

Supporting Information

Na₂CO₃-Promoted Synthesis of Thiocarbamates from Isocyanates and Thiols under Mild Conditions

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General Information

All solvents were dried and distilled before use according to the standard methods. The chemicals were purchased from commercial sources (Aladdin, purity > 97%) and used as received unless otherwise indicated. Flash chromatography columns were packed with 200-300 mesh neutral alumina in petroleum (bp. 60-90 °C) and ethyl acetate. ¹H NMR (600 MHz), ¹³C NMR (150.9 MHz) data were recorded on a BRUKER AVANCE III 600MHz instrument at 298 K with tetramethylsilane as an internal standard. Melting points were determined on a STUART SMP10 melting point apparatus and uncorrected. The crystal data was collected by a Bruker D8 Venture X-ray Single Crystal Diffractometer. High resolution mass spectrometry (HRMS) was performed with ESI in the positive ion mode on the Thermo Scientific Q Exactive instrument. IR spectra was performed on Thermo Scientific Nicolet iS50 (ATR-FTIR) spectrophotometer.

General procedure for synthesis of thiocarbamates from isocyanates and thiols

To a 25 mL sealed tube equipped with a magnetic stir bar was added Na₂CO₃ (5.2 mg, 0.05 mmol), this tube was evacuated and backfilled with N₂ three times. Then, 2-methylphenyl isocyanate (62 μL, 0.5 mmol), benzyl thiol (59 μL, 0.5 mmol) and 1.0 mL of 1, 4-dioxane were added under the N₂ atmosphere, and the reaction tube was sealed and stirred for 1 h at 25 °C. The reaction was carefully quenched with water (10 mL) and extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated. The yields were determined by using the ¹H NMR technique using trichloroethylene (45 μL, 0.5 mmol) as an internal standard. The crude product was purified by silica gel flash chromatography (petroleum ether/ EtOAc: 1/1-10/1). All of the products were characterized by NMR and HRMS techniques.

Crystal data and structure refinement details of 2r and 2s.

Table 1. Single crystal X-ray data and structure refinement details for 2r

| | |
|-----------------------------------|--|
| Identification code | 2r |
| Empirical formula | C ₄₅ H ₄₅ N ₃ O ₆ S ₃ |
| Formula weight | 820.02 |
| Temperature | 273(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 14.2283(6) Å α = 90° b = 14.9598(6) Å β = 94.1990(10)° c = 20.4993(8) Å γ = 90° |
| Volume | 4351.6(3) Å ³ |
| Z | 4 |
| Density (calculated) | 1.252 g/cm ³ |
| Absorption coefficient | 0.220 mm ⁻¹ |
| F(000) | 1728 |
| Crystal size | 0.20 x 0.13 x 0.06 mm ³ |
| Theta range for data collection | 2.72 to 28.20°. |
| Index ranges | -18 ≤ h ≤ 18, -19 ≤ k ≤ 18, -27 ≤ l ≤ 27 |
| Reflections collected | 44821 |
| Independent reflections | 10734 [R(int) = 0.0347] |
| Completeness to theta = 25.04° | 99.0% |
| Data / restraints / parameters | 10734/0/520 |
| Goodness-of-fit on F ² | 1.017 |
| Final R indices [I > 2σ(I)] | R1 = 0.0551, wR2 = 0.1306 |
| R indices (all data) | R1 = 0.0854, wR2 = 0.1527 |

Table 2. Single crystal X-ray data and structure refinement details for **2s**

| | |
|-----------------------------------|--|
| Identification code | 2s |
| Empirical formula | $C_{14}H_{13}NO_2S$ |
| Formula weight | 259.31 |
| Temperature | 273(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | monoclinic |
| Space group | P 21/c |
| Unit cell dimensions | a = 13.3641(8) Å $\alpha = 90^\circ$ b = 11.7805(7) Å $\beta = 107.970(2)^\circ$ c = 8.6325(5) Å $\gamma = 90^\circ$ |
| Volume | 1292.77(13) Å ³ |
| Z | 4 |
| Density (calculated) | 1.332 g/cm ³ |
| Absorption coefficient | 0.243 mm ⁻¹ |
| F(000) | 544 |
| Crystal size | 0.18 x 0.10 x 0.05 mm ³ |
| Theta range for data collection | 3.02 to 28.35°. |
| Index ranges | -17 ≤ h ≤ 17, -15 ≤ k ≤ 15, -10 ≤ l ≤ 11 |
| Reflections collected | 12988 |
| Independent reflections | 3196 [R(int) = 0.0257] |
| Completeness to theta = 25.04° | 98.9% |
| Data / restraints / parameters | 3196/0/165 |
| Goodness-of-fit on F ² | 1.050 |
| Final R indices [I > 2σ(I)] | R1 = 0.0381, wR2 = 0.1099 |
| R indices (all data) | R1 = 0.0455, wR2 = 0.1149 |

ORTEP diagram of compound **2r** and **2s**

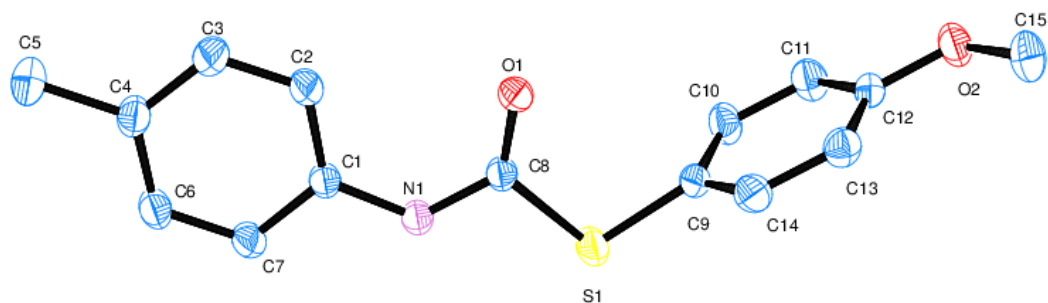


Fig 1. ORTEP diagram of compound **2r** with thermal ellipsoids at 30% probability (H not shown for clarity)

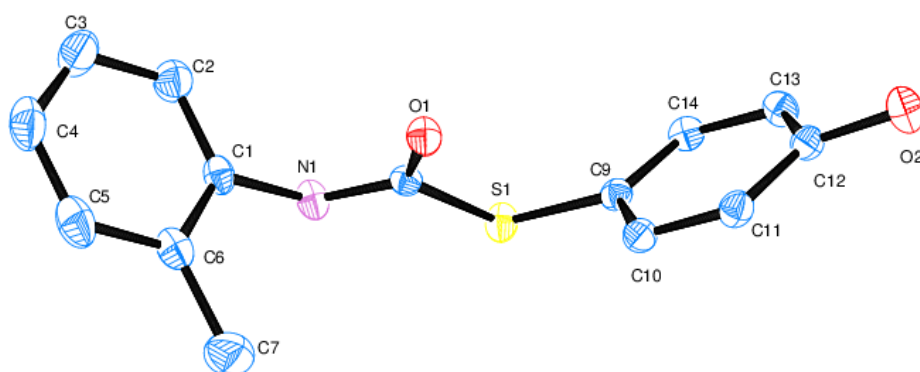
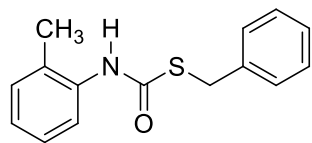


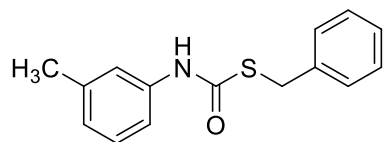
Fig 2. ORTEP diagram of compound **2s** with thermal ellipsoids at 30% probability (H not shown for clarity)

Characterization data of thiocarbamates



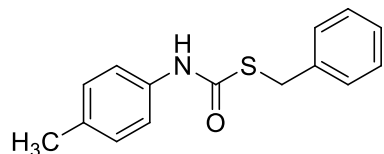
S-benzyl-*o*-tolylcarbamothioate (**2a**)

White solid, yield: 99% (94%). ^1H NMR (600 MHz, CDCl_3) δ 7.57 (s, 1H), 7.32 (d, $J = 7.3$ Hz, 2H), 7.26 (t, $J = 7.3$ Hz, 2H), 7.24-7.19 (m, 1H), 7.18-7.12 (m, 2H), 7.09 (d, $J = 6.5$ Hz, 1H), 7.03 (s, 1H), 4.17 (s, 2H), 2.19 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.72 (s), 138.04 (s), 135.28 (s), 130.70 (s), 128.93 (s), 128.62 (s), 127.29 (s), 126.80 (d, $J = 2.7$ Hz), 34.54 (s), 17.75 (s). HRMS (ESI, m/z) calcd for $\text{C}_{15}\text{H}_{16}\text{NOS}^+$: 258.0947, found: 258.0947. Mp: 84-85 °C. IR (cm^{-1}): 3208.3, 1635.3, 1514.8, 1488.7, 1453.8, 1240.8, 1202.9, 1169.8, 1025.9, 947.0, 913.2, 839.3, 743.8, 709.5, 696.1.



S-benzyl-*m*-tolylcarbamothioate (**2b**)

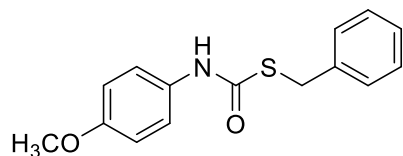
White solid, yield: 98% (90%). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.39 (d, $J = 7.5$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.30-7.26 (m, 2H), 7.23-7.17 (m, 2H), 7.05 (s, 1H), 6.95 (d, $J = 6.9$ Hz, 1H), 4.25 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.37, 139.29, 138.13, 137.68, 129.09, 129.01, 128.77, 127.46, 125.56, 120.79, 117.18, 34.68, 21.56. HRMS (ESI, m/z) calcd for $\text{C}_{15}\text{H}_{16}\text{NOS}^+$: 258.0947, found: 258.0948. Mp: 74-55 °C. IR (cm^{-1}): 3247.1, 2923.1, 1651.3, 1595.4, 1541.9, 1493.3, 1432.0, 1290.9, 1260.7, 1195.7, 1140.8, 903.9, 871.5, 779.5, 692.1.



S-benzyl-*p*-tolylcarbamothioate (**2c**)

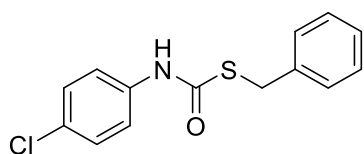
White solid, yield: 94% (89%). ^1H NMR (600 MHz, CDCl_3) δ 7.40 (d, $J = 7.4$ Hz, 3H), 7.36-7.27 (m, 5H), 7.12 (d, $J = 8.2$ Hz, 2H), 4.26 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.45 (s), 137.99 (s), 134.64 (d, $J = 123.5$ Hz), 129.60 (s), 128.92 (s), 128.62 (s), 127.29 (s), 120.22 (s), 34.48 (s), 20.88 (s). HRMS (ESI, m/z)

calcd for $C_{15}H_{16}NOS^+$: 258.0947, found: 258.0947. Mp: 113-114 °C. IR (cm^{-1}): 3245.2, 2922.0, 1647.2, 1598.8, 1532.2, 1510.7, 1406.9, 1310.2, 1294.7, 1246.8, 1158.2.



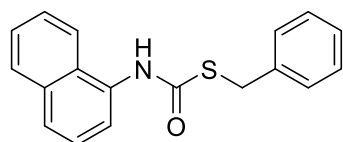
S-benzyl-(4-methoxyphenyl)carbamothioate (**2d**)

White solid, yield: 95% (90%). 1H NMR (600 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.38 (d, $J = 7.4$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 4H), 7.28 (d, $J = 7.2$ Hz, 1H), 6.84 (d, $J = 8.9$ Hz, 2H), 4.24 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.37 (s), 156.69 (s), 138.02 (s), 130.72 (s), 128.91 (s), 128.59 (s), 127.25 (s), 121.68 (s), 114.25 (s), 77.37 (s), 77.16 (s), 76.95 (s), 55.46 (s), 34.43 (s). HRMS (ESI, m/z) calcd for $C_{15}H_{16}NO_2S^+$: 274.0896, found: 274.0896. Mp: 94-95 °C.



S-benzyl-(4-chlorophenyl)carbamothioate (**2e**)

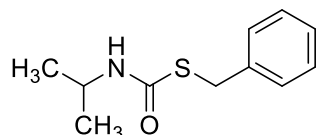
White solid, yield: 92% (87%). 1H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, $J = 7.4$ Hz, 3H), 7.35-7.30 (m, 4H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 8.8$ Hz, 2H), 4.24 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.79 (s), 137.71 (s), 136.22 (s), 129.24 (t, $J = 50.6$ Hz), 128.93 (s), 128.93 (s), 128.74 (s), 127.50 (s), 121.26 (s), 34.58 (s). HRMS (ESI, m/z) calcd for $C_{14}H_{13}ClNOS^+$: 278.0401, found: 278.0400. Mp: 118-119 °C.



S-benzyl-naphthalen-1-ylcarbamothioate (**2f**)

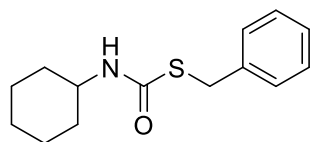
White solid, yield: 91% (85%). 1H NMR (600 MHz, $CDCl_3$) δ 7.91-7.83 (m, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.52 (dd, $J = 9.2, 4.9$ Hz, 3H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 7.3$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 2H), 7.26 (t, $J = 7.2$ Hz, 1H), 4.24 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.76 (s), 137.98 (s), 134.28 (s), 132.04 (s), 129.05 (s), 128.70 (s), 127.39 (s), 126.77 (s), 126.39 (s), 125.64 (s), 121.36 (s), 34.75 (s). HRMS

(ESI, m/z) calcd for C₁₈H₁₆NOS⁺: 294.0947, found: 294.0947. Mp: 132-133 °C. IR (cm⁻¹): 3228.8, 1643.9, 1520.6, 1503.7, 1453.8, 1390.2, 1344.9, 1269.2, 1243.9, 1182.8, 1155.2, 1014.0, 927.4, 896.5, 871.7, 801.9, 769.0, 702.8, 692.5.



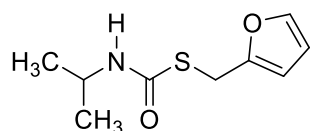
S-benzyl-isopropylcarbamothioate (**2g**)

White solid, yield: 99% (95%). ¹H NMR (600 MHz, CDCl₃) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 5.37 (s, 1H), 4.16 (s, 2H), 4.09 (s, 1H), 1.16 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 165.67 (s), 138.48 (s), 128.85 (s), 128.56 (s), 127.13 (s), 43.90 (s), 34.15 (s), 22.78 (s). HRMS (ESI, m/z) calcd for C₁₁H₁₆NOS⁺: 210.0947, found: 210.0947. Mp: 74-75 °C.



S-benzyl-cyclohexylcarbamothioate (**2h**)

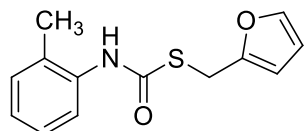
White solid, yield: 99% (94%). ¹H NMR (600 MHz, CDCl₃) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.44 (s, 1H), 4.16 (s, 2H), 3.78 (s, 1H), 1.93 (d, *J* = 10.2 Hz, 2H), 1.70 (d, *J* = 13.6 Hz, 2H), 1.60 (d, *J* = 13.0 Hz, 1H), 1.33 (dd, *J* = 24.8, 12.3 Hz, 2H), 1.14 (q, *J* = 11.9 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 165.60 (s), 138.55 (s), 128.85 (s), 128.55 (s), 127.11 (s), 50.72 (s), 34.18 (s), 33.13 (s), 25.43 (s), 24.82 (s). HRMS (ESI, m/z) calcd for C₁₄H₂₀NOS⁺: 250.1260, found: 250.1259. Mp: 104-105 °C. IR (cm⁻¹): 3293.0, 2925.2, 2854.2, 1636.5, 1600.5, 1515.8, 1452.9, 1311.1, 1247.0, 1206.4, 1159.1, 1073.4, 1208.1, 889.7, 835.5, 818.3, 783.2, 697.5.



S-(furan-2-ylmethyl) isopropylcarbamothioate (**2i**)

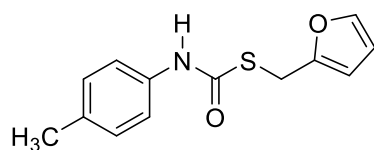
Colourless liquid, yield: 99% (93%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.32-7.27 (m, 1H), 6.28-6.23 (m, 1H), 6.20 (d, *J* = 3.1 Hz, 1H), 5.41 (s, 1H), 4.15 (s, 2H), 4.06

(s, 1H), 1.14 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (151 MHz, Chloroform- d) δ 165.02, 151.42, 142.07, 110.62, 107.68, 44.00, 26.59, 22.77. HRMS (ESI, m/z) calcd for $\text{C}_9\text{H}_{13}\text{NO}_2\text{SNa}^+$: 222.0559, found: 222.0560.



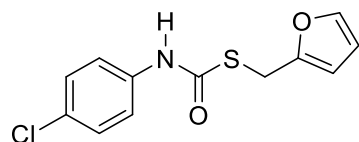
S-(furan-2-ylmethyl)-*o*-tolylcarbamothioate (**2j**)

White solid, yield: 92% (86%). ^1H NMR (600 MHz, CDCl_3) δ 7.58 (s, 1H), 7.34 (s, 1H), 7.17 (dd, $J = 28.0, 6.9$ Hz, 4H), 6.30 (s, 1H), 6.27 (d, $J = 2.6$ Hz, 1H), 4.24 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 165.12(s), 150.92 (s), 142.20 (s), 135.10 (s), 130.71 (s), 126.80 (s), 126.30 (s), 110.66 (s), 107.99 (s), 77.37 (s), 77.16 (s), 76.95 (s), 26.97 (s), 17.75 (s). HRMS (ESI, m/z) calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_2\text{S}^+$: 248.0740, found: 248.0739. Mp: 75-76 $^\circ\text{C}$.



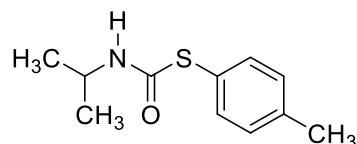
S-(furan-2-ylmethyl)-*p*-tolylcarbamothioate (**2k**)

White solid, yield: 96% (90%). ^1H NMR (600 MHz, Chloroform- d) δ 7.36-7.33 (m, 1H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), 7.04 (s, 1H), 6.30 (s, 1H), 6.27 (s, 1H), 4.25 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, Chloroform- d) δ 166.62, 151.04, 142.37, 135.01, 129.78, 120.25, 110.78, 108.13, 27.10, 20.99. HRMS (ESI, m/z) calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_2\text{S}^+$: 248.0740, found: 248.0739. Mp: 99-100 $^\circ\text{C}$.



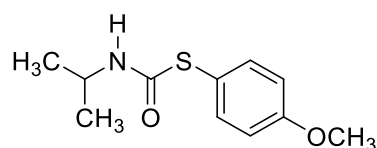
S-(furan-2-ylmethyl)-(4-chlorophenyl)carbamothioate (**2l**)

White solid, yield: 99% (97%). ^1H NMR (600 MHz, Chloroform- d) δ 7.35 (d, $J = 8.9$ Hz, 3H), 7.28-7.24 (m, 2H), 7.21 (s, 1H), 6.33 – 6.25 (m, 2H), 4.25 (s, 2H); ^{13}C NMR (151 MHz, Chloroform- d) δ 165.03, 150.71, 142.47, 136.21, 129.28, 121.30, 110.81, 108.27, 27.13. HRMS (ESI, m/z) calcd for $\text{C}_{12}\text{H}_{11}\text{ClNO}_2\text{S}^+$: 268.0194, found: 268.0190. Mp: 105-106 $^\circ\text{C}$.



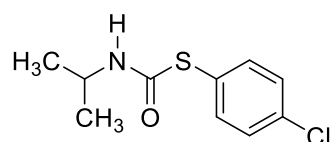
S-(*p*-tolyl) isopropylcarbamothioate (**2m**)

White solid, yield: 97% (93%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.16 (s, 1H), 4.08-3.97 (m, 1H), 2.37 (s, 3H), 1.12 (d, *J* = 6.2 Hz, 6H); ¹³C NMR (151 MHz, Chloroform-*d*) δ 165.55, 140.00, 135.54, 130.32, 125.44, 43.99, 22.77, 21.42. HRMS (ESI, *m/z*) calcd for C₁₁H₁₆NOS⁺: 210.0947, found: 210.0945. Mp: 98-99 °C



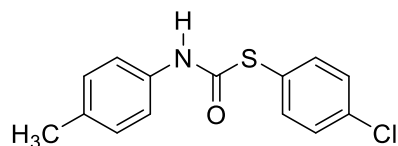
S-(4-methoxyphenyl) isopropylcarbamothioate (**2n**)

White solid, yield: 98% (92%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 1H), 4.06-3.96 (m, 1H), 3.81 (s, 3H), 1.10 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (151 MHz, Chloroform-*d*) δ 165.92, 160.87, 137.22, 119.53, 115.07, 55.43, 43.88, 22.68. HRMS (ESI, *m/z*) calcd for C₁₁H₁₆NO₂S⁺: 226.0896, found: 226.0893. Mp: 94-95 °C.



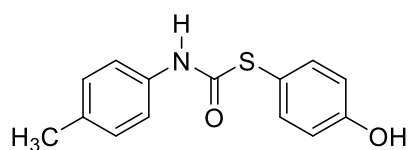
S-(4-chlorophenyl) isopropylcarbamothioate (**2o**)

White solid, yield: 94% (87%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.38-7.34 (m, 2H), 5.33 (s, 1H), 4.09 – 3.95 (m, 1H), 1.15 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (151 MHz, Chloroform-*d*) δ 164.15, 136.59, 135.82, 129.47, 127.26, 44.28, 22.73. HRMS (ESI, *m/z*) calcd for C₁₀H₁₃ClNOS⁺: 230.0401, found: 230.0399. Mp: 146-147 °C. IR (cm⁻¹): 3297.0, 2973.7, 1912.4, 1645.6, 1571.2, 1518.6, 1466.5, 1454.7, 1386.0, 1365.5, 1211.9, 1166.7, 1091.1, 1077.0, 1009.6, 953.5, 874.6, 814.5, 747.8, 701.7.



S-(4-chlorophenyl) *p*-tolylcarbamothioate (**2p**)

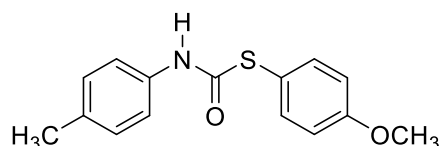
White solid, yield: 95% (90%). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.5$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.18 (s, 1H), 7.11 (d, $J = 8.1$ Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.74, 136.78, 136.29, 134.92, 129.76, 129.65, 126.64, 119.95, 20.97. HRMS (ESI, m/z) calcd for $\text{C}_{14}\text{H}_{13}\text{ClNOS}^+$: 278.0401, found: 278.0400. Mp: 147-148 °C.



S-(4-hydroxyphenyl) *p*-tolylcarbamothioate (**2q**)

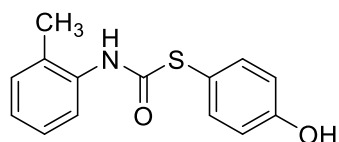
White solid, yield: 96% (90%).

^1H NMR (600 MHz, DMSO-*d*₆) δ 10.28 (s, 1H), 9.87 (s, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 8.3$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-*d*₆) δ 163.62, 158.58, 137.21, 136.42, 132.34, 129.18, 119.02, 116.45, 115.97, 20.34. HRMS (ESI, m/z) calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_2\text{S}^+$: 260.0740, found: 260.0739. Mp: 161-162 °C.



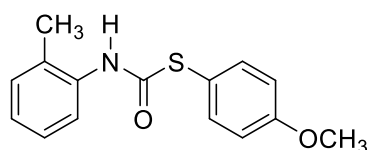
S-(4-methoxyphenyl) *p*-tolylcarbamothioate (**2r**)

White solid, yield: 99% (95%). ^1H NMR (600 MHz, CDCl_3) δ 7.54 (d, $J = 8.8$ Hz, 2H), 7.47 (s, 1H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 8.2$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 165.40, 161.04, 137.36, 135.21, 134.07, 129.49, 119.75, 118.87, 115.13, 55.39, 20.84. HRMS (ESI, m/z) calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2\text{S}^+$: 274.0896, found: 274.0894. Mp: 112-113 °C.



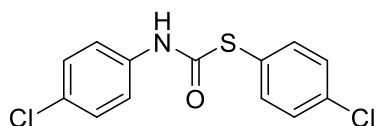
S-(4-hydroxyphenyl) *o*-tolylcarbamothioate (**2s**)

White solid, yield: 98% (93%). ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.85 (s, 1H), 9.68 (s, 1H), 7.33-7.26 (m, 3H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.1 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 2H), 2.20 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 164.83, 158.52, 137.09, 136.03, 130.39, 126.09, 125.91, 116.73, 115.99, 17.69. HRMS (ESI, *m/z*) calcd for C₁₄H₁₄NO₂S⁺: 260.0740, found: 260.0741. Mp: 115-116 °C.



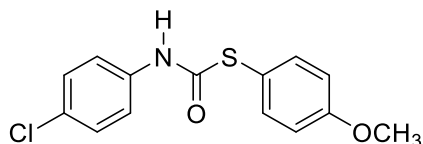
S-(4-methoxyphenyl) *o*-tolylcarbamothioate (**2t**)

White solid, yield: 97% (91%). ¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 7.0 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 1H), 3.85 (s, 3H), 2.00 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.51 (s), 137.68 (s), 135.61 (s), 130.60 (s), 127.08 (s), 125.35 (s), 119.36 (s), 115.55 (s), 55.62 (s), 17.33 (s). HRMS (ESI, *m/z*) calcd for C₁₅H₁₆NO₂S⁺: 274.0896, found: 274.0895. Mp: 121-122 °C.



S-(4-chlorophenyl) (4-chlorophenyl)carbamothioate (**2u**)

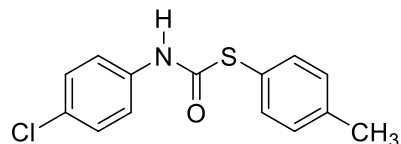
White solid, yield: 98% (94%). ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.72 (s, 1H), 7.59-7.42 (m, 6H), 7.35 (s, 2H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 162.46, 137.55, 136.81, 134.32, 128.75, 127.29, 126.85, 120.63. HRMS (ESI, *m/z*) calcd for C₁₃H₁₀Cl₂NOS⁺: 297.9855, found: 297.9857. Mp: 166-167 °C



S-(4-methoxyphenyl) (4-chlorophenyl)carbamothioate (**2v**)

White solid, yield: 99% (93%). ¹H NMR (600 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.23 (s, 1H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* =

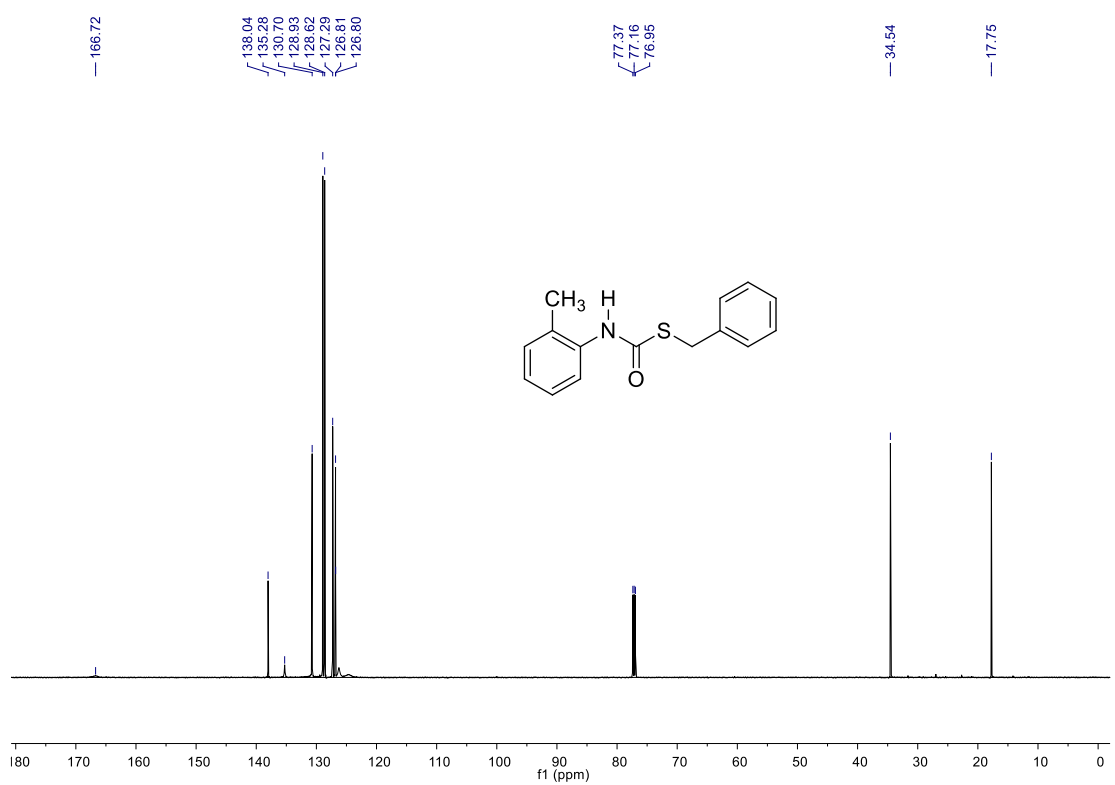
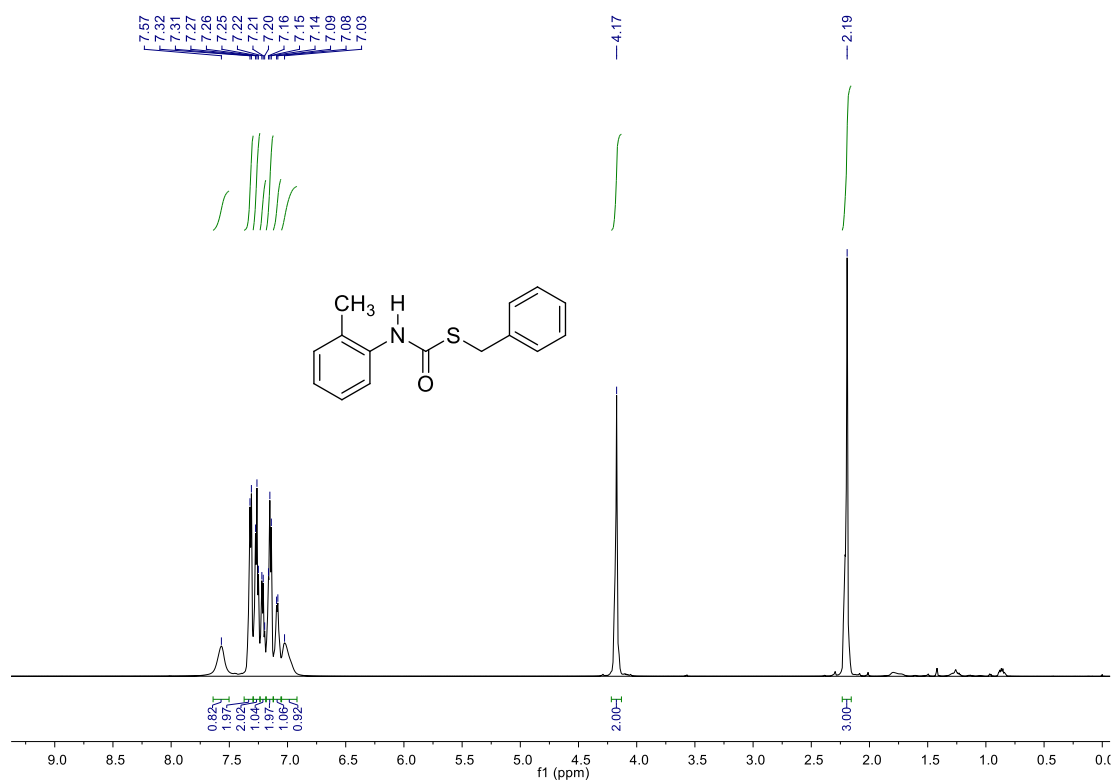
8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.70, 161.37, 137.50, 136.31, 129.58, 129.17, 120.84, 118.43, 115.38, 55.55. HRMS (ESI, *m/z*) calcd for $\text{C}_{14}\text{H}_{13}\text{ClNO}_2\text{S}^+$: 294.0350, found: 294.0348. Mp: 125-126 °C.



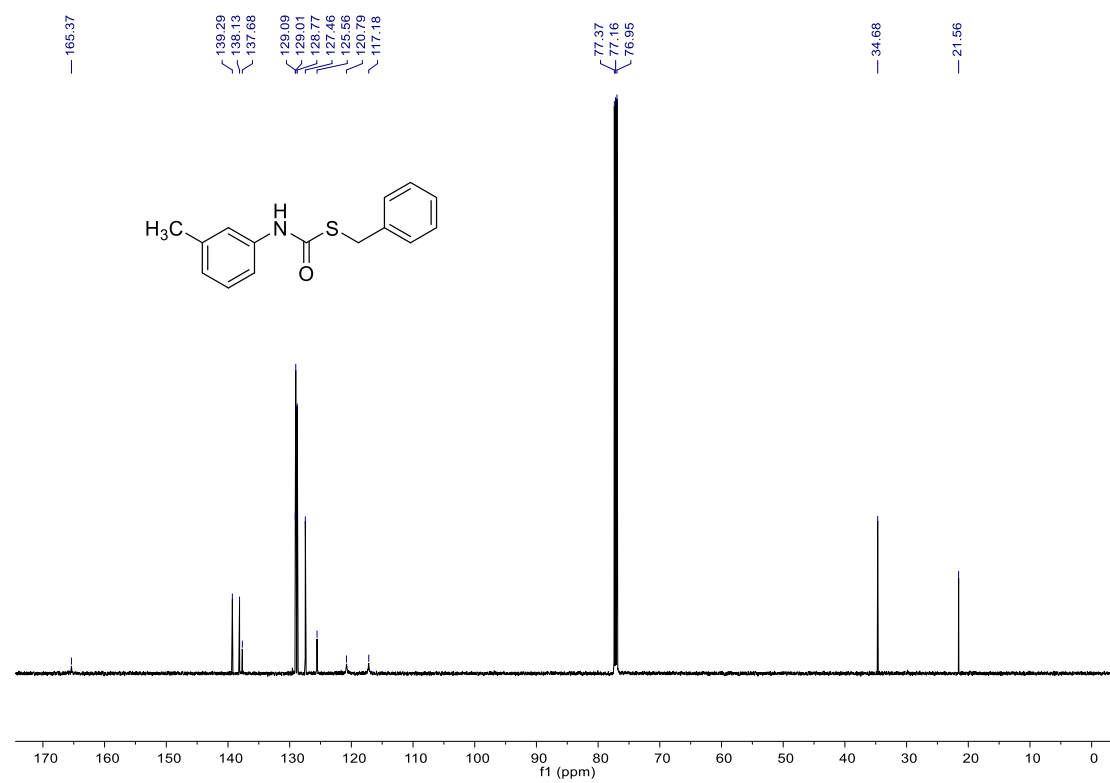
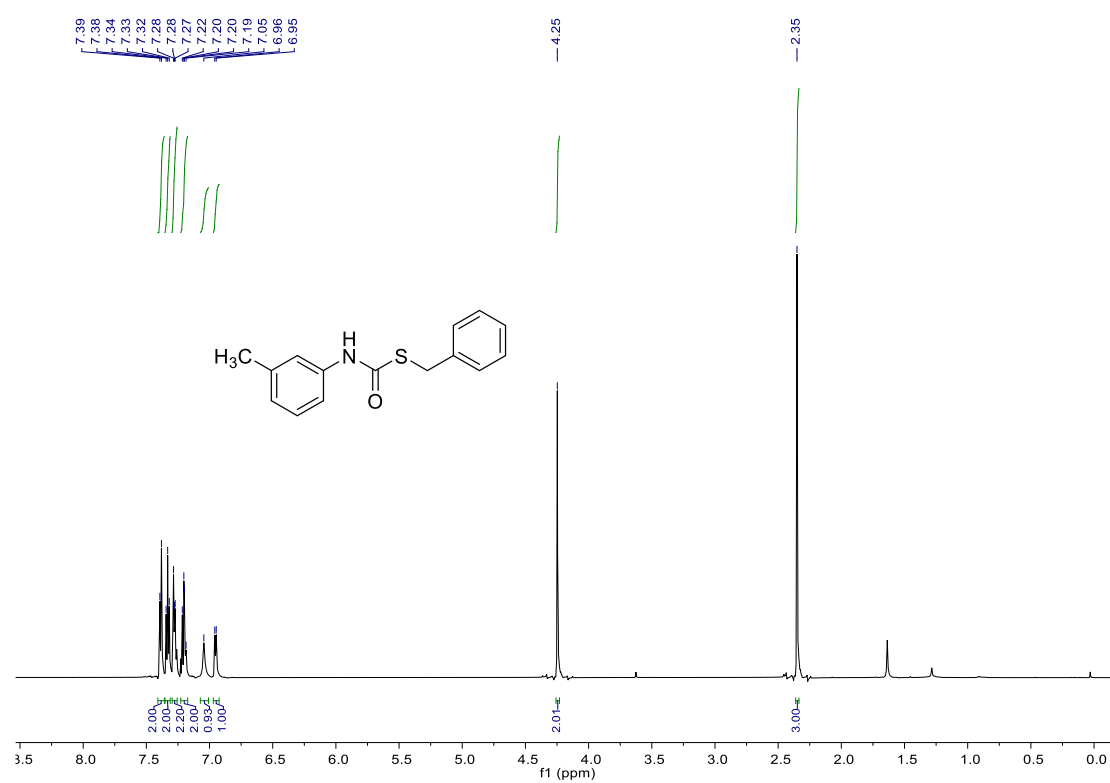
S-(*p*-tolyl) (4-chlorophenyl)carbamothioate (**2w**)

White solid, yield: 98% (94%). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, $J = 8.1$ Hz, 2H), 7.32-7.29 (m, 2H), 7.24 (dd, $J = 11.7, 7.9$ Hz, 4H), 2.38 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.26, 140.72, 136.30, 135.73, 130.57, 129.62, 129.18, 124.34, 120.87, 21.48. HRMS (ESI, *m/z*) calcd for $\text{C}_{14}\text{H}_{13}\text{ClNOS}^+$: 278.0401, found: 278.0400. Mp: 153-154 °C. IR (cm^{-1}): 3291.3, 1650.7, 1588.9, 1514.4, 1488.3, 1395.7, 1277.3, 1243.3, 1149.6, 1088.5, 1010.4, 898.2, 808.7, 678.4.

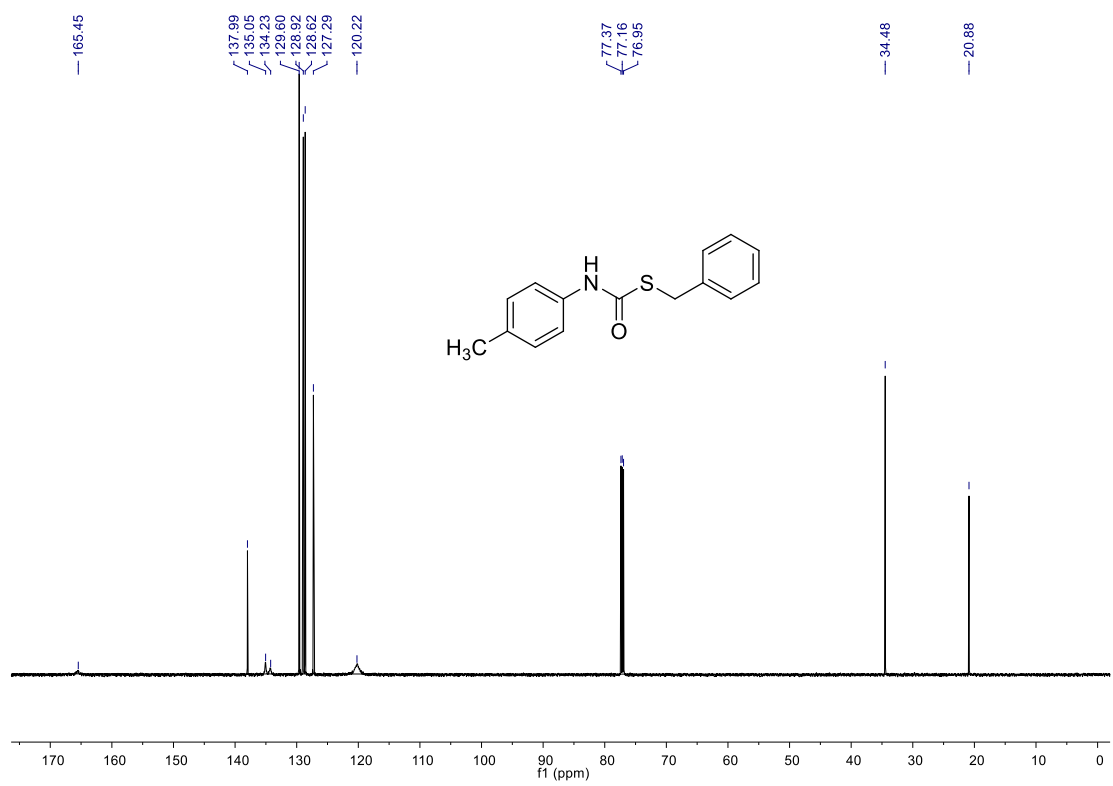
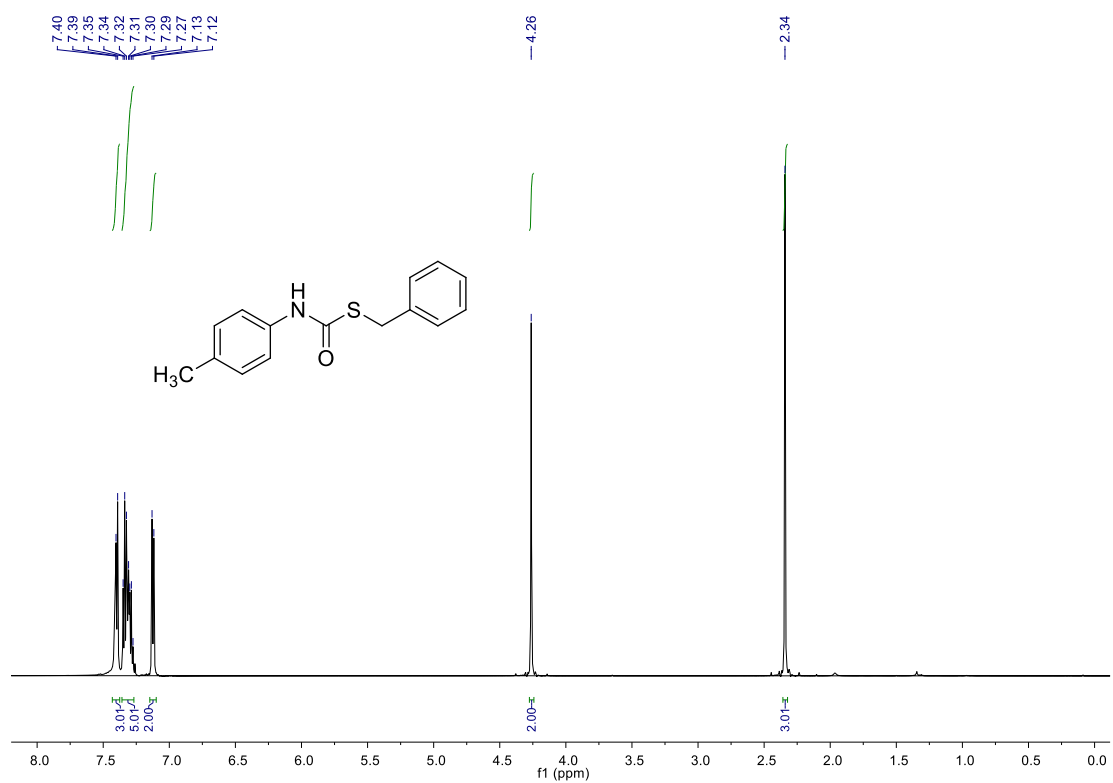
^1H NMR and ^{13}C NMR spectra for thiocarbamates



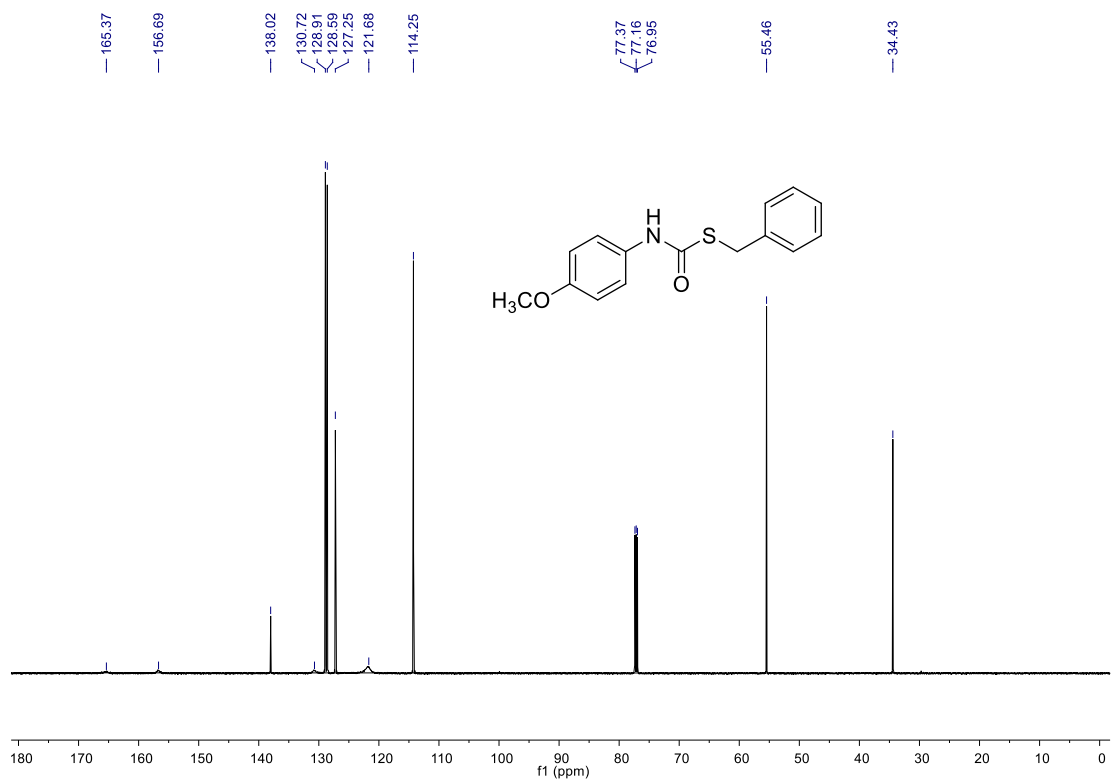
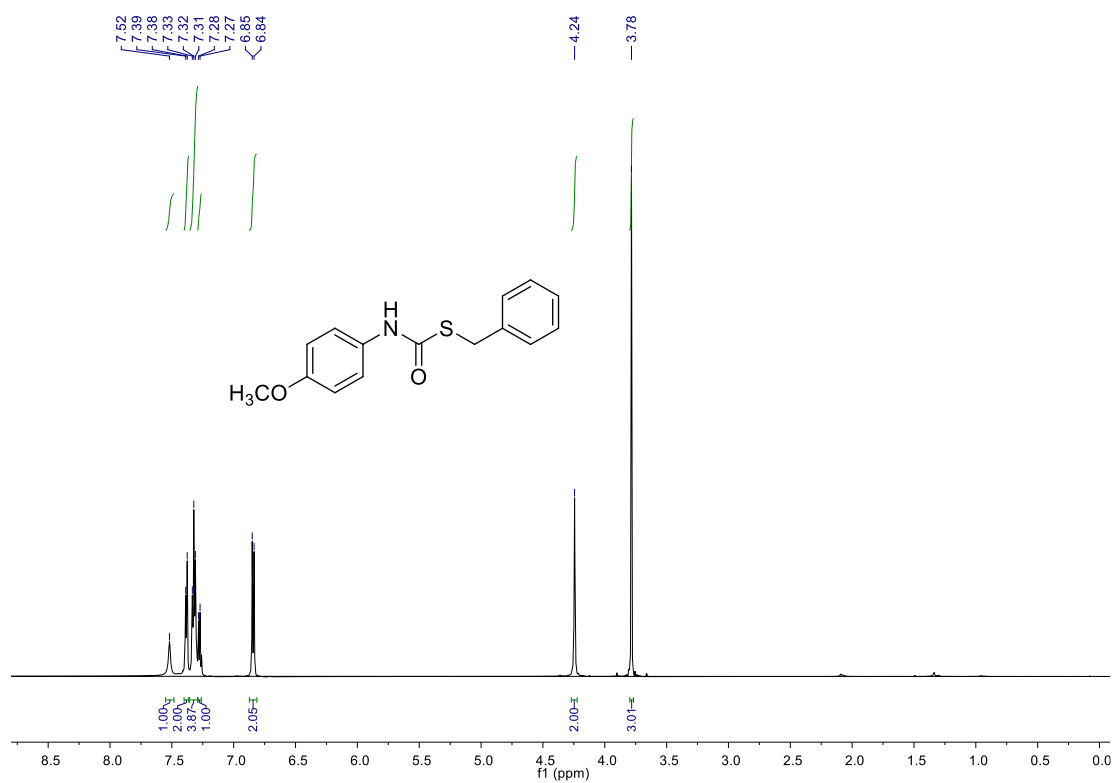
^1H and ^{13}C NMR Spectra of **2a**



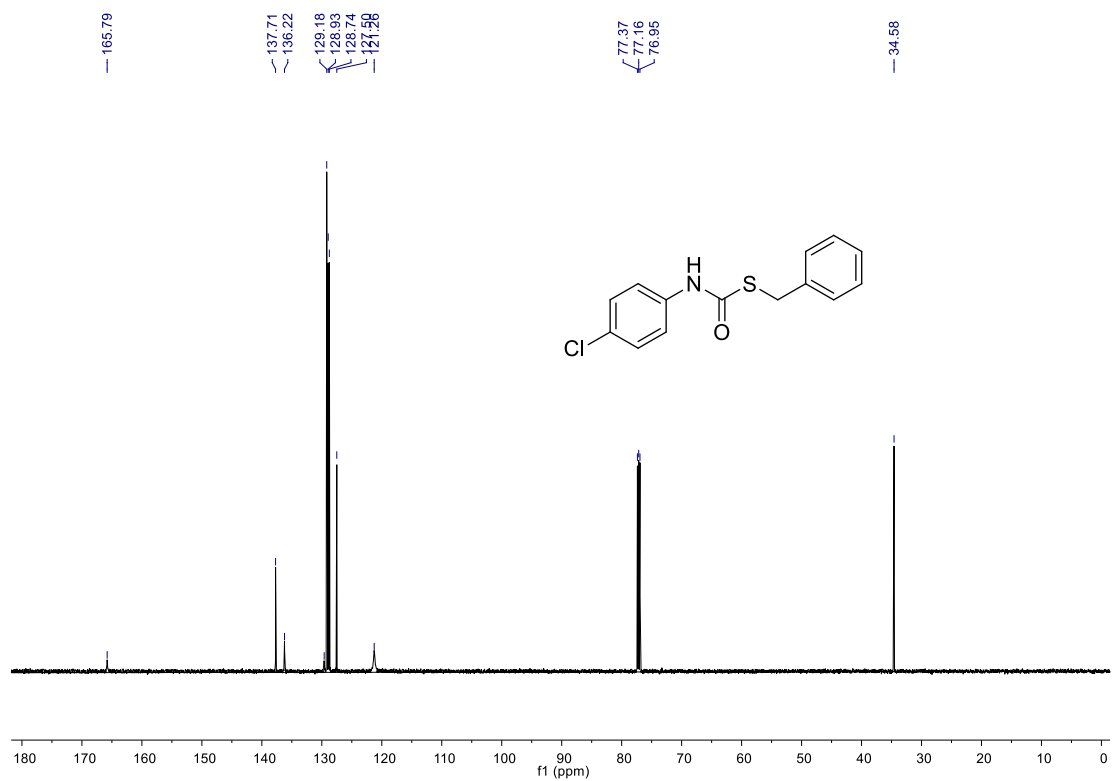
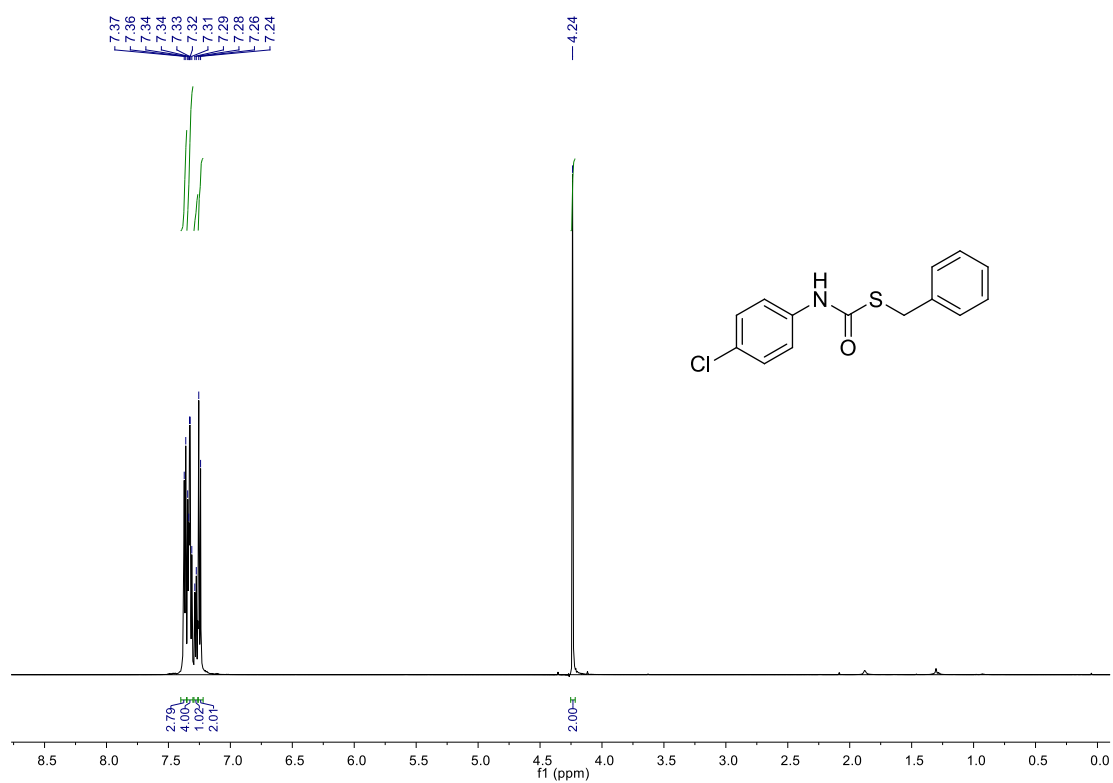
¹H and ¹³C NMR Spectra of **2b**



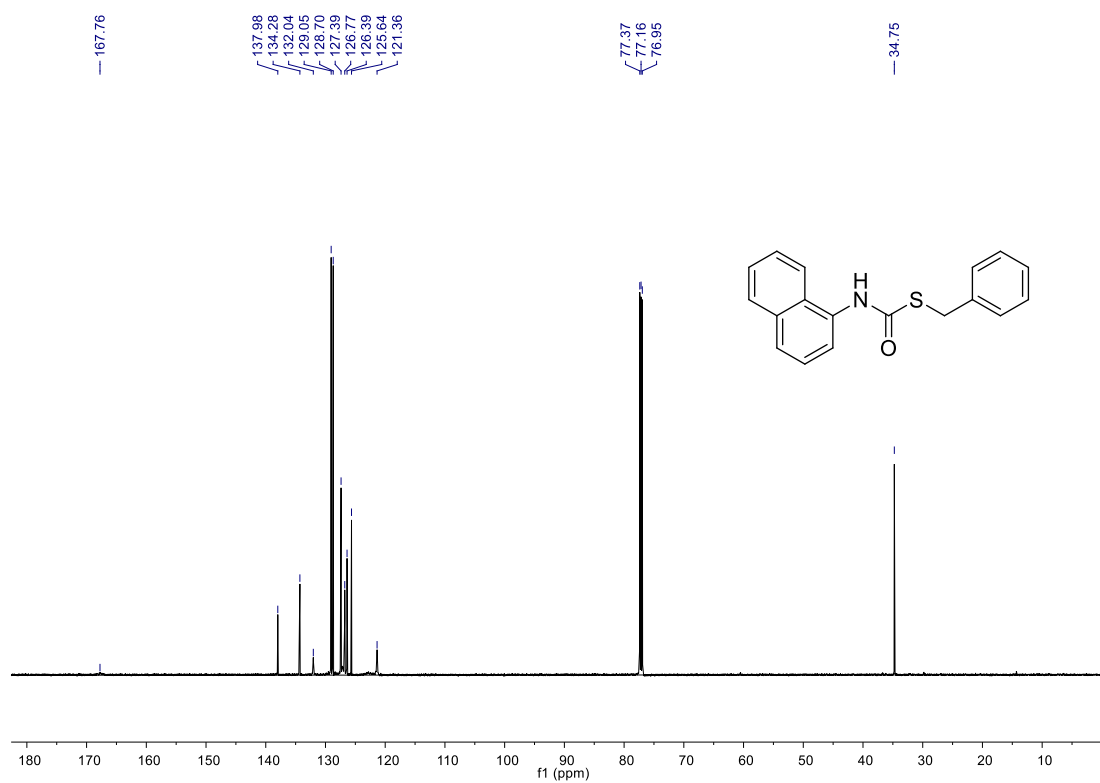
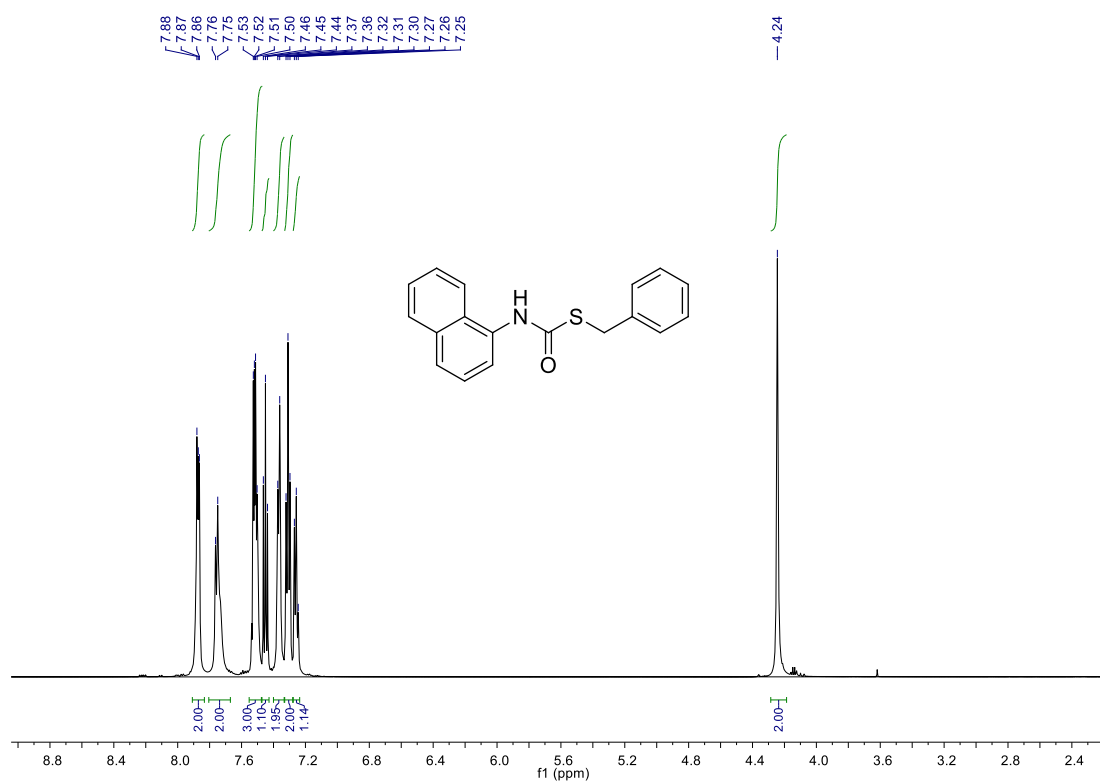
¹H and ¹³C NMR Spectra of 2c



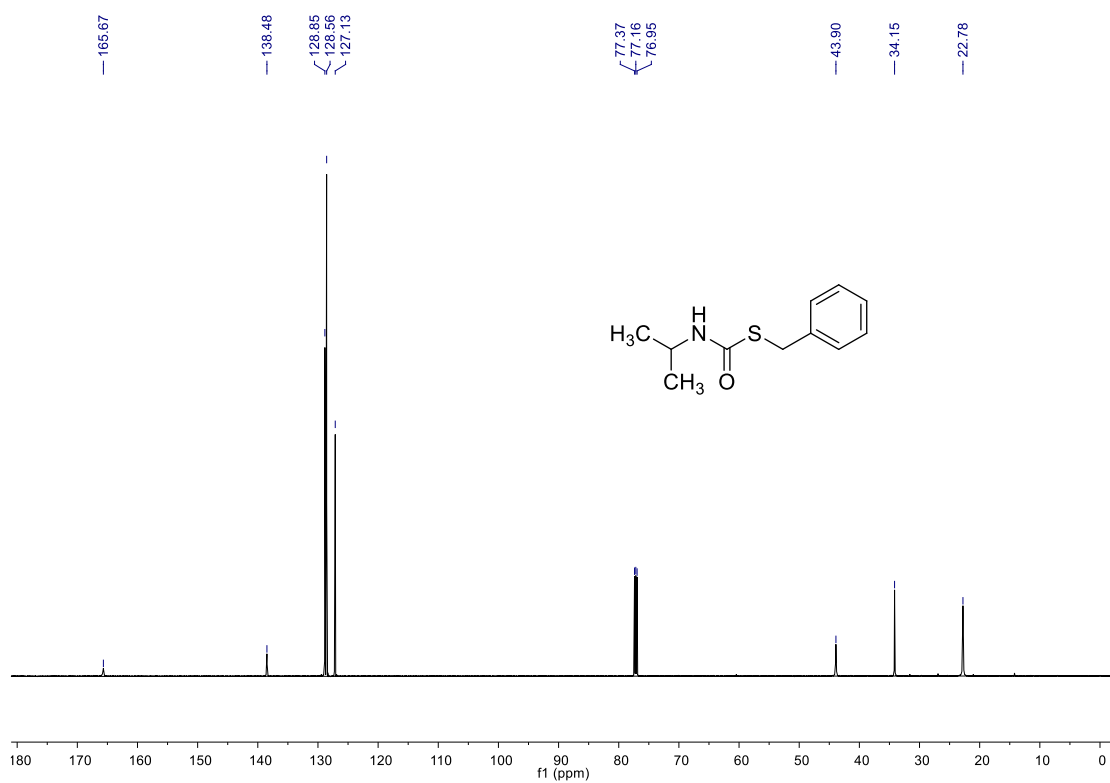
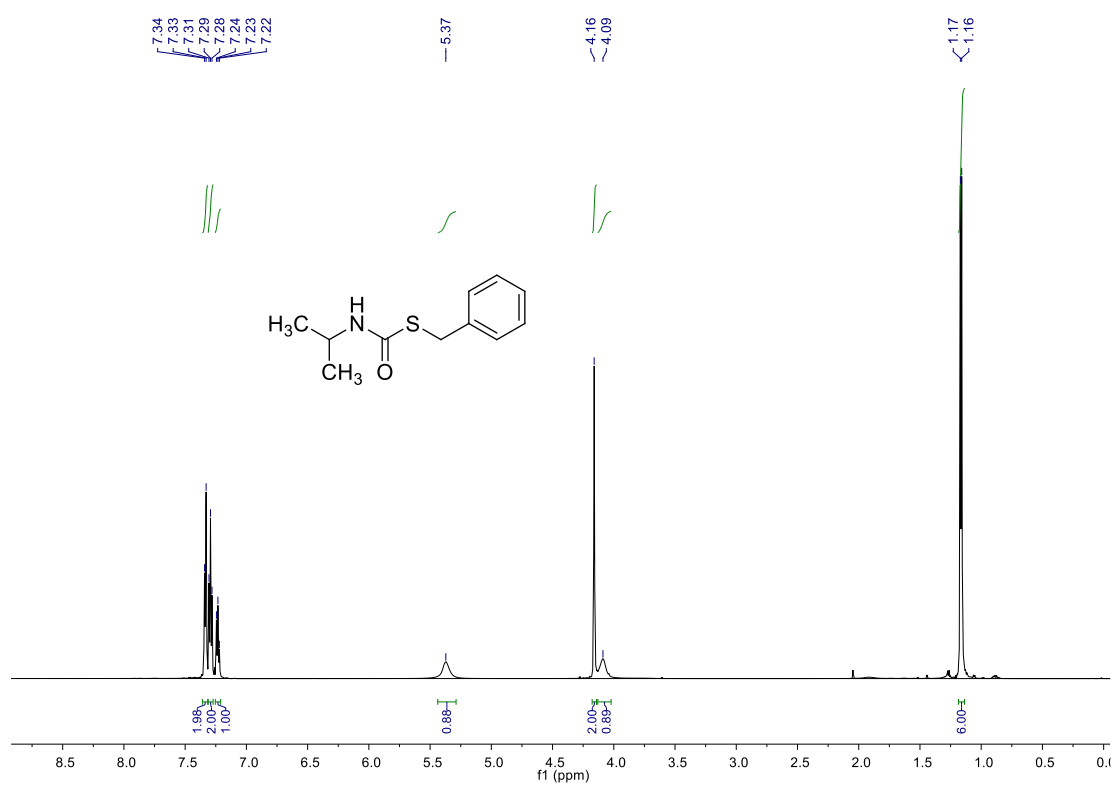
¹H and ¹³C NMR Spectra of **2d**



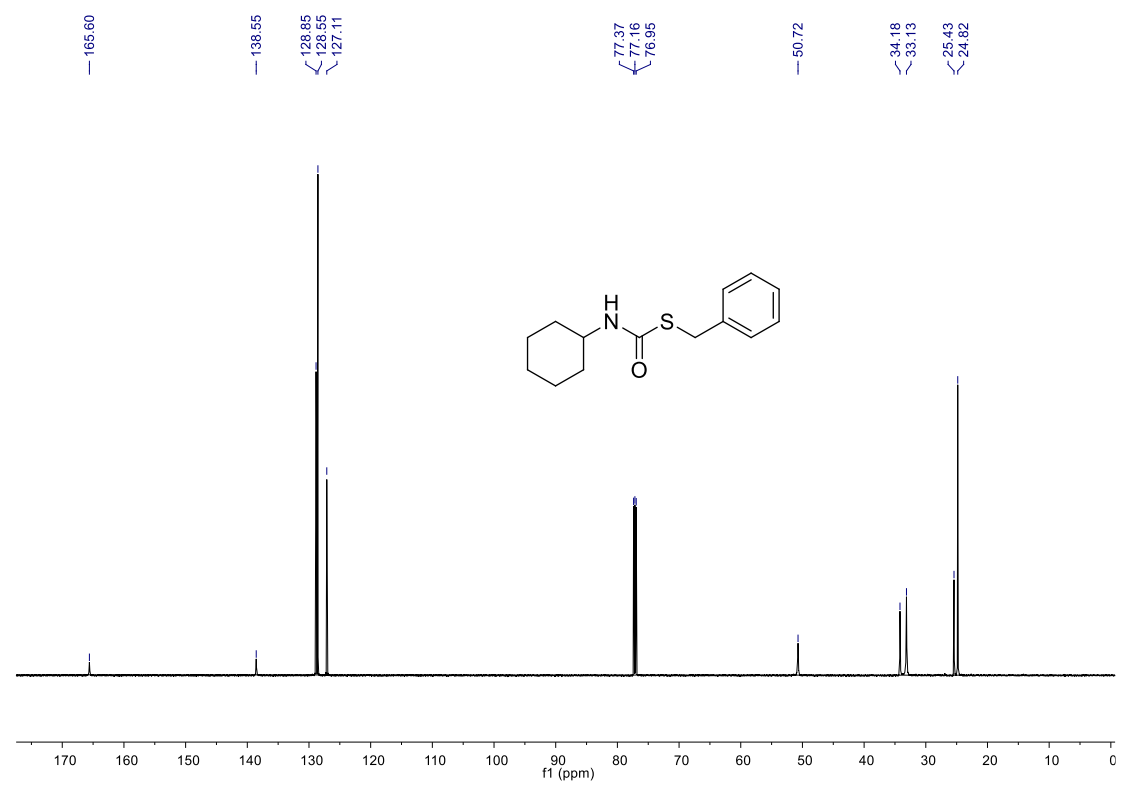
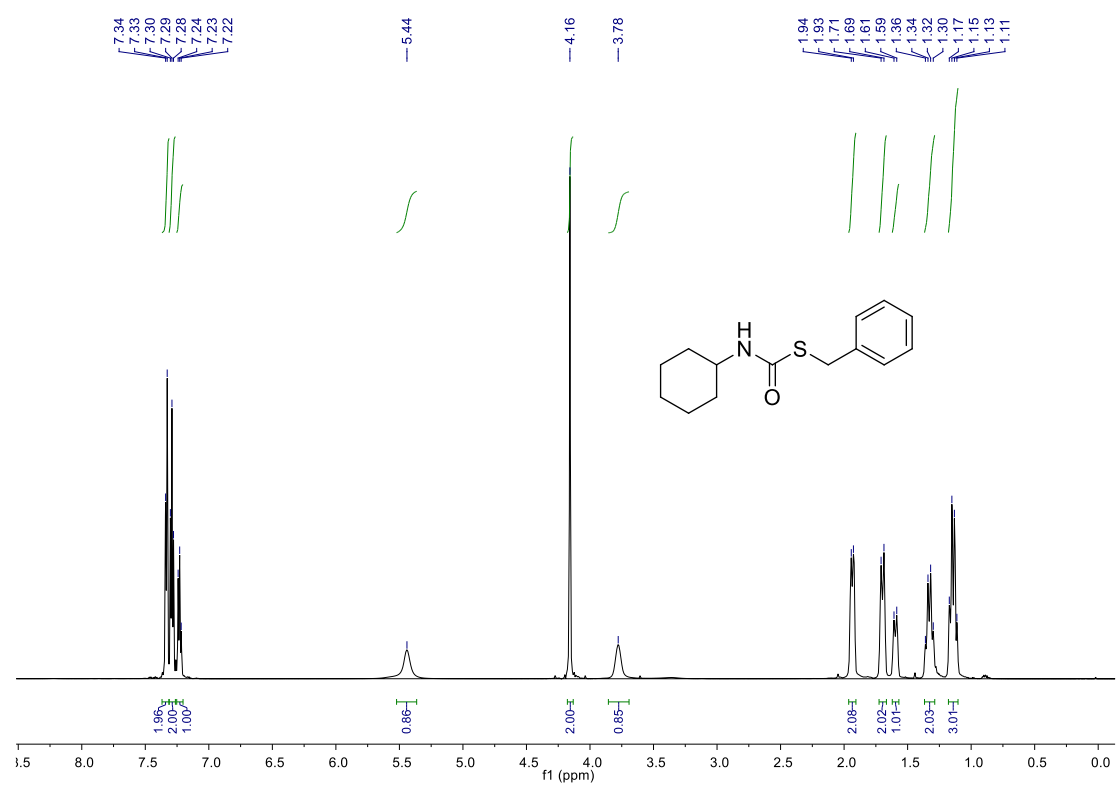
¹H and ¹³C NMR Spectra of 2e



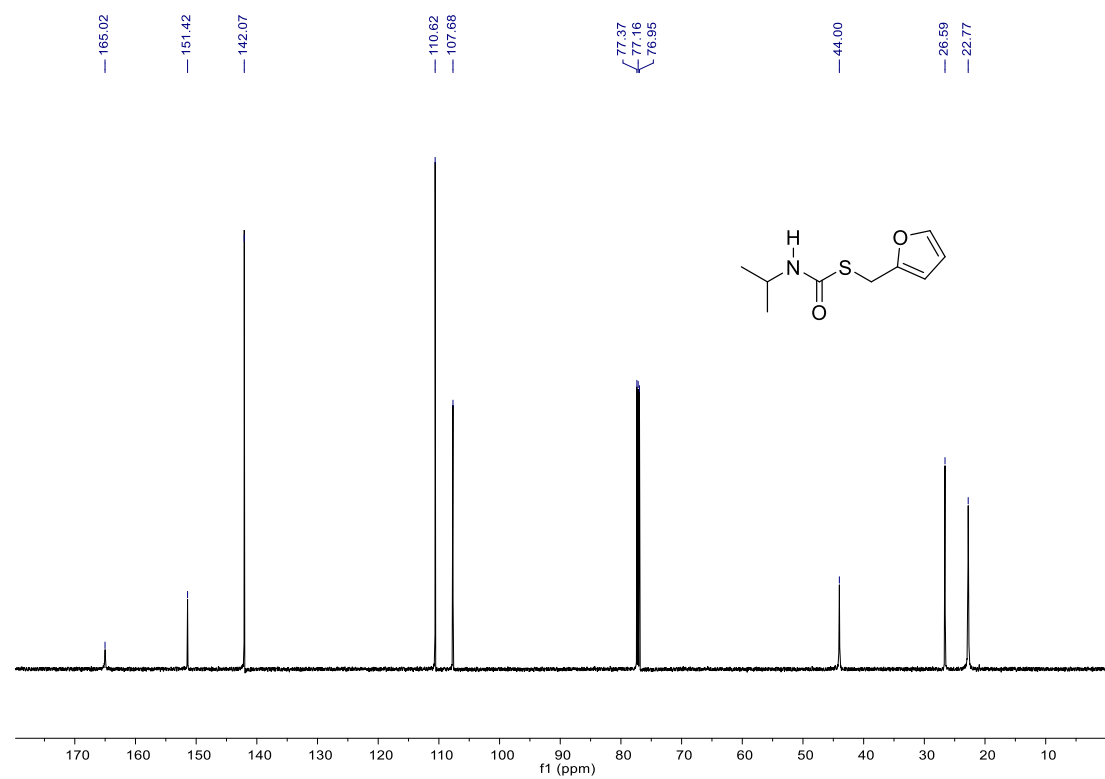
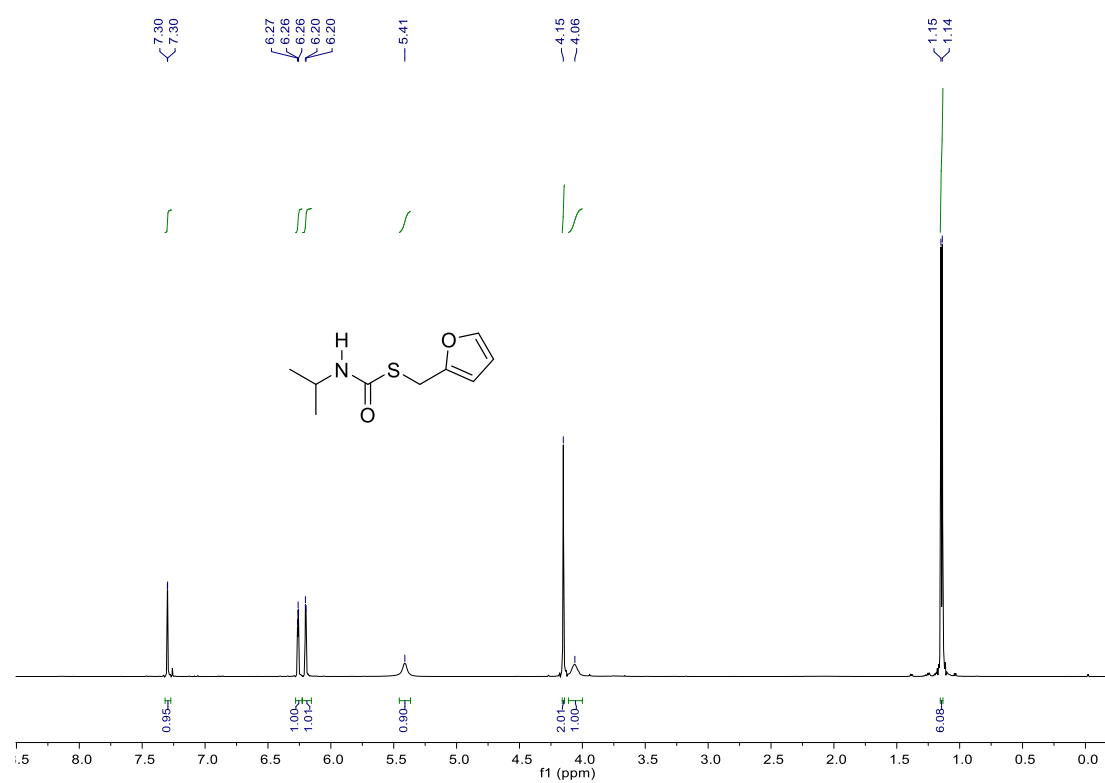
^1H and ^{13}C NMR Spectra of **2f**



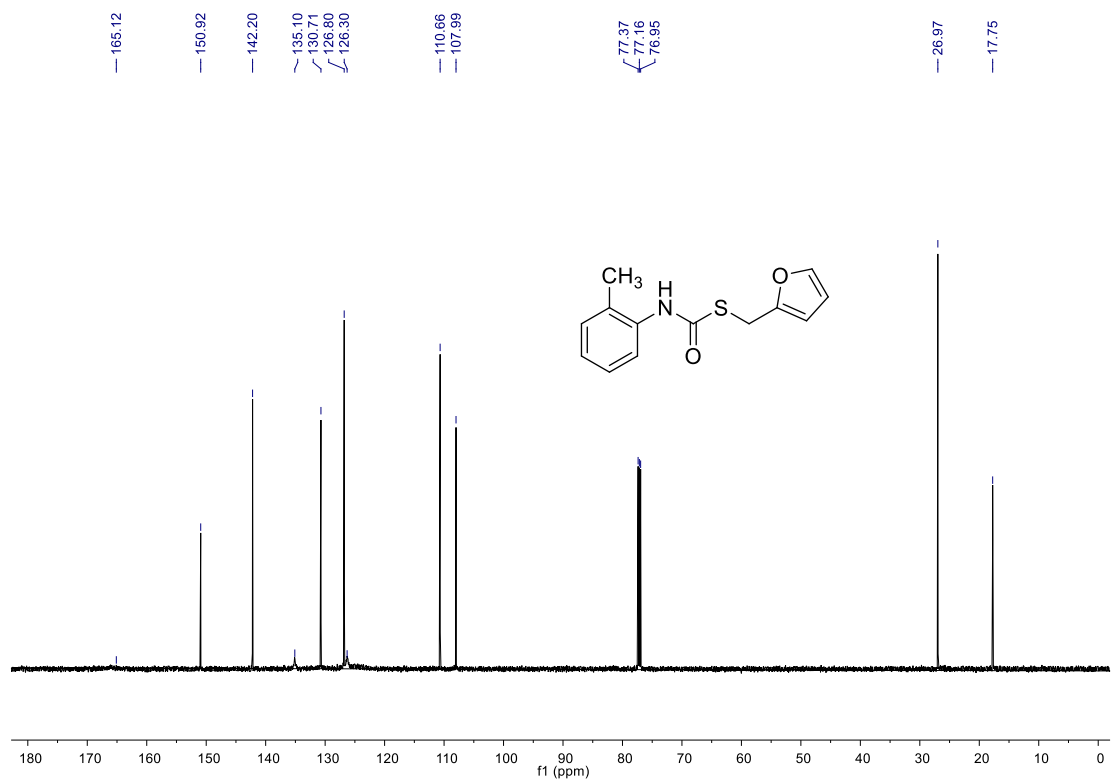
¹H and ¹³C NMR Spectra of **2g**



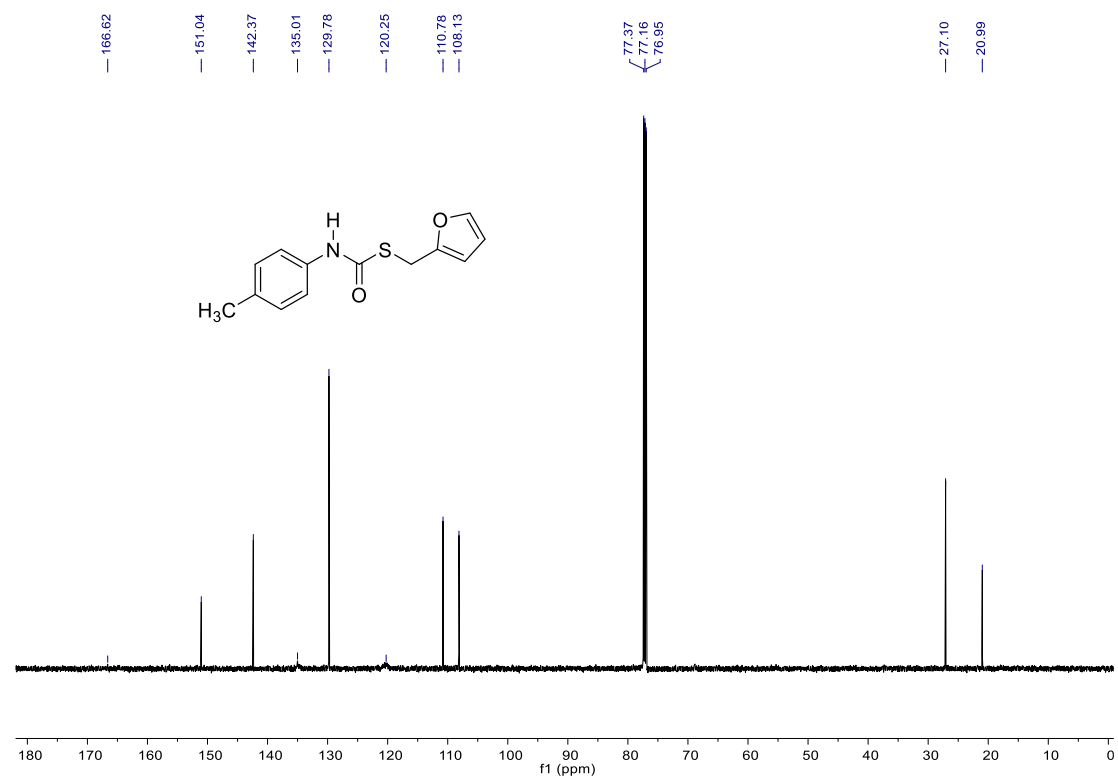
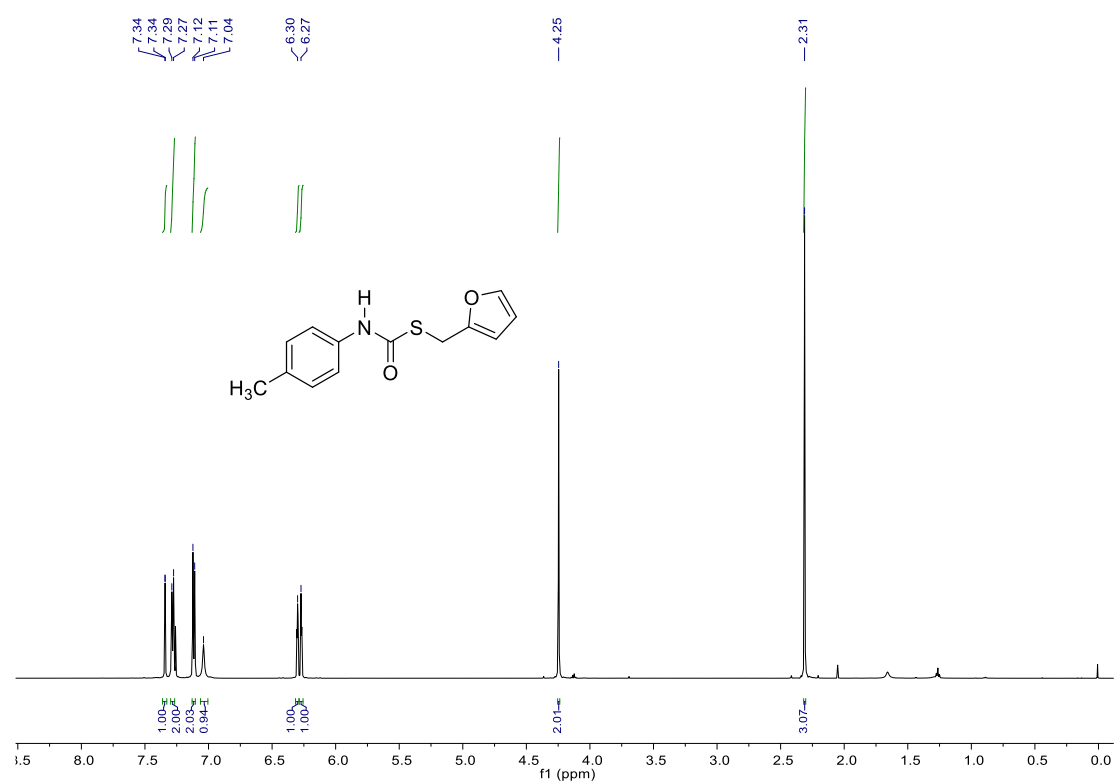
¹H and ¹³C NMR Spectra of 2h



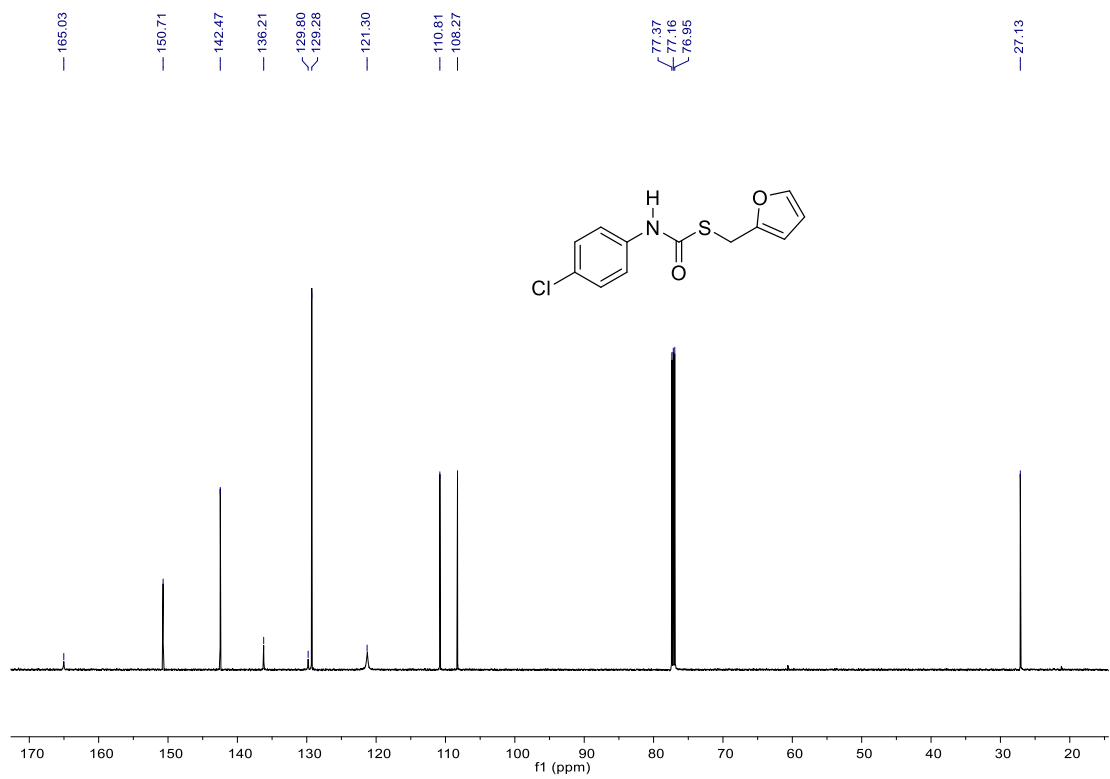
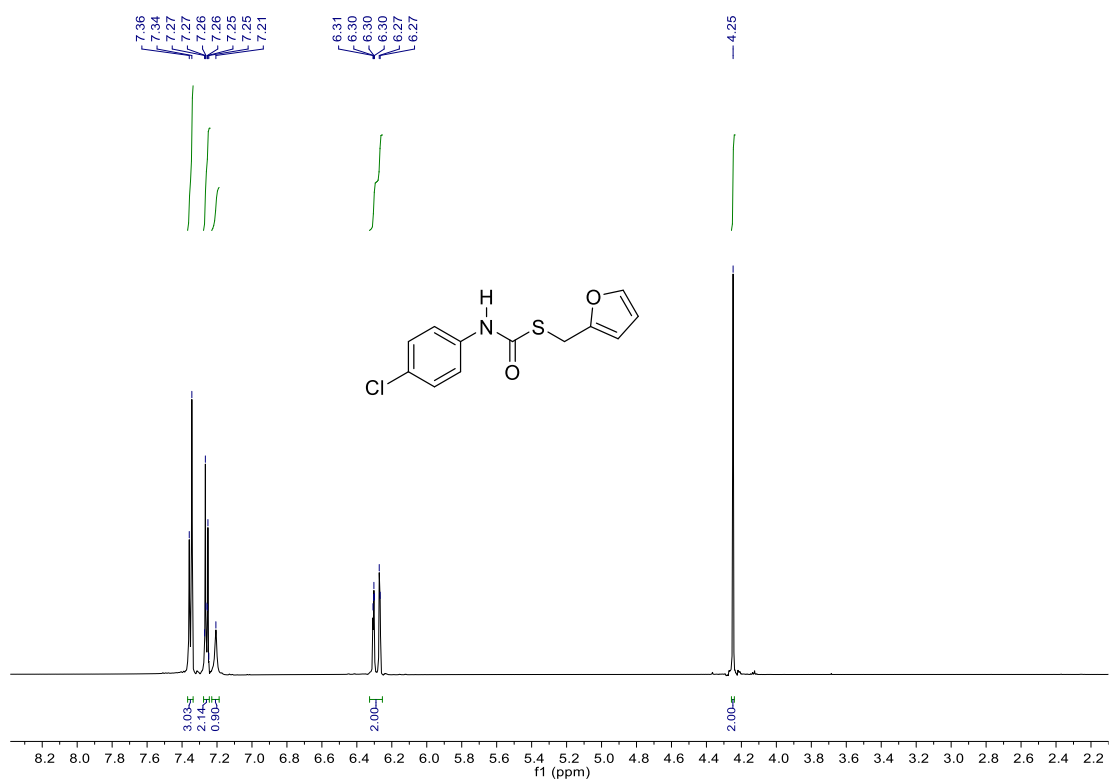
¹H and ¹³C NMR Spectra of **2i**



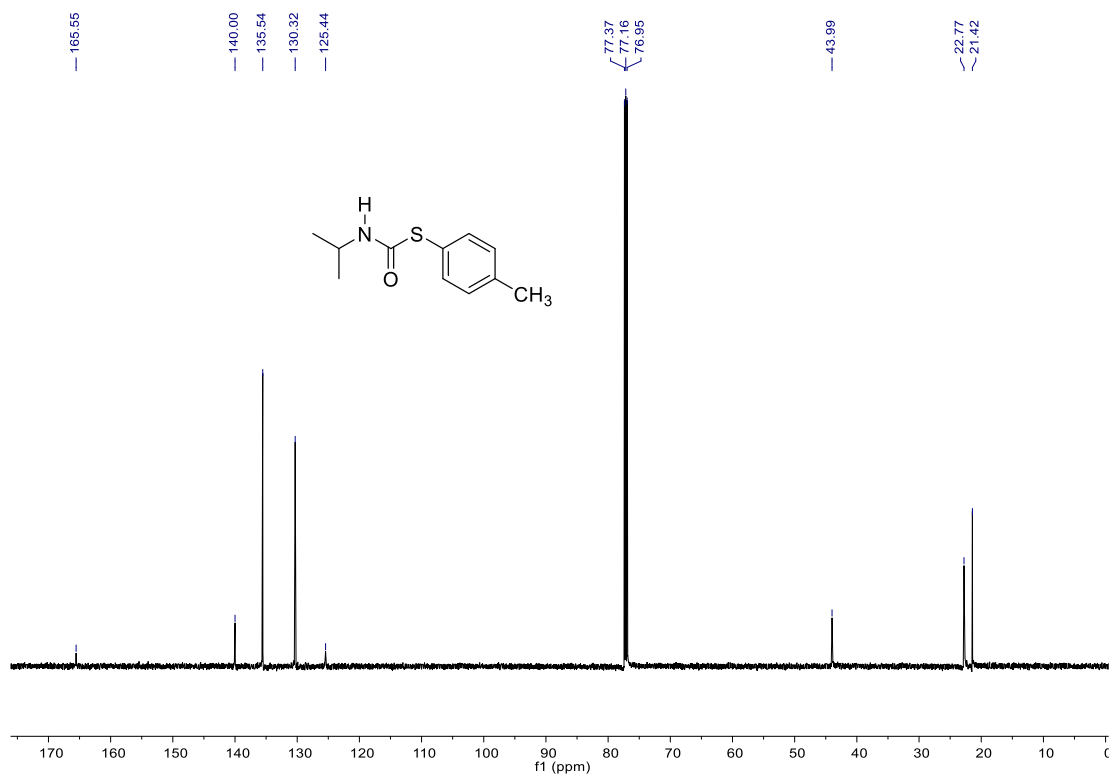
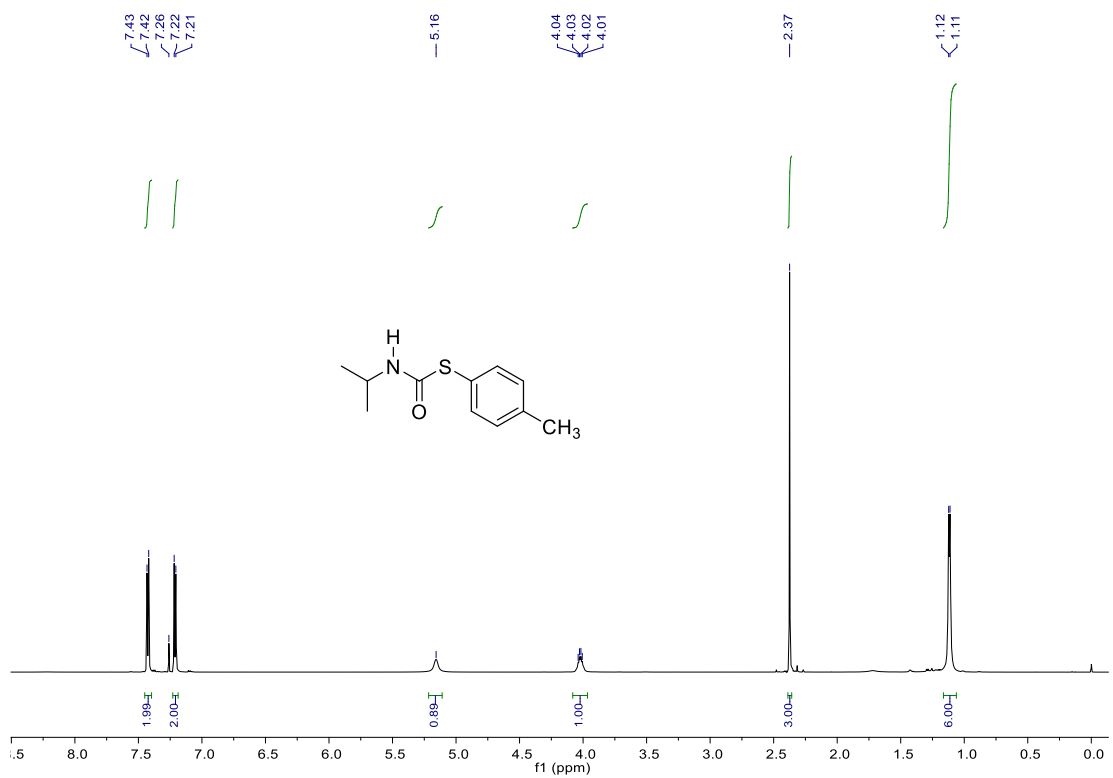
¹H and ¹³C NMR Spectra of **2j**



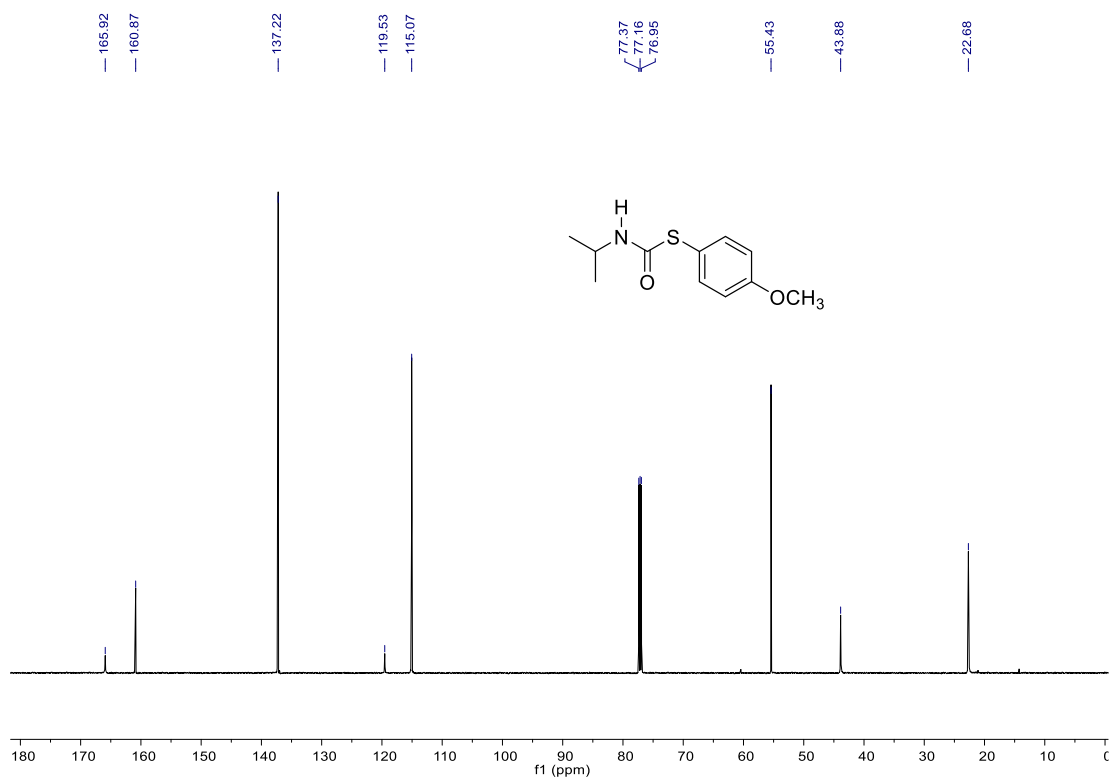
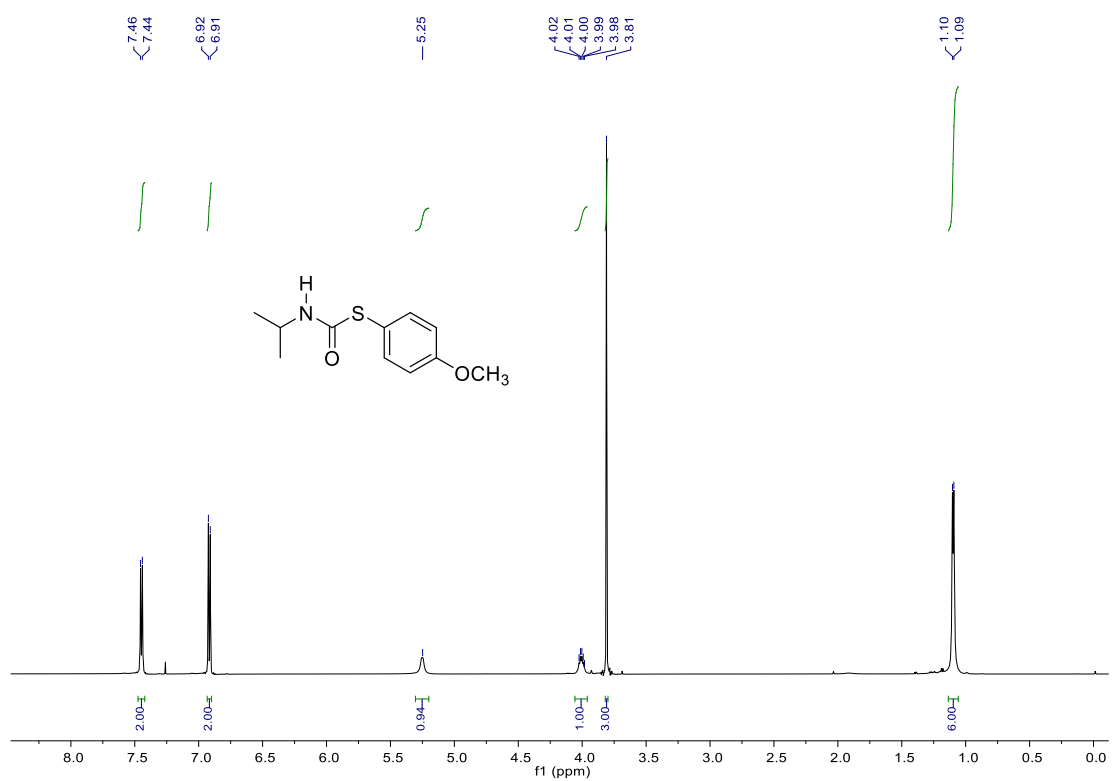
¹H and ¹³C NMR Spectra of **2k**



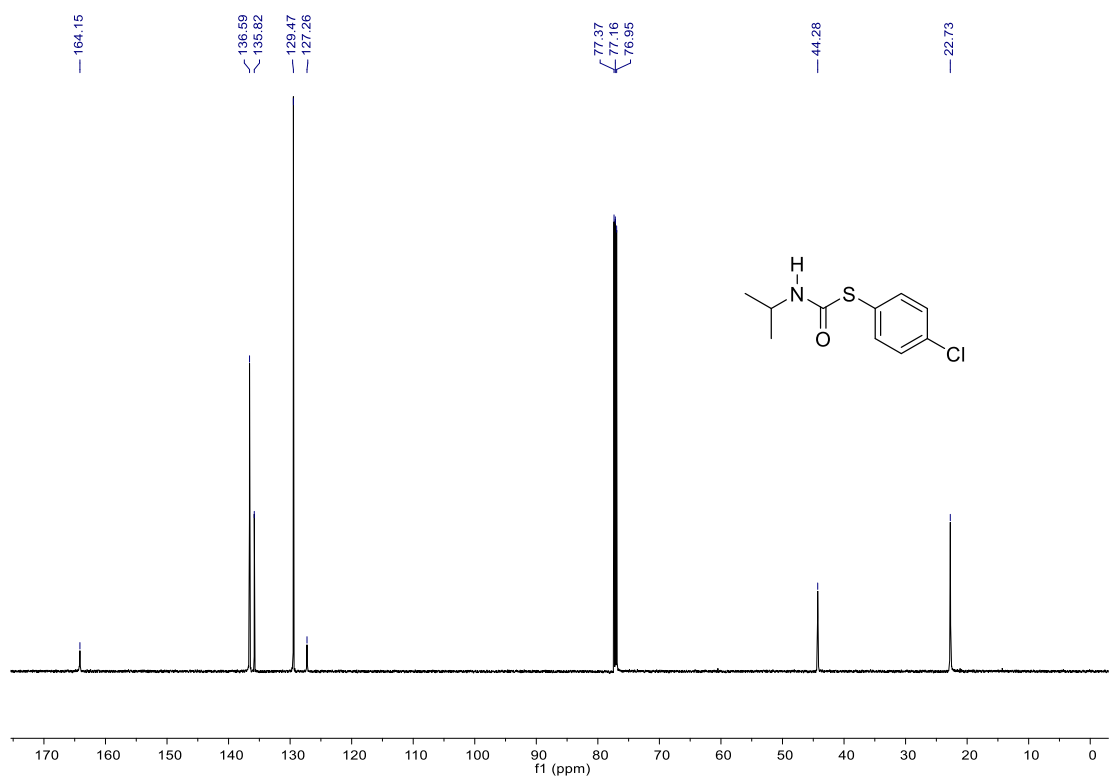
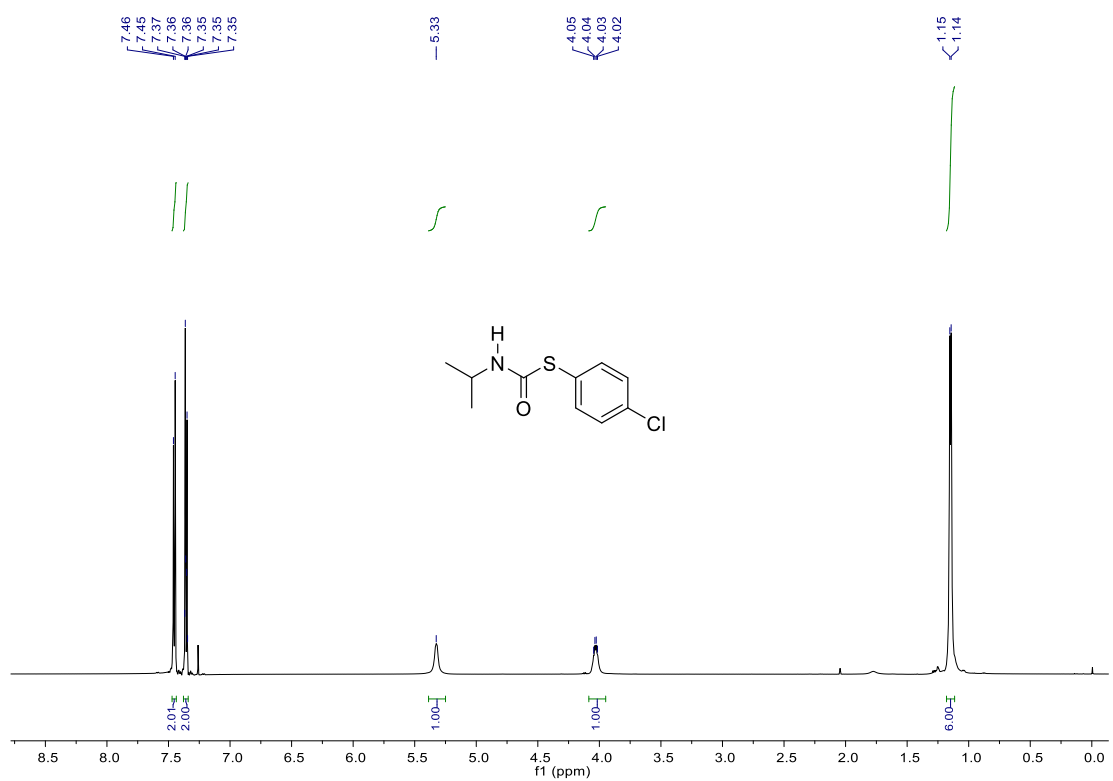
^1H and ^{13}C NMR Spectra of **21**



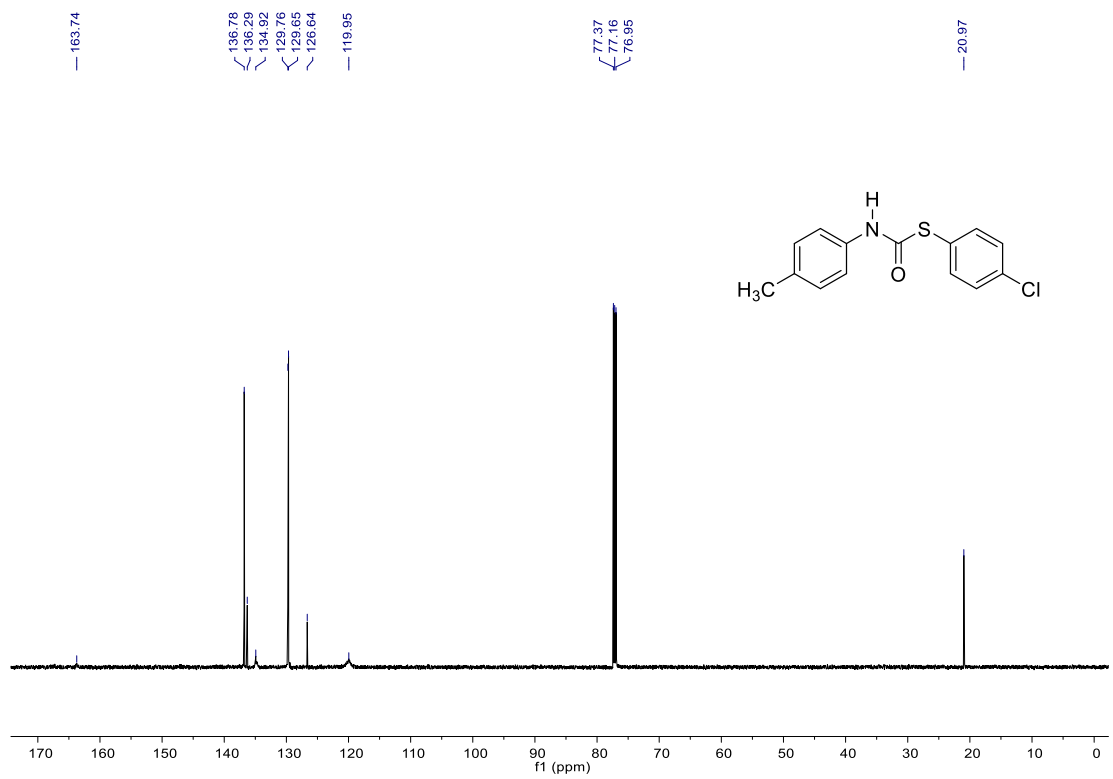
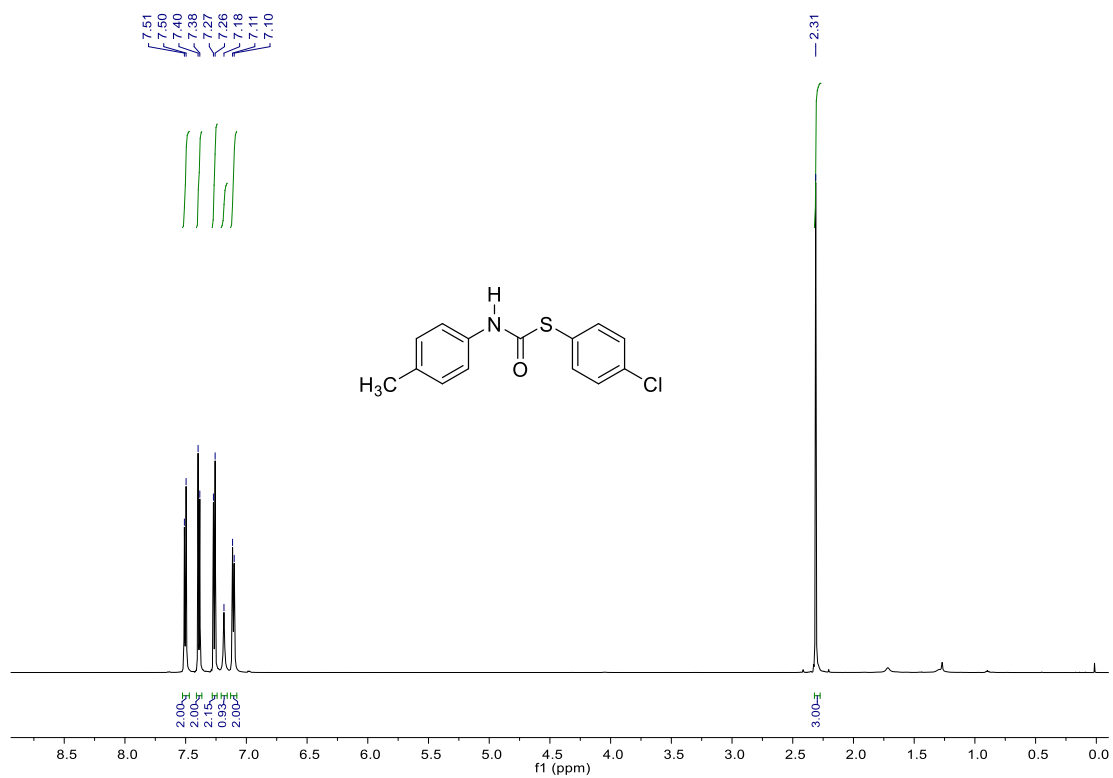
¹H and ¹³C NMR Spectra of **2m**



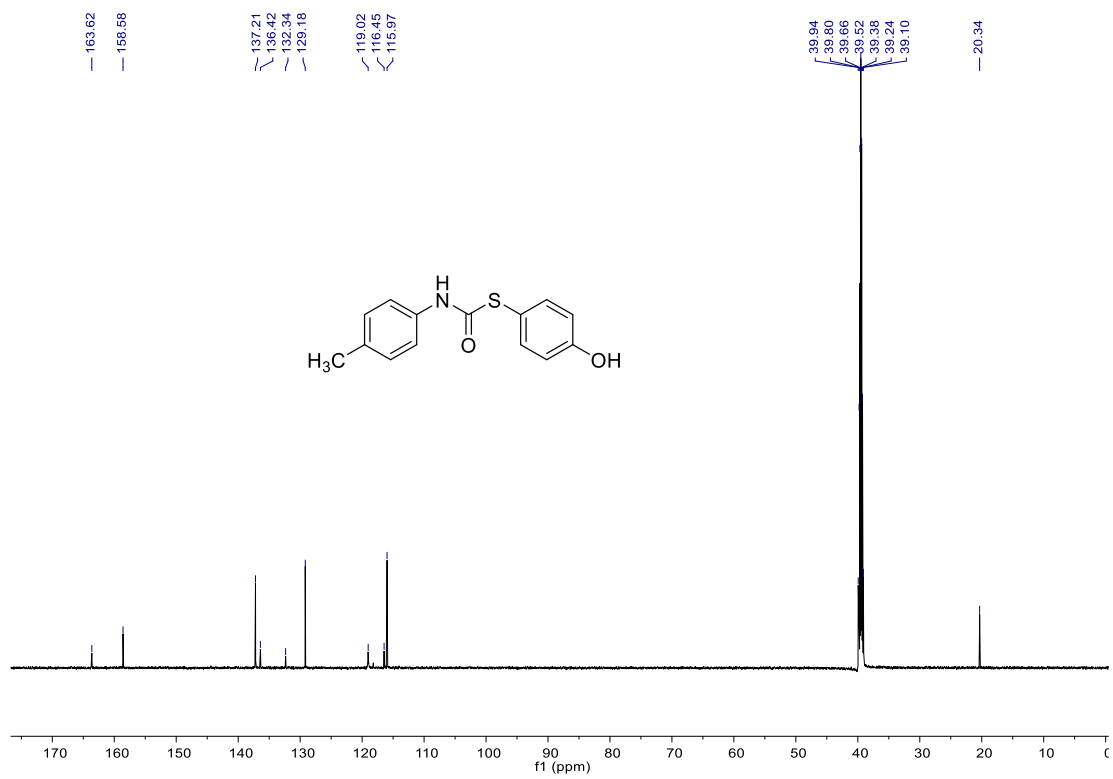
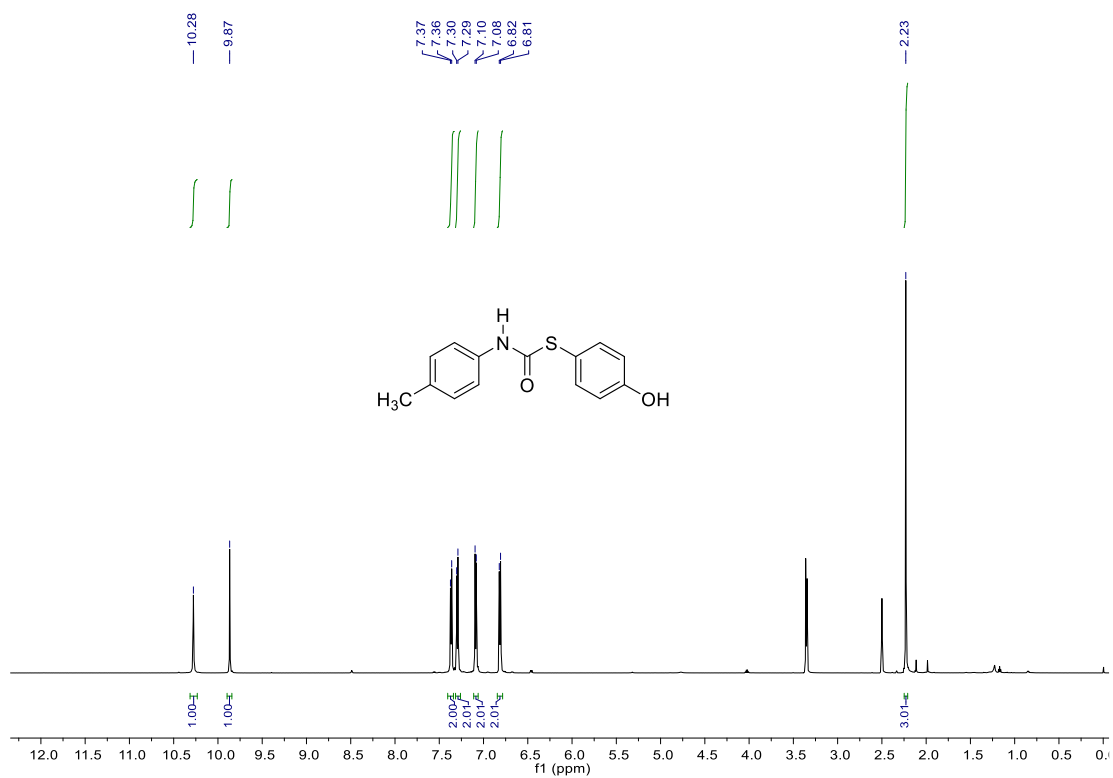
¹H and ¹³C NMR Spectra of **2n**



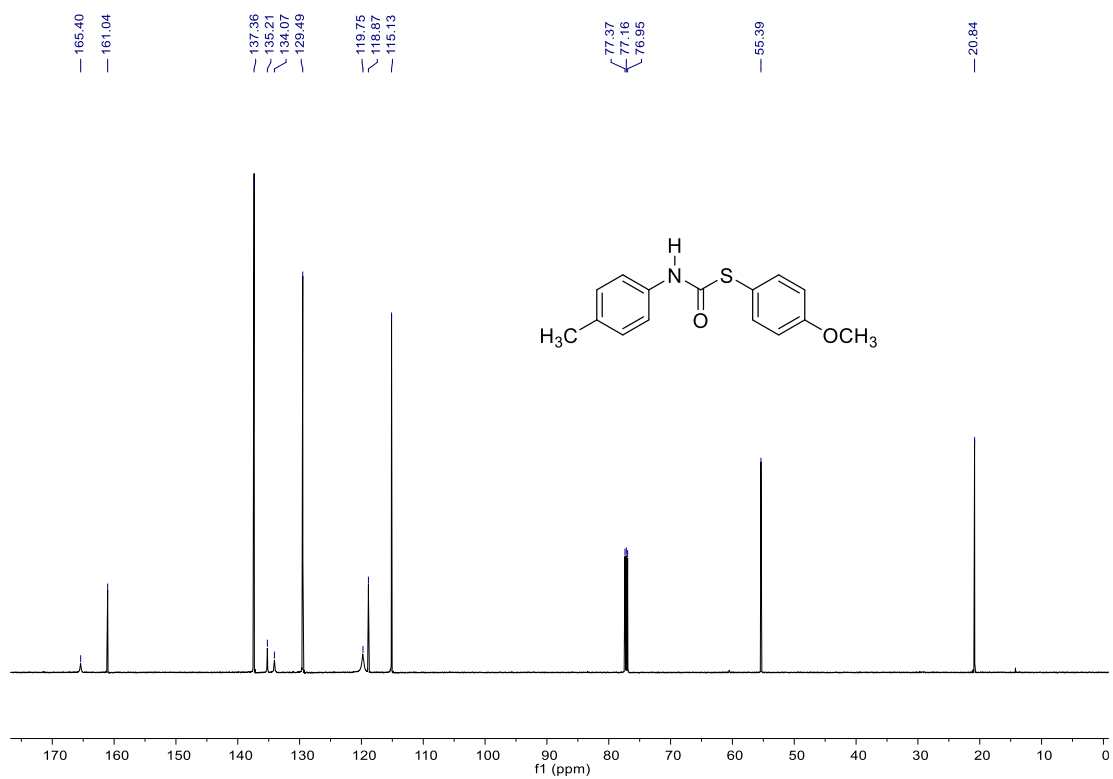
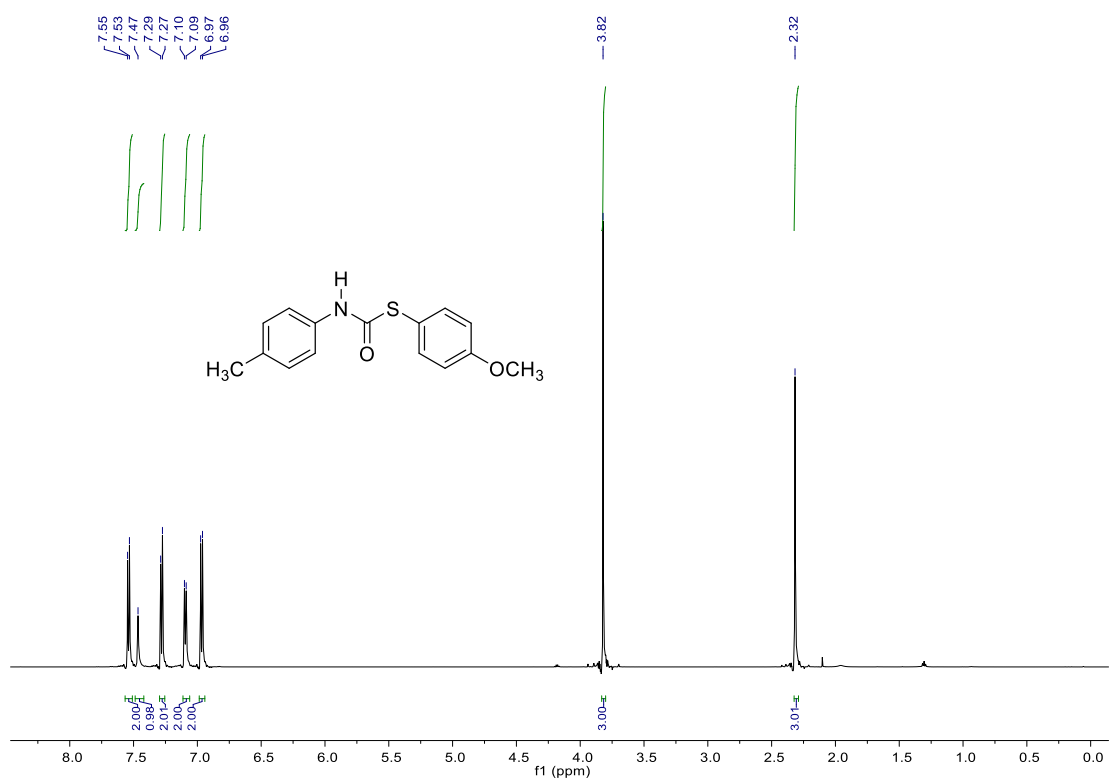
¹H and ¹³C NMR Spectra of 2o



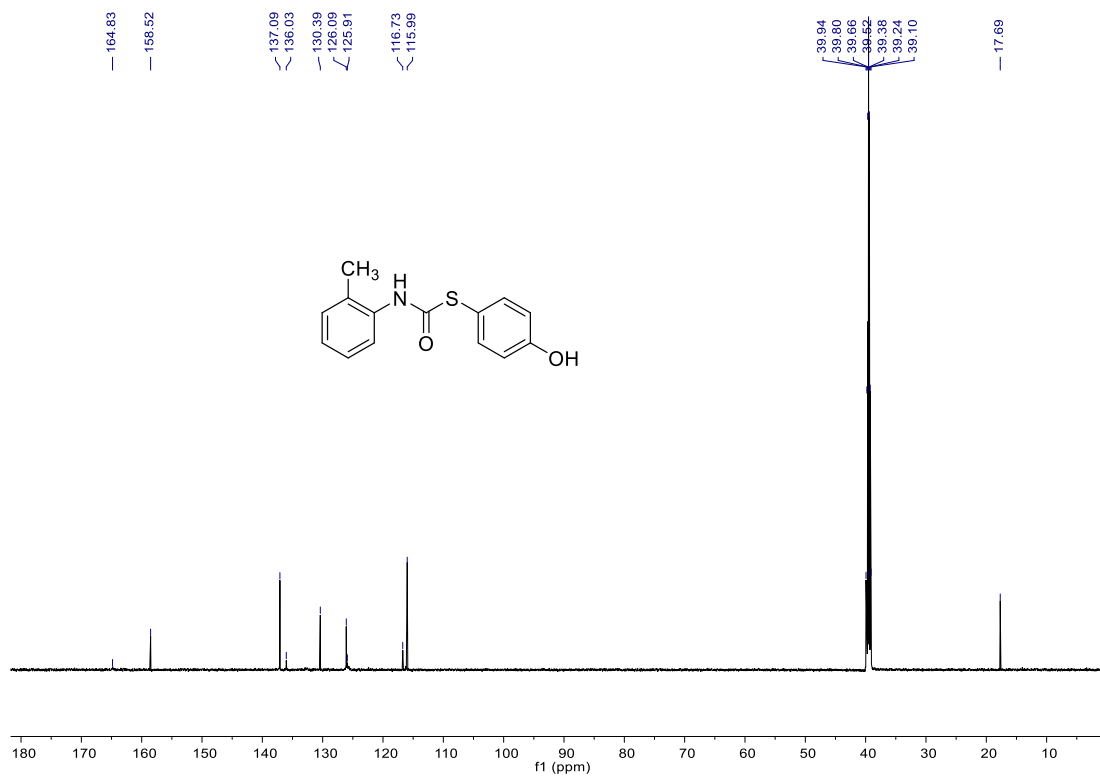
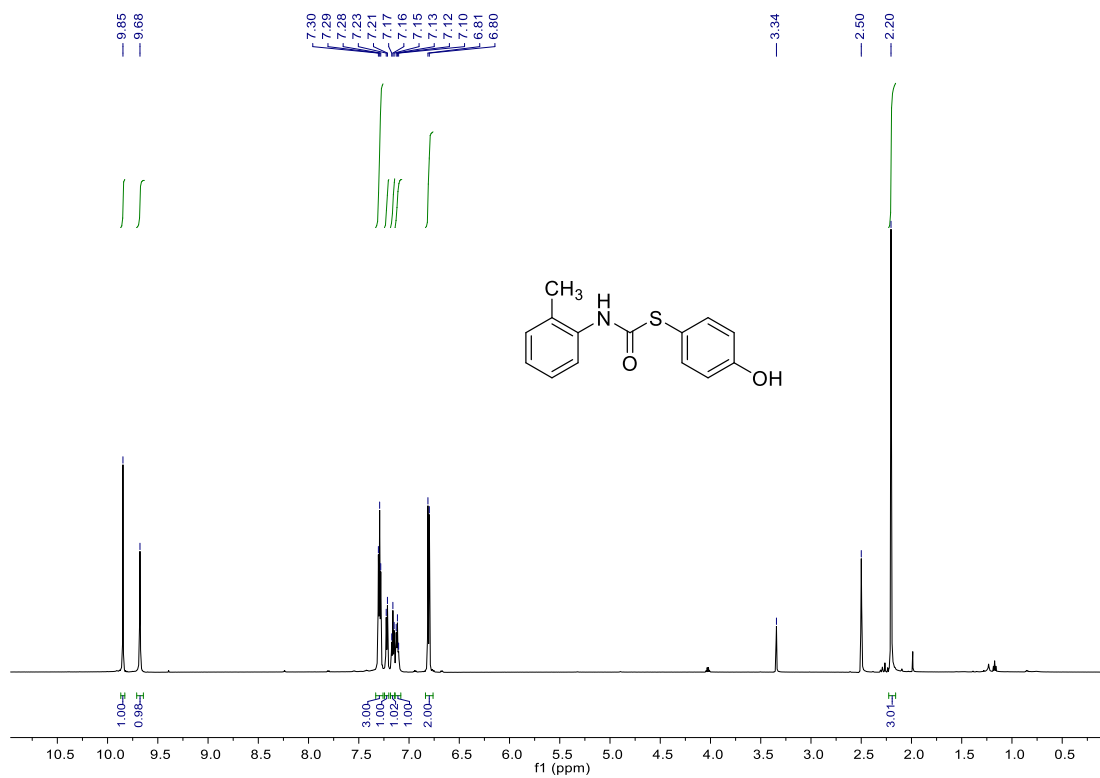
¹H and ¹³C NMR Spectra of **2p**



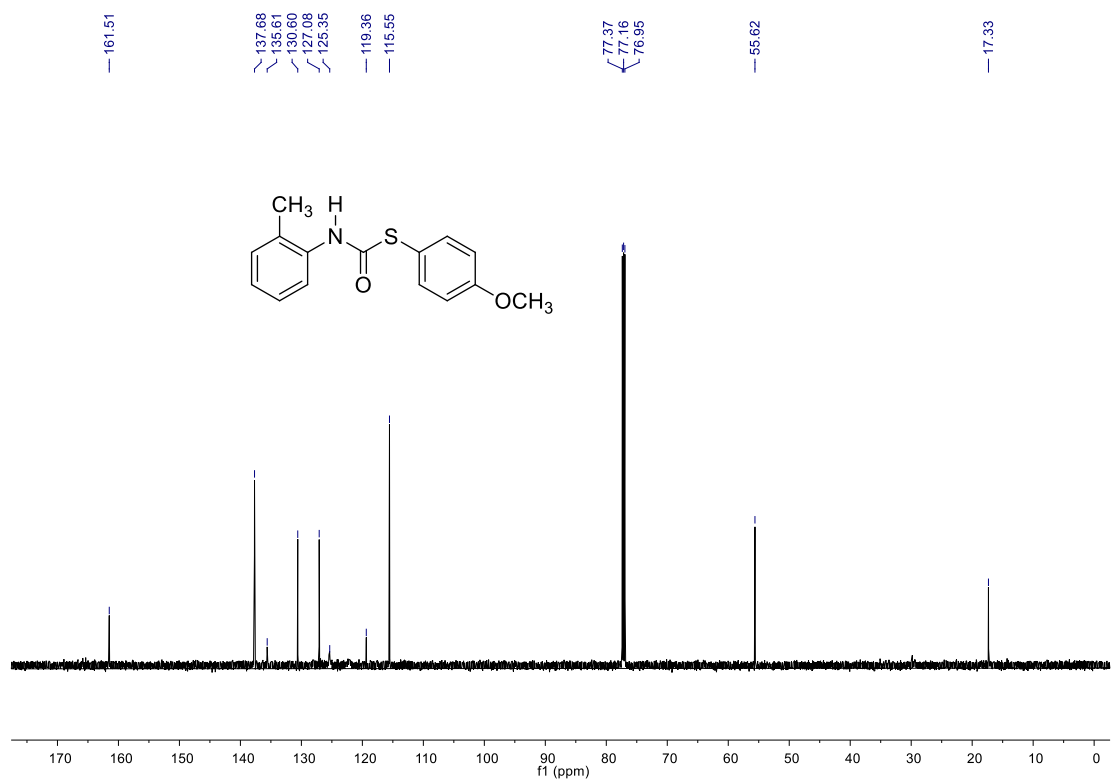
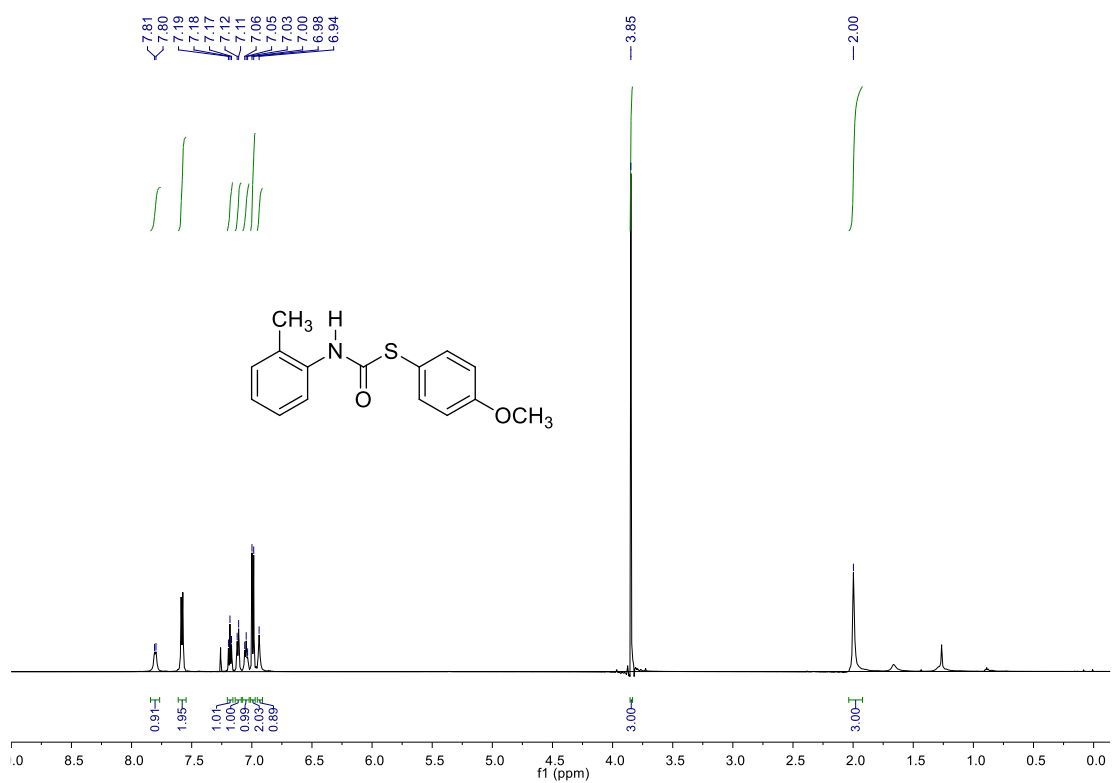
¹H and ¹³C NMR Spectra of 2q



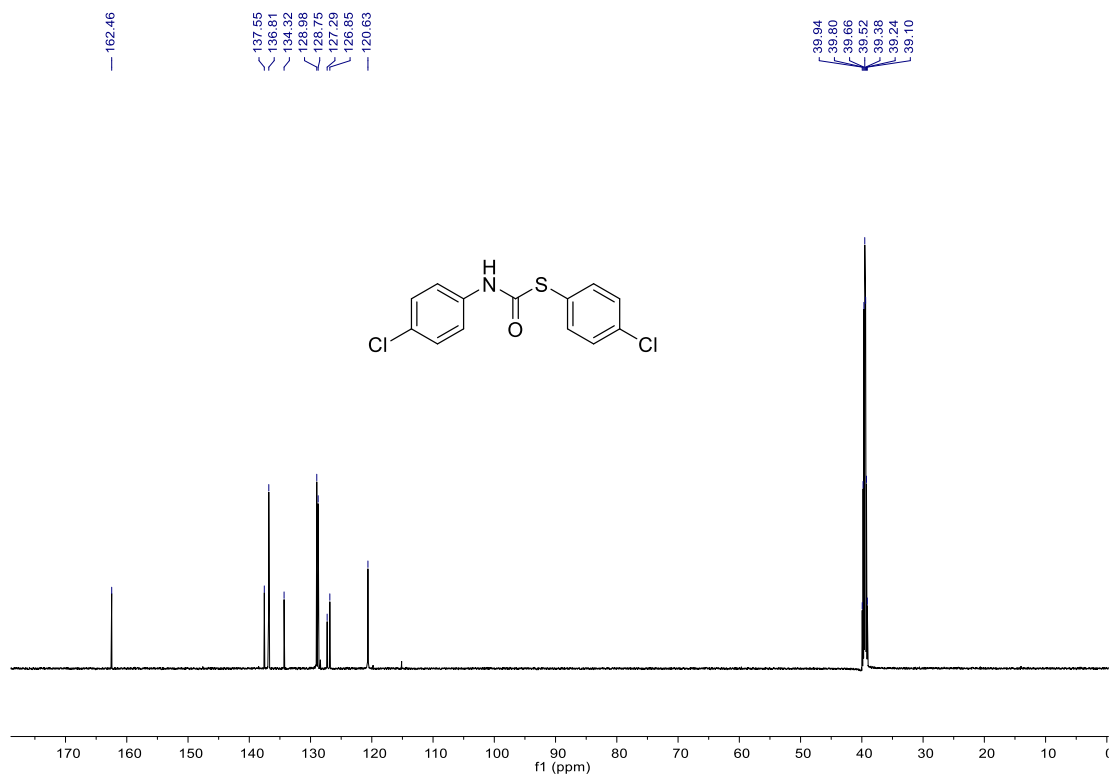
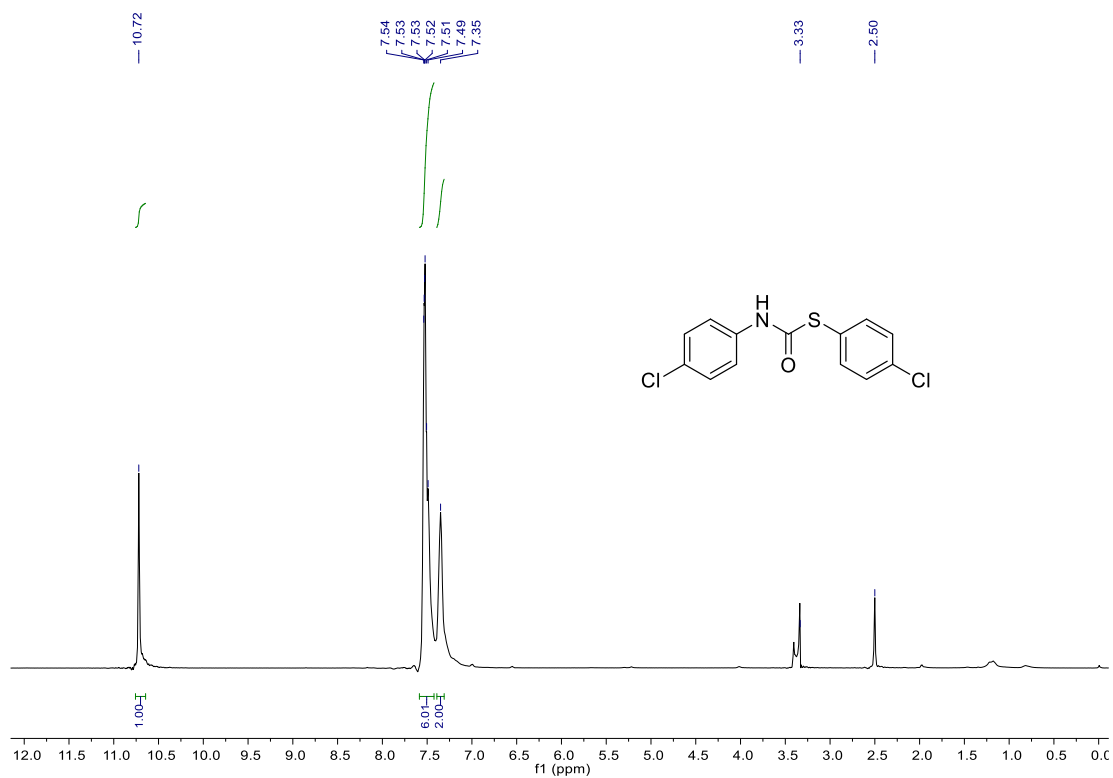
¹H and ¹³C NMR Spectra of **2r**



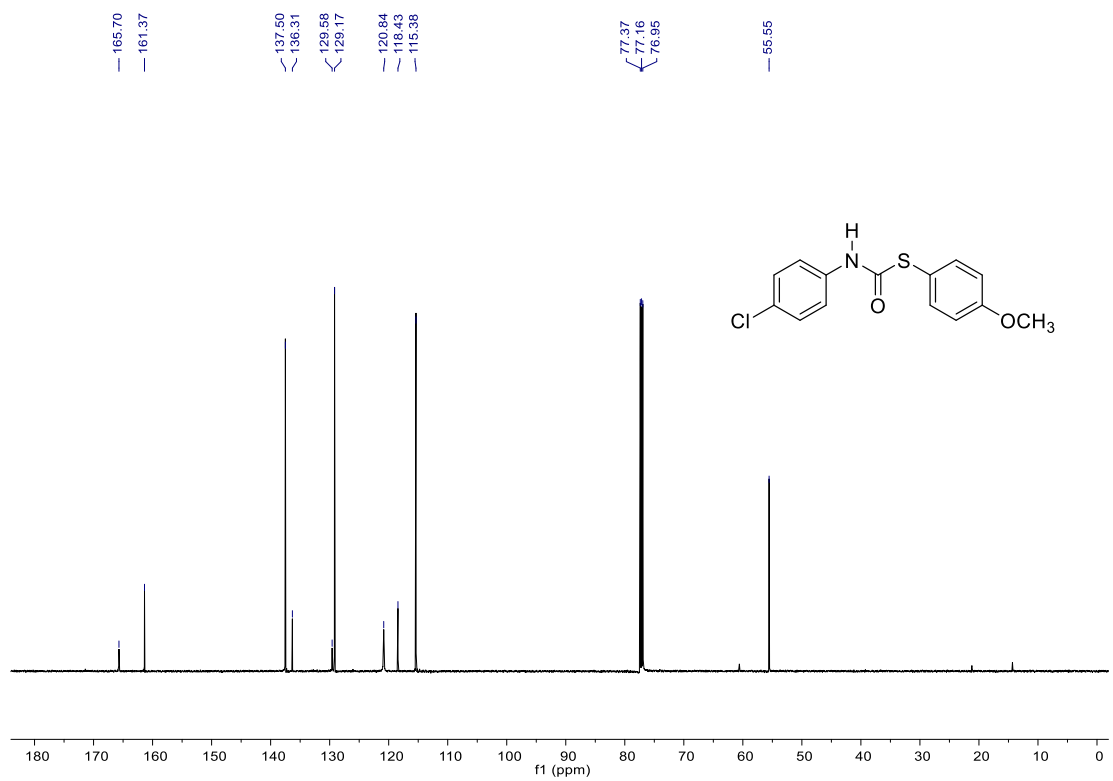
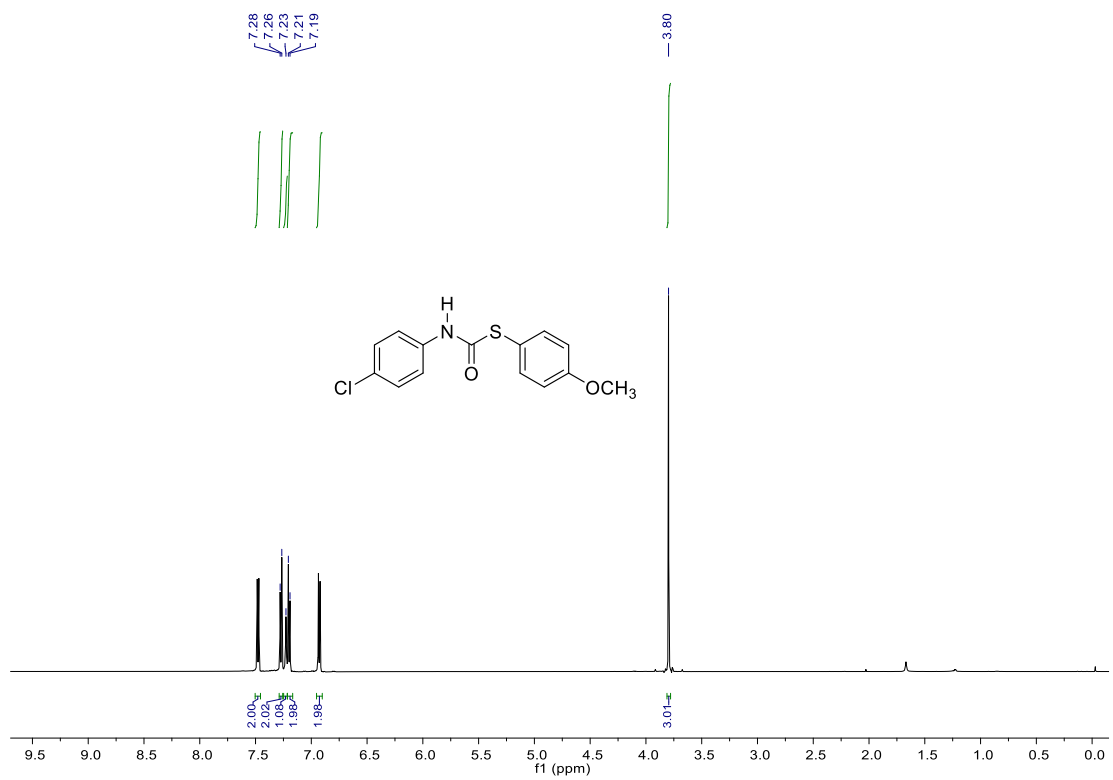
^1H and ^{13}C NMR Spectra of 2s



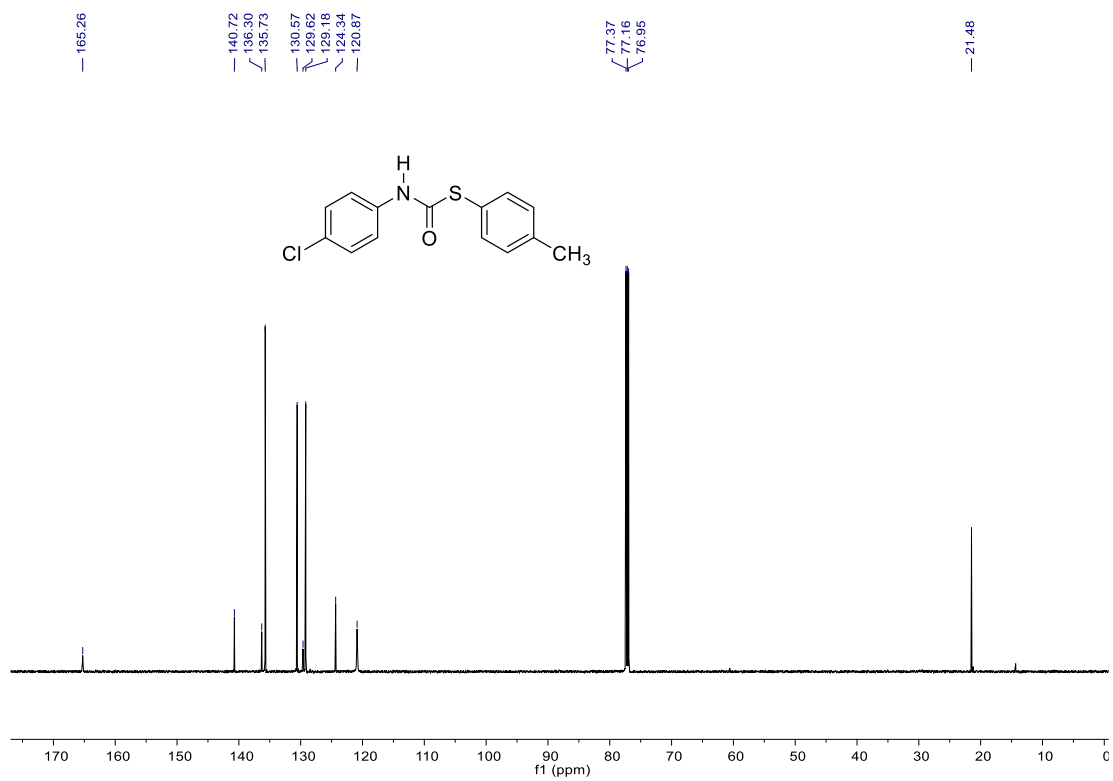
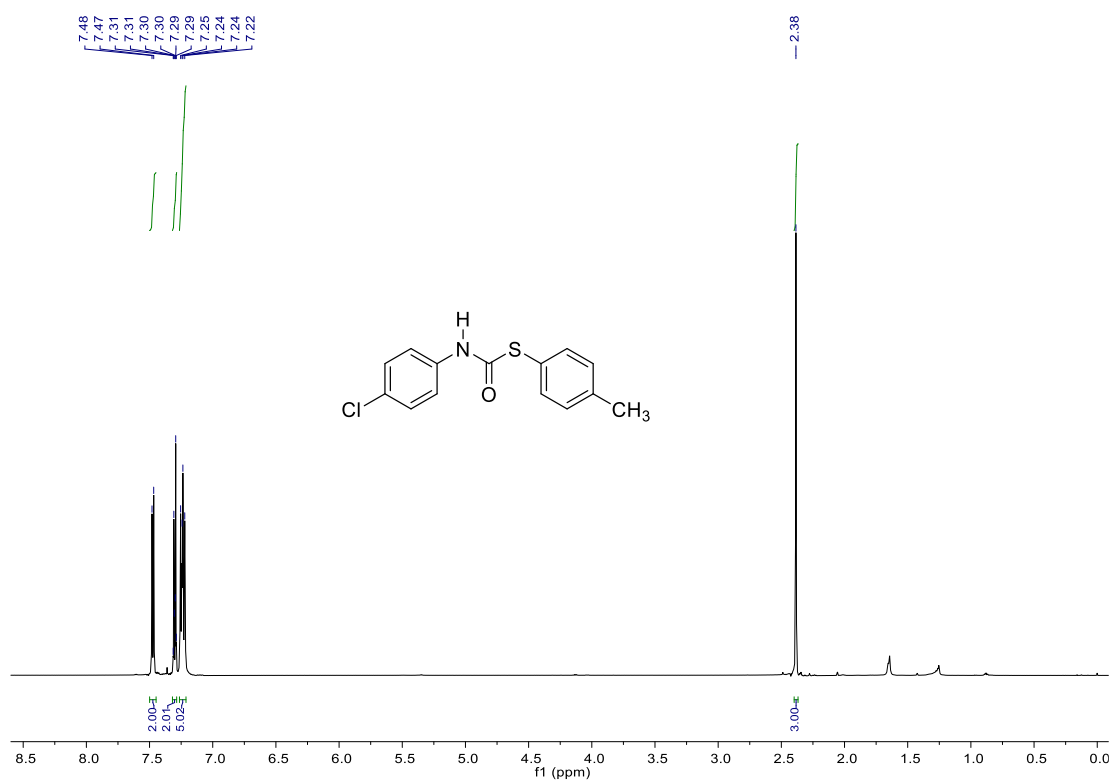
¹H and ¹³C NMR Spectra of **2t**



¹H and ¹³C NMR Spectra of **2u**



¹H and ¹³C NMR Spectra of **2v**



¹H and ¹³C NMR Spectra of 2w