Desymmetrisation of aromatic diamines and synthesis of non-symmetrical thiourea derivatives by click-mechanochemistry

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Supplementary Material

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1. Experimental

1.1 General comments

All chemicals were purchased from commercial sources (Sigma Aldrich or Alfa Aesar) and were used as received (except for 4-nitrophenyl isothiocyanate which was purified by column chromatography). The experiments were carried out in a Retsch MM400 mill at a frequency of 30 Hz using a 10 mL stainless steel grinding jar and a single stainless steel ball of 12 mm diameter (unless otherwise stated). Dry methanol or ethylacetate were used as the liquid phase throughout all liquid-assisted grinding (LAG) experiments. Since the reactivity in mechanochemical milling is dependent on the ratio of the amount (mass or volume) of reacting material and the reaction jar volume, all experiments were systematically designed so as to provide ca. 200 mg of the solid product. Thus, reactions of non-symmetrical mono-substitution were done at 0.90 mmol scale, while the di-substitutions were conducted on half that scale. This facilitates the comparison of reactions by making reaction environments similar across all experiments, and also means that the same number of amino groups is transformed in each experiment.

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance (300 and 600 MHz) spectrometers with tetramethylsilane as an internal standard, while IR spectra were obtained on an ABB Bomem MB102 spectrophotometer (CsI optics, DTGS detector, KBr pellets).

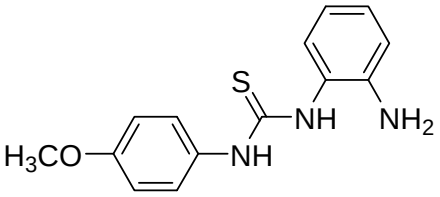
Quantum calculations were carried out with the GAUSSIAN03 program package[1] using Becke's three-parameter exchange functional with the correlation functional of Lee, Yang and Paar (B3LYP). Geometries were fully optimized with the 6-31G(d) valence double ζ-basis set of Pople and Hariharan, and were confirmed to be minima by computing their analytical vibrational frequencies. Single-point calculations were performed with the 6-311+G(d,p) basis set. The zero point vibrational energies computed at the B3LYP/6-31G(d) level were used unscaled. Frontier molecular orbitals (FMO) were obtained at the RHF/6-31G(d)//B3LYP/6-31G(d) level of theory.

1.2 Synthesis of mono-(thio)ureas 1a-e and 3a-b

N^{1}-(2-aminophenyl)-*N*^{2}-(4-methoxyphenyl)thiourea (1a)

An equimolar mixture of *o*-phenylenediamine (0.45 mmol, 48.7 mg) and 4-methoxyphenyl isothiocyanate (0.45 mmol, 62.2 μL) was ground in the presence of 30 μL of dry methanol

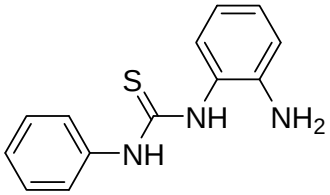
(LAG experiment, η = 0.25 μL mg^{-1}) for 30 minutes. The product was scraped off the walls of the grinding jar affording thiourea **1a** in >98% yield.



δ_H(600 MHz; d_6-DMSO; Me_4Si) 4.85 (2 H, s, NH_2), 6.57 (1 H, t, *J* 7.5, Ar), 6.75 (1 H, d, *J* 7.9, Ar), 6.89 (2 H, d, *J* 8.8, Ar), 6.96 (1 H, t, *J* 7.8, Ar), 7.07 (1 H, d, *J* 7.7, Ar), 7.35 (2 H, d, *J* 8.8, Ar), 8.87 (1 H, s, NH), 9.30 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 55.2, 113.5, 115.8, 116.3, 124.1, 126.0, 127.0, 128.0, 132.3, 143.9, 156.4, 180.3. HRMS-MALDI found: 274.0998; calc. for $C_{14}H_{16}N_3OS$ ($M+H^+$): 274.1008.

N^1-(2-aminophenyl)-*N*^{2}-phenylthiourea (1b)

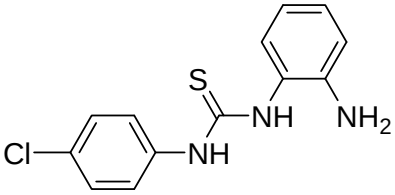
An equimolar mixture of *o*-phenylenediamine (0.6 mmol, 64.8 mg) and phenyl isothiocyanate (0.6 mmol, 72.0 μL) was ground neat for 30 minutes. The product was scraped off the walls of the grinding jar affording thiourea **1b** in >96% yield.



δ_H(600 MHz; d_6-DMSO; Me_4Si) 4.88 (2 H, s, NH_2), 6.57 (1 H, t, *J* 7.5, Ar), 6.75 (1 H, d, *J* 8.0, Ar), 6.97 (1 H, t, *J* 7.6, Ar), 7.03-7.13 (2 H, overlapped Ar), 7.31 (2 H, t, *J* 7.8, Ar), 7.52 (2 H, d, *J* 7.7, Ar), 9.02 (1 H, s, NH), 9.52 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 115.8, 116.3, 123.5, 124.0, 124.2, 127.1, 128.1, 128.3, 139.6, 144.0, 180.0. ν_{max}/cm^{-1}3439, 3389, 3270, 3047, 2974, 2934, 2860, 1618, 1607, 1541, 1501, 1450, 1366, 1315, 1025, 752, 698, 688, 634. HRMS-MALDI found: 244.0905; calc. for $C_{13}H_{14}N_3S$ ($M+H^+$): 244.0903.

N^1-(2-aminophenyl)-*N*^{2}-(4-chlorophenyl)thiourea (1c)

An equimolar mixture of *o*-phenylenediamine (0.45 mmol, 48.7 mg) and 4-chlorophenyl isothiocyanate (0.45 mmol, 76.3 mg) was ground in the presence of 32 μL of dry methanol (LAG experiment, η = 0.25 μL mg^{-1}) for 30 minutes. The product was scraped off the walls of the grinding jar affording thiourea **1c** in >99% yield.

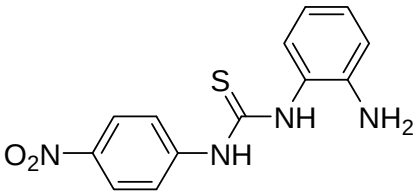


δ_H(300 MHz; d_6-DMSO; Me_4Si) 4.90 (2 H, s, NH_2), 6.56 (1 H, t, *J* 7.5, Ar), 6.75 (1 H, d, *J* 8.0, Ar), 6.97 (1 H, t, *J* 7.6, Ar), 7.07 (1 H, d, *J* 7.8, Ar), 7.35 (2 H, d, *J* 8.8, Ar), 7.55 (2 H, d, *J* 8.8, Ar), 9.11 (1 H, s, NH), 9.61 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 115.8, 116.2, 123.8, 125.1, 127.1, 127.9, 128.1 (2 C

overlapped), 138.7, 143.9, 180.1. HRMS-MALDI found: 278.0522; calc. for $C_{13}H_{13}ClN_3S$ ($M+H^+$): 278.0513.

N^1-(2-aminophenyl)-N^2-(4-nitrophenyl)thiourea (1d)

An equimolar mixture of *o*-phenylenediamine (0.45 mmol, 48.7 mg) and 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg) was ground in the presence of 30 μL of dry methanol (LAG experiment, $\eta = 0.25$ μL mg^{-1}) for 30 minutes. The product was scraped off the walls of the grinding jar affording thiourea **1d** in >98% yield.

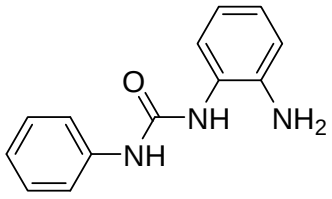


1d: δ_H(600 MHz; d_6-DMSO; Me_4Si) 4.55-5.35 (2 H, brs, NH_2), 6.57 (1 H, t, *J* 7.5, Ar), 6.76 (1 H, d, *J* 8.0, Ar), 6.99 (1 H, t, *J* 7.6, Ar), 7.09 (1 H, d, *J* 7.6, Ar), 7.91 (2 H, d, *J* 9.1, Ar), 8.19 (2 H, d, *J* 9.1, Ar), 9.45 (1 H, s, NH), 9.66-10.52 (1 H, brs, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 115.8, 116.1, 121.3, 123.4, 124.2, 127.3, 128.0, 142.1, 143.9, 146.5, 179.8. HRMS-MALDI found: 289.0746; calc. for $C_{13}H_{13}N_4O_2S$ ($M+H^+$): 289.0754.

N^1-(2-aminophenyl)-N^2-phenylurea (1e)

A 1:1 mixture of *o*-phenylenediamine (0.6 mmol, 64.8 mg) and phenyl isocyanate (0.6 mmol, 71.5 mg, 65.2 μL) was ground neat for 30 minutes. ^{1}H NMR analysis indicated the formation of a mixture of unreacted *o*-phenylenediamine (10%), mono-urea **1e** (78%) and bis-urea **2i** (12%).

The pure urea **1e** was synthesised by a conventional solution-based approach. *o*-Phenylenediamine (3.0 mmol, 324.4 mg) was dissolved in 4 mL and phenyl isocyanate (1.0 mmol, 119.1 mg, 109 μL) in 1 mL of dry dichloromethane. The isocyanate solution was added dropwise to the ***o*-pda** solution with stirring. The stirring was continued for 15 minutes at room temperature, the precipitated product was filtered off, washed with 15 mL of CH_2Cl_2 and dried in air to give mono-urea **1e** in 99% yield.



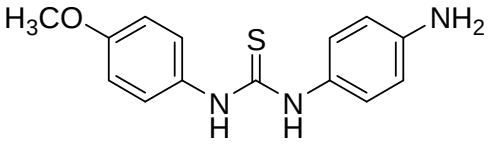
δ_H(300 MHz; d_6-DMSO; Me_4Si) 4.75 (2 H, s, NH_2), 6.57 (1 H, t, *J* 7.8, Ar), 6.74 (1 H, d, *J* 7.9, Ar), 6.84 (1 H, t, *J* 7.2, Ar), 6.94 (1 H, t, *J* 7.3, Ar), 7.26 (2 H, t, *J* 7.5, Ar), 7.33 (1 H, d, *J* 7.9, Ar), 7.44 (2 H, d, *J* 7.7, Ar),7.70 (1 H, s, NH), 8.72 (1 H, s,

NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 115.8, 116.7, 117.9, 121.4, 123.7, 124.3, 124.7, 128.7, 140.0, 140.8, 153.1. HRMS-MALDI found: 228.1133; calc. for $C_{13}H_{14}N_3O$ ($M+H^+$): 228.1131.

N^1-(4-aminophenyl)-N^2-(4-methoxyphenyl)thiourea (3a)

A mixture of *p*-phenylenediamine (0.45 mmol, 48.7 mg), 4-methoxyphenyl isothiocyanate (0.45 mmol, 62.2 μL) and sodium chloride (974 mg, 20×*m*(***p*-pda**)) was ground in the presence of 100 μL of ethylacetate (LAG experiment, η = 0.8 μL mg^{-1}) in a 10 mL teflon grinding jar using a single 10 mm teflon ball (with steel core) for 30 minutes. The resulting mixture was suspended in 10 mL of distilled water and stirred for 10 minutes. Filtration over a sintered funnel and washing with 5 mL of water, followed by drying in air afforded the mono-thiourea **3a** in 97% yield.

Solution synthesis carried out by stirring the equimolar mixture of *p*-phenylenediamine (0.45 mmol, 48.7 mg) and 4-methoxyphenyl isothiocyanate (0.45 mmol, 62.2 μL) in ethylacetate (2 mL) for 24 hours gave mono-thiourea **3a** in 78% yield.

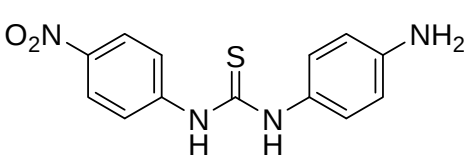


δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.74 (3 H, s, OCH_3), 5.01 (2 H, s, NH_2), 6.52 (2 H, d, *J* 8.6, Ar), 6.87 (2 H, d, *J* 9.0, Ar), 6.98 (2 H, d, *J* 8.6, Ar), 7.29 (2 H, d, *J* 8.9, Ar), 9.12 (1 H, s, NH), 9.20 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 55.2, 113.4, 113.6, 126.1, 126.2, 127.4, 132.4, 146.4, 156.3, 180.0. HRMS-MALDI found: 274.0995; calc. for $C_{14}H_{16}N_3OS$ ($M+H^+$): 274.1008.

N^1-(4-aminophenyl)-N^2-(4-nitrophenyl)thiourea (3b)

A mixture of *p*-phenylenediamine (0.45 mmol, 48.7 mg), 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg) and sodium chloride (974 mg, 20×*m*(***p*-pda**)) was ground either neat (NG experiment) or in the presence of 32 μL of ethylacetate (LAG experiment, η = 0.25 μL mg^{-1}) in a 10 mL teflon grinding jar using a single 10 mm teflon ball (with steel core) for 30 minutes. ^{1}H NMR analysis in both cases indicated the formation of a mixture of unreacted *p*-phenylenediamine, mono-thiourea **3b** (54% NG, 62% LAG) and bis-thiourea **4b**. NG or LAG without NaCl in a stainless steel jar with 12 mm steel ball gave slightly better conversion to **3b** (76% NG, 68% LAG).

The pure thiourea **3b** was therefore synthesised by a conventional solution-based approach. *p*-Phenylenediamine (0.45 mmol, 48.7 mg) was dissolved in 1 mL of dry dichloromethane and 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg) was added to this solution. The stirring was continued for two hours at room temperature, the precipitated product was filtered off and dried in air to give thiourea **3b** in 88% yield.

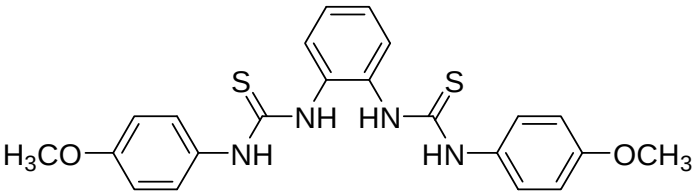


δ_H(300 MHz; d_6-DMSO; Me_4Si) 5.08 (2 H, s, NH_2), 6.54 (2 H, d, *J* 8.6, Ar), 7.04 (2 H, d, *J* 8.5, Ar), 7.82 (2 H, d, *J* 9.2, Ar), 8.17 (2 H, d, *J* 9.2, Ar), 9.88 (1 H, s, NH), 9.99 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 113.6, 121.3, 124.2, 125.7, 126.9, 141.9, 146.6, 146.8, 179.0. HRMS-MALDI found: 289.0759; calc. for $C_{13}H_{13}N_4O_2S$ ($M+H^+$): 289.0754.

1.3 Synthesis of bis-thioureas 2a-h and 4a-d

N^1,*N*^{2}-*bis*[*N*-(4-methoxyphenyl)thiocarbamoyl]-1,2-diaminobenzene (2a)

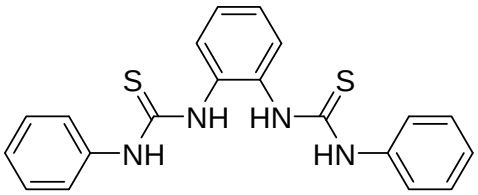
A mixture of 4-methoxyphenyl isothiocyanate (0.9 mmol, 124 μL), *o*-phenylenediamine (0.45 mmol, 48.7 mg) and 80μL of methanol (η = 0.4 μL mg^{-1}) was ground for 540 minutes. The product was then scraped off the walls affording bis-thiourea **2a** in >95% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.73 (6 H, s, OCH_3), 6.88 (4 H, d, *J* 8.6, Ar), 7.15-7.38 (6 H, overlapped Ar), 7.41-7.53 (2 H, m, Ar), 9.02 (2 H, s, NH), 9.76 (2 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 55.2, 113.9, 126.1, 127.9, 131.4, 134.6, 156.8, 180.0. HRMS-MALDI found: 439.1250; calc. for $C_{22}H_{23}N_4O_2S_2$ ($M+H^+$): 439.1257.

N^1,*N*^{2}-*bis*[*N*-phenylthiocarbamoyl]-1,2-diaminobenzene (2b)

A mixture of phenyl isothiocyanate (144μL, 1.2 mmol) and *o*-phenylenediamine (64.8 mg, 0.6 mmol) and 60 μL (η = 0.25 μL mg^{-1}) or 75 μL (η = 0.33 μL mg^{-1}) of methanol was ground for 180 minutes. The product was then scraped off the walls affording bis-thiourea **2b** in >99% yield.

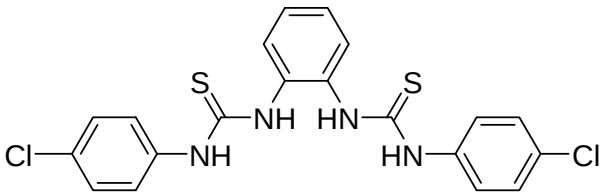


δ_H(600 MHz; d_6-DMSO; Me_4Si) 7.14 (2 H, t, *J* 7.3,

Ar), 7.22-7.28 (2 H, m, Ar), 7.32 (4 H, t, *J* 7.8, Ar), 7.45 (4 H, d, *J* 7.8, Ar), 7.47-7.51 (2 H, m, Ar), 9.18 (2 H, s, NH), 9.97 (2 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 123.8, 124.8, 126.2, 128.1, 128.6, 134.6, 138.9, 179.9.

***N*^{1},*N*^{2}-*bis*[*N*-(4-chlorophenyl)thiocarbamoyl]-1,2-diaminobenzene (2c)**

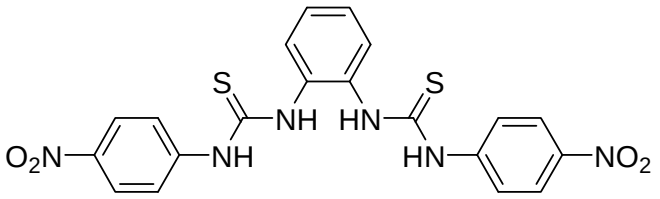
A mixture of 4-chlorophenyl isothiocyanate (0.9 mmol, 152.7 mg), *o*-phenylenediamine (0.45 mmol, 48.7 mg) and 50μL of methanol (η = 0.25 μL mg^{-1}) was ground for 180 minutes. The product was then scraped off the walls affording bis-thiourea **2c** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 7.22-7.31 (2 H, overlapped Ar), 7.36 (4 H, d, *J* 8.6, Ar), 7.43-7.56 (6 H, overlapped Ar), 9.26 (2 H, s, NH), 10.04 (2 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 125.3, 126.3, 128.0, 128.4, 128.6, 134.3, 138.0, 180.0. HRMS-MALDI found: 447.0284; calc. for $C_{20}H_{17}Cl_2N_4S_2$ (M+H$^+$): 447.0266.

***N*^{1},*N*^{2}-*bis*[*N*-(4-nitrophenyl)thiocarbamoyl]-1,2-diaminobenzene (2d)**

A mixture of 4-nitrophenyl isothiocyanate (0.9 mmol, 162.2 mg), *o*-phenylenediamine (0.45 mmol, 48.7 mg) and 53μL of methanol (η = 0.25 μL mg^{-1}) was ground for 180 minutes. The product was then scraped off the walls affording bis-thiourea **2d** in >99% yield.

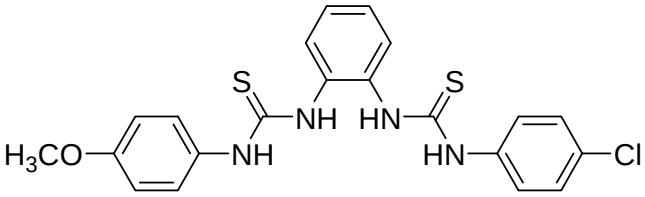


δ_H(300 MHz; d_6-DMSO; Me_4Si) 7.26-7.37 (2 H, m, Ar), 7.48-7.58 (2 H, m, Ar), 7.88 (4 H, d, *J* 9.2, Ar), 8.17 (4 H, d, *J* 9.2 Ar), 9.63 (2 H, s, NH), 10.60 (2 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 121.6, 124.3, 126.7, 128.1, 134.0, 142.5, 145.8, 179.9. HRMS-MALDI found: 491.0547; calc. for $C_{20}H_{16}N_6O_4S_2Na$ (M+Na$^+$): 491.0566.

***N*^{1}-[*N*-(4-chlorophenyl)thiocarbamoyl]-*N*^{2}-[*N*-(4-methoxyphenyl)thiocarbamoyl]-1,2-diaminobenzene (2e)**

An equimolar mixture of mono-thiourea **1a** (0.45 mmol, 123.0 mg) and 4-chlorophenyl isothiocyanate (0.45 mmol, 76.3 mg) was ground in the presence of 50 μL of dry methanol

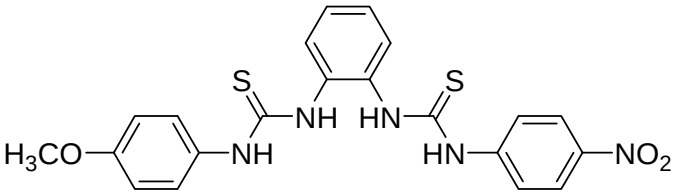
(LAG experiment, η = 0.25 μL mg^{-1}) for 180 minutes. The product was scraped off the walls of the grinding jar affording bis-thiourea **2e** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.71 (3 H, s, OCH_3), 6.87 (2 H, d, *J*8.9, Ar), 7.20-7.30 (4 H, overlapped Ar), 7.37 (2 H, d, *J*8.8, Ar), 7.40-7.45 (1 H, m, Ar), 7.49 (2 H, d, *J*8.8, Ar), 7.52-7.57 (1 H, m, Ar), 8.96 (1 H, s, NH), 9.31 (1 H, s, NH), 9.79 (1 H, s, NH), 10.02 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 55.1, 113.9, 125.2, 126.0, 126.1, 126.2, 127.8, 127.9, 128.3, 128.5, 131.3, 134.1, 134.8, 138.0, 156.9, 179.99, 180.01. HRMS-MALDI found: 465.0591; calc. for $C_{21}H_{19}ClN_4OS_2Na$ (M+Na$^+$): 465.0581.

N^1-[*N*-(4-chlorophenyl)thiocarbamoyl]-N^2-[*N*-(4-methoxyphenyl)thiocarbamoyl]-1,2-diaminobenzene (2f)

An equimolar mixture of mono-thiourea **1a** (0.45 mmol, 123.0 mg) and 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg) was ground in the presence of 50 μL of dry methanol (LAG experiment, η = 0.25 μL mg^{-1}) for 180 minutes. The product was scraped off the walls of the grinding jar affording bis-thiourea **2f** in >99% yield.

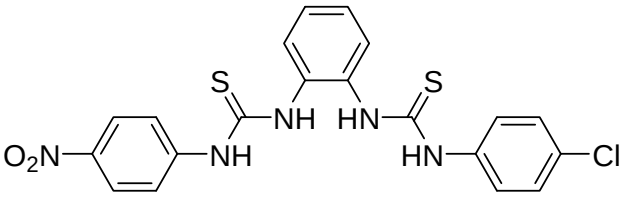


δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.69 (3 H, s, OCH_3), 6.84 (2 H, d, *J* 8.9, Ar), 7.20-7.32 (4 H, overlapped Ar), 7.38-7.45 (1 H, m, Ar), 7.57-7.64 (1 H, m, Ar), 7.85 (2 H, d, *J* 9.2, Ar), 8.20 (2 H, d, *J* 9.2, Ar), 8.92 (1 H, s, NH), 9.67 (1 H, s, NH), 9.83 (1 H, s, NH), 10.56 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 55.1, 113.9, 121.6, 124.2, 126.07, 126.10, 126.5, 127.8, 128.0, 131.2, 133.6, 134.9, 142.4, 145.8, 156.9, 179.9, 180.0. HRMS-MALDI found: 454.1014; calc. for $C_{21}H_{20}N_5O_3S_2$ (M+H$^+$): 454.1002.

N^1-[*N*-(4-chlorophenyl)thiocarbamoyl]-N^2-[*N*-(4-nitrophenyl)thiocarbamoyl]-1,2-diaminobenzene (2g)

An equimolar mixture of mono-thiourea **1d** (0.45 mmol, 129.6 mg) and 4-chlorophenyl isothiocyanate (0.45 mmol, 76.3 mg) was ground in the presence of 50 μL of dry methanol

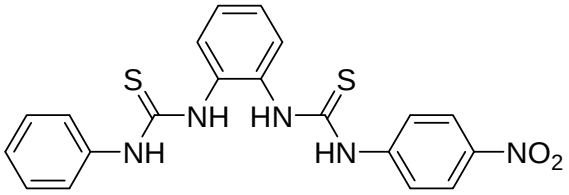
(LAG experiment, η = 0.25 μL mg^{-1}) for 180 minutes. The product was scraped off the walls of the grinding jar affording bis-thiourea **2g** in >97% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 7.24-7.39 (4 H, overlapped Ar), 7.45-7.58 (4 H, overlapped Ar), 7.86 (2 H, d, *J* 9.2, Ar), 8.19 (2 H, d, *J* 9.2, Ar), 9.24 (1 H, s, NH), 9.63 (1 H, s, NH), 10.07 (1 H, s, NH), 10.57 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 121.6, 124.2, 125.2, 126.3, 126.6, 127.9, 128.1, 128.3, 128.6, 133.8, 134.4, 137.9, 142.5, 145.8, 179.9, 180.0. HRMS-MALDI found: 480.0320; calc. for $C_{20}H_{16}ClN_5O_2S_2Na$ (M+Na$^+$): 480.0326.

N^1-[*N*-(4-nitrophenyl)thiocarbamoyl]-N^2-[*N*-phenylthiocarbamoyl]-1,2-diaminobenzene (2h)

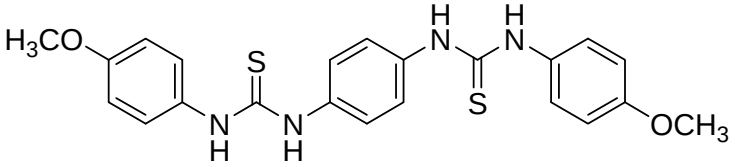
An equimolar mixture of mono-thiourea **1b** (0.45 mmol, 109.5 mg) and 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg) was ground in the presence of 50 μL of dry methanol (LAG experiment, η = 0.25 μL mg^{-1}) for 180 minutes. The product was scraped off the walls of the grinding jar affording bis-thiourea **2h** in >99% yield. The 30-minute reaction resulted in only 68% conversion according to ^{1}H NMR analysis of the reaction mixture.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 7.13 (1 H, t, *J* 7.3, Ar), 7.22-7.37 (4 H, overlapped Ar), 7.39-7.50 (3 H, overlapped Ar), 7.53-7.60 (1 H, m, Ar), 7.86 (2 H, d, *J* 9.2, Ar), 8.19 (2 H, d, *J* 9.2, Ar), 9.14 (1 H, s, NH), 9.64 (1 H, s, NH), 10.03 (1 H, s, NH), 10.58 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 121.6, 123.7, 124.3, 124.9, 126.2, 126.6, 127.9, 128.1, 128.6, 133.8, 134.7, 138.8, 142.5, 145.9, 179.89, 179.94. HRMS-MALDI found: 424.0898; calc. for $C_{21}H_{20}ClN_4OS_2$ (M+H$^+$): 424.0896.

N^1,N^2-*bis*[*N*-(4-methoxyphenyl)thiocarbamoyl]-1,4-diaminobenzene (4a)

A mixture of 4-methoxyphenyl isothiocyanate (0.9 mmol, 124 μL), *p*-phenylenediamine (0.45 mmol, 48.7 mg) and 50μL of methanol (η = 0.25 μL mg^{-1}) was ground for 30 minutes. The product was then scraped

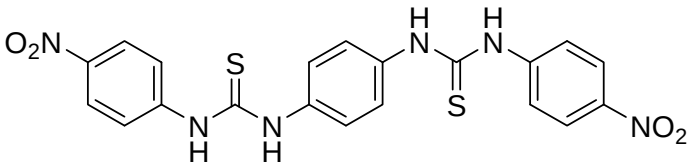


off the walls affording bis-thiourea **4a** in >99% yield.

δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.75 (6 H, s, OCH_3), 6.90 (4 H, d, *J* 8.9, Ar), 7.33 (4 H, d, *J* 8.9, Ar), 7.41 (4 H, s, Ar), 9.52 (2 H, s, NH), 9.56 (2 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 55.2, 113.6, 123.7, 125.9, 132.1, 135.8, 156.5, 179.8. HRMS-MALDI found: 439.1239; calc. for $C_{22}H_{23}N_4O_2S_2$ ($M+H^+$): 439.1257.

***N*^{1},*N*^{2}-*bis*[*N*-(4-nitrophenyl)thiocarbamoyl]-1,4-diaminobenzene (4b)**

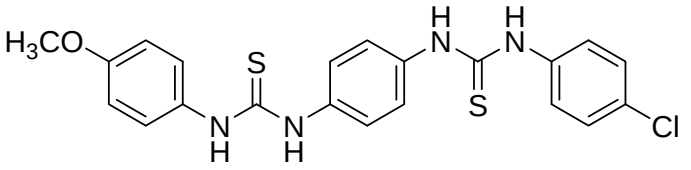
A mixture of 4-nitrophenyl isothiocyanate (0.9 mmol, 162.2 mg), *p*-phenylenediamine (0.45 mmol, 48.7 mg) and 50μL of methanol (η = 0.25 μL mg^{-1}) was ground for 30 minutes. The product was then scraped off the walls affording bis-thiourea **4b** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 7.50 (4 H, s, Ar), 7.84 (4 H, d, *J* 9.2, Ar), 8.20 (4 H, d, *J* 9.2, Ar), 10.25 (2 H, s, NH), 10.37 (2 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 121.4, 123.9, 124.3, 135.8, 142.2, 146.2, 179.2. HRMS-MALDI found: 469.0731; calc. for $C_{20}H_{17}N_6O_4S_2$ ($M+H^+$): 469.0747.

***N*^{1}-[*N*-(4-chlorophenyl)thiocarbamoyl]-*N*^{2}-[*N*-(4-methoxyphenyl)thiocarbamoyl]-1,4-diaminobenzene (4c)**

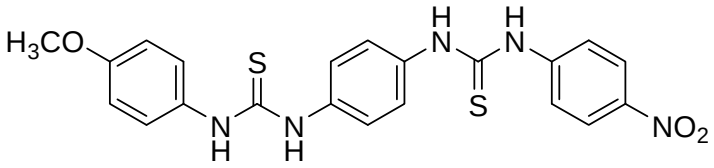
An equimolar mixture of mono-thiourea **3a** (0.45 mmol, 123.0 mg) and 4-chlorophenyl isothiocyanate (0.45 mmol, 76.3 mg) was ground in the presence of 50 μL of dry methanol (LAG experiment, η = 0.25 μL mg^{-1}) for 30 minutes. The product was scraped off the walls of the grinding jar affording bis-thiourea **4c** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.75 (3 H, s, OCH_3), 6.90 (2 H, d, *J* 8.9, Ar), 7.25-7.48 (8 H, m, overlapped Ar), 7.52 (2 H, d, *J* 8.8, Ar), 9.54 (1 H, s, NH), 9.58 (1 H, s, NH), 9.79 (1 H, s, NH), 9.81 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 55.2, 113.6, 123.7 (2 C, overlapped), 125.1, 125.9, 128.1, 128.2, 132.1, 135.5, 136.1, 138.4, 156.5, 179.6, 179.8. HRMS-MALDI found: 443.0775; calc. for $C_{21}H_{20}ClN_4OS_2$ ($M+H^+$): 443.0761.

N^1-[*N*-(4-methoxyphenyl)thiocarbamoyl]-N^2-[*N*-(4-nitrophenyl)thiocarbamoyl]-1,4-diaminobenzene (4d)

An equimolar mixture of mono-thiourea **3a** (0.45 mmol, 123.0 mg) and 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg) was ground in the presence of 50 μL of dry methanol (LAG experiment, $\eta = 0.25$ μL mg^{-1}) for 30 minutes. The product was scraped off the walls of the grinding jar affording bis-thiourea **4d** in >99% yield.

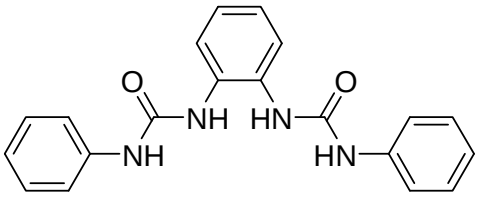


δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.75 (3 H, s, OCH_3), 6.90 (2 H, d, *J* 8.9, Ar), 7.33 (2 H, d, *J* 8.9, Ar), 7.38-7.53 (4 H, overlapped Ar), 7.84 (2 H, d, *J* 9.2, Ar), 8.20 (2 H, d, *J* 9.2, Ar), 9.58 (1 H, s, NH), 9.60 (1 H, s, NH), 10.21 (1 H, s, NH), 10.32 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 55.2, 113.7, 121.4, 123.7, 123.8, 124.3, 125.9, 132.1, 135.1, 136.5, 142.2, 146.3, 156.5, 179.1, 179.8. HRMS-MALDI found: 454.0989; calc. for $C_{21}H_{20}N_5O_3S_2$ ($M+H^+$): 454.1002.

1.4 Synthesis of urea 2i and mixed urea-thioureas 2j-m

N^1,N^2-*bis*[*N*-phenylcarbamoyl]-1,2-diaminobenzene (2i)

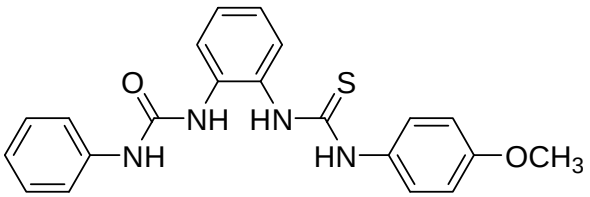
A 1:2 mixture of *o*-phenylenediamine (0.6 mmol, 64.8 mg) and phenyl isocyanate (1.2 mmol, 142.9 mg, 130.4 μL) was ground neat for 30 minutes. The product was scraped off the walls of the grinding jar affording bis-urea **2i** in >99% yield.



δ_H(600 MHz; d_6-DMSO; Me_4Si) 6.96 (2 H, t, *J* 7.4, Ar), 7.05-7.11 (2 H, m, Ar), 7.27 (4 H, t, *J* 7.8, Ar), 7.47 (4 H, d, *J* 7.8, Ar), 7.57-7.63 (2 H, m, Ar), 8.04 (2 H, s, NH), 9.04 (2 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 118.1, 121.7, 123.89, 123.95, 128.7, 131.2, 139.8, 153.1. HRMS-MALDI found: 369.1329; calc. for $C_{20}H_{18}N_4O_2Na$ ($M+Na^+$): 369.1322.

N^1-[*N*-(4-methoxyphenyl)thiocarbamoyl]-N^2-[*N*-phenylcarbamoyl]-1,2-diaminobenzene (2j)

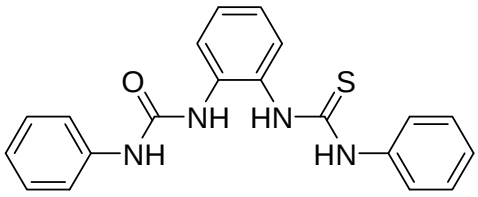
An equimolar mixture of mono-thiourea **1a** (0.45 mmol, 123.0 mg, prepared by milling) and phenyl isocyanate (0.45 mmol, 53.6 mg, 49 μL) was ground neat for 180 minutes. The product was scraped off the walls of the grinding jar affording mixed urea-thiourea **2j** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 3.72 (3 H, s, OCH_3), 6.88 (2 H, d, *J* 8.9, Ar), 6.97 (1 H, t, *J* 7.3, Ar), 7.05 (1 H, t, *J* 7.5, Ar), 7.20 (1 H, t, *J* 7.7, Ar), 7.27 (2 H, t, *J* 7.8, Ar), 7.31-7.50 (5 H, m, overlapped Ar), 7.79 (1 H, d, *J* 7.7, Ar), 8.10 (1 H, s, NH), 9.00 (1 H, s, NH), 9.25 (1 H, s, NH), 9.74 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 55.1, 113.8, 118.2, 121.8, 121.9, 122.7, 126.0, 126.4, 128.7 (2C overlapped), 130.2, 131.7, 134.8, 139.6, 152.8, 156.7, 180.9. HRMS-MALDI found: 393.1376; calc. for $C_{21}H_{20}ClN_4OS_2$ ($M+H^+$): 393.1379.

N^1-[*N*-phenylthiocarbamoyl]-N^2-[*N*-phenylcarbamoyl]-1,2-diaminobenzene (2k)

An equimolar mixture of mono-thiourea **1b** (0.45 mmol, 109.5 mg, prepared by milling) and phenyl isocyanate (0.45 mmol, 53.6 mg, 49 μL) was ground neat for 180 minutes. The product was scraped off the walls of the grinding jar affording mixed urea-thiourea **2k** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 6.97 (1 H, t, *J* 7.3, Ar), 7.05 (1 H, t, *J* 7.5, Ar), 7.13 (1 H, t, *J* 7.4, Ar), 7.17-7.37 (6 H, m, overlapped Ar), 7.42 (2 H, d, *J* 7.5, Ar), 7.54 (2 H, d, *J* 7.7, Ar), 7.84 (1 H, d, *J* 8.2, Ar), 8.10 (1 H, s, NH), 9.17 (1 H, s, NH), 9.26 (1 H, s, NH), 9.93 (1 H, s, NH). δ_C(150 MHz, d_6-DMSO; Me_4Si) 118.2, 121.7, 121.8, 122.6, 123.6, 124.5, 126.6, 128.4, 128.7 (2C overlapped), 129.9, 135.0, 139.1, 139.6, 152.7, 180.8. HRMS-MALDI found: 363.1286; calc. for $C_{21}H_{20}ClN_4OS_2$ ($M+H^+$): 363.1274.

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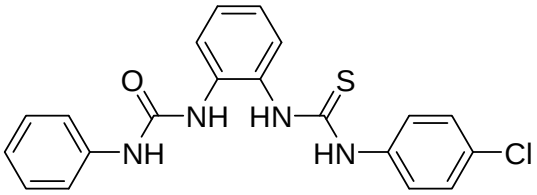
N^1-[*N*-(4-chlorophenyl)thiocarbamoyl]-N^2-[*N*-phenylcarbamoyl]-1,2-diaminobenzene (2l)

An equimolar mixture of mono-thiourea **1c** (0.45 mmol, 125.0 mg, prepared by milling) and phenyl isocyanate (0.45 mmol, 53.6 mg, 49 μL) was ground neat for 180 minutes. The product was scraped off the walls of the grinding jar affording mixed urea-thiourea **2l** in >99% yield.

The title compound was also synthesised by a reverse reaction between equimolar amounts of mono-urea **1e** (0.45 mmol, 102.3 mg) and 4-chlorophenyl isothiocyanate (0.45 mmol, 76.3 mg). LAG by using methanol (45 μL, η = 0.25 μL mg^{-1}) for 30 minutes gave only 65% of **2l** while 180 minutes of milling afforded the mixed urea-thiourea **2l** in >99% yield.

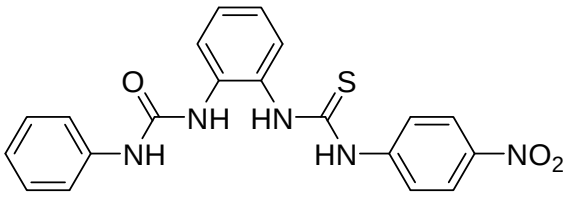


δ_H(300 MHz; d_6-DMSO; Me_4Si) 6.97 (1 H, t, *J* 7.3, Ar), 7.05 (1 H, t, *J* 7.5, Ar), 7.16-7.47 (8 H, m, overlapped Ar), 7.58 (2 H, d, *J* 8.6, Ar), 7.87 (1 H, d, *J* 8.0, Ar), 8.09 (1 H, s, NH), 9.26 (2 H, s, overlapped NH), 10.00 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 118.1, 121.7, 121.8, 122.6, 125.2, 126.7, 128.27, 128.33, 128.66, 128.72, 129.5, 135.1, 138.3, 139.6, 152.7, 180.9. HRMS-MALDI found: 397.0878; calc. for $C_{21}H_{20}ClN_4OS_2$ ($M+H^+$): 397.0884.

N^1-[*N*-(4-nitrophenyl)thiocarbamoyl]-N^2-[*N*-phenylcarbamoyl]-1,2-diaminobenzene (2m)

An equimolar mixture of mono-thiourea **1d** (0.45 mmol, 129.7 mg, prepared by milling) and phenyl isocyanate (0.45 mmol, 53.6 mg, 49 μL) was ground neat for 180 minutes. The product was scraped off the walls of the grinding jar affording mixed urea-thiourea **2m** in >99% yield.

The title compound was also synthesised by a reverse reaction between equimolar amounts of mono-urea **1e** (0.45 mmol, 102.3 mg) and 4-nitrophenyl isothiocyanate (0.45 mmol, 81.1 mg). LAG by using methanol (45 μL, η = 0.25 μL mg^{-1}) for 30 minutes afforded the mixed urea-thiourea **2m** in >99% yield.



δ_H(300 MHz; d_6-DMSO; Me_4Si) 6.96 (1 H, t, *J* 7.3, Ar), 7.06 (1 H, t, *J* 7.6, Ar), 7.21-7.33 (4 H, m, overlapped Ar), 7.43 (2 H, d, *J* 8.6, Ar), 7.90-7.99 (3 H, m, Ar), 8.09 (1 H, s,

NH), 8.20 (2 H, d, *J* 9.2, Ar), 9.24 (1 H, s, NH), 9.59 (1 H, s, NH), 10.54 (1 H, s, NH). δ_C(75 MHz, d_6-DMSO; Me_4Si) 118.1, 121.5, 121.6, 121.8, 122.6, 124.3, 127.1, 128.6, 128.7, 129.0, 135.3, 139.6, 142.4, 146.1, 152.6, 180.8. HRMS-MALDI found: 408.1140; calc. for $C_{20}H_{18}N_5O_3S$ ($M+H^+$): 408.1125.

2. FTIR spectra

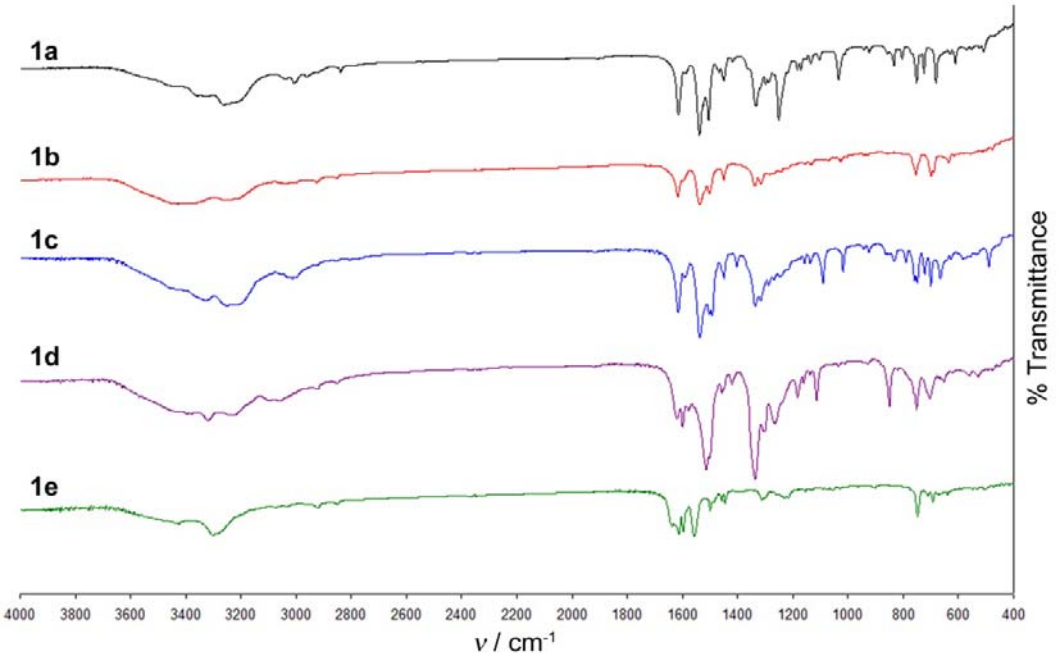


Figure S1. IR spectra of mono-thioureas **1a-e**. The absence of the characteristic isothiocyanate stretching vibration band at 2000–2200 cm^{-1} is notable.

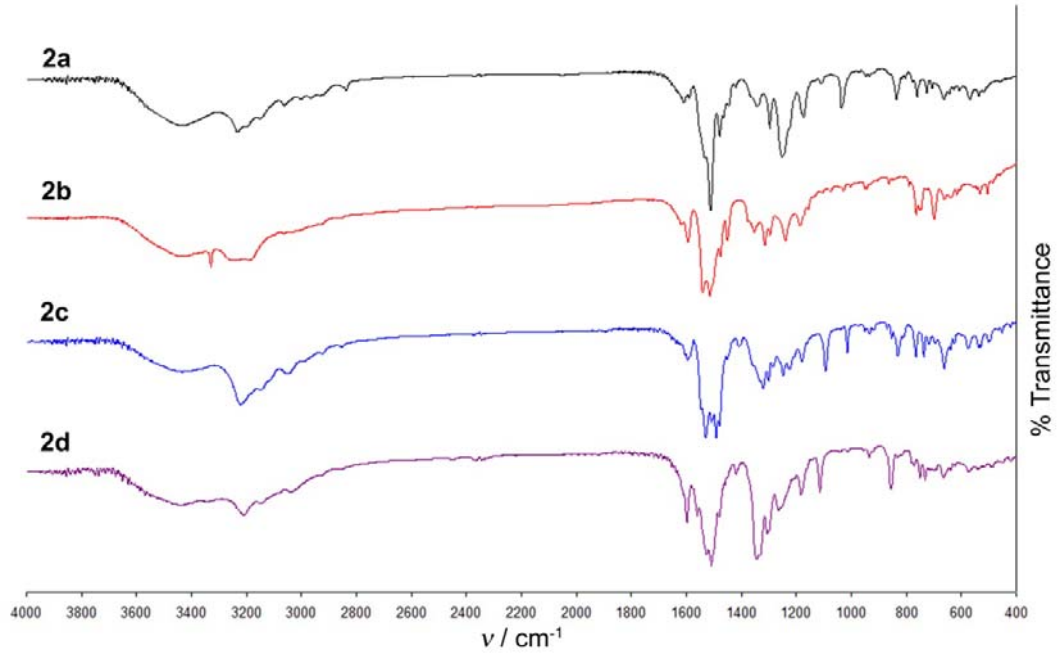


Figure S2. IR spectra of bis-thioureas **2a-d**. The absence of the characteristic isothiocyanate stretching vibration band at 2000–2200 cm^{-1} is notable.

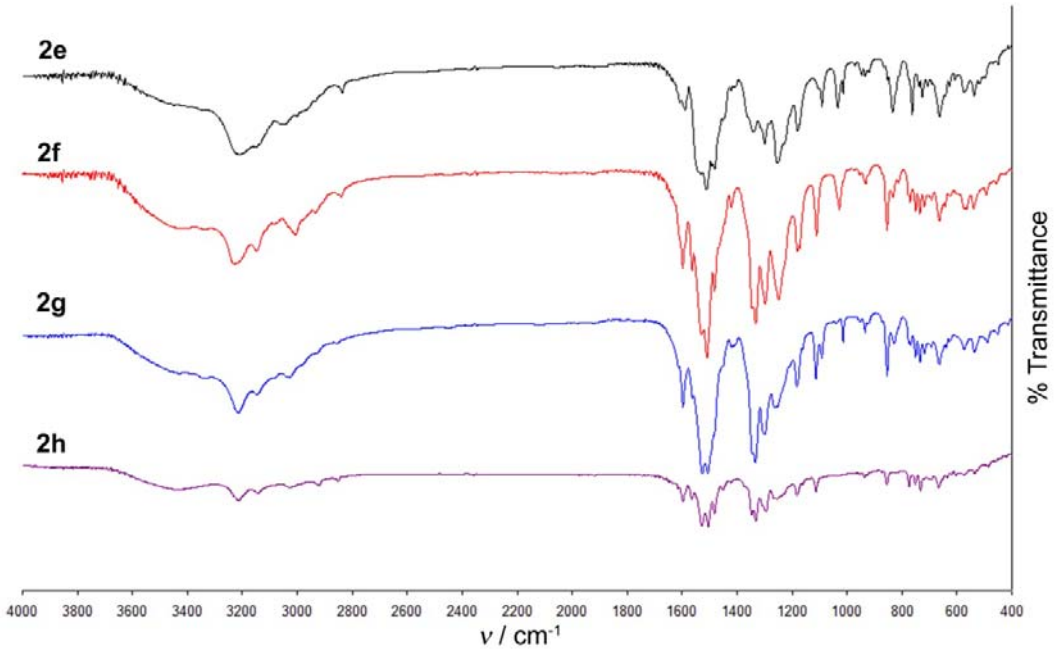


Figure S3. IR spectra of desymmetrised bis-thioureas **2e-h**. The absence of the characteristic isothiocyanate stretching vibration band at 2000–2200 cm^{-1} is notable.

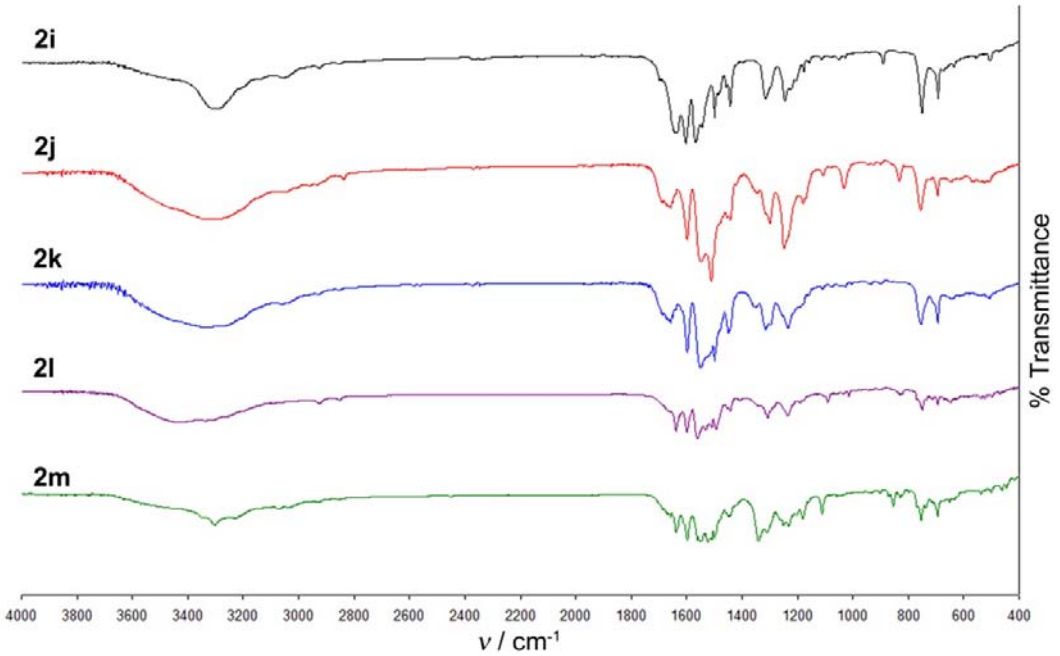


Figure S4. IR spectra of bis-urea **2i** and mixed urea-thioureas **2j-m**. The absence of the characteristic isothiocyanate stretching vibration band at 2000–2200 cm^{-1} is notable.

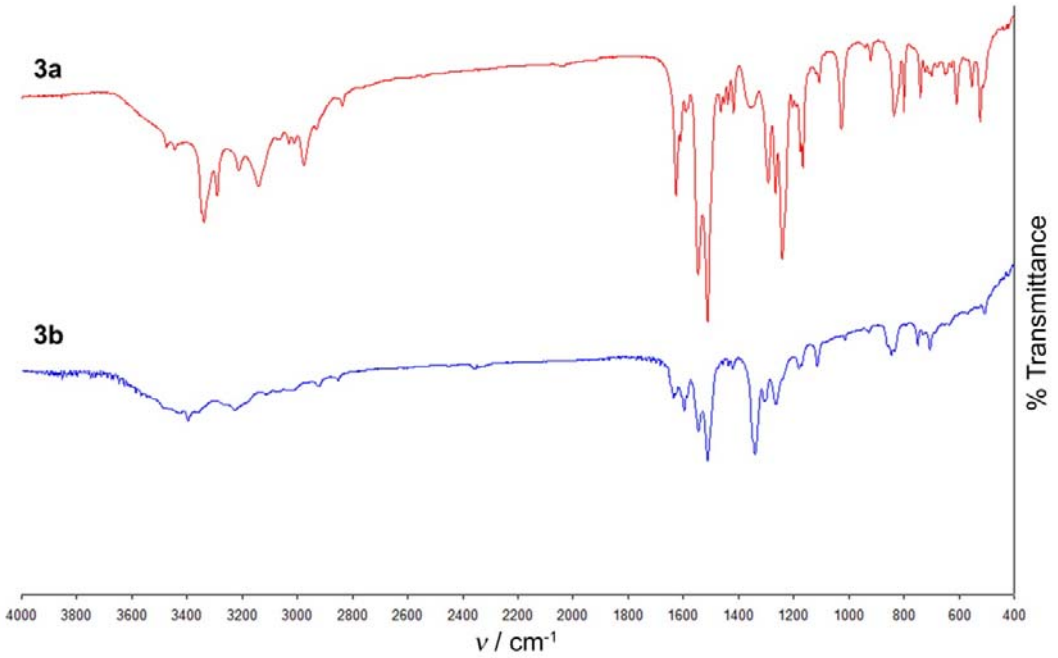


Figure S5. IR spectra of mono-thioureas **3a-b**. The absence of the characteristic isothiocyanate stretching vibration band at 2000–2200 cm^{-1} is notable.

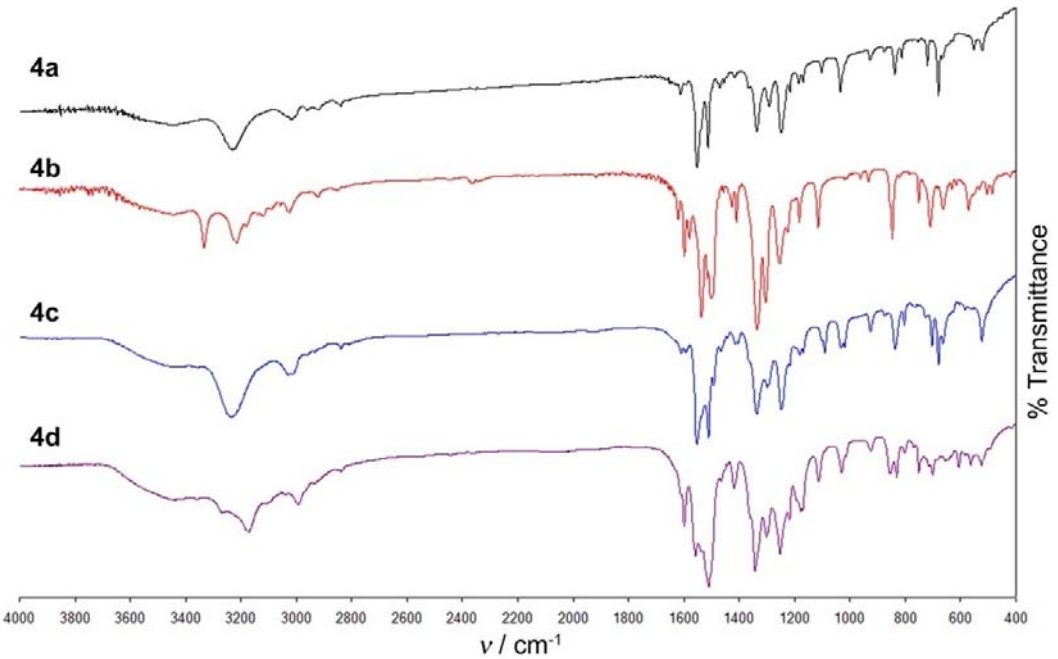


Figure S6. IR spectra of bis-thioureas **4a-d**. The absence of the characteristic isothiocyanate stretching vibration band at 2000–2200 cm^{-1} is notable.

3. ^{1}H and ^{13}C NMR spectra

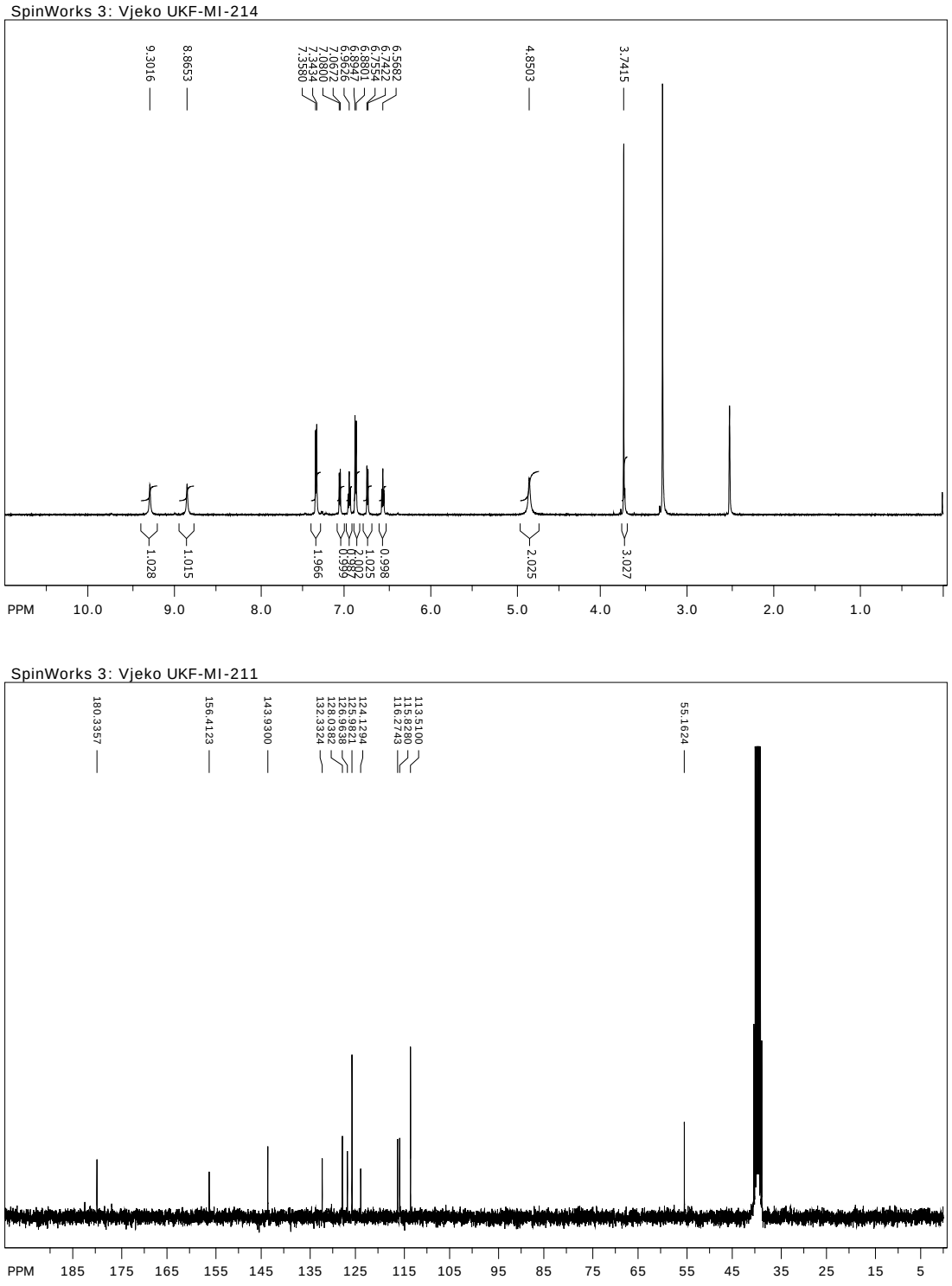


Figure S7. ^{1}H and ^{13}C NMR spectra of mono-thiourea **1a**.

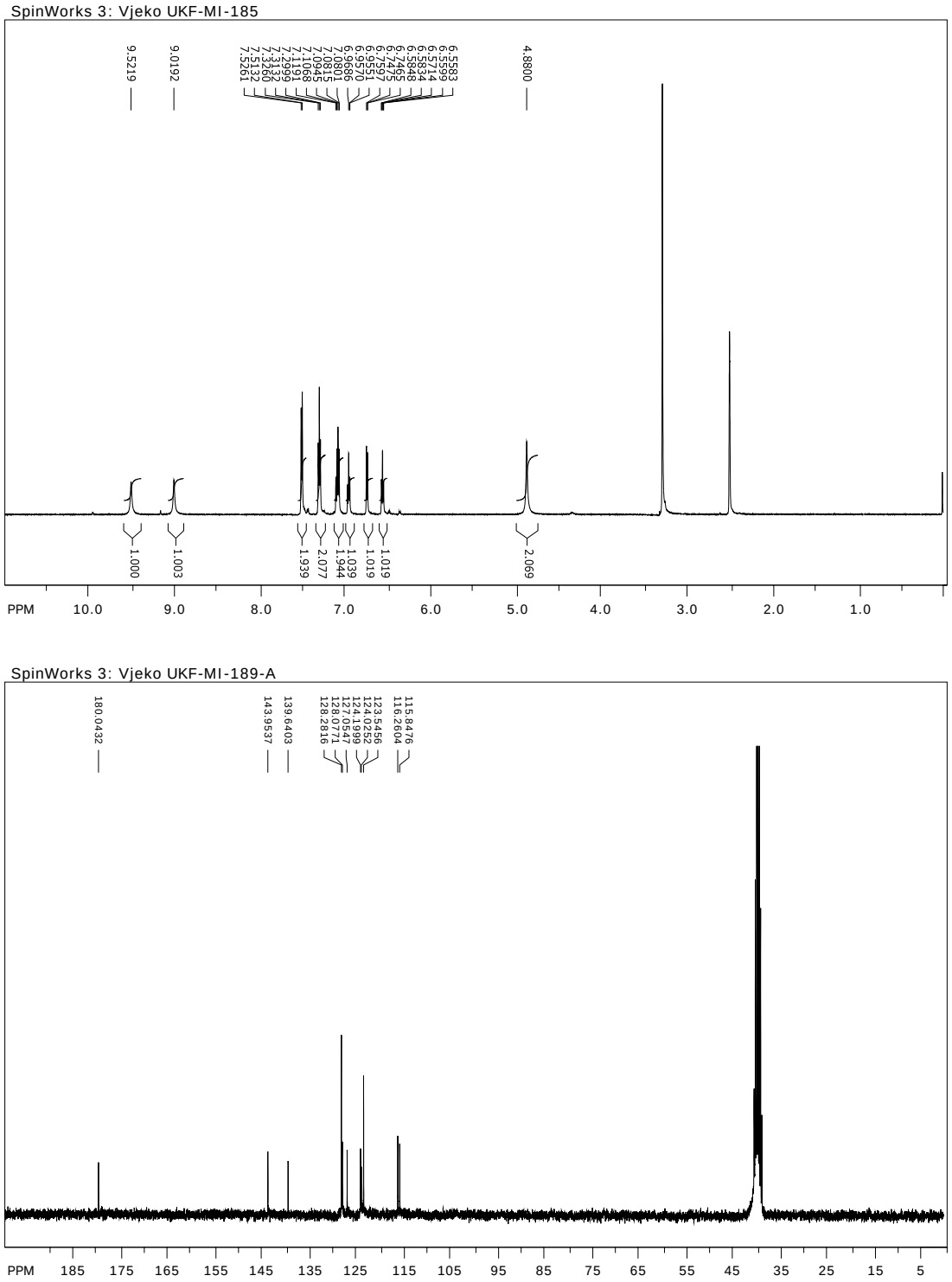


Figure S8. ^{1}H and ^{13}C NMR spectra of mono-thiourea **1b**.

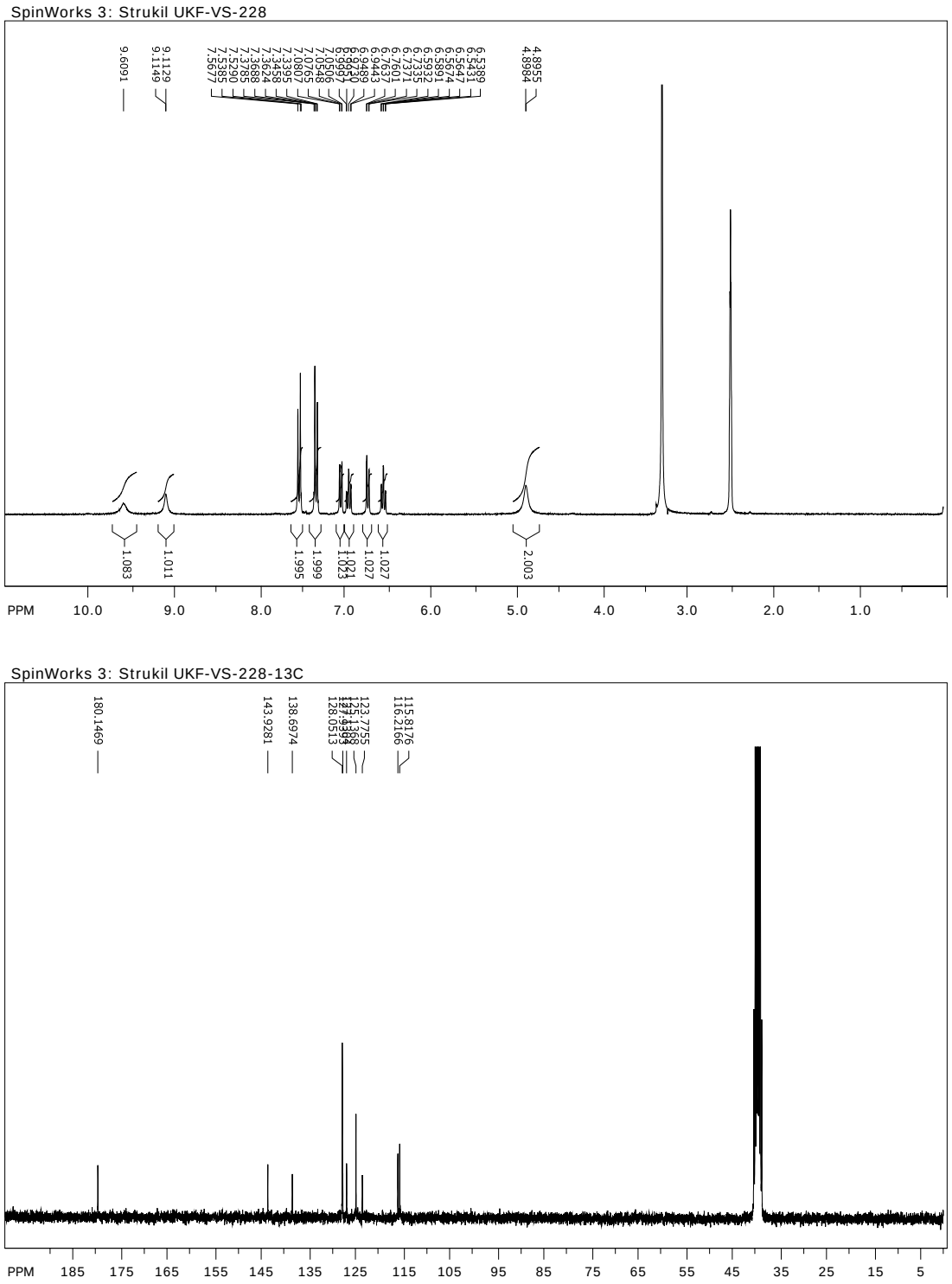


Figure S9. ^{1}H and ^{13}C NMR spectra of mono-thiourea **1c**.

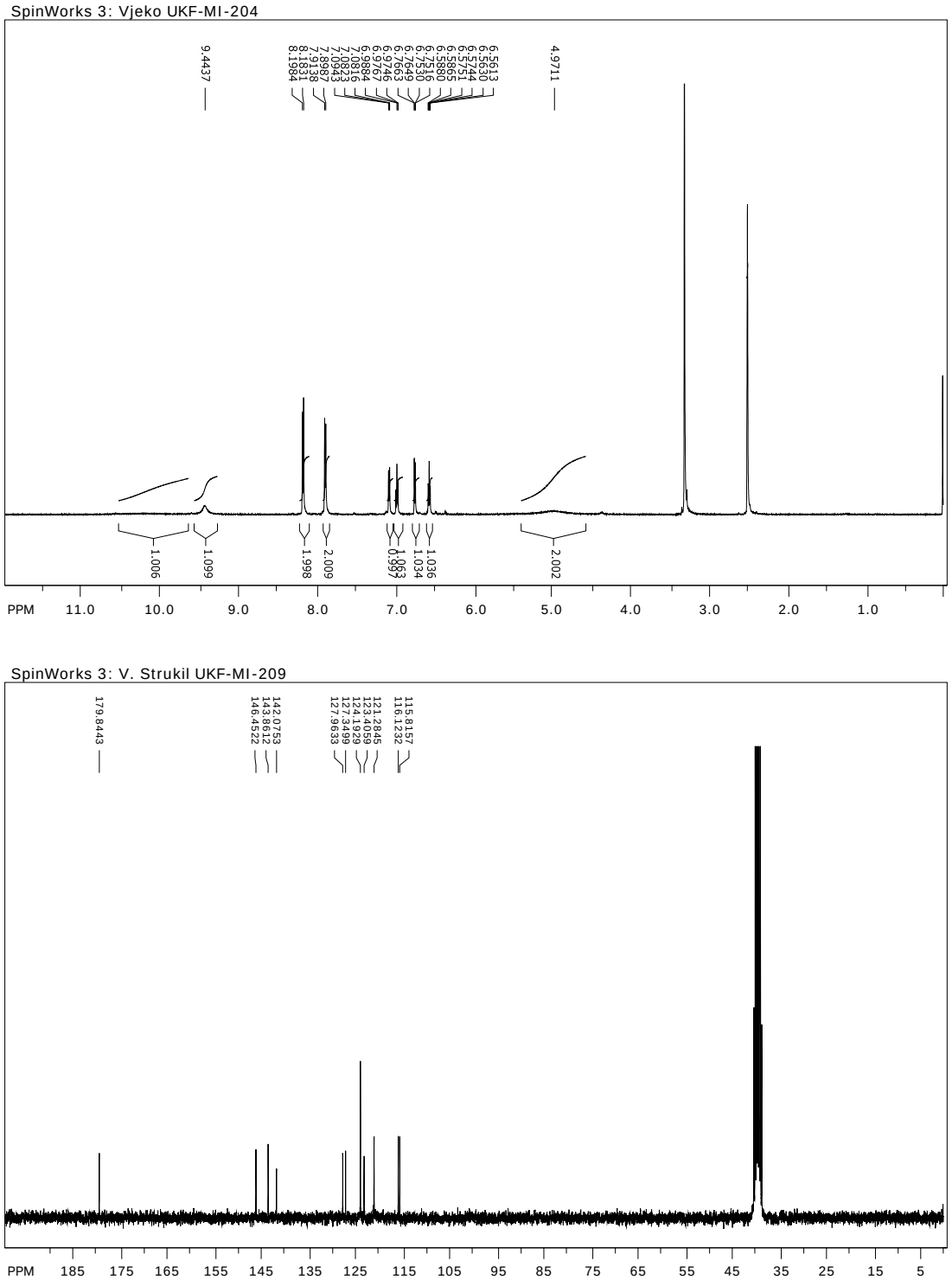


Figure S10. ^{1}H and ^{13}C NMR spectra of mono-thiourea **1d**.

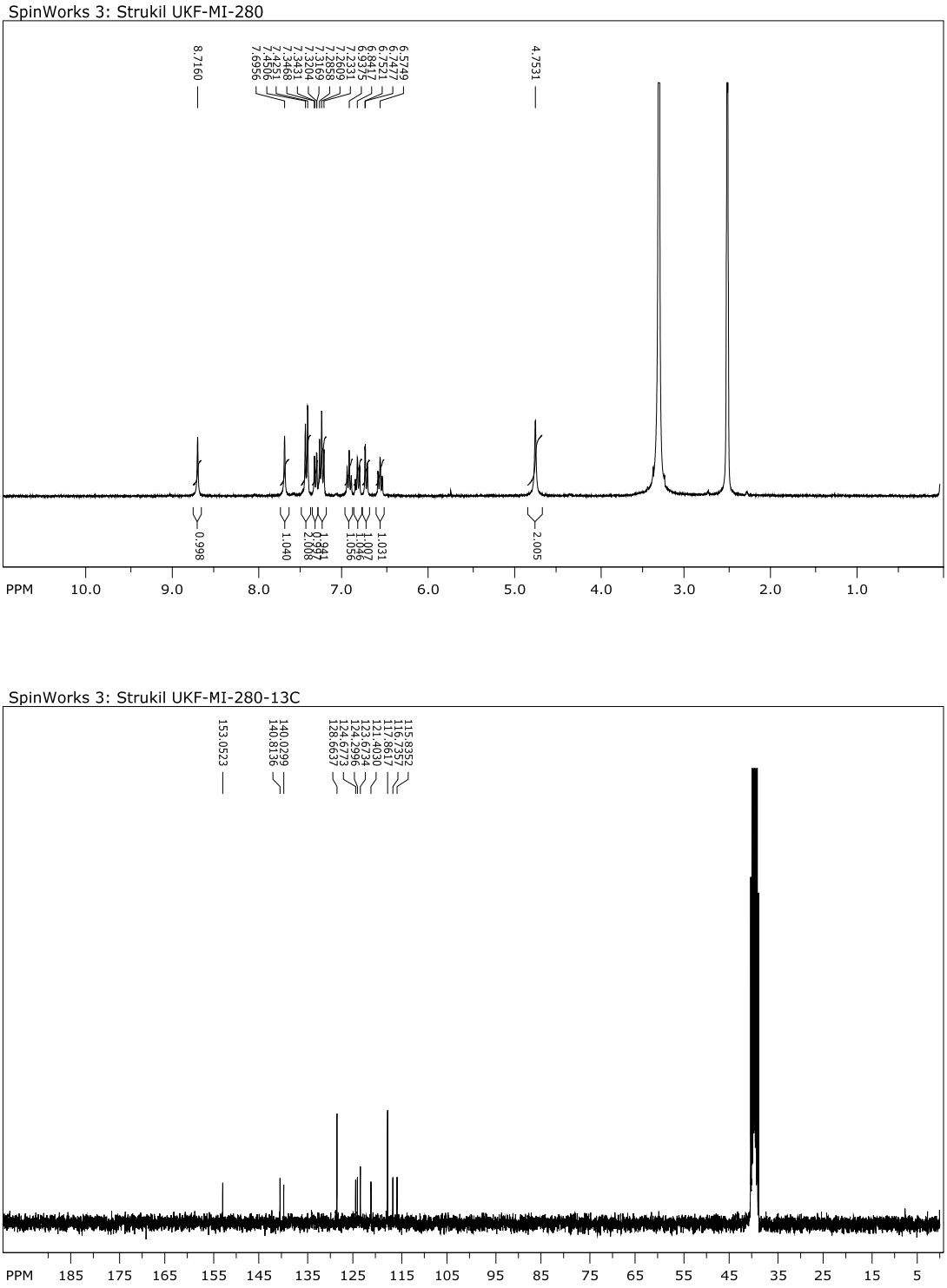


Figure S11. ^{1}H and ^{13}C NMR spectra of mono-urea **1e**.

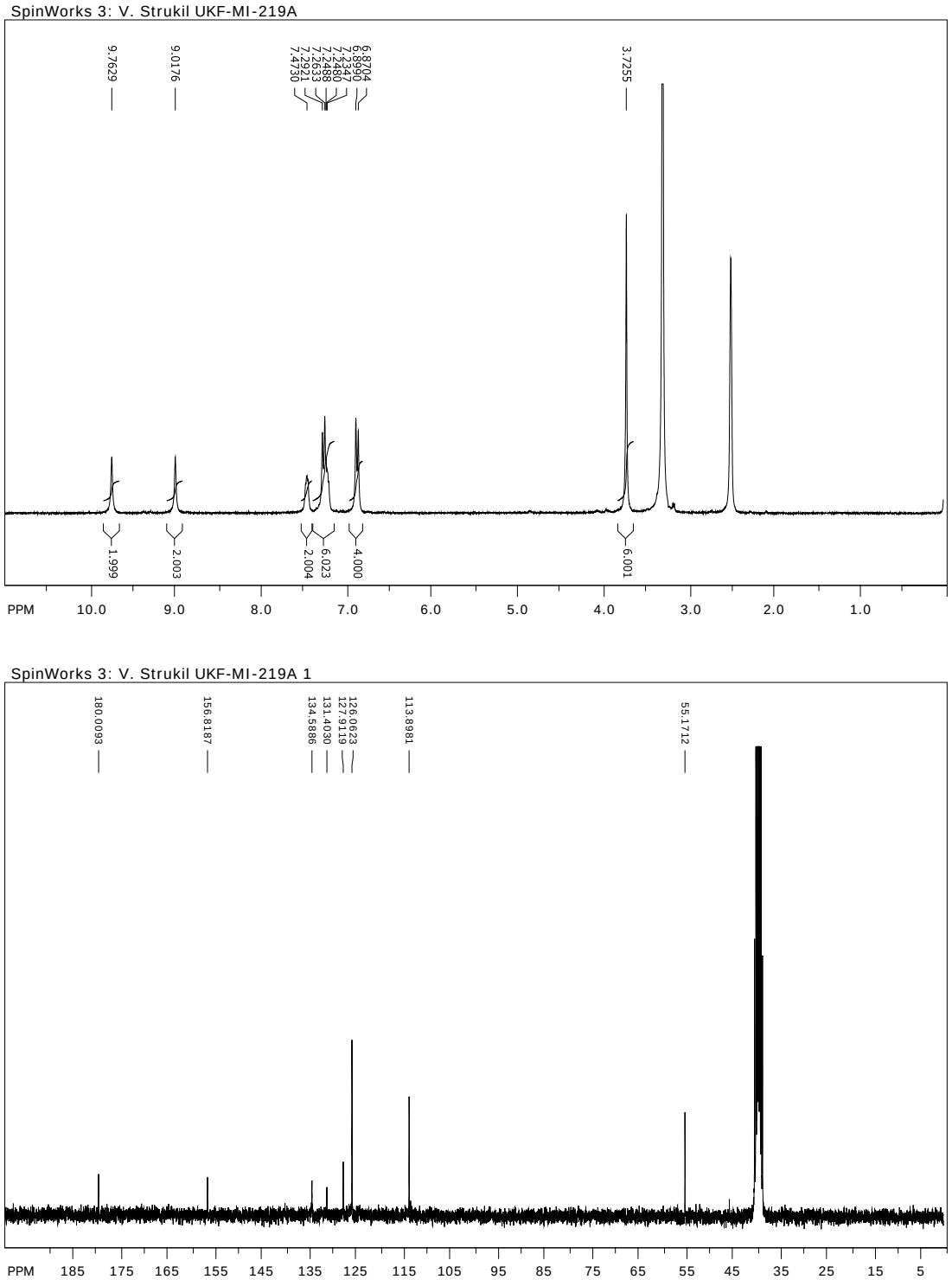


Figure S12. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2a**.

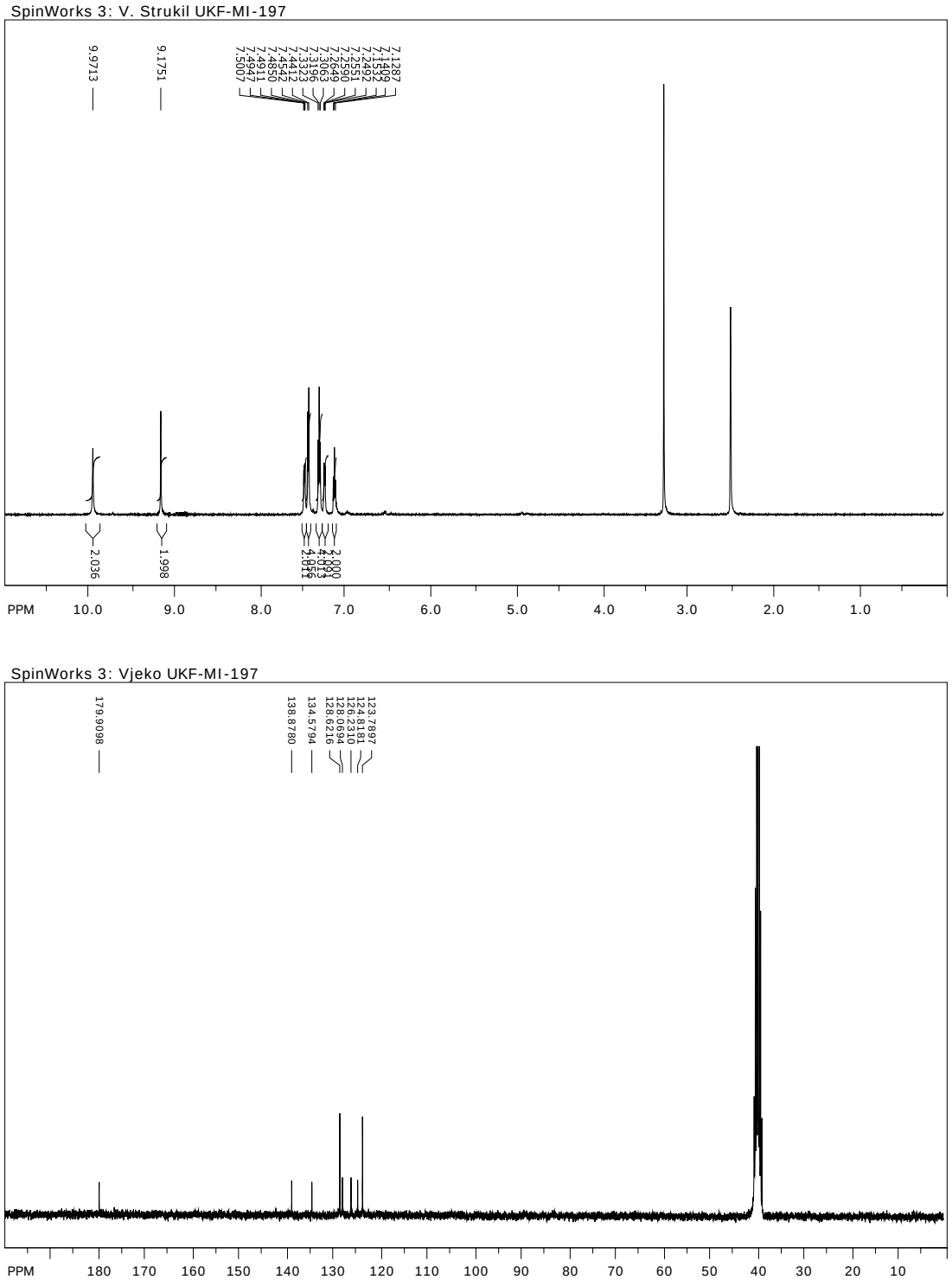


Figure S13. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2b**.

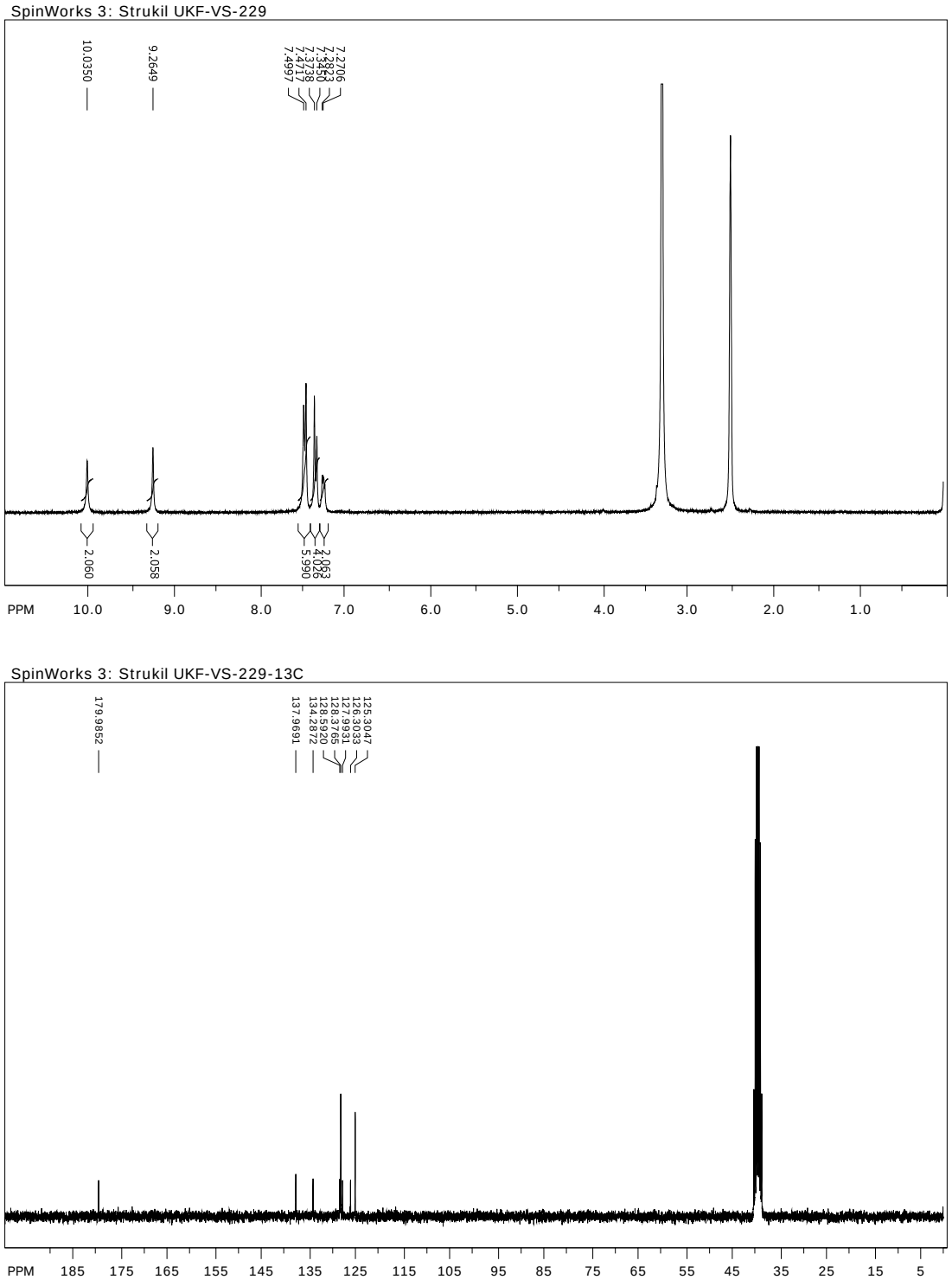


Figure S14. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2c**.

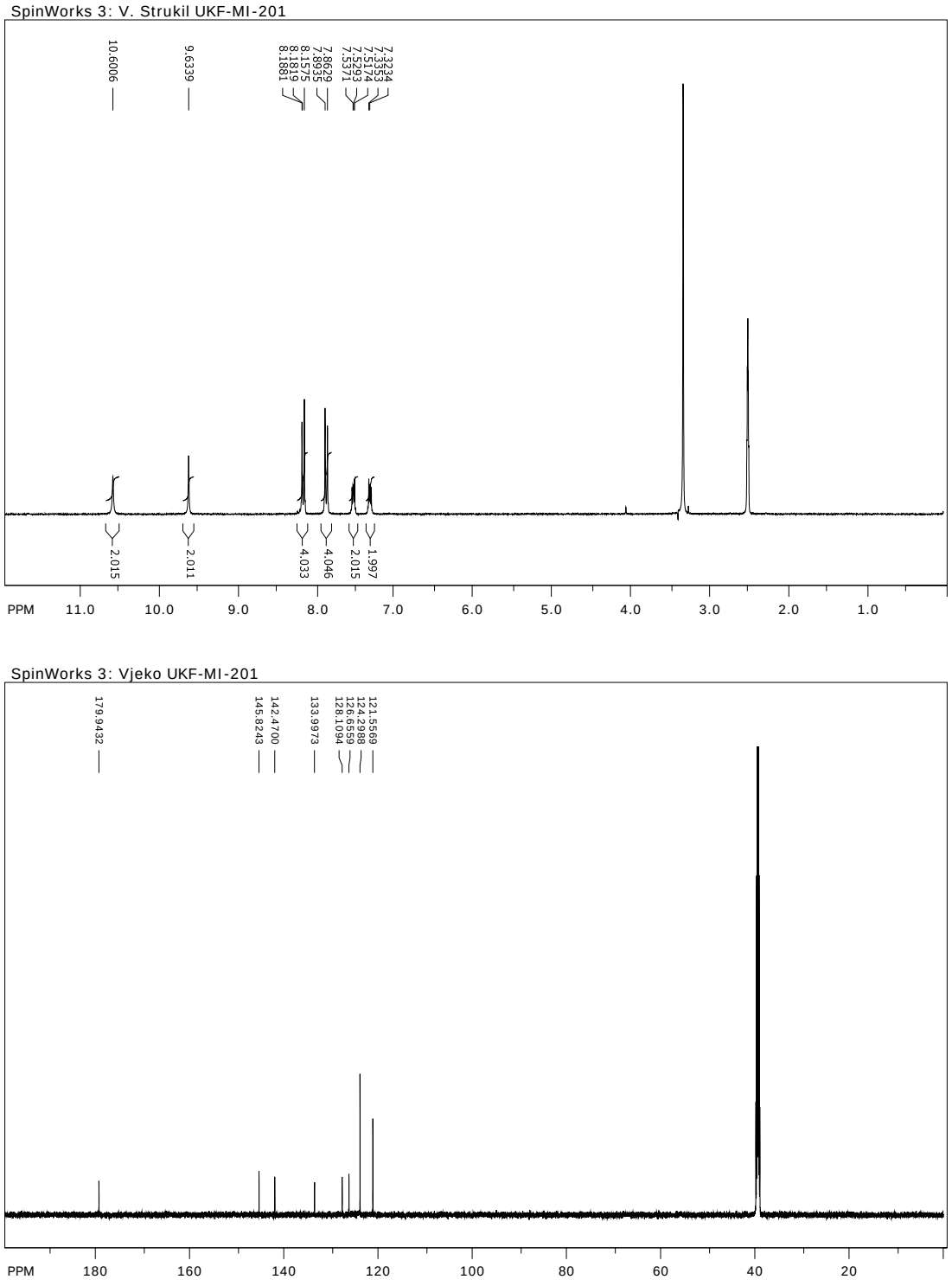


Figure S15. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2d**.

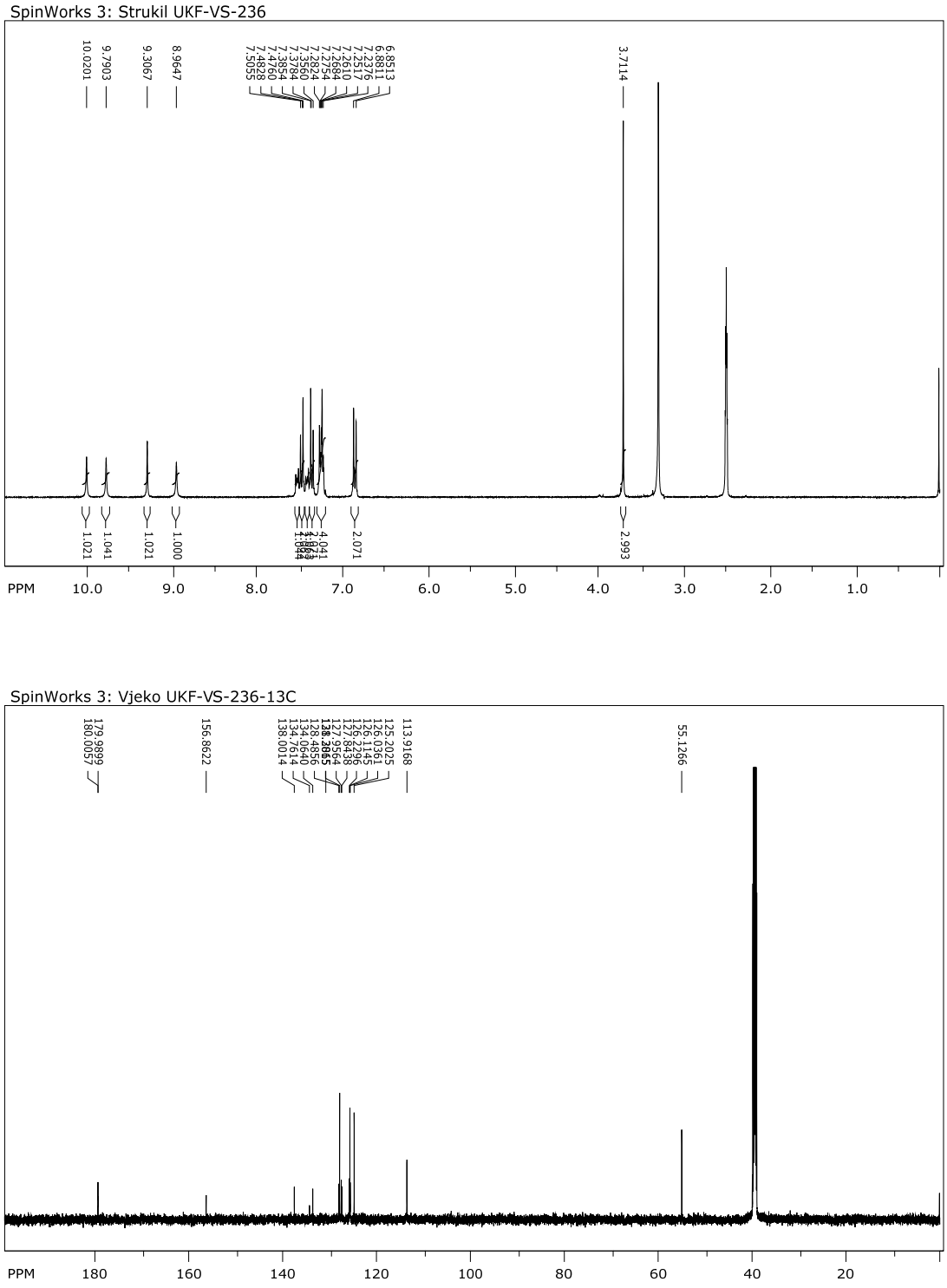


Figure S16. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2e**.

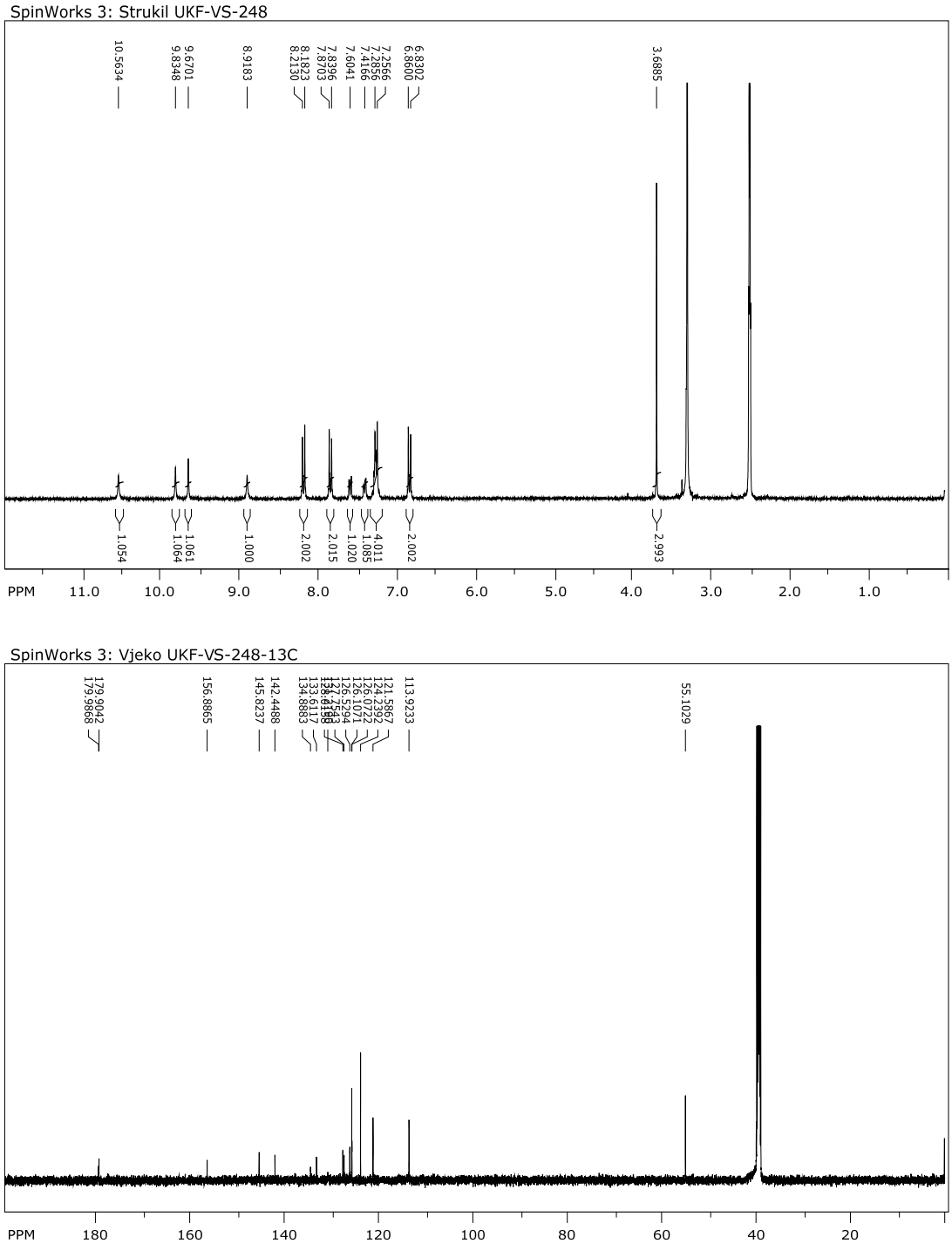


Figure S17. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2f**.

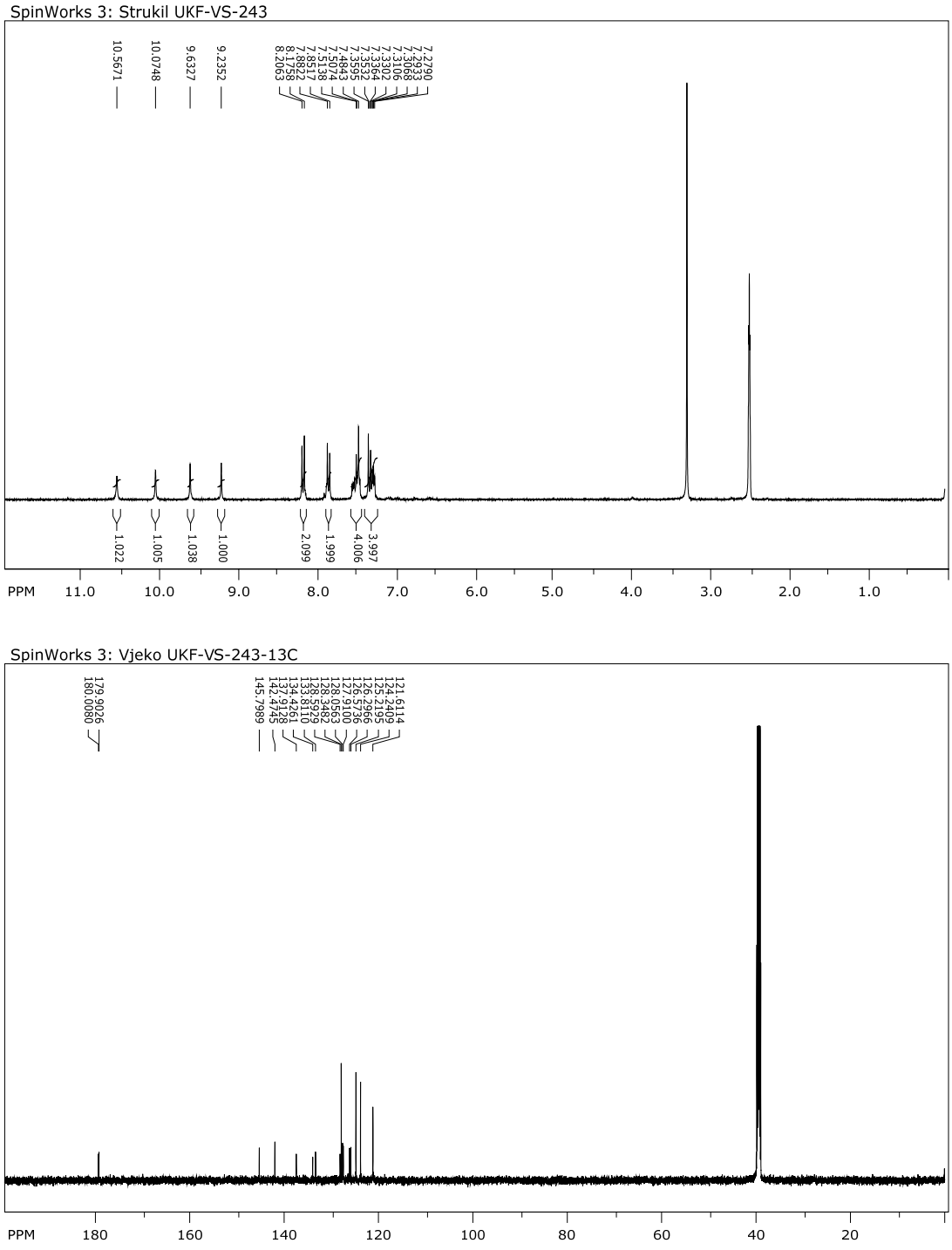


Figure S18. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2g**.

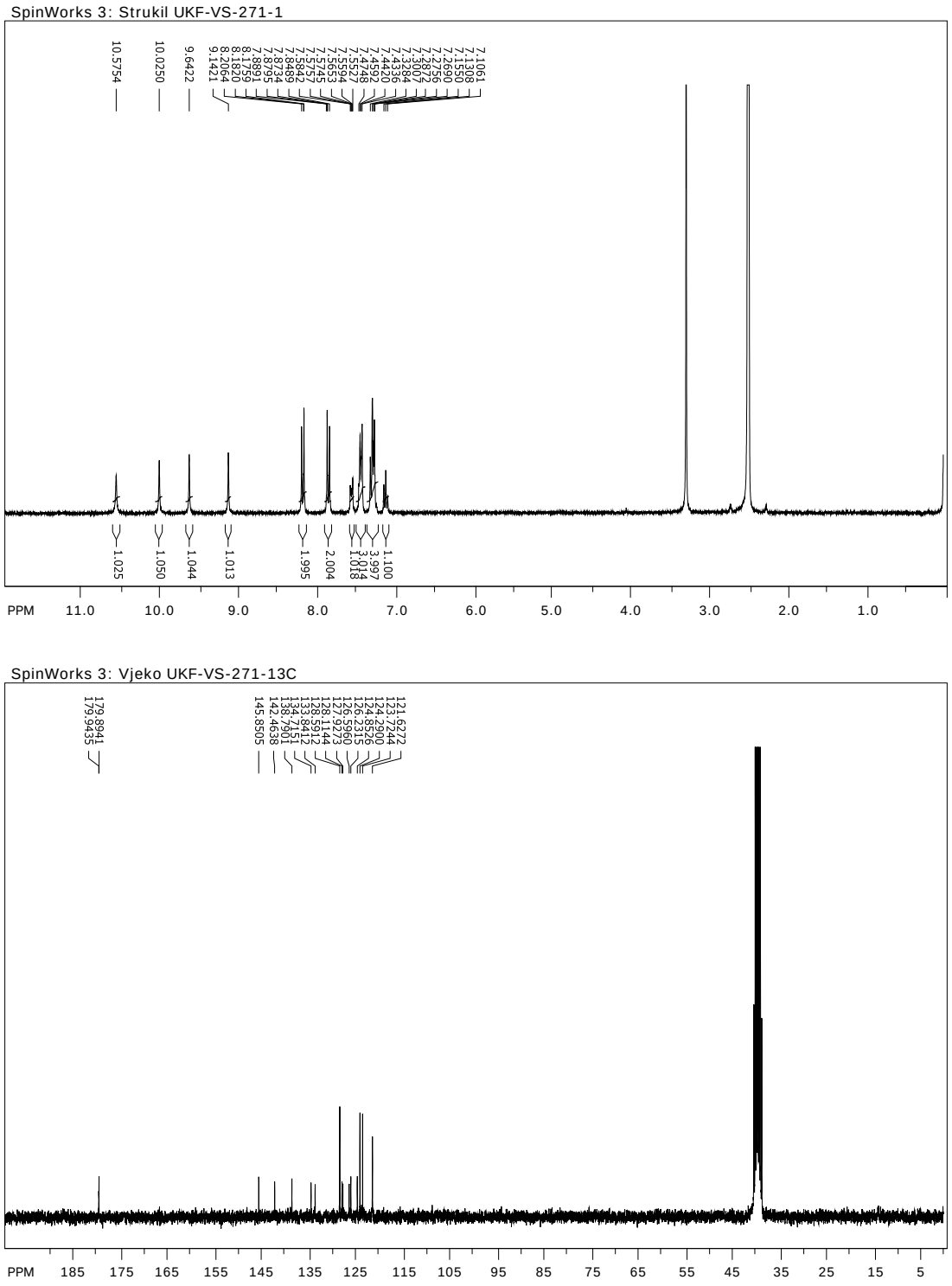
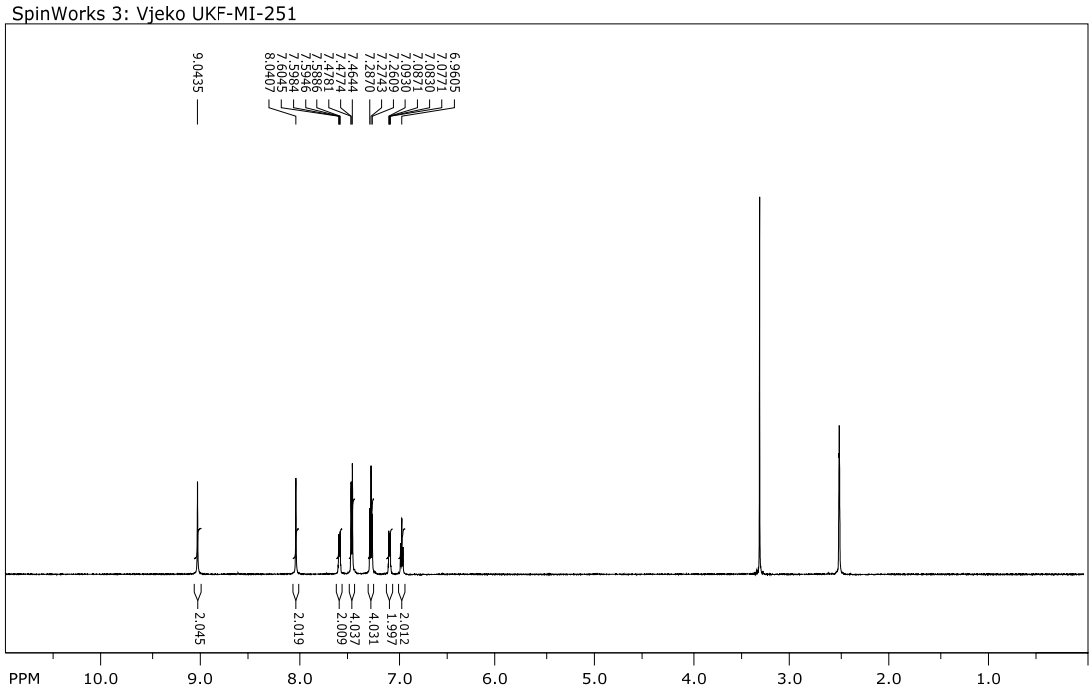


Figure S19. ^{1}H and ^{13}C NMR spectra of bis-thiourea **2h**.



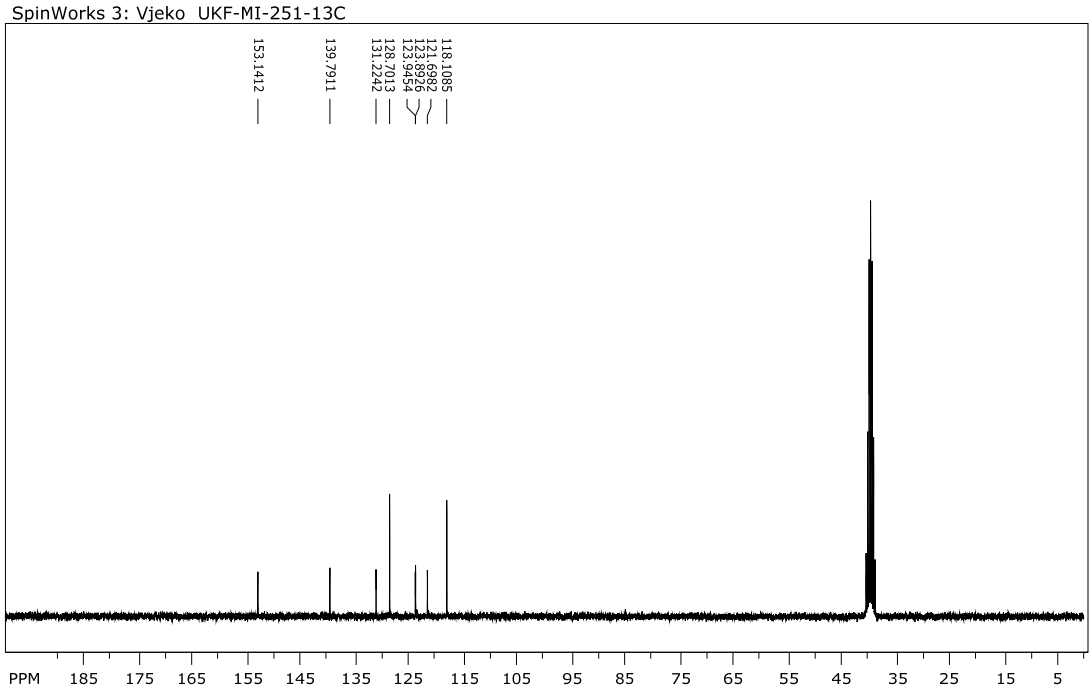


Figure S20. ^{1}H and ^{13}C NMR spectra of bis-urea **2i**.

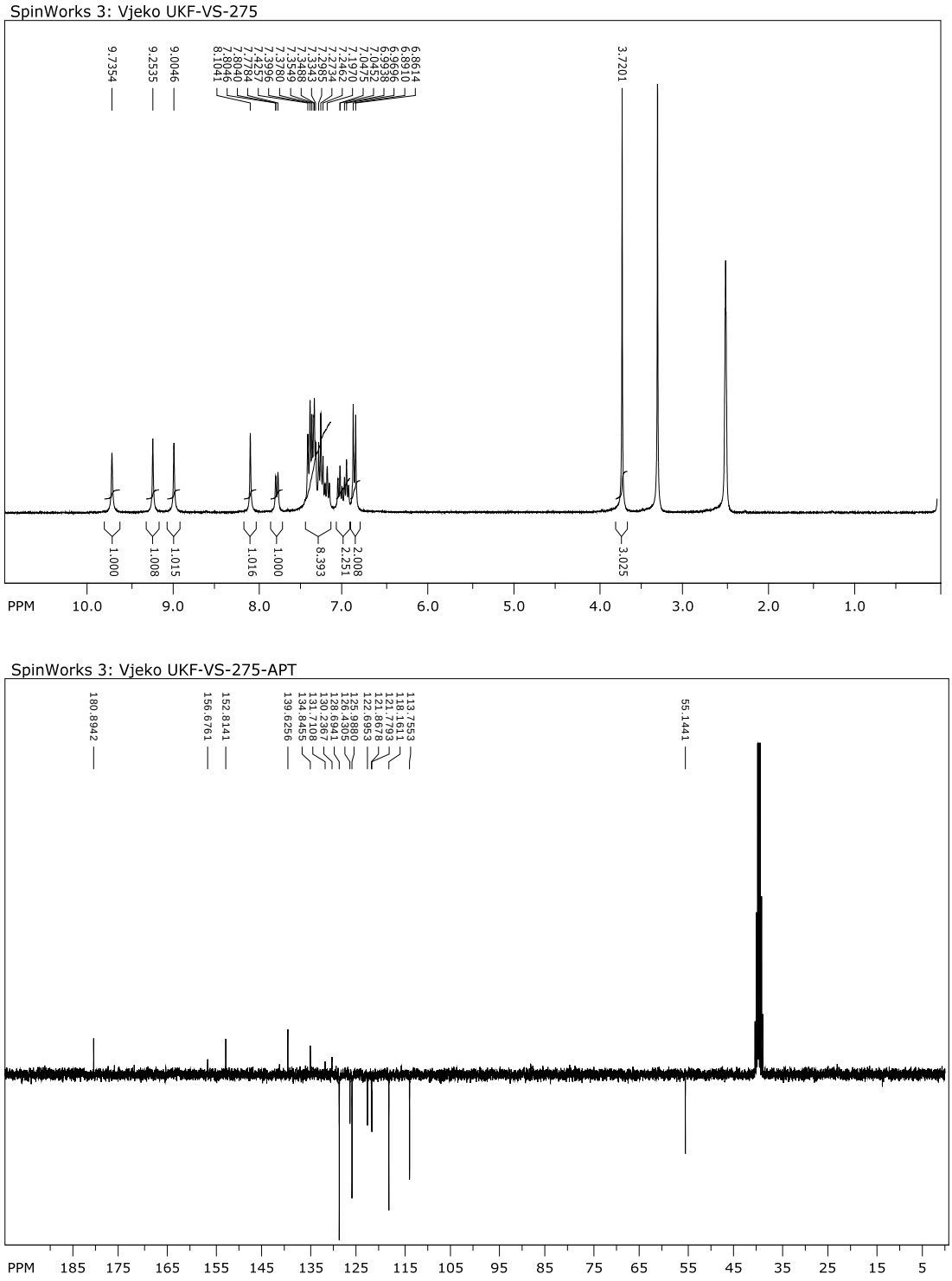


Figure S21. ^{1}H and ^{13}C NMR spectra of mixed urea-thiourea **2j**.

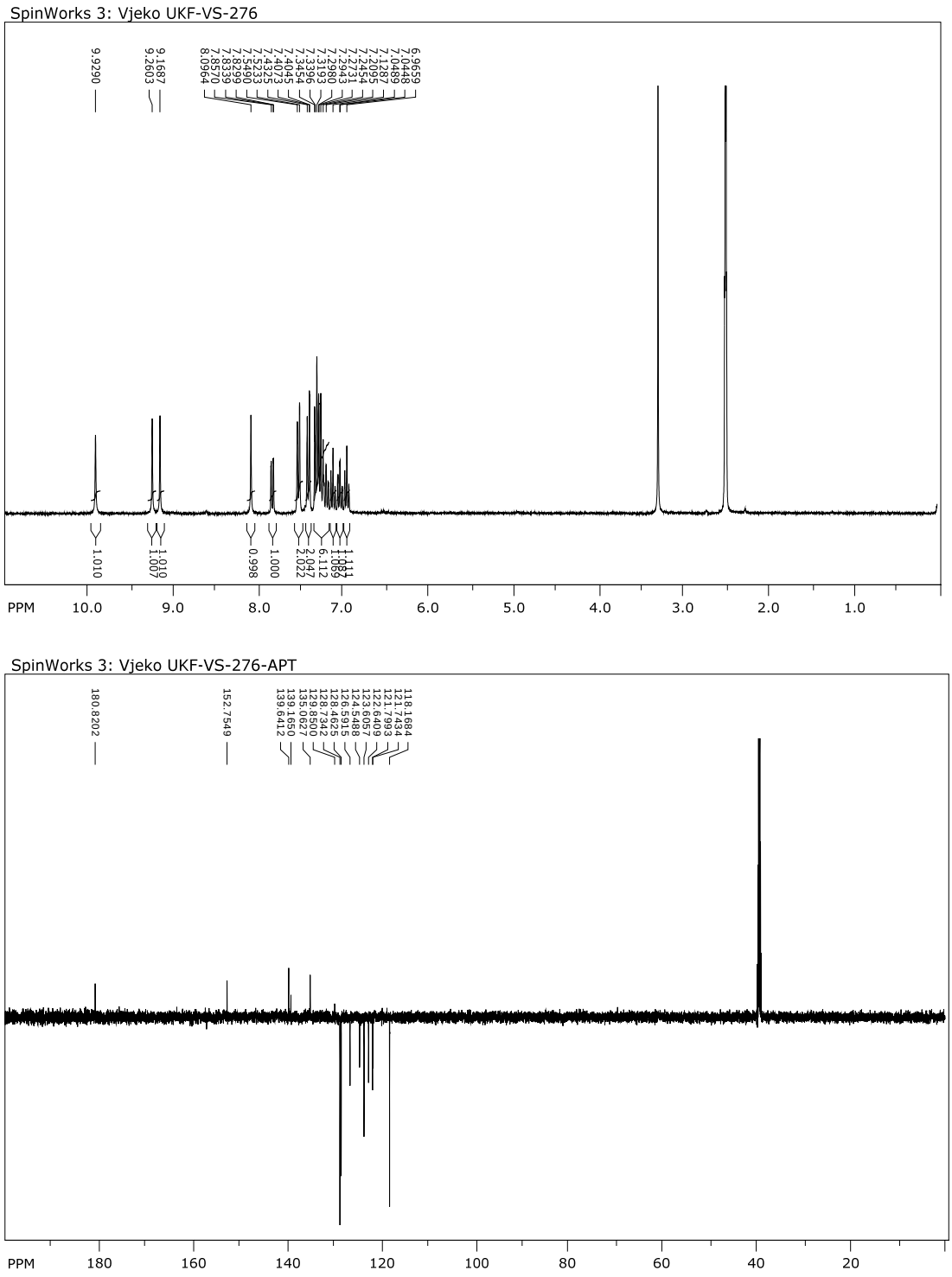


Figure S22. ^{1}H and ^{13}C NMR spectra of mixed urea-thiourea **2k**.

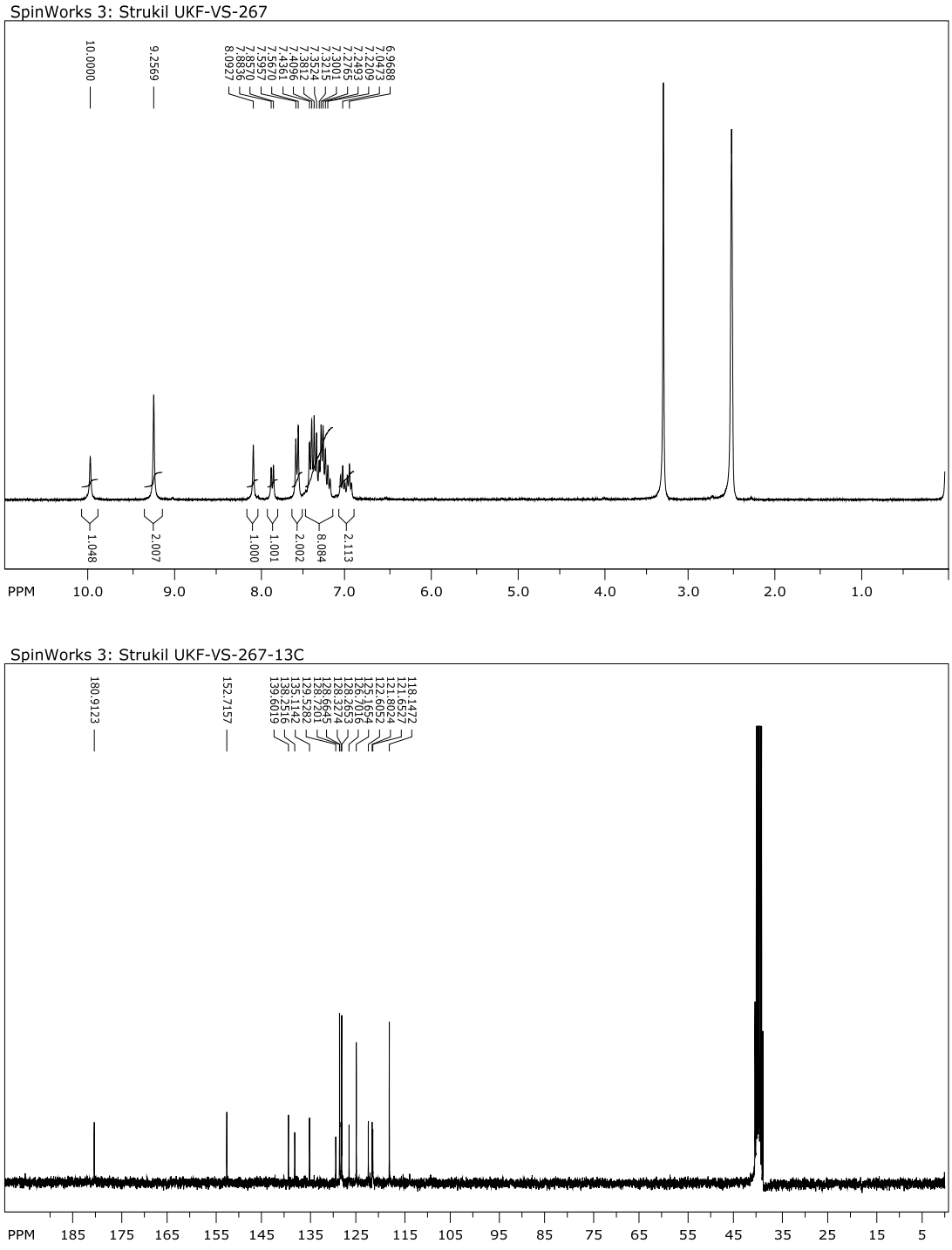


Figure S23. ^{1}H and ^{13}C NMR spectra of mixed urea-thiourea **2l**.

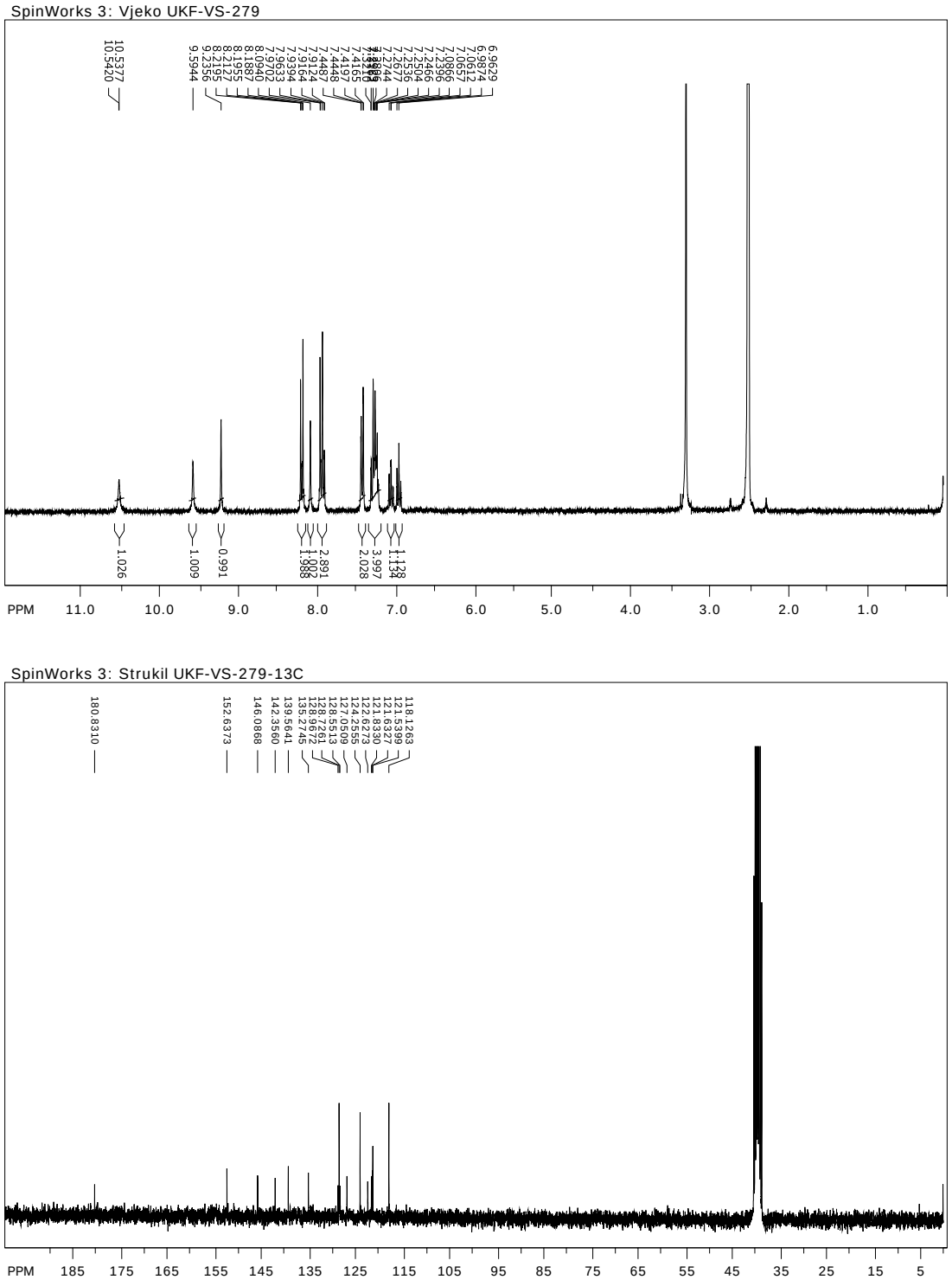


Figure S24. ^{1}H and ^{13}C NMR spectra of mixed urea-thiourea **2m**.

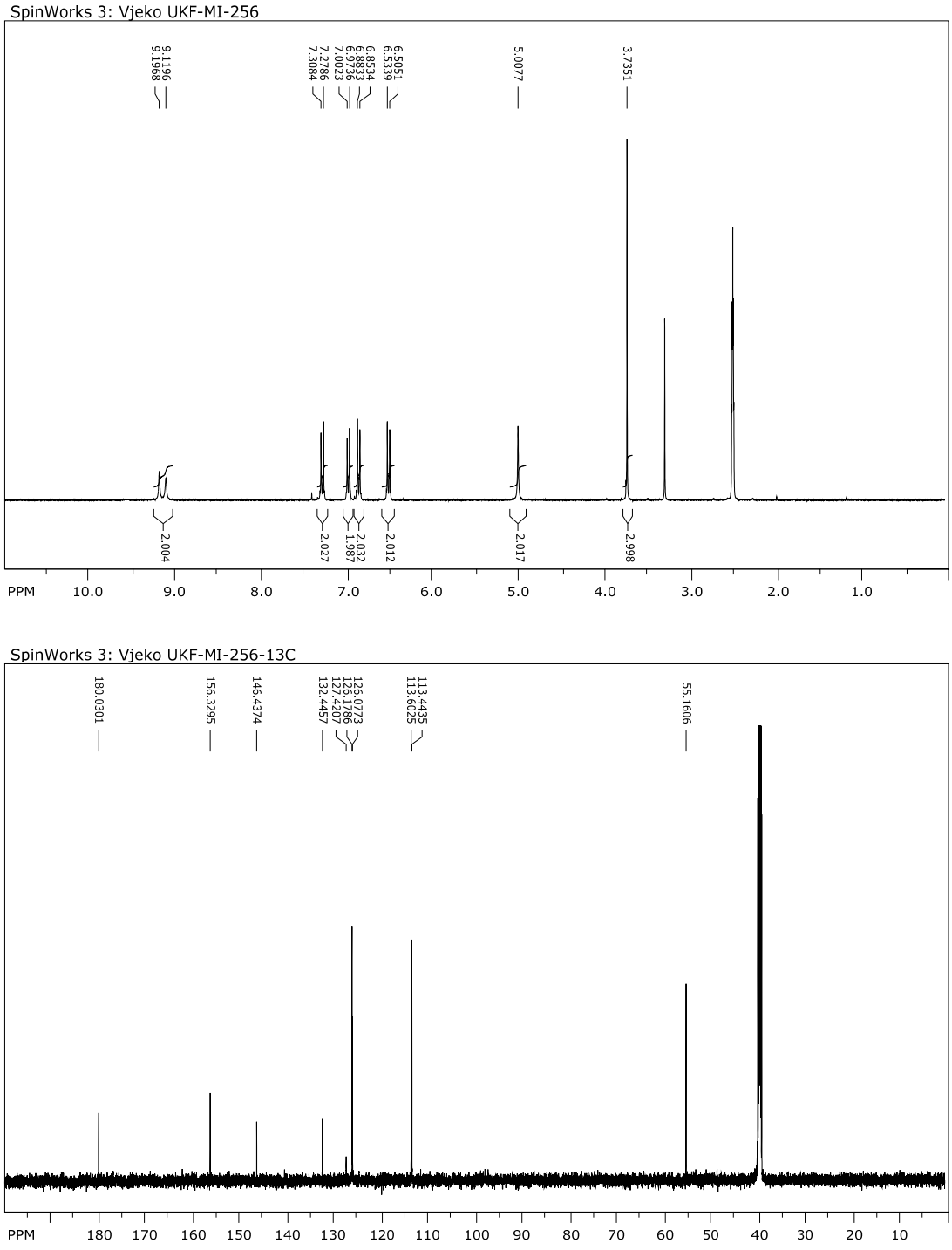


Figure S25. ^{1}H and ^{13}C NMR spectra of mono-thiourea **3a**.

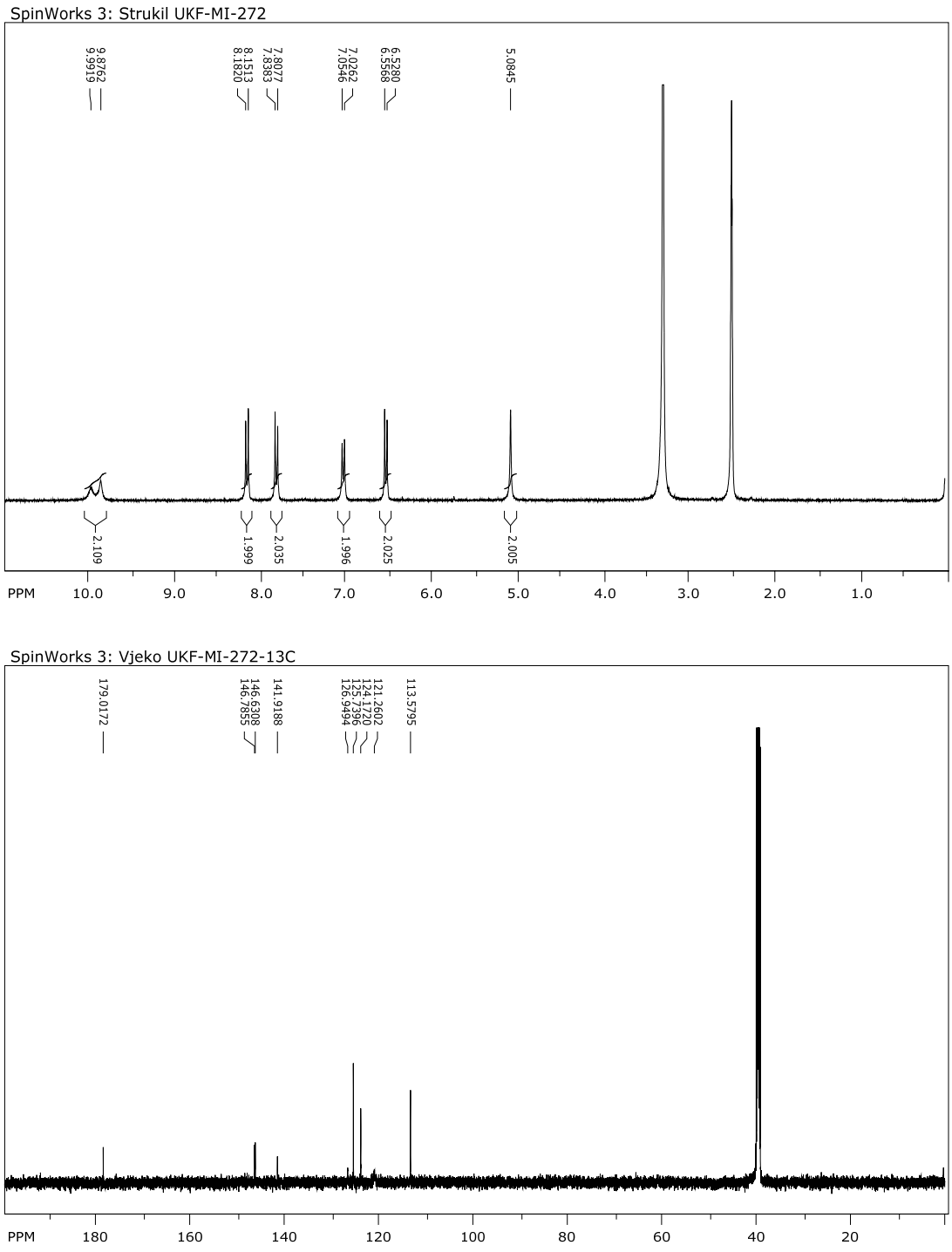


Figure S26. ^{1}H and ^{13}C NMR spectra of mono-thiourea **3b**.

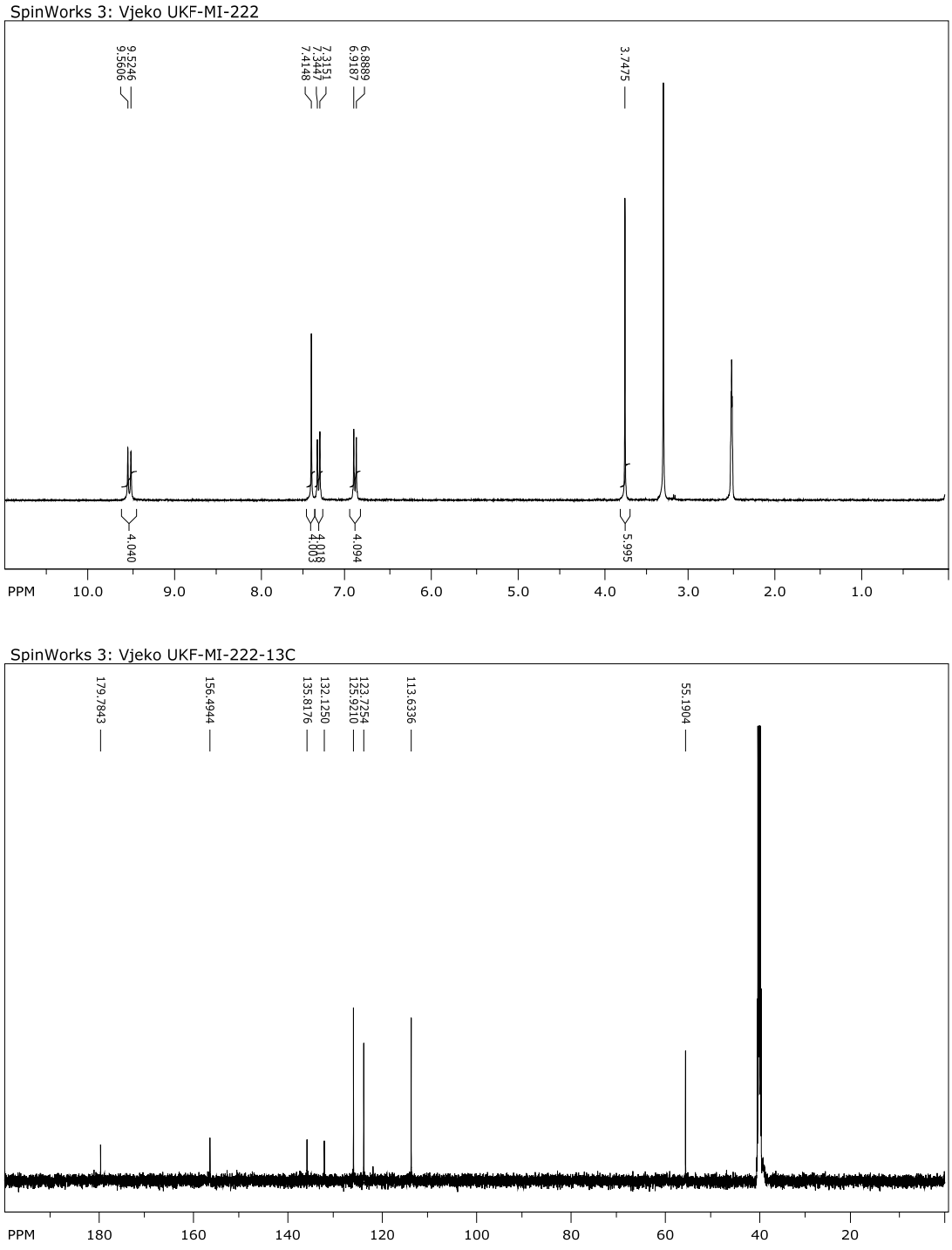


Figure S27. ^{1}H and ^{13}C NMR spectra of bis-thiourea **4a**.

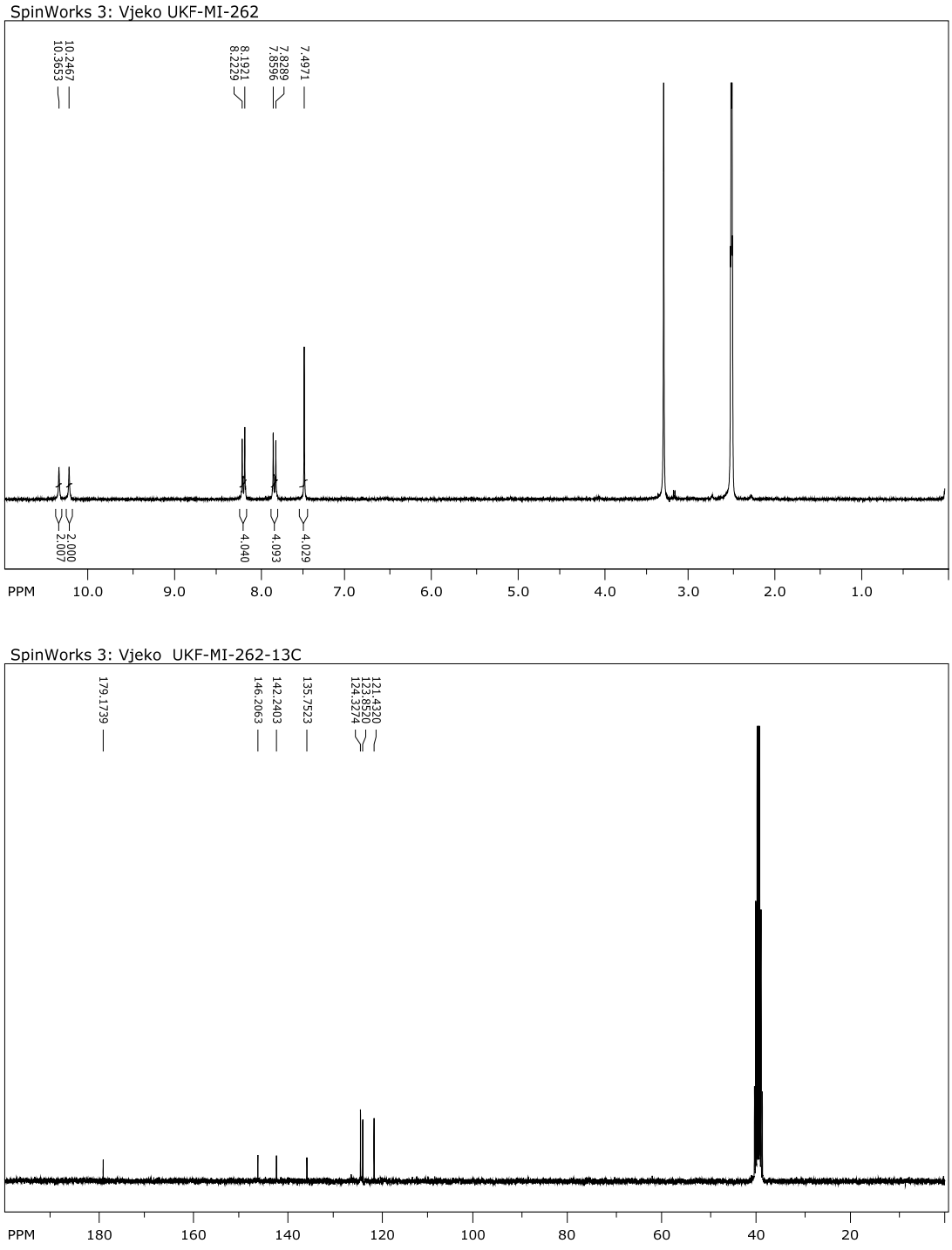


Figure S28. ^{1}H and ^{13}C NMR spectra of bis-thiourea **4b**.

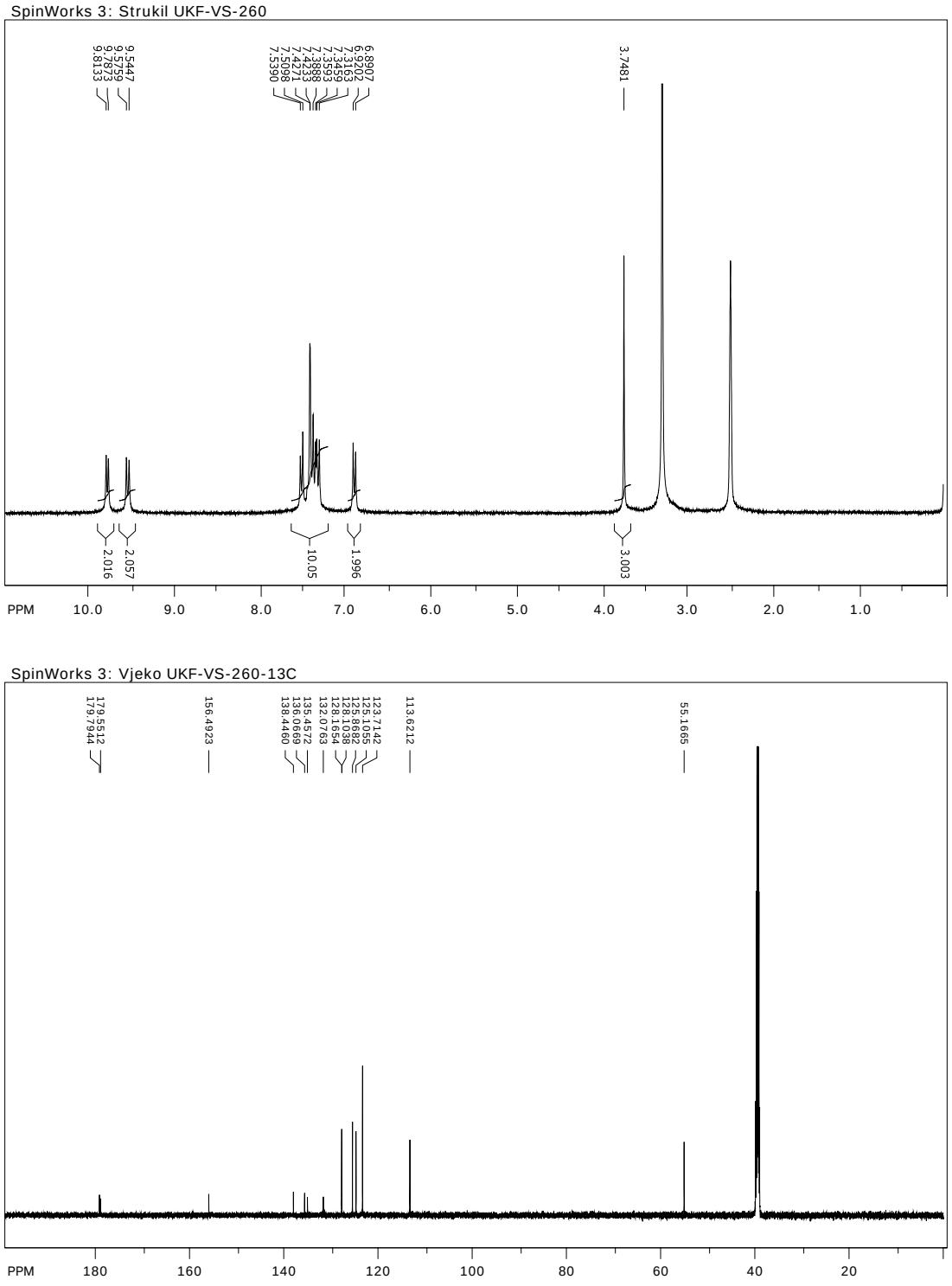


Figure S29. ^{1}H and ^{13}C NMR spectra of bis-thiourea **4c**.

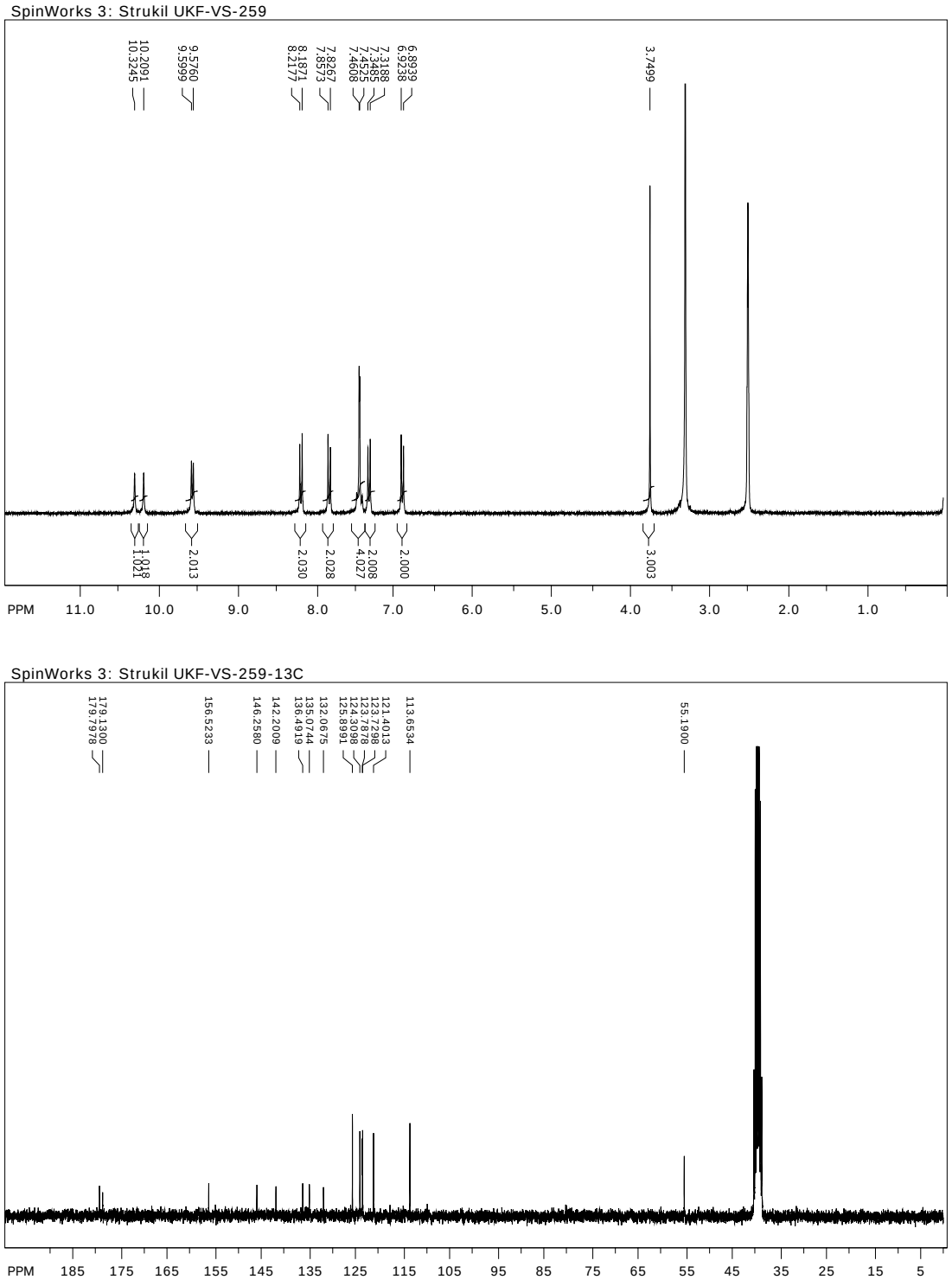


Figure S30. ^{1}H and ^{13}C NMR spectra of bis-thiourea **4d**.

4. DFT quantum chemical calculations

Table 1. Gas phase energies of *p*-methoxyphenyl mono-thiourea conformers **1a** calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

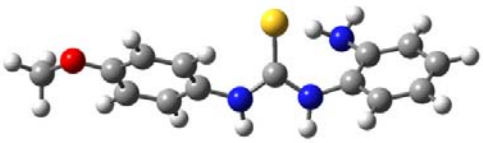
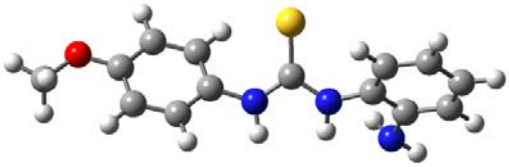
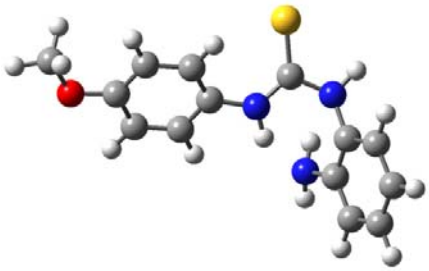
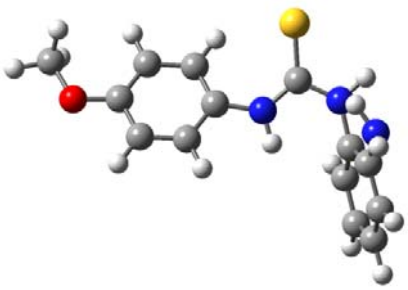
Structure	E_{el} / a.u.	E_{ZPV} / a.u.	E_{tot} / a.u.	E_{rel} / kJ mol^{-1}
 **1a-*cis***	-1180.42926	0.27280	-1180.15646	14.6
 **1a-*cis2***	-1180.42713	0.27315	-1180.15398	21.3
 **1a-*trans***	-1180.43534	0.27328	-1180.16206	0.0
 **1a-*trans2***	-1180.43454	0.27393	-1180.16061	3.8

Table 2. Gas phase energies of phenyl mono-thiourea conformers **1b** calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

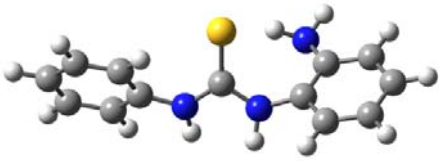
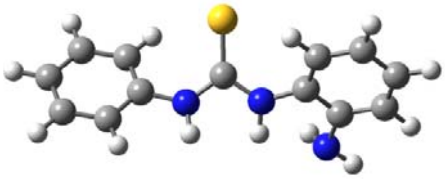
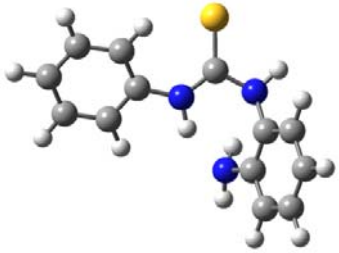
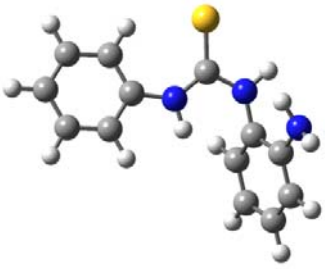
Structure	E_{el} / a.u.	E_{ZPV} / a.u.	E_{tot} / a.u.	E_{rel} / kJ mol^{-1}
 **1b-*cis***	-1065.87375	0.24027	-1065.63348	15.1
 **1b-*cis2***	-1065.87183	0.24055	-1065.63128	20.9
 **1b-*trans***	-1065.87985	0.24060	-1065.63925	0.0
 **1b-*trans2***	-1065.87915	0.24130	-1065.63785	3.8

Table 3. Gas phase energies of *p*-chlorophenyl mono-thiourea conformers **1c** calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

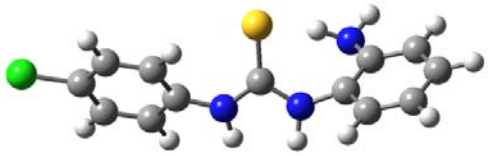
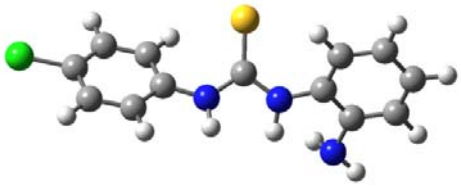
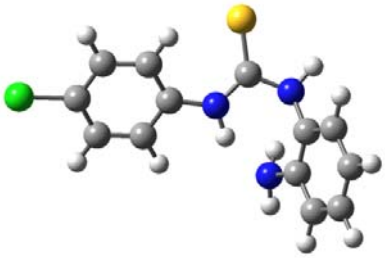
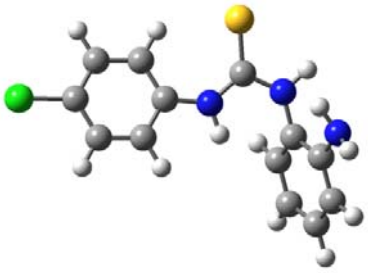
Structure	E_{el} / a.u.	E_{ZPV} / a.u.	E_{tot} / a.u.	E_{rel} / kJ mol^{-1}
 **1c-*cis***	-1525.49604	0.23059	-1525.26545	15.9
 **1c-*cis2***	-1525.49419	0.23086	-1525.26333	21.8
 **1c-*trans***	-1525.50232	0.23076	-1525.27156	0.0
 **1c-*trans2***	-1525.50171	0.23164	-1525.27007	3.8

Table 4. Gas phase energies of *p*-nitrophenyl mono-thiourea conformers **1d** calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

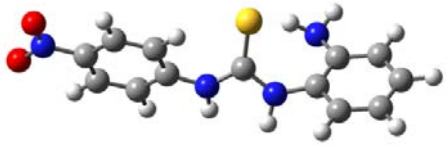
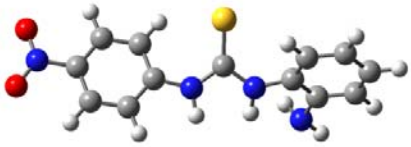
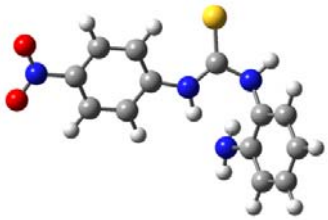
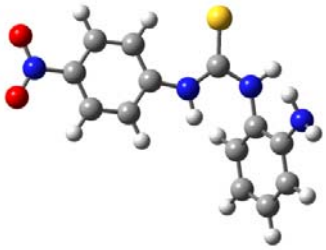
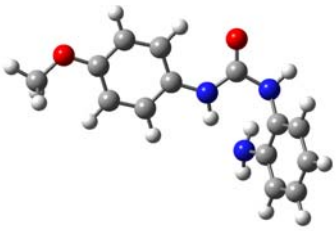
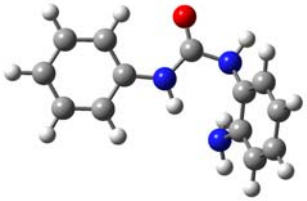
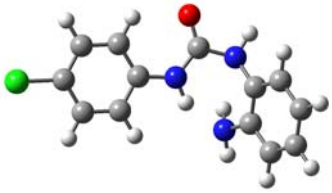
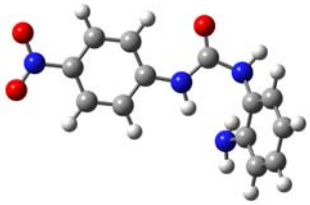
Structure	E_{el} / a.u.	E_{ZPV} / a.u.	E_{tot} / a.u.	E_{rel} / kJ mol^{-1}
 **1d-*cis***	-1270.43813	0.24296	-1270.19517	17.6
 **1d-*cis2***	-1270.43671	0.24330	-1270.19341	22.2
 **1d-*trans***	-1270.44493	0.24311	-1270.20182	0.0
 **1d-*trans2***	-1270.44446	0.24405	-1270.20041	3.8

Table 5. Gas phase energies of *trans*- mono-urea conformers calculated at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory.

Structure	E_{el} / a.u.	E_{ZPV} / a.u.	E_{tot} / a.u.
 **OMe-mono-urea**	-857.48449	0.276438	-857.20805
 **1e (H-mono-urea)**	-742.93029	0.243825	-742.68647
 **Cl-mono-urea**	-1202.55311	0.234142	-1202.31897
 **NO_2-mono-urea**	-947.49683	0.246555	-947.25028

5. Frontier Molecular Orbital (FMO) analysis

Table 6. HOMO and HOMO-1 energies of the most stable *trans*- conformers of mono-thioureas **1a-d** and LUMO energies of *p*-substituted phenyl isothiocyanates calculated at the RHF/6-31G(d)//B3LYP/6-31G(d) level of theory.

Mono-thiourea	HOMO / eV	HOMO-1 / eV	Isothiocyanate	LUMO / eV
1a-*trans* (OMe)	-7.7	-8.3	4-methoxyphenyl	2.6
1b-*trans* (H)	-8.0	-8.4	phenyl	2.3
1c-*trans* (Cl)	-8.2	-8.5	4-chlorophenyl	2.0
1d-*trans* (NO_2)	-8.6	-8.9	4-nitrophenyl	0.6

Table 7. HOMO–LUMO gaps for the reaction of mono-thioureas **1a-d** with *p*-substituted phenyl isothiocyanates calculated at the RHF/6-31G(d)//B3LYP/6-31G(d) level of theory.

Bis-thiourea (mono-thiourea + isothiocyanate)	HOMO–LUMO gap / eV	(HOMO-1)–LUMO gap / eV
2a (OMe + OMe)	10.3	10.9
2b (H + H)	10.3	10.7
2c (Cl + Cl)	10.2	10.5
2d (NO_2 + NO_2)	9.2	9.5
2e (OMe + Cl)	9.7	10.3
2f (OMe + NO_2)	8.3	8.9
2g (NO_2 + Cl)	10.6	10.9
2h (H + NO_2)	8.6	9.0

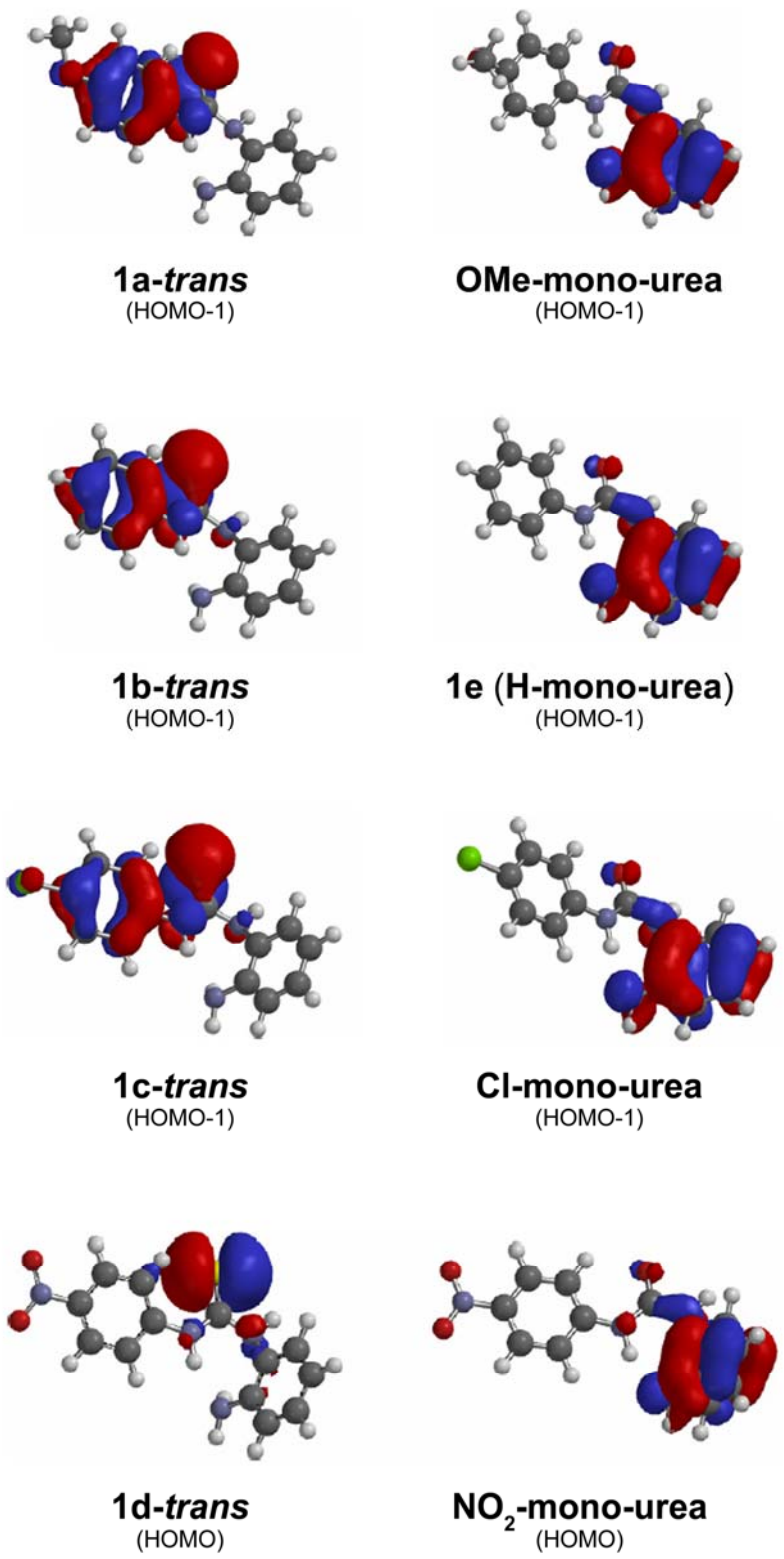


Figure S31. The comparison of the frontier molecular orbitals of *trans*- conformers of mono-thioureas **1a-d** and the corresponding urea analogues. The difference in the relative sizes of the orbital coefficients on the sulfur, oxygen and free NH_2 nitrogen atoms is notable.

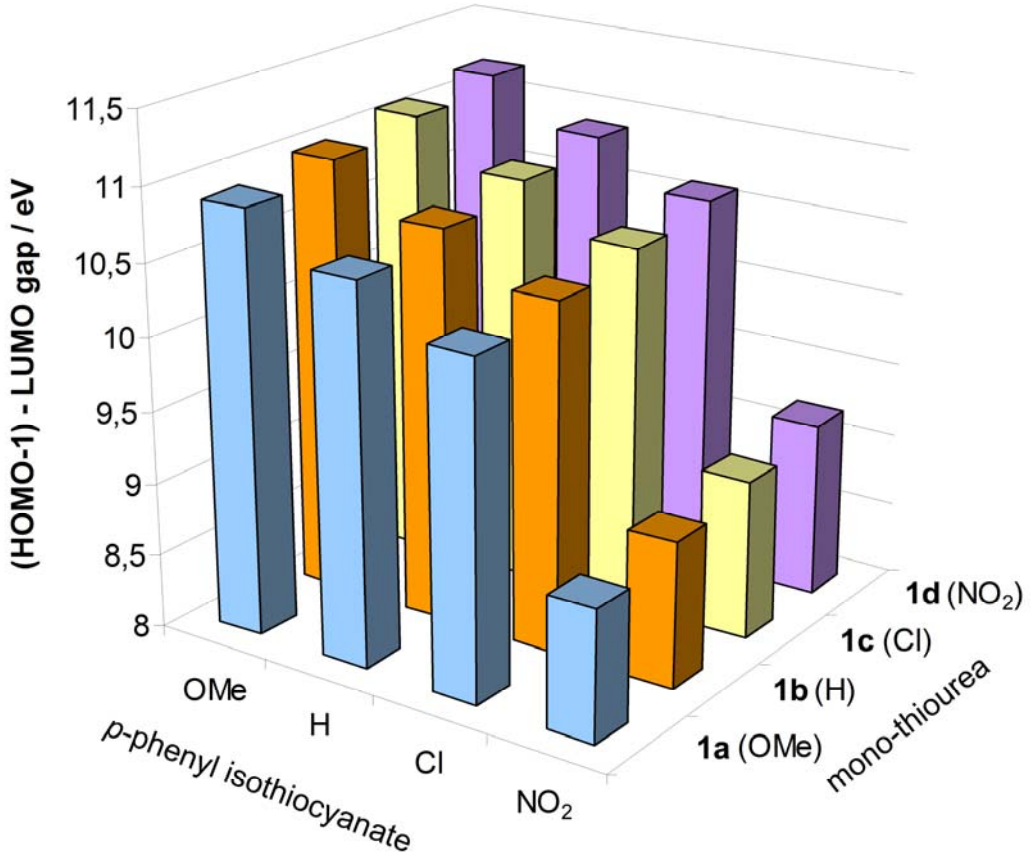


Figure S32. (HOMO-1)–LUMO gaps (calculated at the RHF/6-31G(d)//B3LYP/6-31G(d) level of theory) for different combinations of mono-thioureas **1a-d** and *p*-substituted phenyl isothiocyanates. In the case of NO_2 mono-thiourea **1d** HOMO–LUMO values are displayed.

6. Cartesian coordinates of mono-(thio)ureas

B3LYP/6-31G(d) geometries:

1a-*cis*

C	-1.389543	-0.182379	5.329340
C	-1.448168	-0.437612	3.961564
C	-0.300776	-0.394524	3.165076
C	0.952480	-0.075900	3.737128
C	0.989701	0.192685	5.117416
C	-0.155975	0.131796	5.903420
H	-2.291456	-0.220320	5.932367
H	-2.397938	-0.675478	3.488269
H	1.946287	0.443930	5.570815
H	-0.084775	0.339824	6.967730
N	-0.418228	-0.817441	1.803822
H	-0.912335	-1.695376	1.685794
N	2.120002	-0.099591	2.977345
H	2.007917	0.329632	2.060386
H	2.911051	0.311459	3.460878
C	-0.193913	-0.092101	0.663998
S	0.298125	1.514826	0.667994
N	-0.405462	-0.843577	-0.468198
H	-0.422889	-1.847726	-0.332969
C	-0.299116	-0.447303	-1.829736
C	-0.926700	0.705618	-2.324679
C	-0.847346	1.013994	-3.674474
C	-0.161723	0.172344	-4.564156
C	0.450080	-0.987557	-4.078970
C	0.382886	-1.282312	-2.714774
H	-1.467890	1.356036	-1.649071
H	-1.323336	1.906036	-4.068931
H	0.986950	-1.659046	-4.738769
H	0.877654	-2.175634	-2.339995
O	-0.156019	0.568224	-5.870754
C	0.527300	-0.242243	-6.812471
H	0.407750	0.253497	-7.777529
H	1.596859	-0.322069	-6.576223
H	0.094995	-1.250560	-6.867519

1a-*cis2*

C	-1.428451	-0.807420	4.912789
C	-1.124178	-0.734540	3.553886
C	0.098252	-0.199881	3.139329
C	1.020193	0.278604	4.096319
C	0.709209	0.176417	5.454675
C	-0.508079	-0.366988	5.864393
H	-2.382596	-1.222362	5.224047
H	-1.825215	-1.090410	2.809995
H	1.422935	0.541295	6.190529
H	-0.739276	-0.431390	6.923921
N	0.543107	-0.188157	1.798495
H	1.557202	-0.232896	1.732387

N	2.264042	0.783218	3.632347
H	2.146479	1.584821	3.015197
H	2.872711	1.053472	4.398920
C	-0.147004	0.025958	0.627930
S	-1.724966	0.574959	0.532441
N	0.654296	-0.258567	-0.459237
H	1.439230	-0.870985	-0.270007
C	0.374148	-0.097476	-1.841728
C	-0.188594	1.076214	-2.366763
C	-0.379558	1.203633	-3.734575
C	0.001263	0.177534	-4.612783
C	0.578779	-0.986567	-4.097339
C	0.752646	-1.116324	-2.717083
H	-0.480430	1.877620	-1.700477
H	-0.819720	2.104115	-4.151004
H	0.886001	-1.797933	-4.746743
H	1.185338	-2.032925	-2.321713
O	-0.227012	0.414213	-5.938706
C	0.124145	-0.596882	-6.868159
H	-0.429970	-1.526882	-6.682728
H	-0.145414	-0.207360	-7.851610
H	1.201540	-0.810369	-6.846699

1a-*trans*

C	-0.431922	1.681310	4.621841
C	0.543127	1.160693	3.772977
C	0.285932	0.031162	2.990160
C	-0.968428	-0.607082	3.077774
C	-1.950568	-0.064531	3.917022
C	-1.685214	1.069053	4.681497
H	-0.218188	2.561749	5.219983
H	1.518978	1.633803	3.699609
H	-2.922153	-0.550025	3.977778
H	-2.458382	1.467133	5.332608
N	1.321968	-0.520283	2.167991
H	2.245345	-0.510392	2.585492
N	-1.227540	-1.729314	2.266752
H	-0.414129	-2.332485	2.165168
H	-2.037518	-2.264469	2.560805
C	1.435429	-0.405557	0.780764
S	2.968535	-0.470581	0.093804
N	0.248148	-0.292007	0.131046
H	-0.573067	-0.550644	0.675171
C	-0.018628	-0.160126	-1.256707
C	0.774162	0.579318	-2.136708
C	0.411003	0.703188	-3.479668
C	-0.758107	0.100795	-3.956375
C	-1.564566	-0.626292	-3.069969
C	-1.195320	-0.755749	-1.739112
H	1.679509	1.051909	-1.780608
H	1.050937	1.278099	-4.139111
H	-2.471662	-1.087781	-3.447059
H	-1.821679	-1.329694	-1.060065
O	-1.199139	0.162348	-5.248611

C	-0.412597	0.874941	-6.188960
H	-0.935399	0.789112	-7.143506
H	-0.322194	1.936078	-5.920267
H	0.592307	0.442606	-6.285700

1a-*trans2*

C	-1.961841	-1.389365	3.596024
C	-0.800326	-1.400783	2.825408
C	0.106213	-0.335512	2.880252
C	-0.133445	0.761518	3.742165
C	-1.297138	0.747573	4.530321
C	-2.197905	-0.310435	4.452394
H	-2.661029	-2.217888	3.542883
H	-0.572632	-2.241522	2.175802
H	-1.490813	1.581128	5.201539
H	-3.093648	-0.290342	5.067288
N	1.306624	-0.339800	2.109293
H	2.195663	-0.348374	2.595730
N	0.799825	1.785535	3.836696
H	1.375516	1.922464	3.014254
H	0.457204	2.655111	4.223942
C	1.445560	-0.244228	0.739736
S	2.996463	-0.170735	0.086307
N	0.264389	-0.198285	0.065733
H	-0.559406	-0.168672	0.657711
C	-0.025720	-0.056094	-1.315499
C	0.805127	-0.498526	-2.347469
C	0.412077	-0.352500	-3.680420
C	-0.821678	0.222690	-3.999704
C	-1.663861	0.652007	-2.964287
C	-1.266500	0.516919	-1.642780
H	1.761017	-0.946503	-2.114072
H	1.082577	-0.700661	-4.457737
H	-2.621092	1.095943	-3.218222
H	-1.924611	0.866487	-0.849742
O	-1.295677	0.407809	-5.267833
C	-0.479817	-0.005251	-6.351924
H	0.480272	0.527741	-6.361089
H	-0.289897	-1.086691	-6.326363
H	-1.037467	0.240843	-7.257536

1b-*cis*

C	-1.386953	-0.650626	-4.459876
C	-1.511658	-0.463798	-3.085707
C	-0.497876	0.144741	-2.340449
C	0.689726	0.578430	-2.973488
C	0.803817	0.367027	-4.359543
C	-0.216998	-0.226840	-5.093657
H	-2.185016	-1.125358	-5.022155
H	-2.408774	-0.794026	-2.567170
H	1.714435	0.690321	-4.859477
H	-0.093300	-0.365996	-6.164324
N	-0.766372	0.434395	-0.965854

H	-1.673880	0.858118	-0.805162
N	1.678862	1.259528	-2.267580
H	1.875316	0.850274	-1.356369
H	2.537857	1.363934	-2.796409
C	-0.116548	-0.033335	0.146215
S	1.188586	-1.087722	0.078469
N	-0.654917	0.497196	1.298192
H	-1.207382	1.336416	1.166001
C	-0.362711	0.231449	2.658805
C	-0.039245	-1.043985	3.139154
C	0.177825	-1.228347	4.504009
C	0.061022	-0.166207	5.402362
C	-0.278284	1.099431	4.922696
C	-0.484762	1.299082	3.559532
H	0.044201	-1.875080	2.452250
H	0.432826	-2.220614	4.866071
H	-0.376226	1.938232	5.606360
H	-0.734178	2.291014	3.187480
H	0.229604	-0.323631	6.463775

1b-*cis2*

C	-1.366517	0.794163	-4.142653
C	-1.090863	0.741853	-2.776803
C	0.104826	0.176343	-2.326891
C	1.029106	-0.352652	-3.254473
C	0.747622	-0.270861	-4.620630
C	-0.443163	0.302320	-5.065858
H	-2.300014	1.233310	-4.481911
H	-1.793205	1.138812	-2.055405
H	1.463001	-0.674465	-5.334220
H	-0.651887	0.350509	-6.130873
N	0.524475	0.181241	-0.977557
H	1.538443	0.192257	-0.894669
N	2.247221	-0.884944	-2.754506
H	2.094034	-1.673337	-2.128236
H	2.865756	-1.183463	-3.502487
C	-0.192466	0.006645	0.183121
S	-1.785713	-0.497101	0.253073
N	0.599648	0.303252	1.276624
H	1.393348	0.900673	1.075970
C	0.343817	0.163616	2.661659
C	-0.375788	-0.907811	3.207288
C	-0.529351	-0.998881	4.589976
C	0.036057	-0.049125	5.442806
C	0.765949	1.007838	4.897771
C	0.915654	1.116688	3.517102
H	-0.812349	-1.652197	2.555626
H	-1.093627	-1.831188	5.001959
H	1.215233	1.756642	5.544417
H	1.472858	1.951315	3.095690
H	-0.088883	-0.132907	6.518563

1b-*trans*

C	-0.063512	-1.499255	-4.007492
C	0.803773	-0.996901	-3.039105
C	0.424952	0.071413	-2.220632
C	-0.841185	0.667095	-2.392266
C	-1.715263	0.142312	-3.353242
C	-1.330434	-0.931109	-4.152971
H	0.243184	-2.332576	-4.632070
H	1.787381	-1.437622	-2.898642
H	-2.696607	0.594235	-3.479679
H	-2.020614	-1.316403	-4.898197
N	1.353159	0.606937	-1.268371
H	2.311045	0.662551	-1.594793
N	-1.224715	1.725241	-1.544181
H	-0.454713	2.357574	-1.336457
H	-2.031566	2.240869	-1.879022
C	1.342049	0.400033	0.112054
S	2.800053	0.466296	0.943455
N	0.099601	0.211228	0.633679
H	-0.670050	0.498320	0.030319
C	-0.307257	-0.052755	1.964448
C	0.452128	-0.787721	2.883809
C	-0.065716	-1.041113	4.153679
C	-1.332267	-0.584437	4.521594
C	-2.091962	0.135715	3.598365
C	-1.584237	0.401379	2.329330
H	1.433830	-1.147262	2.608426
H	0.532912	-1.609419	4.860552
H	-3.081492	0.497606	3.864484
H	-2.173522	0.968643	1.612294
H	-1.723359	-0.789032	5.514199

1b-*trans2*

C	-1.822828	-1.325347	2.958216
C	-0.746645	-1.344031	2.072713
C	0.221551	-0.332846	2.100663
C	0.134511	0.712010	3.051636
C	-0.943649	0.703721	3.953344
C	-1.908460	-0.297842	3.901732
H	-2.570730	-2.111255	2.925265
H	-0.635307	-2.149386	1.351855
H	-1.019557	1.497353	4.693075
H	-2.735473	-0.274003	4.606166
N	1.340147	-0.344346	1.215097
H	2.267995	-0.449643	1.609505
N	1.132658	1.675222	3.115706
H	1.629758	1.838411	2.248033
H	0.883630	2.532240	3.592247
C	1.352582	-0.256256	-0.162015
S	2.834450	-0.326580	-0.957239
N	0.116093	-0.089357	-0.710734
H	-0.630936	-0.005811	-0.028671
C	-0.339250	0.053849	-2.042381

C	0.419203	-0.227320	-3.186732
C	-0.160281	-0.072512	-4.446993
C	-1.481130	0.350439	-4.593029
C	-2.236336	0.623022	-3.450748
C	-1.671750	0.477856	-2.187733
H	1.443768	-0.555428	-3.085450
H	0.439229	-0.292586	-5.326325
H	-3.267921	0.952887	-3.539045
H	-2.265606	0.697978	-1.302270
H	-1.917427	0.465441	-5.581102

1c-*cis*

C	-1.291392	-0.765674	-5.268560
C	-1.457465	-0.555981	-3.902269
C	-0.486092	0.106601	-3.146683
C	0.699433	0.573362	-3.759417
C	0.855537	0.338911	-5.137679
C	-0.123275	-0.309119	-5.882932
H	-2.056136	-1.282676	-5.839697
H	-2.353777	-0.910093	-3.398379
H	1.765015	0.687132	-5.622606
H	0.031988	-0.464958	-6.947125
N	-0.798859	0.412726	-1.784644
H	-1.721979	0.812427	-1.653608
N	1.643918	1.306767	-3.044641
H	1.837837	0.923207	-2.121911
H	2.508985	1.439165	-3.557021
C	-0.156633	-0.004592	-0.650611
S	1.185153	-1.012742	-0.661843
N	-0.738670	0.532778	0.479789
H	-1.312863	1.352224	0.319423
C	-0.454169	0.306684	1.846686
C	-0.107741	-0.950067	2.360075
C	0.101892	-1.109901	3.727929
C	-0.050688	-0.023781	4.588568
C	-0.411186	1.228260	4.095378
C	-0.605909	1.387662	2.725770
H	0.001240	-1.796072	1.695371
H	0.373682	-2.082325	4.124025
H	-0.529264	2.069829	4.769135
H	-0.871293	2.368214	2.336513
Cl	0.208560	-0.236016	6.314959

1c-*cis2*

C	-1.394090	0.762396	-4.938373
C	-1.106771	0.723647	-3.574492
C	0.094263	0.164967	-3.130421
C	1.011832	-0.370595	-4.060798
C	0.718226	-0.302491	-5.424992
C	-0.477786	0.263870	-5.864990
H	-2.331437	1.196317	-5.273590
H	-1.803742	1.126512	-2.851239
H	1.428170	-0.711220	-6.141002

H	-0.696085	0.301638	-6.928455
N	0.527913	0.183486	-1.785273
H	1.543261	0.187167	-1.715526
N	2.235770	-0.894913	-3.564826
H	2.090483	-1.691065	-2.946355
H	2.856746	-1.181295	-4.315619
C	-0.176179	0.027124	-0.616504
S	-1.772501	-0.459488	-0.517288
N	0.633466	0.326260	0.466698
H	1.429112	0.916275	0.252561
C	0.385756	0.201753	1.852006
C	-0.337892	-0.859476	2.412997
C	-0.488473	-0.946917	3.795053
C	0.094148	0.011450	4.622946
C	0.829262	1.063966	4.082215
C	0.966596	1.155718	2.699693
H	-0.785103	-1.607828	1.773420
H	-1.051813	-1.767066	4.227041
H	1.280772	1.807547	4.729974
H	1.526964	1.985887	2.275040
Cl	-0.095336	-0.111022	6.367537

1c-*trans*

C	-0.607155	-1.612646	-4.595756
C	0.419764	-1.130274	-3.786548
C	0.226261	-0.009605	-2.973417
C	-1.014200	0.659765	-2.990643
C	-2.047971	0.155527	-3.790182
C	-1.846816	-0.970600	-4.584789
H	-0.443543	-2.487152	-5.217799
H	1.386141	-1.627394	-3.767729
H	-3.009280	0.664500	-3.796510
H	-2.659401	-1.339191	-5.204346
N	1.314160	0.499362	-2.190114
H	2.216161	0.479647	-2.652004
N	-1.206852	1.773473	-2.147255
H	-0.383168	2.369407	-2.095900
H	-2.028099	2.320969	-2.382289
C	1.488315	0.362302	-0.813803
S	3.048886	0.370427	-0.194892
N	0.322058	0.283391	-0.113313
H	-0.505708	0.601989	-0.616824
C	0.099492	0.113346	1.272133
C	0.942510	-0.617436	2.119724
C	0.609855	-0.777078	3.463585
C	-0.565316	-0.219714	3.963559
C	-1.421337	0.497848	3.130528
C	-1.083929	0.661524	1.790420
H	1.854448	-1.051702	1.734504
H	1.264834	-1.341125	4.119012
H	-2.336231	0.927785	3.523822
H	-1.744088	1.226418	1.136739
Cl	-0.976273	-0.426018	5.662558

1c-*trans2*

C	-2.031716	-1.390683	3.462289
C	-0.829737	-1.389352	2.757235
C	0.052457	-0.305663	2.847964
C	-0.253046	0.797059	3.681094
C	-1.459563	0.770877	4.402575
C	-2.334567	-0.304857	4.289093
H	-2.711242	-2.233211	3.382558
H	-0.551058	-2.233298	2.132040
H	-1.705143	1.608215	5.051559
H	-3.263240	-0.294195	4.853188
N	1.295107	-0.297619	2.144208
H	2.156522	-0.332884	2.677436
N	0.654132	1.837995	3.816404
H	1.283390	1.970950	3.033886
H	0.277917	2.706829	4.172504
C	1.508036	-0.240310	0.783820
S	3.089435	-0.227073	0.210220
N	0.356708	-0.172641	0.053402
H	-0.488080	-0.123981	0.614324
C	0.109346	-0.073302	-1.333467
C	1.036612	-0.381987	-2.338216
C	0.669258	-0.276000	-3.679240
C	-0.617803	0.126854	-4.025709
C	-1.554760	0.427179	-3.038252
C	-1.186269	0.327397	-1.701232
H	2.036193	-0.694893	-2.071991
H	1.390463	-0.513913	-4.453944
H	-2.557456	0.739280	-3.309684
H	-1.915799	0.569860	-0.931272
Cl	-1.069091	0.256882	-5.721173

1d-*cis*

C	-5.51714000	-0.47402400	-1.46229700
C	-4.14801700	-0.71849500	-1.40595600
C	-3.40933400	-0.43487800	-0.25389900
C	-4.04010200	0.11897600	0.88331700
C	-5.42175900	0.37063200	0.80198100
C	-6.15071900	0.07219000	-0.34368800
H	-6.07633500	-0.69876900	-2.36500600
H	-3.62906700	-1.13516700	-2.26591000
H	-5.92184500	0.80174400	1.66652200
H	-7.21783400	0.27593800	-0.36497400
N	-2.04031800	-0.85103200	-0.22312800
H	-1.88967400	-1.80650900	-0.52924800
N	-3.33943500	0.33602400	2.06780700
H	-2.42291600	0.75480600	1.92778400
H	-3.86880100	0.87166600	2.74686100
C	-0.92398500	-0.07573800	-0.08484000
S	-0.96323900	1.59412300	0.04013500
N	0.21754400	-0.86170800	-0.02143100
H	0.05059000	-1.82698000	0.23876000
C	1.57969900	-0.52197500	-0.03032200

C	2.09522300	0.63788400	-0.63371000
C	3.46637800	0.86258700	-0.63745300
C	4.32373500	-0.06729700	-0.05121500
C	3.83397200	-1.23029600	0.54169200
C	2.46525500	-1.45042100	0.54999100
H	1.42754200	1.35517000	-1.08829700
H	3.88104300	1.75018800	-1.09912300
H	4.52302000	-1.93541500	0.98940400
H	2.07173400	-2.34899100	1.01980800
N	5.76727900	0.17542000	-0.06284800
O	6.17091500	1.21276700	-0.59042800
O	6.49529200	-0.67394800	0.45503400

1d-*cis2*

C	5.26292400	-1.24554400	-0.86006100
C	3.89027900	-1.00500400	-0.82072300
C	3.39949000	0.11902900	-0.15199300
C	4.28923500	1.00534000	0.49292400
C	5.66310800	0.76086300	0.42434800
C	6.15051100	-0.35740000	-0.25109300
H	5.63590700	-2.12283900	-1.37994700
H	3.19769500	-1.67846200	-1.30891200
H	6.34890000	1.44631400	0.91753300
H	7.22077600	-0.53898200	-0.28855400
N	2.04145900	0.51440700	-0.15798700
H	1.94344900	1.52309500	-0.05908000
N	3.74328700	2.15473500	1.12544200
H	3.13071500	1.91318800	1.90256500
H	4.46757400	2.77746600	1.47041900
C	0.89607400	-0.23563900	-0.08399900
S	0.84057500	-1.86900000	0.25469500
N	-0.20707800	0.57121000	-0.34581300
H	0.00760300	1.41356600	-0.86716800
C	-1.58393900	0.34299200	-0.21377200
C	-2.14942000	-0.59543700	0.66771600
C	-3.53088100	-0.70778800	0.76357600
C	-4.35081700	0.11401700	-0.00846800
C	-3.81117800	1.05835100	-0.88137500
C	-2.43313800	1.16658000	-0.97974900
H	-1.51089600	-1.23091800	1.26333800
H	-3.98229500	-1.42401200	1.43902800
H	-4.47092500	1.68410500	-1.46929000
H	-2.00260400	1.89342800	-1.66492100
N	-5.80434100	-0.00896000	0.10169900
O	-6.25268700	-0.85258200	0.87975700
O	-6.49754800	0.74085000	-0.58944400

1d-*trans2*

C	3.59974900	-2.10657400	-1.36739100
C	2.94664300	-0.87599400	-1.37276200
C	3.07773600	0.00836900	-0.29446500
C	3.90083000	-0.32291400	0.80809200
C	4.56957100	-1.55999800	0.78816800

C	4.41568700	-2.43650700	-0.28082200
H	3.48961600	-2.78766600	-2.20509200
H	2.33263000	-0.57633500	-2.21785500
H	5.21022700	-1.82713600	1.62518800
H	4.93968500	-3.38820700	-0.26485700
N	2.42654900	1.28093400	-0.29368700
H	2.99541400	2.11770300	-0.36079600
N	4.07998100	0.58423000	1.84094300
H	3.33020800	1.25176500	1.97382600
H	4.43015400	0.20278800	2.70978100
C	1.07824900	1.55211300	-0.24790200
S	0.56508400	3.14986400	-0.29351500
N	0.30482800	0.42415300	-0.14197100
H	0.84307700	-0.43597700	-0.09620000
C	-1.07934300	0.20940100	-0.06499000
C	-2.06415500	1.20458700	-0.19044400
C	-3.40830900	0.85793800	-0.10699500
C	-3.77548000	-0.46997200	0.09862600
C	-2.81410800	-1.47352500	0.22292000
C	-1.47548200	-1.12937700	0.14069000
H	-1.77261300	2.23255100	-0.34907800
H	-4.17898200	1.61305700	-0.20222900
H	-3.12544500	-2.49829000	0.38219000
H	-0.71939400	-1.90519200	0.23841300
N	-5.19264400	-0.82311700	0.18601400
O	-6.01937300	0.08317000	0.07252700
O	-5.47768400	-2.00886800	0.36841100

1d-*trans*

C	4.73027900	-0.74792300	1.68168200
C	3.98720600	0.32086900	1.18438800
C	3.19919600	0.17377400	0.03899300
C	3.17785900	-1.06022000	-0.64062700
C	3.90998200	-2.13524500	-0.12183100
C	4.67828900	-1.98129300	1.02978100
H	5.33271400	-0.62085400	2.57568800
H	4.00005900	1.28312000	1.68953000
H	3.88565600	-3.09187000	-0.63884500
H	5.24594400	-2.82557400	1.41019900
N	2.48141700	1.30352400	-0.47840200
H	2.98583800	2.18194000	-0.43766500
N	2.35853700	-1.20305200	-1.78240300
H	2.40000100	-0.39043600	-2.39458800
H	2.54878700	-2.04935700	-2.30931800
C	1.11380800	1.54077900	-0.38335600
S	0.56597700	3.12439500	-0.36885800
N	0.35993000	0.39796500	-0.37178400
H	0.84175500	-0.43184900	-0.72487900
C	-1.01779000	0.20302700	-0.19073200
C	-1.87387000	1.10604000	0.46294100
C	-3.21561200	0.78624200	0.63233400
C	-3.70579600	-0.42904300	0.15676900
C	-2.87144600	-1.34339700	-0.48651100
C	-1.53397300	-1.02361000	-0.65585400
H	-1.49084800	2.04833300	0.82652200

H	-3.88849400	1.46968900	1.13544700
H	-3.27863100	-2.28076600	-0.84436600
H	-0.87246200	-1.72438400	-1.15844100
N	-5.11953700	-0.75748300	0.33918600
O	-5.83417500	0.07004500	0.90740700
O	-5.51547300	-1.84567000	-0.08510600

OMe-mono-urea

C	-1.165064	-0.742130	-5.395993
C	-1.410037	-0.533554	-4.041034
C	-0.456789	0.058018	-3.206045
C	0.800895	0.442521	-3.730728
C	1.036460	0.202312	-5.097150
C	0.072214	-0.367358	-5.921832
H	-1.924319	-1.197689	-6.024257
H	-2.364113	-0.831164	-3.609886
H	2.001131	0.489834	-5.510518
H	0.292646	-0.525251	-6.974159
N	-0.845141	0.350508	-1.864705
H	-1.832907	0.539994	-1.756694
N	1.743773	1.103402	-2.946325
H	1.836175	0.697754	-2.016170
H	2.645513	1.186402	-3.402127
C	-0.145360	0.008367	-0.721181
O	0.979873	-0.489799	-0.745333
N	-0.832497	0.309015	0.440417
H	-1.690171	0.834740	0.343142
C	-0.416986	0.116818	1.778857
C	0.740304	-0.592465	2.144815
C	1.060304	-0.746507	3.487563
C	0.248979	-0.210480	4.496291
C	-0.904184	0.493043	4.137016
C	-1.225345	0.650507	2.787677
H	1.377276	-1.007133	1.376680
H	1.953161	-1.291366	3.778390
H	-1.558349	0.923371	4.886471
H	-2.126197	1.202192	2.523918
O	0.666219	-0.427467	5.781330
C	-0.119796	0.101187	6.834550
H	0.386728	-0.181463	7.759431
H	-0.187514	1.196468	6.780027
H	-1.134314	-0.320711	6.835221

1e (**H-mono-urea**)

C	-1.240966	-0.689177	-4.516874
C	-1.451938	-0.483229	-3.155930
C	-0.464258	0.073709	-2.337333
C	0.793403	0.424288	-2.884811
C	0.993568	0.187440	-4.257540
C	-0.004019	-0.347207	-5.065642
H	-2.026058	-1.117441	-5.132394
H	-2.405359	-0.755378	-2.707040
H	1.957716	0.449049	-4.688855

H	0.189905	-0.503841	-6.123339
N	-0.816545	0.367856	-0.985961
H	-1.792754	0.599480	-0.857217
N	1.771756	1.050456	-2.115697
H	1.872052	0.635591	-1.190617
H	2.665752	1.110985	-2.589889
C	-0.105094	-0.001093	0.139895
O	1.002255	-0.534464	0.091891
N	-0.758922	0.320011	1.318382
H	-1.608214	0.862289	1.238311
C	-0.336951	0.095802	2.646183
C	0.821000	-0.620474	2.986180
C	1.143410	-0.799224	4.331658
C	0.339134	-0.282490	5.347878
C	-0.812036	0.428284	5.004698
C	-1.148460	0.616598	3.667267
H	1.449779	-1.020253	2.203741
H	2.042989	-1.355329	4.582589
H	-1.454218	0.840785	5.778290
H	-2.048562	1.172646	3.409761
H	0.604157	-0.430498	6.390695

Cl-mono-urea

C	-1.083591	-0.805348	-5.378988
C	-1.361961	-0.575212	-4.034299
C	-0.432026	0.038557	-3.189253
C	0.834365	0.424320	-3.690103
C	1.103438	0.162606	-5.046508
C	0.162793	-0.429122	-5.882422
H	-1.824058	-1.278077	-6.016761
H	-2.323317	-0.872752	-3.619832
H	2.075103	0.450398	-5.442718
H	0.408599	-0.603478	-6.926431
N	-0.853936	0.350533	-1.861277
H	-1.840628	0.558494	-1.780892
N	1.753487	1.106130	-2.895585
H	1.833675	0.715220	-1.958503
H	2.662762	1.196355	-3.334676
C	-0.179801	0.035699	-0.699404
O	0.945357	-0.460389	-0.683450
N	-0.893376	0.364081	0.444579
H	-1.756263	0.874866	0.317602
C	-0.514248	0.187128	1.789647
C	0.656833	-0.474802	2.190732
C	0.944076	-0.614814	3.547653
C	0.074852	-0.102593	4.507972
C	-1.091541	0.556025	4.124448
C	-1.379601	0.697129	2.770842
H	1.331182	-0.867864	1.443704
H	1.850195	-1.126348	3.854968
H	-1.767499	0.955034	4.873049
H	-2.291537	1.211977	2.474690
Cl	0.449069	-0.286668	6.218087

NO_2-mono-urea

C	-5.65505400	-1.00389800	-0.89774500
C	-4.31273000	-1.30592600	-0.68720900
C	-3.46650400	-0.42958500	-0.00056600
C	-3.96121700	0.80500200	0.48229000
C	-5.31625600	1.09940800	0.24028400
C	-6.15391500	0.21155200	-0.42520800
H	-6.29503800	-1.70151600	-1.42880900
H	-3.90124400	-2.24268700	-1.05798000
H	-5.70923400	2.04716000	0.60231800
H	-7.19639200	0.47471000	-0.58197700
N	-2.13992800	-0.88158500	0.27894600
H	-2.06588100	-1.87798400	0.43713600
N	-3.16421700	1.66430900	1.23515000
H	-2.22810900	1.77897700	0.85163400
H	-3.60328100	2.56211000	1.40487200
C	-0.97821600	-0.19019900	0.02788200
O	-0.94802400	0.96533300	-0.38672800
N	0.16627100	-0.93165500	0.32345700
H	0.02983300	-1.83013900	0.76669900
C	1.50579500	-0.55559600	0.17406100
C	1.91658700	0.66291800	-0.39941600
C	3.27193100	0.94473500	-0.51624800
C	4.21812400	0.02421600	-0.06758900
C	3.83039600	-1.18853700	0.50225100
C	2.47938800	-1.47217400	0.61971100
H	1.17410800	1.36937200	-0.73996700
H	3.60659800	1.87689800	-0.95474600
H	4.58534700	-1.88622000	0.84274500
H	2.16905500	-2.41597600	1.06268700
N	5.64151200	0.33175200	-0.19522900
O	5.95389600	1.41074200	-0.70214800
O	6.44897800	-0.50681500	0.21189200

1. *Gaussian 03*. Revision C.02. Frisch MJ. Trucks GW. Schlegel HB. Scuseria GE. Robb MA. Cheeseman JR. Montgomery Jr JA. Vreven T. Kudin KN. Burant JC. Millam JM. Iyengar SS. Tomasi J. Barone V. Mennucci B. Cossi M. Scalmani G. Rega N. Petersson GA. Nakatsuji H. Hada M. Ehara M. Toyota K. Fukuda R. Hasegawa J. Ishida M. Nakajima T. Honda Y. Kitao O. Nakai H. Klene M. Li X. Knox JE. Hratchian HP. Cross JB. Bakken V. Adamo C. Jaramillo J. Gomperts R. Stratmann RE. Yazyev O. Austin AJ. Cammi R. Pomelli C. Ochterski JW. Ayala PY. Morokuma K. Voth GA. Salvador P. Dannenberg JJ. Zakrzewski V G. Dapprich S. Daniels AD. Strain MC. Farkas O. Malick DK. Rabuck AD. Raghavachari K. Foresman JB. Ortiz JV. Cui Q. Baboul AG. Clifford S. Cioslowski J. Stefanov BB. Liu G. Liashenko A. Piskorz P. Komaromi I. Martin RL. Fox DJ. Keith T. Al-Laham MA. Peng CY. Nanayakkara A. Challacombe M. Gill PMW. Johnson B. Chen W. Wong MW. Gonzalez C. Pople JA (2004) Gaussian Inc Wallingford CT