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SmI_2-promoted intra- and intermolecular C–C bond formation with chiral *N*-acyl oxazolidinones

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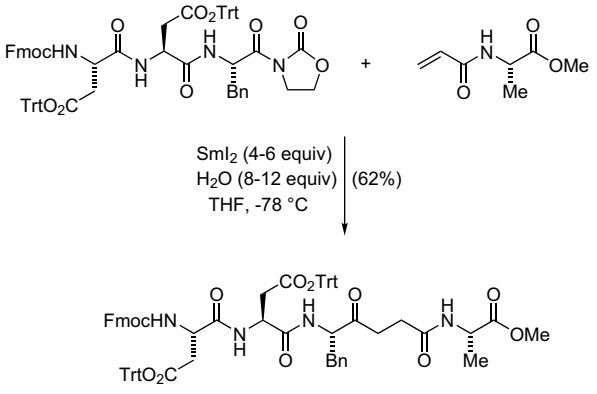
ABSTRACT

The suitability of chiral oxazolidinones in the SmI_2-mediated C–C bond generation between the imide functionality of an *N*-acyl oxazolidinone unit and an olefinic radical acceptor, in both inter- and intramolecular reactions, was investigated. It was shown that the products from an Evans asymmetric alkylation can undergo direct carbon–carbon bond formation with an acrylamide providing chiral acyclic ketones in reasonable yields. These examples represent the first transformation of such *N*-acyl oxazolidinones where this chiral auxiliary is removed under the conditions for ketone formation. 5-*exo*-*trig* Cyclization studies were also undertaken with the same type of substrates, providing *trans*-2,5-disubstituted cyclopentanones in yields of approx. 50%. However, attempts to cyclize heteroatom-containing equivalents were less rewarding.

1. Introduction

Evans chiral oxazolidinones are an important class of compounds, which have been extensively employed as successful chiral auxiliaries in an array of synthetic transformations including asymmetric enolate alkylations, asymmetric aldol reactions, cycloadditions, Michael additions, and others.[1] Whereas there are a variety of protocols for removing the chiral auxiliary direct carbon–carbon bond formation with expulsion of the oxazolidinone requires a minimum of two steps. For example, an initial trimethylaluminum-mediated transamination of the *N*-acyl oxazolidinone with *N*,*N*-methoxymethylamine is required followed by the C–C bond forming step in general with either organomagnesium or -lithium reagents.[2]

Earlier, we have demonstrated the ability of *N*-acyl derivatives of 2-oxazolidinone to undergo direct C–C bond formation with acrylates and acrylamides promoted by the divalent lanthanide reagent, samarium diiodide,[3] leading to γ-keto esters and amides.[4] This reaction was exploited for the synthesis of ketomethylene isosteres of peptides directly from *N*-peptidyl oxazolidinones without epimerization at the stereogenic carbon center adjacent to the keto-functionality in the final product (Scheme 1), which attests to the mildness of the reaction conditions.[5–7] This work led us to consider the possibility of using such reactions with substrates bearing an Evans chiral oxazolidinone, as a short route for the preparation of chiral α-substituted ketones, where the C–C bond formation occurs directly after the asymmetric alkylation step. Thus in this paper, we report our studies on the application of chiral *N*-acyl oxazolidinones in SmI_2-mediated inter- and intramolecular reactions with olefins.



Scheme 1.

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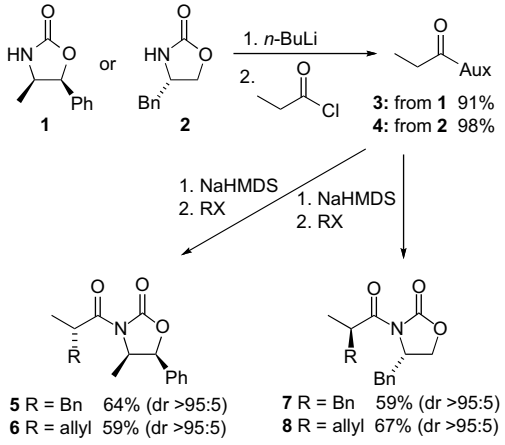
2. Results and discussion

2.1. Intermolecular couplings

To investigate the suitability of this SmI_2-mediated C–C bond forming reaction coupled with Evans asymmetric alkylations for the two-step preparation of chiral acyclic ketones, some simple chiral *N*-acyl oxazolidinones were prepared according to the literature procedures.[8] The two commercially available chiral auxiliaries, (4*R*,5*S*)-4-methyl-5-phenyl-2-oxazolidinone (**1**) and 5-(*S*)-4-benzyl-2-oxazolidinone (**2**), were deprotonated with butyl lithium at −78 °C and subjected to propanoyl chloride providing the corresponding *N*-propionyl oxazolidinones **3** and **4**, respectively (Scheme 2). α-Alkylation was then carried out by first treatment of **3** and **4** with NaHMDS followed by the addition of either allyl or benzyl bromide leading to the desired alkylated products **5**–**8** with high diastereomeric excess.

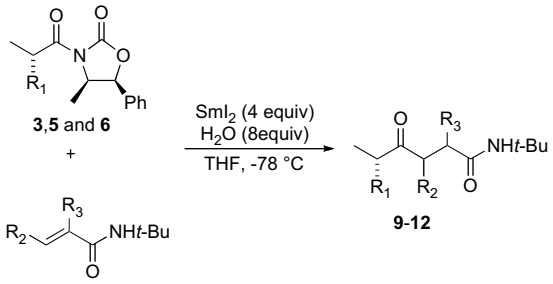


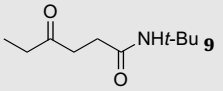
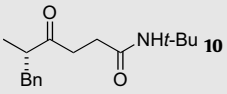
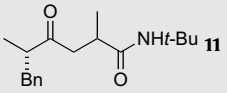
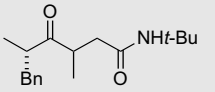
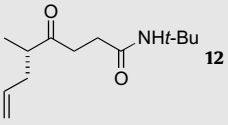
Scheme 2.

Studies on the SmI_2-promoted coupling of these chiral *N*-acyl oxazolidinones derived from auxiliary **1** with acrylamides are shown in Table 1. All reactions were performed according to our previously reported procedure[4a] whereby SmI_2 is added to a cooled THF solution (−78 °C) of the *N*-acyl oxazolidinone and the acrylamide with water as an additive.[4,5] To examine the influence of an additional substituent on the 2-oxazolidinone fragment on these coupling reactions, **3** was first reacted with *N*-*tert*-butyl acrylamide. Gratifyingly, this afforded the ethyl ketone **9** in a 67% yield (entry 1), which is even better than that previously reported with the unsubstituted 2-oxazolidinone.[4a] In agreement with this result, the desired chiral α-substituted ketones **10** and **12** could also be obtained in good yields (entries 2 and 5). Even coupling to an α-substituted acrylamide such as the *N*-*tert*-butyl methacrylamide gave the ketone **11** in a 64% yield though without any control at the new stereogenic carbon center formed under the coupling (entry 3). On the other hand, substitution in the β-position is detrimental as shown with the crotyl derivative, resulting in no carbon–carbon bond formation (entry 4).

Reactions performed with substrates bearing the alternative chiral auxiliary **2** proved also feasible (Table 2) leading to ketones **9**, **13**, and **14**. But in general slightly reduced yields were obtained, which can be attributed to the greater sterical bulk of the 2-oxazolidinone side chain adjacent to the reacting C=O center (benzyl vs methyl). In contrast to what was generally observed in coupling reactions with the simple 2-oxazolidinone, some reduction products of the chiral α-substituted ketones to the corresponding secondary alcohol were isolated in up to 15%. This may likely be a result of a premature collapse of the intermediate hemiaminal

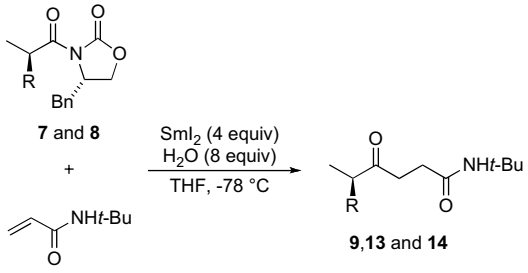
Table 1
Radical addition of *N*-*tert*-butyl acrylamides to *N*-acyl derivatives of (4*R*,5*S*)-4-methyl-5-phenyloxazolidin-2-one **1** promoted by SmI_2/H_2O

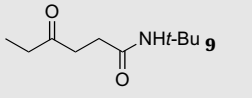
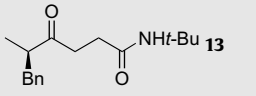
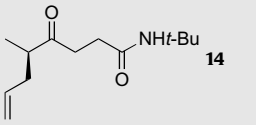


Entry	R_1	R_2	R_3	Product	Yield[a] (%)
1	H	H	H	 **9**	67
2	Bn	H	H	 **10**	72
3	Bn	H	Me	 **11**	64 (dr=1:1[b])
4	Bn	Me	H		0
5	Allyl	H	H	 **12**	65

[a] Isolated yields after column chromatography.
[b] Determined by ^1H NMR.

Table 2
Radical addition of *N*-*tert*-butyl acrylamides to *N*-acyl derivatives of (*S*)-4-benzyloxazolidin-2-one **2** promoted by SmI_2/H_2O

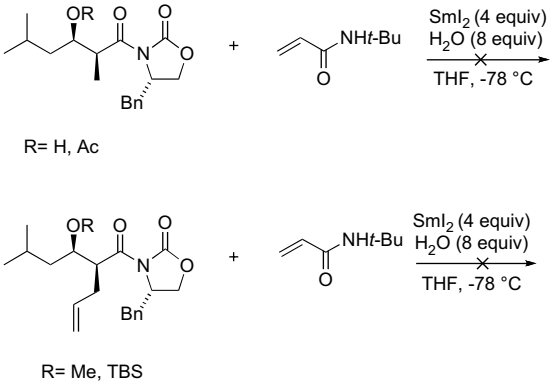


Entry	R	Product	Yield[a] (%)
1	H	 **9**	53
2	Bn	 **13**	61
3	Allyl	 **14**	55

[a] Isolated yields after column chromatography.

after the C–C bond forming step and can possibly be attributed to the increased bulk of the oxazolidinone.

To further investigate the utility of the developed protocol, we attempted the radical addition of substrates prepared from an Evans asymmetric aldol reaction.[9] The aldol substrates were prepared by first *Z*-selective enolization with *n*-Bu_2BOTf and Et_3N followed by subjection to the appropriate aldehyde. However, when subjected to SmI_2/H_2O in the presence of acrylamide reduced and dimerized acrylamide as well as unreacted starting material was obtained (Scheme 3). A range of protecting groups on the secondary alcohol were also tried, i.e., acetyl (Ac), methyl ether, and *tert*-butyl dimethyl silyl ether, but again no coupling product was detected and the starting material was recovered.



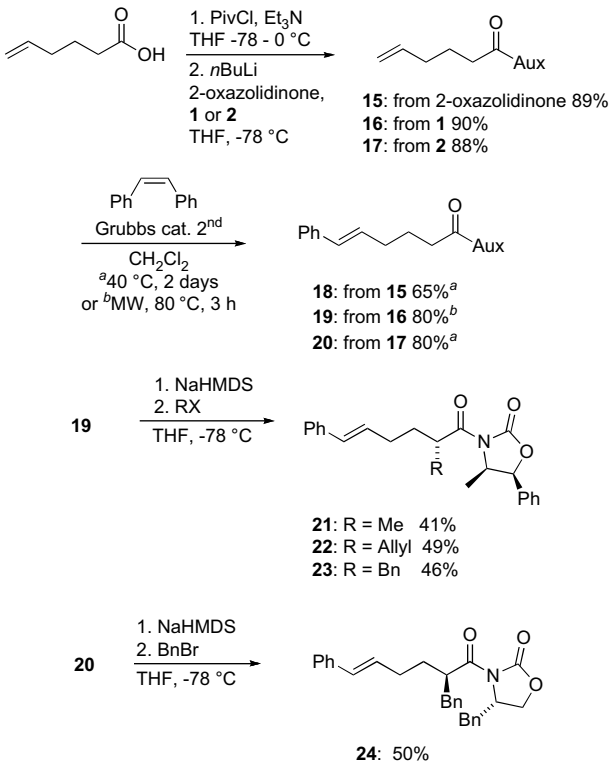
Scheme 3.

Also an intramolecular variant was attempted, the hydroxyl being protected with an acryl moiety. It was contemplated that the resulting acrylate would be reduced in the presence of SmI_2/H_2O and add to the *N*-acyl carbonyl. However, recovery of a product possessing a propanoyl functionalized hydroxyl group led us to conclude that the resulting radical is not suitably oriented to add to this carbonyl.

2.2. Intramolecular additions

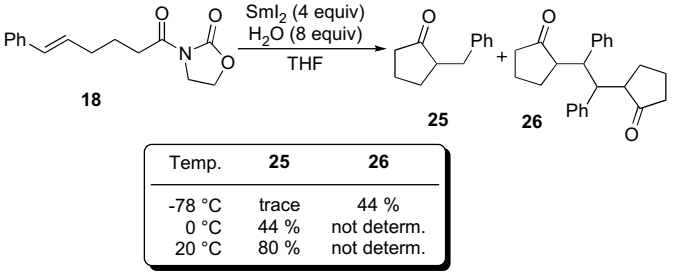
In previous work, we have found that *N*-acyl oxazolidinones could indeed be reduced to the ketyl radical in the absence of acrylates and acrylamides.[4b] The question therefore arose whether such carbon centered radicals could be exploited for intramolecular ketyl radical additions to an olefin for the preparation of chiral cyclic aliphatic ketones, as well as the corresponding heterocyclic systems. To test this possibility, the simple achiral substrate **15** was first synthesized by standard imide formation between 2-oxazolidinone and the commercially available hex-5-enoic acid (Scheme 4). Subsequent installment of the *C*6-phenyl group in **18** was conveniently accomplished via cross-metathesis with *cis*-stilbene using Grubbs second generation catalyst in dichloromethane.[10] Although the reaction was slow and required a period of 2 days, it was nevertheless clean affording the *trans*-styrene derivative in a 65% yield. The reaction time could be lowered to 3 h by running the reaction in a microwave at 80 °C as was achieved in the formation of **19** (Scheme 4).

The *N*-acyl oxazolidinone **18** was then tested for its ability to undergo 5-*exo*-*trig* cyclization at various reaction temperatures using the combination of SmI_2/H_2O in THF, as illustrated in Scheme 5. This ring closure event proved particularly rewarding at 20 °C where an 80% yield of 2-benzylpentanone (**25**) could be isolated after column chromatography. Lowering the reaction temperature had an adverse effect on the isolated yields of **25**, but at −78 °C, it was surprising to observe the formation of the dimer **16** as the



Scheme 4.

major isolated product (44% yield), which likely arises from radical dimerization of the intermediate benzylic radical.[11] Only traces of the desired cyclopentanone **25** could be observed upon ^1H NMR analysis of the crude reaction mixture.



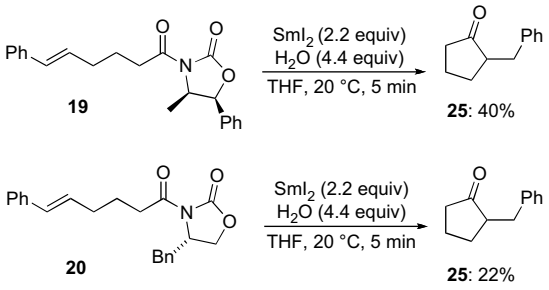
Temp.	25	26
-78 °C	trace	44 %
0 °C	44 %	not determ.
20 °C	80 %	not determ.

Scheme 5.

With these results in hand, we then turned to examine the reactivity of the corresponding chiral *N*-acyl oxazolidinones **19** and **20**, where it was anticipated that the *C*5-substitutent of the 2-oxazolidinone moiety would direct the selective facial attack of the ketyl radical onto the olefinic radical acceptor. These compounds were prepared in an analogous manner as that for compound **18** (Scheme 4).

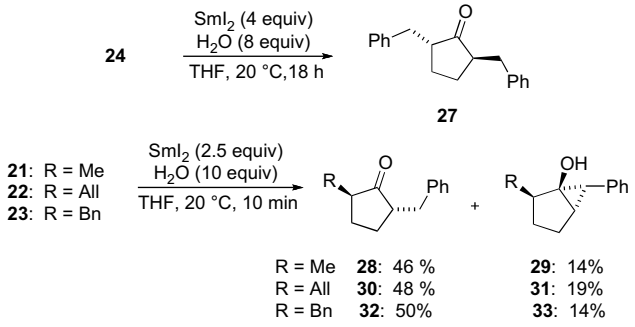
Although both *N*-acyl oxazolidinones **19** and **20** were consumed upon treatment with SmI_2, **19** provided only a moderate 40% yield of the cyclopentanone **25**, whereas the cyclic precursor **20** led to **25** in a poorer yield (Scheme 6). Considerable efforts were undertaken in an attempt to improve the efficiency of this transformation by varying the reaction temperature, as well as the nature of the additives, however, all in vain. In analogy to the intermolecular coupling reactions, the cyclizations were then examined with substrates subjected to an initial asymmetric alkylation. It was our expectation that introduction of this *C*2-substituent could induce

a geometric constraint that might favor the reactive conformation for cyclization. The asymmetric alkylations of **19** and **20** were performed with NaHMDS and with an alkyl halide providing compounds **21**–**24** (Scheme 4).



Scheme 6.

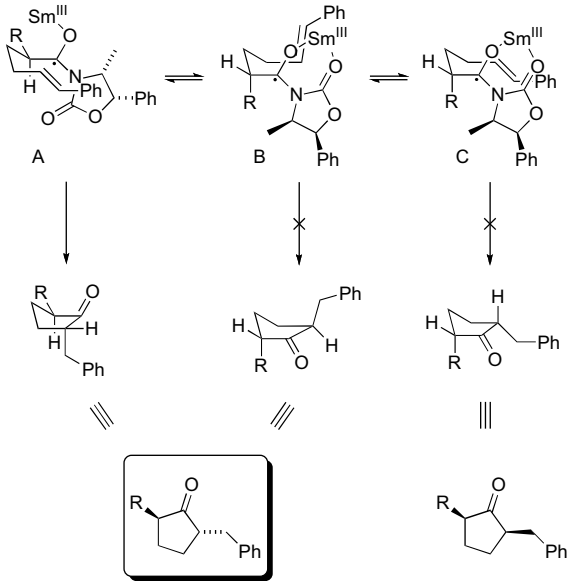
Gratifyingly, cyclization of the *N*-acyl oxazolidinone **24** with SmI_2 increased the ring closing yield to 53%, providing **27** as a single diastereomer according to ^1H NMR analysis (Scheme 7). The relative configuration between the two benzyl substituents on the cyclopentanone ring was assigned to the trans-relationship as a high optical activity was observed for this product. In a similar manner, the enantiomerically pure cyclopentanones **28**, **30**, and **32** could also be secured from the starting *N*-acyl oxazolidinones **21**–**23** in yields from 46 to 50%. However, a second product was isolated from these reactions, identified to possess the [3.1.0] bicyclic ring system, as illustrated with compounds **29**, **31**, and **33** in Scheme 7. The isolation of these products is not entirely surprising, as the intermediary benzylic anion bears a striking resemblance to the intermediate samarium carbanion of the Simmons–Smith type cyclopropanation of samarium enolates developed by Imamoto and Takiyama.[12] This in turn implies that there is partial collapse of the hemiaminal to the ketone, after ketyl radical addition to the alkene, which may be due to the increased sterical bulk of the more functionalized oxazolidinone. Such cyclopropane containing products were not observed with the simple 2-oxazolidinone.



Scheme 7.

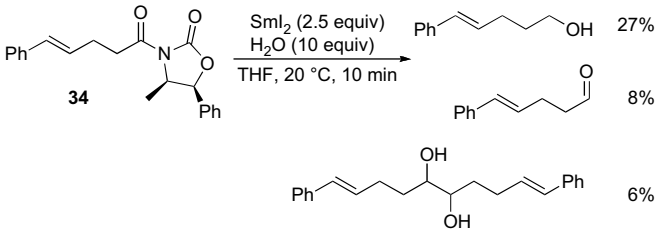
The effect of different proton donor additives was investigated on the cyclization of the *N*-acyl oxazolidinone **23**. When MeOH (10 equiv) was used as an additive, the results were the same as with H_2O, producing the cyclopentanone and the cyclopropanol by-product in 51 and 14% yield, respectively. On the other hand, with PhOH (10 equiv) the isolated yield was lowered to 22%, while the addition of *t*-BuOH (10 equiv) only gave a 7% yield of the desired cyclopentanone. In this latter case, the cyclopropanol was isolated in 25%, the high yield of which may originate from a slower protonation of the intermediary benzylic anion with this less acidic proton source.

A rational for the trans-selectivity observed for the cyclizations of the chiral *N*-acyl oxazolidinones **21**–**24** is given in Scheme 8. In analogy with the previous studies on the ketyl–olefin radical cyclizations performed by Molander and McKie,[13] it can be expected that our ring closures proceed through an envelope transition state with a trans-relationship between the ketyl oxygen and the olefin, as depicted with conformers **A** and **C**. This is explained by electronic repulsion between the anionic oxygen and the forming methylene radical as would occur with conformer **B**. Moreover, **A** has the benefit of having the R substituent in a pseudo-equatorial position as opposed to **B**, which places R in a pseudo-axial orientation. For all cases, we assume that the olefin prefers to approach the ketyl from the side opposite to the protruding *C*5-substituent presented on the oxazolidinone ring. As conformer **C** would lead to the product of cis-selectivity, we therefore and counter intuitively suggest that our samarium diiodide mediated ketyl–olefin cyclizations proceed through a monodentate coordinated samarium species **A** based on the observed stereoselectivity. This suggestion is in agreement with that proposed by Badone and coworkers on the radical cyclizations of chiral oxazoldinone-derived 2-alkeneamides.[14]



Scheme 8.

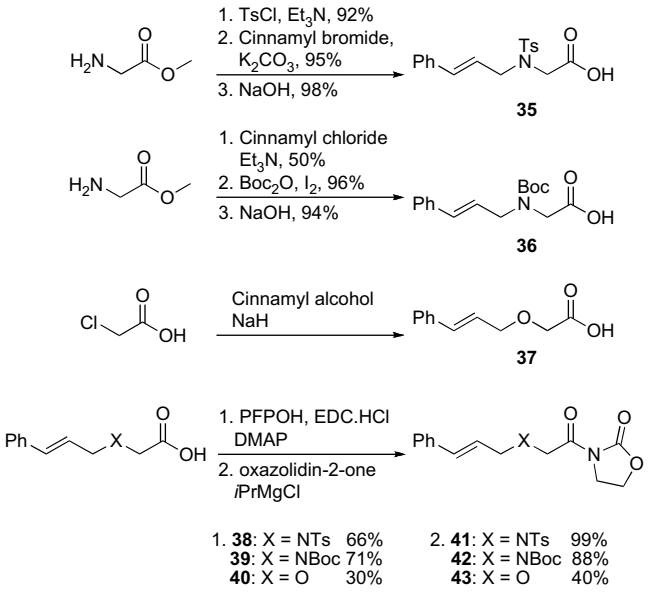
Attempts were also undertaken to examine whether the product from 4-*exo*-*trig* cyclization could also be feasible using these reaction conditions. However, subjecting *N*-acyl oxazolidinone **34** to SmI_2/H_2O did not lead to any ring closing products (Scheme 9). Nonetheless, several by-products derived from reduction of the imide functionality were found including a substantial amount of starting material (38%).



Scheme 9.

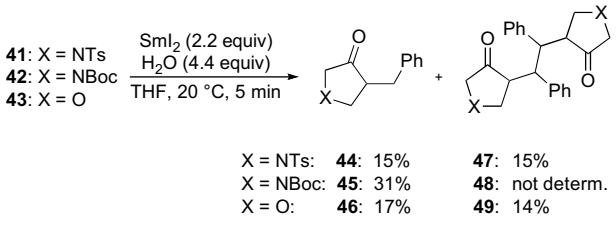
Finally, a small study was initiated to investigate the application of these SmI_2 cyclizations with cyclic precursors possessing a heteroatom in the chain, under the assumption that the rate constant

for 5-*exo* cyclization substrates containing a nitrogen or oxygen is higher than that for the corresponding all carbon chain and therefore cyclization yields were expected to be greater. For this purpose, the carboxylic acids **35**–**37** containing either an NBoc, NTs, or an oxygen in the chain were prepared using standard synthetic transformations (Scheme 10). Subsequent conversion to their PFP-esters **38**–**40** and imide formation with 2-oxazolidinone in the presence of isopropyl magnesium bromide then led to the desired *N*-acyl oxazolidinones **41**–**43**.[5]



Scheme 10.

The substrates **41**–**43** were cyclized according to the same procedure as their carbon analogs, but the yields of the cyclic ketones **44**–**46** were disappointingly low for all three cases (Scheme 11). Considerable efforts were made to optimize the reactions and a slight improvement was found when the substrate **42** was added slowly over a 20 min period by syringe pump to the ethereal solution of SmI_2 and H_2O, leading to a 31% yield of the cyclized product **45**. As observed earlier in the cyclization of the simple *N*-acyl oxazolidinone **18** where also the product **26** of dimerization was observed when the reaction was performed at low temperature, the same series of products **47**–**49** could also be noted for these cyclization studies promoted by SmI_2.



Scheme 11.

3. Conclusion

In summary, we have examined the suitability of chiral oxazolidinones in the SmI_2-mediated carbon–carbon bond generating reactions between the imide functionality of an *N*-acyl oxazolidinone unit with olefinic radical acceptors. Quite pleasingly, we have demonstrated that products from an Evans asymmetric alkylation can undergo direct C–C bond formation with an acrylamide providing chiral acyclic ketones in reasonable yields. This represents the first example of a transformation of such *N*-acyl oxazolidinones where this chiral auxiliary is removed under the conditions for ketone formation. Finally, cyclization studies were also examined with the same type of substrates, providing *trans*-2,5-disubstituted cyclopentanones in yields of approx. 50%. However, attempts to cyclize heteroatom-containing equivalents were less successful.

4. Experimental section

4.1. General methods

Unless otherwise noted all reactions were carried out under inert atmosphere. Solvents were dried according to standard procedures and reactions were monitored by thin-layer chromatographic (TLC) analysis. All other chemicals were used as-received from the appropriate suppliers. Flash chromatography was carried out on silica gel 60 (230–400 mesh). SmI_2 was prepared according to a literature method.[15]

The ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz. The chemical shifts are reported in parts per million downfield to TMS (δ=0) and referenced using the residual $CHCl_3$ resonance (δ=7.26) for ^1H NMR and the central $CDCl_3$ resonance (δ=77.16) for ^{13}C NMR. ^1H NMR spectra are reported as follows: s=singlet, d=doublet, t=triplet, q=quartet, qn=quintet, sx=sextet, sp=septet, br=broad; coupling constant(s) in hertz; integration.

4.2. (4*R*,5*S*)-4-Methyl-3-((*S*)-2-methyl-3-phenylpropanoyl)-5-phenyloxazolidin-2-one (5). General procedure for the asymmetric alkylation of chiral *N*-acyl oxazolidinones[8]

N-Acyl oxazolidinone **3** (2.405 g, 10.31 mmol) was dissolved in THF (35 mL) and cooled to −78 °C, and then NaHMDS (1.0 M in THF, 12.0 mL, 12.0 mmol) was added dropwise to the solution and stirred for 30 min at −78 °C. Then benzyl bromide (3.7 mL, 31 mmol) was added, and the solution was allowed to warm to 0 °C over 60 min, and finally quenched with water (50 mL). The reaction mixture was concentrated in vacuo, and extracted with CH_2Cl_2 (3×50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, obtaining a pale yellow oil. The pure product was obtained by column chromatography (10% EtOAc in pentane as eluant), which gave compound **5** (2.049 g, 6.475 mmol, 64%) as a colorless wax. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.41–4.16 (m, 10H), 5.63 (d, *J*=7.4 Hz, 1H), 4.75 (m, 1H), 4.20–4.09 (m, 1H), 3.11 (dd, *J*=13.3, 6.7 Hz, 1H), 2.66 (dd, *J*=13.3, 8.0 Hz, 1H), 1.19 (d, *J*=6.7 Hz, 3H), 0.73 (d, *J*=6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.4, 152.7, 137.8, 134.9, 128.8 (4C), 128.3 (4C), 126.4 (2C), 78.4, 54.7, 40.2, 37.7, 15.1, 14.9.

*4.2.1. (4R,5S)-4-Methyl-3-((S)-2-methylpent-4-enoyl)-5-phenyloxazolidin-2-one (**6**)*

The reaction was conducted according to the general procedure for asymmetric alkylation of chiral *N*-acyl oxazolidinones: *N*-acyl oxazolidinone **3** (500 mg, 2.15 mmol), NaHMDS (1.0 M in THF, 2.63 mL, 2.63 mmol), and allyl bromide (0.22 mL, 2.6 mmol). The pure product was obtained by column chromatography (5% EtOAc in pentane as eluant), which gave compound **6** (393 mg, 1.4 mmol, 67%) as a white solid. Mp 64–65 °C (EtOAc/hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41–7.25 (m, 5H), 5.83–5.73 (m, 1H), 5.64 (d, *J*=7.3 Hz, 1H), 5.06–4.99 (m, 2H), 4.80–4.73 (m, 1H), 3.91–3.82 (m, 1H), 2.51–2.44 (m, 1H), 2.36–2.16 (m, 1H), 1.18 (d, *J*=6.8 Hz, 3H), 0.84 (d, *J*=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.9, 152.9, 134.9, 134.4, 129.7 (2C), 129.2 (2C), 126.9, 116.8, 78.4,

55.3, 41.8, 37.8, 17.1, 14.1. HRMS $C_{16}H_{19}NO_3$ [M+Na^+] calculated: 296.1263, found: 296.1271.

4.2.2. (S)-4-Benzyl-3-((R)-2-methyl-3-phenylpropanoyl)-oxazolidin-2-one (**7**)

The reaction was conducted according to the general procedure for asymmetric alkylation of chiral *N*-acyl oxazolidinones: *N*-acyl oxazolidinone **4** (500 mg, 2.15 mmol), NaHMDS (1.0 M in THF, 2.63 mL, 2.63 mmol) and benzyl bromide (0.31 mL, 2.6 mmol). The pure product was obtained by column chromatography (10% EtOAc in pentane as eluant), which gave compound **7** (444 mg, 1.4 mmol, 64%) as a white solid. Mp 91–92 °C (EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34–7.05 (m, 10H), 4.70–4.64 (m, 1H), 4.19–4.07 (m, 3H), 3.19 (dd, *J*=13.2, 7.2 Hz, 1H), 3.08 (dd, *J*=13.4, 3.2 Hz, 1H), 2.71 (dd, *J*=13.2, 7.2 Hz, 1H), 2.59 (dd, *J*=13.4, 9.1 Hz, 1H), 1.22 (d, *J*=6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.6, 153.3, 139.5, 135.4, 129.6 (2C), 129.1 (4C), 128.6 (2C), 127.5, 126.6, 66.1, 55.2, 40.1, 39.8, 37.9, 17.1. HRMS $C_{20}H_{21}NO_3$ [M+Na^+] calculated: 346.1419, found: 346.1411.

4.2.3. (S)-4-Benzyl-3-((R)-2-methylpent-4-enoyl)-oxazolidin-2-one (**8**)

Reaction was conducted according to the general procedure for asymmetric alkylation of chiral *N*-acyl oxazolidinones: *N*-acyl oxazolidinone **4** (500 mg, 2.15 mmol), NaHMDS (1.0 M in THF, 2.63 mL, 2.63 mmol) and allyl bromide (0.22 mL, 2.6 mmol). The pure product was obtained by column chromatography (5% EtOAc in pentane as eluant), which gave compound **8** (346 mg, 1.3 mmol, 59%) as a colorless wax. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29–7.16 (m, 5H), 5.84–5.71 (m, 1H), 5.08–5.00 (m, 2H), 4.66–4.60 (m, 1H), 4.15–4.07 (m, 2H), 3.81 (dqn, *J*=13.5, 6.7 Hz, 1H), 3.22 (dd, *J*=13.3, 2.8 Hz, 1H), 2.66 (dd, *J*=13.3, 9.7 Hz, 1H), 2.51–2.44 (m, 1H), 2.22–2.15 (m, 1H), 1.14 (d, *J*=6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.6, 153.3, 135.6, 135.5, 129.6 (2C), 129.1 (2C), 127.5, 117.4, 66.1, 55.5, 38.3, 38.2, 37.3, 16.6. HRMS $C_{16}H_{19}NO_3$ [M+Na^+] calculated: 296.1263, found: 296.1257.

4.2.4. (E)-N-tert-Butylbut-2-enamide

Ethyl *trans*-2-butenoate (125 mg, 1.1 mmol) is dissolved in EtOH (5 mL) followed by addition of NaOH(aq) (2 M, 1.3 mL, 2.6 mmol) and stirred for 4 h, followed by addition of HCl(aq) (2 M, 1.5 mL, 3 mmol). The solution is extracted with CH_2Cl_2 (4×10 mL) and concentrated in vacuo. The crude oil is used without further purification, dissolved in CH_2Cl_2 (10 mL), and cooled to 0 °C followed by addition of NMM (1.7 mL, 1.6 mmol), *tert*-butylamine (117 mg, 1.6 mmol), and EDC (0.3 g, 1.6 mmol). The solution was stirred at room temperature for 6 h, and then washed with water (3×5 mL) and brine (5 mL) and concentrated in vacuo. The pure product was obtained by column chromatography (5% EtOAc in pentane as eluant), which gave the title compound (141 mg, 1.0 mmol, 91%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.81–6.72 (m, 1H), 5.70 (d, *J*=15.0 Hz, 1H), 5.23 (br s, 1H), 1.82 (dd, *J*=6.8, 1.6 Hz, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.6, 141.2, 123.1, 51.9, 29.4 (3C), 18.7. HRMS $C_8H_{15}NO$ [M+Na^+] calculated: 164.1051, found: 164.1042.

4.3. *N-tert*-Butyl-4-oxohexanamide (9). General procedure for coupling with acrylamides[4a]

Water (54 μL, 3 mmol) was added to a solution of *N*-acyl oxazolidinone **3** (129 mg, 0.555 mmol) and *N-tert*-butylacrylamide (48 mg, 0.375 mmol) in THF (5.0 mL), and then the solution was cooled to −78 °C. A solution of SmI_2 (0.1 M, 15 mL, 1.5 mmol) was added dropwise over 1 h. The reaction mixture was then left stirring at −78 °C for 24 h. Excess SmI_2 was oxidized by flushing the mixture with oxygen from a balloon. To the now yellow reaction mixture was added satd NH_4Cl(aq) (4 mL) at −78 °C followed by warming to room temperature. HCl(aq) (1 M, 5 mL) was added followed by extraction with EtOAc (3×10 mL). The combined organic phases were washed with $Na_2S_2O_3$(aq) (10 mL), dried over $MgSO_4$, filtered, and then evaporated in vacuo. The pure product was obtained by column chromatography (15% EtOAc in pentane as eluant), which gave compound **9** (37 mg, 0.198 mmol, 53%) as a colorless solid. Mp 51–52 °C (EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.47 (br s, 1H), 2.74 (t, *J*=6.0 Hz, 2H), 2.58 (m, 4H), 1.30 (s, 9H), 1.09 (t, *J*=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.7, 172.3, 51.7, 37.5, 35.4, 30.8, 29.2 (3C), 7.6. HRMS $C_{10}H_{19}NO_2$ [M+Na^+] calculated: 208.1313, found: 208.1310.

4.3.1. (S)-N-tert-Butyl-5-methyl-4-oxo-6-phenylhexanamide (**10**)

The title compound was prepared using the general method for the SmI_2-promoted coupling with acrylamides, with *N*-acyl oxazolidinone **5** (179 mg, 0.555 mmol) and *N-tert*-butylacrylamide (48 mg, 0.375 mmol). The pure product was obtained by column chromatography (15% EtOAc in pentane as eluant), which gave compound **10** (74 mg, 0.27 mmol, 72%) as a colorless amorphous solid. $[\alpha]_D^{23}$ −9.3 (*c* 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30–7.24 (m, 2H), 7.22–7.16 (m, 1H), 7.16–7.11 (m, 2H), 5.50 (s, 1H), 3.00 (dd, *J*=13.5, 6.9 Hz, 1H), 2.93–2.77 (m, 2H), 2.65–2.52 (m, 2H), 2.39–2.21 (m, 2H), 1.32 (s, 9H), 1.10 (d, *J*=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 213.5, 171.3, 139.7, 129.0 (2C), 128.5 (2C), 126.4, 51.2, 48.2, 39.1, 37.2, 30.9, 28.9 (3C), 16.5. HRMS $C_{17}H_{25}NO_2$ [M+Na^+] calculated: 298.1783, found: 298.1774.

4.3.2. (5S)-N-tert-Butyl-2,5-dimethyl-4-oxo-6-phenylhexanamide (**11**)

The title compound was prepared using the general method for the SmI_2-promoted coupling with acrylamides, with *N*-acyl oxazolidinone **5** (179 mg, 0.555 mmol) and *N-tert*-butylmethacrylamide (53 mg, 0.375 mmol). The pure product was obtained by column chromatography (15% EtOAc in pentane as eluant), which gave compound **11** (69 mg, 0.240 mmol, 64%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27–7.13 (m, 5H), 5.53 (br s, 1H), 3.02–2.41 (m, 5H), 2.13 (dd, *J*=18.0, 4.3 Hz, 1H), 1.30 (s, 9H), 1.09 (d, *J*=7.1 Hz, 3H), 1.06 (d, *J*=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 213.6, 175.0, 139.8, 129.1 (2C), 128.6 (2C), 126.4, 51.1, 48.4, 46.6, 39.2, 36.4, 28.9 (3C), 17.9, 16.3. HRMS $C_{18}H_{27}NO_2$ [M+Na^+] calculated: 312.1939, found: 312.1942.

4.3.3. (S)-N-tert-Butyl-5-methyl-4-oxooct-7-enamide (**12**)

The title compound was prepared using the general method for the SmI_2-promoted coupling with acrylamides, with *N*-acyl oxazolidinone **6** (151 mg, 0.555 mmol) and *N-tert*-butylacrylamide (48 mg, 0.375 mmol). The pure product was obtained by column chromatography (20% EtOAc in pentane as eluant), which gave compound **12** (55 mg, 0.243 mmol, 65%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.77–5.64 (m, 1H), 5.48 (br s, 1H), 5.07–4.94 (m, 2H), 2.87–2.61(m, 3H), 2.42–2.30 (m, 3H), 2.11–2.04 (m, 1H), 1.30 (s, 9H), 1.04 (d, *J*=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 211.2, 172.7, 132.9, 115.9, 52.2, 46.1, 35.7, 35.2, 31.0, 29.7 (3C), 16.7. HRMS $C_{13}H_{23}NO_2$ [M+Na^+] calculated: 248.1626, found: 248.1620.

4.3.4. (R)-N-tert-Butyl-5-methyl-4-oxo-6-phenylhexanamide (**13**)

The title compound was prepared using the general method for the SmI_2-promoted coupling with acrylamides, with *N*-acyl oxazolidinone **7** (179 mg, 0.555 mmol) and *N-tert*-butylacrylamide (48 mg, 0.375 mmol). The pure product was obtained by column chromatography (15% EtOAc in pentane as eluant), which gave compound **13** (63 mg, 0.228 mmol, 61%) as a colorless amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29–7.23 (m, 2H), 7.21–7.15 (m, 1H), 7.15–7.10 (m, 2H), 5.47 (s, 1H), 2.99 (dd, *J*=13.5, 6.9 Hz,

1H), 2.92–2.75 (m, 2H), 2.64–2.51 (m, 2H), 2.37–2.19 (m, 2H), 1.31 (s, 9H), 1.08 (d, J=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 213.5, 171.4, 139.8, 129.1 (2C), 128.6 (2C), 126.5, 51.3, 48.3, 39.2, 37.3, 31.0, 29.1, 29.0 (3C), 16.6. HRMS $C_{17}H_{25}NO_2$ [M+Na$^+$] calculated: 298.1783, found: 298.1774.

4.3.5. (R)-N-tert-Butyl-5-methyl-4-oxooct-7-enamide (**14**)

The title compound was prepared using the general method for the SmI_2-promoted coupling with acrylamides, with *N*-acyl oxazolidinone **8** (151 mg, 0.555 mmol) and *N*-*tert*-butylacrylamide (48 mg, 0.375 mmol). The pure product was obtained by column chromatography (20% EtOAc in pentane as eluant), which gave compound **14** (46 mg, 0.206 mmol, 55%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.73–5.62 (m, 1H), 5.51 (br s, 1H), 5.98–5.03 (m, 2H), 2.84–2.57 (m, 3H), 2.41–2.30 (m, 3H), 2.12–2.03 (m, 1H), 1.30 (s, 9H), 1.07 (d, J=6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 211.4, 172.4, 133.1, 115.7, 52.0, 46.4, 35.2, 34.9, 31.5, 29.2 (3C), 17.0. HRMS $C_{13}H_{23}NO_2$ [M+Na$^+$] calculated: 248.1626, found: 248.1620.

4.4. (*S*)-4-Benzyl-3-hex-5-enoyloxazolidin-2-one (17).[16] General procedure for the synthesis of *N*-acyl oxazolidinones

Hex-5-enoic acid (0.5 mL, 4.2 mmol) was dissolved in THF (17 mL) and cooled to −78 °C. Triethylamine (0.75 mL, 5.4 mmol) and subsequently pivaloyl chloride (0.54 mL, 4.4 mmol) were added and the mixture was stirred for 15 min before it was allowed to warm up to 0 °C. After 1 h at 0 °C, the mixture was cooled to −78 °C again. Then a solution of (*S*)-4-benzyloxazolidin-2-one (815 mg, 4.6 mmol) deprotonated by treatment with *n*-BuLi (2.9 mL of 1.6 M in hexane, 4.6 mmol) in THF (13 mL) at −78 °C for 1 h was added via cannula with N_2 pressure. The mixture was stirred for 20 h at −78 °C and then the reaction was quenched with concentrated acetic acid (1.3 mL, 20 mmol) and allowed to warm up to room temperature. After 3 h, the mixture was poured into NH_4Cl(aq) (13 mL) and extracted three times with Et_2O (50 mL). The combined organic portions were washed two times with $NaHCO_3$(aq) (100 mL) and two times with brine (100 mL), and then dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and purification by flash column chromatography (increasing polarity from 5 to 10% EtOAc in pentane as eluant) provided the desired product **17** as a colorless oil (1.01 g, 3.7 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35–7.20 (m, 5H), 5.82 (ddt, J=16.8, 10.0, 6.8 Hz, 1H), 5.06 (dq, J=16.8, 1.2 Hz, 1H), 5.00 (ddt, J=10.0, 2.0, 1.2 Hz, 1H), 4.67 (ddt, J=9.6, 7.2, 3.2 Hz, 1H), 4.22–4.17 (m, 2H), 3.30 (dd, J=13.2, 3.2 Hz, 1H), 3.03–2.88 (m, 2H), 2.77 (dd, J=13.2, 9.6 Hz, 1H), 2.15 (qt, J=7.2, 1.2 Hz, 2H), 1.87–1.77 (m, 2H).

4.4.1. 3-Hex-5-enoyloxazolidin-2-one (**15**)[17]

The title compound was prepared according to the general method for *N*-acyl oxazolidinones using hex-5-enoic acid (392 mg, 3.43 mmol), triethylamine (0.62 mL, 4.5 mmol) and pivaloyl chloride (0.51 mL, 4.1 mmol) in THF (17 mL). Oxazolidin-2-one (329 mg, 3.78 mmol), *n*-BuLi (1.6 M in hexane, 2.47 mL, 4.6 mmol) in THF (13 mL). Flash column chromatography (20% EtOAc in pentane as eluant) gave the desired product **15** as a colorless oil (561 mg, 3.06 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.79 (ddt, J=16.8, 10.0, 7.2 Hz, 1H), 5.03 (dd, J=16.8, 1.2 Hz, 1H), 4.98 (dd, J=10.0, 1.2 Hz, 1H), 4.41 (t, J=9.2 Hz, 2H), 4.02 (t, J=9.2 Hz, 2H), 2.95 (t, J=7.2 Hz, 2H), 2.15 (q, J=7.2 Hz, 2H), 1.77 (qn, J=7.2 Hz, 2H).

4.4.2. (4R,5S)-3-Hex-5-enoyl-4-methyl-5-phenyloxazolidin-2-one (**16**)

5-Hexenoic acid (0.87 mL, 7.3 mmol) was dissolved in THF (30 mL) under an inert atmosphere of argon. The solution was cooled to −78 °C. Subsequently, Et_3N (1.3 mL, 9.4 mmol) and pivaloyl chloride (0.95 mL, 7.7 mmol) were added. The reaction mixture was left stirring for 15 min at −78 °C, 1 h at 0 °C, and then re-cooled to −78 °C. In a separate flask, oxazolidinone **1** (1.435 g, 8.095 mmol) was dissolved in THF (23 mL) under an inert atmosphere of argon. The solution was cooled to −78 °C and *n*-butyl lithium (1.6 M in hexane, 5.1 mL, 8.2 mmol) was added dropwise. After 1 h of stirring at −78 °C, the solution was transferred to the first solution via cannula and the resulting reaction mixture was left stirring overnight at −78 °C. Quenching of excess base was achieved by adding AcOH (2.2 mL) and the solution was allowed to reach room temperature over 2 h. Then NH_4Cl(aq) (23 mL) and water were added followed by extraction with diethyl ether (3×30 mL). The organic phases were washed with $NaHCO_3$(aq)×3 and brine, and subsequently dried over Na_2SO_4, filtered, and then concentrated in vacuo. The pure product was obtained by column chromatography (10% EtOAc in pentane as the eluant), which gave compound **16** (1.795 g, 6.569 mmol, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45–7.23 (m, 5H), 5.80 (ddt, J=16.9, 10.2, 6.7 Hz, 1H), 5.64 (d, J=7.3 Hz, 1H), 5.03 (ddd, J=17.1, 3.6, 1.6 Hz, 1H), 5.00–4.95 (m, 1H), 4.74 (dq, J=13.3, 6.6 Hz, 1H), 2.94 (qdd, J=17.0, 8.0, 6.9 Hz, 2H), 2.18–2.07 (m, 2H), 1.84–1.70 (m, 2H), 0.87 (d, J=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.9, 153.1, 137.9, 133.5, 128.8, 128.7 (2C), 125.7 (2C), 115.4, 79.0, 54.8, 35.0, 33.1, 23.5, 14.6. HRMS $C_{16}H_{19}NO_3$ [M+Na$^+$] calculated: 296.1257, found: 296.1263.

4.4.3. (E)-3-(6-Phenylhex-5-enoyl)oxazolidin-2-one (**18**)

The title compound was prepared by the same method as described for **20** using terminal alkene **15** (110 mg, 0.60 mmol), *cis*-stilbene (0.22 mL, 1.2 mmol), and Grubbs' second generation catalyst (3 mg, 0.5 mol %). Flash column chromatography (10% EtOAc in pentane as eluant) gave the desired product **18** as a colorless oil (101 mg, 0.39 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35–7.27 (m, 4H), 7.21–7.17 (m, 1H), 6.41 (d, J=15.6 Hz, 1H), 6.20 (dt, J=15.6, 7.2 Hz, 1H), 4.33 (t, J=8.0 Hz, 2H), 3.96 (t, J=8.0 Hz, 2H), 2.99 (t, J=7.2 Hz, 2H), 2.30 (qd, J=7.2, 1.2 Hz, 2H), 1.98 (qn, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.6, 153.8, 137.8, 130.9, 130.0, 128.7 (2C), 127.2, 126.2 (2C), 62.2, 42.7, 34.6, 32.6, 24.1. HRMS $C_{15}H_{17}NO_3$ [M+Na$^+$] calculated: 282.1106, found: 282.1113.

4.4.4. (4R,5S)-4-Methyl-5-phenyl-3-((E)-6-phenylhex-5-enoyl)oxazolidin-2-one (**19**)

Grubbs' second generation catalyst (5.5 mg, 0.0065 mmol) was placed in a 5 mL microwave tube under an inert atmosphere of argon. *N*-Acyl oxazolidinone **16** (299.5 mg, 1.096 mmol) and *cis*-stilbene (0.59 mL, 3.3 mmol) were dissolved in CH_2Cl_2 (2.2 mL) and transferred to the microwave tube. The reaction mixture was heated to 80 °C in a Biotage Initiator™ microwave for 3 h. Finally, it was concentrated with silica in vacuo and transferred directly for column chromatography (increasing polarity from 2 to 40% EtOAc in pentane), which gave **19** (307.3 mg, 0.8795 mmol, 80%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51–7.15 (m, 10H), 6.45 (d, J=15.9 Hz, 1H), 6.24 (dt, J=15.8, 6.9 Hz, 1H), 5.52 (d, J=7.3 Hz, 1H), 4.72 (qn, J=6.7 Hz, 1H), 3.03 (t, J=7.2 Hz, 2H), 2.42–2.26 (m, 2H), 1.93 (qn, J=7.3 Hz, 2H), 0.89 (d, J=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.0, 153.1, 137.7, 133.4, 130.8, 129.9, 128.8, 128.8 (2C), 128.6 (2C), 127.1, 126.1 (2C), 125.7 (2C), 79.0, 54.8, 35.0, 32.5, 24.0, 14.6. HRMS $C_{22}H_{23}NO_3$ [M+Na$^+$] calculated: 372.1570, found: 372.1569.

4.4.5. (S)-4-Benzyl-(E)-3-(6-phenylhex-5-enoyl)-oxazolidin-2-one (**20**)

A solution of terminal alkene **17** (300 mg, 1.09 mmol) in CH_2Cl_2 (2 mL) was transferred by syringe to Grubbs' second generation catalyst (5 mg, 0.5 mol %). *cis*-Stilbene (0.38 mL, 2.19 mmol) was added and the mixture was heated to reflux for 48 h. The solvent

was removed in vacuo and purification by flash column chromatography (5% EtOAc in pentane as eluant) gave the product **20** as a colorless oil (307 mg, 0.88 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.35 (m, 7H), 7.22–7.18 (m, 3H), 6.45 (d, J=15.6 Hz, 1H), 6.24 (dt, J=15.6, 7.2 Hz, 1H), 4.64 (ddt, J=9.6, 7.0, 3.2 Hz, 1H), 4.18–4.08 (m, 2H), 3.28 (dd, J=13.2, 3.2 Hz, 1H), 3.02 (td, J=7.2, 1.6 Hz, 2H), 2.74 (dd, J=13.2, 9.6 Hz, 1H), 2.34 (q, J=7.2 Hz, 2H), 1.92 (qn, J=7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.3, 153.6, 137.7, 135.4, 130.8, 129.8, 129.5 (2C), 129.1 (2C), 128.6 (2C), 127.5, 127.1, 126.1 (2C), 66.3, 55.3, 38.1, 35.0, 32.5, 24.0. HRMS $C_{22}H_{23}NO_3$ [M+Na$^+$] calculated: 372.1576, found: 372.1577.

4.4.6. (4R,5S)-4-Methyl-3-((R,E)-2-methyl-6-phenylhex-5-enoyl)-5-phenyloxazolidin-2-one (**21**)

The reaction was conducted according to the general procedure for asymmetric alkylation of chiral *N*-acyl oxazolidinones, with *N*-acyl oxazolidinone **19** (181.8 mg, 0.5203 mmol), NaHMDS (1 M in THF, 0.62 mL, 0.62 mmol), and methyl iodide (97 μL, 1.6 mmol). The pure product was obtained by column chromatography (increasing polarity from 2 to 10% Et_2O in pentane as the eluant), which gave compound **21** (78.3 mg, 0.215 mmol, 41%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41–7.27 (m, 7H), 7.25–7.20 (m, 1H), 7.16–7.08 (m, 2H), 6.40 (d, J=15.9 Hz, 1H), 6.20 (ddd, J=15.8, 8.3, 5.9 Hz, 1H), 4.99 (d, J=7.2 Hz, 1H), 4.50 (qn, J=6.7 Hz, 1H), 3.83–3.72 (m, 1H), 2.44–2.32 (m, 1H), 2.29–2.17 (m, 1H), 2.17–2.02 (m, 1H), 1.69–1.55 (m, 1H), 1.22 (d, J=6.9 Hz, 3H), 0.80 (d, J=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 177.1, 152.8, 137.6, 133.5, 130.5, 130.3, 128.8 (2C), 128.7 (2C), 127.3, 126.1 (2C), 125.7 (2C), 78.7, 55.0, 37.7, 32.9, 31.8, 18.1, 14.5. HRMS $C_{23}H_{25}NO_3$ [M+Na$^+$] calculated: 386.1727, found: 386.1725.

4.4.7. (4R,5S)-3-((S,E)-2-Allyl-6-phenylhex-5-enoyl)-4-methyl-5-phenyloxazolidin-2-one (**22**)

The reaction was conducted according to the general procedure for the asymmetric alkylation of chiral *N*-acyl oxazolidinones, with *N*-acyl oxazolidinone **19** (176.0 mg, 0.5037 mmol), NaHMDS (1 M in THF, 0.6 mL, 0.6 mmol), and allyl bromide (0.13 mL, 1.5 mmol). The pure product was obtained by column chromatography (increasing polarity from 2 to 10% Et_2O in pentane as the eluant), which gave compound **22** (96.9 mg, 0.249 mmol, 49%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43–7.30 (m, 7H), 7.27–7.22 (m, 1H), 7.13–7.07 (m, 2H), 6.42 (d, J=15.9 Hz, 1H), 6.20 (ddd, J=15.8, 8.6, 5.6 Hz, 1H), 5.84 (ddt, J=17.2, 10.1, 7.2 Hz, 1H), 5.12–4.99 (m, 2H), 4.81 (d, J=7.3 Hz, 1H), 4.49 (p, J=6.6 Hz, 1H), 4.02–3.93 (m, 1H), 2.50–2.37 (m, 2H), 2.37–2.18 (m, 2H), 2.11 (dtd, J=13.7, 9.3, 6.7 Hz, 1H), 1.74 (dddd, J=13.6, 6.8, 5.1, 3.7 Hz, 1H), 0.77 (d, J=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.0, 152.8, 137.5, 135.0, 133.5, 130.5, 130.3, 128.8 (C2), 128.7, 128.6 (C2), 127.3, 126.1 (C2), 125.7 (C2), 117.4, 78.5, 54.9, 42.2, 37.9, 32.1, 30.9, 14.6. HRMS $C_{25}H_{27}NO_3$ [M+Na$^+$] calculated: 412.1883, found: 412.1885.

4.4.8. (4R,5S)-3-((S,E)-2-Benzyl-6-phenylhex-5-enoyl)-4-methyl-5-phenyloxazolidin-2-one (**23**)

The reaction was conducted according to the general procedure for asymmetric alkylation of chiral *N*-acyl oxazolidinones, with *N*-acyl oxazolidinone **19** (691.5 mg, 1.979 mmol), NaHMDS (1 M in THF, 2.4 mL, 2.4 mmol), and benzyl bromide (0.71 mL, 5.9 mmol). The pure product was obtained by column chromatography (increasing polarity from 2 to 10% Et_2O in pentane as the eluant), which gave compound **23** (399.1 mg, 0.9080 mmol, 46%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44–7.16 (m, 13H), 7.06–7.00 (m, 2H), 6.41 (d, J=15.9 Hz, 1H), 6.20 (ddd, J=15.8, 8.6, 5.4 Hz, 1H), 4.76 (d, J=7.3 Hz, 1H), 4.49–4.37 (m, 1H), 4.33–4.24 (m, 1H), 3.02 (dd, J=13.3, 7.3 Hz, 1H), 2.78 (dd, J=13.3, 7.9 Hz, 1H), 2.48–2.32 (m, 1H), 2.29–2.04 (m, 2H), 1.80–1.70 (m, 1H), 0.56 (d, J=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.1, 152.7, 138.7, 137.5, 133.5, 130.5, 130.3, 129.5 (2C), 128.8 (2C), 128.6, 128.6 (2C), 128.4 (2C), 127.3, 126.5, 126.1 (2C), 125.7 (2C), 78.4, 54.7, 44.4, 39.6, 32.1, 30.8, 14.3.

4.4.9. (S)-4-Benzyl-3-((R,E)-2-benzyl-6-phenylhex-5-enoyl)oxazolidin-2-one (**24**)

The preparation was conducted according to the general procedure for asymmetric alkylation of chiral *N*-acyl oxazolidinones: *N*-acyl oxazolidinone **20** (162 mg, 0.464 mmol), NaHMDS (1 M in THF, 0.56 mL, 0.56 mmol), and benzyl bromide (95 mg, 0.56 mmol). The product was obtained by column chromatography (increasing polarity from 0 to 5% Et_2O in pentane as the eluant) (101 mg, 0.230 mmol, 50%), and subjected to the general method for SmI_2-promoted cyclization (vide infra).

4.4.10. 2-Benzylcyclopentane (**25**)[18]

N-Acyl oxazolidinone **18** (50 mg, 0.19 mmol) was dissolved in THF (10 mL) and water (28 μL, 1.54 mmol) at −20 °C and SmI_2 solution (0.1 M in THF, 7.7 mL, 0.77 mmol) was added. After 4 h, the excess SmI_2 was quenched by flushing the flask with O_2, and NH_4Cl(aq) (4 mL) and 1 M HCl(aq) (4 mL) were added. The mixture was extracted three times with EtOAc (50 mL), and the combined organic phase was washed with $Na_2S_2O_3$(aq) (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Purification by flash column chromatography (10% EtOAc in pentane as eluant) gave the desired product as a colorless oil (26 mg, 0.15 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30–7.26 (m, 2H), 7.23–7.16 (m, 3H), 3.15 (dd, J=14.0, 4.0 Hz, 1H), 2.54 (dd, J=14.0, 9.6 Hz, 1H), 2.39–2.30 (m, 2H), 2.13–2.04 (m, 1H), 2.11 (qn, J=8.8 Hz, 1H), 2.00–1.91 (m, 1H), 1.79–1.68 (m, 2H), 1.61–1.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 220.4, 140.2, 129.1 (2C), 128.6 (2C), 126.4, 51.3, 38.4, 35.8, 29.4, 20.8. HRMS $C_{12}H_{11}O$ [M+Na$^+$] calculated: 197.0942, found: 197.0937.

4.4.11. 2,2′-(1,2-Diphenylethane-1,2-diyl)dicyclopentanone (**26**)

The protocol was followed as for **25**, with the exception that the reaction was run at −78 °C yielding the dimer of **25**. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.09–6.88 (m, 10H), 3.96 (s, 2H), 3.11 (t, J=9.9 Hz, 2H), 2.30–2.10 (m, 4H), 1.95–1.78 (m, 2H), 1.69–1.48 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 223.1, 142.1, 129.4 (br), 128.1, 126.3, 50.1, 49.9, 41.2, 28.7, 21.2. HRMS $C_{24}H_{26}O_2$ [M+Na$^+$] calculated: 369.1825, found: 369.1833.

4.4.12. (R,R)-2,5-Dibenzylcyclopentanone (**27**)

N-Acyl oxazolidinone **24** (100 mg, 0.23 mmol) was dissolved in THF (2.3 mL), after which water (33 mg, 1.82 mmol) was added. SmI_2 (1.00 mmol) in THF (0.1 M) was added dropwise over 30 min. The mixture was stirred at room temperature for 18 h, and then the flask was flushed with O_2 to remove excess SmI_2. NH_4Cl(aq) (5 mL) was added and the mixture was poured into 0.5 M HCl(aq) (10 mL) before extraction with EtOAc (3×15 mL). The combined organic portions were washed with $Na_2S_2O_3$(aq) (2×15 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo. Pure product obtained by flash column chromatography (2% EtOAc/pentane) gave the title compound (32 mg, 0.12 mmol, 53%) as a colorless oil. $[\alpha]_D^{23}$ +180.4 (*c* 0.9, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29–7.15 (m, 10H), 3.18 (dd, J=14.0, 4.4 Hz, 2H), 2.62 (dd, J=14.0, 9.2 Hz, 2H), 2.35–2.27 (m, 2H), 2.03–1.97 (m, 2H), 1.47–1.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 220.0, 140.0, 129.0, 128.2, 126.0, 52.0, 36.0, 27.0. HRMS $C_{19}H_{20}O$ [M+Na$^+$] calculated: 287.1412, found: 287.1409.

4.4.13. (2S,5R)-2-Benzyl-5-methylcyclopentanone (**28**)

The reaction was conducted according to the general procedure for SmI_2-promoted cyclization: with chiral *N*-acyl oxazolidinone **21** (128.6 mg, 0.3538 mmol), H_2O (64 μL, 3.6 mmol) and SmI_2 (0.1 M in

THF, 8.8 mL, 0.88 mmol). The pure product was obtained by column chromatography (increasing polarity from 0 to 5% EtOAc in pentane as the eluant), which gave compound **28** (30.8 mg, 0.164 mmol, 46%) as a colorless oil. $[\alpha]_D^{23}$ −213.3 (*c* 1.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.11 (m, 5H), 3.16 (dd, *J*=13.8, 4.2 Hz, 1H), 2.60 (dd, *J*=13.8, 9.2 Hz, 1H), 2.39–2.28 (m, 1H), 2.20–2.10 (m, 1H), 2.09–1.97 (m, 2H), 1.52–1.40 (m, 1H), 1.40–1.27 (m, 1H), 1.12 (d, *J*=7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 221.7, 140.1, 129.1 (2C), 128.5 (2C), 126.2, 50.9, 44.6, 36.3, 30.0, 27.4, 14.6. HRMS $C_{13}H_{16}O$ [M+Na^+] calculated: 211.1093, found: 211.1083.

4.4.14. (1R,2R,5S,6S)-2-Methyl-6-phenylbicyclo[3.1.0]hexan-1-ol (**29**)

From the SmI_2-promoted cyclization affording **28**, a major by-product **29** (9.4 mg, 0.050 mmol, 14%) was isolated. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33–7.24 (m, 2H), 7.23–7.15 (m, 3H), 2.32 (qn, *J*=7.0 Hz, 1H), 2.17–2.08 (m, 1H), 2.07 (d, *J*=4.2 Hz, 1H), 1.79 (t, *J*=4.3 Hz, 1H), 1.66–1.50 (m, 4H), 1.41 (dd, *J*=12.7, 8.3 Hz, 1H), 1.14 (d, *J*=7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 137.9, 128.5 (2C), 128.4 (2C), 125.9, 71.6, 38.4, 31.2, 30.5, 29.3, 24.6, 17.2. LRMS $C_{13}H_{16}O$ [M+Na^+] calculated: 211.3, found: 211.3.

4.4.15. (2S,5S)-2-Allyl-5-benzylcyclopentanone (**30**)

The reaction was conducted according to the general procedure for SmI_2-promoted cyclization: with chiral *N*-acyl oxazolidinone **22** (97.6 mg, 0.251 mmol), H_2O (45 μL, 2.5 mmol), and SmI_2 (0.1 M in THF, 6.3 mL, 0.63 mmol). The pure product was obtained by column chromatography (increasing polarity from 0 to 5% EtOAc in pentane as the eluant), which gave compound **30** (25.9 mg, 0.121 mmol, 48%) as a colorless oil. $[\alpha]_D^{23}$ −243.4 (*c* 1.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.20 (t, *J*=7.4 Hz, 2H), 7.15–7.05 (m, 3H), 5.67 (ddt, *J*=16.9, 10.1, 6.7 Hz, 1H), 5.02–4.90 (m, 2H), 3.09 (dd, *J*=13.8, 4.2 Hz, 1H), 2.52 (dd, *J*=13.9, 9.2 Hz, 1H), 2.49–2.41 (m, 1H), 2.31–2.17 (m, 1H), 2.11–1.91 (m, 4H), 1.46–1.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 220.4, 140.0, 135.9, 129.1 (2C), 128.5 (2C), 126.3, 116.6, 51.6, 49.3, 36.1, 34.4, 27.3, 27.0. HRMS $C_{15}H_{18}O$ [M+Na^+] calculated: 237.1250, found: 237.1257.

4.4.16. (1R,2S,5S,6S)-2-Allyl-6-phenylbicyclo[3.1.0]hexan-1-ol (**31**)

From the SmI_2-promoted cyclization affording **30**, a major by-product **31** (10.1 mg, 0.0471 mmol, 19%) was isolated. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34–7.27 (m, 2H), 7.24–7.16 (m, 3H), 5.89 (dddd, *J*=16.7, 10.1, 7.6, 6.5 Hz, 1H), 5.14–5.06 (m, 1H), 5.06–5.01 (m, 1H), 2.67–2.52 (m, 1H), 2.33–2.25 (m, 1H), 2.12–2.01 (m, 2H), 2.05 (d, *J*=4.3 Hz, 1H), 1.82 (t, *J*=4.3 Hz, 1H), 1.68–1.56 (m, 3H), 1.54–1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 138.2, 137.7, 128.5 (2C), 128.4 (2C), 126.0, 116.0, 70.8, 43.5, 35.4, 31.4, 31.0, 25.9, 25.0. LRMS $C_{15}H_{18}O$ [M+Na^+] calculated: 237.3, found: 237.3.

4.4.17. (2S,5S)-2,5-Dibenzylcyclopentanone (**32**)

The reaction was conducted according to the general procedure for SmI_2-promoted cyclization: with chiral *N*-acyl oxazolidinone **23** (99.8 mg, 0.227 mmol), H_2O (41 μL, 2.3 mmol), and SmI_2 (0.1 M in THF, 5.7 mL, 0.57 mmol). The pure product was obtained by column chromatography (increasing polarity from 1 to 5% EtOAc in pentane as the eluant), which gave compound **32** (30.3 mg, 0.115 mmol, 50%) as a crystalline solid. Mp 62–63 °C (EtOAc/Hexanes). $[\alpha]_D^{23}$ −211.5 (*c* 0.9, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (tt, *J*=8.2, 1.5 Hz, 4H), 7.23–7.14 (m, 6H), 3.19 (dd, *J*=13.9, 4.2 Hz, 2H), 2.63 (dd, *J*=13.9, 9.1 Hz, 2H), 2.36–2.26 (m, 2H), 2.07–1.94 (m, 2H), 1.48–1.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 220.1, 140.0, 129.1 (2C), 128.5 (2C), 126.3, 51.6, 36.1, 27.2. HRMS $C_{19}H_{20}O$ [M+Na^+] calculated: 287.1406, found: 287.1412.

4.4.18. (1R,2S,5S,6S)-2-Benzyl-6-phenylbicyclo[3.1.0]hexan-1-ol (**33**)

From the SmI_2-promoted cyclization to obtain **32**, a major by-product **33** (8.6 mg, 0.033 mmol, 14%) was isolated. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.15 (m, 10H), 3.32–3.22 (m, 1H), 2.60–2.45 (m, 2H), 2.09 (d, *J*=4.2 Hz, 1H), 1.98 (dtd, *J*=4.5, 8.2, 12.5 Hz, 1H), 1.86 (t, *J*=4.3 Hz, 1H), 1.63–1.50 (m, 3H), 1.42–1.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.7, 137.5, 129.5 (C2), 128.5 (C2), 128.4 (C2), 128.4 (C2), 126.1, 125.9, 70.8, 45.7, 36.6, 31.2, 30.8, 25.3, 24.7. LRMS $C_{19}H_{20}O$ [M+Na^+] calculated: 287.3, found: 287.3.

4.4.19. (E)-2-(N-3-Phenylprop-2-enyl-para-toluenesulfonamido)acetic acid (**35**)

Et_3N (26 mL, 0.19 mol) and subsequently cinnamyl chloride (4.50 mL, 32.0 mmol) were added to a stirring solution of glycine methyl ester hydrochloride (20.0 g, 0.16 mol) in CH_3CN. The resulting mixture was heated at reflux for 3 h, and then poured into water (150 mL) and extracted three times with CH_2Cl_2 (150 mL). The combined organic portions were washed with water (200 mL), $NaHCO_3$(aq) (200 mL), and brine (200 mL), and then dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Purification by flash column chromatography (25–60% EtOAc in pentane as eluant) afforded the cinnamyl amine as a pale yellow oil (3.28 g, 16.0 mmol, 50%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36–7.18 (m, 5H), 6.52 (d, *J*=15.6 Hz, 1H), 6.23 (d, *J*=15.6 Hz, 1H), 3.70 (s, 3H), 3.44 (s, 2H), 3.41 (dd, *J*=6.4, 1.2 Hz, 2H) 1.84 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.1, 137.1, 132.3, 128.8 (2C), 127.7, 127.5, 126.5 (2C), 52.1, 51.5, 50.0. HRMS $C_{12}H_{15}NO_2$ [M+H^+] calculated: 206.1181, found: 206.1186.

Cinnamyl amine (1.2 g, 5.8 mmol), Boc_2O (1.4 g, 6.4 mmol), I_2 (0.15 g, 0.58 mmol), and THF (2 mL) were mixed at 0 °C and then stirred for 2 h at room temperature before the reaction mixture was poured into Et_2O (100 mL). The organic phase was washed with $Na_2S_2O_3$(aq) (100 mL) and brine (100 mL). After that it was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Purification by flash column chromatography (0–15% ethyl acetate in pentane as eluant) gave the Boc-protected amine as a colorless oil (1.7 g, 5.6 mmol, 96%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.24 (m, 5H), 6.49 (d, *J*=15.2 Hz, ($^1/_2$)×1H), 6.45 (d, *J*=13.2 Hz, ($^1/_2$)×1H), 6.20–6.12 (m, 1H), 4.14 (d, *J*=7.2 Hz, ($^1/_2$)×2H), 4.06 (d, *J*=6.0 Hz, ($^1/_2$)×2H), 4.00 (s, ($^1/_2$)×2H), 3.88 (s, ($^1/_2$)×2H), 3.71 (s, 3H), 1.49 (s, ($^1/_2$)×9H), 1.45 (s, ($^1/_2$)×9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 155.8/155.4, 136.8, 133.3/132.5, 128.8 (2C), 127.9 (2C), 126.7, 125.4/125.3, 80.7, 52.2, 50.5/50.0, 48.0/47.8, 28.6/28.5 (3C). LRMS $C_{17}H_{23}NO_4$ [M+Na^+] calculated: 328.2, found: 328.2.

The methyl ester was hydrolyzed by the same method used in the preparation of **36**: Methyl ester (1.57 g, 5.1 mmol), 2 M NaOH(aq) (5 mL), and methanol (50 mL). This gave **35** as a colorless solid (1.39 g, 4.8 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.96 (br s, 1H), 7.37–7.24 (m, 5H), 6.51–6.46 (m, 1H), 6.17–6.13 (m, 1H), 4.12 (d, *J*=6.0 Hz, 1H), 4.06 (m, 3H), 3.93 (s, ($^1/_2$)×2H), 1.49 (s, ($^1/_2$)×9H), 1.46 (s, ($^1/_2$)×9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 176.1/175.6, 155.4/155.4, 136.7, 133.5/132.8, 128.8 (2C), 128.0, 126.7, 126.6, 125.1/124.9, 81.2, 50.6/50.0, 47.9, 28.6/28.5 (3C). LRMS $C_{16}H_{21}NO_4$ [M+Na^+] calculated: 314.1, found: 314.1.

4.4.20. N-tert-Butoxycarbonyl((E)-3-phenylprop-2-enyl)aminoacetic acid (**36**)

A solution of triethylamine (5.0 mL, 35 mmol) and *p*-toluenesulfonyl chloride (3.7 g, 19 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of glycine methyl ester hydrochloride (2.00 g, 15.9 mmol) in CH_2Cl_2, and the resulting mixture was refluxed for 24 h. Then it was poured into water (50 mL) and extracted three times with Et_2O. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. Purification by flash column chromatography (increasing polarity from 10 to 60% EtOAc in pentane as eluant) yielded the tosylamide as a colorless solid (3.57 g, 14.7 mmol, 92%). ^1H NMR

(400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J=8.0 Hz, 2H), 7.31 (dd, J=8.0, 0.8 Hz, 2H), 4.09 (br s, 1H), 3.78 (d, J=5.6 Hz, 2H), 3.64 (s, 3H), 2.43 (s, 3H).[19]

Oven dried K_2CO_3 (1.77 g, 12.8 mmol) and cinnamyl bromide (1.9 mL, 12.8 mmol) in THF (5 mL) were added to a solution of the tosylamide (1.56 g, 6.4 mmol) in acetone (60 mL). The resulting mixture was heated at reflux for 18 h and then allowed to cool before water (30 mL) was added. The acetone was removed by rotary evaporation, and Et_2O (50 mL) was added and a colorless solid remained undissolved. Filtration yielded the methyl ester as a colorless solid (2.19 g, 6.09 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, J=8.4 Hz, 2H), 7.32 (d, J=8.4 Hz, 2H), 7.30–7.23 (m, 5H), 6.45 (d, J=15.6 Hz, 1H), 6.03 (dt, J=15.6, 6.8 Hz, 1H), 4.06 (s, 2H), 4.04 (d, J=0.8 Hz, 2H), 3.61 (s, 3H), 3.32 (s, 3H).

NaOH(aq) (2 M, 5 mL) was added to a suspension of the methyl ester (1.01 g, 2.81 mmol) in methanol (50 mL). The resulting mixture was heated at reflux for 1 h, and then it was poured into a mixture of water (50 mL) and CH_2Cl_2 (50 mL). This mixture was extracted three times with water (70 mL), and the combined aqueous portions were acidified with concentrated aq HCl and subsequently extracted four times with CH_2Cl_2 (100 mL). The combined organic portions were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. This afforded the carboxylic acid **36** as a colorless solid (0.947 mg, 2.74 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J=8.4 Hz, 2H), 7.33–7.23 (m, 7H), 6.47 (d, J=15.6 Hz, 1H), 6.01 (dt, J=15.6, 6.8 Hz, 1H), 4.07 (s, 2H), 4.04 (dd, J=6.8, 0.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 175.1, 144.1, 136.8, 136.1, 135.4, 130.0 (2C), 128.9 (2C), 128.5, 127.6 (2C), 126.8 (2C), 123.1, 50.8, 47.1, 21.8. LRMS $C_{16}H_{21}NO_4$ [M+Na^+] calculated: 368.4, found: 368.4.

4.4.21. (E)-3-Phenylprop-2-enyloxyacetic acid (**37**)[20]

Cinnamyl alcohol (3.19 g, 23.8 mmol) in THF (20 mL) was added slowly to a suspension of NaH (33.3 mmol, 1.33 g of 60% NaH in oil, the oil had previously been removed by washing with pentane) in THF (20 mL) at 0 °C. After stirring for 45 min, 2-chloroacetic acid (900 mg, 9.5 mmol) in THF (15 mL) was added over 20 min. The resulting mixture was heated at reflux for 18 h. The volume was reduced by rotary evaporation and Et_2O (100 mL) was added. The organic phase was extracted three times with $NaHCO_3$(aq) (80 mL). The combined aqueous portions were acidified with concentrated aq HCl and extracted three times with Et_2O (200 mL). The combined organic portions were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo yielding 1.0 g of crude product, which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.20 (m), 6.64 (d, J=16.0 Hz, 1H), 6.28 (dt, J=16.0, 6.4 Hz, 1H), 4.29 (d, J=6.4 Hz, 2H), 4.18 (s, 2H).

4.4.22. Pentafluorophenyl (E)-(N-3-phenylprop-2-enyl-para-toluenesulfonamido)acetate (**38**)

The carboxylic acid **35** (785 mg, 2.28 mmol), pentafluorophenol (460 mg, 2.50 mmol), EDC (870 mg, 4.6 mmol), and DMAP (55 mg, 0.46 mmol) were dissolved in CH_2Cl_2 (60 mL), and stirred at room temperature for 16 h. The mixture was poured into $NaHCO_3$(aq) (50 mL) and extracted three times with CH_2Cl_2 (50 mL). The combined organic portions were washed two times with $NaHCO_3$(aq) (100 mL) and once with NaCl(aq) (50 mL) before it was dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the crude product was purified by flash column chromatography (0–50% CH_2Cl_2 in pentane as eluant). This gave the desired product as a colorless oil (0.775 g, 1.52 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, J=8.0 Hz, 2H), 7.33–7.26 (m, 7H), 6.52 (d, J=15.6 Hz, 1H), 6.06 (dt, J=15.6, 6.8 Hz, 1H), 4.47 (s, 2H), 4.10 (d, J=6.8 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.3, 144.0, 139.7 (br), 139.2 (br), 139.0 (br), 138.4 (br), 136.6 (br), 136.3, 135.8, 135.6, 129.8 (2C), 128.6 (2C), 128.3, 127.4 (2C), 126.6 (2C), 122.3, 50.2, 46.2, 21.5.

4.4.23. Pentafluorophenyl N-tert-butoxycarbonyl((E)-(3-phenylprop-2-enyl)amino)acetate (**39**)

The title compound **39** was prepared using the same method for the preparation of compound **38**: carboxylic acid **36** (1.30 g, 4.46 mmol), pentafluorophenol (0.90 g, 4.90 mmol), EDC (1.74 g, 8.9 mmol), and DMAP (0.11 g, 0.89 mmol) in CH_2Cl_2 (60 mL). Flash column chromatography (25–75% CH_2Cl_2 in pentane as eluant) gave the pentafluorophenyl ester **39** as a colorless oil (1.45 g, 3.27 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) major rotamer: 7.39–7.24 (m, 5H), 6.56 (d, J=15.6 Hz, 1H), 6.18 (dt, J=15.6, 6.8 Hz, 1H), 4.25 (s, 2H), 4.19 (d, J=6.8 Hz, 2H), 1.49 (s, 9H); minor rotamer inter alia: 6.52 (m, 1H), 4.36 (s, 2H), 4.12 (d, J=6.0 Hz, 2H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.6/166.5, 155.6/155.0, 142.4 (br), 141.1 (br), 140.1 (br), 139.3 (br), 138.6 (br), 136.9 (br), 136.5, 134.1/133.4, 128.8 (2C), 128.2, 126.7 (2C), 124.5/124.5, 81.7/81.5, 50.6/50.0, 47.4, 28.5/28.3 (3C).

4.4.24. Pentafluorophenyl (E)-3-phenylprop-2-enyloxyacetate (**40**)

The crude of **37** (1 g), pentafluorophenol (1.93 g, 10.5 mmol), EDC (3.71 g, 19 mmol), and DMAP (230 mg, 1.9 mmol) were dissolved in CH_2Cl_2 (30 mL) and stirred for 18 h. The mixture was then poured into $NaHCO_3$(aq) and extracted three times with CH_2Cl_2 (50 mL). The combined organic portions were washed with $NaHCO_3$(aq) (100 mL) and brine (100 mL), and then dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and flash column chromatography (increasing polarity from 10 to 30% CH_2Cl_2 in pentane) gave the desired product **40** as a pale yellow oil (999 mg, 2.8 mmol, 30% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42–7.27 (m, 5H), 6.68 (d, J=16.0 Hz, 1H), 6.31 (dt, J=16.0, 6.4 Hz, 1H), 4.51 (s, 2H), 4.36 (dd, J=6.4, 0.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.1, 142.5 (br), 141.3 (br), 140.0 (br), 139.4 (br), 138.7 (br), 136.9 (br), 136.2, 135.3, 128.8 (2C), 128.4, 126.8 (2C), 123.6, 72.7, 66.1.

4.4.25. (E)-N-3-Phenylprop-2-enyl-N-(2-oxo-2-(2-oxooxazolidin-3-yl)ethyl)-para-toluenesulfonamide (**41**)

i-PrMgCl (2 M in THF, 1.6 mL, 3.2 mmol) was added to a stirred solution of oxazolidin-2-one (280 mg, 3.2 mmol) in THF (20 mL) at −15 °C, and after 20 min the PFP-ester **38** (829 mg, 1.60 mmol) in THF (20 mL) was added over 20 min. The resulting mixture was stirred for 3 h at −15 °C and then poured into $NaHCO_3$(aq) (50 mL). Next it was extracted three times with EtOAc (50 mL), and the combined organic portions were washed with $NaHCO_3$(aq) (100 mL) and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by flash column chromatography (increasing polarity from 20 to 40% EtOAc in pentane as eluant) to give *N*-acyl oxazolidinone **41** as a colorless solid (657 mg, 1.58 mmol, 99%). Mp 58–60 °C (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, J=8.0 Hz, 2H), 7.32 (d, J=8.0 Hz, 2H), 7.29–7.23 (m, 5H), 6.40 (d, J=15.6 Hz, 1H), 5.99 (dt, J=15.6, 6.8 Hz, 1H), 4.63 (s, 2H), 4.37 (t, J=8.4 Hz, 2H), 4.05 (dd, 6.8, 1.2 Hz, 2H), 3.94 (t, J=8.4 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 169.1, 153.8, 143.8, 137.3, 136.2, 134.7, 129.9, 128.8 (2C), 128.3 (2C), 127.7 (2C), 126.7, 123.8, 63.1, 51.1, 49.6, 42.5, 21.8. HRMS $C_{21}H_{21}N_2O_4S$ [M+Na^+] calculated: 437.1147, found: 437.1155.

4.4.26. tert-Butyl 2-oxo-2-(2-oxooxazolidin-3-yl)((E)-3-phenylprop-2-enylethyl)carbamate (**42**)

The title compound **42** was prepared using the method described for the preparation of compound **41**: *i*-PrMgCl (2 M in THF, 3.0 mL), oxazolidin-2-one (521 mg, 6.0 mmol), and **39** (1.37 g, 2.99 mmol) in THF (50 mL). Flash column chromatography (15–40% ethyl acetate in pentane as eluant) gave the *N*-acyl oxazolidinone **42** as a colorless solid (950 mg, 2.64 mmol, 88%). Mp 148–149 °C (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) major rotamer

7.36–7.28 (m, 4H), 7.26–7.23 (m, 1H), 6.46 (br d, J=16.0 Hz, 1H), 6.21–6.13 (m, 1H), 4.57 (s, 2H), 4.41 (t, J=8.0 Hz, 2H), 4.05 (d, J=6.0 Hz, 1H), 4.00 (t, J=8.0 Hz, 2H), 1.49 (s, 9H). Minor rotamer inter alia: 4.51 (s, 2H), 4.40 (t, J=8.0 Hz, 2H), 4.11 (d, J=6.4 Hz, 2H), 3.97 (t, J=8.0 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 169.7/169.6, 155.6/155.2, 153.6/153.6, 136.6, 132.8/132.1, 128.6/128.5 (2C), 127.7 (2C), 126.4/126.4, 125.6/125.6, 80.7/80.5, 63.1, 51.0/50.5, 50.1/50.0, 42.5, 28.6/28.5 (3C). HRMS $C_{19}H_{24}N_2O_5$ [M+Na^+] calculated: 383.1583, found: 383.1577.

*4.4.27. (E)-(3-Phenylprop-2-enyloxyacetyl)oxazolidin-2-one (**43**)*

i-PrMgCl (2 M in THF, 2.8 mL) was added to a solution of oxazolidin-2-one (486 mg, 5.58 mmol) in THF (20 mL) at −15 °C. After 30 min the PFP-ester **40** (0.992 g, 2.79 mmol) in THF (25 mL) was added over 20 min and the resulting mixture was stirred for 3 h at −15 °C. It was then poured into $NaHCO_3$(aq) (50 mL) and extracted three times with Et_2O (50 mL). The combined organic portions were washed with $NaHCO_3$(aq) (100 mL) and brine (100 mL), dried over $MgSO_4$, filtered and the volume reduced in vacuo. Purification by flash column chromatography (increasing polarity from 20 to 40% EtOAc in pentane as eluant) gave the *N*-acyl oxazolidinone **43** as a colorless solid. (294 mg, 1.13 mmol, 40%). Mp 113–114 °C (CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.37 (m, 2H), 7.33–7.29 (m, 2H), 7.26–7.22 (m, 1H), 6.64 (d, J=16.0 Hz, 1H), 6.31 (dt, J=16.0, 6.4 Hz, 1H), 4.44 (t, J=8.0 Hz, 2H), 4.29 (dd, J=6.4, 1.2 Hz, 2H), 4.01 (t, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.2, 153.4, 136.3, 133.5, 128.5 (2C), 127.8, 126.5 (2C), 124.9, 72.1, 69.1, 63.1, 41.9. HRMS $C_{14}H_{15}NO_4$ [M+Na^+] calculated: 284.0899, found: 284. 0905.

4.5. General procedure for SmI_2 cyclizations

A mixture of the *N*-acyl oxazolidinone (0.18 mmol) and water (0.8 mmol) in THF (20 mL) was added dropwise (1 mL/min) to a solution of SmI_2 in THF (0.1 M, 4 mL, 0.40 mmol) at the temperature in question. Immediately after addition was complete excess SmI_2 was quenched with O_2. Then NH_4Cl(aq) (4 mL) and 1 M aq HCl (4 mL) were added and the mixture was extracted three times with EtOAc (50 mL). The combined organic portions were washed with $Na_2S_2O_3$(aq) (100 mL) and brine (100 mL). The organic phase was then dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by flash column chromatography with the stated solvent system.

*4.5.1. 4-Benzyl-1-para-toluenesulfonylpyrrolidin-3-one (**44**)*

The *N*-tosyl pyrrolidinone **44** was prepared by the general procedure for SmI_2-promoted cyclizations using *N*-acyl oxazolidinone **41** (100 mg, 0.24 mmol), water (22 μL, 1.2 mmol), and SmI_2 (0.1 M in THF, 6.0 mL, 0.6 mmol) at room temperature. Purification by flash column chromatography (5% Et_2O in pentane/CH_2Cl_2 1:1 as eluant) yielded the product **44** as a colorless amorphous solid (12 mg, 0.036 mmol, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67 (d, J=8.0 Hz, 2H), 7.35 (dd, J=8.0, 0.8 Hz, 2H), 7.31–7.21 (m, 3H), 7.08 (d, J=6.8 Hz, 2H), 3.75 (d, J=18.0 Hz, 1H), 3.72 (t, J=9.2 Hz, 1H), 3.37(d, J=18.0 Hz, 1H), 3.12 (dd, J=14.0 Hz, 1H), 3.02 (t, J=9.2 Hz, 1H), 2.81 (ddt, J=10.0, 9.6, 4.0 Hz, 1H), 2.54 (dd, J=14.0, 10.0 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 209.2, 144.4, 137.7, 131.6, 130.0 (2C), 128.9 (2C), 128.6 (2C), 127.9 (2C), 127.2, 54.0, 50.2, 33.8, 28.4, 21.6. HRMS $C_{18}H_{19}NO_3$ [M+Na^+] calculated: 352.0983, found: 352.0981.

*4.5.2. tert-Butyl 3-benzyl-4-oxopyrrolidine-1-carboxylate (**45**)*

The *N*-Boc pyrrolidinone **45** was prepared by the general procedure for SmI_2-promoted cyclizations using *N*-acyl oxazolidinone **42** (65 mg, 0.18 mmol), water (14 μL, 0.80 mmol), and SmI_2 (0.1 M in THF, 4.0 mL, 0.40 mmol) at 20 °C. Purification by flash column chromatography (5% Et_2O in pentane/CH_2Cl_2 1:1 as eluant) afforded the title compound **45** as a colorless amorphous solid (16 mg, 0.06 mmol, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.21 (m, 3H), 7.17–7.15 (m, 2H), 3.95–3.88 (m, 2H), 3.66 (br d, J=19.0 Hz, 1H), 3.33 (dd, J=11.6, 8.8 Hz, 1H), 3.18 (dd, J=14.0, 4.0 Hz, 1H), 2.91–2.84 (m, 1H), 2.67 (dd, J=14.0, 9.6 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 212.1 (br), 154.2, 138.1, 128.7 (4C), 126.7, 80.4, 53.1, 49.3, 47.8, 34.4, 28.4 (3C). HRMS $C_{16}H_{21}NO_3$ [M+Na] calculated: 298.1419, found: 298.1426.

*4.5.3. 4-Benzyldihydrofuran-3(2H)-one (**46**)*[21]

The dihydrofuranone **46** was prepared according to the general method for SmI_2-promoted cyclizations using *N*-acyl oxazolidinone **43** (60 mg, 0.23 mmol), water (18 μL, 1.0 mmol) and SmI_2 (0.1 M in THF, 5 mL, 0.5 mmol) at 20 °C. Purification by flash column chromatography (5% Et_2O in pentane:CH_2Cl_2 1:1 as eluant) afforded of the title compound as a colorless amorphous solid. (7 mg, 0.04 mmol, 17%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.21 (m, 3H), 7.17 (m, 2H), 4.31 (br.t, J=8.8 Hz, 1H), 4.07 (dt, J=17.2, 0.4 Hz, 1H), 3.85 (d, J=17.2 Hz, 1H), 3.85 (d, J=8.8 Hz, 1H), 3.16 (dd, J=14.0, 4.0 Hz, 1H), 2.79 (ddt, J=10.0, 8.8, 4.0 Hz, 1H), 2.66 (dd, J=10.0, 8.8 Hz, 1H). HRMS $C_{11}H_{12}O_2$ [M+Na^+] calculated: 199.0735, found: 199.0740.

*4.5.4. 4,4′-(1,2-Diphenylethane-1,2-diyl)bis(1-tosylpyrrolidin-3-one) (**47**)*

Subjecting *N*-acyl oxazolidinone **41** (75 mg, 0.18 mmol) to the general procedure for SmI_2-promoted cyclizations using water (14 μL, 0.8 mmol) and SmI_2 (0.1 M in THF, 4.0 mL, 0.4 mmol) afforded apart from **44** (7 mg, 0.021 mmol, 12%) also by-product **47** (18 mg, 0.027 mmol, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.41 (d, J=8.4 Hz, 4H), 7.20–7.14 (m, 10H), 7.12–7.07 (m, 4H), 3.87 (s, 2H), 3.67 (t, J=9.6 Hz, 2H), 3.42 (d, J=17.2 Hz, 2H), 2.92 (t, J=9.6 Hz, 2H), 2.63 (d, J=17.2 Hz, 2H), 2.46 (t, J=9.6 Hz, 2H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 210.0 (2C), 144.0 (2C), 138.4 (2C), 131.4 (2C), 129.7 (4C), 129.0 (4C), 127.7 (4C), 127.6 (6C), 55.0 (2C), 48.6 (2C), 48.4 (2C), 46.9 (2C), 21.5 (2C). HRMS $C_{36}H_{36}N_2O_6S_2$ [M+Na^+] calculated: 679.1912, found: 679.1938.

*4.5.5. 4,4′-(1,2-Diphenylethane-1,2-diyl)bis(dihydrofuran-3-(2H)-one) (**49**)*

The title compound was a by-product of the general procedure for SmI_2-promoted cyclizations using oxazolidinone **43** (11 mg, 0.03 mmol, 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38–7.27 (m, 10H), 4.21 (t, J=8.8 Hz, 2H), 4.10 (t, J=1.6 Hz, 2H), 3.73 (t, J=8.8 Hz, 2H), 3.71 (d, J=16.8 Hz, 2H), 3.28 (d, J=16.8 Hz, 1H), 2.52 (td, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 216.5 (2C), 139.6 (2C), 129.0 (6C), 127.7 (4C), 72.3 (2C), 70.3 (2C), 47.6 (2C), 46.2 (2C). HRMS $C_{22}H_{22}O_4$ [M+Na^+] calculated: 373.1416, found: 373.1414.

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