Supporting Information for

A Direct and Efficient Preparation of 1-Phenyltetrazol-5-yl Sulfides from Alcohols

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Table of Contents

1. GENERAL EXPERIMENTAL.................................................................................................................... S2
2. EXPERIMENTAL PROCEDURES ............................................................................................................ S2
2.1 \(N\)-(Ethylsulfanylmethylene)-\(N\),\(N\)-dimethylammonium tetrafluoroborate (6)........................................ S2
2.2 General procedure for preparation of 1-phenyl-1(\(H\))-tetrazol-5-yl sulfides........................................ S2
2.2.1 Ethyl 6-(1-phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)hexanoate (8a).......................................................... S2
2.2.2 5-(Hex-5-enylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8b).......................................................... S3
2.2.3 5-(3-Methylbut-3-enylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8c).......................................................... S3
2.2.4 5-(2-Methylpropylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8d).......................................................... S3
2.2.5 1-Phenyl-5-(4-phenylbutan-2-ylsulfanyl)-1(\(H\))-tetrazole (8e).......................................................... S3
2.2.6 3-[Phenyl[2-(1-phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)ethyl]amino]propanenitrile (8f).......................... S4
2.2.7 1-Phenyl-5-[2-(tetrahydro-2(\(H\))-pyran-2-yloxy)ethylsulfanyl]-1(\(H\))-tetrazole (8g)..................... S4
2.2.8 1-Phenyl-5-(tetrahydro-2(\(H\))-pyran-2-ylsulfanyl)-1(\(H\))-tetrazole (9)............................................ S4
2.2.9 tert-Butyl 3-(1-phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)propylcarbamate (8h)......................................... S4
2.2.10 5-(1-Phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)pentan-1-ol (8i).......................................................... S5
2.2.11 5-[(4-Methylphenyl)methylsulfanyl]-1-phenyl-1,2,3,4-tetrazole (8j)............................................. S5
2.2.12 (E)-5-(3-Phenylprop-2-enylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8k)............................................. S5
3. NMR SPECTRA .......................................................................................................................................... S6
3.1 \(N\)-(Ethylsulfanylmethylene)-\(N\),\(N\)-dimethylammonium tetrafluoroborate (6)........................................ S6
3.2 Ethyl 6-(1-phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)hexanoate (8a).......................................................... S8
3.3 5-(Hex-5-enylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8b).......................................................... S10
3.4 5-(3-Methylbut-3-enylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8c).......................................................... S12
3.5 5-(2-Methylpropylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8d).......................................................... S14
3.6 1-Phenyl-5-(4-phenylbutan-2-ylsulfanyl)-1(\(H\))-tetrazole (8e).......................................................... S16
3.7 3-[Phenyl[2-(1-phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)ethyl]amino]propanenitrile (8f).......................... S17
3.8 1-Phenyl-5-[2-(tetrahydro-2(\(H\))-pyran-2-yloxy)ethylsulfanyl]-1(\(H\))-tetrazole (8g)..................... S20
3.9 tert-Butyl 3-(1-phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)propylcarbamate (8h)......................................... S24
3.10 5-(1-Phenyl-1(\(H\))-tetrazol-5-ylsulfanyl)pentan-1-ol (8i).......................................................... S26
3.11 5-[(4-Methylphenyl)methylsulfanyl]-1-phenyl-1,2,3,4-tetrazole (8j)............................................. S26
3.12 (E)-5-(3-Phenylprop-2-enylsulfanyl)-1-phenyl-1(\(H\))-tetrazole (8k)............................................. S30
1. **General Experimental**

All reactions were carried out under argon with dry solvents. Dry toluene, dichloromethane and diethyl ether were obtained by passage through activated alumina columns under nitrogen. All other chemicals were used as obtained from commercial sources.

Flash column chromatography was carried out on silica gel (Kieselgel 600) or weakly acidic alumina (50-200 μm). “Petrol” refers to the fraction of petroleum ether that boils in the range 40–60 °C.

IR spectra were recorded of neat solids or liquids or of solvent casts, using a PerkinElmer Spectrum 100 instrument fitted with an ATR accessory. $^1$H and $^{13}$C NMR spectra were recorded as CDCl$_3$ solutions on a Bruker AVANCE DRX600 spectrometer. Mass spectra were recorded by Dr Lisa Harris of the Christopher Ingold Laboratories on a VG70-SE instrument or a Thermo MAT 900 instrument. Melting points were measured on a Reichert-Jung THERMOVAR instrument or an Electrothermal 9100 apparatus and are uncorrected.

2. **Experimental Procedures**

2.1 **$N$-(Ethylsulfanylmethylene)-$N,N$-dimethylammonium tetrafluoroborate (6)**

\[
\text{EtS=NMMe}_2^+\text{BF}_4^-
\]

To a solution of triethyloxonium tetrafluoroborate (5.57 g, 29.3 mmol) in CH$_2$Cl$_2$ (50 mL) was added $N,N$-dimethylthioformamide 5 (2.3 mL, 26.7 mmol) and the solution stirred at room temperature for 18 h. The mixture was concentrated in vacuo to approximately half of its original volume and then added dropwise to stirred Et$_2$O (100 mL); the solution was then placed in a refrigerator for 2 h. The resulting precipitate was collected by filtration under argon, washed with cold Et$_2$O (2 × 25 mL) and dried in vacuo for 10 min to give salt 6 (5.26 g, 96%) as a white crystalline solid which was stored at –25 ºC under argon; m.pt. 20-21 ºC; $\nu_{\text{max}}$/cm$^{-1}$ (solid) 3076, 1650, 1634, 1463; $\delta_H$(CDCl$_3$, 600 MHz) 1.51 (3H, t, $J=7.5$ Hz, CH$_2$CH$_3$), 3.40 (3H, s, NCH$_3$CH$_3$), 3.41 (2H, q, $J=7.5$ Hz, CH$_2$), 3.73 (3H, s, NCH$_3$CH$_3$), 9.57 (1H, s, CH); $\delta_C$(CDCl$_3$, 150 MHz) 15.6 (CH$_2$C$_6$H$_5$), 30.1 (C$_6$H$_2$), 42.4 and 49.4 (N(C$_6$H$_5$)$_2$), 183.1 (C$_6$); $m/z$ (CI) 118 ([EtSCH=NMMe$_2$]$^+$, 100%), 90 (48); HRMS found 118.0686, C$_5$H$_{12}$NS ([EtSCH=NMMe$_2$]$^+$) requires 118.0691.

2.2 **General procedure for preparation of 1-phenyl-1($H$)-tetrazol-5-yl sulfides.**

To a solution of alcohol 2 in toluene (0.4-0.5 M) were added salt 6 (1.5 equiv.), imidazole (1.0 to 5.0 equiv) and 1-phenyl-1($H$)-tetrazole-5-thiol 7 (1.2 to 2.0 equiv.), and the mixture heated to 90 °C. Upon completion of the reaction (monitored by TLC or $^1$H NMR analysis), the solvent was removed in vacuo. Purification by flash chromatography afforded pure sulfide 8.

2.2.1 **Ethyl 6-(1-phenyl-1($H$)-tetrazol-5-ylsulfanyl)hexanoate (8a)**

\[
\text{EtO}_2\text{C}^\equiv\text{S}^\equiv\text{N}^\equiv\text{PhN}^\equiv\text{N}^\equiv
\]

Purification by flash chromatography (Al$_2$O$_3$, petrol/EtOAc 19:1→9:1) gave sulfide 8a as a yellow oil in 76% yield; $\nu_{\text{max}}$/cm$^{-1}$ (CHCl$_3$ cast) 2980, 2937, 2865, 1729, 1597, 1500; $\delta_H$(CDCl$_3$, 600 MHz) 1.24 (3H, t, $J=7.3$ Hz, CH$_3$), 1.48 (2H, app. quin, $J=7.5$ Hz, CH$_2$CH$_2$CH$_2$S), 1.67 (2H, app. quin, $J=7.5$ Hz, CH$_2$CH$_2$C=O), 1.85 (2H, app. quin, $J=7.5$ Hz, CH$_2$CH$_2$S), 2.30 (2H, t, $J=7.5$ Hz, CH$_2$C=O), 3.39 (2H, t, $J=7.4$ Hz, CH$_2$S), 4.11 (2H, q, $J=7.3$ Hz, CH$_2$CH$_3$), 5.1-7.59 (5H, m, aromatic CH); $\delta_C$(CDCl$_3$, 150 MHz) 14.4 (CH$_3$), 24.4 (CH$_2$CH$_2$C=O), 28.2 (CH$_2$CH$_2$CH$_2$S), 28.9 (CH$_2$CH$_2$S), 33.2 (CH$_3$S), 34.2 (CH$_2$C=O), 60.4 (CH$_2$CH$_3$), 124.0, 129.9 and 130.2 (aromatic CH), 133.8 (aromatic C), 154.5 (NCS), 173.6 (C=O); $m/z$ (CI) 321 (MH$^+$, 100%), 275 (MH$^+$–EtOH, 41), 119 (55); HRMS found 321.1379, C$_{15}$H$_{21}$N$_2$O$_2$S (MH$^+$) requires 321.1385.
2.2.2 5-(Hex-5-ylsulfanyl)-1-phenyl-1(H)-tetrazole (8b)

Purification by flash chromatography (Al₂O₃, petrol→petrol/EtOAc 19:1) gave sulfide 8b as a colorless oil in 70% yield; ν max/cm⁻¹ (CDCl₃ cast) 3071, 2927, 2856, 2640, 1597, 1499; δH (CDCl₃, 600 MHz) 1.54 (2H, app. quin, J 7.4 Hz, CH₂=CHCH₂CH=CH₂), 1.83 (2H, app. quin, J 7.4 Hz, CH₂CH₂S), 2.08 (2H, q, J 7.0 Hz, CH₂CH=CH₂), 3.39 (2H, t, J 7.4 Hz, CH₂S), 4.95 (1H, d, J 10.0 Hz) and 5.00 (1H, d, J 17.1 Hz, CH=CH₂), 5.77 (1H, ddt, J 17.1, 10.0, 7.0 Hz, CH=CH₂), 7.50-7.59 (5H, m, aromatic CH); δC (CDCl₃, 150 MHz) 27.9 (CH₂CH₂CH=CH₂), 28.6 (CH₂CH₂S), 33.2 (CH₂S), 33.3 (CH₂=CHCH₂), 115.2 (CH=CH₂), 123.9, 130.0 and 130.2 (aromatic CH), 133.8 (aromatic C), 138.1 (CH₂=CH₂), 154.6 (NC=S); m/z (CI) 261 (MH⁺, 100%), 207 (28); HRMS found 261.1165, C₁₂H₁₁N₂S (MH⁺) requires 261.1174.

2.2.3 5-(3-Methylbut-3-ylsulfanyl)-1-phenyl-1(H)-tetrazole (8c)

Purification by flash chromatography (SiO₂, petrol→petrol/EtOAc 24:1) gave sulfide 8c as a pale yellow oil in 67% yield; ν max/cm⁻¹ (CDCl₃ cast) 3078, 2960, 2937, 1649, 1597, 1499; δH (CDCl₃, 600 MHz) 1.77 (3H, s, CH₃), 2.53 (2H, t, J 7.5 Hz, CH₂CH₃), 3.53 (2H, t, J 7.3 Hz, CH₂S), 4.77 (1H, s) and 4.83 (1H, s, CH₂CH=CH₂), 7.51-7.59 (5H, m, aromatic CH); δC (CDCl₃, 150 MHz) 22.2 (CH₃), 31.5 (CH₂CH₃), 37.0 (CH₂S), 112.6 (CH=CH₂), 124.0, 129.9 and 130.2 (aromatic CH), 133.8 (aromatic C), 142.6 (CH₂=CH₂), 154.5 (SCN); m/z (EI) 246 (M⁺, 40%), 159 (45), 135 (32), 85 (100); HRMS found 246.0935, C₁₂H₁₄N₂S (M⁺) requires 246.0939.

2.2.4 5-(2-Methylpropylsulfanyl)-1-phenyl-1(H)-tetrazole (8d)

Purification by flash chromatography (SiO₂, petrol→petrol/EtOAc 19:1) gave sulfide 8d as a colorless oil in 75% yield; ν max/cm⁻¹ (film) 2960, 2929, 2871, 1597, 1499; δH (CDCl₃, 600 MHz) 1.05 (6H, d, J 6.8 Hz, CH(CH₃)₂), 2.10 (1H, nonet, J 6.8 Hz, CH(CH₃)₂), 3.31 (2H, d, J 6.8 Hz, CH₂), 7.52-7.60 (5H, m, aromatic CH); δC (CDCl₃, 150 MHz) 21.8 (CH(CH₃)₂), 28.4 (CH₂CH₃), 41.9 (CH₂), 124.0, 129.9 and 130.2 (aromatic CH), 133.9 (aromatic C), 154.8 (SCN); m/z (CI) 235 (MH⁺, 100%); HRMS found 235.1022, C₁₃H₁₃N₂S (MH⁺) requires 235.1017.

2.2.5 1-Phenyl-5-(4-phenylbutan-2-ylsulfanyl)-1(H)-tetrazole (8e)

Purification by flash chromatography (SiO₂, petrol→petrol/EtOAc 24:1) gave sulfide 8e as a colorless oil in 83% yield; ν max/cm⁻¹ (CDCl₃ cast) 3063, 3027, 2926, 2859, 1597, 1499, 1455, 1387; δH (CDCl₃, 600 MHz) 1.56 (3H, d, J 6.8 Hz, CH₃), 2.02 (1H, ddt, J 13.7, 9.5, 6.8 Hz) and 2.14 (1H, ddt, J 13.7, 9.5, 6.8 Hz, CH₂CH₃S), 2.72-2.83 (2H, m, PhCH₂), 4.07 (1H, sext., J 6.8 Hz, CHS), 7.15-7.21 (3H, m), 7.25-7.30 (2H, m) and 7.51-7.60 (5H, m, aromatic CH); δC (CDCl₃, 150 MHz) 21.6 (CH₃), 33.3 (PhCH₂), 38.3 (CH₂CH₃S), 44.5 (CHS), 124.2, 126.3, 128.5, 128.6, 129.9 and 130.2 (aromatic CH), 133.8 and 141.0 (aromatic C), 154.0 (SCN); m/z (CI) 311 (MH⁺, 100%), 119 (58); HRMS found 311.1327, C₁₇H₁₄N₂S (MH⁺) requires 311.1330.

2.2.6 3-[Phenyl[2-(1-phenyl-1(H)-tetrazol-5-ylsulfanyl)ethyl]amino]propanenitrile (8f)

Purification by flash chromatography (SiO2, petrol/EtOAc 17:3→4:1) gave sulfide 8f as a viscous colorless oil in 88% yield; \( \nu_{\text{max}}/\text{cm}^{-1} \) (neat) 3063, 2932, 2248, 1693, 1597, 1499; \( \delta_\text{H} \) (CDCl3, 600 MHz) 2.65 (2H, t, J 6.8 Hz, CH2CN), 3.53 (2H, t, J 7.2 Hz, CH2S), 3.77 (2H, t, J 6.8 Hz, CH2CH2S), 3.89 (2H, t, J 7.2 Hz, CH2CH2S), 6.80-6.84 (3H, m), 7.27-7.32 (2H, m) and 7.53-7.60 (5H, m, aromatic CH); \( \delta_\text{C} \) (CDCl3, 150 MHz) 16.3 (CH2CN), 30.1 (CH2S), 47.6 (CH2CH2CN), 50.9 (CH2CH2S), 113.2 (aromatic CH), 118.4 (CN), 118.7, 123.9, 130.0, 130.0 and 130.4 (aromatic CH), 133.6 (aromatic C(amine)), 145.7 (aromatic C(amine)), 154.0 (SCN); \( m/z \) (ES+) 373 (MNa+, 100%); HRMS found 373.1211, C15H13N6NaS (MNa+) requires 373.1211.

2.2.7 1-Phenyl-5-[2-(tetrahydro-2(H)-pyran-2-yloxy)ethylsulfanyl]-1(H)-tetrazole (8g)

Purification by flash chromatography (Al2O3, petrol/EtOAc 9:1→4:1) gave sulfide 8g as a colorless oil in 80% yield; \( \nu_{\text{max}}/\text{cm}^{-1} \) (CDCl3 cast) 2942, 2871, 1597, 1499; \( \delta_\text{H} \) (CDCl3, 600 MHz) 1.45-1.60 (4H, m, OCH2CH2CH2CH2), 1.68 (1H, m, OCH2CH2CH2), 1.77 (1H, m, OCH2CH2CH2), 3.49 (1H, m, OCH2CH2CH2), 3.61 (1H, dt, J 13.6, 5.9 Hz) and 3.66 (1H, dt, J 13.6, 5.9 Hz, CH2S), 3.80-3.85 (2H, m, OCH2CH2CH2 and OCH2CH2), 4.08 (1H, dt, J 10.7, 5.9 Hz, OCH2CH2S), 4.63 (1H, dd, J 4.1, 2.9 Hz, OCHO), 7.51-7.59 (5H, m, aromatic CH); \( \delta_\text{C} \) (CDCl3, 150 MHz) \( \delta \) 19.5 (OCH2CH2CH2), 25.4 (CH2S), 30.5 (OCH2CH2CH2), 33.6 (CH2S), 62.5 (OCH2CH2CH2), 65.6 (OCH2CH2S), 99.1 (OCHO), 124.0, 129.9 and 130.3 (aromatic CH), 133.8 (aromatic C), 154.4 (SCN); \( m/z \) (ES+) 329 (MNa+, 80%), 301 (31), 223 (100); HRMS found 329.1052, C14H18N2O2S (MNa+) requires 329.1048.

2.2.8 1-Phenyl-5-[tetrahydro-2(H)-pyran-2-ylsulfanyl]-1(H)-tetrazole (9)

Obtained in the reaction of 2f in the presence of 1 equiv. imidazole. Purification by flash chromatography (Al2O3, petrol→petrol/EtOAc 19:1) gave sulfide 9 as a white solid in 39% yield; m.p. 69-71 °C; \( \nu_{\text{max}}/\text{cm}^{-1} \) (solid) 2966, 2941, 2851, 1595, 1498; \( \delta_\text{H} \) (CDCl3, 600 MHz) 1.68 (1H, m, OCH2CH2), 1.73-1.83 (2H, m, OCH2CH2CH2), 2.04 (1H, m, SCHCH), 2.11-2.20 (1H, m, OCH2CH2CH2), 2.36 (1H, dddd, J 13.1 11.8, 10.1, 4.2 Hz, SCHCH), 3.80 (1H, td, J 11.5, 2.7 Hz) and 4.16 (1H, m, OCH2), 5.98 (1H, dd, J 10.1, 2.8 Hz, OCHS), 7.48-7.57 (3H, m) and 7.90-7.93 (2H, m, aromatic CH); \( \delta_\text{C} \) (CDCl3, 150 MHz) \( \delta \) 22.3 (OCH2CH2CH2), 24.8 (OCH2CH2), 29.1 (SCHCH2), 68.5 (OCH2), 83.5 (OCHS), 124.2, 129.4 and 129.8 (aromatic CH), 134.6 (aromatic C), 163.7 (SCN); \( m/z \) (CI) 263 (MH+, 100%), 179 (100), 85 (23); HRMS found 263.0958, C14H13N2O2S (M+) requires 263.0967.

2.2.9 tert-Butyl 3-(1-phenyl-1(H)-tetrazol-5-ylsulfanyl)propylcarbamate (8h)

Purification by flash chromatography (Al2O3, petrol/EtOAc 9:1→17:3) gave sulfide 8h as a cloudy yellow oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) (CDCl3 cast) 3342 br, 2978, 2929, 1696, 1597, 1500; \( \delta_\text{H} \) (CDCl3, 600 MHz) 1.43 (9H, s, C(CH3)3), 2.00-2.07 (2H, m, CH2CH2N), 3.22-3.30 (2H, m, CH2N), 3.43 (2H, td, J 6.9, 2.0 Hz, CH2S), 4.81-5.00 (1H, br s, NH), 7.51-7.60 (5H, m, aromatic CH); \( \delta_\text{C} \) (CDCl3, 150 MHz) 28.5 (C(CH3)3), 29.8 (CH2CH2N), 30.6 (CH2S), 38.9 (CH2N), 79.5 (C(CH3)3), 124.0, 129.9 and 130.3 (aromatic CH), 133.7 (aromatic C), 154.5 (SCN), 156.2 (C=O); \( m/z \) (EI) 335 (M+, 8%), 279 (100); HRMS found 335.1420, C15H17N2O2S (M+) requires 335.1416.
2.2.10 5-(1-Phenyl-1(H)-tetrazol-5-ylsulfanyl)pentan-1-ol (8i)

Purification by flash chromatography (SiO$_2$, petrol/EtOAc 7:3→1:1) gave sulfide 8i as a colorless oil; $\nu_{\text{max}}$/cm$^{-1}$ (CDCl$_3$ cast) 3414 br, 2941, 2865, 1597, 1500; $\delta_{\text{H}}$ (CDCl$_3$, 600 MHz) 1.54 (2H, m, CH$_2$CH$_2$O), 1.62 (2H, m, CH$_2$CH$_2$S), 3.40 (2H, t, $J$ 7.3 Hz, CH$_2$S), 3.66 (2H, t, $J$ 6.3 Hz, CH$_2$O), 7.51-7.60 (5H, m, aromatic CH); $\delta_{\text{C}}$ (CDCl$_3$, 150 MHz) 25.0 (CCH$_2$CH$_2$O), 29.0 (CCH$_2$S), 32.1 (CCH$_2$O), 62.7 (CCH$_2$O), 124.0, 129.9 and 130.0 (aromatic C), 133.8 (aromatic C), 154.5 (SCN); $m/z$ (Cl) 265 (MH$^+$, 100%); HRMS found 265.1114, C$_{12}$H$_{17}$ON$_4$S (MH$^+$) requires 265.1123.

2.2.11 5-[(4-Methylphenyl)methylsulfanyl]-1-phenyl-1(H)-1,2,3,4-tetrazole (8j)$^4$

Purification by flash chromatography (SiO$_2$, petrol→petrol/EtOAc 19:1) gave sulfide 8j as a thick pale yellow oil; $\nu_{\text{max}}$/cm$^{-1}$ (CDCl$_3$ cast) 3043, 2922, 1597, 1515, 1499; $\delta_{\text{H}}$ (CDCl$_3$, 600 MHz) 2.33 (3H, s, CH$_3$), 4.60 (2H, s, CH$_2$), 7.13 (2H, d, $J$ 7.9 Hz, CH$_3$CCH), 7.31 (2H, d, $J$ 7.9 Hz, SCHRCH), 7.50-7.54 (5H, m, aromatic CH); $\delta_{\text{C}}$ (CDCl$_3$, 150 MHz) 21.3 (CH$_3$), 37.6 (CH$_2$), 123.9, 129.3, 129.6, 129.9 and 130.2 (aromatic CH), 132.2 (SCHRCH), 133.7 (NCHR), 135.1 (SCN); $m/z$ (EI) 282 (M$^+$, 30%), 221 (22), 137 (21), 118 (19), 105 (100); HRMS found 282.0927, C$_{15}$H$_{14}$N$_4$S (M$^+$) requires 282.0934.

2.2.12 (E)-5-(3-Phenylprop-2-enylsulfanyl)-1-phenyl-1(H)-tetrazole (8k)$^5$

Purification by flash chromatography (SiO$_2$, petrol→petrol/EtOAc 19:1) gave sulfide 8k as a thick pale yellow oil; $\nu_{\text{max}}$/cm$^{-1}$ (CDCl$_3$ cast) 3060, 3027, 1597, 1499; $\delta_{\text{H}}$ (CDCl$_3$, 600 MHz) 4.21 (2H, dd, $J$ 7.5, 1.1 Hz, SCH$_2$), 6.36 (1H, dt, $J$ 15.7, 7.5 Hz, SCH$_2$), 6.71 (1H, d, $J$ 15.7 Hz, PhCH), 7.24 (1H, m), 7.28-7.32 (2H, m), 7.34-7.37 (2H, m) and 7.51-7.60 (5H, m, aromatic CH); $\delta_{\text{C}}$ (CDCl$_3$, 150 MHz) 36.0 (SCHR), 122.5 (SCHRCH), 124.0, 126.7, 128.3, 128.8, 129.9 and 130.3 (aromatic CH), 133.7 (NCHR), 135.3 (PhCH), 136.1 (CCHR=CH), 153.9 (SCN); $m/z$ (EI) 294 (M$^+$, 17%), 266 (16), 265 (16), 233 (15), 147 (17), 118 (22), 117 (100); HRMS found 294.0925, C$_{16}$H$_{14}$N$_4$S (M$^+$) requires 294.0934.

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3. NMR Spectra
3.1 $N$-(Ethylsulfanylmethylene)-$N,N$-dimethylammonium tetrafluoroborate

[Diagram of NMR spectrum with chemical shifts marked]
3.2 Ethyl 6-(1-phenyl-1H-tetrazol-5-ylsulfanyl)hexanoate (8a)
3.3 5-(Hex-5-enylsulfanyl)-1-phenyl-1H-tetrazole (8b)

\[
\text{\(\text{S} = \text{N} - \text{N}\)}
\]

\[
\text{\(\text{Ph} = \text{N} - \text{N}\)}
\]
3.4  5-(3-Methylbut-3-enylsulfanyl)-1-phenyl-1(\textit{H})-tetrazole (8c)
3.5 5-(2-Methylpropylsulfanyl)-1-phenyl-1(H)-tetrazole (8d)
3.6 1-Phenyl-5-(4-phenylbutan-2-ylsulfanyl)-1(H)-tetrazole (8e)
3.7 3-{Phenyl[2-(1-phenyl-1(H)-tetrazol-5-ylsulfanyl)ethyl]amino}propanenitrile (8f)
3.8 1-Phenyl-5-[2-(tetrahydro-2(H)-pyran-2-yl)oxy]ethylsulfanyl]-1(H)-tetrazole (8g)
3.9 1-Phenyl-5-(tetrahydro-2(\(H\))-pyran-2-ylsulfanyl)-1(\(H\))-tetrazole (9)
3.10 \textit{tert}-Butyl 3-(1-phenyl-1(\textit{H})-tetrazol-5-ylsulfanyl)propylcarbamate (8h)
3.11 5-(1-Phenyl-1(H)-tetrazol-5-ylsulfanyl)pentan-1-ol (8i)
3.12 5-[(4-Methylphenyl)methylsulfanyl]-1-phenyl-1(\textit{H})-1,2,3,4-tetrazole (8j)
3.13  \((E)-5-(3\text{-Phenylprop-2-enylsulfanyl})-1\text{-phenyl-1}(H)\text{-tetrazole}\ (8k)\)