Cobalt(III)-Catalyzed C-H Amidation of *N,N*-Dialkyl Thiobenzamides by Sulfur Coordination

(Supporting Information)

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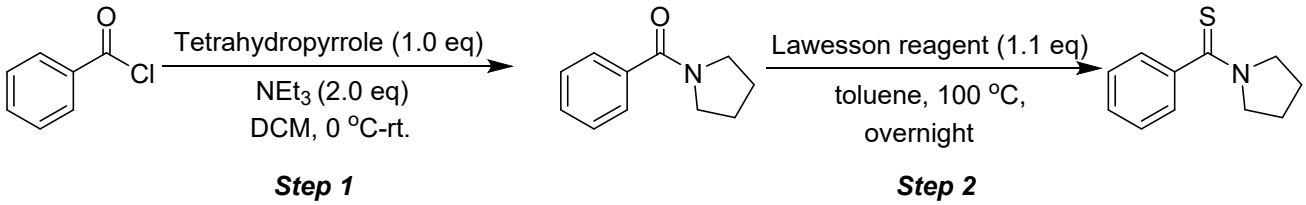
1. General remarks

All manipulations were conducted with sealed tubes. ^{1}H-NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with Chloroform-d. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with Chloroform-d. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

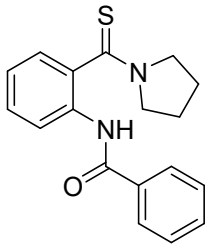
2. Preparation of substrates



Step 1: The solution of tetrahydropyrrole (10 mmol, 0.8 mL) and NEt_3 (20 mol, 2.8 mL) was dissolved in 50 mL dry DCM; and moved to an ice-bath, to this mixture was added the Benzoyl chloride slowly. After additon, the reaction was taken out of the ice-bath, and keeping stirring at 25 °C overnight. Then the reaction was quenched by the saturated sodium bicarbonate and extracted with DCM (50 mL × 2). The combined organic phase was washed with brine and dried over Na_2SO_4 and the solvent was removed under vacuum. The crude product can be used without further purification.[1]

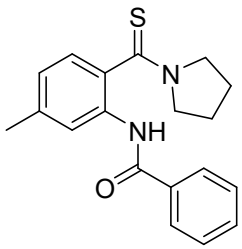
Step 2: The crude product and Lawesson reagent (11 mmol, 4.45 g) was dissolved in 50 mL toluene. Then the reaction was transformed to a preheated oil bath and stirring at 100 °C overnight. Cool down to r.t and concentrated in vacuum. The resulting oil was purified by column chromatography on silica gel (Petroleum ether /ethyl acetate = 20:1) affording **1** as yellow solid.[2]

3. Experimental procedure and characterization data



3a

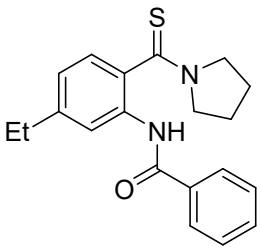
1) *N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benzamide (3a). The reaction of phenyl(pyrrolidin-1-yl)methanethione (1**a**) (0.2 mmol, 38.3 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg,0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3a**; Yellow solid, 55.4 mg, yield: 89%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.81 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.56 -7.37(m, 4H), 7.49 (dd, J = 13.2, 7.6 Hz, 2H), 7.41-7.37 (m, 4H), 7.17-7.12 (m, 2H), 3.96 (t, J = 8.4 Hz, 2H), 3.53 (d, J = 8.0 Hz, 1H), 3.34 (s, 1H), 2.07-1.87 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.2, 165.1, 134.3, 133.6, 133.4, 132.0, 129.6, 128.8, 127.3, 124.9, 124.1, 123.4, 54.1, 53.1, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{18}N_2OSNa$ $[M+Na]^+$ 333.1032, found: 333.1030.



3b

2) *N*-(5-methyl-2-(pyrrolidine-1-carbonothioyl)phenyl)benz-amide (3b). The reaction of pyrrolidin-1-yl(p-tolyl)methanethione (**1b**) (0.2 mmol, 41.1 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3b**;

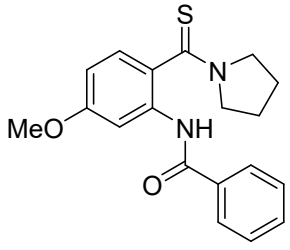
Yellow solid, 60.2 mg, yield: 91%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 8.19 (s, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.56-7.47 (m, 3H), 6.99 (d, J = 19.6, 7.6 Hz, 2H), 3.96 (s, 2H), 3.55 (s, 1H), 3.39 (s, 1H), 2.39 (s, 3H), 2.06-1.88 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.4, 165.0, 140.0, 134.3, 133.4, 131.9, 130.7, 128.7, 127.3, 124.8, 124.8, 123.8, 54.1, 53.1, 26.2, 24.4, 21.5 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{20}N_2OSNa$ $[M+Na]^+$ 347.1189, found: 347.1189.



3c

3) *N*-(5-ethyl-2-(pyrrolidine-1-carbonothioyl)phenyl)benzam-ide (3c).

The reaction of (4-ethylphenyl)(pyrrolidin-1-yl)methanethione (**1c**) (0.2 mmol, 43.9 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3c**; Yellow oil, 39.7 mg, yield: 59%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.95 (s, 1H), 8.22 (s, 1H), 7.95 (t, J = 3.2 Hz, 2H), 7.55-7.47 (m, 3H), 7.06-6.97 (m, 2H), 3.96 (t, J = 7.2 Hz, 2H), 3.56 (s, 1H), 3.40 (s, 1H), 2.69 (d, J = 7.6 Hz, 2H), 2.07-1.88 (m, 4H), 1.28-1.25 (m, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.6, 165.1, 146.3, 134.4, 133.6, 131.9, 131.0, 128.8, 127.3, 124.9, 123.6, 122.8, 54.2, 53.1, 28.9, 26.2, 24.5, 15.3 ppm. **HRMS m/z (ESI)**: calcd. for $C_{20}H_{22}N_2OSNa$ $[M+Na]^+$ 361.1345, found: 361.1335.

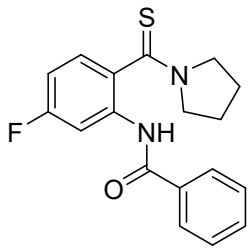


3d

4) *N*-(5-methoxy-2-(pyrrolidine-1-carbonothioyl)phenyl)-

benzamide (3d).

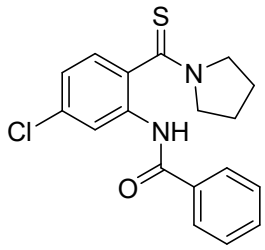
The reaction of (4-methoxyphenyl)(pyrrolidin-1-yl) methanethione (**1d**) (0.2 mmol, 44.3 mg), 3-phenyl-1,4,2- dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3d**; Yellow oil, 18.7 mg, yield: 27%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 10.29 (s, 1H), 8.09 (d, J = 2.8 Hz, 1H), 7.97 (d, J =3.2 Hz, 2H), 7.57-7.47 (m, 3H), 7.04 (d，J = 8.8 Hz, 1H), 6.68 (dd, J = 8.2, 5.6 Hz, 2H), 3.97 (d, J = 7.2 Hz , 2H), 3.88 (d, J = 10 Hz, 3H), 3.56-3.45 (m, 2H), 3.07-1.94 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.1, 165.2, 160.4, 135.7, 134.3, 132.0, 128.8, 127.3, 126.3, 125.2, 110.6, 107.3, 55.5, 54.4, 53.3, 26.2, 24.5 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{20}N_2O_2SNa$ $[M+Na]^+$ 363.1138, found: 363.1132.



3e

5) *N*-(5-fluoro-2-(pyrrolidine-1-carbonothioyl)phenyl)benz-amide (3e). The reaction of (4-fluorophenyl) (pyrrolidin-1-yl) methanethione (**1e**) (0.2 mmol, 41.2 mg), 3-phenyl-1,4,2- dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3e**; Yellow oil, 57.6 mg, yield: 88 %. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 10.08 (s, 1H), 8.26 (dd, J = 2.4, 9.2 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.58-7.48 (m, 3H), 7.10 (dd, J = 6.4, 2.0 Hz, 1H), 6.87-6.82 (m, 1H), 3.98 (s, 2H), 3.55 (s, 1H), 3.37 (s,

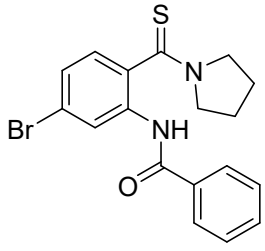
1H), 2.08-1.91 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.4, 165.1, 162.7 (d, $^1J_{C\text{-}F}$ = 246.5 Hz), 135.8 (d, $^3J_{C\text{-}F}$ = 11.7 Hz), 134.0, 132.2, 128.8, 128.6 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 127.3, 126.4 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 110.7 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 110.2 (d, $^2J_{C\text{-}F}$ = 27.0 Hz), 54.3, 53.3, 26.2, 24.4 ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -109.3 ppm (reference: $PhCF_3$). **HRMS m/z (ESI)**: calcd. for $C_{18}H_{17}N_2FOSNa$ $[M+Na]^+$ 351.0938, found: 351.0938.



3f

6) *N*-(5-chloro-2-(pyrrolidine-1-carbonothioyl)phenyl)bez -amide (3f).

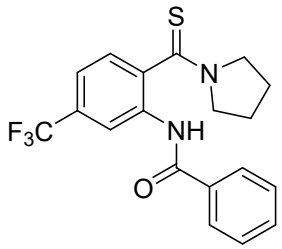
The reaction of (4-chlorophenyl) (pyrrolidin-1-yl) methanethione (**1f**) (0.2 mmol, 45.0 mg), 3-phenyl-1,4,2- dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), $Cp^*Co(CO)I_2$ (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3f**; Yellow oil, 55.3 mg, yield: 80 %. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.93 (s, 1H), 8.49 (s, 1H), 7.93 (dd, J = 3.6, 2.0 Hz, 2H), 7.58-7.48 (m, 3H), 7.14-7.05 (m, 2H), 3.97 (s, 2H), 3.54 (s, 1H), 3.37 (s, 1H), 2.10-1.91 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.2, 165.0, 135.4, 134.9, 133.9, 132.2, 131.1, 128.9, 127.4, 125.9, 124.0, 123.1, 54.2, 53.2, 26.3, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{17}N_2ClOSNa$ $[M+Na]^+$ 367.0642, found: 367.0630.



3g

7) *N*-(5-bromo-2-(pyrrolidine-1-carbonothioyl)phenyl)bez-amide(3g). The reaction of (4-bromophenyl) (pyrrolidin-1-yl) methanethione (**1g**) (0.2 mmol, 54.0 mg), 3-phenyl -1,4,2-

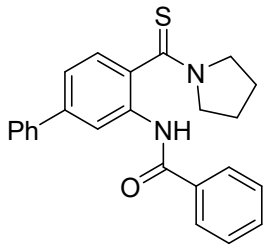
dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3g**; Yellow oil, 44 mg, yield: 56%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.90 (s, 1H), 8.64 (s, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.58-7.48 (m, 3H), 7.28 (dd, J = 6.4, 1.3 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 3.96 (s, 2H), 3.53 (s, 1H), 3.37 (s, 1H), 2.08-1.89 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 192.0, 165.0, 134.9, 133.8, 132.2, 131.4, 128.8, 127.3, 127.0, 126.1, 125.9, 123.4, 54.2, 53.2, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{18}N_2BrOS$ $[M+H]^+$ 389.0318, found: 389.0318.



3h

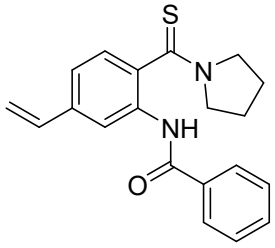
8) *N*-(2-(pyrrolidine-1-carbonothioyl)-5-(trifluoromethyl)phenyl)benzamide (**3h**). The reaction of pyrrolidin-1-yl (4-(trifluoromethyl)phenyl) methanethione (**1h**) (0.2 mmol, 51.8 mg), 3-phenyl-1,4,2- dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3h**; Yellow oil, 37.9 mg, yield: 50%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.81 (s, 1H), 8.75 (s, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.60-7.50 (m, 3H), 7.41 (d, J = 7.6 Hz, 1H), 7.25 (s, 1H), 3.99 (dd, J = 12.4, 5.6 Hz, 2H), 3.54 (s, 1H), 3.34 (s, 1H), 2.12-1.90 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 191.6, 165.2, 135.8, 134.2, 133.8, 132.3, 131.4, 128.9, 127.3, 125.4, 122.2, 120.8 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 120.3 (q, $^3J_{C\text{-}F}$ = 3.2 Hz), 54.1,

53.2, 26.3, 24.4 ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -63.4 ppm (reference: $PhCF_3$). **HRMS m/z (ESI)**: calcd. For $C_{19}H_{17}N_2F_3BrOSNa$ $[M+Na]^+$ 401.0906, found: 401.0904.



3i

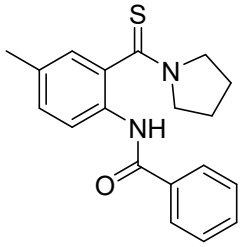
9) *N*-(4-(pyrrolidine-1-carbonothioyl)-[1,1'-biphenyl]-3-yl)-benzamide (**3i**). The reaction of [1,1'-biphenyl]-4-yl(pyrrolidin-1-yl) methanethione (**1i**) (0.2 mmol, 53.5 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3i**; Yellow oil, 50.2 mg, yield: 65%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.98 (s, 1H), 8.65 (s, 1H), 7.88 (d, J = 6.8 Hz, 2H), 7.67 (d, J = 1.2 Hz, 2H), 7.58-7.35 (m, 7H), 7.20 (d, J = 8.0 Hz, 1H), 4.00 (d, J = 6.4 Hz, 2H), 3.61 (s, 1H), 3.46 (s, 1H), 2.08-1.90 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.1, 165.1, 142.6, 140.0, 143.3, 134.0, 132.0, 128.8, 127.8, 127.3, 127.2, 125.4, 122.6, 122.0, 54.2, 53.1, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{24}H_{22}N_2OS$ $[M+H]^+$ 387.1526, found: 387.1515.



3j

10) *N*-(2-(pyrrolidine-1-carbonothioyl)-5-vinylphenyl)benzamide (**3j**). The reaction of pyrrolidin-1-yl (4-vinylphenyl) methanethione (**1j**) (0.2 mmol, 43.5 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as

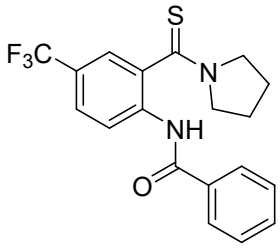
monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3j**; Yellow oil, 29.9 mg, yield: 44%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.92 (s, 1H), 8.44 (s, 1H), 7.96 (d, J = 7.6 Hz, 2H), 7.57-7.48 (m, 3H), 7.20 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.77-6.70 (m, 1H), 5.84 (d, J = 7.6 Hz, 1H), 5.34 (d, J = 7.6 Hz, 1H), 3.97 (s, 2H), 3.56 (s, 1H), 3.40 (s, 1H), 2.07-1.89 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.1, 165.1, 139.1, 136.0, 134.3, 134.0, 132.4, 132.0, 128.8, 127.3, 125.2, 121.7, 121.1, 115.6, 54.1, 53.1, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{20}H_{21}N_2OS$ $[M+H]^+$ 337.1369, found: 337.1358.



3k

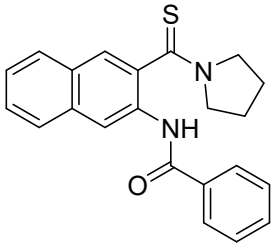
11) *N*-(4-methyl-2-(pyrrolidine-1-carbonothioyl)phenyl)benz-amide(3k). The reaction of pyrrolidin-1-yl(m-tolyl)methanethione (**1k**) (0.2 mmol, 41.1 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3k**; Yellow oil, 48.7 mg, yield: 75%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.56 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.54-7.46 (m, 3H), 7.20 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 3.96 (s, 2H), 3.54 (s, 1H), 3.37 (s, 1H), 2.33 (s, 3H), 2.08-1.87 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.3, 165.0, 134.3, 134.1, 133.8, 131.9, 130.6, 130.3, 128.7, 127.2, 125.1, 123.6, 54.0, 53.0, 26.2, 24.4, 20.9 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{21}N_2OS$ $[M+H]^+$ 325.1369, found: 325.1360.

12) *N*-(2-(pyrrolidine-1-carbonothioyl)-4-(trifluoromethyl)phenyl)benzamide (**3l**).



3l

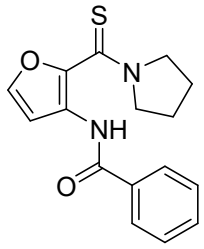
The reaction of pyrrolidin-1-yl(3-(trifluoromethyl)phenyl) methanethione (**1l**) (0.2 mmol, 51.8 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3l**; Yellow oil, 14.4 mg, yield: 19%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.90 (s, 1H), 8.64 (s, 1H), 7.94-7.92 (m, 2H), 7.58-7.48 (m, 3H), 7.30-7.26 (m, 1H), 7.00 (d, J = 8.4 Hz, 1H), 3.96 (s, 2H), 3.53 (s, 1H), 3.36 (s, 1H), 2.08-1.89 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 192.1, 165.0, 134.9, 133.9, 132.2, 130.2 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 126.7 (q, $^2J_{C\text{-}F}$ = 35.2 Hz), 126.1, 126.0, 123.4, 54.2, 53.2, 26.2, 24.4 ppm. **^{19}F NMR** (**377 MHz**, **$CDCl_3$**) δ -62.6 ppm (reference: $PhCF_3$). **HRMS m/z (ESI)**: calcd. for $C_{19}H_{21}N_2OS$ $[M+H]^+$ 379.1086, found: 379.1082.



3m

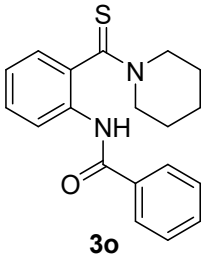
13) *N*-(3-(pyrrolidine-1-carbonothioyl)naphthalen-2-yl) -benzamide (**3m**). The reaction of naphthalen-2-yl (pyrrolidin-1-yl) methanethione (**1m**) (0.2 mmol, 48.3 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3m**; Yellow solid, 53.8 mg, yield: 75%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.87 (s，1H)，

8.88 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 1H),7.74 (d, *J* = 8.4 Hz, 1H), 7.61-7.48 (m, 4H), 7.43 (t, *J* = 14.8 Hz, 1H), 4.06-3.99 (m, 2H)，3.59 (t, *J* = 16.4 Hz, 1H), 3.37-3.33 (m, 1H), 2.12-1.85 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) *δ* 193.1, 165.2, 134.4, 133.7, 133.3, 132.0, 130.5, 129.7, 128.8, 128.0, 127.6, 127.3, 125.9, 124.2, 120.6, 54.3, 53.2, 26.2, 24.5 ppm. **HRMS m/z (ESI)**: calcd. for $C_{22}H_{21}N_2OS$ $[M+H]^+$ 361.1369, found: 361.1360.



3n

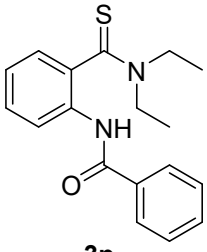
14) *N*-(2-(pyrrolidine-1-carbonothioyl)furan-3-yl)benz -amide(3n). The reaction of furan-2-yl(pyrrolidin-1-yl)methanethione (**1n**) (0.2 mmol, 36.2 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3n**; Yellow oil, 25.0 mg, yield: 42%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) *δ* 12.59 (s, 1H), 8.09-8.07 (m, 2H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.56-7.39 (m, 3H), 7.39 (s, 1H), 4.11 (t, *J* = 18.0 Hz, 2H), 4.01 (t, *J* = 17.6 Hz, 2H), 2.10 (t, *J* = 8.4 Hz, 2H), 2.01 (t, *J* = 13.6 Hz, 3H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) *δ* 177.2, 165.4, 141.8, 135.0, 133.8, 132.0, 128.7, 127.8, 108.1, 54.1, 53.7, 26.8, 23.5 ppm. **HRMS m/z (ESI)**: calcd. for $C_{16}H_{16}N_2O_2SNa$ $[M+Na]^+$ 323.0825, found: 323.0814.



3o

15) 1-Phenyl-2-(2-(piperidine-1-carbonothioyl)phenyl)ethan-1-one (**3o**). The reaction of phenyl(piperidin-1-yl)methanethione (**1o**) (0.2

mmol, 41.0 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3o**; Yellow oil, 21.4 mg, yield: 33%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.37 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.57-7.48 (m, 3H), 7.41-7.37 (m, 1H), 7.18-7.14 (m, 1H), 7.05 (dd, J = 6.4, 1.2 Hz,1H), 4.42 (dd, J = 3.6, 2.8 Hz, 1H), 4.31 (s, 1H), 3.52-3.47 (m, 2H), 1.78-1.57 (m, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.3，165.0，134.2，133.6，133.2，132.0，129.2，128.8，127.2　124.4，124.4，123.8，53.5，50.2，27.0，25.7，24.0 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{21}N_2OS$ $[M+H]^+$ 325.1369, found: 325.1369.

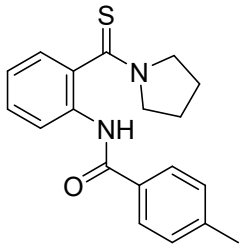


3p

16) *N*,*N*-diethyl-2-(2-oxo-2-phenylethyl)benzothioamide (3p).

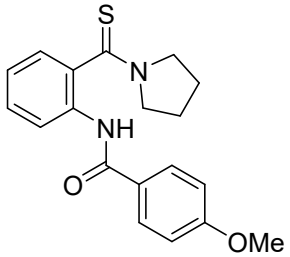
The reaction of *N*,*N*-diethylbenzothioamide (**1p**) (0.2 mmol, 38.7 mg), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3o**; Yellow oil, 42.8 mg, yield: 69%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.14 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 7.2 Hz, 2H), 7.56-7.49 (m, 3H), 7.39 (m, 1H), 7.17 (m, 1H), 7.07 (s, 1H), 4.15-4.11 (m, 2H), 3.42 (t, J = 14.0, 7.2 Hz, 2H), 1.35-1.32 (m, 3H), 1.10-1.07 (m, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.4, 165.0, 134.3, 134.1, 132.6, 132.0, 129.1, 128.8, 127.1, 124.5, 124.3,

123.8, 48.3, 46.1, 13.6, 11.2 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{20}N_2OSNa$ $[M+Na]^+$ 335.1189, found: 335.1183.



4a

17) 4-Methyl-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz -amide (**4a**). The reaction of Phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(p-tolyl)-1,4,2-dioxazol-5-one (**2b**) (0.24 mmol, 42.5 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4a**; Yellow oil, 43.5 mg, yield: 67%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.72 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.40-7.36 (m, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.15-7.11 (m, 2H), 3.95 (t, J = 8.0, 16.0 Hz, 2H), 3.53 (d, J = 7.6 Hz, 1H), 3.34 (s, 1H), 2.41 (s, 3H), 2.07-1.85 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.4, 165.1, 142.5, 133.6, 133.5, 131.5, 129.6, 129.5, 127.3, 124.9, 124.1, 123.5, 54.0, 53.0, 26.2, 24.4, 21.5 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{20}N_2OSNa$ $[M+Na]^+$ 347.1189, found: 347.1174.

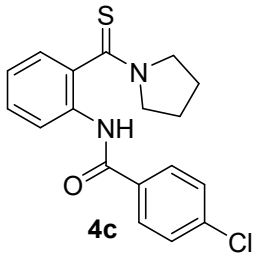


4b

18) 4-Methoxy-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl) -benzamide (**4b**).

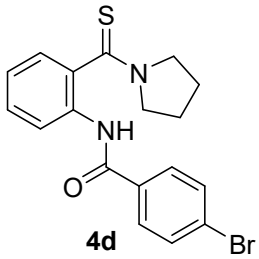
The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (**2c**) (0.24 mmol, 46.3 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4b**; Yellow oil, 61.0 mg, yield: 90%. **^{1}H NMR**

(**400 MHz**, **$CDCl_3$**) δ 9.69 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 9.70 (s, 1H), 8.31 (d, J = 9.2 Hz, 1H), 7.93-7.89 (d, 2H), 7.41-7.36 (m, 1H), 7.15-7.12 (m, 2H), 7.00-6.96 (m, 2H), 3.97 (dd, J = 12 Hz, 4.8, 2H), 3.88 (d, J = 8.8 Hz, 3H), 3.54 (d, J = 7.6 Hz, 1H), 3.55 (s, 1H), 2.10-1.86 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.3, 164.7, 162.5, 133.5, 133.4, 129.5, 129.1, 126.5, 124.9, 123.8, 123.3, 113.9, 55.4, 54.0, 53.0, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{21}N_2O_2S$ $[M+H]^+$ 341.1318, found: 341.1304.



4c

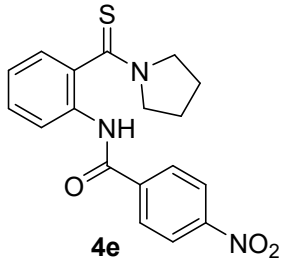
19) 4-Chloro-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz -amide (**4c**). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(4-chlorophenyl)-1,4,2-dioxazol-5-one (**2d**) (0.24 mmol, 47.4 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4c**; Yellow oil, 25.8 mg, yield: 38%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.92 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.47-7.38 (m, 3H), 7.18-7.12 (m, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.55 (s, 1H), 3.37(s, 1H), 2.08-1.87 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.1, 164.0, 138.2, 133.4, 133.2, 132.7, 129.7, 128.7, 125.0, 124.2, 123.3, 54.2, 53.1, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{17}N_2ClOSNa$ $[M+Na]^+$ 367.0642, found: 367.0623.



4d

20) 4-Bromo-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz

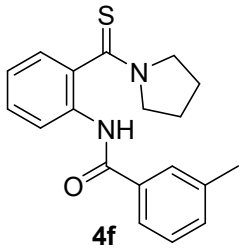
-amide (**4d**). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(4-bromophenyl)-1,4,2-dioxazol-5-one (**2e**) (0.24 mmol, 58.1 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4d**; Yellow oil, 54.1 mg, yield: 69%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.93 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.42-7.38 (m, 1H), 7.17-7.12 (m, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.46 (d, J = 5.6 Hz, 1H), 3.36 (s, 1H), 2.07-1.89 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.0, 164.1, 133.3, 133.2, 133.1, 132.0, 129.7, 128.9, 126.7, 125.0, 124.2, 123.3, 54.2, 53.1, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{18}BrN_2O_2S$ $[M+H]^+$ 389.0318, found: 389.0310.



4e

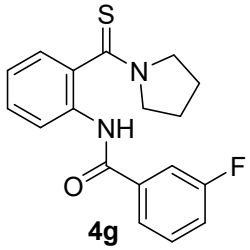
21) 4-Nitro-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz -amide (**4e**). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(4-nitrophenyl)-1,4,2-dioxazol-5-one (**2f**) (0.24 mmol, 49.9 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4e**; Yellow oil, 62.5 mg, yield: 88%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 10.2 (s, 1H), 8.34 (dd, J = 8.8，2.0 Hz, 3H), 8.10 (t, J = 7.2 Hz, 2H), 7.45-7.40 (m, 1H), 7.21-7.15 (m, 2H), 3.98 (d, J = 6.0 Hz, 2H), 3.36 (s, 1H), 3.34 (m,1H), 2.07-1.89 (m, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 192.8, 163.0, 149.8, 139.9, 133.2, 133.0,

129.9, 128.5, 125.2, 124.6, 123.9, 123.3, 54.4, 53.3, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{18}N_3O_3S$ $[M+H]^+$ 356.1063, found: 356.1052.



4f

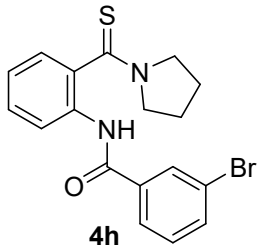
22) 3-Methyl-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz -amide (4f). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(4-nitrophenyl)-1,4,2-dioxazol-5-one (**2g**) (0.24 mmol, 42.5 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4f**; Yellow oil, 42.9 mg, yield: 66%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.91 (s, 1H), 8.26 (d, J = 4.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.45-7.40 (m, 1H), 7.21-7.34 (m, 2H), 7.26 (t, J = 6.0 Hz, 2H), 7.19-7.11 (m, 2H), 3.94 (t, J = 4.8 Hz, 2H), 3.50 (s, 1H), 3.41 (d, J = 4.0 Hz, 1H), 2.53 (s, 3H), 2.09-1.91 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.2, 167.9, 136.7, 135.7, 134.5, 132.9, 131.4, 130.5, 129.4, 127.1, 126.1, 124.9, 124.6, 123.7, 53.8, 52.9, 26.3, 24.5, 20.2 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{20}N_2OSNa$ $[M+Na]^+$ 347.1189, found: 347.1178.



4g

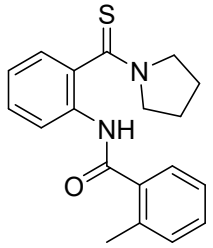
23) 3-Fluoro-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz -amide(4g). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(3-fluorophenyl)-1,4,2-dioxazol-5-one (**2h**) (0.24 mmol, 43.5 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4g**; Yellow oil,

46.6 mg, yield: 71%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 5.2 Hz, 2H), 7.49-7.38 (m, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 6.0 Hz, 2H), 3.97 (s, 2H), 3.56 (s, 1H), 3.37 (s, 1H), 2.08-1.89 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 164.1, 163.8 (d, $^4J_{C\text{-}F}$ = 2.4 Hz), 161.6, 136.7, 136.6, 133.3, 130.5, 129.7, 125.0, 124.3, 123.4, 122.5 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 119.0 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 114.9 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 54.2, 53.1, 26.2, 24.4; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -111.9 ppm (reference: $PhCF_3$). **HRMS m/z (ESI)**: calcd. for $C_{18}H_{18}FN_2OS$ $[M+H]^+$ 339.1118, found: 339.1113.



4h

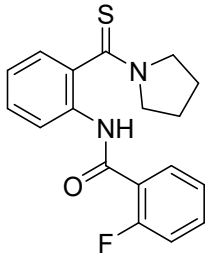
24) 3-Chloro-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz -amide (4h). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(3-bromophenyl)-1,4,2-dioxazol-5-one (**2i**) (0.24 mmol, 47.4 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4h**; Yellow oil, 57.6 mg, yield: 74%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.92 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 6.8 Hz, 1H), 7.15 (d, J = 6.4 Hz, 2H), 3.97 (d, J = 6.0 Hz, 2H), 3.55 (s, 1H), 3.36 (s, 1H), 2.07-1.89 (m, 4H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.0, 164.1, 133.3, 133.2, 133.1, 132.0, 129.7, 128.9, 126.7, 125.0, 124.2, 123.3, 54.2, 53.1, 26.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{18}H_{17}N_2BrOSNa$ $[M+Na]^+$ 389.0318, found: 389.0313.



4i

25) 2-Methyl-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)benz

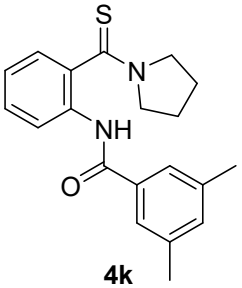
-amide (**4i**). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(o-tolyl)-1,4,2-dioxazol-5-one (**2j**) (0.24 mmol, 42.5 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4i**; Yellow oil, 48.8 mg, yield: 75%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.71 (s, 1H), 8.32 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H), 7.71 (dd, J = 6.4, 2.0 Hz, 1H), 7.42-7.35 (m, 3H), 7.15-7.12 (m, 2H), 3.97 (dd, J = 4.8, 2.0 Hz, 1H), 3.53 (s, 1H), 3.36 (d, J = 4.8 Hz, 1H), 2.43 (s, 3H), 2.09-1.89 (s, 4H) ppm. **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.3, 165.3, 138.7, 134.3, 133.7, 133.4, 132.7, 129.6, 128.7, 128.2, 124.9, 124.2, 124.1, 123.5, 54.0, 53.0, 26.2, 24.4, 21.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{19}H_{20}N_2OSNa$ $[M+Na]^+$ 347.1189, found: 347.1168.



4j

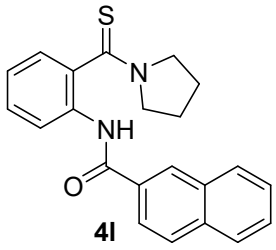
26) 2-Fluoro-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl) -benzamide(4j). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(2-fluorophenyl)-1,4,2-dioxazol-5-one (**2k**) (0.24 mmol, 43.5 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4j**; Yellow oil, 21.7 mg, yield: 33%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.09 (d, J = 11.2 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.10 (t, J = 2.8 Hz, 1H), 7.50 (dd, J = 12.8, 6.8 Hz, 1H), 7.28 (dd, J = 8.0, 1.2 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.21-7.14 (m, 3H), 4.00 (t, J = 2.8 Hz, 2H), 3.44 (t, J = 4.8 Hz, 1H), 3.35 (t, J = 5.6 Hz, 1H), 2.10-1.91 (m, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 161.6, 161.5, 159.0, 135.3, 133.7, 133.6, 132.1, 132.0, 130.1, 129.1, 128.4, 125.0, 123.6, 121.7, 121.6, 116.4, 116.2, 53.3, 52.8, 26.2, 24.5 ppm. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -113.6 ppm (reference: $PhCF_3$). **HRMS m/z (ESI)**: calcd. for $C_{18}H_{18}FN_2OS$ $[M+H]^+$ 339.1118, found: 339.1110.



4k

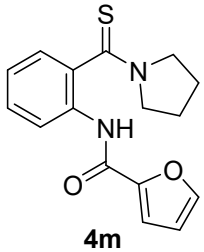
27) 3,5-Dimethyl-*N*-(2-(pyrrolidine-1-carbonothioyl)phenyl) -benzamide (**4k**). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(3,5-dimethylphenyl)-1,4,2-dioxazol-5-one (**2l**) (0.24 mmol, 45.9 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4k**; Yellow oil, 50.9 mg, yield: 75%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.62 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 7.53 (s, 2H), 7.41-7.37 (m, 1H), 7.18 (s, 1H), 7.15-7.12 (m, 3H), 3.97 (dd, J = 12.4, 5.2 Hz, 2H), 3.53 (d, J = 7.6 Hz, 1H), 3.35 (s, 1H), 2.39 (s, 6H), 2.01-1.87 (m, 4H) ppm. **^{13}C NMR (100MHz, $CDCl_3$)** δ 193.3, 165.5, 138.4, 134.3, 133.7, 133.5, 133.3, 129.5, 125.0, 124.9, 124.0, 123.4, 53.9, 53.0, 26.2, 24.4, 21.2 ppm. **HRMS m/z (ESI)**: calcd. for $C_{20}H_{23}N_2OS$ $[M+H]^+$ 339.1526, found: 339.1511.



4l

28) *N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)-2-naphth -amide (**4l**). The reaction of Phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(naphthalen-2-yl)-1,4,2-dioxazol-5-one (**2m**) (0.24 mmol, 51.2 mg), Cp*Co(CO)I_2

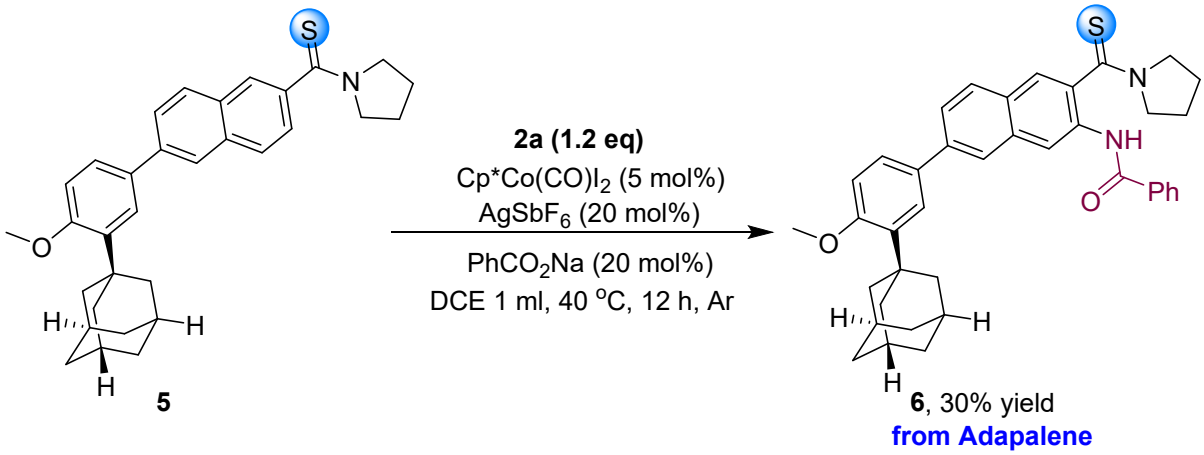
(4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4l**; Yellow oil, 67.0 mg, yield: 93%. **^{1}H NMR** (**400 MHz**, **$CDCl_3$**) δ 9.96 (s, 1H), 8.48 (s, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.01-7.88 (m，4H), 7.61-7.54 (m, 2H), 7.44-7.40 (m, 1H), 7.16 (dd, J = 5.6, 3.2 Hz, 3.98 (t, J = 5.6 Hz, 2H), 3.56 (d, J = 6.8 Hz, 1H), 3.39 (s, 1H), 2.06-1.86 (m, 4H); **^{13}C NMR** (**100 MHz**, **$CDCl_3$**) δ 193.3, 165.2, 135.0, 133.6, 133.5, 132.6，131.5，129.7, 129.3, 128.7, 128.2, 127.9, 127.7, 126.78, 125.0, 124.2，123.6, 123.5，54.1, 53.1, 24.2, 24.4 ppm. **HRMS m/z (ESI)**: calcd. for $C_{22}H_{20}N_2OSNa$ $[M+Na]^+$ 383.1189, found: 383.1170.



4m

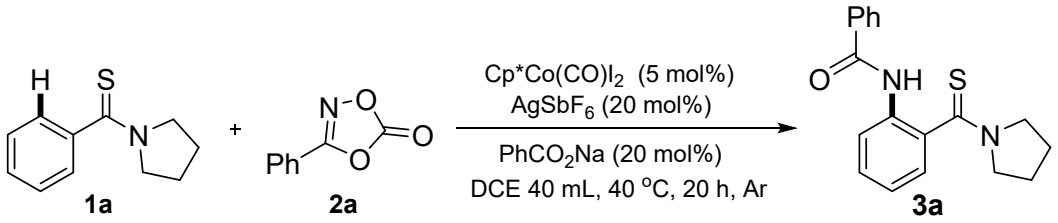
29) *N*-(2-(pyrrolidine-1-carbonothioyl)phenyl)furan-2-car -boxamide (**4m**). The reaction of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.2 mmol, 38.3 mg), 3-(furan-2-yl)-1,4,2-dioxazol-5-one (**2n**) (0.24 mmol, 36.7 mg), Cp*Co(CO)I_2 (4.8 mg, 0.01 mmol), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), and DCE (2 mL) were stirred at 40 °C for 12 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **4m**; Yellow oil, 24.6 mg, yield: 41%. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.93 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.53 (s, 1H), 7.39-7.35 (m, 1H), 7.20 (d, J = 3.2 Hz, 1H), 7.14 (d, J = 4.0 Hz, 2H), 3.99 (t, J = 7.2 Hz, 2H), 3.50 (t, J = 7.2 Hz, 1H), 3.33 (d, J = 4.4 Hz, 1H), 2.10-1.89 (m, 4H) ppm. **^{13}C NMR** (**100 MHz, $CDCl_3$**) δ 168.9, 165.1, 137.7, 134.5, 131.8, 128.7, 127.8, 127.2, 124.0, 122.6, 122.0, 50.4, 46.5, 26.4, 24.2 ppm. **HRMS m/z (ESI)**: calcd. for $C_{12}H_{17}N_2O_2S$ $[M+H]^+$ 301.1005, found: 301.0999.

4. Structural modification of Adapalene



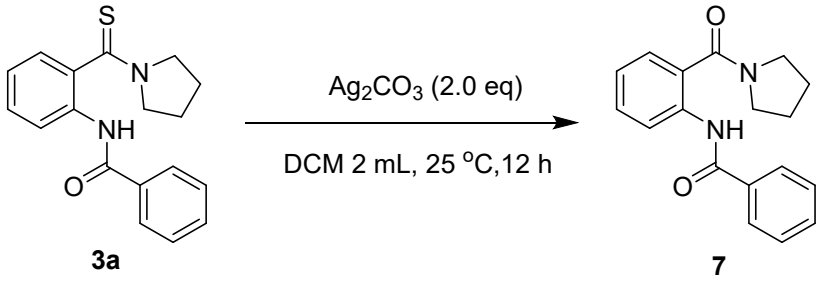
The reaction of (6-(3-((3*R*,5*R*,7*R*)-adamantan-1-yl)-4-methoxyphenyl) naphthalen-2-yl) (pyrrolidin-1-yl)methanethione (**5**) (0.1 mmol, 41.2 mg), 1,4,2-dioxazol-5-one (**2b**) (0.12 mmol, 19.5 mg), Cp*Co(CO)I_2 (2.4 mg, 0.005 mmol), $AgSbF_6$ (6.9 mg, 0.02 mmol), $PhCO_2Na$ (3.6 mg, 0.04 mmol), in 2 mL DCE at 40 °C under Ar for 12 h as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to afford 17.8 mg (30%) of **6** as solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.94 (s, 1H), 8.94 (s, 1H), 8.06-8.00 (dd, J = 17.2, J = 7.2 Hz, 3H), 7.79 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 2.0 Hz, 2H), 7.57-7.50 (m, 4H), 7.00 (d, J = 8.4 Hz, 1H), 4.08-4.12 (dd, J = 18.8 Hz, J = 11.2, 2H), 3.91 (d, J = 6.8 Hz, 3H), 3.65 (d, J = 4.0 Hz, 1H), 3.40 (s, 1H), 2.22 (t, J = 8.0 Hz, 6H), 2.11 (s, 4H), 2.01 (d, J = 4.8 Hz, 2H), 1.84 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.2, 165.2, 158.8, 140.2, 138.9, 134.5, 134.1, 132.8, 132.5, 132.0, 130.8, 128.8, 128.4, 128.0, 127.3, 125.9, 125.6, 125.5, 124.9, 124.0, 120.6, 112.1, 55.1, 54.4, 53.3, 40.6, 37.2, 37.1, 29.7, 29.3, 29.1, 26.2, 24.5 ppm. **HRMS m/z (ESI)**: calcd. for $C_{39}H_{40}N_2O_2SNa$ $[M+H]^+$ 623.2703, found: 623.2720.

5. Gram-scale reaction



The reaction of phenyl(pyrrolidin-1-yl)methanethione (1**a**) (7 mmol, 1.34 g), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (8.4 mmol, 1.37 g), Cp*Co(CO)I_2 (168 mg, 0.35 mmol), $AgSbF_6$ (483 mg, 1.4 mmol), $PhCO_2Na$ (252 mg, 1.4 mmol), and DCE (40 mL) were stirred at 40 °C for 20 h in Ar as monitored by TLC. The resulting mixture was concentrated and purified by flash chromatography on silica gel to **3a**; Yellow solid, 1.80 g, yield: 82%.

6. Transformation of amidated product

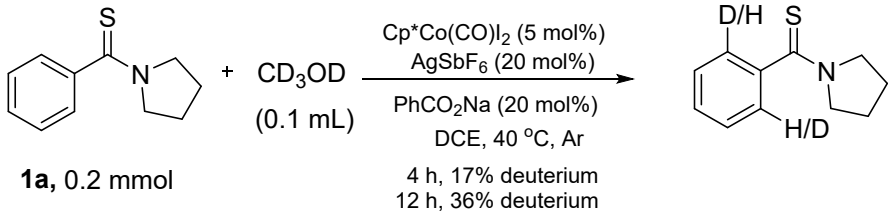


Synthesis of 7: 3a (0.1 mmol), Ag_2CO_3 (0.2 mmol) and DCM (2 mL) was added to a 50 mL Schlenk flask, the mixture was stirred at 25 °C for 12 h. Monitored by TLC until the reaction was complete. The product was purified by flash chromatography (petroleum ether /ethyl acetate =10:1) affording **7**, 58.8 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.56 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 6.8 Hz, 2H), 7.54-7.43 (m, 5H), 7.11 (t, J = 7.6 Hz, 1H), 3.67 (t, J = 6.0 Hz, 2H), 3.54 (t, J = 5.6 Hz, 2H), 1.98 (t, J = 6.0 Hz, 2H), 1.87 (d, J = 5.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) □ 168.9, 165.1, 137.7, 134.5, 131.8, 128.7, 127.8, 127.2, 124.0, 122.6, 122.0,

50.4, 46.5, 26.4, 24.2 ppm.

7. Mechanistic studies

H/D exchange experiments

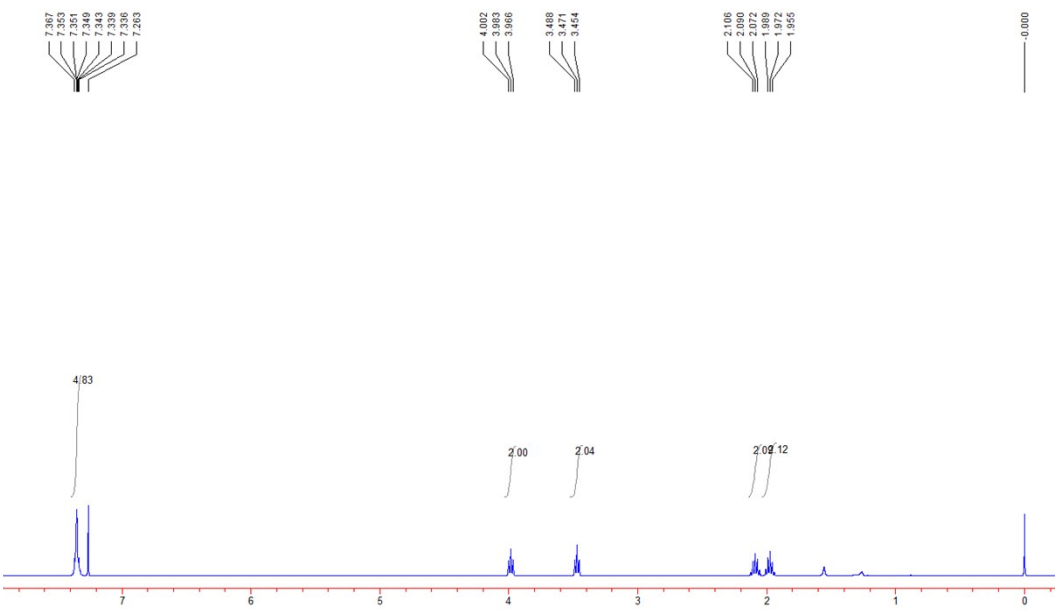


1a, 0.2 mmol

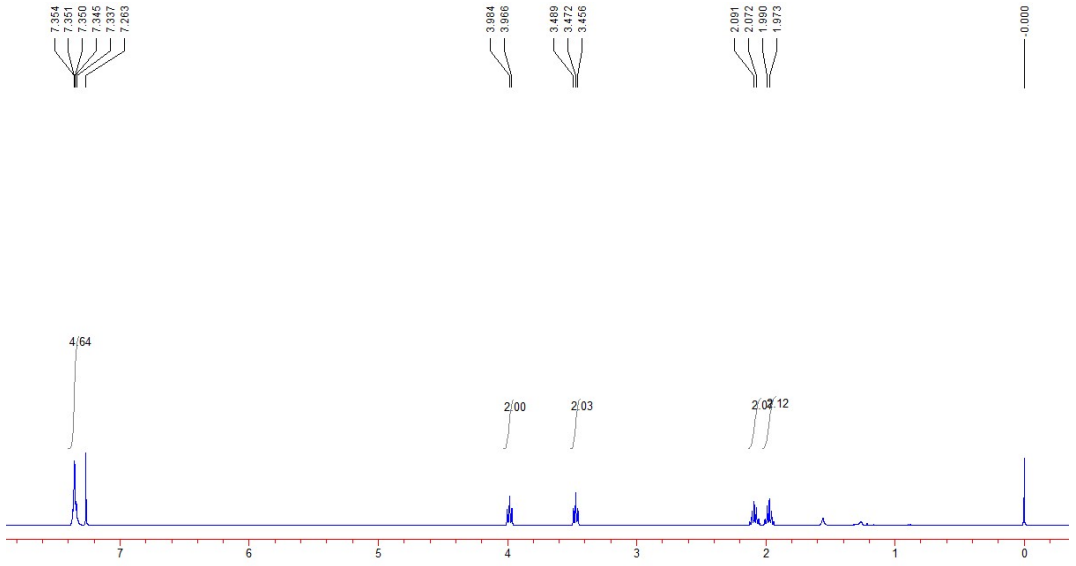
Scheme S1 H/D exchange experiment

To a 25 mL Schlenk tube was added **1a** (0.2 mmol), CD_3OD (0.1 mL), $Cp^*Co(CO)I_2$ (5 mol%), $AgSbF_6$ (20 mol%), $PhCO_2Na$ (20 mol%) and DCE (2 mL), were stirred at 40 °C for 4 h or 12 h in Ar. After cooling to room temperature, the solvent was removed under vacuum. The residue was purified by flash chromatography silica gel. The deuterium incorporation was estimated to be 17% for 4 h and 36% for 12 h.

4h:

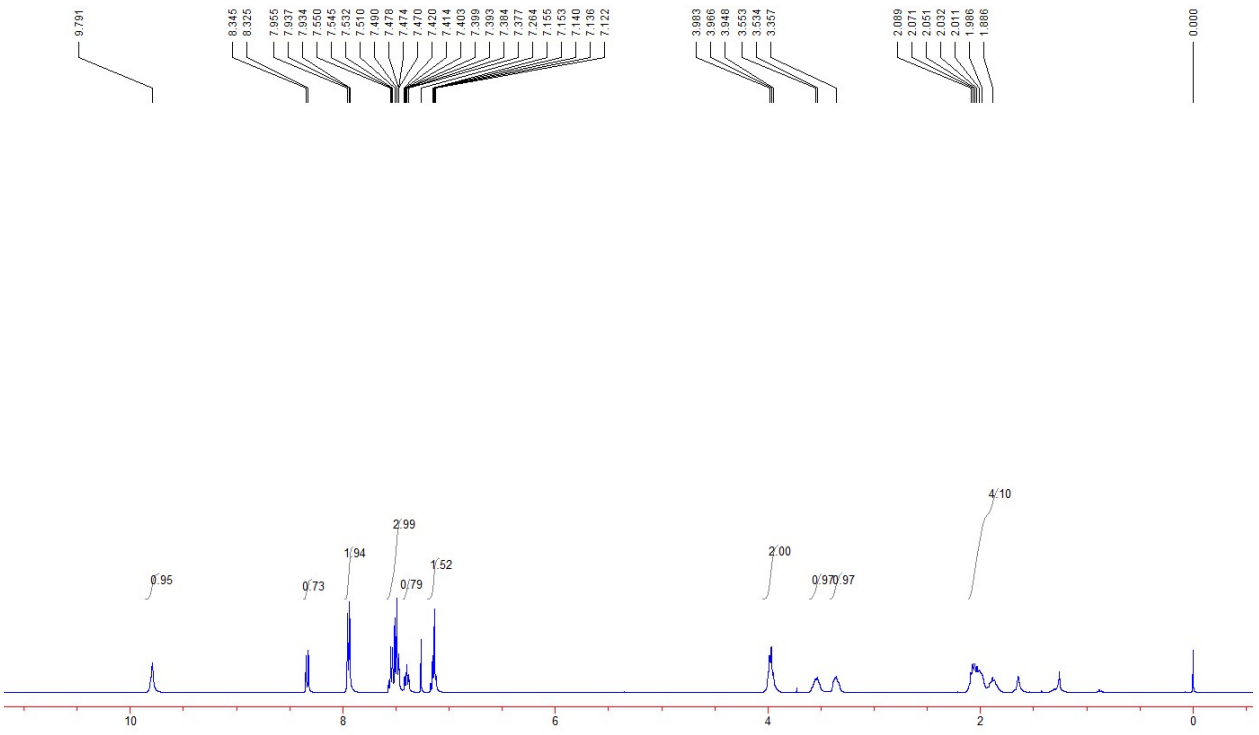


12h:

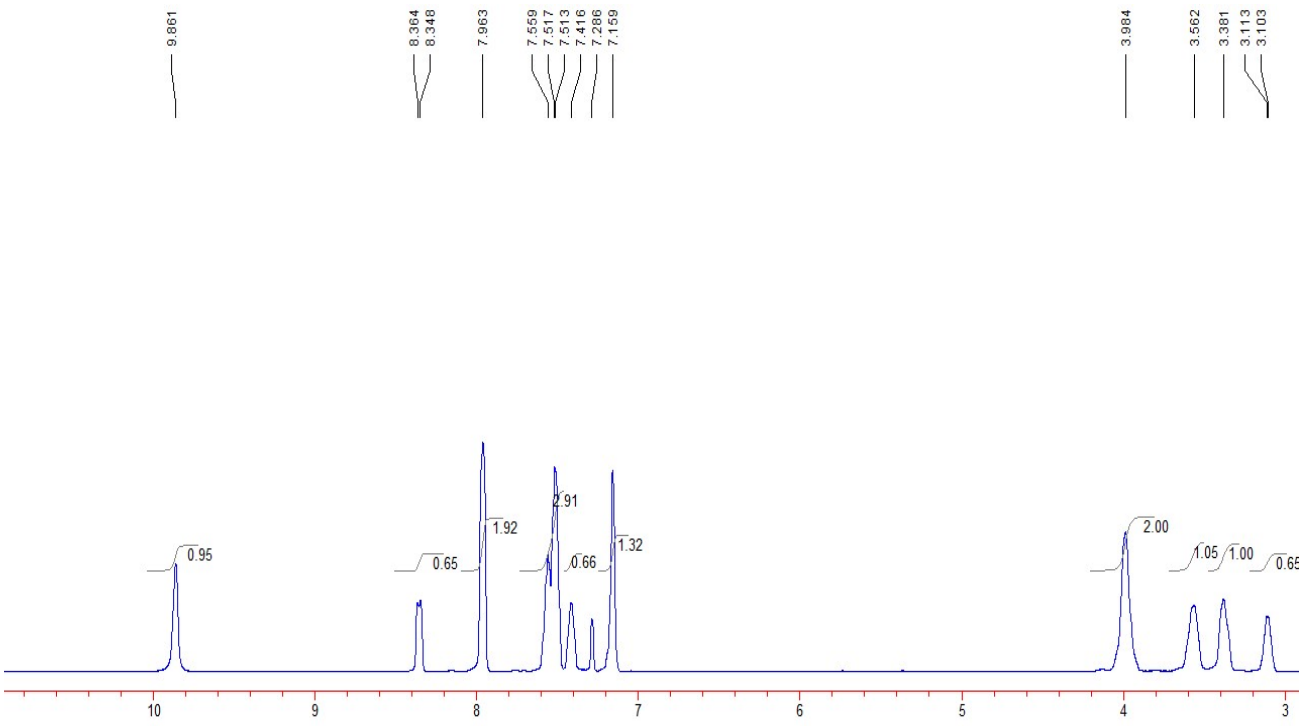


KIE experiments

The reaction of **1a** (19.1 mg, 0.1 mmol) and **1a-d_5** (19.6 mg, 0.1 mmol), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (13.8 mg, 0.04 mmol), $PhCO_2Na$ (7.2 mg, 0.04 mmol), 3-phenyl-1,4,2-dioxazol-5-one (39.1 mg, 0.24 mmol) and DCE (2 mL) were stirred at 40 °C for 4 h in Ar. The volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography. *KIE* value (K_H/K_D = 2.6) was determined on the basis of ^{1}H NMR analysis.



A mixture of phenyl(pyrrolidin-1-yl)methanethione (**1a**) (0.20 mmol) or deuterium-labeled compound [D1]-**1a** (0.20 mmol), 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (0.24 mmol, 39.1 mg), Cp*Co(CO)I_2 (5 mol%), $AgSbF_6$ (20 mol%), $PhCO_2Na$ (20 mol%) and DCE (2 mL) were added into a dry sealed tube. The reactions were stirred at 40 °C in parallel for 4 h. After cooling to room temperature, these two reactions were combined and the solvent was removed under vacuum. The residue was purified by flash chromatography silica gel. 41% starting material was recovered. *KIE* value (K_H/K_D = 1.9) was determined on the basis of ^{1}H NMR analysis.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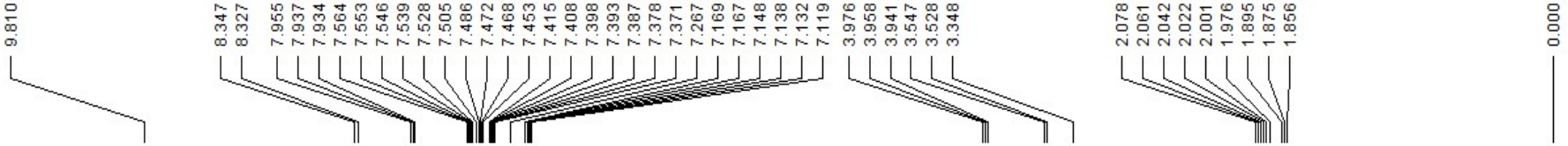
3.113
3.103
0.95
0.65
1.92
2.91
0.66
1.32
2.00
1.05
1.00
0.65
10
9
8
7
6
5
4
3

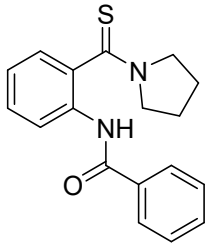
8. References

[1] L. Hie, N. F. Fine Nathel, T. K. Shah, E. L. Baker, X. Hong, Y.-F. Yang, P. Liu, K. N. Houk, N. K. Garg, *Nature*. **2015**, 524, 79-83.

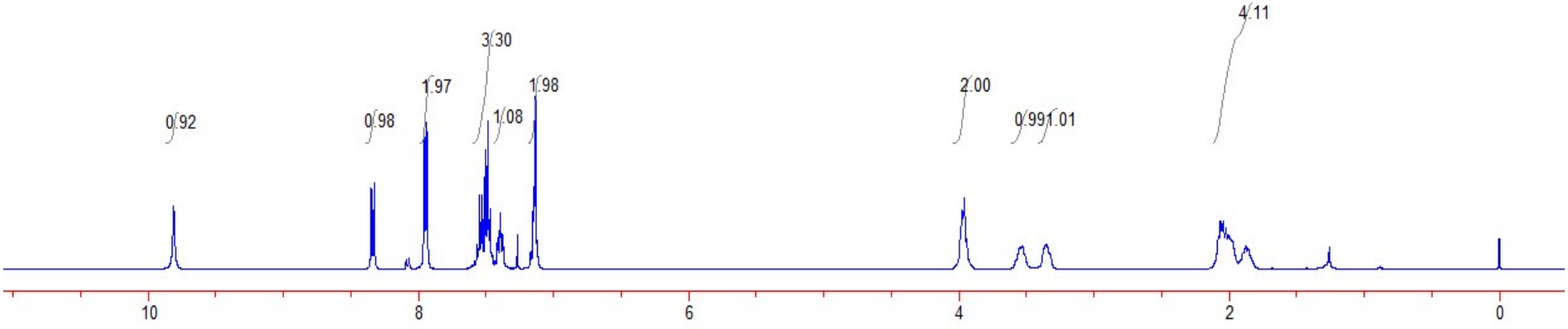
[2] J. E. Spangler, Y. Kobayashi, P. Verma, D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2015**, 137, 11876-11879.

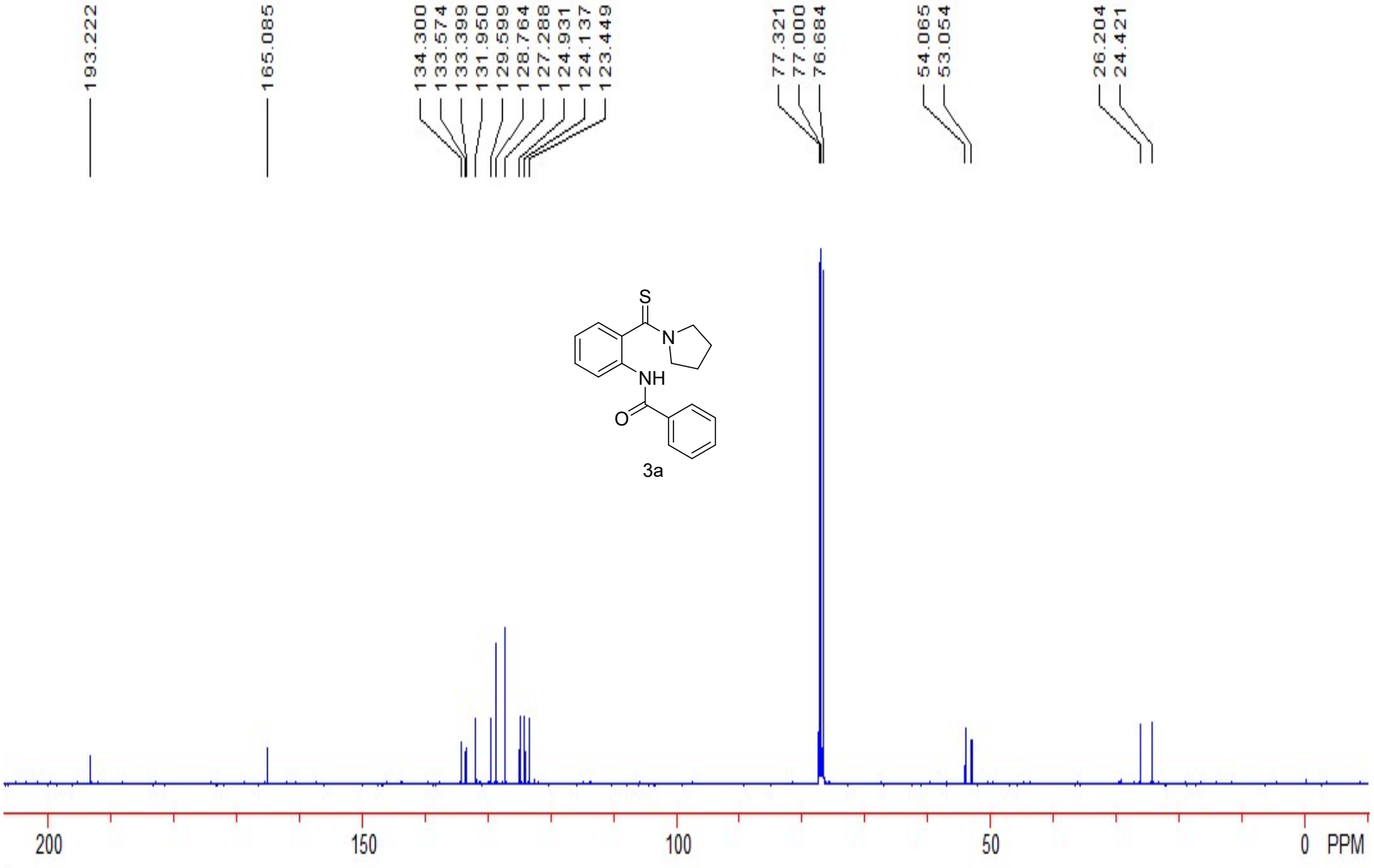
9. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for products





3a

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77.000
76.684
54.065
53.054
26.204
24.421
S
N
NH
O
3a
200
150
100
50
0
PPM


9.920
7.962
8.185
7.943
7.559
7.542
7.525
7.504
7.485
7.468
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7.029
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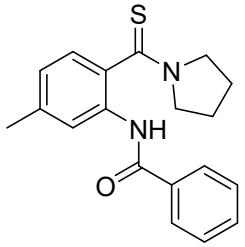
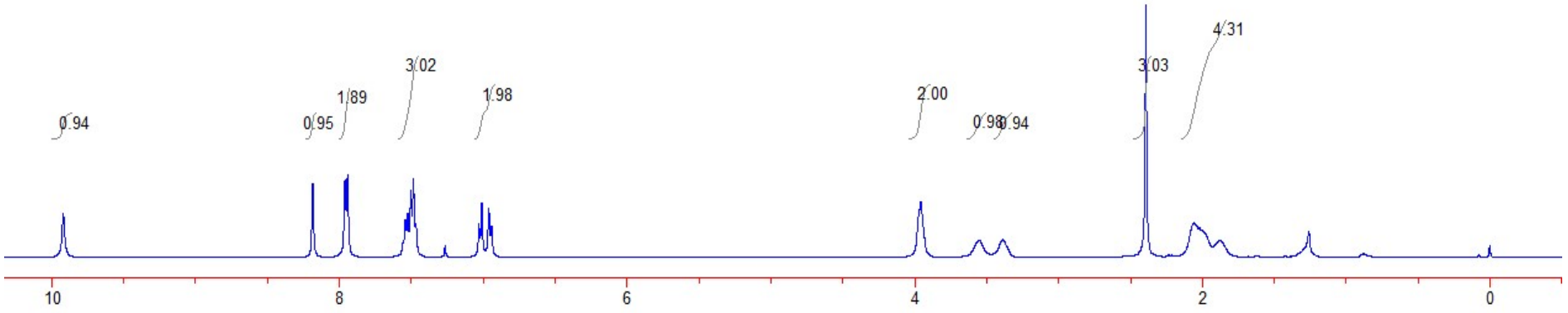

S
N
NH
O

3b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0.95
1.89
3.02
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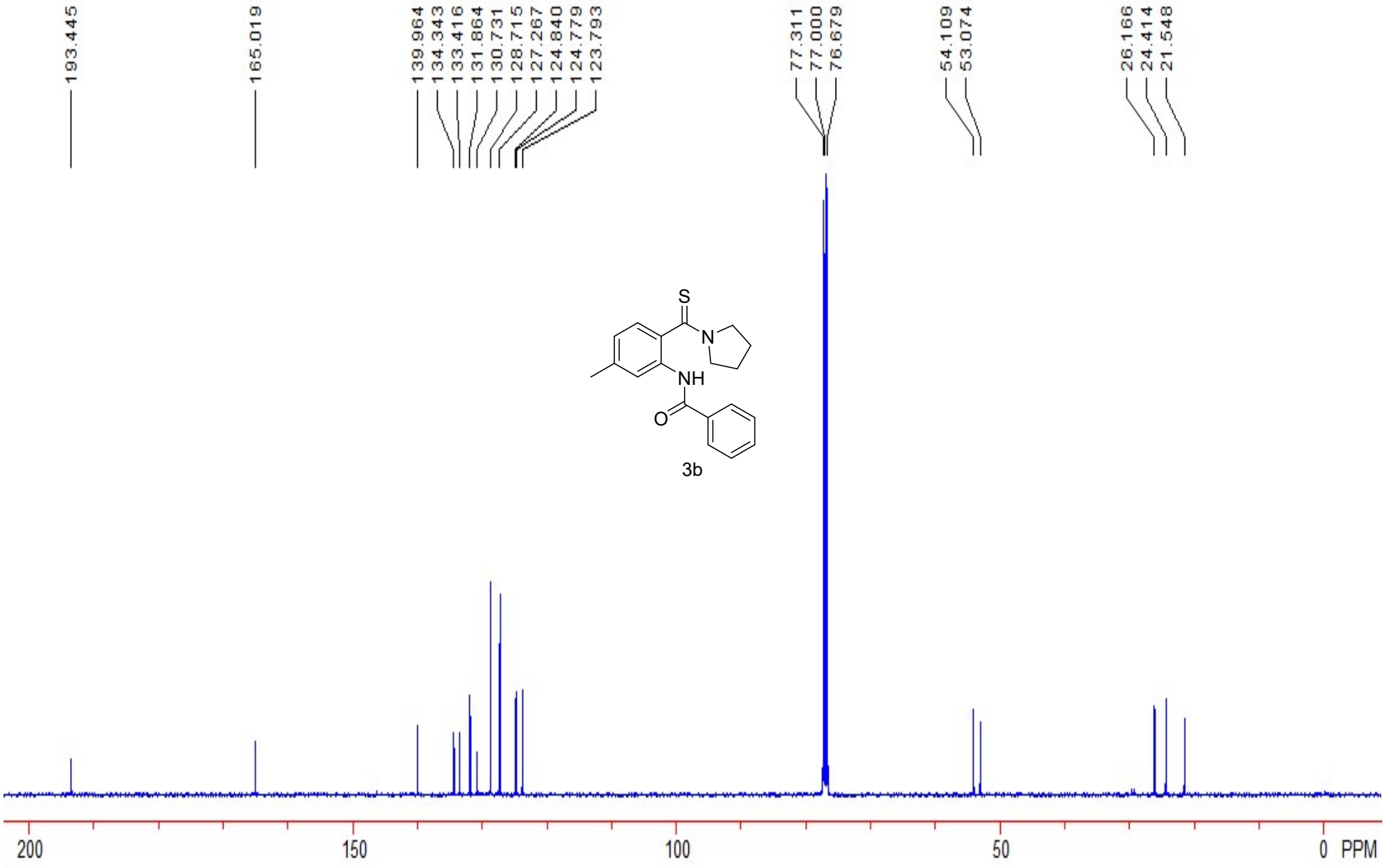
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77.311
77.000
76.679
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NH
O
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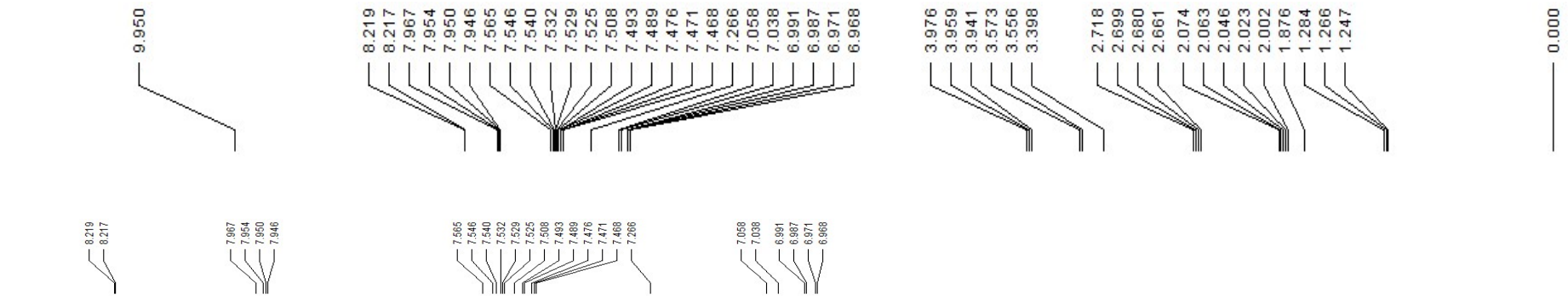
0
PPM

3b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7.471
7.468
7.266
7.058
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6.987
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6.968
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3.959
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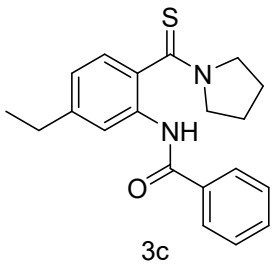
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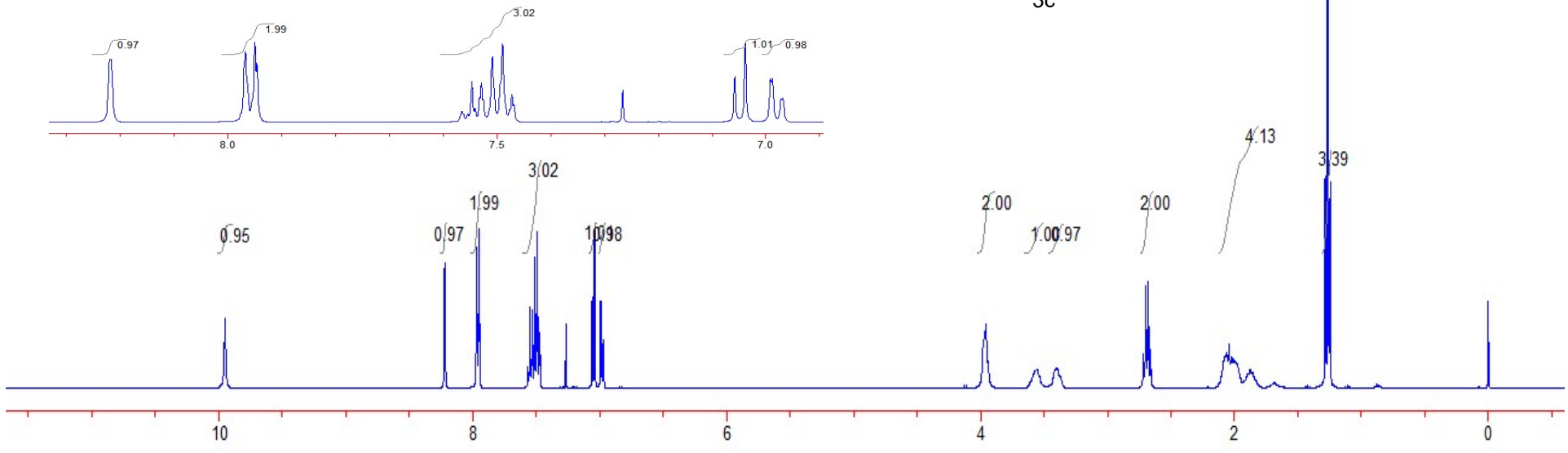
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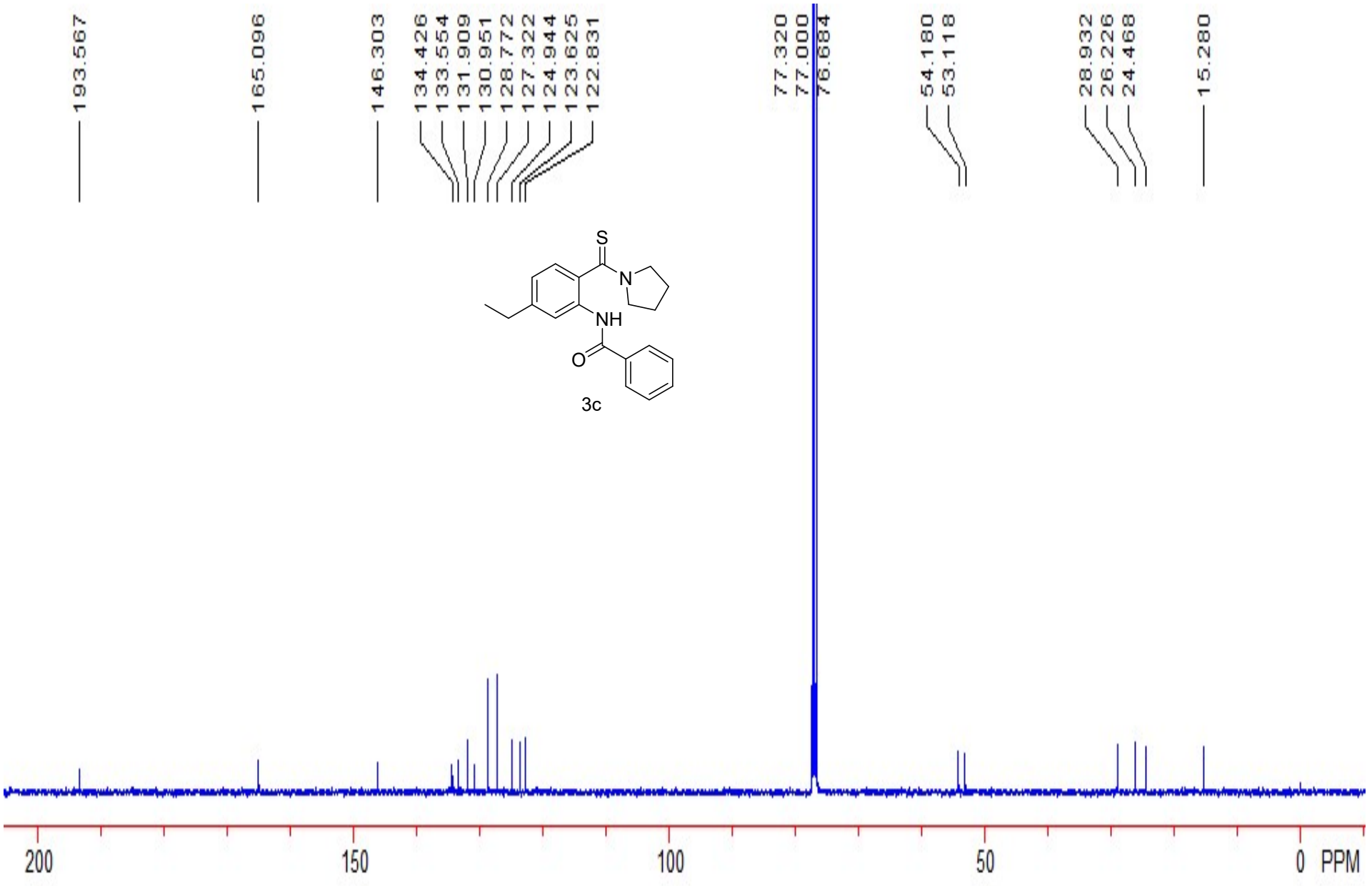
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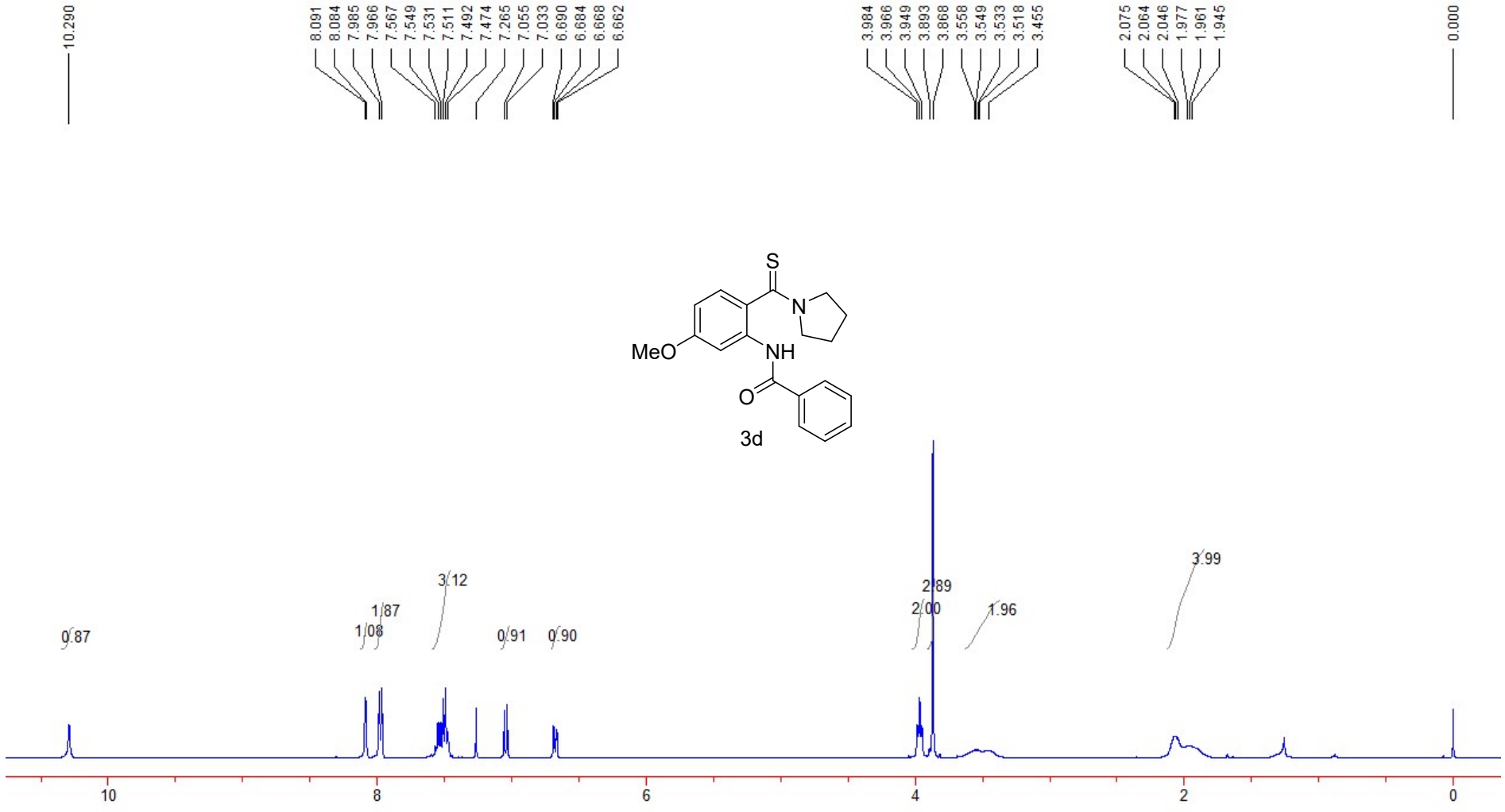
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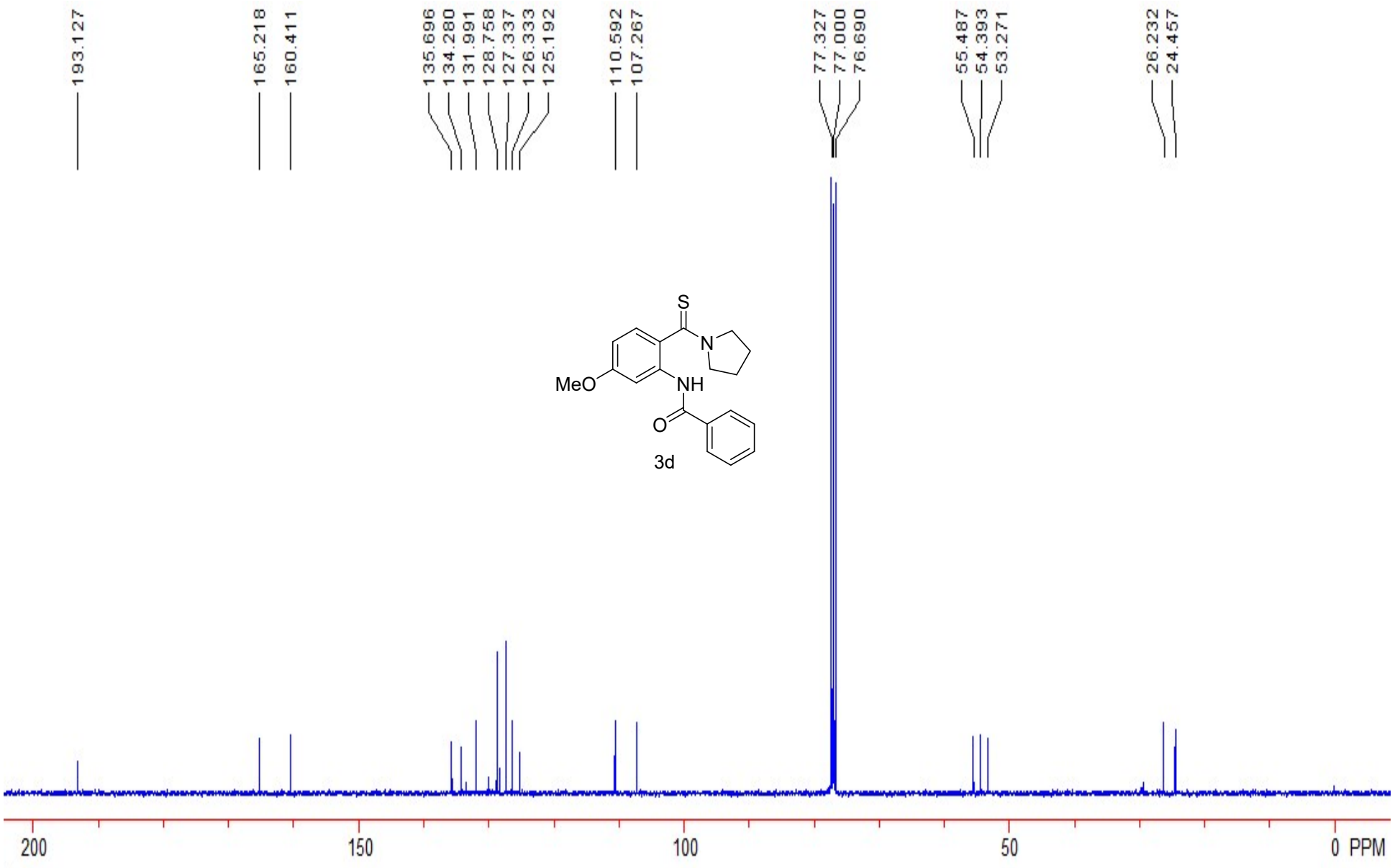
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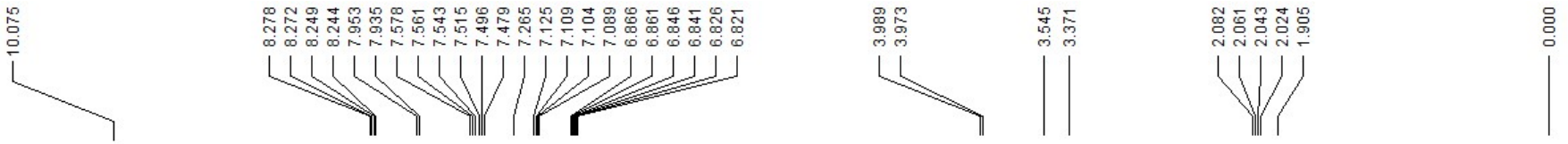
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7.479
7.265
7.125
7.109
7.104
7.089
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6.846
6.841
6.826
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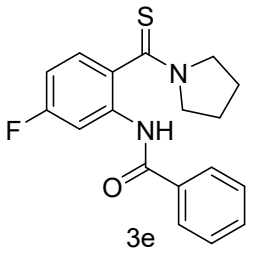
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F
NH
O

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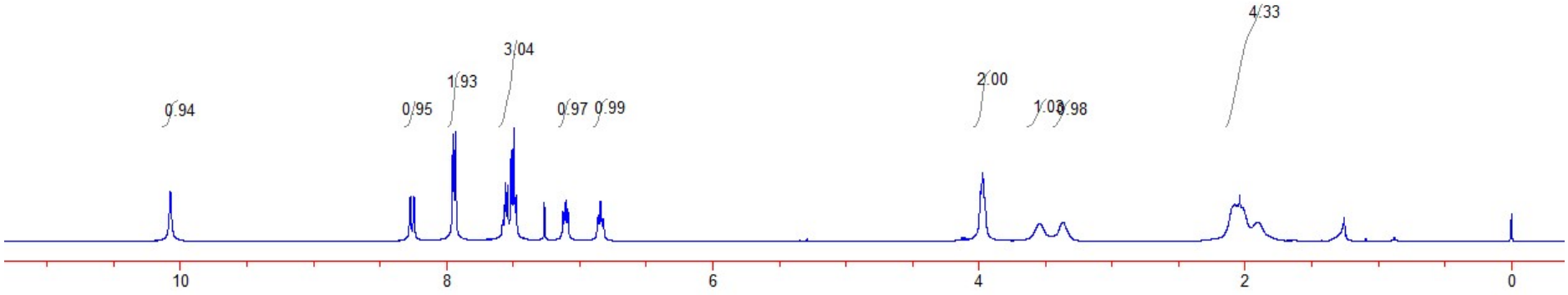
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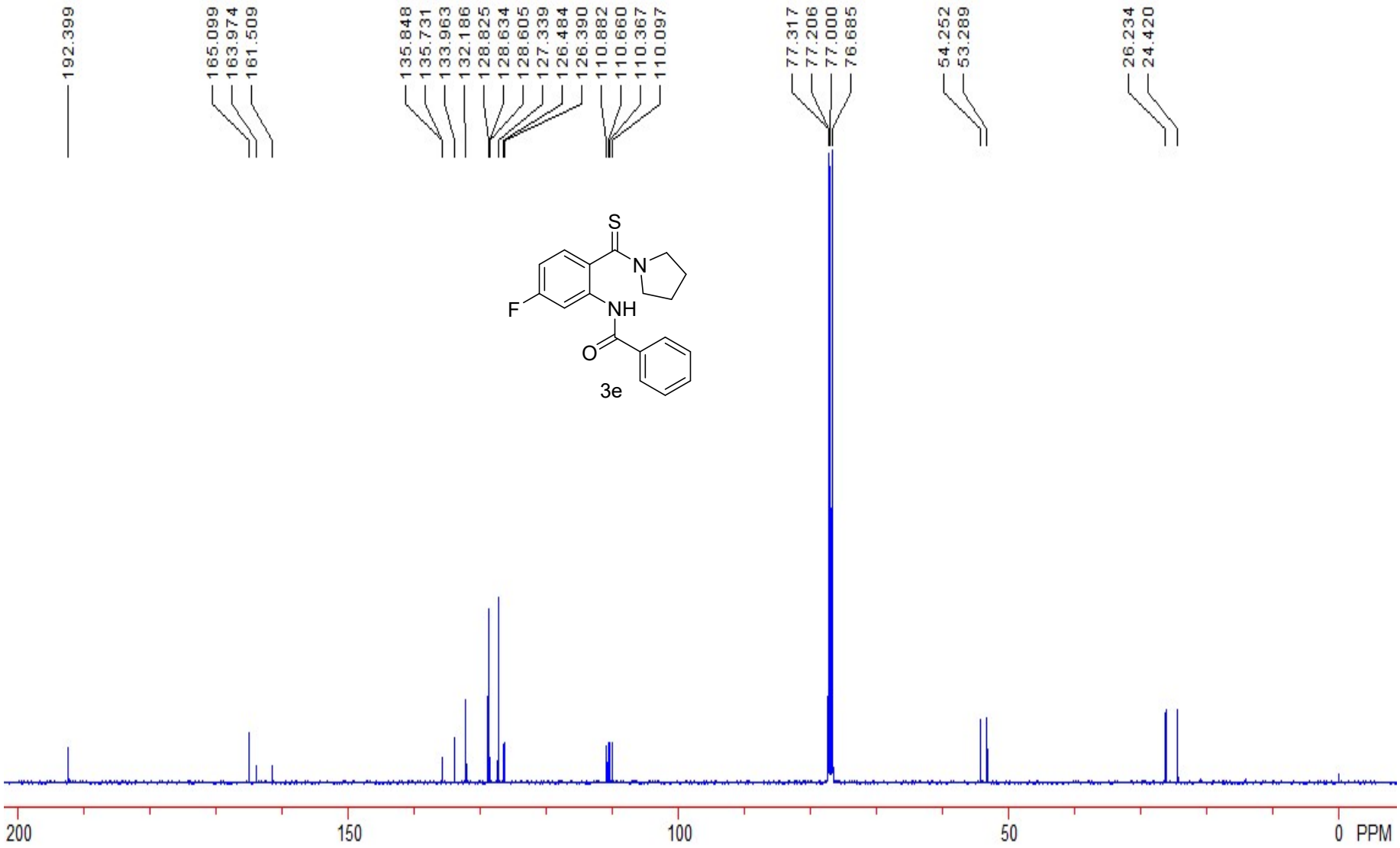
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110.882
110.660
110.367
110.097
77.317
77.206
77.000
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NH
O
3e
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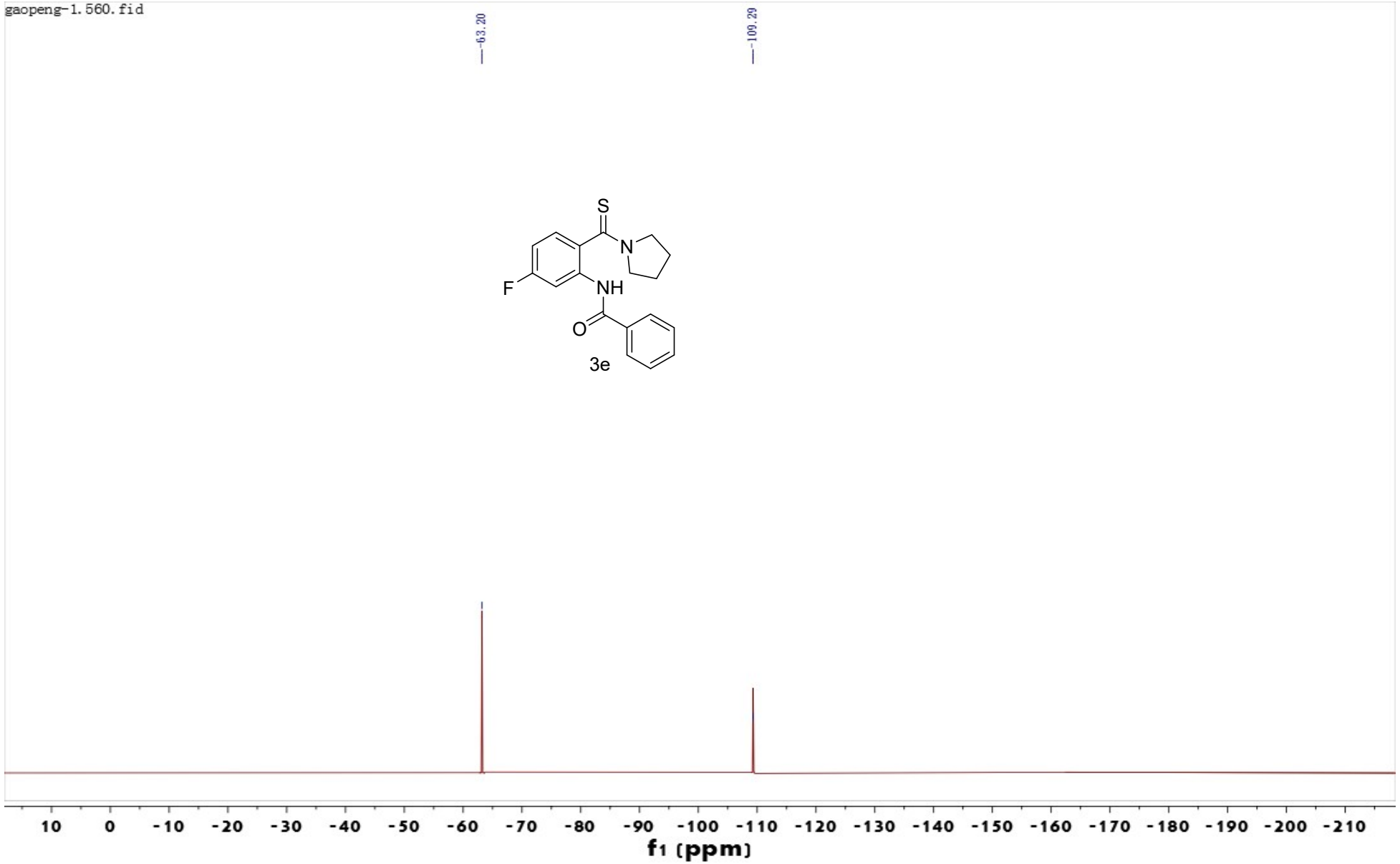
100
50
0 PPM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F
NH
O
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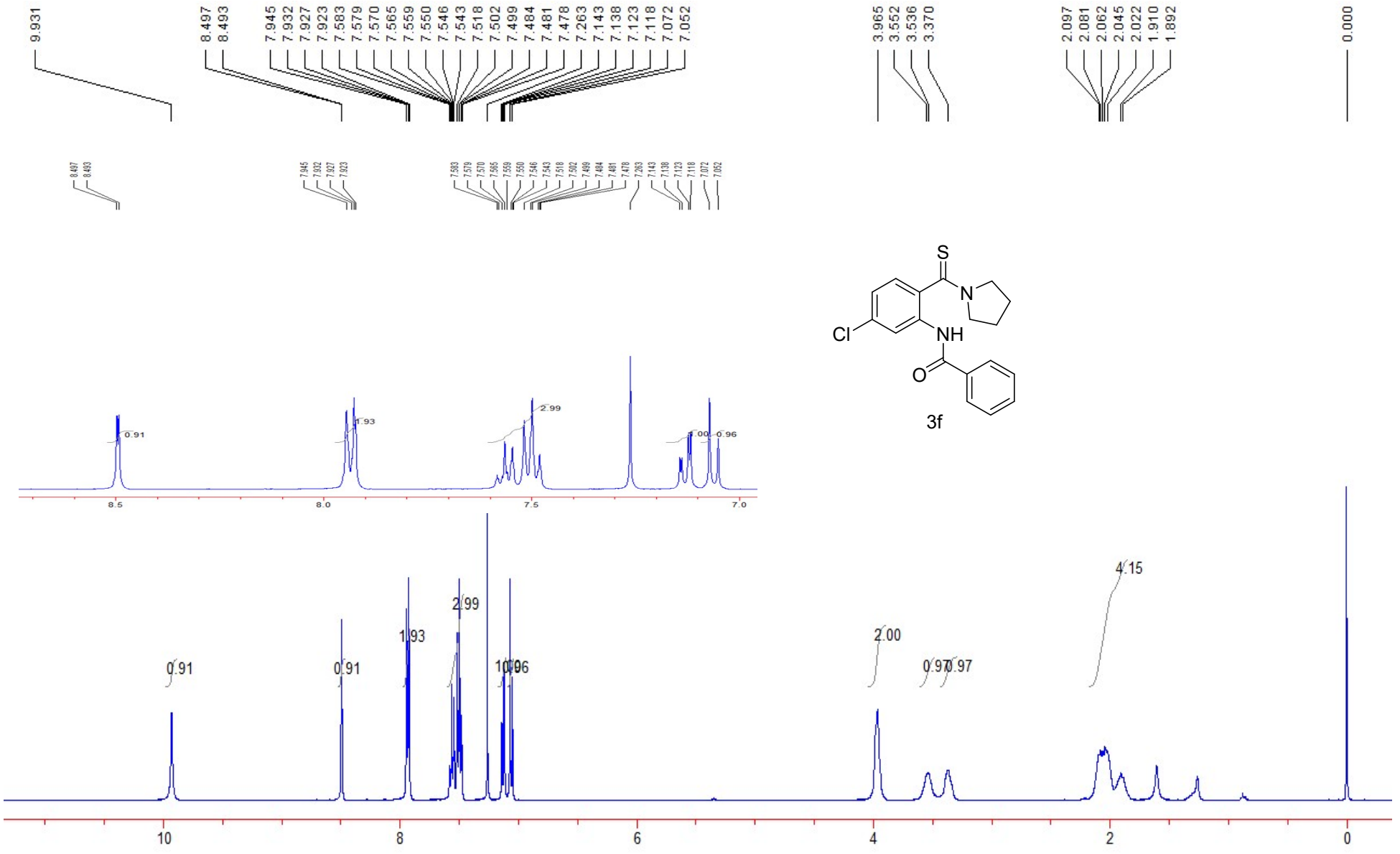
f1 (ppm)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7.546
7.543
7.518
7.502
7.499
7.484
7.481
7.478
7.263
7.143
7.138
7.123
7.118
7.072
7.052
3.965
3.552
3.536
3.370
2.097
2.081
2.062
2.045
2.022
1.910
1.892
0.000
S
N
Cl
NH
O
3f
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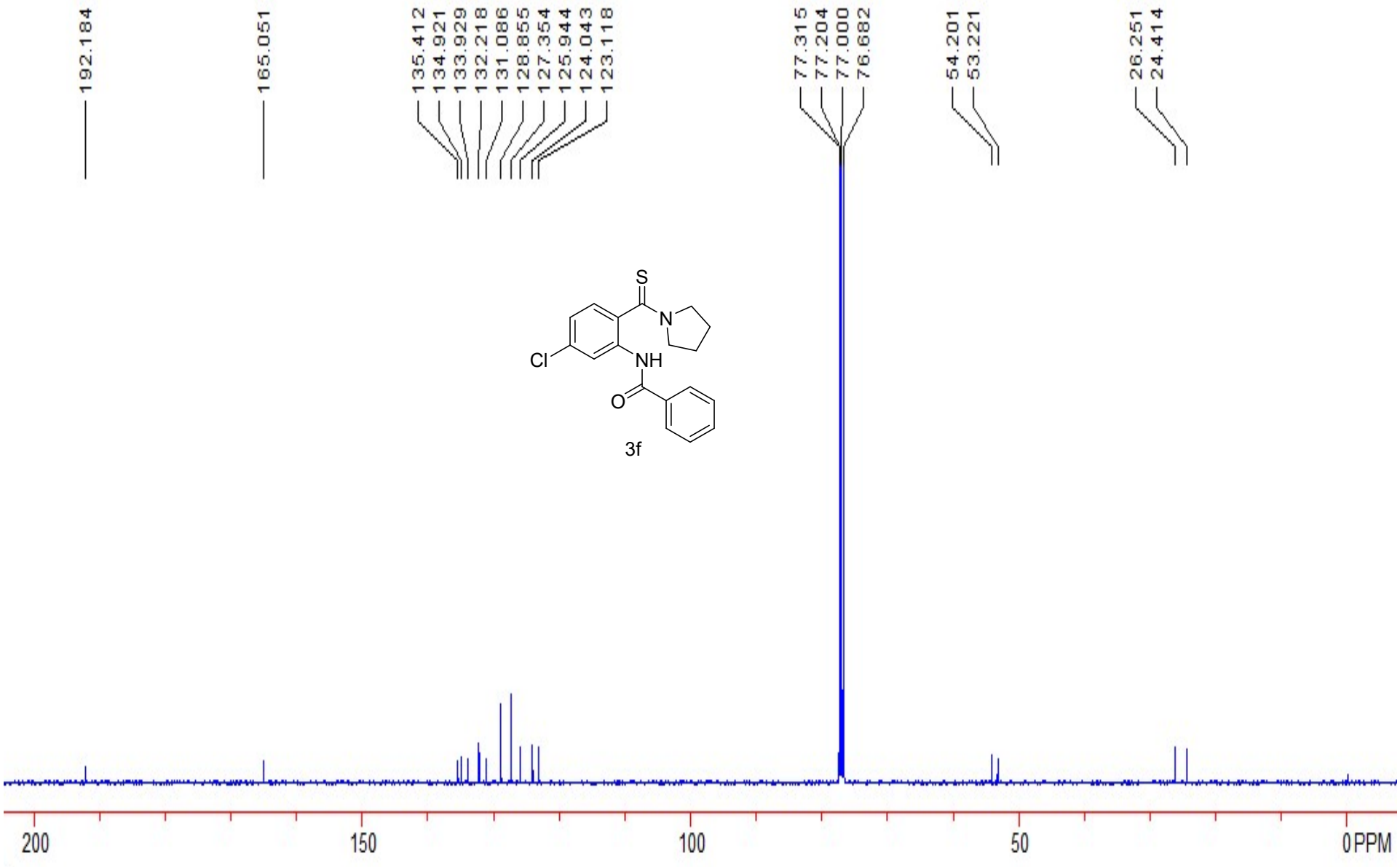
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77.204
77.000
76.682
54.201
53.221
26.251
24.414
S
N
Cl
NH
O
3f
200
150
100
50
0 PPM


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8.643
7.939
7.921
7.580
7.562
7.543
7.515
7.495
7.478
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7.266
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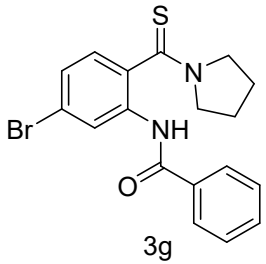
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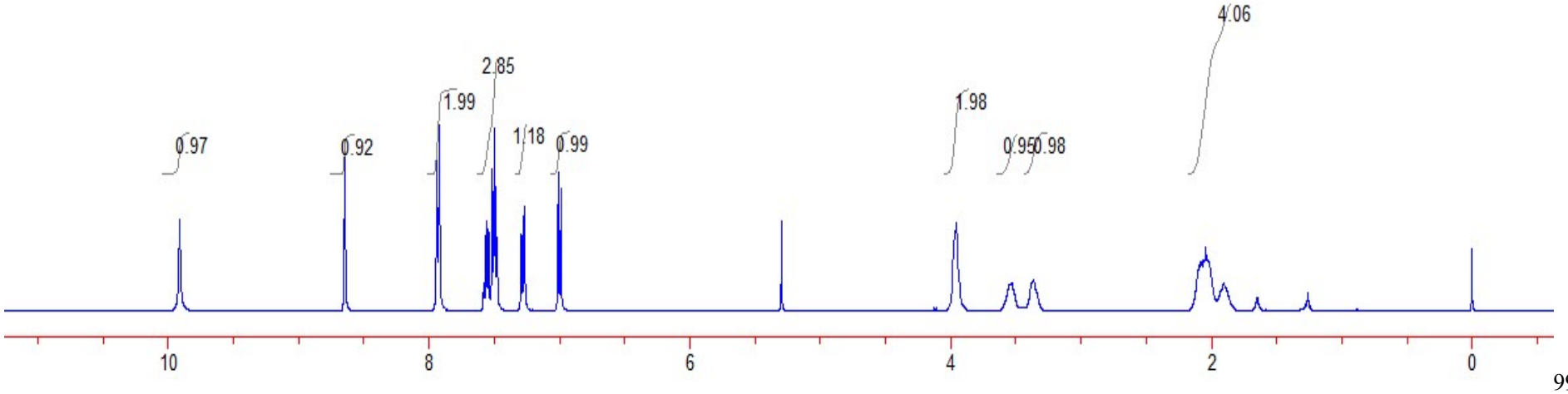
Br
NH
O

3g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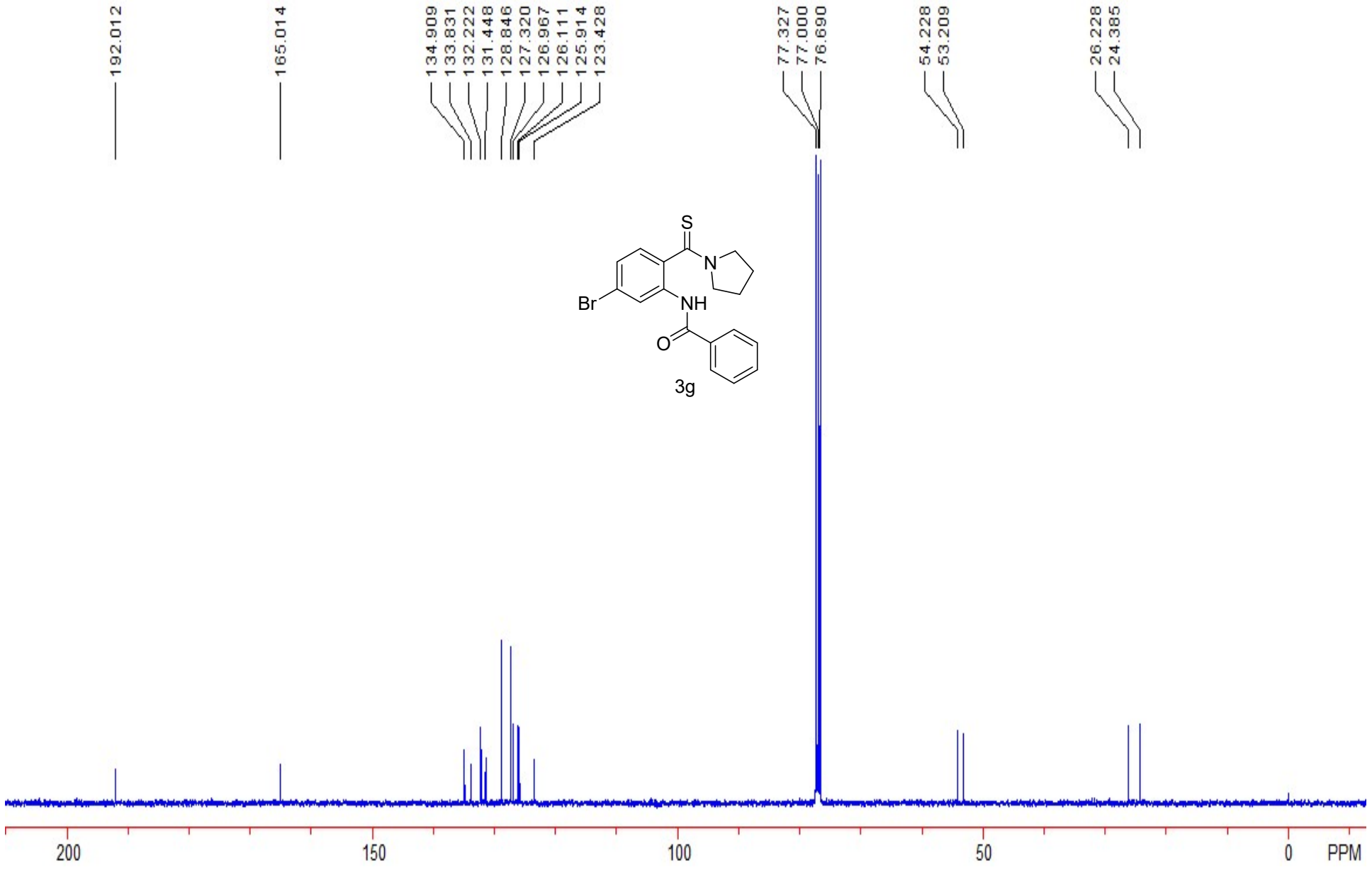
0

999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77.000
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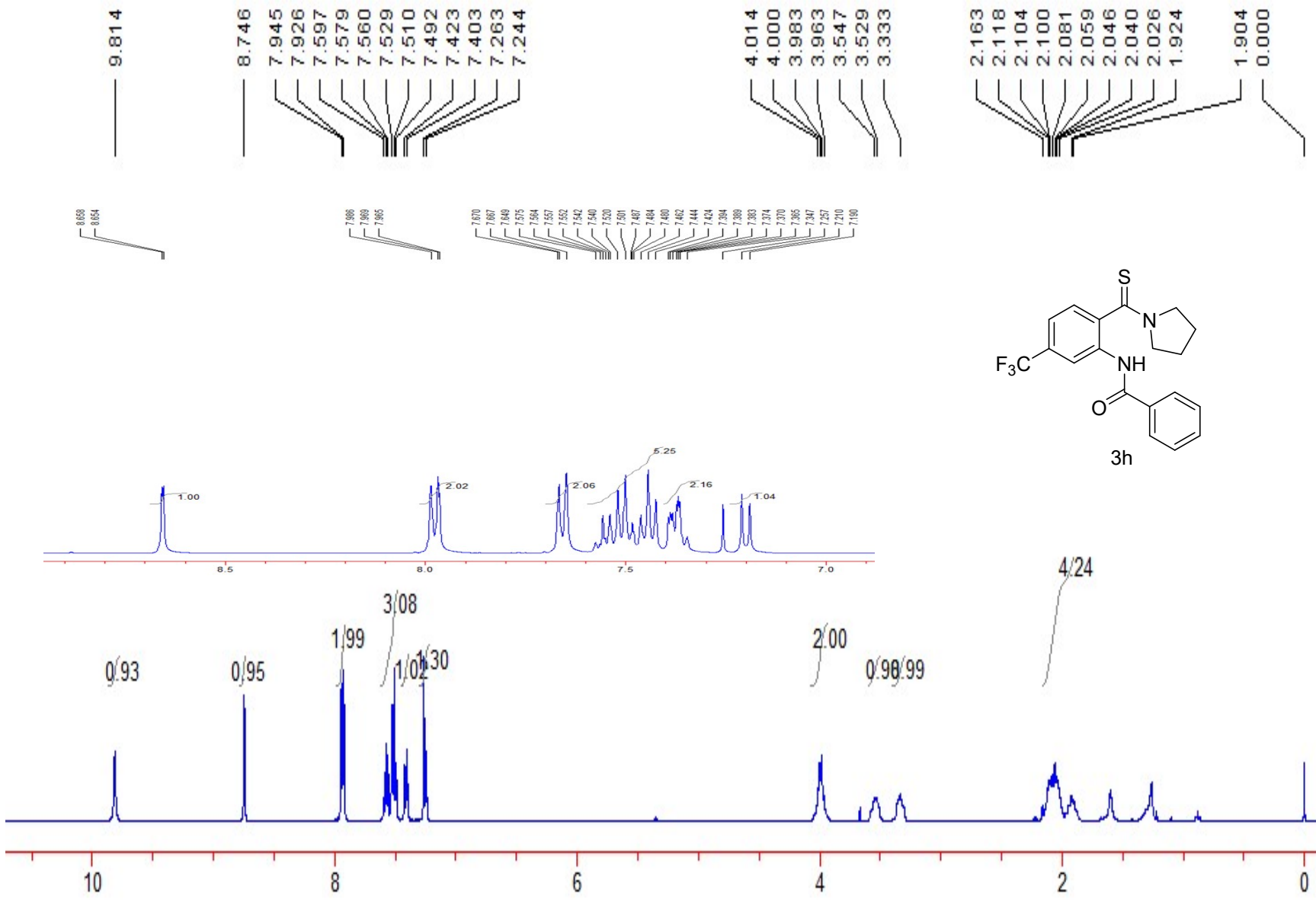
PPM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2.026
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1.904
0.000
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N
F3C
NH
O
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2.06
5.25
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2
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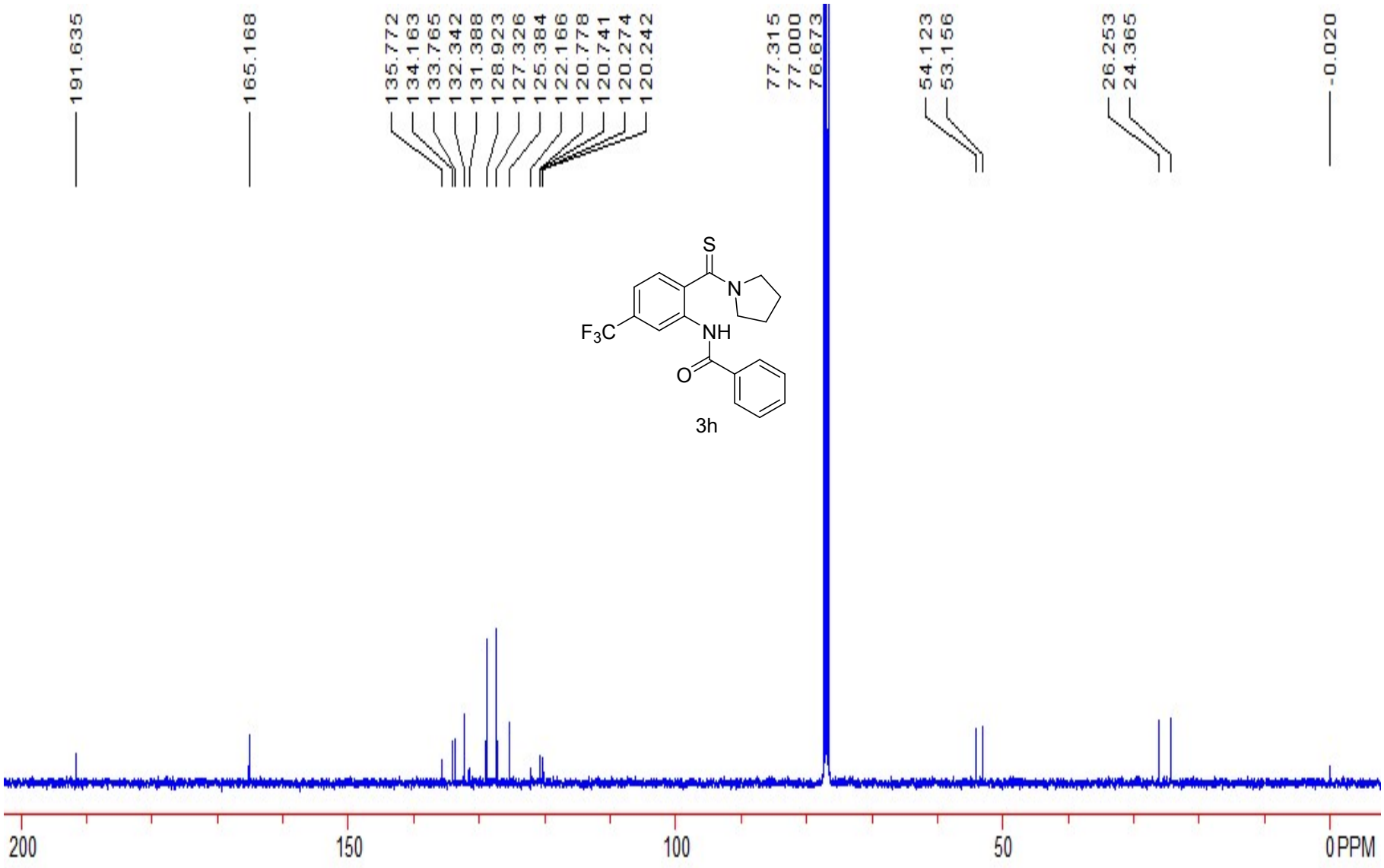
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3h
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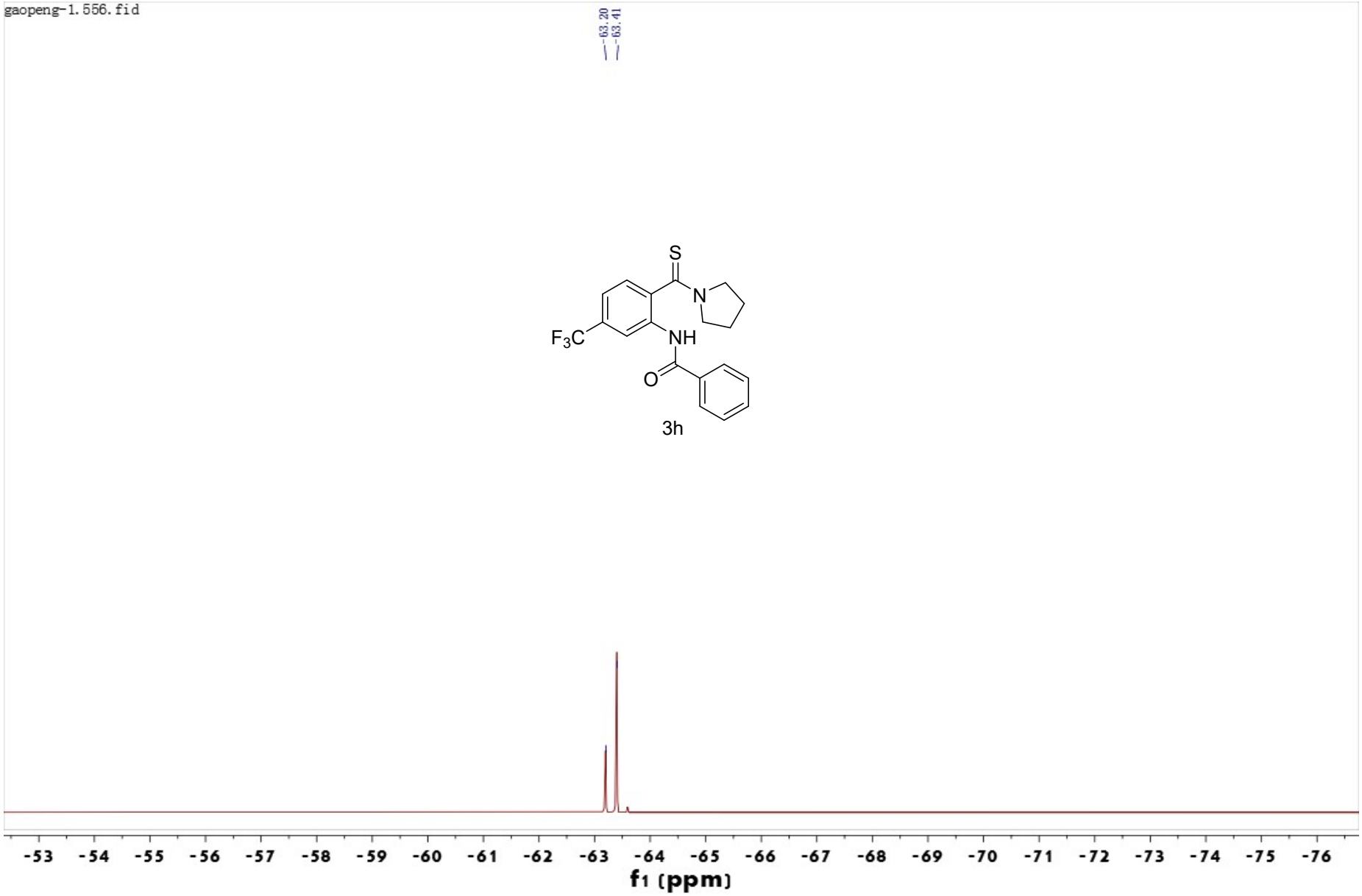
0 PPM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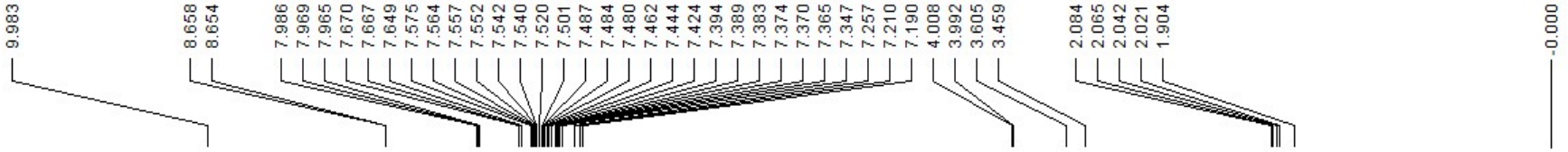
f1 (ppm)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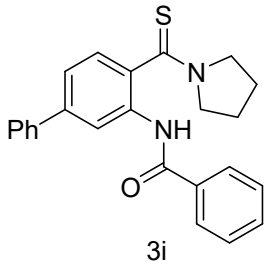
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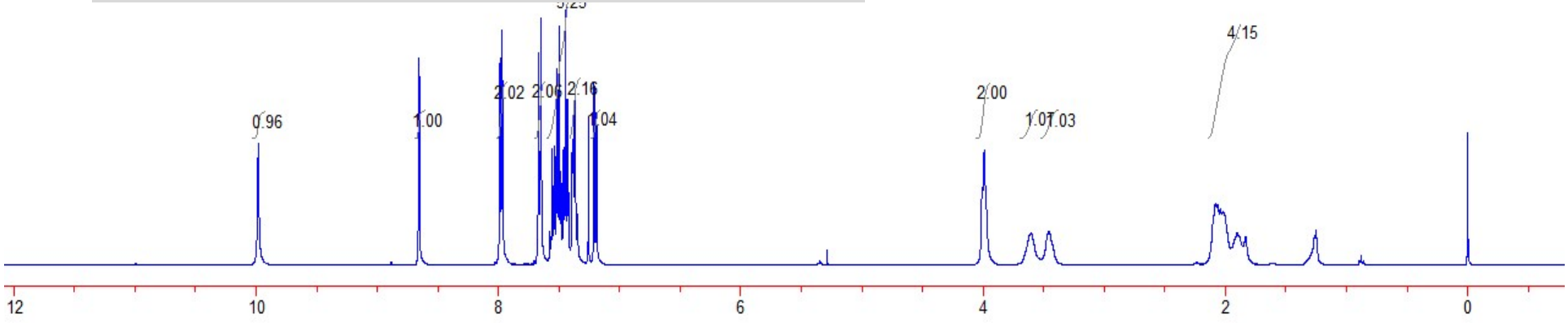
3i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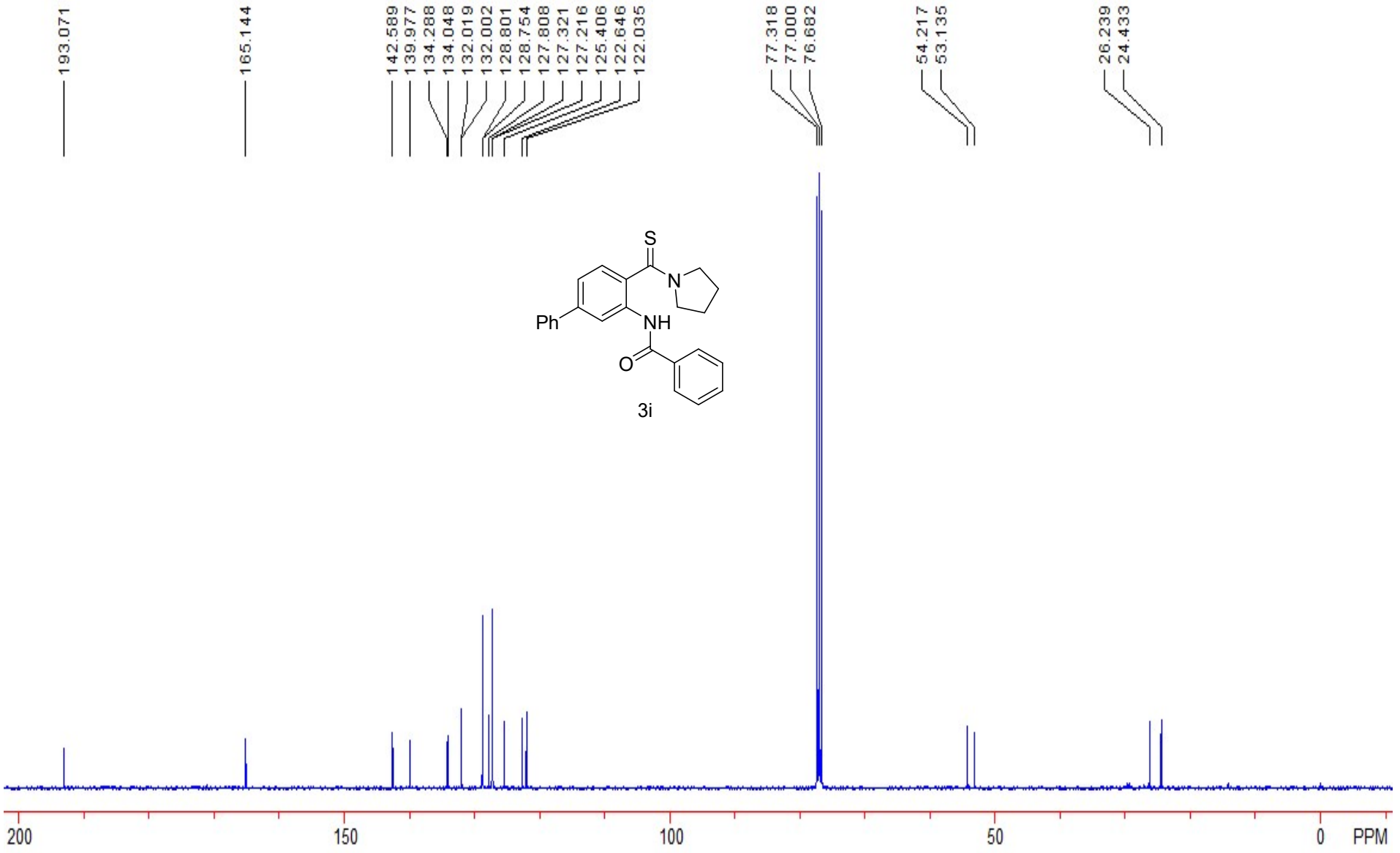
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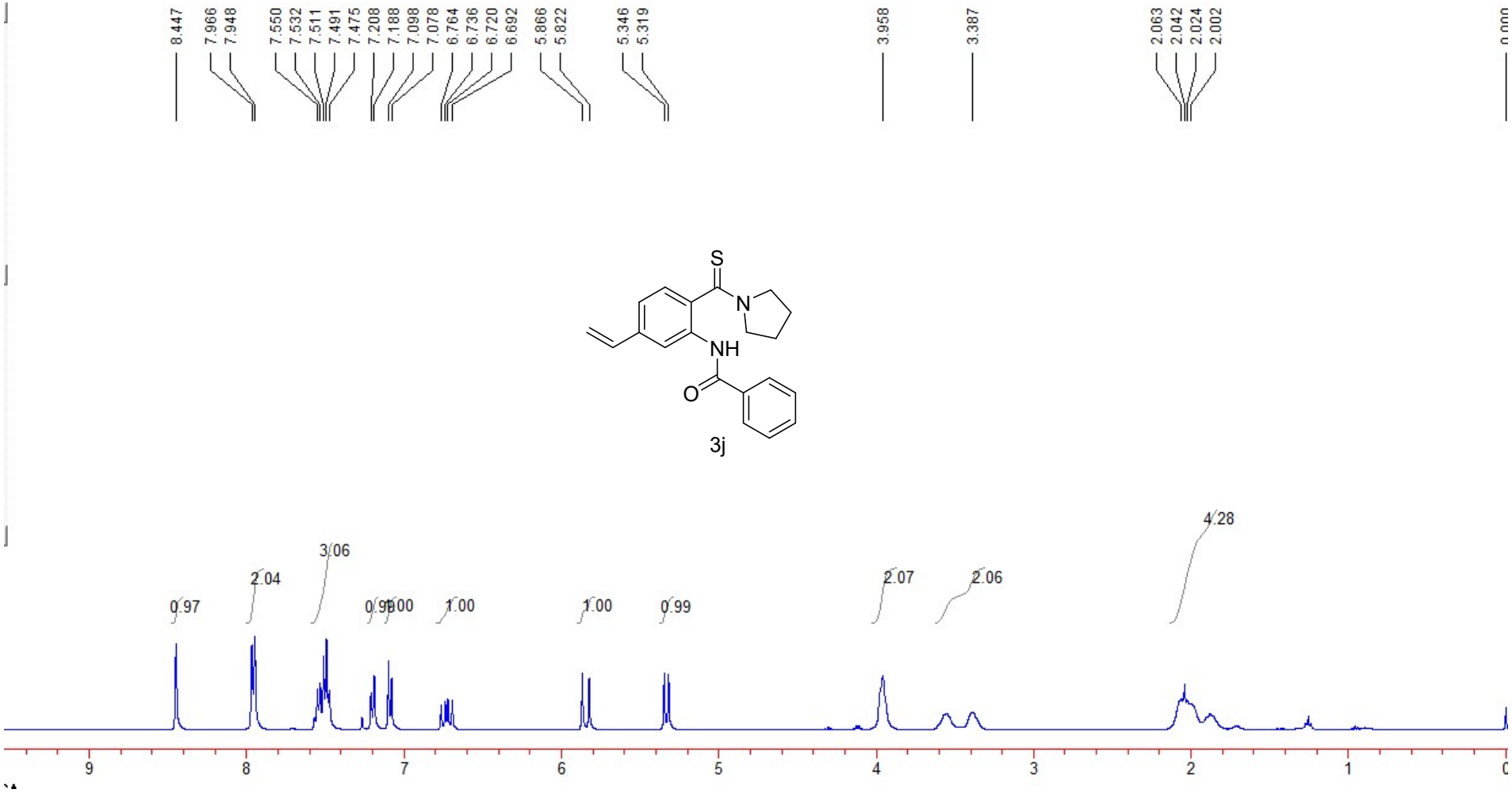
PPM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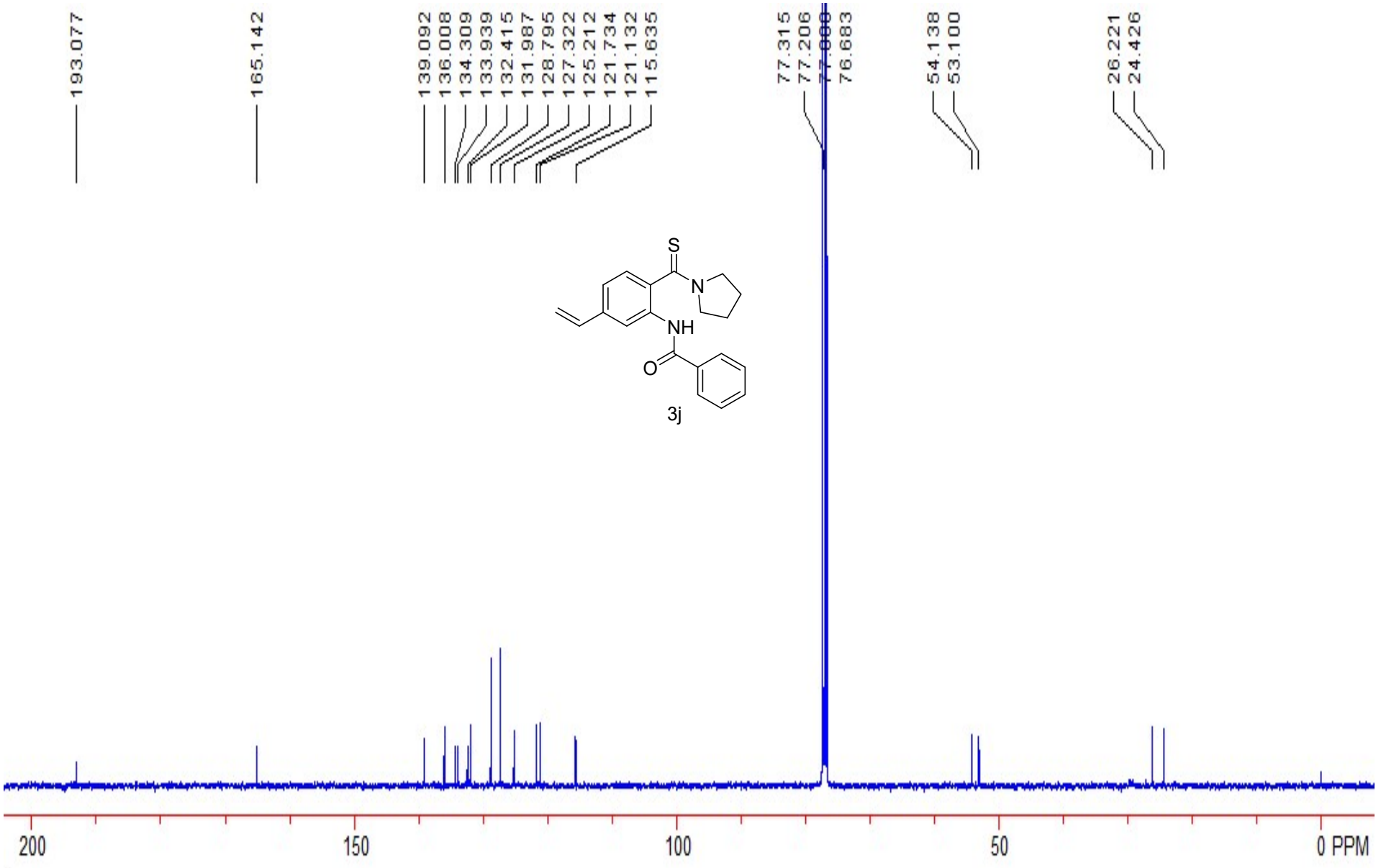
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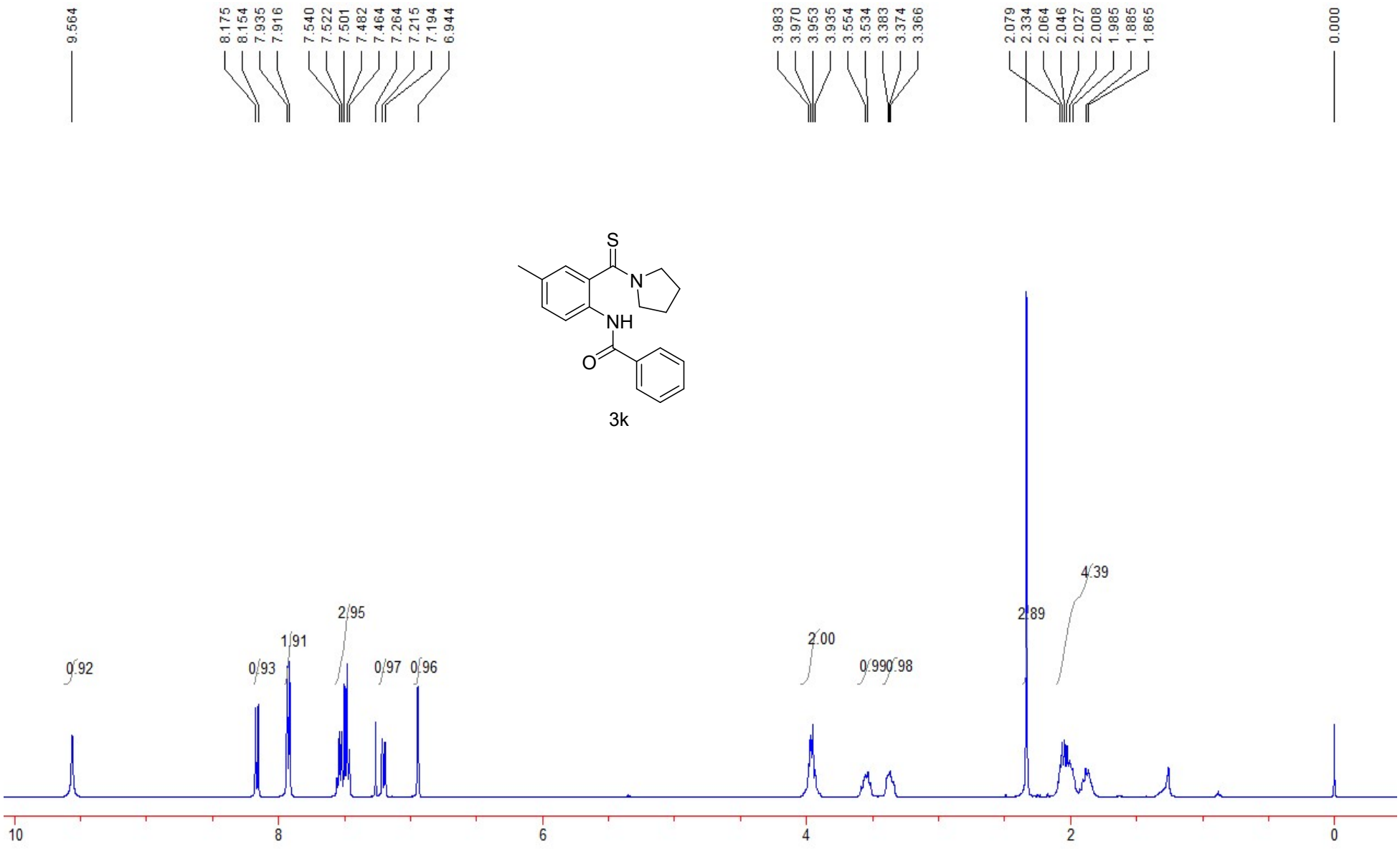
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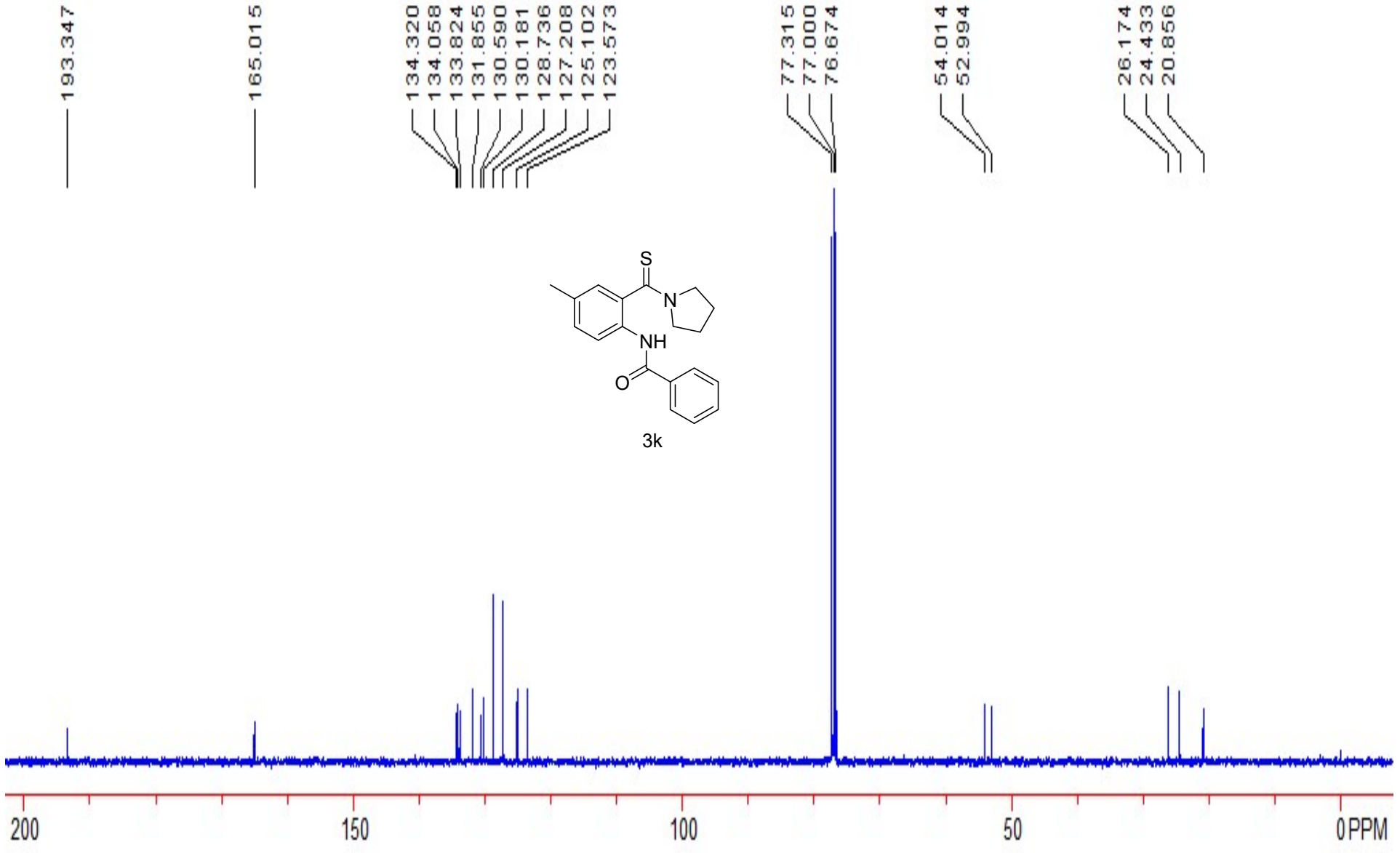
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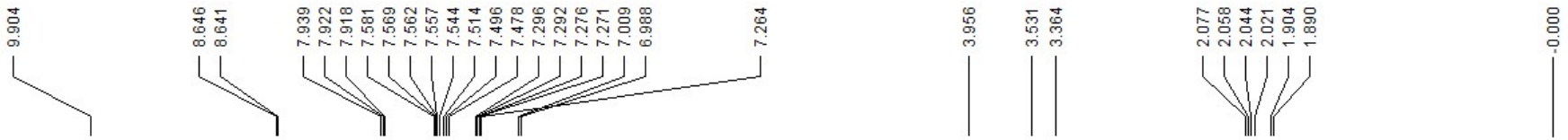
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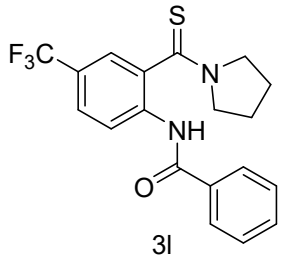
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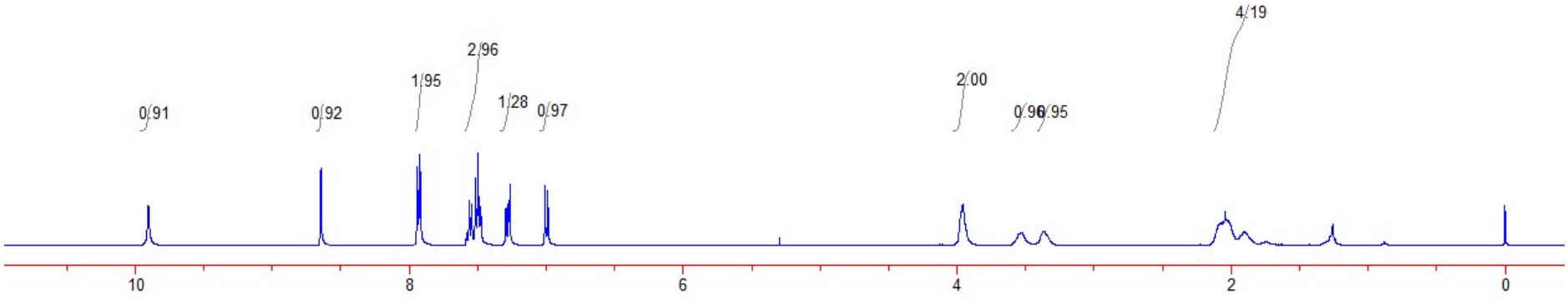
3l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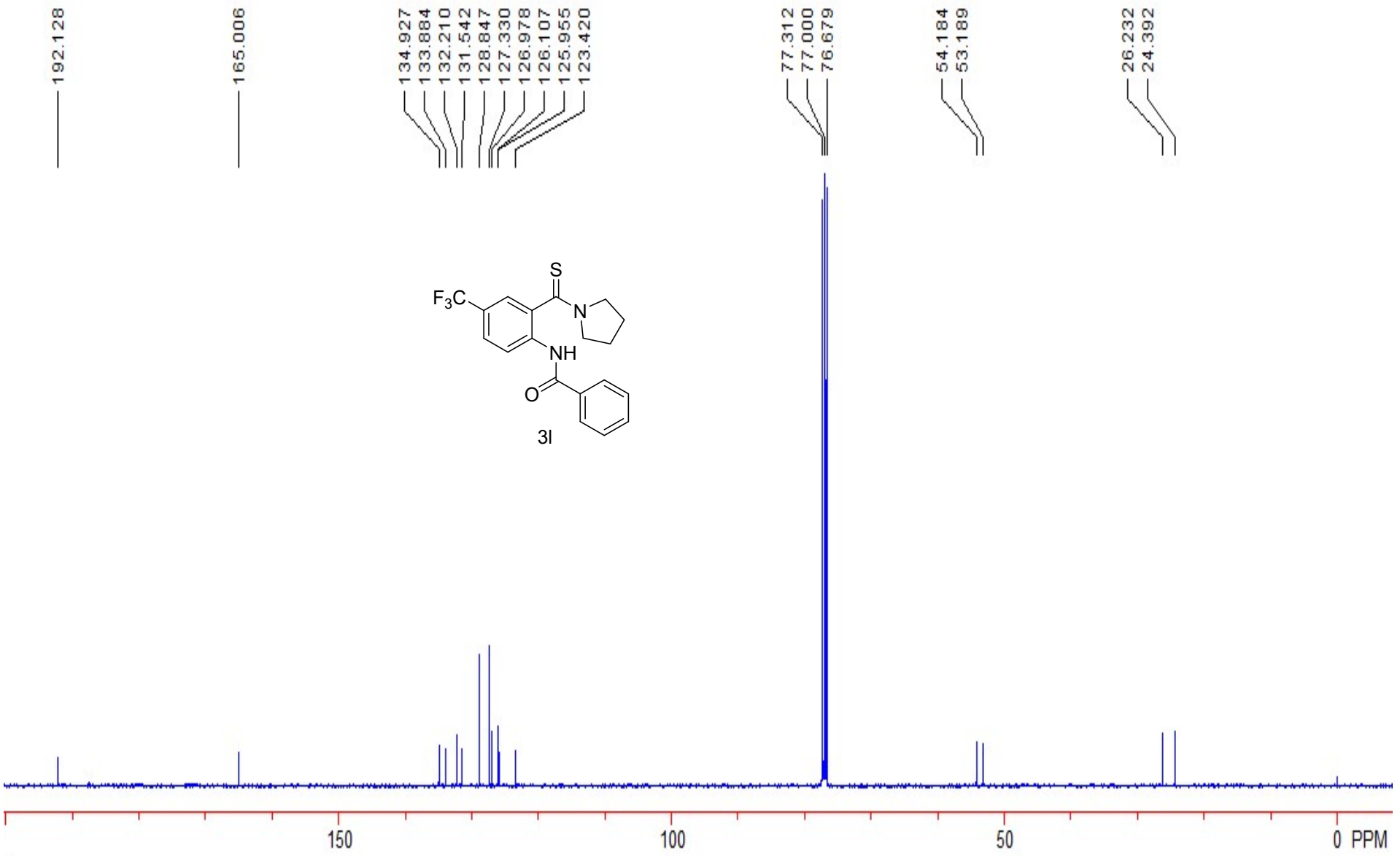
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77.000
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NH
O
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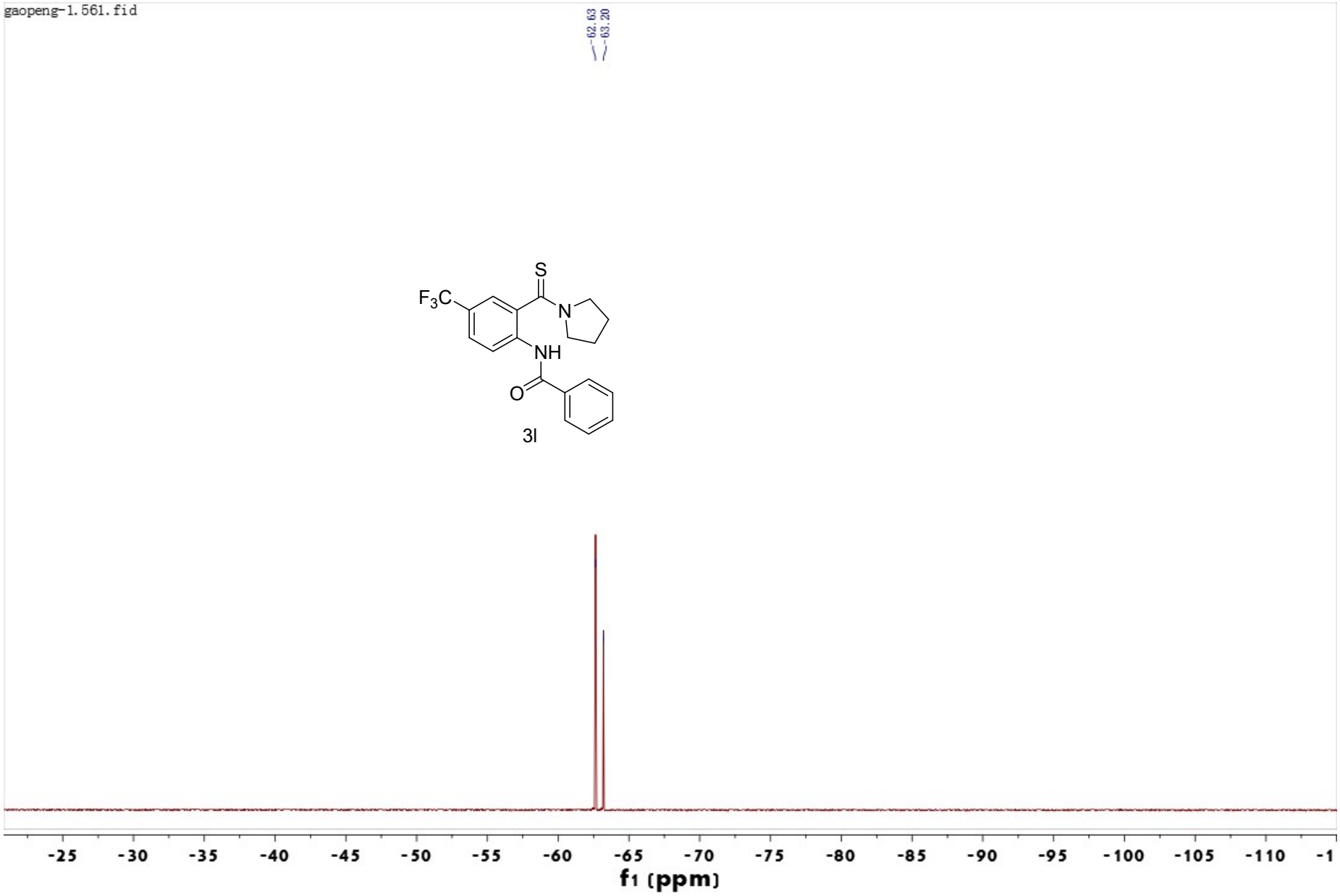
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NH
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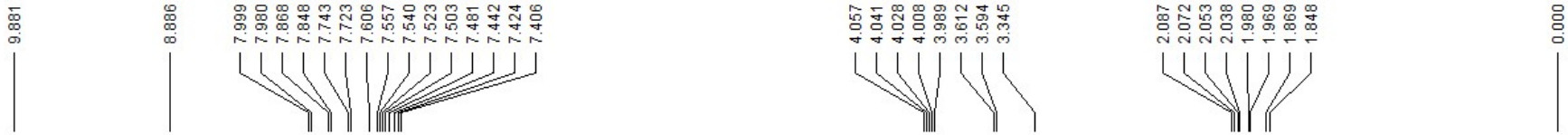
f1 (ppm)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4.041
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4.008
3.989
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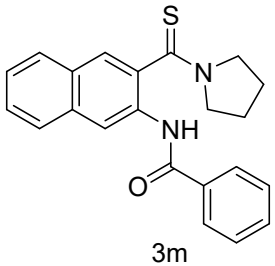
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O

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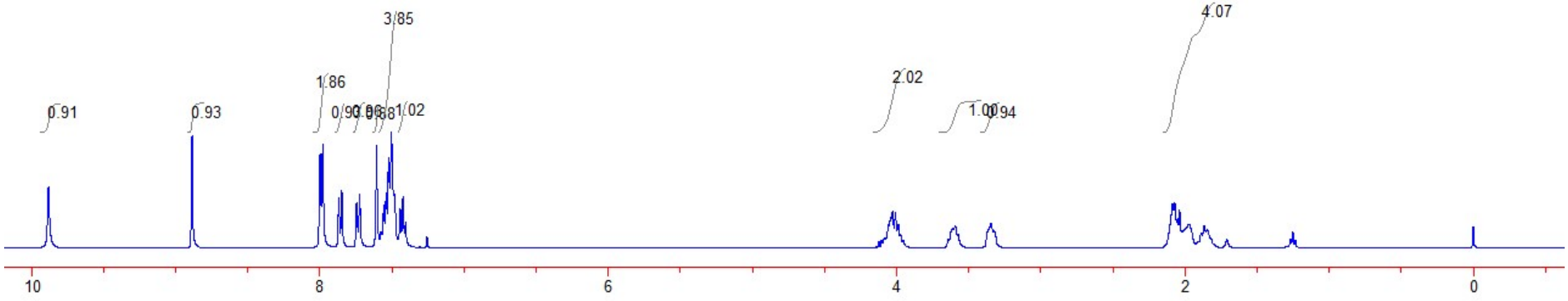
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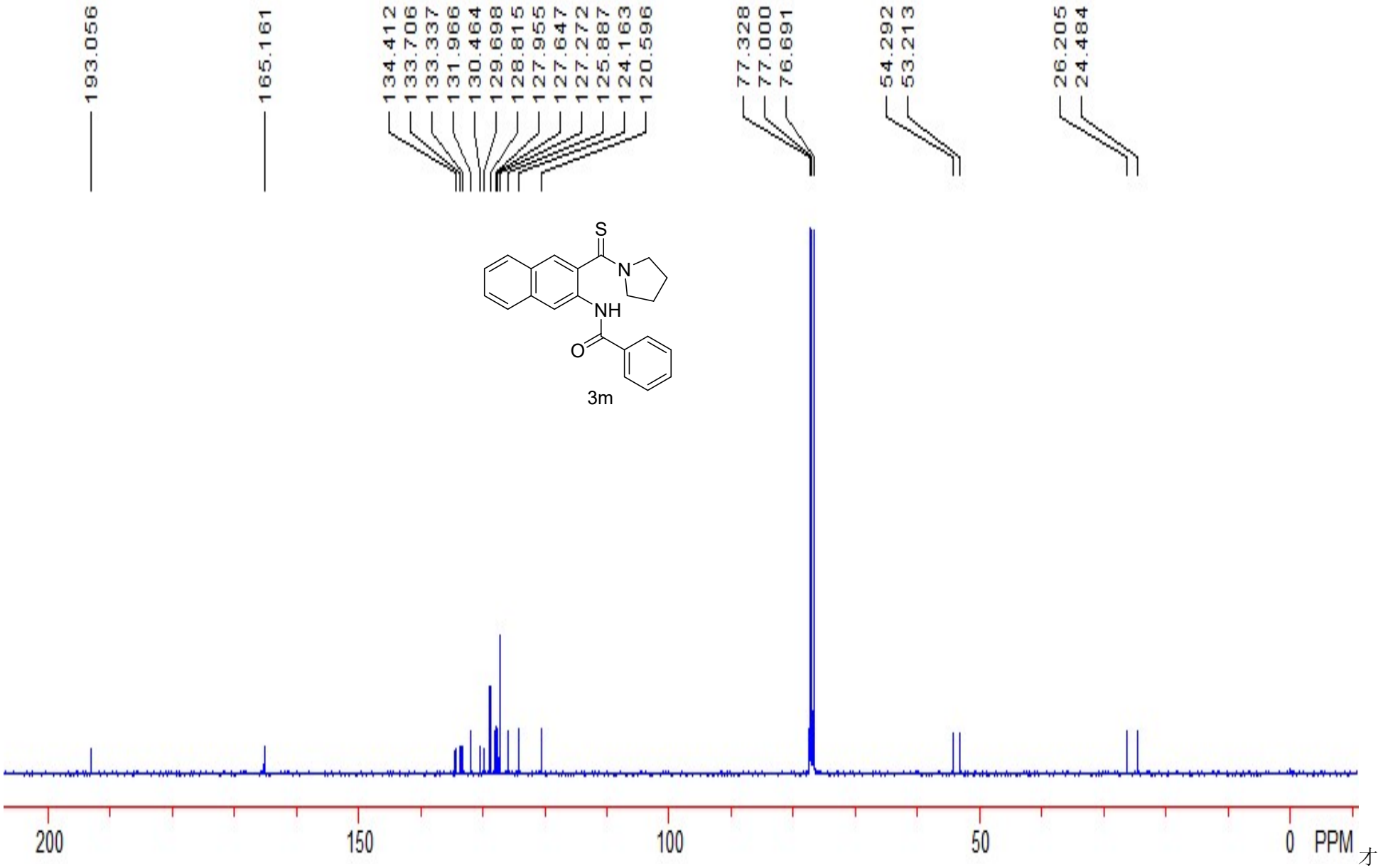
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77.000
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O
3m
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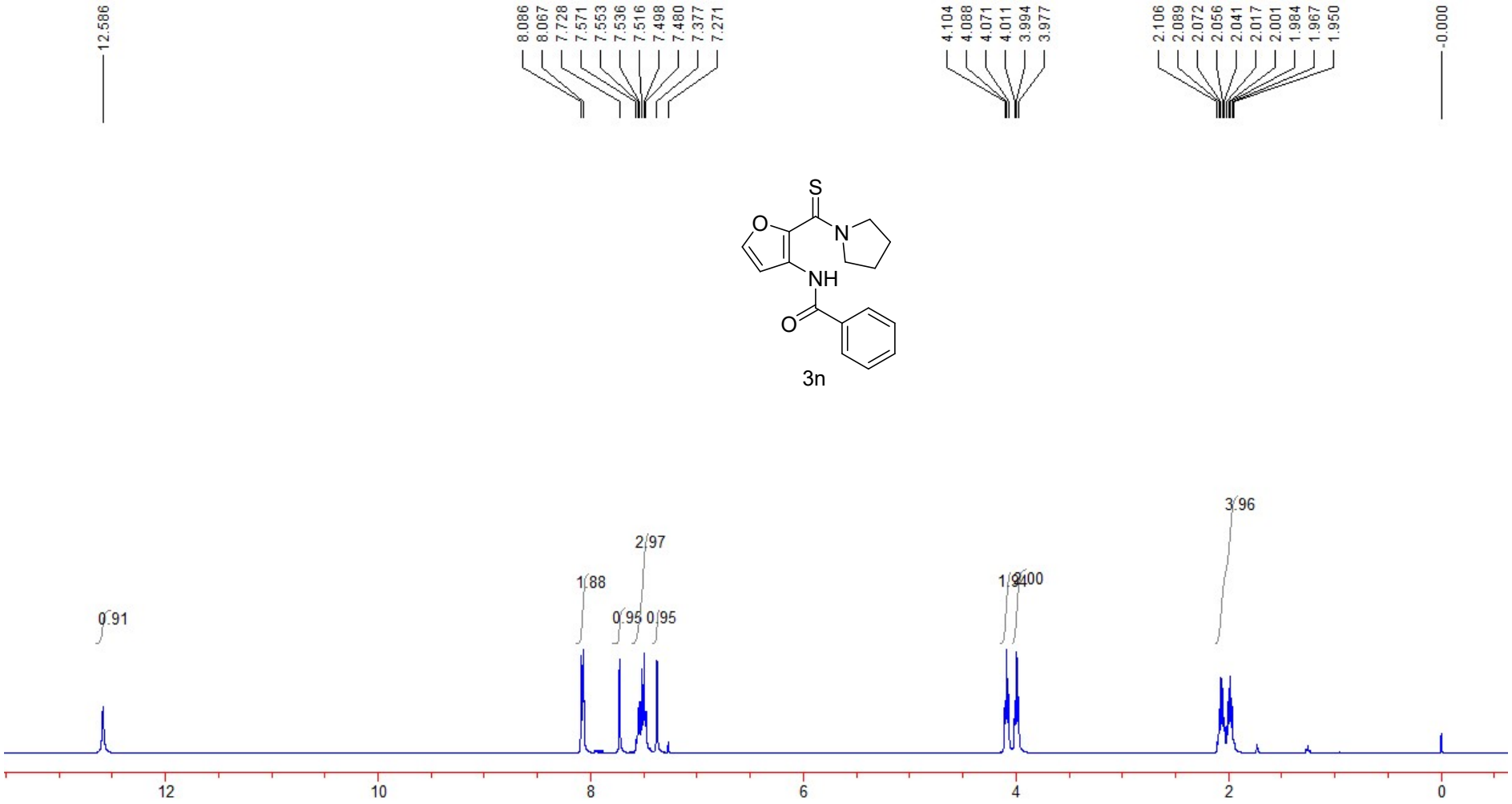
PPM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2.017
2.001
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1.967
1.950
-0.000
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O
N
NH
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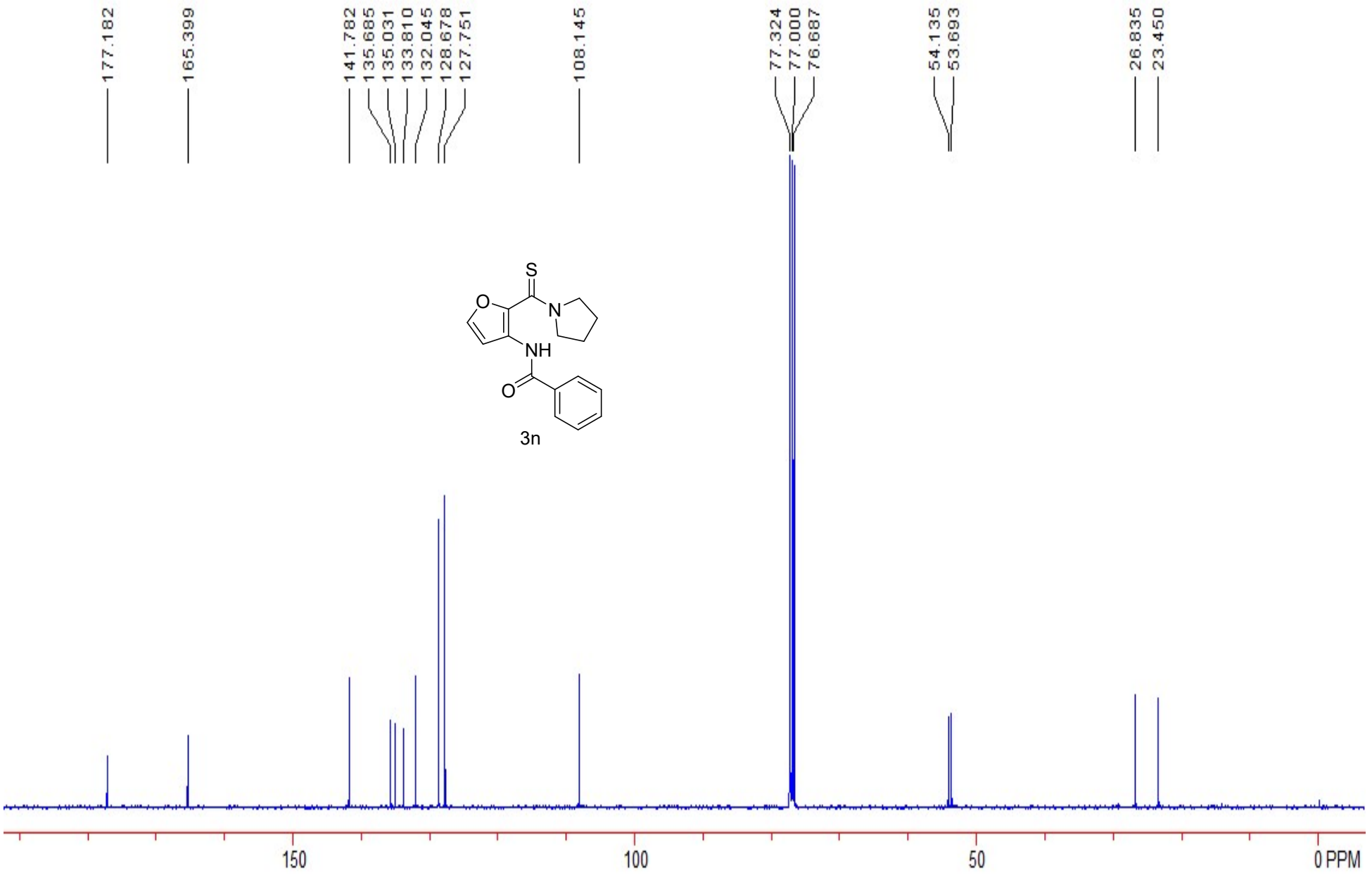
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77.000
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53.693
26.835
23.450
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NH
O
3n
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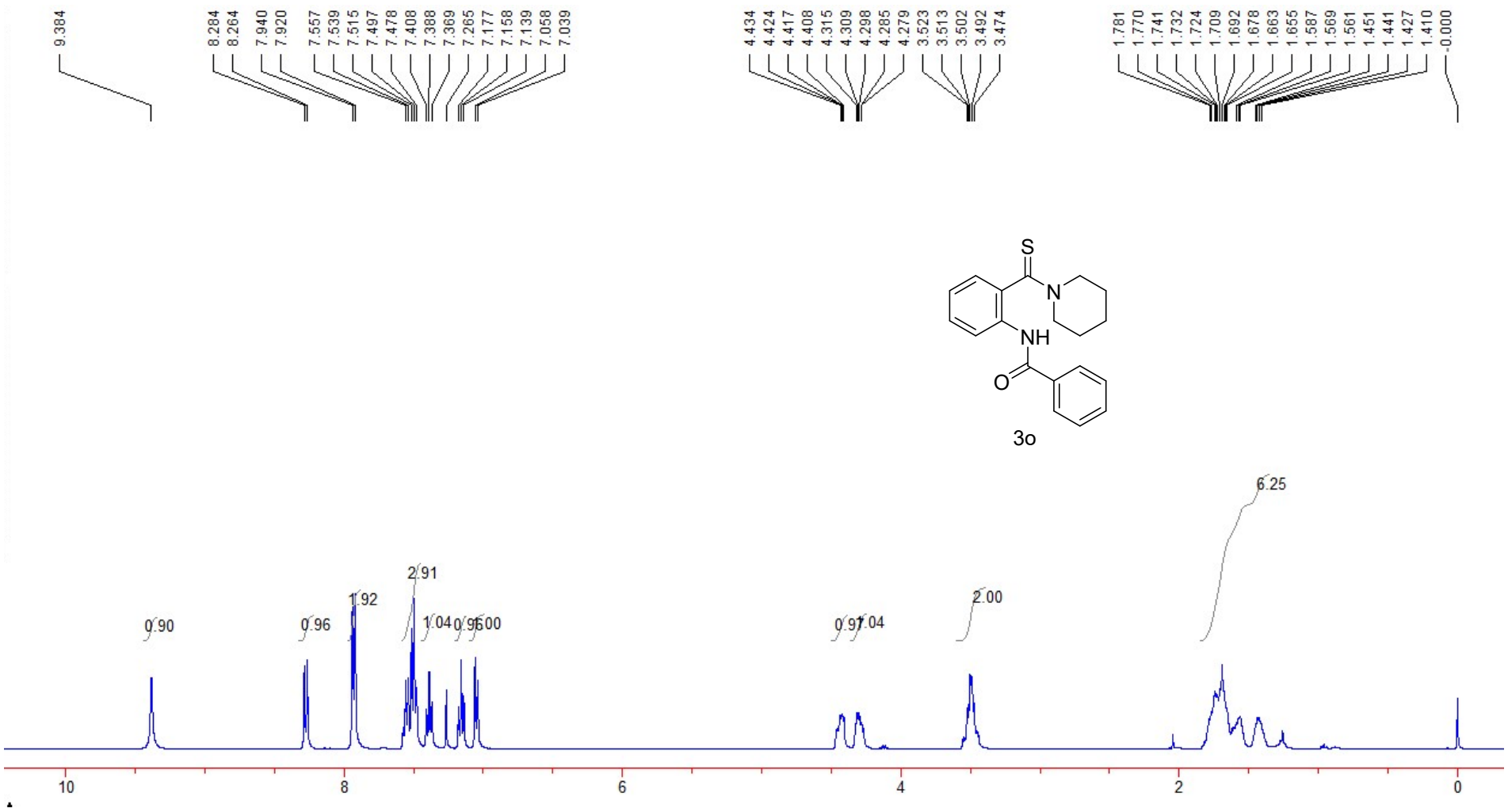
0 PPM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7.515
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7.388
7.369
7.265
7.177
7.158
7.139
7.058
7.039
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4.424
4.417
4.408
4.315
4.309
4.298
4.285
4.279
3.523
3.513
3.502
3.492
3.474
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1.770
1.741
1.732
1.724
1.709
1.692
1.678
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1.441
1.427
1.410
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N
NH
O
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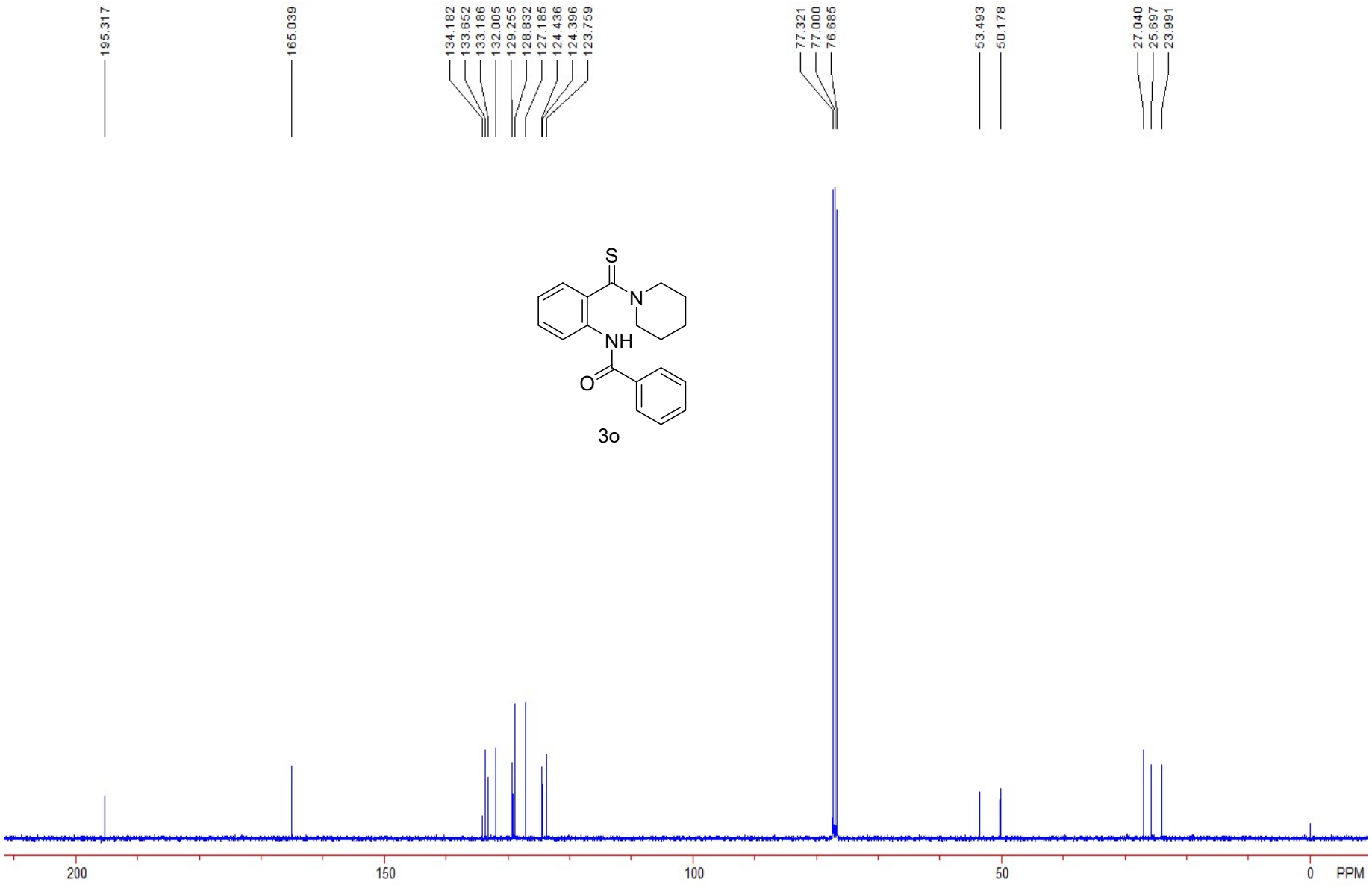
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77.000
76.685
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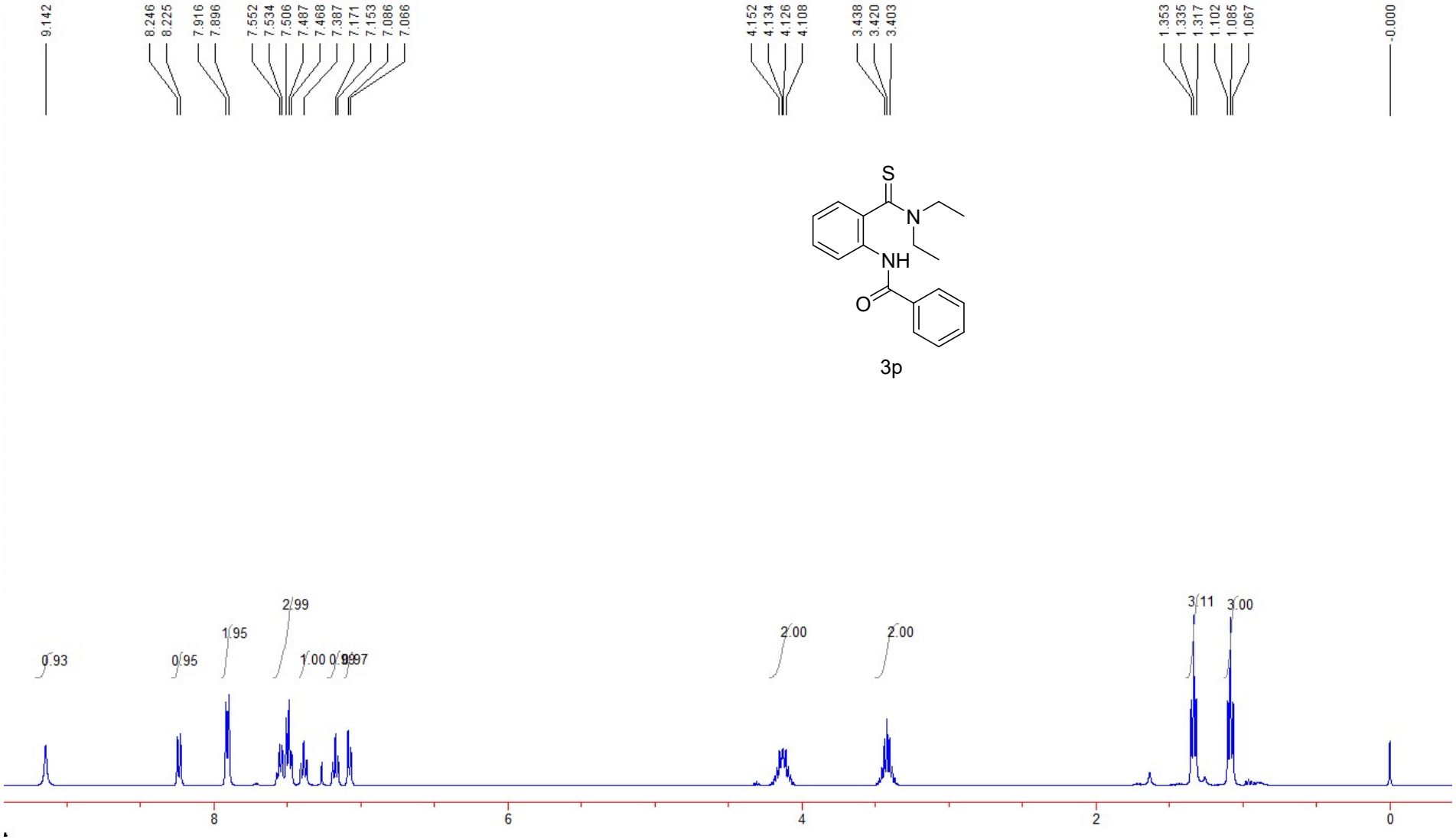
50
0
PPM

3o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7.153
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1.335
1.317
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N
NH
O
3p
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0.95
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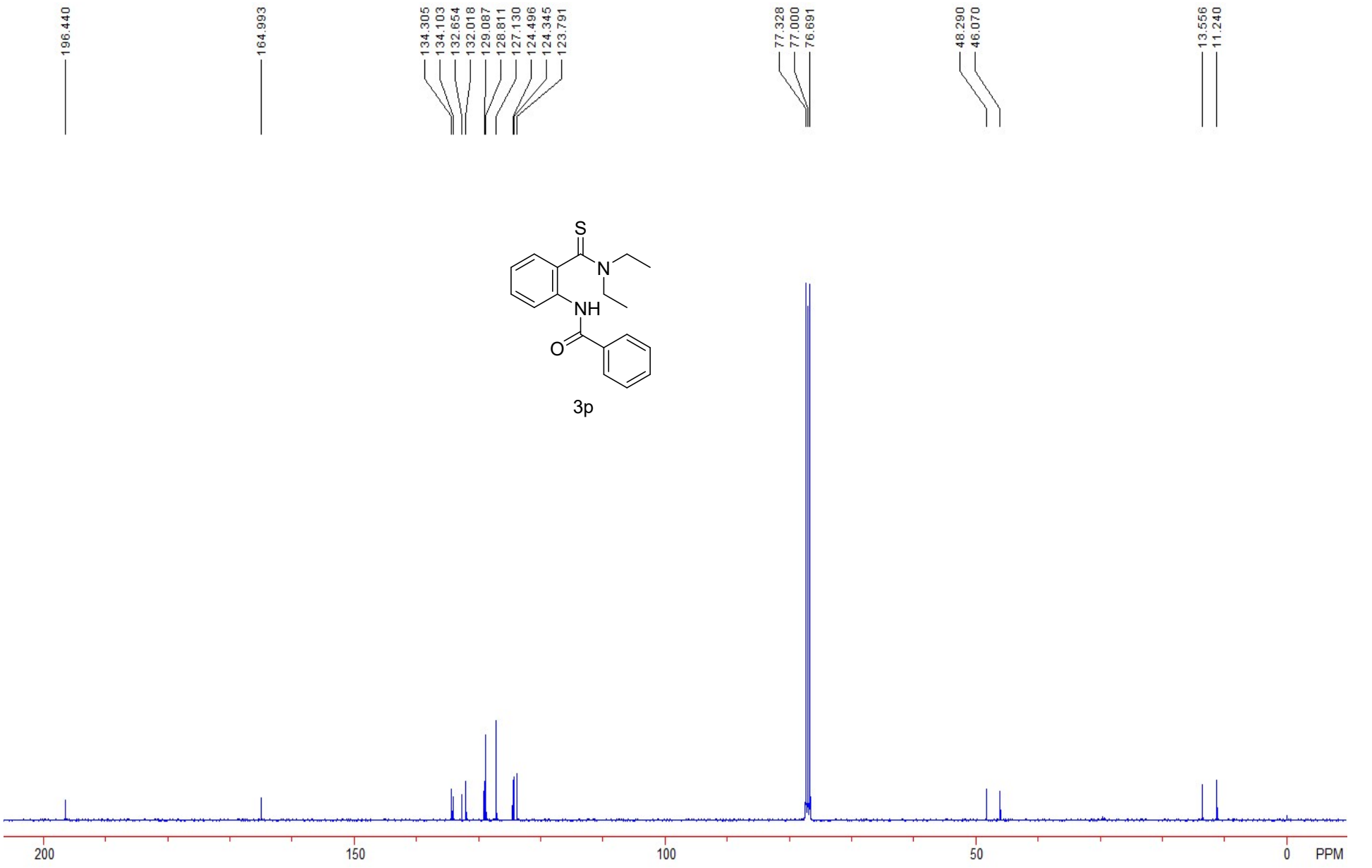
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77.000
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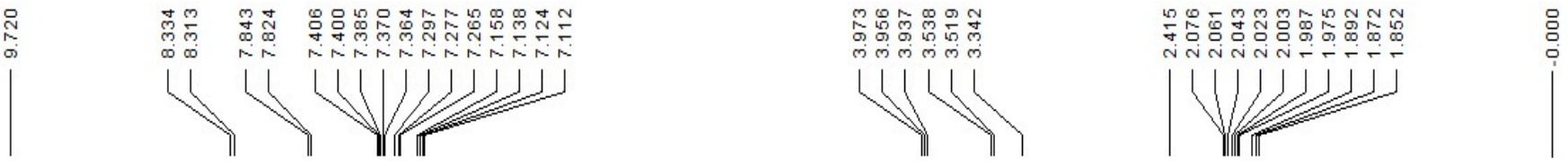
PPM

3p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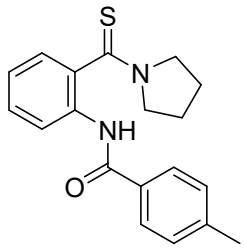
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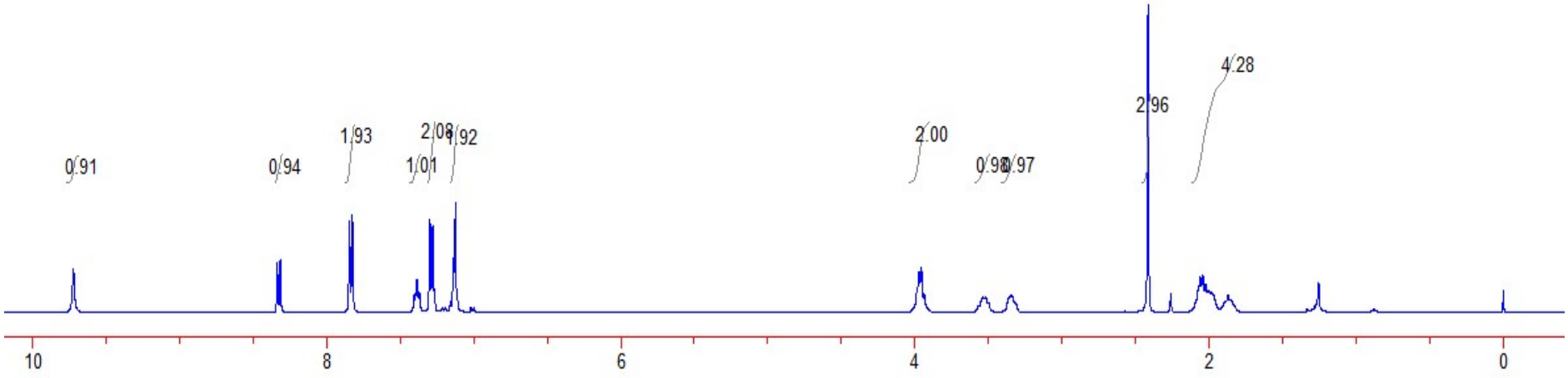
NH
O

4a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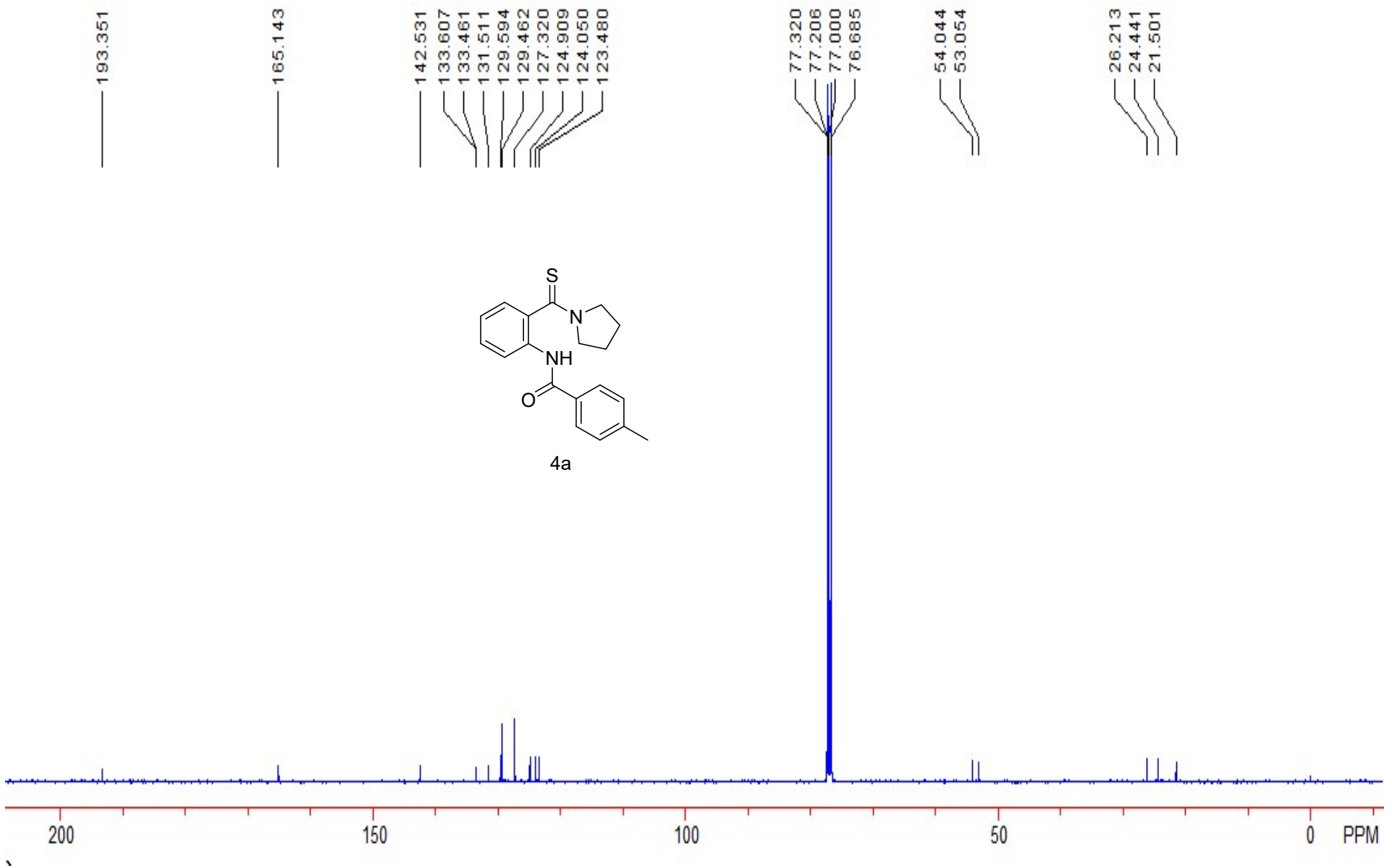
1.92
2.00
0.98
0.97
2.96
4.28
10
8
6
4
2
0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129.462
127.320
124.909
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123.480
77.320
77.206
77.000
76.685
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26.213
24.441
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S
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NH
O
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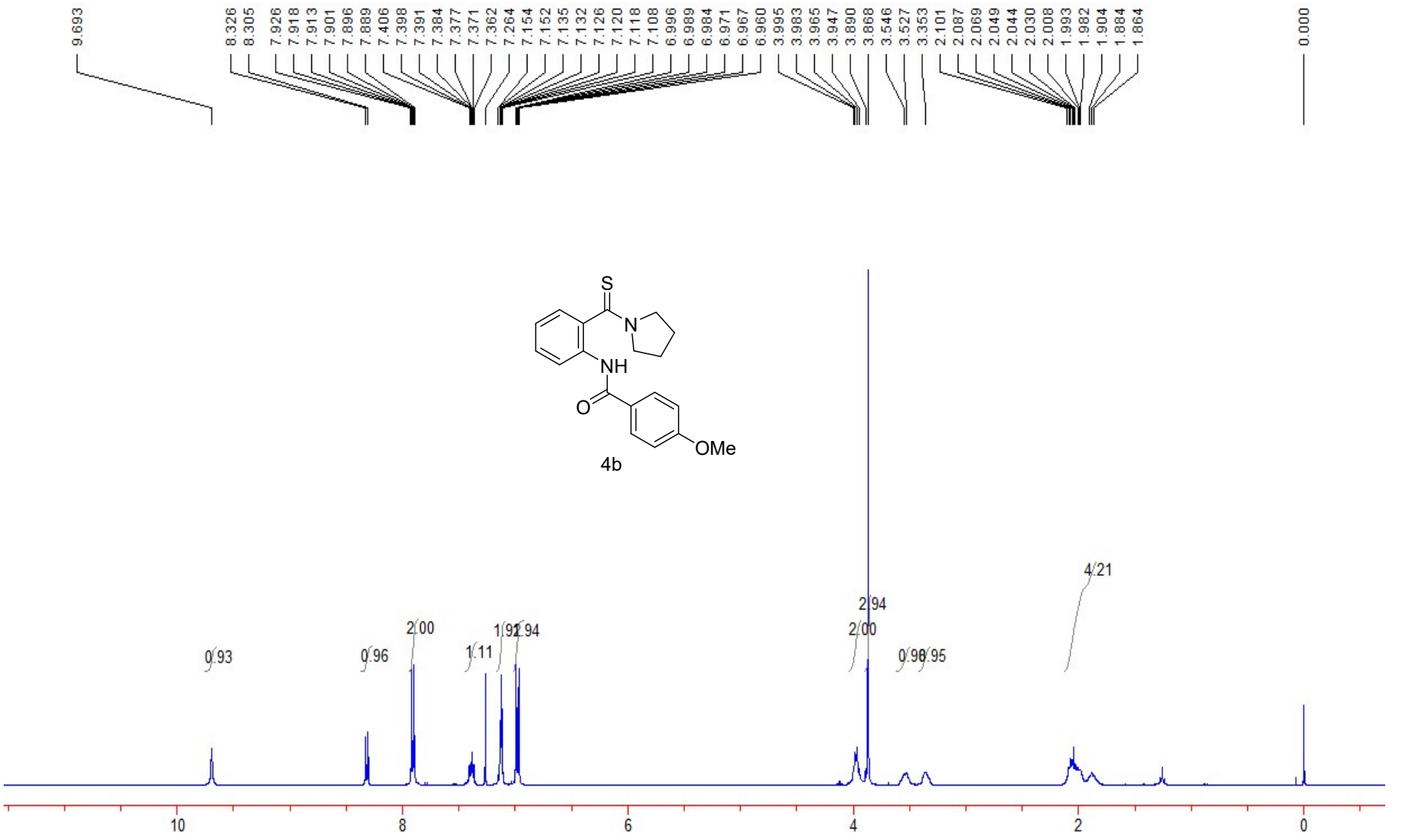
150
100
50
0
PPM

4a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7.152
7.135
7.132
7.126
7.120
7.118
7.108
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6.989
6.984
6.971
6.967
6.960
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3.983
3.965
3.947
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3.546
3.527
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2.087
2.069
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2.044
2.030
2.008
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1.904
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N
NH
O
OMe
4b
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2.00
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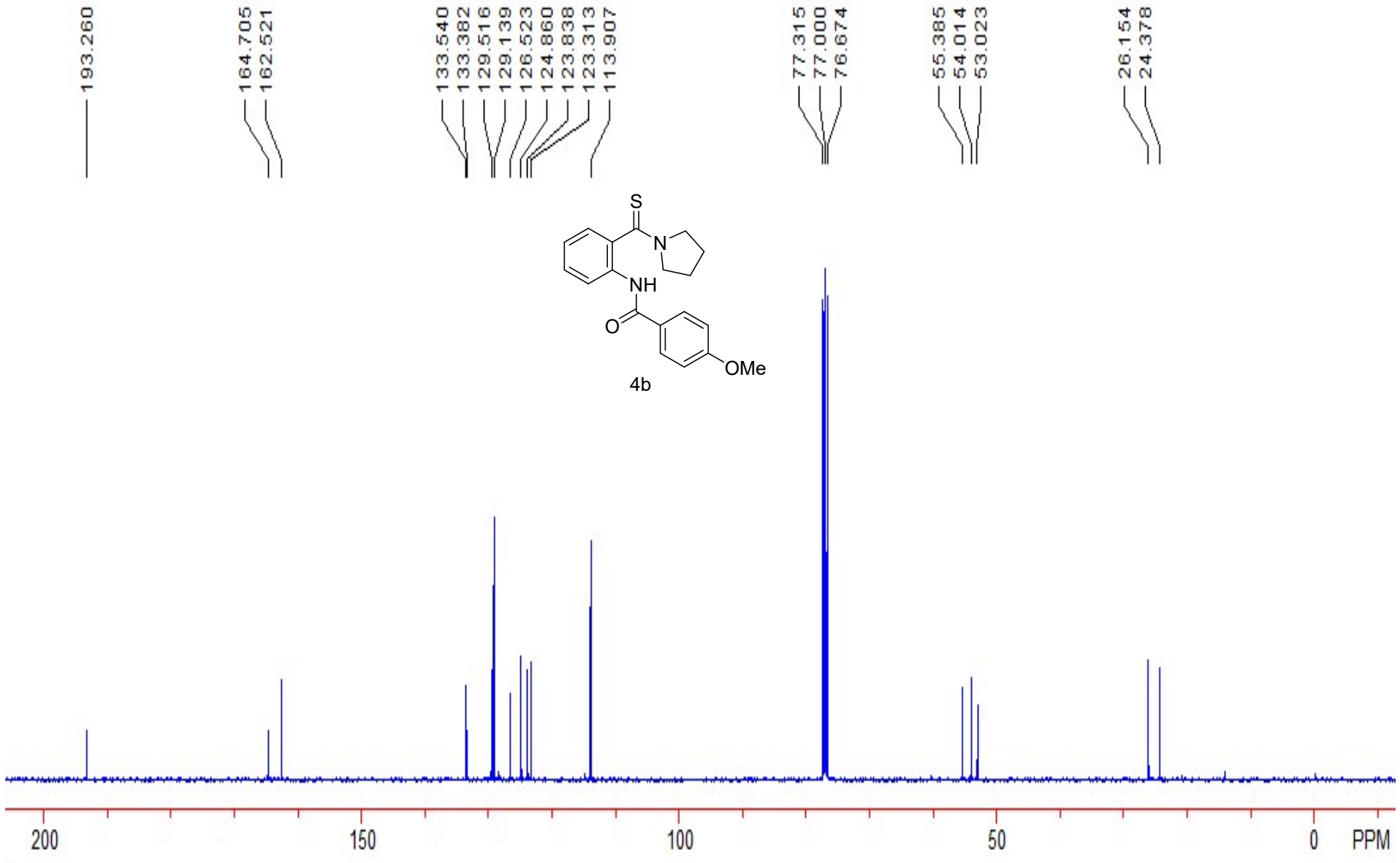
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76.674
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24.378
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OMe
4b
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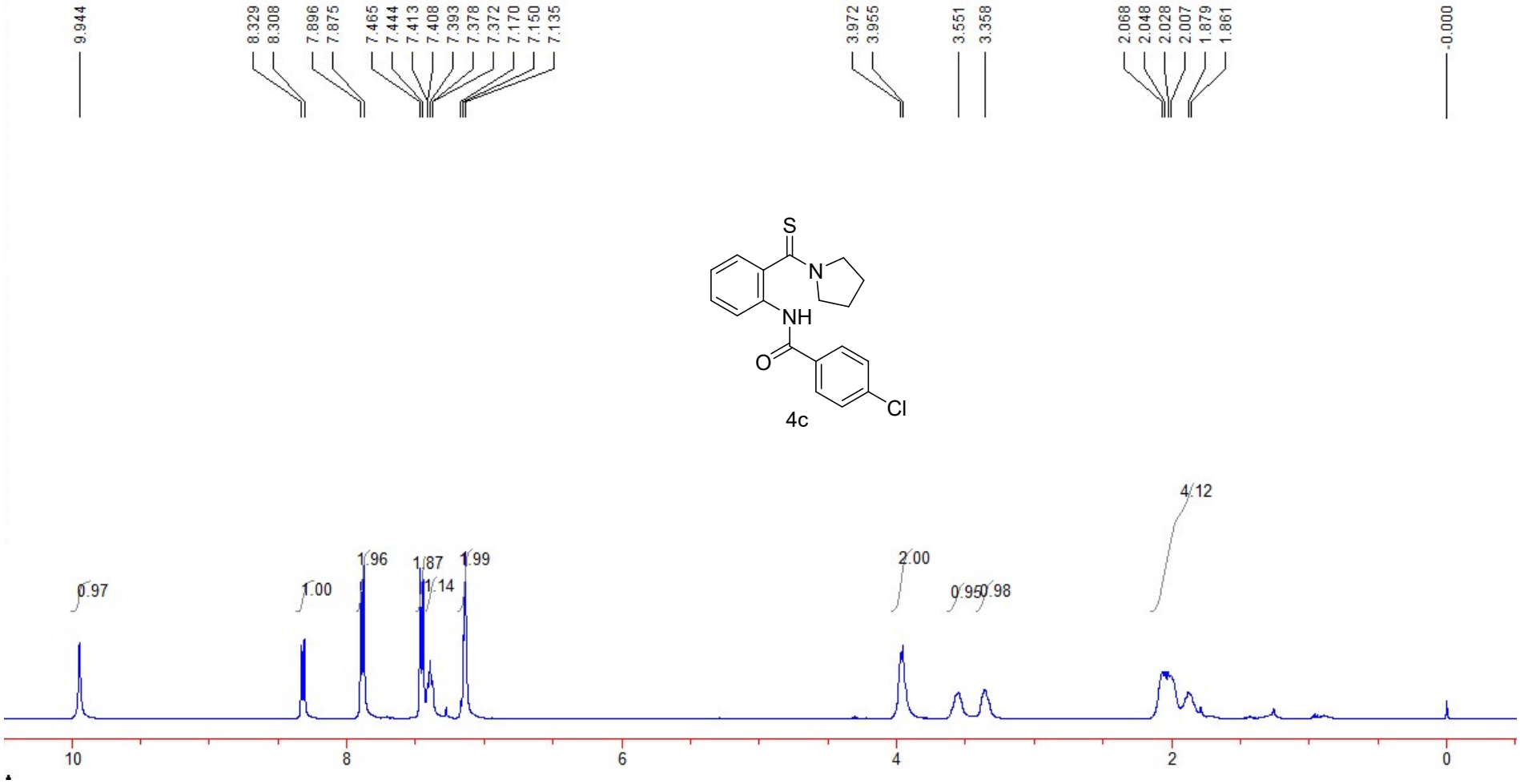
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7.170
7.150
7.135
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2.048
2.028
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1.861
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NH
O
Cl
4c
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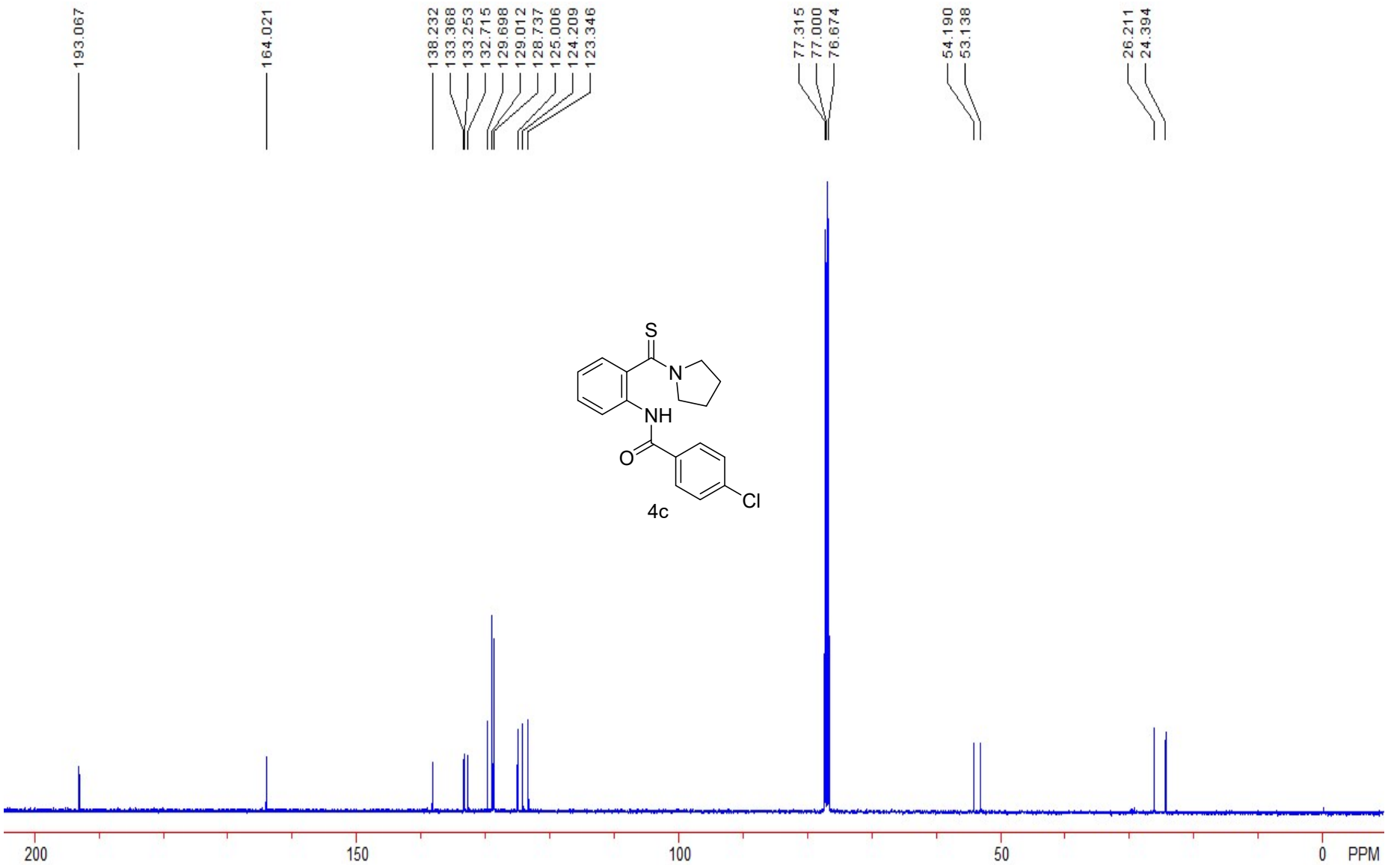
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Cl
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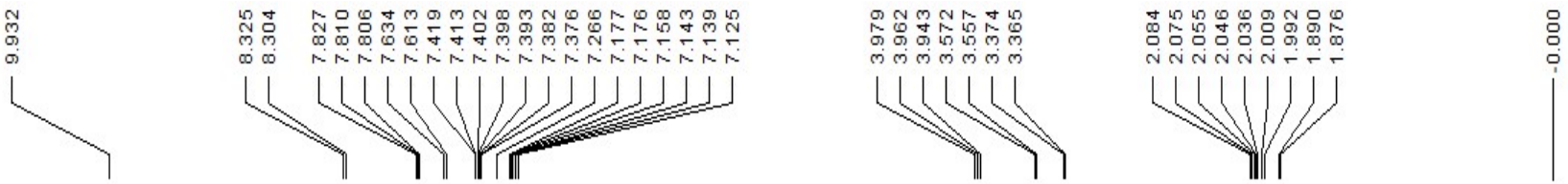
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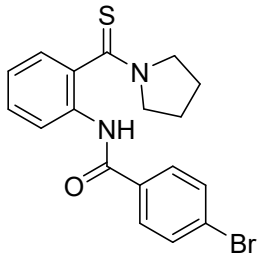
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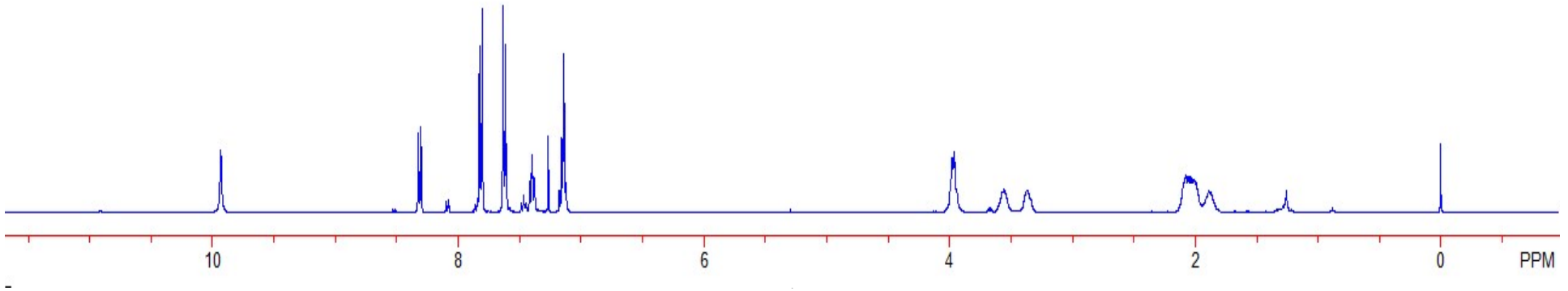
NH
O
Br

4d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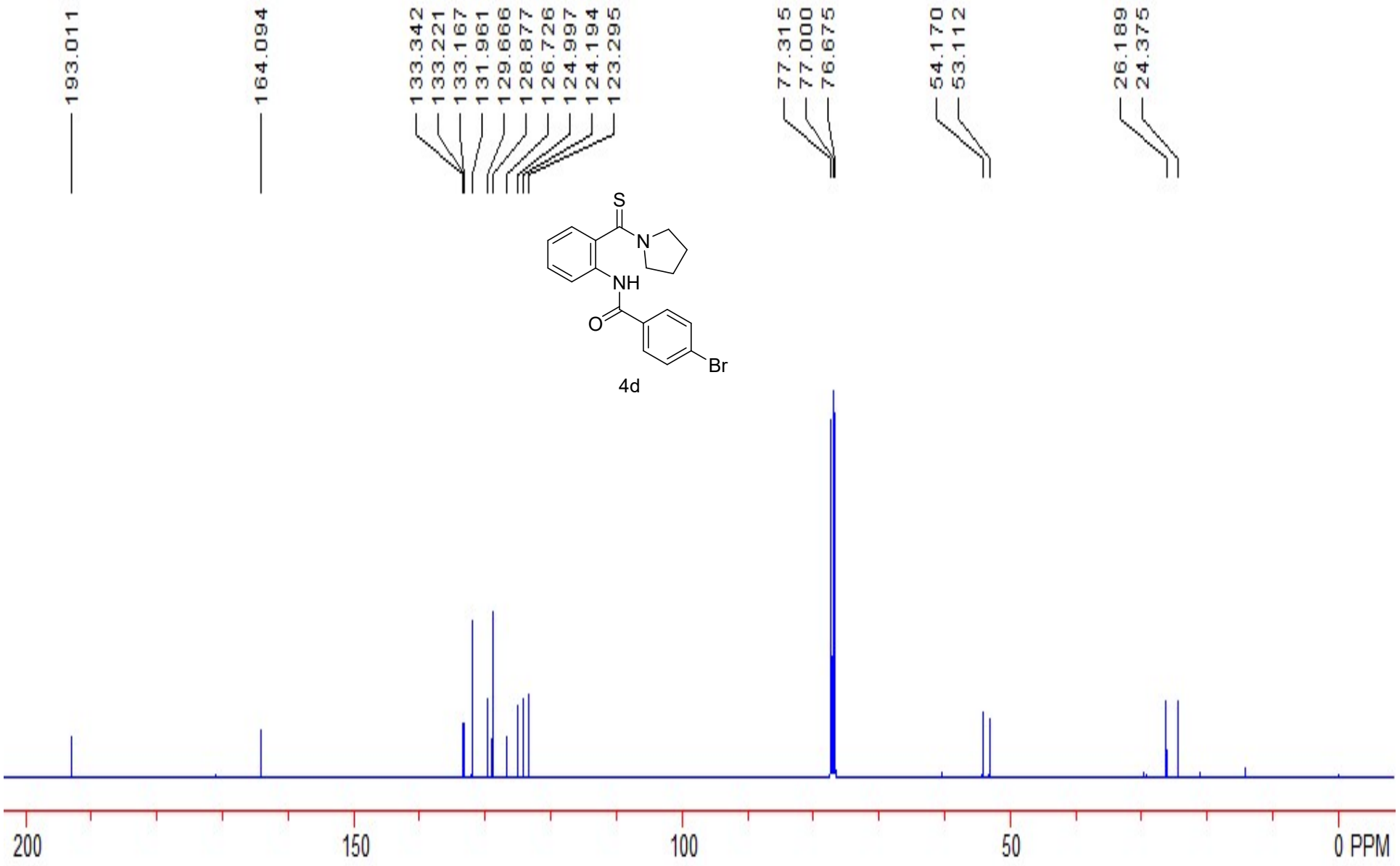
8
6
4
2
0
PPM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77.000
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54.170
53.112
26.189
24.375
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NH
O
Br
4d
200
150
100
50
0 PPM


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8.325
8.132
8.114
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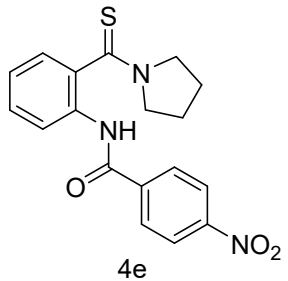
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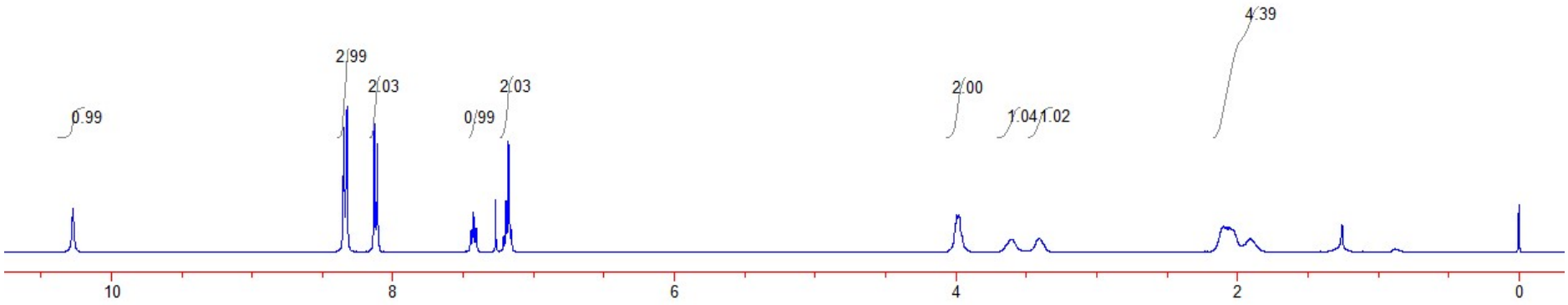
O
NO2

4e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10
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4
2
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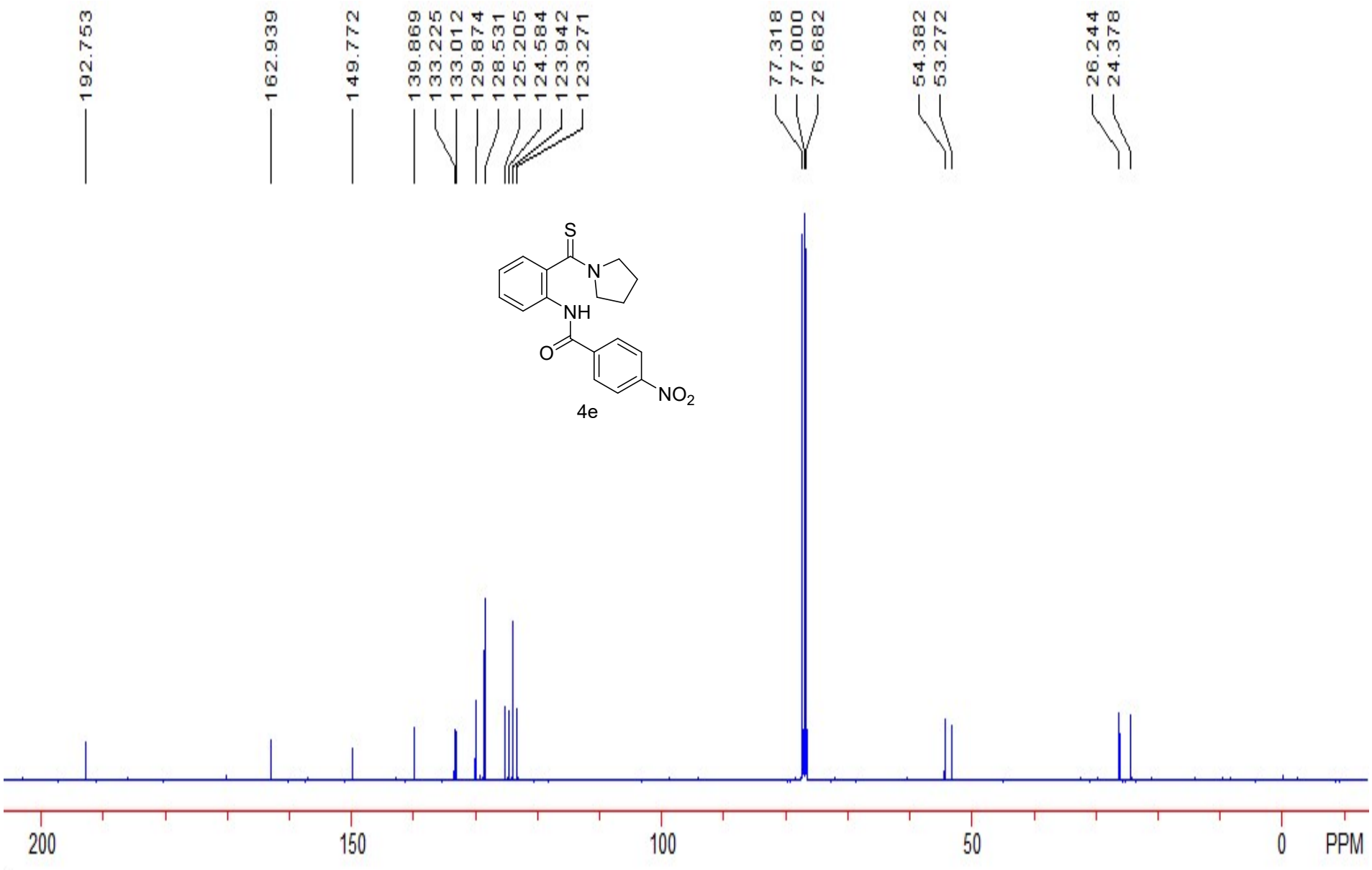
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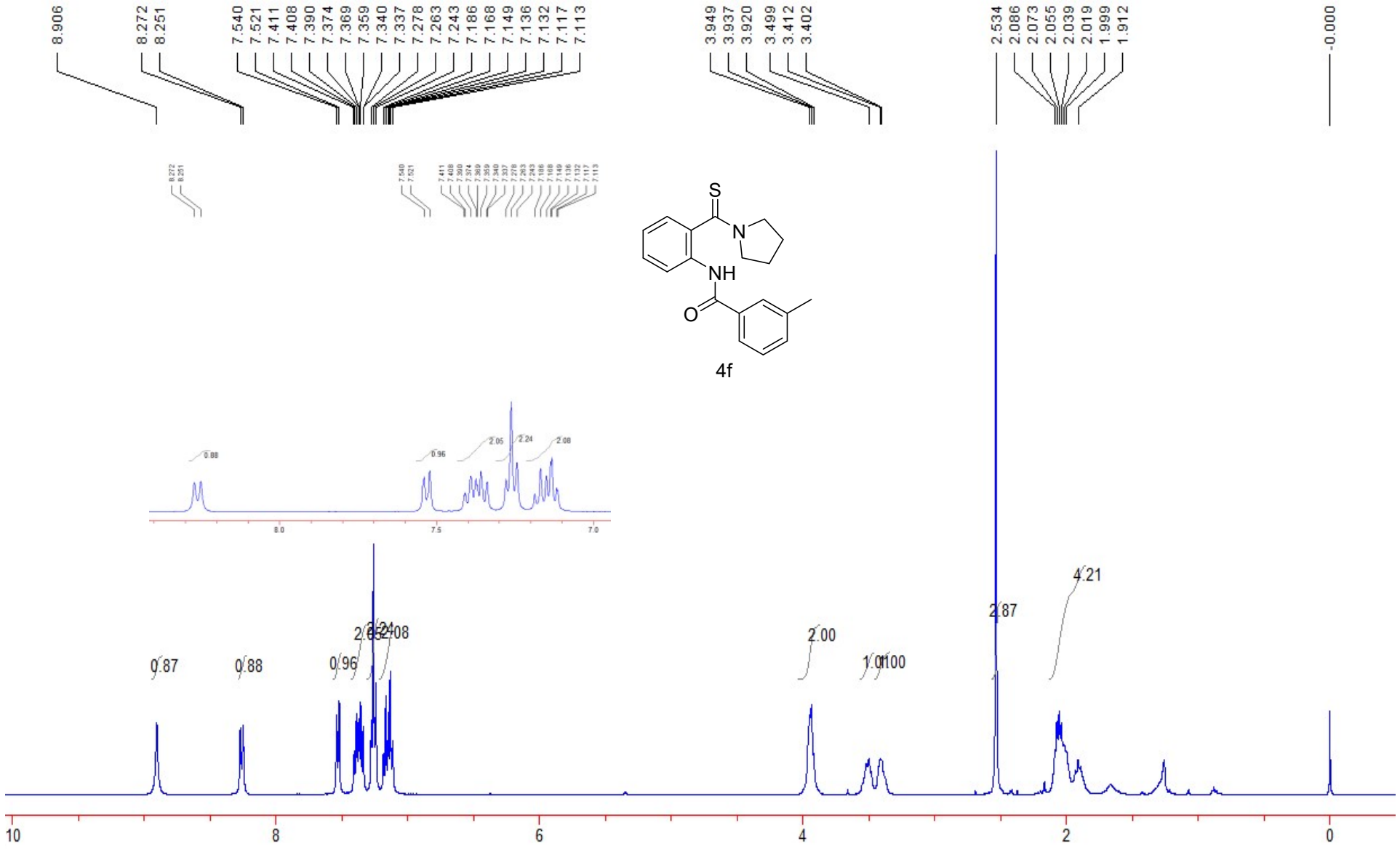
PPM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O
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4
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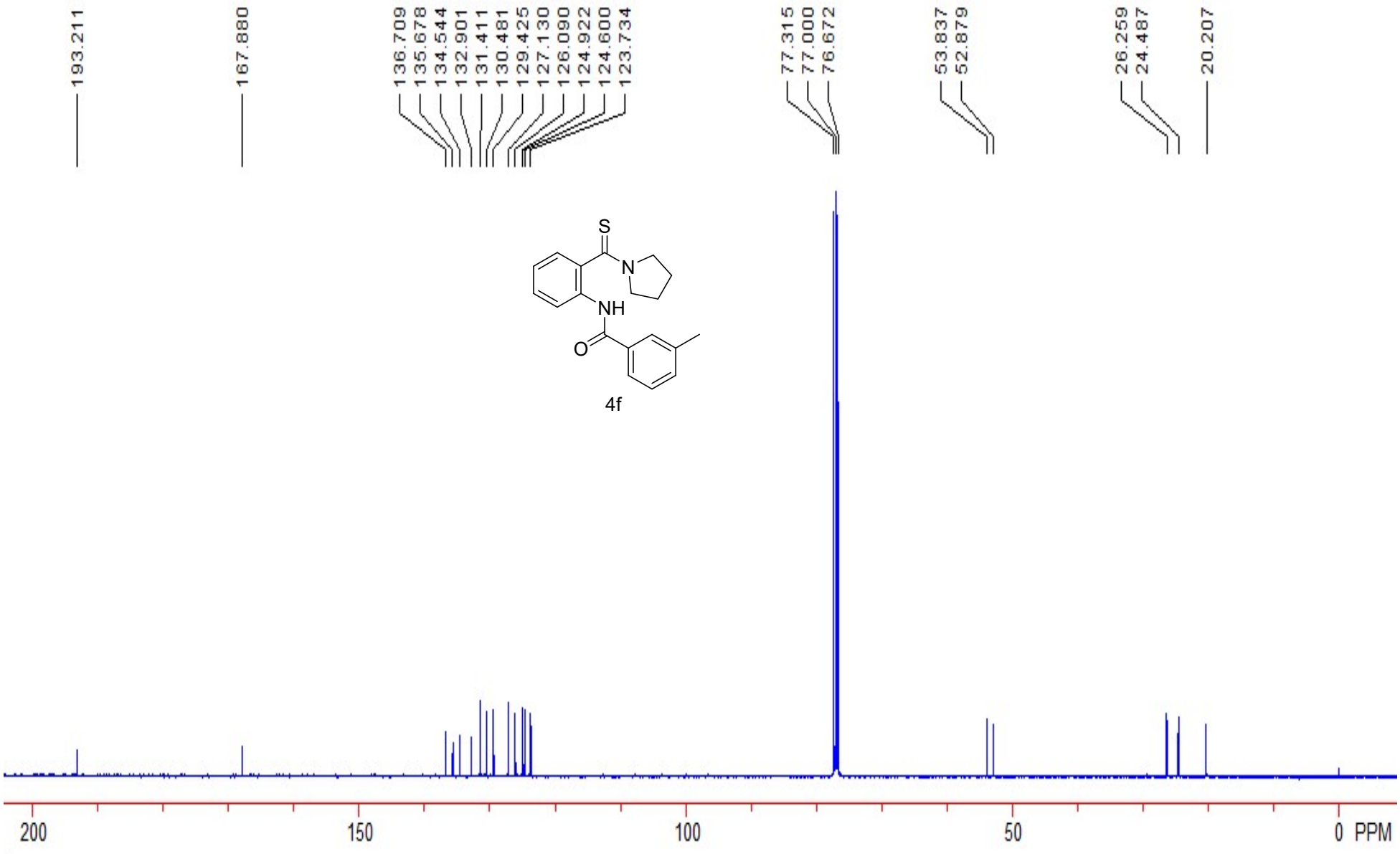
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77.000
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52.879
26.259
24.487
20.207
S
N
NH
O
4f
200
150
100
50
0 PPM


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7.239
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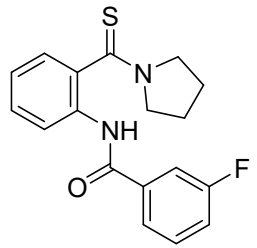
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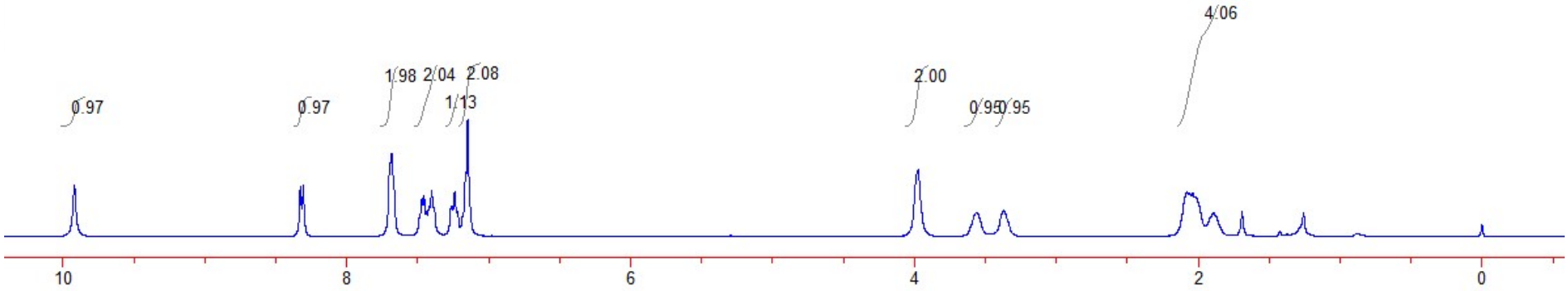
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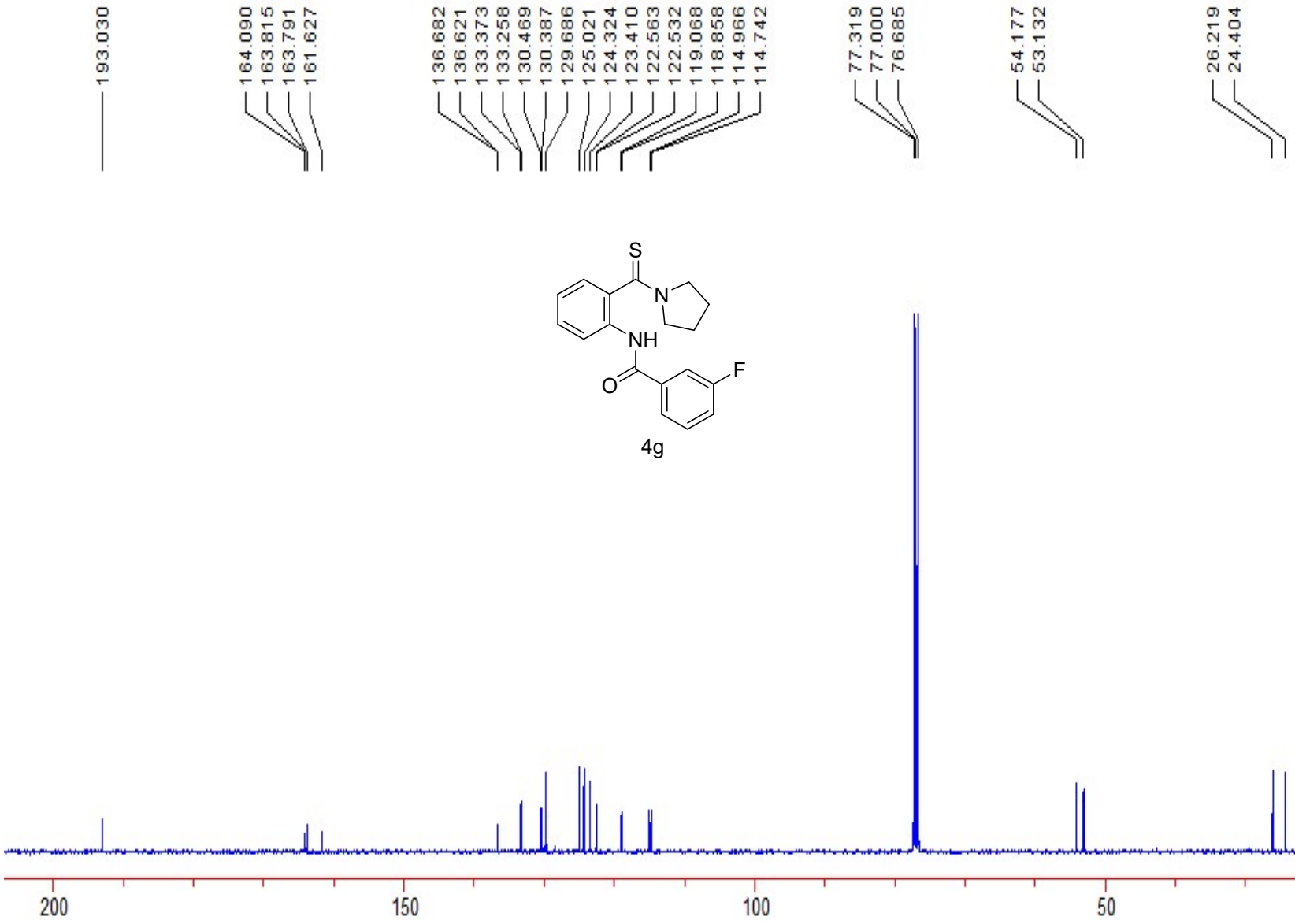
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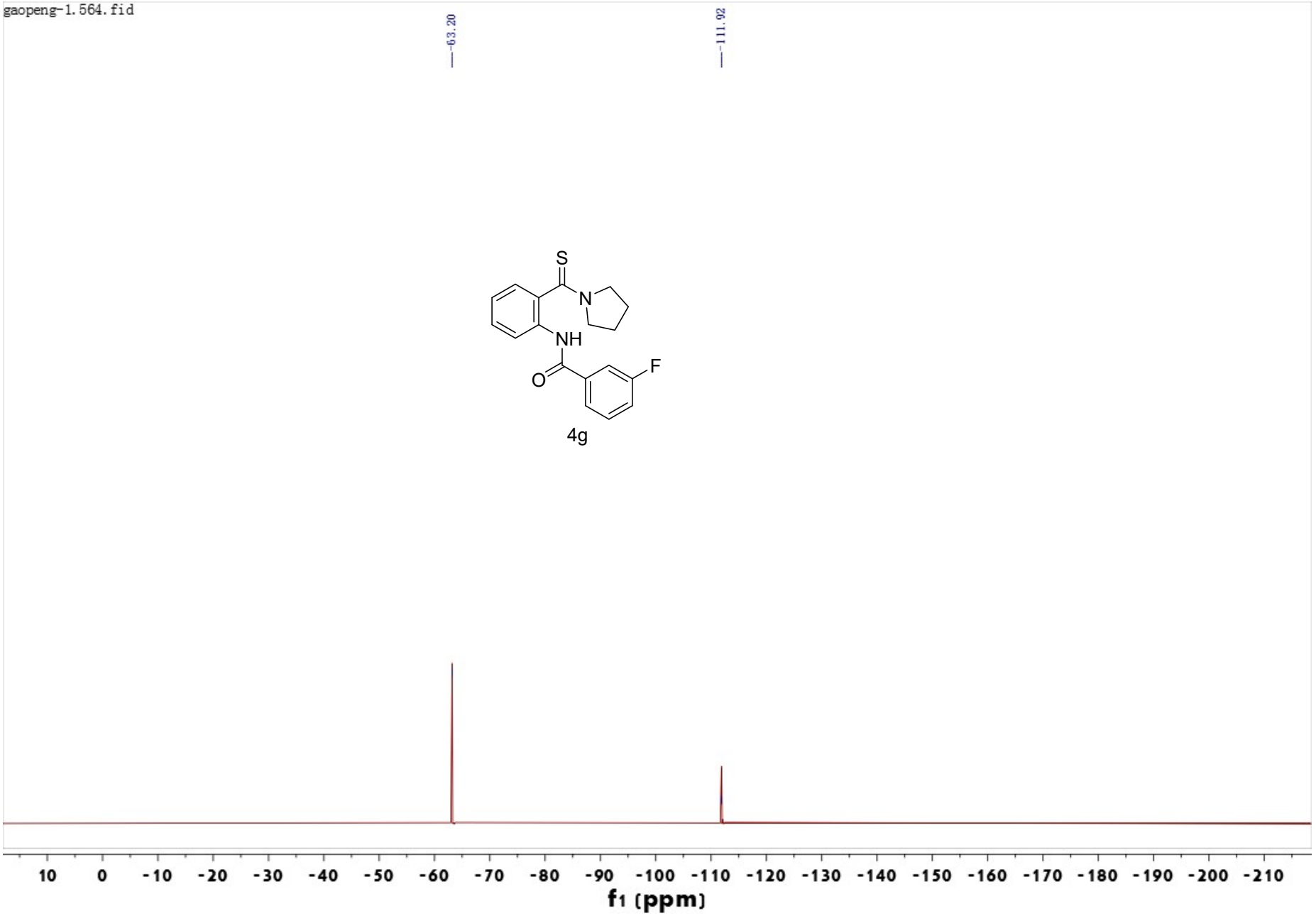
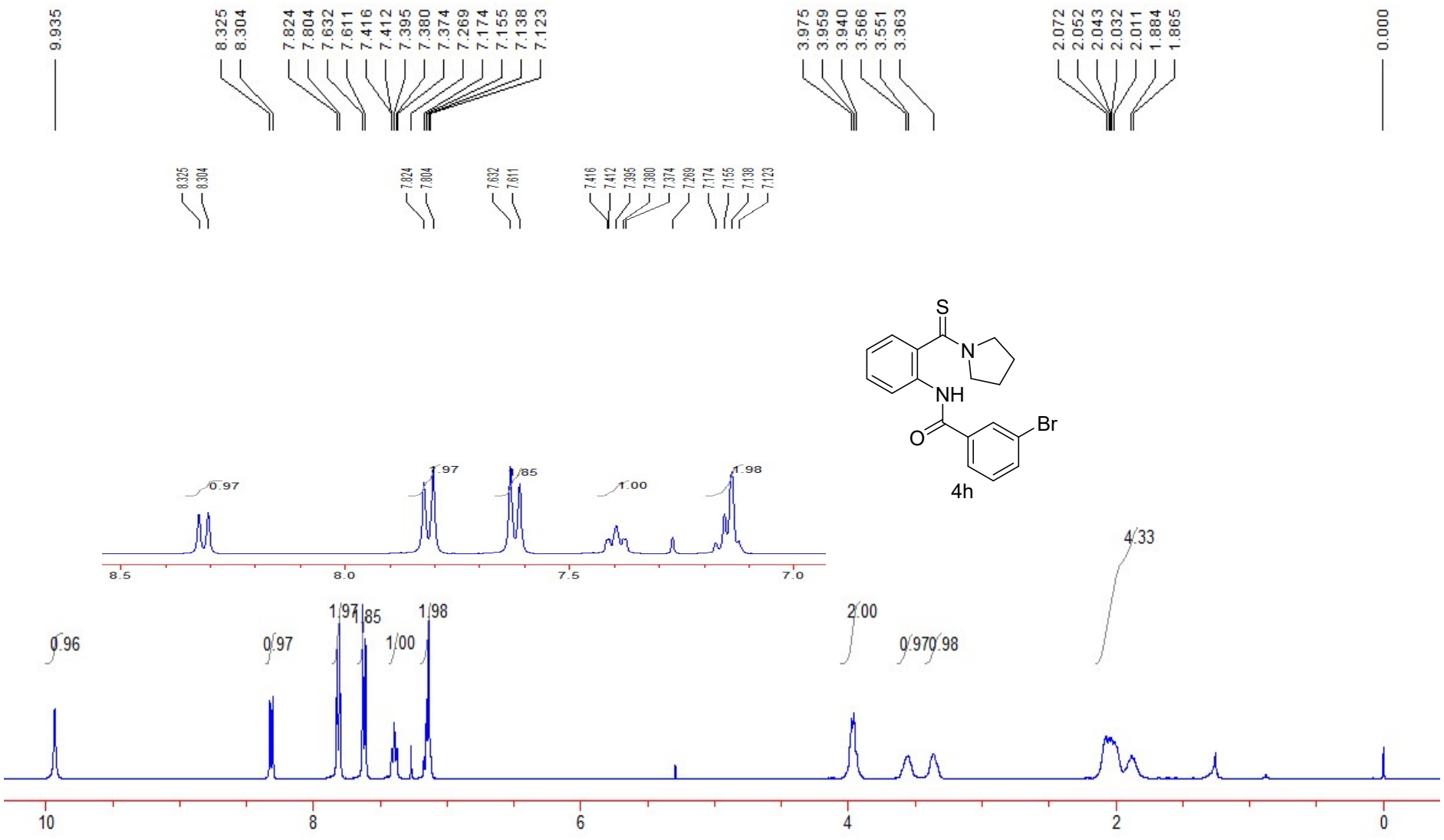
gaopeng-1.564.fid

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7.269
7.174
7.155
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2.052
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2.032
2.011
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1.865
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N
NH
O
Br
4h
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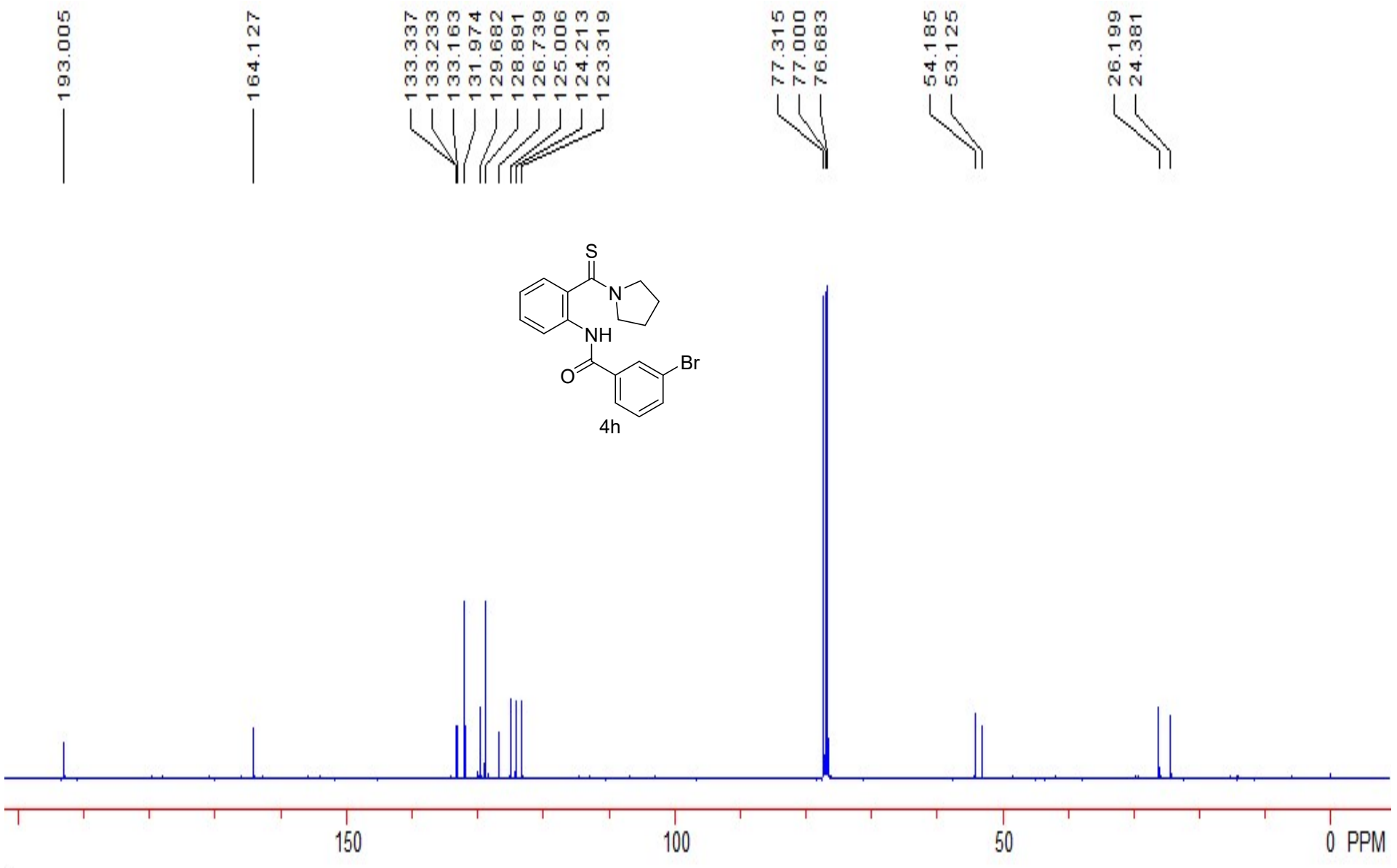
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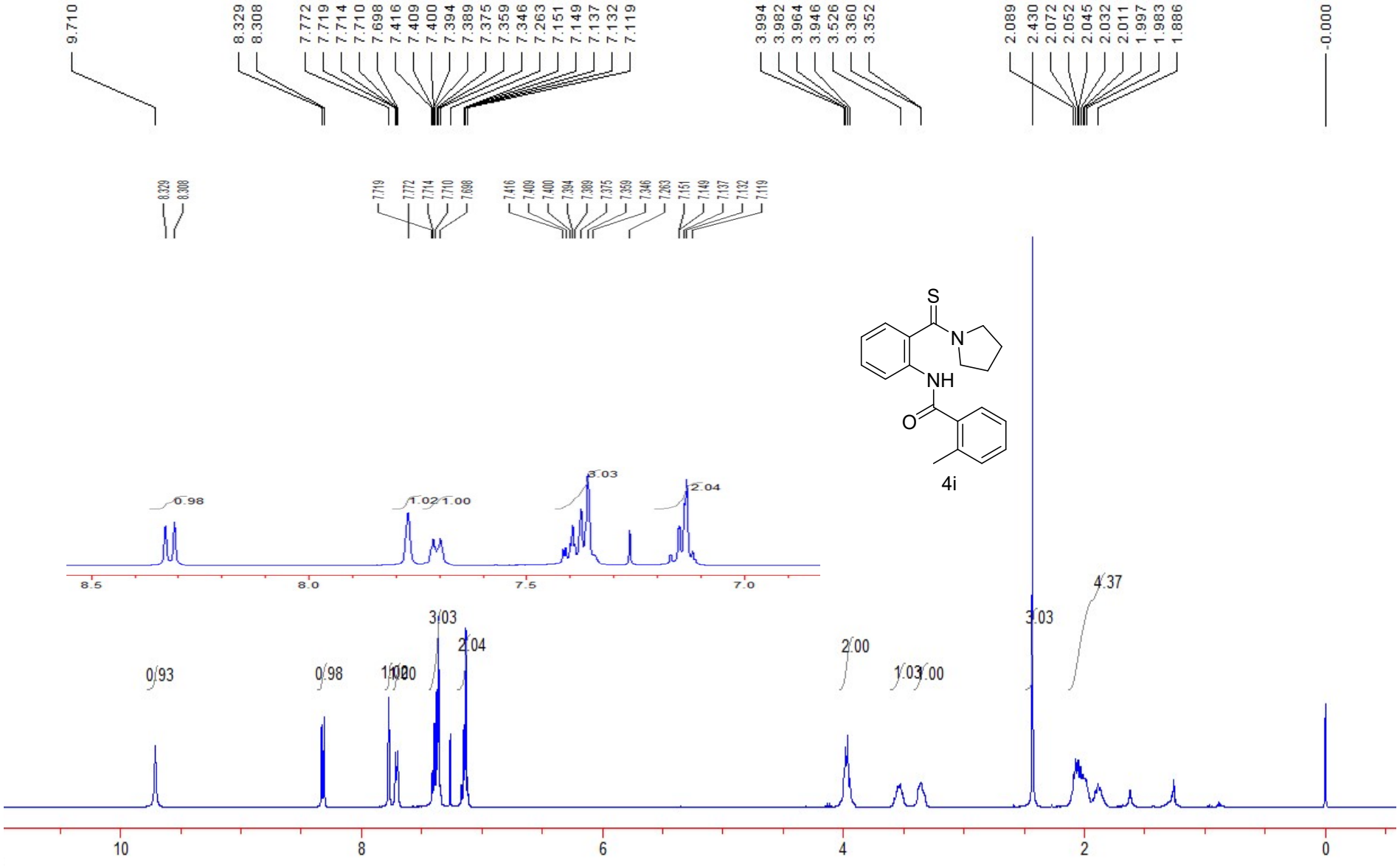
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NH
O
4i
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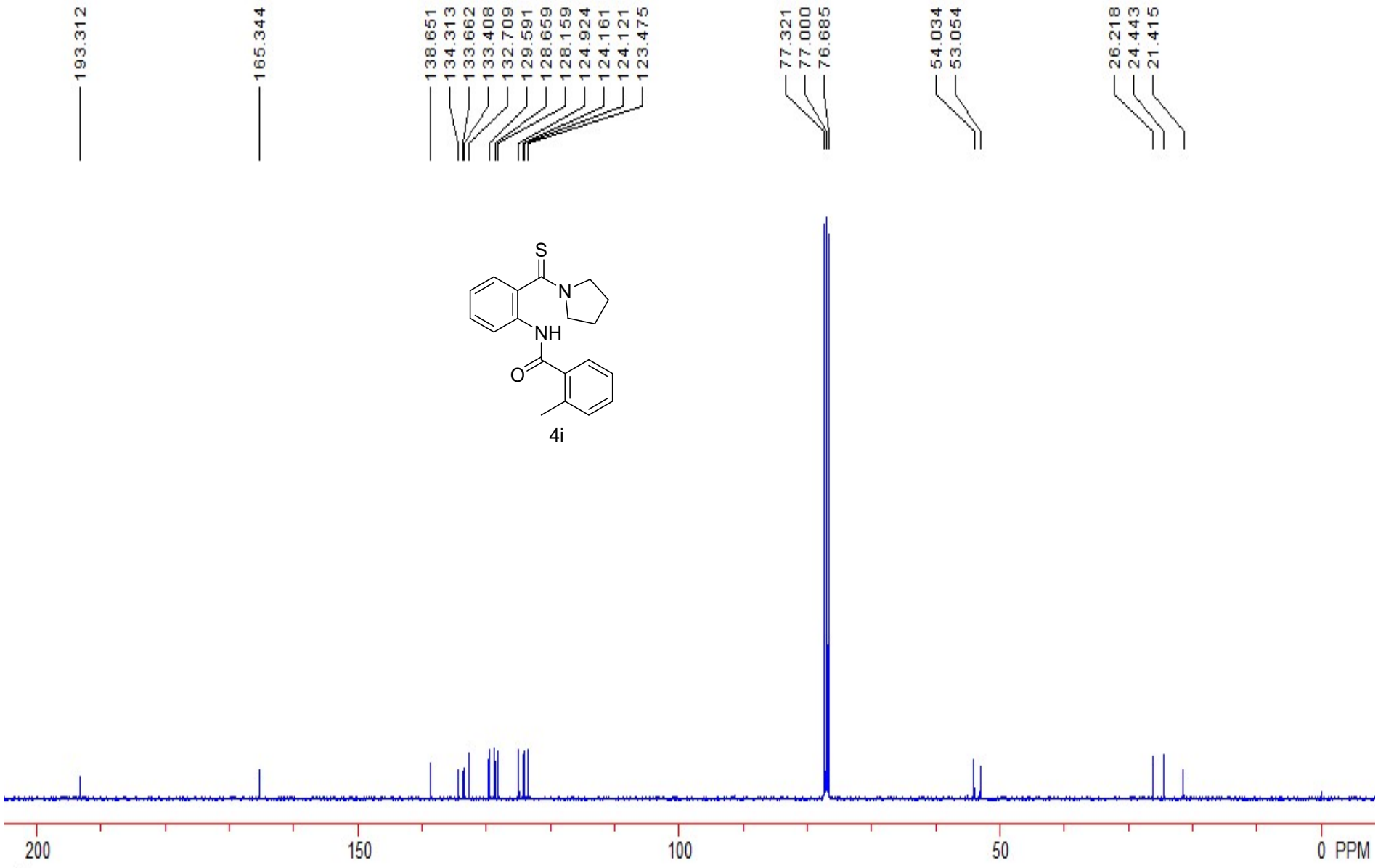
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77.000
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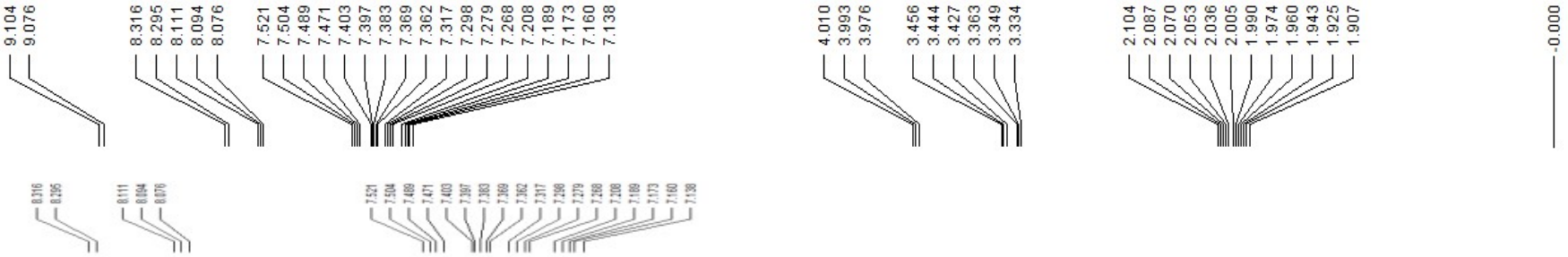
4i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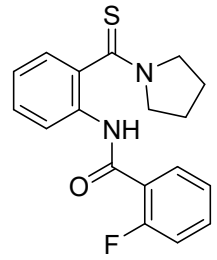
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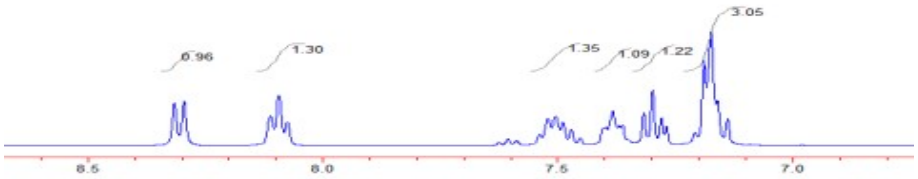
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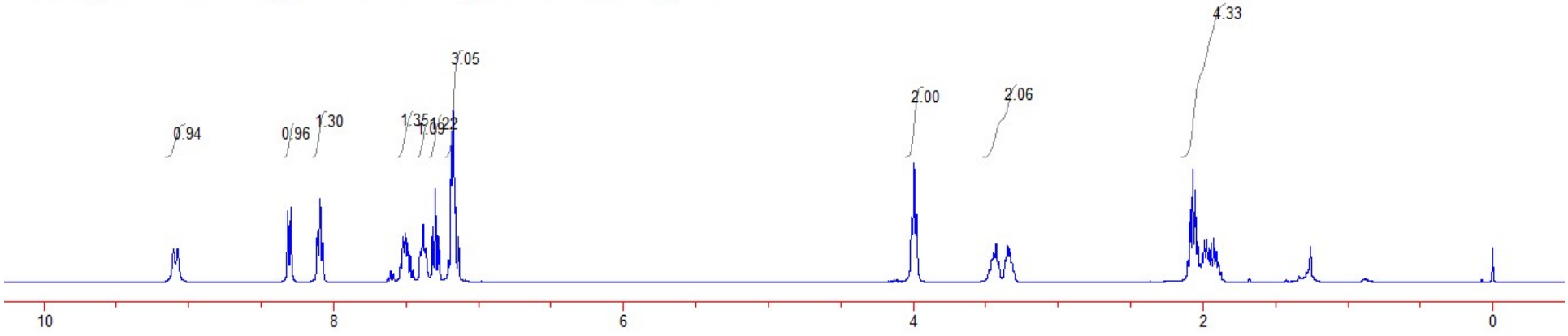
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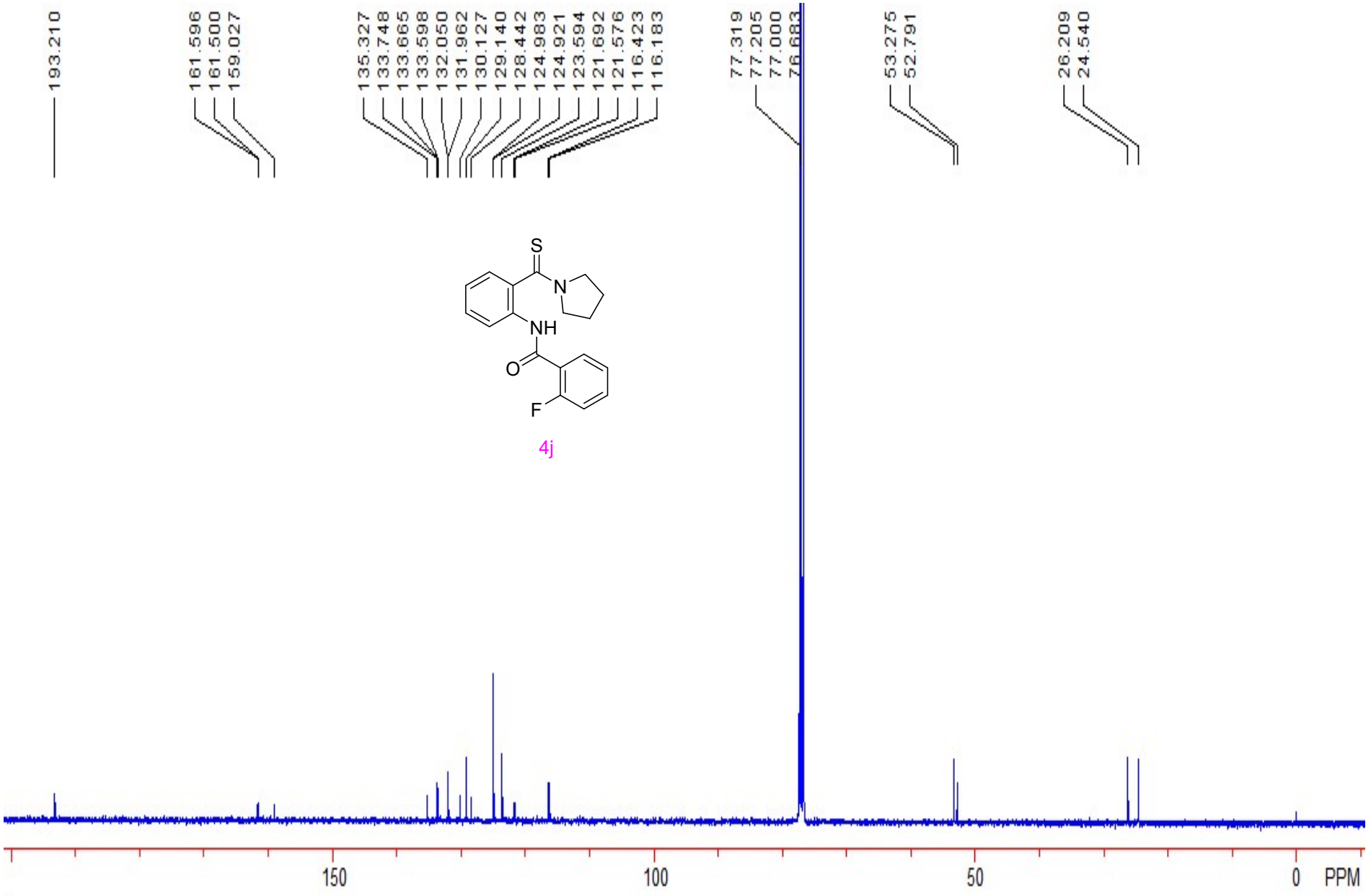
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O
F
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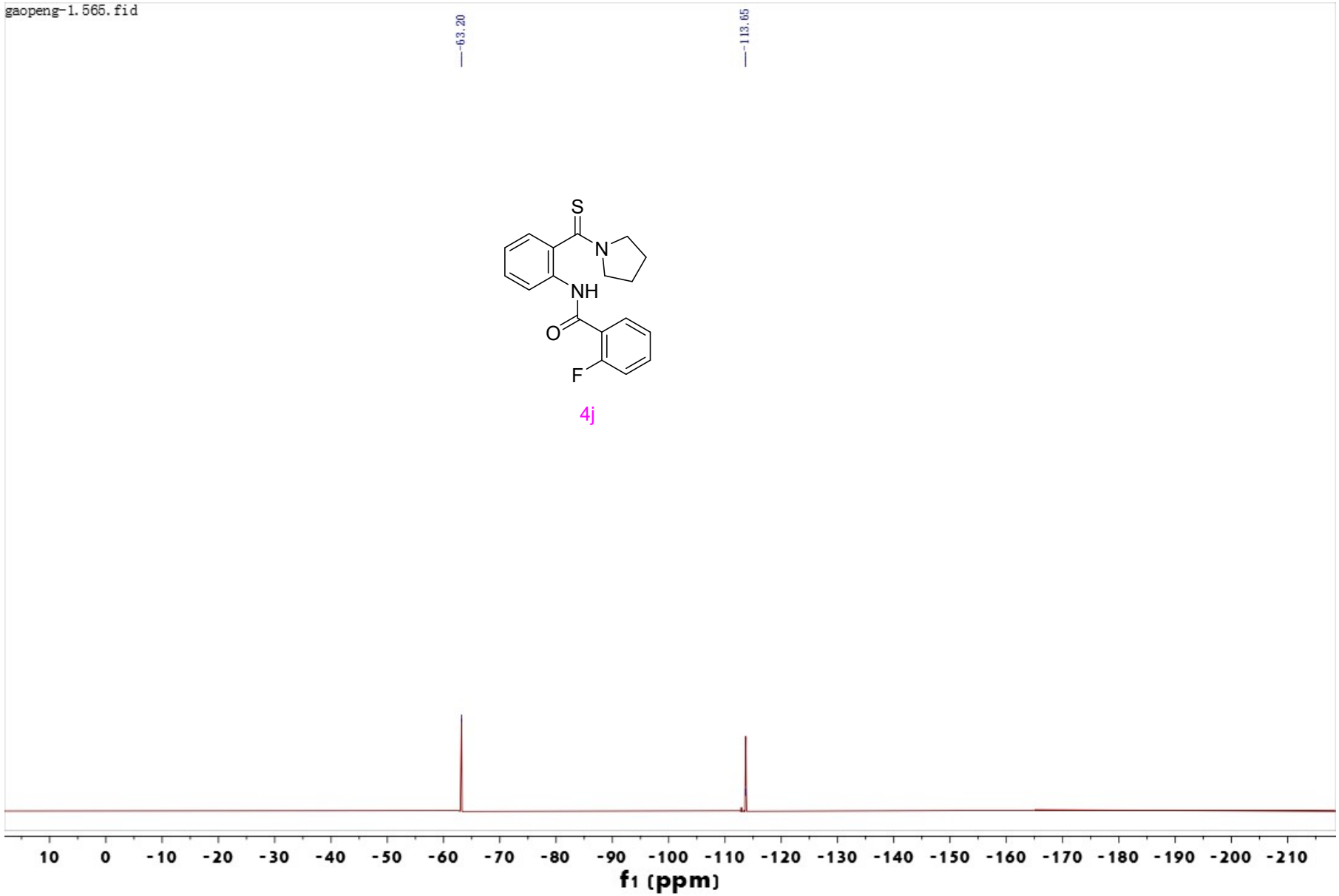
50
0
PPM

4j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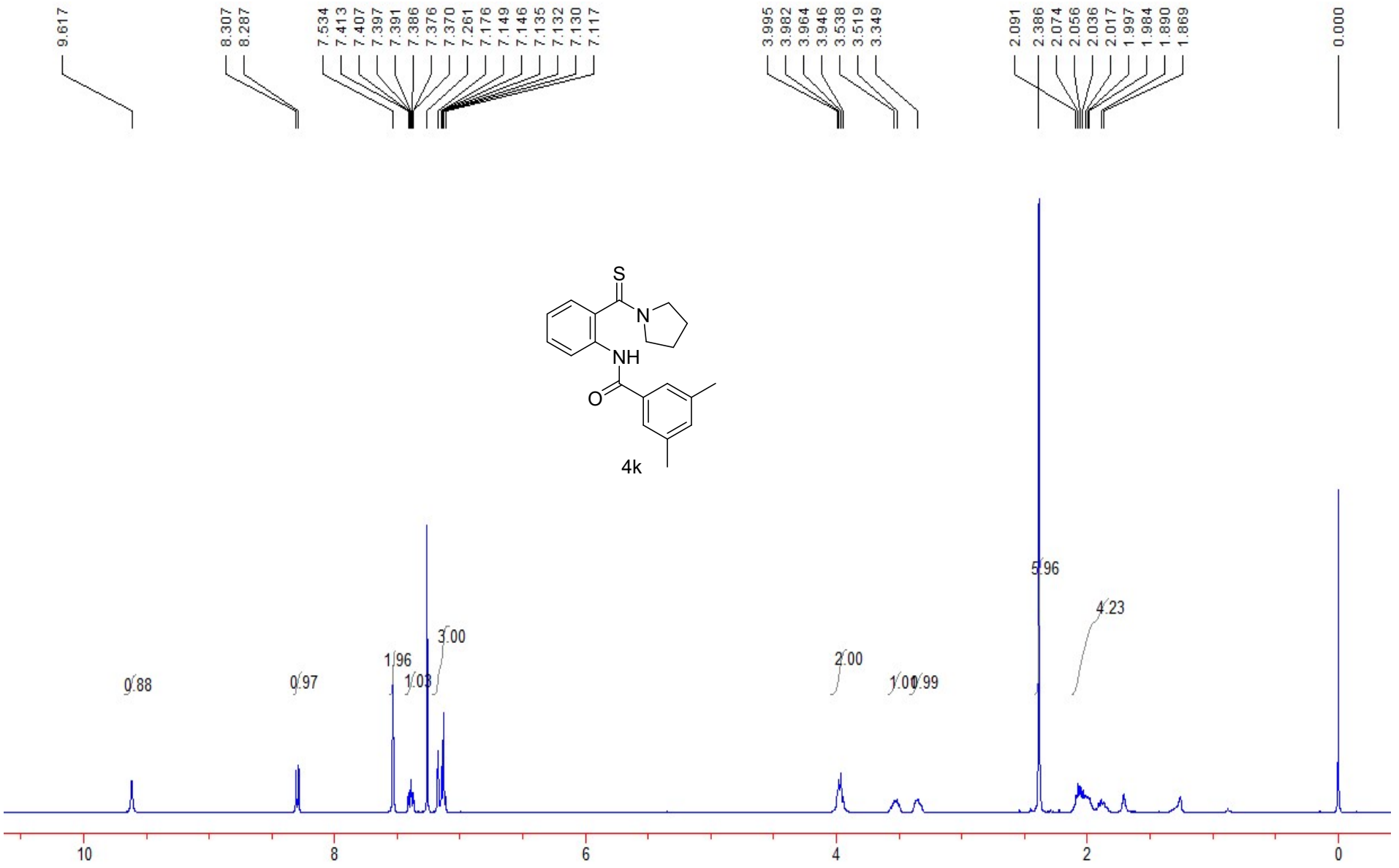
f1 (ppm)

4j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3.519
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NH
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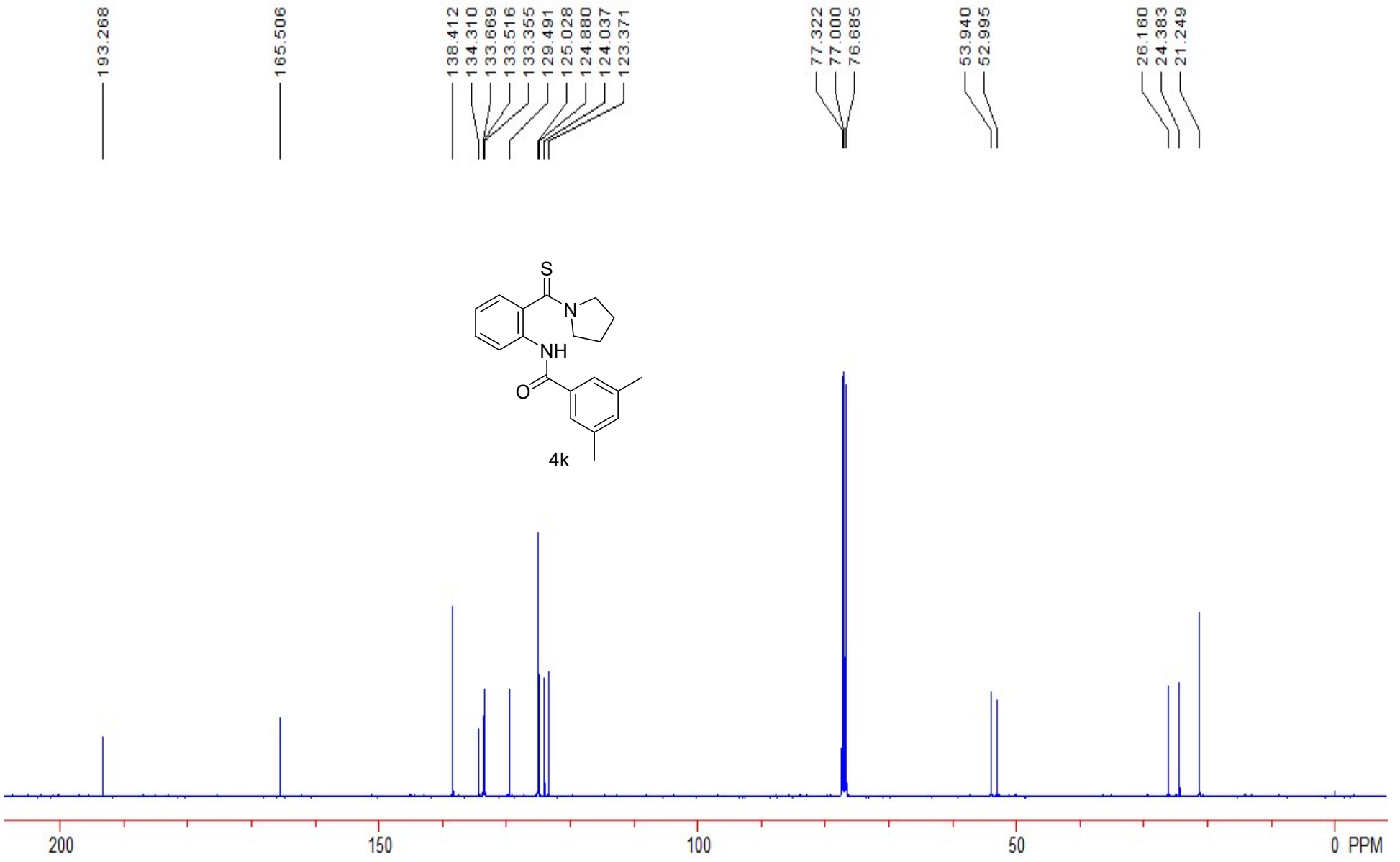
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77.000
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O
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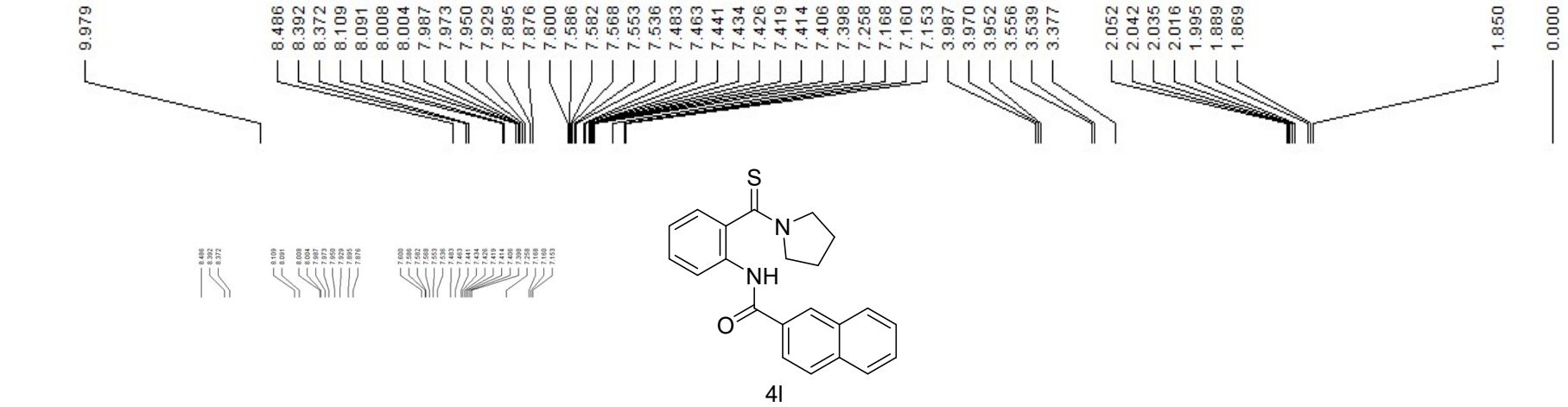
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O

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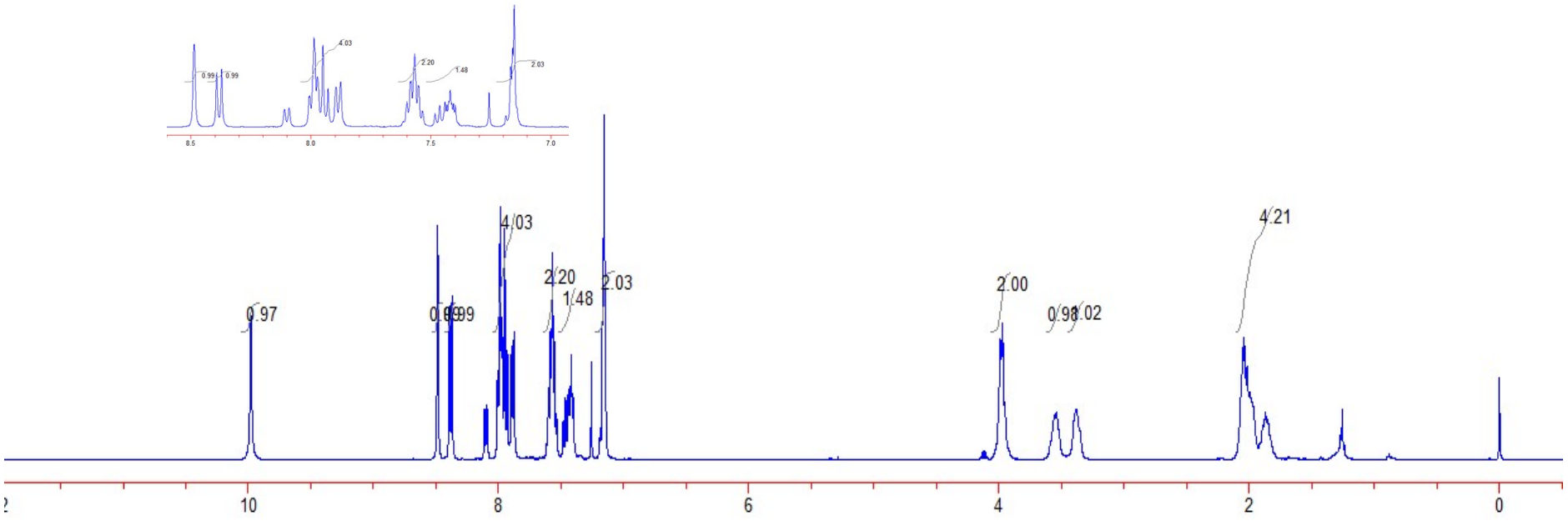
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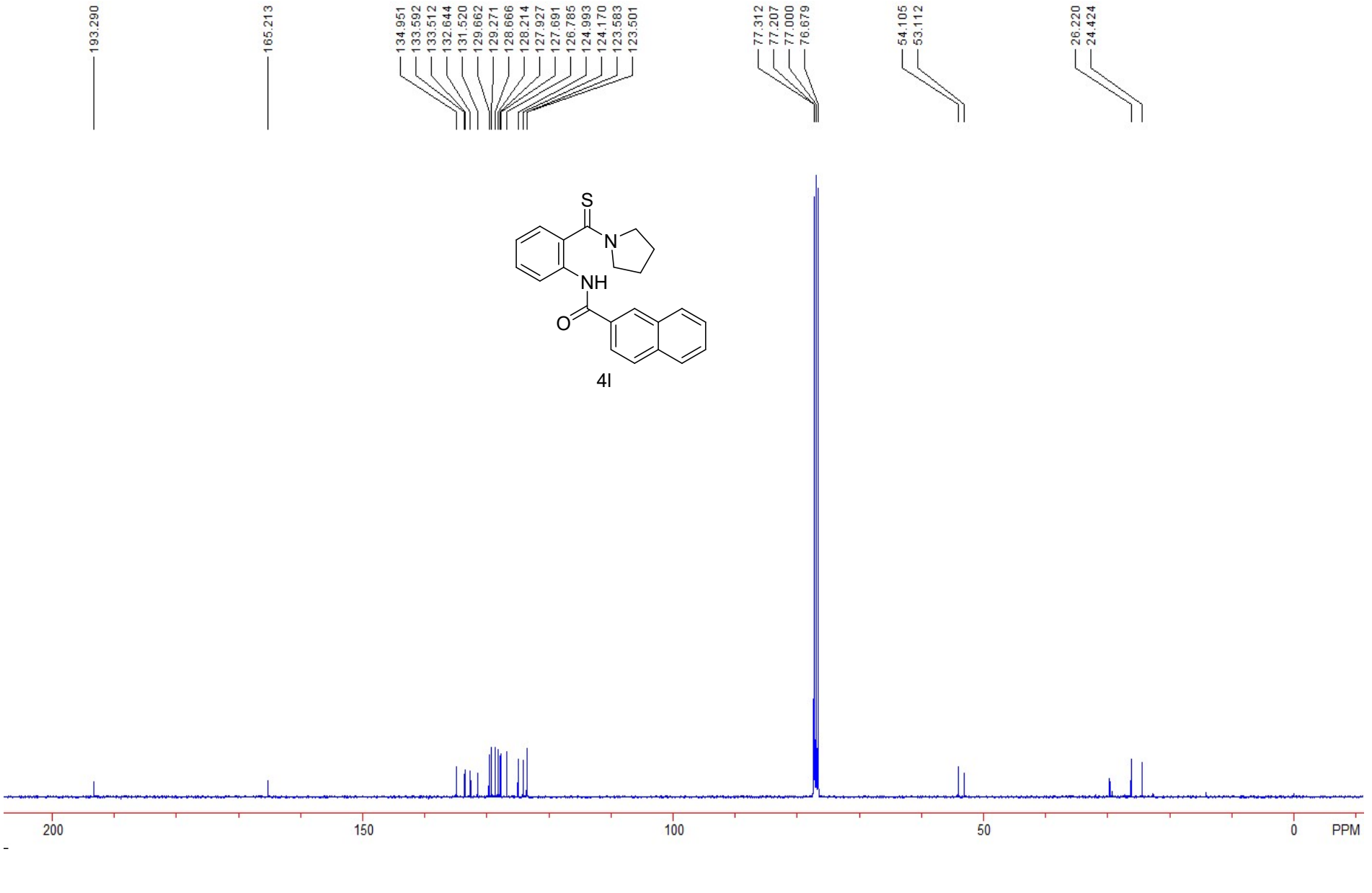
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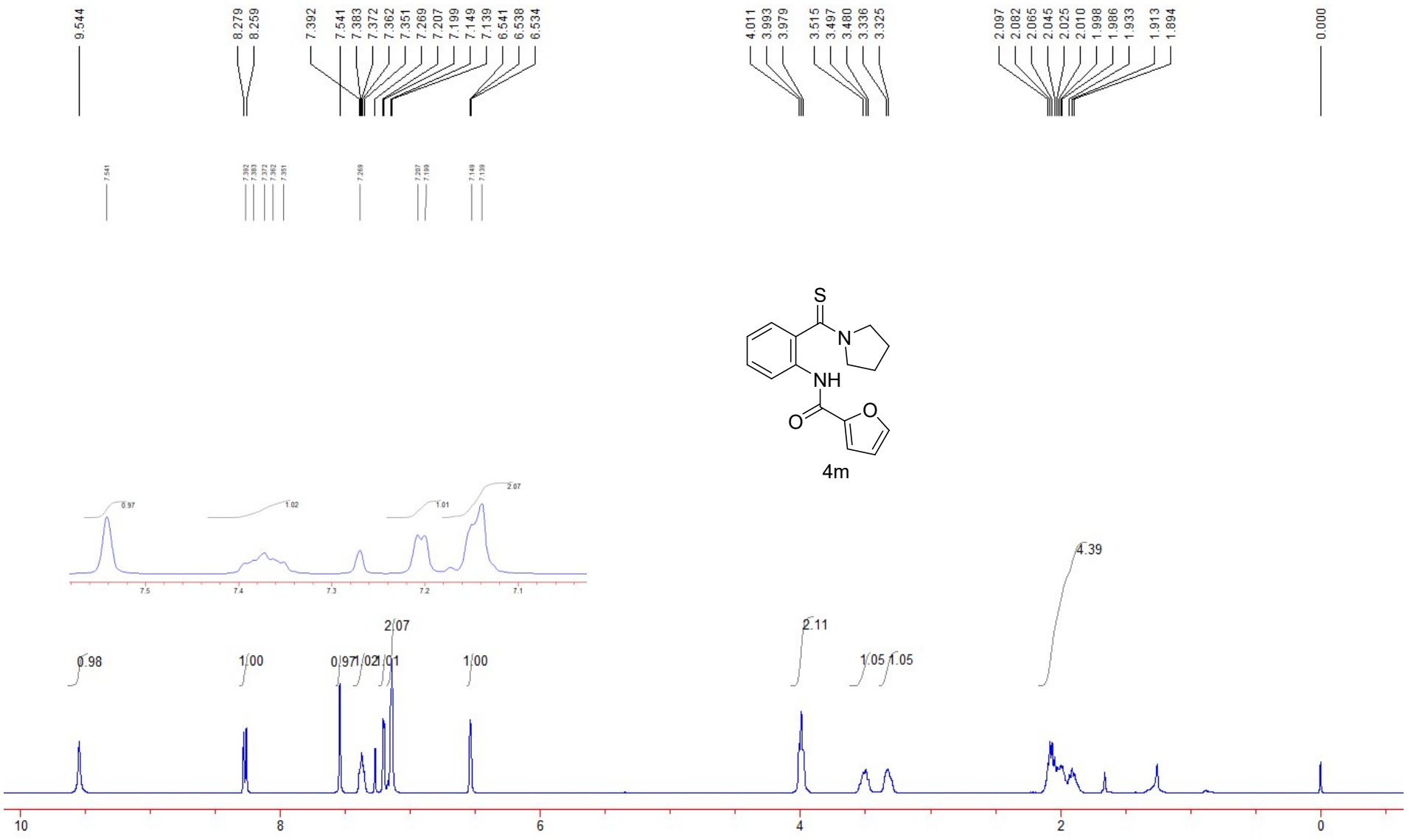
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3.325
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NH
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O
4m
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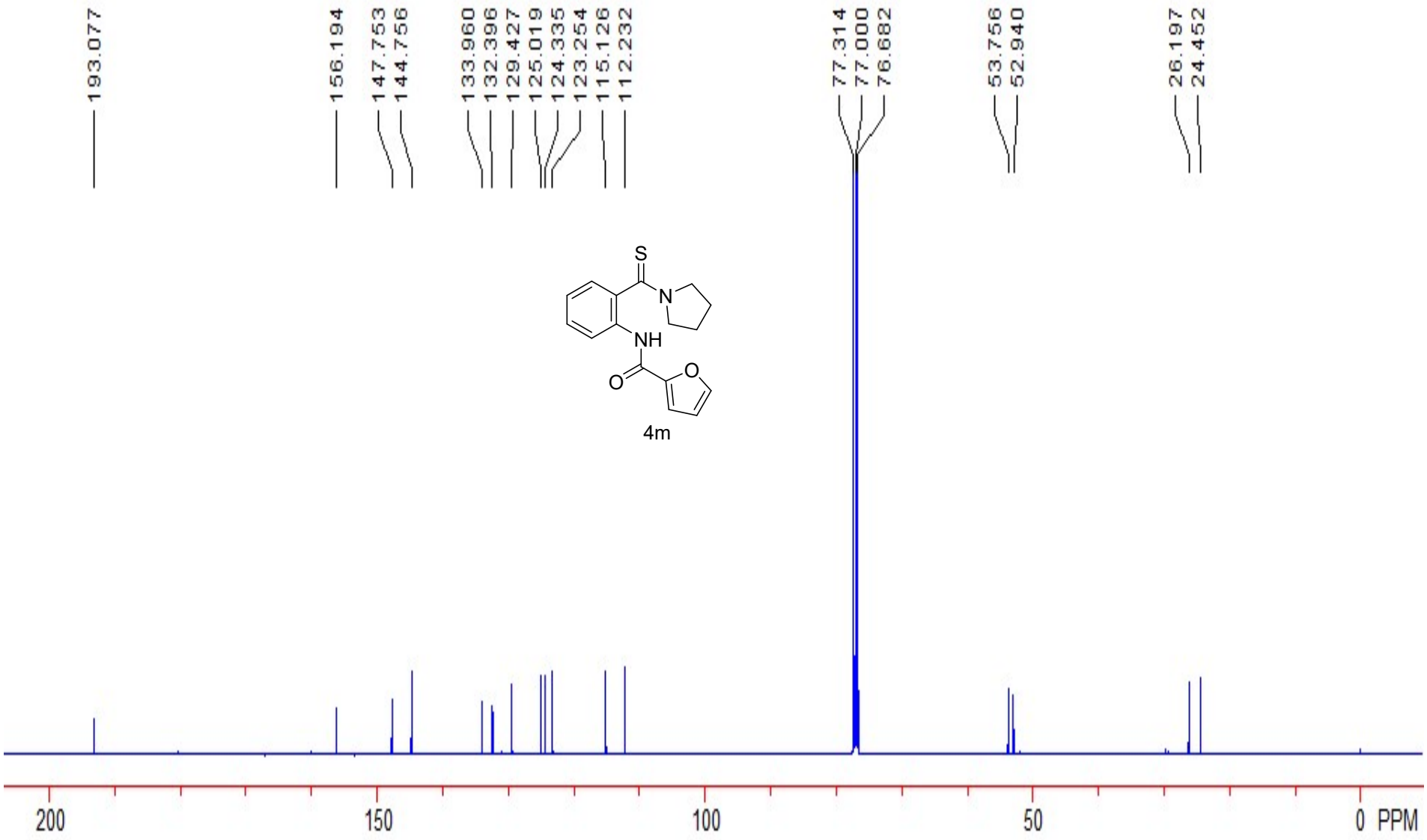
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NH
O
O
4m
200
150
100
50
0 PPM


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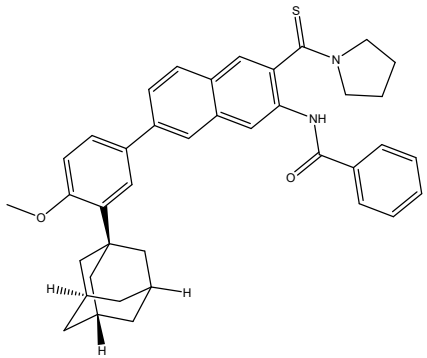
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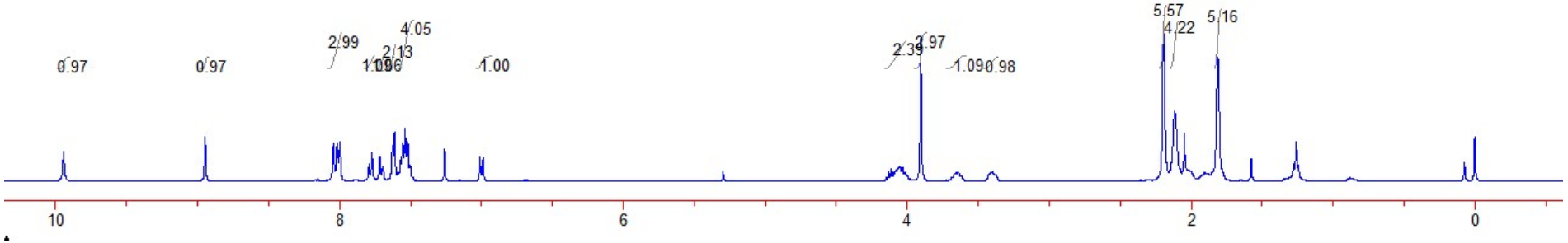
H
H
H

6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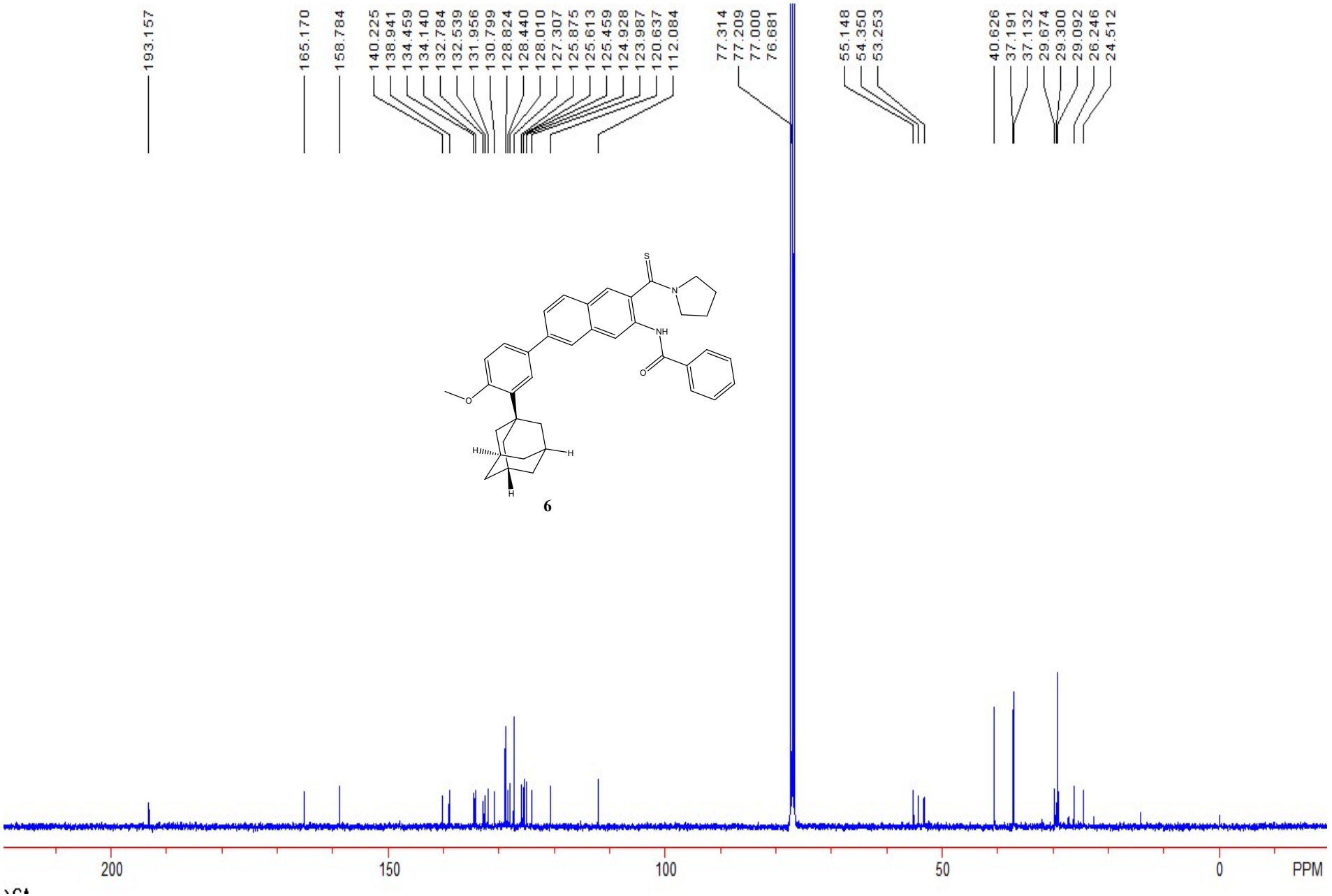
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PPM

6


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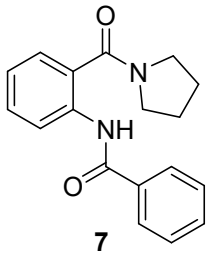
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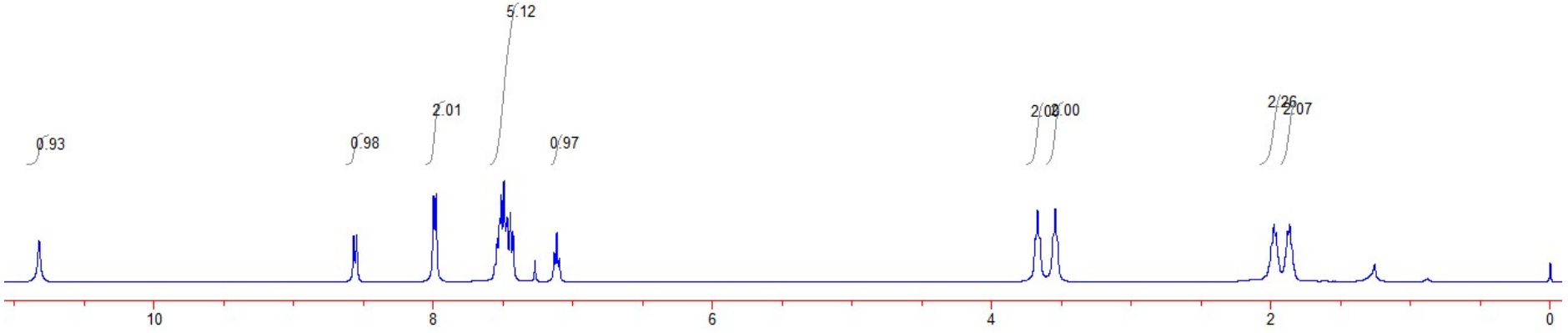
7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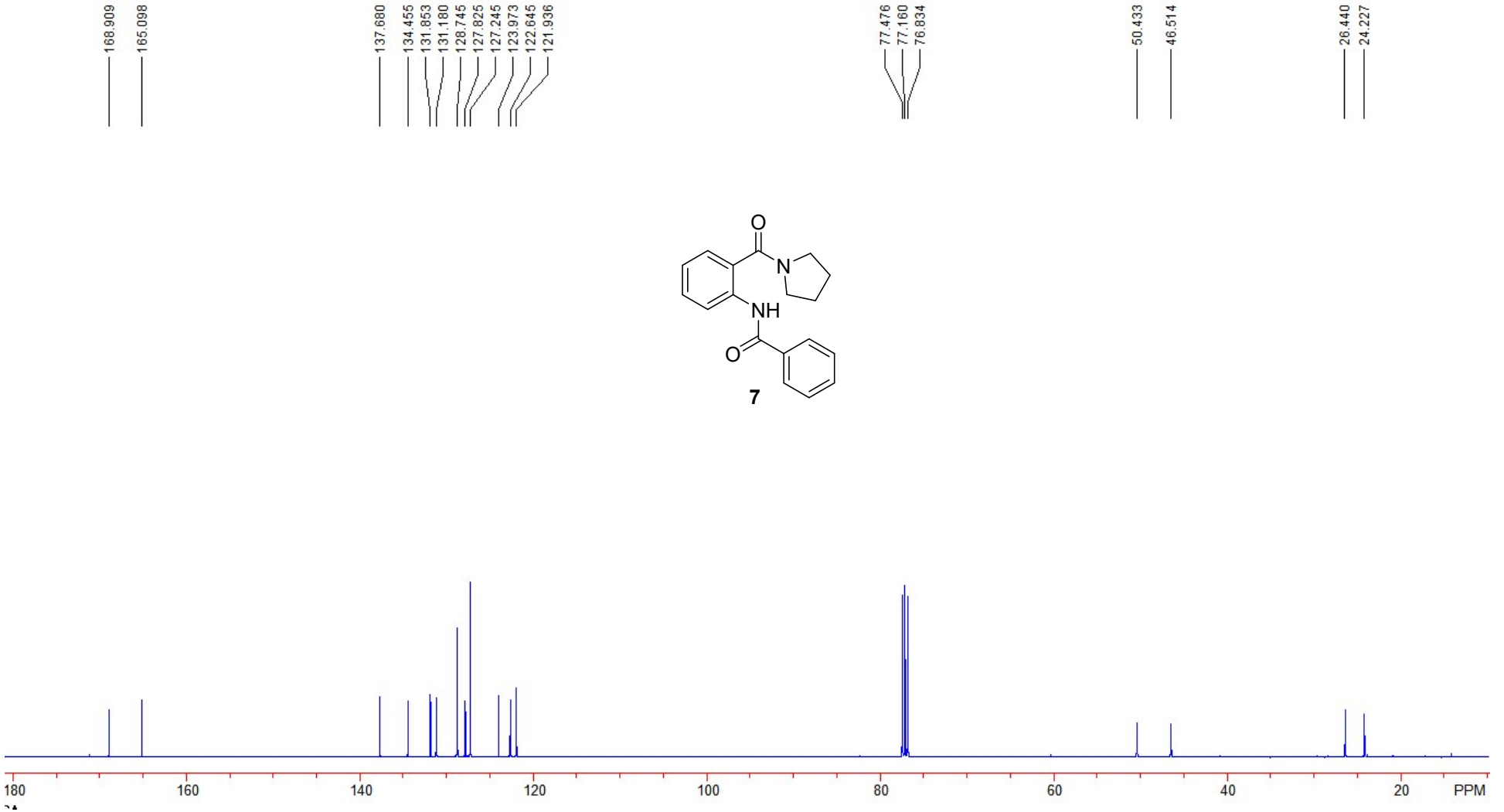
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PPM

7