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Reaction conditions for the regiodivergent direct arylations at C2- or C5-positions of oxazoles using phosphine-free palladium catalysts

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Abstract. Two sets of reaction conditions for the regiodivergent C2- or C5- direct arylations of oxazole are reported. In both cases, phosphine-free catalysts and inexpensive bases were employed allowing the access to the arylated oxazoles in moderate to high yields. Using $Pd(OAc)_2$/KOAc as catalyst and base, regioselective C5-arylations were observed; whereas, using $Pd(acac)_2$/Cs_2CO_3 system, the arylation occurred at the C2-position of oxazole. The higher reactivity of C5-H bond of oxazole as compared to the C2-H bond in the presence of $Pd(OAc)_2$/KOAc system is consistent with a concerted metalation deprotonation mechanism; whereas the C2-arylation likely occurs *via* a simple base deprotonation of the oxazole C2-position. Then, from these C2- or C5-arylated oxazoles, a second palladium-catalyzed direct C-H bond arylation affords 2,5-diaryloxazoles with two different aryl groups. We also applied these sequential arylations to the straightforward synthesis of 2-arylphenanthro[9,10-*d*]oxazoles *via* three C-H bond functionalization steps. The Ru-catalyzed C-H arylation of the aryl unit of 2-aryloxazoles is also described.

Keywords: palladium; oxazole; direct arylation; C-H bond functionalization; C-C bond formation

Introduction

Several aryl-substituted oxazole derivatives exhibit important biological properties, such as Oxaprozin which is a non-steroidal anti-inflammatory drug used to relieve the inflammation associated with arthritis (Figure 1). Therefore, the discovery of general and simple routes to (poly)arylated oxazoles has potential for medicinal chemistry.

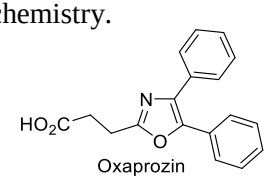

Figure 1. Structure of Oxaprozin.

In recent years, the direct arylation of (hetero)aromatics *via* Pd-catalyzed C–H bond functionalizations has brought a revolution in the access of arylated heteroarenes.[1,2] This methodology is very attractive compared to the Stille, Suzuki or Negishi couplings as they do not require the preliminary synthesis of organometallic derivatives.[3] Several examples of Pd-catalyzed arylations *via* a C-H bond functionalization of substituted oxazoles have been reported.[4] In contrast, only a few examples of Pd-catalyzed direct arylations of unsubstituted oxazole have been described.[5-7] In 2010, Strotman, Chobanian et al. reported a study dealing with the regiodivergent arylation (C2- *vs* C5-arylations) of oxazoles (Scheme 1, top).[5c] They revealed that the C5-arylation is preferred in polar solvents such as DMA associated to 10 mol% 2-di-*tert*-butylphosphino-3,4,5,6-tetramethyl-2′,4′,6′-triisopropyl-1,1′-biphenyl (**L1**) as phosphine ligand; conversely, C2-arylation regioselectively took place in the nonpolar solvent xylene associated to 10 mol% 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (**L2**) as phosphine ligand. In both cases, they employed K_2CO_3/PivOH as base/additive. By contrast, in 2013, Bellina et al. obtained C5-arylated oxazoles regioselectively using $Pd(OAc)_2$ catalyst and Bu_4NOAc as base without adding phosphine ligand.[6b] To our knowledge, regiodivergent direct arylations of oxazole using phosphine-free conditions have not yet been described (Scheme 1, bottom).

As a better understanding of the influence of reaction conditions on the regioselectivity control of the arylation of oxazoles is still needed, we reinvestigated the influence of the catalyst, base and solvent for these couplings. Herein, we report i) conditions for the palladium-catalyzed regiodivergent direct arylation of oxazole using phosphine-free catalysts; ii) on the scope of the regioselectivity of C2-arylation, C5-arylation and one pot C2,C5-diarylation; iii) on the influence of the presence of aryl-substituents at C2- or C5-positions of oxazole on their reactivity for access to C2,C5-diaryloxazoles; iv) on the synthesis of 2-arylphenanthro[9,10-*d*]oxazoles *via* three successive C-H bond functionalization steps; and v) on the Ru-catalyzed C-H arylation of the aryl unit of 2-aryloxazoles.

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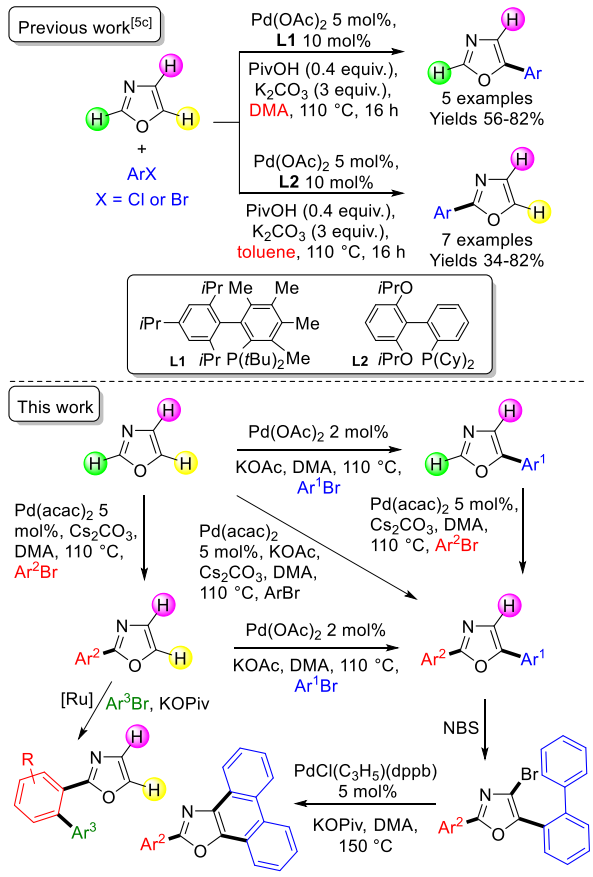

Scheme 1. Pd-catalyzed direct arylations of oxazole.

The free energy of activation for direct arylation of oxazole in the presence of Pd-catalysts *via* Concerted Metalation Deprotonation (CMD)[8] pathway has been calculated by Gorelsky (Figure 2). The energy of activation of the C-H bond flanked by two heteroelements is higher (25.3 kcal mol^{-1}), than the energy of activation of the C-H bond at C5-position (23.5 kcal mol^{-1}). Therefore, due to the lower energy of activation of the C-H bond at C5-position of oxazole, for reactions which proceed *via* a Pd-catalyzed CMD mechanism, we expected to be able to control the regioselectivity in favor of C5-arylation using acetates as base/ligand; whereas, regioselective C2-arylations might be obtained in the presence of a quite strong base, *via* deprotonation of the C2-position of oxazole.

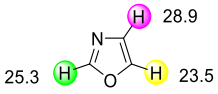

Figure 2. Free energy of activation ($\Delta G^{\ddagger}_{298K}$, kcal mol^{-1}) for direct arylation *via* the CMD pathway involving an acetate ligand with the [Pd(C_6H_5)(PMe_3)(OAc)] catalyst.[8]

Results and Discussion

3-Bromoquinoline (1 equiv.) and oxazole (2 equiv.) were employed as the model substrates for our study (Table 1). We initially examined the influence of the nature of the base on the regioselectivities and yields using phosphine-free $Pd(OAc)_2$ catalyst and DMA as the solvent. We had previously observed that KOAc as base/ligand associated to $Pd(OAc)_2$ in DMA promotes very efficiently the coupling of several heteroarenes with aryl bromides.[9] Under these phosphine-free conditions, DMA and also heteroarenes such as oxazoles and some aryl halides might act as ligands to stabilize catalytically active Pd-species. At 110 °C, the expected C5-heteroarylated oxazole **1a** was obtained with a complete regioselectivity in 78% yield (Table 1, entry 1). In sharp contrast, the use of Cs_2CO_3 (2-3 equiv.) as the base instead of KOAc gives rise to the C2-heteroarylated oxazole **1b** in 98-100% regioselectivity and in 22-37% yields (Table 1, entries 2-4). The higher reactivity of C5-H bond as compared to the C2-H bond of oxazoles in the presence of $Pd(OAc)_2$/KOAc system seems to be in agreement with a CMD mechanism;[10] whereas the oxazole C2-arylation likely occurs *via* a simple base deprotonation of the oxazole C2-position. In order to improve the yield in the C2-arylated oxazole **1b**, the influence of the solvent, base and catalyst was examined. The use of stronger base *t*BuOK, led to a poor conversion of 3-bromoquinoline, and the desired product **1b** was only obtained in trace amount (Table 1, entry 5). The use of $PdCl_2$, $PdCl_2(MeCN)_2$, $PdCl_2(PhCN)_2$ and $Pd(dba)_2$ catalysts using Cs_2CO_3 as base, afforded **1b** in similar regioselectivities and yields than $Pd(OAc)_2$ (Table 1, entries 6-9). The reactions performed in other solvents such as DMF and NMP gave **1b** in poor yields; whereas, the use of xylene was ineffective (Table 1, entries 10-12). $Pd(acac)_2$ catalyst using KOAc as the base gave a mixture of products **1a**, **1b** and **1c** in 59:13:28 ratio (Table 1, entry 14). Conversely, the use of 5 mol% $Pd(acac)_2$ catalyst associated to Cs_2CO_3 (3 equiv.) was very effective, and the target C2-heteroarylated oxazole **1b** was obtained with complete regioselectivity and in 65% yield (Table 1, entry 15). Finally, in order to obtain the C2,C5-diheteroarylated oxazole **1c** *via* a one pot reaction, we employed a mixture of KOAc and Cs_2CO_3 as a mixture of bases (Table 1, entry 16). To our delight, the desired product **1c** was obtained in 80% selectivity and in 74% yield (**1a** was also observed in 19% selectivity). The substrate scope of the C5-arylation of oxazole using a set of (hetero)aryl bromides was investigated (Scheme 2). In the presence of 2 mol% $Pd(OAc)_2$, KOAc as the base in DMA, very regioselective C5-arylation reactions and good yields in the 5-aryloxazoles **2a-7a** were obtained using aryl bromides bearing nitro, cyano, formyl, propionyl, benzoyl or ester *para*-substituents. In all cases, very low amounts of C2-arylated or C2,C5-diarylated oxazoles were detected by GC/MS and ^{1}H NMR analysis of the crude mixtures. Lower yields in **8a-10a** were obtained for the coupling aryl bromides *para*-substituted by trifluoromethyl, chloro or fluoro groups, owing to the formation of significant amounts of 2,5-diaryl oxazoles **8c-10c** in the course of these reactions.

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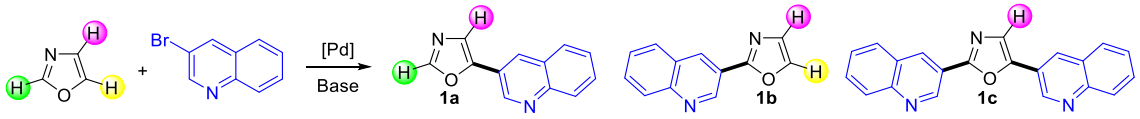
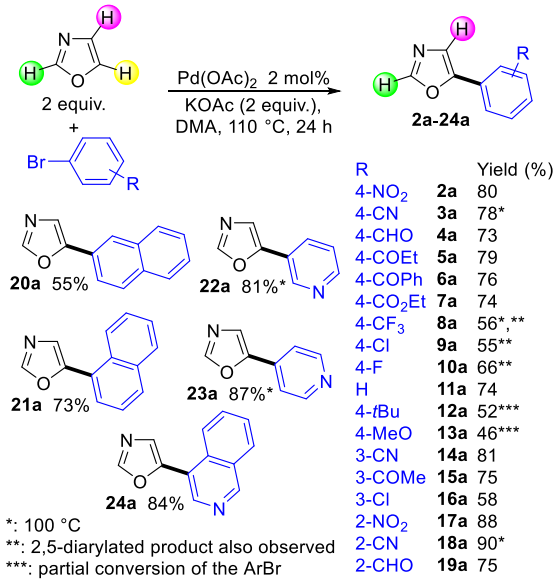
Table 1. Influence of the reaction conditions on the Pd-catalyzed arylation of oxazole with 3-bromoquinoline



Entry	Catalyst (mol%)	Solvent	Base	Conv. (%)	Ratio **1a**:**1b**:**1c**	Yield (%)
1	$Pd(OAc)_2$ (2)	DMA	KOAc	100	100:0:0	**1a** 78[b]
2	$Pd(OAc)_2$(5)	DMA	Cs_2CO_3	38	0:100:0	**1b** 22[a,b]
3	$Pd(OAc)_2$ (5)	DMA	Cs_2CO_3	42	0:100:0	**1b** 33[b]
4	$Pd(OAc)_2$ (5)	DMA	Cs_2CO_3	45	2:98:0	**1b** 37
5	$Pd(OAc)_2$ (5)	DMA	*t*BuOK	9	0:100:0	-
6	$PdCl_2$ (5)	DMA	Cs_2CO_3	33	0:100:0	-
7	$PdCl_2(MeCN)_2$ (5)	DMA	Cs_2CO_3	40	0:100:0	-
8	$PdCl_2(PhCN)_2$ (5)	DMA	Cs_2CO_3	28	0:100:0	-
9	$Pd(dba)_2$ (5)	DMA	Cs_2CO_3	36	0:100:0	-
10	$PdCl_2(MeCN)_2$ (5)	DMF	Cs_2CO_3	31	0:100:0	-
11	$PdCl_2(MeCN)_2$ (5)	NMP	Cs_2CO_3	20	0:100:0	-
12	$PdCl_2(MeCN)_2$ (5)	xylene	Cs_2CO_3	3	-	-
13	Pd/C 10% (5)	DMA	Cs_2CO_3	8	0:100:0	-
14	$Pd(acac)_2$ (5)	DMA	KOAc	100	59:13:28	-
15	$Pd(acac)_2$ (5)	DMA	Cs_2CO_3	100	0:100:0	**1b** 65
16	$Pd(acac)_2$ (5)	DMA	Cs_2CO_3/KOAc	100	19:1:80	**1c** 74[c]

Conditions: 3-Bromoquinoline (1 equiv.), oxazole (2 equiv.), base (3 equiv.), 24 h, 110 °C, conversion of 3-bromoquinoline, isolated yields. [a] 100 °C. [b] Base 2 equiv. [c] 3-Bromoquinoline (3 equiv.), oxazole (1 equiv.), Cs_2CO_3 (3 equiv.) and KOAc (3 equiv.) as mixture of bases, 48 h, conversion of oxazole.

With the electron-rich aryl bromides, 4-*tert*-butylbromobenzene and 4-bromoanisole, the 5-aryloxazoles **12a** and **13a** were also obtained in moderate yields of 52% and 46%, respectively due to a partial conversion of these aryl bromides. Cyano-, acetyl- and chloro-substituents at *meta*-position on the aryl bromide were also tolerated giving access to the corresponding 5-aryloxazoles **14a**-**16a** in 58-81% yields. Reactions with more hindered, 2-bromonitrobenzene, 2-bromobenzonitrile, 2-bromobenzaldehyde and 1-bromonaphthalene were also successful providing the products **17a**-**19a** and **21a** in 73-90% yields.

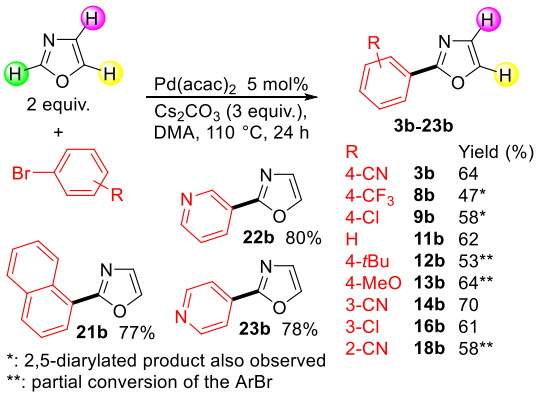


R		Yield (%)
4-NO_2	**2a**	80
4-CN	**3a**	78*
4-CHO	**4a**	73
4-COEt	**5a**	79
4-COPh	**6a**	76
4-CO_2Et	**7a**	74
4-CF_3	**8a**	56*,**
4-Cl	**9a**	55**
4-F	**10a**	66**
H	**11a**	74
4-*t*Bu	**12a**	52***
4-MeO	**13a**	46***
3-CN	**14a**	81
3-COMe	**15a**	75
3-Cl	**16a**	58
2-NO_2	**17a**	88
2-CN	**18a**	90*
2-CHO	**19a**	75

Scheme 2. Scope of the C5-arylation of oxazole.

The *N*-containing heterocycles, 3- or 4-bromopyridines, and 4-bromoisoquinoline also regioselectively afforded the desired C5-arylated oxazole derivatives **22a**-**24a** in 81-87% yields.

Then, the scope of the C2-arylation of oxazole using $Pd(acac)_2$/Cs_2CO_3 as catalytic system was examined (Scheme 3). Lower yields were generally obtained than for the C5-arylations. However, in all cases, very regioselective C2-arylations were observed. From *para*-substituted aryl bromides bearing electron-withdrawing – e.g. cyano or chloro – or electron-donating – e.g. *tert*-butyl or methoxy – groups, similar yields in the C2-arylated oxazoles **b** were obtained. Moreover, *meta*- or *ortho*-substituents on the aryl bromide and also 3- or 4-bromopyridines also afforded the desired products **14b**-**23b** in 58-80% yields.



R		Yield (%)
4-CN	**3b**	64
4-CF_3	**8b**	47*
4-Cl	**9b**	58*
H	**11b**	62
4-*t*Bu	**12b**	53**
4-MeO	**13b**	64**
3-CN	**14b**	70
3-Cl	**16b**	61
2-CN	**18b**	58**

Scheme 3. Scope of the C2-arylation of oxazole.

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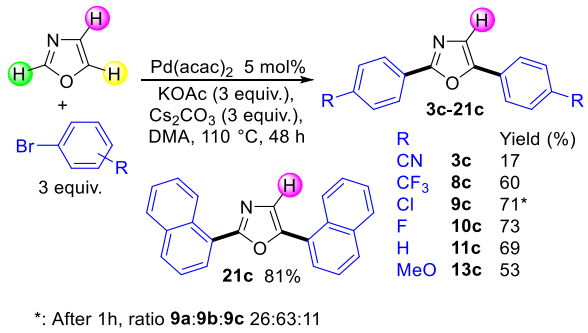
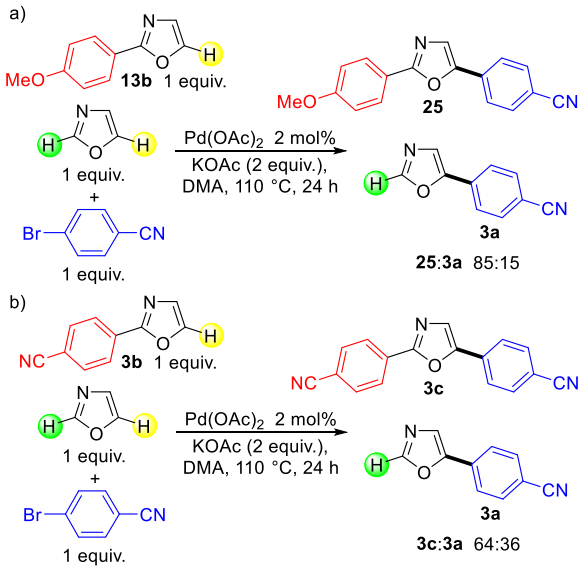
The synthesis of 2,5-diarylated oxazoles from oxazole in a single pot was then examined (Scheme 4). As shown in the table 1 and schemes 2 and 3, the site selectivity for the arylation of oxazole is highly dependent on the presence of acetates for C5-arylation and on the use of a quite strong base for C2-arylation. Based on these results, we assumed that a mixture of KOAc and Cs_2CO_3 as a base might promote the one pot oxazole 2,5-diarylation. The reaction of oxazole with 3 equiv. of 4-bromobenzonitrile, 3 equiv. of KOAc and 3 equiv. of Cs_2CO_3 in the presence of 5 mol% $Pd(acac)_2$ catalyst afforded the desired 2,5-diaryloxazoles **3c** in only 17% yield, revealing that with a highly electron-deficient aryl bromide, the second arylation is much slower than the first one. Conversely, under the same conditions, the reactions with 4-trifluoro-, 4-chloro- and 4-fluoro-substituted aryl bromides afforded the target products **8c**-**10c** in 60-73% yields. 2,5-Diphenyloxazole **11c** was also obtained in good yield using bromobenzene as the aryl source. The use of an excess of the electron-rich aryl bromide, 4-bromoanisole (3 equiv.) in the presence of 5 mol% $Pd(acac)_2$ catalyst gave the desired diarylated product **12c** in 53% yield. 1-Bromonaphthalene was also successfully employed for the one-pot synthesis of the 2,5-diarylated oxazole **21c**. In order to determine the most reactive arylation site under these conditions, the selectivity of the reaction with 4-chlorobromobenzene was measured at 1 h. A mixture of **9a**:**9b**:**9c** with a ratio of 26:63:11 was obtained, indicating that under these conditions, the C2-arylation is favored.



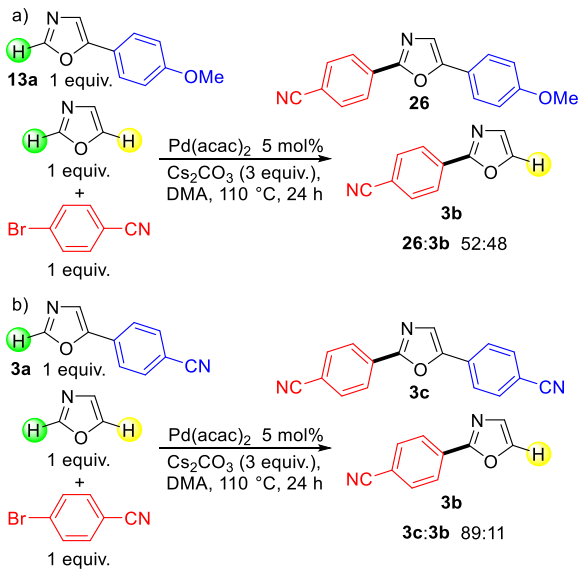
Scheme 4. Scope of the C2,C5-diarylation of oxazole.

We performed two competition reactions to probe the oxazoles C2-substituent preference of the $Pd(OAc)_2$ catalyst for the C5-arylation (Scheme 5). From an equimolar mixture of oxazole and 2-(4-methoxyphenyl)oxazole **13b** using 4-bromobenzonitrile as the aryl source, in the presence of 2 mol% $Pd(OAc)_2$ associated to KOAc as base, the formation of the 2,5-diaryloxazole **25** was observed in 85% selectivity; whereas, 5-aryloxazole **3a** was only produced in 15% selectivity (Scheme 5, a). When an equimolar mixture of oxazole and 4-(oxazol-2-yl)benzonitrile **3b** was used, the ratio between the diaryloxazole **3c** and 5-aryloxazole **3a** was 64:36 (Scheme 5, b). These results indicate that arylated oxazoles react faster than oxazole and that the presence of an electron-rich aryl at the C2-position of oxazole favors the C5-arylation.



Scheme 5. Competition reactions for the C5-arylation of oxazoles.

Then, we performed two competition reactions from an equimolar mixture of oxazole and the 5-aryloxazoles **3a** and **13a** using again 4-bromobenzonitrile as the aryl source, in the presence of 5 mol% $Pd(acac)_2$ associated to Cs_2CO_3 as base (Scheme 6). The formation of the 2,5-diaryloxazoles **26** and **3c** was observed in 52% selectivity from oxazole and **13a**, and 89% selectivity from oxazole and **3a**. The presence of an electron-deficient aryl group at the oxazole C5-position stongly favors the C2-arylation.



Scheme 6. Competition reactions for C2-arylation of oxazoles.

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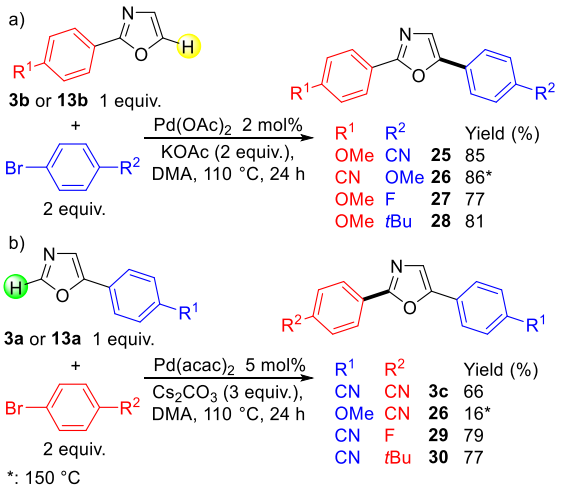
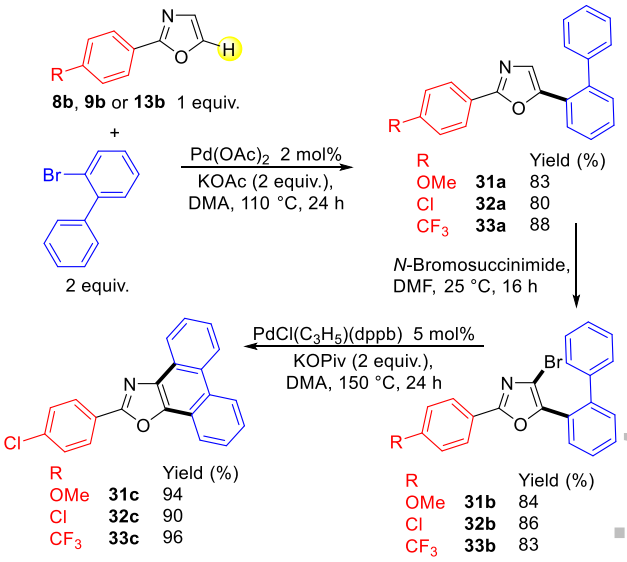
Based on these results, we prepared a set of non-symmetrical 2,5-diaryl oxazoles (Scheme 7). From the C2-arylated oxazoles **3b** and **13b** and a set of electron-rich or -poor aryl bromides, the 2,5-diaryl oxazoles **25-28** were obtained in high yields. We observed in the scheme 6b that an oxazole substituted by an electron-deficient arene at C5-position favors the C2-arylation. Indeed, from **3a** and 4-bromofluorobenzene or 4-*tert*-butylbromobenzene, the products **29** and **30** were obtained in good yields. The synthesis of **3c** *via* successive C5- followed by C2-arylation also afforded the expected product in a good 66% yield. In contrast, the reaction of **13a** with 4-bromobenzonitrile gave the 2,5-diaryl oxazole **26** in only 16% yield. Therefore, the preparation of **26** *via* a C2- followed by C5-arylation sequence should be preferred.



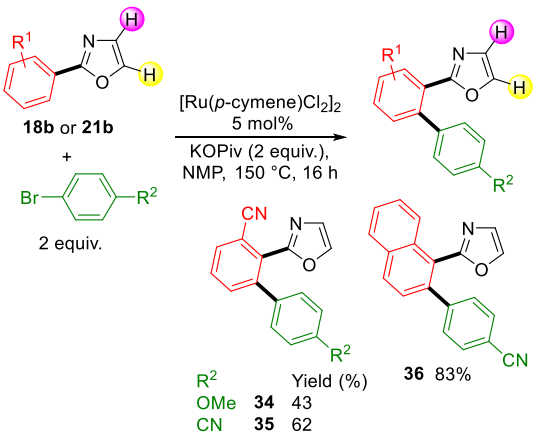
Scheme 7. Synthesis of C2,C5-diaryloxazoles *via* successive arylations.

We also applied the regiocontrolled sequential arylation of oxazole to the synthesis of 2-arylphenanthro[9,10-*d*]oxazoles (Scheme 8). From the previously prepared 2-aryloxazoles **8b**, **9b** and **13b**, the introduction of a biphenyl unit at C5-position proceed in 80-88% yields using 2-bromobiphenyl in the presence of 2 mol% $Pd(OAc)_2$ catalyst. Then, the bromination of the 4-position of the oxazole unit of **31a-33a** with *N*-bromosuccinimide gave the 4-bromooxazoles **31b-33b** in 83-86% yield. Finally, the Pd-catalyzed intramolecular C-H bond arylations of **31b-33b** using 2 mol% of $PdCl(C_3H_5)(dppb)$ [dppb: 1,4-bis(diphenylphosphino)butane] catalyst with 2 equiv. of PivOK as the base in DMA at 150 °C – as it was previously demonstrated that these conditions are very effective to promote the C-H bond cleavage of benzene derivatives[11] – afforded the target π-extended polycyclic heteroaromatic hydrocarbons **31c-33c** in almost quantitative yields. In the course of these synthesis, the three C-H bonds of oxazole were successively arylated.



Scheme 8. Synthesis of 2-arylphenanthro[9,10-*d*]oxazoles *via* successive arylations.

To our knowledge, only two examples of Ru-catalyzed C-H arylations of the aryl unit of 2-aryloxazoles have been reported so far.[12] To demonstrate that, using an appropriate catalytic system, not only the oxazole C-H bonds are reactive, we also studied the reactivity of the aryl substituent of the 2-aryloxazoles **18b** and **21b** in Ru-catalyzed direct arylations (Scheme 9). For these reactions, $[Ru(p\text{-cymene})Cl_2]_2$ was employed as the catalyst and KOPiv as the base. With the electron-rich and -poor aryl bromides 4-bromoanisole and 4-bromobenzonitrile, regioselective arylations of the aryl unit of **18b** were observed affording the products **34** and **35** in moderate yields. A higher yield of 83% in **36** was obtained for the arylation of 2-(naphthalen-1-yl)oxazole **21b**.



Scheme 9. Ru-catalyzed direct arylation of C2-arylated oxazoles.

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Conclusion

In summary, we demonstrated that the regioselectivity of the direct arylation of oxazole can be controlled using the appropriate phosphine-free palladium catalyst/base system. From $Pd(OAc)_2$ catalyst associated to KOAc, regioselective C5-arylations were observed; whereas, the use of $Pd(acac)_2$ catalyst associated to Cs_2CO_3 led to the C2-arylated oxazoles. A wide variety of (hetero)aryl bromides were tolerated by these reaction conditions. The access to 2,5-diaryloxazoles bearing identical or different aryl groups *via* one-pot diarylation or sequential arylations is also described. These sequential arylation allowed the straightforward synthesis of 2-arylphenanthro[9,10-*d*]oxazoles in good yields *via* three C-H bond functionalization steps. Using Ru-catalysis, the C-H arylation of the aryl unit of 2-aryloxazoles is also possible. These phosphine-free regiodivergent procedures employ easily available catalysts, bases and substrates and tolerate a variety of useful functional groups. For these reasons, these protocols provide economically viable and environmentally very attractive accesses to (poly)arylated oxazole derivatives.

Experimental Section

General procedures for palladium-catalyzed direct (di)arylations of oxazoles:

Procedure A: The reaction of the aryl bromide (1 or 2 mmol) (see schemes), oxazole derivative (1 or 2 mmol) (see schemes), KOAc (0.196 g, 2 mmol) in the presence of $Pd(OAc)_2$ (2.4 mg, 0.02 mmol) at 100 or 110 °C (see schemes) during 24 h in DMA (4 mL) under argon affords the coupling products **1a**-**24a**, **25**-**28** and **31a**-**33a** after evaporation of the solvent and purification on silica gel. Eluent heptane:ethyl acetate: 3:7 for **23a**; 4:6 for **22a**; 6:4 for **1a**, **14a**, **24a**; 7:3 for **2a**-**4a**, **6a**, **7a**, **13a**, **15a**, **17a**-**19a**, **25**-**27**; 8:2 for **5a**, **8a**, **10a**-**12a**, **16a**, **20a**, **21a**, **28**, **31a**; 9:1 for **9a**, **32a**, **33a**.

Procedure B: The reaction of the aryl bromide (1 or 2 mmol) (see schemes), oxazole derivative (1 or 2 mmol) (see schemes), Cs_2CO_3 (0.975 g, 3 mmol) in the presence of $Pd(acac)_2$ (15.2 mg, 0.05 mmol) at 110 °C during 24 h in DMA (4 mL) under argon affords the coupling products **1b**-**23b**, **29** and **30** after evaporation of the solvent and purification on silica gel. Eluent heptane:ethyl acetate: 6:4 for **1b**, **22b**; 7:3 for **14b**, **18b**, **29**, **30**; 8:2 for **3b**-**13b**, **16b**, **23b**; 9:1 for **21b**.

Procedure C: The reaction of the aryl bromide (3 mmol), oxazole (0.069 g, 1 mmol), KOAc (0.294 g, 3 mmol) Cs_2CO_3 (0.975 g, 3 mmol) in the presence of $Pd(acac)_2$ (15.2 mg, 0.05 mmol) at 110 °C during 48 h in DMA (4 mL) under argon affords the coupling products **1c**-**21c** after evaporation of the solvent and purification on silica gel. Eluent heptane:ethyl acetate: 3:7 for **1c**, 7:3 for **3c**, **13c**; 8:2 for **8c**, **10c**, **11c**; 9:1 for **9c**, **21c**.

5-(Quinolin-3-yl)oxazole (1a):[17] Following procedure **A**, from 3-bromoquinoline (0.208 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **1a** was obtained in 78% yield (0.153 g) as a brown solid: mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.02 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 149.2, 147.7, 146.7, 130.6, 130.1, 129.5, 128.1, 127.6, 127.5, 122.9, 121.1. LRMS calcd for M^+ $C_{12}H_8N_2O$ 196, found 196.

5-(4-Nitrophenyl)oxazole (2a):[6b] Following procedure **A**, from 4-bromonitrobenzene (0.202 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **2a** was obtained in 80% yield (0.152 g) as a yellow solid: mp 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H), 8.01 (s, 1H), 7.81 (d, *J* = 8.9 Hz, 2H), 7.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 149.5, 147.4, 133.4, 124.8, 124.7, 124.5. LRMS calcd for M^+ $C_9H_6N_2O_3$ 190, found 190.

4-(Oxazol-5-yl)benzonitrile (3a):[13] Following procedure **A**, from 4-bromobenzonitrile (0.182 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **3a** was obtained in 80% yield (0.133 g) as a white solid: mp 151-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 149.8, 132.8, 131.7, 124.7, 124.2, 118.4, 112.0. LRMS calcd for M^+ $C_{10}H_6N_2O$ 170, found 170.

4-(Oxazol-5-yl)benzaldehyde (4a):[14] Following procedure **A**, from 4-bromobenzaldehyde (0.185 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **4a** was obtained in 73% yield (0.126 g) as a white solid: mp 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.99 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 151.6, 150.5, 136.1, 133.1, 130.6, 124.8, 124.2. LRMS calcd for M^+ $C_{10}H_7NO_2$ 173, found 173.

1-(4-(Oxazol-5-yl)phenyl)propan-1-one (5a): Following procedure **A**, from 4-bromopropiophenone (0.213 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **5a** was obtained in 73% yield (0.159 g) as a white solid: mp 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.97 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.49 (s, 1H), 3.01 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 151.2, 150.5, 136.5, 131.6, 128.7, 124.3, 123.4, 31.8, 8.3. Anal. Calcd for $C_{12}H_{11}NO_2$ (201.23): C, 71.63; H, 5.51. Found: C, 71.78; H, 5.39. LRMS calcd for M^+ $C_{12}H_{11}NO_2$ 201, found 201.

(4-(Oxazol-5-yl)phenyl)(phenyl)methanone (6a): Following procedure **A**, from 4-bromobenzophenone (0.261 g, 1 mmol) and oxazole (0.138 g, 2 mmol), KOAc (0.196 g, 2 mmol), product **6a** was obtained in 76% yield (0.189 g) as a yellow solid: mp 129-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.51-7.46 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 151.2, 150.6, 137.4, 137.3, 132.6, 131.2, 130.8, 129.9, 128.4, 124.0, 123.4. Anal. Calcd for $C_{16}H_{11}NO_2$ (249.27): C, 77.10; H, 4.45. Found: C, 77.02; H, 4.66. HRMS calcd for M^+Na $C_{16}H_{11}NNaO_2$ 272.0682, found 272.0683.

Ethyl 4-(oxazol-5-yl)benzoate (7a): Following procedure **A**, from ethyl 4-bromobenzoate (0.229 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **7a** was obtained in 74% yield (0.160 g) as a yellow solid: mp 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.95 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.46 (s, 1H), 4.40 (q, *J* = 7.6 Hz, 2H), 1.40 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 151.1, 150.6, 131.6, 130.3, 130.2, 124.1, 123.3, 61.2, 14.3. Anal. Calcd for $C_{12}H_{11}NO_3$ (217.22): C, 66.35; H, 5.10. Found: C, 66.54; H, 4.89. HRMS calcd for M^+Na $C_{12}H_{11}NNaO_3$ 240.0631, found 240.0632.

5-(4-(Trifluoromethyl)phenyl)oxazole (8a):[15a] Following procedure **A**, from 4-(trifluoromethyl)bromobenzene (0.225 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **8a** was obtained in 56% yield (0.119 g) as a yellow solid: mp 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 150.4, 131.1, 130.6 (q, *J* = 32.5 Hz), 126.1 (q, *J* = 3.7 Hz), 124.7, 124.0 (q, *J* = 272.1 Hz), 122.9. LRMS calcd for M^+ $C_{10}H_6F_3NO$ 213, found 213.

5-(4-Chlorophenyl)oxazole (9a):[15b] Following procedure **A**, from 4-bromochlorobenzene (0.191 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **9a** was obtained in 55% yield (0.098 g) as a white solid: mp 69-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 134.7, 129.4, 126.4, 125.8, 122.0. LRMS calcd for M^+ C_9H_6ClNO 179, found 179.

5-(4-Fluorophenyl)oxazole (10a):[16] Following procedure **A**, from 4-bromofluorobenzene (0.175 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **10a** was obtained in 66% yield (0.107 g) as a white solid: mp 43-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.63 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.29 (s, 1H), 7.12 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, *J* = 249.0 Hz), 150.9, 150.6, 126.4 (d, *J* = 8.3 Hz), 124.2 (d, *J* = 4.5 Hz), 121.3, 116.2 (d, *J* = 22.1 Hz). LRMS calcd for M^+ C_9H_6FNO 163, found 163.

5-Phenyloxazole (11a):[15b] Following procedure **A**, from bromobenzene (0.157 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **11a** was obtained in 74% yield (0.107 g) as a yellow solid: mp 45-47 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.38-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 150.6, 129.1, 128.8, 127.9, 124.5, 121.6. LRMS calcd for M^+ C_9H_7NO 145, found 145.

5-(4-(*tert*-Butyl)phenyl)oxazole (12a):[17] Following procedure **A**, from 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **12a** was obtained in 52% yield (0.104 g) as a yellow solid: mp 43-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.31 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 151.7, 150.2, 125.9, 125.0, 124.2, 121.0, 34.8, 31.2. LRMS calcd for M^+ $C_{13}H_{15}NO$ 201, found 201.

5-(4-Methoxyphenyl)oxazole (13a):[6b] Following procedure **A**, from 4-bromoanisole (0.187 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **13a** was obtained in 46% yield (0.080 g) as an orange solid: mp 63-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 151.7, 150.0, 126.1, 120.7, 120.1, 114.5, 55.5. LRMS calcd for M^+ $C_{10}H_9NO_2$ 175, found 175.

3-(Oxazol-5-yl)benzonitrile (14a):[14] Following procedure **A**, from 3-bromobenzonitrile (0.182 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **14a** was obtained in 81% yield (0.138 g) as a white solid: mp 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.93 (s, 1H), 7.86 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.61 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 149.5, 131.9, 130.0, 129.1, 128.4, 127.9, 123.3, 118.2, 113.6. LRMS calcd for M^+ $C_{10}H_6N_2O$ 170, found 170.

1-(3-(Oxazol-5-yl)phenyl)ethan-1-one (15a): Following procedure **A**, from 3-bromoacetophenone (0.199 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **15a** was obtained in 75% yield (0.140 g) as a white solid: mp 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.95 (s, 1H), 7.90 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.82 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 150.9, 150.7, 137.7, 129.3, 128.6, 128.4, 128.3, 124.0, 122.4, 26.7. Anal. Calcd for $C_{11}H_9NO_2$ (187.20): C, 70.58; H, 4.85. Found: C, 70.69; H, 5.02. LRMS calcd for M^+ $C_{11}H_9NO_2$ 187, found 187.

5-(3-Chlorophenyl)oxazole (16a):[18] Following procedure **A**, from 3-bromochlorobenzene (0.191 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **16a** was obtained in 58% yield (0.104 g) as a white solid: mp 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.64 (t, *J* = 1.4 Hz, 1H), 7.52 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.38 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.30 (dt, *J* = 7.0, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 150.3, 135.0, 130.2, 129.4, 128.6, 124.4, 122.5, 122.4. LRMS calcd for M^+ C_9H_6ClNO 179, found 179.

5-(2-Nitrophenyl)oxazole (17a):[19] Following procedure **A**, from 2-bromonitrobenzene (0.202 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **17a** was obtained in 88% yield (0.167 g) as a yellow solid: mp 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.86 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 (td, *J* = 7.8, 1.0 Hz, 1H), 7.54 (td, *J* = 7.8, 1.5 Hz, 1H), 7.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 147.7, 146.6, 132.7, 129.9, 129.8, 126.0, 124.6, 121.7. LRMS calcd for M^+ $C_9H_6N_2O_3$ 190, found 190.

2-(Oxazol-5-yl)benzonitrile (18a):[14] Following procedure **A**, from 2-bromobenzonitrile (0.182 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **18a** was obtained in 90% yield (0.153 g) as a white solid: mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.94 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 147.8, 134.2, 133.3, 130.5, 128.6, 126.5, 126.2, 118.3, 108.0. LRMS calcd for M^+ $C_{10}H_6N_2O$ 170, found 170.

2-(Oxazol-5-yl)benzaldehyde (19a):[14] Following procedure **A**, from 2-bromobenzaldehyde (0.185 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **19a** was obtained in 75% yield (0.130 g) as a yellow solid: mp 99-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1H), 8.05 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.70-7.63 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 151.9, 148.7, 134.0, 133.5, 129.7, 129.5, 129.1, 129.0, 126.6. LRMS calcd for M^+ $C_{10}H_7NO_2$ 173, found 173.

5-(Naphthalen-2-yl)oxazole (20a):[20] Following procedure **A**, from 2-bromonaphthalene (0.207 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **20a** was obtained in 55% yield (0.107 g) as an orange solid: mp 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.97 (s, 1H), 7.90-7.81 (m, 3H), 7.72 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.55-7.49 (m, 2H), 7.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 150.6, 133.3, 133.2, 128.8, 128.3, 127.8, 126.8, 126.6, 125.0, 123.3, 122.1, 122.0. LRMS calcd for M^+ $C_{13}H_9NO$ 195, found 195.

5-(Naphthalen-1-yl)oxazole (21a):[13] Following procedure **A**, from 1-bromonaphthalene (0.207 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **21a** was obtained in 73% yield (0.142 g) as a yellow solid: mp 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.5 Hz, 1H), 8.07 (s, 1H), 7.93-7.89 (m, 2H), 7.75 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.61-7.52 (m, 3H), 7.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 150.9, 134.0, 130.4, 129.9, 128.9, 127.2, 126.8, 126.4, 125.4, 125.3, 125.0, 124.9. LRMS calcd for M^+ $C_{13}H_9NO$ 195, found 195.

5-(Pyridin-3-yl)oxazole (22a):[14] Following procedure **A**, from 3-bromopyridine (0.158 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **22a** was obtained in 81% yield (0.118 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.59 (d, *J* = 4.1 Hz, 1H), 7.98 (s, 1H), 7.93 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.46 (s, 1H), 7.38 (dd, *J* = 8.0, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 149.7, 148.9, 145.9, 131.6, 124.1, 123.8, 122.9. LRMS calcd for M^+ $C_8H_6N_2O$ 146, found 146.

5-(Pyridin-4-yl)oxazole (23a):[14] Following procedure **A**, from 4-bromopyridine hydrochloride (0.194 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **23a** was obtained in 87% yield (0.127 g) as a brown solid: mp 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (bs, 2H), 8.00 (s, 1H), 7.57 (s, 1H), 7.53 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 150.6, 149.2, 134.6, 124.8, 118.3. LRMS calcd for M^+ $C_8H_6N_2O$ 146, found 146.

5-(Isoquinolin-4-yl)oxazole (24a): Following procedure **A**, from 4-bromoisoquinoline (0.208 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **24a** was obtained in 84% yield (0.164 g) as a white solid: mp 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 1H), 8.78 (s, 1H), 8.24 (d, *J* = 8.2 Hz, 1H), 8.12 (s, 1H), 7.05 (d, *J* = 8.2 Hz, 1H),

7.80 (t, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 151.5, 148.4, 142.5, 132.4, 131.5, 128.4, 128.3, 127.7, 125.7, 123.9, 119.2. Anal. Calcd for $C_{12}H_8N_2O$ (196.21): C, 73.46; H, 4.11. Found: C, 73.28; H, 4.01. HRMS calcd for M^+H $C_{12}H_9N_2O$ 197.0709, found 197.0712.

2-(Quinolin-3-yl)oxazole (1b): Following procedure **B**, from 3-bromoquinoline (0.208 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **1b** was obtained in 65% yield (0.127 g) as a yellow solid: mp 152-154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (d, *J* = 2.0 Hz, 1H), 8.73 (d, *J* = 2.0 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 7.74 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 148.5, 148.0, 139.3, 133.5, 130.7, 129.5, 128.8, 128.5, 127.5, 127.2, 120.7. Anal. Calcd for $C_{12}H_8N_2O$ (196.21): C, 73.46; H, 4.11. Found: C, 73.51; H, 4.05. HRMS calcd for M^+Na $C_{12}H_8N_2NaO$ 219.0529, found 219.0531.

4-(Oxazol-2-yl)benzonitrile (3b):[21] Following procedure **B**, from 4-bromobenzonitrile (0.182 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **3b** was obtained in 64% yield (0.109 g) as a white solid: mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 0.5 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 139.9, 132.8, 131.3, 129.3, 126.9, 118.4, 113.8. LRMS calcd for M^+ $C_{10}H_6N_2O$ 170, found 170.

2-(4-(Trifluoromethyl)phenyl)oxazole (8b):[21] Following procedure **B**, from 4-(trifluoromethyl)bromobenzene (0.225 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **8b** was obtained in 47% yield (0.100 g) as a white solid: mp 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.77 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 139.4, 132.0 (q, *J* = 32.6 Hz), 130.6, 128.9, 126.6, 125.8 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.2 Hz). LRMS calcd for M^+ $C_{10}H_6F_3NO$ 213, found 213.

2-(4-Chlorophenyl)oxazole (9b):[21] Following procedure **B**, from 4-bromochlorobenzene (0.191 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **9b** was obtained in 58% yield (0.104 g) as a white solid: mp 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 138.8, 136.5, 129.1, 128.6, 127.6, 126.0. LRMS calcd for M^+ C_9H_6ClNO 179, found 179.

2-Phenyloxazole (11b):[5c] Following procedure **B**, from bromobenzene (0.157 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **11b** was obtained in 62% yield (0.090 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.03 (m, 2H), 7.71 (s, 1H), 7.49-7.44 (m, 3H), 7.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 138.6, 130.3, 128.8, 128.4, 127.5, 126.4. LRMS calcd for M^+ C_9H_7NO 145, found 145.

2-(4-(*tert*-Butyl)phenyl)oxazole (12b):[22] Following procedure **B**, from 1-bromo-4-*tert*-butylbenzene (0.213 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **12b** was obtained in 53% yield (0.106 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 153.9, 138.4, 128.4, 126.3, 125.9, 124.9, 35.1, 31.3. LRMS calcd for M^+ $C_{13}H_{15}NO$ 201, found 201.

2-(4-Methoxyphenyl)oxazole (13b):[21] Following procedure **B**, from 4-bromoanisole (0.187 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **13b** was obtained in 64% yield (0.112 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 0.5 Hz, 1H), 7.18 (d, *J* = 0.5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 161.4, 138.1, 128.3, 128.1, 120.5, 114.3, 55.5. LRMS calcd for M^+ $C_{10}H_9NO_2$ 175, found 175.

3-(Oxazol-2-yl)benzonitrile (14b):[21] Following procedure **B**, from 3-bromobenzonitrile (0.182 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **14b** was obtained in 70% yield (0.119 g) as a white solid: mp 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (t, *J* = 1.5 Hz, 1H), 8.28 (dt, *J* = 8.4, 1.5 Hz, 1H), 7.77 (s, 1H), 7.72 (dt, *J* = 8.4, 1.5 Hz, 1H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 139.5, 133.4, 130.3, 129.8, 129.7, 128.9, 128.7, 118.0, 113.3. LRMS calcd for M^+ $C_{10}H_6N_2O$ 170, found 170.

2-(3-Chlorophenyl)oxazole (16b):[23] Following procedure **B**, from 3-bromochlorobenzene (0.191 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **16b** was obtained in 61% yield (0.109 g) as a white solid: mp 43-45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.94 (dt, *J* = 8.4, 1.7 Hz, 1H), 7.73 (s, 1H), 7.44-7.37 (m, 2H), 7.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 139.0, 134.9, 130.3, 130.1, 129.1, 128.7, 126.5, 124.4. LRMS calcd for M^+ C_9H_6ClNO 179, found 179.

2-(Oxazol-2-yl)benzonitrile (18b): Following procedure **B**, from 2-bromobenzonitrile (0.182 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **18b** was obtained in 58% yield (0.099 g) as a white solid: mp 51-53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.83 (s, 1H), 7.81 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.70 (td, *J* = 7.8, 1.2 Hz, 1H), 7.54 (td, *J* = 7.8, 1.2 Hz, 1H), 7.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 139.7, 134.8, 132.8, 130.2, 129.3, 129.1, 128.6, 117.9, 109.8. Anal. Calcd for $C_{10}H_6N_2O$ (170.17): C, 70.58; H, 3.55. Found: C, 70.66; H, 3.75. HRMS calcd for M^+Na $C_{10}H_6N_2NaO$ 193.0372, found 193.0372.

2-(Naphthalen-1-yl)oxazole (21b):[24] Following procedure **B**, from 1-bromonaphthalene (0.207 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **21b** was obtained in 77% yield (0.150 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (d, *J* = 8.5 Hz, 1H), 8.21 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.81 (s, 1H), 7.64 (td, *J* = 7.8, 1.2 Hz, 1H), 7.59-7.52 (m, 2H), 7.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 138.3, 133.9, 131.2, 130.2, 128.5, 128.4, 127.8, 127.5, 126.3, 126.2, 125.0, 124.1. LRMS calcd for M^+ $C_{13}H_9NO$ 195, found 195.

2-(Pyridin-3-yl)oxazole (22b):[4a] Following procedure **B**, from 3-bromopyridine (0.158 g, 1 mmol) and oxazole (0.138 g, 2 mmol), product **22b** was obtained in 80% yield (0.117 g) as a yellow solid: mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.67 (d, *J* = 3.9 Hz, 1H), 8.29 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.76 (d, *J* = 0.5 Hz, 1H), 7.39 (dd, *J* = 8.0, 3.9 Hz, 1H), 7.27 (d, *J* = 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 151.2, 147.8, 139.4, 133.7, 128.9, 123.9, 123.7. LRMS calcd for M^+ $C_8H_6N_2O$ 146, found 146.

2-(Pyridin-4-yl)oxazole (23b):[25] Following procedure **B**, from 4-bromopyridine hydrochloride (0.194 g, 1 mmol), oxazole (0.138 g, 2 mmol) and Cs_2CO_3 (1.304 g, 4 mmol), product **23b** was obtained in 78% yield (0.114 g) as a yellow solid: mp 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 6.0 Hz, 2H), 7.88 (d, *J* = 6.0 Hz, 1H), 7.79 (s, 1H), 7.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 150.6, 139.8, 134.2, 129.2, 120.0. LRMS calcd for M^+ $C_8H_6N_2O$ 146, found 146.

2,5-Di(quinolin-3-yl)oxazole (1c): Following procedure **C**, from 3-bromoquinoline (0.624 g, 3 mmol) and oxazole (0.069 g, 2 mmol), product **1c** was obtained in 74% yield (0.239 g) as a yellow solid: mp 265-267 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, *J* = 2.1 Hz, 1H), 9.30 (d, *J* = 2.1 Hz, 1H), 8.90 (d, *J* = 2.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.82 (td, *J* = 7.5, 1.4 Hz, 1H), 7.80-7.75 (m, 2H), 7.68-7.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 149.6, 148.7, 147.9, 147.8, 146.6, 133.6, 131.0, 130.4, 130.2, 129.6, 129.5, 128.5, 128.1, 127.7, 127.6, 127.3, 125.2, 121.1, 120.4. Anal. Calcd for $C_{21}H_{13}N_3O$ (323.36): C, 78.00; H, 4.05. Found: C, 78.25; H, 4.02. HRMS calcd for M^+Na $C_{21}H_{13}N_3NaO$ 346.0951, found 346.0949.

4,4'-(Oxazole-2,5-diyl)dibenzonitrile (3c):[26] Following procedure **C**, from 4-bromobenzonitrile (0.546 g, 3 mmol)

and oxazole (0.069 g, 1 mmol), product **3c** was obtained in 17% yield (0.046 g) as a white solid: mp 265-267 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 150.7, 133.1, 132.9, 131.5, 130.7, 127.1, 126.8, 124.8, 118.5, 118.3, 114.4, 112.4. LRMS calcd for M^+ $C_{17}H_9N_3O$ 271, found 271.

2,5-Bis(4-(trifluoromethyl)phenyl)oxazole (8c):[7a] Following procedure **C**, from 4-(trifluoromethyl)bromobenzene (0.675 g, 3 mmol) and oxazole (0.069 g, 1 mmol), product **8c** was obtained in 60% yield (0.214 g) as a white solid: mp 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 150.6, 132.3 (q, *J* = 32.7 Hz), 130.8 (m), 130.6 (q, *J* = 32.7 Hz), 130.2 (m), 126.7, 126.1 (q, *J* = 3.8 Hz), 125.9 (q, *J* = 3.8 Hz), 125.5, 124.4, 123.8 (q, *J* = 272.0 Hz), 123.7 (q, *J* = 272.0 Hz). LRMS calcd for M^+ $C_{17}H_9F_6NO$ 357, found 357.

2,5-Bis(4-chlorophenyl)oxazole (9c):[27] Following procedure **C**, from 4-bromochlorobenzene (0.573 g, 3 mmol) and oxazole (0.069 g, 2 mmol), product **9c** was obtained in 71% yield (0.206 g) as a white solid: mp 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 150.5, 136.6, 134.4, 129.3, 129.2, 127.6, 126.3, 125.7, 125.4, 123.9. LRMS calcd for M^+ $C_{15}H_9Cl_2NO$ 289, found 289.

2,5-Bis(4-fluorophenyl)oxazole (10c):[28] Following procedure **C**, from 4-bromofluorobenzene (0.525 g, 3 mmol) and oxazole (0.069 g, 2 mmol), product **10c** was obtained in 73% yield (0.188 g) as a white solid: mp 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 8.2 , 5.3 Hz, 2H), 7.69 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.37 (s, 1H), 7.22-7.12 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 162.9 (d, *J* = 249.1 Hz), 161.8 (d, *J* = 250.2 Hz), 150.7, 128.5 (d, *J* = 8.7 Hz), 126.2 (d, *J* = 8.2 Hz), 124.4, 123.9, 123.2, 116.3 (d, *J* = 22.1 Hz), 116.2 (d, *J* = 22.1 Hz). LRMS calcd for M^+ $C_{15}H_9F_2NO$ 257, found 257.

2,5-Diphenyloxazole (11c):[27] Following procedure **C**, from bromobenzene (0.471 g, 3 mmol) and oxazole (0.069 g, 2 mmol), product **11c** was obtained in 69% yield (0.152 g) as a white solid: mp 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.51-7.42 (m, 6H), 7.34 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 151.4, 130.5, 129.1, 129.0, 128.6, 128.2, 127.6, 126.4, 124.4, 123.6. LRMS calcd for M^+ $C_{15}H_{11}NO$ 221, found 221.

2,5-Bis(4-methoxyphenyl)oxazole (13c):[27] Following procedure **C**, from 4-bromoanisole (0.561 g, 3 mmol) and oxazole (0.069 g, 2 mmol), product **13c** was obtained in 53% yield (0.149 g) as a white solid: mp 143-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 160.8, 159.8, 150.9, 127.9, 125.7, 121.9, 121.2, 120.6, 114.5, 114.3, 55.5 (2C). LRMS calcd for M^+ $C_{17}H_{15}NO_3$ 281, found 281.

2,5-Di(naphthalen-1-yl)oxazole (21c):[29] Following procedure **C**, from 1-bromonaphthalene (0.621 g, 3 mmol) and oxazole (0.069 g, 2 mmol), product **21c** was obtained in 81% yield (0.260 g) as a yellow solid: mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (d, *J* = 8.6 Hz, 1H), 8.44 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 8.0, 1.1 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.96-7.87 (m, 4H), 7.72-7.53 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 150.3, 134.0, 134.0, 131.3, 130.3, 130.2, 129.6, 128.8, 128.6, 127.9, 127.7, 127.2, 126.8, 126.5, 126.4, 126.3, 126.2, 125.5, 125.4, 125.1, 125.0, 123.9. LRMS calcd for M^+ $C_{23}H_{15}NO$ 321, found 321.

4-(2-(4-Methoxyphenyl)oxazol-5-yl)benzonitrile (25): Following procedure **A**, from 4-bromobenzonitrile (0.364 g, 2 mmol) and 2-(4-methoxyphenyl)oxazole **13b** (0.175 g, 1 mmol), product **25** was obtained in 85% yield (0.235 g) as a yellow solid: mp 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.55 (s, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 161.9, 148.8, 132.8, 132.1, 128.3, 126.2, 124.2, 119.6, 118.6, 114.4, 111.2, 55.5. Anal. Calcd for $C_{17}H_{12}N_2O_2$ (276.30): C, 73.90; H, 4.38. Found: C, 74.15; H, 4.28. LRMS calcd for M^+ $C_{17}H_{12}N_2O_2$ 276, found 276.

4-(5-(4-Methoxyphenyl)oxazol-2-yl)benzonitrile (26): Following procedure **A**, from 4-bromoanisole (0.374 g, 2 mmol) and 4-(oxazol-2-yl)benzonitrile **3b** (0.170 g, 1 mmol) at 150 °C, product **26** was obtained in 86% yield (0.237 g) a yellow solid: mp 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.38 (s, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 158.6, 152.6, 132.6, 131.3, 126.4, 126.0, 122.7, 120.2, 118.4, 114.6, 113.2, 55.4. Anal. Calcd for $C_{17}H_{12}N_2O_2$ (276.30): C, 73.90; H, 4.38. Found: C, 73.85; H, 4.51. LRMS calcd for M^+ $C_{17}H_{12}N_2O_2$ 276, found 276.

5-(4-Fluorophenyl)-2-(4-methoxyphenyl)oxazole (27): Following procedure **A**, from 4-bromofluorobenzene (0.350 g, 2 mmol) and 2-(4-methoxyphenyl)oxazole **13b** (0.175 g, 1 mmol), product **27** was obtained in 77% yield (0.207 g) as a white solid: mp 131-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.67 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.34 (s, 1H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, *J* = 248.5 Hz), 161.4, 161.3, 149.9, 127.9, 125.9 (d, *J* = 8.2 Hz), 124.5 (d, *J* = 3.3 Hz), 122.9 (d, *J* = 1.3 Hz), 120.2, 116.0 (d, *J* = 22.1 Hz), 114.3, 55.4. Anal. Calcd for $C_{16}H_{12}FNO_2$ (269.28): C, 71.37; H, 4.49. Found: C, 71.56; H, 4.20. LRMS calcd for M^+ $C_{16}H_{12}NO_2$ 269, found 269.

5-(4-(*tert*-Butyl)phenyl)-2-(4-methoxyphenyl)oxazole (28): Following procedure **A**, from 1-bromo-4-*tert*-butylbenzene (0.426 g, 2 mmol) and 2-(4-methoxyphenyl)oxazole **13b** (0.175 g, 1 mmol), product **28** was obtained in 81% yield (0.249 g) as a white solid: mp 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 161.0, 151.5, 150.9, 127.9, 125.8, 125.4, 123.9, 122.8, 120.4, 114.2, 55.4, 34.8, 31.2. Anal. Calcd for $C_{20}H_{21}NO_2$ (307.39): C, 78.15; H, 6.89. Found: C, 77.89; H, 6.98. LRMS calcd for M^+ $C_{20}H_{21}NO_2$ 307, found 307.

4-(2-(4-Fluorophenyl)oxazol-5-yl)benzonitrile (29): Following procedure **B**, from 4-bromofluorobenzene (0.350 g, 2 mmol) and 4-(oxazol-5-yl)benzonitrile **3a** (0.170 g, 1 mmol), product **29** was obtained in 79% yield (0.208 g) as a white solid: mp 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.57 (s, 1H), 7.19 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4 (d, *J* = 252.2 Hz), 161.6, 149.4, 132.8, 131.8, 128.7 (d, *J* = 8.7 Hz), 126.2, 124.3, 123.2 (d, *J* = 3.3 Hz), 118.5, 116.2 (d, *J* = 22.2 Hz), 111.6. Anal. Calcd for $C_{16}H_9FN_2O$ (264.26): C, 72.72; H, 3.43. Found: C, 72.89; H, 3.62. LRMS calcd for M^+ $C_{16}H_9FN_2O$ 264, found 264.

4-(2-(4-(*tert*-Butyl)phenyl)oxazol-5-yl)benzonitrile (30): Following procedure **B**, from 1-bromo-4-*tert*-butylbenzene (0.426 g, 2 mmol) and 4-(oxazol-5-yl)benzonitrile **3a** (0.170 g, 1 mmol), product **30** was obtained in 77% yield (0.232 g) as a yellow solid: mp 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.57 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 154.5, 149.1, 132.8, 132.0, 126.4, 126.3, 125.9, 124.3, 124.1, 118.6, 111.3, 35.0, 31.2. Anal. Calcd for $C_{20}H_{18}N_2O$ (302.38): C, 79.44; H, 6.00. Found: C, 79.65; H, 5.82. LRMS calcd for M^+ $C_{20}H_{18}N_2O$ 302, found 302.

5-([1,1'-Biphenyl]-2-yl)-2-(4-methoxyphenyl)oxazole (31a): Following procedure **A**, from 2-bromobiphenyl

(0.466 g, 2 mmol) and 2-(4-methoxyphenyl)oxazole **13b** (0.175 g, 1 mmol), product **31a** was obtained in 83% yield (0.271 g) as a white solid: mp 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.6 Hz, 3H), 7.49-7.31 (m, 8H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.38 (s, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 160.7, 149.7, 141.6, 139.8, 130.8, 128.9, 128.6, 128.0, 127.9, 127.7, 127.6, 126.8, 126.6, 126.3, 120.2, 114.2, 55.4. Anal. Calcd for $C_{22}H_{17}NO_2$ (327.38): C, 80.71; H, 5.23. Found: C, 80.89; H, 5.05. LRMS calcd for M^+ $C_{22}H_{17}NO_2$ 327, found 327.

5-([1,1'-Biphenyl]-2-yl)-2-(4-chlorophenyl)oxazole (32a): Following procedure **A**, from 2-bromobiphenyl (0.466 g, 2 mmol) and 2-(4-chlorophenyl)oxazole **9b** (0.180 g, 1 mmol), product **32a** was obtained in 80% yield (0.265 g) as a yellow solid: mp 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.45 (td, *J* = 7.6, 1.5 Hz, 1H), 7.42-7.29 (m, 9H), 6.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 150.6, 141.4, 140.0, 136.2, 130.8, 129.0, 128.9, 128.5, 128.4, 127.8, 127.6, 127.4, 126.7, 126.5, 126.4, 125.8. Anal. Calcd for $C_{21}H_{14}ClNO$ (331.80): C, 76.02; H, 4.25. Found: C, 76.31; H, 4.02. LRMS calcd for M^+ $C_{21}H_{14}ClNO$ 331, found 331.

5-([1,1'-Biphenyl]-2-yl)-2-(4-(trifluoromethyl)phenyl)oxazole (33a): Following procedure **A**, from 2-bromobiphenyl (0.466 g, 2 mmol) and 2-(4-(trifluoromethyl)phenyl)oxazole **8b** (0.213 g, 1 mmol), product **33a** was obtained in 88% yield (0.321 g) as a yellow solid: mp 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.49 (td, *J* = 7.6, 1.5 Hz, 1H), 7.45-7.31 (m, 7H), 6.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 151.2, 141.4, 140.2, 131.6 (q, *J* = 32.5 Hz), 130.9, 130.5, 128.9, 128.6, 128.5, 127.8, 127.7, 126.9, 126.7, 126.3, 126.2, 125.7 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.3 Hz). Anal. Calcd for $C_{22}H_{14}F_3NO$ (365.36): C, 72.32; H, 3.86. Found: C, 72.12; H, 4.07. LRMS calcd for M^+ $C_{22}H_{14}NO$ 365, found 365.

5-([1,1'-Biphenyl]-2-yl)-4-bromo-2-(4-methoxyphenyl)oxazole (31b): The reaction of 5-([1,1'-biphenyl]-2-yl)-2-(4-methoxyphenyl)oxazole **31a** (0.245 g, 0.75 mmol), *N*-bromosuccinimide (0.267 g, 1.5 mmol) at 25 °C during 16 h in DMF (4 mL) under argon affords the coupling product **31b** after evaporation of the solvent and purification on silica gel in 84% yield (0.256 g) as a yellow oil. Eluent heptane:ethyl acetate: 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.53-7.44 (m, 3H), 7.36-7.25 (m, 5H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 160.6, 146.4, 141.8, 141.2, 130.8, 130.0, 129.8, 128.7, 128.2, 127.9, 127.3, 127.2, 125.3, 119.1, 114.6, 114.1, 55.4. LRMS calcd for M^+ $C_{22}H_{12}BrNO_2$ 405, found 405.

5-([1,1'-Biphenyl]-2-yl)-4-bromo-2-(4-chlorophenyl)oxazole (32b): The reaction of 5-([1,1'-biphenyl]-2-yl)-2-(4-chlorophenyl)oxazole **32a** (0.248 g, 0.75 mmol), *N*-bromosuccinimide (0.267 g, 1.5 mmol) at 25 °C during 16 h in DMF (4 mL) under argon affords the coupling product **32b** after evaporation of the solvent and purification on silica gel in 86% yield (0.264 g) as a yellow oil. Eluent heptane:ethyl acetate: 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.6 Hz, 1H), 7.57-7.46 (m, 5H), 7.35-7.24 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 147.3, 141.9, 141.1, 136.9, 130.8, 130.1, 130.0, 129.0, 128.7, 128.2, 127.4, 127.3, 127.2, 124.9, 124.8, 114.8. LRMS calcd for M^+ $C_{21}H_{13}ClBrNO$ 411, found 411.

5-([1,1'-Biphenyl]-2-yl)-4-bromo-2-(4-(trifluoromethyl)phenyl)oxazole (33b): The reaction of 5-([1,1'-biphenyl]-2-yl)-2-(4-(trifluoromethyl)phenyl)oxazole **33a** (0.273 g, 0.75 mmol), *N*-bromosuccinimide (0.267 g, 1.5 mmol) at 25 °C during 16 h in DMF (4 mL) under argon affords the coupling product **33b** after evaporation of the solvent and purification on silica gel in 83% yield (0.276 g) as a yellow oil. Eluent heptane:ethyl acetate: 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.58-7.48 (m, 3H), 7.37-7.26 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 148.0, 142.0, 141.1, 132.2 (q, *J* = 32.5 Hz), 130.8, 130.2, 130.0, 129.4, 128.7, 128.3, 127.4, 127.3, 126.3, 125.7 (q, J = 3.7 Hz), 124.8, 124.0 (q, *J* = 272.3 Hz), 115.1. LRMS calcd for M^+ $C_{22}H_{13}BrF_3NO$ 444, found 444.

2-(4-Methoxyphenyl)phenanthro[9,10-*d*]oxazole (31c):[30] The reaction of 5-([1,1'-biphenyl]-2-yl)-4-bromo-2-(4-methoxyphenyl)oxazole **31b** (0.203 g, 0.5 mmol), KOPiv (0.140 g, 1 mmol) in the presence of $PdCl(C_3H_5)$(dppb) (15.2 mg, 0.025 mmol) at 150 °C during 24 h in DMA (4 mL) under argon affords the coupling product **31c** after evaporation of the solvent and purification on silica gel in 94% yield (0.152 g) as a white solid: mp 230-232 °C. Eluent heptane:ethyl acetate: 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (t, *J* = 8.6 Hz, 2H), 8.62 (d, *J* = 7.9 Hz, 1H), 8.32 (d, *J* = 7.0 Hz, 3H), 7.77-7.65 (m, 4H), 7.07 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4, 161.9, 144.6, 135.6, 129.1, 128.9, 128.8, 127.3, 127.2, 126.2, 126.1, 126.0, 123.7, 123.4, 122.9, 121.2, 120.7, 120.3, 114.4, 55.5. LRMS calcd for M^+ $C_{22}H_{15}NO_2$ 325, found 325.

2-(4-Chlorophenyl)phenanthro[9,10-*d*]oxazole (32c):[30] The reaction of 5-([1,1'-biphenyl]-2-yl)-4-bromo-2-(4-chlorophenyl)oxazole **32b** (0.205 g, 0.5 mmol), KOPiv (0.140 g, 1 mmol) in the presence of $PdCl(C_3H_5)$(dppb) (15.2 mg, 0.025 mmol) at 150 °C during 24 h in DMA (4 mL) under argon affords the coupling product **32c** after evaporation of the solvent and purification on silica gel in 90% yield (0.148 g) as a white solid: mp 261-263 °C. Eluent heptane:ethyl acetate: 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (t, *J* = 8.6 Hz, 2H), 8.59 (d, *J* = 7.9 Hz, 1H), 8.40-8.26 (m, 3H), 7.80-7.65 (m, 4H), 7.58 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 145.0, 137.0, 135.5, 129.4, 129.3, 128.9, 128.4, 127.6, 127.5, 126.6, 126.3, 126.2, 126.1, 123.8, 123.5, 122.7, 121.0, 120.8. LRMS calcd for M^+ $C_{21}H_{12}ClNO$ 329, found 329.

2-(4-(Trifluoromethyl)phenyl)phenanthro[9,10-*d*]oxazole (33c): The reaction of 5-([1,1'-biphenyl]-2-yl)-4-bromo-2-(4-(trifluoromethyl)phenyl)oxazole **33b** (0.222 g, 0.5 mmol), KOPiv (0.140 g, 1 mmol) in the presence of $PdCl(C_3H_5)$(dppb) (15.2 mg, 0.025 mmol) at 150 °C during 24 h in DMA (4 mL) under argon affords the coupling product **33c** after evaporation of the solvent and purification on silica gel in 96% yield (0.174 g) as a white solid: mp 223-225 °C. Eluent heptane:ethyl acetate: 9:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (t, *J* = 8.6 Hz, 2H), 8.62 (d, *J* = 7.9 Hz, 1H), 8.47 (d, *J* = 7.4 Hz, 2H), 8.34 (d, *J* = 6.7 Hz, 1H), 7.85-7.65 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 145.3, 135.6, 132.4 (q, *J* = 32.7 Hz), 130.7, 129.6, 129.0, 127.9, 127.6, 127.4, 126.8, 126.4, 126.0, 125.9 (q, *J* = 3.8 Hz), 123.8, 123.7 (q, *J* = 272.6 Hz), 123.5, 122.9, 121.0, 120.9. Anal. Calcd for $C_{22}H_{12}F_3NO$ (363.34): C, 72.73; H, 3.33. Found: C, 72.89; H, 3.20. LRMS calcd for M^+ $C_{22}H_{12}F_3NO$ 363, found 363.

4'-Methoxy-2-(oxazol-2-yl)-[1,1'-biphenyl]-3-carbonitrile (34): The reaction of 4-bromoanisole (0.374 g, 2 mmol), 2-(oxazol-2-yl)benzonitrile **18b** (0.170 g, 1 mmol), KOPiv (0.280 g, 2 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (30.6 mg, 0.05 mmol) at 150 °C during 16 h in NMP (4 mL) under argon affords the coupling product **34** after evaporation of the solvent and purification on silica gel in 43% yield (0.119 g) as a white solid: mp 101-103 °C. Eluent heptane:ethyl acetate: 7:3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.67-7.61 (m, 2H), 7.26 (s, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 159.5, 158.1, 143.7, 139.8, 134.6, 132.0, 131.2, 130.6, 129.7, 129.5, 128.2, 117.2, 114.2, 113.9, 55.2. Anal. Calcd for $C_{17}H_{12}N_2O_2$ (276.30): C, 73.90; H, 4.38. Found: C, 73.68; H, 4.21. LRMS calcd for M^+ $C_{17}H_{12}N_2O_2$ 276, found 276.

2-(Oxazol-2-yl)-[1,1'-biphenyl]-3,4'-dicarbonitrile (35): The reaction of 4-bromobenzonitrile (0.364 g, 2 mmol), 2-(oxazol-2-yl)benzonitrile **18b** (0.170 g, 1 mmol), KOPiv (0.280 g, 2 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (30.6 mg, 0.05 mmol) at 150 °C during 16 h in NMP (4

mL) under argon affords the coupling product **35** after evaporation of the solvent and purification on silica gel in 62% yield (0.168 g) as a white solid: mp 183-185 °C. Eluent heptane:ethyl acetate: 6:4. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.89 (dd, *J* = 6.1, 2.9 Hz, 1H), 7.75-7.68 (m, 2H), 7.67-7.62 (m, 3H), 7.28-7.23 (m, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 157.2, 143.7, 142.0, 140.1, 134.3, 133.6, 132.2, 130.8, 129.7, 129.2, 128.4, 118.4, 116.9, 114.2, 111.9. Anal. Calcd for $C_{17}H_9N_3O$ (271.28): C, 75.27; H, 3.34. Found: C, 75.60; H, 3.54. LRMS calcd for M^+ $C_{17}H_9N_3O$ 271, found 271.

4-(1-(Oxazol-2-yl)naphthalen-2-yl)benzonitrile (36): The reaction of 4-bromobenzonitrile (0.364 g, 2 mmol), 2-(naphthalen-1-yl)oxazole **21b** (0.195 g, 1 mmol), KOPiv (0.280 g, 2 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (30.6 mg, 0.05 mmol) at 150 °C during 16 h in NMP (4 mL) under argon affords the coupling product **36** after evaporation of the solvent and purification on silica gel in 83% yield (0.246 g) as a yellow solid: mp 161-163 °C. Eluent heptane:ethyl acetate: 7:3. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.99-7.90 (m, 2H), 7.66-7.52 (m, 6H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.29 (s, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 159.7, 145.9, 139.3, 139.1, 132.9, 132.4, 132.0, 131.1, 129.5, 128.2, 128.0, 127.9, 127.0, 126.8, 125.7, 124.3, 118.8, 111.0. Anal. Calcd for $C_{20}H_{12}N_2O$ (296.33): C, 81.07; H, 4.08. Found: C, 81.23; H, 4.32. LRMS calcd for M^+ $C_{20}H_{12}N_2O$ 296, found 296.

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FULL PAPER

Reaction conditions for the regiodivergent direct arylations at C2- or C5-positions of oxazoles using phosphine-free palladium catalysts

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