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Diastereoselective photosensitised radical addition to fumaric acid derivatives bearing oxazolidine chiral auxiliaries

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Abstract

Various fumaric acid diamides were alkylated by reaction with photogenerated radicals. The radicals were produced either by benzophenone triplet hydrogen abstraction (from 1,3-dioxolane, 2-methyl-1,3-dioxolane and adamantane) or via photoinduced electron transfer sensitised by DCN/biphenyl from stannanes (*t*-$BuSnPh_3$ and Bu_4Sn). When chiral substrates were employed the reaction occurred with a good degree of stereoselectivity even when acyclic alkyl radicals were involved. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Radical addition to olefins has become a synthetically useful process in organic synthesis, particularly when the reaction occurs with a high degree of diastereoselectivity. Concerning the latter point, satisfactory results have been obtained both in the case of intramolecular addition and for the intermolecular addition of cyclic radicals bearing a substituent on a carbon adjacent to the radical site.[1,2] On the other hand, the stereoselective radical addition to a stereogenic centre on an acyclic alkene has been explored by Porter, Giese and Curran over the last decade. These groups first used chiral fumarate esters,[3a] which gave a poor stereoselectivity, but better results were obtained with chiral amides, through studies which extended the use of chiral auxiliaries previously employed in cycloaddition and in enolate addition reactions.[4,5] In this case, the addition of open chain or cyclic alkyl radicals was found to occur in a good yield as well as with a satisfactory diastereoselectivity.[6] The auxiliaries used included 2,5-disubstituted pyrrolidines,[7–9] 2,2-dimethyl-oxazolidines,[10,11] Oppolzer's camphorsultam,[4b,12] and benzoxazole derivatives.[12,13]

All of these studies involved the generation of alkyl radicals through a chain reaction via tin or mercury derivatives. Therefore, we deemed it worthwhile to extend the scope of the reaction by using different types of radicals and/or different radical precursors. We present here a study of

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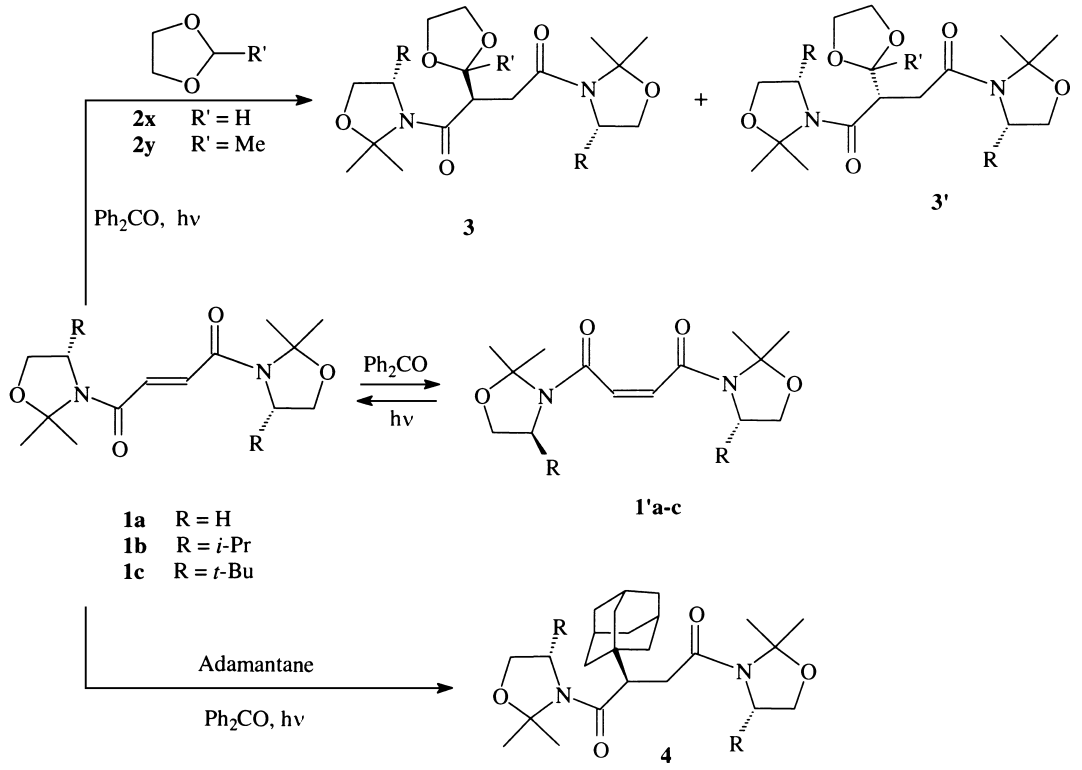
the addition to fumaryl amides of two 2-dioxolanyl radicals and of the adamantyl radical produced by photosensitised benzophenone hydrogen abstraction as well as of two open-chain alkyl radicals produced from alkyltin precursors through photoinduced electron transfer to aromatic sensitisers in their excited states. In this way, the photochemical functionalisation of fumaric acid tethered to chiral oxazolidines was obtained with good to excellent stereoselectivity.

2. Results

2.1. Radical by photosensitised hydrogen abstraction

Three (*E*)-fumaryl-bis(oxazolidines), viz. **1a** (achiral), **1b** and **1c** (both chiral) were used in this study. These were prepared from the corresponding, easily available aminoalcohols in two steps. Irradiation of these fumaryloxazolidines in acetonitrile in the presence of benzophenone as photosensitiser caused geometric isomerisation and led to formation of the corresponding *Z*-isomers (**1′a–c**) (see Experimental).

Irradiation of fumaryloxazolidines **1a–c** in neat 1,3-dioxolane (**2x**) or in a 1 M solution of 2-methyl-1,3-dioxolane (**2y**) in MeCN gave dioxolanylsuccinyloxazolidines **3** (*R* stereochemistry, major product) and **3′** (*S*) in moderate to good yields. The ratio of the two diastereoisomers depended both on the chiral oxazolidine tethered to the alkene and on the dioxolane used (de from 88.9 to >98.5% Scheme 1 and Table 1).



Scheme 1.

Table 1
Products yield by irradiation of derivatives **1a–c**

Substrate	Radical source	Product[(a)]	Product yield %[(b)]	de
1a	**2x**	**3ax**	81.5	-
1a	**2y**	**3ay**	44 (61.7)	-
1a	Adamantane	**4a**	36	-
1a	**5w**	**6aw**	50 (58.9)	-
1a	**5z**	**6az**	47.4 (59.7)	-
1b	**2x**	**3bx**	56	94.1
1'b	**2x**	**3bx**	(c)	94.7
1b	**2y**	**3by** + **3'by**	57.6 (66.6) + 7.4 (8.6)	88.9
1b	Adamantane	**4b**	31	> 98.5[(d)]
1b	**5w**	**6bw**	49.5 (63.4)	88.9
1b	**5z**	**6bz**	43.2 (51)	94.7
1c	**2x**	**3cx**	75	> 98.5[(d)]
1c	**5w**	**6cw**	79	> 98.5[(d)]

(a) The major stereoisomer is indicated. The minor one is detected by GC/MS except in the case of **3'by** where its amount is sufficient for the isolation.

(b) Isolated yield. In parenthesis yields based on recovered alkene.

(c) Product not isolated

(d) The second diastereoisomer could not be detected by GC analysis

Increasing the bulkiness of the substituent in the oxazolidine increased the de with no negative effect on the isolated yield of the alkylated products **3**, which was satisfactory even with hindered **1c**. The de obtained was 94.1 to >98.5% with the unsubstituted dioxolane **2x** and slightly lower, 88.9%, in the reaction of **2y** with the alkene **1b**.

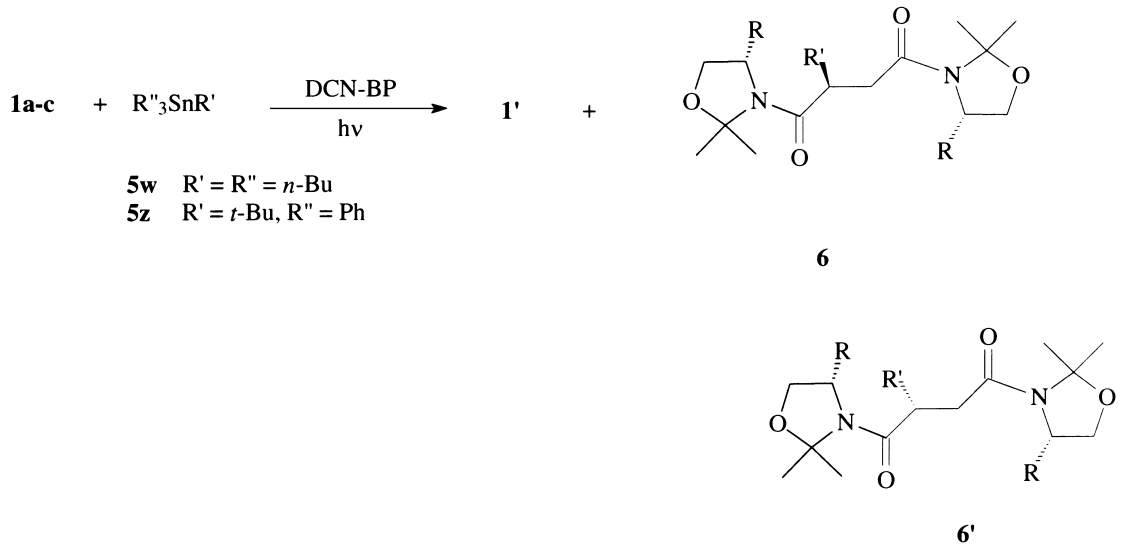
The addition of the adamantyl radical, generated by photosensitised hydrogen abstraction from adamantane by benzophenone, was also explored. In this case, adducts **4a**,**b** were formed in high regio- (attack only by the 1-adamantyl radical) and stereoselectivity (only the *R*-isomer was isolated in the case of **4b**). Product yields were lower in this case, probably due to the steric hindrance of the adamantyl radical, which is known to react efficiently with less crowded electrophylic alkenes.[14]

In all of the above experiments *E*/*Z* isomerisation took place concurrently with alkylation. As an example, in the irradiation of **1a** in dioxolane maleate **1'a** formed at a rate of ca. 1:3 of that of the alkylation to give **3a**. This did not affect the final results since the maleate also underwent

photosensitised alkylation giving the same adducts **3**/**3′** with roughly the same de, as was demonstrated in separate experiments starting from the maleate (see an example concerning **1′b** in Table 1)

2.2. Radical by photoinduced SET

The reaction was also successful with acyclic alkyl radicals produced from tetrasubstituted stannanes **5w** and **5z** by photoinduced SET and using 1,4-dicyanonaphthalene (DCN) and biphenyl (Bp) as sensitisers. Under these conditions the alkylsuccinyloxazolidines (**6**/**6′**) were formed in medium to good chemical yields (Scheme 2). As appears in Table 1, a high degree of stereochemical control was achieved with these open-chain radicals, both straight chain (**6** main stereoisomer, de >88.9%) and branched (94.7%). The highest selectivity and best chemical yields were obtained with the highly hindered *t*-butyloxazolidinyl alkene **1c** as the substrate. Noteworthy, when the less crowded primary radical (*n*-Bu) was added to this alkene, the diastereoselection was satisfactory and significantly increased in going from **1b** to **1c** (de 88.9 and >98.5%, respectively). Only the major isomer was isolated in both cases and to it the same stereochemistry was assigned (the indicator is *R* in the case of *t*-Bu, product **6bz**, and *S* in the case of *n*-Bu, products **6bw** and **6cw**). Also, when using the SET method for the generation of radicals some *E*/*Z* isomerisation of the starting alkene occurred during the irradiation.



Scheme 2.

2.3. Stereochemistry assignment

Assignment of the *R* stereochemistry to the main isomers of succinyl derivatives **3** and **6** was supported by NOE experiments. These gave unambiguous evidence in the case of the isopropyloxazolidinylsuccinates **3bx** and **6bz**. Furthermore, this was supplemented by an X-ray structure determination in the case of product **6bz** (Fig. 1). NMR experiments on the *t*-butyloxazolidinylfumarate **1c** and the corresponding succinyl derivatives showed that these compounds

exist in solution as a mixture of rotamers with a considerable barrier at room temperature. However, this did not affect the stereochemical assignment since the signals attributed to rotamers could be distinguished from those due to diastereoisomers through saturation transfer experiments.

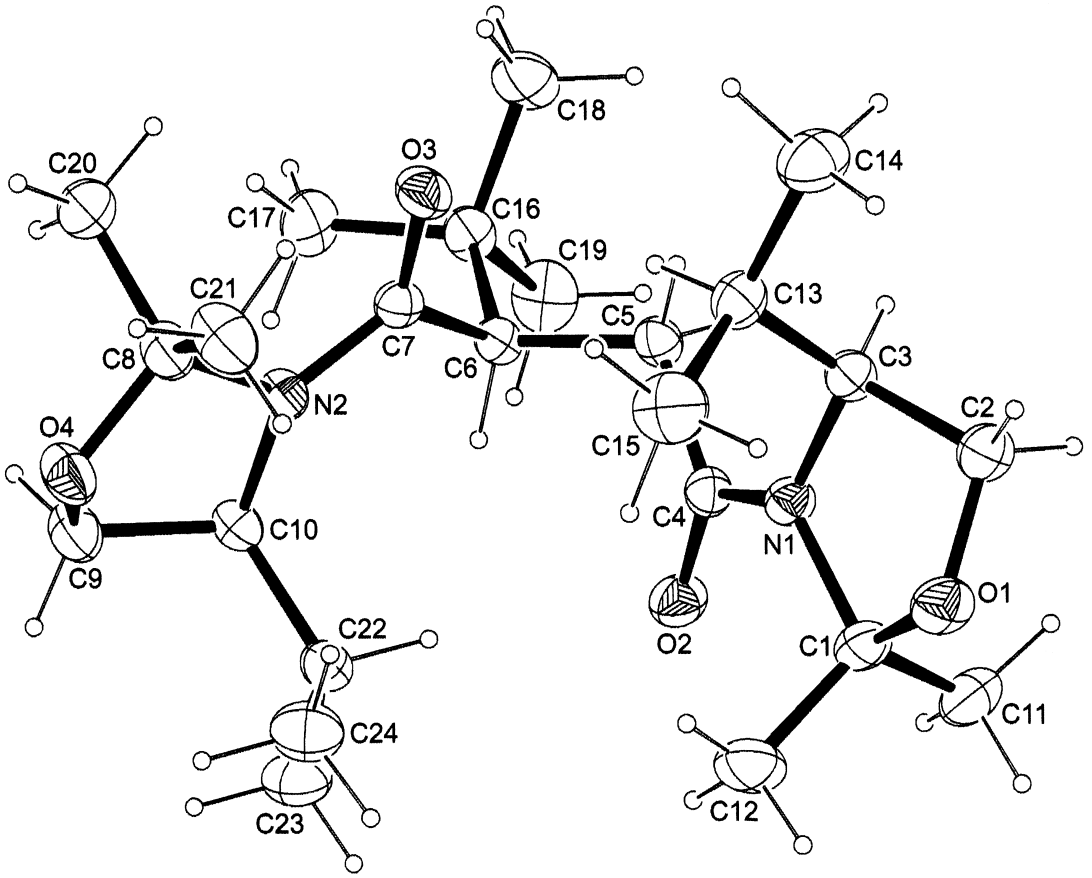


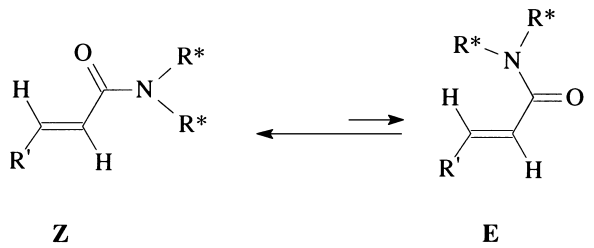
Figure 1. ORTEP view of **6bz**. Ellipsoids are drawn at 20% probability level

3. Discussion

A large number of auxiliaries have been considered in the literature with the aim of reaching good stereoselectivity in radical addition to electron poor alkenes and the current state of the art is as follows.

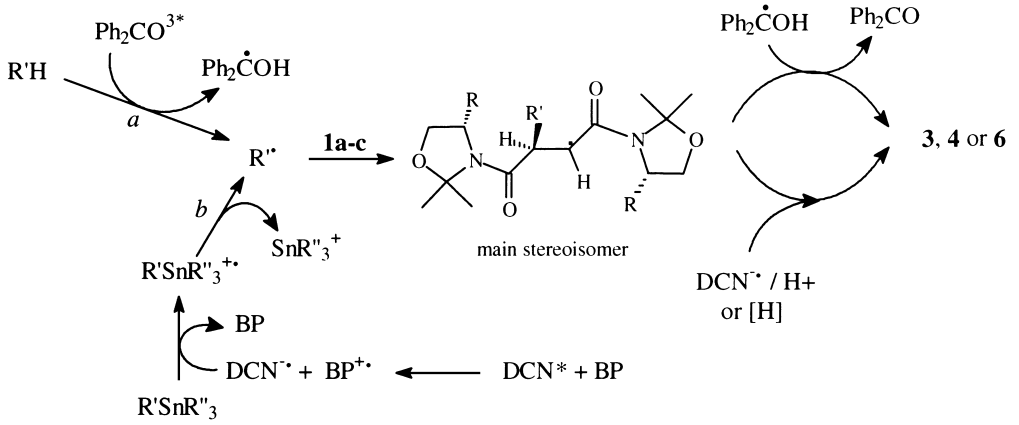
(a) The use of esters derived from chiral alcohol auxiliaries rarely led to a high level of diastereoselectivity;[15] (b) amides from chiral amines are largely used because they show a reduced conformational mobility with respect to esters since the allylic strain largely favours the *Z* conformation with respect to the *E* conformation for the planar R_2N–C(=O)–C=C moiety (see Scheme 3);[16] (c) the synthesis of chiral auxiliaries is often tedious and the requisite of the availability in both enantiomeric forms is very rarely verified; (d) bulkiness of the auxiliaries causes a dramatic

decrease in the efficiency of radical addition when bulky radicals, e.g. *t*-Bu, are used;[9] (e) when the reaction temperature decreases, the de increases but radical chain reactions do not propagate efficiently;[19] and (f) mercury and tin derivatives largely employed in radical chain reactions are highly toxic and their use should be minimised.



Scheme 3.

When confronting some of the limitations listed above it is desirable to develop different radical precursors in connection with different methods for the generation of radicals. We produced the radicals by photochemical means in two different ways, viz. through hydrogen abstraction by triplet benzophenone[21] used in a 40% amount[22] (Scheme 4, path *a*) and through the electron transfer pathway via fragmentation of the radical cations[14a,25–28] (Scheme 4, path *b*).



Scheme 4.

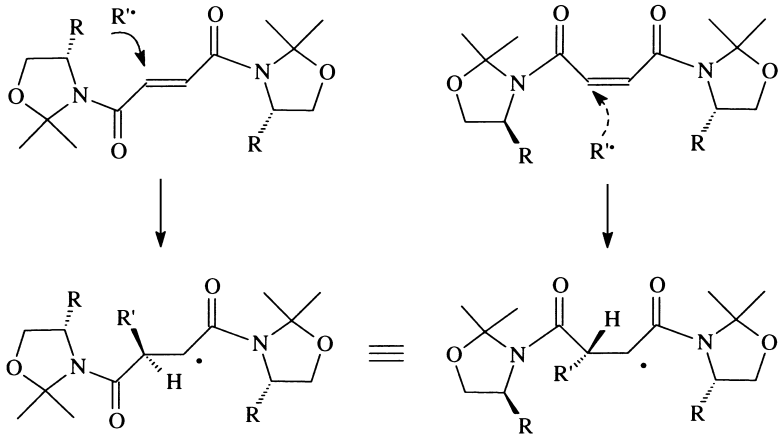
Among the chiral auxiliaries described in the literature we chose 2,2-dimethyl-4-(alkyl)-oxazolidine derivatives because these are quite easily synthesised and their removal is known to occur with little racemisation;[11] furthermore, chiral 2-substituted succinic acids are suitable building blocks for organic synthesis and their structure is present in the skeleton of molecules of biological interest.[29] We considered both the previously reported isopropyl **1b**[11] and the yet more bulky *t*-butyloxazolidine derivative **1c** as well as achiral **1a** for the sake of comparison. Compounds **1b** and **1c** are easily obtained from the corresponding L-amino acid or L-amino-alcohols (see Experimental).

Addition of dioxolanyl and 2-methyldioxolanyl radicals offers an entry for the introduction of masked aldehydes or the methylketone groups. Noteworthy, the monoalkyldioxolane moiety

introduced in this way can be transformed into a carboxylic group in one step[30] or into a -CH_2NH_2 group through the deprotection–oxime formation–reduction sequence.[31]

In the present alkylation reaction the de obtained is high and increases in going from **1b** to **1c** with both alkyl and α,α′-dioxyalkyl radicals. The better stereofacial selection in the latter case is due to the steric hindrance of the two *t*-Bu groups present in the molecule, which induces a pseudoaxial orientation in the half chair oxazolidine conformation.[10]

On the other hand, the de is less affected by the bulkiness of the adding radical than by the bulkiness of the chiral auxiliary. Indeed, similar results are obtained with dioxolanyl and *t*-Bu radicals as compared to 2-methyldioxolanyl and *n*-Bu radicals, respectively. The selectivity observed is in the same direction as observed by Porter et al. in the reaction between thermally generated alkyl radicals and similar substrates[11] and corresponds to that expected by simple visual inspection of the models (Scheme 5). However, the present methods for the photogeneration of radicals allow a better selectivity to be obtained. It appears that the mild conditions of the photochemical method allow the facial selectivity induced by the chiral auxiliary to be fully exploited.



Scheme 5.

Also noteworthy, hydrogen abstraction from adamantane is known to be a non-selective process.[14a,32] In the case of adamantane, both bridged or bridgehead hydrogens have been reported to be extracted, with varying selectivities.[33] However, only succinic acid derivatives incorporating the 1-adamantyl radical are obtained in the present reaction, possibly because the regioselectivity arises at the addition step. Stereoselectivity is complete with this bulky radical.

Compounds **1a**–**c** also undergo *E*/*Z* interconversion and photoisomers **1′** were isolated in some cases by column chromatography (Table 1). This isomerisation occurs both upon direct and upon sensitised irradiation, being faster when benzophenone is used (the triplet sensitised *E*/*Z* isomerisation is well known).[34]

Importantly for the success of the present synthetic approach, such isomerisation has no adverse effect on the stereoselectivity, the addition to both isomers apparently leading to the same adduct radical, again as expected from inspection of the model (see Scheme 5). Control experiments where the irradiation of the alkenes was carried out in neat acetonitrile showed that in the photostationary state the *Z*-isomers (maleic diamides) predominate. As shown in Table 1 the de

obtained starting directly from maleic amides **1′b** is about the same as from the fumaryl derivatives **1b** in the reaction with dioxolane **2x** (see Table 1 and Experimental). In this connection, it is worth mentioning that this is an unprecedented result since the alkylation of chiral maleic amides by any radical method has not been previously reported.

4. Conclusion

A mild functionalisation of fumaryloxazolidines **1a–c** involving the formation of C–C bonds was achieved photochemically in good yield and with a good level of diastereoselection. The addition of radicals, both when they were produced by hydrogen atom abstraction and when they arose via the electron transfer path gave chiral 2-alkyl succinic acid derivatives with a de from 88.9 to >98.5%. This was higher than when obtained through radical chain methods, with no need for lowering the temperature showing that the mild conditions of the photochemical radical generation allow for optimal exploitation of chiral amides for diastereoselective alkylation. The resulting 2-substituted chiral succinic acid derivatives can be elaborated as suitable building blocks for organic synthesis and further studies on this subject are in progress.

5. Experimental

5.1. General

NMR spectra were recorded on a 300 MHz spectrometer. The assignments were made on the basis of ^{1}H and ^{13}C NMR, supported by DEPT-135 and 2D correlated NMR data. Chemical shifts are reported in ppm downfield from TMS. Acetonitrile was refluxed over CaH_2, benzene and Et_2O were refluxed over sodium and distilled just before use while CH_2Cl_2 was dried over molecular sieves. 1,3-Dioxolane, 2-methyl-1,3-dioxolane, Ph_3SnCl, biphenyl, fumaryl chloride and (*S*)-*tert*-leucinol were commercial samples and were used without purification. L-Valinol was prepared by reduction of the corresponding amino acid[35] and DCN from the naphthalene.[36] (*S*)-4-Alkyl-2,2-dimethyl-1,3-oxazolidines were prepared from the corresponding aminoalcohols.[10,11] The photochemical reactions were performed by using nitrogen-purged solution and a multilamp reactor fitted with four to eight 15-W phosphor-coated lamps (maximum of emission, 320 or 360 nm) for the irradiation. The reaction course was followed by TLC (cyclohexane–ethyl acetate) and GC. Workup of the photolytes involved concentration in vacuo and chromatographic separation using Millipore 60 Å 35–70 μm silica gel. The diastereomeric ratio was determined by GC/MS (HP-5, 10 m×0.53 mm×2.65 μm).

The structure of compound **6bz** was assessed by a single crystal X-ray determination. Unit cell parameters and intensity data were obtained on an Enraf–Nonius CAD-4 diffractometer. Calculations were performed with the WinGX-97[37] software. Cell dimensions were determined by least-squares fitting of 25 centred reflections monitored in the range $9.28^\circ < \theta < 13.88^\circ$. Corrections for Lp and empirical absorption were applied.[38] The structure was solved by SIR92.[39] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares using SHELXL-93.[40] All the hydrogen atoms were located in the difference Fourier maps and refined isotropically. Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[41] The diagram of the molecular structure (see Fig. 1) was produced by the ORTEP program.[42]

5.2. Synthesis of fumaryl derivatives **1**. General procedure

Oxazolidines **1a–c** were prepared by the method reported by Porter et al. as detailed below.[11] To a solution of the [(*S*)-4-alkyl]-2,2-dimethyl-1,3-oxazolidine (70.2 mmol) in dry CH_2Cl_2 (200 ml) a solution of Et_3N (11.7 ml, 84.2 mmol) in dry CH_2Cl_2 (40 ml) was added dropwise at 0°C under argon. Fumaryl chloride was then slowly added (4.6 ml, 42.1 mmol) and the resulting dark mixture was stirred for 30 min at 0°C and 3 h at room temperature. The solution was evaporated and the residue taken up with 350 ml of ethyl acetate and washed with water (150 ml), $NaHCO_3$ satd. solution (150 ml) and brine (150 ml). The organic phase was dried and evaporated.

5.2.1. Synthesis of (E)-3,3′-(1,4-dioxo-2-butene-1,4-diyl)bis(2,2-dimethyl)-1,3-oxazolidine **1a**

The substrate was purified by column chromatography (cyclohexane:ethyl acetate, 2:8) and crystallised from cyclohexane/ethyl acetate (27.8% yield, based on the oxazolidine) and isolated as a colourless solid, m.p. 170–172°C.

Compound **1a**: ^1H ($CDCl_3$) δ 1.65 (s, $4CH_3$), 3.8 (t, 4H, $2CH_2$, $J=6$ Hz), 4.05 (t, 4H, $2CH_2$, $J=6$ Hz), 7.2 (s, 2H, 2CH); ^{13}C ($CDCl_3$) δ 24.1 (CH_3), 46.1 (CH_2), 63.1 (CH_2), 95.0, 132.9 (CH), 160.9 (CO). IR (KBr) ν/cm^{-1} 1620, 1416, 1254, 839. Anal. calcd for $C_{14}H_{22}N_2O_4$: C, 59.56; H, 7.85. Found: C, 59.60; H, 7.80.

5.2.2. Synthesis of (E)-3,3′-(1,4-dioxo-2-butene-1,4-diyl)bis[2,2-dimethyl-(S)-4-(1-methylethyl)]-1,3-oxazolidine **1b**

The crude product was purified by column chromatography (cyclohexane:ethyl acetate, 1:1) and crystallised from cyclohexane/ethyl acetate to give a colourless solid, m.p. 78–80°C. Spectral data were identical to those previously reported.[11]

5.2.3. Synthesis of (E)-3,3′-(1,4-dioxo-2-butene-1,4-diyl)bis[2,2-dimethyl-(S)-4-(1,1-dimethylethyl)]-1,3-oxazolidine **1c**

The substrate was purified by column chromatography (cyclohexane:ethyl acetate, 75:25) and isolated in 15% yield (based on the starting aminoalcohol) to give a colourless solid, m.p. 48–50°C.

Compound **1c**: ^1H ($CDCl_3$) (mixture of two rotamers, one largely predominant) δ (the signals of the main one are reported) 0.95 (s, 9H, *t*-Bu), 1.55 (s, 3H, CH_3), 1.8 (s, 3H, CH_3), 3.7–4.1 (m, 3H), 7.3 (s, 1H); ^{13}C ($CDCl_3$) (mixture of two rotamers) δ (the signals of the main one are reported) 22.6 (CH_3), 26.2 (CH_3), 27.2 (CH_3, *t*-Bu), 35.4, 64.8 (CH_2), 65.1 (CH), 96.4, 133.3 (CH), 163.8 (CO). IR (KBr) ν/cm^{-1} 1618, 1418, 1252, 840. Anal. calcd for $C_{22}H_{38}N_2O_4$: C, 66.97; H, 9.71. Found: C, 67.12; H, 9.59.

5.3. Photosensitised isomerisation of alkenes **1**

5.3.1. Isomerisation of **1a**

Compound **1a** (169 mg, 0.6 mmol, 0.05 M) and benzophenone (22 mg, 0.12 mmol, 0.01 M) were dissolved in 12 ml of MeCN and irradiated at 320 nm for 15 h. After evaporation the residue was chromatographed on column (with cyclohexane:ethylacetate from 2:8 to neat ethyl acetate as eluant) to afford 120 mg (71% yield) of **1′a** as a colourless solid, m.p. 103–105°C.

Compound **1′a**: ^1H ($CDCl_3$) δ 1.6 (s, 12H), 3.65 (t, 4H, $J=6$ Hz), 4.00 (t, 4H, $J=6$ Hz), 6.20 (s, 2H); ^{13}C ($CDCl_3$) δ 24.1 (CH_3), 46.3 (CH_2), 63.2 (CH_2), 94.7, 129.6 (CH), 162.9 (CO). IR (KBr) ν/cm^{-1} 1635, 1412, 1242, 824. Anal. calcd for $C_{14}H_{22}N_2O_4$: C, 59.56; H, 7.85. Found: C, 59.69; H, 7.90.

*5.3.2. Isomerisation of **1b***

Compound **1b** (219 mg, 0.6 mmol, 0.05 M) and benzophenone (22 mg, 0.12 mmol, 0.01 M) were dissolved in 12 ml of MeCN and irradiated at 320 nm for 15 h. After evaporation the residue was chromatographed on column (cyclohexane:ethyl acetate, 2:8) to afford 142 mg (65% yield) of **1′b** as a colourless solid, m.p. 128–130°C.

Compound **1′b**: ^{1}H ($CDCl_3$) δ 0.9 (m, 12H), 1.6 (s, 6H), 1.7 (s, 6H), 1.9 (m, 2H), 3.75 (m, 2H), 3.9 (m, 4H), 6.25 (s, 2H); ^{13}C ($CDCl_3$) δ 17.3 (CH_3), 19.7 (CH_3), 22.3 (CH_3), 25.8 (CH_3), 31.6 (CH_3), 63.0 (CH), 64.4 (CH_2), 95.4, 129.1 (CH), 164.0 (CO). IR (KBr) ν/cm^{-1} 1639, 1429, 1068, 838. Anal. calcd for $C_{20}H_{34}N_2O_4$: C, 71.81; H, 10.25. Found: C, 71.71; H, 10.28.

*5.4. Alkylation of **1a–c** via photosensitised hydrogen transfer*

*5.4.1. Synthesis of 3,3′-[2-(2-dioxolanyl)-1,4-dioxo-1,4-butanediyl]bis(2,2-dimethyl)oxazolidine **3ax***

Compound **1a** (1.41 g, 5 mmol, 0.05 M) and benzophenone (364 mg, 2 mmol, 0.02 M) were dissolved in 100 ml of 1,3-dioxolane and irradiated for 45 min at 360 nm. After column chromatography (from cyclohexane:ethyl acetate, 2:8, to neat ethyl acetate as eluants) **3ax** (1.45 g, 81.5% yield) was isolated as a syrup.

Compound **3ax**: ^{1}H ($CDCl_3$) δ 1.5 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 2.5 (dd, 1H, J=4 Hz and 16 Hz), 2.9 (dd, 1H, J=10 Hz and 16 Hz), 3.25 (ddd, 1H, J=4 Hz, 10 Hz and 16 Hz), 3.55 (m, 1H), 3.7 (m, 1H), 3.85 (m, 2H), 4.0 (m, 8H), 5.0 (d, 1H, J=7 Hz); ^{13}C ($CDCl_3$) δ 23.6 (CH_3), 24.0 (CH_3), 24.2 (CH_3), 24.3 (CH_3), 34.8 (CH_2), 45.9 (CH), 46.0 (CH_2), 46.3 (CH_2), 62.8 (CH_2), 62.9 (CH_2), 64.7 (CH_2), 65.0 (CH_2), 94.3, 94.4, 104.7 (CH), 167.4 (CO), 168.1 (CO). IR (neat) ν/cm^{-1} 1643, 1427, 1063, 832. Anal. calcd for $C_{17}H_{28}N_2O_6$: C, 57.29; H, 7.92. Found: C, 57.33; H, 7.91.

*5.4.2. Synthesis of 3,3′-[2-(2-methyl-2-dioxolanyl)-1,4-dioxo-1,4-butanediyl]bis(2,2-dimethyl)-oxazolidine **3ay***

Compound **1a** (843 mg, 3 mmol, 0.05 M), benzophenone (220 mg, 1.2 mmol, 0.02 M) and 2-methyl-1,3-dioxolane (5.4 ml, 60.2 mmol) in 54.6 ml of MeCN were irradiated for 15 h at 360 nm. Column chromatography (cyclohexane:ethyl acetate, 2:8) gave 241 mg of **1′a** and 488 mg of **3ay** (44% yield) as a colourless solid, m.p. 118–120°C.

Compound **3ay**: ^{1}H ($CDCl_3$) δ 1.4 (s, 3H, CH_3), 1.5 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 2.45 (dd, 1H, J=3 Hz and 16 Hz), 3.0 (dd, 1H, J=10 Hz and 16 Hz), 3.35 (dd, 1H, J=3 Hz and 10 Hz), 3.55 (m, 1H), 3.75 (m, 1H), 3.8–4.1 (m, 10H); ^{13}C ($CDCl_3$) δ 22.4 (CH_3), 23.6 (CH_3), 24.0 (CH_3), 24.3 (CH_3), 24.4 (CH_3), 35.3 (CH_2), 46.1 (CH_2), 46.5 (CH_2), 49.0 (CH), 63.0 (CH_2), 63.1 (CH_2), 64.3 (CH_2), 64.4 (CH_2), 94.4, 94.5, 110.3, 168.0 (CO), 168.4 (CO). IR (KBr) ν/cm^{-1} 1645, 1427, 1069, 832. Anal. calcd for $C_{18}H_{30}N_2O_6$: C, 58.36; H, 7.56. Found: C, 58.40; H, 7.51.

*5.4.3. Synthesis of 3,3′-[2-(1-adamantyl)-1,4-dioxo-1,4-butanediyl]bis(2,2-dimethyl)oxazolidine **4a***

Compound **1a** (422 mg, 1.5 mmol, 0.05 M), benzophenone (110 mg, 0.6 mmol, 0.02 M), and adamantane (2.4 g, 17.6 mmol, 0.6 M) in 30 ml of benzene were irradiated for 15 h at 360 nm. After column chromatography (from cyclohexane:ethyl acetate, 6:4 to 3:7) **4a** (226 mg, 36% yield) was isolated as a colourless solid, m.p. 133–135°C.

Compound **4a**: ^{1}H ($CDCl_3$) δ 1.4–1.9 (m, 12 H), 1.5 (s, 6H, $2CH_3$), 1.6 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 2.0 (bs, 3H, CH adam), 2.3 and 2.8 (AB part of an ABX system, 2H), 2.75 (X part of an ABX system, 1H), 3.6 (dt, 1H, $J=6$ Hz and 9 Hz), 3.65–3.8 (m, 3H), 3.95 (m, 4H), 4.1 (m, 1H); ^{13}C ($CDCl_3$) δ 23.3 (CH_3), 24.1 (CH_3), 24.4 (CH_3), 24.8 (CH_3), 28.5 (CH adam), 33.2 (CH_2), 35.2, 36.8 (CH_2 adam), 40.0 (CH_2 adam), 46.2 (CH_2), 47.1 (CH_2), 50.7 (CH), 62.9 (CH_2), 63.0 (CH_2), 94.3, 94.6, 169.1 (CO), 170.8 (CO). IR (KBr) ν/cm^{-1} 2902, 1634, 1412, 1066, 831. Anal. calcd for $C_{24}H_{38}N_2O_4$: C, 68.87; H, 9.15. Found: C, 68.94; H, 9.11.

*5.4.4. Synthesis of 3,3′-[(*R*)-2-(2-dioxolanyl)-1,4-dioxo-1,4-butanediyl)]bis[2,2-dimethyl-(*S*)-4-(1-methylethyl)]oxazolidine* ***3bx***

Compound **1b** (806 mg, 2.2 mmol, 0.05 M) and benzophenone (160 mg, 0.9 mmol, 0.02 M) were dissolved in 44 ml of 1,3-dioxolane and irradiated for 15 h at 360 nm. After column chromatography (cyclohexane:ethyl acetate, 4:6) 542 mg of **3bx** (56% yield) were isolated as an oil. The relative configuration was derived from NOE experiments. Irradiation of H-2 caused unambiguous enhancement of the hydrogen of the isopropyl group in the corresponding 1D-NOE difference spectrum. Small scale experiments irradiating **1′b** instead of **1b** again gave about the same de excess of the final product **3bx** (94.7%).

Compound **3bx**: ^{1}H ($CDCl_3$) δ 0.85–1.1 (m, 12H, $4CH_3$), 1.55 (2s, 6H, $2CH_3$), 1.7 (s, 6H, $2CH_3$), 2.15 (m, 2H), 2.5 (dd, 1H, $J=4$ Hz and 15 Hz), 2.75 (dd, 1H, $J=8$ Hz and 15 Hz), 3.5 (ddd, 1H, $J=4$ Hz, 7 Hz and 8 Hz), 3.75–4.1 (m, 10H), 5.0 (d, 1H, $J=7$ Hz); ^{13}C ($CDCl_3$) δ 16.8 (CH_3), 17.4 (CH_3), 18.7 ($2CH_3$), 22.5 (CH_3), 22.6 (CH_3), 25.8 (CH_3), 25.9 (CH_3), 30.9 (CH), 31.1 (CH), 34,3 (CH_2), 45.7 (CH), 62.5 (CH), 62.7 (CH), 63.9 (CH_2), 64.4 (CH_2), 64.8 (CH_2), 65.1 (CH_2), 95.3, 95.3, 105.8 (CH), 168.8 (CO), 169.2 (CO). IR (neat) ν/cm^{-1} 2976, 1643, 1426, 1064, 832. Anal. calcd for $C_{23}H_{40}N_2O_6$: C, 62.70; H, 9.15. Found: C, 62.81; H, 9.21.

*5.4.5. Synthesis of 3,3′-[(*R/S*)-2-(2-methyl-2-dioxolanyl)-1,4-dioxo-1,4-butanediyl)]bis[2,2-dimethyl-(*S*)-4-(1-methylethyl)]oxazolidine* ***3by*** *and* ***3′by***

Compound **1b** (915 mg, 2.5 mmol, 0.05 M), benzophenone (456 mg, 2.5 mmol, 0.02 M), and 2-methyl-1,3-dioxolane (4.4 ml, 50 mmol) in 45.6 ml of MeCN were irradiated for 22 h at 360 nm. After column chromatography (cyclohexane:ethyl acetate, 7:3) 124 mg of **1′b** as an oil, 654 mg of **3by** (57.6% yield) as an oil and 84 mg of **3′by** (7.4% yield) were isolated.

Compound **3by**: ^{1}H ($CDCl_3$) δ 0.92–1.1 (m, 12H, $4CH_3$), 1.37 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.65 (s, 6H, $2CH_3$), 2.25 (m, 2H) 2.5–2.7 (m, 2H, AB part of an ABX system), 3.65 (m, 1H, X part of an ABX system), 3.8–4.1 (m, 10H); ^{13}C ($CDCl_3$) δ 16.7 (CH_3), 17.6 (CH_3), 19.9 ($2CH_3$), 22.5 (CH_3), 22.6 (CH_3), 22.7 (CH_3), 25.7 (CH_3), 25.9 (CH_3), 30.9 (CH), 31.0 (CH), 34.9 (CH_2), 48.6 (CH), 62.6 (2CH), 63.8 (CH_2), 64.4 (CH_2), 64.8 (CH_2), 65.1 (CH_2), 95.2, 95.8, 111.0, 169.1 (CO), 169.7 (CO). IR (neat) ν/cm^{-1} 2977, 1640, 1422, 1063, 831. Anal. calcd for $C_{24}H_{42}N_2O_6$: C, 63.41; H, 9.31. Found: C, 63.40; H, 9.22.

Compound **3′by**: ^{1}H ($CDCl_3$) δ 0.9–1.1 (m, 12H, $4CH_3$), 1.36 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 2.25 (m, 2H), 2.5–2.7 (m, 2H, AB part of an ABX system), 3.50 (m, 1H, X part of an ABX system), 3.8–4.2 (m, 10H); ^{13}C ($CDCl_3$) δ 16.7 (CH_3), 17.7 (CH_3), 20.0 ($2CH_3$), 22.6 (CH_3), 22.7 (CH_3), 23.1 (CH_3), 25.2 (CH_3), 25.8 (CH_3), 31.1 (2CH), 35.1 (CH_2), 48.7 (CH), 62.7 (2CH), 63.8 (CH_2), 64.5 (CH_2), 64.9 (CH_2), 65.1 (CH_2), 95.2, 95.8, 110.9, 168.8 (CO), 170.0 (CO). IR (neat) ν/cm^{-1} 2975, 1641, 1421, 1063, 830. Anal. calcd for $C_{24}H_{42}N_2O_6$: C, 63.41; H, 9.31. Found: C, 63.30; H, 9.19.

*5.4.6. Synthesis of 3,3′-[(R)-2-(1-adamantyl)-1,4-dioxo-1,4-butanediyl]bis[2,2-dimethyl-(S)-4-(1-methylethyl)]oxazolidine **4b***

Compound **1b** (457 mg, 1.25 mmol, 0.05 M), benzophenone (228 mg, 1.25 mmol, 0.02 M) and adamantane (2 g, 14.7 mmol, 0.6 M) in 25 ml of benzene were irradiated for 15 h at 360 nm. A further portion of benzophenone was added (228 mg) and the irradiation was prolonged for an additional 15 h. After column chromatography (cyclohexane:ethyl acetate, 75:25) the raw product was further purified by washing with cold pentane. At the end 190 mg of **4b** (31% yield) were isolated as a syrup.

Compound **4b**: ^{1}H ($CDCl_3$) δ 0.9 (m, 12H, 4CH_3), 1.2–1.9 (m, 12H, adam), 1.5 (s, 3H, CH_3), 1.6 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.0 (bs, 3H, 3CH), 2.25 (m, 2H), 2.50 (dd, 1H, $J=3$ and 8 Hz), 2.60 (dd, 1H, $J=3$ and 8 Hz), 3.0 (t, 1H, CH), 3.8–4.0 (m, 6H); ^{13}C ($CDCl_3$) δ 16.5 (CH_3), 17.0 (CH_3), 19.9 (CH_3), 22.4 (CH_3), 22.9 (CH_3), 25.6 (CH_3), 25.8 (CH_3), 28.5 (CH, adam), 30.6 (CH), 31.0 (CH), 33.1 (CH_2, adam), 34.2, 36.8 (CH_2, adam), 50.3 (CH), 62.5 (CH), 63.0 (CH), 63.5 (CH_2), 63.6 (CH_2), 95.2, 95.5, 169.6 (CO), 171.6 (CO). IR (neat) ν/cm^{-1} 2903, 1633, 1414, 1066, 830. Anal. calcd for $C_{30}H_{50}N_2O_4$: C, 71.67; H, 10.02. Found: C, 71.71; H, 10.10.

*5.4.7. Synthesis of 3,3′-[(R)-2-(2-dioxolanyl)-1,4-dioxo-1,4-butanediyl]bis[2,2-dimethyl-(S)-4-(1,1-dimethylethyl)]oxazolidine **3cx***

Compound **1c** (312 mg, 0.8 mmol, 0.05 M) and benzophenone (58 mg, 0.32 mmol, 0.02 M) were dissolved in 16 ml of 1,3-dioxolane and irradiated for 15 h at 360 nm. Column chromatography (cyclohexane:ethyl acetate, 75:25) allowed isolation of 276 mg of **3cx** (75% yield) as an oil.

The spectroscopic characterisation of this compound was difficult because in solution it appeared as a mixture of two rotamers (one largely predominant), as confirmed by saturation transfer NMR experiment. In fact, in this case the signals of the acetalic hydrogen of the two rotamers were well separated (4.9 and 5.2 ppm, respectively) in the ^{1}H NMR spectrum. When one of the two signals was irradiated, an intensity change of the second one was observed. This is consistent with the fact that both signals were connected by chemical exchange and belonged to the same diastereomeric species.

Compound **3cx**: ^{1}H ($CDCl_3$) (mixture of two rotamers) δ (the signals of the main one are reported) 1.00 (s, 9H, *t*-Bu), 1.05 (s, 9H, *t*-Bu), 1.51 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.7 (s, 3H, CH_3), 2.3 and 3.05 (m, 3H, ABX system), 3.85 (m, 1H, X part of an ABX system), 3.70–4.10 (m, 10H), 4.9 (d, 1H, $J=7$ Hz); ^{13}C ($CDCl_3$) (mixture of two rotamers) δ (the signals of the main one are reported) 22.5 (CH_3), 22.6 (CH_3), 27.1 (CH_3), 27.3 (CH_3), 27.4 (*t*-Bu), 27.6 (*t*-Bu), 33.3, 33.7, 35.7 (CH_2), 46.3 (CH), 63.9 (CH), 64.1 (CH), 64.8, 65.2, 65.3, 65.9 (CH_2), 96.1, 96.2, 105.8 (CH), 170.9 (CO), 171.3 (CO). IR (neat) ν/cm^{-1} 1644, 1427, 1061, 830. Anal. calcd for $C_{25}H_{44}N_2O_6$: C, 64.07; H, 9.46. Found: C, 64.00; H, 9.59.

*5.5. Alkylation of bisfumaryl **1** via the SET method by using stannanes **5**. General procedure*

The alkenes **1a**–**c** (0.015 M), a stannane **5** (0.02 M), biphenyl (0.1 M) and DCN (0.005 M) were dissolved in MeCN (30 ml) and the solution was divided into two portions that were irradiated (320 nm) in quartz tubes until the stannane was consumed. During the reaction solid tin derivatives separated from the reaction mixture. The solution was then filtered, the solvent removed and the residue purified on a chromatographic column by using cyclohexane–ethyl acetate mixtures as eluants.

5.5.1. Synthesis of t-*butyltriphenylstannane* ***5z***

To a solution of *t*-BuMgCl (60 mmol) in 180 ml of Et_2O, a cloudy solution of Ph_3SnCl (7.7 g, 20 mmol) in Et_2O/benzene was added slowly at 0°C under stirring. After 15 min at 0°C the mixture was stirred for 3 h at room temperature and than poured into NH_4Cl/HCl/ice. The water phase was extracted twice with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. After removal of the solvent the residue was crystallised from benzene/methanol. *t*-Butyltriphenylstannane was obtained in 81.3% yield (6.6 g) as a colourless solid (needles, m.p. 144–145°C).

Compound **5z**: ^1H ($CDCl_3$) δ 1.4 (s, 9H, *t*-Bu), 7.4 (m, 10H), 7.6 (m, 5H). IR (KBr) ν/cm^{-1} 1430, 1077, 725, 700. Anal. calcd for $C_{22}H_{24}Sn$: C, 64.90; H, 5.94. Found: C, 64.87; H, 5.95.

5.5.2. Synthesis of 3,3′-(2-butyl-1,4-dioxo-1,4-butanediyl)bis(2,2-dimethyl)oxazolidine ***6aw***

Compound **1a** (126 mg, 0.45 mmol, 0.015 M), biphenyl (462 mg, 3 mmol, 0.1 M), Bu_4Sn (200 μl, 0.6 mmol, 0.02 M) and DCN (26 mg, 0.15 mmol, 5×10^{-3} M) were dissolved in 30 ml of MeCN and irradiated for 2 days at 320 nm. The crude photolisate was filtered and then chromatographed (cyclohexane:ethyl acetate, 65:35). This allowed isolation of 19 mg of **1′a** and 76 mg (50% yield) of **6aw** as an oil.

Compound **6aw**: ^1H ($CDCl_3$) δ 0.9 (t, 3H, $J=7$ Hz), 1.3 (m, 4H, $2CH_2$), 1.4–1.6 (m, 2H, CH_2), 1.5–1.6 (4s, 12H, $4CH_3$), 2.25 (dd, 1H, $J=4$ Hz and 10 Hz), 2.8 (dd, 1H, $J=10$ Hz and 16 Hz), 3.05 (m, 1H, CH), 3.5–3.8 (3m, 3H, CH_2+CH), 4.05 (m, 5H); ^{13}C ($CDCl_3$) δ 13.8 (CH_3), 22.6 (CH_2), 23.6 (CH_3), 24.0 (CH_3), 24.4 (CH_3), 24.6 (CH_3), 29.2 (CH_2), 32.4 (CH_2), 38.2 (CH_2), 40.8 (CH), 46.1 (CH_2), 46.2 (CH_2), 62.5 (CH_2) 62.6 (CH_2), 94.3, 94.4, 168.2 (CO), 172.3 (CO). IR (neat) ν/cm^{-1} 2979, 1643, 1416, 1064, 831. Anal. calcd for $C_{18}H_{32}N_2O_4$: C, 63.50; H, 9.47. Found: C, 63.53; H, 9.53.

5.5.3. Synthesis of 3,3′-[2-(1,1-dimethylethyl)-1,4-dioxo-1,4-butanediyl)]bis(2,2-dimethyl)oxazolidine ***6az***

Compound **1a** (126 mg, 0.45 mmol, 0.015 M), biphenyl (462 mg, 3 mmol, 0.1 M), **5z** (244 mg, 0.6 mmol, 0.02 M) and DCN (26 mg, 0.15 mmol, 5×10^{-3} M) were dissolved in 30 ml of MeCN and irradiated for 2 days at 320 nm. A further portion of stannane (122 mg) and DCN (13 mg) were then added and the irradiation was continued for a further 24 h. The crude photolisate was filtered and chromatographed (cyclohexane:ethyl acetate, 65:35). This allowed to isolate 26 mg of **1′a** and 72 mg (47.4% yield) of **6az** as an oil.

Compound **6az**: ^1H ($CDCl_3$) δ 1.0 (s, 9H, *t*-Bu), 1.5 (s, 6H, $2CH_3$), 1.55 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 2.3 and 2.85 (m, 2H, AB part of an ABX system), 2.8 (m, 1H, X part of an ABX system), 3.5–3.85 (m, 3H), 4.0 (m, 4H), 4.1 (m, 1H); ^{13}C ($CDCl_3$) δ 23.3 (CH_3), 24.0 (CH_3), 24.4 (CH_3), 24.7 (CH_3), 27.7 (*t*-Bu), 33.2, 34.9 (CH_2), 46.1 (CH_2), 47.8 (CH_2), 49.3 (CH), 62.9 (CH_2), 63.0 (CH_2), 94.3, 94.5, 168.8 (CO), 171.3 (CO). IR (neat) ν/cm^{-1} 2978, 1644, 1418, 1060, 830. Anal. calcd for $C_{18}H_{32}N_2O_4$: C, 63.50; H, 9.47. Found: C, 63.41; H, 9.50.

5.5.4. Synthesis of 3,3′-[(S)-2-butyl-1,4-dioxo-1,4-butanediyl)]bis[2,2-dimethyl-(S)-4-(1-methylethyl)]oxazolidine ***6bw***

Compound **1b** (164 mg, 0.45 mmol, 0.015 M), biphenyl (462 mg, 3 mmol, 0.1 M), Bu_4Sn (200 μl, 0.6 mmol, 0.02 M) and DCN (26 mg, 0.15 mmol, 5×10^{-3} M) were dissolved in 30 ml of MeCN and irradiated for 2 days at 320 nm. A further portion of stannane (100 μl) and DCN (13 mg) were then added and the irradiation was continued for another day. The crude photolisate was

filtered and chromatographed (cyclohexane:ethyl acetate, 8:2). This gave 36 mg of **1′a** and 94 mg (49.5% yield) of **6bw** as an oil.

Compound **6bw**: ^{1}H ($CDCl_3$) δ 0.8–1.05 (m, 15H, $5CH_3$), 1.3 (m, 4H, $2CH_2$), 1.4–1.7 (m, 2H, CH_2), 1.5 (s, 6H, $2CH_3$), 1.7 (s, 6H, $2CH_3$), 2.0–2.3 (m, 2H, 2CH), 2.35–2.7 (m, 2H, ABX), 3.2 (m, 1H, ABX), 3.75–4.0 (m, 6H); ^{13}C ($CDCl_3$) δ 13.8 (CH_3), 16.8 (CH_3), 17.0 (CH_3), 19.6 (CH_3), 19.7 (CH_3), 22.6 (CH_3), 22.7 (CH_3), 22.8 (CH_2), 25.7 (CH_3), 25.9 (CH_3), 29.0 (CH_2), 30.9 (CH), 31.0 (CH), 32.7 (CH_2), 38.1 (CH_2), 41.1 (CH), 62.6 (CH), 62.7 (CH), 63.9 (CH_2), 64.0 (CH), 95.2, 95.3, 168.9 (CO), 173.1 (CO). IR (neat) ν/cm^{-1} 2977, 1642, 1416, 1064, 830. Anal. calcd for $C_{24}H_{44}N_2O_4$: C, 67.89; H, 10.44. Found: C, 67.77; H, 10.52.

*5.5.5. Synthesis of 3,3′-[(*R*)-2-(1,1-dimethylethyl)-1,4-dioxo-1,4-butanediyl]bis[2,2-dimethyl-(*S*)-4-(1-methylethyl)]oxazolidine* ***6bz***

Compound **1b** (164 mg, 0.45 mmol, 0.015 M), biphenyl (462 mg, 3 mmol, 0.1 M), **5z** (244 mg, 0.6 mmol, 0.02 M) and DCN (26 mg, 0.15 mmol, 5×10^{-3} M) were dissolved in 30 ml of MeCN and irradiated for 2 days at 320 nm. A further portion of stannane (122 mg) and DCN (13 mg) were then added and the irradiation was continued for another day. The solution obtained was filtered and then chromatographed (cyclohexane:ethyl acetate, 9:1) and 25 mg of **1′a** and 82 mg (43.2% yield) of **6bz** as a colourless solid (m.p. 107–108°C) were isolated. The relative configuration was derived from NOE and X-ray experiments. First, the irradiation of H-2 caused, in the corresponding 1D-NOE difference spectrum, enhancement for the hydrogen of the isopropyl group similar to the case of compound **3bx**. Second, a single crystal X-ray determination showed that the configuration of the stereogenic centre is opposite with respect of the isopropyl groups in the oxazolidine rings.

Compound **6bz**: ^{1}H ($CDCl_3$) δ 0.8–1.1 (m, 12H, $4CH_3$), 1.05 (s, 9H, *t*-Bu), 1.5 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.7 (s, 3H, CH_3), 2.2 (m, 1H, CH), 2.35 (m, 1H, CH), 2.45 (dd, 1H, $J=5$ Hz and 16 Hz), 2.7 (dd, 1H, $J=6.5$ Hz and 16 Hz), 3.1 (dd, 1H, $J=5$ Hz and 6.5 Hz), 3.7–4.0 (m, 6H); ^{13}C ($CDCl_3$) δ 16.5 (CH_3), 17.0 (CH_3), 19.8 ($2CH_3$), 22.6 (CH_3), 22.7 (CH_3), 23.1 (CH_3), 25.2 (CH_3), 25.8 (CH_3), 27.9 (*t*-Bu), 30.5 (CH), 30.9 (CH), 34.7, 34.8 (CH_2), 48.6 (CH), 62.4 (CH), 63.0 (CH), 63.5 (CH_2), 95.2, 95.4, 169.3 (CO), 172.1 (CO). IR (KBr) ν/cm^{-1} 2981, 1640, 1417, 1062, 832. Anal. calcd for $C_{24}H_{44}N_2O_4$: C, 67.89; H, 10.44. Found: C, 67.92; H, 10.36.

*5.5.6. Synthesis of 3,3′-[(*S*)-2-butyl-1,4-dioxo-1,4-butanediyl]bis[2,2-dimethyl-(*S*)-4-(1,1-dimethylethyl)]oxazolidine* ***6cw***

Compound **1c** (180 mg, 0.45 mmol, 0.015 M), biphenyl (465 mg, 3 mmol, 0.1 M), Bu_4Sn (200 μl, 0.6 mmol, 0.02 M) and DCN (26 mg, 0.15 mmol, 5×10^{-3} M) were dissolved in 30 ml of MeCN and irradiated overnight at 320 nm. The crude photolisate was filtered and then chromatographed (cyclohexane:ethyl acetate, 9:1) and 204 mg of **6cw** (79% yield) was recovered as an oil.

Compound **6cw**: ^{1}H ($CDCl_3$) (mixture of rotamers) δ 0.85 (m, 3H, CH_3), 0.85–1.1 (m, 18H, *t*-Bu), 1.15–1.4 (m, 4H, CH_2), 1.4–1.85 (m, 12H, CH_3), 1.5–1.6 (m, 2H, CH_2), 2.3–3.5 (m, 3H, ABX system), 3.75–4.4 (m, 6H); ^{13}C ($CDCl_3$) (mixture of rotamers) δ 13.8–14.0 (CH_3), 22.5–2.9 (CH_2), 26.0–26.7 (*t*-Bu), 27.3–28.5 (CH_3), 29.0–29.9 (CH_2), 31.8–39.6 ($2CH_2$), 41.5–43.9 (CH), 59.3–60.0 (CH), 61.3–64.8 (CH_2), 64.1–65.9 (CH), 93.9–96.2, 171.2–177.6 (CO). IR (neat) ν/cm^{-1} 2977, 1642, 1416, 1061, 831. Anal. calcd for $C_{26}H_{48}N_2O_4$: C, 68.99; H, 10.69. Found: C, 69.11; H, 10.55.

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