Intramolecular photo[4+2]cycloaddition of an enone with a benzene ring

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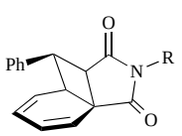
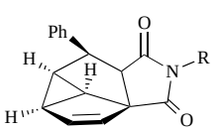
***N*-Benzoyl-*N*-benzylcinnamamides 1, *N*-acetyl-*N*-(1-benzyl)cinnamamides 3 and *N*-[(1-benzyl)-aminocarbonyl]-*N*-(1-benzyl)cinnamamides 5 have been irradiated by a high-pressure mercury lamp in the presence of benzil in benzene at room temperature to give 3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-dien-4-ones 2, 4 and 6 with high stereoselectivity. These are the first photo[4+2]cycloadducts of an enone and a benzene ring.**

Photo-[2+2]- and -[3+2]-cycloadditions of alkenes to benzenes are typical reactions of the latter and many examples have been reported.[1] In contrast, photo[4+2]cycloaddition of benzene is much rarer, the only known examples being photocycloaddition with dienes,[2] furan[3] and dichlorovinylene carbonate;[4] such reactions showed low selectivity and gave poor product yields. Similarly, photo[4+2]cycloadditions of enones are rare compared with the numerous examples of [2+2]cycloadditions with dienes; the only known examples of the former are the cycloadditions of enones with cyclopentadiene and furan;[5] however, both [4+2]- and [2+2]-addition showed poor selectivity. In order to achieve the hitherto unknown photo[4+2]cycloaddition of an enone with a benzene ring, we designed intramolecular photo[4+2]cycloadditions of the cinnamamides **1**, **3** and **5**.

According to MM2 calculation,[6] the [4+2]adduct **2a** is 6.6 kcal mol^{-1} more stable than the [2+2]adduct **2a**′ and 102.8 kcal



2a'



2a"

mol^{-1} more stable than the [3+2]adduct **2a**″. In these reactions the [4+2]adducts, 3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-dien-4-ones **2**, **4** and **6** were obtained as the sole products with perfect regio- and stereo-selectivity. The photo[4+2]cycloaddition of a benzene ring and an enone is novel, although the [4+2] process is symmetry allowed from (i) the excited ethene (S_1 or T_1) with the S_0 benzene or from (ii) the triplet excited benzene with S_0 ethene.[1h,7] Even thermal [4+2]cycloaddition of an enone to a benzene ring is very limited, highly strained benzenes being required to react with reactive dienophiles.[8]

An enone fixed rigidly and closely to a diene moiety was reported by Wollenweber to undergo an intramolecular diene/enone photo[4+2]cycloaddition from the excited state in a stepwise radical reaction.[9] Aoyama *et al*. also reported an intramolecular photo[2+2]cycloaddition of an alkene and a benzene ring connected with a CO–N bond.[1d] If the 2- and 3-carbons of an enone are close enough to the carbons at the 1′- and 4′-position of the benzene ring respectively, a diradical generated from the excited enone must react with the carbons at the 1′- and 4′-positions to give a [4+2]adduct (Fig. 1). Based on this idea, we planned to hold the enone double bond in an

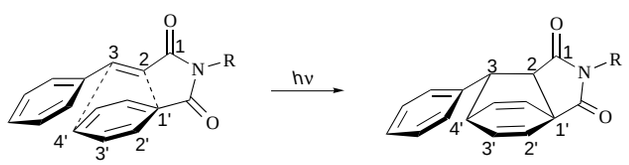
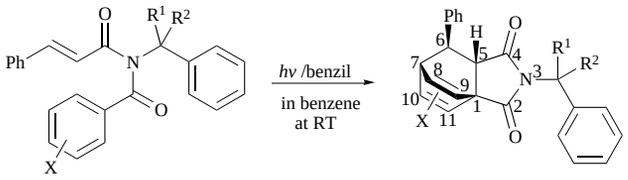


Fig. 1 Mode of photo[4+2]cycloaddition

appropriate position for [4+2]cycloaddition by linking it with a rigid and planar CO–N–CO bond to the benzene ring. To suppress polymerisation of the acryloyl group, a phenyl group was introduced at its 3-position.

The cinnamamides **1a–p** were prepared by condensation of the corresponding acid chlorides and amines. The irradiation was carried out in benzene with a triplet sensitiser (benzil) using a high-pressure mercury lamp under an Ar atmosphere at room temperature. Cycloaddition of the cinnamoyl double bond to the benzoyl-benzene proceeded to give the [4+2]adducts **2** (Table 1). In the reaction of **1a** ($R^1 = R^2 = X = H$), the cycloaddition was attempted with several sensitisers [anthracene ($E_T = 42$ kcal mol^{-1}), benzil ($E_T = 53$ kcal mol^{-1}), naphthalene ($E_T = 61$ kcal mol^{-1}), benzophenone ($E_T = 69$ kcal mol^{-1}) and acetophenone ($E_T = 74$ kcal mol^{-1})]; direct irradiation failed to induce any reaction. Benzil was found to be the only sensitiser for the photo[4+2]cycloaddition, the others sensitising *trans–cis* isomerisation of the cinnamoyl function.[10] The reason why benzil alone sensitised the reaction has yet to be clarified. However, it is obvious that the reaction proceeds from a triplet excited state because of sensitisation by the triplet sensitiser (benzil). Photo[2+2]cycloaddition of maleic anhydride to benzene is known to be a triplet state reaction when the charge-transfer complex is sensitised by benzophenone, the unsensitised process arising from the singlet state of the charge-transfer complex.[7,11] In all cases, perfect stereochemical control was achieved, the stereochemistry being determined by NOE difference spectra (^{1}H NMR spectroscopy). The selected data are shown in Scheme 1 and indicate the *trans*-configuration of the 5- and 6-protons. Although *trans–cis* isomerisation was observed by ^{1}H NMR analysis during the irradiation, the stereochemistry of the 5- and the 6-protons in the tricyclic products **2** was *trans*. The UV spectra of **1a** and **2a** were measured in acetonitrile at room temperature (Scheme 2). The peaks at 250–350 nm disappeared after the cycloaddition. Methoxy, nitro and cyano substituents on the benzoyl function [**1b**, **1i** (X = MeO), **1g**, **1m** (X = NO_2) and **1l** (X = CN)] resulted in complete suppression of the cycloaddition with recovery of

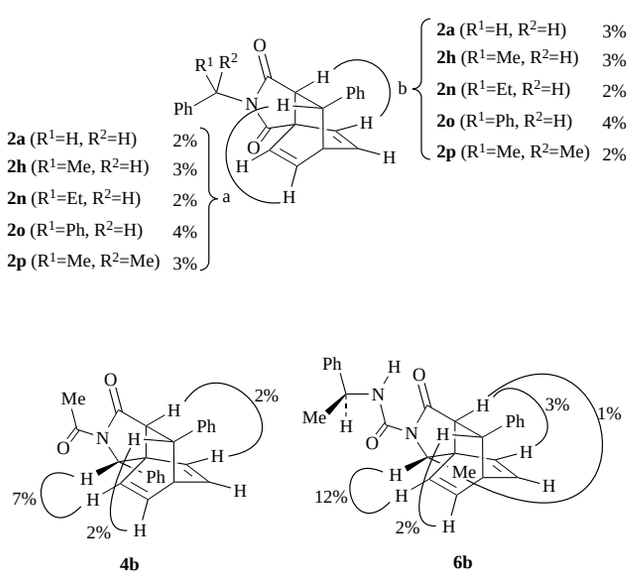


1a-p **2a-p**

Table 1 Photo[4+2]cycloaddition of **1a–p**[a]

Entry	Starting material	R^1	R^2	X	Time (h)	Product	Yield (%)[b]
1	**1a**	H	H	H	3	**2a**	93
2	**1b**			*p*-MeO	16	**2b**	0
3	**1c**			*p*-Me	2	**2c**	99[c]
4	**1d**			*m*-Me	1	**2d**	83
5	**1e**			*o*-Me	2	**2e**	35
6	**1f**			*p*-Cl	6	**2f**	71
7	**1g**			*p*-NO_2	18	**2g**	0
8	**1h**	Me	H	H	2	**2h**	99[c]
9	**1i**			*p*-MeO	8	**2i**	0
10	**1j**			*p*-Me	2	**2j**	99[c]
11	**1k**			*p*-Cl	4	**2k**	92
12	**1l**			*p*-CN	8	**2l**	0
13	**1m**			*p*-NO_2	8	**2m**	0
14	**1n**	Et		H	1	**2n**	87
15	**1o**	Ph		H	1	**2o**	98
16	**1p**	Me	Me	H	1	**2p**	84

[a] A solution of **1** (0.1 mmol) and benzil (1 equiv.) in benzene (5 ml) in a Pyrex test tube was irradiated by a high-pressure mercury lamp under Ar atmosphere at room temperature. [b] The yields are isolated yields. [c] The yield of products was determined by ^{1}H NMR spectroscopy of the solution. The products were thermally unstable.



4b **6b**

Scheme 1 NOE spectra of photo products (selected data)

starting material. In the reactions of **1**, the cinnamoyl group reacted with the benzoyl group, but not with benzyl. The electron density of the benzoyl group might control the reactivity. The stereoselectivity of the cyclisation is controlled by the steric repulsion between the phenyl and carbonyl in the cinnamoyl group. In the case of **1h**, **1n**, **1o** and **1p**, the regioselectivity of the cycloaddition was deduced from the reaction of the deuteriated compounds, the benzoyl group being replaced with [$^2H_5$]benzoyl (**1h′**, **1n′**, **1o′** and **1p′**), difficulties being experienced in determining the stereochemistry of the products by ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra of the adducts (**2h′**, **2n′**, **2o′** and **2p′**) the signals for the protons at the bridgehead-carbons (C-7) and the double bond-carbons (C-8,

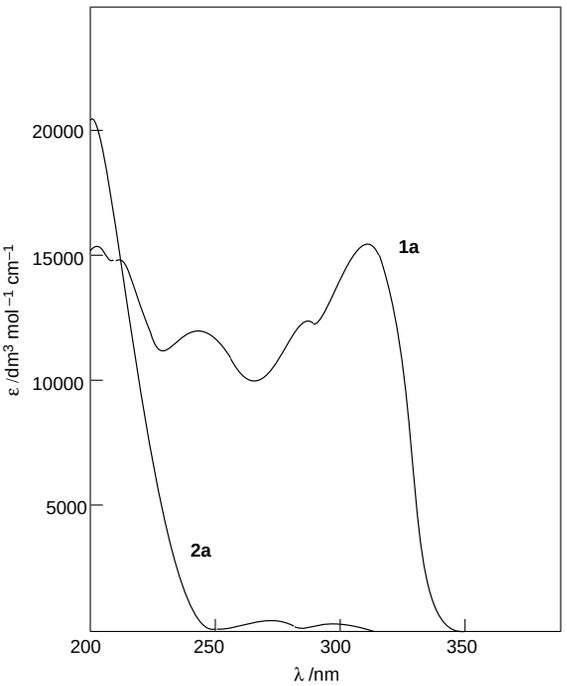
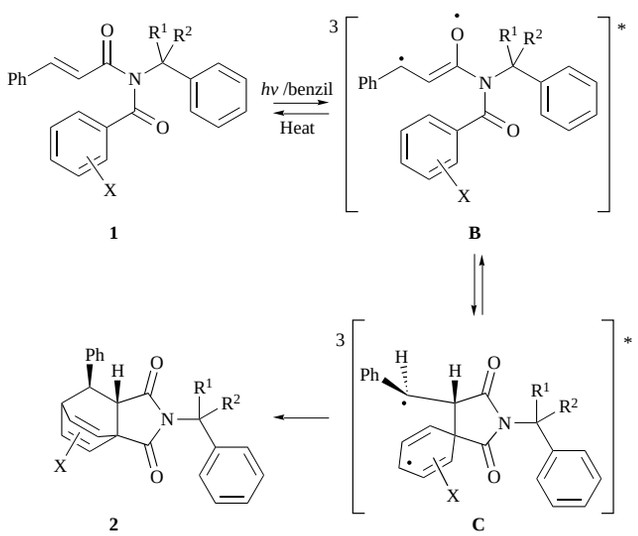


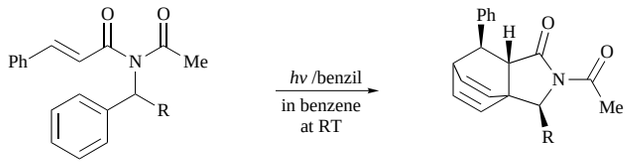
Fig. 2 UV spectra of **1a** and **2a**. Concentration = 1.00 × 10^{-5} M, solvent = acetonitrile, and temperature 20 °C.



Scheme 2 Mechanism for the intramolecular photo[4+2]cycloaddition

C-9, C-10 and C-11) disappeared as a result of replacement. The results indicated that the benzoyl reacted with the cinnamoyl function.

In order to investigate the reactivity of the benzyl group in the photocycloaddition, the benzoyl group was changed to an acetyl group (Table 2). The reaction of *N*-acetyl-*N*-benzylcinnamamide **3a** (R = H) failed to give the [4+2]adduct **4a** under similar reaction conditions. In contrast, *N*-acetyl-*N*-(diphenylmethyl)cinnamamide **3b** (R = Ph) produced the adduct **4b** in low yield. The products were expected to be a mixture of diastereoisomers because of the three asymmetric centres. However, the single diastereoisomer **4b** was obtained and its structure was determined by NOE difference spectroscopy (Scheme 1). The α-substituent of the benzyl group might have some important role for the reactivity and the stereoselectivity. Irradiation of *N*-cinnamoyl-*N*,*N′*-bis(1-phenylethyl)-ureas **5b–e** (R = Me) also gave single diastereoisomers (NOE of **6b** is shown in Scheme 1), [4+2]adducts **6b–e**; however,

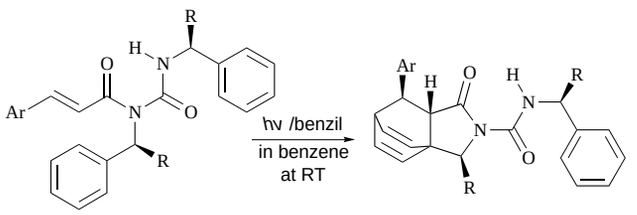


3a-b **4a-b**

Table 2 Photo[4+2]cycloaddition of **3a**,**b**[a]

Entry	Starting material	R	Time (h)	Product	Yield (%)[b]
1	**3a**	H	3	**4a**	0
2	**3b**	Ph	2	**4b**	42

[a] The same procedure in Table 1. [b] Isolated yields.



5a-e Ar = 4-XC_6H_4 **6a-e**

Table 3 Photo[4+2]cycloaddition of cinnamoylureas **5a–e**

Entry	Starting material	R	X	Time (h)	Product	Yield (%)[b]
1	**5a**	H	H	15	**6a**	0
2	**5b**	Me	H	4	**6b**	56
3	**5c**		MeO	6	**6c**	55
4	**5d**		Me	4	**6d**	56
5	**5e**		Cl	4	**6e**	61

[a] A solution of **5** (0.1 mmol) and benzil (1 equiv.) in benzene (5 ml) in a Pyrex test tube was irradiated by a high-pressure mercury lamp under an Ar atmosphere at room temperature. [b] The yields are isolated yields.

N-cinnamoyl-*N*,*N*′-dibenzylurea **5a** (R = H) was inert under similar conditions of irradiation (Table 3). In our previous report, type II photocyclisation was observed in the reaction of *N*-acryloyl-*N*,*N*′-bis(1-phenylethyl)ureas to give β-lactam derivatives.[12] Thus, a 3-phenyl substituent on the acryloyl group completely suppressed the hydrogen abstraction ability of the enone double bond. These results indicate that the α-substituted benzyl group is also reactive with the cinnamoyl group. In the case of **3b** and **5b–e** it is clear that the cinnamoyl group was excited by the sensitiser (benzil) to generate the diradical which reacted with the benzyl group, since the benzyl aromatic ring itself is not excited by benzil. As with these reactions, for compound **1** it also seems that benzil sensitises the cinnamoyl group which reacts with the benzoyl.

The mechanism for the photo[4+2]cycloaddition was postulated as follows (Scheme 2). The cinnamoyl group of **1** is excited by irradiation in the presence of benzil (a triplet sensitiser) to give the diradical **B**. The symmetry-allowed photo[2+2]cycloaddition of an excited maleic anhydride–benzene complex (the triplet state) takes place because the face of the maleic anhydride-double bond and that of benzene smoothly interact. However, in the reaction of **1**, **3** and **5** the face-to-face interaction for charge transfer[7,13] is difficult, because of the rigid junction, and stepwise cyclisation occurs. The stepwise [2+2]cyclisation of **1**, **3** and **5** needs a larger energy than the [4+2]cyclisation (from the MM2 calculation). The radical at the 2-position (more reactive than that at the 3-position),[14] reacts with C-1′ of the benzene ring to generate the spiro intermediate **C**. The methoxybenzoyl group (X = MeO) is not reactive

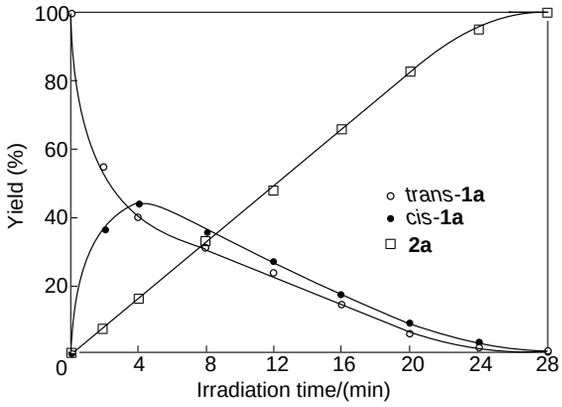
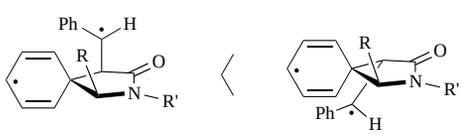


Fig. 3 Monitor of photo[4+2]cycloaddition of **2a**. A solution of *trans*-**1a** (0.03 mmol) and benzil (0.03 mmol) in [$^2H_6$]benzene (1.0 ml) in a Pyrex tube was irradiated by a high-pressure mercury lamp (450 W) under an argon atmosphere. The percentages of *trans*-**1a**, *cis*-**1a** and **2a** were monitored by ^{1}H NMR spectroscopy.

because an electron-rich benzene ring is an unsuitable acceptor of radicals. Suppression of reactivity by the nitro- and cyano-groups (X = NO_2 and CN) is explained in terms of the unreactivity of the diradical in the generated diradical **C** which is stabilised by the electron acceptor groups. In **C** the α-proton is located *cis* to the phenyl group because of steric repulsion. In the photoreaction of *N*-(α-substituted benzyl) cinnamamides **3b** and **5b–e**, the intermediate **E** is more favoured than **D** because of the steric repulsion between the R and the benzyl group (Scheme 3). In the photoreaction of a vinylene carbon-



D (disfavoured) **E** (favoured)

Scheme 3 Diradical intermediates generated from **3b** (R = Ph, R′ = CH_2Ph) and **5b** [R = Me, R′ = CONHCH(CH_3)Ph]

ate and benzene (Scharf *et al.*[4]), the initially generated [2+2]adducts are gradually transformed to the corresponding [4+2]- adducts. Accordingly, the [2+2]adducts may be produced from the intermediate **C** at an early stage. However, from the result of MM2 calculation, the [2+2]adducts are less stable than the [4+2]products and their formation was not detected by monitoring with ^{1}H NMR spectroscopy (Fig. 3). The *trans–cis* isomerisation occurs followed by the [4+2]cycloaddition during the irradiation.

Some of the cinnamamides showed the thermal retro-[4+2]addition at room temperature (*i.e.* **2c**→**1c**, $\tau_{1/2}$ = 3 h). The stereochemistry of the recovered cinnamamide **1c** was the *trans*-form only. Reconstruction of the conjugated system must be the driving force for the retro reaction.

The intramolecular cycloaddition of a benzene ring in cinnamamides gives only the [4+2]adducts and does not produce other by-products ([2+2]- and [3+2]-adducts). Now we are studying its utilisation for the photosensitive materials.

Experimental

General

Mps were determined on a Yanako MP-S3 melting-point apparatus and are uncorrected. ^{1}H NMR (270, 400, 500 MHz) and ^{13}C NMR (22.4, 67.8 MHz) spectra were recorded in $CDCl_3$ or C_6D_6 and were referenced against internal tetramethylsilane. Chemical shifts are reported in ppm on the δ scale. Coupling constants (*J*) are given in Hz. High-performance

liquid chromatography (HPLC) was performed on Merck Lichrosorb Si 60 column (7 μm) eluting with ethyl acetate–hexane. Flash column chromatography (ethyl acetate–hexane) was performed with Fuji silica gel BW-200 (200 mesh). Photoreactions were carried out using a USHIO 450 W high-pressure mercury lamp. All solvents were freshly distilled and stored over 4 Å molecular sieves. *N*-Alkylcinnamamides and *N*-alkylbenzamides were prepared from the corresponding commercially available amines and acid chlorides.

General procedure for the preparation of the cinnamamides 1 and 3

To a solution of *N*-alkylcinnamamide (1 mmol) in benzene (20 ml) was added triethylamine (1.2 equiv.) at room temperature. To the resulting solution was added dropwise the appropriate acyl chloride (1.2 equiv.). The resulting mixture was heated at reflux for 24 h after which it was quenched with saturated aqueous $NaHCO_3$ (20 ml) and washed with 1 M hydrochloric acid (20 ml) and brine (20 ml). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The products were separated by column chromatography on silica gel, and further purification by recrystallisation from ethyl acetate–hexane or HPLC gave the cinnamamides.

***N*-Benzoyl-*N*-benzylcinnamamide 1a.** Colourless crystals (64%); mp 115–116 °C (Found: C, 80.9; H, 5.5; N, 4.4. $C_{23}H_{19}NO_2$ requires C, 80.9; H, 5.6; N, 4.1%); δ_H(270 MHz; $CDCl_3$) 5.15 (2 H, s), 6.30 (1 H, d, $J_{2,3}$ 15.0), 7.10–7.65 (15 H, m) and 7.55 (1 H, d, $J_{2,3}$ 15.0); δ_C(22.4 MHz; $CDCl_3$) 49.2 (t), 121.6 (d), 127.5 (d), 127.9 (d), 128.2 (d), 128.5 (d), 128.7 (d), 128.8 (d), 130.2 (d), 132.6 (d), 134.4 (s), 136.3 (s), 137.5 (s), 143.4 (d), 169.3 (s) and 173.4 (s); ν_{max}(KBr)/cm^{-1} 1695, 1655, 1620, 1350, 1205, 1190, 1140 and 705.

***N*-Benzyl-*N*-(*p*-methoxybenzoyl)cinnamamide 1b.** Colourless crystals (40%); mp 81–82 °C (Found: C, 77.7; H, 5.7; N, 4.0. $C_{24}H_{21}NO_3$ requires C, 77.6; H, 5.7; N, 3.8%); δ_H(270 MHz; $CDCl_3$) 3.80 (3 H, s), 5.15 (2 H, s), 6.30 (1 H, d, $J_{2,3}$ 15.5), 6.90 (2 H, d, *J* 9.0), 7.15 (2 H, dd, *J* 2.0 and 7.5), 7.20–7.35 (6 H, m), 7.40 (2 H, dd, *J* 2.0 and 7.5), 7.55 (1 H, d, $J_{2,3}$ 15.5) and 7.65 (2 H, d, $J_{2',3'}$ 9.0); δ_C(22.4 MHz; $CDCl_3$) 49.3 (t), 55.5 (q), 114.1 (d), 121.6 (d), 127.4 (d), 127.9 (d), 128.2 (d), 128.5 (d), 128.7 (d), 130.1 (d), 131.3 (d), 134.6 (s), 137.7 (s), 142.9 (d), 163.3 (s), 169.2 (s) and 173.0 (s); ν_{max}(KBr)/cm^{-1} 1650, 1610, 1340, 1310, 1255, 1170 and 1035.

***N*-Benzyl-*N*-(*p*-methylbenzoyl)cinnamamide 1c.** Colourless crystals (84%); mp 113–114 °C (Found: C, 81.0; H, 5.9; N, 4.2. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%); δ_H(270 MHz; $CDCl_3$) 2.35 (3 H, s), 5.15 (2 H, s), 6.30 (1 H, d, $J_{2,3}$ 15.5), 7.10–7.45 (12 H, m), 7.55 (1 H, d, $J_{2,3}$ 15.5) and 7.55 (2 H, d, $J_{2',3'}$ 10.0); δ_C(22.4 MHz; $CDCl_3$) 21.6 (q), 49.2 (t), 121.7 (d), 127.4 (d), 127.9 (d), 128.2 (d), 128.5 (d), 128.7 (d), 129.0 (d), 129.5 (d), 130.2 (d), 133.5 (s), 134.6 (s), 137.6 (s), 143.1 (d), 143.5 (s), 169.3 (s) and 173.5 (s); ν_{max}(KBr)/cm^{-1} 1695, 1655, 1620, 1345, 1310, 1185, 1135, 980, 760 and 700.

***N*-Benzyl-*N*-(*m*-methylbenzoyl)cinnamamide 1d.** Colourless crystals (53%); mp 76–77 °C (Found: C, 81.0; H, 5.9; N, 3.9. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%); δ_H(270 MHz; $CDCl_3$) 2.30 (3 H, s), 5.15 (2 H, s), 6.30 (1 H, d, $J_{2,3}$ 15.5), 7.10 (2 H, dd, $J_{4',6'}$ 2.0 and $J_{4',5'}$ 8.0), 7.20–7.45 (12 H, m) and 7.55 (1 H, d, $J_{2,3}$ 15.5); δ_C(22.4 MHz; $CDCl_3$) 21.2 (q), 49.1 (t), 121.7 (d), 125.9 (d), 127.4 (d), 127.8 (d), 128.2 (d), 128.5 (d), 128.6 (d), 129.2 (d), 130.1 (d), 133.2 (d), 134.4 (s), 136.2 (s), 137.6 (s), 138.7 (s), 143.0 (d), 169.3 (s) and 173.6 (s); ν_{max}(KBr)/cm^{-1} 1695, 1655, 1620, 1345 and 1165.

***N*-Benzyl-*N*-(*o*-methylbenzoyl)cinnamamide 1e.** Colourless crystals (48%); mp 94–95 °C (Found: C, 81.0; H, 5.8; N, 3.8. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%); δ_H(270 MHz; $CDCl_3$) 2.30 (3 H, s), 5.10 (2 H, s), 6.50 (1 H, d, $J_{2,3}$ 15.0), 7.10–7.40 (14 H, m) and 7.55 (1 H, d, $J_{2,3}$ 15.0); δ_C(22.4 MHz; $CDCl_3$) 19.3 (q), 48.4 (t), 121.0 (d), 125.9 (d), 127.4 (d), 127.6 (d), 127.9 (d), 128.3 (d), 128.4 (d), 128.6 (d), 130.1 (d), 130.9 (d), 131.2 (d), 134.4 (s), 136.3 (s), 137.4 (s), 143.4 (d), 169.3 (s) and 173.2 (s); ν_{max}(KBr)/cm^{-1} 1695, 1655, 1620, 1345, 1310, 1190, 1145, 1045 and 975.

***N*-Benzyl-*N*-(*p*-chlorobenzoyl)cinnamamide 1f.** Colourless crystals (23%); mp 121–122 °C (Found: C, 73.5; H, 4.7; N, 3.7. $C_{23}H_{18}NO_2Cl$ requires C, 73.5; H, 4.8; N, 3.7%); δ_H(270 MHz; $CDCl_3$) 5.15 (2 H, s), 6.35 (1 H, d, $J_{2,3}$ 15.0), 7.20 (2 H, dd, *J* 2.0 and 8.5), 7.25–7.40 (8 H, m), 7.40 (2 H, d, $J_{2',3'}$ 8.5), 7.55 (2 H, d, $J_{2',3'}$ 8.5) and 7.60 (1 H, d, $J_{2,3}$ 15.0); δ_C(22.4 MHz; $CDCl_3$) 49.1 (t), 121.0 (d), 127.5 (d), 127.9 (d), 128.0 (d), 128.5 (d), 128.7 (d), 128.9 (d), 130.0 (d), 130.4 (d), 134.1 (s), 134.5 (s), 137.2 (s), 138.7 (s), 144.0 (d), 169.0 (s) and 172.3 (s); ν_{max}(KBr)/cm^{-1} 1700, 1650, 1615, 1335, 1310, 1185, 1135 and 975.

***N*-Benzyl-*N*-(*p*-nitrobenzoyl)cinnamamide 1g.** Colourless crystals (21%); mp 107–108 °C (Found: C, 71.5; H, 4.4; N, 7.4. $C_{23}H_{18}N_2O_4$ requires C, 71.5; H, 4.7; N, 7.3%); δ_H(270 MHz; $CDCl_3$) 5.15 (2 H, s), 6.50 (1 H, d, $J_{2,3}$ 15.5), 7.25–7.40 (m, 10 H), 7.60 (1 H, d, $J_{2,3}$ 15.5), 7.75 (2 H, dm, *J* 9.0) and 8.25 (2 H, dm, *J* 9.0); δ_C(22.4 MHz; $CDCl_3$) 44.8 (t), 119.9 (d), 123.7 (d), 127.6 (d), 127.7 (d), 128.0 (d), 128.7 (d), 128.9 (d × 2), 130.8 (d), 133.8 (s), 136.8 (s), 141.8 (s), 145.7 (d), 149.3 (s), 169.0 (s) and 171.4 (s); ν_{max}(KBr)/cm^{-1} 1695, 1655, 1615, 1530, 1345, 1310, 1185, 865 and 715.

***N*-Benzoyl-*N*-(1-phenylethyl)cinnamamide 1h.** Colourless oil (98%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.06 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.11 (1 H, d, $J_{2,3}$ 15.5) and 7.00–7.70 (m, 16 H); δ_C(22.4 MHz; $CDCl_3$) 17.4 (q), 54.7 (d), 122.5 (d), 126.8 (d), 126.9 (d), 127.4 (d), 127.9 (d), 128.3 (d), 128.4 (d), 129.8 (d), 130.1 (d), 132.2 (d), 133.9 (s), 136.9 (s), 140.7 (s), 142.3 (d), 168.7 (s) and 173.0 (s); ν_{max}(neat)/cm^{-1} 1660, 1625, 1380, 1340, 1305, 1275, 1195, 1070, 765 and 700 [Found: MH^+ (FAB), 356.1657. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1650].

***N*-(*p*-Methoxybenzoyl)-*N*-(1-phenylethyl)cinnamamide 1i.** Colourless oil (74%); δ_H(270 MHz; $CDCl_3$) 1.85 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 3.80 (3 H, s), 6.00 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.15 (1 H, d, $J_{2,3}$ 15.5), 6.85 (2 H, dm, $J_{2',3'}$ 9.0), 7.10 (2 H, dd, *J* 2.0 and 8.0), 7.20–7.35 (6 H, m), 7.45 (1 H, d, $J_{2,3}$ 15.5), 7.50 (2 H, dd, *J* 2.0 and 8.0) and 7.65 (2 H, dm, $J_{2',3'}$ 9.0); δ_C(22.4 MHz; $CDCl_3$) 17.8 (q), 55.1 (d), 55.3 (q), 114.0 (d), 122.5 (d), 127.0 (d), 127.2 (d), 127.7 (d), 128.1 (d), 128.2 (d), 128.6 (d), 129.4 (s), 129.9 (d), 131.4 (d), 134.4 (s), 141.0 (s), 142.2 (d), 163.3 (s), 168.6 (s) and 172.9 (s); ν_{max}(neat)/cm^{-1} 1694, 1648, 1622, 1602, 1342, 1306, 1260, 1200, 1168, 788 and 760 [Found: MH^+ (FAB), 386.1762. $C_{25}H_{24}NO_3$ (MH^+) requires 386.1756].

***N*-(*p*-Methylbenzoyl)-*N*-(1-phenylethyl)cinnamamide 1j.** Colourless oil (99%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 2.30 (3 H, s), 6.05 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.10 (1 H, d, $J_{2,3}$ 15.5), 7.05 (2 H, dd, *J* 1.5 and 8.0), 7.15–7.35 (8 H, m), 7.40 (1 H, d, $J_{2,3}$ 15.5), 7.50 (2 H, dd, *J* 1.5 and 8.0) and 7.55 (2 H, dm, $J_{2',3'}$ 8.0); δ_C(22.4 MHz; $CDCl_3$) 17.7 (q), 21.4 (q), 55.0 (d), 122.6 (d), 127.0 (d), 127.2 (d), 127.6 (d), 128.1 (d), 128.5 (d), 129.0 (d), 129.3 (d), 129.9 (d), 134.3 (s), 140.9 (s), 142.3 (d), 143.5 (s), 168.8 (s) and 173.3 (s); ν_{max}(neat)/cm^{-1} 1694, 1658, 1620, 1450, 1374, 1338, 1306, 1272, 1196 and 1176 [Found: MH^+ (FAB), 370.1806. $C_{25}H_{24}NO_2$ (MH^+) requires 370.1807].

***N*-(*p*-Chlorobenzoyl)-*N*-(1-phenylethyl)cinnamamide 1k.** Colourless oil (91%); δ_H(270 MHz; $CDCl_3$) 1.85 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.05 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.10 (1 H, d, $J_{2,3}$ 15.5), 7.10 (2 H, dd, *J* 1.5 and 8.0), 7.20–7.40 (8 H, m), 7.40 (1 H, d, $J_{2,3}$ 15.5), 7.50 (2 H, dd, *J* 1.5 and 8.0) and 7.55 (2 H, dm, $J_{2',3'}$ 8.5); δ_C(22.4 MHz; $CDCl_3$) 17.6 (q), 54.9 (d), 122.1 (d), 127.0 (d), 127.6 (d), 128.1 (d), 128.5 (d), 128.8 (d), 130.0 (d), 130.1 (d), 133.9 (s), 135.3 (s), 138.6 (s), 140.6 (s), 143.1 (d), 168.7 (s) and 172.0 (s); ν_{max}(neat)/cm^{-1} 1696, 1652, 1620, 1340, 1192, 1172 and 758 [Found: MH^+ (FAB), 390.1270. $C_{24}H_{21}NO_2Cl$ (MH^+) requires 390.1261].

***N*-(*p*-Cyanobenzoyl)-*N*-(1-phenylethyl)cinnamamide 1l.** Colourless oil (66%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 6.05 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 6.15 (1 H, d, $J_{2,3}$ 15.5), 7.10 (2 H, dd, *J* 1.5 and 8.0), 7.25–7.40 (7 H, m), 7.50 (2 H, dd, *J* 1.5 and

8.0) and 7.65–7.75 (4 H, m); δ_C(22.4 MHz; $CDCl_3$) 17.6 (q), 54.8 (d), 115.2 (s), 117.4 (s), 121.7 (d), 126.9 (d), 127.7 (d), 128.3 (d), 128.6 (d), 128.7 (d), 130.6 (d), 132.2 (d), 133.6 (s), 140.3 (s), 140.7 (s), 144.3 (d), 169.1 (s) and 171.4 (s); ν_{max}(neat)/cm^{-1} 2225w, 1654, 1340, 1274, 1192, 1174, 788, 762 and 700 [Found: MH^+ (FAB), 381.1605. $C_{25}H_{21}N_2O_3$ (MH^+) requires 381.1603].

***N*-(*p*-Nitrobenzoyl)-*N*-(1-phenylethyl)cinnamamide 1m.** Colourless oil (65%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.05 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.20 (1 H, d, $J_{2,3}$ 15.5), 7.15 (2 H, dd, *J* 1.5 and 7.5), 7.25–7.45 (7 H, m), 7.50 (2 H, dd, *J* 1.5 and 7.5), 7.75 (2 H, dm, $J_{2',3'}$ 9.0) and 8.20 (2 H, dm, $J_{2',3'}$ 9.0); δ_C(22.4 MHz; $CDCl_3$) 17.6 (q), 54.8 (d), 121.4 (d), 123.7 (d), 126.9 (d), 127.4 (d), 127.8 (d), 128.4 (d), 128.7 (d), 129.0 (d), 130.6 (d), 133.6 (s), 140.2 (s), 142.4 (s), 144.7 (d), 149.2 (s), 169.3 (s) and 171.2 (s); ν_{max}(neat)/cm^{-1} 1656, 1622, 1526, 1350, 1306, 1274, 1190, 848, 792, 760, 714 and 700 [Found: MH^+ (FAB), 401.1503. $C_{24}H_{21}N_2O_4$ (MH^+) requires 401.1502].

***N*-Benzoyl-*N*-(1-phenylpropyl)cinnamamide 1n.** Colourless oil (95%); δ_H(270 MHz; $CDCl_3$) 1.05 (3 H, t, $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.30 (1 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 14.0 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.50 (1 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 14.0 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 5.80 (1 H, dd, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5 and $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5), 6.05 (1 H, d, $J_{2,3}$ 15.5), 7.00 (2 H, ddd, *J* 1.5, 1.5 and 7.5), 7.16–7.50 (10 H, m), 7.55 (2 H, ddd, *J* 1.5, 1.5 and 7.5) and 7.65 (2 H, ddd, *J* 2.5, 3.0 and 8.5); δ_C(22.4 MHz; $CDCl_3$) 11.6 (q), 24.6 (t), 61.8 (d), 122.9 (d), 127.2 (d), 127.6 (d), 128.0 (d), 128.5 (d), 128.6 (d), 128.8 (d), 130.0 (d), 132.4 (d), 134.1 (s), 137.2 (s), 140.1 (s), 142.4 (d), 169.5 (s) and 173.1 (s); ν_{max}(neat)/cm^{-1} 1696, 1656, 1620, 1338, 1192, 1176, 788, 760 and 698 [Found: MH^+ (FAB), 370.1804. $C_{25}H_{24}NO_2$ (MH^+) requires 370.1807].

***N*-Benzoyl-*N*-(diphenylmethyl)cinnamamide 1o.** White solid (32%) (Found: C, 82.3; H, 6.0; N, 3.2. $C_{29}H_{23}NO_2 \cdot 1/3H_2O$ requires C, 82.3; H, 5.6; N, 3.3%); δ_H(270 MHz; $CDCl_3$) 6.15 (1 H, d, $J_{2,3}$ 15.5), 7.05 (2 H, dd, *J* 1.5 and 8.0), 7.15–7.50 (17 H, m) and 7.70 (2 H, ddd, *J* 2.5, 4.5 and 8.5); δ_C(22.4 MHz; $CDCl_3$) 63.8 (d), 122.6 (d), 127.4 (d), 127.8 (d), 128.2 (d), 128.6 (d), 128.8 (d), 128.9 (d), 129.0 (d), 130.2 (d), 132.8 (d), 134.3 (s), 137.1 (s), 138.9 (s), 143.2 (d), 169.0 (s) and 172.8 (s); ν_{max}(KBr)/cm^{-1} 3050, 2930, 1695, 1660, 1620, 1340, 1190, 985, 765 and 695.

***N*-Benzoyl-*N*-(1-methyl-l-phenylethyl)cinnamamide 1p.** Colourless oil (73%); δ_H(270 MHz; $CDCl_3$) 1.85 (6 H, s), 6.20 (1 H, d, $J_{2,3}$ 15.5), 7.10–7.65 (13 H, m), 7.45 (1 H, d, $J_{2,3}$ 15.5) and 8.05 (2 H, ddd, *J* 1.5, 3.0 and 8.0); δ_C(22.4 MHz; $CDCl_3$) 29.3 (q), 62.9 (s), 121.5 (d), 125.0 (d), 126.4 (d), 127.7 (d), 128.2 (d), 128.5 (d), 129.0 (d), 129.8 (d), 130.1 (d), 133.8 (d), 134.4 (s), 136.6 (s), 142.7 (d), 147.2 (s), 166.2 (s) and 174.8 (s); ν_{max}(neat)/cm^{-1} 1700, 1662, 1622, 1344, 1268, 1232, 1158, 784, 764 and 698 [Found: MH^+ (FAB), 370.1813. $C_{25}H_{24}NO_2$ (MH^+) requires 370.1807].

***N*-Acetyl-*N*-benzylcinnamamide 3a.** Colourless crystals (26%); mp 92–93 °C (Found: C, 77.4; H, 6.0; N, 4.9. $C_{18}H_{17}NO_2$ requires C, 77.4; H, 6.1; N, 5.0%); δ_H(270 MHz; $CDCl_3$) 2.50 (3 H, s), 5.05 (2 H, s), 7.05 (1 H, d, $J_{2,3}$ 15.5), 7.20–7.40 (8 H, m), 7.50 (1 H, d, *J* 7.5), 7.50 (1 H, d, *J* 7.5) and 7.75 (1 H, d, $J_{2,3}$ 15.5); δ_C(22.4 MHz; $CDCl_3$) 26.0 (q), 47.5 (t), 120.1 (d), 126.2 (d), 127.3 (d), 128.1 (d), 128.7 (d), 130.3 (d), 134.4 (s), 137.0 (s), 145.0 (d), 169.1 (s) and 173.4 (s); ν_{max}(KBr)/cm^{-1} 1700, 1610, 1380, 1340, 1195 and 1085.

***N*-Acetyl-*N*-(diphenylmethyl)cinnamamide 3b.** Colourless oil (99%); δ_H(270 MHz; $CDCl_3$) 2.40 (3 H, s), 6.70 (1 H, d, $J_{2,3}$ 15.5), 7.10 (1 H, s), 7.25–7.35 (15 H, m) and 7.50 (1 H, d, $J_{2,3}$ 15.5); δ_C(22.4 MHz; $CDCl_3$) 26.3 (q), 61.6 (d), 121.6 (d), 127.3 (d), 128.0 (d), 128.2 (d), 128.6 (d), 130.2 (d), 134.1 (s), 138.4 (s), 144.0 (d), 169.9 (s) and 173.0 (s); ν_{max}(neat)/cm^{-1} 1684, 1622, 1378, 1334, 1244, 1172, 784, 760 and 700 [Found: MH^+ (FAB), 356.1652. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1650].

General procedure for the preparation of the cinnamamides 5

To a solution of cinnamic acid (1 mmol) in 5 ml of acetonitrile was added triethylamine (1 equiv.) at room temperature. To a solution of carbodiimide (1.2 equiv.) in acetonitrile (10 ml) was added dropwise the resulting solution. After complete addition, the mixture was further stirred at room temperature for 24 h after which it was acidified with 1 M hydrochloric acid (50 ml) and extracted with diethyl ether (3 × 20 ml). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The products were separated by column chromatography on silica gel and further purification by HPLC gave the cinnamamides.

***N*-Benzyl-*N*-(benzylaminocarbonyl)cinnamamide 5a.** Colourless crystals (76%); mp 111–112 °C (Found: C, 77.6; H, 6.0; N, 7.5. $C_{24}H_{22}N_2O_2$ requires C, 77.8; H, 6.0; N, 7.6%); δ_H(270 MHz; $CDCl_3$) 4.60 (2 H, d, $J_{N'H,N'\text{-}\alpha}$ 5.5), 5.20 (2 H, s), 6.80 (1 H, d, $J_{2,3}$ 15.5), 7.25–7.40 (16 H, m) and 7.70 (1 H, d, $J_{2,3}$ 15.5); δ_C(22.4 MHz; $CDCl_3$) 44.7 (t), 47.6 (t), 118.7 (d), 126.1 (d), 127.3 (d), 127.4 (d), 127.5 (d), 128.1 (d), 128.6 (d), 128.9 (d), 130.5 (d), 134.3 (s), 137.8 (s), 138.3 (s), 145.9 (d), 155.4 (s) and 170.2 (s); ν_{max}(KBr)/cm^{-1} 1640, 1535, 1355, 1185 and 705.

***N*-(1-Phenylethyl)-*N*-[(1-phenylethyl)aminocarbonyl]cinnamamide 5b.** Colourless oil (91%); δ_H(270 MHz; $CDCl_3$) 1.55 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 1.75 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 5.07 (1 H, dq, $J_{N'H,N''\text{-}\alpha}$ 7.0 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 6.30 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.60 (1 H, d, $J_{2,3}$ 16.0), 7.20–7.40 (15 H, m), 7.60 (1 H, d, $J_{2,3}$ 16.0) and 9.00 (1 H, br); δ_C(22.4 MHz; $CDCl_3$) 18.4 (q), 22.6 (q), 50.8 (d), 51.4 (d), 120.3 (d), 126.0 (d), 126.3 (d), 127.1 (d), 127.2 (d), 128.0 (d), 128.5 (d), 128.6 (d), 128.7 (d), 130.1 (d), 134.5 (s), 141.8 (s), 143.2 (s), 144.0 (d), 154.6 (s) and 169.3 (s); ν_{max}(neat)/cm^{-1} 1710, 1656, 1610, 1522, 1498, 1376, 786, 762 and 700 [Found: MH^+ (FAB), 399.2073. $C_{26}H_{27}N_2O_2$ (MH^+) requires 399.2072].

***N*-(1-Phenylethyl)-*N*-[(1-phenylethyl)aminocarbonyl]-4′-methoxycinnamamide 5c.** Colourless oil (75%); δ_H(270 MHz; $CDCl_3$) 1.55 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 1.75 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 3.80 (3 H, s), 5.10 (1 H, dq, $J_{N'H,N''\text{-}\alpha}$ 7.0 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 6.30 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.45 (1 H, d, $J_{2,3}$ 15.0), 6.80 (2 H, d, $J_{2',3'}$ 9.0), 7.20 (2 H, d, $J_{2',3'}$ 9.0), 7.20–7.40 (10 H, m), 7.60 (1 H, d, $J_{2,3}$ 15.0) and 9.15 (1 H, br); δ_C(22.4 MHz; $CDCl_3$) 18.4 (q), 22.6 (q), 50.7 (d), 51.4 (d), 55.3 (q), 114.2 (d), 117.8 (d), 126.0 (d), 127.0 (d), 127.1 (d), 127.3 (d), 128.3 (d), 128.6 (d), 128.7 (d), 130.0 (d), 142.0 (s), 143.4 (s), 143.8 (s), 154.8 (d), 161.3 (s) and 169.7 (s); ν_{max}(neat)/cm^{-1} 1708, 1650, 1598, 1576, 1512, 1452, 782, 762 and 700 [Found: MH^+ (FAB), 433.1674. $C_{27}H_{29}N_2O_3$ (MH^+) requires 433.1683].

***N*-(1-Phenylethyl)-*N*-[(1-phenylethyl)aminocarbonyl]-4′-methylcinnamamide 5d.** Colourless oil (72%); δ_H(270 MHz; $CDCl_3$) 1.55 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 1.80 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 2.30 (3 H, s), 5.10 (1 H, dq, $J_{N'H,N''\text{-}\alpha}$ 7.0 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 6.30 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.55 (1 H, d, $J_{2,3}$ 15.0), 7.10–7.40 (14 H, m), 7.60 (1 H, d, $J_{2,3}$ 15.0) and 9.05 (1 H, br); δ_C(22.4 MHz; $CDCl_3$) 18.4 (q), 21.3 (q), 22.6 (q), 50.7 (d), 51.4 (d), 119.2 (d), 126.0 (d), 127.06 (d), 127.12 (d), 128.0 (d), 128.6 (d), 128.7 (d), 129.5 (d), 131.8 (d), 140.6 (s), 141.9 (s), 143.3 (s), 144.0 (d), 154.7 (s) and 169.6 (s); ν_{max}(neat)/cm^{-1} 1704, 1650, 1602, 1514, 1498, 1368, 812, 786, 760 and 700 [Found: MH^+ (FAB), 413.2233. $C_{27}H_{29}N_2O_2$ (MH^+) requires 413.2229].

***N*-(1-Phenylethyl)-*N*-[(1-phenylethyl)aminocarbonyl]-4′-chlorocinnamamide 5e.** Colourless oil (86%); δ_H(270 MHz; $CDCl_3$) 1.55 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 1.75 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 5.05 (1 H, dq, $J_{N'H,N'\text{-}\alpha}$ 7.5 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 6.30 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 6.55 (1 H, d, $J_{2,3}$ 15.5), 7.10–7.40 (14 H, m), 7.50 (1 H, d, $J_{2,3}$ 15.5) and 8.80 (1 H, br); δ_C(22.4 MHz; $CDCl_3$) 18.3 (q), 22.1 (q), 50.6 (d), 51.6 (d), 120.3 (d), 125.7 (d), 125.96 (d), 126.02 (d), 127.1 (d), 128.1 (d), 128.5 (d), 128.8 (d), 128.9 (d), 132.7 (s), 135.7 (s), 141.7 (s), 142.1 (d), 142.9 (s), 154.1 (s) and 168.1 (s); ν_{max}(neat)/cm^{-1} 1702, 1656, 1610, 1530, 1494, 1372, 1262, 1094, 786, 762 and 700 [Found: MH^+ (FAB), 399.2073. $C_{26}H_{26}N_2O_2Cl$ (MH^+) requires 399.2072].

General procedure for the photocycloaddition of the cinnamamides 2

A solution containing cinnamamide (0.1 mmol) and benzil (1 equiv.) in benzene (5 ml) in a Pyrex test tube was irradiated with

a high-pressure mercury lamp under an Ar atmosphere at room temperature, the reaction being monitored by HPLC and a UV detector. After irradiation, the mixture was evaporated *in vacuo*. The products were separated by column chromatography on silica gel (ethyl acetate–hexane) and purified by HPLC (ethyl acetate–hexane) to give the photocycloadducts.

(5*S,6*R**)-*N*-Benzyl-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2a.** Colourless oil (93%); δ_H(270 MHz; $CDCl_3$) 2.75 (1 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, dd, $J_{6,7}$ 1.0 and $J_{5,6}$ 7.0), 3.90 (1 H, ddddd, $J_{6,7}$ 1.0, $J_{7,9}$ 1.0, $J_{7,11}$ 1.0, $J_{7,8}$ 5.5 and $J_{7,10}$ 6.0), 4.65 (2 H, s), 6.05 (1 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.5), 6.45 (1 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.90 (1 H, dd, $J_{7,10}$ 6.0 and $J_{10,11}$ 7.5), 7.05 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5) and 7.15–7.40 (10 H, m); δ_C(22.4 MHz; $CDCl_3$) 42.2 (t), 44.9 (d), 45.1 (d), 55.8 (s), 57.6 (d), 126.8 (d), 127.1 (d), 127.8 (d), 128.5 (d), 128.6 (d), 132.2 (d), 132.5 (d), 133.8 (d), 136.1 (s), 141.8 (d), 142.6 (s), 175.0 (s) and 176.0 (s); ν_{max}(neat)/cm^{-1} 1712, 1384, 1344, 1131, 794, 758 and 700 [Found: MH^+ (FAB), 342.1478. $C_{23}H_{20}NO_2$ (MH^+) requires 342.1494].

(5*S,6*R**)-*N*-Benzyl-7-methyl-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2c.** Colourless oil (>95%); δ_H(90 MHz; C_6D_6) 1.00 (3 H, s), 2.65 (1 H, d, $J_{5,6}$ 7.5), 2.95 (1 H, d, $J_{5,6}$ 7.5), 4.70 (2 H, d, *J* 2.0), 5.80 (1 H, d, $J_{8,9}$ 7.5), 6.00 (1 H, d, $J_{10,11}$ 7.1), 6.20 (1 H, d, $J_{10,11}$ 7.0), 6.90 (1 H, d, $J_{8,9}$ 7.5) and 6.97–7.31 (10 H, m); the ^{13}C NMR, IR and HRMS spectra were not measured because of the unstable nature of the product.

(1*R,5*S**,6*R**,7*S**)-*N*-Benzyl-10-methyl-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione (a major product of 2d).** Colourless oil (47%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, d, $J_{10\text{-}Me,11}$ 2.0), 2.75 (1 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 7.0), 3.60 (1 H, dddd, $J_{6,7}$ 1.5, $J_{7,9}$ 1.5, $J_{7,11}$ 2.0 and $J_{7,8}$ 5.5), 4.65 (2 H, d, $J_{2,5}$ 2.5), 5.65 (1 H, dd, $J_{7,11}$ 2.0 and $J_{10\text{-}Me,11}$ 2.0), 6.45 (1 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 7.05 (1 H, dd, $J_{7,9}$ 1.5 and $J_{8,9}$ 7.5) and 7.15–7.40 (10 H, m); δ_C(22.4 MHz; $CDCl_3$) 18.5 (q), 42.2 (t), 44.6 (d), 50.6 (d), 56.3 (s), 58.9 (d), 125.1 (d), 126.8 (d), 127.1 (d), 127.8 (d), 128.6 (d), 128.7 (d), 132.1 (d), 134.3 (d), 136.2 (s), 142.9 (s), 152.1 (s), 175.4 (s) and 176.2 (s); ν_{max}(neat)/cm^{-1} 1716, 1386, 1344, 790, 750 and 700 [Found: MH^+ (FAB), 356.1656. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1651].

(1*S,5*S**,6*R**,7*R**)-*N*-Benzyl-8-methyl-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione (a minor product of 2d).** Colourless oil (36%); δ_H(270 MHz; $CDCl_3$) 1.80 (3 H, d, $J_{8\text{-}Me,9}$ 2.0), 3.00 (1 H, d, $J_{5,6}$ 7.0), 3.15 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 7.0), 3.50 (1 H, dddd, $J_{6,7}$ 1.5, $J_{7,11}$ 1.5, $J_{7,9}$ 2.0 and $J_{7,10}$ 5.5), 4.65 (s, 2 H), 6.05 (1 H, dd, $J_{7,11}$ 1.5 and $J_{10,11}$ 7.5), 6.65 (1 H, dd, $J_{7,9}$ 2.0 and $J_{8\text{-}Me,9}$ 2.0), 6.90 (1 H, dd, $J_{7,10}$ 5.5 and $J_{10,11}$ 7.5) and 7.15–7.40 (10 H, m); δ_C(22.4 MHz; $CDCl_3$) 21.6 (q), 42.1 (t), 44.7 (d), 51.7 (d), 51.7 (d), 55.6 (s), 57.6 (d), 126.2 (d), 127.0 (d), 127.1 (d), 127.8 (d), 128.6 (d × 2), 133.0 (d), 136.2 (s), 141.5 (d), 142.1 (s), 142.7 (s), 175.0 (s) and 176.3 (s); ν_{max}(neat)/cm^{-1} 1722, 1386, 1342, 782, 756 and 700 [Found: MH^+ (FAB), 356.1652. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1651].

(1*R,5*S**,6*R**,7*S**)-*N*-Benzyl-11-methyl-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione (a minor product of 2e).** Colourless oil (13%); δ_H(270 MHz; $CDCl_3$) 1.45 (3 H, d, $J_{11\text{-}Me,10}$ 2.0), 2.75 (1 H, d, $J_{5,6}$ 7.5), 3.25 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 7.5), 3.80 (1 H, dddd, $J_{6,7}$ 1.5, $J_{7,9}$ 1.5, $J_{7,8}$ 5.0 and $J_{7,10}$ 6.5), 4.65 (2 H, s), 6.40 (1 H, dd, $J_{11\text{-}Me,10}$ 2.0 and $J_{7,10}$ 6.5), 6.45 (1 H, dd, $J_{7,8}$ 5.0 and $J_{8,9}$ 7.0), 7.05 (1 H, dd, $J_{7,9}$ 1.5 and $J_{8,9}$ 7.0), 7.15–7.35 (8 H, m) and 7.45 (2 H, dd, *J* 2.0 and 7.5); δ_C(22.4 MHz; $CDCl_3$) 16.9 (q), 42.2 (t), 45.0 (d), 45.2 (d), 58.1 (d), 59.0 (s), 126.8 (d), 127.1 (d), 128.0 (d), 128.6 (d), 129.4 (d), 133.3 (d), 134.1 (d), 134.6 (d), 136.0 (s), 140.3 (s), 142.9 (s), 174.6 (s) and 175.5 (s); ν_{max}(neat)/cm^{-1} 1714, 1384, 1342, 1070, 788, 756, 728 and 700 [MH^+ (FAB), 356.1649. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1650].

(1*R,5*S**,6*R**,7*R**)-*N*-Benzyl-9-methyl-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione (a major product of 2e).** Colourless oil (22%); δ_H(270 MHz; $CDCl_3$) 2.10 (3 H, d, $J_{9\text{-}Me,8}$ 1.5), 2.75 (1 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, dd, $J_{6,7}$ 2.0 and $J_{5,6}$ 7.0), 3.75 (1 H, dddd, $J_{6,7}$ 2.0, $J_{7,11}$ 2.0, $J_{7,8}$ 5.5 and $J_{7,10}$ 6.5), 4.65 (2 H, s), 5.95 (1 H, dd, $J_{9\text{-}Me,8}$ 1.5 and $J_{7,8}$ 5.5), 6.00 (1 H, dd, $J_{7,11}$ 2.0 and $J_{10,11}$ 7.0), 6.90 (1 H, dd, $J_{7,10}$ 6.5 and $J_{10,11}$ 7.0) and 7.15–7.40 (10 H, m); δ_C(22.4 MHz; $CDCl_3$) 16.1 (q), 42.1 (t), 44.8 (d), 45.4 (d), 57.1 (d), 57.5 (s), 125.5 (d), 126.7 (d), 127.2 (d), 127.8 (d), 128.6 (d), 128.7 (d), 131.8 (d), 136.2 (s), 142.6 (d), 142.9 (s), 144.8 (s), 175.3 (s) and 175.8 (s); ν_{max}(neat)/cm^{-1} 1718, 1432, 1384, 1348, 1072, 788, 756 and 700 [Found: MH^+ (FAB), 356.1658. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1651].

(5*S,6*R**)-*N*-Benzyl-7-chloro-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2f.** Colourless oil (71%); δ_H(270 MHz; $CDCl_3$) 3.00 (1 H, d, $J_{5,6}$ 7.0), 3.40 (1 H, d, $J_{5,6}$ 7.0), 4.65 (2 H, s), 6.10 (1 H, d, $J_{10,11}$ 7.0), 6.45 (1 H, d, $J_{8,9}$ 8.5), 6.90 (1 H, d, $J_{10,11}$ 7.0), 7.05 (1 H, d, $J_{8,9}$ 8.5) and 7.20–7.35 (10 H, m); the ^{13}C NMR, IR and HRMS spectra were not measured because of the unstable nature of the product.

(5*S,6*R**)-6-Phenyl-*N*-(1-phenylethyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2h.** (99%) *Diastereoisomer A*.— Colourless oil; δ_H(270 MHz; $CDCl_3$) 1.85 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 2.70 (1 H, d, $J_{5,6}$ 7.5), 3.20 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 7.5), 3.90 (1 H, ddddd, $J_{7,9}$ 1.0, $J_{7,11}$ 1.0, $J_{6,7}$ 1.5, $J_{7,8}$ 5.5 and $J_{7,10}$ 6.0), 5.40 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 6.00 (1 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.5), 6.45 (1 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.90 (1 H, dd, $J_{7,10}$ 6.0 and $J_{10,11}$ 7.5), 7.00 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5), 7.10–7.40 (8 H, m) and 7.45 (2 H, dd, *J* 1.0 and 7.0); δ_C(22.4 MHz; $CDCl_3$) 16.9 (q), 45.1 (d), 45.2 (d), 49.8 (d), 55.7 (s), 57.5 (d), 126.9 (d), 127.2 (d), 127.4 (d), 127.7 (d), 128.4 (d), 128.7 (d), 132.0 (d), 132.6 (d), 133.8 (d), 139.5 (s), 141.9 (d), 142.7 (s), 175.2 (s) and 176.1 (s); ν_{max}(neat)/cm^{-1} 3060, 3028, 2972, 1776, 1710, 1500, 1374, 1346, 758 and 698.

Diastereoisomer B.—Colourless oil; δ_H(270 MHz; $CDCl_3$) 1.80 (3 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 2.75 (1 H, d, $J_{5,6}$ 7.5), 3.20 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 7.5), 3.90 (1 H, ddddd, $J_{7,9}$ 1.0, $J_{7,11}$ 1.0, $J_{6,7}$ 1.5, $J_{7,8}$ 5.5 and $J_{7,10}$ 6.0), 5.45 (1 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 6.10 (1 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.5), 6.45 (1 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.90 (1 H, dd, $J_{7,10}$ 6.0 and $J_{10,11}$ 7.5), 7.05 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5), 7.10–7.40 (8 H, m) and 7.45 (2 H, dd, *J* 1.0 and 7.0); δ_C(22.4 MHz; $CDCl_3$) 16.6 (q), 45.0 (d), 45.1 (d), 50.1 (d), 55.7 (s), 57.6 (d), 126.9 (d), 127.2 (d × 2), 127.7 (d), 128.5 (d), 128.7 (d), 132.1 (d), 132.6 (d), 133.9 (d), 140.2 (s), 142.0 (d), 142.7 (s), 175.1 (s) and 176.1 (s); ν_{max}(neat)/cm^{-1} 1715, 1500, 1460, 1378, 1342, 1154, 1050, 1030, 782, 758 and 698 [Found: MH^+ (FAB), 356.1654. $C_{24}H_{22}NO_2$ (MH^+) requires 356.1651].

A mixture of diastereoisomers of (5*S,6*R**)-7,8,9,10,11-pentadeuterio-6-phenyl-*N*-(1-phenylethyl)-3-azatricyclo-[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2h′.** Colourless oil (99%); δ_H(270 MHz; $CDCl_3$) 1.80 (1.5 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 1.85 (1.5 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 2.70 (0.5 H, d, $J_{5,6}$ 7.5), 2.75 (0.5 H, d, $J_{5,6}$ 7.5), 3.15 (0.5 H, dd, $J_{5,6}$ 7.5), 3.20 (0.5 H, d, $J_{5,6}$ 7.5), 5.40 (0.5 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 5.40 (0.5 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 7.15–7.40 (8 H, m) and 7.45 (2 H, dd and *J* 1.0, 7.0) [Found: MH^+ (FAB), 361.1970. $C_{24}H_{17}D_5NO_2$ (MH^+) requires 361.1964].

A mixture of diastereoisomers of (5*S,6*R**)-7-methyl-6-phenyl-*N*-(1-phenylethyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2j.** Colourless oil (>99%); δ_H(270 MHz; C_6D_6) 1.20 (1.5 H, s), 1.20 (1.5 H, s), 2.05 (1.5 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 2.10 (1.5 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 2.95 (0.5 H, d, $J_{5,6}$ 7.0), 3.00 (0.5 H, d, $J_{5,6}$ 7.0), 3.20 (0.5 H, d, $J_{5,6}$ 7.0), 3.25 (0.5 H, d, $J_{5,6}$ 7.0), 5.85 (0.5 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 5.85 (0.5 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.0), 6.00 (1 H, d, $J_{10,11}$ 7.0), 6.25 (0.5 H, d, $J_{10,11}$ 7.0), 6.35 (0.5 H, d, $J_{10,11}$ 7.0), 6.45 (0.5 H, d, $J_{10,11}$ 7.0), 6.45 (0.5 H, d, $J_{10,11}$ 7.0), 7.10 (0.5 H, d, $J_{8,9}$ 7.5), 7.15 (0.5 H, d, $J_{8,9}$ 7.5) and 7.25–7.60 (10 H, m). The ^{13}C NMR, IR and HRMS spectra were not measured because of the unstable nature of the product.

A mixture of diastereoisomers of (5*S,6*R**)-7-chloro-6-phenyl-*N*-(1-phenylethyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2k.** Colourless oil (92%); δ_H(270 MHz; $CDCl_3$) 1.80 (1.5 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 1.80 (1.5 H, d, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 2.95 (0.5 H, d, $J_{5,6}$ 7.0), 2.95 (0.5 H, d, $J_{5,6}$ 7.0), 3.35 (0.5 H, d, $J_{5,6}$ 7.0), 3.40 (0.5 H,

d, $J_{5,6}$ 7.0), 5.35 (0.5 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 5.40 (0.5 H, q, $J_{N\text{-}\alpha,N\text{-}\beta}$ 7.5), 6.00 (0.5 H, d, $J_{10,11}$ 7.0), 6.10 (0.5 H, d, $J_{10,11}$ 7.0), 6.40 (0.5 H, d, $J_{8,9}$ 7.5), 6.45 (0.5 H, d, $J_{8,9}$ 7.5), 6.85 (1 H, d, $J_{10,11}$ 7.0), 7.00 (0.5 H, d, *J* 7.5), 7.05 (0.5 H, d, $J_{10,11}$ 7.5) and 7.20–7.40 (10 H, m); ν_{max}(neat)/cm^{-1} 1718, 1658, 1620, 1378, 1340, 760 and 700. The ^{13}C NMR and HRMS spectra were not measured because of the unstable nature of the product.

A mixture of diastereoisomers of (5*S,6*R**)-6-phenyl-*N*-(1-phenylpropyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2n.** Colourless oil (87%); δ_H(270 MHz; $CDCl_3$) 0.95 (1.5 H, t, $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 0.95 (1.5 H, t, $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.20 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.25 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.45 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.55 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.65 (0.5 H, d, $J_{5,6}$ 7.0), 2.70 (0.5 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, dd, $J_{6,7}$ and $J_{5,6}$ 7.0), 3.85–3.90 (1 H, m), 5.10 (1 H, dd, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5 and $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5), 6.00 (0.5 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.0), 6.10 (0.5 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.0), 6.45 (0.5 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.45 (0.5 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.90 (1 H, dd, $J_{7,10}$ 7.0 and $J_{10,11}$ 7.0), 7.00 (0.5 H, dd, $J_{7,9}$ 1.5 and $J_{8,9}$ 7.5), 7.05 (0.5 H, dd, $J_{7,9}$ 1.5 and $J_{8,9}$ 7.5), 7.18–7.37 (8 H, m) and 7.45 (2 H, d, *J* 7.5); ν_{max}(neat)/cm^{-1} 1714, 1380, 1346, 788, 758 and 700 [Found: MH$^+$ (FAB), 370.1800. $C_{25}H_{24}NO_2$ (MH$^+$) requires 370.1807].

A mixture of diastereoisomers of (5*S,6*R**)-7,8,9,10,11-pentadeuterio-6-phenyl-*N*-(1-phenylpropyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2n′.** Colourless oil (79%); δ_H(270 MHz; $CDCl_3$) 0.95 (1.5 H, t, $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 0.95 (1.5 H, t, $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.20 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.25 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.45 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.55 (0.5 H, ddq, $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5, $J_{N\text{-}\beta1,N\text{-}\beta2}$ 13.5 and $J_{N\text{-}\beta,N\text{-}\gamma}$ 7.5), 2.65 (0.5 H, d, $J_{5,6}$ 7.0), 2.70 (0.5 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, dd, $J_{6,7}$ and $J_{5,6}$ 7.0), 5.10 (1 H, dd, $J_{N\text{-}\alpha,N\text{-}\beta1}$ 6.5 and $J_{N\text{-}\alpha,N\text{-}\beta2}$ 9.5), 7.20–7.35 (8 H, m) and 7.45 (2 H, d, *J* 7.5) [Found: MH$^+$ (FAB), 375.2122. $C_{25}H_{19}D_5NO_2$ (MH$^+$) requires 375.2121].

(5*S,6*R**)-6-Phenyl-*N*-(diphenylmethyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2o.** Colourless oil (98%); δ_H(270 MHz; $CDCl_3$) 2.80 (1 H, d, $J_{5,6}$ 7.0), 3.25 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 7.0), 3.90 (1 H, ddddd, $J_{7,9}$ 1.0, $J_{6,7}$ 1.5, $J_{7,11}$ 1.5, $J_{7,8}$ 6.0 and $J_{7,10}$ 6.5), 6.10 (1 H, dd, $J_{7,11}$ 1.5 and $J_{10,11}$ 7.0), 6.45 (1 H, dd, $J_{7,8}$ 6.0 and $J_{8,9}$ 7.5), 6.55 (1 H, s), 6.95 (1 H, dd, $J_{7,10}$ 6.5 and $J_{10,11}$ 7.0), 7.05 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5) and 7.15–7.40 (15 H, m); δ_C(22.4 MHz; $CDCl_3$) 45.1 (d), 45.2 (d), 55.8 (s), 57.7 (d), 58.1 (d), 126.9 (d), 127.2 (d), 127.7 (d), 127.8 (d), 128.4 (d), 128.5 (d), 128.7 (d), 131.9 (d), 132.7 (d), 133.8 (d), 137.7 (s), 138.0 (s), 142.1 (d), 142.6 (s), 174.9 (s) and 175.7 (s); ν_{max}(neat)/cm^{-1} 1718, 1662, 1498, 1378, 1346, 786, 738 and 700 [Found: MH$^+$ (FAB), 418.1807. $C_{29}H_{24}NO_2$ (MH$^+$) requires 418.1807].

(5*S,6*R**)-7,8,9,10,11-Pentadeuterio-6-phenyl-*N*-(diphenylmethyl)-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2o′.** Colourless oil (99%); δ_H(270 MHz; $CDCl_3$) 2.80 (1 H, d, $J_{5,6}$ 7.0), 3.25 (1 H, d, $J_{5,6}$ 7.0), 6.55 (1 H, s) and 7.15–7.40 (15 H, m) [Found: MH$^+$ (FAB), 423.2122. $C_{29}H_{19}D_5NO_2$ (MH$^+$) requires 423.2121].

(5*S,6*R**)-*N*-(1-Methyl-1-phenylethyl)-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2p.** Colourless oil (84%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, s), 1.95 (3 H, s), 2.70 (1 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, dd, $J_{6,7}$ 0.5 and $J_{5,6}$ 7.0), 3.85 (1 H, ddddd, $J_{6,7}$ 0.5, $J_{7,9}$ 1.0, $J_{7,11}$ 1.0, $J_{7,8}$ 5.5 and $J_{7,10}$ 6.5), 6.20 (1 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.0), 6.45 (1 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.95 (1 H, dd, $J_{7,10}$ 6.5 and $J_{10,11}$ 7.0), 7.00 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5) and 7.20–7.35 (10 H, m); δ_C(22.4 MHz; $CDCl_3$) 28.4 (q), 28.9 (q), 45.1 (d), 45.2 (d), 55.8 (s), 58.0 (d), 61.8 (s), 124.3 (d), 126.8 (d), 127.2 (d), 128.3 (d), 128.6 (d), 131.9 (d), 132.6 (d), 134.1 (d), 142.0 (d), 142.8 (s), 146.3 (s), 175.9 (s) and 176.7 (s); ν_{max}(neat)/cm^{-1} 1780, 1724, 1368, 1328, 1220, 1060, 784, 756 and 700 [Found: MH$^+$ (FAB), 370.1809. $C_{25}H_{24}NO_2$ (MH$^+$) requires 370.1807].

(5*S,6*R**)-7,8,9,10,11-Pentadeuterio-*N*-(1-methyl-1-phenylethyl)-6-phenyl-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-diene-2,4-dione 2p′.** Colourless oil (99%); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, s), 1.95 (3 H, s), 2.70 (1 H, d, $J_{5,6}$ 7.0), 3.20 (1 H, d, $J_{5,6}$ 7.0) and 7.20–7.35 (10 H, m) [Found: MH$^+$ (FAB), 375.2117. $C_{25}H_{19}D_5NO_2$ (MH$^+$) requires 375.2121].

(2*S,5*S**,6*R**)-*N*-Acetyl-2,6-diphenyl-3-azatricyclo[5.2.2.0^{1,5}]-undeca-8,10-dien-4-one 4b.** Colourless oil (42%); δ_H(270 MHz; $CDCl_3$) 2.55 (3 H, s), 2.80 (1 H, d, $J_{5,6}$ 6.0), 3.20 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 6.0), 3.80–3.85 (1 H, m), 5.85 (1 H, s), 6.25–6.30 (3 H, m), 6.85 (1 H, dd, $J_{7,10}$ 6.5 and $J_{10,11}$ 7.5) and 7.15–7.45 (10 H, m); δ_C(22.4 MHz; $CDCl_3$) 25.2 (q), 45.3 (d), 46.5 (d), 51.7 (s), 56.5 (d), 64.5 (d), 126.2 (d), 126.6 (d), 127.3 (d), 128.0 (d), 128.5 (d), 129.0 (d), 132.7 (d), 134.7 (d), 136.0 (d), 141.6 (d), 143.3 (s), 170.7 (s) and 175.0 (s); ν_{max}(neat)/cm^{-1} 2972, 2924, 1744, 1690, 1374, 1334, 1280 and 666 [Found: MH$^+$ (FAB), 356.1638. $C_{24}H_{22}NO_2$ (MH$^+$) requires 356.1650].

(2*S,5*S**,6*R**)-2-Methyl-6-phenyl-*N*-[(1-phenylethyl)aminocarbonyl]-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-dien-4-one 6b.** Colourless oil (56%); δ_H(270 MHz; $CDCl_3$) 1.50 (3 H, d, $J_{2,2\text{-}Me}$ 7.0), 1.50 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 2.75 (1 H, d, $J_{5,6}$ 6.5), 3.15 (1 H, dd, $J_{6,7}$ 2.0 and $J_{5,6}$ 6.5), 3.90 (1 H, ddddd, $J_{7,9}$ 0.5, $J_{7,11}$ 0.5, $J_{6,7}$ 2.0, $J_{7,8}$ 5.5 and $J_{7,10}$ 6.5), 4.85 (1 H, q, $J_{2,2\text{-}Me}$ 7.0), 5.05 (1 H, dq, $J_{N'H,N'\text{-}\alpha}$ 7.5 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 6.15 (1 H, dd, $J_{7,11}$ 0.5 and $J_{10,11}$ 7.5), 6.45 (1 H, dd, $J_{7,8}$ 5.5 and $J_{8,9}$ 7.5), 6.70 (1 H, dd, $J_{7,9}$ 0.5 and $J_{8,9}$ 7.5), 6.80 (1 H, dd, $J_{7,10}$ 6.5 and $J_{10,11}$ 7.5), 7.15–7.35 (10 H, m) and 8.70 (1 H, d, *J* 7.5); δ_C(22.4 MHz; $CDCl_3$) 14.7 (q), 22.9 (q), 44.9 (d), 46.0 (d), 49.7 (d), 51.3 (s), 57.3 (d), 57.5 (d), 125.9 (d), 126.6 (d), 127.2 (d × 2), 128.6 (d × 2), 133.6 (d), 134.5 (d), 136.2 (d), 141.3 (d), 143.5 (s), 152.1 (s) and 176.3 (s); ν_{max}(neat)/cm^{-1} 1714, 1534, 1370, 1342, 1232, 760, 718 and 700 [Found: MH$^+$ (FAB), 399.2077. $C_{26}H_{27}N_2O_2$ (MH$^+$) requires 399.2072].

(2*S,5*S**,6*R**)-2-Methyl-6-(4-methoxyphenyl)-*N*-[(1-phenylethyl)aminocarbonyl]-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-dien-4-one 6c.** Colourless oil (55%); δ_H(270 MHz; $CDCl_3$) 1.50 (3 H, d, $J_{2,2\text{-}Me}$ 7.0 Hz), 1.50 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.3), 2.70 (1 H, d, $J_{5,6}$ 6.5 Hz), 3.13 (1 H, dd, $J_{6,7}$ 1.5 and $J_{5,6}$ 6.5), 3.75 (3 H, s), 3.85 (1 H, ddddd, $J_{6,7}$ 1.5, $J_{7,9}$ 1.5, $J_{7,11}$ 1.5, $J_{7,8}$ 6.0 and $J_{7,10}$ 6.0), 4.85 (1 H, q, $J_{2,2\text{-}Me}$ 7.0), 5.05 (1 H, dq, $J_{N'H,N'\text{-}\alpha}$ 7.5 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 6.15 (1 H, dd, $J_{7,11}$ 1.5 and $J_{10,11}$ 7.5), 6.45 (1 H, dd, $J_{7,8}$ 6.0 and $J_{8,9}$ 7.5), 6.70 (1 H, dd, $J_{7,9}$ 1.5 and $J_{8,9}$ 7.5), 6.80 (2 H, d, $J_{2',3'}$ 9.0), 6.80 (1 H, dd, $J_{7,10}$ 6.0 and $J_{10,11}$ 7.5), 7.15 (2 H, d, $J_{2',3'}$ 9.0), 7.15–7.35 (5 H, m) and 8.70 (1 H, d, *J* 7.5); δ_C(22.4 MHz; $CDCl_3$) 14.7 (q), 22.9 (q), 45.2 (d), 49.7 (d), 51.3 (d), 55.3 (s), 57.4 (d), 57.5 (d), 114.0 (d), 125.9 (d), 127.2 (d), 128.2 (d), 128.6 (d), 133.6 (d), 134.5 (d), 135.7 (d), 136.0 (d), 141.3 (s), 143.6 (s), 152.2 (s), 158.3 (s) and 176.4 (s); ν_{max}(neat)/cm^{-1} 1715, 1520, 1375, 1250, 1180, 765 and 705 [Found: MH$^+$ (FAB), 429.2161. $C_{27}H_{29}N_2O_3$ (MH$^+$) requires 429.2178].

(2*S,5*S**,6*R**)-2-Methyl-6-(4-methylphenyl)-*N*-[(1-phenylethyl)aminocarbonyl]-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-dien-4-one 6d.** Colourless oil (56%); δ_H(270 MHz; $CDCl_3$) 1.50 (3 H, d, $J_{2,2\text{-}Me}$ 6.5), 1.50 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 2.30 (3 H, s), 2.70 (1 H, d, $J_{5,6}$ 6.5), 3.10 (1 H, dd, $J_{6,7}$ 1.0 and $J_{5,6}$ 6.5), 3.85 (1 H, ddddd, $J_{6,7}$ 1.0, $J_{7,9}$ 1.0, $J_{7,11}$ 1.0, $J_{7,8}$ 6.0 and $J_{7,10}$ 6.5), 4.85 (1 H, q, $J_{2,2\text{-}Me}$ 6.5), 5.05 (1 H, dq, $J_{N'H,N'\text{-}\alpha}$ 7.0 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.0), 6.15 (1 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.0), 6.45 (1 H, dd, $J_{7,8}$ 6.0 and $J_{8,9}$ 7.5), 6.70 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5), 6.80 (1 H, dd, $J_{7,10}$ 6.5 and $J_{10,11}$ 7.0), 7.10 (2 H, d, $J_{2',3'}$ 8.5), 7.15 (2 H, d, $J_{2',3'}$ 8.5), 7.15–7.35 (5 H, m) and 8.70 (1 H, d, $J_{N'H,N'\text{-}\alpha}$ 7.0); δ_C(22.4 MHz; $CDCl_3$) 14.7 (q), 20.9 (q), 22.9 (q), 45.0 (d), 45.6 (d), 49.7 (d), 51.3 (s), 57.3 (d), 57.4 (d), 125.9 (d), 127.1 (d), 128.6 (d), 129.2 (d), 133.7 (d), 134.4 (d), 136.1 (d), 136.2 (s), 140.5 (s), 141.3 (d), 143.6 (s), 152.1 (s) and 176.4 (s); ν_{max}(neat)/cm^{-1} 2972, 1716, 1690, 1532, 1372, 1344, 1232 and 762 [Found: MH$^+$ (FAB), 413.2222. $C_{27}H_{29}N_2O_2$ (MH$^+$) requires 413.2229].

(2*S,5*S**,6*R**)-2-Methyl-6-(4-chlorophenyl)-*N*-[(1-phenylethyl)aminocarbonyl]-3-azatricyclo[5.2.2.0^{1,5}]undeca-8,10-dien-4-one 6e.** Colourless oil (61%); δ_H(270 MHz; $CDCl_3$) 1.50 (3 H,

d, $J_{2,2\text{-Me}}$ 7.0), 1.50 (3 H, d, $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 2.65 (1 H, d, $J_{5,6}$ 6.0), 3.10 (1 H, dd, $J_{6,7}$ 1.0 and $J_{5,6}$ 6.0), 3.85 (1 H, ddddd, $J_{6,7}$ 1.0, $J_{7,9}$ 1.0, $J_{7,11}$ 1.0, $J_{7,8}$ 6.0 and $J_{7,10}$ 6.0), 4.85 (1 H, q, $J_{2,2\text{-Me}}$ 7.0), 5.05 (1 H, dq, $J_{N'H,N'\text{-}\alpha}$ 7.5 and $J_{N'\text{-}\alpha,N'\text{-}\beta}$ 7.5), 6.15 (1 H, dd, $J_{7,11}$ 1.0 and $J_{10,11}$ 7.0), 6.45 (1 H, dd, $J_{7,8}$ 6.0 and $J_{8,9}$ 7.5), 6.70 (1 H, dd, $J_{7,9}$ 1.0 and $J_{8,9}$ 7.5), 6.80 (1 H, dd, $J_{7,10}$ 6.0 and $J_{10,11}$ 7.0), 7.15–7.40 (9 H, m) and 8.70 (1 H, d, *J* 7.5); δ_C(22.4 MHz; $CDCl_3$) 14.7 (q), 22.9 (q), 44.7 (d), 45.4 (d), 49.7 (d), 51.3 (s), 57.3 (d), 57.5 (d), 125.9 (d), 127.2 (d), 128.6 (d), 128.6 (d), 132.4 (s), 133.3 (d), 134.9 (d), 136.3 (d), 141.1 (d), 142.0 (s), 143.4 (s), 152.0 (s) and 176.0 (s); ν_{max}(neat)/cm^{-1} 1714, 1530, 1496, 1372, 790, 762, 700 and 666 [Found: MH^+ (FAB), 433.1674. $C_{26}H_{26}N_2O_2Cl$ (MH^+) requires 433.1683].

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