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Para-Selective Cu–catalyzed C–H Aryloxylation of Electron-rich Arenes and Heteroarenes

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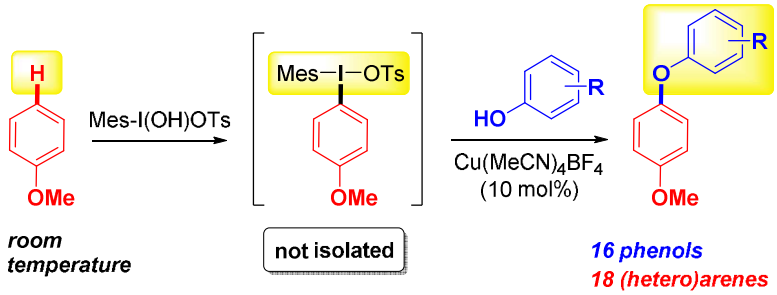


Abstract. Cu-catalyzed reaction of phenols with electron-rich (hetero)arene ligands of unsymmetrical diaryl-λ^3-iodanes is a key step in the developed one-pot two-step method for intermolecular *para*-selective C–H aryloxylation of heteroarenes and arenes.

Introduction

Synthetic methodologies employing hypervalent iodonium species have recently become an important alternative to the transition metal-catalyzed direct C*sp2*–H activation methods for C-O bonds formation.[1,2] Thus, a reaction of diaryliodonium salts with various oxygen nucleophiles such as alcohols and phenols under metal-free conditions has been widely used for synthesis of aryl-alkyl ethers and diarylethers.[3,4] The use of symmetrical diaryliodonium salts in the reaction with oxygen nucleophiles generates one equivalent of aryl iodide side-product together with the desired ether (eq 1).The waste of aryl iodide nucleofuge becomes cost-inefficient for diaryliodonium salts possessing structurally complex aryl moieties. Therefore, unsymmetrical diaryliodonium salts comprising an elaborated aryl moiety and structurally simple nontransferrable or "dummy" arene ligand are often used (eq 2). The nontransferrable aryl moieties should be relatively electron-rich and sterically unhindered, because oxygen nucleophiles such as phenolates react either with the most electron-deficient of the two aryl moieties in the unsymmetrical iodonium salt (electronic control) or with *ortho*-substituted aryl moiety (steric control or so-called *ortho*-effect).[5,6] Such reactivity pattern, however, imparts an important limitation to the transition metal-free methodology: oxygen nucleophiles apparently do not react with electron-rich aryl moieties of unsymmetrical diaryliodonium species.

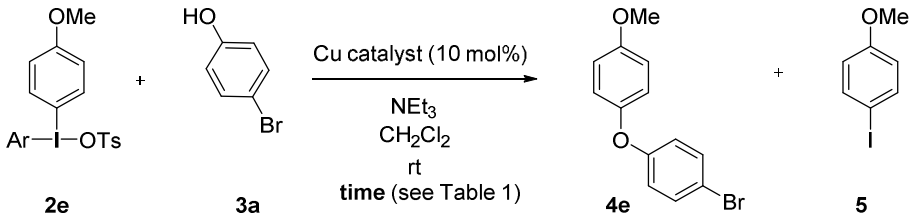
We have recently demonstrated that the selectivity of the reaction between unsymmetrical diaryl-λ^3-iodanes and nitrogen nucleophiles such as azides and amines can be directed to the more electron-rich (hetero)arene moiety by a Cu(I) catalyst.[7,8] We report herein that the most electron-rich of the two aryl ligands in unsymmetrical diaryliodonium species react selectively with oxygen nucleophiles such as phenols in the presence of Cu(I) species.[9] This finding provided new opportunities for Csp^2-H functionalization of arenes given that the unsymmetrical diaryl-λ^3-iodanes can be generated *in situ* directly from relatively electron-rich arenes and hypervalent iodonium reagent such as ArI(OH)OTs.[10] We envisioned that the electron-rich aryl moiety of the *in situ* formed unsymmetrical diaryl-λ^3-iodanes would subsequently react with phenols in the presence of Cu(I) catalyst to afford diarylethers. Indeed, we

found that the transformation of non-prefunctionalized arenes to diarylethers can be performed in sequential two step manner as described below. Furthermore, the developed Csp^2-H aryloxylation approach features high *para*-selectivity of C–O bond formation, and, hence, it is a complementary methodology to transition metal-catalyzed Csp^2–H to Csp^2–O transformations which usually requires the presence of an *ortho*-directing group in the arene.[11]

Results and Discussion.

para-Methoxyphenyl moiety-containing diaryl-λ^3-iodane **2e**[12] was chosen as a model for the development of Csp^2–H aryloxylation method because *para*-anisyl moiety has been frequently used as a "dummy" ligand in the noncatalyzed reactions of unsymmetrical diaryl-λ^3-iodanes with oxygen nucleophiles.[13] Indeed, phenol **3a** reacted preferentially with a mesityl ligand of the λ^3-iodane **2e** to afford mesityl 4-bromophenyl ether and iodoanisole **5** (entry 1, Table 1). The desired **4e** was formed only in less than 5% yield. In sharp contrast, addition of $Cu(MeCN)_4BF_4$ (10 mol%) altered the selectivity of the reaction providing ether **4e** as the major product (**4e**:**5**=2:1, entry 2). Mesityl moiety apparently served as a nontransferable aryl ligand[14] in the Cu(I)-catalyzed reaction of λ^3-iodane **2e** with **3a**. As anticipated, replacement of bulky mesityl ligand for a less sterically hindered phenyl group (iodane **2e-Ph**) resulted in a non-selective reaction (entry 3). Disappointingly, the use of sterically highly hindered triisopropylphenyl (TIPP) ligand as the nontransferable aryl moiety[15] (iodane**2e-TIPP**) resulted in undesired selectivity (**4e**:**5**=1:3, entry 4). Therefore the mesityl group was chosen as the "dummy" ligand in all subsequent experiments. Copper(I) iodide can be used as a catalyst at the expense of slightly diminished yields of the target **4e** (**4e**:**5**=1.4:1, entry 5). Interestingly, catalytic efficiency of copper salts depended on the structure of anion: both Cu(I) and Cu(II) triflates were inferior to $Cu(MeCN)_4BF_4$ (entries 6,7 vs. entry 2). The presence of water (1 equiv) was found to be detrimental for the success of the reaction between λ^3-iodane **2e** and **3a** (entry 8). Hence, moisture-free conditions are critical to obtain the desired product **4e** in good yields. The presence of oxygen had relatively small effect on the reaction outcome (entry 9 vs. entry 2).

Table 1. Reaction of λ^3-iodane **2e** with phenol **3a**.[a]



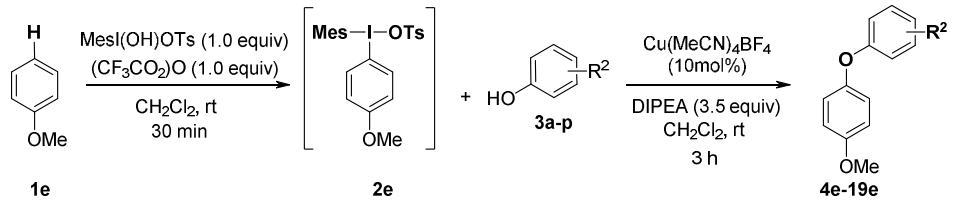
Entry	λ^3-iodane	Cu catalyst	time, h[b]	**4e**, %[c]	**5**, %[c]
1	**2e**	None	168[d]	<5	55[e]
2	**2e**[f]	$Cu(MeCN)_4BF_4$	1.5	60	33
3	**2e-Ph**[g]	$Cu(MeCN)_4BF_4$	1.5	49	47
4	**2e-TIPP**[h]	$Cu(MeCN)_4BF_4$	1.5	30	66
5	**2e**	CuI	1.5	49	36
6	**2e**	$Cu(OTf)_2$	48	30	51
7	**2e**	CuOTf	48	33	50
8[i]	**2e**	$Cu(MeCN)_4BF_4$	48	30	47
9[j]	**2e**	$Cu(MeCN)_4BF_4$	1.5	49	38

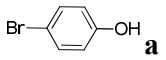
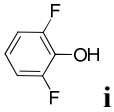
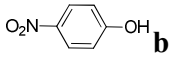
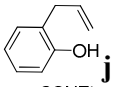
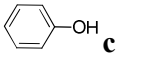
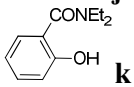
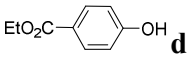
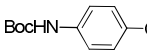
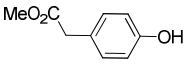
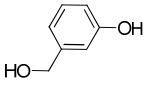
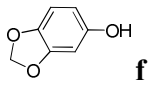
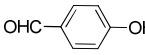
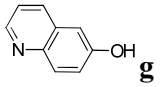
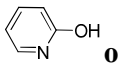
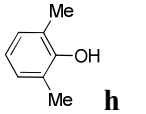
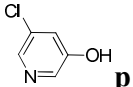
[a] Conditions: λ^3-iodane **2e** (1 equiv), phenol **3a** (1.2 equiv), *i*PrNEt$_2$ (1.5 equiv), CH_2Cl_2 (0.1 M). [b] Full conversion of **2e**. [c] Determined by ^{1}H-NMR using methyl 2-iodobenzoate as an internal standard. [d] 75% conversion of **2e**. [e] Formed together with 20% of mesityl 4-bromophenyl ether. [f] Ar=Mes. [g] Ar=Ph. [h] Ar=TIPP (2,4,6-triisopropyl)phenyl. [i] In the presence of water (1 equiv). [j] Under air.

With the optimized conditions for the reaction between λ^3-iodane **2e** and phenol **3a** in hand, the development of a one-pot sequential synthesis of diarylethers from non-prefunctionalized arenes without isolation of the intermediate λ^3-iodane was addressed. The λ^3-iodane **2e** could be formed from anisole and MesI(OH)OTs (1.1 equiv) in 74% yield within 24 h in anhydrous CH_2Cl_2 at room temperature. Higher yields of **2e** were achieved in the presence of protic acids such as CF_3COOH and TsOH (82% and 91%, respectively).[16] Subsequent reaction of the *in situ* formed **2e** with phenol **3a** in the presence of *i*PrNEt$_2$ (2.5 equiv) and $Cu(MeCN)_4BF_4$ (10 mol%) afforded the desired diarylether **4e** in 57% yield after 18 hours at room temperature. The prolonged reaction time could be decreased substantially by capturing one equivalent of water that is generated during the formation of λ^3-iodane **2e** from anisole and MesI(OH)OTs (compare entries 8 and 2, Table 1). This was achieved by using trifluoroacetic acid anhydride (1 equiv) as an additive. The anhydride reacted with water to form trifluoroacetic acid which, in turn, facilitated the formation of λ^3-iodane **2e** in 70% yield within 3 hours at room temperature (entry 1, Table 2).

Next, the scope of phenols suitable for the reaction with λ^3-iodane **2e** was examined (Table 2). Phenols with both electron-withdrawing groups (entries 2,4,9,11,14) and electron-releasing groups (entries 6, 8, 12) are suitable as nucleophiles. Sterically hindered phenols (entries 8 and 9) afforded lower yields of diarylethers. The C–H aryloxylation conditions are compatible with a variety of functional groups in phenols such as halides (entry 1,9,16), nitro group (entry 2), carboxylic ester (entries 4 and 5), amide (entry 11), benzylic alcohol (entry 13), aldehyde (entry 14), alkene (entry 10) and *N*-Boc protecting group (entry 12). Quinolin-6-ol (entry 7) and hydroxypyridines (entries 15,16) could be also used as nucleophiles.

Table 2. Scope of phenols **3**.[a]



entry	ArOH **3**	yield, %[b]	entry	ArOH **3**	yield, %[b]
1	 **a**	**4e**, 70	9	 **i**	**12e**, 37
2	 **b**	**5e**, 65	10	 **j**	**13e**, 64
3	 **c**	**6e**, 73	11	 **k**	**14e**, 50
4	 **d**	**7e**, 68	12	 **l**	**15e**, 67
5	 **e**	**8e**, 69	13	 **m**	**16e**, 54
6	 **f**	**9e**, 59	14	 **n**	**17e**, 75
7	 **g**	**10e**, 50	15	 **o**	**18e**, 67
8	 **h**	**11e**, 58	16	 **p**	**19e**, 53

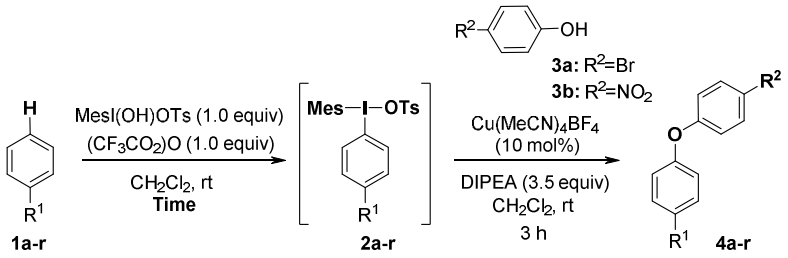
[a] Conditions: Arene **1e** (1.0 equiv); $(CF_3CO)_2O$ (1.0 equiv) and Mes-I(OH)OTs (1.0 equiv) in CH_2Cl_2 (0.25 M) at room temperature for 30 min; then $Cu(MeCN)_4BF_4$ (10 mol%), phenol **3** (1.2 equiv) and DIPEA (3.5 equiv) in CH_2Cl_2 (0.1 M) at rt for 3 h. [b] Average yield of two runs.

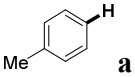
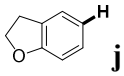
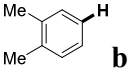
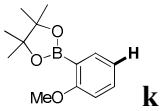
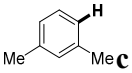
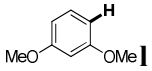
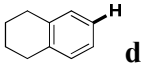
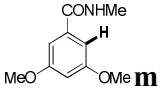
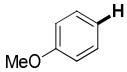
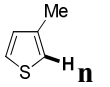
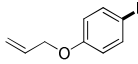
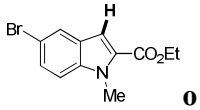
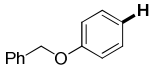
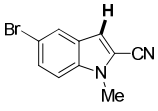
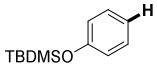
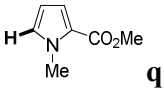
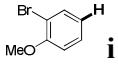
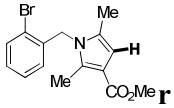
All arenes that react with MesI(OH)OTs reagent in the presence of trifluoroacetic anhydride and form relatively stable λ^3-iodanes are suitable as substrates (Table 3). Toluene **1a** (entry 1) represents a reactivity borderline: less electron-rich arenes than toluene (for example benzene and aryl halides) did not react with MesI(OH)OTs reagent. Time of the formation of λ^3-iodanes **2a–r** correlated well with electronic properties of the starting arenes **1a–r**: the more electron-rich were arenes **1a–r**, the shorter time was required to achieve complete conversion to λ^3-iodanes **2a–r** (compare entries 1, 3, 5 and 12 as well as entries 4 and 10, Table 3). The strong electron-donating effect of methoxy group (σ_p= –0.27)[17] compensated for the presence of deactivating electron-withdrawing substituents such as bromine (entry 9) and amide (entry 13). Relatively electron-rich heterocycles such as thiophene (entry 14), indoles (entries 15, 16) and pyrroles (entries 17, 18) also afforded the C–H aryloxylation products.

Regioselectivity of the C−H aryloxylation is controlled at the stage of the formation of the unsymmetrical diaryl-λ^3-iodane intermediates **2a–r**. Notably, all monosubstituted arenes underwent highly regioselective *para*-C–H aryloxylation and the formation of isomeric *ortho*-substituted products was not observed. The C–O bond formation in multiply substituted arenes proceeded selectively at the *para*-position to the strongest electron-releasing substituent (entries 9–11). In heterocycles the regioselectivity of the C–O bond formation was consistent with that of electrophilic aromatic substitution (S_EAr) reactions: λ^3-iodanes were formed at the β-position of indoles (entries 15 and 16, Table 3), and at the α-position of thiophenes (entry 14) and pyrroles (entry 17). In 2,5-disubstituted pyrrole the C–H aryloxylation occurred at the β-position (entry 18).

The C−H aryloxylation conditions were compatible with the presence of bromine (entries 9, 15, 16, 18) and even pinacolyl boronate moiety (entry 11) in substrates which renders feasible their further functionalization. *O*-Allyl (entry 6), *O*-benzyl (entry 7), *N*-benzyl (entry 18) and even relatively labile *O*-TBDMS (entry 8) protecting groups are tolerated. (Hetero)arenes may contain a range of functional groups such as secondary amides (entry 13), carboxylic esters (entries 15, 17, 18) and nitrile (entry 16).

Table 3. Substrate scope for the synthesis of diarylethers.[a]



entry	arene **1**	ArOH	time, h	yield, %[b]	entry	arene **1**	ArOH	time, h	yield, %[b]
1	 **a**	**3a**	40	63	10	 **j**	**3a**	0.1	57
2	 **b**	**3a**	18	67	11	 **k**	**3a**	2	65[c]
3	 **c**	**3a**	3	72	12	 **l**	**3a**	0.25	55
4	 **d**	**3a**	0.5	51	13	 **m**	**3a**	0.5	28
5	 **e**	**3a**	0.5	70	14	 **n**	**3b**	0.5	50
6	 **f**	**3a**	0.5	73	15	 **o**	**3b**	0.5	71
7	 **g**	**3a**	0.5	78	16	 **p**	**3b**	18	53
8	 **h**	**3a**	0.5	68	17	 **q**	**3b**	0.25	49
9	 **i**	**3a**	18	65	18	 **r**	**3b**	0.5	43

[a] Conditions: (Hetero)arene **1** (1.0 equiv); $(CF_3CO)_2O$ (1.0 equiv) and Mes-I(OH)OTs (1.0 equiv) in CH_2Cl_2 (0.25 M) at room temperature; then $Cu(MeCN)_4BF_4$ (10 mol%), phenol **3** (1.2 equiv) and DIPEA (3.5 equiv) in CH_2Cl_2 (0.1 M) at rt for 3 h. [b] Average yield of two runs. [c] 80% purity according to ^{1}H-NMR; pure product (>95%) was obtained by crystallization.

An important mechanistic question pertains to possible involvement of phenoxy diaryl-λ^3-iodanes in the Cu-catalyzed aryloxylation reaction. Putative phenoxy diaryl-λ^3-iodanes could form from tosyloxy diaryl-λ^3-iodanes **2a**–**r** and phenols by exchange of tosyloxy ligand for phenoxy moiety. Subsequent Cu-catalyzed reductive elimination from phenoxy diaryl-λ^3-iodanes would afford diarylethers and iodo-mesitylene. To verify such a mechanistic scenario, preparation

of phenoxy diaryl-λ^3-iodanes in pure form was attempted. After a considerable work it was found that relatively stable phenoxy diaryl-λ^3-iodanes could be obtained from the corresponding tosylates only if phenols possessing electron-withdrawing substituents were used. Thus, the reaction of sodium *para*-nitrophenolate and iodonium tosylate **2o** afforded crystalline phenoxy diaryl-λ^3-iodane **20**, which could be stored for more than a week at +4 ^{o}C without decomposition. The structure of **20** was confirmed by X-ray crystallographic analysis (Figure 1).[18]

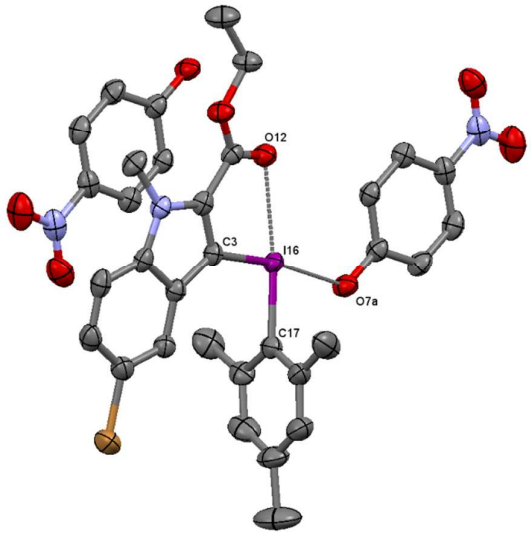
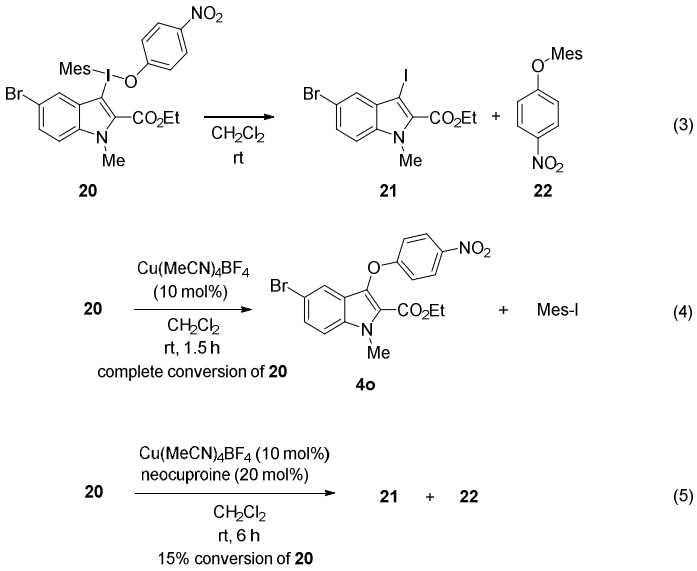


Figure 1. X-ray crystal structure of a 1:1 adduct of λ^3-iodane **20** and phenol **3b** (thermal displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): I16−C3, 2.095(3); I16−C17, 2.102(3); I16−O7a, 2.578(2); I−O12, 2.748(2); C3−I16−C17, 95.0(1). See the Supporting Information for details.

In CH_2Cl_2 solution phenoxy diaryl-λ^3-iodane **20** undergoes slow reductive elimination to form 3-iodoindole **21** and diarylether **22** (eq 3; 25% conversion after 3 h at rt; 100% conversion after 168 h at rt), and the formation of **4o** was not observed. Importantly, addition of $Cu(MeCN)_4BF_4$ (10 mol%) resulted in reversal of selectivity favoring the formation of the desired ether **4o** (**4o**:**21**=5:1) together with Mes-I (eq 4). Furthermore, the copper catalyst considerably decreased the reaction time (complete conversion of **20** was observed already after 1.5 h). These results point toward an involvement of phenoxy diaryl-λ^3-iodane intermediates such as **20** in catalytic cycle of the Cu-catalyzed C-H aryloxylation.



A control experiment has been carried out to determine the oxidation state of catalytically active copper species in the C-H aryloxylation reaction. Accordingly, neocuproine (2 equiv with respect to $Cu(MeCN)_4BF_4$) was added to the λ^3-iodane **20** and Cu(I) catalyst (eq 5). Neocuproine is a highly specific chelating agent for Cu(I) ions, which forms a stable bright orange-colored complex of formula $Cu^I(neocuproine)_2$.[19] The addition of neocuproine considerably decelerated the reaction and only 15% conversion of λ^3-iodane **20** was observed after 6 hours as opposed to the complete conversion of **20** within 1.5 h without the added neocuproine (eq 5 vs. eq 4).[20] Furthermore, 3-iodoindole **21** and ether **22** were the only products observed in the reaction mixture and the desired **4o** was not formed. Evidently, the addition of neocuproine completely inhibited the Cu(I)-catalyzed reaction and λ^3-iodane **20** underwent slow noncatalyzed conversion to **21** and **22**. Based on these results a Cu^I/Cu^{III} catalytic cycle for the reaction between λ^3-iodanes **2** and phenols **3** is plausible. Accordingly, an initially formed Cu(I)-phenolate would undergo oxidative addition of the λ^3-iodane **2** to form the Cu(III) intermediate. Product forming reductive elimination would afford diarylether and regenerate a catalytically active Cu(I) species.

Conclusions.

In summary, electron-rich (hetero)arene ligands of unsymmetrical diaryl-λ^3-iodanes undergo reaction with phenolates in the presence of Cu(I) catalyst. Such reactivity mode of unsymmetrical diaryl-λ^3-iodanes with phenolates cannot be

achieved under metal-free conditions where electronically poor arene ligands react preferentially. Hence, the Cu(I)-catalyzed synthesis of diarylethers from unsymmetrical diaryl-λ^3-iodanes is a complementary method to the metal-free conditions. The Cu(I)-catalyzed reaction between unsymmetrical diaryl-λ^3-iodanes and phenolates was used also as a key step in the development of a one-pot two-step sequential catalytic C-H aryloxylation method. The C-H aryloxylation method comprised an initial formation of unsymmetrical diaryl-λ^3-iodanes directly from non-prefunctionalized electron rich (hetero)arenes and MesI(OH)OTs reagent. Subsequent Cu(I)-catalyzed reaction of the *in situ* formed unsymmetrical diaryl-λ^3-iodanes with phenolates provided the desired diarylethers. The developed C-H aryloxylation method features high *para*-selectivity of C−H aryloxylation of a wide range of relatively electronrich arenes. The *para* regioselectivity is controlled at the stage of the formation of the unsymmetrical diaryl-λ^3-iodane intermediates. Regioselectivity of C−H aryloxylation in heteroarenes in general is consistent with that of electrophilic aromatic substitution (S_EAr) reactions. Given the mild reaction conditions (room temperature) and excellent functional group compatibility, the developed C–H aryloxylation is especially suitable for late-stage *para*-selective functionalization of pharmaceutically relevant (hetero)arenes.

Experimental Section.

General Information.

Unless otherwise noted, all chemicals were used as obtained from commercial sources and all reactions were performed under argon atmosphere. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel F-254 plates. Nuclear magnetic resonance spectra were recorded on NMR spectrometers at the following frequencies: ^{1}H, 400 or 300 MHz; ^{13}C{^{1}H}, 101 or 75 MHz. Chemical shifts are reported in parts per million (ppm) relative to TMS or with the residual solvent peak as an internal reference. Infrared (IR) spectra were recorded with KBr pellet, and wavenumbers were given in cm^{-1}. High resolution mass spectra (HRMS) were recorded on an TOF MS instrument using the ESI technique.

Preparation of unsymmetrical diaryl-λ^3-iodanes.

(4-Methoxyphenyl){[(4-methylphenyl)sulfonyl]oxy}(2,4,6-trimethylphenyl)-λ^3-iodane (2e). To a well-stirred suspension of MesI(OH)OTs (2.17 g, 5.00 mmol, 1.0 equiv) and TsOH●H_2O (951 mg, 5.00 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was added dropwise neat anisole **1e** (543 μL, 5.00 mmol, 1.00 equiv) and the resulting yellow solution was stirred at room temperature. The progress of the reaction was monitored by TLC (disappearance of the MesI(OH)OTs spot, R_f = 0.49, 20:80:5 MeOH/CH_2Cl_2/AcOH) and complete conversion of the starting material was observed within 1 hour. The solution was concentrated to ca. 2/3 of the original volume and Et_2O was added (50 mL). Formed precipitate was filtered, washed with Et_2O (10 mL) and dried *in vacuo* to afford **2e** as a white powder (2.50 g, 95% yield). Pure material was obtained by crystallization from CH_2Cl_2/diethyl ether: mp 180 ^oC dec. ^1H NMR (300 MHz, DMSO-d_6, ppm) δ 7.95 – 7.89 (2H, m), 7.49 – 7.44 (2H, m), 7.19 (2H, s), 7.12 – 7.08 (2H, m), 7.06 – 7.00 (2H, m), 3.78 (3H, s), 2.60 (6H, s), 2.28 (6H, s). ^1H NMR spectrum was in agreement with that reported in the literature.[21]

(4-Methoxyphenyl){[(4-methylphenyl)sulfonyl]oxy}[2,4,6-tris(1-methylethyl)phenyl]-λ^3-iodane (2e-TIPP). Iodane **2e-TIPP** (2.33 g, 77% yield) was synthesized from TIPP-I(OH)OTs[22] (2.59 g, 5.00 mmol, 1.0 equiv), TsOH●H_2O (951 mg, 5.00 mmol, 1.0 equiv) and anisole **1e** (543 μL, 5.00 mmol, 1.00 equiv) as described for iodane **2e**. Pure material was obtained by crystallization from CH_2Cl_2/diethyl ether: mp 168 ^oC dec. ^1H NMR (300 MHz, DMSO-d_6, ppm) δ 7.91 – 7.84 (2H, m), 7.49 – 7.44 (2H, m), 7.28 (2H, s), 7.14 – 7.05 (4H, m), 3.78 (3H, s), 3.49 – 3.38 (2H, m), 3.03 – 2.89 (1H, m), 2.28 (3H, s), 1.26 – 1.17 (18H, m). ^1H NMR spectrum was in agreement with that reported in the literature.[13d]

(4-Methoxyphenyl){[(4-methylphenyl)sulfonyl]oxy}phenyl-λ^3-iodane (2e-Ph). Iodane **2e-Ph** (2.3 g, 95% yield) was synthesized from $PhI(OAc)_2$ (1.61 g, 5.00 mmol, 1.0 equiv), TsOH●H_2O (1.24 g, 6.5 mmol, 1.3 equiv) and anisole **1e** (543 μL, 5.0 mmol, 1.00 equiv) as described for iodane **2e**. Pure material was obtained by crystallization from CH_2Cl_2/diethyl ether: mp 160 ^oC dec. ^1H NMR (300 MHz, DMSO-d_6, ppm) δ 8.23 – 8.13 (4H, m), 7.68 – 7.61 (1H, m), 7.55 – 7.44 (4H, m), 7.14 – 7.04 (4H, m), 3.79 (3H, s), 2.28 (3H, s). ^1H NMR spectrum was in agreement with that reported in the literature.[10a]

Ethyl 5-bromo-1-methyl-3-[(4-nitrophenoxy)(2,4,6-trimethylphenyl)-λ^3-iodanyl]-1*H*-indole-2-carboxylate 1:1 adduct with 4-nitrophenol (20). A solution of ethyl 5-bromo-3-(mesityl(tosyloxy)-λ^3-iodanyl)-1-methyl-1*H*-indole-2-carboxylate[8a] (2.0 g, 2.86 mmol, 1.0 equiv.) in CH_2Cl_2 (50 mL) was extracted twice with a solution of 4-nitrophenol (598 mg, 4.30 mmol, 1.5 equiv.) and NaOH (172 mg, 4.30 mmol, 1.5 equiv) in water (50 mL). Organic layer was dried over Na_2SO_4, concentered *in vacuo* and Et_2O (50 mL) was added to the yellow residue. Formed precipitate was filtered, washed with Et_2O (10 mL) and dried *in vacuo* to afford λ^3-iodane **20** as a yellow powder (1.53 g, 67% yield). Pure material was obtained by crystallization from CH_2Cl_2/diethyl ether: mp 124 ^oC dec. IR (film, cm^{-1}) 1717 (C=O).^1H NMR (400 MHz, $CDCl_3$, ppm) δ 11.25 – 10.50 (1H, br s), 7.99 – 7.94 (4H, m), 7.41 (1H, dd, *J* = 9.0, 1.8 Hz), 7.30 (1H, d, *J* = 9.0 Hz), 7.05 (2H, s), 6.61 – 6.57 (4H, m), 5.96 (1H, d, *J* = 1.8 Hz), 4.58 (2H, q, *J* = 7.1 Hz), 4.08 (3H, s), 2.56 (6H, s), 2.35 (3H, s), 1.50 (3H, t, *J*=7.1 Hz).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 169.71, 169.68, 161.8, 144.9, 143.1, 138.9, 137.9, 129.99, 129.97, 129.0, 127.2, 126.6, 122.3, 119.8, 117.4, 116.5, 113.2, 64.0, 33.6, 27.3, 21.2, 14.5.HRMS-ESI (m/z) calcd for $C_{21}H_{22}NO_2BrI$ [M-$OC_6H_4NO_2$*$HOC_6H_4NO_2$]$^+$ 525.9879, found 525.9878.

Preparation of $Cu(MeCN)_4BF_4$

$[Cu(MeCN)_4]BF_4$ was synthesized in accordance with literature procedure.[23] Thus, to a blue-colored suspension of $Cu(BF_4)_2\bullet 6H_2O$ (2.00 g, 5.79 mmol) in anhydrous MeCN (50 mL) was added copper powder (1.47 g, 23.17 mmol). The resulting suspension was heated under reflux for 4 h under argon atmosphere and then hot-filtered. The pale blue filtrate was then cooled to –20 ^oC whereupon a white solid crystalline material was formed. The white solid was collected by filtration and washed with Et_2O (15 mL). Pure material was obtained by recrystallization from hot MeCN. Yield: 1.73 g (95%).

General Procedure for Sequential One-Pot Two-Step Synthesis of Diarylethers

To a solution of MesI(OTs)OH (217 mg, 0.50 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (1 mL) under argon atmosphere was added a solution of arene **1** (0.50 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (1 mL). Neat TFAA (71 μL, 0.50 mmol, 1.0 equiv) was

then added dropwise (*slowly, within 2-3 minutes; too fast addition of TFAA leads to the formation of side-products*). The resulting solution (color range – pale yellow to dark brown) was stirred at room temperature under argon atmosphere and the progress of the reaction was monitored by TLC (disappearance of the starting I (III) reagent spot; mobile phase 20:80:5 MeOH/DCM/AcOH). Immediately upon disappearance of MesI(OTs)OH reagent (see Table 3 for appropriate time), the reaction mixture was transferred via cannula to another flask which contained pre-weighed solid $[Cu(MeCN)_4]^+BF_4^-$ (16 mg, 0.05 mmol, 10 mol%) and a magnetic stir-bar, and the source flask was rinsed with CH_2Cl_2 (1 mL). To the resulting well-stirred suspension was immediately (!) added a solution of phenol (0.6 mmol, 1.2 equiv) in anhydrous CH_2Cl_2 (2 mL), followed with neat DIPEA (305 μL 1.75 mmol, 3.5 equiv) (*Important! Decomposition of the formed λ^3-iodane begins if the addition of Cu catalyst and/or DIPEA is delayed*). The resulting solution was stirred at room temperature under argon atmosphere and the progress of the reaction was monitored by TLC (mobile phase MeOH/CH_2Cl_2/AcOH=20:80:5; the intermediate λ^3-iodanes have R_f=0.4–0.6). In the most cases the reaction was completed in 3 hours. The solution was poured into a mixture of water (50 mL) and aqueous saturated ammonia solution (20 mL) and extracted with CH_2Cl_2(3x30 mL). Combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel.

1-Bromo-4-(4-methoxyphenoxy)benzene (4e).[24] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **4e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a pale yellow powder (100 mg in the 1st run and 95 mg in the 2nd run, 72% and 68% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.35. Pure material was obtained by crystallization from diethyl ether /petroleum ether: mp 87–88 °C. ^{1}H NMR (300MHz, $CDCl_3$, ppm) δ 7.42 – 7.35 (2H, m), 7.00 – 6.94 (2H, m), 6.92 – 6.86 (2H, m), 6.85 – 6.78 (2H, m), 3.81 (3H, s).

1-Methoxy-4-(4-nitrophenoxy)benzene (5e).[25] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **5e**. Purification of the crude

product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a white powder (75 mg in the 1st run and 85 mg in the 2nd run, 61% and 69% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.29. Pure material was obtained by crystallization from diethyl ether /petroleum ether: mp 113-114 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.21 – 8.15 (2H, m), 7.06-7.00 (2H, m), 6.99-6.92 (4H, m), 3.84 (3H, s).

1-Methoxy-4-phenoxybenzene (6e).[25] Following the general procedure anisole **1e** (54 µL, 0.50 mmol) was converted into **6e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a colorless oil (75 mg in the 1st run and 70 mg in the 2nd run, 75% and 70% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.46. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.33 – 7.27 (2H, m), 7.07 – 7.01 (1H, m), 7.01 – 6.96 (2H, m), 6.96 – 6.91 (2H, m), 6.91 – 6.85 (2H, m), 3.81 (3H, s).

Ethyl 4-(4-methoxyphenoxy)benzoate (7e).[26] Following the general procedure anisole **1e** (54 µL, 0.50 mmol) was converted into **7e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a colorless oil (95 mg in the 1st run and 90 mg in the 2nd run, 70% and 66% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.29. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.02 – 7.95 (2H, m), 7.05 – 6.98 (2H, m), 6.96 – 6.89 (4H, m), 4.35 (2H, q, J = 7.1 Hz), 3.82 (3H, s), 1.38 (3H, t, J = 7.1 Hz).

Methyl [4-(4-methoxyphenoxy)phenyl]acetate (8e).[27] Following the general procedure anisole **1e** (54 µL, 0.50 mmol) was converted into **8e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a colorless oil (91 mg in the 1st run and 95 mg in the 2nd run, 67% and 70% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.21. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.24 – 7.17 (2H, m), 7.01 – 6.94 (2H, m), 6.93 – 6.84 (4H, m), 3.81 (3H, s), 3.70 (3H, s), 3.59 (2H, s).

5-(4-Methoxyphenoxy)-1,3-benzodioxole (9e).[28] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **9e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a colorless oil (70 mg in the 1st run and 75 mg in the 2nd run, 57% and 61% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.33. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.96 – 6.91 (2H, m), 6.88 – 6.84 (2H, m), 6.72 (1H, d, J = 8.4 Hz), 6.53 (1H, d, J = 2.4 Hz), 6.42 (1H, dd, J = 8.4, 2.4 Hz), 5.95 (2H, s), 3.79 (3H, s).

6-(4-Methoxyphenoxy)quinoline (10e). Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **10e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 5% diethyl ether / light petroleum ether to 35% diethyl ether in light petroleum ether afforded product as a grey powder (60 mg in the 1st run and 65 mg in the 2nd run, 48% and 52% yield, respectively); analytical TLC on silica gel, 1:3 diethyl ether /petroleum ether, R_f=0.21. Pure material was obtained by crystallization from diethyl ether /petroleum ether: mp 46–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (1H, dd, J = 4.2, 1.7 Hz), 8.06 (1H, d, J = 9.2 Hz), 7.97 – 7.94 (1H, m), 7.47 (1H, dd, J = 9.2, 2.7 Hz), 7.33 (1H, dd, J = 8.3, 4.2 Hz), 7.09 (1H, d, J = 2.7 Hz), 7.08 – 7.04 (2H, m), 6.96 – 6.91 (2H, m), 3.83 (3H, s).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 157.0, 156.5, 149.6, 148.9, 145.0, 135.1, 131.4, 129.2, 122.7, 121.6, 121.5, 115.2, 111.2, 55.8. HRMS-ESI (m/z) calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1025, found 252.1025.

2-(4-Methoxyphenoxy)-1,3-dimethylbenzene (11e).[29] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **11e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a white powder (68 mg in the 1st run and 63 mg in the 2nd run, 60% and 55% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.50. Pure material was obtained by crystallization from petroleum ether: mp 43–45 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 7.11 – 7.00 (3H, m), 6.82 – 6.76 (2H, m), 6.71 – 6.65 (2H, m), 3.76 (3H, s), 2.13 (6H, s).

1,3-Difluoro-2-(4-methoxyphenoxy)benzene (12e). Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **12e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a colorless oil (45 mg in the 1st run and 41 mg in the 2nd run, 38% and 35% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.38. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.12 (1H, ddt, J = 9.2, 7.7, 5.8 Hz), 7.03 – 6.95 (2H, m), 6.93 – 6.88 (2H, m), 6.85 – 6.80 (2H, m), 3.77 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 156.6 (dd, J = 251.1, 4.6 Hz), 155.4, 152.1, 132.4 (t, J = 14.8 Hz), 124.9 (t, J = 9.1 Hz), 116.5, 114.8, 112.6 (dd, J = 16.7, 5.6 Hz), 55.8. Anal. Calcd. for $C_{13}H_{10}O_2F_2$: C, 66.10; H, 4.27. Found: C, 66.44; H, 4.49.

1-(4-Methoxyphenoxy)-2-prop-2-en-1-ylbenzene (13e).[29] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **13e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a colorless oil (78 mg in the 1st run and 75 mg in the 2nd run, 65% and 63% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/petroleum ether, R_f=0.50. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.24 (1H, dd, J = 7.4, 1.8 Hz), 7.14 (1H, ddd, J = 8.0, 7.5, 1.8 Hz), 7.03 (1H, ddd, J = 7.5, 7.4, 1.1 Hz), 6.93 – 6.84 (4H, m), 6.79 (1H, dd, J = 8.0, 1.1 Hz), 6.00 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.12 – 5.03 (2H, m), 3.80 (3H, s), 3.45 (2H, d, J = 6.6 Hz).

***N*,*N*-Diethyl-2-(4-methoxyphenoxy)benzamide (14e).**[30] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **14e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% CH_2Cl_2 to 15% diethyl ether in CH_2Cl_2 afforded product as a white powder (79 mg in the 1st run and 70 mg in the 2nd run, 53% and 47% yield, respectively); analytical TLC on silica gel, 1:10 diethyl ether/CH_2Cl_2, R_f=0.32. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 62–63 °C. ^{1}H NMR (300 MHz, DMSO-d_6, ppm) δ 7.36 – 7.25 (2H, m), 7.12 (1H, td, J = 7.4, 0.9 Hz), 6.99 – 6.92 (4H, m), 6.78 (1H, dd, J = 8.3, 0.7 Hz), 3.74 (3H, s), 3.54 –

3.33 (2H, m), 3.18 (2H, q, J = 7.0 Hz), 1.07 (3H, t, J = 7.1 Hz), 1.01 (3H, t, J = 7.1 Hz).

***tert*-Butyl [4-(4-methoxyphenoxy)phenyl]carbamate (15e).** Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **15e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 10% EtOAc in light petroleum ether to 35% EtOAc in light petroleum ether afforded product as a white powder (99 mg in the 1st run and 112 mg in the 2nd run, 63% and 71% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.17. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.33 – 7.26 (2H, m), 6.96 – 6.91 (2H, m), 6.92 – 6.88 (2H, m), 6.88 – 6.83 (2H, m), 6.44 (1H, s), 3.79 (3H, s), 1.51 (9H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 155.7, 154.0, 153.1, 151.0, 133.4, 120.5, 120.2, 118.8, 114.9, 80.6, 55.8, 28.5. Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.57; H, 6.72; N, 4.37.

[3-(4-Methoxyphenoxy)phenyl]methanol (16e).[31] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **16e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 5% diethyl ether in light petroleum ether to 35% diethyl ether in light petroleum ether afforded product as a pale yellow oil (64 mg in the 1st run and 60 mg in the 2nd run, 56% and 52% yield, respectively); analytical TLC on silica gel, 1:3 diethyl ether/petroleum ether, R_f=0.33. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.32 – 7.26 (1H, m), 7.06 – 7.02 (1H, m), 7.01 – 6.93 (3H, m), 6.92 – 6.84 (3H, m), 4.65 (2H, d, J = 5.6 Hz), 3.81 (3H, s), 1.64 (1H, t, J = 5.6 Hz).

4-(4-Methoxyphenoxy)benzaldehyde (17e).[32] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **17e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 10% EtOAc in light petroleum ether to 35% EtOAc in light petroleum ether afforded product as a pale yellow powder (82 mg in the 1st run and 88 mg in the 2nd run, 72% and 77% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.17. Pure material was obtained by crystallization from diethyl

ether/petroleum ether: mp 60–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 9.91 (1H, s), 7.85 – 7.79 (2H, m), 7.06 – 6.98 (4H, m), 6.97 – 6.90 (2H, m), 3.83 (3H, s).

2-(4-Methoxyphenoxy)pyridine (18e).[27] Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **18e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 10% diethyl ether in CH_2Cl_2 to 60% diethyl ether in CH_2Cl_2M afforded product as a grey powder (69 mg in the 1st run and 65 mg in the 2nd run, 69% and 65% yield, respectively); analytical TLC on silica gel, 1:1 diethyl ether/ CH_2Cl_2, R_f=0.29. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 111–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.37 (1H, ddd, J = 9.2, 6.6, 2.1 Hz), 7.33 – 7.27 (3H, m), 7.02 – 6.96 (2H, m), 6.67 – 6.61 (1H, m), 6.21 (1H, td, J = 6.7, 1.3 Hz), 3.84 (3H, s).

3-Chloro-5-(4-methoxyphenoxy)pyridine (19e). Following the general procedure anisole **1e** (54 μL, 0.50 mmol) was converted into **19e**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 10% EtOAc in light petroleum ether to 35% EtOAc in light petroleum ether afforded product as a white powder (60 mg in the 1st run and 65 mg in the 2nd run, 51% and 55% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.25. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 54–55 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.35 (1H, d, J = 2.0 Hz), 8.27 (1H, d, J = 2.5 Hz), 7.42 (1H, dd, J = 2.5, 2.3 Hz), 7.14 – 7.11 (2H, m), 7.02 – 6.99 (2H, m), 3.77 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, ppm) δ 156.4, 155.0, 148.0, 142.0, 138.1, 131.2, 123.7, 121.1, 115.4, 55.4. HRMS-ESI (m/z) calcd for $C_{12}H_{11}NO_2Cl$ $[M+H]^+$ 236.0478, found 236.0483.

1-Bromo-4-(4-methylphenoxy)benzene (4a).[33] Following the general procedure toluene **1a** (53 μL, 0.50 mmol) was converted into **4a**. Purification of the crude product by column chromatography (Biotage M+12) using light petroleum ether as a mobile phase afforded product as a white powder (87 mg in the 1st run and 78 mg in the 2nd run, 66% and 59% yield, respectively); analytical TLC on silica gel, light petroleum ether, R_f=0.38. Pure material was obtained by crystallization from

petroleum ether: mp 65–66 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.44 – 7.37 (2H, m), 7.18 – 7.12 (2H, m), 6.94 – 6.88 (2H, m), 6.88 – 6.82 (2H, m), 2.34 (3H, s).

4-(4-Bromophenoxy)-1,2-dimethylbenzene (4b). Following the general procedure *o*-xylene **1b** (60 μL, 0.50 mmol) was converted into **4b**. Purification of the crude product by column chromatography (Biotage M+12) using light petroleum ether as a mobile phase afforded product as a colorless oil (96 mg in the 1st run and 90 mg in the 2nd run, 69% and 65% yield, respectively); analytical TLC on silica gel, light petroleum ether, R_f=0.32. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 – 7.38 (2H, m), 7.10 (1H, d, J = 8.2 Hz), 6.88 – 6.83 (2H, m), 6.81 (1H, d, J = 2.6 Hz), 6.75 (1H, dd, J = 8.2, 2.6 Hz), 2.25 – 2.24 (6H, m). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 157.3, 154.5, 138.5, 132.7, 132.3, 130.9, 120.7, 120.0, 116.7, 115.1, 20.1, 19.2. Anal. Calcd. for $C_{14}H_{13}OBr$: C, 60.67; H, 4.73. Found: C, 60.62; H, 4.76.

1-(4-Bromophenoxy)-2,4-dimethylbenzene(4c). Following the general procedure *m*-xylene **1c** (62 μL, 0.50 mmol) was converted into **4c**. Purification of the crude product by column chromatography (Biotage M+12) using light petroleum ether as a mobile phase afforded product as a colorless oil (103 mg in the 1st run and 96 mg in the 2nd run, 74% and 69% yield, respectively); analytical TLC on silica gel, light petroleum ether, R_f=0.42. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39 – 7.35 (2H, m), 7.08 – 7.06 (1H, m), 7.01 – 6.97 (1H, m), 6.84 – 6.80 (1H, m), 6.78 – 6.73 (2H, m), 2.33 (3H, s), 2.16 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 157.7, 151.6, 134.3, 132.6, 132.4, 130.1, 128.0, 120.4, 118.5, 114.3, 20.9, 16.2. Anal. Calcd. for $C_{14}H_{13}OBr$: C, 60.67; H, 4.73. Found: C, 61.03; H, 4.81.

4-Bromophenyl 5,6,7,8-tetrahydronaphthalen-2-yl ether (4d). Following the general procedure tetraline **1d** (68 μL, 0.50 mmol) was converted into **4d**. Purification of the crude product by column chromatography (Biotage M+12) using light petroleum ether as a mobile phase afforded product as a colorless oil (70 mg in the 1st run and 83 mg in the 2nd run, 46% and 55% yield, respectively); analytical TLC on silica gel, light petroleum ether, R_f=0.29. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.42 – 7.38 (2H, m), 7.04 (1H, d, J = 8.2 Hz), 6.89 – 6.84 (2H, m), 6.75 (1H, dd, J=8.2, 2.6 Hz), 6.72 (1H, d, J = 2.6 Hz), 2.78 – 2.71 (1H, m), 1.82 – 1.77 (4H, m). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 157.3, 154.2 139.0, 132.9, 132.7, 130.5, 120.1,

119.6, 116.8, 115.1, 29.7, 28.9, 23.4, 23.1. Anal. Calcd. for $C_{16}H_{15}OBr$: C, 63.38; H, 4.99. Found: C, 63.42; H, 4.97.

1-Bromo-4-[4-(prop-2-en-1-yloxy)phenoxy]benzene (4f).[34] Following the general procedure *O*-allyl ether **1f** (68 μL, 0.50 mmol) was converted into **4f**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 5% EtOAc in light petroleum ether to 25% EtOAc in light petroleum ether afforded product as a white powder (109 mg in the 1st run and 111 mg in the 2nd run, 72% and 73% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.42. Pure material was obtained by crystallization from petroleum ether: mp 58–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.43 – 7.35 (2H, m), 6.99 – 6.87 (4H, m), 6.86 – 6.78 (2H, m), 6.06 (1H, ddt, *J* = 17.2, 10.5, 5.3 Hz), 5.42 (1H, dq, *J* = 17.3, 1.6 Hz), 5.30 (1H, dq, *J* = 10.5, 1.4 Hz), 4.53 (2H, dt, *J* = 5.3, 1.5 Hz).

1-(Benzyloxy)-4-(4-bromophenoxy)benzene (4g).[35] Following the general procedure *O*-benzyl ether **1g** (92 mg, 0.50 mmol) was converted into **4g**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 5% EtOAc in light petroleum ether to 25% EtOAc in light petroleum ether afforded product as a white powder (135 mg in the 1st run and 140 mg in the 2nd run, 76% and 79% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.35. Pure material was obtained by crystallization from petroleum ether: mp 109–110 °C.^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.46 – 7.33 (7H, m), 6.96 (4H, s), 6.86 – 6.80 (2H, m), 5.06 (2H, s).

[4-(4-Bromophenoxy)phenoxy](*tert*-butyl)dimethylsilane (4h). Following the general procedure *O*-TBDMS phenol **1h**[36] (105 mg, 0.50 mmol) was converted into **4h**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 10% EtOAc in light petroleum ether afforded product as a colorless oil (125 mg in the 1st run and 131 mg in the 2nd run, 66% and 69% yield, respectively); analytical TLC on silica gel, light petroleum ether, R_f=0.25.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41 – 7.37 (2H, m), 6.91 – 6.87 (2H, m), 6.84 – 6.80 (4H, m), 0.99 (9H, s), 0.21 (6H, s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 157.8, 152.2, 150.3, 132.6, 121.2, 120.8, 119.5, 114.9,

25.8, 18.3, -4.3. Anal. Calcd. for $C_{18}H_{23}O_2BrSi$: C, 56.99; H, 6.11. Found: C, 56.98; H, 6.10.

2-Bromo-4-(4-bromophenoxy)-1-methoxybenzene (4i). Following the general procedure 2-bromoanisole **1i** (62 μL, 0.50 mmol) was converted into **4i**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 10% EtOAc in light petroleum ether afforded product as a white powder (125 mg in the 1st run and 109 mg in the 2nd run, 70% and 61% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.50. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 69–70 °C.^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 – 7.39 (2H, m), 7.25 (1H, d, J = 2.8 Hz), 6.96 (1H, dd, J = 8.9, 2.8 Hz), 6.88 (1H, d, J = 8.9 Hz), 6.86 – 6.81 (2H, m), 3.89 (3H, s).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 157.2, 152.8, 150.2, 132.8, 124.9, 119.7, 119.5, 115.6, 112.7, 112.2, 56.8. Anal. Calcd. for $C_{13}H_{10}O_2Br_2$: C, 43.61; H, 2.82. Found: C, 43.54; H, 2.72.

5-(4-Bromophenoxy)-2,3-dihydro-1-benzofuran (4j). Following the general procedure dihydrobenzofuran **1j** (56 μL, 0.50 mmol) was converted into **4j**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 10% EtOAc in light petroleum ether afforded product as a white powder (70 mg in the 1st run and 95 mg in the 2nd run, 48% and 65% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.42. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 54–55 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40 – 7.36 (2H, m), 6.90 – 6.87 (1H, m), 6.83 – 6.79 (2H, m), 6.79 – 6.76 (1H, m), 6.74 (1H, d, J=8.5 Hz), 4.59 (2H, t, J = 8.7 Hz), 3.20 (2H, t, J = 8.7 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 158.3, 156.8, 149.7, 132.6, 128.7, 119.7, 119.1, 117.3, 114.6, 109.8, 71.7, 30.2. Anal. Calcd. for $C_{14}H_{11}O_2Br$: C, 57.76; H, 3.81. Found: C, 57.59; H, 3.72.

2-[5-(4-Bromophenoxy)-2-methoxyphenyl]-4,4,5,5-tetramethyl-1,3,2-dioxa borolane (4k). Following the general procedure pinacolyl boronate **1k**[37] (117 mg, 0.50 mmol) was converted into **4k**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 5% EtOAc in light

petroleum ether to 25% EtOAc in light petroleum ether afforded product as a white powder (142 mg in the 1st run and 122 mg in the 2nd run, 70% and 60% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.10. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40 – 7.33 (3H, m), 7.05 (1H, dd, J = 8.9, 3.1 Hz), 6.84 (1H, d, J = 8.9 Hz), 6.82 – 6.77 (2H, m), 3.83 (3H, s), 1.34 (12H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 161.0, 158.2, 149.0, 132.6, 128.2, 124.1, 119.0, 114.5, 112.0, 83.9, 56.6, 25.0. Anal. Calcd. for $C_{19}H_{22}O_4BBr$: C, 56.33; H, 5.47. Found: C, 56.37; H, 5.45.

1-(4-Bromophenoxy)-2,4-dimethoxybenzene (4l). Following the general procedure resorcinol dimethyl ether **1l** (65 µL, 0.50 mmol) was converted into **4l**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 20% EtOAc in light petroleum ether afforded product as a colorless oil (80 mg in the 1st run and 88 mg in the 2nd run, 52% and 57% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.33. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 – 7.32 (2H, m), 6.95 (1H, d, J = 8.7 Hz), 6.78 – 6.74 (2H, m), 6.58 (1H, d, J = 2.8 Hz), 6.46 (1H, dd, J = 8.7, 2.8 Hz), 3.82 (3H, s), 3.77 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 158.3, 157.8, 152.6, 137.8, 132.4, 122.6, 117.8, 114.1, 104.4, 100.8, 56.1, 55.8. Anal. Calcd. for $C_{14}H_{13}O_3Br$: C, 54.39; H, 4.24. Found: C, 54.24; H, 4.18.

2-(4-Bromophenoxy)-3,5-dimethoxy-*N*-methylbenzamide (4m). Following the general procedure 3,5-dimethoxy-*N*-methylbenzamide (**1m**)[8a] (97 mg, 0.50 mmol) was converted into **4m**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% CH_2Cl_2 to 10% diethyl ether in CH_2Cl_2 afforded product as a white powder (51 mg in the 1st run and 49 mg in the 2nd run, 28% and 27% yield, respectively); analytical TLC on silica gel, 1:10 diethyl ether/CH_2Cl_2, R_f=0.31. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 116–117 °C. IR (film, cm^{-1}) 3324 (N-H), 1638 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 – 7.32 (2H, m), 7.23 (1H, d, J = 3.0 Hz), 7.21 – 7.15 (1H, m), 6.74 – 6.69 (2H, m), 6.65 (1H, d, J = 3.0 Hz), 3.86 (3H, s), 3.68 (3H, s), 2.88 (3H, d, J = 4.9 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 165.2, 157.6,

157.1, 153.0, 135.1, 132.7, 128.6, 117.0, 115.1, 104.8, 104.2, 56.3, 55.9, 27.0. HRMS-ESI (m/z) calcd for $C_{16}H_{17}NO_4Br$ $[M+H]^+$ 366.0341, found 366.0354.

3-Methyl-2-(4-nitrophenoxy)thiophene (4n). Following the general procedure methylthiophene **1n** (48 μL, 0.50 mmol) was converted into **4n**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 100% light petroleum ether to 15% EtOAc in light petroleum ether afforded product as a pale yellow powder (59 mg in the 1st run and 59 mg in the 2nd run, 50% and 50% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.32. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 69–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.23 – 8.19 (2H, m), 7.08 – 7.03 (2H, m), 6.90 (1H, d, *J*=5.9 Hz), 6.77 (1H, d, *J*=5.9 Hz), 2.02 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 163.8, 150.4, 143.1, 128.1, 126.1, 125.6, 117.5, 115.9, 11.8. HRMS-ESI (m/z) calcd for $C_{11}H_{10}NO_3S$ $[M+H]^+$ 236.0381, found 236.0388.

Ethyl 5-bromo-1-methyl-3-(4-nitrophenoxy)-1*H*-indole-2-carboxylate (4o). Following the general procedure indole **1o**[8a] (141 mg, 0.50 mmol) was converted into **4o**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 5% EtOAc in light petroleum ether to 25% EtOAc in light petroleum ether afforded product as a pale yellow powder (140 mg in the 1st run and 155 mg in the 2nd run, 67% and 74% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.17. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 151–152 °C. IR (film, cm^{-1}) 1717 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.22 – 8.16 (2H, m), 7.61 (1H, dd, *J* = 1.9, 0.4 Hz), 7.48 (1H, dd, *J* = 9.0, 1.9 Hz), 7.33 (1H, dd, *J* = 9.0, 0.4 Hz), 7.03 – 6.97 (2H, m), 4.20 (2H, q, *J* = 7.1 Hz), 4.07 (3H, s), 1.05 (3H, t, *J* = 7.1 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 164.1, 160.7, 142.7, 135.9, 135.3, 129.5, 126.0, 121.6, 120.7, 119.2, 115.5, 114.5, 112.3, 61.1, 32.2, 14.0. Anal. Calcd. for $C_{18}H_{15}N_2O_5Br$: C, 51.57; H, 3.61; N, 6.68. Found: C, 51.36; H, 3.52; N, 6.55.

5-Bromo-1-methyl-3-(4-nitrophenoxy)-1*H*-indole-2-carbonitrile (4p). Following the general procedure 2-cyanoindole **1p**[38] (118 mg, 0.50 mmol) was converted into **4p**. Purification of the crude product by column chromatography (Biotage M+12)

using gradient elution from 15% EtOAc in light petroleum ether to 45% EtOAc in light petroleum ether afforded product as a pale yellow powder (100 mg in the 1st run and 95 mg in the 2nd run, 54% and 51% yield, respectively); analytical TLC on silica gel, 1:5 EtOAc/light petroleum ether, R_f=0.16. Pure material was obtained by crystallization from EtOAc/petroleum ether: mp 202–203 °C. IR (film, cm^{-1}) 2220 (C≡N). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.25 – 8.22 (2H, m), 7.53 (1H, dd, *J* = 8.9, 1.9 Hz), 7.48 (1H, dd, *J* = 1.9, 0.6 Hz), 7.29 (1H, dd, *J* = 9.0, 0.5 Hz), 7.12 – 7.09 (2H, m), 3.90 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 162.4, 143.6, 139.6, 135.0, 130.4, 126.3, 121.7, 119.6, 116.3, 115.3, 112.4, 110.7, 103.1, 32.1. Anal. Calcd. for $C_{16}H_{10}N_3O_3Br$: C, 51.64; H, 2.71; N, 11.29. Found: C, 51.55; H, 2.72; N, 10.96.

Methyl 1-methyl-5-(4-nitrophenoxy)-1*H*-pyrrole-2-carboxylate (4q). Following the general procedure methyl 1*H*-pyrrole **1q** (70 mg, 0.50 mmol) was converted into **4q**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 10% EtOAc in light petroleum ether to 30% EtOAc in light petroleum ether afforded product as a pale yellow powder (68 mg in the 1st run and 68 mg in the 2nd run, 49% and 49% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.16. Pure material was obtained by crystallization from diethyl ether /petroleum ether: mp 135–136 °C. IR (film, cm^{-1}) 1716 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 – 8.15 (2H, m), 7.09 – 7.05 (2H, m), 6.69 – 6.67 (2H, m), 3.94 (3H, s), 3.82 (3H, s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm) δ 164.3, 161.3, 142.6, 139.1, 126.0, 120.7, 119.7, 116.0, 109.1, 51.5, 37.2. HRMS-ESI (m/z) calcd for $C_{13}H_{13}N_2O_5$ $[M+H]^+$ 277.0824, found 277.0819.

Methyl 1-(2-bromobenzyl)-2,5-dimethyl-4-(4-nitrophenoxy)-1*H*-pyrrole-3-carboxylate (4r). Following the general procedure 1*H*-pyrrole **1r**[39] (161 mg, 0.50 mmol) was converted into **4r**. Purification of the crude product by column chromatography (Biotage M+12) using gradient elution from 10% EtOAc in light petroleum ether to 30% EtOAc in light petroleum ether afforded product as a pale yellow powder (92 mg in the 1st run and 106 mg in the 2nd run, 40% and 46% yield, respectively); analytical TLC on silica gel, 1:10 EtOAc/light petroleum ether, R_f=0.16. Pure material was obtained by crystallization from diethyl ether/petroleum ether: mp 159–160 °C. IR (film, cm^{-1}) 1700 (C=O). ^{1}H NMR (400 MHz, $CDCl_3$, ppm)

δ 8.21 – 8.16 (2H, m), 7.61 (1H, dd, *J* = 7.8, 1.3 Hz), 7.26 (1H, td, *J* = 7.6, 1.2 Hz), 7.19 (1H, td, *J* = 7.7, 1.7 Hz), 7.02 – 6.97 (2H, m), 6.37 – 6.33 (1H, m), 5.08 (2H, s), 3.57 (3H, s), 2.46 (3H, s), 1.96 (3H, s). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, ppm) δ 164.9, 164.3, 142.2, 135.53, 135.47, 134.3, 133.1, 129.5, 128.4, 126.4, 125.9, 121.7, 119.1, 115.3, 104.6, 50.9, 47.7, 11.3, 8.2. HRMS-ESI (m/z) calcd for $C_{21}H_{20}N_2O_5Br$ $[M+H]^+$ 459.0556, found 459.0551.

Associated Content

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Notes

The authors declare no competing financial interest.

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Supporting Information

^{1}H and ^{13}C spectra, X-ray crystallographic data for λ^3-iodane **20** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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