Simple and Highly Efficient Catalytic Thiocyanation of Aromatic Compounds in Aqueous Media

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Two simple, mild, and efficient procedures for the thiocyanation of N-heterocycles, substituted anilines (electron-rich and electron-deficient), and *N*-substituted aromatic amines at room temperature are reported (*Table 3*). The first uses H_2O_2 as pollution-free oxidant and the second H_5IO_6; both with the reagent potassium thiocyanate in H_2O as solvent. These procedures provided the target thiocyanates after a short reaction time in good to excellent yields and high regioselectivity.

Introduction. – Aryl thiocyanates are useful intermediates in the synthesis of S-containing heterocycles, in which the thiocyanate group will be readily transformed into other S-functionalities [1]. One of the most general way for the direct introduction of an S-atom at aromatic rings is the electrophilic thiocyanation. On the other hand, the nucleophilic attack of thiocyanate ion at an aromatic nucleus *via* displacement reactions is not an easy way to form thiocyanated compounds [2–5]. So, several methods have been developed for the electrophilic thiocyanation of arenes [6][7] such as bromine/potassium thiocyanate [8], *N*-thiocyanatosuccinimide [9], an thiocyanate salt in the presence of ceric ammonium nitrate (CAN) [10], acidic montmorillonite K10 clay [11], I_2/MeOH [2], *Oxone*® [12], pentavalent iodine, *i.e.*, 2-iodoxybenzoic acid (IBX) [13], or potassium peroxydisulfate/copper(II) sulfate [14]. However, these methodologies suffer from one or more drawbacks such as the use of toxic transition metals as oxidants [1], the toxicity of reagents in general [7][8], large excess of catalyst [11], and performances under certain special conditions. Therefore, there is a need to find new, fast, and useful methods with safe and clean oxidants or reagents for the synthesis of aryl thiocyanates.

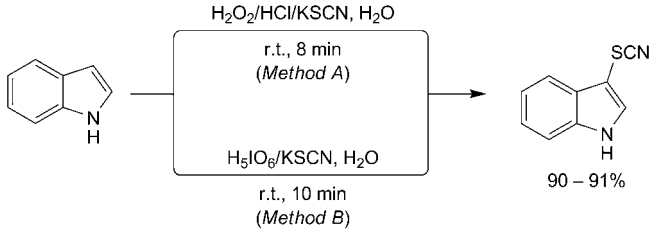
In recent years, the use of 'green' oxidants such as hydrogen peroxide (H_2O_2) has become highly attractive for a number of reasons: it is a cheap, mild, and an environmentally benign oxidant with a high content of active O-atom, and H_2O is formed as only by-product. Hydrogen peroxide was used as an oxidant for a wide range of organic functional groups such as sulfides and thiols [15], 1,4-dihydropyridines [16] and alcohols [17], but expensive catalysts were normally required to affect O-atom transfer from H_2O_2 to the substrate. Therefore, the use of cheap catalysts beside H_2O_2 is a very important topic.

Also, hypervalent iodine compounds such as H_5IO_6 are employed to oxidize various organic substrates with or without catalyst. Very recently, oxidation of alcohols with

H_5IO_6/2,2,6,6-tetramethylpiperidin-1-yl-oxy (TEMPO) [18], H_5IO_6/Fe^{III}/2-picolinic acid [19], or H_5IO_6/CrO_3 [20] and oxidation of sulfides to sulfoxides with $H_5IO_6/FeCl_3$ [21], H_5IO_6/manganese [22] were also reported. The reagent H_5IO_6 has several advantages, such as cost effectiveness, nontoxicity, and an exceedingly simple and clean workup of products.

We now report the thiocyanation of aromatic and heteroaromatic compounds with potassium thiocyanate as a thiocyanating agent. For this purpose, we designed and run the reaction on two general routes: on the one hand with H_2O_2 as oxidant in conjunction with HCl as inexpensive catalysts in H_2O (*Method A*), and on the other hand with H_5IO_6 as oxidant [23–30] in H_2O (*Method B*; *Scheme 1*).

Scheme 1. *Conversion of 1*H-*Indole to 1*H-*Indol-3-yl Thiocyanate*



Results and Discussion. – The conversion of 1*H*-indole into 1*H*-indol-3-yl thiocyanate at room temperature was considered as a model reaction and used to study the solvent influence on the rate and yield of the reaction. Thus the conversions according to *Methods A* and *B* with the same concentration of the reactants but in other solvents then H_2O, *i.e.*, in MeOH, EtOH, MeCN, CH_2Cl_2, $CHCl_3$, and AcOEt suggested that H_2O was the most favorable solvent for the thiocyanation (*Table 1*).

Table 1. *Thiocyanation of 1*H-*Indole in Various Solvents*

Solvent	Time [min]		Yield [%][a])	
	A	*B*	*A*	*B*
MeOH	< 5	5	91	93
EtOH	< 5	7	94	91
MeCN	< 5	10	89	90
$CHCl_3$	30	25	83	85
CH_2Cl_2	45	35	75	80
H_2O	8	10	91	90
AcOEt	20	20	82	90

[a]) Yield of isolated 1*H*-indol-3-yl thiocyanate.

In further experiments, different amounts of catalyst and oxidant were tested in the model conversion. Thus, in the case of *Method A*, only 1–2 drops of conc. aqueous HCl solution was needed to complete the reaction. Changing the molar ratio of the oxidant (*Table 2*) revealed that generally increasing the amount of H_2O_2 or H_5IO_6 shortened the reaction time and increased the yield, the optimum being reached with 3 mmol-

Table 2. *Optimization of Catalyst and Oxidant for the Thiocyanation of 1*H-*Indole*

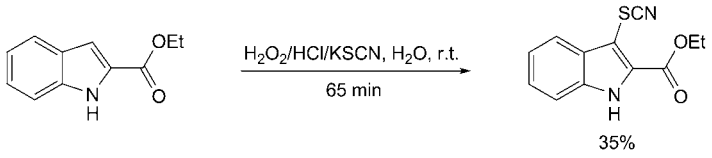
Method A			*Method B*		
H_2O_2[a])	Time [min]	Yield [%][b])	H_5IO_6[a])	Time [min]	Yield [%][b])
1	240	25	0.25	240	30
1.5	240	45	0.5	90	55
2	90	55	0.6	50	79
2.5	30	80	0.75	15	90
3	10	91	1	15	89

[a]) Amount in mmol per mmol of 1*H*-indole. [b]) Yield of isolated 1*H*-indol-3-yl thiocyanate.

equiv. of H_2O_2 after 10 min *Method A*, and with 0.75 mmol-equiv. of H_5IO_6 after 15 min (*Method B*).

Having established the optimal reaction conditions, we treated various N-heterocycles and aromatic amines, including such compounds with electron-releasing and electron-withdrawing substituents as well as halogen atoms at their aromatic rings, with potassium thiocyanate in the presence of H_2O_2/HCl or H_5IO_6 to afford the corresponding aryl thiocyanates in high to excellent yields (75–95%) within relatively short reaction times (8–120 min; *Table 3*). The products from 1*H*-indoles (*Entries 1–4*) showed that the monothiocyanation uniquely occurred at the 3-position of 1*H*-indole. However, the thiocyanation of ethyl 1*H*-indole-2-carboxylate in the presence of H_2O_2/HCl gave only 35% yield, this lower yield being probably due to the steric hindrance of 2-substituted 1*H*-indoles (*Scheme 2*). The 1*H*-pyrrole (*Table 3, Entry 5*) was also easily transformed into 1*H*-pyrrol-2-yl thiocyanate within 10–16 min.

Scheme 2. *Thiocyanation of Ethyl 1*H-*Indole-2-carboxylate*



Aromatic amines were readily converted to the monothiocyanated products with high *para*-selectivity (*Table 3*, *Entries 6–20*). The influence of electron-releasing substituents, electron-withdrawing substituents, and halogen atoms at the aromatic ring of amines was also studied. Thus, electron-donating substituents increased the reaction rate and gave the products in high yields (*Table 3*, *Entries 9–11*). When amines with electron-withdrawing substituents were thiocyanated, the reaction times were longer and the yields slightly decreased (*Table 3*, *Entries 16–20*). *N*-Substituted amines such as *N*-methylaniline, *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, *N*-phenylmorpholine, 1-phenyl-1-aza[15]crown-5, and 2,3-dihydro-1*H*-indole furnished the corresponding aryl thiocyanates in short reaction times and good yields (*Table 3*, *Entries 6–8* and *12–15*).

Table 3. *Application of the in Thiocyanation Reaction to Different Substrates*

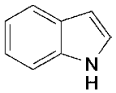
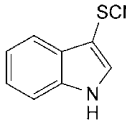
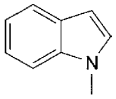
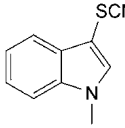
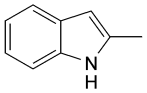
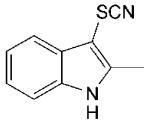
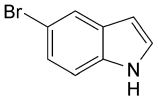
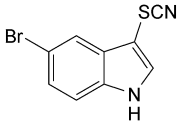
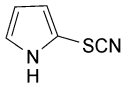
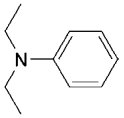
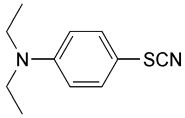
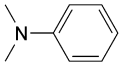
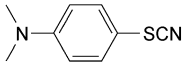
Entry	Substrate	Product	*Method A*		*Method B*		M.p. [°]	
			Time [min]	Yield [%][a])	Time [min]	Yield [%][a])	found	reported
1			10	91	15	90	70–72	71–73 [7]
2			15	89	15	88	79–81	83–84 [31]
3			13	82	15	92	97–99	99–101 [31]
4			14	94	30	85	125–127	127–129 [31]
5			16	87	10	85	liquid	liquid [31]
6			14	95	85	50	82–84	–[b])
7			10	92	70	81	71–72	70–73 [31]

Table 3 (cont.)

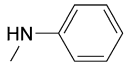
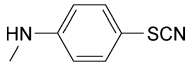
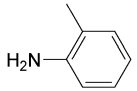
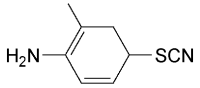
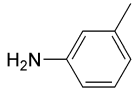
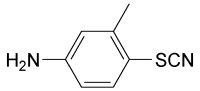
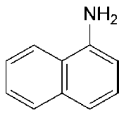
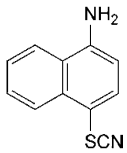
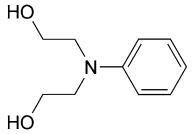
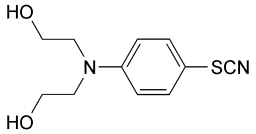
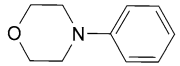
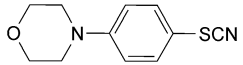
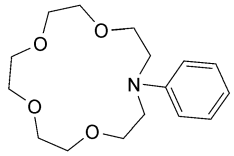
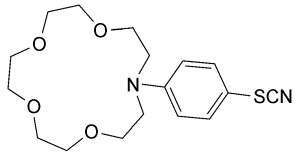
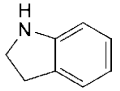
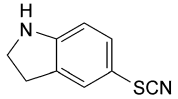
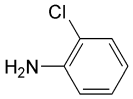
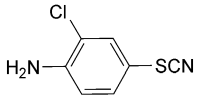
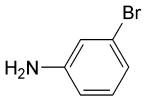
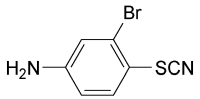
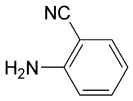
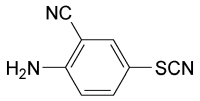
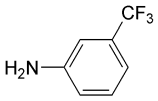
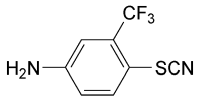
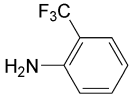
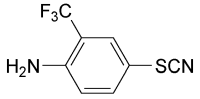
Entry	Substrate	Product	*Method A*		*Method B*		M.p. [°]	
			Time [min]	Yield [%][a])	Time [min]	Yield [%][a])	found	reported
8			35	88	70	85	45–48	46–47 [7c]
9			25	25	30	90	62–64	–[b])
10			35	80	30	90	70–71	–[b])
11			45	83	70	93	191–194	–[b])
12			30	78	35	88	66–69	–[b])
13			40	80	20	90	74–76	–[b])
14			45	95	30	91	77–80	–[b])

Table 3 (cont.)

Entry	Substrate	Product	*Method A*		*Method B*		M.p. [°]	
			Time [min]	Yield [%][a])	Time [min]	Yield [%][a])	found	reported
15			60	75	60	75	59–60	–[b])
16			75	86	90	82	58–60	60–61 [31]
17			65	90	90	85	69–71	71–73 [7]
18			90	83	120	81	58–60	–[b])
19			85	80	120	76	97–99	–[b])
20			75	82	90	80	148–150	–[b])

[a]) Yield of isolated 1*H*-indol-3-yl thiocyanate. [b]) New compounds.

Finally, we compared our results with reported methods which involve other reagents, and toxic solvents or oxidants, some under refluxing conditions or ultrasonic irradiation. As shown in *Table 4*, the methods described in this work occur under very mild and eco-friendly reaction conditions.

Table 4. *Conversion of* 1*H-Indole to* 1*H-Indol-3-yl Thiocyanate with a Thiocyanate Salt by Various Methods*

System	Time [min]	Yield [%]
H_5IO_6/H_2O	10	90
$HCl/H_2O_2/H_2O$	8	91
I_2/MeOH	50	85 [2]
DDQ/MeOH[a])	50	99 [31a][31b]
DEAD/MeCN[b])	45	85 [6]
$Mn(OAc)_3$/AcOH	120	83 [31c]
Oxone®/MeOH	43	98 [12]
K10 clay/MeOH[c]), 0°	120	85 [11]

[a]) DDQ = 4,5-Dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile. [b]) DEAD = Diethyl azodicarboxylate = diethyl diazenedicarboxylate. [c]) K10 clay = montmorillonite K10 clay.

Conclusions. – We developed a mild and straightforward procedure for the synthesis of organic thiocyanate derivatives by a reaction with KSCN in the presence of HCl/H_2O_2 (*Method A*) or H_5IO_6 (*Method B*). The thiocyanates were obtained at room temperature after short reaction times in good to excellent yields and high regioselectivity.

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Experimental Part

General. All chemicals were purchased from *Merck* or *Fluka*. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. TLC: silica gel *SIL G/UV 254* plates. Column chromatography (CC): silica gel *60* (0.063 – 0.200 mm) No. 1.07734, *Merck KGaA*. M.p.: *Büchi-B-545* apparatus; open capillary tubes. IR Spectra: *Perkin–Elmer-17259* FT-IR spectrometer, KBr disks; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-Avance-DPX-250* and *FT-NMR* spectrometer; at 300 (^1H) and 75 MHz (^{13}C); δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. Microanalysis: *Perkin-Elmer-240-B* microanalyzer.

*Thiocyanation of 1*H-*Indole to 1*H-*Indol-3-yl Thiocyanate. Method A* (Typical Procedure). A suspension of 1*H*-indole (0.117 g, 1 mmol), potassium thiocyanate (0.294 g, 3 mmol), 36% HCl soln. (0.04 – 0.07 g, 1 – 2 drops) in H_2O (5 – 7 ml) was stirred at r.t. for 5 min. Then, 30% H_2O_2 soln. (3 mmol) was added dropwise (2 – 5 min). After completion of the reaction (TLC monitoring), the mixture was extracted with $CHCl_3$ (2 × 10 ml), the extract dried (Na_2SO_4 (5 g)) for 20 min and concentrated, and the residue purified by CC (hexane/AcOEt 5 :1): 0.159 g (91%) of *1*H-*indol-3-yl thiocyanate.*

Method B (Typical Procedure). A suspension of 1*H*-indole (0.117 g, 1 mmol), potassium thiocyanate (0.228 g, 3 mmol), and $HIO_4 \cdot 2\ H_2O$ (0.143g, 0.75 mmol) in H_2O (5 – 7 ml) was stirred at r.t. for 10 min. After completion of the reaction (TLC monitoring), the mixture was worked up as described for *Method A:* 0.158 g (90%) of *1*H-*indol-3-yl thiocyanate.* (*Table 3*, *Entry 1*). IR: 2159 (SCN), 3289 (NH).

^{1}H-NMR: 8.87 (*s*, 1 H); 7.83 (*t*, *J* = 3.3, 1 H); 7.46–7.23 (*m*, 4 H). ^{13}C-NMR: 136.0; 131.2; 127.6; 123.8; 121.8; 118.6; 112.2; 91.7. MS: 174 (M^+).

*1-Methyl-1*H-*indol-3-yl Thiocyanate* (*Entry 2*): IR: 2146 (SCN). ^{1}H-NMR: 7.84–7.36 (*m*, 5 H); 3.74 (*s*, 3 H). ^{13}C-NMR: 137.1; 135.2; 128.4; 123.4; 121.6; 118.8; 112.1; 110.3; 33.4. MS: 188 (M^+).

*2-Methyl-1*H-*indol-3-yl Thiocyanate* (*Entry 3*): IR: 2151 (SCN), 3395 (NH), 3395. ^{1}H-NMR: 8.55 (*s*, 1 H); 7.71 (*d*, *J* = 6.9, 1 H); 7.33–7.23 (*m*, 3 H); 2.49 (*s*, 3 H). ^{13}C-NMR: 142.1; 135.1; 128.6; 122.9; 121.5; 118.0; 111.3; 88.7; 12.0. MS: 188 (M^+).

*5-Bromo-1*H-*indol-3-yl Thiocyanate* (*Entry 4*): IR: 2146 (SCN), 3351 (NH). ^{1}H-NMR: 8.87 (*s*, 1 H); 7.90–7.15 (*m*, 4 H). ^{13}C-NMR: 134.6; 132.2; 129.3; 123.1; 121.2; 115.3; 113.7; 111.9; 102.2. MS: 251 (M^+), 253 ($M+2$).

*1*H-*Pyrrole-2-yl Thiocyanate* (*Entry 5*): IR: 2160 (SCN), 3247 (NH). ^{1}H-NMR: 9.04 (*s*, 1 H), 7.04–7.00 (*m*, 1 H); 6.68–6.59 (*m*, 1 H); 6.30–6.29 (*m*, 1 H). ^{13}C-NMR: 121.2; 120.2; 112.2; 110.9; 109.6. MS: 124 (M^+).

4-(Diethylamino)phenyl Thiocyanate (*Entry 6*): IR: 2151 (SCN). ^{1}H-NMR: 7.50–7.34 (*m*, 2 H); 7.20–7.13 (*m*, 1 H), 6.63–6.61 (*m*, 1 H); 3.50 (*q*, *J* = 7.2, 2 H); 3.37 (*q*, *J* = 6.9, 2 H); 1.16 (*t*, *J* = 5.4, 6 H). ^{13}C-NMR: 149.1, 134.9, 125.2, 121.7, 112.6, 44.5, 12.3. MS: 206 (M^+).

4-(Diethylamino)phenyl Thiocyanate (*Entry 7*): IR: 2146 (SCN). ^{1}H-NMR: 7.44 (*d*, *J* = 8.7, 2 H); 6.69 (*d*, *J* = 8.7, 2 H); 3.00 (*s*, 6 H). ^{13}C-NMR: 151.6; 134.5; 113.1; 112.7; 106.3; 40.1. MS: 178 (M^+).

4-(Methylamino)phenyl Thiocyanate (*Entry 8*): IR: 2153 (SCN), 3413 (NH). ^{1}H-NMR: 7.15–7.12 (*m*, 2 H); 7.06–6.82 (*m*, 2 H); 4.70 (*s*, 1 H); 3.32 (*s*, 3 H). ^{13}C-NMR: 150.9; 134.6; 132.8; 117.6; 116.4; 114.8; 113.6; 30.3. MS: 164 (M^+).

4-Amino-3-methylphenyl Thiocyanate (*Entry 9*): IR: 2153 (SCN), 3369, 3456 (NH_2). ^{1}H-NMR: 6.64–7.37 (*m*, 3 H); 3.98 (*s*, 2 H); 2.12 (*s*, 3 H). ^{13}C-NMR: 147.3; 135.1; 132.1; 123.9; 115.8; 112.8; 108.81; 17.2. MS: 164 (M^+).

4-Amino-2-methylphenyl Thiocyanate (*Entry 10*): IR: 2146 (SCN), 3219, 3337 (NH_2). ^{1}H-NMR: 7.37–6.64 (*m*, 3 H); 3.98 (*s*, 2 H); 2.34 (*s*, 3 H). ^{13}C-NMR: 149.7; 143.0; 136.3; 117.3; 112.4; 108.4; 21.2. MS: 164 (M^+).

4-Aminonaphthalen-1-yl Thiocyanato (*Entry 11*): IR: 2146 (SCN), 3358, 3442 (NH_2). ^{1}H-NMR: 7.85–6.70 (*m*, 6 H); 4.58 (*s*, 2 H). ^{13}C-NMR: 136.2; 128.2; 125.8; 125.6; 121.6; 108.9. MS: 200 (M^+).

4-[Bis(2-hydroxyethyl)amino]phenyl Thiocyanate (*Entry 12*): IR: 2153 (SCN), 3300 (OH). ^{1}H-NMR: 7.42 (*d*, *J* = 8.7, 2 H); 6.70 (*d*, *J* = 8.4, 2 H); 4.43 (*s*, 2 H); 3.75–3.60 (*m*, 4 H); 3.55–3.35 (*m*, 4 H). ^{13}C-NMR: 151.8; 132.1; 116.5; 114.3; 111.7; 58.7; 55.9. MS: 238 (M^+).

4-(Morpholin-4-yl)phenyl Thiocyanate (*Entry 13*): IR: 2156 (SCN). ^{1}H-NMR: 7.48 (*d*, *J* = 8.1, 2 H); 6.92 (*d*, *J* = 8.4, 2 H); 3.88 (*t*, *J* = 4.5, 4 H); 3.24 (*t*, *J* = 5.1, 4 H). ^{13}C-NMR: 152.5; 133.7; 116.1; 111.9; 111.1; 67.1; 48.0. MS: 220 (M^+).

4-(1-Aza[15]-crown-5)1-yl Thiocyanate (=1,4,7,10-Tetraoxa-13-azacyclopentadec-13-yl Thiocyanate; *Entry 14*): IR: 2147 (SCN), 1094 (C–O). ^{1}H-NMR: 7.37 (*d*, *J* = 8.4, 2 H); 6.64 (*d*, *J* = 8.1, 2 H); 3.72–3.57 (*m*, 20 H). ^{13}C-NMR: 149.3; 134.7; 112.8; 105.9; 112.6; 71.2; 70.2; 69.9; 68.0; 52.6. MS: 352 (M^+).

*2,3-Dihydro-1*H-*indol-5-yl Thioanate* (*Entry 15*): IR: 2216 (SCN), 3420 (NH). ^{1}H-NMR: 7.19–6.92 (*m*, 3 H); 5.2 (*s*, 1 H); 3.23 (*t*, *J* = 8.4, 2 H); 2.18 (*t*, *J* = 10.5, 2 H). ^{13}C-NMR: 142.1; 128.1; 127.8; 127.4; 122.3; 114.8; 110.3; 50.7; 28.5. MS: 176 (M^+).

4-Amino-3-chlorophenyl Thiocyanate (*Entry 16*): IR: 2159 (SCN), 3379, 3435 (NH_2). ^{1}H-NMR: 7.37–7.19 (*m*, 3 H); 6.80 (*s*, 1 H); 4.47 (*s*, 2 H). ^{13}C-NMR: 145.3; 132.7; 133.8; 119.6; 116.5; 111.8; 109.7. MS: 184 (M^+), 186 ($M+2$).

4-Amino-2-bromophenyl Thioanate (*Entry 17*): IR: 2156 (SCN), 3233, 3376 (NH_2). ^{1}H-NMR: 7.23–7.50 (*m*, 3 H); 6.65 (*s*, 1 H); 4.12 (*s*, 2 H). ^{13}C-NMR: 144.8; 134.5; 132.6; 117.5; 116.1; 112.7; 109.2. MS: 228 (M^+), 230 ($M+2$).

4-Amino-3-cyanophenyl Thiocyanate (*Entry 18*): IR: 2156 (SCN), 2222 (CN), 3360, 3444 (NH_2). ^{1}H-NMR: 7.58–7.28 (*m*, 2 H); 6.83 (*s*, 1 H); 4.96 (*s*, 2 H). ^{13}C-NMR: 151.7; 138.4; 137.2; 117.8; 116.3; 111.3; 109.3; 96.7. MS: 175 (M^+).

4-Amino-2-(trifluoromethyl)phenyl Thiocyanate (*Entry 19*): IR: 2160 (SCN), 3275, 3369 (NH_2). ^{1}H-NMR: 7.82–7.33 (*m*, 3 H); 4.01 (*s*, 2 H). ^{13}C-NMR: 144.6; 135.3; 125.5; 118.8; 117.4; 115.1; 111.7. MS: 218 (M^+).

4-Amino-3-(trifluoromethyl)phenyl Thiocyanate (*Entry 20*): IR: 2158 (SCN) 3395, 3435 (NH_2). ^{1}H-NMR: 7.68–7.28 (*m*, 2 H); 6.80 (*s*, 1 H); 4.57 (*s*, 2 H). ^{13}C-NMR: 146.7; 137.5; 131.9; 125.6; 114.3; 111.6; 109.2. MS: 218 (M^+).

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