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Journal Name

ARTICLE

Synthesis of Oxazolidinones: Rhodium-Catalyzed C–H Amination of *N*-Mesyloxycarbamates.

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N-Mesyloxycarbamates undergo intramolecular C–H amination reactions to afford oxazolidinones in good to excellent yields in the presence of rhodium(II) carboxylate catalysts. The reaction is performed under green conditions and potassium carbonate is used, forming biodegradable potassium mesylate as a reaction by-product. This method enables the production of electron-rich, electron-deficient aromatic and heteroaromatic oxazolidinones in good to excellent yields. Conformationally restricted cyclic secondary *N*-mesyloxycarbamates furnish *cis* oxazolidinones in high yields and selectivity; DFT calculations are provided to account for the observed selectivity. *Trans* oxazolidinones were prepared from acyclic secondary *N*-mesyloxycarbamates using $Rh_2(oct)_4$. The selectivity was reverted with cytoxazone *N*-mesyloxycarbamate precursor using large chiral rhodium(II) carboxylate complexes, affording the corresponding *cis* oxazolidinone. This orthogonal selectivity was used to achieve the formal synthesis of (–)-cytoxazone.

Introduction

Oxazolidinones are found in many important biologically active molecules,[1] such as cytoxazone, a selective immunomodulator inhibiting the signaling pathway of Th2 cells.[2] Recently, oxazolidinones have emerged in a novel class of antibiotics,[3] including FDA-approved linezolid (Figure 1).[4] These antibiotics display a unique mechanism for microbial protein synthesis inhibition, providing a new potent tool against drug-resistant infections. As such, oxazolidinones are relevant to medicinal chemistry, additionally to being commonly used as a source of 1,2-amino alcohols, and as chiral auxiliaries.[5,6]

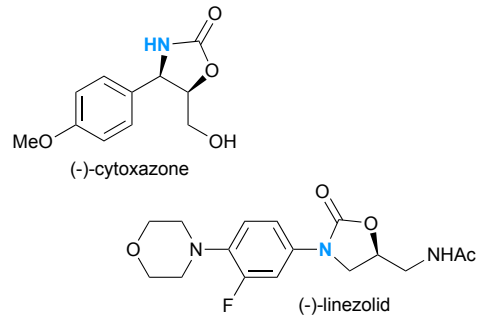

Figure 1 Selected Examples of Biologically Relevant Oxazolidinones

The functionalization of amino alcohols with electrophilic "C=O" reagents is a well-established approach to access oxazolidinones.[6a,7,8,9] Aziridines[10] or epoxides[11] have also been successfully used as substrates. Modern methods have also targeted the formation of C–O or C–N bonds resulting in more convergent approaches.[12,13] For example, Rh(II),[14] and Ag(I)[15] complexes have been reported to catalyze the intramolecular C–H amination of primary carbamates in the presence diacetoxyiodobenzene to produce oxazolidinones.[16] Our group has developed a preoxidized *N*-tosyloxycarbamate reagent that undergoes Rh(II)-catalyzed C–H insertion reactions to produce oxazolidinones in good to high yields.[17] We have recently established that *N*-mesyloxycarbamates are also suitable reagents to perform intermolecular rhodium-catalyzed C–H insertion reactions.[18] Advantages associated with these reagents include ease of synthesis, high stability, easily removable biodegradable low molecular weight by-products, and non-anhydrous mild reaction conditions. Herein we delineate the use of *N*-mesyloxycarbamates in intramolecular C–H amination reactions to produce oxazolidinones in the presence of Rh(II) carboxylate complexes using ethyl acetate or methanol as a solvent. The reactivity of *N*-mesyloxycarbamates derived from primary, secondary and tertiary alcohols is described. The diastereoselectivity of the rhodium-catalyzed C–H amination reaction is also discussed and includes the formal synthesis of (–)-cytoxazone.

Results and Discussion

The *N*-mesyloxycarbamate derived from 2-phenylethanol (**1**) was first prepared and studied in the rhodium-catalyzed intramolecular C–H amination reaction (Table 1). Under the pre-

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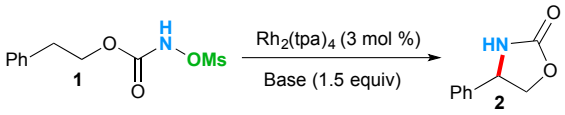
† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data of *N*-mesyloxycarbamates, details of computation, X-ray crystal structures and copies of ^1H and ^{13}C NMR spectra of all new compounds. See DOI: 10.1039/x0xx00000x

viously established optimal reaction conditions, using 6 mol % of rhodium(II) triphenylacetate dimer complex ($Rh_2(tpa)_4$), 3 equiv of K_2CO_3 in CH_2Cl_2, the desired oxazolidinone **2** was obtained in an excellent yield of 90% (entry 1). In comparison, the tosyl derivative afforded the same product in 92% under these reaction conditions.[17] Further reaction optimization was undertaken to develop more environmentally friendly reaction protocols (lower catalyst loading and non-chlorinated solvents). The use of an aqueous saturated solution of K_2CO_3 furnished 86% yield of the desired product using only 3 mol % of $Rh_2(tpa)_4$ (entry 2). Ethyl and isopropyl acetate were tested as alternative solvents (entries 3–6). Using an aqueous saturated solution of K_2CO_3 in ethyl acetate for 16 h, oxazolidinone **2** was isolated in 89% yield. The use of other bases and isopropyl acetate as solvent afforded lower yields of the product (entries 4–6). Conversely, the use of $NOBF_4$ as a catalyst additive in the presence of acetonitrile proved beneficial for the C–H amination producing oxazolidinone **2** in 93% yield (entry 7). Such additives have been used to prepare mixed valent rhodium dimer [Rh(II)–Rh(III)].[19] Although further investigations would be required to establish their exact role, control experiments showed that the use of acetonitrile alone or $AgBF_4$ (instead of $NOBF_4$) did not have a positive effect (entries 8–9). In addition to optimization showed in table 1, a number of other rhodium, iron and silver catalysts were investigated; however, $Rh_2(tpa)_4$ remained the most reactive one.[20]

Table 1. C–H Amination of *N*-Mesyloxycarbamate **1** under Various Reaction Conditions

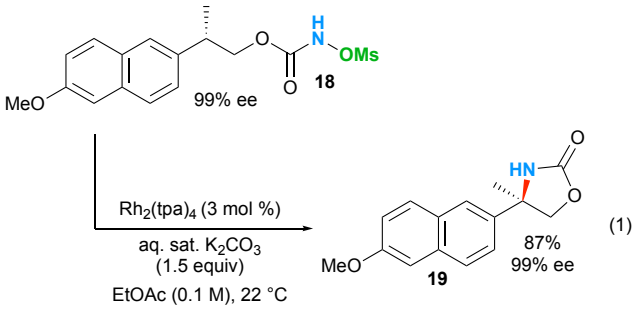


Entry	Conditions [a]	Yield [b]
1	solid K_2CO_3 (3 equiv) [c] CH_2Cl_2, 22 °C, 6 h	90%
2	aq. sat. K_2CO_3 CH_2Cl_2, 22 °C, 6 h	86%
3	**aq. sat. K_2CO_3 EtOAc, 22 °C, 16 h**	**89%**
4	solid KOAc EtOAc, 22 °C, 32 h	71%
5	solid KOAc *i*-PrOAc, 22 °C, 72 h	69%
6	solid sodium 2-ethylhexanoate *i*-PrOAc, 22 °C, 16 h	49%
7	**aq. sat. K_2CO_3, $NOBF_4$ (3 mol %), CH_3CN (20 mol %), EtOAc, 22 °C, 16 h**	**93%**
8	aq. sat. K_2CO_3, CH_3CN (20 mol %), EtOAc, 22 °C, 16 h	78%
9	aq. sat. K_2CO_3, $AgBF_4$ (3 mol %), CH_3CN (20 mol %), EtOAc, 22 °C, 16 h	74%

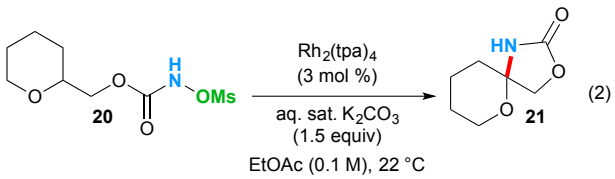
[a] 0.1 M. [b] Isolated yields. [c] $Rh_2(tpa)_4$ (6 mol %).

The optimized reaction conditions (Table 1, entry 3) were used to prepare a variety of diversely substituted aromatic oxazolidinones (Table 2). Substrates containing electron-donating substituted aromatic groups were reacted in good to excellent yields (entries 1, 2, 4, 5). Namely, the reaction conditions were compatible with a TBS-protected phenol derivative, affording **6** in good yields (entry 4). With halo-substituted aromatic groups, the use of $NOBF_4$ and acetonitrile as additives proved advantageous (entries 3, 6–9). It was necessary to decrease the amount of base to obtain a good yield for trifluoromethyl-substituted aryl oxazolidinone **12** (entry 10). *N*-Mesyloxycarbamates containing larger aromatic rings afforded oxazolidinones **13** et **14** in high yields (entries 11, 12). Heterocycles, such as thiophene and protected indoles were compatible with the reaction conditions and the corresponding oxazolidinones were produced in good yields (entries 13–15).[21] This is in sharp contrast with the result obtained with Du Bois's methodology, that afforded the desired oxazolidinone **16** as a minor product (26%), while the corresponding spirocycle was the major product (61%).[22]

The rhodium-catalyzed C–H amination reaction is stereospecific as 99% ee *N*-mesyloxycarbamate **18** afforded the desired oxazolidinone **19** in 92% yield and 99% ee (eq 1).



Non-aromatic substrates derived from primary alcohols were next investigated. When the insertion reaction occurred in a tertiary C–H bond, an excellent yield was obtained (Eq 2). Oxazolidinone **21** was produced in 93% yield using freshly recrystallized $Rh_2(tpa)_4$. It is possible to recover the rhodium complex and to reuse the catalyst to obtain the desired product in similar yields. Moreover, a gram scale reaction was run and oxazolidinone **21** was obtained in 90% yield using only 1 mol % of $Rh_2(tpa)_4$.



Fresly recrystallized $Rh_2(tpa)_4$: 93%
Recycled by flash chromatography $Rh_2(tpa)_4$: 86%
Gram Scale with 1 mol % of $Rh_2(tpa)_4$: 90%

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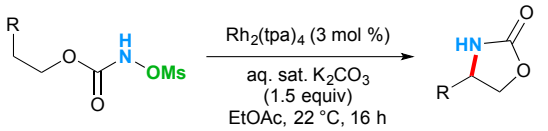
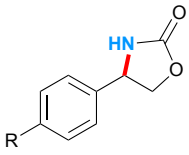
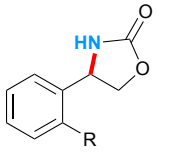
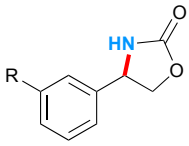
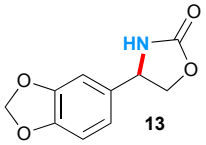
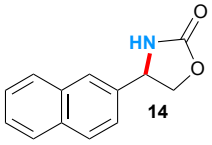
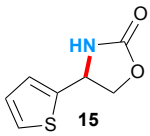
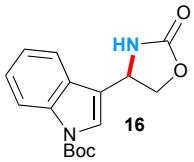
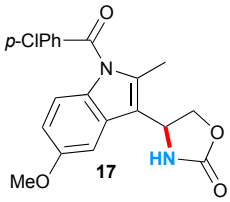
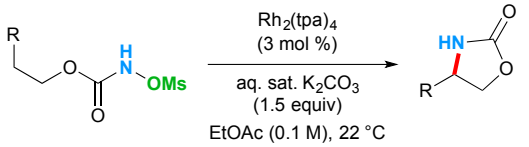
Table 2. Rhodium-Catalyzed C–H Amination of Aromatic *N*-Mesyloxycarbamates



Entry	Oxazolidinone		Yield [a]
1		R = OMe, **3**	79%
2		R = Me, **4**	81%
3 [b]		R = Cl, **5**	83%
4		R = OTBS, **6**	68%
5 [c]		R = OMe, **7**	92%
6 [b]		R = Br, **8**	86%
7 [b]		R = Cl, **9**	70%
8 [b]		R = F, **10**	68%
9 [b]		R = Cl, **11**	70%
10 [d]		R = CF_3, **12**	84%
11 [b]	 **13**		85%
12	 **14**		84%
13 [b]	 **15**		82%
14	 **16**		73%
15	 **17**		67%

[a] Isolated Yields. [b] $NOBF_4$ (5 mol %), CH_3CN (20 mol %). [c] $Rh_2(tpa)_4$ (4 mol %). [d] K_2CO_3 aq. sat. (1.05 equiv, 0.05 M)

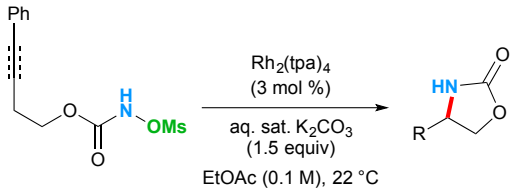
The C–H amination reaction is slower when the insertion occurred in a secondary C–H bond, resulting in lower yields under the standard reactions conditions. For example, oxazolidinone **22** and **23** were isolated with 45% and 60% yield respectively (Eq 3). More forcing reaction conditions (higher temperature or prolonged reaction time) did not improve the yield, as catalyst decomposition was observed. The use of $NOBF_4$ and acetonitrile as additives proved slightly advantageous, as 64% yield of the oxazolidinone **23** was isolated.



(3)

R = OCH_2CH_2OEt, **22**, 45%
R = *n*-Bu, **23**, 60%
R = *n*-Bu, **23**, 64%
($NOBF_4$ (5 mol %), CH_3CN (20 mol %))

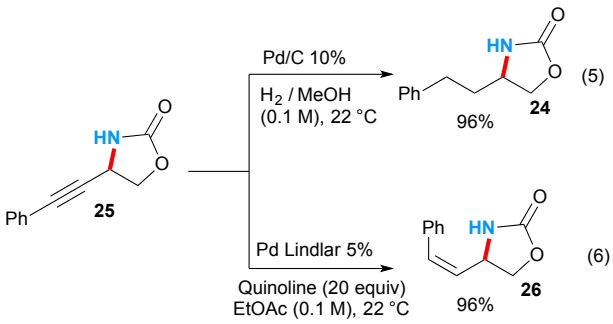
When an aromatic group is present at the end of the alkyl chain, the yield further dropped as a result of a low chemo-selectivity. The desired oxazolidinone **24** was produced in 36% yield, along with other products, including the 6-membered ring derivative (Eq 4). To improve the yield, an alkyne moiety was introduced in the substrate, furnishing oxazolidinone **25** in 74% yield.



(4)

R = CH_2CH_2Ph, **24**, 36%
R = C≡CPh, **25**, 74%

The alkyne can easily be further reduced to afford the saturated oxazolidinone **24** in an excellent yield (eq 5). The overall yield for this 2-steps sequence is higher than the direct C–H amination of the saturated substrate. Furthermore, it is possible to perform a partial hydrogenation using Lindlar catalyst in the presence of quinoline, to produce the *Z*-alkene oxazolidinone **26** (eq 6). Such a product cannot be produced directly by C–H amination from the corresponding carbamate, as the double bond would react to afford the corresponding aziridine product.[18a]



A series of cyclic *N*-mesyloxycarbamates derived from secondary and tertiary alcohols were prepared and investigated (Table 3). The reaction with the indanol derivative afforded oxazolidinone **27** in high yields and selectivity (entry 1). The benzylic C–H amination favored the formation of the

cis isomer under the standard reaction conditions. The C–H amination of simple non-conformationally bias aliphatic derivatives proved to be problematic. The poor reactivity associated with this particular class of substrates had been reported: in some cases, the formation of the corresponding ketone was the major product.[23] For example, the *N*-mesyloxycarbamate derived from cyclopentanol reacted slowly to afford exclusively the *cis* isomer of bicyclo [3.3.0] **28** in 40% yield (entry 2). Catalyst decomposition was observed before the reaction was completed: using $NOBF_4$ and acetonitrile as additives or heating the reaction mixture did not improve the conversion. Conversely the use of the corresponding CF_3-substituted tertiary *N*-mesyloxycarbamate afforded oxazolidinone **29** in an excellent yield and as a single diastereomer (entry 3). This result appears to support the hypothesis of the undesired reactivity of the α-hydrogen in secondary *N*-mesyloxycarbamates.[23] However, introducing a substituent at that position also modifies the conformation of the starting material. With the more flexible *N*-mesyloxycarbamate derived from cyclohexanol, the diastereoselectivity decreased to 80:20 (entry 4). It was possible to isolate the major *cis*-isomer as a single diastereomer in low yield, when heating at 40 °C. DFT calculations of rhodium nitrenes derived from cyclohexyl carbamate and $Rh_2(OAc)_4$ showed that equatorial rhodium nitrene **A** is slightly more stable by 0.8 kcal/mol compared to axial rhodium nitrene **B** (Figure 2).[24]

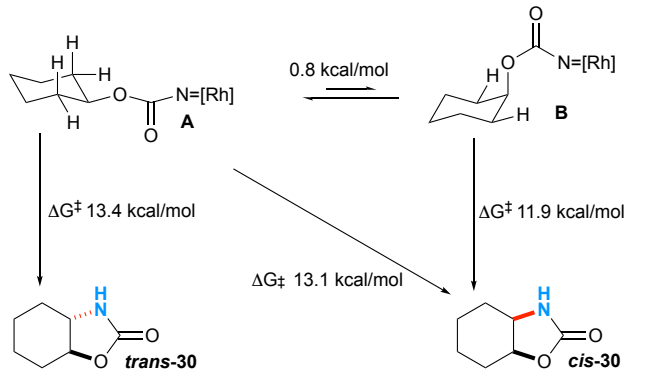


Figure 2. Conformational Equilibrium of Cyclohexyl Carbamate Rhodium Nitrene and $Rh_2(OAc)_4$ with computed relative free energies barriers at the PBEPBE/BS1 level.

Axial rhodium nitrene **B** produced exclusively *cis*-oxazolidinone **30** via an insertion in an equatorial C-H bond ($\Delta G^{‡}$ = 11.9 kcal/mol) (Figure 3). Conversely equatorial rhodium nitrene **A** afforded both *cis*- and *trans*-oxazolidinone **30** with $\Delta G^{‡}$ 13.1 and 13.4 kcal/mol respectively (Figure 4). This is an unusual Curtin-Hammett situation, in which the more stable conformer also afforded the major diastereomer. A late transition state for the insertion in the axial C-H bond is slightly preferred over a transition state in the less hindered equatorial C–H bond.

Tertiary *N*-mesyloxycarbamates derived from 1-methyl- and 1-trifluoromethyl-cyclohexanol were then studied and produced the desired oxazolidinones **31** and **32** in good yields and as a single diastereomer (Table 3, entries 5, 6).

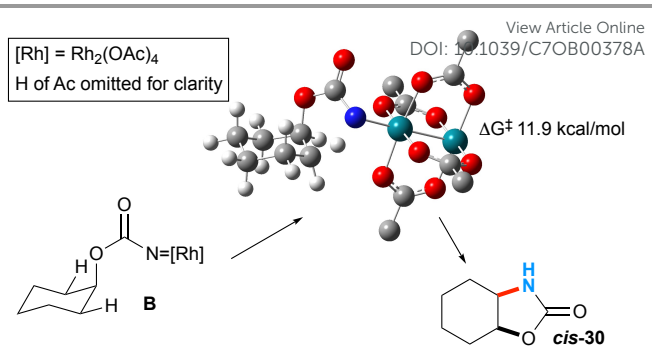


Figure 3. Transition state producing *cis*-oxazolidinone **30** from axial rhodium nitrene **B** with computed relative free energies barriers at the PBEPBE/BS1 level.

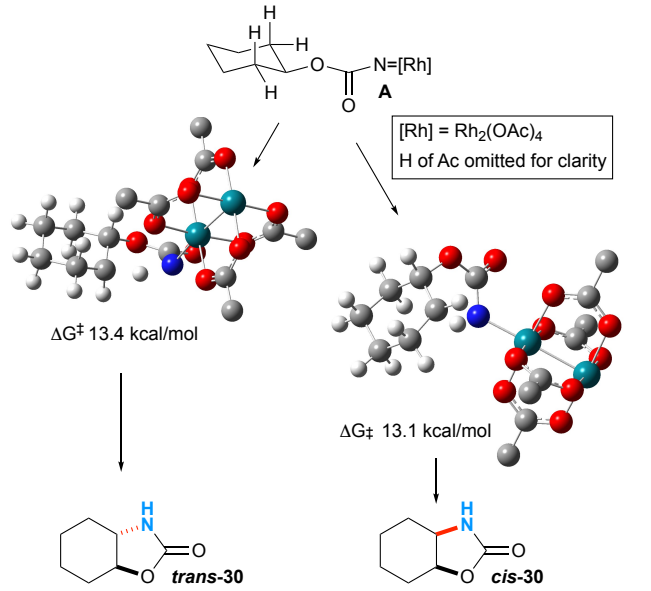


Figure 4. Transition state producing *cis*- and *trans*-oxazolidinone **30** from equatorial rhodium nitrene **A** with computed relative free energies barriers at the PBEPBE/BS1 level.

To establish whether the lack of reactivity of secondary *N*-mesyloxycarbamates is due to the undesired reactivity of the α-hydrogen, or to an unfavored conformation, a series of *N*-mesyloxycarbamates from *cis* and *trans* 4-*t*-butyl-cyclohexanol were synthesized (entries 7–10). In the case of the *trans* 4-*t*-butyl-cyclohexanol derivative, in which the carbamate moiety is forced in the equatorial position, a mixture of diastereomers was observed. *Trans*-oxazolidinone **33** was the major product (isolated in low yields) resulting from the insertion into the less hindered equatorial C–H bond (entry 7). Conversely the *cis* 4-*t*-butyl-cyclohexanol derivative was converted into the corresponding *cis*-oxazolidinone **34** in good yields (entry 8). The axial carbamate can easily undergo an insertion into an equatorial C–H bond affording exclusively the *cis* stereoisomer. The relative stereochemistry of ***cis*-34** was confirmed by the resolution of an X-ray crystal structure.[20] Both *cis* and *trans* isomer of *N*-mesyloxycarbamates derived from 4-*t*-butyl-1-methyl-cyclohexanol, afforded exclusively the corresponding *cis*-oxazolidinone (entries 9-10). The yield for the production of **36**, which resulted from an equatorial C–H bond insertion was slightly better than the one for the axial C–H bond amination affording **35**.

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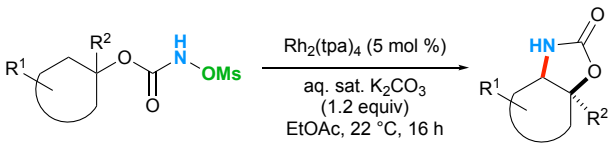
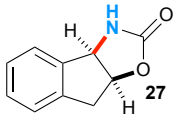
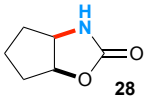
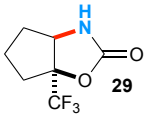
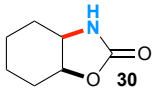
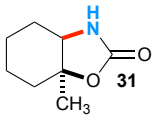
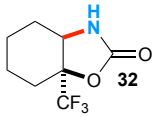
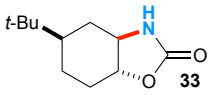
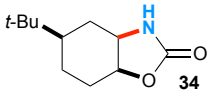
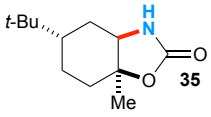
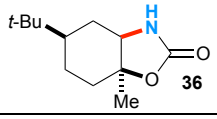
Table 3. Rhodium-Catalyzed C–H Amination of Cyclic *N*-Mesyloxycarbamates



Entry	Oxazolidinone	Crude dr [a]	Yield dr [b]
1 [c]	 **27**	>99 : 1	86% >99 : 1
2	 **28**	>99 : 1	40% >99 : 1
3 [d]	 **29**	>99 : 1	89% >99 : 1
4 [e]	 **30**	80 : 20	33% >99 : 1
5 [f]	 **31**	>99 : 1	81% >99 : 1
6 [d]	 **32**	>99 : 1	84% >99 : 1
7	 **33**	15 : 85	20% <1 : 99
8 [e]	 **34**	>99 : 1	79% >99 : 1
9 [e]	 **35**	>99 : 1	57% >99 : 1
10 [e]	 **36**	>99 : 1	85% >99 : 1

[a] Crude dr (*cis*:*trans*) determined by ^{1}H NMR. [b] Isolated yields and dr (*cis*:*trans*). [c] $Rh_2(tpa)_4$ (3 mol %), K_2CO_3 (1.5 equiv). [d] $Rh_2(oct)_4$ (1 mol %), KOAc (3.0 equiv), MeOH (0.2 M). [e] 40 °C. [f] aq. sat. K_2CO_3 (1.0 equiv).

The results clearly indicated that the conformational bias is the key element to predict reactivity in these cyclic systems. DFT calculations of rhodium nitrenes derived from corresponding *t*-butyl-cyclohexyl carbamates and $Rh_2(OAc)_4$ confirmed the experimental observations.[24] *Trans*-oxazolidinone **33** is favored by 0.6 kcal/mol over the *cis* isomer (Figure 5). A late transition state for the insertion in the less hindered equatorial C–H bond is preferred, over an early transition state into an axial C–H bond. This is in sharp contrast with results obtained with equatorial rhodium nitrene **A** (figure 3), which display a late transition state for the insertion in the axial C–H bond. Steric interaction between the rhodium dimer and the *t*-butyl group might be responsible for the difference in between the two transition states.

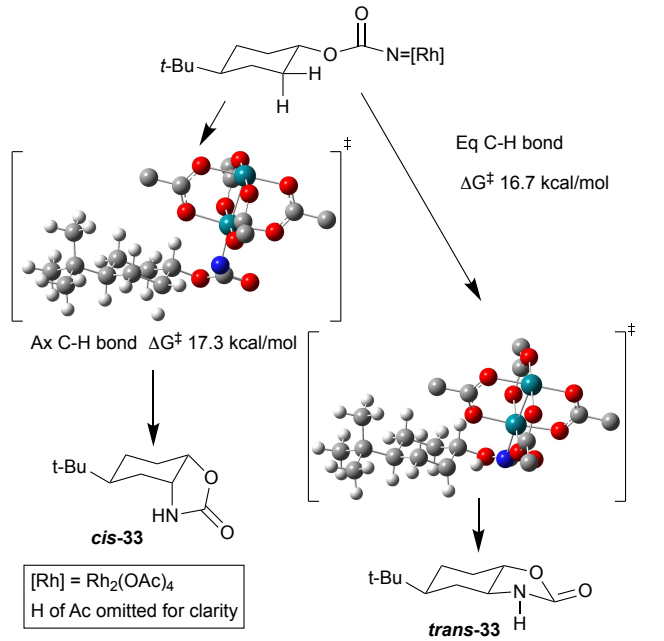


Figure 5. Transition states producing *cis*- and *trans*-oxazolidinone **33** with computed relative free energies barriers at the PBEPBE/BS1 level.

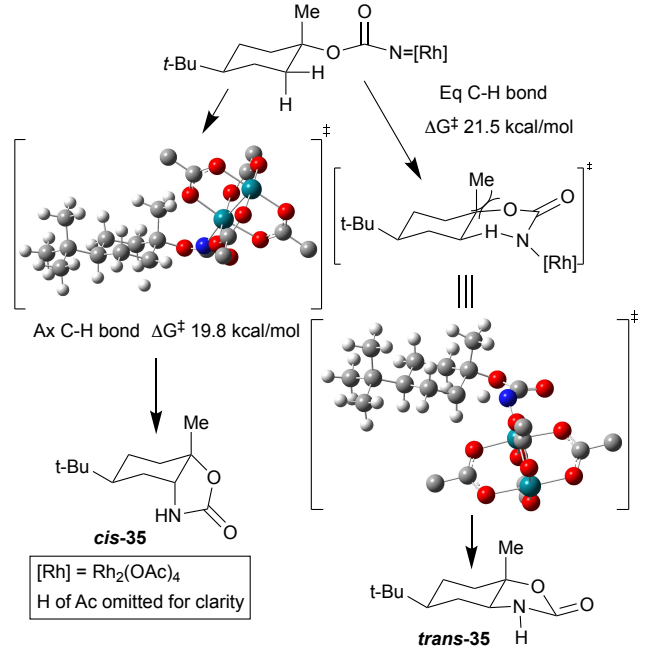


Figure 6. Transition states producing *cis*- and *trans*-oxazolidinone **35** with computed relative free energies barriers at the PBEPBE/BS1 level.

In the case of *trans*-4-*t*-butyl-1-methyl-cyclohexyl carbamate, a gauche interaction with the additional axial methyl group is

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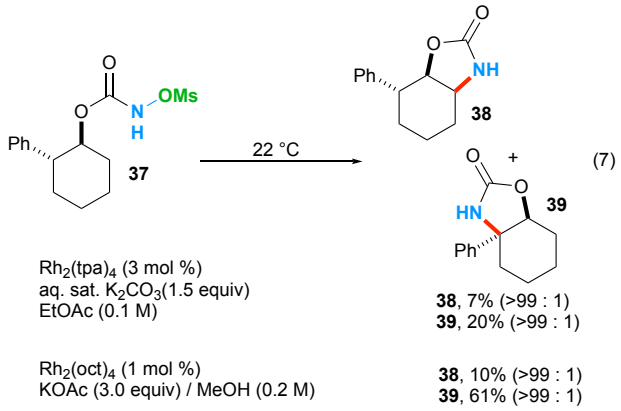
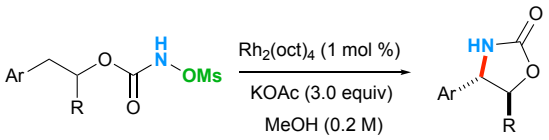
observed in the transition state leading to diastereomer *trans*: the early transition state affording *cis*-oxazolidinone **35** become favored by 1.7 kcal/mol, corresponding to a theoretical ratio of 95:5 (Figure 6). Experimentally, the *trans* isomer was not observed (Table 3, entry 9), but given that $Rh_2(tpa)_4$ was used, it is possible that the bigger rhodium catalyst precluded the formation of the *trans* isomer. Finally, for both *cis*-4-*t*-butyl-cyclohexyl carbamate and *cis*-4-*t*-butyl-1-methyl-cyclohexyl carbamate (affording respectively oxazolidinone **34** and **36**), the transition state leading to the *trans*-oxazolidinone could not be located in agreement with the experimental results (Table 3, entries 8 and 10).

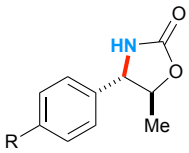
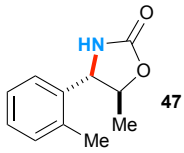
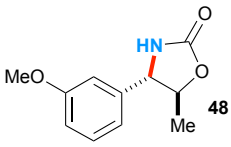
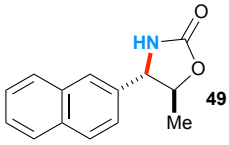
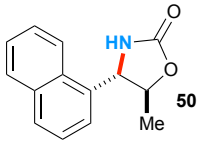
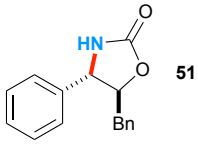
Trans-2-phenylcyclohexanol-derived *N*-mesyloxycarbamate **37** was also studied (Eq 7). Two *cis*-oxazolidinone products were obtained, one resulting from aliphatic C–H insertion, **38**, and the other from benzylic C–H amination reaction, **39**. The later proved to be the major product formed, albeit in low yields using $Rh_2(tpa)_4$. Conversely the use of $Rh_2(oct)_4$ in methanol afforded the desired oxazolidinone **39** as a single diastereomer in 61% yield, along with 10% of oxazolidinone **38**.



When the reactivity of acyclic secondary *N*-mesyloxycarbamate to produce oxazolidinone **40** was examined using $Rh_2(tpa)_4$, a 1:1 mixture of *trans* and *cis* diastereomer was observed. Conversely the use of $Rh_2(oct)_4$ in methanol afforded oxazolidinone **40** as 88:12 favoring the *trans* diastereomer. Similar results were obtained with $Rh_2(OAc)_4$ and other rhodium catalysts produced lower yields and/or dr.[20] The desired *trans* oxazolidinone **40** was isolated in 66% yield as a 98:2 dr (Table 4, entry 1). The relative stereochemistry of ***trans*-40** was confirmed by X-ray crystallography.[20] The reaction conditions tolerated various substituents, electron-donating or electron-withdrawing at the *para* position of the aromatic moiety (entries 2–7). Slightly higher dr was observed for *ortho*-substituted oxazolidinone **47**, where *meta*-substituted oxazolidinone **48** was isolated in 58% yield with 94:6 isolated dr (entries 8, 9). Naphtyl-substituted oxazolidinones **49** and **50** were obtained in good yields and dr (entries 10, 11). The symmetrical 1,3-diphenylpropanol-derived *N*-mesyloxycarbamate produced oxazolidinone **51** in moderate yield (entry 12).

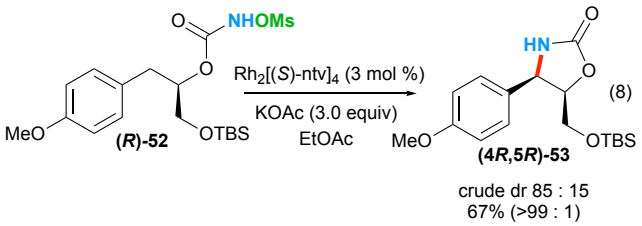
Table 4. Rhodium-Catalyzed C–H Amination of Acyclic Secondary *N*-Mesyloxycarbamates



Entry	Oxazolidinone		Crude dr [a]	Yield (dr) [b]
1		R = H, **40**	89 : 11	66 (98 : 2)
2		R = Me, **41**	90 : 10	76 (96 : 4)
3		R = *t*-Bu, **42**	90 : 10	75 (96 : 4)
4		R = Ph, **43**	90 : 10	75 (98 : 2)
5		R = OMe, **44**	90 : 10	65 (95 : 5)
6		R = Br, **45**	88 : 12	59 (99 : 1)
7		R = CF_3, **46**	89 : 11	59 (99 : 1)
8		**47**	94 : 6	55 (97 : 3)
9		**48**	90 : 10	58 (94 : 6)
10		**49**	89 : 11	76 (97 : 3)
11		**50**	96 : 4	73 (97 : 3)
12		**51**	87 : 13	64 (99 : 1)

[a] Crude dr (*trans*:*cis*) determined by ^1H NMR. [b] Isolated yields and dr (*trans*:*cis*).

The precursor of (–)-cytoxazone, (*R*)-*N*-mesyloxycarbamate **52** was then prepared from the corresponding enantiopur alcohol. As previsouly reported,[2d] the use of $Rh_2(OAc)_4$ afforded mainly the *trans*-oxazolidinone. The diastereoselectivity was inverted when bigger rhodium dimer complexes were used. Whereas $Rh_2(oct)_4$ and $Rh_2(tpa)_4$ afforded oxazolidinone **53** with 60:40 and 74:26 ratio favoring the *cis* isomer, the use of chiral valine derived $Rh_2[(S)\text{-ntv}]_4$ afforded the desired compound with 85:15 dr; *cis*-oxazolidinone **53** was isolated in 67% yield as a single diasteromer (Eq 8). As the deprotection of the TBS has been previously reported,[2b,e] a formal synthesis of (–)-cytoxazone was achieved.



Conclusions

In conclusion, *N*-mesyloxycarbamates proved valuable precursors to undergo intramolecular C–H amination affording oxazolidinones in high yields. Rhodium dimer complexes were the optimal catalysts to be used. In some cases, the facial selectivity could be modulated using different rhodium dimer complexes. Experimental results and DFT calculations confirmed that conformational bias is an important criterion to consider to favor the C–H insertion, especially with cyclic secondary carbamates. A formal synthesis of (–)-cytoxazone was achieved by using a chiral sterically hindered rhodium dimer complex.

Experimental

General Remarks

ACS grade solvents and reagents were used without further purification. Commercially available rhodium(II) octanoate was used without further purification. Rhodium(II) triphenylacetate[25] and Rh_2[(S)-ntv]$_4$,[26] were prepared according to the literature. Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F_{254} TLC plates (visualization using UV absorbance and/or aqueous potassium permanganate solution). Flash chromatography was performed using Silicycle SiliaFlash® P60 silica gel with the indicated solvent system. Optical rotations were measured on an Anton Paar MCP 200 polarimeter and on a Perkin Elmer Model 1343 polarimeter at 589 nm. Data are reported as follows: $[\alpha]_l^{temp.}$, concentration (*c* g/100 mL), and solvent. Infrared spectra were recorded on a Bruker ALPHA Platinum ATR FT-IR spectrometer along with the OPUS software and are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. ^{1}H NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker Avance 500 or a Bruker Avance 400 (respectively 500 and 400 MHz). Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz and integration. ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise noted, on a Bruker Avance 500, a Bruker Avance 400 or a Bruker Avance 300 (125, 100 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. Mass spectra were obtained on a LC-MSD TOF (ESI) Agilent Technologies high resolution from the Centre régional de spectrométrie de masse de l'Université de Montréal. High performance liquid chromatography (HPLC) analyses were performed on a Hewlett Packard 1100 Series quaternary gradient pump with diode-array detector interfaced with HP Chemstation software. Values for enantiomeric excess were determined using a chiral column. Data are reported as follows: column type, flow, solvent used, and retention time (t_r).

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General Procedure A for the Synthesis of Oxazolidinones

In a 15 mL round-bottom flask, equipped with a magnetic stir bar, the *N*-mesyloxycarbamate (1.00 mmol, 1.00 equiv) was dissolved in non-anhydrous EtOAc (10.0 mL). Green $Rh_2(tpa)_4$ (40.7 mg, 0.030 mmol, 3.00 mol %) was added and the resulting mixture was stirred. After complete dissolution of the rhodium dimer, a saturated aqueous K_2CO_3 solution (0.187 mL, 1.50 equiv) was added. The resulting turquoise heterogeneous mixture was stirred at room temperature for 16 hours. The reaction was monitored by TLC (40% EtOAc/hexanes). The crude mixture was filtered through Celite, and the later was thoroughly washed with EtOAc. The solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel eluting with 20% then 40% EtOAc/hexanes.

General Procedure B for the Synthesis of Oxazolidinones

In a 4 mL vial, equipped with a magnetic stir bar, $NOBF_4$ (1.8 mg, 0.015 mmol, 3.0 mol %) was dissolved in non-anhydrous EtOAc (1 mL). $Rh_2(tpa)_4$ (20.4 mg, 0.0150 mmol, 3.00 mol %) was added, followed by CH_3CN (52 µl, 0.20 mmol, 20 mol %). The resulting mixture heterogeneous and was stirred for 30 min. In a 15 mL round-bottom flask, equipped with a magnetic stir bar, the *N*-mesyloxycarbamate (0.500 mmol, 1.00 equiv) was dissolved in non-anhydrous EtOAc (0.5 mL). To this homogeneous solution, was added the heterogeneous Rh catalyst mixture, followed by an aqueous saturated solution of K_2CO_3 (93.4 µL, 0.750 mmol, 1.50 equiv). The resulting mixture was stirred for 16 h. The reaction was monitored by TLC (40% EtOAc/hexanes). The crude mixture was filtered through celite, and the cake was thoroughly washed with EtOAc. The solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel eluting with 20% then 40% EtOAc/hexanes.

General Procedure C for the Synthesis of Oxazolidinones

In a 15 mL round-bottom flask, equipped with a magnetic stir bar, the *N*-mesyloxycarbamate (1.00 mmol, 1.00 equiv) was dissolved in non-anhydrous MeOH (2.5 mL). Green $Rh_2(oct)_4$ (4.0 mg, 5.1 µmol, 1.0 mol %) was added and the resulting mixture was stirred. After complete dissolution of the rhodium dimer, solid potassium acetate (147 mg, 1.50 mmol, 3.00 equiv) was added. The resulting turquoise heterogeneous mixture was stirred at room temperature for 16 hours. The reaction was monitored by TLC (50% EtOAc/hexanes). The crude reaction mixture was quenched with ~10 µL of pyridine and filtered through Celite; the later was thoroughly washed with EtOAc. The solvent was evaporated under reduced

pressure. The residue was chromatographed on silica gel eluting with 40% then 50% EtOAc/hexanes.

Characterization of Oxazolidinones

(±)-4-Phenyloxazolidin-2-one (2).[17a] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **1** (0.130 g, 0.500 mmol), to afford oxazolidinone **2** (0.073 g, 0.445 mmol, 89% yield) as a crystalline white solid after purification by flash chromatography. The title compound was also prepared according to General Procedure B to afford oxazolidinone **2** (0.076 g, 0.465 mmol, 93% yield) as a white solid after purification by flash chromatography. R_f 0.17 (40% EtOAc/Hexanes); mp 135-136 °C (lit. 135-136 °C);[17a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.33 (m, 5H), 5.73 (s (br), 1H), 4.96 (dd, *J* = 8.0, 1H), 4.74 (t, *J* = 8.7 Hz, 1H,), 4.19 (dd, *J* = 8.6, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 139.4, 129.2, 128.9, 126.0, 72.5, 56.4.

(±)-4-(4-Methoxyphenyl)oxazolidin-2-one (3).[7e] The title compound was prepared according to general procedure A starting *N*-mesyloxycarbamate **S1**[20] (0.289 g, 1.00 mmol), to afford oxazolidinone **3** (0.153 g, 0.79 mmol, 79% yield) as a white solid after purification by flash chromatography. R_f 0.16 (40% EtOAc/hexanes); mp 111 °C (lit. 111 °C);[7e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 6.93-6.90 (m, 2H), 5.64 (s (br), 1H), 4.90 (dd, *J* = 8.7, 7.1 Hz, 1H), 4.70 (t, *J* = 8.7 Hz, 1H), 4.15 (dd, *J* = 8.7, 7.1 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.84, 159.82, 131.4, 127.3, 114.4, 72.6, 55.9, 55.3.

(±)-4-Methylphenyloxazolidin-2-one (4).[9c] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S2**[20] (0.137 g, 0.500 mmol), to afford oxazolidinone **4** (0.072 g, 0.405 mmol, 81% yield) as a white solid after purification by flash chromatography. **R_f** 0.4 (40% EtOAc/hexanes); **mp** 109 °C (lit. 110 °C);[7a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.19 (m, 5H), 5.80 (s (br), 1H), 4.91 (dd, *J* = 8.6, 7.0 Hz, 1H), 4.71 (t, *J* = 8.6 Hz, 1H), 4.16 (dd, *J* = 8.6, 7.0 Hz, 1H), 2.35 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 138.7, 136.4, 129.8, 126.0, 72.6, 56.2, 21.1; IR (neat) 3259, 1747, 1708, 1241, 1028, 919, 767 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{12}NO_2$ 178.0863; found 178.0866.

(±)-4-Chlorophenyloxazolidin-2-one (5).[7l] The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S3**[20] (0.147 g, 0.500 mmol), to afford oxazolidinone **5** (0.082 g, 0.415 mmol, 83% yield) as a white solid after purification by flash chromatography. R_f 0.13 (40% EtOAc/hexanes); mp 110-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.29-7.26 (m, 2H), 6.18 (s (br), 1H), 4.94 (d, *J* = 8.7, 6.8 Hz, 1H), 4.72 (t, *J* = 8.7 Hz, 1H), 4.13 (dd, *J* = 8.7, 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 137.9, 134.7, 129.4, 127.4, 72.3, 55.8.

(±)-4-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)oxazolidin-2-one (6).[5c] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S4**[20] (0.390 g, 1.00 mmol), to afford oxazolidinone **6** (0.200 g, 0.68 mmol, 68% yield) as a white solid after purification by flash chromatography. R_f 0.21 (40% EtOAc/hexanes); mp 111-112 °C (lit. 110-112 °C);[5c] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.18 (m, 2H), 6.86-6.84 (m, 2H), 5.52 (s (br), 1H,), 4.89 (dd, *J* = 8.6, 7.1 Hz, 1H), 4.70 (t, *J* = 8.6 Hz, 1H), 4.17 (dd, *J* = 8.6, 7.1 Hz, 1H), 0.98 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 156.2, 131.8, 127.3, 120.7, 72.7, 56.0, 25.6, 18.1, -4.4.

(±)-2-Methoxyphenyloxazolidin-2-one (7). The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S5**[20] (0.145 g, 0.500 mmol) using $Rh_2(tpa)_4$ (27.1 mg, 0.020 mmol, 4.00 mol %), to afford oxazolidinone **7** (0.089 g, 0.461 mmol, 92% yield) as a white solid after purification by flash chromatography. R_f 0.22 (40% EtOAc/hexanes); mp 115-117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H), 7.00 (td, *J* = 7.5, 0.85 Hz, 1H), 6.89 (dd, *J* = 8.2 Hz, 0.75 Hz, 1H), 6.12 (s (br), 1H), 5.24 (dd, *J* = 8.8, 6.5 Hz, 1H), 4.80 (t, *J* = 8.7 Hz, 1H), 4.16 (dd, *J* = 8.6 Hz, 6.4 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 156.4, 129.4, 127.8, 125.5, 120.9, 110.4, 71.5, 55.3, 51.3; IR (neat) 3219, 3123, 1736, 1493, 1228, 1018, 745 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{12}NO_3$ 194.0812; found 194.0817.

(±)-2-Bromo-phenyloxazolidin-2-one (8). The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S6**[20] (0.169 g, 0.500 mmol), to afford oxazolidinone **8** (0.104 g, 0.430 mmol, 86% yield) as a white solid after purification by flash chromatography. R_f 0.2 (40% EtOAc/hexanes); mp 95-97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.39 (td, *J* = 7.6, 1.1 Hz, 1H), 7.21 (td, *J* = 7.7, 1.6 Hz, 1H), 6.86 (s (br), 1H), 5.33 (dd, *J* = 8.8, 6.3 Hz, 1H), 4.89 (t, *J* = 8.8 Hz, 1H), 4.11 (dd, *J* = 8.8, 6.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 138.9, 133.1, 129.9, 128.2, 126.4, 121.8, 71.4, 55.4; IR (neat) 3253, 1773, 751, 727 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9BrNO_2$ 241.9811; found 241.9818.

(±)-2-Chloro-phenyloxazolidin-2-one (9). The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S7**[20] (0.147 g, 0.500 mmol), to afford oxazolidinone **9** (0.069 g, 0.350 mmol, 70% yield) as a white solid after purification by flash chromatography. R_f 0.29 (40% EtOAc/hexanes); mp 103-108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 (td, *J* = 7.6, 1.7 Hz, 1H), 7.16 (s (br), 1H), 5.34 (dd, *J* = 8.9, 6.2 Hz, 1H), 4.86 (t, *J* = 8.9 Hz, 1H), 4.10 (dd, *J* = 8.7, 6.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 137.3, 131.9, 129.7, 129.4, 127.5, 126.1, 71.2, 53.3; IR (neat) 3247, 1741, 1239, 1023, 757 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9ClNO_2$ 198.0316; found 198.0315.

(±)-2-Fluoro-phenyloxazolidin-2-one (10). The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S8**[20] (0.139 g, 0.500 mmol), to afford oxazolidinone **10** (0.062 g, 0.340 mmol, 68% yield) as a beige solid after purification by flash chromatography. R_f 0.25 (40% EtOAc/hexanes); mp 99-101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (td, *J* = 7.6, 1.6 Hz, 1H), 7.34-7.29 (m, 1H), 7.19 (td, *J* = 7.6, 1.0 Hz, 1H), 7.08-7.04 (m, 1H), 6.96 (s (br), 1H), 5.25 (dd, *J* = 8.8, 6.5 Hz, 1H), 4.79 (t, *J* = 8.8 Hz, 1H), 4.18 (dd, *J* = 8.8, 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 160.0 (d, *J* = 247 Hz), 130.0 (d, *J* = 8.2 Hz), 126.8 (d, *J* = 13 Hz), 126.6 (d, *J* = 3.7 Hz), 124.7 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 21 Hz), 71.3 (d, *J* = 1.7 Hz), 50.4 (d, *J* = 4.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -119.44-

-119.49 (m); IR (neat) 3254, 1739, 1712, 1033, 761 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9FNO_2$ 182.0612; found 182.0611.

(±)-3-Chloro-phenyloxazolidin-2-one (11). The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S9**[20] (0.147 g, 0.500 mmol), to afford oxazolidinone **11** (0.069 g, 0.350 mmol, 70% yield) as a white solid after purification by flash chromatography. R_f 0.22 (40% EtOAc/hexanes); mp 90-91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.34 (m, 3 H), 7.25-7.22 (m, 1 H), 5.81 (s (br), 1H), 4.94 (dd, *J* = 8.7, 6.7 Hz, 1H), 4.74 (t, *J* = 8.7 Hz, 1H), 4.17 (dd, *J* = 8.7, 6.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 141.5, 135.2, 130.6, 129.1, 126.3, 124.1, 72.2, 55.8; IR (neat) 3238, 1743, 1709, 1027, 670 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_9H_9ClNO_2$ 198.0316; found 198.0320.

(±)-3-(Trifluoromethyl)phenyloxazolidin-2-one (12). The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S10**[20] (0.164 g, 0.500 mmol) using a saturated aqueous K_2CO_3 solution (0.065 mL, 1.05 equiv) in EtOAc (10.0 mL, 0.05 M), to afford oxazolidinone **12** (0.097 g, 0.420 mmol, 84% yield) as a white solid after purification by flash chromatography. R_f 0.24 (40% EtOAc/hexanes); mp 76-77 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.54 (m, 5 H), 5.65 (s (br), 1H), 5.04 (dd, *J* = 8.8, 6.9 Hz, 1H), 4.78 (t, *J* = 8.8 Hz, 1H), 4.19 (dd, *J* = 8.8, 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 140.6, 131.6 (q, *J* = 33 Hz), 129.9, 129.3, 125.7 (q, *J* = 4 Hz), 123.7 (q, *J* = 272 Hz), 123.0 (q, *J* = 4 Hz), 72.1, 56.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -62.7 (s); IR (neat) 3267, 1721, 1330, 1108, 1028, 704, 661 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_9F_3NO_2$ 232.0580; found 232.0588.

(±)-3,4-(Methylenedioxy)phenyloxazolidin-2-one (13). The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S11**[20] (0.152 g, 0.500 mmol), to afford oxazolidinone **13** (0.088 g, 0.425 mmol, 85% yield) as a white solid after purification by flash chromatography. R_f 0.17 (40% EtOAc/hexanes); mp 139-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (d, *J* = 1.6 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.97 (s, 2H), 5.96 (s (br), 1H), 4.87 (dd, *J* = 8.7, 6.9 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 1H), 4.13 (dd, *J* = 8.6, 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 148.5, 148.0, 133.2, 119.7, 108.5, 106.1, 101.4, 72.6, 56.2; IR (neat) 3241, 1748, 1250, 1028, 923 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{10}NO_4$ 208.0604; found 208.0609.

(±)-4-(Naphthalen-2-yl)oxazolidin-2-one (14).[7c] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S12**[20] (0.309 g, 1.00 mmol), to afford oxazolidinone **14** (0.180 g, 0.84 mmol, 84% yield) as a white solid after purification by flash chromatography. R_f 0.16 (40% EtOAc/hexanes); mp 153 °C, (lit. 146 °C);[7d] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5, 1H), 7.86-7.82 (m, 2H), 7.76 (s, 1H), 7.54-7.49 (m, 2H), 7.42 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.20 (s (br), 1H), 5.09 (dd, *J* = 8.7, 6.8 Hz, 1H), 4.77 (t, *J* = 8.7 Hz, 1H), 4.25 (dd, *J* = 8.7, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 136.7, 133.3, 133.1, 129.4, 127.9, 127.7, 126.7, 126.6, 125.4, 123.2, 72.3, 56.5.

(±)-4-(Thiophen-2-yl)oxazolidin-2-one (15).[9a] The title compound was prepared according to general procedure B starting from *N*-mesyloxycarbamate **S13**[20] (0.133 g, 0.500 mmol), to afford oxazolidinone **15** (0.069 g, 0.410 mmol, 82% yield) as a beige solid. R_f 0.16 (40% EtOAc/hexanes); mp 101 °C (lit. 101-101.5 °C);[9a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7,31 (m, 1H), 7.06-7.05 (m, 1H), 6.99 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.22 (s (br), 1H), 5.24 (dd, *J* = 8.7 Hz, 6.7 Hz, 1H), 4.71 (t, *J* = 8.6 Hz, 1H), 4.28 (dd, *J* = 8.7 Hz, 6.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 142.9, 127.2, 126.0, 125.4, 72.5, 52.3.

(±)-4-(1-*tert*-Butoxycarbonyl-1*H*-indol-3-yl)-oxazolidin-2-one (16). The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S14**[20] (0.398 g, 1.00 mmol), to afford oxazolidinone **16** (0.222 g, 0.730 mmol, 73% yield) as a white solid after purification by flash chromatography. R_f 0.25 (40% EtOAc/hexanes); mp 51-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.25-7.21 (m, 1H), 6.73 (s (br), 1H), 5.16 (dd, *J* = 8.4, 6.7 Hz, 1H), 4.71 (t, *J* = 8.4 Hz, 1H), 4.36 (dd, *J* = 8.4, 6.7 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 149.2, 136.0, 127.2, 124.9, 123.6, 122.9, 118.8, 118.7, 115.5, 84.1, 70.3, 49.5, 28.0; IR (neat) 3261, 2978, 1728, 1366, 1151, 744 cm^{-1}; HRMS (ESI) calc. for $C_{16}H_{19}N_2O_4$ $[M+H]^+$: 303.1339; found: 303.1348.

(±)-4-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)oxazolidin-2-one (17). The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S15**[20] (0.049 g, 0.100 mmol), to afford oxazolidinone **17** (0.026 g, 0.067 mmol, 67% yield) as a white solid after purification by flash chromatography. R_f 0.25 (60% EtOAc/hexanes); mp 156-158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.50-7.47 (m, 2H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.79 (d, *J* = 9.1 Hz, 1H), 6.70 (dd, *J* = 9.1, 2.5 Hz, 1H), 5.30 (dd, *J* = 9.1, 7.1 Hz, 1H), 5.18 (s (br), 1H), 4.76 (t, *J* = 9.0 Hz, 1H), 4.54 (dd, *J* = 8.8, 7.1 Hz, 1H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 158.9, 156.0, 140.0, 136.2, 133.2, 131.4, 131.2, 129.3, 127.4, 115.3, 115.1, 112.4, 101.4, 69.4, 55.7, 48.8, 12.9; IR (neat) 1733, 1678, 1595, 1321, 1214, 1085 cm^{-1}; HRMS (ESI) calc. for $C_{20}H_{18}ClN_2O_4$ $[M+H]^+$: 385.0950; found: 385.0963.

(-)-4-(6-Methoxynaphthalen-2-yl)-4-methyloxazolidin-2-one (19). The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **18** (0.177 g, 0.500 mmol), to afford oxazolidinone **19** (0.112 g, 0.435 mmol, 87% yield) as a white solid after purification by flash chromatography. R_f 0.15 (40% EtOAc/hexanes); mp 181-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.73 (m, 3H), 7.44 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 5.65 (s (br), 1H), 4.42 (s, 2H), 3.93 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.2, 138.1, 133.9, 129.6, 128.4, 128.0, 123.4, 123.2, 119.6, 105.5, 78.2, 60.2, 55.3, 27.3; IR (neat) 3229, 1756, 1366, 1165, 1037, 1027 cm^{-1}; HRMS (ESI) calc. for $C_{15}H_{16}NO_3$ $[M+H]^+$: 258.1125; found: 258.1131; $[\alpha]_D^{20}$ = - 36.0 ° (*c* 1.0, $CHCl_3$); Enantiomeric excess was determined by HPLC analysis: 99% *ee*, Chiracel® OD, 1.00 mL/min, 90 : 10 Hexanes/*i*-PrOH, 210 nm, t_R (minor) = 25.05 min, t_R(major) = 31.34 min.

(±)-3,6-Dioxa-1-azaspiro[4.5]decan-2-one (21).[17a] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **20** (0.253 g, 1.00 mmol), to afford oxazolidinone **21** (0.147 g, 0.930 mmol, 93% yield) as a white solid. *Gram Scale: N*-mesyloxycarbamate **20** (2.03 g, 8.00 mmol) was reacted with $Rh_2(tpa)_4$ (0.111 g, 0.08 mmol, 1.0 mol %) according to general procedure A, to afford oxazolidinone **21** (1.135 g, 7.22 mmol, 90% yield) as a white solid after purification by flash chromatography. R_f 0.12 (40% EtOAc/hexanes); mp 113-114 °C, (lit. 98 °C);[17a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s (br), 1H), 4.30 (d, *J* = 9.2 Hz, 1H,), 4.10 (d, *J* = 9.2 Hz, 1H), 3.79-3.71 (m, 2H), 1.83-1.71 (m, 4H), 1.61-1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 87.1, 76.1, 63.0, 33.5, 24.5, 20.0.

(±)-4-(2-Ethoxyethoxy)oxazolidin-2-one (22). The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S16**[20] (0.136 g, 0.500 mmol), to afford oxazolidinone **22** (39 mg, 0.23 mmol, 45% yield) as a colorless oil after purification by flash chromatography. R_f 0.21 (60% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s (br), 1H), 5.12-5.10 (m, 1H), 4.45 (dd, *J* = 10, 6.0 Hz, 1H), 4.27 (dd, *J* = 10, 1.7 Hz, 1H), 3.75 (ddd, *J* = 12, 5.5, 2.3 Hz, 1H), 3.68-3.58 (m, 2H), 3.54 (q, *J* = 7.0 Hz, 2H), 3.53-3.49 (m, 1H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 84.3, 71.4, 70.3, 68.3, 66.8, 15.0; IR (neat) 3281, 1748, 1099 cm^{-1}; HRMS (ESI) calc. for $C_7H_{14}NO_4$ $[M+H]^+$: 176.0917; found: 176.0921.

(±)-4-Butyloxazolidin-2-one (23).[17a] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S17**[20] (0.120 g, 0.500 mmol), to afford oxazolidinone **23** (0.043 g, 0.30 mmol, 60% yield) as a colorless oil after purification by flash chromatography. The title compound was also prepared according to general procedure B starting from *N*-mesyloxycarbamate **S17**[20] (0.120 g, 0.500 mmol), to afford oxazolidinone **23** (0.046 g, 0.320 mmol, 64% yield) as a colorless oil after purification by flash chromatography. R_f 0.16 (40% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (s (br), 1H), 4.47 (t, *J* = 8.5 Hz, 1H), 4.00 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.89-3.82 (m, 1H), 1.63-1.50 (m, 2H), 1.36-1.23 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 70.3, 52.6, 35.0, 27.3, 22.4, 13.8.

(±)-4-Phenethyloxazolidin-2-one (24).[10b] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S18**[20] (0.287 g, 1.00 mmol), to afford oxazolidinone **24** (0.068 g, 0.36 mmol, 36% yield) as a white solid after purification by flash chromatography. R_f 0.14 (40% EtOAc/hexanes); mp 65-68 °C (lit. 96-97 °C (*S,* 99% ee);[10b] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.23-7.20 (m, 1H), 7.18-7.15 (m, 2H), 6.05 (s (br), 1H), 4.46 (t, *J* = 8.5 Hz, 1H), 4.01 (dd, *J* = 8.5, 6.0 Hz, 1H), 3.90-3.84 (m, 1H), 2.74-2.62 (m, 2H), 1.99-1.86 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 140.1, 128.7, 128.3, 126.5, 70.2, 52.1, 36.9, 31.7; IR (neat) 3224, 1744, 1710, 1241, 1033, 698 cm^{-1}; HRMS (ESI) calc. for $C_{11}H_{13}NNaO_2$ $[M+Na]^+$: 214.0839; found: 214.0839.

(±)-4-(Phenylethynyl)oxazolidin-2-one (25).[9b] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S19**[20] (0.142 g, 0.50 mmol) using an aqueous saturated solution of K_2CO_3 (0.078 mL, 0.63 mmol, 1.25 equiv), to afford oxazolidinone **25** (0.069 g, 0.37 mmol, 74% yield) as a white solid after purification by flash chromatography. R_f 0.24 (40% EtOAc/hexanes); mp 106-107 °C, (lit. 91-93 °C);[9b] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.37-7.30 (m, 3H), 6.24 (s (br), 1H), 4.83 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.63 (t, *J* = 8.5 Hz, 1H), 4.44 (dd, *J* = 8.5, 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 131.8, 129.0, 128.4, 121.5, 85.5, 85.1, 70.3, 44.3; IR (neat) 3335, 1730, 1404, 1205, 930, 751, 691 cm^{-1}; HRMS (ESI) calc. for $C_{11}H_{10}NO_2$ $[M+H]^+$: 188.0706; found: 188.0713.

(3a*R,8a*S**)-3,3a,8,8a-Tetrahydro-2*H*-indeno[1,2-*d*]oxazol-2-one (27).**[17a] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S20**[20] (0.271 g, 0.100 mmol) to afford oxazolidinone **27** (0.15 g, 0.86 mmol, 86% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.14 (40% EtOAc/hexanes); mp 158 °C (lit. 160-162 °C);[17a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 4H), 7.09 (br (s), 1H), 5.44-5.40 (m, 1H), 5.18 (d, *J* = 7.2 Hz, 1H), 3.43 (dd, *J* = 18, 6 Hz, 1H), 3.35 (d, *J* = 17 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 140.3, 139.7, 129.3, 127.8, 125.5, 124.8, 80.6, 61.2, 38.8.

(3a*R,6a*S**)-Hexahydro-2*H*-cyclopenta[*d*]oxazol-2-one (28).**[27] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S21**[20] (0.112 g, 0.500 mmol) using $Rh_2(tpa)_4$ (33.9 mg, 0.025 mmol, 5.00 mol %) and an aqueous saturated K_2CO_3 solution (74.7 µL, 0.600 mmol, 1.20 equiv) to afford oxazolidinone **28** (0.025 g, 0.200 mmol, 40% yield, >99:1 dr) as a white solid after purification by flash chromatography on silica gel (50% EtOAc/hexanes, then 100% EtOAc). R_f 0.35 (EtOAc); mp 85-86°C (lit. 87-88 °C);[28] ^{1}H NMR (500 MHz, $CDCl_3$) 5.10 (s (br), 1H), 5.07 (t, *J* = 6.4 Hz, 1H), 4.27 (t, *J* = 6.4 Hz, 1H), 2.13-2.09 (m, 1H), 1.87-1.72 (m, 3H), 1.68-1.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 82.4, 56.5, 34.7, 33.9, 22.0.

(3a*R,6a*S**)-6a-(Trifluoromethyl)hexahydro-2*H*-cyclopenta-[*d*]oxazol-2-one (29)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S25**[20] (0.146 g, 0.500 mmol), to afford oxazolidinone **29** (0.087 g, 0.445 mmol, 89% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.38 (40% EtOAc/hexanes); mp 88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 6.11 (s (br), 1H), 4.30 (d, 1H, *J* = 6.2 Hz, 1H), 2.23-2.15 (m, 1H), 1.99-1.88 (m, 4H), 1.82-1.74 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 123.8 (q, *J* = 280 Hz), 89.9 (q, *J* = 32 Hz), 57.8, 34.7, 33.1, 22.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -80.8 (s); IR (neat) 3271, 3175, 2981, 2944, 1737, 1367, 1216, 1187, 1160, 990, 959, 934, 849, 702 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_7H_9F_3NO_2$ 196.0580; found 196.0586.

(3a*R,7a*S**)-Hexahydrobenzo[*d*]oxazol-2(3*H*)-one (30).**[7l] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S22**[20] (0.119 g, 0.500 mmol) using $Rh_2(tpa)_4$ (33.9 mg, 0.025 mmol, 5.00 mol %) and an aqueous saturated K_2CO_3 solution (74.7 µL, 0.600 mmol, 1.20 equiv) at 40 °C. The crude dr was determined prior to purification to be 80:20 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 3.75 (maj) and 3.32 (min) ppm).

Oxazolidinone **30** (0.023 g, 0.165 mmol, 33% yield, >99:1 dr) was isolated as a white solid after purification by flash chromatography on silica gel (50% EtOAc/hexanes). R_f 0.24 (40% EtOAc/hexanes); mp 54-55 °C (lit. 54-55 °C);[28] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27 (s (br), 1H), 4.59 (dd, *J* = 11, 5.0 Hz, 1H), 3.74 (dd, *J* = 13, 7.0 Hz, 1H), 2.04-1.98 (m, 1H), 1.86-1.72 (m, 2H), 1.67-1.42 (m, 4H), 1.33-1.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 75.9, 51.7, 28.7, 26.8, 19.8, 19.5.

(3a*R,7a*S**)-7a-Methylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (31)**.[7i] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S26**[20] (0.126 g, 0.500 mmol) using an aqueous saturated K_2CO_3 solution (62.3 µL, 0.500 mmol, 1.00 equiv), to afford oxazolidinone **31** (0.063 g, 0.401 mmol, 81% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.17 (40% EtOAc/hexanes); mp 50-51 °C (lit. 50-51 °C);[29] ^{1}H NMR (500 MHz, $CDCl_3$) 6.01 (s (br), 1H), 3.58 (t, 1H, *J* = 4.2 Hz, 1H), 1.87-1.82 (m, 1H), 1.74-1.50 (m, 5H), 1.45-1.39 (m, 1H), 1.42 (s, 3H), 1.33-1.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 82.3, 57.4, 33.3, 26.8, 24.8, 20.2, 18.5.

(3a*R,7a*S**)-7a-(Trifluoromethyl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (32)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S27**[20] (0.153 g, 0.500 mmol), to afford oxazolidinone **32** (0.088 g, 0.420 mmol, 84% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.5 (40% EtOAc/hexanes); mp 104-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 5.62 (s (br), 1H), 4.09 (t, 1H, *J* = 3.7 Hz, 1H), 2.00-1.88 (m, 2H), 1.79-1.54 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 124.2 (q, *J* = 283 Hz), 80.8 (q, *J* = 31 Hz), 50.6, 25.4, 23.5, 15.4, 14.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -82.8 (s); IR (neat) 3262, 3179, 2947, 1737, 1211, 1173, 1144, 1049, 963, 761, 699 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_8H_{11}F_3NO_2$ 210.0763; found 210.0743.

(3a*R,5*R**,7a*R**)-5-(*tert*-Butyl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (33)**.[30] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S23**[20] (0.147 g, 0.500 mmol) using $Rh_2(tpa)_4$ (33.9 mg, 0.025 mmol, 5.00 mol %) and an aqueous saturated K_2CO_3 solution (74.7 µL, 0.600 mmol, 1.20 equiv). The crude dr was determined prior to purification to be 15:85 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 3.58 and 3.33 ppm). Oxazolidinone **33** was isolated (0.020 g, 0.100 mmol, 20% yield, <1:99 dr) as a white solid after purification by flash chromatography. R_f 0.42 (40% EtOAc/hexanes); mp 122-123 °C (Lit. 123-124 °C);[30] ^{1}H NMR (500 MHz, $CDCl_3$) 4.97 (s (br), 1H), 3.85 (td, *J* = 11, 3.7 Hz, 1H), 3.37-3.32 (m, 1H), 2.24-2.20 (m, 1H), 2.13-2.10 (m, 1H), 1.99-1.95 (m, 1H) 1.69-1.61 (m, 1H), 1.28-1.19 (m, 3H), 0.90 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 83.9, 61.0, 46.0, 32.5, 29.9, 27.9, 27.7 24.8.

(3a*R,5*R**,7a*S**)-5-(*tert*-Butyl)hexahydrobenzo[*d*]oxazol-2(3*H*)-one (34)**.[30] The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S24**[20] (0.147 g, 0.500 mmol) using $Rh_2(tpa)_4$ (33.9 mg, 0.025 mmol, 5.00 mol %) and an aqueous saturated K_2CO_3 solution (74.7 µL, 0.600 mmol, 1.20 equiv) at 40 °C to afford oxazolidinone **34** (0.078 g, 0.395 mmol, 79% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.24 (40% EtOAc/hexanes); mp 173-174 °C (Lit. 172-173 °C);[30] ^{1}H NMR (500 MHz, $CDCl_3$) 5.47 (s (br), 1H), 4.57-4.55 (m, 1H), 3.61-3.57 (m, 1H), 2.30-2.25 (m, 1H), 2.03-1.98 (m, 1H), 1.68-1.60 (m, 2H), 1.28-1.20 (m, 1H), 1.13-1.06 (m, 1H), 0.97-0.90 (m, 1H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 75.8, 53.3, 43.4, 32.3, 31.7, 29.7, 27.2, 21.0.

(3a*R,5*S**,7a*S**)-5-(*tert*-Butyl)-7a-methylhexahydrobenzo-[*d*]oxazol-2(3*H*)-one (35)**. The title compound was prepared according to general procedure A starting from *N*-mesyloxy-carbamate **S28**[20] (0.154 g, 0.500 mmol) using $Rh_2(tpa)_4$ (33.9 mg, 0.025 mmol, 5.00 mol %) and an aqueous saturated K_2CO_3 solution (74.7 µL, 0.600 mmol, 1.20 equiv) at 40 °C to afford oxazolidinone **35** (0.060 g, 0.285 mmol, 57% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.32 (40% EtOAc/hexanes); mp 153-154 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 5.12 (s (br), 1H), 3.32 (dd, *J* = 10, 6.4 Hz, 1H), 2.20-2.15 (m, 1H), 2.03-1.98 (m, 1H), 1.62-1.51 (m, 2H), 1.41 (s, 3H), 1.32-1.24 (m, 1H), 1.15-1.08 (m, 1H), 1.02-0.96 (m, 1H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 81.6, 58.0, 42.8, 33.8, 32.5, 32.4, 27.1, 26.6, 21.8; IR (neat) 3229, 3131, 2961, 2867, 1727, 1362, 1235, 1073, 990, 758, 686, 557 cm-1; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{22}NO_2$ 212.1645; found 212.1636.

(3a*R,5*R**,7a*S**)-5-(*tert*-butyl)-7a-methylhexahydrobenzo-[*d*]oxazol-2(3*H*)-one (36)**. The title compound was prepared according to general procedure A starting from *N*-mesyloxycarbamate **S29**[20] (0.154 g, 0.500 mmol) using $Rh_2(tpa)_4$ (33.9 mg, 0.025 mmol, 5.00 mol %) and an aqueous saturated K_2CO_3 solution (74.7 µL, 0.600 mmol, 1.20 equiv) at 40 °C to afford oxazolidinone **36** (0.090 g, 0.425 mmol, 85% yield, >99:1 dr) as a white solid after purification by flash chromatography. R_f 0.36 (40% EtOAc/hexanes); mp 135-136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 5.18 (s (br), 1H), 3.74 (t, *J* = 3.0 Hz, 1H), 1.86-1.69 (m, 4H), 1.47-1.41 (m, 1H), 1.44 (s, 3H), 1.34-1.28 (m, 1H), 1.10-1.00 (m, 1H), 0.86 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 82.3, 58.3, 38.9, 33.5, 32.2, 27.3, 27.1, 24.6, 21.6. IR (neat) 3343, 2955, 2941, 2866, 1759, 1717, 1382, 1317, 1071, 975, 896. 615, 559, 421 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{22}NO_2$ 212.1645; found 212.1635.

(3a*S,7a*S**)-3a-phenylhexahydrobenzo[*d*]oxazol-2(3*H*)-one (39)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **37**[20] (0.157 g, 0.500 mmol), to afford oxazolidinone **39** (0.066 g, 0.305 mmol, 61% yield, >99:1 dr) as a colorless oil after purification by flash chromatography (50% EtOAc/hexanes). R_f 0.3 (40% EtOAc/ hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) 7.44-7.41 (m, 2H), 7.39-7.35 (m, 2H), 7.31-7.28 (m, 1H), 6.94 (s (br), 1H), 4.68 (t, *J* = 4.1 Hz, 1H), 2.20-2.15 (m, 1H), 2.07-2.02 (m, 1H), 1.90-1.83 (m, 2H), 1.78-1.68 (m, 2H), 1.63-1.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 143.4, 128.7, 127.7, 125.2, 82.1, 61.9, 34.9, 25.8, 19.4, 17.7; IR (neat) 3257, 2938, 2863, 1729, 1495, 1447, 1129, 1098, 996, 979, 698, 656 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}NO_2$ 218.1176; found 218.1182.

(4*S,5*S**)-5-Methyl-4-phenyloxazolidin-2-one (40)**.[7l] The title compound was prepared according to general procedure C

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starting from *N*-mesyloxycarbamate **S30**[20] (0.137 g, 0.500 mmol). The crude dr was determined prior to purification to be 88:12 (determined by ^{1}H NMR (MeOD) evaluation based on ^{1}H signal at 1.48 and 0.90 ppm). Oxazolidinone **40** was isolated (0.057 g, 0.330 mmol, 66% yield, 98:2 dr) as a white solid after purification by flash chromatography. R_f 0.4 (40% EtOAc/hexanes); mp 123-125 °C (lit. 124 °C);[28] ^{1}H NMR (500 MHz, $CDCl_3$) 7.40-7.37 (m, 2H), 7.36-7.32 (m, 3H), 6.28 (s (br), 1H), 4.46 (d, *J* = 7.3 Hz, 1H), 4.43-4.38 (m, 1H), 1.49 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 138.7, 129.1, 128.7, 126.2, 81.6, 64.0, 19.2; IR (neat) 3287, 2925, 1742, 1455, 1382, 1232, 1017, 959, 700 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{12}NO_2$ 178.0863; found 178.0860.

(4*S,5*S**)-5-Methyl-4-(*p*-tolyl)oxazolidin-2-one (41)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S31**[20] (0.143 g, 0.500 mmol). The crude dr was determined prior to purification to be 90:10 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.48 and 0.95 ppm). Oxazolidinone **41** was isolated (0.073 g, 0.380 mmol, 76% yield, 96:4 dr) as a wax after purification by flash chromatography. R_f 0.26 (40% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) 7.25-7.20 (m, 4H), 6.34 (s (br), 1H), 4.45-4.37 (m, 2H), 2.37 (s, 3H), 1.49 (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 138.5, 135.7, 129.6, 126.0, 81.7, 63.7, 21.0, 19.1; IR (neat) 3279, 2978, 2924, 1738, 1380, 1227, 1059, 968, 931, 810, 767, 730, 504 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{13}NO_2$ 192.1019; found 192.1012.

(4*S,5*S**)-4-(4-(*tert*-Butyl)phenyl)-5-methyloxazolidin-2-one (42)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S32**[20] (0.165 g, 0.500 mmol). The crude dr was determined prior to purification to be 90:10 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.50 and 0.97 ppm). Oxazolidinone **42** was isolated (0.087 g, 0.375 mmol, 75% yield, 96:4 dr) as a white solid after purification by flash chromatography. R_f 0.26 (40% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) 7.43-7.41 (m, 2H), 7.29-7.27 (m, 2H), 5.28 (s (br), 1H), 4.47-4.42 (m, 2H), 1.51-1.47 (m, 3H), 1.32 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 152.2, 135.4, 126.1 (2C), 81.7, 63.8, 34.6, 31.3, 19.1; IR (neat) 3274, 2960, 2924, 1750, 1512, 1383, 1282, 1063, 1017 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{20}NO_2$ 234.1489; found 234.1478.

(4*S,5*S**)-4-([1,1'-Biphenyl]-4-yl)-5-methyloxazolidin-2-one (43)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S33**[20] (0.174 g, 0.500 mmol). The crude dr was determined prior to purification to be 90:10 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.53 and 1.01 ppm). Oxazolidinone **43** was isolated (0.095 g, 0.375 mmol, 75% yield, 98:2 dr) as a white solid after purification by flash chromatography. R_f 0.24 (40% EtOAc/hexanes); mp 144-145 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.63-7.61 (m, 2H), 7.58-7.56 (m, 2H), 7.47-7.41 (m, 4H), 7.39-7.36 (m, 1H), 5.77 (s (br), 1H), 4.52-4.45 (m, 2H), 1.53 (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 141.1, 140.2, 137.5, 128.9, 127.9, 127.7, 127.0, 126.7, 81.7, 63.8, 19.2; IR (neat) 3274, 2960, 2924, 1750, 1512, 1383, 1282, 1063, 1017 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_2$ 234.1489; found 234.1478.

(4*S,5*S**)-4-(4-Methoxyphenyl)-5-methyloxazolidin-2-one (44)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S34**[20] (0.151 g, 0.500 mmol). The crude dr was determined prior to purification to be 90:10 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.46 and 0.94 ppm). Oxazolidinone **44** was isolated (0.067 g, 0.325 mmol, 65% yield, 95:5 dr) as a white solid after purification by flash chromatography. R_f 0.24 (40% EtOAc/hexanes); mp 75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.31-7.28 (m, 2H), 6.96-6.93 (m, 2H), 5.61 (s (br), 1H), 4.46-4.40 (m, 2H), 3.84 (s, 3H), 1.51-1.48 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 158.8, 130.4, 127.6, 114.5, 81.9, 63.6, 55.4, 19.0; IR (neat) 3274, 2923, 1740, 1513, 1383, 1117, 1060, 1031, 766 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{14}NO_3$ 208.0968; found 208.0958.

(4*S,5*S**)-4-(4-Bromophenyl)-5-methyloxazolidin-2-one (45)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S35**[20] (0.176 g, 0.500 mmol). The crude dr was determined prior to purification to be 88:12 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.49 and 0.95 ppm). Oxazolidinone **45** was isolated (0.075 g, 0.290 mmol, 59% yield, 99:1 dr) as a white solid after purification by flash chromatography. R_f 0.22 (40% EtOAc/hexanes); mp 93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.55-7.52 (m, 2H), 7.24-7.22 (m, 2H), 5.59 (s (br), 1H), 4.44-4.36 (m, 2H), 1.49 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 137.6, 132.4, 127.9, 122.9, 81.5, 63.5, 19.2; IR (neat) 3287, 2924, 2853, 1750, 1488, 1383, 1229, 1064, 1010, 974, 932, 504 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{10}H_{11}BrNO_2$ 255.9968; found 255.9970.

(4*S,5*S**)-5-Methyl-4-(4-(trifluoromethyl)phenyl)oxazolidin-2-one (46)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S36**[20] (0.171 g, 0.500 mmol). The crude dr was determined prior to purification to be 89:11 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.51 and 0.94 ppm). Oxazolidinone **46** was isolated (0.072 g, 0.290 mmol, 59% yield, 99:1 dr) as a white solid after purification by flash chromatography. R_f 0.24 (40% EtOAc/hexanes); mp 86 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.68 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 5.90 (s (br), 1H), 4.54 (d, *J* = 7.3 Hz, 1H), 4.44-4.38 (m, 1H), 1.53 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 142.6, 131.3 (q, *J* = 33 Hz), 126.6, 126.2 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 242 Hz), 81.4, 63.6, 19.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -62.7 (s); IR (neat) 3280, 2924, 2854, 1750, 1456, 1425, 1351, 1166, 1124, 1067 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{11}F_3NO_2$ 246.0736; found 246.0736.

(4*S,5*S**)-5-Methyl-4-(o-tolyl)oxazolidin-2-one (47)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S37**[20] (0.144 g, 0.500 mmol). The crude dr was determined prior to purification to be 94:6 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.53 and 0.91 ppm). Oxazolidinone **47** was isolated (0.052 g, 0.270 mmol, 55% yield, 97:3 dr) as a white solid after purification by flash chromatography. R_f 0.32 (40%

EtOAc/hexanes); mp 132-133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.44-7.43 (m, 1H), 7.29-7.22 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 5.77 (s (br), 1H), 4.76 (d, *J* = 6.2 Hz, 1H), 4.48-4.43 (m, 1H), 2.36 (s, 3H), 1.53 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 137.0, 135.1, 131.0, 128.4, 127.0, 125.8, 81.3, 59.8, 20.1, 19.3; IR (neat) 3267, 2924, 1748, 1385, 1230, 1060, 1048, 723 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{14}NO_2$ 192.1019; found 192.1011.

(4*S,5*S**)-4-(3-Methoxyphenyl)-5-methyloxazolidin-2-one (48)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S38**[20] (0.152 g, 0.500 mmol). The crude dr was determined prior to purification to be 90:10 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.48 and 0.95 ppm). Oxazolidinone **48** was isolated (0.060 g, 0.290 mmol, 58% yield, 94:6 dr) as a wax after purification by flash chromatography. R_f 0.27 (40% EtOAc/hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) 7.34-7.29 (m, 1H), 6.93-6.89 (m, 3H), 6.21 (s (br), 1H), 4.46-4.40 (m, 2H), 3.83 (s, 3H), 1.51 (d, *J* = 5.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 159.2, 140.3, 130.2, 118.4, 114.1, 111.6, 81.5, 63.9, 55.3, 19.3; IR (neat) 3273, 2976, 2930, 1737, 1601, 1490, 1456, 1284, 1042, 974, 775, 698 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{11}H_{13}NO_3$ 208.0968; found 208.0964.

(4*S,5*S**)-5-Methyl-4-(naphthalen-2-yl)oxazolidin-2-one (49)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S39**[20] (0.162 g, 0.500 mmol). The crude dr was determined prior to purification to be 89:11 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 1.51 and 0.95 ppm). Oxazolidinone **49** was isolated (0.086 g, 0.378 mmol, 76% yield, 97:3 dr) as a white solid after purification by flash chromatography. R_f 0.28 (40% EtOAc/hexanes); mp 166-167 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.90 (d, *J* = 8.6 Hz, 1H), 7.87-7.83 (m, 2H), 7.79 (s, 1H), 7.55-7.50 (m, 2H), 7.47 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.60 (s (br), 1H), 4.62 (d, *J* = 7.3 Hz, 1H), 4.55-4.50 (m, 1H), 1.53 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 135.8, 133.4, 133.1, 129.4, 127.9, 127.8, 126.8, 126.6, 125.7, 123.4, 81.5, 64.2, 19.3; IR (neat) 3269, 2923, 2853, 1740, 1383, 1351, 1303, 1228, 1061, 933, 819, 750, 478 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1019; found 228.1013.

(4*S,5*S**)-5-Methyl-4-(naphthalen-1-yl)oxazolidin-2-one (50)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S40**[20] (0.162 g, 0.500 mmol). The crude dr was determined prior to purification to be 96:4 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 5.82 and 5.27 ppm). Oxazolidinone **50** was isolated (0.083 g, 0.365 mmol, 73% yield, 97:3 dr) as a white solid after purification by flash chromatography. R_f 0.29 (40% EtOAc/hexanes); mp 162-164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.95-7.92 (m, 2H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.60-7.51 (m, 3H), 5.63 (s (br), 1H), 5.30 (d, *J* = 5.8 Hz, 1H), 4.62-4.57 (m, 1H), 1.65 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 134.4, 134.0, 130.4, 129.4, 129.3, 126.8, 126.1, 125.6, 123.6, 121.8, 81.1, 59.8, 20.3; IR (neat) 3269, 2922, 2852, 1740, 1454, 1259, 1063, 1063, 1049, 800, 777, 734 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1019; found 228.1019.

(4*S,5*S**)-5-Benzyl-4-phenyloxazolidin-2-one (51)**. The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate **S41**[20] (0.175 g, 0.500 mmol). The crude dr was determined prior to purification to be 87:13 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 3.17+3.08 and 2.64+2.39 ppm). Oxazolidinone **51** was isolated (0.081 g, 0.320 mmol, 64% yield, 99:1 dr) as a white solid after purification by flash chromatography. R_f 0.34 (40% EtOAc/hexanes); mp 158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.36-7.30 (m, 5H), 7.28-7.23 (m, 3H), 7.17-7.153 (m, 2H), 5.26 (s (br), 1H), 4.62-4.56 (m, 2H), 3.16 (dd, *J* = 14.2, 6.3 Hz, 1H), 3.07 (dd, *J* = 14.2, 5.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 139.1, 135.0, 129.7, 129.1, 128.8, 128.7, 127.2, 126.1, 85.1, 60.6, 39.7; IR (neat) 3262, 2921, 1749, 1496, 1455, 1388, 1157, 1071, 969, 699 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_2$ 254.1176; found 254.1168.

(4*R*,5*R*)-5-(((*tert*-Butyldimethylsilyl)oxy)methyl)-4-(4-methoxyphenyl)oxazolidin-2-one (53).[2e] The title compound was prepared according to general procedure C starting from *N*-mesyloxycarbamate ***R*-52**[20] (105 mg, 0.242 mmol) using Rh_2[(S)-ntv]$_4$ in EtOAc. The crude dr was determined prior to purification to be 85:15 (determined by ^{1}H NMR evaluation based on ^{1}H signal at 4.64 and 4.35 ppm). Oxazolidinone **53** was isolated (55.1 mg, 0.163 mmol, 67% yield, 99:1 dr) as a white solid after purification by flash chromatography. R_f 0.37 (40% EtOAc/hexanes); $[\alpha]^{20}_D$ -25.2 (c 0.73, $CHCl_3$), lit.[2e] $[\alpha]^{28}_D$ -26.4 (c 0.93, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$) 7.20-7.17 (m, 2H), 6.86-6.83 (m, 2H), 6.42 (s (br), 1H), 5.26-5.25 (m, 1H), 4.65-4.61 (m, 1H), 3,79 (s, 3H), 3.08 (dd, *J* = 15, 8.6 Hz, 1H), 2.90 (dd, *J* =15, 5.3 Hz, 1H), 0.93 (s, 9H), 0.14 (s, 3H), 0,09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 158.5, 130.1, 128.6, 113.9, 83.0, 78.2, 55.3, 33.7, 25.6, 17.9, -4.36, -4,89.

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