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Diastereoselective [4+3] Cycloadditions of Enantiopure Nitrogen-Stabilized Oxyallyl Cations

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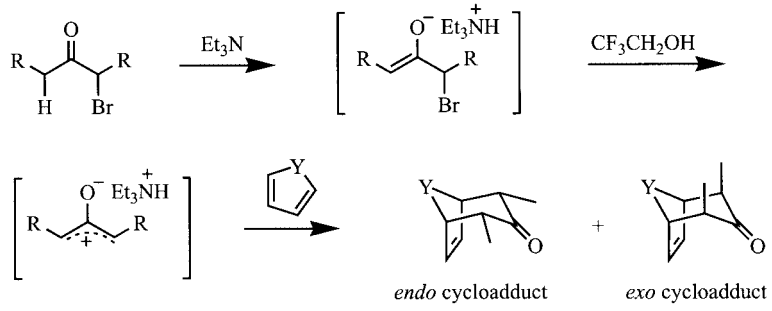
Diastereoselective trapping of chiral enantiopure oxyallyl cations by common dienes is reported. Excellent diastereoselectivities were obtained and depending on which auxiliary was used cycloadditions proceeded through a chelated or non-chelated pathway.

Introduction

[4+3] Cycloadditions between oxyallyl cations and common cyclic 1,3-dienes[1] offer easy access to highly versatile seven-membered rings. Not only are such rings found in a great number of natural products like tropane alkaloids,[2] but also the resulting [3.2.1] bicyclic ketones formed through cycloaddition with cyclic dienes, due to their rigid conformations, are amenable to further regio- and stereospecific transformations.[3] Extensive studies over the past thirty years have provided a good understanding of the relative stereochemical outcome (*endo* vs. *exo*) observed in crude mixtures of [4+3] cycloadditions.[1] A large variety of methods have been developed in order to generate oxyallyl cation intermediates, including reductive, acido-solvolytic or basic conditions.[1] However, it was not until this past decade that the first asymmetric versions appeared in the literature.[4] Most notable are examples using chiral acetals[4] or via epoxidation of enantiopure allenamides,[4] as well as a recent enantioselective variant.[4]

Our laboratories successfully demonstrated the viability of nitrogen-substituted oxyallyl cations a few years ago.[5,6] One of the major advantages of this type of oxyallyl cation was the possibility to include the nitrogen atom in an optically pure heterocycle and potentially induce asymmetry into the reaction. Recently Hsung et al. elegantly showed that heterocycles such as Evans-type oxazolidinones were excellent candidates for this task and that good levels of diastereoselectivity could be achieved.[7]



Scheme 1. Postulated mechanism of [4+3] cycloadditions under Föhlisch conditions.

During this same time period we were working on extending our previous studies on nitrogen-substituted oxyallyl cations to an asymmetric variant. However, unlike Hsung, who generated his oxyallyl cations by low-tempera-

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ture oxidation of allenamides with dimethyldioxirane (DMDO), we were attracted to the more straightforward Föhlisch conditions, α-substituted α-bromo ketones under basic conditions (typically triethylamine or sodium 2,2,2-trifluoroethoxide),[8] in a polar media (MeOH or 2,2,2-trifluoroethanol) (Scheme 1). We wish herein to report our contribution toward the diastereocontrol of [4+3] cycloadditions involving chiral enantiopure oxyallyl cations under such basic conditions and therefore set an alternative entry to Hsung's oxidative procedure.[4]

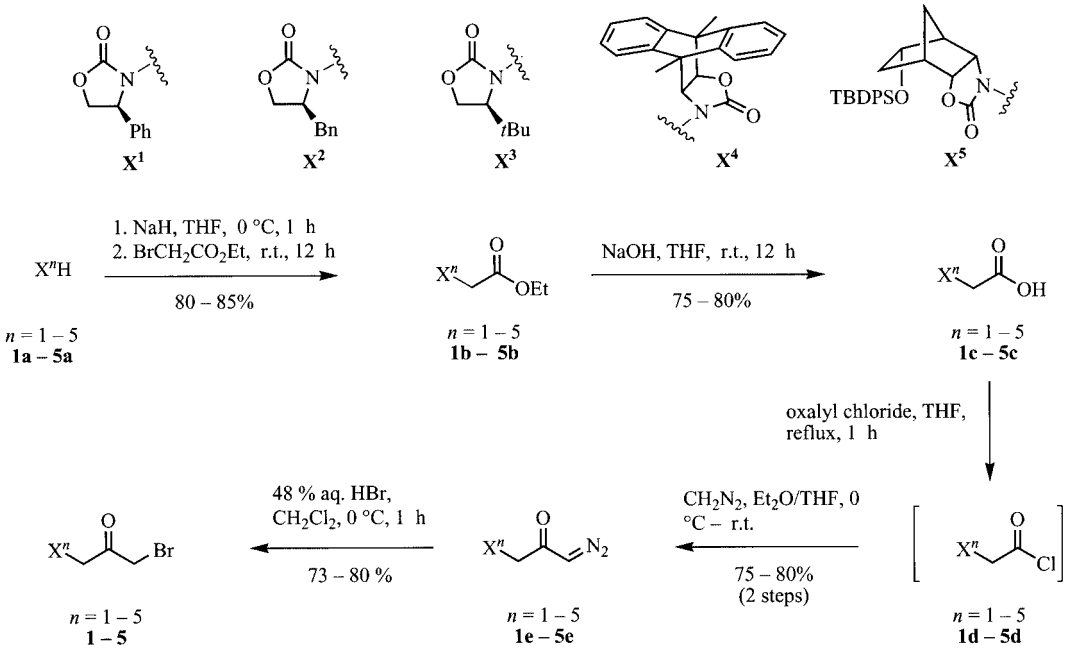
Results and Discussion

Diastereoselective [4+3] Cycloadditions with Furan and Cyclopentadiene

In initial studies, we decided to focus on the common chiral oxazolidinones of type **1a**, **2a** and **3a**, derived respectively from phenylglycine, phenylalanine and *tert*-leucine, because they were shown to be excellent chiral auxiliaries in a variety of other asymmetric processes.[7] The synthesis of our precursors commenced, as depicted in Scheme 2, by alkylation of enantiopure chiral oxazolidinones **1a**, **2a** and **3a**, with ethyl bromoacetate (NaH, THF, 0 °C), affording alkyl esters **1b**, **2b** and **3b** in good yields.[9] Saponification readily occurred upon subjection of these oxazolinyl acetate esters to an alkaline media (NaOH, THF, 0 °C) providing the corresponding acetic acids.[9a] The diazo ketones **1e**, **2e** and **3e** were generated by converting the carboxylic acids **1c**, **2c** and **3c** to their acid chlorides (respectively **1d**, **2d** and **3b**) (oxalyl chloride, THF, reflux), followed by trapping with diazomethane (ethereal solution, 0 °C). These compounds were then easily purified by standard column chromatography on silica without any observed degradation, and could be readily stored for long periods of time in a refrigerator.[9] Gas evolution was immediately observed upon exposure of 48% aqueous HBr to ice-cold dichloromethane solutions of diazo ketones **1e**, **2e** and **3e**, thus providing quick and easy access to the α-bromo ketone intermediates **1**–**3**.[9] The α-bromo ketones were quite sensitive and readily decomposed on standing at room temperature or attempted silica gel chromatography. Consequently once the precursors were prepared they were immediately subjected to the cycloaddition reaction. Although it took 5 steps to generate the requisite precursors, the sequence proceeded in good overall yields and was completely amenable to larger scale preparation.

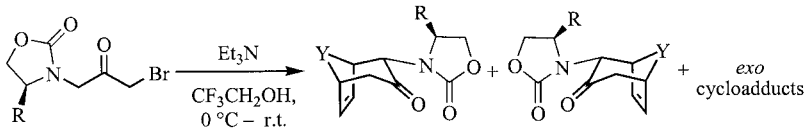
Upon subjection of bromo ketones **1**–**3** to the cycloaddition conditions developed by Föhlisch (CF_3CH_2OH, Et_3N),[8] in the presence of a large excess of diene (10 to 20 equiv.), the expected [4+3] cycloadditions readily occurred, in moderate to good chemical yields (Table 1). Cycloadditions involving **1** and **2** afforded the corresponding bicyclic ketones **6a**–**c**, **7a**–**c**, **9a**–**c** and **10a**–**c** with excellent relative stereoselectivity (*endo* vs. *exo*, see structural assignment, vide supra), but with very moderate facial diastereoselectivities (Table 1).

Surprisingly, a low *endo*/*exo* ratio, unusual under these conditions, was observed during the course of the cycloaddition of **2** and cyclopentadiene (Entry 5). As expected, increasing the steric hindrance lead to significant improvement concerning the facial selectivity and ratios up to 95:5 were observed when the oxyallyl cation derived from the 4-*tert*-butyloxazolidinyl bromo ketone **3** was treated with furan (Entries 3 and 6). In each case, major *endo*-cycloadducts were isolated diastereomerically pure by standard chromatographic techniques or recrystallization in good chemical yields.



Scheme 2. Synthesis of chiral nonracemic oxyallyl precursors **1**–**5**.

Table 1. Diastereoselectivities obtained in [4+3] cycloadditions of **1**, **2**, and **3**.



1 (R = Ph) **2** (R = Bn) **3** (R = *t*Bu)	Y = O	**6a** **7a** **8a**	**6b** **7b** **8b**	**6c** **7c** **8c**
1 (R = Ph) **2** (R = Bn) **3** (R = *t*Bu)	Y = CH_2	**9a** **10a** **11a**	**9b** **10b** **11b**	**9c** **10c** **11c**

Entry	Bromo ketone[a] X^n see Scheme 2	Diene	Products	*endo*/*exo*[c] (**a** + **b**)/**c**	*dr*[c] **a**/**b**	Yield[b] [%]
1	**1**	furan	**6a–c**	93:7	66:34	70
2	**2**	furan	**7a–c**	90:10	67:33	70
3	**3**	furan	**8a–c**	95:5	95:5	80
4	**1**	Cp	**9a–c**	93:7	66:34	65
5	**2**	Cp	**10a–c**	67:3	67:33	65
6	**3**	Cp	**11a–c**	89:11	89:11	70

[a] Typical conditions: 1 equiv. of bromo ketone in diene (0.25 M), trifluoroethanol (0.5 M), followed by 1.5 equiv. of Et_3N. [b] Combined isolated yield. [c] Measured by GC.

X-ray crystallographic analyses of the resulting cycloadducts allowed us to unambiguously assign the absolute stereochemistry of the three new stereogenic centers created during the cycloaddition. Similarly to Hsung's observations,[4] the stereochemical outcome of this type of [4+3] cycloaddition was consistent with a concerted transition state, where the diene approached from the least congested face of the most stable W-form of the oxyallyl cation (Figure 1).[10] The acidity of 2,2,2-trifluoroethanol was presumably sufficient to render the alcoholic proton capable of chelating the two carbonyl units in a seven-membered ring transition state, as predicted by computational calculations previously carried out by our laboratories.[5]

It was felt at this stage that the diastereoselectivity might be improved by the use of stronger chelating Lewis acids such as lithium perchlorate or magnesium bromide, in an aprotic media such as acetonitrile.[11,12] Initial results using oxazolidinyl bromo ketone **1**, with magnesium bromide proved encouraging as facial diastereoselectivities with both furan and cyclopentadiene were significantly improved from a disappointing 2:1 ratio to a more acceptable 4:1 ratio with the inclusion of $MgBr_2$, (Table 2, Entries 2 and 4), albeit with slightly reduced yields and/or relative stereoselectivities. Unfortunately, bromo ketones **2** and **3** did not offer any benefit under such conditions as lower diastereoselectivities were observed along with lower yields.

The decreased diastereoselections observed with **3** might be attributed to a lower propensity of lithium and magnesium oxyallyls to form seven-membered chelating rings or might simply be a consequence of a larger excess of "available chelating agent", because, as in our first series of results, 2,2,2-trifluoroethanol was used as the solvent.

Our efforts towards the organization of a structurally defined transition state therefore lead us to investigate the

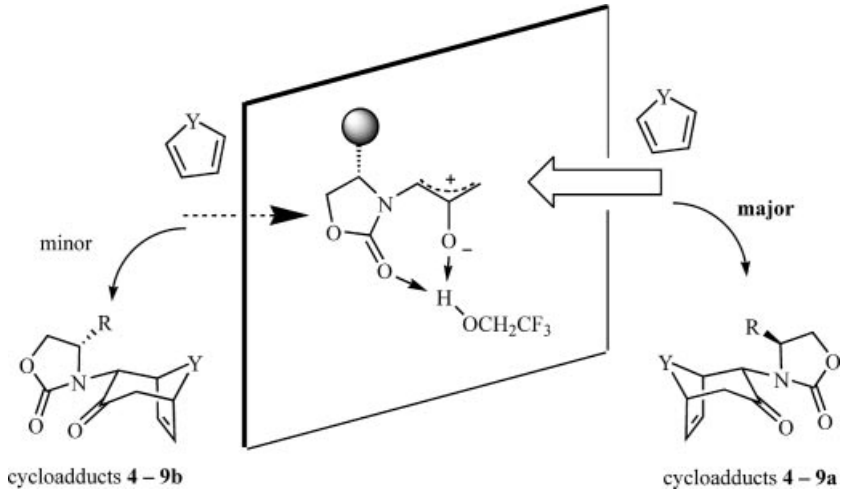
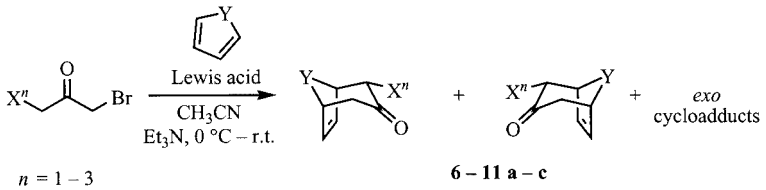


Figure 1. Chelated model proposed for [4+3] cycloaddition with **1**, **2** and **3**.

Table 2. Diastereoselectivities obtained in the presence of Lewis acids.



n = 1 – 3 **6 – 11 a – c**

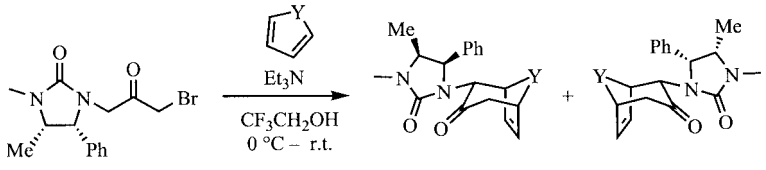
Entry	Bromo ketone[a] X^n see Scheme 2	Diene	Products	Lewis acid	*endo*/*exo*[c] (**a** + **b**)/**c**	*dr*[c] **a**/**b**	Yield[b] [%]
1	**1**	furan	**6a–c**	$LiClO_4$	85:15	67:33	22
2	**1**	furan	**6a–c**	$MgBr_2$	98:2	98:2	40
3	**1**	Cp	**7a–c**	$LiClO_4$	71:29	71:29	45
4	**1**	Cp	**7a–c**	$MgBr_2$	86:14	86:14	50
5	**2**	furan	**8a–c**	$LiClO_4$	88:12	88:12	35
6	**2**	furan	**8a–c**	$MgBr_2$	89:11	89:11	40
7	**2**	Cp	**9a–c**	$LiClO_4$	88:12	88:12	60
8	**2**	Cp	**9a–c**	$MgBr_2$	77:23	77:23	50
9	**3**	furan	**10a–c**	$LiClO_4$	89:11	89:11	25
10	**3**	furan	**10a–c**	$MgBr_2$	77:23	77:23	20
11	**3**	Cp	**11a–c**	$LiClO_4$	83:17	83:17	25
12	**3**	Cp	**11a–c**	$MgBr_2$	83:17	83:17	20

[a] Typical conditions: 1 equiv. of bromo ketone in CH_3CN (0.25 M), 4 equiv. of Lewis acid, 20 equiv. of diene followed by 1.7 equiv. of Et_3N. [b] Combined isolated yield. [c] Measured by GC.

closely related ephedrine-derived imidazolidinone **10**,[13] in which the lone pairs on the carbonyl oxygen should be more basic and thus better adept at chelating with a Lewis acid. Unfortunately reacting this new oxyallyl precursor with furan or cyclopentadiene did not lead to any improvement and only identical diastereomeric ratios as those observed with **1** were obtained. Given this lack of improvement, we abandoned this route, even though it has been shown that replacing the methyl substituent on similar imidazolidinyl auxiliaries have resulted in increased diastereoselection in other processes (Scheme 3).[14]

Examination of Table 1 clearly indicates that increasing the steric bulk of the oxazolidinone five-membered ring results in increased levels of stereoinduction. With this in mind it was felt that if increased steric bulk could be incorporated in the oxazolidinone ring then there was a good chance of getting superior results. Kunieda et al. recently designed two new classes of chiral oxazolidinones, **4a** and **5a**, that are highly sterically congested and conformationally rigid (Scheme 2). These auxiliaries were reported to induce exceptional facial discrimination, particularly in Diels–Alder reactions and organocuprate conjugate addition.[15] Given these successes, it was felt that these types of auxiliaries should be investigated in our [4+3] cycloadditions.

Syntheses of these auxiliaries were achieved according to methods described in the literature [except for the resolution of the tricyclic oxazolidinone **5a**, which was conveniently realized with the readily available (1*S*,4*R*)-camphanic acid chloride,[16] see experimental section for details].[15] Applying our five-step sequence to **4a** and **5a** yielded the expected α-bromo ketones **4** and **5**, respectively, in good overall yields. To our delight, both auxiliary-bound oxyallyl precursors afforded [4+3] cycloadducts with excellent diastereoselectivities, and chemical yields (Table 3). Optimal conditions for cycloaddition of the oxyallyl cation arising from **5** required, however, the increase of the diene amount to 200 equiv. due to a significant amount of 2,2,2-trifluoroethanol by-products. Presumably the amount of diene could be reduced if the solvent was changed to 1,1,1,3,3,3-hexafluoropropanol. *To the best of our knowledge, such facial diastereoselections using chiral nitrogen sub-*



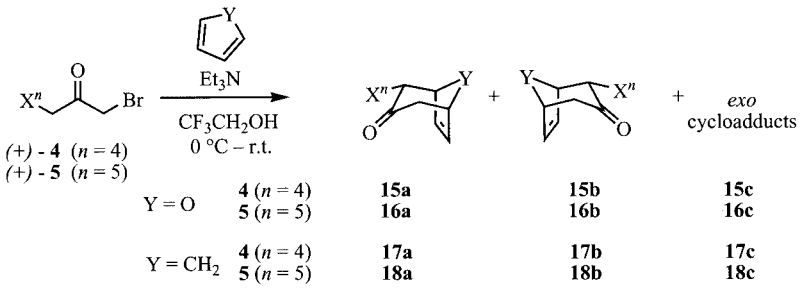
12

Y = O (*endo*:*exo* > 90 : 10) **13a** (21%) **13b** (8%)

Y = CH_2 (*endo*:*exo* > 90 : 10) **14a** (36%) **14b** (20%)

Scheme 3. Imidazolidinone-derived bromo ketone **12**.

Table 3. Diastereoselectivities obtained with **4** and **5**.



Entry	Bromo ketone[a] X^n see Scheme 2	Diene	Products	*endo*/*exo*[c] (**a** + **b**)/**c**	*dr*[c] **a**/**b**	Yield[b] [%]
1	**4**	furan	**15a–c**	93:7	96:4	89
2	**5**	furan	**16a–c**	92:8	97:3	90
3	**4**	Cp	**17a–c**	95:5	> 98:2	94
4	**5**	Cp	**18a–c**	83:17	> 98:2	90

[a] Typical conditions: 1 equiv. of bromo ketone in diene (0.25 M), trifluoroethanol (0.5 M), followed by 1.5 equiv. of Et_3N. [b] Combined isolated yield. [c] 1H NMR ratio and isolated yield.

stituted oxyallyl cations are unprecedented, and it is also noteworthy that examples of [4+3] cycloadditions proceeding in essentially quantitative yields are rare.

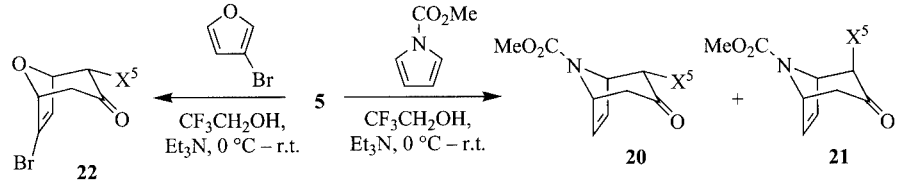
To our surprise, X-ray crystallographic analyses assigned absolute stereochemistries to the cycloadducts **17a** and **18a** consistent with a nonchelated transition state (Figure 2). The reason for this complete reversal of stereochemistry remains unclear. Intervention of some type of chelation by the silicon atom in **5** cannot be ruled out, however, this should be largely unfavoured due to the bulky groups directly linked to this atom, and such a chelation is not possible in **4**. Clearly another as yet unidentified factor must be responsible for this intriguing stereochemical phenomenon. We briefly investigated the possibility of reversing this stereochemical outcome, however, efforts at forcing the reaction to proceed through a chelated pathway by the addition of Lewis acid ($MgBr_2$, $LiClO_4$) remained unsuccessful, because only slight diminutions in diastereoselectivities were obtained.

Given the remarkable ability of the above auxiliaries to effect diastereoselective [4+3] cycloadditon, we were interested in extending this study to other dienes. It was thought that dienes such as 3-bromofuran and methyl 1*H*-pyrrole-1-carboxylate would be of importance because they would provide access to regioselective functionalization of the olefin in the cycloadducts, thus providing a simple "handle" to further manipulate the products, and to the important tropane alkaloid framework, respectively. Reaction of each of these dienes (200 equiv.) with **5** proceeded readily with excellent facial stereoselectivity in favour of the *endo* diastereomers, albeit in modest yields (Table 4).

Structure Determination of the Cycloadducts

The [3.2.1] bicyclic ketones formed were easily determined to be *endo* or *exo* isomers, e.g. **6a–b** and **6c** simply by looking at the ^1H NMR signal of H^1. In *endo* cycloadducts, the dihedral angle between H^1 and H^2, is close to 0°, so H^1 appears as a singlet (axial–equatorial *J* couplings ≈ 0–2 Hz), as opposed to *exo* isomers, in which H^1 appears as a doublet (equatorial–equatorial *J* coupling ≈ 4–5 Hz). It was also usually observed that, like in cyclohexanone compounds, axial α protons are very often found downfield

Table 4. [4+3] Cycloaddition with 3-bromofuran and methyl 1*H*-pyrrole-1-carboxylate.



Entry	Bromo ketone[a] X^5 see Scheme 2	Diene	Products	*endo*/*exo*[c] (**a** + **b**)/**c**	*dr*[c] **a**/**b**	Yield[b] [%]
1	**5**	3-bromofuran	**20–21**	> 98:2	> 98:2	21
2	**5**	methyl 1*H*-pyrrole-1-carboxylate	**22**	90:10	> 98:2	53

[a] Typical conditions: 1 equiv. of bromo ketone in diene (0.25 M), trifluoroethanol (0.5 M), followed by 1.5 equiv. of Et_3N. [b] Combined isolated yield. [c] 1H NMR ratio and isolated yield.

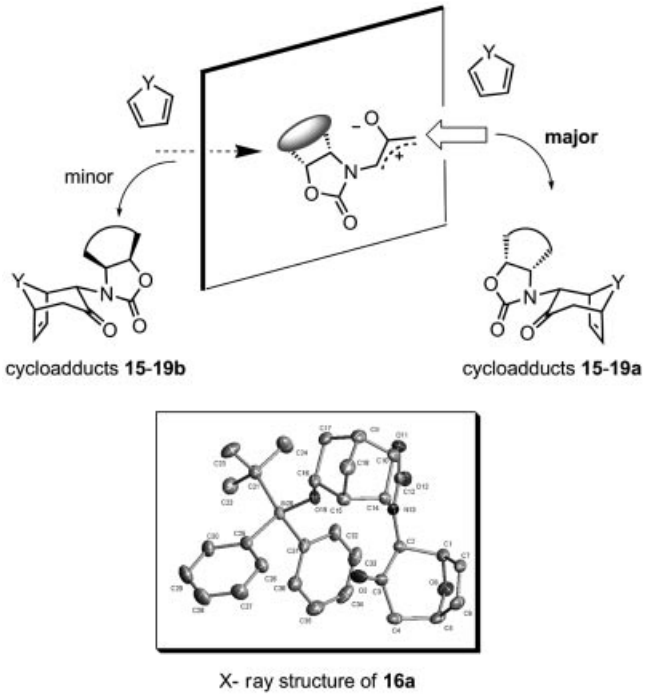


Figure 2. Nonchelated transition state proposed for diastereoselective [4+3] cycloaddition of **4** and **5**.

from equatorial α protons.[17] Assignments of the absolute stereochemistry (unambiguously verified by X-ray crystallography), e.g. **6a** and **6b**, proved to also be possible by common NMR techniques. Strong magnetic anisotropies observed in cycloadducts arising from **1**, have been explained by strong interaction of H^2 with the chiral auxiliary (Figure 3).

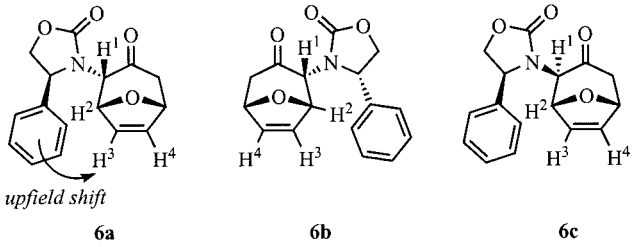


Figure 3. Anisotropic effects on H^3 and H^4.

We corroborated our assumption on the structure of **6a**, by calculation of the ^1H chemical shift of H^3 and H^4 in both **6a** and **6b**, using the GIAO (Gauge Independent Atomic Orbital) method[18] implemented in GAUSSIAN 94.[19] The results (Table 5) were highly consistent with the observed NMR spectrum (see experimental section for details). When the oxazolidinyl bromo ketone **1** was employed, the ^1H NMR spectrum therefore was sufficient to assign both relative and absolute stereochemistries. The olefinic regions of the cycloadducts **13a**–**b** and **14a**–**b** derived from bromo ketone **12** possessed a similar spectroscopic behaviour.

Table 5. Predicted anisotropic effect on H^3 and H^4 chemical shift in cycloadducts **6a** and **6b**.

	Cycloadduct **6a**		Cycloadduct **6b**	
Proton	H^3	H^4	H^3	H^4
Calculated	5.34 ppm	6.13 ppm	7.08 ppm	6.28 ppm
Experimental	5.08 ppm	6.16 ppm	7.58 ppm	6.19 ppm

Conclusions

We have demonstrated that chiral enantiopure nitrogen-stabilized oxyallyl cations can undergo highly diastereoselective [4+3] cycloadditions with common cyclic 1,3-dienes such as furan and cyclopentadiene. Using the bromo ketone **3**, excellent yields of cycloadducts were obtained along with diastereoselectivities as high as 95:5 with furan as a trapping agent, similar to the results obtained by Hsung.[7] The absolute stereochemistries of the resulting bicyclic ketones were consistent with a chelated transition state. Surprisingly, but nevertheless quite fortuitous, a complete reversal of the stereochemical course of the cycloaddition towards a nonchelated pathway was obtained with the enantiopure bromo ketones **4** and **5**. Selective cleavage of oxazolidinone auxiliaries, extension of the scope of the method to substituted oxyallyl precursors, as well as efforts concerning the design of enantioselective processes are currently sustaining our ongoing endeavours.

Experimental Section

General Methods: All reactions were carried out in flame-dried round-bottomed flasks (RBF) or in oven-dried glassware (pyrex) (180 °C, 1 h) unless stated otherwise. Temperatures indicated refer to an external bath. All reaction mixtures were stirred unless stated otherwise. Standard techniques were used for solvent purifications. Diethyl ether, tetrahydrofuran, xylenes, benzene and toluene were distilled over sodium, using benzophenone as an indicator prior to use. Dichloromethane, triethylamine and acetonitrile were distilled over calcium hydride. Tetrahydrofuran, diethyl ether, dichloromethane, methanol, xylene, hexane, benzene and toluene were also available via the use of Grubbs type columns. Air and moisture sensitive reagents were handled via standard techniques. Reagents were purchased from common suppliers and used as received unless stated otherwise. $LiClO_4$ was recrystallized from H_2O, dried overnight at 170 °C in an oven and stored in a dessicator. Diazomethane was prepared according to literature methods.[9b,9c,9d] Analytical thin layer chromatography (TLC) was performed using Merck 60 F-254 silica gel precoated aluminum plates (0.25 mm). Visualization was effected by short-wave UV irradiation, and/or by potassium permanganate or phosphomolybdic acid dip followed by staining on a hot plate. SiO_2 flash chromatography was performed using Silicycle silica gel (30–60 μm particle size) or EM Reagents silica gel 60 (230–400 mesh). Nuclear magnetic resonance (NMR) spectroscopy was performed with a Varian INNOVA 300 MHz or with a Varian UNITY 400 MHz (referred to proton resonance frequency). ^1H NMR spectroscopic data are presented in parts per million (ppm, δ) relative to tetramethylsilane as an internal standard. All proton–proton NMR coupling constants (J) are expressed in Hertz (Hz). ^{13}C NMR spectroscopic data are presented in parts per million (δ) relative to $CDCl_3$ (δ = 77.16 ppm) as an internal standard unless otherwise stated. Infrared spectra (IR) were recorded either with a

Bruker IFS 25 FTIR or a NEXUS 470 FTIR. Main peaks are reported as wavenumbers in cm^{-1}. Mass spectra (MS) were recorded with a Hewlett–Packard 5971 instrument or a Kratos MS50TC mass spectrometer at 70 eV unless otherwise stated, with fragments reported as their m^+/z ratio. Optical rotations were measured with a Perkin–Elmer 241 polarimeter with dichloromethane as solvent unless otherwise stated. Gas chromatographic (GC) analyses were recorded with a Hewlett–Packard 6890 series with a flame ionization detector (FID). Melting points were measured with a Gallenkamp melting-point apparatus and all melting points are uncorrected. X-ray crystallography was performed with a Bruker AXSP4/SMART 1000 diffractometer.

Resolution of (±)-3-Oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one with (+)-(1*S*,4*R*)-Camphanoyl Chloride. Preparation of Enantiopure (–)-(1*R*,2*S*,6*R*,7*S*)-3-Oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one (–)-5a and (+)-(1*S*,2*R*,6*S*,7*R*)-3-Oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one (+)-5a. Step 1: In a 500-mL RBF fitted with a dropping funnel was placed (±)-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one[15b] (7.80 g, 51.6 mmol, 1 equiv.) and THF (65 mL). The slurry was cooled to 0 °C and sodium hydride (60% dispersion in mineral oil, 4.128 g, 103.2 mmol, 2 equiv.) was added in small portions at a rate such that the vigorous foaming was controlled. Stirring was continued for 1 hour at room temp., then the dropping funnel was charged with a solution of (–)-(1*S*,4*R*)-camphanoyl chloride[16] (12.28 g, 56.7 mmol, 1.1 equiv.) in THF (60 mL), which was slowly added dropwise over 30 minutes, producing noticeable heat evolution which was controlled with the aid of a water bath. The reaction mixture was stirred overnight at room temp. and then quenched with MeOH, followed by NH_4Cl. The organic layer was washed with NH_4Cl (1×), brine (1×), dried with Na_2SO_4, and concentrated in vacuo. The resulting crude oil was subjected to SiO_2 chromatography (EtOAc/hexanes, 1:2) to afford 4.485 g (29% yield) and 7.23 g (45% yield) of the two diastereoisomers, both as colourless solids (74% total yield). Data for the least polar diastereoisomer **(1*R*,2*S*,6*R*,7*S*)-5-[(1*S*,4*R*)-7,7-Dimethyl-3-oxo-2-oxabicyclo[2.2.1]hept-1-ylcarbonyl]-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one:** R_f = 0.32 (EtOAc/hexanes, 1:2). $[\alpha]_D^{25}$ = –20.4 (*c* = 5.95, CH_2Cl_2). M.p. 224–226 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2970, 1782, 1693, 1372, 1353, 1283, 1213, 1075, 1020, 929 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.20 (dd, *J* = 3.1, 5.7 Hz, 1 H), 6.13 (dd, *J* = 3.0, 5.6 Hz, 1 H), 4.97 (dd, *J* = 4.2, 8.1 Hz, 1 H), 4.38 (dd, *J* = 3.7, 8.1 Hz, 1 H), 3.52–3.56 (m, 1 H), 3.42–3.46 (m, 1 H), 2.91 (hept, *J* = 4.7 Hz, 1 H), 2.14 (ddt, *J* = 1.8, 4.6, 10.8 Hz, 1 H), 1.89 (ddt, *J* = 2.3, 4.6, 10.7 Hz, 1 H), 1.72–1.82 (m, 2 H), 1.33 (d, *J* = 10.1 Hz, 1 H), 1.20 (s, 3 H), 1.09 (s, 3 H), 1.00 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.0, 168.4, 151.5, 135.3, 134.6, 91.8, 77.0, 59.7, 56.0, 54.0, 46.6, 44.1, 29.3, 17.6, 16.9, 9.8 ppm. LRMS (EI) calcd. for $C_{19}H_{22}NO_5$ (M^+): 331.15, found 331.7. Data for the most polar diastereoisomer **(1*S*,2*R*,6*S*,7*R*)-5-[(1*S*,4*R*)-7,7-Dimethyl-3-oxo-2-oxabicyclo[2.2.1]hept-1-ylcarbonyl]-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one:** R_f = 0.26 (EtOAc/hexanes, 1:2). $[\alpha]_D^{25}$ = +63.8 (*c* = 1.94, CH_2Cl_2). M.p. 232–234 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2979, 1782, 1698, 1366, 1351, 1323, 1284, 1213, 1074, 929 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.25 (dd, *J* = 3.0, 5.8 Hz, 1 H), 6.07 (dd, *J* = 3.0, 5.8 Hz, 1 H), 4.95 (dd, *J* = 4.0, 8.7 Hz, 1 H), 4.77 (dd, *J* = 3.7, 8.7 Hz, 1 H), 3.67 (m, 1 H), 3.30 (m, 1 H), 2.75 (hept, *J* = 4.7 Hz, 1 H), 2.20 (ddt, *J* = 1.8, 4.5, 10.9 Hz, 1 H), 1.90 (ddt, *J* = 2.2, 4.5, 10.8 Hz, 1 H), 1.70–1.79 (m, 2 H), 1.38 (d, *J* = 10.1 Hz, 1 H), 1.19 (s, 3 H), 1.10 (s, 3 H), 1.01 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.1, 167.9, 152.1, 134.8, 134.6, 91.8, 77.0, 59.3, 56.1, 54.0, 46.1, 45.3, 44.5, 29.4, 29.2, 17.4, 16.7, 9.7 ppm.

Step 2: To a 25-mL RBF was added the enantiopure diastereomer from above and THF (135 mL). The clear colourless solution was chilled to 0 °C, and lithium borohydride (4 equiv.) was added in one portion. After 5 minutes, methanol (8 equiv.) was carefully added and the resulting mixture was stirred at room temp. overnight, after which time TLC indicated complete consumption of the starting material. Citric acid (5.6 g) was carefully added in small portions and stirring was continued for an additional 10 minutes. The white solid was filtered and the filtrate was concentrated in vacuo. Purification of the resulting crude solid via column chromatography (CH_2Cl_2/EtOAc, 1:2) afforded the enantiomerically pure oxazolidinones (–)-**5a** and (+)-**5a** as colourless solids in 84% and 82% yield, respectively.

(–)-(1*R*,2*S*,6*R*,7*S*)-3-Oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one and (+)-(1*S*,2*R*,6*S*,7*R*)-3-Oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-one. (–)-5a: R_f = 0.27 (CH_2Cl_2/EtOAc, 1:2). $[\alpha]_D^{25}$ = –71.7 (*c* = 1.1, CH_2Cl_2) (ref.[15b] $[\alpha]_D^{25}$ = –85.5, *c* = 1.0, MeOH). M.p. 181–183 °C (ref.[15b] 189–190 °C). IR ($CDCl_3$): $\tilde{\nu}$ = 3271 (br. s), 2986, 1711, 1392, 1333, 1300, 1239, 1044, 951, 934 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.14 (t, *J* = 1.77 Hz, 2 H), 5.54–5.86 (br. s, 1 H), 4.96 (dd, *J* = 4.2, 8.4 Hz, 1 H), 4.04 (dd, *J* = 3.7, 8.5 Hz, 1 H), 3.21–3.26 (m, 1 H), 2.97–3.02 (m, 1 H), 1.61 (td, *J* = 1.9, 9.8 Hz, 1 H), 1.23 (dquint, *J* = 0.6, 9.9 Hz, 1 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 106.9, 135.2, 133.9, 80.1, 56.4, 46.3, 46.2, 43.8 ppm. HRMS (EI) calcd. for $C_8H_9NO_2$: 151.06332, found: 151.06308. **(+)-5a:** $[\alpha]_D^{25}$ = +73.4 (*c* = 0.75, CH_2Cl_2) (ref.[15b] $[\alpha]_D^{25}$ = +85.3, *c* = 1.0, MeOH).

General Procedure for Formation of the Oxazolidinyl Acetates 1b–5b: A solution of the corresponding substituted 2-oxazolidinone (6.00 mmol) in THF (15 mL) was added to a suspension of NaH (60% dispersion in mineral oil) (320 mg, 13 mmol) in THF (10 mL) at 0 °C. After stirring the mixture at 0 °C for 1 h, ethyl bromoacetate (0.7 mL, 6.3 mmol) was added. The resulting mixture was warmed to room temp. and stirred overnight. The mixture was cooled to 0 °C, quenched with ethanol (1 mL), followed by H_2O (3 mL) and THF was removed in vacuo. The crude mixture was diluted with CH_2Cl_2, washed with brine, dried with $MgSO_4$ and concentrated in vacuo.

Ethyl (*S*)-2-(2-Oxo-4-phenyl-1,3-oxazolidin-3-yl)acetate (1b): Purification by flash chromatography (50% EtOAc/hexanes) yielded ester **1b** (1.19 g, 80%) as a tan liquid. R_f = 0.6 (50% EtOAc/hexanes). IR ($CDCl_3$): $\tilde{\nu}$ = 3476, 2989, 2970, 2244, 1770, 1716, 1420, 1010 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.29 (m, 2 H), 5.07 (dd, *J* = 8.4, 8.4 Hz, 1 H), 4.71 (dd, *J* = 8.7, 8.7 Hz, 1 H), 4.27 (ABq, *J* = 18.0 Hz, 1 H), 4.14 (m, 3 H), 3.37 (ABq, *J* = 18 Hz, 1 H), 1.24 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6, 158.7, 137.0, 129.7, 129.6, 127.5, 70.5, 61.7, 60.3, 43.4, 14.4 ppm. HRMS (EI) calcd. for $C_{12}H_{13}NO_4$ [M^+] 235.2395, found 235.2395.

Ethyl (*S*)-2-(4-Benzyl-2-oxo-1,3-oxazolidin-3-yl)acetate (2b): Purification by flash chromatography (50% EtOAc/hexanes) yielded the ester **2b** (1.26 g, 80%) as a colourless liquid. R_f = 0.6 (50% EtOAc/hexanes). IR ($CDCl_3$): $\tilde{\nu}$ = 2981, 2912, 2257, 1743, 1709, 1427, 1358, 1215, 1094, 1019 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 3 H), 7.18 (m, 2 H), 4.30 (m, 5 H), 4.08 (m, 1 H), 3.71 (d, *J* = 18.0 Hz, 1 H), 3.08 (dd, *J* = 5.4, 13.6 Hz, 1 H), 2.80 (dd, *J* = 7.8, 13.6 Hz, 1 H), 1.29 (t, *J* = 7.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 158.8, 135.7, 129.3, 129.2, 127.5, 67.8, 61.8, 56.6, 44.1, 39.0, 14.4 ppm. HRMS (EI) calcd. for $C_{13}H_{15}NO_4$ [M^+] 249.2664, found 249.2668.

Ethyl (*S*)-2-(4-*tert*-Butyl-2-oxo-1,3-oxazolidin-3-yl)acetate (3b): Purification by flash chromatography yielded the ester **3b** (1.16 g, 85%) as a colourless solid. R_f = 0.6 (50% EtOAc/hexanes). M.p. 72–74 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3674, 3472, 3408, 2967, 2874, 2254,

1763, 1699, 1482, 1427, 1371, 1026 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.41 (ABq, J = 18.0 Hz, 1 H), 4.35 (dd, J = 8.7, 8.7 Hz, 1 H), 4.20 (m, 2 H), 3.84 (ABq, J = 18.0 Hz, 1 H), 3.57 (dd, J = 4.8, 8.7 Hz, 1 H), 1.26 (t, J = 7.3 Hz, 3 H), 0.98 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.0, 160.4, 65.5, 64.3, 61.8, 47.3, 34.8, 25.7, 14.4 ppm. HRMS (EI) calcd. for $C_{10}H_{17}NO_4$ [M^+] 215.2493, found 215.2491.

(+)-Methyl (4*R*,5*S*)-2-(2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl)acetate (4b): Purification by SiO_2 column chromatography gave **4b** (1.457 g, 93%) as a colourless solid. R_f = 0.5 (EtOAc/hexanes, 1:2). $[\alpha]_D^{25}$ = +69 (c = 1.1, CH_2Cl_2). M.p. 197–199 °C. IR (neat): $\tilde{\nu}$ = 3020, 1744, 1524, 1420, 1228, 1200, 924 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.39 (m, 2 H), 7.24 (m, 6 H), 4.55 (d, J = 10.1 Hz, 1 H), 4.32 (d, J = 18.9, 1 Hz, 1 H), 3.88 (d, J = 10.2 Hz, 1 H), 3.84 (d, J = 19.0 Hz, 1 H), 3.71 (s, 3 H), 2.08 (s, 3 H), 2.03 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 159.3, 142.8, 141.5, 140.5, 139.9, 126.9, 126.8, 126.6, 123.9, 122.8, 122.6, 122.1, 81.2, 64.5, 52.5, 46.5, 46.2, 45.6, 15.9, 14.8 ppm. LRMS-FAB: [M^+] 363.4.

(–)-Methyl (1*R*,2*S*,6*R*,7*R*,8*R*)-2-[8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]acetate (5b): Purification by column chromatography afforded the ester **5b** (412 mg, 79%) as a colourless solid. R_f = 0.42 (CH_2Cl_2/EtOAc, 20:1). $[\alpha]_D^{25}$ = –29.6 (c = 1.01, CH_2Cl_2). M.p. 115–118 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2957, 1749, 1429, 1212, 1133, 1109, 1072, 1033, 1012 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.67 (m, 4 H), 7.33–7.46 (m, 6 H), 4.76–4.83 (ddd, J = 1.4, 4.8, 10.5 Hz, 1 H), 4.49–4.57 (ABq, J = 18.1 Hz, 1 H), 4.24–4.32 (m, 1 H), 4.15–4.22 (ddd, J = 1.6, 4.3, 10.5 Hz, 1 H), 3.73–3.80 (ABq, J = 17.1 Hz, 1 H), 3.73 (s, 3 H), 2.46–2.52 (m, 2 H), 1.33–1.51 (m, 3 H), 1.17–1.24 (m, 1 H) 1.08 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 168.5, 136.1, 135.7, 133.8, 133.5, 130.1, 129.9, 127.9, 127.9, 76.6, 75.0, 58.2, 52.3, 45.4, 43.8, 40.8, 33.2, 28.9, 27.3 (3 C), 19.1 ppm. HRMS (EI) calcd. for $C_{23}H_{24}NO_5Si$ [$M^+ - C_4H_9$] 422.1433, found 422.1433.

General Procedure for Formation of the Oxazolidinyl Acetic Acids 1c–5c: Sodium hydroxide (360 mg, 9.00 mmol) was dissolved in H_2O (2.2 mL) and added to a solution of the corresponding ester (4.50 mmol) in THF (9.0 mL). The mixture was stirred at room temperature overnight and THF was removed in vacuo. The aqueous layer was washed with CH_2Cl_2 (10 mL) and then acidified with 6 M HCl. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL) with vigorous stirring for 30 min prior to each extraction. The combined organic layers was washed with brine, dried with $MgSO_4$ and concentrated in vacuo.

(*S*)-2-(2-Oxo-4-phenyl-1,3-oxazolidin-3-yl)acetic Acid (1c): Carboxylic acid **1c** (796 mg, 80%) was isolated as a colourless solid. R_f = 0.2 (75% EtOAc/hexanes). M.p. 106–108 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3036, 2254, 1710, 1747, 1417, 1200, 1096, 1029 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 5.75 (s, 1 H), 5.06 (dd, J = 8.3, 8.3 Hz, 1 H), 4.71 (dd, J = 8.5, 8.5 Hz, 1 H), 4.34 (d, J = 18.0 Hz, 1 H), 4.18 (dd, J = 8.3, 8.3 Hz, 1 H), 3.44 (d, J = 18.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6, 159.4, 136.6, 129.8, 127.6, 70.9, 60.4, 43.2 ppm. HRMS (EI) calcd. for $C_{11}H_{11}NO_4$ [M^+] 221.2126, found 221.2120.

(*S*)-2-(4-Benzyl-2-oxo-1,3-oxazolidin-3-yl)acetic Acid (2c): Carboxylic acid **2c** (847 mg, 75%) was isolated as a colourless solid. R_f = 0.2 (75% EtOAc/hexanes). M.p. 134–136 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2996, 2257, 1737, 1748, 1426, 1362, 1220 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 10.06 (br. s, 1 H) 7.38 (m, 3 H), 7.18 (m, 2 H), 4.33 (m, 3 H), 4.11 (dd, J = 6.8, 6.8 Hz, 1 H), 3.78 (d, J = 18.3 Hz, 1 H), 3.10 (dd, J = 13.5, 5.3 Hz, 1 H), 2.81 (dd, J = 13.5, 7.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.1, 159.3, 135.3, 129.3, 129.2, 127.6, 68.1, 56.8, 43.9, 39.9 ppm. HRMS (EI) calcd. for $C_{12}H_{13}NO_4$ [M^+] 235.2395, found 235.2399.

(*S*)-2-(4-*tert*-Butyl-2-oxo-1,3-oxazolidin-3-yl)acetic Acid (3c): Carboxylic acid **3c** (724 mg, 80%) was isolated as a colourless solid. R_f = 0.3 (75% EtOAc/hexanes). M.p. 166–168 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3110, 2967, 2874, 2647, 1756, 1691, 1483, 1428, 1400, 1242, 1187 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.01 (br. s, 1 H), 4.48 (d, J = 18.3 Hz, 1 H), 4.39 (dd, J = 9.0, 9.0 Hz, 1 H), 4.19 (dd, J = 9.0, 4.9 Hz, 1 H), 3.93 (d, J = 18.3 Hz, 1 H), 3.62 (dd, J = 9.0, 4.9 Hz, 1 H), 1.01 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 160.9, 65.9, 64.6, 47.2, 34.8, 25.8 ppm. HRMS (EI) calcd. for $C_9H_{15}NO_4$ [M^+] 201.2224, found 201.2221.

(+)-(4*R*,5*S*)-2-(2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl)acetic Acid (4c): Carboxylic acid **4c** (1.22 g, 97%) was isolated as a white solid which was of sufficient purity for use in subsequent steps. $[\alpha]_D^{25}$ = +67.1 (c = 1.5, CH_2Cl_2). M.p. 226–229 °C (dec). IR (neat): $\tilde{\nu}$ = 3018, 2970, 1746, 1526, 1416, 1206, 1042, 932 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.36 (m, 2 H), 7.23 (m, 6 H), 4.55 (d, J = 9.1 Hz, 1 H), 4.28 (d, J = 18.3 Hz, 1 H), 3.90 (d, J = 18.4, 1 H), 3.86 (d, J = 9.1 Hz, 1 H), 2.06 (s, 3 H), 2.03 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 173.2, 159.9, 143.0, 141.7, 140.7, 140.2, 127.4, 127.3, 127.2, 127.0, 124.2, 123.2, 123.0, 122.5, 81.8, 65.1, 46.8, 46.5, 45.9, 16.2, 15.1 ppm. LRMS-FAB: [M^+] 348.5.

(–)-(1*R*,2*S*,6*R*,7*R*,8*R*)-2-[8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]acetic Acid (5c): Carboxylic acid **5c** (363 mg, 95%) was isolated as a colourless solid which was of sufficient purity for use in the next step. $[\alpha]_D^{25}$ = –43.0 (c = 0.59, CH_2Cl_2). M.p. 218–219 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3071, 2961, 2857, 1751, 1462, 1427, 1264, 1184, 1129, 1141, 1112, 1071, 1036, 1017 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.67 (m, 4 H), 7.37–7.49 (m, 6 H), 4.77–4.85 (dd, J = 4.7, 10.5 Hz, 1 H), 4.50–4.59 (d, J = 18.4 Hz, 1 H), 4.25–4.34 (m, 1 H), 4.14–4.22 (dd, J = 3.8, 10.9 Hz, 1 H), 3.75–3.85 (d, J = 18.6 Hz, 1 H), 2.46–2.54 (m, 2 H), 1.34–1.52 (m, 3 H), 1.19–1.28 (m, 1 H) 1.08 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 158.8, 136.1, 135.7, 133.7, 133.5, 130.1, 130.0, 128.0, 127.9, 77.4, 77.9, 74.9, 58.4, 45.5, 43.8, 40.7, 33.2, 28.9, 27.3 (3 C), 19.1 ppm. HRMS (EI) calcd. for $C_{22}H_{22}NO_5Si$ [$M^+ - C_4H_9$] 408.1267, found: 408.1272.

General Procedure for the Formation of the Oxazolidinyl Diazo Ketones 1e–5e: Oxalyl chloride (0.31 mL, 3.5 mmol) was added to a solution of the corresponding oxazolidinyl acetic acid (2.3 mmol) in THF (9 mL). The mixture was heated at reflux for 1 h, and then all volatile materials were removed in vacuo. The acid chloride was immediately re-dissolved in THF (9 mL) and added dropwise to a solution of diazomethane in ether cooled to 0 °C. The reaction was warmed to room temperature and stirred overnight to allow for evaporation of excess CH_2N_2. The solvent was removed in vacuo.

(*S*)-2-(2-Oxo-4-phenyl-1,3-oxazolidin-3-yl)acetyl Chloride (1d): An aliquot was removed from the crude reaction mixture for ^1H NMR analysis. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 5.02 (dd, J = 8.3, 8.3 Hz, 1 H), 4.75 (dd, J = 8.8, 8.8 Hz, 1 H), 4.70 (ABq, J = 19.0 Hz, 1 H), 4.23 (dd, J = 8.8, 8.8 Hz, 1 H), 3.81 (ABq, J = 19.0 Hz, 1 H) ppm.

(*S*)-3-(3-Diazo-2-oxopropyl)-4-phenyl-1,3-oxazolidin-2-one (1e): Purification by flash chromatography (75% EtOAc/hexanes) gave the diazo ketone **1e** (446 mg, 79%) as a yellow oil. R_f = 0.4 (50% EtOAc/hexanes). IR ($CDCl_3$): $\tilde{\nu}$ = 3482, 3102, 2911, 2246, 2109, 1737, 1648, 1415, 1362 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 5.29 (br. s, 1 H), 5.05 (dd, J = 8.3, 8.3 Hz, 1 H), 4.73 (dd, J = 8.8, 8.8 Hz, 1 H), 4.25 (ABq, J = 17.0 Hz, 1 H), 4.19 (dd, J = 8.3, 8.3 Hz, 1 H), 3.36 (ABq, J =

17.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.0, 158.8, 137.1, 129.7, 129.6, 127.5, 70.5, 60.7, 54.1, 48.6 ppm. HRMS calcd. for $C_{12}H_{11}N_3O_3$ [M^+] 245.0800, found 245.0878.

(*S*)-2-(4-Benzyl-2-oxo-1,3-oxazolidin-3-yl)acetyl Chloride (2d): An aliquot was removed from the crude reaction mixture for ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (m, 3 H), 7.18 (m, 2 H), 4.58 (ABq, *J* = 19.0 Hz, 1 H), 4.42 (dd, *J* = 8.3, 8.3 Hz, 1 H), 4.29 (m, 1 H), 4.14 (dd, *J* = 6.4, 8.3 Hz, 1 H), 4.05 (ABq, *J* = 19.0 Hz, 1 H), 3.04 (dd, *J* = 6.6, 13.7 Hz, 1 H), 2.87 (dd, *J* = 7.3, 13.7 Hz, 1 H) ppm.

(*S*)-4-Benzyl-3-(3-diazo-2-oxopropyl)-1,3-oxazolidin-2-one (2e): Purification by flash chromatography (75% EtOAc/hexanes) gave the diazo ketone **2e** (447 mg, 75%) as a yellow solid. R_f = 0.4 (50% EtOAc/hexanes). M.p. 101–102.5 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3112, 2920, 2254, 2113, 1750, 1653, 1430, 1377, 1324, 1144, 1102 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (m, 3 H), 7.08 (m, 2 H), 5.34 (br. s, 1 H), 4.36 (dd, *J* = 8.3, 8.3 Hz, 1 H), 4.27 (m, 1 H), 4.20 (ABq, *J* = 17.1 Hz, 1 H), 4.11 (dd, *J* = 5.8, 8.3 Hz, 1 H), 3.71 (ABq, *J* = 17.1 Hz, 1 H), 3.08 (dd, *J* = 4.9, 13.4 Hz, 1 H), 2.73 (dd, *J* = 8.4, 13.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.2, 158.8, 135.5, 129.2(7), 129.2(6), 127.5, 67.8, 57.1, 54.1, 49.6, 39.0 ppm. $C_{13}H_{13}N_3O_3$: calcd. C 60.21, H 5.06, N 16.21; found C 60.08, H 5.05, N 15.96.

(*S*)-2-(4-*tert*-Butyl-2-oxo-1,3-oxazolidin-3-yl)acetyl Chloride (3d): An aliquot was removed from the crude reaction mixture for ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.87 (ABq, *J* = 19.0 Hz, 1 H), 4.42 (dd, *J* = 9.0, 9.0 Hz, 1 H), 4.34 (ABq, *J* = 19.0 Hz, 1 H), 4.23 (dd, *J* = 5.1, 9.0 Hz, 1 H), 3.62 (dd, *J* = 5.1, 8.8 Hz, 1 H), 1.01 (s, 9 H) ppm.

(*S*)-4-*tert*-Butyl-3-(3-diazo-2-oxopropyl)-1,3-oxazolidin-2-one (3e): Purification by flash chromatography (75% EtOAc/hexanes) gave the diazo ketone **3e** (414 mg, 80%) as a yellow solid. R_f = 0.4 (50% EtOAc/hexanes). M.p. 76–78 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3107, 2958, 2246, 2108, 1744, 1652, 1479, 1422, 1376, 1324, 1244, 1146 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.47 (br. s, 1 H), 4.39 (dd, *J* = 9.0, 9.0 Hz, 1 H), 4.36 (ABq, *J* = 17.3 Hz, 1 H), 4.20 (dd, *J* = 3.9, 9.0 Hz, 1 H), 3.93 (ABq, *J* = 17.3 Hz, 1 H), 3.57 (dd, *J* = 3.9, 9.0 Hz, 1 H), 0.99 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.5, 160.6, 65.5, 64.9, 54.1, 52.8, 34.9, 25.8 ppm. HRMS calcd. for $C_{10}H_{15}N_3O_3$ [M^+] 225.1113, found 225.1117.

(4*R*,5*S*)-2-(2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl)acetyl Chloride (4d): An aliquot was removed from the crude reaction mixture for ^{1}H NMR analysis. ^{1}H NMR (300 MHz): δ = 7.38 (m, 2 H), 7.24 (m, 6 H), 4.72 (d, *J* = 18.5 Hz, 1 H), 4.58 (d, *J* = 9.2 Hz, 1 H), 4.29 (d, *J* = 18.1 Hz, 1 H), 3.88 (d, *J* = 9.1 Hz, 1 H), 2.07 (s, 3 H), 2.03 (s, 3 H) ppm.

(4*R*,5*S*)-3-(3-Diazo-2-oxopropyl)-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-2-one (4e): Purification by SiO_2 column chromatography (EtOAc/hexanes, 2:3) gave **4e** as a highly crystalline yellow solid. R_f = 0.3 (EtOAc/hexane, 1:2). $[\alpha]_D^{25}$ = +101.5 (*c* = 1.1, $CHCl_3$). M.p. 220–222 °C (dec). IR (neat): $\tilde{\nu}$ = 3030, 2970, 2106, 1750, 1644, 1524, 1430, 1370, 1228, 920 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.38 (m, 2 H), 7.24 (m, 6 H), 5.14 (s, 1 H), 4.55 (d, *J* = 9.3 Hz, 1 H), 4.00 (d, *J* = 18.5 Hz, 1 H), 3.94 (d, *J* = 18.3 Hz, 1 H), 3.84 (d, *J* = 9.2 Hz, 1 H), 2.08 (s, 3 H), 2.03 (s, 3 H) ppm ^{13}C NMR (75 MHz): δ = 190.1, 159.8, 142.9, 141.8, 141.0, 140.4, 127.4, 127.3, 127.28, 126.5, 124.4, 123.4, 122.9, 122.6, 81.7, 66.5, 54.7, 53.6, 46.5, 46.0, 16.2, 15.0 ppm. LRMS-FAB: [M^+] 348.5.

(1*R*,2*S*,6*R*,7*R*,8*R*)-2-[8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]acetyl Chloride (5d): An aliquot was removed from the reaction mixture for ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.67 (m, 4 H), 7.35–7.49 (m, 6 H), 4.85–4.93 (ABq, *J* = 19.2 Hz, 1 H), 4.78–4.86 (dd, *J* = 4.4, 10.2 Hz, 1 H), 4.28–4.37 (m, 1 H), 4.07–4.16 (m, 1 H), 4.07–4.16 (ABq, *J* = 19.1 Hz, 1 H), 2.45–2.56 (m, 2 H), 1.19–1.59 (m, 4 H), 1.10 (s, 9 H) ppm.

(–)-(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-Butyl(diphenyl)silanyloxy-5-(3-diazo-2-oxopropyl)-3-oxa-5-azatricyclo[5.2.1.02,6]decan-4-one (5e): Purification by flash chromatography of the resulting crude oil (CH_2Cl_2/EtOAc, 4:1) afforded the diazo ketone **5e** (333 mg, 88% yield over 2 steps) as a colourless amorphous solid. R_f = 0.28 (CH_2Cl_2/EtOAc, 5:1). $[\alpha]_D^{25}$ = –12.0 (*c* = 0.71, CH_2Cl_2). M.p. 104–105 °C (dec.). IR ($CDCl_3$): $\tilde{\nu}$ = 3480, 3071, 2959, 2858, 2108, 1750, 1651, 1471, 1428, 1373, 1106, 1072, 1032, 884 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.66 (m, 4 H), 7.34–7.47 (m, 6 H), 5.21–5.29 (br. s, 1 H), 4.75–4.83 (dd, *J* = 0.8, 4.1, 10.3 Hz, 1 H), 4.36–4.38 (ABq, *J* = 16.7 Hz, 1 H), 4.26–4.35 (m, 1 H), 4.12–4.20 (ddd, *J* = 1.0, 3.8, 10.1 Hz, 1 H), 3.58–3.69 (ABq, *J* = 17.5 Hz, 1 H), 2.47–2.55 (m, 2 H), 1.17–1.55 (m, 4 H), 1.08 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.1, 158.3, 136.1 (2 C), 135.7 (2 C), 133.9, 133.4, 131.0, 130.0, 128.9, 127.9 (2 C), 76.7, 74.9, 58.6, 53.8, 51.2, 43.8, 40.8, 33.2, 29.0, 27.3 (3 C), 19.2 ppm. HRMS (EI) calcd. for $C_{23}H_{22}NO_4Si$ [$M^+ - C_4H_9 - N_2$] 404.1318, found: 404.1301.

General Procedure for Formation of the Oxazolidinyl Bromo Ketones: HBr (48% aq.) (0.29 mL, 5.40 mmol) was added dropwise to a solution of the corresponding diazo ketone (0.90 mmol) in CH_2Cl_2 (3.6 mL) cooled to 0 °C (vigorous nitrogen evolution). After 1 h, (monitored by TLC) the reaction was quenched with satd. $NaHCO_3$ (0.5 mL) and washed with brine (1 mL). The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2 × 2 mL). The combined organic layers were dried with $MgSO_4$ and concentrated.

(*S*)-3-(3-Bromo-2-oxopropyl)-4-phenyl-1,3-oxazolidin-2-one (1): Bromo ketone **1** (195 mg, 73%) was isolated as a yellow solid. R_f = 0.6 (50% EtOAc/hexanes). M.p. 92–94 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2911, 2248, 1753, 1706, 1415, 1357, 910 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 5.00 (dd, *J* = 8.3, 8.3 Hz, 1 H), 4.75 (dd, *J* = 8.8, 8.8 Hz, 1 H), 4.55 (ABq, *J* = 19.0 Hz, 1 H), 4.19 (dd, *J* = 8.8, 8.8 Hz, 1 H), 3.87 (s, 2 H), 3.77 (ABq, *J* = 19.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.9, 158.7, 136.9, 129.8, 127.5, 70.6, 60.3, 48.7, 31.2 ppm. HRMS calcd. for $C_{12}H_{12}BrNO_3$ [M^+] 297.0000, found 298.0065. Note: This compound was observed to be unstable.

(*S*)-4-Benzyl-3-(3-bromo-2-oxopropyl)-1,3-oxazolidin-2-one (2): The bromo ketone **2** (210 mg, 75%) was isolated as a yellow solid. R_f = 0.6 (50% EtOAc/hexanes). M.p. 99.5–101.5 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3005, 2960, 2914, 2242, 1751, 1711, 1426, 1358, 1221, 1090, 1039 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.19 (m, 2 H), 4.48 (ABq, *J* = 19.0 Hz, 1 H), 4.44 (dd, *J* = 7.5 Hz, 1 H), 4.27 (dd, *J* = 7.3 Hz, 1 H), 4.10 (dd, *J* = 6.6 Hz, 1 H), 4.04 (ABq, *J* = 18.6 Hz, 1 H), 3.77 (s, 2 H), 3.01 (dd, *J* = 6.1, 13.4 Hz, 1 H), 2.85 (dd, *J* = 6.1, 13.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.9, 158.8, 135.7, 129.3, 129.1, 127.6, 68.1, 56.5, 49.5, 39.5, 31.2 ppm. $C_{13}H_{14}BrNO_3$: calcd. C 50.16, H 4.54, N 4.50; found C 49.66, H 4.69, N 4.46. HRMS calcd. for $C_{13}H_{14}BrNO_3$ [M^+] 311.0157, found 311.0158.

(*S*)-3-(3-Bromo-2-oxopropyl)-4-*tert*-butyl-1,3-oxazolidin-2-one (3): The bromo ketone **3** (199 mg, 80%) was isolated in as a yellow solid. R_f = 0.6 (50% EtOAc/hexanes). M.p. 88–90 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3464, 3405, 2966, 2877, 2253, 1747, 1713, 1480, 1424, 1363, 1223, 1188, 1092, 1052 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.72 (ABq, *J* = 18.8 Hz, 1 H), 4.46 (dd, *J* = 9.0, 9.0 Hz, 1 H), 4.38 (ABq, *J* = 18.8 Hz, 1 H), 4.24 (dd, *J* = 4.4, 9.0 Hz, 1 H), 3.94 (m,

1 H), 3.53 (dd, J = 4.4, 9.0 Hz, 1 H), 0.99 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.3, 160.4, 65.8, 64.4, 52.7, 34.9, 31.2, 25.8 ppm. $C_{10}H_{16}O_3NBr$: calcd. C 43.18, H 5.80, N 5.04; found C 43.42, H 5.80, N 5.04. HRMS calcd. for $C_{10}H_{16}BrNO_3$ [M^+] 277.0313, found 277.0311.

(+)-(4*R*,5*S*)-3-(3-Bromo-2-oxopropyl)-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-2-one (4): The bromo ketone **4** (49 mg, 86%) was isolated as a fine yellow powder. Compound **4** was sensitive to chromatography so it was used immediately in subsequent cycloaddition reactions. R_f = 0.4 (EtOAc/hexanes, 2:3). $[\alpha]_D^{25}$ = +32.3 (c = 1.4, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3036, 2942, 1744, 1542, 1436, 1210, 1010, 926 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.38 (m, 2 H), 7.23 (m, 6 H), 4.61 (d, J = 9.3 Hz, 1 H), 4.43 (d, J = 18.5 Hz, 1 H), 4.33 (d, J = 18.3 Hz, 1 H), 3.94 (d, J = 9.2 Hz, 1 H), 3.83 (s, 2 H), 2.09 (s, 3 H), 2.01 (s, 3 H) ppm. ^{13}C NMR (75 MHz): δ = 196.9, 159.5, 142.8, 141.6, 140.7, 140.1, 127.1, 127.0, 126.7, 124.0, 122.9, 122.8, 122.2, 81.5, 65.1, 52.2, 46.3, 45.7, 31.3, 16.0, 14.9 ppm.

(–)-(1*R*,2*S*,6*R*,7*R*,8*R*)-5-(3-Bromo-2-oxo-propyl)-8-*tert*-butyl(diphenyl)silanyloxy-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (5): The bromo ketone **5** (507 mg, 93% yield) was isolated as a white-brown solid. The material obtained was usually of sufficient purity for direct use in subsequent steps. Purification by flash chromatography (CH_2Cl_2/EtOAc, 5:1) afforded the bromo ketone **5** (464 mg, 85%) as a colourless solid. R_f = 0.47 (CH_2Cl_2/EtOAc, 20:1). $[\alpha]_D^{25}$ = –22.5 (c = 0.67, CH_2Cl_2). M.p. 130–132 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2961, 1747, 1428, 1343, 1262, 1111, 1072, 1032, 884, 858, 821 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.67 (m, 4 H), 7.34–7.47 (m, 6 H), 4.82 (dd, J = 4.9, 10.4 Hz, 1 H), 4.68 (ABq, J = 18.9 Hz, 1 H), 4.29–4.45 (m, 1 H), 4.14 (dd, J = 3.5, 5.8 Hz, 1 H), 4.13 (ddd, J = 1.6, 4.3, 8.9 Hz, 1 H), 4.11 (ABq, J = 18.9 Hz, 1 H), 3.75 (s, 2 H), 2.49–2.55 (m, 1 H), 2.41–2.47 (m, 1 H), 1.54–1.59 (m, 2 H), 1.18–1.42 (m, 2 H), 1.11 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.8, 158.4, 136.1, 135.7, 134.0, 133.4, 131.0, 130.1, 130.0, 128.9, 128.0, 127.9, 76.8, 74.9, 68.3, 58.1, 51.0, 43.9, 40.8, 33.2, 31.2, 29.0, 27.3 (3 C), 19.2 ppm. HRMS (EI) calcd. for $C_{23}H_{23}BrNO_4Si^{79}$ [$M^+ - C_4H_9$] 484.0580, found 484.0577.

General Procedure for Cycloaddition Using CF_3CH_2OH/Et_3N Conditions: The corresponding diene (10 equiv. or 200 equiv.) was added to a solution of the bromo ketone (0.24 mmol) in 2,2,2-trifluoroethanol (0.92 mL) cooled to 0 °C. Et_3N (0.05 mL, 0.39 mmol) was then added dropwise. The resulting mixture was slowly warmed to room temperature and stirred for 12 h. The organic layer was diluted with CH_2Cl_2, washed with brine, dried with $MgSO_4$ and concentrated in vacuo.

General Procedure for Cycloaddition Using $LiClO_4$/Et_3N Conditions: The corresponding diene (10 equiv.) was added to a solution of the bromo ketone (0.23 mmol) and $LiClO_4$ (98 mg, 0.92 mmol) in freshly distilled acetonitrile (0.92 mL) cooled to 0 °C. Et_3N (0.05 mL, 0.39 mmol) was then added dropwise and the resulting mixture was slowly warmed to room temperature and stirred for 12 h. The organic layer was diluted with CH_2Cl_2, washed with brine, dried with $MgSO_4$ and concentrated in vacuo.

General Procedure for Cycloaddition Using $MgBr_2$/Et_3N Conditions: The corresponding diene (10 equiv.) was added to a solution of the bromo ketone (0.23 mmol) and $MgBr_2$ (169 mg, 0.92 mmol) in freshly distilled acetonitrile (0.92 mL) cooled to 0 °C. Et_3N (0.05 mL, 0.39 mmol) was then added dropwise and the resulting mixture was slowly warmed to room temperature and stirred for 12 h. The organic layer was diluted with CH_2Cl_2, washed with brine, dried with $MgSO_4$ and concentrated in vacuo.

(1*R*,2*S*,5*R*)-2-[(4*S*)-2-Oxo-4-phenyl-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (6a): Cycloaddition of **1** with furan was performed according to the general procedure described above. Purification by flash chromatography (40% EtOAc/hexanes) followed by recrystallization (EtOAc/hexanes) gave cycloadduct **6a** as a colourless solid. R_f = 0.3 (50% EtOAc/hexanes). M.p. 166–168 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3405, 2969, 2244, 1738, 1712, 1407, 1355, 1215, 1100 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 6.16 (dd, J = 1.7, 6.1 Hz, 1 H), 5.08 (dd, J = 1.7, 6.1 Hz, 1 H), 4.94 (m, 2 H), 4.82 (dd, J = 4.5, 9.0 Hz, 1 H), 4.78 (dd, J = 1.7, 4.5 Hz, 1 H), 4.73 (dd, J = 8.2, 9.0 Hz, 1 H), 4.13 (dd, J = 4.5, 8.2 Hz, 1 H), 2.88 (dd, J = 5.1, 15.7 Hz, 1 H), 2.46 (d, J = 15.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.1, 159.6, 140.6, 135.0, 132.0, 129.9, 129.4, 126.5, 80.3, 78.4, 71.4, 67.2, 57.9, 46.0 ppm. $C_{16}H_{15}NO_4$: calcd. C 67.36, H 5.30, N 4.91; found C 67.09, H 5.21, N 4.93.

(1*S*,2*R*,5*S*)-2-[(4*S*)-2-Oxo-4-phenyl-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (6b): Purification by flash chromatography (40% EtOAc/hexanes) gave **6b** as a mixture with compound **6a**. R_f = 0.3 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 6.58 (dd, J = 1.7, 6.1 Hz, 1 H), 6.28 (dd, J = 1.7, 6.1 Hz, 1 H), 4.99 (m, 1 H), 4.90 (m, 3 H), 4.75 (m, 1 H), 3.78 (d, J = 4.6 Hz, 1 H), 2.75 (dd, J = 5.1, 15.6 Hz, 1 H), 2.46 (d, J = 15.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.5, 160.8, 137.4, 133.9, 132.4, 129.9, 129.8, 127.6, 81.0, 78.3, 70.4, 66.4, 64.2, 45.7 ppm.

(1*R*,2*S*,5*R*)-2-[(4*S*)-4-Benzyl-2-oxo-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (7a) and (1*S*,2*R*,5*S*)-2-[(4*S*)-4-Benzyl-2-oxo-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (7b): Cycloaddition of **2** with furan was performed according to the general procedure described above. These compounds were isolated as a mixture in a 2:1 ratio via flash chromatography (40% EtOAc/hexanes). Upon recrystallization (EtOAc/hexanes) enhancement of compound **7a** was possible but complete purification was not obtained. R_f = 0.3 (50% EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (m, 6 H), 7.24 (m, 4 H), 6.55 (dd, J = 6.1, 1.9 Hz, 1 H **7b**), 6.46 (m, 2 H **7a**), 6.39 (dd, J = 6.1, 1.7 Hz, 1 H **7b**), 5.17 (dd, J = 4.4, 1.2 Hz, 1 H **7a**), 5.10 (m, 3 H), 4.66 (d, J = 4.4 Hz, 1 H **7a**), 4.28 (m, 3 H), 4.09 (m, 4 H), 2.90 (m, 6 H), 2.54 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6, 158.7, 135.6, 135.4, 133.8, 133.3, 132.3, 129.4, 129.3, 129.2, 129.1, 127.6, 111.7, 111.6, 80.9, 80.4, 78.4, 67.8, 67.7, 67.0, 59.2, 56.4, 45.7, 40.4, 40.8 ppm. HRMS calcd. for $C_{17}H_{17}NO_4$ [M^+] 299.1157, found 299.1157.

(1*R*,2*S*,5*R*)-2-[(4*S*)-4-*tert*-Butyl-2-oxo-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (8a): Cycloaddition of **3** with furan was performed according to the general procedure described above. Purification by flash chromatography (40% EtOAc/hexanes) followed by recrystallization (EtOAc/hexanes) gave cycloadduct **8a** as a colourless solid. R_f = 0.3 (50% EtOAc/hexanes). M.p. 239–241 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2966, 2253, 1758, 1713, 1480, 1416, 1363, 1224, 1171, 1140 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.63 (d, J = 6.1 Hz, 1 H), 6.27 (d, J = 6.1 Hz, 1 H), 5.20 (d, J = 4.1 Hz, 1 H), 5.04 (d, J = 4.6 Hz, 1 H), 4.50 (dd, J = 9.0, 9.0 Hz, 1 H), 4.21 (dd, J = 3.6, 9.0 Hz, 1 H), 4.11 (d, J = 4.1 Hz, 1 H), 3.30 (dd, J = 3.4, 9.0 Hz, 1 H), 2.81 (dd, J = 5.1, 16.1 Hz, 1 H), 2.51 (d, J = 16.3 Hz, 1 H), 1.01 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6, 159.4, 134.1, 131.6, 81.1, 78.4, 71.3, 68.6, 65.3, 45.6, 35.1, 25.5 ppm. $C_{16}H_{15}NO_4$: calcd. C 63.36, H 7.22, N 5.28; found C 63.19, H 7.32, N 5.07.

(1*R*,2*S*,5*R*)-2-[(4*S*)-2-Oxo-4-phenyl-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (9a): Cycloaddition of **1** with cyclopentadiene was performed according to the general procedure described above. Purification by flash chromatography (30% EtOAc/hexanes) followed by recrystallization (EtOAc/hexanes) gave the cycloadduct

9a as a colourless solid. R_f = 0.4 (50% EtOAc/hexanes). M.p. 116–118 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3066, 2957, 2911, 1750, 1603, 1477, 1411, 1191, 1043 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42 (m, 3 H), 7.32 (m, 2 H), 5.98 (dd, J = 2.9, 5.9 Hz, 1 H), 5.02 (dd, J = 2.7, 5.9 Hz, 1 H), 4.91 (d, J = 2.7 Hz, 1 H), 4.74 (m, 2 H), 4.07 (dd, J = 1.7, 6.1 Hz, 1 H), 2.91 (m, 1 H), 2.79 (m, 1 H), 2.58 (dd, J = 3.4, 15.8 Hz, 1 H), 2.45 (ddd, J = 2.6, 2.9, 15.8 Hz, 1 H), 2.15 (m, 1 H), 1.99 (d, J = 11.2 Hz, 1 H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 204.8, 160.4, 141.6, 137.6, 133.6, 129.5, 128.9, 126.2, 71.6, 68.2, 57.7, 45.2, 44.8, 44.4, 39.8. HRMS calcd. for $C_{17}H_{17}NO_3$ [M^+] 283.1208, found 283.1205.

(1*S*,2*R*,5*S*)-2-[(4*S*)-2-Oxo-4-phenyl-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (9b): Purification by flash chromatography (30% EtOAc/hexanes) followed by recrystallization (EtOAc/hexanes) gave cyclaodduct **9b** as a colourless solid. R_f = 0.4 (50% EtOAc/hexanes). M.p. 165–167 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3696, 2952, 1955, 1761, 1602, 1478, 1262, 1106, 1042 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 (m, 5 H), 6.27 (dd, J = 2.7, 5.6 Hz, 1 H), 6.05 (dd, J = 2.7, 5.6 Hz, 1 H), 4.89 (dd, J = 8.5, 8.5 Hz, 1 H), 4.68 (dd, J = 8.5, 8.5 Hz, 1 H), 4.12 (dd, J = 8.5, 8.5 Hz, 1 H), 3.71 (d, J = 2.9 Hz, 1 H) 3.00 (m, 1 H), 2.88 (m, 1 H), 2.46 (m, 2 H), 2.18 (m, 1 H), 1.69 (d, J = 10.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 158.0, 138.0, 135.5, 134.9, 129.5(8), 129.5(1), 127.6, 70.4, 67.7, 64.0, 45.4, 45.3, 44.6, 39.1 ppm. HRMS calcd. for $C_{17}H_{17}NO_3$ [M^+] 283.1208, found 283.1213.

(1*R*,2*S*,5*R*)-2-[(4*S*)-4-Benzyl-2-oxo-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (10a): Cycloaddition of **2** with cyclopentadiene was performed according to the general procedure described above. Purification by flash chromatography (30% EtOAc/hexanes) followed by recrystallization (EtOAc/hexanes) gave **10a** as a colourless solid. R_f = 0.4 (50% EtOAc/hexanes). M.p. 136–138 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3673, 3409, 2957, 2253, 1747, 1724, 1701, 1604, 1479, 1418, 1351, 1290, 1226, 1089 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 3 H), 7.17 (m, 2 H), 6.30 (m, 2 H), 4.61 (d, J = 2.7 Hz, 1 H), 4.09 (m, 3 H), 3.13 (m, 1 H), 3.02 (m, 2 H), 2.69 (dd, J = 9.8, 13.6 Hz, 1 H), 2.58 (dd, J = 3.4, 16.6 Hz, 1 H), 2.52 (ddd, J = 2.7, 2.7, 16.6 Hz, 1 H), 2.40 (m, 1 H), 2.05 (d, J = 11.2 Hz, 1 H) ppm. ^{13}C (75 MHz, $CDCl_3$): δ = 204.8, 158.7, 138.4, 136.4, 134.2, 129.2, 129.1, 127.3, 67.7, 67.3, 57.2, 45.1, 44.9, 44.7, 39.7, 39.1. $C_{18}H_{19}NO_3$: C 7.69; H 6.44, N 4.71; found C 72.13, H 6.47, N 4.72. HRMS calcd. for $C_{18}H_{19}NO_3$ [M^+] 297.1364, found 297.1363.

(1*S*,2*R*,5*S*)-2-[(4*S*)-4-Benzyl-2-oxo-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (10b): Purification by flash chromatography (30% EtOAc/hexanes) gave **10b** as a colourless oil. R_f = 0.4 (50% EtOAc/hexanes). IR ($CDCl_3$): $\tilde{\nu}$ = 2954, 2871, 1949, 1745, 1715, 1603, 1496, 1478, 1290, 1255, 1190, 1102, 1012 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 3 H), 7.17 (m, 2 H), 6.28 (dd, J = 2.7, 5.6 Hz, 1 H), 6.18 (dd, J = 2.7, 5.6 Hz, 1 H), 4.77 (d, J = 2.7 Hz, 1 H), 4.28 (dd, J = 8.5, 8.5 Hz, 1 H), 4.08 (dd, J = 4.4, 8.5 Hz, 1 H), 3.87 (m, 1 H), 3.22 (m, 1 H), 3.05 (m, 2 H), 2.71 (dd, J = 10.5, 13.6 Hz, 1 H), 2.56 (dd, J = 3.2, 15.8 Hz, 1 H), 2.47 (ddd, J = 2.4, 2.7, 15.8 Hz, 1 H), 2.37 (m, 1 H), 2.09 (d, J = 11.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.3, 155.7, 134.8 131.6, 128.6, 124.9, 124.8, 123.1, 64.1, 63.5, 50.3, 40.7, 40.6, 40.4, 36.4, 35.5 ppm. HRMS calcd. for $C_{18}H_{19}NO_3$ [M^+] 297.1364, found 297.1367.

(1*R*,2*S*,5*R*)-2-[(4*S*)-4-*tert*-Butyl-2-oxo-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (11a): Cycloaddition of **3** with cyclopentadiene was performed according to the general procedure described above. Purification by flash chromatography (30% EtOAc/hexanes) followed by recrystallization (EtOAc/hexanes) gave cycloadduct **11a** as a colourless solid. R_f = 0.4 (50% EtOAc/hexanes). M.p. 190–191.5 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3173, 2960, 2874, 2253, 1756, 1716, 1480, 1420, 1362, 1237, 1196, 1115, 1067 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.40 (dd, J = 2.9, 5.6 Hz, 1 H), 6.05 (dd, J = 2.9, 5.6 Hz, 1 H), 4.47 (dd, J = 8.7, 9.0 Hz, 1 H), 4.18 (dd, J = 3.6, 8.7 Hz, 1 H), 3.89 (d, J = 2.6 Hz, 1 H), 3.24 (m, 2 H), 2.94 (m, 1 H), 2.50 (m, 2 H), 2.33 (m, 1 H), 1.85 (d, J = 10.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.0, 159.4, 136.0, 133.8, 72.4, 68.9, 65.1, 45.8, 45.3, 45.2, 39.3, 35.2, 25.5 ppm. $C_{17}H_{17}NO_3$: calcd. C 68.40, H 8.04, N 5.32; found C 68.31, H 8.13, N 5.22.

(1*S*,2*R*,5*S*)-2-[(4*R*,5*S*)-1,5-Dimethyl-2-oxo-4-phenylimidazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (13a): Cycloaddition of **12** with furan was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes, 3:1) afforded cycloadducts **13a** (40.6 mg, 21%) and **13b** (12.7 mg, 7%) as colourless solids. R_f = 0.41 (EtOAc/hexanes, 3:1). $[\alpha]_D^{25}$ = –283 (c = 2.03, CH_2Cl_2). IR ($CDCl_3$): $\tilde{\nu}$ = 2968, 1733, 1695, 1435, 1403, 1340, 1258, 1040, 966, 845, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.42 (m, 5 H), 6.09 (dd, J = 1.7, 6.1 Hz, 1 H), 5.21 (d, J = 4.4 Hz, 1 H), 5.09 (dd, J = 1.8, 6.2 Hz, 1 H), 4.93 (dd, J = 0.9, 5.0 Hz, 1 H), 4.68 (dd, J = 1.8, 4.4 Hz, 1 H), 4.48 (d, J = 8.8 Hz, 1 H), 3.97 (dq, J = 2.1, 6.6 Hz, 1 H), 2.82 (d of ABq, J = 5.8, 20.1 Hz, 1 H), 2.74 (s, 3 H), 2.37 (ABq, J = 15.6 Hz, 1 H), 0.72 (d, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz/$CDCl_3$): δ = 202.9, 162.3, 138.6, 134.4, 132.5, 128.4, 80.9, 78.3, 66.6, 59.7, 57.0, 46.1, 29.2, 15.2 ppm. HRMS (EI) calcd. for $C_{18}H_{20}N_2O_3$ [M^+] 312.1474, found 312.1473.

(1*R*,2*S*,5*R*)-2-[(4*R*,5*S*)-1,5-Dimethyl-2-oxo-4-phenylimidazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (13b): R_f = 0.24 (EtOAc/hexanes, 3:1). $[\alpha]_D^{25}$ = –168 (c = 0.37, CH_2Cl_2). IR ($CDCl_3$): $\tilde{\nu}$ = 2962, 2920, 1725, 1694, 1651, 1446, 1403, 1261, 1025, 801 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.43 (m, 5 H), 6.67 (ddd, J = 0.6, 1.9, 6.1 Hz, 1 H), 6.22 (ddd, J = 0.4, 1.8, 6.0 Hz, 1 H), 5.04 (ddd, J = 0.3, 1.8, 4.6 Hz, 1 H), 4.71 (ddd, J = 0.7, 1.4, 5.1 Hz, 1 H), 4.81 (d, J = 8.8 Hz, 1 H), 3.88 (dq, J = 6.6, 8.8 Hz, 1 H), 3.73 (d, J = 4.6 Hz, 1 H), 2.78 (s, 3 H), 2.59 (d of ABq, J = 5.2, 16.2, 1 H), 2.42 (ABq, J = 16.2 Hz, 1 H), 0.74 (d, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.5, 160.6, 136.4, 134.7, 131.3, 128.9, 128.7, 81.4, 78.1, 68.0, 65.7, 55.8, 45.8, 28.7, 14.5 ppm. HRMS (EI) calcd. for $C_{18}H_{20}N_2O_3$ [M^+] 312.1474, found 312.1465.

(1*S*,2*R*,5*R*)-2-[(4*R*,5*S*)-1,5-Dimethyl-2-oxo-4-phenylimidazolidin-3-yl]bicyclo[3.2.1]oct-6-en-3-one (14a): Cycloaddition of **12** with cyclopentadiene was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes, 1:1) afforded cycloadducts **14a** (65 mg, 36%) and **14b** (36 mg, 20%) as colourless solids. R_f = 0.30 (EtOAc/hexanes, 1:1). $[\alpha]_D^{25}$ = –120.6 (c = 2.32, CH_2Cl_2). IR ($CDCl_3$): $\tilde{\nu}$ = 2949, 1720, 1694, 1435, 1403, 1351, 1253, 1193, 1099, 735 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.44 (m, 4 H), 6.97–7.11 (m, 1 H), 5.92 (dd, J = 2.8, 5.9 Hz, 1 H), 5.11 (dd, J = 2.6, 5.8 Hz, 1 H), 5.03 (d, J = 2.7 Hz, 1 H), 4.39 (d, J = 8.9 Hz, 1 H), 3.96 (dq, J = 2.3, 6.6 Hz, 1 H), 2.81–2.87 (m, 1 H), 2.72 (s, 3 H), 2.63 (quint, J = 2.7 Hz, 1 H), 2.51 (d of ABq, J = 2.6, 15.8 Hz, 1 H), 2.37 (t of ABq, J = 2.9, 15.9 Hz, 1 H), 2.03–2.12 (m, 1 H), 1.95–2.09 (ABq, J = 12.4 Hz, 1 H), 0.70 (d, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.5, 163.0, 139.1, 136.8, 134.3, 128.6, 128.1, 128.0, 127.5, 67.2, 59.7, 57.2, 45.3, 44.8, 44.6, 39.7, 29.3, 15.2 ppm. HRMS (EI) calcd. for $C_{19}H_{22}N_2O_2$ [M^+] 310.1681, found 310.1687.

(1*R*,2*S*,5*S*)-2-[(4*R*,5*S*)-1,5-Dimethyl-2-oxo-4-phenylimidazolidin-3-yl]bicyclo[3.2.1]oct-6-en-3-one (14b): R_f = 0.24 (EtOAc/hexanes, 1:1). IR ($CDCl_3$): $\tilde{\nu}$ = 2944, 1699, 1435, 1402, 1362, 1261, 1028,

762, 704 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.43 (m, 5 H), 6.34 (dd, J = 2.6, 5.6 Hz, 1 H), 5.99 (dd, J = 2.4, 5.5 Hz, 1 H), 4.77 (d, J = 8.9 Hz, 1 H), 3.90 (dq, J = 6.6, 8.9 Hz, 1 H), 3.65 (d, J = 2.9 Hz, 1 H), 3.08 (quint, J = 2.7 Hz, 1 H), 2.86–2.88 (m, 1 H), 2.78 (s, 3 H), 2.37–2.40 (m, 2 H), 2.17 (broad quint, J = 5.7 Hz, 1 H), 1.67 (d, J = 11.2 Hz, 1 H), 0.71 (d, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.0, 161.1, 136.9, 133.9, 128.3 (2 C), 128.3 (2 C), 68.8, 65.5, 63.9, 56.0, 45.6, 45.4, 44.6, 39.0, 28.8, 14.5 ppm. HRMS (EI) calcd. for $C_{19}H_{22}N_2O_2$ [M^+] 310.1681, found 310.1675.

(1*S*,2*R*,5*S*)-2-[(4*R*,5*S*)-2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (15a): Cycloaddition of **4** with furan was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes, 2:3) afforded cycloadducts **15a** (145 mg, 83%), **15b** (6 mg, 3%) and **15c** (4.5 mg, 2.6%) as colourless solids. R_f = 0.22 (EtOAc/hexanes, 2:3). $[\alpha]_D^{25}$ = +44.2 (c = 1.0, CH_2Cl_2). M.p. 199–201 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3054, 2966, 1762, 1715, 1526, 1412, 1362, 1210, 1011, 924 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.38 (m, 4 H), 7.25 (m, 4 H), 6.14 (ddd, J = 1.5, 3.1, 5.4 Hz, 2 H), 5.03 (dd, J = 1.4, 4.5 Hz, 1 H), 4.99 (dt, J = 0.98, 5.35 Hz, 1 H), 4.58 (d, J = 9.2 Hz, 1 H), 4.05 (d, J = 4.5 Hz, 1 H), 3.67 (d, J = 9.2 Hz, 1 H), 2.75 (dd, J = 5.3, 16.6 Hz, 1 H), 2.44 (d, J = 16.6 Hz, 1 H), 2.11 (s, 3 H), 2.06 (s, 3 H) ppm. ^{13}C NMR (75 MHz): δ = 199.5, 158.0, 142.6, 141.7, 140.7, 140.3, 133.6, 131.5, 127.2, 127.1, 127.0, 126.7, 124.3, 124.1, 122.7, 122.3, 81.0, 80.9, 78.2, 69.6, 68.6, 46.4, 45.9, 45.4, 16.0, 14.8 ppm. HRMS (EI) calcd. for $C_{26}H_{23}NO_4$ [M^+] 413.1627, found 413.1622.

(1*R*,2*S*,5*R*)-2-[(4*R*,5*S*)-2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (15b): R_f = 0.2 (EtOAc/hexanes, 2:3). IR ($CHCl_3$): $\tilde{\nu}$ = 3054, 2966, 1764, 1715, 1534, 1408, 1360, 924 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.38 (m, 4 H), 7.24 (m, 4 H), 6.28 (dd, J = 1.6, 6.0 Hz, 1 H), 6.22 (dd, J = 1.5, 6.0 Hz, 1 H), 4.98 (dd, J = 0.84, 5.3 Hz, 1 H), 4.93 (dd, J = 1.5, 5.5 Hz, 1 H), 4.57 (d, J = 8.7 Hz, 1 H), 4.36 (d, J = 4.5 Hz, 1 H), 3.73 (dd, J = 0.86, 8.7 Hz, 1 H), 2.83 (dd, J = 5.4, 16.5 Hz, 1 H), 2.50 (d, J = 16.5 Hz, 1 H), 2.07 (s, 3 H), 1.97 (s, 3 H) ppm. ^{13}C NMR (75 MHz): δ = 198.4, 143.7, 141.5, 140.4, 139.2, 132.9, 127.1, 127.0, 126.5, 124.7, 123.3, 122.9, 122.0, 81.1, 80.3, 78.1, 77.4, 69.0, 66.3, 46.9, 45.8, 15.7, 15.2 ppm.

(1*S*,2*S*,5*S*)-2-[(4*R*,5*S*)-2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (15c): R_f = 0.18 (EtOAc/hexanes, 2:3). IR ($CDCl_3$): $\tilde{\nu}$ = 3050, 2972, 1761, 1716, 1522, 1416, 1350, 1212, 1015, 926 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.37 (m, 2 H), 7.22 (m, 6 H), 6.48 (ddd, J = 0.85, 4.1, 18.6 Hz, 2 H), 5.00 (t, J = 0.5 Hz, 2 H), 4.55 (d, J = 9.3 Hz, 1 H), 3.87 (d, J = 9.5 Hz, 1 H), 3.27 (s, 1 H), 3.07 (dd, J = 7.1, 19.1 Hz, 2 H), 2.06 (s, 3 H), 1.98 (s, 3 H) ppm.

(1*R*,2*S*,5*S*)-2-[(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (16a): Cycloaddition of **5** with furan (200 equiv.) was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes gradient, 1:5, 1:4, 1:3, 1:2 and 1:1) afforded cycloadducts **16a** (50.1 mg, 82%), **16b** (1.6 mg, 3%) and **16c** (2.8 mg, 5%) all as colourless solids. R_f = 0.35 (CH_2Cl_2/EtOAc, 10:1). $[\alpha]_D^{25}$ = +0.4 (c = 1.05, CH_2Cl_2). M.p. 81–84 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3072, 2963, 2858, 2249, 1748, 1725, 1589, 1472, 1262, 1111, 1077, 1029 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.71 (m, 4 H), 7.37–7.47 (m, 6 H), 6.47 (dd, J = 1.7, 6.0 Hz, 1 H), 6.23 (dd, J = 1.7, 6.0 Hz, 1 H), 5.65 (dd, J = 1.8, 4.4 Hz, 1 H), 4.96 (dt, J = 1.5, 4.9 Hz, 1 H), 4.64 (ddd, J = 1.2, 4.9, 10.4 Hz, 1 H), 4.57 (s, 1 H), 4.33–4.37 (m, 1 H), 4.21 (ddd, J = 1.5, 4.1, 10.4 Hz, 1 H), 2.70 (d of ABq, J = 4.9, 14.6 Hz, 1 H), 2.66–2.74 (m, 1 H), 2.43–2.49 (m, 1 H), 2.35 (d of ABq, J = 1.2, 14.6 Hz, 1 H), 1.61 (dd of ABq, J = 3.2, 5.0, 13.8 Hz, 1 H), 1.28–1.47 (m, 2 H), 1.21–1.23 (m, 1 H), 1.11 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.6, 157.9, 136.1, 135.9, 134.0, 133.8, 133.7, 133.5, 130.0, 129.8, 127.9, 127.8, 80.1, 78.7, 75.1, 68.9, 60.4, 47.0, 44.7, 40.8, 33.5, 29.5, 27.4 (3 C), 19.2 ppm. HRMS (EI) calcd. for $C_{27}H_{26}NO_5Si$ [$M^+ - C_4H_9$] 472.1580, found 472.1587.

(1*S*,2*R*,5*R*)-2-[(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (16b): R_f = 0.43 (CH_2Cl_2/EtOAc, 5:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3070, 2953, 2850, 2249, 1748, 1725, 1594, 1472, 1262, 1111, 1075 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.67 (m, 4 H), 7.33–7.46 (m, 6 H), 6.38 (dd, J = 1.8, 6.1 Hz, 1 H), 6.25 (dd, J = 1.6, 6.1 Hz, 1 H), 5.26 (dd, J = 1.6, 4.4 Hz, 1 H), 5.00–5.03 (m, 1 H), 4.95 (d, J = 4.4 Hz, 1 H), 4.86 (ddd, J = 1.2, 4.0, 10.6 Hz, 1 H), 4.34 (m, 1 H), 3.65 (ddd, J = 1.6, 4.0, 10.6 Hz, 1 H), 2.87 (d of ABq, J = 5.0, 15.1 Hz, 1 H), 2.48–2.54 (m, 1 H), 2.39 (ABq, J = 14.4 Hz, 1 H), 2.33–2.38 (m, 1 H), 1.59–1.74 (m, 1 H), 1.17–1.45 (m, 3 H), 1.11 (s, 9 H) ppm.

(1*R*,2*R*,5*S*)-2-[(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (16c): R_f = 0.32 (CH_2Cl_2/EtOAc, 5:1). $[\alpha]_D^{25}$ = +83.3 (c = 0.018, CH_2Cl_2). IR ($CDCl_3$): $\tilde{\nu}$ = 2928, 1749, 1427, 1260, 1223, 1075, 802 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.68 (m, 4 H), 7.36–7.45 (m, 6 H), 6.68 (dd, J = 1.8, 7.7 Hz, 2 H), 6.60 (dd, J = 1.8, 7.7 Hz, 2 H), 6.29 (ddd, J = 0.7, 1.8, 6.0 Hz, 1 H), 5.49 (dd, J = 1.6, 6.0 Hz, 1 H), 5.41–5.42 (m, 1 H), 4.97 (dd, J = 1.8, 5.7 Hz, 1 H), 4.75 (ddd, J = 0.8, 4.6, 10.3 Hz, 1 H), 4.45–4.49 (m, 1 H), 4.21 (s, 1 H), 3.86 (ddd, J = 1.5, 4.0, 10.4 Hz, 1 H), 2.75 (dd of ABq, J = 1.0, 5.8, 17.8 Hz, 1 H), 2.68–2.73 (m, 1 H), 2.55 (broad t, J = 5.0 Hz, 1 H), 2.44 (ABq, J = 17.8 Hz, 1 H), 1.73 (dd of ABq, J = 3.0, 5.0, 13.6 Hz, 1 H), 1.61 (dd of ABq, J = 1.2, 5.1, 13.5 Hz, 1 H), 1.49 (m, 1 H), 1.41 (m, 1 H), 1.23–1.31 (m, 1 H), 1.10 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.6, 159.5, 136.1, 136.0, 135.7, 134.3, 133.4, 131.6, 130.2, 129.8, 128.1, 127.9, 79.5, 77.4, 75.1, 72.2, 61.9, 58.5, 47.1, 44.9, 40.7, 34.1, 29.7, 27.3 (3 C), 19.4 ppm. HRMS (EI) calcd. for $C_{27}H_{26}NO_5Si$ [$M^+ - C_4H_9$] 472.1580, found 472.1584.

(1*S*,2*R*,5*S*)-2-[(4*R*,5*S*)-2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl]bicyclo[3.2.1]oct-6-en-3-one (17a): Cycloaddition of **4** with cyclopentadiene was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes, 2:3) afforded cycloadducts **17a** (167 mg, 89%) and **17b** (9 mg, 5%) as a colourless solids. R_f = 0.33 (EtOAc/hexanes, 2:3). $[\alpha]_D^{25}$ = +23.0 (c = 1.25, $CHCl_3$). M.p. 168–170 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 3052, 2968, 1760, 1716, 1526, 1416, 1364, 1212, 1011, 926 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.32–7.26 (m, 4 H), 7.25–7.21 (m, 4 H), 5.95 (dd, J = 1.2, 0.3 Hz, 2 H), 4.56, (d, J = 9.2 Hz, 1 H), 3.84, (d, J = 2.8 Hz, 1 H), 3.61 (d, J = 9.2 Hz, 1 H), 3.11–3.07 (m, 1 H), 2.92–2.86 (m, 1 H), 2.42 (t, J = 2.8 Hz, 2 H), 2.35–2.30 (m, 1 H), 2.07 (s 3 H), 2.05 (s, 3 H), 1.86 (d, J = 11.1, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 223.1, 158.2, 143.1, 142.0, 141.0, 140.3, 135.7, 133.8, 127.1, 126.9, 126.0, 124.1, 123.1, 122.3, 80.8, 71.2, 69.3, 46.5, 46.0, 45.1, 44.8, 39.1, 15.9, 15.0 ppm. HRMS (EI) calcd. for $C_{27}H_{26}NO_5Si$ [$M^+ - C_4H_9$] 472.1580, found 472.1579.

(1*R*,2*S*,5*R*)-2-[(4*R*,5*S*)-2-Oxo-4,5-[9,10]dimethylanthraceno-1,3-oxazolidin-3-yl]bicyclo[3.2.1]oct-6-en-3-one (17b): R_f = 0.31 (EtOAc/hexanes, 2:3). IR ($CDCl_3$): $\tilde{\nu}$ = 3051, 2970, 1760, 1716, 1524, 1414, 1354, 1210, 1015, 926 cm^{-1}. ^{1}H NMR (300 MHz): δ = 7.37–7.34 (m, 4 H), 7.27–7.23 (m, 4 H), 6.22 (ddd, J = 2.8, 5.5, 15.9 Hz, 2 H), 4.55 (d, J = 9.3 Hz, 1 H), 3.82 (d, J = 9.2 Hz, 1 H), 3.18, (s, 1

H), 2.91 (dd, *J* = 2.9, 4.2 Hz, 1 H), 2.79 (br. q, *J* = 1.5 Hz, 1 H), 2.62 (dd, *J* = 5.1, 18.8 Hz, 1 H), 2.58 (d, *J* = 11.2 Hz, 1 H), 2.31 (d, *J* = 18.4 Hz, 1 H), 2.04 (s, 6 H), 1.80–1.77 (m, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 208.1, 158.8, 143.0, 142.1, 141.2, 140.5, 140.3, 135.3, 127.3, 127.2, 127.17, 126.8, 124.5, 123.0, 122.9, 122.5, 81.6, 69.8, 65.3, 46.6, 46.0, 45.99, 45.4, 37.1, 36.6, 15.9, 15.0 ppm. HRMS (EI) calcd. for $C_{27}H_{26}NO_5Si$ [$M^+ - C_4H_9$] 472.1580, found 472.1580.

(1*S*,2*R*,5*R*)-2-[(1*S*,2*R*,6*S*,7*S*,8*S*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]bicyclo[3.2.1]oct-6-en-3-one (18a): Cycloaddition of **5** with cyclopentadiene (200 equiv.) was performed according to the general procedure described above. Purification by flash column chromatography (EtOAc/hexanes gradient, 1:7, 1:5, 1:4, 1:2 and 1:1) afforded cycloadducts **18a** (30.8 mg, 76% yield) and **18c** (6.1 mg, 14%) as colourless solids. R_f = 0.45 (CH_2Cl_2/EtOAc, 20:1). $[\alpha]_D^{25}$ = –21.4 (*c* = 0.22, CH_2Cl_2). M.p. 71–74 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2956, 2858, 1748, 1589, 1471, 1427, 1439, 1260, 1111, 1076, 911, 860 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.71 (m, 4 H), 7.33–7.54 (m, 6 H), 6.13 (dd, *J* = 2.7, 5.8 Hz, 1 H), 6.05 (dd, *J* = 2.6, 6.0 Hz, 1 H), 4.74 (ddd, *J* = 0.9, 5.0, 10.3 Hz, 1 H), 4.51 (d, *J* = 2.9 Hz, 1 H), 4.36 (ddt, *J* = 1.3, 4.6, 8.8 Hz, 1 H), 4.05 (ddd, *J* = 1.5, 4.0, 10.3 Hz, 1 H), 3.55 (quint, *J* = 2.7 Hz, 1 H), 2.90 (br. t, *J* = 4.0 Hz, 1 H), 2.80–2.86 (m, 1 H), 2.47 (broad t, *J* = 4.6 Hz, 1 H), 2.30 (dd, *J* = 1.6, 3.0 Hz, 1 H), 1.97 (quint, *J* = 5.8 Hz, 1 H), 1.68 (dd of ABq, *J* = 3.3, 4.7, 13.7 Hz, 1 H), 1.43–1.53 (m, 2 H), 1.29 (dt of ABq, *J* = 1.4, 11.2 Hz, 1 H), 1.16 (quint of ABq, *J* = 1.6 Hz, 11.3 Hz, 1 H), 1.07 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 158.3, 136.7, 136.1, 136.0, 134.3, 129.9, 129.6, 127.8, 127.7, 76.8, 74.9, 69.3, 60.8, 46.4, 45.3, 44.1, 40.8, 40.2, 33.6, 29.9, 27.3 (3 C), 19.2 ppm. HRMS (EI) calcd. for $C_{28}H_{28}NO_4Si$ [$M^+ - C_4H_9$] 470.1788, found 470.1800.

(1*S*,2*S*,5*R*)-2-[(1*S*,2*R*,6*S*,7*S*,8*S*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]bicyclo[3.2.1]oct-6-en-3-one (18c): R_f = 0.42 (CH_2Cl_2/EtOAc, 20:1). IR ($CDCl_3$): $\tilde{\nu}$ = 2956, 2856, 1746, 1594, 1470, 1440, 1266, 1114, 1076, 910 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.69 (m, 4 H), 7.35–7.47 (m, 6 H), 6.27 (dd, *J* = 2.7, 5.8 Hz, 1 H), 6.12 (dd, *J* = 2.3, 5.6 Hz, 1 H), 4.76 (dd, *J* = 4.8, 10.0 Hz, 1 H), 4.56 (d, *J* = 2.6 Hz, 1 H), 4.39 (quint, *J* = 4.9 Hz, 1 H), 4.33 (d, *J* = 3.0 Hz, 1 H), 4.18 (ddd, *J* = 1.7, 4.4, 10.7 Hz, 1 H), 3.59–3.65 (m, 1 H), 3.16–3.23 (m, 1 H), 2.83–2.90 (m, 1 H), 2.49–2.56 (m, 1 H), 2.00 (dt, *J* = 5.6, 12.1 Hz, 1 H), 1.62–1.79 (m, 1 H), 1.45–1.47 (m, 5 H), 1.08 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.4, 157.9, 137.3, 136.1 (2 C), 135.9 (2 C), 134.8, 134.5, 133.6, 130.0, 129.8, 127.9 (2 C), 127.8 (2 C), 75.0, 69.6, 60.4, 60.3, 50.5, 45.6, 45.4, 43.6, 40.9, 33.5, 30.0, 27.4 (3 C), 19.4 ppm. HRMS (EI) calcd. for $C_{28}H_{28}NO_4Si$ [$M^+ - C_4H_9$] 470.1788, found 470.1788.

Methyl (1*R*,2*S*,5*S*)-2-[(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]-3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate (20): Cycloaddition of **5** with methyl 1*H*-pyrrole-1-carboxylate (200 equiv.) was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes gradient, 1:5, 1:3, 1:1 and 2:1) afforded cycloadducts **20** (30.6 mg, 32%) and **21** (2.9 mg, 3%) as colourless solids. R_f = 0.46 (EtOAc/hexanes, 2:1). $[\alpha]_D^{25}$ = –0.5 (*c* = 1.47, CH_2Cl_2). M.p. 96–98 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2957, 2880, 2858, 1750, 1728, 1708, 1449, 1392, 1293, 1214, 1113, 1075 cm^{-1}. ^{1}H NMR (300 MHz, DMSO, 80 °C): δ = 7.76 (dd, *J* = 1.7, 7.6 Hz, 2 H), 7.67 (dd, *J* = 1.6, 7.9 Hz, 2 H), 7.41–7.54 (m, 6 H), 6.45 (dd, *J* = 2.5, 6.2 Hz, 1 H), 6.33 (dd, *J* = 2.4, 6.1 Hz, 1 H), 5.09 (dd, *J* = 2.4, 3.9 Hz, 1 H), 4.89 (ddd, *J* = 4.3, 10.3 Hz, 1 H), 4.77 (quint, *J* = 2.3 Hz, 1 H), 4.54 (d, *J* = 4.0 Hz, 1 H), 4.45 (quint, *J* = 5.5 Hz, 1 H), 3.90 (ddd, *J* = 1.5, 4.0, 10.3 Hz, 1 H), 3.70 (s, 3 H), 2.79–2.84 (m, 1 H), 2.68 (d of ABq, *J* = 4.4, 15.7 Hz, 1 H), 2.45–2.51 (m, 1 H), 2.42 (d of ABq, *J* = 1.5, 15.7 Hz, 1 H), 1.32–1.60 (m, 3 H), 1.22–1.29 (m, 1 H), 1.11 (s, 9 H) ppm. ^{13}C NMR (75 MHz, DMSO, 80 °C): δ = 199.7, 157.7, 152.1, 135.1 (2 C), 134.9 (2 C), 133.1, 133.4, 133.2, 132.8, 129.3, 129.1, 127.2 (2 C), 127.1 (2 C), 76.1, 74.5, 67.1, 60.8, 59.5, 56.4, 51.9, 44.2, 44.0, 33.6, 30.4, 29.0, 26.7 (3 C), 18.2 ppm. HRMS (EI) calcd. for $C_{29}H_{29}N_2O_6Si$ [$M^+ - C_4H_9$] 529.1795, found 529.1800.

Methyl (1*R*,2*R*,5*S*)-2-[(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-Butyl(diphenyl)silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]-3-oxo-8-azabicyclo[3.2.1]oct-6-ene-8-carboxylate (21): R_f = 0.44 (EtOAc/hexanes, 2:1). $[\alpha]_D^{25}$ = +7.3 (*c* = 0.15, CH_2Cl_2). IR ($CDCl_3$): $\tilde{\nu}$ = 2961, 2857, 1747, 1731, 1699, 1455, 1410, 1261, 1105, 1071, 1031 cm^{-1}. ^{1}H NMR (300 MHz, DMSO, 80 °C): δ = 7.69–7.78 (m, 4 H), 7.38–7.51 (m, 6 H), 6.46 (dd, *J* = 2.3, 6.0 Hz, 1 H), 6.10 (dd, *J* = 2.5, 6.1 Hz, 1 H), 5.59 (t, *J* = 2.0 Hz, 1 H), 4.88 (t, *J* = 2.2 Hz, 1 H), 4.71 (dd, *J* = 5.0, 9.9 Hz, 1 H), 4.24 (quint, *J* = 4.2 Hz, 1 H), 3.94 (s, 1 H), 3.84 (ddd, *J* = 1.4, 4.1, 10.2 Hz, 1 H), 3.69 (s, 3 H), 2.99 (d of ABq, *J* = 4.5, 16.5 Hz, 1 H), 2.35–2.41 (m, 2 H), 2.24 (m, 2 H), 1.14–1.41 (m, 3 H), 1.07 (s, 9 H) ppm.

(1*R*,2*S*,5*S*)-6-Bromo-2-[(1*R*,2*S*,6*R*,7*R*,8*R*)-8-*tert*-butyl(diphenyl)-silanyloxy-4-oxo-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]dec-5-yl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (22): Cycloaddition of **5** with 3-bromofuran (200 equiv.) was performed according to the general procedure described above. Purification by flash chromatography (EtOAc/hexanes gradient, 1:4, 1:3 and 1:2) afforded cycloadduct **22** (20.8 mg, 21% yield) as an orange solid. R_f = 0.51 (EtOAc/hexanes, 1:3). $[\alpha]_D^{25}$ = +2.72 (*c* = 0.25, CH_2Cl_2). M.p. 140–142 °C. IR ($CDCl_3$): $\tilde{\nu}$ = 2962, 2858, 1748, 1728, 1600, 1471, 1427, 1260, 1112, 1073, 806 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, *J* = 1.5, 7.8 Hz, 2 H), 7.63 (dd, *J* = 1.7, 7.6 Hz, 2 H), 7.34–7.47 (m, 6 H), 6.57 (d, *J* = 2.0 Hz, 1 H), 5.63 (dd, *J* = 2.0, 4.2 Hz, 1 H), 4.73–4.81 (m, 2 H), 4.47 (d, *J* = 4.2 Hz, 1 H), 4.37 (quint, *J* = 5.3 Hz, 1 H), 4.27 (ddd, *J* = 1.5, 4.1, 10.4 Hz, 1 H), 2.60–2.70 (m, 3 H), 2.45–2.50 (m, 1 H), 1.61 (dd of ABq, *J* = 3.2, 4.6, 13.7 Hz, 1 H), 1.45 (dd of ABq, *J* = 5.0, 10.7, 13.7 Hz, 1 H), 1.34 (ABq, *J* = 11.4 Hz, 1 H), 1.18 (ABq, *J* = 11.6 Hz, 1 H), 1.11 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.7, 157.8, 136.0, 135.8, 133.9, 133.7, 132.5, 130.1, 129.9, 127.9, 127.8, 123.6, 82.4, 81.3, 75.1, 67.2, 60.3, 45.3, 44.6, 40.8, 33.5, 29.4, 27.5 (3 C), 19.3 ppm. HRMS (EI) calcd. for $C_{27}H_{25}O_5NSi^{81}Br$ [$M^+ - C_4H_9$] 552.0665, found: 552.0660.

CCDC-607138 to -607140 contain the complete crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] For reviews on [4+3] cycloadditions: a) H. M. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 819–835; b) R. Noyori,

Y. Hayakawa, *Org. React.* **1983**, *29*, 163; c) H. M. R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 1–88; d) J. Mann, *Tetrahedron* **1986**, *42*, 4611–4659; e) A. Hosomi, Y. Tominage, [4+3] cycloadditions, in: *Comprehensive Organic Synthesis*, Eds B. M. Trost, I. Fleming, Pergamon: Oxford, **1991**; vol. 5, chapter 5.1, pp. 593–615; f) M. Lautens, *Synlett* **1993**, 177; g) J. H. Rigby, F. C. Pigge, *Org. React.* **1997**, *51*, 351–478; h) M. Harmata, P. Rashatasakhon, *Tetrahedron* **2003**, *59*, 2371–2395; i) M. Harmata, *Acc. Chem. Res.* **2001**, *34*, 595–605.

[2] a) N. Cramer, S. Laschat, A. Baro, W. Frey, *Synlett* **2003**, *14*, 2175–2177. For tropane alkaloids interest in cocaine medication; b) H. M. L. Davies, A. Gulzar, M. R. Churchill, *J. Am. Chem. Soc.* **1996**, *118*, 10774–10782 and references cited therein.

[3] a) M. Lautens, P. Chiu "Using Ring-Opening Reactions of Oxabicyclic Compounds as a Strategy in Organic Synthesis" in *Topics in Current Chemistry*, **1997**, vol. 190, p. 1 (Ed.: P. Metz), Springer Verlag, New York; b) M. Lautens, T. Rovis, *J. Am. Chem. Soc.* **1997**, *119*, 11090.

[4] For an excellent review on asymmetric [4+3] cycloadditions: a) I. V. Hartung, H. M. R. Hoffmann, *Angew. Chem. Int. Ed.* **2004**, *43*, 1934–1949; b) M. Lautens, S. Ma, *Tetrahedron Lett.* **1996**, *37*, 1727; c) M. Lautens, R. Aspiotis, J. Colucci, *J. Am. Chem. Soc.* **1996**, *118*, 10930–10931; d) A. S. Kende, H. Huang, *Tetrahedron Lett.* **1997**, *38*, 3353–3356; e) C. B. W. Stark, U. Eggert, H. M. R. Hoffmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 1267–1268; f) C. B. W. Stark, U. Eggert, H. M. R. Hoffmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 1337–1339; g) H. Beck, S. Pierau, R. Wartchow, H. M. R. Hoffmann, *Chem. Eur. J.* **2000**, *6*, 684–691; h) H. Beck, C. B. W. Stark, H. M. R. Hoffmann, *Org. Lett.* **2000**, *2*, 883–886; i) M. Harmata, D. E. Jones, M. Kahraman, U. Sharma, C. L. Barnes, *Tetrahedron Lett.* **1999**, *40*, 1831–1834; j) S. Y. Cho, J. C. Lee, J. K. Cha, *J. Org. Chem.* **1999**, *64*, 3394–3395; k) A. G. Myers, J. K. Barbay, *Org. Lett.* **2001**, *3*, 425–428; l) H. Xiong, R. P. Hsung, C. R. Berry, C. Rameshkumar, *J. Am. Chem. Soc.* **2001**, *123*, 7174–7175; m) H. Xiong, J. Huang, S. K. Ghosh, R. P. Hsung, *J. Am. Chem. Soc.* **2003**, *125*, 12964–12965; n) C. Rameshkumar, R. P. Hsung, *Angew. Chem. Int. Ed.* **2004**, *43*, 625–628; o) M. Harmata, S. K. Ghosh, X. Hong, S. Wacharasindhu, P. Kirchhoefer, *J. Am. Chem. Soc.* **2003**, *125*, 2058–2059; p) J. Huang, R. P. Hsung, *J. Am. Chem. Soc.* **2005**, *127*, 50–51.

[5] a) M. A. Walters, H. R. Arcand, *J. Org. Chem.* **1996**, *61*, 1478–1486; b) M. A. Walters, H. R. Arcand, D. J. Lawrie, *Tetrahedron Lett.* **1995**, *36*, 23–26.

[6] For a review on heteroatom substituted oxyallyls see: M. Harmata, *Recent Res. Dev. Org. Chem.* **1997**, *1*, 523–535.

[7] For a review of the use of chiral oxazolidinones in asymmetric synthesis see: a) D. J. Ager, I. Prakash, D. R. Schaad, *Aldrichim. Acta* **1997**, *30*, 3–12. For the seminal work on the use of oxazolidinones to control diastereofacial selectivity in the Diels–Alder cycloaddition reaction see; b) D. A. Evans, K. T. Chapman, J. Bisaha, *J. Am. Chem. Soc.* **1988**, *110*, 1238–1256.

[8] a) K. G. Bowers, J. Mann, A. J. Markson, *J. Chem. Res., Synop.* **1986**, 424–425; b) B. Fohlisch, W. Gottstein, R. Herter, I. Wanner, *J. Chem. Res., Synop.* **1981**, 246–247; c) B. Föhlisch, E. Wolf, *J. Chem. Res., Synop.* **1983**, 166.

[9] a) D. A. Evans, E. Sjogren, *Tetrahedron Lett.* **1985**, *26*, 3783–3786; b) A. McKervey, T. Ye, *Tetrahedron* **1992**, *48*, 8007–8022; c) W. Bradley, G. Schwarzenbach, *J. Chem. Soc.* **1928**, 2904; d) R. A. Volkmann, R. D. Carroll, R. B. Drolet, M. L. Elliott, B. S. Moore, *J. Org. Chem.* **1982**, *47*, 3344–3345; e) K. Balenovic, D. Cerar, L. Filipovic, *J. Org. Chem.* **1953**, *18*, 868–871; f) A. McKervey, Y. Tao, *Chem. Rev.* **1994**, *94*, 1091–1160; g) D. P. Rotella, *Tetrahedron Lett.* **1995**, *36*, 5453.

[10] J. M. Goodman, H. M. R. Hoffmann, J. G. Vinter, *Tetrahedron Lett.* **1995**, *36*, 7757–7760.

[11] R. Herter, B. Föhlisch, *Synthesis* **1982**, 976–979.

[12] For an excellent review of the use of Lewis acids in organic synthesis see: a) M. Santelli, J.-M. Pons, *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: New York, **1996**. For use of Mg^{2+} in asymmetric processes see; b) S. K. Tipparaju, *Synlett* **2004**, *5*, 912–913; c) D. A. Evans, J. S. Tedrow, J. T. Shaw, C. W. Downey, *J. Am. Chem. Soc.* **2002**, *124*, 392–393; d) D. A. Evans, C. W. Downey, J. T. Shaw, J. S. Tedrow, *Org. Lett.* **2002**, *4*, 1127–1130.

[13] G. Cardillo, A. D'Amico, M. Orena, S. Sandri, *J. Org. Chem.* **1988**, *53*, 2354–2356.

[14] A. A.-M. Abdel-Aziz, J. Okuno, S. Tanaka, T. Ishizuka, H. Matsunaga, T. Kunieda, *Tetrahedron Lett.* **2000**, *41*, 8533–8537.

[15] a) K. Kimura, K. Murata, K. Otsuka, T. Ishizuka, M. Haratake, T. Kunieda, *Tetrahedron Lett.* **1992**, *33*, 4461–4464; b) T. Nakamura, N. Hashimoto, T. Ishizuka, T. Kunieda, *Tetrahedron Lett.* **1997**, *38*, 559–562.

[16] H. Gerlach, D. Kappes, R. K. Boeckman Jr, G. N. Maw (Ed.: L. E. Overman), *Org. Synth.* **1992**, *71*, 48.

[17] R. U. Lemieux, R. K. Kullnig, H. J. Burnstein, W. J. Schneider, *J. Am. Chem. Soc.* **1958**, *80*, 6098.

[18] For discussion of this technique (also known as the gauge-including atomic orbital method) as applied to ^{1}H NMR see: a) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260; For a recent review on ab initio calculations of NMR chemical shift see; b) A. C. De Dios, A. C. *Progress in Nuclear Magnetic Resonance Spectroscopy* **1996**, *29*, 229–278.

[19] Gaussian 94, Revision D.3: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc, Pittsburgh PA, **1995**.

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