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Hypervalent Iodine Mediated Oxidative Cyclization of Acrylamide *N*-Carbamates to 5,5-Disubstituted Oxazolidine-2,4-diones

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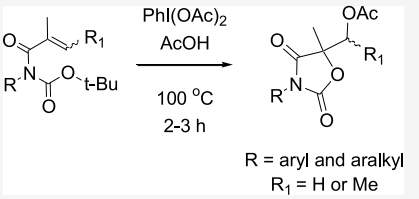
ABSTRACT: A metal-free oxidative cyclization of *N*-Boc-acrylamides with (diacetoxyiodo)benzene in acetic acid produced 5,5-disubstituted oxazolidine-2,4-diones with the formation of a C−O bond in moderate to excellent yields. In addition, the reaction was diastereospecific with *N*-Boc-2,3-dimethylacrylamides and proceeded with phenyl migration in the case of an *N*-Boc-2-phenylacrylamide to generate a 5-acetoxy-5-benzyloxazolidine-2,4-dione.



In recent years, transition metal (TM) catalyzed and metal-free oxidative cyclization via C−H activation of *N*-phenylacrylamides has emerged as an efficient method for the construction of 3,3-disubstituted oxindoles (Figure 1A).[1−3] For example, Jaegli et al. utilized Pd-catalysis to affect the reaction rate, and this was further used in a spirooxindole synthesis.[4] In addition, Cao et al.[5] reported a metal-free example of this reaction, while Zhang et al. have generated aminooxylated oxindoles using a similar strategy.[6] Alternatively, *N*-Boc acrylamides have been found to undergo cyclization with the alkene generating a variety of 5,5′-disubstituted oxazolidine-2,4-diones with the introduction of C−F, C−N, and C−I bonds (Figure 1B).[7−9] We now report that metal-free hypervalent iodine mediated oxidative cyclization of *N*-Boc-acrylamides provides an efficient route to 5,5-disubstituted oxazolidine-2,4-diones with the formation of a C−O bond (Figure 1C).[10] Furthermore, the reaction takes place with an array of N-substituents, is diastereospecific with *N*-Boc-2,3-dimethylacrylamides, and occurs with phenyl migration in the case of an *N*-Boc-2-phenylacrylamide.

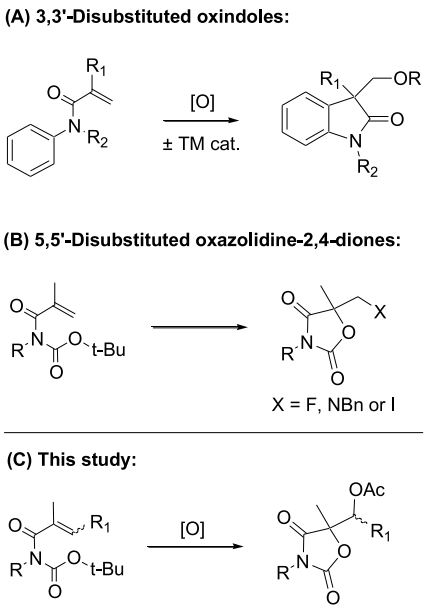


Figure 1. Previous studies on (A) TM catalyzed and metal-free oxidative cyclizations of *N*-phenylacrylamides and (B) Cyclizations of *N*-Boc-acrylamides with the formation of C−F, C−N, and C−I bonds. (C) Current study on metal-free oxidative cyclizations of *N*-Boc-acrylamides producing 5,5-disubstituted oxazolidine-2,4-diones with the introduction of a C−O bond.

5,5-Disubstituted oxazolidine-2,4-diones are an interesting class of heterocycles that has been recognized as a "privileged medicinal chemistry scaffold"[11] found in various pharmacologically active compounds.[12−14] For example, 5,5-disubstituted oxazolidine-2,4-diones have been reported as potent and selective mineralocorticoid receptor antagonists with potential use in the treatment of chronic kidney disease, hypertension, and congestive heart failure.[15−17] For these reasons, the efficient construction of 5,5-disubstituted oxazolidine-2,4-diones is of interest within the synthetic organic chemistry community.

N-2,3-Dimethoxybenzyl-*N*-Boc-methacrylamide (**1**) was selected as the initial substrate for this study. Exposure of this material, at a concentration of 0.1 M in acetic acid, to 10 mol % $Pd(OAc)_2$ and 2 equiv of $PhI(OAc)_2$ at 100 °C for 3 h generated 5,5-disubstituted oxazolidine-2,4-dione **2** as the

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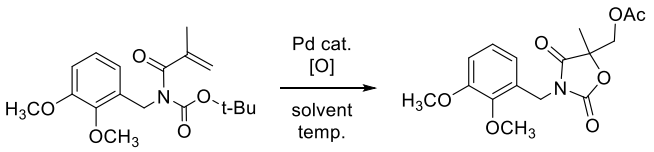
Table 1. Analysis of Reaction Conditions and Reagents[a]



1 2

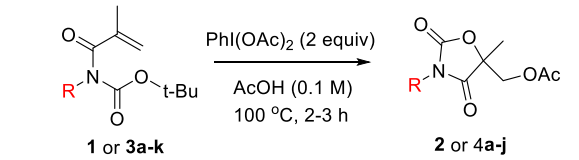
Entry	Oxidant	Catalyst	Solvent	Temp (°C)	Time (h)	Yield of **2** (%)
1	$PhI(OAc)_2$	$Pd(OAc)_2$	AcOH	100	3	70
2	$PhI(OAc)_2$	$Pd(OAc)_2$	AcOH	rt	24	75
3	$PhI(OAc)_2$	$Pd(OAc)_2$	CH_3CN	100	27	<5
4	$PhI(OAc)_2$	$Pd(OAc)_2$	1,4-dioxane	100	72	n.d.[b]
5	Oxone	$Pd(OAc)_2$	AcOH	100	2	22
6	$K_2S_2O_8$	$Pd(OAc)_2$	AcOH	100	2	n.d.
7	$PhI(OAc)_2$	None	AcOH	100	16	71
8	$PhI(OAc)_2$	None	AcOH	100	3	83
9	$PhI(OAc)_2$[c]	None	AcOH	100	6	48
10[d]	$PhI(OAc)_2$	None	AcOH	100	3	84

[a]Reaction conditions: **1** (1.0 equiv), oxidant (2.0 equiv), catalyst (10 mol %) in solvent (0.1 M under argon). [b]n.d. = not detected. [c]1.0 equiv. [d]Methyl carbamate of **1** used as substrate.

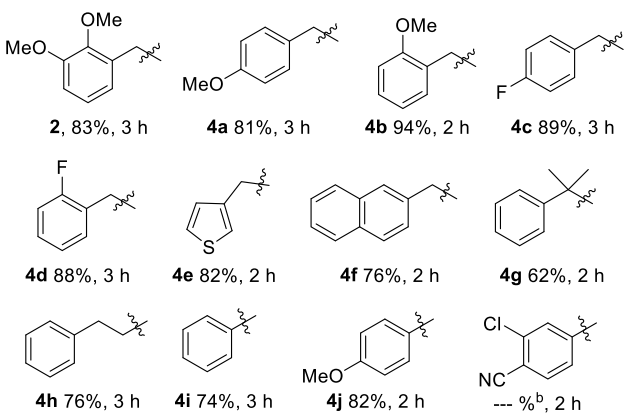
major product in 70% yield (Table 1, entry 1) with no detection of the corresponding 3,3-disubstituted oxindole. In order to confirm the structure assignment of **2** as a 5,5-disubstituted oxazolidine-2,4-dione, a crystal structure was obtained (*cf.* Figure S1). In addition, a minor overoxidized product (<5%) was detected.[18] Encouraged by these initial results, a number of reaction parameters (e.g., solvent, oxidant, temperature, and necessity of the palladium catalyst) were examined. The reaction proceeded at room temperature, although additional time was needed to achieve similar product yield (entry 2). However, the reaction was adversely affected when nonacidic less polar solvents (e.g., acetonitrile or 1,4-dioxane) were used in place of acetic acid (entries 3 and 4). Similarly, replacement of $PhI(OAc)_2$ with other oxidants, such as potassium peroxymonosulfate (e.g., Oxone) or potassium persulfate, resulted in significantly lower product yields (entries 5 and 6). The reaction was conducted in the absence of a palladium catalyst producing **2** in comparable yields (entries 7 and 8) demonstrating that the reaction proceeds in metal-free conditions. Over-oxidation was observed in the absence of a Pd-catalyst, but only during extended reaction time (entry 7). Reducing the equivalents of $PhI(OAc)_2$ was detrimental (entry 9). Finally, the methyl carbamate also gave a similar yield of **2** (entry 10).

Following an analysis of reaction conditions and reagents, the structure−reactivity relationship (SRR) of the N-substituent was explored. *N*-Benzyl groups with a 2- or 4-methoxy (e.g., **3a** and **3b**) were well tolerated producing **4a** and **4b** in good yields without generation of oxidized byproducts as observed with substrate **1** (Table 2). Electron-withdrawing groups in the 2- or 4-position of the *N*-benzyl, as well as replacement of the benzyl with a heterocycle (e.g., 2-thiophenylmethyl) or a fused aromatic hydrocarbon (e.g., 2-naphthylmethyl), were well tolerated generating products **4c**−**f**, respectively, in good yields. The additional steric hindrance on the benzylic carbon or extending the linker to a phenethyl resulted in corresponding 5,5-disubstituted oxazolidine-2,4-diones **4g** and **4h** in moderate yields. Finally, the attachment of the phenyl group directly to the nitrogen was also tolerated (**4i** and **4j**). However, a similar substrate containing several

Table 2. Reaction Substrate Scope: N-Substituents[a]



1 or **3a-k** **2** or **4a-j**



2, 83%, 3 h **4a** 81%, 3 h **4b** 94%, 2 h **4c** 89%, 3 h
4d 88%, 3 h **4e** 82%, 2 h **4f** 76%, 2 h **4g** 62%, 2 h
4h 76%, 3 h **4i** 74%, 3 h **4j** 82%, 2 h --- %[b], 2 h

[a]Reaction conditions: $PhI(OAc)_2$ (2 equiv) in AcOH (0.1 M) at 100 °C for 2−3 h. [b]N-de-Boc starting material was isolated (80%).

electron-withdrawing groups resulted in isolation of only the corresponding *N*-de-Boc starting material.

Next, the scope of the alkene was analyzed. For example, alkene **5a** generated **6a** in quantitative yield (Table 3). The SRR of the alkene geometry was also examined. The *E*-substituted alkene substrate **5b** underwent diastereospecific reaction to generate **6b**, albeit in only 27% yield. In addition to the desired product, another 5,5-disubstituted oxazolidine-2,4-dione **7a** was generated in 44% yield. The *Z*-isomer **5c** gave the other diastereomer **6c** in 42% yield, again with generation of **7a** in a similar yield. The trisubstituted alkene **5d** and tetra-substituted alkene **5e** only yielded alkene products **7b** and **7c**, respectively.

Assignment of the relative stereochemistry of **6b** and **6c** was difficult to confirm via 1D, 2D, and NOE NMR experiments,

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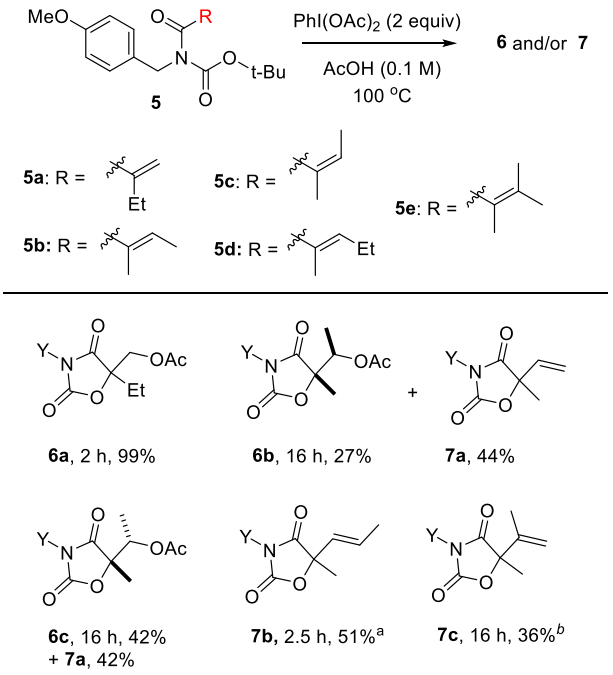
Table 3. Reaction Substrate Scope: Alkenes[a]



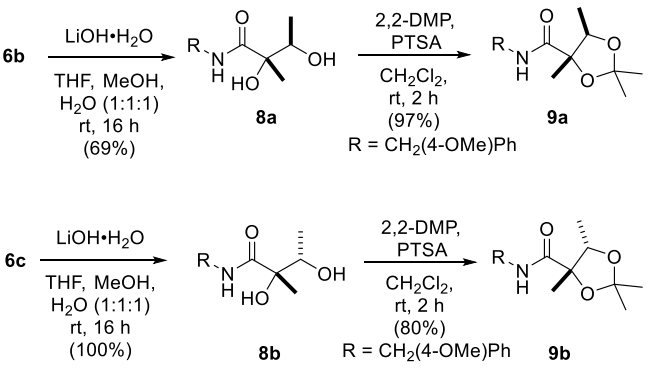
[a]Y: CH_2(4-OMe)Ph. [b]de-Boc starting material recovered.

so ^{1}H and ^{13}C NMR chemical shift calculations were performed on the two diastereomers of interest, *rel*-(*R*,*S*) and *rel*-(*S*,*S*), which for the calculations we labeled **6RS** and **6SS**, respectively. The gauge independent atomic orbital (GIAO)[19] method at the mPW1PW91/6-311+G(d,p) level of theory[20] was used for the chemical shift calculations, using Boltzmann weighting for all low-energy conformations. $CHCl_3$ was used as a solvent with the polarizable continuum solvent model (PCM). The computed chemical shifts of **6RS** and **6SS** were compared with the experimental values of **6b** and **6c**, utilizing mean absolute error (MAE), CP3[21] and DP4+[22] probability analyses (for DP4+, we used total or tDP4+ to be the sum of the scaled, sDP4+, and unscaled, uDP4+, NMR chemical shifts). The scaled chemical shifts were calculated by applying empirical scaling using the slope and intercept of the regression line obtained by plotting chemical shift values of ^{1}H and ^{13}C (calculated vs experimental). This computational approach has been reported for addressing the stereochemical assignment of other isomeric compounds.[23,24]

Comparing the results (*cf.* Tables S1−S22, Supporting Information) obtained with either tDP4+ probability analysis or "scaled shift only" sDP4+ probability data of **6SS** (96.86% probability, Table S20) showed close agreement with the experimental data of **6c**, whereas sDP4+ also predicted **6RS** to match **6c** (83.67% probability, Table S19), a confusing result. The only case of DP4+ calculations in which **6RS** matched with experimental results for **6b** was for sDP4+ carbon-only data, and for these data **6SS** matched with **6c** as well. Similarly, for scaled chemical shifts the carbon corrected mean absolute error (CMAE) data of **6SS** matched **6c**, but the data of **6RS** did not match **6b**. Moreover, tDP4+ probability analysis predicted **6SS** to match **6c** with 99.78% probability but did not predict **6RS** calculated chemical shifts to match with **6b** experimental values. Finally, considering results from CP3 (a method that simultaneously assigns structures for two diastereomers when experimental chemical shifts are available for both), **6RS** matched **6b** and **6SS** matched **6c** with 100% probability when carbon-only or all chemical shift data were used (*cf.* Tables S23−S24).

In order to verify the relative stereochemistry of these materials, **6b** was hydrolyzed with lithium hydroxide in THF/MeOH/H_2O to diol **8a** (Scheme 1). The structure of **8a** was

Scheme 1. Synthesis of Dimethyl Ketals 9a and 9b



confirmed as *rel*-(*R*,*S*) by X-ray crystallography (*cf.* Figure S2). Furthermore, this material was converted to dimethyl ketal **9a**, which by 1D-NOE experiments indicated the relative stereochemistry was *rel*-(*R*,*S*). Diastereomer **6c** was likewise converted to diol **8b** and then to dimethyl ketal **9b**. 1D-NOE experiments of **9b** were consistent with the relative stereochemistry of *rel*-(*S*, *S*). ^{1}H and ^{13}C NMR chemical shift calculations were performed for the two diastereomers of interest, *rel*-(*S*,*R*) and *rel*-(*S*,*S*), which for the calculations we labeled **8RS** and **8SS**, respectively. Comparing the results (*cf.* Tables S17−S18 and S21−S22) obtained with DP4+ probability analysis and "scaled only" sDP4+ probability data, sDP4+ chemical shift data for **8RS** with **8a** (53.06% probability) and for **8SS** with **8b** (72.77% probability) showed agreement, whereas the sDP4+ calculations for scaled carbon-only data matched **8RS** with **8a** but **8SS** also with **8b**. In addition, tDP4+ probability analysis predicted **8RS** to match **8a** with a 94.62% probability. The CMAE data for scaled chemical shifts matched **8RS** with **8a** and **8SS** with **8b**. Unlike for the **6b**/**6c** assignment, for **8a**/**8b** the CP3 probabilities (*cf.* Tables S23−S24) were unhelpful. The CP3 ^{1}H data and all data (considering together both ^{1}H and ^{13}C data) predicted that **8SS** matched with **8a** and **8RS** matched with **8b**, though the CP3 ^{13}C only data did match correctly with what was learned from the crystal structure of **8a**—that **8RS** should match with **8a** and **8SS** with **8b**.

The diastereospecificity and formation of the alkene byproducts observed in these reactions provide some insights into the potential mechanism of this transformation. Presumably the (diacetoxyiodo)benzene coordinates with the alkene via intermediate **A** (Scheme 2) that can undergo cyclization with loss of isobutylene to generate an intermediate such as **B**. This is consistent with the stereochemical course reported for the ICl-induced iodo-cyclization of similar *N*-Boc-acrylamide substrates.[9] This could be followed by S_N2-like substitution of PhI(OAc) with stereocenter inversion resulting in **6b**. Intermediate **B** could also undergo elimination generating **7a**.

Finally, the *N*-Boc-2-phenylacrylamide substrate **10** was subjected to the same reaction conditions. However, the phenyl-migration product **11** was generated in 75% yield

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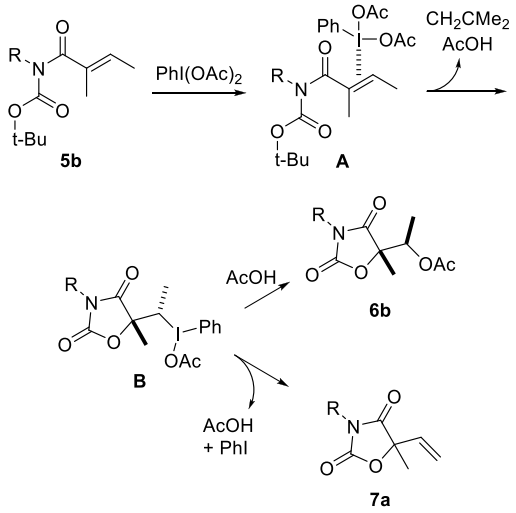
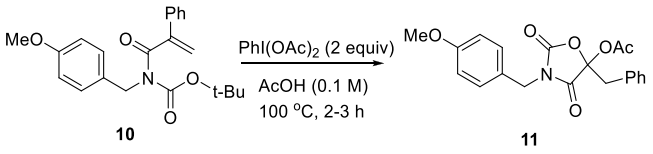
Scheme 2. Proposed Mechanism for the Conversion of 5b to 6b and 7a[a]



[a]R = CH_2(4-OMe)Ph.

(Scheme 3). The structure of **11** was confirmed by X-ray crystallography (*cf.* Figure S3). This reaction likely occurs via a

Scheme 3. Synthesis of 11



phenonium ion intermediate reminiscent of a similar reaction of 4-aryl-4-pentenoic acids with a hypervalent iodine reagent reported by Boye et al.[25]

In conclusion, a method for (diacetoxyiodo)benzene-mediated oxidative cyclization of *N*-Boc-acrylamides in acetic acid to produce 5,5-disubstituted oxazolidine-2,4-diones was developed. The reaction scope was modestly broad with respect to the amide N-substituents. In addition, the reaction was diastereospecific with *N*-Boc-2,3-dimethylacrylamide substrates. However, more highly substituted *N*-Boc-acrylamides gave alkene-containing 5,5-disubstituted oxazolidine-2,4-diones. A proposed mechanism was provided that is consistent with the observed diastereospecificity of the reaction and formation of the alkene byproducts. Finally, in the case of an *N*-Boc-2-phenylacrylamide substrate, phenyl migration was observed generating a 5-acetoxy-5-benzyl oxazolidine-2,4-dione. Hopefully, the results of this study will encourage further examination of these reactions (e.g., employing more reactive or catalytic hypervalent iodine reagents and expanding the scope), as well as medicinal chemistry applications of the products.

EXPERIMENTAL SECTION

General Information. All reactions involving air-sensitive reagents were carried out with magnetic stirring and oven-dried glassware with rubber septa under argon, unless otherwise stated. All commercially available chemicals and reagent grade solvents were used directly without further purification, unless otherwise specified. Reactions were monitored by thin-layer chromatography (TLC) on Baker-flex silica gel plates (IB2-F) using UV-light (254 and 365 nm) detection or visualizing agents (phosphomolybdic acid stain). Flash chromatography was conducted with silica gel (230−400 mesh) using a Teledyne ISCO CombiFalsh Rf instrument. NMR spectra were recorded at room temperature using JEOL ECA-600 or 500 or 400 instruments (^{1}H NMR at 600 or 500 or 400 MHz; ^{13}C NMR at 150 or 125 or 100 MHz; ^{19}F NMR at 564 MHz) with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given in parts per million (ppm) with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26 ppm), CD_3OD (3.31 ppm), DMSO-d_6 (2.50 ppm); ^{13}C NMR: $CDCl_3$ (77.0 ppm), CD_3OD (49.2 ppm), DMSO-d_6 (39.5 ppm)]. Signal patterns are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants (J) are given in Hz. Nuclear Overhauser enhancement spectroscopy (NOESY) spectra were obtained to observe correlations between proton signals. High-resolution mass spectra (HRMS) were obtained by the University of Texas at Austin mass spectrometry facility using an ESI quadrupole mass spectrometer with a time-of-flight tube and reported as m/z (relative intensity) for the molecular ion [M].

*General Procedure A: Preparation of tert-Butyl Carbamates **1**, **3a−h**, **3k**, **5a−e**, and **10**.*[26] To a solution of the corresponding amine (1 equiv) in anhydrous dichloromethane was added Et_3N (1.3 equiv) at 0 °C. Then the corresponding acryloyl chloride (1.0−1.5 equiv) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 2−4 h. After completion of the reaction, water was added and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude compound was purified by chromatography using hexane/ethyl acetate as eluent. To a solution of the acrylamide (1 equiv) in anhydrous THF was added LiHMDS (1.3 equiv, 1.0 M in THF) at −78 °C. The reaction mixture was stirred for 20 min at this temperature. Then di-*tert*-butyl dicarbonate (1.3 equiv dissolved in THF) was added slowly to the reaction mixture, which was then allowed to warm to 0 °C. Stirring was continued for 1−2 h. Reaction progress was monitored by TLC (30% EtOAc/hexane). After reaction completion saturated NH_4Cl solution was added and the mixture was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude compounds were purified by chromatography using hexane/ethyl acetate as eluent to obtain compounds **1**, **3a−h**, **3k**, **5a−e**, and **10**.

*tert-Butyl (2,3-Dimethoxybenzyl)(methacryloyl)carbamate (**1**).* 21%; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.0 (t, J = 8.0 Hz, 1H), 6.80 (dd, J = 20.6 Hz, 8.2 Hz, 2H), 5.28 (s, 1H), 5.20 (s, 1H), 4.92 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.04 (s, 3H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.2, 153.4, 152.5, 146.7, 143.2, 131.5, 123.9, 119.4, 116.4, 111.2, 83.3, 60.4, 55.7, 43.2, 27.7, 19.3. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{25}NO_5Na$, 358.1625; found, 358.1634.

*tert-Butyl Isobutyryl(4-methoxybenzyl)carbamate (**3a**).* 69%; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.15 (s, 2H), 4.77 (s, 2H), 3.78 (s, 3H), 1.99 (s, 3H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.2, 158.8, 153.4, 143.3, 129.8, 129.5, 116.2, 113.6, 83.3, 55.2, 47.5, 27.9, 19.2. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{23}NO_4Na$, 328.1519; found, 328.1526.

*tert-Butyl Isobutyryl(2-methoxybenzyl)carbamate (**3b**).* 74%; white solid; mp: 65−66 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (td, J = 8.0 Hz, 2.0 Hz, 1H), 7.15 (dd, J = 7.5 Hz, 1.5 Hz, 1H), 6.92−6.89 (m, 1H), 6.85−6.83 (m, 1H), 5.27−5.26 (m, 1H), 5.20 (m, 1H), 4.86 (s, 2H), 3.80 (s, 3H), 2.02−2.04 (m, 3H), 1.38 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 174.2, 156.9, 153.5, 143.3, 128.1, 127.8, 125.9, 120.3, 116.5, 110.0, 83.0, 55.2, 43.6, 27.7, 19.3. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{23}NO_4Na$, 328.1519; found, 328.1526.

*tert-Butyl (4-Fluorobenzyl)(methacryloyl)carbamate (**3c**).* 96%; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.31 (m, 2H), 7.01−6.96 (m, 2H), 5.17−5.16 (m, 2H), 4.80−4.78 (m, 2H), 2.00 (s, 3H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 173.9, 162.0 (d, J_{CF} = 244.2 Hz), 153.2, 143.1, 133.4 (d, J_{CF} = 2.9 Hz), 129.8 (d,

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J_{CF} = 8.7 Hz), 116.3, 115.1 (d, J_{CF} = 20.4 Hz), 83.7, 47.3, 27.6, 19.1. ^{19}F NMR (564 MHz, $CDCl_3$): δ −115.0 (s). HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{20}FNO_3Na$, 316.1319; found, 316.1317.

*tert-Butyl (2-Fluorobenzyl)(methacryloyl)carbamate (**3d**).* 23%; white solid; mp: 51−52 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28−7.21 (m, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.03 (t, J = 9.3 Hz, 1H), 5.26 (s, 1H), 5.22 (s, 1H), 4.92 (s, 2H), 2.03 (s, 3H), 1.39 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 174.2, 160.5 (d, J_{CF} = 245.6 Hz), 153.1, 143.0, 129.2 (d, J_{CF} = 4.3 Hz), 128.9 (d, J_{CF} = 8.6 Hz), 124.8(d, J_{CF} = 14.4 Hz), 124.1 (d, J_{CF} = 2.9 Hz), 116.7, 115.2 (d, J_{CF} = 21.5 Hz), 83.6, 41.8 (d, J_{CF} = 4.4 Hz), 27.7, 19.3. ^{19}F NMR (564 MHz, $CDCl_3$): δ −118.3 (s). HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{20}FNO_3Na$, 316.1319; found, 316.1317.

*tert-Butyl Methacryloyl(thiophen-3-ylmethyl)carbamate (**3e**).* 81%; colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25−7.22 (m, 2H), 7.10 (dd, J = 5.0 Hz, 1.5 Hz, 1H), 5.17−5.14 (m, 2H), 4.81 (s, 2H), 1.99 (s, 3H), 1.43 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 174.0, 153.2, 143.2, 138.1, 127.9, 125.5, 123.3, 116.3, 83.5, 43.2, 27.7, 19.2. HRMS (ESI): m/z [M + K]$^+$ calcd for $C_{14}H_{19}NO_3SK$, 320.0717; found, 320.0720.

*tert-Butyl Methacryloyl(naphthalen-2-ylmethyl)carbamate (**3f**).* 85%; pale yellow solid; mp 85−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82−7.78 (m, 4H), 7.49−7.44 (m, 3H), 5.21−5.18 (m, 2H), 4.99 (s, 2H), 2.02 (s, 3H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.2, 153.4, 143.3, 135.1, 133.2, 132.7, 128.2, 127.9, 127.6, 127.0, 126.1, 126.0, 125.8, 116.5, 83.5, 48.3, 27.7, 19.3. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{23}NO_3Na$, 348.1570; found, 348.1577.

*tert-Butyl Methacryloyl(2-phenylpropan-2-yl)carbamate (**3g**).* 37%; yellow solid; mp 87−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49−7.47 (m, 2H), 7.33−7.29 (m, 2H), 7.22−7.18 (m, 1H), 5.77 (s, 1H), 5.50 (s, 1H), 2.0 (s, 3H), 1.76 (s, 6H), 1.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.1, 153.5, 147.7, 144.3, 128.1, 126.3, 124.8, 121.3, 82.4, 61.9, 29.2, 27.7, 18.6. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{25}NO_3Na$, 326.1727; found, 326.1725.

*tert-Butyl Methacryloyl(phenethyl)carbamate (**3h**).* 89%; yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.19 (m, 5H), 5.13 (s, 1H), 5.09 (s, 1H), 3.89 (t, J = 7.8 Hz, 2H), 2.90 (t, J = 7.8 Hz, 2H), 1.97 (s, 3H), 1.44 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.2, 153.3, 143.4, 138.5, 129.0, 128.4, 126.4, 115.9, 83.7, 46.2, 34.9, 27.8, 19.3. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{23}NO_3Na$, 312.1570; found, 312.1576.

*tert-Butyl (3-Chloro-4-cyanophenyl)(methacryloyl)carbamate (**3k**).* 77%; white solid; mp 105−107 °C ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (dd, J = 8.2 Hz, 1.3 Hz, 1H), 7.36 (m, 1H), 7.19 (dt, J = 8.3 Hz, 1.7 Hz, 1H), 5.61 (s, 1H), 5.51 (s, 1H), 2.07 (s, 3H), 1.47 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 173.0, 152.0, 143.4, 142.4, 137.3, 134.2, 128.7, 126.0, 120.5, 115.5, 111.9, 85.1, 27.7, 18.7. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{17}ClN_2O_3Na$, 343.0820; found, 343.0819.

*tert-Butyl 4-Methoxybenzyl(2-methylenebutanoyl)carbamate (**5a**).* 79%; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.16 (dt, J = 17.2 Hz, 1.6 Hz, 2H), 4.78 (s, 2H), 3.78 (s, 3H), 2.36 (qt, J = 7.2 Hz, 1.6 Hz, 2H), 1.40 (s, 9H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.1, 158.8, 153.4, 149.0, 129.9, 129.5, 113.9, 113.6, 83.2, 55.1, 47.5, 27.7, 25.5, 11.5. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{25}NO_4Na$, 342.1676; found, 342.1683.

*(E)-tert-Butyl 4-Methoxybenzyl(2-methylbut-2-enoyl)carbamate (**5b**).* 84%; colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.88 (qq, J = 7.0 Hz, 2.0 Hz, 1H), 4.74 (s, 2H), 3.78 (s, 3H), 1.84 (m, 3H), 1.70 (dd, J = 7.0 Hz, 1.0 Hz, 3H), 1.39 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 175.1, 158.8, 153.7, 135.5, 130.1, 129.6, 128.8, 113.6, 82.6, 55.2, 47.9, 27.8, 13.6, 13.3. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{25}NO_4Na$, 342.1676; found, 342.1686.

*(Z)-tert-Butyl 4-methoxybenzyl(2-methylbut-2-enoyl)carbamate (**5c**).* 85%; colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 6.9 Hz, 2H), 6.83 (d, J = 6.9 Hz, 2H), 5.38−5.33 (m, 1H), 4.83 (s, 2H), 3.78 (s, 3H), 1.91 (s, 3H), 1.51 (d, J = 6.9 Hz, 3H), 1.43 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 173.4, 158.8, 152.7, 134.8, 129.9, 129.8, 122.9, 113.6, 83.4, 55.2, 46.6, 27.7, 20.6, 14.2. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{25}NO_4Na$, 342.1676; found, 342.1686.

*(E)-tert-Butyl 4-Methoxybenzyl(2-methylpent-2-enoyl)-carbamate (**5d**).* 87%; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.77 (tq, J = 7.2 Hz, 1.6 Hz, 1H), 4.74 (s, 2H), 3.78 (s, 3H), 2.14−2.06 (m, 2H), 1.84 (m, 3H), 1.39 (s, 9H), 0.99 (t, J = 7.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.3, 158.7, 153.7, 135.8, 133.9, 130.1, 129.6, 113.6, 82.7, 55.2, 48.0, 27.8, 21.3, 13.5, 13.0. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{27}NO_4Na$, 356.1832; found, 356.1842.

*tert-Butyl (2,3-Dimethylbut-2-enoyl)(4-methoxybenzyl)-carbamate (**5e**).* 95%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.83 (s, 2H), 3.78 (s, 3H), 1.79 (s, 3H), 1.66 (s, 3H), 1.57 (s, 3H), 1.41 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.5, 158.8, 152.8, 130.0, 129.8, 129.5, 128.0, 113.6, 82.7, 55.2, 46.7, 27.8, 21.3, 19.8, 16.2. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{27}NO_4Na$, 356.1832; found, 356.1839.

*tert-Butyl 4-Methoxybenzyl(2-phenylacryloyl)carbamate (**10**).* 61%; colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 7.29−7.27 (m, 5H), 6.87 (d, J = 8.4 Hz, 2H), 5.68 (s, 1H), 5.48 (s, 1H), 4.88 (s, 2H), 3.80 (s, 3H), 1.18 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 172.4, 158.9, 152.7, 147.1, 136.0, 130.0, 129.7, 128.3, 128.2, 126.4, 115.9, 113.7, 83.6, 55.2, 47.5, 27.4. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{22}H_{25}NO_4Na$, 390.1676; found, 390.1683.

*General Procedure B: Preparation of tert-Butyl Carbamates **3i−j**.*[8] To a solution of the corresponding amine, carboxylic acid (1.0 equiv each) and HOBt·H_2O (0.3 equiv) in acetonitrile was added EDC (1.2 equiv) at 0 °C. After 5 min, Et_3N (1.0 equiv) was added and the reaction mixture was allowed to warm slowly to room temperature and then stir for 1 h. Reaction progress was monitored by TLC (50% EtOAc/hexane). After reaction completion, water was added and the mixture was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude compound was purified by chromatography using hexane/ethyl acetate as eluent. To a solution of acrylamide (1.0 equiv) in anhydrous dichloromethane was added a catalytic amount of DMAP. Then di-*tert*-butyl dicarbonate (2.0 equiv) was added, and the reaction mixture was allowed to stir overnight at room temperature. Reaction progress was monitored by TLC 30% EtOAc/hexane. After reaction completion, water was added and the mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under reduced pressure, and the crude material was purified by chromatography to obtain **3i−j**.

*tert-Butyl Methacryloyl(phenyl)carbamate (**3i**).* 73%; white solid; mp 65−67 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (br t, J = 7.8 Hz, 2H), 7.32 (br t, J = 7.5 Hz, 1H), 7.17−7.15 (m, 2H), 5.56 (s, 1H), 5.38 (s, 1H), 2.06 (s, 3H), 1.44 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 173.8, 153.2, 142.9, 138.6, 129.1, 127.7, 127.6, 118.6, 83.6, 27.8, 19.0. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{19}NO_3Na$, 284.1257; found, 284.1261.

*tert-Butyl Methacryloyl(4-methoxyphenyl)carbamate (**3j**).* 47%; colorless viscous liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.07 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.51 (s, 1H), 5.34 (s, 1H), 3.80 (s, 3H), 2.05 (s, 3H), 1.43 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 173.9, 158.8, 153.4, 142.9, 131.2, 128.8, 118.2, 114.3, 83.4, 55.4, 27.7, 19.1. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{21}NO_4Na$, 314.1363; found, 314.1371.

*General Procedure C: Preparation of 5,5 Disubstituted Oxazolidine-2,4-diones (**2**, **4a−j**, **6a−c**, **7a−c**, and **11**).*[4] To a solution of the corresponding *tert*-butyl carbamate substrate (1.0 equiv) in acetic acid (0.1 M) at room temperature was added (diacetoxyiodo)benzene (2.0 equiv). The reaction mixture was heated in an oil bath to 100 °C for 2−3 h. Reaction progress was monitored by TLC (30−40% EtOAc/hexane). Upon reaction completion, the

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volatiles were removed under reduced pressure and then the crude materials were purified by chromatography.

*3-(2,3-Dimethoxybenzyl)-5-methyl-2,4-dioxooxazolidin-5-yl)-methyl Acetate (**2**).* Compound **2** was synthesized from **1** (50 mg, 0.15 mmol), $PhI(OAc)_2$ (96 mg, 0.30 mmol), and acetic acid (1.49 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to provide **2** (42.3 mg, 83%). White solid; mp 99−100 °C. ^{1}H NMR(500 MHz, $CDCl_3$): δ 7.01−6.98 (m, 1H), 6.88−6.85 (m, 2H), 4.79 (s, 2H), 4.32 (dd, J = 54.0 Hz, 12.0 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 1.96 (s, 3H), 1.58 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.1, 169.8, 154.2, 152.8, 147.2, 128.1, 124.1, 120.6, 112.5, 83.8, 65.1, 60.7, 55.8, 38.8, 20.4, 18.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{20}NO_7$, 338.1240; found, 338.1230.

*(3-(4-Methoxybenzyl)-5-methyl-2,4-dioxooxazolidin-5-yl)methyl Acetate (**4a**).* Compound **4a** was synthesized from **3a** (50 mg, 0.16 mmol), $PhI(OAc)_2$ (106 mg, 0.33 mmol), and acetic acid (1.64 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **4a** (40.7 mg, 81%) as a white solid; mp 103−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.63 (dd, J = 34.8 Hz, 14.6 Hz, 2H), 4.27 (dd, J = 38.0 Hz, 12.4 Hz, 2H), 3.78 (s, 3H), 1.72 (s, 3H), 1.55 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.9, 169.5, 159.6, 154.3, 130.2, 126.9, 114.0, 83.8, 65.0, 55.2, 43.3, 19.9, 18.4. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{17}NO_6Na$, 330.0948; found, 330.0954.

*(3-(2-Methoxybenzyl)-5-methyl-2,4-dioxooxazolidin-5-yl)methyl Acetate (**4b**).* Compound **4b** was synthesized from **3b** (50 mg, 0.16 mmol), $PhI(OAc)_2$ (106 mg, 0.33 mmol), and acetic acid (1.64 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−15% ethyl acetate in hexane) to yield **4b** (47.6 mg, 94%) as a white solid; mp 82−83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.22 (m, 2H), 6.92−6.87 (m, 2H), 4.77 (s, 2H), 4.32 (dd, J = 50.8 Hz, 12.0 Hz, 2H), 3.84 (s, 3H), 1.95 (s, 3H), 1.57 (s, 3H);$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.8, 169.5, 157.0, 154.2, 129.4, 128.6, 122.2, 120.3, 110.5, 83.5, 64.9, 55.3, 39.1, 20.3, 18.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{17}NO_6Na$, 330.0948; found, 330.0954.

*(3-(4-Fluorobenzyl)-5-methyl-2,4-dioxooxazolodin-5-yl)methyl Acetate (**4c**).* Compound **4c** was synthesized from **3c** (50 mg, 0.17 mmol), $PhI(OAc)_2$ (113 mg, 0.35 mmol), and acetic acid (1.70 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **4c** (45 mg, 89%) as a white solid; mp 93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.40 (m, 2H), 7.05−7.01 (m, 2H), 4.66 (dd, J = 36.0 Hz, 14.4 Hz, 2H), 4.28 (dd, J = 45.6 Hz, 12.4 Hz, 2H), 1.72 (s, 3H), 1.56 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.8, 169.4, 162.7 (d, J_{CF} = 246.2 Hz), 154.1, 130.7 (d, J_{CF} = 8.8 Hz), 130.6 (d, J_{CF} = 2.9 Hz), 115.7 (d, J_{CF} = 21.4 Hz), 83.9, 65.0, 43.0, 20.0, 18.4. ^{19}F NMR (564 MHz, $CDCl_3$): δ −112.9 (s). HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_{14}FNO_5Na$, 318.0748; found, 318.0750.

*(3-(2-Fluorobenzyl)-5-methyl-2,4-dioxooxazolidin-5-yl)methyl Acetate (**4d**).* Compound **4d** was synthesized from **3d** (50 mg, 0.17 mmol), $PhI(OAc)_2$ (113 mg, 0.35 mmol), and acetic acid (1.70 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **4d** (44.3 mg, 88%) as a white solid; mp 94−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.35 (td, J = 7.2 Hz, 1.2 Hz, 1H), 7.34−7.28 (m, 1H), 7.14−7.05 (m, 2H), 4.80 (dd, J = 23.2 Hz, 14.8 Hz, 2H), 4.31 (dd, J = 52.4 Hz, 12.0 Hz, 2H), 1.88 (s, 3H), 1.59 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.6, 169.4, 160.5 (d, J_{CF} = 247.1 Hz), 153.9, 130.3 (d, J_{CF} = 2.9 Hz), 130.2 (d, J_{CF} = 8.8 Hz), 124.2 (d, J_{CF} = 3.9 Hz), 121.3 (d, J_{CF} = 14.6 Hz), 115.6 (d, J_{CF} = 21.4 Hz), 83.9, 65.0, 37.6 (d, J_{CF} = 4.9 Hz), 20.1, 18.5. ^{19}F NMR (564 MHz, $CDCl_3$): δ −116.8 (s). HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_{14}FNO_5Na$, 318.0748; found, 318.0740.

*(5-Methyl-2,4-dioxo-3-(thiophen-3-ylmethyl)oxazolidin-5-yl)-methyl Acetate (**4e**).* Compound **4e** was synthesized from **3e** (50 mg, 0.18 mmol), $PhI(OAc)_2$ (144 mg, 0.45 mmol), and acetic acid (1.78 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **4e** (41.3 mg, 82%) as a white solid; mp 90 °C. ^{1}H NMR 500 MHz, $CDCl_3$): δ 7.38−7.36 (m, 1H), 7.29−7.27 (m, 1H), 7.15−7.13 (m, 1H), 4.75 (dd, J = 14.5 Hz, 3.0 Hz, 1H), 4.67 (dd, J = 14.5 Hz, 2.5 Hz, 1H), 4.32 (dd, J = 12.0 Hz, 3.5 Hz, 1H), 4.23 (dd, J = 12.0 Hz, 3.5 Hz, 1H), 1.74 (d, J = 3.5 Hz, 3H), 1.56 (d, J = 2.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.6, 169.4, 154.1, 134.8, 127.7, 126.4, 124.9, 83.9, 65.0, 38.3, 19.9, 18.3. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{12}H_{13}NO_5SNa$, 306.0407; found, 306.0406.

*(5-Methyl-3-(naphthalen-2-ylmethyl)-2,4-dioxooxazolidin-5-yl)-methyl Acetate (**4f**).* Compound **4f** was synthesized from **3f** (50 mg, 0.15 mmol), $PhI(OAc)_2$ (99 mg, 0.307 mmol), and acetic acid (1.5 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **4f** (38 mg, 76%) as a white solid; mp 110−112 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.83−7.79 (m, 3H), 7.53−7.47 (m, 3H), 4.86 (dd, J = 42.0 Hz, 14.5 Hz, 2H), 4.27 (dd, J = 46.0 Hz, 13.0 Hz, 2H), 1.56 (s, 3H), 1.53 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.9, 169.5, 154.3, 133.1, 133.0, 132.0, 128.7, 128.1, 127.9, 127.6, 126.5, 126.1, 83.9, 65.0, 44.0, 19.8, 18.4. HRMS (ESI): m/z $[M + K]^+$ calcd for $C_{18}H_{17}NO_5K$, 366.0738; found, 366.0743.

*(5-Methyl-2,4-dioxo-3-(2-phenylpropan-2-yl)oxazolidin-5-yl)-methyl Acetate (**4g**).* Compound **4g** was synthesized from **3g** (50 mg, 0.16 mmol), $PhI(OAc)_2$ (106 mg, 0.329 mmol), and acetic acid (1.65 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **4g** (34 mg, 62%) as a white solid; mp 78−80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.32 (m, 4H), 7.28−7.25 (m, 1H), 4.28 (dd, J = 82.5 Hz, 12.0 Hz, 2H), 2.07 (s, 3H), 1.97 (s, 6H), 1.52 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 173.8, 169.5, 153.7, 144.6, 128.5, 127.3, 124.4, 81.6, 65.3, 62.8, 28.4, 27.8, 20.5, 18.9. HRMS (ESI): m/z $[M + K]^+$ calcd for $C_{16}H_{19}NO_5K$, 344.0895; found, 344.0895.

*(5-Methyl-2,4-dioxo-3-phenethyloxazolidin-5-yl)methyl Acetate (**4h**).* Compound **4h** was synthesized from **3h** (50 mg, 0.17 mmol), $PhI(OAc)_2$ (111 mg, 0.34 mmol), and acetic acid (1.72 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−15% ethyl acetate in hexane) to yield **4h** (38 mg, 76%) as a white solid; mp 82−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.29 (m, 2H), 7.26−7.22 (m, 3H), 4.25 (dd, J = 58.4 Hz, 12.0 Hz, 2H), 3.82 (td, J = 7.6 Hz, 2.4 Hz, 2H), 2.99 (br t, J = 7.4 Hz, 2H), 1.99 (s, 3H), 1.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.9, 169.6, 154.2, 136.7, 128.8, 128.7, 127.0, 83.6, 64.8, 41.0, 33.2, 20.4, 18.6. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{17}NO_5Na$, 314.1003; found, 314.0999.

*(5-Methyl-2,4-dioxo-3-phenyloxazolidin-5-yl)methyl Acetate (**4i**).* Compound **4i** was synthesized from **3i** (50 mg, 0.19 mmol), $PhI(OAc)_2$ (123 mg, 0.381 mmol), and acetic acid (1.9 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−15% ethyl acetate in hexane) to yield **4i** (37 mg, 74%) as a white solid; mp 118−120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (br t, J = 7.5 Hz, 2H), 7.46−7.40 (m, 3H), 4.41 (dd, J = 55.0 Hz, 12.0 Hz, 2H), 2.07 (s, 3H), 1.69 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.1, 169.5, 153.2, 130.7, 129.4, 129.1, 125.4, 83.5, 65.3, 20.4, 18.6. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{13}H_{13}NO_5Na$, 286.0686; found, 286.0686.

*(3-(4-Methoxyphenyl)-5-methyl-2,4-dioxooxazolidin-5-yl)methyl Acetate (**4j**).* Compound **4j** was synthesized from **3j** (180 mg, 0.618 mmol), $PhI(OAc)_2$ (398 mg, 1.235 mmol), and acetic acid (6.18 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−15% ethyl acetate in hexane) to yield **4j** (150 mg, 82%) as an off-white solid; mp 111−113 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 4.40 (dd, J = 67.2 Hz, 12.0 Hz, 2H), 3.83 (s, 3H), 2.07 (s, 3H), 1.67 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.3, 169.5, 159.8, 153.5, 126.9, 123.2, 114.7, 83.5, 65.4, 55.5, 20.4, 18.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_{15}NO_6Na$, 316.0792; found, 316.0797.

*(5-Ethyl-3-(4-methoxybenzyl)-2,4-dioxooxazolidin-5-yl)methyl Acetate (**6a**).* Compound **6a** was synthesized from **5a** (50 mg, 0.157

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mmol), $PhI(OAc)_2$ (104 mg, 0.322 mmol), and acetic acid (1.57 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−15% ethyl acetate in hexane) to yield **6a** (48 mg, 99%) as a colorless liquid; ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 4.64 (dd, J = 37.5 Hz, 14.5 Hz, 2H), 4.28 (dd, J = 59.0 Hz, 12.0 Hz, 2H), 3.77 (s, 3H), 1.94−1.85 (m, 2H), 1.73 (s, 3H), 0.88 (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.4, 169.5, 159.6, 154.6, 130.2, 126.9, 114.0, 87.0, 64.5, 55.2, 43.2, 25.2, 20.0, 6.5. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{19}NO_6Na$, 344.1105; found, 344.1104.

*rel-(R)-1-((S)-3-(4-Methoxybenzyl)-5-methyl-2,4-dioxazolidin-5-yl)ethyl Acetate (**6b**).* Compound **6b** was synthesized from **5b** (100 mg, 0.313 mmol), $PhI(OAc)_2$ (201 mg, 0.62 mmol), and acetic acid (3.13 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **6b** (27 mg, 27%) as a colorless liquid and **7a** (36 mg, 44%) as a colorless liquid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.07 (q, J = 6.6 Hz, 1H), 4.59 (dd, J = 20.4 Hz, 14.4 Hz, 2H), 3.76 (s, 3H), 1.52 (s, 3H), 1.50 (s, 3H), 1.32 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 173.3, 169.1, 159.6, 154.6, 130.5, 127.0, 114.1, 86.4, 71.0, 55.3, 43.2, 20.1, 18.6, 13.4. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{19}NO_6Na$, 344.1105; found, 344.1110.

*3-(4-Methoxybenzyl)-5-methyl-5-vinyloxazolidine-2,4-dione (**7a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.92 (dd, J = 17.2 Hz, 10.8 Hz, 1H), 5.41 (dd, J = 75.2 Hz, 16.8 Hz, 1H), 4.59 (s, 2H), 3.78 (s, 3H), 1.61 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 173.4, 159.5, 154.3, 133.0, 130.0, 126.8, 117.6, 114.1, 85.2, 55.2, 43.2, 22.5. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_{15}NO_4Na$, 284.0893; found, 284.0900.

*rel-(S)-1-((S)-3-(4-Methoxybenzyl)-5-methyl-2,4-dioxo-oxazolidin-5-yl)ethyl Acetate (**6c**).* Compound **6c** was synthesized from **5c** (100 mg, 0.313 mmol), $PhI(OAc)_2$ (201 mg, 0.62 mmol), and acetic acid (3.13 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−20% ethyl acetate in hexane) to yield **6c** (42 mg, 42%) as a colorless liquid and **7a** (34 mg, 42%) as a colorless liquid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 5.12 (q, J = 6.4 Hz, 1H), 4.61 (dd, J = 48.6 Hz, 14.2 Hz, 2H), 3.78 (s, 3H), 1.75 (s, 3H), 1.54 (s, 3H), 1.30 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.6, 169.4, 159.5, 154.4, 130.2, 126.9, 114.0, 85.8, 71.9, 55.2, 43.1, 20.3, 18.8, 14.2. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{19}NO_6Na$, 344.1105; found, 344.1110.

*(E)-3-(4-Methoxybenzyl)-5-methyl-5-(prop-1-en-1-yl)-oxazolidine-2,4-dione (**7b**).* Compound **7b** was synthesized from **5d** (100 mg, 0.30 mmol), $PhI(OAc)_2$ (193 mg, 0.60 mmol), and acetic acid (3.0 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−10% ethyl acetate in hexane) to yield **7b** (42 mg, 51%) as a colorless liquid along with **4d** (12 mg, 17%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.93−5.86 (dq, J = 15.5 Hz, 6.5 Hz, 1H), 5.54 (dq, J = 15.5 Hz, 2.0 Hz, 1H), 4.59 (s, 2H), 3.79 (s, 3H), 1.72 (dd, J = 7.0 Hz, 2.0 Hz, 3H), 1.58 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 174.0, 159.5, 154.4, 130.0, 129.5, 126.9, 126.0, 114.1, 85.1 55.2, 43.2, 22.7, 17.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{17}NO_4Na$, 298.1050; found, 298.1053.

*3-(4-Methoxybenzyl)-5-methyl-5-(prop-1-en-2-yl)oxazolidine-2,4-dione (**7c**).* Compound **7c** was synthesized from **5e** (107 mg, 0.30 mmol), $PhI(OAc)_2$ (193 mg, 0.60 mmol), and acetic acid (3.0 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−15% ethyl acetate in hexane) to yield **7c** (32 mg, 36%) as a colorless liquid; ^1H NMR (500 MHz, $CDCl_4$): δ 7.32 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 5.21 (br s, 1H), 5.06−5.04 (m, 1H), 4.60 (s, 2H), 3.79, (s, 3H), 1.77 (t, J = 1.5 Hz, 3H), 1.65 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 173.5, 159.5, 154.5, 139.5, 130.0, 126.9, 114.8, 114.1, 87.0, 55.2, 43.2, 21.3, 18.1. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{15}H_{17}NO_4Na$, 298.1050; found, 298.1051.

*5-Benzyl-3-(4-methoxybenzyl)-2,4-dioxooxazolidin-5yl Acetate (**11**).* Compound **11** was synthesized from **10** (58 mg, 0.157 mmol), $PhI(OAc)_2$ (101 mg, 0.315 mmol), and acetic acid (1.57 mL, 0.1 M) according to general procedure C. The crude compound was purified by chromatography (0−10% ethyl acetate in hexane) to yield **11** (44 mg, 75%) as a white solid; mp 100−101 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 7.66−7.62 (m, 2H), 7.44−7.35 (m, 5H), 7.19−7.12 (m, 5H), 6.88−6.84 (m, 4H), 6.72−6.70 (m, 2H), 4.70−4.66 (m, 1H), 4.60−4.57 (m, 1H), 4.55−4.52 (m, 1H), 4.45−4.42 (m, 1H), 4.37 (s, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.31 (dd, J = 50.5 Hz, 18 Hz, 2H), 2.15 (s, 3H), 1.72 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.1, 169.4, 168.8, 168.4, 159.6, 159.1, 154.1, 152.7, 131.4, 130.4, 130.2, 129.8, 129.5, 129.4, 129.0, 128.6, 128.1, 126.7, 125.9, 124.9, 114.0, 113.8, 99.9, 86.0, 66.4, 55.2, 55.1, 43.5, 43.1, 40.3, 20.4, 20.0. HRMS (ESI): m/z $[M + K]^+$ calcd for $C_{20}H_{19}NO_6K$, 408.0844; found, 408.0853.

*rel-(2S,3R)-2,3-Dihydroxy-N-(4-methoxybenzyl)-2-methyl-butanamide (**8a**).* To a solution of **6b** (136 mg, 0.423 mmol) in THF and MeOH (8 mL, 1:1) was added $LiOH{\cdot}H_2O$ (480 mg, 11.42 mmol, dissolved in 4.0 mL water) at room temperature. The reaction mixture was stirred at room temperature overnight. Upon reaction completion, volatiles were removed under reduced pressure and the crude compound was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated, and the crude material was purified by chromatography (0−50% ethyl acetate in hexane) to yield **8a** (74 mg, 69%) as a white solid; mp 112−114 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H), 7.12 (br s, 1H), 6.86 (d, J = 8.4 Hz, 2H), 4.39 (td, J = 15.6 Hz, 6.0 Hz, 2H), 4.11 (q, J = 6.6 Hz, 6.0 Hz, 1H), 3.79 (s, 3H), 3.21 (s, 1H), 2.76 (d, J = 6.0 Hz, 1H), 1.37 (s, 3H), 1.18 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 175.7, 159.0, 130.0, 128.9, 114.1, 77.4, 71.3, 55.3, 42.7, 23.0, 16.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{13}H_{19}NO_4Na$, 276.1206; found, 276.1213.

*rel-(4S,5R)-N-(4-Methoxybenzyl)-2,2,4,5-tetramethyl-1,3-dioxolane-4-carboxamide (**9a**).*[27] To a solution of **8a** (35 mg, 0.14 mmol) in 1.5 mL of CH_2Cl_2 was added 2,2-DMP (28 mg, 0.27 mmol) and a catalytic amount of PTSA at room temperature. The reaction mixture was stirred for 2 h. Upon reaction completion, sat. $NaHCO_3$ solution was added and the mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the crude material was purified by chromatography (0−20% ethyl acetate in hexane) to yield **9a** (39 mg, 97%) as a colorless liquid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.19 (d, J = 8.4 Hz, 2H), 7.02 (br s, 1H), 6.87 (d, J = 8.4 Hz, 2H), 4.36 (ddd, J = 24.6 Hz, 17.4 Hz, 7.2 Hz, 2H), 4.17 (q, J = 7.20 Hz, 1H), 3.80 (s, 3H), 1.44 (s, 3H), 1.37 (d, J = 6.6 Hz, 3H), 1.33 (s, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 173.4, 159.0, 130.1, 128.8, 114.1, 108.0, 83.4, 76.4, 55.2, 42.3, 28.2, 25.7, 19.5, 14.9. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{23}NO_4Na$, 316.1519; found, 316.1522.

*rel-(2S,3S)-2,3-Dihydroxy-N-(4-methoxybenzyl)-2-methyl-butanamide (**8b**).* To a solution of **6c** (70 mg, 0.42 mmol) in THF and MeOH (4 mL, 1:1) was added $LiOH{\cdot}H_2O$ (24 mg, 11.44 mmol, dissolved in 2 mL water) at room temperature. The reaction mixture was stirred at room temperature overnight. Upon reaction completion, volatiles were removed under reduced pressure and the crude material was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated, and the crude compound was purified by chromatography (0−50% ethyl acetate in hexane) to yield **8b** (58 mg, 100%) as a colorless viscous liquid. ^1H NMR (600 MHz, $CDCl_3$): δ 7.22 (br s, 1H), 7.18 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.35 (ddd, J = 16.2 Hz, 15.6 Hz, 6.0 Hz, 2H), 3.94 (q, J = 6.6 Hz, 1H), 3.78 (s, 3H), 3.30 (s, 1H), 3.13 (br s, 1H), 1.43 (s, 3H), 1.15 (d, J = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 174.9, 159.0, 129.9, 129.0, 114.0, 76.7, 71.4, 55.3, 42.6, 22.3, 17.2. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{13}H_{19}NO_4Na$, 276.1206; found, 276.1213.

*rel-(4S,5S)-N-(4-Methoxybenzyl)-2,2,4,5-tetramethyl-1,3-dioxolane-4-carboxamide (**9b**).* To a solution of **8b** (40 mg, 0.158 mmol) in 1.5 mL of CH_2Cl_2 was added 2, 2-DMP (33 mg, 0.316 mmol) and

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a catalytic amount of PTSA at room temperature. The reaction mixture was stirred for 2 h. Upon reaction completion, sat. $NaHCO_3$ solution was added and the mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the crude material was purified by chromatography (0−20% ethyl acetate in hexane) to yield **9b** (37 mg, 80%) as a colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (d, J = 8.4 Hz, 2H), 7.01 (br s, 1H), 6.86 (d, J = 8.4 Hz, 2H), 4.44 (dd, J = 6.6 Hz, 14.4 Hz, 1H), 4.31 (dd, J = 14.4 Hz, 5.4 Hz,1H), 4.13 (q, J = 6.6 Hz, 1H), 3.79 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.33 (d, J = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 171.9, 159.0, 130.2, 128.8, 114.1, 108.4, 84.4, 80.5, 55.2, 42.6, 27.6, 25.7, 23.7, 16.0. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{23}NO_4Na$, 316.1519; found, 316.1522.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c00581.

^{1}H, ^{13}C NMR spectra of compounds **1**, **2**, **3a−k**, **4a−j**, **5a−e**, **6a−c**, **7a−c**, **8a−b**, **9a−b**, **10**, and **11**; DP4+ and CP3 experimental data (PDF)

Crystal structure data for compound **2** (CIF)

Crystal structure data for compound **8a** (CIF)

Crystal structure data for compound **11** (CIF)

Accession Codes

CCDC-1936130 (**2**), CCDC-1877266 (**8a**), and CCDC-1936131 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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