Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolizable ketones by hydrogen peroxide/KSCN in water

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Table of content

General Information

All chemicals used in this study were analytical grade, commercially available and used without further purification. Graphite (CAS No. 7782-42-5, particle size: <50μm) was purchased from Merck. Most of the products were purified by column chromatography from appropriate solvents and were identified by ^{1}H NMR, ^{13}C NMR and elemental analyses. Progress of the reactions was monitored by TLC using silica gel polygrams SIL G/UV 254 plates. FT-IR spectra were recorded on Shimadzu DR-8001 Spectrometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz Instrument in $CDCl_3$ or DMSO-*d6* solvents using TMS as internal standard. Chemical shifts were reported in ppm (δ), and coupling constants (*J*), in Hz. Elemental analyses were determined in our department using ThermoFinnigan Flash EA 1112 Series. The surface morphology of graphite and graphene oxide was analyzed by using a Field emission scanning electron microscopy (FESEM, SIGMA, ZEISS, Germany) and Atomic force microscope (AFM, DUALSCOPE™ DS 95-50-E, DME, Denmark). X-ray diffraction (XRD) patterns were recorded on a XRD-D8 (BRUKER, Germany) employing a scanning rate of 0.05° s^{-1} from 10° to 90° with CuKα radiation. The absorbance of graphene oxide solutions was detected by UV-Vis Spectrophotometer (Pharmacia Biotech Ultraspec 4000). Dispersive Raman Microscope (SENTERRA, BRUKER, Germany) was used to characterize functional groups and structural information. The analysis system was equipped with high-energy laser diodes. Melting points were determined in open capillaries with a Galen-Kamp melting point apparatus and are not corrected.

Synthesis of graphene oxide (GO):

natural flake graphite (1g, particle size: <50μm; from Merck), $NaNO_3$ (fine mesh, 1.0 g) and H_2SO_4 (48 ml, 98%) was cooled to 0 °C by stirring in an ice bath for 15 min. 3.0 g finely meshed $KMnO_4$ powder was added slowly with vigorous stirring while keeping the temperature below 20 °C (a dark colored mixture was obtained). After 1.5 h, the mixture was warmed to 35±3 °C for 30 min. Then 180 ml water was added slowly, the temperature rose gradually and was kept in 95 °C for another 30 min. Then 400 ml water was added. Finally aqueous solution of hydrogen peroxide (H_2O_2, 35%, 10 mL) was added to convert the unreacted permanganate and manganese dioxide into soluble sulfates. The

vibrant yellow mixture was then filtered and the precipitate washed with an aqueous HCl solution (5%, 200 mL). The prepared GO was dialyzed in a dialysis bag for 1 week to ensure the complete removal of acid and residual metal ions. The final precipitate was kept in the dark until further use. For using in the reactions, the graphite oxide aqueous suspension was ultrasonicated (200 mL, 10 mg mL^{-1}) for 1 h to form graphene oxide.

FT-IR spectrum of graphene oxide (GO): The FTIR spectrum of GO in Figure 1, shows a broad peak appeared at 3429 cm^{-1} in the high frequency area attributed to the stretching mode of O-H bond, reveals the presence of hydroxyl groups in graphene oxide. The band observed at 1720 cm^{-1} was assigned to the carboxyl group. The sharp peak found at 1615 cm^{-1} is a resonance peak that can be assigned to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide. The peak at 1356 cm^{-1} arises from C-OH group. The peak at 1225 cm^{-1} denotes C-O-C stretching and the peak at 1056 cm^{-1} corresponds to the vibrational mode of the C-O group.

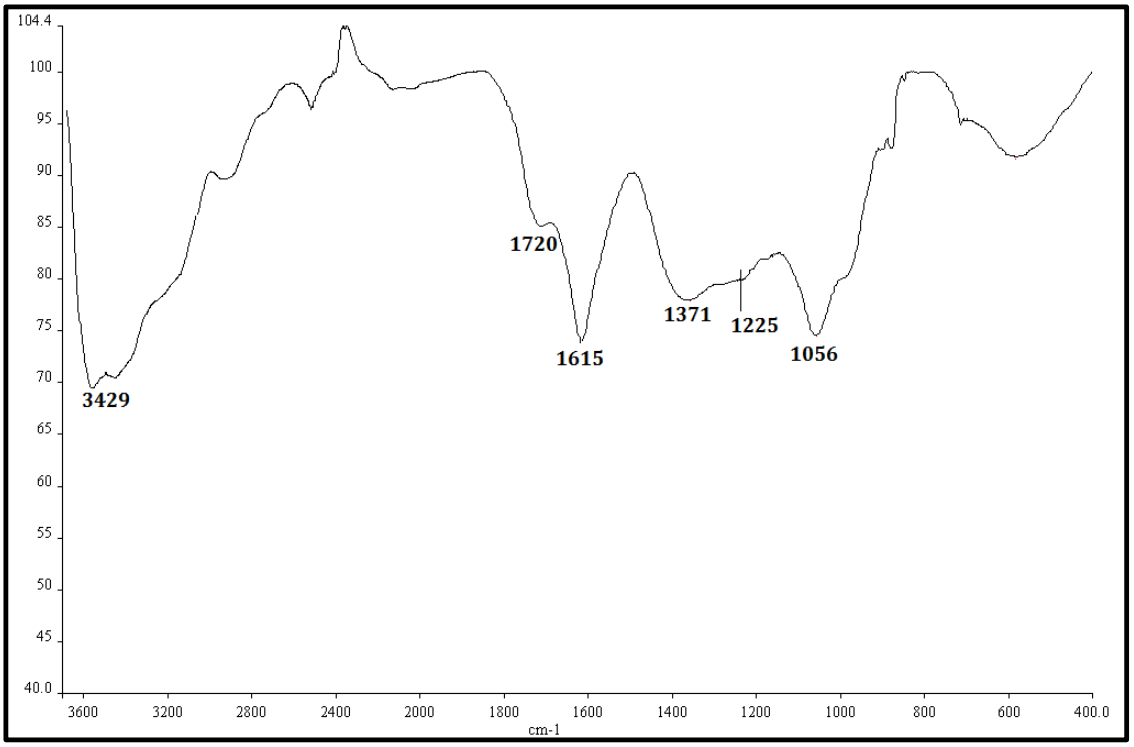

Figure 1: IR spectrum of graphene oxide

UV-Vis spectrum of graphene oxide:

The UV-Vis spectrum of graphene oxide is also shown in Figure 2. According to the absorbance spectra, the main spectrum of graphene oxide has an strong absorption peak at 233 nm, attributed to π-$\pi*$ transition of the C–C conjugated aromatic domains and weak absorption (shoulder) at 305 nm due to n-$\pi*$ transition of C=O bond. Thus, similar to the FTIR, UV-vis spectra provided evidence of the presence of an ample number of oxygen functionalities, such as hydroxyl, carboxyl, epoxide, and carbonyl on graphene oxid.

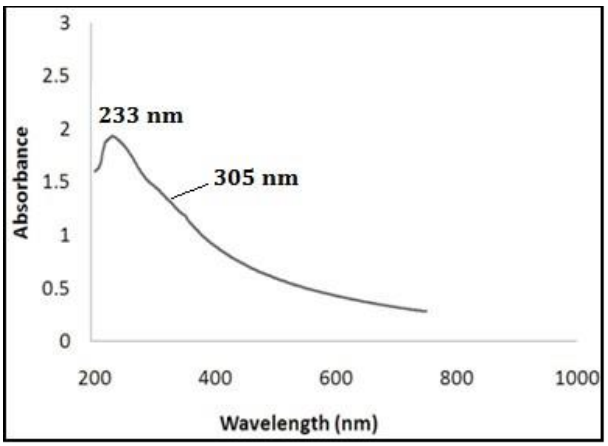

Figure 2: UV-Vis spectrum of graphene oxide

Raman spectrum of graphene oxide: Raman spectroscopy is a standard non-destructive technique that is widely used to obtain structural information about carbon-based materials. Figure 3 shows Raman spectra of graphene oxide. The graphene oxide shows an intense tangential mode (G band) at 1587 cm^{-1}, with a disordered-induced peak (D band) at 1355 cm^{-1}. The G band of graphene oxide broadens and up-shifts in comparison to those observed in graphite (strong G band at 1577 cm^{-1} due to first order scattering of the E_{2g} mode). A possible explanation of this behavior is the presence of isolated double bonds which resonate at higher frequencies. Furthermore, the D band at 1355 cm^{-1} becomes prominent, indicating that the oxidation process influences the size of the in-plane sp^2 domains.

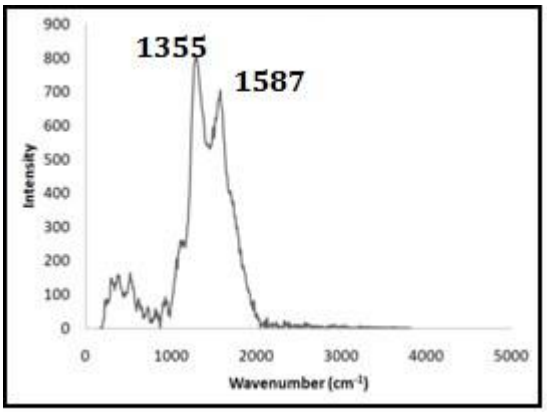

Figure 3: Raman spectra of graphene oxide

On the other hand, because of the breaking of the stacking order which is due to the oxidation reaction, the intensity of the 2D band is smaller after oxidation.

AFM image of graphene oxide: The AFM topography of the GO sample is shown in Figure 4. The surface image and height profiles of AFM for graphene oxide show the existence of irregularly sheet like morphology and lateral dimension of a few micrometers with the presence of mono layers and few layered of graphene oxide. The presence of a few layers in the sample is due to the aggregation or self assembly of two or three layers of graphene oxide during the drying process in the specimen preparation. The height profiles along the straight line depicted in Figure 4 show that the height of graphene oxide is about 1.45 nm, ompatible well with the reported value.

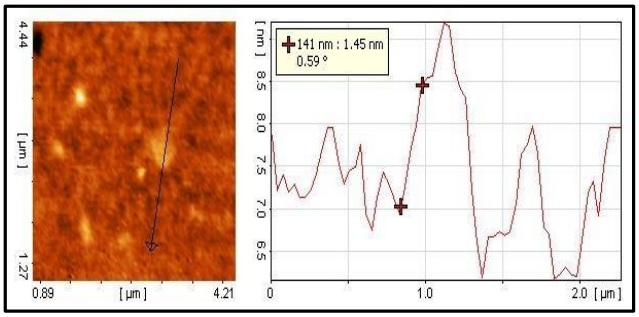

Figure 4: AFM image of exfoliated graphene oxide sheets on mica surface with height profile

XRD analysis of graphene oxide: XRD analysis was used to characterize the crystalline nature and phase purity of the as-synthesized graphene oxide. Pure graphite has a strong

and sharp diffraction peak at 2θ = 26.55°, corresponds to the (002) plane of hexagonal graphite structure with the interlayer spacing of 0.34 nm. After the chemical oxidation and exfoliation into graphene oxide, the 26.55° peak disappeared and a wide diffraction peak at 11.78° appeared instead, revealing a *d*-spacing of 0.83 nm. An increased interlayer distance between consecutive carbon basal planes is attributed to the intercalation of oxygen functional groups and water molecules into carbon layer structure.

Thiocyanation reaction (test reaction) in the absence of arene: In a typical preparation, a 5 mL reaction tube equipped with a magnetic stir bar was charged with GO (24 mg), KSCN (2.5 mmol, 243 mg) and H_2O_2 (30%, aq., 3 mmol, 0.26 mL). After stirring for 10 min, a yellow precipitate was produced. Then the latter solid was dissolved in DMSO (3 mL) and solution containing final product was obtained by filtration of GO form the reaction mixture. Evaporation of the solvent gave OH-SCN as a yellow precipitate. Anal. Calcd. for CHNOS: C, 16.00; H, 1.34; N, 18.65%. Found: C, 15.83; H, 1.50; N, 18.54 %.

4-Thiocyanoaniline (**2a**):[1] mp 58-60 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ d 3.93 (br s, 2H), 6.65 (d, 2H, *J* = 7.5 Hz), 7.33 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 148.9, 134.5, 116.1, 112.4, 108.3. Anal. Calcd. for $C_7H_6N_2S$: C, 55.98; H, 4.03; N, 18.65%. Found: C, 55.76; H, 3.9; N, 18.82%.

2-Methoxy-4-thiocyanato-aniline (**2b**):[2] mp 50-52 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.85 (s, 3H), 4.07 (br s, 2H), 6.66 (d, 1H, *J* = 9.5 Hz), 6.94 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 8.1, 2.0 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 147.6, 139.1, 126.8, 123.5, 121.3, 114.5, 110.7, 55.7. Anal. Calcd. for $C_8H_8N_2OS$: C, 53.32; H, 4.47; N, 15.54%. Found: C, 53.19; H, 4.61; N, 15.60%.

3-Methoxy-4-thiocyanato-aniline (**2c**):[3] mp 100-102 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.88 (s, 3H), 4.04 (br s, 2H), 6.18 (d, 1H, *J* = 2.0 Hz), 6.31 (dd, *J* = 8.0, 2.1 Hz, 2H), 7.29 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 148.4, 144.1, 130.0, 126.7, 123.0, 119.3, 114.7,

55.4; Anal. Calcd. for $C_8H_8N_2OS$: C, 53.32; H, 4.47; N, 15.54%. Found: C, 53.25; H, 4.59; N, 15.43%.

6-Methoxy-1,3-benzothiazol-2-amine (**2d'**):[4] mp 160-162 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 3.38 (br s, 2H), 3.80 (s, 3H), 6.71-6.77 (m, 1H), 7.22-7.34 (m, 2H); ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 165.1, 155.5, 146.0, 133.2, 120.3, 113.8, 105.6, 55.9. Anal. Calcd. for $C_8H_8N_2OS$: C, 53.32; H, 4.47; N, 15.54%. Found: C, 53.20; H, 4.55; N, 15.48%.

2-Methyl-4-thiocyanatoaniline (**2e**):[5] mp 69-71 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.93 (br s, 2H), 6.71-7.29 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 147.0, 134.8, 131.6, 124.3, 115.7, 112.8, 109.0, 17.4; Anal. Calcd. for $C_8H_8N_2S$: C, 58.51; H, 4.91; N, 17.06%. Found: C, 58.39; H, 5.07; N, 17.17%.

3-Methyl-4-thiocyanatoaniline (**2f**):[6] mp 81-83 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.94 (br s, 2H), 6.48 (dd, *J* = 9.0, 2.5 Hz, 2H), 6.57 (d, 1H, *J* = 2.5 Hz), 7.34 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 149.5, 143.0, 136.3, 117.3, 113.7, 112.2, 108.8, 21.0; Anal. Calcd. for $C_8H_8N_2S$: C, 58.51; H, 4.91; N, 17.06%. Found: C, 58.64; H, 4.98; N, 16.90%.

2-Chloro-4-thiocyanatoaniline (**2g**):[6] mp 65-67 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.27 (br s, 2H), 6.68 (d, 1H, *J* = 8.2 Hz), 7.19 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.40 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 145.1; 132.7; 134.1; 119.3; 116.8; 112.2; 109.9; Anal. Calcd. for $C_7H_5ClN_2S$: C, 45.54; H, 2.73; N, 15.17%. Found: C, 45.69; H, 2.66; N, 15.25%.

N-methyl-4-thiocyanatoaniline (**2h**):[6] mp 46-48 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.27 (s, 3H), 4.73(br s, 2H), 6.91-7.11 (m, 2H), 7.19-7.25 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.7; 133.1; 132.0; 118.2; 116.8; 114.1; 113.6; 30.5; Anal. Calcd. for $C_8H_8N_2S$: C, 58.51; H, 4.91; N, 17.06%. Found: C, 58.40; H, 5.08; N, 17.12%.

N-ethyl-4-thiocyanatoaniline (**2i**):[7] mp 54-56 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.26 (3H, t, *J*=7.3 Hz), 3.30 (2H, q, *J*=7.3 Hz), 4.03 (1H, s, NH), 6.49-6.63 (m, 2H), 7.26-7.34 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 150.1, 134.5, 113.1, 112.5, 106.8, 38.4, 14.7; Anal. Calcd. for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.72%. Found: C, 60.78; H, 5.52; N, 15.80%.

N-phenyl-4-thiocyanatoaniline (**2j**):[7] mp 61-63 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.99 (1H, s, NH), 6.90 (d, 2H, *J* = 8.5 Hz), 6.98 (t, 1H, *J* = 7.5 Hz), 7.07 (d, 2H, *J* = 8.0 Hz), 7.24 (t, 2H, *J* = 8.0 Hz), 7.35 (d, 2H, *J* = 8.5 Hz) ; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 145.2, 142.6, 132.1, 129.6,

122.0, 121.4, 120.7, 114.2, 111.8; Anal. Calcd. for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38%. Found: C, 69.15; H, 4.33; N, 12.50%.

N,N-dimethyl-4-thiocyanatoaniline (**2k**):[8] mp 70-72 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.03 (s, 6H), 6.72 (d, 2H, *J* = 9.1 Hz), 7.40 (d, 2H, *J* = 9.2 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 150.9, 134.7,112.8, 112.8, 106.0, 39.9. Anal. Calcd. for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.72%. Found: C, 60.77; H, 5.49; N, 15.86%.

4-Thiocyanatophenol (**2l**):[9] mp 60-62 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.00 (br s, 1H, OH), 6.77-6.81 (m, 2H), 7.45-7.50 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ157.3, 133.8, 117.3, 112.9, 112.0; Anal. Calcd. for C_7H_5NOS: C, 55.61; H, 3.33; N, 9.26%. Found: C, 55.55; H, 3.22; N, 9.16%.

2-Methyl-4-thiocyanato-phenol (**2m**):[10] mp 70-72 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.18 (s, 3H), 6.06(br s, 1H, OH), 6.74 (d, 2H, *J* = 8.5 Hz), 7.20 (dd, 2H, *J* = 8.5, 2.5 Hz), 7.35 (d, 2H, *J* = 2.6 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 155.8, 134.6, 131.7, 127.3, 116.5, 112.8, 112.0, 15.6. Anal. Calcd. for C_8H_7NOS: C, 58.16; H, 4.27; N, 8.48%. Found: C, 58.01; H, 4.40; N, 8.39%.

2,6-Dimethyl-4-thiocyanato-phenol (**2n**):[11] mp 100-102 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.18 (s, 6H), 4.87 (br s, 1H, OH), 7.25 (s, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 154.5, 130.1, 125.8, 119.0, 111.5, 15.9. Anal. Calcd. for C_9H_9NOS: C, 60.31; H, 5.06; N, 7.81%. Found: C, 60.43; H, 4.91; N, 7.94%.

4-thiocyanatoanisole (**2o**):[12] mp 43-45 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.99(d, *J* = 8.9 Hz, 2H), 7.60(d, *J* = 8.9 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 135.6, 132.4, 116.9, 114.0, 111.6; Anal. Calcd. for C_8H_7NOS: C, 58.16; H, 4.27; N, 8.48%. Found: C, 58.05; H, 8.60; N, 8.33%.

2-Methyl-4-thiocyanatoanisole (**2p**):[12] Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.19 (s, 3H), 3.84 (s, 3H, -OCH_3), 6.80 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.39 (dd, *J* = 8.5, 2.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 159.1, 133.6, 130.8, 129.4, 113.2, 111.4, 55.8, 15.9; Anal. Calcd. for C_9H_9NOS: C, 60.31; H, 5.06; N, 7.81%. Found: C, 60.45; H, 4.93; N, 7.70%.

3-Thiocyanatoindole (**2q**):[6] mp 75-77 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.13-7.25 (m, 4H), 7.64 (t, *J* = 3.5 Hz, 1H), 9.22 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 136.5, 131.5, 127.6,

124.0, 121.7, 118.5, 112.4, 91.0; Anal. Calcd. for $C_9H_6N_2S$: C, 62.05; H, 3.47; N, 16.08%. Found: C, 61.91; H, 3.59; N, 16.16%.

2-Methyl-3-thiocyanatoindole (**2r**):[3] mp 100-102 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.35 (s, 3H), 7.03-7.19 (m, 3H), 7.53 (d, *J* = 8.0 Hz, 1H), 9.43 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 142.4, 135.3, 128.7, 122.6, 121.2, 117.9, 11.35, 88.0, 13.9; Anal. Calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88%. Found: C, 63.94; H, 4.35; N, 14.72%.

N-methyl-3-thiocyanatoindole (**2s**):[6] mp 80-82 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.72 (s, 3H), 7.25-7.71 (m, 5H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 136.7, 134.9, 128.7, 123.0, 120.9, 118.5, 112.1, 110.7, 33.7; Anal. Calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.88%. Found: C, 63.70; H, 4.41; N, 14.75%.

2-Thiocyanatopyrole (**2t**):[13] Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.35 (m, 1H), 6.62 (m, 1H), 7.04 (m, 1H), 8.90 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 122.2, 120.5, 111.8, 110.6, 108.9; Anal. Calcd. for $C_5H_4N_2S$: C, 48.37; H, 3.25; N, 22.56%. Found: C, 48.31; H, 3.38; N, 22.43%.

2,5-dithiocyanatopyrrole (**2t'**):[3] mp 101-103 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.87 (d, *J* = 1.7 Hz, 2H), 8.96 (s, 1H, NH); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 119.3, 112.1, 107.6; Anal. Calcd. For $C_6H_3N_3S_2$: C, 39.76; H, 1.67; N, 23.19%. Found: C, 40.02; H, 1.54; N, 23.31%

α-Thiocyanatoacetophenone (**4a**):[14] mp 72-74 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.69 (s, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 192.3, 135.3, 133.7, 128.6, 128.0, 111.9, 42.8; Anal. Calcd. for C_9H_7NOS: C, 61.00; H, 3.98; N, 7.90%. Found: C, 61.13; H, 3.77; N, 8.05%.

2-Thiocyanatocyclopentanone (**4b**):[15] Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.79-2.36 (m, 5H), 2.63-2.68 (m, 1H), 3.75 (t, *J* = 8.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 207.4, 112.3, 53.3, 39.0, 31.2, 10.9; Anal. Calcd. for C_6H_7NOS: C, 51.04; H, 5.00; N, 9.92%. Found: C, 50.93; H, 5.16; N, 10.01%.

2-Thiocyanatocyclohexanone (**4c**):[15] Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.64-1.75 (m, 2H), 1.87-2.00 (m, 2H), 2.12-2.19 (m, 1H), 2.30-2.42 (m, 1H), 2.62-2.69 (m, 1H), 2.73-2.84 (m, 1H), 4,38 (dd, *J* = 6.5, 5.5 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 204.3, 111.5, 59.0, 42.1, 41.4, 39.8, 32.9; Anal. Calcd. for C_7H_9NOS: C, 54.17; H, 5.84; N, 9.02%. Found: C, 54.03; H, 6.01; N, 8.90%.

3-Methyl-2-oxocyclohexyl thiocyanate (**4d**):[16] Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.04 (d, *J* = 1.9 Hz, 3H), 1.19-2.70 (m, 7H), 4.26 (t, *J* = 6.1 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 207.8, 111.8, 51.4, 44.3, 35.4, 33.6, 21.2, 15.5; Anal. Calcd. for $C_8H_{11}NOS$: C, 56.78; H, 6.55; N, 8.28%. Found: C, 57.00; H, 6.48; N, 8.16%.

1-Phenyl-2-thiocyanato-propan-1-one (**4e**):[17] Oil; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.28 (d, *J* = 6.0 Hz, 3H), 4.70 (q, *J* = 6.0 Hz, 1H), 7.24–7.40 (m, 3H) 7.77–7.90 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 195.7, 137.6, 133.1, 128.8, 112.1, 51.5, 19.2; Anal. Calcd. for $C_{10}H_9NOS$: C, 62.80; H, 4.74; N, 7.32%. Found: C, 62.89; H, 4.81; N, 7.17%.

3-Thiocyanato-2,4-pentanedione (**4f**):[15] readily decomposed.

Ethyl-2-thiocyanato-3-oxobutanoate (**4g**): IR (ν_{max}): 2152 (SCN str.) cm^{-1}; readily decomposed on workup and purification.

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