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Stereoselective α-Fluorination of *N*-Acyloxazolidinones at Room Temperature within 1 h

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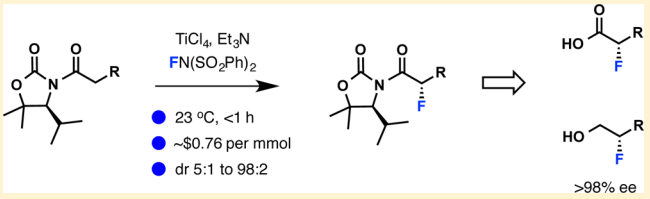
Supporting Information

ABSTRACT: A direct α-fluorination of *N*-acyloxazolidinones based on the unique reactivity of group IVa metal enolates has been developed. The reaction is an experimentally simple, low-cost, quick, and energy-efficient alternative for asymmetric α-fluorination of *N*-acyloxazolidinones. Preliminary studies have shown compatibility with alkyl, alkenyl, and alkynyl, aromatic, and several heteroaromatic substituents. High diastereoselectivities have been achieved with most substrates tested, and the reaction is typically complete within 1 h at ambient temperature.



INTRODUCTION

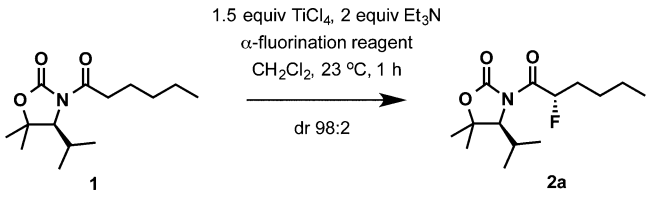
The importance of organofluorine compounds has been amply validated by broad application in medicinal sciences, materials, and agrochemicals.[1] Fluorine incorporation is typically performed to acquire the unique physical and chemical properties that fluorine substitution imparts on organic compounds. Although many methods for fluorination have already been reported in the literature,[1a,b,m,2] future advancements in the discovery and application of fluorinated materials require the availability of new methods for economical and selective fluorination. Despite the broad utility of fluorine-containing organic compounds, stereoselective incorporation of the fluorine atom at the α-position of the carbonyl group has remained an ongoing challenge; several notable recent developments exploit reagent, catalyst, or substrate control in α-fluorination reactions.[3] Following early work on diastereoselective electrophilic α-fluorination of lithium enolates with *N*-fluoro-*o*-benzenedisulfonimide (NFOBS) as the fluorinating reagent,[4] a number of elegant alternatives describing the use of *N*-fluoropyridinium 2,8-diazobicyclo[2,2,2]octane and sulfonamide reagents as the electrophilic source of fluorine were developed.[5] In all, these methods expanded the repertoire of selective α-monofluorination for a diverse range of carbonyl compounds, at the same time highlighting their unique patterns of reactivity. On the other hand, issues of practicality, limitations in substrate scope, high cost of reagents, extended reaction time, and energy efficiency (use of cryogenic conditions or high temperatures) remain persistent, stimulating continued progress in this area.

Recently, we have demonstrated the efficacy of group IVa metal enolates generated by soft enolization[6] in ruthenium-catalyzed radical trichloromethylation, trifluoromethylation, and perfluoroalkylation reactions.[7] Using an experimentally simple protocol, good to high yields of various α-haloalkylation products can be achieved with high diastereoselectivity. Herein, we describe the utility of group IVa metal enolates derived from *N*-acyloxazolidinones in rapid economical and operationally simple electrophilic α-fluorination reactions that take place at room temperature and display high diastereoselectivity.

RESULTS AND DISCUSSION

The aim of initial experiments was to identify the optimal electrophilic source of fluorine, with the chemical efficiency of the α-fluorination reaction and reagent cost being the most important factors (Table 1). Examination of the most common commercial sources of electrophilic fluorine, summarized in Table 1, revealed that *N*-fluorobenzenesulfonimide (NFSI), the

Table 1. Identification of Optimal Fluorinating Reagent[a]



entry	reagent	conversion[b] (%)	$/mmol
1	NFSI	99	$0.35[c]
2	Selectfluor	70[d]	$0.82[e]
3	1-fluoro-2,4,6-trimethylpyridinium triflate	<1	$3.67[f]
4	1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate	<1	$4.09[f]

[a]Standard conditions: **1** (0.50 mmol), $TiCl_4$ (1.5 equiv), Et_3N (2.0 equiv), CH_2Cl_2 (0.5 M), reagent (2.0 equiv), mixed and stirred at room temperature for 1 h. [b]Determined by the 600 MHz NMR analysis of the crude mixture of products. [c]Oakwood Products. [d]Reaction solvent was a 1:1 mixture of acetonitrile/CH_2Cl_2, dr 5:1. [e]Apollo Scientific. [f]TCI America.

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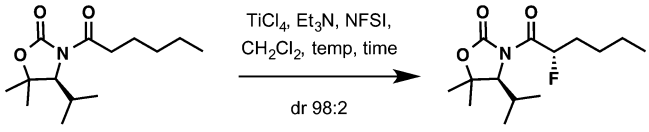
most inexpensive reagent tested, displayed superior performance by a substantial margin. Under standard conditions, complete conversion in the α-fluorination of **1** was achieved with NFSI within 1 h at room temperature. The reaction occurred with a diastereoselectivty of 98:2. Selectfluor, the second best reagent, provided 70% conversion with a decrease of diastereoselectivity to 5:1, whereas both 1-fluoro-2,4,6-trimethylpyridinium triflate and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate were not efficient sources of electrophilic fluorine due to lack of solubility in dichloromethane.

Early experimentation also revealed a rather high reactivity of titanium enolates in the α-fluorination reaction. In contrast to other reported stereoselective α-fluorinations of carbonyl compounds,[2−5] the reaction reaches 90% conversion within 30 min at room temperature while maintaining high diastereoselectivity (Table 2, entry 1). Full conversion requires

Table 2. Optimization of α-Fluorination Reaction



1 **2a**

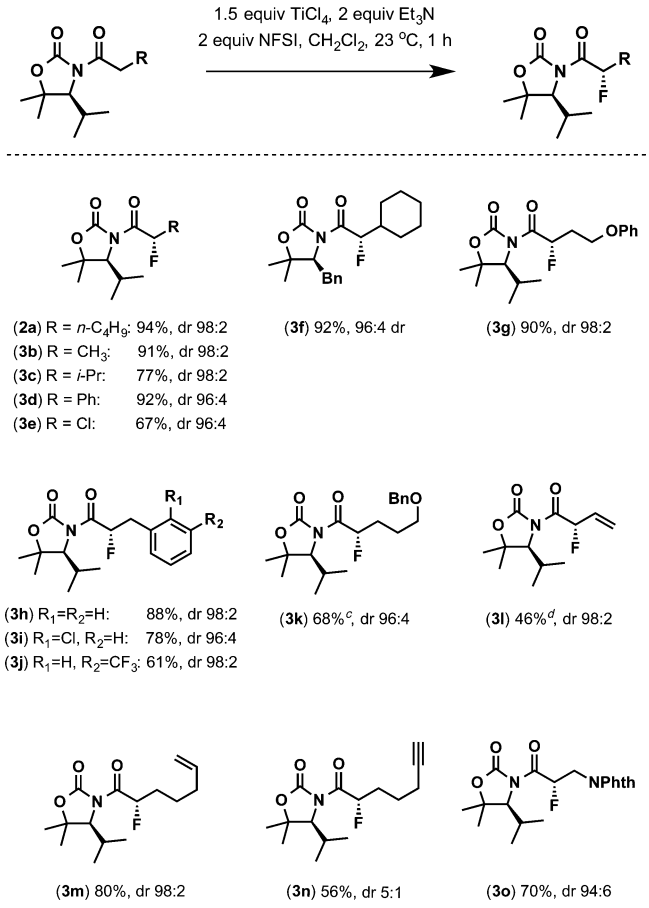
entry	$TiCl_4$ (equiv)	Et_3N (equiv)	NFSI (equiv)	time (h)	conversion[b] (%)
1	2.0	3.0	2.0	0.5	90
2	2.0	3.0	2.0	1	99
3	2.0	2.0	2.0	1	99
4	2.0	3.0	1.25	1	50
5	1.5	2.0	2.0	1	99
6	1.25	2.0	2.0	1	93
7	1.5	1.5	1.5	1	77
8	0.5	3.0	2.0	12	40[c]
9	1.0	3.0	2.0	12	80[c]
10	1.5 ($ZrCl_4$)[d]	2.0	2.0	1	87
11	1.5 ($HfCl_4$)[e]	2.0	2.0	1	78
12	1.5	2.0	2.0	1	99[f]

[a]Standard conditions: **1** (0.50 mmol), CH_2Cl_2 (0.5 M), mixed and stirred at room temperature. [b]Determined by the 600 MHz ^{1}H NMR analysis of the crude mixture of products. [c]Reactions were performed at 45 °C. [d]$ZrCl_4$ was used in place of $TiCl_4$. [e]$HfCl_4$ was used in place of $TiCl_4$. [f]3-propionyl-5,5-dimethyl-4-benzyloxazolidin-2-one was used (dr 96:4).

60 min at 23 °C(Table 2, entry 2). Under optimized conditions, 1.5 equiv of $TiCl_4$ and 2 equiv each of Et_3N and NFSI are required for full conversion (Table 2, entry 5), and reduction in the stoichiometry of any of these reagents erodes conversion (Table 2, entries 4 and 6−9) with the strongest effect observed for NFSI (Table 2, entry 4).[8] Similar results, including high diastereoselectivity of 98:2, were noted when $ZrCl_4$ and $HfCl_4$ (Table 2, entries 10 and 11) were used for enolate generation under identical conditions, although conversions were lower by about 10%.[9] All three common oxazolidinones surveyed (3-propionyl-5,5-dimethyl-4-benzyl- (Table 2, entry 12), 3-propionyl-5,5-dimethyl-4-isopropyl-, and 3-propionyl-4-benzyloxazolidin-2-ones (Table 2, entry 13) showed high diastereoselectivity (>10:1), with the 5,5-dimethyl-4-isopropyl derivative related to **1** giving the highest stereoselectivity (dr 98:2). Therefore, further studies were carried out with NFSI as the fluorinating reagent and the 5,5-dimethyl-4-isopropyl-substituted oxazolidinone as the stereodirecting group.

Substrates derived from simple unfunctionalized alkanoic acids generally afford high yields of α-fluorination products with high diastereoselectivity under standard conditions at room temperature within 1 h (Table 3, **2a**, **3b**,**c**,**f**). The

Table 3. Scope of *N*-Acyloxazolidinones in the α-Fluorination Reaction[a,b]



[a]Standard conditions: substrate (0.50 mmol), $TiCl_4$ (1.5 equiv), Et_3N (2.0 equiv), NFSI (2.0 equiv), CH_2Cl_2 (0.5 M), mixed and stirred at room temperature for 1 h. [b]Yields of isolated products are reported. Diastereomer ratios were determined by 600 MHz ^{1}H NMR analysis of the crude mixture of products. [c]1.5 equiv of $ZrCl_4$ was used in place of $TiCl_4$. [d](*S*)-3-(2-Butenoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was used as the starting material.

derivative of isovaleric acid (Table 3, **3c**) afforded a somewhat depressed yield of 77% due to competitive formation of α-chlorination product (10% yield, >99:1 dr). 3-Phenylacetyl-5,5-dimethyl-4-isopropyloxazolidinone afforded α-fluorination product **3d** in high yield and diastereoselectivity. A unique derivative of α-chloro-α-fluoroacetic acid has been prepared by this procedure with high stereoselectivity (**3e**). An example, **3f**, illustrates that analogues in which the stereodirecting 4-isopropyl substituent is replaced with a benzyl group provide comparable yields and diastereomeric ratios of α-fluorination products. Aryl ether groups are well tolerated (**3g**). A number of compounds produced from hydrocinnamic acids are also good substrates for the α-fluorination reaction (**3h**−**j**), while benzyl ethers undergo partial debenzylation, which can be mitigated by replacing $TiCl_4$ with $ZrCl_4$ (Table 3, **3k**).

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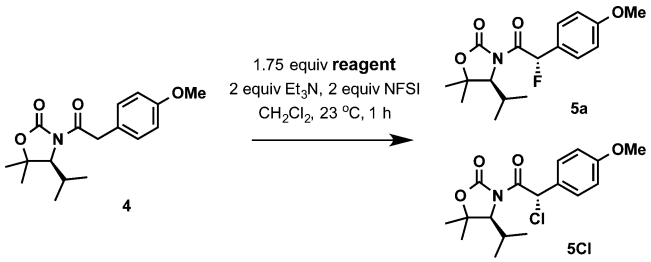
α-Fluorination via titanium enolates of substrates containing unsaturation can be accomplished efficiently in the presence of double bonds (**3l**–**m**), yet terminal alkynes can display notably lower yields (**3n**). Although no specific byproducts have presently been isolated, the lower efficiency can hypothetically be ascribed to the competitive formation of alkynyltitanium species under the reaction conditions. The protected form of α-fluoro-β-alanine can be prepared in 70% yield and 94:6 diastereomeric ratio (**3o**). In most cases, the product can be isolated as the isomerically pure diastereomer either by recrystallization or flash column chromatography.

In contrast to the unfunctionalized phenylacetic acid derivative (cf. Table 3, **3d**), substitution in the phenyl ring resulted in substantially different reactivity under the standard conditions. In fact, the attempted α-fluorination of 4-methoxyphenyl analogue **4** resulted in the exclusive formation of α-chlorination product **5Cl** as a 1:1 mixture of diastereomers (Table 4, entry 1). The hypothesis that replacing $TiCl_4$ with an alternative titanium(IV) Lewis acid would minimize the competitive chlorination was put to the test next. Delightfully, a significant improvement in α-fluorination was achieved when $Ti(OPr\text{-}i)_2Cl_2$, prepared by a reaction of equimolar amounts of $TiCl_4$ and $Ti(OPr\text{-}i)_4$,[10] was used for enolate generation (Table 4, entry 2). When diisopropoxytitanium dichloride was prepared by an alternative procedure from $TiCl_4$, 2 equiv of 2-propanol, and 2 equiv of triethylamine, a further improvement was achieved (Table 4, entry 3).[11] The use of triisopropoxytitanium chloride, isopropoxytitanium trichloride, or zirconium tetrachloride led to either low reactivity or exclusive formation of the α-chlorination product (Table 4, entries 4–6).

Table 4. Optimization of α-Fluorination of 3-(4-Methoxyphenylacetyl)-5,5-dimethyl-4-isopropyloxazolidin-2-one 4[a,b]



entry	reagent	% **4a** (dr)[b,c]	% **4Cl** (dr)[b,c]
1	$TiCl_4$	0	82 (1:1)
2	$Ti(OPr\text{-}i)_2Cl_2$	52 (93:7)	41 (1:1)
3	$Ti(OPr\text{-}i)_2Cl_2{\cdot}2Et_3NHCl$	77 (93:7)	17 (1:1)
4	$Ti(OPr\text{-}i)_3Cl{\cdot}3Et_3NHCl$	17 (93:7)	0
5	$Ti(OPr\text{-}i)Cl_3{\cdot}Et_3NHCl$	0	100 (1:1)
6	$ZrCl_4$	0	100 (1:1)

[a]Standard conditions: **4** (0.50 mmol), Ti reagent (1.75 equiv), Et_3N (2.0 equiv), NFSI (2.0 equiv), CH_2Cl_2 (0.5 M), mixed and stirred at room temperature for 1 h. [b]Percent composition of the compound in the crude mixture of products as determined by 600 ^{1}H NMR analysis. [c]Diastereomeric ratio (dr) was determined by the 600 MHz ^{1}H NMR analysis of the crude mixture of products.

With the protocol utilizing the $Ti(OPr\text{-}i)_2Cl_2{\cdot}2Et_3NHCl$ reagent, a range of substituted phenylacetic acid derivatives can be effectively α-fluorinated with very good diastereocontrol (Table 5). Modification of the phenyl group with electron-donating or mildly electron-withdrawing substituents in the ortho-, meta-, and para-positions is tolerated (**5a-g,i**). Diastereoselectivities are lower than with substrates represented in Table 3 but still in the practically useful range of greater than 10:1, and in most cases, the diastereomers are separable by column chromatography.

In addition, heteroaromatic substituents can effectively afford α-fluorination products with high diastereoselectivity, as demonstrated with the derivatives of 3-furanacetic acid (**5h**) and 2-(benzo[*d*]oxazol-5-yl)acetic acid (**5j**). On the other hand, fluorination of oxazolidinone derived from 2-(benzo[*d*]-oxazol-2-yl)acetic acid (**5k**) afforded a 2:1 mixture of diastereomers. The reduction in diastereoselectivity may be attributed to increased C–H acidity of this compound resulting in the enolization of products. Isolation of difluorination products observed for these examples supports this hypothesis.

A plausible mechanism outlined in Scheme 1 accounts for the experimental observations, including higher than expected reactivity of titanium enolates in the electrophilic fluorination as well as the appearance of α-chlorination byproduct **5Cl**. Soft enolization of 4-methoxyphenyl derivative **4** with $TiCl_4$ and Et_3N affords affords the expected Ti enolate. This newly formed Lewis acid could activate NFSI directly to form **6A**, or NFSI could be activated by excess $TiCl_4$ to form **6B**. The latter mode of activation may explain the need for 1.5–1.75 equiv of the reagent required for complete conversion. Activation of the NSFI by Lewis acid was documented to be essential for electrophilic fluorination of enolates by others.[3e,12] Subsequent electrophilic fluorination typically affords **5a** as the major product. Concurrently, a group exchange between $Cl–TiL_n$ reagent (**6A**, **6B**, or other) and NFSI may take place giving rise to chlorine(I) fluoride, which is an electrophilic source of chloronium. When ClF reacts with the titanium enolate, α-chlorination product **5Cl** is formed.[13] The kinetics of these processes is likely affected by the identity of the Ti reagent among other reaction parameters.

Conversion of the reaction products to broadly useful fluorinated building blocks for organic synthesis is illustrated by examples in Scheme 2. These include hydrolytic and reductive removal of the chiral auxiliary. The monofluorinated derivative **3d** could be readily reduced using sodium borohydride in aqueous THF, delivering the corresponding fluoroalcohol **7a** in high yields and with a high level of retention of stereochemical integrity. Compound **3d** could also be hydrolyzed with a $LiOH–H_2O_2$ reagent system to yield the corresponding acid **7b** in high yields and virtually complete preservation of stereochemistry. Notably, these transformations are characterized by excellent yields and nearly quantitative recovery of the chiral auxiliary.

■ CONCLUSIONS

We have reported an operationally simple asymmetric α-fluorination reaction of *N*-acyloxazolidinones based on the unique reactivity of group IVa metal enolates. From a practical perspective, the reaction requires inexpensive reagents, mild conditions, short reaction times at ambient temperatures, and delivers α-fluorination products directly in good yields and high diastereoselectivities.[14,15] Ongoing studies are directed at defining a more detailed picture of the mechanism for the fluorination of α-arylacetic acid derivatives and determination of the structure and function of the $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$ complex.

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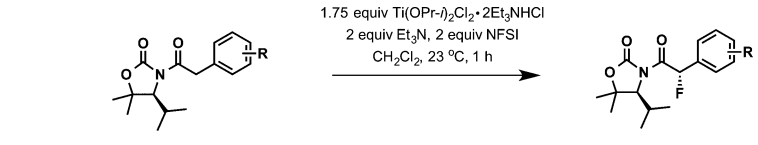
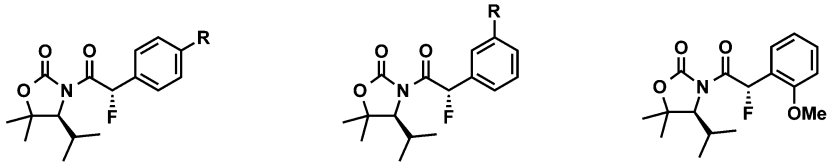
Table 5. Scope of α-Fluorination of α-Aryl Acetic Acid *N*-Acyloxazolidinone Derivatives[a,b,c]

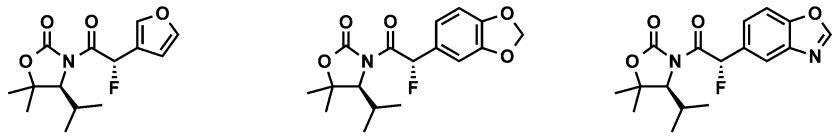




(**5a**) R = OMe, 63%, dr 93:7
(**5b**) R = F: 71%, dr 91:9
(**5c**) R = Cl: 61%, dr 91:9

(**5d**) R = F: 69%, dr 93:7
(**5e**) R = CF_3: 65%, dr 91:9
(**5f**) R = OPh: 62%, dr 95:5

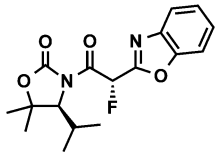
(**5g**) 80%, dr 91:9



(**5h**) 54%, dr 91:9

(**5i**) 64%, dr 91:9

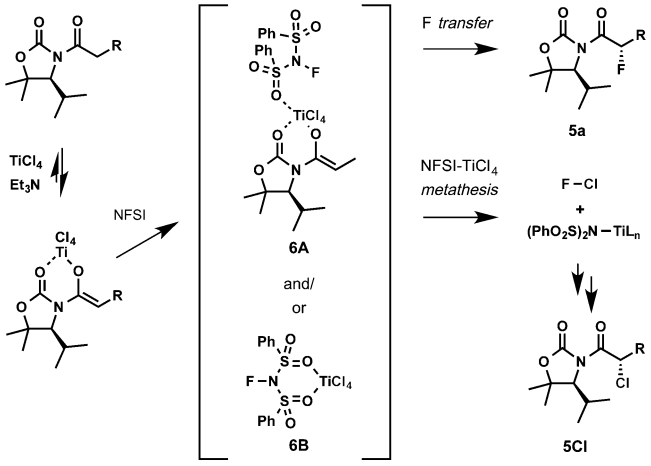
(**5j**) 87%, dr 92:8 [d]



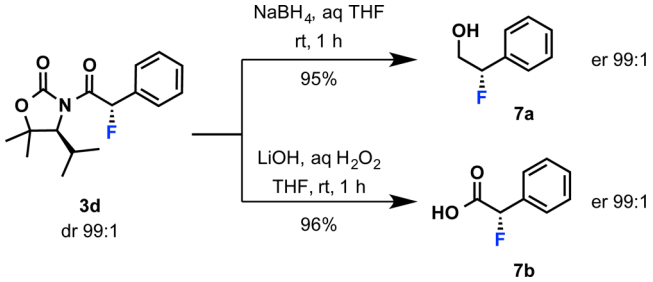
(**5k**) 63%, dr 2:1

[a]Yields are of isolated pure major diastereomers unless indicated otherwise. Diastereomer ratios were determined by 600 MHz ^{1}H NMR analysis of the crude mixture of products. [b]Standard conditions: substrate (0.50 mmol), $TiCl_2(O^iPr)_2$·$2Et_3NHCl$ (1.75 equiv), Et_3N (2.0 equiv), NFSI (2.0 equiv), CH_2Cl_2 (0.5 M), mixed and stirred at room temperature for 1 h. [c]Less than 10% of chlorinated products were observed along with products **4b–k**. [d]Ti(OPr-*i*)$_2$Cl$_2$ (1.75 equiv) was used; product isolated as a mixture of diastereomers.

Scheme 1. Mechanistic Hypothesis for the α-Fluorination Reaction



Scheme 2. Preparation of Enantioenriched Fluorinated Building Blocks via Hydrolytic and Reductive Removal of the Chiral Auxiliary



EXPERIMENTAL SECTION[16]

(*S*)-4-Isopropyl-5,5-dimethyloxazolidin-2-one. (S1). Thionyl chloride (31.1 mL, 0.427 mol) was added dropwise to a solution of L-valine (25.0 g, 0.213 mol) in methanol (430 mL) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, then heated to reflux for 4 h. The solution was cooled to rt and methanol was removed in vacuo. The crude residue was submitted to the next step without purification.

Sodium hydrogen carbonate (53.7 g, 0.640 mol) was added to a solution of crude substrate (0.213 mol) in a 4:1 mixture of THF/MeOH (560 mL) at 0 °C and was stirred for 5 min. Di-*tert*-butyl dicarbonate (47.0 g, 0.215 mol) was added to the mixture at 0 °C. The reaction mixture was warmed to rt, stirred for 2 h, and then quenched with water. The layers were separated. The aqueous layer was

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extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with saturated sodium bicarbonate and brine, dried with magnesium sulfate, and concentrated in vacuo to afford a yellow oil. The crude residue was submitted to the next step without further purification.

Methylmagnesium bromide (3.0 M in Et_2O, 250 mL, 0.750 mol) was added (as a slow stream) to a solution of the crude substrate (0.213 mol) in THF (500 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, then warmed to rt and stirred for 48 h. The solution was cooled to 0 °C and quenched with saturated ammonium chloride (two clear layers should form). The layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and concentrated in vacuo to deliver a light yellow oil. The crude residue was submitted to the next step without further purification.

Potassium *tert*-butoxide (26.8 g, 0.239 mol) was added to a solution of the crude substrate (0.213 mol) in THF (575 mL) at 0 °C. The reaction mixture was warmed to rt and stirred for 2.5 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride. The layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (silica, 40% ethyl acetate in hexanes−75% ethyl acetate in hexanes) to afford the white/yellow solid oxazolidinone **S1** (28.1 g, 0.179 mol, 84%).

Standard Procedure 1: Synthesis of *N*-Acyloxazolidinones via Acyl Chloride. *n*-Butyllithium (2.48 M in hexanes, 2.88 mL, 7.14 mmol, 1.1 equiv) was added to a precooled solution (−78 °C) of oxazolidinone **S1** (1.02 g, 6.49 mmol, 1.0 equiv) in tetrahydrofuran (22.0 mL, 0.30 M) under argon. The solution was warmed to 0 °C and stirred for an additional 30 min. The solution was cooled to −78 °C, and the corresponding acyl chloride (7.78 mmol, 1.2 equiv) was added dropwise to the reaction mixture and stirred for 1 h at −78 °C. The reaction solution was warmed to rt and stirred for an additional 2 h. The reaction was quenched with saturated ammonium chloride, and the layers were separated. The aqeuous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over sodium sulfate, concentrated in vacuo, and purified by column chromatography to give the corresponding *N*-acyloxazolidinone.

*(S)-3-Hexanoyl-4-isopropyl-5,5-dimethyloxazolidin-2-one (**1**).* The title compound was prepared from commercially available hexanoyl chloride (1.08 mL, 7.78 mmol) following standard procedure 1 for the synthesis of *N*-acyloxazolidinones via acyl chloride. (*S*)-3-Hexanoyl-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a yellow oil (1.36 g, 5.32 mmol, 82%) after purification by column chromatography (silica, 6% ethyl acetate in hexanes−12% ethyl acetate in hexanes): $[\alpha]_D^{27}$ +31.21 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (d, *J* = 3.3 Hz, 1H), 3.01−2.92 (m, 1H), 2.87−2.79 (m, 1H), 2.15−2.06 (m, 1H), 1.69−1.59 (m, 2H), 1.47 (s, 3H), 1.34 (s, 3H), 1.33−1.29 (m, 4H), 0.99 (dd, *J* = 7.0, 3.5 Hz, 3H), 0.91 (dd, *J* = 6.8, 3.5 Hz, 3H), 0.88−0.84 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8 (s), 153.5 (s), 82.6 (s), 66.1 (s), 35.3 (s), 31.2 (s), 29.5 (s), 28.7 (s), 24.3 (s), 22.3 (s), 21.4 (s), 21.3 (s), 16.9 (s), 13.8 (s); HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{25}NO_3Na$ $[M + Na]^+$ 278.1732, found 278.1728.

*(S)-4-Isopropyl-5,5-dimethyl-3-propionyloxazolidin-2-one (**S3**).* The title compound was prepared from commercially available propionoyl chloride (0.68 mL, 7.78 mmol) following standard procedure 1 for the synthesis of *N*-acyloxazolidinones via acyl chloride. (S)-4-Isopropyl-5,5-dimethyl-3-propionyloxazolidin-2-one was obtained as a white solid (1.22 g, 5.72 mmol, 88%) after purification by column chromatography (silica, 10% ethyl acetate in hexanes−15% ethyl acetate in hexanes): $[\alpha]_D^{25}$ +38.28 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.13 (d, *J* = 3.3 Hz, 1H), 2.99 (dddd, *J* = 17.4, 7.4 Hz, 1H), 2.89 (dddd, *J* = 17.4, 7.3 Hz, 1H), 2.13 (ddd, *J* = 13.8, 6.9, 3.4 Hz, 1H), 1.49 (s, 3H), 1.36 (s, 3H), 1.17 (dd, *J* = 9.6, 5.2 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6 (s), 153.6 (s), 82.7 (s), 66.2 (s), 29.5 (s), 29.1 (s), 28.8 (s), 21.4 (s), 21.4 (s), 17.0 (s), 8.7 (s); HRMS (ESI-TOF) *m*/*z* calcd for $C_{11}H_{19}NO_3Na$ $[M + Na]^+$ 236.1263, found 236.1268.

*(S)-3-(2-Chloroacetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S4**).* *n*-Butyllithium (2.48 M in hexanes, 2.88 mL, 7.14 mmol, 1.1 equiv) was added to a solution of **S1** (1.02 g, 6.49 mmol, 1.0 equiv) in diethyl ether (22.0 mL, 0.30 M) at −78 °C. The solution was warmed to 0 °C and stirred for an additional 30 min. The solution was cooled to −78 °C, and the corresponding acyl chloride (7.78 mmol, 1.2 equiv) was added dropwise to the reaction mixture and stirred for 1 h at −78 °C. The reaction solution was warmed to rt and stirred for an additional 2 h. The reaction was quenched with saturated ammonium chloride and the layers were separated. The aqeuous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over sodium sulfate, concentrated in vacuo, and purified by column chromatography to give (*S*)-3-(2-chloroacetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one as a yellow oil (1.25 g, 5.38 mmol, 83%) after purification by column chromatography (silica, 10% ethyl acetate in hexanes -15% ethyl acetate in hexanes): $[\alpha]_D^{27}$ +39.55 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.75 (ddd, *J* = 15.3 Hz, 2H), 4.16 (d, *J* = 3.2 Hz, 1H), 2.22−2.14 (m, 1H), 1.54 (s, 3H), 1.42 (s, 3H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (s), 152.9 (s), 83.9 (s), 66.8 (s), 43.4 (s), 29.4 (s), 28.6 (s), 21.3 (s), 21.2 (s), 16.7 (s); HRMS (ESI-TOF) *m*/*z* calcd for $[M + Na]^+$ $C_{10}H_{16}ClNO_3Na$ 256.0716, found 256.0700.

*(S)-4-Isopropyl-5,5-dimethyl-3-(3-phenylpropanoyl)oxazolidin-2-one (**S5**).* The title compound was prepared from commercially available hydrocinnamoyl chloride (1.16 mL, 7.78 mmol) following standard procedure 1 for the synthesis of *N*-acyloxazolidinones via acyl chloride. (*S*)-4-Isopropyl-5,5-dimethyl-3-(3-phenylpropanoyl)-oxazolidin-2-one was obtained as a yellow oil (1.41 g, 4.87 mmol, 74%) after purification by column chromatography (silica, 10% ethyl acetate in hexanes−18% ethyl acetate in hexanes): $[\alpha]_D^{27}$ +36.16 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.26 (m, 3H), 7.25 (s, 1H), 7.21−7.17 (m, 1H), 4.13 (d, *J* = 3.3 Hz, 1H), 3.34 (ddd, *J* = 16.5, 9.0, 6.3 Hz, 1H), 3.29−3.22 (m, 1H), 3.08−2.93 (m, 2H), 2.12 (dddd, *J* = 13.8, 6.9, 3.5 Hz, 1H), 1.50 (s, 3H), 1.32 (s, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9 (s), 153.5 (s), 140.4 (s), 128.5 (s), 128.4 (s), 126.2 (s), 82.8 (s), 66.3 (s), 36.8 (s), 30.7 (s), 29.5 (s), 28.7 (s), 21.4 (s), 17.0 (s); HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{23}NO_3Na$ $[M + Na]^+$ 312.1576, found 312.1559.

*(S)-4-Isopropyl-3-(2-(4-methoxyphenyl)acetyl)-5,5-dimethyloxazolidin-2-one (**S6**).* The title compound was prepared from commercially available 4-methoxyphenylacetyl chloride (1.19 mL, 7.78 mmol) following standard procedure 1 for the synthesis of *N*-acyloxazolidinones via acyl chloride. (*S*)-4-Isopropyl-3-(2-(4-methoxyphenyl)acetyl)-5,5-dimethyloxazolidin-2-one was obtained as a yellow oil (1.02 g, 3.34 mmol, 52%) after purification by column chromatography (silica, 15−22% ethyl acetate in hexanes: $[\alpha]_D^{26}$ 70.63 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.26−7.25 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.30 (d, *J* = 15.0 Hz, 1H), 4.19 (d, *J* = 15.0 Hz, 1H), 4.12 (d, *J* = 3.1 Hz, 1H), 3.79 (s, 3H), 2.10 (ddd, *J* = 10.5, 6.8, 3.4 Hz, 1H), 1.49 (s, 3H), 1.31 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1 (s), 158.6 (s), 153.5 (s), 130.6 (s), 125.9 (s), 113.9 (s), 82.8 (s), 66.4 (s), 55.1 (s), 40.6 (s), 29.5 (s), 28.7 (s), 21.4 (s), 21.3 (s), 16.8 (s); HRMS (EI) *m*/*z* calcd for $C_{17}H_{23}NO_4$ $[M]^+$ 305.1627, found 305.1637.

*(S)-3-(2-(4-Fluorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S7**).* The title compound was prepared from commercially available 4-fluorophenylacetyl chloride (1.07 mL, 7.78 mmol) following standard procedure 1 for the synthesis of *N*-acyloxazolidinones via acyl chloride. (*S*)-3-(2-(4-Fluorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a colorless oil (1.06 g, 3.61 mmol, 56%) after purification by column chromatography (silica, 9% ethyl acetate in hexanes−13% ethyl acetate in hexanes): $[\alpha]_D^{27}$ +45.86 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.01 (dd, *J* = 8.7 Hz, 2H), 4.35 (d, *J* = 15.1 Hz, 1H),

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4.20 (d, J = 15.1 Hz, 1H), 4.13 (d, J = 3.1 Hz, 1H), 2.14−2.06 (m, 1H), 1.50 (s, 3H), 1.32 (s, 3H), 0.95 (d, J = 7.0 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5 (s), 162.9 (s), 160.9 (s), 153.4 (s), 131.2 (d, J = 8.0 Hz), 129.6 (d, J = 3.2 Hz), 115.3 (d, J = 21.4 Hz), 82.9 (s), 66.4 (s), 40.6 (s), 29.5 (s), 28.8 (s), 21.4 (s), 21.2 (s), 16.7 (s); HRMS (EI) m/z calcd for C16H$_{20}$FNO3 $[M]^+$ 293.1427, found 293.1435.

Standard Procedure 2: Synthesis of *N*-Acyloxazolidinones via Mixed Anhydride. *Solution A.* In a flame-dried flask, trimethylacetyl chloride (1.45 equiv) was added dropwise to a precooled (−20 °C) reaction mixture of carboxylic acid (1.20 equiv) and triethylamine (4.80 equiv) in tetrahydrofuran (0.15 M) under argon. The solution was allowed to stir at −20 °C for an additional 2 h.

Solution B. In a separate flame-dried flask, *n*-butyllithium (1.10 equiv) was added dropwise to a precooled (−78 °C) reaction mixture of oxazolidione **S1** (1.00 equiv) in tetrahydrofuran (0.30 M) under argon. The mixture was allowed to warm to 0 °C and then stir at 0 °C for an additional 30 min.

Solution B (lithiated oxazolidinone), was transferred (via cannula) to the precooled (−20 °C) solution A (mixed anhydride) reaction mixture. After the addition was complete, the reaction mixture was warmed to room temperature and stirred at room temperature for 3 h. The reaction was quenched with saturated ammonium chloride, and the layers were separated. The aqeuous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over sodium sulfate, concentrated in vacuo, and purified by column chromatography to give the corresponding *N*-acyloxazolidinone.

*(S)-4-Isopropyl-5,5-dimethyl-3-(3-methylbutanoyl)oxazolidin-2-one (**S9**).* The title compound was prepared from commercially available 3-methylbutanoic acid (0.84 mL, 7.63 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-4-Isopropyl-5,5-dimethyl-3-(3-methylbutanoyl)-oxazolidin-2-one was obtained as a colorless oil (1.34 g, 3.64 mmol, 88%) after purification by column chromatography (silica, 10% ethyl acetate in hexanes−15% ethyl acetate in hexanes): $[\alpha]_D^{25}$ +30.87 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 (d, J = 3.2 Hz, 1H), 2.91 (dd, J = 15.6, 6.7 Hz, 1H), 2.76 (dd, J = 15.6, 7.1 Hz, 1H), 2.25−2.16 (m, 1H), 2.14 (ddd, J = 16.9, 8.5, 5.2 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H), 1.06−0.96 (m, 9H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1 (s), 153.5 (s), 82.5 (s), 66.2 (s), 43.8 (s), 29.5 (s), 28.8 (s), 25.3 (s), 22.5 (s), 22.3 (s), 21.5 (s), 21.3 (s); HRMS (ESI+TOF) m/z calcd for $C_{13}H_{23}NO_3Na$ $[M + Na]^+$ 264.1576, found 264.1561.

*(S)-3-(Hept-6-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S10**).* The title compound was prepared from commercially available 6-heptenoic acid (0.63 mL, 7.63 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(Hept-6-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a colorless oil (1.53 g, 3.38 mmol, 90%) after purification by column chromatography (silica, 9% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +32.15 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (dddd, J = 16.9, 10.2, 6.7 Hz, 1H), 5.02−4.91 (m, 2H), 4.13 (d, J = 3.3 Hz, 1H), 2.99 (ddd, J = 16.1, 8.5, 6.4 Hz, 1H), 2.90−2.82 (m, 1H), 2.16−2.04 (m, 3H), 1.75−1.60 (m, 2H), 1.49 (s, 3H), 1.48−1.42 (m, 2H), 1.36 (s, 3H), 1.00 (d, J = 7.0 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H.); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7 (s), 153.5 (s), 138.4 (s), 114.6 (s), 82.7 (s), 66.2 (s), 35.3 (s), 33.4 (s), 29.5 (s), 28.8 (s), 28.3 (s), 24.1 (s), 21.4 (s), 21.6 (s), 17.0 (s); HRMS (ESI+TOF) m/z calcd for $C_{15}H_{25}NO_3Na$ $[M + Na]^+$ 290.1732, found 290.1720.

*(S)-3-(5-(Benzyloxy)pentanoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S11**).* The title compound was prepared from 6-heptenoic acid (2.08 g, 10.0 mmol) following the standard procedure for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(5-(Benzyloxy)pentanoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a white solid (2.71 g, 7.81 mmol, 78%) after purification by column chromatography (silica, 15% ethyl acetate−hexanes): $[\alpha]_D^{26}$ +24.09 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 4.4 Hz, 4H), 7.28 (dd, J = 8.3, 4.1 Hz, 1H), 7.25 (s, 1H), 4.50 (s, 2H), 4.14 (d, J = 3.3 Hz, 1H), 3.51 (t, J = 6.2 Hz, 2H), 3.03 (ddd, J = 16.8, 8.1, 6.5 Hz, 1H), 2.91 (ddd, J = 16.8, 8.2, 6.3 Hz, 1H), 2.13 (dddd, J = 13.8, 6.9, 3.4 Hz, 1H), 1.82−1.74 (m, 2H), 1.73−1.66 (m, 2H), 1.50 (s, 3H), 1.37 (s, 3H), 1.02 (d, J = 7.0 Hz, 3H), 0.93 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6 (s), 153.5 (s), 138.6 (s), 128.3 (s), 127.6 (s), 127.5 (s), 82.7 (s), 72.9 (s), 69.9 (s), 66.2 (s), 35.2 (s), 29.5 (s), 29.1 (s), 28.8 (s), 21.5 (s), 21.4 (s), 21.4 (s), 17.1 (s); HRMS (ESI+TOF) m/z Calcd for $C_{20}H_{29}NO_4Na$ $[M + Na]^+$ 370.1994, found 370.2002.

*(S)-3-(Hept-6-ynoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S12**).* The title compound was prepared from commercially available 6-heptynoic acid (0.69 g, 5.42 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(Hept-6-ynoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a colorless oil (1.41 g, 2.15 mmol, 75%) after purification by column chromatography (silica, 10% ethyl acetate in hexanes−18% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +33.58 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.15 (d, J = 3.3 Hz, 1H), 3.03 (ddd, J = 16.6, 8.4, 6.5 Hz, 1H), 2.91 (ddd, J = 16.7, 8.3, 6.6 Hz, 1H), 2.24 (ddd, J = 7.1, 2.6 Hz, 2H), 2.14 (dtd, J = 13.8, 6.9, 3.4 Hz, 1H), 1.95 (dd, J = 2.6 Hz, 1H), 1.86−1.74 (m, 2H), 1.66−1.59 (m, 2H), 1.51 (s, 3H), 1.38 (s, 3H), 1.02 (d, J = 7.0 Hz, 3H), 0.94 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3 (s), 153.5 (s), 83.9 (s), 82.7 (s), 68.5 (s), 66.2 (s), 34.9 (s), 29.5 (s), 28.8 (s), 27.9 (s), 23.7 (s), 21.5 (s), 21.4 (s), 18.2 (s), 17.0 (s); HRMS (ESI+TOF) m/z calcd for $C_{15}H_{23}NO_3Na$ $[M + Na]^+$ 288.1576, found 288.1571.

*(S)-2-(3-(4-Isopropyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-3-oxopropyl)isoindoline-1,3-dione (**S13**).* The title compound was prepared from commercially available 3-(1,3-dioxo-1,3-dihydro-2*H*-isoindol-2-yl)-propanoic acid (8.69 g, 39.7 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-2-(3-(4-Isopropyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-3-oxopropyl)isoindoline-1,3-dione was obtained as a white solid (6.78 g, 18.9 mmol, 48%) after purification by column chromatography (silica, 20% ethyl acetate in hexanes−25% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +18.79 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86−7.83 (m, 2H), 7.73−7.69 (m, 2H), 4.13 (d, J = 3.2 Hz, 1H), 4.09−4.05 (m, 2H), 3.43−3.35 (m, 1H), 3.29 (ddd, J = 17.1, 7.5 Hz, 1H), 2.14 (ddd, J = 13.9, 6.9, 3.2 Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H), 1.02 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (s), 167.9 (s), 153.4 (s), 133.9 (s), 132.0 (s), 123.2 (s), 83.2 (s), 66.3 (s), 34.2 (s), 33.4 (s), 29.5 (s), 28.8 (s), 21.4 (s), 21.2 (s), 16.9 (s); HRMS (ESI+TOF) m/z calcd for $C_{19}H_{22}N_2O_5Na$ $[M + Na]^+$ 381.1426, found 381.1427.

*(S)-4-Isopropyl-5,5-dimethyl-3-(3-(3-(trifluoromethyl)phenyl)-propanoyl)oxazolidin-2-one (**S14**).* 3-Trifluoromethylcinnamic acid (1.65 g, 7.63 mmol) was submitted to standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. The resultant crude oil was submitted to the next reaction without further purification.

Ethanol (28.0 mL, 0.2 M) was added to the mixture of crude substrate (7.63 mmol) and palladium on carbon (10 wt %, 0.20 g). Hydrogen gas was then bubbled through the reaction mixture for 2 min at room temperature. The reaction mixture was pressurized with hydrogen gas. The reaction mixture was stirred for 3 h at room temperature. The reaction mixture was filtered through Celite, and the solvent was removed in vacuo. (S)-4-Isopropyl-5,5-dimethyl-3-(3-(3-(trifluoromethyl)phenyl)propanoyl)oxazolidin-2-one was obtained as a clear oil (1.98 g, 5.54 mmol, 88%) after purification by column chromatography (silica, 15% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +25.37 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.45 (d, J = 7.7 Hz, 2H), 7.41−7.37 (m, 1H), 4.13 (d, J = 3.4 Hz, 1H), 3.37 (ddd, J = 16.9, 8.6, 6.6 Hz, 1H), 3.24 (ddd, J = 16.9, 8.2, 6.7 Hz, 1H), 3.14−2.99 (m, 2H), 2.11 (dddd, J = 13.8, 6.9, 3.4 Hz, 1H), 1.49 (s, 3H), 1.32 (s, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4 (s), 153.5 (s), 141.4 (s), 132.0 (d, J = 1.3 Hz), 130.7 (q, J = 32.0 Hz), 128.8 (s), 125.2 (q, J = 3.8 Hz), 123.2−122.7 (m), 82.9 (s), 66.3 (s), 36.6 (s), 30.3 (s), 29.5 (s), 28.7 (s), 21.4 (s), 21.3 (s), 16.9 (s); HRMS (ESI+TOF) m/z calcd for $C_{18}H_{22}F_3NO_3Na$ $[M + Na]^+$ 380.1449, found 380.1450.

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*(S,E)-3-(But-2-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S15**).* The title compound was prepared from commercially available crotonoic acid (0.517 g, 6.00 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*,*E*)-3-(But-2-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a white solid (0.770 g, 3.42 mmol, 68%) after purification by column chromatography (silica, 10% ethyl acetate in hexanes−30% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +52.90 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$); δ (ppm): 7.29 (ddd, *J* = 15.2, 3.2, 1.5 Hz, 1H), 7.12 (dddd, *J* = 15.1, 6.9 Hz, 1H), 4.19 (d, *J* = 3.4 Hz, 1H), 2.13 (dddd, *J* = 13.8, 6.9, 3.5 Hz, 1H), 1.93 (dd, *J* = 6.9, 1.6 Hz, 3H), 1.49 (s, 3H), 1.36 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5 (s), 153.5 (s), 146.4 (s), 121.9 (s), 82.6 (s), 66.2 (s), 29.6 (s), 28.7 (s), 21.4 (s), 21.3 (s), 18.4 (s), 17.0 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{12}H_{19}NO_3Na$ $[M + Na]^+$ 248.1263, found 248.1255.

*(S)-4-Isopropyl-5,5-dimethyl-3-(2-phenylacetyl)oxazolidin-2-one (**S16**).* The title compound was prepared from commercially available phenyl acetic acid (1.51 g, 11.1 mmol) following standard procedure 2 for the synthesis of N-acyloxazolidinones via mixed anhydride. (*S*)-4-Isopropyl-5,5-dimethyl-3-(2-phenylacetyl)oxazolidin-2-one was obtained as yellow oil (2.24 g, 8.1 mmol, 81%) after purification by column chromatography (silica, 15% ethyl acetate−hexanes): $[\alpha]_D^{26}$ +36.65 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.30 (m, 4H), 7.27−7.24 (m, 1H), 4.37 (d, *J* = 15.0 Hz, 1H), 4.26 (d, *J* = 15.0 Hz, 1H), 4.13 (d, *J* = 3.3 Hz, 1H), 2.11 (dddd, *J* = 13.8, 6.9, 3.3 Hz, 1H), 1.49 (s, 3H), 1.31 (s, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8 (s), 153.5 (s), 134.0 (s), 129.6 (s), 128.5 (s), 127.1 (s), 82.9 (s), 66.5 (s), 41.6 (s), 29.6 (s), 28.8 (s), 21.4 (s), 21.4 (s), 16.9 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{16}H_{21}NO_3Na$ $[M + Na]^+$ 298.1419, found 298.1414

*(S)-3-(2-(4-Chlorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S17**).* The title compound was prepared from commercially available 2-(4-chlorophenyl)acetic acid (1.30 g, 7.63 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(2-(4-Chlorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as green solid (0.54 g, 1.7 mmol, 28%) after purification by column chromatography (silica, 20−25% ethyl acetate in hexanes): $[\alpha]_D^{27}$ +37.17 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.0 Hz, 4H), 4.35 (d, *J* = 15.1 Hz, 1H), 4.20 (d, *J* = 15.1 Hz, 1H), 4.13 (d, *J* = 3.2 Hz, 1H), 2.14−2.06 (m, 1H), 1.50 (s, 3H), 1.33 (s, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.05 (s), 1533 (s), 132.8 (s), 132.3 (s), 130.9 (s), 128.4 (s), 82.8 (s), 66.3 (s), 40.7 (s), 29.4 (s), 28.6 (s), 21.3 (s), 21.1 (s), 16.7 (s); HRMS (EI) *m*/*z* calcd for $C_{16}H_{20}ClNO_3$ $[M]^+$ 309.1132, found 309.1132.

*(S)-3-(2-(Benzo[d][1,3]dioxol-5-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S18**).* The title compound was prepared from commercially available 2-(benzo[1,3]dioxol-5-yl)acetic acid (1.65 g, 7.63 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(2-(Benzo[*d*][1,3]-dioxol-5-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a white solid (1.43 g, 4.45 mmol, 71%) after purification by column chromatography (silica, 11% ethyl acetate in hexanes): $[\alpha]_D^{23}$ +39.58 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (d, *J* = 1.3 Hz, 1H), 6.81−6.78 (m, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.93 (s, 2H), 4.27 (d, *J* = 15.1 Hz, 1H), 4.17 (s, 1H), 4.13 (d, *J* = 3.2 Hz, 1H), 2.15−2.07 (m, 1H), 1.50 (s, 3H), 1.33 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8 (s), 153.5 (s), 147.6 (s), 146.6 (s), 127.5 (s), 122.8 (s), 110.1 (s), 108.2 (s), 100.9 (s), 82.9 (s), 66.5 (s), 41.1 (s), 29.6 (s), 28.8 (s), 21.4 (s), 21.3 (s), 16.9 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{17}H_{21}NO_5Na$ $[M + Na]^+$ 342.1317, found 342.1306.

*(S)-4-Isopropyl-5,5-dimethyl-3-(2-(3-phenoxyphenyl)acetyl)-oxazolidin-2-one (**S19**).* The title compound was prepared from commercially available 2-(3-phenoxyphenyl)acetic acid (0.326 g, 1.43 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-4-Isopropyl-5,5-dimethyl-3-(2-(3-phenoxyphenyl)acetyl)oxazolidin-2-one was obtained as a yellow oil (0.36 g, 0.98 mmol, 76%) after purification by column chromatography (silica, 12% ethyl acetate in hexanes): $[\alpha]_D^{22}$ +52.08 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.26 (m, 3H), 7.09 (dd, *J* = 7.4 Hz, 2H), 7.02−6.97 (m, 3H), 6.91 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.36 (d, *J* = 15.1 Hz, 1H), 4.22 (d, *J* = 15.1 Hz, 1H), 4.14 (d, *J* = 3.2 Hz, 1H), 2.11 (dddd, *J* = 13.8, 6.9, 3.3 Hz, 1H), 1.49 (s, 3H), 1.33 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3 (s), 157.2 (s), 157.1 (s), 153.4 (s), 129.7 (s), 129.6 (s), 124.6 (s), 123.1 (s), 120.1 (s), 118.8 (s), 117.6 (s), 82.9 (s), 66.4 (s), 41.4 (s), 29.6 (s), 28.7 (s), 21.4 (s), 21.3 (s), 16.9 (s); HRMS (ESI+TOF) *m*/*z* Calcd for $C_{22}H_{25}NO_4Na$ $[M + Na]^+$ 390.1681, found 390.1698.

*(S)-3-(2-(3-Fluorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S20**).* The title compound was prepared from commercially available 2-(3-fluorophenyl)acetic acid (1.17 g, 7.60 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(2-(3-Fluorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as yellow oil (1.46 g, 4.97 mmol, 79%) after purification by column chromatography (silica, 12% ethyl acetate in hexanes): $[\alpha]_D^{23}$ +48.61 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.26 (m, 1H), 7.25 (s, 1H), 7.11 (dd, *J* = 7.7, 0.4 Hz, 1H), 7.08−7.04 (m, 1H), 6.98−6.93 (m, 1H), 4.37 (d, *J* = 15.1 Hz, 1H), 4.23 (d, *J* = 15.1 Hz, 1H), 4.13 (d, *J* = 3.3 Hz, 1H), 2.11 (dddd, *J* = 13.8, 6.9, 3.3 Hz, 1H), 1.49 (s, 3H), 1.33 (s, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.07 (s), 162.7 (d, *J* = 245.8 Hz), 153.4 (s), 136.2 (d, *J* = 7.9 Hz), 129.9 (d, *J* = 8.4 Hz), 125.3 (d, *J* = 3.1 Hz), 116.6 (d, *J* = 21.8 Hz), 114.1 (d, *J* = 21.0 Hz), 82.9 (s), 66.5 (s), 41.2 (d, *J* = 2.0 Hz), 29.6 (s), 28.7 (s), 21.4 (s), 21.3 (s), 16.8 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{16}H_{20}FNO_3Na$ $[M + Na]^+$ 316.1325, found 316.1324.

*(S)-3-(2-(Furan-3-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S21**).* The title compound was prepared from commercially available 3-furylacetic acid (0.191 g, 1.51 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(2-(Furan-3-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained after purification by column chromatography (silica, 20% ethyl acetate in hexanes) as a clear oil (0.266 g, 1.00 mmol, 66%): $[\alpha]_D^{21}$ +39.04 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 0.5 Hz, 1H), 7.34 (t, *J* = 1.6 Hz, 1H), 6.37 (d, *J* = 1.1 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 4.10 (d, *J* = 3.2 Hz, 1H), 4.04 (d, *J* = 16.0 Hz, 1H), 2.09 (dtd, *J* = 13.8, 6.9, 3.3 Hz, 1H), 1.46 (s, 3H), 1.30 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0 (s), 153.3 (s), 142.7 (s), 140.9 (s), 117.1 (s), 111.3 (s), 82.8 (s), 66.3 (s), 31.6 (s), 29.5 (s), 28.6 (s), 21.3 (s), 21.2 (s), 16.7 (s); HRMS (EI) *m*/*z* calcd for $C_{14}H_{19}NO_4$ $[M]^+$ 265.1314, found 265.1318.

*(S)-3-(2-(Benzo[d]oxazol-5-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S22**).* Pd/C (20 mol %) was added to a solution of ethanol/ethyl acetate (1:1, 0.16 M) and methyl 2-(4-hydroxy-3nitrophenyl)acetate (1.37 g, 6.48 mmol) at room temperature. The reaction mixture was placed under an atmosphere of H_2 and stirred for 14 h. The reaction mixture was then filtered through a pad of Celite, and the remaining residue was washed using a solvent system of EtOH/EtOAc (1:1). The filtrate was concentrated in vacuo providing a crude dark brown solid (1.08 g, 99%). The crude product was used without further purification.

Triethyl orthoformate (13.3 mL, 0.8 M) was added to the crude substrate (10.6 mmol). The reaction mixture was heated to reflux and stirred for 18 h. The reaction mixture was cooled to room temperature and was then transferred to a separatory funnel containing water (90 mL). Layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo providing a light brown oil (1.75 g, 10.5 mmol, 99%). The crude product was used without further purification.

An aqueous solution of NaOH was added (0.4 M, 11.36 mmol, 1.2 equiv) to a solution of crude substrate (1.81 g, 9.47 mmol) in methanol (0.37 M), at room temperature. The mixture was stirred for 12 h. The reaction mixture was diluted with H_2O to a concentration of 0.035 M. Concentrated aqueous HCl was added until a pH of ∼4 was

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achieved. The solution was allowed to stir for 1 h, and the solids were collected by filtration and washed with cold water to provide the crude acid as a tan solid (0.673 g, 3.52 mmol, 41%).

The title compound was prepared from the crude acid (0.375 g, 2.11 mmol) following standard procedure 2 for the synthesis of *N*-acyloxazolidinones via mixed anhydride. (*S*)-3-(2-(Benzo[*d*]oxazol-5-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a white solid (0.433 g, 1.37 mmol, 65%) after purification by column chromatography (silica, 24% ethyl acetate to 30% ethyl acetate in hexanes): $[\alpha]_D^{21}$ +29.80 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.73 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 4.47 (d, *J* = 15.4 Hz, 1H), 4.33 (d, *J* = 15.4 Hz, 1H), 4.11 (d, *J* = 3.1 Hz, 1H), 2.11−2.03 (m, 1H), 1.45 (s, 3H), 1.29 (s, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5 (s), 153.4 (s), 152.8 (s), 149.0 (s), 140.2 (s), 130.6 (s), 127.3 (s), 121.5 (s), 110.6 (s), 82.9 (s), 66.4 (s), 41.3 (s), 29.4 (s), 28.7 (s), 21.4 (s), 21.2 (s), 16.8 (s). HRMS (ESI+TOF) *m*/*z* calcd $C_{17}H_{20}N2O_4Na$ $[M + Na]^+$ 339.1321, found 339.1314.

Standard Procedure 3: Synthesis of *N*-Acyloxazolidinones via Prepared Acyl Chloride. Oxalyl chloride (1.65 equiv) was added dropwise to a precooled (0 °C) solution of carboxylic acid (1.50 equiv), dimethylformamide (10 μL), and dichloromethane (2.0 M). The reaction mixture was allowed to stir for 10 min at 0 °C, and then the solution was warmed to room temperature and stirred for an additional 45 min (or until bubbling stops). The solution was carefully concentrated in vacuo.

In a separate flask, *n*-butyllithium (1.05 equiv) was added dropwise to a precooled (−78 °C) solution of oxazolidinone **S1** (1.00 equiv) in THF (0.35 M) under argon. The solution was stirred for 30 min at −78 °C. A solution of the crude acyl chloride in THF (0.6 M total, 3 rinses) was added dropwise at −78 °C. After being stirred at −78 °C for 2 h, the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous ammonium chloride. The layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and concentrated in vacuo. The resultant oil or solid was purified by column chromatography to give the corresponding *N*-acyloxazolidinone.

*(S)-3-(3-(2-Chlorophenyl)propanoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S23**).* The title compound was prepared from commercially available 3-(2-chlorophenyl)propanoic acid (1.29 g, 7.00 mmol) following the standard procedure for the synthesis of *N*-acyloxazolidinones via prepared acyl chloride. (*S*)-3-(3-(2-Chlorophenyl)propanoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained as a yellow oil (1.77 g, 5.46 mmol, 74%) after purification by column chromatography (silica, 15% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +30.14 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.27 (m, 2H), 7.16 (ddd, *J* = 13.5, 10.5, 6.2 Hz, 2H), 4.15 (d, *J* = 3.1 Hz, 1H), 3.38−3.20 (m, 2H), 3.12 (dt, *J* = 9.0, 6.0 Hz, 2H), 2.14 (ddd, *J* = 10.3, 8.3, 5.1 Hz, 1H), 1.50 (s, 3H), 1.36 (s, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7 (s), 153.5 (s), 138.1 (s), 134.0 (s), 130.5 (s), 129.5 (s), 127.7 (s), 126.8 (s), 82.9 (s), 66.4 (s), 35.2 (s), 29.5 (s), 28.8 (s), 28.3 (s), 21.4 (s), 17.1 (s). HRMS (ESI+TOF) *m*/*z* calcd for $C_{17}H_{22}ClNO_3Na$ $[M + Na]^+$ 346.1186, found 346.1189.

*(S)-4-Isopropyl-5,5-dimethyl-3-(4-phenoxybutanoyl)oxazolidin-2-one (**S24**).* The title compound was prepared from commercially available 4-phenoxybutanoic acid (2.70 g, 15.0 mmol) following the standard procedure for the synthesis of *N*-acyloxazolidinones via prepared acyl chloride. (*S*)-4-Isopropyl-5,5-dimethyl-3-(4-phenoxybutanoyl)oxazolidin-2-one was obtained as a white solid (2.95 g, 0.92 mmol, 92%) after purification by column chromatography (silica, 5−25% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +29.90 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.27 (m, 1H), 7.25 (dd, *J* = 4.7, 2.6 Hz, 1H), 6.95−6.88 (m, 3H), 4.15 (d, *J* = 3.4 Hz, 1H), 4.04 (dd, *J* = 6.2 Hz, 2H), 3.16 (ddddd, *J* = 17.5, 7.8, 6.8 Hz, 2H), 2.22−2.11 (m, 3H), 1.50 (s, 3H), 1.37 (s, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2 (s), 158.8 (s), 153.5 (s), 129.4 (s), 120.6 (s), 114.5 (s), 82.8 (s), 66.6 (s), 66.3 (s), 32.1 (s), 29.5 (s), 28.8 (s), 28.8 (s), 24.2 (s), 21.44 (s), 21.37 (s), 17.1 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{18}H_{25}NO_4Na$ $[M + Na]^+$ 342.1681, found 342.1679.

*(S)-4-Isopropyl-3-(2-(2-methoxyphenyl)acetyl)-5,5-dimethyloxazolidin-2-one (**S25**).* The title compound was prepared from commercially available 2-(2-methoxyphenyl)acetic acid (0.73 g, 4.00 mmol) following standard procedure 3 for the synthesis of *N*-acyloxazolidinones via prepared acyl chloride. (*S*)-4-Isopropyl-3-(2-(2-methoxyphenyl)acetyl)-5,5-dimethyloxazolidin-2-one was obtained as white solid (0.51 g g, 1.67 mmol, 42%) after purification by column chromatography (silica, 15% ethyl acetate in hexanes): $[\alpha]_D^{26}$ +25.03 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28−7.25 (m, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.92 (dd, *J* = 7.1 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.25 (ddd, *J* = 17.3 Hz, 2H), 4.17 (d, *J* = 3.2 Hz, 1H), 3.78 (s, 3H), 2.18−2.12 (m, 1H), 1.53 (s, 3H), 1.42 (s, 3H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7 (s), 157.4 (s), 153.8 (s), 131.2 (s), 128.5 (s), 123.3 (s), 120.5 (s), 110.3−109.8 (m), 82.8 (s), 66.5 (s), 55.3 (s), 37.2 (s), 29.6 (s), 28.7 (s), 21.5 (s), 21.3 (d, *J* = 6.5 Hz), 16.9 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{17}H_{23}NO_4Na$ $[M + Na]^+$ 328.1525, found 328.1522.

*(S)-4-Isopropyl-5,5-dimethyl-3-(2-(3-(trifluoromethyl)phenyl)-acetyl)oxazolidin-2-one (**S26**).* The title compound was prepared from commercially available 2-(3-trifluoromethyl)acetic acid (1.71 g, 8.40 mmol) following standard procedure 3 for the synthesis of *N*-acyloxazolidinones via prepared acyl chloride. (*S*)-4-Isopropyl-5,5-dimethyl-3-(2-(3-(trifluoromethyl)phenyl)acetyl)oxazolidin-2-one was obtained as yellow oil (1.01 g, 2.94 mmol, 35%) after purification by column chromatography (silica, 30% ethyl acetate in hexanes): $[\alpha]_D^{23}$ +33.10 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.44 (dd, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 15.4 Hz, 1H), 4.29 (d, *J* = 15.4 Hz, 1H), 4.15 (d, *J* = 3.2 Hz, 1H), 2.15−2.09 (m, 1H), 1.50 (s, 3H), 1.34 (s, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9 (s), 153.4 (s), 134.9 (s), 133.3 (d, *J* = 1.2 Hz), 131.3−130.2 (m), 128.9 (d, *J* = 7.3 Hz), 126.3 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 3.8 Hz), 124.0 (d, *J* = 272.2 Hz), 83.1, (s), 66.5 (s), 41.3 (s), 29.6 (s), 28.8 (s), 21.4 (s), 21.3 (s), 16.8 (s); HRMS (ESI+TOF) *m*/*z* calcd for $C_{17}H_{20}F_3NO_3Na$ $[M + Na]^+$ 366.1293, found 366.1292.

*(S)-3-(2-(Benzo[d]oxazol-2-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S27**).* *n*-Butyllithium (4.5 mL, 2.33 M in hexanes, 10.5 mmol, 1.1 equiv) was added dropwise to a precooled (−78 °C) solution of **S1** (1.5 g, 9.54 mmol) in tetrahydrofuran (0.3 M) under argon. The reaction mixture was stirred for 30 min. Acetyl chloride (0.82 mL, 11.45 mmol, 1.2 equiv) was added dropwise to the reaction mixture at −78 °C and was then stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched with saturated ammonium chloride, and the layers were separated. The aqeuous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo. (*S*)-3-Acetyl-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained after purification by column chromatography (silica, 12% ethyl acetate to 14% ethyl acetate in hexanes) as a colorless oil (1.4 g, 7.03 mmol, 74%).

NaHMDS (0.6 M in toluene, 8.3 mL, 5 mmol, 2 equiv) was added dropwise to a precooled (0 °C) solution of (*S*)-3-acetyl-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.500 g, 2.50 mmol) and 2-chlorobenzoxazole (0.385 g, 2.50 mmol) in toluene (11 mL) under argon. The reaction mixture was stirred at 0 °C for 2 h and then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with 1 N NH_4Cl solution (38 mL, 15.3 equiv). The layers were separated. The aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. (*S*)-3-(2-(Benzo[*d*]oxazol-2-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained after purification by column chromatography (silica, 21% ethyl acetate to 25% ethyl acetate in hexanes as a green solid (0.510 g, 1.61 mmol, 65%): $[\alpha]_D^{20}$ +49.79 (*c* 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68−7.64 (m, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 7.32−7.27 (m, 2H), 4.73 (d, *J* = 17.1 Hz, 1H), 4.55 (d, *J* = 17.1 Hz, 1H), 4.20 (d, *J* = 2.5 Hz, 1H), 2.21−2.15 (m, 1H), 1.52 (d, *J* = 6.3 Hz, 3H), 1.47 (s, 3H), 1.06 (d, *J* = 7.0 Hz, 3H),

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0.99 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6 (s), 159.9 (d, J = 0.9 Hz), 153.4 (s), 151.0 (s), 141.1 (s), 124.9 (s), 124.2 (s), 119.9 (s), 110.5 (s), 83.6 (s), 66.8 (s), 36.8 (s), 29.6 (s), 28.7 (s), 21.4 (s), 21.3 (s), 16.9 (s); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{20}N2O_4Na$ $[M + Na]^+$ 339.1321, found 339.1331.

*(S)-3-(2-(Benzo[d]oxazol-2-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S28**).* *n*-Butyllithium (4.5 mL, 2.33 M in hexanes, 10.5 mmol, 1.1 equiv) was added dropwise to a precooled (−78 °C) solution of **S1** (1.5 g, 9.54 mmol) in tetrahydrofuran (0.3 M) under argon. The reaction mixture was stirred for 30 min. Acetyl chloride (0.82 mL, 11.45 mmol, 1.2 equiv) was added dropwise to the reaction mixture at −78 °C and was then stirred for 1 h. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched with saturated ammonium chloride, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated in vacuo. (*S*)-3-Acetyl-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained after purification by column chromatography (silica, 12% ethyl acetate to 14% ethyl acetate in hexanes) as a colorless oil (1.4 g, 7.03 mmol, 74%).

NaHMDS (0.6 M in toluene, 8.3 mL, 5 mmol, 2 equiv) was added dropwise to a precooled (0 °C) solution of (*S*)-3-acetyl-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.500 g, 2.50 mmol) and 2-chlorobenzoxazole (0.385 g, 2.50 mmol) in toluene (11 mL) under argon. The reaction mixture was stirred at 0 °C for 2 h and then warmed to room temperature and stirred for an additional 12 h. The reaction was quenched with 1 N NH_4Cl solution (38 mL, 15.3 equiv). The layers were separated. The aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. (*S*)-3-(2-(Benzo[*d*]oxazol-2-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one was obtained after purification by column chromatography (silica, 21% ethyl acetate to 25% ethyl acetate in hexanes as a green solid (0.510 g, 1.61 mmol, 65%): $[\alpha]_D^{20}$ +49.79 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68−7.64 (m, 1H), 7.48 (d, J = 5.0 Hz, 1H), 7.32−7.27 (m, 2H), 4.73 (d, J = 17.1 Hz, 1H), 4.55 (d, J = 17.1 Hz, 1H), 4.20 (d, J = 2.5 Hz, 1H), 2.21−2.15 (m, 1H), 1.52 (d, J = 6.3 Hz, 3H), 1.47 (s, 3H), 1.06 (d, J = 7.0 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6 (s), 159.9 (d, J = 0.9 Hz), 153.4 (s), 151.0 (s), 141.1 (s), 124.9 (s), 124.2 (s), 119.9 (s), 110.5 (s), 83.6 (s), 66.8 (s), 36.8 (s), 29.6 (s), 28.7 (s), 21.4 (s), 21.3 (s), 16.9 (s); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{20}N2O_4Na$ $[M + Na]^+$ 339.1321, found 339.1331.

*(S)-3-(2-Cyclohexylacetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (**S29**).* The title compound was prepared from commerically available 2-cyclohexylacetic acid following known literature protocols:[7c] ^{1}H NMR (500 MHz, $CDCl_3$); δ ppm): 7.32−7.26 (m, 4H), 7.26−7.25 (m, 1H), 7.22 (ddd, J = 8.5, 3.8, 1.8 Hz, 1H), 4.51 (dd, J = 9.6, 3.9 Hz, 1H), 3.13 (dd, J = 14.4, 3.8 Hz, 1H), 2.91−2.75 (m, 3H), 1.88−1.78 (m, 1H), 1.74−1.60 (m, 5H), 1.36 (s, 3H), 1.34 (s, 3H), 1.31−1.21 (m, 2H), 1.18−1.10 (m, 1H), 1.04−0.95 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8 (s), 152.6 (s), 136.9 (s), 129.0 (s), 128.6 (s), 126.7 (s), 81.9 (s), 77.3 (s), 77.0 (s), 76.8 (s), 63.5 (s), 42.7 (s), 35.4 (s), 34.4 (s), 33.0 (d, J = 10.0 Hz), 28.5 (s), 26.1 (d, J = 10.4 Hz), 22.2 (s).

Standard Procedure for α-Fluorination of *N*-Acyloxazolidinones. In a flame-dried flask, $TiCl_4$ (1.0 M in CH_2Cl_2, 0.75 mL, 0.75 mmol, 1.5 equiv) was added dropwise to the solution of *N*-acyloxazolidinone (0.50 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C under argon. The mixture was stirred for 5 min at 0 °C. Triethylamine (0.14 mL, 1.00 mmol, 2.0 equiv) was added at 0 °C, and the solution was stirred for 30 min. *N*-Fluorosulfonimide (0.315 g, 1.00 mmol, 2.0 equiv) was added in one portion at 0 °C (CAUTION: vigorous gas evolution may be observed upon addition). The mixture was warmed to 23 °C and stirred for 1 h. The reaction mixture was filtered through a 1.5 cm silica plug column, and the plug was rinsed with CH_2Cl_2 (10 mL) and EtOAc (50 mL). The combined filtrate was concentrated in vacuo. Analysis of the crude mixture of products by ^{1}H NMR spectroscopy showed the diastereoselectivity of the reaction. The crude residue was purified by flash column chromatography to give the corresponding α-monofluorinated *N*-acyloxazolidinone

Table 2, Entry 2a. The title compound was prepared from (*S*)-3-hexanoyl-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.128 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 15% ethyl acetate in hexanes) to afford the product as a colorless oil (0.128 g, 0.47 mmol, 94%, single diastereomer): $[\alpha]_D^{24}$ +13.60 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.99 (d, J = 51.4 Hz, 1H), 4.10 (d, J = 3.0 Hz, 1H), 2.20 (dtd, J = 13.8, 6.9, 3.1 Hz, 1H), 1.87−1.76 (m, 2H), 1.55−1.33 (m, 10H), 1.07 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5 (d, J = 22.7 Hz), 153.1 (s), 89.1 (d, J = 178.5 Hz), 84.0 (s), 66.9 (s), 32.0 (d, J = 22.1 Hz), 29.5 (s), 28.9 (s), 26.9 (d, J = 1.9 Hz), 22.1 (s), 21.4 (s), 21.3 (s), 16.9 (s), 13.8 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −192.24 to −192.48 (m, 1F); HRMS (ESI+TOF) m/z calcd for $C_{14}H_{24}FNO_3Na$ $[M + Na]^+$ 296.1638, found 296.1633.

Table 3, Entry 3b. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-propionyloxazolidin-2-one (0.107 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 11% ethyl acetate in hexanes) to afford the product as a white solid (0.105 g, 0.46 mmol, 91%, single diastereomer: $[\alpha]_D^{26}$ +14.78 (*c* 0.42, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$); δ (ppm): 6.08 (dddd, J = 49.2, 6.5 Hz, 1H), 4.11 (d, J = 3.2 Hz, 1H), 2.19 (dddd, J = 13.9, 7.0, 3.2 Hz, 1H), 1.57 (dd, J = 23.8, 6.5 Hz, 3H), 1.53 (s, 3H), 1.39 (s, 3H), 1.06 (d, J = 7.0 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 172.8 (d, J = 22.4 Hz), 154.8 (s), 87.6 (d, J = 176.6 Hz), 85.9 (s), 68.6 (s), 31.3 (s), 30.7 (s), 23.2 (s), 23.1 (s), 19.9 (d, J = 23.6 Hz), 18.7 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −183.56 to −183.80 (m, 1F); HRMS (ESI+TOF) m/z calcd for $C_{11}H_{18}FNO_3Na$ $[M + Na]^+$ 254.1168, found 254.1164.

Table 3, Entry 3c. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(3-methylbutanoyl)oxazolidin-2-one (0.121 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr >98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 6% ethyl acetate in hexanes) to afford the product as a colorless oil (0.100 g, 0.39 mmol, 77%, single diastereomer): $[\alpha]_D^{26}$ +42.22 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.89 (dd, J = 49.6, 3.2 Hz, 1H), 4.11 (d, J = 3.0 Hz, 1H), 2.23−2.11 (m, 2H), 1.53 (s, 3H), 1.38 (s, 3H), 1.11 (d, J = 6.9 Hz, 3H), 1.08 (d, J = 7.0 Hz, 3H), 0.97 (dd, J = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7 (d, J = 23.0 Hz), 153.1 (s), 92.3 (dd, J = 181.2, 19.7 Hz), 83.9 (s), 67.03 (d, J = 19.1 Hz), 30.6 (t, J = 20.2 Hz), 29.5 (d, J = 19.9 Hz), 28.9 (d, J = 11.6 Hz), 21.4 (d, J = 6.6 Hz), 21.2 (s), 18.9 (d, J = 18.9 Hz), 16.9 (d, J = 17.4 Hz), 15.3 (d, J = 16.3 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ −204.40 (dd, J = 50.2, 28.3 Hz, 1F). HRMS (ESI+TOF) m/z calcd for $C_{13}H_{22}FNO_3Na$ $[M + Na]^+$ 282.1481, found 282.1489.

Table 3, Entry 3d. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(2-phenylacetyl)oxazolidin-2-one (0.138 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 96:4) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 3% diethyl ether in toluene−5% diethyl ether in toluene) to afford the product as a yellow solid (0.135 g, 0.46 mmol, 92%, single diastereomer): $[\alpha]_D^{26}$ +132.53 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 4.9 Hz, 2H), 7.38 (d, J = 5.4 Hz, 3H), 6.98 (d, J = 48.8 Hz, 1H), 3.99 (d, J = 3.1 Hz, 1H), 2.18 (dddd, J = 13.8, 6.9, 3.2 Hz, 1H), 1.44 (s, 3H), 1.12 (d, J = 7.0 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8 (d, J = 26.9 Hz), 152.9 (s), 133.4 (d, J = 20.2 Hz), 130.1 (d, J = 3.1 Hz), 128.8 (s), 128.8 (s), 128.5 (s), 128.5 (s), 88.9 (d, J = 180.2 Hz), 84.2 (s), 67.5 (s), 29.8 (s), 28.4 (s), 21.4 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −172.63 (d, J = 48.8 Hz, 1F); HRMS (ESI+TOF) m/z Calcd for $C_{16}H_{20}FNO_3Na$ $[M + Na]^+$ 316.1325, found 316.1324.

Table 3, Entry 3e. The title compound was prepared from (*S*)-3-(2-chloroacetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.117 g, 0.50

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mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 15% ethyl acetate in hexanes−25% ethyl acetate in hexanes) to afford the product as a white solid (84 mg, 0.34 mmol, 67%, single diastereomer): $[\alpha]_D^{26}$ +38.40 (*c* 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 51.6 Hz, 1H), 4.08 (d, *J* = 3.0 Hz, 1H), 2.24−2.18 (m, 1H), 1.56 (s, 3H), 1.45 (s, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (d, *J* = 26.3 Hz), 152.6 (s), 90.3 (d, *J* = 248.8 Hz), 85.2 (s), 67.7 (s), 29.5 (s), 28.9 (s), 21.5 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −149.72 (dd, *J* = 51.6, 3.6 Hz, 1F); HRMS (ESI +TOF) *m*/*z* Calcd for $C_{10}H_{15}FClNO_3Na$ $[M + Na]^+$ 274.0622, found 274.0610.

Table 3, Entry 3f. The title compound was prepared from (*S*)-4-benzyl-3-(2-cyclohexylacetyl)-5,5-dimethyloxazolidin-2-one (0.165 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 96:4) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 20% ethyl acetate in hexanes−25% ethyl acetate in hexanes) to afford the product as a white solid (0.160 g, 0.46 mmol, 92%, single diastereomer): $[\alpha]_D^{26}$ +19.05 (*c* 0.42, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33−7.27 (m, 4H), 7.24 (dd, *J* = 7.1 Hz, 1H), 5.83 (dd, *J* = 49.6, 3.6 Hz, 1H), 4.46 (dd, *J* = 9.9, 3.0 Hz, 1H), 3.25 (dd, *J* = 14.5, 2.8 Hz, 1H), 2.93 (dd, *J* = 14.5, 9.9 Hz, 1H), 1.84 (dddd, *J* = 58.1, 34.1, 16.5, 8.1 Hz, 4H), 1.65 (dd, *J* = 21.0, 12.8 Hz, 2H), 1.44−1.35 (m, 7H), 1.35−1.27 (m, 2H), 1.23−1.11 (m, 2H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 169.54 (d, *J* = 23.5 Hz), 152.1 (s), 136.6 (s), 129.0 (s), 128.8 (s), 126.9 (s), 92.1 (d, *J* = 180.8 Hz), 83.5 (s), 64.1 (s), 40.3 (d, *J* = 20.8 Hz), 35.0 (s), 28.6 (d, *J* = 3.3 Hz), 28.5 (s), 26.1 (d, *J* = 4.3 Hz), 26.0 (s), 25.8 (s), 25.8 (s), 22.2 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −201.83 (dd, *J* = 50.1, 26.9 Hz, 1F); HRMS (ESI+TOF) *m*/*z* calcd for $C_{20}H_{26}FNO_3Na$ $[M + Na]^+$ 370.1794, found 370.1800.

Table 3, Entry 3g. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(4-phenoxybutanoyl)oxazolidin-2-one (0.160 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1.5% diethyl ether in toluene) to afford the product as a white solid (0.155 g, 0.46 mmol, 92%, single diastereomer): $[\alpha]_D^{26}$ +31.81 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 6.95 (dd, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.21 (ddd, *J* = 49.0, 5.3 Hz, 1H), 4.22−4.14 (m, 2H), 4.13 (d, *J* = 3.0 Hz, 1H), 2.41 (ddd, *J* = 5.9 Hz, 1H), 2.37 (ddd, *J* = 5.9 Hz, 1H), 2.21 (ddd, *J* = 13.8, 8.4, 5.0 Hz, 1H), 1.53 (s, 3H), 1.41 (s, 3H), 1.08 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5 (d, *J* = 22.6 Hz), 158.4 (s), 153.0 (s), 129.4 (s), 121.1 (s), 114.8 (d, *J* = 0.7 Hz), 86.3 (d, *J* = 178.7 Hz), 84.2 (s), 66.9 (s), 62.9 (d, *J* = 3.3 Hz), 32.0 (d, *J* = 21.8 Hz), 29.4 (s), 28.9 (s), 21.4 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −192.47 to −192.69 (m, 1F); HRMS (ESI+TOF) *m*/*z* calcd for $C_{18}H_{24}FNO_4Na$ $[M + Na]^+$ 360.1587, found 360.1594.

Table 3, Entry 3h. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(3-phenylpropanoyl)oxazolidin-2-one (0.145 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 12% ethyl acetate in hexanes−15% ethyl acetate in hexanes) to afford the product as a colorless oil after purification (0.136 g, 0.44 mmol, 88%, single diastereomer): $[\alpha]_D^{26}$ +37.73 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34−7.29 (m, 4H), 7.25 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.22 (ddd, *J* = 49.5, 8.6, 3.3 Hz, 1H), 4.10 (d, *J* = 3.0 Hz, 1H), 3.14 (dddd, *J* = 22.9, 19.4, 14.3, 6.0 Hz, 2H), 2.19 (dddd, *J* = 13.7, 6.9, 3.2 Hz, 1H), 1.51 (s, 3H), 1.30 (s, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5 (d, *J* = 22.5 Hz), 152.9 (s), 135.1 (d, *J* = 1.9 Hz), 129.4 (s), 128.5 (s), 127.1 (s), 89.2 (d, *J* = 181.1 Hz), 84.0 (s), 66.7 (s), 38.5 (d, *J* = 22.5 Hz), 29.4 (s), 28.7 (s), 21.3 (s), 21.2 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −188.75 (ddd, *J* = 49.6, 33.6, 19.4 Hz, 1F); HRMS (ESI+TOF) *m*/*z* calcd for $C_{17}H_{22}FNO_3Na$ $[M + Na]^+$ 330.1481, found 330.1485.

Table 3, Entry 3i. The title compound was prepared from (*S*)-3-(3-(2-chlorophenyl)propanoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.162 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 96:4) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 12% diethyl ether in toluene−15% diethyl ether in toluene) to afford the product as a colorless oil (0.133 g, 0.39 mmol, 78%, single diastereomer): $[\alpha]_D^{25}$ +26.92 (*c* 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.25−7.18 (m, 2H), 6.32 (ddd, *J* = 48.7, 8.2, 4.2 Hz, 1H), 4.13 (d, *J* = 3.1 Hz, 1H), 3.46 (ddd, *J* = 18.6, 14.7, 8.1 Hz, 1H), 3.30 (ddd, *J* = 30.1, 14.6, 4.1 Hz, 1H), 2.21 (dddd, *J* = 13.8, 5.1 Hz, 1H), 1.53 (s, 3H), 1.35 (s, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3 (d, *J* = 22.6 Hz), 152.8 (s), 134.5 (s), 132.8 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 1.3 Hz), 129.6 (s), 128.6 (s), 126.9 (s), 87.7 (d, *J* = 181.0 Hz), 83.9 (s), 66.9 (s), 35.2 (d, *J* = 22.7 Hz), 29.5 (s), 28.9 (s), 21.5 (s), 21.3 (s), 16.9 (s). ^{19}F NMR (564 MHz, $CDCl_3$) δ −187.68 to −187.87 (m, 1F); HRMS (ESI+TOF) *m*/*z* calcd for $C_{17}H_{21}FClNO_3Na$ $[M + Na]^+$ 364.109, found 364.1102.

Table 3, Entry 3j. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(3-(3-(trifluoromethyl)phenyl)propanoyl)-oxazolidin-2-one (0.179 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1.5% diethyl ether in toluene) to afford the product as a white solid (0.115 g, 0.31 mmol, 61%, 98:2 dr): $[\alpha]_D^{26}$ +25.27 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.56−7.51 (m, 2H), 7.45 (dd, *J* = 7.7 Hz, 1H), 6.18 (ddd, *J* = 49.4, 8.7, 2.5 Hz, 1H), 4.12 (d, *J* = 2.9 Hz, 1H), 3.19 (dddd, *J* = 34.6, 23.1, 14.5, 5.7 Hz, 2H), 2.21 (dddd, *J* = 13.7, 6.9, 3.2 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2 (d, *J* = 22.5 Hz), 153.1 (s), 136.2 (d, *J* = 1.0 Hz), 133.0 (s), 130.9 (q, *J* = 32.2 Hz), 129.0 (s), 126.3 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 3.8 Hz), 124.0 (d, *J* = 273.42 Hz), 89.0 (d, *J* = 181.9 Hz), 84.3 (s), 66.9 (s), 38.2 (d, *J* = 22.5 Hz), 29.5 (s), 28.9 (s), 21.4 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −62.65 (s, 3F), −189.13 (ddd, *J* = 49.5, 34.0, 20.1 Hz, 1F); HRMS (ESI+TOF) *m*/*z* calcd for $C_{18}H_{21}F_4NO_3Na$ $[M + Na]^+$ 398.1355, found 398.1356.

Table 3, Entry 3k. The title compound was prepared from (*S*)-3-(5-(benzyloxy)pentanoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.174 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 15% ethyl acetate in hexanes hexanes−25% ethyl acetate in hexanes) to afford the product as a colorless oil (0.124 g, 0.34 mmol, 68%, single diastereomer): $[\alpha]_D^{25}$ +30.86 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35−7.30 (m, 4H), 7.29−7.26 (m, 1H), 6.10−5.99 (m, 1H), 4.49 (d, *J* = 2.8 Hz, 2H), 4.10 (d, *J* = 3.0 Hz, 1H), 3.57−3.49 (m, 2H), 2.20 (dddd, *J* = 13.9, 7.0, 3.2 Hz, 1H), 2.02−1.91 (m, 2H), 1.90−1.79 (m, 2H), 1.53 (s, 3H), 1.36 (s, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 171.9 (d, *J* = 22.7 Hz), 154.9 (s), 140.2 (s), 130.1 (s), 129.4 (s), 129.3 (s), 90.7 (d, *J* = 178.8 Hz), 85.9 (s), 74.6 (s), 70.9 (s), 68.7 (s), 31.3 (s), 31.0 (d, *J* = 22.1 Hz), 30.7 (s), 26.8 (d, *J* = 2.0 Hz), 23.2 (s), 23.1 (s), 18.8 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −192.32 (ddd, *J* = 50.1, 30.1, 24.4 Hz, 1F); HRMS (ESI+TOF) *m*/*z* Calcd for $C_{20}H_{28}FNO_4Na$ $[M + Na]^+$ 388.1900, found 388.1901.

Table 3, Entry 3l. The title compound was prepared from (*S*,*E*)-3-(but-2-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.113 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr >98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 15% ethyl acetate in hexanes−25% ethyl acetate in hexanes) to afford the product as a clear oil (56 mg, 0.23 mmol, 46%, single diastereomer): $[\alpha]_D^{25}$ +36.44 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.46 (dd, *J* = 48.7, 6.2 Hz, 1H), 6.07−5.97

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(m, 1H), 5.65 (dd, J = 17.3, 3.2 Hz, 1H), 5.46 (d, J = 10.7 Hz, 1H), 4.07 (d, J = 2.9 Hz, 1H), 2.19 (dddd, J = 13.7, 6.9, 3.1 Hz, 1H), 1.52 (s, 3H), 1.34 (s, 3H), 1.08 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4 (d, J = 24.7 Hz), 153.0 (s), 129.9 (d, J = 19.8 Hz), 121.8 (d, J = 10.9 Hz), 87.7 (d, J = 179.0 Hz), 84.3 (s), 67.2 (s), 29.5 (s), 28.9 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −186.01 (ddd, J = 49.0, 14.3, 3.6 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{12}H_{18}FNO_3Na$ $[M + Na]^+$ 266.1168, found 266.1158.

Table 3, Entry 3m. The title compound was prepared from (*S*)-3-(hept-6-enoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.134 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 98:2) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 9% ethyl acetate in hexanes−11% ethyl acetate in hexanes) to afford the product as a colorless oil (0.114 g, 0.40 mmol, 80%, single diastereomer): $[\alpha]_D^{26}$ +31.46 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.05−5.94 (m, 1H), 5.78 (dddd, J = 16.9, 10.2, 6.6 Hz, 1H), 4.99 (dd, J = 32.4, 13.7 Hz, 2H), 4.10 (d, J = 2.9 Hz, 1H), 2.19 (dddd, J = 10.3, 7.2, 3.3 Hz, 1H), 2.16−2.05 (m, 2H), 1.88−1.77 (m, 2H), 1.70−1.60 (m, 2H), 1.53 (s, 3H), 1.38 (s, 3H), 1.07 (d, J = 7.0 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3 (d, J = 22.6 Hz), 153.1 (s), 137.8 (s), 115.1 (s), 89.0 (d, J = 178.7 Hz), 84.0 (s), 66.9 (s), 32.9 (s), 31.7 (d, J = 22.1 Hz), 29.5 (s), 28.9 (s), 24.0 (d, J = 1.9 Hz), 21.4 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −192.17 to −192.40 (m, 1F); HRMS (ESI+TOF) m/z calcd for $C_{15}H_{24}FNO_3Na$ $[M + Na]^+$ 308.1638, found 308.1642.

Table 3, Entry 3n. The title compound was prepared from (*S*)-3-(hept-6-ynoyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.132 g, 0.50 mmol) following the standard α-fluorination procedure. The diastereoselectivity (dr 5:1) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 12% ethyl acetate in hexanes) to afford the product as a colorless oil (79 mg, 0.28 mmol, 56%, single diastereomer): $[\alpha]_D^{26}$ +30.73 (c 0.316, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$), δ ppm): 6.02 (ddd, J = 50.1, 7.4, 3.6 Hz, 1H), 4.11 (d, J = 2.8 Hz, 1H), 2.28 (dt, J = 16.7, 8.0 Hz, 2H), 2.24−2.18 (m, 1H), 2.06−1.89 (m, 3H), 1.78 (ddd, J = 22.5, 14.4, 7.0 Hz, 2H), 1.54 (s, 3H), 1.40 (s, 3H), 1.08 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 170.0 (d, J = 22.6 Hz), 153.1 (s), 88.8 (d, J = 179.1 Hz), 84.1 (s), 83.4 (s), 69.0 (s), 66.9 (s), 31.3 (d, J = 22.1 Hz), 29.5 (s), 29.0 (s), 23.8 (d, J = 2.0 Hz), 21.4 (s), 21.3 (s), 18.0 (s), 16.9 (s). ^{19}F NMR (564 MHz, $CDCl_3$) δ −192.21 (ddd, J = 50.0, 31.2, 23.3 Hz). HRMS (ESI+TOF) m/z calcd for $C_{15}H_{22}FNO_3Na$ $[M + Na]^+$ 306.1481, found 306.1476

Table 3, Entry 3o. The title compound was prepared from (*S*)-2-(3-(4-isopropyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-3-oxopropyl)-isoindoline-1,3-dione (0.179 g, 0.50 mmol) following the standard α−luorination procedure. The diastereoselectivity (dr 94:6) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 5% diethyl ether in toluene−10% diethyl ether in toluene) to afford the product as a white solid (0.132 g, 0.35 mmol, 70%, single diastereomer): $[\alpha]_D^{22}$ +13.20 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (ddd, J = 72.2, 5.3, 3.1 Hz, 4H), 6.22 (ddd, J = 46.7, 4.4, 1.9 Hz, 1H), 4.38 (ddd, J = 15.3, 10.7, 4.7 Hz, 1H), 4.26 (ddd, J = 31.6, 15.2, 1.6 Hz, 1H), 4.16 (d, J = 2.8 Hz, 1H), 2.19 (dddd, J = 6.8, 3.9 Hz, 1H), 1.69 (s, 3H), 1.55 (s, 3H), 1.01 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7 (s), 167.5 (d, J = 23.2 Hz), 153.5 (s), 134.1 (s), 131.7 (s), 123.5 (s), 85.9 (d, J = 183.8 Hz), 84.7 (s), 66.7 (s), 38.1 (d, J = 21.7 Hz), 29.4 (s), 28.8 (s), 21.8 (s), 21.2 (s), 17.0 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −194.2 (ddd, J = 44.1, 32.2, 11.3 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{19}H_{21}FN_2O_5Na$ $[M + Na]^+$ 399.1332, found 399.1339.

Standard Procedure for α-Fluorination of *N*-(Arylacetyl)-oxazolidinones. *Preparation $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$.* In a flame-dried reaction vessel, *i*-PrOH (0.184 mL, 2.40 mmol, 2.0 equiv) was added dropwise to $TiCl_4$ (1.0 M in CH_2Cl_2, 1.20 mL, 1.20 mmol, 1.0 equiv) at 23 °C over 5 min under argon (HCl gas evolution is observed). The mixture was stirred for an additional 10 min. Triethylamine (0.335 mL, 2.40 mmol, 2.0 equiv) was added dropwise to the solution at 23 °C over 10 min. The mixture was stirred for an additional 30 min (most of the initially formed white precipiate eventually redissolves).

α-Fluorination Reaction. In a separate flame-dried flask, $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$ (1 M in CH_2Cl_2, 0.875 mL, 0.875 mmol, 1.75 equiv) was added dropwise to the solution of *N*-arylacetyl oxazolidinone (0.50 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C under argon (solution should become a deep red upon complete addition). The reaction mixture was stirred for 5 min. Triethylamine (0.14 mL, 1.0 mmol, 2.0 equiv) was added dropwise to the reaction mixture at 0 °C, and the solution was stirred for 30 min. *N*-Fluorobenzenesulfonimide (0.315 g, 1.00 mmol, 2.0 equiv) was added in one portion to the reaction at 0 °C (CAUTION: vigorous gas evolution may be observed upon addition). The reaction mixture was warmed to 23 °C and stirred for 1 h. After filtration of the reaction mixture through a 1.5 cm silica plug column, the plug was rinsed with CH_2Cl_2 (10 mL) and EtOAc (50 mL). The combined filtrate was concentrated in vacuo. Analysis of the crude mixture of products by ^{1}H NMR spectroscopy show the diastereoselectivity of the reaction. The residue was purified by flash column chromatography to give the desired α-fluorinated product.

Table 5, Entry 5a. The title compound was prepared from (*S*)-4-isopropyl-3-(2-(4-methoxyphenyl)acetyl)-5,5-dimethyloxazolidin-2-one (0.153 g, 0.50 mmol) following the standard α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 93:7) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 4% diethyl ether in toluene) to afford the product as a colorless oil (0.102 g, 0.31 mmol, 63%, single diastereomer): $[\alpha]_D^{26}$ +141.92 (c 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 6.91 (d, J = 48 Hz, 1 H), 6.89 (d, J = 8.5 Hz, 2H), 4.01 (d, J = 3.0 Hz, 1H), 3.81 (s, 3H), 2.18 (dddd, J = 13.8, 6.9, 3.2 Hz, 1H), 1.45 (s, 3H), 1.12 (d, J = 7.1 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H), 0.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1 (d, J = 27.8 Hz), 160.9 (d, J = 2.9 Hz), 152.9 (s), 130.3 (s), 130.2 (s), 125.6 (d, J = 21.0 Hz), 114.2 (s), 114.1 (s), 88.6 (d, J = 179.9 Hz), 84.1 (s), 67.5 (s), 55.3 (s), 29.50 (s), 28.5 (s), 21.5 (s), 21.3 (s), 17.0 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −169.50 (d, J = 49.4 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{22}FNO_4Na$ $[M + Na]^+$ 346.1431, found 346.1439.

Table 5, Entry 5b. The title compound was prepared from (*S*)-3-(2-(4-fluorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.146 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 10:1) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1% diethyl ether in toluene) to afford the product as a white solid (0.110 g, 0.36 mmol, 71%, single diastereomer): $[\alpha]_D^{25}$ +141.77 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53−7.49 (m, 2H), 7.06 (dd, J = 8.4 Hz, 2H), 6.94 (d, J = 48.6 Hz, 1H), 3.99 (d, J = 2.9 Hz, 1H), 2.17 (ddd, J = 10.5, 6.8, 3.3 Hz, 1H), 1.44 (s, 3H), 1.10 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.97 (s, 3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7 (d, J = 27.2 Hz), 163.6 (dd, J = 250.0, 3.2 Hz), 152.9 (s), 130.7 (d, J = 4.3 Hz), 130.6 (d, J = 4.3 Hz), 129.5 (dd, J = 20.9, 3.3 Hz), 115.9 (d, J = 1.7 Hz), 115.7 (d, J = 1.7 Hz), 88.0 (d, J = 180.5 Hz), 84.3 (s), 67.4 (s), 29.4 (s), 28.4 (s), 21.4 (s), 21.2 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −110.25 to −110.31 (m, 1F), −171.32 (dd, J = 48.6, 5.4 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{16}H_{19}F_2NO_3Na$ $[M + Na]^+$ 334.1234, found 334.1240.

Table 5, Entry 5c. The title compound was prepared from (*S*)-3-(2-(4-chlorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.155 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 10:1) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 3% diethyl ether in toluene−5% diethyl ether in toluene) to afford the product as green crystals (0.100 g, 0.31 mmol, 61%, 10:1 dr, single diastereomer): $[\alpha]_D^{26}$ +125.38 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 48.5 Hz, 1H), 4.00 (d, J = 2.7 Hz, 1H), 2.21−2.15 (m, 1H), 1.45 (s, 3H), 1.11 (d, J = 7.0 Hz, 3H), 1.00−0.99 (m, 6H); ^{13}C NMR (151

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MHz, $CDCl_3$) δ 168.5 (d, J = 26.9 Hz), 152.9 (s), 136.2 (d, J = 3.5 Hz), 131.9 (d, J = 20.6 Hz), 129.9 (s), 129.9 (s), 129.1 (s), 129.0 (s), 88.0 (d, J = 180.6 Hz), 84.3 (s), 67.5 (s), 29.5 (s), 28.5 (s), 21.4 (s), 21.2 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −172.51 (d, J = 48.5 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{16}H_{19}FClNO_3Na$ $[M + Na]^+$ 350.0935, found 350.0928.

Table 5, Entry 5d. The title compound was prepared from (*S*)-3-(2-(3-fluorophenyl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.147 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 93:7) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1% diethyl ether in toluene) to afford the product as a white solid (0.107 g, 0.35 mmol, 69%, single diastereomer): $[\alpha]_D^{26}$ +126.11 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.29 (m, 2H), 7.26−7.22 (m, 1H), 7.08 (ddddd, J = 9.6, 5.6, 1.4 Hz, 1H), 6.98 (d, J = 48.5 Hz, 1H), 3.99 (d, J = 3.2 Hz, 1H), 2.18 (dddd, J = 13.9, 6.9, 3.2 Hz, 1H), 1.45 (s, 3H), 1.10 (d, J = 7.0 Hz, 3H), 1.02−0.97 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3 (d, J = 26.6 Hz), 162.6 (dd, J = 247.8, 1.5 Hz), 152.9 (s), 135.7 (dd, J = 20.6, 7.4 Hz), 130.4 (dd, J = 8.1, 1.4 Hz), 124.1 (dd, J = 4.8, 3.2 Hz), 117.2 (dd, J = 21.1, 2.8 Hz), 115.3 (dd, J = 22.7, 4.8 Hz), 87.9 (dd, J = 181.1, 1.8 Hz), 84.4 (s), 67.5 (s), 29.5 (s), 28.5 (s), 21.4 (s), 21.2 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −111.55 (td, J = 9.6, 6.0 Hz, 1F), −173.59 (d, J = 48.9 Hz); HRMS (ESI+TOF) m/z calcd for $C_{16}H_{19}F_2NO_3Na$ $[M + Na]^+$ 334.1231, found 334.1241.

Table 5, Entry 5e. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(2-(3-(trifluoromethyl)phenyl)acetyl)-oxazolidin-2-one (0.172 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 10:1) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1% diethyl ether in toluene) to afford the product as a white solid (0.117 g, 0.33 mmol, 65%, 10:1 dr, single diastereomer): $[\alpha]_D^{26}$ +140.82 (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.72 (m, 2H), 7.67 (d, J = 7.4 Hz, 1H), 7.54 (dd, J = 7.8 Hz, 1H), 7.04 (d, J = 48.5 Hz, 1H), 4.03 (d, J = 3.2 Hz, 1H), 2.20 (dddd, J = 13.9, 6.9, 3.2 Hz, 1H), 1.46 (s, 3H), 1.12 (d, J = 7.0 Hz, 3H), 1.01 (d, J = 7.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2 (d, J = 26.4 Hz), 152.9 (s), 134.6 (d, J = 20.6 Hz), 132.2 (dd, J = 4.5, 1.1 Hz), 131.8−130.9 (m), 129.4 (d, J = 1.2 Hz), 126.9−126.6 (m), 125.02−124.76 (m), 123.6 (d, J = 272.5 Hz), 88.1 (d, J = 181.2 Hz), 84.5 (s), 67.5 (s), 29.5 (s), 28.4 (s), 21.4 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −62.85 (s, 3F), −173.31 (d, J = 48.5 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{19}F_4NO_3Na$ $[M + Na]^+$ 384.1199, found 384.1196.

Table 5, Entry 5f. The title compound was prepared from (*S*)-4-isopropyl-5,5-dimethyl-3-(2-(3-phenoxyphenyl)acetyl)oxazolidin-2-one (0.184 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 95:5) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1% diethyl ether in toluene) to afford the product as a white solid (0.119 g, 0.31 mmol, 62%, single diastereomer): $[\alpha]_D^{26}$ +148.96 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$); δ (ppm): 7.30−7.25 (m, 3H), 7.19 (d, J = 7.9 Hz, 1H), 7.13 (s, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.1 Hz, 1H), 6.90 (dd, J = 28.3, 20.4 Hz, 3H), 3.94 (d, J = 3.0 Hz, 1H), 2.13 (dtd, J = 13.8, 6.9, 3.1 Hz, 1H), 1.40 (s, 3H), 1.05 (d, J = 7.0 Hz, 3H), 0.97 (s, 3H), 0.94 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5 (d, J = 26.7 Hz), 157.6 (d, J = 1.6 Hz), 156.7 (s), 152.9 (s), 135.2 (d, J = 20.3 Hz), 130.2 (d, J = 1.6 Hz), 129.8 (s), 123.7 (s), 123.2 (d, J = 4.6 Hz), 120.4 (d, J = 3.0 Hz), 118.9 (s), 118.8 (d, J = 4.6 Hz), 88.5 (d, J = 180.8 Hz), 84.3 (s), 67.5 (s), 29.5 (s), 28.5 (s), 21.4 (s), 21.3 (s), 17.0 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −172.83 (d, J = 48.8 Hz, 1F). HRMS (ESI+TOF) m/z calcd for $C_{22}H_{24}FNO_4Na$ $[M + Na]^+$ 408.1587, found 408.1600.

Table 5, Entry 5g. The title compound was prepared from (*S*)-4-isopropyl-3-(2-(2-methoxyphenyl)acetyl)-5,5-dimethyloxazolidin-2-one (0.153 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 10:1) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1.5% diethyl ether in toluene−3% diethyl ether in toluene) to afford the product as a colorless oil (0.129 g, 0.40 mmol, 80%, single diastereomer: $[\alpha]_D^{26}$ +158.73 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (dd, J = 7.8 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 48.5 Hz, 1H), 6.94 (dd, J = 14.7, 7.7 Hz, 2H), 4.11 (d, J = 3.0 Hz, 1H), 3.86 (s, 3H), 2.20 (dddd, J = 13.7, 6.9, 2.9 Hz, 1H), 1.46 (s, 3H), 1.21 (s, 3H), 1.11 (d, J = 7.0 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9 (d, J = 25.6 Hz), 157.7 (d, J = 3.7 Hz), 152.6 (s), 131.4 (d, J = 3.4 Hz), 128.1 (d, J = 5.0 Hz), 122.4 (d, J = 19.1 Hz), 120.5 (d, J = 1.2 Hz), 111.4 (s), 84.8 (d, J = 177.7 Hz), 83.8 (s), 67.1 (s), 55.8 (s), 29.5 (s), 28.6 (s), 21.4 (s), 21.3 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −177.76 (d, J = 48.4 Hz, 1F); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{22}FNO_4Na$ $[M + Na]^+$ 346.1431, found 346.1436.

Table 5, Entry 5h. Preparation $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$. In a flame-dried reaction vessel, *i*-PrOH (0.184 mL, 2.40 mmol, 2.0 equiv) was added dropwise to $TiCl_4$ (1.0 M in CH_2Cl_2, 1.20 mL, 1.20 mmol, 1.0 equiv) at 23 °C over 5 min under argon (HCl gas evolution is observed). The mixture was stirred for an additional 10 min. Triethylamine (0.335 mL, 2.40 mmol, 2.0 equiv) was added dropwise to the solution at 23 °C over 10 min. The mixture was stirred for an additional 30 min (most of the initially formed white precipitate eventually redissolves).

α-Fluorination Reaction. In a separate flame-dried flask, $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$ (1 M in CH_2Cl_2, 0.33 mL, 0.33 mmol, 1.75 equiv) was added dropwise to the solution of (*S*)-3-(2-(furan-3-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (50 mg, 0.19 mmol, 1.0 equiv) in CH_2Cl_2 (0.38 mL) at 0 °C under argon (solution should become a deep red upon complete addition). The reaction mixture was stirred for 2 min. Triethylamine (53 μL, 0.38 mmol, 2.0 equiv) was added dropwise to the reaction mixture at 0 °C, and the solution was stirred for 2 min. *N*-Fluorobenzenesulfonimide (0.120 g, 0.38 mmol, 2.0 equiv) was added in one portion to the reaction at 0 °C (CAUTION: vigorous gas evolution may be observed upon addition). The reaction mixture was warmed to 23 °C and stirred for 30 min. After filtration of the reaction mixture through a 1.5 cm silica plug column, the plug was rinsed with CH_2Cl_2 (10 mL) and EtOAc (50 mL). The combined filtrate was then concentrated in vacuo. The diastereoselectivity (10:1) was determined by ^{1}H NMR analysis of the crude mixture of products. The residue was purified by column chromatography (silica, 4% diethyl ether in toluene) to afford the product as a white solid (29 mg, 0.103 mmol, 54%, single diastereomer): $[\alpha]_D^{20}$ +61.94 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 4.0 Hz, 1H), 7.41 (d, J = 1.1 Hz, 1H), 6.99 (d, J = 48.6 Hz, 1H), 6.52 (s, 1H), 4.02 (d, J = 2.5 Hz, 1H), 2.22−2.13 (m, 1H), 1.48 (s, 3H), 1.10 (d, J = 5.8 Hz, 6H), 1.00 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6 (d, J = 27.2 Hz), 153.0 (s), 143.8 (d, J = 7.4 Hz), 143.3 (d, J = 8.7 Hz), 118.9 (d, J = 24.2 Hz), 108.8 (s), 84.3 (s), 82.0 (dd, J = 177.6, 10.1 Hz), 67.3 (d, J = 12.0 Hz), 29.5 (s), 28.6 (s), 21.4 (s), 21.3 (d, J = 2.7 Hz), 16.9 (d, J = 4.1 Hz).^{19}F NMR (564 MHz, $CDCl_3$) δ −176.65 (d, J = 4.8 Hz), −176.73 (d, J = 4.8 Hz); HRMS (ESI+TOF) m/z calcd for $C_{14}H_{18}FNO_4Na$ $[M + Na]^+$ 306.1118, found 306.1122.

Table 5, Entry 5i. The title compound was prepared from (*S*)-3-(2-(benzo[*d*][1,3]dioxol-5-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.160 g, 0.50 mmol) following the standard procedure for α-fluorination of *N*-(arylacetyl)oxazolidinones. The diastereoselectivity (dr 10:1) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 1.5% diethyl ether in toluene−2% diethyl ether in toluene) to afford the product as a white solid (0.107 g, 0.32 mmol, 64%, single diastereomer): $[\alpha]_D^{26}$ +138.76 (c 0.83, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, J = 9.2 Hz, 2H), 6.88 (d, J = 48.7 Hz, 1H), 6.80 (d, J = 7.8 Hz, 1H), 5.98 (s, 2H), 4.01 (d, J = 3.1 Hz, 1H), 2.21−2.15 (m, 1H), 1.47 (s, 3H), 1.12 (d, J = 7.0 Hz, 3H), 1.05 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 206.9 (s), 168.9 (d, J = 27.8 Hz), 152.9 (s), 148.5 (dd, J = 224.9, 2.4 Hz), 127.1 (d, J = 20.9 Hz), 123.1 (d, J = 5.2 Hz), 108.6 (dd, J = 89.3, 2.9 Hz), 101.5 (s), 88.5 (d, J = 180.6 Hz), 84.2 (s), 67.5 (s), 30.9 (s), 29.5 (s), 28.6 (s), 21.5

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(s), 21.3 (s), 17.0 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −169.32 to −169.84 (m, 1F); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{20}FNO_5Na$ $[M + Na]^+$ 360.1223, found 360.1226

Table 5, Entry 5j. Preparation $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$. In a flame-dried reaction vessel, *i*-PrOH (0.184 mL, 2.40 mmol, 2.0 equiv) was added dropwise to $TiCl_4$ (1.0 M in CH_2Cl_2, 1.20 mL, 1.20 mmol, 1.0 equiv) at 23 °C over 5 min under argon (HCl gas evolution is observed). The mixture was stirred for an additional 10 min. Triethylamine (0.335 mL, 2.40 mmol, 2.0 equiv) was added dropwise to the solution at 23 °C over 10 min. The mixture was stirred for an additional 30 min (most of the initially formed white precipiate eventually redissolves).

α-Fluorination Reaction. In a separate flame-dried flask, $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$ (1 M in CH_2Cl_2, 0.33 mL, 0.33 mmol, 1.75 equiv) was added dropwise to the solution of (*S*)-3-(2-(benzo[d]oxazol-5-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.10 g, 0.31 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL) at 0 °C under argon (solution should become a deep red upon complete addition). The reaction mixture was stirred for 2 min. Triethylamine (86 μL, 0.62 mmol, 2.0 equiv) was added dropwise to the reaction mixture at 0 °C, and the solution was stirred for 2 min. *N*-Fluorobenzenesulfonimide (0.195 g, 0.62 mmol, 2.0 equiv) was added in one portion to the reaction at 0 °C (CAUTION: vigorous gas evolution may be observed upon addition). The reaction mixture was warmed to 23 °C and stirred for 1 h. After filtration of the reaction mixture through a 1.5 cm silica plug column, the plug was rinsed with CH_2Cl_2 (10 mL) and EtOAc (50 mL). The combined filtrate was then concentrated in vacuo. The diastereoselectivity (dr 92:8) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by column chromatography (silica, 4% diethyl ether in toluene) to afford the product as a white solid (0.119 g, 0.31 mmol, 87%, mixture of diastereomers): $[\alpha]_D^{21}$ +115.77 (*c* 1.0, $CHCl_3$);^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.98 (s, 1H), 7.61 (s, 2H), 7.10 (d, *J* = 48.6 Hz, 1H), 4.03 (d, *J* = 2.9 Hz, 1H), 2.25−2.15 (m, 1H), 1.44 (s, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.95 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7 (d, *J* = 27.1 Hz), 153.4 (s), 152.9 (s), 150.9−150.7 (m), 140.4 (s), 130.4 (d, *J* = 20.8 Hz), 126.5 (d, *J* = 4.2 Hz), 121.2 (d, *J* = 4.6 Hz), 111.4 (d, *J* = 1.5 Hz), 88.6 (d, *J* = 180.9 Hz), 84.3 (s), 67.4 (s), 29.50 (s), 28.6 (s), 21.4 (s), 21.2 (s), 16.9 (s).^{19}F NMR (564 MHz, $CDCl_3$) δ −169.22 (s), −169.31 (s); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{19}FN_2O_4Na$ $[M + Na]^+$ 357.1227, found 357.1224.

Table 5, Entry 5k. Preparation $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$. In a flame-dried reaction vessel, *i*-PrOH (0.184 mL, 2.40 mmol, 2.0 equiv) was added dropwise to $TiCl_4$ (1.0 M in CH_2Cl_2, 1.20 mL, 1.20 mmol, 1.0 equiv) at 23 °C over 5 min under argon (HCl gas evolution is observed). The mixture was stirred for an additional 10 min. Triethylamine (0.335 mL, 2.40 mmol, 2.0 equiv) was added dropwise to the solution at 23 °C over 10 min. The mixture was stirred for an additional 30 min (most of the initially formed white precipiate eventually redissolves).

α-Fluorination Reaction. In a separate flame-dried flask, $TiCl_2(OPr\text{-}i)_2{\cdot}2Et_3NHCl$ (1 M in CH_2Cl_2, 0.44 mL, 0.44 mmol, 1.75 equiv) was added dropwise to the solution of (*S*)-3-(2-(benzo[*d*]oxazol-2-yl)acetyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one (0.158 g, 0.50 mmol, 1.0 equiv) in CH_2Cl_2 (1.0 mL) at 0 °C under argon (solution should become a deep red upon complete addition). The reaction mixture was stirred for 2 min. Triethylamine (0.14 mL, 1.0 mmol, 2.0 equiv) was added dropwise to the reaction mixture at 0 °C, and the solution was stirred for 2 min. *N*-Fluorobenzenesulfonimide (0.14 mL, 1.0 mmol, 2.0 equiv) was added in one portion to the reaction at 0 °C (CAUTION: vigorous gas evolution may be observed upon addition). The reaction mixture was warmed to 23 °C and stirred for 30 min. After filtration of the reaction mixture through a 1.5 cm silica plug column, the plug was rinsed with CH_2Cl_2 (10 mL) and EtOAc (50 mL). The combined filtrate was then concentrated in vacuo. The diastereoselectivity (dr 2:1) was determined by ^{1}H NMR analysis of the crude product. The residue was purified by column chromatography (silica, 4% diethyl ether in toluene) to afford the product as a white solid (0.105 g, 0.32 mmol, 63%, single diastereomer: $[\alpha]_D^{21}$ +77.97 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 50.4 Hz, 1H), 4.30 (d, *J* = 3.0 Hz, 1H), 2.24 (dq, *J* = 6.8, 3.8 Hz, 1H), 1.59 (s, 3H), 1.53 (s, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (d, *J* = 23.3 Hz), 158.1 (d, *J* = 21.8 Hz), 153.7 (s), 151.1 (s), 126.5 (d, *J* = 1.2 Hz), 124.9 (s), 120.8 (d, *J* = 0.9 Hz), 111.3 (d, *J* = 0.9 Hz), 85.7 (s), 82.9 (d, *J* = 183.5 Hz), 67.3 (s), 29.6 (s), 28.8 (s), 21.6 (s), 21.4 (s), 16.9 (s); ^{19}F NMR (564 MHz, $CDCl_3$) δ −185.48 (s), −185.57 (s); HRMS (ESI+TOF) m/z calcd for $C_{17}H_{19}FN_2O_4Na$ $[M + Na]^+$ 357.1227, found 357.1216.

*(S)-2-Fluoro-2-phenylethanol.(**7a**).* Sodium borohydride (63.7 mg, 1.68 mmol) was added to a solution of the substrate (0.175 g, 0.561 mmol) in a 3:1 mixture of THF:H_2O (8.50 mL) at 0 °C, and the reaction mixture was stirred for 10 min. The reaction mixture was warmed to rt and stirred an additional 1 h. The reaction was quenched with aqueous 1 M HCl (5 mL). The layers were separated. The aqueous layer was extracted with diethyl ether (3 × 5 mL). The organic layers were combined and washed with brine, dried with sodium sulfate, and concentrated in vacuo, and the residue was purified by column chromatography (silica, 50% diethyl ether in pentane−80% diethyl ether in pentane) to afford the desired alcohol (72.2 mg, 0.52 mmol, 93%) and the purified oxazolidinone (83 mg, 0.53 mmol, 95%): $[\alpha]_D^{23}$ +51.03 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dt, *J* = 17.5, 7.3 Hz, 5H), 5.57 (ddd, *J* = 48.7, 7.8, 2.8 Hz, 1H), 3.98−3.89 (m, 1H), 3.83 (dd, *J* = 30.1, 12.5 Hz, 1H), 2.38 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3 (d, *J* = 19.6 Hz), 128.7 (d, *J* = 1.7 Hz), 128.5 (s), 125.7 (d, *J* = 7.0 Hz), 94.8 (d, *J* = 171.9 Hz), 66.5 (d, *J* = 24.7 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ −186.89 (ddd, *J* = 49.5, 30.6, 19.1 Hz); HRMS (EI) m/z calcd for C_8H_9FO $[M]^+$ 140.0637, found 140.0634.

Determination of er for the Product. 2-Naphthoyl chloride (3.0 equiv) was added to a solution of the purified alcohol, triethylamine (3.0 equiv), and 4-(dimethylamino)pyridine (0.5 equiv) in dichloromethane (0.1 M) at 0 °C. After 10 min, the reaction mixture was warmed to rt and stirred for 30 min. The reaction was quenched with aqueous ammonium chloride, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried with sodium sulfate, concentrated in vacuo, and purified by column chromatography chromatography (silica, 15% ethyl acetate in hexanes) to afford the desired naphthoyl ester derivative. HPLC analysis of the 2-naphthoyl ester derivative (OJ-H, 2.5% ^{i}PrOH−hexanes, 1.0 mL/min, 254 nm) indicated an er of 0.8:99.2: t_R (minor) = 37.5 min, t_R (major) = 45.5 min.

*(S)-2-Fluoro-2-phenylacetic acid (**7b**).* Lithium hydroxide monohydrate (32.1 mg, 0.765 mmol) was added to a solution of the substrate (0.117 g, 0.373 mmol), hydrogen peroxide (30%, 0.40 mL), and water (0.40 mL) in THF (1.50 mL) at 0 °C, and the mixture was stirred for 5 min. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with aqueous sodium sulfite (1.5 M, 3.0 mL) and HCl (1 M, 3.0 mL) and allowed to stir for 5 min until two transparent layers were visible. The layers were separated, and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The organic layer was extracted with aqueous sodium hydroxide (3 M, 3 × 3 mL) and water (3 × 5 mL). The aqueous extractions were combined and set aside. The organic layer was washed with HCl (1 M) and brine, dried with sodium sulfate, and concentrated in vacuo to recover the oxazolidinone auxiliary (56.6 mg, 0.36 mmol, 97%). The previously saved aqueous layers were acidified with aqueous HCl (1 M). The aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and concentrated in vacuo to afford the desired pure carboxylic acid (55.2 mg, 0.358 mmol, 96%): $[\alpha]_D^{21}$ +116.06 (c 0.843, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.46 (d, *J* = 34.7 Hz, 5H), 5.83 (d, *J* = 47.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1 (d, *J* = 28.0 Hz), 133.4 (d, *J* = 20.5 Hz), 129.9 (d, *J* = 30.1 Hz), 128.8 (d, *J* = 31.6 Hz), 126.7 (d, *J* = 33.8 Hz), 88.8 (dd, *J* = 186.7, 15.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ

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−180.78 (d, J = 47.8 Hz); HRMS (EI) m/z calcd for $C_8H_7FO_2[M]^+$ 154.0430, found 154.0434.

Determination of er for the Acid. A solution of the (*S*)-2-fluoro-2-phenylacetic acid (1.0 equiv) in diethyl ether (0.2 M) was added to a solution of lithium aluminum hydride (4.0 equiv) in diethyl ether (0.5 M) at 0 °C, and the mixture was stirred for 10 min. The reaction mixture was warmed to room temperature, stirred for 10 min, and quenched using the Feiser workup: the reaction mixture was cooled to 0 °C, H_2O (1:1 volume/weight to $LiAlH_4$) was added dropwise (CAUTION: highly exothermic), and the mixture was stirred for 5 min. A solution (1:1 by volume/weight to $LiAlH_4$) of aqueous NaOH (15 wt % NaOH in H_2O) was added dropwise and the mixture stirred for 5 min. Finally, H_2O (3:1 by volume/weight to $LiAlH_4$) was added dropwise. The solution was warmed to room temperature and allowed to stir for 1 h until a white precipitate formed. The reaction mixture was filtered and concentrated in vacuo. No further purification was done. 2-Naphthoyl chloride (5.0 equiv) was added to a solution of the crude alcohol, triethylamine (5.0 equiv), and 4-dimethylaminopyridine (1.0 equiv) in dichloromethane (0.1 M) at 0 °C. After 10 min, the reaction mixture was warmed to room temperature and stirred for 30 min. The mixture was quenched with aqueous ammonium chloride, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried with sodium sulfate, concentrated in vacuo, and purified by column chromatography (silica, 12.5% ethyl acetate in hexanes) to afford the desired naphthoyl ester derivative. HPLC analysis of the 2-naphthoyl ester derivative (OJ-H, 2.5% ^{i}PrOH–hexanes, 1.0 mL/min, 254 nm) indicated er 1.1:98.9: t_R (minor) = 35.9 min, t_R (major) = 46.4 min.

■ ASSOCIATED CONTENT

Supporting Information

Details on general experimental methods. ^{1}H and ^{13}C NMR spectra for all compounds and ^{19}F NMR spectra for fluorinated products. Chiral HPLC traces to determine ee for compounds **7a** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Triethylamine: \$0.10/g (\$0.01/mmol, EMD); CH_2Cl_2: \$0.002/g (\$0.0002/mmol, Fisher).

(15) Reaction cost calculated based on typical 0.50 mmol scale: 0.75 mmol $TiCl_4$ ($0.0075), 1.00 mmol Et_3N ($0.01), 1.00 mmol NFSI ($0.35), 27.3 mmol CH_2Cl_2 ($0.0055). Starting material is not factored into costs.
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