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Elemental sulfur as a trigger and reagent in cyclization of γ-amino acetylenic ketones to 1,2-dihydro-3*H*-pyrrole-3-thiones

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All reactions were carried out under an argon atmosphere. Potassium hydroxide and elemental sulfur are commercial reagents (Aldrich, Acros Organics). Amino acetylenic ketones **1a-f,h,j,k** were prepared from propargylic amines and acyl chlorides as previously described.[S1]

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometers (400.13 and 100.62 MHz, respectively) in $CDCl_3$ solutions and referenced to HMDS (^{1}H, ^{13}C). The assignment of signals in ^{1}H spectra was performed using 2D homonuclear correlation method COSY. Resonance signals of ^{13}C were assigned with application of 2D heteronuclear correlation methods HSQC and HMBC. FT-IR spectra were obtained with a Varian 3100 FT-IR spectrometer. The C, H, N microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The Cl ans S contents were determined by the combustion method.

The preparation of 1,2-dihydro-3*H*-pyrrole-3-thiones 2 from γ-amino acetylenic ketones 1, elemental sulfur and KOH·0.5H$_2$O. A suspension of elemental sulfur (35.2 mg, 1.1 mmol) and KOH·0.5H_2O (143 mg, 2.2 mmol) in EtOH (3 mL) was stirred under argon atmosphere at 50–55 °C for 4 h. Then, γ-amino acetylenic ketone **1a-k** (1.0 mmol) was added to the obtained suspension and the reaction mixture was stirred at 20–25 °C for 6–20 h. After completion of the reaction (TLC monitoring, eluent: toluene/Et_2O, 10:1), the solvent was removed under reduced pressure. The residue was purified by column chromatography on SiO_2 (eluent: toluene/Et_2O, 10:1), the proper fractions were concentrated *in vacuo* to obtain the corresponding 1,2-dihydro-3*H*-pyrrole-3-thione **2a-k**.

5-Cyclohexyl-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2a). Yield: 205 mg (59%); waxy product. The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{23}H_{25}NS$: C, 79.49; H, 7.25; N, 4.03; S, 9.23. Found: C, 79.63; H, 7.38; N, 3.82; S, 9.60.

2-Methyl-1,2,5-triphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2b). Yield: 256 mg (75%); crimson powder, mp 154–155 °C (reprecipitated from CCl_4 to hexane). The ^{1}H and

^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{23}H_{19}NS$: C, 80.90; H, 5.61; N, 4.10; S, 9.39. Found: C, 80.68; H, 5.58; N, 4.16; S, 9.58.

5-(Furan-2-yl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2c). Yield: 206 mg (62%); waxy product. The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{21}H_{17}NOS$: C, 76.10; H, 5.17; N, 4.23; S, 9.67. Found: C, 76.38; H, 5.11; N, 4.31; S, 9.84.

2-Methyl-1,2-diphenyl-5-(thiophen-2-yl)-1,2-dihydro-3*H*-pyrrole-3-thione (2d). Yield: 246 mg (71%); burgundy powder, mp 155–156 °C (reprecipitated from CCl_4 to hexane). The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{21}H_{17}NS_2$: C, 72.58; H, 4.93; N, 4.03; S, 18.46. Found: C, 72.24; H, 4.98; N, 4.00; S, 18.42.

5-(4-Chlorophenyl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2e). Yield: 229 mg (61%); dark red powder, mp 85–86 °C (reprecipitated from CCl_4 to hexane). The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{23}H_{18}ClNS$: C, 73.49; H, 4.83; Cl, 9.43; N, 3.73; S, 8.53. Found: C, 73.68; H, 4.77; Cl, 9.20; N, 3.68; S, 8.22.

5-(4-Ethylphenyl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2f). Yield: 269 mg (73%); red powder, mp 152–153 °C (reprecipitated from CCl_4 to hexane). The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{25}H_{23}NS$: C, 81.26; H, 6.27; N, 3.79; S, 8.68. Found: C, 81.29; H, 6.30; N, 3.76; S, 8.51.

5-(4-Methoxyphenyl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2g). Yield: 252 mg (68%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.75 (s, 3H, Me); 3.80 (s, 3H, MeO); 6.65 (br.d, 2H, H_o, PhN, ^{3}J = 7.7 Hz); 6.68 (s, 1H, H-4, pyrrolethione); 6.80–6.83 (m, 2H, H-3,5, PhC-5); 7.12–7.16 (m, 2H, H_m, PhN); 7.17–7.21 (m, 1H, H_p, PhN); 7.30–7.38 (m, 7H, H-2,6, PhC-5; $H_{o,m,p}$, PhC-2). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 24.9 (Me); 55.5 (MeO); 86.6 (C-2, pyrrolethione); 114.4 (C-3,5, PhC-5); 120.4 (C-4, pyrrolethione); 121.7 (C-1, PhC-5); 126.4 (C_o, PhC-2); 127.5 (C_o, PhN); 128.3 (C_p, PhN); 128.4 (C_p, PhC-2); 128.8 (C_m, PhC-2); 129.2 (C_m, PhN); 131.3 (C-2,6, PhC-5); 139.3 (C_i, PhN); 139.9 (C_i, PhC-2); 162.2 (C-4, PhC-5); 172.0 (C-5, pyrrolethione); 223.7 (C=S). IR (film): ν = 3059, 2930, 2850, 1606, 1576, 1493, 1478, 1449, 1404, 1351, 1299, 1259, 1212, 1180, 1142, 1119, 1093, 1074, 1027, 1003, 911, 856, 838, 804, 796, 777, 760, 733, 725, 697, 657, 636, 593, 558, 540 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NOS$: C, 77.60; H, 5.70; N, 3.77; S, 8.63. Found: C, 77.45; H, 5.78; N, 3.71; S, 8.25.

2,2-Dimethyl-1-(naphthalen-1-yl)-5-phenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2i). Yield: 200 mg (61%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.32, 1.71 (s, 6H, Me); 6.73 (s, 1H, H-4, pyrrolethione); 7.08–7.12 (m, 2H, H_m, PhC-5); 7.19–7.23 (m, 1H, H_p, PhC-5); 7.33–7.35 (m, 2H, H_o, PhC-5); 7.35–7.43 (m, 2H, H-3,6, napht); 7.51–7.58 (m, 3H, H-2,7,8,

napht); 7.81 (d, 1H, H-4, napht, ^3J = 8.3 Hz); 7.88 (dd, 1H, H-5, napht, ^3J = 7.2 Hz, ^4J = 2.2 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 26.0, 28.9 (Me); 84.3 (C-2, pyrrolethione); 119.5 (C-4, pyrrolethione); 123.4 (C-2, napht); 125.2 (C-8, napht); 126.7 (C-3, napht); 127.2 (C-7, napht); 127.8 (C-5, napht); 128.3 (C_m, PhC-5); 128.5 (C_o, PhC-5); 126.6 (C-4, napht); 129.7 (C-6, napht); 130.2 (C-9, napht); 131.3 (C_p, PhC-5); 131.4 (C-10, napht); 134.6 (C-1, napht); 135.0 (C_i, PhC-5); 172.7 (C-5, pyrrolethione); 223.9 (C=S). IR (film): ν = 3058, 2924, 2851, 1519, 1469, 1424, 1395, 1352, 1284, 1256, 1191, 1157, 1119, 1074, 1053, 1020, 1001, 964, 939, 911, 871, 858, 803, 776, 766, 731, 693, 647, 568, 548, 534, 508 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.25; S, 9.73. Found: C, 80.42; H, 5.75; N, 4.31; S, 9.45.

1-Phenyl-2-(thiophen-2-yl)-1-azaspiro[4.5]dec-2-ene-4-thione (2j). Yield: 224 mg (66%); waxy product. The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{20}H_{20}NS_2$: C, 70.77; H, 6.20; N, 4.14; S, 18.79. Found: C, 70.55; H, 6.28; N, 4.10; S, 18.89.

5-Isopropyl-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (2k). Yield: 141 mg (46%); waxy product. The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S2] data. Anal. Calcd for $C_{20}H_{21}NS$: C, 78.13; H, 6.88; N, 4.56; S, 10.43. Found: C, 78.34; H, 6.98; N, 4.43; S, 10.21.

Synthesis of γ-amino acetylenic ketones 1g,i. To a solution of propargylic amine (2.0 mmol) and acyl chloride (2.0 mmol) in toluene (5 mL), CuI (0.016 g, 0.08 mmol), $PdCl_2$ (0.006 g, 0.04 mmol), Ph_3P (0.01 g, 0.04 mmol), and Et_3N (1 mL) were added. The mixture was stirred under an argon atmosphere at 40–45 °C for 3 h. After completion of the reaction (TLC monitoring, eluent: hexane/Et_2O, 2:1), the solvent was removed under reduced pressure, the residue was purified by flash-chromatography on basic Al_2O_3 (eluent: toluene), the proper fractions were concentrated *in vacuo* to give the corresponding amino acetylenic ketone **1g,i**.

1-(4-Methoxyphenyl)-4-phenyl-4-(phenylamino)pent-2-yn-1-one (1g). Yield: 624 mg (88%); grey powder, mp 140–141 °C (reprecipitated from CCl_4 to hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.94 (s, 3H, Me); 3.83 (s, 3H, MeO); 4.40 (br.s, 1H, NH); 6.62–6.64 (m, 2H, H_o, PhN); 6.75–6.77 (m, 2H, H-3,5, 4-$MeOC_6H_4$); 6.79–6.83 (m, 1H, H_p, PhN); 7.11–7.14 (m, 2H, H_m, PhN); 7.30–7.34 (m, 1H, H_p, PhC*); 7.37–7.41 (m, 2H, H_m, PhC*); 7.75–7.76 (m, 2H, H_o, PhC*); 7.77–7.79 (m, 2H, H-2,6, 4-$MeOC_6H_4$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 35.2 (Me); 55.5 (MeO); 56.6 (C*); 81.9 (≡<u>C</u>-C(O)); 95.8 (C*-<u>C</u>≡); 113.8 (C-3,5, 4-$MeOC_6H_4$); 116.3 (C_o, PhN); 119.1 (C_p, PhN); 125.4 (C_o, PhC*); 127.7 (C_p, PhC*); 128.8 (C_m, PhC*); 128.9 (C_m, PhN); 130.1 (C-1, 4-$MeOC_6H_4$); 132.1 (C-2,6, 4-$MeOC_6H_4$); 143.3 (C_i, PhC*); 145.2 (C_i, PhN); 164.4 (C-4, 4-$MeOC_6H_4$); 176.6 (C=O). IR (film): ν = 3058, 2976, 2925, 2841, 2207, 1641, 1634, 1600, 1574, 1511, 1505, 1463, 1447, 1422, 1368, 1316, 1304, 1259, 1218, 1180, 1164, 1105, 1075, 1145,

1026, 996, 912, 877, 844, 802, 749, 741, 699, 648, 630, 621, 598, 501 cm^{-1}. Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.25; H, 5.90; N, 3.98.

4-Methyl-4-(naphthalen-1-ylamino)-1-phenylpent-2-yn-1-one (1i). Yield: 450 mg (72%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.89 (s, 6H, Me); 4.45 (br.s, 1H, NH); 7.33–7.37 (m, 2H, H_m); 7.37–7.41 (m, 3H, H-2,3,4, napht); 7.47–7.49 (m, 2H, H-6,7, napht); 7.52–7.55 (m, 1H, H_p); 7.83–7.85 (m, 1H, H-5, napht); 7.88–7.91 (m, 1H, H-8, napht); 7.96–7.98 (m, 2H, H_o). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 30.1 (C(Me)$_2$); 48.8 (C*); 81.2 (≡C-C(O)); 98.1 (C*-C≡); 110.8 (C-2, napht); 119.8 (C-4, napht); 120.3 (C-8, napht); 125.3 (C-7, napht); 125.5 (C-9, napht); 125.9 (C-6, napht); 126.1 (C-3, napht); 128.6 (C_m); 128.9 (C-5, napht); 129.7 (C_o); 134.1 (C_p); 134.6 (C-10, napht); 136.7 (C_i); 139.9 (C-1, napht); 178.1 (C=O). IR (film): ν = 3059, 2984, 2934, 2867, 2208, 1644, 1597, 1580, 1526, 1483, 1463, 1450, 1408, 1383, 1365, 1346, 1314, 1264, 1222, 1174, 1150, 1098, 1055, 1023, 1001, 969, 937, 909, 868, 850, 787, 772, 732, 702, 682, 647, 617, 610, 579, 566, 421 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.05; H, 6.16; N, 4.52.

References

S1. (*a*) P. A. Volkov, K. O. Khrapova, I. A. Bidusenko, A. A. Telezhkin, E. Yu. Schmidt, A. I. Albanov and B. A. Trofimov, *Russ. Chem. Bull.*, 2022, **71**, 1514; https://doi.org/10.1007/s11172-022-3558-3; (*b*) P. A. Volkov, K. O. Khrapova, A. A. Telezhkin, I. A. Bidusenko, E. Yu. Schmidt, A. I. Albanov and B. A. Trofimov, *Adv. Synth. Catal.*, 2023, **365**, 53; https://doi.org/10.1002/adsc.202201179.

S2. P. A. Volkov, K. O. Khrapova, E. M. Vyi, A. A. Telezhkin, I. A. Bidusenko, A. I. Albanov, E. Yu. Schmidt and B. A. Trofimov, *Org. Biomol. Chem.*, 2023, **21**, 6903; https://doi.org/10.1039/D3OB01061A.

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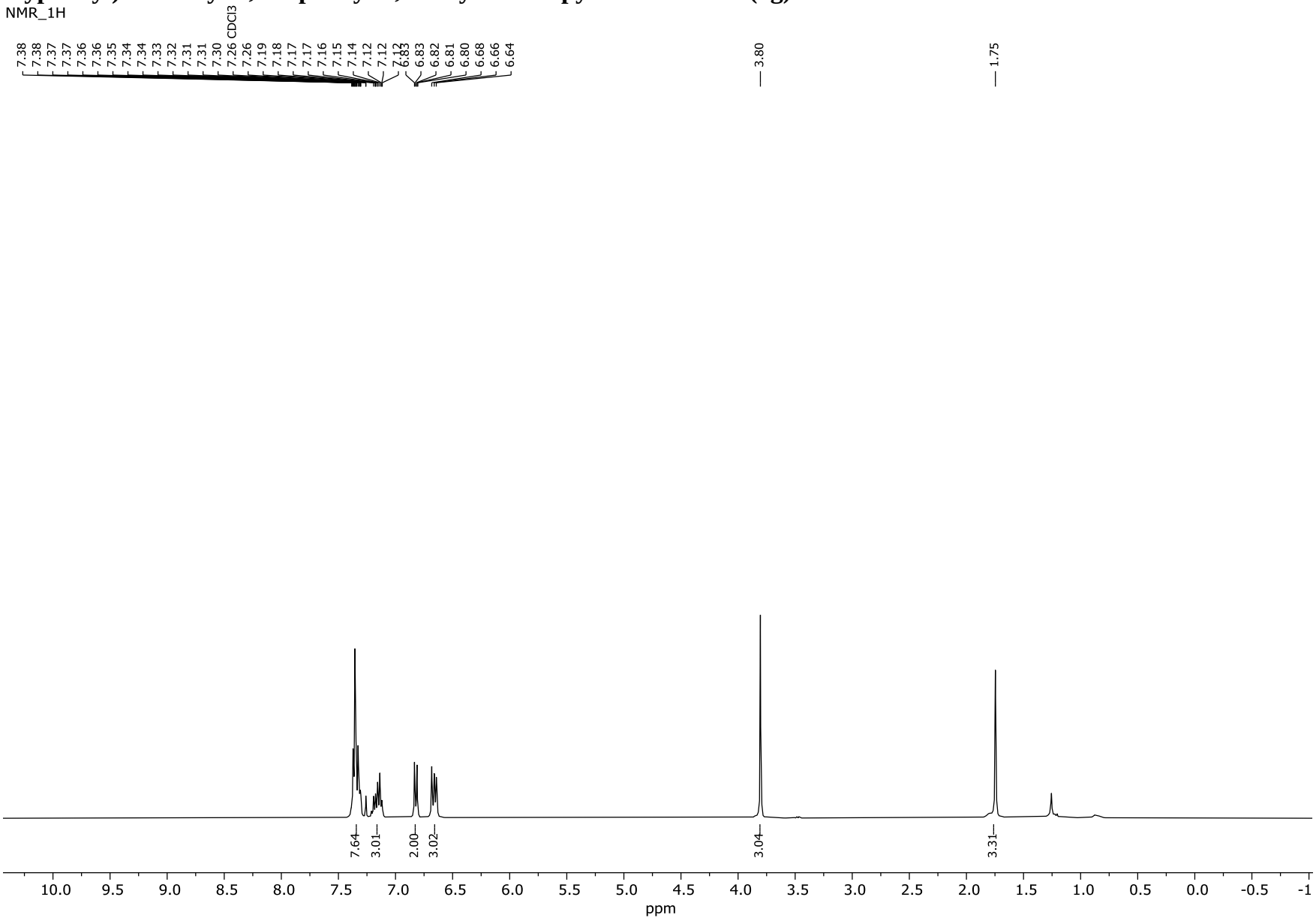

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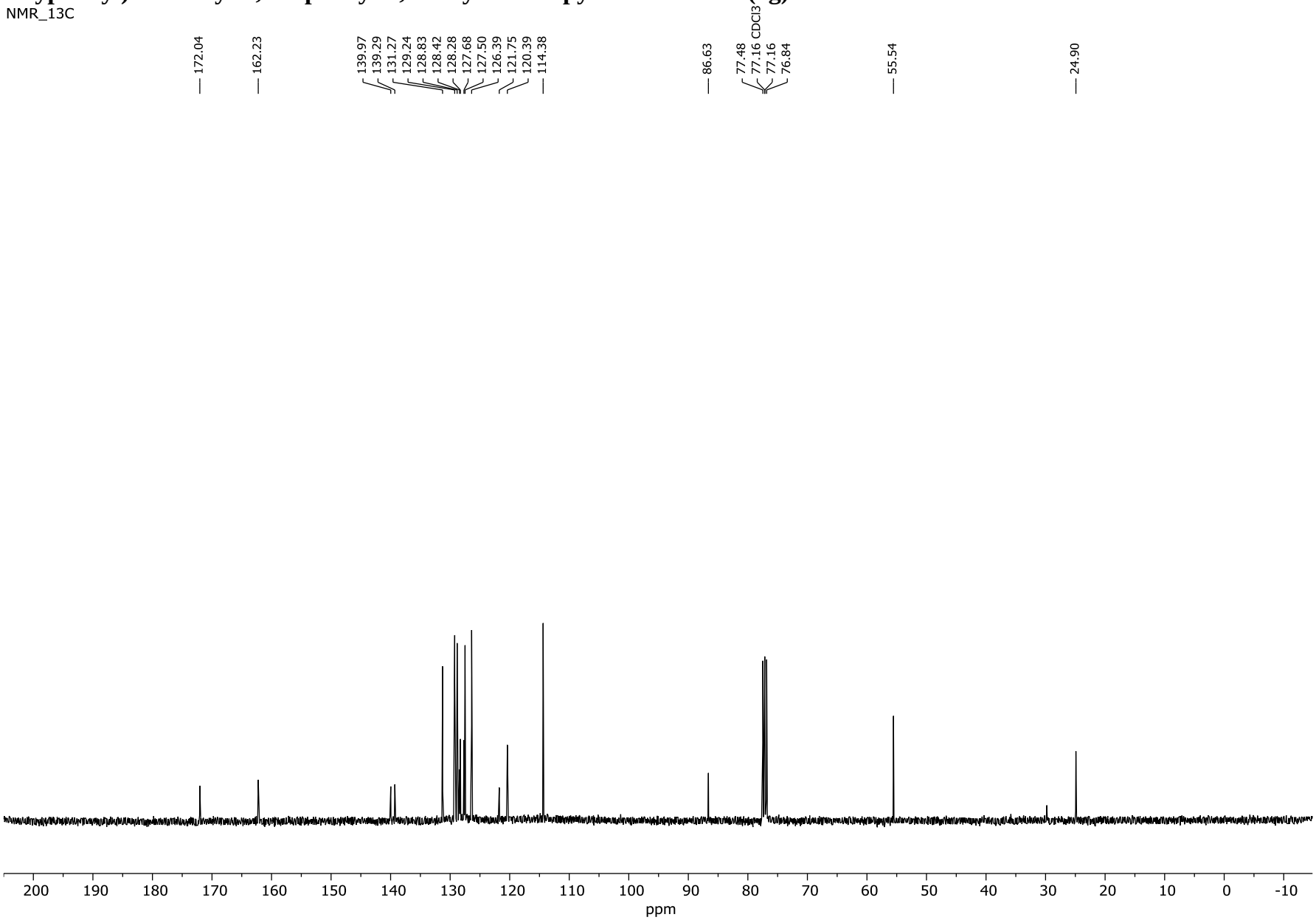

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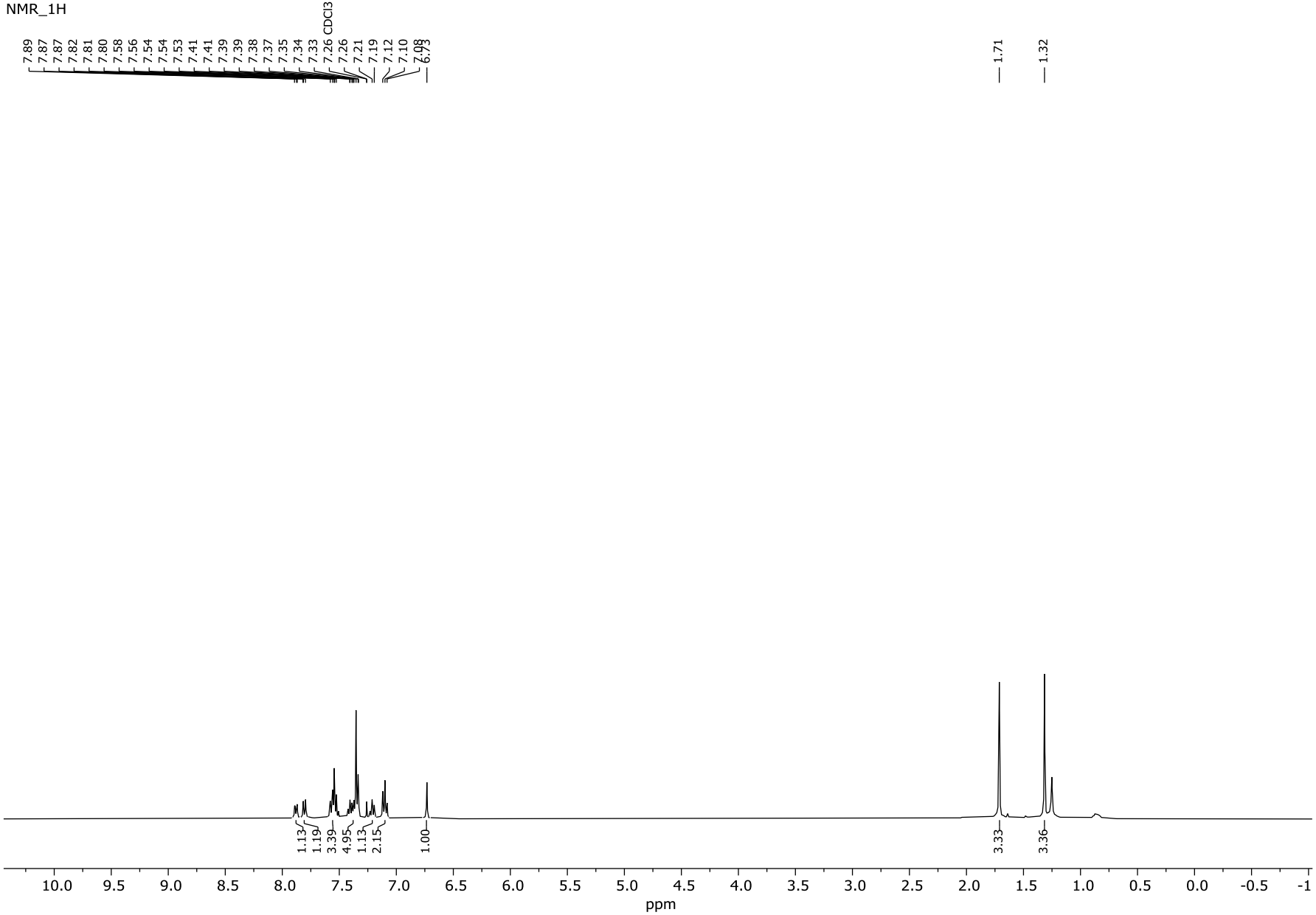

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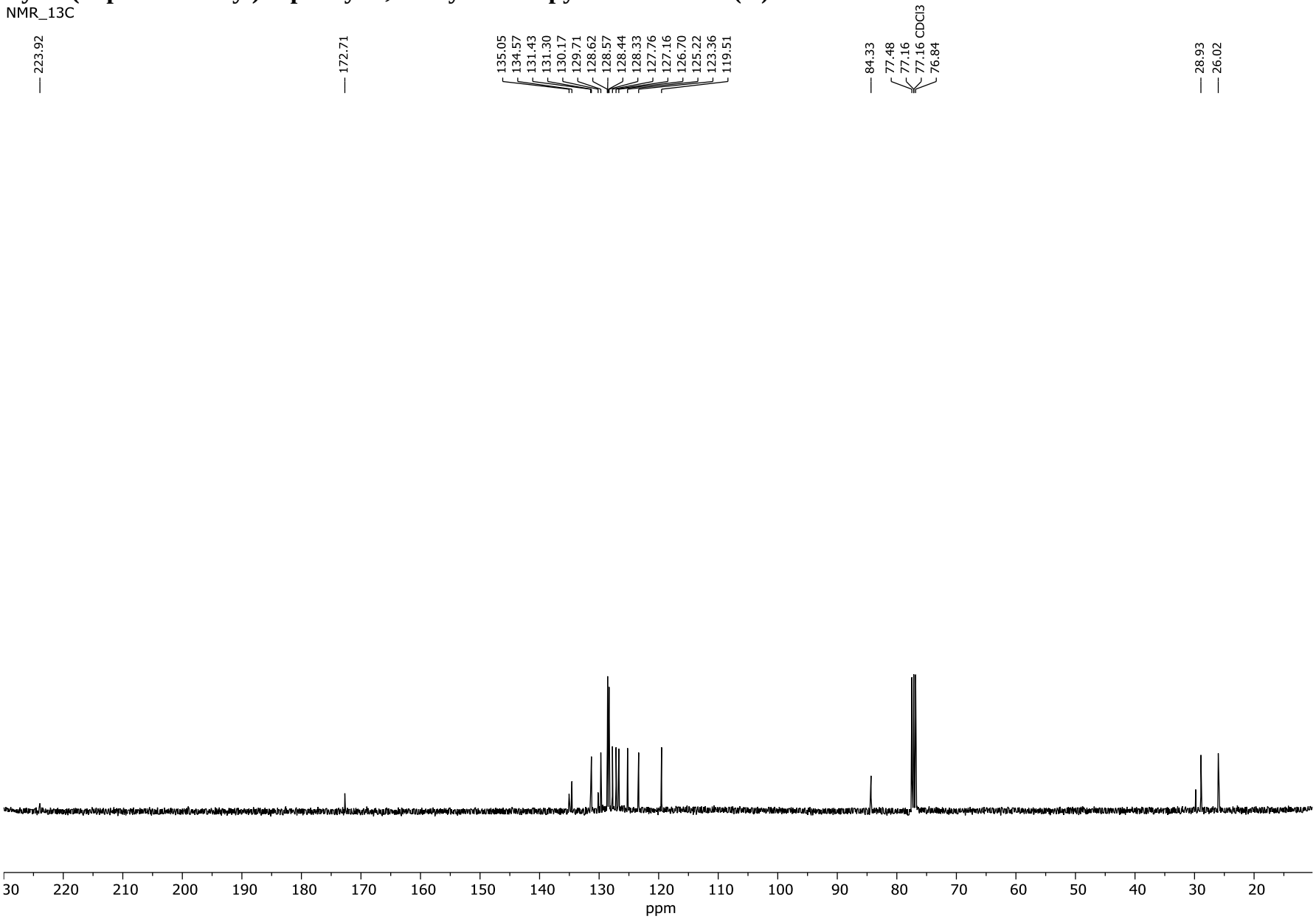

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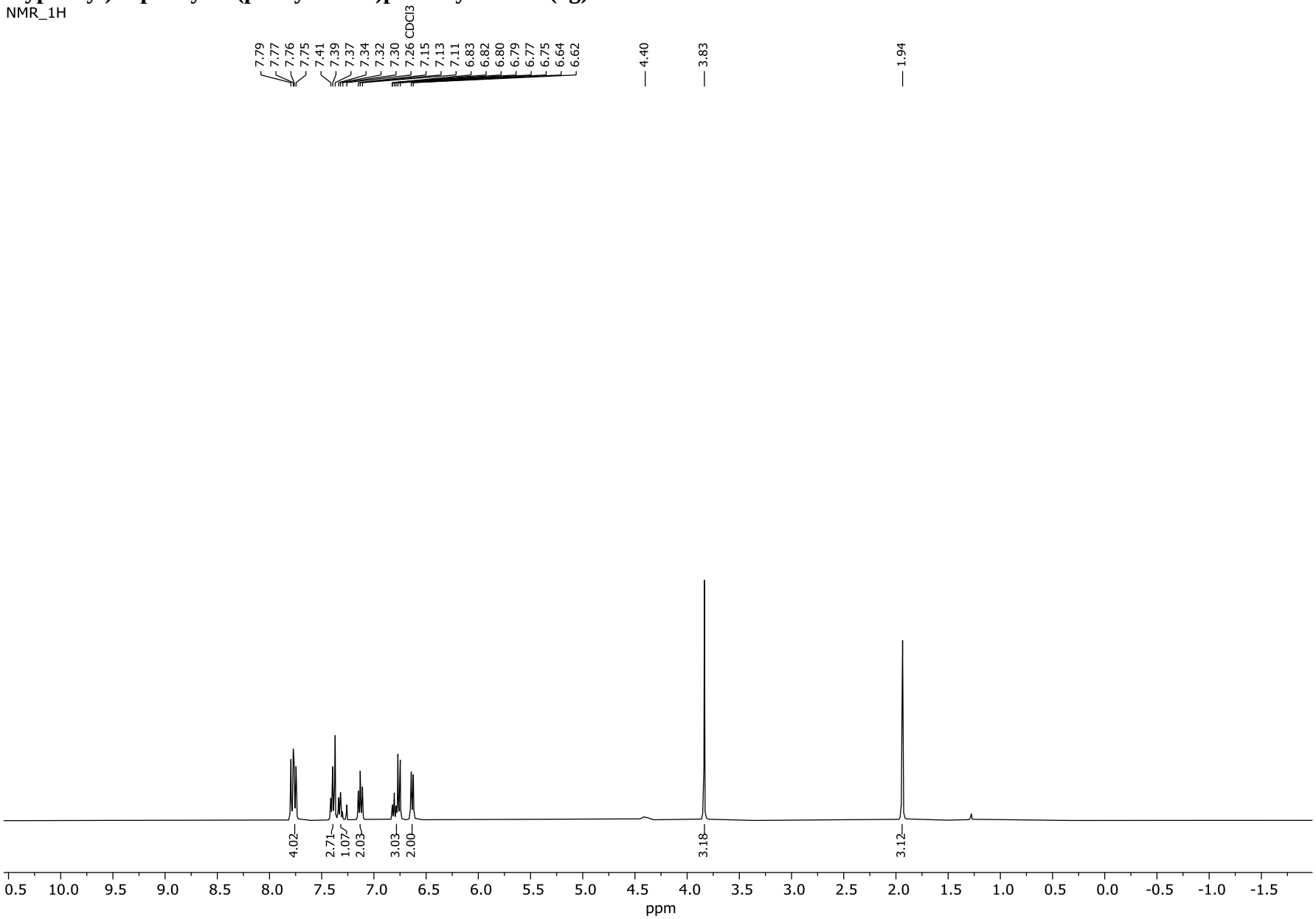

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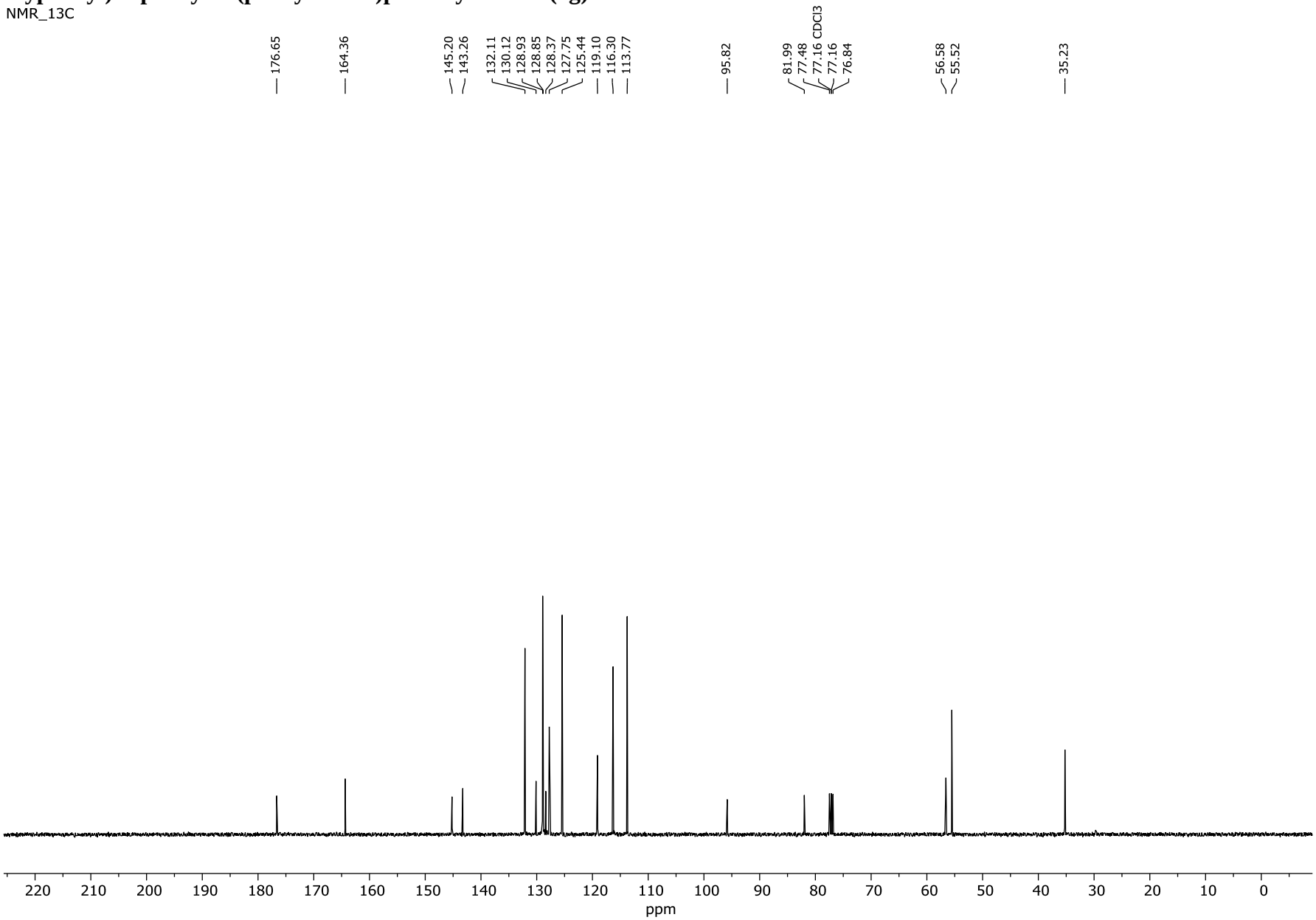

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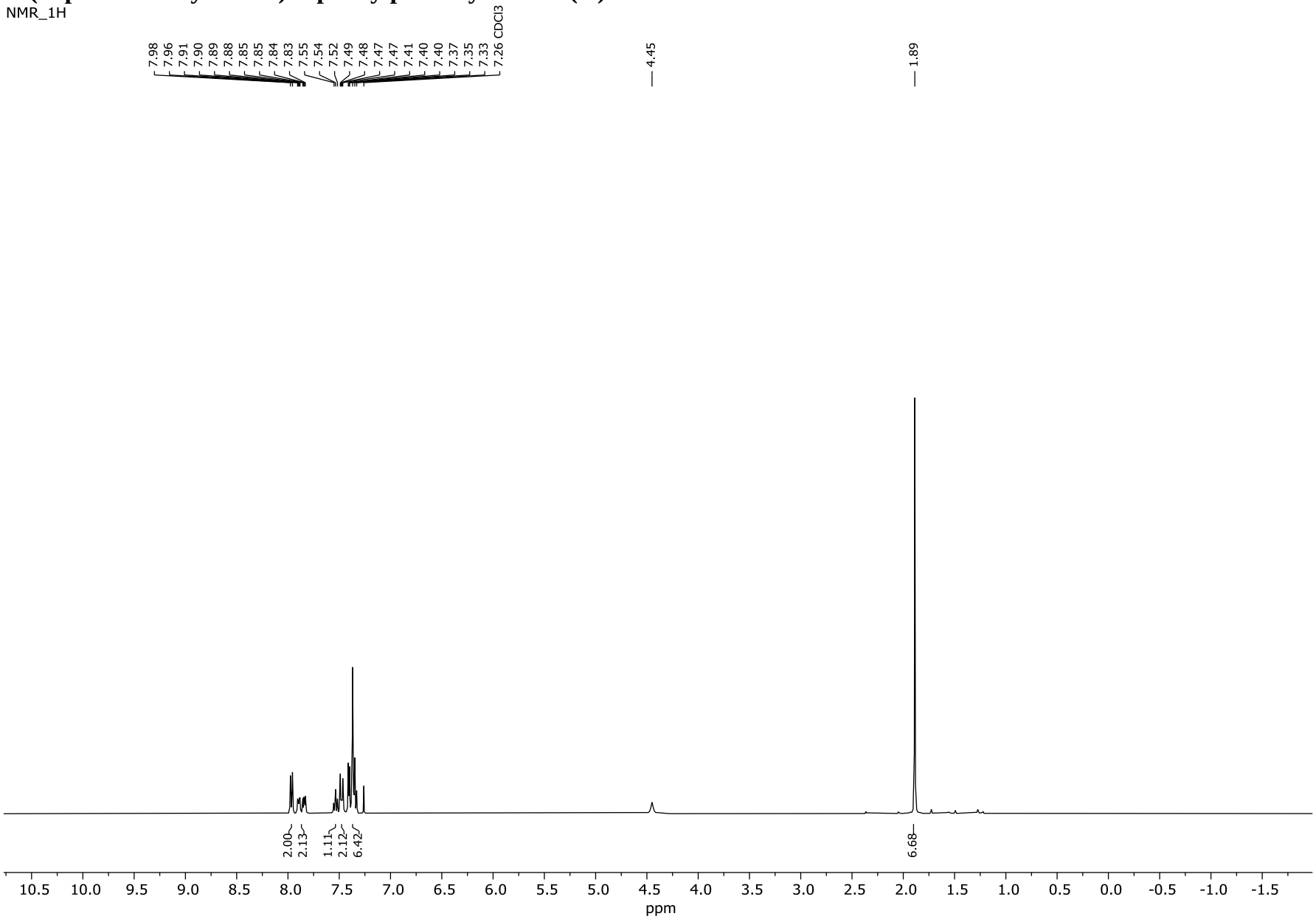

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