Direct Arylations of Heteroarenes with Benzenesulfonyl Chlorides Using Pd/C Catalyst

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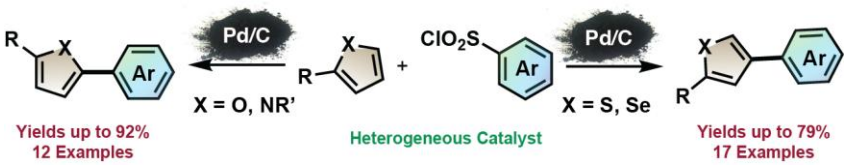


The reactivity of heteroaromatics in direct arylation with benzenesulfonyl chlorides using 10% Pd/C as catalyst was explored. With (benzo)thiophenes, (benzo)furans, pyrroles and selenophenes, high yields in arylated heteroarenes were obtained. These arylations were performed using only 5 mol% Pd/C and Li_2CO_3 as inexpensive base. The regioselectivities are similar to those observed with homogeneous palladium catalysts. Better yields were obtained with electron-deficient benzenesulfonyl chlorides than with the electron-rich ones. Notably, useful substituents such as bromo or iodo on the benzenesulfonyl chloride were tolerated, as no cleavage of the C-Br or C-I bonds was observed under these conditions. The use of Pd/C presents several advantages compared to the previously employed homogeneous palladium catalysts, as it can be easily removed by filtration at the end of the reaction. The major side-products of the reaction are HBr associated to Li_2CO_3. Therefore, this new protocol affords a very attractive synthetic scheme in terms of cost, simplicity and low environmental impact for the access to arylated heteroaromatics.

Introduction

Many drugs contain an aryl substituent on a 5-membered ring heteroarene (Fig. 1). For example, Atorvastatin which is used to prevent cardiovascular diseases is one of the most prescribed drugs. Canagliflozin is a medication used to treat type 2 diabetes. Saprisartan is an AT1 receptor antagonist. Raloxifene is a medication used to prevent and treat osteoporosis, and Lapatinib is an orally active drug used against breast cancer and other solid tumors. In addition, aryl-substituted heteroarenes are ubiquitous units in organic material science.[1] Therefore, the development of new procedures using easily accessible and easy to handle inexpensive reagents that allow access to such structures in a few steps is of great interest to pharmacochemists as well as to researchers working in the field of organic materials.

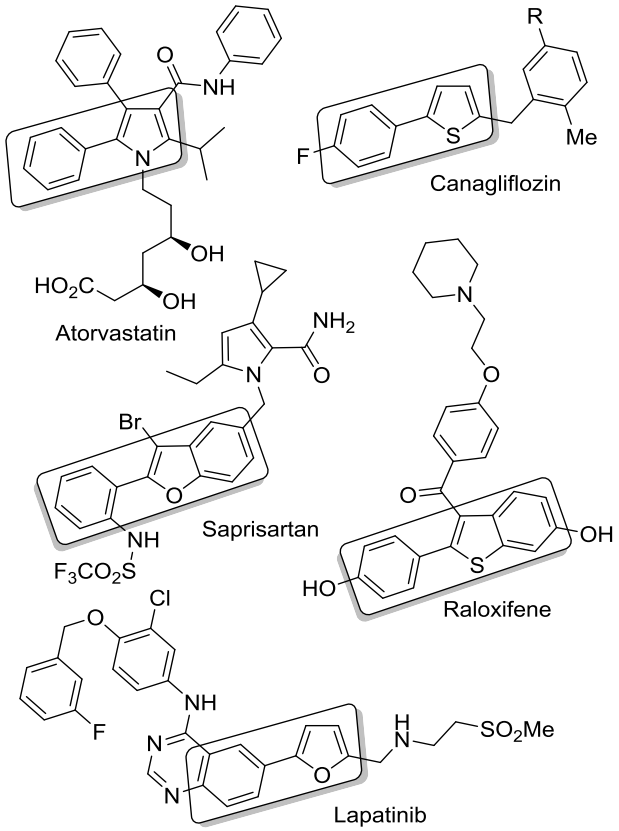
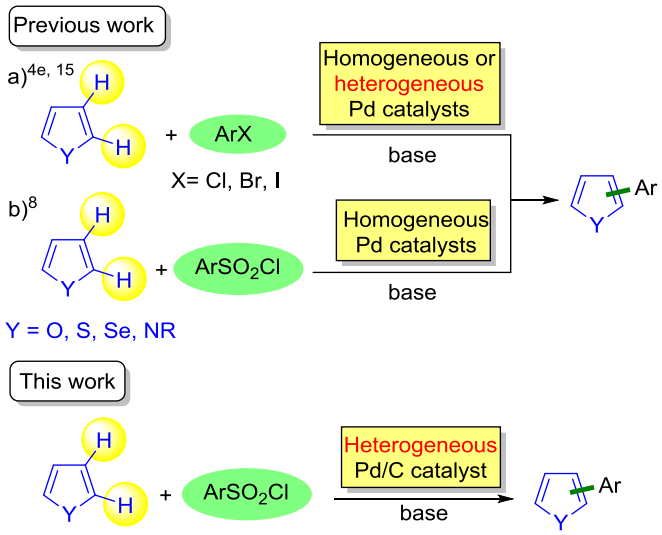


Figure 1. Representative examples of drugs containing an aryl-substituted heteroarene

The Pd-catalyzed reactions such as Stille, Suzuki and Negishi cross-couplings are very effective tools for the access to aryl-substituted heteroarenes. These coupling reactions tolerate many useful functional groups and high yields in target products are often obtained. However, one of the major drawback of such couplings is that they require the preliminary synthesis of organometallic or boron derivatives.[2] In 1985, Ohta et al. described the Pd-catalyzed arylation of heteroarenes *via* the cleavage of C-H bonds using aryl bromides as aryl sources[3] Since this seminal report, the so-called "direct arylations" of heteroarenes using Pd-catalysis was demonstrated to be a very effective method for the preparation of arylated heteroarenes (Scheme 1, a).[4-7] For these arylations, in addition to aryl halides, a variety of aryl sources such as benzenesulfonyl chlorides can be employed. The use of benzenesulfonyl chlorides is very attractive as in some cases, the regioselectivity of the arylation is modified and as they allow the synthesis of molecules containing several halo-substituents including iodo, due to the C-halo bond tolerance of the reactions performed with these substrates.[8-10] To the best of our knowledge, in all cases the Pd-catalyzed direct arylations of heteroarenes by benzenesulfonyl chlorides were performed using homogeneous catalysts (Scheme 1, b).[8]

Pd/C catalyst displays several advantages over homogeneous palladium catalysts:[11] 1) it is easy to handle because it is not sensitive to air or moisture, 2) it is readily available on a large scale and at an affordable cost, 3) it can be removed by simple filtration, 4) recycling of the recovered Pd/C residues is possible in some cases or they can be reconditioned. However, to date the Pd-catalyzed direct arylation of heteroarenes using Pd/C is limited to the reactions with aryl halides.[12-15] A few other heterogeneous Pd-catalysts such as $Pd(OH)_2$, zeolites or nanoparticles have also been successfully employed for the direct arylation of heteroaromatics with aryl halides.[16,17]

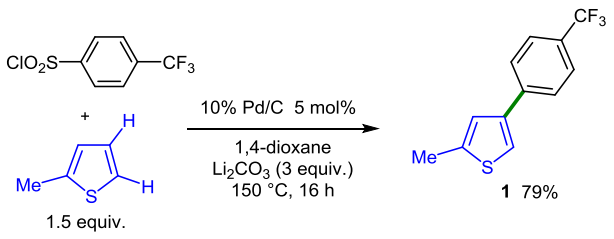
As the efficacy of the Pd/C catalyst in direct heteroarene arylations by benzenesulfonyl chlorides has not yet been described, we investigated its potential using a set of heteroarenes (Scheme 1, bottom).



Scheme 1. Pd-catalyzed direct arylations of heteroarenes

Results and Discussion

Using reaction conditions similar to those employed with homogeneous palladium catalyst,[9] we first studied the reactivity of 2-methylthiophene (1.5 equiv.) using 4-(trifluoromethyl)benzenesulfonyl chloride (1 equiv.) as the aryl source in the presence of 5 mol% Pd/C (10%) (Scheme 2). With Li_2CO_3 as the base at 150 °C, the C4-arylated thiophene **1** was regioselectively obtained in 79% yield. It should be noted that this regioselectivity (C4-arylation) is different from the regioselectivity observed with aryl bromide and Pd/C (C5-arylations). This difference of regioselectivity for the arylation of thiophenes using benzenesulfonyl chlorides or aryl bromides had already been observed with homogeneous Pd-catalysts.[9] The use of a lower reaction temperature of 130 °C, or the use of cyclopentyl methyl ether as the solvent afforded the desired coupling product **1** in lower yields of 68% and 15%, respectively. We also studied the possibility of recycling the Pd/C catalyst. The Pd/C recovered by filtration on filter paper was used for a second run which afforded **1** in a lower yield of 44%.



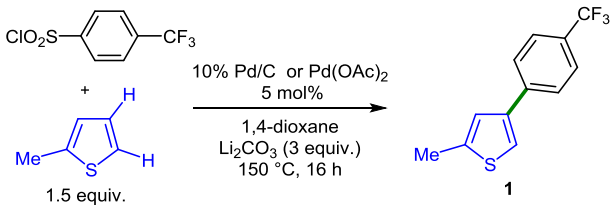
Variations from above conditions	Yield (%)
$ArSO_2Cl$ 1.5 equiv., 2-methylthiophene 1 equiv.	32
130 °C	68
Reaction in cyclopentyl methyl ether	15
Addition of 1 drop of Hg	0
Using Pd/C recovered by filtration	44

Scheme 2. Pd/C-catalyzed coupling of 2-methylthiophene with benzenesulfonyl chlorides

The mechanism of the direct arylations of heteroarenes using Pd/C catalyst has not yet been elucidated. In 2003 Conlon et al. studied the mechanism of the Suzuki-Miyaura reaction using Pd/C.[18a] They suggested that this reaction might have a homogeneous component due to the formation of soluble palladium-species coming from the desorption of the palladium from Pd/C to produce soluble Pd(II) species. Such desorption may occur after the oxidative addition of the aryl halide on the Pd/C surface. The direct arylation of heteroarenes might proceed *via* a similar mechanism.

In order to better understand the mechanism of the coupling using benzenesulfonyl chlorides with Pd/C, the mercury poisoning test was applied to this reaction. When a drop of Hg was added to the reaction mixture, no formation of product **1** was detected by GC/MS, and ^{1}H NMR analysis of the crude mixture (Scheme 2). Such reaction inhibition is generally observed when the catalytic cycle involves heterogeneous species including colloidal Pd(0).[19a] However, in a few cases, Hg(0) interaction with soluble molecular Pd-complexes was also found to inhibit catalytic reactions.[19b,19c]

The kinetics of the formation of product **1** using both Pd/C and $Pd(OAc)_2$ catalysts was measured (Scheme 3, a). With Pd/C, an induction period was observed with <1% yield in **1** after 15 minutes. Conversely, with $Pd(OAc)_2$ after 15 minutes 4% of **1** was obtained. At 4 h the yields in **1** with Pd/C and $Pd(OAc)_2$ were 17% and 33%, respectively; whereas after 16 h, similar yield in **1** were obtained with these two catalysts. The induction period for the Pd/C catalyzed reaction might come from a slow leaching to produce catalytically active palladium clusters or nanoparticles. In order to confirm the formation of soluble clusters or nanoparticles, a hot filtration test[20] was performed (Scheme 3, b). The yield in **1** with Pd/C at 150 °C after 4 h was 13%; then, the reaction mixture was filtered through a pad of Celite, and 1 equiv. of Li_2CO_3 was added to the solution which was heated again at 150 °C during 4 h. The filtrate was catalytically active, as after 8 h the reaction progressed to 21% yield. This result supports the formation of catalytically active soluble clusters or nanoparticles from Pd/C.[21]



a) Kinetics with Pd/C and $Pd(OAc)_2$ catalysts:

	Yield in **1** (%)	
Time	Pd/C	$Pd(OAc)_2$
5 min.	<1	2
15 min.	<1	4
30 min.	3	7
1 h	6	12
2 h	10	19
4 h	17	33
8 h	30	58
16 h	64	77

b) Hot filtration test with 10% Pd/C 5 mol%:

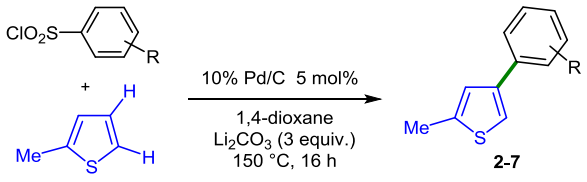
Time	Yield in **1** (%)
4 h	13*
8 h	21

*: At 4 h, hot filtration on Celite and addition of 1 equiv. of Li_2CO_3

Scheme 3. Kinetics of the direct arylation of 2-methylthiophene with 4-(trifluoromethyl)benzenesulfonyl chloride using Pd/C or $Pd(OAc)_2$ catalysts and hot filtration test

Then, a set of benzenesulfonyl chlorides was reacted with 2-methylthiophene using Pd/C (Scheme 4). From benzenesulfonyl chlorides bearing chloro or fluoro *para*-substituents, the desired products **2** and **3** were obtained in 62% and 77 % yield, respectively. By contrast, the reaction of electron-rich 4-

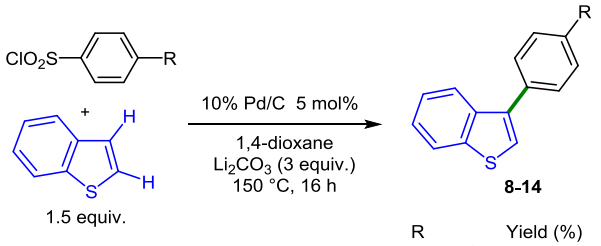
methoxybenzenesulfonyl chloride gave the product **5** in only 21% yield, due to a low conversion of this benzenesulfonyl chloride. As the use of benzenesulfonyl chlorides in Pd-catalyzed direct arylations tolerates bromo-substituents,[8] the behavior of 3-bromo- and 4-bromo-benzenesulfonyl chlorides was also investigated. With 4-bromobenzenesulfonyl chloride, a moderate yield in the target product **6** was obtained due to a poor conversion. Conversely, the use of 3-bromobenzenesulfonyl chloride afforded the product **7** in 79% yield. In both cases, no cleavage of the C-Br bond was observed.



R		Yield (%)
4-Cl	**2**	62
4-F	**3**	77
H	**4**	75
4-MeO	**5**	21
4-Br	**6**	38
3-Br	**7**	79

Scheme 4. Pd/C-catalyzed coupling of 2-methylthiophene with benzenesulfonyl chlorides

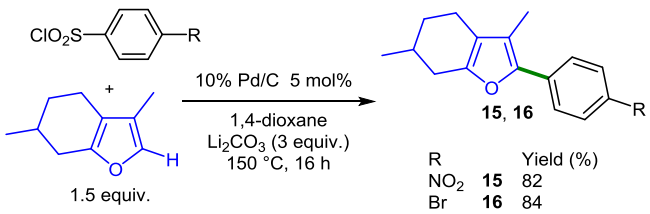
Under the same reaction conditions using Pd/C, the direct arylation of benzothiophene with benzenesulfonyl chlorides regioselectively gave the C3-arylated benzothiophenes (Scheme 5). Again, the use of benzenesulfonyl chlorides as the aryl source instead of aryl bromides modifies the regioselectivity of the arylation. In the presence of aryl bromides and Pd/C, regioselective C2-arylations of benzothiophene had been previously observed.[9] The reaction tolerates a range of substituents on the benzenesulfonyl chloride. However, again higher yields in desired coupling products were obtained in the presence of electron-withdrawing groups such as trifluoromethyl or chloro than with 4-methoxybenzenesulfonyl chloride. From 4-bromo- and even 4-iodo-benzenesulfonyl chlorides, the halo-containing 3-arylbenzothiophenes **13** and **14** were obtained in moderate yields.



R		Yield (%)
CF_3	**8**	71
Cl	**9**	63
F	**10**	60
H	**11**	61
MeO	**12**	41
Br	**13**	45
I	**14**	54

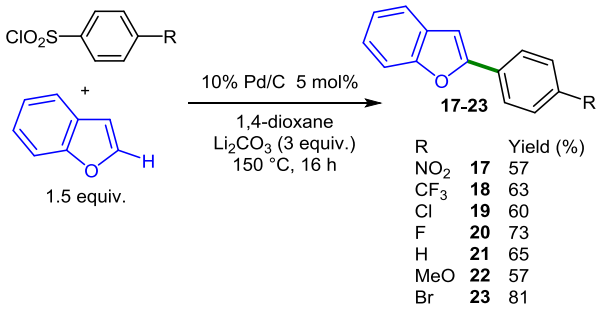
Scheme 5. Pd/C-catalyzed coupling of benzothiophene with benzenesulfonyl chlorides

The reactivity of Menthofuran, which is a natural compound found in mint oil, using Pd/C was then investigated (Scheme 6). The influence of nitro and bromo *para*-substituents on the benzenesulfonyl chloride was examined, and both reactions produced the expected C5-arylated Menthofuran derivatives **15** and **16** in high yields.



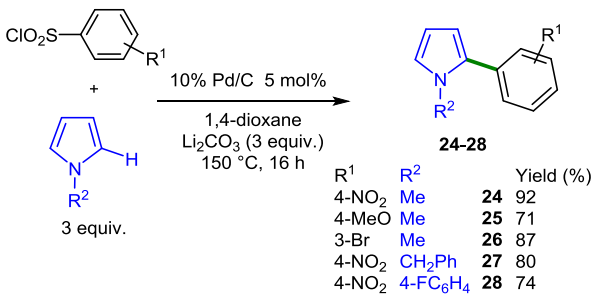
Scheme 6. Pd/C-catalyzed coupling of menthofuran with benzenesulfonyl chlorides

The regioselective Pd-catalyzed direct arylation of benzofuran with aryl halides is a challenging reaction. Such couplings generally led to mixtures of C2- and C3-arylation products together with C2,C3-diarylation products, as C2- and C3-positions of benzofuran display quite similar reactivity.[22] We have reported a few years ago that the use of benzenesulfonyl chlorides instead of aryl halides using the homogeneous catalyst $PdCl_2(MeCN)_2$ allows to control the regioselectivity of the Pd-catalyzed arylation of benzofurans in favor of C2-position.[22] When Pd/C was used for the direct arylation of benzofuran with benzenesulfonyl chlorides, the C2-arylated benzofurans were also regioselectively produced (Scheme 7). At 150 °C after 16 h, the 2-arylbenzofurans **17-20** were obtained in 57-73% yields, from benzenesulfonyl chlorides bearing nitro, trifluoromethyl, chloro or fluoro *para*-substituents. Similar yields in products **21** and **22** were obtained from benzenesulfonyl chloride and 4-methoxybenzenesulfonyl chloride. Notably, from 4-bromobenzenesulfonyl chloride, the bromo-substituted 2-arylbenzofuran **23** was isolated in 81% yield.



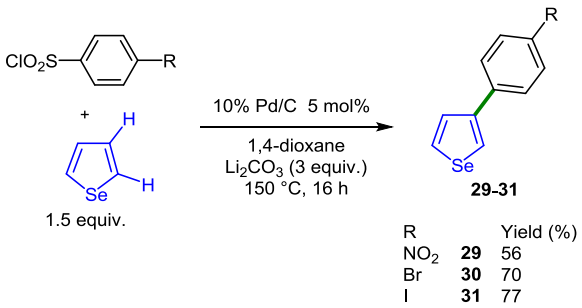
Scheme 7. Pd/C-catalyzed coupling of benzofuran with benzenesulfonyl chlorides

Then, the reactivity of pyrrole derivatives with benzenesulfonyl chlorides using Pd/C was examined (Scheme 8). For these reactions, an excess (3 equiv.) of pyrrole derivative was employed in order to avoid the formation of 2,5-diarylated pyrrole derivatives. From 1-methylpyrrole and 4-nitro-, 4-methoxy- and 3-bromo-benzenesulfonyl chlorides, the C2-arylated pyrroles **24**-**26** were obtained in 71-92% yields. The reaction also tolerated benzyl or fluorobenzene substituents on the nitrogen atom of pyrrole, providing the products **27** and **28** in good yields. Under these conditions, no debenzylation was observed.



Scheme 8. Pd/C-catalyzed coupling of pyrrole derivatives with benzenesulfonyl chlorides

In the presence of aryl halides, the Pd-catalyzed direct arylation of selenophene proceed at C2-position;[18] whereas with benzenesulfonyl chlorides using the homogeneous catalyst $Pd(OAc)_2$, C3-arylated selenophenes had been obtained.[19] We observed that using Pd/C and benzenesulfonyl chlorides, the arylation of selenophene also occurred regioselectively at C3-position of selenophene (Scheme 9). Nitro and bromo *para*-substituents on the benzenesulfonyl chloride were successfully employed affording the products **29** and **30** in 56% and 70% yield, respectively. A 4-iodo substituent on the benzenesulfonyl chloride was also tolerated giving rise to the 3-arylselenophene **31** in 77% yield.



Scheme 9. Pd/C-catalyzed coupling of selenophene with benzenesulfonyl chlorides

Conclusion

Pd/C catalyst was successfully employed to promote the direct arylation of a range of heteroaromatics using benzenesulfonyl chlorides as the aryl source. To our knowledge these are the first examples of desulfitative direct arylations of heteroaromatics using a heterogeneous pre-catalyst. These couplings likely proceed *via* the formation of homogeneous catalytically active soluble clusters or nanoparticles from Pd/C. Good to high yields in arylated heteroaromatics were obtained using a variety of benzenesulfonyl chlorides. With (benzo)thiophenes and selenophene, the arylation occurred at β-positions; whereas, with (benzo)furans and pyrroles α-arylated compounds were obtained. These regioselectivities are similar to those observed with the homogeneous palladium catalysts $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$ when benzenesulfonyl chlorides were employed as the aryl sources. This protocol is attractive as 1) Pd/C can be easily removed by simple filtration, 2) the catalyst, base and reactants are air-stable and easily available, 3) the reaction tolerates useful functional groups such as nitro, trifluoromethyl, methoxy or even bromo and iodo substituents. For these reasons, this new procedure provides an economically viable and environmentally very attractive access to arylated heteroaromatics.

Experimental Section

1,4-Dioxane (99%) and Li_2CO_3 (99%) were purchased from Fischer. 10% Pd/C was purchased from Aldrich (Reference 205699 which is expect to conform to the following: approximately 90% <60 µm and 10% <5 µm with an average particle size of 15 µm). These compounds were not purified before use.

Typical experiment for coupling reactions: The reaction of the benzenesulfonyl chloride (1 mmol), heteroaromatic (1.5 or 3 mmol) (see schemes) and Li_2CO_3 (0.222 g, 3 mmol) in the presence of 10% Pd/C (0.055 g, 5 mol%) in 1,4-dioxane under argon at 150 °C during 16 h, affords the corresponding product after cooling, evaporation of the solvent and filtration on silica gel (pentane/ether).

2-Methyl-4-(4-(trifluoromethyl)phenyl)thiophene (1)[9]

4-(Trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **1** in 79% (0.191 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 1.4 Hz, 1H), 7.07 (d, *J* = 1.4 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 140.5, 139.4, 128.6 (q, *J* = 32.6 Hz), 126.5, 125.7 (q, *J* = 3.2 Hz), 124.3, 124.0 (q, *J* = 271.6 Hz), 119.6, 15.4. LRMS calcd for M^+ $C_{12}H_9F_3S$ 242, found 242.

4-(4-Chlorophenyl)-2-methylthiophene (2)[9]

4-Chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **2** in 62% (0.129 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 1.4 Hz, 1H), 7.04 (d, *J* = 1.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.8, 134.6, 132.7, 128.8, 127.4, 124.4, 118.3, 15.4. LRMS calcd for M^+ $C_{11}H_9ClS$ 208, found 208.

4-(4-Fluorophenyl)-2-methylthiophene (3)[9]

4-Fluorobenzenesulfonyl chloride (0.194 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **3** in 77% (0.148 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.13 (d, *J* = 1.4 Hz, 1H), 7.06 (t, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 1.4 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, *J* = 245.4 Hz), 141.0, 140.7, 132.3 (d, *J* = 3.3 Hz), 127.6 (d, *J* = 8.1 Hz), 124.5, 117.7, 115.5 (d, *J* = 21.3 Hz), 15.3. LRMS calcd for M^+ $C_{11}H_9FS$ 192, found 192.

2-Methyl-4-phenylthiophene (4)[9]

Benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **4** in 75% (0.131 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 1.4 Hz, 1H), 7.08 (d, *J* = 1.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 140.5, 136.1, 128.7, 126.9, 126.2, 124.6, 118.0, 15.5. LRMS calcd for M^+ $C_{11}H_{10}S$ 174, found 174.

4-(4-Methoxyphenyl)-2-methylthiophene (5)[9]

4-Methoxybenzenesulfonyl chloride (0.206 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **5** in 21% (0.043 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 1.4 Hz, 1H), 7.00 (d, *J* = 1.4 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 3.83 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 141.7, 140.3, 129.0, 127.3, 124.6, 116.6, 114.1, 55.3, 15.4. LRMS calcd for M^+ $C_{12}H_{12}OS$ 204, found 204.

4-(4-Bromophenyl)-2-methylthiophene (6)[9]

4-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **6** in 38% (0.096 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 1.4 Hz, 1H), 7.02 (d, *J* = 1.4 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.8, 135.0, 131.8, 127.8, 124.3, 120.8, 118.4, 15.4. LRMS calcd for M^+ $C_{11}H_9BrS$ 252, found 252.

4-(3-Bromophenyl)-2-methylthiophene (7)[23]

3-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol) affords **7** in 79% (0.200 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 1.4 Hz, 1H), 7.03 (d, *J* = 1.4 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 140.6, 138.2, 130.4, 129.9, 129.4, 124.9, 124.5, 123.0, 119.1, 15.6. LRMS calcd for M^+ $C_{11}H_9BrS$ 252, found 252.

3-(4-(Trifluoromethyl)phenyl)benzo[*b*]thiophene (8)[9]

4-(Trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **8** in 71% (0.197 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 1H), 7.91-7.85 (m, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.48 (s, 1H), 7.45-7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 139.6, 137.4, 136.6, 129.5 (q, *J* = 32.6 Hz), 128.8, 125.7 (q, *J* = 4.0 Hz), 124.7, 124.6 (m), 124.1 (q, *J* = 271.8 Hz), 123.1, 122.5. LRMS calcd for M^+ $C_{15}H_9F_3S$ 278, found 278.

3-(4-Chlorophenyl)benzo[*b*]thiophene (9)[9]

4-Chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **9** in 63% (0.154 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.90 (m, 1H), 7.90-7.83 (m, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.43-7.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.6, 136.8, 134.4, 133.5, 129.9, 128.9, 124.5, 124.4, 123.7, 123.0, 122.6. LRMS calcd for M^+ $C_{14}H_9ClS$ 244, found 244.

3-(4-Fluorophenyl)benzo[*b*]thiophene (10)[24]

4-Fluorobenzenesulfonyl chloride (0.194 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **10** in 60% (0.137 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.90 (m, 1H), 7.89-7.82 (m, 1H), 7.55 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.43-7.38 (m, 2H), 7.38 (s, 1H), 7.18 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, *J* = 246.6 Hz), 140.8, 138.0, 137.1, 132.2, 130.4 (d, *J* = 8.1 Hz), 124.6, 124.5, 123.6, 123.1, 122.8, 115.8 (d, *J* = 21.5 Hz). LRMS calcd for M^+ $C_{14}H_9FS$ 228, found 228.

3-Phenylbenzo[*b*]thiophene (11)[9]

Benzenesulfonyl chloride (0.177 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **11** in 61% (0.128 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.90 (m, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.9 Hz, 2H), 7.44-7.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 138.1, 137.9, 136.0, 128.7, 128.5, 127.5, 124.4, 124.3, 123.4, 122.9. LRMS calcd for M^+ $C_{14}H_{10}S$ 210, found 210.

3-(4-Methoxyphenyl)benzo[*b*]thiophene (12)[9]

4-Methoxybenzenesulfonyl chloride (0.206 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **12** in 41% (0.098 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.90 (m, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.43-7.36 (m, 2H), 7.35 (s, 1H), 7.04 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

159.1, 140.6, 138.1, 137.7, 129.8, 128.5, 124.3, 124.2, 122.9, 122.8, 122.5, 114.1, 55.3. LRMS calcd for M^+ $C_{15}H_{12}OS$ 240, found 240.

3-(4-Bromophenyl)benzo[*b*]thiophene (13)[9]

4-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **13** in 45% (0.130 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.90 (m, 1H), 7.90-7.82 (m, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.43-7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.5, 136.8, 134.8, 131.9, 130.2, 124.6, 124.5, 123.7, 123.0, 122.6, 121.6. LRMS calcd for M^+ $C_{14}H_9BrS$ 288, found 288.

3-(4-Iodophenyl)benzo[*b*]thiophene (14)

4-Iodobenzenesulfonyl chloride (0.302 g, 1 mmol) and benzothiophene (0.201 g, 1.5 mmol) affords **14** in 54% (0.181 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.89 (m, 1H), 7.89-7.83 (m, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.45-7.37 (m, 3H), 7.33 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.9, 137.5, 136.9, 135.5, 130.5, 124.6, 124.5, 123.8, 123.0, 122.6, 93.1. Anal. Calcd for $C_{14}H_9IS$ (336.19): C, 50.02; H, 2.70; found: C, 67.34; H, 3.80.

3,6-Dimethyl-2-(4-nitrophenyl)-4,5,6,7-tetrahydrobenzofuran (15)[10b]

4-Nitrobenzenesulfonyl chloride (0.221 g, 1 mmol) and menthofuran (0.225 g, 1.5 mmol) affords **15** in 82% (0.222 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 2.80-2.60 (m, 1H), 2.50-2.24 (m, 3H), 2.23 (s, 3H), 2.00-1.80 (m, 2H), 1.50-1.30 (m, 1H), 1.12 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 145.1, 145.0, 138.4, 124.3, 124.2, 121.2, 121.1, 31.6, 31.2, 29.2, 21.5, 120.0, 10.5. LRMS calcd for M^+ $C_{16}H_{17}NO_3$ 271, found 271.

2-(4-Bromophenyl)-3,6-dimethyl-4,5,6,7-tetrahydrobenzofuran (16)[10b]

4-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and menthofuran (0.225 g, 1.5 mmol) affords **16** in 84% (0.256 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 2.80-2.70 (m, 1H), 2.50-2.20 (m, 3H), 2.15 (s, 3H), 2.10-1.85 (m, 2H), 1.50-1.35 (m, 1H), 1.12 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 145.9, 131.7, 131.5, 126.5, 120.2, 119.7, 117.0, 31.6, 31.4, 29.8, 21.7, 20.2, 10.1. LRMS calcd for M^+ $C_{16}H_{17}BrO$ 304, found 304.

2-(4-Nitrophenyl)benzofuran (17)[22]

4-Nitrobenzenesulfonyl chloride (0.221 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **17** in 57% (0.136 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 153.4, 147.4, 136.4, 128.8, 126.0, 125.3, 124.5, 123.7, 121.8, 111.6, 105.2. LRMS calcd for M^+ $C_{14}H_9NO_3$ 239, found 239.

2-(4-(Trifluoromethyl)phenyl)benzofuran (18)[22]

4-(Trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **18** in 63% (0.165 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 154.3, 133.8, 130.2 (q, *J* = 32.5 Hz), 129.0, 126.0 (q, *J* = 2.1 Hz), 125.2, 125.1, 124.1 (q, *J* = 271.8 Hz), 123.4, 111.5, 103.4. LRMS calcd for M^+ $C_{15}H_9F_3O$ 262, found 262.

2-(4-Chlorophenyl)benzofuran (19)[22]

4-Chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **19** in 60% (0.137 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.01 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.9, 134.4, 129.2 (2C), 129.1, 126.3, 124.7, 123.2, 121.1, 111.3, 101.9. LRMS calcd for M^+ $C_{14}H_9ClO$ 228, found 228.

2-(4-Fluorophenyl)benzofuran (20)[22]

4-Fluorobenzenesulfonyl chloride (0.194 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **20** in 73% (0.155 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 5.8, 5.5 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, *J* = 248.7 Hz), 155.1, 155.0, 129.3, 126.9, 126.8 (d, *J* = 8.3 Hz), 124.4, 123.2, 121.0, 116.1 (d, *J* = 21.7 Hz), 111.3, 101.1 (d, *J* = 1.7 Hz). LRMS calcd for M^+ $C_{14}H_9FO$ 212, found 212.

2-Phenylbenzofuran (21)[22]

Benzenesulfonyl chloride (0.177 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **21** in 65% (0.126 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.04 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 155.0, 130.6, 129.3, 128.9, 128.7, 125.1, 124.4, 123.1, 121.0, 111.3, 101.4. LRMS calcd for M^+ $C_{14}H_{10}O$ 194, found 194.

2-(4-Methoxyphenyl)benzofuran (22)[22]

4-Methoxybenzenesulfonyl chloride (0.206 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **22** in 57% (0.128 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.89 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 156.2, 154.8, 129.6, 126.6, 123.9, 123.5, 123.0, 120.7, 114.4, 111.1, 99.8, 55.5. LRMS calcd for M^+ $C_{15}H_{12}O_2$ 224, found 224.

2-(4-Bromophenyl)benzofuran (23)[22]

4-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and benzofuran (0.177 g, 1.5 mmol) affords **23** in 81% (0.221 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 154.9, 132.1, 129.5, 129.2, 126.5, 124.7, 123.2, 122.6, 121.2, 111.3, 102.0. LRMS calcd for M^+ $C_{14}H_9BrO$ 272, found 272.

1-Methyl-2-(4-nitrophenyl)pyrrole (24)[10a]

4-Nitrobenzenesulfonyl chloride (0.221 g, 1 mmol) and 1-methylpyrrole (0.243 g, 3 mmol) affords **24** in 92% (0.186 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 6.82 (m, 1H), 6.42 (dd, *J* = 3.4, 1.7 Hz, 1H), 6.25 (t, *J* = 3.4 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 139.7, 132.4, 128.1, 126.6, 124.0, 111.5, 108.9, 35.7. LRMS calcd for M^+ $C_{11}H_{10}N_2O_2$ 202, found 202.

2-(4-Methoxyphenyl)-1-methylpyrrole (25)[10a]

4-Methoxybenzenesulfonyl chloride (0.206 g, 1 mmol) and 1-methylpyrrole (0.243 g, 3 mmol) affords **25** in 71% (0.133 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.74 (m, 1H), 6.23 (t, *J* = 3.4 Hz, 1H), 6.20 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.89 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 134.4, 130.1, 126.0, 123.1, 113.9, 108.1, 107.6, 55.4, 35.0. LRMS calcd for M^+ $C_{12}H_{13}NO$ 187, found 187.

2-(3-Bromophenyl)-1-methylpyrrole (26)[25]

3-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and 1-methylpyrrole (0.243 g, 3 mmol) affords **26** in 87% (0.205 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.75 (s, 1H), 6.30-6.20 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.5, 133.1, 131.4, 130.0, 129.7, 127.1, 124.5, 122.5, 109.5, 108.1, 35.2. LRMS calcd for M^+ $C_{11}H_{10}BrN$ 235, found 235.

1-Benzyl-2-(4-nitrophenyl)pyrrole (27)[10a]

4-Nitrobenzenesulfonyl chloride (0.221 g, 1 mmol) and 1-benzylpyrrole (0.471 g, 3 mmol) affords **27** in 80% (0.222 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.40-7.26 (m, 3H), 7.04 (dd, *J* = 7.4, 1.6 Hz, 2H), 6.91 (dd, *J* = 2.7, 1.8 Hz, 1H), 6.49 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.37 (dd, *J* = 3.7, 2.7 Hz, 1H), 5.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 138.5, 137.0, 131.5, 127.9, 127.3, 126.7, 125.1, 124.8, 122.8, 110.6, 108.4, 50.1. LRMS calcd for M^+ $C_{17}H_{14}N_2O_2$ 278, found 278.

1-(4-Fluorophenyl)-2-(4-nitrophenyl)pyrrole (28)

4-Nitrobenzenesulfonyl chloride (0.221 g, 1 mmol) and 1-(4-fluorophenyl)pyrrole (0.483 g, 3 mmol) affords **28** in 74% (0.209 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 7.21-7.15 (m, 2H), 7.10 (t, *J* = 8.2 Hz, 2H), 7.00 (dd, *J* = 2.7, 1.7 Hz, 1H), 6.65 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.43 (dd, *J* = 3.6, 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, *J* = 248.0 Hz), 145.6, 138.9, 136.0 (d, *J* = 3.2 Hz), 131.6, 127.7, 127.3 (d, *J* = 8.5 Hz), 126.9, 123.6, 116.3 (d, *J* = 22.8 Hz), 113.3, 110.2. Anal. Calcd for $C_{16}H_{11}FN_2O_2$ (282.27): C, 68.08; H, 3.93; N, 9.92; found: C, 68.25; H, 3.99; N, 10.08.

3-(4-Nitrophenyl)selenophene (29)[10c]

4-Nitrobenzenesulfonyl chloride (0.221 g, 1 mmol) and selenophene (0.196 g, 1.5 mmol) affords **29** in 56% (0.141 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (dd, *J* = 2.5, 1.3 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 2H), 8.15 (dd, *J* = 5.5, 2.5 Hz, 1H), 7.71 (dd, *J* = 5.5, 1.3 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 143.3, 142.4, 132.2, 129.1, 128.9, 127.1, 124.4. LRMS calcd for M^+ $C_{10}H_7NO_2Se$ 253, found 253.

3-(4-Bromophenyl)selenophene (30)[10c]

4-Bromobenzenesulfonyl chloride (0.255 g, 1 mmol) and selenophene (0.196 g, 1.5 mmol) affords **30** in 70% (0.200 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 2.5, 1.3 Hz, 1H), 8.09 (dd, *J* = 5.5, 2.5 Hz, 1H), 7.63 (dd, *J* = 5.5, 1.3 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 136.2, 132.0, 131.4, 129.4, 128.3, 125.9, 121.1. LRMS calcd for M^+ $C_{10}H_7BrSe$ 286, found 286.

3-(4-Iodophenyl)selenophene (31)[10c]

4-Iodobenzenesulfonyl chloride (0.302 g, 1 mmol) and selenophene (0.196 g, 1.5 mmol) affords **31** in 77% (0.256 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.09 (m, 1H), 8.08 (dd, *J* = 5.5, 2.5 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.62 (dd, *J* = 5.5, 1.3 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.9, 136.8, 131.4, 129.3, 128.6, 126.0, 92.5. LRMS calcd for M^+ $C_{10}H_7ISe$ 334, found 334.

Supporting information

Copies of ^{1}H and ^{13}C NMR spectra of new compounds and ^{1}H NMR spectra of known compounds.

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