PERKIN 1

Diastereoselective intramolecular [4 + 4] photocycloaddition reaction of *N*-(naphthylcarbonyl)anthracene-9-carboxamides: temperature effects and reversal of diastereoselectivity

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Intramolecular diastereoselective [4 + 4] photocycloadditions of acyclic imides **1a** and **1b** possessing anthracene and naphthalene moieties were carried out in the solid state and in solution. For **1a**, novel reversal of diastereoselectivity was observed on changing the reaction phase. The diastereomeric excess was changed from −60% de in the solid state at 60 °C to 70% de in acetone at −78 °C. Almost 100% de was observed for the solid-state photocycloaddition of **1b**. The reactivity of **1a** in the solid state was discussed based on its single crystal X-ray analysis.

Introduction

Control of stereoselectivity is currently a topic of great interest in organic photochemistry. Asymmetric induction has been carried out successfully in solid-state photochemistry of some chiral crystals formed by spontaneous resolution of chiral substrates on crystallisation.[1] Diastereoselective reactions have also been achieved in solid-state photochemistry using covalently bound chiral auxiliaries[2] or with noncovalent linkers forming organic salts,[3] which causes conformational biases of the transition states. However, the reversal of diastereoselectivity starting from the same compound is rarely attained in photochemical reactions by merely changing the reaction conditions. However, there are numerous examples of this in ground-state organic chemistry, especially in aldol condensations.[4] In order to obtain the other diastereomer as a photoproduct, the reaction should be carried out with the chiral auxiliary possessing the opposite absolute configuration, as is usual in asymmetric synthesis. One promising exception was the temperature dependent enantioselective photoisomerization of cyclooctene in which the entropy term of the reaction was not negligible, thus the enantioselectivity was inverted according to the increase of the reaction temperature.[5] In thermal reactions, similar temperature dependent diastereofacial selectivity has also been reported.[6] A reversal of de was observed in the addition reaction of butyllithium.[7]

As a continuation of our study on the photochemistry of aromatic amides,[8] we have examined the diastereoselective intramolecular photocycloaddition of acyclic imides possessing anthracene and naphthalene moieties as 4π reactants. Among the photocycloadditions of aromatic compounds,[9] the [4 + 4] and [4 + 2] cycloadditions of anthracene[10] and naphthalene derivatives[11] are well known reactions. Diastereoselective [4 + 4][12] and [4 + 2][13] cycloadditions of anthracene derivatives using chiral auxiliaries have been reported, intermolecularly in the solid state and intramolecularly in solution, respectively. In this paper, we report on temperature effects on the [4 + 4] photocycloaddition reaction of anthracene–naphthalene system both in solution and in the solid state, and the reversal of the diastereoselectivity.

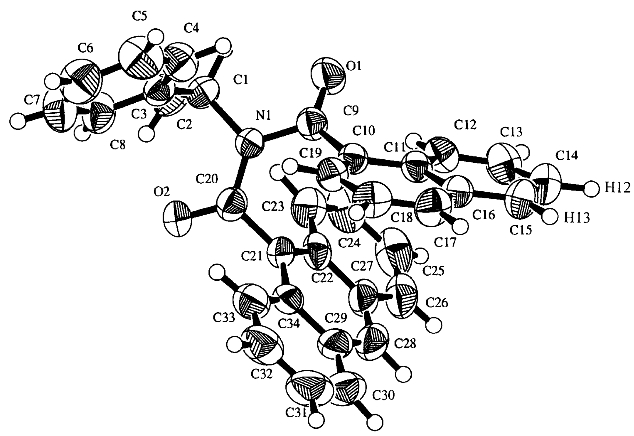
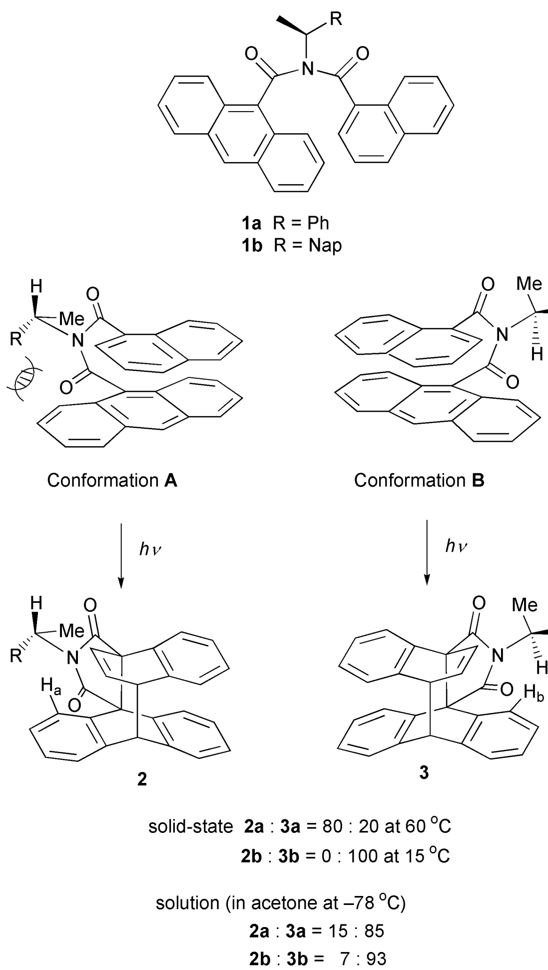


Fig. 1 ORTEP diagram of the molecular structure of **1a** with thermal ellipsoids drawn at the 50% probability level. The distances between two reaction sites: C10–C21, 2.89 Å; C17–C28, 4.80 Å. The torsion angle, C17–C10–C21–C28, 42.8°.

Results and discussion

In order to have efficient overlap of π-orbitals of two chromophores, the anthracene and naphthalene moieties, we planned to connect them with an iminodicarbonyl linkage, and thus prepared acyclic imides **1a** and **1b**. The single crystal X-ray structure of **1a** possessing an *N*-(1*S*)-1-phenylethyl group as a chiral auxiliary shows that the naphthalene and anthracene rings face each other with a torsion angle (C17–C10–C21–C28) of 42.8° and distances of 2.89 and 4.80 Å for C10–C21 and C17–C28, respectively (Fig. 1). Due to the π–π interactions between the two aromatic rings, these two rings are located preferentially in positions in which they face each other. Moreover, this orientation of the aromatic rings can also be influenced by the nature of the iminodicarbonyl group which may be considered to be a sequence of two amide functions. Therefore, the two carbonyls tend to be located in nearly the same plane in a W-shape due to electronic repulsion. Similar *cis* favorable conformations were observed in *N*-methyl aromatic amides and *N*,*N*′-dimethyl aromatic ureas.[14] In contrast, similar aromatics possessing amino,[15] propylene,[16] and ester[17] linkages instead of an iminodicarbonyl were reported to lack this tendency in their crystalline structures. In addition to these, **1a** has the following features. After the [4 + 4] cycloaddition, the iminodicarbonyl linkage creates a five-membered imido ring, a favorable ring formation in photocycloaddition according to the Rule of Five.[18] Carbonyl groups contribute to the construction of networks which assist the formation of the crystal structure owing to their C–H···O interactions.[19] Interatomic distances (between the two molecules) of 2.46 and 2.37 Å were observed for O1–H13 and O2–H12, respectively, which indicated the existence of such interactions.

If the photocycloaddition proceeds stereoselectively from this conformation (the conformation in the crystal structure shown as conformation A in Scheme 1) **1a** should afford the



Scheme 1

[4 + 4] cycloadduct **2a** predominantly. Powdered single crystals of **1a** were sandwiched between two Pyrex cover glasses wrapped with a polyethylene bag and irradiated for 6 h in an ice–water bath. However, almost no reaction (conversion of 2% with 60% de) occurred at this temperature. The lack of reactivity is probably due to the larger torsion angle between the anthracene and the naphthalene rings and the long C10–C21 distance (4.80 Å) which is longer than the distance limit (4.2 Å) between two double bonds for photocycloaddition.[20] These cause ineffective overlap between the π-orbitals. We considered that the photocycloaddition might proceed at an elevated temperature upon irradiation since the molecule would be forced to vibrate in the crystal lattice and to locate two π planes in suitable positions for the cycloaddition by reducing the C10–C21 distance and the torsion angle between the anthracene and the naphthalene rings. Fig. 2 shows the conversion yields and the diastereoselectivity (% de) of the photocycloaddition of **1a** in the solid state at various reaction temperatures. The diastereoselectivity was determined based on the comparison of the integration of methyl groups after 6 h at various reaction temperatures. Melting of the resulting reaction mixture was not observed during or after the irradiation. Up to 50% conversion (reaction temperature below 74 °C), the de was in the range of 45–60%. With an increase of the reaction temperature, the conversion yield increased. Complete conversion was observed at 87 °C with 24% de.

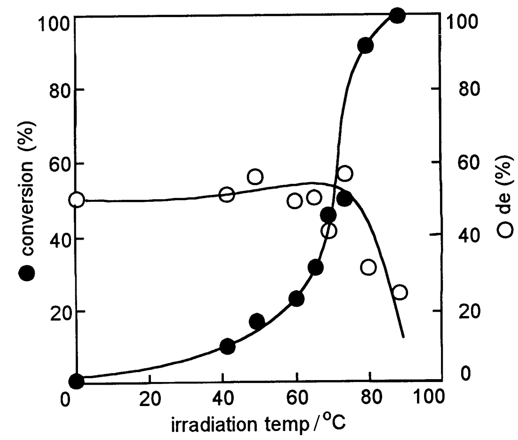


Fig. 2 Temperature effect on the conversion and diastereoselectivity of the solid-state photocycloaddition of **1a** after 6 h irradiation.

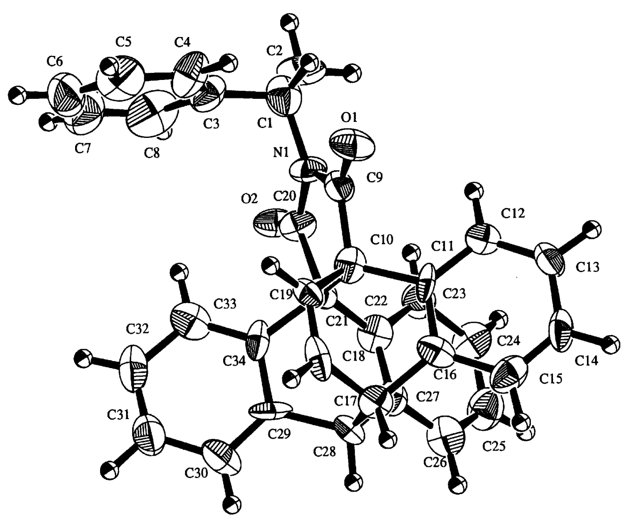


Fig. 3 ORTEP diagram of the molecular structure of **2a** with thermal ellipsoids drawn at the 50% probability level.

Two diastereomeric cycloadducts were separated by HPLC and their absolute configurations were determined to be **2a** and **3a** as the major and minor isomers, respectively by their single crystal X-ray analyses. Their space groups belong to the chiral space group $P2_12_12_1$. Fig. 3 and 4 show the ORTEP diagrams of the major and minor diastereomers **2a** and **3a**, respectively. Their absolute configurations were deduced from the known chiral centre, the attached (1*S*)-1-phenylethyl group. Their configurations indicate that the photocycloaddition proceeds predominantly from the conformation **A** as observed in the X-ray structure of **1a**. In spite of the existence of disorder originating in the higher reaction temperature and the progress of the reaction, moderate diastereoselectivity was observed after complete conversion. The ^{1}H NMR spectrum of **2a** was almost identical to that of **3a** except for the chemical shifts of the methyl group of the 1-phenylethyl group (δ_{Me} **2a**: 2.12, **3a**: 2.16) and one of the aromatic protons which showed an up-field shift of 0.15 ppm (δ_{Ha} **2a**: 6.37, δ_{Hb} **3a**: 6.52) compared to that of **3a**. This up-field shift could be interpreted in terms of

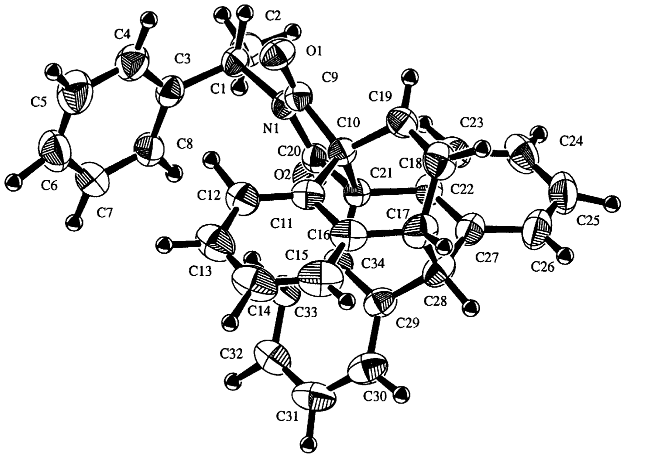


Fig. 4 ORTEP diagram of the molecular structure of **3a** with thermal ellipsoids drawn at the 50% probability level.

the slightly stronger shielding effect caused by the phenyl group of the 1-phenylethyl group of **2a** than that of **3a** on the facing *peri*-position of aromatic proton H_a and H_b, respectively.

Recrystallisation of acyclic imide **1b** with the bulkier chiral auxiliary, 1-naphthylethyl group, gave powdery fine crystals which were not appropriate for single crystal X-ray analysis. In contrast to the solid-state photocycloaddition of **1a**, the intramolecular [4 + 4] photocycloaddition of **1b** proceeded in the solid state even at lower temperatures (*ca.* 15 °C) with almost 100% de within experimental error after complete conversion. Since the cycloadduct did not afford a suitable single crystal for X-ray diffraction analysis, the configurational determination of [4 + 4] cycloadduct was carried out based on ^{1}H NMR study. Unlike the solid-state photocycloaddition, two diastereomers were obtained in the reaction of **1b** in solution. Irradiation of a toluene solution of **1b** at 15 °C for 10 min gave a mixture of two diastereomeric isomers in a 74:26 ratio in almost quantitative yield. These two diastereomers were hard to separate by HPLC. The major diastereomer was the same as obtained from the solid-state photochemical reaction and its configuration was deduced to be **3b** from the following ^{1}H NMR spectral comparison. As mentioned above, the aromatic proton of **2a** (H_a) appears at higher field than that of **3a** (H_b). A similar shielding tendency should be observed in diastereomers **2b** and **3b**. Therefore, the diastereomer possessing the aromatic proton (H_a) whose chemical shift was 0.27 ppm higher than the other (H_b) was assigned as **2b** (δ_{Ha}: 5.98, δ_{Hb}: 6.25). As for the methyl protons, this was also consistent with the observations for those of **2a** and **3a**. The methyl protons of **3b** (δ 2.28) appeared at slightly lower field than that of **2b** (δ 2.25). The results indicate that **1b** has the conformation **B** in its solid state, which is different from that of **1a**.

In order to examine the selectivity of the cycloaddition in different reaction phases, either in the solid state or in solution, and also the temperature effect, the photocycloaddition of **1a** and **1b** was examined in solution. Three solvents, acetone (47 to −78 °C), chloroform (47 to −78 °C), and toluene (90 to −78 °C) were employed at various reaction temperatures. The irradiation was performed using a high-pressure mercury lamp to afford [4 + 4] cycloadducts with various diastereoisomeric ratios in almost quantitative yields. The best diastereoselectivities were observed in acetone at −78 °C and were 70 and 86% de for **1a** and **1b** affording **2b** and **3b**, respectively. In all solvents, the 1-naphthylethyl derivative **1b** resulted in a better diastereoselectivity. At higher reaction temperature, the decrease of diastereoselectivity was observed for both **1a** and **1b** in all three solvents. However, the reversal of diastereoselectivity, from 19% de at −78 °C to −4% de at 90 °C, was observed for **1a** in toluene. Except for **1a** in toluene, the cycloadducts derived from the conformation **B** were obtained

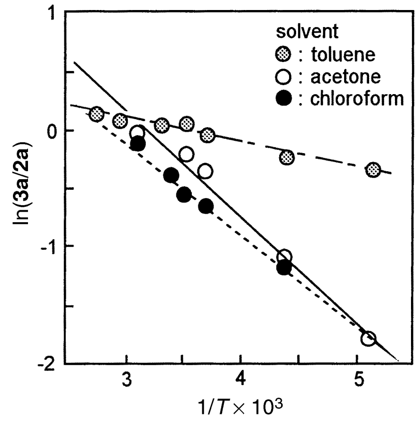


Fig. 5 Arrhenius plots of the ratio of diastereomers (**3a**:**2a**) against 1/*T*.

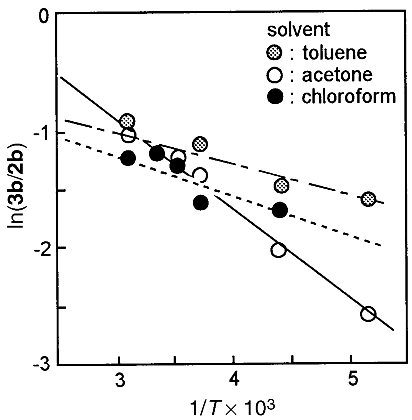


Fig. 6 Arrhenius plots of the ratio of diastereomers (**3b**:**2b**) against 1/*T*.

as the major diastereomers, in contrast to the solid-state cycloaddition of **1a** in which **2a** was the major diastereomer. Solvation of **1a** with toluene *via* π–π stacking might affect the conformation of the transition state. The diastereoselectivity of the photocycloaddition can be explained by the steric hindrance between the anthracene ring and the phenyl of the 1-phenylethyl group or the naphthyl of the 1-(1-naphthyl)ethyl group in the conformation **B**. Arrhenius plots were carried out, plotting the logarithm of the ratios of diastereomers (**3a**:**2a** or **3b**:**2b**) against 1/*T* (Fig. 5 and Fig. 6). The differences in activation energy (ΔE_a) between the formation of two diastereomers were 0.5, 0.4, and 0.1 kcal mol^{-1} for **1a** in acetone, chloroform, and toluene, respectively, and 0.4, 0.2, 0.2 kcal mol^{-1} for **1b** in acetone, chloroform, and toluene, respectively.

Since **1a** and **1b** contain two chromophores, it is conceivable that the reaction involves an excited naphthyl or anthryl moiety. Therefore, the effect of irradiation wavelength was examined in solution. The UV spectra of **1a** and **1b** showed absorptions at 380 (379) and 399 nm corresponding to the anthryl group, which was missing in the related carboxamide with two naphthyl moieties[21] instead of one anthryl and one naphthyl moieties. Thus, selective irradiation of the anthryl moiety was carried out in benzene with a high-pressure Hg lamp through the UV cut-off filter (Toshiba L-39: transmittance 85 and 1% at 405 and 365 nm, respectively) at 0 °C. Almost the same results were obtained as in the irradiation of them with a Pyrex filter. Diastereoselectivities of (−8) ± 2% de and 61 ± 2% de were obtained independent of irradiation wavelengths for the reactions of **1a** and **1b**, respectively. Therefore, the photocycloadditions should involve the excited anthryl moiety. The PM3 calculation of **1a** showed that the molecular orbital of its LUMO localised completely on the anthryl moiety.

The present findings show the novel temperature effect on the photocycloaddition in the solid state and the reversal of the diastereoselectivity depending on the reaction phases.

Experimental

General

Mps were determined on a Yanaco MP-S3 apparatus and are uncorrected. IR spectra were recorded on a Hitachi I-2000 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL GSX-400 and GSX-500 spectrometers in $CDCl_3$ with Me_4Si as an internal standard; *J* values are given in Hz. EI mass spectra were measured with a Hitachi RMU-7M mass spectrometer. Reaction mixtures were concentrated on a rotary evaporator at 10–15 mmHg. Chromatographic separations were accomplished by flash column chromatography on silica gel (Fuji gel BW 200; 150–350 mesh). Separation of diastereomers was carried out by a preparative HPLC run; column Merck Si 60 (7 µm, 10 × 250 mm), hexane–ethyl acetate as eluent. Photocycloaddition reactions were carried out using a USHIO 450 W high-pressure mercury lamp. All solvents were freshly distilled and stored over 4 Å molecular sieves.

Preparation of carboxamide 1

***N*-((1*S*)-1-Phenylethyl)-*N*-(1-naphthylcarbonyl)anthracene-9-carboxamide 1a.** To a solution of *N*-((1*S*)-1-phenylethyl)-anthracene-9-carboxamide (0.400 g, 1.23 mmol; prepared from (1*S*)-1-phenylethylamine and anthracene-9-carbonyl chloride) in toluene (30 cm^3) was added triethylamine (2.0 equiv.) at room temperature. To the resulting solution was added dropwise naphthalenecarbonyl chloride (0.37 cm^3, 2.46 mmol). The resulting mixture was heated at reflux for 15 h and then it was quenched with saturated $NaHCO_3$ (20 cm^3) and washed with 1 M hydrochloric acid (20 cm^3) and brine (20 cm^3). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The product was recrystallised from *n*-hexane–ethyl acetate to give yellow crystals of **1a** (0.613 g, 65%); mp 195–196 °C (from *n*-hexane–ethyl acetate) (Found: C, 84.89; H, 5.19; N, 2.92. $C_{34}H_{25}NO_2$ requires C, 85.15; H, 5.25; N, 2.92%); λ_{max}(CH_3CN)/nm 262.5 (ε/dm^3 mol^{-1} cm^{-1} 41 100), 326 (6500), 380 (4800) and 399 (4500); ν_{max}(KBr)/cm^{-1} 1660 (C=O); δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.29 (3 H, br s, Me), 6.39 (1 H, br), 6.52–6.57 (2 H, m), 6.65 (1 H, td, *J* 8.0 and 1.0,), 6.86 (1 H, d, *J* 8.0), 7.02 (2 H, t, *J* 7.1), 7.15–7.50 (12 H, m), 7.84 (1 H, d, *J* 8.8) and 7.96 (2 H, br); δ_C (125 MHz; $CDCl_3$; Me_4Si) 17.86 (q), 55.68 (d), 123.02 (d), 123.24 (d), 124.96 (d), 125.35 (d), 125.42 (d), 126.15 (d), 126.86 (d), 127.10 (d), 127.97 (d), 128.11 (s), 128.18 (s), 128.31 (s), 128.36 (d), 128.42 (d), 129.10 (d), 129.31 (d), 130.06 (s), 130.33 (s), 132.14 (s), 133.11 (s), 171.36 (s) and 173.77 (s); *m*/*z* (EI) 479 (M$^+$, 46%), 374 (100), 331 (24), 303 (9), 205 (57), 177 (49), 155 (35) and 127 (32).

Crystallographic data for 1a.† $C_{34}H_{25}NO_2$, $M = 479.58$, orthorhombic, space group $P2_12_12_1$ (#19), $a = 13.9906(9)$, $b = 22.060(1)$, $c = 8.082(1)$ Å, $V = 2494.2(4)$ Å^3, $Z = 4$, $D_{calc} = 1.277$ g cm^{-3}, $T = 296.2$ K, $\mu = 6.23$ cm^{-1} (CuKα = 1.5418 Å), $R = 0.040$ ($Rw = 0.038$) for 1864 observed reflections [$I > 2.00\sigma(I)$].

***N*-((1*S*)-1-Naphthylethyl)-*N*-(1-naphthylcarbonyl)anthracene-9-carboxamide 1b.** In a similar manner as for the preparation of **1a**, **1b** was prepared from *N*-((1*S*)-1-naphthylethyl)anthracene-9-carboxamide with naphthalenecarbonyl chloride as yellow needles; mp 170–172 °C (from *n*-hexane–ethyl acetate) (Found: C, 86.03; H, 5.02; N, 2.61. $C_{38}H_{27}NO_2$ requires C, 86.18; H, 5.14; N, 2.64%); λ_{max}(CH_3CN)/nm 262.5 (ε/dm^3 mol^{-1} cm^{-1} 37 000), 283 (13 800), 295 (10 300), 327 (5500), 379 (4500) and 399 (3800); ν_{max}(KBr)/cm^{-1} 1650 (C=O); δ_H(400 MHz; $CDCl_3$ Me_4Si) 2.59 (3 H, br), 5.95 (1 H, br), 6.25 (1 H, br), 6.48 (1 H, d, *J* 7.8), 6.58 (1 H, t, *J* 7.8), 6.68–6.67 (1 H, md, *J* 6.4), 6.96 (1 H, t, *J* 7.2,), 7.07 (1 H, d, *J* 7.6), 8.11–7.15 (16 H, m) and 8.92 (1 H, br); δ_C(125 MHz; $CDCl_3$; Me_4Si) 18.34 (q), 51.25 (d), 122.60 (d), 122.83 (d), 123.46 (d), 123.51 (d), 123.77 (d), 124.82 (d), 124.95 (d), 125.07 (d), 125.17 (d), 125.63 (d), 125.70 (d), 125.99 (d), 126.51 (d), 126.55 (s), 126.60 (d), 126.89 (d), 127.13 (d), 128.03 (s), 128.15 (d), 128.24 (d), 128.73 (d), 128.90 (d), 129.31 (d), 129.67 (s), 130.09 (s), 130.19 (s), 131.76 (s), 131.82 (s), 132.56 (s), 133.81 (s), 170.78 (s) and 173.82 (s); *m*/*z* (EI) 529 (M$^+$, 41%), 408 (6), 374 (98), 331 (37), 303 (17), 205 (49), 177 (80), 155 (99), 127 (100) and 57 (49).

Photocycloaddition of 1a and 1b

For preparative runs, a benzene solution (15 cm^3) of **1a** or **1b** (0.30 mmol) was irradiated through Pyrex glass filter for 20 min. The reaction was almost quantitative and the evaporation of solvent gave the corresponding [4 + 4] cycloadducts. Solid-state photoreaction of **1a** was carried out as follows. Carboxamide **1a** (10.0 mg, 0.021 mmol) was sandwiched between two Pyrex slide glasses which were placed in a polyethylene bag and irradiated in a temperature controlled water bath (±0.5 °C) for 6 h (3 h for each side). The ratio of diastereomer was determined based on the comparison of integrals of methyl protons of both diastereomers in their ^{1}H NMR spectra. For solution photoreaction, carboxamide **1a** or **1b** (1.25 × 10^{-2} M) in an appropriate solvent was irradiated under bubbling of argon through Pyrex filter for 20 min and the diastereomer ratio was determined by ^{1}H NMR spectroscopy.

[4 + 4] Cycloadduct 2a. Colorless crystals; mp 187–189 °C (from *n*-hexane–ethyl acetate) (Found: C, 84.91; H, 5.19; N, 2.78. $C_{34}H_{25}NO_2$ requires C, 85.15; H, 5.25; N, 2.92%); δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.12 (3 H, d, *J* 7.3), 4.11 (1 H, ddd, *J* 10.7, 7.3 and 1.5), 4.50 (1 H, d, *J* 10.7), 5.86–5.97 (2 H, m), 6.18 (1 H, dd, *J* 8.4 and 7.3), 6.37 (1 H, d, *J* 7.6), 6.69–7.24 (11 H, m), 7.38 (1 H, t, *J* 7.6), 7.45 (2 H, t, *J* 8.0) and 7.68 (2 H, d, *J* 7.5); δ_C(125 MHz; $CDCl_3$; Me_4Si) 16.75 (q), 48.01 (d), 50.85 (d), 53.02 (d), 63.31 (s), 66.89 (s), 124.16 (d), 124.39 (d), 125.44 (d), 125.59 (d), 125.79 (d), 126.11 (d), 126.48 (d), 126.56 (d), 127.02 (d), 127.17 (d), 127.32 (d), 127.57 (d), 128.11 (d), 128.59 (d), 134.05 (d), 137.83 (d), 139.23 (s), 139.77 (s), 140.92 (s), 141.14 (s), 143.02 (s), 143.06 (s), 143.75 (s), 176.44 (s) and 177.62 (s); *m*/*z* (EI) 479 (M$^+$, 42%), 374 (92), 331 (19), 303 (11), 205 (84), 177 (100), 155 (93), 127 (81), 105 (66), 77 (29).

Crystallographic data for 2a.† $C_{34}H_{25}NO_2$, $M = 479.58$, orthorhombic, space group $P2_12_12_1$ (#19), $a = 13.294(2)$, $b = 15.467(2)$, $c = 12.047(1)$ Å, $V = 2477.0(5)$ Å^3, $Z = 4$, $D_{calc} = 1.286$ g cm^{-3}, $T = 296.2$ K, $\mu = 6.19$ cm^{-1} (CuKα = 1.5418Å), $R = 0.088$ ($Rw = 0.089$) for 1589 observed reflections [$I > 0.70\sigma(I)$].

[4 + 4] Cycloadduct 3a. Colorless crystals; mp 187–189 °C (from *n*-hexane–ethyl acetate) (Found: C, 84.87; H, 5.21; N, 2.91. $C_{34}H_{25}NO_2$ requires C, 85.15; H, 5.25; N, 2.92%); ν_{max}(KBr)/cm^{-1} 1700 (C=O); δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.16 (3 H, d, *J* 7.3), 4.15 (1 H, ddd, *J* 10.8, 7.2 and 1.5), 4.53 (1 H, d, *J* 11.0), 5.89 (2 H, dd, *J* 8.3 and 1.4), 5.93 (1 H, q, *J* 7.2), 6.20 (1 H, dd, *J* 8.4 and 7.3), 6.52 (1 H, d, *J* 7.8), 6.61–7.25 (11 H, m), 7.38 (1 H, t, *J* 7.6), 7.46 (2 H, t, *J* 8.0), 7.70 (2 H, d, *J* 7.6); δ_C(125 MHz; $CDCl_3$; Me_4Si) 17.13 (q), 48.07 (d), 51.30 (d), 53.09 (d), 63.41 (s), 66.87 (s), 124.24 (d), 124.45 (d), 125.45 (d), 125.64 (d), 125.80 (d), 126.17 (d), 126.53 (d), 127.06 (d), 127.25 (d), 127.32 (d), 127.35 (d), 127.42 (d), 128.03 (d), 128.70 (d), 134.09 (d), 137.80 (d), 139.49 (s), 139.84 (s), 140.95 (s), 141.20

† CCDC reference number 207/496. See http://www.rsc.org/suppdata/p1/b0/b005142j/ for crystallographic files in .cif format.

(s), 142.97 (s), 143.17 (s), 143.83 (s), 176.49 (s) and 177.57 (s); *m*/*z* (EI) 479 (M^+, 41%), 374 (100), 331 (27), 303 (11), 205 (66), 177 (53), 155 (44), 127 (37), 105 (43), 77 (16).

Crystallographic data for 3a.† $C_{34}H_{25}NO_2$, $M = 479.58$, orthorhombic, space group $P2_12_12_1$ (#19), $a = 12.384(2)$, $b = 21.405(2)$, $c = 9.292(2)$ Å, $V = 2463.2(6)$ Å^3, $Z = 4$, $D_{calc} = 1.293$ g cm^{-3}, $T = 296.2$ K, $\mu = 6.27$ cm^{-1} (CuKα = 1.5418Å), $R = 0.039$ ($Rw = 0.040$) for 1589 observed reflections [$I > 3.00\sigma(I)$].

[4 + 4] Cycloadduct 2b. Characteristic peaks assigned for the minor diastereomer **2b** from the ^{1}H NMR spectrum of the mixture of **2b** and **3b** (together with those of major **3b** for comparison); δ_H(500 MHz; $CDCl_3$; Me_4Si) Me; 2.25 (d, *J* 7.3, **2b**), 2.28 (d, *J* 7.3, **3b**); C*H*; 4.07 (ddd, *J* 10.7, 7.1, 1.2, **2b**), 4.10 (ddd, *J* 10.9, 7.2 and 1.0, **3b**); C*H*; 4.46 (**2b**),* 4.49 (d, *J* 10.9, **3b**); CH=C*H*; 5.88 (dd, *J* 8.5 and 1.2, **2b**), 5.81 (dd, *J* 8.5 and 1.2, **3b**); C*H*=CH; 6.15 (**2b**),* 6.14 (dd, *J* 8.5 and 7.2, **3b**) (*due to the overlap of peaks, coupling constants were difficult to determine).

[4 + 4] Cycloadduct 3b. Colorless crystals; mp 178–181 °C (from *n*-hexane–ethyl acetate) (Found: C, 85.80; H, 5.04; N, 2.57. $C_{38}H_{27}NO_2$ requires C, 86.18; H, 5.14; N, 2.64%); ν_{max}(KBr)/cm^{-1} IR 1705 (C=O); δ_H(400 MHz; $CDCl_3$; Me_4Si) 2.28 (3 H, d, *J* 7.3), 4.10 (1 H, ddd, *J* 10.9, 7.2 and 1.0), 4.49 (1 H, d, *J* 10.9), 5.81 (1 H, dd, *J* 8.5 and 1.2), 6.14 (1 H, dd, *J* 8.5 and 7.2), 6.25 (1 H, d, *J* 7.5), 6.58 (1 H, td, *J* 7.8 and 1.2), 6.66 (2 H, q, *J* 7.3), 6.72–6.83 (5 H, m), 7.08–7.18 (3 H, m), 7.22 (1 H, d, *J* 7.0), 7.55–7.62 (2 H, m), 7.69 (1 H, td, *J* 7.0 and 1.4), 7.91 (1 H, d, *J* 8.2), 7.95 (1 H, d, *J* 8.3), 8.15 (1 H, d, *J* 7.3) and 8.48 (1 H, d, *J* 8.6); δ_C(125 MHz; $CDCl_3$; Me_4Si) 17.87 (q), 47.58 (d), 48.05 (d), 53.07 (d), 63.35 (s), 66.80 (s), 123.20 (d), 124.44 (d), 124.59 (d), 125.24 (d), 125.32 (d), 125.50 (d), 125.75 (d), 126.11 (d), 126.44 (d), 126.58 (d), 126.90 (d), 126.97 (d), 127.20 (d), 127.24 (d), 127.26 (d), 128.95 (d), 129.19 (d), 131.13 (s), 133.62 (s), 133.90 (s), 134.13 (d), 137.71 (d), 139.81 (s), 140.89 (s), 141.17 (s), 142.88 (s), 143.08 (s), 143.75 (s), 176.56 (s) and 177.73 (s); *m*/*z* (EI) 529 (M^+, 18%), 374 (100), 331 (19), 303 (9), 205 (32), 177 (39), 155 (76) and 127 (49).

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