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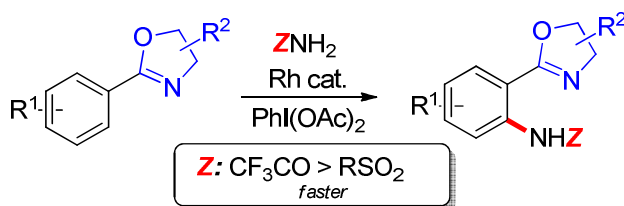
Abstract

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-Hartwig cross-coupling represents a powerful and complementary *C-N* bond forming alternative (scheme 1b). However, the methodology requires the use of a pre-functionalized coupling partner in the form of a halide/pseudo halide.[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 towards 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]

Scheme 1: *N*-Arylsulfonamide synthetic methods
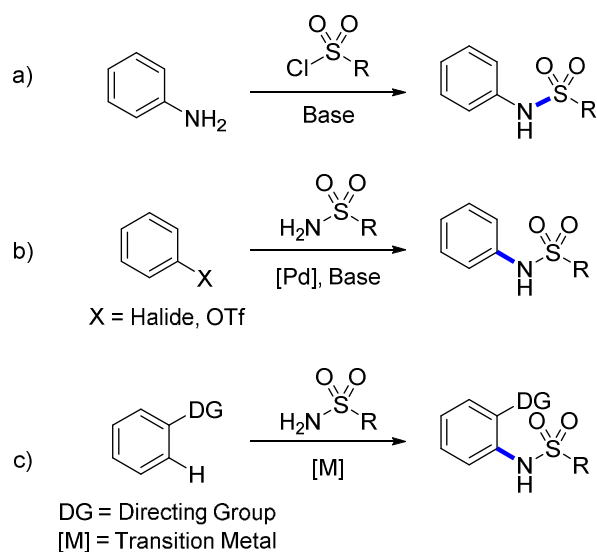
We recently disclosed an efficient and regioselective rhodium-catalyzed *C-H* amidation/cyclization sequence to afford functionalized quinazoline and quinazolinone derivatives.[6] We also recently described the successful applicability of our methodology on

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*-aryl sulfonamides 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-phenyl pyridines with an array of functionalized sulfonamides.[8] In addition, a small selection of aryl oxazolines were disclosed (4 examples) that were employed in conjunction with *para*-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 °C 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 *para*-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 was found to proceed well at 100 °C affording 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.

Scheme 2: Comparative study of reaction temperature on the reactivity of trifluoroacetamide and *para*-toluenesulfonamide
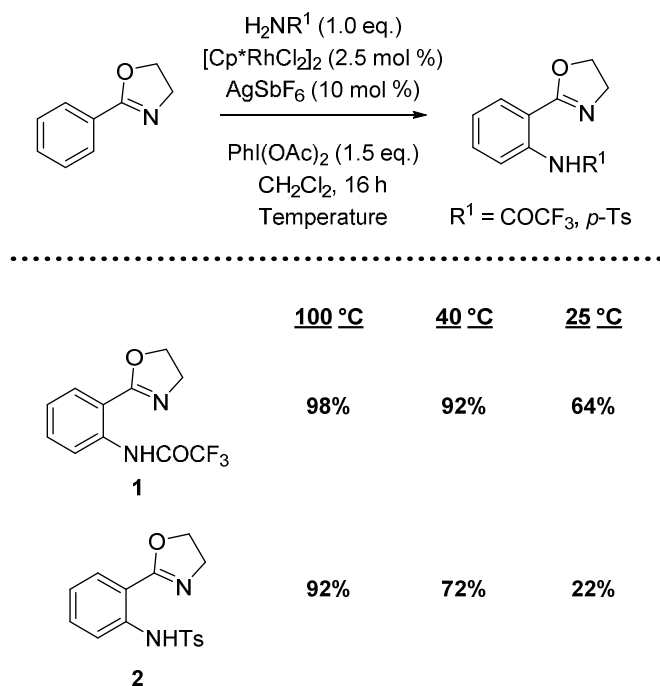
We next decided to investigate the nature of sulfonamides which could be used in conjunction with aryl oxazolines in the rhodium-promoted system (scheme 3). Pleasingly, a range of aromatic sulfonamides could be used alongside the *gem*-dimethyl oxazoline directing group at the optimum reaction temperature of 100 °C and only mono-aminated 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, *ortho*-, *meta*- and *para*-methyl functionalized sulfonamides afforded the *C-H* aminated products in good to excellent yield. Finally, alkyl sulfonamides were found to

be viable substrates in combination with both the unsubstituted and *gem*-dimethyl oxazoline

directing group.

Scheme 3: Sulfonamide scope
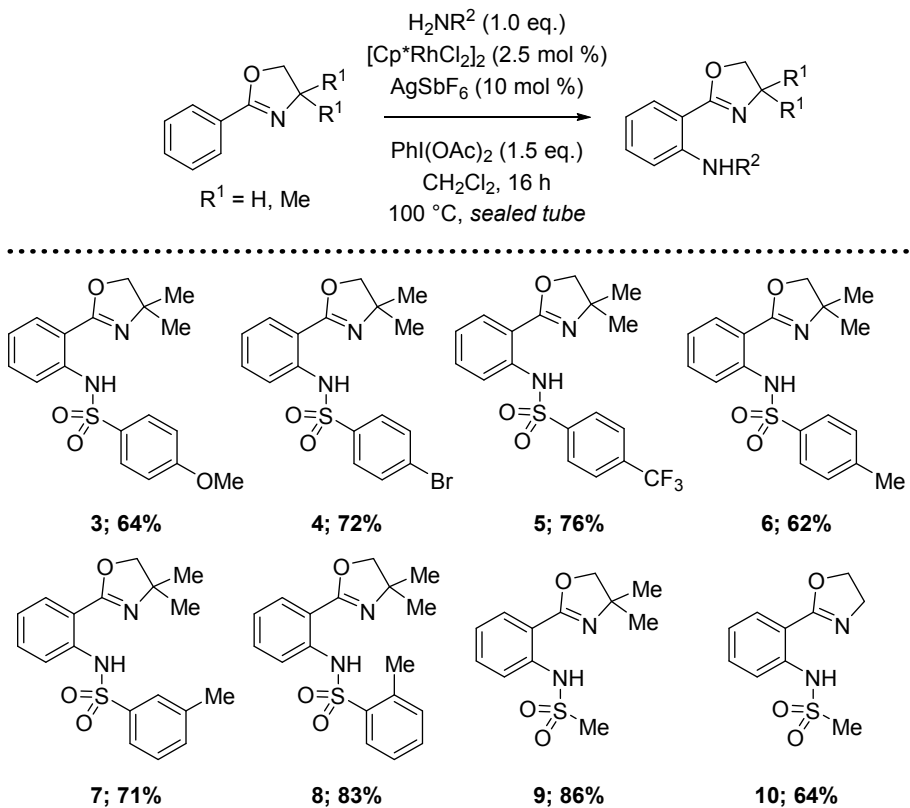
We then turned our attention to the functionalities on the aryl oxazoline (scheme 4).

Pleasingly under the optimum reaction conditions, we found a small selection of

electronically distinct aryl oxazolines 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**).

Scheme 4: Oxazoline scope

11; 78%   **12; 72%**   **13; 66%**   **14; 80%**
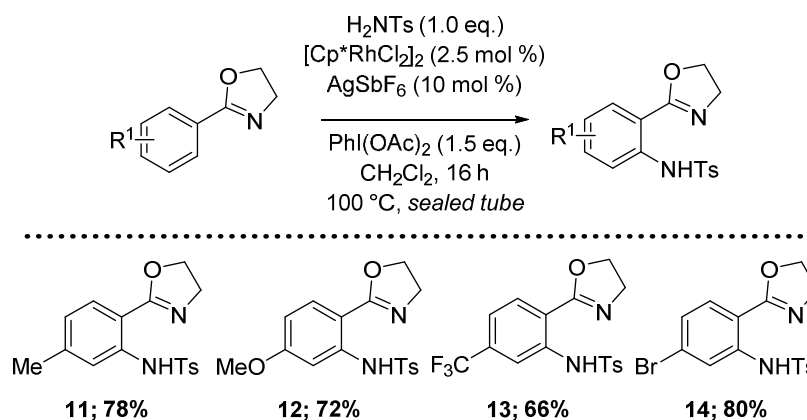
In an effort to demonstrate utility of this particular transformation we targeted the synthesis of sulfonamide **16**, a known potassium ion channel inhibitor.[10] We envisaged that the employment of our optimal *C-H* amidation conditions for sulfonamides would readily deliver **16** from 3-methoxy substituted aryl oxazoline **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-phenyl oxazoline **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 aryl oxazoline **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, 4-methoxyphenyl oxazoline **20** was found to show good reactivity towards 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.

Scheme 5: Initial investigations into the effect of electron donating groups on oxazoline reactivity
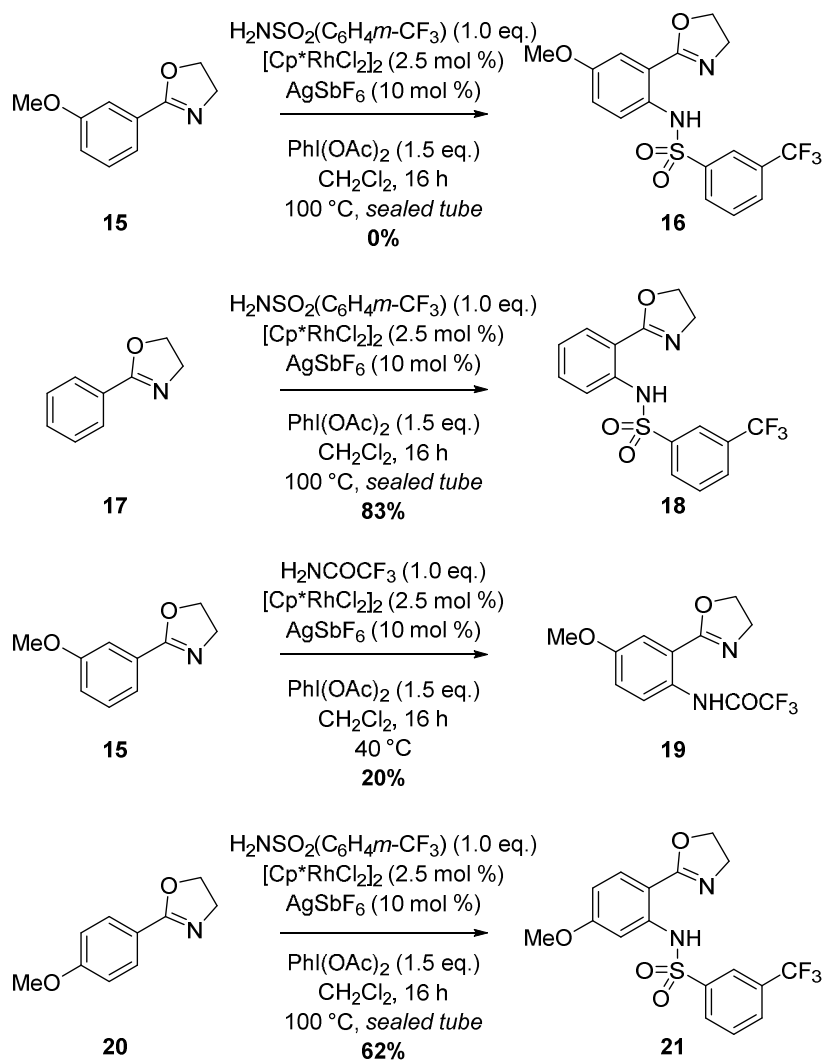
In order to explore the generality of this observation, an array of *para-* and *meta*-substituted

aryl oxazolines 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 *para*-toluenesulfonamide at 100 °C and trifluoroacetamide at 40 °C.

As shown in scheme 6 and in a similar manner to above, the incorporation of an electron

donating methoxy group *para-* to the oxazoline was highly successful with both amino

sources delivering the corresponding products in high yield. In contrast, 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 a *meta*-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 *para*-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-fluro substituted oxazoline and *para*-toluenesulfonamide was unambiguously confirmed by X-ray crystallography.[11] Notably, selective insertion into the 2-position of similar *meta*-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 is subjected to *C-H* amidation conditions with stoichiometric Cu(OAc)$_2$ and *para*-toluenesulfonamide.[13]

Scheme 6: Comparative study of *meta*-substituted versus *para*-substituted substrates

H$_2$NR^2(1.0 eq.)
[Cp*RhCl$_2$]$_2$ (2.5 mol %)
AgSbF$_6$ (10 mol %)

PhI(OAc)$_2$ (1.5 eq.)
CH$_2$Cl$_2$, 16 h
100 °C (*sealed tube*) or 40 °C   R^2 = Ts or COCF$_3$

22; R^1=Me$_2$N; R^2=Ts 0%
23; R^1=Me$_2$N; R^2=COCF$_3$ 24%

24; R^1=Me$_2$N; R^2=Ts 0%
25; R^1=Me$_2$N; R^2=COCF$_3$ 12%

12; R^1=MeO; R^2=Ts 72%
26; R^1=MeO; R^2=COCF$_3$ 100%

27; R^1=MeO; R^2=Ts 0%
19; R^1=MeO; R^2=COCF$_3$ 20%

11; R^1=Me; R^2=Ts 78%
28; R^1=Me; R^2=COCF$_3$ 84%

29; R^1=Me; R^2=Ts 47%
30; R^1=Me; R^2=COCF$_3$ 72%

31; R^1=MeO$_2$C; R^2=Ts 73%
32; R^1=MeO$_2$C; R^2=COCF$_3$ 92%

33; R^1=MeO$_2$C; R^2=Ts 57%
34; R^1=MeO$_2$C; R^2=COCF$_3$ 77%

35; R^2 = Ts 72%
36; R^2 = COCF$_3$ 97%

37; R^2 = Ts 61%
38; R^2 = COCF$_3$ 60%

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 *meta*-methoxy aromatic substrates, together with the unusual regioselectivity observed with the *meta*-fluoro substrate were particularly intriguing and warranted further investigation. Accordingly, we decided to conduct deuterium labelling experiments and these are shown in Scheme 7.[8,14] We conducted the reaction between 3-methoxy aryloxazoline **15** and *para*-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 di-deuterated materials **39** and **40**. This result confirms that rhodacycle

formation proceeds under the reaction conditions, but suggests that the problematic step in

the catalytic cycle is related to the formation of Rh(V)-nitrenoid species **B**. Although the

origin of this effect await further study, it may be that the presence of an electron donating

meta-substituent (with respect to the directing group) results in a strengthening 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 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 cyclometallation is occurring in this case. Finally, carrying out the

deuterium labelling experiment with the *meta*-fluoro aryloxazoline we were able to observe a

mixture which contained *C-H* amidation product **37** and a 1:1 mixture of recovered starting

material and mono *C*2 deuterated starting material. The observation of *C*2-selective mono

deuteration indicated that it is likely that selective rhodacycle formation gives rise to the

observed product, rather than 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.

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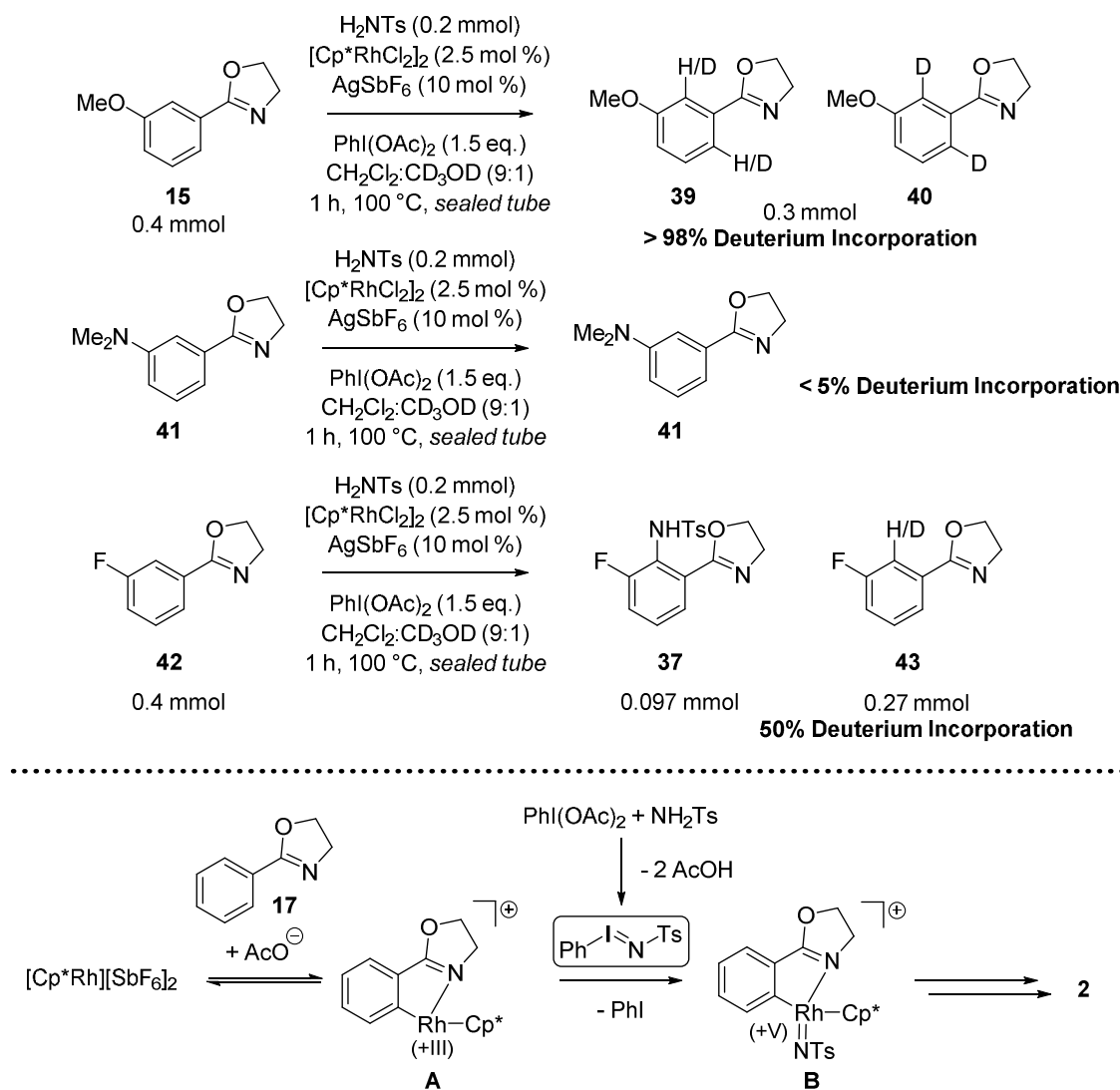
Finally, in order to show the potential of this method for synthesis of functionalized scaffolds we targeted the *C-H* amidation of 2-chloropyridine **44** (scheme 8). This substrate underwent smooth amidation and in high regiocontrol to generate **45**.[7] Subsequent hydrolysis of the acetamide followed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

Scheme 8: Synthesis of multi-functionalized heterocycles
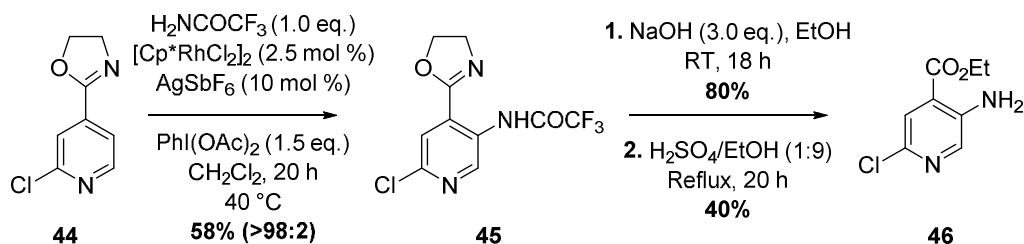
In conclusion, we have described the extension of our rhodium-promoted *C-H* amidation conditions to sulfonamide amino sources. We found a reaction temperature of 100 °C was key to affording efficient amidation with a range of aryl and alkyl sulfonamides, and that a range of functionalized oxazoline scaffolds were well tolerated. Through investigation and comparative study, we found aryl oxazolines with electron donating *meta*-substituents were incompatible with the reaction system whilst 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 procedures 2-(*p*-tolyl)-4,5-dihydrooxazole[6], 2-(4-methoxyphenyl)-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 eq.) and heated to 55 °C with stirring. Upon reaching the desired temperature ethanolamine (1.5 eq.) was added slowly via syringe and the reaction was stirred for 3 h before cooling to room temperature, and stirring for a further 18 hours. The crude reaction mixture was then

purified by recrystallisation 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]. Following 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 eq.) in dry dichloromethane (0.2 M) at 0 °C was added oxalyl chloride (3.0 eq.) and DMF (few drops). The reaction was allowed to warm to room temperature and stirred for a period of 3 hours before removing the solvent *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 eq.) was then added, followed by ethanolamine (3.0 eq.) 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-dimethylaminobenzoic acid (1.00 g, 6.05 mmol), oxalyl chloride (2.31 g, 18.2 mmol) and DMF (few drops) in dichloromethane (30 mL), 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: v_{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]$^+$ $C_{11}H_{17}N_2O_2$ calcd. 209.1285, found 209.1288.

Synthesis of 3-(dimethylamino)-N-(2-hydroxyethyl)benzamide. Following general procedure B, using 3-dimethylaminobenzoic acid (1.00 g, 6.05 mmol), oxalyl chloride (2.31 g, 18.2 mmol) and DMF (few drops) in dichloromethane (30 mL), 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: v_{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]$^+$ $C_{11}H_{17}N_2O_2$ 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), then ethanolamine (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: v_{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 was added

amide (1.0 eq.) and dry dichloromethane (0.6 M). With stirring NEt$_3$ (1.9 eq.) was then

added, followed by DMAP (0.2 eq.) and *p*-TsCl (1.7 eq.). 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 layers partitioned. The

aqueous layer was further extracted with dichloromethane. The combined organic layers were

dried over anhydrous MgSO$_4$, filtered and the solvent was removed *in vacuo*. The crude

residue was dissolved in MeOH (0.5 M) and NaOH pellets (3.0 eq.) were added in one

portion. The reaction mixture was stirred at room temperature for 1 – 3 h before removing the

solvent *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$_4$, 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. Following 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), then using 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: v_{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: v_{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), then using 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%). M.p.: 60 − 61 °C (lit., 59 − 60

°C)[4]; ^{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); $^{13}C\{^1H\}$ 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: v_{max}/ cm^{-1} (neat) 2991 (w), 2912 (w), 1649 (m), 1585 (s), 1270 (s), 1185 (s), 1055 (s), 949 (s), 842 (s), 715 (s); ^1H 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); $^{13}C\{^1H\}$ 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), then using NaOH pellets (116 mg, 6.42 mmol) and MeOH (6 mL), the oxazoline product was afforded as a colorless amorphous solid (409 mg, 68%). ^1H 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); $^{13}C\{^1H\}$ 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 was added oxazoline (2.0 eq.), [Cp*RhCl$_2$]$_2$ (2.5 mol %), AgSbF$_6$ (10 mol %), PhI(OAc)$_2$ (1.5 eq.) and sulfonamide

(1.0 eq.). 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 cooling 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%). M.p.: 74 – 75 °C (pentane); FTIR: v_{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-methyl-benzenesulfonamide (**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%). M.p.: 191 – 193 °C (lit.,[19] 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); $^{13}C\{^1H\}$ 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-methoxy-benzenesulfonamide (**3**). Following general procedure D, using 4-methoxybenzene sulfonamide (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.p.: 106 – 108 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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); $^{13}C\{^1H\}$ 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-bromo-benzenesulfonamide (**4**). Following general procedure D, using 4-bromobenzene sulfonamide (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%). M.p.: 111 – 114 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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); $^{13}C\{^1H\}$ 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-trifluoromethylbenzene sulfonamide (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%). M.p.: 80 – 81 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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-methyl-benzenesulfonamide (**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%). M.p.: 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-methylbenzene sulfonamide (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%). M.p.: 98 –

99 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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-methylbenzene sulfonamide (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%). M.p.: 96 –

97 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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%). M.p.: 86 – 88 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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]$^+$ $C_{12}H_{17}N_2O_3S$ 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%). M.p.: 149 – 150 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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]$^+$ $C_{10}H_{13}N_2O_3S$ 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%). M.p.: 117 –118 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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: v_{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%). M.p.: 160 – 161 °C (dichloromethane/petroleum ether (40/60));

FTIR: v_{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%). M.p.: 142

– 143 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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%). M.p.: 140

– 141 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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%). M.p.: 125

– 126 °C (pentane); FTIR: v_{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%). M.p.: 152 – 153 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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%). M.p.: 132 – 133 °C (pentane); FTIR: v_{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%). M.p.: 119 – 120 °C (pentane); FTIR: v_{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-dihydro-oxazole]-acetamide (**26**)[6]. Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(4-methoxyphenyl)-4,5-dihydro-oxazole (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%). M.p.: 103 – 104 °C (pentane); FTIR: v_{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%). M.p.: 120 – 121 °C (pentane); FTIR: v_{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%). M.p.: 128 – 129 °C (pentane); FTIR: v_{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-dihydro-oxazole]-acetamide (**30**)[6].
Following general procedure D, using trifluoroacetamide (65 mg, 0.20 mmol) and 2-(3-

methylphenyl)-4,5-dihydro-oxazole (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%). M.p.: 145 –

146 °C (pentane); FTIR: v_{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%). M.p.: 136

– 137 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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 (49mg, 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%). M.p.: 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%). M.p.: 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%). M.p.: 212 – 213 °C (pentane); FTIR: v_{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-methylbenzene sulfonamide

(**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%). M.p.: 145

– 146 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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-dihydro-oxazole]-acetamide (**36**)[6].

Following general procedure D, using trifluoroacetamide (23 mg, 0.20 mmol) and 2-(4-

fluorophenyl)-4,5-dihydro-oxazole (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%). M.p.: 121 – 122 °C (pentane); FTIR: v_{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%). M.p.: 109 – 110 °C (dichloromethane/petroleum ether (40/60)); FTIR: v_{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%). M.p.: 119 – 120 °C (pentane); FTIR: v_{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 colourless solid (34 mg, 58%). M.p.: 98 – 99 °C; FTIR: v_{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); ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.18 (1H, s, N*H*), 9.73 (1H, s, C*H*$_{ar}$), 7.75 (1H, s, C*H*$_{ar}$), 4.51 (2H, t, J = 9.5 Hz, C*H*$_2$), 4.24 (2H, t, J = 9.5 Hz, C*H*$_2$); ^{19}F NMR (376.5 MHz, CDCl$_3$): δ – 75.8; ^{13}C{^{1}H} 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 was added *N*-(6-chloro-4-(4,5-dihydrooxazol-2-yl)pyridine-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 hours. The reaction mixture was concentrated, dissolved in ethyl acetate and deionised 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 $MgSO_4$, filtered and the solvent was removed *in vacuo* to afford the aniline product as colourless solid (364 mg, 80%). M.p.: 184 – 185 °C; FTIR: v_{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); ^{1}H NMR (400 MHz, d^6-DMSO): 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{^{1}H} NMR (100.6 MHz, d^6-DMSO): δ 162.0, 144.0, 138.8, 135.0, 121.6, 115.6, 66.7, 55.3; HRMS: *m/z* [MH]$^+$ $C_8H_9{}^{35}ClN_3O$ 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_2SO_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 neutralised 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 $MgSO_4$, 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); ^{1}H 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{^{1}H} 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.

Supporting Information Available: ^{1}H, ^{13}C, ^{19}F NMR spectra for selected compounds, X-Ray Crystallography data and details of deuterium labelling experiments. This material is available free of charge via the Internet at http://pubs.acs.org

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