.0), 133 (6.8) (Found: C, 74.96; H, 4.41; N, 9.78. $C_{18}H_{12}N_2O_2$ requires C, 74.99; H, 4.20; N, 9.72%).

Irradiation of 4a with methyl acrylate (38). The mixture of **39** and **40** was subjected to stepwise crystallization from petroleum ether (bp 60–90 °C)–ethyl acetate to give pure samples of the two isomers.

Methyl (1S,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo[1,3]-benzoxazolo[3,2-b]cyclobuta[c]isoquinoline-1-carboxylate* ***39***. Colorless needles, mp 140–142 °C; ν_{max}/cm^{-1} 3040, 2980, 2930, 1718, 1663, 1595, 1478, 1395, 1332, 1289, 1218, 749, 690; δ_H (500 MHz) 2.915–2.960 (3H, m, H^2, H^3 and H^4), 3.863 (3H, s, CO_2CH_3), 4.596 (1H, br, H^1), 6.942 (1H, d, *J* 7.5, ArH), 7.012 (1H, t, *J* 7.5, ArH), 7.088 (1H, t, *J* 7.5, ArH), 7.355 (1H, d, *J* 7.5, ArH), 7.448 (1H, t, *J* 7.5, ArH), 7.592 (1H, t, *J* 7.5, ArH), 7.910 (1H, d, *J* 7.5, ArH), 8.284 (1H, d, *J* 7.5, ArH); *m*/*z* (%) 321 (M$^+$, 0.6), 262 (2.3), 235 (100), 207 (7.1), 179 (6.3), 178 (8.8), 152 (5.1), 133 (2.2) (Found: C, 71.03; H, 4.79; N, 4.42. $C_{19}H_{15}NO_4$ requires C, 71.02; H, 4.71; N, 4.36%).

Methyl (1R,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo[1,3]-benzoxazolo[3,2-b]cyclobuta[c]isoquinoline-1-carboxylate* ***40***. Colorless plates, mp 169–170 °C; ν_{max}/cm^{-1} 3030, 2910, 1730, 1659, 1592, 1479, 1390, 1269, 1202, 1165, 1031, 757, 742, 690; δ_H (500 MHz) 2.696 (1H, ddd, *J* 4, 8, 12, 1/2 H^{3}H^4), 3.025 (1H, t, *J* 12, 1/2 H^{3}H^4), 3.512 (3H, s, CO_2CH_3), 3.887 (1H, ddd, *J* 8, 9, 12, H^2), 4.591 (1H, dd, *J* 4, 9, H^1), 6.927 (1H, d, *J* 7.5, ArH), 7.009 (1H, t, *J* 7.5, ArH), 7.071 (1H, t, *J* 7.5, ArH), 7.144 (1H, d, *J* 7.5, ArH), 7.440 (1H, t, *J* 7.5, ArH), 7.515 (1H, t, *J* 7.5, ArH), 7.951 (1H, d, *J* 7.5, ArH), 8.307 (1H, d, *J* 7.5, ArH); *m*/*z* (%) 321 (M$^+$, 6.0), 306 (9.4), 273 (11.7), 262 (6.5), 236 (20.3), 235 (100), 207 (5.5), 179 (5.0), 178 (6.4), 152 (3.8), 133 (2.7) (Found: C, 71.03; H, 4.93; N, 4.21. $C_{19}H_{15}NO_4$ requires C, 71.02; H, 4.71; N, 4.36%).

Irradiation of 5 with acrylonitrile (35). The mixture of **40** and **41** was subjected to stepwise crystallization from petroleum ether (bp 60–90 °C)–acetone to give pure samples of the two isomers.

(1S,2aR,13bS*)-1,2,9,13b-Tetrahydro-9-oxo[1,3]benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1-carbonitrile* ***41***. Colorless prisms, mp 191.5–192.5 °C; ν_{max}/cm^{-1} 3090, 3020, 2998, 2900, 2210, 1650, 1458, 1352, 1300, 1190, 745, 690; δ_H (500 MHz) 2.935 (1H, ddd, *J* 3, 5, 12, 1/2 H^{3}H^4), 3.131 (1H, dt, *J* 10, 5, H^2), 3.257 (1H, dd, *J* 10, 12, 1/2 H^{3}H^4), 4.573 (1H, br, H^1), 7.160 (1H, t, *J* 7.5, ArH), 7.221 (1H, t, *J* 7.5, ArH), 7.288 (1H, d, *J* 7.5, ArH), 7.325 (1H, d, *J* 7.5, ArH), 7.505 (1H, t, *J* 7.5, ArH), 7.632 (1H, t, *J* 7.5, ArH), 8.164 (1H, d, *J* 8, ArH), 8.322 (1H, d, *J* 8, ArH); *m*/*z* (%) 304 (M$^+$, 0.4), 276 (1.8), 275 (3.2), 251 (100), 223 (19.2), 222 (10.2), 195 (2.2), 156 (5.3), 149 (5.3), 128 (6.4) (Found: C, 70.90; H, 4.09; N, 9.25. $C_{18}H_{12}N_2OS$ requires C, 71.03; H, 3.97; N, 9.20%).

(1R,2aR,13bS*)-1,2,9,13b-Tetrahydro-9-oxo[1,3]benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1-carbonitrile* ***42***. Colorless needles, mp 217–218 °C; ν_{max}/cm^{-1} 3030, 2980, 2210, 1645, 1458, 1375, 1245, 758, 749, 687; δ_H (500 MHz) 2.992 (1H, ddd, *J* 2, 7, 11, 1/2 H^{3}H^4), 3.097 (1H, t, *J* 11, 1/2 H^{3}H^4), 3.727 (1H, ddd, *J* 7, 9, 11, H^2), 4.496 (1H, dd, *J* 2, 9, H^1), 7.134 (1H, t, *J* 7.5, ArH), 7.214–7.283 (2H, m, ArH), 7.384 (1H, d, *J* 7.5, ArH), 7.553 (1H, t, *J* 7.5, ArH), 7.696 (1H, t, *J* 7.5, ArH), 8.350 (1H, d, *J* 8, ArH), 8.405 (1H, d, *J* 8, ArH); *m*/*z* (%) 304 (M$^+$, 1.0), 276 (2.2), 275 (3.7), 251 (100), 223 (16.7), 222 (8.0), 190 (2.4), 156 (5.4), 149 (6.3), 128 (5.3) (Found: C, 71.04; H, 3.97; N, 9.24. $C_{18}H_{12}N_2OS$ requires C, 71.03; H, 3.97; N, 9.20%).

Irradiation of 5 with methyl acrylate (38). The mixture of **43** and **44** was crystallized from petroleum ether (bp 60–90 °C)–ethyl acetate to give a pure sample of **43**. The mother liquor was carefully chromatographed on a silica gel column with petroleum ether (bp 60–90 °C)–ethyl acetate as eluents. The first half of the fractions gave a further crop of **43**, the second half of the fractions afforded crude **44**, which contained a small amount of **43** and was recrystallized in petroleum ether (bp 60–90 °C)–ethyl acetate to give a pure sample of **44**.

Methyl (1S,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo[1,3]-benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1-carboxylate* ***43***. Colorless prisms, mp 120–122 °C; ν_{max}/cm^{-1} 3050, 2990, 2970, 2945, 1725, 1659, 1602, 1582, 1465, 1368, 1325, 1298, 1235, 1170, 764; δ_H (500 MHz) 2.842 (1H, ddd, *J* 3, 5, 12, 1/2 H^{3}H^4), 3.105 (1H, dt, *J* 10, 5, H^2), 3.170 (1H, dd, *J* 10, 12, 1/2 H^{3}H^4), 3.808 (3H, s, CO_2CH_3), 4.582 (1H, br, H^1), 7.113 (1H, t, *J* 7.5, ArH), 7.185 (1H, t, *J* 7.5, ArH), 7.228–7.254 (2H, m, ArH), 7.420 (1H, t, *J* 7.5, ArH), 7.551 (1H, t, *J* 7.5, ArH), 8.145 (1H, d, *J* 8, ArH), 8.296 (1H, d, *J* 8, ArH); *m*/*z* (%) 337 (M$^+$, 0.2), 309 (1.1), 308 (3.5), 278 (2.9), 252 (47.4), 251 (100), 250 (17.1), 223 (38.6), 222 (16.3), 115 (11.1) (Found: C, 67.65; H, 4.45; N, 4.14. $C_{19}H_{15}NO_3S$ requires C, 67.64; H, 4.48; N, 4.15%).

Methyl (1R,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo[1,3]-benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1-carboxylate* ***44***. Colorless needles, mp 119.5–120.5 °C; ν_{max}/cm^{-1} 3140, 3060, 3008, 1730, 1656, 1463, 1368, 1282, 1263, 1245, 1196, 1039, 750, 690; δ_H (500 MHz) 2.698 (1H, ddd, *J* 3, 7, 12, 1/2 H^{3}H^4), 3.237 (1H, t, *J* 12, 1/2 H^{3}H^4), 3.498 (3H, s, CO_2CH_3), 3.714 (1H, ddd, *J* 7, 9, 12, H^2), 4.586 (1H, dd, *J* 3, 9, H^1), 7.079–7.118 (2H, m,

ArH), 7.182–7.256 (2H, m, ArH), 7.426 (1H, t, *J* 7.5, ArH), 7.495 (1H, t, *J* 7.5, ArH), 8.338–8.370 (2H, m, ArH); *m/z* (%) 337 (M^+, 0.3), 308 (2.0), 278 (1.2), 252 (19.5), 251 (100), 250 (8.6), 223 (16.1), 222 (6.6), 115 (4.1) (Found: C, 67.61; H, 4.47; N, 4.15. $C_{19}H_{15}NO_3S$ requires C, 67.64; H, 4.48; N, 4.15%).

Irradiation of 5 with dimethyl fumarate (F), and dimethyl maleate (M). Flash chromatographic separation of the reaction mixture afforded **48** and a mixture of cycloadducts **45**, **46** and **47**. After determination of the total yield and product ratio of the cycloadducts, the mixture was allowed to crystallize from petroleum ether (bp 60–90 °C)–ethyl acetate. The crystals were filtered off and subjected to stepwise crystallization from petroleum ether (bp 60–90 °C)–ethyl acetate to give pure samples of **45** and **47**. The mother liquor, which mainly contained **46**, was evaporated and the residue carefully separated by chromatography on a silica gel column with petroleum ether (bp 60–90 °C)–ethyl acetate as eluents. The middle fractions gave crude **46** which was recrystallized from petroleum ether (bp 60–90 °C)–ethyl acetate to afford the analytically pure sample of **46**.

Dimethyl (1R,2R,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo-[1,3]benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1,2-dicarboxylate* ***45***. Colorless needles, mp 203–204 °C; ν_{max}/cm^{-1} 3040, 2930, 2900, 1748, 1733, 1680, 1460, 1363, 1330, 1209, 1178, 1025, 759, 739, 688; δ_H (500 MHz) 3.381 (3H, s, CO_2CH_3), 3.568 (3H, s, CO_2CH_3), 3.881 (1H, dd, *J* 9.5, 10.5, H^2), 4.152 (1H, d, *J* 10.5, H^3), 4.521 (1H, d, *J* 9.5, H^1), 7.092 (1H, t, *J* 7.5, ArH), 7.137 (1H, d, *J* 7.5, ArH), 7.188–7.231 (2H, m, ArH), 7.465 (1H, t, *J* 7.5, ArH), 7.533 (1H, t, *J* 7.5, ArH), 8.359–8.384 (2H, m, ArH); *m/z* (%) 395 (M^+, 73.7), 336 (78.3), 322 (36.4), 304 (12.5), 276 (100), 251 (6.5), 250 (10.5), 249 (16.8), 248 (37.2), 247 (11.4) (Found: C, 63.85; H, 4.36; N, 3.57. $C_{21}H_{17}NO_5S$ requires C, 63.79; H, 4.33; N, 3.54%).

Dimethyl (1S,2S,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo-[1,3]benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1,2-dicarboxylate* ***46***. Colorless prisms, mp 109–111 °C; ν_{max}/cm^{-1} 3040, 2980, 2930, 1720, 1665, 1458, 1352, 1299, 1225, 1185, 1023, 755, 739, 689; δ_H (500 MHz) 3.317 (3H, s, CO_2CH_3), 3.605 (1H, dd, *J* 7.5, 8, H^2), 3.793 (3H, s, CO_2CH_3), 3.850 (1H, d, *J* 8, H^3), 4.531 (1H, d, *J* 7.5, H^1), 7.138–7.211 (2H, m, ArH), 7.277–7.308 (2H, m, ArH), 7.445 (1H, t, *J* 7.5, ArH), 7.574 (1H, d, *J* 7.5, ArH), 7.955 (1H, d, *J* 7.5, ArH), 8.274 (1H, d, *J* 7.5, ArH); *m/z* (%) 251 (100), 223 (25.4), 222 (11.5), 113 (33.8) (Found: C, 63.77; H, 4.37; N, 3.54. $C_{21}H_{17}NO_5S$ requires C, 63.79; H, 4.33; N, 3.54%).

Dimethyl (1S,2R,2aR,13bS*)-1,2,9,13b-tetrahydro-9-oxo-[1,3]benzothiazolo[3,2-b]cyclobuta[c]isoquinoline-1,2-dicarboxylate* ***47***. Colorless needles, mp 175–177 °C; ν_{max}/cm^{-1} 3050, 2940, 1740, 1729, 1654, 1462, 1360, 1214, 1195, 1169, 1158, 752; δ_H (500 MHz) 3.290 (1H, dd, *J* 6, 10, H^2), 3.520 (3H, s, CO_2CH_3), 3.827 (3H, s, CO_2CH_3), 4.100 (1H, d, *J* 10, H^3), 4.734 (1H, d, *J* 6, H^1), 7.130 (1H, t, *J* 7.5, ArH), 7.205–7.231 (2H, m, ArH), 7.360 (1H, d, *J* 7.5, ArH), 7.464 (1H, t, *J* 7.5, ArH), 7.599 (1H, t, *J* 7.5, ArH), 8.133 (1H, d, *J* 7.5, ArH), 8.314 (1H, d, *J* 7.5, ArH); *m/z* (%) 395 (M^+, 0.2), 251 (100), 223 (24.3), 222 (11.4), 113 (45.1) (Found: C, 63.81; H, 4.38; N, 3.44. $C_{21}H_{17}NO_5S$ requires C, 63.79; H, 4.33; N, 3.54%).

Dimethyl 2-(11H-[1,3]benzothiazolo[3,2-b]isoquinolin-11-on-6-yl)butanedioate ***48***. Yellow prisms from petroleum ether (bp 60–90 °C)–acetone, mp 221–223 °C; ν_{max}/cm^{-1} 3130, 3080, 3000, 2970, 1740, 1730, 1670, 1614, 1550, 1490, 1464, 1343, 1300, 1258, 1230, 1175, 779, 768; δ_H (500 MHz) 2.737 (1H, dd, *J* 5.5, 17, 1/2CH_2), 3.591 (1H, dd, *J* 8, 17, 1/2CH_2), 3.667 (3H, s, CO_2CH_3), 3.719 (3H, s, CO_2CH_3), 4.425 (1H, br, unexchangable, CH), 7.370–7.757 (6H, m, ArH), 8.839 (1H, d, *J* 8, ArH), 9.192 (1H, d, *J* 8, ArH); *m/z* (%) 395 (M^+, 75.4), 336 (74.6), 322 (35.6), 304 (13.6), 276 (100), 251 (6.8), 250 (12.3), 249 (15.9), 248 (30.7), 247 (11.3) (Found: C, 63.86; H, 4.47; N, 3.74. $C_{21}H_{17}NO_5S$ requires C, 63.79; H, 4.33; N, 3.54%).

Crystal structure of 37

$C_{18}H_{12}N_2O_2$, $M = 288.30$. Orthorhombic, space group *Pbca* with $a = 14.488(2)$, $b = 8.605(2)$, $c = 22.048(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2748.7(9)$ Å^3, $Z = 8$, $D_c = 1.393$ g cm^{-3}. Absorption coefficient 0.093 mm^{-1}, $F(000) = 1200$. A transparent needle shaped crystal of 0.15 × 0.20 × 0.80 mm was used. Data were collected on a Siemens SHELXTL P4 diffractometer equipped with graphite-monochromated Mo-Kα radiation in the range of θ 1.85–24.99°. The structure was solved by direct method (SHELXTL version 5.0) and refined on F^2 by full-matrix least-squares method. A total of 2417 independent reflections [R(int) = 0.0365] were used in the refinement which converged with $R = 0.0573$ and $wR = 0.1412$.¶

Crystal structure of 45

$C_{21}H_{17}NO_5S$, $M = 395.42$. Monoclinic, space group $P2(1)/c$ with $a = 9.280(2)$, $b = 11.797(2)$, $c = 16.781(3)$ Å, $\alpha = 90°$, $\beta = 95.03(3)°$, $\gamma = 90°$, $V = 1830.0(6)$ Å^3, $Z = 4$, $D_c = 1.435$ g cm^{-3}. Absorption coefficient 0.211 mm^{-1}, $F(000) = 824$. A crystal of 1.50 × 0.25 × 0.18 mm was used. Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromatized Mo-Kα in the range of θ 2.11–25.97°. The structure was solved by direct method (SHELXTL version 5.0) and refined on F^2 by full-matrix least-squares method. A total of 3587 independent reflections [R(int) = 0.0185] were used in the refinement which converged with $R = 0.0478$ and $wR = 0.1235$.¶

Acknowledgements

Project supported by the National Natural Science Foundation of China (29772016) and the Natural Science Foundation of Jiangsu Province (BK97017).

¶ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/275. See http://www.rsc.org/suppdata/perkin1/1998/4147 for crystallographic files in .cif format.

References

1 See, for example, (*a*) H. L. Blewitt, *Special Topics in Heterocyclic Chemistry*, vol. 30, eds. A. Weissberger and E. C. Taylor, John Wiley, New York, 1979, pp. 117–170; (*b*) J. A. Montgomery and J. A. Secrist III, in *Comprehensive Heterocyclic Chemistry*, vol. 5, eds. A. R. Katritzky and C. W. Rees, Pergamon Press, New York, 1984, p. 680; (*c*) J. J. Kamiski and A. M. Doweyko, *J. Med. Chem.*, 1997, **40**, 427; (*d*) B. Blank, N. W. DiTullio, A. J. Krog and H. L. Saunders, *J. Med. Chem.*, 1978, **21**, 489.

2 (*a*) M. F. Sartori, A. Oken and H. E. Schroeder, *J. Org. Chem.*, 1966, **31**, 1498; (*b*) V. N. Bubnovskaya, V. A. Ol'shevskaya and F. S. Babichev, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1977, **43**, 43 (*Chem. Abstr.*, 1977, **86**, 171331p); (*c*) E. Schefczik, *Justus Liebigs Ann. Chem.*, 1969, **729**, 83.

3 (*a*) V. N. Babnovskaya and F. S. Babichev, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1971, **37**, 1024 (*Chem. Abstr.*, 1971, **76**, 34150h); (*b*) V. N. Babnovskaya, G. N. Miskevich and F. S. Babichev, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1973, **39**, 188 (*Chem. Abstr.*, 1973, **78**, 147860z); (*c*) K. W. Bentley, *Nat. Prod. Rep.*, 1992, **9**, 365; (*d*) K. W. Bentley, *Nat. Prod. Rep.*, 1993, **10**, 449.

4 M. F. Grundon, *The Alkaloids*, eds. R. H. F. Manske and R. G. A. Rodrigo, vol. XVII, Academic Press, New York, 1977, pp. 142, 183.

5 (*a*) K. Q. Ling, G. Ji, H. Cai and J. H. Xu, *Tetrahedron Lett.*, 1998, **39**, 2381; (*b*) K. Q. Ling, H. Cai, J. H. Ye and J. H. Xu, *Tetrahedron*, in press.

6 (*a*) Y. Tamura, M. Sasho, K. Nakagawa, T. Tsugoshi and Y. Kita, *J. Org. Chem.*, 1984, **49**, 473; (*b*) Y. Tamura, A. Wada, M. Sasko, K. Fukunaga, H. Maeda and Y. Kita, *J. Org. Chem.*, 1982, **47**, 4376.

7 A. Geogieva, E. Stanoeva, S. Spassov, M. Haimova, N. De Kimpe, M. Boelens, M. Keppens, A. Kemme and A. Mishnev, *Tetrahedron*, 1995, **51**, 6099 and references cited therein.
8 E. Stanoeva and M. Khaimova, *Khim. Geterotsikl. Soedin.*, 1984, 1587 (Russ.) (*Chem. Abstr.*, 1984, **102**, R148999c).
9 See, for example, M. Veda, M. Takahashi, S. Hishiki and Y. Imai, *J. Polym. Sci. Polym. Chem. Ed.*, 1979, **17**, 2459.
10 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214.
11 M. J. Frisck, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *GAUSSIAN 94, Revision B.3*, Gaussian, Inc., Pittsburgh, PA, 1995.
12 I. Fleming, *Frontier Obitals and Organic Chemical Reactions*, Wiley, Chichester, 1978.
13 D. A. Tysse and M. M. Baizer, *J. Org. Chem.*, 1974, **39**, 2819.
14 R. C. Larson, R. T. Iwamoto and R. N. Adams, *Anal. Chim. Acta*, 1961, **25**, 371.
15 D. Sazou and P. Karabinas, *Collect. Czech. Chem. Commun.*, 1987, **52**, 2132.
16 A. Weller, *Z. Phys. Chem.* (*Wiesbaden*), 1982, **133**, 193.
17 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Co., Inc., 1978, p. 314.
18 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.

Paper 8/05865B