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Pd-catalysed desulfitative Heck reaction tolerant to aryl C-Halo bonds for access to (poly)halo-substituted stilbene or cinnamate derivatives

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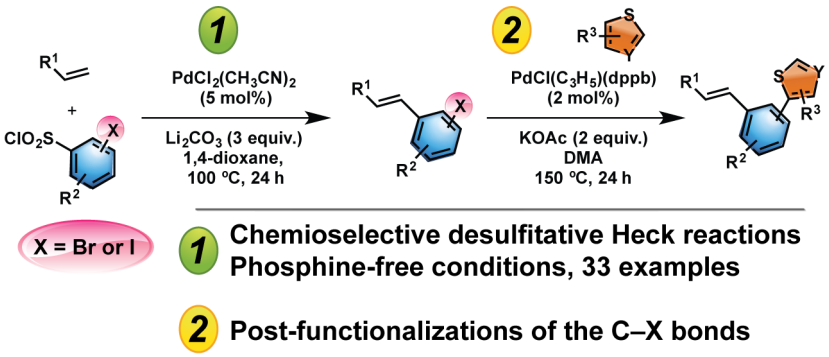
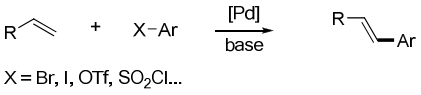


Abstract The palladium-catalysed desulfitative Heck type reaction of (poly)halo-substituted benzenesulfonyl chlorides with alkenes was investigated. Styrene or acrylates in the presence of bromo- or iodo-benzenesulfonyl chlorides and a phosphine-free palladium catalyst were found to afford the expected *β*-arylated Heck type products with complete regio- and stereo-selectivities. The reaction tolerates a variety of substituents on the halobenzenesulfonyl chloride. Moreover, no cleavage of the C-Br and C-I bonds was observed in the course of these reactions, allowing further transformations. Using 4-bromobenzenesulfonyl chloride as the central unit, consecutive desulfitative Heck type reaction followed by palladium-catalysed direct arylation allowed to prepare heteroarylated stilbene derivatives in only two steps.

Key words Palladium, catalysis, desulfitative Heck reaction, halobenzenesulfonyl chlorides, alkenes

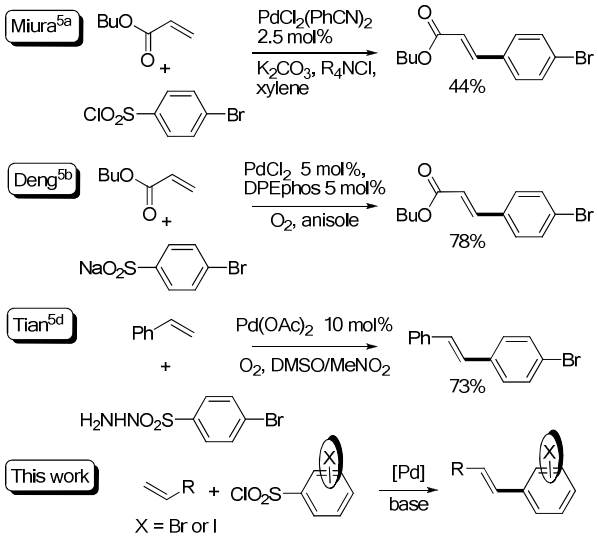
Introduction

Mizoroki-Heck reaction is certainly one of the most powerful methods for the preparation of stilbene or cinnamate derivatives.[1,2] For such reactions, in most cases, aryl halides were employed as the aryl source (Scheme 1); however, the reactivity of benzenesulfonyl derivatives was also studied. For example, Miura and co-workers reported in 1989 the Heck type Pd-catalysed desulfitative reaction of acrylates with benzenesulfonyl chlorides for the synthesis of 3-aryl-2-propenoates.[3a] A few years later, Vogel et al. extended these Pd-catalysed desulfitative Heck reactions to styrene and substituted acrylates.[3b] Jafarpour et al. recently reported that the reaction of methylacrylate with benzenesulfonyl chloride in the presence of $PdCl_2$ and $Cu(OAc)_2$ as catalytic system also affords the Heck type products.[3c] The arylation of glycals under Pd-catalysed desulfitative Heck conditions has also been reported.[3d]



Scheme 1

The synthesis of halo-substituted stilbene or cinnamate derivatives is an important field for research in organic chemistry as they give access to important building blocks for biochemists. Therefore, reaction conditions promoting Heck type reaction, tolerant to C-Halo bonds, would provide a straightforward access to halo-substituted arenes. However, although desulfitative couplings are known to tolerate both bromo and iodo substituents on benzenesulfonyl chlorides,[4] surprisingly to our knowledge, only one example of desulfitative Pd-catalysed Heck-type reaction employing a bromobenzenesulfonyl chloride has been reported (Scheme 2, top).[5a] Rare examples of such Pd-catalysed reactions using a 4-bromobenzenesulfinate or bromobenzenesulfonyl hydrazides have been described (Scheme 2, middle).[5b,5d] A few examples of Rh- or Ru-catalysed Heck type reactions in the presence of halo-substituted arylation agents, but without cleavage of the C-halo bond, have also been reported.[6,7]



Scheme 2

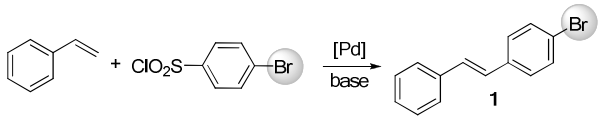
As the use of (poly)halobenzenesulfonyl chlorides as reactants in Pd-catalysed reactions presents several attractive features - 1) many of them are commercially available at an affordable cost, 2) they can be easily prepared from sulfonic acids or sulphur substrates by chlorination, 3) there are generally no cleavage of the C-halo bonds in Pd-catalysed reactions - the reaction outcome using such benzenesulfonyl chlorides in Heck-type reaction needed to be investigated in more details (Scheme 2, bottom).

Herein, we report on the influence of the position of the halo-substituent on the benzenesulfonyl chlorides in the Pd-catalysed desulfitative Heck reaction. The influence of other additional substituents and the reactivity of some di- and tri-bromobenzenesulfonyl chlorides were also investigated.

Results and discussion

Based on our previous results on the Pd-catalysed desulfitative[8] coupling with heteroarene derivatives,[9,10] the influence of several reaction conditions, using 5 mol% $PdCl_2(MeCN)_2$ catalyst and Li_2CO_3 as the base, on the products formation was first examined (Table 1). From 1 equiv. of 4-bromobenzenesulfonyl chloride and 1.5 equiv. of styrene at 100 °C during 24 h, the desired Heck type product **1** was obtained in 62% yield with complete regio- and stereo-selectivity in favour of the formation of the *E*-isomer and without cleavage of the C-Br bond (Table 1, entry 1). A lower reaction temperature of 80 °C also gave selectively **1**, but in very low yield due to a poor conversion (Table 1, entry 2). We also investigated the influence of the nature of the solvent. DMF and CPME were ineffective, as with these two solvents, **1** could not be isolated (Table 1, entries 3 and 4). The reaction performed in ethylbenzene and diethyl carbonate gave **1** in poor 22% and 12% yields, respectively (Table 1, entries 5 and 6). The use of 5 mol% $Pd(OAc)_2$, afforded **1**, in a slightly higher yields of 65%; whereas, a reaction performed with $PdCl_2$ gave **1** in 41% yield (Table 1, entries 7 and 8). When K_2CO_3 or Cs_2CO_3 were used as bases instead of Li_2CO_3, **1** was obtained in quite low yields (Table 1, entries 10 and 11). This difference between carbonated bases might be due to the higher solubility of Cs_2CO_3 compared with Li_2CO_3 or K_2CO_3 in dioxane. A similar trend had been previously observed in Pd-catalysed desulfitative Heck reaction or direct arylation.[3d,9a,11]

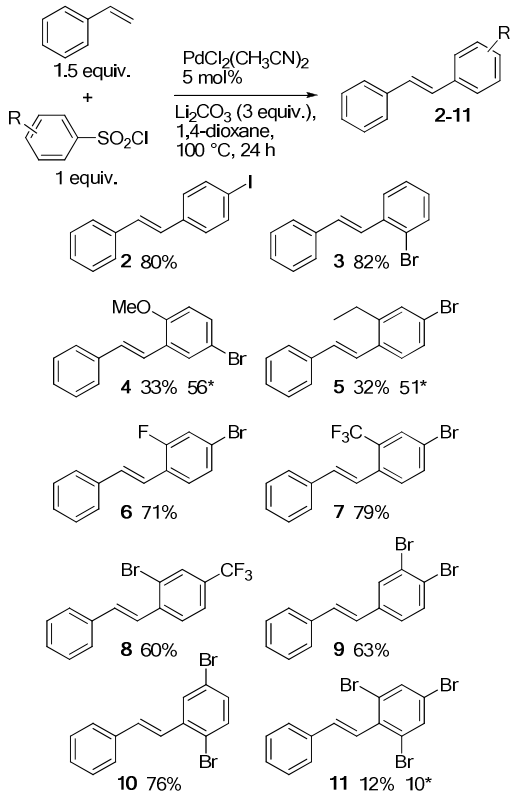
Table 1. Influence of the conditions on the Pd-catalysed desulfitative reaction of styrene with 4-bromobenzenesulfonyl chloride.



Entry	Catalyst	Solvent	Base	Temp. (°C)	Yield in **1** (%)
1	$PdCl_2(CH_3CN)_2$	1,4-dioxane	Li_2CO_3	100	67 (62)
2	$PdCl_2(CH_3CN)_2$	1,4-dioxane	Li_2CO_3	80	5
3	$PdCl_2(CH_3CN)_2$	DMF	Li_2CO_3	150	trace
4	$PdCl_2(CH_3CN)_2$	CPME[a]	Li_2CO_3	120	0
5	$PdCl_2(CH_3CN)_2$	Ethylbenzene	Li_2CO_3	100	22
6	$PdCl_2(CH_3CN)_2$	Diethyl carbonate	Li_2CO_3	150	12
7	$Pd(OAc)_2$	1,4-dioxane	Li_2CO_3	100	69 (65)
8	$PdCl_2$	1,4-dioxane	Li_2CO_3	100	41
9	-	1,4-dioxane	Li_2CO_3	100	0
10	$PdCl_2(CH_3CN)_2$	1,4-dioxane	K_2CO_3	100	33
11	$PdCl_2(CH_3CN)_2$	1,4-dioxane	Cs_2CO_3	100	8

Condition: [Pd] 5 mol%, 4-bromobenzenesulfonyl chloride (1 equiv.), styrene (1.5 equiv.), Li_2CO_3 (3 equiv.), yield determined by GC and crude ^1H NMR, 24 h, yields in parenthesis are isolated. [a] CPME: cyclopentyl methyl ether.

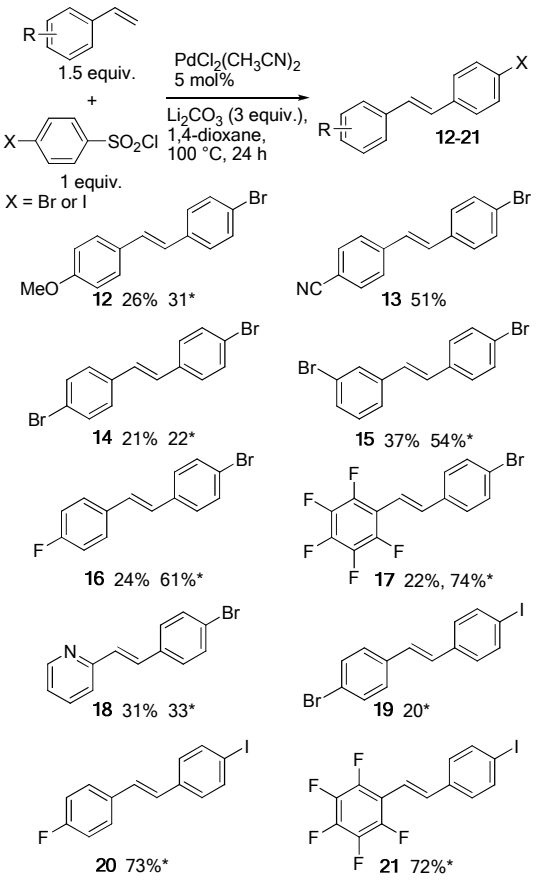
Then, the scope of the Pd-catalysed desulfitative Heck reaction of styrene with a variety of halo-substituted benzenesulfonyl chlorides was investigated (Scheme 3). A high yield of 80% in **2** was obtained for the reaction of 4-iodobenzenesulfonyl chloride with styrene. Moreover, no cleavage of the C-I bond was observed. *Ortho*-substituents often exhibit an important influence on Pd-catalysed reactions due to their coordination and/or steric properties. Therefore, the reactivity of 2-bromobenzenesulfonyl chloride and of a set of 2-substituted 4-bromobenzenesulfonyl chlorides was investigated. 2-Bromobenzenesulfonyl chloride afforded the desired product **3** in 82% yield. Lower yields of 33% and 32% in **4** and **5** were obtained in the presence of 2-methoxy- or 2-ethyl-substituted 4-bromobenzenesulfonyl chlorides. These poor yields are probably due to the formation of quite large amounts of oligomers or polymers of styrene as side-products. However, with these two substrates, the use of a larger excess of styrene (3 equiv.) using $Pd(OAc)_2$ as catalyst allowed to increase the yield in **4** and **5** to 56% and 51% yields, respectively. On the other hand, 4-bromo-2-fluorobenzenesulfonyl chloride and more congested 4-bromo-2-(trifluoromethyl)benzenesulfonyl chloride afforded **6** and **7** in 71% and 79% yields, respectively. From 2-bromo-4-(trifluoro)benzenesulfonyl chloride, the desired product **8** was also obtained in good yield. It should be mentioned that for all these reactions, no cleavage of the C-halo bonds was observed allowing further transformations. As both 2,5- and 3,4-dibromobenzene-1-sulfonyl chlorides can be easily prepared by reaction of 1,4- and 1,2-dibromobenzenes with chlorosulfonic acid,[12a] their reactivity for desulfitative Heck reaction was also evaluated. In both cases, the expected products **9** and **10** were obtained in high yields without cleavage of both C-Br bonds. Moreover, the reaction of 2,4,6-tribromobenzene-1-sulfonyl chloride with styrene was found to afford **11** with the three C-Br bonds untouched, but in only 12% yield. Currently, such polyhalo-substituted styrenes are generally prepared using multi-steps syntheses *via* Wittig reaction as the key step.[12b,12c]



*: Styrene derivative 3 equiv., 40 h, $Pd(OAc)_2$ 5 mol%

Scheme 3

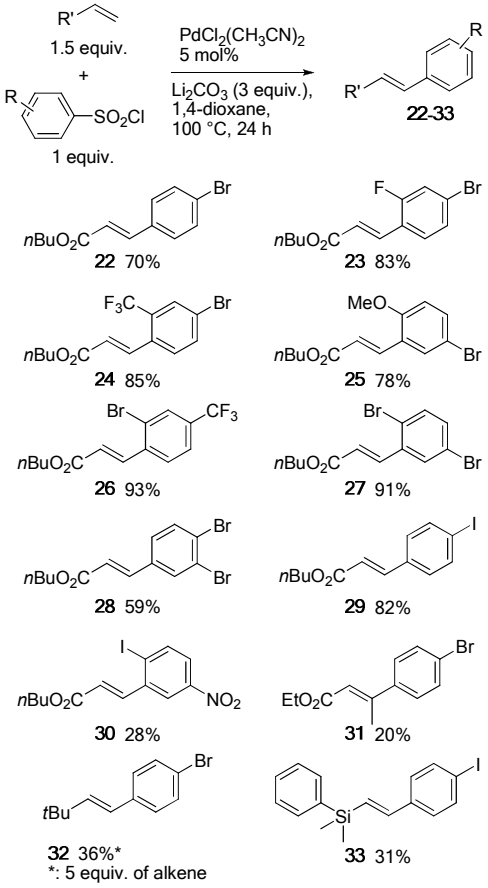
The influence of some styrene substituents on their reactivity for this reaction was then examined (Scheme 4). Lower yields than with styrene were obtained with both 4-methoxy- and 4-cyano-styrenes, as **12** and **13** were isolated in only 26% and 51% yields, respectively. However, a bromo substituent on styrene was tolerated allowing the synthesis of dibromostilbenes. From 4- and 3-bromostyrenes and 4-bromobenzenesulfonyl chloride as reaction partner, the desired dibromostilbenes **14** and **15** were obtained in low to moderate yields, due to the low conversions of these two bromobenzenesulfonyl chlorides. It should be mentioned that the use of a larger excess of 3-bromostyrene using $Pd(OAc)_2$ as catalyst allowed to increase the yield in **15** to 54%. Both 4-fluorostyrene and 2,3,4,5,6-pentafluorostyrene were also successfully reacted with 4-bromobenzenesulfonyl chloride affording **16** and **17** in good yields. Again, the use of 3 equiv. of alkene with 5 mol% $Pd(OAc)_2$ catalyst gave the highest yields. A moderate yield in **18** was obtained using 2-vinylpyridine and 4-bromobenzenesulfonyl chloride as reaction partners. Then, we compared the reactivity of 4-bromobenzenesulfonyl chloride and 4-iodobenzenesulfonyl chloride in the presence of three styrene derivatives. Similar yields than with 4-bromobenzenesulfonyl chloride were obtained in all cases. Moreover, no cleavage of the C-I bond was observed. For example, 4-fluorostyrene and 2,3,4,5,6-pentafluorostyrene reacted with 4-iodobenzenesulfonyl chloride gave **20** and **21** in 73% and 72% yields, respectively. Again, in the presence of 4-bromostyrene, a low yield in desired product **19** was obtained.



*: Styrene derivative 3 equiv., 40 h, $Pd(OAc)_2$ 5 mol%

Scheme 4

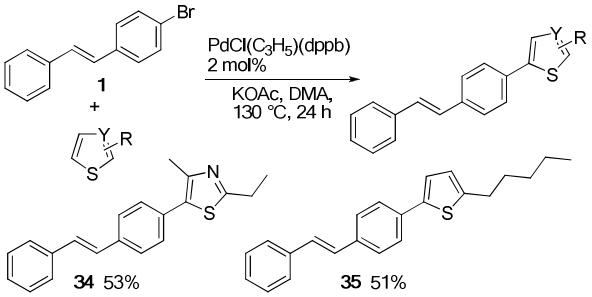
The reactivity of a few other alkenes for such reactions was also investigated (Scheme 5). The reaction of *n*-butylacrylate with 4-bromobenzenesulfonyl chloride gave the cinnamate derivative **22** in 70% yield. Again a complete regio- and stereo-selectivity in favour of the formation of the *E*-isomer was observed. A set of substituents at C2 of 4-bromobenzenesulfonyl chloride, for reaction with *n*-butylacrylate, was also tolerated affording the bromo-substituted cinnamates **23**-**25** in 78-85% yields. A high yield of 93% in **26** was also obtained for the reaction of *n*-butylacrylate with 2-bromo-4-(trifluoromethyl)benzenesulfonyl chloride. Both 2,5- and 3,4-dibromobenzene-1-sulfonyl chlorides were also successfully coupled with *n*-butylacrylate affording **27** and **28** in 91% and 59% yields, respectively. The reaction of *n*-butylacrylate with 4-iodobenzenesulfonyl chloride gave Heck type product **29** in 82% yield, without C-I bond cleavage. Even the electron-deficient 2-iodo-5-nitrobenzenesulfonyl chloride gave the target product **30** without cleavage of the very reactive C-I bond. If terminal alkenes are reactive under these conditions in Pd-catalysed desulfitative Heck reaction, on the other hand, ethyl *trans*-2-butenoate[13] exhibits a poor reactivity affording **31** in only 20% yield. However, the reaction was found to be fully regio- and stereo-selective. The reaction of 3,3-dimethylbut-1-ene with 4-bromobenzenesulfonyl chloride gave **32** in only 36% yield. Due to the low boiling point of 3,3-dimethylbut-1-ene, 5 equiv. of this alkene were employed for this reaction. From dimethyl(phenyl)(vinyl)silane and 4-iodobenzenesulfonyl chloride, *E*-isomer **33** was also stereoselectively obtained, but in low yield (31%) is due to the partial *in-situ* desilylation of **30** affording 4-iodostyrene as side-product.



Scheme 5

Although the mechanism is not yet elucidated, we assume that in the first step an oxidative addition of $ArSO_2Cl$ to Pd(II) affords a Pd(IV) species. Such oxidative addition on Pd(II) have been reported to proceed even at room temperature.[14] Then, after elimination of SO_2, the coordination of the alkene followed by insertion in the Pd-Ar bond might afford a Pd-$CHRCH_2Ar$ intermediate. Then, β-H elimination followed by reductive elimination assisted by the base would produces the β-arylated alkene derivative with regeneration of a Pd(II) species.

Since one decade, Pd-catalysed direct arylation of heteroaromatics with aryl halides *via* a C–H bond activation has become a popular method for generating carbon-carbon bonds.[15] In order to further demonstrate the synthetic potential of the halo-substituted stilbenes prepared by our method, Pd-catalysed direct arylations using **1** as aryl source was also studied (Scheme 6). Using 2 mol% $PdCl(C_3H_5)_2(dppb)$[16] catalyst in the presence of KOAc in DMA, **1** was coupled with 2-ethyl-4-methylthiazole and 2-pentylthiophene to afford **34** and **35** in 53% and 51% yields, respectively. In both cases, a regioselective C5-arylation of the heteroarene, without isomerisation of the stilbene double bond, was observed.



Scheme 6

Conclusion

In summary, we report here phosphine-ligand free, ammonium-salt free and oxidant-free conditions allowing desulfitative palladium-catalysed Heck type reactions using both bromo- and iodo-substituted benzenesulfonyl chlorides, in the presence of styrenes or acrylates, as the reaction partners. In the course of these reactions, no cleavage of the benzenesulfonyl chlorides C-Br or C-I bonds was observed allowing further transformations. The reaction was found to proceed with easily accessible $Pd(MeCN)_2Cl_2$ catalyst and Li_2CO_3 as inexpensive base. Moreover, this procedure tolerates a variety of substituents on the halobenzenesulfonyl chlorides. Due to the wide availability of diversely functionalized (poly)halo-substituted benzenesulfonyl chlorides at an affordable cost, such simple reaction conditions (no expensive base and ligand) should be very attractive to synthetic chemists for access to (poly)halo-substituted stilbene or cinnamate derivatives, compared to more classical methods, such as Wittig reaction, which requires several steps and, in some cases, affords mixtures of stereoisomers.

Experimental section

General Remarks:

All reactions were run under argon in Schlenk tubes using vacuum lines. Dioxane analytical grade was not distilled before use. Li_2CO_3 (>99%) was used. Commercial alkene derivatives and halobenzenesulfonyl chlorides were used without purification. The reactions were followed by GC and NMR. ^1H and ^{13}C spectra were recorded with a Bruker 400 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (7.26 for ^1H NMR and 77.0 for ^{13}C NMR). Flash chromatography was performed on silica gel (230–400 mesh).

General procedure for desulfitative reactions: In a typical experiment, the alkene derivative (1.5 mmol), halobenzenesulfonyl chloride derivative (1 mmol), Li_2CO_3 (0.222 g, 3 mmol) and $PdCl_2(MeCN)_2$ (12.9 mg, 0.05 mmol), were dissolved in 1,4-dioxane (2 mL) under an argon atmosphere. The reaction mixture was stirred at 100 °C for 24 h. After evaporation of the solvent, the product was purified by silica gel column chromatography.

Preparation of the $PdCl(C_3H_5)(dppb)$ catalyst:[16] An oven-dried 40 mL Schlenk tube equipped with a magnetic stirring bar under argon atmosphere, was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). 10 mL of anhydrous dichloromethane were added, then, the solution was stirred at room temperature for twenty minutes. The solvent was removed in vacuum. The yellow powder was used without purification. ^{31}P NMR (81 MHz, $CDCl_3$) δ= 19.3 (s).

(*E*)-1-Bromo-4-styrylbenzene (1)[17]

From styrene (0.156 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **1** was obtained in 62% (0.160 g) yield as a white solid (mp: 141-143 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.51 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.40-7.33 (m, 4H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 16.4 Hz, 1H), 7.03 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ137.0, 136.3, 131.8, 129.4, 128.7, 128.0, 127.9, 127.4, 126.6, 121.3.

(*E*)-1-Iodo-4-styrylbenzene (2)[18]

From styrene (0.156 g, 1.5 mmol) and 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol), product **2** was obtained in 80% (0.244 g) yield as a white solid (mp: 156-159 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.72 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.43-7.25 (m, 5H), 7.14 (d, *J* = 16.4 Hz, 1H), 7.04 7.14 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ137.8, 137.0, 136.9, 129.6, 128.9, 128.3, 128.0, 127.6, 126.7, 91.9.

(*E*)-1-Bromo-2-styrylbenzene (3)[19]

From styrene (0.156 g, 1.5 mmol) and 2-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **3** was obtained in 82% (0.212 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.70 (d, *J* = 8.5 Hz, 1H), 7.65-7.58 (m, 3H), 7.55 (d, *J* = 16.4 Hz, 1H), 7.46-7.32 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ137.3, 137.2, 133.2, 131.6, 128.9, 128.8, 128.2, 127.7, 127.6, 127.0, 126.8, 124.3.

(*E*)-4-Bromo-1-methoxy-2-styrylbenzene (4)[20]

From styrene (0.156 g, 1.5 mmol) and 2-methoxy-5-bromobenzenesulfonyl chloride (0.285 g, 1 mmol), product **4** was obtained in 33% (0.095 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.70 (d, *J* = 2.5 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.42-7.25 (m, 5H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ156.0, 137.5, 131.1, 130.4, 129.0, 128.8, 128.7, 127.9, 126.8, 122.2, 113.4, 112.7, 55.9.

(*E*)-1-Bromo-2-ethyl-4-styrylbenzene (5)

From styrene (0.156 g, 1.5 mmol) and 2-ethyl-4-bromobenzenesulfonyl chloride (0.284 g, 1 mmol), product **5** was obtained in 32% (0.092 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.52 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.43-7.25 (m, 6H), 6.99 (d, *J* = 16.4 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ144.0, 137.5, 134.9, 131.7, 130.8, 129.3, 128.9, 128.0, 127.4, 126.7, 125.2, 121.6, 26.4, 15.2.

$C_{16}H_{15}Br$ (287.19): Calcd C 66.91, H 5.26; Found C 67.12, H 5.15.

(*E*)-4-Bromo-2-fluoro-1-styrylbenzene (6)

From styrene (0.156 g, 1.5 mmol) and 2-fluoro-4-bromobenzenesulfonyl chloride (0.273 g, 1 mmol), product **6** was obtained in 71% (0.197 g) yield as a white solid (mp: 78-80 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.52 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.35-7.25 (m, 3H), 7.17 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ160.1 (d, *J* = 254.1 Hz), 137.0, 131.6 (d, *J* = 4.8 Hz), 128.9, 128.3, 128.1 (d, *J* = 4.3 Hz), 127.7 (d, *J* = 3.6 Hz), 126.8, 124.5 (d, *J* = 12.0 Hz), 121.1 (d, *J* = 9.9 Hz), 120.0 (d, *J* = 3.4 Hz), 119.5 (d, *J* = 25.4 Hz).

$C_{14}H_{10}BrF$ (277.13): Calcd C 60.68, H 3.64; Found C 60.47, H 3.80.

(*E*)-4-Bromo-1-styryl-2-(trifluoromethyl)benzene (7)

From styrene (0.156 g, 1.5 mmol) and 2-trifluoromethyl-4-bromobenzenesulfonyl chloride (0.323 g, 1 mmol), product **7** was obtained in 79% (0.258 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.81 (s, 1H), 7.66 (s, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.45-7.35 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ136.6, 135.5 (q, *J* = 1.7 Hz), 135.1, 133.4, 129.3 (q, *J* = 6.0 Hz), 129.1 (q, *J* = 31.0 Hz), 128.9, 128.7, 128.6, 127.1, 123.4 (q, *J* = 274.4 Hz), 123.3 (q, *J* = 2.0 Hz), 120.9.

$C_{15}H_{10}BrF_3$ (327.14): Calcd C 55.07, H 3.08; Found C 55.00, H 3.22.

(*E*)-2-Bromo-1-styryl-4-(trifluoromethyl)benzene (8)

From styrene (0.156 g, 1.5 mmol) and 2-bromo-4-trifluoromethylbenzenesulfonyl chloride (0.323 g, 1 mmol), product **8** was obtained in 60% (0.196 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.86 (d, *J* = 1.7 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.60-7.55 (m, 3H), 7.47 (d, *J* = 16.4 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ140.8, 136.5, 133.9, 130.5 (q, *J* = 33.1 Hz), 130.2 (q, *J* = 3.0 Hz), 128.9, 128.8, 127.2, 126.9, 126.2, 124.5 (q, *J* = 3.7 Hz), 124.0, 123.2 (q, *J* = 272.4 Hz).

$C_{15}H_{10}BrF_3$ (327.14): Calcd C 55.07, H 3.08; Found C 55.30, H 3.07.

(*E*)-1,2-Dibromo-4-styrylbenzene (9)

From styrene (0.156 g, 1.5 mmol) and 3,4-dibromobenzene-1-sulfonyl chloride (0.334 g, 1 mmol), product **9** was obtained in 63% (0.213 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.76 (d, *J* = 2.1 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.35-7.25 (m, 2H), 7.11 (d, *J* = 16.4 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ138.3, 136.6, 133.8, 131.4, 130.8, 128.9, 128.4, 126.8, 126.5, 126.1, 125.2, 123.3.

$C_{14}H_{10}Br_2$ (338.04): Calcd C 49.74, H 2.98; Found C 49.89, H 3.12.

(*E*)-1,4-Dibromo-2-styrylbenzene (10)

From styrene (0.156 g, 1.5 mmol) and 2,5-dibromobenzene-1-sulfonyl chloride (0.334 g, 1 mmol), product **10** was obtained in 76% (0.257 g) yield as a yellow solid (mp: 62-64 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.79 (d, *J* = 2.3 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.46-7.20 (m, 7H), 7.04 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ139.2, 136.7, 134.5, 132.8, 131.6, 129.6, 128.9, 128.6, 127.1, 126.3, 122.7, 121.6.

$C_{14}H_{10}Br_2$ (338.04): Calcd C 49.74, H 2.98; Found C 49.47, H 3.18.

(*E*)-1,3,5-Tribromo-2-styrylbenzene (11)

From styrene (0.156 g, 1.5 mmol) and 2,4,6-tribromobenzene-1-sulfonyl chloride (0.620 g, 1 mmol), product **11** was obtained in 12% (0.050 g) yield as a white solid (mp: 80-82 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.76 (s, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.92 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ137.5, 137.4, 136.3, 134.9, 128.9, 128.7, 126.9, 126.1, 124.5, 121.0.

$C_{14}H_9Br_3$ (416.93): Calcd C 40.33, H 2.18; Found C 40.54, H 2.01.

(*E*)-1-Bromo-4-(4-methoxystyryl)benzene (12)[21]

From 4-methoxystyrene (0.201 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **12** was obtained in 26% (0.075 g) yield as a white solid (mp: 207-209 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.47 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.93-6.87 (m, 3H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ159.7, 136.8, 131.9, 129.9, 129.1, 127.9, 127.8, 125.4, 120.9, 114.3, 55.5.

(*E*)-4-(4-Bromostyryl)benzonitrile (13)[22]

From 4-cyanostyrene (0.194 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **13** was obtained in 51% (0.145 g) yield as a yellow solid (mp: 192-194 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.61 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H),7.39 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 16.4 Hz, 1H), 7.07 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ141.6, 135.4, 132.7, 132.1, 131.2, 128.5, 127.6, 127.1, 122.7, 119.1, 111.0.

(*E*)-1,2-Bis(4-bromophenyl)ethane (14)[23]

From 4-bromostyrene (0.183 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **14** was obtained in 21% (0.071 g) yield as a white solid (mp: 216-219 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.48 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 4H), 7.02 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ136.1, 132.0, 128.3, 128.2, 121.8.

(*E*)-1-Bromo-3-(4-bromostyryl)benzene (15)[24]

From 3-bromostyrene (0.366 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **15** was obtained in 54% (0.182 g) yield as a white solid (mp: 97-100 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.65 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.43-7.38 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 16.4 Hz, 1H), 6.99 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ139.3, 135.9, 132.0, 130.8, 130.3, 129.4, 129.0, 128.2, 127.9, 125.4, 123.1, 121.9.

(*E*)-1-Bromo-4-(4-fluorostyryl)benzene (16)[25]

From 4-fluorostyrene (0.244 g, 3 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **16** was obtained in 61% (0.169 g) yield as a white solid (mp: 138-140 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.53-7.45 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.09-7.02 (m, 3H), 6.92 (d, *J* = 16.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ162.6 (d, *J* = 257.5 Hz), 136.3, 133.3, 132.0, 128.4, 128.2 (d, *J* = 8.0 Hz), 128.0, 127.4 (d, *J* = 2.4 Hz), 121.5, 115.8 (d, *J* = 21.9 Hz).

(E)-1-(4-bromostyryl)-2,3,4,5,6-pentafluorobenzene (17)[23]

From 2,3,4,5,6-pentafluorostyrene (0.582 g, 3 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **17** was obtained in 74% (0.258 g) yield as a white solid (mp: 104-106 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.53 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 16.8 Hz, 1H), 6.97 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ146.9 (dm, *J* = 250.0 Hz), 140.0 (dm, *J* = 250.0 Hz), 137.2 (dm, *J* = 250.0 Hz), 138.6 (m), 137.7, 132.0, 128.3, 123.0, 113.4 (m), 112.0 (t, *J* = 13.6 Hz).

(*E*)-2-(4-Bromostyryl)pyridine (18)[26]

From 2-vinylpyridine (0.158 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **18** was obtained in 31% (0.081 g) yield as a brown solid (mp: 106-108 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ8.61 (d, *J* = 5.1 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.74 (td, *J* = 7.7, 1.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 14.9 Hz, 1H), 7.42 (d, *J* = 14.9 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.28 (dd, *J* = 7.7, 5.1 Hz), 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ150.9, 150.5, 141.2, 139.5, 137.2, 132.8, 131.5, 129.6, 129.0, 125.7, 125.3.

(*E*)-1-Bromo-4-(4-iodostyryl)benzene (19)[27]

From 4-bromostyrene (0.366 g, 3 mmol) and 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol), product **19** was obtained in 20% (0.077 g) yield as a white solid (mp: 240-242°C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.67 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.97 (d, *J* = 16.3 Hz, 1H).

(*E*)-1-Fluoro-4-(4-iodostyryl)benzene (20)[28]

From 4-fluorostyrene (0.244 g, 3 mmol) and 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol), product **20** was obtained in 73% (0.236 g) yield as a white solid (mp: 165-167 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.68 (d, *J* = 8.3 Hz, 2H), 7.47 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.10-7.03 (m, 3H), 6.92 (d, *J* = 16.4 Hz, 1H).

(*E*)-1,2,3,4,5-Pentafluoro-6-(4-iodostyryl)benzene (21)

From 2,3,4,5,6-pentafluorostyrene (0.582 g, 3 mmol) and 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol), product **21** was obtained in 72% (0.285 g) yield as a white solid (mp: 107-110 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 16.8 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 16.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ144.9 (dm, *J* = 250.0 Hz), 140.1 (dm, *J* = 250.0 Hz), 138.2, 137.8 (dm, *J* = 250.0 Hz), 136.1 (m), 128.6, 113.5, 112.3 (t, *J* = 13.6 Hz), 94.8.

$C_{14}H_6F_5I$ (396.09): Calcd C 42.45, H 1.53; Found C 42.55, H 1.41.

(*E*)-Butyl 3-(4-bromophenyl)acrylate (22)[7]

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **22** was obtained in 70% (0.198 g) yield as a white solid (mp: 37-39 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.60 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.9, 143.2, 133.5, 132.2, 129.5, 124.5, 119.1, 64.7, 30.9, 19.3, 13.9.

(*E*)-Butyl 3-(4-bromo-2-fluorophenyl)acrylate (23)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 2-fluoro-4-bromobenzene-1-sulfonyl chloride (0.273 g, 1 mmol), product **23** was obtained in 83% (0.250 g) yield as a white solid (mp: 36-38 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.72 (d, *J* = 16.0 Hz, 1H), 7.41 (t, *J* = 9.0 Hz, 1H), 7.33-7.26 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.8, 160.9 (d, *J* = 258.4 Hz), 136.1 (d, *J* = 2.5 Hz), 130.0 (d, *J* = 3.6 Hz), 128.0 (d, *J* = 3.7 Hz), 124.4 (d, *J* = 9.7 Hz), 121.8 (d, *J* = 11.8 Hz), 121.5 (d, *J* = 6.6 Hz), 120.1 (d, *J* = 25.3 Hz), 64.8, 30.9, 19.3, 13.8.

$C_{13}H_{14}BrFO_2$ (301.15): Calcd C 51.85, H 4.69; Found C 51.59, H 4.87.

(*E*)-Butyl 3-(4-bromo-2-(trifluoromethyl)phenyl)acrylate (24)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 2-trifluoromethyl-4-bromobenzenesulfonyl chloride (0.323 g, 1 mmol), product **24** was obtained in 85% (0.298 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.95 (d, *J* = 16.0 Hz, 1H), 7.83 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.22 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.0, 138.9, 135.4, 132.5, 130.4 (q, *J* = 31.1 Hz), 129.6 (q, *J* = 5.8 Hz), 129.5, 123.8, 123.3, 123.0 (q, *J* = 274.7 Hz), 65.0, 30.8, 19.3, 13.9.

$C_{14}H_{14}BrF_3O_2$ (351.16): Calcd C 47.88, H 4.02; Found C 47.79, H 4.14.

(*E*)-Butyl 3-(5-bromo-2-methoxyphenyl)acrylate (25)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 5-bromo-2-methoxybenzene-1-sulfonyl chloride (0.285 g, 1 mmol), product **25** was obtained in 78% (0.244 g) yield as a white solid (mp: 60-62 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.88 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 2.5 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 7.6 Hz, 2H), 3.86 (s, 3H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ167.2, 157.4, 138.4, 133.8, 131.2, 125.6, 120.2, 113.1, 113.0, 64.5, 55.9, 30.9, 19.3, 13.9.

$C_{14}H_{17}BrO_3$ (313.19): Calcd C 53.69, H 5.47; Found C 53.48, H 5.38.

(*E*)-Butyl 3-(2-bromo-4-(trifluoromethyl)phenyl)acrylate (26)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 2-bromo-4-trifluoromethylbenzenesulfonyl chloride (0.323 g, 1 mmol), product **26** was obtained in 93% (0.326 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.99 (d, *J* = 16.0 Hz, 1H), 7.87 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.24 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.1, 141.6, 138.3, 132.9 (q, *J* = 33.5 Hz), 130.5 (q, *J* = 3.0 Hz), 128.2, 125.2, 124.6 (q, *J* = 3.7 Hz), 123.6, 123.0 (q, *J* = 272.7 Hz), 65.0, 30.8, 19.3, 13.9.

$C_{14}H_{14}BrF_3O_2$ (351.16): Calcd C 47.88, H 4.02; Found C 47.98, H 4.19.

(*E*)-Butyl 3-(2,5-dibromophenyl)acrylate (27)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 1,4-dibromobenzene-1-sulfonyl chloride (0.334 g, 1 mmol), product **27** was obtained in 91% (0.329 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.93 (d, *J* = 16.0 Hz, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.24 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.9, 141.5, 136.5, 134.7, 133.9, 130.6, 123.8, 122.4, 121.7, 64.8, 30.8, 19.3, 13.8.

$C_{13}H_{14}Br_2O_2$ (362.06): Calcd C 43.13, H 3.90; Found C 43.01, H 3.87.

(*E*)-Butyl 3-(3,4-dibromophenyl)acrylate (28)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 3,4-dibromobenzene-1-sulfonyl chloride (0.334 g, 1 mmol), product **28** was obtained in 59% (0.214 g) yield as a yellow solid (mp: 38-41 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.76 (d, *J* = 2.1 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 16.0 Hz, 1H), 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.21 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.8, 141.8, 135.4, 134.2, 132.9, 127.7, 126.6, 125.6, 120.4, 64.8, 30.9, 19.3, 13.9.

$C_{13}H_{14}Br_2O_2$ (362.06): Calcd C 43.13, H 3.90; Found C 43.20, H 3.99.

(*E*)-*n*-Butyl 3-(4-iodophenyl)acrylate (29)[7]

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol), product **29** was obtained in 82% (0.271 g) yield as a white solid (mp: 39-41 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.70 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 16.0 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 7.6 Hz, 2H), 1.68 (quint., *J* = 7.6 Hz, 2H), 1.41 (sext., *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.8, 143.4, 138.2, 134.0, 129.6, 119.2, 96.5, 64.6, 30.8, 19.3, 13.8.

(*E*)-Butyl 3-(2-iodo-5-nitrophenyl)acrylate (30)

From *n*-butylacrylate (0.192 g, 1.5 mmol) and 2-iodo-5-nitrobenzene-1-sulfonyl chloride (0.347 g, 1 mmol), product **30** was obtained in 28% (0.105 g) yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ8.30 (d, *J* = 2.3Hz, 1H), 8.14 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.04 (d, *J* = 16.0 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ165.8, 148.6, 139.2, 138.2, 135.6, 128.4, 125.5, 125.0, 122.1, 65.2, 30.8, 19.3, 13.9.

$C_{13}H_{14}NIO_4$ (375.16): Calcd C 41.62, H 3.76; Found C 41.66, H 3.99.

(*E*)-Ethyl 3-(4-bromophenyl)but-2-enoate (31)[29]

From ethyl *trans*-2-butenoate (0.171 g, 1.5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **31** was obtained in 20% (0.054 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.50 (d, *J* = 6.5 Hz, 2H), 7.34 (d, *J* = 6.5 Hz, 2H), 6.11 (s, 1H), 4.21 (q, *J* = 6.7 Hz, 2H), 2.54 (d, *J* = 1.3 Hz, 3H), 1.31 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ166.8, 154.2, 141.2, 131.8, 128.0, 123.3, 117.8, 60.1, 17.9, 14.5.

(*E*)-1-Bromo-4-(3,3-dimethylbut-1-enyl)benzene (32)[30]

From 3,3-dimethylbut-1-ene (0.420 g, 5 mmol) and 4-bromobenzenesulfonyl chloride (0.255 g, 1 mmol), product **32** was obtained in 36% (0.086 g) yield as a white solid (mp: 62-65 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.40 (d, *J* = 6.3 Hz, 2H), 7.22 (d, *J* = 6.3 Hz, 2H), 6.24 (s, 2H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ142.8, 137.2, 131.6, 127.7, 123.7, 120.5, 33.6, 29.6.

(*E*)-(4-Iodostyryl)dimethyl(phenyl)silane (33)

From dimethyl(phenyl)(vinyl)silane (0.243 g, 1.5 mmol) and 4-iodobenzenesulfonyl chloride (0.303 g, 1 mmol), product **33** was obtained in 31% (0.113 g) yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.60-7.53 (m, 2H), 7.40-7.35 (m, 3H), 7.18 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 19.1 Hz, 1H), 6.59 (d, *J* = 19.1 Hz, 1H), 0.44 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 138.3, 137.8, 137.7, 134.0, 129.3, 128.6, 128.4, 128.0, 93.8, -2.5.

$C_{16}H_{17}ISi$ (364.30): Calcd C 52.75, H 4.70; Found C 52.64, H 4.48.

(*E*)-2-Ethyl-4-methyl-5-(4-styrylphenyl)thiazole (34)

(*E*)-1-Bromo-4-styrylbenzene **1** (0.259 g, 1 mmol), 2-ethyl-4-methylthiazole (0.191 g, 1.5 mmol), KOAc (0.196 g, 2 mmol), and $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol), were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 130 °C for 24 h. After evaporation of the solvent, the product was purified by silica gel column chromatography affording **34** in 53% (0.162 g) yield as a yellow solid (mp: 112-114 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.47-7.35 (m, 4H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 16.4 Hz, 1H), 7.14 (d, *J* = 16.4 Hz, 1H), 3.04 (q, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 147.1, 137.3, 136.8, 131.7, 130.9, 129.5, 129.4, 128.9, 128.0, 127.9, 126.8, 126.7, 27.1, 16.4, 14.5.

$C_{20}H_{19}NS$ (305.44): Calcd C 78.65, H 6.27; Found C 78.79, H 6.09.

(*E*)-2-Pentyl-5-(4-styrylphenyl)thiophene (35)

(*E*)-1-Bromo-4-styrylbenzene **1** (0.259 g, 1 mmol), 2-pentylthiophene (0.231 g, 1.5 mmol), KOAc (0.196 g, 2 mmol), and $PdCl(C_3H_5)$(dppb) (12.2 mg, 0.02 mmol), were dissolved in DMA (2 mL) under an argon atmosphere. The reaction mixture was stirred at 130 °C for 24 h. After evaporation of the solvent, the product was purified by silica gel column chromatography affording **35** in 51% (0.169 g) yield as a brown solid (mp: 190-192 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.46 (m, 6H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.11 (s, 2H), 6.75 (d, *J* = 3.5 Hz, 1H), 2.81 (t, *J* = 7.6 Hz, 2H), 1.77-1.65 (m, 2H), 1.44-1.33 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 141.5, 137.5, 136.1, 134.1, 128.8, 128.5, 128.3, 127.7, 127.1, 126.6, 125.7, 125.2, 122.8, 31.5, 31.4, 30.4, 22.6, 14.2.

$C_{23}H_{24}S$ (332.50): Calcd C 83.08, H 7.28; Found C 82.94, H 7.30.

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Supporting Information

YES (this text will be updated with links prior to publication)

References

(1) (a) de Vries J. G. *Can. J. Chem.* **2001**, *79*, 1086-1092; (b) Oestreich, M. The Mizoroki–Heck Reaction, Wiley, New York, 2009; (c) Le Bras J.; Muzart, J. *Chem. Rev.*, **2011**, *111*, 1170-1214; (d) Mc Cartney, D.; Guiry, P. J. *Chem; Soc. Rev.* **2011**, *40*, 5122-5150; (e) Hussain, M.; Van Sung, T.; Langer, P. *Synlett* **2012**, *23*, 2735-2745.

(2) For Heck type reactions with aryl sulfinic acids: Wang G.-W.; Miao, T. *Chem. Eur. J.*, **2011**, *17*, 5787-5790.

(3) For Heck type reaction with benzenesulfonyl chlorides: (a) Miura, M.; Hashimoto, H.; Itoh K.; Nomura, M. *Tetrahedron Lett.*, **1989**, *30*, 975-976; (b) Dubbaka, S. R.; Zhao, D.; Fei, Z.; Volla, C. M. R.; Dyson P. J.; Vogel, P. *Synlett*, **2006**, 3155-3157; (c) Jafarpour, F.; Olia M. B. A.; Hazrati, H. *Adv. Synth. Catal.*, **2013**, *355*, 3407-3412; (d) Kusunuru, A. K.; Yousuf, S. K.; Tatina, M.; Mukherjee, D. *Eur. J. Org. Chem.* **2015**, 459-462.

(4) For a review on metal-catalysed desulfitative direct arylation: Yuan, K.; Soulé J. F.; Doucet, H. *ACS Catal.*, **2015**, *5*, 978-991.

(5) For a single example of Pd-catalysed Heck type reaction with a 4-bromobenzenesulfonyl chloride: (a) Miura, M.; Hashimoto, H.; Itoh K.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2207-2211; For an example of Pd-catalysed Heck type reaction with a 4-bromobenzenesulfinate : (b) Zhou, X.; Luo, J.; Liu, J.; Peng S.; Deng, G.-J. *Org. Lett.*, **2011**, *13*, 1432-1435; (c) Hu, S.; Xia, P.; Cheng K.; Qi, C. *Appl. Organomet. Chem.*, **2013**, *27*, 188-190. For examples of Pd-catalysed Heck type reaction with a 4-bromobenzenesulfonyl hydrazide: (d) Yang, F.-L.; Ma X.-T.; Tian, S.-K. *Chem. Eur. J.*, **2012**, *18*, 1582-1585.

(6) For a single example of Rh-catalysed Heck type reaction with a 4-bromobenzenesulfonyl chloride: Dubbaka S. R.; Vogel, P. *Chem. Eur. J.*, **2005**, *11*, 2633-2641.

(7) For examples of Ru-catalysed Heck type reaction with halo-substituted arylboronic acids: Farrington, E. J.; Barnard, C. F. J.; Rowsell, E.; Brown, J. M. *Adv. Synth. Catal.* **2005**, *347*, 185-195.

(8) For a review on transition-metal mediated C-S bond activation: Wang, L.; He W.; Yu, Z. *Chem. Soc. Rev.*, **2013**, *42*, 599-921.

(9) For selected examples of Pd-catalysed direct arylations via desulfitative coupling from our laboratory: (a) Yuan K.; Doucet, H. *Chem. Sci.*, **2014**, *5*, 392-396; (b) Loukotova, L.; Yuan, K.; Doucet, H. *ChemCatChem*, **2014**, *6*, 1303-1309; (c) Hfaiedh, A.; Yuan, K.; Ben Ammar, H.; Ben Hassine, B.; Soulé, J.-F.; Doucet H. *ChemSusChem* **2015**, *8*, 1794-1804.

(10) For Pd-catalysed conjugate addition using benzenesulfonyl chlorides and enones: Yuan, K.; Sang, R.; Soulé, J.-F.; Doucet H. *Cat. Sci. Technol.* **2015**, *5*, 2904-2912.

(11) Amatore, C.; Jutand A.; Le Duc, G. *Chem. Eur. J.* **2012**, *18*, 6616-6625.

(12) (a) Loeser, R.; Bergmann, R.; Frizler, M.; Mosch, B.; Dombrowski, L.; Kuchar, M.; Steinbach, J.; Guetschow, M.; Pietzsch, J. *ChemMedChem* **2013**, *8*, 1330-1344; (b) Nielsen, C. B.; Johnsen, M.; Arnbjerg, J.; Pittelkow, M.; McIlroy, S. P.; Ogilby, P. R.; Jorgensen, M. *J. Org. Chem.* **2005**, *70*, 7065-7079; (c) Biet, T.; Fihey, A.; Cauchy, T.; Vanthuyne, N.; Roussel, C.; Crassous, J.; Avarvari, N. *Chem. Eur. J.* **2013**, *19*, 13160-13167.

(13) For selected examples of Heck type reactions with disubstituted alkenes: (a) Melpolder, J.; Heck, R. *J. Org. Chem*. **1976**, *41*, 265-272; (b) Cortese N.; Ziegler, C.; Hrnjez, B., Heck, R. *J. Org. Chem*. **1978**, *43*, 2952-2958; (c) Cacchi, S.; Arcadi, A. *J. Org. Chem*. **1983**, *48*, 4236-4270; (d) Amorese, A.; Arcadi, A.; Bernocchi, E.; Cacchi, S.; Cerrini, S.; Fereli, W.; Ortar, G. *Tetrahedron* **1989**, *45*, 813-828; (e) Beller, M.; Riermeier, T. *Tetrahedron Lett*. **1996**, *37*, 6535-6538; (f) Beller, M.; Riermeier, T. *Eur. J. Inorg. Chem*. **1998**, *1*, 29-35; (g) Netherton, M.; Fu, G. *Org. Lett*. **2001**, *3*, 4295-4298; (h) Berthiol, F; Doucet, H; Santelli, M *Eur. J. Org. Chem.* **2003**, 1091-1096; (i) Kondolff, I, Doucet, H; Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 8487-8491.

(14) Zhao X.; Dong, V. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 932-934.

(15) For reviews: (a) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200-205; (b) Li, B.-J.; Yang, S.-D.; Shi, Z.-J. *Synlett* **2008**, 949-957; (c) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269-10310; (d) Ackermann, L.; Vicente, R.; Kapdi, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792-9826; (e) Joucla, L.; Djakovitch, L. *Adv. Synth. Catal.* **2009**, *351*, 673-714; (f) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315-1345; (g) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 10236-10254; (h) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936-946; (i) Wencel-Delord, J.; Glorius, F. *Nature Chem.* **2013**, *5*, 369-375; (j) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C. *Adv. Synth. Catal.* **2014**, *356*, 17-117; (k) He, M.; Soulé, J.-F.; Doucet, H. *ChemCatChem* **2014**, 6, 1824-1859; (l) Miura, M.; Satoh, T.; Hirano, K. *Bull. Chem. Soc. Jpn* **2014**, *87*, 751-764; (m) Bheeter, C. B.; Chen, L.; Soulé, J.-F.; Doucet, H. *Cat. Sci. Technol.* **2016**, DOI:10.1039/C5CY02095F.

(16) Cantat, T.; Génin, E.; Giroud, C.; Meyer G.; Jutand, A. *J. Organomet. Chem.* **2003**, *687*, 365-376.

(17) Sugihara, T.; Satoh, T.; Miura, M.; Nomura, M. *Adv. Synth. Catal.* **2004**, *346*, 1765-1772.

(18) Cella, R.; Stefani, H. A. *Tetrahedron* **2006**, *62*, 5656-5662.

(19) Berthiol, F.; Kondolff, I.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2004**, *689*, 2786-2798.

(20) Kohno, T.; Togashi, K.; Fukamiya, N. *Nat. Prod. Res.* **2007**, *21*, 606-615.

(21) Gigante, B.; Esteves, M. A.; Pires, N.; Davies, M. L.; Douglas, P.; Fonseca, S. M.; Burrows, H. D.; Castro, R. A. E.; Pina, J.; Seixas de Melo, J. *New J. Chem.* **2009**, *33*, 877-885.

(22) Yang, J.-S.; Hwang, C.-Y.; Hsieh, C.-C.; Chiou, S.-Y. *J. Org. Chem.* **2004**, *69*, 719-726.

(23) Patureau, F. W.; Nimphius, C.; Glorius, F. *Org. Lett.* **2011**, *13*, 6346-6349.

(24) Aydin, J.; Larsson, J. M.; Selander, N.; Szabo, K. J. *Org. Lett.* **2009**, *11*, 2852-2854.

(25) Kalkhambkar, R. G.; Laali, K. K. *Tetrahedron Lett.* **2011**, *52*, 1733-1737.

(26) Aun, C. E.; Clarkson, T. J.; Happer, D. A. R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 645-649.

(27) Wang, H.-W.; Yeh, M.-Y.; Chen, C.-H.; Lim, T.-S.; Fann, W.; Luh, T.-Y. *Macromolecules* **2008**, *41*, 2762-2770.

(28) Ebraheem, K. A. K.; Webb, G. A. *J. Mol. Struct.* **1975**, *25*, 387-96.

(29) Metternich, J. B.; Gilmour R. *J. Am. Chem. Soc.* **2015**, 137, 11254-11257.

(30) Mai, W.-P.; Song, G.; Sun, G.-C.; Yang, L.-R.; Yuan, J.-W.; Xiao, Y.-M.; Mao, P.; Qu, L.-B. *RSC Advances* **2013**, *3*, 19264-19267.