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One-Pot Conversions of Olefins to Cyclic Carbonates and Secondary Allylic and Homoallylic Amines to Cyclic Carbamates

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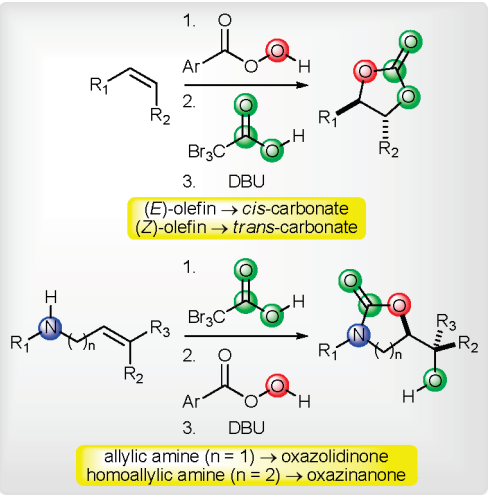

Sequential treatment of a 1,2-disubstituted olefin with *m*-CPBA, Br_3CCO_2H, and DBU results in the one-pot, stereospecific conversion of the olefin to the corresponding disubstituted cyclic carbonate (1,3-dioxolan-2-one). The reaction proceeds via an initial epoxidation followed by S_N2-type epoxide ring opening by Br_3CCO_2H and subsequent base-promoted carbonate formation upon elimination of bromoform. When a solution of a secondary allylic or homoallylic amine and Br_3CCO_2H is sequentially treated with *m*-CPBA then DBU, the product of the reaction is a cyclic carbamate (1,3-oxazolidin-2-one or 1,3-oxazinan-2-one).

Introduction

Cyclic carbonates are useful intermediates within organic synthesis[1] and are often employed as protecting groups for 1,2-diols.[2] Interest in their synthesis has increased recently as they have been employed as polar aprotic solvents for a variety of reactions and as electrolytes for lithium ion batteries.[3] Methods for their preparation often rely on the treatment of a 1,2-diol with phosgene (or an equivalent),[2] although more recently the metal-catalyzed insertion of CO_2 gas into an epoxide ring has been developed into an efficient synthetic route.[4]

As part of an ongoing research program directed toward the chemo- and diastereoselective functionalization of allylic and homoallylic amines at the olefin,[5] we have previously developed an ammonium-directed olefinic oxidation of allylic

(1) Clements, J. H. *Ind. Eng. Chem. Res.* **2003**, *42*, 663.
(2) Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951.
(3) Schäffner, B.; Schäffner, F.; Verevkin, S. P.; Börner, A. *Chem. Rev.* **2010**, *110*, 4554.
(4) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618. Zhou, C.-H.; Beltramini, J. N.; Fana, Y. X.; Lu, G. Q. *Chem. Soc. Rev.* **2008**, *37*, 527.
(5) For examples of chemo- and diastereoselective cyclopropanations of allylic amines from this laboratory, see: (a) Davies, S. G.; Ling, K. B.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Chem. Commun.* **2007**, 4029. (b) Csatayová, K.; Davies, S. G.; Lee, J. A.; Ling, K. B.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Tetrahedron* **2010**, *66*, 8420.

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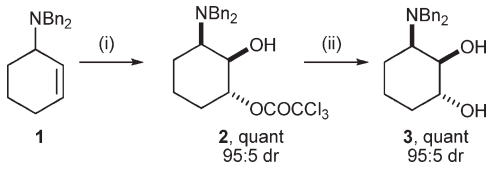
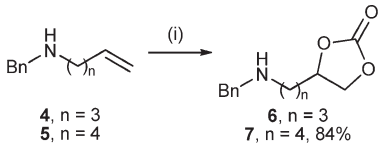
SCHEME 1[a]



[a]Reagents and conditions: (i) Cl_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 21 h, then $NaHCO_3$ (0.1 M, aq); (ii) K_2CO_3, MeOH, rt, 16 h.

SCHEME 2[a]



[a]Reagents and conditions: (i) Cl_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 21 h, then $NaHCO_3$ (0.1 M, aq).

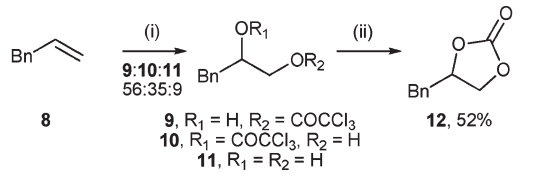
and homoallylic amines[6] to facilitate the synthesis of amino diol units.[7] For instance, treatment of 3-*N*,*N*-dibenzylaminocyclohex-1-ene **1** with Cl_3CCO_2H followed by *m*-CPBA and basic aqueous workup using $NaHCO_3$ gave trichloroacetate ester **2** in 95:5 dr and quantitative yield. Transesterification of **2** upon treatment with K_2CO_3 in MeOH gives amino diol **3** in 95:5 dr and quantitative yield[7a] (Scheme 1).

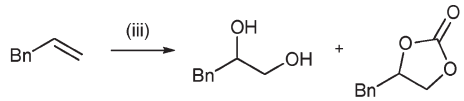
Upon application of this protocol to bis- and trishomoallylic amines **4** and **5** we noted that cyclic carbonates **6** and **7** were produced as the major products, rather than the expected trichloroacetate esters (Scheme 2).[8] We were surprised to note that this result represents only the second reported example of the formation of a 1,3-dioxolan-2-one upon treatment of an α-trichloroacetoxy alcohol with base[9] (in contrast, treatment of an α-trichloroacetamido alcohol with base to form a 1,3-oxazolidin-2-one has been well documented).[10] In this light, we proposed that the transformation could be developed into a one-pot protocol for the conversion of an olefin to a cyclic carbonate and delineate herein the results of our studies in this area.

Results and Discussion

One-Pot Conversion of Olefins to Cyclic Carbonates. The application of our oxidation protocol to allylbenzene **8** (as a model substrate) was examined. Under our literature conditions[7a]

SCHEME 3[a]





run	acid	base	ratio 11:12	yield 12 %
1	F_3CCO_2H	Et_3N	100 : 0	0
2	Cl_3CCO_2H	Et_3N	20 : 80	55
3	Br_3CCO_2H	Et_3N	0 : 100	80
4	Cl_3CCO_2H	DBU	5 : 95	83
5	Br_3CCO_2H	DBU	0 : 100	84

[a]Reagents and conditions: (i) Cl_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 21 h, then $NaHCO_3$ (0.1 M, aq); (ii) Et_3N, CH_2Cl_2, rt, 2 h; (iii) acid, *m*-CPBA, CH_2Cl_2, rt, 18 h, then base, 0 °C to rt, 2 h (see table).

(i.e., those employed for **1**, **4**, and **5**), oxidation of **8** resulted in a 56:35:9 mixture of the regioisomeric trichloroacetate esters **9** and **10** and diol **11**, with no trace of the corresponding cyclic carbonate **12**. The absence of any cyclization suggested that the presence of the amine function within **4** and **5** may have been important in promoting carbonate formation. Indeed, when the mixture of trichloroacetate esters **9** and **10** (and diol **11**) was treated with Et_3N in CH_2Cl_2, conversion of both **9** and **10** to carbonate **12** occurred, and **12** was isolated in 52% yield after purification. This transformation was next developed into a one-pot procedure for the formation of carbonate **12** from olefin **8**: the optimal protocol involved the treatment of allylbenzene **8** with *m*-CPBA followed by Br_3CCO_2H, followed finally by the introduction of excess DBU to the reaction flask (as both a base and sacrificial reducing agent to scavenge any remaining peracid).[11] These conditions proved more efficacious in promoting carbonate formation than when employing either F_3CCO_2H or Cl_3CCO_2H as the acid and/or than when employing Et_3N as both the reducing agent and base. No trihaloacetate ester products were observed in any of these optimization studies, presumably due to in situ hydrolysis upon aqueous workup (Scheme 3).

The mechanism and course of the reaction was followed by ^1H NMR spectroscopic analysis. Addition of *m*-CPBA to allylbenzene **8** in $CDCl_3$ promoted complete conversion of starting material to epoxide **13** after 3 h. Subsequent addition of Br_3CCO_2H produced a 65:35 mixture of tribromoacetate esters **14** and **15** in quantitative conversion. When the oxidation reaction was repeated using *m*-CPBA in the presence of Br_3CCO_2H, however, a reaction time of 7 h was required before complete consumption of starting material (to give a 65:35 mixture of tribromoacetate esters **14** and **15**), indicating that the epoxidation reaction occurs faster in the absence of Br_3CCO_2H, presumably due to competitive

(6) We also developed a protocol for the diastereoselective oxidation of the corresponding tertiary amine *N*-oxides; see: Aciro, C.; Davies, S. G.; Kurosawa, W.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Org. Lett.* **2009**, *11*, 1333.

(7) (a) Aciro, C.; Claridge, T. D. W.; Davies, S. G.; Roberts, P. M.; Russell, A. J.; Thomson, J. E. *Org. Biomol. Chem.* **2008**, *6*, 3751. (b) Aciro, C.; Davies, S. G.; Roberts, P. M.; Russell, A. J.; Smith, A. D.; Thomson, J. E. *Org. Biomol. Chem.* **2008**, *6*, 3762. (c) Bond, C. W.; Cresswell, A. J.; Davies, S. G.; Kurosawa, W.; Lee, J. A.; Fletcher, A. M.; Roberts, P. M.; Russell, A. J.; Smith, A. D.; Thomson, J. E. *J. Org. Chem.* **2009**, *74*, 6735. (d) Bagal, S. K.; Davies, S. G.; Lee, J. A.; Roberts, P. M.; Russell, A. J.; Scott, P. M.; Thomson, J. E. *Org. Lett.* **2010**, *12*, 136.

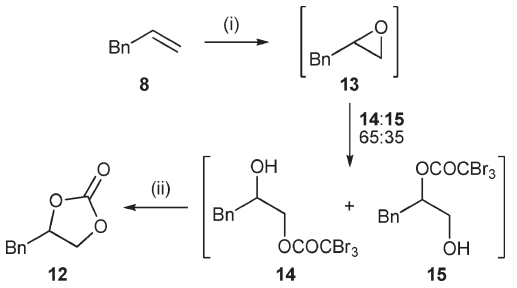
(8) Although carbonate **7** could be isolated in pure form (84% yield), an analytical sample of **6** could not be obtained even after exhaustive flash column chromatography due to the presence of residual unidentified impurities (~10%).

(9) Bailey, S.; Helliwell, M.; Teerawutgulrag, A.; Thomas, E. J. *Org. Biomol. Chem.* **2005**, *3*, 3654.

(10) For instance, see: Oishi, T.; Ando, K.; Inomiya, K.; Sato, H.; Iida, M.; Chida, N. *Org. Lett.* **2002**, *4*, 151. Sakaguchi, H.; Tokuyama, H.; Fukuyama, T. *Org. Lett.* **2007**, *9*, 1635. Shih, T.-L.; Li, H.-Y.; Ke, M.-S.; Kuo, W.-S. *Synth. Commun.* **2008**, *38*, 4139.

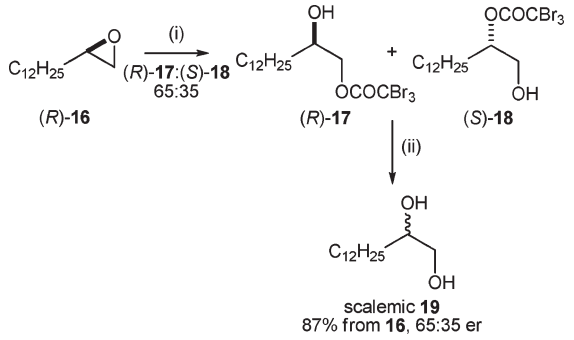
(11) Wefelscheid, U. K.; Woodward, S. *J. Org. Chem.* **2009**, *74*, 2254.

SCHEME 4[a]



[a]Reagents and conditions: (i) Br_3CCO_2H, *m*-CPBA, $CDCl_3$, rt, 3 or 7 h; (ii) DBU, 0 °C to rt, 2 h.

SCHEME 5[a]



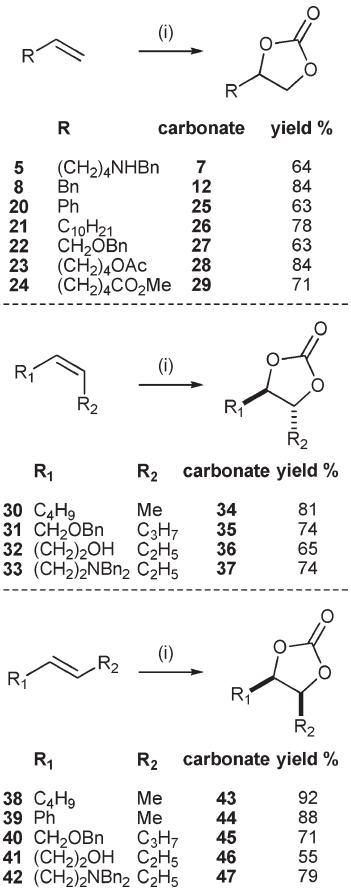
[a]Reagents and conditions: (i) Br_3CCO_2H, $CDCl_3$, rt, 12 h; (ii) K_2CO_3, MeOH rt, 2 h.

hydrogen bonding of the carboxylic acid to the peracid disrupting the intramolecularly hydrogen-bonded, reactive conformer of the latter.[12] Subsequent addition of DBU promoted complete conversion to carbonate **12**, establishing that carbonate formation occurs only upon basic workup. The observation that a 65:35 mixture of tribromoacetate esters **14** and **15** is formed in both of these reactions suggests that either the intermediate epoxide **13** does not undergo regioselective ring opening or regioselective ring opening occurs followed by an equilibration process (Scheme 4). To determine which of these mechanistic scenarios was in operation, enantiopure tetradec-1-ene oxide (*R*)-**16** (commercially available) was treated with Br_3CCO_2H in $CDCl_3$, which resulted in a 65:35 mixture of tribromoacetate esters **17** and **18**, respectively. Transesterification of this mixture upon treatment with K_2CO_3 in MeOH gave the common diol **19** in 65:35 er,[13] demonstrating that the ring opening of epoxide **16** occurs in a nonregioselective manner and hence results in erosion of the stereochemical integrity of the final product **19** (Scheme 5); the observation of a 65:35 mixture of tribromoacetate esters **14** and **15** from the epoxidation and ring opening of allylbenzene **8** is therefore most likely also due to nonregioselective ring opening of the intermediate epoxide **13** rather than an equilibration process.

(12) Poluektov, P. T.; Gonsovskaya, T. B.; Ponomarev, F. G.; Gusev, Y. K. *Polym. Sci. USSR* **1973**, *15*, 686. Bach, R. D.; Dmitrenko, O.; Adam, W.; Schambony, S. *J. Am. Chem. Soc.* **2003**, *125*, 924.

(13) The enantiomeric excess of diol **19** was determined by Chiral HPLC analysis of the corresponding mono-*p*-nitrobenzoate derivative. For full details see the Supporting Information.

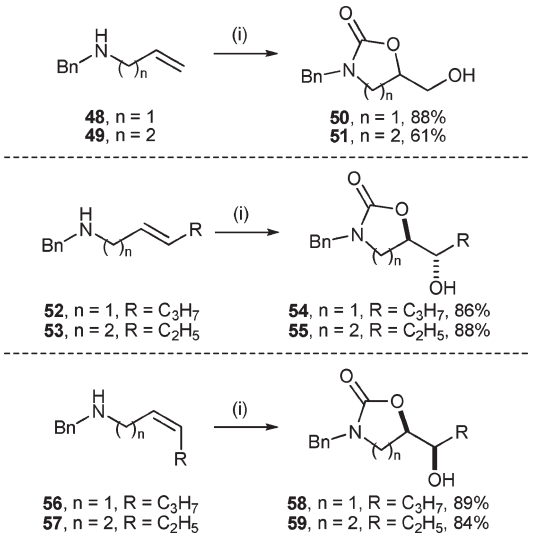
SCHEME 6[a]



[a]Reagents and conditions: (i) Br_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 18 h, then DBU, 0 °C to rt, 2 h.

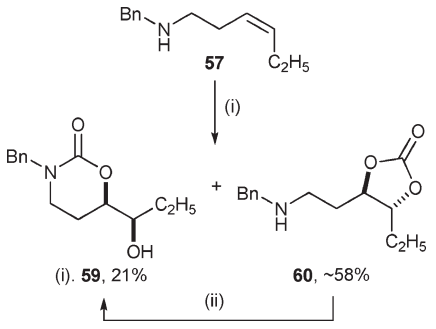
The optimized reaction conditions were applied to a range of mono- and disubstituted olefins bearing a variety of functional groups. In these reactions, *m*-CPBA was added to a solution of the olefin in CH_2Cl_2 followed by the addition of Br_3CCO_2H, except in the cases of unsaturated amines **5**, **33**, and **42**, in which Br_3CCO_2H *must be added first* to prevent competing N-oxidation.[7a] In each case, conversion to the corresponding carbonate was observed. Carbonate formation from (*Z*)-olefins **30**−**33** resulted in the corresponding *trans*-configured carbonates **34**−**37**, while (*E*)-olefins **38**−**42** gave the corresponding *cis*-configured carbonates **43**−**47**, as single diastereoisomers. These stereochemical assignments could be made confidently on the basis of ^{1}H NMR NOE analyses of **34**−**37** and **43**−**47**: *cis*-configured carbonates (1,3-dioxolan-2-ones) **43**−**47** gave strong reciprocal enhancements between C(4)*H* and C(5)*H* and between the C(4)- and C(5)-substituents (generally two methylene groups), while in the *trans*-configured compounds **34**−**37** strong reciprocal enhancements were noted between C(4)*H* and the C(5)-substituent and between the C(4)-substituent and C(5)*H*. The results from these experiments establish that carbonate formation is a stereospecific (rather than stereoselective) process, as would be expected for a mechanism of formation involving epoxidation of the olefin, S_N2-type epoxide ring opening, and cyclization upon basification via attack of the free hydroxyl group on the tribromoacetate ester followed by loss of bromoform (Scheme 6).

SCHEME 7[a]



[a]Reagents and conditions: (i) Br_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 18 h, then DBU, 0 °C to rt, 2 h.

SCHEME 8[a]



[a]Reagents and conditions: (i) Cl_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 21 h, then $NaHCO_3$ (0.1 M, aq); (ii) stand in $CDCl_3$.

One-Pot Conversion of Secondary Allylic and Homoallylic Amines to Oxazolidinones and Oxazinanones. When this procedure was applied to secondary allylic and homoallylic amines **48** and **49**, the corresponding carbamates (oxazolidinone **50** and oxazinanone **51**, respectively) were produced as the major products. Similarly, oxidation of secondary allylic amines **52** and **56** gave the diastereoisomeric oxazolidinones **54** and **58**, while oxidation of secondary homoallylic amines **53** and **57** gave the diastereoisomeric oxazinanones **55** and **59** in good isolated yield and as single diastereoisomers in each case (Scheme 7). The relative configurations within **58** and **59** were unambiguously established by single-crystal X-ray analyses.[14] Therefore, given the diastereoisomeric nature of **54** and **58**, and of **55** and **59**, the relative configurations within **54** and **55** could confidently be assigned and are consistent with the reaction proceeding via an *anti*-dihydroxylation event with respect to the double bond in each case.

The formation of carbamate products in these reactions is in contrast to our initial observations concerning the oxidation of secondary bis- and trishomoallylic amines **4** and **5** which gave carbonates **6** and **7**, respectively, as the major products. To investigate these observations further, secondary homoallylic amine **57** was sequentially treated with Cl_3CCO_2H and *m*-CPBA followed by workup with aqueous $NaHCO_3$ (i.e., under the conditions initially employed for oxidation of **4** and **5**). This resulted in a mixture of products which included carbamate **59** and carbonate **60** and as the major components in an approximate 12:88 ratio, respectively.[15] Purification via flash column chromatography gave carbamate **59** in 21% isolated yield and an impure sample of carbonate **60** in ~58% yield (the major impurity in this sample was carbamate **59**). The isolated yield of carbamate **59** (21%) was significantly higher than the proportion indicated by analysis of the crude reaction mixture, suggesting that carbonate **60** may undergo rearrangement to carbamate **59** during chromatography.[16] Consistent with this hypothesis, a sample of **60** in $CDCl_3$ was observed by ^1H NMR spectroscopic analysis to rearrange to **59** over time; the rate of the rearrangement process increased markedly in the presence of triethylamine (Scheme 8).

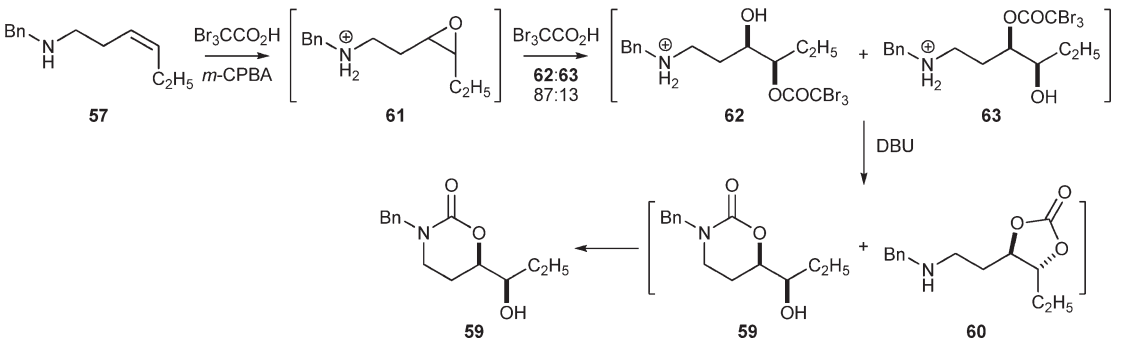
These results offer some insight into the mechanism of formation of carbamate **59** upon sequential treatment with Br_3CCO_2H, *m*-CPBA, and DBU, which was further investigated by monitoring the reaction by ^1H NMR spectroscopy. Thus, a solution of homoallylic amine **57** and Br_3CCO_2H in $CDCl_3$ was treated with *m*-CPBA, which resulted in the formation of an 87:13 mixture of tribromoacetate esters **62** and **63**, respectively, with complete consumption of starting material noted within 3 h. The appearance and disappearance of an intermediate species was also observed; this intermediate was tentatively assigned as being epoxide **61**. Addition of DBU to the reaction mixture resulted in the immediate (< 5 min) formation of a mixture of carbonate **60** (ca. 10%) and carbamate **59** (ca. 90%); within a further 2 h, the major species present was carbamate **59** (> 95%). A general reaction pathway may therefore be proposed. Initial epoxidation of homoallylic amine **57** gives epoxide **61**. Ring opening via an S_N2-type process gives rise to a mixture of regioisomeric tribromoacetate esters **62** and **63**. Addition of DBU to the reaction mixture results in deprotonation of ammoniums **62** and **63** to reveal the nucleophilic nitrogen atom within. Attack of the free amino group at the carbonyl within the conjugate base of **63** leads directly to the corresponding six-ring carbamate **59**, although attack of the hydroxyl group onto the carbonyl group results in formation of the five-membered carbonate **60**. Direct formation of carbamate **59** from the conjugate base of **62** (the major product of the oxidation reaction) is not possible and therefore presumably proceeds via the initial formation of carbonate **60**. Subsequent rearrangement of carbonate **60** to carbamate **59** is driven by formation of the more thermodynamically favorable product (Scheme 9). Rearrangement of carbonates **6** and **7**, derived from bis- and trishomoallylic amines **4** and **5** in this manner, is presumably disfavored (e.g., through kinetic

(14) Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 784948 (**58**) and CCDC 784949 (**59**).

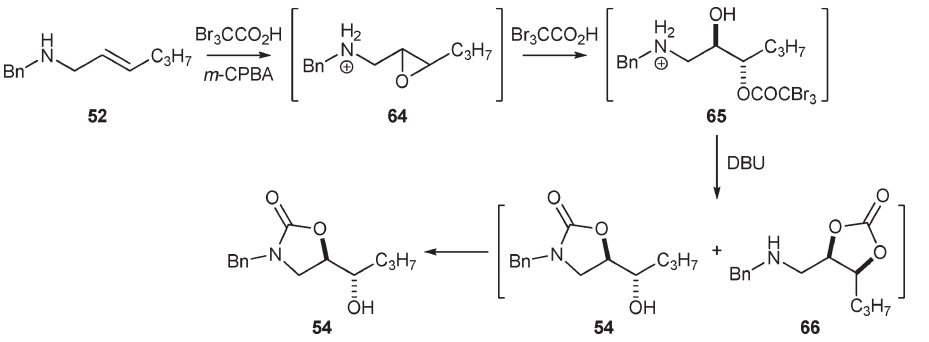
(15) The ratio of carbamate **59** to carbonate **60** was found to vary upon several runs of this reaction, and a sample of carbonate **60** was not always isolated upon purification: conversion to carbamate **59** during purification was assumed to be complete in these cases.

(16) *O*- to *N*-acyl migration has been previously reported. For instance, see: Yakura, T.; Yoshimoto, Y.; Ishida, C.; Mabuchi, S. *Tetrahedron* **2007**, *63*, 4429. Yu, D.-S.; Xu, W.-X.; Liu, L.-X.; Huang, P.-Q. *Synlett* **2008**, 1189. Gonzalez-Gomez, J. C.; Foubelo, F.; Yus, M. *J. Org. Chem.* **2009**, *74*, 2547.

SCHEME 9



SCHEME 10

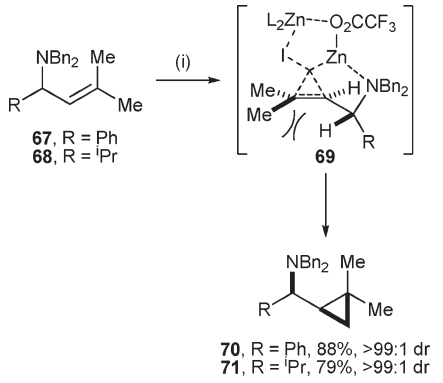


retardation) due to the requirement to form a seven- or eight-membered ring, respectively, thus accounting for the differences in reactivity in the oxidation reactions of unsaturated amines **4**, **5**, and **57** carried out with *m*-CPBA in the presence of Cl_3CCO_2H followed by workup with aqueous $NaHCO_3$.

Analogous observations were made when the reaction of allylic amine **52** was monitored by ^1H NMR spectroscopy. Addition of *m*-CPBA to a solution of **52** and Br_3CCO_2H in $CDCl_3$ resulted in the formation of epoxide **64** and tribromoacetate ester **65** as a single regioisomer;[7] within 2 h complete consumption of starting material was noted, and within a further 4 h ring opening of the intermediate epoxide **64** to give tribromoacetate ester **65** had also reached completion. The observation of a single regioisomeric tribromoacetate ester **65** in this reaction is consistent with ring opening of the intermediate epoxide **64** occurring at the carbon atom distal to the protonated *N*-benzyl amino moiety,[7] where its destabilizing inductive electron-withdrawing influence on the late transition state is less pronounced.[17] Addition of DBU to the reaction mixture gave a mixture of products, although after 2 h the only species present was carbamate **54**, consistent with the conversion of tribromoacetate ester **65** to carbamate **54** occurring via initial formation of carbonate **66** (Scheme 10).

Diastereoselective Synthesis of Carbonates from Chiral Allylic Amines. We have recently shown that the substrate-directed cyclopropanation of tertiary allylic amines **67** and **68** (having a stereogenic center at the allylic position) proceeds with very high levels of diastereoselectivity to give the corresponding *syn*-cyclopropanes **70** and **71**, consistent with the directed reaction proceeding via transition state model **69**

SCHEME 11[a]



[a]Reagents and conditions: (i) Et_2Zn, CH_2I_2, F_3CCO_2H, CH_2Cl_2, rt, 1 h.

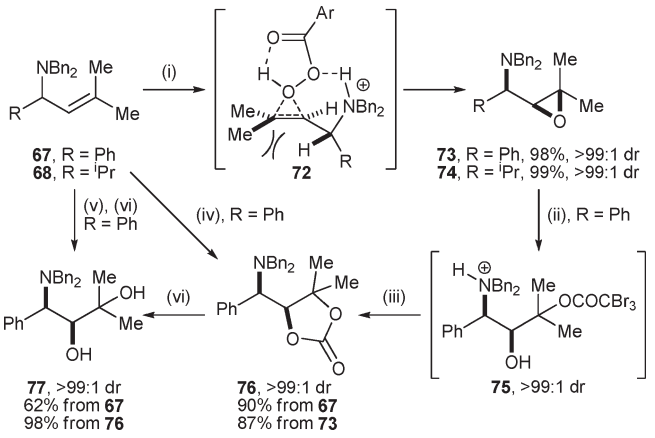
in which 1,3-allylic strain is minimized (Scheme 11).[5b] Given the excellent levels of substrate control elicited in these systems, it was envisaged that application of our oxidation methodology to chiral allylic amines such as **67** and **68** would result in a diastereoselective version of this protocol that would be applicable to the preparation of enantiopure carbonates:[18] the protonated amino group has the capacity to effect hydrogen-bonded delivery of the oxidant and promote ring opening of the so-formed epoxide distal to itself.[7]

Oxidation of **67** and **68** with *m*-CPBA in the presence of Cl_3CCO_2H at room temperature gave complete conversion to the corresponding epoxides **73** and **74** in > 99:1 dr in both cases. The relative configuration within **74** was established

(17) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737. Addy, J. K.; Parker, R. E. *J. Chem. Soc.* **1963**, 915.

(18) The preparation of enantiopure tertiary allylic amines (with structures similar to **67** and **68**) from α-amino acids has been demonstrated; see: Barluenga, J.; Barangaña, B.; Concellón, J. M. *J. Org. Chem.* **1995**, *60*, 6696.

SCHEME 12[a]



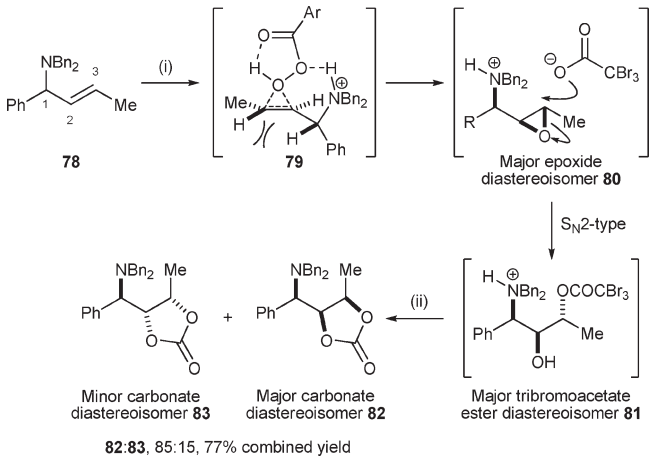
[a]Reagents and conditions: (i) Cl_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 1 h (R = Ph) or 21 h (R = ^{i}Pr); (ii) Br_3CCO_2H, $CDCl_3$, rt, 12 h; (iii) DBU, $CDCl_3$, 0 °C to rt, 1 h; (iv) Br_3CCO_2H, *m*-CPBA CH_2Cl_2, rt, 18 h, then DBU, 0 °C to rt, 2 h; (v) Cl_3CCO_2H, *m*-CPBA, CH_2Cl_2, 40 °C, 21 h; (vi) K_2CO_3, MeOH, 60 °C 16 h.

unambiguously by single-crystal X-ray analysis,[19] and the relative configuration within **73** was assigned by analogy. The stereochemical outcomes of these oxidation reactions are therefore consistent with an ammonium-directed process proceeding via transition state model **72** in which 1,3-allylic strain is minimized. Treatment of a sample of epoxide **73** in $CDCl_3$ with Br_3CCO_2H revealed quantitative conversion to tribromoacetate ester **75** as a single regio- and diastereoisomer within 12 h. The connectivity within **75** was established by ^{1}H NMR COSY and HMBC analyses. Subsequent treatment of **75** with DBU gave quantitative conversion to carbonate **76** within 1 h. Interestingly, under analogous conditions, epoxide **74** showed a distinct recalcitrance to undergo ring opening upon treatment with Br_3CCO_2H, and the use of more forcing conditions resulted only in starting material degradation. In light of these results, application of our previously optimized one-pot protocol for the formation of carbonates from allylic amines was investigated for **67**, although this was found to give a 2:1 mixture of epoxide **73** (>99:1 dr) and carbonate **76** (>99:1 dr); when the reaction was repeated using 10 equiv of Br_3CCO_2H to promote the ring-opening reaction, complete conversion to carbonate **76** (>99:1 dr) was observed, and **76** was isolated in 90% yield as a single diastereoisomer whose relative configuration was unambiguously assigned by single-crystal X-ray analysis;[20] this analysis also affirmed the regioselectivity of the epoxide ring-opening reaction [i.e., that formation of tribromoacetate ester **75** from epoxide **73** occurs by preferential epoxide ring opening distal to the ammonium moiety (as predicted) rather than via a process involving ring opening proximal to the ammonium moiety followed by migration of the tribromoacetate group]. Treatment of carbonate **76** with K_2CO_3 in MeOH gave diol **77** whose relative configuration was

(19) Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784950.

(20) Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784951.

SCHEME 13[a]



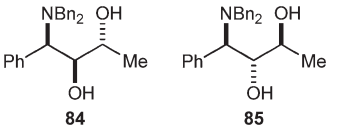
[a]Reagents and conditions: (i) Br_3CCO_2H, *m*-CPBA, CH_2Cl_2, rt, 3 days, then DBU, 0 °C to rt, 2 h.

unambiguously established by single-crystal X-ray analysis;[21] diol **77** was also prepared directly from allylic amine **67** upon treatment with *m*-CPBA in the presence of Cl_3CCO_2H at 40 °C followed by transesterification (K_2CO_3/MeOH), consistent with a mechanism involving completely diastereoselective epoxidation followed by completely regioselective ring opening (Scheme 12).

It is noteworthy that even in the absence of significant 1,3-allylic strain it is possible to obtain modest levels of diastereoselectivity within systems similar in structure to tertiary allylic amines **67** and **68**. For example, under optimized conditions, sequential treatment of tertiary allylic amine **78** with Br_3CCO_2H and *m*-CPBA at rt for 3 days followed by DBU gave a chromatographically inseparable 85:15 mixture of carbonates **82** and **83**,[22] which were isolated in 77% combined yield. The relative configuration within the major diastereoisomeric carbonate **82** was assigned upon the assumption that the reaction proceeds by an analogous mechanism to that delineated for **67**, via epoxidation transition state model **79** that places the allylic C−H bond (i.e., C(1)*H*) of **78** coplanar with the olefinic C−H bond (i.e., C(3)*H*) to minimize allylic 1,3-strain (i.e., directly analogous to transition state model **72**) to give the major epoxide diastereoisomer **80**. Ring opening of the epoxide via an S_N2-type process at the carbon atom distal to the ammonium moiety

(21) Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784952.

(22) The crude reaction mixture also contained an 85:15 mixture of diols **84** and **85** (the ratio of carbonates **82** and **83** to diols **84** and **85** was 88:12); chromatography allowed isolation of the major diastereoisomeric diol **84** in 7% yield and >99:1 dr, in addition to the 85:15 mixture of carbonates **82** and **83**. The production of diols **84** and **85** in this reaction is presumably a result of competitive hydrolysis of the corresponding carbonates **82** and **83** or the intermediate tribromoacetate esters. Treatment of an 85:15 mixture of carbonates **82** and **83** with K_2CO_3 in MeOH gave an 85:15 mixture of diols **84** and **85**.



gives tribromoacetate ester **81**, which undergoes elimination of bromoform upon treatment with base to give carbonate **82** as the major product (Scheme 13).

Conclusion

In conclusion, sequential treatment of a 1,2-disubstituted olefin with *m*-CPBA, Br_3CCO_2H, and DBU results in the one-pot, stereospecific conversion of the olefin to the corresponding disubstituted cyclic carbonate (1,3-dioxolan-2-one). The reaction proceeds via an initial epoxidation followed by S_N2-type epoxide ring opening by Br_3CCO_2H and subsequent base-promoted carbonate formation upon elimination of bromoform. When a solution of a secondary allylic or homoallylic amine and Br_3CCO_2H is sequentially treated with *m*-CPBA then DBU, the product of the reaction is a cyclic carbamate (1,3-oxazolidin-2-one or 1,3-oxazinan-2-one).

Experimental Section

General Experimental Details. *m*-CPBA was supplied as a 70−77% slurry in water and titrated according to the procedure of Swern[23] immediately before use. Water was purified by an Elix UV-10 system. Organic solvents were used as supplied (analytical or HPLC grade) without prior purification. Organic layers were dried over $MgSO_4$. Thin layer chromatography was performed on aluminum plates coated with 60 F_{254} silica. Plates were visualized using UV light (254 nm), iodine, 1% aqueous $KMnO_4$, or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed either on Kieselgel 60 silica on a glass column or on an automated flash column chromatography platform.

Melting points are uncorrected. IR spectra were recorded as either a thin film on NaCl plates (film) or a KBr disk (KBr), as stated. Selected characteristic peaks are reported in cm^{-1}. NMR spectra were recorded in the deuterated solvent stated. The field was locked by external referencing to the relevant deuteron resonance. $^1H-^1H$ COSY and $^1H-^{13}C$ HMQC analyses were used to establish atom connectivity.

General Procedure 1 for Oxidation of Olefins. *m*-CPBA was added to a stirred solution of olefin in CH_2Cl_2, and the resultant mixture was stirred at rt for 10 min. Br_3CCO_2H was added in one portion, and the reaction mixture was stirred at rt for 18 h. DBU was added at 0 °C, and the resultant mixture was stirred at rt for 2 h. Satd aq $NaHCO_3$ and CH_2Cl_2 were added, and the layers were separated. The organic layer was washed with satd aq $NaHCO_3$ and brine and then dried, filtered, and concentrated in vacuo.

General Procedure 2 for Oxidation of Unsaturated Amines. Br_3CCO_2H was added to a stirred solution of olefin in CH_2Cl_2, and the resultant mixture was stirred at rt for 10 min. *m*-CPBA was added in one portion, and the reaction mixture was stirred at rt for 18 h. DBU was added at 0 °C, and the resultant mixture was stirred at rt for 2 h. Satd aq $NaHCO_3$ and CH_2Cl_2 were added, and the layers were separated. The organic layer was washed with satd aq $NaHCO_3$ and brine and then dried, filtered, and concentrated in vacuo.

(*RS*)-4-(4′-*N*-Benzylaminobutyl)-1,3-dioxolan-2-one 7. Method A. Cl_3CCO_2H (2.13 g, 13.2 mmol) was added to **5** (500 mg, 2.64 mmol) in CH_2Cl_2 (5 mL) at rt, and the solution was stirred for 30 min. *m*-CPBA (985 mg, 75%, 4.22 mmol) was added, and the resultant solution was stirred at rt for 21 h. The mixture was then diluted with CH_2Cl_2 (100 mL) and washed with satd aq Na_2SO_3 (100 mL portions) until starch-iodide paper indicated that no *m*-CPBA was present. The organic layer was then washed with 0.1 M aq $NaHCO_3$ (4 × 100 mL), dried, and concentrated in vacuo. Purification via flash column chromatography (eluent EtOAc) gave **7** as a colorless oil (553 mg, 84%): ν_{max} (film) 2937 (C−H), 1796 (C═O); δ_H (400 MHz, $CDCl_3$) 1.36−1.45 (1H, m, C(2′)H_A), 1.46−1.54 (1H, m, C(2′)H_B), 1.54−1.61 (2H, m, C(3′)H_2), 1.63−1.70 (1H, m, C(1′)H_A), 1.71−1.82 (1H, m, C(1′)H_B), 2.65 (2H, t, *J* 7.2, C(4′)H_2), 3.79 (2H, s, NCH_2Ph), 4.03 (1H, dd, *J* 8.3, 7.2, C(5)H_A), 4.49 (1H, app t, *J* 8.3, C(5)H_B), 4.63−4.71 (1H, m, C(4)*H*), 7.23−7.35 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 22.2 (*C*(2′)), 29.0 (*C*(3′)), 33.7 (*C*(1′)), 48.5 (*C*(4′)), 53.5 (N*C*H_2Ph), 69.3 (*C*(5)), 77.0 (*C*(4)), 127.3, 128.3, 128.5 (*o*,*m*,*p*-*Ph*), 139.1 (*i*-*Ph*), 155.0 (*C*(2)); *m*/*z* (ESI^+) 250 ($[M + H]^+$, 100%); HRMS (ESI^+) $C_{14}H_{20}NO_3^+$ requires 250.1438; found 250.1439.

Method B. Following general procedure 2, **5** (189 mg, 1.00 mmol) in CH_2Cl_2 (6.7 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol) followed by DBU (2.0 mL). Purification via flash column chromatography (eluent EtOAc) gave **7** as a colorless oil (159 mg, 64%).

(*RS*)-4-Benzyl-1,3-dioxolan-2-one 12. Following general procedure 1, **8** (80.2 mg, 0.678 mmol) in CH_2Cl_2 (4.5 mL) was treated with Br_3CCO_2H (1.00 g, 3.39 mmol) and *m*-CPBA (233 mg, 75%, 1.01 mmol) followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 4:1) gave **12** as a colorless oil (101 mg, 84%):[24] δ_H (400 MHz, $CDCl_3$) 2.99 (1H, dd, *J* 14.0, 6.5, CH_ACH_BPh), 3.15 (1H, dd, *J* 14.0, 6.1, CH_ACH_BPh), 4.17 (1H, dd, *J* 8.5, 6.8, C(5)H_A), 4.44 (1H, dd, *J* 8.5, 7.9, C(5)H_B), 4.90−4.97 (1H, m, C(4)*H*), 7.21−7.38 (5H, m, *Ph*).

Tetradecane-1,2-diol 19. Br_3CCO_2H (147 mg, 0.50 mmol) was added to a solution of (*R*)-1,2-epoxytetradecane **16** (21 mg, 0.10 mmol) in $CDCl_3$ (0.6 mL). The reaction was monitored by ^1H NMR analysis for 12 h. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and washed with satd aq Na_2SO_3 (10 mL), followed by satd aq NH_4Cl (10 mL). The organic layer was dried and concentrated in vacuo. The residue was dissolved in MeOH (2.0 mL). K_2CO_3 (138 mg, 1.0 mmol) was added, and the mixture was stirred at rt for 16 h and then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (10 mL) and washed with satd aq $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried and concentrated in vacuo to give **19** as white solid (20.0 mg, 87%, 65:35 er):[25] mp 60−62 °C {lit.[25] mp 62−64 °C}; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.0, CH_3), 1.19−1.45 (22H, m, CH_2), 3.25−3.35 (1H, m, C(1)H_A), 3.65−3.78 (2H, m, C(1)H_B, C(2)*H*).

The enantiomeric excess of **19** was determined by Chiral HPLC of the corresponding mono-*p*-nitrobenzoate derivative, giving resolution of both enantiomers: OD-H Daicel chiral column, flow rate 1.5 mL/min (*iso*-propanol/hexane 3:97), (*S*)-enantiomer t_R = 17.1 min and (*R*)-enantiomer t_R = 22.7 min.

Data for 2-hydroxytetradecyl 4-nitrobenzoate: *p*-Nitrobenzoyl chloride (80 mg, 0.43 mmol) was added to a solution of diol **19** (20 mg, 0.09 mmol) in pyridine (1.0 mL) and CH_2Cl_2 (1.0 mL). The reaction mixture was stirred at rt for 8 h, diluted with CH_2Cl_2 (10 mL), and washed with satd aq $CuSO_4$ (10 mL) and brine (10 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc 8:1) gave 2-hydroxytetradecyl 4-nitrobenzoate as a white solid (17 mg, 53%): mp 63−65 °C; ν_{max} (KBr) 3475 (O−H), 2955 (C−H), 1697 (C═O), 1543; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.0, CH_3), 1.19−1.38 (20H, m, CH_2), 1.57−1.59 (2H, m, C(3)H_2), 4.01−4.02 (1H, m, C(2)*H*), 4.28 (1H, dd, *J* 11.5, 7.1, C(1)H_A), 4.43 (1H, dd, *J* 11.5, 3.0, C(1)H_B), 8.22 (2H, d, *J* 8.8, *Ar*), 8.30 (2H, d, *J* 8.8, *Ar*); δ_C (100 MHz, $CDCl_3$) 14.1 (*C*(14)), 22.6, 25.4, 29.1, 29.3, 29.5, 29.6, 29.7, 31.9, 33.5 (*C*(3)−*C*(13)), 69.9 (*C*(2)), 70.0 (*C*(1)), 123.6,

(23) Swern, D. *Org. React.* **1953**, *VII*, 392.

(24) Paddock, R. L.; Hiyama, Y.; McKay, J. M.; Nguyen, S. T. *Tetrahedron Lett.* **2004**, *45*, 2023.

(25) Kawashima, M.; Horikawa, Y. *Biotechnol. Lett.* **1993**, *15*, 1039.

130.8, 135.3 (*o,m,p-Ar*), 150.6 (*i-Ar*), 164.8 (*C*=O); *m*/*z* (ESI$^+$) 402 ([M + Na]$^+$, 90%); HRMS (ESI$^+$) $C_{21}H_{33}NNaO_5^+$ ([M + Na]$^+$) requires 402.2251; found 402.2252.

(***RS*)-4-Phenyl-1,3-dioxolan-2-one 25.** Following general qprocedure 1, **20** (105 mg, 1.00 mmol) in CH_2Cl_2 (6.7 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 4:1) gave **25** as a colorless oil (103 mg, 63%):[26] δ_H (400 MHz, $CDCl_3$) 4.36 (1H, app t, *J* 8.4, C(5)H_A), 4.81 (1H, app t, *J* 8.4, C(5)H_B), 5.69 (1H, app t, *J* 8.4, C(4)*H*), 7.21−7.38 (5H, m, *Ph*).

(***RS*)-4-Decyl-1,3-dioxolan-2-one 26.** Following general procedure 1, **21** (151 mg, 0.90 mmol) in CH_2Cl_2 (6 mL) was treated with Br_3CCO_2H (1.33 g, 4.50 mmol) and *m*CPBA (309 mg, 75%, 1.35 mmol), followed by DBU (1.5 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc 5:1) gave **26** as a colorless oil (160 mg, 78%): ν_{max} (film) 2925 (C−H), 1800 (C=O), 1065; δ_H (400 MHz, $CDCl_3$) 0.86 (3H, t, *J* 6.9, C(10′)H_3), 1.22−1.36 (15H, m, CH_2), 1.42−1.50 (1H, m, C(2′)-H_A), 1.67−1.69 (1H, m, C(1′)H_A), 1.77−1.89 (1H, m, C(1′)H_B), 4.07 (1H, t, *J* 8.5, C(5)H_A), 4.52 (1H, t, *J* 8.5, C(5)H_B), 4.67−4.72 (1H, m, C(4)*H*); δ_C (100 MHz, $CDCl_3$) 14.1 (*C*(10′)), 22.6, 24.3, 29.1, 29.2, 29.3, 29.4, 29.5, 31.8 (*C*(2′)−*C*(9′)), 33.9 (*C*(1′)), 69.4 (*C*(4)), 76.7 (*C*(5)), 155.6 (*C*(2)); *m*/*z* (ESI$^+$) 251 ([M + Na]$^+$, 100%); HRMS (ESI$^+$) $C_{13}H_{24}NaO_3^+$ ([M + Na]$^+$) requires 251.1618; found 251.1616.

(***RS*)-4-(Benzyloxymethyl)-1,3-dioxolan-2-one 27.** Following general procedure 1, **22** (107 mg, 0.72 mmol) in CH_2Cl_2 (4.8 mL) was treated with Br_3CCO_2H (1.06 g, 3.60 mmol) and *m*-CPBA (506 mg, 75%, 2.19 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 4:1) gave **27** as a colorless oil (94 mg, 63%):[27] δ_H (400 MHz, $CDCl_3$) 3.62 (1H, dd, *J* 11.0, 3.7, CH_AH$_B$OBn), 3.71 (1H, dd, *J* 11.0, 3.7, CH$_A$$H_B$OBn), 4.38 (1H, dd, *J* 8.6, 6.2, C(5)H_A), 4.48 (1H, app t, *J* 8.6, C(5)H_B), 4.58 (2H, AB system, *J* 12.2, OCH_2Ph), 4.79−4.84 (1H, m, C(4)*H*), 7.30−7.40 (5H, m, *Ph*).

(***RS*)-4-(4′-Acetoxybutyl)-1,3-dioxolan-2-one 28.** Following general procedure 1, **23** (70 mg, 0.50 mmol) in CH_2Cl_2 (3.3 mL) was treated with Br_3CCO_2H (740 mg, 2.5 mmol) and *m*-CPBA (172 mg, 75%, 0.75 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 1:1) gave **28** as an opaque oil (85 mg, 84%): ν_{max} (film) 2917 (C−H), 1793 (C=O, carbonate), 1731 (C=O, ester); δ_H (400 MHz, $CDCl_3$) 1.41−1.50 (1H, m, CH_2), 1.53−1.61 (1H, m, CH_2), 1.66−1.76 (4H, m, CH_2), 2.04 (3H, s, CO*Me*), 4.05−4.08 (3H, m, C(5)H_A, C(4′)H_2), 4.53 (1H, t, *J* 9.4, C(5)H_B), 4.47−4.74 (1H, m, C(4)*H*); δ_C (100 MHz, $CDCl_3$) 20.9 (*Me*), 21.1, 28.1, 33.5 (*C*(1′)−*C*(3′)), 63.7 (*C*(4′)), 69.3 (*C*(5)), 76.8 (*C*(4)), 154.9 (*C*(2)), 171.1 (*C*OMe); *m*/*z* (ESI$^+$) 225 ([M + Na]$^+$, 100%); HRMS (ESI$^+$) $C_9H_{14}NaO_5^+$ ([M + Na]$^+$) requires 225.0733; found 225.0732.

(*RS*)-Methyl 5-(1′,3′-dioxolan-2′-one-4′-yl)pentanoate 29. Following general procedure 1, **24** (142 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 2:1) gave **29** as a yellow oil (143 mg, 71%): ν_{max} (film) 2917 (C−H), 1793 (C=O, carbonate), 1731 (C=O, ester); δ_H (400 MHz, $CDCl_3$) 1.38−1.59 (2H, m, C(4)H_2), 1.64−1.86 (4H, m, C(3)H_2, C(5)H_2), 2.32 (2H, t, *J* 7.2, C(2)H_2), 3.65 (3H, s, O*Me*), 4.05 (1H, dd, *J* 10.8, 7.2, C(5′)H_A), 4.52 (1H, dd, *J* 10.8, 8.4, C(5′)H_B), 4.66−4.73 (1H, m, C(4′)*H*); δ_C (100 MHz, $CDCl_3$) 23.9, 24.3 (*C*(3), *C*(4), *C*(5)), 33.5 (*C*(2)), 51.6 (O*Me*), 69.3 (*C*(5′)), 76.7 (*C*(4′)), 155.0 (*C*(2′)), 173.6 (*C*(1)); *m*/*z* (ESI$^+$) 225 ([M + Na]$^+$, 100%); HRMS (ESI$^+$) $C_9H_{14}NaO_5^+$ ([M + Na]$^+$) requires 225.0733; found 225.0732.

(*RS*,*RS*)-4-Butyl-5-methyl-1,3-dioxolan-2-one 34. Following general procedure 1, **30** (72 mg, 0.72 mmol) in CH_2Cl_2 (4.8 mL) was treated with Br_3CCO_2H (1.06 g, 3.61 mmol) and *m*-CPBA (250 mg, 75%, 1.08 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 5:1) gave **34** as a colorless oil (93 mg, 81%, >99:1 dr): ν_{max} (film) 2959 (C−H), 1802 (C=O); δ_H (400 MHz, $CDCl_3$) 0.89 (3H, t, *J* 6.5, C(4′)H_3), 1.30−1.40 (4H, m, C(2′)H_2, C(3′)H_2), 1.42 (3H, d, *J* 6.1, C(5)*Me*), 1.59−1.77 (2H, m, C(1′)H_2), 4.16 (1H, dt, *J* 6.9, 5.1, C(4)*H*), 4.36 (1H, dq, *J* 6.9, 6.1, C(5)*H*); δ_C (100 MHz, $CDCl_3$) 13.7 (*C*(4′)), 19.0 (*C*(5)*Me*), 22.2 (*C*(2′)), 26.7 (*C*(3′)), 32.8 (*C*(1′)), 78.4 (*C*(5)), 83.5 (*C*(4)), 154.6 (*C*(2)); *m*/*z* (ESI$^+$) 181 ([M + Na]$^+$, 100%); HRMS (ESI$^+$) $C_8H_{14}NaO_3^+$ ([M + Na]$^+$) requires 181.0835; found 181.0836.

(*RS*,*RS*)-4-(Benzyloxymethyl)-5-propyl-1,3-dioxolan-2-one 35. Following general procedure 1, **31** (190 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.5 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 4:1) gave **35** as a colorless oil (185 mg, 74%, >99:1 dr): ν_{max} (film) 2962 (C−H), 1797 (C=O); δ_H (500 MHz, $CDCl_3$) 0.96 (3H, t, *J* 7.0, C(3″)H_3), 1.38−1.44 (1H, m, C(2″)H_A), 1.57−1.66 (2H, m, C(2″)H_B, C(1″)H_A), 1.79−1.85 (1H, m, C(1″)H_B), 3.64−3.71 (2H, m, CH_2OBn), 4.57−4.58 (2H, m, OCH_2Ph), 4.70−4.73 (2H, m, C(4)*H*, C(5)*H*), 7.30−7.45 (5H, m, *Ph*); δ_C (125 MHz, $CDCl_3$) 13.7 (*C*(3″)H_3), 19.2 (*C*(2″)), 30.5 (*C*(1″)), 66.7 (*C*H$_2$OBn), 73.8 (*C*H$_2$Ph), 76.7, 79.2 (*C*(4), *C*(5)), 127.7, 128.0, 128.5 (*o,m,p-Ph*), 137.0 (*i-Ph*), 154.5 (*C*(2)); *m*/*z* (ESI$^+$) 273 ([M + Na]$^+$, 90%); HRMS (ESI$^+$) $C_{14}H_{18}NaO_4^+$ ([M + Na]$^+$) requires 273.1097; found 273.1095.

(*RS*,*RS*)-5-(2′-Hydroxyethyl)-4-ethyl-1,3-dioxolan-2-one 36. Following general procedure 1, **32** (100 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 1:1) gave **36** as a pale yellow oil (83 mg, 65%, >99:1 dr): ν_{max} (film) 3424 (O−H), 2972 (C−H), 1790 (C=O); δ_H (400 MHz, $CDCl_3$) 1.02 (3H, t, *J* 7.5, *Me*), 1.74 (2H, q, *J* 7.5, C(1″)H_2), 1.91−1.98 (2H, m, C(1′)H_2), 3.78−3.81 (2H, m, C(2′)H_2), 4.30 (1H, dd, *J* 12.6, 7.5, C(5)*H*), 4.47−4.52 (1H, m, C(4)*H*); δ_C (100 MHz, $CDCl_3$) 8.8 (*C*(2″)), 26.5 (*C*(1″)), 36.2 (*C*(1′)), 57.9 (*C*(2′)), 79.1 (*C*(4)), 83.4 (*C*(5)), 155.0 (*C*(2)); *m*/*z* (ESI$^+$) 183 ([M + Na]$^+$, 100%); HRMS (ESI$^+$) $C_7H_{12}NaO_4^+$ ([M + Na]$^+$) requires 180.0628; found 180.0636.

(*RS*,*RS*)-4-(2′-Dibenzylaminoethyl)-5-ethyl-1,3-dioxolan-2-one 37. Following general procedure 2, **33** (279 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.5 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 6:1) gave **37** as a colorless oil (252 mg, 74%, >99:1 dr): ν_{max} (film) 2969 (C−H), 1801 (C=O); δ_H (500 MHz, $CDCl_3$) 0.98 (3H, t, *J* 7.4, C(2″)H_3), 1.46−1.58 (2H, m, C(1″)H_2), 1.71−1.86 (1H, m, C(1′)H_A), 1.88−1.94 (1H, m, C(1′)H_B), 2.59−2.63 (2H, m, C(2′)H_2), 3.61 (4H, AB system, J_{AB} 13.5, N(CH_2-Ph)$_2$), 4.05−4.09 (1H, m, C(5)*H*), 4.28−4.32 (1H, m, C(4)*H*), 7.26−7.34 (10H, m, *Ph*); δ_C (125 MHz, $CDCl_3$) 8.9 (*C*(2″)H_3), 26.5 (*C*(1″)H_2), 31.9 (*C*(1′)), 49.0 (*C*(2′)), 58.8 (N(*C*H$_2$Ph)$_2$), 79.8 (*C*(5)), 82.8 (*C*(4)), 127.1, 128.4, 128.8 (*o,m,p-Ph*), 139.0 (*i-Ph*), 154.7 (*C*(2)); *m*/*z* (ESI$^+$) 362 ([M + Na]$^+$, 100%); HRMS (ESI$^+$) $C_{21}H_{26}NO_3^+$ ([M + H]$^+$) requires 340.1907; found 340.1911.

(*RS*,*SR*)-4-Butyl-5-methyl-1,3-dioxolan-2-one 43. Following general procedure 1, **38** (71 mg, 0.72 mmol) in CH_2Cl_2 (4.8 mL) was treated with Br_3CCO_2H (1.06 g, 3.61 mmol) and *m*-CPBA (250 mg, 75%, 1.08 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C

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petrol/EtOAc, 5:1) gave **43** as a colorless oil (105 mg, 92%, >99:1 dr): ν_{max} (film) 2959 (C−H), 1799 (C=O); δ_H (400 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.2, C(4′)H_3), 1.36 (3H, d, *J* 6.7, C(5)*Me*), 1.35−1.44 (4H, m, C(2′)H_2, C(3′)H_2), 1.51−1.57 (1H, m, C(1′)H_A), 1.67−1.77 (1H, m, C(1′)H_B), 4.63 (1H, ddd, *J* 10.2, 7.0, 3.4, C(4)*H*), 4.83 (1H, dq, 7.0, 6.7, C(5)*H*); δ_C (100 MHz, $CDCl_3$) 13.8 (*C*(4′)), 14.5 (C(5)*Me*), 22.3 (*C*(2′)), 27.6 (*C*(3′)), 28.5 (*C*(1′)), 76.0 (*C*(5)), 80.0 (*C*(4)), 154.7 (*C*(2)); *m*/*z* (ESI^+) 181 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_8H_{14}NaO_3^+$ ($[M + Na]^+$) requires 181.0835; found 181.0831.

(***RS,SR*)-4-Phenyl-4-methyl-1,3-dioxolan-2-one 44.** Following general procedure 1, **39** (118 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.2 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 5:1) gave **44** as a colorless oil (157 mg, 88%, >99:1 dr): ν_{max} (film) 2984, 2936 (C−H), 1806 (C=O); δ_H (400 MHz, $CDCl_3$) 1.54 (3H, dt, *J* 6.1, 1.5, C(5)*Me*), 4.56−4.64 (1H, m, C(5)*H*), 5.14 (1H, d, *J* 8.1, C(4)*H*), 7.34−7.37 (2H, m, *Ph*), 7.41−7.44 (3H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 18.3 (C(5)*Me*), 80.8 (*C*(5)), 84.9 (*C*(4)), 126.0, 129.1, 129.7 (*o*,*m*,*p-Ph*), 135.0 (*i-Ph*), 154.3 (*C*(2)); *m*/*z* (ESI^+) 201 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{10}H_{10}NaO_3^+$ ($[M + Na]^+$) requires 201.0522; found 201.0524.

(***RS,SR*)-4-(Benzyloxymethyl)-5-propyl-1,3-dioxolan-2-one 45.** Following general procedure 1, **40** (190 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.5 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 4:1) gave **45** as a colorless oil (178 mg, 71%, >99:1 dr): ν_{max} (film) 2959 (C−H), 1793 (C=O), 1051; δ_H (500 MHz, $CDCl_3$) 0.97 (3H, t, *J* 7.0, C(3″)H_3), 1.38−1.44 (2H, m, C(2″)H_2), 1.60−1.70 (1H, m, C(1″)H_A), 1.70−1.80 (1H, m, C(1″)H_B), 3.60 (1H, dd, *J* 10.9, 1.9, C(1′)H_A), 3.68 (1H, dd, *J* 10.9, 1.9, C(1′)H_B), 4.34−4.37 (1H, m, C(4)*H*), 4.52−4.61 (3H, m, OCH_2Ph, C(5)*H*), 7.30−7.44 (5H, m, *Ph*); δ_C (125 MHz, $CDCl_3$) 13.6 (*C*(3″)), 17.8 (*C*(2″)), 36.0 (*C*(1″)), 68.7 (*C*H_2OBn), 73.7 (O*C*H_2Ph), 78.6 (*C*(5)), 79.9 (*C*(4)), 127.7, 128.0, 128.6 (*o*, *m*,*p-Ph*), 137.0 (*i-Ph*), 154.5 (*C*(2)); *m*/*z* (ESI^+) 273 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{14}H_{18}NaO_4^+$ ($[M + Na]^+$) requires 273.1097; found 273.1095.

(***RS,SR*)-4-(2′-Hydroxyethyl)-5-ethyl-1,3-dioxolan-2-one 46.** Following general procedure 1, **41** (100 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (1.5 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 1:1) gave **46** as a colorless oil (88 mg, 55%, >99:1 dr): ν_{max} (film) 3417 (O−H), 2974 (C−H), 1792 (C=O); δ_H (400 MHz, $CDCl_3$) 1.08 (3H, t, *J* 7.6, C(2″)H_3), 162−1.72 (2H, m, C(1″)H_2), 1.73−1.92 (2H, m, C(1′)H_2), 3.79−3.87 (2H, m, C(2′)H_2), 4.59−4.65 (1H, m, C(4)*H*), 4.90−4.96 (1H, m, C(5)*H*); δ_C (100 MHz, $CDCl_3$) 10.0 (*C*(2″)), 22.4 (*C*(1″)), 31.3 (*C*(1′)), 58.4 (*C*(2′)), 76.7 (*C*(4)), 81.2 (*C*(5)), 154.7 (*C*(2)); *m*/*z* (ESI^+) 183 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_7H_{12}NaO_4^+$ ($[M + Na]^+$) requires 183.0628; found 183.0629.

(***RS,SR*)-4-(2′-Dibenzylaminoethyl)-5-ethyl-1,3-dioxolan-2-one 47.** Following general procedure 2, **42** (279 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.5 mmol), followed by DBU (1.5 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 6:1) gave **47** as a colorless oil (270 mg, 79%, >99:1 dr): ν_{max} (film) 2971, 2803 (C−H), 1798 (C=O); δ_H (500 MHz, $CDCl_3$) 0.95 (3H, t, *J* 7.3, C(2″)H_3), 1.30−1.35 (1H, m, C(1″)H_A), 1.50−1.57 (1H, m, C(1″)H_B), 1.67−1.69 (1H, m, C(1′)H_A), 1.80−1.85 (1H, m, C(1′)H_B), 2.57−2.68 (2H, m, C(2′)H_2), 3.61 (4H, br s, N(CH_2Ph)$_2$), 4.26−4.30 (1H, m, C(5)*H*), 4.72−4.76 (1H, m, C(4)*H*), 7.26−7.34 (10H, m, *Ph*); δ_C (125 MHz, $CDCl_3$) 9.96 (C(2″)), 22.2 (*C*(1″)), 27.0 (*C*(1′)), 49.7 (*C*(2′)), 58.9 (N(*C*H_2Ph)$_2$), 77.8 (*C*(5)), 80.3 (*C*(4)), 127.3, 128.2, 129.7 (*o*,*m*,*p-Ph*), 139.0 (*i-Ph*), 154.6 (*C*(2)); *m*/*z* (ESI^+) 362 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{21}H_{26}NO_3^+$ ($[M + H]^+$) requires 340.1907; found 340.1911.

(***RS*)-*N*(3)-Benzyl-5-(hydroxymethyl)-1,3-oxazolidin-2-one 50.** Following general procedure 2, **48** (147 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (344 mg, 75%, 1.50 mmol), followed by DBU (2.0 mL). Purification via flash column chromatography (gradient elution, 50%→100% EtOAc in 30−40 °C petrol) gave **50** as a colorless oil (157 mg, 88%): ν_{max} (film) 3408 (O−H), 2924, 2874 (C−H), 1731 (C=O); δ_H (400 MHz, $CDCl_3$) 3.35 (1H, app t, *J* 8.6, C(4)H_A), 3.42 (1H, app t, *J* 8.6, C(4)H_B), 3.57 (1H, dd, *J* 12.5, 4.3, C(1′)H_A), 3.78 (1H, dd, *J* 12.5, 3.2, C(1′)H_B), 4.36 (2H, AB system, J_{AB} 15.0, NCH_2Ph), 4.53−4.57 (1H, m, C(5)*H*), 7.25−7.33 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 45.2 (*C*(4)), 48.2 (N*C*H_2Ph), 62.8 (*C*(1′)), 73.8 (*C*(5)), 127.9, 128.0, 128.8 (*o*,*m*, *p-Ph*), 135.6 (*i-Ph*), 158.3 (*C*(2)); *m*/*z* (ESI^+) 230 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{11}H_{13}NNaO_3^+$ ($[M + Na]^+$) requires 230.0788; found 230.0788.

(***RS*)-*N*(3)-Benzyl-6-(hydroxymethyl)-1,3-oxazinan-2-one 51.** Following general procedure 2, **49** (100 mg, 0.620 mmol) in CH_2Cl_2 (4.1 mL) was treated with Br_3CCO_2H (917 mg, 3.10 mmol) and *m*-CPBA (213 mg, 75%, 0.93 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (gradient elution, 50%→100% EtOAc in 30−40 °C petrol) gave **51** as a pale yellow solid (83 mg, 61%): mp 95−97 °C; ν_{max} (KBr) 3384 (O−H), 2928, 2872 (C−H), 1672 (C=O); δ_H (400 MHz, $CDCl_3$) 1.89−2.17 (2H, m, C(5)H_2), 3.20−3.23 (1H, m, C(4)H_A), 3.28−3.31 (1H, ddd, *J* 16.7, 11.5, 5.3, C(4)H_B), 3.67 (1H, dd, *J* 12.3, 5.2, C(1′)H_A), 3.83 (1H, dd, *J* 12.3, 3.4, C(1′)H_B), 4.34−4.38 (1H, m, C(6)*H*), 4.55 (2H, AB system, J_{AB} 14.9, NCH_2Ph), 7.26−7.50 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 23.4 (*C*(5)), 43.6 (*C*(4)), 52.6 (N*C*H_2Ph), 64.3 (*C*H_2OH), 77.7 (*C*(6)), 127.7, 128.0, 128.7 (*o*,*m*,*p-Ph*), 136.4 (*i-Ph*), 153.8 (*C*(2)); *m*/*z* (ESI^+) 244 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{12}H_{15}NNaO_3^+$ ($[M + Na]^+$) requires 244.0944; found 244.0943.

(***RS,SR*)-*N*(3)-Benzyl-5-(1′-hydroxybutyl)-1,3-oxazolidin-2-one 54.** Following general procedure 2, **52** (100 mg, 0.528 mmol) in CH_2Cl_2 (3.5 mL) was treated with Br_3CCO_2H (778 mg, 2.64 mmol) and *m*-CPBA (181 mg, 75%, 0.79 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (gradient elution, 50%→100% EtOAc in 30−40 °C petrol) gave **54** as a colorless oil (113 mg, 86%, >99:1 dr): ν_{max} (film) 3418 (O−H), 2957 (C−H), 1726 (C=O); δ_H (400 MHz, $CDCl_3$) 0.91 (3H, app t, *J* 7.0, C(4′)H_3), 1.31−1.38 (3H, m, C(2′)H_2, C(3′)H_A), 1.51−1.55 (1H, m, C(3′)H_B), 3.32 (1H, t, *J* 8.7, C(4)H_A), 3.45−3.47 (1H, m, C(4)H_B), 3.86−3.89 (1H, m, C(1′)*H*), 4.33 (1H, d, *J* 14.9, NC$H_A$$H_B$Ph), 4.40 (1H, ddd, *J* 16.3, 8.7, 3.7, C(5)*H*), 4.52 (1H, d, *J* 14.9, NCH$_A$$H_B$Ph), 7.23−7.50 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 13.9 (*C*(4′)), 18.6 (*C*(3′)), 33.5 (*C*(2′)), 44.0 (*C*(4)), 48.3 (NCH_2Ph), 70.4 (*C*(1′)), 75.7 (*C*(5)), 127.9, 128.1, 128.8 (*o*,*m*,*p-Ph*), 135.6 (*i-Ph*), 158.0 (*C*(2)); *m*/*z* (ESI^+) 272 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{14}H_{19}NNaO_3^+$ ($[M + Na]^+$) requires 272.1257; found 272.1254.

(***RS,SR*)-*N*(3)-Benzyl-6-(1′-hydroxypropyl)-1,3-oxazinan-2-one 55.** Following general procedure 2, **53** (120 mg, 0.630 mmol) in CH_2Cl_2 (4.1 mL) was treated with Br_3CCO_2H (932 mg, 3.15 mmol) and *m*-CPBA (216 mg, 75%, 0.95 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (gradient elution, 50%→100% EtOAc in 30−40 °C petrol) gave **55** as a colorless oil (138 mg, 88%, >99:1 dr): $C_{14}H_{19}NO_3$ requires C, 67.45; H, 7.7; N, 5.6%; found C, 67.5; H, 7.6; N, 5.4%; ν_{max} (film) 3392 (O−H), 3030 (C−H), 2966 (C−H), 1672 (C=O); δ_H (400 MHz, $CDCl_3$) 1.02 (3H, t, *J* 5.5, C(3′)H_3), 1.45−1.56 (2H, m, C(2′)H_2), 1.89−2.05 (2H, m, C(5)H_2), 3.18−3.25 (2H, m, C(4)H_2), 3.73 (1H, app quintet, *J* 3.8, C(1′)*H*),

4.15 (1H, dt, *J* 10.8, 3.8, C(6)*H*), 4.53 (2H, AB system, J_{AB} 14.9, NCH_2Ph), 7.27−7.35 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 10.2 (*C*(3′)), 21.2 (*C*(2′)), 24.9 (*C*(5)), 43.6 (*C*(4)), 52.5 (NCH_2Ph), 73.2 (*C*(1′)), 79.9 (*C*(6)), 127.7, 128.0, 128.7 (*o*,*m*,*p*-*Ph*), 136.5 (*i*-*Ph*), 154.1 (*C*=O); *m*/*z* (ESI^-) 248 ($[M - H]^-$, 100%); HRMS (ESI^-) $C_{14}H_{18}NO_3^-$ ($[M - H]^-$) requires 248.1292; found 248.1291.

(*RS*,*RS*)-*N*(3)-Benzyl-5-(1′-hydroxybutyl)-1,3-oxazolidin-2-one 58. Following general procedure 2, **56** (100 mg, 0.528 mmol) in CH_2Cl_2 (3.5 mL) was treated with Br_3CCO_2H (778 mg, 2.64 mmol) and *m*-CPBA (181 mg, 75%, 0.79 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (gradient elution, 50%→100% EtOAc in 30−40 °C petrol) gave **58** as a colorless oil (117 mg, 89%, >99:1 dr): ν_{max} (film) 3418 (O−H), 2957 (C−H), 1726 (C=O); δ_H (400 MHz, $CDCl_3$) 0.92 (3H, t, *J* 7.1, C(4′)H_3), 1.39−1.54 (4H, m, C(2′)H_2, C(3′)H_2), 3.30 (1H, app t, *J* 7.5, C(4)H_A), 3.41 (1H, app t, *J* 7.5, C(4)H_B), 3.53−3.56 (1H, m, C(1′)*H*), 4.36 (1H, d, *J* 15.0, NC$H_A$$H_B$Ph), 4.36−4.38 (1H, m, C(5)*H*), 4.49 (1H, d, *J* 15.0, NCH$_A$$H_B$Ph), 7.26−7.38 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 13.8 (*C*(4′)), 18.7 (*C*(3′)), 34.5 (*C*(2′)), 45.7 (*C*(4)), 48.3 (NCH_2Ph), 72.1 (*C*(1′)), 75.7 (*C*(5)), 127.9, 128.0, 128.8 (*o*,*m*,*p*-*Ph*), 135.6 (*i*-*Ph*), 157.7 (*C*(2)); *m*/*z* (ESI^+) 250 ($[M + H]^+$, 100%); HRMS (ESI^+) $C_{14}H_{20}NO_3^+$ ($[M + H]^+$) requires 250.1438; found 250.1436.

X-ray Crystal Structure Determination for 58. Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo Kα radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions. The structure was refined using CRYSTALS.[28]

X-ray crystal structure data for **58** [$C_{14}H_{19}NO_3$]: M = 498.62, triclinic, space group $P\bar{1}$, a = 9.6645(4) Å, b = 11.3513(4) Å, c = 12.7583(5) Å, α = 101.4022(16)°, β = 104.9826(16)°, γ = 90.623(2)°, V = 1322.54(9) Å^3, Z = 4, μ = 0.088 mm^{-1}, colorless block, crystal dimensions = 0.12 × 0.16 × 0.24 mm^3. A total of 5982 unique reflections were measured for 5 < θ < 27, and 2904 reflections were used in the refinement. The final parameters were wR_2 = 0.134 and R_1 = 0.127 [$I > 2.5\sigma(I)$].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784948. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(*RS*,*RS*)-*N*(3)-Benzyl-6-(1′-hydroxypropyl)-1,3-oxazinan-2-one 59. Following general procedure 2, **57** (120 mg, 0.630 mmol) in CH_2Cl_2 (4.2 mL) was treated with Br_3CCO_2H (932 mg, 3.15 mmol) and *m*-CPBA (216 mg, 75%, 0.95 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (gradient elution, 50%→100% EtOAc in 30−40 °C petrol) gave **59** as a colorless oil (132 mg, 84%, >99:1 dr): $C_{14}H_{19}NO_3$ requires C, 67.45; H, 7.7; N, 5.6%; found C, 67.4; H, 7.6; N, 5.6%; ν_{max} (film) 3390 (O−H), 3031 (C−H), 2934 (C−H), 1681 (C=O); δ_H (400 MHz, $CDCl_3$) 0.99 (3H, t, *J* 7.0, C(3′)H_3), 1.53−1.64 (2H, m, C(2′)H_2), 1.87−1.91 (2H, m, C(5)H_2), 3.17−3.22 (1H, m, C(4)H_A), 3.21−3.30 (1H, m, C(4)H_B), 3.49−3.53 (1H, m, C(1′)*H*), 4.11−4.16 (1H, m, C(6)*H*), 4.54 (2H, AB system, J_{AB} 15.0, NCH_2Ph), 7.26−7.35 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 9.9 (*C*(3′)), 23.8 (*C*(2′)), 25.5 (*C*(5)), 43.7 (*C*(4)), 52.5 (NCH_2Ph), 74.2 (*C*(1′)), 79.8 (*C*(6)), 127.6, 128.1, 128.7 (*o*,*m*,*p*-*Ph*), 136.5 (*i*-*Ph*), 153.8 (*C*(2)); *m*/*z* (ESI^-) 248 ($[M-H]^-$, 100%); HRMS (ESI^-) $C_{14}H_{18}NO_3^-$ ($[M-H]^-$) requires 248.1292; found 248.1292.

X-ray Crystal Structure Determination for 59. Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo Kα radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions. The structure was refined using CRYSTALS.[28]

X-ray crystal structure data for **61** [$C_{14}H_{19}NO_3$]: M = 249.31, monoclinic, space group $P2_1/n$, a = 12.0044(4) Å, b = 9.1663(4) Å, c = 12.0881(5) Å, β = 92.7130(18)°, V = 1328.63(9) Å^3, Z = 4, μ = 0.087 mm^{-1}, colorless plate, crystal dimensions = 0.13 × 0.18 × 0.21 mm^3. A total of 3016 unique reflections were measured for 5 < θ < 27, and 3016 reflections were used in the refinement. The final parameters were wR_2 = 0.141 and R_1 = 0.065 [$I > -3.0\sigma(I)$].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784949. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(*RS*,*SR*)-1-*N*,*N*-Dibenzylamino-1-phenyl-2,3-epoxy-3-methylbutane 73. Cl_3CCO_2H (1.20 g, 7.33 mmol) was added to a solution of **67** (500 mg, 1.47 mmol) in CH_2Cl_2 (10 mL) at rt, and the solution was stirred for 30 min. *m*-CPBA (1.08 g, 70%, 4.40 mmol) was added, and the solution was stirred at rt for 1 h. The mixture was then diluted with CH_2Cl_2 (20 mL) and washed with satd aq Na_2SO_3 (50 mL portions) until starch-iodide paper indicated that no *m*-CPBA was present. The organic layer was washed with satd aq $NaHCO_3$ (4 × 50 mL), dried, and concentrated in vacuo. Purification via flash column chromatography (gradient elution, 1%→5% Et_2O in 30−40 °C petrol) gave **73** as a colorless oil (516 mg, 98%, >99:1 dr): ν_{max} (film) 3041 (C−H), 2961 (C−H), 1493; δ_H (400 MHz, $CDCl_3$) 0.91 (3H, s, *Me*), 1.45 (3H, s, *Me*), 3.34 (1H, d, *J* 9.0, C(2)*H*), 3.65 (1H, d, *J* 9.0, C(1)*H*), 3.80 (4H, AB system, J_{AB} 13.5, N(CH_2Ph)$_2$), 7.14−7.49 (15H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 18.8 (*Me*), 24.8 (*Me*), 53.9 (N(*C*H_2Ph)$_2$), 56.2 (*C*(3)), 60.3 (*C*(1)), 63.2 (*C*(2)), 126.7, 127.2, 127.8, 128.1, 128.3, 129.0 (*o*,*m*,*p*-*Ph*), 139.9, 140.0 (*i*-*Ph*); *m*/*z* (ESI^+) 358 ($[M + H]^+$, 100%); HRMS (ESI^+) $C_{25}H_{28}NO^+$ ($[M + H]^+$) requires 358.2165; found 358.2167.

(*RS*,*SR*)-1-*N*,*N*-Dibenzylamino-1-isopropyl-2,3-epoxy-3-methylbutane 74. Cl_3CCO_2H (265 mg, 1.63 mmol) was added to a solution of **68** (100 mg, 0.33 mmol) in CH_2Cl_2 (2 mL) at rt, and the solution was stirred for 30 min. *m*-CPBA (120 mg, 70%, 0.48 mmol) was added, and the solution was stirred at rt for 21 h. The mixture was then diluted with CH_2Cl_2 (10 mL) and washed with satd aq Na_2SO_3 (20 mL portions) until starch-iodide paper indicated that no *m*-CPBA was present. The organic layer was washed with satd aq $NaHCO_3$ (4 × 20 mL), dried, and concentrated in vacuo. Purification via flash column chromatography (gradient elution, 1%→5% Et_2O in 30−40 °C petrol) gave **73** as a white solid (105 mg, 99%, >99:1 dr): mp 74−77 °C; ν_{max} (film) 2958 (C−H), 2927 (C−H), 1493; δ_H (400 MHz, $CDCl_3$) 0.78 (3H, d, *J* 6.7, *Me*CHMe), 1.02 (3H, d, *J* 6.7, MeCH*Me*), 1.15 (3H, s, C(3)*Me*), 1.36 (3H, s, C(3)*Me*), 1.80−1.89 (1H, m, C*H*Me$_2$), 2.11 (1H, app t, *J* 9.8, C(1)*H*), 2.92 (1H, d, *J* 9.8, C(2)*H*), 3.90 (4H, AB system, J_{AB} 13.1, N(CH_2Ph)$_2$), 7.20−7.49 (10H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 19.5 (*Me*), 19.8 (*Me*), 20.9 (*Me*), 24.5 (*Me*), 28.8 (*C*HMe$_2$), 54.7 (N(CH_2Ph)$_2$), 56.6 (*C*(3)), 60.8 (*C*(1)), 66.3 (*C*(2)), 126.6, 128.0, 129.2 (*o*,*m*,*p*-*Ph*), 140.6 (*i*-*Ph*); *m*/*z* (ESI^+) 346 ($[M + Na]^+$, 100%); HRMS (ESI^+) $C_{22}H_{30}NO^+$ ($[M + H]^+$) requires 324.2322; found 324.2325.

X-ray Crystal Structure Determination for 74. Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo Kα radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with

(28) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, C. K.; Watkin, D. J. *CRYSTALS*; Chemical Crystallography Laboratory, University of Oxford: U.K., 2010; Issue 14.

anisotropic thermal parameters. Hydrogen atoms were added at idealized positions. The structure was refined using CRYSTALS.[28]

X-ray crystal structure data for **74** [$C_{22}H_{29}NO$]: M = 323.48, monoclinic, space group $P21/c$, a = 12.1182(2) Å, b = 10.2863(2) Å, c = 15.4746(3) Å, β = 97.3039(8)°, V = 1913.28(6) Å^3, Z = 4, μ = 0.068 mm^{-1}, colorless plate, crystal dimensions = 0.18 × 0.21 × 0.28 mm^3. A total of 4354 unique reflections were measured for $5 < \theta < 27$, and 2864 reflections were used in the refinement. The final parameters were wR_2 = 0.090 and R_1 = 0.043 [$I > -3.0\sigma(I)$].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784950. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(*RS*,*SR*)-4,4-Dimethyl-5-[(*N*,*N*-dibenzylamino)(phenyl)methyl]-1,3-dioxolan-2-one 76. Following general procedure 2, **67** (170 mg, 0.500 mmol) in CH_2Cl_2 (3.3 mL) was treated with Br_3CCO_2H (1.48 g, 5.00 mmol) and *m*-CPBA (184 mg, 70%, 0.75 mmol), followed by DBU (1.0 mL). Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 5:1) gave **43** as a white solid (180 mg, 90%, >99:1 dr): mp 126−128 °C; ν_{max} (KBr) 2981 (C−H), 1797 (C=O); δ_H (400 MHz, $CDCl_3$) 0.97 (3H, s, C(5)Me_A), 1.13 (3H, s, C(5)Me_B), 3.19 (2H, d, J 13.7, N(CH_AH$_B$Ph)$_2$), 3.99 (2H, d, J 13.7, N(CH$_A$$H_B$Ph)$_2$), 4.07 (1H, d, J 11.1, C(1′)*H*), 5.11 (1H, d, J 11.1, C(5)*H*), 7.10−7.49 (15H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 21.4 (*Me*), 26.8 (*Me*), 53.5 (N(CH_2Ph)$_2$), 60.2 (*C*(1′)), 84.1 (*C*(4)), 84.2 (*C*(5)), 127.2, 127.5, 128.4, 128.8, 129.3, 130.3 (*o*,*m*,*p*-*Ph*), 138.1, 139.0 (*i*-*Ph*), 153.9 (*C*(2)); m/z (ESI$^+$) 424 ([M + Na]$^+$, 70%); HRMS (ESI$^+$) $C_{26}H_{28}NO_3^+$ ([M + H]$^+$) requires 402.2064; found 402.2067.

X-ray Crystal Structure Determination for 76. Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo Kα radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions. The structure was refined using CRYSTALS.[28]

X-ray crystal structure data for **76** [$C_{26}H_{27}NO_3$]: M = 401.51, triclinic, space group $P\bar{1}$, a = 8.7549(2) Å, b = 9.8380(3) Å, c = 14.0722(5) Å, α = 85.2408(11)°, β = 83.4949(12)°, γ = 66.4693(13)°, V = 1103.16(6) Å^3, Z = 2, μ = 0.078 mm^{-1}, colorless block, crystal dimensions = 0.21 × 0.24 × 0.27 mm^3. A total of 4962 unique reflections were measured for $5 < \theta < 27$, and 4962 reflections were used in the refinement. The final parameters were wR_2 = 0.100 and R_1 = 0.063 [$I > -3.0\sigma(I)$].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784951. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(*RS*,*SR*)-1-*N*,*N*-Dibenzylamino-1-phenyl-3-methyl-butane-2,3-diol 77. Method A. Cl_3CCO_2H (253 mg, 1.55 mmol) was added to **67** (106 mg, 0.310 mmol) in CH_2Cl_2 (2 mL) at rt, and the resultant solution was stirred for 30 min. *m*-CPBA (80 mg, 73%, 0.34 mmol) was added, and the reaction mixture was stirred at 40 °C for 21 h. The mixture was then cooled to rt, diluted with CH_2Cl_2 (10 mL), and washed with satd aq Na_2SO_3 (10 mL portions) until starch-iodide paper indicated that no *m*-CPBA was present. The organic layer was washed with satd aq $NaHCO_3$ (4 × 10 mL), dried, and concentrated in vacuo. The residue was dissolved in MeOH (4.0 mL); K_2CO_3 (428 mg, 3.1 mmol) was added; and the mixture was stirred at rt for 16 h and then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (10 mL) and washed with satd aq $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried and concentrated in vacuo. Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 5:1) gave **77** as a white solid (72 mg, 62%, >99:1 dr): mp 90−94 °C; ν_{max} (film) 3315 (O−H), 2971 (C−H); δ_H (400 MHz, $CDCl_3$) 0.64 (3H, s, C(3)Me_A), 0.98 (3H, s, C(3)Me_B), 2.99−3.02 (2H, m, N(CH_AH$_B$Ph)$_2$), 3.84 (1H, d, J 9.4, C(1)*H*), 3.87−3.91 (2H, m, N(CH$_A$$H_B$Ph)$_2$), 4.07 (1H, J 9.4, C(2)*H*), 7.25−7.47 (15H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 24.7 (*Me*), 27.9 (*Me*), 52.9 (N(CH_2Ph)$_2$), 53.6 (N(CH_2Ph)$_2$), 60.0 (*C*(1)), 73.3 (*C*(2)), 127.2, 127.5, 128.0, 128.3, 128.6, 130.3 (*o*,*m*,*p*-*Ph*), 138.2, 139.8 (*i*-*Ph*); m/z (ESI$^+$) 376 ([M + H]$^+$, 100%); HRMS (ESI$^+$) $C_{25}H_{30}NO_2^+$ ([M + H]$^+$) requires 376.2271; found 376.2270.

Method B. K_2CO_3 (127 mg, 0.92 mmol) was added to a solution of **76** (37 mg, 0.09 mmol) in MeOH (2.0 mL). The mixture was heated to 60 °C for 16 h and then concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (10 mL) and washed with satd aq $NaHCO_3$ (10 mL) and brine (10 mL). The organic layer was dried and concentrated in vacuo. Purification via flash column chromatography (eluent 40−60 °C petrol/EtOAc, 5:1) gave **77** as a white solid (34 mg, 98%, >99:1 dr).

X-ray Crystal Structure Determination for 77. Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo Kα radiation using standard procedures at 150 K. The structure was solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealized positions. The structure was refined using CRYSTALS.[28]

X-ray crystal structure data for **77** [$C_{25}H_{29}NO_2$]: M = 375.51, monoclinic, space group $P21/c$, a = 10.14550(10) Å, b = 8.47320(10) Å, c = 24.9311(4) Å, β = 97.0646(6)°, V = 2126.93(5) Å^3, Z = 4, μ = 0.073 mm^{-1}, colorless block, crystal dimensions = 0.20 × 0.20 × 0.20 mm^3. A total of 4820 unique reflections were measured for $5 < \theta < 27$, and 2564 reflections were used in the refinement. The final parameters were wR_2 = 0.046 and R_1 = 0.040 [$I > 3.0\sigma(I)$].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 784952. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(4*RS*,5*SR*,1′*SR*)-4-[(*N*,*N*-Dibenzylamino)(phenyl)methyl]-5-methyl-1,3-dioxolan-2-one 82. Br_3CCO_2H (2.96 g, 10.0 mmol) was added to a stirred solution of **78** (265 mg, 1.00 mmol) in CH_2Cl_2 (6.6 mL), and the resultant mixture was stirred at rt for 10 min. *m*-CPBA (367 mg, 70%, 1.50 mmol) was added in one portion, and the reaction mixture was stirred at rt for 3 days. DBU was added at 0 °C, and the resultant mixture was stirred at rt for 2 h. Satd aq $NaHCO_3$ (10 mL) was added, and the layers were separated. The organic layer was washed with satd aq $NaHCO_3$ (2 × 10 mL) and brine (10 mL) and then dried and concentrated in vacuo to give an 85:15 mixture of **82** and **83** as a colorless oil (298 mg, 77%, **82**:**83**, 85:15). An analytical sample of **82** (>95:5 dr) was obtained after exhaustive flash column chromatography: ν_{max} (film) 2986 (C−H), 1803 (C=O); δ_H (400 MHz, $CDCl_3$) 0.94 (3H, d, J 9.3, C(5)*Me*), 3.29 (2H, d, J 13.5, N(CH_AH$_B$Ph)$_2$), 3.95 (2H, d, J 13.5, N(CH$_A$$H_B$Ph)$_2$), 4.07 (1H, app d, J 9.3, C(1′)*H*), 5.11 (1H, q, J 9.3, C(5)*H*), 5.43−5.55 (1H, m, C(4)*H*), 7.10−7.49 (15H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 14.5 (*Me*), 53.6 (N(CH_2Ph)$_2$), 59.3 (*C*(1′)), 75.6 (*C*(5)), 77.7 (*C*(4)), 127.1, 128.4, 128.5, 128.8, 128.9, 133.5 (*o*,*m*,*p*-*Ph*), 138.9, 139.0 (*i*-*Ph*), 154.6 (*C*(2)); m/z (ESI$^+$) 388 ([M + H]$^+$, 100%); HRMS (ESI$^+$) $C_{25}H_{26}NO_3^+$ ([M + H]$^+$) requires 388.1907; found 388.1904.

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Supporting Information Available: Full details of all experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra, and crystallographic information files (for structures CCDC 784948−784952). This material is available free of charge via the Internet at http://pubs.acs.org.