

Preparation of Organostannanes by Intermolecular Radical Substitution Reactions

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Abstract: A new approach to the synthesis of aromatic stannanes *via* novel radical substitution reaction of aromatic sulfones is presented. Thus, α -heterocyclic aromatic sulphones derived from indole, pyrrole, pyrazole, furans and thiophenes undergo rapid and high yielding *ipso*-substitution to furnish organostannanes. This methodology has been extended to β -heterocyclic aromatic sulfones derived from indoline and dibenzofuran. The methodology has some limitations as shown in the lack of reactivity of 3-phenylsulfonyl indole derivative **17** and some phenylthio-substituted heteroaromatic systems **22-24**. Phenylsulfinyl substituted indoles can also undergo the desired substitution reaction as shown in the successful transformation of **25** to the corresponding stannane **4a**.

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Introduction

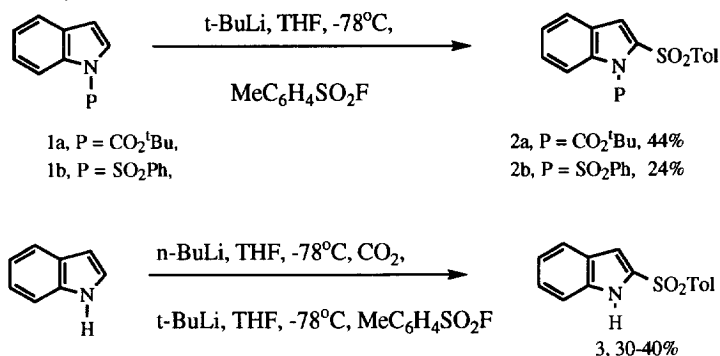
Free-radicals have gained widespread use in organic synthesis and in particular the development of a large number of cyclization reactions has led to a proliferation in the utilisation of these intermediates in natural product and target-synthesis.¹ Many of the advantages associated with these reactions stem from the mild and neutral conditions under which these transformations proceed. As part of our interest in free-radical based reactions for organic synthesis we have been examining a range of unimolecular² and bimolecular substitution reactions as methods for preparing heterocyclic aromatic compounds. We have been particularly interested in using such an approach for the synthesis of substituted aromatic compounds and have recently developed a new approach to heteroaromatic stannanes.³ The synthetic versatility of aromatic stannanes lies in their ability to undergo a range of interesting and valuable transformations; of particular note is the palladium catalysed cross-coupling technology pioneered by Stille and co-workers.⁴ Herein we provide further details of the radical substitution method for preparing aromatic stannanes with some indication of the scope and limitation of the process.

Results and Discussion

Our initial work was directed toward examining the *ipso*-substitution reaction of 2-tolylsulfonyl-indoles as a possible method for preparing 2-indolyl-stannanes. There were two reasons for this: the first was to evaluate the feasibility of the transformation; and the second to illustrate its applicability to a class of compounds which may be useful for preparing functionalised indoles. Subsequent to initial reports^{5,6,7} on the preparation of these compounds, a number of workers have reported the use of such stannanes for the preparation of functionalised indoles.⁸

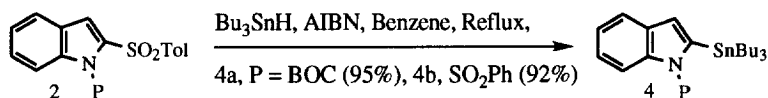
Although the transmetalation approach generally used is a more direct route to aryl stannanes we believed that by gaining a greater understanding of the radical substitution reaction we would be able to develop a complementary method for their preparation. Certainly the ability to transform an aromatic sulfone into an aromatic stannane would be a useful transformation given the ready availability of the former and the sensitivity of the latter.⁹ The mild conditions utilised in the formation of the stannane under radical conditions are also likely to be more compatible with highly functionalised synthetic precursors than those associated with existing procedures.

We prepared the desired sulfones **2a,b** *via* an intermediate lithio-species; the use of tosyl chloride to introduce the sulfone moiety is known to proceed to give the chloride¹⁰ and demands the use of tosyl fluoride or anhydride.¹¹ The yields, which have not been optimised were moderate, therefore we developed an alternative and more direct approach by protection of 2-tosyl-indole¹² **3** which is available directly from indole *via* the Katritzky reaction (scheme 1).¹³



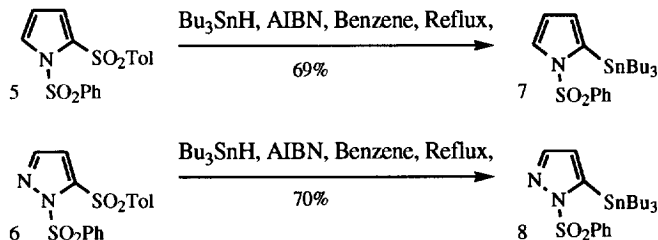
Scheme 1

We found that treatment of these compounds with tri-*n*-butyltin hydride led to the isolation of the desired stannanes **4a,b** in good yields; the stability of the stannanes to the reaction conditions is a testament to the mildness of the reaction conditions (scheme 2).



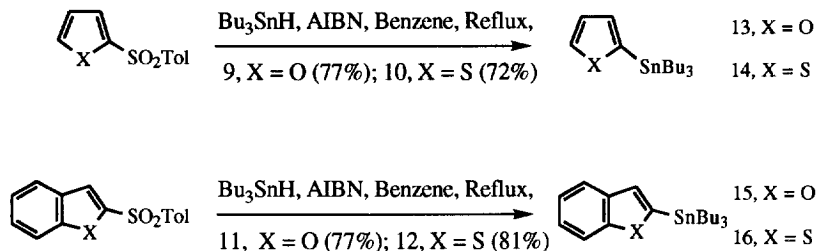
Scheme 2

We then decided to explore this substitution reaction a little further and prepared the pyrrole and pyrazole sulfones **5** and **6** *via* lithiation/sulfonation of the parent heterocycles.¹⁴ The radical displacements proceed to give the organostannanes **7** and **8** in good yields (scheme 3).



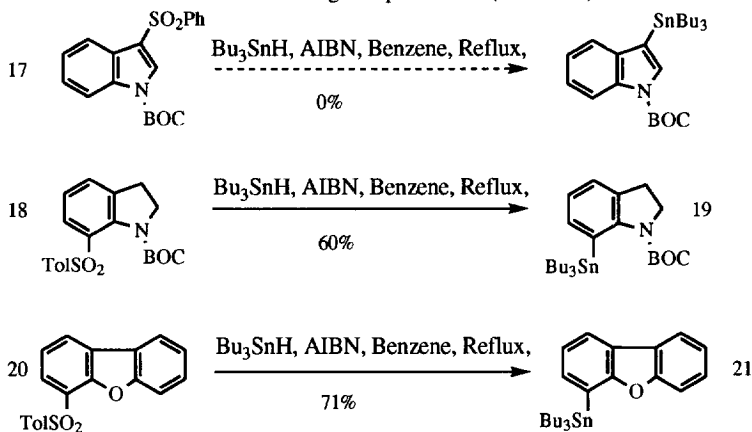
Scheme 3

In order to extend this methodology to other heteroaromatic systems we prepared oxygen and sulfur heterocyclic sulfones **9**, **10**, **11** and **12** by the lithiation/sulfonation approach in unoptimised yields. All of these compounds subsequently participated in the radical substitution reaction providing **13-16** in reasonable yields, illustrating that this substitution has some generality for commonly encountered heterocyclic systems (scheme 4).



Scheme 4

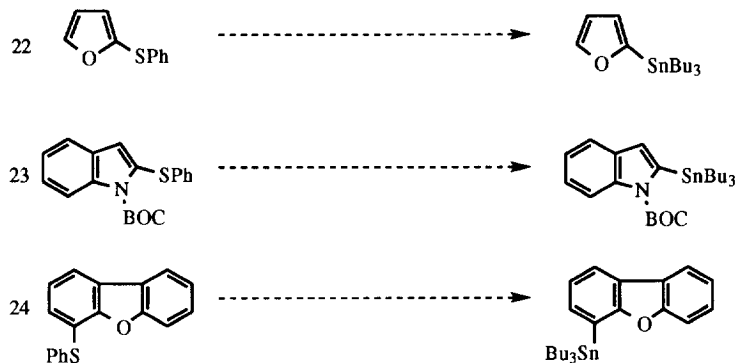
The examples described thus far involve *ipso*-substitution of an α -heterocyclic aryl sulfone and we sought to further examine the scope of the process. We found that the 3-phenylsulfonyl-indole derivative **17** did not participate in the substitution and the only products isolated from these investigations were either the starting sulfone or, with prolonged heating, complex unidentifiable mixtures. However, in contrast we found that the indoline-sulfone **18**,¹² prepared *via* regioselective lithiation of Boc-indoline as described by Beak,⁵ underwent smooth substitution to give **19** in reasonable yield.¹⁵ Thus β -sulfonyl-substituted heterocycles can undergo substitution and it was encouraging to note the successful displacement using dibenzofuran sulfone **20** to give **21**. However it appears that there may be some limitations with β -heteroatom substituents as illustrated in the failure of sulfone **17** to undergo displacement (scheme 5).



Scheme 5

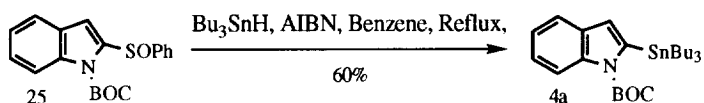
In order to further examine the types of functional group which will participate in the substitution reaction we also examined phenylthio-substituted heterocycles **22**, **23** and **24**. None of these precursors reacted as desired; unidentifiable mixture of products were isolated, although we were usually able to detect some phenylthiotributylstannane in these reactions (scheme 6). We were never able to isolate any of the "reduced" heteroaromatic portion, indeed in the indole case which we attempted on numerous occasions, we were unable to account for the indole fragment. This is particularly surprising, in view of the elegant work of

Jones and co-workers who have clearly demonstrated that 2-indolyl radicals are easy to generate and can be used for synthetic purposes.¹⁶



Scheme 6: Unsuccessful Substitution Reactions with Phenylsulfonyl-Heterocycles

However we did find that the phenylsulfonyl substituted indole **25** does undergo substitution to give the product stannane **4a** in reasonable yield (scheme 7).



Scheme 7

Conclusions

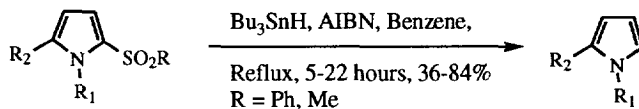
We have shown that sulfone-substituted heteroaromatics can undergo a regioselective substitution with TBTH under radical conditions. There are limitations to the generality of this process, for example certain heteroaromatic sulfones do not participate for reasons which are not clear at the present time. There is no evidence from this study that the phenylsulfonyl-substituted analogues will be useful for this type of transformation, although it should be noted that the groups of Sweeney and Harrowven have elegantly shown that phenylthio-substituted aromatics or alkenes can undergo *ipso* substitution with the organostannyl radical.¹⁷ It is interesting to note that we have previously shown that intramolecular substitution with carbon-centred radicals does proceed even with the phenylthio substituted indoles, albeit in much reduced yields.¹⁸ We have been tempted to draw analogies between our work on the intramolecular substitution and the intermolecular examples described herein. Obviously the results obtained in this study show that there are considerable differences between the two classes of reaction. The success of the sulfonyl-substituted indole derivative bodes well for the development of alternative *ipso* substitution reactions.

In the majority of cases described herein these compounds are available *via* transmetalation approach¹⁹ and in no sense do we propose that this methodology should be used for the preparation of these compounds. However it is likely that this work, which shows the feasibility of the sulfone to stannane transformation, may be attractive to workers who need to prepare sensitive organostannanes, avoiding a direct lithiation approach. The use of stannyl-substituted indoles to prepare functionalised indoles *via* cross coupling technology is now well established and stannyl-substituted pyrroles and thiophenes are particularly valuable in the preparation of conducting polymers.²⁰ This type of methodology may become particularly valuable if

functionalised monomers are required which incorporate sensitive functional groups which preclude a direct lithiation approach.

The mechanisms of the substitution reactions are unclear; although we favour an addition-elimination pathway we cannot rule out the electron-transfer pathway initially proposed by Ueno for related *ipso*-substitution reactions.²¹

It is useful to draw attention to work described by Muchowski and co-workers in which they highlight a very interesting desulfonylation reaction mediated by TBTH (scheme 8).²²



Scheme 8

It is possible that this transformation proceeds *via* an initial *ipso*-substitution reaction to give an intermediate stannane which then undergoes rapid destannylation either under the reaction conditions or on chromatographic purification. The reactions are carried out at elevated temperatures for prolonged periods (5-22 hours) and indeed we have found that yields of our products are generally lowered if the reactions are subjected to prolonged heating with the destannylated compound often observed as a by-product. In accord with these workers we have also found that diphenylsulfone does not undergo any significant reaction with TBTH with prolonged heating.

Overall our work has shown that heteroaromatic sulfones can participate in intermolecular *ipso* substitution reactions to provide organostannanes. The methodology provides a useful alternative to more conventional methods and may represent a useful addition to the armoury of methods currently available to the synthetic chemist for the preparation of this useful class of compound.

Acknowledgements

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Experimental

Glassware used in the reactions are oven dried for at least 4 hours (200 °C) or flame dried. All reactions are carried out under a positive atmosphere of argon or nitrogen unless otherwise stated. All solvents used in the reactions are dry, THF and ether are freshly distilled from sodium/benzophenone. Dichloromethane, dimethylformamide, and toluene are distilled from calcium hydride. Petrol refers to petroleum ether b.p. 40 - 60°C. All reagents are used as purchased or are purified using standard methods. Standard or usual work-up involves addition of water then extraction with six portions of diethyl ether (25ml per mmol) and drying with potassium carbonate or magnesium sulfate. Filtration and removal of the solvent "in vacuo" gives the crude product. Proton NMR spectra are recorded at 500, 360, 270 or 200MHz, carbon spectra are recorded at 125MHz. Chemical shifts are reported downfield in parts per million using tetramethylsilane as internal reference. Melting points are uncorrected. Analytical thin layer chromatography was performed using pre-coated glass-backed plates and visualised by ultra-violet light, potassium permanganate or iodine as appropriate. Silica-gel chromatography is carried out using flash silica (mesh 40) and under slight pressure.

General procedure: lithiation and sulfonation/sulfonation of heterocycles

To a stirred solution of heterocycle in THF at -78 °C was added *n*-butyllithium or *t*-butyllithium at -78°C and thence *p*-toluenesulfonyl fluoride or diphenyldisulfide in THF dropwise; the mixture was allowed to warm to room temperature. Standard work-up and purification (SiO₂/ReX) gave the product

1-(Phenylsulfonyl)-2-[(4-methylphenyl)sulfonyl]-1H-indole, 2b

Compound **2b** was prepared in 24% according to the general procedure from: **1b** (15.6 mmol) in THF (156 ml); *t*-BuLi (18.7 mmol) 60 minutes then *p*-toluenesulfonyl fluoride (18.7 mmol) in THF (10.0 ml), -78°C 1hr, r.t. 2.5 hrs. Purification (SiO₂) (petrol : CH₂Cl₂, 1:1), white solid m.p. 137-138 °C (petrol : ether); Rf (SiO₂) 0.22, (petrol : ether, 3:1); V_{max} (cm⁻¹) 3498, 2285, 1596, 1514, 1472, 1449, 1384, 1184, 1151, 1127, 1086, 1016, 814, 752, 727; ¹H NMR (C₆D₆) 8.19 (1H, d, J = 8.2), 8.06 (2H, d, J = 7.42), 7.91 (2H, d, J = 8.6), 7.78 (1H, d, J = 0.79), 7.66 (1H, d, J = 7.82), 7.58 - 7.40 (4H, m), 7.39 - 7.26 (3H, m), 2.43 (3H, s); ¹³C NMR (CDCl₃) 144.5, 139.0, 138.2, 137.9, 137.8, 134.3, 129.4, 129.2, 128.6, 128.5, 127.8, 126.6, 124.6, 123.2, 122.7, 115.4, 21.69; HRMS Calcd for C₂₁H₁₇NO₄S₂ 411.0599 found 411.0599

1,1-Dimethylethyl-2-[(4-methylphenyl)sulfonyl]-1H-indole-1-carboxylate, 2a

Compound **2a** was prepared in 44% according to the general procedure from: **1a** (18.3 mmol) in THF (150 ml); *t*-BuLi (22.0 mmol) 45 minutes then *p*-toluenesulfonyl fluoride (22.0 mmol) in THF (10.0 ml), -78 °C 1hr, r.t. 2.5 hrs. Purification (SiO₂) (petrol : ether 50:1, 20:1, 10:1, 6:1, 3:1), white solid m.p. 137-138 °C (petrol : ether). Rf (SiO₂) 0.34, (petrol : ether, 3:1); V_{max} (cm⁻¹) 2980, 2932, 1752, 1598, 1519, 1494, 1326, 1153, 1090, 1019; ¹H NMR (CDCl₃) 8.06 (1H, d, J = 8.06), 7.90 (2H, d, J = 8.3), 7.78 (1H, d, J = 8.21), 7.62 (1H, d, J = 7.9), 7.48 - 7.43 (1H, m), 7.36 - 7.27 (2H, m), 7.2 (1H, s), 2.46 (3H, s), 1.60 (9H, s); ¹³C NMR (CDCl₃) 148.20, 144.2, 138.4, 137.8, 137.4, 129.3, 128.5 (m-C's), 127.8, 126.2, 123.6, 122.7, 118.8, 115.8, 86.10, 27.98, 21.64; HRMS calcd for C₂₀H₂₁NO₄S: 371.1191 found 371.1168; Anal. Calcd for C₂₀H₂₁NO₄S C 64.67, H 5.69, N 3.79 found: C 64.64, H 5.53, N 3.61.

1-Phenylsulfonyl, 2-[(4-methylphenyl)sulfonyl]-pyrrole 5

Compound **5** was prepared in 27% according to the general procedure from: *1*-[phenylsulfonyl]pyrrole (10.1 mmol) in THF (100 ml); *t*-BuLi (15.1 mmol) 40 minutes then *p*-toluenesulfonyl fluoride (12.2 mmol) in THF (20.0 ml), -78°C 4hr. Purification (SiO₂) (petrol : ether 5:1, 4:1, 3:1, 2:1), white solid m.p. 102.5°C (MeOH) ; Rf 0.11 (SiO₂, petrol:ether 3:1);

V_{\max} (cm^{-1}) 3066, 2924, 1449, 1377, 1157, 1144, 814, 705; ^1H NMR (CDCl_3) 7.97 (2H, d, $J = 7$), 7.83 (2H, d, $J = 8.2$), 7.52 (2H, m), 7.40 (2H, m), 7.25 (3H, m), 6.3 (1H, t, $J = 3.5$), 2.32 (3H, s); ^{13}C NMR (CDCl_3) 144.3, 138.34, 138.11, 134.54, 132.23, 130.1, 129.45, 129.24, 128.28, 128.05, 126.35, 111.5, 21.6; HRMS calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4\text{S}_2$ 361.0443 found 361.0440.

1-Phenylsulfonyl, 5-[(4-methylphenyl)sulfonyl]-1H-pyrazole 6

Compound **6** was prepared in 34% according to the general procedure from: 1-(phenylsulfonyl)pyrazole (4.6 mmol) in THF (50 ml); t-BuLi (5.1 mmol) 10 minutes then *p*-toluenesulfonyl fluoride (6.9 mmol) in THF (10 ml), -78°C , 4h. Purification (SiO_2) (petrol : ether, 3:1, 2:1, 1:1), Rf 0.06 (petrol : ether 4:1); V_{\max} (cm^{-1}) 3133, 1450, 1363, 1153, 815, 728; ^1H NMR (CDCl_3) 8.1 (2H, d, $J = 2.7$), 8.0 (2H, dd, $J = 8.5, 1.3$), 7.9 (1H, d, $J = 8.4$), 7.7 (1H, m), 7.55 (2H, t, $J = 8.1$), 7.3 (2H, d, $J = 8$), 6.8 (1H, d, $J = 2.7$), 2.4 (3H, s); ^{13}C NMR (CDCl_3) 158.7, 144.6, 137.9, 136.3, 134.8, 133.5, 132.6, 129.9, 129.7, 129.4, 129.13, 129.0, 128.9, 128.5, 108.6, 21.1; HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}_2$ 362.0395 found 362.0402.

2-[(4-Methylphenyl)sulfonyl]furan 9

Compound **9** was prepared in 19% according to the general procedure from: furan (2.05 mmol) in THF (8 ml); n-BuLi (2.22 mmol) 120 minutes -20°C , then *p*-toluenesulfonyl fluoride (2.22 mmol) in THF (5 ml), -20°C 1hr, r.t. 1 hr. Purification (SiO_2 , petrol : ether, 3:1). Rf 0.25 (SiO_2 , petrol : ether, 3:1); V_{\max} (cm^{-1}) 1329, 1152, 1194, 1058, 883, 815, 751; ^1H NMR (CDCl_3) 7.86 (2H, dd, $J = 8.6, 2$), 7.5 (1H, dd, $J = 1.8, 1$), 7.3 (2H, dd, $J = 8.6, 1$), 7.16 (1H, dd, $J = 3.5, 1$), 6.46 (1H, dd, $J = 3.7, 2$), 2.4 (3H, s); ^{13}C NMR (CDCl_3) 152, 147.15, 144.8, 129.9, 127.9, 116.9, 111.48, 77.16, 21.44; HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{SO}_3$ 222.0351 found 222.0357.

2-[(4-Methylphenyl)sulfonyl]-thiophene 10

Compound **10** was prepared in 10% according to the general procedure from: thiophene (6.46 mmol) in THF (4.8 ml); n-BuLi (7.11 mmol) -40°C 60 minutes, then *p*-toluenesulfonyl fluoride (7.11 mmol) in THF (5 ml), -78°C 1hr, r.t. 2 hrs. Purification (SiO_2 , petrol : ether, 3:1). Rf 0.3 (SiO_2 , petrol : ether); V_{\max} (cm^{-1}) 1342, 1152, 857, 818, 728; ^1H NMR (CDCl_3) 7.87 (2H, dd, $J = 6.6, 2$), 7.7 (1H, dd, $J = 3.7, 1.4$), 7.6 (1H, dd, $J = 5, 1.6$), 7.3 (2H, d, $J = 8$), 7.1 (1H, dd, $J = 4, 5$), 2.4 (3H, s); ^{13}C NMR (CDCl_3) 144.3, 139.2, 133.5, 133.0, 129.9, 127.7, 127.4, 127.3, 21.6; HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{S}_2$ 238.0122 found 238.0122.

2-[(4-methylphenyl)sulfonyl]-benzofuran 11

Compound **11** was prepared in 30% according to the general procedure from: benzofuran (1.54 mmol) in diethyl ether (5 ml); n-BuLi (1.84 mmol) -10°C , 60 minutes, then *p*-toluenesulfonyl fluoride (1.84 mmol) in diethyl ether (5 ml), -50°C 1hr, r.t. 18 hrs. Purification (SiO_2 , petrol : ether, 3:1) white solid, m.p. $95-96^\circ\text{C}$ (Et_2O). Rf 0.27 (SiO_2 , petrol : ether, 3:1); V_{\max} (cm^{-1}) 1335, 1257, 1157, 1111, 857, 813, 751; ^1H NMR (CDCl_3) 7.96 (2H, d, $J = 6.6, 2$), 7.74 (1H, dt, $J = 8, 1$), 7.53-7.36 (3H, m), 7.34 (2H, d, $J = 8.2$), 7.31-7.26 (1H, m), 2.42 (3H, s); ^{13}C NMR (CDCl_3) 156.4, 152.0, 145.2, 136.4, 130.0, 128.3, 127.9, 126, 124.2, 123.0, 112.8, 112.4, 22.0; HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{O}_3\text{S}$ 272.0507 found 272.0511.

2-[(4-methylphenyl)sulfonyl]-benzo[b]thiophene 12

Compound **12** was prepared in 55% according to the general procedure from: benzo[b]thiophene (5.5 mmol) in THF (5 ml); n-BuLi (6.1 mmol) -30°C 60 minutes, then *p*-toluenesulfonyl fluoride (6.1 mmol) in THF (5 ml), -70°C 1hr, r.t. 2 hrs. Purification (SiO_2 , petrol : ether, 3:1) white solid, m.p. $158-159^\circ\text{C}$ (Et_2O). Rf 0.35 (SiO_2 , petrol : ether, 3:1); V_{\max} (cm^{-1}) 2987, 1326, 1153, 994, 897; ^1H NMR (CDCl_3) 7.95 (2H, d, $J = 4$), 7.9 (1H, s), 7.88-7.78 (3H, m), 7.48-7.38 (2H, m), 7.3 (2H, dd, $J = 8.6, 1$), 2.4 (3H, s);

^{13}C NMR (CDCl_3) 144.7, 143.5, 142.7, 138.5, 137.7, 130.0, 127.7, 127.4, 125.9, 125.5, 122.7, 21.6; HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{S}_2$ 288.0280 found 288.0279.

1,1-Dimethylethyl-3-[(phenylthio)-1H-indole-1-carboxylate

To a stirred solution of 3-phenylthio-indole²³ (2.7 mmol), DMAP (0.5 mmol) and Et_3N (3.2 mmol) in CH_2Cl_2 (20 ml) at 0 °C was added di-*tert*-butyldicarbonate (2.9 mmol) and the reaction stirred at room temperature for 30 minutes. Water (10 ml) was added, the aqueous layer was extracted with CH_2Cl_2 , the organic layers dried and the solvent removed *in vacuo* to give the crude product. Purification was carried out by silica-gel chromatography (petrol : ether, 4:1) to give the title compound (87%). Rf 0.94 (SiO_2 , petrol : ether, 4:1); V_{max} (cm^{-1}) 3584, 3567, 2522, 2411, 2360, 2127, 2055, 1869, 1845, 1793, 1685, 1654, 1636, 1606, 1583, 1541, 1525, 1508, 1024, 853; ^1H NMR (CDCl_3) 8.27 (1H, d, $J = 8.2$), 7.96 (1H, s), 7.57 (1H, dq, $J = 8, 1.2, 0.8$), 7.47-7.41 (1H, m), 7.3 (1H, d, $J = 7$) 7.28-7.15 (5H, m), 1.77 (9H, s); HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_2\text{S}$ 325.1137 found 325.1144.

1,1-Dimethylethyl-3-(phenylsulfonyl)-1H-indole-1-carboxylate 17

To a stirred solution of 1,1-dimethylethyl-3-[(phenylthio)-1H-indole-1-carboxylate (1.65 mmol) in methanol (6 ml) at 0 °C was added oxoneTM (4.12 mmol) in water (6 ml). The reaction mixture was stirred for 3 days and the reaction was quenched with aqueous sodium bisulfite. The aqueous layer was extracted with CH_2Cl_2 and washed with brine, water, dried (Na_2SO_4) and the solvent removed *in vacuo* to give the crude product. Purification was carried out using silica-gel chromatography (petrol : ether, 3:1) to give **17** as a white solid (86%) m.p. 112-113 °C. Rf 0.3 (SiO_2 , petrol : ether, 4:1); V_{max} (cm^{-1}) 2987, 1736, 1397, 1373, 1220, 1065; ^1H NMR (CDCl_3) 8.29 (1H, s), 8.17 (1H, dd, $J = 7, 1$), 8.1 (2H, dd, $J = 8, 1.6$), 7.9-7.88 (1H, m), 7.59-7.46 (1H, m), 7.5 (2H, d, $J = 7.4$), 7.42-7.29 (2H, m), 1.68 (9H, s); ^{13}C NMR (CDCl_3) 148.4, 142, 133.1, 133.1, 130.8, 129.2, 127.1, 125.9, 124.9, 124.4, 121.6, 119.9, 115.6, 85.9, 28.0; HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_4\text{S}$ 357.1035 found 357.1038.

4-[(4-Methylphenyl)sulfonyl]-dibenzofuran 20

Compound **20** was prepared in 49% according to the general procedure from: dibenzofuran (5.95 mmol) in THF (8 ml); *n*-BuLi (7.14 mmol) -60 °C, 10 minutes, 0 °C 1 hour, then *p*-toluenesulfonyl fluoride (6.6 mmol) in THF (5 ml), -60°C 1hr, r.t. 2 hrs. Purification (SiO_2 , petrol : ether, 3:1), white solid, m.p. 178-179 °C (Et_2O). Rf 0.32 (SiO_2 , petrol : ether, 3:1); V_{max} (cm^{-1}) 2987, 1320, 1191, 1154, 1062; ^1H NMR (CDCl_3) 8.15-8.07 (2H, m), 8.12 (2H, d, $J = 7.8$), 7.92 (1H, dd, $J = 7.0, 1$), 7.68 (1H, dd, $J = 9.2, 1$), 7.55-7.3 (3H, m), 7.3 (2H, dd, $J = 8.6, 1$), 2.4 (3H, s); ^{13}C NMR (CDCl_3) 156.4, 151.5, 144.5, 138.3, 129.6, 128.2, 126.5, 126.4, 126.4, 126, 123.6, 122.7, 120.7, 112.2, 21.5; HRMS calcd for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{S}$ 322.0664 found 322.0671.

2-Phenylthio-furan 22

Compound **22** was prepared in 39% according to the general procedure from: furan (20.6 mmol) in THF (10 ml); *n*-BuLi (21.3 mmol) -20°C, then $(\text{PhS})_2$ (21 mmol) in THF (5 ml), -20 °C 1hr, r.t. 1 hr. Purification (bulb to bulb distillation), colourless liquid, b.pt. 120 °C @ 0.6 mm. Rf 0.82 (SiO_2 , petrol : ether, 3:1); V_{max} (cm^{-1}) 2610, 2365, 1944, 1869, 1786, 1757, 1698, 1554, 1369, 1329, 1301, 1216, 882, 822, 667; ^1H NMR (CDCl_3) 7.58 (1H, dd, $J = 2, 1$); 7.28-7.13 (5H, m), 6.75 (1H, dd, $J = 3, 1$), 6.47 (1H, dd, $J = 3, 2$); ^{13}C NMR (CDCl_3) 146.5, 129, 127.5, 126.3, 112.4, 111.8; HRMS calcd for $\text{C}_{10}\text{H}_8\text{OS}$ 176.0296 found 176.0301.

1,1-Dimethylethyl-2-(phenylthio)-1H-indole -1-carboxylate 23

Di-*tert*-butyldicarbonate (0.55 mmol) in dichloromethane (1.5 ml) was added to an ice cold solution of 2-*phenylthio-indole*,²³ (0.50 mmol), triethylamine (1.33 mmol) and 4-dimethylamino pyridine (DMAP) (0.1 mmol) in dichloromethane (3.0 ml). The reaction mixture was allowed to warm to room temperature after twenty minutes and after a further two and a half hours another portion of DMAP (0.1 mmol) was added, and stirring was continued at room temperature overnight (tlc, petrol : ether, 5:1). After the standard work-up, purification of the crude mixture by flash column chromatography (neat petrol, petrol : ether, 30:1) gave the title compound as a white solid (72%) m.p. 69 - 71 °C; Rf 0.4 (SiO₂, petrol : ether, 20:1); V_{max} (cm⁻¹) 2978, 2927, 1739, 1541, 1514, 1447, 1329, 1292, 1112, 1025; ¹H NMR (CDCl₃) 8.27 (1H, d, J = 7.8), 7.58-7.55 (2H, m), 7.42-7.39 (3H, m), 7.28-7.12 (4H, m), 1.67 (9H, s); ¹³C NMR (CDCl₃) 136.9, 136.5, 135.3, 133.7, 133.4, 129.5, 128.7, 128.4, 123.2, 123.0, 119.1, 115.1, 108.9, 85.1, 28.2; HRMS calcd for C₁₉H₂₀NO₂S [M+H]⁺ 326.1216 found 326.1225.

4-Phenylthio-dibenzofuran 24

Compound **24** was prepared in 40% according to the general procedure from: *dibenzofuran* (5.95 mmol) in THF (10 ml); *n*-BuLi (6.5 mmol) -60°C, 10 minutes, 0°C 1 hour, then (PhS)₂ (5.9 mmol) in THF (2 ml), -60°C 1hr, r.t. 2 hrs. Purification (SiO₂, petrol : ether, 3:1), white solid, m.p. 50-51°C. Rf 0.9 (SiO₂, petrol : ether, 3:1); V_{max} (cm⁻¹) 3944, 3735, 3690, 3649, 3583, 2686, 2522, 2411, 2306, 1654, 1578, 1508, 1422, 1189, 1157, 1057, 879, 667; ¹H NMR (CDCl₃) 7.96 (1H, dq, J = 8, 1.4, 0.7), 7.9 (1H, dd, J = 7.6, 1.4), 7.6 (1H, m), 7.50-7.39 (2H, m), 7.38-7.19 (7H, m); ¹³C NMR (CDCl₃) 156.1, 155.3, 134.8, 130.9, 130.4, 129.2, 127.5, 126.9, 124.9, 124.1, 124, 123.0, 120.8, 120.3, 112.1; HRMS calcd for C₁₈H₁₂OS 276.0609 found 276.0615;

2-(Phenylsulfinyl)-1H-indole

A solution of oxoneTM (0.73 mmol) in THF/methanol (4 ml, 1:1) was added to a solution of 2-*phenylthio indole*,²³ (0.73 mmol) at 0 °C in THF/methanol (4 ml, 1:1). The reaction mixture was allowed to stir for ten minutes at 0 °C (SiO₂, petrol : ether, 1:1). After the standard work-up, purification of the crude mixture by silica-gel chromatography (petrol : ether, 5:1, 3:1, 2:1, 1:1) gave the title compound as a white solid (64%) m.p. 139 - 140 °C; Rf (SiO₂) 0.32 (petrol : ether, 1:1); V_{max} (cm⁻¹) 3436, 2903, 2106, 1642, 1620, 1504, 1416, 1345, 1231, 1032; ¹H NMR (CDCl₃) 9.78 (1H, bs), 7.71 - 7.68 (2H, m), 7.63 (1H, d, J = 7.0), 7.49 - 7.44 (m, 3H), 7.39 (1H, d, J = 8.2), 7.28 - 7.25 (1H, m), 7.15 - 7.09 (1H, m), 6.92 (1H, d, J = 0.8); ¹³C NMR (CDCl₃) 140.7, 137.8, 136.4, 131.1, 129.3, 127.0, 124.8, 121.7, 120.8, 112.2, 106.8; HRMS Calcd for C₁₄H₁₁NOS 242.0640 found 242.0643.

1,1-Dimethylethyl-2-(phenylsulfinyl)-1H-indole-1-carboxylate 25

Di-*tert*-butyldicarbonate (0.36 mmol) in dichloromethane (1.5 ml) was added to a cooled solution (0 °C) of 2-*phenylsulfinyl-indole*, (0.3 mmol), triethylamine (0.4 mmol) and 4-dimethylamino pyridine (DMAP) (0.1 mmol) in dichloromethane (3.0 ml). The reaction mixture was allowed to warm to room temperature over twenty minutes and after a further two and a half hours another portion of DMAP (0.1 mmol) was added. The reaction mixture was allowed to stir at room temperature overnight (SiO₂, petrol : ether 2 : 1). After the standard work-up, purification of the crude mixture by flash column chromatography (petrol : ether 100:0, 2:1, 1.5:1, 1:1) afforded **25** as a white solid (78%) m.p. 100 - 102 °C (petrol : ether); Rf 0.22 (SiO₂, petrol : ether, 2:1); V_{max} (cm⁻¹) 3442, 2935, 1620, 1475, 1445, 1379, 1124, 1032, 1023; ¹H NMR (CDCl₃) 7.96 (1H, d, J = 8.1), 7.96 - 7.76 (2H, m), 7.67 (1H, d, J = 7.1), 7.44 - 7.42 (3H, m), 7.36 - 7.27 (3H, m), 1.60

(9H, s); ^{13}C NMR (CDCl_3) 149.6, 145.4, 143.0, 137.4, 131.2, 129.0, 128.5, 126.8, 125.8, 123.4, 121.9, 115.9, 112.1, 85.9, 27.9; HRMS calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3\text{S}$ 341.1086 found 341.1086.

General procedure: preparation of tri-*n*-butylstannyl heterocycles

A solution of TBTH (2 equivs), AIBN (0.1-1 equiv) in toluene (1-3 ml) was added to the sulfone (1 equiv) in toluene (1-2 ml) at reflux 1-8 hrs and the mixture heated at reflux until complete (tlc analysis). The reaction was allowed to cool to room temperature and the solvent removed *in vacuo*. Chromatography was carried out on SiO_2 (normal or C_{18} bonded) or Al_2O_3 to give the product.

1,1-Dimethylethyl-2-(tri-*n*-butylstannyl)-1H-indole-1-carboxylate 4a (1 hour, 0.27 mmol, 95%);

Rf 0.26 (C_{18} , MeOH); Vmax (cm^{-1}) 1714, 1373, 744; ^1H NMR (CDCl_3) 8.18 (1H, d, $J = 8.2$), 7.7 (1H, d, $J = 7.0$), 7.42 (1H, dd, $J = 7.8, 7.4$), 7.35 (1H, dd, $J = 7.8, 7.4$), 6.94 (1H, s), 1.9 (s, 9H), 1.79 (6H, m), 1.58 (6H, m), 1.36 (6H, m), 1.11 (9H, m); ^{13}C NMR (CDCl_3) 152.2, 143.3, 137.4, 132.4, 123.2, 122.1, 120.0, 118.6, 115.2, 83.7, 29.1, 28.2, 27.3, 13.70, 11.60; HRMS calcd for $\text{C}_{25}\text{H}_{41}\text{NO}_2\text{Sn}$ 507.2159 found 507.2179. Anal. Calcd for $\text{C}_{25}\text{H}_{41}\text{NO}_2\text{Sn}$ C 57.16, H 6.83, N 2.56 found C 57.32, H 6.83, N 2.65.

1-(Phenylsulfonyl)-2-(tri-*n*-butylstannyl)-1H-indole 4b; (4 hours, 0.05 mmol, 92%);

Rf 0.39 (C_{18} , MeOH); Vmax (cm^{-1}) 2956, 2922, 2871, 2852, 1362, 1169, 1130, 1093, 747, 728, 588; ^1H NMR (C_6D_6) 8.1 (1H, m), 7.5 (1H, d, $J = 7.8$), 7.5 (1H, d, $J = 8.4$), 7.37 (1H, m), 7.0 (2H, m), 6.93 (1H, s), 6.66 (3H, m), 1.68 (6H, m), 1.38 (12H, m), 0.98 (9H, m); ^{13}C NMR (CDCl_3) 143.6, 139.4, 138.4, 133.3, 131.9, 129.0, 126.3, 123.9, 123.0, 120.6, 120.3, 113.7, 29.0, 27.4, 13.7, 11.9; HRMS calcd for $\text{C}_{26}\text{H}_{37}\text{NO}_2\text{SSn}$ 547.1567 found 547.1561.

1-(Phenylsulfonyl)-2-(tri-*n*-butylstannyl)-1H-pyrrole 7 (1 hour, 0.26 mmol, 69%);

Rf 0.85 (SiO_2 , petrol : ethyl acetate, 5:1); Vmax (cm^{-1}) 2956, 2923, 2871, 2854, 1458, 1448, 1419, 1361, 1200, 1174, 1146, 1076, 963, 753, 728, 686, 594, 563; ^1H NMR (C_6D_6) 7.5-7.4 (3H, m), 6.8-6.6 (3H, m), 6.5 (1H, dd, $J = 3.1, 1.4$), 6.25 (1H, t, $J = 3$), 1.65-1.5 (6H, m), 1.4-1.2 (12H, m), 0.95-0.85 (9H, t); ^{13}C NMR (CDCl_3) 142, 136, 132.9, 129.1, 128.3, 125.9, 125.3, 114.9, 29.4, 27.7, 13.9, 11.6.

1-(Phenylsulfonyl)-5-(tri-*n*-butylstannyl)-1H-pyrazole 8 (6 hours, 0.25 mmol, 70%);

Rf 0.71 (SiO_2 , petrol : ether, 3:1); Vmax (cm^{-1}) 2957, 2927, 1458, 1340, 1187, 728; ^1H NMR (C_6D_6) 8.02 (1H, d, $J = 2.7$), 7.92 (2H, m), 6.77 (3H, m), 6.12 (1H, d, $J = 2.7$), 1.47 (6H, m), 1.27 (6H, m), 1.02 (6H, m), 0.84 (9H, m); ^{13}C NMR (CDCl_3) 139.0, 133.6, 130.8, 129, 128.2, 116.1, 29.2, 27.4, 13.8, 10.3; HRMS calcd for $\text{C}_{21}\text{H}_{34}\text{N}_2\text{O}_2\text{SSn}$ 498.1363 found 498.1349.

2-(Tri-*n*-butylstannyl)furan 13 (3 hours, 1.4 mmol, 77%)

Rf 0.65 (Al_2O_3 , petrol); Vmax (cm^{-1}) 2957, 2853, 803, 733; ^1H NMR (CDCl_3) 7.71 (1H, d, $J = 1.6$), 6.53 (1H, d, $J = 3.1$), 6.39 (1H, d, 3.1), 1.59-1.47 (6H, m), 2.37-1.23 (6H, m), 1.12-1.0 (6H, m), 0.9-0.84 (9H, t); ^{13}C NMR (C_6D_6) 160.4, 147.3, 121.8, 109.5, 29.3, 27.5, 13.8, 10.3; HRMS calcd for $\text{C}_{16}\text{H}_{30}\text{SnO}$ 357.1240 found 357.1248.

2-(Tri-*n*-butylstannyl)thiophene 14 (2.5 hours, 0.76 mmol, 72%)

Rf 0.87 (Al_2O_3 , petrol); Vmax (cm^{-1}) 2957, 2853, 821, 746; ^1H NMR (CDCl_3) 7.63 (1H, d, $J = 4.7$), 7.25 (1H, m), 7.17 (1H, m), 1.57-1.51 (6H, m), 1.38-1.26 (6H, m), 1.11-1.10 (6H, m), 0.89-0.84 (9H, m), ^1H NMR (C_6D_6) 7.49 (1H, d, $J = 4.7$), 7.30 (1H, d, $J = 3.5$), 7.22 (1H, m), 1.72-1.63 (6H, m), 1.46-1.32 (6H, t) 1.20-1.13 (6H, m), 0.97-0.92 (9H, m); ^{13}C NMR (C_6D_6) 135.6, 131, 128.2, 29.5, 27.6, 13.8, 11; HRMS calcd for $\text{C}_{12}\text{H}_{21}\text{SSn} [\text{M-Bu}]^+$ 317.0386 found 317.0394.

2-(Tri-*n*-butylstannyl)benzofuran 15 (2.5 hours, 0.25 mmol, 77%)

Rf 0.87 (Al₂O₃, petrol); Vmax (cm⁻¹) 2957, 2853, 1466, 1438, 1154, 1073, 780, 752; ¹H NMR (CDCl₃) 7.6-7.5 (2H, m), 7.23-7.15 (2H, m), 6.9 (1H, d, J = 0.8), 1.66-1.54 (6H, m), 1.43-1.29 (6H, m), 1.19-1.13 (6H, m), 0.2-0.88 (9H, m); ¹³C NMR (C₆D₆) 159.4, 136.8, 128.3, 123.9, 122.7, 120.7, 118.7, 111.4, 29.3, 27.5, 13.8, 10.4; HRMS calcd for C₁₆H₂₃OSn [M-Bu]⁺ 351.0771 found 351.0781.

2-(Tri-*n*-butylstannyl)benzothiophene 16; (2 hours, 0.7 mmol, 81%);

Rf 0.84 (Al₂O₃, petrol); Vmax (cm⁻¹) 2956, 2852, 743, 727; ¹H NMR (CDCl₃) 7.86 (1H, d, J = 7.8), 7.79 (1H, d, J = 7.0), 7.37 (1H, s), 7.33-7.27 (2H, m), 1.63-1.53 (6H, m), 1.4-1.3 (6H, m), 1.21-1.02 (6H, m), 0.91-0.85 (9H, m); ¹³C NMR (C₆D₆) 144.9, 141.7, 139.4, 132.6, 124.1, 123.8, 123.7, 122.2, 29.4, 27.6, 13.8, 11; HRMS calcd for C₁₆H₂₃SSn [M-Bu]⁺ 367.0542 found 367.0542.

1,1-Dimethylethyl-2,3-dihydro-7-(tri-*n*-butylstannyl)-1H-indole-1-carboxylate 19 (1 hour, 0.1 mmol, 60%);

Rf 0.88 (SiO₂, petrol : ether, 3:1); Vmax (cm⁻¹) 2958, 2927, 2871, 1693, 1456, 1412, 1392, 1340, 1248, 1146, 1014, 766; ¹H NMR (CDCl₃) 7.34-7.32 (1H, d, J = 7.2), 7.12-7.10 (1H, d, J = 7.2), 6.97-6.93 (1H, t, J = 7.3), 3.99-3.95 (2H, t, J = 8.4), 3.04-2.99 (2H, t, J = 8.4), 1.52 (9H, s), 1.59-1.46 (6H, m), 1.37-1.27 (6H, m), 1.06-0.96 (6H, m), 0.95-0.86 (9H, m); ¹³C NMR (CDCl₃) 153.6, 149.0, 136.4, 131.4, 130.4, 124.4, 122.6, 80.5, 47.9, 29.2, 28.5, 28.1, 27.3, 13.7, 12.9; HRMS calcd for C₂₅H₄₃NO₂Sn 509.2316 found 509.2320.

4-(Tri-*n*-butylstannyl)dibenzofuran 21; (2 hours, 0.46 mmol, 71%);

Rf 0.9 (Al₂O₃, petrol); Vmax (cm⁻¹) 2956, 2853, 782, 756, 732; ¹H NMR (C₆D₆) 7.74-7.60 (3H, m), 7.43 (1H, m), 7.27 (1H, m), 7.13-7.06 (2H, m), 1.75-1.63 (6H, m), 1.46-1.28 (12H, m), 0.91-0.86 (9H, m); ¹³C NMR (C₆D₆) 162.7, 156.4, 135.2, 127.1, 123.3, 122.7, 121.1, 121.0, 111.7, 29.5, 27.6, 13.8, 10.2; HRMS calcd for C₂₀H₂₅SnO [M-Bu]⁺ 401.0927 found 401.0931.

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