Oxazoline-Promoted Rh-Catalyzed C−H Amidation of Benzene Derivatives with Sulfonamides and Trifluoroacetamide. A Comparative Study

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Ⓢ *Supporting Information*

ABSTRACT: A Rh-catalyzed *ortho*-amidation of 2-aryloxazolines offers an efficient and direct route to a range of sulfonamides. The scope of the reaction is very broad with respect to sulfonamide substrate, but the position and electronic nature of the substituents on the aryl moiety of the oxazoline lead to a surprising modulation of reactivity. The reactivity of sulfonamides in comparison to trifluoroacetamide is compared, the latter undergoing Rh-catalyzed amidation more rapidly.
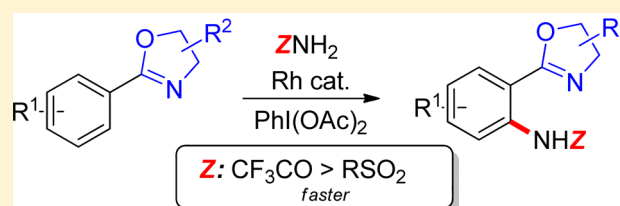
INTRODUCTION

Sulfonamides represent an important functional group within organic chemistry as evidenced by their prevalence within natural and non-natural compounds.[1] Typical synthetic approaches rely on the functionalization of anilines or amines with reactive sulfonyl chlorides (Scheme 1a).[2] Buchwald−

Scheme 1. N-Arylsulfonamide Synthetic Methods
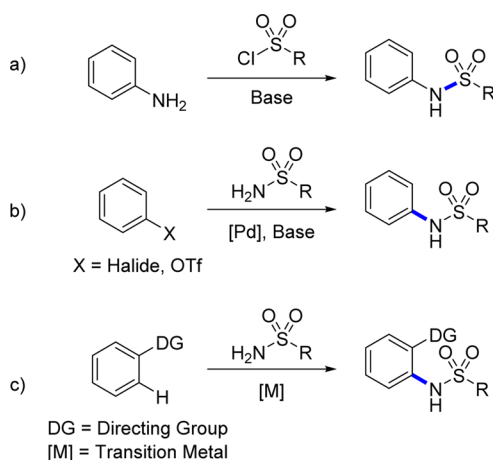
Hartwig cross-coupling represents a powerful and complementary C−N bond forming alternative (Scheme 1b). However, the methodology requires the use of a prefunctionalized coupling partner in the form of a halide/pseudohalide.[3] An alternative means of introducing of the sulfonamide group is by C−H activation (Scheme 1c). C−H activation has emerged as a very successful approach toward the synthesis of complex molecular scaffolds.[4] In particular, C−H amidation protocols represent a powerful strategy for the formation of C(sp[2])−N

bonds in which sulfonamides have been demonstrated to be successful coupling partners.[5]

We recently disclosed an efficient and regioselective rhodium-catalyzed C−H amidation/cyclization sequence to afford functionalized quinazoline and quinazolinone derivatives.[6] We also recently described the successful applicability of our methodology on 2-substituted pyridines.[7] Within our rhodium-catalyzed C−H amidation step, we chose the trifluoroacetamide as the amino source because of the ease of hydrolysis of this functionality. However, we recognized the potential of this strategy to directly deliver a range of N-arylsulfonamides and report herein the scope of this process. Moreover, we highlight some surprising reactivity differences with regard to the substrate amine donors and aryl acceptors.

Our investigations were inspired by Su and co-workers, who demonstrated the successful Rh-catalyzed reaction of 2-phenylpyridines with an array of functionalized sulfonamides.[8] In addition, a small selection of aryloxazolines were disclosed (four examples) that were employed in conjunction with *p*-toluenesulfonamide. Given the potential for oxazolines to be used as surrogates for carboxylic acid derivatives,[9] we decided to fully investigate the scope of the oxazoline-directed rhodium-catalyzed C−H amidation of aromatic compounds with aryl sulfonamides.

RESULTS AND DISCUSSION

Our previous work had highlighted that oxazolines promote an unusually mild amidation reaction when trifluoroacetamide is employed; the product yields are similar when the reactions are conducted at 100 or 40 °C.[6] Furthermore, the reaction was found to proceed quite efficiently at room temperature. We

decided to carry out a similar investigation using *p*-toluenesulfonamide in order to identify an optimal reaction temperature and to compare the reactivity of this amine source with trifluoroacetamide. As depicted in Scheme 2, the reaction

Scheme 2. Comparative Study of Reaction Temperature on the Reactivity of Trifluoroacetamide and *p*-Toluenesulfonamide
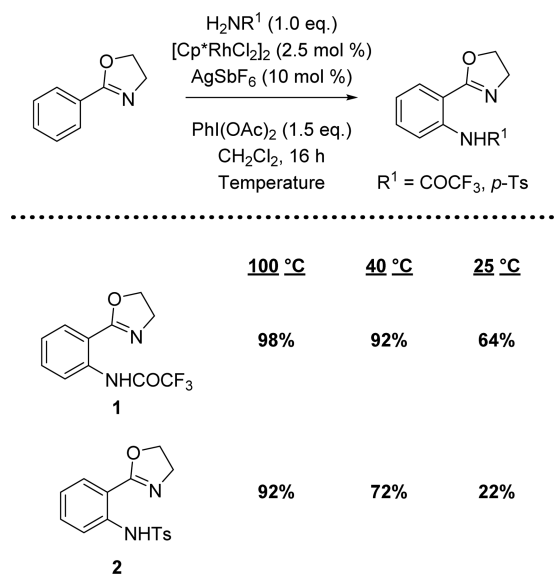
was found to proceed well at 100 °C to afford the C—H-amidated product in an excellent yield of 92%. In contrast to trifluoroacetamide, however, lowering the temperature to 40 °C led to a significant drop in yield. Moreover, conducting the reaction at 25 °C resulted in a poor isolated yield of 22%, highlighting the sluggish nature of this substrate at ambient temperature. Overall, we were interested to note that the reaction conditions required to afford efficient C—(sp^2)N bond formation were harsher in the case of the sulfonamide versus trifluoroacetamide, implicating a key role of the amine donor's role in dictating reactivity.

We next decided to investigate the nature of sulfonamides that could be used in conjunction with aryloxazolines in the rhodium-promoted system (Scheme 3). Pleasingly, a range of aromatic sulfonamides could be used alongside the *gem*-dimethyloxazoline directing group at an optimum reaction temperature of 100 °C, and only monoaminated products were observed in all cases. Under the standard reaction conditions, both electron-withdrawing and electron-donating functionalities were well tolerated by the sulfonamide group. Additionally, *o*-, *m*- and *p*-methyl-functionalized sulfonamides afforded the C—H-amidated products in good to excellent yield. Finally, alkyl sulfonamides were found to be viable substrates in combination with both the unsubstituted and *gem*-dimethyloxazoline directing group.

We then turned our attention to the functionalities on the aryloxazoline (Scheme 4). Pleasingly, under the optimum reaction conditions, we found a small selection of electronically distinct aryloxazolines were well tolerated. Both electron-poor and electron-rich aryl systems were successful, as demonstrated by the methoxy- and trifluoromethyl-substituted examples (12 and 13).

In an effort to demonstrate the utility of this particular transformation, we targeted the synthesis of sulfonamide 16, a
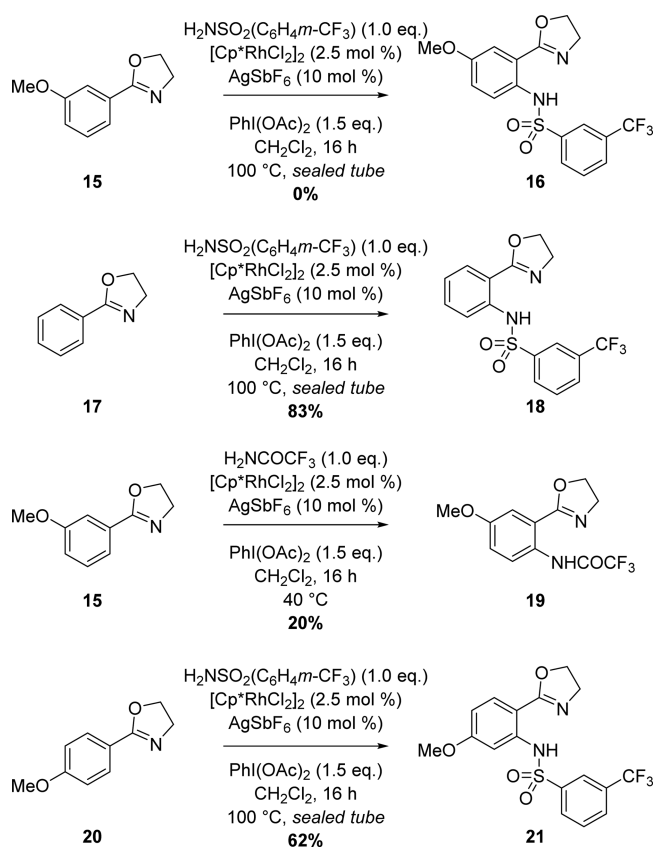
**Scheme 3. Sulfonamide Scope**
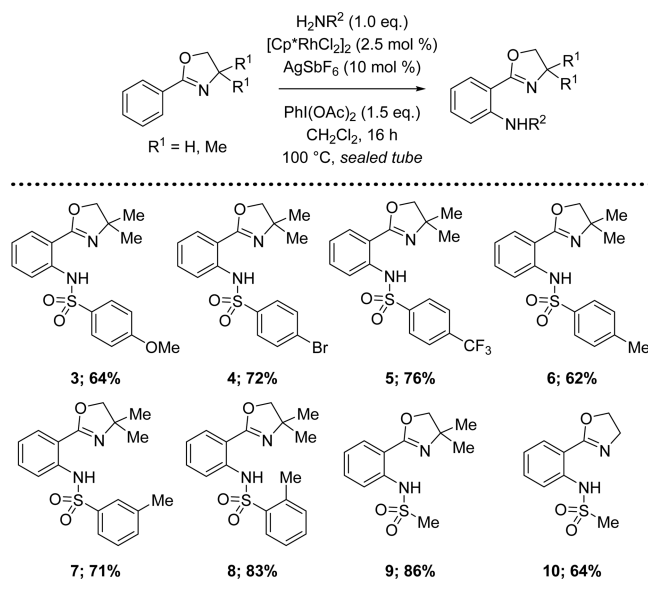
Scheme 4. Oxazoline Scope
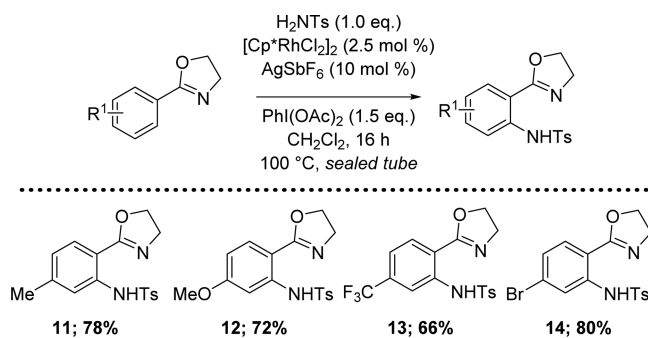
known potassium ion channel inhibitor.[10] We envisaged that the employment of our optimal C—H amidation conditions for sulfonamides would readily deliver 16 from 3-methoxy-substituted aryloxazoline 15 and 3-(trifluoromethyl)-benzenesulfonamide (Scheme 5). In the event, we were surprised to find that this reaction failed to proceed, even after heating over an extended time period. In order to rule out the sulfonamide as the source of low reactivity, 3-(trifluoromethyl)benzenesulfonamide was reacted with 2-phenyloxazoline 17. This reaction proceeded smoothly to afford the corresponding product 18 in an excellent yield of 83%. We next decided to further examine the reactivity of 3-methoxy-substituted aryloxazoline 15 by subjecting it to our standard reaction conditions with trifluoroacetamide. Interestingly, in this case, we observed only a poor yield of 20% of product 19. Finally, 2-(4-methoxyphenyl)oxazoline 20 was found to show good reactivity toward 3-(trifluoromethyl)-benzenesulfonamide, affording compound 21 in 62% yield. Taken together, these results indicated that the C—H amidation reaction could be retarded by the presence of an electron-donating substituent situated *meta* to the oxazoline directing group.

In order to explore the generality of this observation, an array of *para*- and *meta*-substituted aryloxazolines bearing both electron-donating and electron-withdrawing functionalities were prepared. For the purpose of comparison, each substrate was subjected to the optimum reaction conditions with *p*-

Scheme 5. Initial Investigations into the Effect of Electron-Donating Groups on Oxazoline Reactivity

Scheme 6. Comparative Study of *Meta*-Substituted versus *Para*-Substituted Substrates


toluenesulfonamide at 100 °C and trifluoroacetamide at 40 °C. As shown in Scheme 6, substrates containing a dimethylamino group were found to be unreactive; sulfonamides **22** and **24** were not formed while trifluoroacetamides **23** and **25** were generated in low yield. In contrast, the incorporation of a methoxy group para to the oxazoline was highly successful, with both amino sources delivering the corresponding products in high yield. However, when the methoxy group was *meta* to the directing group, the reaction was significantly retarded. These data clearly show that the positioning of the functional group can have a profound effect on reactivity. Next, the reactivity of methyl-substituted oxazolines was investigated. We observed better overall reactivity in these cases; however, the combination of an *m*-methyl group and the less reactive sulfonamide resulted in product **29** being generated in rather modest yield. Switching to an electron-withdrawing ester substituent, we were interested to note that both *para*- and *meta*-functionalized examples afforded similar reaction outcomes. Both substrates were reactive, and the desired compounds were isolated in good yields. Finally, we wanted to explore the effect of a fluorine group on the C−H amidation reaction. In this series, the *para*-functionalized example produced the C−H-amidated products with both amino sources in good to excellent yield. However, in the case of the *meta*-functionalized example, we observed insertion at the more hindered position between the oxazoline and the fluoride. This regioselectivity was surprising as we had not observed the analogous regiochemical C−H insertion in any of our other *meta*-substituted examples. The outcome was independent of amine source, and both *p*-toluenesulfonamide and trifluoroacetamide inserted into the 2-position of the aryl ring with
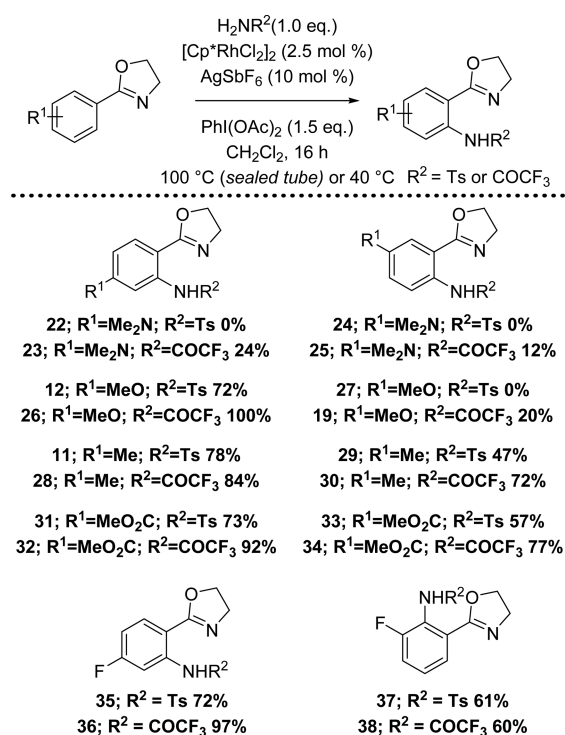
high selectivity and yield. The structure of the C−H amination product arising from the reaction between 3-fluoro-substituted oxazoline and *p*-toluenesulfonamide was unambiguously confirmed by X-ray crystallography.[11] Notably, selective insertion into the 2-position of similar *m*-fluoro scaffolds by C−H activation methodologies has received only scant precedent. Reports by Sanford and others demonstrated insertion into the 6-position under palladium-catalyzed C−H activation.[12] A single report by Yu described a mixture of insertion products (1:1.5 C_2/C_6) when N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-2-fluorobenzamide was subjected to C−H amidation conditions with stoichiometric $Cu(OAc)_2$ and *p*-toluenesulfonamide.[13]

We were interested to note that in all of the cases examined the trifluoroacetamide is superior to that of the sulfonamide, both in terms of milder conditions and higher yield. The reactivity and selectivity trends observed in the C−H amidation of various aromatic oxazolines with trifluoroacetamide and sulfonamides is intriguing, and our observations highlight some unexpected trends. In particular, we felt that the low reactivity observed in the cases of dimethylamino-functionalized aromatics, and the *m*-methoxy aromatic substrates, together with the unusual regioselectivity observed with the *m*-fluoro substrate were particularly intriguing and warranted further investigation. Accordingly, we decided to conduct deuterium-labeling experiments, and these are shown in Scheme 7.[8,14] We conducted the reaction between 2-(3-methoxyaryl)oxazoline (**15**) and *p*-toluenesulfonamide in the presence of deuterated methanol and observed 74% mass recovery. The mixture did not contain amidation product, but we observed almost quantitative deuterium incorporation affording a mixture of mono- and dideuterated materials **39** and **40**. This result confirms that rhodacycle formation proceeds under the reaction conditions but suggests that the problematic step in the

Scheme 7. Deuterium Incorporation Studies and Abbreviated Mechanism
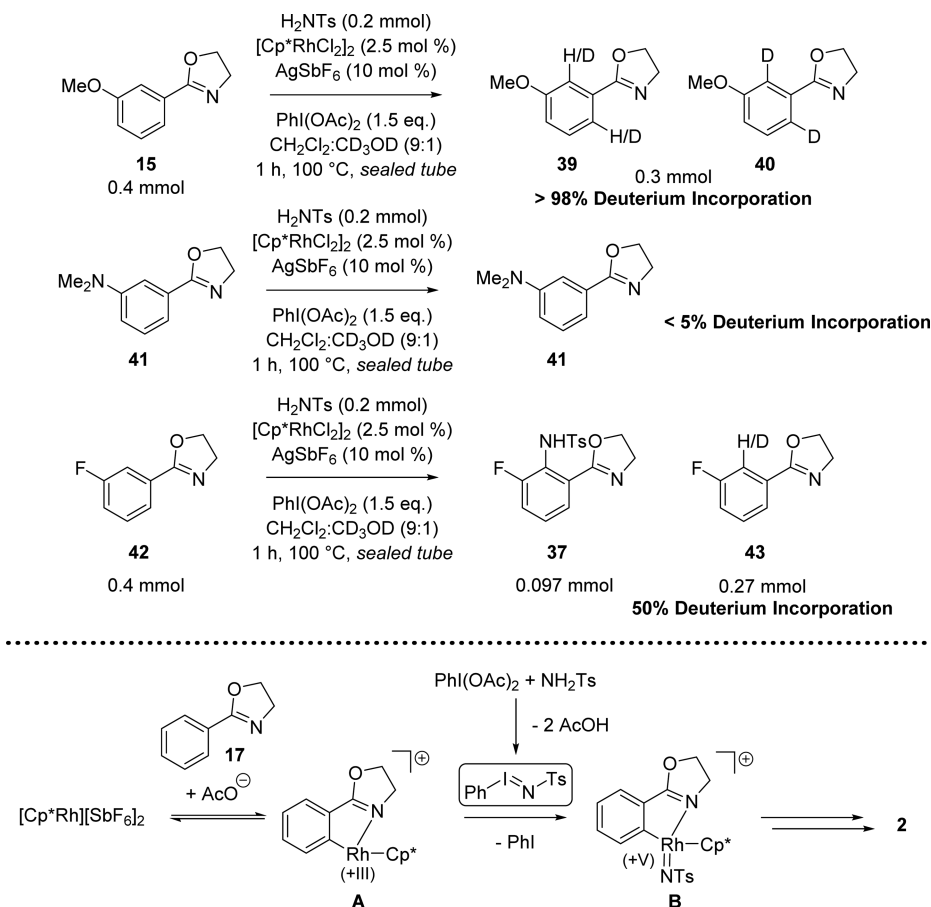
Scheme 8. Synthesis of Multifunctionalized Heterocycles
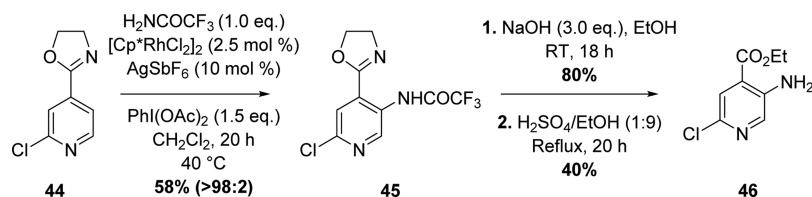
catalytic cycle is related to the formation of Rh(V) nitrenoid species **B**. Although the origin of this effect awaits further study, it may be that the presence of an electron-donating *meta*-substituent (with respect to the directing group) results in a strengthening of the carbon–rhodium bond in rhodacycle **A** retarding nitrene insertion or that strong electron donation reduces the propensity for formation of Rh–nitrenoid intermediates. In addition, running the same reaction of 2-[3-(dimethylamino aryl]oxazoline **41** resulted in <5% deuterium incorporation (as judged by 400 MHz ^{1}H NMR spectroscopy) and only recovery of the starting material, suggesting that slow cyclometalation is occurring in this case. Finally, carrying out the deuterium-labeling experiment with the (*m*-fluoroaryl)-oxazoline, we were able to observe a mixture that contained C–H amidation product **37** and a 1:1 mixture of recovered starting material and mono C2-deuterated starting material. The observation of C2-selective monodeuteration indicated that it is likely that selective rhodacycle formation gives rise to the observed product rather than the product determining nitrene insertion. We believe the selective rhodacycle formation is a

result of the enhanced acidity of the proton *ortho* to the fluoro substituent.

Finally, in order to show the potential of this method for synthesis of functionalized scaffolds, we targeted the C–H amidation of 2-chloropyridine **44** (Scheme 8). This substrate underwent smooth amidation and in high regiocontrol to generate **45**.[7] Subsequent hydrolysis of the acetamide followed by the oxazoline delivered aza-anthranilic ester **46** in acceptable overall yield.

In conclusion, we have described the extension of our rhodium-promoted C–H amidation conditions to sulfonamide amino sources. We found that a reaction temperature of 100 °C was key to affording efficient amidation with a range of aryl and alkyl sulfonamides, and that a range of functionalized oxazoline scaffolds were well tolerated. Through investigation and comparative study, we found aryloxazolines with electron-donating *meta*-substituents were incompatible with the reaction system, while their *para*-substituted counterparts were highly successful. Mechanistic studies suggested this could be due to the inhibition of the formation of key Rh(V)–nitrenoid species,

or a slow nitrene insertion step. Additionally, we observed the opposite regioselectivity of amide insertion with 3-fluoro aryloxazoline and determined this observation to be the result of regioselective rhodacycle formation.

■ EXPERIMENTAL SECTION

The following substrates were prepared according to a previously reported procedure: 2-(p-tolyl)-4,5-dihydrooxazole,[6] 2-(4-methoxy-phenyl)-4,5-dihydrooxazole (**20**),[6] 2-(4-trifluoromethylphenyl)-4,5-dihydrooxazole,[6] 2-(4-bromophenyl)-4,5-dihydrooxazole,[6] 2-(m-tolyl)-4,5-dihydrooxazole,[6] 2-(4-fluorophenyl)-4,5-dihydrooxazole,[6] methyl 3-(4,5-dihydrooxazol-2-yl)benzoate,[6] and 2-(2-chloropyridin-4-yl)-4,5-dihydrooxazole (**44**).[7]

General Procedure A: Amide Synthesis. To a dried, round-bottomed flask was added ester (1.0 equiv) and then heated to 55 °C with stirring. When the desired temperature was reached, ethanol-amine (1.5 equiv) was added slowly via syringe, and the reaction was stirred for 3 h before being cooled to room temperature and stirred for a further 18 h. The crude reaction mixture was then purified by recrystallization or flash column chromatography on silica gel eluting with dichloromethane and methanol (1% MeOH to 20% MeOH) or ethyl acetate (100%) to afford the amide products.

Synthesis of N-(2-Hydroxyethyl)-3-methoxybenzamide.[15] Follow-ing general procedure A, using ethyl 3-methoxybenzoate (3.09 g, 17.2 mmol) and ethanolamine (1.57 g, 25.8 mmol), the amide product was afforded as a yellow oil (3.18 g, 95%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (1H, s), 7.29 (2H, dd, J = 4.0, 2.5 Hz), 7.05−6.93 (2H, m), 3.82−3.77 (5H, m), 3.58 (2H, app dd, J = 10.0, 5.0 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 168.7, 159.9, 135.7, 129.7, 119.0, 117.9, 112.5, 62.2, 55.5, 43.0.

Synthesis of 3-Fluoro-N-(2-hydroxyethyl)benzamide.[16] Following general procedure A, using ethyl 3-fluorobenzoate (2.29 g, 13.6 mmol) and ethanolamine (1.25 g, 20.4 mmol) the amide product was afforded as a yellow oil (1.62 g, 65%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.53 (1H, s), 7.74−7.68 (1H, m), 7.65 (1H, ddd, J = 10.0, 2.5, 1.5 Hz), 7.51 (1H, td, J = 8.0, 6.0 Hz), 7.42−7.32 (1H, m), 3.51 (2H, q, J = 6.0 Hz), 3.33 (2H, q, J = 6.0 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6): δ 164.9 (d, J = 2.0 Hz), 161.9 (d, J = 244.0 Hz), 136.9 (d, J = 6.5 Hz), 130.4 (d, J = 8.0 Hz), 123.3 (d, J = 2.5 Hz), 117.9 (d, J = 21.0 Hz), 114.0 (d, J = 22.5 Hz), 59.6, 42.3. ^{19}F NMR (376.5 MHz, DMSO-d_6) δ −113.0.

General Procedure B: Amide Synthesis. To a stirred solution of benzoic acid (1.0 equiv) in dry dichloromethane (0.2 M) at 0 °C were added oxalyl chloride (3.0 equiv) and DMF (few drops). The reaction was allowed to warm to room temperature and stirred for a period of 3 h before the solvent was removed in vacuo. The crude residue was then dissolved in dry dichloromethane (0.2 M) and cooled to 0 °C using an ice bath. Triethylamine (3.0 equiv) was then added followed by ethanolamine (3.0 equiv) via syringe. The reaction was allowed to warm to room temperature and stir overnight. The reaction mixture was then dry loaded onto silica gel and purified by flash column chromatography on silica gel eluting with dichloromethane and methanol (0 to 10% MeOH) to afford the amide products.

Synthesis of 4-(Dimethylamino)-N-(2-hydroxyethyl)benzamide. Following general procedure B, using 4-(dimethylamino)benzoic acid (1.00 g, 6.05 mmol), oxalyl chloride (2.31 g, 18.2 mmol), and DMF (few drops) in dichloromethane (30 mL) and then ethanolamine (1.11 g, 18.2 mmol), triethylamine (1.84 g, 18.2 mmol), and dichloromethane (30 mL), the amide product was afforded as a colorless amorphous solid (763 mg, 61%). FTIR: ν_{max} cm^{-1} (neat) 3362 (m), 2943 (w), 2871 (w), 1609 (m), 1521 (m), 1205 (m), 1056 (m). ^{1}H NMR (400 MHz, MeOD-d_4). δ 7.89−7.50 (2H, m), 6.93−6.52 (2H, m), 3.69 (2H, t, J = 6.0 Hz), 3.48 (2H, t, J = 6.0 Hz), 3.00 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, MeOD-d_4): δ 170.7, 154.3, 129.7, 121.9, 112.1, 61.9, 43.4, 40.2. HRMS: m/z [MH]$^+$ C$_{11}$H$_{17}$N$_2$O$_2$ calcd 209.1285, found 209.1288.

Synthesis of 3-(Dimethylamino)-N-(2-hydroxyethyl)benzamide. Following general procedure B, using 3-(dimethylamino)benzoic acid (1.00 g, 6.05 mmol), oxalyl chloride (2.31 g, 18.2 mmol), and DMF

(few drops) in dichloromethane (30 mL) and then ethanolamine (1.11 g, 18.2 mmol), triethylamine (1.84 g, 18.2 mmol), and dichloromethane (30 mL), the amide product was afforded as a yellow oil (626 mg, 50%). FTIR: ν_{max} cm^{-1} (neat) 2807 (w), 1636 (m), 1598 (m), 1350 (m), 1055 (s), 994 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29−7.22 (2H, m), 7.02 (1H, d, J = 8.0 Hz), 6.87 (1H, d, J = 8.0, 2.5 Hz), 6.68 (1H, br s), 3.85−3.80 (2H, app m), 3.62 (2H, app dd, J = 10.0, 5.5 Hz), 2.99 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 169.6, 150.6, 135.2, 129.4, 115.8, 114.7, 111.7, 62.8, 43.2, 40.9. HRMS: m/z [MH]$^+$ C$_{11}$H$_{17}$N$_2$O$_2$ calcd 209.1285, found 209.1286.

Synthesis of Methyl 4-((2-Hydroxyethyl)carbamoyl)benzoate. Following general procedure B, using 4-(methoxycarbonyl)benzoic acid (1.00 g, 5.55 mmol), oxalyl chloride (2.11 g, 16.6 mmol), and DMF (few drops) in dichloromethane (28 mL) and then ethanol-amine (1.01 g, 16.7 mmol), triethylamine (1.68 g, 16.7 mmol), and dichloromethane (28 mL), the amide product was afforded as a colorless amorphous solid (820 mg, 66%). FTIR: ν_{max} cm^{-1} (neat) 3330 (w), 3287 (w), 1714 (m), 1633 (m), 1550 (m), 1283 (s), 1111 (s), 1052 (s). ^{1}H NMR (400 MHz, MeOD-d_4): δ 8.11−8.07 (2H, m), 7.94−7.90 (2H, m), 3.93 (3H, s), 3.72 (2H, t, J = 6.0 Hz), 3.52 (2H, t, J = 6.0 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, MeOD-d_4): δ 169.5, 167.7, 139.9, 133.9, 130.6, 128.5, 61.5, 52.9, 43.7. HRMS: m/z [MH]$^+$ C$_{11}$H$_{14}$NO$_4$ calcd 224.0917, found 224.0920.

General Procedure C: Oxazoline Synthesis. To a dried round bottomed flask were added amide (1.0 equiv) and dry dichloro-methane (0.6 M). With stirring, NEt$_3$ (1.9 equiv) was then added, followed by DMAP (0.2 equiv) and p-TsCl (1.7 equiv). The reaction mixture was allowed to stir at room temperature overnight before being diluted with dichloromethane and water. The mixture was then transferred to a separating funnel, and the layerswere partitioned. The aqueous layer was further extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO$_4$ and filtered, and the solvent was removed in vacuo. The crude residue was dissolved in MeOH (0.5 M), and NaOH pellets (3.0 equiv) were added in one portion. The reaction mixture was stirred at room temperature for 1−3 h before the solvent was removed in vacuo. The residue was dissolved in dichloromethane and water and transferred to a separating funnel. The layers were partitioned, and the aqueous layer was further extracted with dichloromethane and ethyl acetate. The combined organic layers were dried over anhydrous MgSO$_4$ and filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether (40/60) and ethyl acetate (0% ethyl acetate to 100% ethyl acetate) to afford the oxazoline products.

Synthesis of 4-(4,5-Dihydrooxazol-2-yl)-N,N-dimethylaniline. Fol-lowing general procedure C, using 4-(dimethylamino)-N-(2-hydroxyethyl)benzamide (690 mg, 3.31 mmol), p-TsCl (1.07 g, 5.63 mmol), NEt$_3$ (636 mg, 6.29 mmol), DMAP (81 mg, 0.66 mmol), and dichloromethane (5.5 mL) and then NaOH pellets (400 mg, 9.93 mmol) and MeOH (6.6 mL), the oxazoline product was afforded as a colorless amorphous solid (347 mg, 55%). FTIR: ν_{max} cm^{-1} (neat) 2970 (w), 1641 (m), 1603 (s), 1530 (m), 1354 (m), 1324 (m), 1187 (s), 1159 (s), 1066 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79−7.73 (2H, m), 6.64−6.58 (2H, m), 4.30 (2H, t, J = 9.5 Hz), 3.94 (1H, t, J = 9.5 Hz), 2.94 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 165.0, 152.1, 129.4, 114.8, 111.0, 67.1, 54.6, 40.0. HRMS: m/z [MH]$^+$ C$_{11}$H$_{15}$N$_2$O calcd 191.1179, found 191.1180.

Synthesis of 3-(4,5-Dihydrooxazol-2-yl)-N,N-dimethylaniline (41). Following general procedure C, using 3-(dimethylamino)-N-(2-hydroxyethyl)benzamide (577 mg, 2.77 mmol), p-TsCl (898 mg, 4.71 mmol), NEt$_3$ (532 mg, 5.26 mmol), DMAP (68 mg, 0.55 mmol) and dichloromethane (5.0 mL), then using NaOH pellets (332 mg, 8.31 mmol) and MeOH (6.0 mL), the oxazoline product 41 was afforded as a colorless amorphous solid (272 mg, 52%). FTIR: ν_{max} cm^{-1} (neat) 2977 (w), 1646 (m), 1591 (s), 1496 (s), 1433 (s), 1367 (s), 1350 (s), 1253 (s), 1238 (s), 1066 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36−7.33 (1H, m), 7.32−7.27 (2H, m), 6.86 (1H, dt, J = 7.0, 2.5 Hz), 4.44 (2H, t, J = 9.5 Hz), 4.07 (2H, t, J = 9.5 Hz), 3.00 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 165.5, 150.5, 129.1,

128.4, 116.5, 115.6, 112.0, 67.6, 54.9, 40.7. HRMS: m/z [MH]$^+$ C$_{11}$H$_{15}$N$_2$O calcd 191.1179, found 191.1180.

Synthesis of 2-(3-Methoxyphenyl)-4,5-dihydrooxazole (15).[17] Following general procedure C, using N-(2-hydroxyethyl)-3-methoxybenzamide (1.00 g, 5.12 mmol), p-TsCl (1.66 g, 8.71 mmol), NEt$_3$ (984 mg, 1.36 mmol), DMAP (125 mg, 1.02 mmol), and dichloromethane (8.5 mL) and then NaOH pellets (614 mg, 15.4 mmol) and MeOH (10.2 mL), the oxazoline product **15** was afforded as a colorless solid (572 mg, 63%). Mp: 60−61 °C (lit.[4] mp 59−60 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49−7.45 (1H, m), 7.43 (1H, dd, J = 2.5, 1.5 Hz), 7.24 (1H, t, J = 8.0 Hz), 6.95 (1H, ddd, J = 8.0, 2.5, 1.0 Hz), 4.33 (2H, t, J = 9.5 Hz), 3.97 (2H, t, J = 9.5 Hz), 3.76 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.5, 159.4, 129.3, 128.9, 120.5, 117.9, 112.5, 67.6, 55.3, 54.8.

Synthesis of 2-(3-fluorophenyl)-4,5-dihydrooxazole (42). Following general procedure C, using 3-fluoro-N-(2-hydroxyethyl)benzamide (1.00 g, 5.46 mmol), p-TsCl (1.77 g, 9.28 mmol), NEt$_3$ (1.05 g, 10.4 mmol), DMAP (133 mg, 1.09 mmol) and dichloromethane (9.1 mL), then using NaOH pellets (655 mg, 16.4 mmol) and MeOH (11 mL), the oxazoline product **42** was afforded as a yellow oil (688 mg, 76%). FTIR: ν_{max} cm^{-1} (neat) 2991 (w), 2912 (w), 1649 (m), 1585 (s), 1270 (s), 1185 (s), 1055 (s), 949 (s), 842 (s), 715 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (1H, d, J = 8.0 Hz), 7.65−7.58 (1H, m), 7.35 (1H, td, J = 8.0, 5.5 Hz), 7.14 (1H, td, J = 8.5, 2.5 Hz), 4.41 (2H, t, J = 9.5 Hz), 4.04 (2H, t, J = 9.5 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 163.7 (d, J = 3.0 Hz), 162.6 (d, J = 246.0 Hz), 130.0 (d, J = 8.0 Hz), 124.0 (d, J = 3.0 Hz), 118.3 (d, J = 21.0 Hz), 115.3 (d, J = 23.5 Hz), 67.9, 55.0. ^{19}F NMR (376.5 MHz, CDCl$_3$); δ −112.7. HRMS: m/z [MH]$^+$ C$_9$H$_9$FNO calcd 166.0663, found 166.0664.

Synthesis of Methyl 4-(4,5-Dihydrooxazol-2-yl)benzoate.[18] Following general procedure C, using methyl 4-((2-hydroxyethyl)-carbamoyl)benzoate (650 mg, 2.91 mmol), p-TsCl (945 mg, 4.95 mmol), NEt$_3$ (559 mg, 5.53 mmol), DMAP (71 mg, 0.58 mmol), and dichloromethane (5 mL) and then NaOH pellets (116 mg, 6.42 mmol) and MeOH (6 mL), the oxazoline product was afforded as a colorless amorphous solid (409 mg, 68%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07−8.01 (2H, m), 8.00−7.93 (2H, m), 4.42 (2H, t, J = 9.5 Hz), 4.05 (2H, t, J = 9.5 Hz), 3.89 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 166.5, 163.9, 132.5, 131.8, 129.6, 128.2, 67.9, 55.2, 52.4.

General Procedure D: C−H Amidation. To a dried Schlenk tube were added oxazoline (2.0 equiv), [Cp*RhCl$_2$]$_2$ (2.5 mol %), AgSbF$_6$ (10 mol %), PhI(OAc)$_2$ (1.5 equiv), and sulfonamide (1.0 equiv). The tube was fitted with a rubber septum and placed under an atmosphere of nitrogen followed by the addition of dry dichloromethane via syringe (0.1 M). The septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at 40−45 °C for 18 h. After the mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel eluting with petroleum ether (40/60) followed by dichloromethane or petroleum ether (40/60) and ethyl acetate (0% ethyl acetate to 40% ethyl acteate) to afford the aminated products.

Synthesis of 2,2,2-Trifluoro-N-[2-(4,5-dihydro-2-oxazolyl)phenyl]-acetamide (1).[6] Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-phenyl-2-oxazoline (59 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product **1** was isolated as a colorless solid (48 mg, 92%). Mp: 74−75 °C (pentane). FTIR: ν_{max} cm^{-1} (neat) 3054 (w), 2915 (w), 1734 (s), 1260 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.69 (1H, s), 8.68 (1H, dd, J = 8.5 and 1.0 Hz), 7.90 (1H, dd, J = 8.5 and 1.0 Hz), 7.52 (1H, t, J = 8.5 Hz), 7.21 (1H, t, J = 8.5 Hz), 4.43 (2H, t, J = 9.5 Hz), 4.16 (2H, t, J = 9.5 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.7, 155.7 (q, J = 37.5 Hz), 137.7, 132.9, 129.4, 124.5, 120.3, 116.1 (q, J = 288.5 Hz), 114.5, 66.8, 54.5. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.0. HRMS: m/z [MH]$^+$ C$_{11}$H$_{10}$N$_2$O$_2$F$_3$ calcd 259.0694, found 259.0704.

Synthesis of N-[2-(4,5-Dihydro-2-oxazolyl)phenyl]-4-methylbenzenesulfonamide (2).[8] Following general procedure D, using p-

toluenesulfonamide (34 mg, 0.20 mmol) and 2-phenyl-2-oxazoline (59 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **2** was isolated as a colorless solid (58 mg, 92%). Mp: 191−193 °C (lit.[19] mp 195−199 °C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.36 (1H, s), 7.78−7.70 (3H, m), 7.64 (1H, dd, J = 8.0 and 1.0 Hz), 7.37−7.29 (1H, m), 7.20 (2H, d, J = 8.0 Hz), 6.99 (1H, td, J = 8.0 and 1.0 Hz), 4.39−4.31 (2H, m), 4.16−4.08 (2H, m), 2.34 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.5, 143.5, 139.1, 136.9, 132.4, 129.5, 129.4, 127.2, 122.3, 117.8, 113.5, 66.5, 54.5, 21.5.

Synthesis of N-[2-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-4-methoxybenzenesulfonamide (3). Following general procedure D, using 4-methoxybenzenesulfonamide (37 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **3** was isolated as a colorless solid (46 mg, 64%). M: 106−108 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2974 (w), 2849 (w), 1336 (s), 1157 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.22 (1H, s), 7.79−7.68 (4H, m), 7.39−7.31 (1H, m), 7.04−6.97 (1H, m), 6.87−6.80 (2H, m), 4.02 (2H, s), 3.79 (3H, s), 1.40 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 162.1, 161.6, 139.1, 132.4, 131.7, 129.4, 129.3, 122.7, 118.8, 114.3, 114.1, 78.1, 68.1, 55.6, 28.6. HRMS: m/z [MH]$^+$ C$_{18}$H$_{21}$N$_2$O$_4$S calcd 361.1222, found 361.1237.

Synthesis of N-[2-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-4-bromobenzenesulfonamide (4). Following general procedure D, using 4-bromobenzenesulfonamide (47 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **4** was isolated as a colorless solid (59 mg, 72%). Mp: 111−114 °C (dichloromethane/petroleum ether (40/60)); FTIR: ν_{max} cm^{-1} (neat) 3099 (w), 2961 (w), 2890 (w), 1336 (s), 1160 (s), 1064 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.37 (1H, s), 7.76−7.65 (4H, m), 7.55−7.49 (2H, m), 7.41−7.34 (1H, m), 7.08−7.01 (1H, m), 4.03 (2H, s), 1.39 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 161.9, 139.0, 138.8, 132.5, 132.2, 129.5, 128.8, 127.7, 123.2, 118.8, 114.5, 78.2, 68.1, 28.6. HRMS: m/z [MH]$^+$ C$_{17}$H$_{18}$N$_2$O$_3$S^{79}Br calcd 409.0222, found 409.0216.

Synthesis of N-(2-(4,4-Dimethyl-1,5-dihydrooxazol-2-yl)phenyl)-4-(trifluoromethyl)benzenesulfonamide (5). Following general procedure D, using 4-(trifluoromethyl)benzenesulfonamide (45 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **5** was isolated as a colorless solid (46 mg, 76%). Mp: 80−81 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2980 (w), 1628 (m), 1506 (m), 1340 (m), 1321 (s), 1161 (s), 1129 (s), 1059 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.50 (1H, s), 7.94 (2H, d, J = 8.0 Hz), 7.77−7.72 (2H, m), 7.65 (2H, d, J = 8.0 Hz), 7.39 (1H, ddd, J = 8.5, 7.5, 1.5 Hz), 7.06 (1H, td, J = 8.0, 1.0 Hz), 4.03 (2H, s), 1.39 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 162.0, 143.6, 138.6, 134.5 (q, J = 33.0 Hz), 132.6, 129.5, 127.7, 126.1 (q, J = 3.5 Hz), 123.4, 123.3 (q, J = 273.0 Hz), 118.9, 114.5, 78.2, 68.1, 28.6. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −63.1. HRMS: m/z [MH]$^+$ C$_{18}$H$_{18}$N$_2$O$_3$F$_3$S calcd 399.0990, found 399.0986.

Synthesis of N-[2-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-4-methylbenzenesulfonamide (6).[8] Following general procedure D, using p-toluenesulfonamide (34 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **6** was isolated as a colorless solid (43 mg, 62%). Mp: 104−106 °C (dichloromethane/petroleum ether (40/60)); ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.29 (1H, s), 7.71 (4H, m), 7.42−7.31 (1H, m), 7.17 (2H, d, J = 8.5 Hz), 7.07−6.96 (1H, m), 4.02 (2H, s), 2.33 (3H, s), 1.42 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 161.9, 143.6, 139.3,

137.1, 132.4, 129.5, 129.3, 127.3, 122.7, 118.8, 114.3, 78.1, 68.1, 28.6, 21.6.

Synthesis of N-(2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-3-methylbenzenesulfonamide (7). Following general procedure D, using 3-methylbenzenesulfonamide (39 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.20 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 7 was isolated as a colorless solid (49 mg, 71%). Mp: 98−99 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2971 (w), 1631 (m), 1500 (m), 1340 (s), 1280 (m), 1161 (s), 1062 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.30 (1H, s), 7.76−7.69 (2H, m), 7.65−7.63 (1H, m), 7.62−7.59 (1H, m), 7.36 (1H, ddd, J = 8.5, 7.5, 1.5 Hz), 7.29−7.23 (2H, m), 7.01 (1H, ddd, J = 8.5, 7.5, 1.0 Hz), 4.02 (2H, s), 2.32 (3H, s), 1.39 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 161.9, 139.9, 139.2, 139.0, 133.6, 132.4, 129.3, 128.7, 127.5, 124.4, 122.8, 118.8, 114.4, 78.1, 68.1, 28.6, 21.4. HRMS: m/z [MH]$^+$ C$_{18}$H$_{21}$N$_2$O$_3$S calcd 345.1273, found 345.1288.

Synthesis of N-(2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)phenyl)-2-methylbenzenesulfonamide (8). Following general procedure D, using 2-methylbenzenesulfonamide (34 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.20 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 8 was isolated as a colorless solid (57 mg, 83%). Mp: 96−97 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2967 (w), 1631 (m), 1500 (m), 1337 (s), 1270 (s), 1158 (s), 1136 (s), 1056 (s), 1043 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.64 (1H, s), 8.12 (1H, dd, J = 8.0, 1.5 Hz), 7.74 (1H, dd, J = 8.0, 1.5 Hz), 7.56 (1H, dd, J = 8.5, 1.0 Hz), 7.39 (1H, td, J = 7.5, 1.5 Hz), 7.33−7.24 (2H, m), 7.21 (1H, d, J = 7.5 Hz), 6.95 (1H, ddd, J = 8.5, 7.5, 1.0 Hz), 4.06 (2H, s), 2.66 (3H, s), 1.41 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 162.0, 139.1, 137.8, 137.6, 133.0, 132.7, 132.5, 130.3, 129.4, 126.0, 121.8, 116.3, 112.8, 78.1, 68.1, 28.6, 20.2. HRMS: m/z [MH]$^+$ C$_{18}$H$_{21}$N$_2$O$_3$S calcd 345.1273, found 345.1270.

Synthesis of N-[2-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-4-methanesulfonamide (9). Following general procedure D, using methane sulfonamide (19 mg, 0.20 mmol) and 4,4-dimethyl-2-phenyl-2-oxazoline (70 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 9 was isolated as a colorless solid (46 mg, 86%). Mp: 86−88 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2971 (w), 2872 (w), 1322 (m), 1142 (s), 1047 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.01 (1H, s), 7.85 (1H, dd, J = 8.0 and 1.5 Hz), 7.72 (1H, dd, J = 8.5 and 1.0 Hz), 7.50−7.40 (1H, m), 7.16−7.06 (1H, m), 4.07 (2H, s), 3.01 (3H, s), 1.39 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 161.9, 139.4, 132.7, 129.7, 122.8, 118.1, 114.1, 78.2, 68.1, 39.9, 28.6. HRMS: m/z [MH]$^+$ C$_{12}$H$_{17}$N$_2$O$_3$S calcd 269.0960, found 269.0959.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-methanesulfonamide (10). Following general procedure D, using methane sulfonamide (19 mg, 0.20 mmol) and 2-phenyl-2-oxazoline (59 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 10 was isolated as a colorless solid (31 mg, 64%). Mp: 149−150 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 1634 (m), 1583 (m), 1494 (m), 1319 (s), 1251 (s), 1142 (s), 1055 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.11 (1H, s), 7.89 (1H, dd, J = 8.0, 1.5 Hz), 7.75 (1H, dd, J = 8.5, 1.0 Hz), 7.52−7.43 (1H, app m), 7.13 (1H, td, J = 8.0, 1.0 Hz), 4.42 (2H, t, J = 9.5 Hz), 4.15 (2H, t, J = 9.5 Hz), 3.05 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.7, 139.5, 132.9, 129.9, 122.6, 117.4, 113.6, 66.7, 54.6, 40.0. HRMS: m/z [MH]$^+$ C$_{10}$H$_{13}$N$_2$O$_3$S calcd 241.0641, found 241.0647.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-5-methylphenyl)-4-methylbenzenesulfonamide (11).[8] Following general procedure D, using p-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(p-tolyl)-4,5-dihydrooxazole (65 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30

mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 11 was isolated as a colorless solid (52 mg, 78%). Mp: 117−118 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2950 (w), 1641 (m), 1591 (m), 1507 (m), 1360 (m), 1324 (s), 1263 (s), 1149 (s), 1058 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.30 (1H, s), 7.74 (2H, d, J = 8.0 Hz), 7.60 (1H, d, J = 8.0 Hz), 7.47 (1H, s), 7.20 (2H, d, J = 8.0 Hz), 6.80 (1H, dd, J = 8.0, 1.0 Hz), 4.32 (2H, t, J = 9.5 Hz), 4.10 (2H, t, J = 9.5 Hz), 2.34 (3H, s), 2.30 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.5, 143.6, 143.3, 139.1, 137.1, 129.6, 129.2, 127.3, 123.4, 118.5, 111.2, 66.5, 54.5, 22.0, 21.6. HRMS: m/z [MH]$^+$ C$_{17}$H$_{19}$N$_2$O$_3$S calcd 331.1111, found 331.1117.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-5-methoxyphenyl)-4-methylbenzenesulfonamide (12). Following general procedure D, using p-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(4-methoxyphenyl)-4,5-dihydrooxazole (71 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 12 was isolated as a colorless oil (50 mg, 72%). FTIR: ν_{max} cm^{-1} (neat) 2970 (w), 1633 (s), 1606 (m), 1573 (s), 1512 (s), 1333 (s), 1142 (s), 1067 (s), 1036 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.50 (1H, s), 7.76 (2H, d, J = 8.0 Hz), 7.63 (1H, d, J = 9.0 Hz), 7.21 (1H, s), 7.20−7.17 (2H, app m), 6.50 (1H, dd, J = 9.0, 2.5 Hz), 4.31 (2H, t, J = 9.5 Hz), 4.08 (2H, t, J = 9.5 Hz), 3.77 (3H, s), 2.34 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.5, 162.7, 143.7, 141.0, 137.0, 130.8, 129.6, 127.4, 108.8, 106.5, 102.8, 66.4, 55.5, 54.4, 21.6. HRMS: m/z [MH]$^+$ C$_{17}$H$_{19}$N$_2$O$_4$S calcd 347.1060, found 347.1068.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-5-(trifluoromethyl)phenyl)-4-methylbenzenesulfonamide (13). Following general procedure D, using p-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(4-trifluoromethylphenyl)-4,5-dihydrooxazole (86 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 13 was isolated as a colorless solid (51 mg, 66%). Mp: 160−161 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 3089 (w), 2965 (w), 1646 (m), 1588 (m), 1522 (m), 1418 (s), 1321 (s), 1253 (s), 1159 (s), 1121 (s), 1083 (s), 1063 (s), 959 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.43 (1H, s), 7.94 (1H, s), 7.85 (1H, d, J = 8.0 Hz), 7.77 (2H, d, J = 8.0 Hz), 7.25−7.20 (3H, m), 4.40 (2H, t, J = 9.5 Hz), 4.18 (2H, t, J = 9.5 Hz), 2.36 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 163.7, 144.0, 139.4, 136.5, 133.85 (q, J = 33.0 Hz), 130.0, 129.7, 127.3, 123.3 (q, J = 273.0 Hz), 118.6 (d, J = 3.5 Hz), 115.9, 114.4 (d, J = 4.0 Hz), 66.7, 54.6, 21.5. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −63.4. HRMS: m/z [MH]$^+$ C$_{17}$H$_{16}$F$_3$N$_2$O$_3$S calcd 385.0828, found 385.0834.

Synthesis of N-(5-Bromo-2-(4,5-dihydrooxazol-2-yl)phenyl)-4-methylbenzenesulfonamide (14). Following general procedure D, using p-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(4-bromophenyl)-4,5-dihydrooxazole (90 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 14 was isolated as a colorless solid (64 mg, 80%). Mp: 142−143 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 3051 (w), 2980 (w), 1641 (s), 1593 (m), 1570 (m), 1489 (m), 1395 (m), 1357 (m), 1324 (s), 1256 (s), 1151 (s), 1086 (s), 1060 (s), 936 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.40 (1H, s), 7.84 (1H, d, J = 2.0 Hz), 7.76 (2H, d, J = 8.0 Hz), 7.57 (1H, d, J = 8.5 Hz), 7.23 (2H, d, J = 8.0 Hz), 7.11 (1H, dd, J = 8.5, 2.0 Hz), 4.35 (2H, t, J = 9.5 Hz), 4.11 (2H, t, J = 9.5 Hz), 2.36 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.2, 144.0, 140.2, 136.7, 130.6, 129.8, 127.3, 126.9, 125.5, 120.6, 112.2, 66.7, 54.6, 21.7. HRMS: m/z [MH]$^+$ C$_{16}$H$_{16}^{79}$BrN$_2$O$_3$S calcd 395.0060, found 395.0063.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)phenyl)-3-(trifluoromethyl)benzenesulfonamide (18). Following general procedure D, using 3-(trifluoromethyl)benzenesulfonamide (45 mg, 0.20 mmol) and 2-phenyl-2-oxazoline (59 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 18 was isolated as a colorless solid (61 mg, 83%). Mp: 140−141 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 3087 (w), 1639 (m), 1588 (w), 1502 (m), 1433 (w),

1329 (s), 1279 (s), 1253 (s), 1154 (s), 1124 (s), 1103 (s), 1068 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.42 (1H, s), 8.13 (1H, s), 7.98 (1H, d, J = 8.0 Hz), 7.73 (2H, dd, J = 8.0, 1.5 Hz), 7.69 (1H, dd, J = 8.0, 1.0 Hz), 7.53 (1H, t, J = 8.0 Hz), 7.42−7.35 (1H, m), 7.06 (1H, td, J = 8.0, 1.0 Hz), 4.35 (2H, t, J = 9.0 Hz), 4.12 (2H, t, J = 9.0 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.7, 141.1, 138.5, 132.7, 131.6 (q, J = 33.5 Hz), 130.5, 129.7, 129.6, 129.5 (q, J = 3.5 Hz), 124.4 (q, J = 4.0 Hz), 123.5, 123.3 (q, J = 273.0 Hz), 119.0, 114.5, 66.7, 54.5. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −62.9. HRMS: m/z [MH]$^+$ C$_{16}$H$_{14}$F$_3$N$_2$O$_3$S calcd 371.0672, found 371.0676.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-4-methoxyphenyl)-2,2,2-trifluoroacetamide (19). Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(3-methoxyphenyl)-4,5-dihydrooxazole (43 mg, 0.24 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 19 was isolated as a colorless solid (12 mg, 20%). Mp: 125−126 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 2975 (w), 1712 (m), 1601 (m), 1558 (m), 1372 (m), 1276 (m), 1218 (m), 1131 (s), 1058 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.40 (1H, s), 8.60 (1H, d, J = 9.0 Hz), 7.40 (1H, d, J = 3.0 Hz), 7.05 (1H, dd, J = 9.0, 3.0 Hz), 4.42 (2H, t, J = 9.5 Hz), 4.15 (2H, t, J = 9.5 Hz), 3.82 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.5, 156.0, 155.2 (q, J = 37.5 Hz), 131.1, 121.8, 118.4, 116.2 (q, J = 288.5 Hz), 115.7, 114.1, 66.8, 55.7, 54.6. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −75.9. HRMS: m/z [MH]$^+$ C$_{12}$H$_{12}$F$_3$N$_2$O$_3$ calcd 289.0795, found 289.0794.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-5-methoxyphenyl)-3-(trifluoromethyl)benzenesulfonamide (21). Following general procedure D, using 3-(trifluoromethyl)benzenesulfonamide (45 mg, 0.20 mmol) and 2-(3-methoxyphenyl)-4,5-dihydrooxazole (71 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 21 was isolated as a colorless solid (50 mg, 62%). Mp: 152−153 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 3081 (w), 2977 (w), 1644 (m), 1610 (m), 1577 (m), 1514 (m), 1370 (m), 1319 (s), 1260 (m), 1154 (s), 1109 (s), 1061 (s), 1035 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.62 (1H, s), 8.16 (1H, s), 8.00 (1H, d, J = 8.0 Hz), 7.74 (1H, d, J = 8.0 Hz), 7.64 (1H, dd, J = 9.0 Hz), 7.55 (1H, t, J = 8.0 Hz), 7.22 (1H, d, J = 2.5 Hz), 6.56 (1H, dd, J = 9.0, 2.5 Hz), 4.33 (2H, t, J = 9.5 Hz), 4.09 (2H, t, J = 9.5 Hz), 3.80 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.6, 162.8, 141.1, 140.3, 131.6 (q, J = 33.5 Hz), 130.9, 130.5, 129.8, 129.5 (q, J = 3.5 Hz), 124.5 (q, J = 3.5 Hz), 123.3 (q, J = 273.0 Hz), 109.7, 107.2, 103.8, 66.6, 55.6, 54.2. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −62.9. HRMS: m/z [MH]$^+$ C$_{17}$H$_{16}$F$_3$N$_2$O$_4$S calcd 401.0777, found 401.0784.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-5-(dimethylamino)-phenyl)-2,2,2-trifluoroacetamide (23). Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 4-(4,5-dihydrooxazol-2-yl)-N,N-dimethylaniline (46 mg, 0.24 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product 26 was isolated as a colorless solid (15 mg, 24%). Mp: 132−133 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 2883 (w), 1710 (m), 1616 (m), 1580 (m), 1535 (m), 1370 (s), 1238 (m), 1149 (s), 1121 (s), 1063 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.84 (1H, s), 8.08 (1H, d, J = 2.5 Hz), 7.69 (1H, d, J = 9.0 Hz), 6.45 (1H, dd, J = 2.5, 9.0 Hz), 4.35 (2H, t, J = 9.5 Hz), 4.08 (2H, t, J = 9.5 Hz), 3.05 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 165.1, 155.8 (app d, J = 37.5 Hz), 153.0, 139.0, 130.3, 116.1 (app d, J = 288.5 Hz), 107.3, 103.0, 102.4, 66.4, 54.2, 40.2. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.0. HRMS: m/z [MH]$^+$ C$_{13}$H$_{15}$F$_3$N$_3$O$_2$ calcd 302.1111, found 302.1111.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-4-(dimethylamino)-phenyl)-2,2,2-trifluoroacetamide (25). Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 3-(4,5-dihydrooxazol-2-yl)-N,N-dimethylaniline (46 mg, 0.24 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product 26 was isolated as an orange solid (8 mg, 12%). Mp:

119−120 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 3006 (w), 2982 (w), 1712 (m), 1597 (m), 1539 (m), 1264 (m), 1139 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.32 (1H, s), 8.56 (1H, d, J = 9.0 Hz), 7.23 (1H, d, J = 2.5 Hz), 6.89 (1H, dd, J = 9.0, 2.5 Hz), 4.42 (2H, t, J = 9.5 Hz), 4.16 (2H, t, J = 9.5 Hz), 2.98 (6H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.8, 154.6 (app d, J = 37.0 Hz), 147.0, 127.6, 121.5, 116.3, 116.2 (app d, J = 288.5 Hz), 115.3, 112.5, 66.6, 54.4, 40.7. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −75.8. HRMS: m/z [MH]$^+$ C$_{13}$H$_{14}$F$_3$N$_3$O$_2$ calcd 302.1111, found 302.1115.

Synthesis of 2,2,2-Trifluoro-N-[2-(4-methoxyphenyl)-4,5-dihydrooxazole]acetamide (26).[6] Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(4-methoxyphenyl)-4,5-dihydrooxazole (71 mg, 0.400 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product 26 was isolated as a colorless solid (57 mg, 100%). Mp: 103−104 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 3117 (w), 2979 (w), 1714 (m), 1637 (m), 1181 (s), 1145 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.84 (1H, s), 8.31 (1H, d, J = 2.5 Hz), 7.79 (1H, d, J = 8.5 Hz), 6.73 (1H, dd, J = 8.5, 2.5 Hz), 4.39 (2H, t, J = 9.5 Hz), 4.12 (2H, t, J = 9.5 Hz), 3.87 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.7, 162.9, 155.8 (q, J = 37.5 Hz), 139.4, 130.6, 116.0 (q, J = 288.5 Hz), 111.0, 107.4, 105.3, 66.6, 55.7, 54.3. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.0. HRMS: m/z [MH]$^+$ C$_{12}$H$_{12}$N$_2$O$_3$F$_3$ calcd 289.0800, found 289.0799.

Synthesis of 2,2,2-Trifluoro-N-[2-(4-methylphenyl)-4,5-dihydro-oxazole]acetamide (28).[8] Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 4,5-dihydro-2-(4-methylphenyl)oxazole (65 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product 28 was isolated as a colorless solid (46 mg, 84%). Mp: 120−121 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 3046 (w), 2958 (w), 1721 (s), 1637 (s), 1153 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.66 (1H, s), 8.52 (1H, s), 7.77 (1H, d, J = 8.0 Hz), 7.02 (1H, d, J = 8.0 Hz), 4.41 (2H, t, J = 9.5 Hz), 4.14 (2H, t, J = 9.5 Hz), 2.42 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): 164.8, 155.6 (q, J = 37.5 Hz), 143.8, 137.5, 129.2, 125.3, 120.8, 116.1 (q, J = 289.0 Hz), 112.0, 66.7, 54.4, 22.1. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.0. HRMS: m/z [MH]$^+$ C$_{12}$H$_{12}$N$_2$O$_2$F$_3$ calcd 273.0851, found 273.0861.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (29). Following general procedure D, using p-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(m-tolyl)-4,5-dihydrooxazole (65 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product 29 was isolated as a colorless solid (31 mg, 47%). Mp: 128−129 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 2985 (w), 2914 (w), 1633 (s), 1514 (m), 1334 (s), 1253 (s), 1152 (s), 1061 (s), 941 (m). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.10 (1H, s), 7.71 (2H, d, J = 8.0 Hz), 7.55 (1H, d, J = 8.5 Hz), 7.53 (1H, d, J = 1.5 Hz), 7.18 (2H, d, J = 8.0 Hz), 7.15 (1H, dd, J = 8.5, 1.5 Hz), 4.33 (2H, t, J = 9.5 Hz), 4.11 (2H, t, J = 9.5 Hz), 2.34 (3H, s), 2.25 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.6, 143.5, 137.1, 136.7, 133.2, 132.1, 129.7, 129.6, 127.3, 118.4, 113.8, 66.5, 54.6, 21.6, 20.7. HRMS: m/z [MH]$^+$ C$_{17}$H$_{19}$N$_2$O$_3$S calcd 331.1111, found 331.1116.

Synthesis of 2,2,2-Trifluoro-N-[2-(3-methylphenyl)-4,5-dihydrooxazole]acetamide (30).[6] Following general procedure D, using trifluoroacetamide (65 mg, 0.20 mmol) and 2-(3-methylphenyl)-4,5-dihydrooxazole (104 mg, 0.400 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product 30 was isolated as a colorless solid (39 mg, 72%). Mp: 145−146 °C (pentane). FTIR: ν$_{max}$ cm$^{−1}$ (neat) 3096 (w), 2993 (w), 2887 (w), 1714 (m), 1615 (m), 1138 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.56 (1H, s), 8.55 (1H, d, J = 8.5 Hz), 7.70 (1H, d, J = 2.0 Hz), 7.32 (1H, dd, J = 8.5, 2.0 Hz), 4.42 (2H, t, J = 9.5 Hz), 4.15 (2H, t, J = 9.5 Hz), 2.36 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.7, 155.4 (q, J = 288.5 Hz), 135.3, 134.3, 133.4, 129.7, 120.3, 116.9 (q, J = 37.5 Hz),

114.4, 66.7, 54.5, 20.9. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.0. HRMS: m/z [MH]$^+$ C$_{12}$H$_{12}$N$_2$O$_2$F$_3$ calcd 273.0851, found 273.0859.

Synthesis of Methyl 4-(4,5-Dihydrooxazol-2-yl)-3-(4-methylphenylsulfonamido)benzoate (31). Following general procedure D, using *p*-toluenesulfonamide (34 mg, 0.20 mmol) and methyl 4-(4,5-dihydrooxazol-2-yl)benzoate (82 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **31** was isolated as a colorless solid (55 mg, 73%). Mp: 136−137 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 3016 (w), 2990 (w), 1720 (s), 1639 (s), 1578 (m), 1512 (m), 1327 (s), 1238 (s), 1157 (s), 1093 (s), 1063 (s), 944 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.30 (1H, s), 8.29 (1H, d, J = 1.5 Hz), 7.81−7.75 (3H, m), 7.63 (1H, dd, J = 8.0, 1.5 Hz), 7.22 (2H, d, J = 8.0 Hz), 4.38 (2H, t, J = 9.5 Hz), 4.16 (2H, t, J = 9.5 Hz), 3.91 (3H, s), 2.35 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 166.1, 164.1, 143.9, 139.3, 136.8, 133.5, 129.7, 129.6, 127.4, 123.1, 118.6, 116.9, 66.8, 54.7, 52.6, 21.6. HRMS: m/z [MH]$^+$ C$_{18}$H$_{19}$N$_2$O$_5$S calcd 375.1009, found 375.1014.

Synthesis of Methyl 4-(4,5-Dihydrooxazol-2-yl)-3-(2,2,2-trifluoroacetamido)benzoate (32). Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and methyl 4-(4,5-dihydrooxazol-2-yl)benzoate (49 mg, 0.24 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **32** was isolated as a colorless solid (58 mg, 92%). Mp: 129−130 °C (pentane). FTIR: ν_{max} cm^{-1} (neat) 2982 (w), 2961 (w), 1733 (m), 1715 (m), 1588 (m), 1297 (m), 1249 (s), 1158 (s), 1112 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.64 (1H, s), 9.26 (1H, d, J = 1.5 Hz), 7.93 (1H, d, J = 8.0 Hz), 7.84 (1H, dd, J = 8.0, 1.5 Hz), 4.46 (2H, t, J = 9.5 Hz), 4.18 (2H, t, J = 9.5 Hz), 3.94 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 166.0, 164.2, 155.7 (q, J = 38.0 Hz), 137.7, 133.9, 129.5, 125.4, 121.0, 117.8, 115.9 (q, J = 288.5 Hz), 67.0, 54.6, 52.7. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −76.1. HRMS: m/z [MH]$^+$ C$_{13}$H$_{12}$F$_3$N$_2$O$_4$ calcd 317.0744, found 317.0746.

Synthesis of Methyl 3-(4,5-Dihydrooxazol-2-yl)-4-(4-methylphenylsulfonamido)benzoate (33). Following general procedure D, using *p*-toluenesulfonamide (34 mg, 0.20 mmol) and methyl 3-(4,5-dihydrooxazol-2-yl)benzoate (82 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **33** was isolated as a colorless solid (43 mg, 57%). Mp: 180−181 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 3084 (w), 2957 (w), 1710 (s), 1639 (s), 1593 (m), 1499 (m), 1438 (s), 1375 (m), 1339 (m), 1306 (s), 1281 (s), 1154 (s) 929 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.72 (1H, s), 8.43 (1H, d, J = 2.0 Hz), 7.98 (1H, dd, J = 9.0, 2.0 Hz), 7.78 (2H, d, J = 8.0 Hz), 7.66 (1H, d, J = 9.0 Hz), 7.23 (2H, d, J = 8.0 Hz), 4.41 (2H, t, J = 9.5 Hz), 4.17 (2H, t, J = 9.5 Hz), 3.86 (3H, s), 2.35 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 166.0, 164.3, 144.2, 143.0, 136.8, 133.6, 131.4, 129.8, 127.4, 123.8, 116.7, 112.9, 66.8, 54.7, 52.3, 21.7. HRMS: m/z [MH]$^+$ C$_{18}$H$_{19}$N$_2$O$_5$S calcd 375.1009, found 375.1015.

Synthesis of 2,2,2-Trifluoro-N-[3-(4,5-dihydro-2-oxazolyl)methyl ester benzoic acid]acetamide (34).[6] Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 3-(4,5-dihydro-2-oxazolyl)methyl ester benzoic acid (104 mg, 0.400 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product **34** was isolated as a colorless solid (49 mg, 77%). Mp: 212−213 °C (pentane). FTIR: ν_{max} cm^{-1} (neat) 2961 (w), 2891 (w), 1715 (s), 1646 (m), 1594 (m), 1155 (s), 1139 (s), 767 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.90 (1H, s), 8.74 (1H, d, J = 9.0 Hz), 8.57 (1H, d, J = 2.0 Hz), 8.17 (1H, dd, J = 9.0, 2.0 Hz), 4.47 (2H, t, J = 9.5 Hz), 4.19 (2H, t, J = 9.5 Hz), 3.93 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 165.8, 164.3, 156.0 (q, J = 38.0 Hz), 141.3, 134.0, 131.1, 126.2, 120.1, 116.4 (q, J = 288.5 Hz), 114.5, 67.0, 54.6, 52.4. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.0. HRMS: m/z [MH]$^+$ C$_{13}$H$_{12}$N$_2$O$_4$F$_3$ calcd 317.0744, found 317.0743.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-5-fluorophenyl)-4-methylbenzenesulfonamide (35). Following general procedure D,

using *p*-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(4-fluorophenyl)-4,5-dihydrooxazole (66 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **35** was isolated as a colorless solid (48 mg, 72%). Mp: 145−146 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 2985 (w), 2914 (w), 1644 (s), 1598 (s), 1509 (s), 1423 (m), 1367 (s), 1329 (s), 1276 (s), 1261 (s), 1147 (s), 1058 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.58 (1H, s), 7.79−7.75 (2H, app m), 7.72 (1H, dd, J = 9.0, 6.5 Hz), 7.39 (1H, dd, J = 11.0, 2.5 Hz), 7.23 (2H, d, J = 8.0 Hz), 6.67 (1H, ddd, J = 9.0, 8.0, 2.5 Hz), 4.36 (2H, t, J = 9.5 Hz), 4.12 (2H, t, J = 9.5 Hz), 2.36 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 164.9 (d, J = 252.0 Hz), 164.1, 144.0, 141.4 (d, J = 12.0 Hz), 136.8, 131.5 (d, J = 10.5 Hz), 129.8, 127.3, 109.7 (d, J = 2.5 Hz), 109.5 (d, J = 22.0 Hz), 105.0 (d, J = 27.5 Hz) 66.6, 54.5, 21.6. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −104.1. HRMS: m/z [MH]$^+$ C$_{16}$H$_{16}$FN$_2$O$_3$S calcd 336.0890, found 336.0893.

Synthesis of 2,2,2-Trifluoro-N-[2-(4-fluorophenyl)-4,5-dihydrooxazole]acetamide (36).[6] Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(4-fluorophenyl)-4,5-dihydrooxazole (66 mg, 0.400 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 16 h, product **36** was isolated as a colorless solid (54 mg, 97%). Mp: 121−122 °C (pentane). FTIR: ν_{max} cm^{-1} (neat) 3124 (w), 2993 (w), 1721 (m), 1637 (m), 1142 (s), 757 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.86 (1H, s), 8.47 (1H, dd, J = 11.0, 2.5 Hz), 7.89 (1H, dd, J = 9.0, 7.0 Hz), 6.91 (1H, ddd, J = 9.0, 7.0, 2.5 Hz), 4.43 (2H, t, J = 9.5 Hz), 4.15 (2H, t, J = 9.5 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 166.1, 163.9 (d, J = 57.0 Hz), 155.9 (q, J = 37.5 Hz), 139.5 (d, J = 12.0 Hz), 131.3 (d, J = 10.5 Hz), 115.1 (q, J = 288.5 Hz), 111.7 (d, J = 22.0 Hz), 110.9, 108.2 (d, J = 28.5 Hz), 66.9, 54.4. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −76.1, −103.3. HRMS: m/z [MH]$^+$ C$_{11}$H$_9$N$_2$O$_2$F$_4$ calcd 277.0600, found 277.0601.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-6-fluorophenyl)-4-methylbenzenesulfonamide (37). Following general procedure D, using *p*-toluenesulfonamide (34 mg, 0.20 mmol) and 2-(3-fluorophenyl)-4,5-dihydrooxazole (66 mg, 0.40 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **37** was isolated as a colorless solid (40 mg, 61%). Mp: 109−110 °C (dichloromethane/petroleum ether (40/60)). FTIR: ν_{max} cm^{-1} (neat) 3071 (w), 2980 (w), 2962 (w), 1639 (m), 1473 (s), 1449 (s), 1327 (s), 1268 (s), 1152 (s), 1088 (s), 991 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.54 (1H, s), 7.76 (2H, d, J = 8.0 Hz), 7.55 (1H, d, J = 8.0 Hz), 7.26 (2H, d, J = 8.0 Hz), 7.21−7.14 (1H, m), 7.08 (1H, td, J = 8.0, 5.0 Hz), 4.30 (2H, t, J = 9.5 Hz), 4.05 (2H, t, J = 9.5 Hz), 2.41 (3H, s). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 163.7 (d, J = 3.5 Hz), 155.5 (d, J = 250.0 Hz), 143.4, 138.1, 129.2, 127.7 (d, J = 14.0 Hz), 127.3 (d, J = 1.5 Hz), 124.7 (d, J = 3.0 Hz), 124.7 (d, J = 3.0 Hz), 119.9 (d, J = 20.5 Hz), 119.3 (d, J = 3.5 Hz), 66.8, 54.6, 21.7. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −115.7. HRMS: m/z [MH]$^+$ C$_{16}$H$_{16}$FN$_2$O$_3$S calcd 335.0860, found 335.0866.

Synthesis of N-(2-(4,5-Dihydrooxazol-2-yl)-6-fluorophenyl)-2,2,2-trifluoroacetamide (38). Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(3-fluorophenyl)-4,5-dihydrooxazole (40 mg, 0.24 mmol) with [Cp*RhCl$_2$]$_2$ (3 mg, 0.005 mmol), AgSbF$_6$ (7 mg, 0.02 mmol), and PhI(OAc)$_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 100 °C for 16 h, product **38** was isolated as a colorless solid (33 mg, 60%). Mp: 119−120 °C (pentane). FTIR: ν_{max} cm^{-1} (neat) 1742 (s), 1644 (m), 1532 (s), 1532 (s), 1474 (s), 1362 (s), 1271 (s), 1205 (s), 1129 (s). ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.84 (1H, s), 7.68 (1H, dd, J = 7.0, 2.0 Hz), 7.36−7.27 (2H, m), 4.44 (2H, t, J = 9.5 Hz), 4.15 (2H, t, J = 9.5 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ 163.6 (d, J = 3.5 Hz), 155.7 (d, J = 254.5 Hz), 154.9 (q, J = 38.0 Hz), 126.9 (d, J = 8.0 Hz), 124.8 (d, J = 3.0 Hz), 124.0 (d, J = 14.5 Hz), 120.3 (d, J = 3.5 Hz), 120.2 (d, J = 20.5 Hz), 116.1 (q, J = 287.0 Hz), 67.1, 54.8. ^{19}F NMR (376.5 MHz; CDCl$_3$): δ −75.5, −111.0. HRMS: m/z [MH]$^+$ C$_{11}$H$_9$F$_4$N$_2$O$_2$ calcd 277.0595, found 277.0596.

Synthesis of N-(6-Chloro-4-(4,5-dihydrooxazol-2-yl)pyridine-3-yl)-2,2,2-trifluoroacetamide (45).[7] Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(2-chloropyridin-4-yl)-4,5-dihydrooxazole 44 (44 mg, 0.24 mmol) with $[Cp*RhCl_2]_2$ (3 mg, 0.005 mmol), $AgSbF_6$ (7 mg, 0.02 mmol), and $PhI(OAc)_2$ (97 mg, 0.30 mmol) in dichloromethane (2 mL) at 40 °C for 20 h, product 45 was isolated as a colorless solid (34 mg, 58%). Mp: 98−99 °C. FTIR: ν_{max} cm^{-1} (neat) 3097 (w), 2921 (w), 2882 (w), 1726 (s), 1589 (m), 1565 (m), 1522 (m), 1307 (s), 1143 (s), 1123 (s), 944 (s), 741 (s). ^1H NMR (400 MHz, CDCl$_3$): δ 13.18 (1H, s, NH), 9.73 (1H, s, CH$_{ar}$), 7.75 (1H, s, CH$_{ar}$), 4.51 (2H, t, J = 9.5 Hz, CH$_2$), 4.24 (2H, t, J = 9.5 Hz, CH$_2$). ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −75.8. $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl$_3$): δ 162.6, 155.5 (q, J = 38.5 Hz), 147.1, 142.4, 132.2, 123.4, 122.9, 115.7 (q, J = 288.5 Hz), 67.6, 54.8. HRMS: m/z [MH]$^+$ C$_{10}$H$_8$^{35}ClF$_3$N$_3$O$_2$ calcd 294.0252, found 294.0252.

Synthesis of 6-Chloro-4-(4,5-dihydrooxazol-2-yl)pyridin-3-amine.[7] To a round-bottomed flask were added N-(6-chloro-4-(4,5-dihydrooxazol-2-yl)pyridin-3-yl)-2,2,2-trifluoroacetamide (45) (680 mg, 2.31 mmol) and methanol (23 mL). NaOH pellets (277 mg, 6.93 mmol) were then added, and the reaction mixture was stirred at room temperature for 18 h. The reaction mixture was concentrated, dissolved in ethyl acetate and deionized water, and transferred to a separating funnel. The layers were partitioned, and the aqueous layer was further extracted with ethyl acetate. The combined organic layers were dried over anhydrous MgSO$_4$ and filtered, and the solvent was removed in vacuo to afford the aniline product as colorless solid (364 mg, 80%). Mp: 184−185 °C. FTIR: ν_{max} cm^{-1} (neat) 3347 (w), 3151 (w), 2980 (w), 1643 (m), 1614 (m), 1475 (s), 1364 (s), 1290 (m), 1247 (m), 1111 (m), 951 (s), 869 (s). ^1H NMR (400 MHz, DMSO-d$_6$): δ 8.02 (1H, s, CH$_{ar}$), 7.37 (1H, s, CH$_{ar}$), 7.11 (2H, s, NH$_2$), 4.36 (2H, t, J = 9.5 Hz, CH$_2$), 4.07 (2H, t, J = 9.5 Hz, CH$_2$). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d$_6$): δ 162.0, 144.0, 138.8, 135.0, 121.6, 115.6, 66.7, 55.3. HRMS: m/z [MH]$^+$C$_8$H$_9$^{35}ClN$_3$O calcd 198.0429, found 198.0428.

Synthesis of Ethyl 5-Amino-2-chloroisonicotinate (46). To a round-bottomed flask equipped with a reflux condenser was added 6-chloro-4-(4,5-dihydrooxazol-2-yl)pyridin-3-amine (50 mg, 0.25 mmol) followed by ethanol (6.3 mL) and concentrated H$_2$SO$_4$ (0.7 mL). The reaction mixture was stirred and heated at reflux for 20 h. The reaction was then allowed to cool to room temperature and diluted with water. The reaction mixture was then neutralized to pH 6 using a saturated aqueous solution of NaHCO$_3$ and transferred to a separating funnel with ethyl acetate. The layers were partitioned, and the aqueous layer was further extracted with ethyl acetate. The combined organic layers were then dried over anhydrous MgSO$_4$ and filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether (40/60) and ethyl acetate (0% to 40% ethyl acetate) to afford the ester product 46 as an orange amorphous solid (20 mg, 40%). FTIR: ν_{max} cm^{-1} (neat) 2989 (w), 1701 (m), 1274 (m), 767 (s). ^1H NMR (400 MHz, CDCl$_3$): δ 7.97−7.96 (1H, m, CH$_{ar}$), 7.66−7.65 (1H, m, CH$_{ar}$), 5.12 (2H, br s, NH$_2$), 4.37 (2H, q, J = 7.0 Hz, CH$_2$), 1.40 (3H, t, J = 7.0 Hz, CH$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl$_3$): δ 166.0, 143.9, 139.9, 137.9, 123.5, 119.0, 61.7, 14.3. HRMS: m/z [MH]$^+$ C$_8$H$_{10}$^{35}ClN$_2$O$_2$ calcd 201.0425, found 201.0429.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02481.

> ^1H, ^{13}C, and ^{19}F NMR spectra for selected compounds, X-ray crystallographic data, and details of deuterium-labeling experiments (PDF)
> X-ray crystallographic data for compound 37 (CIF)

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Notes

The authors declare no competing financial interest.

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