# Synthesis of aryl thiocyanates using $Al_2O_3$/$MeSO_3H$ (AMA) as a novel heterogeneous system

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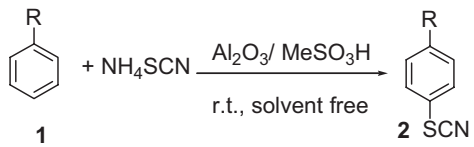
Indoles and various aromatic and heteroaromatic compounds undergo smooth thiocyanation with ammonium thiocyanate in the presence of a mixture of $Al_2O_3$/$MeSO_3H$ (AMA) under mild conditions without use of any organic solvents to afford the corresponding aryl thiocyanates in excellent yields and with high selectivity. The reactions proceed rapidly at room temperature.

**Keywords:** $Al_2O_3$, $MeSO_3H$, aromatic compounds, thiocyanation, indoles, solvent-free conditions

Aromatic or heteroaromatic thiocyanates are useful intermediates in the synthesis of sulfur-containing heterocycles.[1,2] Furthermore, aryl thiocyanates can be easily transformed into various sulfur functional groups[3,4] such as thiophenols by reduction with lithium aluminium hydride and aryl nitriles/disulfides by reaction with aromatic Grignard reagents. Thus, the direct thiocyanation of aromatic systems is of importance. In view of the versatility of the thiocyanate group in heterocycle construction,[2,5] it is of significance to probe the direct thiocyanation of aromatic and heteroaromatic compounds. Several methods have been developed for the thiocyanation of arenes and indoles,[6-15] including bromine/potassium thiocyanate[6] and *N*-thiocyanatosuccinimide (only for 5-methoxy-2-methylindole and accompanied by two bis-thiocyanates)[7] and (each with ammonium thiocyanate) ceric ammonium nitrate (CAN),[8] acidic K-10 clay,[9] iodine/MeOH (only for indoles and aryl amines),[10] oxone®[11] and iron(III)chloride (only for indoles and aryl amines).[12] However, these methodologies suffer from one or more drawbacks such as the lack of availability or difficult preparation of starting materials,[6,7] the requirement for a large excess of strong oxidising reagents, low yields for some compounds,[8] and reactions under certain special conditions.[9] Furthermore, some require high temperatures and the use of a large amount of organic solvents to obtain satisfactory results. Since organosulfur compounds have become increasingly useful and important in the field of drugs and pharmaceuticals, the development of simple, convenient and efficient approaches are desirable. In the present work, we report a novel, efficient, and regioselective thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocyanate in the presence of $Al_2O_3$/$MeSO_3H$ (AMA).

We have recently reported that (AMA) was an effective reagent for many useful organic reactions such as the Fries-rearrangement,[16] the Beckmann rearrangement,[17] the preparation of amides from nitriles,[18] the mono-esterification of diols,[19] the conversion of aldehydes into monoesters,[20] the synthesis of macrocyclic polyether-diesters[21] and the synthesis of coumarins.[22] This paper reports its application in the thiocyanation of various aromatic compounds (Scheme 1).




**Scheme 1**

Initially, the reaction of anisole (**1a**) with ammonium thiocyanate was chosen as a model reaction and its behaviour was studied under a variety of conditions by TLC and $^1$H NMR spectroscopy (Table 1).

As shown in Table 1, the best results were obtained using a mixture of $Al_2O_3$ and $MeSO_3H$ in 1:5 molar ratio, when carried out at room temperature for 10 min (entry 7).

A typical experimental procedure is as follows: to a mixture of $MeSO_3H$ (1 ml, 15 mmol) and $Al_2O_3$ (acidic type 540 C, 0.27 g, 3 mmol) was added anisole (**1a**) (1 mmol) and ammonium thiocyanate (1 mmol). The mixture was stirred for 10 min. Then the reaction mixture was extracted with ethyl acetate and after evaporation of the organic layer 4-thiocyanatoanisole (**2a**) was obtained in an excellent yield.

Under the best reaction conditions described above, various aromatic and heteroaromatic compounds (Table 2, 1–15) were converted into the corresponding aryl thiocyanates. The products were identified by $^1$H and $^{13}$C NMR, MS and IR analysis. The IR spectra showed the characteristic peak of –SCN near 2080 cm$^{-1}$ and the –C–S stretching near 730 cm$^{-1}$. The results are listed in Table 2.

The results summarised in Table 2 reveal that excellent yields were obtained with aromatic and heteroaromatic compounds. All of the aromatic compounds reacted very rapidly within 5–73 min. In all cases, the reactions proceeded smoothly at room temperature with high regioselectivity. This method is very clean and free from side products.

**Table 1** Thiocyanation of anisole (1 mmol) with ammonium thiocyanate (1 mmol) under various reaction conditions

| Entry | Catalyst/reagent | Solvent | Time | Yield/%[a] |
|---|---|---|---|---|
| 1 | $I_2$, r.t. | MeOH | 24 h | 0 |
| 2 | $FeCl_3$, r.t. | $CH_2Cl_2$ | 24 h | 5 |
| 3 | Sulfamic acid | None | 24 h | 0 |
| 4 | Alumina sulfonic acid (ASA)[23,24] | None | 24 h | 0 |
| 5 | $Al_2O_3$ (3 mmol), r.t. | None | 24 h | 0 |
| 6 | $MeSO_3H$, (15 mmol), r.t. | None | 24 h | 65 |
| 7 | $Al_2O_3$ (3 mmol)/$MeSO_3H$ (15 mmol), r.t. | None | 10 min | 98 |
| 8 | $Al_2O_3$ (2 mmol)/$MeSO_3H$ (15 mmol), r.t. | None | 1 h | 80 |
| 9 | $Al_2O_3$ (1 mmol)/$MeSO_3H$ (15 mmol), r.t. | None | 2 h | 80 |
| 10 | No catalyst/reagent | None | 24 h | 0 |

[a]Isolated yields.

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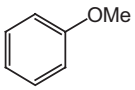
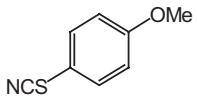
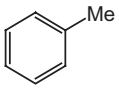
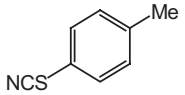
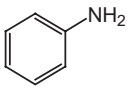
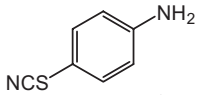
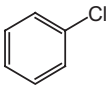
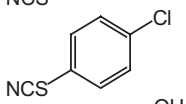
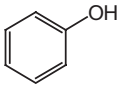
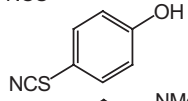
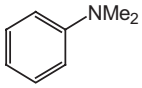
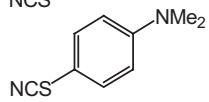
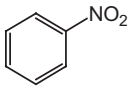
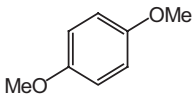
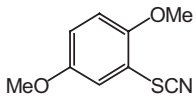
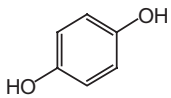
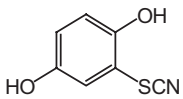
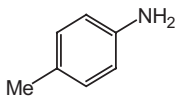
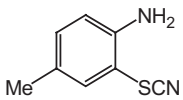
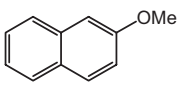
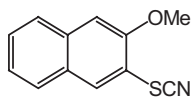
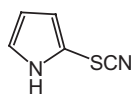
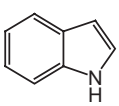
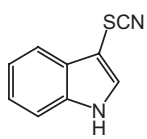
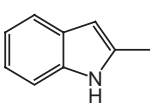
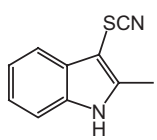
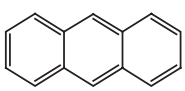
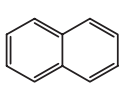
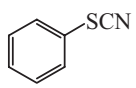
**Table 2** Thiocyanation of aromatic compounds using AMA

| Entry | Substrates | | Products | | Time/min | Yield/%[a] |
|---|---|---|---|---|---|---|
| 1 |  | **1a** |  | **2a** | 10 | 98 |
| 2 |  | **1b** |  | **2b** | 65 | 80 |
| 3 |  | **1c** |  | **2c** | 4 | 98 |
| 4 |  | **1d** |  | **2d** | 35 | 95 |
| 5 |  | **1e** |  | **2e** | 5 | 97 |
| 6 |  | **1f** |  | **2f** | 10 | 85 |
| 7 |  | **1g** | No reaction | | | |
| 8 |  | **1h** |  | **2h** | 25 | 98 |
| 9 |  | **1i** |  | **2i** | 45 | 98 |
| 10 |  | **1j** |  | **2j** | 5 | 94 |
| 11 |  | **1k** |  | **2k** | 20 | 94 |
| 12 |  | **1l** |  | **2l** | 15 | 94 |
| 13 |  | **1m** |  | **2m** | 10 | 98 |
| 14 |  | **1n** |  | **2n** | 20 | 90 |
| 15 |  | **1o** |  | **2o** | 73 | 81 |
| 16 |  | **1p** | No reaction | | | |
| 17 |  | **1q** | No reaction | | | |
| 18 |  | **1r** |  | **2r** | 30 | 84 |

[a]Yields are of the isolated compounds.

It was very exciting to find that unactivated benzenes such as chlorobenzene reacted smoothly in the presence of AMA to afford the corresponding thiocyanato aromatics in high yields (Table 2, entry 4). Thicyanation occurs exclusively at the position *para* to –OMe, –Me, –OH, $–NH_2$, $–NMe_2$ and –Cl for all of the compounds studied in excellent yields. However, in cases where the *para* positions are blocked (Table 2, entries 8–11), the thiocyano group is introduced in the *ortho* position. This procedure can also be used for the thiocyanation of heterocyclic compounds such as furan, pyrrole, and indoles (entries 12–15). In the case of indoles, the products were obtained with mono-thiocyanation at the 3-position of the indole ring. The thiocyanation of nitrobenzene, anthracene, and naphthalene with ammonium thiocyanate seemed more difficult to perform perhaps because of inherent reactivity or mixing problems (entries 7, 16 and 17). The present method provides a useful means for the regioselective thiocyanation of aromatic compounds. We believe that this constitutes the first satisfactory method for the direct conversion of arenes to the corresponding thiocyanoarenes. Exhaustive search of Chemical Abstracts has led us to this conclusion.

Another interesting behaviour of alumina lies in the fact that it can be reused after simple washing with AcOEt and $H_2O$, thus rendering the process more economic. The yields of 4-thiocyanatoanisole (**1a**) in the 2nd, 3rd, 4th, and 5th use of the alumina were almost the same as that in the 1st use. It should be noted that $MeSO_3H$ was not adsorbed on the alumina during the reaction and, after extraction with AcOEt, $MeSO_3H$ was not found on the alumina; thus, it is necessary to add $MeSO_3H$ again in the use of recovered alumina.

In conclusion, we have demonstrated that a readily available and inexpensive reagent AMA is very effective and highly selective for the thiocyanation of aromatic compounds. The extremely high regioselectivity of this reaction may be very useful in organic synthesis. The low cost and availability of the reagent, the easy procedure and work-up, the lack of solvent in the reaction step, and the high yields and short reaction times make this method a useful addition to the present methodologies. Hence, we believe that it will find wide application in organic synthesis as well as in industry.

## Experimental

*General*

$^1$H NMR and $^{13}$C NMR spectra were measured on a Bruker Advance DPX FT 250 and 62.9 MHz spectrometer with TMS as an internal standard. IR spectra were obtained on Perkin–Elmer or FTIR-800 instruments. Mass spectra were obtained on a Shimadzu GCMS0QP 1000EX at 20 and/or 70 eV. Elemental analyses were performed on PerkinElmer 240-B microanalyser. $Al_2O_3$ (acidic type 540 C) was purchased from Merck company.

*General procedure for thiocyanation of aromatic and heteroaromatic compounds*

To a mixture of $MeSO_3H$ (1.0 ml) and $Al_2O_3$ (0.27 g, 3.0 mmol) were added the aromatic compound (1 mmol) and $NH_4SCN$ (1 mmol). The mixture was stirred at room temperature for the appropriate time (Table 2). Then the mixture was poured into water and extracted twice with ethyl acetate or chloroform (20 ml). The organic layer was washed with a saturated solution of sodium bicarbonate (20 ml). Then the organic layer dried over $CaCl_2$ and evaporated under reduced pressure. The resulting product was purified by column chromatography on silica gel (Merck, 100-2—mesh, EtOAc–hexane, 1 : 9) to afford the pure thiocyanato derivative. For $^1$H NMR spectra of AA'XX' systems $J^* = J_{23} + J_{25}$.

*4-Thiocyanatoanisole* (**2a**): Yellow crystalline solid; m.p. 131–133°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3168, 2076, 1619, 790; $^1$H NMR (250 MHz, $d_6$-DMSO): δ 7.98 (m, 2H, $J^*$ = 8.7 Hz, ArH), 6.99 (m, 2H, $J^*$ = 8.7 Hz, ArH), 3.84 (s, 3H, –OC*H*$_3$); $^{13}$C NMR (62.9 MHz, $d_6$-DMSO): δ 55.3 (–O*C*H$_3$), 112.9 (–S*C*N), 113.4, 129.3, 131.2, 161.8; GC-Ms/EI: *m/z* (%) = 167 (M$^+$ + 2, 97.8), 166 (M$^+$ + 1, 24.9), 165 (M$^+$, 12.0), 151 (43.2), 150 (13.7), 134 (100), 83 (20.1), 76 (11.3), 57 (48.4); Anal. Calcd for $C_8H_7NOS$: C, 58.2; H, 4.3. Found: C, 58.0; H, 4.0%.

*4-Thiocyanatotoluene* (**2b**): Yellow crystalline solid; m.p. 46–55°C (lit.[14] 54 °C); IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3168, 2077, 1613; 790; $^1$H NMR (250 MHz, $CDCl_3$): δ 7.88 (m, 2H, $J^*$ = 8.8 Hz, ArH), 7.45 (m, 2H, $J^*$ = 8.8 Hz, ArH), 3.38 (s, 3H, –C*H*$_3$); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 61.7(–*C*H$_3$), 119.3 (–S*C*N), 128.8, 131.8, 132.8, 155.4; GC-Ms/EI: *m/z* (%) = 151 (M$^+$ + 2, 96.0), 150 (M$^+$ + 1, 23.7), 149 (M$^+$, 11.7), 135 (43.2), 134 (100), 133 (21.9), 83 (41.0), 57 (51.0); Anal. Calcd for $C_8H_7NS$: C, 64.4; H, 4.7. Found: C, 64.2; H, 4.5%.

*4-Thiocyanatoaniline* (**2c**): Yellow crystalline solid; m.p. 52–55°C (lit.[11] 49–51°C); IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3623, 3412, 2071, 782; $^1$H NMR (250 MHz, $d_6$-DMSO): δ 6.94 (m, 2H, $J^*$ = 8.5 Hz, ArH), 7.46 (m, 2H, $J^*$ = 8.5 Hz, ArH), 4.56 (s, brs, 2H, –N*H*$_2$); $^{13}$C NMR (62.9 MHz, $d_6$-DMSO): δ 115.9 (–S*C*N), 122.7, 128.3, 128.5, 156.6; GC-Ms/EI: *m/z* (%) = 151 (M$^+$ + 1, 2.4), 150 (M$^+$, 36.2), 149 (M$^+$, 38.6), 108 (31.5), 71 (64.6), 84 (44.1), 57 (100), 56 (50.4); Anal. Calcd for $C_7H_6N_2S$: C, 56.0; H, 4.0. Found: C, 55.9; H, 4.0%.

*1-Chloro-4-thiocyanatobenzene* (**2d**): Yellow crystalline solid; m.p. 73–78°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 2080, 7879; $^1$H NMR (250 MHz, $CDCl_3$): δ 7.36 (m, 2H, $J^*$ = 8.5 Hz, ArH), 7.08 (m, 2H, $J^*$ = 8.5 Hz, ArH); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 113.1(–S*C*N), 121.8, 129.3, 132.3, 134.6; GC-Ms/EI: *m/z* (%) = 169 (M$^+$, 19.6), 167 (18.6), 149 (52.0), 129 (20.6), 97 (30.4),81 (44.1), 57 (100), 55 (81.4); Anal. Calcd for $C_7H_4ClNS$: C, 49.6; H, 2.4. Found: C, 49.2; H, 2.1%.

*4-Thiocyanatophenol* (**2e**): Yellow crystalline solid; m.p. 148–152°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3341, 2077, 782; $^1$H NMR (250 MHz, $CDCl_3$): δ 7.46 (m, 2H, $J^*$ = 7.6 Hz, ArH), 6.81 (m, 2H, $J^*$ = 7.6 Hz, ArH), 4.14 (brs, 1H, –O*H*). $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 114.3 (–S*C*N), 117.3, 122.7, 129.6, 160.5; GC-Ms/EI: *m/z* (%) = 153 (M$^+$ + 2, 4.2), 152 (M$^+$ + 1, 14.1), 151 (M$^+$, 13.2), 150 (60.4), 137 (43.60), 134 (100), 123 (6.7), 91 (4.7), 57 (56.1); Anal. Calcd for $C_7H_5NOS$: C, 55.6; H, 3.3. Found: C, 55.4; H, 3.1%.

*N,N-Dimethyl-4-thiocyanatonaniline* (**2f**): Yellow crystalline solid; m.p. 73–75°C (lit.[12] 72–74°C); IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3234, 3060, 2092, 765; $^1$H NMR ($CDCl_3$): δ 6.88 (m, 2H, $J^*$ = 8.4 Hz, ArH), 6.97 (m, 2H, $J^*$ = 8.4 Hz, ArH) 3.7 (s, 6H, –C*H*$_3$); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 55.2 (–*C*H$_3$), 113.0 (–S*C*N), 114.5, 116.2, 130.4, 153.2; GC-Ms/EI: *m/z* (%) = 179 (M$^+$ + 1, 1.1), 178 (M$^+$, 0.5), 165 (8.7), 129 (12.9), 111 (17.0), 83 (36.3), 57 (100), 55 (90.1); Anal. Calcd for $C_9H_{10}N_2S$: C, 60.6; H, 5.7. Found: C, 60.5; H, 5.4%.

*1,4-Dimethoxy-2-thiocyanatobenzene* (**2h**): Orange crystalline solid; m.p. 72–75°C (lit.[15] 68–69°C); IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3404, 3184, 2073, 1631, 711; $^1$H NMR (250 MHz, $CDCl_3$): δ 6.76–6.77 (m, 3H, ArH), 3.70 (s, 6H, –OMe); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 55.8 (–O*C*H$_3$), 56.6(–O*C*H$_3$), 113.1 (–S*C*N), 114.6, 116.9, 119.6, 120.4, 151.1, 153.7; GC-MS/EI: *m/z* (%) = 196 (M$^+$ + 1, 5.9), 195 (M$^+$, 8.3), 166 (24.6), 165 (7.3), 150 (27.7), 123 (16.6), 97 (37.2), 71 (44.8), 55 (100); Anal. Calcd for $C_9H_9NO_2S$: C, 55.4; H, 4.7. Found: C, 55.1; H, 4.3%.

*1,4-Dihydroxy 2-thiocyanatobenzene-1,4-diol* (**2i**): Yellow crystalline solid; m.p. 126–128°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3348, 3168, 2092, 1618, 759; $^1$H NMR (250 MHz, $d_6$-DMSO): δ 8.82 (s, 1H, –O*H*), 8.61 (s, 1H, –O*H*), 6.13–6.37 (m, 3H, ArH); $^{13}$C NMR (62.9 MHz, $d_6$-DMSO): δ 115.1 (-S*C*N), 115.6, 116.1, 120.6, 123.3, 149.1, 154.7; GC–MS/EI: *m/z* (%) = 168 (M$^+$ + 1, 1.2), 167 (M$^+$, 1.2), 150 (21.9), 135 (21.4), 107 (14.7), 85 (43.9), 57 (100); Anal. Calcd for $C_7H_5NO_2S$: C, 50.3; H, 3.0. Found: C, 50.0; H, 3.0%.

*4-Methyl-2-thiocyanatoaniline* (**2j**): Yellow crystalline solid; m.p. 146–150°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3224, 3130, 2077, 1631, 844; $^1$H NMR (250 MHz, $d_6$-DMSO): δ 7.29 (d, 1H, $J$ = 8.3 Hz, ArH), 7.20 (s, 1H, ArH), 6.88 (d, 1H, $J$ = 8.3 Hz, ArH), 4.18 (brs, 2H, –N*H*$_2$), 3.13 (s, 3H, –C*H*$_3$); $^{13}$C NMR (62.9 MHz, $d_6$-DMSO): δ 25.7 (–*C*H$_3$), 111.4, 114.6(-S*C*N), 121.7, 125.8, 130.2, 135.9, 150.2; GC–MS/EI: *m/z* (%) = 164 (M$^+$, 20.8), 132 (21.9), 107 (27.9), 97 (31.7), 71 (48.6), 59 (89.1), 57 (69.4), 55 (100); Anal. Calcd for $C_8H_8N_2S$: C, 58.5; H, 4.9. Found: C, 58.1; H, 4.65%.

*2-Methoxy-3-thiocyanatonaphthalene* (**2k**): Yellow crystalline solid; m.p. 150–152°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3390, 3257, 2077, 1622, 7598; $^1$H NMR (250 MHz, $CDCl_3$): δ 8.04 (d, 1H, $J$ = 7.8 Hz, ArH), 7.83 (s, 1H, ArH), 7.75 (s, 1H, ArH), 7.25–7.40 (m, 3H, ArH), 3.99 (s, 3H, –OC*H*$_3$); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 56.8 (–O*C*H$_3$), 108.2, 111.4, 113.1 (–S*C*N), 118.1, 124.0, 124.2, 127.5, 127.8, 130.7, 139.6, 150.2; GC–MS/EI: *m/z* (%) = 217 (M$^+$ + 2, 52.5), 216 (M$^+$ + 1, 61.7), 215 (M$^+$, 5.0), 183 (39.2), 140 (50.8), 113 (25.8), 83 (37.5), 60 (43.3), 57 (100), 55 (80.0); Anal. Calcd for $C_{12}H_9NOS$: C, 66.95; H, 4.2. Found: C, 66.7; H, 4.0%.

*2-Thiocyanatofuran* (**2l**): Yellow crystalline solid; m.p. 65–67°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3379, 3276, 2100, 1626, 767. $^1$H NMR (250 MHz, $d_6$-DMSO): δ 7.57 (s, 1H, ArH), 6.98 (s, 1H, ArH), 6.35 (s, 1H, ArH); $^{13}$C NMR (62.9 MHz, DMSO): δ 112.6 (–S*C*N), 112.9, 116.8,

145.5, 151.7; GC–MS/EI: *m/z* (%) = 127 ($M^+$ + 2, 8.0), 126 ($M^+$ + 1, 3.7) 125 ($M^+$, 5.7), 97 (25.0), 96 (10.9), 95 (18.0), 73 (30.7), 71 (52.2), 69 (65.9), 57 (100), 55 (70.2); Anal. Calcd for $C_5H_3NOS$: C, 48.0; H, 2.4. Found: C, 47.7; H, 2.2%.

*2-Thiocyanato-pyrrole* (**2m**): Colourless liquid[11] IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3379, 3276, 2100, 1626, 767; $^1$H NMR (250 MHz, $d_6$-DMSO): δ 7.05 (s, 1H, ArH), 6.87 (s, 1H, ArH), 6.03 (s, 1H, ArH); $^{13}$C NMR (62.9 MHz, $d_6$-DMSO): δ 112.5 (–S*C*N), 113.1, 117.2, 145.4, 151.6; GC–MS/EI: *m/z* (%) = 126 ($M^+$ + 2, 17.6), 125 ($M^+$ + 1, 3.5) 124 ($M^+$, 12.6), 107 (27.6), 97 (31.2), 82 (50.8), 57 (100), 55 (87.9); Anal. Calcd for $C_5H_4N_2S$: C, 48.4; H, 3.25. Found: C, 48.2; H, 3.0%.

*3-Thiocyanato-indole* (**2n**): Red crystalline solid; m.p. 123–125°C (lit.[12] 125–127°C); IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3342, 3109, 2920, 1620, 758; $^1$H NMR (250 MHz, $CDCl_3$): δ 8.9 (s, brs, 1H, –N*H*), 7.88 (d, 1H, *J* = 8.0 Hz, ArH), 7.32–7.70 (m, 4H, ArH); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 83.0, 113.2, 113.5 (–S*C*N), 118.9, 122.4, 122.8, 127.3, 127.6, 145.4; GC–MS/EI: *m/z* (%) = 175 ($M^+$ + 1, 41.2), 174 (M + , 30), 155 (21), 141 (30), 97 (20), 85 (22), 71 (35), 57 (98), 43 (100); Anal. Calcd for $C_9H_6N_2S$: C, 62.05; H, 3.5. Found: C, 61.9; H, 3.2%.

*2-Methyl-3-thiocyanato-indole* (**2o**): Red crystalline solid; m.p. 100–103°C (lit.[12] 102–103°C); IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3340, 2922, 1620, 750; $^1$H NMR (250 MHz, $CDCl_3$): δ 8.50 (s, brs, 1H, –N*H*), 7.73 (d, 1H, *J* = 8.0 Hz, ArH), 7.20–7.54 (m, 3H, ArH), 2.52 (s, 3H, –C*H*$_3$); $^{13}$C NMR (62.9 MHz, $CDCl_3$): δ 16.3 (–*C*H$_3$), 78.0, 113.6 (–S*C*N), 119.5, 122.2, 122.8, 127.5, 129.1, 135.4, 139.1; GC–MS/EI: *m/z* (%) = 189 ($M^+$ + 1, 32.2), 188 (M + , 24.3), 156 (15.0), 57 (98), 55 (100); Anal. Calcd for $C_{10}H_8N_2S$: C, 63.80; H, 4.3. Found: C, 63.5; H, 4.0%.

*Thiocyanatobenzene* (**2r**): Yellow crystalline solid; m.p. 210–212°C; IR(KBr) ($\nu_{max}$/cm$^{-1}$): 3162, 2074, 1615, 792; $^1$H NMR (250 MHz, $d_6$-DMSO): δ 7.53 (d, 2H, *J* = 8.0 Hz, ArH), 7.32 (m, 3H, ArH); $^{13}$C NMR (62.9 MHz, $d_6$-DMSO): δ 113.2 (–S*C*N), 125.1, 130.4, 131.5,131.8; GC–MS/EI: *m/z* (%) = 137 (12.0), 136 (14.9), 135 (M + ,53.2), 121 (33.2), 83 (100); Anal. Calcd for $C_8H_7NOS$: C, 62.2; H, 3.7. Found: C, 62.0; H, 3.5%.

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## References

1 J.L. Wood, *Organic reactions,* Wiley: New York, 1967. Vol. III, pp. 240-266.
2 J.L Wood,. *Organic reactions*, eds R. Adams, John Wiley and Sons, New York, 1946. Vol. 3, Chapter 6.
3 F.D. Toste, F. Laronde and W.J. Still, *Tetrahedron Lett.,* 1995, **36**, 2949.
4 M.S. Grant and H.R. Snyder, *J. Am. Chem. Soc*., 1960, **82**, 2742.
5 R.G. Guy, *The chemistry of cyanates and their thio derivatives,* ed. S. Patai, John Wiley & Sons, New York, 1977. Part 2, Chapter 18.
6 M.S. Grant and H.R. Snyder *J. Am. Chem. Soc.,* 1960, **82**, 2742.
7 F.D. Toste, V.D. Stefano and I.W.J. Still, *Synth. Commun*., 1995, **25**, 1277.
8 V. Nair, T.G. George, L.G. Nair and S.B. Panicker, *Tetrahedron Lett*., 1999, **40**, 1195.
9 M. Chakraburty and S. Sarkar, *Tetrahedron Lett.,* 2003, **44**, 8131.
10 J.S. Yadav, B.V.S. Reddy, S. Shubashree and K. Sadashiv, *Tetrahedron Lett.,* 2004, **45**, 2951.
11 G. Wu, Q. Liu, Y. Shen and L. Wentao, *Tetrahedron Lett.,* 2005, **46**, 5831.
12 J.S. Yadav, B.V.S. Reddy, A.D. Krishna, Ch. S. Reddy and A.V. Narsaiah, *Synthesis*, 2005, **6**, 961.
13 V.K. Jadhav; R.R. Pal, P.P. Wadgaonkar and M.M. Salunkhe, *Synth. Commun*., 2001, **31**, 3041.
14 A. Khazei, A. Alizadeh and R.G. Vaghei, *Molecules,* 2001, **6**, 253.
15 Y. Kita, T. Takada, S. Mihara, B.A. Whelan and H. Tohma, *J. Org. Chem*., 1995, **60**, 7144.
16 H. Sharghi and B. Kaboudin, *J. Chem. Res.(S),* 1998, 628.
17 H. Sharghi and M. Hosseini Sarvari, *J. Chem. Res.(S*), 2001, 446.
18 H. Sharghi and M. Hosseini Sarvari *Synth. Commun*., 2003, **33**, 207.
19 H. Sharghi and M. Hosseini Sarvari *Tetrahedron*, 2003, **59**, 3627.
20 H. Sharghi and M. Hosseini Sarvari *J. Org. Chem*., 2003, **68**, 4096.
21 H. Sharghi and M. Hosseini Sarvari *Synthesis*, 2003, **6**, 879.
22 H. Sharghi and M. Jokar *Heterocycles*, 2007, **71**, 2721.
23 H. Sharghi, M. Hosseini-Sarvari and E. Eskandari *J. Chem. Res.,* 2005, 482.
24 M. Hosseini-Sarvari and H. Sharghi *J. Chem. Res.,* 2006, 205.