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A Facile Access to Ortho-Hydroxyanilnes Based on Ir(III)-Catalyzed Direct C−H Amidation of 2-Phenoxypyridines

Lianhui Wang,[a] Zi Yang,[a] Mengqi Yang,[a] Miaodou Tian,[a] Changsheng Kuai[a] and Xiuling Cui*[a]

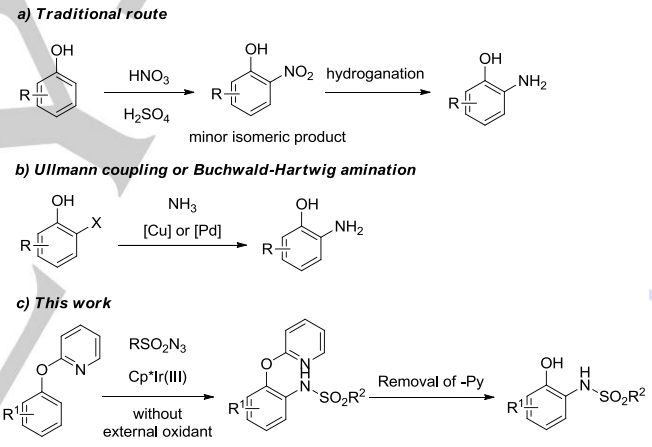
Dedication ((optional))

Abstract: A highly efficient and regioselective C−H amidation of 2-phenoxypyridines catalyzed by Ir(III) has been developed using sulfonyl azides as readily amino source. The amidated products were provided in good to excellent yields with broad functional group tolerance. Furthermore, the 2-pyridyl moiety in the amidated products can readily be removed, offering an efficient route to the synthetically useful *ortho*-hydroxyanilnes, which is important building block in organic synthesis.

Introduction

Nitrogen-containing molecules are widely present in natural products, pharmaceuticals, agrochemicals, and functional materials.[1] Especially, *ortho*-hydroxyaniline and its derivatives are one of the important intermediates for organic synthesis.[2] As a result, the development of efficient and selective amination procedures has been the focus of intensive research in the past decades. Traditional procedures to syethesize *ortho*-hydroxyanilines usually start from aromatic nitration, followed by reduction (**Scheme 1, a**),[3] which suffer from side reaction and harsh reaction conditions and fussy chemical process.[4] Recently, transition metal-catalyzed amination of aryl(preudo)halides,[5] typically palladium-catalyzed Buchwald-Hartwig coupling reactions[6] and copper-catalyzed Ullman-type transformations,[7] are among the most reliable and widely used methods (**Scheme 1, b**). However, aryl (pseudo)halides are required and they are not always readily accessible. Moreover, stoichiometric amounts of (preodo)halogen salt as by-product are generated in these process.[8,9]

As a consequence, the direct amination of C− H bonds to form C− N bonds represents a straightforward and promising approach, which obviates the pre-functionalization of substrates and greatly improves the reaction efficiency.[10] Very recently, inspired by the work from Chang group,[11] a new catalyst system using Ir(III) species was rapidly developed for the direct C−H amination of arenes or alkenes with organic azides under exceptionally mild conditions, in which molecular nitrogen is released as a sole by-product external oxidants are avoided.[12] Among these reports, the use of coordinating moieties as directing group has become an efficient strategy to improve the region-selectivity. However, the structural diversity of the corresponding products is severely limited because it is nontrivial to remove and functionalize the coordinating moieties.[13] Thus, the development of removable or modifiable directing groups would be highly desirable.[14] In our continuing efforts to develop highly efficient amination reaction as well as removable directing groups,[15] we herein explored an iridium-catalyzed direct C− H amination of 2-phenoxypyridines[16] with sulfonyl azides as amino source and internal oxidant. Notably, the 2-pyridyl group can be removed to deliver the corresponding *ortho*-hydroxy-(*N*-sulfonyl)anilnes (**Scheme 1, c**).



Scheme 1. Strategies for the preparation of *ortho*-hydroxyanilines

Results and Discussion

Initially, we commenced our study to examine the various reaction conditions in a model reaction of 2-(2-fluorophenoxy)pyridine (**1a**) with tosyl azide (TsN_3, **2a**) (**Table 1**) We were pleased to find that a cationic Ir species generated *in situ* from $[Cp^*IrCl_2]_2$ (0.5 mol%) and $AgSbF_6$ (2.0 mol%) displayed catalytic activity, and the amidated product **3aa** was obtained in 92% yield in 1,2-DCE at 80 °C (entry 1). **3aa** was not formed in the absence of either $[Cp^*IrCl_2]_2$ or $AgSbF_6$ (entries 2 and 3), implying that both $[Cp^*IrCl_2]_2$ and $AgSbF_6$ are crucial in this current transformation. While increasing the amount of $[Cp^*IrCl_2]_2$ from 0.5 mol% to 1.0 mol% did not significantly improve the yield of the target product (entry 4), reducing the catalytic loadings to 0.1 mol% yet afforded **3aa** in a moderate yield (entry 5). In view of the importance of $AgSbF_6$ in the catalytic system, various metal additives were screened as well. As shown in **Table 1**, $AgNTf_2$ behaved similar to $AgSbF_6$ in

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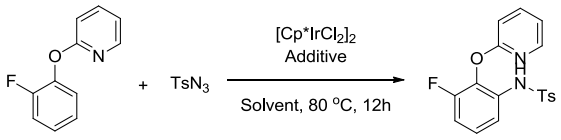
efficiency, leading to **3aa** in 91% yield (entry 6). Whereas, other metal salts, such as AgOAc, $AgBF_4$ and KPF_6, resulted in complete inefficiency (entries 7−9). Using the combination of $[Cp^*IrCl_2]_2$ and $AgSbF_6$, several nonpolar (1,2-DCE, PhMe and DCM) and polar (DMF and *t*-AmOH) solvents were then evaluated (entries 10−13). The most efficient catalysis was accomplished in nonpolar reaction media, with 1,2-DCE being ideal (entry 1). In previous observation by Chang and co-workers, acetate additives can promote the C−H bond activation.[11g] However, to our disappointment, the use of catalytic amounts of NaOAc or a combination of AcOH and Li_2CO_3 in this case solely resulted in decreased product yield (entries 14−15). Finally, the reaction temperature and time were evaluated. The yield was reduced to some extent when the reaction temperature decreased to 70 °C (entry 18), and the yield was not improved evidently by prolonging or shortening the reaction time (entry 5 vs. entries 16 and 17). It should be mentioned that several popular transition metal catalysts including $Pd(OAc)_2$, $[RuCl_2(p\text{-Cymene})]_2$, $[Cp^*RhCl_2]_2$ and $[Cp^*CoI_2(CO)]$ were explored as well, however, were totally unsuccessful for the present reaction. Thus, the optimal conditions were identified as following: 0.5 mol% $[Cp^*IrCl_2]_2$, 2.0 mol% $AgSbF_6$, 1.2 equiv. of TsN_3 in 1.2-DCE at 80°C for 12 h.

Table 1. Optimization of various reaction parameters[a]



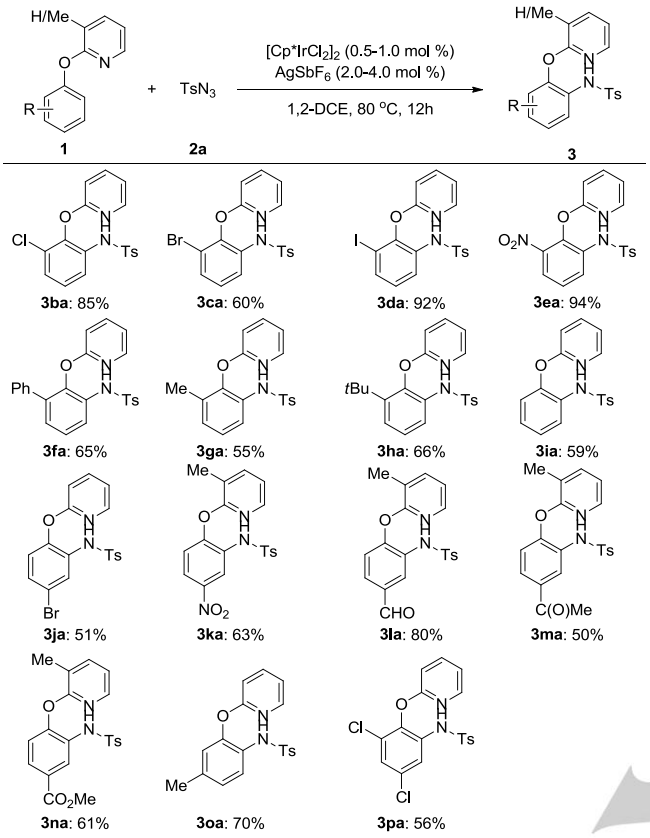
1a **2a** **3aa**

Entry	$[Cp^*IrCl_2]_2$/mol %	Additive/mol %	Solvent	**3aa**/%
1	0.5	$AgSbF_6$/2.0	1,2-DCE	92
2	0.5	—	1,2-DCE	0
3	—	$AgSbF_6$/2.0	1,2-DCE	0
4	1.0	$AgSbF_6$/4.0	1,2-DCE	94
5	0.1	$AgSbF_6$/0.4	1,2-DCE	54
6	0.5	$AgNTf_2$/2.0	1,2-DCE	91
7	0.5	AgOAc/2.0	1,2-DCE	0
8	0.5	$AgBF_4$/2.0	1,2-DCE	0
9	0.5	KPF_6/2.0	1,2-DCE	0
10	0.5	$AgSbF_6$/2.0	*t*-AmOH	35
11	0.5	$AgSbF_6$/2.0	DMF	0
12	0.5	$AgSbF_6$/2.0	DME	56
13	0.5	$AgSbF_6$/2.0	PhMe	0
14[b]	0.5	$AgSbF_6$/4.0	1,2-DCE	42
15[c]	0.5	$AgSbF_6$/4.0	1,2-DCE	9
16[d]	0.1	$AgSbF_6$/1.0	1,2-DCE	56
17[e]	0.1	$AgSbF_6$/1.0	1,2-DCE	47
18[f]	0.5	$AgSbF_6$/2.0	1,2-DCE	76

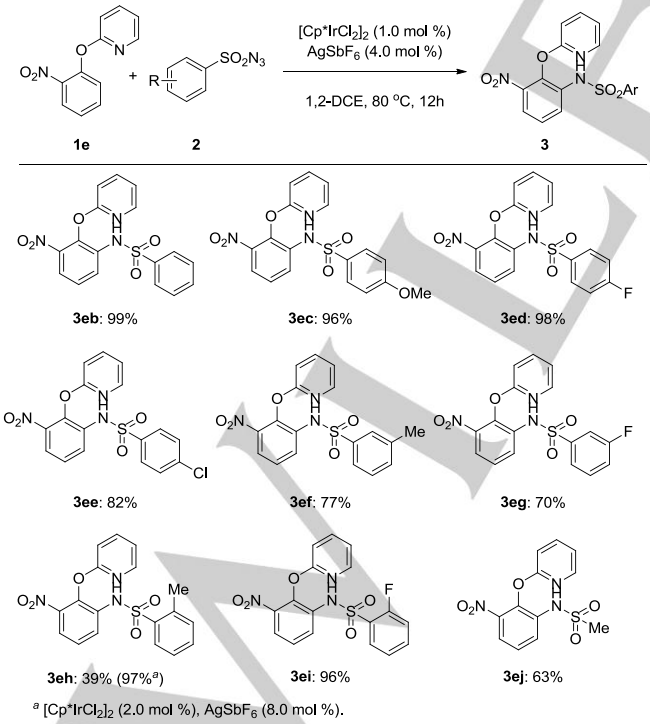
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[Cp^*IrCl_2]_2$ (0.1-1.0 mol %), Additive (0.4-4.0 mol %), Solvent (2.0 mL), 80 °C, 12 h, isolated yields based on substrate **1a**; [b] NaOAc (30 mol %) was added; [c] AcOH (30 mol %) and Li_2CO_3 (30 mol %) were added. [d] 16h. [e] 10h. [f] 70 °C.

With the optimized reaction conditions in hand, we next investigated the scope of diaryl ethers with tosyl azide (TsN_3, **2a**) and representative data are shown in **Scheme 2**. A variety of functional groups, such as halide (**1b**-**d**, **1j** and **1p**), nitro (**1e** and **1k**), aldehyde (**1l**), ketone (**1m**) and ester (**1n**), were well tolerated with this transformation. To investigate the influence of substituents at the arene core, sulfonyl azide **2a** was reacted with various substrates **1b**-**h** with electron-withdrawing or -donating groups, equipped at the ortho position. Diaryl ethers (**1b**-**f**) with electron-withdrawing substituents worked well, providing the desired products in good to excellent yields. Electron-donating groups, such as methyl- (**1g**) and *tert*-Butyl- (**1h**), only afforded moderate yields presumably due to the steric hindrance. Moreover, functional groups at the para position were examined. It should be emphasized that the two reactants, namely 2-phenoxypyridine **1** and azide **2**, were used in a ratio of 1.5:1.0 to reduce the diamidation quantities in these transformations. The amidation of 2-phenoxypyridine (**1i**) and 2-(4-bromophenoxy)pyridine (**1j**) with TsN_3 (**2a**) produced the target products **3ia** and **3ja** in 59% and 51% yields. Interestingly, some substrates with 2-methyl pyridyl group (**1k**-**n**) could perform with good regioselectivity, and deliver to the monoamidation products **3ka−3na** in moderate to good yields. Aldehyde, ketone and ester in substrates **1l**, **1m** and **1n** did not act as a directing group, with the *ortho*-aminated product **3** relative to 2-pyridyl formed exclusively. To our delight, the amidation occurred selectively at the steric C−H bonds when the *meta* position was substituted by a methyl group (**1o**), affording the sole regioisomer **3oa** in 70% yield. Finally, dichloro-substituted substrate **1p** was also facile (**3pa)**, indicating that the amidation was not significantly influenced by the electronic variation of substrates.

Encouraged by the successful results in **Scheme 1**, we further explored the scope of organic azides **2** with 2-(2-nitrophenoxy)pyridine (**1e**) in the presence of 1.0 mol% of $[Cp^*IrCl_2]_2$ (**Scheme 3**). Likewise, versatile functional groups, such as fluoro (**2d**, **2g** and **2i**) and chloro (**2e**) were compatible under the standard reaction conditions. In regard to para-substituted arenesulfonyl azides, both electron-donating and -withdrawing groups readily participated in the amidation with excellent efficiency (**3eb−3ee**). Similarly, substrates substituted



Scheme 2. Amidation of diaryl ethers **1** with TsN_3 (**2a**).

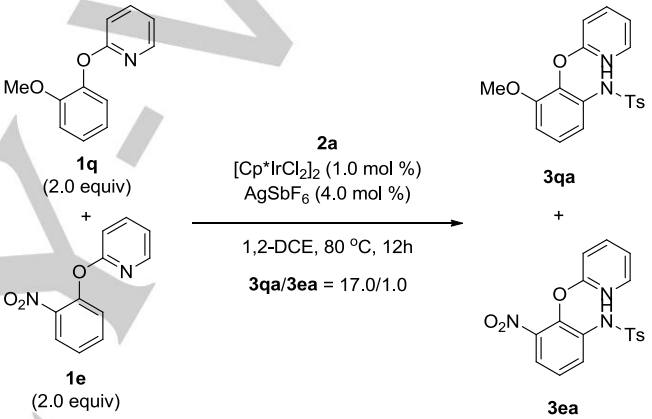


[a] $[Cp^*IrCl_2]_2$ (2.0 mol %), $AgSbF_6$ (8.0 mol %).

Scheme 3. Amidation of diaryl ether **1e** with sulfonyl azides **2**.

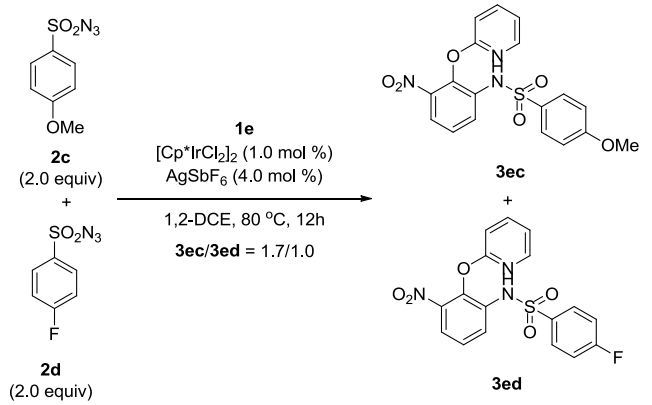
with methyl (**2f**) or fluoro (**2g**) group at the meta-position proceeded smoothly. Treatment of **1e** with 2-fluorobenzenesulfonyl azide (**2i**) afforded the desired product **3ei** in 96% yield. 2-Me substituted substrate **1h** gave 39% yield, probably owing to steric effect. We are pleased to find that the yield of **3eh** steadily increased to 97% with a higher $[Cp^*IrCl_2]_2$ loading (2.0 mol%). Furthermore, aliphatic sulfonyl azide **2j** was also successfully applied to the current iridium-catalyzed conditions and afforded the product **3ej** in 63% yield. Other amino sources, such as acyl and aryl azides, were not reactive, leading to negligible product yields (3%). Only benzyl sulfonyl azide exihibited moderate reactivity (39% yield).

To gain insight into the reaction pathway, preliminary mechanistic studies were investigated. The intermolecular competition experiment between 2-phenoxypyridines **1q** and **1e** with tosyl azide (**2a**) were performed (**Scheme 4**). The ratio of products (**3qa**/**3ea** = 17) indicated that electron-rich substrate **1q** was transformed preferentially, hence rendering an electrophilic-type iridiation manifold.



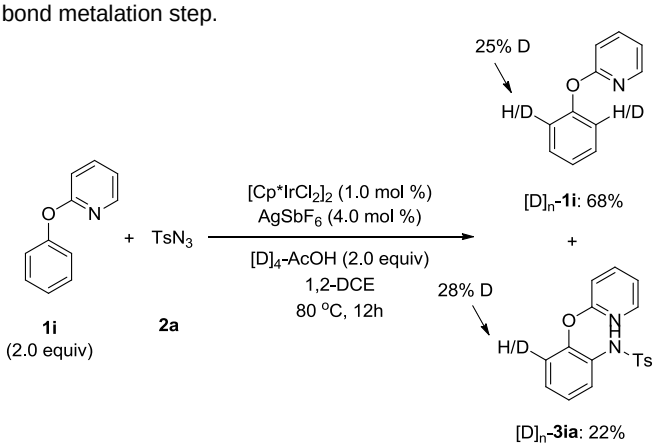
Scheme 4. Intermolecular competition experiment with diaryl ethers **1q** and **1e**

In addition, a competitive experiment between differently substituted sulfonyl azides **2c**/**2d** that differ in electronic effects was conducted (**Scheme 5**). The ratio of products (**3ec**/**3ed** = 1.7) were obtained, which indicated electron-donating substituents to be beneficial as well.



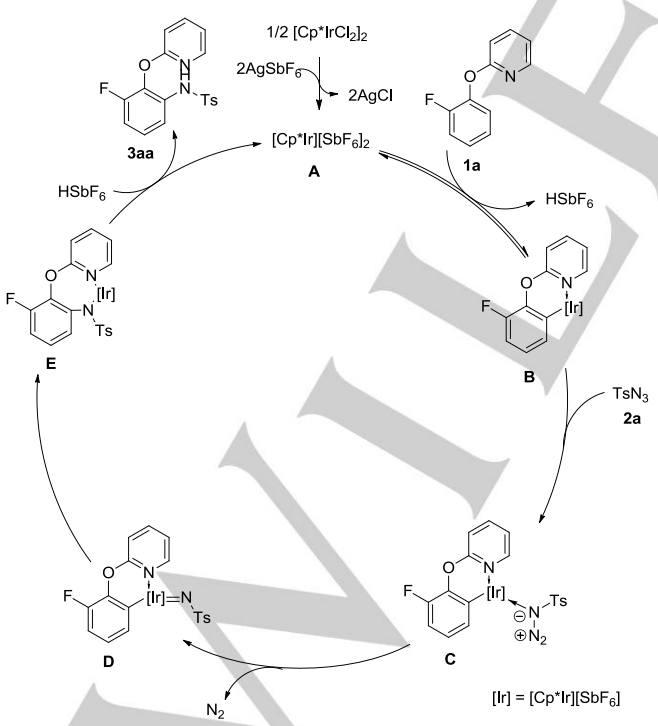
Scheme 5. Intermolecular competition experiment with azides **2c** and **2d**.

Furthermore, deuterium-labeling experiments were conducted. The amidation of 2-phenoxypyridine (**1i**) with tosyl azide (**2a**) in the presence of $[D]_4$-AcOH under the standard reaction conditions was conducted (**Scheme 6**). Significant deuterium was observed for the product $[D]_n$-**3ia** (28% D) or recycled substrate $[D]_n$-**1i** (25% D), being indicative of a reversible C−H bond metalation step.



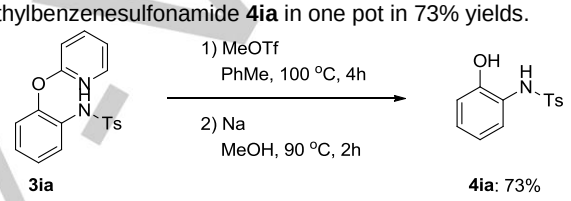
Scheme 6. Iridium-catalyzed direct *ortho*-C–H amidation azide **2a** with diaryl ether **1i** in the presence of $[D]_4$-AcOH.

On the basis of the above mechanistic studies and the related reports on iridium-catalyzed direct C−H amidation,[11,12] a possible mechanistic pathway is proposed in **Scheme 7**. First, a cationic Ir(III) species **A**, in situ generated by treating the dimeric precursor $[Cp^*IrCl_2]_2$ with $AgSbF_6$, undergoes a reversible C−H bond activation of diaryl ether **1a** via the chelation assistance of the pyridine nitrogen atom to generate a six-membered iridacycle **B**. Next, coordination of tosyl azide (**2a**) to the iridium center gives the complex **C**, which may undergo extrusion of one molecular N_2 to provide an iridium−nitrenoid intermediate **D**. The subsequent intramolecular insertion of nitrenoid moiety into iridacycle forms a new C−N bond to deliver the seven-membered iridacyclic species **E**. Finally, protonolysis of **E** provides the amination product **3aa** with the regeneration of the active iridium species **A**.



Scheme 7. Plausible mechanism for the iridium-catalyzed direct *ortho*-C–H amidation reaction.

Finally, we were pleased to find that the 2-pyridyl moiety can be efficiently cleaved (**Scheme 8**).[16k,16n] Compound **3ia** was treated with methyl trifluoromethanesulfonate (MeOTf) to form 1-methyl-2-{2-(4-methylphenylsulfonamido)phenoxy}pyridin-1-ium in toluene. Then, the crude intermediate was added into a refluxing Na/MeOH solution to generate N-(2-hydroxyphenyl)-4-methylbenzenesulfonamide **4ia** in one pot in 73% yields.



Scheme 8. Removal of the 2-pyridyl moiety.

Conclusions

In conclusion, an iridium-catalyzed direct C−H amidation of 2-phenoxypyridines using a range of synthetically valuable sulfonyl azides as amino source has been reported. Mild reaction conditions, low catalyst loading as well as good tolerance of various functional groups are the remarkable features of this method. Another attractive feature of this present approach turned out to be a facile route to the synthetically versatile *ortho*-hydroxyaniline derivatives upon the removal of the 2-pyridyl moieties.

Experimental Section

General information: Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Melting points were determined in open glass capillaries and were uncorrected. ^{1}H NMR spectra were recorded on 400 MHz spectrometers, and ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard at room temperature. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70−230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254).

Diaryl ether compounds **1a-q**[17] and sulfonyl azides **2a-j**[18] were prepared according to the known procedures.

The Representative procedure for the synthesis of compounds 3: A flame-dried sealed tube was cooled to ambient temperature and filled with N_2. To this flask were added 2-(2-fluorophenoxy)pyridine (**1a**) (94.5 mg, 0.5 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[Cp^*IrCl_2]_2$ (2.0 mg, 0.0025 mmol), $AgSbF_6$ (3.5 mg, 0.01 mmol) and 1,2-DCE (2.0 mL). Then the sealed tube was heated at 80 °C. After 12 h, the reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc = 5:1→2:1) to afford the desired product **3aa** (165 mg, 92%) as a white solid.

***N*-{3-fluoro-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3aa):** M. p. = 139−140 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.13 (br s, 1H), 8.32 (d, J = 5.3 Hz, 1H), 7.94 (ddd, J = 7.6, 7.6, 0.7 Hz, 1H), 7.74 (d, J = 3.9 Hz, 1H), 7.48 (d, J = 4.2 Hz, 2H), 7.41−7.36 (m, 1H), 7.33−7.27 (m, 1H), 7.23 (d, J = 4.2 Hz, 2H), 6.87−6.79 (m, 1H), 7.09 (dd, J = 9.8, 8.4 Hz, 1H), 2.42 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.6 (C_q), 153.3 (d, $^1J_{C-F}$ = 242 Hz, C_q), 147.2 (CH), 144.5 (C_q), 144.4 (C_q), 140.4 (CH), 135.9 (C_q), 129.6 (CH), 128.1 (d, $^4J_{C-F}$ = 3 Hz, CH), 128.0 (CH), 125.1 (CH), 124.0 (CH), 118.8 (d, $^3J_{C-F}$ = 8 Hz, CH), 128.6 (d, $^2J_{C-F}$ = 18 Hz, CH), 21.7 (CH_3) (One C_q is invisible). ^{19}F-NMR (376 MHz, $CDCl_3$): δ = −113.5 (s). HRMS (ESI) m/z calcd for $C_{18}H_{16}FN_2O_3S$ $[M + H]^+$: 359.0866, Found 359.0867.

***N*-{3-chloro-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3ba):** The representative procedure was followed using 2-(2-chlorophenoxy)pyridine (**1b**) (103.0 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 30:1:1) to afford the desired product **3ba** (159 mg, 85%) as a white solid. M. p. = 155−156 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.52 (br s, 1H), 8.33 (d, J = 4.9 Hz, 1H), 7.94 (ddd, J = 7.8, 7.7, 1.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.44−7.42 (m, 1H), 7.41−7.34 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.85 (dd, J = 8.0, 8.0 Hz, 1H), 2.43 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.5 (C_q), 152.0 (C_q), 147.2 (CH), 144.4 (C_q), 140.2 (CH), 135.7 (C_q), 131.6 (CH), 131.5 (CH), 129.5 (CH), 128.0 (CH), 127.3 (C_q), 125.1 (CH), 124.0 (CH), 123.6 (C_q), 119.7 (CH), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}ClN_2O_3S$ $[M + H]^+$: 375.0570, Found 375.0572.

***N*-{3-bromo-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3ca):** The representative procedure was followed using 2-(2-bromophenoxy)pyridine (**1a**) (125.0 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2c**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3ca** (127 mg, 60%) as a white solid. M. p. = 145−146 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.64 (br s, 1H), 8.33 (d, J = 5.3 Hz, 1H), 7.94 (ddd, J = 7.7, 7.6, 1.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 8.0, 1.4 Hz, 1H), 7.48 (dd, J = 8.0, 1.4 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.39 (dd, J = 7.5, 5.7 Hz, 1H), 7.23 (d, J = 8.2 Hz, 2H), 6.80 (dd, J = 8.0, 8.0 Hz, 1H), 2.43 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.5 (C_q), 152.9 (C_q), 147.2 (CH), 144.4 (C_q), 140.2 (CH), 135.7 (C_q), 134.5 (CH), 132.4 (CH), 129.5 (CH), 128.0 (CH), 126.9 (C_q), 125.1 (CH), 124.0 (CH), 120.4 (CH), 112.8 (C_q), 21.7 (s, CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}BrN_2O_3S$ $[M + H]^+$: 419.0065, Found 419.0057.

***N*-{3-iodo-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3da):** The representative procedure was followed using 2-(2-iodophenoxy)pyridine (**1d**) (145.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3da** (214 mg, 92%) as a white solid. M. p. = 156−157 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.84 (br s, 1H), 8.32 (dd, J = 5.0, 1.2 Hz, 1H), 7.94 (ddd, J = 7.9, 7.9, 1.4 Hz, 1H), 7.78−7.71 (m, 2H), 7.50 (dd, J = 7.9, 1.3 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.40−7.36 (m, 1H), 7.23 (d, J = 8.4 Hz, 2H), 6.67 (dd, J = 7.9, 7.9 Hz, 1H), 2.44 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 155.1 (C_q), 153.5 (C_q), 147.1 (CH), 144.4 (C_q), 140.6 (CH), 140.2 (CH), 135.5 (C_q), 133.5 (CH), 129.5 (CH), 128.0 (CH), 125.4 (C_q), 125.2 (CH), 124.0 (CH), 121.3 (CH), 87.1 (C_q), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}IN_2O_3S$ $[M + H]^+$: 466.9926, Found 466.9926

4-Methyl-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ea): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 5:1:1) to afford the desired product **3ea** (181 mg, 94%) as a yellow solid. M. p. = 158−159 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.11 (br s, 1H), 8.29 (dd, J = 5.0, 2.0 Hz, 1H), 8.19 (dd, J = 8.6, 1.6 Hz, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.82 (dd, J = 7.8, 1.7 Hz, 1H), 7.67 (ddd, J = 7.8, 7.8, 2.0 Hz, 1H), 7.31 (d J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 1H), 7.13−7.06 (m, 2H), 2.45 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.2 (C_q), 153.1 (C_q), 148.0 (CH), 144.3 (C_q), 140.7 (CH), 138.4 (CH), 137.0 (C_q), 135.5 (C_q), 129.4 (CH), 129.2 (C_q), 128.5 (CH), 126.0 (CH), 120.7 (CH), 119.3 (CH), 117.4 (CH), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}N_3O_5S$ $[M + H]^+$: 386.0811, Found 386.0812.

4-Methyl-*N*-{2-(pyridin-2-yloxy)-[1,1'-biphenyl]-3-yl}benzenesulfonamide (3fa): The representative procedure was followed using 2-([1,1'-biphenyl]-2-yloxy)pyridine (**1f**) (123.0 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3fa** (136 mg, 65%) as a white solid. M. p. = 162−163 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.85 (br s, 1H), 8.28 (dd, J = 5.0, 1.1 Hz, 1H), 7.92 (ddd, J = 7.8, 7.8, 2.0 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.51 (dd, J = 7.9, 1.5 Hz, 1H), 7.44−7.31 (m, 7H), 7.26 (d, J = 8.3 Hz, 2H), 6.99 (dd, J = 7.7, 7.7 Hz, 1H) 2.47 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.9 (C_q), 152.7 (C_q), 147.3 (CH), 144.1 (C_q), 139.9 (CH), 138.2 (C_q), 136.0 (C_q), 132.1 (CH), 132.0 (CH), 132.0 (C_q), 129.4 (CH), 129.2 (CH), 128.3 (CH), 128.0 (CH), 127.1 (CH), 126.4 (C_q), 124.9 (CH), 123.7 (CH), 119.9 (CH), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2O_3S$ $[M + H]^+$: 417.1273, Found 417.1275.

4-Methyl-*N*-{3-methyl-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ga): The representative procedure was followed using 2-(*o*-tolyloxy)pyridine (**1g**) (92.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3ga** (98 mg, 55%) as a white solid. M. p. = 109−111 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.26 (br s, 1H), 8.34 (dd, J = 5.0, 2.0 Hz, 1H), 7.87 (ddd, J = 7.8, 7.8, 2.0 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 8.3 Hz, 2H), 7.32 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.28 (dd, J = 7.8, 1.0 Hz, 1H), 7.23 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 7.5 Hz, 1H), 6.80 (dd, J = 7.8, 7.6 Hz, 1H), 2.43 (s, 3H), 2.18 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.0 (C_q), 153.5 (C_q), 147.5 (CH), 144.0 (C_q), 139.8 (CH), 136.2 (C_q), 132.0 (CH), 129.9 (CH), 129.3 (CH), 128.2 (CH), 128.0 (C_q), 125.7 (C_q), 124.5 (CH), 123.6 (CH), 119.4 (CH), 21.7 (CH_3), 16.4 (CH_3). HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$: 355.1116, Found 355.1113.

***N*-{3-(*tert*-butyl)-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3ha):** The representative procedure was followed using 2-{2-(*tert*-

butyl)phenoxy}pyridine (**1h**) (113.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:0:1 → 10:1:1) to afford the desired product **3ha** (131 mg, 66%) as a white solid. M. p. = 131−132 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.47 (br s, 1H), 8.35 (d, *J* = 4.9 Hz, 1H), 7.90 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.39−7.32 (m, 2H), 7.29−7.25 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.84 (dd, *J* = 7.9, 7.9 Hz, 1H), 2.41 (s, 3H), 1.29 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.4 (C_q), 154.1 (C_q), 147.3 (CH), 143.9 (C_q), 139.7 (CH), 139.3 (C_q), 136.2 (C_q), 130.4 (CH), 129.3 (CH), 128.2 (CH), 128.1 (CH), 126.5 (C_q), 124.8 (CH), 123.6 (CH), 119.0 (CH), 34.9 (C_q), 29.3 (CH_3), 21.6 (CH_3). HRMS (ESI) m/z calcd for $C_{22}H_{25}N_2O_3S$ $[M + H]^+$: 397.1586, Found 397.1587.

4-Methyl-*N*-{2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ia): The representative procedure was followed using 2-phenoxypyridine (**1i**) (128.2 mg, 0.75 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:0:1 → 10:1:1) to afford the desired product **3ia** (100 mg, 59%) as a white solid. M. p. = 166−167 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.38 (br s, 1H), 8.33 (dd, *J* = 5.1, 1.8 Hz, 1H), 7.89 (ddd, *J* = 7.8, 7.7, 2.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.34 (ddd, *J* = 7.6, 5.0, 1.0 Hz, 1H), 7.25 (d, *J* = 7.9 Hz), 7.21 (d, *J* = 8.4 Hz, 2H), 6.91−6.86 (m, 2H), 2.42 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 152.2 (CH), 154.0 (C_q), 147.4 (CH), 144.1 (C_q), 139.8 (CH), 136.2 (C_q), 132.8 (C_q), 131.0 (CH), 129.4 (CH), 128.1 (CH), 126.1 (C_q), 124.9 (CH), 123.7 (CH), 120.2 (CH), 119.1 (CH), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{17}N_2O_3S$ $[M + H]^+$: 341.0960, Found 341.0959.

***N*-{5-bromo-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3ja):** The representative procedure was followed using 2-(4-bromophenoxy)pyridine (**1j**) (187.5 mg, 0.75 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3ja** (108 mg, 51%) as a white solid. M. p. = 156−157 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.72 (br s, 1H), 8.33 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.94 (ddd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.39 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.34 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 1H), 2.44 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.7 (C_q), 153.5 (C_q), 147.4 (CH), 144.4 (C_q), 140.1 (CH), 135.9 (C_q), 135.3 (CH), 133.9 (CH), 129.5 (CH), 128.1 (CH), 127.2 (C_q), 125.2 (CH), 124.1 (CH), 120.6 (CH), 111.0 (C_q), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}BrN_2O_3S$ $[M + H]^+$: 419.0065, Found 419.0065.

4-Methyl-*N*-{2-((3-methylpyridin-2-yl)oxy)-5-nitrophenyl}benzenesulfonamide (3ka): The representative procedure was followed using 3-methyl-2-(4-nitrophenoxy)pyridine (**1k**) (172.5 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3ka** (126 mg, 63%) as a white solid. M. p. = 194−195 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 12.41 (br s, 1H), 8.52 (d, *J* = 2.5 Hz, 1H), 8.24 (d, *J* = 4.4 Hz, 1H), 8.14 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.44− 7.39 (m, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 1H), 2.75 (s, 3H), 2.46 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.2 (C_q), 151.4 (C_q), 144.7 (C_q), 144.6 (CH), 142.5 (CH), 140.3 (C_q), 136.4 (C_q), 135.7 (C_q), 129.7 (CH), 129.6 (CH), 128.2 (CH), 126.7 (CH), 125.3 (CH), 124.6 (C_q), 119.1 (CH), 21.7 (CH_3), 18.4 (CH_3). HRMS (ESI) m/z calcd for $C_{19}H_{18}N_3O_5S$ $[M + H]^+$: 400.0967, Found 400.0967.

***N*-{5-formyl-2-[(3-methylpyridin-2-yl)oxy]phenyl}-4-methylbenzenesulfonamide (3la):** The representative procedure was followed using 4-{(3-methylpyridin-2-yl)oxy}benzaldehyde (**1l**) (159.8 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol) , $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3la** (153 mg, 80%) as a white solid. M. p. = 196−197 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 12.02 (br s, 1H), 9.91 (br s, 1H), 8.24 (dd, *J* = 5.0, 1.3 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.80 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 1H), 2.75 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 189.9 (C_q), 161.7 (C_q), 151.8 (C_q), 144.7 (CH), 144.4 (C_q), 142.2 (CH), 136.5 (CH), 136.2 (C_q), 136.0 (C_q), 131.7 (CH), 129.5 (CH), 129.5 (C_q), 128.2 (CH), 125.1 (C_q), 125.1 (CH), 119.7 (CH), 21.7 (CH_3), 18.3 (CH_3). HRMS (ESI) m/z calcd for $C_{20}H_{19}N_2O_4S$ $[M + H]^+$: 383.1066, Found 383.1063.

***N*-{5-acetyl-2-[(3-methylpyridin-2-yl)oxy]phenyl}-4-methylbenzenesulfonamide (3ma):** The representative procedure was followed using 1-{4-[(3-methylpyridin-2-yl)oxy]phenyl}ethanone (**1m**) (170.2 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ma** (99 mg, 50%) as a white solid. M. p. = 167−168 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.76 (br s, 1H), 8.23 (d, *J* = 5.0 Hz, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 7.88 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 1H) 2.74 (s, 3H), 2.59 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 195.9 (C_q), 160.4 (C_q), 152.0 (C_q), 144.7 (CH), 144.3 (C_q), 142.1 (CH), 136.1 (C_q), 136.1 (C_q), 134.4 (CH), 131.3 (CH), 129.9 (C_q), 129.4 (CH), 128.2 (CH), 125.0 (CH), 124.5 (C_q), 118.9 (CH), 26.3 (CH_3), 21.7 (CH_3), 18.4 (CH_3). HRMS (ESI) m/z calcd for $C_{21}H_{21}N_2O_4S$ $[M + H]^+$: 397.1222, Found 397.1225.

Methyl 3-(4-methylphenylsulfonamido)-4-{(3-methylpyridin-2-yl)oxy}benzoate (3na): The representative procedure was followed using methyl 4-{(3-methylpyridin-2-yl)oxy}benzoate (**1n**) (182.2 mg, 0.75 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3na** (126 mg, 61%) as a white solid. M. p. = 157−158 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.68 (br s, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 8.23 (d, *J* = 4.0 Hz, 1H), 7.93 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 1H) 3.92 (s, 3H), 2.75 (s, 3H), 2.45 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 156.2 (C_q), 160.2 (C_q), 152.1 (C_q), 144.7 (CH), 144.2 (C_q), 142.0 (CH), 136.2 (C_q), 136.2 (C_q), 135.2 (CH), 132.6 (CH), 129.4 (CH), 128.2 (CH), 124.9 (CH), 124.5 (C_q), 122.1 (C_q), 118.8 (CH), 52.0 (CH_3), 21.7 (CH_3), 18.4 (CH_3). HRMS (ESI) m/z calcd for $C_{21}H_{21}N_2O_5S$ $[M + H]^+$: 413.1171, Found 413.1171.

4-Methyl-*N*-{4-methyl-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3oa): The representative procedure was followed using 2-(*m*-tolyloxy)pyridine (**1o**) (92.5 mg, 0.5 mmol) and *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3oa** (124 mg, 70%) as a white solid. M. p. = 123−124 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.24 (br s, 1H), 8.33 (d, *J* = 4.9 Hz, 1H), 7.89 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.37− 7.31 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.73 (s, 1H), 6.72 (d, *J* = 8.2 Hz, 1 H), 2.43 (s, 3H), 2.30 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.7 (C_q), 154.1 (C_q), 147.4 (CH), 144.0

(C_q), 141.5 (C_q), 139.8 (CH), 136.3 (C_q), 132.4 (CH), 129.4 (CH), 128.1 (CH), 124.8 (CH), 123.6 (CH), 123.5 (C_q), 121.2 (CH), 119.5 (CH), 21.7 (CH_3), 21.3 (CH_3). HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2O_3S$ $[M + H]^+$: 355.1116, Found 355.1117.

***N*-{3,5-dichloro-2-(pyridin-2-yloxy)phenyl}-4-methylbenzenesulfonamide (3pa):** The representative procedure was followed using 2-(2,4-dichlorophenoxy)pyridine (**1p**) (120.0 mg, 0.50 mmol), TsN_3 (**2a**) (127.8 mg, 0.6 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) yielded **3pa** (116 mg, 56%) as a white solid. M. p. = 153−154 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.77 (br s, 1H), 8.32 (d, *J* = 5.0 Hz, 1H), 7.97 (ddd, *J* = 7.8, 7.8, 1.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.53− 7.40 (m, 4H), 7.37 (d, *J* = 2.7 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.1 (C_q), 151.1 (C_q), 147.2 (CH), 144.7 (C_q), 140.4 (CH), 135.5 (C_q), 131.4 (CH), 131.2 (CH), 129.6 (CH), 128.0 (CH), 127.6 (C_q), 125.3 (CH), 124.3 (CH), 123.6 (C_q), 21.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{15}Cl_2N_2O_3S$ $[M + H]^+$: 409.0180, Found 409.0171.

***N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3eb):** The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), benzenesulfonyl azide (**2b**) (109.8 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 40:1:1 → 20:1:1) to afford the desired product **3eb** (184 mg, 99%) as a yellow solid. M. p. = 159−160 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.09 (br s, 1H), 8.29 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.19 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 (ddd, *J* = 7.8, 7.8, 2.0 Hz, 1H), 7.63 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.52 (dd, *J* = 7.8, 7.5 Hz, 2H), 7.26 (dd, *J* = 8.6, 8.6 Hz, 1H), 7.16− 7.05 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.1 (C_q), 153.1 (C_q), 148.0 (CH), 140.7 (CH), 140.0 (C_q), 138.4 (CH), 135.5 (C_q), 133.3 (CH), 129.0 (C_q), 128.8 (CH), 128.5 (CH), 126.1 (CH), 120.8 (CH), 119.3 (CH), 117.4 (CH). HRMS (ESI) m/z calcd for $C_{17}H_{14}N_3O_5S$ $[M + H]^+$: 372.0654, Found 372.0653.

4-Methoxy-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ec): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 4-methoxybenzenesulfonyl azide (**2c**) (127.8 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ec** (192 mg, 96%) as a yellow solid. M. p. = 144−145 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.13 (br s, 1H), 8.29 (d, *J* = 5.0 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.66 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.12− 7.04 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.5 (C_q), 153.2 (C_q), 153.1 (C_q), 147.9 (CH), 140.7 (CH), 138.4 (CH), 135.6 (C_q), 131.4 (C_q), 130.8 (CH), 129.2 (C_q), 126.0 (CH), 120.6 (CH), 119.3 (CH), 117.2 (CH), 113.9 (CH), 55.6 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}N_3O_6S$ $[M + H]^+$: 402.0760, Found 402.0761.

4-Fluoro-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ed): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 4-fluorobenzenesulfonyl azide (**2d**) (120.6 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ed** (190 mg, 98%) as a yellow solid. M. p. = 161−162 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.07 (br s, 1H), 8.31 (dd, *J* = 5.2, 1.7 Hz, 1H), 8.22 (dd, *J* = 8.6, 1.1 Hz, 1H), 8.11− 8.01 (m, 2H), 7.83 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.66 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.6, 8.6 Hz, 2H), 7.15− 7.07 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.6 (d, $^1J_{C-F}$ = 256 Hz, C_q), 153.1 (C_q), 148.0 (CH), 140.7 (CH), 138.5 (CH), 136.1 (d, $^4J_{C-F}$ = 3 Hz, C_q), 135.5 (C_q), 131.6 (d, $^3J_{C-F}$ = 9 Hz, CH), 128.8 (C_q), 126.3 (CH), 120.8 (CH), 119.5 (CH), 116.8 (CH), 115.9 (d, $^2J_{C-F}$ = 22 Hz, CH) (One C_q is invisible). ^{19}F-NMR (376 MHz, $CDCl_3$) δ = −(104.0−104.2) (m). HRMS (ESI) m/z calcd for $C_{17}H_{13}FN_3O_5S$ $[M + H]^+$: 390.0560, Found 390.0557.

4-Chloro-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ee): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 4-chlorobenzenesulfonyl azide (**2e**) (130.6 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ee** (166 mg, 82%) as a yellow solid. M. p. = 153−154 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.04 (br s, 1H), 8.31 (d, *J* = 5.0 Hz, 1H), 8.22 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.82 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.65 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.09− 7.01 (m, 3H). ^{13}C-NMR (100 MHz $CDCl_3$): δ = 153.1 (C_q), 153.0 (C_q), 148.0 (CH), 140.7 (CH), 139.8 (C_q), 138.7 (C_q), 138.5 (CH), 135.4 (C_q), 130.2 (CH), 129.0 (CH), 128.8 (C_q), 126.3 (CH), 120.8 (CH), 119.5 (CH), 116.7 (CH). HRMS (ESI) m/z calcd for $C_{17}H_{13}ClN_3O_5S$ $[M + H]^+$: 406.0264, Found 406.0264.

3-Methyl-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ef): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 3-methylbenzenesulfonyl azide (**2f**) (118.2 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ef** (148 mg, 77%) as a yellow solid. M. p. = 143−144 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.14 (br s, 1H), 8.29 (d, *J* = 5.0 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.69 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.46− 7.37 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.14− 7.06 (m, 2H), 2.43 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.1 (C_q), 148.0 (CH), 140.6 (CH), 139.8 (C_q), 139.0 (C_q), 138.4 (CH), 135.6 (C_q), 134.2 (CH), 129.1 (C_q), 128.7 (CH), 128.7 (CH), 126.1 (CH), 125.5 (CH), 120.9 (CH), 119.3 (CH), 117.6 (CH), 21.4 (CH_3) (One C_q is invisible). HRMS (ESI) m/z calcd for $C_{18}H_{16}N_3O_5S$ $[M + H]^+$: 386.0811, Found 386.0808.

3-Fluoro-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3eg): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 3-fluorobenzenesulfonyl azide (**2g**) (120.6 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 8:1:1) to afford the desired product **3eg** (136 mg, 70%) as a yellow solid. M. p. = 140−141 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.07 (br s, 1H), 8.32 (d, *J* = 4.1 Hz, 1H), 8.23 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.88− 7.73 (m, 3H), 7.67 (ddd, *J* = 8.0, 7.6, 1.8 Hz, 1H), 7.55− 7.48 (m, 1H), 7.33 (d, *J* = 8.2, 8.2, 1.5 Hz, 1H), 7.17− 7.07 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 162.2 (d, $^1J_{C-F}$ = 251 Hz, C_q), 153.0 (C_q), 152.9 (C_q), 148.1 (CH), 142.1 ($^3J_{C-F}$ = 7 Hz, C_q), 140.7 (CH), 138.5 (CH), 135.5 (C_q), 130.4 (d, $^3J_{C-F}$ = 7 Hz, CH), 128.7 (C_q), 126.3 (CH), 124.3 (d, $^4J_{C-F}$ = 3 Hz, CH), 121.0 (CH), 120.5 (d, $^2J_{C-F}$ = 24 Hz, CH), 119.5 (CH), 117.0 (CH), 116.1 (d, $^2J_{C-F}$ = 24 Hz, CH). ^{19}F-NMR (376 MHz, $CDCl_3$) δ = −(109.9− 110.0) (m). HRMS (ESI) m/z calcd for $C_{17}H_{13}FN_3O_5S$ $[M + H]^+$: 390.0560, Found 390.0561.

2-Fluoro-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3eh): A) The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 2-methylbenzenesulfonyl azide (**2h**) (118.2 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h,

purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3eh** (74 mg, 39%) as a yellow solid. B) The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 2-methylbenzenesulfonyl azide (**2h**) (118.2 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (8.0 mg, 0.01 mmol) and $AgSbF_6$ (13.8 mg, 0.04 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3eh** (187 mg, 97%) as a yellow solid. M. p. = 100−101 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.22 (br s, 1H), 8.30 (d, J = 4.1 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.73 (dd, J = 8.0, 7.5 Hz, 1H), 7.49 (dd, J = 7.7, 7.5 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.30− 7.25 (m, 1H), 7.15 (dd, J = 7.1, 6.8 Hz, 1H), 7.04 (dd, J = 8.0, 8.0 Hz, 1H), 2.56 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.3 (C_q), 153.0 (C_q), 148.0 (CH), 140.4 (CH), 138.5 (C_q), 138.4 (CH), 138.3 (C_q), 135.6 (C_q), 133.3 (CH), 132.8 (CH), 130.4 (CH), 129.0 (C_q), 126.1 (CH), 125.9 (CH), 121.4 (CH), 119.5 (CH), 119.1 (CH), 20.7 (CH_3). HRMS (ESI) m/z calcd for $C_{18}H_{16}N_3O_5S$ $[M + H]^+$: 386.0811, Found 386.0809.

2-Fluoro-*N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (3ei): The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), 2-fluorobenzenesulfonyl azide (**2i**) (120.6 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ei** (186 mg, 96%) as a yellow solid. M. p. = 177−178 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.11 (br s, 1H), 8.26 (dd, J = 5.0, 1.1 Hz, 1H), 8.19 (dd, J = 8.6, 1.5 Hz, 1H), 8.06 (ddd, J = 7.6, 7.4, 1.5 Hz, 1H), 7.91 (dd, J = 7.8, 1.3 Hz, 1H), 7.68 (ddd, J = 7.8, 7.8, 1.8 Hz, 1H), 7.66− 7.59 (m, 1H), 7.35− 7.23 (m, 2H), 7.20 (dd, J = 9.3, 9.3 Hz, 1H), 7.14− 7.07 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 159.2 (d, $^1J_{C-F}$ = 258 Hz, C_q), 153.2 (C_q), 153.1 (C_q), 147.9 (CH), 140.8 (d, $^4J_{C-F}$ = 2 Hz, CH), 138.4 (CH), 135.7 (d, $^3J_{C-F}$ = 8 Hz, CH), 135.4 (C_q), 131.9 (CH), 128.8 (C_q), 128.4 (d, $^2J_{C-F}$ = 13 Hz, C_q), 126.1 (CH), 124.2 (d, $^3J_{C-F}$ = 4 Hz, CH), 121.0 (CH), 119.3 (CH), 117.5 (CH), 117.2 (d, $^2J_{C-F}$ = 21 Hz, CH). ^{19}F-NMR (376 MHz, $CDCl_3$) δ = −(106.9−107.1) (m). HRMS (ESI) m/z calcd for $C_{17}H_{13}FN_3O_5S$ $[M + H]^+$: 390.0560, Found 390.0560.

***N*-{3-nitro-2-(pyridin-2-yloxy)phenyl}methanesulfonamide (3ej):** The representative procedure was followed using 2-(2-nitrophenoxy)pyridine (**1e**) (108.0 mg, 0.5 mmol), methanesulfonyl azide (**2j**) (72.6 mg, 0.6 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol). After 12 h, purification by column chromatography on silica gel (PE/EtOAc/DCM: 20:1:1 → 10:1:1) to afford the desired product **3ej** (98 mg, 63%) as a yellow solid. M. p. = 120−121 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.01 (br s, 1H), 8.44 (d, J = 3.8 Hz, 1H), 8.24 (dd, J = 8.2, 1.1 Hz, 1H), 7.87 (dd, J = 7.8, 1.1 Hz, 1H), 7.62 (dd, J = 7.8, 7.8 Hz, 1H), 7.16 (dd, J = 8.2, 8.2 Hz, 1H), 7.09 (dd, J = 7.8, 7.8 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 3.65 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.9 (C_q), 152.7 (C_q), 148.1 (CH), 141.6 (CH), 138.5 (CH), 135.1 (C_q), 128.7 (C_q), 126.2 (CH), 119.9 (CH), 119.7 (CH), 113.8 (CH), 42.9 (CH_3). HRMS (ESI) m/z calcd for $C_{12}H_{12}N_3O_5S$ $[M + H]^+$: 310.0498, Found 310.0498.

Intermolecular competition experiment with diaryl ethers 1q and 1e (Scheme 4): The mixture of 2-(2-methoxyphenoxy)pyridine (**1q**) (201.0 mg, 1.0 mmol), 2-(2-nitrophenoxy)pyridine (**1e**) (216.0 mg, 1.0 mmol), *para*-toluenesulfonyl azide (**2a**) (98.5 mg, 0.5 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and 1,2-DCE (2.0 mL) was stirred at 80 °C under N_2 for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→10:1:1→6:1:1) to yield **3ea** (5 mg, 2%) as a yellow solid and **3qa** (62 mg, 34%) as a white solid.

Intermolecular competition experiment with azides 2c and 2d (Scheme 5): The mixture of 2-(2-nitrophenoxy)pyridine (**1e**) (92.5 mg, 0.5 mmol), 4-methoxybenzenesulfonyl azide (**2c**) (213.0 mg, 1.0 mmol), 4-fluorobenzenesulfonyl azide (**2d**) (201.0 mg, 1.0 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol) and 1,2-DCE (2.0 mL) was stirred at 80 °C under N_2 for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 20:1:1→8:1:1) to yield **3ed** (66 mg, 34%) as a yellow solid and **3ec** (121 mg, 60%) as a yellow solid.

Iridium-catalyzed direct *ortho*-C–H amidation azide 2a with diaryl ether 1i in 1,2-DCE and $[D]_4$-AcOH (Scheme 6): A mixture of 2-phenoxypyridine (**1i**) (342.0 mg, 2.0 mmol), *para*-toluenesulfonyl azide (**2a**) (197.0 mg, 1.0 mmol), $[Cp^*IrCl_2]_2$ (8.0 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), 1,2-DCE (2.0 mL) and $[D]_4$-AcOH (112 µL, 2.0 mmol) was stirred at 80 °C under N_2 for 12 h. The reaction mixture was cooled to ambient temperature, filtered through a pad of celite and silica gel, and washed with EtOAc (3 x 10 mL). The solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 40:1:1→20:1:1) to give $[D]_n$-**1i** (117 mg, 68%) as a white solid and $[D]_n$-**3ia** (74 mg, 22%) as a white solid. The deuterium incorporation was estimated by ^{1}H-NMR spectroscopy.

Removal of the directing group (Scheme 8): [16k,16n] To a solution of 4-methyl-*N*-{2-(pyridin-2-yloxy)phenyl}benzenesulfonamide (**3ia**) (170.0 mg 0.5 mmol) in PhMe (10.0 mL) under N_2 was added MeOTf (100 µL, 0.88 mmol). The reaction mixture was stirred under N_2 at 100 °C for 4 h. The reaction mixture was allowed to cool to ambient temperature. Evaporation of the solvent *in vacuo* yielded a white solid. The solid was dissolved in dry MeOH (5.0 mL) and was added under N_2 to a solution of Na (276 mg, 12 mmol) in dry MeOH (20.0 mL). The reaction mixture was heated at 90 °C for 2 h. The reaction mixture was allowed to cool to ambient temperature and the solvent was evaporated *in vacuo*. H_2O (50 mL) was added, and the resulting mixture was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the residue was purified by silica gel column chromatography (PE/EtOAc/DCM = 10:1:1→6:1:1) to afford *N*-(2-hydroxyphenyl)-4-methylbenzenesulfonamide (**4ia**) (97 mg, 73%) as a white solid. M. p. = 142−143 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.07 (dd, J = 7.8, 7.8 Hz, 1H), 6.94− 6.85 (m, 2H), 6.76 (d, J = 7.8 Hz, 1H), 6.73 (br s, 1H), 6.59 (br s, 1H), 2.40 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 150.2 (C_q), 144.3 (C_q), 135.0 (C_q), 129.6 (CH), 127.9 (CH), 127.5 (CH), 125.2 (CH), 123.0 (C_q), 121.0 (CH), 116.9 (CH), 21.6 (CH_3). HRMS (ESI) m/z calcd for $C_{13}H_{14}NO_3S$ $[M + H]^+$: 264.0694, Found 264.0692. The spectral data were in accordance with those reported in the literature.[19]

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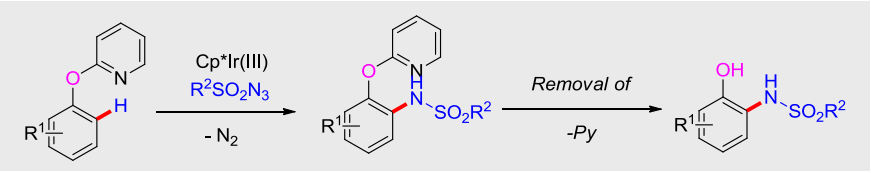

A highly efficient and regioselective C−H amidation of 2-phenoxypyridines with sulfonyl azides catalyzed by Ir(III) was developed, offering the synthetically useful *ortho*-hydroxyanilnes after removal of the 2-pyridyl moiety.

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A Facile Access to Ortho-Hydroxyanilnes Based on Ir(III)-Catalyzed Direct C−H Amidation of 2-Phenoxypyridines