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Pyrrolylsulfonium salts: stable, accessible and versatile pseudohalides for Stille couplings†

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Pyrrolyl halides can be difficult to synthesise in a regioselective manner and are often unstable, which has hampered their application in cross-coupling. Here we introduce pyrrolylsulfonium salts as advantageous pseudohalide coupling partners and showcase their applicability in Stille couplings. Benefits of these salts include their straightforward synthesis *via* an "interrupted Pummerer" process, their high stability, and the ability to selectively introduce the sulfonium group at either the pyrrole α- or β- position as required. The Stille coupling has been demonstrated for aryl, heteroaryl and alkynylstannanes, and the effect of the pyrrole substituents on the regioselectivity of S–C bond activation has been investigated. Conditions to effect *N*-desulfonylation of *N*-trisyl coupling products have been identified.

Introduction

The pyrrole ring system is commonly found in organic materials,[1] as well as in natural products[2] and drug substances[3] (Fig. 1). For example, GS70 is a pyrrole-based electron acceptor which has been used to fabricate organic solar cells that can achieve high power conversion efficiencies,[4] P(DKPP-TPTH) is a pyrrole-containing polymer which has been used to construct organic field-effect transistors,[5] and OCF_3-BnPyV is a viologen-substituted pyrrole which has been used in electrochromic devices.[6] The natural products cycloprodigiosin[7] and heronapyrrole A[8] have immunosuppressant and antibiotic properties, respectively. The licensed drug vonoprazan[9] is a potassium-competitive acid blocker indicated for gastroduodenal ulcers and the investigational drug resminostat is in trials for oncology indications.[10]

Many synthetic strategies to access pyrrole-containing targets have been reported. These may be divided into *de novo* pyrrole syntheses[11] (where the pyrrole ring is formed with substituents already in place) and pyrrole functionalization approaches (where substituents are introduced onto a pre-existing pyrrole ring). In this latter category, S_EAr and pyrrole metalation protocols are well developed.[12] Transition metal-catalysed cross-couplings have also been studied for pyrrole functionalization,[13] although some shortcomings remain to be overcome. For example, the use of pyrrolyl halides as classical electrophilic cross-coupling partners may be hindered by difficulties of synthetic access and/or instability. Thus, halogenation of *N*-H pyrrole or simple *N*-alkyl/*N*-aryl derivatives with a variety of electrophilic halogen sources reportedly often leads to complex mixtures of mono- and polyhalopyrroles. Moreover, the parent *N*-H-2-halopyrroles are markedly unstable, decomposing upon attempted isolation (Scheme 1a).[14,15] Selectivity for halogenation at C2 *vs.* C3 can also vary depending on the substrate and synthetic method, and separation is usually challenging. Whilst *N*-halosuccinmides can exhibit good selectivity for halogenation at **C2** over **C3**, overreaction to the 2,4-dihalopyrrole can occur.[14] To access 3-halopyrroles, an acid-mediated isomerization ("halogen dance") of the 2-halo isomer can sometimes be employed, but this can also induce a degree of disproportionation (Scheme 1b).[14,16] Halopyrroles substituted with electron-withdrawing groups can be more stable in some cases. For example, pyrroles bearing a carbonyl at **C2** generally undergo electrophilic halogenation to give stable products, but regioselectivity between **C4** and **C5** depends on the halogenating agent and on the nature of the carbonyl (Scheme 1c).[15,16a,17] Alternatively, use of an electron-withdrawing protecting group on nitrogen can sometimes increase stability. For example, considering bromopyrroles specifically, *N*-Boc-2-bromopyrrole[18] can reportedly be stored as a solution in hexane at −10 °C,[19] and *N*-tosyl-2-bromopyrrole[20] is stable in pure form. *N*-Tosyl-3-bromopyrrole may be synthesized by treating *N*-tosylpyrrole with Br_2 under acidic conditions,[21] and *N*-Boc-3-bromo-

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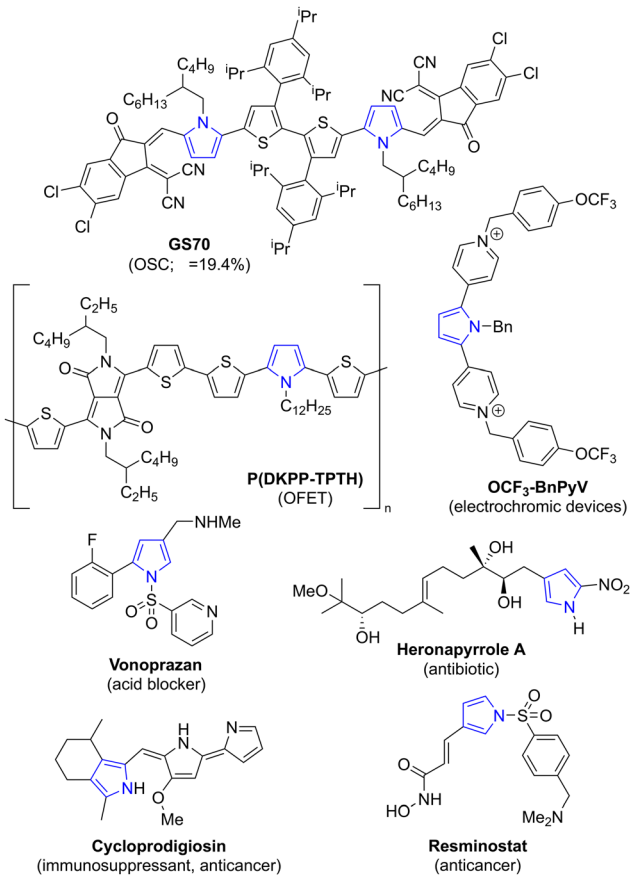
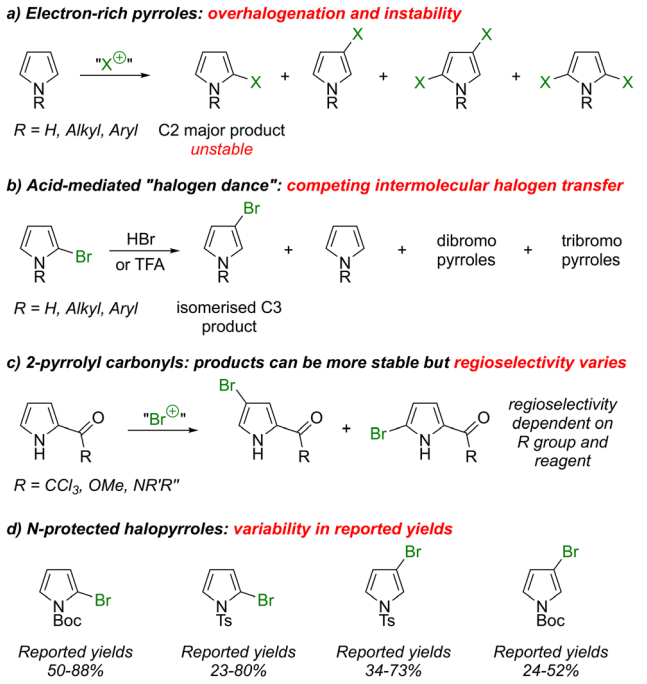


Fig. 1 A selection of pyrrole-containing molecules.

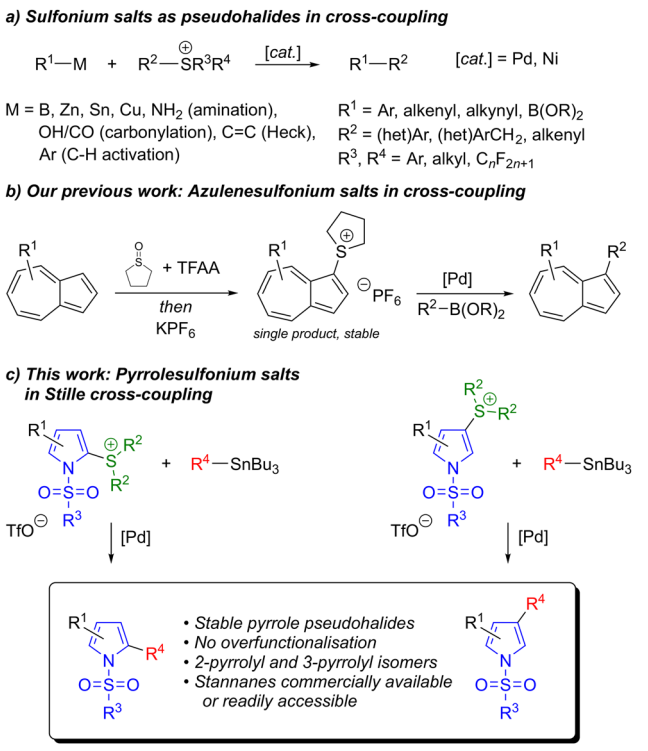
pyrrole is synthesized from *N*-TIPS-3-bromopyrrole by protecting group exchange[22] (Scheme 1d). However, all of these examples have in common that the yields reported for their preparation (by the same procedure) vary appreciably.

Whilst some cross-couplings of halopyrroles such as those in Scheme 1 have been reported,[23] their more widespread utilisation has been hampered by the issues described above. An alternative approach is the use of a pyrrole pseudohalide for cross-coupling. Thus far, there are some examples of pyrrole triflates being used as pseudohalides in cross-couplings,[24] primarily in natural product total synthesis, but the preparation of the substrates has not been generalised. Pyrrole C–H functionalisation approaches have also been developed, each with varying scope in substrate, coupling partner, catalyst, *etc.*[25]

Sulfonium salts have become established as pseudohalides that can have advantages over classical halide coupling partners. Cross-coupling of sulfonium salts was first reported by Liebeskind *et al.*,[26] who demonstrated Stille, Suzuki–Miyaura and Negishi couplings with aryl, heteroaryl, alkenyl and benzyl sulfonium salts. Since then the scope of sulfonium salt cross-coupling has been expanded to include various other nucleophilic coupling partners, carbonylative couplings, reductive cross-electrophile couplings, *etc.*, employing both Pd and Ni (Scheme 2a).[27,28] Sulfonium salts are also synthetically useful in other contexts, and their chemistry has been reviewed.[29] We previously reported the synthesis of azulenesulfonium salts and their use in cross-coupling.[30] These salts proved superior to azulene halides in terms of their stability and ease of syn-



Scheme 1 Stability and selectivity problems in the formation of halopyrroles.



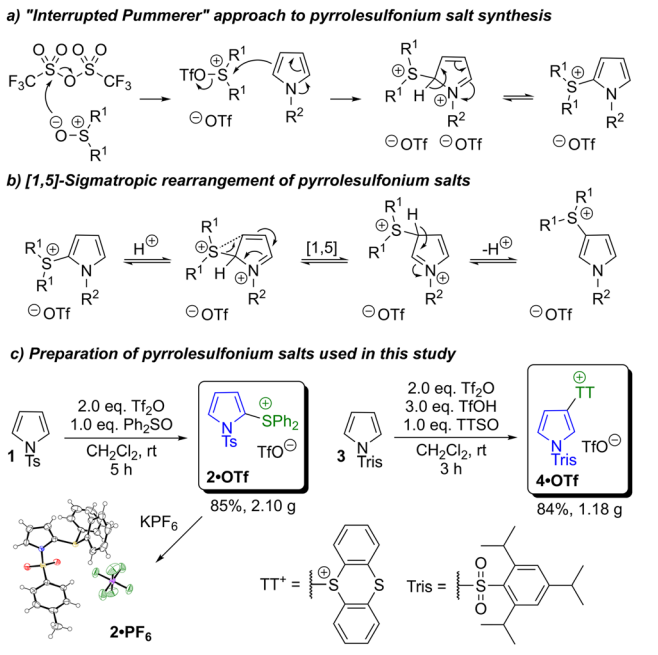
Scheme 2 Sulfonium salts are competent pseudohalides in cross-coupling.

thesis. Synthesis of azulene halides by S_EAr reaction on the electron-rich five-membered ring typically leads to overhalogenation, and the products are unstable (unless electron-withdrawing groups are also present). In contrast azulenesulfonium salts may be synthesised in good yield, as the sole products, and are stable without any special handling/storage precautions (Scheme 2b). The cationic sulfonium substituent serves to reduce the electron density of the aromatic system, thereby imparting stability. We recognised that many of the drawbacks of azulene halides (instability, difficulty of synthesis/purification) were shared with pyrrolyl halides, which also comprise an electron-rich five-membered aromatic ring. Therefore we sought to develop pyrrolylsulfonium salts for use in cross-coupling, anticipating that they would share the advantages of azulenesulfonium salts. The results of these studies are reported here (Scheme 2c). Pyrrolylsulfonium salts are known,[31] but to date they have been primarily used as radical precursors, in sigmatropic rearrangements or as substrates for dealkylation to give pyrrolyl thioethers.

Results and discussion

Aryl sulfonium salts can be synthesised by various approaches, including reaction of aryl thiols/thioethers with electrophiles, or activation of sulfoxides and attack by nucleophiles.[29j] For the synthesis of pyrrolylsulfonium salts we opted to employ an "interrupted Pummerer" reaction,[32] wherein a sulfoxide is activated by an acid anhydride, followed by attack at sulfur by a nucleophilic (*i.e.* electron-rich) arene, loss of an oxygen leaving group and rearomatisation (Scheme 3a). In Pummerer reactions the sulfoxide is most commonly activated with a carboxylic acid anhydride, but in this case we employed a sulfonic acid anhydride (specifically triflic anhydride). This was due to our previous findings that use of a carboxylic acid anhydride can promote an alternative reaction pathway affording Δ^3-pyrrol-2-one products.[33]

A key advantage of pyrrolylsulfonium salts as reagents for cross-coupling is easy access to both the 2-pyrrolyl and 3-pyrrolyl regioisomers. The interrupted Pummerer process typically installs the sulfonium salt at the 2-position, in keeping with the established S_EAr reactivity of pyrrole. This product may then be isomerised to the 3-pyrrolylsulfonium salt *via* a Brønsted acid-catalysed [1,5]-sigmatropic rearrangement (Scheme 3b).[31b–d] Analogous migrations of various other functional groups on the pyrrole ring have been reported,[34] although stability of the substrates to the highly acidic reaction conditions varies. In contrast, pyrrolylsulfonium salts are robust under these conditions and may be isomerised in high yield. Furthermore the interrupted Pummerer/rearrangement reaction cascade may be performed as a one-pot process. We prepared and screened multiple pyrrolylsulfonium salts to identify optimal reagents for cross-coupling that (a) are easily prepared in good yield on gram scale; (b) exhibit good stability; (c) have good solubility in the solvents to be used for cross-coupling; and (d) undergo oxidative addition into the correct C–S bond. From this screening we identified the novel salt diphenyl (*N*-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)sulfonium triflate **2·OTf** as an ideal reagent for the preparation of 2-substituted pyrroles, which was prepared on a gram scale (Scheme 3c). Reaction workup involved straightforward partitioning between MeCN and hexane,[35] followed by recrystallisation from methanol. The reaction generates an equivalent of triflic acid as a byproduct, which might be expected to catalyse the [1,5]-sigmatropic rearrangement shown in Scheme 3b. However, we found the specific combination of *N*-tosyl and diphenyl sulfonium substituents disfavoured the rearrangement under these reaction conditions, and hence 2-pyrrolyl (non-rearranged) salt **2·OTf** could be isolated in 85% yield. In contrast, we found that thianthrenium salts underwent the rearrangement more readily and that additional triflic acid facilitated the process. Formation of the 3-pyrrolylthianthrenium salt with an *N*-tosyl protecting group occurred in variable yield and the product was only sparingly soluble. Switching to a more sterically demanding *N*-trisyl group improved product solubility and rendered the synthesis reproducible and also scalable to gram scale. We thus identified the novel 5-(*N*-(2,4,6-triisopropylphenylsulfonyl)-1*H*-pyrrol-3-yl)-5*H*-thianthrenium triflate **4·OTf** as an ideal reagent for the preparation of 3-substituted pyrroles (Scheme 3c). Amongst the various sulfonium groups used as synthetic handles in the literature, the thianthrenium group has been extensively exploited due to its particular properties.[36–38] For example, its introduction onto an aromatic ring typically proceeds in an exceptionally regioselective manner.[28,39] In the case of *N*-trisyl pyrrole, NMR studies indicate that the initial thianthrenation affords a mixture of **4·OTf** and its 2-pyrrolyl regioisomer. This then



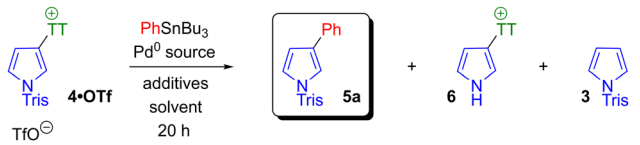
Scheme 3 Synthesis of sulfonium salts by "interrupted Pummerer" reaction and their isomerisation by [1,5]-sigmatropic rearrangement. TTSO = thianthrene-*S*-oxide.

undergoes rearrangement to **4·OTf**, such that after 3 hours **4·OTf** is the only product present.[31m,o] Introduction of a bulky group at nitrogen is known to favour 3-substituted products in pyrrole S_EAr reactions.[22]

To establish the applicability of pyrrolylsulfonium salts **2·OTf** and **4·OTf** in cross-coupling, we employed them as pseudohalides in the Migita–Kosugi–Stille coupling.[40,41] Examples of pyrrolyl halide Stille couplings are known,[42] although competing dehalogenation can reportedly be significant in some cases.[23p] Organostannanes are advantageous coupling partners due to their stability to air and moisture, as well as their availability from commercial sources or through straightforward syntheses.[43] The robust nature of the Stille coupling and its efficiency under mild reaction conditions mean it has proven successful in many instances where other cross-coupling methodologies have failed.[44] Whilst the (variable) toxicity of organostannanes[45] necessitates the thorough removal of tin residues from active pharmaceutical ingredients prepared through Stille coupling, methods to achieve this are well developed.[46]

We selected phenyltributylstannane as an archetypal aryl stannane reagent for reaction optimisation. Reaction parameters were varied as shown in Scheme 4 and Table 1. Initial attempts using $Pd(PPh_3)_4$ and 1.3 equivalents of stannane showed the coupling was viable in DMF, toluene and *t*-butanol (entries 1–3). Desired product **5a** formed in each case, with the highest conversion in DMF. Formation of byproducts was also observed, either as a result of *N*-sulfonyl group cleavage (giving **6**) or reductive cleavage of the thianthrenium group (giving **3**). This latter process is analogous to the dehalogenation sometimes observed with classical halide substrates. The beneficial effects of copper salt additives on Stille couplings are well documented,[47] so we evaluated the effect of CuI as an additive in DMF and toluene (entries 4 and 5), but no improvement in conversion was observed. Fluoride salts are also known to promote Stille couplings,[48] and synergistic effects arising from the presence of both copper and fluoride salts have been reported.[49] Multiple conditions including caesium fluoride as an additive were evaluated (entry 6), but formation of desired product **5a** was negligible in each case, with *N*-sulfonyl cleavage dominating instead to give **6**. Use of an alternative Cu(I) source did not increase conversion to **5a** (entries 7–10). Use of triphenylarsine as ligand[50] in conjunction with $Pd_2(dba)_3$ as palladium source in DMF gave greater conversion to **5a** (entries 11–15). Reaction temperature could be lowered to 50 °C without a reduction in conversion, and 2 mol% loading of $Pd_2(dba)_3$ (*i.e.* 4 mol% of Pd) was identified as optimal. Finally, a change in reaction stoichiometry to 2.2 equivalents of stannane increased conversion to 84% of **5a** and suppressed formation of byproducts **3** and **6** (entry 15).

An analogous reaction optimisation was carried out for the coupling of phenyltributylstannane with 2-pyrrolyl sulfonium salt **2·OTf**. Reaction parameters were varied as shown in Scheme 5 and Table 2. An initial attempt using $Pd(PPh_3)_4$ in DMF showed the coupling to be viable, with desired 2-phenylpyrrole **7a** forming in moderate yield (entry 1). Three byproducts were also identified, namely the *N*-sulfonyl cleavage product **8**, the sulfonium reductive cleavage product **1** and the parent pyrrole **9**. This latter byproduct (which was not observed in the coupling of **4·OTf**) presumably arises from *N*-sulfonyl cleavage from **1**, highlighting the greater stability of



Scheme 4 Stille coupling of **4·OTf** to form desired 3-phenylpyrrole **5a** and byproducts **6** and **3**.

Table 1 Optimisation of Stille coupling of 3-pyrrolyl thianthrenium salt **4·OTf**

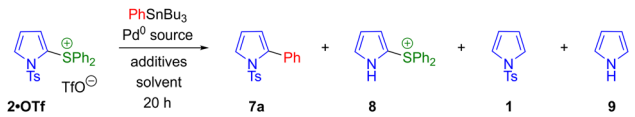
Entry	Pd(0) source	$PhSnBu_3$ (equiv.)	Additive	Ligand	Solvent	Conc. (M)	Temp. (°C)	Conv.% **5a**	Conv.% **6**	Conv.% **3**
1	$Pd(PPh_3)_4$ (4 mol%)	1.3	—	—	DMF	0.12	110	64	<5	7
2	$Pd(PPh_3)_4$ (4 mol%)	1.3	—	—	Toluene	0.12	110	58	23	10
3[a]	$Pd(PPh_3)_4$ (4 mol%)	1.3	—	—	^{t}BuOH	0.12	80	38	—	6
4	$Pd(PPh_3)_4$ (4 mol%)	1.3	CuI (16 mol%)	—	DMF	0.12	110	38	<5	8
5	$Pd(PPh_3)_4$ (4 mol%)	1.3	CuI (16 mol%)	—	Toluene	0.12	110	50	—	6
6	$Pd(PPh_3)_4$ (4 mol%)	1.3	CsF (2.2 eq.) with/without CuI	—	DMF/ toluene	0.12	80–110	<5	10–50	<5
7	$Pd(PPh_3)_4$ (4 mol%)	1.3	Cu(OTf)·Tol (16 mol%)	—	Toluene	0.12	110	46	<5	5
8	$Pd(PPh_3)_4$ (8 mol%)	1.3	Cu(OTf)·Tol (16 mol%)	—	Toluene	0.12	85	24	8	5
9	$Pd(PPh_3)_4$ (4 mol%)	1.3	Cu(OTf)·Tol (16 mol%)	—	Toluene	0.12	80	44	16	6
10	$Pd(PPh_3)_4$ (4 mol%)	1.3	Cu(OTf)·Tol (16 mol%)	—	Toluene	0.07	110	47	16	10
11	$Pd_2(dba)_3$ (2 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	0.12	80	71	6	5
12	$Pd_2(dba)_3$ (2 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	0.12	50	70	3	6
13	$Pd_2(dba)_3$ (1 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	0.12	50	57	—	21
14	$Pd_2(dba)_3$ (4 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	0.12	50	69	5	10
15	**$Pd_2(dba)_3$ (2 mol%)**	**2.2**	—	**$AsPh_3$ (16 mol%)**	**DMF**	**0.12**	**50**	**84**	—	—

Conversions obtained from crude ^{1}H-NMR spectra by comparison to an internal standard (mesitylene). Cu(OTf)·Tol = copper(I) trifluoromethanesulfonate–toluene complex. [a] 13% of starting material **4** remained.

Table 2 Optimisation of Stille coupling of 2-pyrrolyl sulfonium salt **2·OTf**

Entry	Pd(0) source	$PhSnBu_3$ (equiv.)	Additive	Ligand	Solvent	Temp. (°C)	Conv% **7a**	Conv% **8**	Conv% **1**	Conv% **9**
1	$Pd(PPh_3)_4$ (4 mol%)	1.3	—	—	DMF	80	31	6	23	7
2	$Pd(PPh_3)_4$ (4 mol%)	1.3	CsF (2.2 eq.) Cu(OTf)·Tol (16 mol%)	—	DMF/ toluene	50–110	Trace	20–60	Trace	—
3	$Pd_2(dba)_3$ (2 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	50	64	14	15	—
4	$Pd_2(dba)_3$ (4 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	50	58	6	16	—
5	$Pd_2(dba)_3$ (2 mol%)	1.3	—	$AsPh_3$ (16 mol%)	DMF	80	53	10	18	—
6	$Pd_2(dba)_3$ (2 mol%)	1.3	CuI (16 mol%)	$AsPh_3$ (16 mol%)	DMF	50	24	16	25	6
7	$Pd_2(dba)_3$ (2 mol%)	1.3	CuI (16 mol%)	$AsPh_3$ (16 mol%)	DMF	25	7	—	12	3
8	**$Pd_2(dba)_3$ (2 mol%)**	**2.2**	—	**$AsPh_3$ (16 mol%)**	**DMF**	**50**	**74**	4	3	—

Conversions obtained from crude ^{1}H-NMR spectra by comparison to an internal standard (mesitylene). Cu(OTf)·Tol = copper(I) trifluoromethanesulfonate–toluene complex.



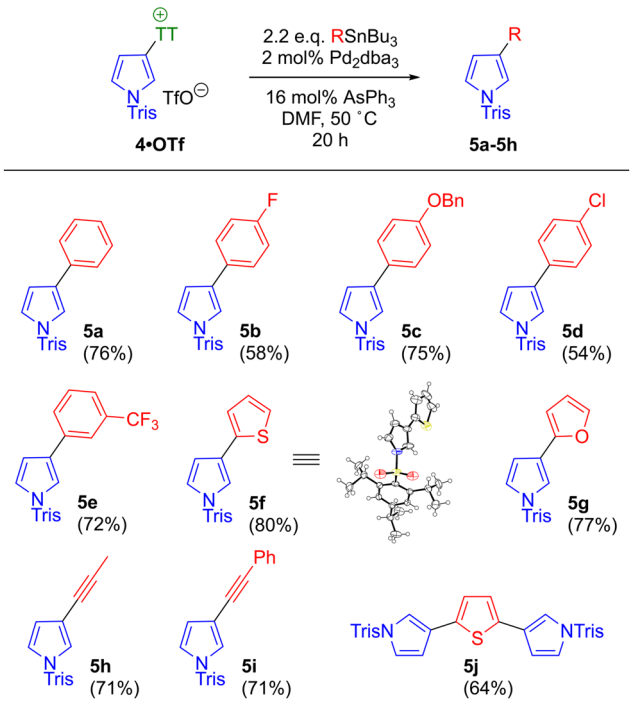
Scheme 5 Stille coupling of **2·OTf** to form desired 2-phenylpyrrole **7a** and byproducts **8**, **1** and **9**.

the *N*-trisyl group compared to *N*-tosyl.‡ Use of a fluoride additive with a copper(I) source was once again unproductive (entry 2). Use of $AsPh_3/Pd_2(dba)_3$ in DMF proved superior to the $Pd(PPh_3)_4$ system, and no increase in conversion was observed when the loading of $Pd_2(dba)_3$ was increased beyond 2 mol% or the temperature was increased beyond 50 °C (entries 3–5). With this palladium/ligand combination, copper(I) additives again proved deleterious (entries 6 and 7). However, a change in reaction stoichiometry to 2.2 equivalents of stannane was beneficial (as was the case for the coupling of **4·OTf**), increasing conversion to 74% of **7a** and minimising byproduct formation.

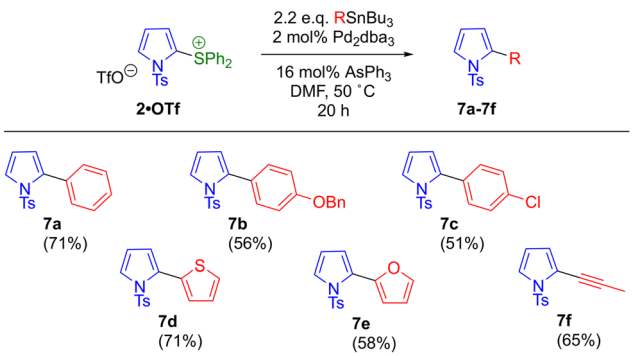
With optimised conditions in hand for the coupling of both salts, substrate scope for the couplings was examined using a range of commercially available stannanes. For the coupling of **4·OTf** (Scheme 6), both (substituted) phenyl (**5a–5e**) and heteroaryl (**5f–5g**) products were isolated in good yield. In the formation of chlorophenyl pyrrole **5d**, no evidence was seen of unwanted C–Cl bond activation in the product.[51] Alkynyl stannanes were also competent coupling partners (**5h–5i**). Use of a bis(stannyl)thiophene effected a double coupling to give **5j**. To the best of our knowledge, the heteroaryl triad in **5j** with this particular connectivity (2,5-bis(3-pyrrolyl)thiophene) is a previously unknown structural motif outside the field of porphyrin chemistry.[52]

For the coupling of **2·OTf** (Scheme 7), here also (substituted) phenyl (**7a–7c**), heteroaryl (**7d–7e**) and alkynyl (**7f**) products were accessible in good to moderate yield.

‡An alternative explanation for the formation of **9** would be by reductive cleavage of the sulfonium group from **8**. However, this appears less likely since if the reductive cleavage occurs by Pd-mediated S–C bond activation in the first step, then in **8** this would be expected to favour the S–Ph bond over the S–pyrrole bond, on the basis of the results shown in Scheme 9.



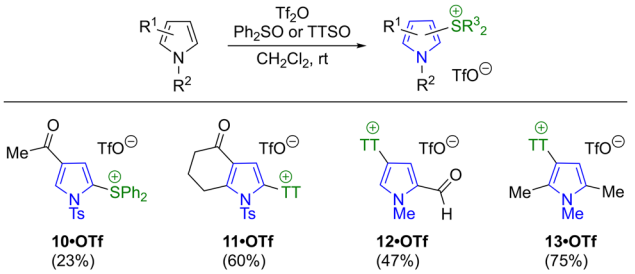
Scheme 6 Coupling of **4·OTf** with a range of stannanes. Yields in parentheses are isolated yields.



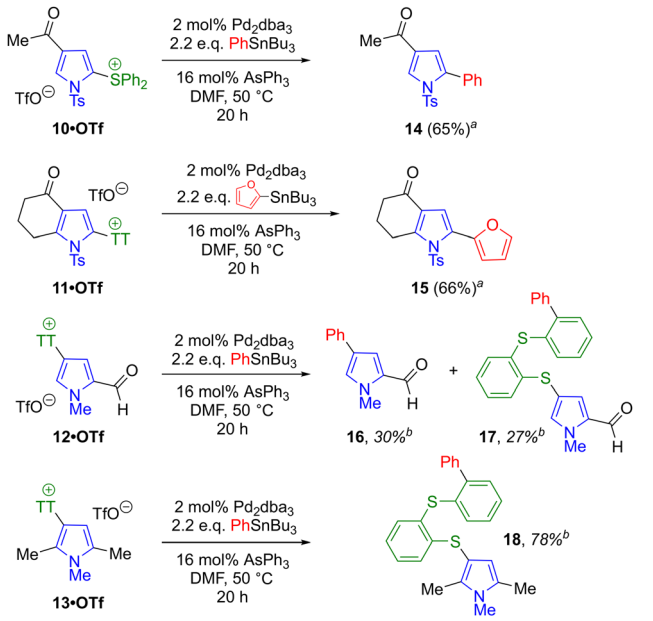
Scheme 7 Coupling of **2·OTf** with a range of stannanes. Yields in parentheses are isolated yields.

Preparation of sulfonium salts from C-substituted pyrroles was next attempted (Scheme 8). An *N*-tosyl pyrrole bearing a methyl ketone formed diphenylsulfonium salt **10·OTf** in low yield, along with byproducts potentially arising from enol triflate formation, although **10·OTf** was nevertheless isolable in pure form after chromatography. In contrast, a similar ketone-bearing substrate formed thianthrenium salt **11·OTf** in a much better yield. Here, the presence of electron-withdrawing groups at both N1 and C3 seemingly disfavours the migration of the sulfonium group. Pyrrole substrates lacking *N*-sulfonyl protection were also examined, with salts **12·OTf** and **13·OTf** forming from the corresponding *N*-methyl pyrroles. Salt **13·OTf** is the only regioisomer that can form from the corresponding substrate (1,2,5-trimethylpyrrole). However, **12·OTf** forms from 2-formyl-*N*-methylpyrrole, which has 3 potential sites of attachment. As such, the exclusive isolation of the product with the thianthrenium group at C4 is noteworthy, given that the regioselectivity of S_EAr reactions on 2-pyrrolyl carbonyls can vary (see Scheme 1c).

The successful cross-coupling of salts **2·OTf** and **4·OTf** requires that the initial oxidative addition step of the catalytic cycle is selective for the correct S–C bond. That is to say, palladium must insert into the bond between sulfur and the pyrrole ring, and not into a bond between sulfur and a phenyl ring (of the diphenyl sulfonium or thianthrenium group). During optimisation of the coupling conditions and during preparation of the products in Schemes 6 and 7, only products arising from activation of the correct S–C bond were isolated, and no products from coupling at the "wrong" S–C bond were ever detected. To determine the structural motif(s) responsible for regioselectivity in S–C bond activation, sulfonium salts from Scheme 8 were cross-coupled under the established conditions. Results with **2·OTf** and **4·OTf** indicate that with a sulfonium group at either C2 or C3, when the only other substituent is an electron-withdrawing (sulfonyl) group at N1, the desired regioselectivity is observed. Salts **10·OTf** and **11·OTf** are both substrates with a sulfonium handle at C2 as well as electron-withdrawing groups at N1 and C4. Coupling of **10·OTf** with $PhSnBu_3$ led to isolation of **14** and coupling of **11·OTf** with 2-furyl-$SnBu_3$ led to isolation of **15** as the sole product in each case (Scheme 9), illustrating that the desired regioselectivity is observed in this scenario also. In contrast, salt **12·OTf** possesses a sulfonium handle at C4 and an electron-withdrawing group at C2, but lacks an electron-withdrawing group at N1. This salt underwent the coupling to give two products in approximately equal conversion, namely the desired product **16** and the product arising from ring cleavage of the thianthrenium motif, **17**. Under the same reaction conditions, salt **13·OTf** (lacking any electron-withdrawing groups) formed only the thianthrene ring cleavage product **18**, in high conversion.

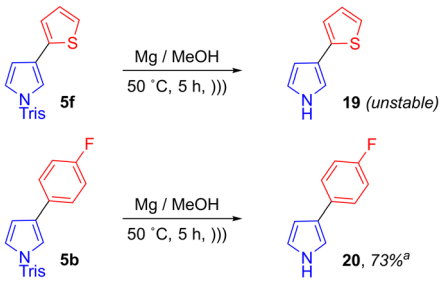


Scheme 8 Synthesis of sulfonium salts from substituted pyrroles. TTSO = thianthrene-*S*-oxide. Yields in parentheses are isolated yields.

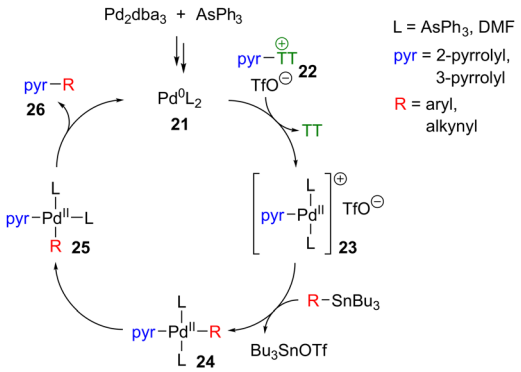


Scheme 9 Coupling of C-substituted pyrrolylsulfonium salts. [a]Isolated yield. [b]Conversion by ^{1}H-NMR.

Formation of the products depicted in Scheme 9 highlights the role of the *N*-sulfonyl group in ensuring that the desired regioselectivity in the S–C bond activation step is achieved. Therefore, since pyrrolylsulfonium couplings of the type reported here are likely to be carried out on *N*-sulfonyl substrates specifically, we investigated removal of the *N*-sulfonyl group from selected coupling products. For *N*-tosyl pyrroles of the type shown in Scheme 7, conditions for *N*-deprotection are widely reported in the literature using, for example, sodium hydroxide in ethanol.[20a–c] However for *N*-trisyl pyrroles of the type shown in Scheme 6, the additional steric bulk renders the *N*-sulfonyl group much more resistant to removal. Attempted deprotection of thienylpyrrole **5f** under basic hydrolysis conditions (NaOH/MeOH/Δ) led to recovery of starting material. A reported procedure for *N*-sulfonyl cleavage using triflic acid led to decomposition.[53] Attempts at reductive S–N bond cleavage using SmI_2 or complexes thereof also returned starting material.[54] However, use of Mg in MeOH at 50 °C under sonication[55] was successful at removing the *N*-trisyl group to give 3-(2-thienyl)pyrrole **19**. Instability of this substance in air or upon attempted purification hampered quantitation of its formation. Therefore a less electron-rich *N*-trisylpyrrole was selected for deprotection (*p*-fluorophenyl product **5b**). The resultant deprotection product **20** exhibited greater stability



Scheme 10 *N*-Deprotection of *N*-trisylpyrroles. [a]Conversion by ^{1}H-NMR.



Scheme 11 Proposed mechanistic cycle for pyrrolylsulfonium Stille couplings.

than **19**, and it was determined to have formed in 73% conversion (Scheme 10).

A possible mechanism for a representative pyrrolylsulfonium Stille coupling is depicted in Scheme 11. The Pd^0 active catalyst **21** will engage in oxidative addition into the C–S bond of a pyrrolylsulfonium salt such as **22** to give Pd^{II} complex **23**. Whereas oxidative addition with a classical halide coupling partner would form a neutral Pd^{II} complex with a Pd–X bond, we propose that use of pyrrolylsulfonium pseudohalide **22** may instead lead to a cationic tricoordinate complex of type **23**. In the specific case of thianthrenium salts, Ritter *et al.* have presented evidence that thianthrene ("TT") is notably non-coordinating towards Pd^{II} complexes (less coordinating than triflate),[56] although this may not necessarily apply for other sulfonium salts such as the diphenylsulfonium salts **2·OTf** and **10·OTf**. Transmetallation with the stannane reagent would afford tetracoordinate **24**, which after isomerisation could undergo reductive elimination to give product **26**. DMF is reportedly a non-innocent solvent in Stille couplings, and transmetallation can occur from a Pd^{II} complex in which DMF occupies a coordination site (*i.e.* L = DMF).[50b] Accordingly we do not speculate as to the specific identity of the "L" substituents in each of the complexes in Scheme 11. The mechanism shown is most likely a simplification of the true process, which may vary depending on the nature of the pyrrolylsulfonium salt and stannane used.[40b,57] Accordingly the mechanism of this process merits further study.

Conclusions

We have described the straightforward synthesis of multiple pyrrolylsulfonium salts and demonstrated their applicability as pseudohalides in Stille couplings. The approach used for the synthesis of these salts allows for their regioselective installation at either the pyrrole α- or β-position, through the choice of appropriate sulfonium substituents and reaction conditions for the pyrrole in question. The salts are formed in good yield and exhibit good stability, and the synthesis is not prone to overfunctionalisation; these are all significant advantages over the classical pyrrolyl halide coupling partners. Additionally, we have identified reaction conditions that are able to effect the Stille coupling of the pyrrolylsulfonium salts with a range of (hetero)aryl- and alkynyl-stannanes. When the pyrrolylsulfonium salt possesses an *N*-sulfonyl substituent, cross-coupling occurs at the desired S–C bond only. The sulfide byproduct is therefore recoverable and could be recycled for the synthesis of additional pyrrolylsulfonium salt, if required. Both the *N*-tosyl and *N*-trisyl groups have been shown to be removable subsequent to the coupling step. Furthermore, variants of this methodology may be applicable to other heterocycles. For example, while Stille couplings of other arylthianthrenium salts are unknown so far, we note that indolyl thianthrenium salts have been reported.§ For the reasons listed above we anticipate that the methodology described here may find applications in various synthetic contexts.

Author contributions

S.E.L. and J.L.H. conceived the project. J.L.H. carried out the synthesis. C.L.L. and J.L.H acquired and interpreted NMR data. G.K.-K. carried out X-ray crystallography. S.E.L. wrote the manuscript with input from all authors.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for **2·PF$_6$** and **5f** have been deposited at the CCDC under 2382855 and 2382856.†

Conflicts of interest

There are no conflicts to declare.

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§The synthesis of indol-3-ylthianthrenium tetrafluoroborate is reported in the ESI† for ref. 39.

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