Supporting Information

A simple and straightforward synthesis of phenyl isothiocyanates, symmetrical and unsymmetrical thioureas under ball milling

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1. General Information

NMR spectra were recorded on a Bruker AV300 NMR spectrometer in $CDCl_3$. IR spectra were recorded on a Bruker VECTOR-22 instrument in KBr pellet. All melting points were determined on a XT-4 binocular microscope (Beijing Tech Instrument Co., China) and are not corrected. High-resolution mass spectra (HRMS) were recorded on a Micromass GCT-MS spectrometer with ESI mode. Analytical TLC and column chromatography were performed on silica gel GF254, and silica gel H60, respectively. HPLC was conducted on an Agilent 1100 liquid chromatograph with a diode-array detector using a Zorbax Eclipse XDB-C18 (4.6 mm × 250 mm) with *n*-hexane:2-propanol (4:1) as the eluent (2 mL/min), and was monitored at 254 nm. The mixer mill MM 400 (Retsch GmbH, Germany) was used for all ball-milling reactions. Commercially available CS_2, Et_3N, THF, CH_2Cl_2, CH_3OH and all liquid anilines were further purification in standard manners before use.

2. Typical procedures for synthesis of 3a-3l, 4a-4l and 5a-5l

(1) Typical procedure for synthesis of isothiocyanates 3a-3l (3g as an exmaple)

4-methyl aniline **1g** (10.0 mmol), CS_2 (50.0 mmol) and KOH (10.0 mmol), together with a stainless ball of 7.0 mm in diameter, were introduced into a stainless jar (25 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 40 minutes. The resulting reaction mixtures were combined for direct separation through short column chromatography over silica gel (eluent: hexane/ethyl acetate, v/v = 20:1), affording 2.86 g (96%) of the desired product **3g** as a pale solid. m. p. 27–28 ^{o}C; IR (KBr) *v* 3033, 2099, 1503, 930, 813, 791 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (br, 4H, ArH), 2.35 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 134.2, 130.2, 128.0, 125.5, 21.3.

(2) Typical procedure for synthesis of symmetrical thiourea 4a-4l (4g as an exmaple)

4-methyl aniline (**1g**) (5.0 mmol), CS_2 (5.0 mmol) and KOH (6.0 mmol), together with a stainless ball of 7.0 mm in diameter, were introduced into a stainless jar (25 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 40 minutes. The resulted reaction mixtures were combined and immersed into 30 mL diluted HCl (~5%) with the aid of ultrasonic irradiation, and the desired solid products were collected by Büchner filtration and dried in a desiccator to afford 2.38 g (93%) of **4g** as white solid. m. p. 177–179 ^{o}C; IR (KBr) *v* 3149, 3053, 2965, 1591, 1566, 1509, 1485, 1247, 1142, 811 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (brs, 2H, NH), 7.19–7.26 (m, 8H, ArH), 2.31 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 136.1, 133.5, 128.7, 124.5, 20.0.

(3) Typical procedure for synthesis of unsymmetrical thiourea 5a-5l (5d as an exmaple)

A stainless reaction jar (25 mL) containing aniline **1** (10.0 mmol), CS_2 (50.0 mmol), KOH (10.0 mmol) and a stainless ball (7.0 mm in diameter) was vibrated vigorously at 30 Hz for 40 minutes via Retsch MM400 ball miller. The vessel was opened and 4-bromobenzenamine (10.0 mmol) was added into this resulted mixture, and the sealed vessel was continued to vibrate for 45 minutes at 30 Hz. The reaction mixtures combined from two parallel vessels were immersed in 5% HCl (30 mL) with the aid of ultrasonic irradiation, and the desired solid products were collected by Büchner filtration and dried in a desiccator to give 5.76 g (90%) of the desired product **5d** as a pale solid. m. p. 181–182 ^{o}C; IR (KBr) *v*3277, 3035, 2938, 1593, 1523, 1487, 1237, 1055, 936, 742 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 7.87 (brs, 1H, NH), 7.59 (brs, 1H, NH), 7.40 (d, *J* = 8.1 Hz, 2H, ArH), 7.22 (d, *J* = 8.1 Hz, 2H, ArH), 7.17 (m, 4H, ArH), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz, *d*-DMSO) 180.0, 139.5, 137.1, 134.3, 131.5, 129.4, 126.0, 124.4, 116.7, 21.0.

3. Analytical data for 3a-3l, 4a-4l and 5a-5l

phenyl isothiocyanate (3a)

Oil; IR (KBr) *v* 3045, 2083, 1594, 1516, 1491, 1452, 1070, 927, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.31 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 130.3, 128.5, 126.3, 124.7.

2-methyl-phenyl isothiocyanate (3b)

Oil; IR (KBr) *v* 3029, 2089, 1601, 1491, 936, 765 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (br, 4H, ArH), 2.39 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 133.8, 130.7, 129.7, 127.4, 126.9, 125.9, 18.4.

2-methoxyphenyl isothiocyanate (3c)

Oil; IR (KBr) *v* 3052, 2092, 1603, 1521, 1479, 1102, 936, 768 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.30 (m, 1H, ArH), 7.13–7.16 (m, 1H, ArH), 6.90–6.96 (m, 2H, ArH), 3.94 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 137.9, 129.3, 125.8, 121.1, 119.3, 112.5, 56.4.

2-chlorophenyl isothiocyanate (3d)

Oil; IR (KBr) *v* 3045, 2090, 1588, 1483, 1068, 937, 751 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.37 (m, 1H, ArH), 7.11–7.18 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 131.0, 129.6, 129.1, 126.9, 126.6, 125.6.

3-methyl-phenyl isothiocyanate (3e)

Oil; IR (KBr) *v* 3042, 2100, 1605, 1484, 965, 810, 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01–7.25 (m, 4H, ArH), 2.34 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.8, 134.6, 131.1, 130.2, 128.6, 127.9, 123.3, 21.8.

3-chlorophenyl isothiocyanate (3f)

m. p. 39–41 ^{o}C (Lit.[1] 45 ^{o}C); IR (KBr) *v* 3058, 2095, 1596, 1472, 1070, 960, 864, 752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 8.1 Hz, 1H, ArH), 7.33 (s, 1H, ArH), 7.26 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.06 (d, J = 8.1 Hz, 1H, ArH),; ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 135.0, 132.6, 130.5, 127.4, 125.8, 123.8.

4-methyl-phenyl isothiocyanate (3g)

m. p. 27–28 ^{o}C (Lit.[2] 26–28 ^{o}C); IR (KBr) *v* 3033, 2098, 1503, 930, 813, 791 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (br, 4H, ArH), 2.35 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 134.2, 130.2, 128.0, 125.5, 21.3.

4-methoxyphenyl isothiocyanate (3h)

Oil; IR (KBr) *v* 3022, 2092, 1603, 1504, 1463, 1297, 1034, 931, 828 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 8.6 Hz, 2H, ArH), 6.85 (d, J = 8.6 Hz, 2H, ArH), 3.80 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 133.9, 127.0, 123.5, 114.8, 55.6.

4-bromophenyl isothiocyanate (3i)

m. p. 56–57 ^{o}C (Lit.[3] 58 ^{o}C); IR (KBr) ν 3072, 3050, 2082, 1593, 1467, 1062, 1010, 923, 818 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J = 8.1 Hz, 2H, ArH), 7.27 (d, J = 8.1 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 132.8, 130.1, 127.2, 120.8.

4-chlorophenyl isothiocyanate (3j)

m. p. 44–46 ^{o}C (Lit.[4] 46.5 ^{o}C); IR (KBr) ν 3063, 2079, 1595, 1483, 1089, 929, 823 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.2 Hz, 2H, ArH), 7.16 (d, J = 8.2 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5, 132.4, 129.6, 129.0, 128.1.

4-nitrophenyl isothiocyanate (3k)

m. p. 112–113 ^{o}C (Lit.[5] 110–112 ^{o}C); IR (KBr) ν 3033, 2099, 1533, 1354, 1078, 930, 813, 749 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 8.1 Hz, 2H, ArH), 7.09 (d, J = 8.1 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 137.9, 127.0, 126.4, 125.3.

3, 4-dichlorophenyl isothiocyanate (3l)

m. p. 74–77 ^{o}C (Lit.[6] 75–79 ^{o}C); IR (KBr) ν 3037, 2102, 1591, 1472, 1356, 1108, 938, 846, 754 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 1H, ArH), 7.35 (d, J = 2.2 Hz, 1H, ArH), 7.09 (d, J = 8.6 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 134.3, 132.6, 131.7, 130.8, 127.4, 124.8.

1-*o*-tolyl-3-*p*-tolylthiourea (5a)

m. p. 130–132 ^{o}C (Lit. [7] 132 ^{o}C); IR (KBr) ν 3177, 3035, 2938, 1593, 1523, 1487, 1237, 1055, 936, 742 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (brs, 2H, NH), 7.38 (m, 1H, ArH), 7.18–7.27 (m, 7H, ArH), 2.35 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4, 136.0, 134.6, 134.4, 133.7, 130.2, 129.0, 127.2, 126.8, 126.1, 124.6, 20.1, 17.0.

1-*m*-tolyl-3-*p*-tolylthiourea (5b)

m. p. 147–148 ^{o}C (Lit. [8] 148 ^{o}C); IR (KBr) ν 3148, 3054, 2922, 1601, 1509, 1476, 1247, 1025, 876, 812 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (brs, 2H, NH), 7.10–7.31 (m, 7H, ArH), 7.08 (d, J = 7.2 Hz, 1H, ArH), 2.35 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.7, 138.6, 136.1, 136.0, 133.6, 129.1, 128.3, 126.7, 124.8, 124.5, 121.3, 20.4, 20.1.

1-(4-methoxyphenyl)-3-*p*-tolylthiourea (5c)

m. p. 158–160 ^{o}C (Lit. [9] 161 ^{o}C); IR (KBr) ν 3207, 3063, 2943, 1597, 1556, 1478, 1237, 1074, 915, 707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (brs, 2H, NH), 7.10–7.21 (m, 6H, ArH), 6.83–6.86 (m, 2H, ArH), 3.73 (s, 3H, OCH_3), 2.27 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.5, 157.6, 136.1, 133.5, 129.1, 129.0, 126.5, 124.5, 113.7, 54.5, 20.0.

1-(4-bromophenyl)-3-*p*-tolylthiourea (5d)

m. p. 181–182 ^{o}C (Lit. [10] 184 ^{o}C); IR (KBr) ν3145, 3042, 2956, 1603, 1523, 1490, 1246, 1103, 928, 725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (brs, 1H, NH), 7.59 (brs, 1H, NH), 7.40 (d, J = 8.1 Hz, 2H, ArH),

7.22 (d, *J* = 8.1 Hz, 2H, ArH), 7.17 (m, 4H, ArH), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz, *d*-DMSO) δ 180.0, 139.5, 137.1, 134.3, 131.5, 129.4, 126.0, 124.4, 116.7, 21.0.

1-(4-chlorophenyl)-3-*p*-tolylthiourea (5e)

m. p. 177–178 ^{o}C (Lit.[11] 174–175 ^{o}C); IR (KBr) *v* 3155, 3058, 2944, 1599, 1505, 1377, 1124, 878, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (brs, 1H, NH), 7.61 (brs, 1H, NH), 7.26 (brs, 4H, ArH), 7.15 (brs, 4H, ArH), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.0, 136.9, 135.1, 132.6, 131.1, 129.6, 128.3, 125.5, 124.6, 20.1.

1-(4-methylphenyl)-3-phenylthiourea (5f)

m. p. 138–139 ^{o}C (Lit.[12] 141 ^{o}C); IR (KBr) *v* 3200, 3074, 2953, 2944, 1601, 1407, 1224, 965, 738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (brs, 2H, NH), 7.43 (m, 4H, ArH), 7.28–7.33 (m, 5H, ArH), 2.39 (s, 3H, CH_3); ^{13}C NMR (125 MHz, *d*-DMSO) δ 179.6, 139.6, 136.8, 133.7, 128.8, 128.4, 124.4, 123.9, 121.7, 20.6.

1-(4-chlorophenyl)-3-(4-methoxyphenyl)thiourea (5g)

m. p. 179–180 ^{o}C (Lit.[13] 176–178 ^{o}C); IR (KBr) *v* 3215, 3058, 2923, 1603, 1554, 1383, 1065, 972, 784 cm^{-1}; ^{1}H NMR (300 MHz, *d*-DMSO) δ 9.70 (brs, 2H, NH), 7.51 (d, *J* = 9.0 Hz, 2H, ArH), 7.36 (d, *J* = 8.8 Hz, 2H, ArH), 7.31 (d, *J* = 8.8 Hz, 2H, ArH), 6.91 (d, *J* = 9.0 Hz, 2H, ArH), 3.74 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, *d*-DMSO) δ 179.9, 156.7, 138.6, 132.0, 128.3, 128.1, 126.1, 125.3, 113.8, 55.3.

1-(3-chlorophenyl)-3-(4-methoxyphenyl)thiourea (5h)

m. p. 173–175 ^{o}C ; IR (KBr) *v* 3225, 3061, 3002, 1612, 1574, 1321, 1064, 886, 705 cm^{-1}; ^{1}H NMR (300 MHz, *d*-DMSO) δ 9.79 (s, 1H, NH), 9.76 (s, 1H, NH), 7.71 (d, *J* = 1.8 Hz, 1H, ArH), 7.34–7.41 (m, 2H, ArH), 7.32 (d, *J* = 6.7 Hz, 2H, ArH), 7.13–7.17 (m, 1H, ArH),, 6.92 (d, *J* = 6.7 Hz, 2H, ArH), 3.77 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, *d*-DMSO) δ 179.8, 156.7, 141.2, 132.5, 131.9, 129.9, 126.1, 123.8, 122.9, 121.9, 113.8, 55.2.

1-(2-chlorophenyl)-3-(4-methoxyphenyl)thiourea (5i)

m. p. 168–170 ^{o}C (Lit.[9] 173 ^{o}C); IR (KBr) *v* 3155, 3058, 2944, 1599, 1505, 1377, 1124, 878, 695 cm^{-1}; ^{1}H NMR (300 MHz, *d*-DMSO) δ 9.90 (s, 1H, NH), 9.30 (s, 1H, NH), 7.70 (d, *J* = 7.4 Hz, 1H, ArH), 7.50 (d, *J* = 7.5 Hz, 1H, ArH), 7.42 (d, *J* = 8.3 Hz, 2H, ArH), 7.33 (t, *J* = 7.1 Hz, 1H, ArH), 7.03 (t, *J* = 7.4 Hz, 1H, ArH), 6.95 (d, *J* = 8.4 Hz, 2H, ArH), 3.75 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, *d*-DMSO) δ 180.5, 156.8, 136.5, 131.8, 129.6, 129.4, 129.0, 127.7, 127.1, 126.2, 113.8, 55.3.

1-(4-bromophenyl)-3-(4-methoxyphenyl)thiourea (5j)

m. p. 178–179 ^{o}C (Lit.[13] 182–184 ^{o}C); IR (KBr) *v* 3199, 3053, 2947, 1605, 1505, 1377, 1125, 978, 864, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (brs, 2H, NH), 7.53 (d, *J* = 8.2 Hz, 2H, ArH), 7.48 (d, *J* = 8.0 Hz, 2H, ArH), 7.30 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.2 Hz, 2H, ArH), 3.83 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, *d*-DMSO) δ 179.8, 156.6, 139.1, 131.2, 131.1, 126.0, 125.6, 116.5, 113.7, 55.2.

1-(3-methylphenyl)-3-(4-methoxyphenyl)thiourea (5k)

m. p. 148–149 °C (Lit. [14] 150 °C); IR (KBr) *v* 3195, 3044, 2958, 1601, 1542, 1385, 1226, 873, 692 cm^{-1}; ^1H NMR (300 MHz, *d*-DMSO) δ 7.88 (brs, 1H, NH), 9.57 (brs, 2H, NH), 7.32 (d, *J* = 8.7 Hz, 2H, ArH), 7.17–7.27 (m, 3H, ArH), 6.95 (s, 1H, ArH), 6.90 (d, *J* = 8.7 Hz, 2H, ArH), 3.74 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz, *d*-DMSO) δ 179.8, 156.5, 139.4, 137.7, 132.2, 128.3, 126.1, 125.1, 124.2, 120.9, 113.6, 55.2, 21.1.

1-(3-methylphenyl)-3-(4-bromophenyl)thiourea (5l)

m. p. 163–164 °C (Lit. [14] 151 °C); IR (KBr) *v* 3220, 3064, 2953, 1610, 1522, 1380, 1066, 932, 759 cm^{-1}; ^1H NMR (300 MHz, *d*-DMSO) δ 9.84 (s, 1H, NH), 9.82 (s, 1H, NH), 7.50 (d, *J* = 9.0 Hz, 2H, ArH), 7.45 (d, *J* = 9.0 Hz, 2H, ArH), 7.21–7.26 (m, 3H, ArH), 6.96 (d, *J* = 6.5 Hz, 1H, ArH), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz, *d*-DMSO) δ 179.5, 139.1, 139.0, 137.8, 131.2, 128.4, 125.6, 125.4, 124.2, 120.9, 116.3, 21.1.

1,3-bis(phenyl)thiourea (4a)

m. p. 154–155 °C (Lit.[15] 153–156 °C); IR (KBr) *v* 3208, 3035, 3004, 1599, 1550, 1451, 1344, 1025, 934, 757, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (brs, 2H, NH), 7.25–7.44 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7, 137.2, 129.6, 127.0, 125.3.

1,3-bis(2-methylphenyl)thiourea (4b)

m. p. 165–166 °C (Lit.[16] 165–167 °C); IR (KBr) *v* 3301, 3025, 2956, 1587, 1527, 1498, 1266, 1043, 927, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (brs, 2H, NH), 7.42–7.45 (m, 2H, ArH),7.22–7.35 (m, 6H, ArH), 2.33 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9, 135.7, 131.3, 130.7, 128.3, 128.0, 127.1, 18.0.

1,3-bis(2-methoxyphenyl)thiourea (4c)

m. p. 138–139 °C (Lit.[17] 134 °C); IR (KBr) *v* 3189, 3035, 2958, 1594, 1518, 1486, 1263, 1073, 923, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (brs, 2H, NH), 7.16–7.26 (m, 2H, ArH), 6.91–7.03 (m, 6H, ArH), 3.82 (s, 6H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 156.3, 139.7, 128.4, 125.4, 120.7, 111.5, 55.9.

1,3-bis(2-chlorophenyl)thiourea (4d)

m. p. 128–130 °C (Lit.[18] 130.5 °C); IR (KBr) *v* 3215, 3046, 2939, 1601, 1523, 1214, 944, 737 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70–7.88 (br, 2H, NH), 7.16–7.39 (m, 6H, ArH), 6.92 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 130.7, 129.1, 128.7, 127.0, 126.6, 125.6.

1,3-bis(3-methylphenyl)thiourea (4e)

m. p. 110–112 °C (Lit.[19] 111.5–112.5 °C); IR (KBr) *v* 3213, 3055, 2946, 1597, 1535, 1376, 1049, 867 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (brs, 2H, NH), 7.25–7.32 (m, 2H, ArH), 7.17–7.21 (m, 4H, ArH), 7.07–7.10 (m, 2H, ArH), 2.36 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8, 139.7, 137.1, 129.3, 127.8, 125.9, 122.4, 21.4.

1,3-bis(3-chlorophenyl)thiourea (4f)

m. p. 131–133 °C (Lit.[19] 131.5 °C); IR (KBr) *v* 3181, 3046, 2963, 1602, 1515, 1345, 1064, 844 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (brs, 2H, NH), 7.24–7.39 (m, 8H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7, 138.1, 135.1, 130.5, 127.3, 125.2, 123.3.

1,3-bis-(4-methylphenyl)thiourea (4g)

m. p. 177–179 °C (Lit.[20] 178–180 °C); IR (KBr); IR (KBr) *v* 3149, 3053, 2965, 1591, 1536, 1509, 1485, 1247, 1142, 811 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (brs, 2H, NH), 7.19–7.26 (m, 8H, ArH), 2.31 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.2, 136.1, 133.5, 128.7, 124.5, 20.0.

1,3-bis(4-methoxyphenyl)thiourea (4h)

m. p. 185–186 °C (Lit.[19] 186.5 °C); IR (KBr) *v* 3199, 3032, 2934, 1589, 1521, 1487, 1052, 936, 763 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (brs, 2H, NH), 7.34 (d, J = 8.7 Hz, 4H, ArH), 6.95 (d, J = 8.7 Hz, 4H, ArH), 3.84 (s, 6H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 151.3, 126.5, 124.0, 111.2, 55.8.

1,3-bis(4-bromophenyl)thiourea (4i)

m. p. 188–190 °C (Lit.[21] 188 °C); IR (KBr) *v* 3238, 3044, 2950, 1594, 1531, 1479, 1243, 1056, 921, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (s, 2H, NH), 7.53 (d, J = 7.5 Hz, 4H, ArH), 6.38 (d, J = 7.5 Hz, 4H, ArH); ^{13}C NMR (125 MHz, *d*-DMSO) δ 179.4, 138.9, 131.3, 125.6, 116.5.

1,3-bis(4-chlorophenyl)thiourea (4j)

m. p. 177–178 °C (Lit.[19] 176 °C); IR (KBr) *v* 3277, 3035, 2938, 1593, 1523, 1487, 1237, 1055, 936, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (brs, 2H, NH), 7.30–7.40 (m, 8H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 139.2, 129.6, 129.3, 126.4.

1,3-bis(4-nitrophenyl)thiourea (4k)

m. p. 194–196 °C (Lit.[22] 195–196 °C); IR (KBr) *v* 3290, 3035, 2958, 1597, 1552, 1532, 1487, 1353, 1229, 1076, 954, 787 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.55 (brs, 2H, NH), 7.93 (d, J = 8.4 Hz, 4H, ArH), 6.63 (d, J = 8.4 Hz, 4H, ArH); ^{13}C NMR (125 MHz, *d*-DMSO) δ 179.3, 145.7, 142.8, 126.5, 122.1.

2(1H)benzoimidazolinethione (4l)

m. p. 301–302 °C (Lit.[23] 304 °C); IR (KBr) *v* 3397, 3057, 2954, 1644, 1529, 1447, 1310, 742, 720 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.43 (brs, 2H, NH), 7.24–7.39 (m, 4H, ArH); ^{13}C NMR (125 MHz, *d*-DMSO) δ 168.3, 132.4, 122.7, 109.8.

4. References

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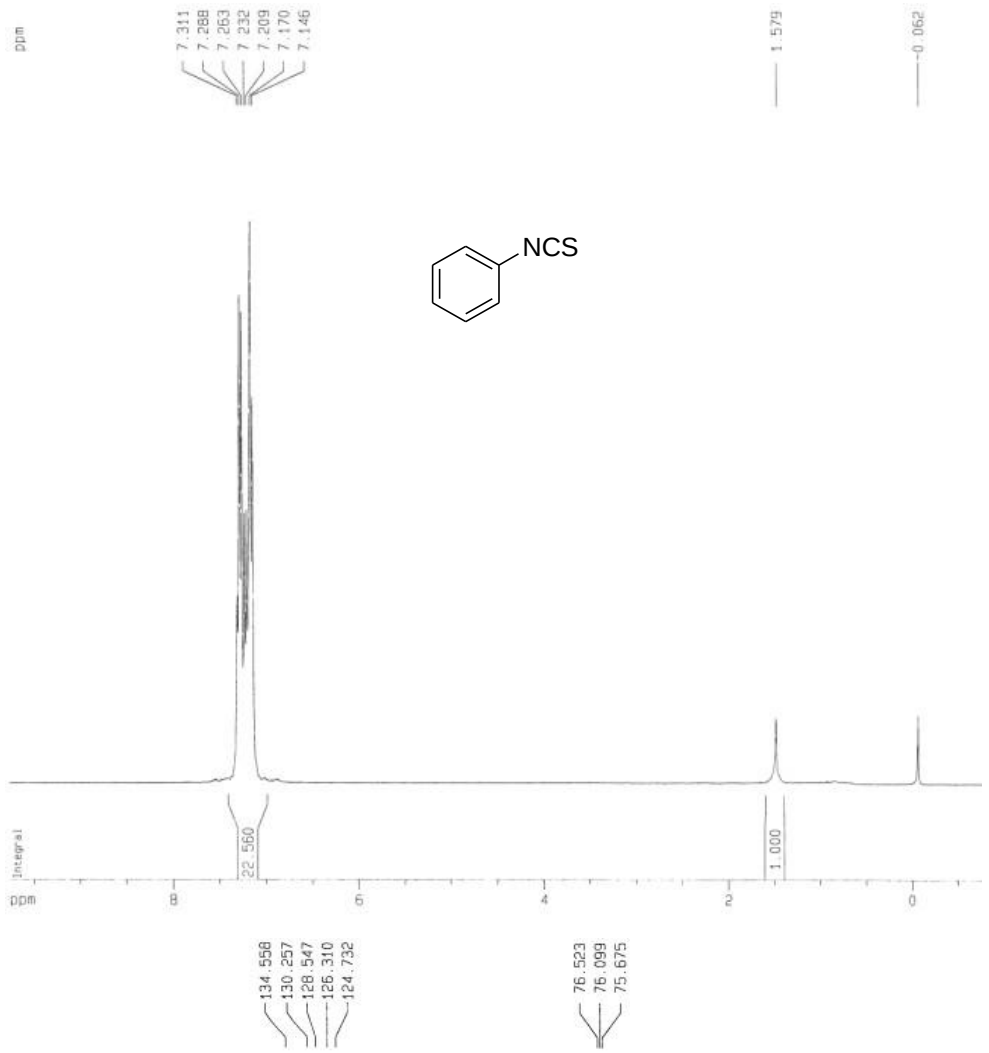
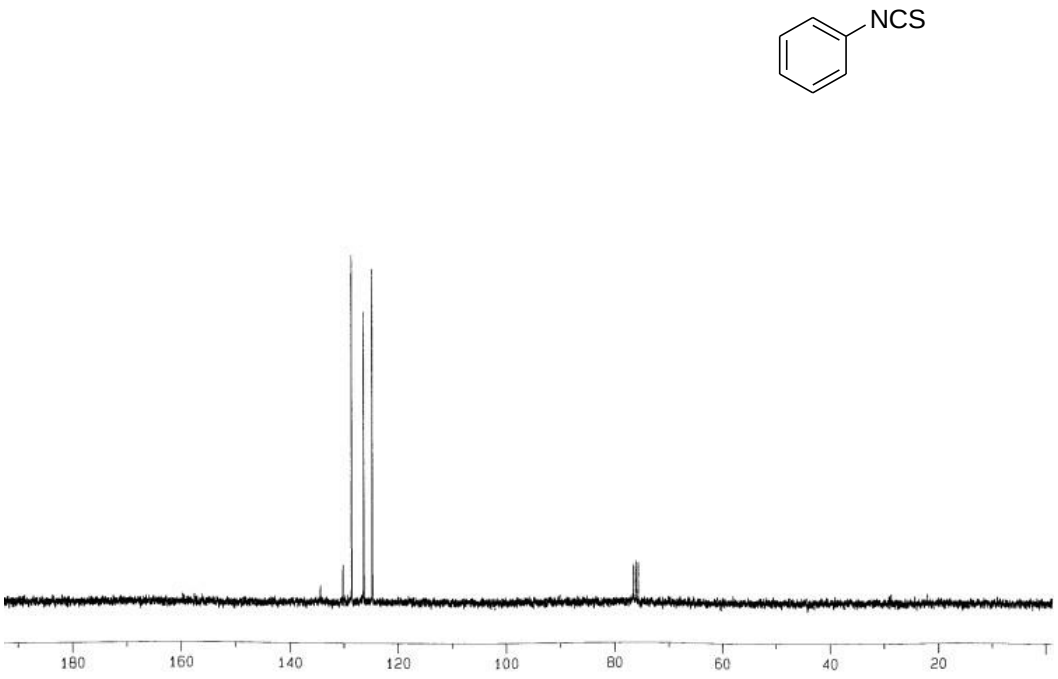
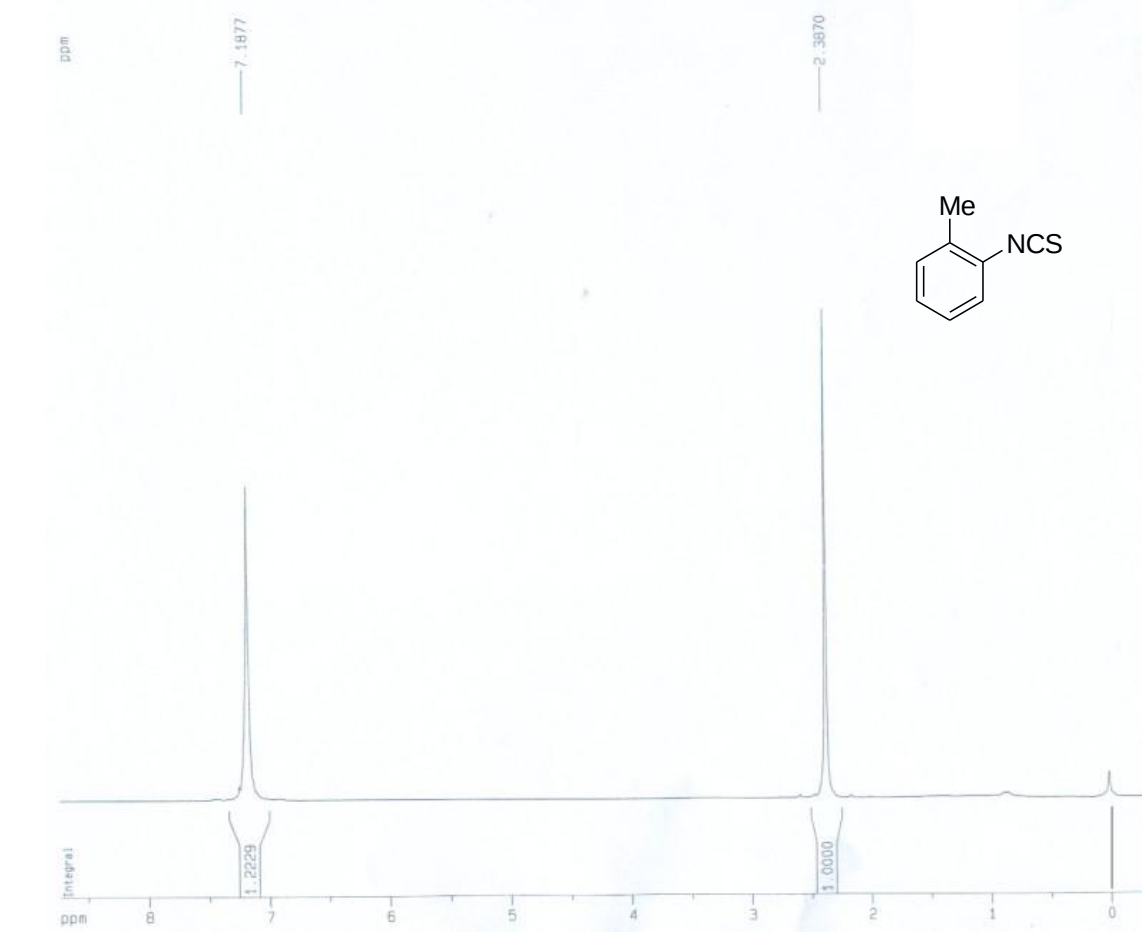
5. ^{1}HNMR and ^{13}CNMR spectra for compounds 3a-3l and 5a-5e



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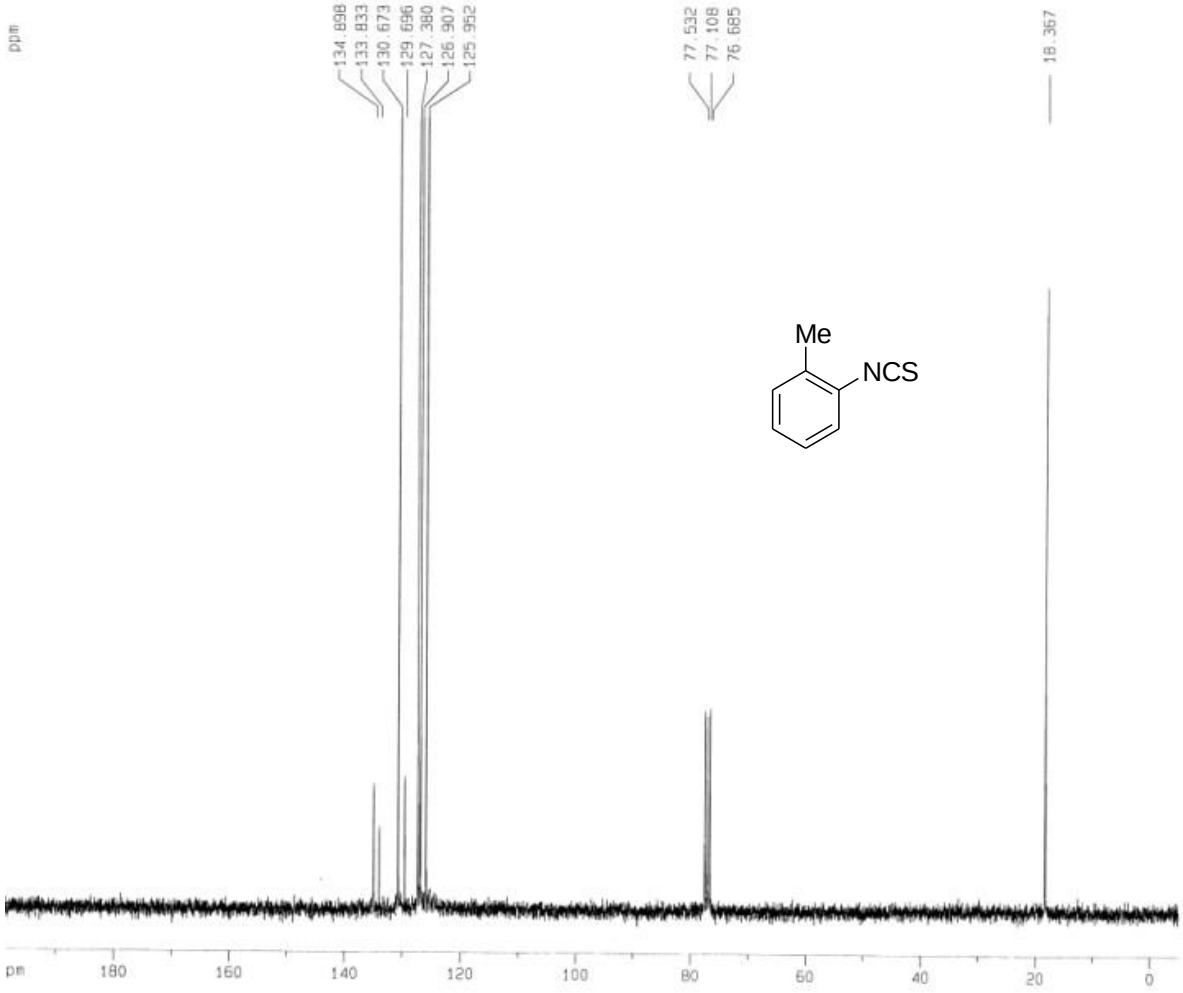
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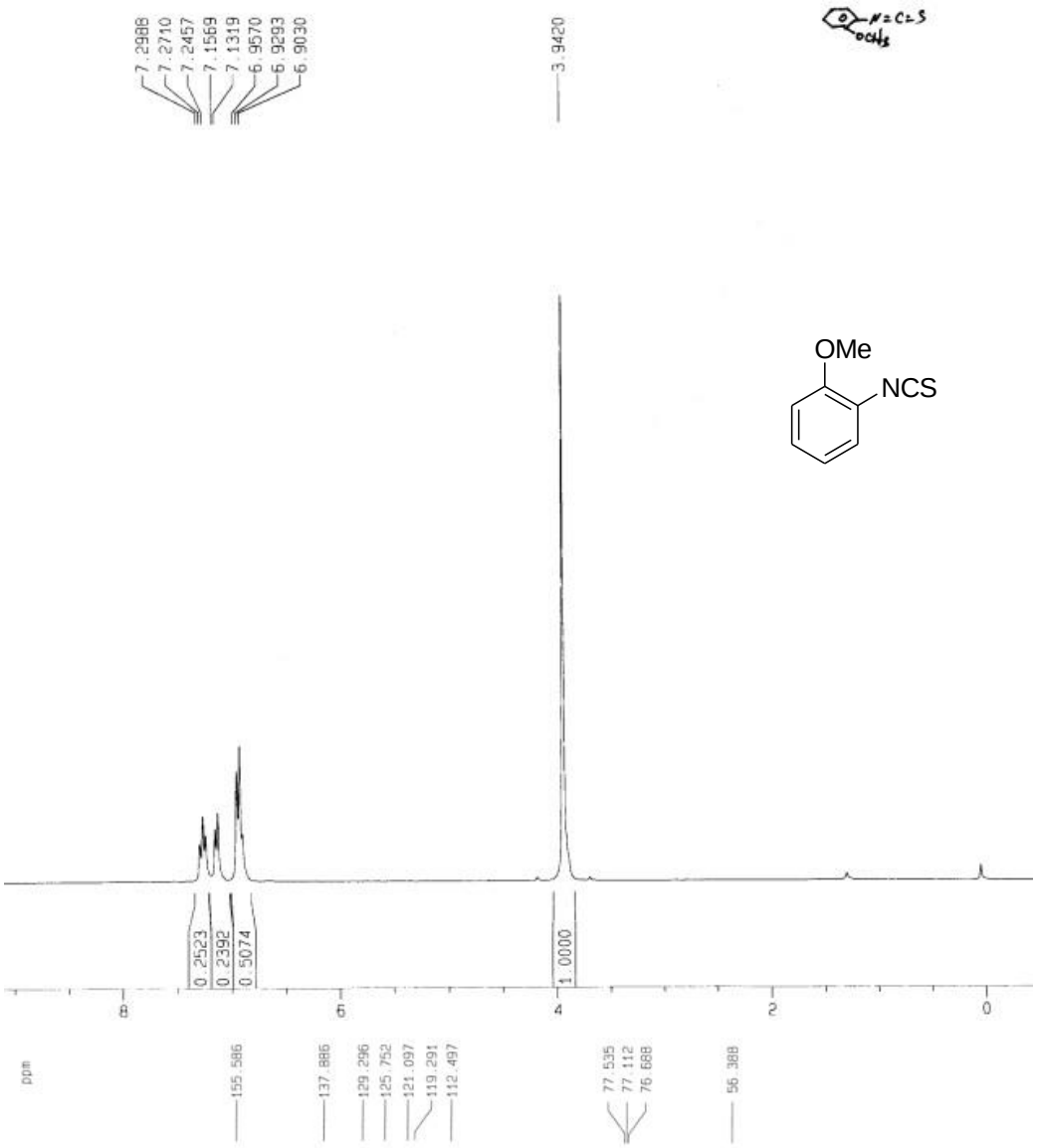
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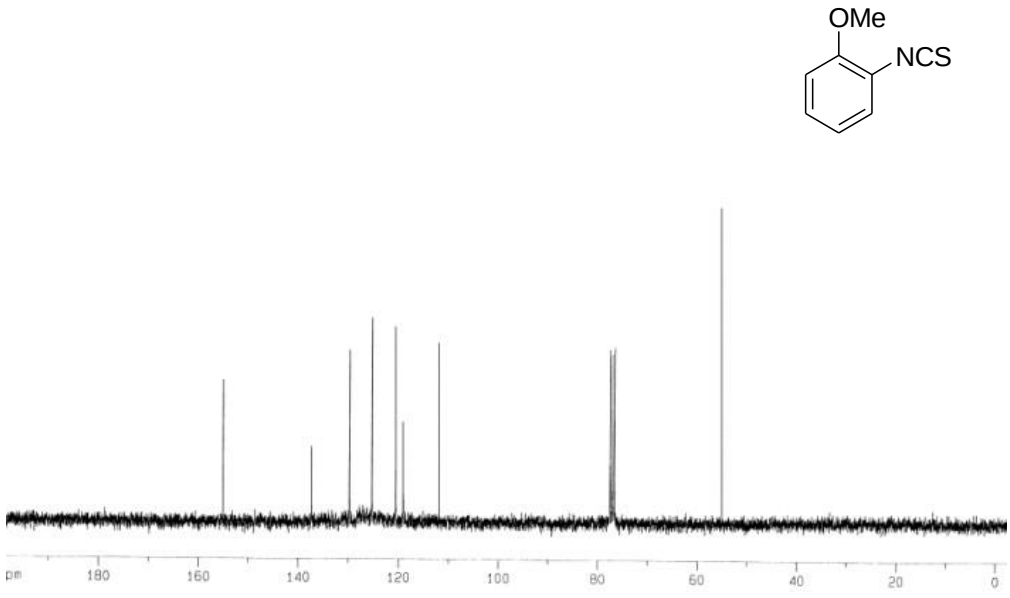
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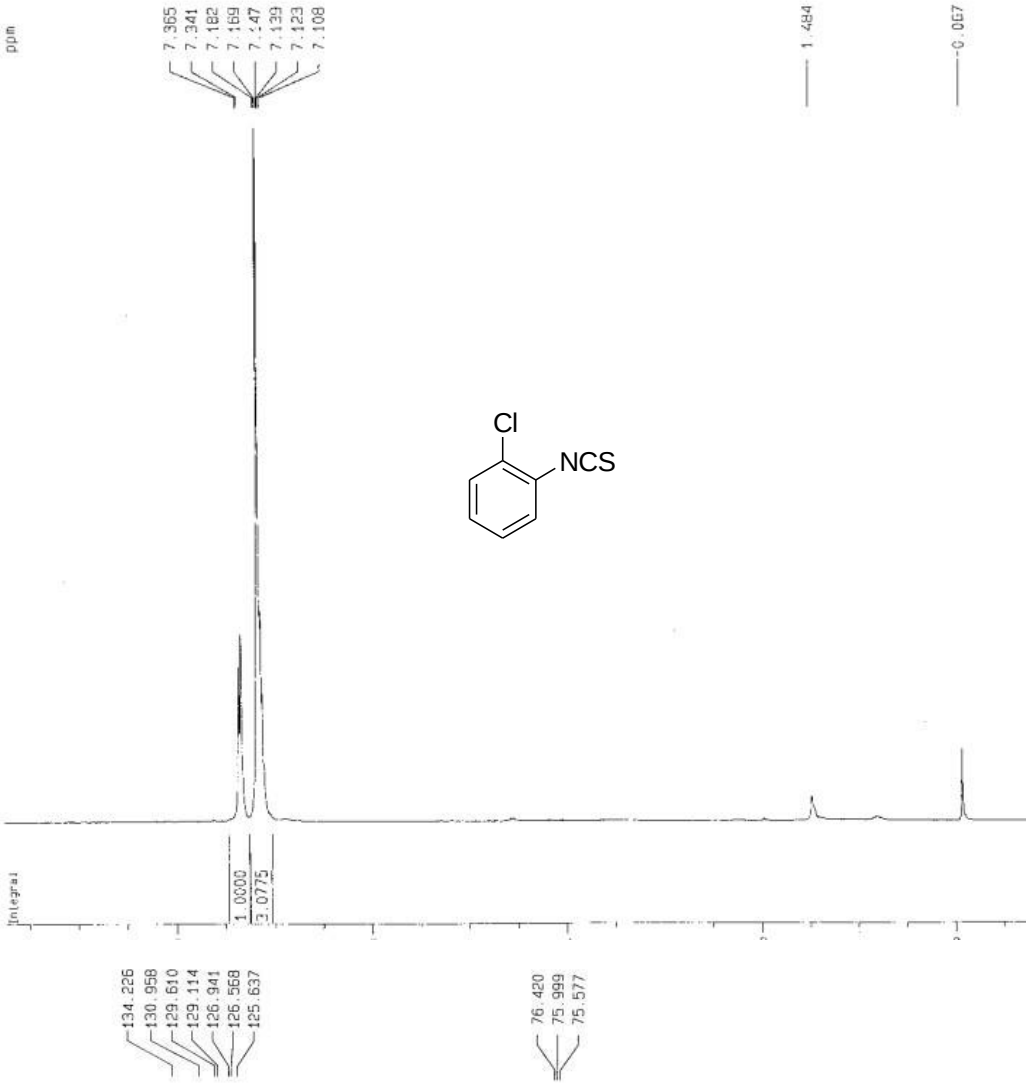

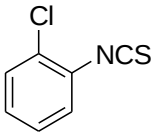

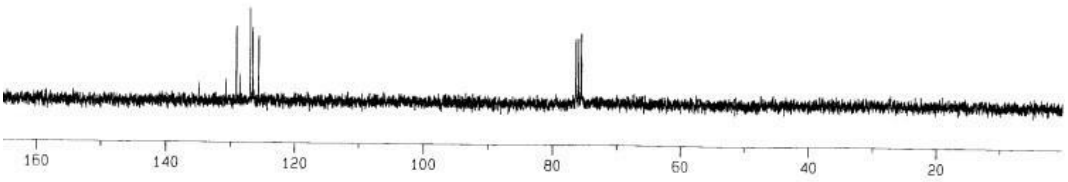

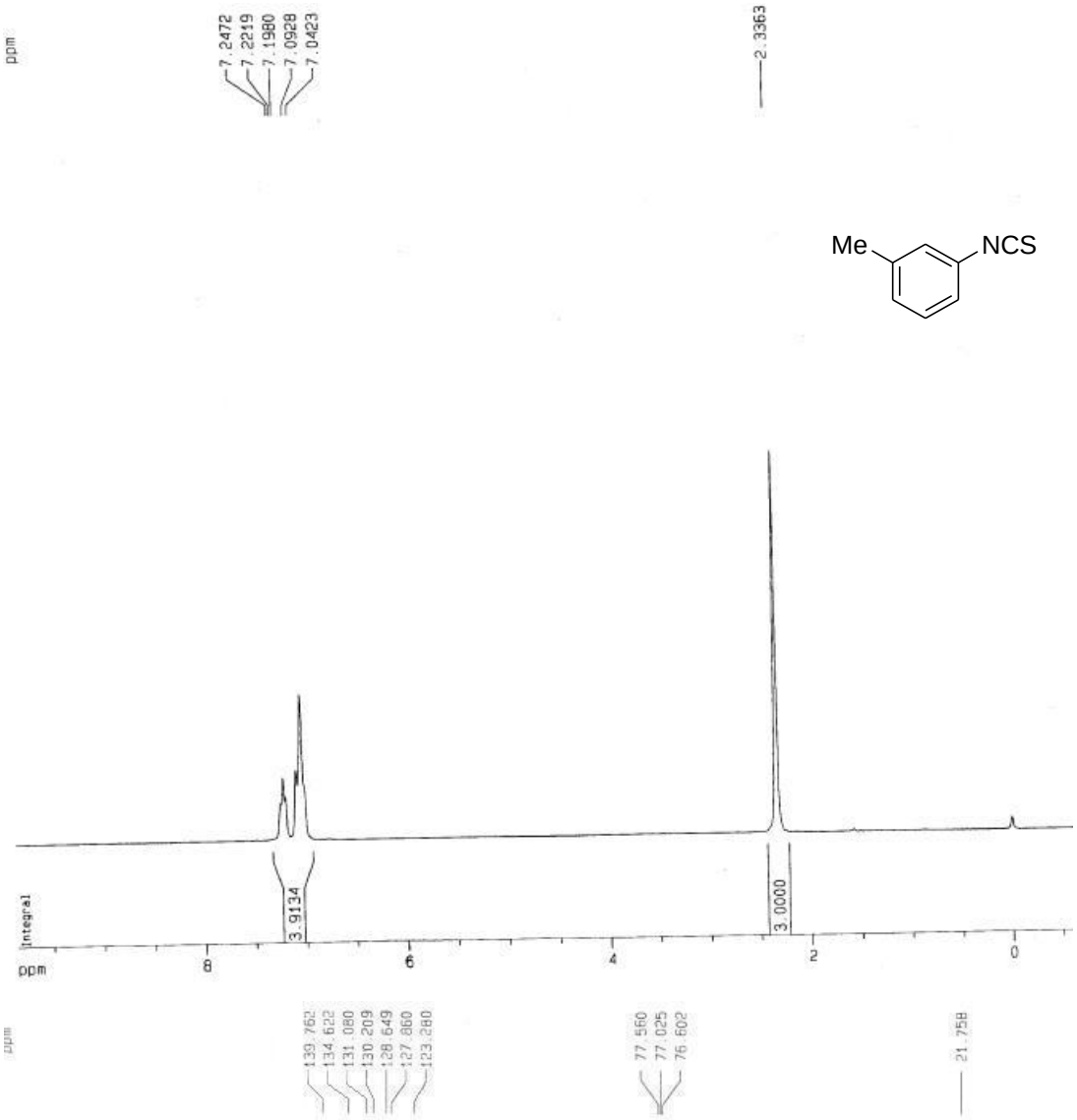

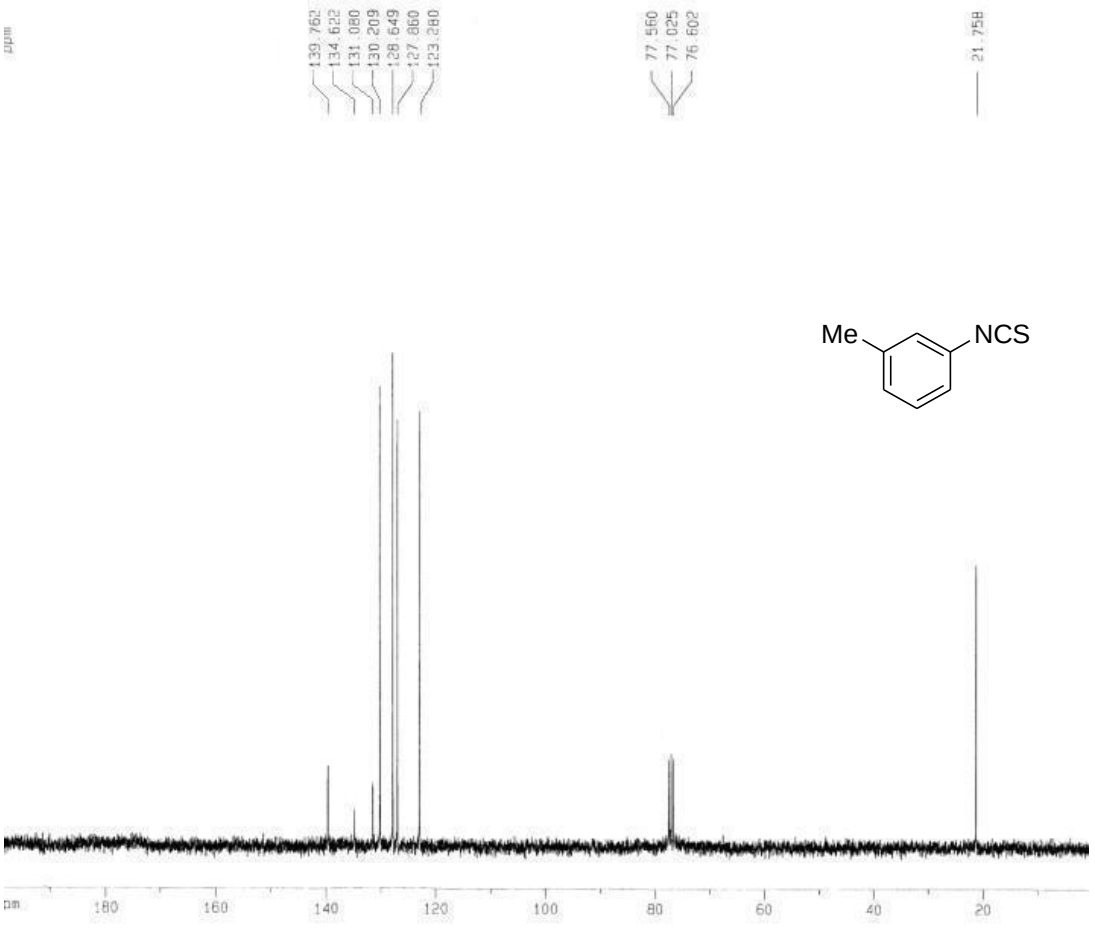


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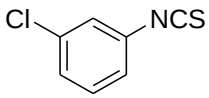
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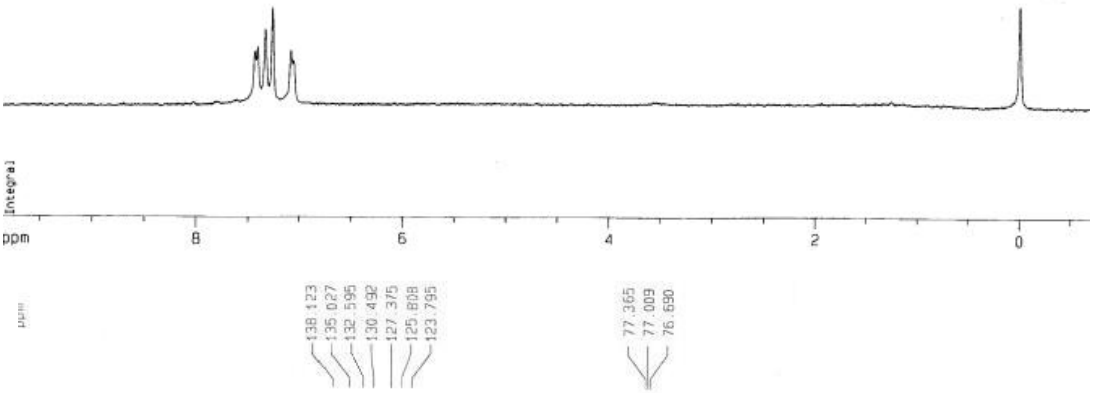
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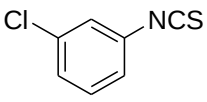
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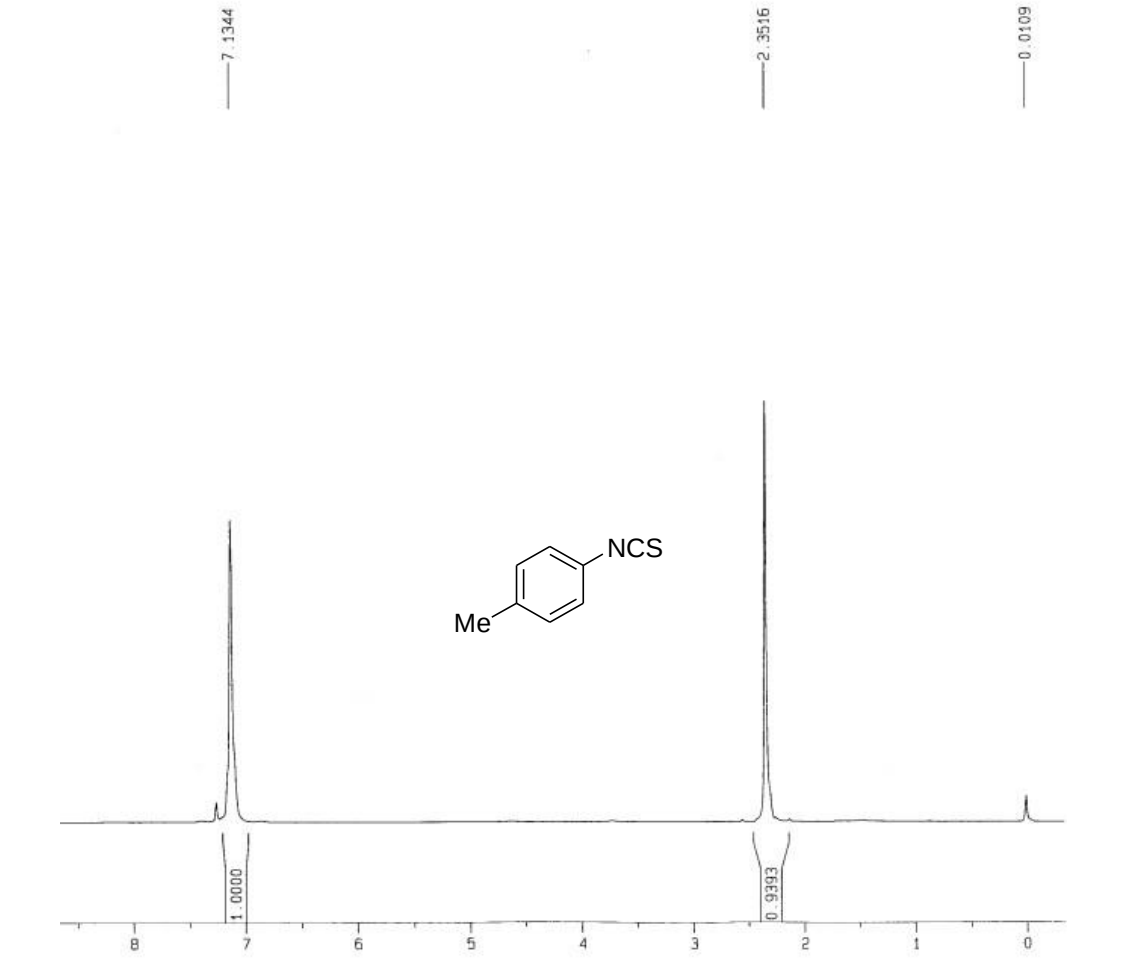

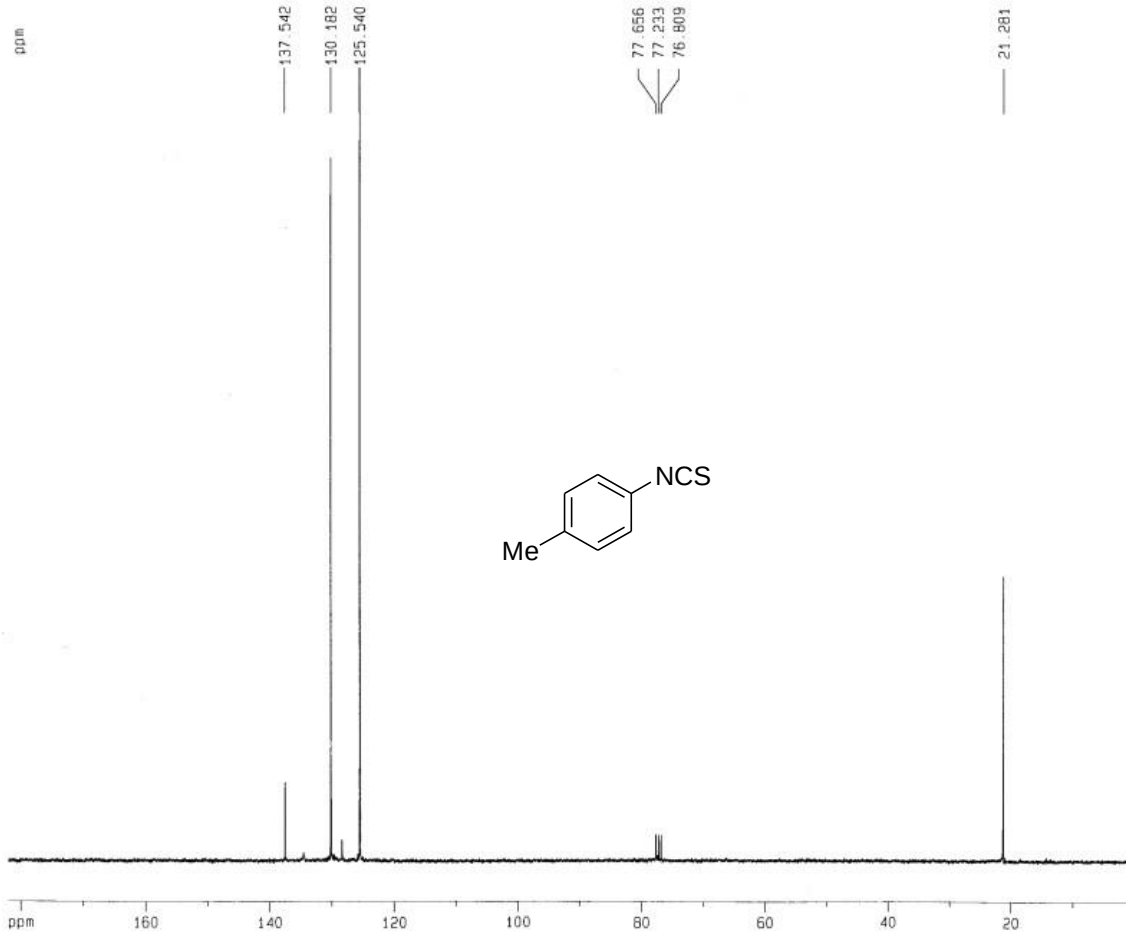

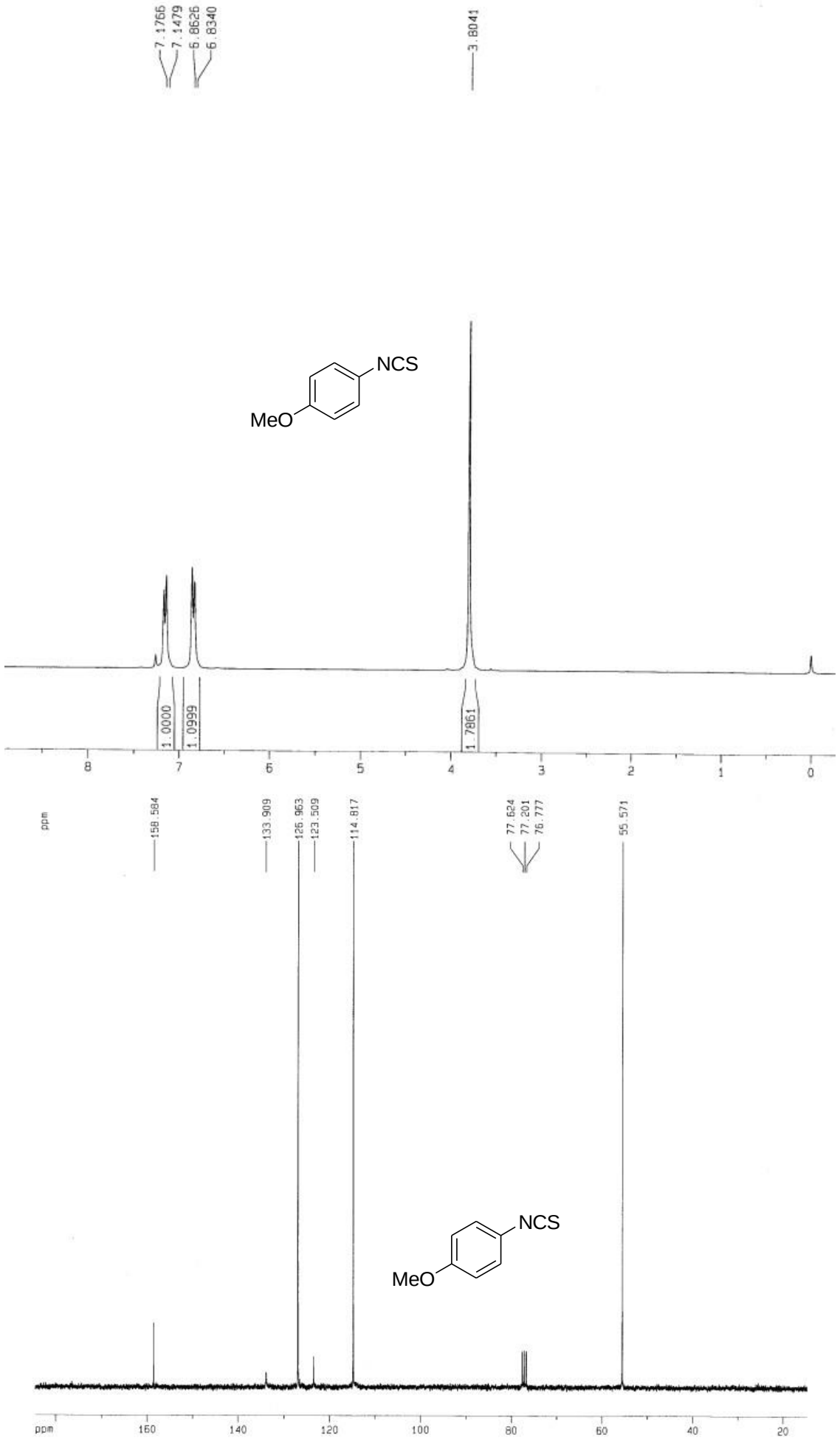

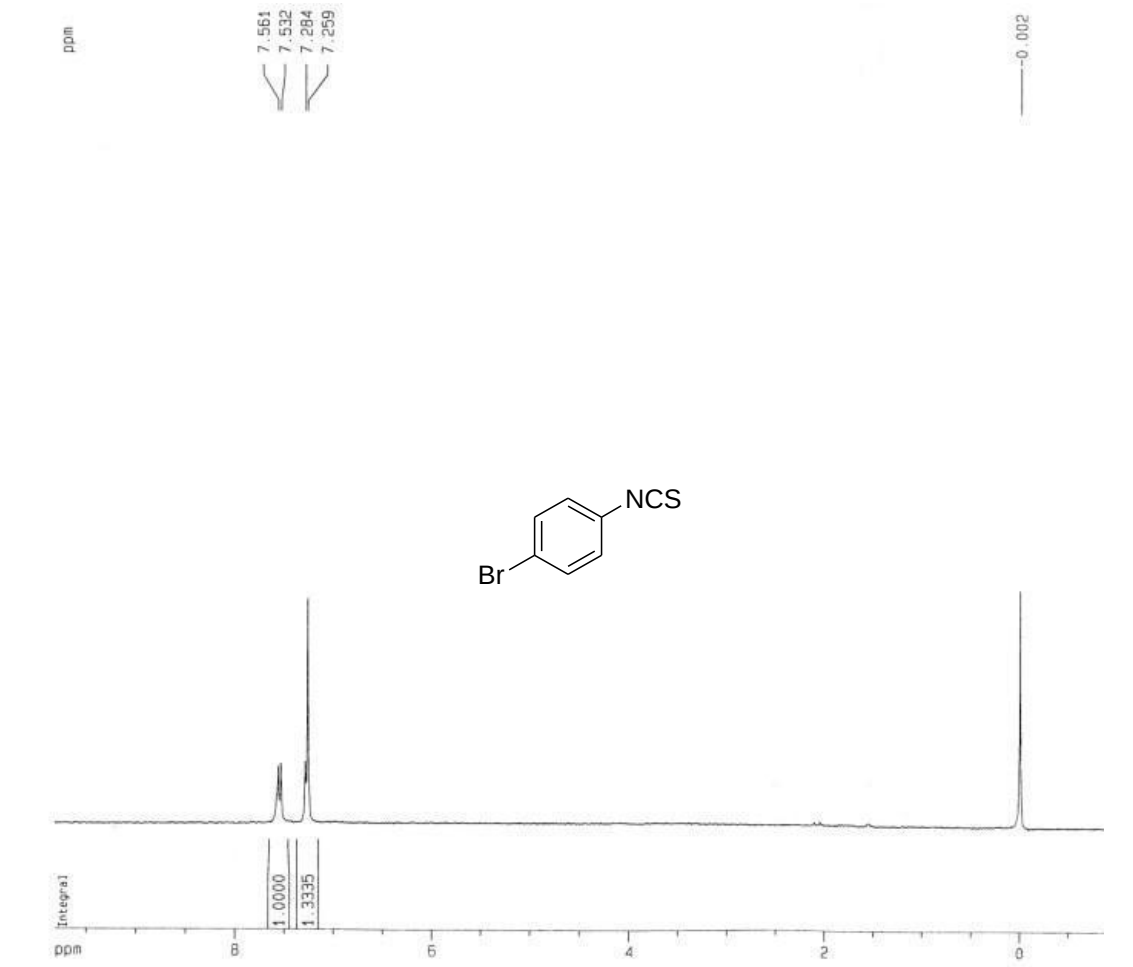

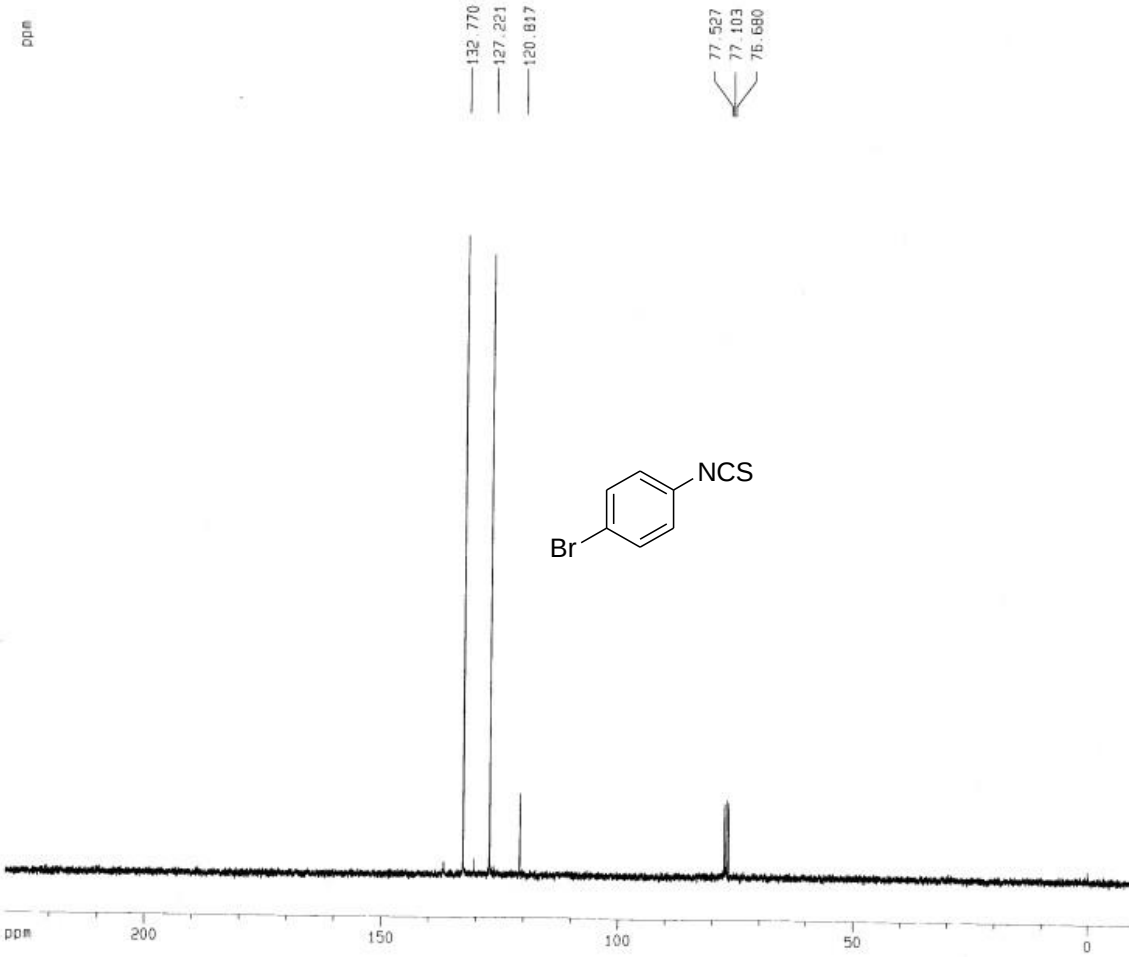

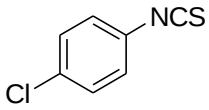

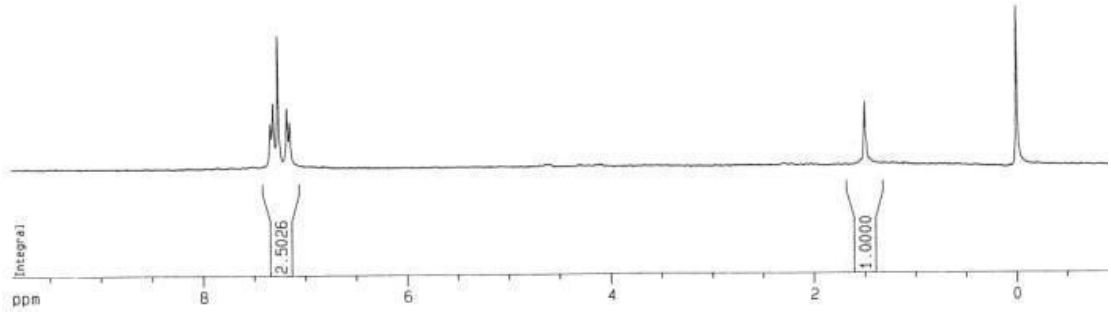

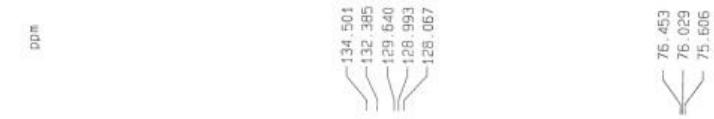

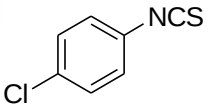

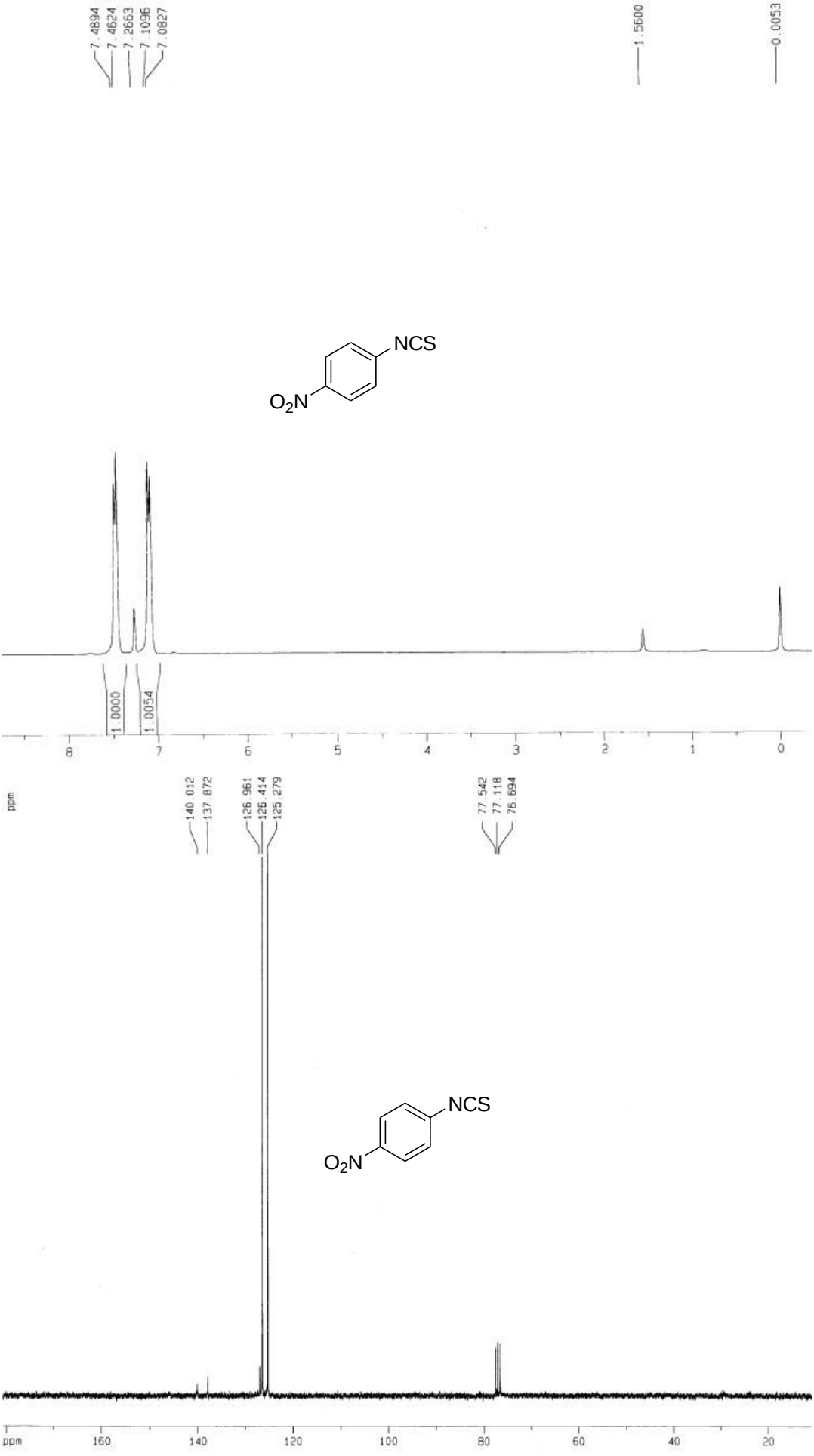
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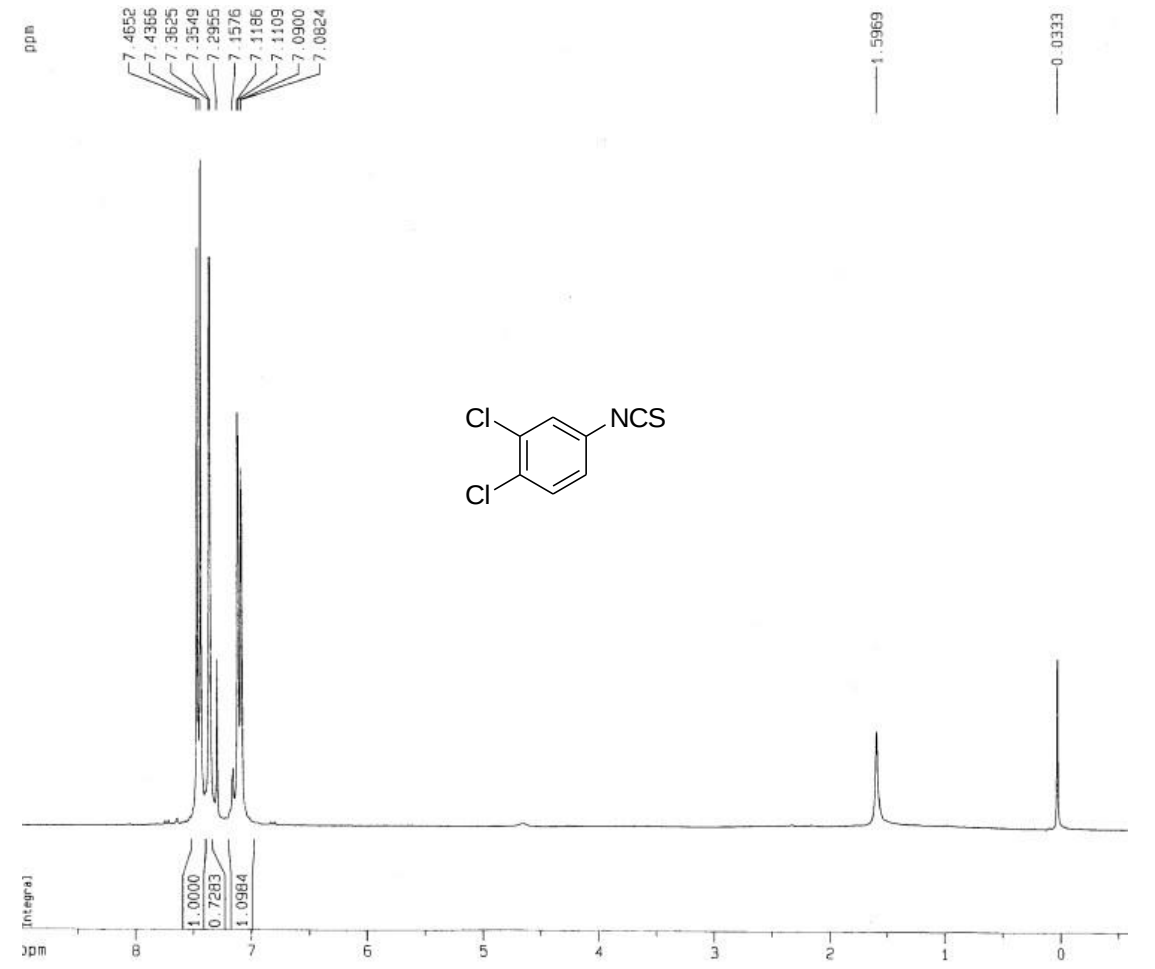

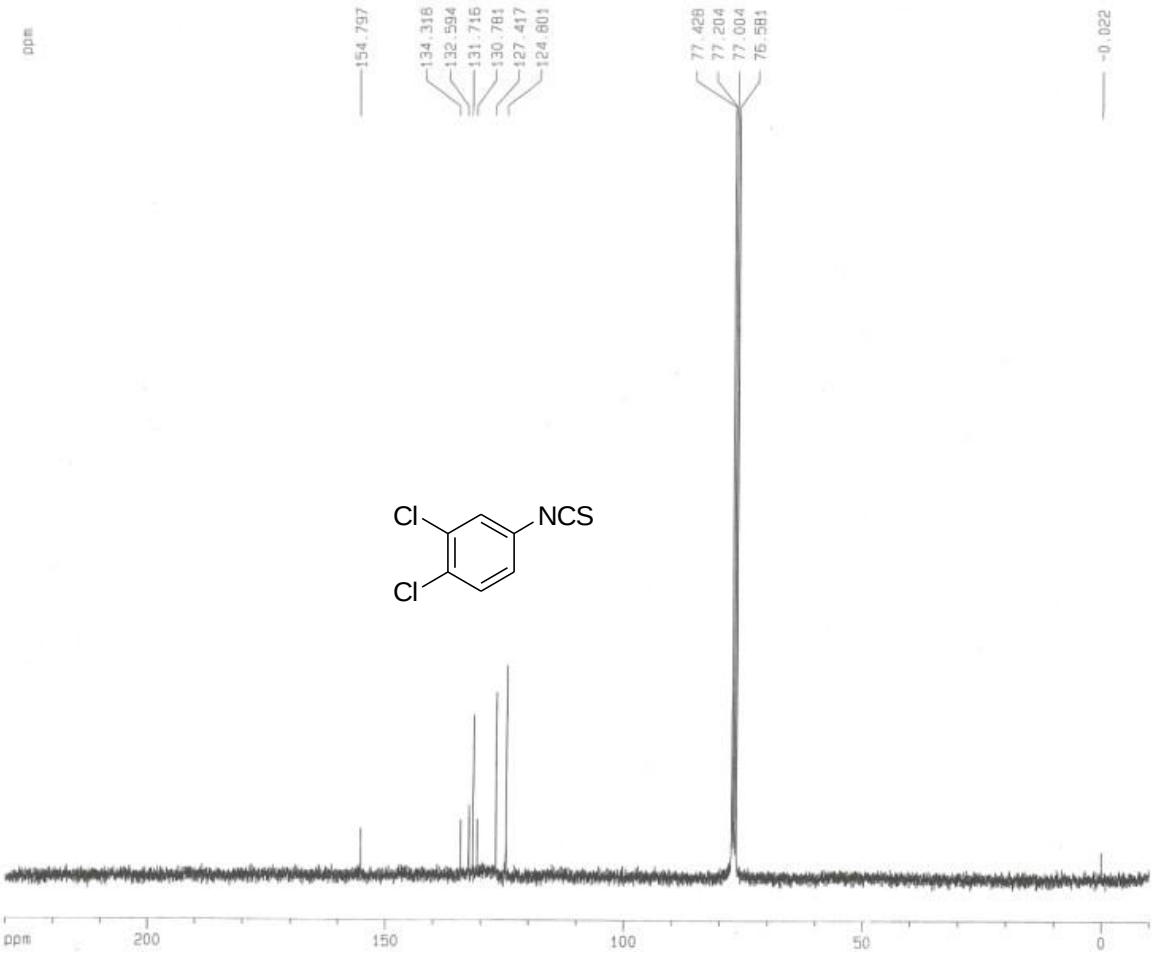

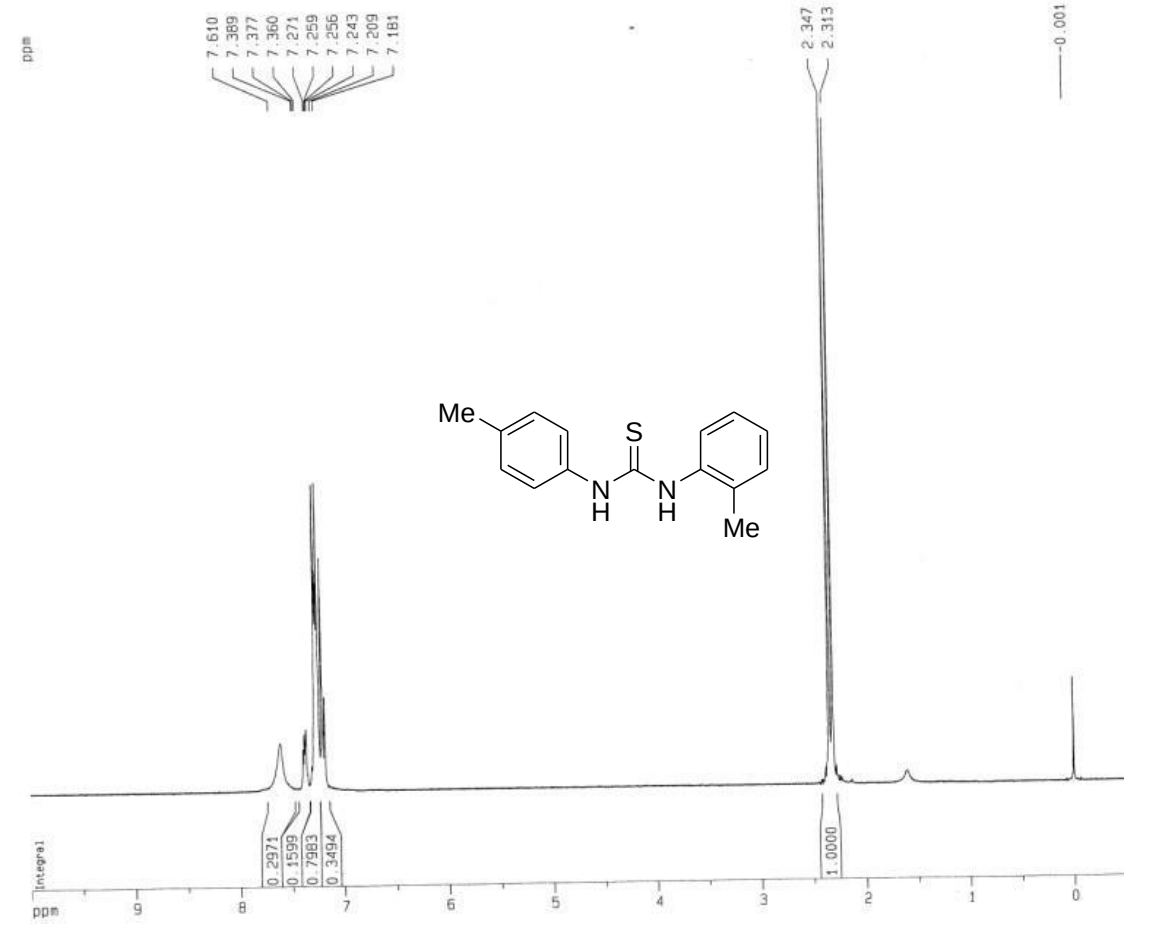

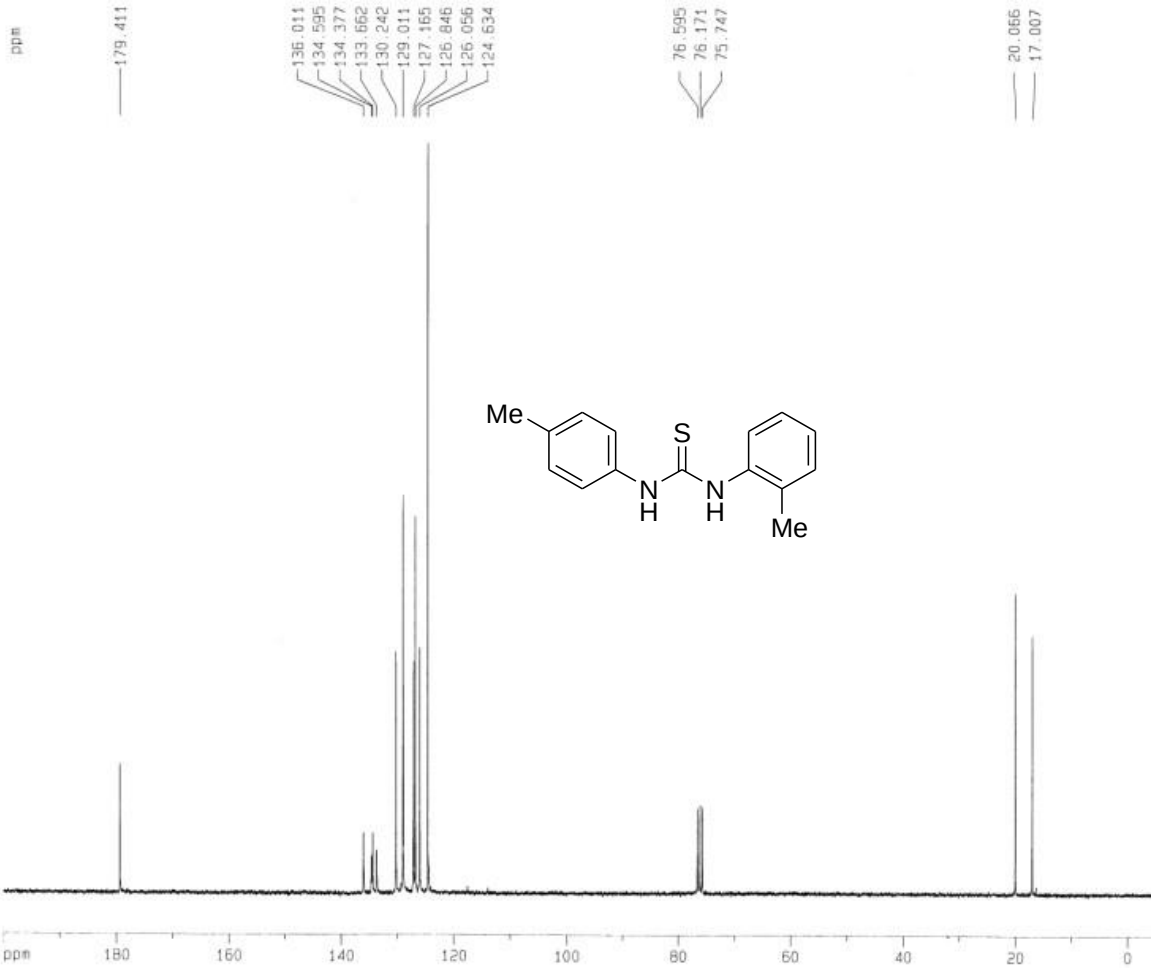

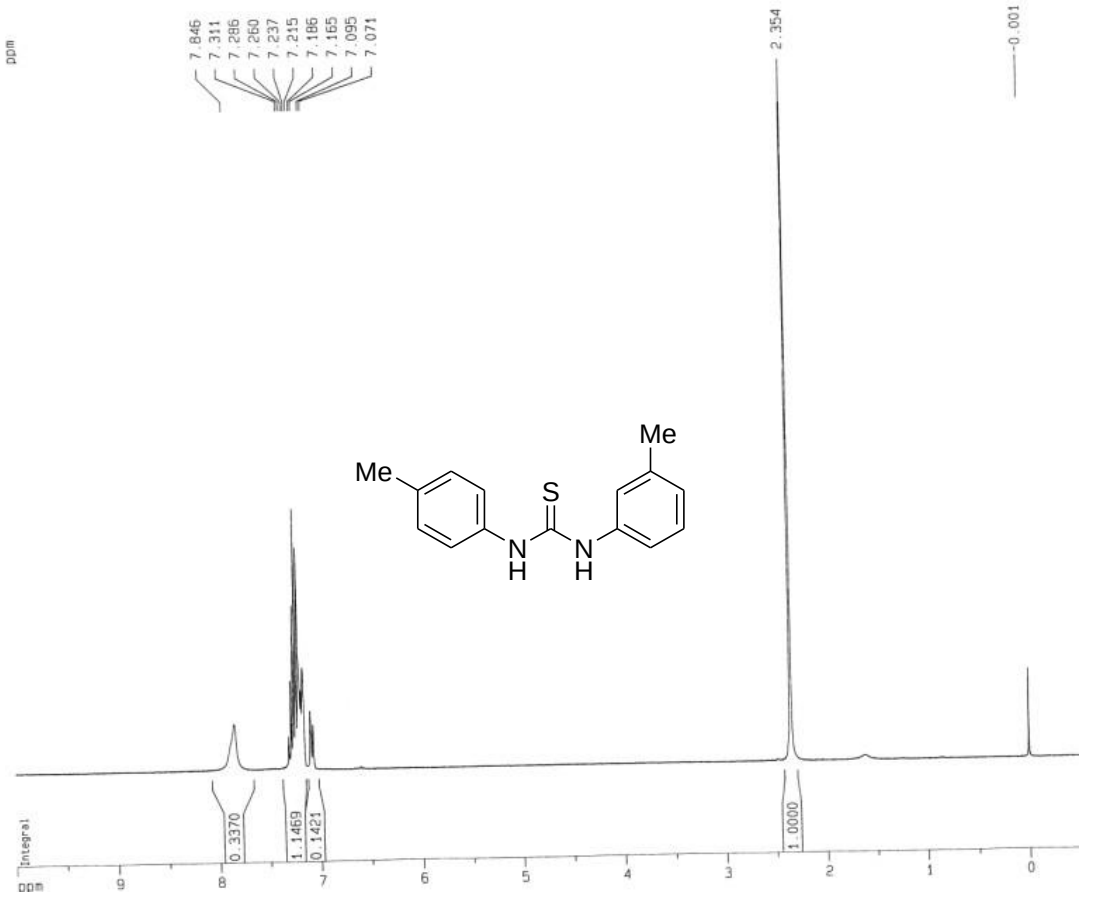
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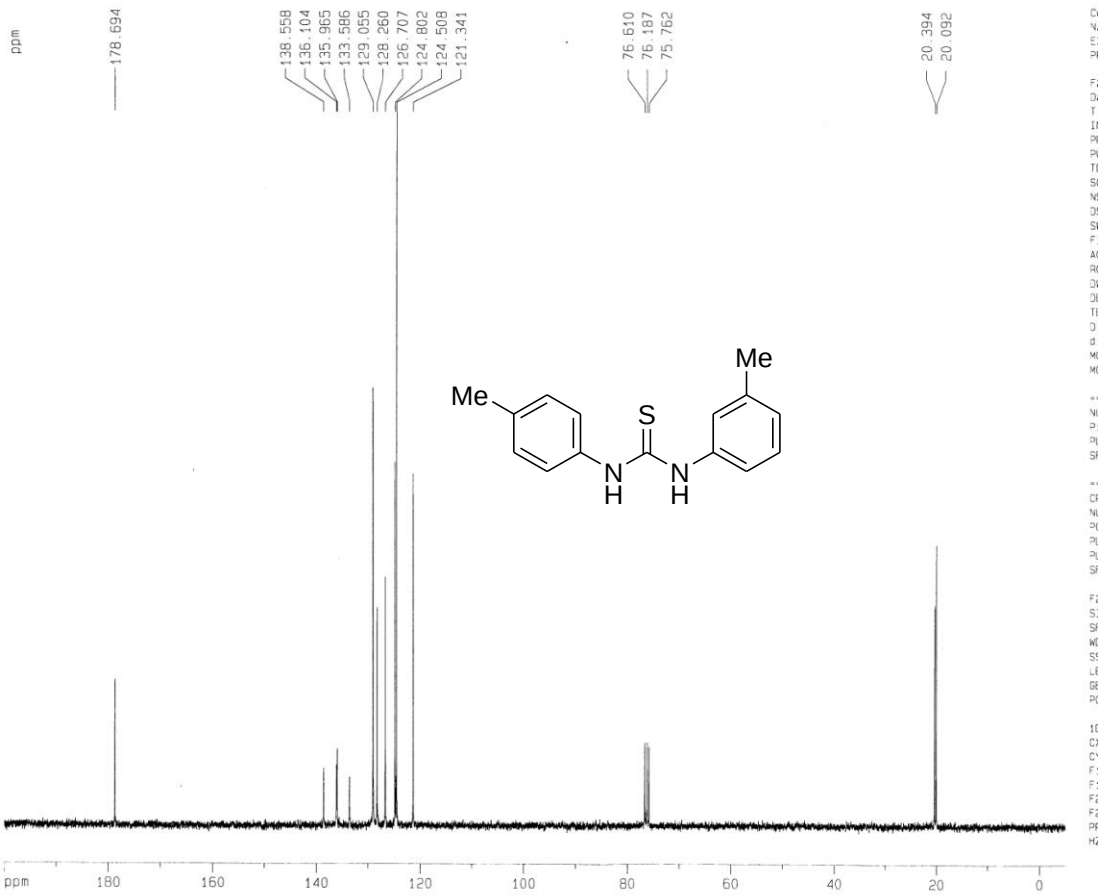
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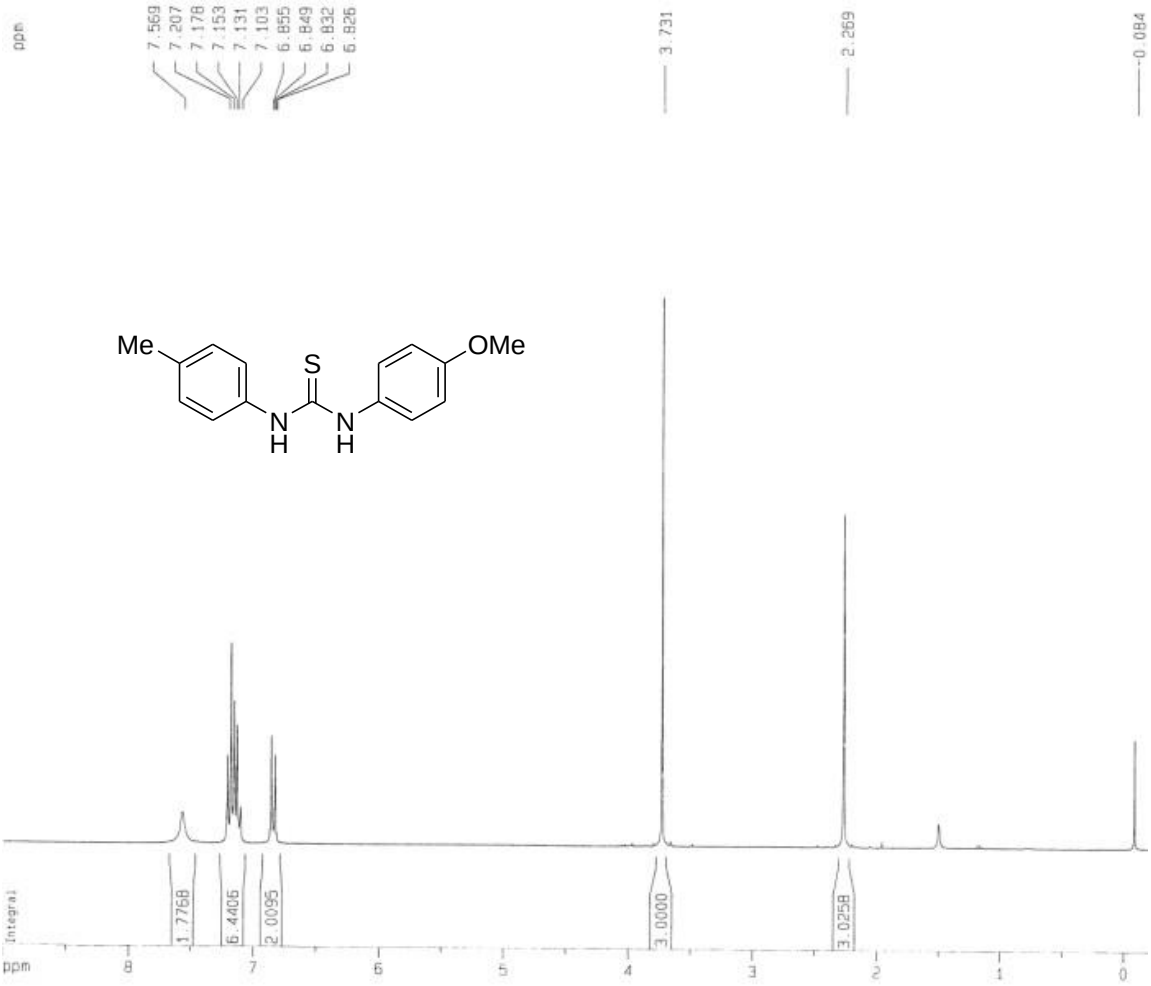
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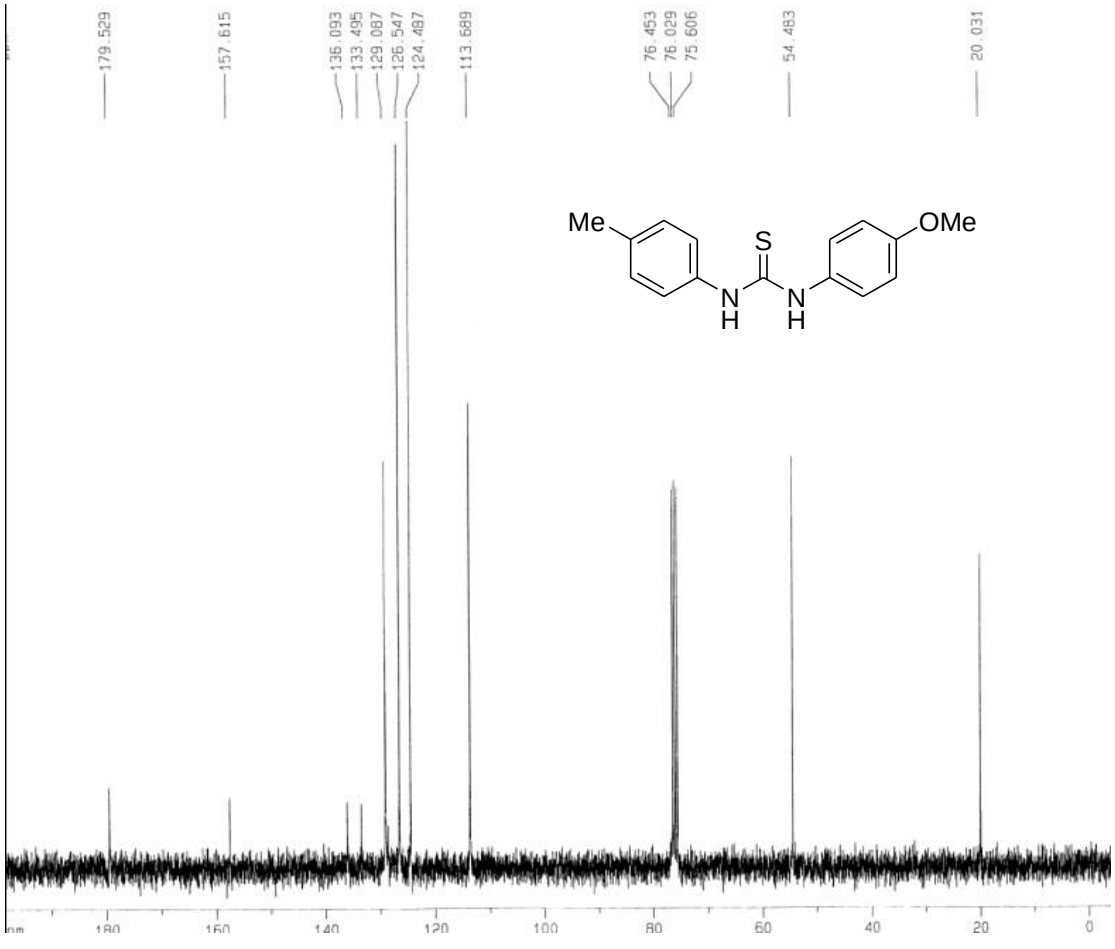
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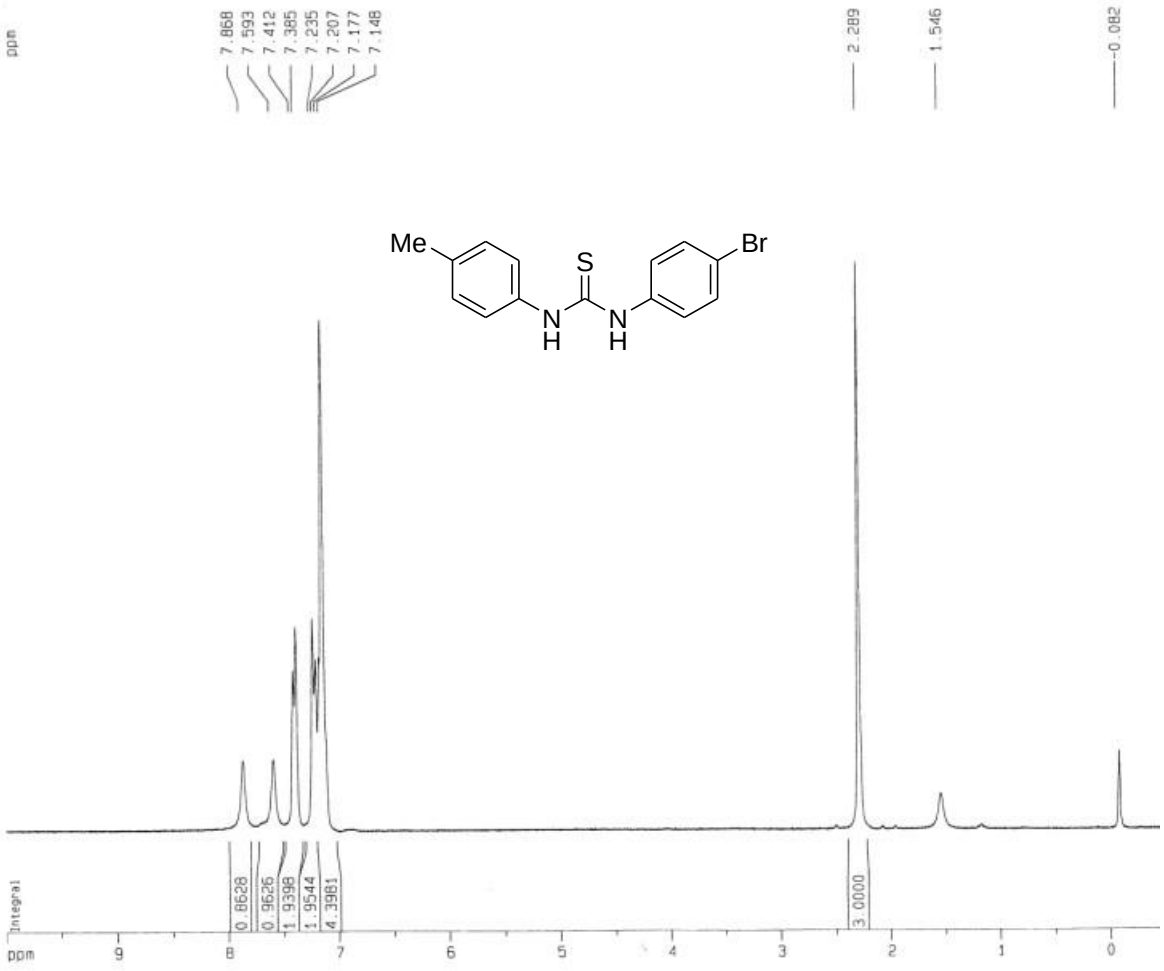

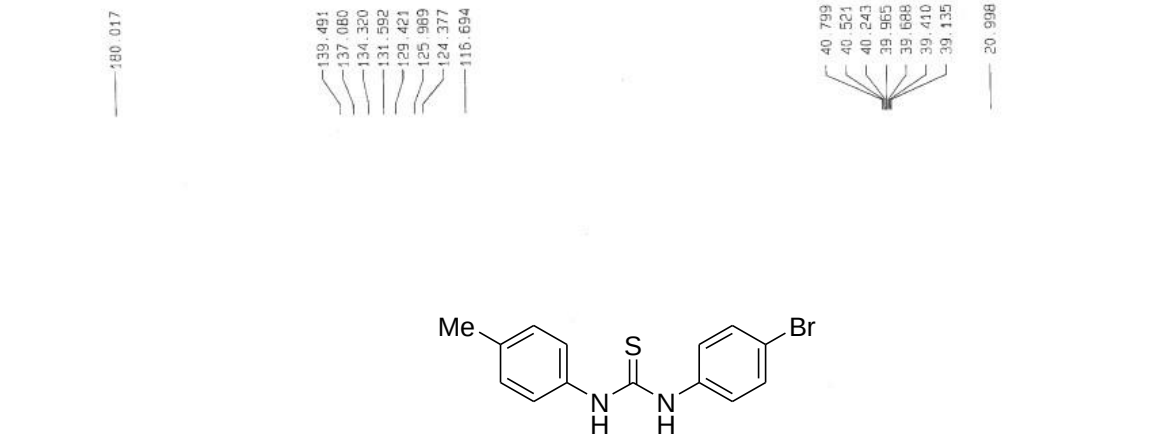

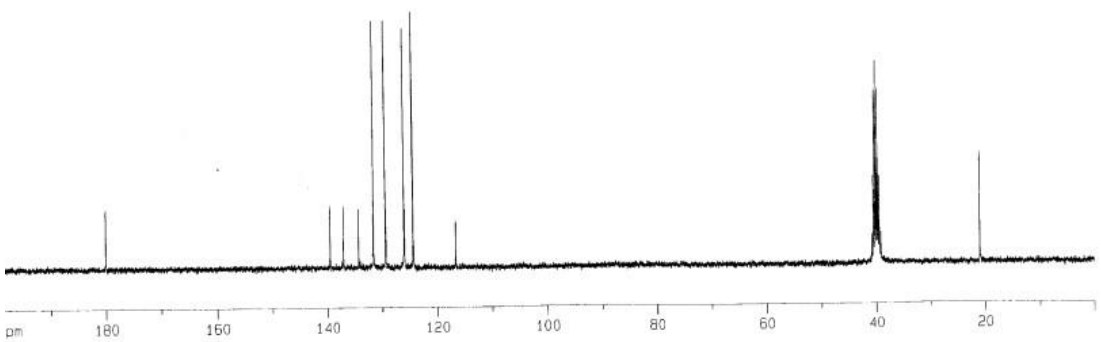

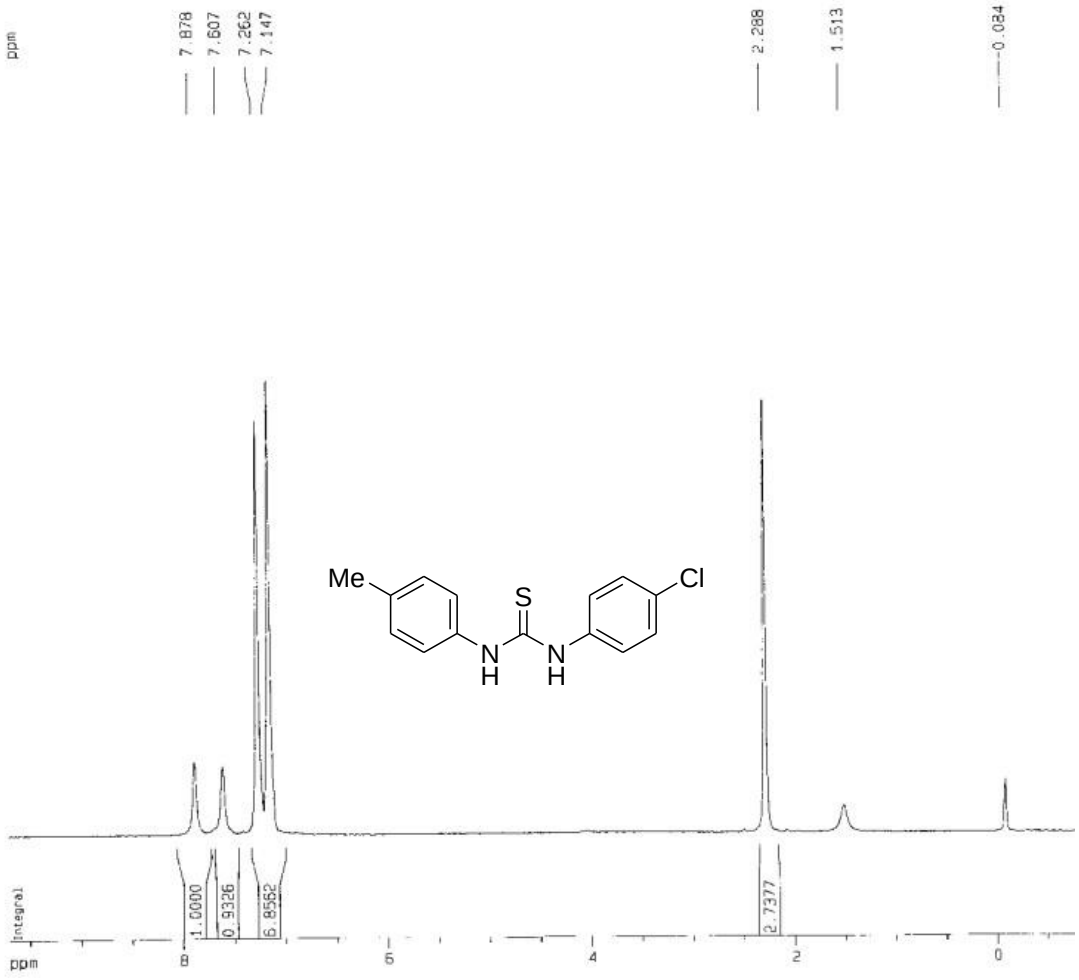
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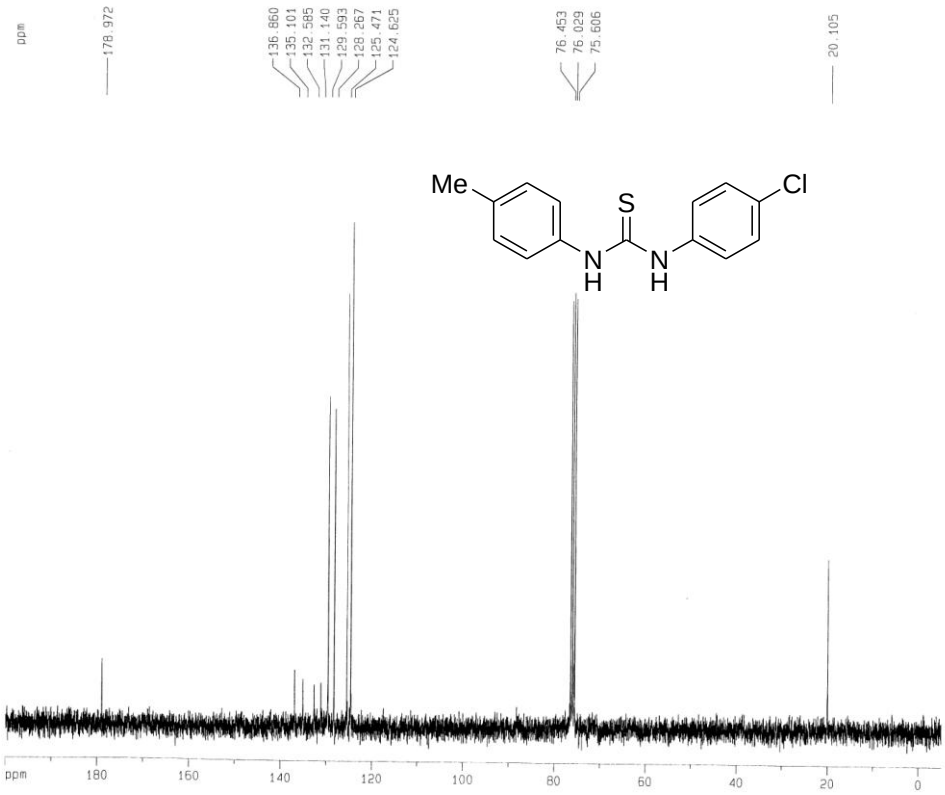
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132.585
131.140
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125.471
124.625
76.453
76.029
75.606
20.105
Me
S
N
H
N
H
Cl
ppm
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140
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100
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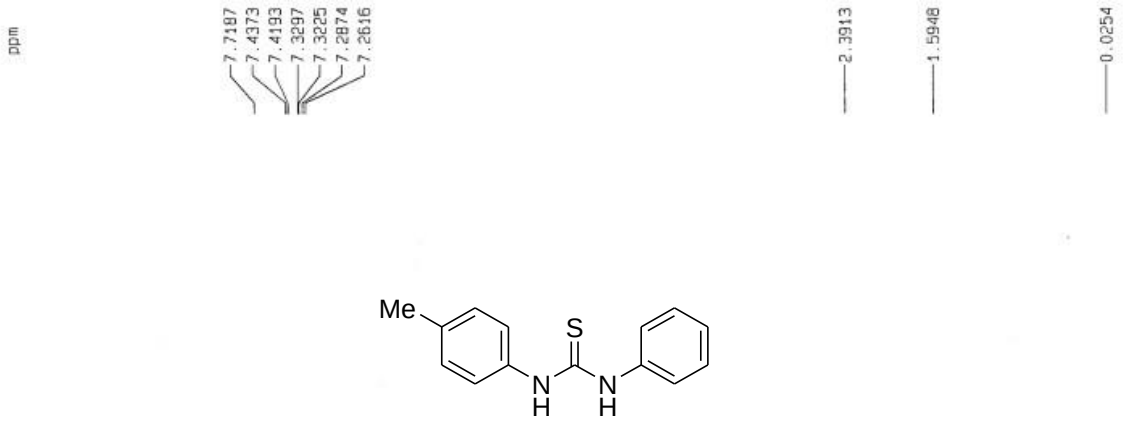
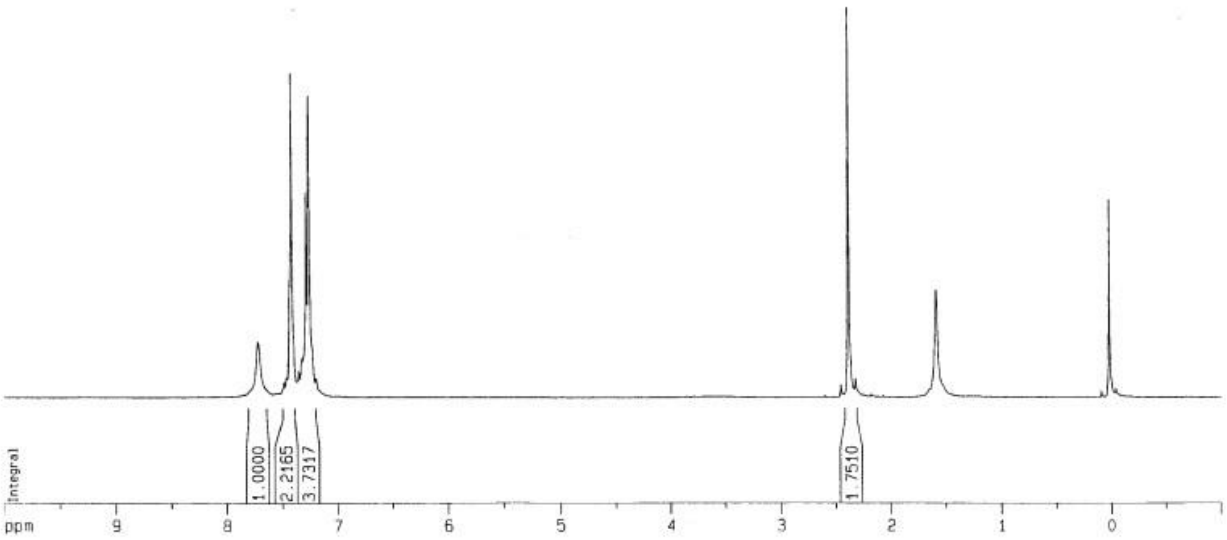
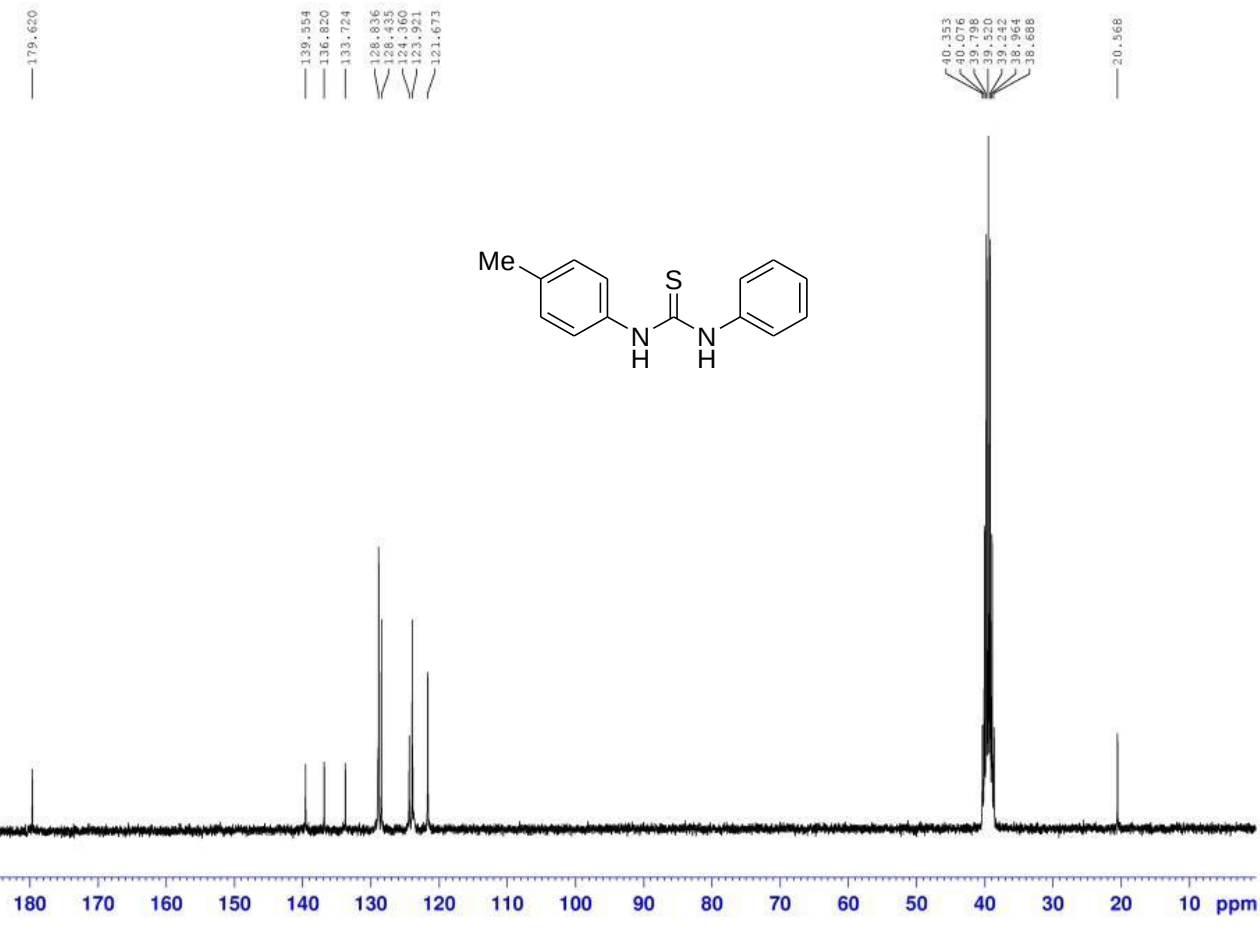
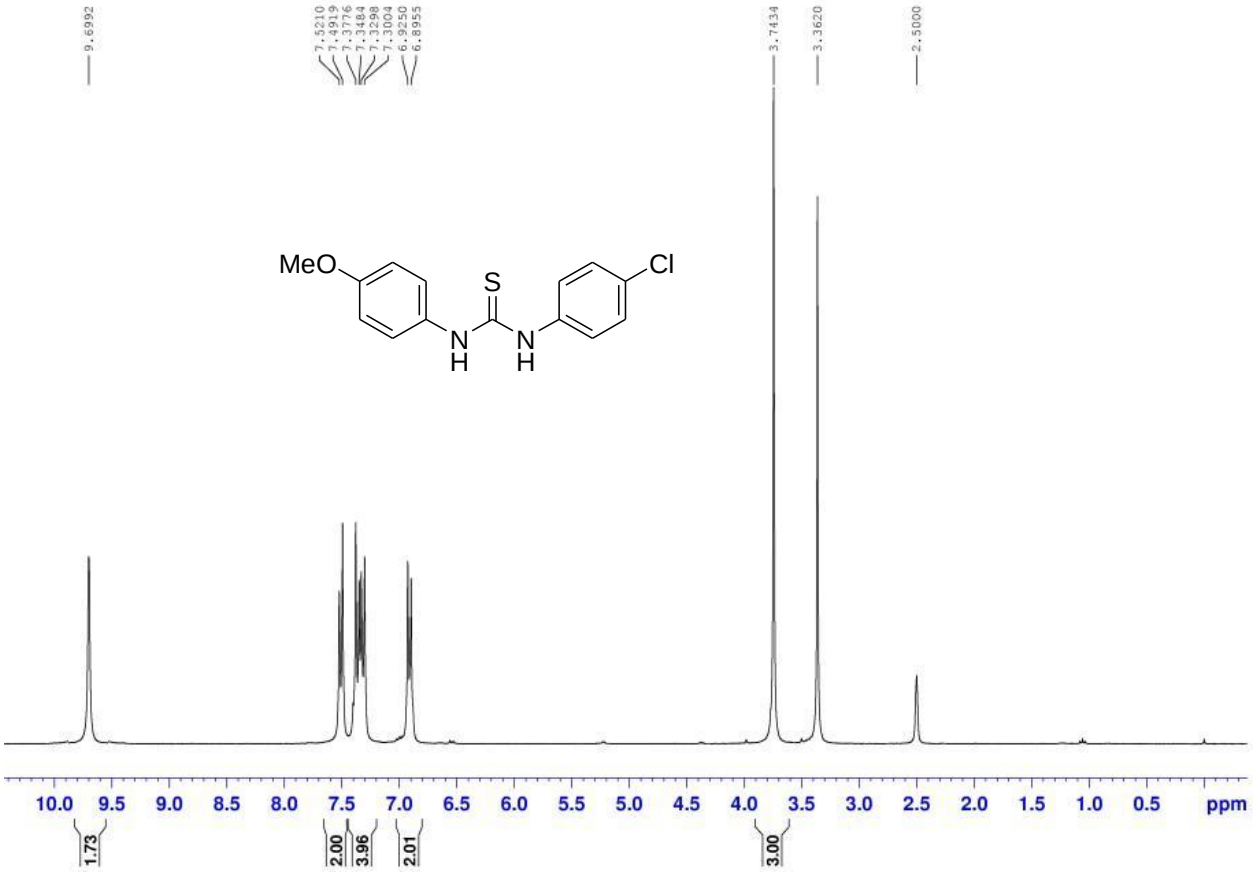
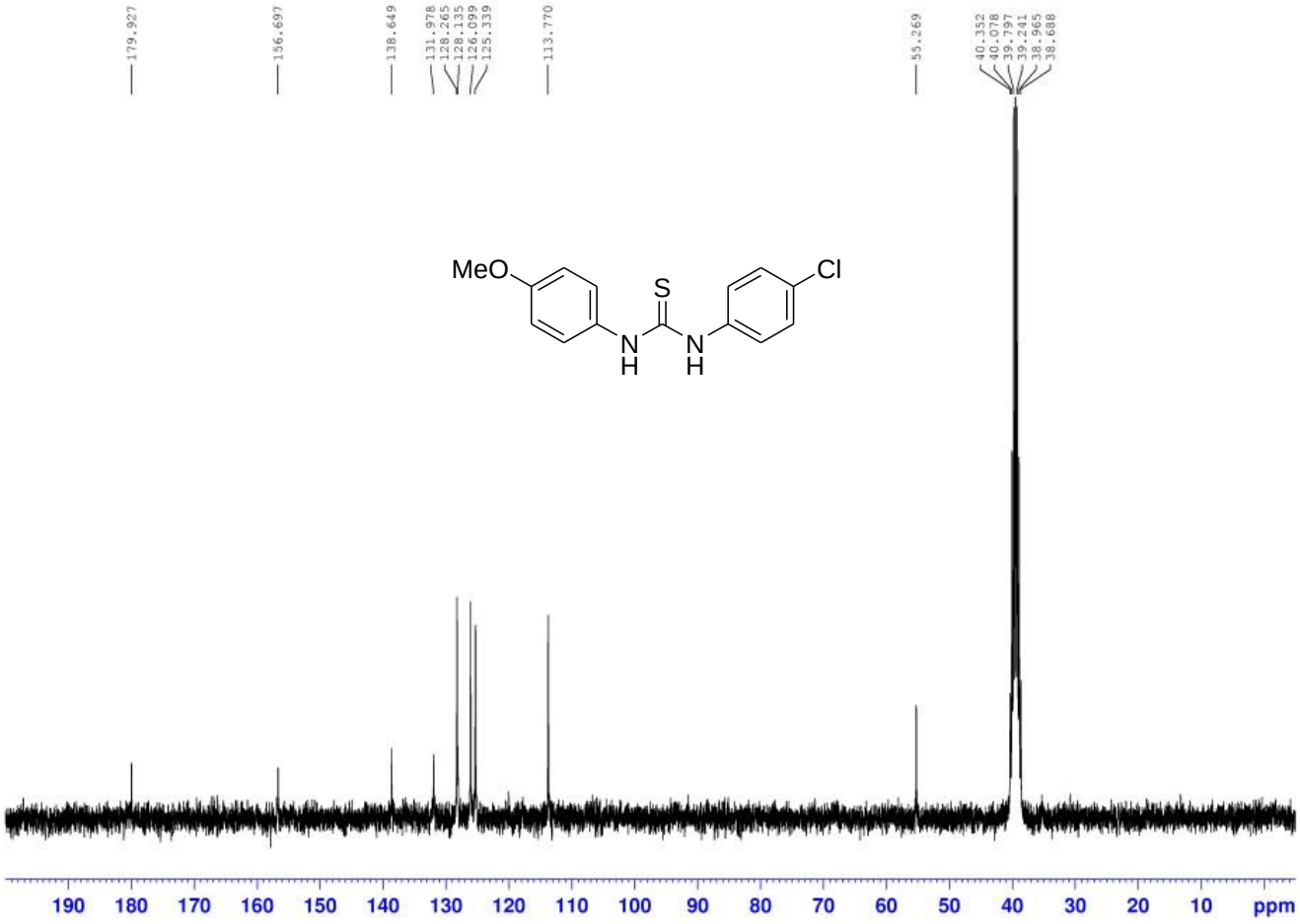
60
40
20
0

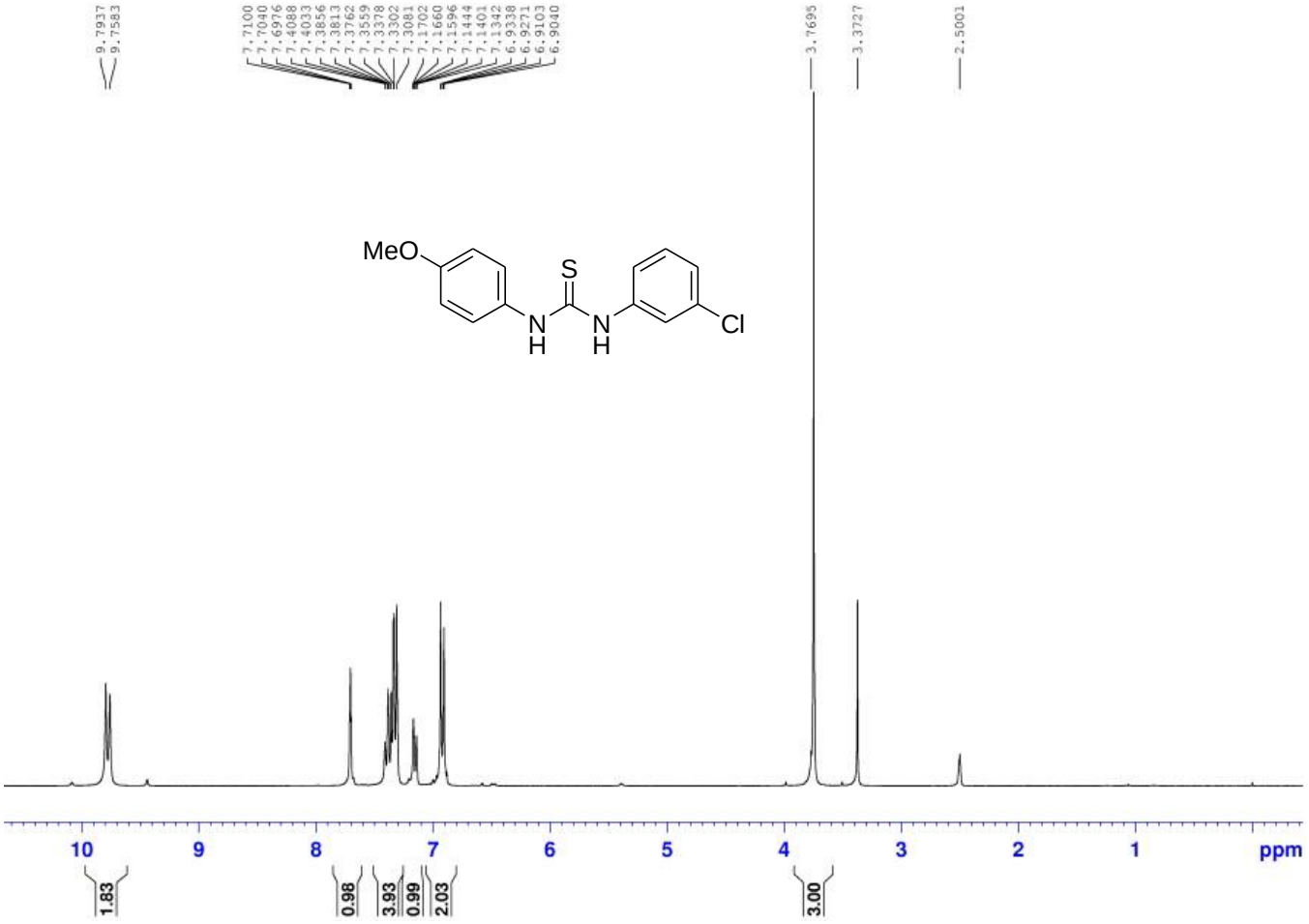


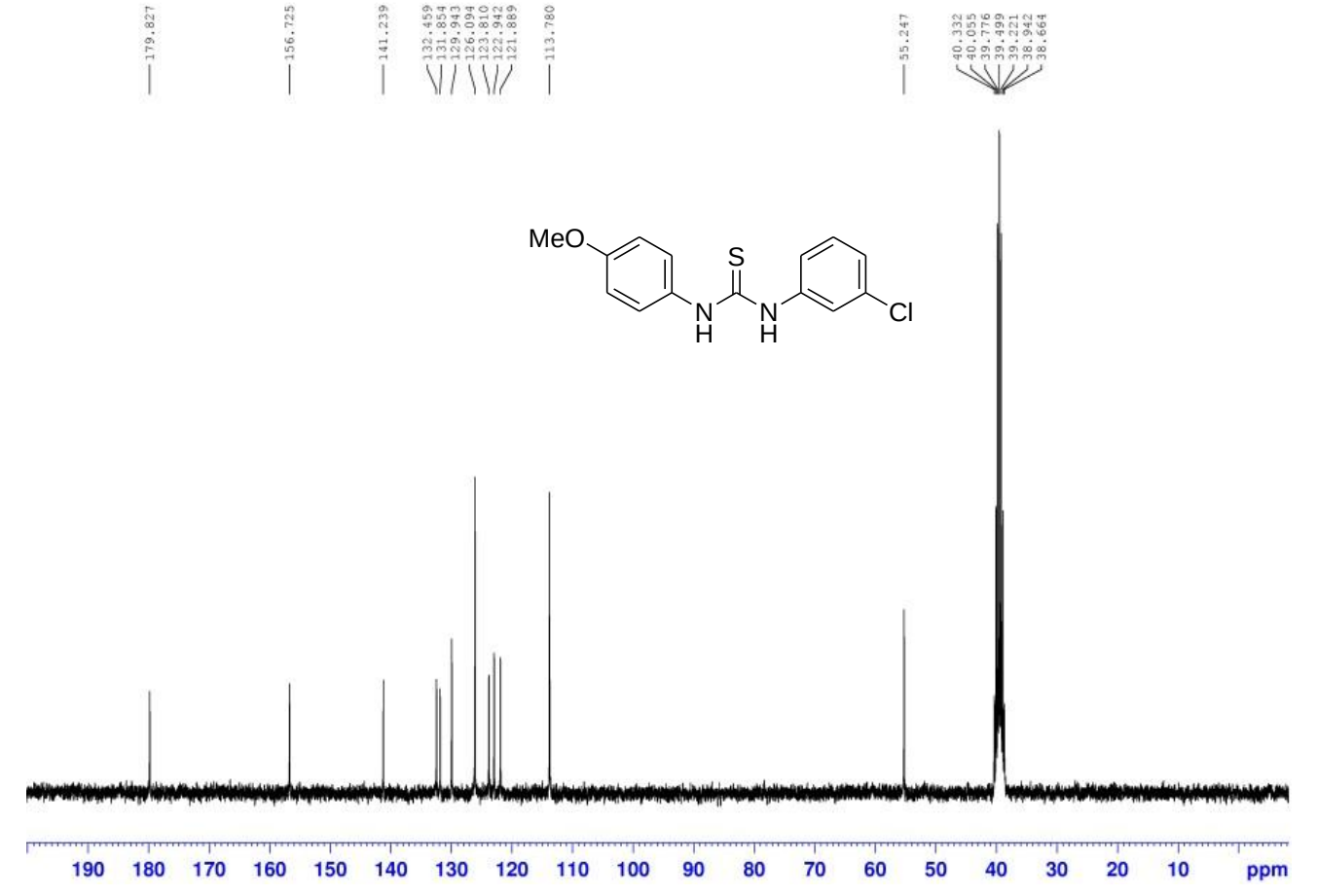


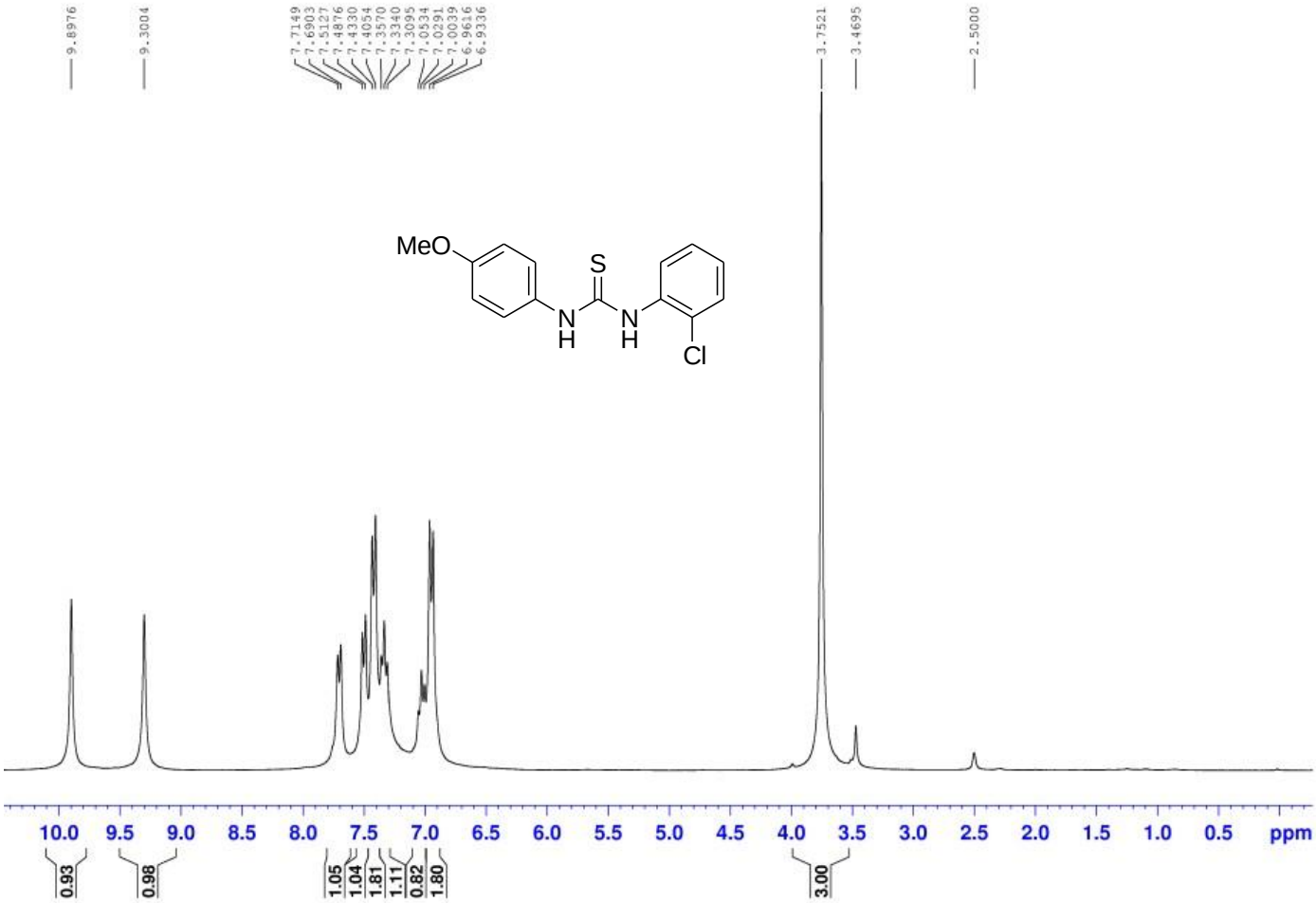


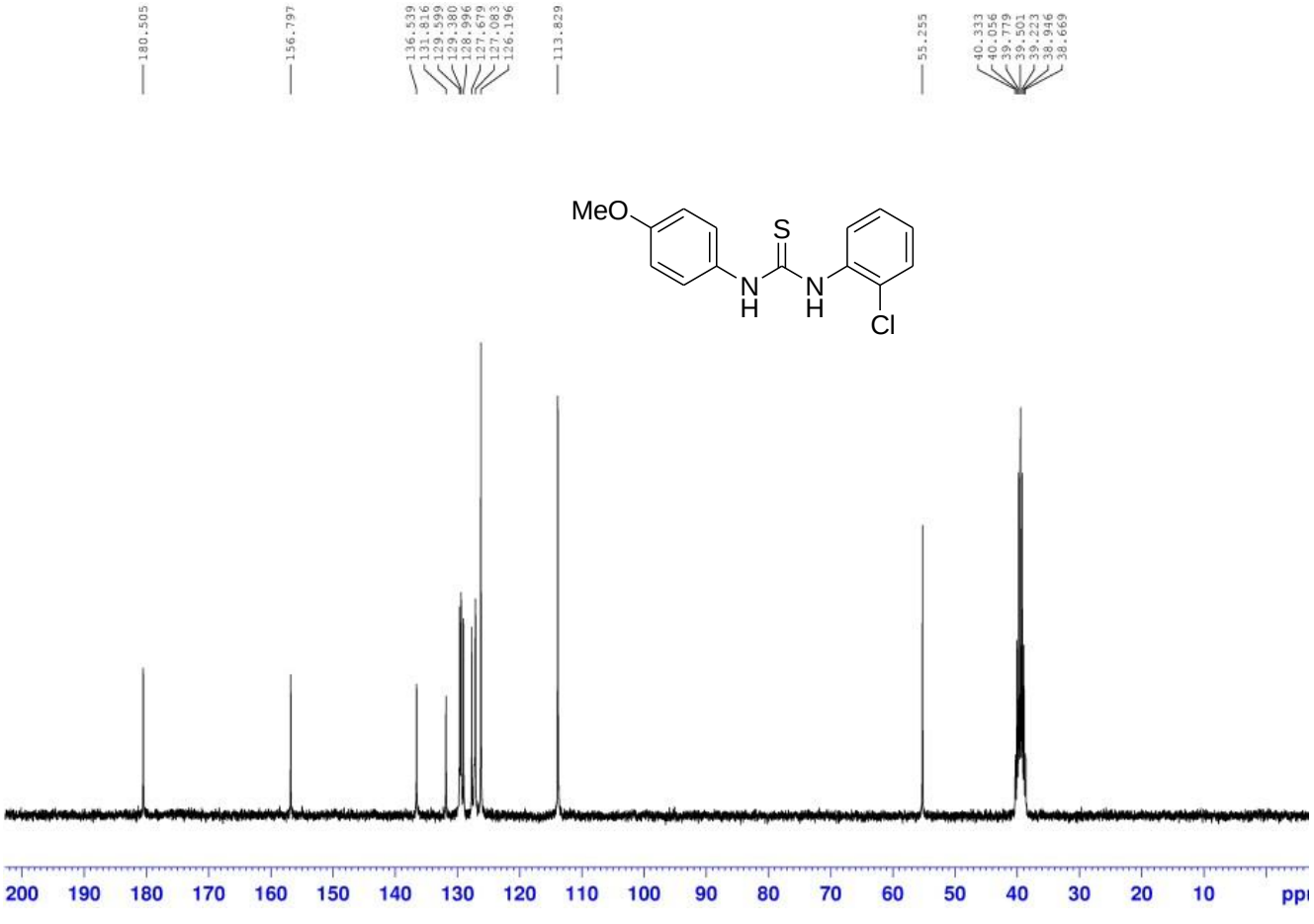


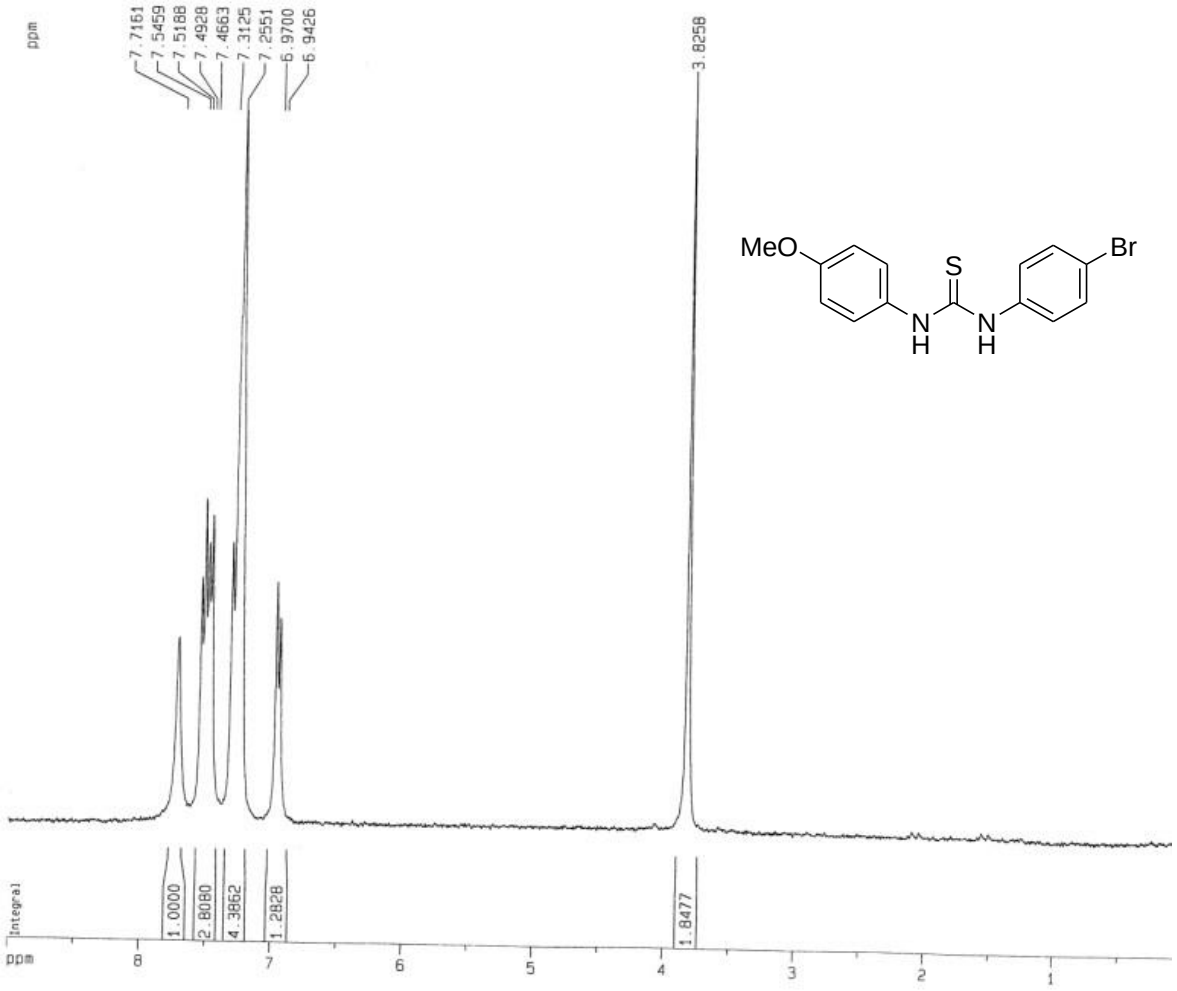








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7.4928
7.4663
7.3125
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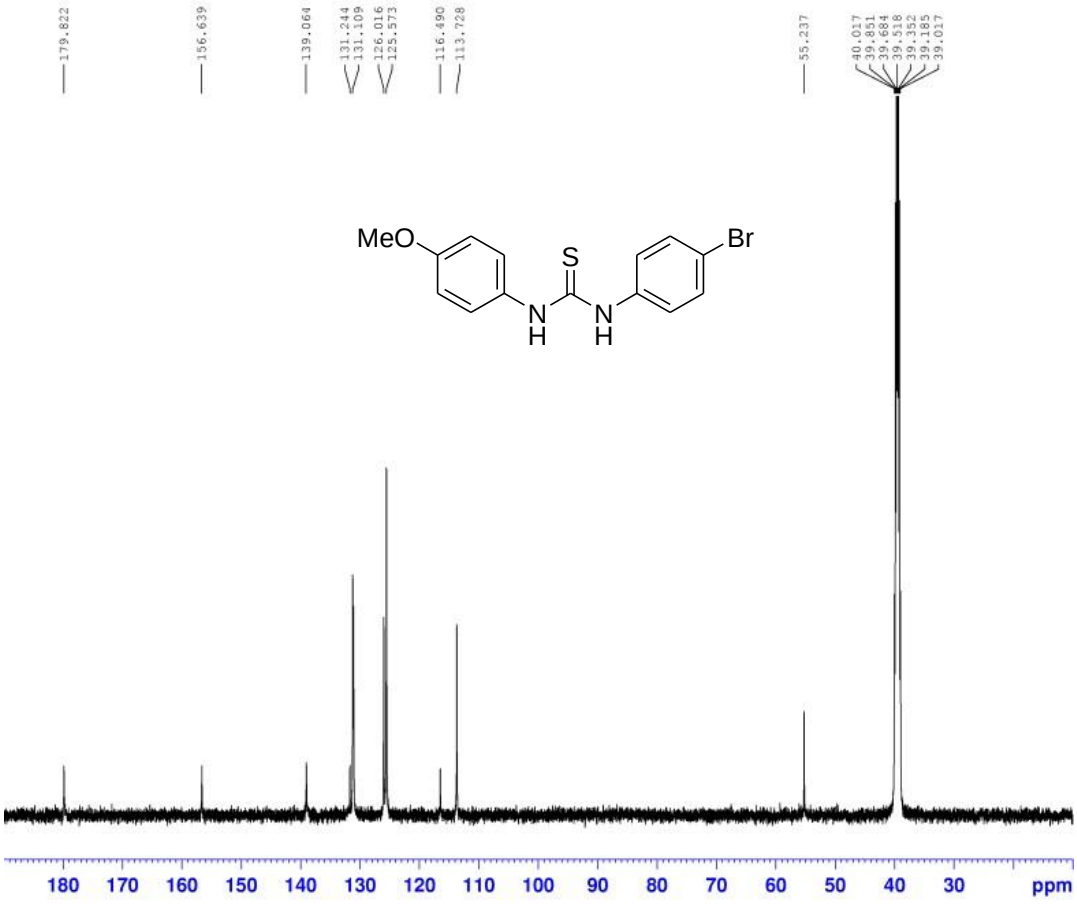
6.9700
6.9426
3.8258
MeO
Br
S
N
H
N
H
Integral
1.0000
2.8080
4.3862
1.2828
1.8477
ppm
8
7
6
5
4
3
2
1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166.639
139.064
131.244
131.109
126.016
125.573
116.490
113.728
55.237
40.017
39.851
39.684
39.518
39.352
39.185
39.017
MeO
Br
S
N
H
N
H
180
170
160
150
140
130
120
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90
80
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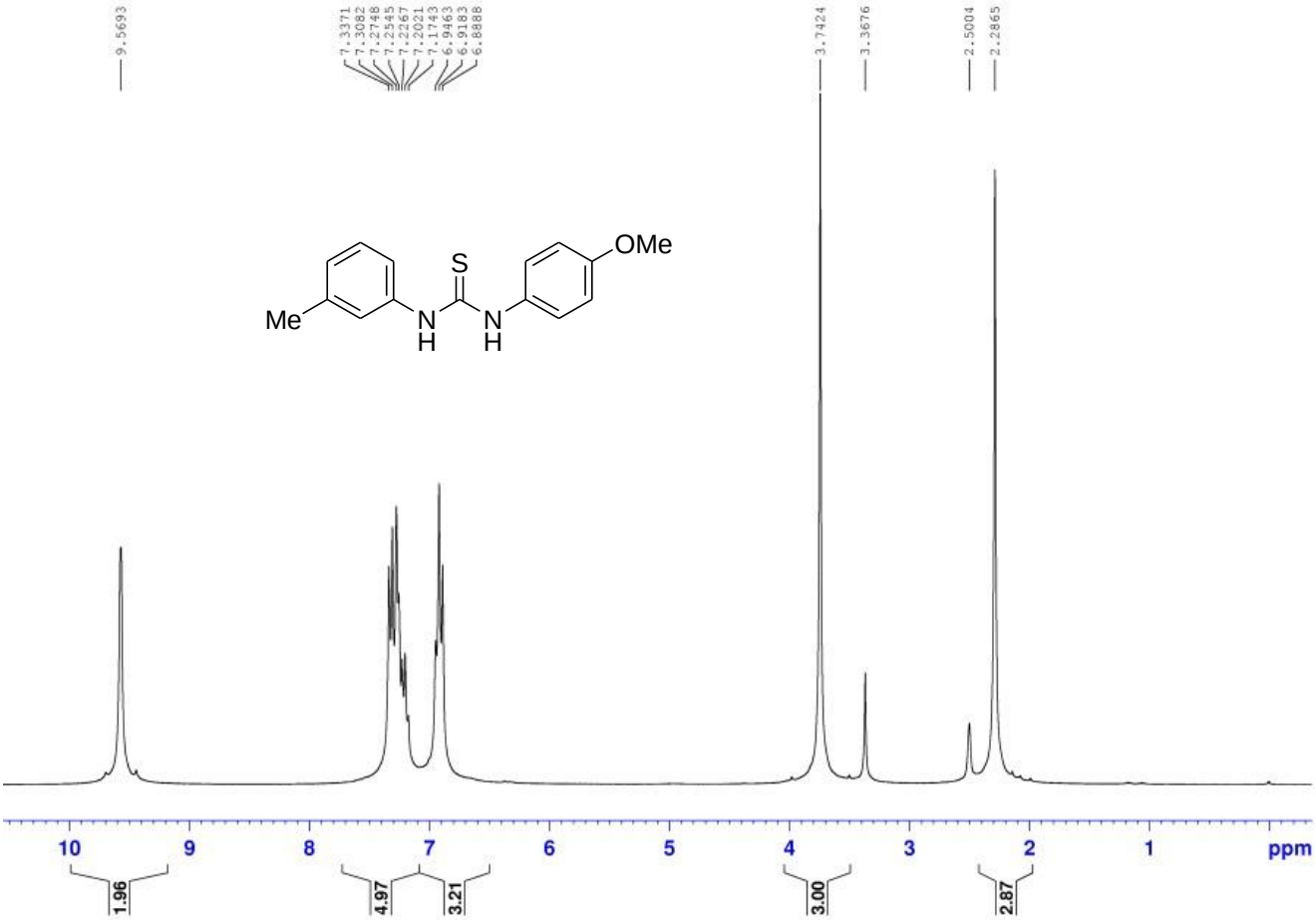
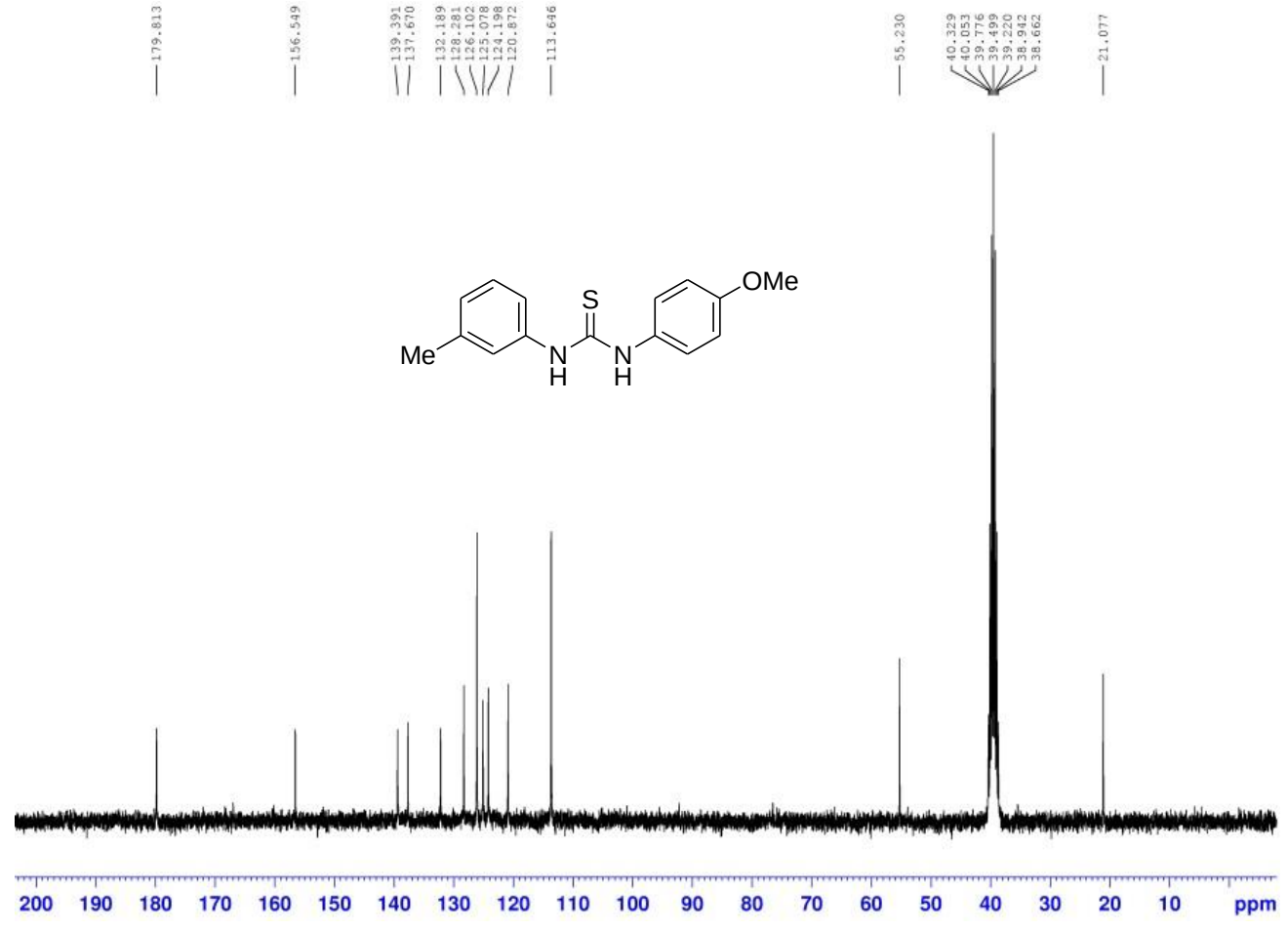
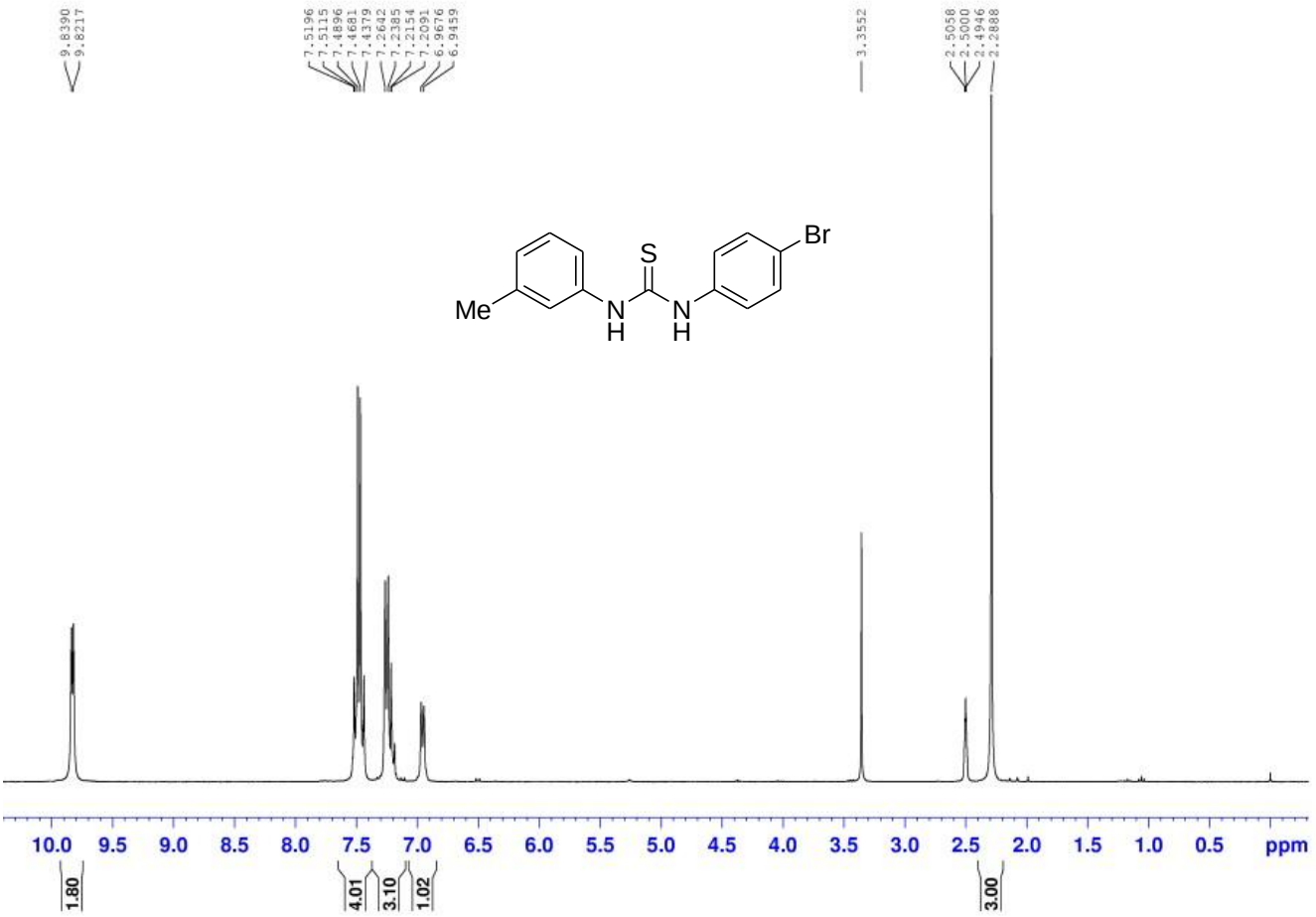
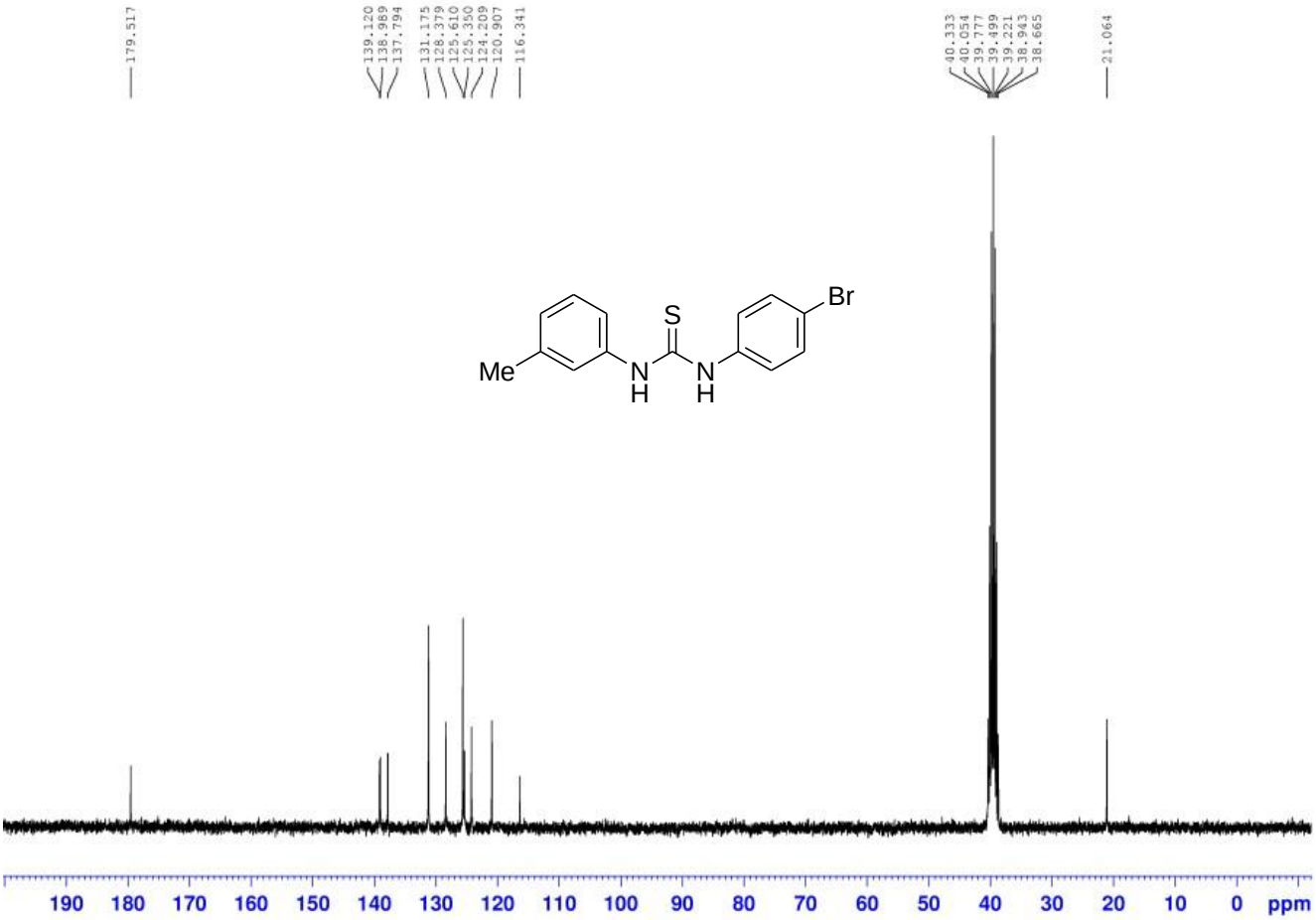
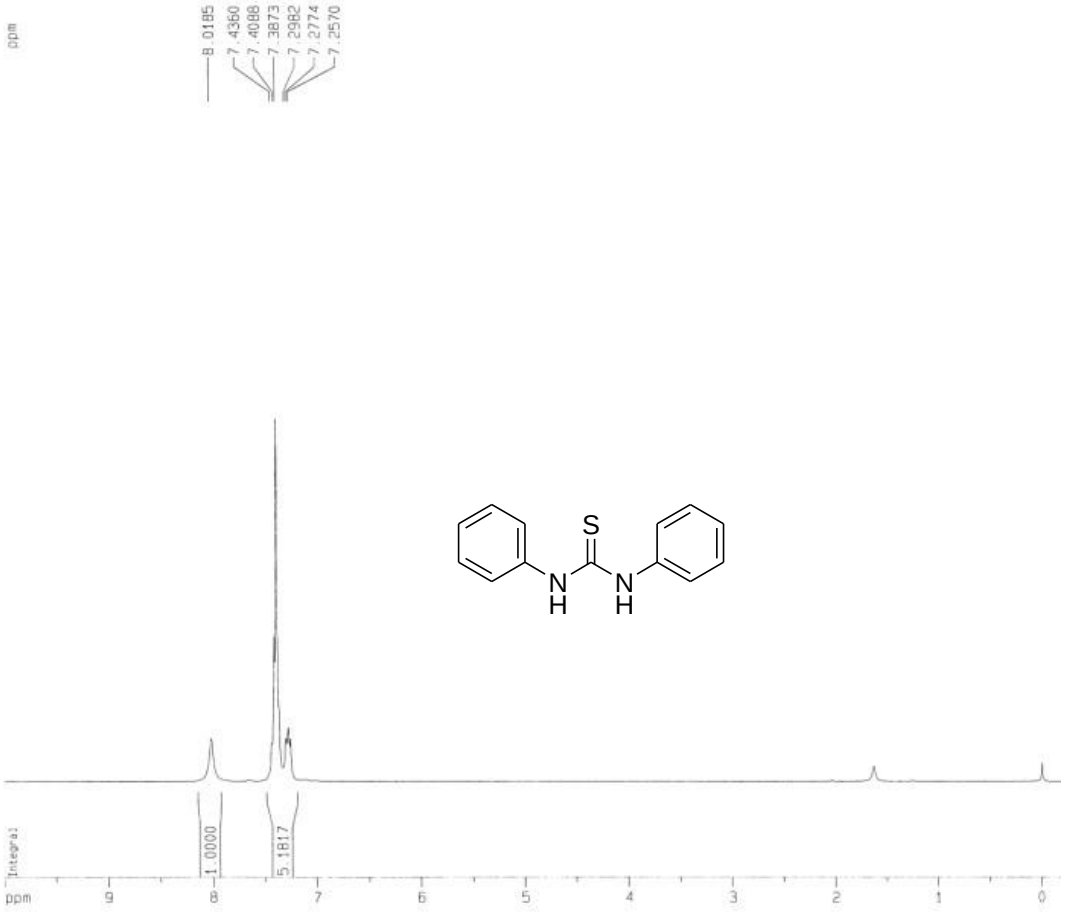
50
40
30
ppm

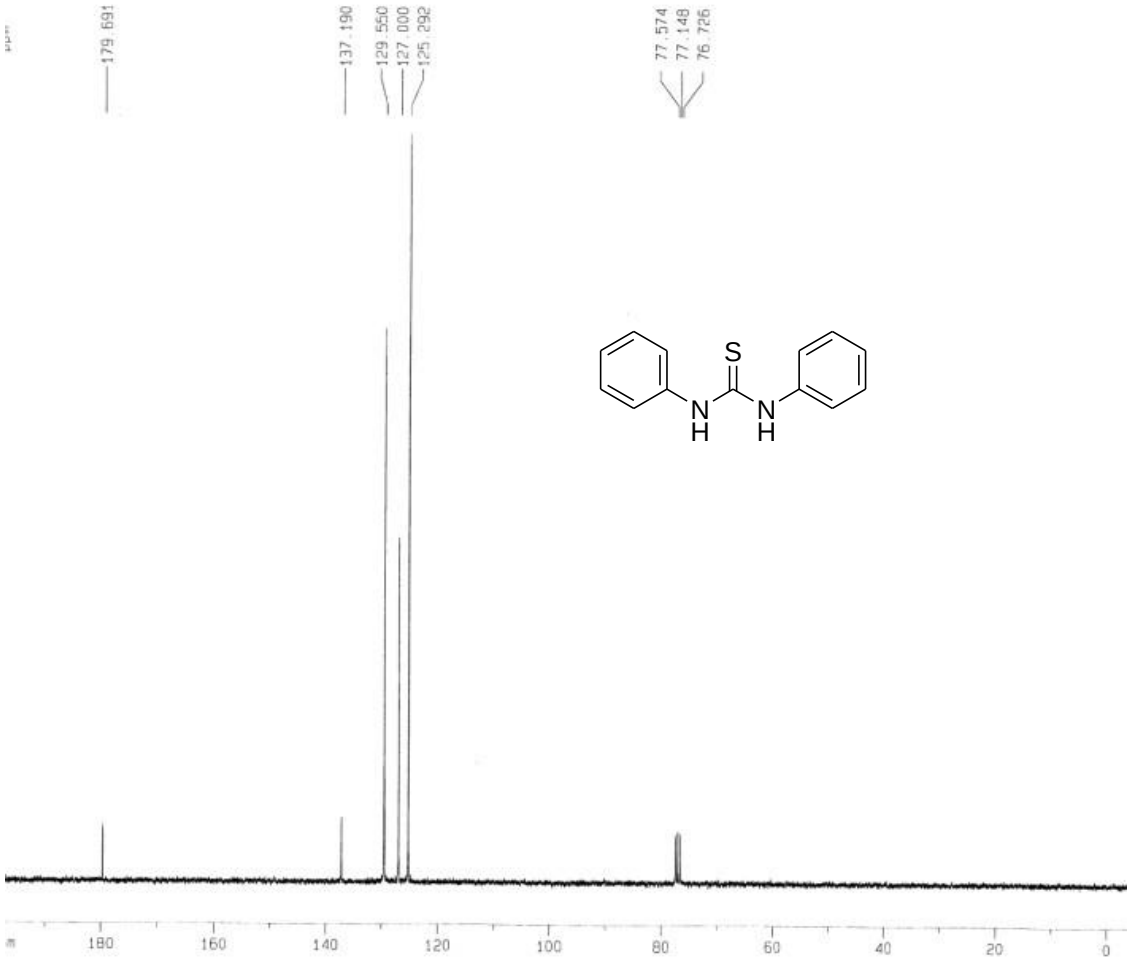









8.0185
7.4360
7.4088
7.3873
7.2982
7.2774
7.2570
S
N
H
N
H
Integral
1.0000
5.1817
ppm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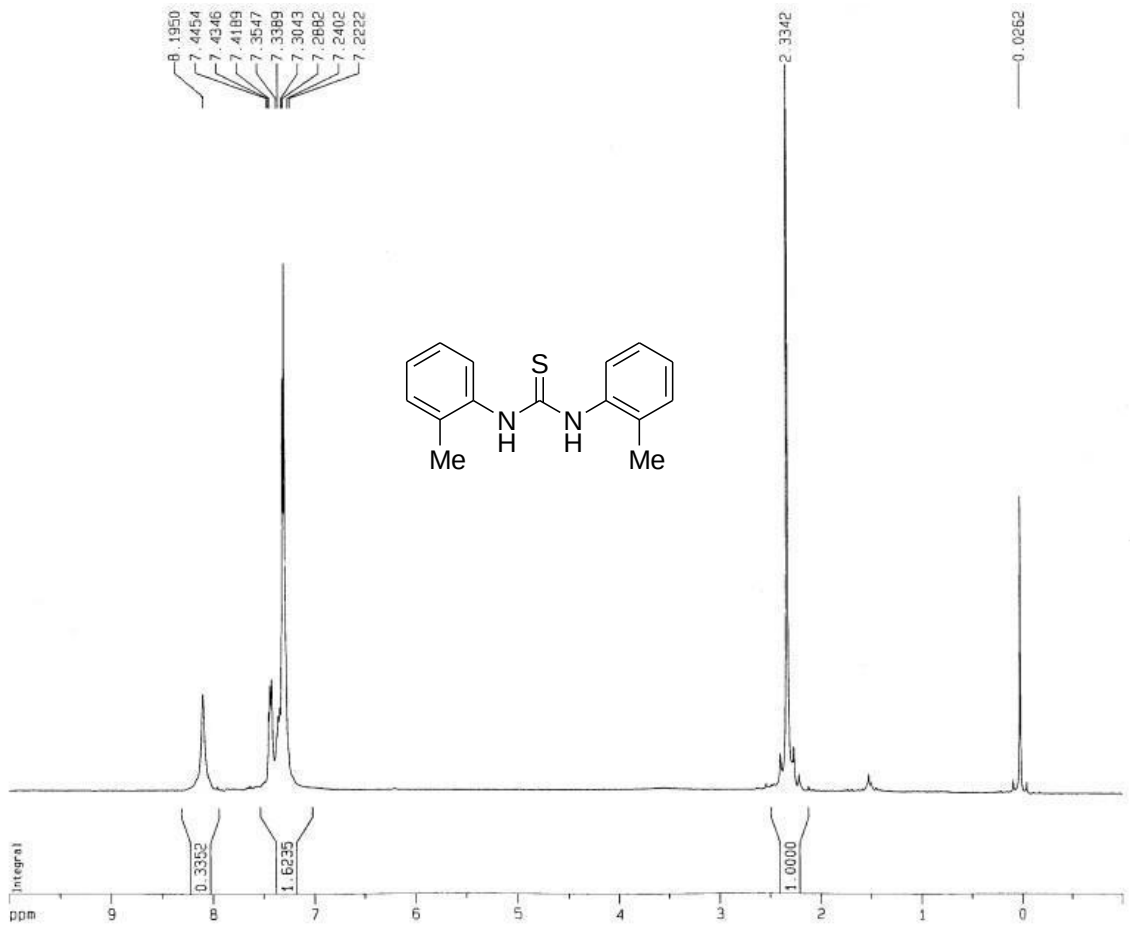
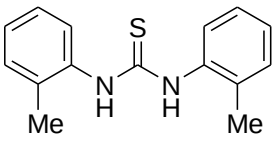
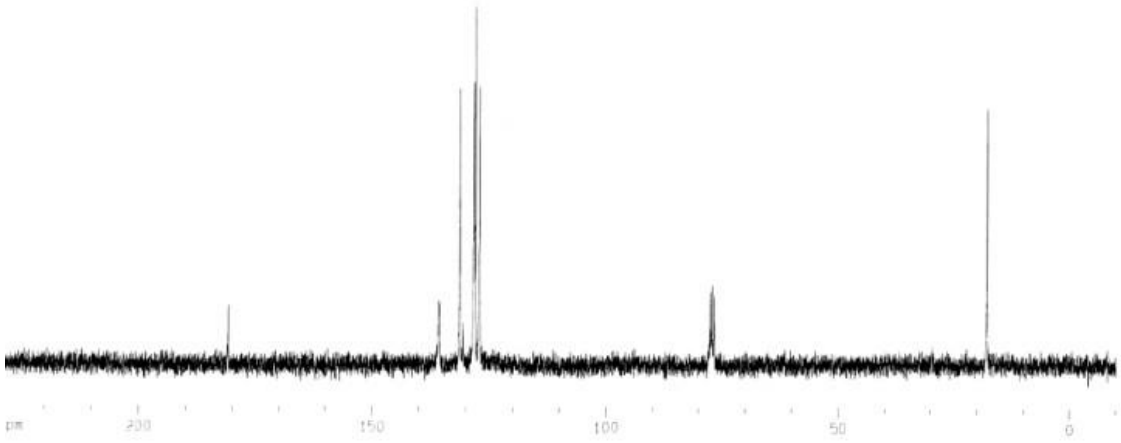
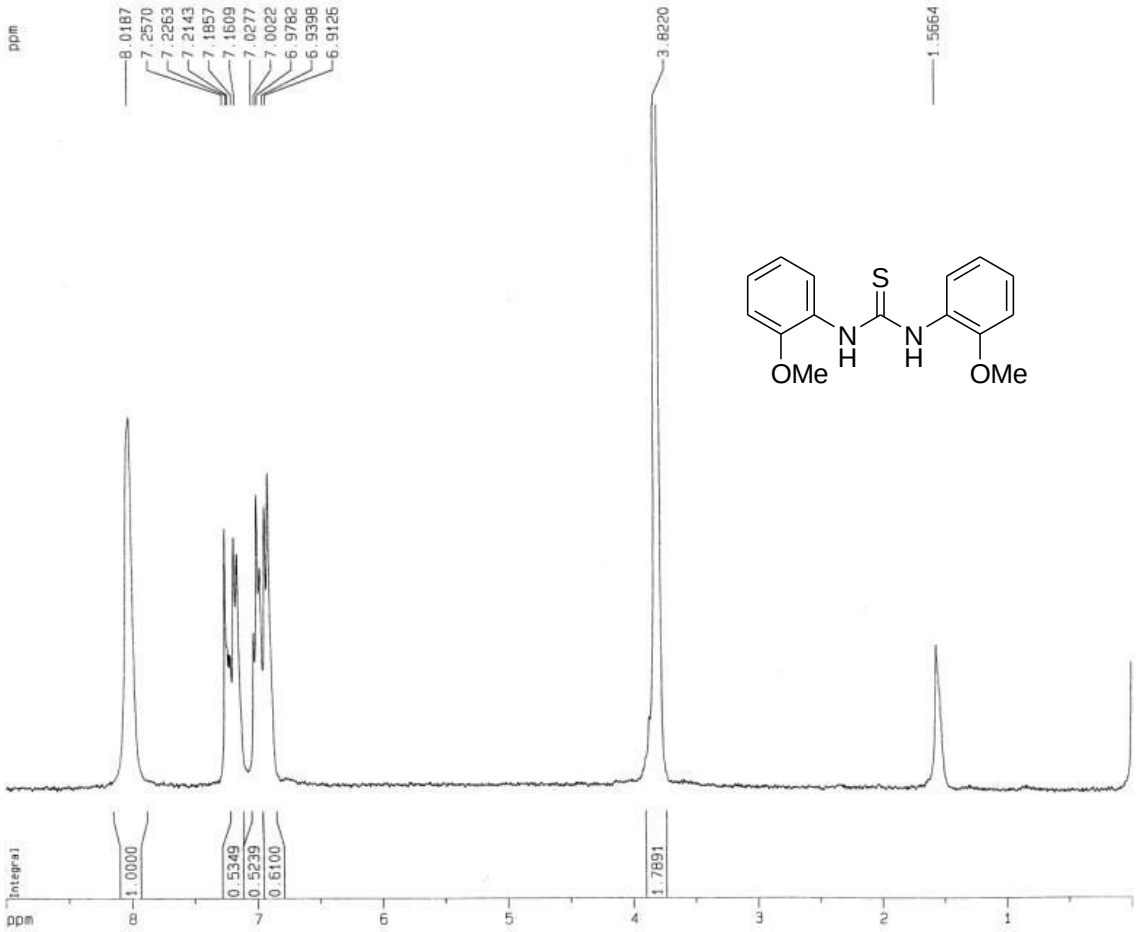
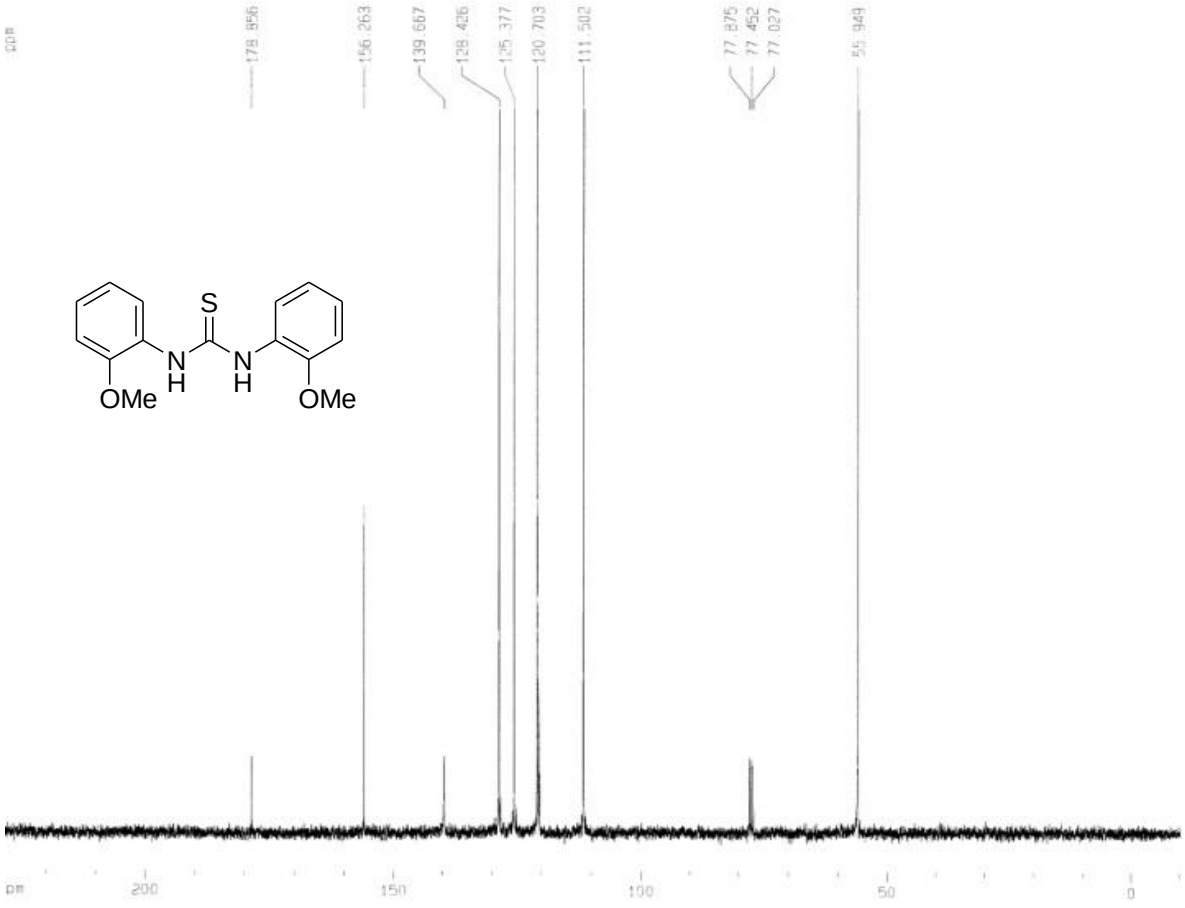
129.550
127.000
125.292
77.574
77.148
76.726
S
N
H
N
H

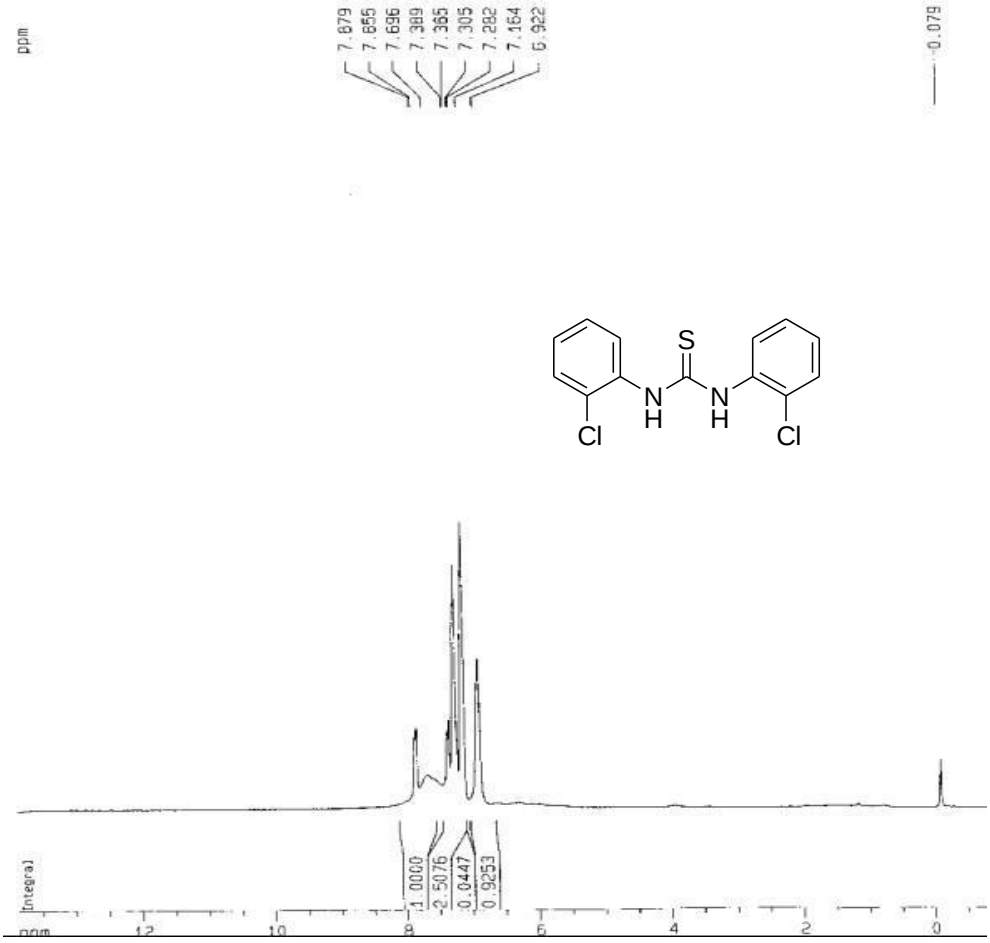








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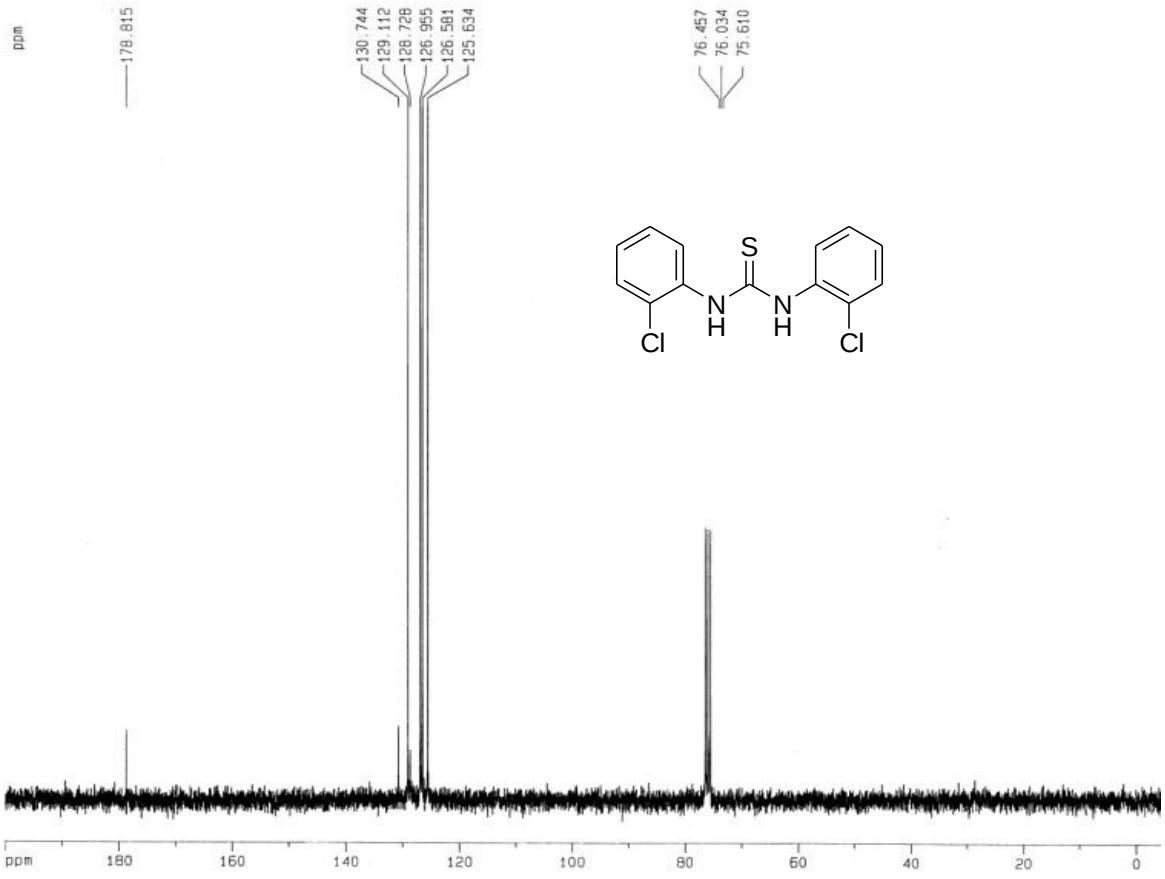
7.164
6.922
0.079
S
N
H
N
H
Cl
Cl
Integral
1.0000
2.5076
0.0447
0.9253
12
10
8
6
4
2
0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126.955
126.581
125.634
76.457
76.034
75.610
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H
N
H
Cl
Cl
ppm
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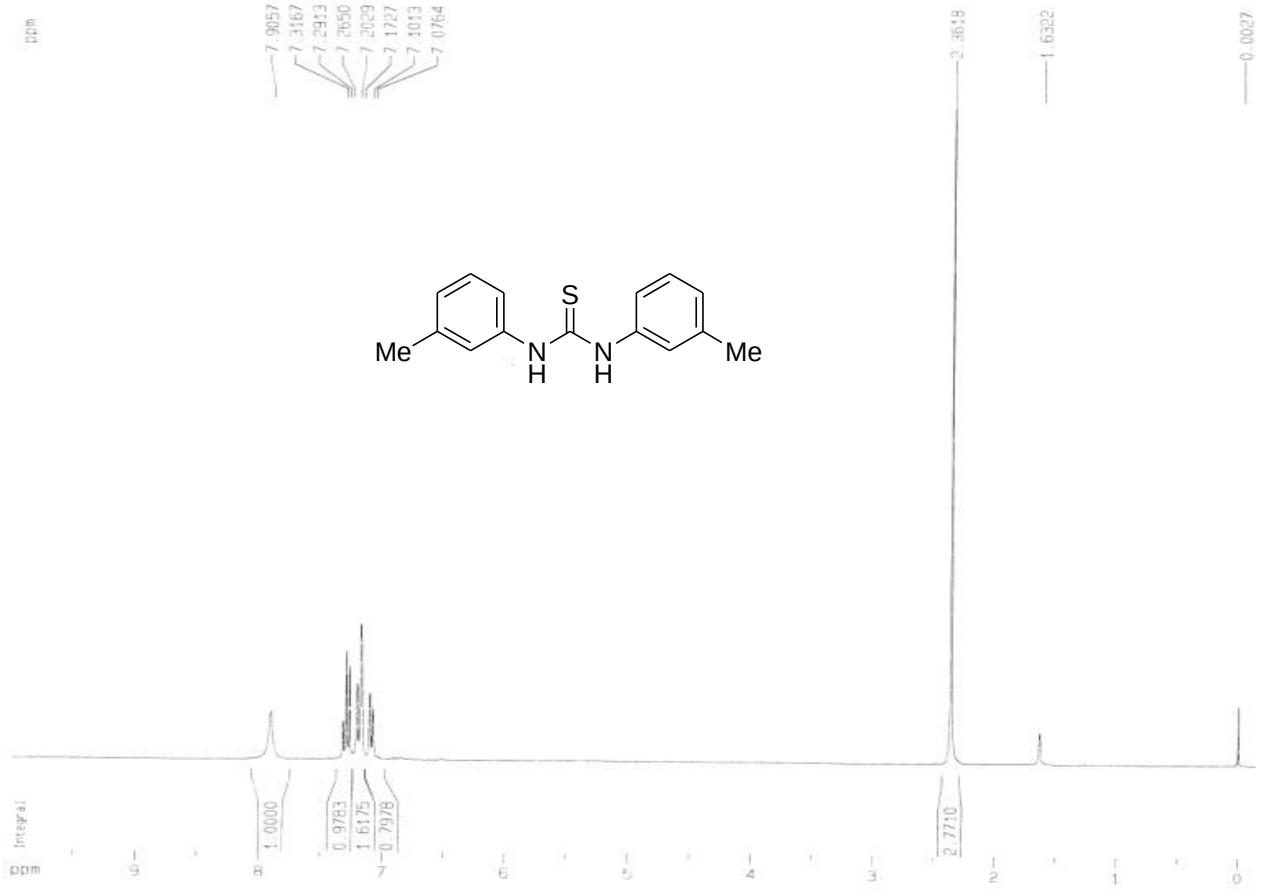
140
120
100
80
60
40
20
0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7.2650
7.2029
7.1727
7.1013
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2.3619
1.6322
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Me
S
N
H
N
H
Me
Integral
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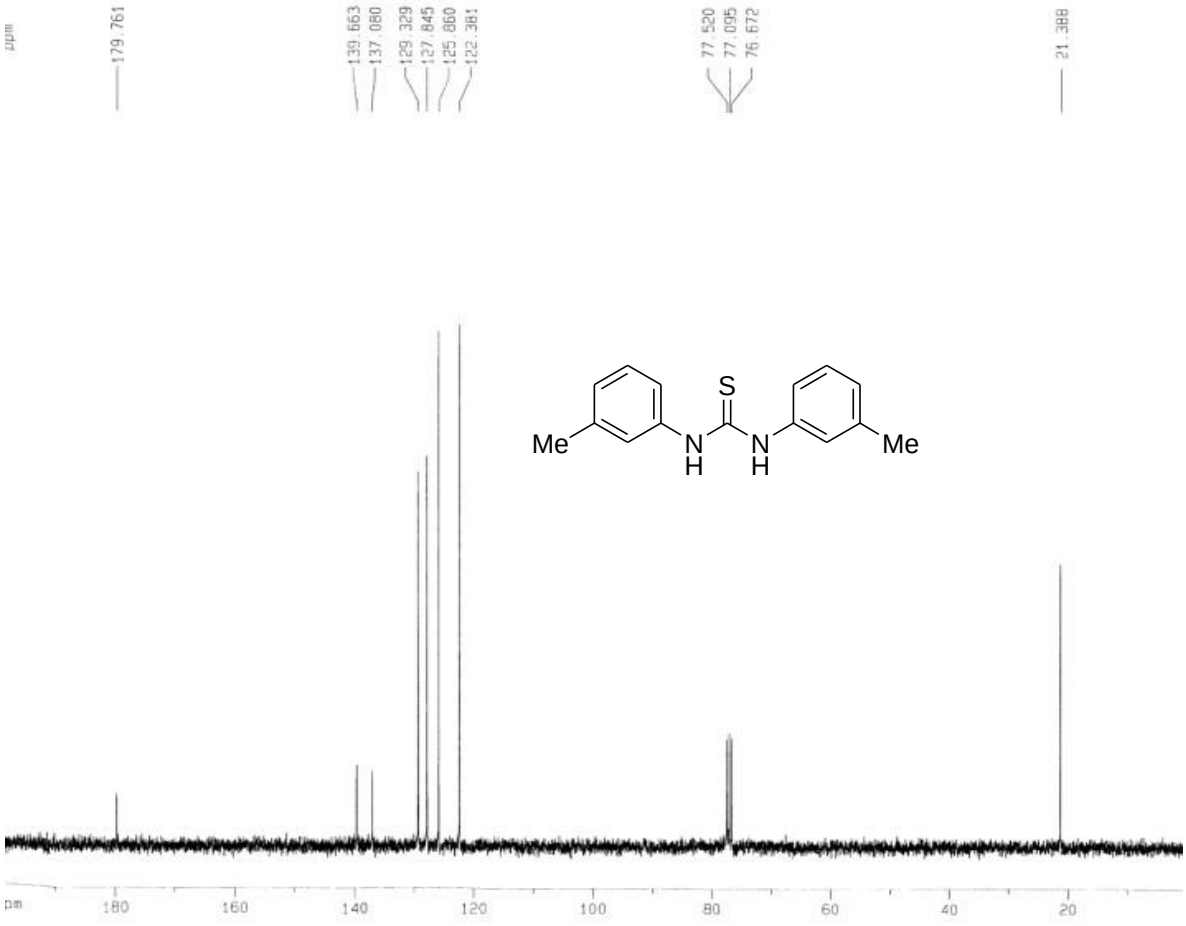
2.7710
ppm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129.329
127.845
125.860
122.361
77.520
77.095
76.672
21.388
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S
N
H
N
H
Me
ppm
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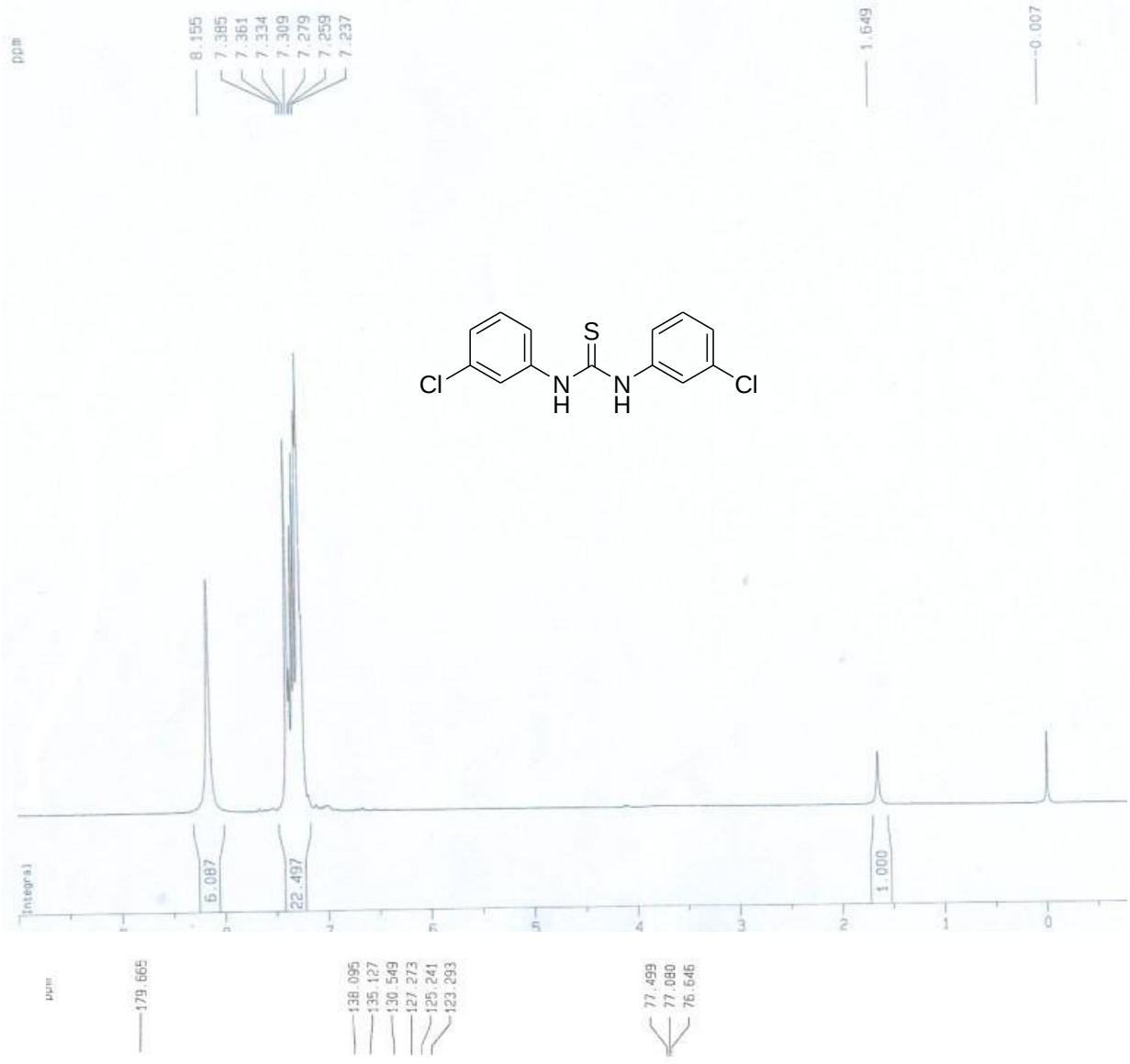
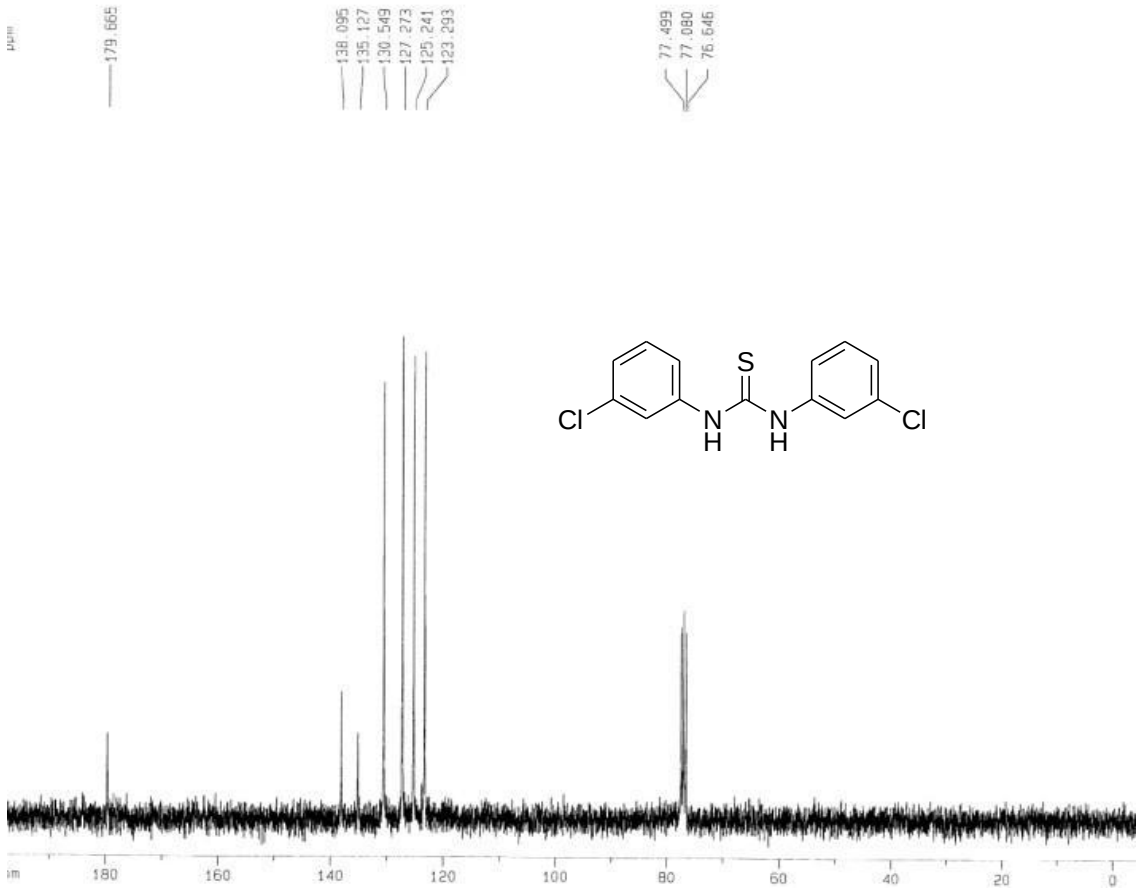
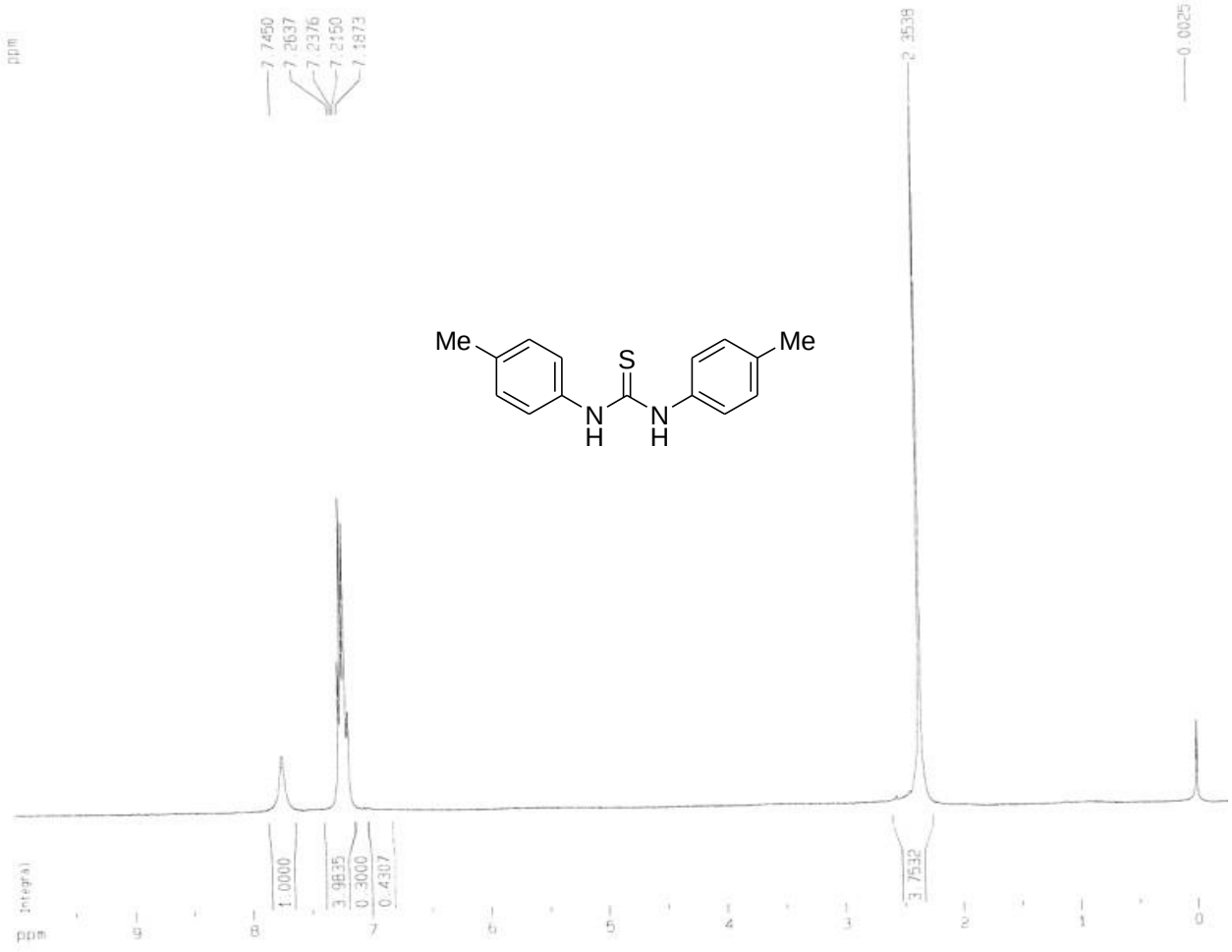
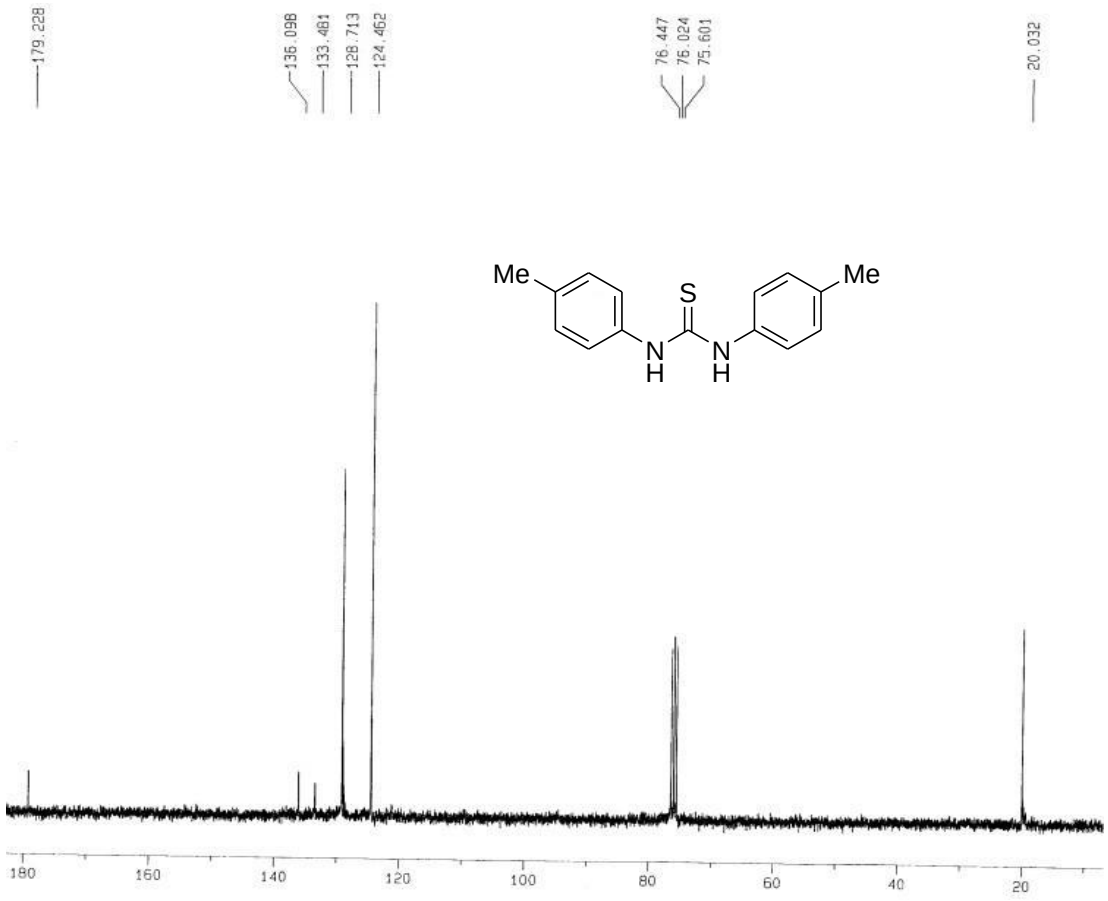
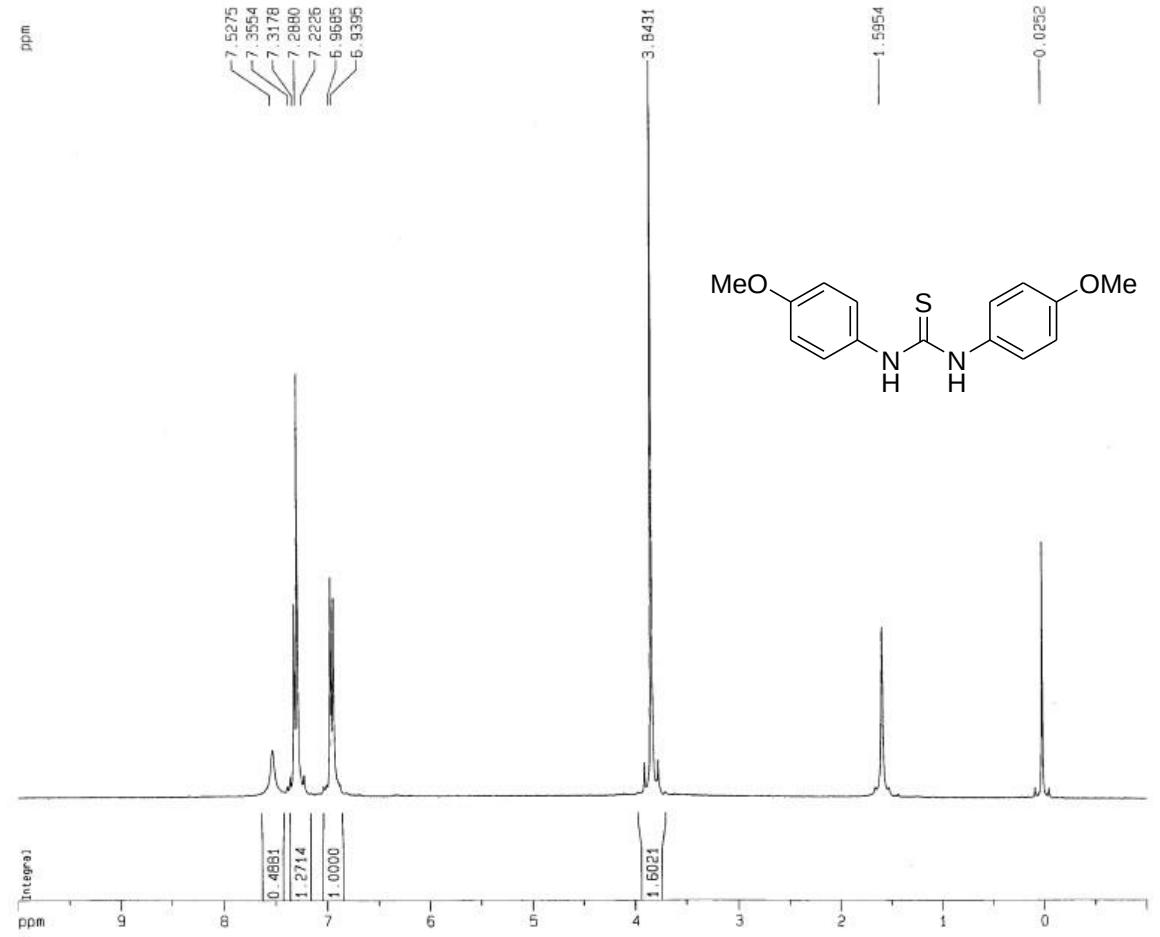
160
140
120
100
80
60
40
20







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7.2880
7.2225
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6.9395
3.8431
1.5954
0.0252
MeO
OMe
S
N
H
N
H
Integral
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1.2714
1.0000
1.6021
ppm
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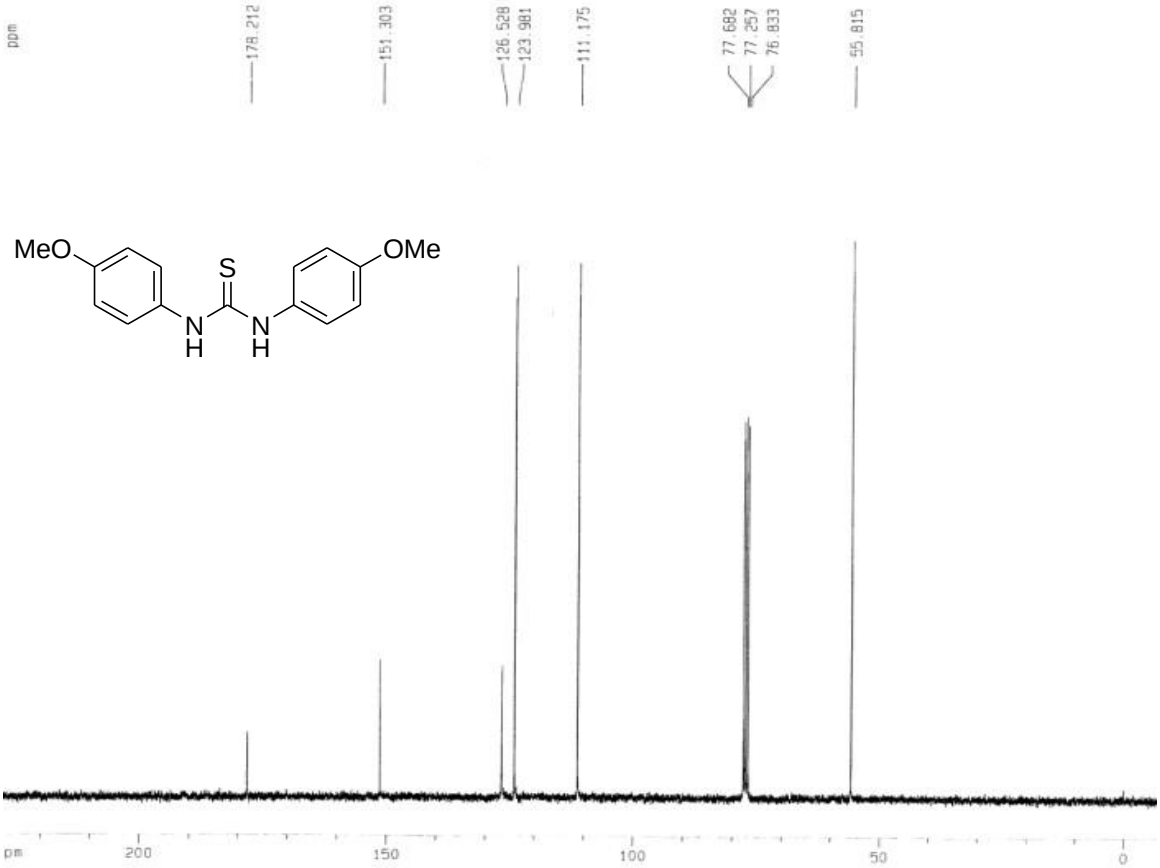
8
7
6
5
4
3
2
1
0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126.528
123.981
111.175
77.682
77.257
76.833
55.815
MeO
OMe
S
N
H
N
H
ppm
200
150
100
50
0