

SUPPORTING INFORMATION

A novel dual-nano assisted synthesis of symmetrical disulfides from aryl/alkyl halides

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Characterization of Synthesized Compounds, 2a-2u:

Diphenyl disulfide¹⁻⁵ (2a)

White solid; yield: 125 mg (94%); mp 60-61°C (lit. 57-59°C); Anal. calcd for C₁₂H₁₀S₂: C, 66.01; H, 4.62. Found: C, 66.05; H, 4.57. ¹H NMR (400 MHz, CDCl₃): δ 7.17-7.04 (m, 6H, Ph), 7.43-7.32 (m, 4H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ 127.3, 127.6, 129.0, 137.0. HRMS (EI, m/z) for [M]⁺ calcd 218.02; Found: 218.0555.

Dibenzyl disulfide³ (2b)

White solid; yield: 137 mg (92%); mp 69-72°C; Anal. calcd for C₁₄H₁₄S₂: C, 68.25; H, 5.73; Found: C, 68.20; H, 5.72. ¹H NMR (400 MHz, CDCl₃): δ 7.23-7.24 (d, *J* = 6.72 Hz, 4H, Ph), 7.27-7.29 (t, *J* = 7.32 Hz, 2H, Ph), 7.30-7.32 (t, *J* = 7.32 Hz, 4H, Ph), 3.5989 (s, 4H, CH₂). ¹³C NMR (400 MHz, CDCl₃): δ 43.30 (2C), 127.49 (2C), 128.55 (4H), 129.49 (4H), 137.43 (2H).

Bis-(2-aminophenyl) disulfide^{1-2,5} (2c)

Light yellow solid; yield: 138 mg (91%); mp 95-96°C (lit. 93-94°C); Anal. calcd for C₁₂H₁₂N₂S₂: C, 58.03; H, 4.87; Found: C, 57.98; H, 4.88. ¹H NMR (400 MHz, CDCl₃): 4.24 (br s, 4H, NH₂), 6.45-6.52 (m, 2H, Ph), 6.57-6.61 (m, 2H, Ph), 6.96-7.00 (m, 4H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ 115.0, 117.8, 119.1, 131.6, 136.3, 148.2.

Bis-(2-methylphenyl) disulfide² (2d)

White solid; yield: 141 mg (95%); mp 43-45°C; Anal. calcd for C₁₄H₁₄S₂: C, 68.25; H, 5.73; Found: C, 68.20; H, 5.71. ¹H NMR (400 MHz, CDCl₃): δ 2.42 (s, 6H, CH₃), 7.08-7.12 (m, 4H, Ph), 7.17-7.21 (m, 4H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ 47.6, 119.9, 123.1, 128.1, 129.2, 132.0, 136.0.

Bis-(4-methylphenyl) disulfide²⁻⁶ (2e)

Off white solid; yield: 146 mg (>98%); mp 43-45°C; Anal. calcd for C₁₄H₁₄S₂: C, 68.25; H, 5.73; Found: C, 68.23; H, 5.77. ¹H NMR (400 MHz, CDCl₃): 2.30 (s, 6H, CH₃), 7.01-7.12 (m, 4H, Ph), 7.32-7.35 (m, 4H, Ph). ¹³C NMR (100 MHz, CDCl₃): δ 21.4, 128.8, 129.7, 133.3, 137.6. HRMS (EI, m/z) for [M]⁺ calcd 246.39; Found: 246.0897

Bis-(4-*tert*-butyl) disulfide⁴ (2f)

Colorless crystals; yield: 180 mg (90%); mp 87-89°C; Anal. calcd for C₂₀H₂₆S₂: C, 72.67; H, 7.93; Found: C, 72.70; H, 7.90. ¹H NMR (400 MHz, CDCl₃): 1.28 (s, 18H, CH₃), 7.32 (d, *J* = 8.4 Hz, 4H,

Ph), 7.45 (d, $J = 8.4$ Hz, 4H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 31.6, 35.0, 127.5, 128.2, 134.0, 151.6.

Bis-(3-methoxyphenyl) disulfide⁶ (2g)

White solid; yield: 151 mg (90%); mp 105-107°C; Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}_2$: C, 60.40; H, 5.07; Found: C, 60.37; H, 5.10. ^1H NMR (400 MHz, CDCl_3): 3.76 (s, 6H, OCH_3), 6.89-6.94 (m, 2H, Ph), 7.08-7.15 (m, 4H, Ph), 7.25-7.33 (m, 2H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 55.8, 115.0, 127.4, 131.8, 134.0, 134.4, 160.6.

Bis-(4-methoxyphenyl) disulfide^{1,3-6} (2h)

White solid; yield: 160 mg (95%); mp 38-40°C (lit. 41-43°C); Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}_2$: C, 60.40; H, 5.07; Found: C, 60.30; H, 5.09. ^1H NMR (400 MHz, CDCl_3): δ 3.73 (s, 6H, OCH_3), 6.89 (d, $J = 8.8$ Hz, 4H, Ph), 7.31 (d, $J = 8.7$ Hz, 4H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 133.0, 128.6, 114.5, 54.8.

Bis(4-acetylphenyl) disulfide⁷ (2i)

Yellow oil; yield: 161 mg (88%); Anal. calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}_2$: C, 63.55; H, 4.67; Found: C, 63.52; H, 4.59. ^1H NMR (400 MHz, CDCl_3): 2.54 (s, 6H, CH_3CO), 7.52 (d, $J = 8.4$ Hz, 4H, Ph), 7.83 (d, $J = 8.5$ Hz, 4H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 26.6, 125.8, 130.1, 139.2, 143.4, 193.5.

Bis-(3-chlorophenyl) disulfide² (2j)

White solid; yield: 157 mg (91%); mp 81-83°C; Anal. calcd for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{S}_2$: C, 50.18; H, 2.18; Found: C, 50.15; H, 2.20. ^1H NMR (400 MHz, CDCl_3): 7.08-7.11 (m, 4H, Ph), 7.15-7.23 (m, 2H, Ph), 7.41-7.47 (m, 2H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 125.1, 127.2, 128.2, 131.8, 136.1, 138.4.

Bis-(4-chlorophenyl) disulfide^{1-4,6} (2k)

White solid; yield: 153 mg (89%); mp 73-75°C (lit. 72-74°C); Anal. calcd for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{S}_2$: C, 50.18; H, 2.18; Found: C, 50.23; H, 2.88. ^1H NMR (400 MHz, CDCl_3): δ 7.16-7.23 (m, 4H, Ph), 7.35-7.44 (m, 4H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 129.3, 129.6, 133.7, 136.0.

Bis-(4-fluorophenyl) disulfide⁵ (2l)

Off white solid; yield: 122 mg (80%); Anal. calcd for $\text{C}_{12}\text{H}_8\text{F}_2\text{S}_2$: C, 56.67; H, 3.17; Found: C, 56.69; H, 3.15. ^1H NMR (400 MHz, CDCl_3): δ 6.51-6.57 (m, 4H, Ph), 6.80-6.85 (m, 4H, Ph). ^{13}C NMR (100 MHz, CDCl_3): δ 116.4 (d, $J = 21.3$ Hz), 131.3 (d, $J = 8.6$ Hz), 132.5 (d, $J = 2.8$ Hz), 162.4 (d, $J = 244.2$ Hz).

Bis-(2-nitrophenyl) disulfide¹ (2m)

Yellow solid; yield: 155 mg (84%); mp 190-193°C; Anal. calcd for C₁₂H₈N₂O₄S₂: C, 46.74; H, 2.62; N, 9.09; Found: C, 46.71; H, 2.60; N, 9.08. ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.42 (t, *J* = 7.8 Hz, 2H), 7.57-7.60 (t, *J* = 7.8 Hz, 7.5 Hz, 2H), 7.84-7.86 (d, *J* = 8.3 Hz, 2H), 8.33-8.35 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (500 MHz, CDCl₃): δ 120.63 (2C), 124.99 (2C), 126.23 (2C), 131.22 (2C), 139.46 (2C), 150.15 (2C).

Bis-(4-nitrophenyl) disulfide¹ (2n)

Light yellow solid; yield: 160 mg (86%); mp 167-169°C (lit. 176-178 °C); Anal. calcd for C₁₂H₈N₂O₄S₂: C, 46.74; H, 2.62; N, 9.09; Found: C, 46.71; H, 2.60; N, 9.08. ¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, *J*=8.7 Hz, 4H, Ph), 8.17 (d, *J*=8.6 Hz, 4H, Ph), ¹³C NMR (500 MHz, CDCl₃): δ 123.158 (4C), 131.743 (4C), 141.989 (2C), 147.008 (2C).

Bis-(2,4-dinitrophenyl) disulfide¹ (2o)

Yellow powder; yield: 183 mg (76%); mp > 240 °C; Anal. calcd for C₁₂H₆N₄O₈S₂: C, 36.18; H, 1.52; N, 14.07; Found: C, 36.13; H, 1.55; N, 14.08. ¹H NMR (400 MHz, CDCl₃): δ 7.51-7.53 (d, *J* = 8.84 Hz, 2H, Ph), 8.39-8.41 (dd, *J* = 9.16 Hz, 2H, Ph), 9.0356 (s, 2H).

Bis-(2-naphthyl) disulfide^{2,5} (2p)

White solid; yield: 170 mg (88%); Anal. calcd for C₂₀H₁₄S₂: C, 75.43; H, 4.43; Found: C, 75.40; H, 4.42. ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.47 (t, *J* = 7.32 Hz, 4H), 7.60-7.63 (dd, *J* = 8.56 Hz, 2H), 7.72-7.74 (d, *J* = 9.16 Hz, 2H), 7.77-7.79 (d, *J* = 8.52 Hz, 4H), 7.98 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 125.77 (2C), 126.37 (2C), 126.65 (2C), 126.87 (2C), 127.59 (2C), 127.90 (2C), 129.11 (2C), 132.62 (2C), 133.59 (2C), 134.38 (2C).

Bis-(2-carboxyphenyl) disulfide (2q)

White solid; yield: 151 mg (82%); Anal. calcd for C₁₄H₁₀O₄S₂: C, 54.89; H, 3.29; Found: C, 54.92; H, 3.30. ¹H NMR (500 MHz, DMSO): δ 7.31-7.33 (t, *J* = 7.25 Hz, 2H), 7.53-7.56 (t, *J* = 7.52 Hz, 2H), 7.61-7.63 (d, *J* = 8.05 Hz, 2H), 8.01-8.03 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (500 MHz, DMSO): δ 123.379 (2C), 124.298 (2C), 126.484 (2C), 129.914 (2C), 131.556 (2C), 137.321 (2C), 165.958 (2C). HRMS (EI, *m/z*) for [M-OH]⁺ calcd 290.01; Found: 289.0426.

3,3'-dipyridyl disulfide⁷ (2s)

Yellow oil; yield: 114 mg (86%); Anal. calcd for $C_{10}H_8N_2S_2$: C, 54.52; H, 3.66; N, 12.72; Found: C, 54.62; H, 3.60; N, 12.71. 1H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 2H, py), 7.75-7.84 (m, 2H, py), 8.55-8.58 (m, 4H, py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.8, 127.2, 140.0, 149.3, 152.8.

5,5'-Dibromo-2,2'-dipyridyl disulfide⁸(2t)

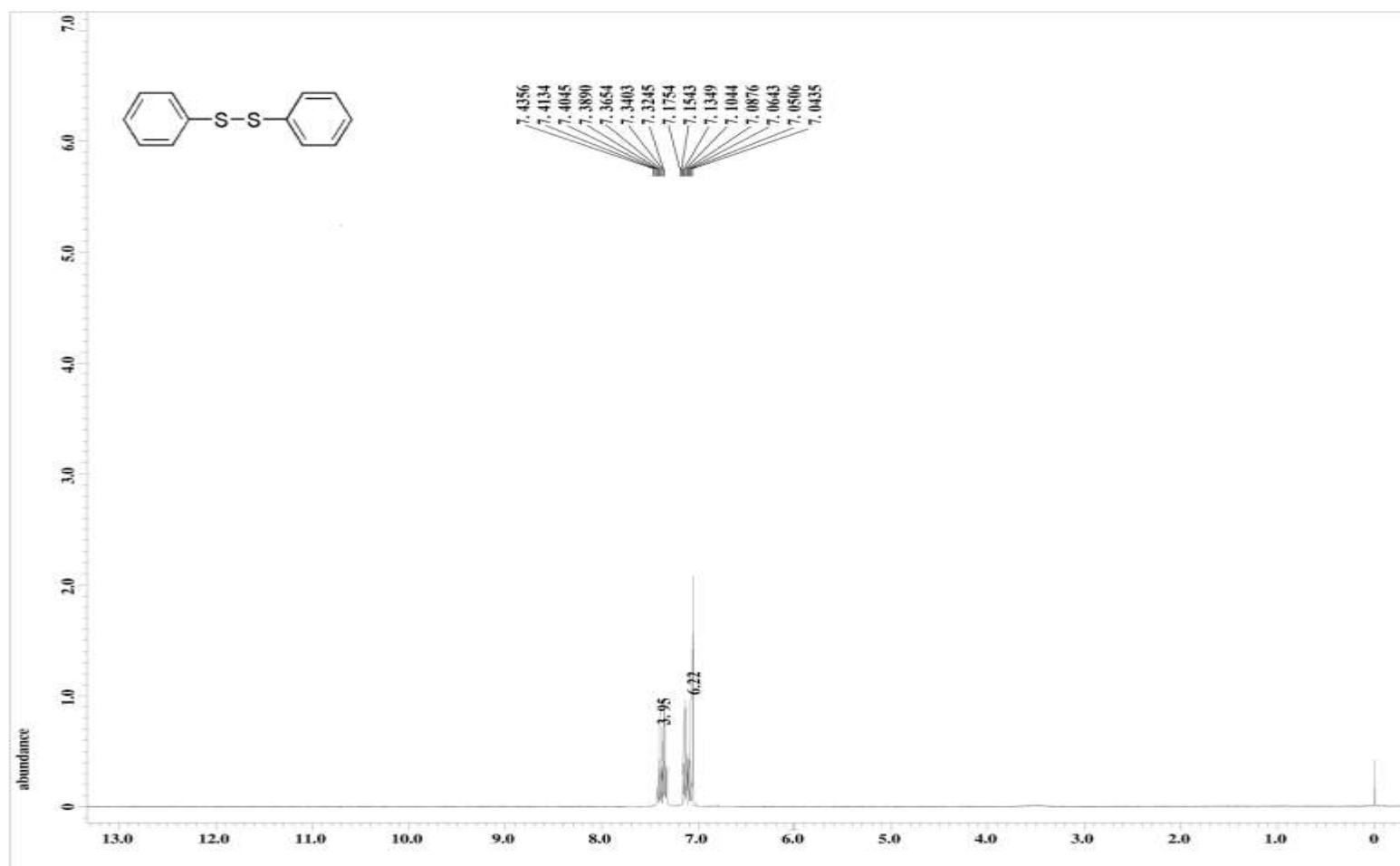
Colorless crystals; yield: 186 mg (82%); mp 84-86°C; Anal. calcd for $C_{10}H_6Br_2N_2S_2$: C, 31.77; H, 1.60; N, 7.41; Found: C, 31.73; H, 1.61; N 7.43. 1H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 9.4 2H, py), 7.64 (d, J = 9.6 2H, py), 8.45 (d, J = 14.5 2H, py). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.7, 121.5, 139.4, 150.2, 157.1.

Dicyclohexyl disulfide^{2,3} (2u)

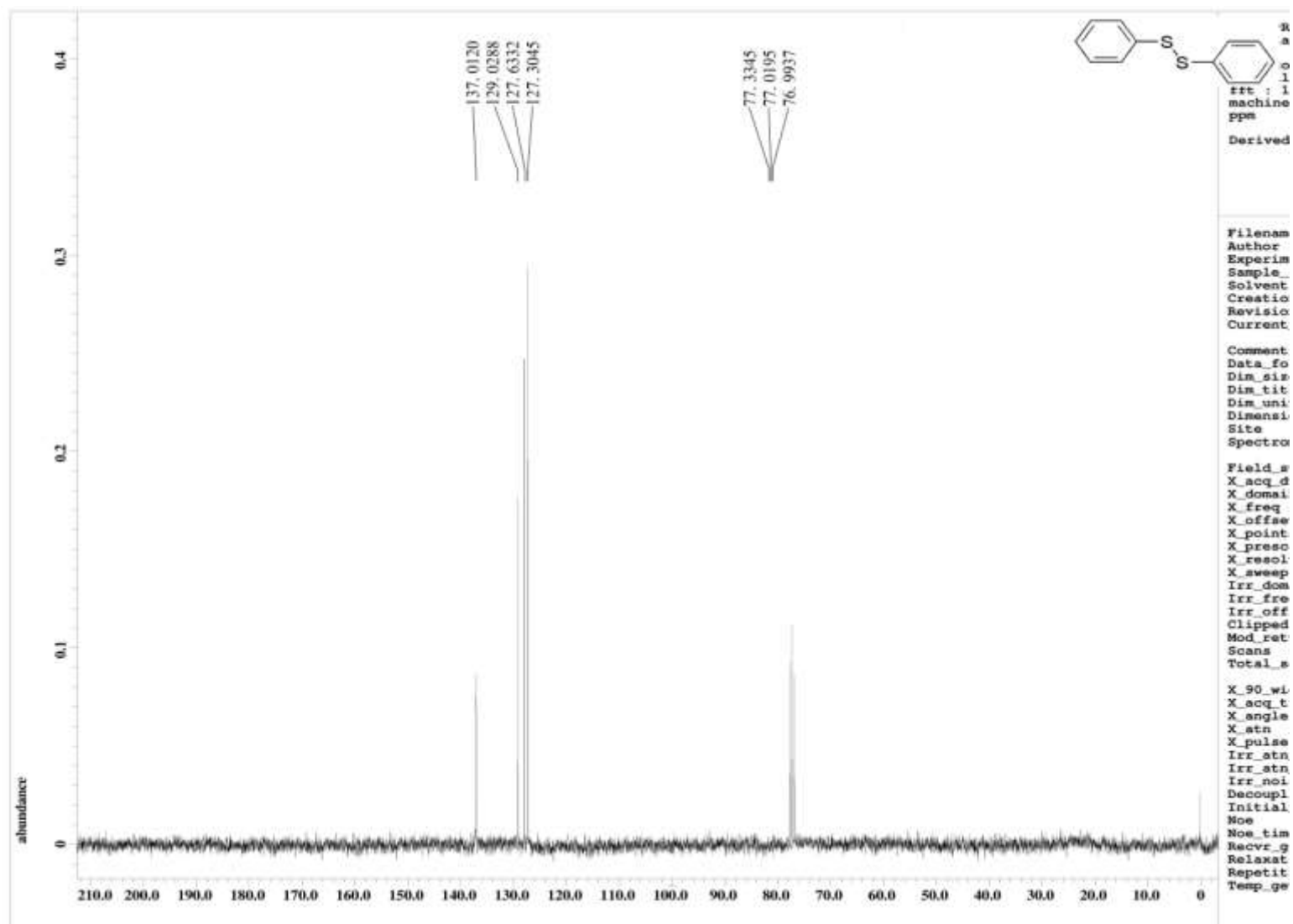
Colorless oil, yield: 123 mg (89%); Anal. calcd for $C_{12}H_{22}S_2$: C, 62.55; H, 9.62; Found: C, 62.58; H, 9.65. 1H NMR (400 MHz, $CDCl_3$): δ 1.25-1.28 (m, 10H), 1.69 (br s, 4H), 1.73 (br s, 2H), 2.03 (br s, 4H), 2.63-2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.8, 27.0, 33.3, 49.3.

References

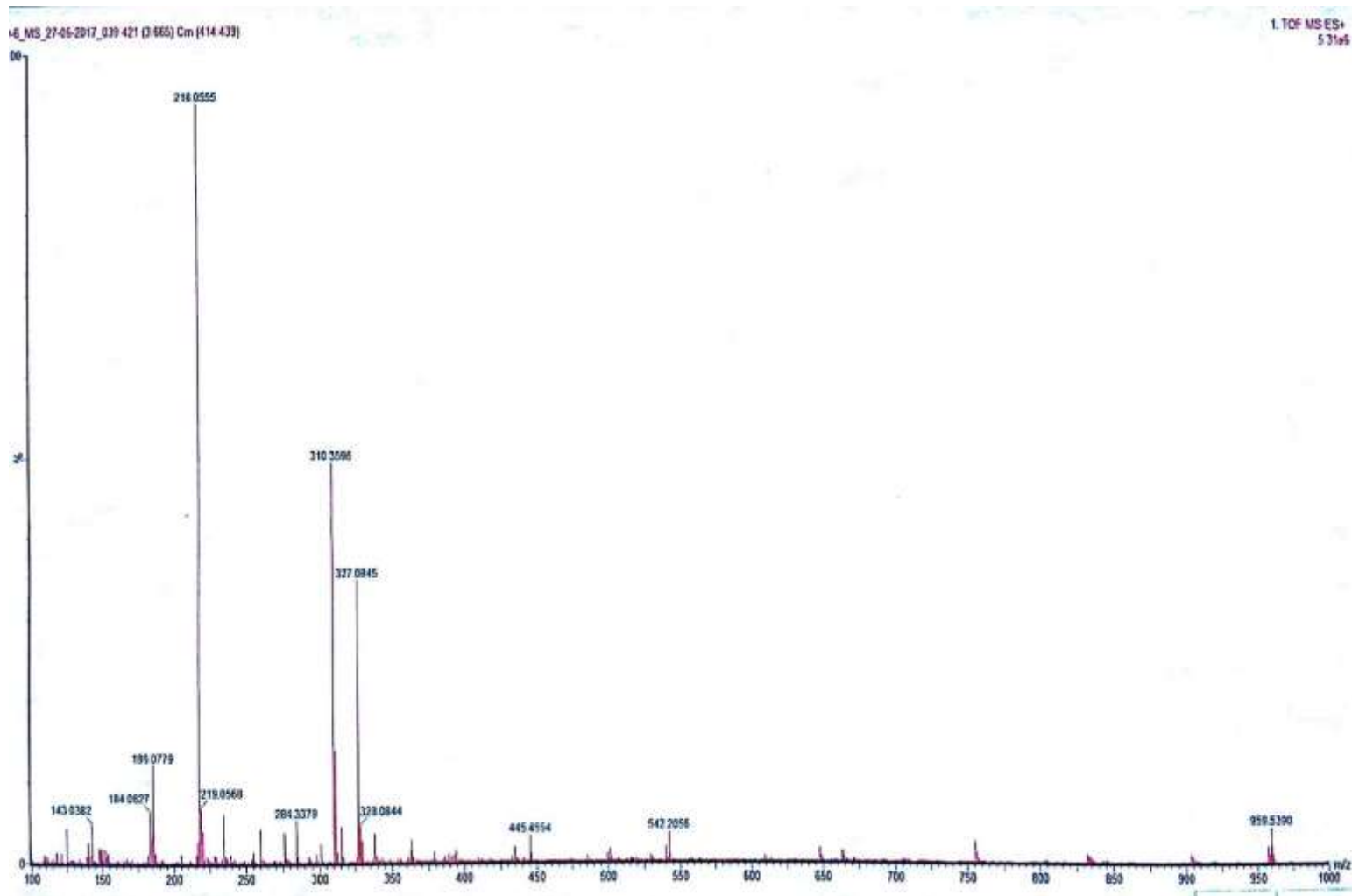
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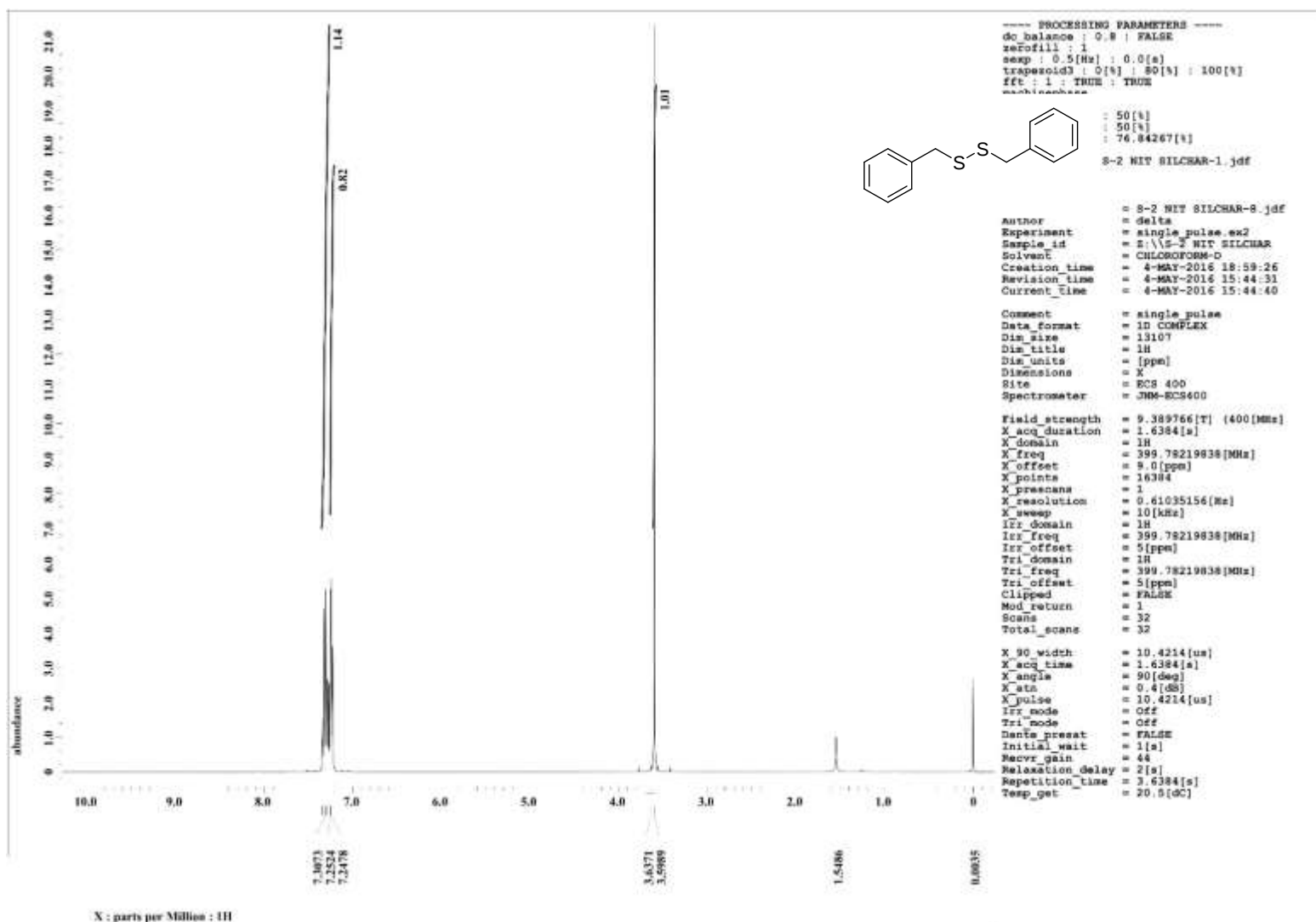
^1H NMR (400 MHz, CDCl_3) of Diphenyl disulfide **2a**



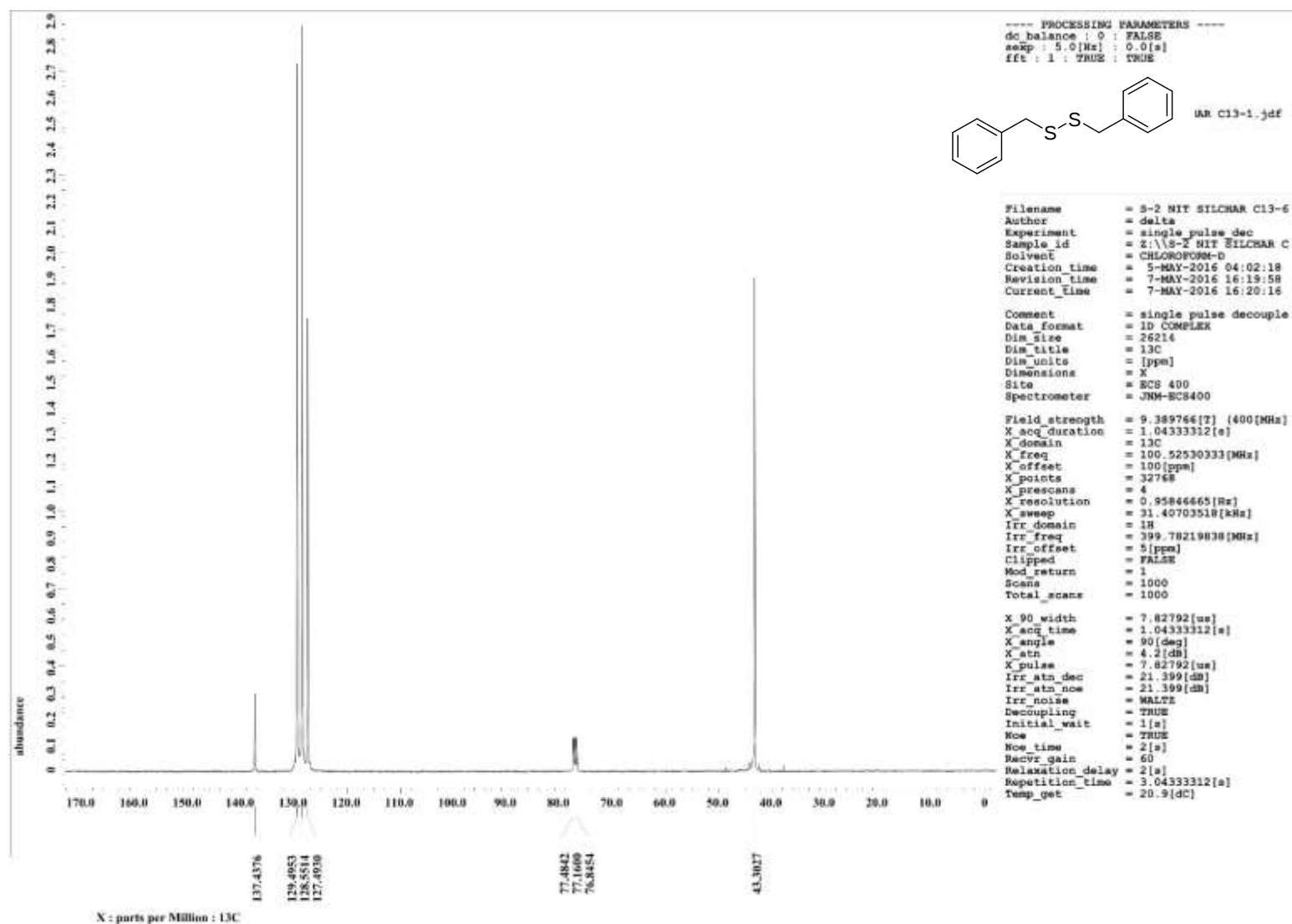
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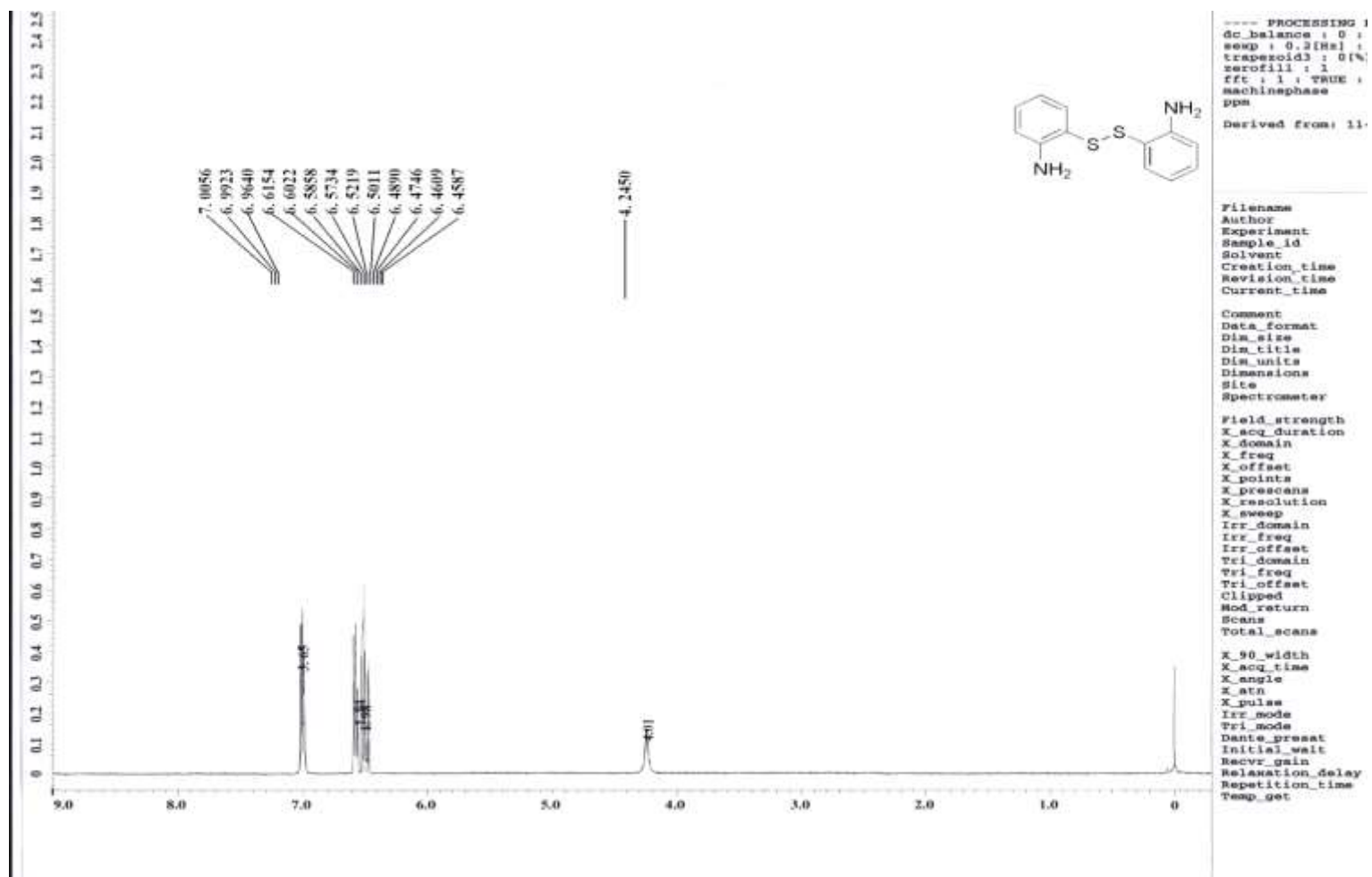
HRMS of Diphenyl disulfide **2a**



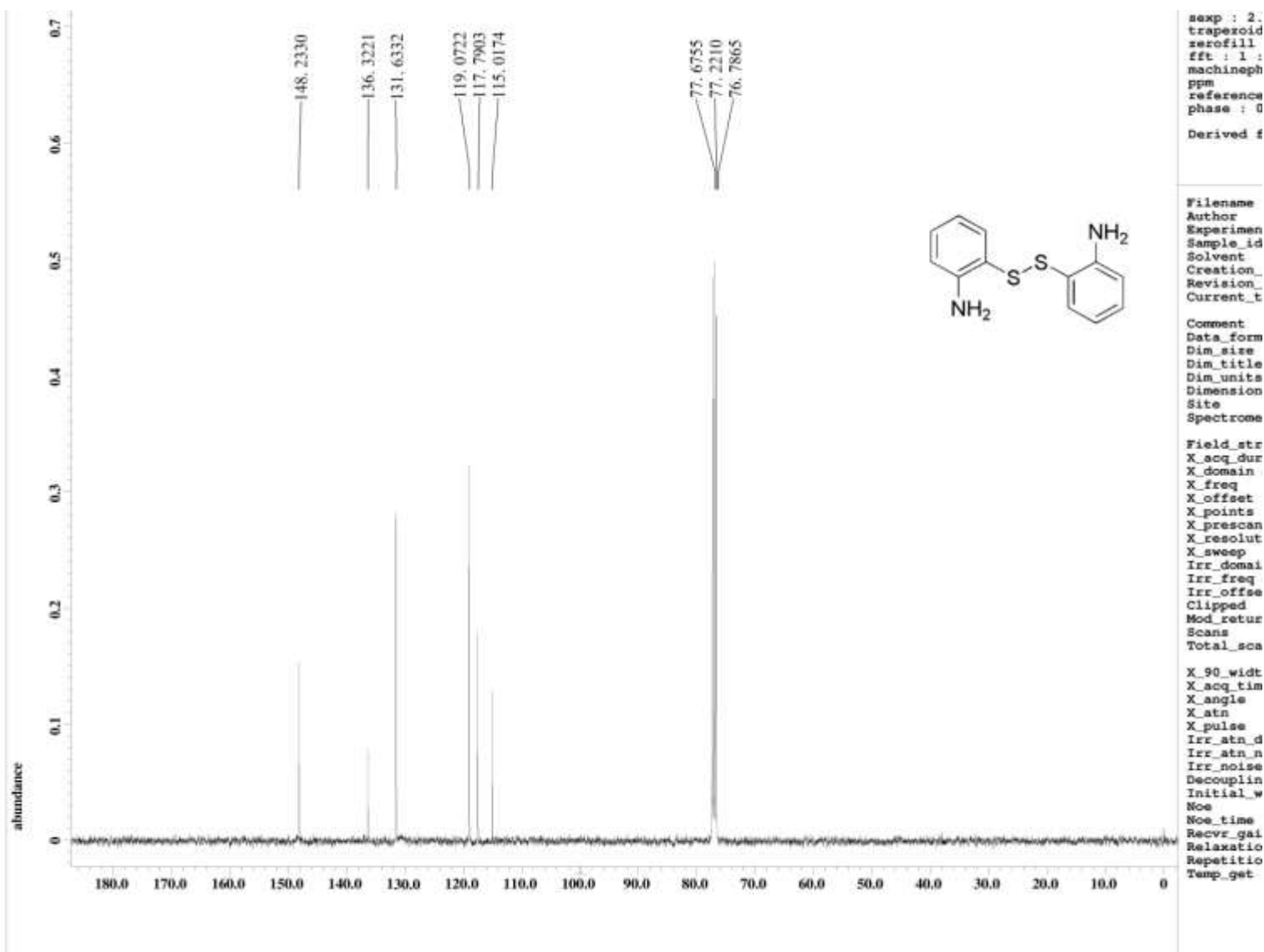
^1H NMR (400 MHz, CDCl_3) of Dibenzyl disulfide **2b**



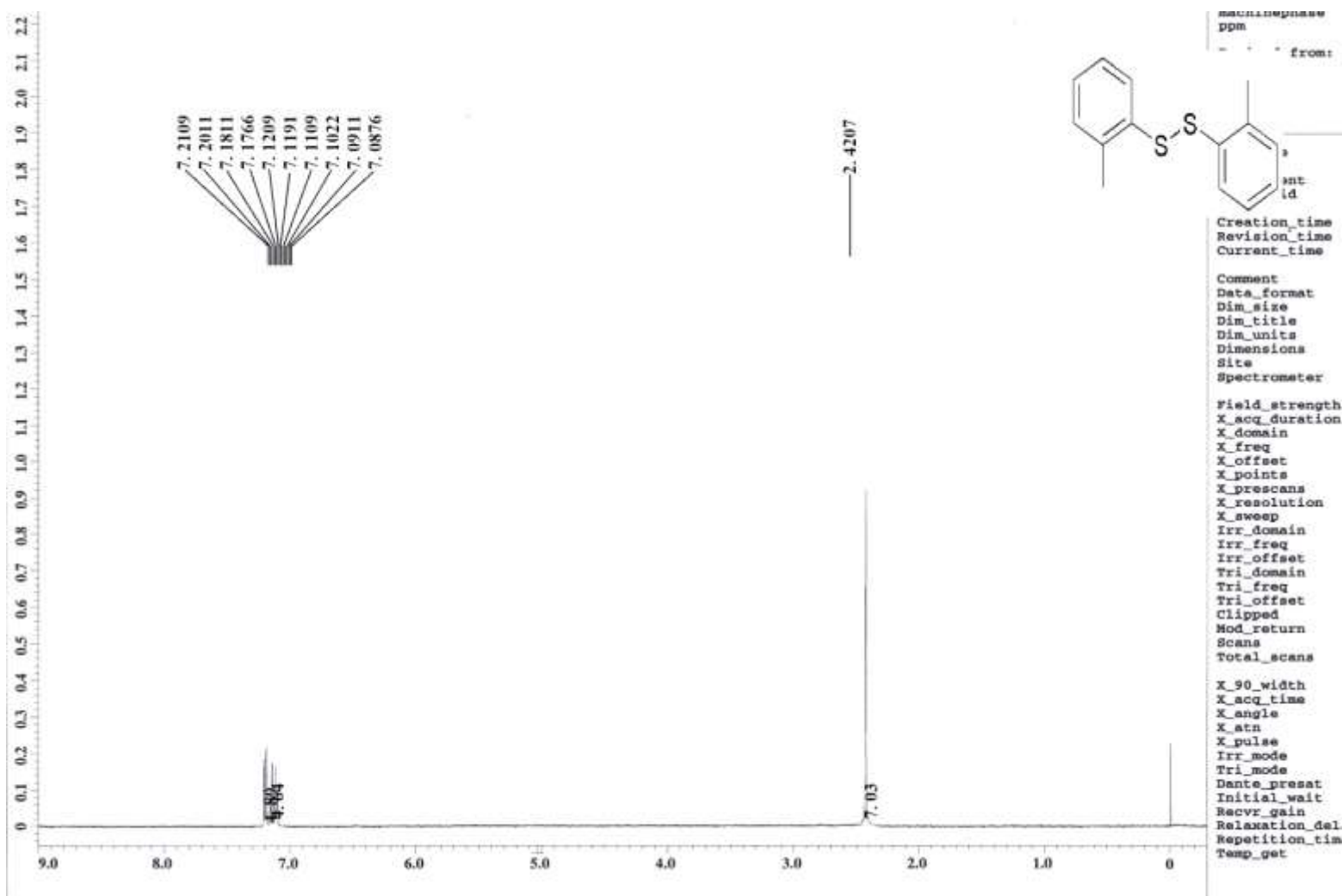
^{13}C NMR (400 MHz, CDCl_3) of Dibenzyl disulfide **2b**



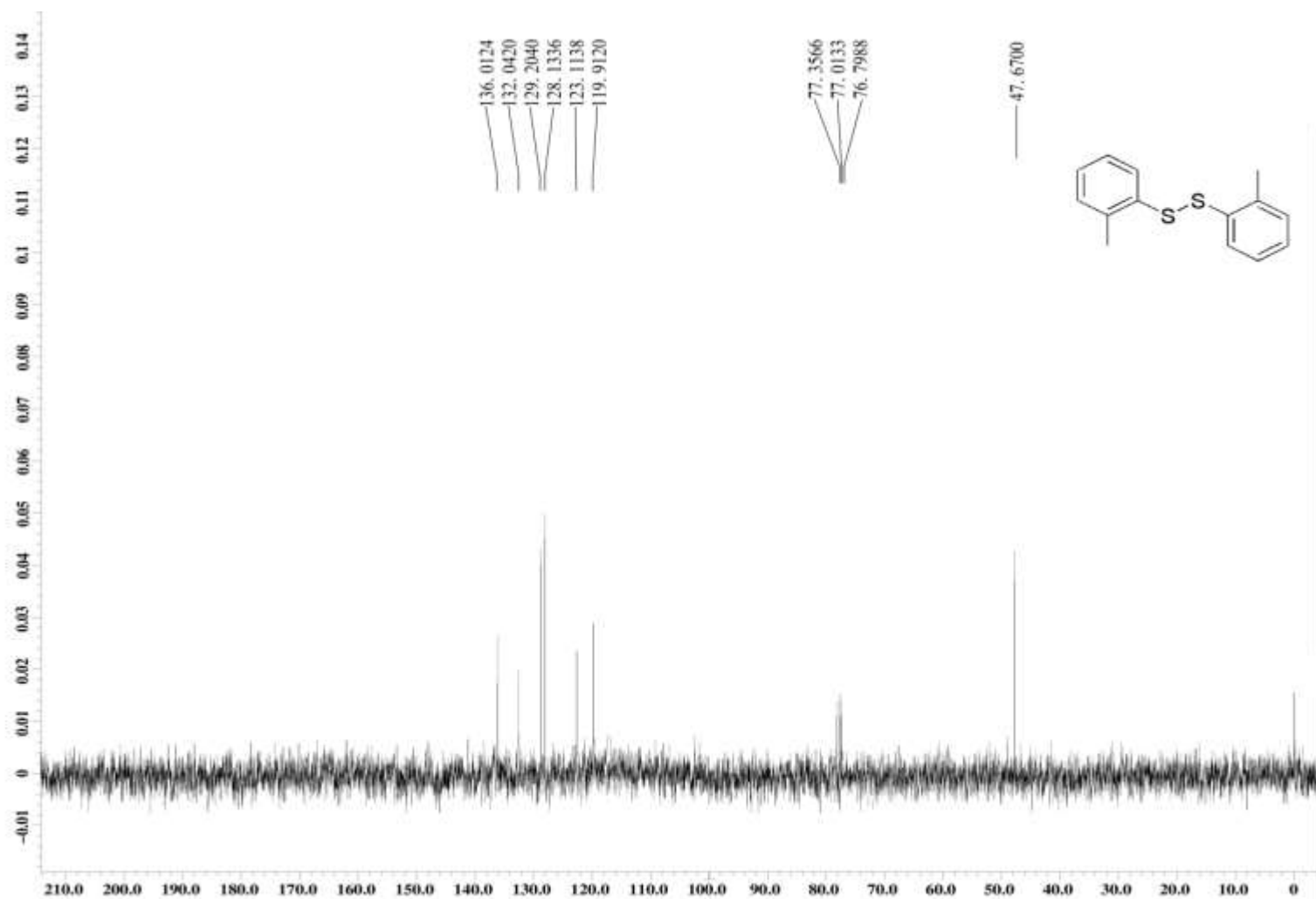
¹H NMR (400 MHz, CDCl₃) of bis-(2-aminophenyl) disulfide 2c



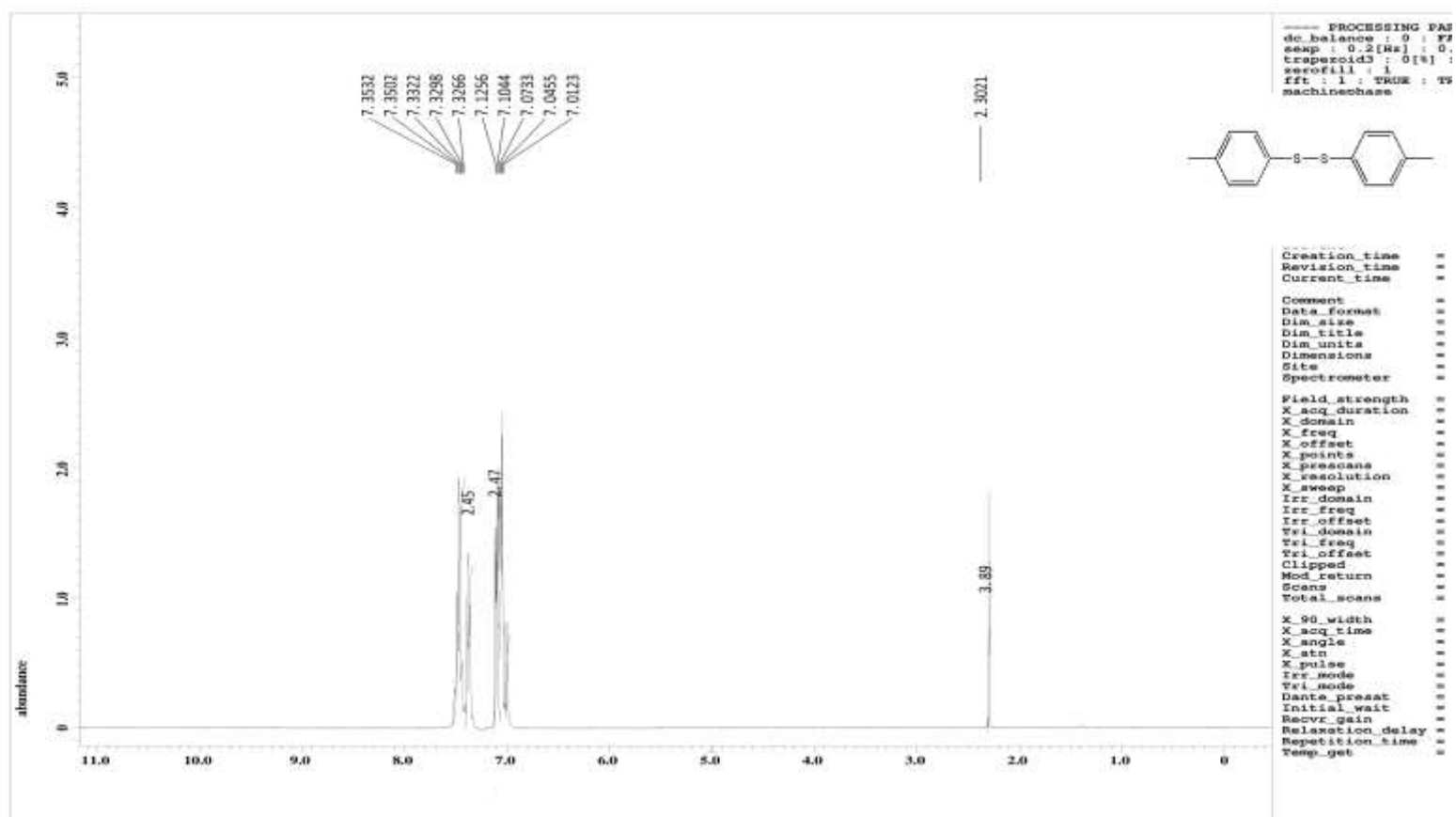
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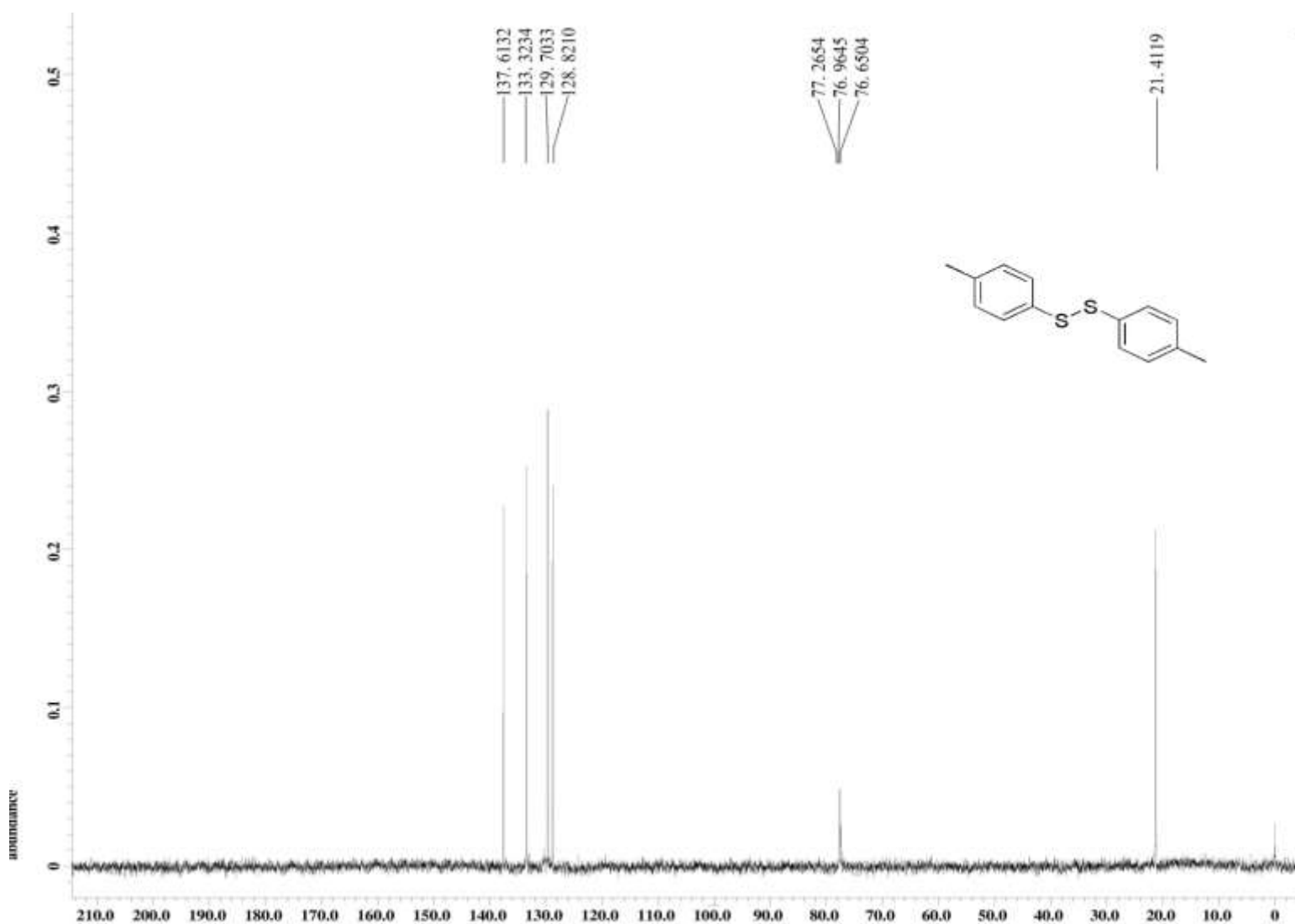
¹H NMR (400 MHz, CDCl₃) of bis-(2-methylphenyl) disulfide **2d**



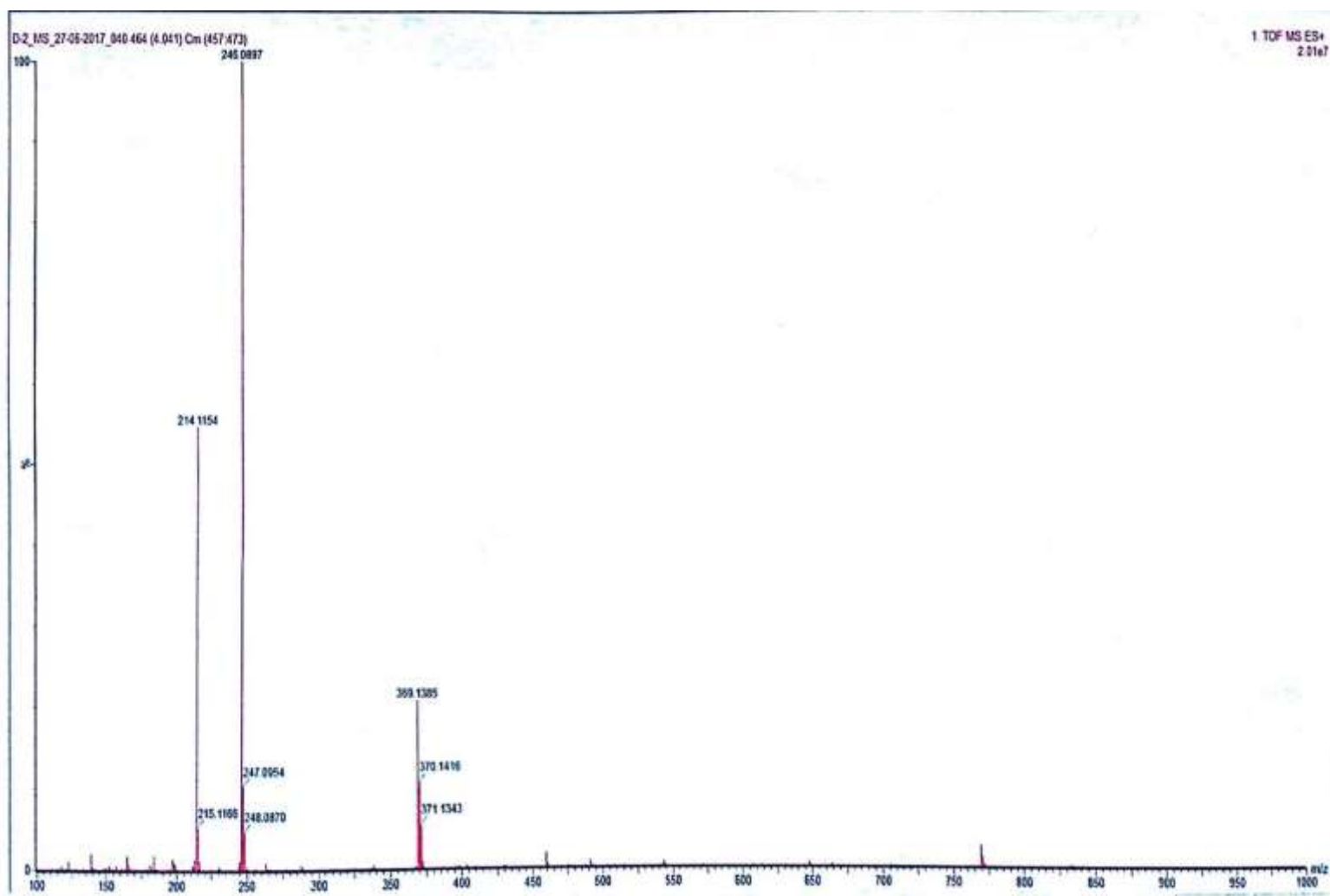
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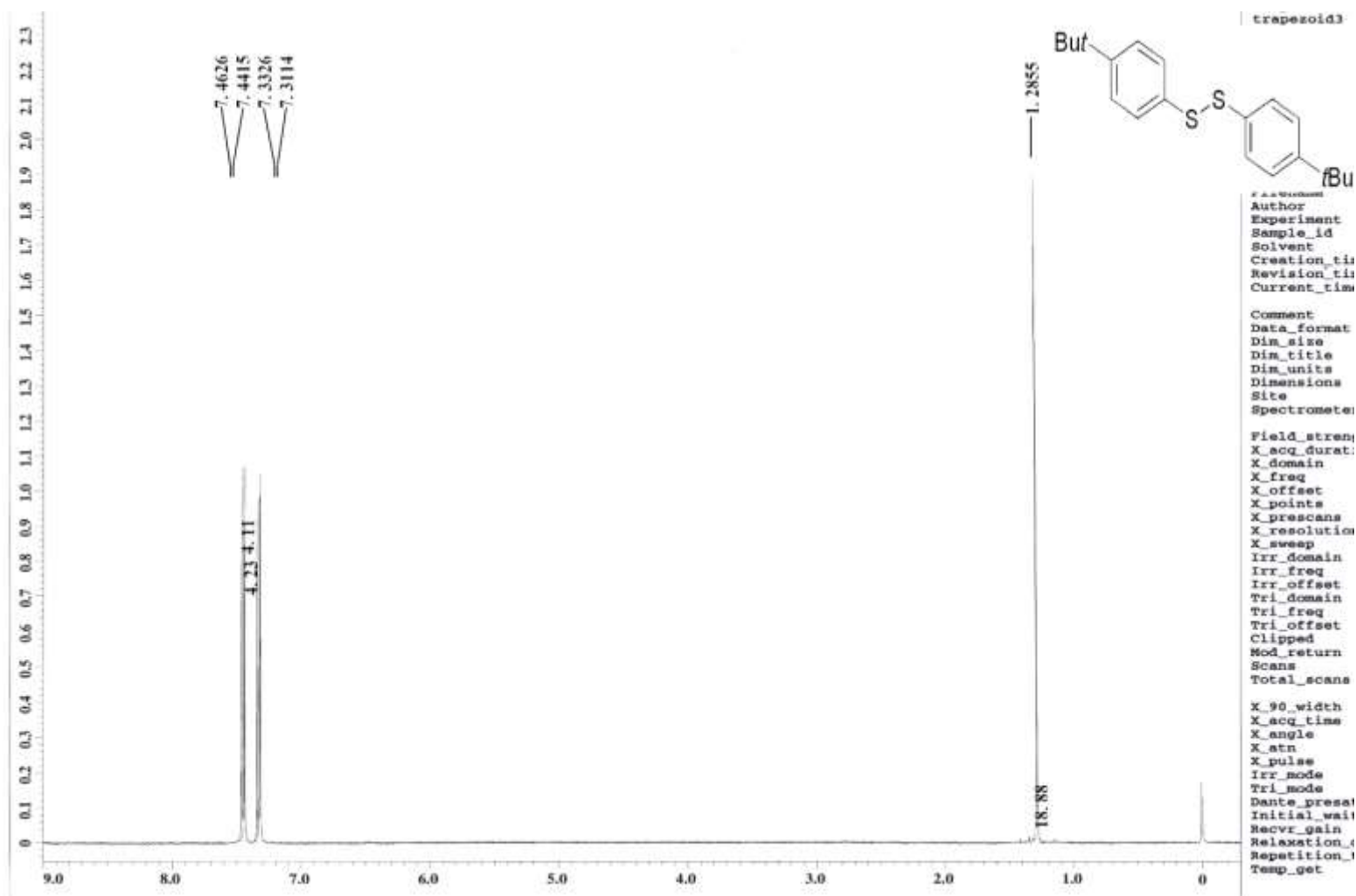
^1H NMR (400 MHz, CDCl_3) of bis-(4-methylphenyl) disulfide **2e**



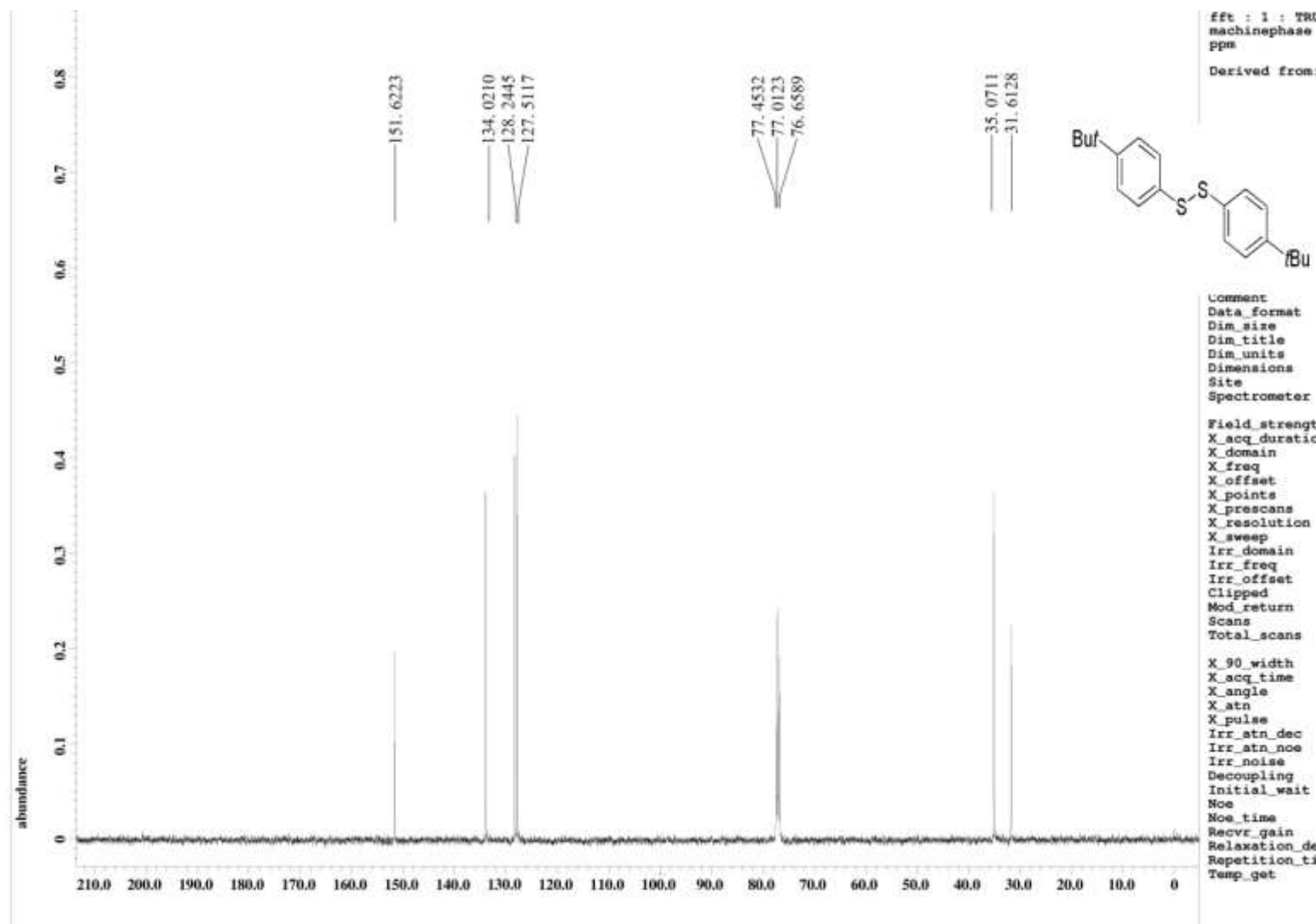
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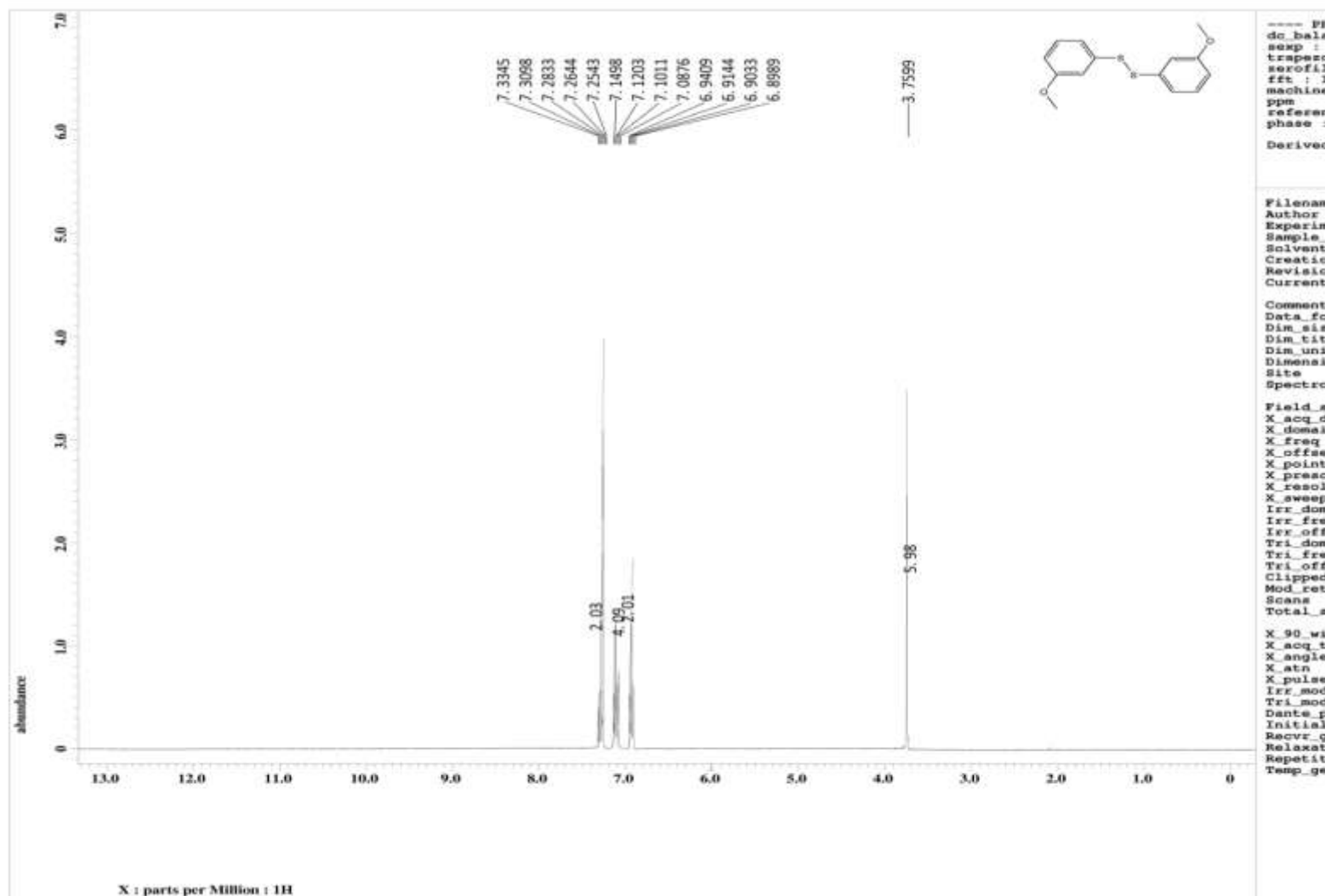
HRMS of bis-(4-methylphenyl) disulfide **2e**



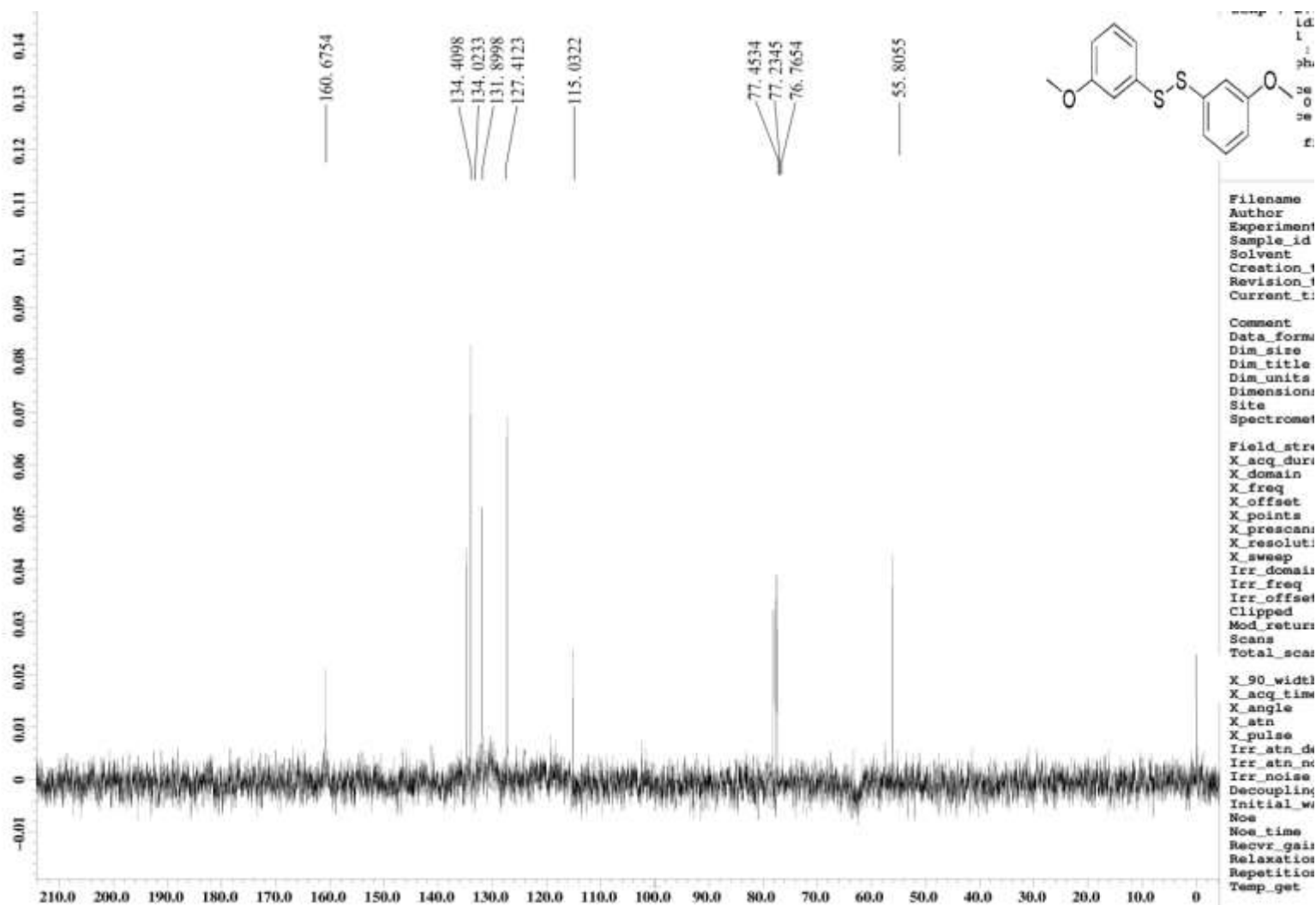
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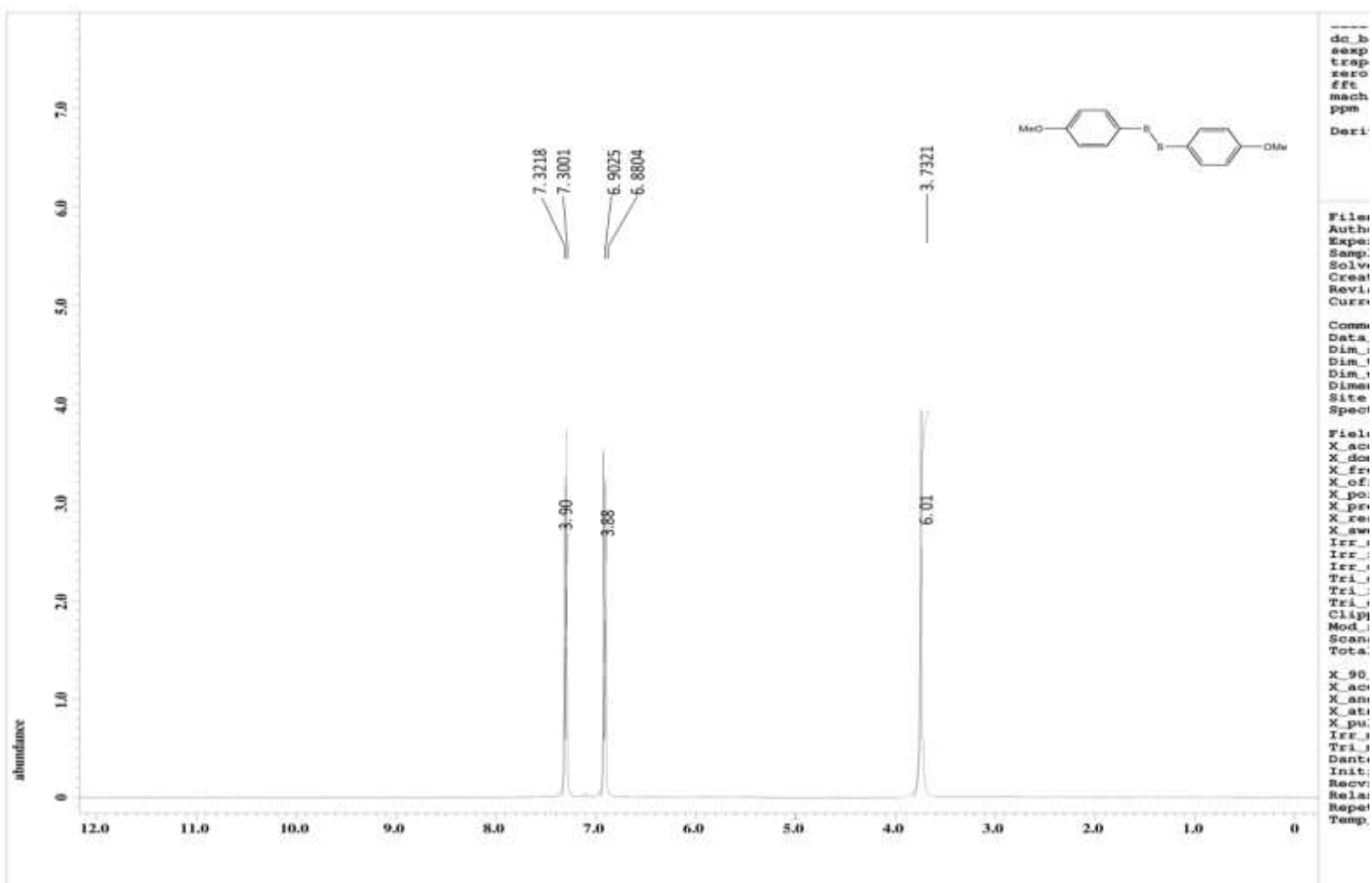
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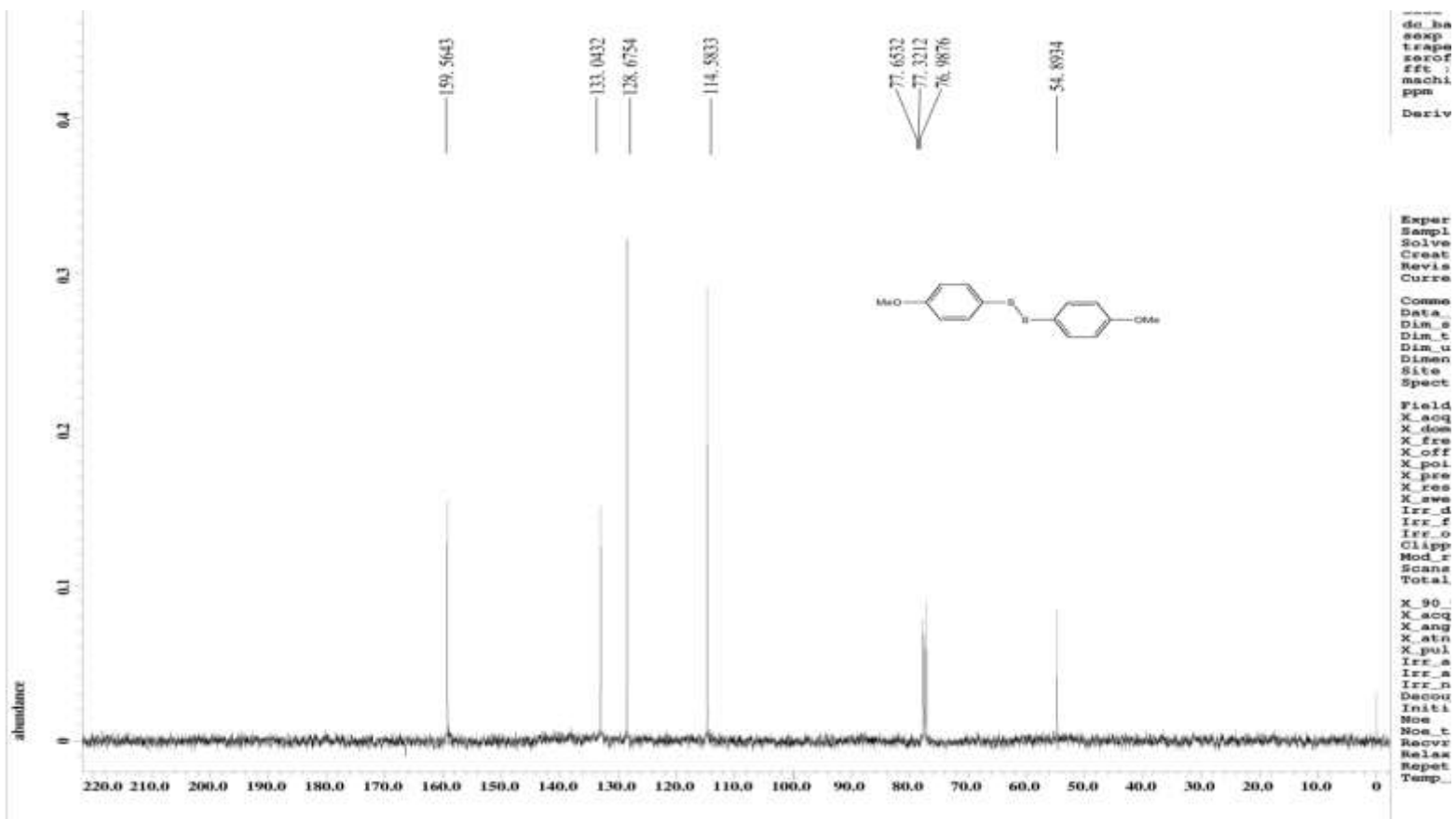
¹H NMR (400 MHz, CDCl₃) of bis-(3-methoxyphenyl) disulfide **2g**



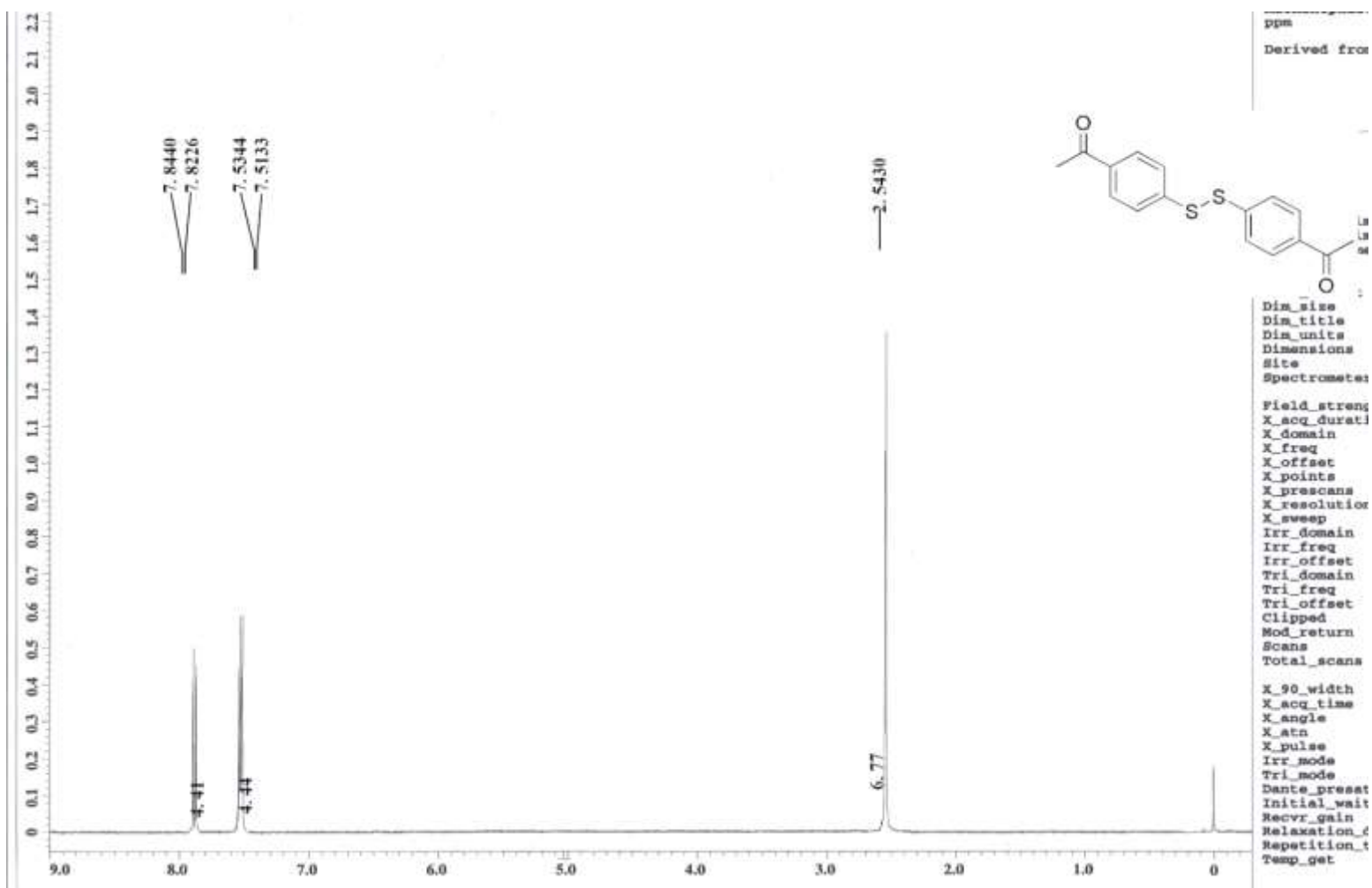
^{13}C NMR (100 MHz, CDCl_3) of bis-(3-methoxyphenyl) disulfide **2g**



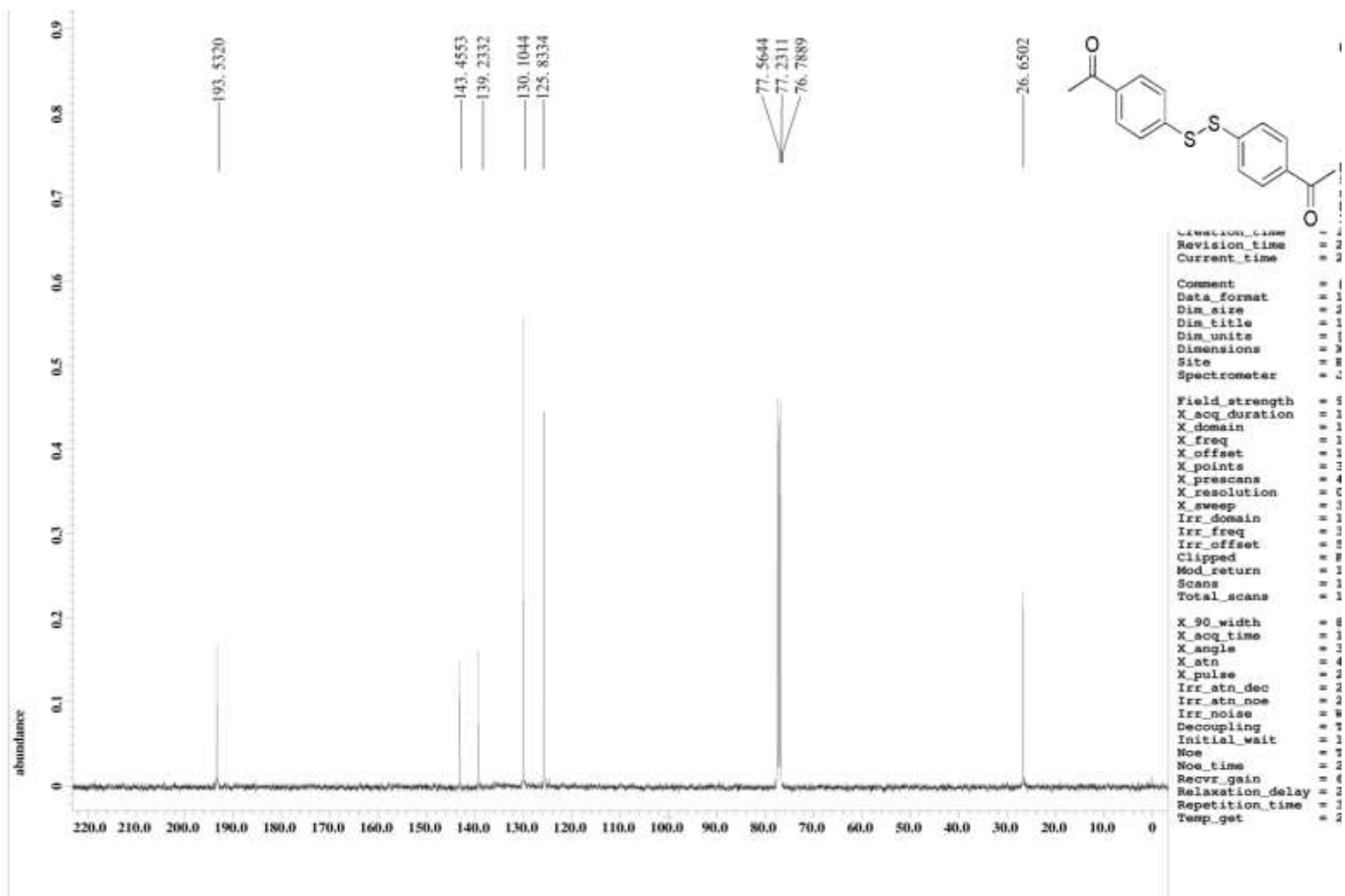
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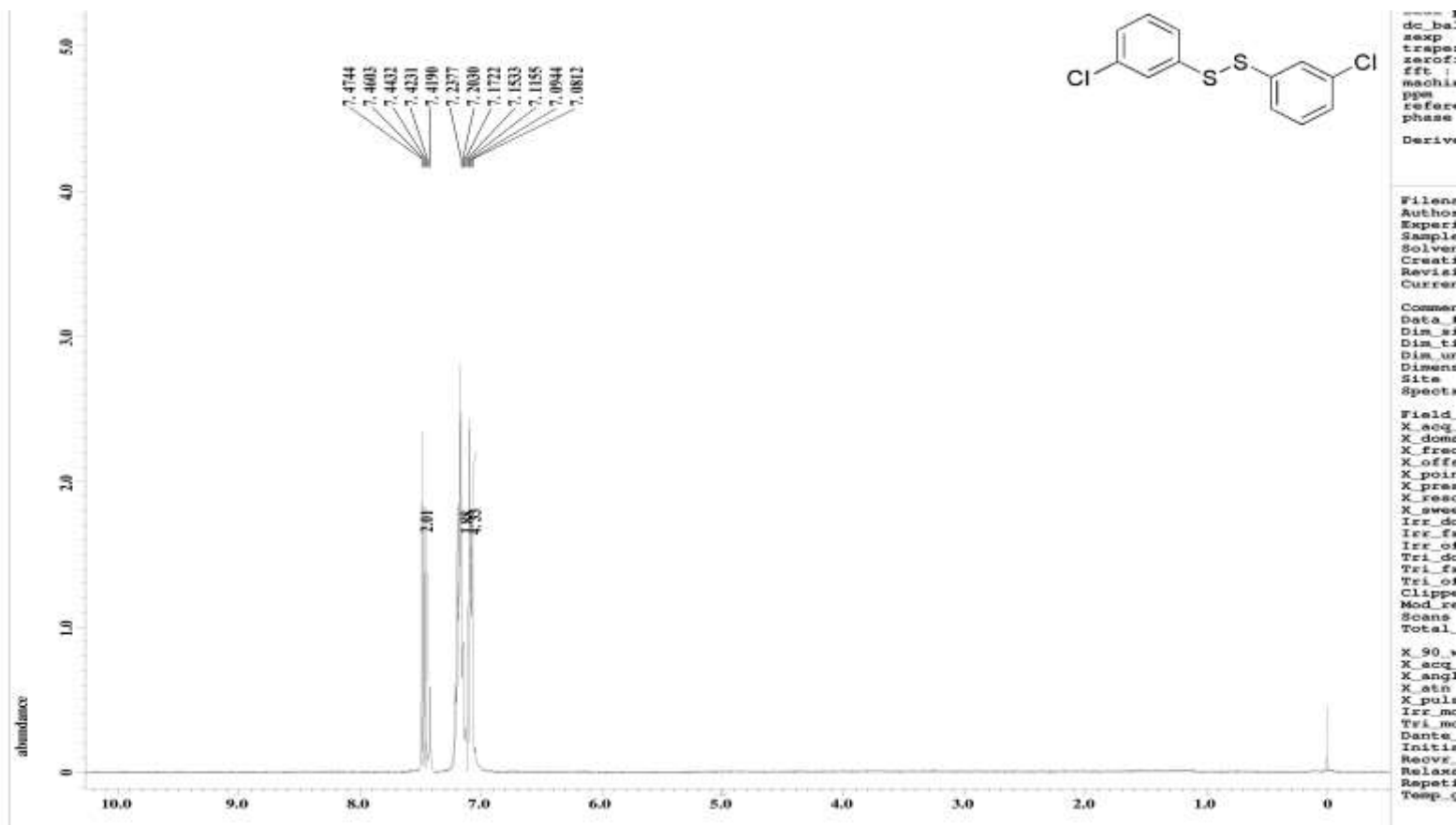
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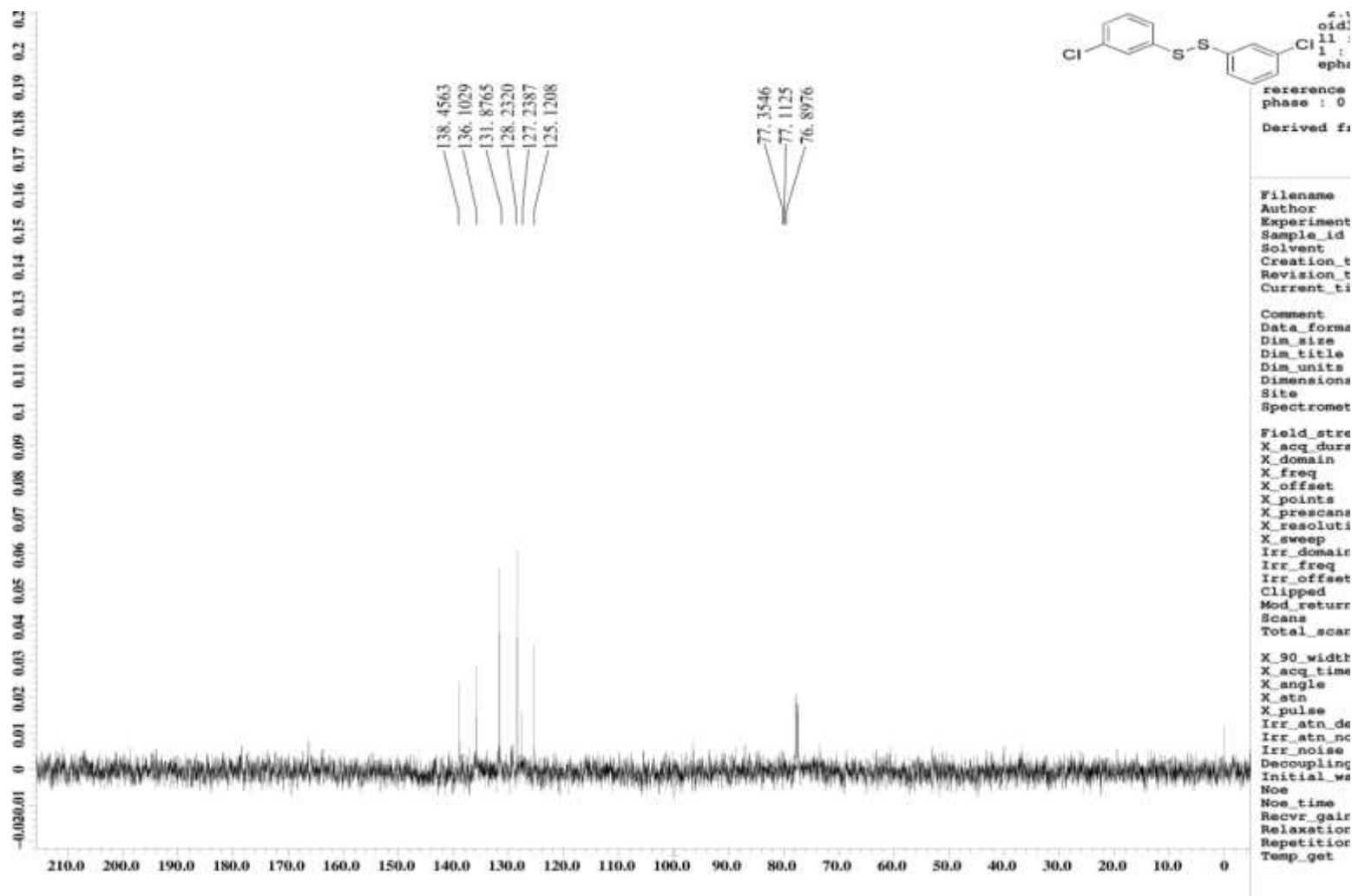
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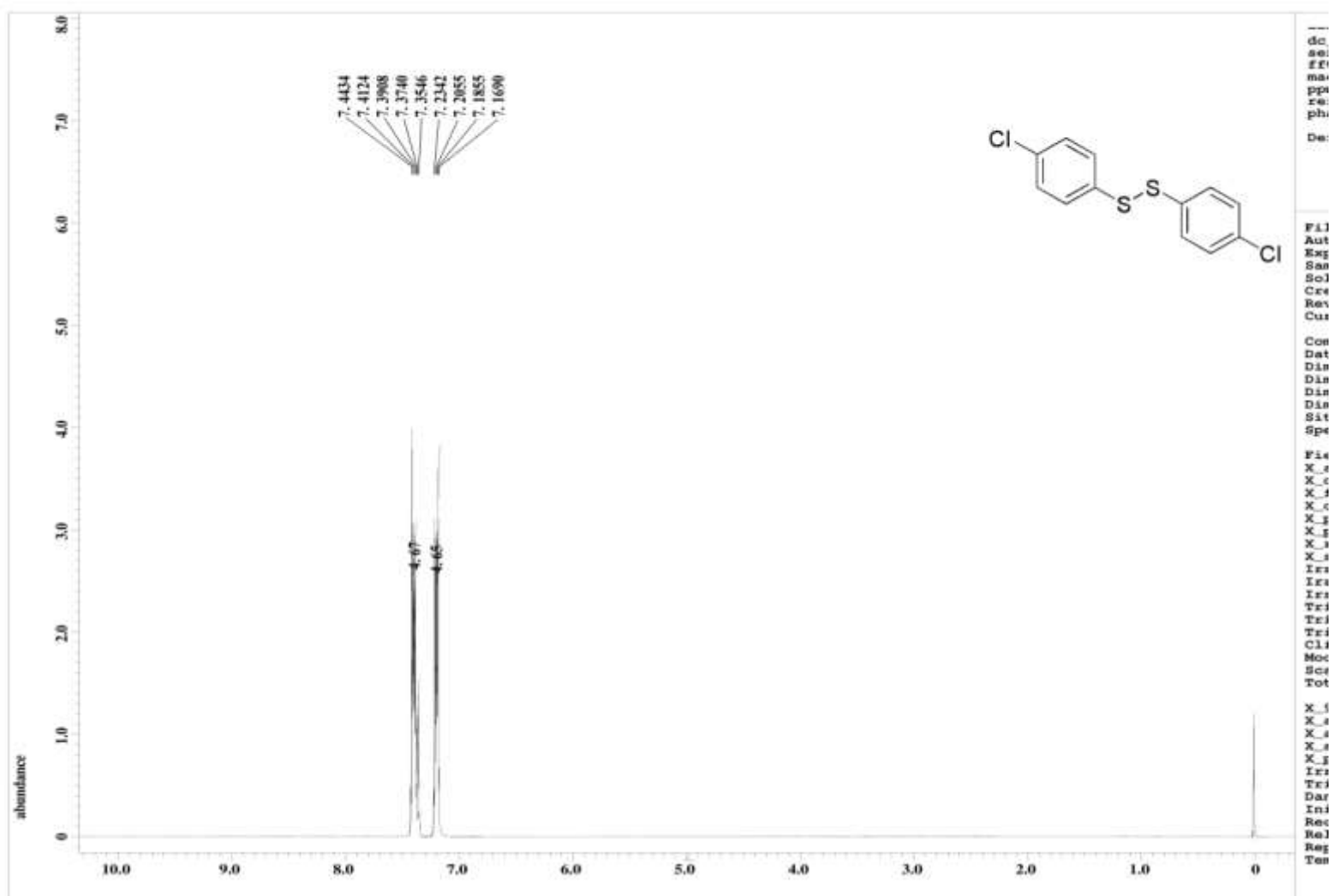
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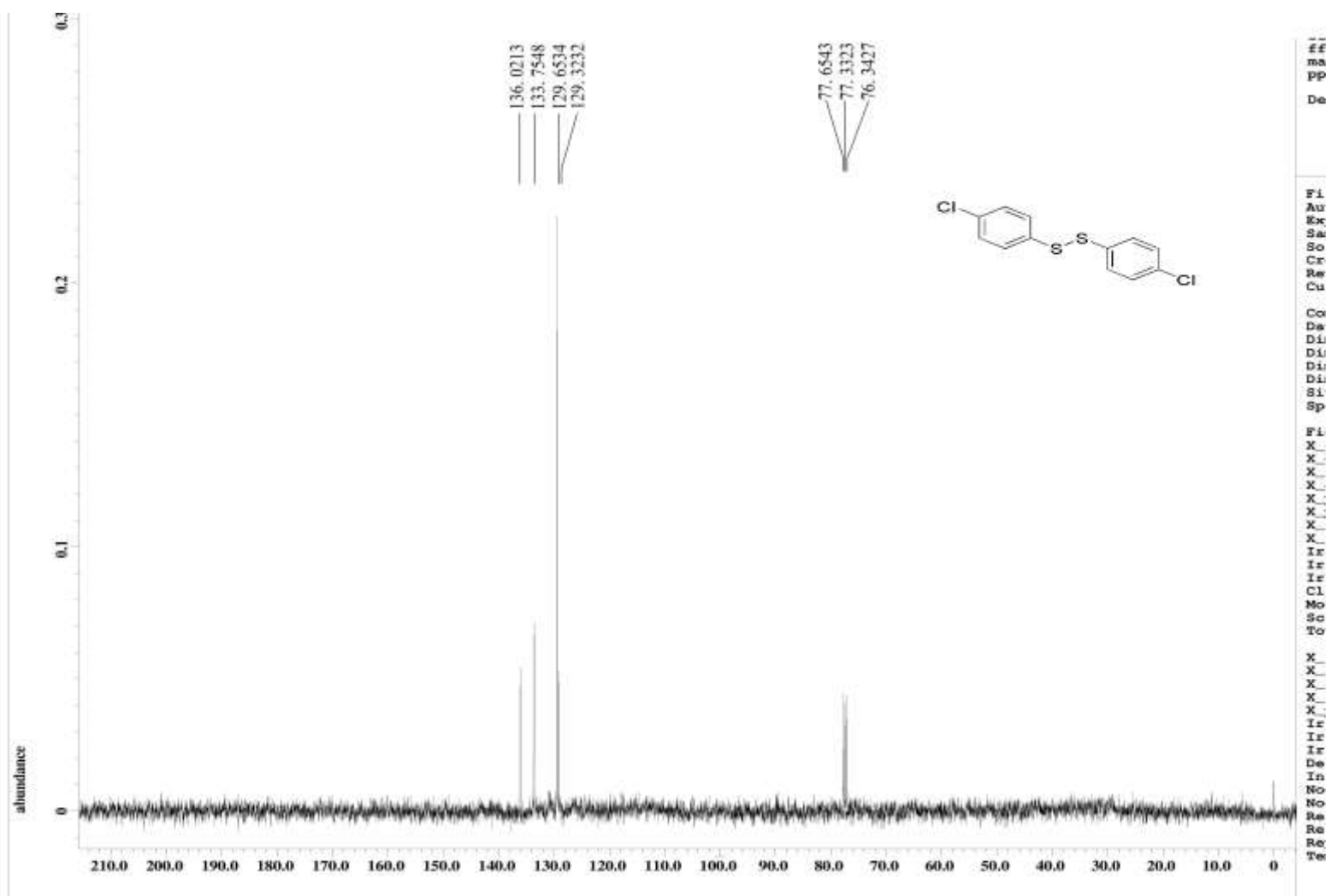
¹H NMR (400 MHz, CDCl₃) of bis-(3-chlorophenyl) disulfide **2j**



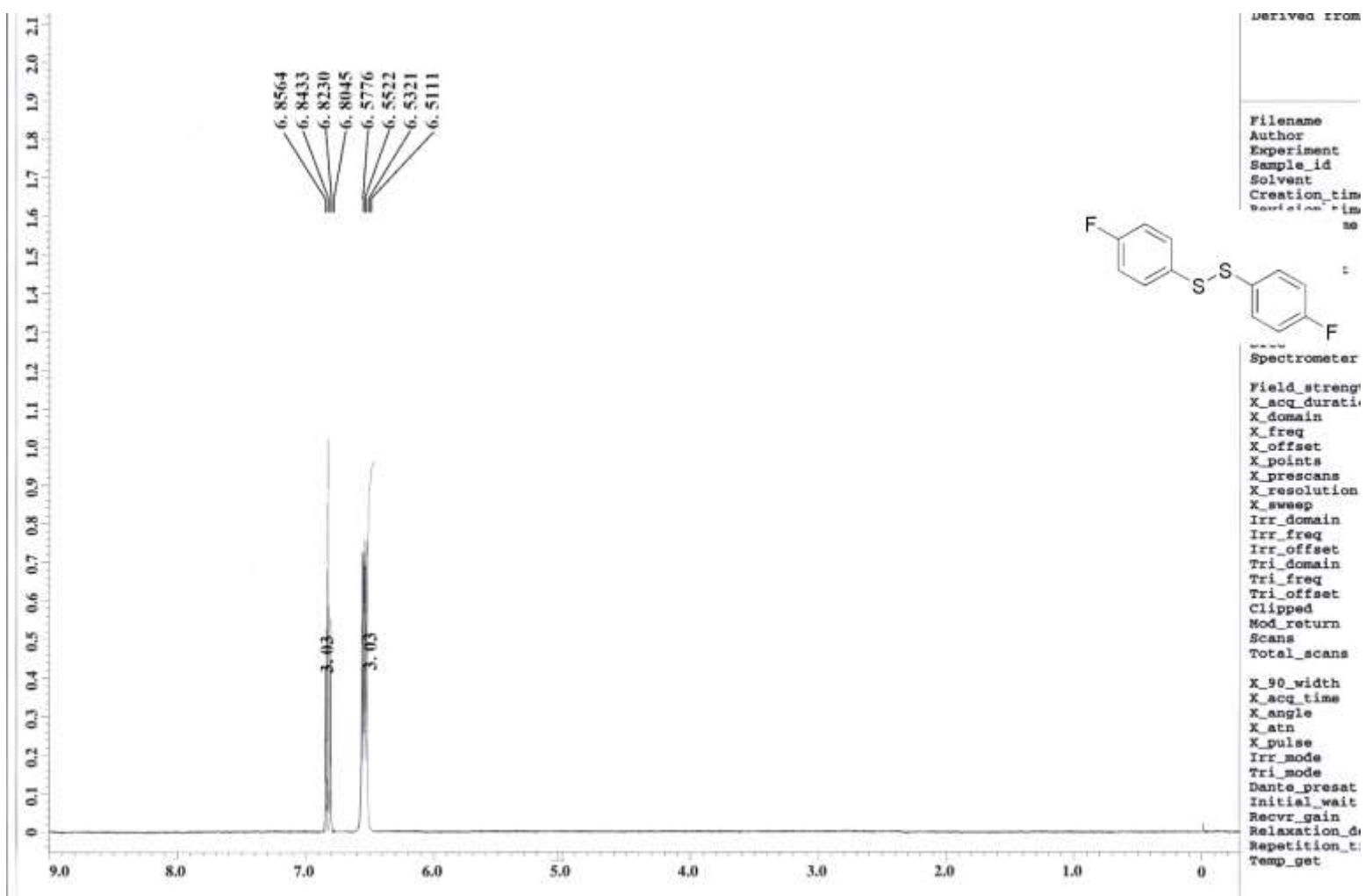
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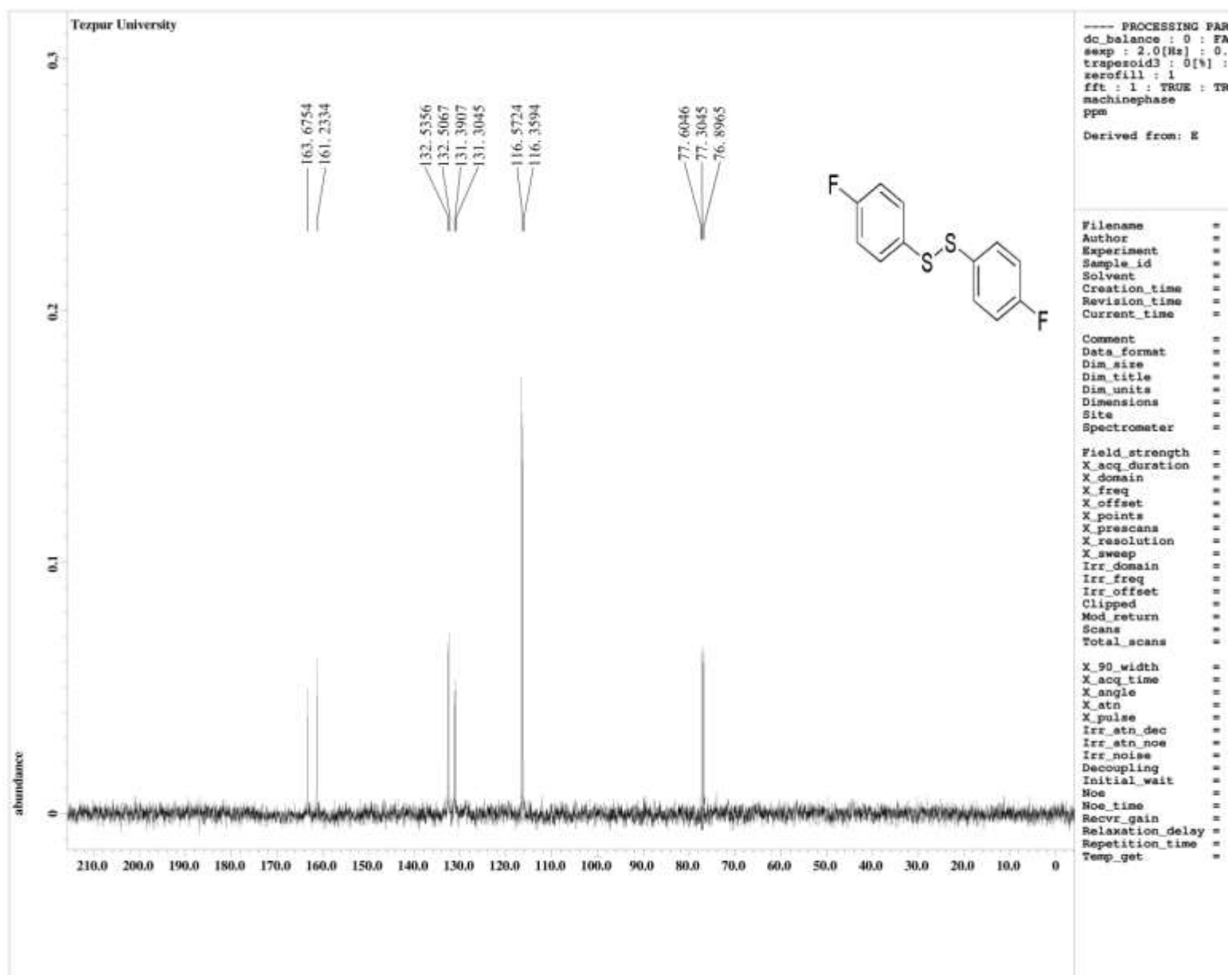
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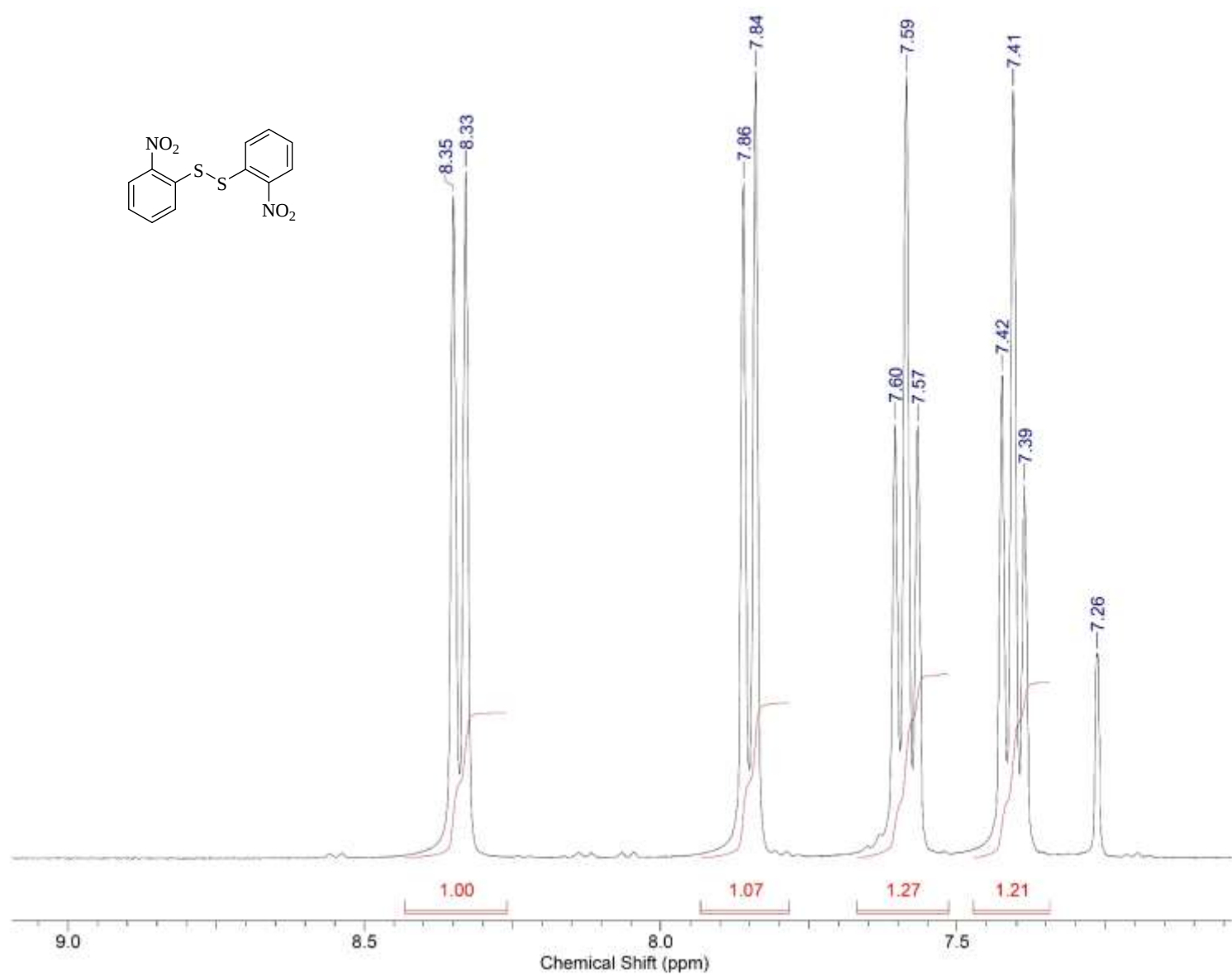
^{13}C NMR (100 MHz, CDCl_3) of bis-(4-chlorophenyl) disulfide **2k**



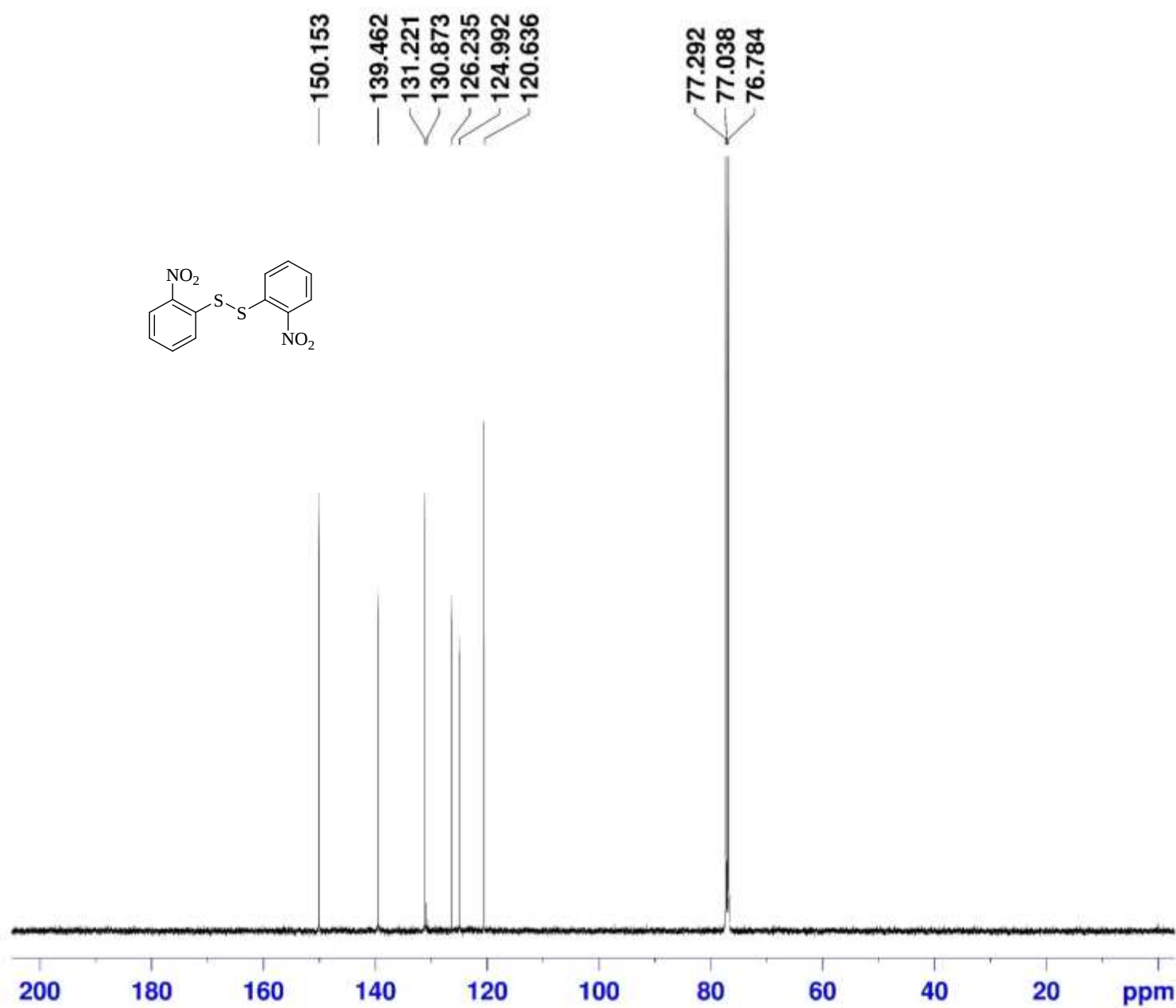
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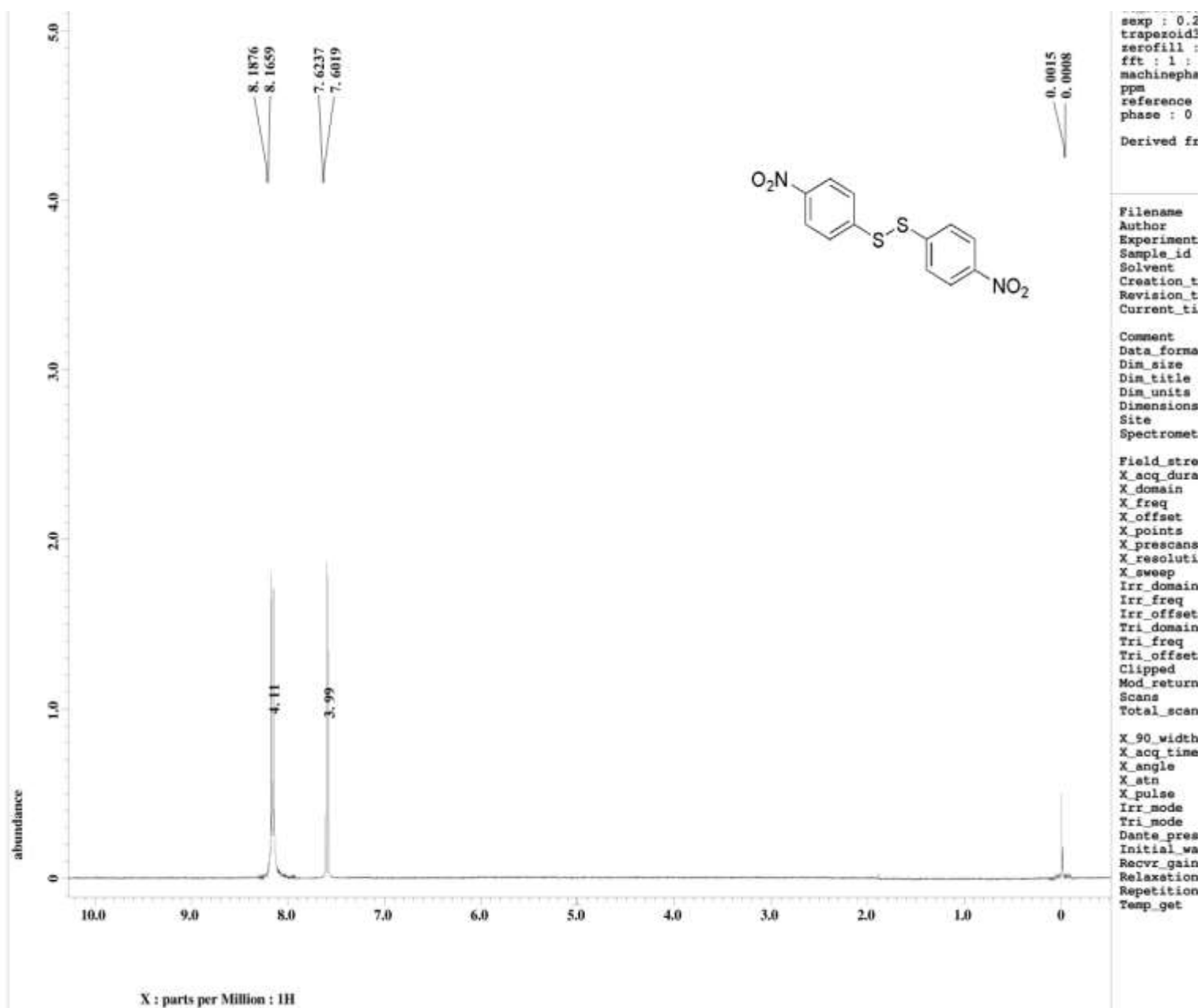
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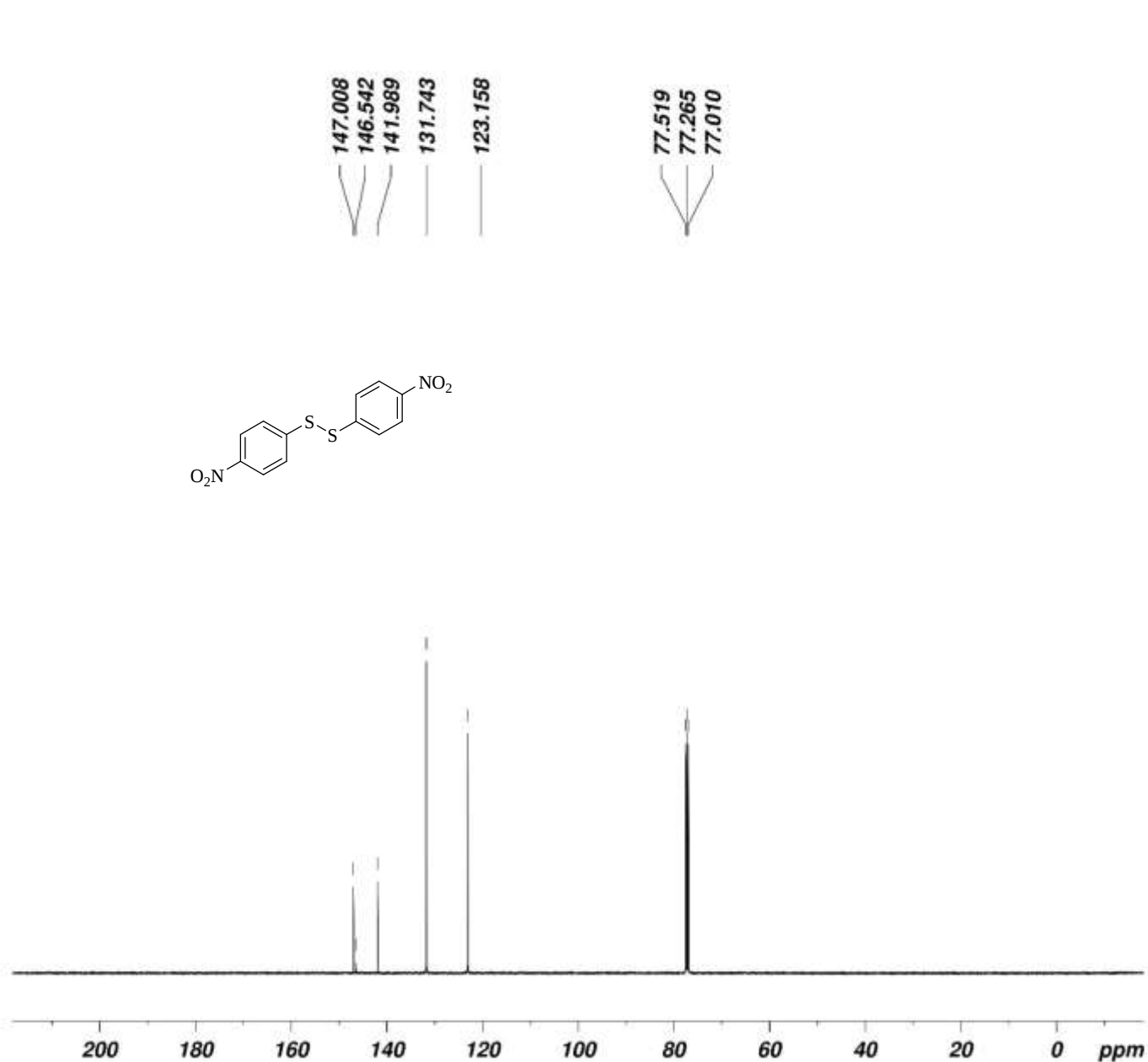
¹H NMR (400 MHz, CDCl₃) of bis-(2-nitrophenyl) disulfide **2m**



¹³C NMR (500 MHz, CDCl₃) of bis-(2-nitrophenyl) disulfide **2m**



¹H NMR (400 MHz, CDCl₃) of bis-(4-nitrophenyl) disulfide **2n**



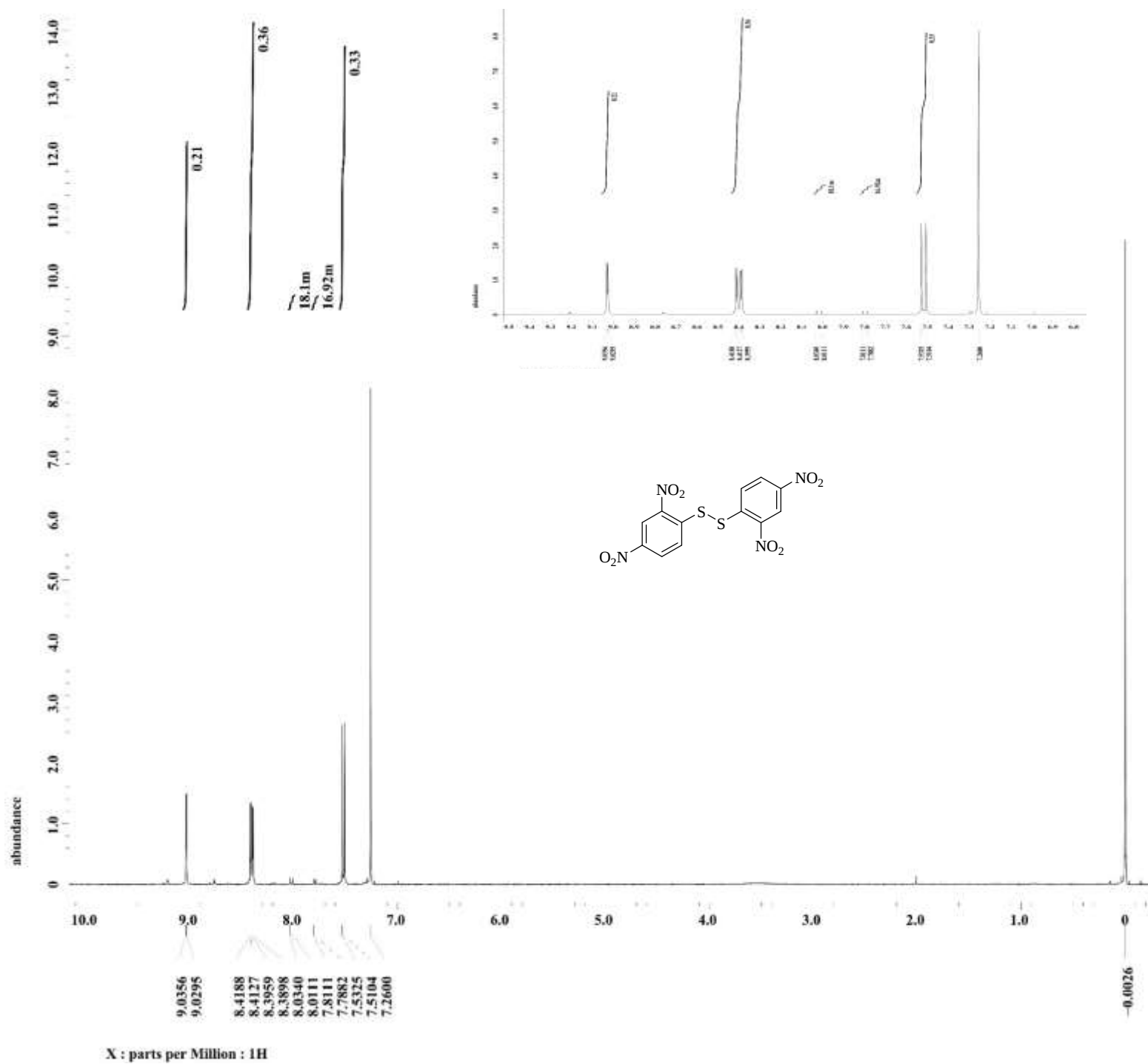
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D1 2.0
D11 0.
TD0

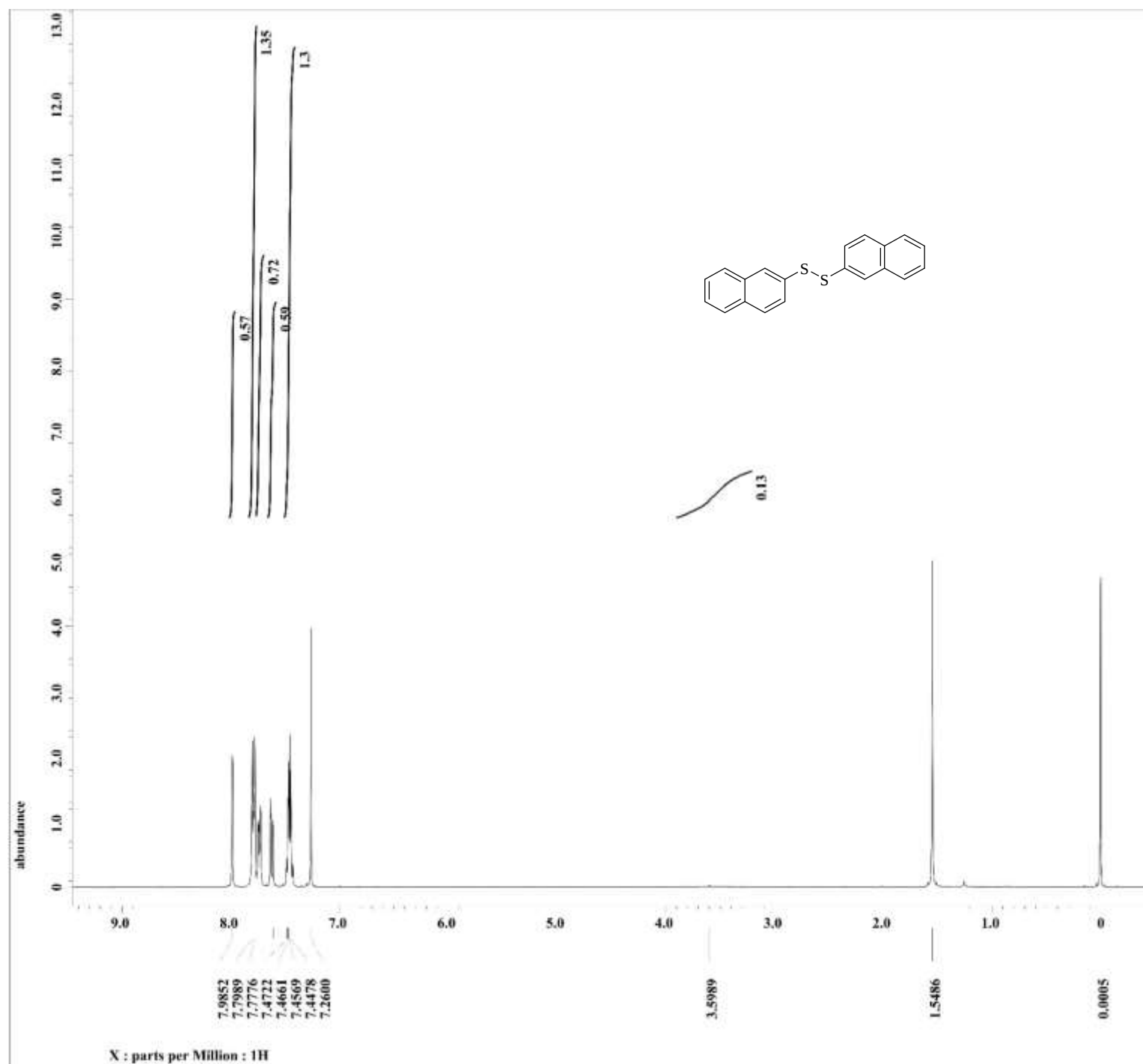
=====
NUC1
P1
PL1
PL1W 7
SFO1 1.

=====
CPDPRG2
NUC2
PCPD2
PL2
PL12
PL13
PL2W 2
PL12W
PL13W
SFO2 5

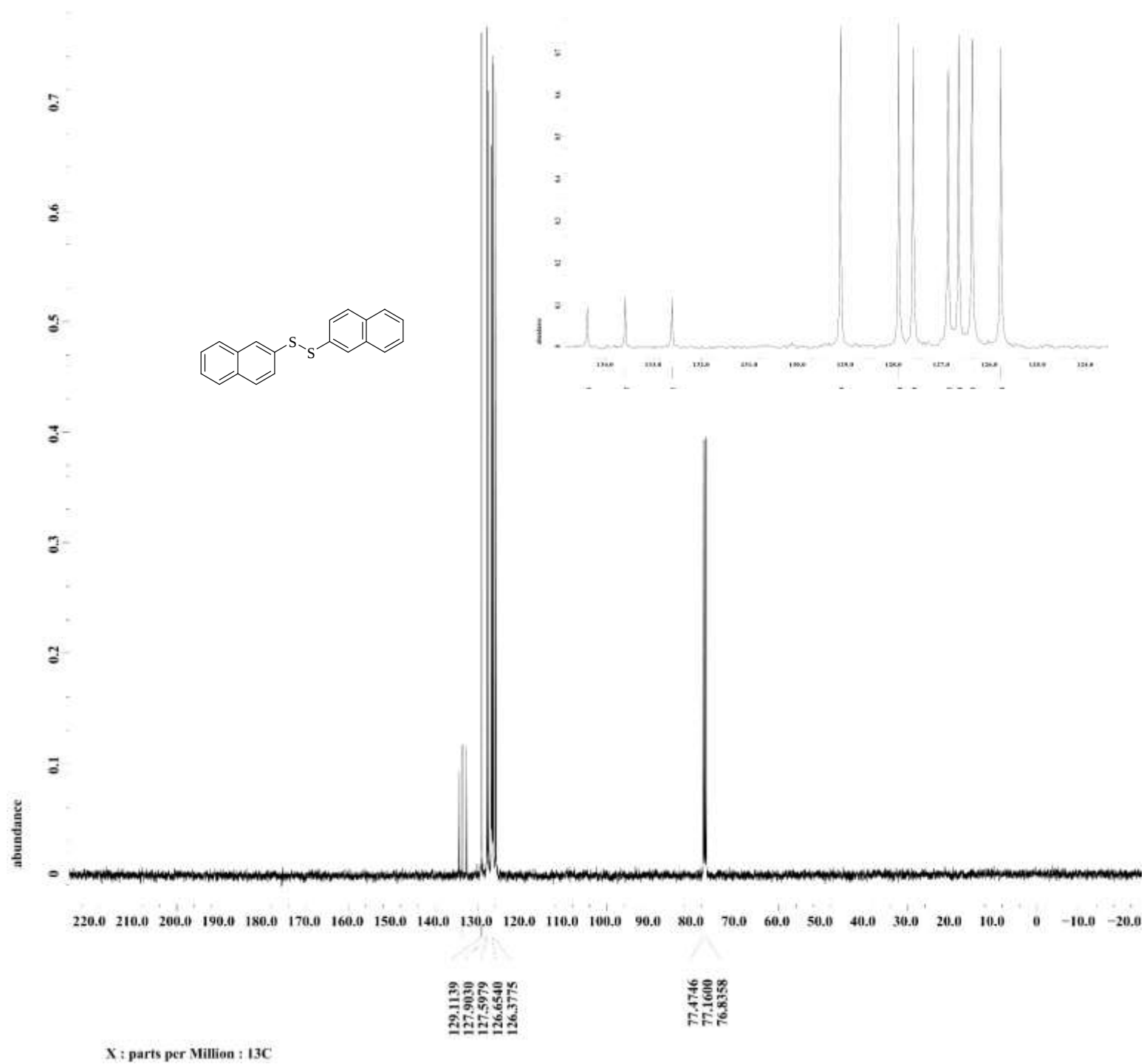
¹³C NMR (500 MHz, CDCl₃) of bis-(4-nitrophenyl) disulfide **2n**



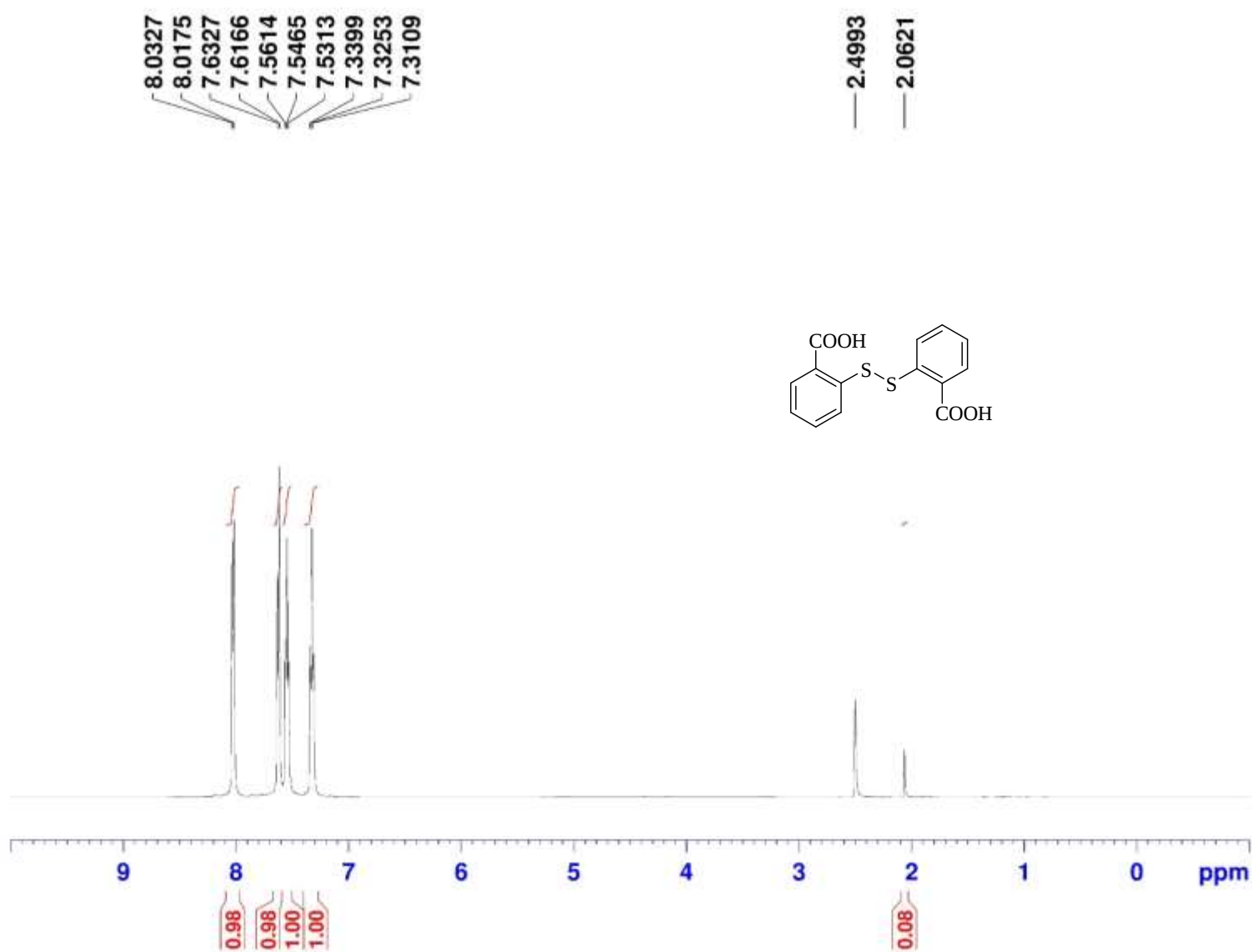
¹H NMR (400 MHz, CDCl₃) of bis-(2,4-dinitrophenyl) disulfide **2o**



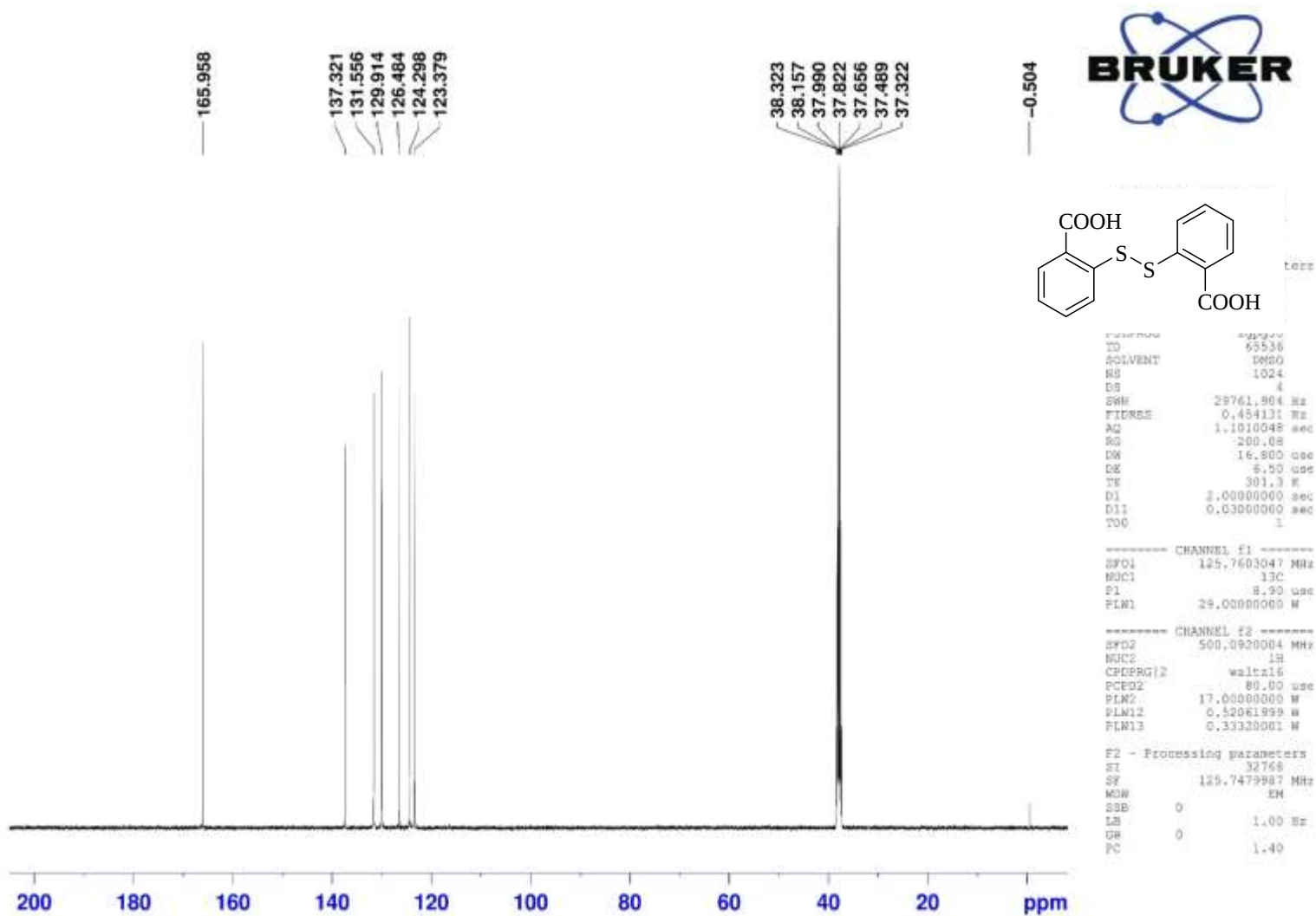
¹H NMR (400 MHz, CDCl₃) of Bis-(2-naphthyl) disulfide **2p**



^{13}C NMR (400 MHz, CDCl_3) of Bis-(2-naphthyl) disulfide **2p**



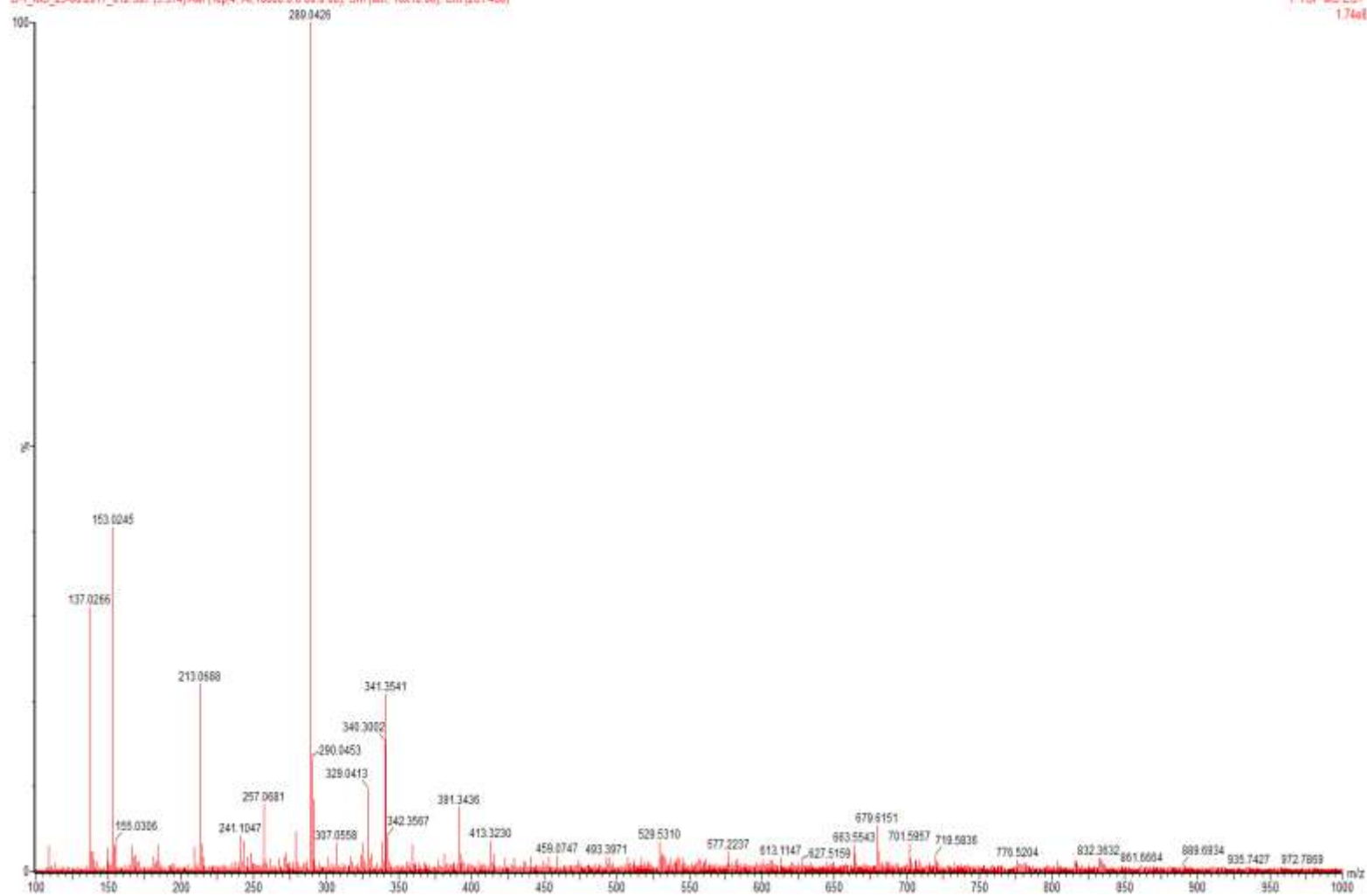
¹H NMR (500 MHz, DMSO) of Bis-(2-carboxyphenyl) disulfide **2q**



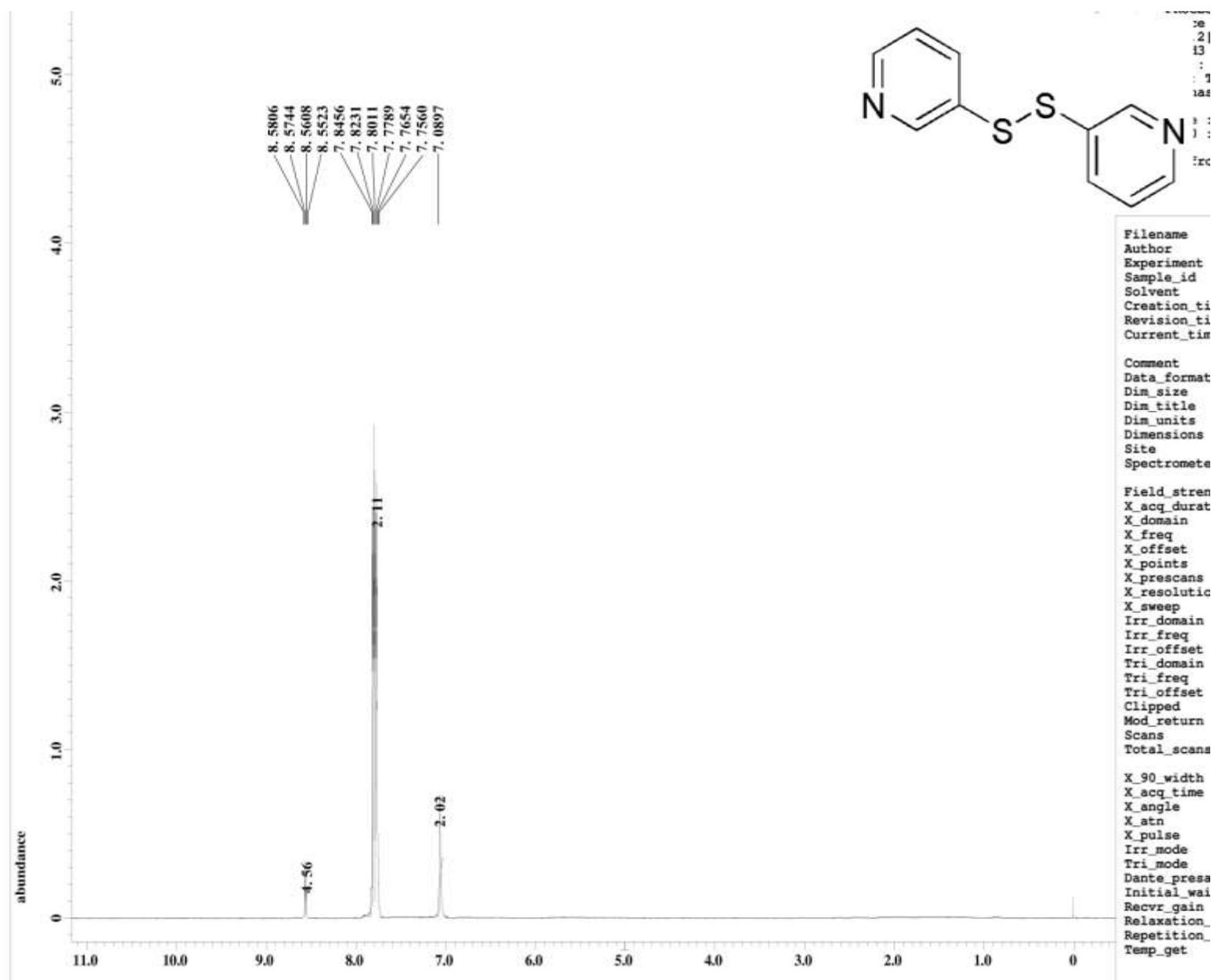
¹³C NMR (500 MHz, DMSO) of Bis-(2-carboxyphenyl) disulfide **2q**

D-1_NIS_29-06-2017_012.387 (3.374) AM (Top 4, Ac 10000.0 0.00.0 00); 5m (Mn, 10x10.00); Cm (261.480)

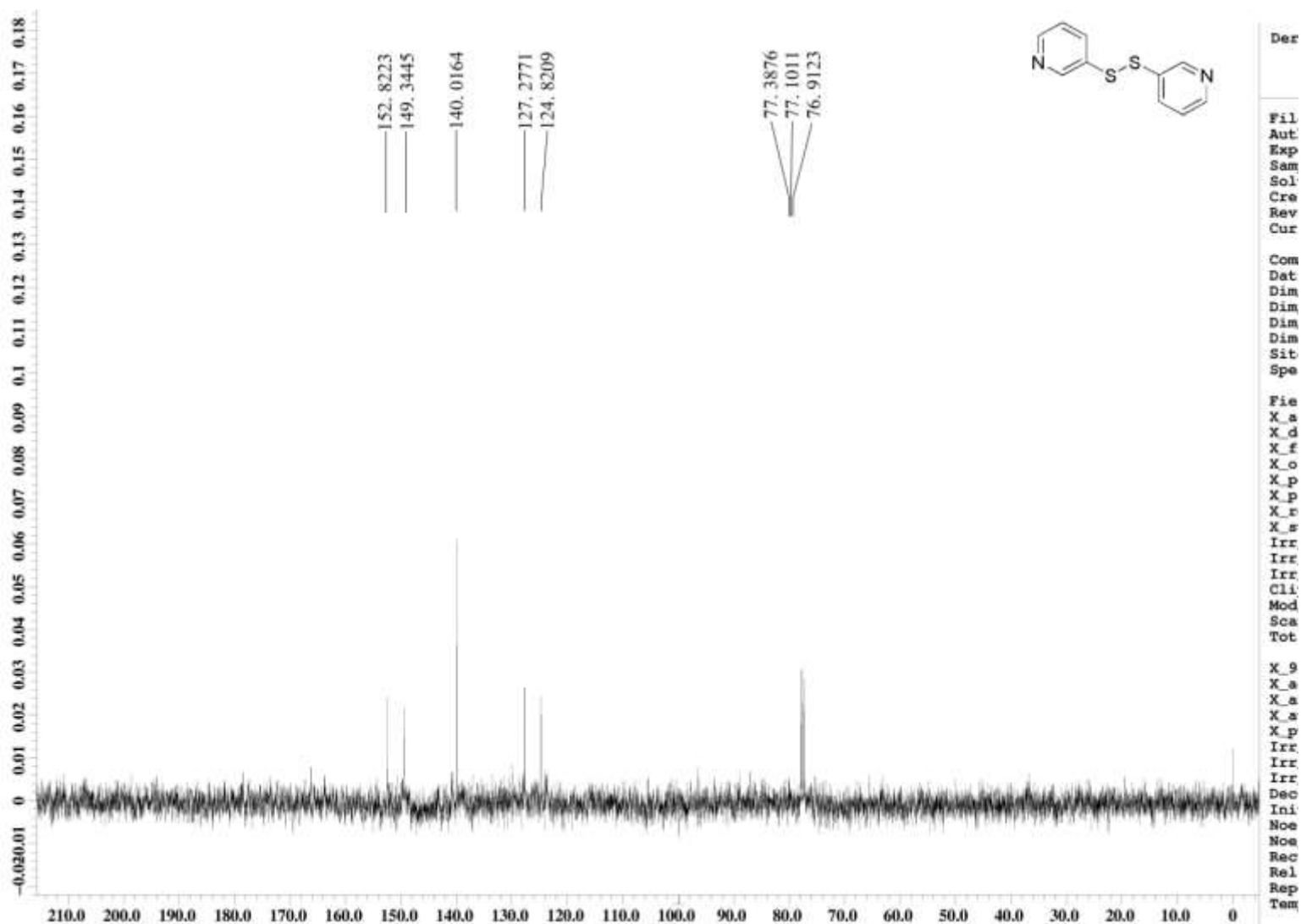
1-TOF MS ES+
1.74e6



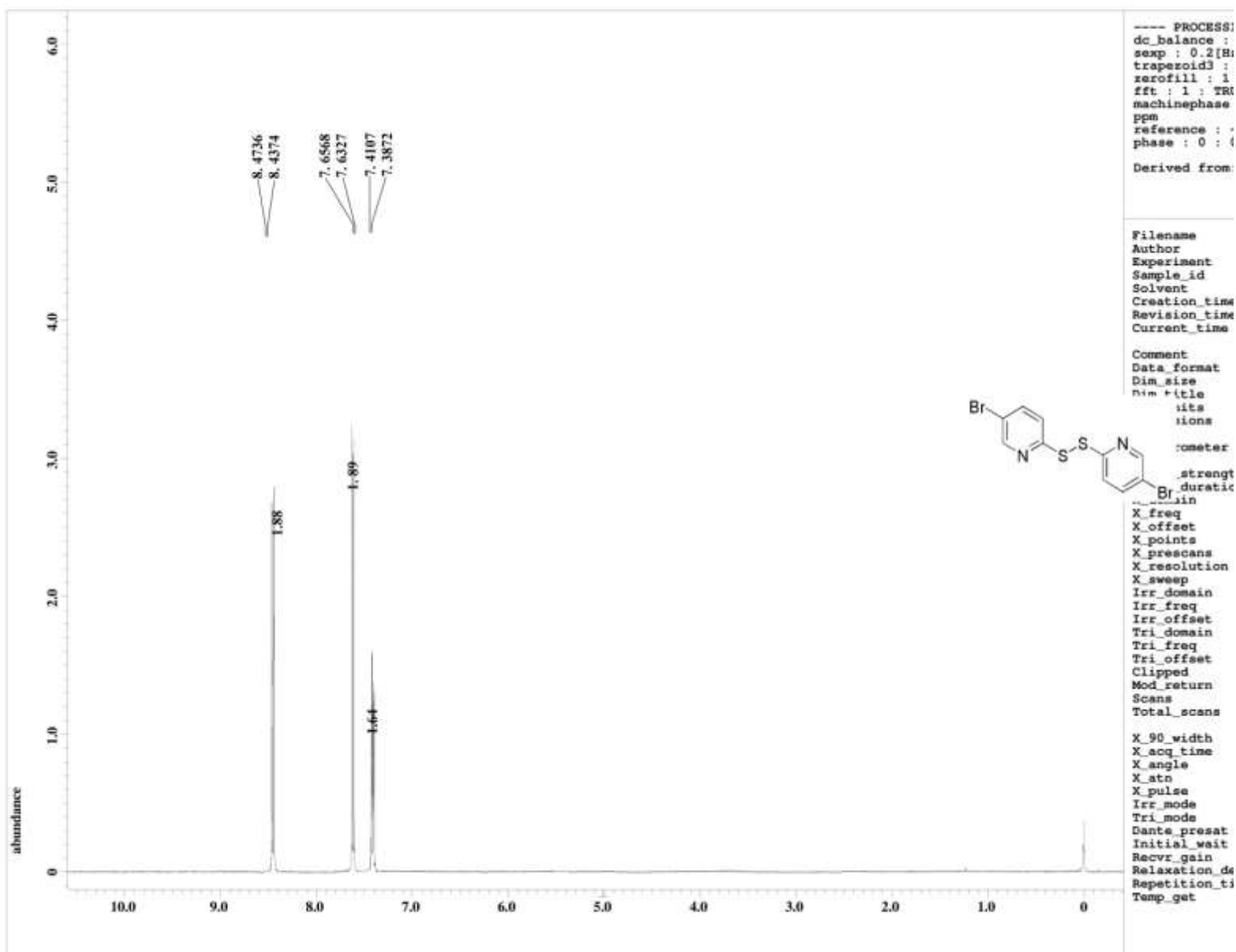
HRMS of Bis-(2-carboxyphenyl) disulfide **2q**



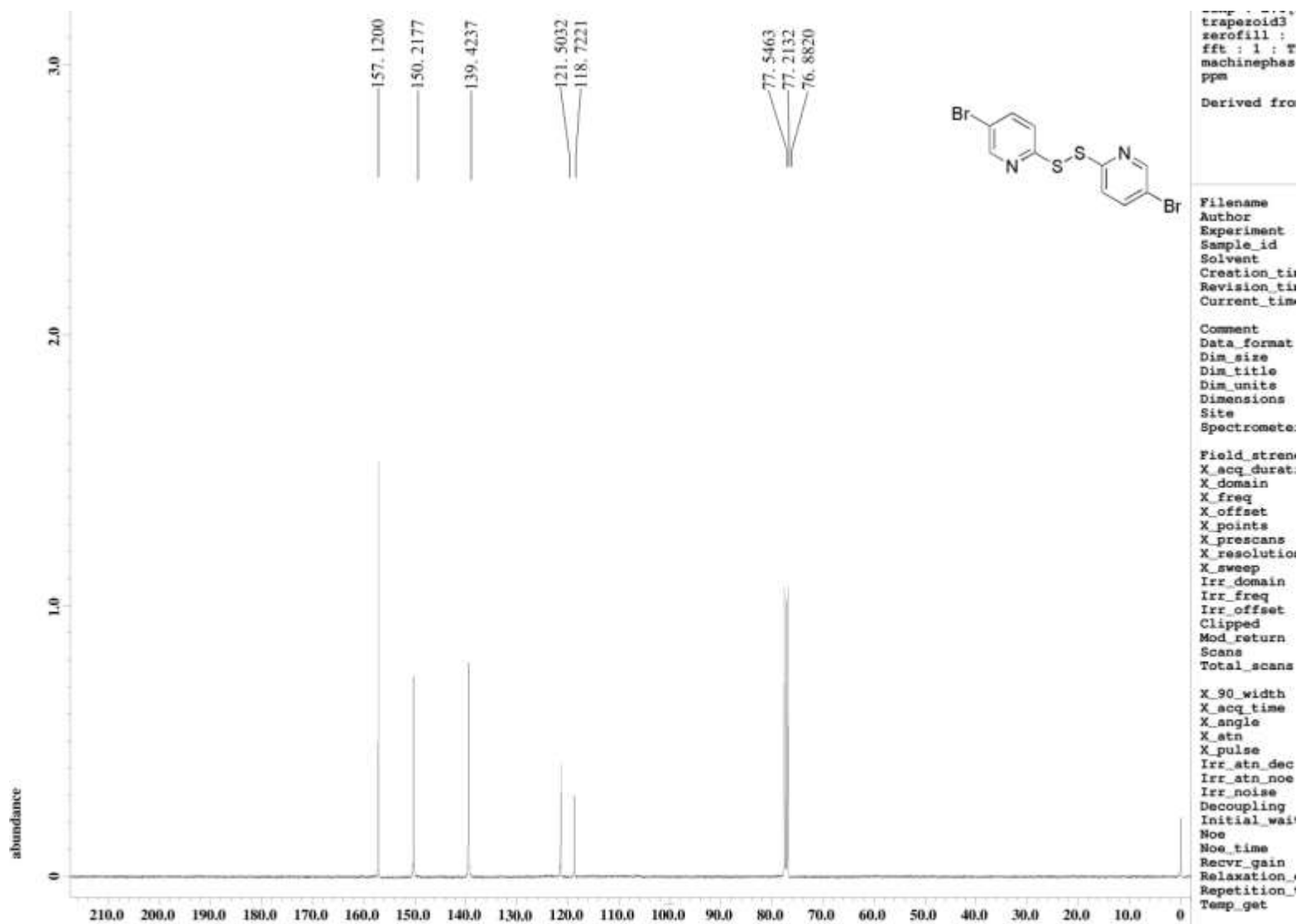
¹H NMR (400 MHz, CDCl₃) of 3,3'-dipyridyl disulfide **2s**



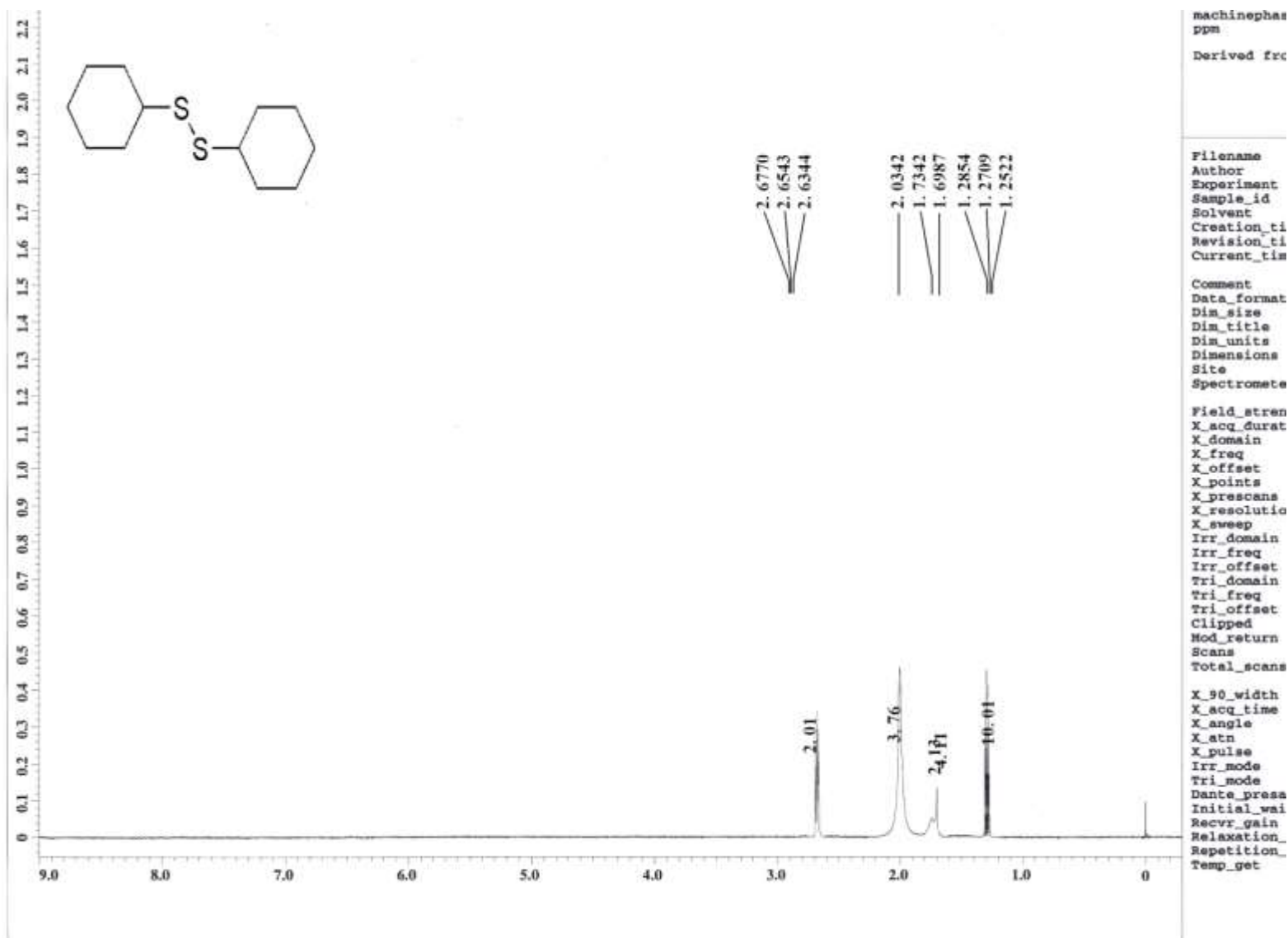
^{13}C NMR (100 MHz, CDCl_3) of 3,3'-dipyridyl disulfide **2s**



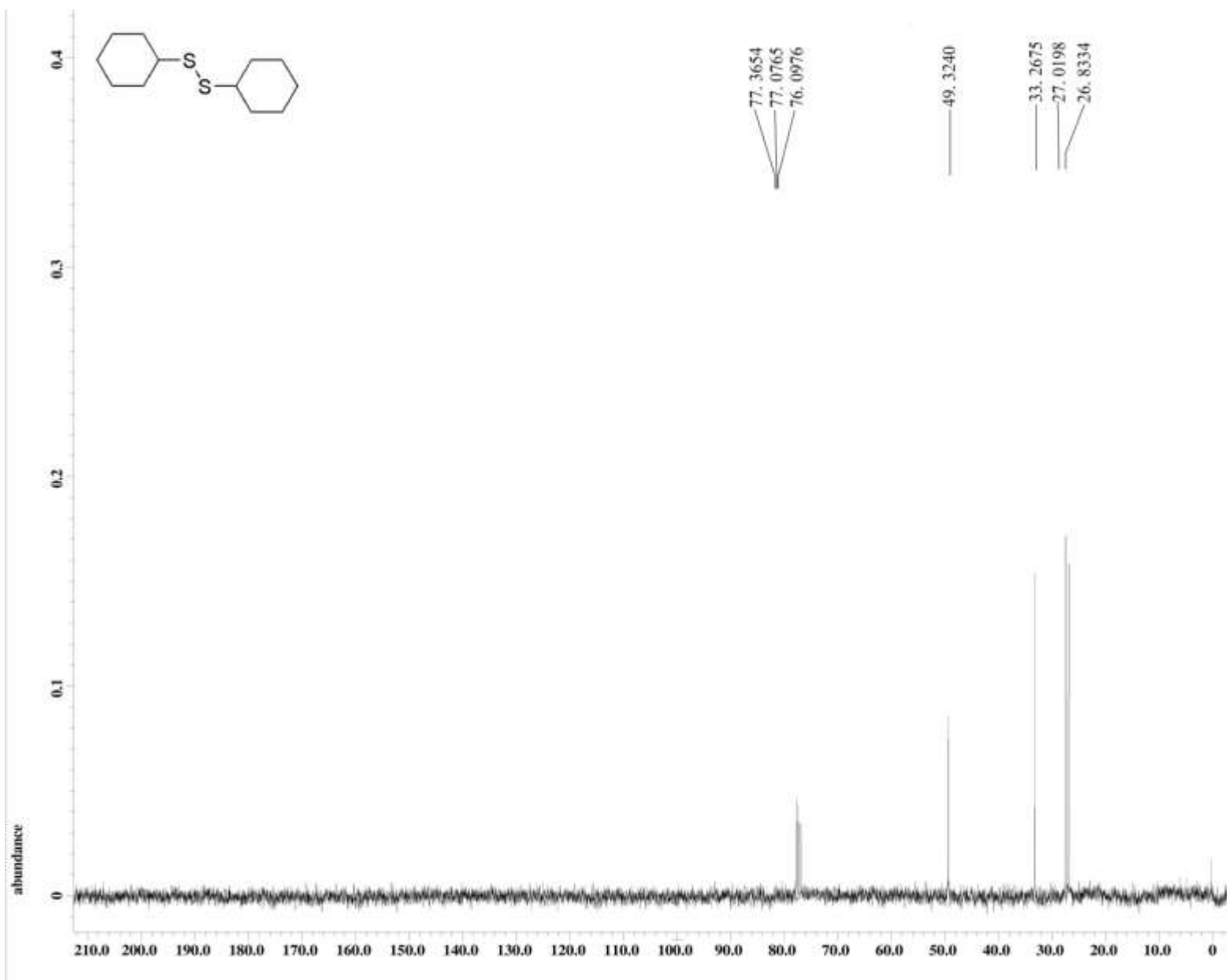
^1H NMR (400 MHz, CDCl_3) of 5,5'-Dibromo-2,2'-dipyridyl disulfide 2t



^{13}C NMR (100 MHz, CDCl_3) of 5,5'-Dibromo-2,2'-dipyridyl disulfide **2t**



¹H NMR (400 MHz, CDCl₃) of Dicyclohexyl disulfide **2u**



^{13}C NMR (100 MHz, CDCl_3) of Dicyclohexyl disulfide **2u**