PERKIN 1

Highly *peri*- and stereoselective intramolecular photocycloaddition and cyclisation of *N*-(1-naphthylethyl)prop-2-enamides

Shigeo Kohmoto,* Yoshiyuki Miyaji, Masaru Tsuruoka, Keiki Kishikawa, Makoto Yamamoto and Kazutoshi Yamada

*Department of Materials Technology, Faculty of Engineering, Chiba University, 1-33,
Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*

Received (in Cambridge, UK) 18th January 2001, Accepted 3rd July 2001
First published as an Advance Article on the web 9th August 2001

Control of three modes of intramolecular reactions, [2+2] and [4+2] cycloadditions, and Type-II cyclisation, is attempted in the photochemical reaction of *N*-(naphthylethyl)prop-2-enamides. The reactions are affected by the enamide substituents and the sensitisation conditions used. Acryloyl derivatives undergo [2+2] cycloaddition and Type-II cyclisation. The two reactions occur selectively depending on the sensitiser used, benzophenone sensitisation affording the [2+2] cycloadducts whereas the Type-II cyclisation products are obtained exclusively by benzene sensitisation. In contrast, photolysis of cinnamoyl derivatives results in the formation of [4+2] cycloadducts.

Introduction

Bichromophoric compounds have been investigated considerably as models for the study of key photochemical processes, especially for intramolecular energy-, electron-, or proton-transfer.[1] They may undergo different modes of photochemical reaction depending on the excited state of the chromophore involved. Control of the mode of photochemical reactions by selective excitation of one of the chromophores is interesting from both mechanistic and synthetic viewpoints. In order to carry out the above-mentioned control of the mode of photochemical reactions, either wavelength-dependent photochemical reaction[2] or selective sensitisation of chromophores may be required.

As a part of our study of *peri*- and stereoselective organic photochemical reactions,[3] we have investigated the control of three types of intramolecular reaction, *viz.* [2+2] and [4+2] cycloadditions and Type-II cyclisation in the photoreaction of *N*-(naphthylethyl)prop-2-enamide derivatives **1** based on selective sensitisation and substituent effect. One of the chromophores of **1**, the naphthalene π-system, is well known to act as a 2π or 4π unit in [2+2] or [4+2] photocycloadditions with alkenes, respectively,[4] and also to undergo [3+2] photocycloaddition at the 1,8- and 4,5-positions of the naphthalene ring substituted with electron-withdrawing groups.[5] The other chromophore, the acrylamide moiety, reacts not only with the naphthalene moiety as a 2π unit, but also undergoes Type-II cyclisation *via* hydrogen abstraction by olefinic carbon.[6] Therefore, some different intramolecular photochemical reactions could occur in this system.

Results and discussion

Photoreaction of acryloyl derivatives

Irradiation of compounds **1a**–**c** in benzene with a high-pressure Hg lamp through Pyrex filter ($\lambda > 280$ nm) gave two types of products, [2+2] photocycloadducts, **2a**–**c**, and azetidin-2-ones, **3a**–**c** (for **3a** as a diastereomeric mixture) derived from the Type-II cyclisation (Scheme 1). The product ratio **2** : **3** depended on irradiation time. Prolonged irradiation gave a higher yield of **3** and a lower yield of **2**. The results indicated the presence of a retro-[2+2] photocycloaddition[7] under the reaction conditions.

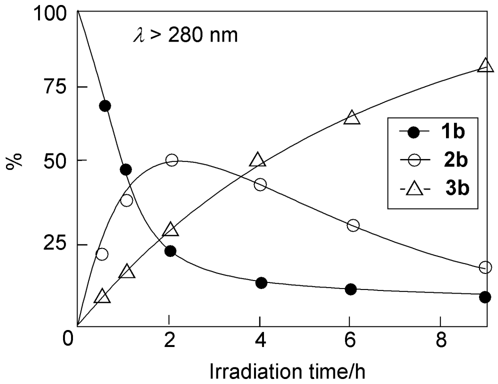
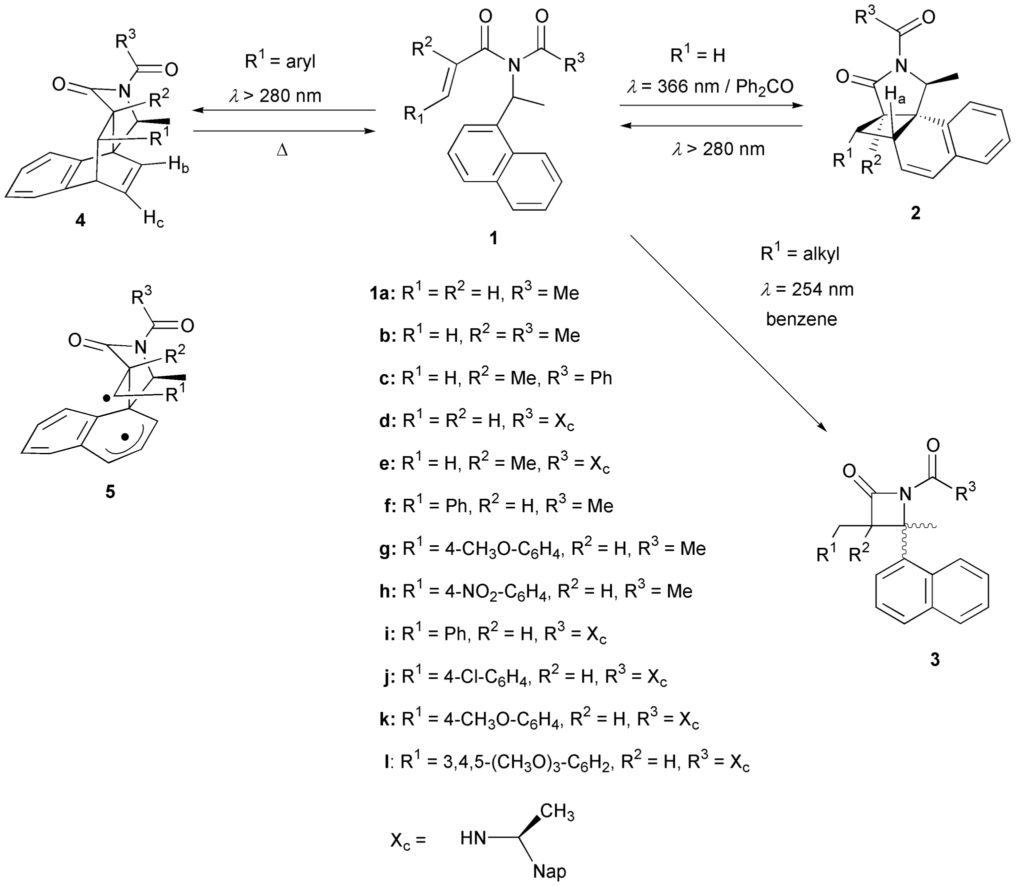


Fig. 1 Irradiation time-dependent product ratios of the photochemical reaction of **1b** in benzene-d_6 irradiated by a high-pressure Hg lamp through Pyrex.

In order to confirm this, the progress of the reaction was monitored by ^{1}H NMR spectroscopy. Fig. 1 shows the results for **1b** in benzene-d_6. In the early stage of the reaction, both **2b** and **3b** were formed, but after 2 h, the amount of **2b** started to decrease, whereas the amount of **3b** continued to increase, which indicated that the formation of **3b** was irreversible. Further confirmation of a retro-[2+2] photocycloaddition of **2b** to **1b** was achieved when **2b** was irradiated in benzene-d_6 and the formation of **1b** was observed (Fig. 2). In order to carry out the photoreaction selectively, photosensitisation of the reaction was examined. Since **1b** has almost no absorption at 366 nm (absorbance < 0.05) even at the initial concentration (6.7×10^{-2} M), no reaction was observed when the irradiation was carried out through combination filters (cut-off range; 340 nm $< \lambda < 380$ nm). In the direct irradiation through Pyrex filter, the emitted light of 313 nm from a high-pressure Hg lamp should be utilised for the photoreaction. Fig. 3 shows the UV spectra of **1b** and **2b**. However, addition of benzophenone as a sensitiser afforded **2b** without the formation of **3b** (entry 3 in Table 1). In contrast, benzene sensitisation of the reaction of **1b** (irradiation of **1b** by a low-pressure Hg lamp, sample in benzene) resulted in the exclusive formation of **3b** accompanied by a tiny amount of **2b** which was subsequently transformed to **3b** *via* **1b** (Fig. 4). Thus, complete conversion of **1b** to **3b** was accomplished. It is

DOI: 10.1039/b100678i



Scheme 1

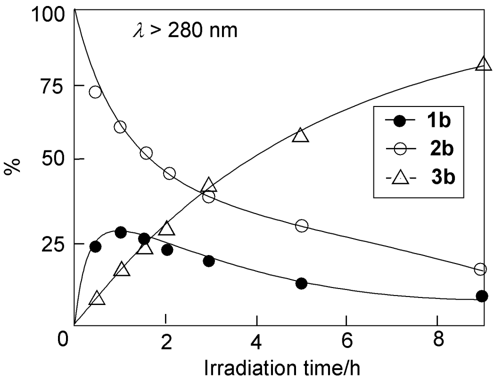


Fig. 2 Irradiation time-dependent product ratios of the photochemical reaction of **2b** in benzene-d_6 irradiated by a high-pressure Hg lamp.

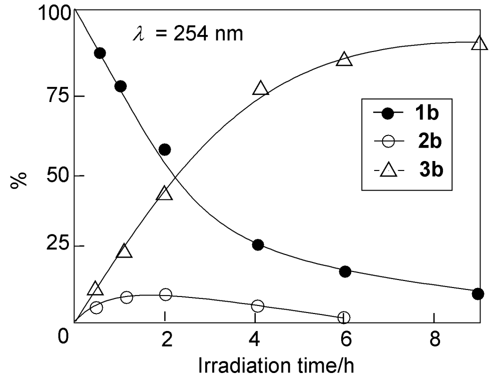


Fig. 4 Irradiation time-dependent product ratios of the photochemical reaction of **1b** in benzene-d_6 irradiated by a low-pressure Hg lamp.

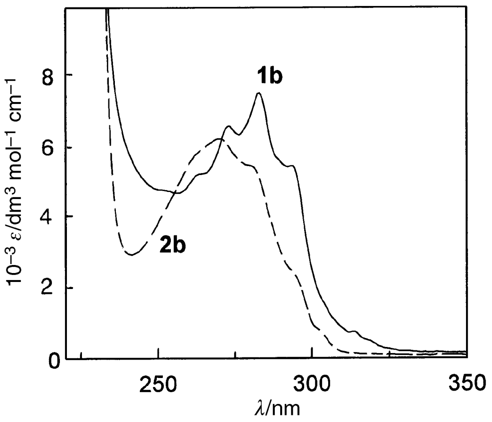


Fig. 3 The UV spectra of **1b** and **2b** in acetonitrile.

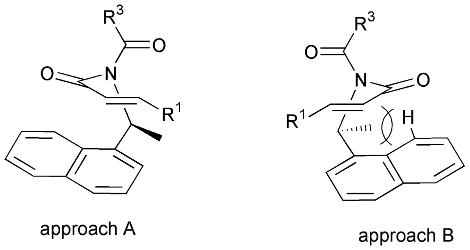
noteworthy that the Type-II cyclisation was the unique reaction observed in benzophenone sensitisation of acrylamide with an *N*-1-phenylethyl instead of an *N*-1-naphthylethyl group.[8] However, in the present system, we did not observe any Type-II cyclisation by benzophenone sensitisation; instead, the [2+2] cycloaddition was the unique reaction. Benzophenone might sensitise the naphthyl group rather than the enone moiety, whereas benzene might sensitise the enone more efficiently than the naphthalene moiety for the Type-II cyclisation.

In order to apply this reaction for diastereoselective [2+2] photocycloaddition, *p*-methoxyacetophenone-sensitised reactions of chiral molecules, **1d** and **1e**, were carried out. *p*-Methoxyacetophenone was chosen as an easily separable sensitiser from the products by silica gel chromatography. Single diastereomers, **2d** and **2e**, were obtained in 78 and 82% yield from **1d** and **1e**, respectively. Their stereochemistry was deduced from NOESY spectroscopy. The NOE relation between the methyl of the pyrrolidin-2-one and the proton H_a

Table 1 Isolated product yields in the intramolecular photochemical reaction of **1**

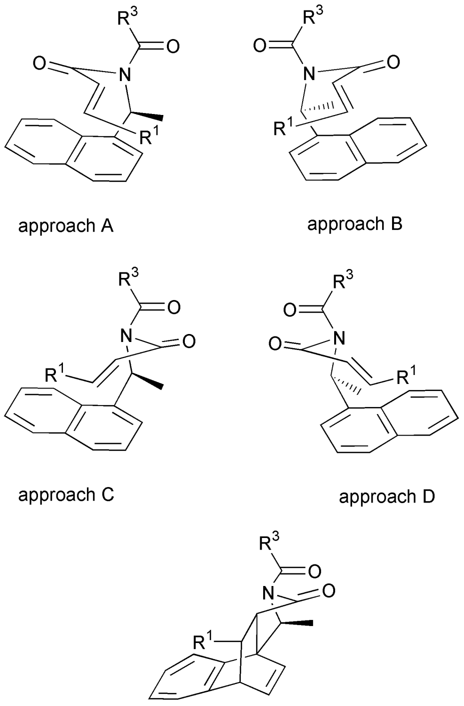
Entry	Compd	R^1	R^2	R^{3a}	Time (*t*/h)	**2** (%)	**3** (%)	**4** (%)
1	**1a**	H	H	Me	8	19	59^b	0
2	**1b**	H	Me	Me	5	58	23	0
3					0.5^c	82	0	0
4	**1c**	H	Me	Ph	8	47	46	0
5	**1d**	H	H	X_c	1^d	78	0	0
6	**1e**	H	Me	X_c	1^d	82	0	0
7	**1f**	Ph	H	Me	1.5	0	0	94
8	**1g**	$4\text{-}CH_3OC_6H_4$	H	Me	1.5	0	0	96
9	**1h**	$4\text{-}NO_2C_6H_4$	H	Me	1.5	0	0	97
10	**1i**	Ph	H	X_c	1.5	0	0	92
11	**1j**	$4\text{-}ClC_6H_4$	H	X_c	1.5	0	0	75
12	**1k**	$4\text{-}CH_3OC_6H_4$	H	X_c	1.5	0	0	86
13	**1l**	$3,4,5\text{-}(CH_3O)_3C_6H_2$	H	X_c	1.5	0	0	97

[a] X_c = (*S*)-1-(1-naphthyl)ethylamino. [b] Diastereomer ratio; *syn*-**3a** : *anti*-**3a** = 4 : 5. [c] With one molar equiv. of benzophenone as sensitizer (340 nm < λ < 380 nm). [d] With one molar equiv. of *p*-methoxyacetophenone as sensitizer.



approach A approach B

Fig. 5 Orientation of the double bond to the naphthalene moiety in [2+2] cycloaddition of **1**.



approach A approach B

approach C approach D

6

Fig. 6 Orientation of the double bond to the naphthalene moiety in [4+2] cycloaddition of **1**.

established their relationship to be *syn*. The diastereoselectivity was governed by the steric hindrance between the hydrogen atom at the *peri*-position of the naphthalene ring and the methyl of the 1-naphthylethyl group. In the two approaches of the enone moiety to the naphthalene, approach **A** is preferable to avoid the above-mentioned steric hindrance (Fig. 5).

Photoreaction of cinnamoyl derivatives

It is reported that substitution on the β carbon of α,β-unsaturated amides inhibits the hydrogen abstraction by the β carbon under photolysis, causing no photochemical reaction to occur.[9] We did not observe the Type-II photocyclisation in our cinnamoyl amide series, whereas we did find [4+2] cycloaddition. Irradiation of a benzene solution of **1f–l** by a high-pressure Hg lamp through a Pyrex filter afforded the corresponding [4+2] cycloadducts, **4f–l** in 75–97% yield as a single diastereomer. Benzophenone and benzene sensitisation also resulted in the formation of [4+2] cycloadducts with no trace of the corresponding [2+2] or Type-II cyclisation products. Their stereochemistries were deduced by NOESY spectroscopy. For the cycloadduct **4i**, it is confirmed that the methyl group is located *cis* to R^2 (=H) and H_b, and away from the *peri*-position of the naphthalene ring from the NOE relations between the methyl and R^2, the methyl and H_b, and R^2 and H_b. The stereochemistry of the phenyl group (=R^1) was determined to be *anti* to the adjacent carbonyl from the NOE relation between H_c and the phenyl (R^1) proton. Among four possible approaches (**A–D**) of the cinnamoyl double bond to the naphthalene ring for the [4+2] cycloaddition, the cycloaddition proceeded *via* approach **A** (Fig. 6). It is easily understood that approaches **B** and **D** are unfavourable due to the steric repulsion between the methyl group and the hydrogen atom at the *peri*-position of the naphthalene moiety. Approach **C** seems to be sterically unfavourable compared with approach **A**. The heat of formation calculated by PM3 for **4c** is 1.1 kcal mol^{-1}† smaller than that for **6** which might be derived *via* approach **C** though it was not obtained. Since a [4+2] cycloaddition is photochemically forbidden if the reaction is supra, supra, the reaction should be stepwise. The biradical **5** might be the intermediate in which the stereochemistry of the carbon substituted with the phenyl group should be lost. Including the stereochemistry of the phenyl group, eight possible diastereomers might be formed if there is no such stereocontrol.

In our cinnamoyl amides, only one diastereomer was obtained out of eight possible ones. In order to investigate how the *Z–E* configuration of the cinnamoyl double bond affects the stereochemistry of the phenyl substituent, the progress of the reaction of **1l** was monitored by ^1H NMR spectroscopy in benzene-d_6. We found that a *Z–E* isomerisation of **1l** occurred in addition to the [4+2] cycloaddition. However, the resulting [4+2] cyloadduct **4l** had the stereochemistry of the phenyl *anti* to the adjacent carbonyl. For further confirmation of this fact, the isolated *cis*-**1l** was irradiated under the same conditions. The same [4+2] cycloadduct **4l** was obtained as a single diastereomer. Since the radical site loses its original stereochemical information, the same biradical intermediate should be formed from both (*E*)-**1l** and (*Z*)-**1l**, which results in the formation of the same sterically favourable cycloadduct. A

---

† 1 cal = 4.184 J.

thermal retro-[4+2] cycloaddition of the [4+2] adducts was observed upon heating. The half-life of **1g** was determined to be 3.0 h at 150 °C in $CDCl_3$ in a sealed tube by monitoring with ^1H NMR spectroscopy.

For the formation of the [4+2] cycloadduct, the sensitised photorearrangement of the [2+2] to [4+2] cycloadduct was reported.[10] However, the possibility of this kind of rearrangement may be eliminated in our case, since the [2+2] cycloadducts obtained from acryloyl derivatives were stable under irradiation with a sensitiser. Recently, photocycloaddition of 2-morpholinoacrylonitrile to substituted 1-acenaphthones was reported to give [2+2] or [4+2] cycloadducts depending on the position of the substituent at the naphthalene ring either at C-2 or C-4.[11] The *peri*-selectivity was explained by steric hindrance encountered in a proposed exciplex intermediate. Again, such a steric effect is not the controlling factor in the present system.

Though the controlling factor to differentiate the mode of reaction, either the [2+2] or [4+2] cycloaddition, is not yet clear, it is possible to carry out three types of photochemical reaction selectively in *N*-(naphthylethyl)prop-2-enamides. *peri*-Selectivity of either the [2+2] or [4+2] cycloaddition is dependent on the substituents of the enone moiety, acryloyl or cinnamoyl. In acryloyl derivatives, two types of reactions are possible, but both reactions can be induced selectively by sensitisation. Stereoselectivity of the [2+2] and [4+2] photocycloadditions has been controlled perfectly.

Experimental

General

Mps were determined on a Yanaco MP-S3 apparatus and are uncorrected. IR spectra were recorded on a Hitachi I-2000 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL EX-90, FX-270 and GSX-400 spectrometers for samples in $CDCl_3$ with Me_4Si as an internal standard; *J*-values are given in Hz. Mass spectra were measured with an Hitachi RMU-7M mass spectrometer. Optical rotations were measured on a Horiba SEPA 300 polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Elemental analyses were performed on a Perkin-Elmer 240 analyser. Reaction solutions were concentrated on a rotary evaporator at 10–15 mmHg. Chromatographic separation was accomplished by flash column chromatography on silica gel (Fuji gel BW 200; 150–350 mesh) and further purification was carried out by a preparative HPLC run; column Merck Si 60 (7 µm; 10 × 250 mm), hexane–ethyl acetate as eluent. All solvents were freshly distilled and stored over 4 Å molecular sieves.

General procedure for the preparation of *N*-(1-naphthylethyl)-prop-2-enamides 1

Achiral enamides were prepared as follows. To a solution of the carboxamide, prepared from (±)-1-(1-naphthyl)ethylamine and acryloyl chloride or cinnamoyl chloride (2 mmol), in benzene (30 cm^3) was added triethylamine (1.2 equiv.) at room temperature. To the resulting solution was added dropwise acetyl chloride or benzoyl chloride (1.2 equiv.). The resulting mixture was refluxed overnight and was then quenched with saturated aq. $NaHCO_3$ (30 cm^3) and washed successively with 1 M hydrochloric acid (30 cm^3) and brine (30 cm^3). The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. The products were separated by column chromatography on silica gel [ethyl acetate–hexane (1 : 4)]. Crystalline compounds were recrystallised from ethyl acetate–hexane (≈1 : 7).

Chiral enamides, **1d**, **1e**, **1i**, **1j**, **1k** and **1l**, were prepared as reported[12] from *N*,*N*′-bis[(*S*)-1-naphthylethyl]carbodiimide with the appropriate carboxylic acids.

***N*-(1-Naphthylethyl)-*N*-prop-2-enoylacetamide 1a.** Colourless oil (65%); ν_{max} (film)/cm^{-1} 1690 (C=O) and 1616 (C=C); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.89 (3 H, d, *J* 6.9), 2.19 (3 H, s), 5.52 (1 H, dd, *J* 10.1 and 1.5), 6.04 (1 H, dd, *J* 17.0 and 1.5), 6.24 (1 H, dd, *J* 17.0 and 10.1), 6.52 (1 H, q, *J* 6.9), 7.41–7.54 (3 H, m), 7.63–7.68 (1 H, m) and 7.75–7.91 (3 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 18.02 (q), 26.28 (q), 50.42 (d), 122.59 (d), 124.50 (d), 125.27 (d), 125.93 (d), 126.29 (d), 128.35 (d), 128.58 (d), 128.88 (t), 130.70 (s), 131.75 (d), 133.36 (s), 134.52 (s), 169.79 (s) and 172.38 (s); *m*/*z* (FAB) 268.1339 (MH$^+$. $C_{17}H_{18}NO_2$ requires *m*/*z*, 268.1337).

***N*-(2-Methylprop-2-enoyl)-*N*-(1-naphthylethyl)acetamide 1b.** Colourless oil (52%); ν_{max} (film)/cm^{-1} 1705 (C=O) and 1664 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.72 (3 H, s), 1.90 (3 H, d, *J* 7.0), 2.10 (3 H, s), 5.15 (1 H, s), 5.23 (1 H, s), 6.60 (1 H, q, *J* 7.0), 7.40–7.86 (6 H, m) and 8.12 (1 H, d, *J* 8.5); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 17.90 (q), 18.29 (q), 26.79 (q), 50.72 (d), 123.10 (d), 124.56 (t), 124.95 (d), 125.54 (d), 126.53 (d), 126.71 (d), 128.50 (d), 128.88 (d), 131.48 (s), 133.60 (s), 134.34 (s), 143.32 (s), 171.61 (s) and 175.46 (s); *m*/*z* (FAB) 282.1480 (MH$^+$. $C_{18}H_{20}NO_2$ requires *m*/*z*, 282.1494).

***N*-(2-Methylprop-2-enoyl)-*N*-(1-naphthylethyl)benzamide 1c.** Colourless crystals (58%); mp 150–151 °C (Found: C, 80.62; H, 6.33; N, 4.09. $C_{23}H_{21}NO_2$ requires C, 80.44; H, 6.16; N, 4.08%); ν_{max} (KBr)/cm^{-1} 1695 (C=O) and 1650 (C=O); δ_H (90 MHz; $CDCl_3$; Me_4Si) 1.39 (3 H, s), 2.04 (3 H, d, *J* 7.0), 4.95 (1 H, q, *J* 1.5), 5.15 (1 H, q, *J* 1.5), 6.74 (1 H, q, *J* 7.0), 7.10–8.00 (11 H, m) and 8.51 (1 H, d, *J* 7.9); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 17.93 (q), 18.02 (q), 51.91 (d), 122.50 (t), 122.98 (d), 124.71 (d), 125.21 (d), 126.23 (d), 126.80 (d), 128.29 (d), 128.67 (d), 131.36 (d), 133.45 (s), 134.31 (s), 138.25 (s), 144.52 (s), 173.28 (s) and and 174.20 (s); *m*/*z* (FAB) 344.1658 (MH$^+$. $C_{23}H_{22}NO_2$ requires *m*/*z*, 344.1650).

***N*-[(*1S*)-1-Naphthylethyl]-*N*-{[(*1S*)-1-naphthylethyl]-carbamoyl}prop-2-enamide 1d.** Colourless amorphous (34%); mp 49–51 °C; $[\alpha]_D^{21}$ −81.7 (*c* 1.00 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3284 (NH), 1698 (C=O), 1658 (C=O) and 1620 (C=C); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.42 (1 H, d, *J* 7.3), 1.87 (3 H, d, *J* 7.3), 5.60 (1 H, dq, *J* 7.3 and 7.3), 5.67 (1 H, dd, *J* 8.8 and 3.1), 6.07 (1 H, d, *J* 7.3), 6.39 (1 H, dd, *J* 17.0 and 3.1), 6.49 (1 H, dd, *J* 17.0 and 8.8), 6.53 (1 H, q, *J* 7.3), 6.70 (1 H, d, *J* 7.3), 6.92 (1 H, t, *J* 7.7) and 7.10–7.92 (13 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 17.93 (q), 20.88 (q), 46.18 (d), 49.40 (d), 121.84 (d), 122.77 (d), 124.65 (d), 125.15 (d), 125.57 (d), 125.63 (d), 126.32 (d), 126.80 (d), 127.96 (d), 128.59 (d), 128.67 (d), 128.85 (t), 129.36 (d), 130.38 (s), 131.00 (s), 133.48 (s), 133.75 (s), 134.49 (s), 137.27 (s), 153.56 (s) and 166.15 (s); *m*/*z* (EI) 422.1999 (M$^+$. $C_{28}H_{26}N_2O_2$ requires *M*, 422.1996).

***N*-[(*1S*)-1-Naphthylethyl]-*N*-{[(*1S*)-1-naphthylethyl]-carbamoyl}-2-methylprop-2-enamide 1e.** Colourless crystals (40%); mp 122–123 °C (Found: C, 79.69; H, 6.47; N, 6.17. $C_{29}H_{28}N_2O_2$ requires C, 79.79; H, 6.47; N, 6.42%); $[\alpha]_D^{21}$ +16.1 (*c* 1.02 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3364 (NH), 1700(C=O), 1648 (C=O), and 1624 (C=C); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.30 (3 H, d, *J* 7.0), 1.70 (3 H, d, 7.0), 2.00 (3 H, s), 4.85 (1 H, d, *J* 7.0), 5.15 (1 H, s), 5.22 (1 H, s), 5.50 (1 H, dq, *J* 7.0 and 7.0), 6.41 (1 H, q, *J* 7.0), 6.60–6.74 (2 H, m), 6.87 (1 H, d, *J* 7.0), 7.20–7.30 (2 H, m) and 7.40–8.00 (9 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 17.36 (q), 19.57 (q), 20.02 (q), 45.76 (d), 48.81 (d), 116.65 (t), 122.02 (d), 122.95 (d), 123.07 (d), 124.65 (d), 125.15 (d), 125.84 (d), 126.53 (d), 126.88 (d), 128.23 (d), 128.61 (d), 128.79 (d), 128.88 (d), 130.61 (s), 131.09 (s), 133.57 (s), 133.84 (s), 134.52 (s), 136.94 (s), 142.46 (s), 154.21 (s) and 172.44 (s); *m*/*z* (EI) 438 (M + 2, 2%), 437 (M + 1, 1), 436 (M$^+$, 5), 282 (15), 238 (12), 224 (9), 195 (15), 182 (12), 170 (25) and 100 (100).

***N*-(1-Naphthylethyl)-*N*-[(*E*)-3-phenylprop-2-enoyl]acetamide 1f.** Colourless oil (55%); ν_{max} (film)/cm^{-1} 1695 (C=O), 1660

(C=O) and 1620 (C=C), 1510, 1455, 1375, 1335, 1265, 1190, 1115, 1085, 1025, 980 and 770; δ_H (270 MHz; CDCl$_3$; Me$_4$Si) 1.92 (3 H, d, *J* 7.0), 2.27 (3 H, s), 6.41 (1 H, d, *J* 16.2), 6.63 (1 H, q, *J* 7.0), 7.28 (1 H, d, *J* 16.2), 7.20–7.83 (11 H, m) and 7.97 (1 H, d, *J* 8.5); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.40 (q), 26.25 (q), 50.33 (d), 122.05 (d), 123.10 (d), 124.74 (d), 125.66 (d), 126.02 (d), 126.65 (d), 128.02 (d), 128.70 (d), 128.88 (d), 130.43 (d), 131.12 (s), 133.72 (s), 133.96 (s), 134.97 (s), 144.25 (d), 170.95 (s) and 172.38 (s); *m*/*z* (FAB) 344.1638 (MH$^+$. $C_{23}H_{22}NO_2$ requires *m*/*z*, 344.1650).

***N*-[(*E*)-3-(4-Methoxyphenyl)prop-2-enoyl]-*N*-(1-naphthylethyl)acetamide 1g.** Colourless oil (63%); ν_{max} (film)/cm^{-1} 1740 (C=O), 1660 (C=O) and 1600 (C=C); δ_H (270 MHz; CDCl$_3$; Me$_4$Si) 1.92 (3 H, d, *J* 7.0), 2.26 (3 H, s), 3.78 (3 H, s), 6.22 (1 H, d, *J* 15.6), 6.64 (1 H, q, *J* 7.0), 6.80 (2H, dt, *J* 8.6 and 2.2), 7.16 (2 H, d, *J* 8.6), 7.22 (1 H, d, *J* 15.6), 7.36–7.58 (3H, m), 7.67 (1H, d, *J* 7.4), 7.73 (1H, d, *J* 8.4), 7.81 (1H dd, *J* 8.4 and 1.5) and 8.00 (1 H, d, *J* 8.4); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.34 (q), 26.01 (q), 50.12 (d), 55.13 (q), 114.08 (d), 119.64 (d), 123.12 (d), 124.71 (d), 125.51 (d), 125.93 (d), 126.53 (d), 128.52 (d), 128.79 (d), 129.78 (d), 131.15 (s), 133.63 (s), 135.03 (s), 144.37 (d), 161.52 (s), 171.25 (s) and 171.99 (s); *m*/*z* (FAB) 374.1766 (MH$^+$. $C_{24}H_{24}NO_3$ requires *m*/*z*, 374.1761).

***N*-(1-Naphthylethyl)-*N*-[(*E*)-3-(4-nitrophenyl)prop-2-enoyl]-acetamide 1h.** Yellow crystals (46%); mp 128–129 °C (Found: C, 71.26; H, 5.19; N, 7.26. $C_{23}H_{20}N_2O_4$ requires C, 71.12; H, 5.19; N, 7.21%); ν_{max} (KBr)/cm^{-1} 1685 (C=O) 1625 (C=C), 1520 (NO$_2$) and 1380 (NO$_2$); δ_H (270 MHz; CDCl$_3$; Me$_4$Si) 1.93 (3 H, d, *J* 7.0), 2.27 (3 H, s), 6.59 (1 H, d, *J* 15.4), 6.60 (1 H, q, *J* 7.0), 7.30 (1 H, d, *J* 15.4), 7.35–7.90 (9 H, m) and 8.15 (2 H, d, *J* 8.5); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.43 (q), 26.19 (q), 50.63 (d), 122.89 (d), 123.84 (d), 124.74 (d), 125.87 (d), 126.82 (d), 128.44 (d), 128.97 (d), 130.85 (s), 133.72 (s), 134.85 (s), 139.98 (d), 140.28 (s), 148.19 (s), 169.73 (s) and 173.04 (s); *m*/*z* (FAB) 389.1498 (MH$^+$. $C_{23}H_{21}N_2O_4$ requires *m*/*z*, 389.1501).

***N*,*N*′-Bis[(*1S*)-1-naphthylethyl]-*N*-[(*2E*)-3-phenylprop-2-enoyl]urea 1i.** Colourless crystals (56%); mp 164–165 °C (Found: C, 82.14; H, 6.05; N, 5.99. $C_{34}H_{30}N_2O_2$ requires C, 81.90; H, 6.06; N, 5.62%); $[\alpha]^{21}_D$ +88.6 (*c* 0.90 in CHCl$_3$); ν_{max} (KBr)/cm^{-1} 3344 (NH), 1708 (C=O), 1652 (C=O) and 1610 (C=C); δ_H (270 MHz; CDCl$_3$; Me$_4$Si) 1.52 (3 H, d, *J* 7.0), 1.89 (3 H, d, *J* 7.0), 5.70 (1 H, dq, *J* 7.0 and 7.0), 6.55 (1 H, br s), 6.64 (1 H, q, *J* 7.0), 6.75 (1 H, d, *J* 15.4), 6.81 (1 H, d, *J* 7.3), 7.00–7.10 (1 H, m), 7.65 (1 H, d, *J* 15.4) and 7.20–8.00 (17 H, m); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.34 (q), 21.39 (q), 46.36 (d), 49.79 (d), 119.43 (d), 121.99 (d), 122.95 (d), 123.01 (d), 124.77 (d), 125.30 (d), 125.66 (d), 125.72 (d), 126.47 (d), 126.88 (d), 127.99 (d), 128.67 (d), 128.79 (d), 128.94 (d), 130.05 (d), 130.52 (s), 131.18 (s), 133.67 (s), 133.87 (s), 134.64 (s), 135.18 (s), 137.63 (s), 143.56 (d), 154.00 (s) and 166.83 (s); *m*/*z* (EI) 499 (M + 1, 3%), 344 (2), 302 (2), 197 (31), 182 (54), 170 (75), 155 (77), 131 (100) and 103 (65).

***N*-[(*E*)-3-(4-Chlorophenyl)prop-2-enoyl]-*N*,*N*′-bis[(*1S*)-1-naphthylethyl]urea 1j.** Colourless crystals (90%); mp 164.5–165.5 °C; $[\alpha]^{21}_D$ +105.8 (*c* 1.33 in CHCl$_3$); ν_{max} (KBr)/cm^{-1} 3260 (NH), 1708 (C=O), 1658 (C=O) and 1616 (C=C); δ_H (270 MHz; CDCl$_3$; Me$_4$Si) 1.51 (3 H, d, *J* 7.0), 1.86 (3 H, d, *J* 7.0), 5.71 (1 H, dq, *J* 7.0 and 7.0), 6.46 (1 H, s), 6.64 (1 H, q, *J* 7.0), 6.69 (1 H, d, *J* 15.4), 6.85 (1 H, d, *J* 7.3), 7.00–7.10 (1 H, m), 7.59 (1 H, d, *J* 15.4), 7.15–8.00 (16 H, m); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.29 (q), 21.18 (q), 46.24 (d), 49.79 (d), 117.10 (d), 119.78 (d), 122.14 (d), 122.89 (d), 124.83 (d), 125.27 (d), 125.48 (d), 125.66 (d), 125.75 (d), 126.53 (d), 126.82 (d), 128.08 (d), 128.64 (d), 128.79 (d), 128.91 (d), 129.00 (d), 129.33 (d), 129.63 (d), 130.55 (s), 131.09 (s), 132.94 (s), 133.63 (s), 133.84 (s), 135.39 (s), 135.75 (s), 137.45 (s), 141.95 (d), 153.86 (s) and 166.36 (s); *m*/*z* (EI) 532.1910 (M$^+$. $C_{34}H_{29}{}^{35}ClN_2O_2$ requires *M*, 532.1917).

***N*-[(*E*)-3-(4-Methoxyphenyl)prop-2-enoyl]-*N*,*N*′-bis[(*1S*)-1-naphthylethyl]urea 1k.** Colourless solid (71%); $[\alpha]^{21}_D$ +126.0 (*c* 1.41 in CHCl$_3$); ν_{max} (KBr)/cm^{-1} 3350 (NH), 1692 (C=O), 1650 (C=O) and 1600 (C=C); δ_H (270 MHz; CDCl$_3$; Me$_4$Si) 1.52 (3 H, d, *J* 7.0), 1.88 (3 H, d, *J* 7.0), 3.80 (3 H, s), 5.72 (1 H, dq, *J* 7.0 and 7.0), 6.59 (1 H, d, *J* 15.4), 6.63 (1 H, q, *J* 7.0), 6.77–6.84 (3 H, m), 7.05–7.13 (1 H, m), 7.58 (1 H, d, *J* 15.4) and 7.20–8.00 (15 H, m); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.22 (q), 21.30 (q), 46.21 (d), 49.67 (d), 55.16 (q), 114.08 (d), 116.74 (d), 121.81 (d), 122.80 (d), 122.92 (d), 124.62 (d), 125.15 (d), 125.45 (d), 126.26 (d), 126.67 (d), 127.24 (s), 127.81 (d), 128.46 (d), 128.61 (d), 128.76 (d), 129.51 (d), 130.34 (s), 131.06 (s), 133.51 (s), 133.72 (s), 135.18 (s), 137.56 (s), 143.26 (s), 154.00 (s), 161.07 (s) and 167.01 (s); *m*/*z* (FAB) 529.2940 (MH$^+$. $C_{35}H_{33}N_2O_3$ requires *m*/*z*, 529.2942).

***N*,*N*′-Bis[(1*S*)-1-naphthylethyl]-*N*-[(*E*)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]urea 1l.** Colourless crystals (34%); mp 149–150 °C (Found: C, 75.22; H, 6.35; N, 4.51. $C_{37}H_{36}N_2O_5$ requires C, 75.49; H, 6.16; N, 4.76%); $[\alpha]^{21}_D$ +114.0 (*c* 0.71 in CHCl$_3$); ν_{max} (KBr)/cm^{-1} 3420 (NH), 1700 (C=O), 1655 (C=O), 1610 (C=C); δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 1.55 (3 H, d, *J* 6.8), 1.89 (3 H, d, *J* 7.0), 3.83 (6 H, s), 3.87 (3 H, s), 5.71 (1 H, dq, *J* 7.0 and 7.0 Hz), 6.62 (1 H, q, *J* 6.8), 6.63 (1 H, d, *J* 15.0), 6.75 (1 H, br s), 6.85 (1 H, d, *J* 7.2), 7.03–7.08 (1 H, m), 7.61 (1 H, d, *J* 15.0), 7.20–7.80 (14 H, m); δ_C (22.4 MHz; CDCl$_3$; Me$_4$Si) 18.26 (q), 21.24 (q), 46.18 (d), 49.70 (d), 55.73 (q), 60.59 (q), 104.87 (d), 118.32 (d), 121.66 (d), 122.59 (d), 124.59 (d), 125.06 (d), 125.36 (d), 125.45 (d), 126.17 (d), 126.59 (d), 127.72 (d), 128.35 (d), 128.53 (d), 128.67 (d), 129.84 (s), 130.41 (s), 130.85 (s), 133.36 (s), 133.57 (s), 135.09 (s), 137.39 (s), 139.62 (s), 143.41 (d), 153.00 (d), 153.83 (s) and 166.33 (s); *m*/*z* (FAB) 589.2696 (MH$^+$. $C_{37}H_{37}N_2O_5$ requires *m*/*z*, 589.2703).

***N*,*N*′-Bis[(1*S*)-1-naphthylethyl]-*N*-[(*Z*)-3-(3,4,5-trimethoxyphenyl)prop-2-enoyl]urea [(*Z*)-1l].** Colourless oil; ν_{max} (KBr)/cm^{-1} 3440 (NH), 1710 (C=O), 1650 (C=O) and 1585 (C=C); δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 1.56 (3 H, d, *J* 6.8), 1.89 (3 H, d, *J* 7.0), 3.61 (6 H, s), 3.84 (3 H, s), 5.70 (1 H, dq, *J* 7.0 and 7.0), 5.89 (1 H, d, *J* 12.6), 6.42 (1 H, d, *J* 12.6), 6.53 (1 H, q, *J* 6.8), 6.57 (2 H, s), 6.96 (1 H, d, *J* 7.0) and 7.20–7.90 (14 H, m); *m*/*z* (FAB) 589.2700 (MH$^+$. $C_{37}H_{37}N_2O_5$ requires *m*/*z*, 589.2703).

General procedure for the photochemical reaction of 1

Preparative photochemical reactions were carried out in benzene (15 cm^3) with *ca.* 1.0 mmol of an enamide **1** in a Pyrex test tube (1.5 cm diameter × 16.5 cm) under bubbling of argon irradiated externally using a Ushio 450 W high-pressure mercury lamp. The reaction tube was cooled externally in a water-bath. For the reaction of **1d** and **1e**, *p*-methoxyacetophenone (1 equiv.) was added as a sensitiser. The progress of the reaction was monitored by TLC. After irradiation, the solvent was removed *in vacuo*. The products were separated by column chromatography on silica gel [ethyl acetate–hexane (1 : 4)]. The [2+2] cycloadducts **2** and azetidin-2-ones **3** were separated and purified by HPLC [ethyl acetate–hexane (1 : 6)]. The crystalline compounds were recrystallised from ethyl acetate–hexane (≈1 : 7).

The monitoring experiments by ^{1}H NMR spectroscopy (90 MHz) were performed on *ca.* 0.1 M **1** in benzene-d_6. The sample solution was purged by argon for 15 min prior to irradiation. For benzophenone sensitisation, a combination of glass filters, Toshiba UV-35 and UV-D36A (340 nm < λ < 380 nm), was applied to select the 366 nm mercury arc light. A Ushio 6 W low-pressure mercury lamp was used for the 254 nm irradiation.

[2+2] Cycloadduct 2a. Colourless crystals; mp 131.5–132.5 °C (Found: C, 76.68; H, 6.34; N, 5.03. $C_{17}H_{17}NO_2$ requires C, 76.38; H, 6.41; N, 5.24%); ν_{max} (KBr)/cm^{-1} 1734 (C=O) and 1690 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.32 (3 H, d, *J* 6.2), 2.32 (1 H, ddd, *J* 11.3, 8.5, 1.7), 2.50 (1 H, ddd, *J* 11.3, 10.0, 8.9), 2.60 (3 H, s), 3.24 (1 H, m), 3.36 (1 H, m), 4.24 (1 H, q, *J* 6.2), 5.83 (1 H, dd, *J* 9.9, 5.9), 6.33 (1 H, d, *J* 9.9), 7.06–7.10 (1 H, m) and 7.10–7.28 (3 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 13.81 (q), 26.22 (q), 31.47 (t), 34.13 (d), 45.91 (s), 53.82 (d), 64.08 (d), 127.15 (d), 127.27 (d), 127.72 (d), 128.29 (d), 133.63 (s), 134.19 (s), 172.44 (s) and 177.75 (s).

[2+2] Cycloadduct 2b. Colourless crystals; mp 129–130 °C (Found: C, 77.01; H, 6.94; N, 5.00. $C_{18}H_{19}NO_2$ requires C, 76.84; H, 6.81; N, 4.98%); ν_{max} (KBr)/cm^{-1}1724 (C=O) and 1706 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.12 (3 H, s), 1.30 (3 H, d, *J* 7.0), 1.95 (1 H, dd, *J* 11.2 and 10.0), 2.45 (1 H, dd, *J* 11.2 and 8.5), 2.60 (3 H, s), 3.20 (1 H, ddd, *J* 10.0, 8.5 and 5.8), 4.19 (1 H, q, *J* 7.0), 5.83 (1 H, dd, *J* 10.0 and 5.8), 6.30 (1 H, d, *J* 10.0), 7.00–7.12 (2 H, m) and 7.20–7.30 (2 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 13.81 (q), 18.85 (q), 26.34 (d), 31.92 (q), 39.41 (t), 49.46 (s), 56.00 (s), 62.65 (d), 126.85 (d), 127.48 (d), 127.63 (d), 127.72 (d), 127.78 (d), 128.61 (d), 130.97 (s), 134.37 (s), 172.74 (s) and 180.71 (s); *m*/*z* (EI) 282 (M + 1, 4%), 281 (M^+, 12), 238 (14), 212 (39), 170 (41), 155 (39), 127 (18), 69 (55) and 43 (100).

[2+2] Cycloadduct 2c. Colourless crystals; mp 161–162 °C (Found: C, 80.53; H, 6.21; N, 3.96. $C_{23}H_{21}NO_2$ requires C, 80.44; H, 6.16; N, 4.08%); ν_{max} (KBr)/cm^{-1} 1730 (C=O) and 1675 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.07 (3 H, s), 1.29 (3 H, d, *J* 6.3), 2.03 (1 H, dd, *J* 11.4 and 10.3), 2.56 (1 H, dd, *J* 11.4 and 8.7), 3.47 (1 H, ddd, *J* 10.3, 8.7 and 5.5), 4.41 (1 H, q, *J* 6.3), 5.90 (1 H, dd, *J* 9.9 and 5.5), 6.34 (1 H, d, *J* 9.9), 7.04–7.12 (2 H, m), 7.22–7.27 (2 H, m), 7.42–7.50 (2 H, m), 7.53–7.61 (1 H, m) and 7.75–7.80 (2 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 12.29 (q), 18.46 (q), 31.65 (d), 39.88 (t), 49.82 (s), 55.73 (s), 62.20 (s), 126.85 (d), 127.39 (d), 127.69 (d), 127.75 (d), 127.84 (d), 128.08 (d), 128.52 (d), 129.27 (d), 130.67 (s), 132.64 (d), 134.25 (s), 135.03 (s), 171.82 (s) and 179.66 (s); *m*/*z* (FAB) 344.1646 (MH^+. $C_{23}H_{22}NO_2$ requires *m*/*z*, 344.1651).

[2+2] Cycloadduct 2d. Colourless solid; $[\alpha]_D^{21}$ −48.3 (*c* 0.58 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3284 (NH) and 1712 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.39 (3 H, d, *J* 6.2), 1.72 (3 H, d, *J* 7.7), 2.25 (1 H, ddd, *J* 11.6, 8.5 and 1.5), 2.45 (1 H, ddd, *J* 11.6, 9.3 and 9.3), 3.30 (2 H, m), 4.35 (1 H, q, *J* 6.2), 5.75 (1 H, dd, *J* 9.6 and 6.2), 5.95 (1 H, dq, *J* 7.7 and 7.7), 6.30 (1 H, d, *J* 9.6), 7.01 (1 H, d, *J* 7.2), 7.15–7.65 (7 H, m), 7.80 (1 H, d, *J* 8.3), 7.88 (1 H, d, *J* 8.3), 8.19 (1 H, d, *J* 8.5) and 8.96 (1 H, d, *J* 8.0); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.38 (q), 21.98 (q), 31.35 (t), 33.98 (d), 45.58 (d), 46.03 (s), 54.30 (d), 64.77 (d), 122.53 (d), 123.24 (d), 125.39 (d), 125.66 (d), 126.29 (d), 127.15 (d), 127.72 (d), 128.08 (d), 128.29 (d), 128.85 (d), 130.82 (s), 133.66 (s), 133.96 (s), 134.19 (s), 138.82 (s), 152.15 (s) and 178.86 (s); *m*/*z* (EI) 422.2003 (M^+; $C_{28}H_{26}N_2O_2$ requires *M*, 422.1996).

[2+2] Cycloadduct 2e. Colourless solid; $[\alpha]_D^{21}$ −15.3 (*c* 0.88 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3480 (NH) and 1712 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.13 (3 H, s), 1.36 (3 H, d, *J* 6.2), 1.72 (3 H, d, *J* 7.0), 1.88 (1 H, dd, *J* 11.2 and 10.0), 2.38 (1 H, dd, *J* 11.2 and 8.5), 3.15 (1 H, ddd, *J* 10.0, 8.5 and 5.8), 4.29 (1 H, q, *J* 6.2), 5.78 (1 H, dd, *J* 10.4 and 5.8), 5.93 (1 H, dq, *J* 7.7 and 7.7), 6.28 (1 H, d, *J* 10.4), 7.00–7.30 (4 H, m), 7.45–7.60 (4 H, m), 7.80 (1 H, d, *J* 8.1), 7.89 (1 H, d, *J* 8.1), 8.19 (1 H, d, *J* 8.5) and 8.90 (1 H, d, *J* 7.7); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.35 (q), 18.70 (q), 22.01 (q), 31.65 (d), 39.23 (t), 45.58 (d), 49.52 (s), 56.47 (s), 63.34 (d), 122.47 (d), 123.21 (d), 125.39 (d), 125.66 (d), 126.29 (d), 126.77 (d), 127.45 (d), 127.57 (d), 127.66 (d), 127.72 (d), 128.02 (d), 128.73 (d), 128.85 (d), 130.85 (s), 133.96 (s), 134.34 (s), 138.91 (s), 152.27 (s) and 181.60 (s); *m*/*z* (EI) 436.2143 (M^+. $C_{29}H_{28}N_2O_2$ requires *M*, 436.2152).

The azetidin-2-one *syn*-3a. Colourless crystals; mp 139–140 °C (Found: C, 76.28; H, 6.25; N, 5.18. $C_{17}H_{17}NO_2$ requires C, 76.38; H, 6.41; N, 5.24%); ν_{max} (KBr)/cm^{-1} 1790 (C=O) and 1700 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 0.94 (3 H, q, *J* 7.6), 2.25 (3 H, s), 2.62 (3 H, s), 3.60 (1 H, q, *J* 7.6), 7.23–7.53 (4 H, m), 7.68–7.92 (3 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 11.66 (q), 25.39 (q), 25.65 (q), 56.98 (d), 68.86 (s), 125.06 (d), 125.24 (d), 125.30 (d), 125.48 (d), 128.67 (d), 129.36 (d), 129.57 (s), 134.28 (s), 134.37 (s), 169.37 (s) and 169.97 (s); *m*/*z* (FAB) 268.1332 (MH^+. $C_{17}H_{18}NO_2$ requires *m*/*z*, 268.1337).

The azetidin-2-one *anti*-3a. Colourless crystals; mp 135.5–136.5 °C (Found: C, 76.04; H, 6.34; N, 5.14. $C_{17}H_{17}NO_2$ requires C, 76.38; H, 6.41; N, 5.24%); ν_{max} (KBr)/cm^{-1} 1785 (C=O) and 1705 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.69 (3 H, d, *J* 7.6), 2.06 (3 H, s), 2.60 (3 H, s), 3.41 (1 H, q, *J* 7.6), 7.35–7.56 (4 H, m), 7.60–7.65 (1 H, m), 7.75–7.82 (1 H, m) and 7.85–7.95 (1 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 10.50 (q), 19.66 (q), 25.27 (q), 55.22 (d), 67.84 (s), 123.60 (d), 123.75 (d), 125.15 (d), 125.36 (d), 125.90 (d), 128.50 (d), 129.00 (s), 129.63 (d), 134.28 (s), 139.21 (s), 169.46 (s) and 169.94 (s); *m*/*z* (FAB) 268.1330 (MH^+. $C_{17}H_{18}NO_2$ requires *m*/*z*, 268.1337).

The azetidin-2-one 3b. Colourless oil; ν_{max} (film)/cm^{-1} 1784 (C=O) and 1708 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 0.92 (3 H, s), 1.70 (3 H, s), 2.15 (3 H, s), 2.62 (3 H, s) and 7.20–7.90 (7 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 18.20 (q), 20.31 (q), 22.19 (q), 25.57 (q), 57.55 (s), 72.29 (s), 124.41 (d), 125.00 (d), 125.24 (d), 125.30 (d), 125.51 (d), 128.41 (d), 129.36 (d), 129.90 (s), 134.37 (s), 136.55 (s), 169.55 (s) and 173.28 (s); *m*/*z* (FAB) 282.1488 (MH^+. $C_{18}H_{20}NO_2$ requires *m*/*z*, 282.1494).

The azetidin-2-one 3c. Colourless solid; ν_{max} (KBr)/cm^{-1} 1790 (C=O) and 1680 (C=O); δ_H (90 MHz; $CDCl_3$; Me_4Si) 1.03 (3 H, s), 1.70 (3 H, s), 2.32 (3 H, s), 7.20–8.10 (12 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 18.05 (q), 20.88 (q), 23.33 (q), 56.95 (s), 72.05 (s), 124.05 (d), 125.06 (d), 125.33 (d), 125.42 (d), 125.63 (d), 128.08 (d), 128.41 (d), 129.42 (d), 129.60 (d), 129.99 (s), 133.00 (d), 133.78 (s), 134.52 (s), 136.82 (s), 168.18 (s) and 171.99 (s); *m*/*z* (FAB) 344.1645 (MH^+. $C_{23}H_{22}NO_2$ requires *m*/*z* 344.1651).

[4+2] Adduct 4f. Colourless crystals; mp 188.5–189.5 °C (Found: C, 80.08; H, 6.24; N, 3.90. $C_{23}H_{21}NO_2$ requires C, 80.44; H, 6.16; N, 4.08%); ν_{max} (KBr)/cm^{-1} 1755 (C=O) and 1695 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.57 (3 H, d, *J* 6.6), 2.42 (3 H, s), 2.98 (1 H, d, *J* 7.0), 3.14 (1 H, dd, *J* 7.0 and 1.5), 4.22 (1 H, ddd, *J* 5.4, 1.5 and 1.5), 5.44 (1 H, q, *J* 6.6), 6.72 (1 H, dd, *J* 8.0 and 5.4), 6.79 (1 H, dd, *J* 8.0 and 1.5) and 7.10–7.40 (9 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.29 (q), 25.12 (q), 46.24 (d), 47.31 (d), 50.75 (s), 51.82 (d), 57.49 (d), 121.25 (d), 122.47 (d), 125.66 (d), 126.47 (d), 126.71 (d), 127.18 (d), 128.64 (d), 134.61 (d), 134.88 (d), 138.76 (s), 143.50 (s), 146.93 (s), 170.95 (s) and 173.43 (s); *m*/*z* (FAB) 344.1647 (MH^+. $C_{23}H_{22}NO_2$ requires *m*/*z*, 344.1650).

[4+2] Adduct 4g. Colourless crystals; mp 163.5–164.5 °C (Found: C, 77.18; H, 6.06; N, 3.65. $C_{24}H_{23}NO_3$ requires C, 77.19; H, 6.21; N, 3.75%); ν_{max} (KBr)/cm^{-1} 1745 (C=O) and 1700 (C=O); δ_H (90 MHz; $CDCl_3$; Me_4Si) 1.58 (3 H, d, *J* 6.5), 2.41 (3 H, s), 2.95 (1 H, d, *J* 6.9), 3.09 (1 H, dd, *J* 6.9 and 1.5), 3.79 (3 H, s), 4.19 (1 H, ddd, *J* 5.6, 1.5 and 1.5), 5.44 (1 H, q, *J* 6.5), 6.71 (1 H, dd, *J* 7.7 and 5.6), 6.79 (1 H, dd, *J* 7.7 and 1.5), 6.86 (2 H, d, *J* 8.6), 7.26 (2 H, d, *J* 8.6) and 7.28 (4 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.20 (q), 25.03 (q), 45.40 (d), 47.55 (d), 50.63 (s), 51.73 (d), 55.10 (q), 57.52 (d), 113.94 (d), 121.13 (d), 122.35 (d), 125.51 (d), 126.35 (d), 128.08 (d), 134.52

(d), 134.79 (d), 135.57 (s), 138.61 (s), 146.93 (s), 158.30 (s), 170.83 (s) and 173.37 (s); *m*/*z* (FAB) 374.1758 (MH^+. $C_{24}H_{24}NO_3$ requires *m*/*z*, 374.1756).

[4+2] Adduct 4h. Colourless crystals; mp 180–184 °C; ν_{max} (KBr)/cm^{-1} 1740 (C=O), 1695 (C=O), 1520 (NO_2) and 1360 (NO_2); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.60 (3 H, d, *J* 7.0), 2.43 (3 H, s), 2.93 (1 H, d, *J* 7.0), 3.24 (1 H, d, *J* 7.0), 4.25 (1 H, ddd, *J* 5.8, 1.5 and 1.5), 5.48 (1 H, q, *J* 7.0), 6.74 (1 H, dd, *J* 8.1 and 5.8), 6.88 (1 H, dd, *J* 8.1 and 1.5), 7.13–7.30 (4 H, m), 7.48–7.55 (2 H, m) and 8.15–8.25 (2 H, m); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.35 (q), 25.12 (q), 46.15 (d), 46.69 (d), 50.78 (s), 51.94 (d), 57.49 (d), 121.48 (d), 122.62 (d), 123.90 (d), 126.05 (d), 126.74 (d), 128.17 (d), 133.99 (d), 135.92 (d), 138.46 (s), 146.22 (s), 146.81 (s), 151.05 (s), 170.83 (s) and 172.86 (s); *m*/*z* (FAB) 389.1499 (MH^+. $C_{23}H_{21}N_2O_4$ requires *m*/*z*, 389.1451).

[4+2] Adduct 4i. Colourless solid; $[\alpha]_D^{21}$ −39.2 (*c* 1.05 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3464 (NH), 1716 (C=O) and 1686 (C=O); δ_H (270 MHz; $CDCl_3$; Me_4Si) 1.56 (3 H, d, *J* 6.6), 1.63 (3 H, d, *J* 7.0), 2.99 (1 H, d, *J* 7.0), 3.10 (1 H, dd, *J* 7.0 and 1.5), 4.19 (1 H, ddd, *J* 5.4, 1.5 and 1.5), 5.45 (1 H, q, *J* 6.6), 5.90 (1 H, dq, *J* 7.7, 7.0), 6.68 (1 H, dd, *J* 7.7, 5.4), 6.75 (1 H, dd, *J* 7.7, 1.5), 7.15–7.55 (13 H, m), 7.71 (1H, d, *J* 7.7), 7.81 (1 H, dd, *J* 8.5 and 1.5), 8.13 (1 H, d, *J* 8.5) and 8.63 (1 H, d, *J* 7.7); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.65 (q), 22.13 (q), 45.58 (d), 46.06 (d), 47.40 (d), 51.28 (s), 52.42 (d), 57.70 (d), 121.72 (d), 122.14 (d), 122.35 (d), 123.01 (d), 125.33 (d), 125.57 (d), 125.72 (d), 126.23 (d), 126.44 (d), 126.74 (d), 127.15 (d), 127.90 (d), 128.79 (d), 130.64 (s), 133.87 (s), 134.40 (d), 135.09 (d), 138.82 (s), 139.06 (s), 143.47 (s), 147.08 (s), 151.86 (s) and 175.19 (s); *m*/*z* (EI) 498.2296 (M^+. $C_{34}H_{30}N_2O_2$ requires *M*, 498.2309).

[4+2] Adduct 4j. Colourless solid; $[\alpha]_D^{21}$ −40.7 (*c* 1.38 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3310 (C=O) and 1715 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.57 (3 H, d, *J* 6.6), 1.62 (3 H, d, *J* 7.0), 2.93 (1 H, d, *J* 7.2), 3.07 (1 H, dd, *J* 7.2 and 1.5), 4.18 (1 H, ddd, *J* 5.9, 1.5 and 1.3), 5.46 (1 H, q, *J* 6.6), 5.90 (1 H, dq, *J* 7.9 and 7.0), 6.68 (1 H, dd, *J* 7.9 and 5.7), 6.81 (1 H, dd, *J* 7.9 and 1.3), 7.18–7.60 (12 H, m), 7.74 (1 H, d, *J* 7.5), 7.84 (1 H, d, *J* 8.4), 8.14 (1 H, d, *J* 8.2) and 8.57 (1 H, d, *J* 7.9); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.62 (q), 22.07 (q), 45.44 (d), 45.55 (d), 47.20 (d), 51.22 (s), 52.42 (d), 57.70 (d), 121.75 (d), 122.11 (d), 122.35 (d), 122.98 (d), 125.30 (d), 125.57 (d), 125.84 (d), 126.23 (d), 126.50 (d), 127.90 (d), 128.53 (d), 128.73 (d), 130.61 (s), 132.52 (s), 133.87 (s), 134.04 (d), 135.45 (d), 138.61 (s), 139.00 (s), 141.95 (s), 146.75 (s), 151.74 (s) and 174.92 (s); *m*/*z* (FAB) 533.1987 (MH^+. $C_{34}H_{30}{}^{35}ClN_2O_2$ requires *m*/*z*, 533.1996).

[4+2] Adduct 4k. Colourless solid; $[\alpha]_D^{21}$ −40.4 (*c* 0.86 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3310 (NH), 1715 (C=O) and 1615 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.57 (3 H, d, *J* 7.0), 1.61 (3 H, d, *J* 7.0), 2.96 (1 H, d, *J* 7.0), 3.06 (1 H, dd, *J* 7.0 and 1.5), 3.78 (3 H, s), 4.18 (1 H, dd, *J* 5.8 and 1.5), 5.45 (1 H, q, *J* 7.0), 5.90 (1 H, dq, *J* 7.0 and 7.0), 6.70 (1 H, dd, *J* 8.5 and 5.9), 6.78 (1 H, dd, *J* 8.1 and 1.5), 6.83 (2H, m), 7.20–7.60 (10H, m), 7.73 (1 H, d, *J* 7.7), 7.83 (1 H, d, *J* 8.5), 8.13 (1 H, d, *J* 8.5) and 8.62 (1 H, d, *J* 7.7); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.68 (q), 22.13 (q), 45.35 (d), 45.58 (d), 47.79 (d), 51.28 (s), 52.45 (d), 55.25 (q), 57.85 (d), 114.09 (d), 121.72 (d), 122.17 (d), 122.35 (d), 123.04 (d), 125.36 (d), 125.60 (d), 125.72 (d), 126.26 (d), 126.44 (d), 127.90 (d), 128.14 (d), 128.82 (d), 130.67 (s), 133.93 (s), 134.43 (s), 135.12 (s), 135.66 (s), 138.76 (d), 139.12 (d), 147.20 (s), 151.92 (s), 158.42 (s) and 175.31 (s); *m*/*z* (FAB) 529.2495 (MH^+. $C_{35}H_{33}N_2O_3$ requires *m*/*z*, 529.2491).

[4+2] Adduct 4l. Colourless crystals; mp 191–192 °C (Found: C, 75.58; H, 6.31; N, 4.63. $C_{37}H_{36}N_2O_5$ requires C, 75.49; H, 6.16; N, 4.76%); $[\alpha]_D^{21}$ −47.8 (*c* 1.12 in $CHCl_3$); ν_{max} (KBr)/cm^{-1} 3300 (NH), 1720 (C=O) and 1685 (C=O); δ_H (400 MHz; $CDCl_3$; Me_4Si) 1.59 (3 H, *J* 6.4), 1.62 (3 H, d, *J* 6.8), 2.98 (1 H, d, *J* 7.2), 3.02 (1 H, dd, *J* 7.2 and 1.5), 3.80 (3 H, s), 3.84 (6 H, s), 4.18 (1 H, ddd, *J* 5.9, 1.5 and 1.3), 5.47 (1 H, q, *J* 6.4), 5.91 (1 H, dq, *J* 7.9 and 6.8), 6.54 (2 H, s), 6.72 (1 H, dd, *J* 8.1 and 5.9), 6.82 (1 H, dd, *J* 8.1 and 1.3), 7.18–7.58 (8 H, m), 7.75 (1 H, d, *J* 7.5), 7.85 (1 H, d, *J* 8.1), 8.15 (1 H, d, *J* 8.2), 8.58 (1 H, d, *J* 7.9); δ_C (22.4 MHz; $CDCl_3$; Me_4Si) 14.73 (q), 22.10 (q), 45.58 (d), 46.36 (d), 47.70 (d), 51.34 (s), 52.42 (d), 56.18 (q), 57.76 (d), 60.77 (q), 104.30 (d), 121.75 (d), 122.14 (d), 122.35 (d), 123.04 (d), 125.33 (d), 125.60 (d), 125.81 (d), 126.26 (d), 126.50 (d), 127.93 (d), 128.82 (d), 130.70 (s), 133.90 (s), 134.28 (d), 135.30 (d), 136.94 (s), 138.70 (s), 139.06 (s), 139.24 (s), 146.99 (s), 151.86 (s), 153.29 (s) and 175.10 (s); *m*/*z* (FAB) 589.2684 (MH^+. $C_{37}H_{37}N_2O_5$ requires *m*/*z*, 589.2702).

References

1 S. Speiser, *Chem. Rev.*, 1996, **96**, 1953; M. C. Jimenez, M. A. Miranda and R. Tormos, *J. Org. Chem.*, 1998, **63**, 1323.

2 N. J. Turro, V. Ramanurthy, W. Cherry and W. Farneth, *Chem. Rev.*, 1978, **78**, 125; W. G. Dauben and S. Hecht, *J. Org. Chem.*, 1998, **63**, 6102.

3 S. Kohmoto, T. Kobayashi, T. Nishio, I. Iida, K. Kishikawa, M. Yamamoto and K. Yamada, *J. Chem. Soc., Perkin Trans. 1*, 1996, 529; K. Kishikawa, S. Akimoto, S. Kohmoto, M. Yamamoto and K. Yamada, *J. Chem. Soc., Perkin Trans. 1*, 1997, 77; S. Kohmoto, H. Masu, C. Tatsuno, K. Kishikawa, M. Yamamoto and K. Yamaguchi, *J. Chem. Soc., Perkin Trans. 1*, 2000, 4464; S. Kohmoto, T. Kobayashi, J. Minami, X. Ying, K. Yamaguchi, T. Karatsu, A. Kitamura, K. Kishikawa and M. Yamamoto, *J. Org. Chem.*, 2001, **66**, 66.

4 T. R. Chamberlain and J. J. McCullough, *Can. J. Chem.*, 1973, **51**, 2578; D. Döpp, C. Krüger, H. R. Memarian and Y.-H. Tsay, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 1048; D. Döpp and M. Pies, *J. Chem. Soc., Chem. Commun.*, 1987, 1734; A. Gilbert, P. Heath, A. Kashoulis-Koupparis, G. C. R. Ellis-Davies and S. M. Firth, *J. Chem. Soc., Perkin Trans. 1*, 1988, 31; D. Döpp, H. R. Memarian, C. Krüger and E. Raabe, *Chem. Ber.*, 1989, **122**, 585; P. J. Wagner and M. Sakamoto, *J. Am. Chem. Soc.*, 1989, **111**, 9254; K. Mizuno, K. Nakanishi, M. Yasueda, H. Miyata and Y. Otsuji, *Chem. Lett.*, 1991, 2001; J. J. McCullough, T. B. McMurry and D. N. Work, *J. Chem. Soc., Perkin Trans. 1*, 1991, 461; N. Zupancic and B. Sket, *J. Chem. Soc., Perkin Trans. 1*, 1992, 179; K. Mizuno, S. Konishi, T. Takata and H. Inoue, *Tetrahedron Lett.*, 1996, **37**, 7775; T. Noh, D. Kim and Y.-J. Kim, *J. Org. Chem.*, 1998, **63**, 1212; A. Yokoyama and K. Mizuno, *Org. Lett.*, 2000, **2**, 3457.

5 Y. Kubo, T. Inoue and H. Sakai, *J. Am. Chem. Soc.*, 1992, **114**, 7660; Y. Kubo, M. Yoshioka, K. Kikuchi, S. Nakajima and I. Inamura, *Tetrahedron Lett.*, 1999, **40**, 527; Y. Kubo, M. Yoshioka, S. Nakajima and I. Inamura, *Tetrahedron Lett.*, 1999, **40**, 2335.

6 T. Hasegawa, H. Aoyama and Y. Omote, *Tetrahedron Lett.*, 1975, 1901; H. Aoyama, Y. Arata and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1165.

7 E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, 1970, **92**, 704.

8 S. Kohmoto, T. Kreher, Y. Miyaji, M. Yamamoto and K. Yamada, *J. Org. Chem.*, 1992, **57**, 3490.

9 T. Hasegawa, M. Watabe, H. Aoyama and Y. Omote, *Tetrahedron*, 1977, **33**, 485.

10 H.-D. Scharf, H. Leismann, W. Frb, H. W. Gaidetzka and J. Aretz, *Pure Appl. Chem.*, 1975, **41**, 581.

11 H. R. Memarian, M. Nasr-Esfahani, R. Boese and D. Döpp, *Liebigs Ann./Recl.*, 1997, 1023.

12 K. Kishikawa, M. Yamamoto, S. Kohmoto and K. Yamada, *J. Org. Chem.*, 1989, **54**, 2428.