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BENZOTRIAZOLE-ASSISTED SYNTHESIS OF *N*-(α-CYANOALKYL)SULFONAMIDES

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Abstract - *N*-(α-Benzotriazol-1-ylalkyl)sulfonamides, readily available from benzotriazole, an aldehyde and a sulfonamide, are converted into the corresponding *N*-(α-cyanoalkyl)sulfonamides in good yields by treatment with potassium cyanide.

α-Substituted *N*-(α-cyanoalkyl)sulfonamides are both valuable building blocks for the organic synthesis and compounds of useful biological activity, as herbicides,[1-3] plant-growth retarders,[4] and fungicides.[5] Syntheses of some classes of analgesic or antiinflammatory agents,[6] inhibitors of 5-lipohydrogenase,[7] hepatic agents[8] and anthelmintic substances used in veterinary medicine[9] rely on the use of α-cyanomethylene sulfonamides as intermediates. (Tosylamido)acetonitrile was successfully used as an inhibitor of fibrin cross-linking,[1] as well as a

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plasticizer for linear condensation products with recurring amide groups such as polyamide and polyurethane.[11] Other α-substituted sulfonamidoacetonitriles are utilized as intermediates in the synthesis of secondary amines,[12] heterocycles,[13-16] and fluorescence labeling agents.[17] Recently, Reetz *et al.* obtained enantiomerically pure α,β-diamino acids from α-substituted *p*-tolyl-sulfonamidoacetonitriles.[18]

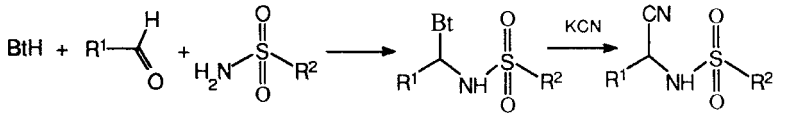
Synthetic approaches to α-substituted tolylsulfonamidoacetonitriles rely on classical reactions of carbonyl compounds and their derivatives: (i) three-component synthesis from aldehyde, potassium cyanide and *p*-toluenesulfonamide;[19,20] (ii) two component synthesis from α-aminonitriles and *p*-toluenesulfonyl chloride;[21-23] (iii) addition of Me_3SiCN to aldimines in the presence of Lewis acids.[18] The nature of the aldehyde strongly conditions the yield.

Earlier work in our group utilized benzotriazole methodology in the preparation of α-acylamino nitriles[24] and unsymmetrical secondary amines,[25] and related work has appeared.[26] We now propose a general, versatile and high yielding method for the preparation of α-substituted *p*-tolyl-sulfonamidoacetonitriles from *N*-(α-benzotriazol-1-ylalkyl)sulfonamides, *via* displacement of benzotriazole by the cyanide ion.

Results and Discussion

Benzotriazole adducts **3a-h** were prepared by the reactions of equimolar amounts of benzotriazole, an aldehyde (**1a-h**) and a

sulfonamide (**2a-h**) in ethanol at room temperature or in toluene at reflux, in a Dean-Stark apparatus.



1a-h **2a-h** **3a-h** **4a-h**

	R^1	R^2	yields (lit) **3**	yields (lit) **4**
a	H	CH_3	98 (84)[27]	100 by NMR
b	H	*p*-CH_3-C_6H_4	95	80 (60)[10]
c	CH_3	*p*-CH_3-C_6H_4	91	94
d	C_2H_5	*p*-CH_3-C_6H_4	95	98 (na)[22-23]
e	$C_3H_7^i$	C_6H_5	90 (84)[27]	90 (na)[26]
f	C_6H_5	*p*-CH_3-C_6H_4	90 (61)[27]	98 (73)[15]
g	*p*-CH_3-C_6H_4	*p*-CH_3-C_6H_4	94	95
h	α-$C_{10}H_7$	*p*-CH_3-C_6H_4	55	65

Previously described procedures[27] were improved as follows: a) benzotriazole adducts of formaldehyde (**3a-b**) can be easily obtained by mixing a large excess of formaldehyde solution (40 %) with benzotriazole and the corresponding sulfonamide in ethanol. The slurry thus formed was vigorously stirred for 48 hr, after which it contained exclusively the benzotriazole adduct as a precipitate, pure by NMR. The two-step method previously proposed[27] for the synthesis of the mentioned compounds necessitated the preparation of benzotriazol-1-ylmethanol, which was subsequently reacted with the appropriate sulfonamide; b) benzotriazole adducts (**3c-e**) from low molecular weight aldehydes were

also obtained by mixing the three components in ethanol. The precipitation of the product started in less than 24 hr., and the reaction went to completion in about 48 hr.

The reaction of benzotriazole adducts **3a-h** with KCN was attempted in polar solvents: ethanol, water, DMSO. Using ethanol and solid KCN, the reaction went to completion in less than 2 hr (as shown by NMR), but the products **4a-h** were difficult to isolate. Suspending the solid starting material in an aqueous solution of KCN 1N, the reaction occurred in high yields for compounds **3c-h**, but not for the benzotriazole-formaldehyde adducts **3a-b**. Using DMSO as a solvent and solid KCN, the products **4a-h** could be isolated in good yields: this method is recommended for the preparation of **4b** and **4h**. *N*-(Benzotriazol-1-ylmethyl)methanesulfonamide (**3a**) quantitatively reacted with solid KCN in DMSO (as shown by ^{1}H and ^{13}C NMR spectra of the reaction mixture), but the expected methanesulfonamidoacetonitrile (**4a**) decomposed during attempts for separation from benzotriazole.

The benzotriazole adducts **3a-h** and the α-substituted sulfonamidoacetonitriles **4b-h** were all characterized by elemental analyses (when necessary) and ^{1}H and ^{13}C NMR spectra. The benzotriazole adducts **3a-e** display the characteristic Bt-1 pattern in the aromatic region: ^{1}H NMR shows two triplets and two doublets. The Bt-C<u>H</u> proton in the ^{1}H NMR spectra is displayed at about 6-7 ppm, while the Bt-<u>C</u>H carbon occurs in

the ^{13}C NMR spectra between 60-70 ppm. When this carbon bears an aryl substituent, the adduct undergoes rapid isomerization *via* an ion-pair and compounds **3f-h** display the signals characteristic for free benzotriazole - broad signals at 7.9 ppm (2H) and 7.45 ppm (2H). The peaks corresponding to the carbon atoms of the benzotriazole ring are not observable in the ^{13}C NMR spectra; they must be broad lines dumped into the baseline due to the particular combination of exchange rates and frequency separations. These spectra are similar to the corresponding imines (Bt-C<u>H</u> at *ca.* 9 ppm and Bt-<u>C</u>H at *ca.* 170 ppm).[27] α-Substituted sulfonamidoacetonitriles **4a-h** display the characteristic signal for the cyano group at 115-118 ppm, whereas the α-cyanomethyne proton is shifted to a higher field (4-5 ppm) compared to Bt-C<u>H</u>.

In conclusion, improved procedures for the preparation of benzotriazol-1-ylmethylene sulfonamides were defined, allowing convenient syntheses of such compounds derived from aliphatic aldehydes. A novel synthesis using these compounds was applied to a wide variety of α-substituted N-(α-cyanoalkyl)sulfonamides and provided already known derivatives in overall yields superior to previously reported methods.

Experimental

^{1}H And ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, on a Varian Gemini 300 spectrometer with tetramethylsilane

as the internal standard. TLC was carried out on pre-coated plates (silica gel G60) purchased from Fisher using as solvent a mixture $CHCl_3$:Et_2O (97:3). Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Formaldehyde (aqueous solution 40 %) was purchased from Fisher. The sulfonamides and aldehydes used as starting materials were purchased from Aldrich.

General Procedure for the Preparation of Compounds 3a-h.

Method A: Benzotriazole (6 g, 0.05 mole), the sulfonamide (0.05 mole) and the corresponding aldehyde (0.15 to 0.25 mole) in 100 mL ethanol (95%), were stirred at room temperature for 24-48 hr. The solid was filtered and washed with ethanol (20 mL), then with ethanol:diethyl ether (1:1, 3x20 mL). The crude products were recrystallized from ethanol as a mixture of Bt-1 and Bt-2 isomers.

Method B: Benzotriazole (11.9 g, 0.1 mole), the sulfonamide (0.1 mole) and the corresponding aldehyde (0.15 mol) in 60 mL toluene, were refluxed for 48 hr in a Dean-Stark apparatus in the presence of PTSA (300 mg), until about 1.8 mL of water was removed azeotropically. The product precipitated upon cooling, and was filtered and washed with ethanol (40 mL) and ethanol:diethyl ether (1:1, 3x50 mL). The resulting solid was recrystallized from ethanol.

***N*-(Benzotriazol-1-ylmethyl)methanesulfonamide (3a).** *Method A* (five-fold excess of formaldehyde), precipitated from the reaction mixture

as a crystallohydrate. Yield 98 % (lit.[27] yield 84 %). White crystals (ethanol), m.p. 163-164 °C (lit.[27] m.p. 161-164°C). ^{1}H NMR (DMSO-d_6) δ (ppm) 2.98 (s,3H), 6.06 (d, 2H, *J* = 7.5 Hz), 6.88 (br s, 2H, $\underline{H_2}O$), 7.28 (t, 1H, *J* = 7.5 Hz), 7.45 (t, 1H, *J* = 7.7 Hz), 7.60 (t, 1H, *J* = 7.7 Hz), 7.94 (d, 1H, *J* = 8.3 Hz), 8.10 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 43.2, 70.3 (Bt-C$\underline{H_2}$), 111.0, 119.2, 124.2, 127.5, 132.4, 145.6.

***N*-(Benzotriazol-1-ylmethyl)-*p*-toluenesulfonamide** (**3b**). *Method A*; precipitated from the reaction mixture as a crystallohydrate. Yield 95 %. White crystals (ethanol), m.p. 192-193 °C. ^{1}H NMR (acetone-d_6) δ (ppm) 2.4 (s, 3H), 6.16 (d, 1H, *J* = 7 Hz), 6.18 (d, 1H, *J* = 6.8 Hz), 6.26 (dd, 1H, *J* = 6.8, 7.0 Hz - different *J* and δ values for C$\underline{H_2}$-NH due to the hydrogen bonding of a H_2O molecule to the sulfonamide moiety), 6.53 (br s, 2H, $\underline{H_2}O$), 7.34 (d, 2H, *J* = 8 Hz), 7.41 (t, 1H, *J* = 8 Hz), 7.56 (t, 1H, *J* = 8 Hz), 7.78 (d, 2H, *J* = 8 Hz), 7.84 (d, 1H, *J* = 8 Hz), 8.05 (d, 1H, *J* = 8 Hz); ^{13}C NMR (acetone-d_6) δ (ppm) 21.2, 71.4 (Bt-C$\underline{H}$), 111.3, 120.0, 124.7, 126.9, 128.1, 130.1, 133.5, 142.3, 143.2, 147.0. (Found: C, 55.53; H, 4.50; N, 18.36. Calc. for $C_{14}H_{14}N_4O_2S$: C, 55.62; H, 4.63; N, 18.54).

***N*-[1-(Benzotriazol-1-yl)ethyl]-*p*-toluenesulfonamide** (**3c**). *Method A*. Yield 91 %. White crystals (ethanol), m.p. 168-172 °C. ^{1}H NMR ($CDCl_3$) δ (ppm) 1.98 (d, 3H, *J* = 9.4 Hz), 2.16 (s, 3H), 6.15 (bd, 1H, *J* = 9.4 Hz, N$\underline{H}$), 6.30-6.40 (m, 1H), 6.76 (d, 2H, *J* = 8 Hz), 7.23 (d, 2H, *J* = 8 Hz), 7.29 (t,

1H, J = 8.3 Hz), 7.42 (t, 1H, J = 8.3 Hz), 7.51 (d, 1H, J = 8.3 Hz), 7.86 (d, 1H, J = 8.3 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 20.5, 20.7, 64.4 (Bt-C<u>H</u>), 110.7, 118.6, 123.4, 125.4, 126.7, 128.4, 130.6, 136.8, 142.1, 145.3. (Found: C, 56.66; H, 5.17; N, 17.90. Calc. for $C_{15}H_{16}N_4O_2S$: C, 56.95; H, 5.10; N, 17.71).

***N*-[1-(Benzotriazol-1-yl)propyl]-*p*-toluenesulfonamide (3d).** *Method A.* Yield 95 %. White crystals (ethanol), m.p. 128-129 °C. ^{1}H NMR (DMSO-d_6) δ (ppm) 0.72 (t, 3H, J = 7.2 Hz), 2.14 (s, 3H), 2.14-2.25 (m, 2H), 6.19 (t, 1H, J = 7.5 Hz), 6.87 (d, 2H, J = 8.0 Hz), 7.27 (d, 2H, J = 8.0 Hz), 7.32 (t, 1H, J = 8.3 Hz), 7.45 (t, 1H, J = 8.3 Hz), 7.85 (d, 1H, J = 8.3 Hz), 7.87 (d, 1H, J = 8.3 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 9.7, 20.8, 27.3, 69.5 (Bt-C<u>H</u>), 110.9, 119.0, 123.9, 125.6, 127.1, 128.8, 131.1, 137.2, 142.4, 145.4. (Found: C, 58.19; H, 5.43; N, 16.98. Calc. for $C_{16}H_{18}N_4O_2S$: C, 58.18; H, 5.49; N, 16.96).

***N*-[1-(Benzotriazol-1-yl)-2-methylpropyl]benzenesulfonamide (3e).** *Method A.* Yield 90 % (lit.[27] yield 84 %). Yellow crystals (ethanol), m.p. 164-166 °C (lit.[27] m.p. 165-166 °C). ^{1}H NMR (DMSO-d_6) δ (ppm) 0.45 (d, 3H, J = 9 Hz), 1.12 (d, 3H, J = 9 Hz), 2.49-3.12 (m, 1H), 5.88 (d, 1H, J = 11 Hz), 7.09 (t, 2H, J = 8.0 Hz), 7.22 (t, 1H, J = 8.0 Hz), 7.31 (t, 1H, J = 8.3 Hz), 7.35 (d, 2H, J = 8.0 Hz), 7.45 (t, 1H, J = 8.3 Hz), 7.86 (d, 1H, J = 8.3 Hz), 7.90 (d, 1H, J = 8.3 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 17.8, 19.1,

32.2, 73.4 (Bt-C<u>H</u>), 110.8, 119.0, 123.9, 125.5, 127.1, 128.3, 131.4, 131.9, 140.0, 145.0.

***N*-[(Benzotriazol-1-yl)phenylmethyl]-*p*-toluenesulfonamide** (**3f**). *Method B.* Yield 90 % (lit.[27] yield 61 %). White crystals (ethanol), m.p. 141 °C (lit.[27] m.p. 141-144°C). ^{1}H NMR (acetone-d_6) δ (ppm) 2.42 (s, 3H), 7.45 (br d, 4H, *J* = 8.0 Hz), 7.58 (t, 2H, *J* = 8.0 Hz), 7.70 (t, 1H, *J* = 8.0 Hz), 7.87 (d, 2H, *J* = 8.0 Hz), 7.92 (br d, 2H), 8.04 (d, 2H, *J* = 8.0 Hz); 9.10 (s, 1H); ^{13}C NMR (acetone-d_6) δ (ppm) 21.5, 127.2, 128.8, 130.1. 130.8, 131.9, 134.0, 135.7, 145.5, 171.4 (Bt^{+}C<u>H</u>=N). The peaks corresponding to the carbon atoms of the benzotriazole ring are not observable.

***N*-[(Benzotriazol-1-yl)-*p*-tolylmethyl]-*p*-toluenesulfonamide** (**3g**). *Method B.* Yield 94 %. White crystals (ethanol), m.p. 145-146 °C. ^{1}H NMR (DMSO-d_6) δ (ppm) 2.40 (br s, 6H), 7.39 (d, 2H, *J* = 8.0 Hz), 7.47 (br d, 4H, *J* = 8.0 Hz), 7.83 (d, 2H, *J* = 8.0 Hz), 7.92 (br d, 4H, *J* = 8.0 Hz), 9.10 (s, 1H); ^{13}C NMR (DMSO-d_6) δ (ppm) 21.1, 21.5, 125.4, 127.6, 129.6, 130.0, 131.1, 131.4, 144.5, 146.5, 171.2 (Bt^{+}C<u>H</u>=N). The peaks corresponding to the carbon atoms of the benzotriazole ring are not observable. (Found: C, 64.13; H, 5.09; N, 14.17. Calc. for $C_{21}H_{20}N_4O_2S$: C, 64.27; H, 5.14; N, 14.28).

***N*-[(Benzotriazol-1-yl)(1-naphthyl)methyl]-*p*-toluenesulfonamide** (**3h**). *Method B.* Yield 55 %. White-beige crystals (ethanol), m.p. 133 °C.

^{1}H NMR (acetone-d_6) δ (ppm) 2.02 (s, 3H), 7.00-7.10 (m, 3H), 7.20-7.35 (m, 4H), 7.50-7.65 (m, 5H), 7.80-7.90 (m, 2H), 8.70 (d, 1H, J = 10 Hz), 9.20 (s, 1H); ^{13}C NMR (acetone-d_6) δ (ppm) 21.5, 115.7, 125.2, 126.2, 127.8, 128.6, 128.8, 129.6, 129.7, 130.0, 130.7, 132.3, 134.8, 137.0, 145.4, 171.4 ($Bt^+C\underline{H}$=N). (Found: C, 67.06; H, 4.80; N, 12.97. Calc. for $C_{24}H_{20}N_4O_2S$: C, 67.27; H, 4.70; N, 13.07).

General Procedure for the Preparation of *N*-(α-cyanomethylene)-sulfonamides 4a-h.

Method A: The α-substituted *N*-(benzotriazol-1-yl)methyl)-*p*-toluenesulfonamide (2 mmol) was dissolved in 2 mL DMSO and treated with 2.2 mmol of solid KCN for 24 hr. The solution was treated with HCl 5% (2mL) when the product precipitated out. The reaction mixture was left overnight in the refrigerator in order to complete the precipitation; afterwards the precipitate was filtered and washed with ethanol (5 mL) and/or ethanol:diethyl ether (1:1, 5-10 mL). The solid thus obtained was pure by NMR.

Method B: The α-substituted *N*-(benzotriazol-1-yl)methyl)-*p*-toluenesulfonamide (2 mmol) was suspended in 2 mL aq. KCN 1N (170 mg, 2 mmol) for 24 hr (for compounds **1b-d** 3mL KCN 1N). The precipitate formed was then filtered and washed with ethanol and/or ethanol:diethyl ether (1:1). The solid thus obtained was pure by NMR.

Method C: The α-substituted *N*-(benzotriazol-1-ylmethyl)-*p*-

toluenesulfonamide (2 mmol), was suspended in 2 mL aq. KCN 1N for 24 hr (for compounds **3b-d** 3mL KCN 1N). The suspension was then treated with methylene chloride (50 mL), and the organic layer was subsequently washed with an aqueous solution 10% of sodium hydroxide (50 mL), and saturated aqueous solution of ammonium chloride (2x50 mL). The organic layer was dried (Na_2SO_4 anh.) and the solvent was evaporated *in vacuo* to yield the pure compound.

***N*-(α-Cyanomethyl)-*p*-toluenesulfonamide** (**4b**). *Method A.* Yield 80 % (lit.[10] yield 60 %). White crystals (ethanol), m.p. 140 °C (lit.[10] m.p. 140-140.5 °C). ^{1}H NMR (DMSO-d_6) δ (ppm) 2.38 (s, 3H), 4.05 (d, 2H, J = 7.5 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 8.4 Hz), 8.52 (t, 1H(N-H), J = 7.5 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 20.9, 30.3, 116.7 (CN), 126.7, 129.7, 136.5, 143.4.

***N*-(α-Cyanoethyl)-*p*-toluenesulfonamide** (**4c**). *Method B, C.* Yield 94 %. White crystals (ethanol), m.p. 142-150 °C. ^{1}H NMR (DMSO-d_6) δ (ppm) 1.48 (d, 3H, J = 7.1 Hz), 2.40 (s, 3H), 4.26 (q, 2H, J = 7.1 Hz), 5.78 (br s, 1H), 7.30 (d, 2H, J = 8 Hz), 7.78 (d, 2H, J = 8 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 20.0, 21.4, 39.7, 118.3 (CN), 127.1, 129.8, 135.9, 144.2. (Found: C, 53.24; H, 5.35; N, 12.63. Calc. for $C_{10}H_{12}N_2O_2S$: C, 53.55; H, 5.39; N, 12.49).

***N*-(α-Cyanopropyl)-*p*-toluenesulfonamide** (**4d**). *Method B, C.* Yield 98 % (lit.[22,23] yield not available). White crystals (ethanol), m.p.156-158 °C

(lit. m.p. not available). ^{1}H NMR (DMSO-d_6) δ (ppm) 1.05 (t, 3H, J = 7.4 Hz), 1.83 (cvintet, 2H, J = 7.4 Hz), 2.44 (s, 3H), 4.14 (br s, 1H, N-H), 4.15 (t, 1H, J = 7.4 Hz), 7.35 (d, 2H, J = 8.3 Hz), 7.80 (d, 2H, J = 8.3 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 9.6, 21.6, 27.4, 45.7, 117.4 (CN), 127.2, 130.0, 136.0, 144.5. (Found: C, 55.56; H, 5.88. Calc. for $C_{11}H_{14}N_2O_2S$: C, 55.46; H, 5.88).

***N*-(α-Cyano-2-methylpropyl)benzenesulfonamide** (**4e**). *Method A.* Yield 90 % (lit.[26] yield not available). White crystals (ethanol), m.p. 156-158 °C (lit. m.p. not available). ^{1}H NMR (DMSO-d_6) δ (ppm) 0.90 (d, 3H, J = 6.7 Hz), 0.94 (d, 3H, J = 6.6 Hz), 1.88 (octet, 1H, J = 6.7 Hz), 3.5 (br s, 1H), 4.19 (d, 1H, J = 6.6 Hz), 7.59-7.70 (m, 3H), 7.87 (d, 2H, J = 6.7 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 17.9, 18.1, 31.8, 49.9, 117.8 (CN), 126.6, 129.2, 132.8, 140.3. (Found: C, 55.59; H, 5.75. Calc. for $C_{11}H_{14}N_2O_2S$: C, 55.46; H, 5.88).

***N*-(α-Cyano-phenylmethyl)-*p*-toluenesulfonamide** (**4f**). *Method B.* Yield 98 % (lit.[15] yield 73 %). White crystals (ethanol), m.p. 133 °C (lit.[15] m.p. 132-134 °C). ^{1}H NMR (DMSO-d_6) δ (ppm) 2.40 (s, 3H), 5.85 (s, 1H), 7.35-7.45 (m, 7H), 7.77 (d, 2H, J = 8.4 Hz), 9.22 (br s, NH); ^{13}C NMR (DMSO-d_6) δ (ppm) 21.0, 47.0, 117.7 (CN), 126.7, 127.0, 128.1, 129.0, 129.7, 133.9, 137.2, 143.4.

***N*-[α-Cyano-(*p*-tolyl)methyl]-*p*-toluenesulfonamide** (**4g**). *Method B.* Yield 95 %. White crystals (ethanol), m.p. 140-142 °C. ^{1}H NMR (DMSO-

d_6) δ (ppm) 2.30 (s, 3H), 2.40 (s, 3H), 3.50 (br s, 1H), 5.75 (br s, 1H), 7.21 (d, 2H, J = 8 Hz), 7.27 (d, 2H, J = 8 Hz), 7.41 (d, 2H, J = 8 Hz), 7.76 (d, 2H, J = 8 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm) 20.7, 21.1, 47.0, 117.9, 126.8, 127.0, 129.5, 129.7, 131.0, 137.3, 138.7, 143.4. (Found: C, 63.97; H, 5.26. Calc. for $C_{16}H_{16}N_2O_2S$: C, 64.00; H, 5.33).

***N*-[α-Cyano-(1-naphthyl)methyl]-*p*-toluenesulfonamide (4h).** *Method C.* Yield 65 %. Yellow crystals (ethanol), m.p. 128-132 °C. ^{1}H NMR ($CDCl_3$) δ (ppm) 2.45 (s, 3H), 4.85 (br s, 1H), 6.10 (s, 1H), 7.33 (d, 2H, J = 8 Hz), 7.43 (t, 1H, J = 7.6 Hz), 7.50-7.64 (m, 2H), 7.72 (d, 1H, J = 7.4 Hz), 7.82 (d, 2H, J = 8 Hz), 7.86-7.94 (m, 2H), 8.04 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 21.5, 46.1, 116.4, 122.3, 124.8, 126.5 (2C), 126.9, 127.2, 127.6, 128.9, 129.4, 129.7, 130.9, 133.7, 135.6, 144.3. (Found: C, 67.51; H, 4.87; N, 8.50. Calc. for $C_{19}H_{16}N_2O_2S$: C, 67.84; H, 4.79; N, 8.33).

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