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Substituted *N*-aryl alk-1-enesulfinamides: preparation, properties and conversion into the corresponding indole compounds [1]

Jean-Bernard Baudin, Marie-Gabrielle Comménil, Sylvestre A Julia, Robert Lorne, Laurent Mauclaire

Laboratoire de chimie, École Normale Supérieure, 24, rue Lhomond, 75231 Paris cedex 05, France

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Summary — Reaction of vinylic organometallic derivatives with *N*-sulfinyl arenamines **2** affords the title sulfinamides **3**. On heating their solutions in selected solvents to 80–124 °C, these sulfinamides are converted into the corresponding indoles **6**, probably via a [3.3]-sigmatropic rearrangement to intermediates VIII which undergo an intramolecular carbophilic reaction of the nitrogen atom with the neighboring sulfine group, followed by elimination of HSOH. The triethyloxonium tetrafluoroborate- or boron trifluoride etherate catalyzed conversion **3** → **6** can be carried out at a much lower temperature.

***N*-sulfinyl-arenamine / vinylic organometallic derivative / substituted *N*-aryl alk-1-enesulfinamide / [3.3]-sigmatropic rearrangement / substituted 1*H*-indole**

Résumé — ***N*-Aryl alc-1-ènesulfinamides: préparation, propriétés et transformations en composés indoliques correspondants [1].** *Les sulfinamides **3** du titre ont été préparés par action de réactifs organométalliques vinyliques sur les N-sulfinylamines aromatiques **2**. Par chauffage de leurs solutions dans certains solvants entre 80 et 124 °C, ces sulfinamides sont transformés en indoles correspondants **6**, probablement par une transposition sigmatropique [3.3] en intermédiaires VIII qui subissent une réaction carbophile intramoléculaire de l'atome d'azote avec la fonction sulfine suivie d'une élimination de HSOH. Les transformations **3** → **6** catalysées par le tétrafluoroborate de triéthyloxonium ou l'éthérate de trifluorure de bore peuvent être effectuées à basse température.*

***N*-sulfinylamine aromatique / dérivé organométallique vinylique / *N*-aryl alc-1-ènesulfinamide substitué / transposition sigmatropique [3.3] / indole substitué**

Introduction

Numerous important compounds in biochemistry and pharmacology are characterized by the presence of an indole ring, which explains the considerable quantity of work concerning the preparation of various substituted indoles. Two reviews have recently exposed the numerous procedures of indolization [2, 3] and we will limit our discussion to methods which bring about [3.3]-sigmatropic rearrangements of the hetero-Cope type [4] from substrates I where X is a heteroatom N, O or S (fig 1).

The case where R^1 = H and X = NH corresponds to Fischer's ancient reaction which has been extensively

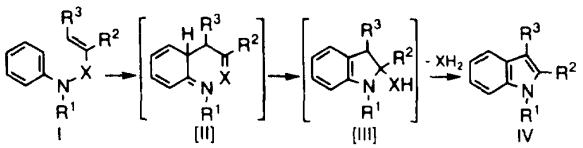

Fig 1

studied; the limits of application were determined [3] and in particular the simple indole cannot be prepared from phenylhydrazine and acetaldehyde. In the case of two different substituents R^2 and R^3, the selectivity of this synthesis was recently improved using diethylaluminum 2,2,6,6-tetramethylpiperidide under mild conditions. However this procedure is limited to compounds carrying an R^1 substituent on nitrogen [5].

The substrates I with X = O, necessary for the 1-aza-1′-oxa Cope rearrangement, were prepared from phenylhydroxylamine derivatives and the majority of the known examples of this procedure have been summarized in a review [4]. An easy synthesis of functionalized indoles was recently achieved from arylhydroxylamines and α-acetylenic carbonyl compounds [6].

The *N*-aryl ethenesulfenamides I, X = S, R^1 = R^2 = R^3 = H, were studied in our laboratory [7]. Upon heating in a solvent between 85 and 135 °C, they did not give the expected 1-aza-1′-thia [3.3]-sigmatropic rearrangement. The two *N*-(1-naphthyl)ethenesulfenamides (fig 2) however were converted into the corresponding 1*H*-benz[*g*]indoles, probably due to the presence of the

naphthalene ring system which allows easier provisional dearomatization into the γ-iminothioaldehyde.

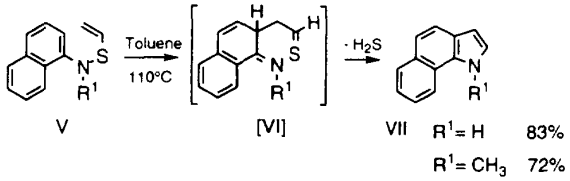

Fig 2

This led us to investigate the properties of *N*-aryl alk-1-enesulfinamides I, X = SO, where the polar sulfinyl group and the weak N–S bond should facilitate the [3.3]-sigmatropic rearrangement and thus the formation of the corresponding indoles (fig 3). We now present the details corresponding to a preliminary communication published in 1986 [8] and additional studies with regard to the scope of this new synthesis of indole compounds.

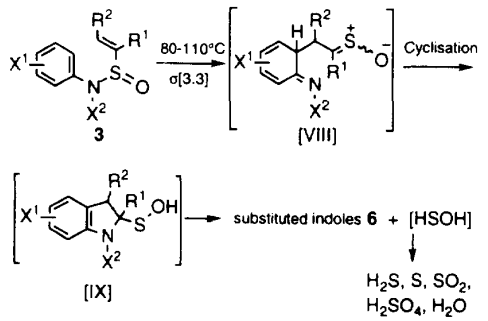

Fig 3

Preparation of the *N*-aryl alk-1-enesulfinamides 3

The *N*-sulfinylarenamines **2** are easily obtained from arenamines **1** and thionyl chloride [9]. Many additions of various organometallic reagents to *N*-sulfinylarenamines are known: saturated aliphatic and aromatic [10], perfluoroalkyl [11], allyl or benzyl [12] and acetylenic [13] Grignard reagents; acetylenic [14], aromatic [15] or heteroaromatic [16] lithioderivatives and allenylcopper(I) species [17]. We prepared the various *N*-aryl alk-1-enesulfinamides **3a–s** by reaction of *N*-sulfinylarenamines **2a–s** with vinylic Grignard derivatives [18] or diisobutylalanes [19] (fig 4, table I). These reactions are facile and give very good yields. In general the sulfinamides **3aa–sc** are reasonably stable and can be stored at −18 °C for a few weeks. They are well characterized by their ^{1}H and ^{13}C NMR spectra. For the following reactions, it is preferable to use the freshly prepared samples of sulfinamides **3**.

The above sulfinamides **3** have an NH group which can be deprotonated and subsequent reaction with appropriate electrophiles leads to the introduction of

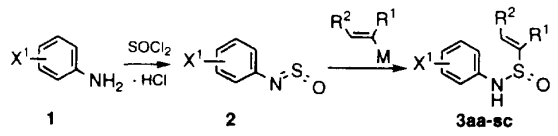

Fig 4

a new X^2 substituent on the nitrogen (fig 5). The base:solvent:electrophile combinations which gave us the best results are shown in table II. Sodium hydride in 1,2-dimethoxyethane (DME) followed by alkyl halide [20] was an efficient method (entries 40, 41, 43–46). During our work, some *N*-alkylation procedures for *N*-monosubstituted arenesulfinamides were published, using *n*-butyllithium [21] or potassium carbonate and allyl bromide in acetone [22].

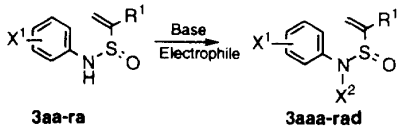

Fig 5

With regard to the *N*-trialkylsilylation of sulfinamides **3** (entries 47, 48, 50 and 51), we used a mixture of chlorotrimethylsilane and hexamethyldisilazane [23]. The crude compounds (**3aab, cac, hab, rac**) were found to be very unstable; their ^{1}H NMR spectra were consistent with the proposed structures and with the spectrum of *N*-trimethylsilyl ethenesulfinamide **5**. By slightly modifying the published conditions [24], reaction of methyl chlorosulfite with lithium bis-(trimethylsilyl)amide gave in situ the *N*-sulfinyl *N*-trimethylsilylamine **4** and then addition of vinylmagnesium bromide easily afforded the compound **5** which was well characterized by spectroscopic data (fig 6).

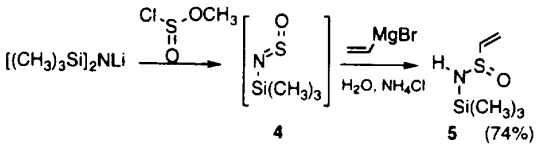

Fig 6

Thermal conversion of *N*-aryl alk-1-enesulfinamides into the corresponding indole compounds

The following procedure is representative: an anhydrous 0.2 M solution of sulfinamide **3** in toluene was slowly distilled with concomitant slow addition of fresh toluene, over the time necessary for the disappearance of the starting material (TLC), generally 1 h but occasionally shorter (fig 7, table III). The azeotropic distillate contained a little acidic water as indicated by pH paper and the condenser contained a small quan-

Table I. Preparation of *N*-aryl alk-1-enesulfinamides **3aa–sc**.

Entry	*Substrates*	X^1	*Organometallic reagents* R^1	R^2	*M*	*Products*	*Yields* (%)
1	**2a**	H	H	H	MgBr	**3aa**	90
2	**2a**	H	CH_3	H	MgBr	**3ab**	95
3	**2a**	H	-(CH=CH)$_2$-		MgBr	**3ac**	96
4	**2a**	H	-(CH$_2$)$_4$-		MgBr	**3ad**	92
5	**2a**	H	H	nC_4H_9	Al(iBu)$_2$	**3ae**	82
6	**2a**	H	C_2H_5	C_2H_5	Al(iBu)2	**3af**	72
7	**2a**	H	C_6H_5	H	MgBr	**3ag**	90
8	**2b**	2-CH_3	H	H	MgBr	**3ba**	93
9	**2c**	4-CH_3	H	H	MgBr	**3ca**	96
10	**2c**	4-CH_3	CH_3	H	MgBr	**3cb**	96
11	**2c**	4-CH_3	H	nC_4H_9	Al(iBu)$_2$	**3cc**	76
12	**2c**	4-CH_3	C_2H_5	C_2H_5	Al(iBu)$_2$	**3cd**	65
13	**2c**	4-CH_3	C_6H_5	H	MgBr	**3ce**	88
14	**2d**	2,3-(CH=CH)$_2$-	H	H	MgBr	**3da**	97
15	**2e**	4-F	H	H	MgBr	**3ea**	96
16	**2f**	2-Cl	H	H	MgBr	**3fa**	97
17	**2g**	3-Cl	H	H	MgBr	**3ga**	96
18	**2h**	4-Cl	H	H	MgBr	**3ha**	96
19	**2h**	4-Cl	CH_3	H	MgBr	**3hb**	78
20	**2h**	4-Cl	H	nC_4H_9	Al(iBu)$_2$	**3hc**	85
21	**2h**	4-Cl	C_2H_5	C_2H_5	Al(iBu)$_2$	**3hd**	64
22	**2i**	2,3-Cl$_2$	H	H	MgBr	**3ia**	95
23	**2j**	2,4-Cl$_2$	H	H	MgBr	**3ja**	92
24	**2k**	2,5-Cl$_2$	H	H	MgBr	**3ka**	81
25	**2l**	3,5-Cl$_2$	H	H	MgBr	**3la**	96
26	**2m**	3-Br	H	H	MgBr	**3ma**	92
27	**2n**	4-Br	H	H	MgBr	**3na**	95
28	**2o**	4-I	H	H	MgBr	**3oa**	92
29	**2p**	2-MeO	H	H	MgBr	**3pa**	94
30	**2q**	3-MeO	H	H	MgBr	**3qa**	95
31	**2r**	4-MeO	H	H	MgBr	**3ra**	94
32	**2r**	4-MeO	CH_3	H	MgBr	**3rb**	85
33	**2r**	4-MeO	H	nC_4H_9	Al(iBu)$_2$	**3rc**	56
34	**2r**	4-MeO	C_2H_5	C_2H_5	Al(iBu)$_2$	**3rd**	62
35	**2r**	4-MeO	C_6H_5	H	MgBr	**3re**	93
36	**2r**	4-MeO	-(CH=CH-C(Me)=CH)-		MgBr	**3rf**	93
37	**2s**	2-[MeOC(O)]	H	H	MgBr	**3sa**	94*
38	**2s**	2-[MeOC(O)]	CH_3	H	MgBr	**3sb**	94*
39	**2s**	2-[MeOC(O)]	H	nC_4H_9	Al(iBu)$_2$	**3sc**	70*

* The sulfinamides **3sa–3sc** are very unstable; after standing at room temperature for several hours, they decomposed giving methyl anthranilate.
Note: the first letter of each sulfinamide corresponds to the specific substituent(s) of the aromatic ring and the second corresponds to the nature of the side chain linked to the sulfur.

tity of an unidentified solid compound (mp ≈ 210 °C whereas sulfur has mp = 112 °C). After cooling to room temperature, the black-brown heterogeneous solution was evaporated under reduced pressure. The mixture of crude products was then separated by flash chromatography on silica gel, affording the indole compounds **6** and variable quantities of polar arenamines **1**.

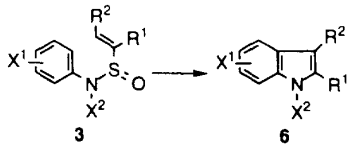

Fig 7

Before commenting on the results of table III, one should consider our hypothesis on the intermediates of the thermal conversion **3** → **6**: along these lines there would be firstly a [3.3]-sigmatropic rearrangement of the unsaturated sulfinamides **3** into iminosulfines [VIII], then cyclization [VIII → IX] and elimination of the unstable species HSOH to give finally the indole compounds **6** together with water, sulfur dioxide and sulfuric acid (fig 3).

The formation and decomposition [25] of the species HSOH should explain not only the acidity of the azeotropic distillate but also the formation of arenamines **1** in variable quantities, owing to the known easy acidic hydrolysis of sulfinamides. We often isolated these arenamines **1**, but not in all cases. To prevent this secondary reaction in acidic medium, we tried heating the sulfinamide **3aa** in benzene with 1 equiv of triethylamine or dry sodium bicarbonate at reflux for 90 min. We were a little surprised to find unchanged starting material in these cases; similarly the sulfinamide **3caa** was stable after heating with triethylamine in benzene

Table II. *N*-Alkylation of *N*-aryl alk-1-enesulfinamides.

Entry	*Substrates*	X^1	R^1	*Conditions*	X^2	*Products*	*Yields (%)*
40	**3aa**	H	H	NaH (1 equiv), DME 45–50 °C, 2 h; CH_3I (1.2 equiv), 0 °C, 1 h	CH_3	**3aaa**	93
41	**3ca**	4-CH_3	H	idem	CH_3	**3caa**	80
42	**3ca**	4-CH_3	H	NaH, DMSO, 45–50 °C, 2 h; $ClCH_2Ph$ (1 equiv)	CH_2-Ph	**3cab**	65
43	**3ha**	4-Cl	H	NaH (1 equiv), DME, 45–50 °C, 2 h; CH_3I (1.2 equiv), 0 °C, 1 h	CH_3	**3haa**	84
44	**3ra**	4-CH_3O	H	idem	CH_3	**3raa**	82
45	**3ra**	4-CH_3O	H	NaH (1 equiv), DME, 45–50 °C, 2 h; C_2H_5I (1.2 equiv), 0 °C, 1 h	C_2H_5	**3rab**	66
46	**3re**	4-CH_3O	C_6H_5	NaH (1 equiv), DME, 45–50 °C, 2 h; CH_3I (1.2 equiv), 0 °C, 1 h	CH_3	**3rea**	42
47	**3aa**	H	H	$(Me_3Si)_2NH$ (1.1 equiv), THF; Me_3SiCl (1.1 equiv), 18 °C, 15 h	$(CH_3)_3Si$	**3aab**	55*
48	**3ca**	4-CH_3	H	idem	$(CH_3)_3Si$	**3cac**	82*
49	**3ca**	4-CH_3	H	NaH (1 equiv), THF/Et_2O (50:50); 45–50 °C, 2 h; $Me_3C(Me_2)SiCl$ (1.2 equiv), 18 °C, 20 h	$Me_3C(Me_2)Si$	**3cad**	76
50	**3ha**	4-Cl	H	$(Me_3Si)_2NH$ (1.1 equiv), THF; Me_3SiCl (1.1 equiv), 18 °C, 15 h	$(CH_3)_3Si$	**3hab**	64*
51	**3ra**	4-CH_3O	H	idem during 1 h	$(CH_3)_3Si$	**3rac**	90*
52	**3ra**	4-CH_3O	H	idem entry 49	$Me_3C(Me_2)Si$	**3rad**	76

* Estimated yields from ^1H NMR spectra of crude products.

and the *N*-sodio derivative of sulfinamide **3ca** in DME after reflux for 3 h.

From table III, we note several interesting observations:

The presence of one or two halogen atoms on the aromatic ring leads to a reduction or even a canceling out of the yields in indolic compounds.

The results of entries 104–106 show that the presence of an electron-withdrawing group completely prevents the conversion, perhaps due to a hydrogen bond between the carbonyl and the secondary amine which would ease a radical split of the N–S bond [26a]. This split would also explain the result of entry 103 (fig 8).

The starred note for entry 72 shows the conversion of *N*-(1-naphthyl)ethenesulfinamide **3da** which was carried out at room temperature. This remarkably easy conversion shows a certain similarity with those of *N*-(1-naphthyl)ethenesulfinamides shown in figure 2; the presence of the naphthalene ring system would ease the provisional dearomatization occurring during formation of iminosulfine of the type VIII.

Many of the experiments in toluene or benzene gave low yields, and we therefore tried heating some sulfinamides in other solvents. Compound **3aa** remained stable after heating in absolute ethanol for 90 min, but entry 65 shows that heating sulfinamide **3ca** in 2-methoxyethanol gave 5-methylindole with a yield comparable with that from entry 63 carried out in toluene. It seemed likely that the presence of one or two methoxy groups in the solvent formula could buffer the acidity of the reaction mixture and improve the yields in indole compounds. Entries 62, 64, 77, 89, 93 and 95 report the experiments carried out in refluxing 1,2-dimethoxyethane, but the yields were generally lower than those obtained in toluene, except in the case of entry 93 which gave 6-methoxyindole **6qa** (53%) and

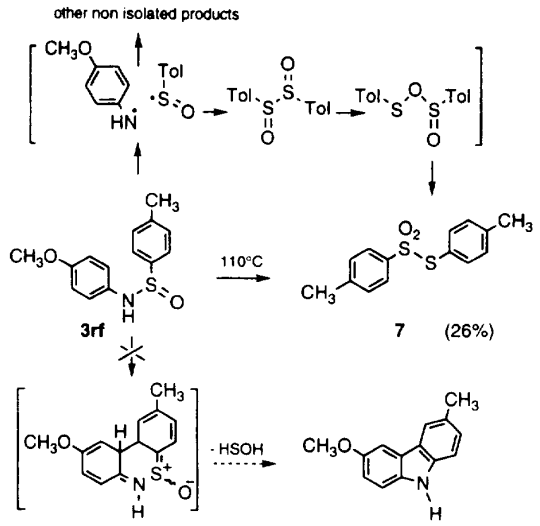

Fig 8

4-methoxyindole **6'qa** (11%). The use of THF (entry 91) or dioxane (entry 92) gave slightly better results than obtained in toluene.

The influence of substituents R^1 and R^2 of the aliphatic chain of sulfinamides **3** is noteworthy. When $R^1 = CH_3$ and $R^2 = H$, the yields were lowered (entries 56, 68 and 79) except for entry 98. This is the same for sulfinamides with $R^1 = C_6H_5$ and $R^2 = H$ (entries 60, 71) except entry 101. When $R^1 = H$ and $R^2 = n\text{-}C_4H_9$, the yield is clearly lowered (entries 59, 80, 99) except for entry 69. When R^1, $R^2 = C_2H_5$, C_2H_5 or $-(CH_2)_4-$, no indole formation was observed (entries 58, 70 and 100).

Table III. Products of thermolysis of *N*-aryl alk-1-enesulfinamides **3**.

Entry	*Substrates*	*Conditions*	*Indoles*	X^1	X^2	R^1	R^2	*Yield (%)*
53	**3aa**	A	**6aa**	H	H	H	H	75
54	**3aa**	B	**6aa**					74
55	**3aaa**	A	**6aaa**	H	CH_3	H	H	41
56	**3ab**	A	**6ab**	H	H	CH_3	H	27
57	**3ac**	A		H	H	-(CH=CH)$_2$-		0
58	**3ad**	A		H	H	-(CH$_2$)$_4$-		0
59	**3ae**	A	**6ae**	H	H	H	nC_4H_9	19
60	**3ag**	A	**6ag**	H	H	C_6H_5	H	41
61	**3ba**	A	**6ba**	7-CH_3	H	H	H	55
62	**3ba**	E (20 min)	**6ba**					30
63	**3ca**	A	**6ca**	5-CH_3	H	H	H	51
64	**3ca**	E (30 min)	**6ca**					46
65	**3ca**	F (30 min)	**6ca**					43
66	**3caa**	B	**6caa**	5-CH_3	CH_3	H	H	83
67	**3cab**	B	**6cab**	5-CH_3	CH_2-Ph	H	H	65
68	**3cb**	A	**6cb**	5-CH_3	H	CH_3	H	20
69	**3cc**	A	**6cc**	5-CH_3	H	H	nC_4H_9	66
70	**3cd**	A (20 min)		5-CH_3	H	C_2H_5	C_2H_5	0
71	**3ce**	A	**6ce**	5-CH_3	H	C_6H_5	H	37
72	**3da**	A	**6da**	2,3-(CH=CH)$_2$-	H	H	H	49*
73	**3ea**	A	**6ea**	5-F	H	H	H	43
74	**3fa**	A	**6fa**	7-Cl	H	H	H	30
75	**3ga**	A	**6ga**	6-Cl	H	H	H	18
			6′ga	4-Cl	H	H	H	18
76	**3ha**	A	**6ha**	5-Cl	H	H	H	48
77	**3ha**	E (90 min)	**6ha**					28
78	**3haa**	B_1 (30 min)	**6haa**	5-Cl	CH_3	H	H	28
79	**3hb**	A (10 min)	**6hb**	5-Cl	H	CH_3	H	25
80	**3hc**	A	**6hc**	5-Cl	H	H	nC_4H_9	15
81	**3ia**	A	**6ia**	6,7-(Cl)$_2$	H	H	H	14
82	**3ja**	A		5,7-(Cl)$_2$	H	H	H	0
83	**3ka**	A		4,7-(Cl)$_2$	H	H	H	0
84	**3la**	A	**6la**	4,6-(Cl)$_2$	H	H	H	30
85	**3ma**	A	**6ma**	6-Br	H	H	H	40**
			6′ma	4-Br	H	H	H	
86	**3na**	A	**6na**	5-Br	H	H	H	49
87	**3oa**	A	**6oa**	5-I	H	H	H	40
88	**3pa**	A	**6pa**	7-CH_3O	H	H	H	45
89	**3pa**	E (20 min)	**6pa**					34
90	**3qa**	A	**6qa**	6-CH_3O	H	H	H	25
			6′qa	4-CH_3O	H	H	H	5
91	**3qa**	C (3 h)	**6qa**					40
			6′qa					7
92	**3qa**	D (15 min)	**6qa**					44
			6′qa					12
93	**3qa**	E (15 min)	**6qa**					53
		azéo. distil.	**6′qa**					11
94	**3ra**	A	**6ra**	5-CH_3O	H	H	H	52
95	**3ra**	E (1 h)	**6ra**					42
96	**3raa**	B_1 (30 min)	**6raa**	5-CH_3O	CH_3	H	H	55
97	**3rac**	A_1 (1 h)	**6ra**	5-CH_3O	H	H	H	37
98	**3rb**	A (10 min)	**6rb**	5-CH_3O	H	CH_3	H	62
99	**3rc**	A (20 min)	**6rc**	5-CH_3O	H	H	nC_4H_9	10
100	**3rd**	A (15 min)		5-CH_3O	H	C_2H_5	C_2H_5	0
101	**3re**	A	**6re**	5-CH_3O	H	C_6H_5	H	62
102	**3rea**	A (45 min)	**6rea**	5-CH_3O	CH_3	C_6H_5	H	41
103	**3rf**	A (20 min)		5-CH_3O	H	-(CH=CH-C(Me)=CH)-		***
104	**3sa**	G		7-[MeOC(O)]	H	H	H	0
105	**3sb**	G		7-[MeOC(O)]	H	CH_3	H	0
106	**3sc**	G		7-[MeOC(O)]	H	H	nC_4H_9	0

A: Slow distillation of an anhydrous solution of sulfinamide in toluene with concomitant slow addition of fresh toluene over an hour. A_1: Refluxing in toluene. B: Same operation as A but in anhydrous benzene for 90 min. B_1: Refluxing in benzene. C: In refluxing tetrahydrofuran. D: In refluxing dioxane. E: In refluxing 1,2-dimethoxyethane (bp = 85 °C). F: In refluxing 2-methoxyethanol (bp = 124 °C). G: At room temperature in toluene, sulfinamides **3sa–sc** were converted into methyl anthranilate (see table I). * On standing under vacuum (0.01 mm Hg) at room temperature, the crude product changed appearance and its ^{1}H NMR spectrum was found to be that of 1*H*-benzo[*g*]indole **6da** (92%). ** Inseparable mixture. *** Flash chromatography of the crude product gave *S*-(4-methylphenyl)-4-methylbenzenethiosulfonate **7** (26%) and 4-methoxybenzenamine.

Table IV. Estimation of the rates of thermal conversion of some sulfinamides **3** in boiling benzene: ratios of sulfinamides **3**:indoles **6**:amines **1**.

Time (min)	*Entry 107 (0.05 M)* **3aa:6aa:1a***	*Entry 108 (0.05 M)* **3ca:6ca:1c**	*Entry 111 (0.025 M)* **3ca:6ca:1c**	*Entry 109 (0.05 M)* **3ha:6ha:1h**	*Entry 110 (0.05 M)* **3ra:6ra:1r**
2	96:4:0	80:15:5		100:0:0	84:14:2
4	79:21	53:37:10		100:0:0	57:32:11
5			54:41:5		
6	67:33	39:50:11		100:0:0	40:45:15
8		27:54:19		100:0:0	29:52:19
10	45:55	23:58:19	26:65:9	100:0:0	18:60:22
12		16:59:25		100:0:0	10:61:28
15	27:73		17:68:15		
18					trace:61:39
20	13:87	4:67:29	7:70:23	36:32:32	
25			4:73:23		
30		4:67:29			
35			0:72:28		
40		3:68:29			

* The ratios of products are evaluated only for the sulfinamide and indole.

Also it seemed likely that the substituents on the aromatic ring of sulfinamides **3** have an influence on the ease of the [3.3]-sigmatropic process **3** → [VIII]. Thus, we judged it useful to compare the rates of this conversion in a series of four sulfinamides **3aa**, **3ca**, **3ha** and **3ra** carrying in the *para* position some representative substituents: H, CH_3, Cl and CH_3O (fig 9). In fact, the amounts of indoles **6** should correspond to those of the intermediate iminosulfines [VIII] and the secondary products formed are simply the arenamines **1** due to the acid-catalyzed hydrolysis of the sulfinamides. The procedure is the following: a 0.05 M solution of sulfinamide in anhydrous benzene was heated with slow distillation of the solvent. After 2 min we stopped heating and took a small amount of the residual solution which was quenched with aqueous sodium bicarbonate and worked up. After continuation of heating with distillation for a further 2 min, we proceeded in the same manner to take a sample and repeated the process. Analysis of the ^1H NMR spectra of the crude samples allowed us to estimate the ratios of sulfinamides:indoles:arenamines (fig 9, table IV).

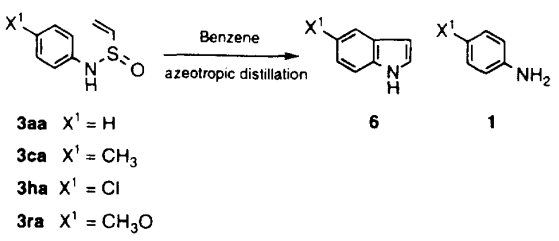

Fig 9

The results of table IV clearly show that the *N*-aryl sulfinamides **3ca** and **3ra** bearing a *para* electron-donating group (CH_3 and CH_3O respectively) are transformed faster than the non-substituted sulfinamide **3aa**. On the other hand, the presence of a *para*-chloro substituent clearly slowed down the reaction rate due to its electron-withdrawing effect, which is in agreement with the results of entries 104–106 which concern the *N*-aryl sulfinamides bearing an *ortho*-methoxycarbonyl group. Concerning the influence of the solvent and the concentration, the following observations were made. An attempt at heating a 0.05 M solution of sulfinamide **3ca** in THF with distillation showed that after 12 min this sulfinamide remained intact. The heating of a 0.025 M solution of sulfinamide **3ca** in benzene did not produce a notable change to the rate of transformation (entry 111), but for the compound **3ha** a reduction in rate was observed: after 35 min of heating, only the sulfinamide **3ha** was present.

It was important to verify that the conversion into indole compounds was truly intramolecular and did not occur via a possible mechanism involving splitting the N–S bond followed by combination of the nitrogeneous and sulfurous fragments [26b]. This led us to investigate the products of heating equimolar mixtures of two different *N*-aryl alk-1-enesulfinamides in toluene. Figures 10, 11 and table V show the results obtained.

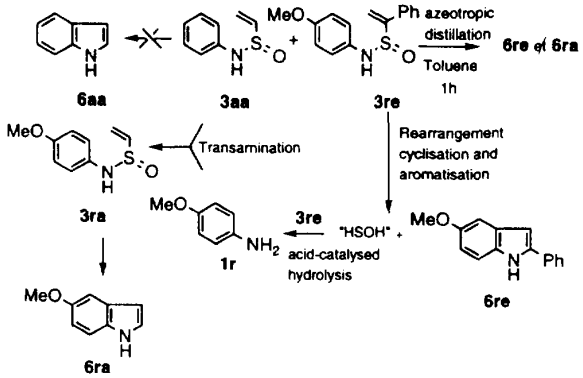

Fig 10

The experiment 112 (fig 10) gave the expected formation of 5-methoxy-2-phenylindole **6re** and slightly surprisingly 5-methoxyindole **6ra**; the expected indole

Table V. Crossing and transamination experiments.

Entry	*Substrates*	*Conditions*	*Products (yields %) [ratios]*
112	**3aa** + **3re**	A (1 h)	**6ra** + **6re** (54) [50:50]
113	**3aa** + **3ce**	A (1 h)	**6aa** + **6ag** + **6ca** + **6ce** (52) [36:9:19:36]
114	**1r** + **3aa**	A (1 h)	**1r** (34); **6ra** (53)
115	**1r** + **3aa**	CH_2Cl_2 18 °C 4 h	**1r** (73); **3aa** (87); **3ra** (10)
116	**1r** + **8a**	Toluene 60 °C 2 h	**1r** (43); **1c** (11); **8a** (31); **8b** (47)
117	**3aaa** + **3rea**	A (1 h)	**6raa** + **6rea** (26) [71:29]

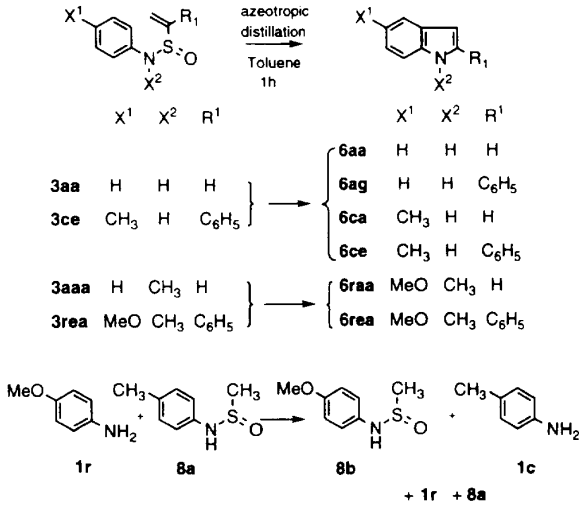

Fig 11

6aa was not formed. Taking into account the kinetics shown above (table IV), we are led to believe that the methoxysulfinamide **3re** reacts faster than **3aa** and gives **6re**; the acidity thus formed may catalyze the hydrolysis of the remaining sulfinamide **3re** into 4-methoxybenzenamine **1r** which, by transamination of the sulfinamide **3aa**, yields in situ a new sulfinamide **3ra** responsible for the formation of **6ra**.

We have verified that the above evoked transamination is possible. The result of entry 114 shows that heating 4-methoxybenzenamine **1r** and sulfinamide **3aa** together produced only the 5-methoxyindole **6ra** (53% isolated). The same reaction at room temperature for 4 h produced methoxysulfinamide **3ra** (10%) (entry 115). Transamination of *N*-(4-methylphenyl)-methanesulfinamide **8a** by 4-methoxybenzenamine for 2 h at 60 °C gave sulfinamide **8b** (47%) (entry 116, fig 11). The experiment 113 was carried out with the sulfinamides **3aa** and **3ce**, the latter bearing a *para*-methyl group which should slightly accelerate the [3.3]-sigmatropic rearrangement (see table IV). Indeed we obtained a mixture of the four indole compounds with the two 5-methyl compounds as the major components **6ce** + **6ca**:**6aa** + **6ag** = 55:45.

Concerning the above transamination reaction, it is also pertinent to remark upon an observation from the Cram group [27]: a pair of (+)-*N*-phenyl-4-methylbenzenesulfinamide and (+)-*N*-(1-naphthyl)-naphthalene-1-sulfinamide solution in benzene gave, after standing at room temperature for 30 h, the four crossing products.

The above transamination reactions called into question the existence of hydrogen bonds [28] between two *N*-monosubstituted sulfinamides. Thus the pair of *N*-methyl-sulfinamides **3aaa** and **3rea** were examined: after heating, they led only to the pair of 5-methoxy-indole compounds (entry 117). Here again, the influence of the methoxy group is analogous to that observed for experiment 112. Thus this transamination reaction makes the analysis of the conversion of **3** into **6** still more intricate and does not allow us to conclude that it is intramolecular in nature.

Now upon examining the hypothetical intermediates shown in figure 3, we notice particularly that the iminosulfine [VIII] and its aromatized isomer, the arenaminosulfine, should give rise to a carbophilic reaction of the nitrogen function with the neighboring sulfine: [VIII] → [IX] to yield the final indole compounds. Recent reviews [25] on the chemistry of sulfines pointed out that the reactivity of simple sulfines with amines was practically unknown; however our examination of the literature data, which was as thorough as possible, gave the following information. Some thiophilic additions were established after reaction of lithium diisopropyl amide with 9-thiofluorenone- or substituted thiobenzophenone-*S*-oxides [29, 30]. Some carbophilic additions of amines to sulfines should also be mentioned:

- two former publications [31, 32] reported the transformation of two arylmethanethial-*S*-oxides by an acid solution of 2,4-dinitrophenylhydrazine into 2,4-dinitrophenyl-hydrazones of the corresponding aldehydes.
- the Metzner group recorded the efficient transformation of 1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione *S*-oxide by primary aliphatic amines into the corresponding imines [33].
- we have studied the reaction of primary aliphatic amines with several aliphatic or aromatic thioaldehyde-*S*-oxides, authentic or formed in situ, to obtain the corresponding imines [34]. Although 4-methoxybenzenamine and 3-ethenyloctanethial-*S*-oxide did not give us the corresponding imine [35], it seems likely that the reaction [VIII → IX] (fig 3) is facilitated by its intramolecular character.

Conversion of *N*-aryl alk-1-enesulfinamides into indole compounds by triethyloxonium tetrafluoroborate

The results of the previous paragraph have indicated the drawbacks of the thermal procedure. To avoid these and at the same time find milder conditions, it seemed likely that the [3.3]-sigmatropic rearrangement would

Table VI. Treatment of sulfinamides **3** with triethyloxonium tetrafluoroborate.

Entry	*Substrates*	*$Et_3O^+BF_4^-$ (equiv)*	*Temperature*	*Products*	*X^1*	*X^2*	*Yields (%)*
118	**3aab**	1.2	−10 °C	**6aa**	H	H	40
119	**3ca**	1.2	−30 °C	**6ca**	5-CH_3	H	30[i]
120	**3cac**	1.1	−10 °C	**6ca**	5-CH_3	H	44
121	**3cad**	1.2	−30 °C	**6ca**	〃	〃	22[ii]
122	**3cad**	1.2	−10 °C	**6ca**	〃	〃	16
123	**3hab**	1.1	−10 °C	**6ha**	5-Cl	H	35
124	**3rac**	1.2	−30 °C	**6ra**	5-CH_3O	H	52
125	**3rac**	1.2	−10 °C	**6ra**	〃	〃	64
126	**3rad**	1.2	−10 °C	**6ra**	〃	〃	13
127	**3raa**	1.2	−30 °C	**6raa**	5-CH_3O	CH_3	41
128	**3rab**	1.2	−30 °C	**6rab**	5-CH_3O	C_2H_5	71

i) *N,N*-diethyl-4-methylbenzenamine was also isolated. ii) starting sulfinamide **3cad** was also isolated (48%).

be facilitated in the case of aminoalkoxysulfonium salts [X] (fig 12). Indeed some allyl vinyl sulfonium salts are known to give a charge-accelerated [3.3]-sigmatropic rearrangement [38, 39].

The literature indicated that the conversion of some *N,N*-dialkylarenesulfinamides into the corresponding aminoalkoxysulfonium salts was possible with methyl triflate [40] or triethyloxonium tetrafluoroborate [41]. We unsuccessfully tried the reaction of triethyloxonium tetrafluoroborate with certain simple *N*-arylsulfinamides: 4-$CH_3OC_6H_4N(CH_3)S(O)R$ with R = CH_3 or 4-$CH_3C_6H_4$. Meanwhile we tried this operation on some sulfinamides **3** assuming that the reactions shown in figure 12 can occur.

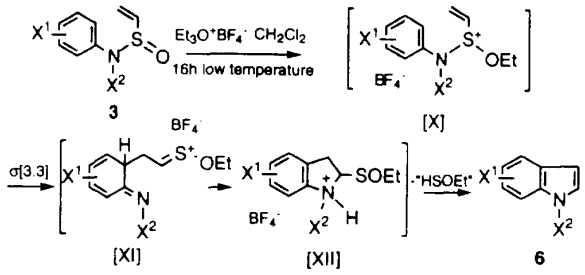

Fig 12

The results of table VI show that the indole compounds can be formed under very mild conditions, but that the yields are often low and that this procedure also gives significant quantities of *N*-mono- and *N,N*-diethylarenamines. The latter are probably formed by reaction of the electrophile with the arenamines developed in situ by acid-catalyzed hydrolysis of the sulfinamides **3**. The experiments with the *N*-trialkylsilylated sulfinamides did not bring about a notable improvement and the corresponding indole compounds were desilylated.

We have also examined the products formed by treatment of the sulfinamide **3ca** with 1.1 equiv of diethoxycarbenium tetrafluoroborate [42] which has been reported to be a more efficient alkylating agent than the trialkyloxonium salts [43]. This reaction gave 5-methylindole **6ca** (25%) and compound **9ca** (20%) which was the product of the classic dimerization of indoles in acidic medium [44] (fig 13).

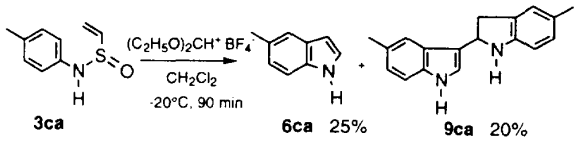

Fig 13

The above reactions often gave modest yields, but nevertheless some facts are worthy of note: the salts of the transient aminoalkoxysulfoniums [X] have clearly shown that they were capable of undergoing [3.3]-sigmatropic rearrangement under mild conditions to produce the intermediate salt [XI] (fig 12). This intermediate can be considered as an analog of the classical intermediate salt of the Pummerer reaction [45] and logically leads to the functionalized indoline [XII], the precursor of the final indole compound.

Conversion of substituted *N*-aryl alk-1-ene-sulfinamides into indole compounds in presence of Lewis acids

Among other methods for achieving the conversion **3** → **6** under mild conditions via an activated sulfinamide species, we were interested in the use of boron trifluoride diethyl etherate which gave very good results for esterification with alcohols [46] and hydrolysis with water or deuterium oxide [47].

Treatment of the sulfinamides **3** with BF_3:OEt_2 in dichloromethane at low temperature in the absence of any nucleophile at low temperature gave the results shown in figure 14 and table VII. The substrates with $R^1 = R^2 = H$ not only gave the indole compounds **6** with yields inferior to these obtained by the thermal route, but also the dimerization products **9** (entries 132 and 139). In order to avoid the formation of these secondary products, we examined the behavior of the *N*-(*t*-butyldimethylsilyl)sulfinamide **3rad**; in this case, no dimer **9** was found but the yield of desilylated indole **6ra** was very small. Treatment of the sulfinamides **3** carrying one or two substituents R^1, R^2 with BF_3:OEt_2

Table VII. Treatment of sulfinamides **3** with boron trifluoride diethyl etherate.

Entry	*Starting sulfinamides*					*Conditions*	*Products (yields %)*	
	3	X^1	X^2	R^1	R^2			
129	**3ab**	H	H	CH_3	H	2 equiv, −30 °C, 2 h	**6ab** (30)	
130	**3ae**	H	H	H	nC_4H_9	1.7 equiv, −40 °C, 2 h	**6ae** (26)	
131	**3af**	H	H	C_2H_5	C_2H_5	1.7 equiv, −40 °C, 2 h	**6af** (23)	
132	**3ca**	4-CH_3	H	H	H	1.2 equiv, −30 °C, 30 min	**6ca** (40)	**9ca** (40)
133	**3cc**	4-CH_3	H	H	nC_4H_9	1.7 equiv, −40 °C, 2 h	**6cc** (48)	
134	**3cd**	4-CH_3	H	C_2H_5	C_2H_5	1.7 equiv, −30 °C, 4 h	**6cd** (59)	
135	**3ha**	4-Cl	H	H	H	1 equiv, −25 °C, 30 min	**6ha** (16)	
136	**3hb**	4-Cl	H	CH_3	H	1.7 equiv, −30 °C, 4 h	**6hb** (71)	
137	**3hc**	4-Cl	H	H	nC_4H_9	1.7 equiv, −40 °C, 2 h	**6hc** (24)	
138	**3hd**	4-Cl	H	C_2H_5	C_2H_5	1.7 equiv, −40 °C, 2 h	**6hd** (20)	
139	**3ra**	4-CH_3O	H	H	H	1 equiv, −25 °C, 30 min	**6ra** (41)	**9ra** (24)
140	**3rad**	4-CH_3O	Me_3CSiMe_2	H	H	1.2 equiv, −25 °C, 30 min	**6ra** (12)	
141	**3rb**	4-CH_3O	H	CH_3	H	1.7 equiv, −30 °C, 4 h	**6rb** (75)	
142	**3rc**	4-CH_3O	H	H	nC_4H_9	1.7 equiv, −40 °C, 2 h	**6rc** (19)	
143	**3rd**	4-CH_3O	H	C_2H_5	C_2H_5	1.7 equiv, −40 °C, 2 h	**6rd** (15)	
144	**3rf**	4-CH_3O	H	-[CH=CH-C(Me)CH]-		1.7 equiv, −30 °C, 4 h	**7** (29)	

gave the corresponding indole compounds with yields often higher than these obtained by the thermal route (table VIII). Indeed the presence of the substituents R^1, R^2 prevented the formation of dimers **9** [98].

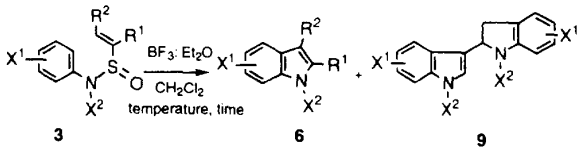

Fig 14

Table VIII. Comparison of some results in tables III and VII.

Substrates	*Yields (%) of substituted indoles obtained after heating in toluene*	*after treatment with boron trifluoride diethyl etherate*
3ab	27	30
3ae	19	26
3af	0	23
3ca	**6ca** (51)	**6ca** (40) + **9ca** (40)
3cc	66	48
3cd	0	59
3ha	48	**6ha** (16)
3hb	25	71
3hc	15	24
3hd	0	20
3ra	**6ra** (52)	**6ra** (41) + **9ra** (24)
3rb	62	75
3rc	10	19
3rd	0	15

We also investigated the use of other Lewis acids; zinc chloride (1.2 equiv) in dichloromethane/ether at room temperature or at reflux did not bring about a notable improvement in the yields: **3ba** → **6ba** (41%); **3ca** → **6ca** (39–45%); **3qa** → **6qa** (60%) and **6′qa** (8%); **3ra** → **6ra** (54%). Attempts at heating the sufinamides **3** in the presence of methyl borate (4 equiv) in toluene at 85 °C for 1 h gave good results in somes cases (entries 145, 146, 148, 149 and 160) (table IX). Without doubt, methyl borate in excess not only plays the role of a weak Lewis acid but also buffers the acidity developed during the reaction, thus diminishing the amounts of arenamines. Meanwhile it totally blocks the transformation of the dichlorosulfinamides **3ia** and **3la**.

Table IX. Treatment of sulfinamides **3** with methyl borate (4 equiv) in warm toluene.

Entry	*Substrates*	*Products*	*Yields*	*Yields of thermal treatment (table III)*
145	**3aa**	**6aa**	78	75
146	**3ab**	**6ab**	37	27
147	**3ba**	**6ba**	55	55
148	**3ca**	**6ca**	90	51
149	**3da**	**6da**	70	49
150	**3ea**	**6ea**	40	43
151	**3ga**	**6ga** + **6′ga**	48	36
152	**3ha**	**6ha**	37	48
153	**3ia**	–	0	14
154	**3ja**	–	0	0
155	**3ka**	–	0	0
156	**3la**	–	0	30
157	**3ma**	**6ma** + **6′ma**	40	40
158	**3oa**	**6oa**	35	40
159	**3qa**	**6qa** + **6′qa**	58 + 10	25 + 5
160	**3ra**	**6ra**	65	52

Conclusion

The above investigations have provided some appreciable results:

- on the efficient preparation of various substituted *N*-aryl alk-1-enesulfinamides **3** which are fairly fragile;
- on the easy conversion of these sulfinamides, by thermolysis or in the presence of certain catalysts, to various substituted indoles often with modest yields. Our relatively simple procedure is valuable for the preparation of certain indoles not substituted at the 1, 2 or 3 positions, in particular the 6-methoxyindole **6qa**, which is an important starting material for the synthesis

of indole and indoline alkaloids and for which a fairly long-winded preparation was described in 1986 [48];

– finally on the likelihood of the new intermediate iminosulfines [VIII] as reaction intermediates. We have not been able to prove their existence, but we have presented several arguments in their favor. The ease of [3.3]-sigmatropic rearrangements of the sulfinamides **3** relative to that of the sulfenamides (I, X = S) is to be compared with those of the 1-alkenyl 2-alkenyl sulfoxides [49, 50] which are easier than these of 1-alkenyl-2-alkenyl sulfides [51].

Experimental section

The general experimental conditions have been described previously [1b].

N-*sulfinylarenamines* **2**; *typical procedure [9a]*

A solution of thionylchloride (4.76 g; 2.92 mL; 40 mmol) in anhydrous benzene (40 mL) was slowly added to a stirred solution of arenamine **1** (20 mmol) in anhydrous benzene (20 mL) at room temperature. The reaction was slightly exothermic and the arenamine hydrochloride crystallized out. The reaction mixture was heated to reflux; the significant release of hydrochloric acid lessened and ceased after 3 h at reflux and the mixture became homogeneous. After heating for a further 1 h, the solvent and excess thionyl chloride were distilled at atmospheric pressure. The *N*-sulfinylarenamine **2** was then distilled under vacuum with generally good yields.

- N-*Sulfinylbenzenamine* **2a**

Bp_{10} = 75 °C; Lit [9a]: bp_{12} = 80 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.92–7.80 (m, 2H); 7.50–7.35 (m, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.2 (s); 130.1 (d); 128.8 (d); 126.7 (d).

MS (EI); *m/z*: 139 (M^+, 56); 93 (31); 91 (25); 86 (47); 84 (100).

- *2-Methyl*-N-*sulfinylbenzenamine* **2b**

$Bp_{0,3}$ = 49–50 °C; Lit [52]: bp_{15} = 99.5 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.4–8.3 (m, 1H); 7.30–7.15 (m, 3H); 2.35 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.2 (s); 134.5 (s); 130.3 (d); 129.9 (d); 127.4 (d); 126.2 (d); 18.2 (q).

MS (EI); *m/z*: 153 (M^+, 33); 136 (100); 104 (54); 78 (71); 77 (50).

- *4-Methyl*-N-*sulfinylbenzenamine* **2c**

Bp_3 = 62–64 °C; Lit [53]: bp_2 = 55 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.85–7.75 (m, 2H); 7.25–7.15 (m, 2H); 2.35 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.8 (s); 140.3 (s); 129.3 (d); 126.7 (d); 21.5 (q).

MS (EI); *m/z*: 153 (M^+, 93); 138 (81); 104 (62); 92 (35); 91 (35); 79 (34); 78 (100); 77 (74).

- N-*Sulfinyl-1-naphthalenamine* **2d**

$Bp_{0,1}$ = 110 °C; mp = 30–31 °C; Lit [54]: bp_1 = 150–152 °C; mp = 33 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.8–8.7 (m, 1H); 8.54–8.42 (m, 1H); 8.02–7.84 (m, 2H); 7.7–7.5 (m, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 138.6 (s); 133.8 (s); 130.8 (d); 128.8 (s); 127.7 (d); 127.3 (d); 126.8 (d); 125.3 (d); 125.4 (d); 123.6 (d).

MS (CI, CH_4); *m/z*: 189 (M^+, 100).

- *4-Fluoro*-N-*sulfinylbenzenamine* **2e**

$Bp_{0,5}$ = 46 °C; Lit [55]: bp_{16} = 107 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.82 (m, 2H); 7.18–7.0 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 162.4 (d, J_{CF} = 252 Hz); 139.1 (s); 129.1 (d); 115.8 (d, J_{CF} = 22 Hz).

MS (CI, CH_4); *m/z*: 157 (M^+, 100).

- *2-Chloro*-N-*sulfinylbenzenamine* **2f**

$Bp_{0,3}$ = 74–76 °C; Lit [56]: bp_{14} = 118–120 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.4–8.3 (m, 1H); 7.60–7.46 (m, 1H); 7.40–7.26 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 139.1 (s); 130.4 (d); 130.0 (d); 129.5 (s); 128.0 (d); 127.1 (d).

MS (EI); *m/z*: 175 (M^+, 5); 173 (14); 138 (100); 110 (46); 90 (48).

- *3-Chloro*-N-*sulfinylbenzenamine* **2g**

$Bp_{0,3}$ = 78–60 °C; Lit [53]: bp_2 = 107 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.84–7.78 (m, 1H); 7.75–7.65 (m, 1H); 7.30–7.25 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.7 (s); 134.5 (s); 130.1 (d); 129.8 (d); 126.6 (d); 124.8 (d).

MS (EI); *m/z*: 175 (M^+, 15); 173 (35); 138 (100); 127 (35); 110 (35); 90 (35); 86 (50); 84 (77).

- *4-Chloro*-N-*sulfinylbenzenamine* **2h**

Bp_3 = 70 °C; Lit [53]: bp_2 = 66 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.86–7.76 (m, 2H); 7.42–7.32 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.8 (s); 137.8 (s); 131.1 (d); 130.0 (d).

MS (EI); *m/z*: 175 (M^+, 15); 173 (50); 138 (87); 110 (67); 90 (75); 84 (60); 63 (100).

- *2,3-Dichloro*-N-*sulfinylbenzenamine* **2i** *[57]*

Mp = 67 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.23 (dd, J = 8 and 1.5 Hz, 1H); 7.52 (dd, J = 8 and 1.5 Hz, 1H); 7.3 (t, J = 8 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.3 (s); 131.1 (s); 130.8 (s); 130.8 (d); 127.2 (d); 125.8 (d).

MS (EI); *m/z*: 209 (M^+, 16); 207 (20); 174 (40); 172 (100); 146 (10); 144 (33); 126 (17); 124 (45).

- *2,4-Dichloro*-N-*sulfinylbenzenamine* **2j**

Mp = 69 °C; Lit [56]: mp = 71 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.4 (d, J = 8.5 Hz, 1H); 7.56 (d, J = 2.5 Hz, 1H); 7.34 (dd, J = 8.5 and 2.5 Hz, 1H).

^{13}C NMR (90 MHz, $CDCl_3$) δ: 137.8 (s); 135.7 (s); 130.8 (s); 129.9 (d); 128.8 (d); 127.5 (d).

MS (EI); *m/z*: 209 (M^+, 8); 207 (11); 174 (20); 172 (58); 163 (10); 161 (17); 146 (17); 144 (40); 126 (35); 124 (100).

- *2,5-Dichloro*-N-*sulfinylbenzenamine* **2k** *[57]*

Mp = 51 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.25 (d, J = 2 Hz, 1H); 7.4 (d, J = 8.5 Hz, 1H); 7.26 (dd, J = 8.5 and 2 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 139.4 (s); 132.6 (s); 130.7 (d); 130.3 (d); 127.9 (s); 127.4 (d).

MS (EI); m/z: 209 (M^+, 17); 207 (25); 174 (40); 172 (100); 163 (16); 161 (25); 146 (8); 144 (20); 126 (13); 124 (22).

• *3,5-Dichloro-N-sulfinylbenzenamine* **2l**

Mp = 48–49 °C; Lit [56]: mp = 48 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8 (d, J = 2 Hz, 2H); 7.45 (t, J = 2 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.7 (s); 135.7 (s); 129.9 (d); 124.9 (d).

MS (EI); m/z: 209 (M^+, 28); 207 (40); 174 (38); 172 (100); 163 (8); 161 (14); 146 (15); 144 (40); 126 (31); 124 (87).

• *3-Bromo-N-sulfinylbenzenamine* **2m**

Mp = 34 °C; Lit [53]: bp_2 = 81 °C; mp = 32 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.04 (t, J = 2 Hz, 1H); 7.0 (ddd, J = 8, 2 and 1.5 Hz, 1H); 7.56 (ddd, J = 8, 2 and 1.5 Hz, 1H); 7.32 (t, J = 8 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.8 (s); 133.0 (d); 130.1 (d); 129.5 (d); 125.3 (d); 122.3 (s).

MS (EI); m/z: 219 (M^+, 30); 217 (29); 138 (100); 110 (50); 90 (35).

• *4-Bromo-N-sulfinylbenzenamine* **2n**

Mp = 60 °C; Lit [53]: mp = 60–61 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.78–7.68 (m, 2H); 7.58–7.48 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.1 (s); 132.2 (d); 128.2 (d); 124.2 (s).

MS (EI); m/z: 219 (M^+, 37); 217 (37); 138 (100); 110 (83); 90 (75).

• *4-Iodo-N-sulfinylbenzenamine* **2o**

Mp = 73–74 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.86–7.76 (m, 2H); 7.68–7.58 (m, 2H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.7 (s); 138.3 (d); 128.3 (d); 96.7 (s).

MS (CI, CH_4); m/z: 265 (M^+ + 1, 100).

• *2-Methoxy-N-sulfinylbenzenamine* **2p**

$Bp_{0.3}$ = 108 °C; Lit [59]: bp = 244 °C; mp = 30 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.4–8.3 (m, 1H); 7.45–7.35 (m, 1H); 7.06–6.96 (m, 2H); 3.92 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 152.3 (s); 131.7 (s); 131.2 (d); 127.8 (d); 120.2 (d); 111.4 (d); 55.7 (q).

MS (EI); m/z: 169 (M^+, 75); 120 (100); 78 (50).

• *3-Methoxy-N-sulfinylbenzenamine* **2q**

$Bp_{0.5}$ = 75 °C; Lit [53]: bp_2 = 98 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.50–7.36 (m, 2H); 7.34–7.22 (m, 1H); 7.0–6.9 (m, 1H); 3.76 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 159.3 (s); 143.0 (s); 129.3 (d); 119.3 (d); 116.8 (d); 111.4 (d); 55.2 (q).

MS (EI); m/z: 169 (M^+, 100); 141 (20).

• *4-Methoxy-N-sulfinylbenzenamine* **2r**

Bp_3 = 100 °C; Lit [53]: bp_2 = 94 °C; mp = 26 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.9 (m, 2H); 7.0–6.9 (m, 2H); 3.87 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 160.5 (s); 137.0 (s); 129.2 (d); 113.9 (d); 55.4 (q).

MS (EI); m/z: 159 (M^+, 100); 154 (22); 121 (32); 106 (34); 98 (20); 80 (40); 78 (32).

• *Methyl 2-(sulfinylamino)benzoate* **2s**

$Bp_{0.1}$ = 85 °C (94%); Lit [60]: bp_9 = 145 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.88 (dd, J = 7.88 and 1.35 Hz, 1H); 7.69–7.61 (m, 1H); 7.52 (td, J = 7.37 and 1.60 Hz, 1H); 7.34 (td, J = 7.68 and 1.38 Hz, 1H); 3.87 (s, 3H).

N-Aryl alk-1-enesulfinamides **3**; *typical procedures*

A solution of *N*-sulfinyl arenamine **2** (2.5 mmol) in anhydrous THF (10 mL) was rapidly added to a stirred 0.49 M solution of vinyl magnesium bromide in THF (5.6 mL; 2.75 mmol) at −78 °C. The cooling bath was then removed and the mixture was allowed to warm to room temperature over a period of 2 h. A saturated aqueous ammonium chloride solution (20 mL) was added and the mixture was extracted with dichloromethane (3 × 30 mL). The extracts were dried (K_2CO_3), filtered through celite and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, Merck) using pentane/ether/acetone, 50:50:0 to 0:98:2. The yields are reported in table I.

A 1M solution of DIBAL-H in hexane (18 mL; 18 mmol) was slowly added to a solution of 1-hexyne (1.35 g; 1.9 mL; 16.5 mmol) in toluene at 0 °C. The mixture was stirred at room temperature for 20 min and at 50 °C for 2 h then cooled to room temperature. A cold (0 °C) solution of *N*-sulfinylarenamine **2** (15 mmol) in toluene (15 mL) was added and the mixture stirred at room temperature for 15 h. A saturated aqueous ammonium chloride solution (15 mL) was added; then after addition of dilute cold sulfuric acid (until pH ≈ 4), the mixture was extracted with dichloromethane (3 × 30 mL) and worked up as above. The yields are reported in table I.

• *N-Phenylethenesulfinamide* **3aa**

Mp = 79.5–80.5 °C (ether).

IR (KBr, cm^{-1}): 3 170, 1 600, 1 510, 1 210, 1 060, 960, 830.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.32–7.20 (m, 2H); 7.15–7.0 (m, 3H); 6.8 (dd, J = 17 and 10 Hz, 1H); 6.42 (s large, 1H); 6.25 (d, J = 17 Hz, 1H); 6.02 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.8 (d); 140.4 (s); 128.9 (d); 123.6 (t); 122.8 (d); 118.2 (d).

MS (EI); m/z: 167 (M^+, 13); 140 (4); 92 (100); 77 (8); 65 (60).

Anal calc for C_8H_9NOS: C 57.46; H 5.42; N 8.38. Found: C 57.34; H 5.41; N 8.25.

• *1-Methyl-N-phenylethenesulfinamide* **3ab**

Mp = 63.5 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.36–7.22 (m, 2H); 7.16–7.0 (m, 3H); 6.22 (s large, 1H); 6.1–6.0 (m, 1H); 5.75–5,65 (m, 1H); 2.05 (m, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 148.2 (s); 141.1 (s); 128.9 (d); 122.6 (d); 118.8 (t); 118.1 (t); 15.8 (q).

MS (EI); m/z: 181 (M^+, 43); 133 (22); 132 (33); 93 (82); 92 (100); 65 (72).

Anal calc for $C_9H_{11}NOS$: C 72.89; H 6.12; N 7.73. Found: C 72.93; H 6.01; N 7.81.

• *N-Phenylbenzenesulfinamide* **3ac**

Mp = 110–112 °C; Lit [10]: mp = 113–114 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.9–7.85 (m, 2H); 7.75–7.6 (m, 3H); 7.4–7.3 (m, 2H); 7.35–7.1 (m, 3H); 7.05 (s large, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 144.2 (s); 140.4 (s); 130.9 (d); 129.0 (d); 128.7 (d); 125.3 (d); 123.2 (d); 118.7 (d).

• N-*Phenylcyclohex-1-ene-1-sulfinamide* **3ad**

Mp = 88 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.35–7.20 (m, 2H); 7.12–7.0 (m, 3H); 6.72–6.64 (m, 1H); 6.32 (s large, 1H); 2.3–2.1 (m,4H); 1.8–1.5 (m, 4H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.8 (s); 141.3 (s); 131.9 (d); 128.9 (d); 122.6 (d); 118.4 (d); 25.2 (t); 22.7 (t); 22.1 (t); 21.6 (t).

MS (EI); *m/z*: 221 (M^+, 10); 173 (23); 172 (23); 129 (15); 93 (100); 92 (30).

Anal calc for $C_{12}H_{15}NOS$: C 65.12; H 6.83; N 6.33. Found: C 65.03; H 6.93; N 6.28.

• N-*Phenylhex-1-enesulfinamide* **3ae**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.3–7.2 (m, 2H); 7.1–7.0 (m, 3H); 6.7 (dt, J = 15 and 8.3 Hz, 1H); 6.4 (dt, J = 15 and 1.2 Hz, 1H); 6.0 (s large, 1H); 2.3–2.2 (m, 2H); 1.5–1.3 (m, 4H); 0.9 (t, J = 7 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.1 (d); 140.7 (s); 132.6 (d); 129.3 (d); 123.3 (d); 118.8 (d); 31.3 (t); 30.1 (t); 22.1 (t); 13.8 (q).

MS (CI, NH_3); *m/z*: 241 (M^+ + 18, 22); 225 (M^+ + 2, 13); 224 (M^+ + 1, 86); 111 (100).

• N-*Phenyl-1-ethylbut-1-enesulfinamide* **3af**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.3–7.2 and 7.09–7.06 (2m, 5H); 6.4 (t, J = 7.5 Hz, 1H); 5.73 (s large, 1H); 2.6–2.1 (m, 4H); 1.15 (t, J = 7.5 Hz, 3H); 1.09 (t, J = 7.6 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 143.8 (s); 141.4 (s); 135.3 (d); 129.2 (d); 122.9 (s); 118.4 (d); 21.2 (t); 19.8 (t); 13.8 (q); 13.5 (q).

MS (CI, NH_3); *m/z*: 224 (M^+ + 1, 17); 197 (30); 111 (100).

• N,*1-Diphenylethenesulfinamide* **3ag**

Mp = 101–103 °C (CH_2Cl_2/pentane).

IR (KBr, cm^{-1}): 1 600, 1 490, 1 380, 1 280, 1 225, 1 080 (large), 760.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.44–7.29 (m, 5H); 7.24–7.14 (m, 2H); 7.04–6.91 (m, 3H); 6.30 (s, 1H); 6.23 (s large, 1H); 6.04 (s, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.0 (s); 140.8 (s); 133.9 (s); 129.3 (d); 129.1 (d); 128.8 (d); 126.9 (d); 123.5 (d); 119.1 (d); 118.9 (t).

MS (CI, NH_3); *m/z*: 261 (M^+ + 18, 6); 244 (M^+ + 1; 100); 226 (6); 153 (8).

Anal calc for $C_{14}H_{13}NOS$: C 69.11; H 5.38; N 5.76. Found: C 69.02; H 5.44; N 5.83.

• N-*(2-Methylphenyl)ethenesulfinamide* **3ba**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.40–7.30 (m, 1H); 7.20–7.10 (m, 2H); 7.10–7.0 (m, 1H); 6.82 (dd, J = 17 and 10 Hz, 1H); 6.45 (s large, 1H); 6.24 (d, J = 17 Hz, 1H); 5.88 (d, J = 10 Hz, 1H); 2.22 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.4 (d); 138.5 (s); 130.1 (d); 128.8 (s); 126.1 (d); 123.6 (d); 123.5 (d); 120.3 (s); 17.3 (q).

MS (EI); *m/z*: 181 (M^+, 4); 107 (18); 106 (100); 79 (23); 78 (15); 77 (40).

• N-*(4-Methylphenyl)ethenesulfinamide* **3ca**

Mp = 76–77 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.14–6.98 (m, 4H); 6.78 (dd, J = 17 and 10 Hz, 1H); 6.24 (d, J = 17 Hz, 1H); 5.93 (d, J = 10 Hz, 1H); 5.87 (s large, 1H); 2.28 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.0 (d); 137.5 (s); 132.5 (s); 129.3 (d); 123.5 (t); 119.0 (d); 20.6 (q).

MS (EI); *m/z*: 181 (M^+, 7); 120 (11); 106 (100); 79 (40); 77 (42).

Anal calc for $C_9H_{11}NOS$: C 59.65; H 6.12; N 7.73. Found: C 59.57; H 6.04; N 7.64.

• *1-Methyl*-N-*(4-methylphenyl)ethenesulfinamide* **3cb**

Mp = 68 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.0–6.84 (m, 4H); 6.78 (s large, 1H); 5.95–5.85 (m, 1H); 5.55–5.50 (m, 1H); 2.24 (s, 3H); 1.94 (s large, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 148.3 (s); 138.1 (s); 132.2 (s); 129.3 (d); 118.8 (d); 118.4 (t); 20.7 (q); 16.1 (q).

MS (CI, NH_3); *m/z*: 196 (M^+ + 1, 70); 146 (100).

Anal calc for $C_{10}H_{13}NOS$: C 61.50; H 6.71; N 7.17. Found: C 61.39; H 6.66; N 7.28.

• N-*(4-Methylphenyl)hex-1-enesulfinamide* **3cc**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.12–7.09 and 7.02–6.9 (2m, 4H); 6.6 (dt, J = 14.8 and 6.9 Hz, 1H); 6.4 (dt, J = 15.4 and 1.6 Hz, 1H); 5.8 (s large, 1H); 2.3 (s, 3H); 2.3–2.2 (m, 2H); 1.5–1.3 (m, 4H); 0.9 (t, J = 7.1 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.8 (d); 138.1 (s); 132.9 (d); 132.8 (s); 129.7 (d); 119.3 (d); 31.2 (t); 30.1 (t); 22.1 (t); 20.8 (q); 13.7 (q).

MS (CI, NH_3); *m/z*: 255 (M^+ + 18, 1); 238 (M^+ + 1, 13); 150 (14); 125 (36); 108 (100).

• *1-Ethyl*-N-*(4-methylphenyl)but-1-enesulfinamide* **3cd**

Mp = 52–53 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.1–7.0 and 6.99–6.96 (2m, 4H); 6.04 (t, J = 7.5 Hz, 1H); 5.5 (s large, 1H); 2.5–2.2 (m, 4H); 2.3 (s, 3H); 1.1 (t, J = 6.9 Hz, 3H); 1.0 (t, J = 7.6 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 143.9 (s); 138.6 (s); 135.1 (d); 132.7 (s); 129.7 (d); 119.2 (d); 21.2 (q); 20.6 (t); 19.8 (t); 13.6 (q); 13.5 (q).

MS (CI, NH_3); *m/z*: 238 (M^+ + 1, 17); 150 (4); 125 (30); 108 (100).

Anal calc for $C_{13}H_{19}NOS$: C 65.78; H 8.07; N 5.90. Found: C 65.85; H 7.98; N 6.01.

• N-*(4-Methylphenyl)-1-phenylethenesulfinamide* **3ce**

Mp = 81–82 °C.

IR (KBr, cm^{-1}): 3 140, 1 610, 1 570, 1 500, 1 220, 1 050 (large), 780, 715.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.49–7.35 (m, 5H); 7.12–7.02 (m, 2H); 6.93–6.83 (m, 2H); 6.30 (s, 1H); 6.07 (s, 1H); 5.62 (s large, 1H); 2.27 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.2 (s); 137.9 (s); 134.0 (s); 133.4 (s); 129.8 (d); 129.0 (d); 128.8 (d); 126.9 (d); 119.7 (d); 118.9 (t); 20.7 (q).

MS (CI, NH_3); *m/z*: 258 (M^+ + 1, 6); 210 (4); 170 (5); 153 (18); 137 (75); 108 (100).

Anal calc for $C_{15}H_{15}NOS$: C 70.01; H 5.87; N 5.44. Found: C 69.92; H 5.92; N 5.51.

• N *(1-Naphthyl)ethenesulfinamide* **3da**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.2–8.1 (m, 2H); 7.9–7.7 (m, 2H); 7.7–7.5 (m, 3H); 6.81 (dd, J = 17 and 10 Hz, 1H); 6.27 (d, J = 17 Hz, 1H); 6.02 (d, J = 10 Hz, 1H).

MS (CI, NH_3); *m/z*: 235 (M^+ + 18, 5); 218 (M^+ + 1, 31); 145 (100).

• N-*(4-Fluorophenyl)ethenesulfinamide* **3ea**

Mp = 79–80 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.15–6.95 (m, 4H); 6.8 (dd, J = 17 and 10 Hz, 1H); 6.36 (s large, 1H); 6.35 (d, J = 17 Hz, 1H); 6.06 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 159.0 (s, J_{CF} = 242 Hz); 140.7 (d); 136.3 (s); 124.1 (t); 120.9 (d, J_{CF} = 6 Hz); 115.6 (d, J_{CF} = 23 Hz).

MS (EI); m/z: 185 (M^+, 10); 111 (15); 110 (100); 83 (25).

Anal calc for C_8H_8FNOS: C 51.90; H 4.35; N 7.57. Found: C 51.74; H 4.34; N 7.40.

• N-*(2-Chlorophenyl)ethenesulfinamide* **3fa**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.5 (dd, J = 8 and 1.5 Hz, 1H); 7.37 (dd, J = 8 and 1.5 Hz, 1H); 7.25 (td, J = 8 and 1.5 Hz, 1H); 7.0 (td, J = 8 and 1.5 Hz, 1H); 6.84 (dd, J = 17 and 10 Hz, 1H); 6.64 (s large, 1H); 6.35 (d, J = 17 Hz, 1H); 6.1 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.5 (d); 137.0 (s); 129.1 (d); 127.2 (d); 124.1 (s); 123.4 (d); 123.1 (t); 118.6 (d).

MS (EI); m/z: 203 (M^+, 30); 201 (8); 128 (35); 127 (40); 126 (100); 101 (30); 99 (90).

• N-*(3-Chlorophenyl)ethenesulfinamide* **3ga**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8–7.7 (m, 1H); 7.2–7.06 (m, 2H); 7.04–6.9 (m, 2H); 6.76 (dd, J = 17 and 10 Hz, 1H); 6.2 (d, J = 17 Hz, 1H); 5.96 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.0 (s); 140.5 (d); 134.4 (s); 129.9 (d); 123.9 (t); 122.5 (d); 117.9 (d); 116.9 (d).

MS (EI); m/z: 203 (M^+, 5); 201 (13); 128 (35); 127 (27); 126 (100); 101 (22); 99 (68).

• N-*(4-Chlorophenyl)ethenesulfinamide* **3ha**

Mp = 98–98.5 °C (ether).

IR (KBr, cm^{-1}): 3 160, 1 600, 1 495, 1 240, 1 060 (large), 830.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.30–7.20 (m, 2H); 7.10–7.00 (m, 2H); 6.94 (s large, 1H); 6.8 (dd, J = 17 and 10 Hz, 1H); 6.26 (d, J = 17 Hz, 1H); 6.04 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.0 (d); 139.2 (s); 129.3 (d); 128.8 (s); 124.5 (t); 120.2 (d).

MS (EI); m/z: 203 (M^+, 3); 201 (8); 153 (10); 151 (27); 129 (23); 128 (36); 127 (72); 126 (100); 101 (20); 99 (72).

Anal calc for C_8H_8ClNOS: C 47.64; H 4.00; N 6.94. Found: C 47.65; H 4.05; N 6.78.

• N-*(4-Chlorophenyl)-1-methylethenesulfinamide* **3hb**

Mp = 132 °C.

IR (KBr, cm^{-1}): 3 180, 3 150, 1 640, 1 595, 1 490, 1 080, 1 070, 930, 830, 515.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.30–7.20 (m, 2H); 7.05–6.95 (m, 2H); 6.07 (s large, 1H); 5.7 (s large, 1H); 2.05 (s large, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 148.5 (s); 139.5 (s); 129.3 (d); 128.6 (s); 120.1 (d); 119.2 (t); 16.0 (q).

MS (EI); m/z: 215 (M^+, 10); 128 (31); 126 (100).

Anal calc for $C_9H_{10}ClNOS$: C 50.58; H 4.71; N 6.55. Found: C 50.17; H 4.63; N 6.49.

• N-*(4-Chlorophenyl)hex-1-enesulfinamide* **3hc**

Mp = 109 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.3–7.2 and 7.0–6.9 (2m, 4H); 6.6 (dt, J = 15 and 6.9 Hz, 1H); 6.3 (dt, J = 14.7 and 1.2 Hz, 1H); 6.2 (s large, 1H); 2.3–2.2 (m, 2H); 1.9–1.2 (m, 4H); 0.9 (t, J = 7 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.9 (d); 139.4 (s); 132.3 (d); 129.2 (d); 125.2 (s); 119.8 (d); 31.3 (t); 30.0 (t); 22.1 (t); 13.7 (q).

MS (CI, NH_3); m/z: 275 (M^+ + 18, 10); 260 (M^+ + 3, 12); 258 (M^+ + 1, 27); 130 (43); 129 (20); 128 (100); 127 (26).

Anal calc for $C_{12}H_{16}ClNOS$: C 56.35; H 6.31; N 5.48. Found: C 56.27; H 6.39; N 5.58.

• N-*(4-Chlorophenyl)-1-ethylbut-1-enesulfinamide* **3hd**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.32–7.2 (m, 2H); 7.0–6.9 (m, 2H); 6.4 (t, J = 7.5 Hz, 1H); 5.7 (s large, 1H); 2.5–2.1 (m, 4H); 1.1 (t, J = 7.5 Hz, 3H); 1.0 (t, J = 7.5 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 143.4 (s); 139.9 (s); 153.8 (d); 129.1 (d); 128.1 (s); 119.8 (d); 21.2 (t); 19.7 (t); 13.8 (q); 13.5 (q).

MS (CI, NH_3); m/z: 258 (M^+ + 1, 10); 130 (26); 119 (16); 128 (100); 127 (33).

• N-*(2,3-Dichlorophenyl)ethenesulfinamide* **3ia**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.45–7.35 (m, 1H); 7.25–7.10 (m, 2H); 6.84 (dd, J = 17 and 10 Hz, 1H); 6.76 (s large, 1H); 6.4 (d, J = 17 Hz, 1H); 6.16 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.4 (d); 138.9 (s); 133.1 (s); 127.4 (d); 124.7 (d); 124.0 (t); 121.4 (s); 115.9 (d).

MS (EI); m/z: 237 (M^+, 13); 235 (20); 162 (67); 160 (100); 135 (45); 133 (77).

• N-*(2,4-Dichlorophenyl)ethenesulfinamide* **3ja**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.35 (s, 1H); 7.02–6.96 (m, 2H); 6.86–6.74 (m, 1H); 6.57 (d, J = 2 Hz, 1H); 6.28 (d, J = 17 Hz, 1H); 6.1 (d, J = 9.5 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.3 (d); 138.2 (s); 133.2 (s); 130.1 (d); 124.9 (t); 123.4 (d); 121.0 (s); 117.9 (d).

MS (EI); m/z: 237 (M^+, 20); 235 (M^+, 25); 163 (25); 162 (70); 161 (40); 160 (100).

• N-*(2,5-Dichlorophenyl)ethenesulfinamide* **3ka**

Mp = 82 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.5 (d, J = 2.5 Hz, 1H); 7.3 (d, J = 8.5 Hz, 1H); 6.98 (dd, J = 8.5 and 2.5 Hz, 1H); 6.84 (dd, J = 17 and 10 Hz, 1H); 6.7 (s large, 1H); 6.4 (d, J = 17 Hz, 1H); 6.16 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.3 (d); 138.2 (s); 133.2 (s); 130.1 (d); 124.9 (t); 123.4 (d); 121.0 (s); 117.9 (d).

MS (EI); m/z: 237 (M^+, 17); 235 (25); 163 (25); 162 (70); 161 (40); 160 (100); 135 (50); 133 (60).

Anal calc for $C_8H_7Cl_2NOS$: C 41.04; H 3.01; N 5.98. Found: C 40.91; H 2.93; N 6.03.

• N-*(3,5-Dichlorophenyl)ethenesulfinamide* **3la**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.35 (s large, 1H); 7.02 (t, J = 2 Hz, 1H); 6.98 (d, J = 2 Hz, 2H); 6.8 (dd, J = 17 and 10 Hz, 1H); 6.28 (d, J = 17 Hz, 1H); 6.1 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.6 (s); 140.1 (d); 135.4 (s); 124.8 (t); 122.8 (d); 116.0 (d).

MS (EI); m/z: 237 (M^+, 10); 235 (14); 189 (20); 188 (20); 187 (33); 186 (25); 162 (63); 161 (29); 160 (100); 135 (52); 133 (87).

• N-*(3-Bromophenyl)ethenesulfinamide* **3ma**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.64 (s large, 1H); 7.15–7.05 (m, 1H); 7.04–6.8 (m, 3H); 6.62 (dd, J = 17 and 10 Hz, 1H); 6.06 (d, J = 17 Hz, 1H); 5.84 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.8 (s); 140.5 (d); 130.3 (d); 125.9 (d); 124.3 (t); 122.7 (s); 121.0 (d); 116.7 (d).

MS (EI); m/z: 247 (M^+, 5); 245 (4); 173 (20); 172 (50); 171 (20); 170 (50); 91 (100); 65(33); 64 (42); 63 (60).

• N-*(4-Bromophenyl)ethenesulfinamide* **3na**

Mp = 100–101 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.4–7.3 (m, 2H); 7.08 (s, large, 1H); 7.0–6.90 (m, 2H); 6.76 (dd, J = 17 and 10 Hz, 1H); 6.22 (d, J = 17 Hz, 1H); 6.0 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.3 (d); 139.7 (s); 132.3 (d); 124.4 (t); 120.7 (d); 116.4 (s).

MS (EI); m/z: 247 (M^+, 10); 245 (10); 197 (15); 195 (15); 173 (25); 172 (90); 171 (30); 170 (92); 91 (92); 65 (55); 64 (62); 63 (100).

Anal calc for C_8H_8BrNOS: C 39.36; H 3.30; N 5.74. Found: C 39.48; H 3.36; N 5.84.

• N-*(4-Iodophenyl)ethenesulfinamide* **3oa**

Mp = 138–140 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.66–7.56 (m, 2H); 6.94–6.84 (m, 2H); 6.8 (dd, J = 17 and 10 Hz, 1H); 6.32 (d, J = 17 Hz, 1H); 6.14 (s large, 1H); 6.08 (d, J = 10 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 140.8 (d); 140.4 (s); 138.2 (d); 124.6 (t); 120.7 (d); 86.5 (s).

MS (EI); m/z: 293 (M^+, 15); 219 (60); 218 (100); 127 (20); 92 (43); 91 (52).

Anal calc for C_8H_8INOS: C 32.78; H 2.75; N 4.78. Found: C 32.99; H 2.87; N 4.64.

• N-*(2-Methoxyphenyl)ethenesulfinamide* **3pa**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.40–7.30 (m, 1H); 7.10–6.85 (m, 3H); 6.84 (dd, J = 17 and 10 Hz, 1H); 6.46 (s, large, 1H); 6.33 (d, J = 17 Hz, 1H); 6.07 (d, J = 10 Hz, 1H); 3.84 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 148.3 (s); 141.0 (d); 129.4 (s); 123.2 (t); 122.6 (d); 120.2 (d); 116.7 (d); 110.3 (d); 54.9 (q).

MS (EI); m/z: 197 (M^+, 15); 123 (40); 122 (100); 107 (45); 94 (70); 92 (52).

Anal calc for $C_9H_{11}N_2OS$: C 54.85; H 5.63; N 7.11. Found: C 54.68; H 5.78; N 6.91.

• N-*(3-Methoxyphenyl)ethenesulfinamide* **3qa**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.3 (s large, 1H); 7.2–7.1 (m, 1H); 6.78 (dd, J = 17 and 10 Hz, 1H); 6.85–6.75 (m, 2H); 6.65–6.55 (m, 1H); 6.22 (d, J = 17 Hz, 1H); 5.96 (d, J = 10 Hz, 1H); 3.72 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 159.9 (s); 141.8 (s); 140.8 (d); 129.5 (d); 123.4 (t); 110.3 (d); 108.3 (d); 103.9 (d); 54.9 (q).

MS (EI); m/z: 197 (M^+, 12); 147 (97); 132 (100); 122 (80); 107 (31); 104 (59); 95 (82).

• N-*(4-Methoxyphenyl)ethenesulfinamide* **3ra**

Mp = 82–82.5 °C (ether).

IR (KBr, cm^{-1}): 3 130, 1 615, 1 515, 1 250 (large), 1 040 (large).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.15–7.05 (m, 2H); 6.90–6.80 (m, 2H); 6.80 (dd, J = 17 and 10 Hz, 1H); 6.30 (s large, 1H); 6.24 (d, J = 17 Hz, 1H); 6.02 (d, J = 10 Hz, 1H); 3.78 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 155.2 (s); 141.2 (d); 133.0 (s); 123.7 (t); 122.1 (d); 114.2 (d); 55.2 (q).

MS (EI); m/z: 197 (M^+, 2); 147 (12); 123 (21); 122 (100); 107 (22).

Anal calc for $C_9H_{11}NO_2S$: C 54.85; H 5.63; N 7.11. Found: C 54.86; H 5.62; N 7.02.

• N-*(4-Methoxyphenyl)-1-methylethenesulfinamide* **3rb**

Mp = 94 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.1–7.0 (m, 2H); 6.90–6.80 (m, 2H); 6.02 (s large, 1H); 5.66 (q, J = 1.5 Hz, 1H); 5.56 (s large, 1H); 3.8 (s, 3H); 2.08 (s large, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 156.5 (s); 148.9 (s); 133.4 (s); 122.3 (d); 118.7 (t); 114.5 (d); 55.4 (q); 16.1 (q).

MS (EI); m/z: 211 (M^+, 2); 123 (12); 122 (100).

Anal calc for $C_{10}H_{13}NO_2S$: C 56.85; H 6.20; N 6.63. Found: C 56.97; H 6.16; N 6.64.

• N-*(4-Methoxyphenyl)hex-1-enesulfinamide* **3rc**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.1–7.0 and 6.9–6.8 (2m, 4H); 6.6 (dt, J = 15 and 8.1 Hz, 1H); 6.3 (dt, J = 15.2 and 1.1 Hz, 1H); 5.9 (s, large, 1H); 3.8 (s, 3H); 2.3–2.2 (m, 2H); 1.5–1.3 (m, 4H); 0.9 (t, J = 7.1 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 156.4 (s); 141.8 (d); 133.2 (s); 132.8 (d); 122.4 (d); 114.4 (d); 55.4 (q); 31.3 (t); 30.1 (t); 22.1 (t); 13.7 (q).

MS (CI, NH_3); m/z: 254 (M^+ + 1, 2); 141 (24); 124 (100); 123 (17).

• *1-Ethyl*-N-*(4-methoxyphenyl)but-1-enesulfinamide* **3rd**

Mp = 58 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.0–6.9 and 6.8–6.7 (2m, 4H); 6.4 (t, J = 7.6 Hz, 1H); 5.7 (s large, 1H); 3.7 (s, 3H); 2.5–2.1 (m, 4H); 1.1 (t, J = 7.5 Hz, 3H); 1.0 (t, J = 7.5 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 156.1 (s); 143.7 (s); 135.1 (d); 133.9 (s); 121.9 (d); 114.3 (d); 55.4 (q); 21.1 (t); 19.8 (t); 13.8 (q); 13.4 (q).

MS (CI, NH_3); m/z: 254 (M^+ + 1, 5); 141 (28); 124 (100); 123 (18).

Anal calc for $C_{13}H_{19}NO_2S$: C 61.63; H 7.56; N 5.53. Found: C 61.71; H 7.50; N 5.48.

• N-*(4-Methoxyphenyl)-1-phenylethenesulfinamide* **3re**

IR (film, cm^{-1}): 3 200, 1 620, 1 500, 1 250, 1 050 (large), 830, 780.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.48–7.33 (m, 5H); 6.97–6.87 (m, 2H); 6.83–6.73 (m, 2H); 6.25 (s, 1H); 6.04 (s, 1H); 5.59 (s large, 1H); 3.77 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 156.6 (s); 152.8 (s); 134.2 (s); 133.1 (s); 128.9 (d); 128.7 (d); 126.9 (d); 122.7 (d); 119.2 (t); 114.3 (d); 55.4 (q).

MS (CI, NH_3); m/z: 291 (M^+ + 18, 5); 274 (M^+ + 1; 38); 224 (6); 170 (15); 161 (11); 153 (21); 141 (3); 124 (100); 108 (4).

• N-*(4-Methoxyphenyl)-4-methylbenzenesulfinamide* **3rf**

Mp = 102 °C, Lit [61]: mp = 120 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.7–7.6 (m, 2H); 7.35–7.25 (m, 2H); 7.1–7.0 (m, 2H); 6.9–9.8 (m, 2H); 5.9 (s large, 1H); 3.77 (s, 3H); 2.43 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 156.6 (2s); 141.5 (s); 133.1 (s); 129.6 (d); 125.6 (d); 122.6 (d); 114.5 (d); 55.4 (q); 21.3 (q).

• *Methyl 2-[(ethenylsulfinyl)amino]benzoate* **3sa**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.01 (dd, J = 8.1 and 1.48 Hz, 1H); 7.95 (s large, 1H); 7.64–7.46 (m, 2H); 7.08–6.98 (m, 1H); 6.88 (dd, J = 16.4 and 9.6 Hz, 1H); 6.4 (d, J = 16.4 Hz, 1H); 6.15 (d, J = 9.6 Hz, 1H); 3.92 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 168.3 (s); 144.8 (s); 141.0 (d); 134.5 (d); 131.4 (d); 124.3 (t); 121.2 (d); 116.2 (d); 114.9 (s); 52.2 (q).

• *Methyl 2-[(1-methylethenyl)sulfinylamino]benzoate* **3sb**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.88 (dd, J = 8 and 1.3 Hz, 1H); 7.59–7.44 (m, 2H); 7.04–6.95 (m, 1H); 6.10 (d, J = 1.6 Hz, 1H); 5.74 (d, J = 1.6 Hz, 1H); 3.90 (s, 3H); 2.08 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 168.4 (s); 148.8 (s); 145.4 (s); 134.5 (d); 131.4 (d); 121.0 (d); 120.0 (t); 117.0 (d); 114.6 (s); 52.1 (q); 15.3 (q).

• *Methyl 2-[(hex-1-enylsulfinyl)amino]benzoate* **3sc**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.89 (dd, J = 8 and 1.5 Hz, 1H); 7.53–7.34 (m, 2H); 6.96–6.84 (m, 1H); 6.65 (dt, J = 15 and 6.8 Hz, 1H); 6.34 (dt, J = 15 and 1.3 Hz, 1H); 3.82 (s, 3H); 2.33–2.16 (m, 2H); 1.51–1.19 (m, 4H); 0.85 (t, J = 7 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 168.3 (s); 145.1 (s); 142.5 (d); 134.5 (d); 132.2 (d); 131.4 (d); 121.0 (d); 116.2 (d); 114.7 (s); 52.1 (q); 31.4 (t); 30.2 (t); 22.1 (t); 13.7 (q).

N-*Alkylation of* N-*aryl alk-1-enesulfinamides; typical procedures*

A solution of sulfinamide **3** (2.76 mmol) in 1,2-dimethoxyethane (5.5 mL) was added to a suspension of sodium hydride (0.066 g; 2.76 mmol) in 1,2-dimethoxyethane (2.76 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min then at 45–50 °C for 2 h. After cooling to 0 °C, the alkylating agent (3.31 mmol; 1.2 equiv; table II) was added and stirring was continued at 0 °C for 1 h. Water (10 mL) was added and the majority of the solvent was evaporated under reduced pressure. The mixture was extracted with ether (3 × 25 mL); the extracts were washed with water (15 mL), dried (K_2CO_3) and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, pentane/dichloromethane/acetone, 50:50:0 to 0:80:20).

Hexamethyldisilazane (0.532 g; 0.7 mL; 3.3 mmol) and chloromethylsilane (0.358 g; 0.42 mL; 3.3 mmol) were added to a solution of sulfinamide **3aa** (1.67 g, 10 mmol) in anhydrous THF (20 mL). After stirring at room temperature for 15 h, the mixture was filtered through celite and evaporated under reduced pressure. The labile product **3aab** could not be purified by flash chromatography on silica gel and was used crude.

A solution of sulfinamide **3ra** (1.182 g; 6 mmol) in diethyl ether/THF (50:50; 18 mL) was added to a stirred suspension of sodium hydride (0.144 g; 6 mmol) in diethyl ether/THF (50:50; 8 mL) at 0 °C. The mixture was stirred at 0 °C for 15 min then at 45–50 °C for 2 h. After cooling to 0 °C, a solution of *tert*-butyldimethylsilyl chloride (1.17 g; 7.8 mmol) in diethyl ether/THF (50:50; 4 mL) was added. Stirring at room temperature for 20 h, usual work up and flash chromatography (silica gel; dichloromethane/acetone, 98:2 to 80:20) afforded the pure compound **3rad** (1.41 g; 76%).

• N-*Methyl*-N-*phenylethenesulfinamide* **3aaa**

Mp = 64.5–66 °C.

IR (KBr, cm^{-1}): 1 595, 1 495, 1 270, 1 080, 975, 775.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.44–7.06 (m, 5H); 6.60 (dd, J = 16.5 and 9.6 Hz, 1H); 6.20 (d, J = 16.5 Hz, 1H); 6.08 (d, J = 9.6 Hz, 1H); 3.06 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 145.6 (s); 140.9 (d); 129.2 (d); 125.2 (t); 124.2 (d); 120.9 (d); 31.1 (q).

MS (CI, NH_3); m/z: 199 (M^+ + 18, 3); 182 (M^+ + 1; 100); 166 (2); 108 (35); 100 (5).

Anal calc for $C_9H_{11}NOS$: C 59.64; H 6.12; N 7.73. Found: C 59.59; H 6.22; N 7.69.

• N-*Phenyl*-N-*(trimethylsilyl)ethenesulfinamide* **3aab**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.2–7.1 (m, 2H); 7.1–7.0 (m, 3H); 6.3 (dd, J = 16.5 and 9.5 Hz, 1H); 5.77 (d, J = 16.5 Hz, 1H); 5.66 (d, J = 9.5 Hz, 1H); 0.28 (s, 9H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.6 (d); 138.8 (s); 129.2 (d); 128.0 (d); 125.1 (d); 122.6 (t); 0.3 (q).

MS (EI); m/z: 239 (M^+, 5); 212 (8); 91 (100).

• N-*Methyl*-N-*(4-methylphenyl)ethenesulfinamide* **3caa**

Mp = 51–52 °C (ether).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.3–7.2 (s large, 4H); 6.62 (dd, J = 17 and 10 Hz, 1H); 6.20 (d, J = 17 Hz, 1H); 6.05 (d, J = 10 Hz, 1H); 3.04 (s, 3H); 2.33 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.7 (s); 140.6 (d); 133.8 (s); 129.3 (d); 124.5 (t); 121.4 (d); 31.9 (q); 20.7 (q).

MS (EI); m/z: 195 (M^+, 13); 145 (19); 144 (18); 121 (40); 120 (100); 91 (40).

Anal calc for $C_{10}H_{13}NOS$: C 61.51; H 6.71; N 7.17. Found: C 61.47; H 6.66; N 7.23.

• N-*(4-Methylphenyl)*-N-*(phenylmethyl)ethenesulfinamide* **3cab**

Flash chromatography afforded a fraction containing sulfinamide **3cab** (90%) and *N*-(phenylmethyl)-4-methylbenzenamine (10%).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.35–7.15 (m, 5H); 7.1–7.0 (m, 4H); 6.64 (dd, J = 17 and 10 Hz, 1H); 6.08 (d, J = 17 Hz, 1H); 5.86 (d, J = 10 Hz, 1H); 4.62 (s, 2H); 2.25 (s, 3H).

• N-*(4-Methylphenyl)*-N-*(trimethylsilyl)ethenesulfinamide* **3cac**

Oil containing *N*-(4-methylphenyl)ethenesufinamide (5%).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.2–7.1 (m, 2H); 7.06–6.96 (m, 2H); 6.31 (dd, J = 17 and 10 Hz, 1H); 5.79 (d, J = 17 Hz, 1H); 5.66 (d, J = 10 Hz, 1H); 2.33 (s, 3H); 0.27 (s, 9H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 141.8 (d); 135.9 (s); 134.8 (s); 129.6 (d); 128.8 (d); 122.5 (t); 20.9 (q); 0.4 (q).

MS (EI); m/z: 253 (M^+, 3); 226 (6); 131 (15); 130 (20); 107 (20); 106 (100); 79 (35); 77 (45).

• N-*(4-Methylphenyl)*-N-*(tert-butyldimethylsilyl)ethenesulfinamide* **3cad**

Same procedure as that described for preparation of compound **3rad** (cf above typical procedure).

IR (film, cm^{-1}): 1 500, 1 250, 1 215, 1 090, 950, 910, 880.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.11–7.04 (m, 2H); 7.01–6.93 (m, 2H); 6.28 (dd, J = 16.6 and 9.7 Hz, 1H); 5.71 (d, J = 16.6 Hz, 1H); 5.62 (d, J = 9.7 Hz, 1H); 2.3 (s, 3H); 0.98 (s, 9H); 0.3 (s, 3H); 0.13 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 142.0 (d); 136.5 (s); 130.6 (d); 129.9 (s); 129.0 (d); 123.0 (t); 26.6 (q); 21.0 (q); 19.2 (s); −3.8 (q); −4.0 (q).

MS (CI, NH_3); m/z: 313 (M^+ + 18, 4); 296 (M^+ + 1, 100); 280 (1); 222 (34); 182 (10); 125 (11); 108 (39).

• N-*(4-Chlorophenyl)*-N-*methylethenesulfinamide* **3haa**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.40-7.30 (m, 2H); 7.25–7.15 (m, 2H); 6.64 (dd, J = 16.5 and 9.5 Hz, 1H); 6.25 (d, J = 16.5 Hz, 1H); 6.12 (d, J = 9.5 Hz, 1H); 3.04 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 143.9 (s); 140.1 (d); 128.7 (d); 128.6 (s); 125.0 (t); 121.4 (d); 30.6 (q).

MS (CI, NH_3); m/z: 217 (M^+ + 2, 35); 215 (M^+, 88); 188 (17); 142 (32); 140 (100); 111 (15); 105 (13); 77 (30).

• N-*(4-Chlorophenyl)*-N-*(trimethylsilyl)ethenesulfinamide* **3hab**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.4–7.3 (m, 2H); 7.15–7.05 (m, 2H); 6.3 (dd, J = 16.5 and 9.5 Hz, 1H); 5.8 (d, J = 16.5 Hz, 1H); 5.71 (d, J = 10 Hz, 1H); 0.28 (s, 9H).

• N-*(4-Methoxyphenyl)*-N-*methylethenesulfinamide* **3raa**

IR (film, cm^{-1}): 1 610, 1 520, 1 250, 1 030, 830.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.17–7.06 (m, 2H); 6.89–6.75 (m, 2H); 6.51 (dd, J = 16.5 and 9.5 Hz, 1H); 6.05 (d, J = 16.5 Hz, 1H); 5.93 (d, J = 9.5 Hz, 1H); 3.74 (s, 3H); 2.99 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 157.3 (s); 141.0 (d); 138.8 (s); 124.7 (d); 123.0 (t); 114.3 (d); 55.4 (q); 33.6 (q).

MS (CI, NH_3); m/z: 211 (M^+, 1); 195 (3); 146 (30); 136 (30); 137 (43); 122 (100); 118 (52); 108 (8); 94 (24).

• N-*Ethyl*-N-*(4-methoxyphenyl)ethenesulfinamide* **3rab**

IR (film, cm^{-1}): 1 605, 1 510, 1 380, 1 210 (large), 1 080, 830.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.17–7.07 (m, 2H); 6.81–6.74 (m, 2H); 6.44 (dd, J = 16.5 and 9.6 Hz, 1H); 5.92 (d, J = 16.5 Hz, 1H); 5.78 (d, J = 9.6 Hz, 1H); 3.73 (s, 3H); 3.46 (q, 2H); 1.04 (t, J = 7.21 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 158.1 (s); 141.4 (d); 135.0 (s); 128.5 (d); 124.1 (t); 114.1 (d); 55.3 (q); 45.4 (t); 14.4 (q).

MS (CI, NH_3); m/z: 243 (M^+ + 18, 17); 226 (M^+ + 1, 68); 208 (45); 176 (100); 169 (48).

• N-*(4-Methoxyphenyl)*-N-*(trimethylsilyl)ethenesulfinamide* **3rac**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.1-7.0 (m, 2H); 6.92–6.82 (m, 2H); 6.32 (dd, J = 16.5 and 9.5 Hz, 1H); 5.78 (d, J = 16.5 Hz, 1H); 5.68 (d, J = 9.5 Hz, 1H); 3.80 (s, 3H); 0.36 (s, 9H).

• N-*(4-Methoxyphenyl)*-N-*(*tert*-butyldimethylsilyl)ethenesulfinamide* **3rad**

IR (film, cm^{-1}): 1 610, 1 505, 1 250, 1 215, 1 100, 1 040, 950.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.04–6.96 (m, 2H); 6.83–6.75 (m, 2H); 6.28 (dd, J = 16.6 and 9.7 Hz, 1H); 5.69 (d, J = 16.6 Hz, 1H); 5.62 (d, J = 9.7 Hz, 1H); 3.78 (s, 3H); 0.96 (s, 9H); 0.28 (s, 3H); 0.1 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 158.2 (s); 142.0 (d); 131.8 (d); 130.4 (s); 123.0 (t); 113.4 (d); 55.2 (q); 26.6 (q); 19.1 (s); −3.9 (q); −4.1 (q).

MS (CI, NH_3); m/z: 312 (M^+ + 1, 18); 296 (2); 238 (58); 182 (4); 141 (15); 124 (100); 108 (9).

• N-*(4-Methoxyphenyl)*-N-*methyl-1-phenylethenesulfinamide* **3rea**

IR (film, cm^{-1}): 1 610, 1 515, 1 250, 1 040, 830.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.38 (s, 5H); 7.02–6.90 (m, 2H); 6.82–6.70 (m, 2H); 6.12 (s, 1H); 6.02 (s, 1H); 3.78 (s, 3H); 2.92 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 157.1 (s); 152.2 (s); 138.9 (s); 134.8 (s); 128.6 (d); 126.9 (d); 124.3 (d); 120.7 (s); 116.4 (d); 114.2 (t); 55.4 (q); 32.6 (q).

MS (CI, NH_3); m/z: 288 (M^+ + 1, 7); 170 (42); 153 (11); 138 (100); 124 (14); 100 (5).

• N-*(Trimethylsilyl)ethenesulfinamide* **5**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 6.53 (dd, J = 16.5 and 9.5 Hz, 1H); 5.93 (d, J = 16.5 Hz, 1H); 5.71 (d, J = 9.5 Hz, 1H); 3.75–3.65 (broad s, 1H); 0.13 (s, 9H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 146.0 (d); 120.2 (t); 0.25 (q).

MS (EI); m/z: 163 (M^+, 1); 136 (21); 115 (20); 75 (33); 73 (100).

Preparation of indole compounds **6**

• *Typical thermal procedure*

Slow distillation of an anhydrous 0.2 M solution of sulfinamide **3** in toluene with concomitant slow addition of fresh toluene over 1 h, afforded an azeotropic distillate containing acidic water and a white powder inside the condenser. The remaining brown-black heterogenous solution was evaporated under reduced pressure and the crude product was purified by flash chromatography (silica gel, pentane/dichloromethane/acetone, 50:50:0 to 0:98:2). The yields are reported in table III.

• *Typical procedure using triethyloxonium tetrafluoroborate*

A 1.47 M solution of triethyloxonium tetrafluoroborate [96] in dichloromethane (1.5 mL; 2.16 mmol) was added to a solution of sulfinamide **3raa** (0.38 g; 1.8 mmol) in dichloromethane (18 mL) at −30 °C. After stirring at −30 °C for 16 h, 1M aqueous sodium hydroxide (10 mL) was added. The usual work-up with dichloromethane and flash chromatography (silica gel, pentane/dichloromethane, 80:20 to 0:100) yielded 5-methoxy-1-methyl-1*H*-indole **6raa** (0.12 g; 41%).

For other substrates, see the conditions and yields reported in table VI.

• *Typical procedure using boron trifluoride diethyl etherate*

Boron trifluoride etherate (0.3 mL; 2.4 mmol) was added to a solution of sulfinamide **3ca** (0.362 g; 2 mmol) in dichloromethane (20 mL) at −30 °C. After stirring at −30 °C for 30 min, 1M aqueous sodium hydroxide (5 mL) was added. The usual work-up with dichloromethane and flash chromatography (silica gel, pentane/dichloromethane/acetone, 50:50:0 to 0:98:2) yielded 5-methyl-1*H*-indole **6ca** (0.105 g; 40%), dimer **9ca** (0.104 g; 40%) and 4-methylbenzenamine (0.043 g; 20%).

For other substrates, see the conditions and yields reported in table VII.

• *Thermal procedure using trimethyl borate*

A solution of sulfinamide **3ca** (0.362 g; 2 mmol) and anhydrous trimethyl borate (0.83 g; 8 mmol) in toluene (20 mL) was treated at 85 °C for 1 h. The solvent was evaporated under reduced pressure and the crude product was dissolved in dichloromethane and washed with water. The usual work-up and purification by flash chromatography yielded 5-methyl-1*H*-indole **6ca** (0.208 g; 90%).

For other examples, see table IX.

• *1H-Indole* **6aa**

Mp = 52 °C; Lit [62]: mp = 52 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.10 (s large, 1H); 7.75–7.65 (m, 1H); 7.40–7.30 (m, 1H); 7.30–7.06 (m, 3H); 6.62–6.54 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 135.4 (s); 127.5 (s); 124.1 (d); 121.6 (d); 120.4 (d); 119.5 (d); 110.9 (d); 102.1 (d).

MS (EI); *m/z*: 117 (M^+, 100); 90 (45); 89 (45); 63 (42); 58 (40).

• *1-Methyl-1H-indole* **6aaa** *[63]*

IR (KBr, cm^{-1}): 1 610, 1 510, 1 460, 1 330, 1 320, 1 245, 770, 745.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.61 (dd, J = 7.91 and 0.87 Hz, 1H); 7.32–7.04 (m, 3H); 6.99 (d, J = 3.1 Hz, 1H); 6.46 (d, J = 3.1 Hz, 1H); 3.72 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 136.7 (s); 128.8 (d); 128.5 (s); 121.5 (d); 120.9 (d); 119.3 (d); 109.2 (d); 100.9 (d); 32.8 (q).

MS (CI, NH_3); *m/z*: 132 (M^+ + 1, 100); 131 (M^+, 15); 108 (2); 70 (3).

• *2-Methyl-1H-indole* **6ab**

Mp = 57–58 °C; Lit [64]: mp = 59–60 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.9–7.8 (m, 1H); 7.58–7.5 (m, 1H); 7.34–7.26 (m, 1H); 7.20–7.06 (m, 2H); 6.30–6.22 (m, 1H); 2.43 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 136.2 (s); 134.9 (s); 129.2 (s); 121.0 (d); 119.7 (d); 119.7 (d); 110.2 (d); 100.5 (d); 13.6 (q).

MS (EI); *m/z*: 131 (M^+, 65); 130 (100); 104 (7); 103 (14); 102 (11) 89 (10); 77 (20).

• *3-Butyl-1H-indole* **6ae**

Oil; Lit [65]: bp_1 = 130 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.8 (m, 1H); 7.75–7.65 (m, 1H); 7.4–7.3 (m, 1H); 7.3–7.0 (m, 2H); 7.0–6.9 (m, 1H); 2.70 (t, J = 7 Hz, 2H); 1.8–1.4 (m, 2H); 1.4–1.1 (m, 2H); 0.93 (t, J = 7 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 136.0 (s); 128.0 (s); 121.6 (d); 121.5 (d); 118.9 (d); 118.6 (d); 116.6 (s); 110.9 (d); 31.5 (t); 30.0 (t); 21.5 (t); 13.2 (q).

MS (CI, NH_3); *m/z*: 174 (M^+ + 1, 100).

• *2,3-Diethyl-1H-indole* **6af**

Oil; Lit [66]: mp = 29 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8 (s large, 1H); 7.6–7.5 (m, 1H); 7.5–7.25 (m, 1H); 7.2–7.0 (m, 2H); 2.9–2.7 (m, 4H); 1.4–1.2 (m, 6H).

MS (CI, NH_3); *m/z*: 175 (M^+ + 2, 11); 174 (M^+ + 1, 100).

• *2-Phenyl-1H-indole* **6ag**

Mp = 186.5–188 °C (pentane/CH_2Cl_2); Lit [67a]: mp = 186 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.33 (s large, 1H); 7.72–7.61 (m, 3H); 7.50–7.08 (m, 6H); 6.84 (d, J = 1.5 Hz, 1H); [67b].

^{13}C NMR (62 MHz, $CDCl_3$) δ: 137.9 (s); 136.8 (s); 132.4 (s); 129.3 (s); 129.0 (d); 127.7 (d); 125.1 (d); 122.3 (d); 120.7 (d); 120.3 (d); 110.9 (d); 100.0 (d); [67c].

• *7-Methyl-1H-indole* **6ba**

Mp = 86 °C; Lit [68, 65]: mp = 84–85 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.9 (m, 1H); 7.5–7.4 (m, 1H); 7.15–6.9 (m, 3H); 6.52–6.48 (m, 1H); 2.4 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 135.6 (s); 127.3 (s); 123.8 (d); 122.4 (d); 120.1 (s); 119.9 (d); 118.4 (d); 103.0 (d); 16.6 (q).

MS (EI); *m/z*: 131 (M^+, 90); 130 (100); 77 (28).

• *5-Methyl-1H-indole* **6ca**

Mp = 59 °C; Lit [65, 69]: mp = 56–58 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.42–7.38 (m, 1H); 7.46–7.32 (m, 1H); 7.08–6.96 (m, 2H); 6.88–6.80 (m, 1H); 6.44–6.36 (m, 1H); 2.42 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 133.8 (s); 128.7 (s); 127.8 (s); 124.1 (d); 123.3 (d); 120.1 (d); 110.5 (d); 101.7 (d); 21.5 (q).

MS (EI); *m/z*: 131 (M^+, 87); 130 (100); 78 (37); 63 (22); 51 (37).

• *1,5-Dimethyl-1H-indole* **6caa**

Oil; Lit [70]: bp_{17} = 138 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.42–7.38 (m, 1H); 7.12 (dd, J = 8.5 and 0.5 Hz, 1H); 7.02 (dd, J = 8.5 and 1 Hz, 1H); 6.86 (d, J = 3 Hz, 1H); 6.36 (dd, J = 3 and 1 Hz, 1H); 3.56 (s, 3H); 2.42 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 134.8 (s); 128.4 (s); 128.4 (d); 127.9 (s); 122.8 (d); 120.2 (d); 108.6 (d); 100.1 (d); 32.6 (q); 21.5 (q).

MS (EI); *m/z*: 145 (M^+, 90); 144 (100); 128 (20); 77 (18); 64 (97).

• *5-Methyl-1-(phenylmethyl)-1H-indole* **6cab**

Oil [71].

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.5–7.35 (m, 5H); 7.35–7.25 (m, 1H); 7.1 (dd, J = 8.5 and 0.5 Hz, 1H); 6.98 (dd, J = 8.5 and 1 Hz, 1H); 6.9 (d, J = 3 Hz, 1H); 6.35 (dd, J = 3 and 1 Hz, 1H); 5.16 (s, 2H); 2.46 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 137.7 (s); 134.7 (s); 129.0 (s); 128.8 (s); 128.8 (d); 128.2 (d); 127.4 (d); 126.6 (d); 122.2 (d); 120.6 (d); 109.3 (d); 101.0 (d); 50.0 (t); 21.3 (q).

MS (EI); *m/z*: 221 (M^+, 17); 91 (100); 65 (32).

Anal calc for $C_{16}H_{15}N$: C 86.84; H 6.83; N 6.33. Found: C 86.79; H 6.90; N 6.31.

• *2,5-Dimethyl-1H-indole* **6cb**

Mp = 112 °C; Lit [72]: mp = 114–115 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.46–7.38 (m, 1H); 7.32–7.28 (m, 1H); 7.10–7.0 (m, 1H); 7.0–6.9 (m, 1H); 6.14–6.08 (m, 1H); 2.43 (s, 3H); 2.3 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 134.9 (s); 134.1 (s); 129.0 (s); 128.4 (s); 122.1 (d); 119.1 (d); 109.8 (d); 99.6 (d); 21.6 (q); 13.6 (q).

MS (EI); *m/z*: 145 (M^+, 80); 140 (100); 130 (23); 115 (17).

• *3-Butyl-5-methyl-1H-indole* **6cc**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.78 (s large, 1H); 7.43 (s, 1H); 7.27 (d, J = 8.5 Hz, 1H); 7.1 (dd, J = 8.5 and 1.3 Hz, 1H); 6.95 (d, J = 2.2 Hz, 1H); 2.76 (t, J = 7.8 Hz,

2H); 2.5 (s, 3H); 1.7–1.6 (m, 2H); 1.5–1.4 (m, 2H); 0.9 (t, J = 7.3 Hz, 3H) [73].

^{13}C NMR (62 MHz, $CDCl_3$) δ: 134.7 (s); 128.2 (s); 127.9 (s); 123.4 (d); 121.3 (d); 118.7 (d); 116.6 (s); 110.8 (d); 32.5 (t); 24.9 (t); 22.8 (t); 21.6 (q); 14.1 (q).

• *2,3-Diethyl-5-methyl-1*H*-indole* **6cd**

Oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.7 (s large, 1H); 7.55 (d, J = 11 Hz, 1H); 7.3–7.2 (m, 1H); 7.1 (d, J = 8 Hz, 1H); 2.9–2.7 (m, 4H); 2.6 (s, 3H); 1.5–1.2 (m, 6H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 136.2 (s); 133.5 (s); 128.7 (s); 128.1 (s); 122.3 (d); 118.0 (d); 112.7 (s); 110.0 (d); 21.6 (q); 19.4 (t); 17.3 (t); 15.8 (q); 14.5 (q).

MS (CI, NH_3); m/z: 189 (M^+ + 2, 17); 188 (M^+ + 1, 100).

Anal calc for $C_{13}H_{17}N$: C 83.37; H 9.15; N 7.48. Found: C 83.42; H 9.11; N 7.47.

• *5-Methyl-2-phenyl-1*H*-indole* **6ce** *[74]*

IR (KBr. cm^{-1}): 3 425, 1 600, 1 450, 1 320, 805. 765.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.24 (s large, 1H); 7.68–7.60 (m, 2H); 7.48–7.38 (m, 3H); 7.35–7.26 (m, 2H); 7.05–6.97 (m, 1H); 6.75 (d, J = 1.78 Hz, 1H); 2.43 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 137.5 (s); 135.2 (s); 132.5 (s); 129.5 (s); 129.4 (s); 129.0 (d); 127.5 (d); 125.0 (d); 124.0 (d); 120.3 (d); 110.5 (d); 99.5 (d); 21.4 (q).

• *1*H*-Benz[g]indole* **6da**

Mp = 172 °C; Lit [75]: mp = 179 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 9.02–8.9 (m, 1H); 8.04 (dd, J = 8 and 1.1 Hz, 1H); 7.98 (dd, J = 8 and 1.1 Hz, 1H); 7.77 (d, J = 9 Hz, 1H); 7.57 (ddd, J = 8, 7.5 and 1.1 Hz, 1H); 7.56 (d, J = 9 Hz, 1H); 7.47 (ddd, J = 8, 7.5 and 1 Hz, 1H); 7.32 (dd, J = 3 and 3 Hz, 1H); 6.74 (dd, J = 3 and 2 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 130.5 (s); 130.5 (s); 128.9 (s); 125.4 (d); 123.9 (s); 123.5 (d); 122.2 (d); 121.8 (d); 120.8 (d); 120.8 (d); 119.3 (d); 104.3 (d).

MS (EI); m/z: 168 (M^+ + 1, 17); 167 (M^+, 100); 166 (24); 140 (15); 139 (31).

• *5-Fluoro-1*H*-indole* **6ea**

Mp = 43 °C; Lit [76]: mp = 46–47 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.2–8.1 (m, 1H); 7.35–7.15 (m, 3H); 7.0–6.85 (m, 1H); 6.52–6.44 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 158.8 (s, J_{CF} = 230 Hz); 132.2 (s); 128.0 (s, J_{CF} = 10 Hz); 126.1 (d); 111.7 (d, J_{CF} = 10 Hz); 110.1 (d, J_{CF} = 30 Hz); 105.2 (d, J_{CF} = 25 Hz); 102.4 (d).

MS (EI); m/z: 135 (M^+, 100); 108 (56); 107 (45).

• *7-Chloro-1*H*-indole* **6fa**

Mp = 55 °C; Lit [77]: mp = 57–58 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.1–7.9 (m, 1H); 7.15–7.0 (m, 3H); 6.86–6.8 (m, 1H); 6.56–6.5 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 135.4 (s); 128.8 (s); 125.1 (d); 121.3 (d); 120.4 (d); 118.1 (d); 117.7 (s); 101.7 (d).

MS (EI); m/z: 143 (M^+, 33); 141 (100); 116 (25).

• *6-Chloro- and 4-chloro-1*H*-indoles* **6ga** *and* **6′ga** *[64b, 77b, 78]*

Inseparable mixture.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.4–8.0 (m, 2H); 7.6–7.5 (m, 1H); 7.4–7.3 (m, 1H); 7.3–7.1 (m, 6H); 6.8–6.7 (m, 1H); 6.6–6.5 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 136.2 (s); 135.8 (s); 127.3 (s); 126.4 (s); 126.1 (s); 125.5 (s); 125.0 (d); 124.8 (d); 122.3 (d); 121.3 (d); 120.2 (d); 119.3 (d); 110.8 (d); 109.7 (d); 102.2(d); 100.6 (d).

• *5-Chloro-1*H*-indole* **6ha**

Mp = 69 °C; Lit [79]: mp = 72–73 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.12–8.0 (m, 1H); 7.64–7.58 (m, 1H); 7.22–7.04 (m, 3H); 6.52–6.44 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 133.9 (s); 128.7 (s); 125.3 (d); 125.1 (s); 122.0 (d); 119.8 (d); 111.8 (d); 102.0 (d).

MS (EI); m/z: 143 (M^+, 33); 141 (100); 116 (18); 89 (30).

• *5-Chloro-1-methyl-1*H*-indole* **6haa** *[80]*

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.64 (dd, J = 2 and 0.8 Hz, 1H); 7.24–7.16 (m, 2H); 7.07 (d, J = 3 Hz, 1H); 6.45 (dd, J = 3 and 1 Hz, 1H); 3.72 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 135.0 (s); 130.0 (d); 129.3 (s); 124.9 (s); 121.7 (d); 120.0 (d); 110.1 (d); 100.5 (d); 32.8 (q).

MS (EI); m/z: 167 (M^+, 33); 166 (20); 165 (100); 164 (60).

• *5-Chloro-2-methyl-1*H*-indole* **6hb**

Mp = 129 °C; Lit [69]: mp = 99–100.5 °C; [64a]: mp = 117–119 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.8 (m, 1H); 7.47 (d, J = 2 Hz, 1H); 7.2 (d, J = 7 Hz, 1H); 7.06 (dd, J = 7 and 2 Hz, 1H); 6.2–6.16 (m, 1H); 2.45 (s large, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 136.6 (s); 134.3 (s); 130.1 (s); 125.2 (s); 121.1 (d); 119.0 (d); 111.1 (d); 100.2 (d); 13.7 (q).

MS (CI); m/z: 169 (M^+ + 2, 3); 168 (M^+ + 2, 27); 167 (M^+ + 1, 12); 166 (M^+ + 1, 100).

• *3-Butyl-5-chloro-1*H*-indole* **6hc**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8 (s, 1H); 7.3–6.9 (m, 3H); 2.7 (t, J = 7.7 Hz, 2H); 1.7–1.6 (m, 2H); 1.5–1.3 (m, 2H); 0.9 (t, J = 7 Hz, 3H).

Anal calc for $C_{12}H_{14}ClN$: C 69.39; H 6.79; N 6.74. Found: C 69.44; H 6.87; N 6.59.

• *5-Chloro-2,3-diethyl-1*H*-indole* **6hd** *[81]*

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8 (s large, 1H); 7.5 (d, J = 1.8 Hz, 1H); 7.2 (d, J = 10.5 Hz, 1H); 7.0 (dd, J = 8.4 and 1.9 Hz, 1H); 2.8–2.6 (m, 4H); 1.3–1.2 (m, 6H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 137.6 (s); 133.5 (s); 129.6 (s); 124.6 (s); 120.9 (d); 117.7 (d); 113.1 (s); 111.1 (d); 19.3 (t); 17.1 (t); 15.6 (q); 14.2 (q).

MS (CI, NH_3); m/z: 211 (M^+ + 2, 4); 210 (M^+ + 2, 27); 209 (M^+ + 1, 17); 208 (M^+ + 1, 100).

• *6,7-Dichloro-1*H*-indole* **6ia** *[82]*

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.2–8.0 (m, 1H); 7.15–7.05 (m, 2H); 6.83–6.75 (m, 1H); 6.5–6.4 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 137.2 (s); 126.9 (s); 126.2 (s); 125.2 (d); 120.2 (d); 119.4 (d); 114.5 (s); 101.9 (d).

MS (EI); m/z: 189 (M^+, 12); 187 (70); 185 (100); 150 (42); 115 (35).

• *4,6-Dichloro-1*H*-indole* **6la**

Oil; Lit [83]: bp_4 = 130–132 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.2–8.0 (m, 1H); 7.2–7.1 (m, 3H); 6.63–6.58 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 135.9 (s); 127.3 (s); 126.1 (s); 125.2 (d); 124.8 (s); 119.8 (d); 109.6 (d); 101.2 (d).

MS (EI); m/z: 189 (M^+, 12); 187 (70); 185 (100); 150 (50); 125 (65); 123 (65); 115 (30); 114 (33).

• *6-Bromo- and 4-bromo-1*H*-indoles* **6ma** *and* **6′ma** *[64b, 83, 84]*

Inseparable mixture.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.95–7.75 (m, 1H); 7.75–7.55 (m, 1H); 7.45–7.35 (m, 1H), 7.3–7.05 (m, 3H); 7.0–6.85 (m, 2H); 6.55–6.45 (m, 1H); 6.45–6.35 (m, 1H).

• *5-Bromo-1*H*-indole* **6na**

Mp = 89 °C; Lit [85]: mp = 90–92 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.08–7.98 (m, 1H); 7.70–7.64 (m, 1H); 7.2–7.04 (m, 3H); 6.45–6.38 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 134.1 (s); 129.3 (s); 125.2 (d); 124.5 (d); 122.9 (d); 112.7 (s); 112.3 (d); 102.0 (d).

MS (EI); m/z: 197 (M^+, 93); 195 (94); 116 (100); 89 (55).

• *5-Iodo-1*H*-indole* **6oa**

Mp = 89 °C; Lit [86]: mp = 99–100 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.2–8.1 (m, 1H); 8.0–7.94 (m, 1H); 7.5–7.4 (m, 1H); 7.2–7.1 (m, 2H); 6.5–6.44 (m, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 134.8 (s); 130.5 (s); 130.2 (d); 129.4 (d); 125.0 (d); 112.3 (d); 101.9 (d); 83.2 (s).

MS (EI); m/z: 243 (M^+, 85); 127 (15); 116 (100); 89 (35).

• *7-Methoxy-1*H*-indole* **6pa**

Oil; Lit [87]: $bp_{0.2}$ = 108–110 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.4–8.3 (m, 1H); 7.3–7.22 (m, 1H); 7.18–7.1 (m, 1H); 7.1–7.0 (m,1H); 6.68–6.6 (m, 1H); 6.55–6.5 (m, 1H); 3.96 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 146.1 (s); 129.2 (s); 126.4 (s); 123.7 (d); 120.1 (d); 113.4 (d); 102.7 (d); 101.7 (d); 55.2 (q).

MS (EI); m/z: 147 (M^+, 100); 132 (63); 104 (72).

• *6-Methoxy-1*H*-indole* **6qa**

Mp = 91 °C; Lit [64b, 77b]: mp = 91–92 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.9 (m, 1H); 7.56–7.48 (m, 1H); 7.06–7.0 (m,1H); 6.85–6.75 (m, 1H); 6.5–6.45 (m, 1H); 3.82 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 155.8 (s); 136.2 (s); 123.0 (d); 121.9 (s); 120.9 (d); 109.6 (d); 101.9 (d); 94.5 (d) 55.6 (q).

MS (CI, NH_3); m/z: 148 (M^+ + 1, 100).

• *4-Methoxy-1*H*-indole* **6′qa**

Mp = 65 °C; Lit [64b, 77b, 83]: mp = 67–69 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.15–8.05 (m, 1H); 7.15–6.95 (m, 3H); 6.65–6.6 (m, 1H); 6.55–6.45 (m, 1H); 3.90 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.5 (s); 137.3 (s); 122.8 (d); 122.6 (s); 118.7 (d); 104.5 (d); 99.9 (d); 99.7 (d) 55.3 (q).

MS (EI); m/z: 147 (M^+, 100); 132 (75); 104 (60).

• *5-Methoxy-1*H*-indole* **6ra**

Mp = 53 °C; Lit [77b]: mp = 54–55 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.15–8.00 (m, 1H); 7.26 (d, J = 8.8 Hz, 1H); 7.18 (t, J = 2.8 Hz, 1H); 7.12 (d, J = 2.4 Hz, 1H); 6.86 (dd, J = 8.8 and 2.4 Hz, 1H); 6.50–6.46 (m, 1H); 3.86 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 154.1 (s); 131.0 (s); 128.2 (s); 125.0 (d); 112.2 (d); 111.7 (d); 102.6 (d); 102.1 (d); 55.8 (q).

MS (EI); m/z: 147 (M^+, 100); 132 (80); 104 (63); 78 (17); 51 (32).

• *5-Methoxy-1-methyl-1*H*-indole* **6raa**

Mp = 95–96.5 °C (pentane/CH_2Cl_2); Lit [88a,b]: mp = 103–104 °C.

IR (KBr, cm^{-1}): 1 625, 1 500, 1 420, 1 250, 1 105, 1 030, 805, 730.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.25–7.17 (m, 1H); 7.10 (d, J = 2.41 Hz, 1H); 7.03 (d, J = 3.03 Hz, 1H); 6.89 (dd, J = 8.76 and 2.41 Hz, 1H); 6.40 (d, J = 3.03 Hz, 1H); 3.85 (s, 3H); 3.75 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.9 (s); 132.0 (s); 129.3 (d); 128.9 (s); 111.8 (d); 109.9 (d); 102.4 (d); 100.3 (d); 55.8 (q); 32.9 (q).

MS (CI, NH_3); m/z: 162 (M^+ + 1, 30); 161 (M^+, 100); 146 (87); 118 (99); 103 (15).

• *1-Ethyl-5-methoxy-1*H*-indole* **6rab** *[89]*

Mp = 64.5–65 °C (pentane/CH_2Cl_2).

IR (KBr, cm^{-1}): 1 625, 1 580, 1 500, 1 250, 1 160, 1 035.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.30–7.22 (m, 1H); 7.14–7.08 (m, 2H); 6.89 (dd, J = 8.95 and 2.45 Hz, 1H); 6.43 (d, J = 2.98 Hz, 1H); 4.16 (q, J = 7.3 Hz, 2H); 3.88 (s, 3H); 1.47 (t, J = 7.3 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.9 (s); 131.1 (s); 129.0 (s); 127.5 (d); 111.7 (d); 110.0 (d); 102.6 (d); 100.5 (d); 55.9 (q); 41.1 (t); 15.5 (q).

MS (CI, NH_3); m/z: 176 (M^+ + 1, 100); 175 (M^+, 8); 160 (5); 152 (2).

• *5-Methoxy-2-methyl-1*H*-indole* **6rb**

Mp = 65 °C; Lit [90]: mp = 69 °C.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8–7.7 (m, 1H); 7.18 (d, J = 9 Hz, 1H); 7.02 (d, J = 2.5 Hz, 1H); 6.77 (dd, J = 9 and 2.5 Hz, 1H); 6.18–6.15 (s large, 1H); 3.86 (s, 3H); 2.44 (s large, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 154.1 (s); 136.0 (s); 131.2 (s); 129.5 (s); 110.8 (d); 110.6 (d); 101.9 (d); 100.2 (d); 55.9 (q); 13.7 (q).

• *3-Butyl-5-methoxy-1*H*-indole* **6rc**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.9 (s large, 1H); 7.3 (d, J = 8.7 Hz, 1H); 7.2 (d, J = 2.2 Hz, 1H); 7.0–6.9 (m, 2H); 4.0 (s, 3H); 2.8 (t, J = 7.7 Hz, 2H); 1.9–1.7 (m, 2H); 1.6–1.5 (m, 2H); 1.1 (t, J = 7.3 Hz, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.7 (s); 131.5 (s); 128.0 (s); 121.9 (d); 116.8 (s); 111.8 (d); 111.6 (d); 101.0 (d); 55.9 (q); 32.2 (t); 24.8 (t); 22.6 (t); 13.9 (q).

MS (EI); m/z: 203 (M^+, 100); 188 (3); 145 (26); 130 (11); 117 (29).

Anal calc for $C_{13}H_{17}NO$: C 76.81; H 8.43; N 6.89. Found: C 77.03; H 8.31; N 7.01.

• *2,3-Diethyl-5-methoxy-1*H*-indole* **6rd**

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.8 (s large, 1H); 7.2 (d, J = 9 Hz, 1H); 7.0 (d, J = 3 Hz, 1H); 6.8 (dd, J = 9 and 2 Hz, 1H); 3.9 (s, 3H); 2.8–2.7 (m, 4H); 1.3–1.2 (m, 6H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.7 (s); 137.2 (s); 130.4 (s); 128.8 (s); 112.7 (s); 111.0 (d); 110.3 (d); 100.8 (d); 56.0 (q); 19.4 (t); 17.3 (t); 15.6 (q); 14.4 (q).

MS (CI, NH_3); m/z: 205 (M^+ + 2, 21); 204 (M^+ + 1, 100).

• *5-Methoxy-2-phenyl-1H-indole* **6re**

Mp = 165.5–167 °C (pentane/CH_2Cl_2); Lit [90]: mp = 166 °C; [91]: mp = 168 °C; [92]: mp = 154 °C.

IR (KBr, cm^{-1}): 3 420, 1 620, 1 590, 1 480, 1 450, 1 220, 1 155, 850, 770.

^1H NMR (250 MHz, $CDCl_3$) δ: 8.22 (s large, 1H); 7.70–7.58 (m, 2H); 7.74–7.26 (m, 4H); 7.09 (d, J = 2.29 Hz, 1H); 6.85 (dd, J = 8.85 and 2.29 Hz, 1H); 6.75 (d, J = 1.58 Hz, 1H); 3.86 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 154.5 (s); 138.6 (s); 132.4 (s); 132.0 (s); 129.7 (s); 129.0 (d); 127.6 (d); 125.0 (d); 112.6 (d); 111.6 (d); 102.3 (d); 99.8 (d); 55.8 (q).

MS (CI, NH_3); m/z: 224 (M^+ + 1, 100); 180 (3).

• *5-Methoxy-1-methyl-2-phenyl-1H-indole* **6rea**

Mp = 120–122 °C; Lit [93]: mp = 124–125 °C.

^1H NMR (250 MHz, $CDCl_3$) δ: 7.54–7.45 (m, 5H); 7.30–7.22 (m, 1H); 7.10 (d, J = 2.43 Hz, 1H); 6.91 (dd, J = 8.8 and 2.43 Hz, 1H); 6.49 (s, 1H); 3.87 (s, 3H); 3.72 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 169.0 (s); 154.4 (s); 142.4 (s); 133.8 (s); 132.9 (s); 129.3 (d); 128.5 (d); 127.8 (d); 111.9 (d); 110.3 (d); 102.2 (d); 101.3 (d); 55.9 (q); 31.3 (q).

Estimated rates for thermal conversions **3** → **6**

The procedure is described in the theoretical section and no fresh solvent was added during the distillation. For each sample, the solvent was evaporated under reduced pressure and the ratios sulfinamides:indole:arenamines were estimated from ^1H NMR spectra of the crude residues by way of the following characteristic signals: for sulfinamide **3aa**: 6.8 (dd, J = 17 and 10 Hz, 1H); 6.25 (d, J = 17 Hz, 1H); 6.02 (d, J = 10 Hz, 1H); for indole **6aa**: 7.75–7.65 (m, 1H) and 6.62–6.54 (m, 1H); for sulfinamide **3ca**: 2.28 (s, 3H); for indole **6ca**: 2.42 (s, 3H); for amine **1c**: 2.20 (s, 3H); for sulfinamide **3ha**: 6.8 (dd, J = 17 and 10 Hz, 1H); 6.26 (d, J = 17 Hz, 1H); 6.04 (d, J = 10 Hz, 1H); for indole **6ha**: 6.52–6.44 (m, 1H); for amine **1h**: 6.70–6.60 (m, 2H); for sulfinamide **3ra**: 3.78 (s, 3H); for indole **6ra**: 3.84 (s, 3H); for amine **1r**: 3.75 (s, 3H).

Experiments on crossing reactions and transaminations

Entry 112: A solution of sulfinamides **3aa** (0.188 g; 1.13 mmol) and **3re** (0.308 g; 1.13 mmol) in anhydrous toluene (23 mL) was heated at atmospheric pressure and the solvent was slowly distilled for 1 h with concomitant slow addition of fresh toluene. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography yielding a fraction (0.209 g) containing a mixture of the indoles **6ra** and **6re** (^1H NMR: ratios ≈ 50:50).The identity of these two indoles was confirmed by comparison of their retention times (HPLC) with these of authentic compounds **6aa**, **6ag**, **6ra** and **6re**.

Entry 114: A solution of sulfinamide **3aa** (0.167 g; 1 mmol) and 4-methoxybenzenamine (0.123 g; 1 mmol) in toluene (20 mL) was treated as above (entry 112). Flash chromatography yielded 5-methoxyindole **6ra** (0.78 g; 53%) and 4-methoxybenzenamine (0.042 g; 34%).

Entry 115: A solution of sulfinamide **3aa** (0.167 g; 1 mmol) and 4-methoxybenzenamine **1r** (0.123 g; 1 mmol) in dichloromethane (8 mL) was stirred at room temperature for 4 h. Flash chromatography of the crude product yielded firstly a fraction (0.164 g) containing the sulfinamides **3aa** and **3ra** (^1H NMR), then a fraction (0.09 g) which was the amine **1r**. The final yields are reported in table V.

Entry 116: A solution of sulfinamide **8a** (0.169 g; 1 mmol) and 4-methoxybenzenamine **1r** (0.123 g; 1 mmol) in toluene (20 mL) was heated at 60 °C for 2 h. Flash chromatography gave first a fraction (0.139 g) containing both the sulfinamides **8a** and **8b** (^1H NMR) then two fractions (0.065 g) containing amines **1r** and **1c**.

• *S-(4-Methylphenyl)-4-methylbenzene-1-thiosulfonate* **7**

Mp = 70–72 °C; Lit [94]: mp = 76 °C.

The ^1H NMR spectrum (250 MHz) was identical with that described previously [95].

• *N-(4-Methylphenyl)methanesulfinamide* **8a**

Mp = 113–114 °C; Lit [12]: mp = 113–115 °C.

^1H NMR (250 MHz, $CDCl_3$) δ: 7.12–7.01 (m, 2H); 7.01–6.89 (m, 2H); 6.72 (broad s, 1H); 2.8 (s, 3H); 2.29 (s, 3H).

• *N-(4-Methoxyphenyl)methanesulfinamide* **8b**

Prepared following a described procedure [12].

Mp = 107–108 °C.

^1H NMR (250 MHz, $CDCl_3$) δ: 7.06–6.97 (m, 2H); 6.84–6.76 (m, 3H); 3.78 (s, 3H); 2.78 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 156.4 (s); 133.5 (d); 122.0 (s); 114.6 (d); 55.5 (q); 41.9 (q).

MS (CI, NH_3); m/z: 203 (M^+ + 18, 10); 187 (M^+ + 2, 8); 186 (M^+ + 1, 69); 140 (20); 124 (26); 123 (100); 122 (68).

Anal calc for $C_8H_{11}NO_2S$: C 51.87; H 5.98; N 7.56. Found: C 51.78; H 6.02; N 7.73.

• *5-Methyl-3-(5-methylindolin-2-yl)-1H-indole* **9ca**

Mp = 129 °C (ether).

^1H NMR (250 MHz, $CDCl_3$) δ: 7.9–7.82 (broad s, 1H); 7.41 (broad s, 1H); 7.28–7.22 (m, 1H); 7.15–7.10 (m, 1H); 7.08–7.0 (m, 1H); 6.98 (broad s, 1H); 6.9–6.82 (m, 2H); 6.58 (d, J = 7 Hz, 1H); 5.2 (t, J = 9 Hz, 1H); 3.4 (dd, J = 15 and 9 Hz, 1H); 3.2 (dd, J = 15 and 9 Hz, 1H); 2.42 (s, 3H); 2.28 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 148.7 (s); 135.1 (s); 129.4 (s); 128.8 (s); 128.1 (s); 127.7 (d); 126.1 (s); 125.5 (d); 123.9 (d); 121.3 (d); 119.2 (d); 118.9 (s); 110.9 (d); 109.2 (d); 56.8 (d); 37.7 (t); 21.5 (q); 20.8 (q).

MS (EI); m/z: 262 (M^+, 52); 247 (9); 131 (100); 130 (72); 122 (37); 121 (42); 103 (11).

Anal calc for $C_{18}H_{18}N_2$: C 82.40; H 6.91; N 10.68. Found: C 82.45; H 6.86; N 10.68.

• *5-Methoxy-3-(5-methoxyindolin-2-yl)-1H-indole* **9ra**

Mp = 154 °C (ether).

^1H NMR (250 MHz, $CDCl_3$) δ: 8.0–7.9 (broad s, 1H); 7.3–7.2 (m, 2H); 7.15–7.10 (m, 1H); 6.94–6.8 (m, 2H); 6,7–6.6 (m, 2H); 5.19 (dd, J = 9 and 9 Hz, 1H); 3.76 (s, 3H); 3.72 (s, 3H); 3.48 (dd, J = 15 and 9 Hz, 1H); 3.2 (dd, J = 15 and 9 Hz, 1H).

^{13}C NMR (62 MHz, $CDCl_3$) δ: 153.9 (s); 153.6 (s); 144.8 (s); 131.8 (s); 130.7 (s); 125.9 (s); 122.0 (d); 119.4 (s); 112.6 (d); 112.4 (d); 112.0 (d); 111.5 (d); 109.9 (d); 101.3 (d); 56.8 (d); 56.0 (q); 55.7 (q); 37.9 (t).

MS (EI); m/z: 294 (M^+, 23); 279 (8); 147 (100); 132 (75); 104 (77).

Anal calc for $C_{18}H_{18}N_2O_2$: C 73.44; H 6.16; N 9.52. Found: C 73.55; H 6.06; N 9.48.

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