SUPPORTING INFORMATION

Hypervalent Iodine Mediated Intramolecular Cyclization of Thioformanilides: Expeditious Approach to 2-substituted Benzothiazoles

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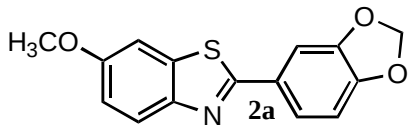
General Remarks:

Commercial reagents and all solvents were analytically pure grade and were used without further purification unless otherwise indicated. Anhydrous conditions were not required for this reaction. ^{1}H and ^{13}C NMR spectra were recorded in deuterated $CDCl_3$. Chemicals shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (δ 0.0) as an internal standard. Coupling constants (*J*) are reported to the nearest 0.1 Hz. The following abbreviations are used to describe multiplicities, s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Low-resolution mass spectra (ESI-MS) and HRMS were recorded using electronspray ionisation (ESI). Melting points were reported and are uncorrected. Elemental analyses were performed on elemental analyzer. Column chromatography was carried out using 60-120 mesh silica gel with eluents as indicated. Thin-layer chromatography (TLC) was performed using Merck 60 F-254 silica gel plates.

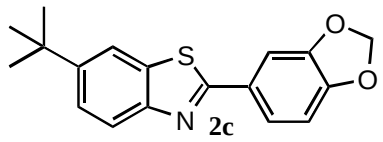
General procedure for the preparation of substituted 2-aryl benzothiazole (**2a**-**h**): Dess-Martin periodinane (5.5 mmol) was added to a stirred solution of thioformanilide (5.0 mmol) in CH_2Cl_2 at room temperature. The progress of the reaction was monitored by TLC. After completion, it was washed diluted with H_2O (2 x 5ml) and the reaction mixture was extracted with CH_2Cl_2 (2 x 10ml). The combined organic phase was dried with anhydrous Na_2SO_4 and the solvent was removed in *vacuo*, to afford the crude product which was purified by column chromatography on silica gel using petroleum ether: EtOAc, 8:1 as eluent to give 2-arylbenzothiazole (85-95%).



2a

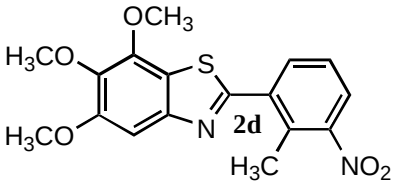
m.p. 164-166 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 3H), 6.02 (s, 2H), 6.83 (d, 1H, *J* = 8.3Hz), 7.02 (dd, 1H, *J* = 2.26 Hz), 7.25 (1H, d, *J* = 3.0 Hz), 7.48-7.58 (m, 2H), 7.85 (d, 1H, *J* = 9.0Hz). ^{13}C NMR (75 MHz): δ 55.8, 101.6, 104.4, 107.3, 108.6, 115.4, 122.0, 123.5, 128.3, 136.3, 148.4, 148.7, 149.8, 157.7. MS (EI): m/z (%) = 285 (M^{+}, 100), 270 (80),

242 (15), 143 (13), 95 (20). Anal. Calcd for $C_{15}H_{11}NO_3S$: C, 63.14; H, 3.88; N, 4.90; S, 11.24. Found: C, 63.05; H, 3.82; N, 4.96; S, 11.15.



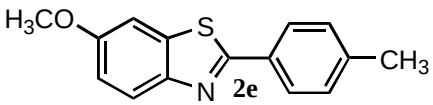
2c

m.p. 97-99 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9H), 6.04 (s, 2H), 6.85-6.87(d, 1H, *J* = 7.9 Hz), 7.46-7.49(dd, 1H, *J* = 7.9 Hz), 7.53-7.56 (dd, 1H, *J* = 9.82 Hz), 7.58-7.60 (m, 1H), 7.80-7.82 (m, 1H) 7.86-7.89 (m, 1H). ^{13}C NMR (75 MHz): δ 29.67, 31.56, 101.65, 107.49, 108.60, 117.59, 122.24, 122.30, 124.40, 128.30, 134.93, 148.34, 148.49, 152.03, 166.90. MS (EI): m/z (%) = 311 (M^+, 10), 294 (40), 178 (20), 164 (40), 155 (50), 148 (85), 71 (38), 43 (100). Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.43; H, 5.50; N, 4.50; S, 10.29. Found: C, 69.35; H, 5.48; N, 4.44; S, 10.20.



2d

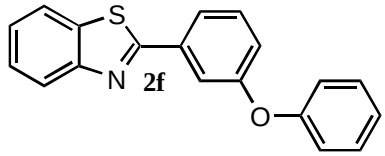
m.p. 163-165 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 3H), 3.92 (s, 3H), 3.98 (s, 3H), 7.34 (s, 1H), 7.41-7.47 (m, 1H), 7.82-7.88 (m, 2H). ^{13}C NMR (75 MHz): δ 16.7, 56.3, 60.7, 61.5, 100.9, 125.2, 126.6, 131.6, 134.2, 136.1, 140.1, 146.6, 150.0, 151.8, 154.3, 165.1. MS (ESI): m/z (%) = 361 (M^+, 100), 101 (80), 79 (35). Anal. Calcd for $C_{17}H_{16}N_2O_5S$: C, 56.65; H, 4.47; N, 7.77; S, 8.89. Found: C, 56.59; H, 4.42; N, 7.73; S, 8.84.



2e

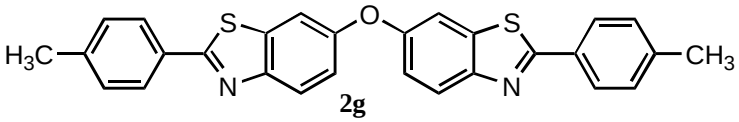
m.p. 99-101 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 3.90 (s, 3H), 7.00-7.05 (dd, 1H, *J* =

12.08 Hz), 7.22-7.29 (m, 3H), 7.86-7.93 (m, 3H). ^{13}C NMR (75 MHz): δ 21.38, 55.71, 104.20, 115.40, 123.47, 127.10, 129.60, 131.08, 136.27, 140.83, 148.72, 157.62, 165.68. MS (ESI): m/z (%) = 256 (M^+, 42), 142 (35), 101 (100), 79 (40). Anal. Calcd for $C_{15}H_{13}NOS$: C, 70.56; H, 5.13; N, 5.48; S, 12.55. Found: C, 70.51; H, 5.11; N, 5.44; S, 12.51.



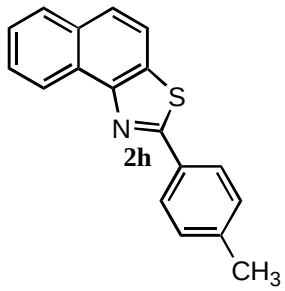
2f

m.p. 87-88 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.04-7.18 (m, 4H), 7.35-7.53 (m, 5H), 7.74-7.82 (m, 2H), 7.89 (d, 1H, *J* = 7.5Hz), 8.06 (d, 1H, *J* = 8.3Hz). ^{13}C NMR (75 MHz): δ 117.7, 119.1, 121.2, 121.6, 122.4, 123.4, 123.7, 125.3, 126.4, 129.9, 130.4, 135.1, 154.1, 156.9, 158.0 MS (ESI): m/z (%) = 303 (M^+, 100), 239 (25), 141 (10). Anal. Calcd for $C_{19}H_{13}NOS$: C, 75.22; H, 4.32; N, 4.61; S, 10.56. Found: C, 75.14; H, 4.28; N, 4.57; S, 10.48.



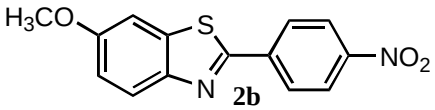
2g

m.p. 216-217 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 3H), 7.18-7.28 (m, 3H), 7.51 (s, 1H), 7.89-8.02 (m, 3H). ^{13}C NMR (75 MHz): δ 21.5, 111.0, 118.7, 124.0, 127.3, 129.7, 130.9, 141.4, 150.3, 155.3. MS (ESI): m/z (%) = 465 (M^+, 55), 145 (100), 102 (78). Anal. Calcd for $C_{28}H_{20}N_2OS_2$: C, 72.38; H, 4.34; N, 6.02; S, 13.80. Found: C, 72.32; H, 4.30; N, 5.94; S, 13.72.



2h

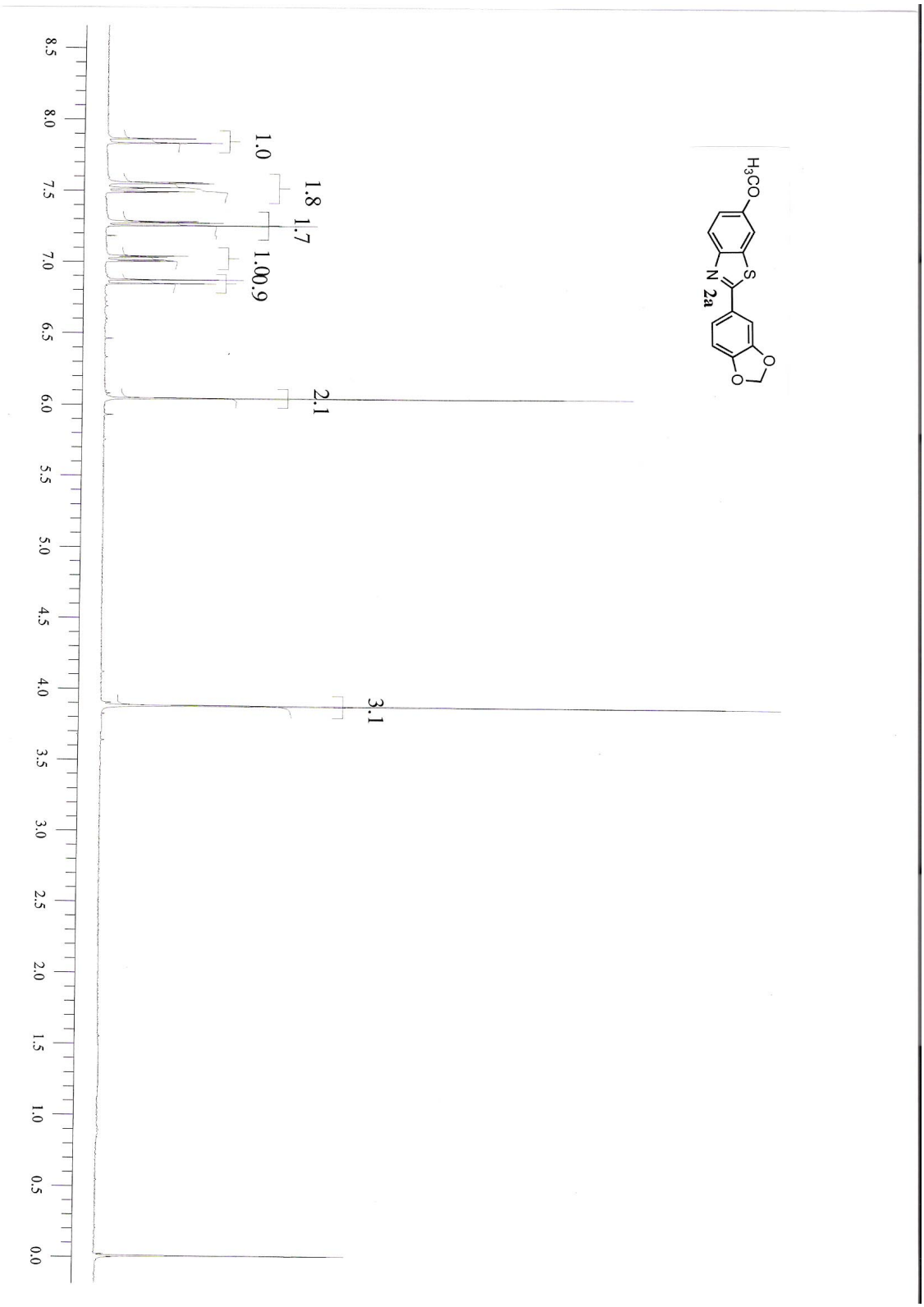
m.p. 78-80 ^{o}C; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H), 7.24-7.30 (m, 2H), 7.51-7.57 (m, 1H), 7.61-7.68 (m, 1H), 7.72-7.77 (m, 1H), 7.86-7.92 (m, 2H), 8.04-8.08 (m, 2H), 8.88 (d, 1H, *J* = 8.3 Hz). ^{13}C NMR (75 MHz): δ 21.46, 118.91, 124.05, 125.62, 125.99, 126.80, 127.22, 128.00, 128.75, 129.65, 131.39, 131.44, 132.05, 140.88, 150.43, 167.21. MS (ESI): m/z (%) = 276 (M^+, 100), 193 (10), 145 (15), 126 (15). Anal. Calcd for $C_{18}H_{13}NS$: C, 78.51; H, 4.76; N, 5.08; S, 11.64. Found: C, 78.43; H, 4.69; N, 5.05; S, 11.62.



2b

m.p. 214-216 ^{o}C (lit. m.p.[(a)] 216-217 ^{o}C); ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3H), 7.09-7.14 (dd, 1H, *J* = 9.06 Hz), 7.34-7.36 (d, 1H, *J* = 2.26 Hz), 7.95-7.99 (d, 1H, *J* = 9.06 Hz), 8.19-8.24 (m, 2H), 8.31-8.36 (m, 2H). MS (EI): m/z (%) = 286 (M^+, 100), 271 (32), 240 (28), 225 (30), 197 (30). Anal. Calcd for $C_{14}H_{10}N_2O_3S$: C, 58.73; H, 3.52; N, 9.78; S, 11.20. Found: C, 58.69; H, 3.51; N, 9.73; S, 11.18.

(a) *J. Med. Chem.* **1996**, *39*, 3375-3384.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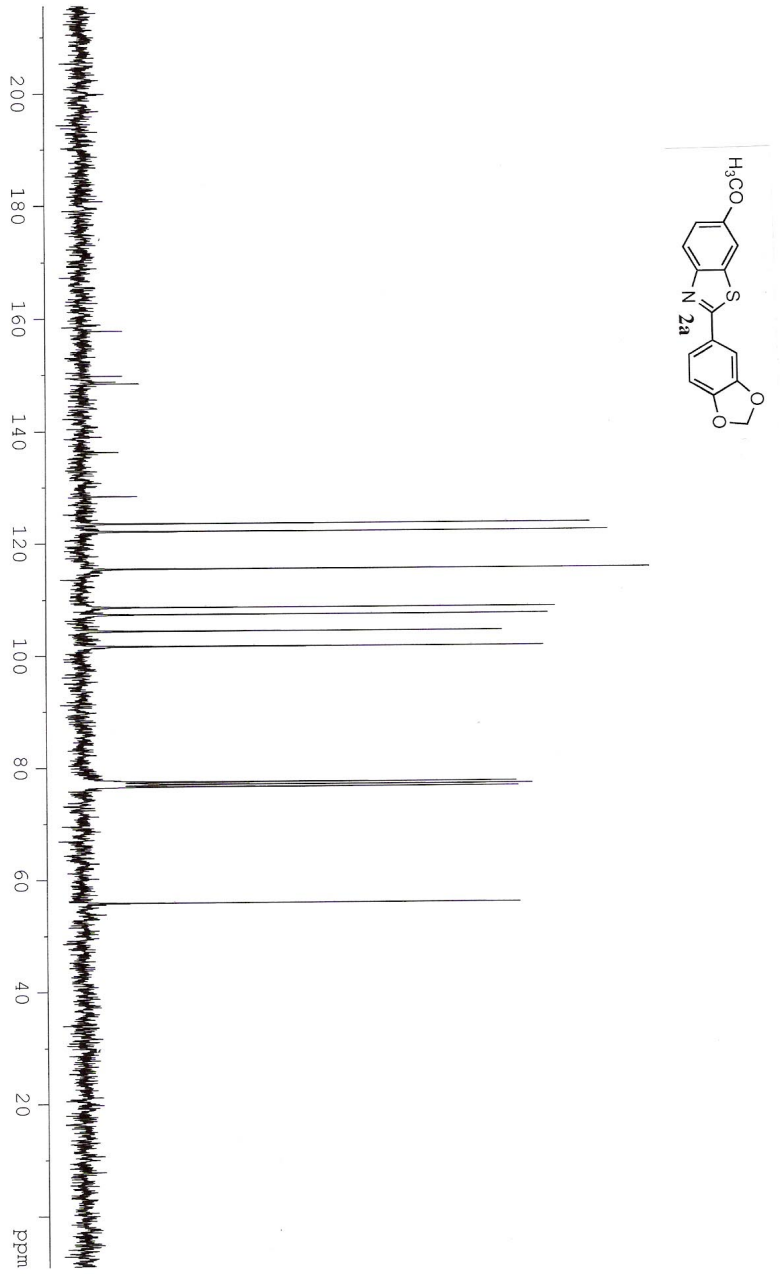
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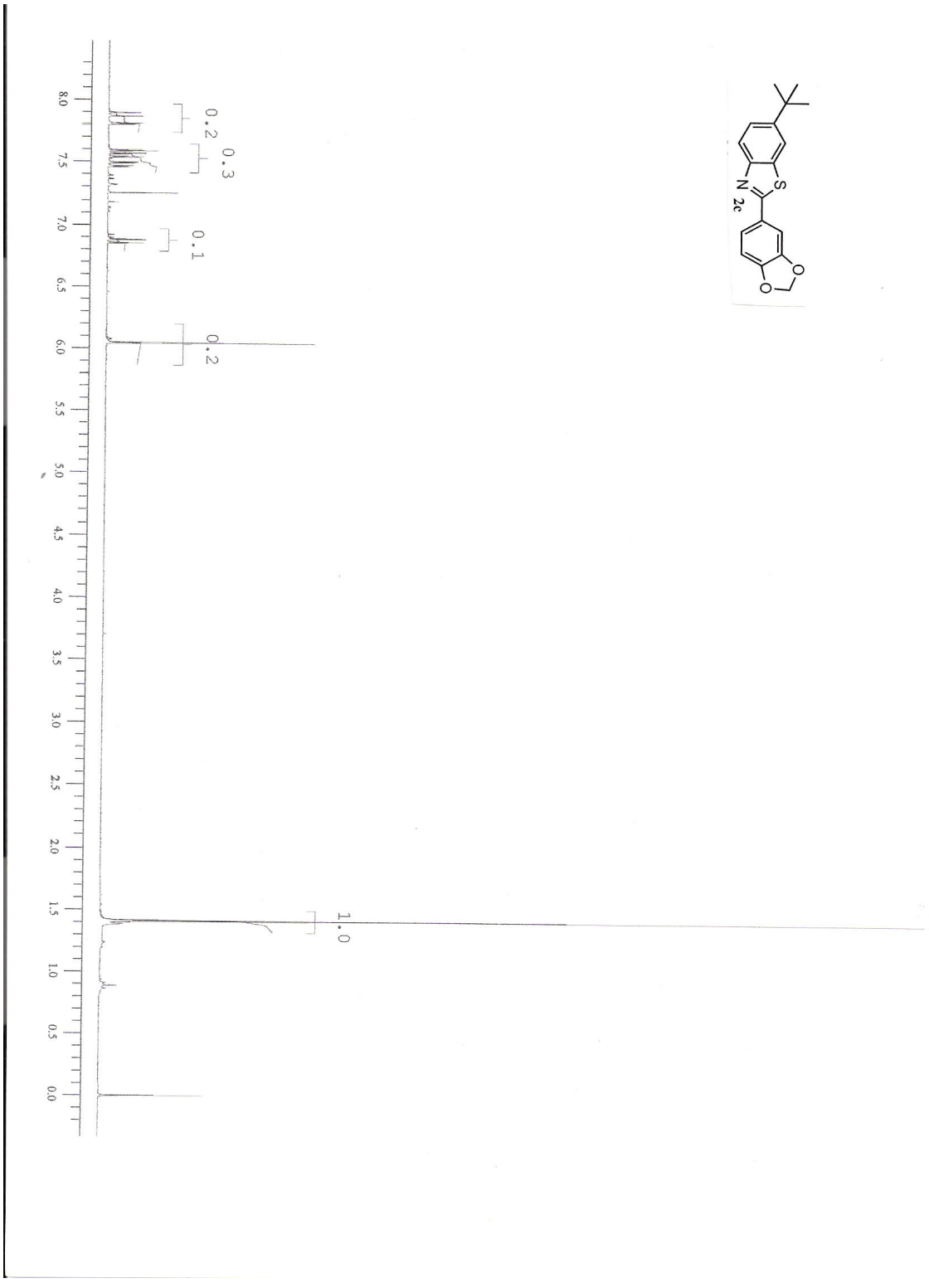
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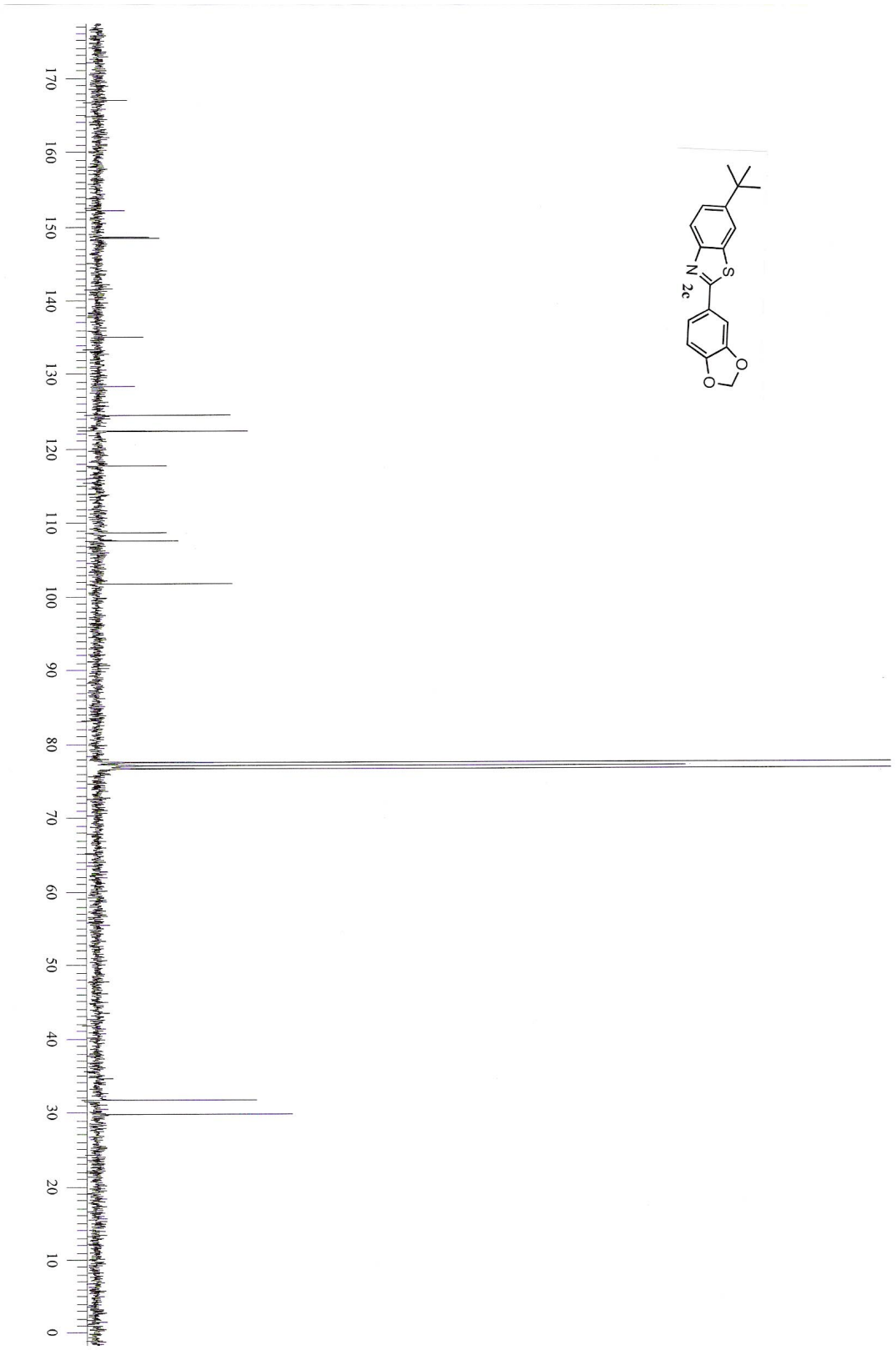
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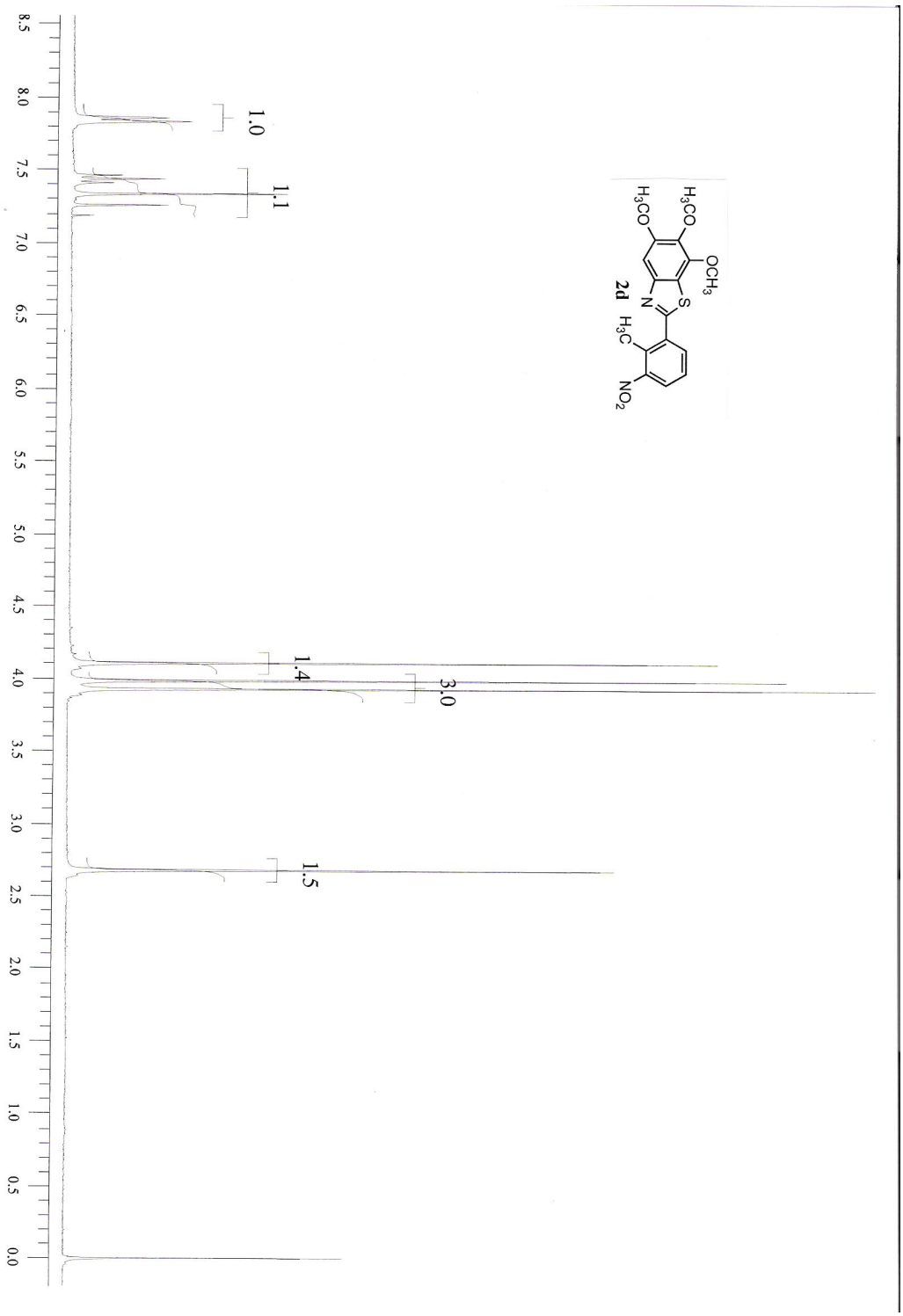
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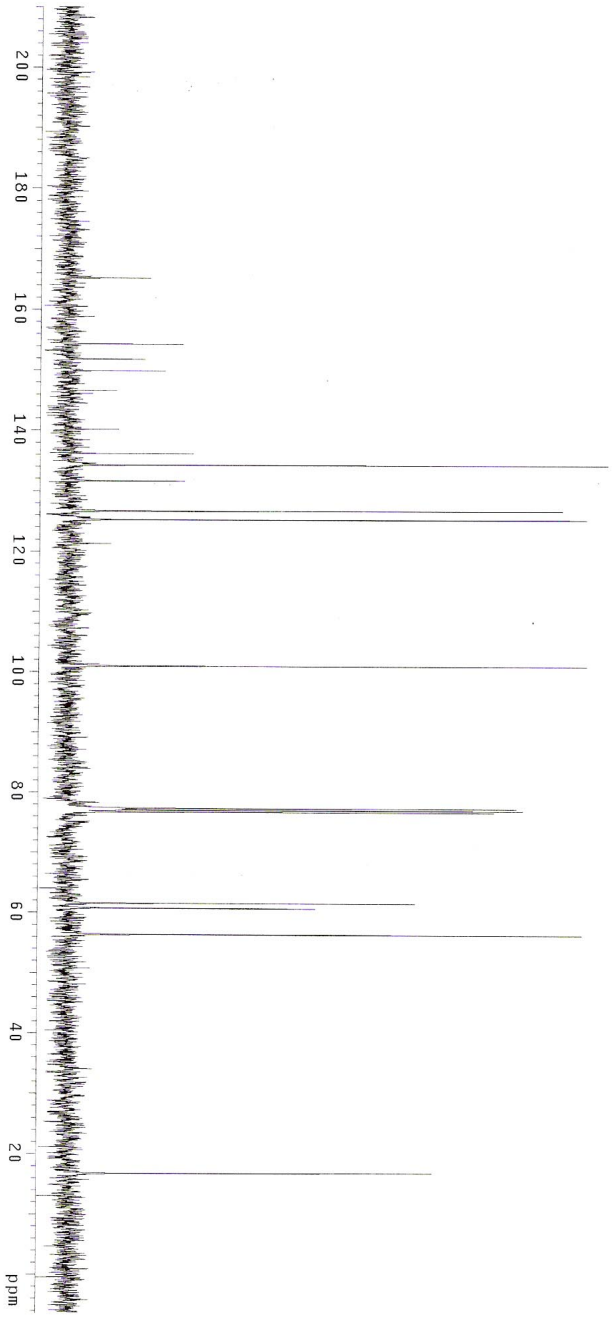
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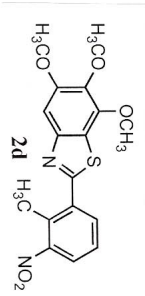
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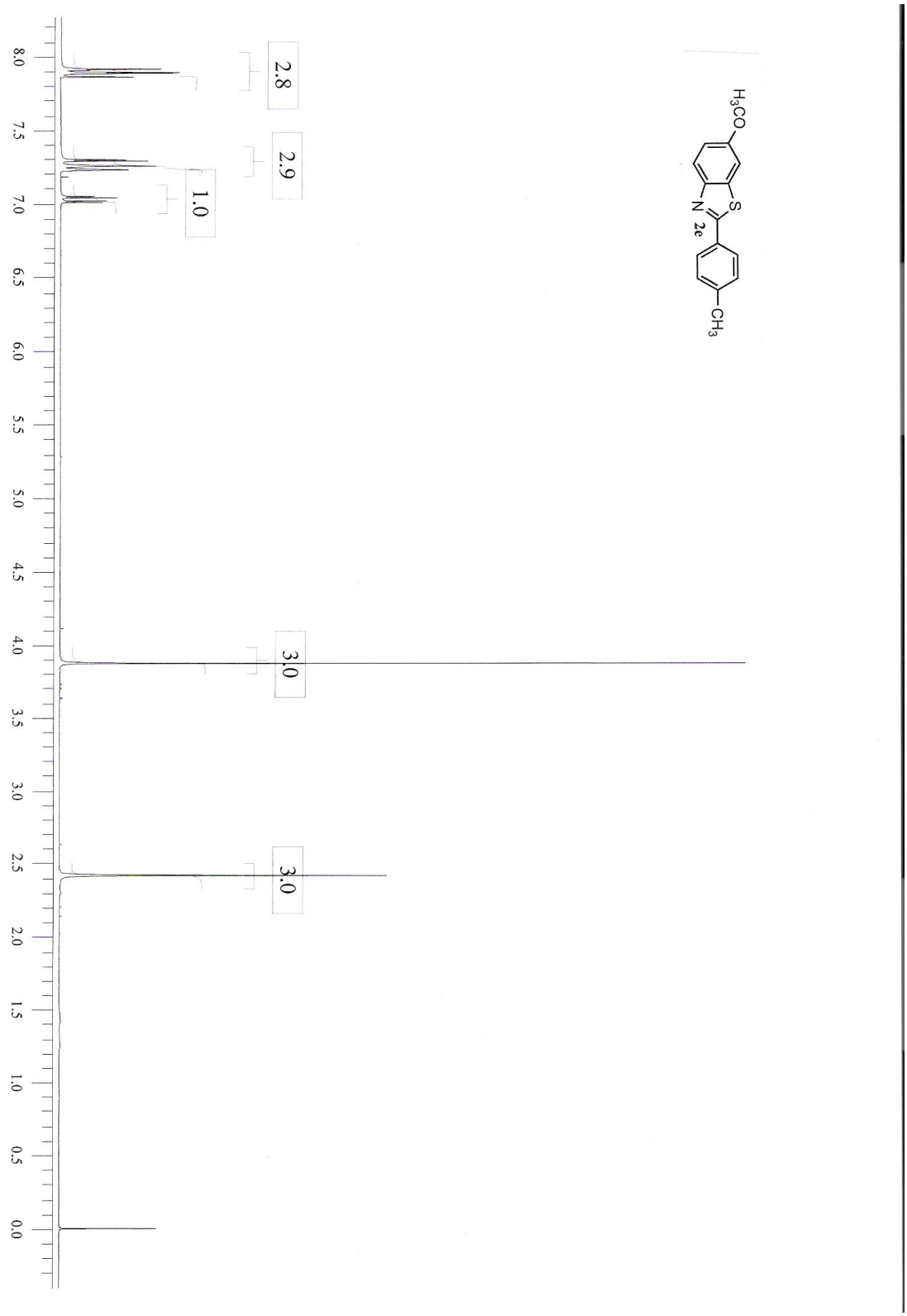
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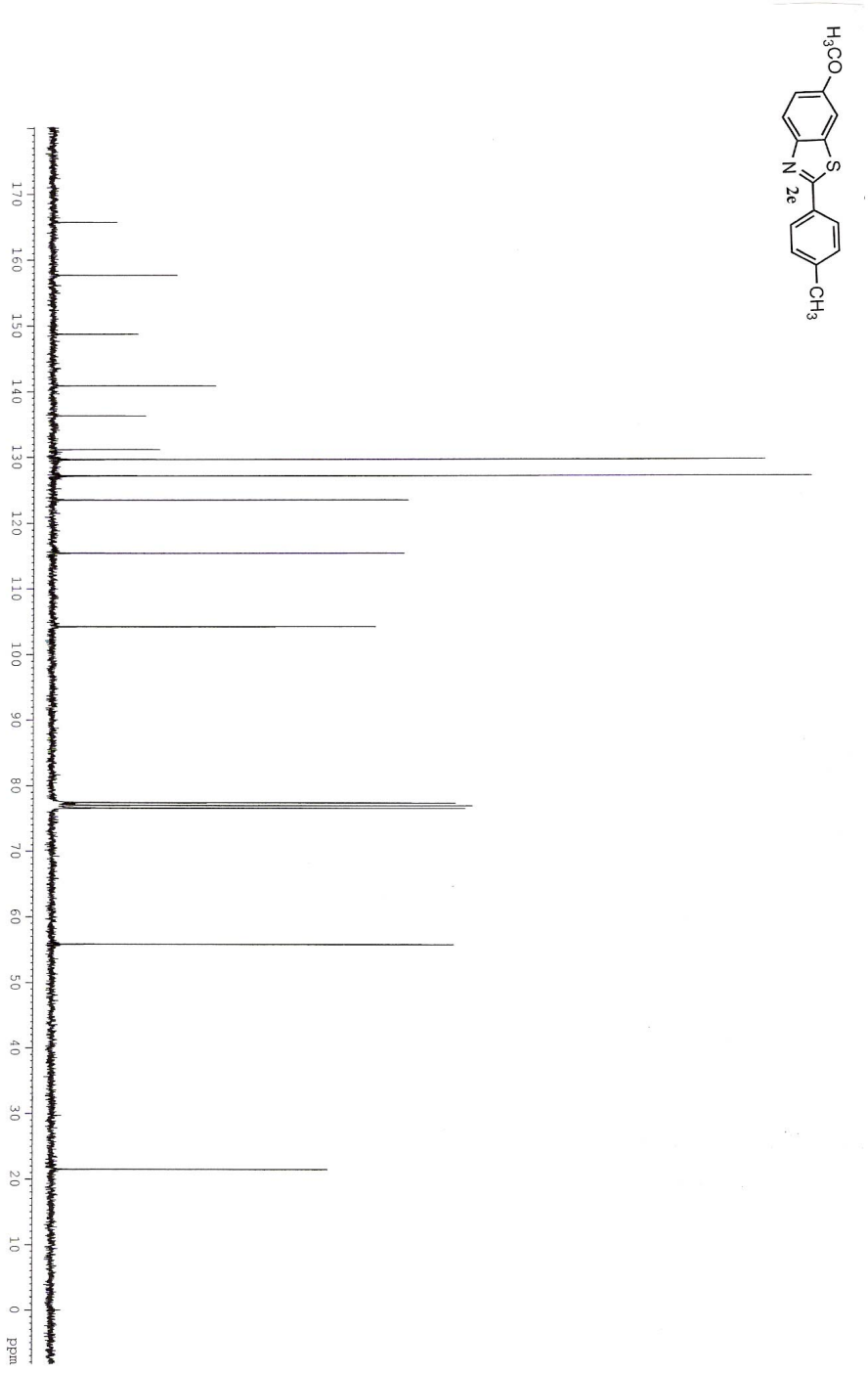
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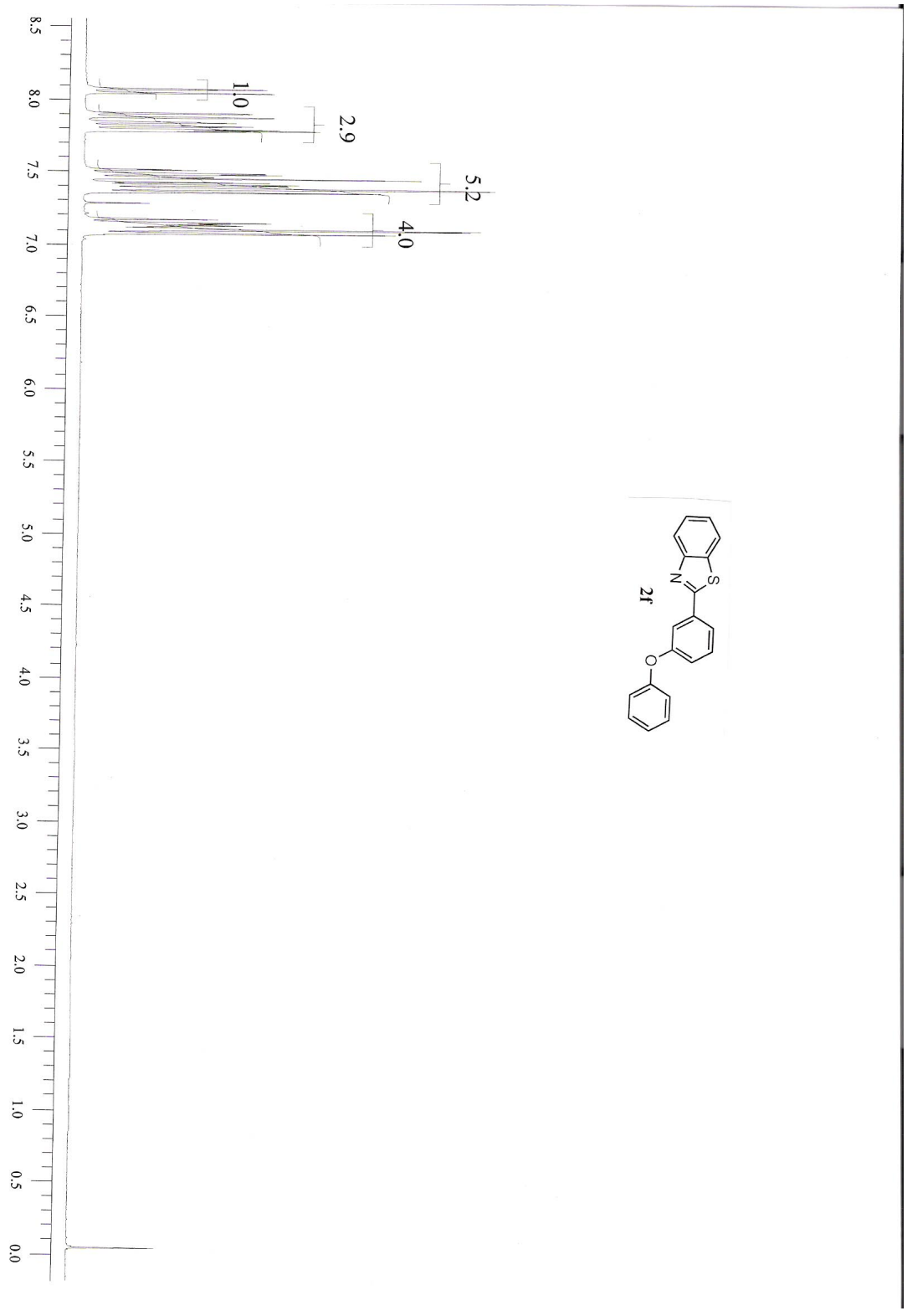
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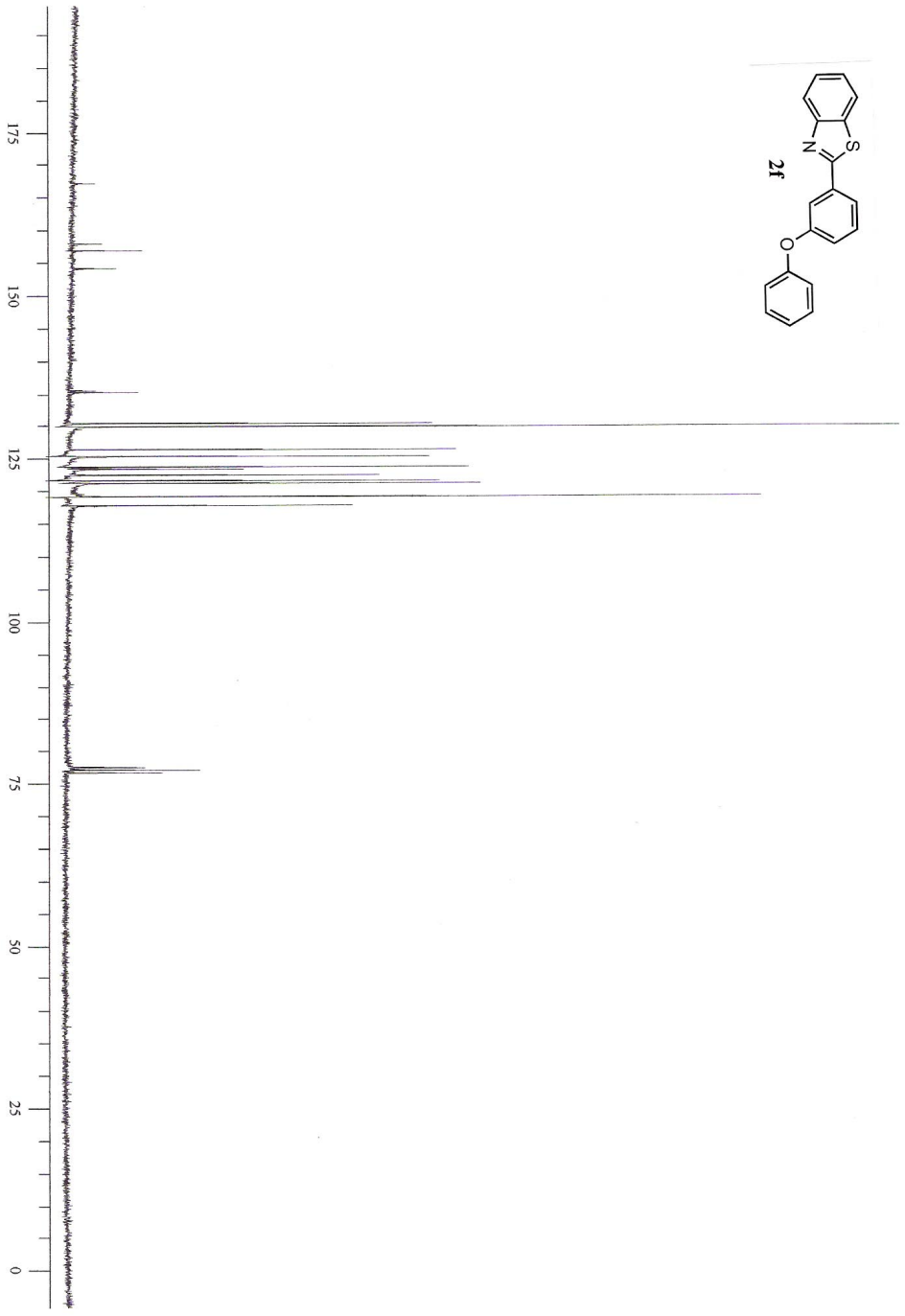

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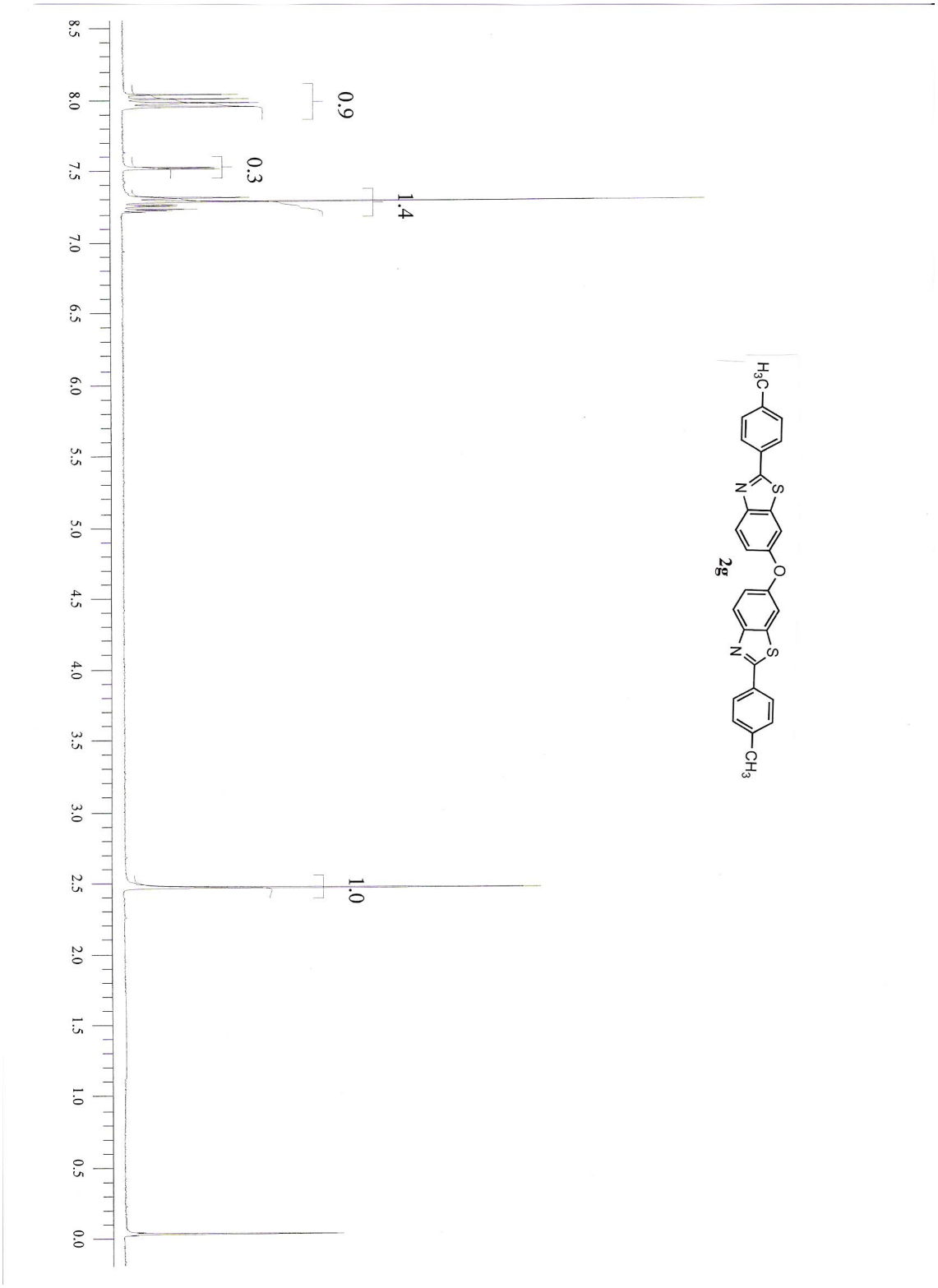
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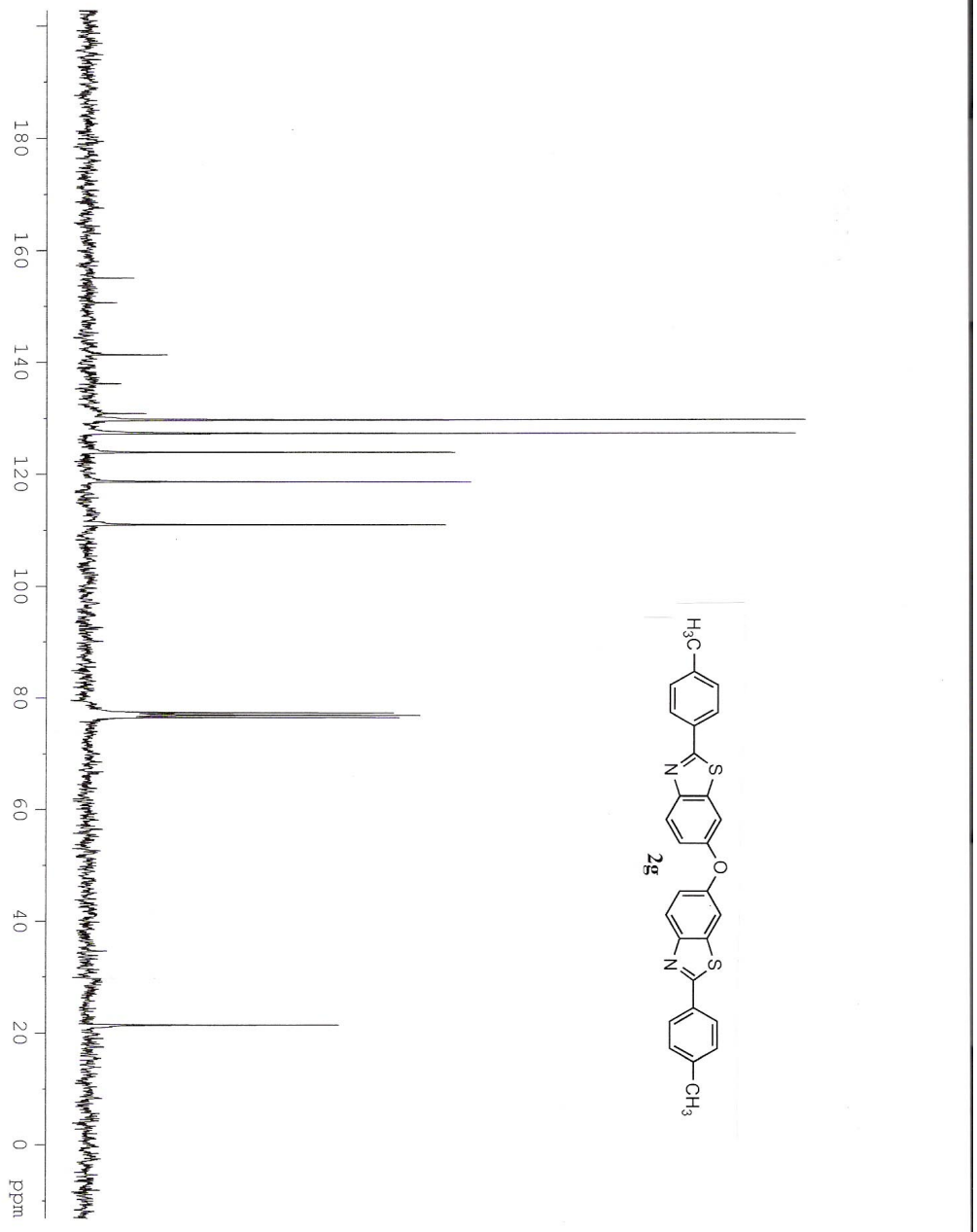
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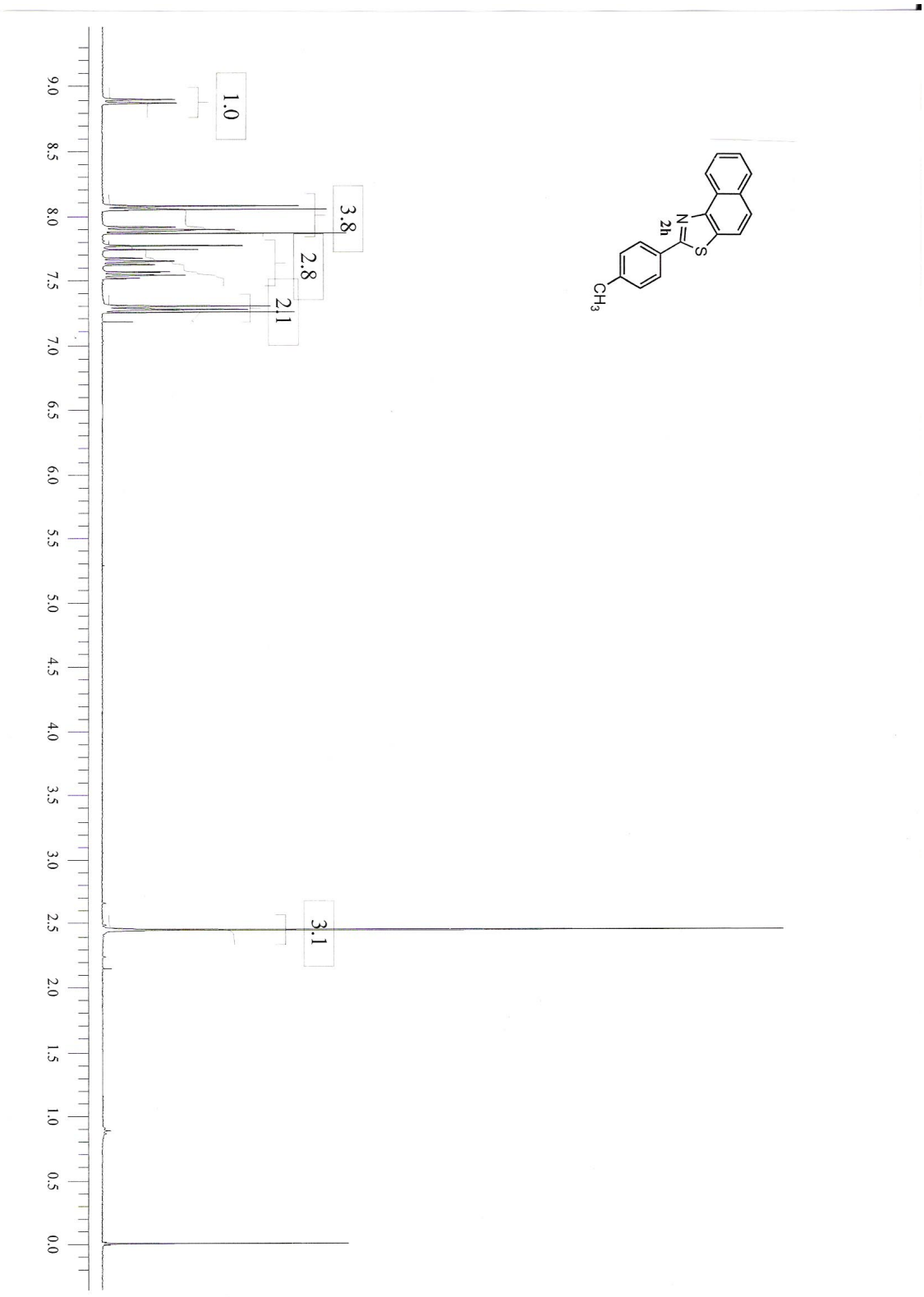
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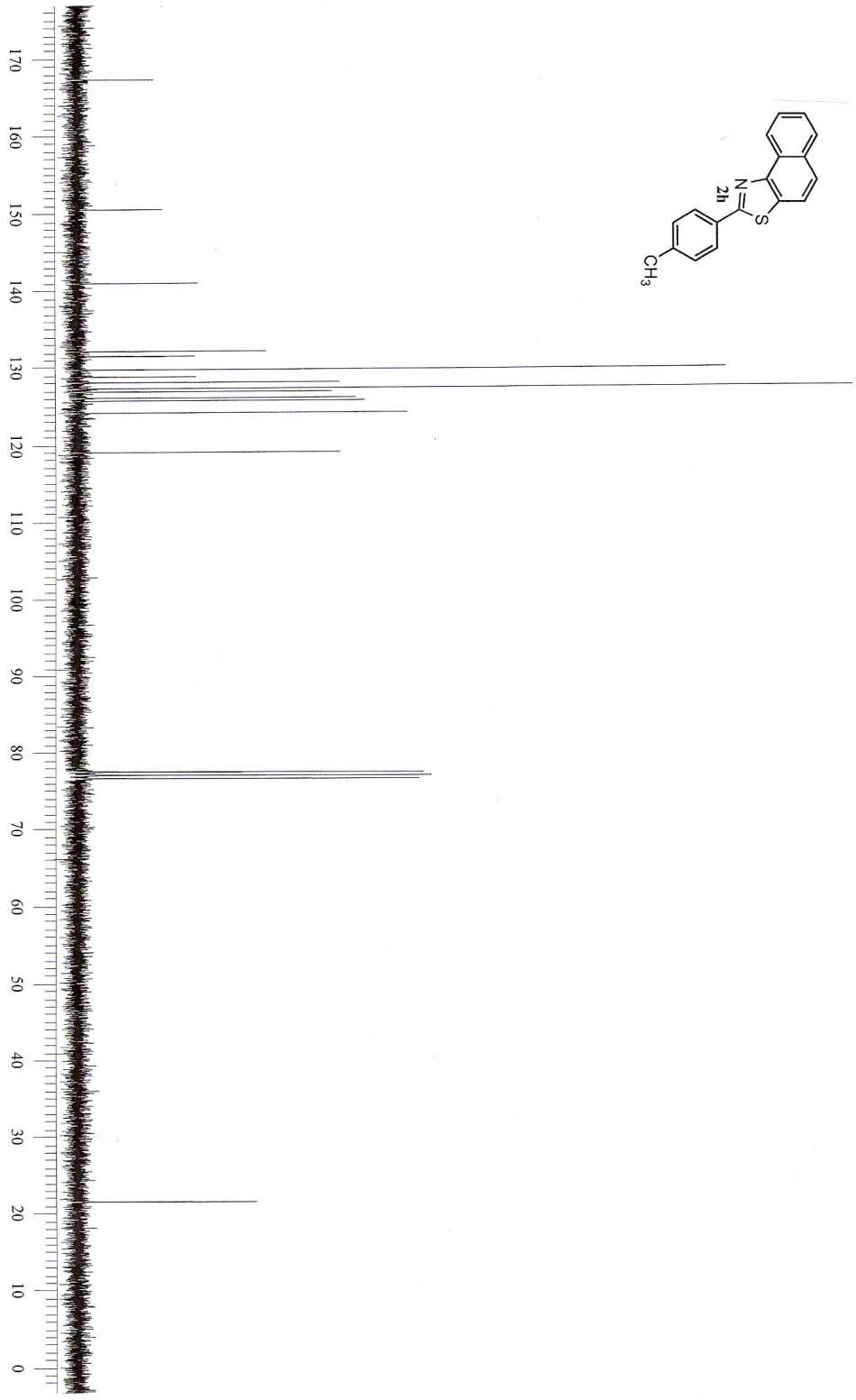
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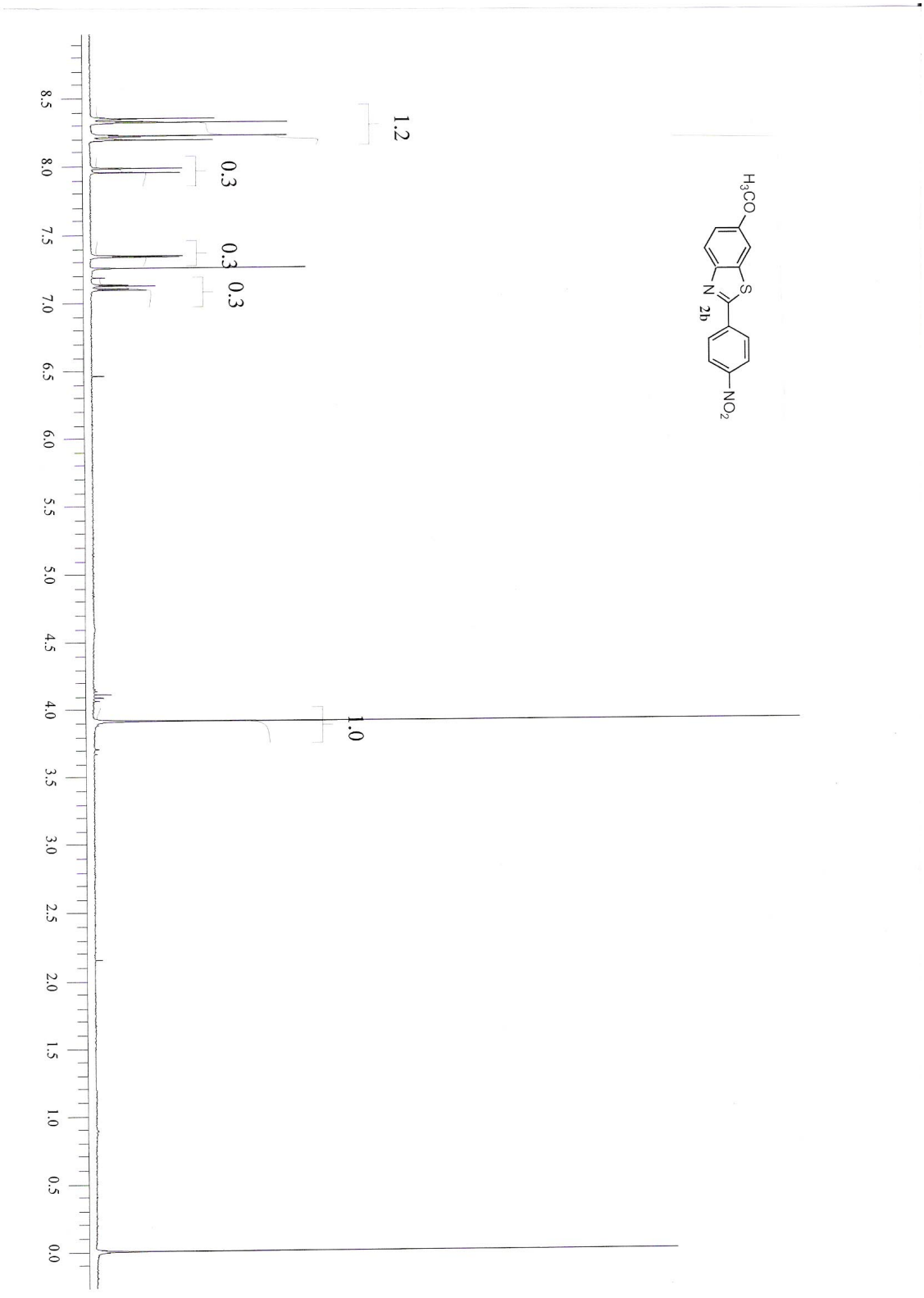
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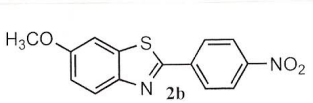

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