

Supporting Information

Photocatalytic synthesis of unsymmetrical thiourea derivatives via visible-light irradiation using nitrogen-doped ZnO nanorods

Mehdi Koohgard^a, Abdollah Masoudi Sarvestani^a and Mona Hosseini-Sarvari^{*a}

[†]*Department of Chemistry, Shiraz University, Shiraz 7194684795, I.R. Iran.*

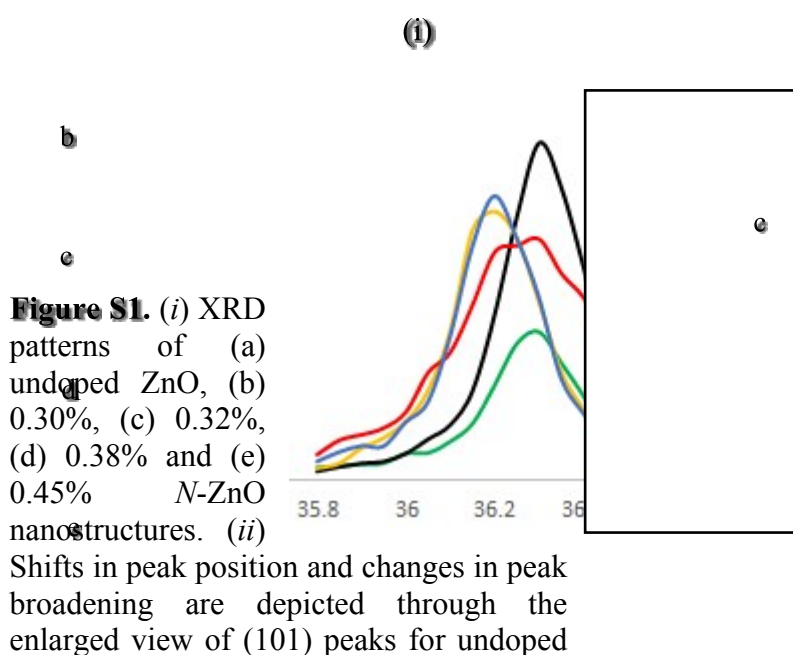
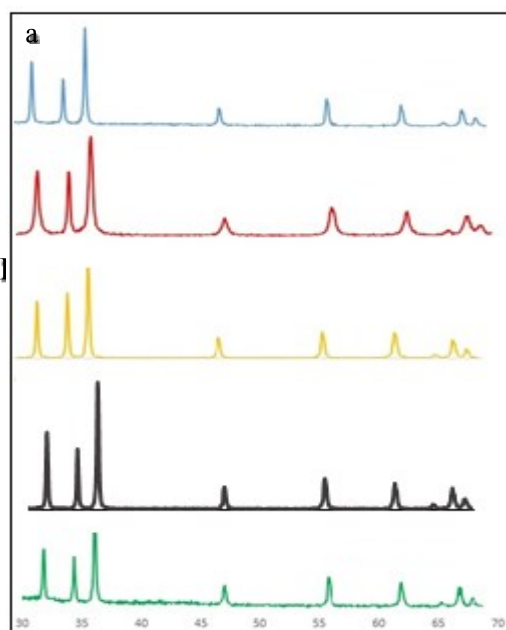
^{*}*Correspondence to: Mona Hosseini-Sarvari; E-mail: hossaini@shirazu.ac.ir*

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XRD analysis.

Figure S1 (i) illustrates the XRD spectrum of (0.30%), (0.32%), (0.38), and (0.45%) N-ZnO and undoped ZnO crystallite. In all diffractograms, prominent XRD lines were observed at 31.61° , 34.31° , 36.11° , 47.41° , 56.41° , 62.71° , 66.21° , 67.81° and 68.91° . These lines were indexed respectively as (100), (002), (101), (102), (110), (103), (200), (112) and (201) and correspond to hexagonal wurtzite phase of ZnO (space group P63mc; JCPD 36-1451).¹ Therefore, undoped and N doped samples prepared by us, possess the abovementioned hexagonal ZnO phase. Furthermore, neither extraneous impurity nor any secondary phase exists in prepared materials. In order to determine the alterations in crystal parameters, the prominent (101) peak of prepared materials was analysed.^{2,3} A careful observation of the enlarged view of this peak for various samples, as presented through Figure S1 (ii), indicates the shift in peak positions as well as change in peak broadening. As evident though the dashed line (b) in Figure S2 (ii) that (101) peak position shift to right for (0.30%) N-ZnO, as compared to that for undoped ZnO. Also for other N-ZnO, shift is seen at (101) peak position. However, shift in the peak position is clearly seen for all of N-ZnO samples. In line with aforesaid concept, this is the first clear indication of N doping into ZnO lattice.¹



and N-ZnO nanostructures.

FT-IR analysis

The FT-IR spectrum of undoped ZnO, (0.30%), (0.32%), (0.38%), and (0.45%) N-ZnO in the region of $400-4000\text{ cm}^{-1}$ is shown in Figure S2. FT-IR spectrum reveals the presence of stretching vibrational bond of O-H (3422 cm^{-1}), C-O (1650 cm^{-1}), C-H (1381 cm^{-1}) and Zn-O (473 and 532 cm^{-1}) in ZnO and N-ZnO. In case of FT-IR spectrum of N-

ZnO samples there is no peak corresponding to nitrogen which accords well with the XRD analysis. This may be due to the low nitrogen doping in ZnO.

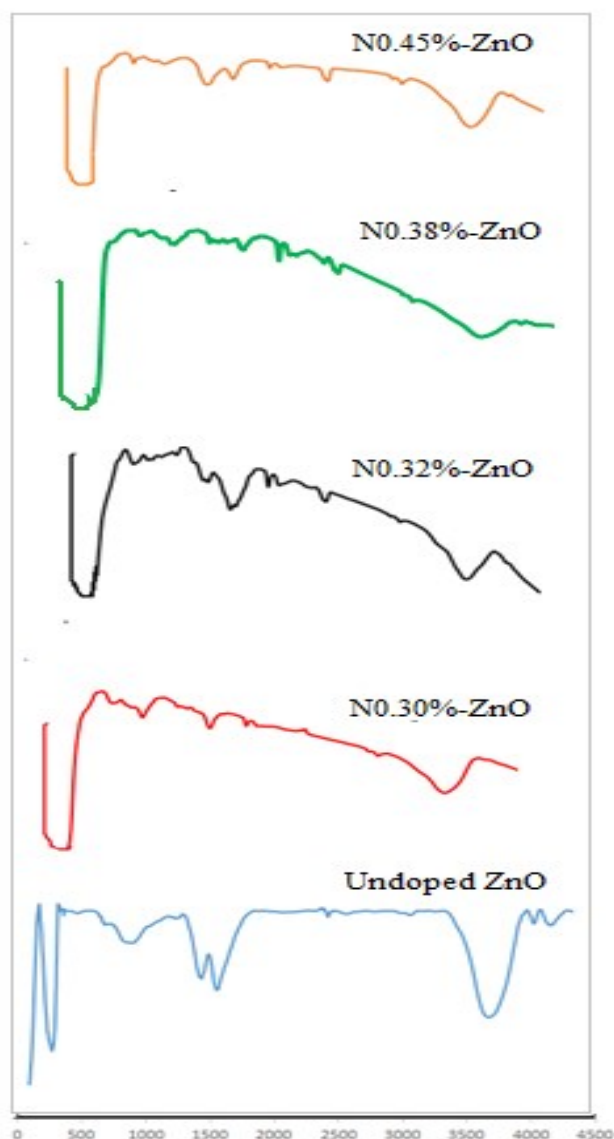


Figure S2. FT-IR spectra of undoped ZnO, (0.30%), (0.32%), (0.38%) and (0.45%) N-ZnO nanostructure.

1) Experimental information

General Information

All chemicals were purchased from Fluka, Aldrich, Acros, and Merck and all solvents were obtained from commercial sources and purified using standard methods. Most of the products were purified by short column or thin-layer chromatography. The progress of the reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates. Optical characteristics of catalysts were determined by UV/vis spectrophotometer (UV

2601, Ray Leigh). IR spectra were run on a Shimadzu FT-IR 8300 spectrophotometer and Perkin Elmer spectrum RXI. $^1\text{H-NMR}$ and spectra were recorded in CDCl_3 using a Bruker Avance DPX instrument (operating at 250 MHz for ^1H). All the coupling constants (J) are in Hertz. Melting points were determined in open capillary tubes in a Buchi-510 oil melting point apparatus. Catalysts were characterized by power X-ray diffraction (XRD) on a Bruker D8-advance X-ray diffractometer with Cu Ka ($\lambda=1.54178 \text{ \AA}$) incident radiation. The distribution morphology of the product was analyzed by scanning electron microscope (SEM, XL-30 FEG SEM, Philips, at 20 kV) and transmission electron microscopy (TEM, Philips model 30M-10, 100KV TEM instrument). The specific surface areas (SSABET; (m^2/g)) of the nanopowders were determined with the nitrogen adsorption measurement applying the BET method at 77 K (BELsorp-mini II). The lamps for irradiation were compact fluorescent lamp (CFL) 15 W white, blue LED 12 W, green LED 12 W and red LED 12 W.

General procedure for the synthesis of ZnO nanorods

In a typical experiment for the synthesis of ZnO nano-rods, zinc acetate dehydrate $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1 g) and PEG 2000 (0.30 g) was dissolved in 140 mL deionized water at room temperature to form a transparent solution. Then 1.5 ml ammonium hydroxide NH_3 (25%) was added dropwise to the solution. The mixture was refluxed for 6 h at 80°C . It was cooled by cold water to stop the reaction. The product was centrifuged and washed with deionized water and absolute ethanol. Then 90 ml deionized water was added and the mixture was refluxed for 9 h. It was cooled by cold water, centrifuged and washed. Then the ZnO nano-rods powders were allowed to drying at 100°C in an oven.⁴

General procedure for the synthesis of N-ZnO NRs

Typically, nitrogen-doped ZnO was prepared by heating a mixture of 0.5 g ZnO NRs and 1 g urea at 600°C in a tubular furnace for 4 h.⁵ The reaction was allowed to cool down to room temperature; the solid photocatalyst was centrifuged and washed with deionized water and then ethanol four times and dried at 70°C for 5 h on a vacuum oven. The pink-colored product was then obtained and denoted as 0.30% N-ZnO. Moreover, 0.32% N-ZnO, 0.38% N-ZnO, and 0.45% N-ZnO were prepared by heating ZnO (0.5 g) with different amounts of urea (2, 4 and 8g), respectively.

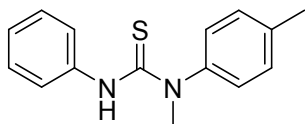
General procedure for the synthesis of thiourea

A mixture of N,N-dimethyl-para-tuloidine (3 mmol), phenyl-iso-thiocyanate (1 mmol), EtOH (4 mL) and (0.45%) N-ZnO NRs nanostructure was stirred under white CFL 15 W until the reaction was completed (monitored by TLC). Then the reaction mixture was diluted with CH_2Cl_2 and centrifuged to remove the catalyst. The filtrate was extracted

with CH₂Cl₂ and water. The organic layer was dried with Na₂SO₄. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:2) to afford the desired pure product.

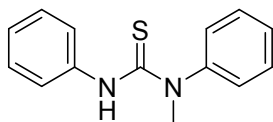
2) Characterization of compounds

1-Methyl-3-phenyl-1-(*p*-tolyl)thiourea (3a)



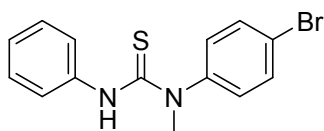
Yellow oil; IR (neat, cm⁻¹): 3371 (NH), 2589, 1519, 1334, 1210 (CS), 1103, 1025, 763, 694, 547. ¹H NMR (250 MHz, CDCl₃) δ (ppm) 2.34 (s, 3H), 3.66 (s, 3H), 6.92 (s, 1H), 7.26-7.07 (m, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 21.1, 43.5, 125.6, 125.9, 126.7, 128.5, 131.3, 139.0, 139.2, 140.1, 181.3.

1-Methyl-1,3-diphenylthiourea (3b)



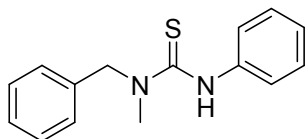
Yellow oil; IR (neat, cm⁻¹): 3355 (NH), 1589, 1504, 1342, 1211 (CS), 1095, 1094, 763, 745, 683. ¹H NMR (250 MHz, CDCl₃) δ (ppm) 3.66 (s, 3H), 6.90 (s, 1H), 7.49-7.06 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 43.6, 125.7, 126.0, 127.0, 128.6, 128.8, 130.8, 139.2, 142.9, 181.4.

1-(4-Bromophenyl)-1-methyl-3-phenylthiourea (3c)



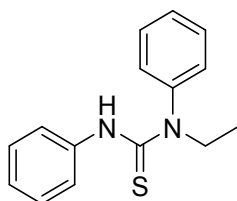
Yellow oil; IR (neat, cm⁻¹): 3213 (NH), 2902, 1597, 1515, 1491, 1386, 1271 (CS), 1085, 822, 688. ¹H NMR (250 MHz, CDCl₃) δ (ppm) 3.65 (s, 3H) 6.86 (s, 1H), 7.09-7.25 (m, 7H), 7.58 (dd, J= 8.7, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 43.8, 125.1, 126.0, 126.2, 127.7, 128.9, 129.2, 139.6, 142.6, 180.0.

1-Benzyl-1-methyl-3-phenylthiourea (3d)



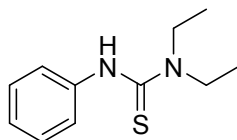
White solid; m.p. = 85-88 °C, IR (KBr, cm⁻¹): 3232 (NH), 3028, 2812, 1643, 1597, 1496, 1423, 1330, 1247 (CS), 1018, 860, 745, 655. ¹H NMR (250 MHz, CDCl₃) δ (ppm) 3.16 (s, 3H), 4.97 (s, 2H), 6.98 (s, 1H), 7.16-7.24 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 44.7, 60.5, 125.3, 125.8, 127.2, 128.7, 129.0, 129.6, 136.7, 138.5, 180.0.

1-Ethyl-1,3-diphenylthiourea (3e)



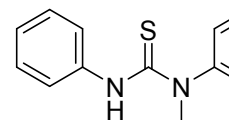
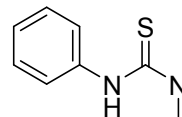
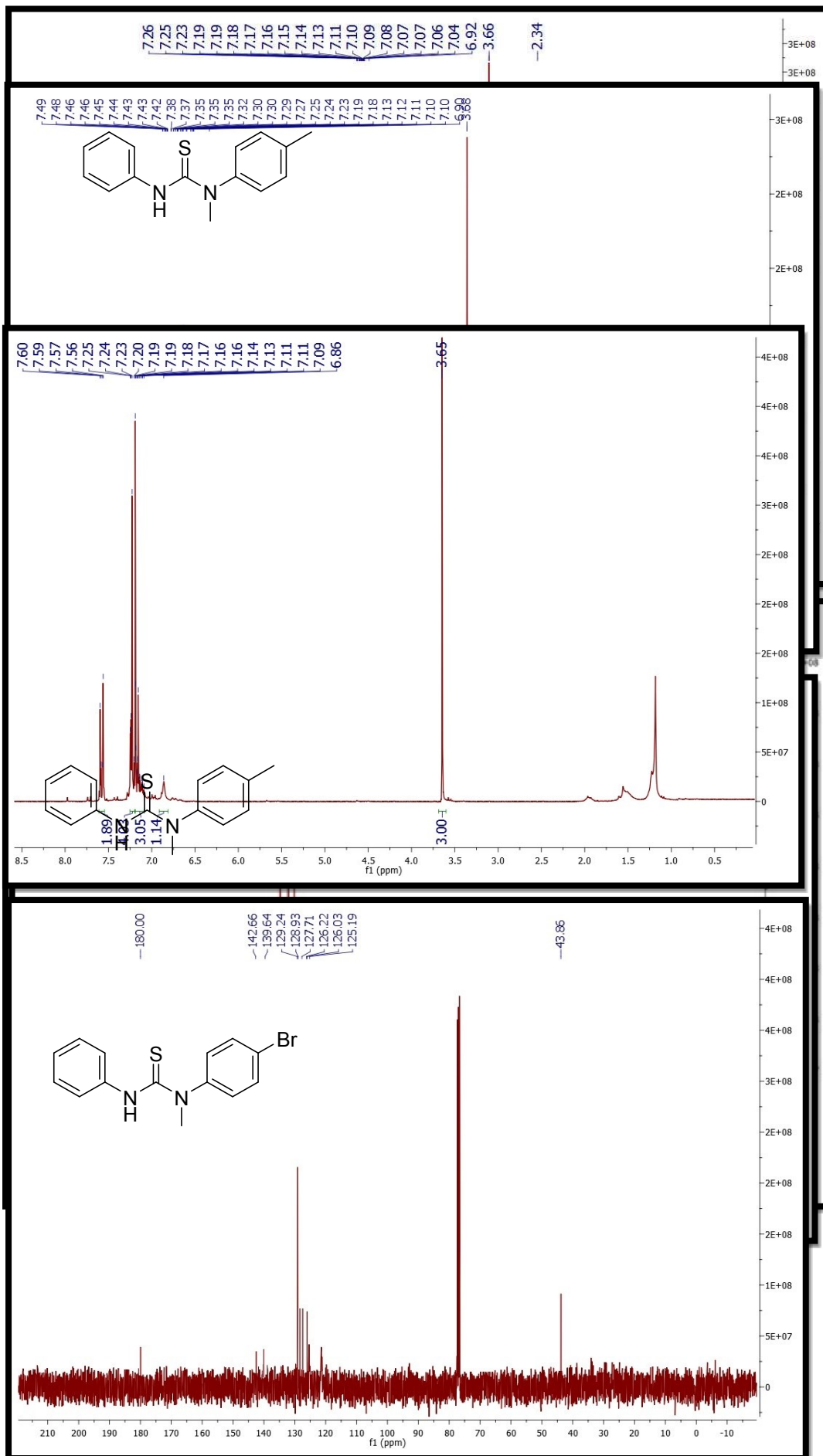
Yellow oil; IR (neat, cm⁻¹): 3242 (NH), 3031, 2912, 1654, 1597, 1496, 1434, 1319, 1247 (CS), 1118, 860, 745, 688. ¹H NMR (250 MHz, CDCl₃) δ (ppm) 1.34 (t, J= 7.5 Hz 3H), 4.56 (q, J= 5 Hz 2H), 6.80 (s, 1H), 7.04-7.30 (m, 10H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 13.30, 43.5, 125.5, 125.6, 126.2, 128.6, 128.7, 133.9, 139.0, 142.0, 180.6.

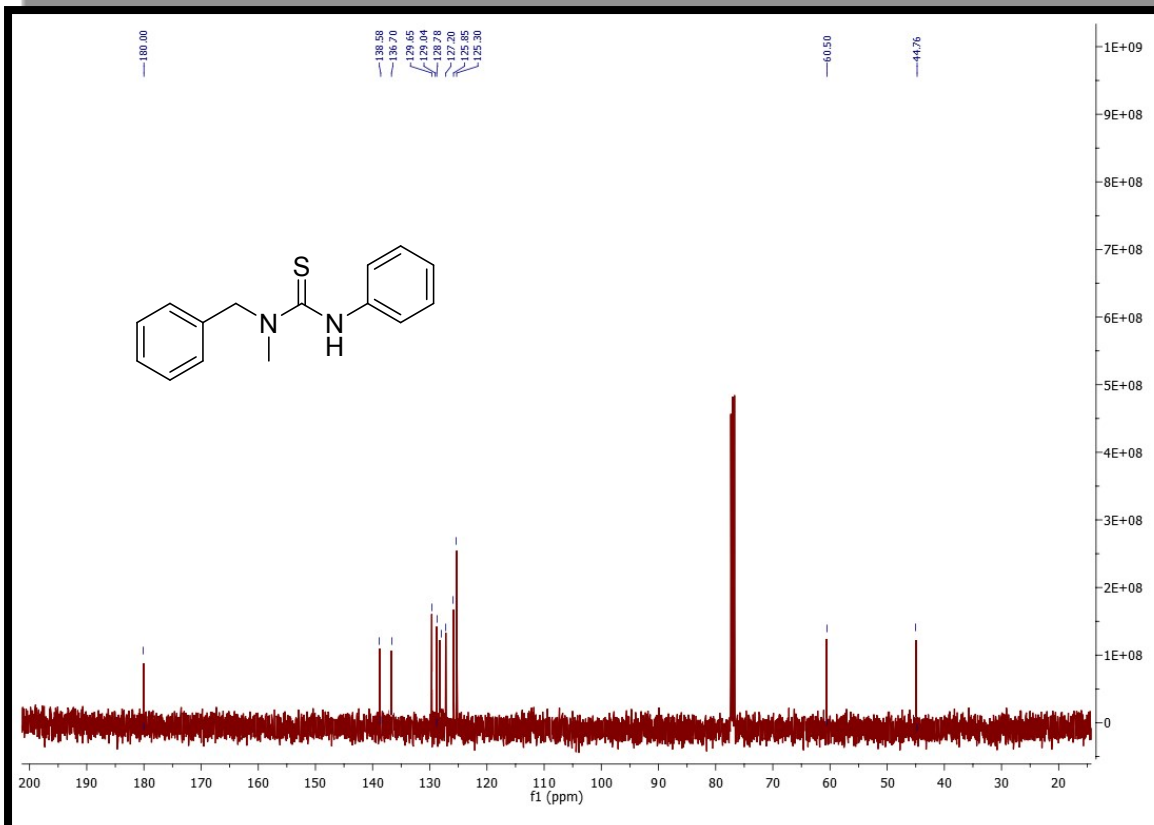
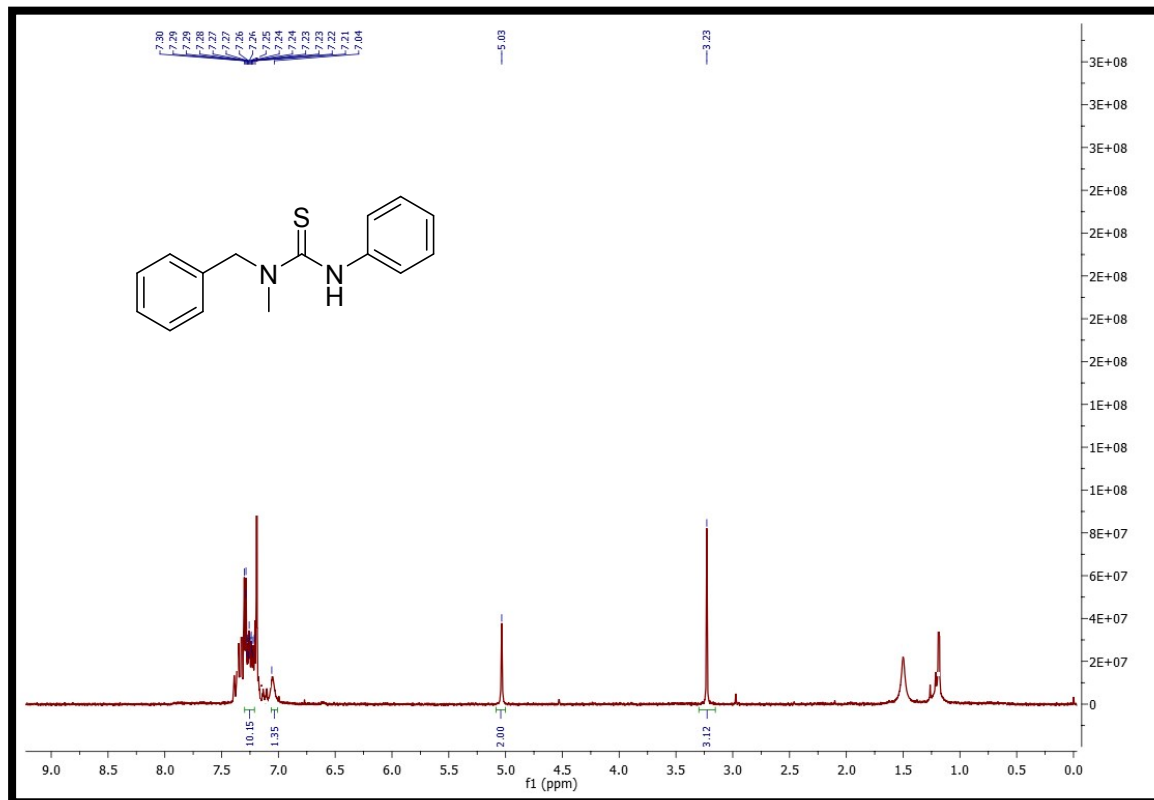
1,1-Diethyl-3-phenylthiourea (3f)

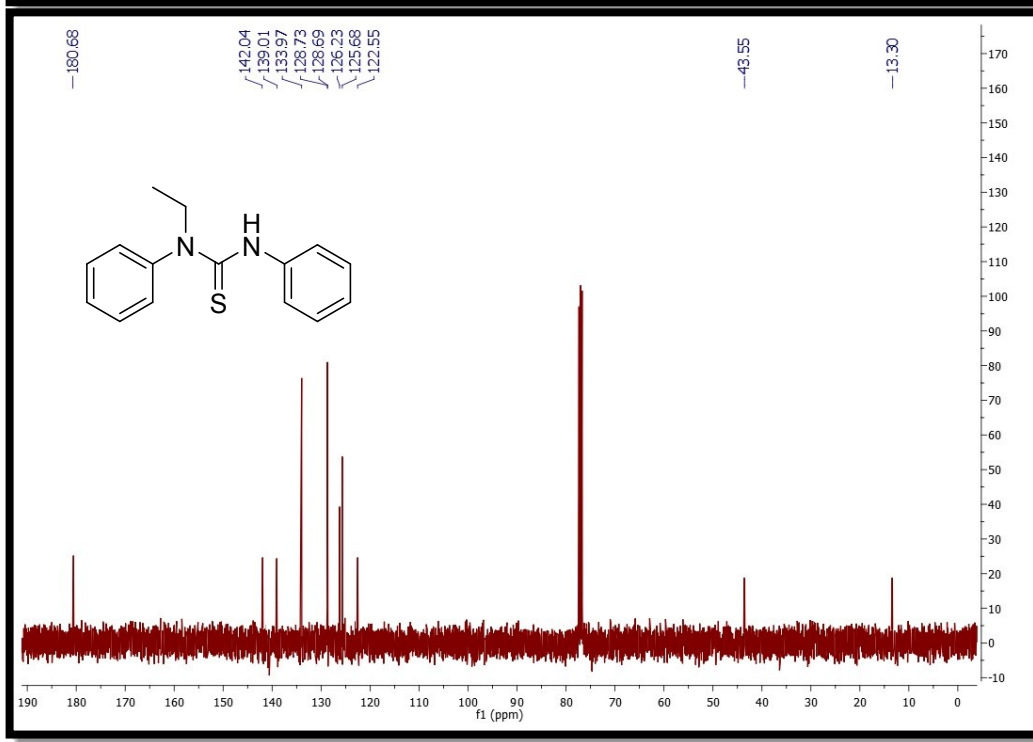
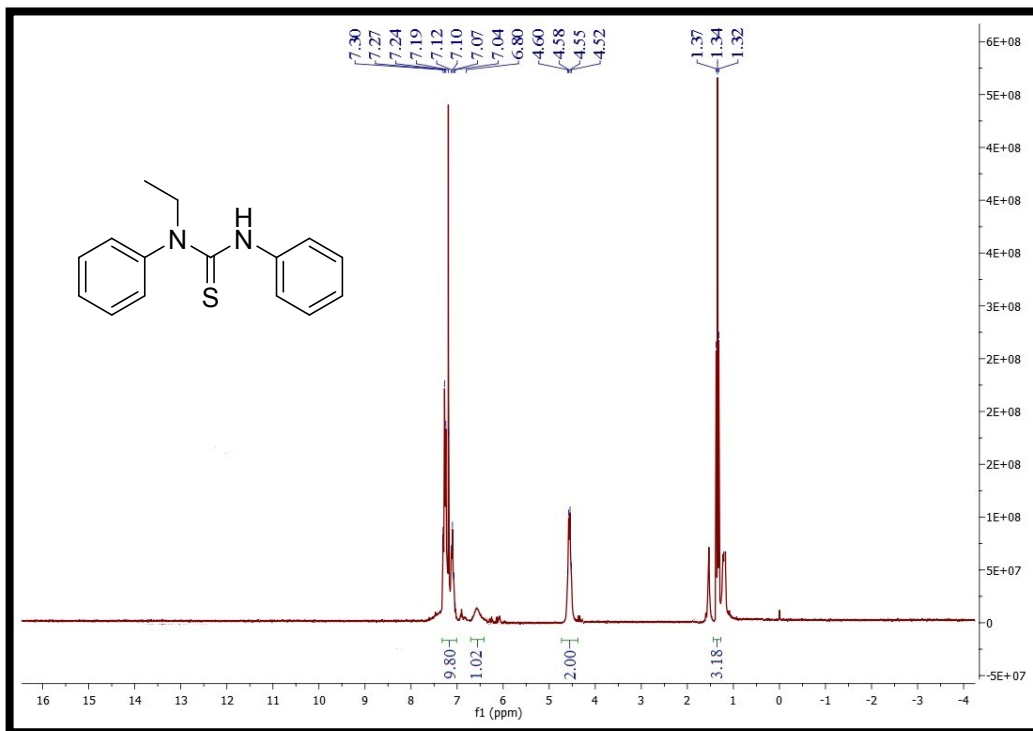


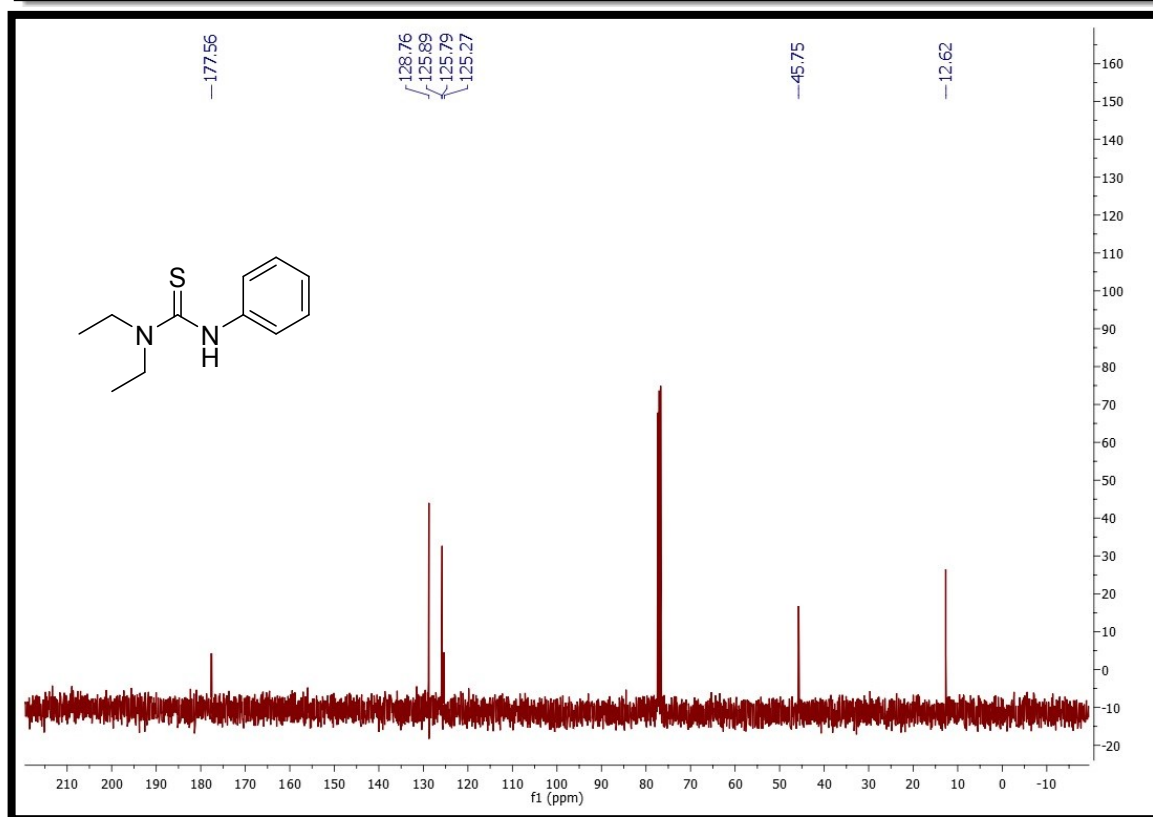
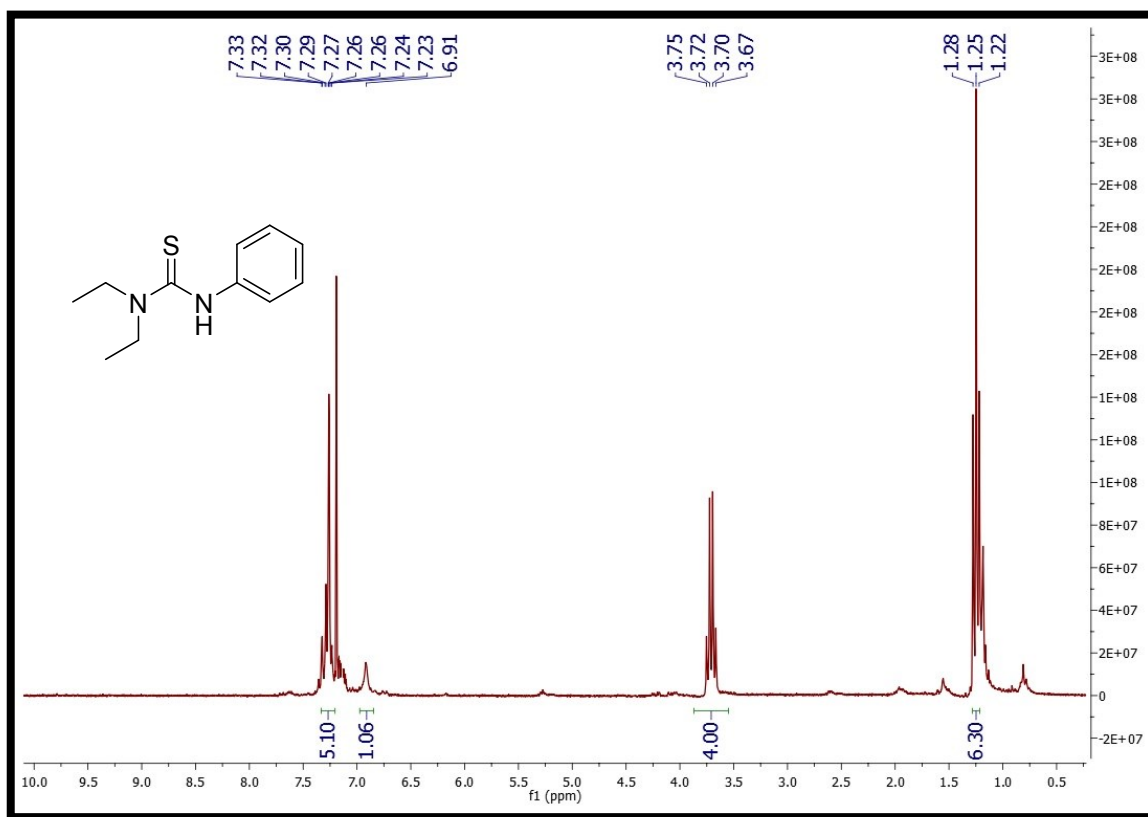
Yellow oil; IR (neat, cm⁻¹): 3229 (NH), 3038, 2975, 2931, 1695, 1518, 1452, 1404, 1350, 1137 (CS), 1075, 1004, 910, 896, 761, 698. ¹H NMR (250 MHz, CDCl₃) δ (ppm) 1.25 (t, J= 5 Hz, 6H), 3.71 (q, J= 7.5 Hz, 4H), 6.91 (s, 1H), 7.23-7.33 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 12.6, 45.7, 125.2, 125.7, 125.8, 177.5.

3) ¹H and ¹³C NMR Spectra of Products

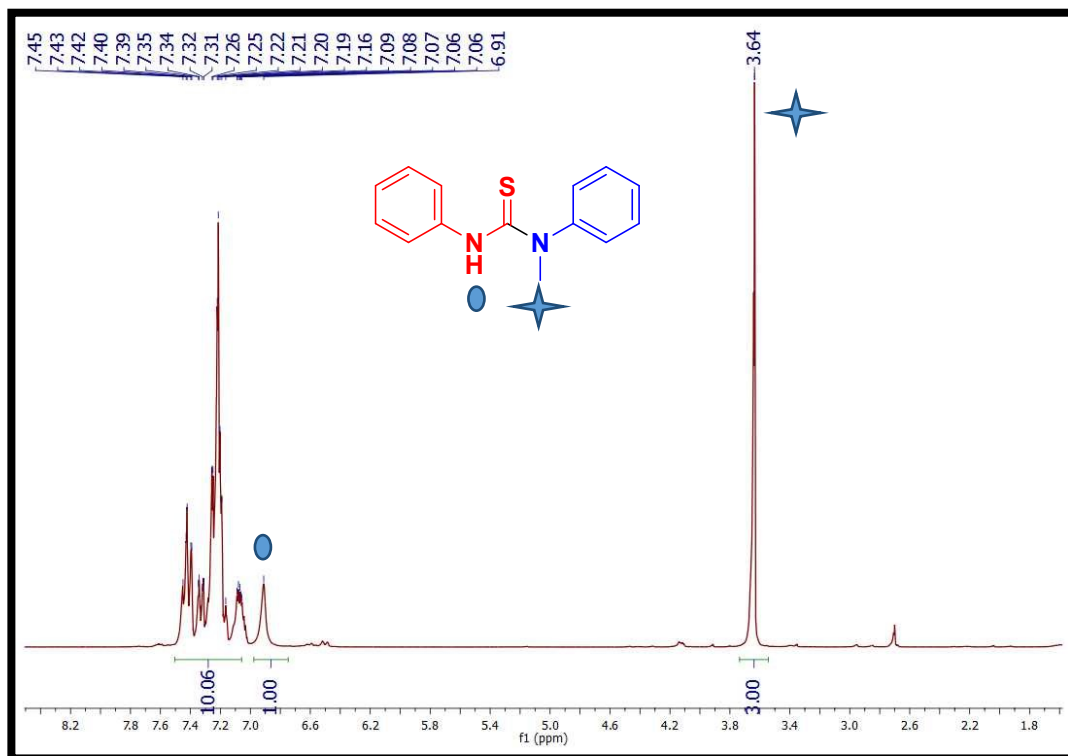




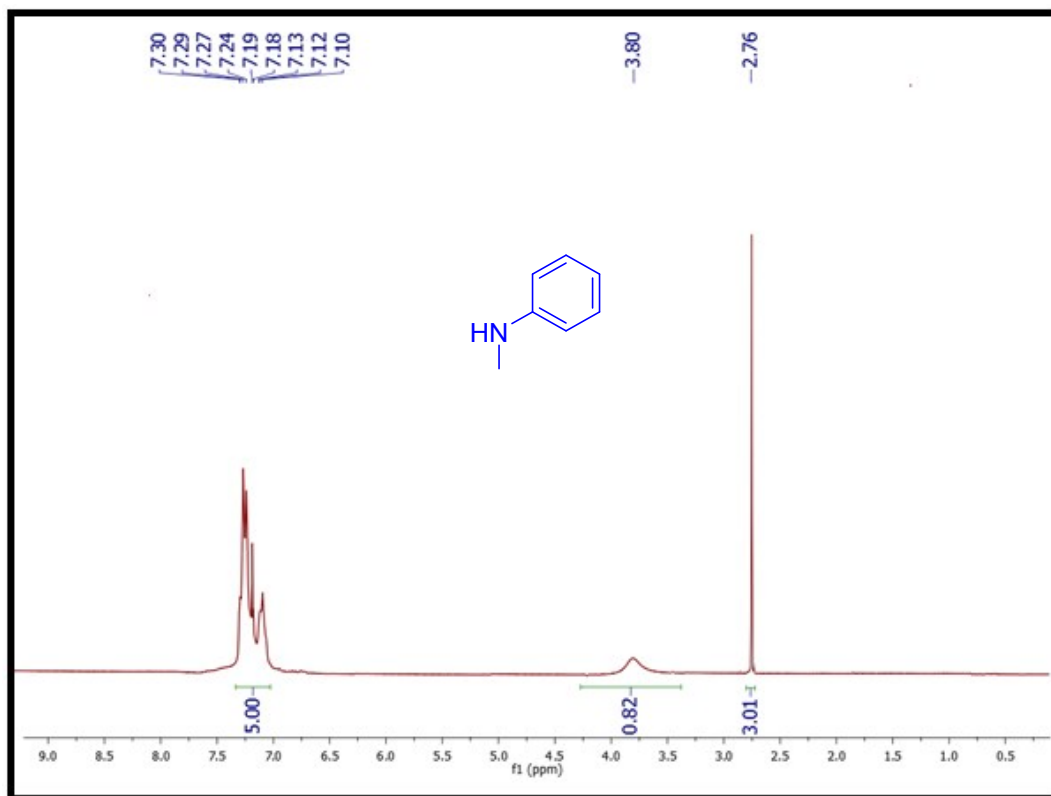




4) ^1H NMR spectrum of product 5



5) ^1H NMR spectrum of product 7



6) References

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