

Diaryl dithiocarbamates: Synthesis, oxidation to thiuram disulfides, Co(III) complexes $[\text{Co}(\text{S}_2\text{CNAr}_2)_3]$ and their use as single source precursors to CoS_2

Electronic supplementary information

Experimental section

General procedures

All solvents and chemicals were purchased from Sigma-Aldrich, Alfa Aesar and used without further purification. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer using residual protons from either DMSO-d_6 or CDCl_3 as solvents for reference. IR analyses were conducted using a Perkin Elmer Spectrum 2 FTIR, or Shimadzu Affinity IR spectrophotometer. The mass spectrum was obtained on a Micromass 70-SE spectrometer utilising Electrospray Ionisation (ESI). Elemental analyses were performed by Flash 2000 Organic Elemental Analyzer of the Science Centre at London Metropolitan University. All measurements were carried out at ambient room temperature. PXRD patterns were measured on a Bruker AXS D4 diffractometer using $\text{CuK}\alpha 1$ radiation and were compared to database standards. TEM images were obtained using a JEOL-1010 microscope at 100 kV equipped with a Gatan digital camera. A 4 mL droplet of nanoparticle suspension (CHCl_3) was placed on a holey carbon-coated copper TEM grid and allowed to evaporate in air under ambient laboratory conditions for several minutes.

Synthesis of $\text{LiS}_2\text{CNAr}_2$ (**1a-1g**)

As a representative example we give the synthesis of $\text{LiS}_2\text{CNPh}_2$ (**1a**). A solution of Ph_2NH (0.846 g, 5.0 mmol) in THF (6 mL) was cooled to $-70\text{ }^\circ\text{C}$ and to this was added $n\text{BuLi}$ (2.5 M hexane solution) (2 mL, 5.0 mmol). The resulting pale-yellow solution was warmed to room temperature before being re-cooled to $0\text{ }^\circ\text{C}$. Carbon disulfide (0.3 mL, 5.0 mmol) was slowly added resulting in formation of a thick orange precipitate. Removal of volatiles under reduced pressure and addition of toluene (10 mL) gave a clear orange solution with gentle heating. Cooling to room temperature over 2 h gave small orange crystals which were isolated by filtration to give **1a** (1.50 g, ca. 100 %). Other DTC salts, $\text{LiS}_2\text{CNAr}_{2,n}(\text{H}_2\text{O})$ (**1b-1g**) were

prepared in an analogous fashion. The amount of toluene required to redissolve the crude material varied, but otherwise preparations were similar. Reactions are easily scaled up and we routinely carried them out on a 20 mmol scale.

1a (Ar = Ph): Orange crystals, 1.50g, 100% yield. Elemental Analysis: Anal. Calcd for **1a**.3H₂O: C, 51.14; H, 5.28; N, 4.59 %. Found: C, 51.61; H, 4.71; N, 4.58 %. IR (cm⁻¹): 692, 748, 1045, 1272, 1305, 1490, 1636. ¹H NMR (DMSO-d₆): δ 7.21 (m, 8 H), 7.03 (m, 2 H). ¹³C{¹H} NMR (DMSO-d₆): δ 219.0 (C=N), 150.4, 129.6, 128.5, 125.2. ESI-MS: *m/z* 244.02 (M⁺ - Li, 20%) 170.09 (100 %).

1b (Ar = p-tolyl): Orange crystals, 1.49g, 99 % yield. Elemental Analysis: Anal. Calcd for **1b**.H₂O: C, 60.59; H, 5.42; N, 4.71 %. Found: C, 59.66; H, 5.41; N, 4.45 %. IR (cm⁻¹): 519, 551, 668, 758, 809, 887, 1045, 1273, 1300, 1321, 1506, 1625. ¹H NMR (DMSO-d₆): δ 7.08 (d, *J* = 8 Hz, 4 H), 6.99 (d, *J* = 8 Hz, 4 H), 2.22 (s, 6 H). ¹³C{¹H} NMR (DMSO-d₆): δ 218.9 (C=N), 148.0, 134.0, 129.2, 129.0, 21.0. ESI-MS: *m/z* 274.07 (M⁺ - Li, 50%), 239.15 (100%), 198.13 (100%).

1c (Ar = p-MeOC₆H₄): Orange crystals, 1.78 g, 100% yield. Elemental Analysis: Anal. Calcd for **2.1c**.3H₂O: C, 49.31; H, 5.52; N, 3.83%. Found: C, 49.77; H, 5.62; N, 3.92 %. IR (cm⁻¹): 550, 1034, 1238, 1501, 1601. ¹H NMR (DMSO-d₆): δ 7.21 (d, *J* = 8 Hz, 4 H), 6.75 (d, *J* = 8 Hz, 4 H), 3.69 (s, 6 H). ¹³C{¹H} NMR (DMSO-d₆): δ 219.1 (C=N), 156.7, 143.8, 130.1, 113.7, 55.5. ESI-MS: *m/z* 303.21 (M⁺-Li, 15%), 609.10 (M⁺-Li+ (MeOC₆H₄)₂NCS₂, 100%).

1d (Ar = 2,2'-dinaphthyl): Orange crystals, 2.01 g, 99% yield. Elemental Analysis: Anal. Calcd for **1d**.3H₂O: C, 62.21; H, 4.97; N, 3.45 %. Found: C, 63.32; H, 4.77; N, 2.97 %. IR (cm⁻¹): 476, 746, 864, 1034, 1312, 1362, 1437, 1504, 1597, 1635. ¹H NMR (DMSO-d₆): δ 7.79 (m, 6 H), 7.65 (m, 4 H), 7.39 (m, 4 H). ¹³C{¹H} NMR (DMSO-d₆): δ 218.8 (C=N), 147.7, 137.4, 133.4, 130.8, 130.1, 129.2, 128.9, 128.3, 127.4, 127.2, 127.1, 126.9, 162.2, 125.7, 125.6, 125.33, 125.30, 124.9, 124.7, 124.6. ESI-MS: *m/z* 344.06 (M⁺ - Li, 100 %), 268.11 (20%).

1e (Ar = Ph, m-MeOC₆H₄): Orange crystals, 1.66 g, 99% yield. Elemental Analysis: Anal. Calcd for **1e**.3H₂O: C, 50.14; H, 5.41; N, 4.18 %. Found: C, 50.36; H, 5.30; N, 4.20 %. IR (cm⁻¹): 687, 704, 735, 772, 833, 924, 1036, 1136, 1225, 1288, 1325, 1485, 1584, 1603. ¹H NMR (DMSO-d₆): δ 7.20 (m, 4 H), 7.11 (t, *J* = 8 Hz, 1H), 7.03 (m, 1 H), 6.79 (m, 2 H), 6.62 (dd, *J* = 8, 4 Hz, 1 H), 3.68 (s, 3 H). ¹³C{¹H} NMR (DMSO-d₆): δ 218.4 (C=N), 159.1, 150.9, 149.8, 129.1, 128.6, 128.0, 124.8, 121.6, 115.3, 110.2, 55.0. ESI-MS: *m/z* 274.04 (M⁺-Li, 100%), 242.06 (10v%), 186.96 (25 %), 158.96 (50 %), 139.99 (70 %), 128.95 (90%).

1f (Ar = Ph, 1-Naphthyl): Orange crystals, 1.76 g, 99% yield. Elemental Analysis: Anal. Calcd for **1f**.3H₂O: C, 57.45; H, 5.11; N, 3.94 %. Found: C, 56.91; H, 5.17; N, 3.84 %. IR (solid) (cm⁻¹): 694, 729, 766, 785, 893, 1005, 1022, 1057, 1082, 1198, 1271, 1306, 1391, 1485, 1587, 1624. ¹H NMR (DMSO-d₆): δ 8.15 (d, *J* = 8 Hz, 1 H), 7.85 (d, *J* = 8 Hz, 1 H), 7.67 (d, *J* = 8 Hz, 1 H), 7.38 (m, 6 H), 7.16 (m, 2 H), 6.99 (m, 1 H). ¹³C{¹H} NMR (DMSO-d₆): δ 219.2 (C=N), 149.7, 146.9, 134.1, 131.1, 129.1, 128.3, 127.8, 126.5, 125.9, 125.7, 125.6, 125.5, 125.2, 124.6. ESI-MS: *m/z* 294.04 (M⁺ - Li, 100%), 262.09 (10%).

1g (Ar = Ph, 2-Naphthyl): Orange crystals, 1.75 g, 99% yield. Elemental Analysis: Anal. Calcd for **1g**.3H₂O: C, 57.45; H, 5.11; N, 3.94 %. Found: C, 58.64; H, 4.45; N, 3.89 %. IR (solid) (cm⁻¹): 475, 556, 689, 718, 745, 820, 853, 1034, 1275, 1331, 1366, 1435, 1483, 1506, 1595. ¹H NMR (DMSO-d₆): δ 7.80 (m, 1 H), 7.74 (m, 2 H), 7.57 (m, 2 H), 7.39 (m, 2 H), 7.30 (m, 2 H), 7.22 (m, 2 H), 7.04 (m, 1 H). ¹³C{¹H} NMR (DMSO-d₆): δ 218.7 (C=N), 149.9, 147.9, 133.4, 130.9, 129.3, 129.2, 128.1, 127.4, 127.2, 126.8, 125.6, 125.6, 125.3, 124.7. ESI-MS: *m/z* 294.04 (M⁺ - Li, 100%), 218.10 (30 %).

Synthesis of KS₂CN(p-tolyl)₂ (**1h**)

A solution of (p-tolyl)₂NH (0.986 g, 5.0 mmol), KO^tBu (0.561 g, 5.0 mmol) and CS₂ (0.3 mL, 5.0 mmol) in THF (6 mL) was stirred for 24 h at room temperature to give a yellow suspension. Removal of THF under reduced pressure and addition of toluene (10 mL) gave clear yellow solution and leaving overnight to crystallise gave small pale-yellow crystals which were isolated by filtration to give **1h** (1.10 g, ca. 70%). **1h**: Pale-yellow crystals. Elemental Analysis: Anal. Calcd for **1h**.3H₂O: C, 49.29; H, 5.52; N, 3.83 %. Found: C, 49.47; H, 5.69; N, 3.88 %. ¹H NMR (DMSO-d₆): δ 7.07 (d, *J* = 8 Hz, 4 H), 6.99 (d, *J* = 8 Hz, 4 H), 2.21 (s, 6 H). ¹³C{¹H} NMR (DMSO-d₆): δ 218.3 (C=N), 147.5, 133.6, 128.7, 128.5, 20.6. ESI-MS: *m/z* 274.04 (M⁺ - K, 100%).

Synthesis of (Ar₂NCS₂)₂ (**2a-g**)

As a representative example we give the synthesis of (Ph₂NCS₂)₂ (**2a**). An aqueous solution of K₃[Fe(CN)₆] (ca. 0.6 M) (ca. 6 cm³) was added dropwise to **2a**.3H₂O (1.51 g, 5 mmol) suspended in water (20 mL) until the solution remained yellow. An off-white muddy precipitate was formed. After extraction with CH₂Cl₂ (3 x 10 cm³) and drying over MgSO₄ an equal volume of hexane was added. Removal of solvent under reduced pressure gave **2a** as a dry

pale-yellow solid (0.82 g, 68 %). Similar scales and procedures were followed for other **2b-2g**). Unlike other diaryl-DTCs, the 2-naphthyl-N-phenyl derivative **2h** oxidised through ortho-cyclisation and gave 3-phenylnaphtho[2,1-d]thiazole-2(3H)-thione (**2g**) along with thiuram disulfide (**2g**) from the similar work up and reaction. Thus, after recrystallization a mixture of crystals of **2g** and **2h** resulted which were separated manually.

2a (Ar = Ph): Pale-yellow solid, 829 mg, 68% yield. Elemental Analysis: Anal. Calcd. for **2a**. $\frac{1}{2}$ CH₂Cl₂: C, 59.92; H, 3.99; N, 5.27 %. Found: C, 60.06; H, 3.71; N, 5.81 %. IR (cm⁻¹): 486, 515, 610, 646, 689, 750, 1022, 1034, 1261, 1304, 1346, 1447, 1487, 1585. ¹H NMR (CDCl₃): δ 7.30-7.48 (m, 20 H). ¹³C{¹H} NMR (CDCl₃): δ 197.6 (C=N), 129.8, 128.7, 127.9. ESI-MS: *m/z* 488.05 (M⁺+1, 100%).

2b (Ar = p-tolyl): Yellow solid, 1.20 g, 88% yield. Elemental Analysis: Anal. Calcd. for C₃₀H₂₈N₂S₄: C, 66.14; H, 5.18; N, 5.14; Found: C, 65.95; H, 4.84; N, 4.81%. IR (cm⁻¹): 552, 590, 731, 813, 1026, 1349, 1501. ¹H NMR (CDCl₃): δ 7.34 (d, *J* = 8 Hz, 8 H), 7.20 (d, *J* = 8 Hz, 8 H), 2.35 (s, 6 H). ¹³C{¹H} NMR (CDCl₃): δ 197.8 (C=N), 130.4, 127.5, 21.4. ESI-MS: *m/z* 816.17 (M⁺ + Tol₂NCS₂; i.e. (Tol₂NCS₂)₃, 50 %), 545.12 (M⁺, 80%), 240.08 (M⁺ – Tol₂NCS₃, 100 %).

2c (Ar = p-MeOC₆H₄): Yellow solid, 731 mg, 48% yield. Elemental Analysis: Anal. Calcd for **2c**. $\frac{1}{4}$ CH₂Cl₂: C, 57.67; H, 4.56; N, 4.45 %. Found: C, 58.24; H, 4.59; N, 4.52 %. IR (cm⁻¹): 520, 563, 594, 745, 781, 810, 827, 1028, 1107, 1161, 1236, 1345, 1501, 1601. ¹H NMR (CDCl₃): δ 7.44 (m, 8 H), 6.99 (m, 8 H), 3.76 (s, 12 H). ¹³C{¹H} NMR (CDCl₃): δ 196.2 (CS₂), 152.8, 138.0, 129.5, 118.0, 114.5, 55.4. ESI-MS: *m/z* 609.10 (M⁺+1, 100%), 272.07 (M⁺- p-Anisyl₂NCS₃, 72%).

2e (Ar = Ph, m-MeOC₆H₄): Pale-yellow crystals, 540 mg, 39 % yield. Elemental Analysis: Anal. Calcd. for **2e**. $\frac{1}{4}$ CH₂Cl₂: C, 59.53; H, 4.33; N, 4.91 %. Found: C, 60.03; H, 4.42; N, 4.82 %. IR (cm⁻¹): 501, 613, 685, 696, 729, 772, 995, 1032, 1045, 1078, 1148, 1231, 1275, 1312, 1321, 1342, 1446, 1485, 1584, 1601. ¹H NMR (CDCl₃): δ 7.52 (d, *J* = 8 Hz, 4 H), 7.44 (t, *J* = 8 Hz, 4 H), 7.35 (m, 4 H), 7.11 (d, *J* = 8 Hz, 4 H), 6.93 (d, *J* = 8 Hz, 2 H), 3.81 (s, 6 H). ¹³C{¹H} NMR (CDCl₃): δ 197.2 (CS₂), 160.3, 130.3, 129.6, 128.5, 127.5, 119.8, 114.5, 113.4, 55.5. ESI-MS: *m/z* 548.09 (M⁺+1, 100%).

2f (Ar = Ph, 1-Naphthyl): Red crystals, 700 mg, 47% yield. Elemental Analysis: Anal. Calcd. for **2f**. $\frac{1}{3}$ CH₂Cl₂: C, 66.85; H, 4.03; N, 4.54 %. Found: C, 66.87; H, 4.04; N, 4.57 %. IR (cm⁻¹): 525, 606, 691, 725, 775, 1003, 1096, 1267, 1339, 1352, 1389, 1489, 1591. ¹H NMR (CDCl₃): δ 8.22 (t, *J* = 8 Hz, 2 H), 7.89 (m, 4 H), 7.55 (m, 12 H), 7.37 (t, *J* = 8 Hz, 4 H), 7.28

(m, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 197.9 (CS_2), 134.8, 134.8, 129.6, 128.7, 127.8, 127.2, 126.9, 125.8, 123.9. ESI-MS: m/z 589.09 ($\text{M}^+ + 1$, 40%).

2g (Ar = Ph, 2-Naphthyl): Red crystals. Elemental Analysis: Anal. Calcd. for **2g**: C, 69.35; H, 4.11; N, 4.76 %. Found: C, 71.90; H, 4.14; N, 5.04 %. IR (cm^{-1}): 470, 512, 530, 589, 650, 690, 740, 790, 1003, 1070, 1136, 1223, 1260, 1270, 1290, 1340, 1487, 1593. ^1H NMR (CDCl_3): δ 7.90 (m, 2 H), 7.82 (m, 1 H), 7.75 (m, 4 H), 7.65 (m, 9 H), 7.54 (m, 4 H), 7.45 (m, 6 H), 7.34 (m, 3 H), 7.23 (m, 1 H), 7.18 (m, 2 H), 7.01 (m, 1 H), 6.89 (d, $J = 12$ Hz, 2 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 197.5 (CS_2), 143.1, 141.0, 140.7, 137.1, 134.78, 131.0, 130.4, 130.1, 129.6, 129.3, 129.2, 128.6, 128.2, 128.1, 127.8, 126.8, 126.6, 126.6, 126.3, 123.8, 123.6, 123.5, 121.6, 120.2, 118.4. ESI-MS: m/z 589.08 ($\text{M}^+ + 1$, 50%).

2h (Ar = Ph, 2-Naphthyl): Red crystals. Elemental Analysis: Anal. Calcd. for **2h**: C, 69.59; H, 3.78; N, 4.77 %. Found: C, 71.95; H, 4.14; N, 5.00 %. IR (cm^{-1}): 420, 501, 530, 555, 586, 648, 694, 737, 799, 1003, 1070, 1134, 1213, 1260, 1269, 1288, 1344, 1489, 1585. ^1H NMR (CDCl_3): δ 7.90 (m, 1 H), 7.82 (m, 1 H), 7.75 (m, 1 H), 7.65 (m, 4 H), 7.54 (m, 1 H), 7.45 (m, 2 H), 6.89 (d, $J = 12$ Hz, 1 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 189.5 (C=S), 141.0, 140.7, 137.1, 134.78, 131.0, 130.1, 129.6, 129.2, 128.6, 126.8, 126.6, 123.6, 123.5, 121.6, 120.2, 118.4. ESI-MS: m/z 294.03 ($\text{M}^+ + 1$, 100%).

Synthesis of $[\text{Co}(\text{S}_2\text{CNAr}_2)_3]$ (**3a-g**)

1a (126 mg, 0.50 mmol) and $[\text{Co}(\text{CH}_3\text{CO}_2)_2]\cdot 4\text{H}_2\text{O}$ (43 mg, 0.17 mmol) were dissolved in water (10 mL) and stirred for 10 min at room temperature. A green precipitate obtained was filtered, washed with water, the residual water was allowed to evaporate and the green solid $[\text{Co}(\text{S}_2\text{CNPh}_2)_3]$ (**3a**) (132 mg, 98 % yield) was dried in fume hood. A similar scale and procedure was followed for **3b-g**. NMR spectra are broad and quaternary carbon signal of the DTC ligand could not be observed.

3a (Ar = Ph): Green crystals, 132 mg, 98% yield. Elemental Analysis: Anal. Calcd for **3a**. CHCl_3 : C, 52.72; H, 3.43; N, 4.61 %. Found: C, 53.51; H, 3.46; N, 4.81 %. IR (solid) (cm^{-1}): 690, 749, 1034, 1051, 1341, 1490. ^1H NMR (CDCl_3): δ 7.41 (br, m, 20 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.8, 129.4, 127.9, 127.7. ESI-MS: m/z 791.01 (M^+ , 10%), 546.98 ($\text{M}^+ - \text{Ph}_2\text{NCS}_2$, 100%).

3b (Ar = p-tolyl): Green crystals, 147 mg, 99% yield. Elemental Analysis: Anal. Calcd for **3b**. CHCl_3 : C, 55.50; H, 4.35; N, 4.22 %. Found: C, 55.52; H, 4.69; N, 4.26 %. IR (solid) (cm^{-1}): 768, 1034, 1320, 1507. ^1H NMR (CDCl_3): δ 7.24 (m, br, 24H), 2.36 (s, 18 H). $^{13}\text{C}\{^1\text{H}\}$

NMR (DMSO- d_6): δ 139.5, 137.9, 130.1, 127.4, 21.3. ESI-MS: m/z 875.11 (M^+ , 15%), 603.04 (M^+ -Tol $_2$ NCS $_2$, 100%).

3c (Ar = p-MeOC $_6$ H $_4$): Green crystals, 117 mg, 71% yield. Elemental Analysis: Anal. Calcd for **3c**.2CH $_2$ Cl $_2$: C, 49.43; H, 4.06; N, 3.68 %. Found: C, 48.87; H, 4.09; N, 3.67 %. IR (solid) (cm $^{-1}$): 598, 817, 1034, 1203, 1330, 1501. 1 H NMR (CDCl $_3$): δ 7.20 (br, s, 12 H), 6.86 (br, s, 12 H), 3.74 (br, s, 18 H). 13 C{ 1 H} NMR (CDCl $_3$): δ 159.0, 128.7, 114.6, 55.6. ESI-MS: m/z 971.07 (M^+ , 40%) 667.02 (M^+ - (MeOC $_6$ H $_4$) $_2$ NCS $_2$, 100%).

3d (Ar = 2,2'-dinaphthyl): Green crystals, 114 mg, 63%. Elemental Analysis: Anal. Calcd for **3d**.2CHCl $_3$: C, 58.65; H, 3.33; N, 3.16 %. Found: C, 58.65; H, 3.50; N, 3.18 %. IR (solid) (cm $^{-1}$): 474, 748, 789, 1034, 1229, 1275, 1327, 1364, 1507. ESI-MS: m/z 1091.17 (M^+).

3e (Ar = Ph, m-MeOC $_6$ H $_4$): Green crystals, 90 mg, 60%. Elemental Analysis: Anal. Calcd for **3e**.2CH $_2$ Cl $_2$: C, 50.24; H, 3.83; N, 3.99 %. Found: C, 50.52; H, 3.49; N, 4.11 %. IR (solid) (cm $^{-1}$): 473, 503, 617, 662, 689, 737, 1036, 1140, 1227, 1283, 1310, 1350, 1487, 1991, 1595. ESI-MS: m/z 881.14 (M^+).

3f (Ar = Ph, 1-Naphthyl): Green crystals, 75 mg, 47%. Elemental Analysis: Anal. Calcd for **3f**.CHCl $_3$: C, 58.84; H, 3.51; N, 3.96 %. Found: C, 58.54; H, 3.54; N, 3.94 %. IR (solid) (cm $^{-1}$): 474, 529, 555, 664, 691, 735, 791, 812, 1036, 1217, 1267, 1330, 1364, 1489, 1506, 1591.

3g (Ar = Ph, 2-Naphthyl): Green crystals, 126 mg, 79%. Elemental Analysis: Anal. Calcd for **3g**.CHCl $_3$: C, 58.84; H, 3.51; N, 3.96 %. Found: C, 58.41; H, 3.67; N, 3.85 %. IR (solid) (cm $^{-1}$): 474, 556, 691, 737, 810, 1036, 1217, 1231, 1271, 1333, 1366, 1489, 1591. ESI-MS: m/z 944.08 (M^+).

Solvothermal heat-up (HU) process

3b (25 mM) was added to OLA (20 mL) in a three-neck round bottom flask attached to a condenser and evacuated and refilled with nitrogen repeatedly for 15 minutes. The solution was heated to 230 °C and held there for 1 h. The mixture was allowed to cool to room temperature slowly, whereupon methanol (80 mL) was added with stirring. The mixture was centrifuged and then the solution decanted leaving behind the resultant nanoparticles. This procedure was repeated four times (3 \times 80 mL MeOH, 1 \times 80 mL CH $_2$ Cl $_2$) and finally the material was allowed to dry in air.

Solvothermal hot-injection (HI) process

15 mL OLA was added into a 3-necked round bottom flask attached to a water condenser and evacuated and refilled with N₂ (gas) repeatedly by a dynamic Schlenk line system for ca. 15 minutes. When the temperature rose to 230 °C, 300 mg of **3b** (dissolved in 5 mL OLA, heated for 15 minutes in oven at 80 °C) was injected into the 3-necked round bottom flask. The solution was heated to 230 °C and held there for 1 h. The mixture was allowed to cool to room temperature slowly, whereupon methanol (80 mL) was added with stirring. The mixture was centrifuged and then the solution decanted leaving behind the resultant nanoparticles. This procedure was repeated four times (3 × 80 mL MeOH, 1 × 80 mL CH₂Cl₂) and finally the material was allowed to dry in air.

Single Crystal X-ray Crystallography

We thank the EPSRC UK National Crystallography Service at the University of Southampton for the collection of the crystallographic data [1]. Hardware used: a Rigaku FRE+ diffractometer (Mo-K_α radiation, 0.71073 Å) equipped with HF Varimax confocal mirrors, an AFC12 goniometer, HG Saturn 724+ detector, and an Oxford Cryosystems low-temperature device. Datasets were processed using CrysAlisPro [2] solutions were solved and refined using Olex-2 [3]. CCDC reference numbers 2175347 (**2b**), 2175344 (**2c**), 2175345 (**2h**), 2175346 (**3b**) and 2175348 (**3e**) contain crystallographic data in CIF format, which is summarized in Table 1.

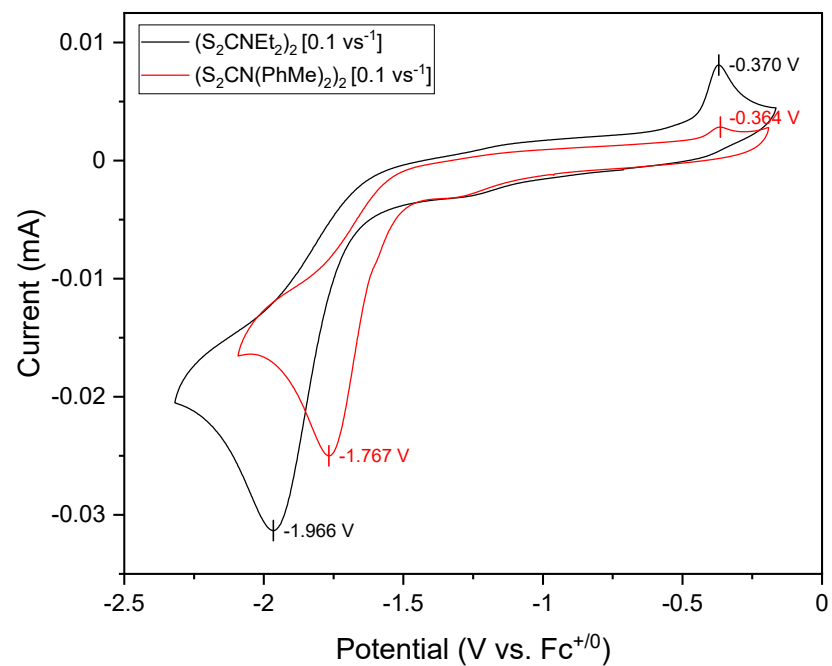
In **2b**, a second orientation of the molecule is present as a minor component in the asymmetric unit. The ratio between the two orientations is ~84:16 and the major difference between the two components is a different C–S–S–C torsion angle image. A few DFIX and ISOR restraints were needed to ensure sensible bond lengths and angles in the minor component. In **2c**, two small areas of residual electron density remained in the asymmetric unit after all atoms had been assigned. These were too small to correspond to any realistic solvent molecule (only 8 electrons per unit cell). Use of the solvent mask feature in Olex-2 did result in slightly better metrics (lower R₁ and wR₂) but led to fractional values of F(000) hence the mask was not used. No twin laws were detected.

- 1 S.J. Coles and P.A. Gale. *Chem. Sci.*, **2012**, 3, 683-689.
- 2 CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.

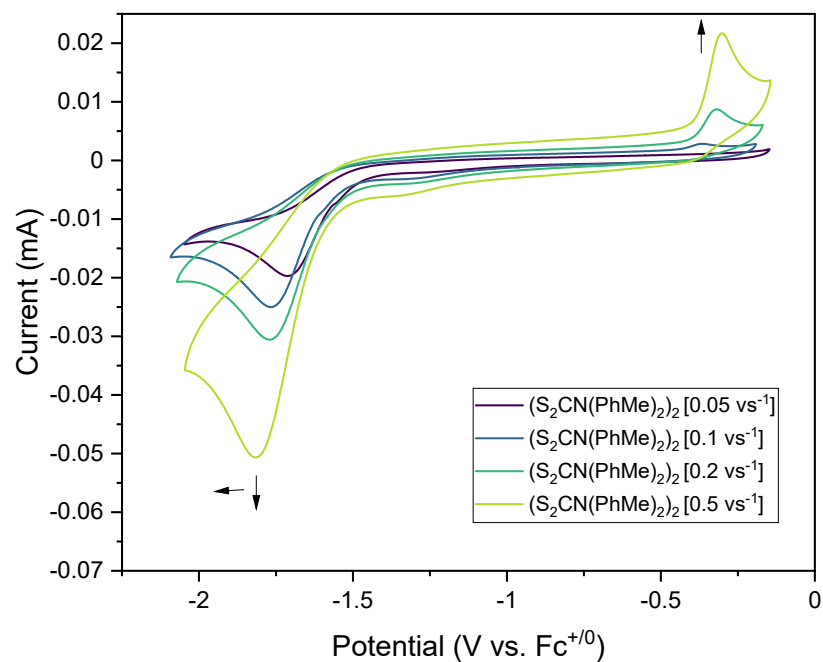
- 3 O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table 1: Crystallographic data and structure refinement

	2b	2c	2h	3b	3e
Empirical formula	C ₃₀ H ₂₈ N ₂ S ₄	C ₃₀ H ₂₈ N ₂ O ₄ S ₄	C ₁₇ H ₁₁ NS ₂	C ₄₅ H ₄₂ N ₃ S ₆ Co	C ₄₂ H ₃₆ N ₃ O ₃ S ₆ Co
Formula weight (Å)	544.78	608.78	293.39	876.10	882.03
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	triclinic	trigonal	trigonal
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -31c	<i>R</i> -3
<i>a</i> (Å)	11.8983(3)	8.5740(6)	11.5301(2)	15.6733(3)	13.9005(7)
<i>b</i> (Å)	12.7382(3)	9.6486(6)	15.3915(3)	15.6733(3)	13.9005(7)
<i>c</i> (Å)	18.6419(7)	11.1360(5)	25.5188(5)	32.6686(7)	37.791(2)
α (°)	90	68.656(5)	72.472(2)	90	90
β (°)	104.692(3)	89.217(5)	81.684(1)	90	90
γ (°)	90	64.833(6)	74.729(2)	120	120
Volume (Å ³)	2733.04(14)	765.65(9)	4155.45(15)	6950.0(3)	6323.8(7)
<i>Z</i>	4	1	12	6	6
Density (calculated) (g/cm ³)	1.324	1.320	1.407	1.256	1.390
Absorption coefficient	0.370	0.347	0.371	0.674	0.746
<i>F</i> (000)	1144	318	1824	2736	2736
Crystal size (mm)	0.15 × 0.13 × 0.04	0.4 × 0.10 × 0.08	0.1 × 0.1 × 0.06	0.21 × 0.09 × 0.04	0.13 × 0.03 × 0.02
θ Range for data collection (°)	4.518 to 66.61	5.08 to 54.96	3.926 to 61.018	3.25 to 54.954	5.482 to 54.972
Index ranges	-18 ≤ <i>h</i> ≤ 17 -19 ≤ <i>k</i> ≤ 19 -28 ≤ <i>l</i> ≤ 28	-11 ≤ <i>h</i> ≤ 11 -12 ≤ <i>k</i> ≤ 12 -14 ≤ <i>l</i> ≤ 14	-14 ≤ <i>h</i> ≤ 16 -21 ≤ <i>k</i> ≤ 21 -34 ≤ <i>l</i> ≤ 36	-14 ≤ <i>h</i> ≤ 20, -20 ≤ <i>k</i> ≤ 14, -42 ≤ <i>l</i> ≤ 42	-18 ≤ <i>h</i> ≤ 18 -18 ≤ <i>k</i> ≤ 17 -48 ≤ <i>l</i> ≤ 48
Reflections collected	92783	17250	81514	63142	29688
Independent reflections	9857	3512	25303	5336	3225
Data / restraints / parameters	9857/14/638	3512/0/183	25303/0/1081	5336/0/253	3225/12/226
Goodness-of-fit on <i>F</i> ²	1.066	1.037	1.015	1.044	1.048
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0389 w <i>R</i> ₂ = 0.0946	<i>R</i> ₁ = 0.0465 w <i>R</i> ₂ = 0.1252	<i>R</i> ₁ = 0.0523 w <i>R</i> ₂ = 0.1130	<i>R</i> ₁ = 0.0454, w <i>R</i> ₂ = 0.1157	<i>R</i> ₁ = 0.0596 w <i>R</i> ₂ = 0.1474
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0529 w <i>R</i> ₂ = 0.1031	<i>R</i> ₁ = 0.0498 w <i>R</i> ₂ = 0.1287	<i>R</i> ₁ = 0.0835 w <i>R</i> ₂ = 0.1271	<i>R</i> ₁ = 0.0538, w <i>R</i> ₂ = 0.1203	<i>R</i> ₁ = 0.1003 w <i>R</i> ₂ = 0.1671
Largest diff. peak and hole (e.Å ⁻³)	0.41/-0.37	1.80/-0.25	0.63/-0.67	0.76/-0.35	0.77/-0.47



(a)



(b)

Figure S1. CVs of (a) Et_4TDS (black) and $\mathbf{2b}$ (red) in MeCN at 0.1 V s^{-1} and (b) $\mathbf{2b}$ at scan rates between 0.05 and 0.5 V s^{-1}

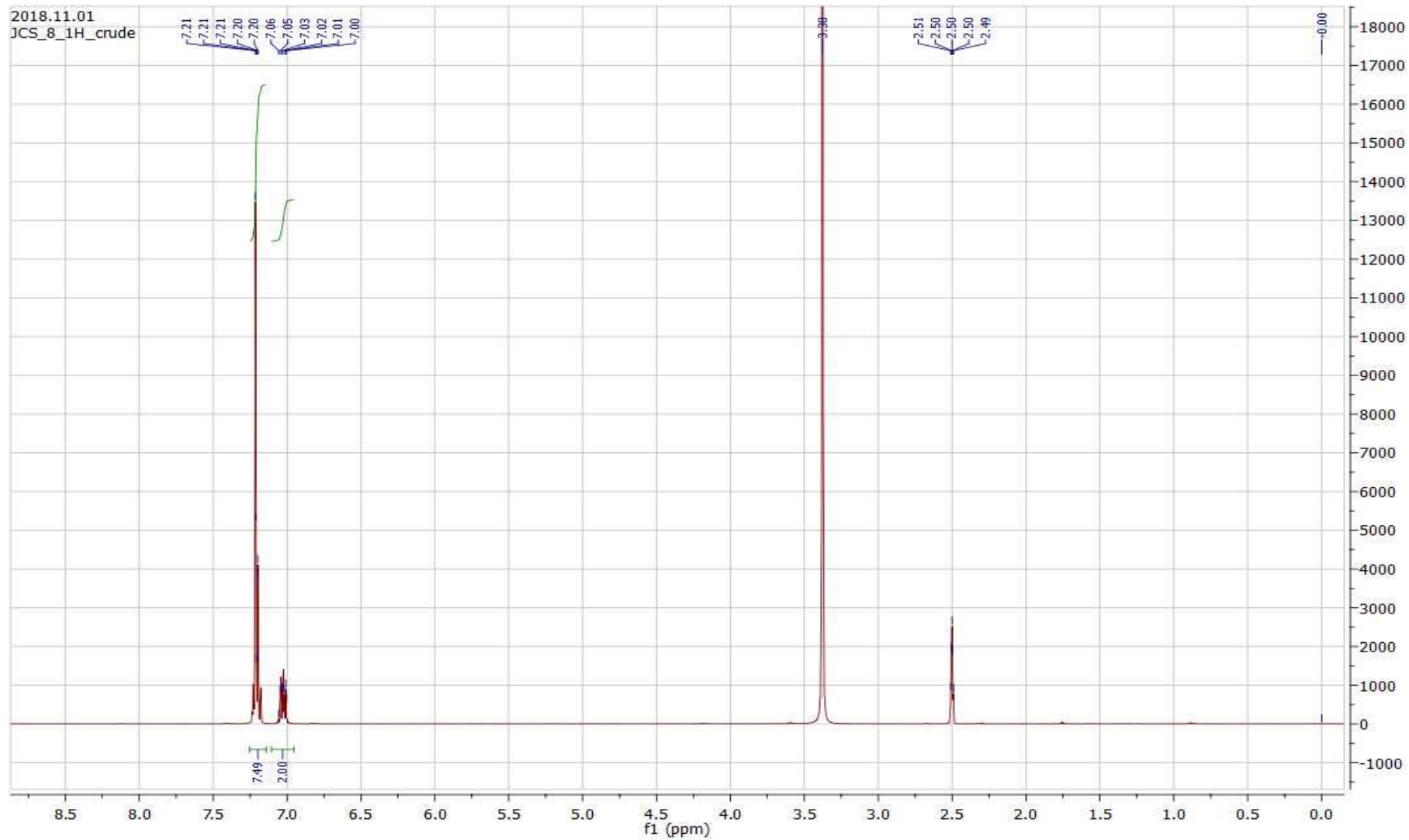


Figure S2. ^1H NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh}_2$ (**1a**)

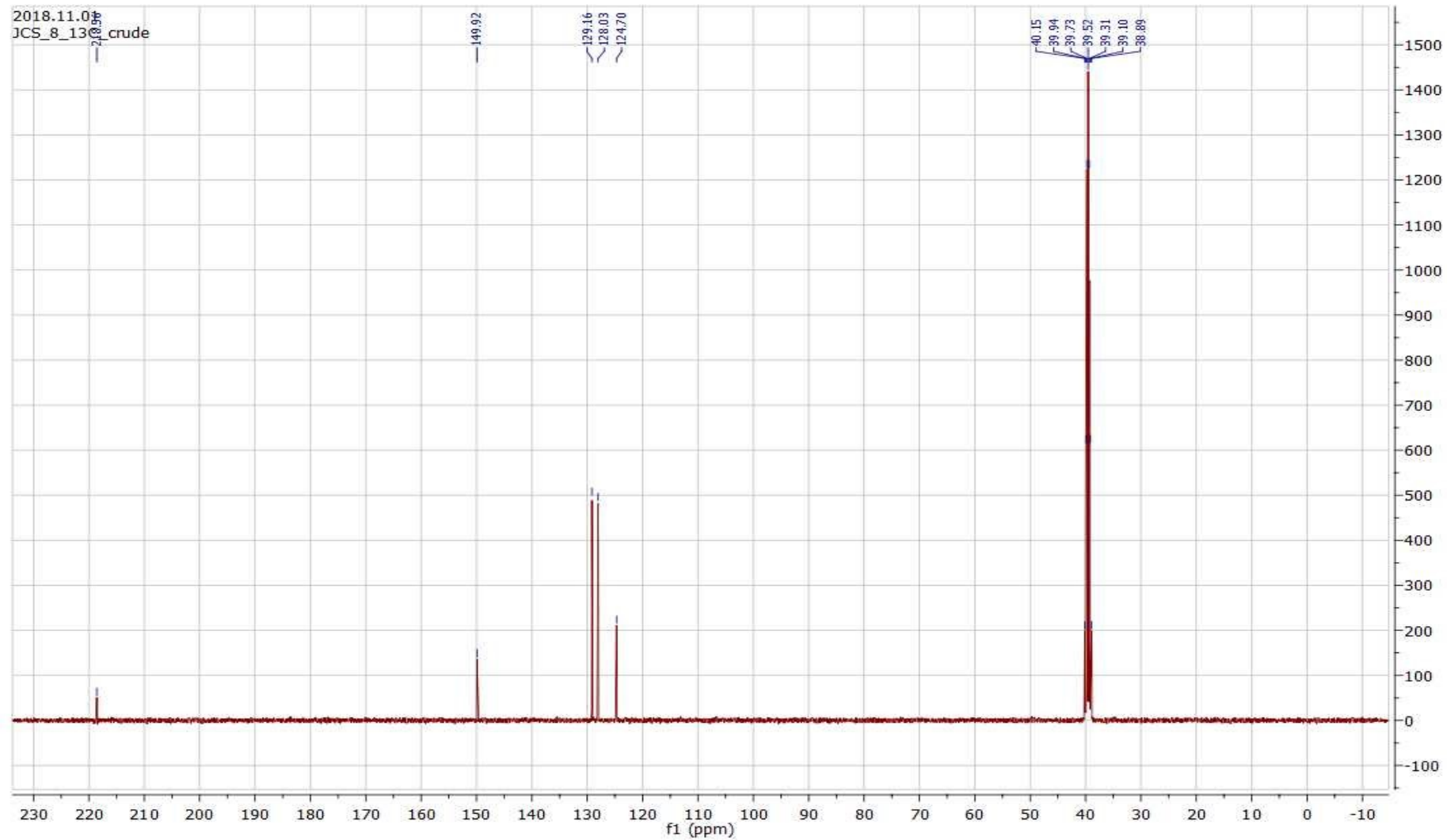


Figure S3. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh}_2$ (**1a**)

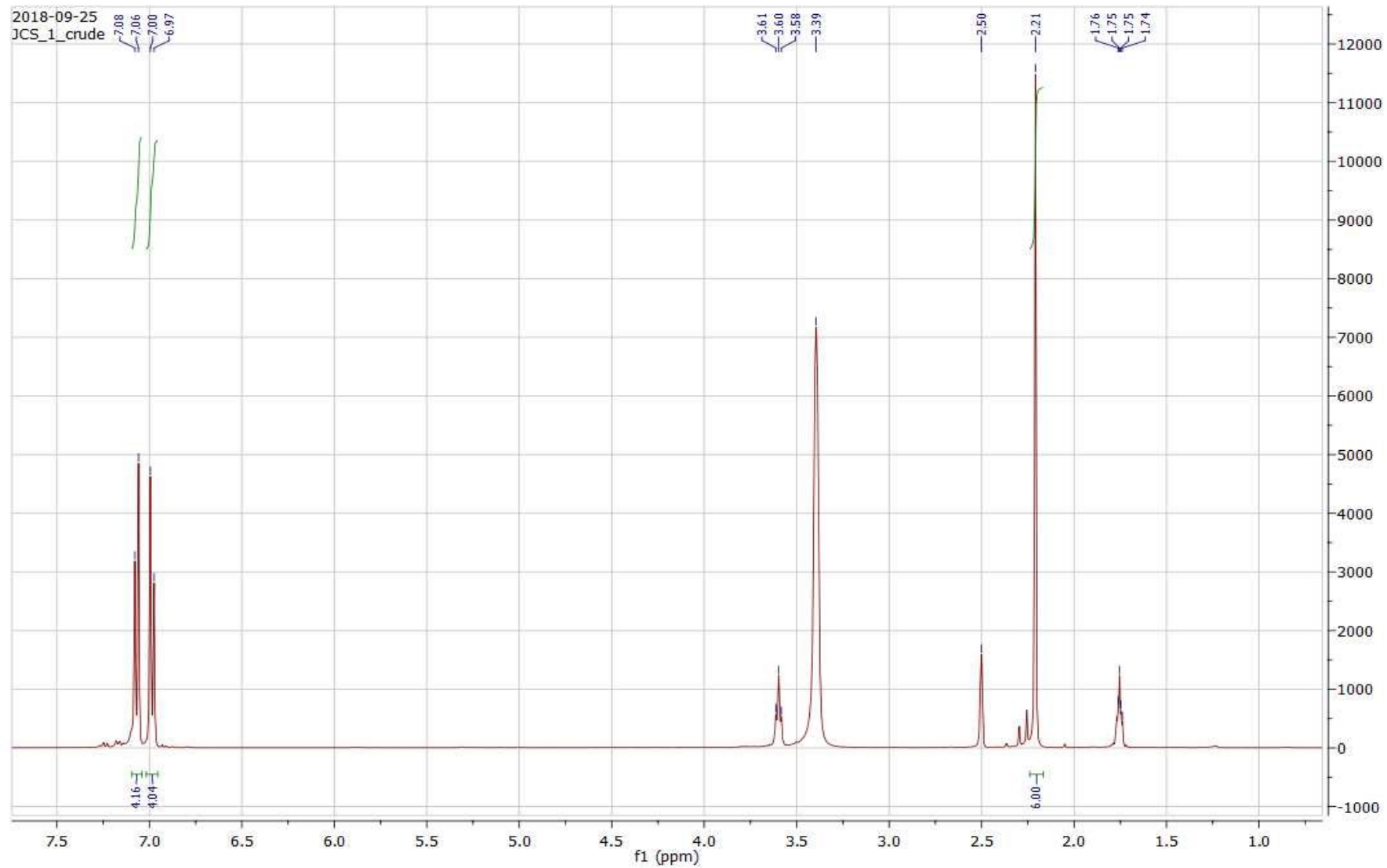


Figure S4. ^1H NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CN}(\text{p-tolyl})_2$ (**1b**)

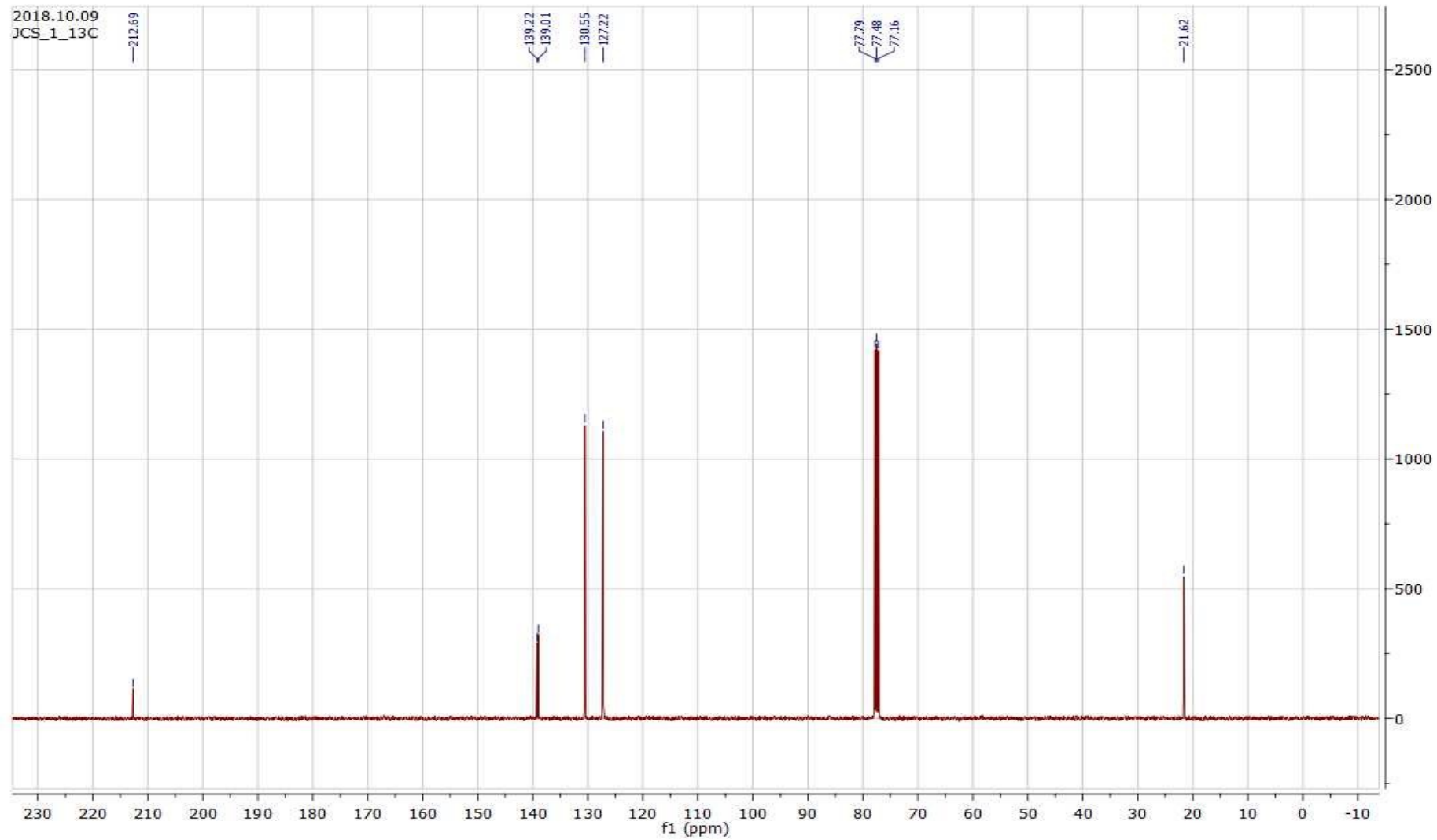


Figure S5. ^{13}C NMR (in CDCl_3) spectrum of of $\text{LiS}_2\text{CN}(\text{p-tolyl})_2$ (**1b**)

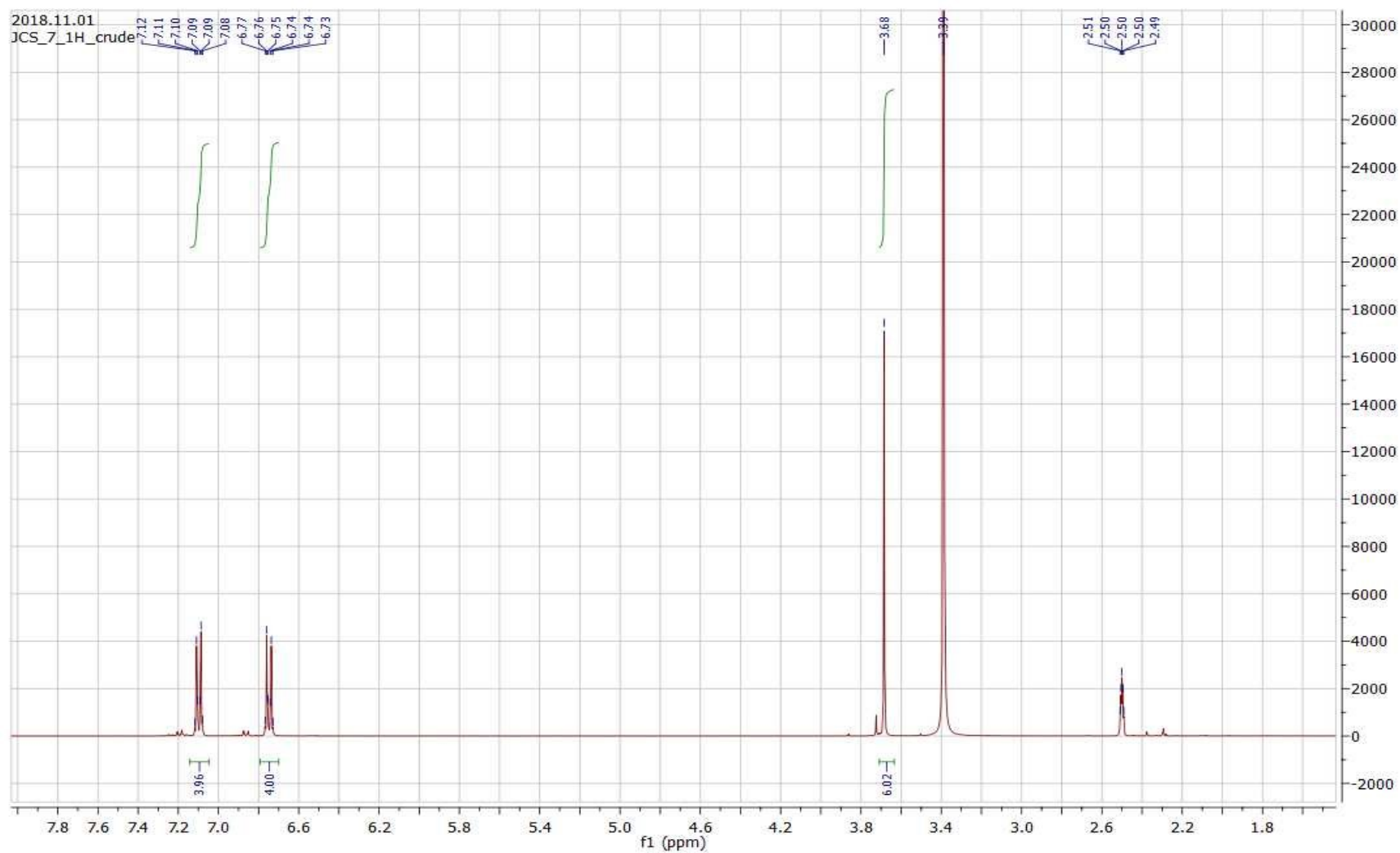


Figure S6. ^1H NMR (in DMSO-d_6) spectrum of $\text{Li}_2\text{CN}(\text{p-anisyl})_2$ (**1c**)

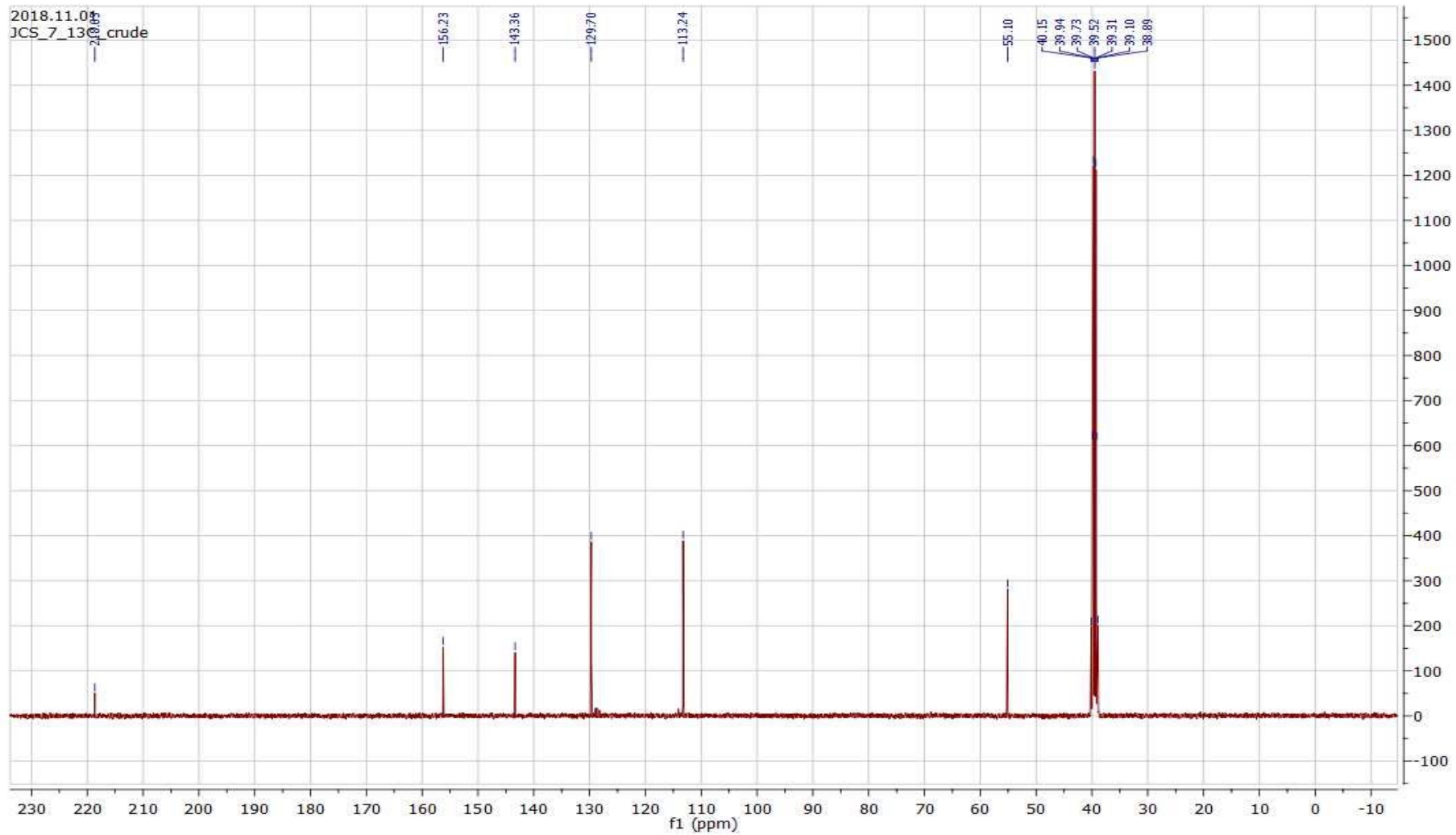


Figure S7. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CN}(\text{p-anisyl})_2$ (**1c**)

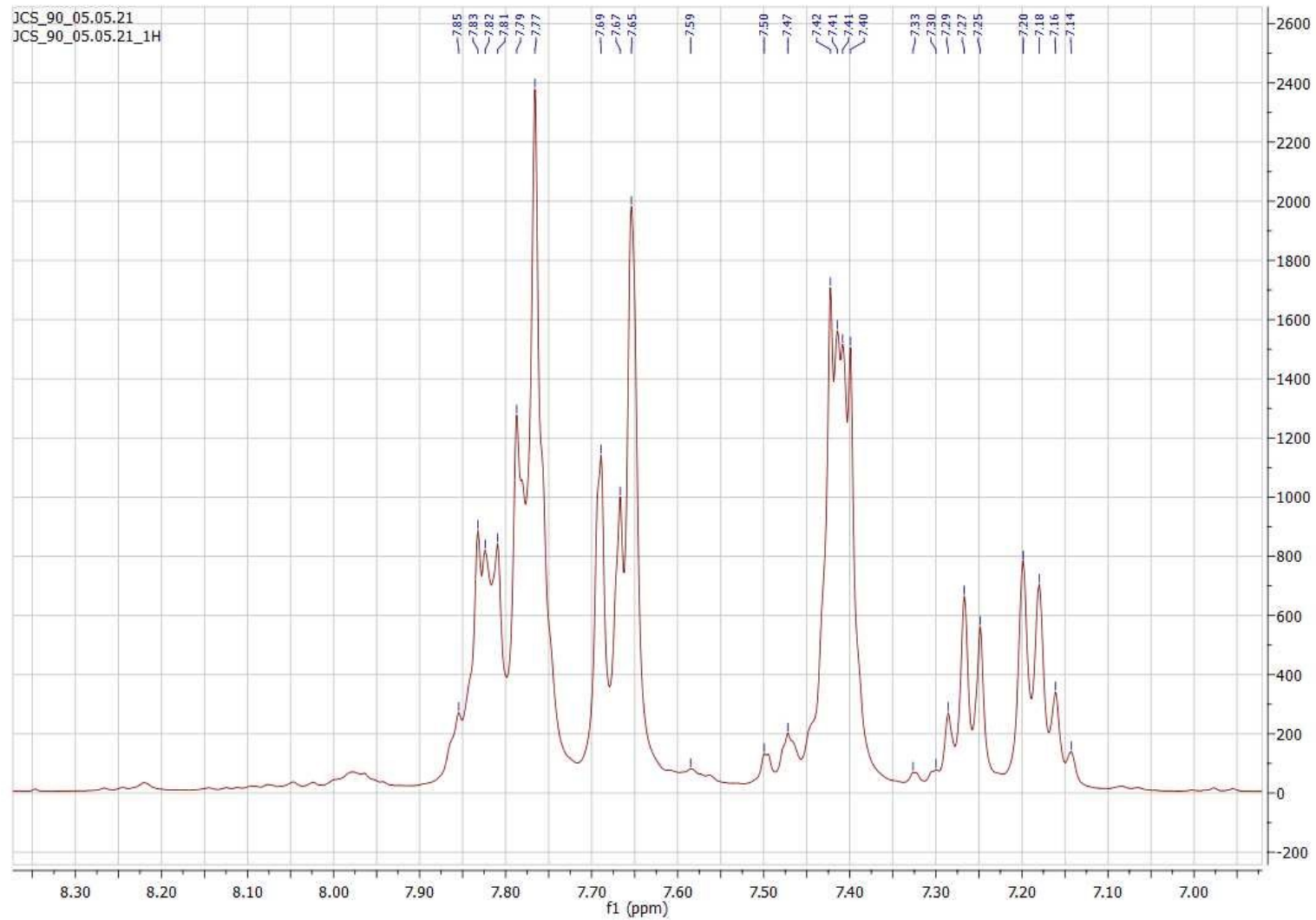


Figure S8. ^1H NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CN}(2\text{-naphthyl})_2$ (**1d**)

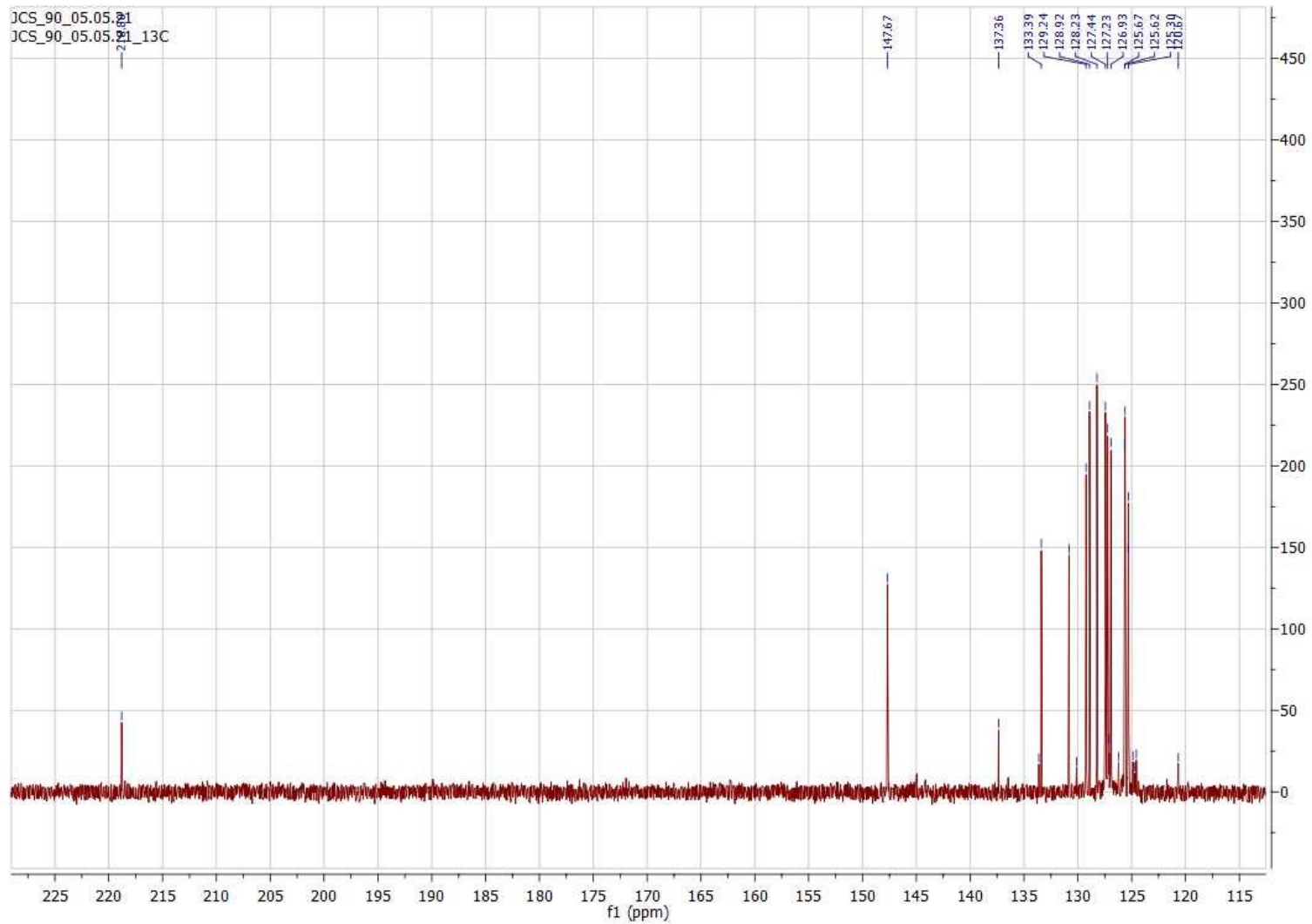


Figure S9. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CN}(2\text{-naphthyl})_2$ (**1d**)

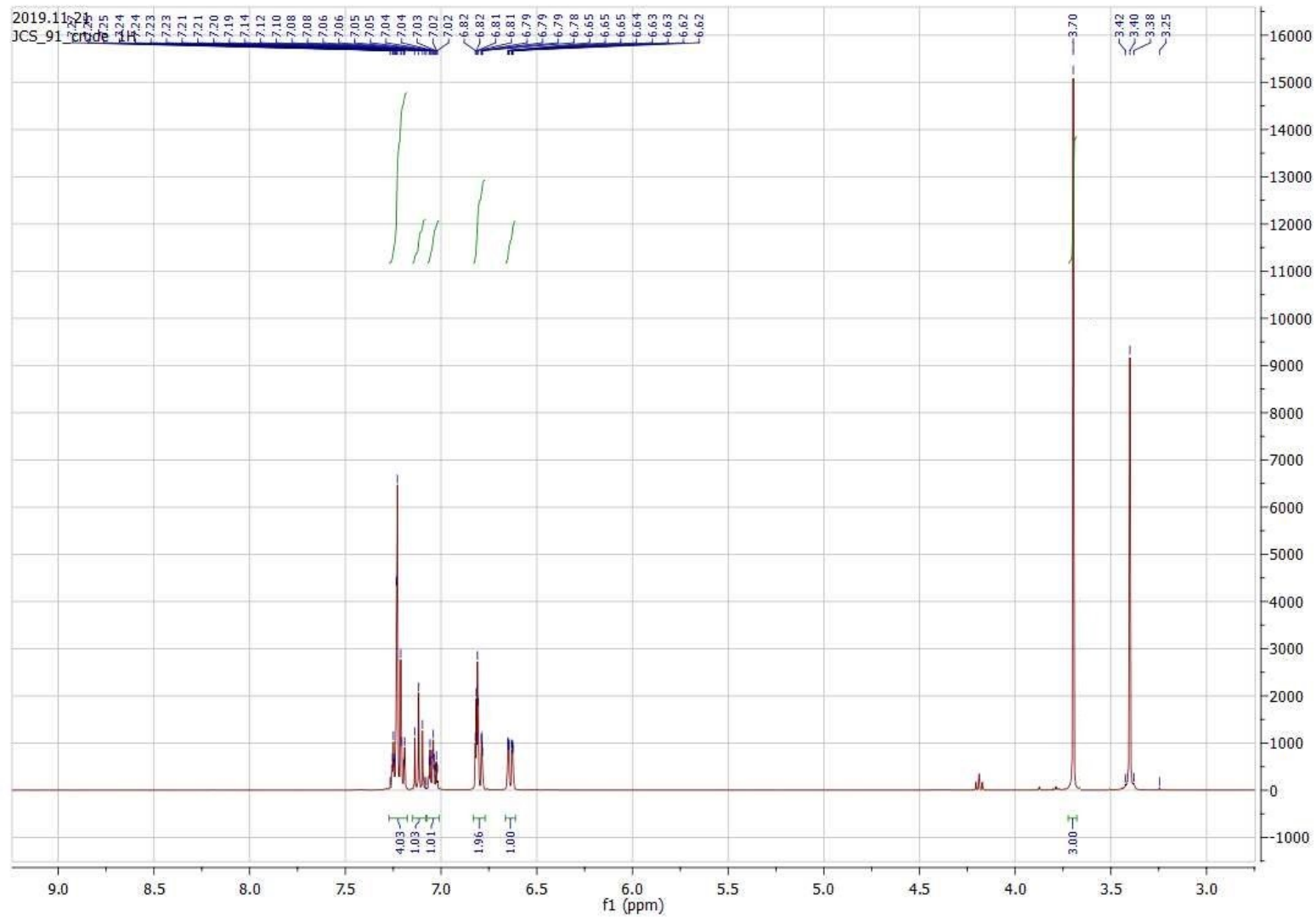


Figure S10. ^1H NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh(m-anisyl)}$ (**1e**)

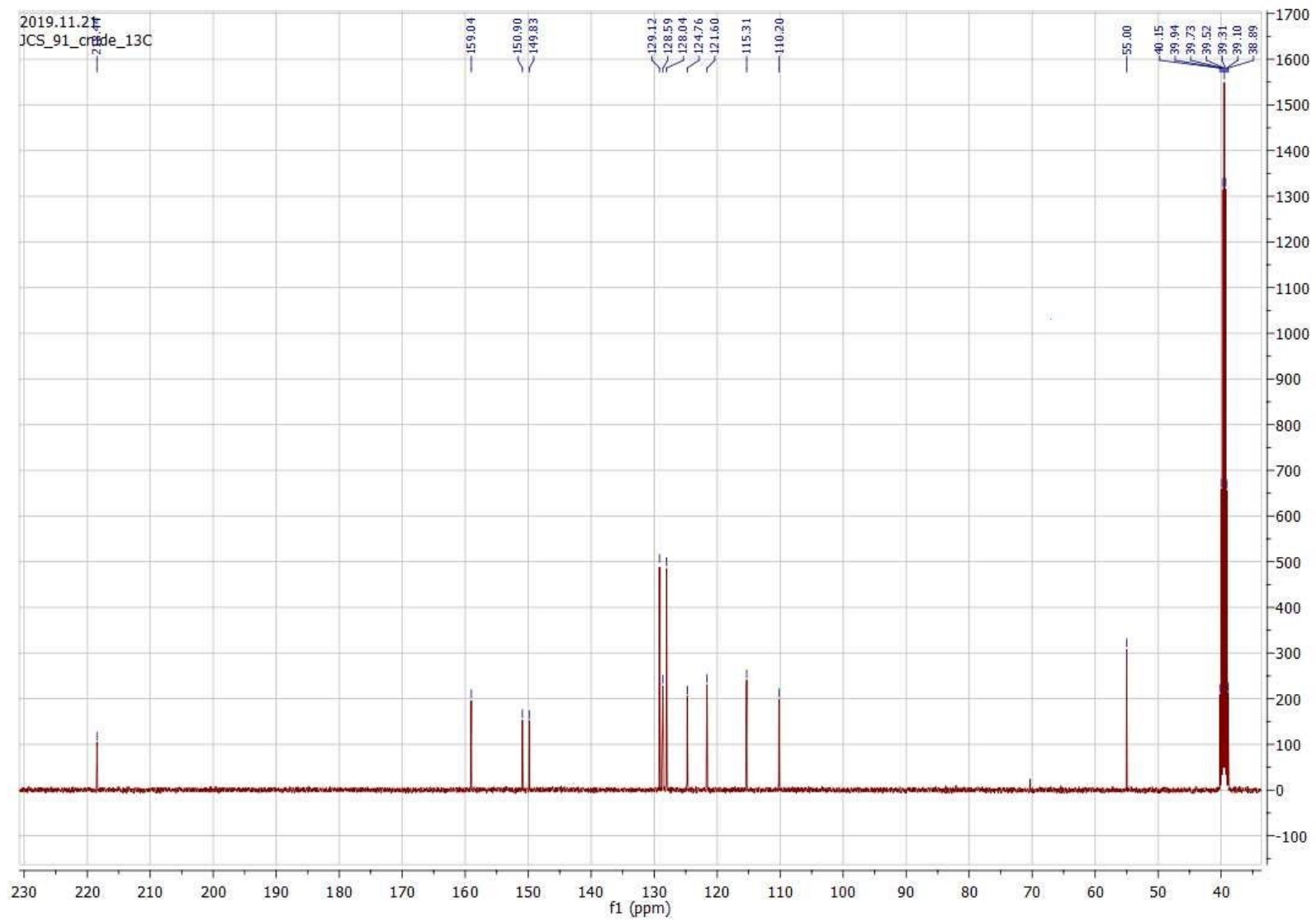


Figure S11. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh(m-anisyl)}$ (**1e**)

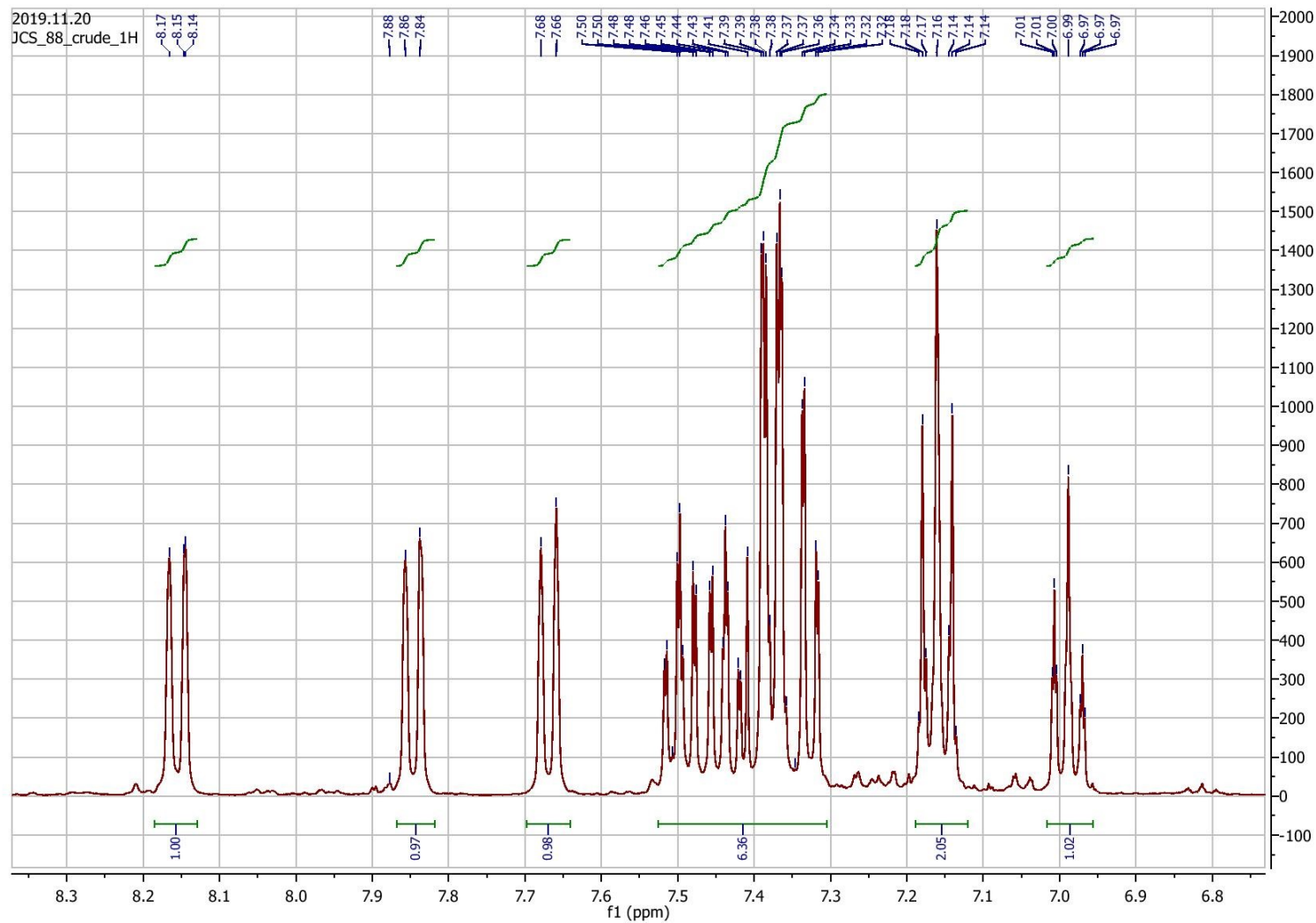


Figure S12. ^1H NMR (in DMSO-d_6) spectrum of $\text{Li}_2\text{CNPh}(1\text{-naphthyl})$ (**1f**)

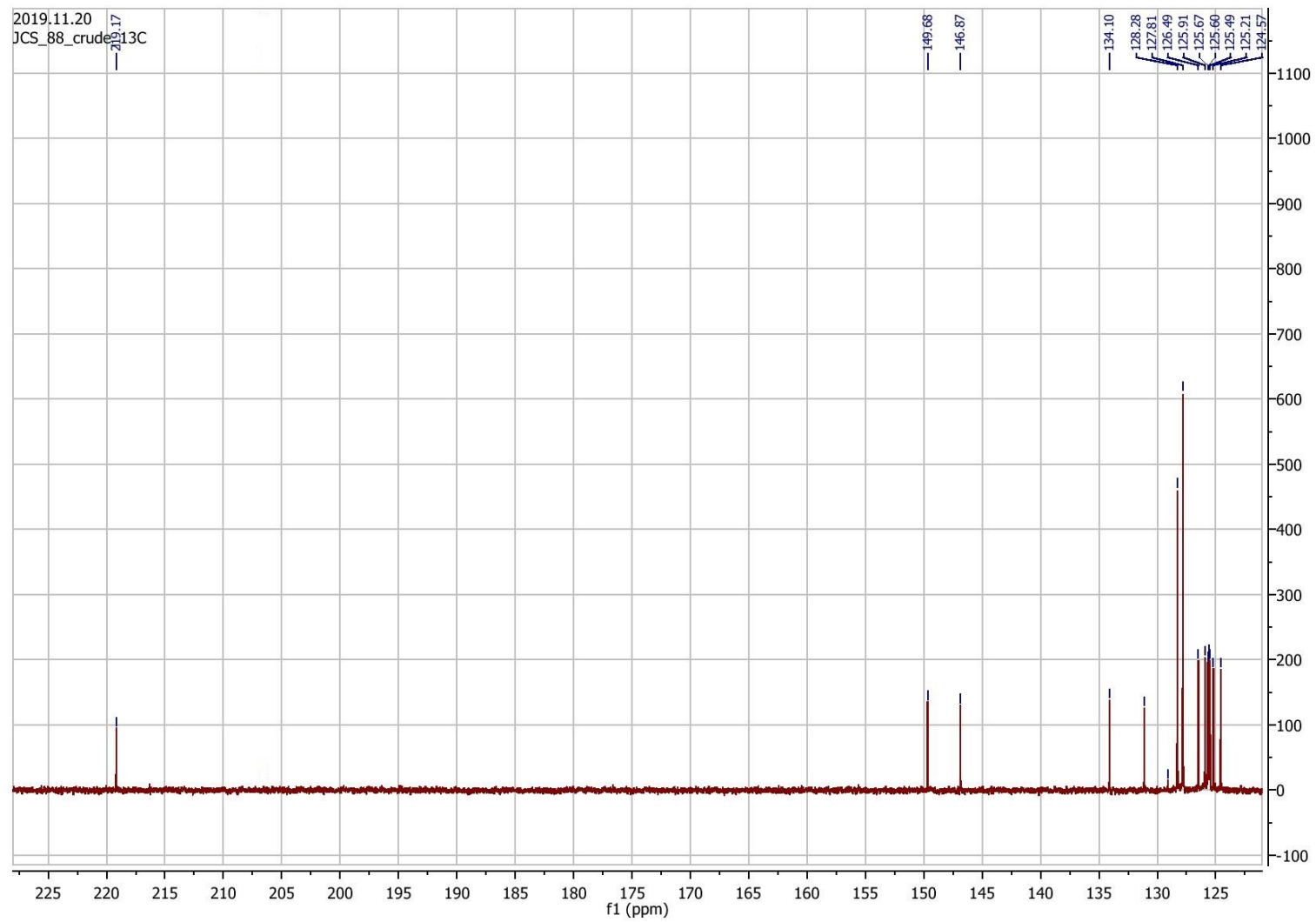


Figure S13. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh}(1\text{-naphthyl})$ (**1f**)

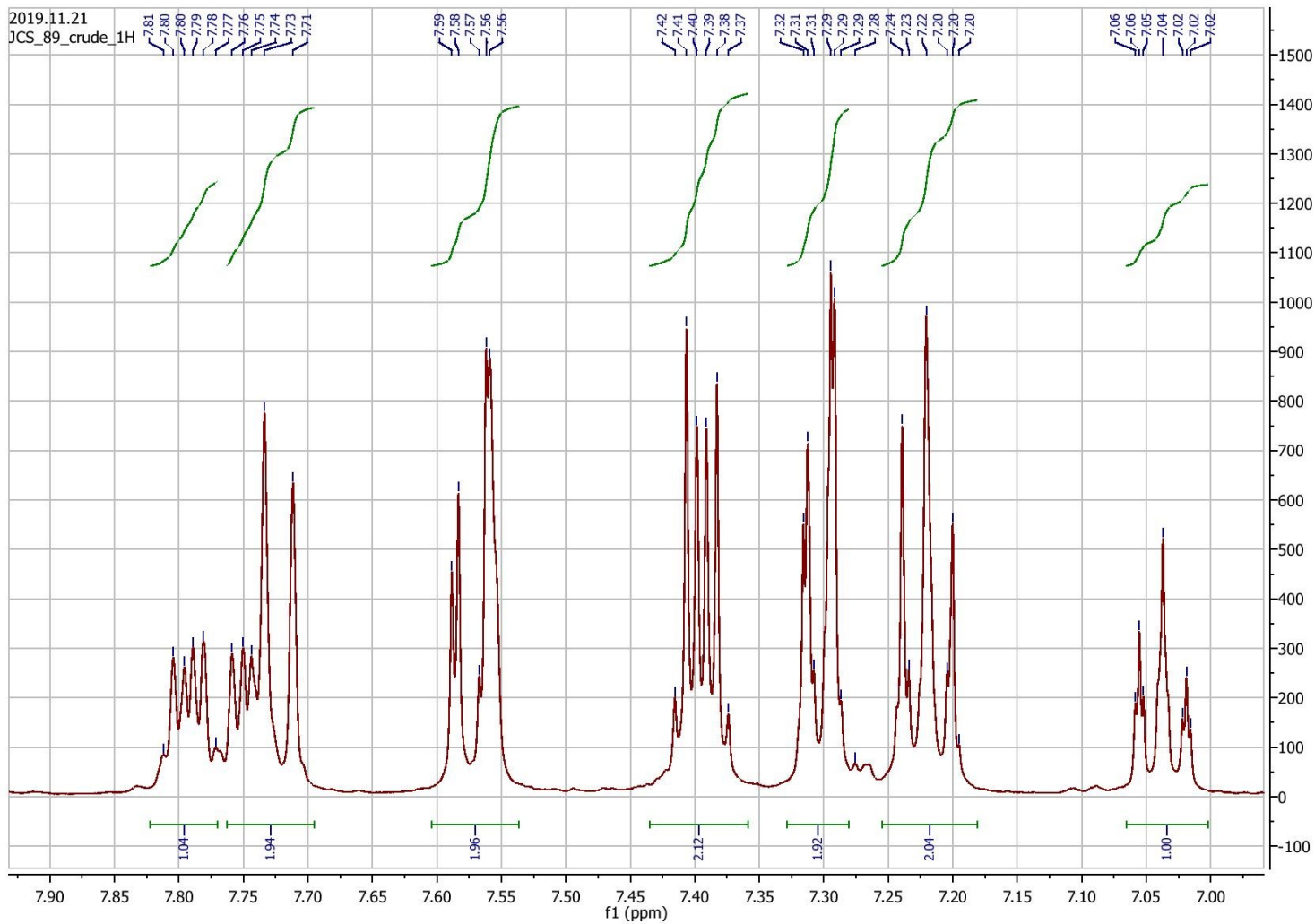


Figure S14. ^1H NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh(2-naphthyl)}$ (**1g**)

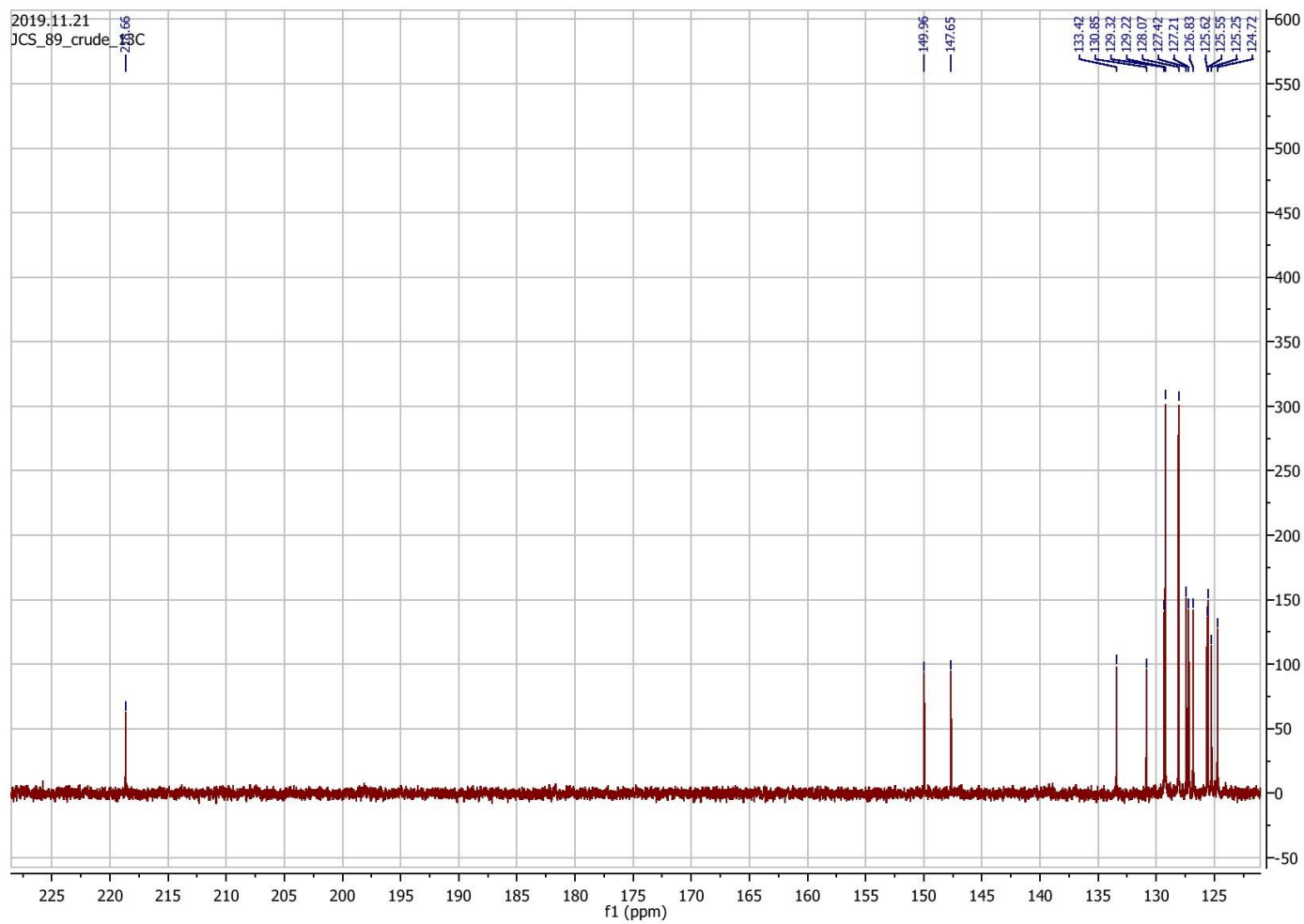


Figure S15. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{LiS}_2\text{CNPh}(2\text{-naphthyl})$ (**1g**)

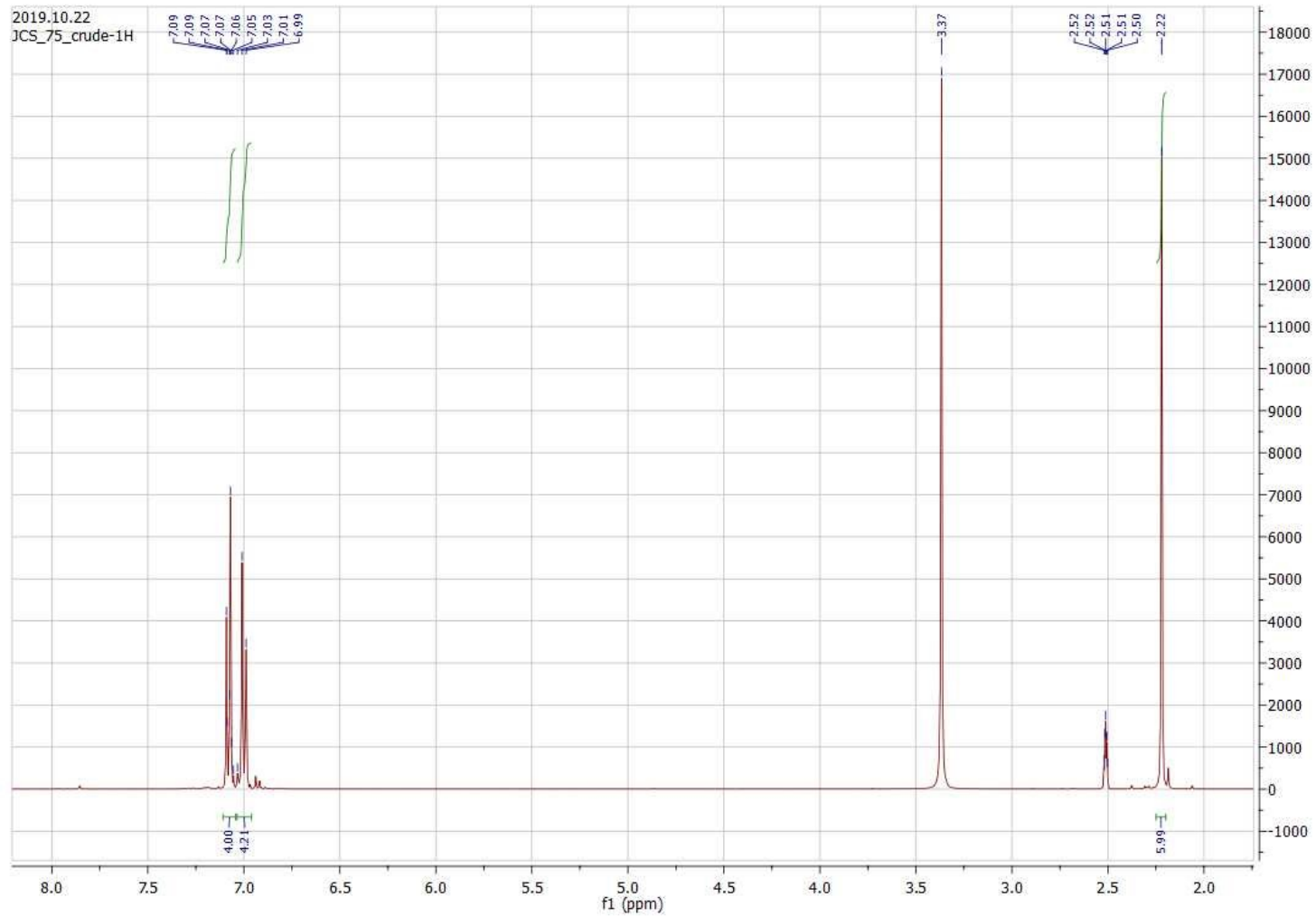


Figure S16. ^1H NMR (in DMSO-d_6) spectrum of $\text{KS}_2\text{CN}(\text{p-tolyl})_2$ (**1h**)

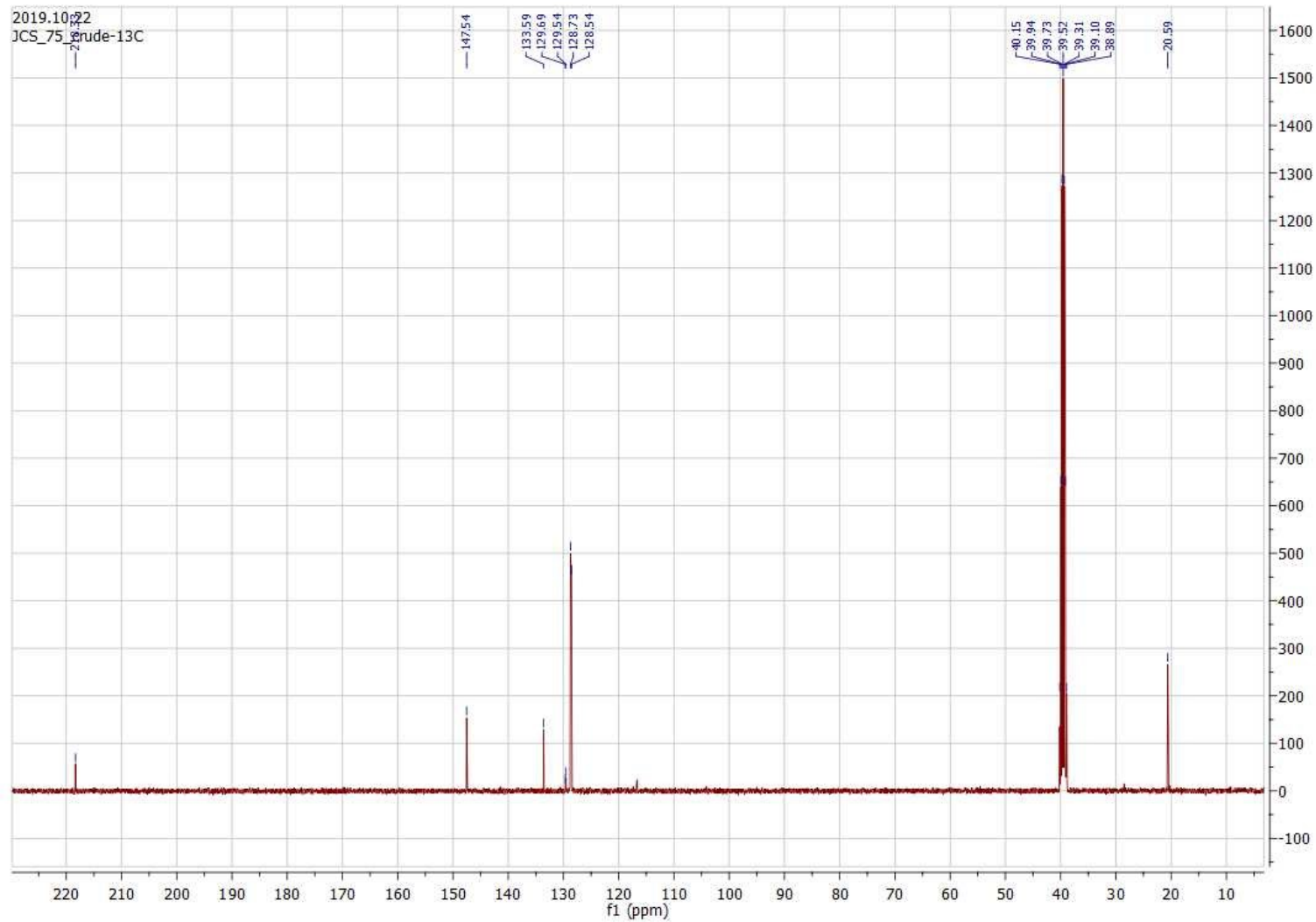


Figure S17. ^{13}C NMR (in DMSO-d_6) spectrum of $\text{KS}_2\text{CN}(\text{p-tolyl})_2$ (**1h**)

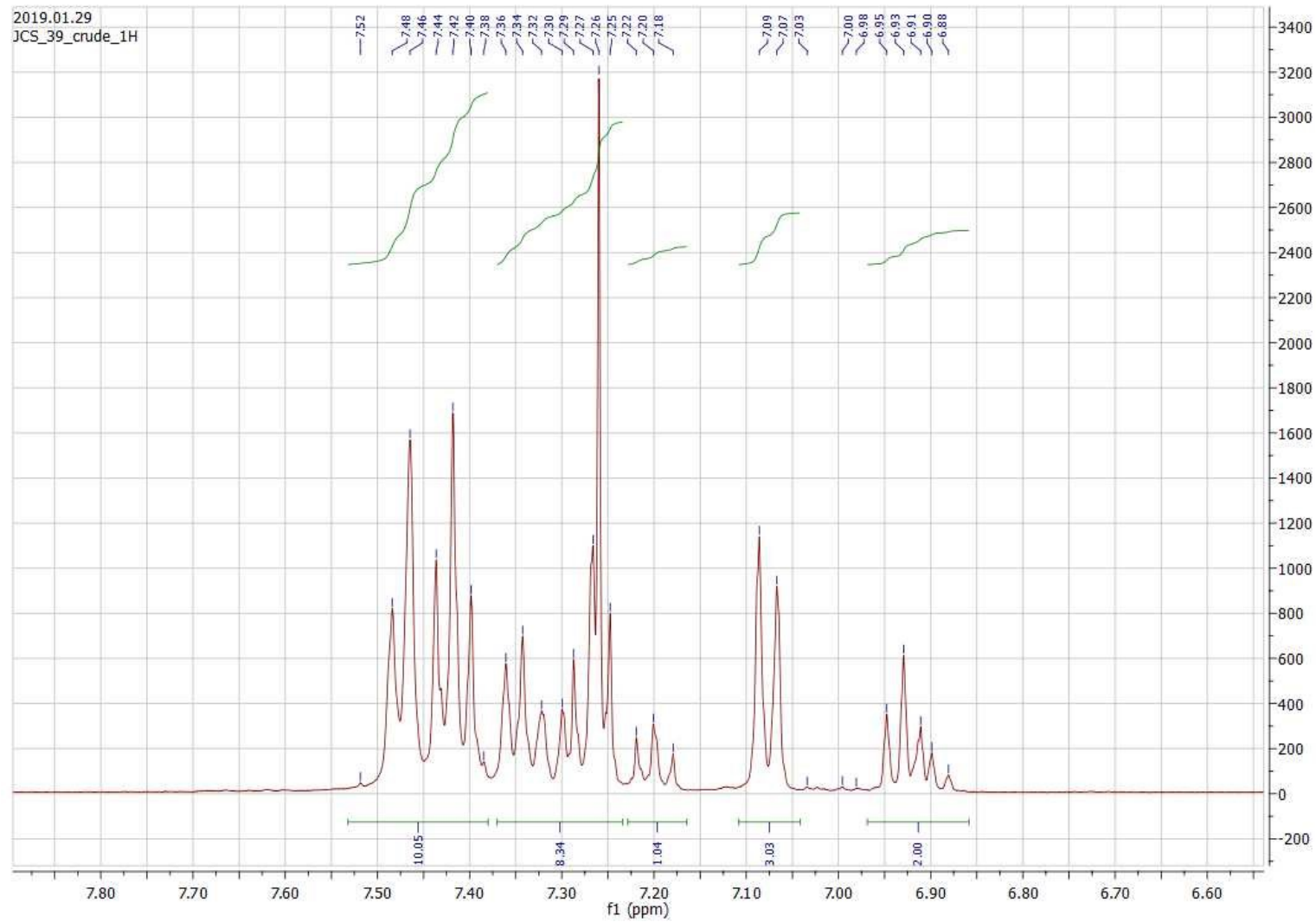


Figure S18. ^1H NMR (in CDCl_3) spectrum of $(\text{Ph}_2\text{NCS}_2)_2$ (**2a**)

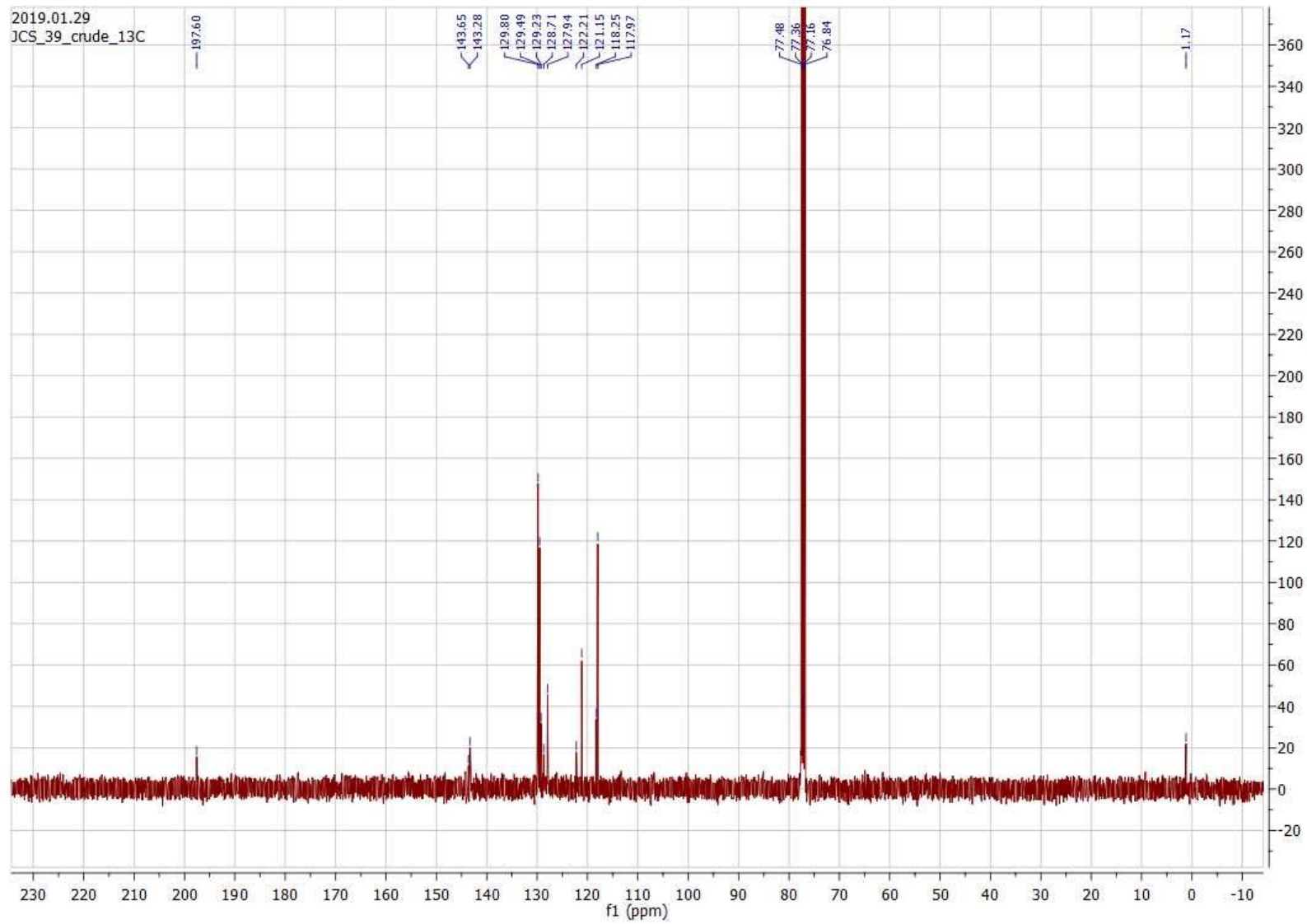


Figure S19. ^{13}C NMR (in CDCl_3) spectrum of $(\text{Ph}_2\text{NCS}_2)_2$ (**2a**)

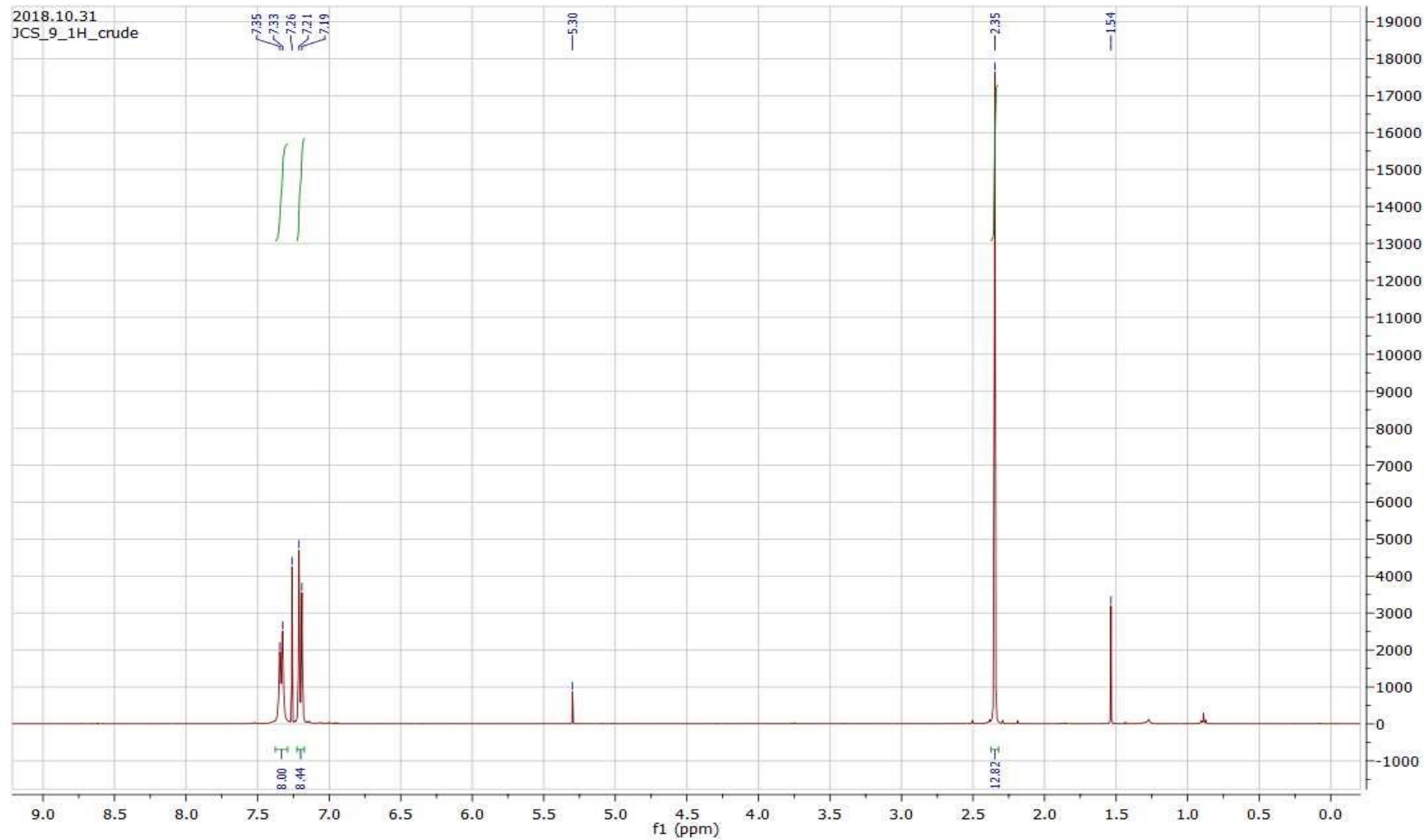


Figure S20. ^1H NMR (in CDCl_3) spectrum of $[(p\text{-tolyl})_2\text{NCS}_2]_2$ (**2b**)

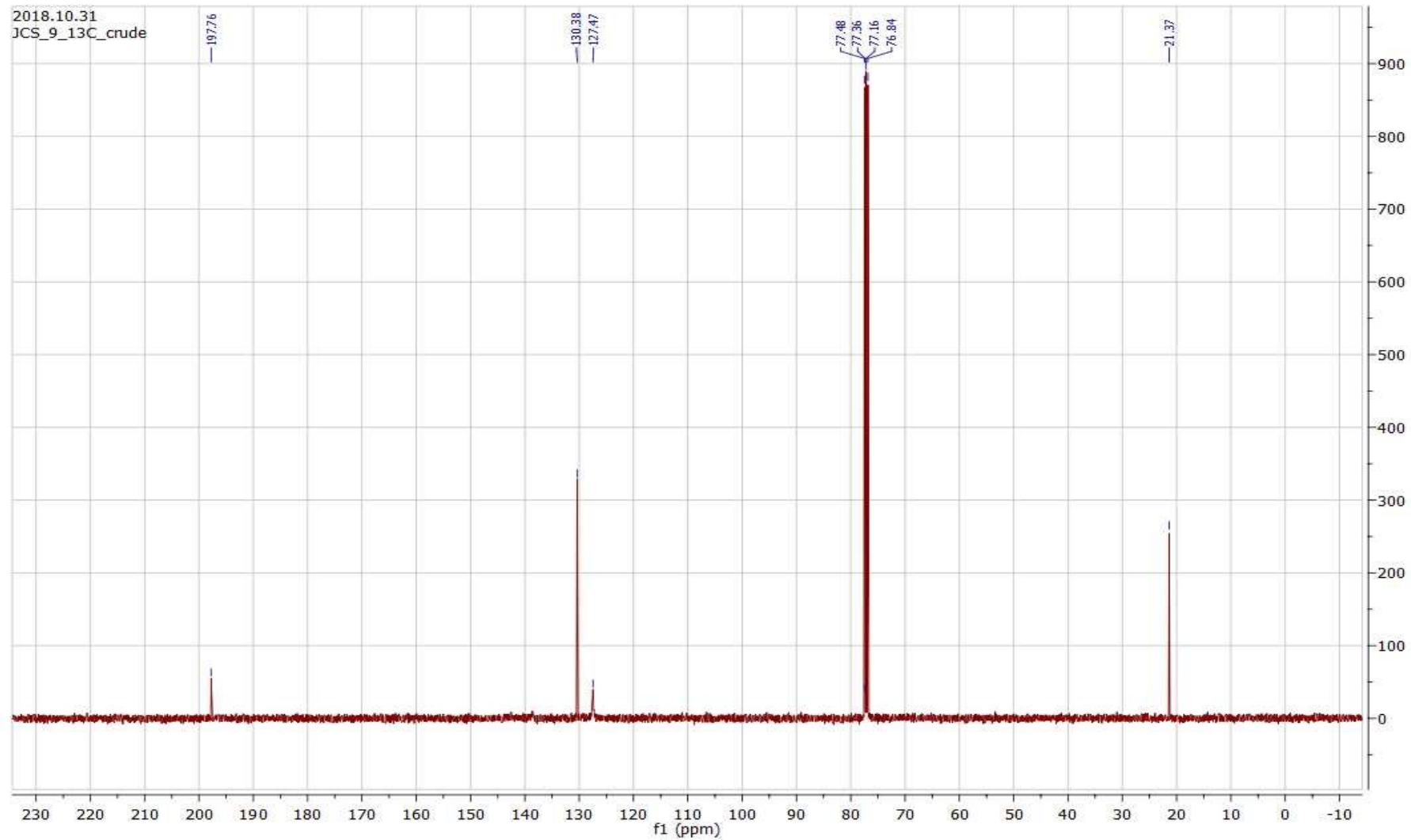


Figure S21. ^{13}C NMR (in CDCl_3) spectrum of $[(p\text{-tolyl})_2\text{NCS}_2]_2$ (**2b**)

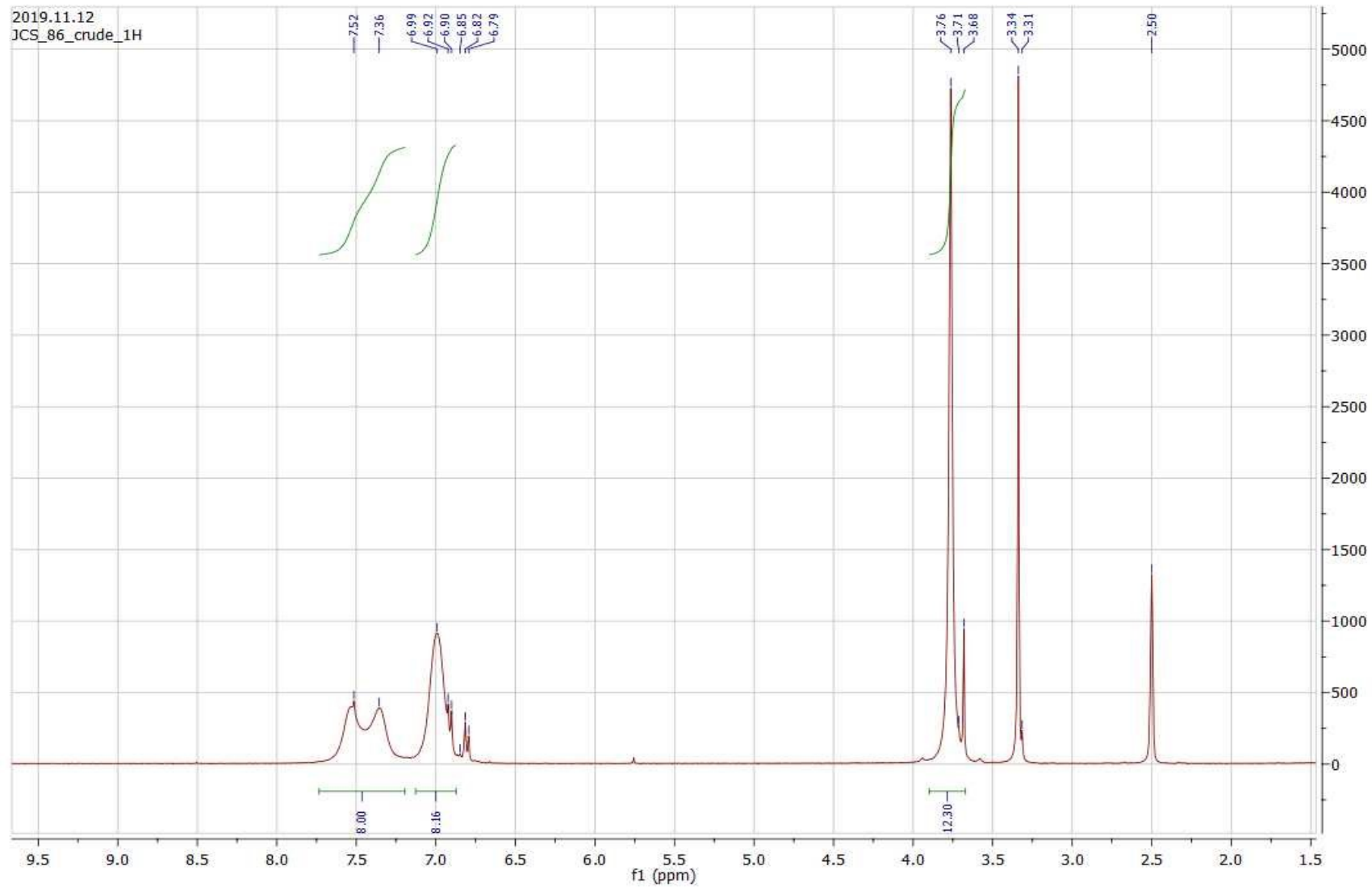


Figure S22. ^1H NMR (in CDCl_3) spectrum of $[(p\text{-anisyl})_2\text{NCS}_2]_2$ (**2c**)

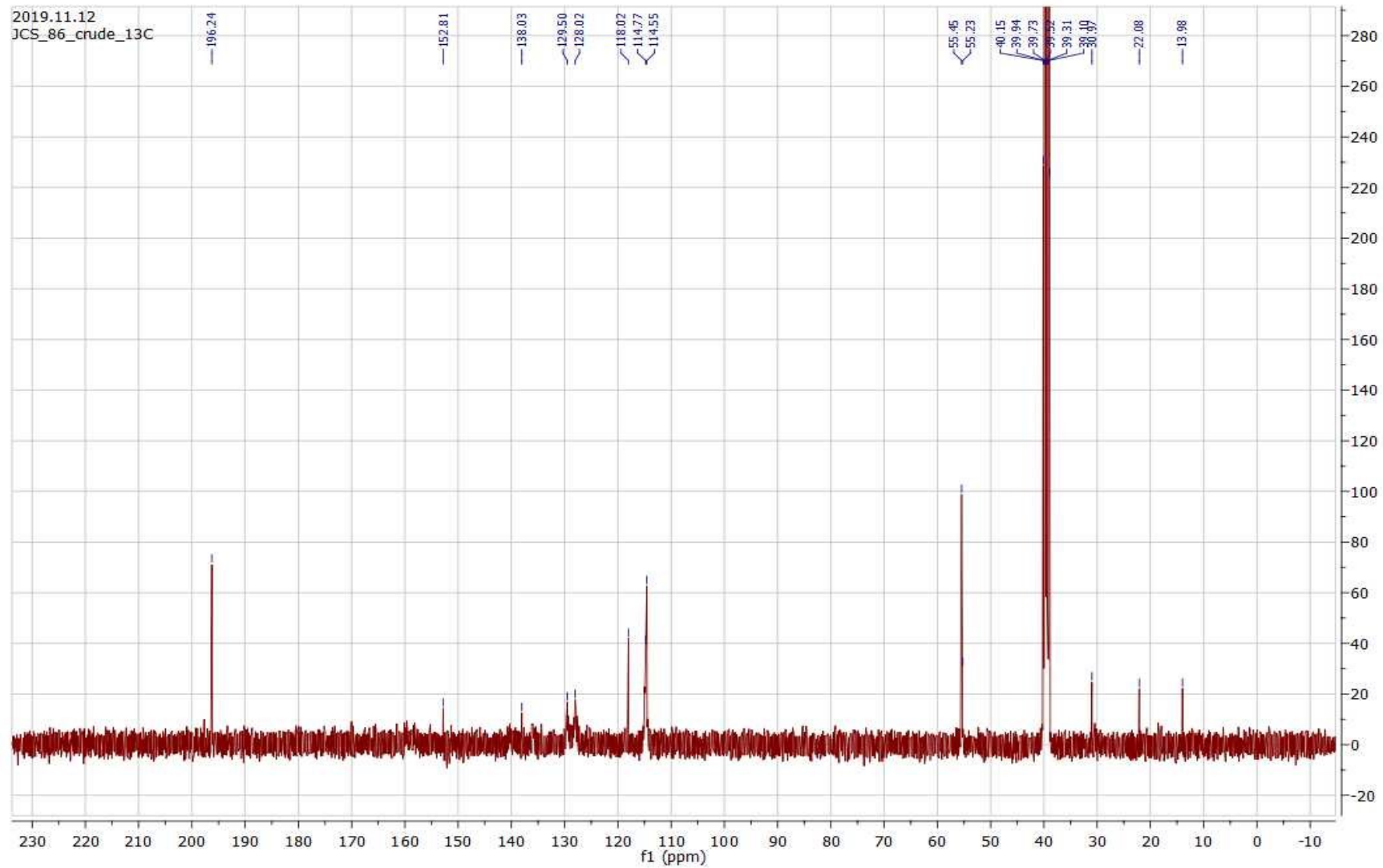


Figure S23. ^{13}C NMR (in CDCl_3) spectrum of $[(p\text{-anisyl})_2\text{NCS}_2]_2$ (**2c**)

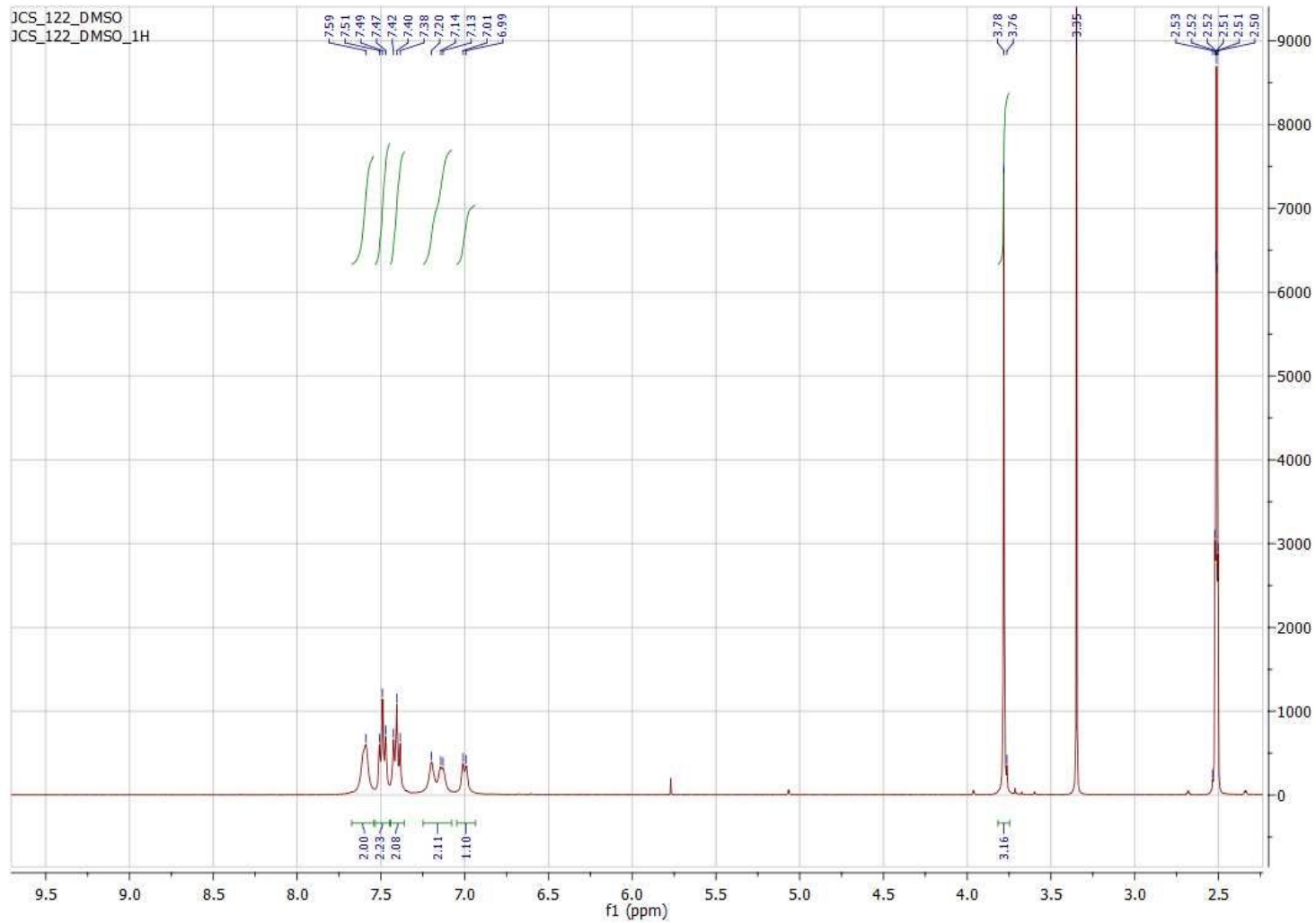


Figure S24. ^1H NMR (in CDCl_3) spectrum of $[(m\text{-anisyl})\text{PhNCS}_2]_2$ (**2e**)

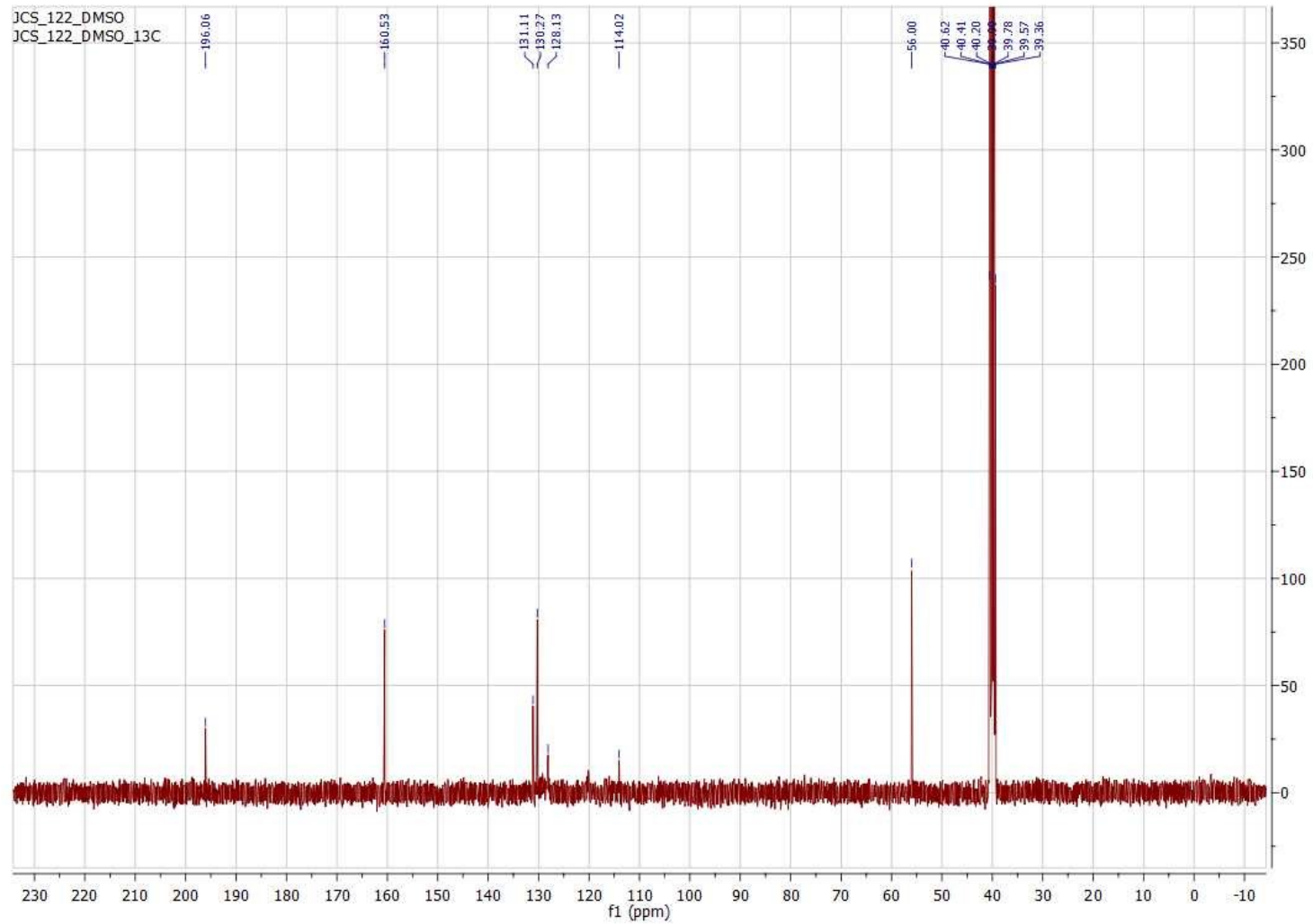


Figure S25. ^{13}C NMR (in CDCl_3) spectrum of $[(m\text{-anisyl})\text{PhNCS}_2]_2$ (**2e**)

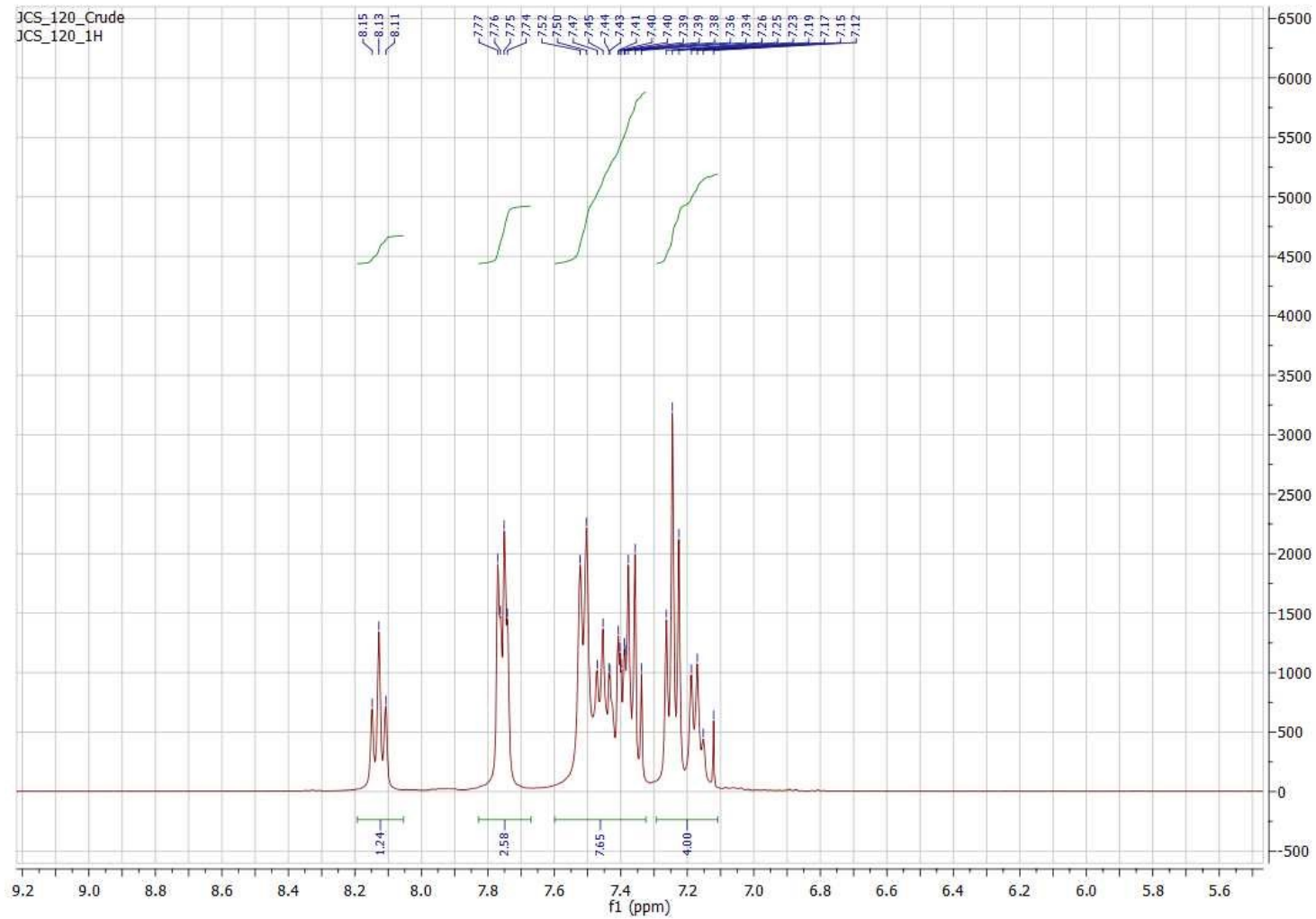


Figure S26. ^1H NMR (in CDCl_3) spectrum of $[\text{Ph}(1\text{-naphthyl})\text{NCS}_2]_2$ (**2f**)

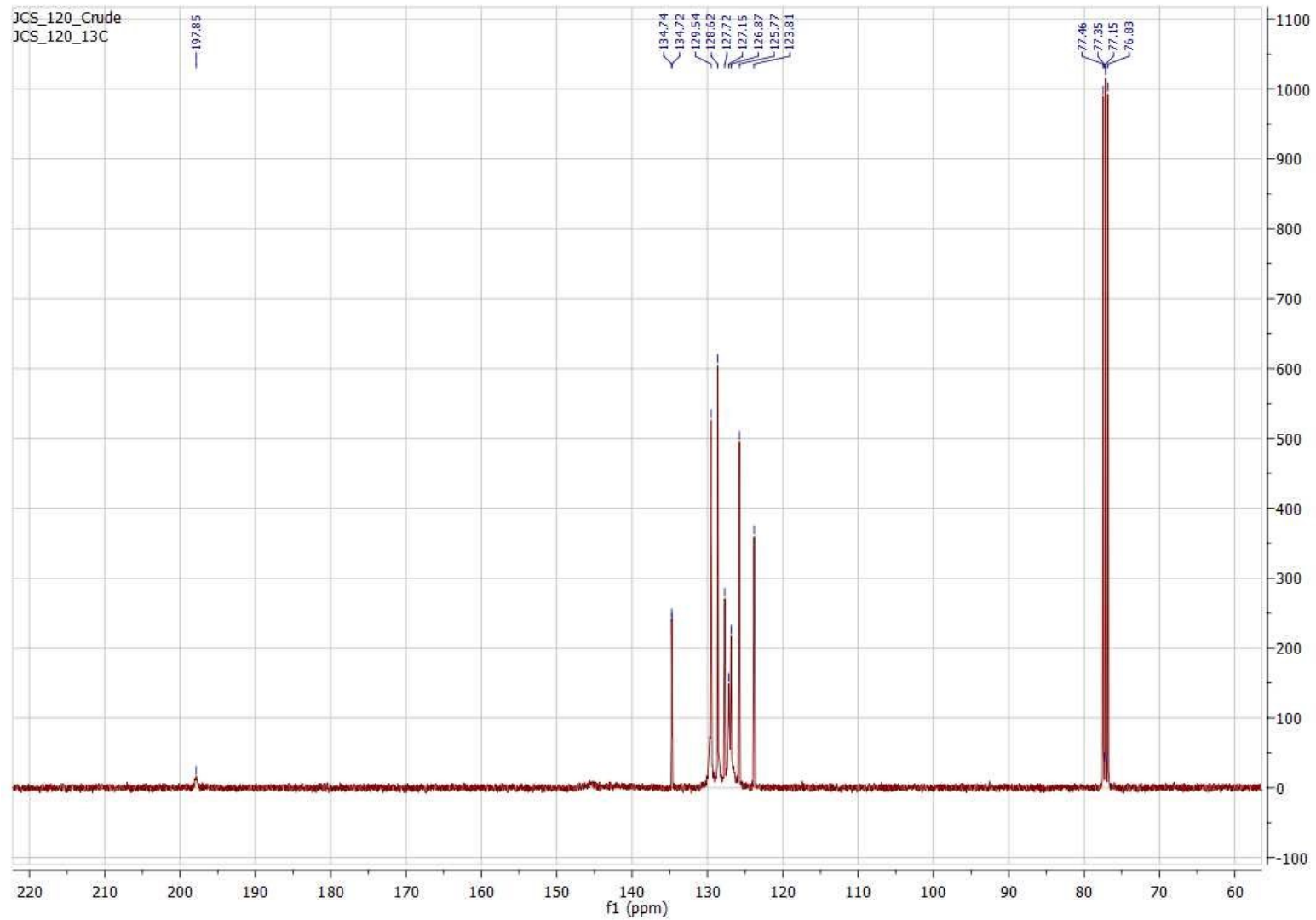


Figure S27. ^{13}C NMR (in CDCl_3) spectrum of $[\text{Ph}(1\text{-naphthyl})\text{NCS}_2]_2$ (**2f**)

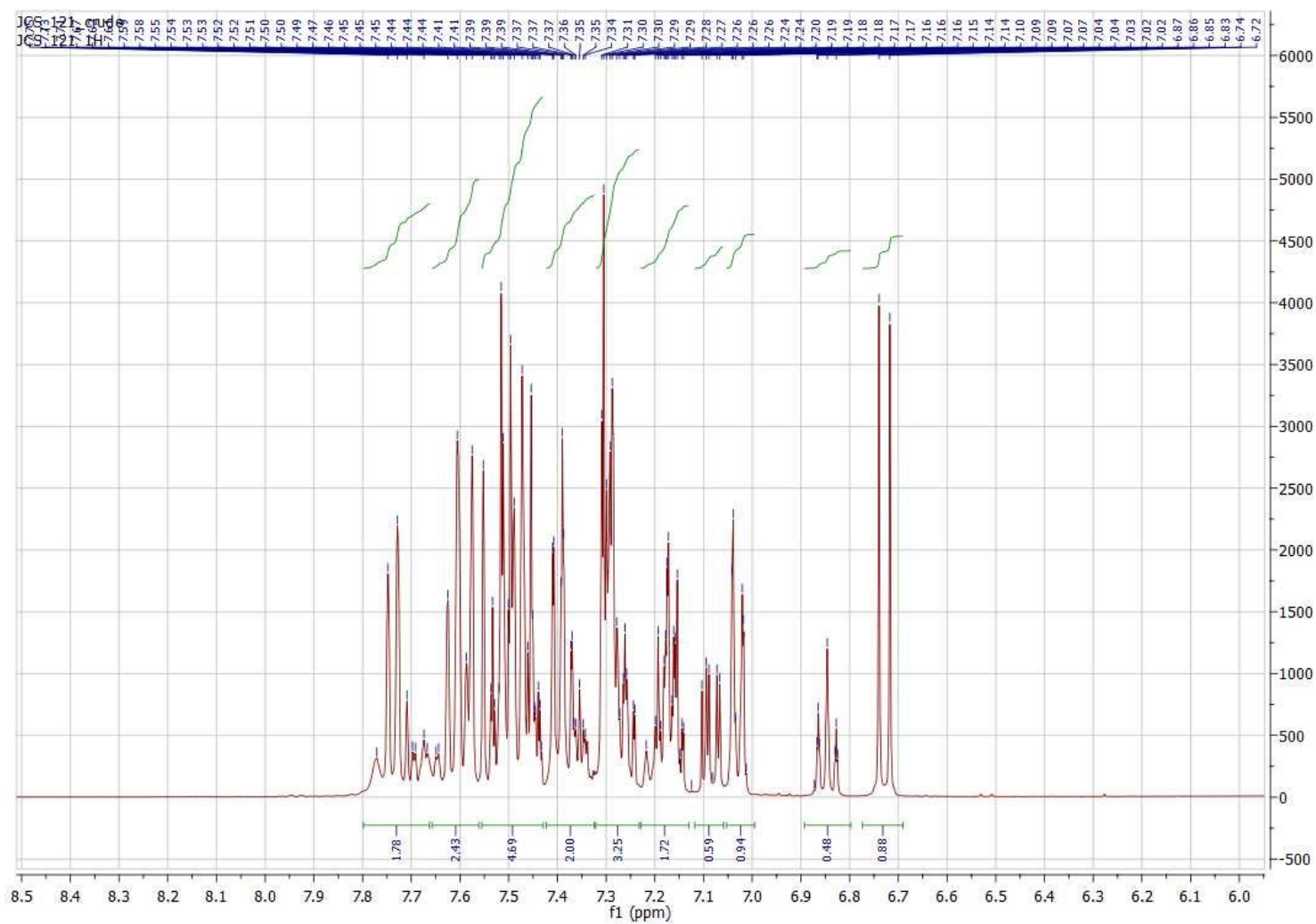


Figure S28. ^1H NMR (in CDCl_3) spectrum of $[\text{Ph}(2\text{-naphthyl})\text{NCS}_2]_2$ (**2g**)

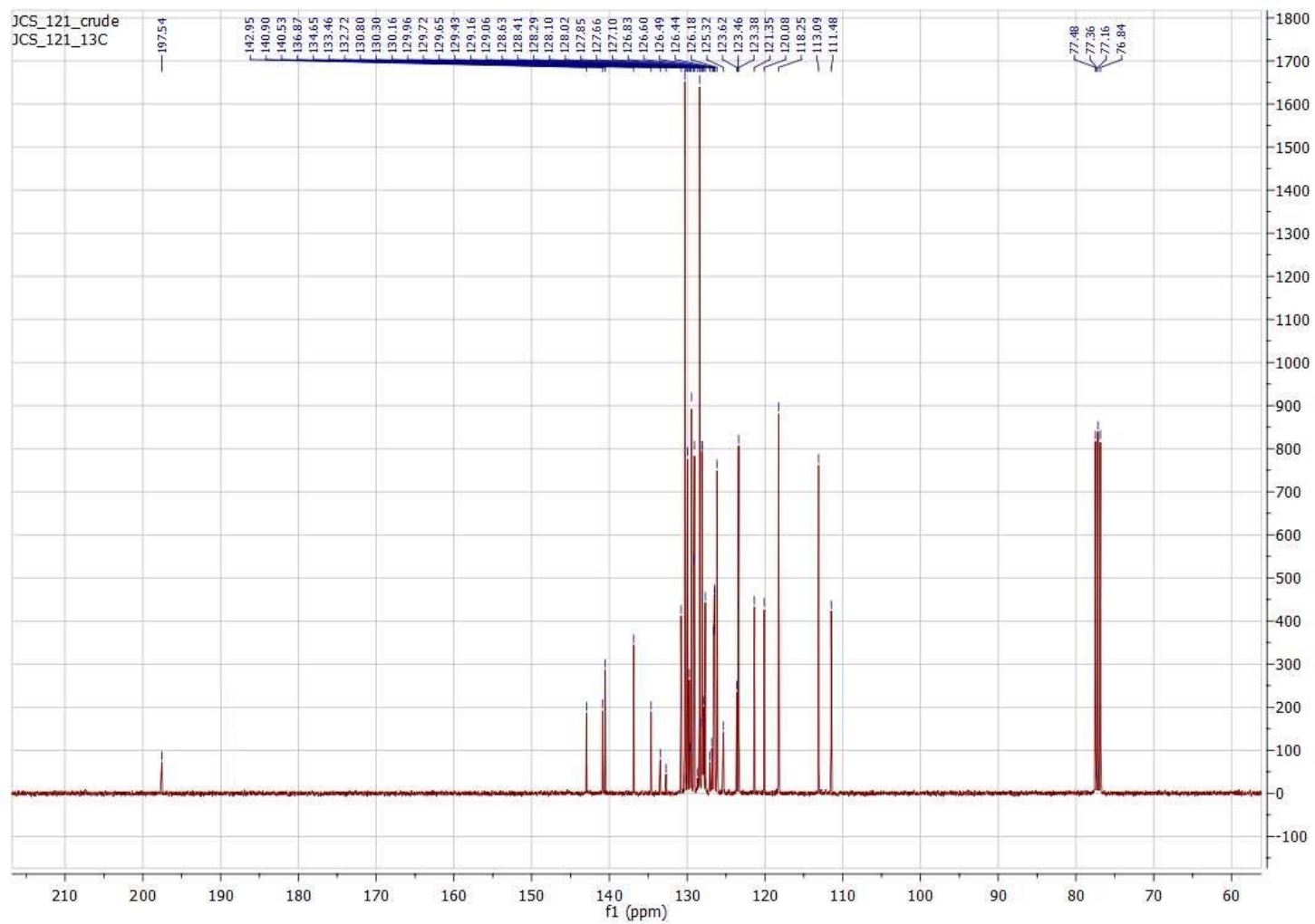


Figure S29. ^{13}C NMR (in CDCl_3) spectrum of $[\text{Ph}(2\text{-naphthyl})\text{NCS}_2]_2$ (**2g**)

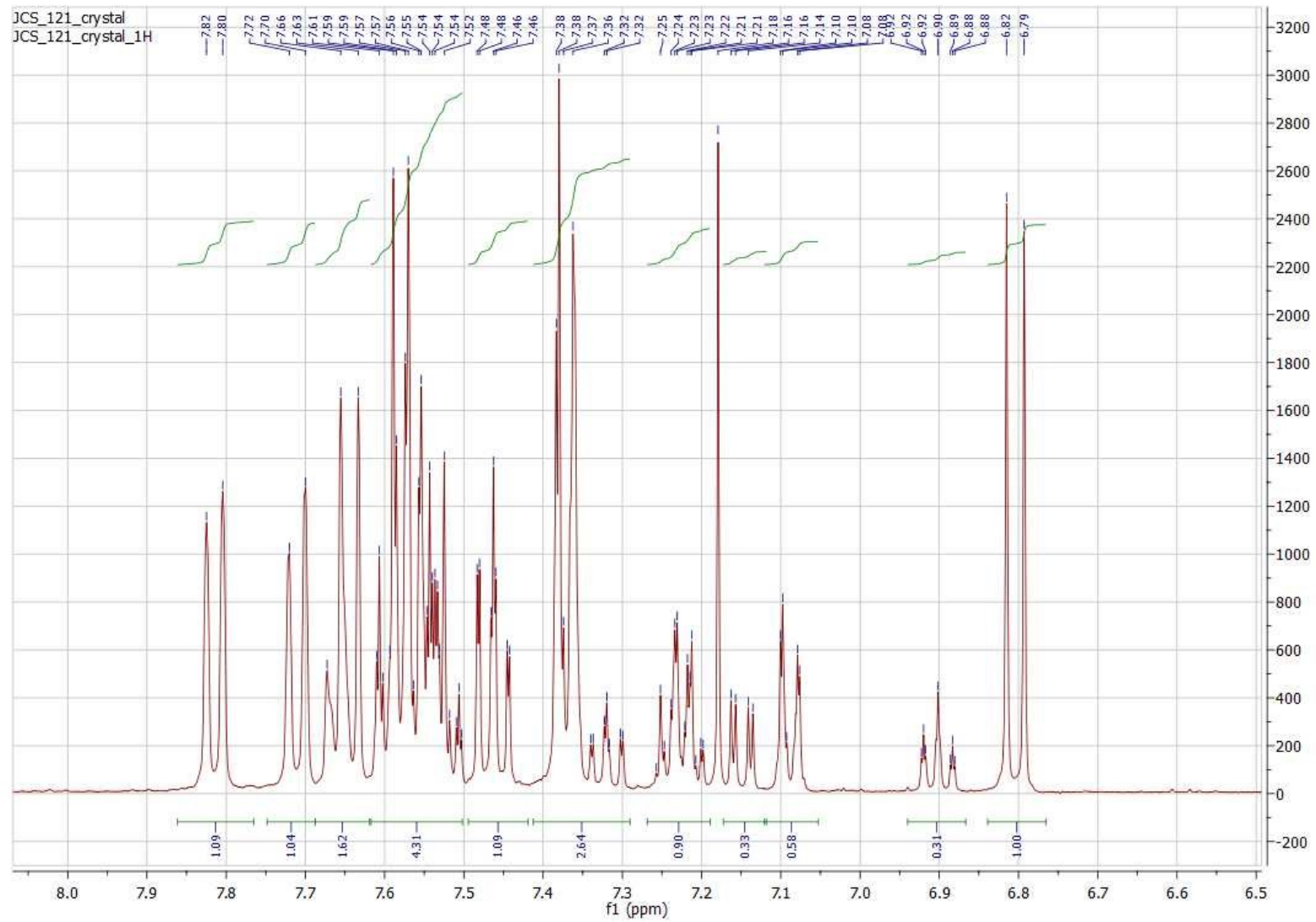


Figure S30. ^1H NMR (in CDCl_3) spectrum of $\text{C}_{17}\text{H}_{11}\text{NS}_2$ (**2h**)

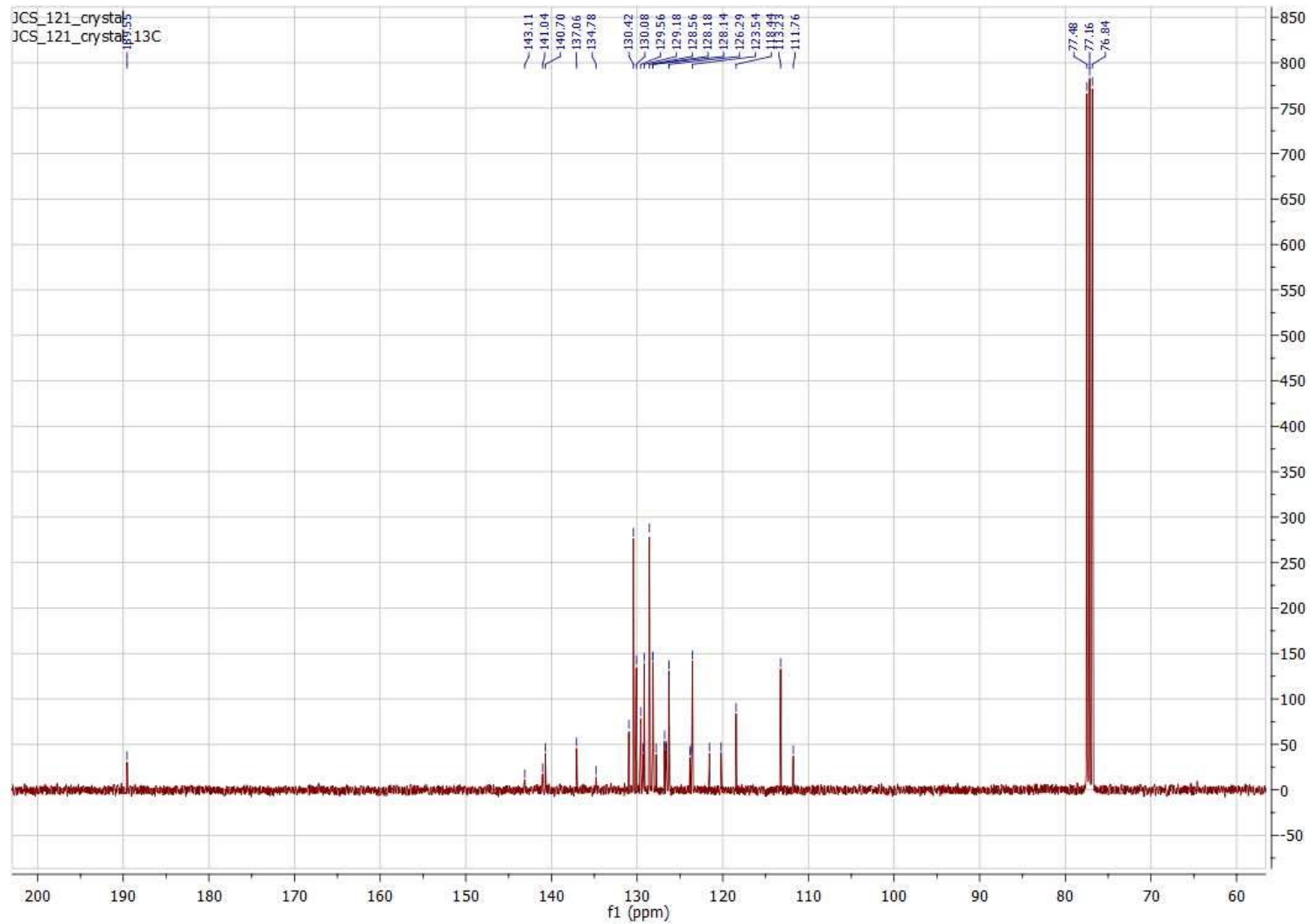


Figure S31. ^{13}C NMR (in CDCl_3) spectrum of $\text{C}_{17}\text{H}_{11}\text{NS}_2$ (**2h**)

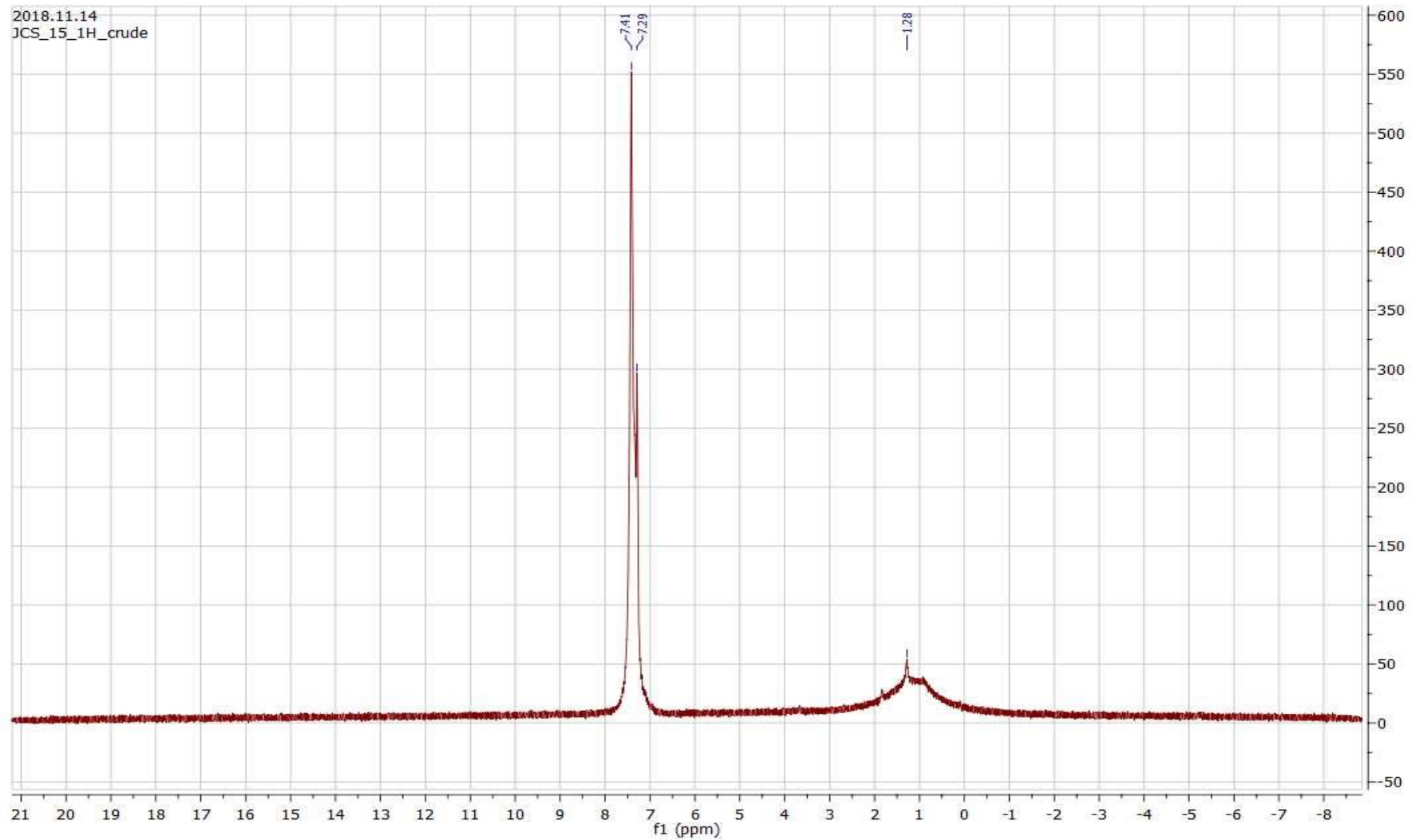


Figure S32. ^1H NMR (in CDCl_3) spectrum of $\text{Co}[\text{S}_2\text{CNPh}_2]_3$ (**3a**)

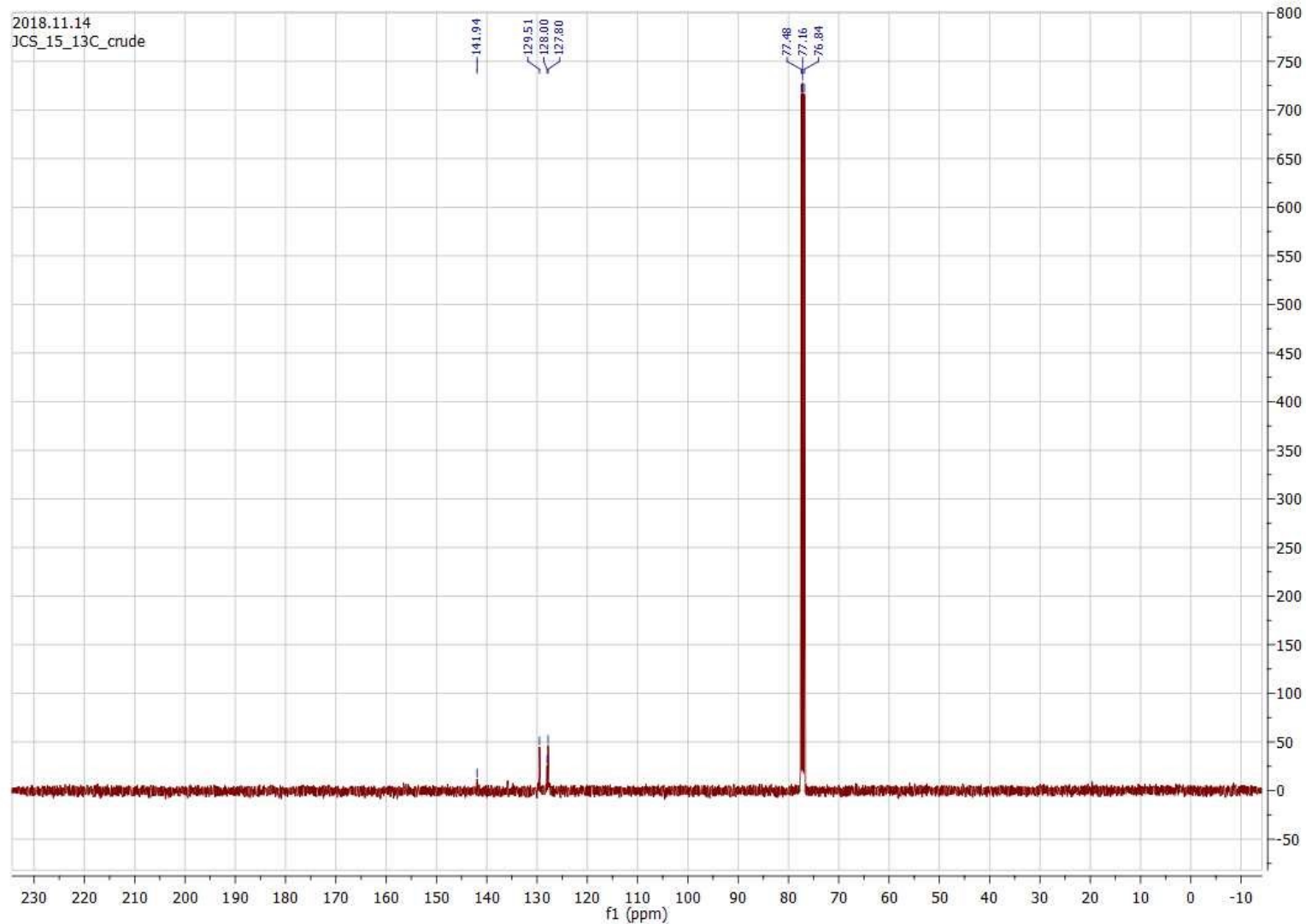


Figure S33. ^{13}C NMR (in CDCl_3) spectrum of $\text{Co}[\text{S}_2\text{CNPh}_2]_3$ (**3a**)

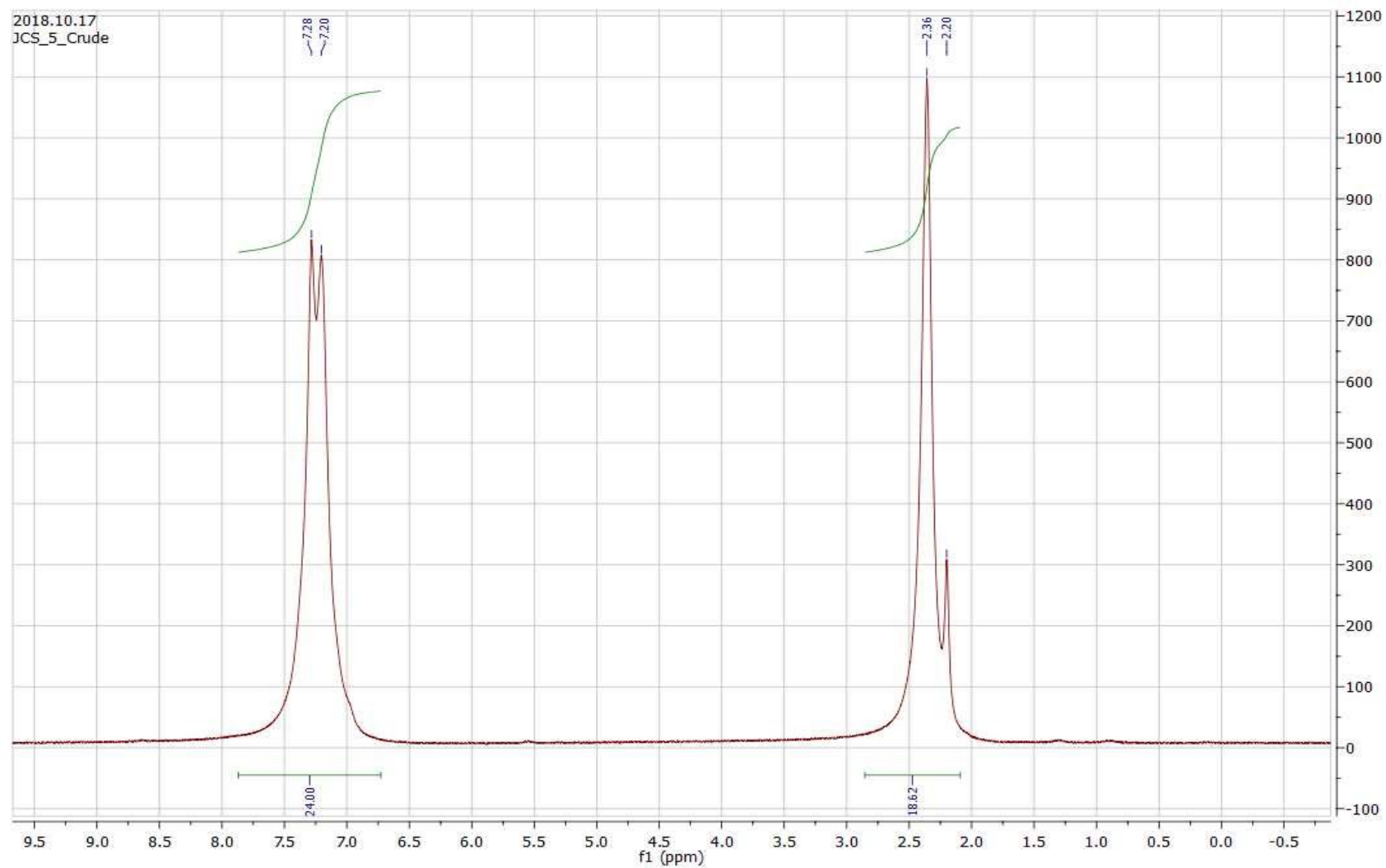


Figure S34. ^1H NMR (in CDCl_3) spectrum of $\text{Co}[\text{S}_2\text{CN}(\text{p-tolyl})_2]_3$ (**3b**)

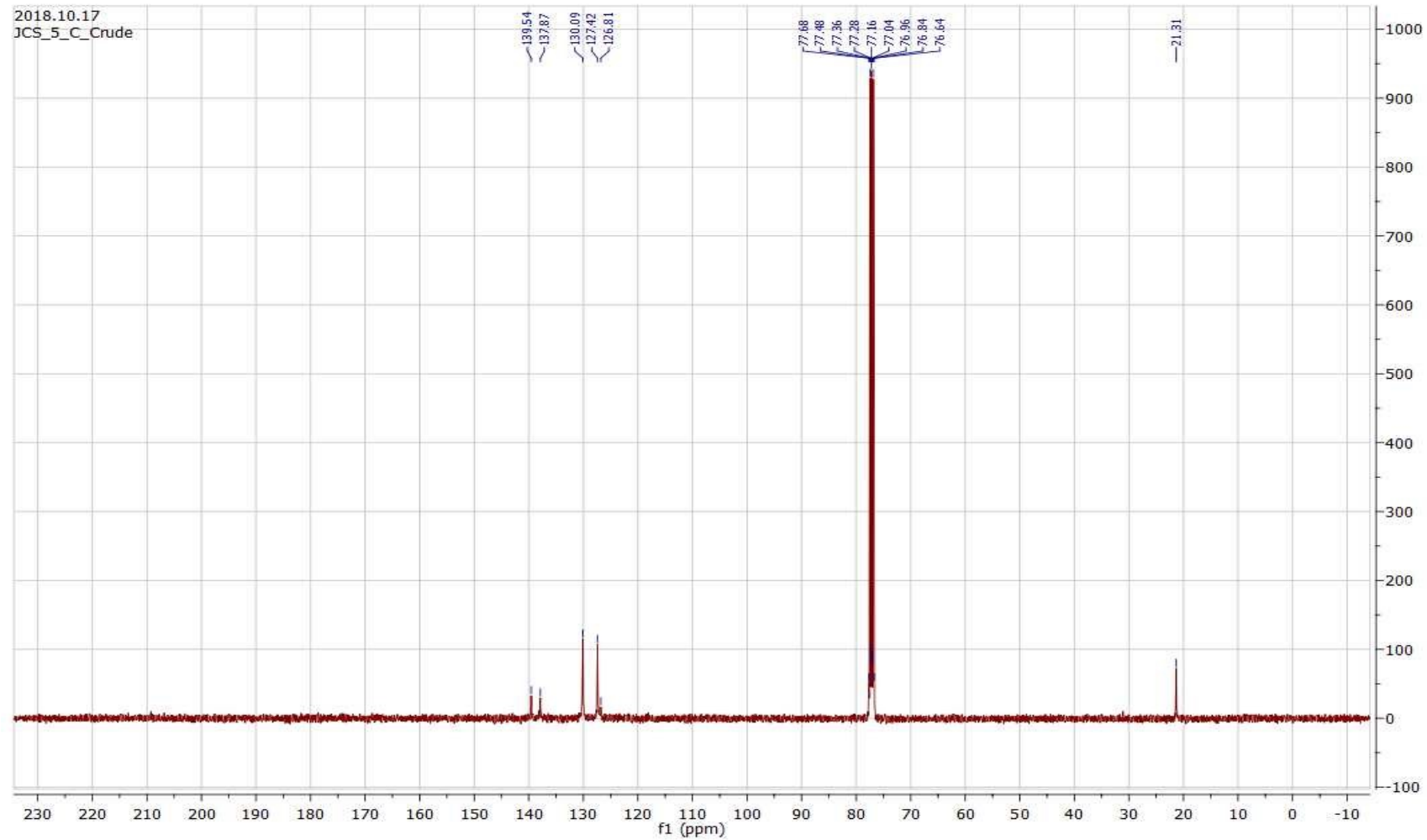


Figure S35. ^{13}C NMR (in CDCl_3) spectrum of $\text{Co}[\text{S}_2\text{CN}(\text{p-tolyl})_2]_3$ (**3b**)

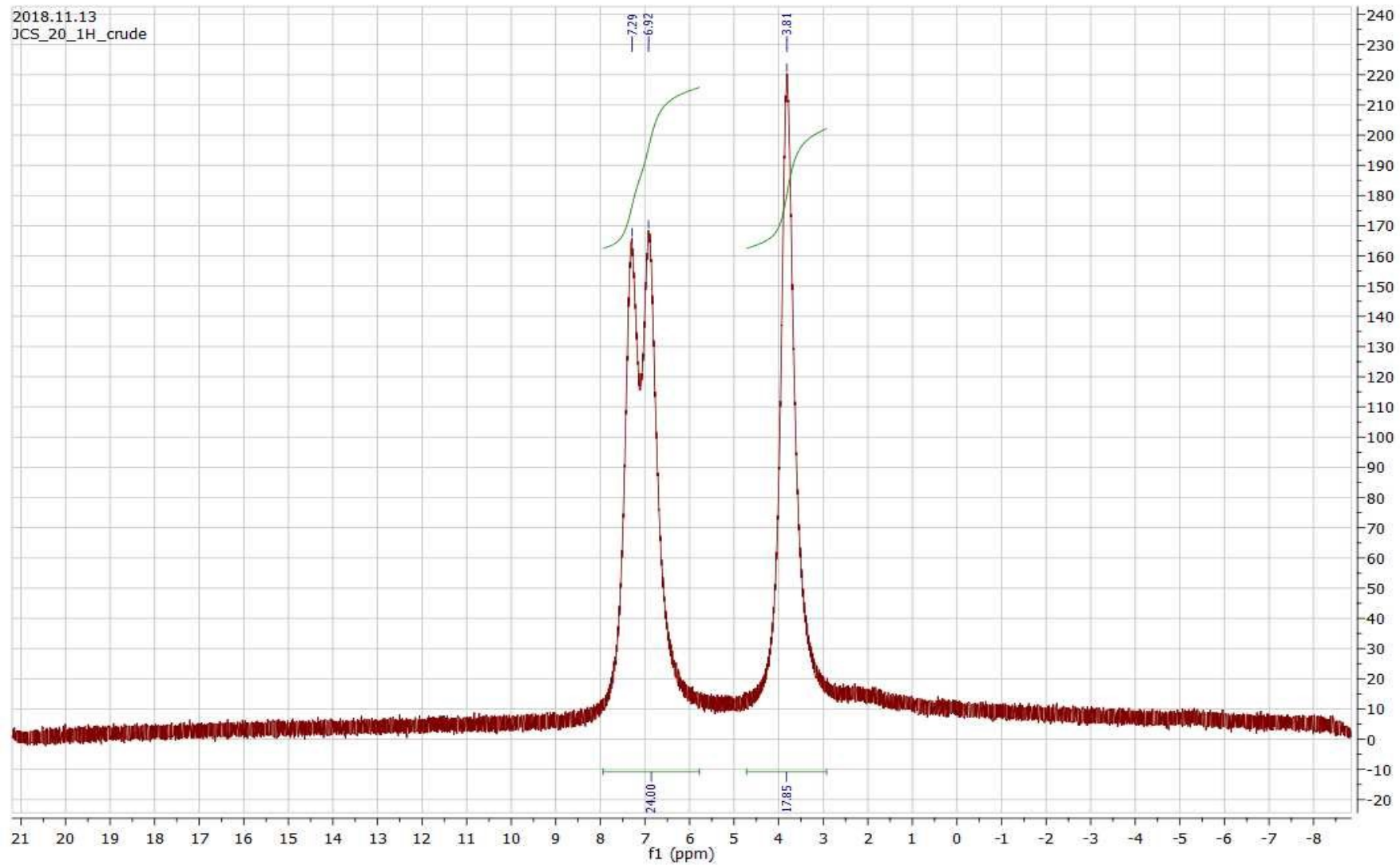


Figure S36. ^1H NMR (in CDCl_3) spectrum of $\text{Co}[\text{S}_2\text{CN}(\text{p-anisyl})_2]_3$ (**3c**)

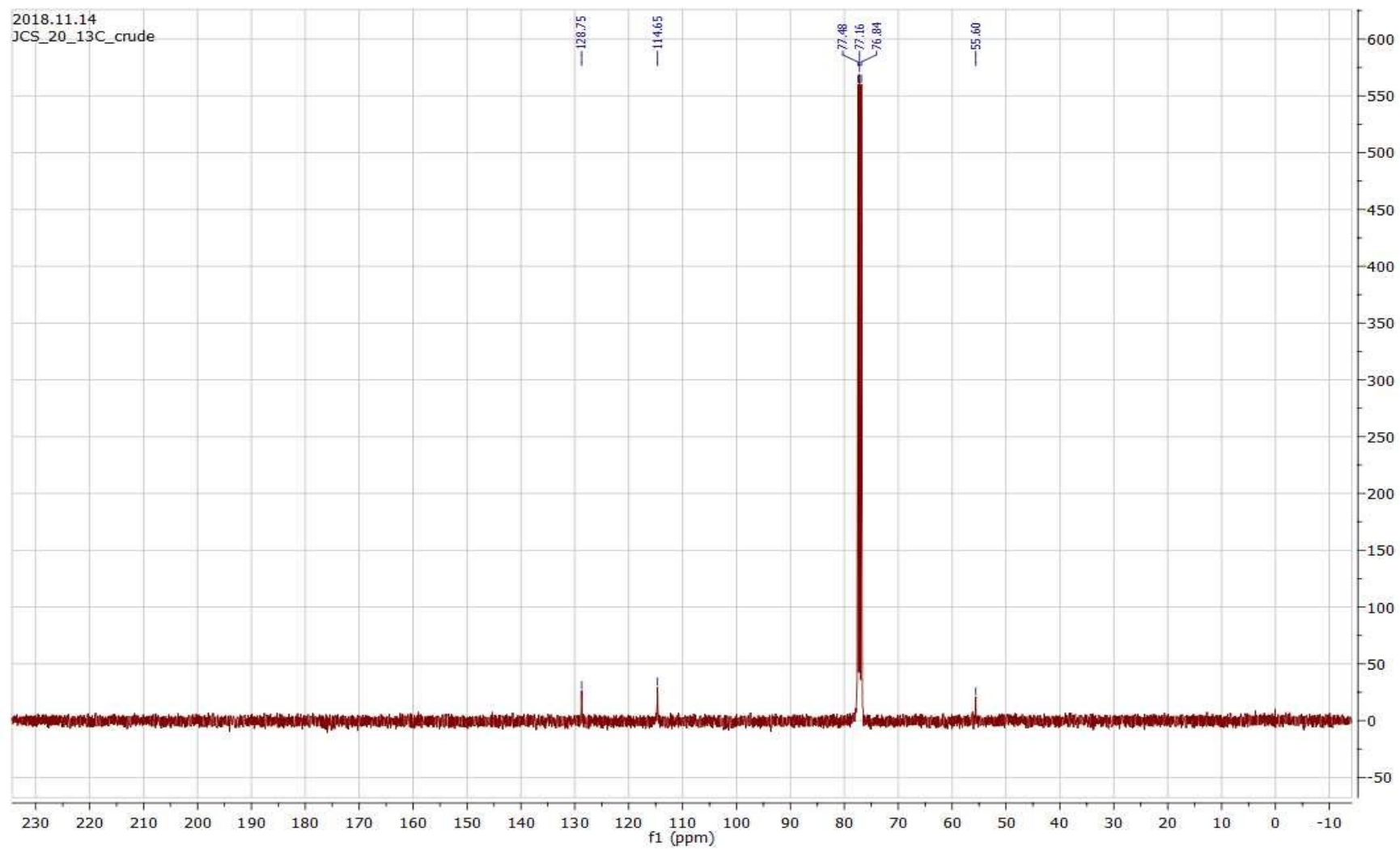


Figure S37. ¹H NMR (in CDCl₃) spectrum of Co[S₂CN(p-anisyl)₂]₃ (**3c**)

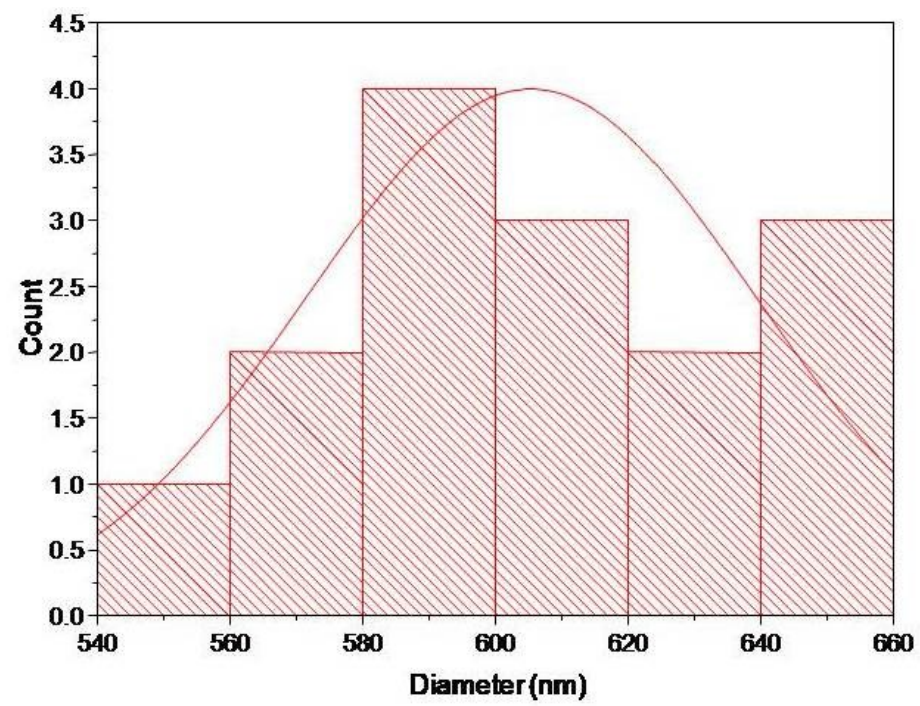


Figure S38. Histogram for nanosphere produced from **3b** by HI