Electronic Supplementary Information

Silver–Mediated Oxidative Vinylic C-H Bond Sulfenylation of Enamides with Disulfides

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1. General information

Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). GC-MS (EI) were collected on a Agilent 7890-5973 instrument. Elemental analyses were performed at the Analytical Laboratory of the Xiangtan University. Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ

77.16 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

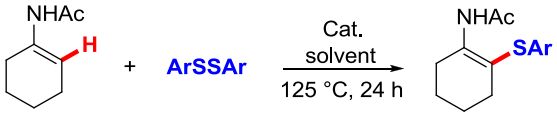
Reagents: Unless stated otherwise, substituted disulfides were synthesized from the corresponding thiophenol with H_2O_2 in CH_3CN/H_2O.[1] Enamides were synthesized starting from ketones according to the method reported by S. M. Weinreb *et. al.*[2] AgOAc and other reagents were purchased and used directly.

2. General experimental procedures for the synthesis of 3a-3h，4b-4i, 5a-5e

An oven-dried reaction vessel was charged with enamide **1** (0.2 mmol), dichloroethane (DCE, 0.6 mL), disulfide **2** (0.4 mmol), AgOAc (1.2 equiv, 0.24 mmol) under argon atmosphere. The vessel was sealed and heated at 125°C for 24 h. The resulting mixture was cooled to room temperature, transferred to silica gel column and eluted with petroleum ether and ethyl acetate (4:1) to give the desired sulfenylation products **3**.

3. Detailed optimization of the oxidative vinylic C-H sulfenylation

Table S1 Detailed optimization of the oxidative vinylic C-H sulfenylation



1a **2a** Ar = *p*-Cl-C_6H_4

entry	Cat. (equiv)	solvent	yield [%][b]
1	$Cu(OTf)_2$ (0.1)	DCE	15
2	$Pd(OAc)_2$ (0.1)	DCE	32
3	AgOAc (0.1)	DCE	21
4	AgOAc (1.0)	DCE	76
5	**AgOAc (1.2)**	**DCE**	**82**
6	Ag_2O (1.2)	DCE	17
7	Ag_2CO_3 (1.2)	DCE	36
8[c]	AgOAc (1.2)	DCE	68
9[d]	AgOAc (1.2)	DCE	47

[1] V. Kesavan, D. Bonnet-Delpon, J.-P. Begue, *Synthesis* **2000**, 223-225.

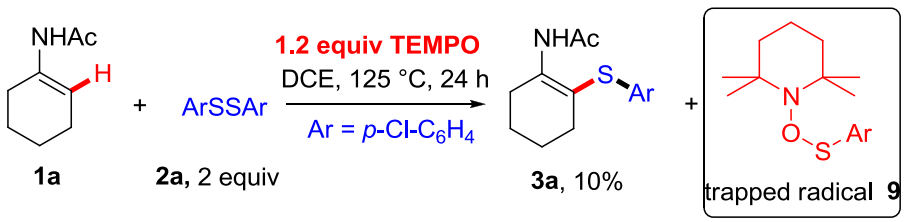
[2] C. Sun, S. M. Weinreb, *Synthesis* **2006**, 3585-3588.

10	AgOAc (1.2)	PhCl	38
11	AgOAc (1.2)	Toluene	44
12	AgOAc (1.2)	THF	26
13	AgOAc (1.2)	*t*-BuOH	14
14	AgOAc (1.2)	DMF	60
15	**CuI (0.1)**	**DCE**	**4**
16	**CuCl (0.1)**	**DCE**	**5**
17	**$CuCl_2$ (0.1)**	**DCE**	**<2**
18	**$Cu(OAc)_2$ (0.1)**	**DCE**	**6**
19	**AgOTf (0.1)**	**DCE**	**12**
20	**$AgBF_4$ (0.1)**	**DCE**	**8**
21	**AgSPh (0.1)**	**DCE**	**<2**
22	**AgCl (0.1)**	**DCE**	**<2**
23[e]	**AgOAc (1.2)**	**DCE**	**11**
24[f]	**AgOAc (1.2)**	**DCE**	**15**

[a] Conditions: **1a** (0.2 mmol), **2a** (2 equiv, 0.4 mmol), solvent (0.6 mL), reacted for 24 h at 125°C under argon atmosphere unless otherwise noted. [b] Isolated yields. [c] 1.5 equiv. of disulfide (**2a**) was used. [d] Reacted at 110 °C. [e] O_2 atmosphere. [f] Air atmosphere.

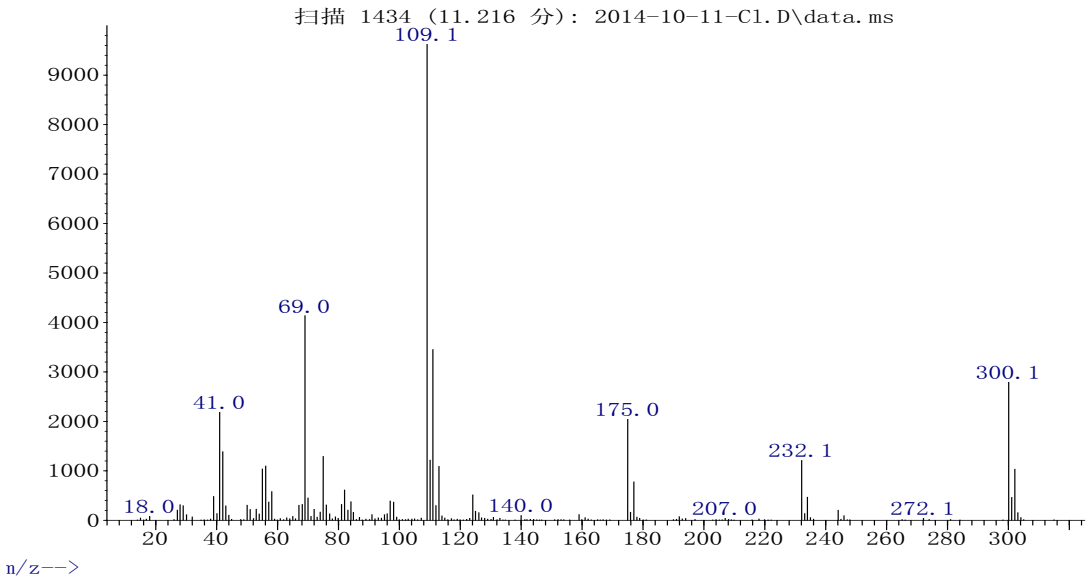
4. Radical trappling experiments

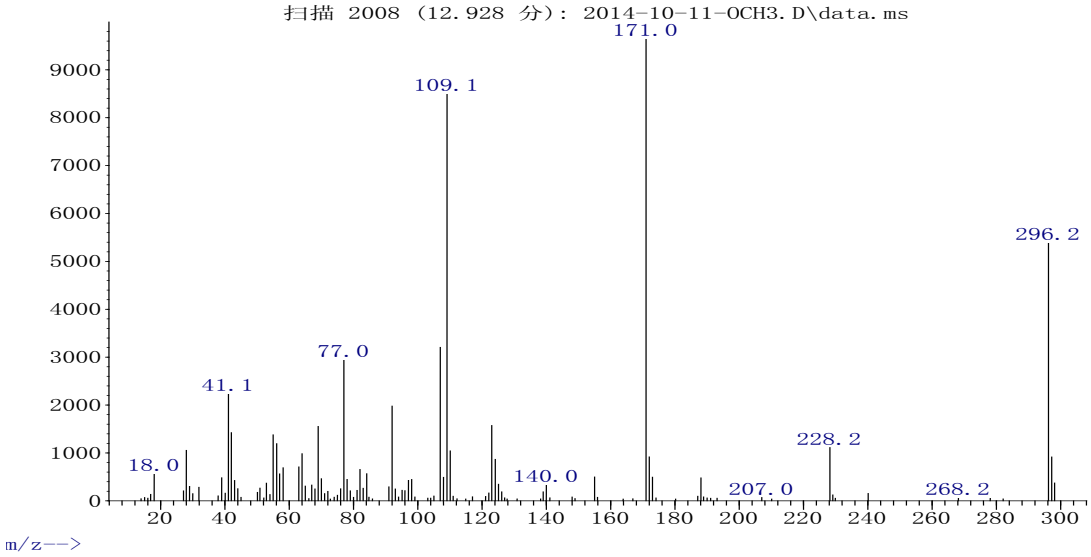
While TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, 1.2 equiv) as radical inhibitor was subjected to the standard procedure, arylsulfide radical (ArS•) was trapped by the TEMPO to afford 4-arylthiooxy-2,2,6,6-tetramethylpiperidine **9a**, **9d** and **9e** determined by the GC-MS. The attempted isolation of these products was failed.

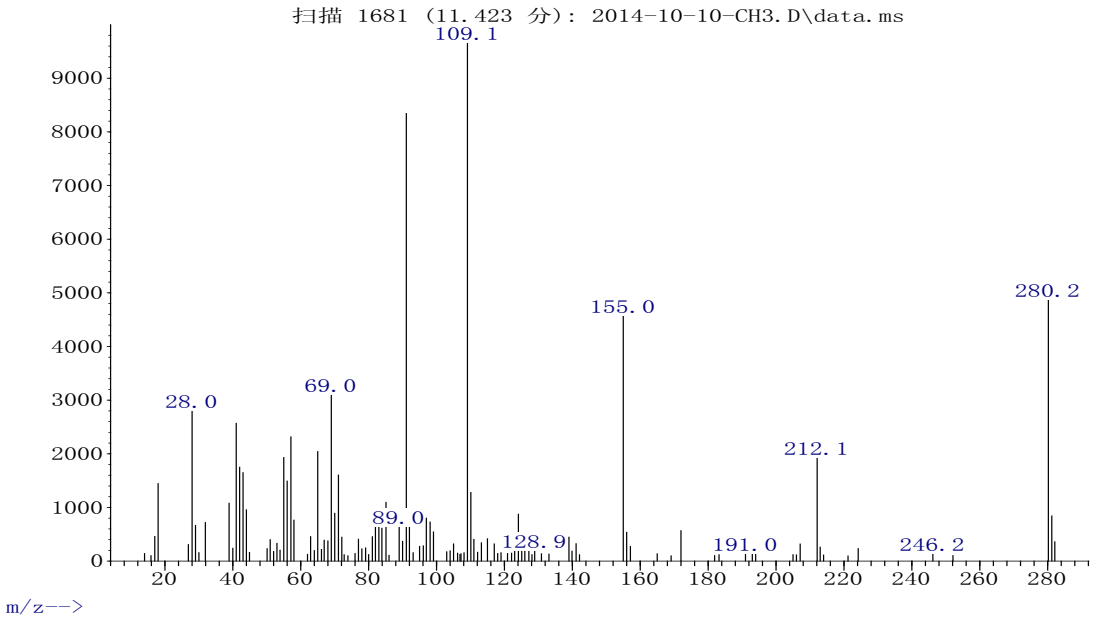


		GC-MS (EI) m/z: $[M+H]^+$	calcd for	found
2a	R = *p*-Cl-C_6H_4	**9a**	**300.1**	**300.1**
2d	R = *p*-CH_3O-C_6H_4	**9d**	**296.2**	**296.2**
2e	R = *p*-CH_3-C_6H_4	**9e**	**280.2**	**280.2**

The GC-MS (EI) of 9a, 9b and 9 were copied c as follow:

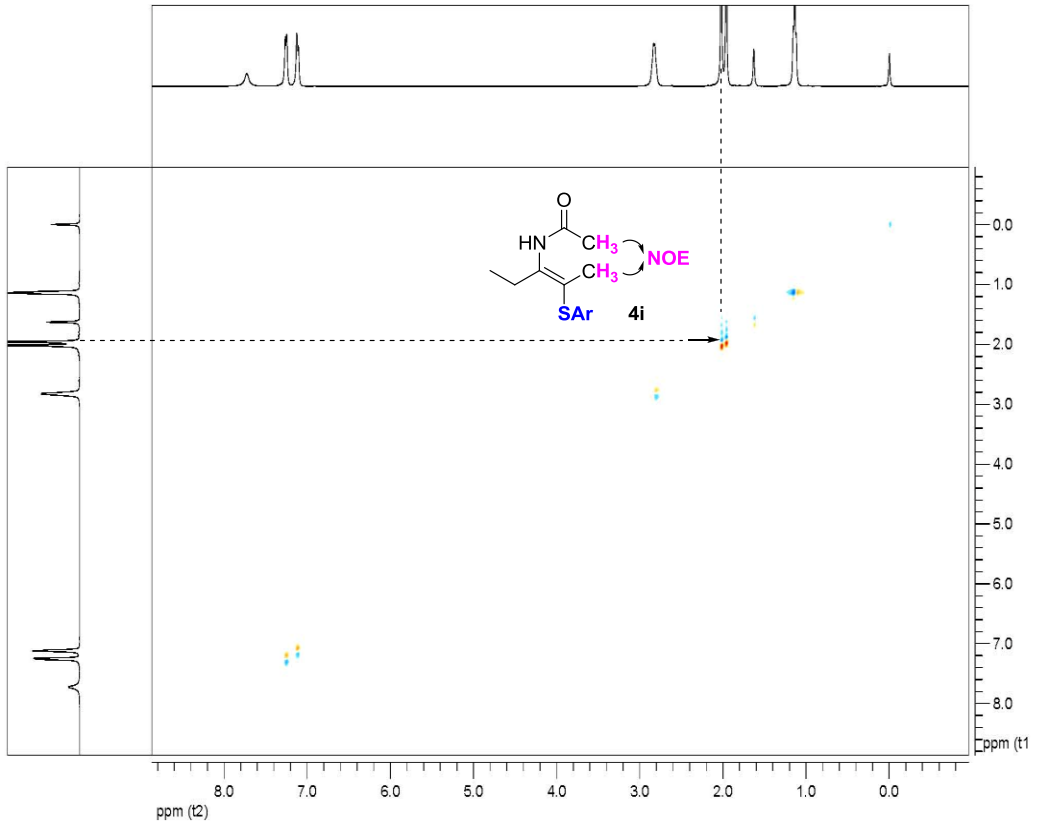

扫描 1434 (11.216 分): 2014-10-11-Cl.D\data.ms
109.1
69.0
41.0
175.0
300.1
232.1
18.0
140.0
207.0
272.1
m/z-->

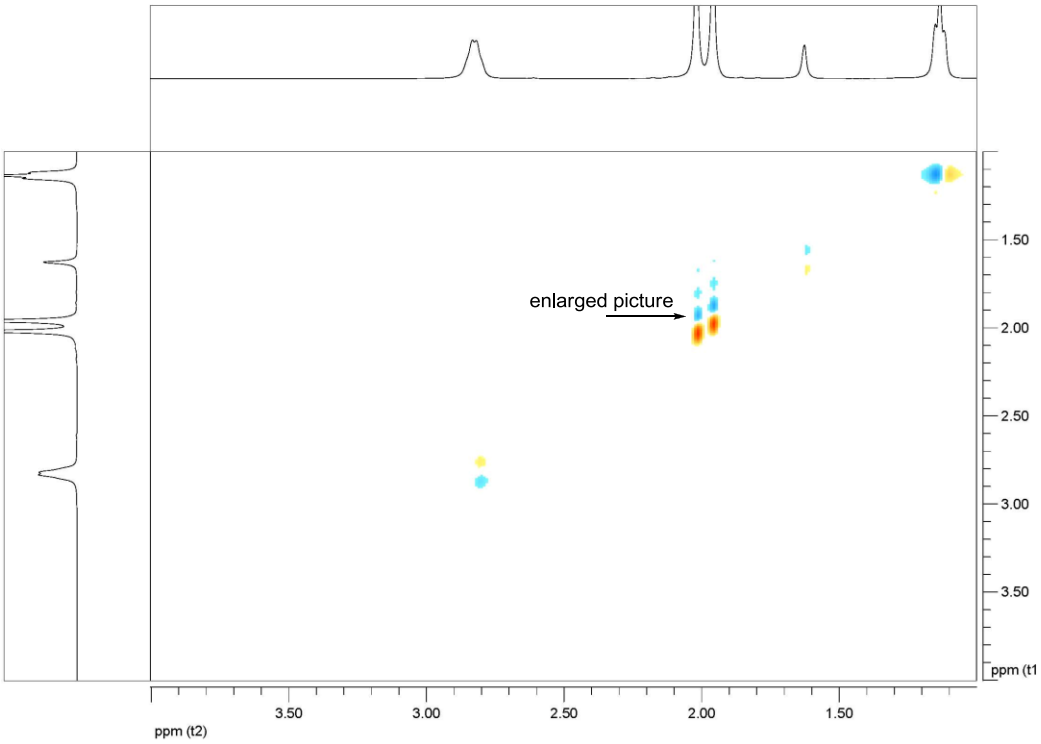

扫描 2008 (12.928 分): 2014-10-11-OCH3.D\data.ms
171.0
109.1
296.2
77.0
41.1
228.2
18.0
140.0
207.0
268.2
m/z-->


扫描 1681 (11.423 分): 2014-10-10-CH3.D\data.ms
109.1
280.2
155.0
69.0
28.0
212.1
89.0
128.9
191.0
246.2
m/z-->

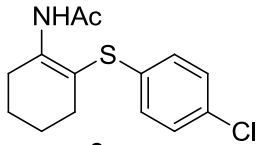
5. The determination of the stereochemistry of poduct 4i

The E configuration of product **4i** was determined by NOE of the adjacent protons on the two methyl groups.



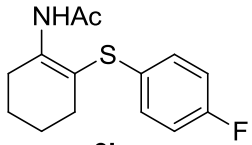


6. Characterization data of products 3a-3h，4b-4i, 5a-5e.



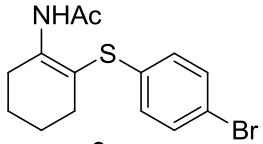
3a

3a: White solid (46.2 mg, 82 % yield); m. p. 130-132℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (s, 1H), 7.26 (d, *J* = 6.8 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 2.89 (s, 2H), 2.22 (s, 2H), 2.01 (s, 3H), 1.73-1.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.21, 142.67, 133.22, 131.86, 129.22, 129.01, 109.78, 30.64, 28.54, 24.56, 23.30, 22.42; MS (EI) m/z (%): 283 (1), 281 (3), 240 (1), 238 (4), 138 (100), 96 (25), 67 (8); IR: 3228 cm^{-1}, 1661 cm^{-1}, 1523 cm^{-1}, 1359 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}ClNOS$, 282.0714, found: 282.0708.



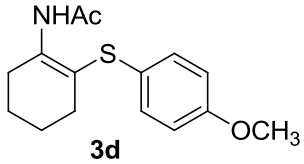
3b

3b: White solid (21.7 mg, 41 % yield); m. p. 101-103℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (s, 1H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 2.87 (s, 2H), 2.20 (s, 2H), 2.03 (s, 3H), 1.71 (d, *J* = 5.6 Hz, 2H), 1.65 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.32 (s), 163.09 (s), 160.64 (s), 141.80 (s), 130.44 (d, *J* = 30.4 Hz), 116.41 (d, *J* = 88.4 Hz), 109.53 (s), 30.75 (s), 28.68 (s), 24.68 (s), 23.49 (s), 22.64 (s); MS (EI) m/z (%): 265 (3) $[M]^+$, 222 (5), 190 (8), 162 (7), 138 (100), 96 (32), 67 (9); IR: 3245 cm^{-1}, 1663 cm^{-1}, 1531 cm^{-1}, 1366 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}FNOS$, 266.1009, found: 266.1005.



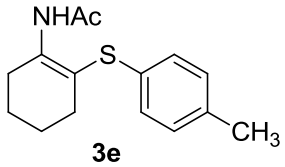
3c

3c: White solid (23.5 mg, 36 % yield); m. p. 143-145℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 2.90 (s, 2H), 2.23 (s, 2H), 2.02 (s, 3H), 1.73 (d, *J* = 6.0 Hz, 2H), 1.70-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ168.31, 143.21, 134.05, 132.31, 129.26, 119.83, 109.18, 30.82, 28.63, 24.81, 23.44, 22.55; MS (EI) m/z (%): 327 (1), 325 (1), 284 (1), 282 (1), 138 (100), 96 (23), 67 (7); IR: 3230 cm^{-1}, 1660 cm^{-1}, 1522 cm^{-1}, 1363 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}BrNOS$, 326.0209, found: 326.0204.



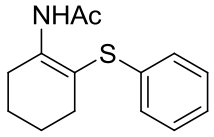
3d

3d: White solid (39.3 mg, 71 % yield); m. p. 127-129℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.99 (s, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.84 (s, 2H), 2.17 (s, 2H), 2.04 (s, 3H), 1.69 (d, *J* = 4.8 Hz, 2H), 1.61 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ168.26, 158.83, 139.97, 131.17, 124.64, 114.83, 112.42, 55.40 30.33, 28.47, 24.63, 23.40, 22.56; MS (EI) m/z (%): 277 (3) $[M]^+$, 234 (2), 202 (4), 138 (100), 96 (31); IR: 3239 cm^{-1}, 1656 cm^{-1}, 1526 cm^{-1}, 1367 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}NO_2S$, 278.1209, found: 278.1204.



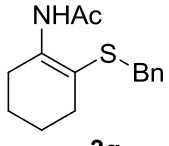
3e

3e: White solid (33.4 mg, 64 % yield); m. p. 127-129℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.03 (s, 1H), 7.10 (s, 4H), 2.88 (s, 2H), 2.32 (s, 3H), 2.22 (s, 2H), 2.01 (s, 3H), 1.71 (d, *J* = 5.6 Hz, 2H), 1.65 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ168.31, 141.76, 136.24, 130.95, 130.04, 128.41, 110.50, 30.71, 28.52, 24.78, 23.45, 22.63, 21.08; MS (EI) m/z (%): 261 (4) $[M]^+$, 218 (4), 186 (6), 138 (100), 96 (41), 67 (8); IR: 3236 cm^{-1}, 1654 cm^{-1}, 1525 cm^{-1}, 1362 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}NOS$, 262.1260, found: 262.1257.



3f

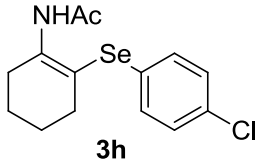
3f: White solid (22.7 mg, 46 % yield); m. p. 94-96℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.04 (s, 1H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 3H), 2.91 (s, 2H), 2.26 (s, 2H), 2.01 (s, 3H), 1.75-1.71 (m, 2H), 1.67 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ168.29, 142.58, 134.74, 129.24, 127.72, 126.04, 109.65, 30.83, 28.52, 24.73, 23.42, 22.57; MS (EI) m/z (%): 247 (3) $[M]^+$, 204 (6), 172 (8), 138 (100), 96 (47), 67 (12); IR: 3231 cm^{-1}, 1654 cm^{-1}, 1522 cm^{-1}, 1364 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{18}NOS$, 248.1104, found: 248.1101.



3g

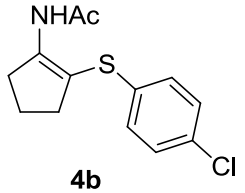
3g: Light yellow liquid (9.4 mg, 18 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (s, 1H), 7.30 (t, *J* = 6.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 3H), 3.71 (s, 2H), 2.68 (s, 2H), 2.30 (s, 2H), 1.78 (s,

3H), 1.63 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.47, 157.74, 151.80, 136.75, 129.44, 120.78, 109.06, 30.64, 28.57, 24.48, 24.41, 23.34, 22.52; MS (EI) m/z (%): 261 (6) $[M]^+$, 218 (2), 170 (32), 138 (37), 128 (100), 91 (33); IR: 2932 cm^{-1}, 1669 cm^{-1}, 1493 cm^{-1}, 1368 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{20}NOS$, 262.1260, found: 262.1257.



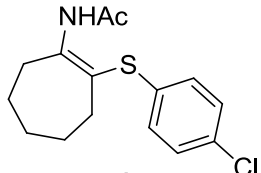
3h

3h: White solid (18.4 mg, 28 % yield); m. p. 132-134°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (s, 1H), 7.28-7.23 (m, 4H), 2.84 (s, 2H), 2.33 (s, 2H), 1.99 (s, 3H), 1.73 (d, *J* = 5.2 Hz, 2H), 1.65 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ168.38, 140.90, 133.12,, 132.17, 129.64, 128.22, 110.02, 33.03, 28.89, 24.59, 24.08, 22.70; MS (EI) m/z (%): 331 (1), 329 (2), 327 (1), 288 (1), 286 (2), 284 (1), 138 (100), 96 (45); IR: 3235 cm^{-1}, 1657 cm^{-1}, 1521 cm^{-1}, 1362 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}ClNOSe$, 330.0158, found: 330.0152.



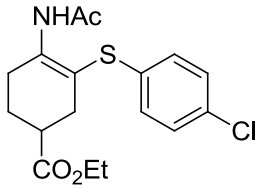
4b

4b: White solid (32.6 mg, 61 % yield); m. p. 131-132°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 6.8 Hz, 2H), 3.15 (t, *J* = 6.8 Hz, 2H), 2.39 (t, *J* = 7.6 Hz, 2H), 2.08 (s, 3H), 2.02-1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.69, 146.35, 133.54, 132.02, 129.34, 128.84, 106.87, 33.18, 33.10, 24.34, 21.47; MS (EI) m/z (%): 269 (18), 267 (53), 227 (12), 225 (32), 194 (10), 192 (28), 124 (100), 82 (97); IR: 3277 cm^{-1}, 1671 cm^{-1}, 1625 cm^{-1}, 1490 cm^{-1}, 1338 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}ClNOS$, 268.0557, found: 268.0551.



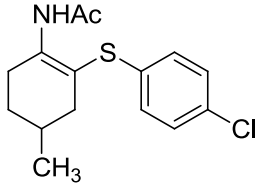
4c

4c: White solid (36.0 mg, 61 % yield); m. p. 115-117°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 2.85 (t, *J* = 5.2 Hz, 2H), 2.41 (t, *J* = 4.8 Hz, 2H), 2.02 (s, 3H), 1.75 (d, *J* = 4.4 Hz, 2H), 1.71 (t, *J* = 4.8 Hz, 2H), 1.51 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.82, 146.95, 133.55, 132.31, 129.93, 129.32, 117.93, 35.26, 31.79, 31.45, 26.81, 25.39, 24.29; MS (EI) m/z (%): 297 (1), 295 (2), 254 (1), 252 (2), 152 (100), 110 (10); IR: 3238 cm^{-1}, 1662 cm^{-1}, 1525 cm^{-1}, 1363 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}ClNOS$, 296.0870, found: 296.0872.



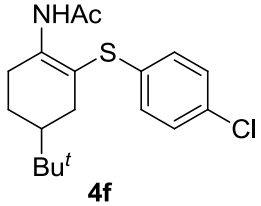
4d

4d: yellow liquid (35.3 mg, 50 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.13 (t, *J* = 2.4 Hz, 2H), 3.07 (d, *J* = 18.4 Hz, 1H), 2.94 (d, *J* = 18.0 Hz, 1H), 2.64 (d, *J* = 8.8 Hz, 1H), 2.53 (t, *J* = 8.8 Hz, 1H), 2.44 (t, *J* = 4.4 Hz, 1H), 2.11 (d, *J* = 13.6 Hz, 1H), 2.03 (s, 3H), 1.87-1.77 (m, 1H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.33, 168.35, 142.47, 132.82, 132.47, 129.53, 129.32, 107.64, 60.74, 39.84, 32.62, 27.44, 25.04, 24.71, 14.30; MS (EI) m/z (%): 355 (1), 353 (3), 312 (1), 310 (3), 268 (1), 266 (4), 240 (2), 238 (6), 210 (100), 168 (26); IR: 3273 cm^{-1}, 1725 cm^{-1}, 1629 cm^{-1}, 1473 cm^{-1}, 1367 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{20}ClNNaO_3S$, 376.0745, found: 376.0741.



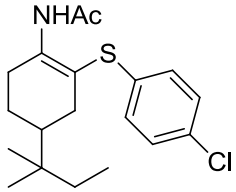
4e

4e: White solid (44.9 mg, 76 % yield); m. p. 100-102°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.97 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.03 (d, *J* = 13.2 Hz, 1H), 2.85 (d, *J* = 6.8 Hz, 1H), 2.24 (d, *J* = 16.4 Hz, 1H), 2.02 (s, 3H), 1.91 (t, *J* = 10.0 Hz, 1H), 1.82 (d, *J* = 11.6 Hz, 1H), 1.78 (d, *J* = 11.6 Hz, 2H), 1.37-1.27 (m, 1H), 0.94 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.24, 142.66, 133.38, 132.15, 129.41, 129.18, 108.84, 39.06, 30.60, 29.49, 28.33, 24.68, 21.13; MS (EI) m/z (%): 297 (1), 295 (2), 254 (1), 252 (3), 152 (100), 110 (30); IR: 3260 cm^{-1}, 1659 cm^{-1}, 1515 cm^{-1}, 1368 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}ClNOS$, 296.0870, found: 296.0871.



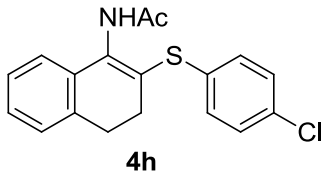
4f

4f: White solid (40.5 mg, 60 % yield); m. p. 112-115°C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.97 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.11 (d, *J* = 18.0 Hz, 1H), 2.78 (t, *J* = 13.6 Hz, 1H), 2.20 (d, *J* = 14.4 Hz, 1H), 2.08 (t, *J* = 13.2 Hz, 1H), 2.01 (s, 3H), 1.94 (d, *J* = 9.2 Hz, 1H), 1.42-1.38 (m, 1H), 1.36-1.20 (m, 1H), 0.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.25, 143.36, 133.57, 132.00, 129.46, 128.68, 109.24, 45.19, 32.70, 29.66, 27.23, 24.68, 24.02; MS (EI) m/z (%): 339 (1), 337 (2), 296 (1), 294 (2), 194 (100), 152 (5), 96 (11); IR: 3255 cm^{-1}, 1664 cm^{-1}, 1521 cm^{-1}, 1368 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{25}ClNOS$, 338.1340, found: 338.1338.



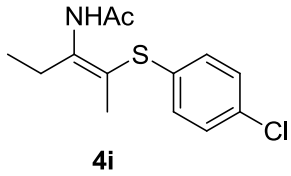
4g

4g: White solid (52.0 mg, 74 % yield); m. p. 91-94℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (s, 1H), 7.26 (d, *J* = 6.4 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.10 (d, *J* = 17.6 Hz, 1H), 2.78 (t, *J* = 11.2 Hz, 1H), 2.16-2.05 (m, 1H), 2.01 (s, 3H), 1.90 (d, *J* = 9.6 Hz, 1H), 1.52-1.45 (m, 1H), 1.31-1.20 (m, 4H), 0.77 (d, *J* = 16.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.28, 143.48, 133.55, 131.88, 129.44, 128.51, 109.05, 42.46, 34.65, 32.50, 32.19, 29.68, 24.78, 23.95, 23.77, 23.57, 8.16; MS (EI) m/z (%): 353 (1), 351 (2), 310 (1), 308 (2), 208 (100), 166 (4), 96 (13); IR: 3236 cm^{-1}, 1664 cm^{-1}, 1525 cm^{-1}, 1367 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{27}ClNOS$, 352.1496, found: 352.1495.



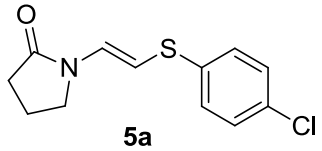
4h

4h: White solid (15.8 mg, 24 % yield; 36.9 mg, 56 % yield); m. p. 204-205℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.12 (m, 8H), 6.90 (s, 1H), 2.82 (s, 2H), 2.43 (s, 2H), 2.22 (s, 2H), 1.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.95, 135.39 134.50, 132.79, 132.77, 129.52, 128.06, 127.68, 126.78, 126.74, 123.18, 123.11, 28.96, 28.77, 23.36; MS (EI) m/z (%): 331 (1), 329 (2), 288 (1), 286 (2), 186 (100), 144 (25), 115 (42); IR: 3235 cm^{-1}, 1651 cm^{-1}, 1521 cm^{-1}, 1369 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{17}ClNOS$, 330.0714, found: 330.0711.



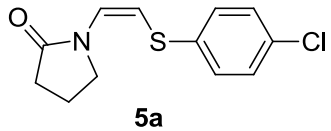
4i

4i: White solid (23.7 mg, 44 % yield); m. p. 103-105℃; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (s, 1H), 7.27 (d, *J* = 6.4 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 2.84 (d, *J* = 6.8 Hz, 2H), 2.04 (s, 3H), 1.98 (s, 3H), 1.15 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.17, 145.30, 133.34, 132.39, 129.70, 129.44, 109.36, 24.51, 22.89, 18.85, 12.74; MS (EI) m/z (%): 271 (1), 269 (2), 228 (1), 226 (3), 126 (100), 108 (10), 84 (49); IR: 3249 cm^{-1}, 1661 cm^{-1}, 1517 cm^{-1}, 1363 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{17}ClNOS$, 270.0714, found: 270.0713.



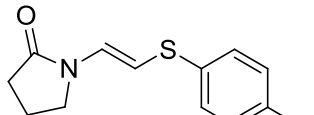
5a

5a: Light yellow liquid (41.1 mg, 81 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.44 (d, *J* = 14.4 Hz, 1H), 7.24 (t, *J* = 4.8 Hz, 4H), 5.57 (d, *J* = 13.6 Hz, 1H), 3.61 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 8.0 Hz, 2H), 2.20-2.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.04, 136.18, 132.32, 132.01, 129.12, 129.01, 100.99, 45.33, 30.91, 17.61; MS (EI) m/z (%): 255 (4), 253 (13), 170 (2), 168 (7), 145 (3), 143 (8), 110 (100); IR: 3041 cm^{-1}, 1694 cm^{-1}, 1473 cm^{-1}, 1393 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}ClNOS$, 254.0401, found: 254.0401.



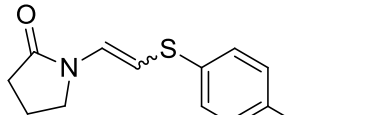
5a

5a: Light yellow liquid (3.5 mg, 7 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.29-7.23 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 1H), 5.46 (d, *J* = 8.8 Hz, 1H), 4.04 (t, *J* = 6.4 Hz, 2H), 2.44 (t, *J* = 8.0 Hz, 2H), 2.14-2.06 (m, 2H); MS (EI) m/z (%): 255 (3), 253 (9), 170 (2), 168 (5), 145 (2), 143 (6), 110 (100); IR: 3050 cm^{-1}, 1696 cm^{-1}, 1606 cm^{-1}, 1473 cm^{-1}, 1384 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}ClNOS$, 254.0401, found: 254.0401.



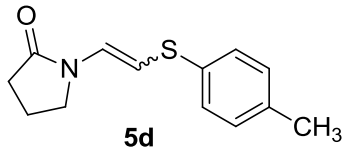
5b

5b: Light yellow liquid (29.4 mg, 62 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41 (d, *J* = 14.4 Hz, 1H), 7.31-7.27 (m, 2H), 6.99 (t, *J* = 8.4 Hz, 2H), 5.59 (d, *J* = 14.4 Hz, 1H), 3.58 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.19-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.06(s), 163.04(s), 131.29(s), 130.33 (d, *J* = 30.8 Hz), 116.15 (d, *J* = 87.6 Hz), 110.12(s), 102.42(s), 45.34(s), 30.96(s), 17.60(s); MS (EI) m/z (%): 237 (20) $[M]^+$, 152 (18), 139 (5), 127 (22), 110 (100); IR: 3053 cm^{-1}, 1697 cm^{-1}, 1607 cm^{-1}, 1486 cm^{-1}, 1385 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}FNOS$, 238.0696, found: 238.0696.



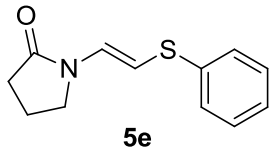
5c

5c: Light yellow liquid (40.8 mg, 82 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31 (t, *J* = 8.8 Hz, 3H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.60 (d, *J* = 14.0 Hz, 1H), 3.79 (s, 3H), 3.55 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 8.4 Hz, 2H), 2.16-2.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.86, 159.03, 131.32, 129.38, 114.86, 114.80, 104.48, 55.49, 45.36, 30.99, 17.58; MS (EI) m/z (%): 249 (18) $[M]^+$, 164 (7), 151 (4), 139 (5), 121 (12), 110 (100); IR: 2939 cm^{-1}, 1693 cm^{-1},1607 cm^{-1}, 1491 cm^{-1}, 1386 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}NO_2S$, 250.0896, found: 250.0895.



5d

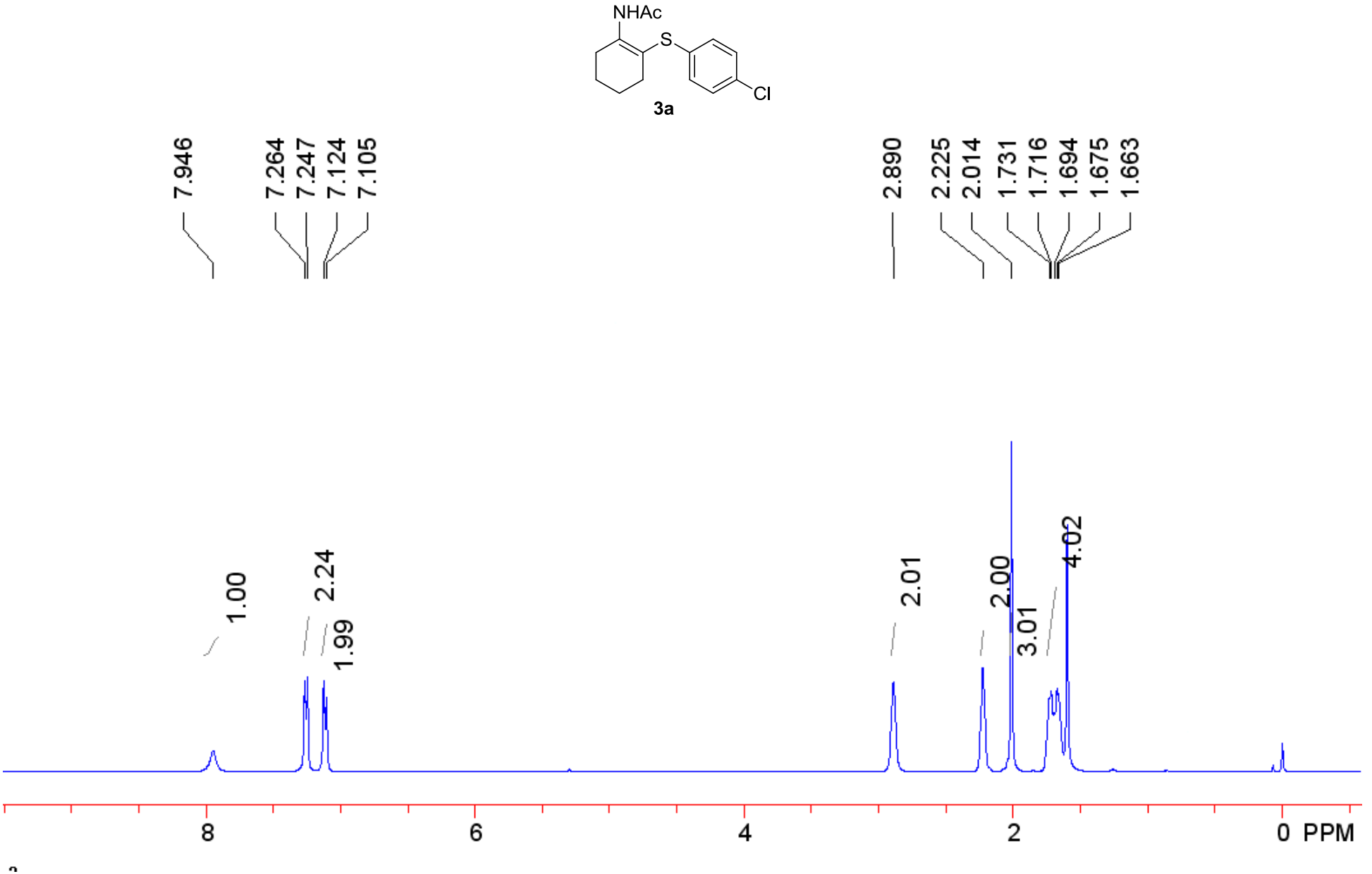
5d: Light yellow liquid (31.7 mg, 68 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38 (d, *J* = 14.0 Hz, 1H), 7.29-7.20 (m, 2H), 7.15-7.09 (m, 2H), 5.61 (d, *J* = 13.6 Hz, 1H), 3.60 (t, *J* = 9.6 Hz, 2H), 2.51 (t, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 2.18-2.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.95, 136.31, 133.44, 130.52, 129.86, 128.60, 103.03, 45.36, 31.00, 21.08, 17.61; MS (EI) m/z (%): 233 (16) $[M]^+$, 148 (8), 135 (4), 123 (5), 110 (100); IR: 3051 cm^{-1}, 1697 cm^{-1}, 1607 cm^{-1}, 1490 cm^{-1}, 1385 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{16}NOS$, 234.0947, found: 234.0944.

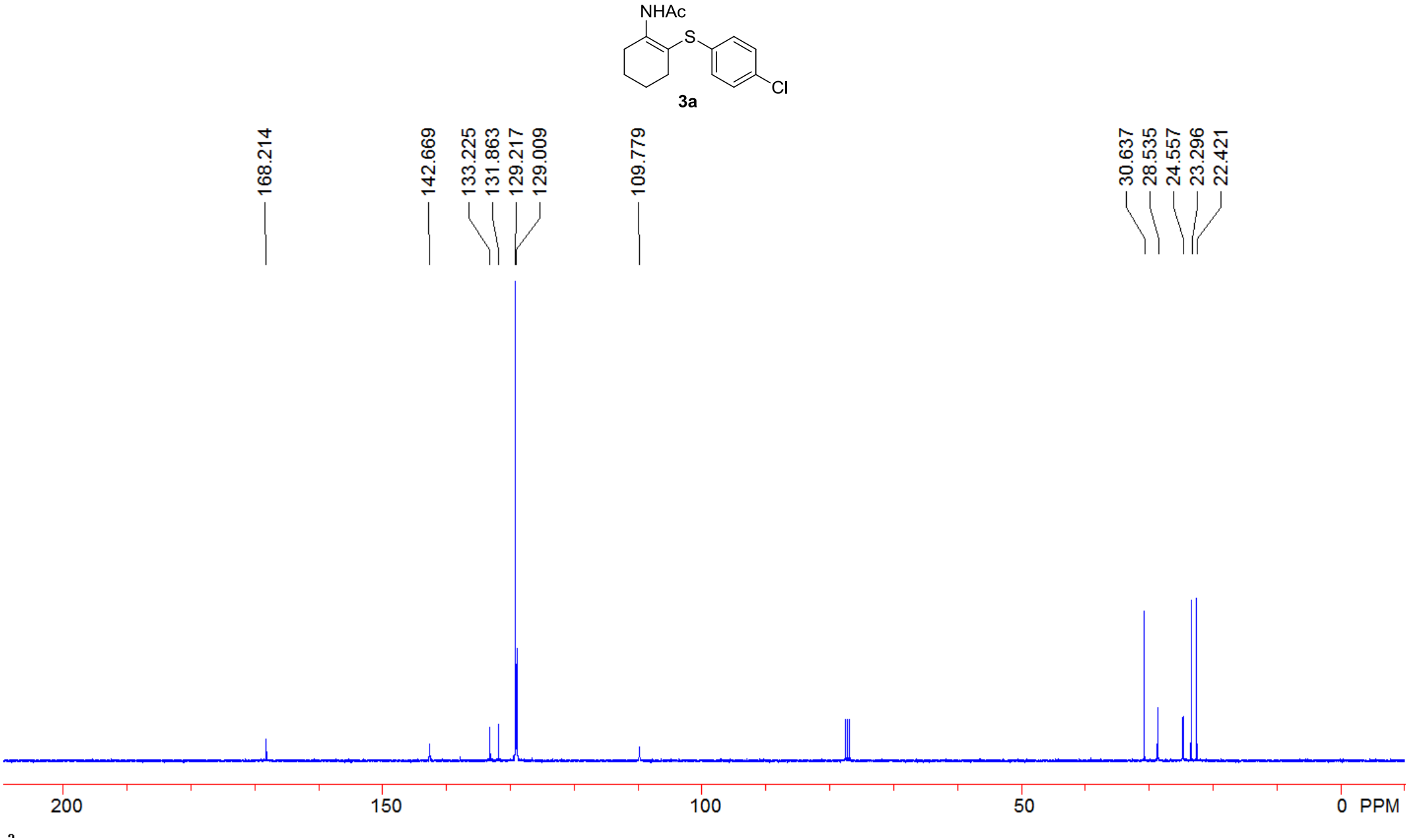


5e

5e: Light yellow liquid (24.1 mg, 55 % yield); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.43 (d, *J* = 14.0 Hz, 1H), 7.28 (t, *J* = 6.0 Hz, 4H), 7.17 (t, *J* = 6.8 Hz, 1H), 5.62 (d, *J* = 14.4 Hz, 1H), 3.60 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.19-2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.78, 137.42, 131.49, 129.06, 127.87, 126.11, 101.90, 45.37, 30.99, 17.63; MS (EI) m/z (%): 219 (16) $[M]^+$, 134 (8), 121 (3), 110 (100); IR: 3052 cm^{-1}, 1697 cm^{-1}, 1607 cm^{-1}, 1582 cm^{-1}, 1385 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}NOS$, 220.0791, found: 220.0791.

7. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3h，4b-4i, 5a-5e.

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23.296
22.421
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100
50
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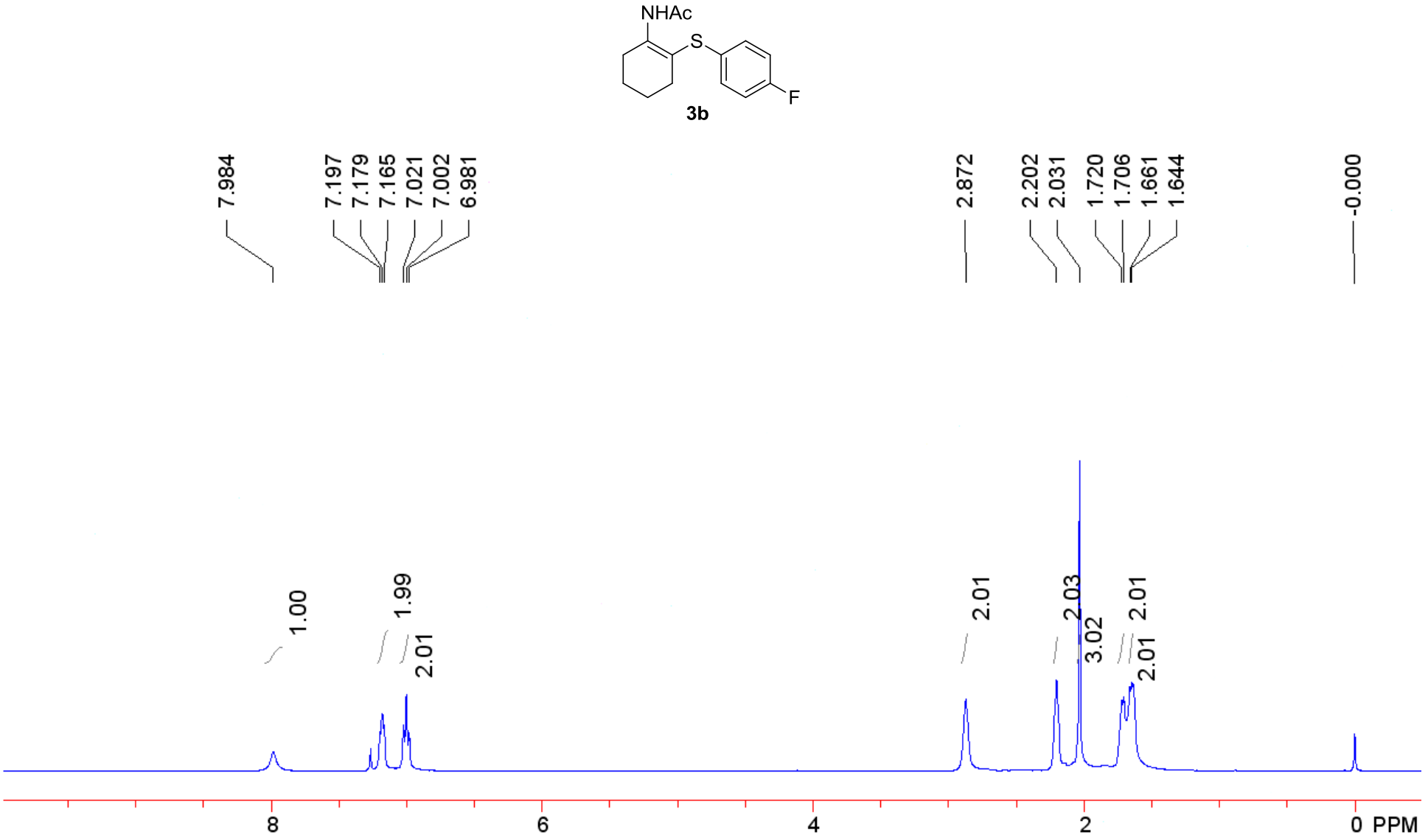
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1.706
1.661
1.644
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2.01
2.03
3.02
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2.01
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4
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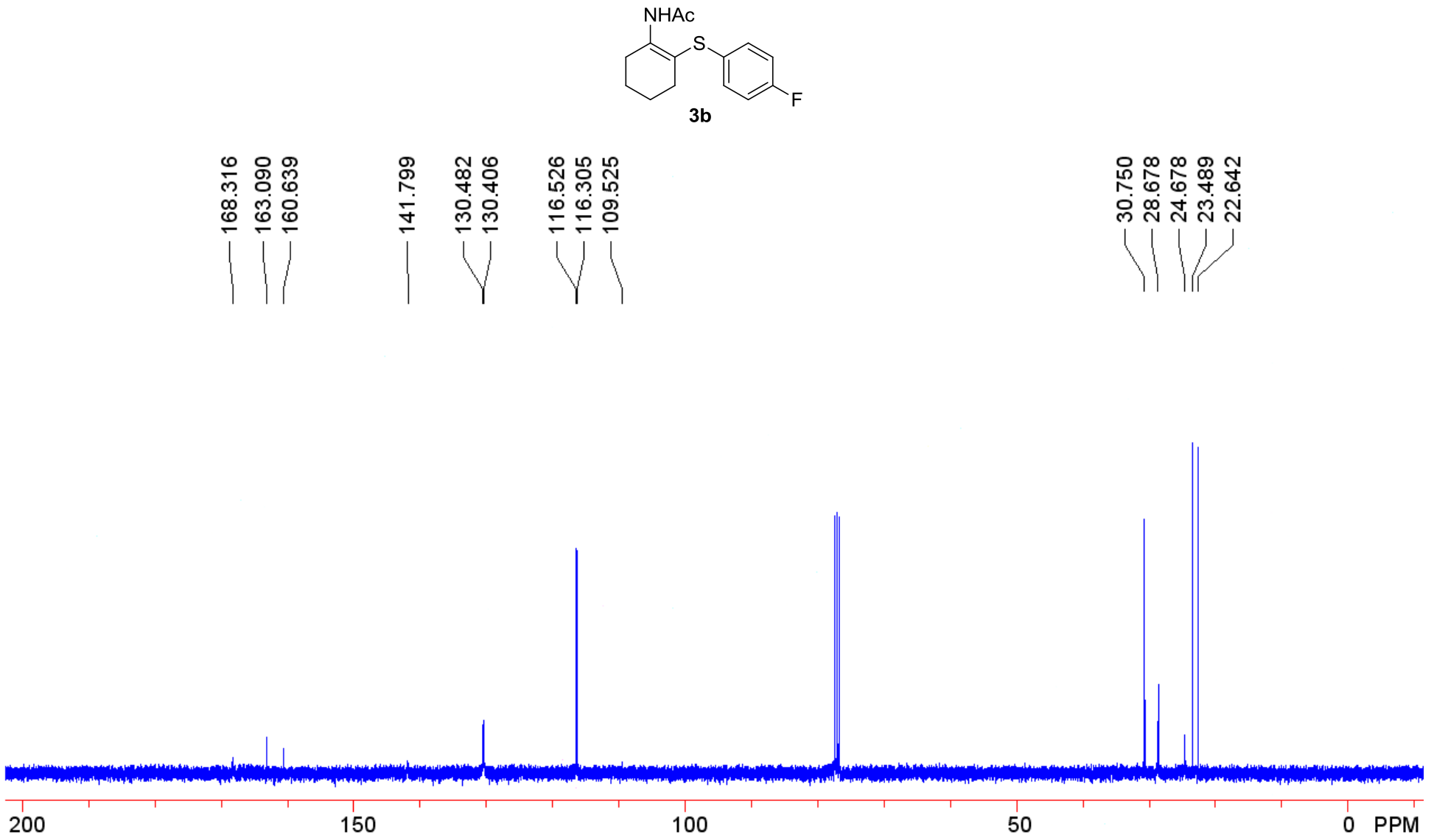
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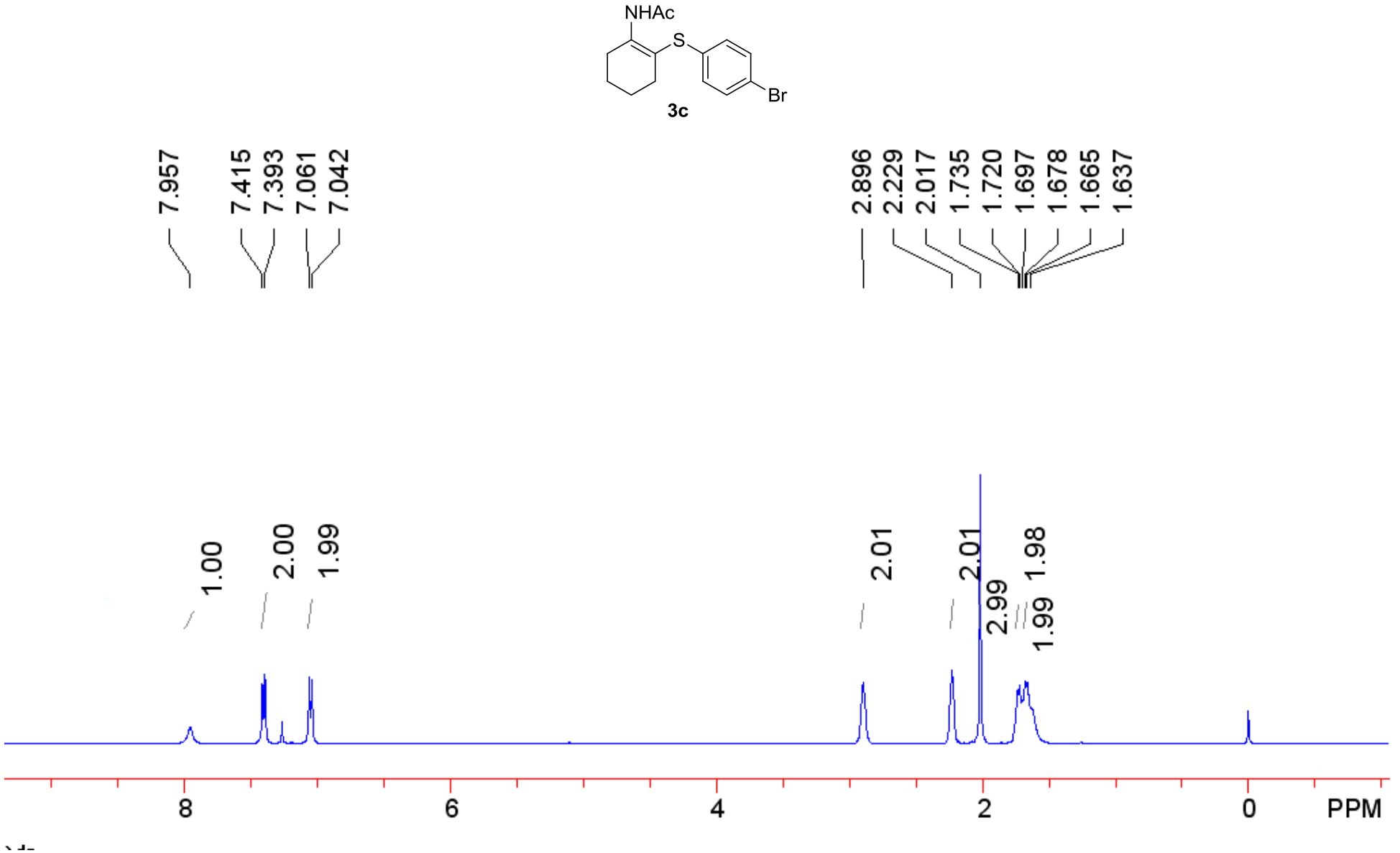
PPM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1.665
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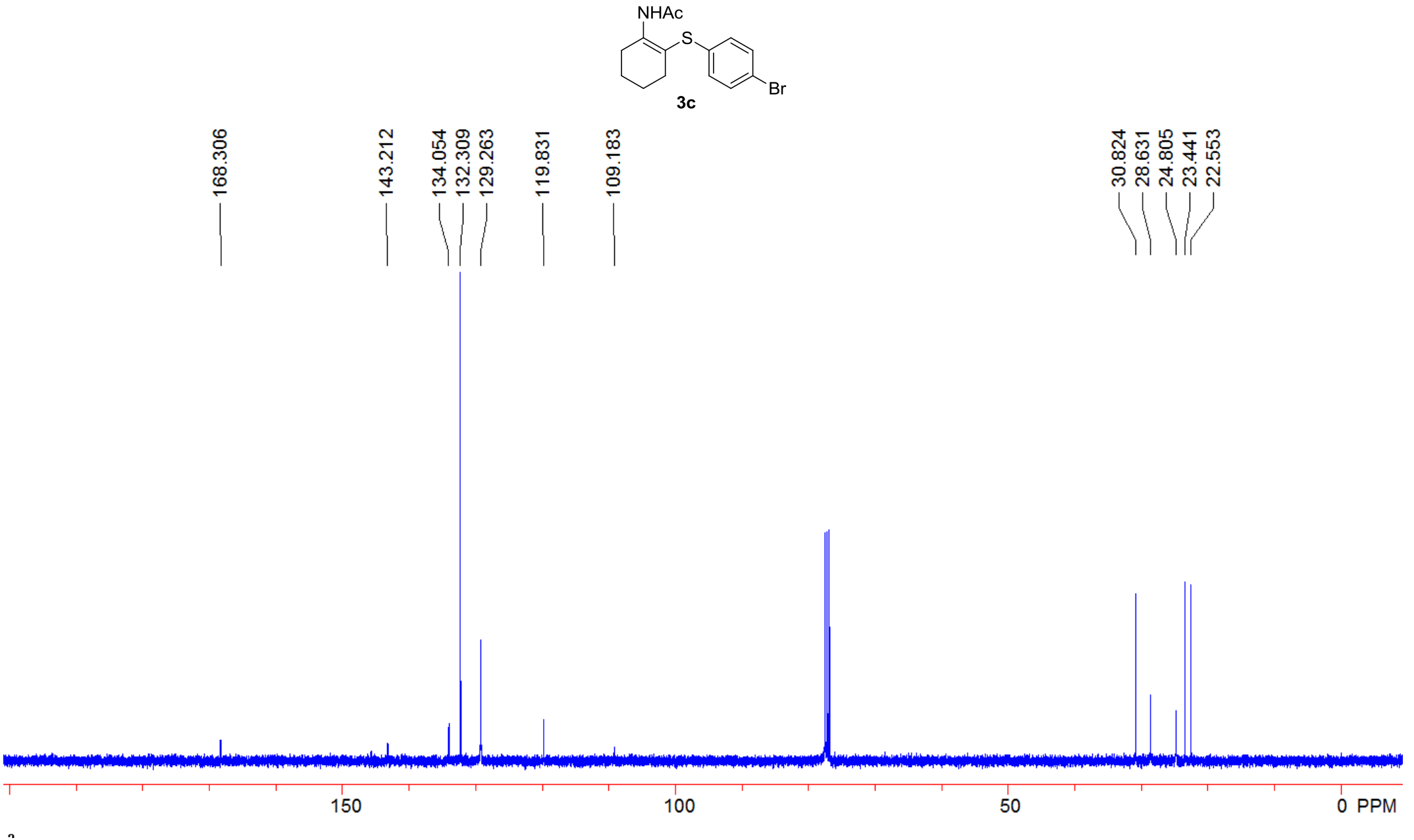
PPM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150
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50
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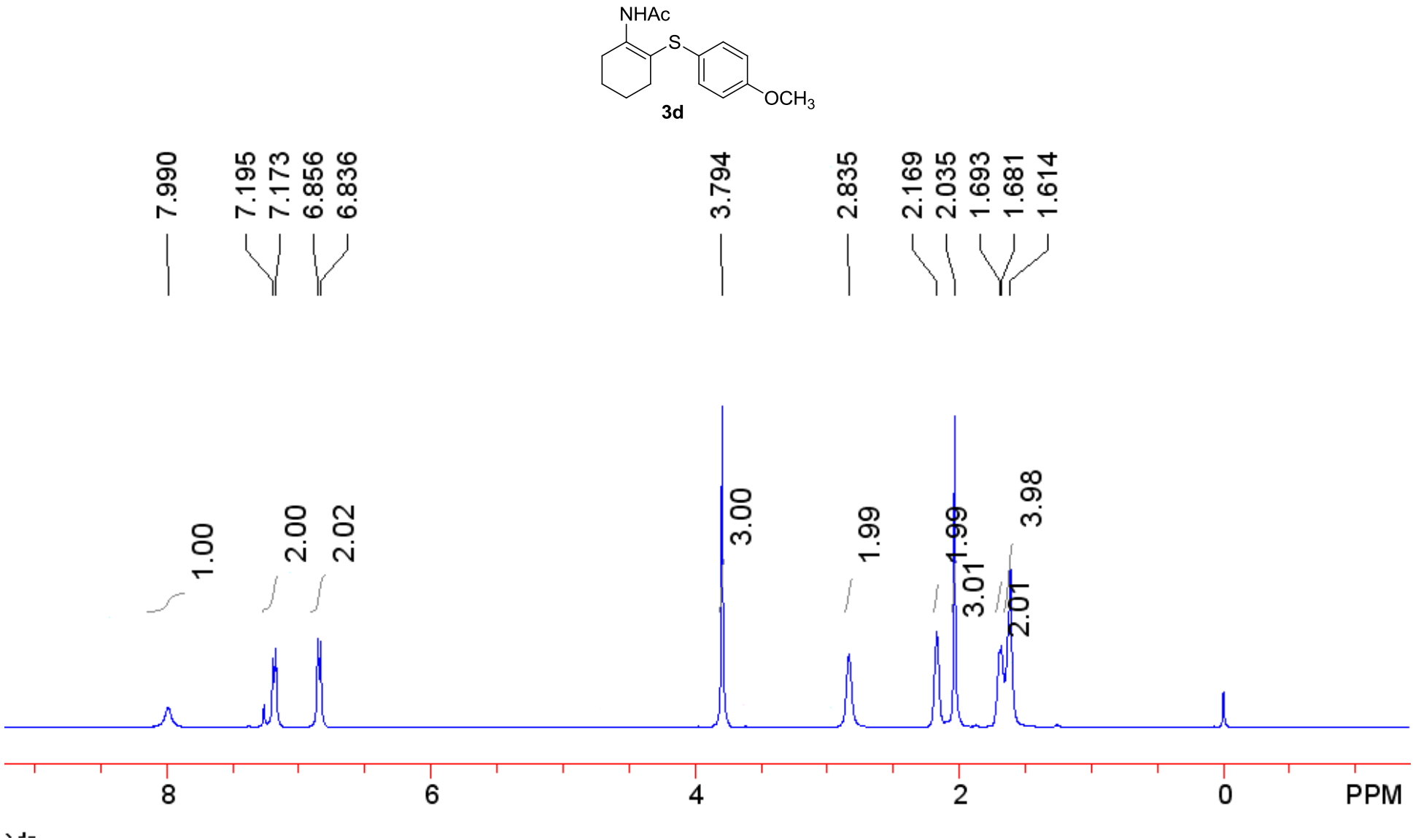
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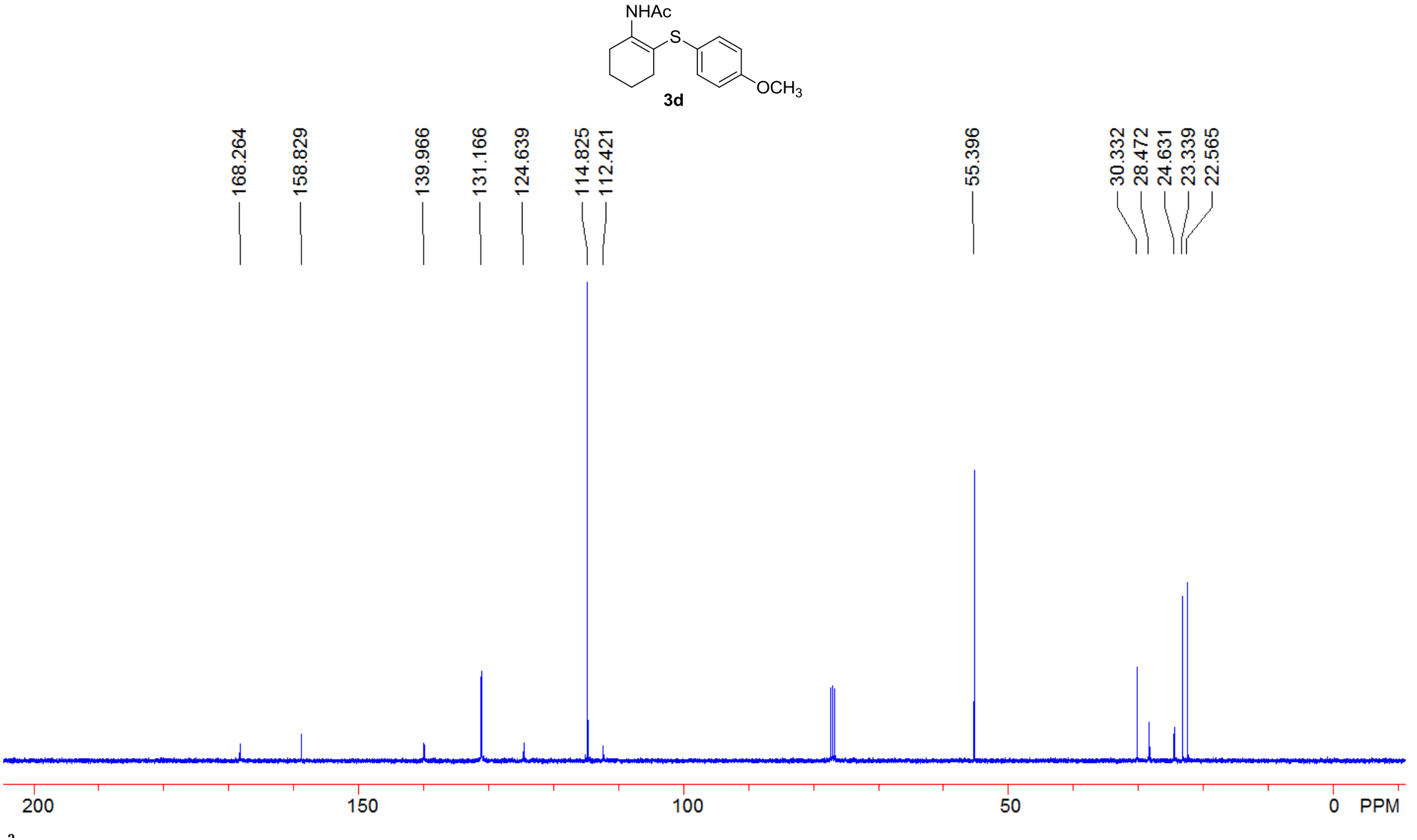
PPM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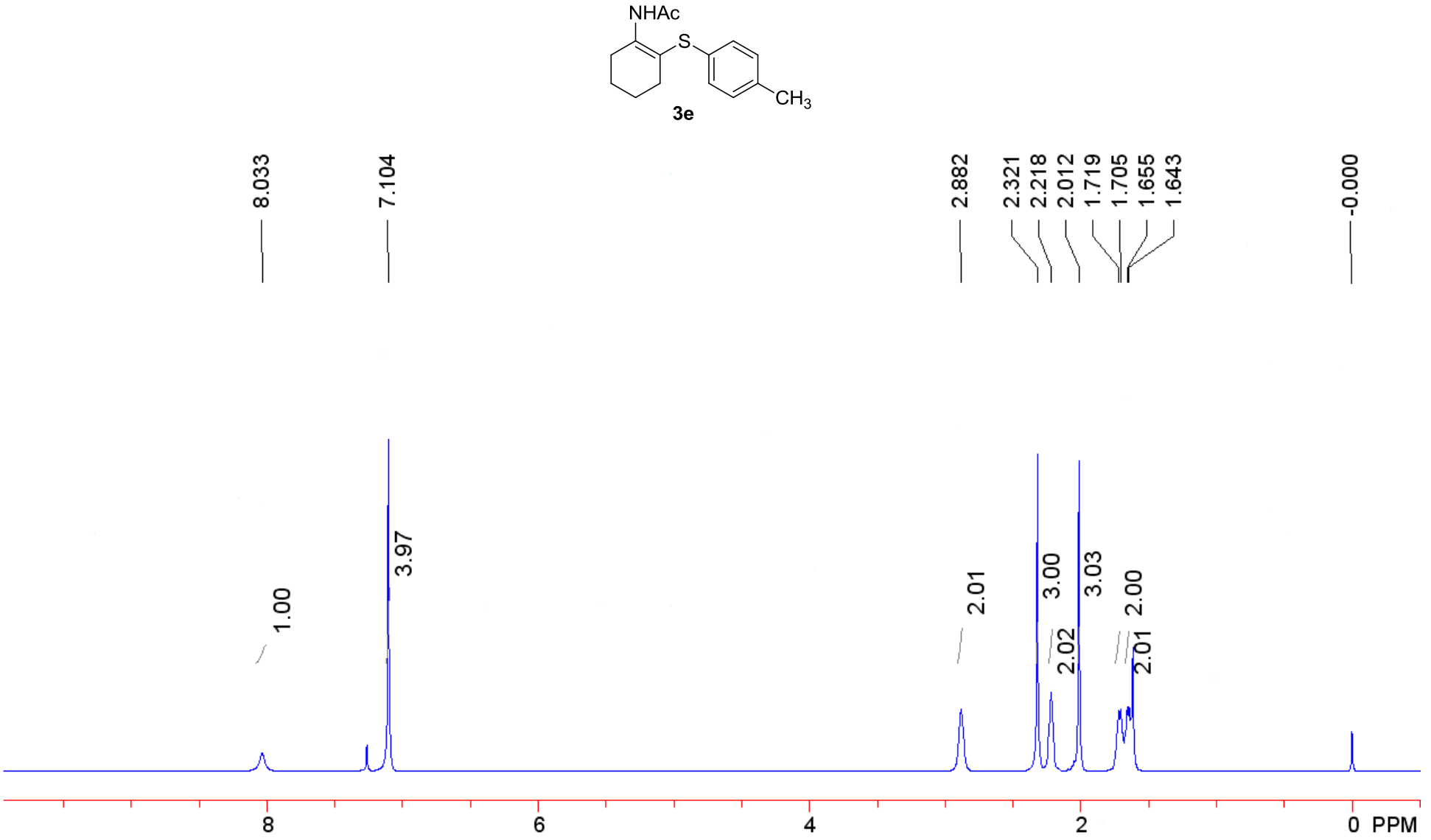
PPM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2.01
3.00
2.02
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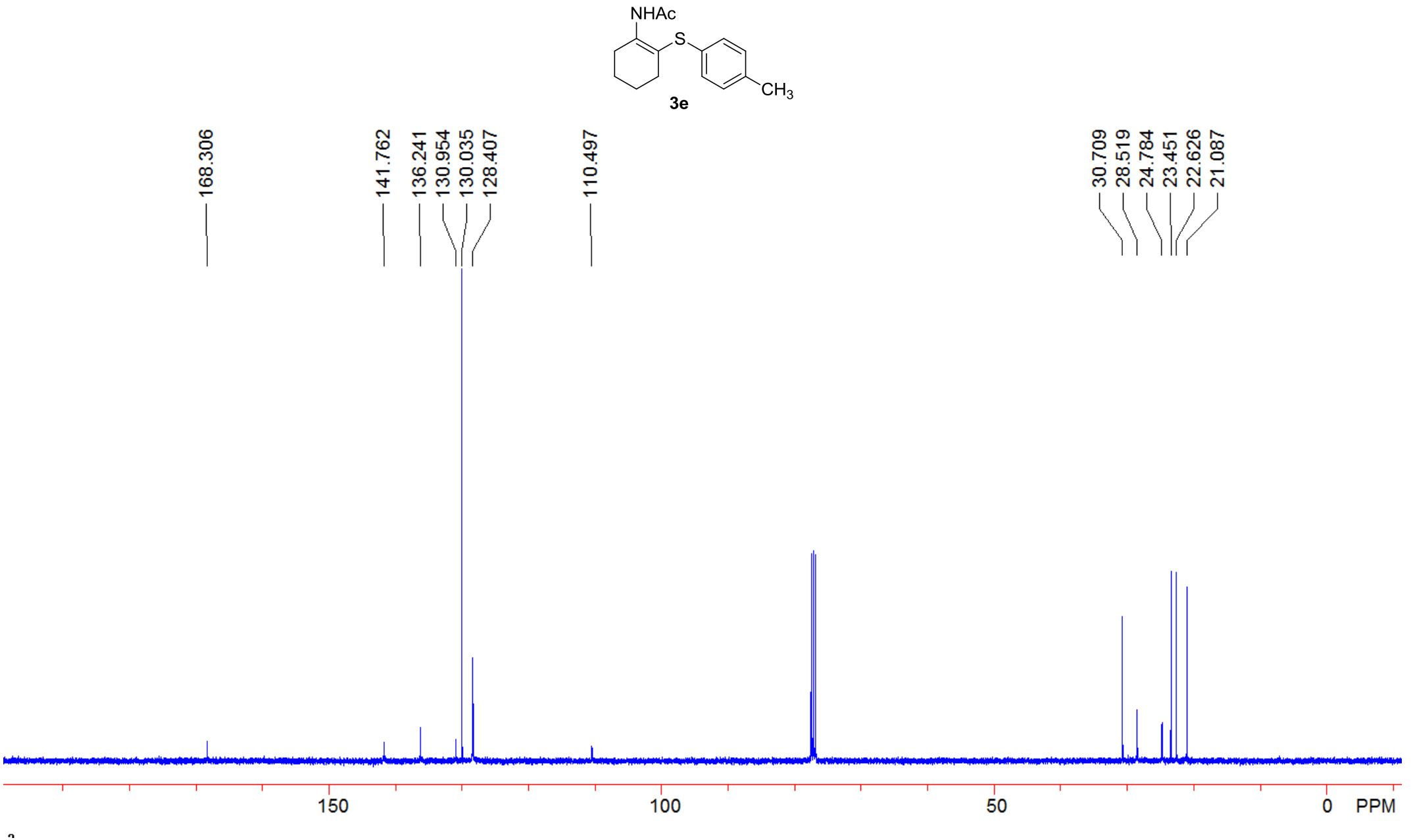
2.01
8
6
4
2
0 PPM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23.451
22.626
21.087
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100
50
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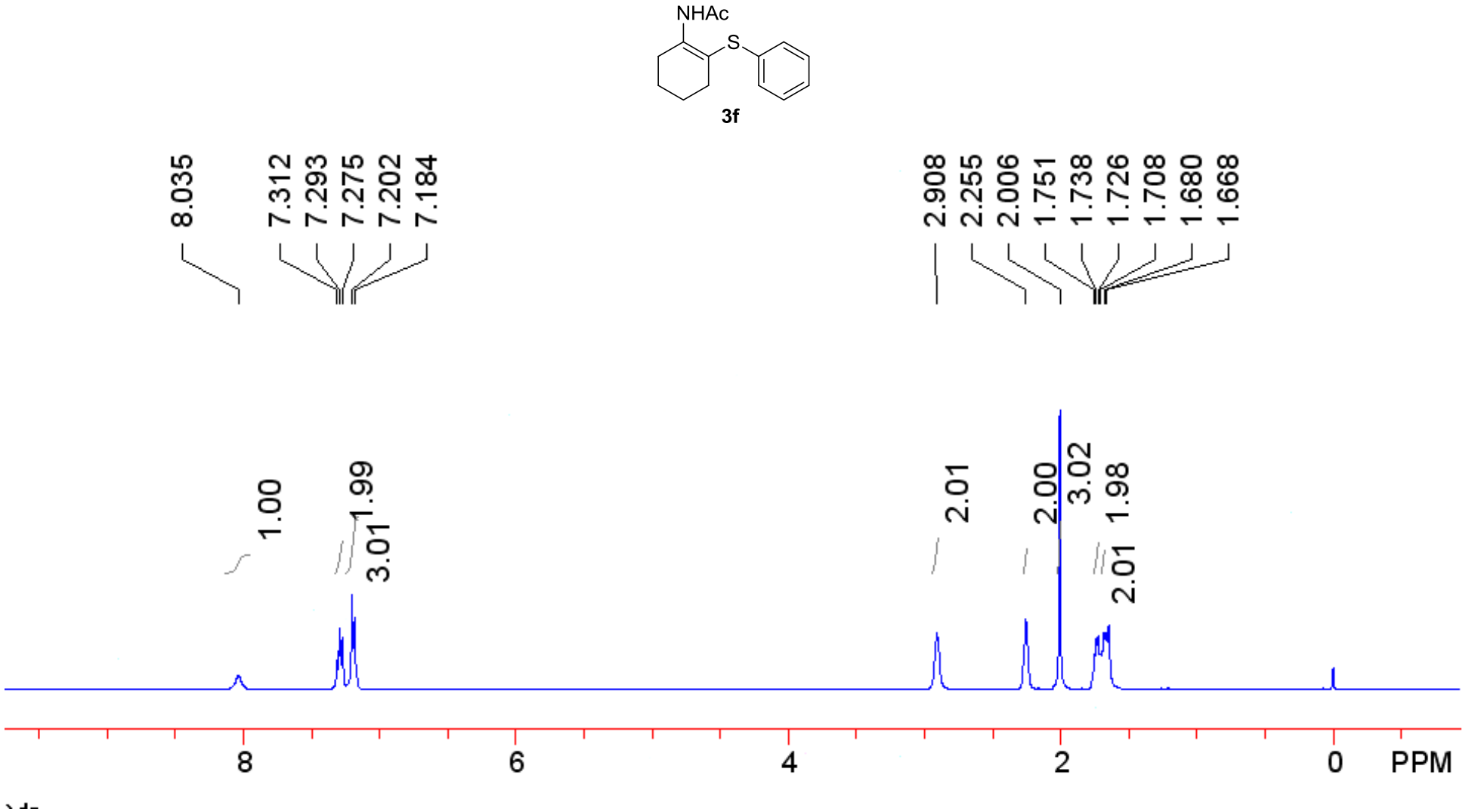
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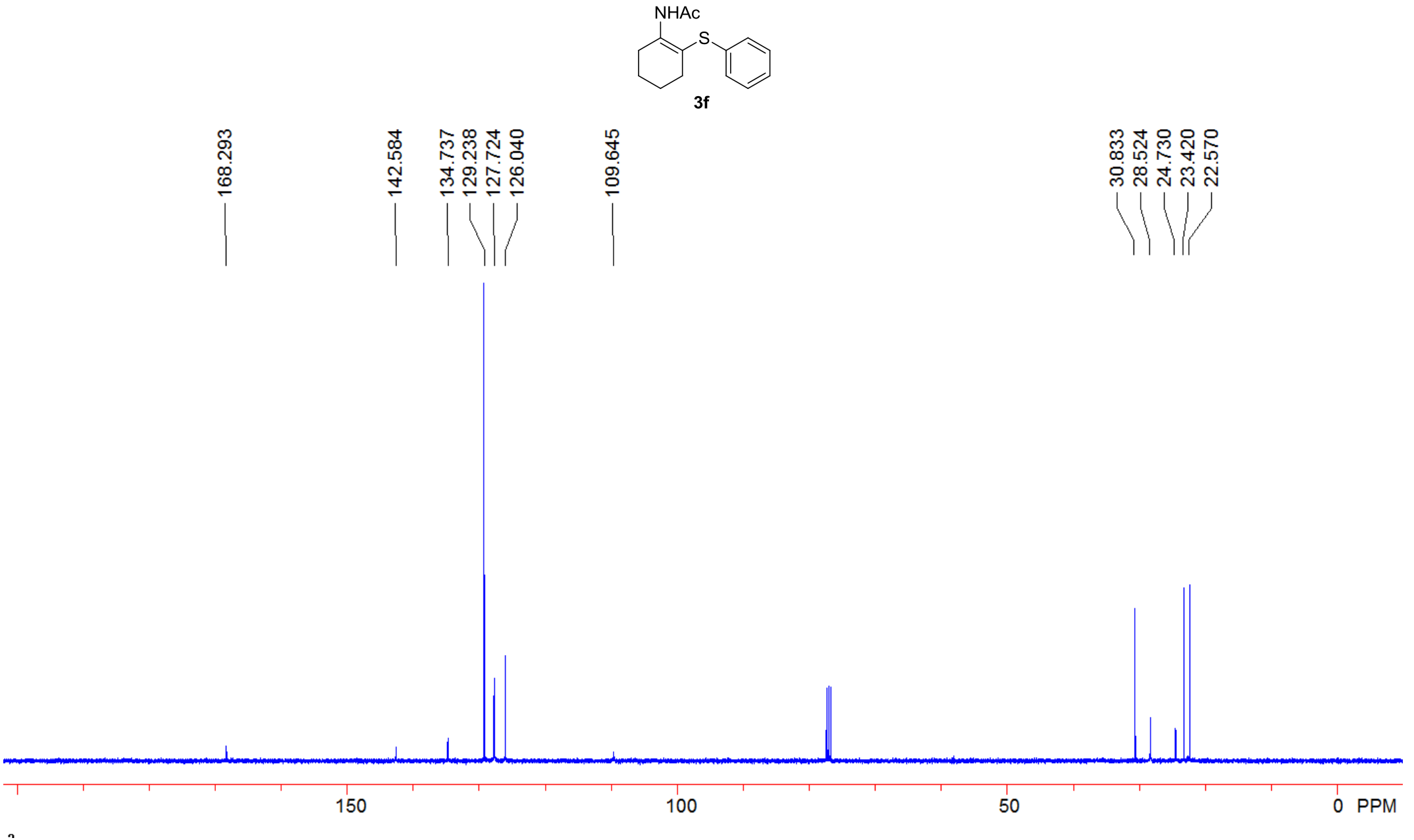
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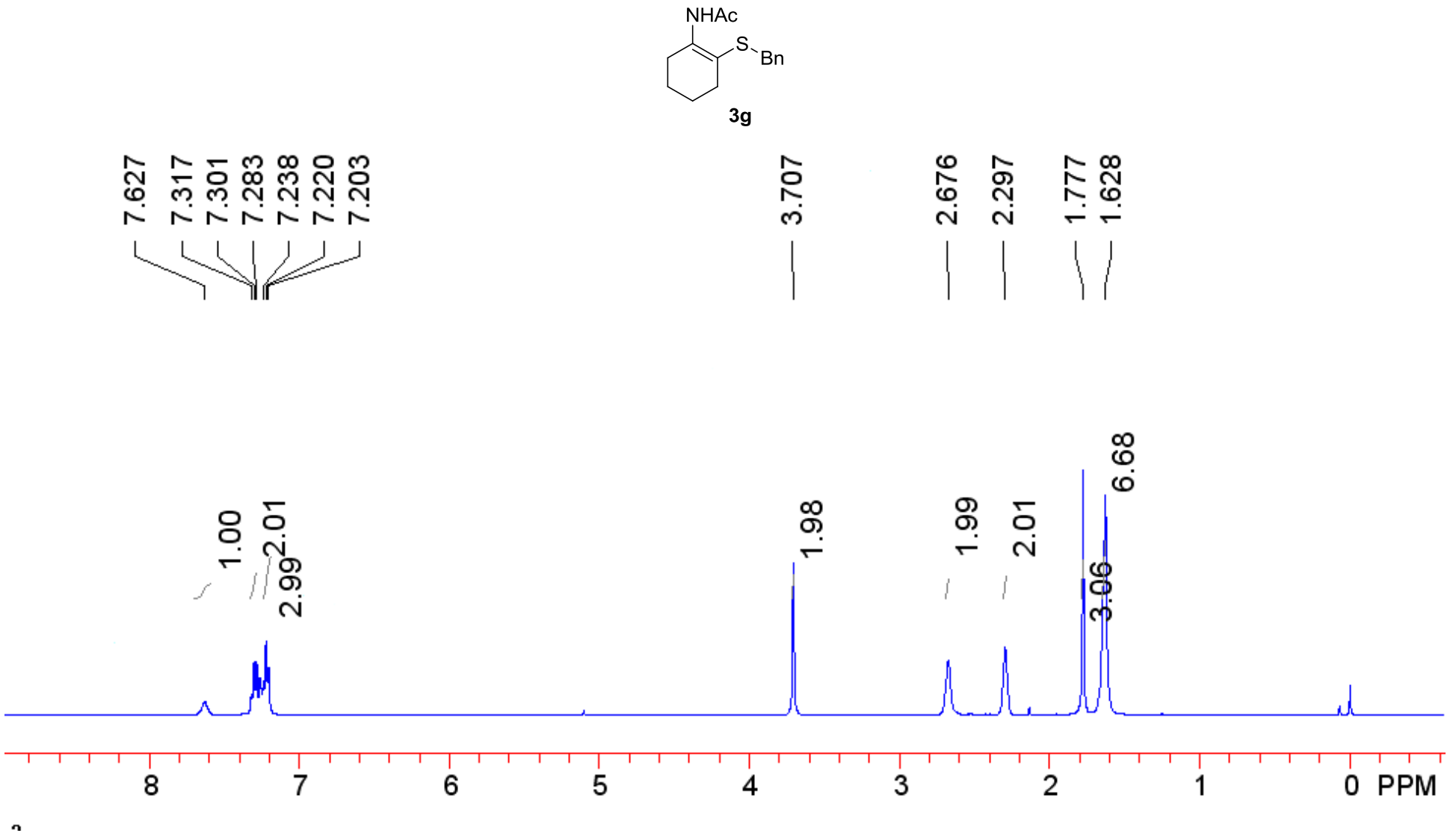
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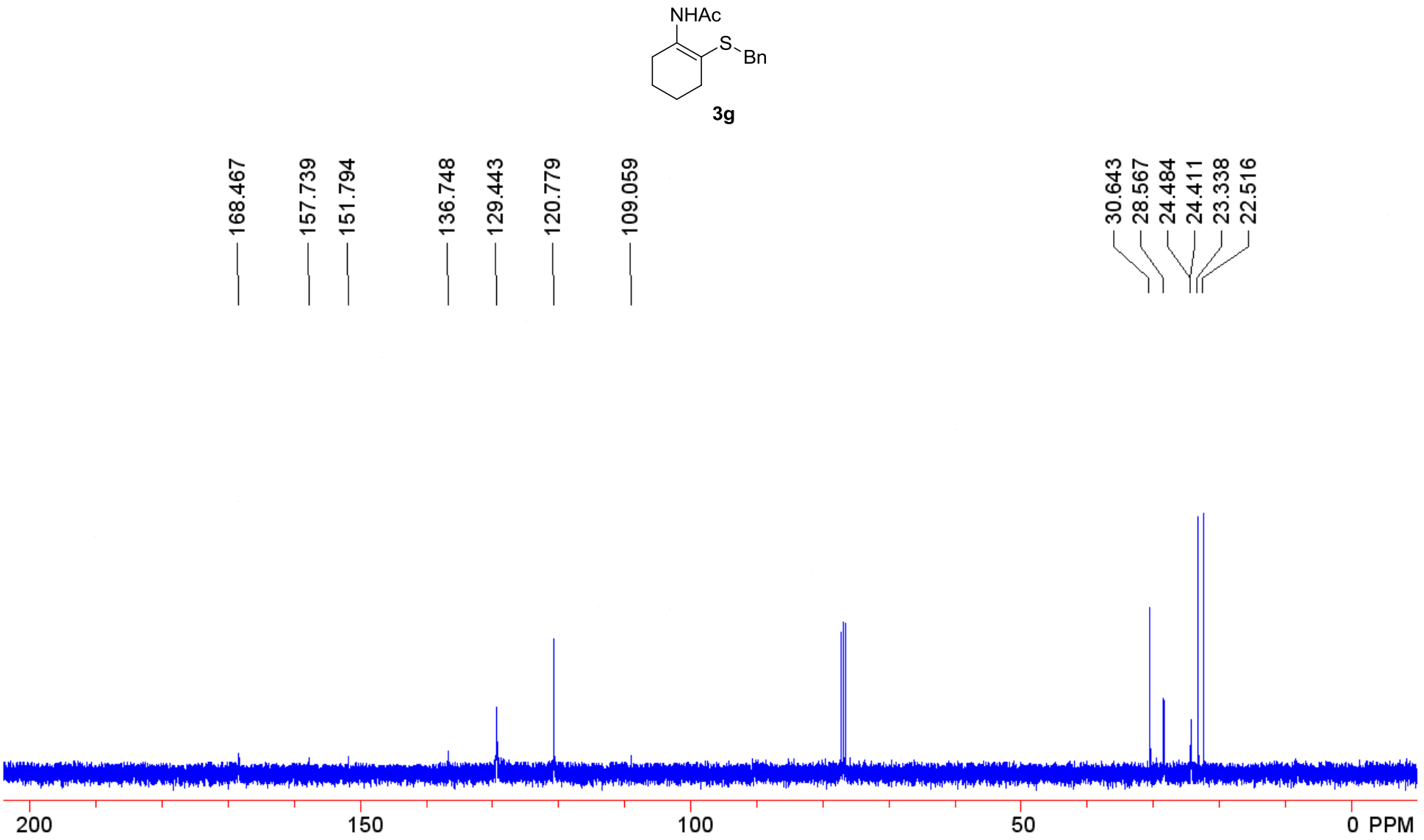
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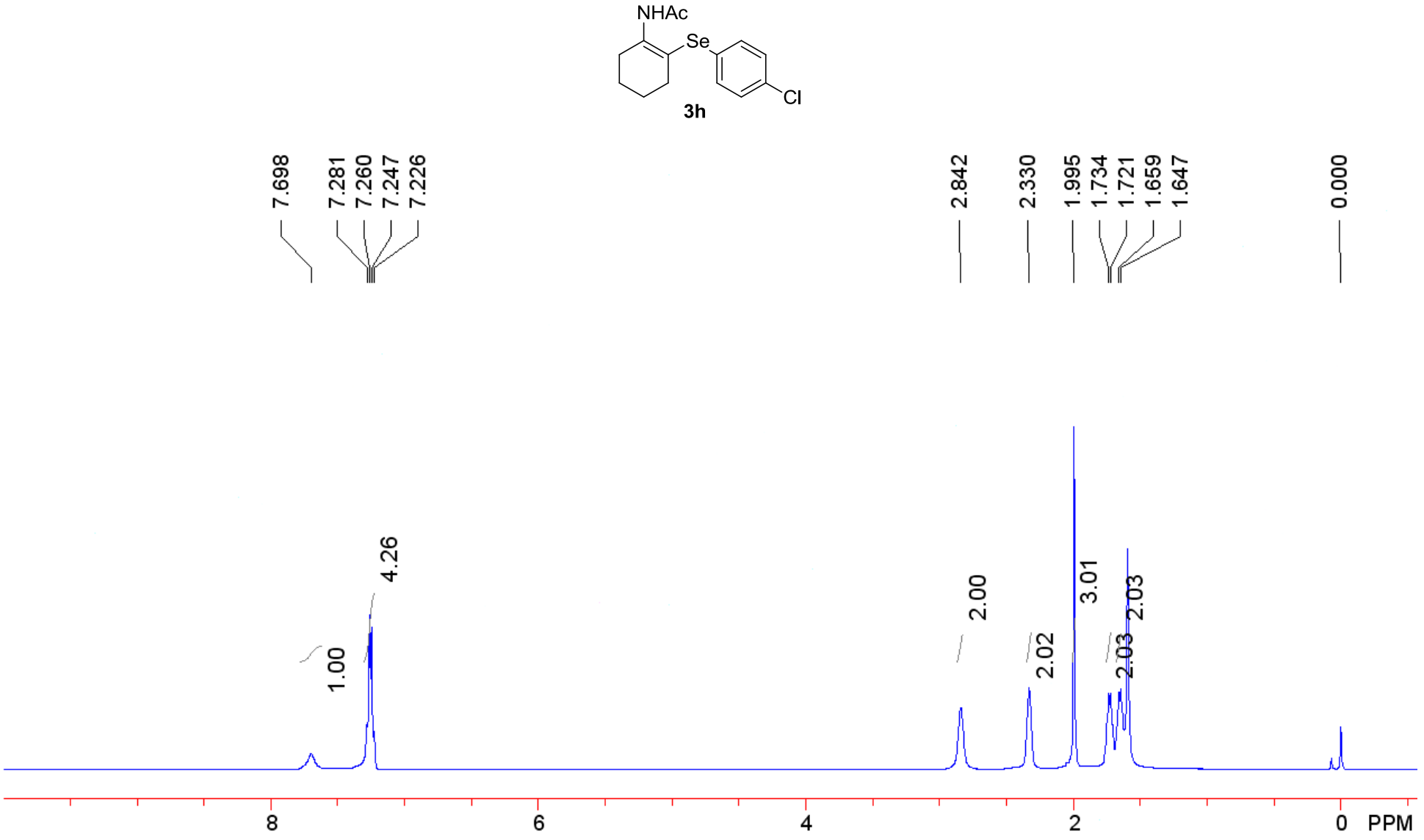
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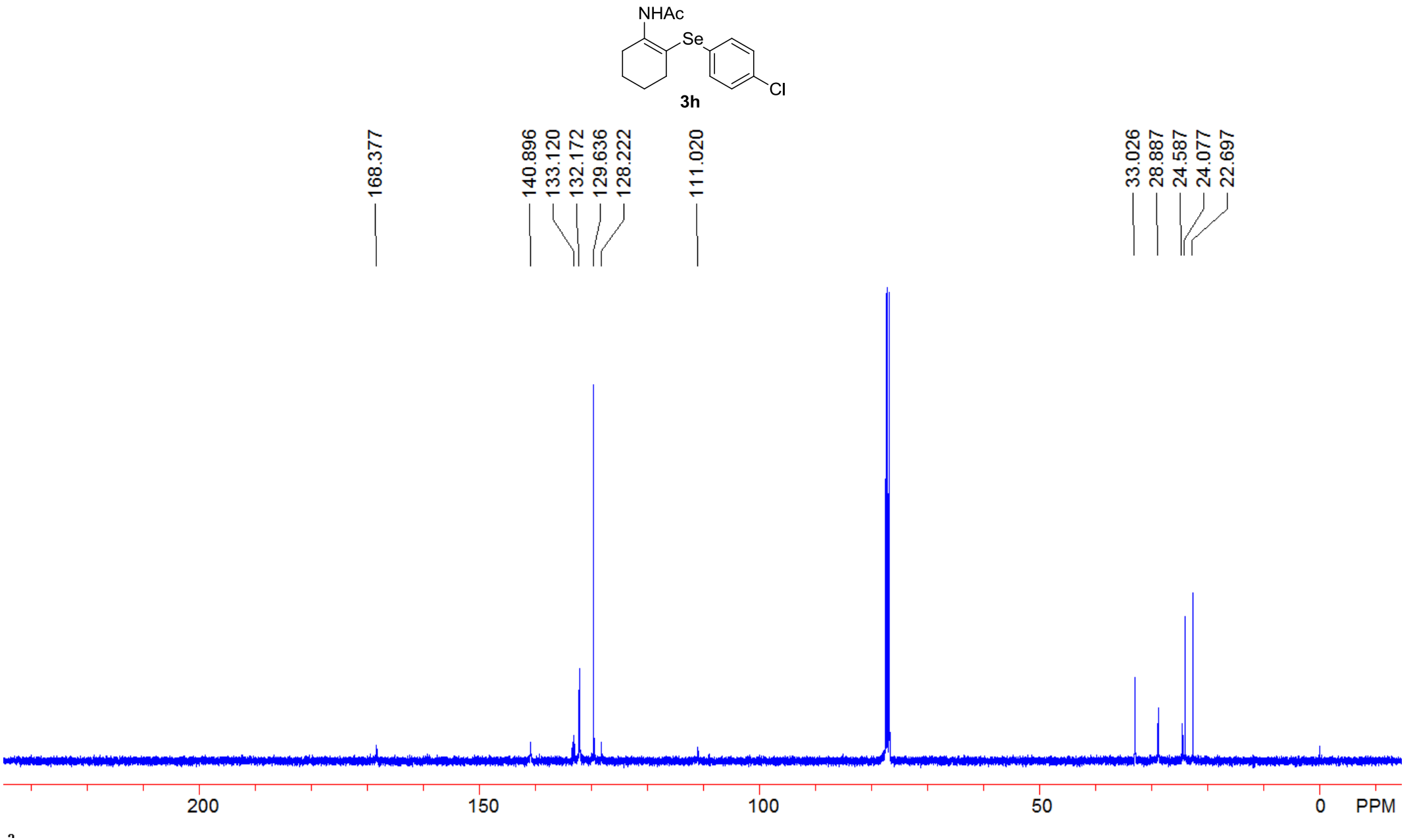
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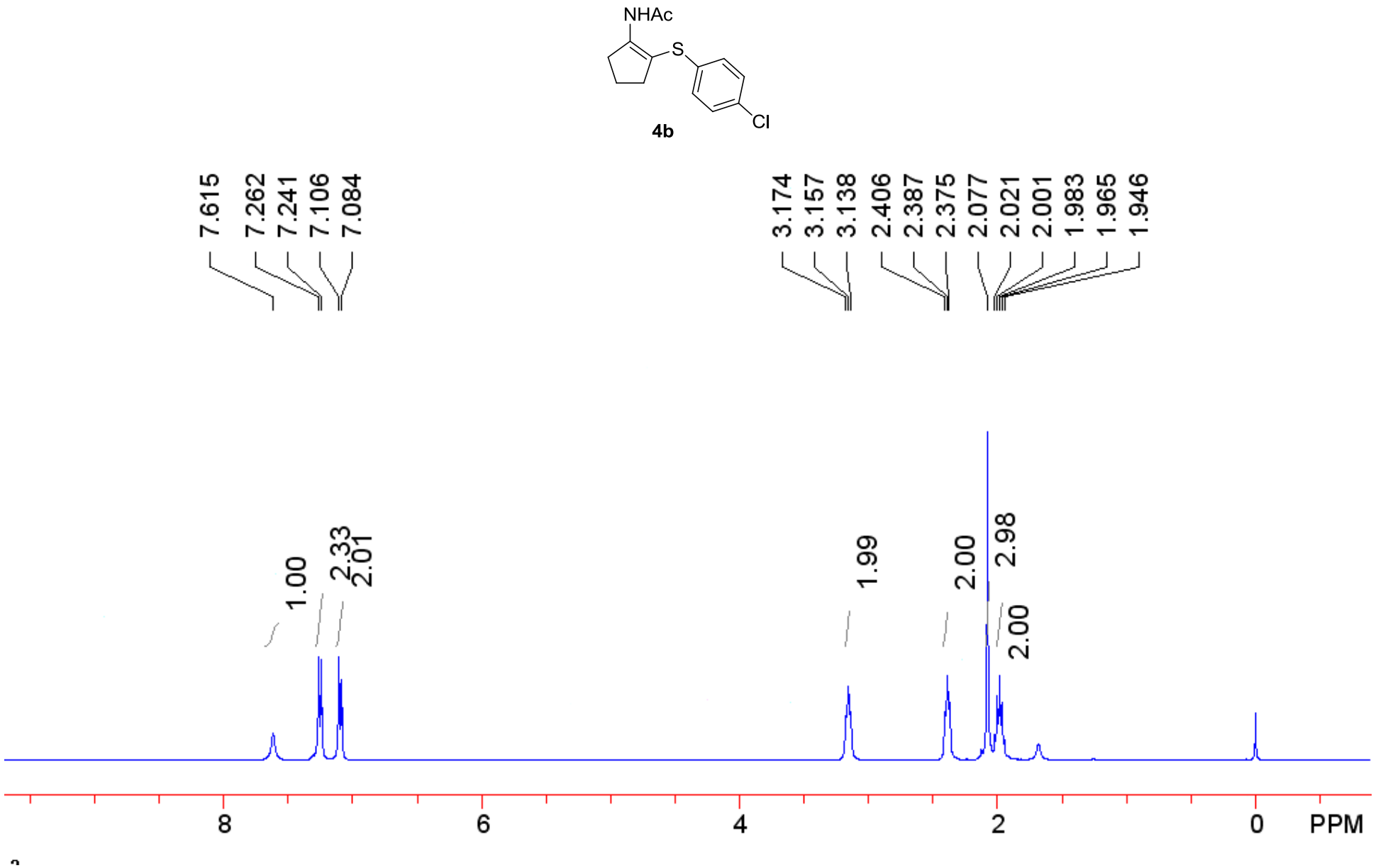
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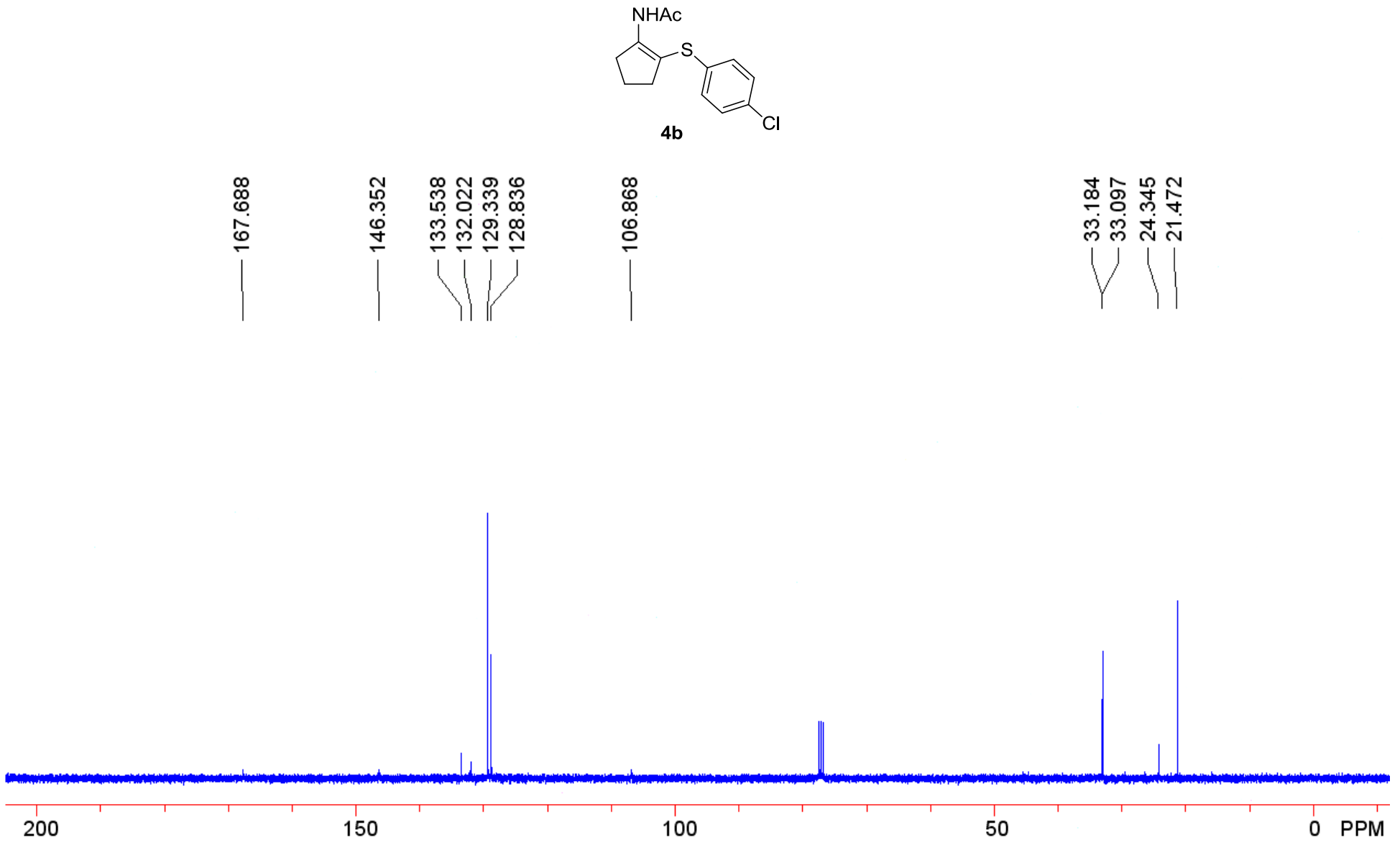
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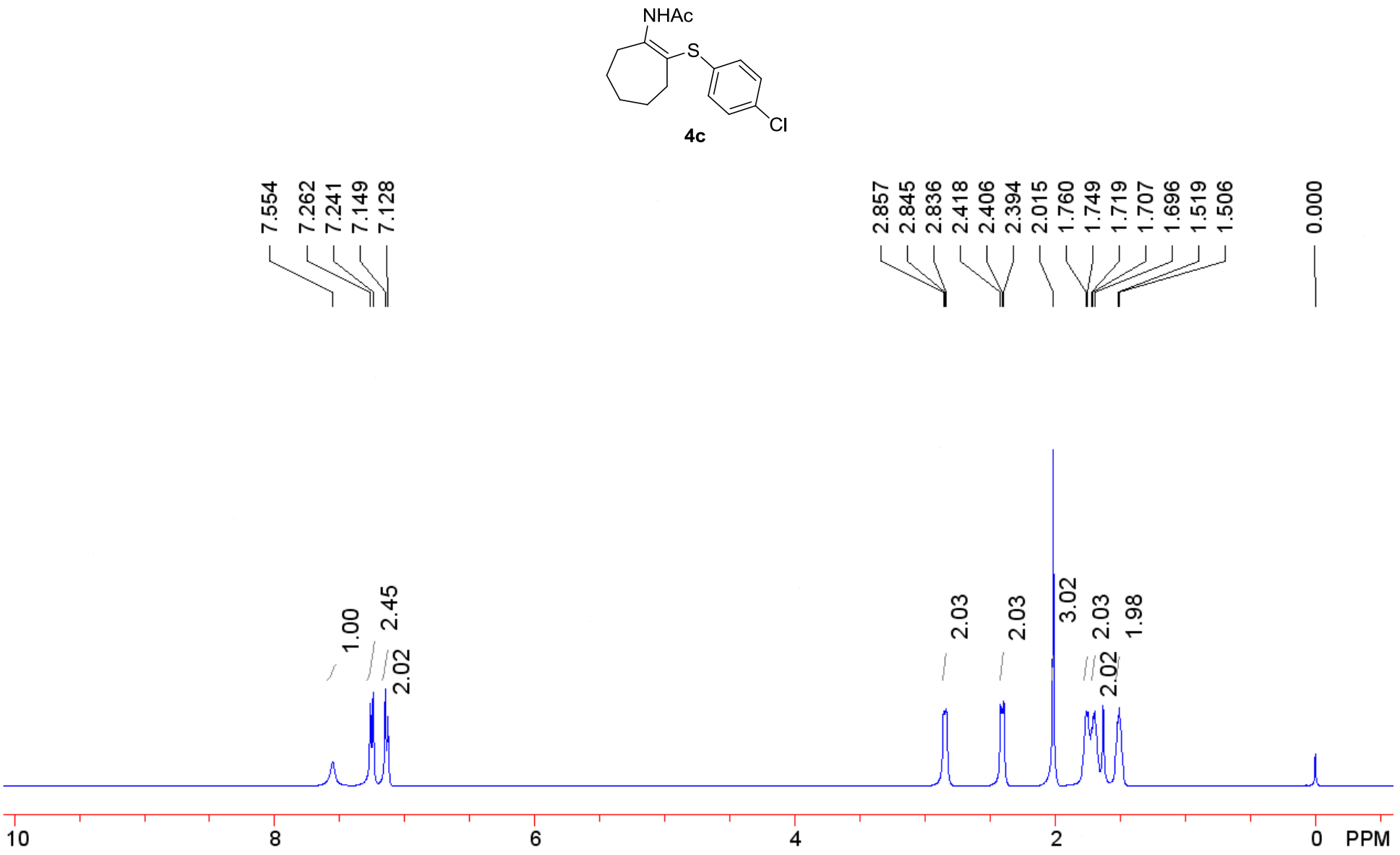
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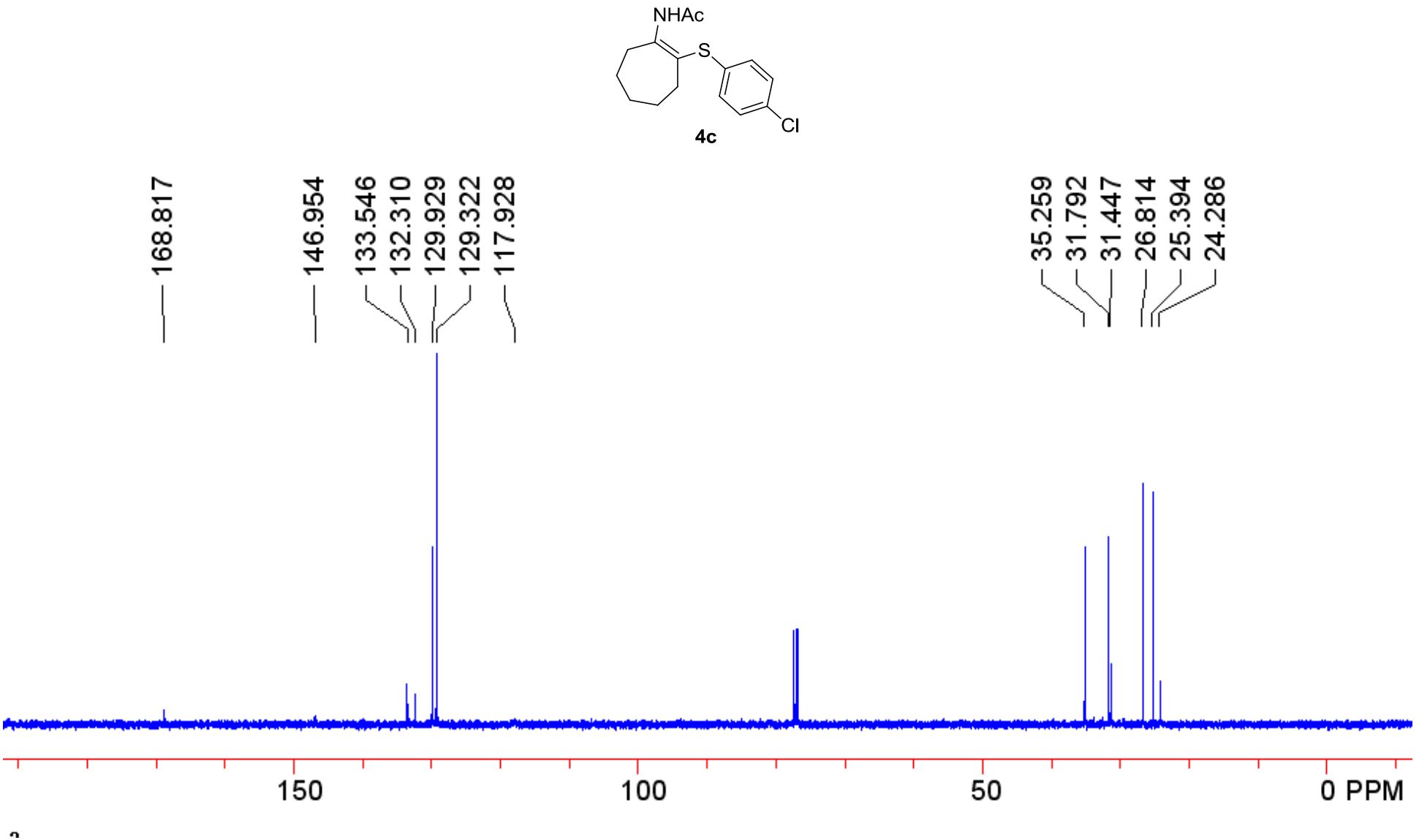
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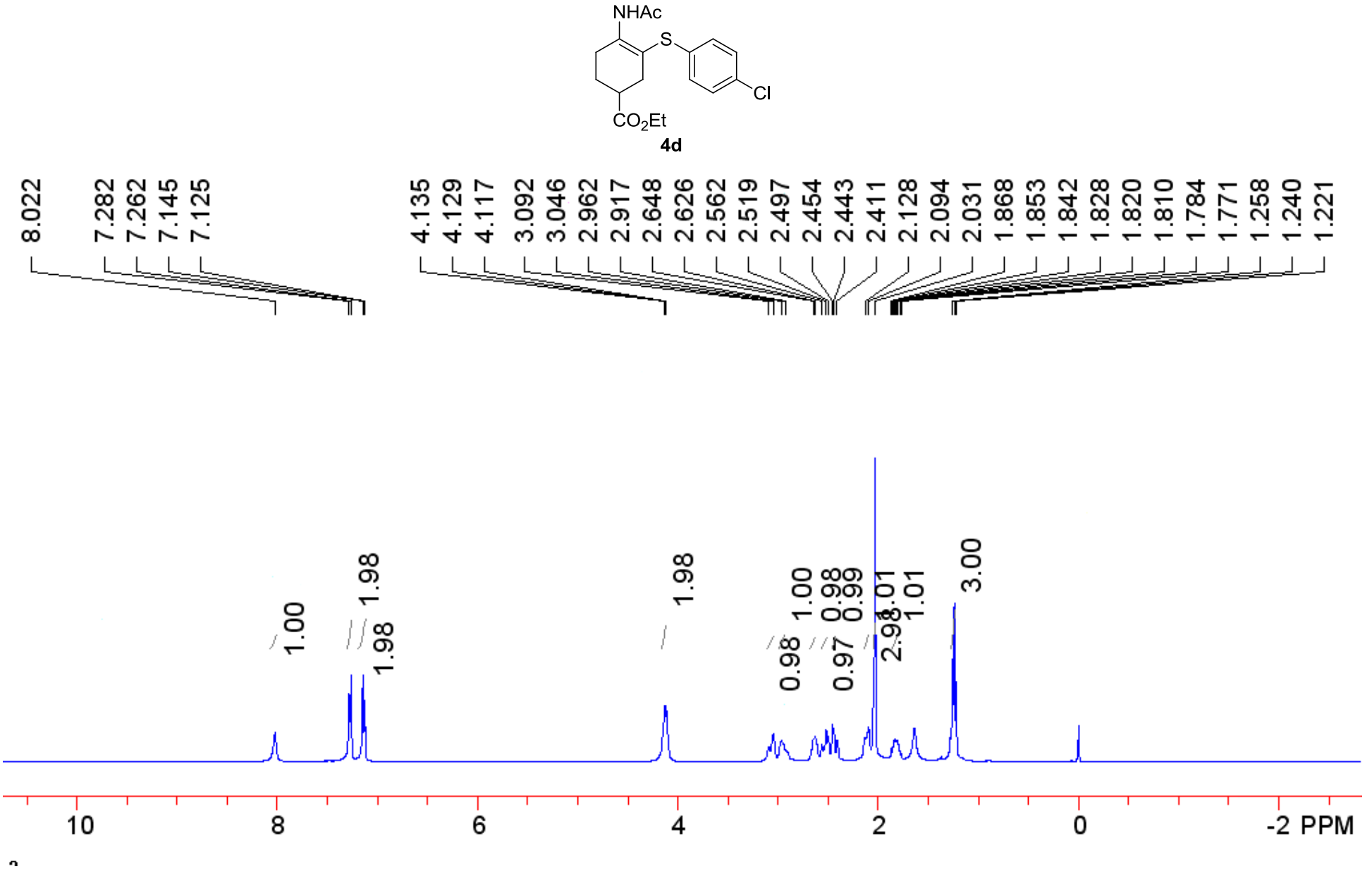
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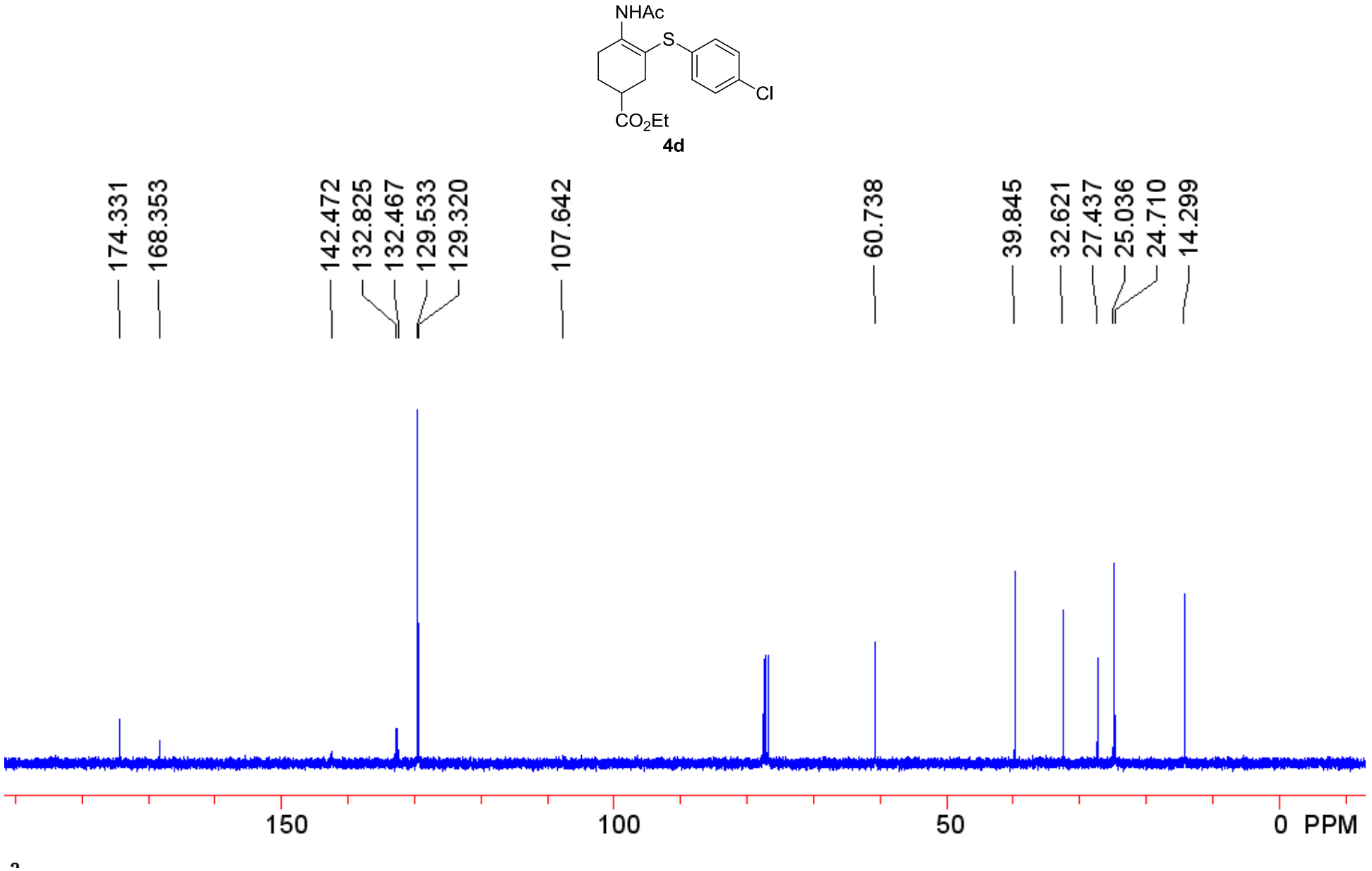
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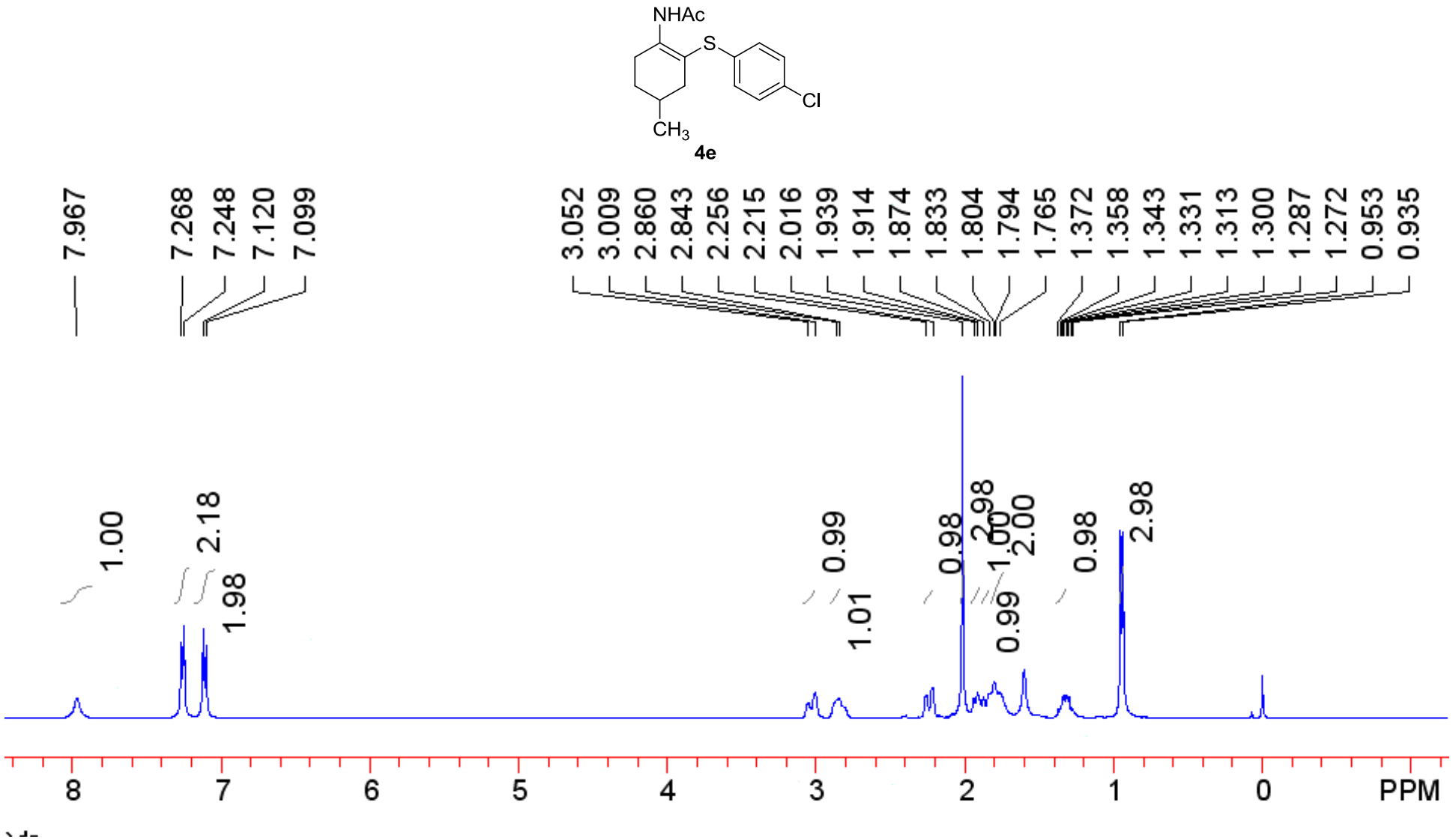
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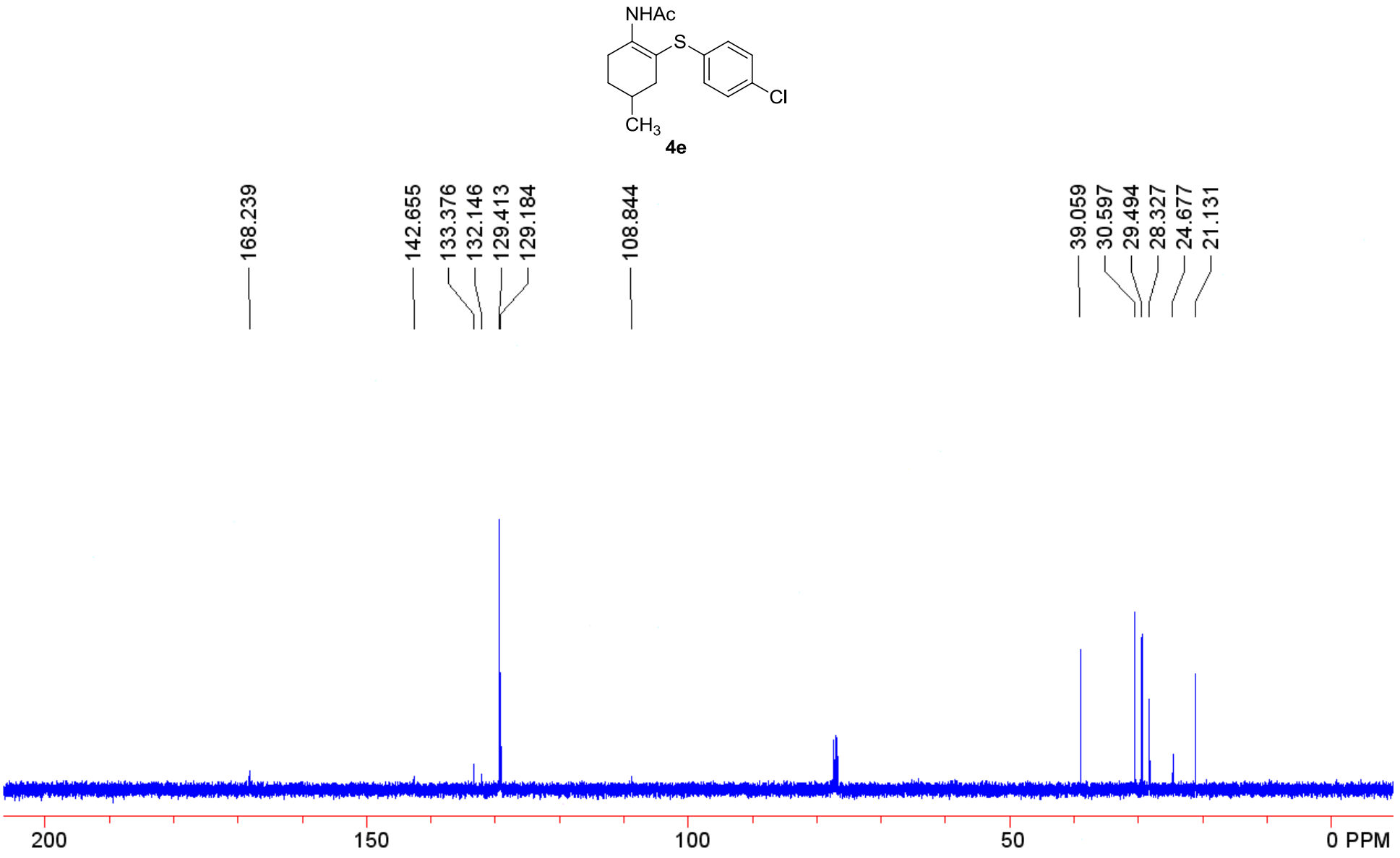
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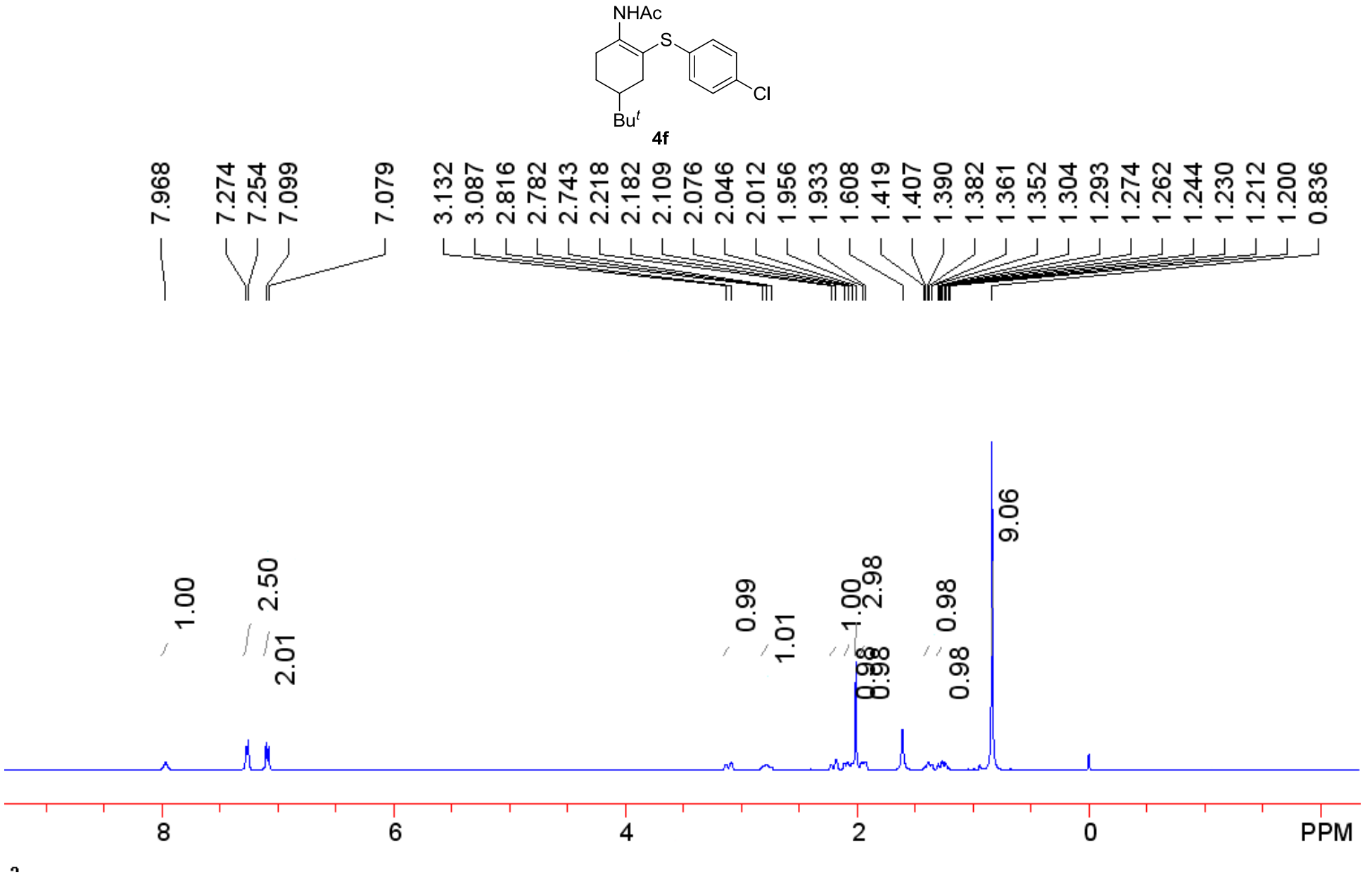
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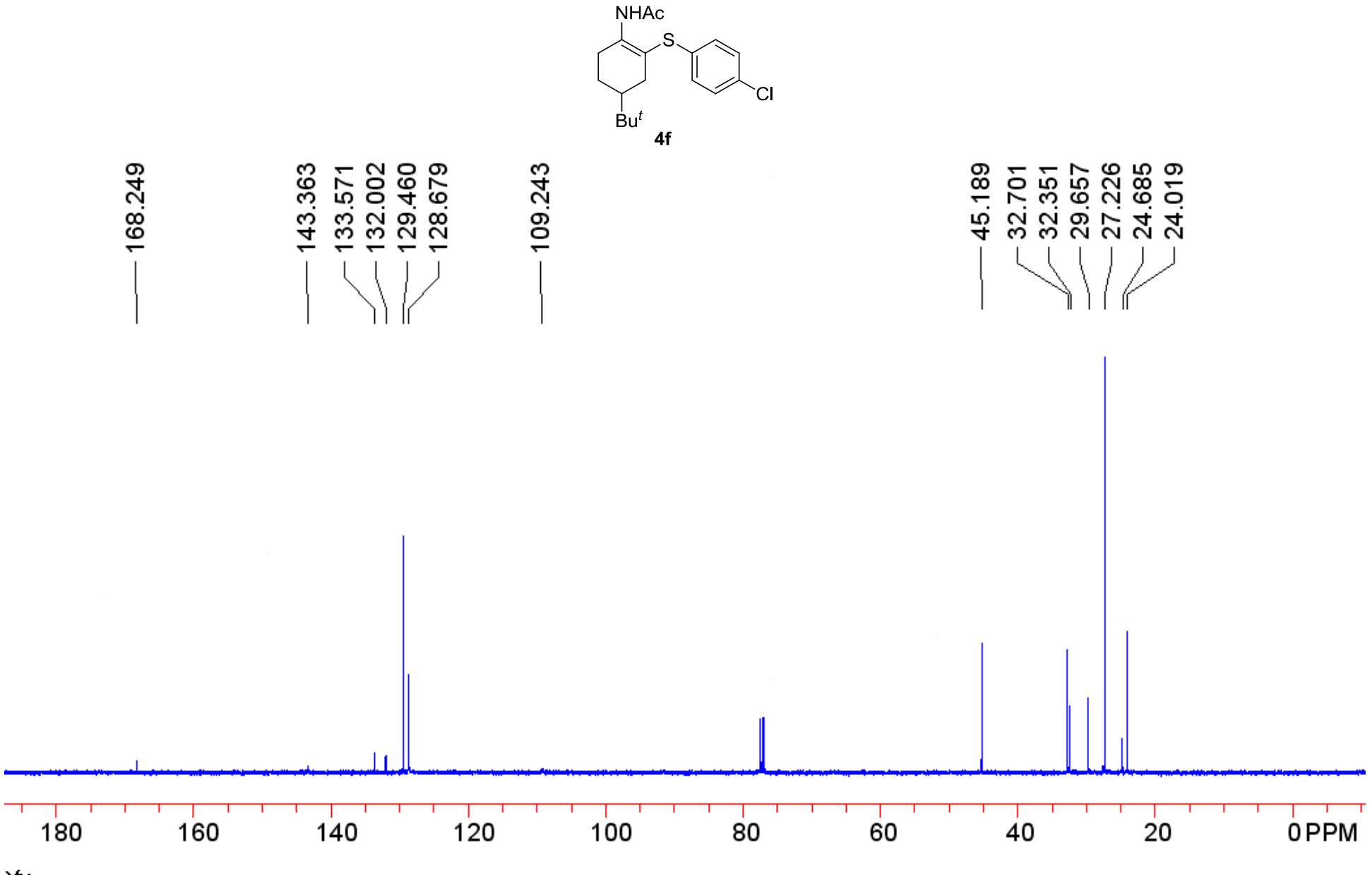
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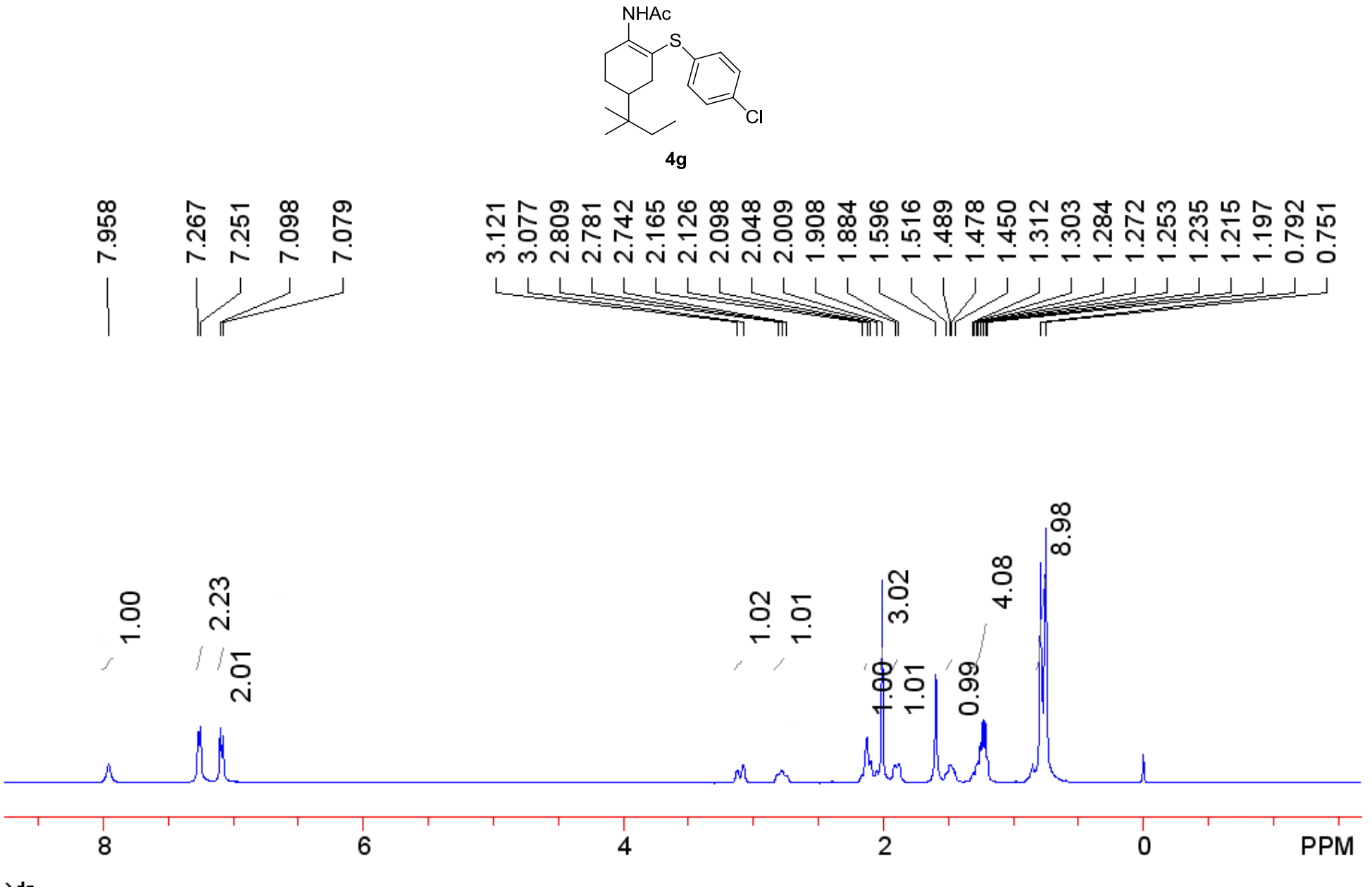
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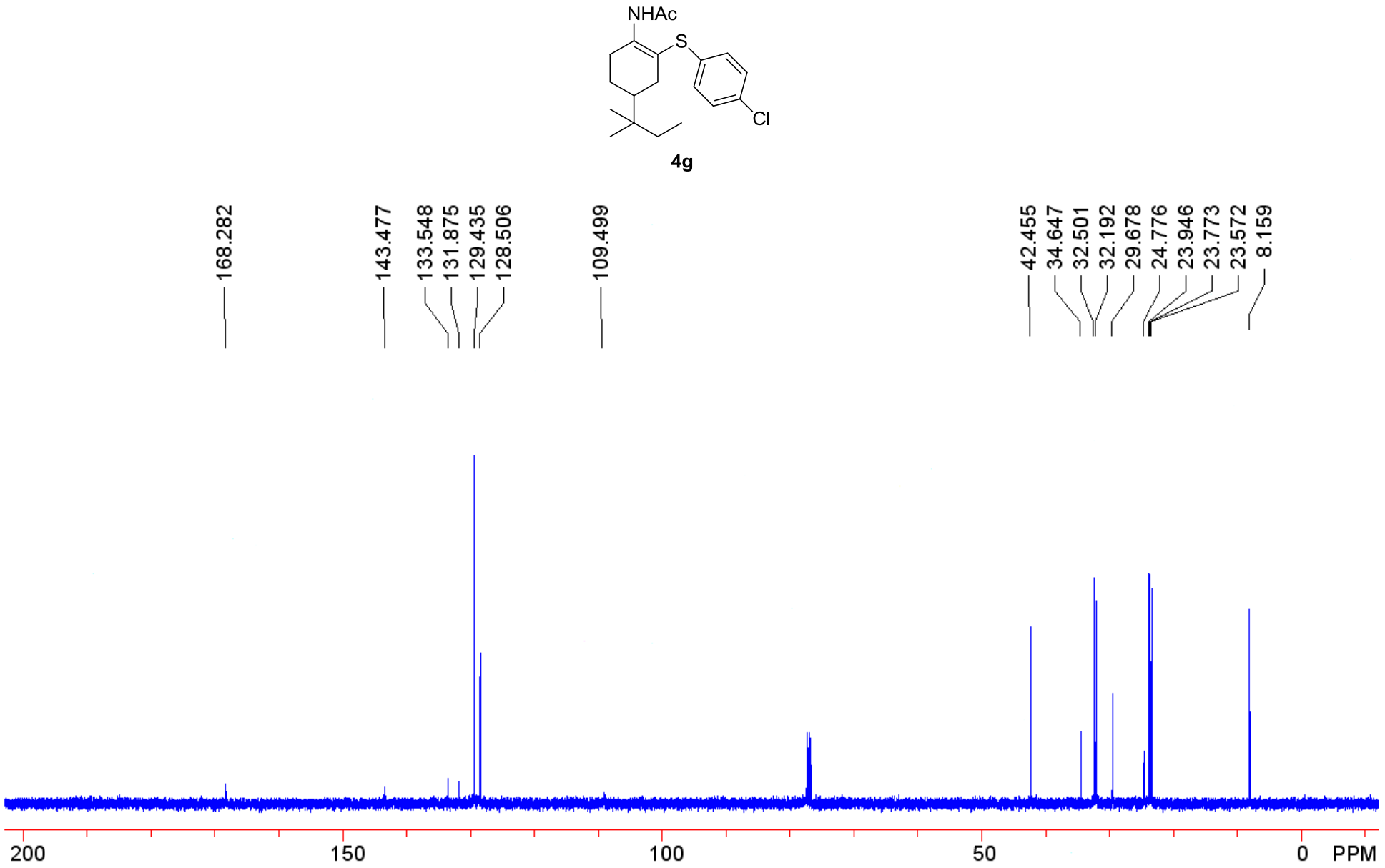
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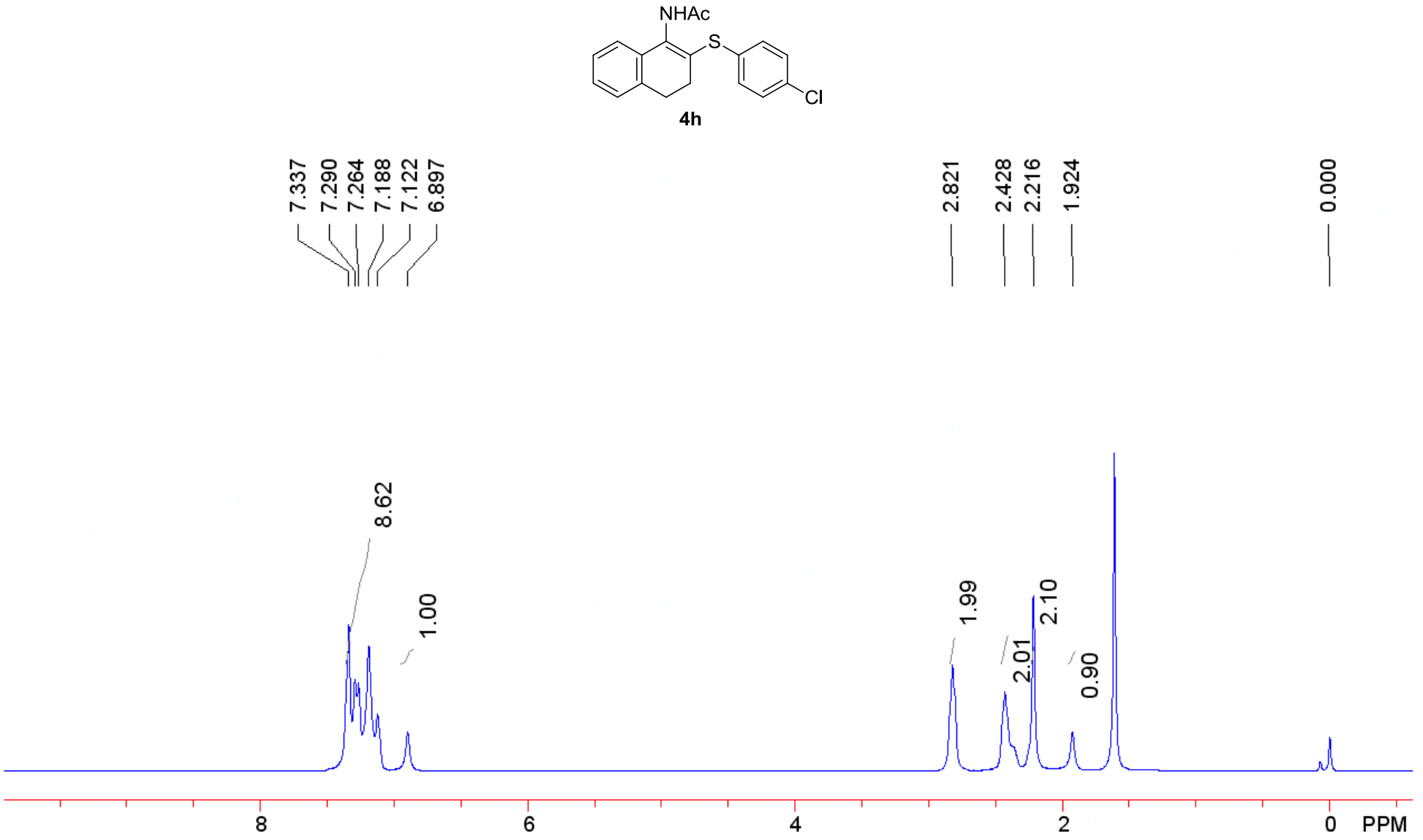
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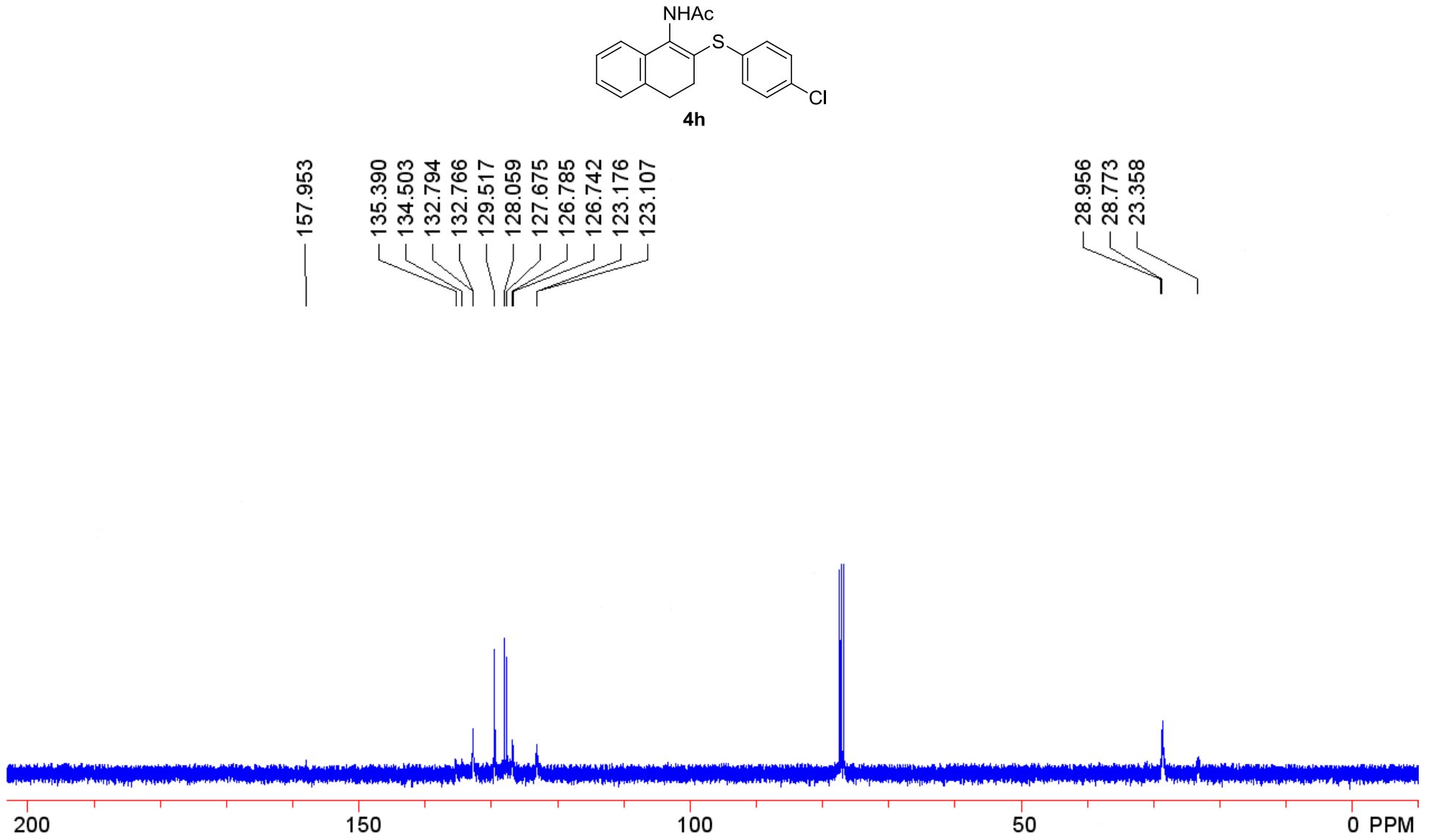
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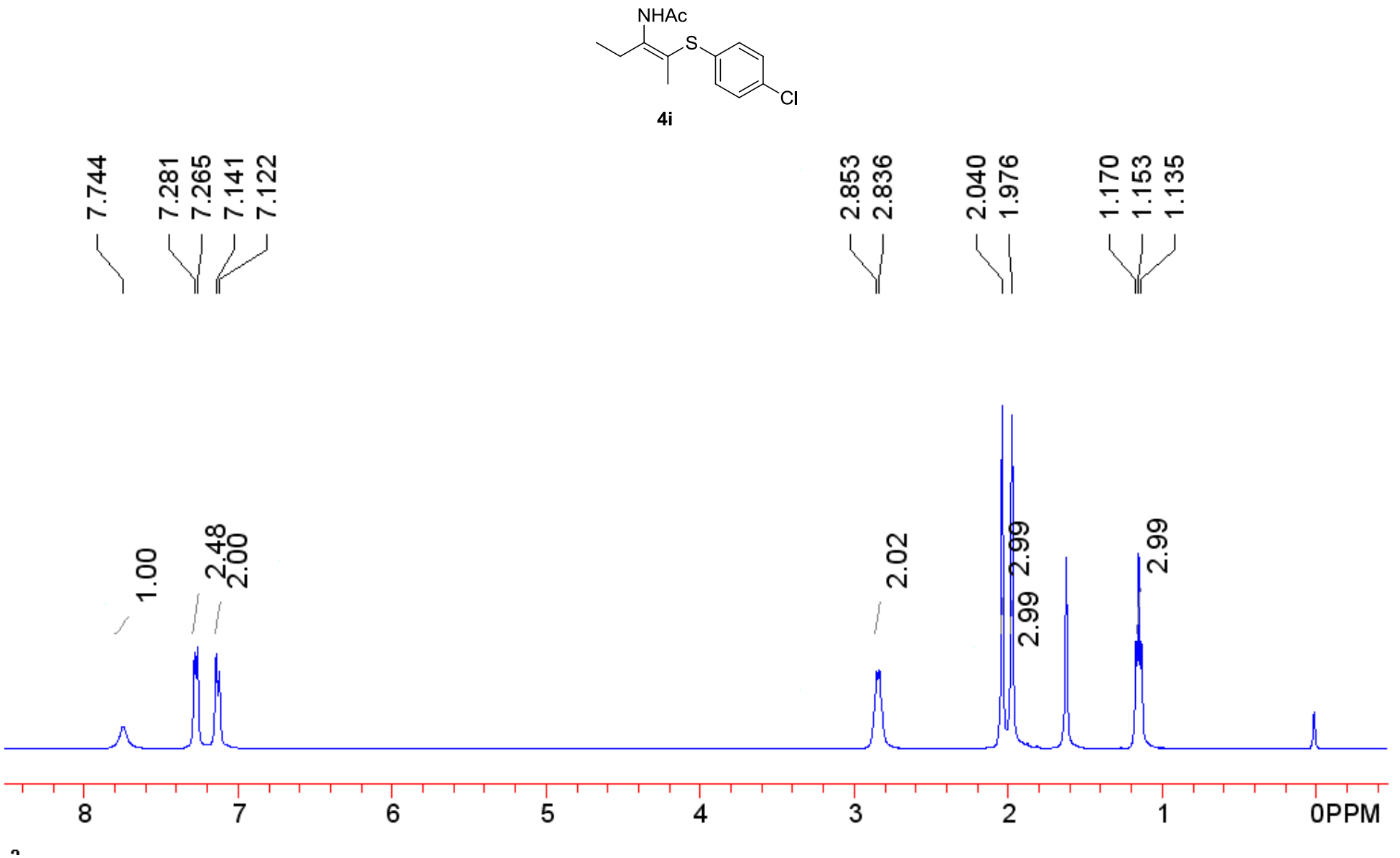
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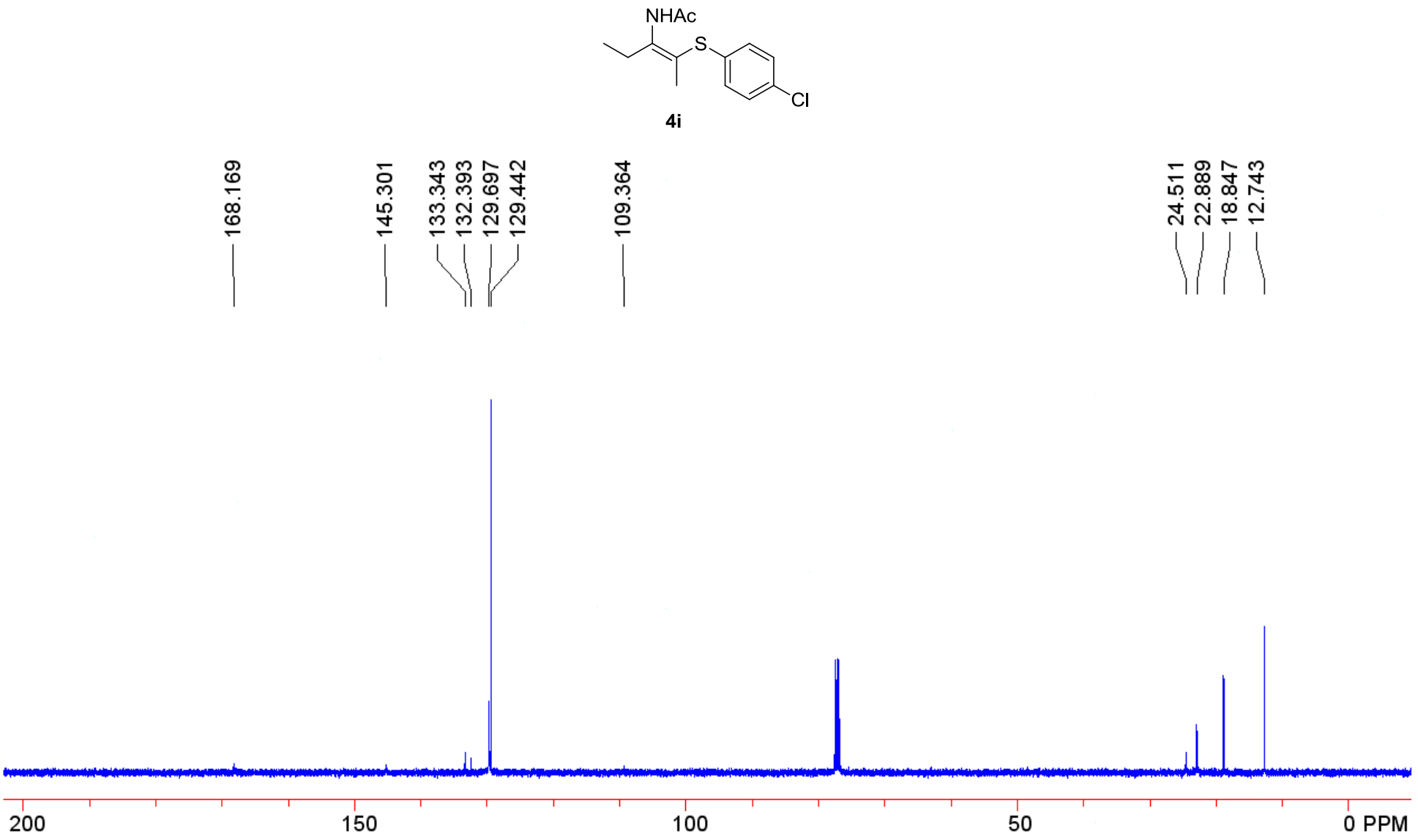
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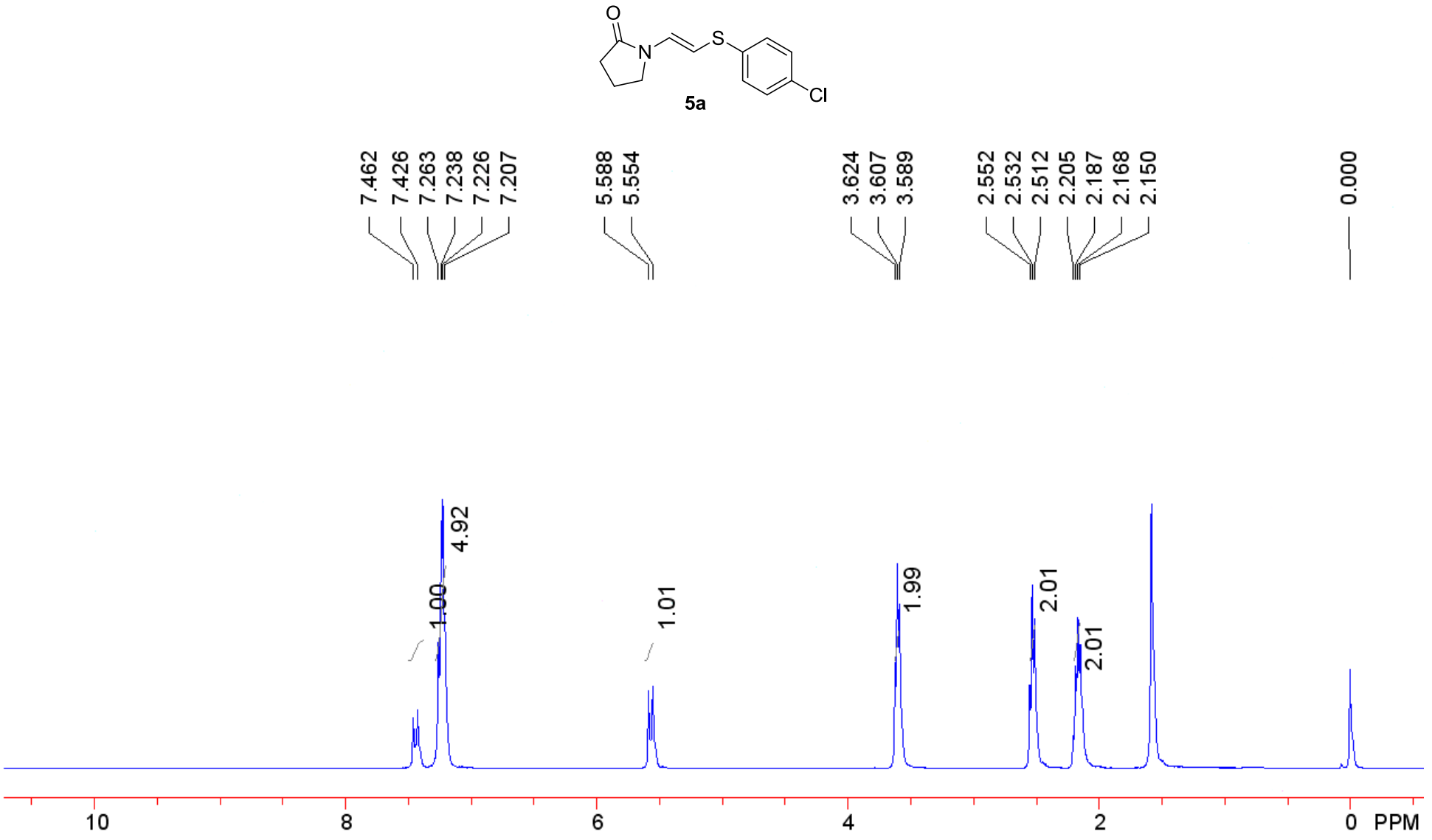
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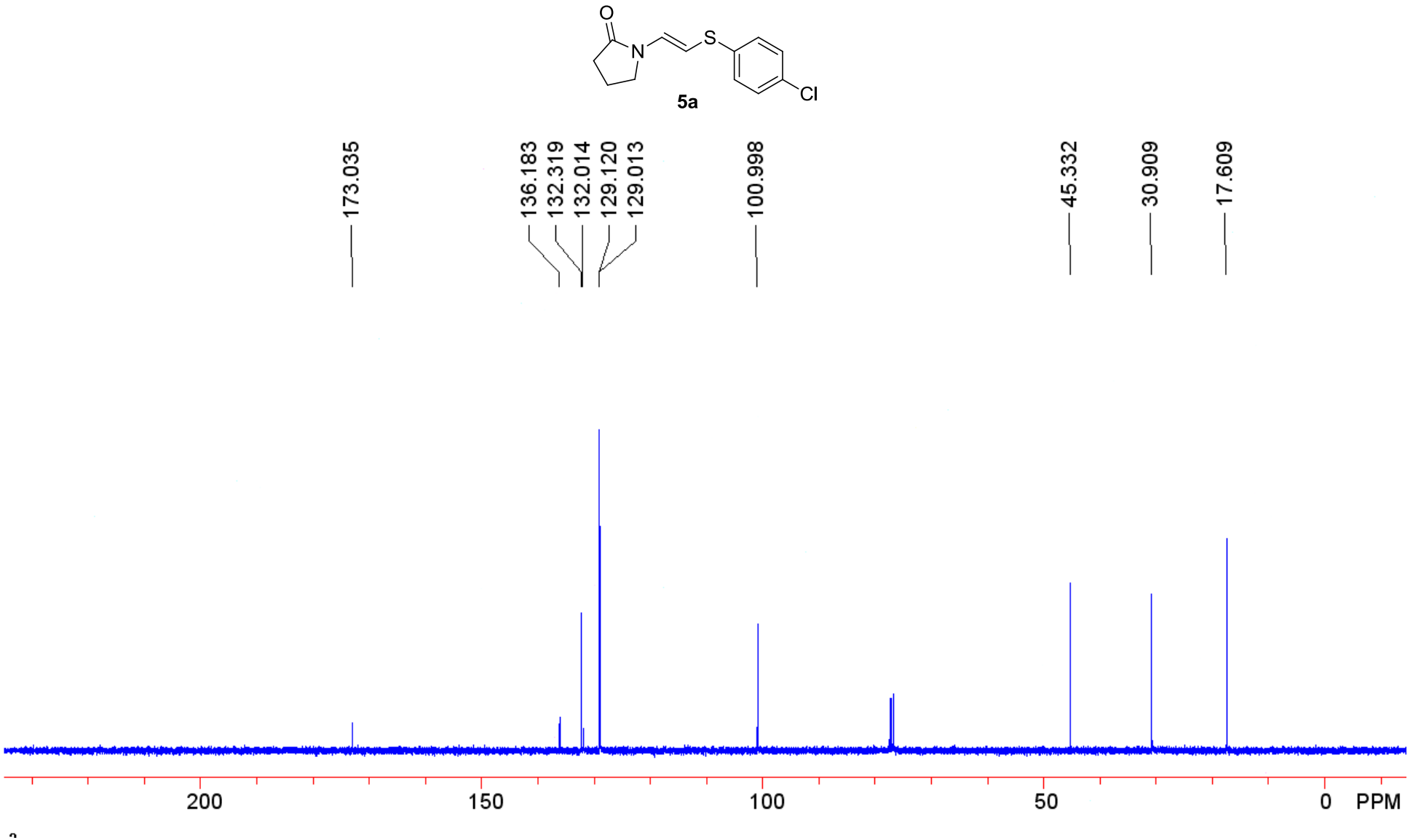
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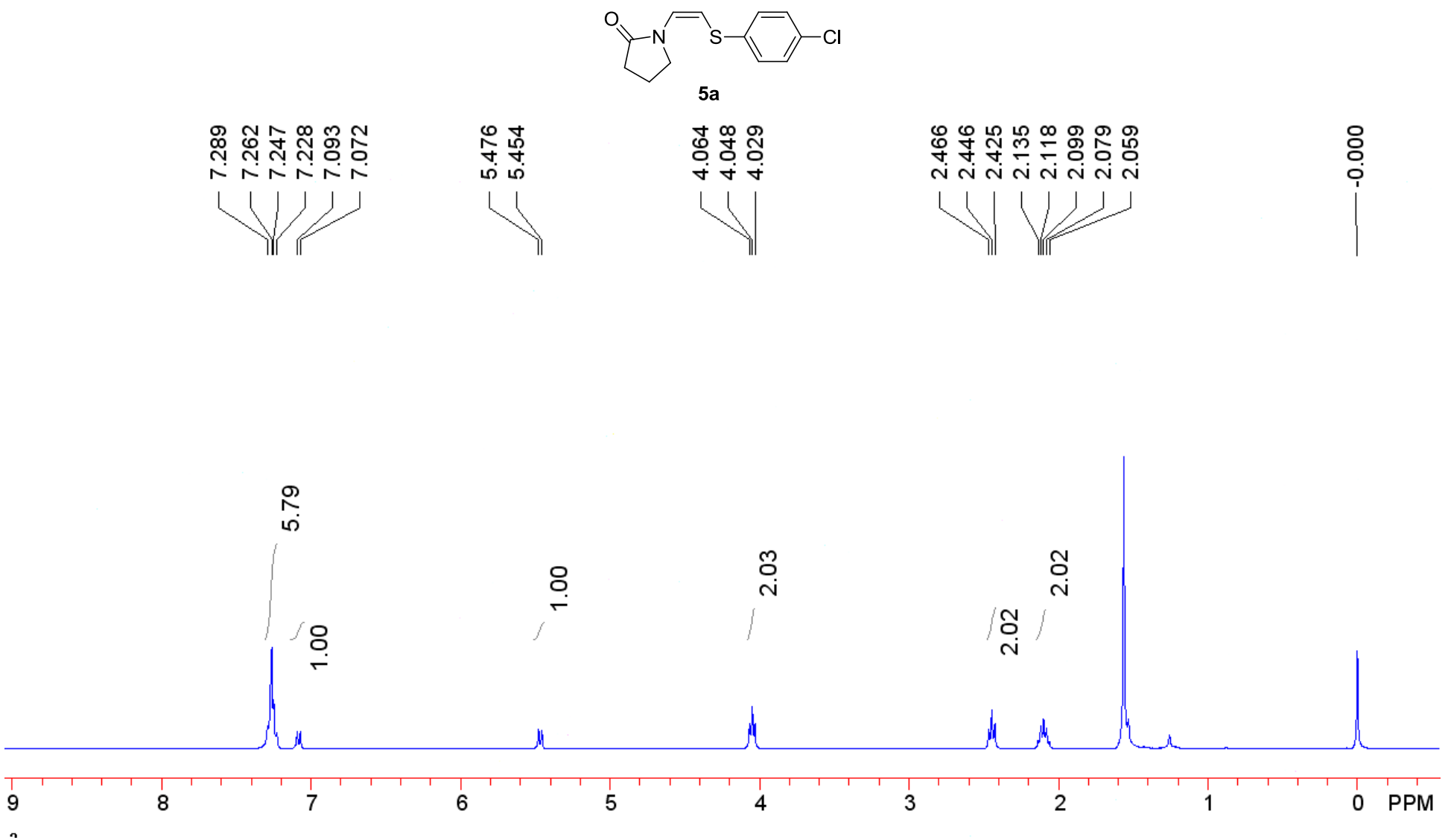
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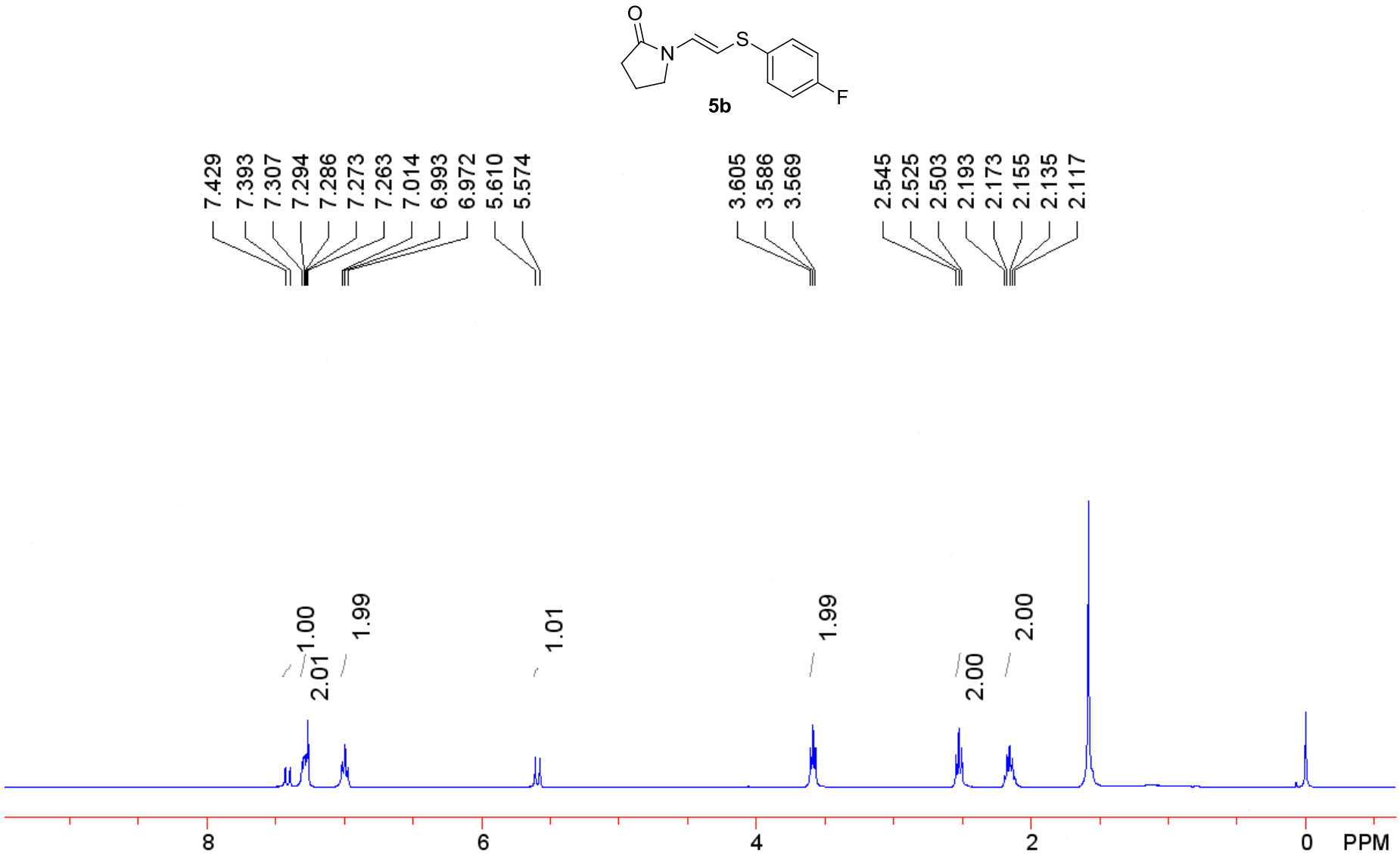
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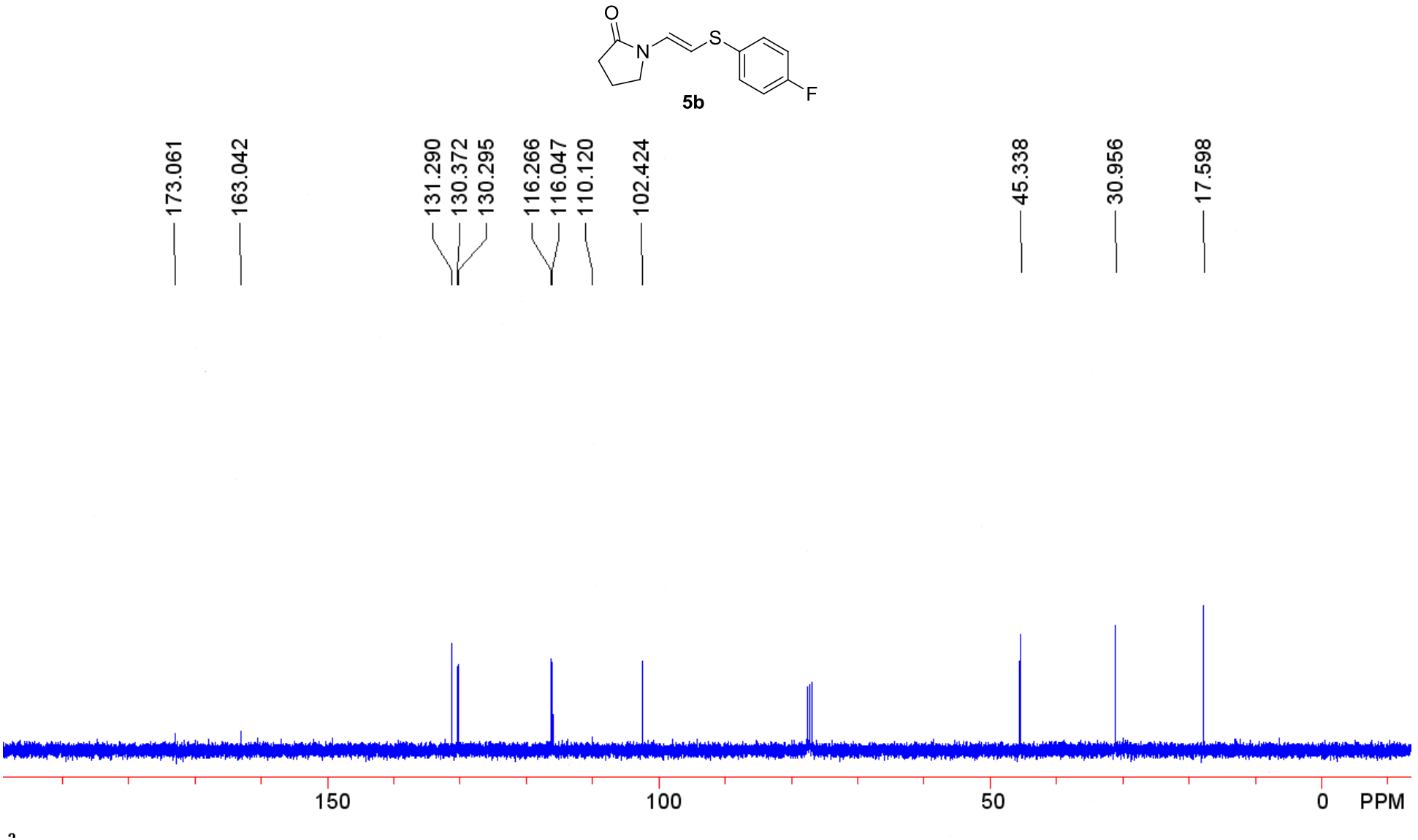
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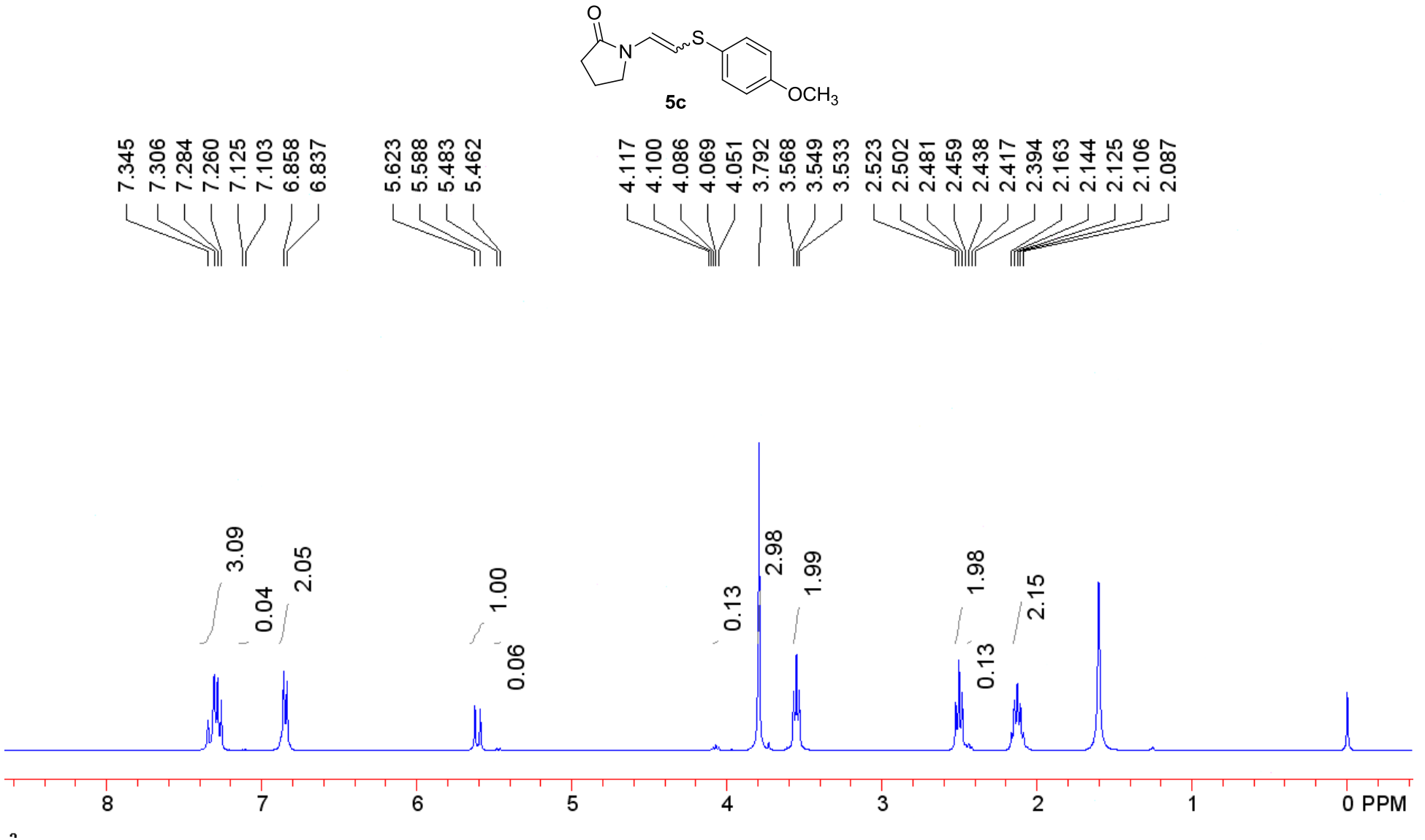
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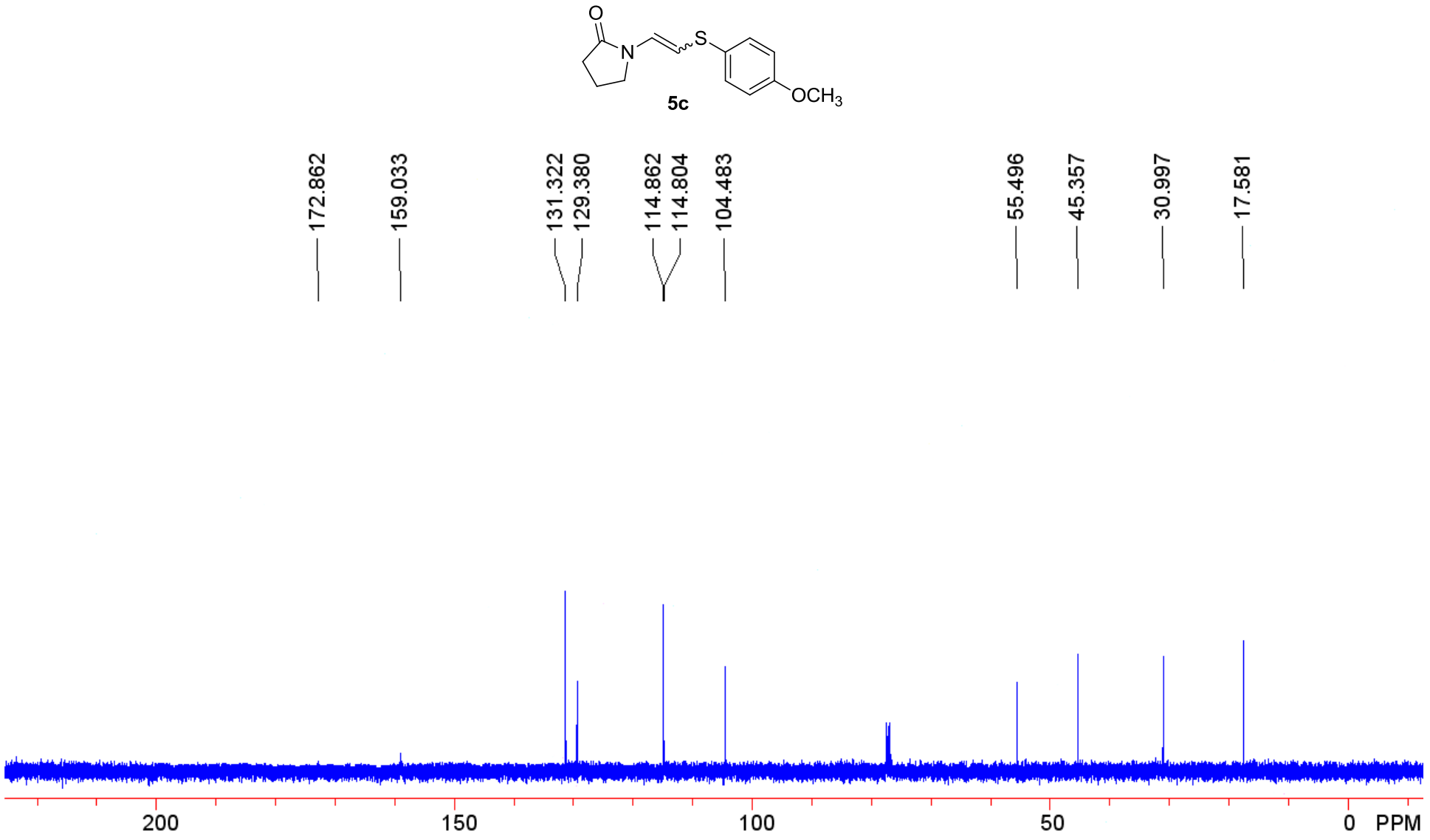
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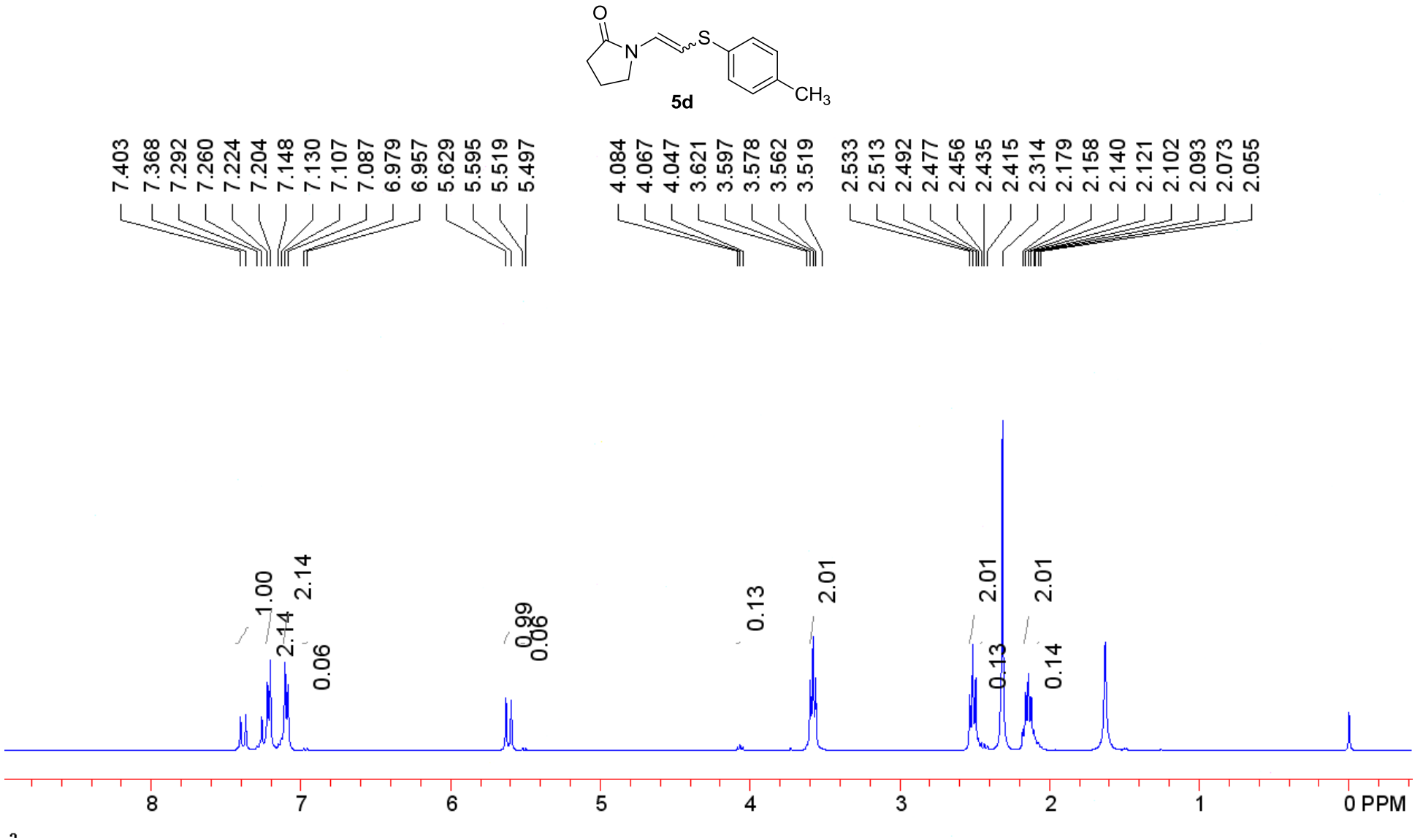
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N
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4.067
4.047
3.621
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3.578
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3.519
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2.055
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0.99
0.06
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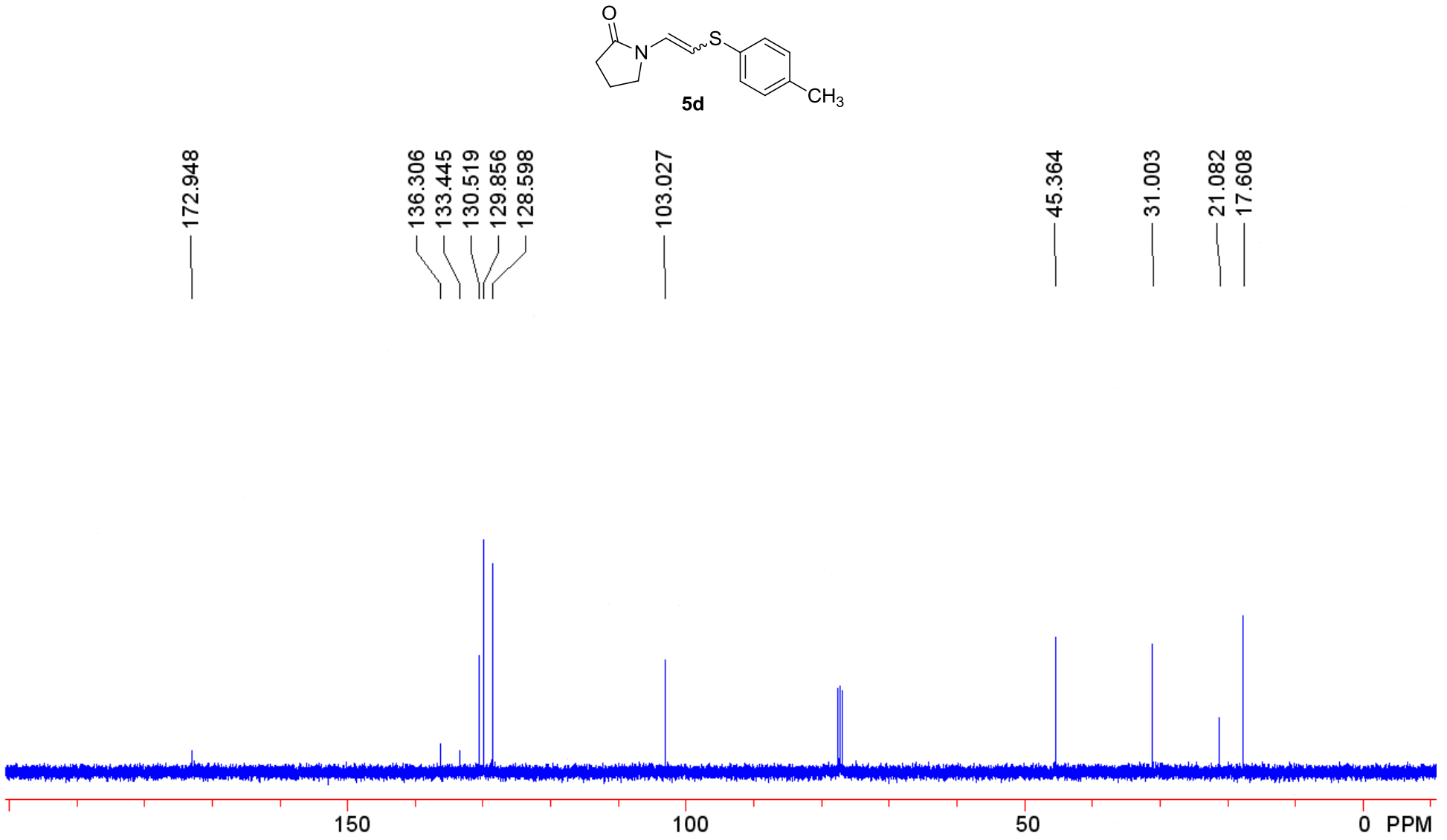
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CH3
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150
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50
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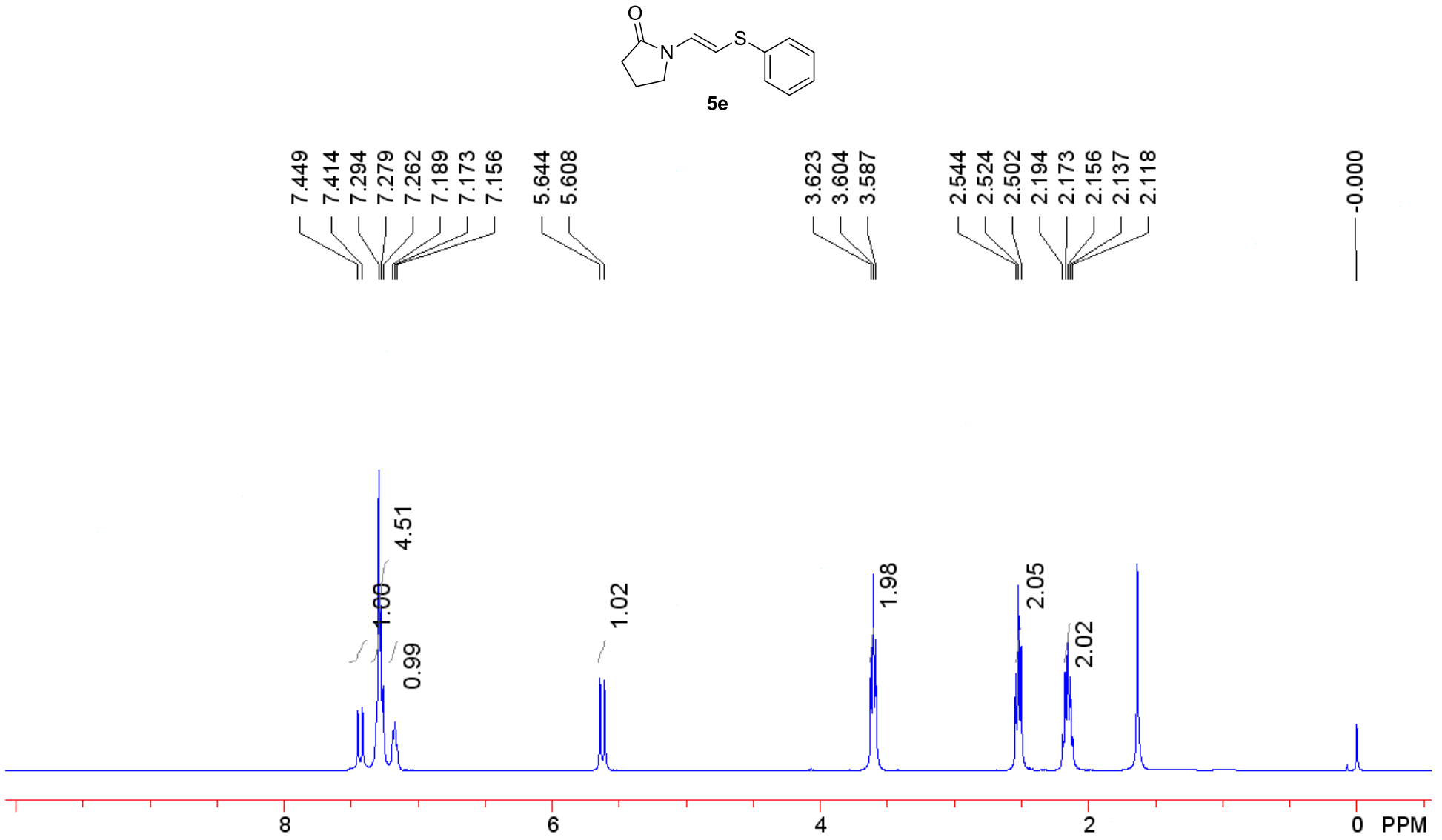
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S
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3.623
3.604
3.587
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2.524
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2.194
2.173
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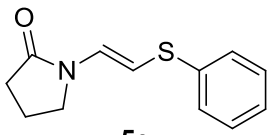
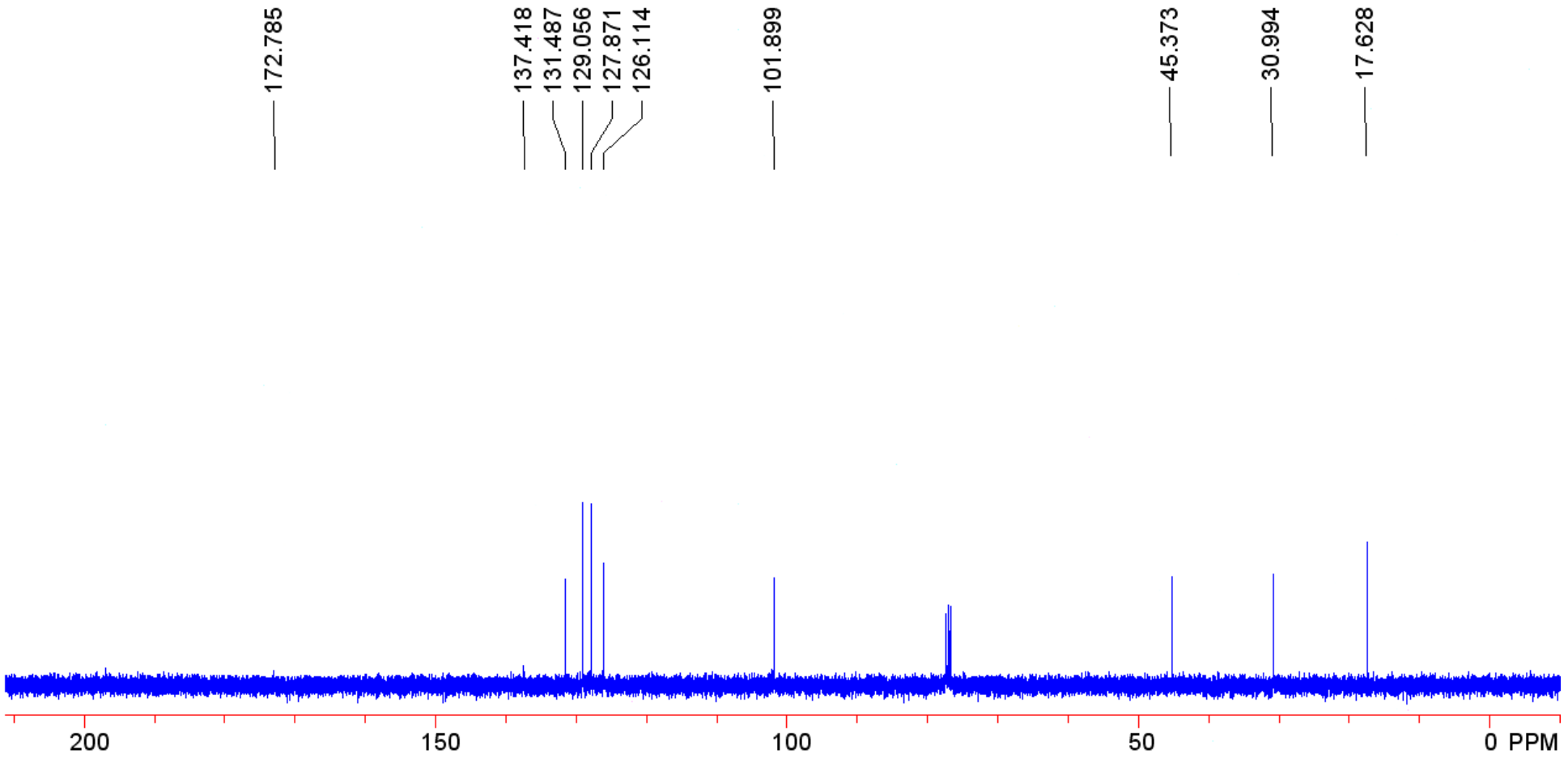

O
N
S

5e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200
150
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50
0 PPM