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Graphical Abstract

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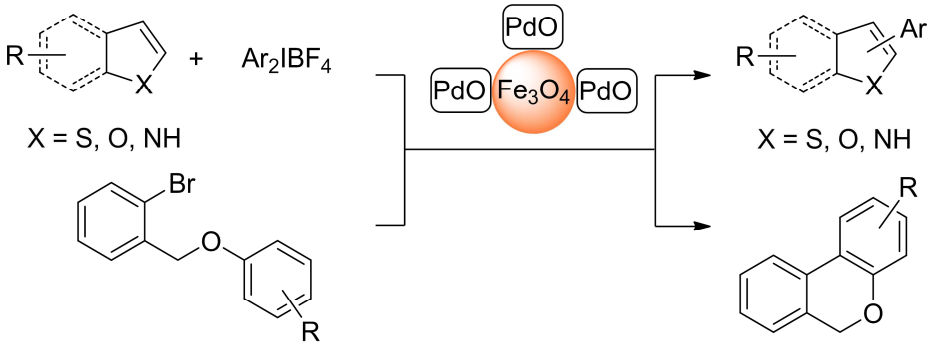

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Impregnated palladium on magnetite as catalyst for direct arylation of heterocycles

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ABSTRACT

Palladium impregnated on magnetite is an efficient, cheap and easy to prepare catalyst for the direct arylation of heterocycles. Good yields are afforded under relatively mild conditions and a broad substrate scope is evident. The catalyst is regioselective in many cases, affording arylated products, at the C2- or C3-position (depending of the heterocycle used). The methodology can be extended to prepare chromenes through an intramolecular direct arylation reaction. Some evidence is provided for two catalyst deactivation pathways, which prevents efficient recycling.

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1. Introduction

The formation of aryl-aryl (Ar-Ar') bonds and heteroaryl (Ar-Het and Het-Het') analogues is an important transformation in organic synthesis due to number of compounds containing these moieties in the pharmaceutical and other industries.[1] Traditional methods[2] for the introduction of the Ar-Ar' bond (e.g. Suzuki-Miyaura, Stille, Negishi and other named reactions) suffer from drawbacks as they require the installation of activating groups on both coupling partners. The associated waste (B, Sn, Zn-based) is also a major problem for the pharmaceutical and other industries. A modern, efficient and environmentally friendly alternative is termed Direct Arylation (DA).[3] Through catalytic C–H activation,[4] DA avoids the preactivation steps, establishing a convenient pathway to arylated compounds in terms of atom economy and environmental impact.[5]

In the last decade a broad number of catalytic systems have been used for the DA of heterocycles.[6] However, most of these methodologies are based on homogeneous catalysis and harsh reaction conditions. Homogeneous catalysis suffers from a number of drawbacks. Deactivation because of metal aggregation and precipitation[7] and separation of the catalyst from the API product[8] seriously impede scale-up of many potentially useful transformations. Heterogeneous catalysis[9] on the other hand, offers a more attractive approach. Heterogeneous catalysts possesses good thermal stability and can usually be removed from the reaction media and can, in principle, be recycled.

Recently notable progress has been made in the search for heterogeneous systems for DA.[10] Palladium has been the most employed transition-metal to accomplish this transformation. Examples include Pd supported on zeolite,[11] modified silica,[12] metal organic frameworks,[13] carbon[14] and mesocellular foam.[15] Pd has been incorporated within a bimetallic heterodimer with magnetite using thermal decomposition.[16] Discerning whether the catalyst behaves in a homogeneous or heterogeneous manner is difficult and complex.[10] In many cases, heterogeneous catalyst precursors are used, but leaching to homogeneous species[17] (e.g. soluble nanoparticles) is likely, although both Glorius[14b] and Bäckvall[15] have provided good evidence for a heterogeneous pathway in Pd-catalysed DA reactions in their systems. However in both cases recycling of the catalyst was not possible (Pd/C and PD/mesocellular foam respectively). Other heterogeneous systems used are based on copper,[18] nickel[19] and TiO_2.[20] Even a transition-metal-free arylation methodology has been reported with similar overall objectives.[21]

As part of our ongoing project on the use of magnetite[22] and impregnated-metal magnetite[23] as catalysts for organic synthesis, we report here a simple, versatile and easy to recover catalyst for the direct arylation of heterocycles and other aryls under relatively mild reaction conditions.

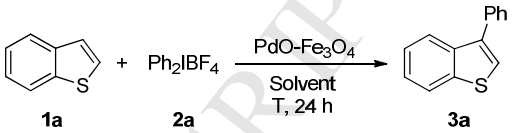
2. Results and discussion

2.1. Direct arylation of heterocycles

The supported catalyst was prepared as previously published.[23c] We chose the arylation of benzothiophene (**1a**) using diphenyliodonium tetrafluoroborate (**2a**) as a model reaction (Table 1). Our first attempt gave the corresponding arylated heterocycle (**3a**) after 24h. Arylation occurred selectively at C3 but in a low yield (entry 1). Increasing the equivalents of **2a** achieved a small increase in yield (entries 2 and 3). A reduction of palladium loading (3 mol%) gave a lower conversion (entry 4) and an increase (10 mol%) improved the yield (entry 5). With the optimised catalyst loading in hand, the iodonium salt was modified (entry 6). The yield of **3a** was increased to 62% with the addition of 3 equivalents of the salt. The temperature effect was evaluated at this point. Increasing the temperature to 100 ºC only gave a slightly higher yield (entry 7). However the best yield was obtained at 60 ºC (entry 8). Unfortunately, it was not possible to reduce the temperature without a significant reduction in yield (entries 9 and 10). The impact of the solvent was evaluated (entries 11–13). The reaction failed in dioxane, water and toluene. Finally, with the best conditions in hand a reaction was performed in the absence of catalyst (entry 14). Only starting material was recovered, confirming the catalytic role of the palladium on magnetite.

Table 1

Optimization of the reaction conditions[a]



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

Entry	**2a** (mol%)	Solvent	T (º C)	Pd (mol%)	Yield (%)[b]
1	110	EtOH	80	6	22
2	220	EtOH	80	6	45
3	300	EtOH	80	6	31
4	220	EtOH	80	3	11
5	220	EtOH	80	10	59
6	300	EtOH	80	10	62
7	300	EtOH	100	10	65
8	**300**	**EtOH**	**60**	**10**	**71**
9	300	EtOH	40	10	39
10	300	EtOH	25	10	0
11	300	Dioxane	60	10	0
12	300	H_2O	60	10	0
13	300	PhMe	60	10	0
14[c]	300	EtOH	60	0	0

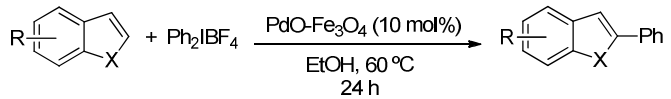
[a] Reaction carried out using compound **1a** (0.5 mmol), **2a** (0.6 mmol), in 1.5 mL of solvent, unless otherwise stated. [b] Isolated yield after column chromatography. [c] Reaction performed in absence of catalyst.

Once the best reaction conditions were found for this process, a number of impregnated metal catalysts were tested (see SI). Only the palladium on magnetite showed high activity. However, the bimetallic palladium-copper catalyst did give a small amount of arylated product. Finally the reaction was also performed using Pd-free magnetite nanoparticles (see SI) to confirm the role of Pd. No product was observed.

The optimised protocol was then applied to other prominent heterocycles. When benzofuran was used as substrate, the arylated product was isolated in an excellent yield of 99% (entry 1). The reaction was completely regioselective for the C2 position. Indoles containing electron withdrawing substituents coupled well (entries 2-4), affording the arylated products in yields from 58-83% and no issues were apparent with these compounds bearing free NH groups. For all the indoles tried, the arylation took place at the C-2 position selectively.

Table 2

Substrate scope: arylation of different heterocycles[a]



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

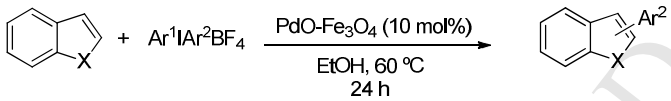
Entry	X	R	Product	Yield (%)[b]
1	O	H	**3b**	99
2	NH	7-CO_2Me	**3c**	83
3	NH	5-F	**3d**	79
4	NH	4-Br	**3e**	58

[a] Reaction carried out using the corresponding heterocycle **1** (0.5 mmol), **2a** (1.5 mmol), in 1.5 mL of EtOH. [b] Isolated yield after column chromatography.

The use of other iodonium salts was also studied (Table 3). Chemoselective arylation could be performed by introducing one non-transferable aryl group such as 2,3,5-triisopropylphenyl (TRIP).[14b, 15] Using this approach, an arylated benzothiophene was isolated in low yield (entry 1, 38%). Better yields (66 and 71%) were obtained using benzofuran and methyl phenyl groups (entries 2 and 3). An electron poor aryl group was also shown to work reasonably well (55% yield, entry 4). Finally an electron rich aryl group was transferred in 84% yield, this time using a symmetrical iodonium salt (entry 5). The catalyst facilitated excellent regioselectivity in all the cases (arylation of benzofuran at C2-position and thiophene at C3).

Table 3

Substrate scope: use of different diaryliodonium salts[a]



1 **2** **3**

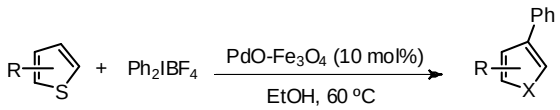
Entry	X	Ar^1	Ar^2	Ar^2 position	Product	Yield (%)[b]
1	S	TRIP	4-MeC_6H_4	C3	**3f**	38
2	O	TRIP	4-MeC_6H_4	C2	**3g**	71
3	O	TRIP	2-MeC_6H_4	C2	**3h**	66
4	O	TRIP	4-ClC_6H_4	C2	**3i**	55
5	O	4-$MeOC_6H_4$	4-$MeOC_6H_4$	C2	**3j**	84

[a] Reaction carried out using the corresponding heterocycle **1** (0.5 mmol), **2** (1.5 mmol), in 1.5 mL of EtOH. [b] Isolated yield after column chromatography.

The protocol was then extended to the arylation of simple thiophenes under the same conditions (Table 4). Using thiophenes, the process was not as high yielding or selective as with previous substrates and a mixture of the mono- and diarylated heterocycles was obtained in 39% overall yield (entry 1). With 2-bromothiophene, only 18% of the mono-arylated heteocycle was recovered (entry 2). Better yield was obtained with the 3-bromothiophene (entry 3). In both cases the bromine remained intact, allowing for further functionalisation. Finally, 2,2'-bithiophene gave the corresponding monoarylated product selectively in 48% yield (entry 4).

Table 4

Substrate scope: arylation of tiophenes[a]



4 **2a** **5**

Entry	R	Product	Yield (%)
1	H	**5a**	39
2	2-Br	**5b**	18
3	3-Br	**5c**	51
4		**5d**	48

[a] Reaction carried out using the corresponding heterocycle **4** (0.5 mmol), **2a** (1.5 mmol), in 1.5 mL of EtOH. [b] Isolated yield after column chromatography.

Once the substrate scope was evaluated, the recyclability of the catalyst was tested. After a standard reaction using benzofuran as heterocycle, the catalyst was retained in the reaction vessel using a magnet and washed several times with ethanol. The vessel was then charged with a new set of reagents and the standard conditions applied. The corresponding product **3b** was obtained in 49% yield after the second cycle and 18% after the third. These results show deactivation of the catalyst. While others have shown that heterogeneous catalysis and recyclability can prove mutually exclusive, no examination of the reasons for deactivation have been proposed in these systems.

We thus sought to examine the catalyst structure before and after the reaction. Transmission electron microscopy (TEM) analysis showed that pre- and post-reaction particles displayed a similar appearance. Also no sinterization of the particles could be observed post-reaction. Additionally both pre- and post-reaction particles showed an identical particle-size distribution. X-ray photoelectron spectroscopy (XPS) analysis of the catalyst did not show any change in oxidation state of the palladium on the magnetite surface. The XPS spectra of the post-reaction sample showed, after deconvolution, two peaks at 337.0 and 342.1 eV, which correspond to the binding energies of PdO $3d_{5/2}$ and PdO $3d_{3/2}$ respectively. The spectra is identical to that taken of the catalyst pre-reaction (See SI). Thus we cannot attribute deactivation of the catalyst to an oxidation change at the surface.[24]

We then hypothesised that leaching of the Pd from the support might be occurring, rendering the insoluble catalyst framework inactive, when reused. The phenomenon of leaching was studied by inductively coupled plasma mass spectrometry (ICP-MS). Here, the reaction mixture was filtered hot after the reaction and the homogeneous solution was tested by dissolved Pd. Only 1.96% of the initial amount of palladium was detected. This amount seems insufficient to explain the deactivation given the lower turnover numbers observed when lower Pd loading was used (Table 1). The inability of the solution phase to catalyse the arylation of benzofuan was confirmed by observation of the reaction progress after filtration. Thus after two hours, the catalyst was filtered hot. No reaction progress was observed after this point confirming that no active species were solubilised under the reaction conditions. The above tests point strongly to heterogeneous catalysis, in line with the conclusion made by Glorius is his arylation of 2-butylthiophene.[14b]

Clearly, if leaching is ruled out, some change at the surface must occur which deactivates the catalyst.[25] X-ray fluorescence

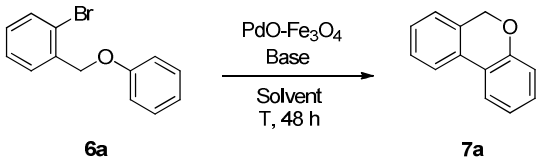
(XRF) was then used to gain further insight at the catalyst surface. More specifically, 5.4% of iodine was detected at the catalyst surface. The adsorbance of halides on the surface of Pd catalysts has previously been shown to affect the activity of heterogeneous catalysts and we believe this to be this case here also.[26]

2.2. Intramolecular direct arylation

Encouraged by the success that we obtained in the direct arylation of heterocycles, we decided to apply palladium on magnetite to an intramolecular arylation.[6d,27] A different mechanism is operative here and thus application to this reaction would give a good indication of the broad utility of the catalyst. We chose the intramolecular arylation of haloether **6a** to obtain the corresponding chromene **7a** (Table 5) as a suitable reaction.

Table 5

Optimization of the reaction conditions for intramolecular direct arylation[a]



6a **7a**

Entry	Base (mol%)	Solvent	T (° C)	Pd (mol%)	Yield (%)[b]
1	KOAc (200)	DMA	140	0.1	5
2	KOAc (200)	DMA	140	1	9
3	KOAc (200)	DMA	140	2	20
4	KOAc (200)	DMA	140	5	61
5	**KOAc (200)**	**DMA**	**140**	**10**	**85**
6	KOAc (200)	DMA	140	15	77
7	KOAc (100)	DMA	140	10	64
8	KOAc (300)	DMA	140	10	71
9	KOH (200)	DMA	140	10	5
10	NaOH (200)	DMA	140	10	0
11	NaOAc (200)	DMA	140	10	56
12	K_2CO_3 (200)	DMA	140	10	0
13	KOAc (200)	PhMe	140	10	0
14	KOAc (200)	DMF	140	10	74
15	KOAc (200)	*t*BuOH	140	10	25
16	KOAc (200)	DMA	160	10	75
17	KOAc (200)	DMA	120	10	63
18[c]	KOAc (200)	DMA	140	0	0

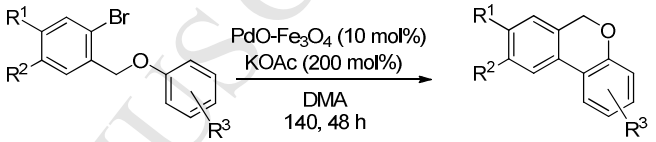
[a] Reaction carried out using compound **6a** (0.5 mmol), KOAc (1 mmol), in 2 mL of solvent, unless otherwise stated. [b] Isolated yield after column chromatography. [c] Reaction performed in absence of catalyst.

Firstly, the optimum catalyst loading was established (entry 1–6). Again 10 mol% of Pd was needed to obtain the best chemical yield of 85% (entry 5). Then the effect of the base was tested (entries 7–12). When 1 equivalent of base was used the yield of **7a** was reduced to 64% (entry 7). The addition of 3 equivalents was not beneficial for the cyclisation process (entry 8). Different bases were tried, but none were as efficient as KOAc (entries 9–12). The impact of the solvent was studied (entries 13–15). Only DMF gave a comparable yield (74%), but was slightly lower to the one obtained with *N*,*N*-dimethylacetamide (DMA). Finally the temperature was modified. Neither a higher, nor lower temperature gave better yields (entries 16 and 17). As a control test, the reaction was performed in the absence of catalyst under the optimised conditions (entry 18). Only starting material was recovered confirming the role of palladium in this process.

The best reaction conditions were then applied to different substrates to evaluate the reaction scope (Table 6). First we studied the tolerance of substituents on the phenoxy group. The presence of a methoxy group was tolerated with only a small detriment in yield (entry 2). Good yield was obtained with a methyl group at the 4-position of the ring (entry 3). The introduction of electron-withdrawing groups had a beneficial effect on the process, and excellent yields were achieved (93 and 92%, entries 4 and 5). Then the effect of substitution on the phenoxy group was evaluated. Similarly good results were obtained using electron-withdrawing groups (87-92%, entries 5-7), although a mixture of regioisomers was obtained when a *meta*-F substituent was present. Little impact on the yields was observed on substitution of the halo-aryl either, and very good yields were observed (84 and 77%, entries 8 and 9).

Table 6

Substrate scope for intramolecular direct arylation[a]



6 **7**

Entry	R^1	R^2	R^3	Product	Yield (%)[b]
1	H	H	H	**7a**	85
2	H	H	4-MeO	**7b**	75
3	H	H	4-Me	**7c**	86
4	H	H	4-Cl	**7d**	93
5	H	H	4-F	**7e**	92
6	H	H	3-F	**7f**	89[c]
7	H	H	2-F	**7g**	87
8	H	CF_3	H	**7h**	84
9	F	H	H	**7i**	77

[a] Reaction carried out using compound **6** (0.5 mmol), KOAc (1 mmol), in 2 mL of DMA. [b] Isolated yield after column chromatography. [c] A mixture of isomers was obtained: 1-Fluoro-6*H*-benzo[*c*]chromene (**7f**) and 3-Fluoro-6*H*-benzo[*c*]chromene (**7f'**) (45:55).

The recyclability of the catalyst was also investigated in this case also. In a similar way to the intermolecular reaction, the catalyst was removed using a magnet and reused using the standard conditions (as in Table 5, entry 5). Again deactivation of the catalyst was observed. This time no product was detected after the second cycle of reaction. ICP-MS analysis of the reaction solution showed 3.3% of the Pd has leached. Post-reaction TEM analysis revealed substantial sintering of palladium nanoparticles had occurred (See SI for particle distribution). XPS analysis also showed a distinctive change and four peaks were observed. Two peaks at 336.9 and 342.2 eV, correspond to the binding energies of PdO $3d_{5/2}$ and PdO $3d_{3/2}$ respectively. The two other peaks at 334.9 and 340.1 eV, correspond to the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ respectively. The ratio between the two oxidation states was Pd:PdO 2:1. Clearly some reduction of the PdO species had occurred perhaps forming inactive Pd-black aggregates. The hot filtration test determined that no reaction progress occurred after filtration. Thus, we believe that changes in the oxidation state of Pd during the reaction renders

the recovered Pd/magnetite unable to catalyse subsequent reactions.

3. Conclusion

In conclusion, we have demonstrated that palladium impregnated on magnetite is a cheap, selective and versatile catalyst for the direct arylation of heterocycles under mild conditions. The process can be applied to a number of substrate and reaction types. In addition, the magnetic properties of the catalyst allow its separation from the reaction media very easily. Decreased yields are observed on reuse of the catalysts in the intermolecular arylation of heterocycles using iodonium salts and no reuse is possible in the intramolecular arylation reactions tested using aryl halides. Preliminary studies suggest that halide ligation to the Pd surface may inhibit subsequent reaction when using iodonium salts. In intramolecular DA reactions using aryl halides, substantial changes to the Pd particle distribution and size are observed. A change in oxidation state of the Pd may also be a cause of inhibition. These dramatic changes in the nature of the catalyst are inevitable considering the conditions required (140 ºC in DMA). Work is ongoing to utilise the insights gathered here to allow for full and convenient recycling of Pd/magnetite.

4. Experimental section

4.1. General information

Solvents and reagents were used as obtained from commercial sources and without purification. ^{1}H NMR (400 MHz) spectra and ^{1}H NMR (300 MHz) spectra were recorded on Bruker Avance 400 and Bruker Avance 300 NMR spectrometers respectively in proton coupled mode. ^{13}C NMR (150 MHz) spectra and ^{13}C NMR (75.5 MHz) spectra were recorded on Bruker Avance 400 and Bruker Avance 300 NMR spectrometers respectively in proton decoupled mode at 20 °C in deuterated chloroform using tetramethysilane as internal standard; chemical shifts are given in δ (parts per million) and coupling constants (*J*) in Hertz Low-resolution mass spectra were recorded on a Waters Quattro Micro triple quadropole instrument in electrospray ionisation (ESI) mode using 50% acetonitrile-water containing 0.1% formic acid as eluent; samples were made up in acetonitrile. High resolution precise mass spectra (HRMS) were recorded on a Waters LCT Premier Tof LC-MS instrument in electrospray ionisation (ESI) mode using 50% acetonitrile-water containing 0.1% formic acid as eluent; samples were made up in acetonitrile. Infrared spectra were measured as pressed potassium bromide (KBr) for solids or thin films on sodium chloride plates for liquids on a Perkin-Elmer FT-IR spectrometer. Melting points were obtained with a Reichert Thermovar apparatus. XPS analyses were carried out on a VG-Microtech Mutilab. XRD analyses were obtained on a BRUKER D-8 ADVANCE diffractometer with Göebel mirror, with a high temperature chamber (up to 900ºC), with a X-ray generator KRISTALLOFLEX K 760-80F (3KW, 20-60KV and 5-80mA). TEM images were obtained on a JEOL, model JEM-2010 equipped with an X-ray detector OXFORD INCA Energy TEM 100 for microanalysis (EDS). XRF analyses were obtained on a PHILIPS MAGIX PRO (PW2400) X-ray spectrometer equipped with a rhodium X-ray tube and a beryllium window. BET isotherms were carried out on a AUTOSORB-6 (Quantachrome), using N_2. The chromatographic analyses (GLC) were determined with a Hewlett Packard HP-5890 instrument equipped with a flame ionization detector and 12 m HP-1 capillary column (0.2 mm diam, 0.33 mm film thickness, OV-1 stationary phase), using nitrogen (2 mL/min) as a carrier gas, $T_{injector}$ = 275 ºC, $T_{detector}$ = 300ºC, T_{column} = 60ºC (3 min) and 60-270 ºC (15 ºC/min), P = 40 kPa. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light, staining with phosphomolybdic acid [25 g phosphomolybdic acid, 10 g $Ce(SO_4)_2$ 4 H_2O, 60 mL of concentrated H_2SO_4 and 940 mL H_2O]. Column chromatography was performed using silica gel 60 of 40-63 mesh. The ICP-MS analyses were carried out on a Thermo Elemental VGPQ-ExCell spectrometer.

4.2. General procedure for the preparation of impregnated palladium on magnetite catalyst.

To a stirred solution of $PdCl_2$ (177 mg, 1 mmol), KCl (1 g, 13 mmol, to increase the palladium solubility) in deionized water (120 mL) was added Fe_3O_4 (4 g, 17 mmol, powder <5 mm, BET area: 9.86 m^2/g). After 10 min at room temperature, the mixture was slowly basified with NaOH (1 M) until pH around 13. The mixture was stirred during 1 day at room temperature in air. After that, the catalyst was filtered and washed with deionized water (3 x 10 mL). The solid was dried at 100 ºC during 24 h in a standard glassware oven, obtaining the expected catalyst: incorporation of palladium of 3.0% according to XRF; by XPS the palladium on the surface was determined as 24.8%; the BET area surface was 13.6 m^2/g.

4.3. General prodecure for the preparation of the diaryliodonium tetrafluoroborates

The diaryliodonium tetrafluoroborates were prepared following the procedures described by Olofsson et al.[28] and Gaunt et al.[29]

*4.3.1. Diphenyliodonium tetrafluoroborate (**2a**)[28].* *m*-CPBA (24 mmol, 5.120 g) was dissolved in CH_2Cl_2 (80 mL). To the solution was added iodobenzene (21.6 mmol, 2.48 mL) followed by slow addition of $BF_3{\cdot}OEt_2$ (54.4 mmol, 6.8 mL) at room temperature. The resulting yellow solution was stirred at room temperature for 30 min and then cooled to 0 ºC and $PhB(OH)_2$ (24 mmol, 2.960 g) was added. After 15 min of stirring at room temperature, the crude mixture was applied on a silica plug (20 g) and eluted with CH_2Cl_2 (2 x 100 mL) followed by CH_2Cl_2/MeOH (2 x 100 mL). The latter solution was concentrated and diethyl ether (40 mL) was added to the residue to induce precipitation. The solution was allowed to stir for 15 min, and then the solid was filtered and washed several times with diethyl ether and then dried in vacuo. White solid; yield 5.960 g (75 %); m.p. = 133-135ºC (Hexane); IR (KBr): ν 1559, 1471, 1443, 1287, 1167, 1053, 740 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO) δ: 7.54 (4H, t, J = 7.6 Hz), 7.68 (2H, t, J = 7.4 Hz), 8.25 (4H, d, J = 7.3 Hz). ^{13}C-NMR (75 MHz, DMSO) δ: 116.4 (2C), 131.7 (4C), 132.0 (2C), 135.1 (4C). ^{19}F NMR (282 MHz, DMSO): δ -148.2 (br. s), -148.3 (dd, J = 2.3, 1.2 Hz).

The appropriate iodoarene (5 mmol) was added to a stirred solution of *m*-CPBA (7.5 mmol, 1.6 g) in acetic anhydride (10 ml) and the solution was stirred for 1 h at room temperature after which 1,3,5-triisopropyl benzene (6.5 mmol, 1.32 mL) was added and the solution cooled to 0 ºC. Tetrafluoroboric acid (50% aqueous, 10 mmol, 1.25 mL) was added over 15 min *via* syringe pump and the solution stirred at 0 ºC for 30 min before being allowed to warm to rt. After 6 h the solution was recooled to 0 ºC and water (100 mL) was slowly added with fast stirring. The solution was extracted with CH_2Cl_2 (2 x 50 ml) and the combined organic extracts dried ($MgSO_4$) and evaporated. The pure iodonium tetrafluoroborate salts were precipitated with Et_2O from a concentrated solution of hot CH_2Cl_2 and obtained by

filtration followed by washed with generous amounts of Et_2O on the filter.

*4.3.2. p-Tolyl(2,4,6-trisopropylphenyl)iodonium tetrafluoroborate (**2b**).* White solid; yield 1.413 g (56 %); m.p. = 189-191ºC (Hexane); IR (KBr): ν 1585, 1571, 1480, 1463, 1057, 1023, 998, 985 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO) δ: 1.22 (18H, app. t, *J* = 6.8 Hz), 2.33 (3H, s), 2.97 (1H, hept, *J* = 6.8 Hz), 3.40 (2H, hept, *J* = 6.8 Hz), 7.30 (2H, s), 7.35 (2H, d, *J* = 8.2 Hz), 7.82 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (75 MHz, DMSO) δ: 20.7, 23.5 (2C), 24.0 (4C), 33.3, 38.6 (2C), 111.3, 123.2, 124.5 (2C), 132.5 (2C), 134.0 (2C), 142.2, 151.1 (2C), 154.1. ^{19}F NMR (282 MHz, DMSO): δ -148.3 (br. s), -148.3 (dd, *J* = 2.3, 1.2 Hz). HRMS calcd. (%) for $C_{22}H_{30}I$: 421.1387; found: 421.1368.

4.3.3. o-*Tolyl(2,4,6-trisiopropylphenyl)iodonium tetrafluoroborate (**2c**).* White solid; yield 1.573 g (31 %); m.p. = 154-155ºC (Hexane); IR (KBr): ν 1586, 1572, 1560, 1467, 1426, 1058, 979 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO) δ: 1.21 (18H, 2 x d, *J* = 6.7 and 6.9 Hz, respectively), 2.63 (3H, s), 2.98 (1H, hept, *J* = 6.9 Hz), 3.31 (2H, hept, *J* = 6.9 Hz), 7.25-7.35 (3H, m), 7.50-7.60 (2H, m), 7.77 (1H, d, *J* = 7.9 Hz). ^{13}C-NMR (75 MHz, DMSO) δ: 23.5 (2C), 24.0 (4C), 24.4, 33.3, 38.9 (2C), 119.4, 123.0, 124.8 (2C), 129.6, 132.0, 132.3, 135.4, 140.4, 151.1 (2C), 154.2. ^{19}F NMR (282 MHz, DMSO): δ -148.3 (br. s), -148.3 (dd, *J* = 2.3, 1.1 Hz). HRMS calcd. (%) for $C_{22}H_{30}I$: 421.1387; found: 421.1368.

*4.3.4. (4-Chlorophenyl)(2,4,6-triisopropylphenyl)iodonium tetrafluoroborate (**2d**)*[14b]. White solid; yield 1.572 g (30 %); m.p. = 180-181ºC (Hexane); IR (KBr): ν 1585, 1570, 1471, 1427, 1389, 1369, 1087, 1055, 1011, 817 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.26 (12H, d, *J* = 6.8 Hz), 1.29 (6H, d, *J* = 7.0 Hz), 2.79 (1H, hept, *J* = 6.9 Hz), 3.26 (2H, hept, *J* = 6.7 Hz), 7.20 (2H, s), 7.42 (2H, d, *J* = 8.9 Hz), 7.64 (2H, d, *J* = 8.9 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 23.6 (2C), 24.3 (4C), 32.4, 39.7 (2C), 108.6, 119.7, 125.5 (2C), 132.6 (2C), 133.9 (2C), 139.0, 152.7 (2C), 156.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ -146.7 (br. s), -146.8 (dd, *J* = 3.3, 1.6 Hz).

*4.3.5. Bis(4-methoxyphenyl)iodonium tetrafluoroborate (**2e**)*[28]. *m*-CPBA (6 mmol, 1.280 g) was dissolved in CH_2Cl_2 (20 mL). To the solution was added 1-iodo-4-methoxybenzene (5.4 mmol, 1.264 g). The mixture was placed then on a pre-heated oil bath at 80 ºC and stirred for 10 min. The mixture was cooled at -78 ºC. A 0 ºC cooled mixture of $BF_3{\cdot}OEt_2$ (13.6 mmol, 1.7 mL) and 4-methoxybenzeneboronic acid (6 mmol, 912 mg) in 20 mL of CH_2Cl_2 was added dropwise. The resulting solution was stirred at -78 ºC for 30 min Then was allowed to warm to room temperature and was applied on a silica plug (12 g) and eluted with CH_2Cl_2 (2 x 50 mL) followed by CH_2Cl_2/MeOH (2 x 50 mL). The latter solution was concentrated and diethyl ether (40 mL) was added to the residue to induce precipitation. The solution was allowed to stir for 15 min, and then the solid was filtered and washed several times with diethyl ether and then dried in vacuo. Grey solid; yield 846 mg (37 %); m.p. = 177-180ºC (Hexane); IR (KBr): ν 1572, 1487, 1441, 1406, 1302, 1258, 1177, 1062, 1022, 825 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO) δ: 3.80 (6H, s), 7.07 (4H, d, *J* = 9.2 Hz), 8.13 (4H, d, *J* = 9.1 Hz). ^{13}C-NMR (75 MHz, DMSO) δ: 55.7 (2C), 105.9 (2C), 117.3 (4C), 136.8 (4C), 161.8 (2C). ^{19}F NMR (282 MHz, DMSO): δ -148.2 (br. s), -148.3 (dd, *J* = 2.3, 1.1 Hz).

4.4. General procedure for the direct arylation of heterocycles

To a stirred solution of the corresponding heterocycle (**1** or **4**, 0.5 mmol) in ethanol (1.5 mL) were added the corresponding diaryliodonium tetrafluoroborate (**2**, 1.5 mmol) and PdO-Fe_3O_4 (180 mg, 10 mol% Pd). The mixture was stirred at 60 ºC for 24 h. The catalyst was removed by a magnet and the solvent evaporated under reduced pressure. The corresponding products **3** or **5** were usually purified by chromatography on silica gel (hexane/ ethyl acetate).

*4.4.1. 3-Phenylbenzo[*b*]thiophene (**3a**)*[14b]. Colourless oil; yield 75 mg (71 %); IR (KBr): ν 1600, 1524, 1484, 1442, 1425, 1348, 834 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.40-7.50 (4H, m), 7.50-7.55 (2H, m), 7.60-7.65 (2H, m), 7.90-8.00 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 122.90, 122.90, 123.4, 124.3, 124.4, 127.5, 128.7 (4C), 136.0, 137.9, 138.1, 140.7; HRMS calcd. (%) for $C_{14}H_{11}S$: 211.0581; found: 211.0573.

*4.4.2. 2-Phenylbenzofuran (**3b**)*[14b]. White solid; yield 96.5 mg (99 %); m.p. = 122-124ºC (Hexane); IR (KBr): ν 1605, 1562, 1491, 1471, 1455, 1259, 1020 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.02 (1H, d, ^4J = 0.7 Hz), 7.15-7.40 (3H, m), 7.40-7.50 (2H, m), 7.52 (1H, d, *J* = 8.1 Hz), 7.55-7.60 (1H, m), 7.85-7.90 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 101.3, 111.2, 120.9, 122.9, 124.2, 124.9 (2C), 128.5, 128.8 (2C), 129.2, 130.4, 154.9, 155.9.

*4.4.3. Methyl 2-phenyl-1H-indole-7-carboxylate (**3c**).* White solid; yield 104.4 mg (83 %); m.p. = 72-74ºC (Hexane); IR (ATR): ν 3435, 1699, 1438, 1268 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.99 (3H, s), 6.85 (1H, d, *J* = 2.4 Hz), 7.14 (1H, t, *J* = 7.7 Hz), 7.30-7.35 (1H, m), 7.40-7.50 (2H, m), 7.70-7.75 (2H, m), 7.80-7.90 (2H, m), 10.11 (1H, br s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 51.9, 99.5, 112.2, 119.4, 124.2, 125.3 (2C), 126.1, 128.0, 129.0 (2C), 130.3, 131.9, 136.9, 139.0, 168.0. HRMS calcd. (%) for $C_{16}H_{13}NO_2$: 251.0946; found: 251.0951.

*4.4.4. 5-Fluoro-2-phenyl-1H-indole (**3d**)*[30]. White solid; yield 83.2 mg (79 %); m.p. = 175-177ºC (Hexane); IR (ATR): ν 3434, 1624, 1586, 1472, 1457 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 6.77 (1H, dd, *J* = 2.0, 0.6 Hz), 6.93 (1H, m), 7.25-7.40 (3H, m), 7.40-7.45 (2H, m), 7.60-7.65 (2H, m), 8.30 (1H, br s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 100.0 (d, $^4J_{(C,F)}$ = 4.7 Hz), 105.4 (d, $^2J_{(C,F)}$ = 23.6 Hz), 110.6 (d, $^2J_{(C,F)}$ = 26.4 Hz), 111.5 (d, $^3J_{(C,F)}$ = 9.7 Hz), 125.2 (2C), 128.0, 129.1 (2C), 129.6 (d, $^3J_{(C,F)}$ = 10.4 Hz), 132.0, 133.3, 139.6, 158.2 (d, $^1J_{(C,F)}$ = 235.0 Hz).

*4.4.5. 4-Bromo-2-phenyl-1H-indole (**3e**)*[31]. White solid; yield 79.1 mg (58 %); m.p. = 100-102ºC (Hexane); IR (ATR): ν 3443, 1597, 1568, 1456, 1452 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 6.85 (1H, d, *J* = 1.8 Hz), 7.01 (1H, t, *J* = 7.9 Hz), 7.25-7.50 (3H, m), 7.40-7.45 (2H, m), 7.60-7.65 (2H, m), 8.40 (1H, br s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 100.1, 110.0, 114.5, 123.1 (2C), 125.2 (2C), 128.1, 129.0 (2C), 130.0, 131.6, 136.8, 138.4.

*4.4.6. 3-(p-Tolyl)benzo[b]thiophene (**3f**)*[14a]. Colourless oil; yield 42 mg (38 %); IR (NaCl): ν 1532, 1495, 1456, 1425, 1344, 1060, 1021, 819 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.43 (3H, s), 7.29 (2H, d, *J* = 7.8 Hz), 7.35-7.40 (3H, m), 7.48 (2H, d, *J* = 8.0 Hz), 7.85-8.95 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 21.2, 122.89, 122.94, 123.0, 124.2, 124.3, 128.6 (2C), 129.4 (2C), 133.1, 137.3, 138.0, 138.1, 140.7.

*4.4.7. 2-(p-Tolyl)benzofuran (**3g**)*[32]. White solid; yield 74 mg (71 %); m.p. = 115-117ºC (Hexane); IR (KBr): ν 1613, 1587, 1504, 1451, 1257, 1033, 801 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.38 (3H, s), 6.94 (1H, s), 7.15-7.30 (4H, m), 7.50 (1H, d, *J* = 7.9 Hz), 7.55 (1H, d, *J* = 7.0 Hz), 7.75 (2H, d, *J* = 7.9 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 21.4, 100.5, 111.1, 120.7, 122.8, 124.0, 124.9 (2C), 127.8, 129.3, 129.5 (2C), 138.6, 154.8, 156.2.

*4.4.8. 2-(o-Tolyl)benzofuran (**3h**)*[33]. Colourless oil; yield 69 mg (66 %); IR (NaCl): ν 1605, 1575, 1489, 1473, 1454, 1259, 1019, 921, 805 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.56 (3H, s), 6.87 (1H, s), 7.15-7.35 (5H, m), 7.51 (1H, d, *J* = 7.2 Hz), 7.58 (1H, d,

J = 6.7 Hz), 7.75-7.90 (1H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 21.9, 105.1, 111.1, 120.9, 122.8, 124.2, 126.1, 128.2, 128.5, 129.2, 129.9, 131.2, 135.8, 154.4, 155.7.

*4.4.9. 2-(4-Chlorophenyl)benzofuran (**3i**)*[32]. White solid; yield 63 mg (55 %); m.p. = 135-138ºC (Hexane); IR (KBr): ν 1602, 1581, 1487, 1450, 1404, 1256, 1104, 1094, 1031, 1010, 836, 804 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 6.99 (1H, d, ^4J = 0.8 Hz), 7.22 (1H, td, *J* = 7.4 Hz, ^4J = 1.2 Hz), 7.29 (1H, td, *J* = 7.7 Hz, ^4J = 1.6 Hz), 7.40 (2H, d, *J* = 8.8 Hz), 7.45-7.50 (1H, m), 7.55-7.60 (1H, m), 7.77 (2H, d, *J* = 8.7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 101.7, 111.2, 121.0, 123.1, 124.5, 126.1 (2C), 128.98, 129.02 (2C), 129.05, 134.3, 154.8, 154.9.

*4.4.10. 2-(4-Methoxyphenyl)benzofuran (**3j**)*[32]. White solid; yield 94 mg (84 %); m.p. = 147-148ºC (Hexane); IR (KBr): ν 1610, 1593, 1505, 1453, 1440, 1248, 1180, 1023, 835, 799 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.82 (3H, s), 6.85 (1H, s), 6.95 (2H, d, *J* = 8.5 Hz), 7.15-7.30 (2H, m), 7.49 (1H, d, *J* = 7.6 Hz), 7.53 (1H, d, *J* = 7.1 Hz), 7.78 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 55.3, 99.7, 111.0, 114.2 (2C), 120.5, 122.8, 123.3, 123.7, 126.4 (2C), 129.5, 154.7, 156.0, 160.0.

*4.4.11. 3-Phenylthiophene (**5a**)*[14b]. White solid; yield 12.2 mg (15 %); m.p. = 91-92ºC (Hexane); IR (ATR): ν 3059, 3033, 1597, 1530, 1493 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.25-7.40 (2H, m), 7.40-7.50 (4H, m) 7.60-7.65 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 120.3, 126.2, 126.3, 126.4 (2C), 127.2, 128.8 (2C), 135.9, 142.4.

*4.4.12. 3,4-Diphenylthiophene (**5a'**)*[14b]. White solid; yield 29.0 mg (24 %); m.p. = 112-114ºC (Hexane); IR (ATR): ν 3049, 3023, 1670, 1598, 1508 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.15-7.25 (10H, m), 7.31 (2H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 124.0, 126.9. 128.1 (2C), 129.0 (2C), 136.5, 141.7.

*4.4.13. 2-Bromo-4-phenylthiophene (**5b**)*[30]. White solid; yield 21.5 mg (18 %); m.p. = 48-50ºC (Hexane); IR (ATR): ν 3082, 3057, 1596, 1492, 1446 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.30-7.35 (3H, m), 7.35-7.40 (2H, m), 7.50-7.55 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 112.9, 121.4, 126.2 (2C), 127.6, 128.9 (2C), 129.2, 134.9, 142.8.

*4.4.14. 3-Bromo-4-phenylthiophene (**5c**)*[34]. White solid; yield 60.9 mg (51 %); m.p. = 57-59ºC (Hexane); IR (ATR): ν 3058, 3030, 1600, 1523, 1482 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.24 (1H, d, *J* = 3.5 Hz), 7.35 (1H, d, *J* = 3.5 Hz), 7.40-7.45 (3H, m), 7.45-7.50 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 111.0, 123.4, 124.0, 127.8, 128.2 (2C), 129.0 (2C), 135.1, 142.0.

*4.4.15. 4-Phenyl-2,2'-bithiophene (**5d**)*[35]. Pale brown solid; yield 58.1 mg (48 %); m.p. = 72-74ºC (Hexane); IR (ATR): ν 3063, 3029, 1596, 1491 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.02 (1H, dd, *J* = 5.0, 3.7 Hz), 7.20-7.25 (2H, m), 7.30-7.35 (2H, m), 7.35-7.40 (2H, m), 7.44 (1H, d, *J* = 1.4 Hz), 7.55-7.65 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 119.1, 122.9, 123.9, 124.5, 126.3 (2C), 127.3, 127.8, 128.8 (2C), 135.5, 137.3, 138.0, 142.9.

*4.5. General procedure for the preparation of the haloethers (**6**)*

The haloethers were prepared following the procedure described by Fagnou *et al*.[36]

To a mixture of potassium carbonate (5 mmol, 690 mg) and the appropriate phenol (5 mmol), was added acetone (5 mL). To the stirring mixture was added the required benzyl bromide (2.5 mmol) followed by heating to 50 ºC overnight. The reaction mixture was then cooled to room temperature, poured into a solution of NaOH (2M), and extracted three times with ether. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purification was done by column chromatography using hexane/ethyl acetate (9:1) mixtures to afford the halo ethers **6**.

*4.5.1. 1-Bromo-2-(phenoxymethyl)benzene (**6a**)*[37]. White solid; yield 3.085 g (73 %); m.p. = 39-40ºC (Hexane); IR (KBr): ν 1597, 1585, 1570, 1497, 1482, 1447, 1437, 1379, 1303, 1245, 1171, 1154, 1056, 1044, 1024, 750 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.14 (2H, s), 6.95-7.00 (3H, m), 7.15-7.20 (1H, m), 7.25-7.35 (3H, m), 7.55-7.60 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 69.3, 114.9 (2C), 121.2, 122.2, 127.5, 128.8, 129.1, 129.5 (2C), 132.6, 136.4, 158.4.

*4.5.2. 1-Bromo-2-((4-methoxyphenoxy)methyl)benzene (**6b**)*[38]. Colourless oil; yield 679 mg (93 %); IR (NaCl): ν 1593, 1570, 1506, 1465, 1455, 1441, 1381, 1230, 1108, 1042, 823, 749 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.76 (3H, s), 5.08 (2H, s), 6.84 (2H, d, *J* = 9.3 Hz), 6.92 (2H, d, *J* = 9.3 Hz), 7.17 (1H, dd, *J* = 7.9 Hz, ^4J = 1.7 Hz), 7.32 (1H, dd, *J* = 7.5 Hz, ^4J = 1.2 Hz), 7.56 (2H, app. t, *J* = 7.3 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 55.7, 70.1, 114.7 (2C), 115.9 (2C), 122.3, 127.5, 128.9, 129.1, 132.6, 136.6, 152.6, 154.2.

*4.5.3. 1-Bromo-2-((p-tolyloxy)methyl)benzene (**6c**)*[37]. Colourless oil; yield 605 mg (96 %); IR (NaCl): ν 1586, 1570, 1510, 1441, 1380, 1297, 1239, 1044, 1025, 817, 747 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.28 (3H, s), 5.09 (2H, s), 6.87 (2H, d, *J* = 8.5 Hz), 7.08 (2H, d, *J* = 8.6 Hz), 7.15 (1H, dd, *J* = 7.7 Hz, ^4J = 1.5 Hz), 7.30 (1H, dd, *J* = 7.6 Hz, ^4J = 0.8 Hz), 7.50-7.60 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 20.5, 69.5, 114.7 (2C), 122.2, 127.5, 128.8, 129.1, 129.9 (2C), .130.4, 132.5, 136.6, 156.3.

*4.5.4. 1-Bromo-2-((4-chlorophenoxy)methyl)benzene (**6d**)*[37]. Colourless oil; yield 667 mg (90 %); IR (NaCl): ν 1599, 1493, 1439, 1291, 1249, 1174, 1096, 1044 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.10 (2H, s), 6.90 (2H, d, *J* = 9.0 Hz), 7.18 (1H, td, *J* = 7.9 Hz, ^4J = 1.7 Hz), 7.24 (2H, d, *J* = 9.1 Hz), 7.32 (1H, td, *J* = 7.6 Hz, ^4J = 1.1 Hz), 7.51 (1H, d, *J* = 7.7 Hz), 7.58 (1H, dd, *J* = 7.9 Hz, ^4J = 1.1 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 69.7, 116.2 (2C), 122.3, 126.1, 127.6, 128.8, 129.36, 129.41 (2C), 132.7, 135.9, 157.0.

*4.5.5. 1-Bromo-2-((4-fluorophenoxy)methyl)benzene (**6e**)*[37]. Pale yellow oil; yield 540 mg (77 %); IR (NaCl): ν 1602, 1571, 1505, 1469, 1440, 1381, 1298, 1247, 1220, 1097, 1044, 1025, 827 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.09 (2H, s), 6.85-7.05 (4H, m), 7.18 (1H, td, *J* = 7.9 Hz, ^4J = 1.7 Hz), 7.32 (1H, td, *J* = 7.6 Hz, ^4J = 1.2 Hz), 7.52 (1H, d, *J* = 7.7 Hz), 7.57 (1H, dd, *J* = 7.9 Hz, ^4J = 1.1 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 70.1, 115.9 (2C, d, $^2J_{(C,F)}$ = 21.2 Hz), 116.0 (2C, d, $^3J_{(C,F)}$ = 10.0 Hz), 122.3, 127.6, 128.9, 129.3, 132.6, 136.1, 154.6 (d, $^4J_{(C,F)}$ = 2.1 Hz), 157.5 (d, $^1J_{(C,F)}$ = 238.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -123.3 (tt, $^3J_{(H,F)}$ = 8.0 Hz, , $^4J_{(H,F)}$ = 4.5).

*4.5.6. 1-Bromo-2-((3-fluorophenoxy)methyl)benzene (**6f**)*[38]. Pale yellow oil; yield 616 mg (88 %); IR (NaCl): ν 1611, 1595, 1490, 1440, 1280, 1263, 1166, 1136, 1027, 748 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.18 (2H, s), 6.85-7.15 (4H, m), 7.17 (1H, td, *J* = 7.9 Hz, ^4J = 1.7 Hz), 7.32 (1H, td, *J* = 7.6 Hz, ^4J = 1.2 Hz), 7.55-7.65 (2H, m). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 70.6, 115.7 (d, $^4J_{(C,F)}$ = 1.6 Hz), 116.3 (d, $^2J_{(C,F)}$ = 18.2 Hz), 121.7 (d, $^2J_{(C,F)}$ = 6.9 Hz), 122.1, 124.3 (d, $^3J_{(C,F)}$ = 3.9 Hz), 127.6, 128.8, 129.3, 132.5, 135.9, 146.5 (d, $^3J_{(C,F)}$ = 10.6 Hz), 152.9 (d, $^1J_{(C,F)}$ = 246.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -133.9 (m).

*4.5.7. 1-Bromo-2-((2-fluorophenoxy)methyl)benzene (**6g**)*[39]. Colourless oil; yield 576 mg (82 %); IR (NaCl): ν 1591, 1571, 1504, 1456, 1442, 1380, 1313, 1284, 1260, 1206, 1110, 1024, 745 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.11 (2H, s), 6.60-6.80

(3H, m), 7.15-7.25 (2H, m), 7.33 (1H, td, *J* = 7.6 Hz, ^4J = 1.2 Hz), 7.53 (1H, d, *J* = 1.7 Hz), 7.68 (1H, d, *J* = 7.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 20.9, 68.5, 117.1, 121.9, 122.6, 123.6, 124.6, 127.5, 128.3, 130.1, 130.3, 131.3, 131.6, 152.6.

4.6.4. 2-Chloro-6H-benzo[c]chromene ***(7d)***[37]. Colourless oil; yield 93 mg (86 %); IR (NaCl): ν 2842, 1591, 1487, 1445, 1408, 1249, 1259, 1247, 1200, 1093, 1020, 815 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.10 (2H, s), 6.91 (1H, d, *J* = 8.6 Hz), 7.14 (1H, d, *J* = 7.5 Hz), 7.17 (1H, dd, *J* = 8.6 Hz, ^4J = 2.5 Hz), 7.30 (1H, td, *J* = 7.4 Hz, ^4J = 1.3 Hz), 7.38 (1H, td, *J* = 7.6 Hz, ^4J = 1.4 Hz), 7.64 (1H, d, *J* = 7.5 Hz), 7.67 (1H, d, *J* = 2.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.5, 118.7, 122.1, 123.1, 124.3, 124.7, 127.1, 128.3, 128.6, 129.1, 131.3 (2C), 153.3.

4.6.5. 2-Fluoro-6H-benzo[c]chromene ***(7e)***[37]. Colourless oil; yield 92 mg (92 %); IR (NaCl): ν 2842, 1619, 1577, 1495, 1448, 1426, 1285, 1247, 1173, 1021, 902, 867, 815 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.08 (2H, s), 6.85-6.95 (2H, m), 7.14 (1H, d, *J* = 7.3 Hz), 7.30 (1H, t, *J* = 7.4 Hz), 7.35-7.40 (2H, m), 7.60 (1H, d, *J* = 7.7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.5, 109.6 (d, $^2J_{(C,F)}$ = 24.2 Hz), 115.8 (d, $^2J_{(C,F)}$ = 23.5 Hz), 118.4 (d, $^3J_{(C,F)}$ = 8.3 Hz), 122.2, 124.1 (d, $^3J_{(C,F)}$ = 8.1 Hz), 124.7, 128.3, 128.5, 129.4 (d, $^4J_{(C,F)}$ = 2.2 Hz), 131.5, 150.7 (d, $^4J_{(C,F)}$ = 2.0 Hz), 158.2 (d, $^1J_{(C,F)}$ = 238.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -121.5.

4.6.6. 1-Fluoro-6H-benzo[c]chromene ***(7f)*** *and 3-Fluoro-6H-benzo[c]chromene* ***(7f')*** *(45:55).* Colourless oil; yield 89 mg (89 %); IR (NaCl): ν 2842, 1618, 1591, 1508, 1486, 1459, 1440, 1262, 1144, 1039, 1025, 966, 793, 763 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.07 (2H, s), 5.12 (2H, s), 6.65-6.85 (4H, m), 7.10-7.20 (3H, m), 7.25-7.45 (4H, m), 7.63 (1H, d, *J* = 7.8 Hz), 7.67 (1H, dd, *J* = 8.6, 6.4 Hz), 8.04 (1H, d, *J* = 7.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.7, 68.8, 104.8 (d, $^2J_{(C,F)}$ = 24.3 Hz), 109.3 (d, $^2J_{(C,F)}$ = 22.0 Hz), 109.7 (d, $^2J_{(C,F)}$ = 23.3 Hz), 112.3 (d, $^3J_{(C,F)}$ = 13.7 Hz), 113.1 (d, $^4J_{(C,F)}$ = 3.2 Hz), 119.2 (d, $^4J_{(C,F)}$ = 3.2 Hz), 121.7, 124.4 (d, $^3J_{(C,F)}$ = 10.0 Hz), 124.6, 124.7, 126.2, 126.3, 127.0 (d, $^4J_{(C,F)}$ = 3.0 Hz), 127.5, 127.9 (d, $^4J_{(C,F)}$ = 1.1 Hz), 128.5, 129.0 (d, $^3J_{(C,F)}$ = 11.1 Hz), 129.5, 130.4, 131.5, 156.0 (d, $^3J_{(C,F)}$ = 12.1 Hz), 156.6 (d, $^3J_{(C,F)}$ = 6.6 Hz), 160.7 (d, $^1J_{(C,F)}$ = 250.7 Hz), 163.3 (d, $^1J_{(C,F)}$ = 247.3 Hz) . ^{19}F NMR (282 MHz, $CDCl_3$): δ -111.5 (m), 115.1 (m). HRMS calcd. (%) for $C_{13}H_8FO$: 199.0559; found: 199.0551.

4.6.7. 4-Fluoro-6H-benzo[c]chromene ***(7g)***. Colourless oil; yield 87 mg (87 %); IR (NaCl): ν 2843, 1617, 1593, 1575, 1488, 1467, 1438, 1299, 1279, 1258, 1221, 1014, 900, 753 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.19 (2H, s), 6.97 (1H, td, $^3J_{(H,H)}$ = 8.0 Hz, $^4J_{(H,F)}$ = 5.1 Hz), 7.04 (1H, ddd, $^3J_{(H,F)}$ = 10.1 Hz, $^3J_{(H,H)}$ = 8.1 Hz, $^4J_{(H,H)}$ = 1.6 Hz), 7.17 (1H, d, $^3J_{(H,H)}$ = 7.4 Hz), 7.31 (1H, td, $^3J_{(H,H)}$ = 7.4 Hz, $^4J_{(H,H)}$ = 1.3 Hz), 7.39 (1H, td, $^3J_{(H,H)}$ = 7.4 Hz, $^4J_{(H,H)}$ = 1.3 Hz), 7.49 (1H, dt, $^3J_{(H,H)}$ = 7.8 Hz, $^4J_{(H,H)}$ = $^5J_{(H,F)}$ = 1.3 Hz), 7.68 (1H, d, $^3J_{(H,H)}$ = 7.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.7, 115.9 (d, $^2J_{(C,F)}$ = 18.2 Hz), 118.4 (d, $^4J_{(C,F)}$ = 3.5 Hz), 121.6 (d, $^3J_{(C,F)}$ = 7.2 Hz), 122.3, 124.8, 125.4 (d, $^4J_{(C,F)}$ = 2.1 Hz), 128.2, 128.6, 129.3 (d, $^3J_{(C,F)}$ = 3.2 Hz), 131.1, 142.6 (d, $^2J_{(C,F)}$ = 11.5 Hz), 152.1 (d, $^1J_{(C,F)}$ = 245.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -136.0 (ddd, $^3J_{(H,F)}$ = 10.2 Hz, $^4J_{(H,F)}$ = 5.2 Hz, $^5J_{(H,F)}$ = 1.1 Hz). HRMS calcd. (%) for $C_{13}H_8FO$: 199.0559; found: 199.0559.

4.6.8. 8-(Trifluoromethyl)-6H-benzo[c]chromene ***(7h)***[40]. White solid; yield 105 mg (87 %); m.p. = 68-70 ºC (Hexane); IR (NaCl): ν 2851, 1607, 1483, 1424, 1333, 1246, 1164, 1076, 757 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.14 (2H, s), 7.02 (1H, dd, *J* = 8.1 Hz, ^4J = 0.9 Hz), 7.08 (1H, td, *J* = 7.6 Hz, ^4J = 1.2 Hz), 7.30 (1H, td, *J* = 7.8 Hz, ^4J = 1.5 Hz), 7.41 (1H, s), 7.61 (1H, d, *J* = 8.3 Hz), 7.74 (1H, dd, *J* = 8.0 Hz, ^4J = 1.5 Hz), 7.77 (1H, d, *J* = 9.0 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.0, 117.6, 121.6, 121.7

4.5.8. 1-Bromo-2-(phenoxymethyl)-4-(trifluoromethyl)benzene ***(6h)***. White solid; yield 823 mg (99 %); m.p. = 70-72ºC (Hexane); IR (KBr): ν 1600, 1586, 1498, 1484, 1459, 1449, 1417, 1342, 1304, 1248, 1173, 1154, 1128, 1060, 1022, 904, 831 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.10 (2H, s), 6.95-7.05 (3H, m), 7.31 (2H, t, *J* = 7.8 Hz), 7.41 (1H, d, *J* = 8.3 Hz), 7.67 (1H, d, *J* = 8.3 Hz), 7.86 (1H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.8, 114.9 (2C), 121.6, 123.8 (q, $^1J_{(C,F)}$ = 272.4 Hz), 125.5 (q, $^3J_{(C,F)}$ = 3.8 Hz), 125.73, 125.74 (q, $^3J_{(C,F)}$ = 3.8 Hz), 129.6 (2C), 130.2 (q, $^2J_{(C,F)}$ = 33.0 Hz), 133.1, 137.7, 158.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.6 (s).

4.5.9. 2-Bromo-4-fluoro-1-(phenoxymethyl)benzene ***(6i)***. Colourless oil; yield 548 mg (78 %); IR (NaCl): ν 1601, 1496, 1457, 1304, 1238, 1171, 1054, 1032, 812, 752 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.08 (2H, s), 6.90-7.10 (4H, m), 7.25-7.35 (3H, m), 7.52 (1H, dd, *J* = 8.6, 6.0 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.8,.114.7 (d, $^2J_{(C,F)}$ = 21.0 Hz), 114.9 (2C), 119.9 (d, $^2J_{(C,F)}$ = 24.6 Hz), 121.3, 122.4 (d, $^3J_{(C,F)}$ = 9.6 Hz), 129.6 (2C), 130.0 (d, $^3J_{(C,F)}$ = 8.5 Hz), 132.3 (d, $^4J_{(C,F)}$ = 3.5 Hz), 158.3, 161.9 (d, $^1J_{(C,F)}$ = 250.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -112.5 (m).

4.6. General procedure for the intramolecular direct arylation

To a stirred solution of the corresponding arene (**6**, 0.5 mmol) in *N*,*N*-dimethylacetamide (2 mL) were added KOAc (1 mmol, 98 mg) and PdO-Fe_3O_4 (180 mg, 10 mol% Pd). The mixture was stirred at 140 ºC for 48 h. The catalyst was removed by a magnet and the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The corresponding products **7** were usually purified by chromatography on silica gel (hexane/ ethyl acetate).

4.6.1. 6H-Benzo[c]chromene ***(7a)***[36]. Colourless oil; yield 71 mg (78 %); IR (NaCl): ν 2842, 1607, 1594, 1487, 1440, 1245, 1198, 1018, 755 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.09 (2H, s), 6.98 (1H, dd, *J* = 8.1 Hz, ^4J = 1.2 Hz), 7.03 (1H, td, *J* = 7.5 Hz, ^4J = 1.3 Hz), 7.11 (1H, d, *J* = 7.4 Hz), 7.20-7.25 (2H, m), 7.34 (1H, td, *J* = 7.6 Hz, ^4J = 1.4 Hz), 7.67 (1H, d, *J* = 7.5 Hz), 7.71 (1H, dd, *J* = 7.7 Hz, ^4J = 1.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.4, 117.3, 122.0, 122.1, 122.9, 123.3, 124.6, 127.6, 128.4, 129.4, 130.1, 131.4, 154.8.

4.6.2. 2-Methoxy-6H-benzo[c]chromene ***(7b)***[38]. Colourless oil; yield 79 mg (75 %); IR (NaCl): ν 2835, 1614, 1572, 1496, 1450, 1219, 1194, 1049, 1037 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.84 (3H, s), 5.07 (2H, s), 6.81 (1H, dd, *J* = 8.8 Hz, ^4J = 2.9 Hz), 6.94 (1H, d, *J* = 8.8 Hz), 7.16 (1H, d, *J* = 7.4 Hz), 7.25-7.30 (2H, m with td at 7.30, *J* = 7.4 Hz, ^4J = 1.2 Hz), 7.38 (1H, td, *J* = 7.6 Hz, ^4J = 1.3 Hz), 7.66 (1H, d, *J* = 7.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 55.8, 68.6, 108.3, 115.0, 118.0, 122.1, 123.6, 124.7, 127.8, 128.4, 130.2, 131.9, 148.9, 154.8.

4.6.3. 2-Methyl-6H-benzo[c]chromene ***(7c)***[37]. Colourless oil; yield 84 mg (86 %); IR (NaCl): ν 2840, 1607, 1593, 1573, 1498, 1449, 1246, 1199, 1021 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.36 (3H, s), 5.08 (2H, s), 6.88 (1H, d, *J* = 8.2 Hz), 7.03 (1H, dd, *J* = 8.2 Hz, ^4J = 2.0 Hz), 7.13 (1H, d, *J* = 7.4 Hz), 7.26 (1H, td, *J* = 7.4 Hz, ^4J = 1.2 Hz), 7.36 (1H, td, *J* = 7.6 Hz, ^4J = 1.1 Hz),

(q, $^{3}J_{(C,F)}$ = 3.8 Hz), 122.3, 122.4, 123.8, 124.1 (q, $^{1}J_{(C,F)}$ = 272.1 Hz), 125.3 (q, $^{3}J_{(C,F)}$ = 3.8 Hz), 129.5 (q, $^{2}J_{(C,F)}$ = 32.6 Hz), 130.7, 131.8, 133.7, 155.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.5.

*4.6.9. 9-Fluoro-6H-benzo[c]chromene (**7i**)*[41]. Colourless oil; yield 77 mg (77 %); IR (NaCl): ν 2846, 1598, 1574, 1504, 1455, 1422, 1246, 1180, 1040, 1015, 757 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 5.07 (2H, s), 6.90-7.15 (4H, m), 7.20-7.30 (1H, m), 7.35 (1H, dd, $^{3}J_{(H,F)}$ = 9.9 Hz, $^{4}J_{(H,H)}$ = 2.5 Hz), 7.63 (1H, dd, $^{3}J_{(H,H)}$ = 7.7 Hz, $^{4}J_{(H,H)}$ = 1.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 67.9, 109.0 (d, $^{2}J_{(C,F)}$ = 23.2 Hz), 114.3 (d, $^{2}J_{(C,F)}$ = 22.1 Hz), 117.5, 122.1 (d, $^{4}J_{(C,F)}$ = 2.5 Hz), 122.3, 123.5, 126.2 (d, $^{3}J_{(C,F)}$ = 8.5 Hz), 127.0 (d, $^{4}J_{(C,F)}$ = 2.9 Hz), 130.1, 132.3 (d, $^{3}J_{(C,F)}$ = 8.3 Hz), 154.7, 163.1 (d, $^{1}J_{(C,F)}$ = 244.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -113.5 (m).

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Supplementary data

Catalyst full characterisation data can be found at the supplementary data associated with article.

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