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Synthesis of biaryls via intramolecular free radical *ipso*-substitution reactions

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ABSTRACT

A variety of functionalised biaryls and heterobiaryls are prepared by intramolecular free radical [1,5]-*ipso*-substitution using sulfonamide and sulfonate derived tethering chains. The overall efficiency of the process is determined by appropriately positioned substituents on the aromatic acceptor ring. The extension of the process to benzylic sulfonates and their corresponding *N*-methylsulfonamide alternatives as substrates in potential [1,6]-*ipso*-substitution reactions leads mainly to the alternative [1,7] addition products.

1. Introduction

The biaryl moiety is a common feature in natural products, functioning as an integral part of a diverse range of compounds, with vastly different structures, chemical properties, biological functions and biosynthetic origin, including, for example, polyketides, terpenes, lignans, coumarins, flavonoids, tannins and alkaloids.[1] The properties of this important class of compounds and their derivatives have been extensively studied over the years. Their importance is exemplified in their numerous applications, for example, as biologically active natural products, as chiral reagents,[2] as crown ethers,[3] as polymers,[4] as organic materials for non-linear optics[5] and also as the foundation of chiral liquid crystals.[6]

As a consequence of their enormous importance and widespread use, a wide variety of methods have been developed for biaryl construction.[7,8] Nowadays, the most frequently adopted strategy for preparing both symmetrical and unsymmetrical functionalised biaryls revolves around the use of transition metal mediated coupling reactions.[9] Nevertheless, problems may still arise when the two rings are of incompatible electronic character and/or especially when severely hindered products are required.[10]

Over the last four decades, the importance of free radicals in new carbon–carbon bond formation for synthetic organic chemistry has been well documented.[11] The rise of interest in this area has almost certainly resulted as a direct consequence of the availability of a range of mild methods for the generation of carbon centred free radicals.[12] Moreover, it is now well established that these reactive intermediates possess a number of important advantages for the organic chemist. We reasoned that the ability of free radicals to operate with impunity in hindered environments of widely differing polarity could overcome some of the disadvantages encountered when applying transition metals mediated coupling reactions to the synthesis of biaryls.

Our interest in this area was aroused by the early observation from Speckamp that an apparently straightforward free radical chain reduction of a primary iodide by Bu_3SnH also afforded significant quantities of the products **2** and **3** via 1,5-*ipso*-substitution and 1,6-addition processes (Scheme 1).[13]

We therefore envisaged that modification of this reaction could lead to a general biaryl synthesis, using an intramolecular free radical *ipso*-substitution[14] approach for the formation of the aryl–aryl bond and featuring the selection of a sulfonyl substituted

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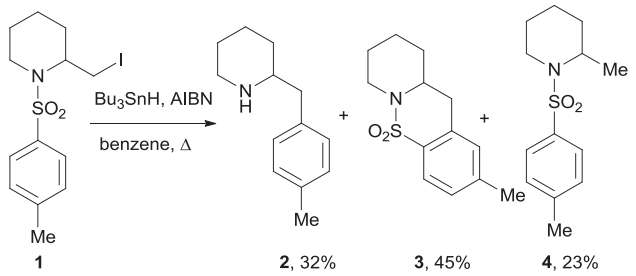
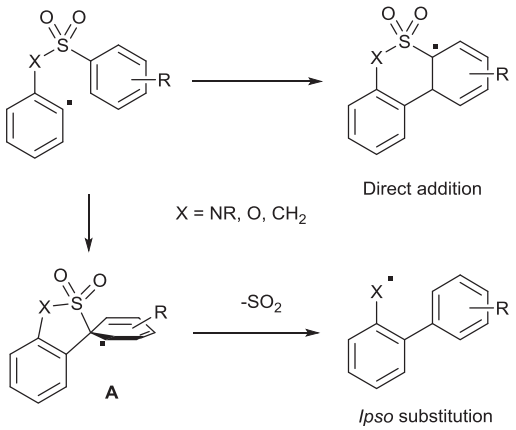


Scheme 1. Speckamp's study.

aromatic acceptor for the *ortho* substituted aryl radical, with subsequent extrusion of sulfur dioxide from the resultant spirocyclic intermediate **A** (Scheme 2).[14h,15] The study of such a system had the added attraction that the factors affecting the regiochemical outcome of the reaction could be probed. For example, it seemed plausible that variation of the length and nature of bridging group intermediate **A** could affect the distribution of products resulting from processes such as 1,5-*ipso*-substitution or 1,6-addition and thus, if this were the case, the reasons for such control might be ascertained.[16]



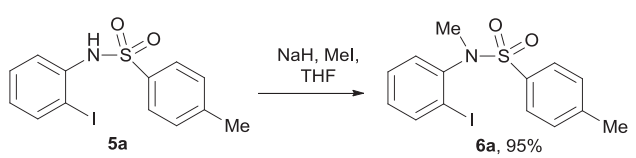
Scheme 2. This work.

2. Results and discussion

2.1. 1,5-*ipso*-Substitution versus 1,6-addition

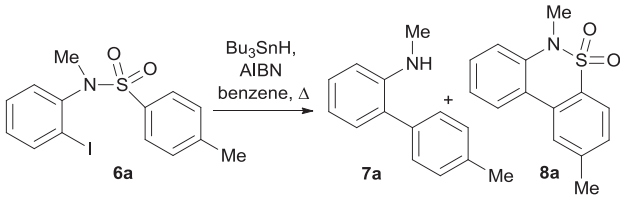
Initially, we decided to synthesise the rearrangement precursor **5a**, easily prepared in 79% yield by stirring 2-iodoaniline and tosyl chloride in pyridine. The addition over 15 h of Bu_3SnH (2.5 equiv, 0.2 M) and AIBN (0.7 equiv) in benzene to a solution of **5a** in refluxing benzene (0.05 M) led to extensive decomposition. Therefore, we methylated the nitrogen atom in **5a** (Scheme 3), the supposition being that the tertiary nitrogen atom in **6a** would have a closer electronic disposition to that of compound **1**. On this occasion the outcome of the radical reaction proved to be of greater interest as outlined in Table 1, entry a.

In an attempt to increase the yield of the 1,5-*ipso*-substitution product, **7a**, relative to that produced via 1,6-addition, **8a**, we



Scheme 3. Synthesis of **6a**.

Table 1
Attempts to increase the ratio 1,5-*ipso* (**7a**) versus 1,6-addition (**8a**) product

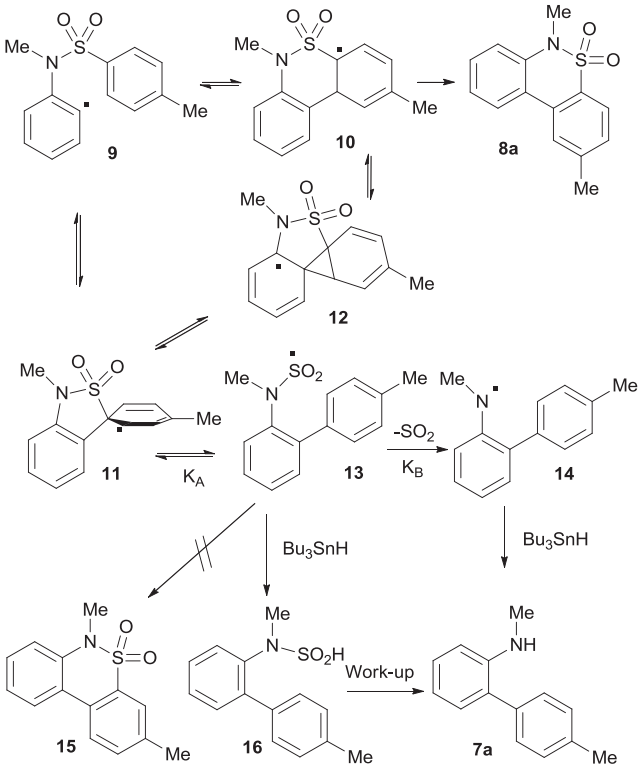


Entry	Concentration[a]	Time[b]	Stannane[c]	AIBN[d]	**7a**	**8a**	**6a**
1	0.2	15	2.5	0.7	34	39	25
2	0.2	15	2.5	0.1	—	—	90
3	0.2	15	1.2	0.7	27	30	30
4	0.8	19	1.2	0.7	46	25	13
5	0.2	0.5	1.2	0.7	39	22	18
6[e]	0.2	15	1.2	0.7	44	30	15
7[f]	0.25	15	1.2	0.7	11	38	44

[a] Concentration of stannane solution.
[b] Addition time (hours).
[c] Equivalents of stannane.
[d] Equivalents of AIBN.
[e] Refluxing anisole was used.
[f] TTMSH was used as reductor.

altered the rate of addition of the solution of stannane reagent, the concentration of this solution, with respect to the stannane and to AIBN, and the temperature and solvent used during the radical reaction (Table 1). The implications of these results were:

1. The conversion of starting sulfonamide **6a** into products is heavily dependent upon the quantity of radical initiator used, implying that the chain processes involved are extremely inefficient (compare entries 1 and 2 in Table 1).
2. Whether one or more equivalents of Bu_3SnH are used appears to be irrelevant in terms of product distribution (compare entries 1 and 3 in Table 1).
3. The fact that raising the concentration of the stannane solution (either reducing the solvent or increasing the addition rate, entries 4 and 5) increases the ratio of products derived from 1,5-*ipso*-substitution/1,6-addition suggests that one or more of the steps outlined in Scheme 4 are reversible. It is known that trichloromethylsulfonyl radical abstracts hydrogen atoms from hydrocarbons.[17] Therefore, it is possible to envisage intermediate **13** being trapped by Bu_3SnH and, as the concentration of the stannane solution is raised, the probability of this occurrence would also be expected to increase. The sulfinic acid **16** would then lose SO_2 on work up to yield the amine **7a**. For this explanation to be valid, the rate constant for the reaction depicted in Scheme 4 must be of approximately the same order of magnitude as those for steps K_A and K_B. A further requirement is that a mechanism must exist by which the spirocyclic intermediate **11** can convert into the sultam intermediate **10**.[18] The conversion of the spirocyclic intermediate **11** into the sultam intermediate **10** might occur via two different mechanisms, either via collapse of **11** back to the initial aryl radical followed by 1,6-ring closure, or via the cyclopropyl intermediate **12**.[19]
4. In his studies, Speckamp noticed a temperature dependence on the ratio of products.[13b] Thus, the increase of temperature led to an important increase in the 1,5-*ipso*-substitution product, the best result being obtained in refluxing diphenylether (190 °C). Entropy should become more important at higher temperatures, and so SO_2 would be released more easily from the postulated intermediate **13** hence denying it the opportunity to recyclise to the intermediate **11**. Even though we did notice the same trend in our system using refluxing anisole



Scheme 4. Proposed mechanism for 1,5-*ipso*-substitution and 1,6-addition.

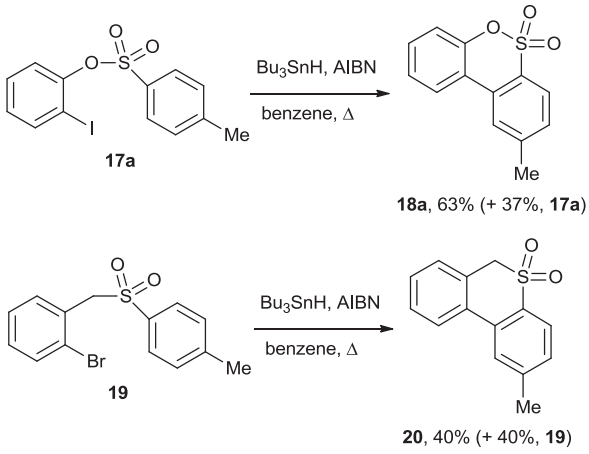
(154 °C), this beneficial effect was less important than in Speckamp's system (compare entries 3 and 6).

5. The use of Chatgilialoglu's reagent led to an increase of the amount of 1,6-addition product (entry 7). The reduction of **13** might be less able to compete with ring closure to the spirocyclohexadienyl radical intermediate **11** when Chatgilialoglu's reagent, a poorer hydrogen atom donor than Bu_3SnH, is used.[20]

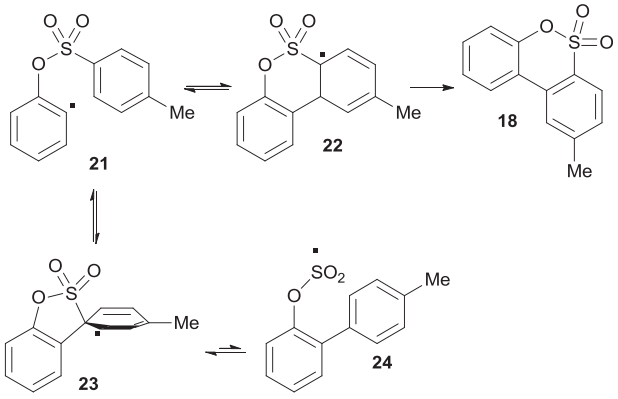
The initial success with sulfonamide **6a** led us to study the effect of the heteroatoms in the linking bridge on the course of the rearrangement reaction. To this end, compounds **17a** and **19** were synthesised and subjected to similar reaction conditions. Surprisingly, in neither instance products resulting from 1,5-*ipso*-substitution were detected. The behaviour of sulfonate **17a** under differing conditions was studied briefly but the product derived via 1,5-*ipso*-substitution was not detected in any experiment.

It is known that carbamoyloxyl radicals lose CO_2 faster than the analogous oxygen radical.[21] If the same was true of $RNMeSO_2\cdot$ and $ROSO_2$, then intermediate **13** would lose SO_2 faster than **24**. Hence, intermediate **24** would have more opportunity to recyclise to **23** and more chance of being converted to the 1,6-addition product **18** than intermediate **13** would have of rearranging to 1,6-addition product **8** via the intermediacy of **11** (Schemes 4 and 6).

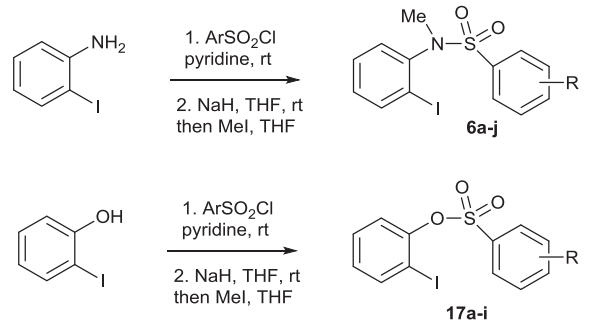
It has been suggested that the outcome of intramolecular radical reactions leading to the formation of aryl–aryl bonds is governed less by polar than ring strain effects in the transition state.[22] In order to understand the steric and electronic factors, which control the regioselectivity of our radical rearrangement reaction, we decided to study the effect of substituents on the acceptor ring. Thus, sulfonamides **6a**–**j** and sulfonates **17a**–**i** were prepared in high overall yield using standard methodology (Scheme 7). Table 2 collects the results of the stannane induced reductive rearrangements of **6a**–**j** and **17a**–**i**.



Scheme 5. Radical reaction of **17a** and **19**.



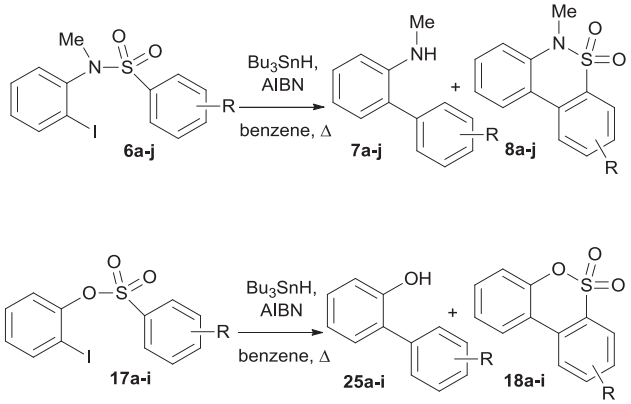
Scheme 6. Proposed mechanism for 1,5-*ipso*-substitution and 1,6-addition.



Scheme 7. Synthesis of **6a**–**j** and **17a**–**i**.

A comparison of the reaction of compounds **6a** and **17a**, both carrying a methyl group *para* on the acceptor ring, with **6b** and **17b**, with a methyl located *ortho* on the acceptor ring, clearly reveals that the site specific location of even a single *ortho* methyl group favours *ipso*-substitution in a remarkable fashion. Since there are two possible sites for the alternative [1,6] addition process and only that bearing the *ortho* methyl group should be more kinetically disfavoured, a possible explanation for the above trend is that the buttressing effect of the *ortho* methyl group and the sulfonyl group in an intermediate of type **26** (Scheme 8) leads to steric acceleration of the reverse reaction and hence channels a greater proportion of the reaction pathway via the corresponding spirocyclic intermediate. Since the *para* derivative **17a** gave the cyclic sultone **18a** as the only product, the effect of the substituent on the *ortho*

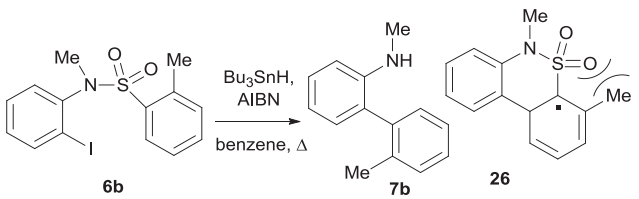
Table 2
Results of the stannane induced radical rearrangements



Substrate	*ipso*-Substitution (yield %)	Addition product (yield %)	Recovered starting material (yield %)
6a, R=4-CH_3	**7a** (46%)	**8a** (25%)	(13%)
6b, R=2-CH_3	**7b** (57%)	—	(10%)
6c, R=2-CO_2CH_3	**27** (65%)	**8c** (19%)	(11%)
6d, R=2,4,6-CH_3	**7d** (65%)	—	—
6e, R=4-F	**7e** (21%)	**8e** (34%)	(26%)
6f, R=4-OCH_3	**7f** (29%)	**8f** (10%)	(34%)
6g, R=3,4-OCH_3	**7g** (33%)	**8g** (8%)	(24%)
6h, R=2,5-OCH_3	**7h** (63%)	—	(26%)
6i, R=3-CO_2CH_3	**7i** (28%)	**8i** (37%)	**33** (11%)
6j, R=4-NO_2	**7j** (31%)	—	(47%)
17a, R=4-CH_3	—	**18a** (63%)	(37%)
17b, R=2-CH_3	**25b** (23%)	**18b** (36%)	(8%)
17c, R=2-CO_2CH_3	**28** (42%)	**18c** (21%)	(37%)
17d, R=2,4,6-CH_3	**25d** (50%)	—	(33%)
17e, R=4-F	—	**18e** (50%)	**29** (9%)
17f, R=4-OCH_3	**25f** (18%)	**18f** (24%)	(31%)
17g, R=3,4-OCH_3	**25g** (19%)	**18g** (34%)[a]	(13%)
17h, R=2,5-OCH_3	**25h** (43%)	**18h** (7%)	
17i, R=3-CO_2CH_3		**18i** (52%)	**33** (19%)

[a] Mixture of two isomers.

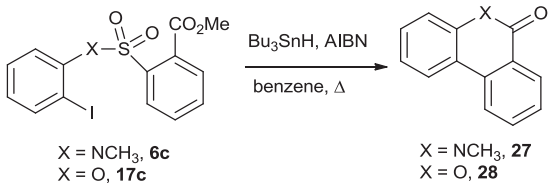
position is clearly revealed as an important contributor to the formation of 1,5-*ipso*-substitution product.[23]



Scheme 8. Radical reaction of **6b**.

The same trend is observed in **6c** and **17c**, which have an *ortho*-carbomethoxy substituent on the acceptor ring. In these examples a better selectivity for the 1,5-*ipso*-substitution reaction was observed, probably both by an electronic stabilisation effect and by its location in the *ortho* position. Interestingly, both *ipso* products were isolated as the corresponding lactam, **27**, or lactone, **28**, presumably formed via base induced cyclisation during fluoride anion treatment to remove tin residues (Scheme 9). Lactones such as **28** have been shown to be important precursors for the synthesis of optically active biaryl natural products.[8]

As anticipated from the above observations, reaction of the corresponding mesityl derivatives, **6d** and **17d**, led to a cumulative enhancement of this tendency and only *ipso*-substitution products were isolated.

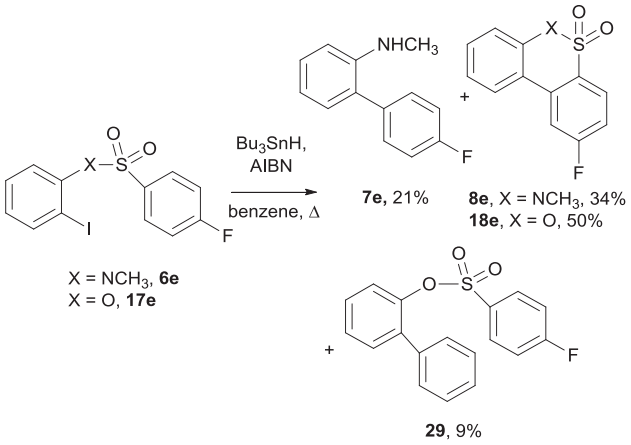


Scheme 9. Radical reaction of **6c** and **17c**.

By way of contrast, however, the *para* fluoro substituent present in **6e** and **17e** appears to disfavour [1,5]-*ipso*-substitution, to retard [1,6] addition, and even to allow capture of the initial σ-radical by benzene solvent, as witnessed by the isolation of **29** in low yield (9%) from reaction of **17e** (Scheme 10).

We next examined the effect of an electron-donating methoxy group. It seemed most likely that such a substituent would promote 1,5-*ipso*-substitution by stabilising the spirocyclic intermediate. Indeed, comparison of **6f** and **6a** shows that the *para* methoxy group was more efficient in promoting *ipso*-substitution than a *para* methyl group and this beneficial effect was also observed on the sulfonate series. However, a poor conversion of starting material was observed.

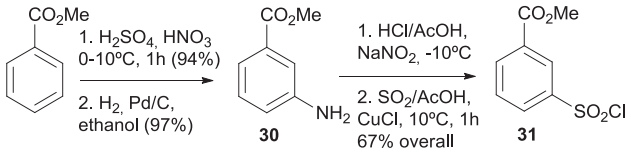
Dimethoxy derivatives **6g** and **17g** were of particular interest because the internal competition between *ipso*-substitution and addition both lead in the first instance to direct stabilisation of the intermediate radical by an α-methoxy group. The results obtained clearly indicate once again that the location of the group adjacent to



Scheme 10. Radical reaction of **6e** and **17e**.

the sulfonyl group is exerting a dominant directing effect, which either minimises or totally eliminates [1,6] addition products, even in the presence of the second methoxy group.

We have previously mentioned that the location of the carbomethoxy group adjacent to the sulfonyl moiety in the acceptor ring was a highly efficient '*ipso director*'. It was therefore of interest to examine the influence of a *meta* carbomethoxy group, using compounds **6i** and **17i**. Since the synthesis of these compounds required methyl 3-(chlorosulfonyl)benzoate, **31**, which was not commercially available, it was prepared by standard procedures from methyl benzoate, as shown in Scheme 11.



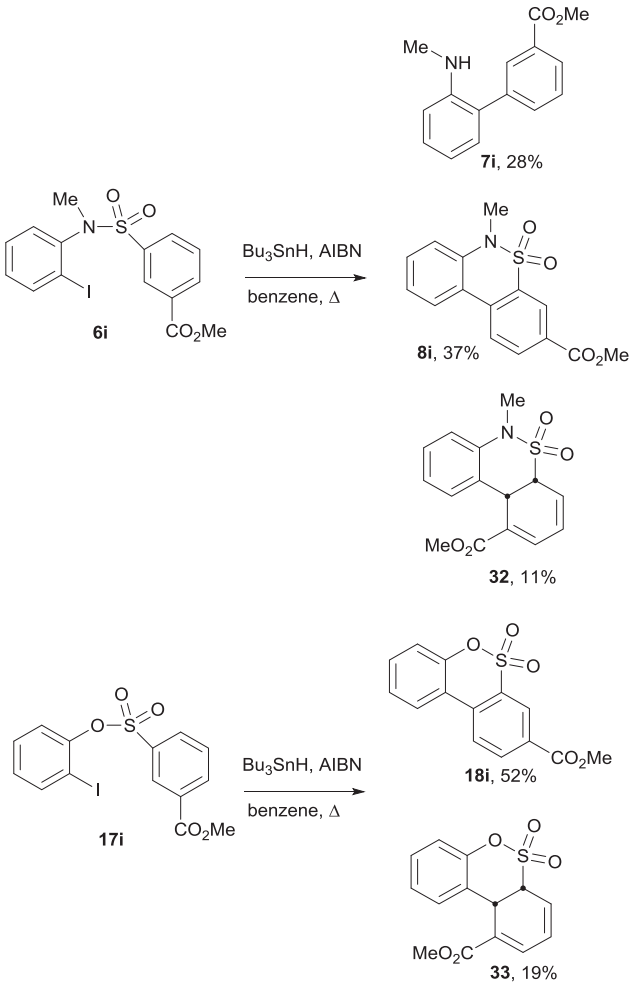
Scheme 11. Synthesis of **31**.

The reaction of sulfonamide **6i** under the standard tin hydride conditions favoured the 1,6-addition product. The addition occurred on the two possible positions, to give compounds **8i** and **32** in 37% and 11% yields, respectively. As expected, the corresponding sulfonate **17i** also showed a product distribution favouring [1,6] addition (Scheme 12).

The isolation of the 'oxidised' **8i** and **18i** is a common phenomenon in the direct addition process even although the dihydroaromatic derivatives should be anticipated products under reducing conditions. This aspect has been fully discussed by Bowman[24] who proposed a pseudo $S_{RN}1$ mechanism to account for similar oxidations in other radical reactions. An alternative mechanism has been suggested by Curran that involves the oxidation of cyclohexadienyl radicals by the initiator (AIBN) or an initiator-derived radical.[25] Thus, the poor propagation and short kinetic chain lengths of these reactions with the consequent need for very large amounts of AIBN could be related with the rearomatization of the cyclohexadienyl radical leading to the addition product.

In compounds **32** and **33**, it is clear that the oxidative process is more difficult, presumably as a consequence of the fact that aromatisation would have led to the introduction of a severe *peri* interaction from the carbomethoxy group.

In the light of the usually slow reduction of aromatic nitro compounds under free radical conditions,[26] often requiring 2 or 3 equiv of the stannane, we examined, in the sufonamides series, the effect of a *para* nitro group on the acceptor ring. Reaction of **6j** under the standard tin hydride conditions afforded only the



Scheme 12. Radical reaction of **6i** and **17i**.

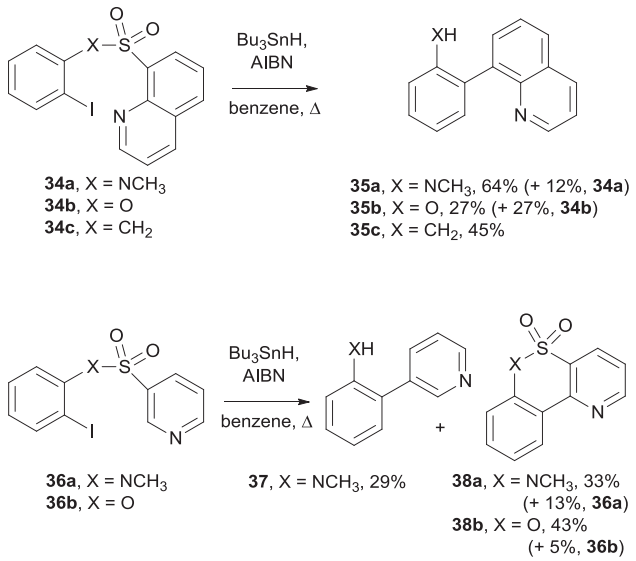
1,5-*ipso* product in low yield, together with significant recovery of starting sulfonamide.

In view of the foregoing examples in the biaryl series, we reasoned that the location of an appropriately cited heteroatom could make such a strategy ideally suited for the synthesis of heterobiaryls. Following standard procedures, we prepared a series of heterosulfonates and heterosulfonamides, which were submitted to the radical reaction conditions. The examples studied reinforce the previously established reactivity patterns. Thus, the reactions of the 8-quinoline derivatives **34a**–**c** can be readily understood by analogy with the behaviour of the *ortho* substituted sulfonyl acceptor, which leads exclusively to *ipso*-substitution products (Scheme 13). The isolation of **35c** in 45% yield is especially noteworthy taking into account the result obtained with its congeneric derivative **19** (Scheme 5). The case of the *meta* substituted pyridine leads, as expected, to a preference for [1,6] addition.

Observation of the thiophene, thiazole and isoxazole derivatives (Scheme 14), all of which gave only [1,5]-*ipso*-substitution products, further highlights the utility of this approach for the construction of sterically congested heterobiaryls.

The isolation of **43** and **46**, in which the cyanoisopropyl radical derived from the AIBN is incorporated into the *para* position of the aniline ring, is also of interest and is presumably a reflection of the inefficiency of the chain propagation sequence and the relatively large quantity of AIBN used under these conditions. Structure of **43** was confirmed by a single X-ray diffraction analysis (Fig. 1).[27]

A reasonable mechanism for the formation of **43** and **46** is outlined in Scheme 15. Thus, the intermediate anilino radical **47** can



Scheme 13. Radical reaction of **34a**–**c** and **36a**,**b**.

either abstract a hydrogen atom from Bu_3SnH to give the biaryl **42a** and thus regenerate the chain carrier in a chain propagation step, or alternatively, undergo AIBN capture at the least sterically hindered *para* position. Presumably, subsequent [1,5]-H migration then follows to afford biaryl **43**.

2.2. 1,6-*ipso*-Substitution versus 1,7-addition

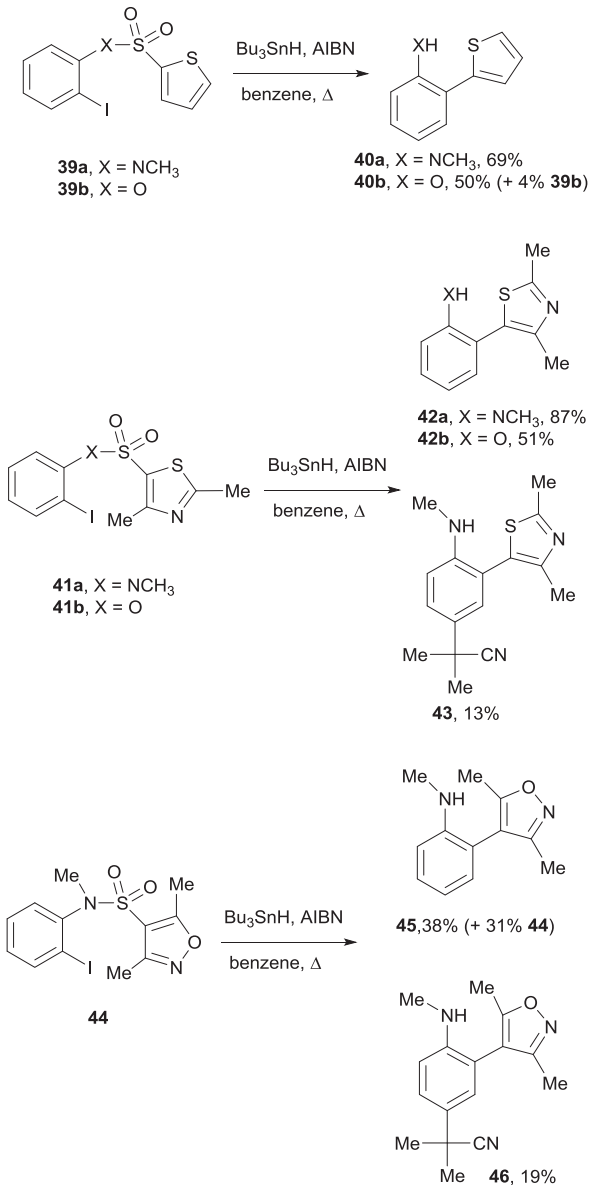
We have shown that although steric and electronic effects around the sulfonyl substituted aromatic acceptor can play a significant role in the synthesis of biaryls and heterobiaryls, in every single case, the selection of the sulfonamide tethering chain led to higher isolated yields of [1,5]-*ipso*-substitution products and improved substitution versus addition ratios than the corresponding sulfonates.

In view of these observations, and since the geometry, nature and number of atoms in the tethering chain can play a profound role, per se, in controlling the outcome of any intramolecular reaction, it was of interest to probe the reactivity pattern of systems in which intramolecular [1,6]-*ipso*-substitution competes with [1,7] addition. By increasing the size of the connecting chain between the aryl radical and the acceptor ring the *ipso*-substitution would be predicted to be the favoured process, since a six-membered ring transition state is usually favoured over the seven-membered ring. We studied five different atom connectivity sequences (Scheme 16).

First, the insertion of an additional carbonyl into the sulfonamide chain was examined. Compound **49** was easily prepared in high yield by stirring tosyl chloride with the amide anion derived from the reaction of 2-iodo-*N*-methylbenzamide and sodium hydride in THF at room temperature. Reaction of **49** under the standard tin hydride conditions afforded a mixture of 1,5-*ipso* product, **50**, and starting material in 37% and 34% yields, respectively, together with an 8% of phenanthridone **51** (Scheme 17).

The mechanism of formation of **50** and **51** involves a 1,6-*ipso* attack with extrusion of SO_2 affording the amidyl radical **53**, which can be reduced to amide **50** or undergo a 1,6-addition process to the aromatic ring (Scheme 18). The formation of amidyl radicals via *ipso*-substitution had already been described in the intramolecular attack of an aryl radical onto aromatic residue with cleavage of a carbon–nitrogen bond.[28] It was also known that amidyl radicals add to aromatic rings.[29]

Compound **54**, prepared in a similar way, was also studied and when exposed to standard radical conditions, afforded compounds



Scheme 14. Radical reaction of **39a**,**b**, **41a**,**b** and **44**.

55 and **56** in 25 and 22% yields, respectively. In this case, the 1,6-addition of the amidyl radical is favoured since amidyl radicals are electrophilic species and the aromatic ring has an electron-donating group on the position *para* to the site of attack. The

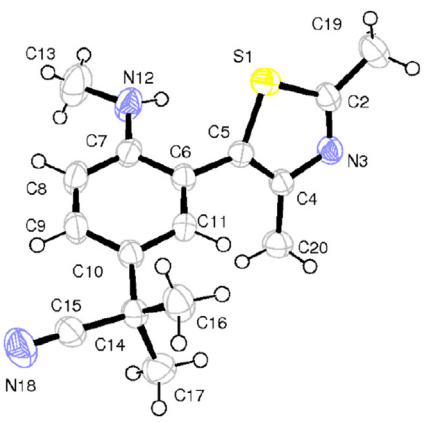
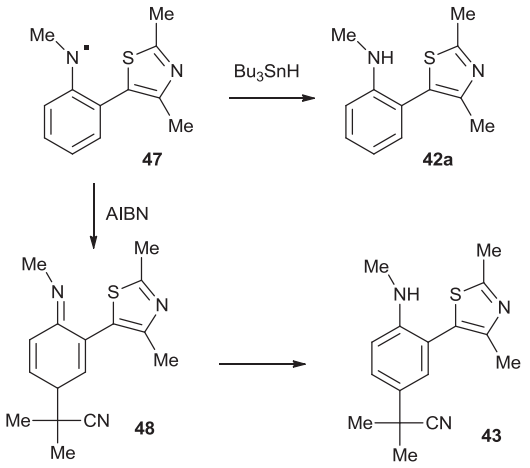
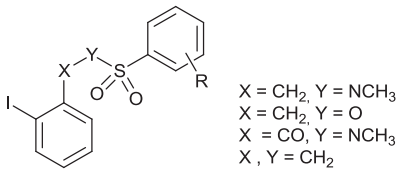


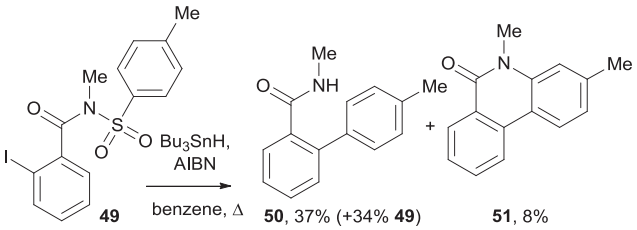
Fig. 1. X-ray diffraction structure (ORTEP) of **43**.



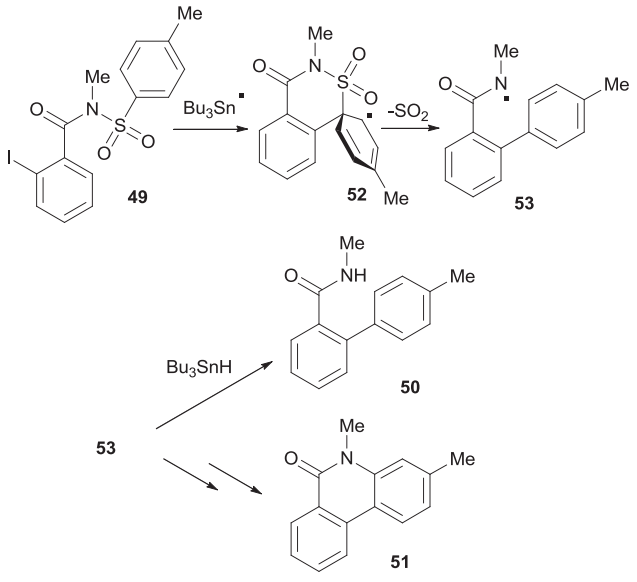
Scheme 15. Proposed mechanism for the formation of **43**.



Scheme 16. General sulfonyl substituted aromatic derivatives.

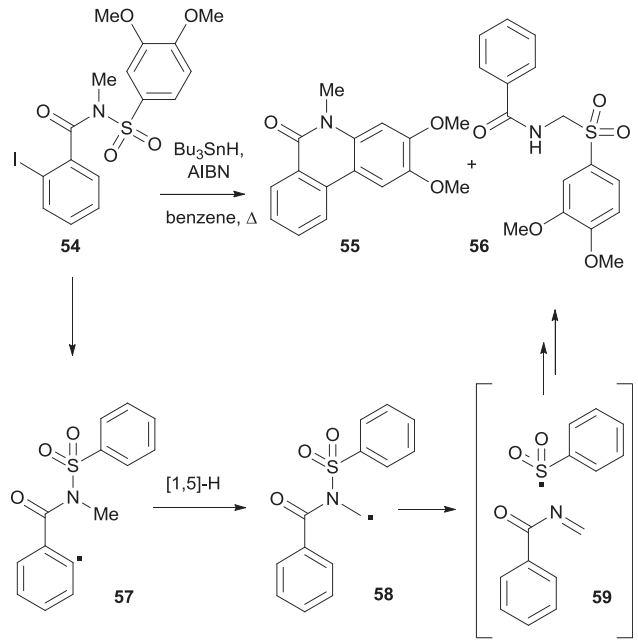


Scheme 17. Radical reaction of **49**.



Scheme 18. Proposed mechanism for the formation of **50** and **51**.

second product formed in the reaction, **56**, has an unusual feature, inasmuch as the sulfonyl group is separated from the nitrogen atom by a methylene group. A possible mechanism for the formation of this compound is represented in Scheme 19. The proposed mechanism would involve a 1,5-hydrogen atom abstraction from the methyl group on the nitrogen atom, with formation of an α-aminomethyl radical,[30] **58**, followed by elimination of the sulfonyl group, which is a good radical leaving group.[31] Recombination of the two species in a cage would give **56**. A similar recombination of two radical species is observed in the photo-Fries rearrangement of sulfonamides and sulfonates.[32] Alternatively, a rearrangement of **58** may led to **56**.



Scheme 19. Proposed mechanism for the formation of **56**.

Surprisingly, radical reaction of **60** and **61** led to complex reaction mixtures in both cases together with a poor mass balance of less than 50%. In order to encourage *ipso*-substitution, compounds **62** and **64** were prepared. However, treatment of **62** under the usual tin hydride conditions did not give any product from *ipso* substitution or addition, and the only identifiable compounds in the reaction mixture were *N*-methylbenzamide, **63**, and starting material. Exposure of **64** to the usual cyclisation conditions resulted in only a 25% yield of the biaryl together with an 11% of *N*-methylbenzamide. An additional example featuring a pyridine acceptor ring was also investigated but once again *N*-methylbenzamide in 16% and starting material in 28% yield were the major products. However, in this case, an 8% of **67**, arisen from 1,6-*ipso*-substitution followed by 1,6-addition reaction was isolated (Scheme 20).

Caddick has shown the lability of heterocyclic-sulfonate linkages in the presence of tri-*n*-butylstannyl radicals.[33] Based on his observation, the most likely mechanism of formation of **63** is illustrated in Scheme 21. Thus, the sulfone moiety is evidently an efficient *ipso*-nucleofuge for the intermolecular addition of tributylstannyl radicals, with subsequent homolytic β-fragmentation of the heterocyclic-sulfonate linkage.

In view of the rather baffling previous results we abandoned these studies. We then decided to add a methylene to the sulfonamide or sulfonate chain. The reduction of the two *ortho* iodo benzylic sulfonates **72a** and **72b**, prepared from the corresponding sulfonyl chlorides and 2-iodobenzyl alcohol, afforded extremely complex mixtures with a very poor mass balance and the only isolated product were that derived from 1,7-addition (Scheme 22). The structure of **74** is based on NMR evidence, since one of the protons of the methylene group of the dihydroaromatic ring (δ 3.23 ppm) is coupled with the neighbouring proton (δ 4.15 ppm).

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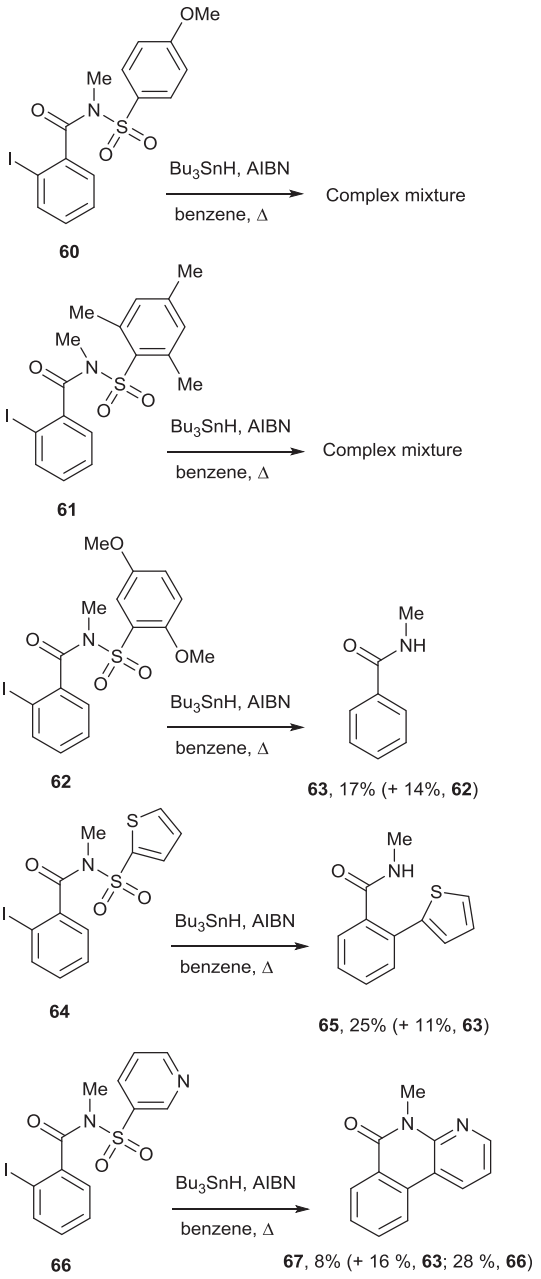
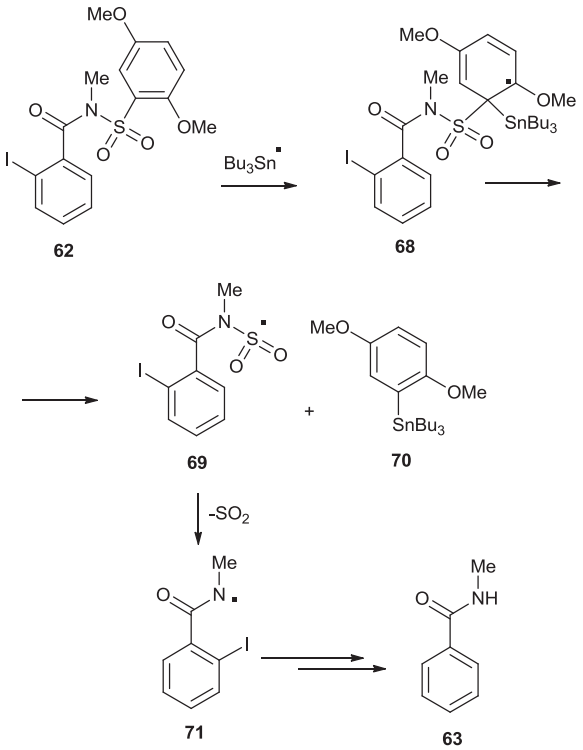


Scheme 20. Radical reaction of **60**, **61**, **62**, **64** and **66**.



Scheme 21. Proposed mechanism for the formation of **63**.

In order to check the effect of *ortho* substituents in this tethering chain we prepared sulfonates **75** and **78** (Scheme 22). Gratifyingly, the tendency for addition observed in **72a**,**b** was effectively counteracted once again by the introduction of *ortho* substituents. Submitting sulfonate **75** to the standard radical conditions afforded two products, **76** and **77**, both formed via 1,6-*ipso*-substitution, in 76% and 14% yields, respectively, with the major product being formed by subsequent lactonisation. The powerful directing effect exerted by the *ortho*-carbomethoxy substituent in the high yielding conversion of the sulfonate **75** is particularly noteworthy in this series. Radical rearrangement of **78** furnished only biaryl **79** in 36% yield. Both examples provide further evidence that this strategy is especially suited for the preparation of more hindered biaryls and heterobiaryls.

Finally, we also prepared the quinoline derivative **80**. Exposure of **80** to the usual radical conditions afforded the desired biaryl in 46% yield together with recovered starting sulfonate and, surprisingly, benzyl alcohol (Scheme 22). The isolation of the latter species may be indicative of the competitive stannyl radical induced cleavage of the heterocyclic. We have already seen a similar behaviour in the carbonyl series (see Scheme 21).

In continuation of our study of the nature of the linking chain, our attention was then directed towards the reaction of the analogous series of *N*-methylsulfonamide derivatives. Thus, compounds **84a**,**b** were prepared from the corresponding sulfonyl chloride, via the methyl sulfonamide, followed by deprotonation with sodium hydride in THF an addition of *o*-bromobenzyl bromide (Scheme 23).

On the basis of our earlier studies involving [1,5]-*ipso*-substitution we anticipated that these sulfonamides would also exhibit an increased preference for [1,6]-*ipso*-substitution, when compared with the corresponding sulfonates. To our initial surprise, however, examination of the literature revealed a very unfavourable precedent in the form of the example shown in Scheme 24. In this case, Huppatz observed exclusive [1,7] addition in a very closely related framework.[34] Interestingly, the transient aryl radical species generated in his study were derived from a diazotisation process at low temperature.

In our hands, however, both sulphonamides **84a** and **84b**, under standard radical conditions, afforded extremely complex mixture where neither [1,6]-*ipso*-substitution nor [1,7] addition products were detected. This suggests that the substrate underwent decomposition, perhaps by a process involving a 1,5-hydrogen atom abstraction from the *N*-methyl group of the sulfonamide by the aryl radical and subsequent elimination of the sulfonyl group. Substitution of the methyl group on the nitrogen by an alternative functionality could provide a solution to this problem. Nevertheless, an isolated example of an intramolecular Pschorr reaction using an *N*-phenylbenzylamine derived benzenesulfonamide has been reported to favour [1,7] addition, the [1,6]-*ipso*-substitution product being not detected (Scheme 25).[35]

In an effort to increase the rate of aryl radical substitution, we therefore elected to study the use of some heteroaromatic derivatives. The construction of these benzylic sulfonamides necessitated a reliable synthesis of 2-iodo-*N*-methylbenzylamine, **85**, since it is not commercially available. Although this compound was

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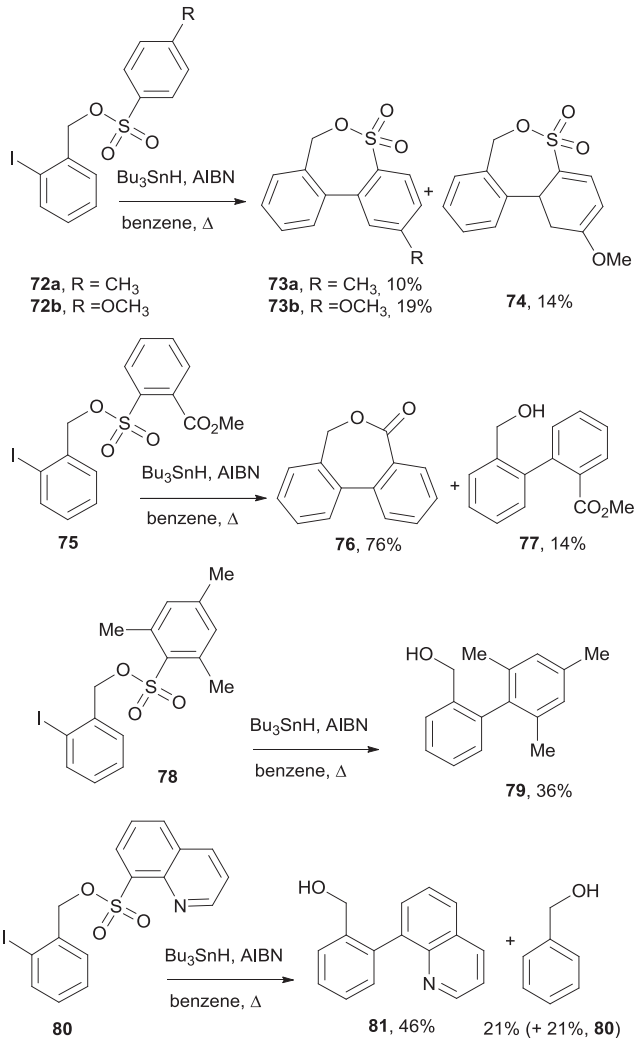
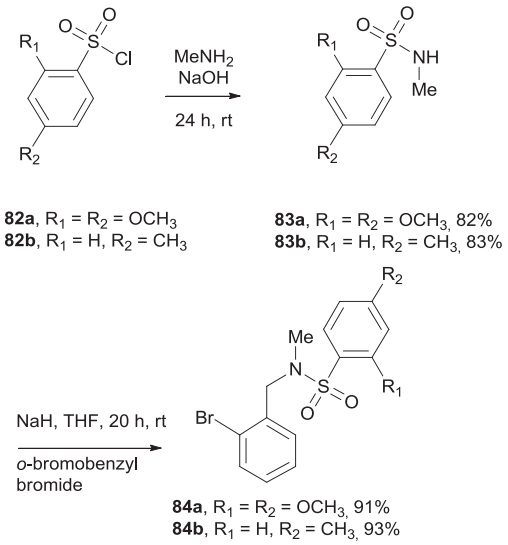
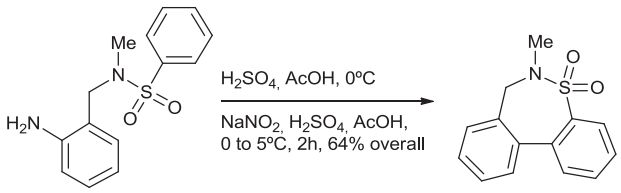


Scheme 22. Radical reaction of **72a**,**b**, **75**, **78** and **80**.

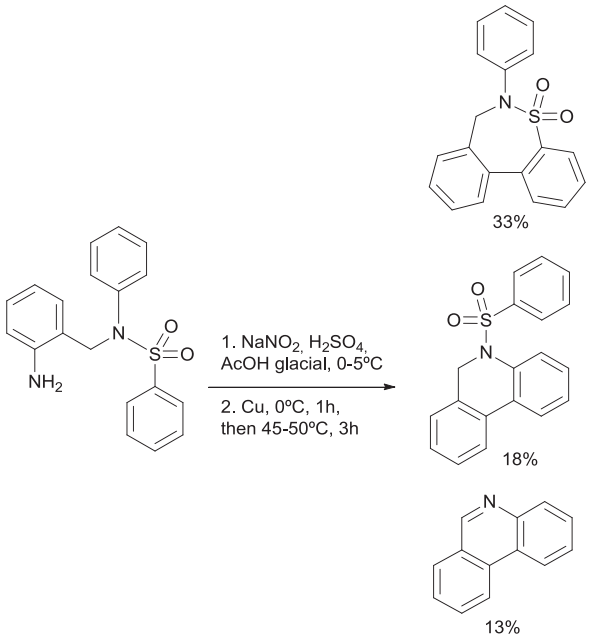


Scheme 23. Synthesis of compounds **84a**,**b**.

known, the only two previously reported syntheses were practically unattractive.[36] We conveniently synthesised **85** in near quantitative yield by dropwise addition of 2-iodobenzyl chloride to a large excess of aqueous methylamine.



Scheme 24. Example by Huppatz.



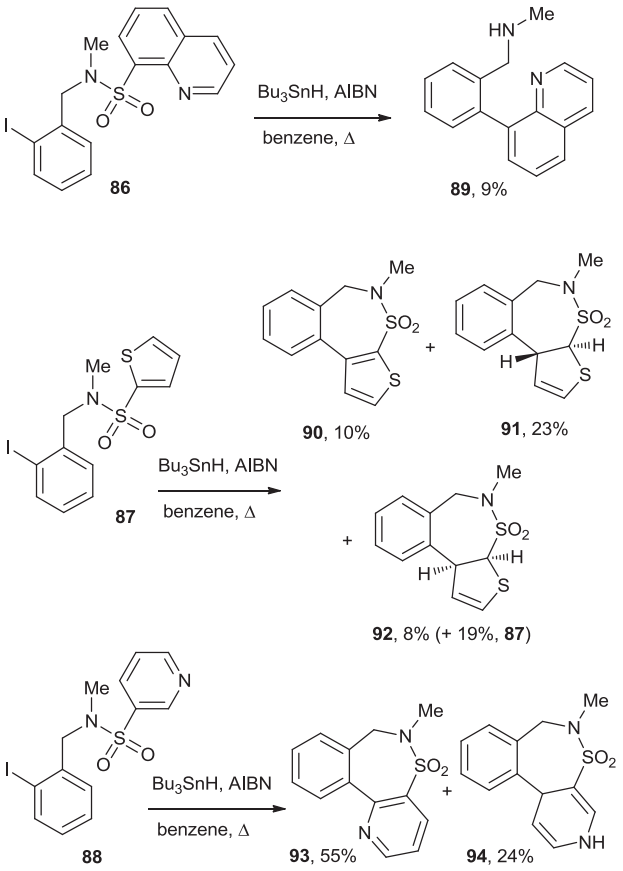
Scheme 25. Intramolecular Pschorr reaction.

Coupling of **85** with the required sulfonyl chloride furnished the corresponding sulfonamides, **86**, **87** and **88**. Unfortunately, subsequent treatment of **86** with Bu_3SnH and AIBN in refluxing benzene led to a very complex mixture of products. Nevertheless, product corresponding to [1,7] addition **89** could be isolated in 9% yield (Scheme 26). The complex behaviour of this quinoline derivative is amazing, providing a remarkable contrast to the benzylic sulfonate and with the entire series of [1,5]-*ipso*-substitution examples in which the sulfonamide linkage had performed so well.

Treatment of **87** with Bu_3SnH and AIBN in refluxing benzene led to a mixture of [1,7] addition derived products together with starting material (Scheme 26). Dihydrothiophene structures **91** and **92** were rigorously proven by single crystal X-ray diffraction analysis (Figs. 2 and 3).[37–39]

Finally in these series, subsequent organostannane induced rearrangement of **88** afforded a mixture of two products both deriving exclusively from [1,7] addition (Scheme 26). Characterisation of the normal [1,7] addition/oxidation product **93** proved trivial due to instant recognition of the familiar three-proton spin system found in earlier derivatives. Interestingly, isolation of the dihydro pyridine **94** shattered our initial expectations of site selectivity at the pyridine ring. However, the lack of regioselectivity observed with pyridine ring as a radicophile in an intramolecular addition reaction had also been noticed by Abramovitch in a study examining the viability of 1,4-*ipso*-substitution processes.[40] Interestingly, the ratio of products corresponding to α- and γ-attack in his study correlates well to the value observed in our example.

We also examined the effect of incorporating a double methylene spacer in the connecting tether. Thus, sulfone **95** was constructed in two steps by methylation of sodium *p*-toluenesulfinate



Scheme 26. Radical reaction of **86**, **87** and **88**.

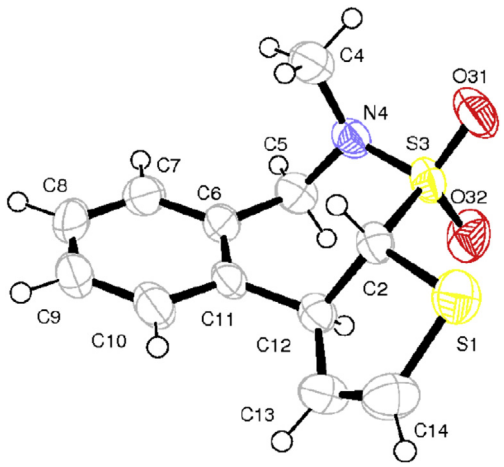


Fig. 2. X-ray diffraction structure of (ORTEP) **91**.

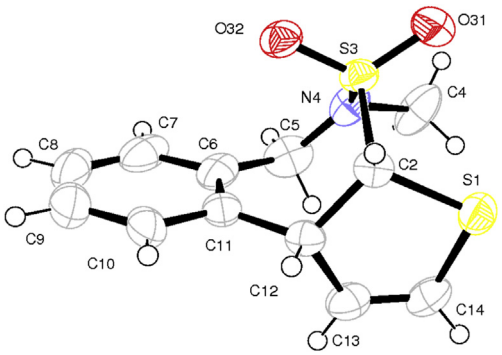
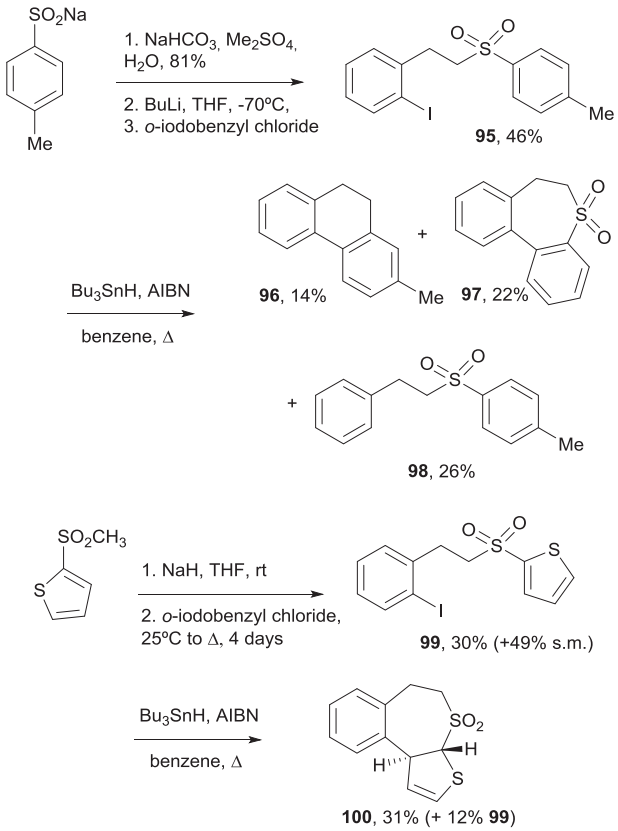


Fig. 3. X-ray diffraction structure of (ORTEP) **92**.



Scheme 27. Synthesis of **95** and **99** and radical reactions.

with dimethyl sulfate, followed by deprotonation with butyl lithium and reaction with *o*-iodobenzyl chloride. Sulfone **99** was prepared in one step albeit by a low yielding method involving 2-methylsulphonylthiophene deprotonation and benzylation. Attempts to improve this yield using either DMF as reaction solvent or *n*-BuLi as base were fruitless.

Reaction of **95** under the usual tin hydride conditions afforded a mixture of products from [1,6]-*ipso*-substitution (**96**, 14%), [1,7] addition (**97**, 22%) and direct reduction (**98**, 26%), as shown in Scheme 27. This was the first example of an attempted [1,6]-*ipso*-substitution reaction in which the direct reduction product could be isolated, indicating that for this type of chain the cyclisation step of the aryl radical competes with hydrogen atom abstraction. The formation of **96** involves an *ipso* attack followed by [1,6] addition of the alkyl radical to the aromatic ring.

Radical rearrangement of sulfone **99** afforded a mixture of starting material and **100**, product derived from [1,7] addition (Scheme 27). As in the foregoing example, this type of chain has favoured the [1,7]-addition process. Once again, isolation of a dihydroheteroaromatic product was observed, presumably as a consequence of the fact that aromatisation would have led to the introduction of severe *peri* interactions.

From the foregoing results, it is clear that simplistic ideas relating to a kinetically driven pathway and a preference for six-membered ring formation over seven are invalid. Stereoelectronic and conformational factors in the tethering chain control the final outcome of the reaction. Although on the basis of the present work [1,7] addition is the inherently favoured pathway over [1,6]-*ipso*-

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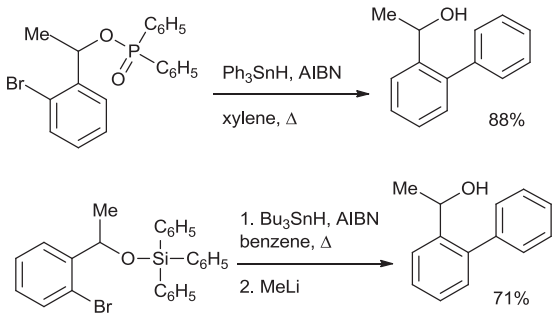
substitution, Clive and Studer have independently shown that synthesis of biaryls by [1,6]-*ipso*-substitution is a viable process by choosing different tethering chains (Scheme 28).[15f,15h]



Scheme 28. Synthesis of biaryls reported by Clive and Studer.

3. Conclusions

In summary, our results show that intramolecular free radical [1,5]-*ipso*-substitution offers a flexible approach to hindered biaryl and heterobiaryls using readily prepared sulfonate and sulfonamide tethering chains. The method is not only tolerant of, but also encouraged by, appropriately sited electron-donating and/or electron-withdrawing groups on the *ortho* positions on the acceptor ring. Extension of this approach to benzylic sulfonates and their corresponding *N*-methylsulfonamides as substrates in potential free radical [1,6]-*ipso*-substitution reactions revealed a preference for the alternative [1,7] addition mode.

4. Experimental

4.1. General methods

^{1}H NMR were recorded in $CDCl_3$ unless otherwise stated at 200, 250, 270, 300, 400 and 500 MHz on spectrometers Varian XL-200, Bruker WM 250, Jeol GSX 270, Bruker AC 300, Varian VXR-400, Jeol GX 400 and Bruker AM 500, respectively. Residual protic solvent was used as internal reference. Coupling constants were measured in hertz (Hz). ^{13}C NMR were recorded in $CDCl_3$ unless otherwise stated at 67.9, 75.4 and 100.6 on spectrometers Jeol GSX 270, Bruker AC 300 and Varian VXR-400, respectively, using the resonances of the solvent as internal reference. IR spectra were recorded on Perkin Elmer 983G, Perkin Elmer 881 and Perkin Elmer 1600 FT-IR instruments. MS spectra were recorded using VG-7070B, VG 12-253, VG ZAB-E, Jeol DX303, VG TRIO-1 and VG-Autospec instruments. Melting points were determined on Reichert and Gallenkamp hot stage instruments and are uncorrected. Microanalyses were performed at Imperial College Chemistry Department microanalytical laboratory and at UCL Chemistry Department microanalytical laboratory. Flash column chromatography was performed on Merck Kieselgel 60 (230–400 mesh) at low positive pressure. Analytical TLC was performed on pre-coated glass plates (Merck 60 F_{254}) and visualised using ultraviolet light (245 nm), iodine and potassium permanganate, as appropriate. 'Petrol' refers to petroleum ether (bp 30–40 °C) and 'ether' refers to diethyl ether. Diethyl ether, THF and benzene solvents were distilled from sodium–benzophenone ketyl; dicholoromethane from phosphorus pentoxide, toluene from sodium, acetonitrile from calcium hydride and methanol from magnesium. All radical reactions were carried out in glassware oven dried and degassed with dry argon or nitrogen for approximately 20 min, which was maintained for the entire period of the reaction.

4.2. General procedure for the synthesis of biaryls derivatives, from *N*-(2-iodophenyl)-*N*-methylarylsulfonamides, 6a–j, 34a, 36a, 39a, 41a and 44, from *N*-(2-iodophenyl)arylsulfonates, 17a–j, 34b, 36b,39b, 41b and from *N*-(2-halobenzyl)arylsulfonamides 19 and 34c

To a stirred solution of iodophenyl-*N*-methylarylsulfonamide or *N*-(2-iodophenyl)arylsulfonate (1 mmol) in benzene (20 mL) at reflux, was added a solution of *n*-Bu_3SnH (0.34 mL, 1.30 mmol) and AIBN (114 mg, 0.7 mmol) in benzene (5 mL) dropwise over 15 h, via a needle placed directly above the refluxing solution. After a further 1 h, the reaction mixture was cooled to room temperature. CCl_4 (15 mL) and a few crystals of iodine were added and stirring was continued for a further 1 h. The solvent was removed in vacuo, and the residue washed with saturated aqueous KF (15 mL) and extracted with diethyl ether (3×60 mL). The combined organic fractions were dried over $MgSO_4$ and the solved evaporated. The residue was purified by column chromatography.

From **6a**. Column chromatography (petrol/CH_2Cl_2 1:1) furnished, in order of elution *N-methyl-2-(4-methylphenyl)aniline*, ***7a*** (46%) as a colourless oil. Found C 85.2, H 7.95, N 7.1. $C_{14}H_{15}N$ requires C 85.2, H 7.7, N 7.1%. ν_{max} (film)/cm^{-1} 3440, 1661, 1579, 1515, 1492, 1312, 1285, 1167. δ_H (300 MHz): 2.40 (3H, s, CH_3), 2.79 (3H, s, CH_3N), 3.77 (1H, br s, NH), 6.69 (1H, dd, *J* 9.1 and 1.0, H-6), 6.77 (1H, ddd, *J* 7.5, 7.4 and 1.1, H-4), 7.08 (1H, dd, *J* 7.4 and 1.6, H-3), 7.23–7.34 (5H, complex signal, H-5, H-2′, H-3′, H-5′, H-6′); δ_C (75.4 MHz): 24.2 (CH_3Ar), 36.7 (CH_3N), 118.4 (CH), 122.6 (CH), 125.8 (2CH), 126.4 (CH), 129.1 (CH), 131.7 (2CH), 139.3 (C), 139.6 (C), 143.0 (C), 146.2 (C). *m*/*z*: 197 (M^+, 100), 181 (10), 167 (11). Found $(M)^+$ 197.1203. $C_{14}H_{15}N$ requires (M) 197.1204, **6a** (13%), and *2,6-dimethyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide*, ***8a*** (25%) as white crystals (mp 82–84 °C, ether). ν_{max} (KBr)/cm^{-1} 1600, 1515, 1468, 1443, 1325, 1170. δ_H (400 MHz): 2.53 (3H, s, CH_3Ar), 3.43 (3H, s, CH_3N), 7.30 (1H, d, *J* 8.2, H-7), 7.33 (1H, td, *J* 7.8 and 1.1, H-9), 7.37 (1H, dd, *J* 7.9 and 1.4, H-3), 7.49 (1H, td, *J* 7.8 and 1.5, H-10), 7.76 (1H, d, *J* 1.4, H-1), 7.89 (1H, d, *J* 8.2, H-8), 8.00 (1H, d, *J* 7.9, H-4); δ_C (100.6 MHz): 22.0 (CH_3Ar), 32.7 (CH_3N), 119.4 (CH), 122.6 (CH), 124.0 (CH), 124.6 (CH), 125.5 (CH), 129.1 (CH), 130.3 (CH), 131.7 (C), 132.3 (C), 139.4 (C), 139.6 (C), 143.0 (C). *m*/*z*: 259 (M^+), 245, 197. Found $(M)^+$ 259.0664. $C_{14}H_{13}NO_2S$ requires (M) 259.0667.

From **6b**. Column chromatography (petrol/CH_2Cl_2 1:1) furnished, in order of elution, *N-methyl-2-(2-methylphenyl)aniline*, ***7b*** (57%) as an oil. ν_{max} (film)/cm^{-1} 3426, 2919, 1512, 742. δ_H (400 MHz): 2.11 (3H, s, CH_3), 2.76 (3H, s, CH_3N), 3.40 (1H, br s, NH), 6.67 (1H, d, *J* 8.2, H-6), 6.74 (1H, dt, *J* 7.4 and 1.1, H-4), 6.97 (1H, dd, *J* 7.3 and 1.5, H-3), 7.17 (1H, m, H–Ar′), 7.21–7.29 (4H, complex signal, H-5, 3H–Ar′); δ_C(100.6 MHz): 19.6 (CH_3Ar), 30.6 (CH_3N), 109.4 (CH), 116.4 (CH), 126.2 (CH), 127.1 (C), 127.6 (CH), 128.5 (CH), 129.5 (CH), 130.2 (CH), 130.3 (CH), 137.2 (C), 138.5 (C), 146.2 (C). *m*/*z*: 197 (M^+, 100), 182, 167. Found $(M)^+$ 197.1204. $C_{14}H_{15}N$ requires (M) 197.1204, and **6b** (10%).

From **6c**. Column chromatography (CH_2Cl_2) furnished, in order of elution, **6c** (11%), *6-methyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide*, ***8c*** (19%) as white crystals (mp 151–153 °C, CH_2Cl_2). ν_{max} (KBr)/cm^{-1} 2952, 1734, 1605, 1591, 1465, 1431, 1333, 1292, 1167, 774. δ_H (400 MHz): 3.36 (3H, s, CH_3N), 4.04 (3H, s, CH_3O), 7.28–7.41 (2H, H-10, H-8 or H-9), 7.52 (1H, ddd, *J* 7.7, 6.8 and 1.4, H-2), 7.66–7.77 (2H, complex signal, H-7, H-8 or H-9), 7.93 (1H, dd, *J* 7.7 and 1.4, H-1), 8.01 (1H, dd, *J* 6.8 and 2.5, H-3); δ_C (100.6 MHz): 36.2 (CH_3N), 51.2 (CH_3O), 117.1 (CH), 123.8 (C), 125.5 (CH), 125.6 (CH), 127.1 (CH), 128.6 (CH), 131.5 (CH), 132.1 (CH), 140.4 (C), 141.3 (C), 142.2 (C), 144.3 (C), 160.2. *m*/*z* (EI): 303 (M^+, 100), 272. Found $(M+H)^+$ 304.3107. $C_{15}H_{14}NO_4S$ requires (M+H) 304.3111, and *5-methyl-5H-phenanthridine-6-one*, ***27*** (65%) as white prisms (mp 106–107 °C, CH_2Cl_2, lit.,[41] 108 °C). ν_{max} (KBr)/cm^{-1} 1638, 1609, 1586, 1491, 1353, 1335, 1318, 1214, 1100, 1043. δ_H (400 MHz): 3.82 (3H, s, CH_3N), 7.12

(1H, dd, *J* 8.1 and 1.1, H-4), 7.43 (1H, dd, *J* 8.4 and 1.0, H-1), 7.53–7.62 (2H, complex signal, H-3, H-10), 7.76 (1H, ddd, *J* 8.4, 7.0 and 1.4, H-2), 8.27–8.31 (2H, complex signal, H-8, H-9), 8.56 (1H, dd, *J* 7.9 and 1.6, H-7); δ_C (100.6 MHz): 40.2 (CH_3N), 119.4 (CH), 124.5 (C), 125.9 (CH), 127.4 (CH), 127.6 (CH), 128.2 (CH), 130.2 (CH), 130.5 (CH), 133.6 (C), 135.3 (CH), 141.2 (C), 142.3 (C), 165.2 (C). *m/z*: 209 (M^+, 100), 178, 166, 152, 139. Found $(M)^+$ 209.0844. $C_{14}H_{11}NO$ requires (M) 209.0841.

From **6d**. Column chromatography (petrol/CH_2Cl_2 1:1) furnished, *N-methyl-2-(2,4,6-trimethylphenyl)aniline*, ***7d*** (65%) as white needles (mp 46–48 °C, ether). ν_{max} (film)/cm^{-1} 3406, 2915, 1598, 1575, 1429, 1312, 1270, 1159, 745. δ_H (400 MHz): 1.97 (6H, s, CH_3), 2.32 (3H, s, CH_3), 2.75 (3H, s, CH_3N), 3.3 (1H, br s, NH), 6.67 (1H, dd, *J* 8.0 and 0.8, H-6), 6.75 (1H, ddd, *J* 7.5, 7.3 and 0.8, H-4), 6.86 (1H, dd, *J* 7.3 and 1.5, H-3), 6.95 (2H, s, H-3′, H-5′), 7.25 (1H, ddd, *J* 8.0, 7.5 and 1.5, H-5); δ_C (100.6 MHz): 20.0 [2 CH_3–C2′ (6′)], 21.0 (CH_3Ar), 30.7 (CH_3N), 109.6 (CH), 117.0 (CH), 125.9 (C), 128.2 (CH), 128.4 (2CH), 129.4 (CH), 134.7 (C), 136.9 (C), 137.2 (2C), 146.0 (C). *m/z*: 226 (M^{+1}, 57), 225 (M^+, 100), 224 (20), 208 (18), 194 (10). Found $(M)^+$ 225.1512. $C_{16}H_{19}N$ requires (M) 225.1517.

From **6e**. Column chromatography (petrol/CH_2Cl_2 1:1) furnished, in order of elution, *2-(4-fluorophenyl)-N-methylaniline*, ***7e*** (21%) as a white crystalline solid (mp 60–61 °C, CH_2Cl_2). ν_{max} (film)/cm^{-1} 3491, 2913, 1599, 1576, 1498, 1459, 1424, 1314, 1284, 1221, 1157, 1005, 837, 746. δ_H (250 MHz): 2.81 (3H, s, CH_3N), 3.86 (1H, br s, NH), 6.70 (1H, d, *J* 8.1, H-6), 6.77 (1H, ddd, *J* 7.7, 7.7 and 1.1, H-4), 7.06 (1H, dd, *J* 7.3 and 1.7, H-3), 7.14 (2H, m, H-3′, H-5′), 7.28 (1H, ddd, *J* 7.7, 7.7 and 1.5, H-5), 7.39 (2H, m, H-2′, H-6′). *m/z*: 201 (M^+), 185, 183, 170, 157, 149, 133. Found $(M)^+$ 201.0960. $C_{13}H_{12}FN$ requires (M) 201.0954, starting material, **6e** (26%) and *2-fluoro-6-methyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide*, ***8e*** (34%) as white crystals (mp 131–133 °C, CH_2Cl_2/petrol). ν_{max} (KBr)/cm^{-1} 1586, 1481, 1442, 1414, 1328, 1294, 1271, 1171, 1119, 1059, 905, 763, 715. δ_H (250 MHz): 3.46 (3H, s, CH_3N), 7.18–7.40 (3H, complex signal, H-3, H-7 and H-8 or H-9), 7.54 (1H, ddd, *J* 7.7, 7.7 and 1.4, H-8 or H-9), 7.62 (1H, dd, *J* 10.0 and 2.3, H-1), 7.94 (1H, dd, *J* 7.7 and 1.1, H-10), 8.01 (1H, dd, *J* 8.8 and 5.5, H-4). *m/z*: 263 (M^+), 232, 198, 182, 170, 167, 158, 149, 143, 133. Found $(M)^+$ 263.0422. $C_{13}H_{10}FNO_2S$ requires (M) 263.0416.

From **6f**. Column chromatography (petrol/CH_2Cl_2 1:1) furnished, in order of elution, *2-(4-methoxyphenyl)-N-methylaniline*, ***7f*** (29%) as a colourless oil.[42] Found C 78.9, H 6.8, N 6.5. $C_{14}H_{15}NO$ requires C 78.8, H 7.1, N 6.6%. ν_{max} (film)/cm^{-1} 3426, 2922, 1603, 1504, 1243, 1171, 1035, 748. δ_H (400 MHz): 2.80 (3H, s, CH_3N), 3.86 (3H, s, CH_3O), 4.01 (1H, br s, NH), 6.70 (1H, dd, *J* 8.0 and 1.0, H-6), 6.78 (1H, ddd, *J* 7.5, 7.2 and 1.2, H-4), 6.98 (2H, m, H-3′, H-5′), 7.08 (1H, dd, *J* 7.5 and 1.8, H-3), 7.26 (1H, ddd, *J* 8.0, 7.5 and 1.5, H-5), 7.35 (2H, m, H-2′, H-6′); δ_C (100.6 MHz): 30.7 (CH_3N), 55.2 (CH_3O), 109.6 (CH), 114.1 (2CH), 116.7 (CH), 125.3 (C), 128.4 (CH), 129.9 (CH), 130.4 (2CH), 131.5 (C), 146.3 (C), 158.7 (C). *m/z*: 214 (M^{+1}, 71), 213 (M^+, 100), 212 (16), 199 (17), 167 (11), 112 (14). Found $(M)^+$ 213.1159. $C_{14}H_{15}NO$ requires (M) 213.1154, starting material, **6f** (34%) and *2-methoxy-6-methyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide*, ***8f*** (10%) as white crystals (mp 105–106 °C, ether). ν_{max} (KBr)/cm^{-1} 1592, 1444, 1312, 1168, 1121, 891, 743, 553. δ_H (400 MHz): 3.43 (3H, s, CH_3N), 3.94 (3H, s, CH_3O), 7.04 (1H, m, H-7), 7.22–7.40 (2H, complex signal, H-3, H-8), 7.39 (1H, d, *J* 2.1, H-1), 7.51 (1H, ddd, *J* 9.0, 8.0 and 1.4, H-9), 7.93 (1H, d, *J* 8.6, H-4), 7.95 (1H, dd, *J* 8.0 and 1.8, H-10); δ_C (100.6 MHz): 32.5 (CH_3N), 55.6 (CH_3O), 110.2 (CH), 113.8 (CH), 119.3 (CH), 123.7 (C), 124.5 (CH), 124.6 (CH), 125.4 (CH), 126.8 (C), 130.5 (CH), 134.3 (C), 139.7 (C), 162.5 (C). *m/z*: 276 (M^{+1}, 98), 275 (M^+, 42), 228 (13), 212 (72), 211 (100), 210 (88), 197 (76), 196 (68), 183 (33), 181 (28), 180 (21), 168 (37), 167 (47), 154 (16), 153 (17), 152 (14), 136 (14). Found $(M+H)^+$ 276.0685. $C_{14}H_{14}NO_3S$ requires (M+H) 276.0694.

From **6g**. Column chromatography (CH_2Cl_2/petrol 3:1 to 1:0, then CH_2Cl_2/methanol 99:1) furnished, in order of elution, and inseparable mixture of *2-(3,4-dimethoxyphenyl)-N-methylaniline*, ***7g***, and ***8g***, which was resolved by HPLC and **6g** (24%). Compound **7g** (33%) as white prisms (mp 95–96 °C, petrol/CH_2Cl_2). ν_{max} (film)/cm^{-1} 3415, 2933, 1504, 1249, 1169. δ_H (400 MHz): 2.79 (3H, s, CH_3N), 3.87 (3H, s, CH_3O), 3.91 (3H, s, CH_3O), 4.00 (1H, br s, NH), 6.67 (1H, d, *J* 8.2, H-6), 6.75 (1H, dt, *J* 7.5 and 1.1, H-4), 6.91–6.94 (3H, complex signal, H-2′, H-5′, H-6′), 7.08 (1H, dd, *J* 7.6 and 1.5, H-3), 7.25 (1H, dt, *J* 8.1 and 1.6, H-5); δ_C (100.6 MHz): 30.8 (CH_3N), 55.9 ($2CH_3O$), 109.8 (CH), 111.4 (CH), 112.6 (CH), 116.7 (CH), 121.4 (CH), 127.4 (C), 128.6 (CH), 129.9 (CH), 131.9 (C), 146.2 (C), 148.1 (C), 149.1 (C). *m/z*: 243 (M^+), 84 (100), 86 (100). Found $(M)^+$ 243.1253. $C_{15}H_{17}NO_2$ requires (M) 243.1259; *1,2-dimethoxy-6-methyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide*, ***8g*** (8%) as a clear oil. ν_{max} (film)/cm^{-1} 2941, 1456, 1325, 1264, 1147. δ_H (400 MHz): 3.35 (3H, s, CH_3N), 3.71 (3H, s, CH_3O), 3.97 (3H, s, CH_3O), 7.08 (1H, d, *J* 8.7, H-3), 7.27–7.32 (2H, complex signal, H-7, H-8 or H-9), 7.46 (1H, dt, *J* 7.5 and 1.5, H-8 or H-9), 7.75 (1H, d, *J* 8.7, H-4), 8.61 (1H, dd, *J* 7.9 and 1.5, H-10); δ_C (100.6 MHz): 32.8 (CH_3N), 56.3 (CH_3O), 60.4 (CH_3O), 111.6 (CH), 119.4 (CH), 119.5 (CH), 122.6 (C), 124.6 (CH), 126.0 (C), 128.3 (C), 129.9 (CH), 130.1 (CH), 139.5 (C), 146.3 (C), 156.6 (C). *m/z* (EI): 305 (M^+), 290, 149 (100). Found $(M+H)^+$ 306.0803. $C_{15}H_{16}NO_4S$ requires (M+H) 306.0800.

From **6h**. Column chromatography (CH_2Cl_2) furnished, in order of elution, *2-(2,5-dimethoxyphenyl)-N-methylaniline*, ***7h*** (63%) as an oil. ν_{max} (film)/cm^{-1} 3428, 2935, 1603, 1579, 1494, 1460, 1313, 1267, 1224, 1047, 807, 749. δ_H (270 MHz): 2.81 (3H, s, CH_3), 3.71 (3H, s, CH_3O), 3.78 (3H, s, CH_3O), 6.71–6.80 (2H, complex signal, H-3, H-5), 6.82 (1H, d, *J* 2.7, H-6′), 6.88 (1H, dd, *J* 9.0 and 2.7, H-4′), 6.94 (1H, d, *J* 9.0 and 1.5, H-3′), 7.08 (1H, dd, *J* 7.6 and 1.7, H-4), 7.28 (1H, dt, *J* 7.6 and 1.7, H-6); δ_C (67.5 MHz): 30.7 (CH_3N), 55.5 (CH_3O), 56.4 (CH_3O), 109.8 (CH), 112.8 (CH), 113.7 (CH), 116.5 (CH), 117.1 (CH), 124.4 (C), 128.6 (CH), 129.0 (C), 130.3 (CH), 146.7 (C), 151.0 (C), 153.8 (C). *m/z*: 243 (M^+), 212 (100), 197, 168. Found $(M)^+$ 243.1261. $C_{15}H_{17}NO_2$ requires (M) 243.1259, and **6h** (26%).

From **6i**. Column chromatography (CH_2Cl_2/petrol 1:1 to 1:0, then petrol/ethyl acetate 8:2) furnished, in order of elution, *methyl 3-(2-methylaminophenyl)benzoate*, ***7i*** (28%) as white prisms (mp 93–95 °C, petrol/CH_2Cl_2). ν_{max} (film)/cm^{-1} 3423, 2950, 1722, 1511, 1462, 1305, 1260, 1231. δ_H (270 MHz): 2.80 (3H, s, CH_3N), 3.92 (3H, s, CH_3O), 6.71 (1H, d, *J* 8.5, H-3′), 6.79 (1H, t, *J* 7.3, H-5′), 7.08 (1H, dd, *J* 7.3 and 1.5, H-6′), 7.29 (1H, ddd, *J* 8.5, 7.8 and 1.7, H-6), 7.51 (1H, t, *J* 7.6, H-5), 7.62 (1H, td, *J* 7.6 and 1.5, H-4), 8.02 (1H, td, *J* 7.8 and 1.7, H-4), 8.10 (1H, t, *J* 1.7, H-2); δ_C (67.5 MHz): 30.7 (CH_3N), 52.0 (CH_3O), 109.9 (CH), 116.8 (CH), 126.4 (C), 128.3 (CH), 128.9 (CH), 129.1 (CH), 129.9 (CH), 130.5 (CH), 130.7 (C), 133.9 (CH), 139.7 (C), 145.9 (C), 166.8 (C). *m/z*: 367 (M^+), 266, 241 (100). Found $(M)^+$ 241.1103. $C_{15}H_{15}NO_2$ requires (M) 241.1103, *methyl 6-methyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide-3-carboxylate*, ***8i*** (37%) as white prisms (mp 178–180 °C, petrol/CH_2Cl_2). ν_{max} (KBr)/cm^{-1} 1720, 1292, 1166. δ_H (270 MHz): 3.46 (3H, s, CH_3N), 3.97 (3H, s, CH_3O), 7.30–7.37 (2H, complex signal, H-10, H-8 or H-9), 7.54 (1H, dt, *J* 7.3 and 1.7, H-8 or H-9), 8.00–8.04 (2H, complex signal, H-1, H-7), 8.33 (1H, dd, *J* 8.3 and 2.0, H-2), 8.65 (1H, d, *J* 2.0, H-4); δ_C (67.5 MHz): 32.7 (CH_3N), 52.5 (CH_3O), 119.4 (CH), 123.2 (C), 124.0 (CH), 124.8 (CH), 125.6 (CH), 126.0 (CH), 129.8 (C), 131.4 (CH), 132.9 (C), 134.2 (C), 136.2 (C), 139.9 (C), 169.4 (C). *m/z* (EI): 303 (M^+, 100), 272, 238, 208, 180. Found $(M)^+$ 303.0576. $C_{15}H_{13}NO_4S$ requires (M) 303.0565, and methyl *(4aRS,10bRS)-4a,10b-dihydro-6-methyl-6H-dibenzo[c,e][1,2]thiazine-5,5-dioxide-1-carboxylate*, ***32*** (11%) as a clear oil. ν_{max} (film)/cm^{-1} 2948, 1707, 1335, 1138. δ_H (270 MHz): 3.38 (3H, s, CH_3N), 3.91 (3H, s, CH_3O), 4.30 (1H, td, *J* 8.0 and 2.0, H-4a), 4.81 (1H, d, *J* 7.8, H-10b), 6.16 (1H, ddd, *J* 9.5, 2.0 and 1.0, H-4), 6.26 (1H, ddd, *J* 9.5, 5.1 and 2.7, H-3), 6.98 (1H, *d*, J 8.1, H–Ar), 7.00–7.02 (2H, complex signal, H–Ar), 7.22–7.30 (2H, complex signal, H–Ar); δ_C (67.5 MHz): 32.2 (CH), 34.3 (CH_3N), 52.5 (CH), 57.3 (CH_3O), 117.1 (CH), 123.7 (CH), 124.9 (C), 125.9 (CH), 127.5 (CH), 128.1 (CH), 128.3 (CH), 129.1 (C), 134.3 (CH), 140.6 (C), 166.9 (C). *m/z* (CI): 323 (MNH_4^+), 224 (100).

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Found $(M+NH_4)^+$ 323.1066. $C_{15}H_{19}N_2O_4S$ requires $(M+NH_4)$ 323.1066.

From **6j**. Column chromatography (petrol/CH_2Cl_2 1:1 to 2:8) furnished, in order of elution, *2-(4-nitrophenyl)-N-methylaniline*, ***7j*** (31%) as orange crystals (mp 154–157 °C, from CH_2Cl_2/petrol). Found C 68.2, H 5.4, N 12.0. $C_{13}H_{12}N_2O_2$ requires C 68.4, H 5.3, N 12.3%. ν_{max} (NaCl/film)/cm^{-1} 3408, 3064, 2919, 1594, 1505, 1344, 1310, 1168, 1101, 1001, 855, 753, 698. δ_H (270 MHz): 2.82 (3H, s, CH_3N), 3.86 (1H, s, NH), 6.73 (1H, d, *J* 8.1, H-6), 6.81 (1H, dt, *J* 7.3 and 1.0, H-4), 7.09 (1H, dd, *J* 7.3 and 1.5, H-3), 7.33 (1H, ddd, *J* 8.1, 7.3 and 1.7, H-5), 7.63 (2H, m, H-2′, H-6′), 8.29 (2H, m, H-3′, H-5′); δ_C (126 MHz): 30.7 (CH_3N), 110.4 (CH), 117.2 (CH), 124.1 (2CH), 125.0 (C), 129.9 (CH), 130.0 (CH), 130.2 (2CH), 145.8 (C), 146.7 (C), 146.8 (C). *m*/*z* (EI): 228 (M^+, 100), 182 (13), 181 (14), 167 (34), and **6j** (47%).

From **34a**. Column chromatography (petrol/ether 1:9 to 1:1) furnished, in order of elution, *N-methyl-2-(quinolin-8-yl)aniline*, ***35a*** (64%) as green crystals (mp 134–135 °C, from CH_2Cl_2/petrol). Found C 82.1, H 5.9, N 11.7. $C_{16}H_{14}N_2$ requires C 82.0, H 6.0, N 12.0%. ν_{max} (NaCl/film)/cm^{-1} 3424, 1600, 1575, 1509, 1455, 1425, 1380, 1310, 1285, 1250, 1167, 830, 796, 748. δ_H (270 MHz): 2.77 (3H, s, CH_3N), 3.90 (1H, s, NH), 6.85 (1H, t, *J* 8.0, H-4 or H-5), 6.88 (1H, t, *J* 7.6, H-4 or H-5), 7.19 (1H, dd, *J* 7.3 and 1.5, H-3 or H-6), 7.36 (1H, dd, *J* 7.8 and 1.5, H-3 or H-6), 7.43 (1H, dd, *J* 8.3 and 4.2, H-3′), 7.63 (1H, t, *J* 7.4, H-6′), 7.71 (1H, dd, *J* 7.1 and 1.7, H-5′ or H-7′), 7.87 (1H, dd, *J* 7.8 and 1.6, H-5′ or H-7′), 8.23 (1H, dd, *J* 8.3 and 1.7, H-4′), 8.94 (1H, dd, *J* 4.2 and 1.7, H-2′); δ_C (δ_C (67.5 MHz): 31.0 (CH_3N), 110.5 (CH), 117.2 (CH), 121.2 (CH), 126.5 (C), 126.9 (CH), 128.0 (CH), 128.7 (C), 129.2 (CH), 131.1 (CH), 131.9 (CH), 136.6 (CH), 139.3 (C), 147.4 (C), 150.7 (2CH). *m*/*z* (EI): 234 (M^+, 78), 233 (100), 218 (33), 204 (70), 191 (15), and **34a** (12%).

From **36a**. Column chromatography (petrol/ether 4:6) furnished, in order of elution, *6-methylbenzo[c]pyrido[2,3-e][1,2]thiazine-5,5-dioxide*, ***38a*** (33%) as colourless crystals (mp 134–135 °C, from CH_2Cl_2/petrol). Found C 58.6, H 3.9, N 11.3. $C_{12}H_{10}N_2O_2S$ requires C 58.5, H 4.1, N 11.4%. ν_{max} (NaCl/film)/cm^{-1} 1602, 1572, 1442, 1321, 1282, 1213, 1169, 1140, 1083, 1042, 869, 802, 754, 720. δ_H (250 MHz): 3.43 (3H, s, CH_3N), 7.31 (1H, dd, *J* 8.0 and 0.7, H-7 or H-10), 7.39 (1H, ddd, *J* 8.2, 7.5 and 1.1, H-8 or H-9), 7.48 (1H, dd, *J* 8.0 and 4.8, H-3), 7.59 (1H, ddd, *J* 8.3, 7.4 and 1.7, H-8 or H-9), 8.26 (1H, dd, *J* 8.1 and 1.8, H-7 or H-10), 8.64 (1H, dd, *J* 8.0 and 1.7, H-4), 8.93 (1H, dd, *J* 4.8 and 1.7, H-2); δ_C (126 MHz): 32.5 (CH_3N), 118.4 (CH), 122.5 (CH), 124.3 (C), 124.5 (CH), 127.2 (CH), 130.2 (C), 130.4 (CH), 132.1 (CH), 139.9 (C), 149.0 (C), 152.9 (CH). *m*/*z* (EI): 246 (M^+, 100), 182 (25), 181 (77), 154 (11), 127 (13), ***36a*** (13%), and *N-methyl-2-(3-pyridyl)aniline*, ***37a*** (29%) as yellow crystals (mp 71–74 °C, from CH_2Cl_2/petrol). Found C 78.1, H 6.3, N 14.9. $C_{12}H_{12}N_2$ requires C 78.2, H 6.6, N 15.2%. ν_{max} (NaCl/film)/cm^{-1} 3315, 2917, 2809, 1600, 1576, 1507, 1473, 1403, 1312, 1285, 1168, 997, 807, 748, 715. δ_H (250 MHz): 2.80 (3H, s, CH_3N), 3.81 (1H, br s, NH), 6.72 (1H, d, *J* 8.1, H–Ar), 6.80 (1H, dt, *J* 7.4 and 1.1, H-4), 7.07 (1H, dd, *J* 7.6 and 0.6, H–Ar), 7.31 (1H, dd, *J* 7.4 and 1.5, H–Ar), 7.35 (1H, ddd, *J* 7.9, 4.9 and 0.8, H-4′), 7.76 (1H, dt, *J* 7.6 and 2.0, H–Ar), 8.60 (1H, br d, *J* 4.5, H-6′), 8.67 (1H, br d, *J* 0.9, H-2′); δ_C (126 MHz): 30.7 (CH_3N), 110.1 (CH), 117.1 (CH), 123.6 (CH), 123.7 (C), 129.6 (CH), 130.2 (CH), 135.2 (C), 136.9 (CH), 146.3 (C), 148.4 (CH), 150.4 (CH). *m*/*z* (EI): 184 (M^+, 100), 169 (12), 168 (20), 156 (11), 154 (10).

From **39a**. Column chromatography (petrol/ether, 95:5) furnished, *N-methyl-2-(2-thienyl)aniline*, ***40a*** (69%) as a yellow oil. ν_{max} (NaCl/film)/cm^{-1} 3417, 3068, 2980, 2911, 2811, 1599, 1576, 1502, 1456, 1421, 1347, 1313, 1288, 1264, 1235, 1191, 1168, 1125, 1066, 1040, 952, 847, 798, 748, 700. δ_H (250 MHz): 2.86 (3H, s, CH_3N), 4.42 (1H, s, NH), 6.72 (1H, d, *J* 8.4, H–Ar), 6.77 (1H, d, *J* 7.5, H–Ar), 7.14 (1H, dd, *J* 5.0 and 3.6, H-4′), 7.18 (1H, dd, *J* 3.6 and 1.4, H-3′), 7.29 (2H, complex signal, H–Ar), 7.37 (1H, dd, *J* 5.1 and 1.4, H-5′); δ_C (126 MHz): 30.7 (CH_3N), 109.9 (CH), 116.6 (CH), 119.6 (C), 125.3 (CH), 126.0 (CH), 127.5 (CH), 129.4 (CH), 130.9 (CH), 140.9 (C), 146.7 (C). *m*/*z* (EI): 189 (M^+, 100), 173 (18), 156 (43), 144 (22), 130 (30), 117 (49), 77 (10). Found $(M)^+$ 189.0613. $C_{11}H_{11}NS$ requires (M) 189.0612.

From **41a**. Column chromatography (petrol/ether 1:1 to 0:1) furnished, in order of elution, *2-(2,4-dimethylthiazol-5-yl)-N-methylaniline*, ***42a*** (87%) as colourless crystals (mp 99–101 °C, from CH_2Cl_2/petrol). Found C 66.1, H 6.3, N 12.8. $C_{12}H_{14}N_2S$ requires C 66.0, H 6.5, N 12.8%. ν_{max} (NaCl/film)/cm^{-1} 3344, 2855, 2802, 1603, 1575, 1513, 1478, 1316, 1180, 1073, 958, 743. δ_H (500 MHz): 2.22 (3H, s, CH_3Ar), 2.69 (3H, s, CH_3Ar), 2.83 (3H, s, CH_3N), 3.80 (1H, s, NH), 6.67 (1H, d, *J* 8.2, H-6), 6.72 (1H, dt, *J* 7.4 and 1.0, H-4), 7.09 (1H, dd, *J* 7.5 and 1.6, H-3), 7.29 (1H, dt, *J* 7.4 and 1.6, H-5); δ_C (126 MHz): 15.4 (CH_3Ar), 19.2 (CH_3Ar), 30.5 (CH_3N), 109.8 (CH), 116.0 (C), 116.3 (CH), 127.0 (C), 130.0 (CH), 131.6 (CH), 147.5 (C), 149.6 (C), 164.9 (C). *m*/*z* (EI): 218 (M^+, 100), 177 (25), 162 (32), 144 (74), 117 (15), 77 (10). Found $(M)^+$ 218.0878. $C_{12}H_{14}N_2S$ requires (M) 218.0878, and *2-[3-(2,4-dimethylthiazol-5-yl)-4-methylaminophenyl]-2-methylpropionitrile*, ***43*** (12%) as colourless crystals (mp 149–150 °C, from CH_2Cl_2/petrol). Found C 67.0, H 6.5, N 14.5. $C_{16}H_{19}N_3S$ requires C 67.3, H 6.5, N 14.7%. ν_{max} (NaCl/film)/cm^{-1} 3317, 2980, 2814, 2234, 1612, 1577, 1521, 1476, 1404, 1373, 1317, 1284, 1214, 1178, 813. δ_H (500 MHz): 1.69 (6H, s, CH_3C), 2.22 (3H, s, CH_3Ar), 2.69 (3H, s, CH_3Ar), 2.83 (3H, s, CH_3N), 3.86 (1H, br s, NH), 6.65 (1H, d, *J* 8.6, H-5′), 7.16 (1H, d, *J* 2.4, H-2′), 7.37 (1H, dd, *J* 8.6 and 2.5, H-6′); δ_C (126 MHz): 15.5 (CH_3Ar), 19.2 (CH_3Ar), 29.2 ($2CH_3C$), 30.5 (CH_3N), 36.1 (C), 109.9 (CH), 116.3 (C), 124.9 (C), 126.4 (C), 126.8 (CH), 128.3 (CH), 129.0 (C), 146.9 (C), 149.9 (C), 165.1 (C). *m*/*z* (EI): 285 (M^+, 56), 270 (100), 229 (10). Found $(M)^+$ 285.1300. $C_{16}H_{19}N_3S$ requires (M) 285.1300.

From **44**. Column chromatography (petrol/ether 1:1 to 0:1) furnished, in order of elution, *2-(3,5-dimethylisoxazol-4-yl)-N-methylaniline*, ***45*** (38%) as colourless crystals (mp 145–147 °C, from CH_2Cl_2/petrol). Found C 71.2, H 7.0, N 13.8. $C_{12}H_{14}N_2O$ requires C 71.3, H 7.0, N 13.85%. ν_{max} (NaCl/film)/cm^{-1} 3370, 2925, 2815, 1633, 1596, 1576, 1514, 1414, 1315, 1288, 1227, 1168, 1066, 991, 879, 753. δ_H (500 MHz): 2.13 (3H, s, CH_3Ar), 2.27 (3H, s, CH_3Ar), 2.81 (3H, d, *J* 5.2, CH_3N), 3.56 (1H, br d, *J* 4.4, NH), 6.69 (1H, d, *J* 8.2, H-6), 6.75 (1H, dt, *J* 7.4 and 1.1, H-4), 6.95 (1H, dd, *J* 7.4 and 1.6, H-3), 7.30 (1H, dt, *J* 8.2 and 1.6, H-5); δ_C (126 MHz): 10.4 (CH_3Ar), 11.4 (CH_3Ar), 30.5 (CH_3N), 109.8 (CH), 113.1 (C), 114.2 (C), 116.7 (CH), 129.7 (CH), 131.0 (CH), 147.6 (C), 160.2 (C), 166.7 (C). *m*/*z* (EI): 202 (M^+, 93), 187 (25), 171 (14), 159 (40), 145 (22), 131 (14), 118 (100), 91 (36), 77 (17). Found $(M)^+$ 202.1106. $C_{12}H_{14}N_2O$ requires (M) 202.1106, **44** (31%), and *2-[3-(3,5-dimethylisoxazol-4-yl)-4-methylaminophenyl]-2-methylpropionitrile*, ***46*** (19%) as beige needles (mp 184–186 °C, from CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 3361, 2986, 2930, 2226, 1637, 1613, 1527, 1445, 1398, 1368, 1325, 1289, 1217, 1177, 1064, 881, 820, 734. δ_H (500 MHz): 1.70 (6H, s, CH_3C), 2.14 (3H, s, CH_3Ar), 2.29 (3H, s, CH_3Ar), 2.82 (3H, d, *J* 5.1, CH_3N), 3.60 (1H, br d, *J* 4.8, NH), 6.67 (1H, d, *J* 8.6, H-5′), 7.04 (1H, d, *J* 2.5, H-2′), 7.38 (1H, dd, *J* 8.6 and 2.5, H-6′); δ_C (126 MHz): 10.4 (CH_3Ar), 11.5 (CH_3Ar), 29.2 ($2CH_3C$), 30.6 (CH_3N), 36.1 (C), 109.9 (CH), 112.8 (C), 114.9 (C), 124.9 (C), 126.4 (CH), 127.7 (CH), 129.4 (C), 147.0 (C), 160.0 (C), 166.9 (C). *m*/*z* (EI): 269 (M^+, 48), 254 (100), 239 (15), 226 (13), 211 (27), 197 (12), 185 (11), 117 (828). Found $(M)^+$ 269.1528. $C_{16}H_{19}N_3O$ requires (M) 269.1528.

From **17a**. Column chromatography (petrol/CH_2Cl_2 2:1) furnished, in order of elution, starting sulfonate **17a** (37%), *9-methyldibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***18a*** (63%) as white crystals (mp 126–127 °C, CH_2Cl_2). Found C 63.6, H 3.9. $C_{13}H_{10}O_3S$ requires C 63.4, H 4.1%. ν_{max} (NaCl/film)/cm^{-1} 1602, 1585, 1444, 1402, 1169, 1149, 1114, 1079, 1032, 999. δ_H (270 MHz): 2.53 (3H, s, CH_3Ar), 6.96–7.49 (4H, complex signal, H-2, H-3, H-4, H-8), 7.73 (1H, s, H-10), 7.88 (1H, d, *J* 8.1, H-7), 7.93 (1H, dd, *J* 7.6 and 1.7, H-1). *m*/*z* (EI): 246 (M^+), 181.

From **17b**. Column chromatography (petrol/CH_2Cl_2 7:3) furnished, in order of elution, starting material **17b** (8%), *7-methyldibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***18b*** (36%) as white

needles (mp 119–121 °C, CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 1367, 1177, 790, 757. δ_H (400 MHz): 2.75 (3H, s, CH_3), 7.30 (1H, dd, *J* 8.0 and 1.3, H-4), 7.34–7.38 (2H, complex signal, H-2 and H-8), 7.44 (1H, dt, J 7.7 and 1.6, H-3), 7.59 (1H, d, *J* 7.8, H-9), 7.76 (1H, d, *J* 8.1, H-10), 7.86 (1H, dd, *J* 7.9 and 1.5, H-1); δ_C (100.6 MHz): 21.0 (CH_3), 119.7 (CH), 122.0 (C), 122.8 (CH), 125.7 (CH), 126.6 (CH), 128.1 (C), 129.1 (C), 130.9 (CH), 132.2 (CH), 133.1 (CH), 136.5 (C), 149.1 (C). *m*/*z* (EI): 246 (M^+, 100), 181 (100). Found $(M)^+$ 246.0351. $C_{13}H_{10}O_3S$ requires (M) 246.0351, and *2-(2-methylphenyl)phenol*, ***25b*** (23%) as a colourless oil. ν_{max} (NaCl/film)/cm^{-1} 3501, 3434, 3060, 2922, 1472, 1185, 754. δ_H (400 MHz): 2.43 (3H, s, CH_3), 5.06 (1H, s, OH), 7.22–7.26 (2H, complex signal, H–Ar), 7.37 (1H, dd, *J* 7.3 and 1.4, H-6), 7.49–7.60 (5H, complex signal, H–Ar); δ_C (100.6 MHz): 19.7 (CH_3), 115.2 (CH), 120.4 (CH), 126.4 (CH), 127.6 (C), 128.5 (CH), 129.1 (CH), 130.1 (CH), 130.4 (CH), 130.6 (CH), 135.6 (C), 137.4 (C), 152.4 (C). *m*/*z* (EI): 184 (M^+, 100), 169. Found $(M)^+$ 184.0900. $C_{13}H_{12}O$ requires (M) 184.0888.

From **17c**. Column chromatography (petrol/CH_2Cl_2 1:2) furnished, in order of elution, *dibenzo[b,d]pyran-6-one*, ***28*** (42%), as white crystals (mp 88–90 °C, from CH_2Cl_2/petrol) (lit.,[43] 92 °C). ν_{max} (NaCl/film)/cm^{-1} 1729, 1605, 1482, 1431, 1304, 1236, 1093, 1076, 1032, 744, 717, 683; δ_H (270 MHz): 7.30–7.40 (2H, complex signal, H-4, H-2 or H-3), 7.48 (1H, m, H-2 or H-3), 7.59 (1H, ddd, *J* 7.7, 7.6 and 1.1, H-8), 7.83 (1H, ddd, *J* 7.7, 7.7 and 1.5, H-9′), 8.07 (1H, dd, *J* 7.9 and 1.5, H-1 or H-10), 8.13 (1H, d, *J* 8.0, H-1 or H-10), 8.41 (1H, dd, *J* 7.6 and 1.3, H-7); *m*/*z*: 196 (M^+), 168, 149. Found $(M)^+$ 196.0527. $C_{13}H_8O_2$ requires (M) 196.0524, starting methyl benzoate, **17c** (37%) and *methyl dibenzo[c,e][1,2]oxathiine-6,6-dioxide-7-carboxylate*, ***18c*** (21%) as a white solid (mp 121–123 °C, CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 3068, 2952, 1735, 1610, 1582, 1454, 1431, 1324, 1297, 1203, 1177, 876. δ_H (500 MHz): 3.88 (3H, s, CH_3O), 7.32–7.40 (2H, complex signal, H-4, H-10), 7.43 (1H, ddd, *J* 7.7, 7.7 and 1.3, H-2 or H-3), 7.51 (1H, ddd, *J* 7.8, 7.8 and 1.6, H-2 or H-3), 7.80 (1H, m, H-9), 7.89 (1H, dd, *J* 7.9 and 1.5, H-1), 8.03 (1H, dd, *J* 6.9 and 2.4, H-8). *m*/*z* (EI): 290 (M^+), 259, 230, 226, 221, 199, 195. Found $(M)^+$ 290.0247. $C_{14}H_{11}O_5S$ requires (M) 290.0249.

From **17d**. Column chromatography (petrol/CH_2Cl_2 1:1 to 1:2) furnished, in order of elution, starting material, **17d** (33%) and *2-(2,4,6-trimethylphenyl)phenol*, ***25d*** (50%) as an oil. ν_{max} (NaCl/film)/cm^{-1} 3493, 2920, 755. δ_H (270 MHz): 2.01 (6H, s, CH_3), 2.34 (3H, s, CH_3), 4.62 (1H, s, OH), 6.94–7.03 (5H, complex signal, H–Ar), 7.27 (1H, m, H-6); δ_C (67.5 MHz): 20.2 ($2CH_3$), 21.1 (CH_3), 115.1 (CH), 120.7 (CH), 126.4 (C), 128.7 (CH), 128.9 (CH), 130.0 (CH), 131.6 (C), 137.8 (C), 138.1 (C), 152.5 (C); *m*/*z* (EI): 215 (M^+), 197 (100), 182, 119. Found $(M)^+$ 212.1209. $C_{15}H_{16}O$ requires (M) 212.1201.

From **17e**. Column chromatography (petrol/CH_2Cl_2 1:1 to 1:2) furnished, in order of elution *(biphenyl-2-yl)-4-fluorobenzenesulfonate*, ***29*** (9%) as a colourless oil. ν_{max} (NaCl/film)/cm^{-1} 3104, 3067, 2926, 1722, 1591, 1491, 1474, 1431, 1408, 1378, 1239, 1196, 1167, 1157, 1091, 861. δ_H (270 MHz): 6.80 (2H, dd, *J* 8.7 and 8.7, H-3, H-5), 7.09–7.13 (2H, m, H–Ar), 7.23–7.30 (6H, complex signal, H–Ar), 7.34 (1H, ddd, *J* 7.3, 7.3 and 1.7, H–Ar), 7.40 (1H, ddd, *J* 7.6, 7.6 and 2.0, H–Ar), 7.53 (1H, dd, *J* 7.3 and 1.4, H–Ar). *m*/*z* (EI): 328 (M^+), 252, 169, 159, 149, 141, 115, 95. Found $(M)^+$ 328.0572. $C_{18}H_{13}FO_3S$ requires (M) 328.0569, and *9-fluorodibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***18e*** (50%) as white crystals (mp 111–115 °C, CH_2Cl_2). Found C 57.8, H 3.0. $C_{12}H_7FO_3S$ requires C 57.6, H 2.8%. ν_{max} (NaCl/film)/cm^{-1} 1591, 1571, 1483, 1447, 1418, 1367, 1195, 1169, 1131, 1077, 856, 763. δ_H (500 MHz): 7.28 (1H, ddd, *J* 8.4, 8.3 and 2.5, H-8), 7.36 (1H, dd, *J* 8.2 and 1.2, H-4), 7.43 (1H, ddd, *J* 7.9, 7.7 and 1.2, H-2), 7.53 (1H, ddd, *J* 8.2, 7.7 and 1.6, H-3), 7.61 (1H, dd, *J* 9.5 and 2.4, H-10), 7.87 (1H, dd, J 7.9 and 1.5, H-1), 8.02 (1H, dd, *J* 8.7, and 5.3, H-7). *m*/*z* (EI): 250 (M^+), 252, 186, 169, 95.

From **17f**. Column chromatography (petrol/CH_2Cl_2 1:1 to 1:2) furnished, in order of elution, starting material, **17f** (31%), *9-methoxydibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***18f*** (24%) as white crystals (mp 154–156 °C, CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 1596, 1486, 1351, 1197, 1182, 1022, 901, 851, 797. δ_H (250 MHz): 3.97 (3H, s, CH_3O), 7.07 (1H, dd, *J* 8.8 and 2.5, H-8), 7.38 (1H, d, *J* 2.6, H-10), 7.31–7.44 (2H, complex signal, H-4, H-2 or H-3), 7.49 (1H, ddd, *J* 7.8, 7.8 and 1.8, H-2 or H-3), 7.90 (1H, dd, *J* 7.7 and 1.7, H-1), 7.94 (1H, d, *J* 8.9, H-7). *m*/*z* (EI): 262 (M^+), 193, 183, 166, 149. Found $(M)^+$ 262.0299. $C_{13}H_{10}O_4S$ requires (M) 262.0300 and *2-(4-methoxyphenyl)phenol*, ***25f*** (18%) as white crystals (mp 63–64 °C, CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 3428, 3033, 2998, 1704, 1605, 1513, 1481, 1450, 1297, 1274, 1246, 1178, 755. δ_H (500 MHz): 3.88 (3H, s, CH_3O), 5.19 (1H, s, OH), 6.94–7.01 (2H, complex signal, H-4, H-6), 7.02 (2H, m, H-3′, H-5′), 7.21–7.26 (2H, complex signal, H-4, H-6), 7.40 (2H, m, H-2′, H-6′). *m*/*z* (EI): 200 (M^+), 185, 169. Found $(M)^+$ 200.0834. $C_{13}H_{12}O_2$ requires (M) 200.0837.

From **17g**. Column chromatography (petrol/CH_2Cl_2 1:1 to 0:1) furnished, in order of elution, *9,10-dimethoxydibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***18g*** (10%) as white prisms (mp 144–145 °C, CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 2945, 1493, 1414, 1370, 1183. δ_H (270 MHz): 3.79 (3H, s, CH_3O), 3.99 (3H, s, CH_3O), 7.09 (1H, d, *J* 8.5, H-8), 7.30–7.49 (3H, complex signal, H-2, H-3, H-4), 7.75 (1H, d, *J* 8.5, H-7), 8.62 (1H, dd, *J* 7.8 and 1.5, H-1); δ_C (67.5 MHz): 56.3 (CH_3O), 60.4 (CH_3O), 112.0 (CH), 119.8 (CH), 120.5 (C), 121.0 (CH), 125.1 (C), 125.6 (C), 126.4 (CH), 129.5 (CH), 130.8 (CH), 146.6 (C), 149.3 (C), 157.5 (C). *m*/*z* (EI): 292 (M^+, 100), 277. Found $(M)^+$ 292.0414. $C_{14}H_{12}O_5S$ requires (M) 292.0405, *8,9-dimethoxydibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***113*** (10%) as white needles (mp 218–219 °C, CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 2939, 2850, 1603, 1515, 1368, 1170, 1030, 861. δ_H (270 MHz): 3.98 (3H, s, CH_3O), 4.03 (3H, s, CH_3O), 7.28–7.41 (5H, complex signal, H–Ar), 7.81 (1H, dd, *J* 7.6 and 1.7, H-1); δ_C (67.5 MHz): 56.4 (CH_3O), 56.5 (CH_3O), 106.0 (CH), 106.7 (CH), 119.9 (CH), 121.5 (C), 124.5 (CH), 125.3 (C), 126.4 (CH), 130.3 (CH), 149.4 (C), 149.7 (C), 153.3 (C), a quaternary carbon was not observed. *m*/*z* (EI): 292 (M^+, 100), 277, 228. Found $(M)^+$ 292.0420. $C_{14}H_{12}O_5S$ requires (M) 292.0405, starting material, **17g** (13%), and *2-(3,4-dimethoxyphenyl)phenol*, ***25g*** (19%) as orange prisms (mp 121–122 °C, CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 3439, 2935, 1268, 1220. δ_H (270 MHz): 3.89 (3H, s, CH_3O), 3.92 (3H, s, CH_3O), 5.4 (1H, br s, OH), 6.95–7.03 (5H, complex signal, H-4, H-6, H-2′, H-5′, H-6′), 7.21–7.25 (2H, complex signal, H-3, H-5); δ_C (67.5 MHz): 55.9 ($2CH_3O$), 111.7 (CH), 112.3 (CH), 115.6 (CH), 120.6 (CH), 121.1 (CH), 127.9 (C), 128.8 (CH), 129.5 (C), 130.0 (CH), 148.7 (C), 149.5 (C), 152.5 (C); *m*/*z* (EI): 230 (M^+, 100), 215. Found $(M)^+$ 230.0943. $C_{14}H_{14}O_3$ requires (M) 230.0943.

From **17h**. Column chromatography (petrol/ether 7:3 to 0:1) furnished, in order of elution, *2-(2,5-dimethoxyphenyl)phenol*, ***25h*** (43%) as an oil. ν_{max} (NaCl/film)/cm^{-1} 3393, 2941, 1271, 1219. δ_H (400 MHz): 3.81 (3H, s, CH_3O), 3.84 (3H, s, CH_3O), 6.54 (1H, br s, OH), 6.90–6.95 (2H, complex signal, H-4′, H-6′), 7.00 (1H, d, *J* 8.7, H-3′), 7.01–7.06 (2H, complex signal, H-4, H-6), 7.28–7.33 (2H, complex signal, H-3, H-5); δ_C (100.6 MHz): 55.7 (CH_3), 57.1 (CH_3), 113.4 (CH), 114.3 (CH), 117.6 (CH), 117.7 (CH), 121.0 (CH), 126.2 (C), 128.3 (C), 129.3 (CH), 131.1 (CH), 149.6 (C), 153.7 (C), 154.7 (C); *m*/*z* (EI): 230 (M^+, 100), 215, 200, 184. Found $(M)^+$ 230.0943. $C_{14}H_{14}O_3$ requires (M) 230.0943, starting material, **17h** (32%) and *7,10-dimethoxydibenzo[c,e][1,2]oxathiine-6,6-dioxide*, ***18h*** (7%) as white needles (mp 155–156 °C, CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 2944, 1374, 1257, 1175. δ_H (270 MHz): 3.91 (3H, s, CH_3O), 3.97 (3H, s, CH_3O), 7.05 (1H, d, *J* 9.3, H-9), 7.24 (1H, d, *J* 9.3, H-8), 7.27–7.44 (3H, complex signal, H-2, H-3, H-4), 8.48 (1H, dd, *J* 8.1 and 1.7, H-1); δ_C (100.6 MHz): 56.7 (CH_3O), 57.2 (CH_3O), 113.6 (CH), 117.9 (CH), 119.4 (CH), 120.4 (C), 121.8 (C), 123.1 (C), 125.8 (CH), 129.9 (CH), 130.3 (CH), 148.2 (C), 150.3 (C), 150.6 (C). *m*/*z* (EI): 292 (M^+, 100), 277. Found $(M)^+$ 292.0420. $C_{14}H_{12}O_5S$ requires (M) 292.0405.

From **17i**. Column chromatography (petrol/CH_2Cl_2 7:3) furnished, in order of elution, *methyl dibenzo[c,e][1,2]oxathiine-6,6-dioxide-8-carboxylate*, ***18i*** (52%) as white prisms (mp 183–185 °C,

CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 2956, 1728, 1377, 1202, 1176, 758. δ_H (400 MHz): 3.99 (3H, s, CH_3O), 7.37 (1H, dd, *J* 8.1 and 1.2, H-4), 7.44 (1H, dt, *J* 7.6 and 1.5, H-2), 7.53 (1H, dt, *J* 8.1 and 1.7, H-3), 7.98 (1H, dd, *J* 7.8 and 1.7, H-1), 8.03 (1H, d, *J* 8.3, H-10), 8.40 (1H, dd, *J* 8.3 and 1.7, H-9), 8.65 (1H, d, *J* 1.7, H-7); δ_C (100.6 MHz): 52.8 (CH_3), 120.2 (CH), 120.9 (2C), 125.1 (CH), 125.7 (2CH), 126.9 (CH), 130.7 (C), 132.3 (CH), 134.4 (CH), 135.4 (C), 150.1 (C), 164.7 (C). *m*/*z* (EI): 290 (M^+, 100), 259, 195, 139. Found $(M)^+$ 290.0238. $C_{14}H_{10}O_5S$ requires (M) 290.0249, and *methyl (4aRS,10bRS)-4a,10b-dihydrodibenzo[c,e][1,2]oxathiine-6,6-dioxide-8-carboxylate*, ***33*** (19%) as white prisms (mp 125–126 °C, CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 1710, 1375, 1227, 1156. δ_H (270 MHz): 3.93 (3H, s, CH_3O), 4.37 (1H, d, *J* 7.8, H-6a), 4.83 (1H, d, *J* 7.3, H-10a), 6.31 (2H, complex signal, *J* 2.9, H-7, H-8), 6.99 (1H, dd, *J* 8.3 and 1.2, H-1 or H-4), 7.06 (1H, d, *J* 7.8, H-1 or H-4), 7.13 (1H, dt, *J* 7.3 and 1.2, H-2 or H-3), 7.24–7.28 (2H, complex signal, H-9, H-2 or H-3); δ_C (100.6 MHz): 33.9 (CH), 52.6 (CH), 55.9 (CH_3), 118.6 (CH), 121.7 (C), 125.2 (CH), 125.9 (CH), 128.1 (CH), 128.4 (CH), 128.5 (C), 129.1 (CH), 134.4 (CH), 150.9 (C), 166.6 (C). *m*/*z* (EI): 292 (M^+), 290, 196 (100), 168.

From **34b**. Column chromatography (petrol/ether 6:4 to 2:8) furnished, in order of elution, *2-(quinolin-8-yl)phenol*, ***35b*** (27%) as bright yellow crystals (mp 111–114 °C, petrol/ether). Found C 81.6, H 4.8, N 6.1. $C_{15}H_{11}NO$ requires C 81.4, H 5.0, N 6.3%. ν_{max} (NaCl/film)/cm^{-1} 3048, 1571, 1498, 1459, 1372, 1279, 1233, 968, 793, 757. δ_H (270 MHz): 7.07 (1H, dt, *J* 7.6 and 1.4, H–Ar), 7.20 (1H, dd, *J* 8.1 and 1.4, H–Ar), 7.41 (2H, complex signal, H–Ar), 7.52 (1H, dd, *J* 8.3 and 4.3, H-3′), 7.70 (1H, t, *J* 7.7, H–Ar), 7.82 (2H, complex signal, Ar–H), 8.33 (1H, dd, *J* 8.4 and 1.8, H-4′), 8.92 (1H, dd, *J* 4.3 and 1.8, H-2′); δ_C (67.5 MHz): 119.6 (CH), 120.9 (CH), 121.1 (CH), 127.5 (CH), 127.7 (CH), 128.2 (C), 128.6 (C), 129.9 (CH), 132.6 (CH), 133.3 (CH), 138.5 (CH), 138.9 (C), 145.2 (C), 149.2 (CH), 155.1 (C); *m*/*z* (EI): 221 (M^+, 27), 220 (22), 204 (100), 191 (13), and starting material, **34b** (56%).

From **36b**. Column chromatography (petrol/ether 6:4 to 4:6) furnished, in order of elution, *benzo[e]pyrido[3,2-c][1,2]oxathiin-5,5-dioxide*, ***38b*** (43%) as colourless crystals (mp 173–175 °C, petrol/CH_2Cl_2). Found C 56.4, H 2.9, N 5.9. $C_{11}H_7NO_3S$ requires C 56.65, H 3.0, N 6.0%. ν_{max} (NaCl/film)/cm^{-1} 3064, 2922, 1608, 1579, 1553, 1485, 1361, 1276, 1244, 1198, 1165, 1146, 1081, 1049,874, 785, 758, 712, 682, 627. δ_H (270 MHz): 7.36 (1H, dd, *J* 8.1 and 1.2, H-7 or H-10), 7.46 (1H, dt, *J* 7.6 and 1.5, H-9 or H-8), 7.51 (1H, dd, *J* 8.1 and 4.9, H-3), 7.58 (1H, dd, *J* 7.8 and 1.7, H-8 or H-9), 8.26 (1H, dd, *J* 8.1 and 1.7, H-4), 8.50 (1H, dd, *J* 7.8 and 1.7, H-7 or H-10), 8.96 (1H, dd, *J* 4.9 and 1.7, H-2); δ_C (67.5 MHz): 119.4 (CH), 122.1 (C), 123.3 (CH), 126.8 (CH), 127.2 (CH), 132.1 (C and CH), 133.1 (CH), 148.7 (C), 150.6 (C), 154.1 (CH); *m*/*z* (EI): 233 (M^+, 100), 169 (57), 140 (20), 114 (17), and starting material, **36b** (5%).

From **39b**. Column chromatography (petrol ether 7:3 to 1:1) furnished, in order of elution, *2-(thien-2-yl)phenol*, ***40b*** (50%) as a green oil. ν_{max} (NaCl/film)/cm^{-1} 3505, 3100, 2921, 2850, 1581, 1523, 1479, 1449, 1369, 1289, 1255, 1187, 1100, 1042, 960, 855, 816, 753, 700. δ_H (270 MHz): 6.98 (1H, dt, *J* 8.1 and 1.3, H–Ar), 6.99 (1H, dt, *J* 7.6 and 1.2, H–Ar), 7.15 (1H, dd, *J* 5.1 and 3.4, H-4′), 7.23 (1H, dd, *J* 7.8 and 1.7, H–Ar), 7.31 (1H, dd, *J* 3.4 and 1.0, H-3′), 7.41 (1H, dd, *J* 5.1 and 1.2, H-5′), 7.44 (1H, dd, *J* 8.1 and 1.7, H–Ar); δ_C (100.6 MHz): 116.2 (CH), 121.0 (CH), 126.1 (CH), 126.3 (CH and C), 127.9 (CH), 129.4 (CH), 130.1 (CH), 138.8 (C), 152.5 (C); *m*/*z* (EI): 176 (M^+, 100), 147 (26), 131 (35), 115 (23). Found $(M)^+$ 176.0296. $C_{10}H_8OS$ requires (M) 176.0296, and starting material, **39b** (4%).

From **41b**. Column chromatography (petrol/ether 6:4 to 2:8) furnished *2-(2,4-dimethylthiazol-5yl)phenol*, ***42b*** (51%) as a cream solid (mp 208–210 °C, petrol/ether). Found C 62.7, H 5.4, N 6.9. $C_{11}H_{11}NOS$ requires C 63.0, H 5.5, N 6.7%. ν_{max} (NaCl/film)/cm^{-1} 2923, 2694, 1287, 1256, 1198, 1154, 1107, 967, 828, 749, 675. δ_H (270 MHz, DMSO-d_6): 2.15 (3H, s, CH_3), 2.52 (3H, s CH_3), 6.77 (1H, dt, *J* 7.6 and 1.0, H-6), 6.87 (1H, dd, *J* 7.6 and 1.0, H-4), 7.11 (2H, complex signal, H-3, H-5), 9.73 (1H, s, OH); δ_C (100.6 MHz): 15.9 (CH_3), 18.5 (CH_3), 115.8 (CH), 118.4 (C), 119.0 (CH), 126.6 (C), 129.4 (CH), 131.4 (CH), 147.8 (C), 154.8 (C), 162.7 (C); *m*/*z* (EI): 205 (M^+, 100), 164 (50), 163 (48), 131 (55), 121 (21), 91 (36), 77 (21). Found $(M)^+$ 205.0561. $C_{11}H_{11}NOS$ requires (M) 205.0561.

From **19**. Column chromatography (petrol/ether 7:3 to 1:1) furnished, in order of elution, starting material, **19** (40%), and *2-methyl-6H-dibenzo[b,d]thiine-5,5-dioxide*, ***20*** (40%) as white crystals (mp 163–168 °C, petrol/ether). ν_{max} (NaCl/film)/cm^{-1} 1598, 1443, 1388, 1306, 1201, 1160, 1145, 1131, 1103, 1076, 815, 770, 725, 646, 631. δ_H (250 MHz): 2.52 (3H, s, CH_3), 4.40 (2H, s, CH_2), 7.27–7.46 (3H, complex signal, H-3, H-7, H-8 or H-9), 7.50 (1H, ddd, *J* 7.6, 7.6 and 1.3, H-8 or H-9), 7.68 (1H, br s, H-1), 7.86 (1H, d, *J* 7.7, H-10), 7.96 (1H, d, *J* 7.7, H-4); *m*/*z* (EI): 244 (M^+), 196, 180, 165, 149, 139, 115. Found $(M)^+$ 244.0562. $C_{14}H_{12}O_2S$ requires (M) 244.0558.

From **34c**. Column chromatography (CH_2Cl_2) furnished, *8-(2-methylphenyl)quinoline*, ***35c*** (45%), as colourless needles (mp 54–56 °C, petrol/CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 3046, 1595, 1494, 1461, 1380, 1315, 1130, 1049, 966, 832, 797, 756, 725. δ_H (270 MHz): 2.06 (3H, s, CH_3), 7.32 (4H, complex signal, H–Ar), 7.39 (1H, dd, *J* 8.3 and 4.2, H-3), 7.60 (2H, complex signal, H–Ar), 7.86 (1H, m, H–Ar), 8.20 (1H, dd, *J* 8.3 and 1.7, H-4), 8.91 (1H, dd, *J* 4.2 and 1.7, H-2); *m*/*z* (EI): 219 (M^+, 46), 218 (88), 204 (100), 109 (30). Found $(M)^+$ 219.1048. $C_{16}H_{13}N$ requires (M) 219.1048.

4.3. General procedure for the reaction of benzamides 49, 54, 62, 64 and 66 with Bu_3SnH

To a stirred solution of the required benzamide (0.9 mmol) in benzene (18 mL) at reflux, was added over 11 h a solution of AIBN (104 mg, 0.6 mmol) and Bu_3SnH (0.31 mL, 1.13 mmol) in benzene (4.7 mL), via uniform motor-driven syringe addition. After a further 2 h, the reaction mixture was cooled to room temperature and CCl_4 (10 mL) and a few crystals of iodine were added and stirred continuously for 2 h. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 (40 mL) and washed with satd aq KF (3×25 mL) and water (30 mL), dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography.

From **49**. Column chromatography (petrol/ether 7:3 to 0:1) furnished, in order of elution, starting benzamide, **49** (34%), *3,5-dimethyl-5H-phenanthridin-6-one*, ***51*** (8%) as white needles (mp 112–114 °C, CH_2Cl_2/petrol) (lit.,[44] 110–112 °C). Found C 80.6, H 5.95, N 6.1. $C_{15}H_{13}NO$ requires C 80.2, H 5.8, N 6.2%. ν_{max} (NaCl/film)/cm^{-1} 1646, 1608, 1417, 1336, 1100, 768. δ_H (270 MHz): 2.52 (3H, s, CH_3), 3.81 (3H, s, CH_3N), 7.15 (1H, dd, *J* 8.2 and 1.1, H-2), 7.23 (1H, s, H-4), 7.55 (1H, ddd, *J* 8.0, 7.0 and 1.0, H-8), 7.74 (1H, ddd, *J* 8.3, 7.1 and 1.4, H-9), 8.17 (1H, d, *J* 8.2, H-1 or H-7), 8.24 (1H, d, *J* 8.2, H-1 or H-7), 8.54 (1H, dd, *J* 8.0 and 1.4, H-10); *m*/*z* (CI): 224 (M^{+1}, 100). Found $(M)^+$ 223.1002. $C_{15}H_{13}NO$ requires (M) 223.0997, and *N-methyl-2-(4-methylphenyl)benzamide*, ***50*** (37%) as white crystals (mp 105–107 °C, CH_2Cl_2/petrol) (lit.,[8] 107–109 °C). ν_{max} (NaCl/film)/cm^{-1} 3309, 2922, 1635, 1545, 1128, 759. δ_H (500 MHz): 2.40 (3H, s, CH_3), 2.69 (3H, s, NCH_3), 2.70 (3H, s, NCH_3), 5.20 (1H, br s, NH), 7.23 (2H, m, H-3′, H-5′), 7.31 (2H, m, H-2′, H-6′), 7.36 (1H, dd, *J* 7.7 and 1.2, H-3), 7.39 (1H, ddd, *J* 7.6, 7.6 and 1.4, H-4 or H-5), 7.46 (1H, ddd, *J* 7.6, 7.5 and 1.5, H-4 or H-5), 7.69 (1H, dd, *J* 7.6 and 1.4, H-6); *m*/*z* (EI): 225 (M^+), 195, 167. Found $(M)^+$ 225.1159. $C_{15}H_{15}NO$ requires (M) 225.1154.

From **54**. Column chromatography (petrol/ethyl acetate 9:1 to 4:6) furnished, in order of elution, starting benzamide, **54** (5%), *N-[(3,4-dimethoxyphenyl)sulfonylmethyl]benzamide*, ***56*** (22%) as a foam. Found C 57.5, H 5.2, N 4.3. $C_{16}H_{17}NO_5S$ requires C 57.3, H 5.1, N 4.2%. ν_{max} (NaCl/film)/cm^{-1} 3343, 3061, 2936, 1669, 1508, 1320, 1263, 1130. δ_H (400 MHz): 3.74 (3H, s, CH_3O), 3.90 (3H, s, CH_3O), 4.86 (2H, d, *J* 6.7, CH_2), 6.91 (2H, complex signal, NH, H-5′), 7.26 (1H, d, *J* 2.2, H-2′), 7.42 (2H, m, H-3, H-5), 7.49–7.54 (2H, complex signal,

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H-4, H-6′), 7.66 (2H, m, H-2, H-6); δ_C (100.6 MHz): 56.1 (CH_3), 56.2 (CH_3), 61.0 (CH_2), 110.8 (2CH), 123.0 (CH), 127.1 (2CH(2CH), 128.2 (C), 128.7 (2CH), 132.4 (CH), 132.7 (C), 149.2 (C), 153.9 (C), 166.4 (C), and *2,3-dimethoxy-5-methyl-5H-phenanthridin-6-one*, ***55*** (25%) as a clear oil. ν_{max} (NaCl/film)/cm^{-1} 2970, 1639, 1528, 1493, 1256. δ_H (270 MHz): 3.70 (3H, s, NCH_3), 3.96 (6H, s, $2OCH_3$), 6.72 (1H, s, H-1), 7.46 (1H, dt, *J* 8.1 and 1.0, H-5), 7.50 (1H, s, H-4), 7.65 (1H, dt, *J* 8.3 and 1.2, H-8), 7.98 (1H, d, *J* 8.3, H-7), 8.45 (1H, dd, *J* 8.1 and 1.0, H-10); δ_C (100.6 MHz): 29.9 (CH_3), 55.9 (CH_3), 56.2 (CH_3), 98.4 (CH), 105.1 (CH), 111.7 (C), 120.8 (CH), 124.5 (C), 126.7 (CH), 128.8 (CH), 132.1 (CH), 132.8 (C), 133.3 (C), 144.9 (C), 150.6 (C), 161.4 (C); *m*/*z* (EI): 269 (M^+, 100), 254, 226. Found $(M)^+$ 269.1052. $C_{16}H_{15}NO_3$ requires (M) 269.1052.

From **62**. Column chromatography (petrol/ethyl acetate 9:1 to 6:4) furnished, in order of elution, starting benzamide, **62** (14%) and *N-methyl-benzamide*, ***63*** (17%), as white needles (mp 75–76 °C, ethyl acetate/petrol). ν_{max} (NaCl/film)/cm^{-1} 3320, 2938, 1643, 1549, 1310, 694; δ_H (270 MHz): 3.00 (3H, s, NCH_3), 6.23 (1H, br s, NH), 7.38–7.48 (3H, complex signal, H-3, H-4, H-5), 7.76 (2H, m, H-2, H-6); δ_C (100.4 MHz): 26.8 (CH_3), 126.8 (2CH), 128.5 (2CH), 131.3 (CH), 134.6 (C), 169.4 (C).

From **64**. Column chromatography (petrol/ether 1:1 to 0:1) furnished, in order of elution, *N-methyl-2-(thien-2-yl)benzamide*, ***65*** (25%) as colourless needles (mp 134–135 °C, THF/petrol). ν_{max} (NaCl/film)/cm^{-1} 3266, 1632, 1544, 1402, 1319, 1268, 1158, 762, 697. δ_H (500 MHz): 2.80 (3H, s, NCH_3), 5.50 (1H, br s, NH), 7.07 (1H, dd, *J* 5.2 and 3.6, H-4′), 7.16 (1H, dd, *J* 3.6, and 1.3, H-3′), 7.35 (1H, dd, *J* 5.2 and 1.2, H-5′), 7.37 (1H, dt, *J* 7.5 and 1.5, H-3), 7.43 (1H, dt, *J* 7.4 and 1.5, H-4), 7.47 (1H, dd, *J* 7.4 and 1.5, H-5), 7.58 (1H, dd, *J* 7.3 and 1.4, H-6); *m*/*z* (EI): 235 (M^{+1}, 100), 187 (43), 115 (24). Found $(M+H)^+$ 218.0640. $C_{12}H_{12}NOS$ requires (M) 218.0640, and *N-methyl-benzamide*, ***63*** (11%).

From **66**. Column chromatography (petrol/ether 1:1 to 0:1) furnished, in order of elution, *5-methyl-5H-benzo[c][1,8]naphthyridin-6-one*, ***67*** (8%) as colourless needles (mp 133–134 °C, THF/petrol). ν_{max} (NaCl/film)/cm^{-1} 1649, 1581, 1477, 1428, 1334, 1283, 1108, 1005, 771. δ_H (500 MHz): 3.94 (3H, s, NCH_3), 7.27 (1H, dd, *J* 7.9 and 4.6, H-3), 7.64 (1H, dt, *J* 7.2, and 1.0, H-6 or H-7), 7.79 (1H, dt, *J* 7.4 and 1.4, H-6 or H-7), 8.23 (1H, d, *J* 7.8, H-4), 8.52 (1H, dd, *J* 7.9 and 1.7, H-4), 8.57 (1H, dd, *J* 8.3 and 1.4, H-8), 8.59 (1H, dd, *J* 4.6 and 1.6, H-2); *m*/*z* (CI, NH_3): 228 ($M + NH_4^+$), 211 (M^{+1}, 100), 182 (17), 181 (24). Found $(M+H)^+$ 211.0871. $C_{13}H_{11}N_2O$ requires (M) 211.0871, starting benzamide, **66**, and *N-methyl-benzamide*, ***63*** (16%).

4.4. General procedure for the reaction of 2-iodobenzyl arylsulfonates 72a,b, 75, 78 and 80 with Bu_3SnH

To a stirred solution of the required sulfonate (0.9 mmol) in benzene (18 mL) at reflux was added over 11 h a solution of AIBN (104 mg, 0.6 mmol) and Bu_3SnH (0.32 mL, 1.17 mmol) in benzene (4.7 mL), via uniform motor-driven syringe addition. After a further 2 h, the reaction mixture was cooled to room temperature and CCl_4 (10 mL) and a few crystals of iodine were added and stirred continuously for 3 h. The solvent was removed in vacuo, the residue dissolved in ethyl acetate (15 mL) and stirred vigorously with satd aq KF (15 mL). After filtration, the organic layer was separated and washed with satd aq KF (25 mL) and water (20 mL), dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography.

From **72a**. Column chromatography (petrol/ethyl acetate 1:0 to 0:1) furnished, in order of elution, starting material **72a** (3%) and *2-methyl-7H-dibenzo[c,e]oxathiepin-5,5-dioxide*, ***73a*** (10%) as white prisms (mp 148–150 °C, petrol/CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 2925, 1351, 1179, 936, 770. δ_H (500 MHz): 2.53 (3H, s, CH_3), 5.03 (2H, s, H-7), 7.37–7.49 (4H, complex signal, H–Ar), 7.56–7.60 (2H, complex signal, H–Ar), 8.04 (1H, d, *J* 8.1, H-4); δ_C (125.7 MHz): 21.6 (CH_3), 72.8 (CH_2), 128.5 (CH), 128.6 (CH), 129.2 (CH), 129.3 (CH), 130.5 (CH), 130.7 (CH), 131.0 (CH), 131.8 (C), 132.0 (C), 138.8 (C), 140.6 (C), 145.2 (C); *m*/*z* (EI): 260 (M^+), 195 (100), 181, 165. Found $(M)^+$ 260.0531. $C_{14}H_{12}O_3S$ requires (M) 260.0507.

From **72b**. Column chromatography (petrol/CH_2Cl_2 9:1 to 8:2) furnished, in order of elution, *1,11b-dihydro-2-methoxy-7H-dibenzo[c,e]oxathiepin-5,5-dioxide*, ***74*** (14%) as beige prisms (mp 160–162 °C, petrol/CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 1567, 1349, 1171, 1157, 1022. δ_H (400 MHz): 2.87 (1H, d, *J* 17.2, H-1), 3.23 (1H, ddd, *J* 17.2, 8.4 and 2.2, H-1), 3.80 (3H, s, OCH_3), 4.15 (1H, d, *J* 8.4, H-11b), 5.03 (1H, AB, *J* 13.5, CH_2), 5.05 (1H, dd, *J* 6.7 and 2.2, H-3), 5.63 (1H, AB, *J* 13.5, CH_2), 6.87 (1H, d, *J* 6.7, H-4), 7.16 (1H, d, *J* 7.6, H-11), 7.32 (1H, d, *J* 7.0, H-8), 7.37–7.43 (2H, complex signal, H-9 and H-10); δ_C (100.6 MHz): 30.7 (CH_2), 34.4 (CH), 55.9 (CH_3), 72.3 (CH_2), 90.4 (CH), 125.5 (CH), 127.4 (CH), 129.9 (CH), 131.2 (CH), 132.5 (CH), 132.6 (CH), 133.4 (C), 139.1 (C), 163.2 (C); *m*/*z* (EI): 278 (M^+), 214, 165, 152, 91 (100). Found $(M)^+$ 278.0613. $C_{14}H_{14}O_4S$ requires (M) 278.0613, and *2-methoxy-7H-dibenzo[c,e]oxathiepin-5,5-dioxide*, ***73b*** (19%) as white prisms (mp 164–165 °C, petrol/CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 2945, 1593, 1563, 1350, 1177, 769. δ_H (270 MHz): 3.95 (3H, s, OCH_3), 5.03 (2H, s, CH_2), 7.04 (1H, dd, *J* 8.8 and 2.7, H-3), 7.11 (1H, d, *J* 2.4, H-1), 7.48–7.50 (2H, complex signal, H–Ar), 7.57–7.60 (2H, complex signal, H–Ar), 8.08 (1H, d, *J* 8.8, H-4); δ_C (100.6 MHz): 55.8 (CH_3), 72.6 (CH_2), 113.0 (CH), 115.9 (CH), 126.6 (C), 128.4 (CH), 129.5 (CH), 130.6 (CH), 130.8 (CH), 131.0 (CH), 131.8 (C), 140.4 (C), 140.9 (C), 163.8 (C); *m*/*z* (EI): 276 (M^+), 212, 211 (100). Found $(M)^+$ 276.0467. $C_{14}H_{12}O_4S$ requires (M) 276.0456.

From **75**. Column chromatography (petrol/CH_2Cl_2 1:1 to 1:2) furnished, in order of elution, *5H-dibenzo[c,e]oxepin-7-one*, ***76*** (76%) as white needles (mp 133–135 °C, petrol/CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 1715, 1277, 1111, 739. δ_H (400 MHz): 5.03 (1H, d, *J* 11.3, H-5), 5.05 (1H, d, *J* 11.3, H-5), 7.39–7.45 (2H, complex signal, H–Ar), 7.48–7.54 (2H, complex signal, H–Ar), 7.58–7.67 (3H, complex signal, H–Ar), 7.97 (1H, dd, *J* 7.9 and 1.3, H-8); δ_C (100.6 MHz): 69.2 (CH_2), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 130.1 (CH), 130.6 (C), 131.9 (CH), 132.5 (CH), 132.5 (CH), 134.8 (C), 137.2 (C), 138.9 (C), 170.2 (C); *m*/*z* (EI): 210 (M^+, 100), 181, 165, 152. Found $(M)^+$ 210.0684. $C_{14}H_{10}O_2$ requires (M) 210.0681, and *methyl 2-(2-hydroxymethylphenyl)benzoate*, ***77*** (14%) as an oil. ν_{max} (NaCl/film)/cm^{-1} 3411, 2951, 1722, 1309, 1244, 749. δ_H (400 MHz): 3.90 (3H, s, OCH_3), 4.58 (2H, d, *J* 3.6, CH_2), 7.26 (1H, dd, *J* 7.5 and 1.5, H–Ar), 7.35 (1H, dt, *J* 7.5 and 1.7, H–Ar), 7.40 (1H, dt, *J* 7.4 and 1.4, H–Ar), 7.48 (1H, t, *J* 7.8, H–Ar), 7.56 (2H, complex signal, H–Ar), 8.03 (2H, complex signal, H–Ar); δ_C (100.6 MHz): 52.2 (CH_3), 63.0 (CH_2), 127.8 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.4 (C), 130.0 (CH), 130.2 (CH), 133.6 (CH), 137.9 (C), 140.2 (C), 140.9 (C), 166.9 (C); *m*/*z* (EI): 242 (M^+), 224, 165 (100). Found $(M)^+$ 242.0941. $C_{15}H_{14}O_3$ requires (M) 242.0943.

From **78**. Column chromatography (petrol/CH_2Cl_2 1:1 to 1:2) furnished *2-(2,4,6-trimethylphenyl)benzyl alcohol*, ***79*** (36%) as an oil. ν_{max} (NaCl/film)/cm^{-1} 3340, 2918, 1613, 1451, 1377. δ_H (270 MHz): 1.95 (6H, s, CH_3), 2.36 (3H, s, CH_3), 4.33 (2H, s, CH_2), 6.97 (2H, s, H-3′, H-5′), 7.05–7.08 (1H, m, H–Ar), 7.36–7.42 (2H, complex signal, H-4 and H-5), 7.57 (1H, m, H-3); δ_C (100.6 MHz): 20.3 (CH_3), 20.9 (CH_3), 62.9 (CH_2), 127.2 (CH), 127.3 (CH), 127.6 (CH), 128.0 (2CH), 129.3 (CH), 135.7 (2C), 136.6 (C), 136.7 (C), 138.3 (C), 139.1 (C); *m*/*z* (EI): 226 (M^+), 208, 193 (100), 178, 165. Found $(M)^+$ 226.1361. $C_{16}H_{18}O$ requires (M) 226.1358.

From **80**. Column chromatography (petrol/ethyl acetate 7:3 to 1:1) furnished, in order of elution, benzyl alcohol (22%), starting sulfonate, **80** (21%) and *2-(8-quinolinyl)benzyl alcohol*, ***81*** (46%) as a colourless oil. ν_{max} (NaCl/film)/cm^{-1} 3364, 3062, 2930, 1672, 1598, 1578, 1496, 1448, 1382, 1316, 1262, 1202, 1100, 1014, 970, 912, 832, 796, 758. δ_H (400 MHz, DMSO-d_6): 3.95 (1H, s, OH), 4.30 (2H, m, CH_2), 7.21 (1H, dd, *J* 7.8 and 4.2, H-3), 7.32 (1H, dt, *J* 7.3 and 0.9, H-4), 7.42 (1H, dt, *J* 7.3 and 1.2, H-5), 7.48 (1H, dd, *J* 8.3 and 4.2, H-3′), 7.61

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(1H, dd, J 7.3 and 1.7, H-6), 7.63 (2H, m, H-6′, H-7′), 7.94 (1H, dd, *J* 7.8 and 1.6, H-5′), 8.33 (1H, dd, *J* 8.3 and 1.8, H-4′), 8.81 (1H, dd, *J* 4.2 and 1.6, H-2′); δ_C (100.6 MHz): 64.0 (CH_2), 121.3 (CH), 126.5 (CH), 127.9 (CH), 128.0 (CH), 128.3 (C), 128.5 (CH), 129.7 (CH), 130.8 (CH), 131.4 (CH), 137.1 (CH), 138.8 (C), 139.6 (C), 140.4 (C), 146.5 (C), 150.5 (CH); *m*/*z* (EI): 235 (M^+), 204 (100), 130 (12). Found $(M)^+$ 235.0990. $C_{16}H_{13}NO$ requires (M) 235.0997.

4.5. General procedure for the reaction of *N*-(2-iodobenzyl)-*N*-methylarylsulfonamides, 86–88 with Bu_3SnH

A solution of AIBN (0.10 g, 0.61 mmol) and Bu_3SnH (0.29 mL, 1.1 mmol) in benzene (9 mL) was introduced over 15 h, via uniform motor-driven syringe addition, to a rapidly stirred solution of the sulfonamide (0.89 mmol) in benzene (18 mL) at reflux. After a further 6 h, the reaction mixture was cooled to room temperature and CCl_4 and a few crystals of iodine were added. The reaction mixture was then evaporated in vacuo, the residue diluted with ether (20 mL) and stirred vigorously with satd aq KF (10 mL). After filtration, the organic layer was separated and the aqueous phase extracted with ether (3×50 mL). The combined organic layer was washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography.

From **86**. Column chromatography (CH_2Cl_2) furnished *6,7-dihydro-6-methylbenzo[4,5][1,2]thiazepine[6,7-h]quinoline-5,5-dioxide*, ***89*** (9%) as yellow prisms (mp >230 °C, petrol/CH_2Cl_2). Found C 63.9, H 4.6, N 8.7. $C_{17}H_{14}N_2O_2S\cdot 1/2H_2O$ requires C 63.9, H 4.7, N 8.8%. ν_{max} (NaCl/film)/cm^{-1} 2927, 1681, 1607, 1540, 1457, 1336, 1152, 1101, 987, 915, 843, 764, 729. δ_H (500 MHz): 2.75 (3H, s, NCH_3), 4.36 (2H, s, H-7), 7.40 (1H, dd, *J* 7.4 and 1.2, H-8 or H-11), 7.45 (1H, dt, *J* 7.4 and 1.2, H-9 or H-10), 7.53 (1H, dd, *J* 8.2 and 4.1, H-2), 7.54 (1H, dt, *J* 7.6 and 1.4, H-9 or H-10), 7.66 (1H, dd, *J* 7.7 and 0.6, H-8 or H-11), 7.70 (1H,d, *J* 8.6, H-12 or H-13), 8.03 (1H, d, *J* 8.6, H-12 or H-13), 8.20 (1H, dd, *J* 8.3 and 1.8, H-1), 9.23 (1H, dd, *J* 4.2 and 1.8, H-3); δ_C (125.7 MHz): 35.4 (NCH_3), 53.3 (CH_2), 122.0 (CH), 128.2 (C), 128.9 (CH), 129.2 (CH), 129.5 (CH), 130.3 (CH), 131.7 (CH), 131.9 (CH), 135.8 (CH), 136.7 (C), 138.5 (C), 139.6 (C), 145.9 (C), 151.6 (CH); *m*/*z* (CI, NH_3): 311 (M^{+1}, 100), 247 (46), 231 (19), 218 (13). Found $(M+H)^+$ 311.0854. $C_{17}H_{15}N_2O_2S$ requires (M+H) 311.0854.

From **87**. Column chromatography (petrol/ether 7:3 to 6:4) furnished, in order of elution, starting material, **87** (19%), *(3aRS, 10bRS)-3a,5,6,10b-tetrahydro-5-methylbenzo[d]thieno[3,2-f][1,2]thiazepine-4,4-dioxide*, ***91*** (23%) as beige crystals (mp 157–158 °C, petrol/CH_2Cl_2). Found C 53.7, H 4.7, N 5.2. $C_{12}H_{13}NO_2S_2$ requires C 53.9, H 4.9, N 5.2%. ν_{max} (NaCl/film)/cm^{-1} 3070, 2940, 1453, 1352, 1181, 1153, 1127, 1090, 1035, 973, 921, 863, 812, 759, 733, 706, 618. δ_H (500 MHz): 2.59 (3H, s, NCH_3), 3.92 (1H, d, *J* 15.7, H-6), 4.57 (1H, d, *J* 12.4, H-3a), 4.97 (1H, dt, *J* 12.4 and 2.6, H-10b), 4.99 (1H, d, *J* 15.7, H-6), 5.83 (1H, dd, *J* 6.2 and 2.2, H-2), 6.32 (1H,dd, *J* 6.2 and 3.0, H-1), 7.29 (1H, d, *J* 7.1, H-7 or H-10), 7.34 (1H, dt, *J* 7.4 and 2.7, H-8 or H-9), 7.34 (1H, dt, *J* 7.4 and 2.7, H-8 or H-9), 7.41 (2H, complex signal, H-7 or H-10, H-8 or H-9); δ_C (125.7 MHz): 34.9 (NCH_3), 53.6 (CH_2), 54.2 (CH), 68.6 (CH), 121.5 (CH), 125.8 (CH), 127.0 (CH), 127.9 (CH), 129.5 (CH), 131.4 (CH), 133.7 (C), 139.4 (C); *m*/*z* (EI): 267 (M^+, 2), 202 (100), 188 (55), 171 (77), 157 (15), 141 (11), 128 (28), 77 (12). Found $(M)^+$ 267.0388. $C_{12}H_{13}NO_2S_2$ requires (M) 267.0388, *5,6-dihydro-5-methylbenzo[d]thieno[3,2-f][1,2]thiazepine-4,4-dioxide*, ***90*** (10%) as beige crystals (mp 189–191 °C, petrol/CH_2Cl_2). Found C 54.2, H 3.9, N 5.25. $C_{12}H_{11}NO_2S_2$ requires C 54.3, H 4.2, N 5.3%. ν_{max} (NaCl/film)/cm^{-1} 1449, 1316, 1186, 1158, 1132, 1022, 987, 768, 740, 686, 647. δ_H (500 MHz): 2.69 (3H, s, NCH_3), 4.53 (2H, s, H-6), 7.34 (1H, d, *J* 5.3, H-2), 7.35 (1H,dd, *J* 7.4 and 1.2, H-7 or H-10), 7.38 (1H, dt, *J* 7.5 and 1.3, H-8 or H-9), 7.47 (1H, dt, *J* 7.5 and 1.7, H-8 or H-9), 7.61 (1H, d, *J* 5.2, H-1), 7.72 (1H, dd, *J* 7.9 and 0.8, H-7 or H-10); δ_C (125.7 MHz): 34.6 (NCH_3), 53.8 (CH_2), 128.4 (CH), 128.8 (CH), 129.2 (CH), 129.3 (CH), 129.9 (CH), 130.6 (CH), 133.0 (C), 134.0 (C), 137.8 (C), 138.0 (C); *m*/*z* (EI): 265 (M^+, 15), 200 (100), 185 (22), 171 (16), 115 (12). Found $(M)^+$ 265.0231. $C_{12}H_{11}NO_2S_2$ requires (M) 265.0231, and *(3aRS, 10bSR)-3a,5,6,10b-tetrahydro-5-methylbenzo[d]thieno[3,2-f][1,2]thiazepine-4,4-dioxide*, ***92*** (8%) as yellow crystals (mp 160–161 °C, petrol/CH_2Cl_2). ν_{max} (NaCl/film)/cm^{-1} 2933, 1474, 1387, 1327, 1197, 1128, 1006, 880, 807, 763, 674. δ_H (500 MHz): 3.09 (3H, s, NCH_3), 4.13 (1H, d, *J* 12.8, H-6), 4.45 (1H, d, *J* 12.8, H-6), 4.78 (1H, dt, *J* 9.4 and 2.4, H-10b), 5.02 (1H, d, *J* 9.4, H-3a), 5.59 (1H, dd, *J* 6.0 and 2.2, H-2), 6.38 (1H,dd, *J* 6.0 and 3.3, H-1), 7.28 (1H, m, H–Ar), 7.32 (3H, complex signal, H–Ar); δ_C (125.7 MHz): 39.1 (NCH_3), 55.3 (CH_2), 57.4 (CH), 71.0 (CH), 122.7 (CH), 125.3 (CH), 128.6 (CH), 128.8 (CH), 130.1 (CH), 130.8 (CH), 135.1 (C), 136.3 (C); *m*/*z* (EI): 267 (M^+, 1), 202 (100), 188 (43), 185 (100), 171 (8), 154 (34), 144 (21), 141 (21), 128 (34), 115 (39), 77 (19). Found $(M)^+$ 267.0388. $C_{12}H_{13}NO_2S_2$ requires (M) 267.0388.

From **88**. Column chromatography (petrol/ether 3:7 to 2:8) furnished, in order of elution, *3,6,7,11b-tetrahydro-6-methylbenzo[d]pyrido[4,3-f][1,2]thiazepine-5,5-dioxide*, ***94*** (24%) as yellow needles (mp 209–210 °C, petrol/CH_2Cl_2). Found C 58.5, H 5.1, N 10.5. $C_{13}H_{15}N_2O_2S\cdot 1/4H_2O$ requires C 58.5, H 5.5, N 10.5%. ν_{max} (NaCl/film)/cm^{-1} 3423, 2928, 1669, 1614, 1470, 1316, 1282, 1148, 1068, 1026, 973, 915, 842, 765, 722, 623. δ_H (500 MHz): 2.31 (3H, s, NCH_3), 3.90 (1H, d, *J* 15.6, H-7), 4.75 (1H, d, *J* 5.7, H-11b), 4.93 (1H, dt, *J* 5.8 and 1.6, H-1), 5.12 (1H, d, *J* 15.6, H-7), 5.81 (1H, br s, NH), 6.50 (1H, ddd, *J* 6.3, 4.8 and 0.7, H-2), 6.92 (1H,d, *J* 5.7, H-4), 7.23 (2H, complex signal, H–Ar), 7.38 (1H, dt, *J* 6.6 and 2.3, H-9 or H-10), 7.48 (1H, d, *J* 7.7, H-8 or H-11); δ_C (125.7 MHz): 34.0 (NCH_3), 35.0 (CH), 53.9 (CH_2), 100.6 (CH), 106.2 (C), 126.4 (CH), 126.5 (CH), 126.8 (CH), 128.7 (CH), 131.3 (CH), 132.6 (CH), 134.3 (C), 142.6 (C); *m*/*z* (EI): 261 (M^+, 7), 197 (84), 195 (77), 183 (83), 168 (43), 154 (23), 139 (13), 127 (15), 115 (11), 91 (31), 79 (100). Found $(M+H)^+$ 263.0864. $C_{13}H_{15}N_2O_2S$ requires (M+H) 263.0854, and *6,7-dihydro-6-methylbenzo[d]pyrido[2,3-f][1,2]thiazepine-5,5-dioxide*, ***93*** (55%) as beige crystals (mp 156–158 °C, petrol/CH_2Cl_2). Found C 59.9, H 4.4, N 10.5. $C_{13}H_{12}N_2O_2S$ requires C 60.0, H 4.65, N 10.8%. ν_{max} (NaCl/film)/cm^{-1} 3067, 1572, 1550, 1441, 1412, 1378, 1341, 1224, 1167, 1133, 1100, 1045, 983, 786, 758, 720. δ_H (500 MHz): 2.91 (3H, s, NCH_3), 3.90 (2H, s, H-7), 7.41 (1H, dd, *J* 7.4 and 0.7, H-8 or H-11), 7.48 (1H,dd, *J* 7.8 and 4.6, H-3), 7.51 (1H, dt, *J* 7.2 and 1.4, H-9 or H-10), 7.56 (1H, dt, *J* 7.6 and 1.3, H-9 or H-10), 7.85 (1H, d, *J* 7.7 and 1.3, H-8 or H-11), 8.28 (1H, dd, *J* 7.9 and 1.6, H-4), 8.93 (1H, dd, *J* 4.8 and 1.7, H-2); δ_C (125.7 MHz): 38.7 (NCH_3), 55.7 (CH_2), 122.6 (CH), 129.6 (CH), 129.7 (CH), 130.2 (CH), 130.4 (CH), 132.5 (C), 133.3 (C), 135.6 (CH), 139.9 (C), 153.2 (CH), 155.9 (C); *m*/*z* (EI): 260 (M^+, 5), 195 (100), 181 (16), 167 (16). Found $(M+H)^+$ 261.0698. $C_{13}H_{13}N_2O_2S$ requires (M+H) 261.0698.

4.6. General procedure for the reaction of sulfones, 95 and 99 with Bu_3SnH

To a stirred solution of the required sulfone (0.9 mmol) in benzene (18 mL) at reflux, was added over 11 h a solution of AIBN (110 mg, 0.67 mmol) and Bu_3SnH (0.32 mL, 1.17 mmol) in benzene (4.7 mL), via uniform motor-driven syringe addition. After a further 2 h, the reaction mixture was cooled to room temperature and CCl_4 (10 mL) and a few crystals of iodine were added and stirred continuously for 3 h. The solvent was removed in vacuo, the residue dissolved in ethyl acetate (15 mL) and stirred vigorously with satd aq KF (15 mL). After filtration, the organic layer was separated and washed with satd aq KF (25 mL) and water (20 mL), dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography.

From **95**. Column chromatography (petrol/CH_2Cl_2 1:1 to 0:1) furnished, in order of elution, *2-methyl-9,10-dihidrophenanthrene*, ***96*** (14%) as an oil. ν_{max} (NaCl/film)/cm^{-1} 2933, 1484, 764. δ_H (400 MHz): 2.39 (3H, s, CH_3), 2.87 (4H, m, $2CH_2$), 7.08 (1H, br s, H-1),

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7.13 (1H, d, *J* 7.9, H-3), 7.21–7.32 (3H, complex signal, H-6, H-7, H-8), 7.66 (1H, d, *J* 8.0, H-4 or H-5), 7.74 (1H, d, *J* 7.7, H-4 or H-5); δ_C (100.6 MHz): 21.2 (CH_3), 29.0 (CH_2), 29.1 (CH_2), 123.4 (CH), 123.6 (CH), 126.8 (CH), 126.9 (CH), 127.6 (CH), 128.0 (CH), 128.8 (CH), 131.7 (C), 134.5 (C), 137.0 (C), 137.1 (C), 137.3 (C); *m*/*z* (EI): 194 (M^+, 100), 179. Found $(M)^+$ 194.1104. $C_{15}H_{14}$ requires (M) 194.1096, *4-methylphenyl phenylethyl sulfone*, ***98*** (26%), as an oil. ν_{max} (NaCl/film)/cm^{-1} 1302, 1149, 1084. δ_H (400 MHz): 2.44 (3H, s, CH_3), 3.01 (2H, m, CH_2), 3.32 (2H, m, SCH_2), 7.09 (2H, m, H-2, H-6), 7.20–7.26 (3H, complex signal, H-3, H-4, H-5), 7.34 (2H, m, H-3′, H-5′), 7.79 (2H, m, H-2′ or H-6′); δ_C (100.6 MHz): 21.6 (CH_3), 28.8 (CH_2), 57.6 (CH_2), 126.8 (CH), 128.1 (2CH), 128.2 (2CH), 128.7 (2CH), 129.9 (2CH), 135.9 (C), 137.5 (C), 144.8 (C); *m*/*z* (EI): 260 (M^+), 180 (100), 91 (100). Found $(M)^+$ 260.0869. $C_{15}H_{16}O_2S$ requires (M) 260.0871 and *2-methyl-6,7-dihydrodibenzo[b,d]thiepin-5,5-dioxide*, ***97*** (22%) as white prisms (mp 134–135 °C, from CH_2Cl_2/petrol). ν_{max} (NaCl/film)/cm^{-1} 1303, 1152, 1125. δ_H (400 MHz): 2.51 (3H, s, CH_3), 2.98 (2H, br s, CH_2), 3.77 (2H, m, SCH_2), 7.32–7.44 (6H, complex signal, H–Ar), 8.02 (1H, d, *J* 7.8, H-4); δ_C (100.6 MHz): 21.6 (CH_3), 29.6 (CH_2), 63.6 (CH_2), 128.0 (CH), 128.4 (CH), 128.5 (CH), 128.8 (CH), 128.9 (2CH), 131.5 (CH), 134.2 (C), 135.3 (C), 139.5 (C), 140.3 (C), 145.1 (C); *m*/*z* (EI): 258 (M^+), 193 (100). Found $(M)^+$ 258.0709. $C_{15}H_{14}O_2S$ requires (M) 258.0714.

From **99**. Column chromatography (petrol/CH_2Cl_2 1:1 to 0:1) furnished, in order of elution, starting sulfone, **99** (12%) and *(3aRS, 10bRS)-3a,10b-dihydrobenzo[d]thieno[2,3-b]thiepane-4,4-dioxide*, ***100*** (31%) as yellow needles (mp 196–199 °C, from CH_2Cl_2/petrol). Found C 57.25, H 4.7. $C_{12}H_{12}O_2S_2$ requires C 57.1, H 4.8%. ν_{max} (NaCl/film)/cm^{-1} 2925, 1486, 1451, 1326, 1293, 1183, 1144, 1125, 912, 833, 754,725, 696. δ_H (500 MHz): 3.02 (1H, ddd, *J* 14.2, 12.5 and 1.2, H-5), 3.08 (1H, ddd, *J* 15.9, 7.6 and 1.2, H-6), 3.42 (1H, dd, *J* 15.9 and 12.7, H-6), 3.49 (1H, ddd, *J* 13.6, 7.4 and 1.1, H-5), 4.64 (1H, d, *J* 11.5, H-3a), 5.02 (1H, dt, *J* 11.5 and 2.6, H-10b), 5.80 (1H, dd, *J* 6.0 and 2.3, H-2), 6.29 (1H, dd, *J* 6.0 and 2.9, H-1), 7.31 (4H, complex signal, H–Ar); δ_C (125.7 MHz): 29.2 (CH_2), 53.9 (CH), 54.6 (CH_2), 74.1 (CH), 122.0 (CH), 125.3 (CH), 126.4 (CH), 128.4 (2CH), 130.7 (CH), 137.4 (C), 139.9 (C); *m*/*z* (EI): 252 (M^+), 187 (100), 173 (69), 155 (56), 153 (59), 142 (36), 141 (36), 128 (66), 115 (60), 77 (30)

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.07.048.

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39. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1407379 (compound **43**), 1407380 (compound **92**) and 1407381 (compound **91**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk)
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