A Simple and Efficient Preparation of 3-Aryl-3-Trifluoromethyl-3*H*-Diazirinyl Sulfoxides and Sulfones

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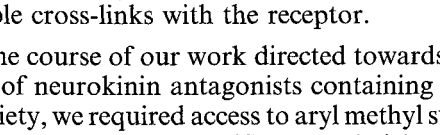
All regioisomers of 3-aryl-3-trifluoromethyl-3*H*-diazirinyl sulfoxides and sulfones have been prepared in five steps from the corresponding bromothioanisoles in excellent overall yields. The key step involves a simultaneous oxidation of sulfide and diaziridine moieties respectively, to yield either the diazirine sulphoxide or sulphone, depending on reaction conditions.

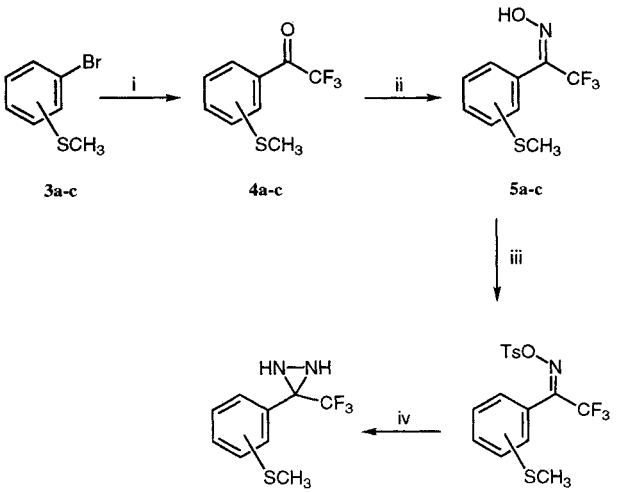
3-Aryl-3-trifluoromethyl-3*H*-diazirines have become widely established as extremely efficient and convenient sources of carbenes, which are proving particularly useful for the photolabelling of biological receptors.[1] Upon photolysis, these systems give rise to carbenes which do not readily rearrange, allowing the formation of chemically stable cross-links with the receptor.

During the course of our work directed towards the preparation of neurokinin antagonists containing a photolabile moiety, we required access to aryl methyl sulfoxides and sulfones containing a trifluoromethyl-3*H*-diazirine moiety at various positions on the aromatic ring (**1** and **2**, Figure 1).



1 **2**

Figure 1



3a-c **4a-c** **5a-c** **7a-c** **6a-c** **1a-c** **2a-c**

a ortho b meta c para

Reagents:
i) BuLi/THF/-78°C/Et_2NCOCF_3 ii) $NH_2OH.HCl$/py iii) TsCl iv) NH_3
v) t-BuOCl (2 equivs) vi) t-BuOCl (4 equivs)

Scheme 1

In addition to our own specific requirements for our particular antagonists, these systems clearly offer wide scope for the synthesis of various 3-aryl-3-trifluoromethyl-3*H*-diazirines via alkylation of the corresponding α-sulfinyl and -sulfonyl carbanions.

The planned route to compounds **1** and **2** (Figure 1) is summarised in Scheme 1.

Clearly, following this route, a key requirement was to be able to effect oxidation of the diaziridine and sulfide moieties in compounds **7** with control over the extent of oxidation at sulfur. It has been shown that an almost quantitative yield of methyl phenyl sulfoxide can be obtained from oxidation of the corresponding sulfide using *tert*-butyl hypochlorite, without the formation of any sulfone.[2] Recent work by Hatanaka[3,4] using an excess of *tert*-butyl hypochlorite with triethylamine has shown that diaziridines can be oxidised to diazirines in high yields. However, employing the conditions described by Skattebol et al[2] for their oxidations of sulfides to sulfoxides, and using two equivalents of *tert*-butyl hypochlorite, we were able to obtain almost quantitative yields of the diazirine-sulfoxides **1**. A crucial requirement for clean production of the sulfoxide is the slow addition of *tert*-butyl hypochlorite. An increase in the amount of *tert*-butyl hypochlorite used enables the diazirine-sulfones **2** to be formed in excellent yields.

Thus, treatment of bromides **3** with BuLi followed by *N,N*-diethyltrifluoroacetamide affords the trifluoromethyl ketones **4** in excellent yields. Conversion to the oximes **5** using hydroxylamine hydrochloride followed by reaction with *p*-toluenesulfonyl chloride yields the tosylates **6** as mixtures of *E*/*Z*-isomers. Reaction of these isomer mixtures with liquid ammonia gives almost quantitative

yields of the diaziridines **7**. An exception was found in the case of the ortho-substituted tosylate **6a**, where intriguingly, only the *Z*-isomer underwent efficient transformation into diaziridine **7a**. Treatment of the diaziridines **7** with *tert*-butyl hypochlorite yields either the diazirine-sulfoxide **1** or -sulfone **2** depending on the amount of *tert*-butyl hypochlorite used.

In summary, under the optimised conditions described above, usefully functionalised 3-aryl-3-trifluoromethyl-3*H*-diazirines are now easily accessible in high yields from readily available starting materials.

tert-Butyl hypochlorite was prepared as previously reported.[5]

NMR spectra were recorded on a General Electric QE 300 instrument; chemical shifts are given with respect to TMS. IR spectra were recorded on a Perkin-Elmer 1420 Spectrometer (Nujol mulls and liquid films) and a Biorad FTS7 (KBr). Mass spectra were obtained on a VG Autospec (EI and FAB+) and a Hewlett Packard MS-Engine Thermospray. UV spectra were recorded on a Pye-Unicam PU 8800 Spectrometer. Microanalyses were obtained using an Elemental Analyzer 1106. Melting points were recorded on a Reichert Hot Stage and are uncorrected. Column chromatography was carried out using flash silica (mesh 230–400).

2,2,2-Trifluoro-1-(methylsulfanylphenyl)ethanones (4a–c); General Procedure:

To a stirred solution of the bromothioanisole (2.03 g, 10 mmol) in anhydr. THF (20 mL) at −78 °C was added BuLi (1.6 M in cyclohexane, 6.9 mL, 11 mmol) dropwise over 10 min under Ar. After stirring for 1 h, a solution of *N,N*-diethyltrifluoroacetamide (2.03 g, 12 mmol) in anhydr. THF (2 mL) was added dropwise over 1 h at −78 °C. The mixture was then stirred for a further 1 h at −78 °C before being quenched with NH_4Cl (2/3 sat., 20 mL). Stirring was continued until the mixture had reached r.t. Extraction was carried out using Et_2O, the ethereal extract dried ($MgSO_4$), filtered and the solvent removed in vacuo to leave the crude compound. This was then purified by column chromatography on silica gel [pet. ether (40–60)/Et_2O, 95:5]. All compounds gave satisfactory microanalyses: for **4a–c**; C ± 0.29, H ± 0.20, F ± 0.22, S ± 0.21, for **5a–c**, **6a–c**, **7a–c**, **1a–c**, **2a–c**; C ± 0.25, H ± 0.23, N ± 0.26.

2,2,2-Trifluoro-1-(2-methylsulfanylphenyl)ethanone **(4a)**:

Yellow crystalline solid, yield: 2.10 g (96%). Small amount recrystallised from pentane to give a yellow crystalline solid, mp 66–67.5 °C.

IR (Nujol): ν = 3000–2800 (C–H), 1680 (C=O), 1585, 1200–1100 (C–F), 925, 740 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 2.50 (3H, s, SCH_3), 7.27 (1H, dd, J = 8.0 Hz, ArH), 7.42 (1H, d, J = 8.2 Hz, ArH), 7.62 (1H, m, ArH), 8.03 (1H, m, ArH).

MS (EI): m/z (%) = 221 (M^{+1}, 5.2), 220 (M^+, 45.1), 151 (100), 108 (21.7), 69 (14.6), 45 (47.2).

2,2,2-Trifluoro-1-(3-methylsulfanylphenyl)ethanone **(4b)**:

Distilled using Kugelrohr. Yellow oil, yield: 2.05 g (93%), bp 90 °C at 0.2 mmHg.

IR (neat): ν = 3000–2800 (C–H), 1710 (C=O), 1580, 1230–1100 (C–F), 980, 960, 750, 700 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 2.55 (3H, s, SCH_3), 7.46 (1H, dd, J = 7.9 Hz, ArH), 7.57 (1H, d, J = 8.1 Hz, ArH), 7.81 (1H, d, J = 7.6 Hz, ArH), 7.90 (1H, s, ArH).

MS (EI): m/z (%) = 222 (M^{+2}, 9.1), 221 (M^{+1}, 17.9), 220 (M^+, 100), 151 (76.9), 123 (44.1), 108 (22.6), 79 (23.3), 45 (34.1).

2,2,2-Trifluoro-1-(4-methylsulfanylphenyl)ethanone **(4c)**:

Pale yellow crystalline solid, yield: 1.96 g (89%). Small amount recrystallised from pentane to give slender colourless needles, mp 46.8–47.8 °C.

IR (Nujol): ν = 3000–2800 (C–H), 1695 (C=O), 1585, 1200–1100 (C–F), 940, 755 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 2.55 (3H, s, SCH_3), 7.32 (2H, d, J = 8.5 Hz, ArH), 7.70 (2H, d, J = 8.5 Hz, ArH).

MS (EI): m/z (%) = 221 (M^{+1}, 5.9), 220 (M^+, 55.5), 151 (100), 108 (19.3), 69 (13.9), 45 (22.5).

2,2,2-Trifluoro-1-(methylsulfanylphenyl)ethanone Oximes (5a–c); General Procedure:

A stirred solution of the 2,2,2-trifluoro-1-(methylsulfanylphenyl)-ethanone (1.90 g, 8.6 mmol), hydroxylamine hydrochloride (1.90 g, 27 mmol), EtOH (19 mL) and pyridine (1.9 mL) was refluxed for 3 h. EtOH was removed under reduced pressure, the residue taken up in Et_2O and washed with water. The Et_2O extract was dried ($MgSO_4$), filtered and the Et_2O removed in vacuo. The pyridine was removed via azeotroping with toluene and the crude oximes purified by column chromatography on silica gel (hexane/acetone, 3:1).

2,2,2-Trifluoro-1-(2-methylsulfanylphenyl)ethanone Oxime **(5a)**:

Refluxed for 6 h. Yellow oil (a mixture of *E*/*Z*-isomers), yield: 1.95 g (96%).

IR (neat): ν = 3200 (O–H), 3100–2800 (C–H), 1590 (C=N), 1210–1090 (C–F), 1000, 960, 940, 750, 730 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 2.48/2.49 (3H, 2s, SCH_3), 7.16–7.50 (4H, m, ArH), 8.28/8.61 (1H, 2s, OH).

MS (EI): m/z (%) = 235 (M^+, 22.9), 218 (100), 203 (47.9), 117 (70.6), 89 (65.7), 71 (54.3), 55 (29.9).

2,2,2-Trifluoro-1-(3-methylsulfanylphenyl)ethanone Oxime **(5b)**:

Yellow oil (a mixture of *E*/*Z*-isomers), yield: 1.93 g (95%).

IR (neat): ν = 3300 (O–H), 3100–2800 (C–H), 1560 (C=N), 1220–1090 (C–F), 1020, 960, 780, 730 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 2.50 (3H, s, SCH_3), 7.21–7.42 (4H, m, ArH), 8.38/8.59 (1H, 2s, OH).

MS (EI): m/z (%) = 237 (M^{+2}, 5.6), 236 (M^{+1}, 11.4), 235 (M^+, 100), 219 (30.2), 188 (19.3), 150 (41.2), 123 (23.4), 99 (24.6), 79 (24.3), 73 (46.0), 45 (50.3).

2,2,2-Trifluoro-1-(4-methylsulfanylphenyl)ethanone Oxime **(5c)**:

Yellow crystalline solid, yield: 1.98 g (98%). Small amount recrystallised from pentane to give a colourless crystalline solid (a mixture of *E*/*Z*-isomers), mp 64.5–77.5 °C.

IR (Nujol): ν = 3220 (O–H), 3100–2800 (C–H), 1590 (C=N), 1200–1100 (C–F), 1000, 820, 730 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 2.51 (3H, s, SCH_3), 7.24–7.34 (2H, m, ArH), 7.40–7.50 (2H, m, ArH), 8.37/8.47 (1H, 2s, OH).

MS (EI): m/z (%) = 237 (M^{+2}, 5.3), 236 (M^{+1}, 11.5), 235 (M^+, 100), 149 (57.1), 124 (19.2), 69 (17.8), 45 (20.3).

2,2,2-Trifluoro-1-(methylsulfanylphenyl)ethanone Oxime Tosylates (6a–c); General Procedure:

To a stirred solution of the oxime (1.80 g, 7.7 mmol), Et_3N (940 mg, 9.3 mmol) and *N,N*-dimethylaminopyridine (81 mg, 0.67 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added *p*-toluenesulfonyl chloride (1.70 g, 8.7 mmol) in small portions. After addition, the reaction mixture was stirred at r.t. for 2 h before quenching with H_2O. The mixture was extracted with CH_2Cl_2, washed with H_2O, dried ($MgSO_4$), filtered and the solvent removed in vacuo. The crude tosylates were purified by column chromatography on silica gel (hexane/acetone, 3:1).

2,2,2-Trifluoro-1-(2-methylsulfanylphenyl)ethanone Oxime Tosylate **(6a)**:

Stirred for 4 h. Pale yellow crystalline solid, yield: 2.81 g (94%). Small amount recrystallised from pet. ether/EtOAc to give a colourless crystalline solid (a mixture of *E*/*Z*-isomers). If recrystallised from EtOH one of the isomers can be obtained > 95% pure. The other isomer can be obtained pure from the diaziridine reaction, (ratio 58:42).

Isomer from EtOH recrystallisation (*Z*-isomer);

^1H NMR ($CDCl_3$/TMS): δ = 2.30 (3H, s, $ArCH_3$), 2.46 (3H, s, SCH_3), 7.14 (1H, d, J = 7.5 Hz, ArH), 7.24–7.51 (6H, m, ArH), 7.88 (2H, d, J = 8.3 Hz, ArH).

Isomer from diaziridine reaction (*E*-isomer);

^{1}H NMR ($CDCl_3$/TMS): δ = 2.41 (3 H, s, $ArCH_3$), 2.49 (3 H, s, SCH_3), 7.08 (1 H, d, J = 7.7 Hz, ArH), 7.24–7.51 (6 H, m, ArH), 7.88 (2 H, d, J = 8.3 Hz, ArH).

IR (Nujol): ν = 3000–2800 (C–H), 1585 (C=N), 1370, 1210–1120 (C–F), 895, 810, 755 cm^{-1}.

MS (EI): m/z (%) = 389 (M^+, 9.7), 218 (27.4), 203 (61.2), 155 (34.7), 91 (100), 65 (22.0).

2,2,2-Trifluoro-1-(3-methylsulfanylphenyl)ethanone Oxime Tosylate **(6b)**:

Pale yellow crystalline solid (a mixture of *E*/*Z*-isomers), yield: 2.80 g (94%). Small amount recrystallised from EtOH to give a colourless crystalline solid (one isomer, mp 82–85 °C).

Isomer from recrystallisation;

IR (Nujol): ν = 3000–2800 (C–H), 1585 (C=N), 1370, 1200–1110 (C–F), 880, 760, 680 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.49 (6 H, s, SCH_3, $ArCH_3$), 7.10–7.19 (2 H, m, ArH), 7.38 (4 H, m, ArH), 7.89 (2 H, d, J = 8.3 Hz, ArH).

MS (EI): m/z (%) = 391 (M^{+2}, 5.4), 390 (M^{+1}, 9.1), 389 (M^+, 42.6), 219 (16.7), 155 (92.7), 91 (100), 65 (17.7).

2,2,2-Trifluoro-1-(4-methylsulfanylphenyl)ethanone Oxime Tosylate **(6c)**:

Pale yellow crystalline solid, yield: 2.87 g (96%). Small amount recrystallised from EtOH to give a colourless crystalline solid (a mixture of *E*/*Z*-isomers), mp 87.5–98 °C.

IR (Nujol): ν = 3000–2800 (C–H), 1580 (C=N), 1375, 1210–1110 (C–F), 1080, 890, 810, 750, 685 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.46–2.52 (6 H, m, SCH_3, $ArCH_3$), 7.22–7.45 (7 H, m, ArH), 7.89 (2 H, d, J = 8.2 Hz, ArH).

MS (EI): m/z (%) = 390 (M^{+1}, 5.7), 389 (M^+, 26.8), 155 (75.3), 105 (8.4), 91 (100), 77 (7.9), 65 (21.3).

3-(Methylsulfanylphenyl)-3-trifluoromethyldiaziridines (7a–c); General Procedure:

A mixture of tosylate (2.34 g, 6 mmol), dry CH_2Cl_2 (30 mL) and NH_3 (l) (20 mL) at −78 °C in a flask fitted with a condenser held at −78 °C, was stirred for 16 h. The cooling vessels were removed and the NH_3 allowed to evaporate. The mixture was taken up in CH_2Cl_2, washed with H_2O (×3), dried ($MgSO_4$), filtered and the solvent removed in vacuo.

3-(2-Methylsulfanylphenyl)-3-trifluoromethyldiaziridine **(7a)**:

Column (CH_2Cl_2). Pure tosylate (*E*-isomer) as well as diaziridine as pale yellow solid, yield: 760 mg (54%), mp 60–67 °C.

IR (Nujol): ν = 3220, 3165 (N–H), 3000–2800 (C–H), 1200–1070 (C–F), 725 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.52 (3 H, s, SCH_3), 2.57 (1 H, br d, J = 8.7 Hz, NH), 2.89 (1 H, br d, J = 8.7 Hz, NH), 7.22 (1 H, dd, J = 7.5 Hz, ArH), 7.32 (1 H, br d, J = 7.8 Hz, ArH), 7.42 (1 H, dd, J = 7.7 Hz, ArH), 7.49 (1 H, br d, J = 7.6 Hz, ArH).

MS (EI): m/z (%) = 235 (M^{+1}, 0.6), 234 (M^+, 3.0), 233 ($M^+ - 1$, 1.3), 203 (23.7), 187 (23.1), 165 (62.3), 150 (49.2).

3-(3-Methylsulfanylphenyl)-3-trifluoromethyldiaziridine **(7b)**:

Colourless crystalline solid, yield: 1.37 g (97%), mp < 31.0 °C.

IR (neat): ν = 3220 (N–H), 3000–2800 (C–H), 1590, 1565, 1385, 1250–1060 (C–F), 950, 780, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.24 (1 H, br d, J = 9.2 Hz, NH), 2.51 (3 H, s, SCH_3), 2.80 (1 H, br d, J = 7.8 Hz, NH), 7.31–7.40 (3 H, m, ArH), 7.48 (1 H, s, ArH).

MS (EI): m/z (%) = 235 (M^{+1}, 7.5), 234 (M^+, 48.2), 233 ($M^+ - 1$, 43.3), 219 (86.7), 167 (36.8), 150 (100), 135 (43.9), 135 (43.9), 114 (40.2), 91 (20.2), 70 (58.8), 57 (52.3).

3-(4-Methylsulfanylphenyl)-3-trifluoromethyldiaziridine **(7c)**:

Colourless crystalline solid, yield: 1.38 g (97%), mp 105–107.5 °C.

IR (Nujol): ν = 3220, 3170 (N–H), 3000–2800 (C–H), 1200–1100 (C–F), 940, 805 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): ν = 2.20 (1 H, bs, NH), 2.50 (3 H, s, SCH_3), 2.80 (1 H, br s, NH), 7.27 (2 H, d, J = 8.4 Hz, ArH), 7.52 (2 H, d, J = 8.4 Hz, ArH).

MS (EI): m/z (%) = 236 (M^{+2}, 3.2), 235 (M^{+1}, 11.7), 234 (M^+, 61.7), 233 ($M^+ - 1$, 100), 213 (44.5), 165 (54.0), 150 (49.2), 118 (38.9).

3-(Methylsulfinylphenyl)-3-trifluoromethyl-3*H*-diazirines (1a–c); General Procedure:

(In the dark).

The diaziridine (774 mg, 3.3 mmol) was dissolved in MeOH (20 mL) and stirred at −78 °C. *tert*-Butyl hypochlorite (78 µl, 6.6 mmol) was added dropwise over 10 min; once addition was complete sodium bicarbonate was added (400 mg) and the solution removed from the cooling vessel and stirred for 1.5 h. The solvent was removed in vacuo, the residue taken up in Et_2O, dried ($MgSO_4$) and passed through a short pad of silica gel.

3-(2-Methylsulfinylphenyl)-3-trifluoromethyl-3H-diazirine **(1a)**:

Yellow oil, yield: 785 mg (96%).

IR (neat): ν = 3000–2800 (C–H), 1620 (N=N), 1320, 1210–1130 (C–F), 1070, 1045 (S=O), 925, 755 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.81 (3 H, s, $SOCH_3$), 7.62 (1 H, dd, J = 7.4 Hz, ArH), 7.76 (2 H, m, ArH), 8.17 (1 H, d, J = 7.7 Hz, ArH).

MS (FAB): m/z (%) = 251 (MH^{+2}, 3.4), 250 (MH^{+1}, 7.1), 249 (MH^+, 76.1), 221 ($MH^+ - N_2$, 13.9), 157 (47.1), 109 (23.4), 95 (39.6), 83 (49.3), 81 (49.7), 69 (88.9), 57 (82.0), 55 (100).

UV (EtOH): diazirine n-π* 310 nm (shoulder).

3-(3-Methylsulfinylphenyl)-3-trifluoromethyl-3H-diazirine **(1b)**:

Yellow oil, yield: 784 mg (96%).

IR (neat): ν = 3000–2800 (C–H), 1600 (N=N), 1320, 1220–1130 (C–F), 1050 (S=O), 950, 785 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.74 (3 H, s, $SOCH_3$), 7.40 (1 H, d, J = 7.6 Hz, ArH), 7.45 (1 H, s, ArH), 7.62 (1 H, dd, J = 7.8 Hz, ArH), 7.69 (1 H, d, J = 7.9 Hz, ArH).

MS (EI): m/z (%) = 248 (M^+, 6.0), 232 (6.2), 220 ($M^+ - N_2$, 19.9), 203 (47.3), 157 (100), 145 (37.5), 137 (71.3), 107 (23.0), 91 (19.2).

UV (EtOH): diazirine n-π* 345 nm.

3-(4-Methylsulfinylphenyl)-3-trifluoromethyl-3H-diazirine **(1c)**:

Yellow oil, yield: 796 mg (97%).

IR (neat): ν = 3000–2800 (C–H), 1600 (N=N), 1340, 1220–1130 (C–F), 1040 (S=O), 930 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 2.73 (3 H, s, $SOCH_3$), 7.36 (2 H, d, J = 8.4 Hz, ArH), 7.69 (2 H, d, J = 8.4 Hz, ArH).

MS (EI): m/z (%) = 248 (M^+, 4.4), 220 ($M^+ - N_2$, 40.1), 174 (27.6), 157 (100), 145 (85.5), 137 (53.5), 107 (29.8), 87 (25.6), 69 (17.6).

UV (EtOH): diazirine n-π* 345 nm.

3-(Methylsulfonylphenyl)-3-trifluoromethyl-3*H*-diazirines (2a–c); General Procedure:

(In the dark).

The diaziridine (234 mg, 1 mmol) was dissolved in MeOH (8 mL) and stirred at −78 °C. *tert*-Butyl hypochlorite (480 µl, 4 mmol) was added followed by sodium bicarbonate (240 mg) and the solution removed from the cooling vessel and stirred for 1.5 h. The solvent was removed in vacuo, the residue taken up in CH_2Cl_2, dried ($MgSO_4$) and purified by column chromatography on silica gel (CH_2Cl_2).

3-(2-Methylsulfonylphenyl)-3-trifluoromethyl-3H-diazirine **(2a)**:

Colourless crystalline solid, yield: 220 mg (83%), mp 59–66 °C.

IR (KBr): ν = 3100–2900 (C–H), 1600 (N=N), 1320 (SO_2), 1230–1130 (C–F, SO_2), 550 cm^{-1}.

^{1}H NMR ($CDCl_3$/TMS): δ = 3.13 (3 H, s, SO_2CH_3), 7.67–7.81

(2H, m, ArH), 7.92 (1H, br d, $J = 7.5$ Hz, ArH), 8.13 (1H, dd, $J = 7.5$, 2.0 Hz, ArH).

MS (thermospray): $m/z = 282$ (MNH_4^+).

UV (EtOH): diazirine n-π^* 310 nm (shoulder).

3-(3-Methylsulfonylphenyl)-3-trifluoromethyl-3H-diazirine (**2b**):

Column (Et_2O/pet.ether, 1:1). Colourless crystalline solid, yield: 223 mg (84%), mp 55–59 °C.

IR (KBr): $\nu = 3100–2900$ (C–H), 1600 (N=N), 1310 (SO_2), 1230–1140 (C–F, SO_2), 540 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): $\delta = 3.06$ (3H, s, SO_2CH_3), 7.58 (1H, br d, $J = 7.6$ Hz, ArH), 7.66 (1H, dd, $J = 7.6$ Hz, ArH), 7.72 (1H, br s, ArH), 8.02 (1H, d, $J = 7.5$ Hz, ArH).

MS (thermospray): $m/z = 282$ (MNH_4^+).

UV (EtOH): diazirine n-π^* 345 nm.

3-(4-Methylsulfonylphenyl)-3-trifluoromethyl-3H-diazirine (**2c**):

Colourless crystalline solid, yield: 234 mg (88%), mp 70–77 °C.

IR (KBr): $\nu = 3100–2900$ (C–H), 1600 (N=N), 1320 (SO_2), 1230–1130 (C–F, SO_2), 550 cm^{-1}.

^1H NMR ($CDCl_3$/TMS): $\delta = 3.07$ (3H, s, SO_2CH_3), 7.41 (2H, d, $J = 8.2$ Hz, ArH), 8.01 (2H, d, $J = 8.2$ Hz, ArH).

MS (thermospray): $m/z = 282$ (MNH_4^+).

UV (EtOH): diazirine n-π^* 345 nm.

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