Efficient Syntheses of New CF_3-containing Diazolopyrimidines

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Abstract: A new simple and efficient way to CF_3-containing pyrimido[1,2-*a*]benzimidazole and pyrazolo[1,5-*a*]pyrimidines, by the reaction of 1,1,1-trifluoro-4-sulfonyl-but-3-ene-2,2-dioles **1a**,**b** with aminoheterocycles is described. The influence of reaction conditions and nature of the aminoheterocycles on regiochemistry was investigated.

Key words: cycloaddition, heterocycles, pyrimido[1,2-*a*]benzimidazole, pyrazolo[1,5-*a*]pyrimidines, sulfones

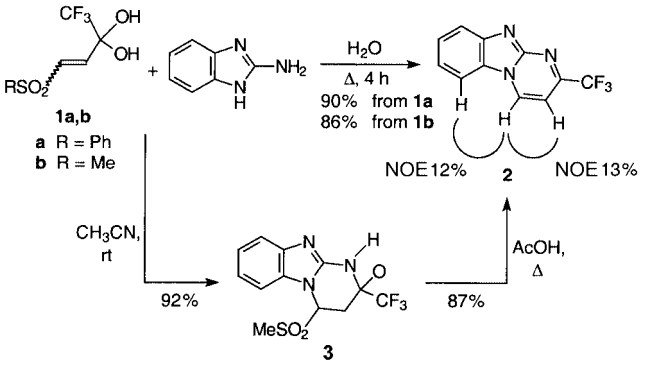
The synthesis of condensed pyrazoles has recently been reviewed.[1,2] The development of new methods for the synthesis of trifluoromethyl-substituted pyrimidines and condensed cyclic derivatives is a topic of current interest[3–5] because of their activity as herbicides[6] and plant growth regulators.[7] The substitution pattern of the azolopyrimidine greatly influences the degree of activity and the mode of action, so it is important to develop syntheses with regioselective control. The reported methods for the synthesis of substituted azolopyrimidines usually involve cyclocondensation of aminoazoles with three carbon 1,3-electrophilic fragments such as β-ketoesters, β-diketones, β-ketoaldehydes, enolethers, acetal esters, ketoesters[8–16] or α,β-unsaturated carbonyl compounds.[1,16–19] A limitation of these approaches is the difficulty of establishing products resulting from reaction of non-symmetrical systems with aminopyrazoles. Several new pyrazolopyrimidines were synthesized via the reaction of aminopyrazoles with 3-dimethylaminopropiophenone and tetracyanoethene.[17] Some reactions involving regiospecific modification of initially prepared azolopyrimidines ring have also been developed recently.[12,18]

There is only a limited amount of literature on the regiospecific synthesis of 7- and 5-substituted azolopyrimidines. Therefore there is a definite need to develop new methods for the synthesis of this class of compounds.

We report now the results of our investigation of the reaction of 1,1,1-trifluoro-4-sulfonyl-but-3-ene-2,2-dioles **1a**,**b** with 2-amino-1*H*-benzimidazol and aminopyrazoles.

In recent work we have prepared some β-trifluoroacetylvinylsulfones by oxidation of the readily available sulfanes.[20] We have found that these alkenes **1a**,**b** are very powerful electrophiles, reacting with heteroarenes such as pyrrole, indole and furan.[21] Also, we have recently described a new simple and efficient regiospecific synthesis of 2-CF_3-imidazo[1,2-*a*]pyridines and 2-CF_3-imidazo[1,2-*a*]quinolines by the reaction of sulfones **1a**,**b** with various 2-aminopyridines and 2-aminoquinoline.[22] It was therefore considered that the reactivity of dioles **1a**,**b** with aminoazoles might result in improved regioselectivity yielding only one regioisomer.

The reaction of 2-amino-1*H*-benzimidazol with sulfones **1a**,**b** proceeds at room temperature in acetonitrile to give the cyclic product tetrahydropyrimido[1,2-*a*]benzimidazol-2-ol **3** in high yield. We investigated the possibility of the preparation of aromatic heterocycle **2** from the cycloadduct **3**. The best results were obtained under reflux in acetic acid. In this case tandem elimination of water and sulfinic acid take place to give cycloadduct **3** in 80% total yield from 2-aminobenzimidazole. We also found reaction conditions to perform a one-step procedure for the preparation of **2** from 2-amino-1*H*-benzimidazol and sulfones **1a,b** under reflux in water (Scheme 1).



Scheme 1

The molecular structure of heterocycles **2** and **3** were determined by spectroscopy and structure **2** was assigned by ^{1}H NMR on the basis of the double resonance and NOE.

To extend the scope of this reaction, we performed other condensations of **1a**,**b** with various aminopyrazoles as nucleophiles.

The treatment of sulfones **1a**,**b** with different 3-aminopyrazoles in acetic acid under reflux gave 7-CF_3 substituted cycloadducts **4a**–**m** accompanied by 5-trifluoromethyl compounds **5a**–**m** as minor isomers. The total yields of these reactions are almost quantitative (Scheme 2). It is worth mentioning, that in the case of aryl-substituted aminopyrazoles, the reaction proceeds regiospecifically to

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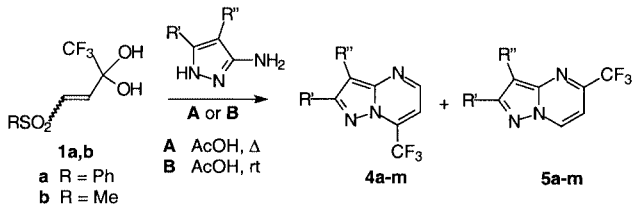
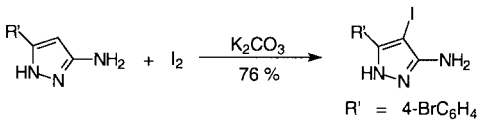
form compounds **4d**–**m** as the only regioisomer. However, 5-alkyl-3-aminopyrazoles under these conditions gave mixtures of the regioisomers **4a**–**c** and **5a**–**c**. Nevertheless, we succeded in providing regioselective formation of 7-CF_3 pyrazolopyrimidines of the more sterically hindered sulfone **1a** with 5-alkyl-3-aminopyrazoles at room temperature leading to regioselective formation of the 7-CF_3 substituted products. The worst ratio in the reaction with 2-amino-5-methylpyrazole was 100:3 and the pure 7-CF_3 substituted isomer, can be easily obtained by recrystallization from benzene (Table 1).



Scheme 2

Iodopyrazolopyrimidines are valuable compounds from biological and pharmaceutical points of view,[12,23] due to their specificificity in anxiolytic activity, being devoid of analgesic, anticonvulsant, or muscle-relaxant properties common to benzodiazepines.[23] Also they could be used in cross-coupling reactions to open up the possibility for the synthesis of analogues (3-position modification). Electrophilic substitution of pyrazolopyrimidines are well known,[12,15] but the treatment of these rings with iodine monochloride afforded the corresponding 3-iodopyrazolo[1,5-*a*]pyrimidines in low yield.[12] Thus, we initially developed a mild and efficient method for the synthesis of 3-amino-4-iodopyrazoles, by treatment of parent aminopyrazoles with iodine/potassium carbonate in water at room temperature (Scheme 3). Under these reaction conditions a model pyrazole was iodinated in 76% yield.



Scheme 3

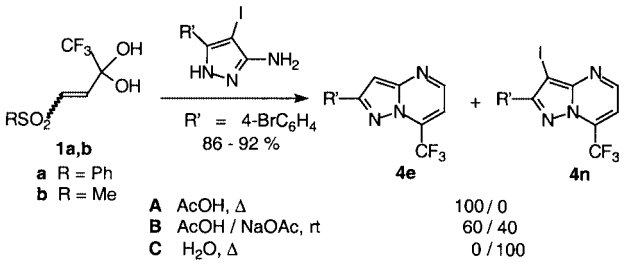
Surprisingly, in the reaction of sulfones **1a**,**b** with 5-(4-bromophenyl)-4-iodo-1*H*-pyrazol-3-amine in acetic acid

Table 1 Yields and Regioisomeric Ratio of Cycloadducts **4** and **5**

R'	R"	Entry	Method	from **1a**		from **1b**	
				4:**5** [a]	Yield, %	**4**:**5** [a]	Yield, %
CH_3	H	**a**	**A**	100 :15	86	100:35	80
			B	**100 :3**	84	100:20	76
cy-Pr	H	**b**	**A**	100:11	88	100:28	82
			B	**100:1**	80	100:15	78
t-Bu	H	**c**	**A**	100;5	94	100:14	84
			B	**100:0**	92	100:2	83
C_6H_5	H	**d**	**A**	100;0	94	100:0	90
			B	100:0	90	100:0	86
4-BrC_6H_4	H	**e**	**A**	100;0	95	100:0	92
2,4-diMeC_6H_3	H	**f**	**A**	100:0	92	-	-
4-MeC_6H_4	H	**g**	**A**	100:0	92	-	-
2-ClC_6H_4	H	**h**	**A**	100:0	92	-	-
4-$MeOC_6H_4$	H	**i**	**A**	100:0	92	-	-
4-$NO_2C_6H_4$	H	**j**	**A**	100:0	89	-	-
H	C_6H_5	**k**	**A**	100:0	93	100/0	88
H	4-ClC_6H_4	**l**	**A**	100:0	93	-	-
H	2-MeC_6H_4	**m**	**A**	100:9	90	100/21	91
			B	100:0	92	-	-

[a] Structure of products and ratios were determined by ^1H NMR.

under reflux only iodine free pyrazolopyrimidine **4e** was obtained in good yield instead of the expected product **4n**. At room temperature in the presence of sodium acetate the formation of a mixture of **4n** and **4e** was observed. Under neutral conditions - in water - the corresponding iodine product was successfully prepared in good yields (Scheme 4). This is due to the electrophilic substitution of iodine by hydrogen under acidic conditions.



Scheme 4

The reaction was found to be equivually facile for the synthesis of 2-, 3- and 2,3-disubstituted-7-(trifluoromethyl)pyrazolo[1,5-*a*]pyrimidine, when the corresponding aminopyrazoles were reacted with sulfones **1a**,**b** under analogous reaction conditions.

All results are in good agreement with literature data[1,17] that is, the ring nitrogen in aminopyrazoles is the most basic and the most hindered site in the molecule. Thus, the endocyclic nitrogen of azoles attacks the less hindered and most electrophilic carbonyl group of sulfones **1a**,**b**.

In summary, sulfones **1a**,**b** were shown to be excellent 1,3-bielectrophiles in their reaction with benzaminoimidazole and aminopyrazoles affording a one-stage synthesis of various diazolopyrimidine derivatives. A novel method for the preparation of iodine-substituted pyrazolopyrimidines for the synthesis of CF_3-containing azolopyrimidines was elaborated. The advantages of this novel method are the simple experimental layout, environmental friendly conditions, reasonable reaction times, regiospecific formation of target products and high yields (Table 2).

Melting points were determined in sealed capillaries and are uncorrected. NMR spectra were recorded on Varian VXR-400 spectrometer with TMS as an internal standard. The IR spectra were obtained with UR-20 spectrometer as films. Column chromatography was performed on silica gel (63–200 mesh, Merck). All solvents used were dried and distilled according to standard procedures. Silica gel Merck 60 and Merck $60F_{254}$ plates were used for conventional and analytical (TLC) chromatography, respectively.

2-(Trifluoromethyl)pyrimido[1,2-*a*]benzimidazole (2)
To a solution of vinylsulfone **1a,b** (1 mmol) in H_2O (20 mL) 1*H*-benzimidazol-2-amine (1 mmol) was added. The mixture was stirred 4 h under reflux. The precipitate was filtered off, washed with H_2O, and the residue was chromatographed with CH_2Cl_2.

4-(Methylsulfonyl)-2-(trifluoromethyl)-1,2,3,4-tetrahydropyrimido[1,2-*a*]benz-imidazol-2-ol (3)
To a solution of vinylsulfone **1b** (1 mmol) in CH_3CN (7 mL) 1*H*-benzimidazol-2-amine (1 mmol) was added. The mixture was stirred 12 h at r.t. The precipitate was filtered off, washed with CH_3CN (2×3 mL) and dried in the air.

Preparation of 2 from 3
4-(Methylsulfonyl)-2-(trifluoromethyl)-1,2,3,4-tetrahydropyrimido[1,2-*a*]benz-imidazol-2-ol (**3**) (1 mmol) was dissolved in glacial HOAc (10 mL). The mixture was stirred for 1 h under reflux. The solvent was evaporated under reduced pressure. The residue was chromatographed with CH_2Cl_2.

(Trifluoromethyl)pyrazolo[1,5-*a*]pyrimidine 4; General Procedure
To a solution of vinylsulfone **1a,b** (1 mmol) in HOAc (20 mL) the corresponding 1*H*-pyrazol-3-amine (1 mmol) was added. The mixture was stirred for an appropriate time under reflux (method **A**) or at r.t. (method **B**). The solvent was evaporated under reduced pressure and the residue chromatographed with CH_2Cl_2.

5-(4-Bromophenyl)-4-iodo-1*H*-pyrazol-3-amine
To a solution of 3-amino-5-(4-bromophenyl)-1*H*-pyrazol (1 mmol) in H_2O (20 mL) iodine (1.1 mmol) and K_2CO_3 (1.1 equiv) were added. The mixture was stirred at room temperature for 24 h. The brown precipitate formed was filtered off, washed with H_2O (2×20 mL), dried on air and the residue was chromatographed with CH_2Cl_2.

2-(4-Bromophenyl)-3-iodo-5-(trifluoromethyl)pyrazolo[1,5-*a*]pyrimidine (4n)
To a solution of vinylsulfone **1a**,**b** (1 mmol) in H_2O (20 mL) 3-amino-5-(4-bromophenyl)-4-iodo-1*H*-pyrazol (1 mmol) was added. The mixture was stirred under reflux 24 h. The precipitate formed was filtered off, dried on air, and chromatographed with CH_2Cl_2.

Acknowledgement

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Table 2 Analytical Data for Compounds **2** – **5**

^{1}H NMR (DMSO-d_6/TMS) δ, *J* (Hz)[a,b,c]	^{13}C NMR (DMSO-d_6/TMS) δ, *J* (Hz)[a]	mp, °C
2: 7.44 (d, 1 H, *J* = 7.0, CH-3), 7.50 (dd, 1 H, *J* = 7.1, 8.4, CH-7), 7.62 (dd, 1 H, *J* = 7.1, 8.3, CH-8), 7.92 (d, 1 H, *J* = 8.3, CH-9) , 8.34 (d, 1 H, *J* = 8.4, CH-6), 9.68 (d, 1 H, *J* = 7.0, CH-4)	**2**: 108.2 111.3, 124.4 (q, *J* = 286.6, CF_3), 125.6, 127.4, 131.6, 133.4, 142.2, 142.4, 147.9, 164.2 (q, *J* = 40.1, CF_3)	290–292
3: 2.91 (dd, 1 H, *J* = 7.0, 15.9, CH_2), 3.18 (s, 3 H, CH_3), 3.22 (br d, 1 H, *J* = 15.9, CH_2), 6.03 (br d, 1 H, *J* = 7.0, CH), 7.45–7.50 (m, 2 H, Ar), 7.60–7.64 (m, 1 H, Ar), 7.69–7.73 (m, 1 H, Ar)	**3**: 28.2, 40.8, 69.3, 79.8 (q, *J* = 37.3 Hz, C–OH), 113.4, 114.1, 123.8 (q, *J* = 385.4, CF_3), 126.0, 127.2, 129.6, 129.9, 147.3	244–246
4a: 2.48 (s, 3 H, CH_3), 6.62 (s, 1 H, CH-9), 7.19 (d, 1 H, *J* = 4.1, CH-6), 8.51 (d, 1 H, *J* = 4.1, CH-5) **5a**: 2.47 (s, 3 H, CH_3), 6.61 (s, 1 H, CH-9), 7.12 (d, 1 H, *J* = 7.3 Hz, CH-6), 8.85 (d, 1 H, *J* = 7.3, CH-7)	**4a** (major isomer): 14.8, 98.4, 105.5, 120.3 (q, *J* = 274.7, CF_3), 134.4 (q, *J* = 36.4, C-CF_3), 136.5, 148.4, 157.5	Oil
4b: 0.90–0.97 (m, 2 H, CH_2), 1.06–1.11 (m, 2 H, CH_2), 2.14–2.21 (m, 2 H, CH–cyPr), 6.45 (s, 1 H, CH-9), 7.01 (d, 1 H, *J* = 4.3, CH-6), 8.45 (d, 1 H, *J* = 4.3, CH-5) **5b**: 0.90–0.97 (m, 2 H, CH_2), 1.06–1.11 (m, 2 H, CH_2), 2.14–2.21 (m, 2 H, CH–cyPr), 6.50 (s, 1 H, CH-9), 6.98 (d, 1 H, *J* = 7.2, CH-6), 8.68 (d, 1 H, *J* = 7.2, CH-7)	**4b** (major isomer): 9.9, 10.1, 94.4, 105.2, 119.9 (q, *J* = 274.7, CF_3), 134.3 (q, *J* = 36.1, C-CF_3), 148.3, 151.1, 164.2	72–74
4c: 1.41 (s, 9 H, 3 × CH_3), 6.70 (s, 1 H, CH-9), 7.03 (d, 1 H, *J* = 4.2, CH-6), 8.48 (d, 1 H, *J* = 4.2, CH-5) **5c**: 1.41 (s, 9 H, 3 × CH_3), 6.75 (s, 1 H, CH-9), 7.00 (d, 1 H, *J* = 7.1, CH-6), 8.82 (d, 1 H, *J* = 7.1, CH-7)	**4c** (major isomer): 29.7, 32.4, 93.8, 104.6, 119.9 (q, *J* = 274.1 Hz, CF_3), 133.3 (q, *J* = 36.5 Hz, C–CF_3), 147.9, 150.4, 169.4	131–133
4d: 7.25 (s, 1 H, CH-9), 7.31 (d, 1 H, *J* = 4.3 Hz, CH-6), 7.46 (t, 1 H, *J* = 7.2, Ph), 7.52 (t, 2 H, *J* = 7.2, Ph), 8.04 (d, 2 H, *J* = 4.3, Ph), 8.61 (d, 1 H, *J* = 4.3, CH-5)	**4d**: 96.2, 108.5, 121.7 (q, *J* = 274.0, CF_3), 128.3, 130.7, 131.3, 134.0, 138.0 (q, *J* = 36.8, C-CF_3), 150.9, 152.9, 158.6	152–153
4e: 7.22 (s, 1 H, CH-9), 7.32 (d, 1 H, *J* = 4.2, CH-6), 7.64 (d, 2 H, *J* = 8.4, Ar), 7.92 (d, 2 H, *J* = 8.4, Ar), 8.61 (d, 1 H, *J* = 4.2, CH-5)	**4e**: 95.7, 108.1, 121.9 (q, *J* = 274.1, CF_3), 124.0, 128.7, 129.1, 133.0, 136.2 (q, *J* = 37.0, C-CF_3), 150.2, 151.9, 163.7	150–151
4f: 2.31 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 7.01 (s, 1 H, CH-9), 7.08 (d, 1 H, *J* = 7.9, Ar), 7.12 (br. s, 1 H, Ar), 7.24 (d, 1 H, *J* = 4.3, CH-6), 7.56 (d, 1 H, *J* = 7.9, Ar), 8.56 (d, 1 H, *J* = 4.3, CH-5)	**4f**: 21.3, 21.6, 98.8, 108.0, 121.5 (q, J = 274.0 Hz, CF_3), 128.4, 130.6, 131.4, 133.6, 134.6 (q, *J* = 37.1, C–CF_3), 138.2, 140.9, 150.5, 151.9, 159.3	108–109
4g: 2.39 (s, 3 H, CH_3), 7.19 (s, 1 H, CH-9), 7.28 (d, 1 H, *J* = 4.3, CH-6), 7.32 (d, 2 H, *J* = 8.0, Ar), 7.92 (d, 2 H, *J* = 8.0, Ar), 8.58 (d, 1 H, *J* = 4.3, CH-5)	**4g**: 21.4, 95.8, 108.2, 121.6 (q, *J* = 274.1, CF_3), 128.0, 130.9, 131.3, 135.5 (q, *J* = 36.4, C–CF_3), 141.4, 150.8, 152.8, 158.5	134–136
4h: 7.37 (s, 1 H, CH-9), 7.38 (d, 1 H, *J* = 4.2, CH-6), 7.45 (m, 2 H, Ar), 7.57 (m, 1 H, Ar), 7.92 (m, 1 H, Ar), 8.65 (d, 1 H, *J* = 4.2, CH-5)	**4h**: 98.8, 108.2, 120.9 (q, *J* = 274.1, CF_3), 128.2, 131.4, 131.5, 132.0, 132.2, 133.3, 134.0 (q, *J* = 36.7, C–CF_3), 150.1, 150.9, 155.1	106–108
4i: 3.82 (s, 3 H, CH_3), 6.99 (d, 2 H, *J* = 7.5, Ar), 7.14 (s, 1 H, CH-9), 7.29 (d, 1 H, *J* = 4.3, CH-6), 7.92 (d, 2 H, *J* = 7.5, Ar), 8.58 (d, 1 H, *J* = 4.3, CH-5)	**4i**: 56.3, 94.8, 107.9, 116.0, 121.2 (q, *J* = 274.1 Hz, CF_3), 125.8, 129.8, 139.7 (q, *J* = 36.9 Hz, C–CF_3), 150.3, 151.4, 159.0, 163.0	150–152
4j: 7.52 (s, 1 H, CH-9), 7.61 (d, 1 H, *J* = 5.0 Hz, CH-6), 8.23 (d, 2 H, *J* = 8.5, Ar), 8.29 (d, 2 H, *J* = 8.5, Ar), 8.90 (d, 1 H, *J* = 5.0, CH-5)	**4j**: 104.4, 108.2, 121.4 (q, *J* = 274.3, CF_3), 129.8, 132.2, 138.5, 140.7 (q, *J* = 36.5, C–CF_3), 145.9, 151.6, 159.9, 163.4	289-290
4k: 7.33 (t, 1 H, *J* = 7.4, Ph), 7.38 (d, 1 H, *J* = 4.1 Hz, CH-6), 7.48 (t, 2 H, *J* = 7.2, Ph), 8.08 (d, 2 H, *J* = 7.5, Ph), 8.65 (s, 1 H, CH-8), 8.71 (d, 1 H, *J* = 4.1 Hz, CH-5)	**4k**: 105.7, 108.5, 121.5 (q, *J* = 274.1, CF_3), 126.3, 126.6, 129.7, 132.1, 140.0 (q, *J* = 36.7, C–CF_3), 145.3, 151.0, 151.6	158–160
4l: 7.41 (d, 1 H, *J* = 4.2 Hz, CH-6), 7.48 (d, 2 H, *J* = 8.4, Ar), 8.09 (d, 2 H, *J* = 8.4, Ar), 8.66 (s, 1 H, CH-8), 8.75 (d, 1 H, *J* = 4.2, CH-5)	**4l**: 105.0, 108.4, 121.4 (q, *J* = 274.2, CF_3), 128.9, 129.9, 132.0, 135.8, 139.2 (q, *J* = 37.0, C–CF_3), 144.2, 150.4, 156.7	198–200
4m: 2.33 (s, 3 H, CH_3), 7.26–7.49 (m, 5 H, Ar, CH-6), 8.38 (s, 1 H, CH-8), 8.65 (d, 1 H, *J* = 4.3, CH-5) **5m**: 2.33 (s, 3 H, CH_3), 7.26–7.49 (m, 5 H, Ar, CH-6), 8.41 (s, 1 H, CH-8), 9.07 (d, 1 H, *J* = 7.3, CH-5)	**4m** (major isomer): 20.9, 108.6, 112.2, 121.0 (q, *J* = 274.1 Hz, CF_3), 127.4, 129.4, 132.0, 132.5, 132.9, 133.0, 138.0 (q, *J* = 37.1 Hz, C–CF_3), 138.9, 146.8, 150.6	101–103
4n: 7.40 (d, 1 H, J = 4.1, CH-6), 7.65 (d, 2 H, *J* = 8.5, Ar), 7.93 (d, 2 H, *J* = 8.5, Ar), 8.67 (d, 1 H, *J* = 4.1, CH-5)	**4n**: 62.8, 105.1, 119.9 (q, *J* = 274.2, CF_3), 120.4, 125.7, 129.0, 133.4, 136.7 (q, *J* = 36.9, C–CF_3), 145.2, 150.4, 156.2	138–140

[a] **a**–**c** in $CDCl_3$, **d**–**h**, **k**, **m** in CD_3CN, **i**, **j**, **l**, **n** in CD_3CN–CF_3COOH, (95:5).
[b] Satisfactory microanalyses were obtained: C, ± 0.28; H, ± 0.25.
[c] IR (film, cm^{-1}) for **3**: 3240 (br. s, OH), 1381 (s, SO_2).

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