# Installation of Protected Ammonia Equivalents onto Aromatic & Heteroaromatic Rings Enabled by Micellar Catalysis

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# Supporting Information

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## I. General Information

Unless otherwise noted, all reactions were performed under an atmosphere of argon. All commercially available reagents were used without further purification. A 2 wt % TPGS-750-M/$H_2O$ solution was prepared by dissolving 4 g TPGS-750-M in 196 g water (HPLC grade), followed by degassing with argon. TPGS-750-M was made as previously described.[1] TPGS-750-M is also available commercially.[2] Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 $F_{254}$ plates (Merck, 0.25 mm thick). The developed chromatogram was analyzed by UV lamp (254 nm). For non-UV active compounds were visualized by aqueous potassium permanganate ($KMnO_4$), vanillin, or ninhydrin stain developed by heat with a heat gun. Flash chromatography was performed in glass columns using Silica Flash® P60 (SiliCycle, 40-63 µm). GC-MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). As capillary column a HP-5MS cross-linked 5% phenylmethylpolysiloxanediphenyl column (30 m x 0.250 mm, 0.25 micron, Agilent Technologies) was employed. Helium was used as carrier gas at a constant flow of 1 mL/min. Retention times ($t_R$) refer to the following temperature program: 50 °C for 5 min; heating rate 20°C/min; 300 °C for 20 min; injection temperature 250 °C; detection temperature 280 °C. $^1H$ and $^{13}C$ NMR were recorded at 22 °C on a Varian UNITY INOVA 400 MHz, 500 MHz, or 600 MHz. Chemical shifts in $^1H$ NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.26 or 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sep = septet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of $^{13}C$ NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.23 ppm) on the δ scale. Chiral HPLC data was collected using a Shimadzu SPD-m20a Prominence diode array detector. Chiral GC analysis was performed using a Restek RT-*beta*DEXcst column (30 m x 0.250 mm, 0.25 micron). Retention times ($t_R$) are from compound dependent temperature programs; split-inlet at 200 °C at 11.60 psi ($H_2$, constant pressure) with 20:1 split, FID 290 °C. High resolution mass analyses were obtained using an APE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI, or a GCT Premier TOF MS (Waters Corp) for FI.

1) Lipshutz, B. H.; Ghorai, S.; Abela, A. R.; Moser, R.; Nishikata, T.; Duplais, C.; and Krasovskiy, A. *J. Org. Chem.* **2011**, *76*, 4379.
2) TPGS-750-M: Aldrich catalog numbers 733857 and 763918.

# II. Experimental procedures

## General Procedure A

**1 ($A_1$).** Inside a dry box, a flame-dried 5 mL round bottom flask or 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with [(π-allyl)PdCl]$_2$ (0.5 mol %), cBRIDP (2 mol %), the base (1.5 equiv), the carbamate (1.2 equiv) and the aryl bromide (0.3 mmol). Outside the dry box, under a positive flow of Ar were added *via* syringe the 2 wt % TPGS-750M/$H_2O$ solution (0.3 mL, 1 *M*) and TIPS-OH (90 μL, 1.5 equiv) if KOH was used as base. After being stirred vigorously at 50 °C for 24 h or 48 h, the mixture was diluted with EtOAc and filtered through a pad of silica gel. Purification by silica gel column chromatography (eluent: EtOAc/hexanes) afforded the desired product.
**2 ($A_2$).** The same procedure was applied using 2 mol % of [(π-allyl)PdCl]$_2$ and 4 mol % of cBRIDP.
**3 ($A_3$).** The same procedure was applied using 0.6 mL (0.5 *M*) of the 2 wt % TPGS-750-M/$H_2O$ solution.

## General Procedure B

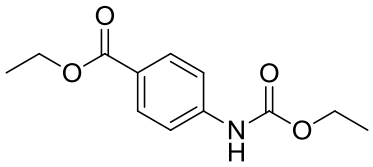
**1 ($B_1$).** Inside a dry box, a flame-dried 5 mL round bottom flask flask or 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with [(π-allyl)PdCl]$_2$ (0.5 mol %), cBRIDP (2 mol %), the base (1.5 equiv), the carbamate (1.2 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750M/$H_2O$ solution (0.3 mL, 1 *M*), the aryl bromide (0.3 mmol) and TIPS-OH (90 μL, 1.5 equiv) if KOH was used as base. After being stirred vigorously at 50 °C for 24 h or 48 h, the mixture was diluted with EtOAc and filtered through a pad of silica gel. Purification by silica gel column chromatography (eluent: EtOAc/hexanes) afforded the desired product.
**2 ($B_2$).** The same procedure was applied, using 2 mol % of [(π-allyl)PdCl]$_2$ and **4 mol %** of cBRIDP.
**3 ($B_3$).** The same procedure was applied, using 0.6 mL (0.5 *M*) of the 2 wt % TPGS-750M/$H_2O$ solution.

## General Procedure C

Inside a dry box, a flame-dried 5 mL round bottom flask or 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), the base (1.5 equiv), the carbamate (1.2 equiv). Outside the dry box, under a positive flow of argon were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.3 mL, 1 *M*), the heteroaryl bromide (0.3 mmol) and TIPS-OH (90 μL, 1.5 equiv) if KOH was used as base. After being stirred vigorously at 50 °C for 24 h to 48 h, the mixture was diluted with EtOAc and filtered through a pad of silica gel. Purification by silica gel column chromatography (eluent: EtOAc/hexanes) afforded the desired product.

# III. Substrate Scope

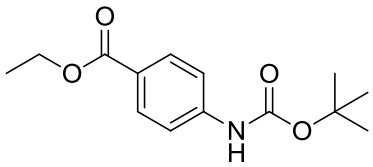
### Synthesis of ethyl 4-((ethoxycarbonyl)amino)benzoate



The title compound was obtained according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.54 mol %), cBRIDP (2.3 mg, 2.15 mol %), ethyl-4-bromobenzoate (49 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (43.6 mg, 0.45 mmol, 1.5 equiv) and urethane (32.1 mg, 0.35 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (70.5 mg, 99% yield). *Note: transesterification with NaO-t-Bu was observed with excess heat and prolonged reaction times.*

**mp:** 127.5 ± 0.5 °C.
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.01 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 2H), 6.79 (br. s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 166.4, 153.3, 142.3, 131.1, 125.3, 117.6, 61.8, 61.0, 14.7, 15.5.
**IR (KBr disk):** 3318, 2978, 2920, 2851, 1728, 1694, 1593, 1535, 1416, 1366, 1316, 1277, 1219, 1060 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{12}H_{15}NO_4Na$ 260.0901, found 260.0885.

### Synthesis of ethyl 4-((*t*-butoxycarbonyl)amino)benzoate

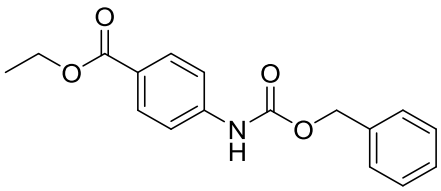


The title compound was obtained according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.56 mol %), cBRIDP (2.2 mg, 2.08 mol %), ethyl-4-bromobenzoate (49 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (45.4 mg, 0.47 mmol, 1.6 equiv) and *t*-butyl carbamate (41.5 mg, 0.35 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (77.9 mg, 98% yield). Spectral data for the titled compound matched that previously reported in literature. *Note: transesterification with NaO-t-Bu was observed with excess heat and prolonged reaction times.*

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.98 (dt, *J* = 8.8, 2.5 Hz, 2H, $H_{Arom.}$), 7.43 (d, *J* = 8.8 Hz, 2H, $H_{Arom.}$), 6.65 (br. s, 1H, NH), 4.36 (q, *J* = 7.2 Hz, 2H, $CH_2$), 1.54 (s, 9H, $(CH_3)_3$), 1.39 (t, *J* = 7.2 Hz, 3H, $CH_3$).

Ref: Grehn, L.; Gunnarsson, K.; Ragnarsson, U. Acta *Chemica Scandinavica, Series B: Organic Chemistry and Biochemistry* **1987**, *41*, 18-23.

## Synthesis of ethyl 4-(((benzyloxy)carbonyl)amino)benzoate



The title compound was obtainied according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.5 mol %), cBRIDP (2.1 mg, 2 mol %), ethyl-4-bromobenzoate (49 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (46.7 mg, 0.48 mmol, 1.6 equiv), benzyl carbamate (56.0 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 5 to 20% EtOAc/hexanes) to provide the desired compound as a white powder (69.5 mg, 77% yield). *Note: transesterification with NaO-t-Bu was observed with excess heat and prolonged reaction times.*

**mp:** 138.5 ± 0.5 °C.

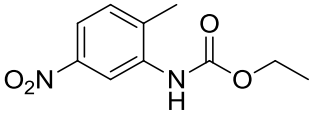
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.0 (dt, *J* = 8.8, 2 Hz, 2H, $H_{Arom.}$), 7.47 (d, *J* = 8.8 Hz, 2H, $H_{Arom.}$), 7.43-7.36 (m, 5H, $H_{Benzyl}$), 6.95 (br. s, 1H, NH), 5.22 (s, 2H, $CH_2$), 4.36 (q, *J* = 7.2 Hz, 2H, O-$CH_2$), 1.39 (t, *J* = 7.2 Hz, 3H, $CH_3$).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 166.2, 152.9, 142.0, 135.7, 130.9, 128.7, 128.5, 128.4, 125.2, 117.5, 67.3, 60.8, 14.3.

**IR (KBr disk):** 3298, 1736, 1694, 1597, 1539, 1416, 1319, 1292, 1223, 1045 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{17}H_{17}NO_4Na$ 322.11, found 322.1051.

## Synthesis of ethyl (2-methyl-5-nitrophenyl)carbamate

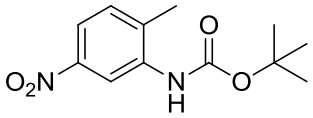


The title compound was obtained according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.58 mol %), cBRIDP (2.3 mg, 2.13 mol %), 2-bromo-4-nitrotoluene (64 mg, 0.3 mmol, 1 equiv), KOH (25.3 mg, 0.45 mmol, 1.5 equiv), urethane (34.1 mg, 0.38 mmol, 1.3 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (65.9 mg, 98% yield).

**mp:** 135.5 ± 0.5 °C.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.81 (s, 1H, $H_{Arom}$), 7.86 (dd, *J* = 8.3, 2.5 Hz, 1H, $H_{Arom}$), 7.30 (d, *J* = 8.3 Hz, 1H, $H_{Arom}$), 6.54 (s, 1H, NH), 4.28 (q, *J* = 7.3 Hz, 2H, $CH_2$), 3.36 (s, 3H, $CH_3$), 1.35 (t, *J* = 7.3 Hz, 3H, $CH_2$-$CH_3$).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$153.5, 147.3, 137.2, 131.0, 118.5, 115.3, 62.1, 29.9, 18.1, 14.7.
**IR (KBr disk):** 3295, 2990, 1694, 1600, 1535, 1346, 1261, 1099, 1061 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{10}H_{12}N_2O_4Na$ 247.07, found 247.0691.

### Synthesis of *t*-butyl (2-methyl-5-nitrophenyl)carbamate

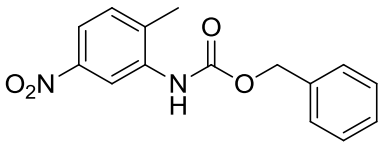


The title compound was obtained according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.55 mol %), cBRIDP (2.2 mg, 2.02 mol %), 2-bromo-4-nitrotoluene (66.8 mg, 0.31 mmol, 1 equiv), KOH (26.3 mg, 0.47 mmol, 1.5 equiv), *t*-butyl carbamate (43.0 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (76.6 mg, 98% yield). Spectral data for the titled compound matched that previously reported in literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.84 (s, 1H, $H_{Arom}$), 7.84 (dd, *J* = 8.3, 2.2 Hz, 1H, $H_{Arom}$), 7.28 (d, *J* = 8.3 Hz, 1H, $H_{Arom}$), 6.42 (br. s, 1H, NH), 2.35 (s, 3H, $CH_3$), 1.56 (s, 9H, $(CH_3)_3$).

Ref: Yu, C.; Liu, B.; Hu, L. *J. Org. Chem.* **2001**, *66*, 919-924.

### Synthesis of benzyl (2-methyl-5-nitrophenyl)carbamate

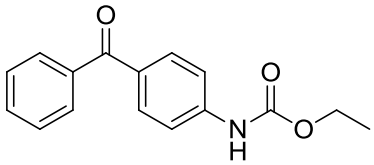


The title compound was obtained according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.56 mol %), cBRIDP (2.2 mg, 2.02 mol %), 2-bromo-4-nitrotoluene (66.9 mg, 0.31 mmol, 1 equiv), KOH (25.5 mg, 0.45 mmol, 1.5 equiv), benzyl carbamate (55.1 mg, 0. 37 mmol, 1.2 equiv) . The crude product was purified by silica gel column chromatography (eluent: gradient from 5 to 20% EtOAc/hexanes) to provide the desired compound as a white powder (87.8 mg, 99% yield).

**mp:** 144.5 ± 0.5 °C.
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.84 (br. s, 1H, $H_{Arom}$), 7.88 (dd, *J* = 8.3, 2.2 Hz, 1H, $H_{Arom}$), 7.45-7.37 (m, 5H, $H_{Benzyl}$), 7.30 (d, *J* = 8.3 Hz, 1H, $H_{Arom}$), 6.64 (br. s, 1H, NH), 5.26 (s, 1H, $CH_2$), 2.34 (s, 3H, $CH_3$).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 153.3, 47.3, 137.0, 135.7, 131.0, 128.9, 128.8, 128.8, 128.3, 118.7, 115.4, 67.9, 18.1.
**IR (KBr disk):** 3295, 1693, 1535, 1346, 1312, 1246, 1057 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{15}H_{14}N_2O_4Na$ 309.09, found 309.0839.

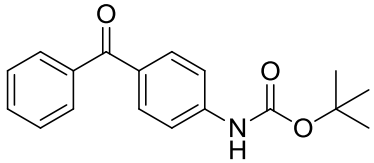
### Synthesis of ethyl (4-benzoylphenyl)carbamate



The title compound was obtained according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.57 mol %), cBRIDP (2.3 mg, 2.21 mol %), 4-bromobenzophenone (78.5 mg, 0.3 mmol, 1 equiv), NaO-*t*-Bu (43.6 mg, 0.45 mmol, 1.5 equiv), urethane (33.6 mg, 0.38 mmol, 1.3 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (79.1 mg, 98% yield).

**mp:** 193 ± 0.5 °C.
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.82 (dt, *J* = 8.3, 2.5 Hz, 2H, $H_{Arom}$), 7.77 (d, *J* = 7.2 Hz, 2H, $H_{Phenyl}$), 7.58 (tt, *J* = 7.3, 1.3 Hz, 1H, $H_{Phenyl}$), 7.53-7.47 (m, 4H, $H_{Phenyl}$ & $H_{Arom.}$), 6.95 (br. s, 1H, NH), 4.26 (q, *J* = 7.3 Hz, 2H, $CH_2$), 1.33 (t, *J* = 7.3 Hz, 3H, $CH_3$).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 195.8, 153.3, 142.3, 138.1, 132.3, 132.3, 132.0, 130.0, 128.4, 117.6, 61.8, 14.7.
**IR (KBr disk):** 3298, 2357, 1724, 1643, 1589, 1531, 1416, 1315, 1223, 1065 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{16}H_{15}NO_3Na$ 292.11, found 292.0943.

### Synthesis of *t*-butyl (4-benzoylphenyl)carbamate



The title compound was obtained according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.56 mol %), cBRIDP (2.2 mg, 2.12 mol %), 4-bromobenzophenone (78.8 mg, 0.3 mmol, 1 equiv.), NaO-*t*-Bu (47.1 mg, 0.49 mmol, 1.6 equiv), *tert*-butyl carbamate (42.9 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (67.1 mg, 75% yield).

**mp:** 180 ± 0.5 °C.

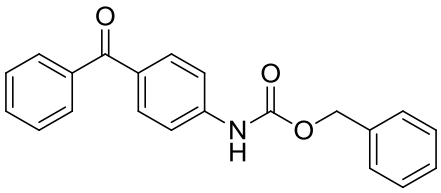
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.81 (d, *J* = 8.5 Hz, 2H, $H_{Arom}$), 7.77 (d, *J* = 7.5 Hz, 2H, $H_{Phenyl}$), 7.59-7.56 (m, 1H, $H_{Phenyl}$), 7.50-7.46 (m, 4H, $H_{Arom}$ & $H_{Phenyl}$), 6.78 (br. s, 1H, NH), 1.54 (s, 9H, $(CH_3)_3$).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 195.8, 142.7, 138.3, 132.24, 132.1, 132.0, 130.1, 130.0, 128.4, 117.5, 105.2, 28.5.

**IR (KBr disk):** 3322, 2361, 2338, 1721, 1647, 1589, 1528, 1416, 1316, 1234, 1157 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{18}H_{19}NO_3Na$ 320.13, found 320.1253.

## Synthesis of benzyl (4-benzoylphenyl)carbamate



The title compound was obtained according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.5 mol %), cBRIDP (2.2 mg, 2.03 mol %), 4-bromobenzophenone (79.1 mg, 0.3 mmol, 1 equiv), NaO-*t*-Bu (45.9 mg, 0.48 mmol, 1.6 equiv), benzyl carbamate (55.4 mg, 0.37 mmol, 1.2 equiv) . The crude product was purified by silica gel column chromatography (eluent: gradient from 2 to 20% EtOAc/hexanes) to provide the desired compound as a white powder (79.5 mg, 80% yield).

**mp:** 123 ± 0.5 °C.

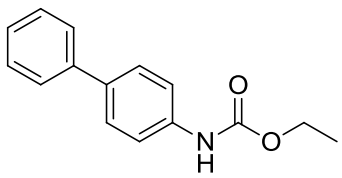
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.82 (dt, *J* = 8.5, 2 Hz, 2H, $H_{Arom}$), 7.78-7.76 (m, 2H, $H_{Phenyl}$), 7.60-7.57 (m, 1H, $H_{Phenyl}$), 7.53-7.47 (m, 4H, $H_{Arom}$ & $H_{Phenyl}$), 7.44-7.35 (m, 5H, $H_{Benzyl}$), 6.94 (br. s, 1H, NH), 5.24 (s, 2H, $CH_2$).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 195.7, 153.1, 142.0, 138.1, 135.8, 132.6, 132.3, 132.0, 130.0, 128.4, 128.8, 128.6, 128.4, 117.7, 67.6.

**IR (KBr disk):** 3310, 1740, 1643, 1597, 1532, 1412, 1316, 1281, 1219, 1053 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{21}H_{17}NO_3Na$ 354.11, found 354.1105.

## Synthesis of ethyl 4-biphenylcarbamate

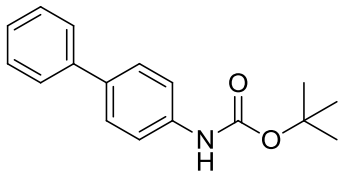


The title compound was obtained according to the general procedure **$A_1$** (50 °C, 48 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.55 mol %), cBRIDP (2.2 mg, 2.03 mol %), 4-bromobiphenyl (72.0 mg, 0.31 mmol, 1 equiv), KOH (26.4 mg, 0.47 mmol, 1.5 equiv), urethane (33.7 mg, 0.38 mmol, 1.2 equiv). The crude product was

purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (62.7 mg, 84% yield).
Following the procedure **$A_2$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2.1 mg, 1.87 mol %), cBRIDP (4.2 mg, 3.93 mol %), 4-bromobiphenyl (70.0 mg, 0.3 mmol, 1 equiv), KOH (25.1 mg, 0.45 mmol, 1.5 equiv), urethane (33.5 mg, 0.38 mmol, 1.3 equiv), the desired compound was obtained in high yield (66.7 mg, 92% yield).

**mp:** 116.5 ± 0.5 °C.
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.58-7.55 (m, 4H), 7.48-7.42 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.34 (t , *J* = 7.2 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$153.8, 140.7, 137.5, 136.5, 129.0, 127.9, 127.2, 127.0, 119.1, 61.5, 14.8.
**IR (KBr disk):** 3318, 2978, 1709, 1597, 1543, 1489, 1323, 1246, 1088 $cm^{-1}$.
HRMS-ESI (*m/z*) $[M + Na]^+$ calculated for $C_{15}H_{15}NO_2Na$ 264.1000, found 264.0988.

## Synthesis of *t*-butyl 4-biphenylcarbamate

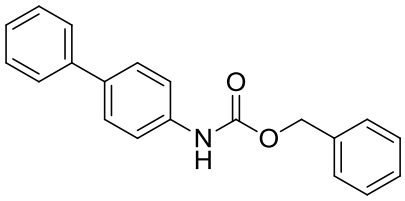



The title compound was obtaining according to the general procedure **$A_1$** (50 °C, 48 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.55 mol %), cBRIDP (2.3 mg, 2.13 mol %), 4-bromobiphenyl (70.3 mg, 0.3 mmol, 1 equiv), KOH (25.2 mg, 0.45 mmol, 1.5 equiv), *t*-butyl carbamate (44.0 mg, 0.38 mmol, 1.3 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 8% EtOAc/hexanes) to provide the desired compound as a white powder (72.9 mg, 90% yield).
Following the procedure **$A_3$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.52 mol %), cBRIDP (2.3 mg, 2.20 mol %), 4-Bromobiphenyl (70.6 mg, 0.3 mmol, 1 equiv), KOH (25.6, 0.46 mmol, 1.5 equiv), *t*-butyl carbamate (42.6 mg, 0.36 mmol, 1.2 equiv), the compound was obtained in similar yield (71.6 mg, 89% yield). Spectral data for compound matched that previously reported in literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.58-7.53 (m, 4H, $H_{Phenyl}$), 7.48-7.41 (m, 4H, $H_{Phenyl}$), 7.33 (tt, *J* = 7.5, 1.3 Hz, 1H, $H_{Phenyl}$), 6.53 (br. s, 1H, NH), 1.55 (s, 9H, $(CH_3)_3$).

Ref: Boz, S.; Stoehr, M.; Soydaner, U.; Mayor, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3179-3183.

**Synthesis of benzyl 4-biphenylcarbamate**

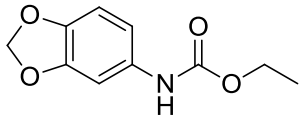


The title compound was obtaining according to the general procedure **$A_1$** (50 °C, 48 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.5 mol %), cBRIDP (2.2 mg, 2. 06 mol %), 4-Bromobiphenyl (70.3 mg, 0.3 mmol, 1 equiv), KOH (25.8 mg, 1.5 equiv), benzyl carbamate (56.2 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 0 to 7% EtOAc/hexanes) to provide the desired compound as a white powder (75.7 mg, 83% yield).
Following the procedure **$A_2$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2.1 mg, 1.9 mol %), cBRIDP (4.1 mg, 3.9 mol %), 4-bromobiphenyl (70.3 mg, 0.3 mmol, 1 equiv), KOH (25.4, 0.45 mmol, 1.5 equiv), benzyl carbamate (55.90 mg, 0.37 mmol, 1.2 equiv), the compound was obtained in high yield (82.2 mg, 90% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.59-7.55 (m, 4H, $H_{Phenyl}$), 7.49-7.32 (m, 10H, $H_{Phenyl}$ & $H_{Benzyl}$), 6.76 (br. s, 1H, NH), 5.24 (s, 2H, $CH_2$).

Ref: Tanimoto, T.; Fukuda, H.; Kawamura, J.; Nakao, M.; Shimada, U.; et al. *Chemical & Pharmaceutical Bulletin* **1984**, *32*, 1032-1039.

**Synthesis of ethyl (1,3-benzodioxolan-5-yl)carbamate**

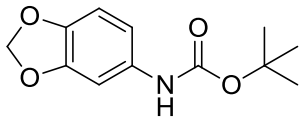


The title compound was obtaining according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.58 mol %), cBRIDP (2.2 mg, 2.08 mol %), 1-bromo-3,4-(methylenedioxy)benzene (36.5 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (44.8 mg, 0.47 mmol, 1.5 equiv), urethane (34.3 mg, 0.38 mmol, 1.3 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a brown-tan solid (19.3 mg, 30%).
Following the procedure **$B_2$** (50 °C, 48 h), $[(\pi\text{-allyl})PdCl]_2$ (2.0 mg, 1.85 mol %), cBRIDP (4.1 mg, 3.86 mol %), 1-bromo-3,4-(methylenedioxy)benzene (36.5 μL, 0.3 mmol, 1 equiv), KOH (25.5, 0.46 mmol, 1.5 equiv), urethane (34.0 mg, 0.38 mmol, 1.3 equiv), the compound was obtained in good yield (53.52 mg, 85% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.09 (br. s, 1H, $H_{Arom}$), 6.73 (d, *J* = 8 Hz, 1H, $H_{Arom}$), 6.68 (d, *J* = 8 Hz, 1H, $H_{Arom}$), 6.50 (br. s, 1H, NH), 5.94 (s, 2H, O-$CH_2$-O), 4.21 (q, J = 7.3 Hz, 2H, $CH_2$), 1.31 (t, *J* = 7.3 Hz, 3H, $CH_3$).

Ref: Broggini, G.; Colombo, F.; Marchi, I. D.; Galli, S.; Martinelli, M.; Zecchi, G. *Tetrahedron: Asymmetry* **2007**, *18*, 1495-1501

## Synthesis of *t*-butyl (1,3-benzodioxolan-5-yl)carbamate

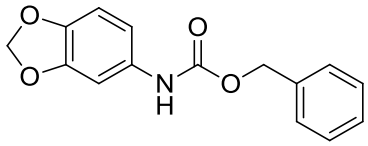


The title compound was obtained according to general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.56 mol %), cBRIDP (2.2 mg, 2.08 mol %), 1-bromo-3,4-(methylenedioxy)benzene (36.5 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (46.5 mg, 0.48 mg, 1.6 equiv), *tert*-butyl carbamate (43.2 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a brown-tan solid (66.5 mg, 93% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.07 (br. s, 1H, $H_{Arom}$), 6.72 (d, *J* = 8.1 Hz, 1H, $H_{Arom}$), 6.66 (d, *J* = 8.1 Hz, 1H, $H_{Arom}$), 6.37 (br. s, 1H, NH), 5.93 (s, 2H, $CH_2$), 1.51 (s, 9H, $(CH_3)_3$).

Ref: Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653-6655.

## Synthesis of benzyl (1,3-benzodioxolan-5-yl)carbamate



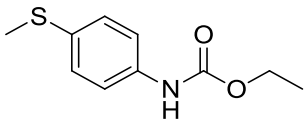
The title compound was obtaining according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.5 mol %), cBRIDP (2.3 mg, 2.14 mol %), 1-bromo-3,4-(methylenedioxy)benzene (36.5 μL, 0.3 mmol, 1 equiv), NaO*t*Bu (46.2 mg, 0.48 mmol, 1.6 equiv), benzyl carbamate (55.2 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (41.36 mg, 50% yield).

Following the procedure **$B_2$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2.1 mg, 1.89 mol %), cBRIDP (4.1 mg, 3.86 mol %), 1-Bromo-3,4-(methylenedioxy)benzene (36.5 μL, 0.3 mmol, 1 equiv.), KOH (25.9 mg, 0.46 mmol, 1.5

equiv), benzyl carbamate (54.6 mg, 0.36 mmol, 1.2 equiv), the compound was obtained in high yield (73.9 mg, 91% yield).

**mp:** 104.5 ± 0.5 °C.
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.41-7.34 (m, 5H, $H_{Benzyl}$), 7.10 (br. s, 1H, $H_{Arom}$), 6.73 (d, *J* = 8.1 Hz, 1H, $H_{Arom}$), 6.68 (d, *J* = 8.1 Hz, 1H, $H_{Arom}$), 6.58 (br. s, 1H, NH), 5.95 (s, 2H, O-$CH_2$-O), 5.2 (s, 2H, $CH_2$).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 148.2, 136.2, 132.2, 128.8, 128.54, 128.50, 112.1, 108.2, 102.0, 101.4, 67.2, 29.9.
**IR (KBr disk):** 3295, 1701, 1539, 1505, 1455, 1269, 1238, 1103, 1061, 1038 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{15}H_{13}NO_4Na$ 294.07, found 294.0737.

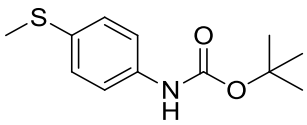
## Synthesis of ethyl (4-(methylthio)phenyl)carbamate



The title compound was obtaining according to the general procedure **$B_3$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), 4-bromothioanisole (51 mg, 0.25 mmol), TIPS-OH/KOH (1.5 equiv), *t*-butyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (51 mg, 97% yield).

**mp:** 81-82 ± 0.5 °C.
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.33-7.32 (m, 2H, $H_{Arom}$), 7.24-7.22 (m, 2H, $H_{Arom}$), 6.71 (br. s, 1H, NH), 4.22 (q, 2H, O-$CH_2$-), 2.46 (s, 3H, $CH_3$-S-), 1.31 (t, 3H, $CH_3$).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 153.8, 135.9, 132.5, 128.6, 127.2, 119.5, 61.4, 17.1, 14.7;
**IR: (neat):** 3320, 3177, 3057, 2982, 1694, 1591, 1479, 1233, 811 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{10}H_{13}NO_2SNa$ 234.0565, found 234.0558.

## Synthesis of *t*-butyl (4-(methylthio)phenyl)carbamate



The title compound was obtaining according to the general procedure **$B_3$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), 4-bromothioanisole (51 mg, 0.25 mmol), TIPS-OH/KOH (1.5 equiv), *t*-butyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (56 mg, 94% yield).

**mp:** 111-112 ± 0.5 °C.

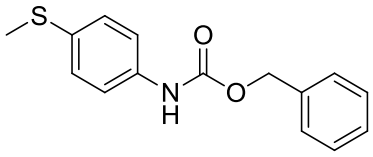
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.35-7.33 (m, 2H, $H_{Arom}$), 7.27-7.26 (m, 2H, $H_{Arom}$), 6.57 (br. s, 1H, NH), 2.49 (s, 3H, $CH_3$-S-), 1.56 (s, 9H, $(CH_3)_3$).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$152.9, 136.4, 132.0, 128.7, 119.4, 80.7, 28.5, 17.3.

**IR (KBr disk):** 3372, 2986, 2924, 1697, 1582, 1512, 1161, 818 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{12}H_{17}NO_2SNa$ 262.0878, found 262.0866.

## Synthesis of benzyl (4-(methylthio)phenyl)carbamate




The title compound was obtaining according to the general procedure **$B_3$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), 4-bromothioanisole (51 mg, 0.25 mmol), TIPS-OH/KOH (1.5 equiv), benzyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (54 mg, 84% yield).

**mp:** 110 – 111 ± 0.5 °C.

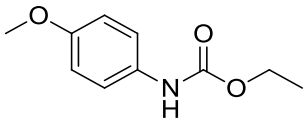
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.41-7.33 (m, 6H, $H_{Arom}$), 7.55-7.23 (m, 3H, $H_{Arom}$), 6.78 (br. s, 1H, NH), 5.20 (s, 2H, -O-$CH_2$-Ph), 2.47 (s, 3H, $CH_3$-S-).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$153.5, 136.1, 135.7, 132.7, 128.8, 128.5, 128.5, 128.4, 119.5, 67.2, 17.0.

**IR (KBr disk):** 3306, 1694, 1524, 1234, 1069, 814, 694 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{15}H_{15}NO_2SNa$ 296.0721, found 296.0716.

## Synthesis of ethyl *p*-methoxyphenylcarbamate

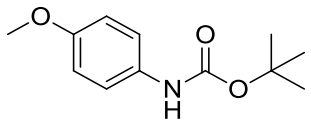



The title compound was obtaining according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), 4-bromoanisole (58 mg, 0.25 mmol), NaO-*t*-Bu (1.5 equiv), urethane (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (55 mg, 94% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.29 (br. s, 2H,), 6.87-6.85 (m (pseudo d), 2H), 6.45 (br. s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H, -O-$CH_3$), 1.31 (t, *J* = 7.2 Hz, 3H). The broad singlet at 7.29 ppm overlaps with the residual $CDCl_3$ peak.

Ref: Chilin, A.; Marzaro, G.; Zanatta, S.; Barbieri, V.; Pastorini, G.; Manzini, P.; Guiotto, A. *Tetrahedron* **2006**, *62*, 12351-12356.

### Synthesis of *t*-butyl *p*-methoxyphenylcarbamate

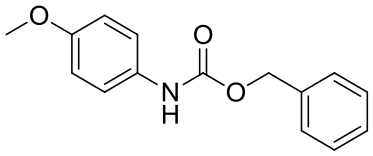


The title compound was obtaining according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.55 mol %), cBRIDP (2.2 mg, 2.05 mol %), 4-bromoanisole (37.5 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (43.9 mg, 0.46 mg, 1.5 equiv), *t*-butyl carbamate (42.9 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 0 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (66.9 mg, 99% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.30-7.26 (m, 2H, $H_{Arom}$), 6.86-6.83 (m, 2H, $H_{Arom}$), 6.33 (br. s, 1H, NH), 3.79 (s, 3H, $CH_3$), 1.52 (s, 9H, $(CH_3)_3$).

Ref: Varala, R.; Nuvula, S.; Adapa, S. R. *J. Org. Chem.* **2006**, *71*, 8283-8286.

### Synthesis of benzyl *p*-methoxyphenylcarbamate

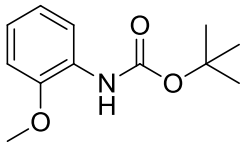


The title compound was obtaining according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.55 mol %), cBRIDP (2.2 mg, 2.08 mol %), 4-bromoanisole (37.5 μL, 0.3 mmol, 1 equiv), NaO-*t*-Bu (46.8 mg, 0.49 mmol, 1.6 equiv), benzyl carbamate (55.7 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white powder (42.4 mg, 52% yield). Spectral data for compound matched that previously reported in literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.42-7.29 (m, 7H, $H_{Arom}$ & $H_{Benzyl}$), 6.86 (m, 2H, $H_{Benzyl}$), 6.57 (br. s, 1H, NH), 5.20 (s, 2H, $CH_2$), 3.79 (s, 3H, $CH_3$).

Ref: Wipf, P.; Maciejewski, J. P. *Org. Lett.* **2008**, *10*, 4383-4386.

**Synthesis of *t*-butyl *o*-methoxyphenylcarbamate**

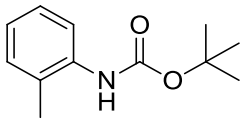


The title compound was obtaining according to the general procedure **$A_2$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2.2 mg, 2 mol %), cBRIDP (4.2 mg, 4 mol %), 2-bromoanisole (37.5 μL, 0.3 mmol, 1 equiv.), NaO-*t*-Bu (47.0 mg, 0.49 mmol, 1.6 equiv), *t*-butyl carbamate (42.4 mg, 0.36 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (62.4 mg, 93% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.09 (d, *J* = 8.4 Hz, 1H, $H_{Arom}$), 7.10 (br. s, 1H, NH), 6.98-6.93 (m, 2H, $H_{Arom}$), 6.86 (dd, *J* = 9.3, 2.4 Hz, 1H, $H_{Arom}$), 3.87 (s, 3H, $CH_3$), 1.54 (s, 9H, $(CH_3)_3$).

Ref: Kondo, Y.; Kojima, S.; Sakamoto, T. *J. Org. Chem.* **1997**, *62*, 6507-6511.

**Synthesis of ethyl *o*-methylphenylcarbamate**

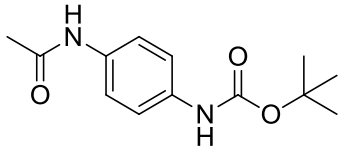


The title compound was obtaining according to the general procedure **$B_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), 2-bromotoluene (43 mg, 0.25 mmol ), TIPS-OH/KOH (1.5 equiv), *t*-butyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent**:** 50% DCM/hexanes) to provide the desired compound as a white powder (48 mg, 94% yield).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.81 (d, *J* = 7.5 Hz, 1H, $H_{Arom}$), 7.20 (t, *J* = 7.5 Hz, 1H, $H_{Arom}$), 7.15 (d, *J* = 7.5, 1H, $H_{Arom}$), 7.0 (t, *J* = 7.5 Hz, 1H, $H_{Arom}$), 6.27 (br. s, 1H, NH), 2.26 (s, 3H, $CH_3$), 1.54 (s, 9H, $(CH_3)_3$).

Ref: Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575-5580.

**Synthesis of *t*-butyl 4-acetamidophenylcarbamate**

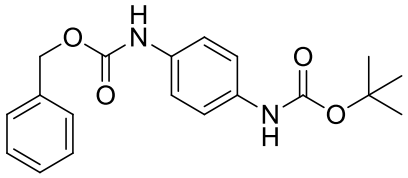


The title compound was obtaining according to the general procedure **$A_1$** (50 °C, 30 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.51 mol %), cBRIDP (2.1 mg, 1.92 mol %), *N*-(4-bromophenyl)acetamide (65.6 mg, 0.31 mmol, 1 equiv.), NaO-*t*-Bu (46.8 mg, 1.5 equiv), *t*-butyl carbamate (43.8 mg, 0.37 mmol, 1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 10 to 50% EtOAc/hexanes) to provide the desired compound as a white powder (72.1 mg, 93% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.42 (d, *J* = 8.7 Hz, 2H, $H_{Arom}$), 7.31 (d, *J* = 8.7 Hz, 2H, $H_{Arom}$), 7.15 (br. s, 1H, NH), 6.45 (br. s, 1H, NH), 2.16 (s, 3H, $CH_3$), 1.52 (s, 9H, $(CH_3)_3$).

Ref: Zeng, H.; Shao, H.; Li, Y. *Syn. Comm.* **2012**, *42*, 25-32.

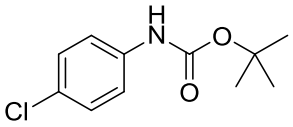
**Synthesis of benzyl *t*-butyl 1,4-phenylenedicarbamate**



The title compound was obtaining according to the general procedure **$A_1$** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (0.6 mg, 0.52 mol %), cBRIDP (2.1 mg, 2 mol %), *N*-(*t*-butoxycarbonyl)-4-bromoaniline (81.8 mg, 0.3 mmol, 1 equiv), NaO-*t*-Bu (44.6 mg, 0.46 mmol, 1.5 equiv), benzyl carbamate (56.8 mg, 0.38 mmol, 1.3 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 12% EtOAc/hexanes) to provide the desired compound as a white semi-solid (92.1 mg, 90% yield).

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.55 (br. s, 1H, $H_{Phenyl}$), 7.40-7.34 (m, 5H, $H_{Arom}$ & $H_{Phenyl}$), 7.19 (t, *J* = 8 Hz, 1H, $H_{Phenyl}$), 7.09-7.05 (m, 2H, $H_{Phenyl}$), 6.88 (br. s, 1H, NH), 6.64 (br. s, 1H, NH), 5.19 (s, 2H, $CH_2$), 1.52 (s, 9H, $(CH_3)_3$).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 153.4, 152.8, 139.3, 139.0, 136.2, 129.6, 128.7, 128.4, 80.7, 67.1, 28.5.
**IR (KBr disk):** 3322, 2978, 2361, 1709, 1609, 1535, 1493, 1424, 1234, 1161, 1057 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{19}H_{22}N_2O_4Na$ 365.1480, found 365.1471.

**Synthesis of *t*-butyl (4-chlorophenyl)carbamate**

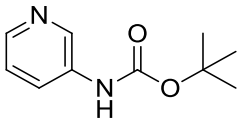


The title compound was obtained according to the general procedure **C** (0.5 *M*, 20 h, 50 °C, 0.25 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv), carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexanes) to provide the desired compound as a white solid (56 mg, 98% yield).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.32-7.28 (m, 2H), 7.26-7.23 (m, 2H), 6.50 (br. s, 1H), 1.51 (s, 9H).

Ref: Roosen, P. C.; Kallepalli, V. A.; Chattopadhyay, B.; Singleton, D. A.; Maleczka, R. E., Jr.; Smith, M. R., III *J. Am. Chem. Soc.* **2012**, *134*, 11350-11353.

**Synthesis of *t*-butyl *N*-(pyridin-3-yl)carbamate**

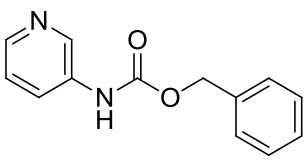


The title compound was obtaining according to the general procedure **C** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), *t*-butyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 15% EtOAc/hexanes) to provide the desired compound as a white powder (44 mg, 91% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.44 (s, 1H, $H_{Pyridine}$), 8.29 (d, $J$ = 4 Hz, 1H, $H_{Pyridine}$), 7.98 (br. s, 1H, $H_{Pyridine}$), 7.27-7.23 (m, 1H, $H_{Pyridine}$), 6.52 (br. s, 1H, NH), 1.54 (s, 9H, $(CH_3)_3$).

Ref: Lemire, A.; Grenon, M.; Pourashraf, M.; Charette, A. *Org.Lett.* **2004**, *6*, 3517-3520.

**Synthesis of Benzyl *N*-(pyridin-3-yl)carbamate**

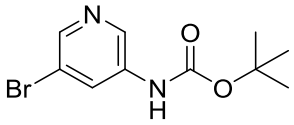


The title compound was obtained according to the general procedure **C** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), benzyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 15% EtOAc/hexanes) to provide the desired compound as a white powder (50 mg, 88% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.48 (s, 1H, $H_{Pyridine}$), 8.32 (s, 1H, $H_{Pyridine}$), 7.99 (br. s, 1H, $H_{Pyridine}$), 7.42-7.25 (m, 6H, $H_{Pyridine}$ & $H_{Arom.}$), 6.75 (br. s, 1H, NH), 5.22 (s, 2H, $CH_2$).

Ref: Salvatore, R. N.; Chu, F.; Nagle, A. S.; Kapxhiu, E. A.; Cross, R. M.; Jung, K. *Tetrahedron* **2002**, *58*, 3329-3348

**Synthesis of *tert*-butyl (5-bromopyridin-3-yl)carbamate**

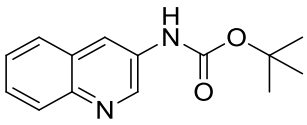



The title compound was obtained according to the general procedure **C** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), benzyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 0 to 60% EtOAc/hexanes) to provide the desired compound as a white powder (32 mg, 47% yield). Spectral data for compound matched that previously reported in the literature.

**$^1$H NMR (400 MHz, $CDCl_3$):** $\delta$ 8.34 (d, J = 1.5 Hz, 1H, $H_{Pyridine}$), 8.31 (s, 2H, $H_{Pyridine}$), 6.90 (br. s, 1H, NH), 1.53 (s, 3H, $(CH_3)_{3.}$).

Ref: Young, B. M.; Hyatt, J. L.; Bouck, D. C.; Chen, T.; Hanumesh, P.; Price, J.; Boyd, V. A.; Potter, P. M.; Webb, T. R. *J. Med. Chem.* **2010**, *53*, 8709-8715.

**Synthesis of *t*-butyl *N*-(quinolin-3-yl)carbamate**



The title compound was obtained according to the general procedure **C** (50 °C, 24 h), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), *t*-butyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 15% EtOAc/hexanes) to provide the desired compound as a white powder (66 mg, 90% yield).

**mp:** 153 – 154 ± 0.5 °C.

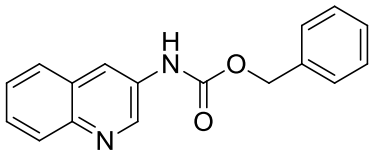
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.65 (d, J = 2.4 Hz, 1H, $H_{2\text{-Quinoline}}$), 8.53 (br. s, 1H, $H_{4\text{-Quinoline}}$), 8.0 (d, *J* = 8.4 Hz, 1H, $H_{5\text{-Quinoline}}$), 7.78 (d, *J* = 8.4 Hz, 1H, $H_{8\text{-Quinoline}}$), 7.61-7.59 (m, 1H, $H_{6\text{-Quinoline}}$), 7.53-7.51 (m, 1H, $H_{7\text{-Quinoline}}$), 6.87 (br. s, 1H, NH), 1.57 (s, 9H, $(CH_3)_3$).

**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 152.9, 144.9, 143.6, 132.2, 129.2, 128.6, 127.9, 127.7, 127.4, 121.8, 81.6, 28.5.

**IR (neat):** 3416, 3336, 3195, 2923, 2859, 1720, 1688, 1254, 1189, 1058, 781 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{14}H_{16}N_2O_2Na$ 267.1109, found 267.1102.

## Synthesis of benzyl *N*-(quinolin-3-yl)carbamate



The title compound was obtaining according to the general procedure **C**, $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), benzyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 15% EtOAc/hexanes) to provide the desired compound as a white powder (50.1 mg, 60% yield).

**mp:** 188 – 190 ± 0.5 °C.

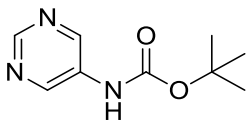
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.70 (br s, 1H,$H_{Arom}$), 8.53 (br. s, 1H, $H_{Arom}$), 8.05 (d, *J* = 8.4 Hz, 1H, $H_{Arom}$), 7.80 (d, *J* = 7.8 Hz, 1H, $H_{Arom}$), 7.63 (t, *J* = 7.2 Hz, 1H, $H_{Arom}$), 7.54 (t, *J* = 7.8 Hz, 1H,$H_{Arom}$), 7.45-7.33 (m, 5H, $H_{Arom}$), 7.01 (br. s, 1H, NH), 5.28 (s, 2H, O-$CH_2$-Ph).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ 145.1, 135.8, 129.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.7, 127.5, 120.7, 67.7.

**IR (neat):** 3416, 3336, 3273, 2923, 2859, 1720, 1616, 1294, 1254, 1058, 781, 742, 696 $cm^{-1}$.

**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{17}H_{14}N_2O_2Na$ 301.0953, found 301.0946.

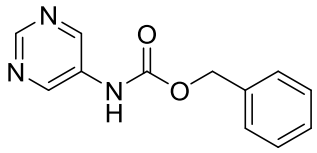
## Synthesis of *t*-butyl *N*-(pyrimidin-3-yl)carbamate



The title compound was obtaining according to the general procedure **C**, $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), *t*-butyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 15% EtOAc/hexanes) to provide the desired compound as a white/yellow powder (13.5 mg, 23% yield).

**mp:** 164 – 165 ± 0.5 °C.
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.92 (br. s, 1H,$H_{Arom}$), 8.85 (br. s, 2H, $H_{Arom}$), 6.76 (br. s, 1H, NH), 1.54 (s, 9H, O-$(CH_3)_3$).
**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ 153.4, 152.3, 146.7, 134.1, 120.7, 28.4.
**IR (neat):** 3221, 3152, 3039, 2975, 2929, 2852, 1726, 1591, 1431, 1418, 1249, 1149, 894, 721, 623 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_9H_{13}N_3O_2Na$ 218.0905, found 218.0893.

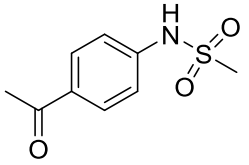
## Synthesis of benzyl *N*-(pyrimidin-3-yl)carbamate



The title compound was obtaining according to the general procedure **C**, $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv.), benzyl carbamate (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 15% EtOAc/hexanes) to provide the desired compound as a white/yellow powder (38.5 mg, 56% yield).

**mp:** 192 – 193 ± 0.5 °C.
**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.96 (br. s, 1H,$H_{Arom}$), 8.87 (br. s, 2H, $H_{Arom}$), 7.42-7.37 (m, 5H, $H_{Arom}$), 5.25 (s, 2H, O-$(CH_2)$-Ph).
**$^{13}$C NMR (100 MHz, $CDCl_3$):** $\delta$ 153.9, 153.1, 146.9, 135.4, 135.5, 128.9, 128.7, 68.2.
**IR (neat):** 3174, 3234, 3067, 2923, 2781, 1723, 1581, 1232, 1033, 694 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{12}H_{11}N_3O_2Na$ 252.0749, found 252.0733.

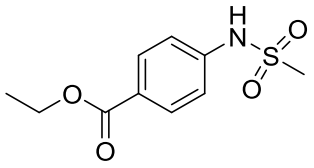
## Synthesis of *N*-(4-acetylphenyl)methanesulfonamide



The title compound was obtaining according to the general procedure **C** (0.5 *M*, 24 h, 50 °C), [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv), sulfonamide (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexanes) to provide the desired compound as a white/yellow powder (45 mg, 85% yield). The product can also be purified by recrystallization using DCM layered with hexanes.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.98 (d, *J* = 9 Hz, 2H), 7.28 (d, *J* = 9 Hz, 2H), 7.03 (br. s, 1H), 3.11 (s, 3H), 2.60 (s, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 196.9, 141.4, 133.6, 130.6, 118.4, 40.2, 26.6.
**IR (KBr disk):** 3220, 3025, 2929, 2982, 1665, 1601, 1328, 1150, 963, 916, 520 cm$^{-1}$.
**HRMS-ESI (*m/z*)** [M + Na]$^+$ calculated for $C_9H_{11}NO_3SNa$ 236.0357, found 236.0355.

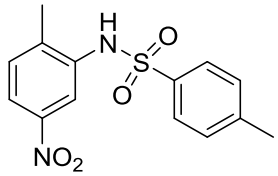
## Synthesis of ethyl 4-(methylsulfonamido)benzoate



The title compound was obtaining according to the general procedure **C** (0.5 *M*, 48 h, 50 °C), [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), NaO-*t*-Bu (1.5 equiv.), sulfonamide (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexanes) to provide the desired compound as a white/yellow powder (53 mg, 87% yield).

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.02 (d, *J* = 9 Hz, 2H), 7.50 (br. s, 1H), 7.26 (d, *J* = 9 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.08 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 166.2, 141.4, 131.5, 126.7, 118.5, 61.3, 40.0, 14.5.
**IR (KBr disk):** 2991, 2942, 2891, 2865, 1592, 1456, 1330, 1061, 881, 786, 586 cm$^{-1}$.
**HRMS-ESI (*m/z*)** [M + Na]$^+$ calculated for $C_{10}H_{13}NO_4SNa$ 266.0463, found 266.0438.

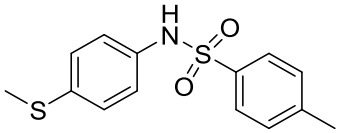
**Synthesis of 4-methyl-*N*-(2-methyl-5-nitrophenyl)benzenesulfonamide**



The title compound was obtained according to the general procedure **C** (0.5 *M*, 24 h, 50 °C), [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv.), TIPSOH (1.5 equiv), sulfonamide (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexanes) to provide the desired compound as a white solid (71 mg, 93% yield).

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 8.17 (d, *J* = 2.4 Hz, 1H), 7.91 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.68 (br. s, 1H), 2.42 (s, 3H), 2.20 (s, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 144.9, 137.9, 136.1, 135.9, 131.6, 130.2, 129.9, 127.5, 120.5, 117.8, 21.8, 18.2.
**IR (neat):** 3276, 3103, 3053, 2925, 2852, 1597, 1520, 1345, 1160, 815, 740, 665, 570, 544 cm$^{-1}$.
**HRMS-ESI (*m/z*)** [M + Na]$^+$ calculated for $C_{14}H_{14}N_2O_4SNa$ 329.0572, found 329.0564.

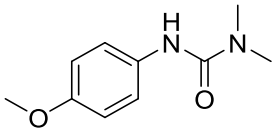
**Synthesis of 4-methyl-*N*-(4-(methylthio)phenyl)benzenesulfonamide**



The title compound was obtaining according to the general procedure **C** (0.5 *M*, 24 h, 50 °C), [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv), sulfonamide (1.2 equiv). The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexanes) to provide the desired compound as a white solid (34 mg, 47% yield, 91% brsm). Starting material was recovered (25 mg).

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.32 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 9 Hz, 1H), 6.99 (d, J = 9 Hz, 1H), 6.43 (br. s, 1H), 2.44 (s, 3H), 2.40 (s, 3H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 144.1, 136.2, 136.0, 133.8, 129.9, 127.8, 127.5, 123.1, 21.7, 16.3.
**IR (neat):** 3259, 3036, 2922, 1602, 1493, 1161, 1091, 814, 575 cm$^{-1}$.
**HRMS-ESI (*m/z*)** [M + Na]$^+$ calculated for $C_{14}H_{15}NO_2S_2Na$ 316.0442, found 316.0456.

**Synthesis of 3-(4-methoxyphenyl)-1,1-dimethylurea**

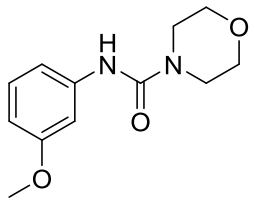


The title compound was obtained according to the general procedure **C** (0.5 *M*, 24 h, 50 °C, 0.25 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient 20-80% EtOAc/hexanes) to provide the desired compound as a white solid (20 mg, 41%). The product can additionally be recrystallized with toluene.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.28 (d, *J* = 9.6 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.16 (br s, 1H), 3.79 (s, 3H), 3.03 (s, 3H).

Ref: Houlden, C. E.; Bailey, C. D.; Ford, J. G.; Gagné, M. R. Lloyd-Jones, G. C.; Booker-Milburn, K. I. *J. Am. Chem. Soc.* **2008**, *130*, 10066-10067.

**Synthesis of *N*-(3-methoxyphenyl)morpholine-4-carboxamide**

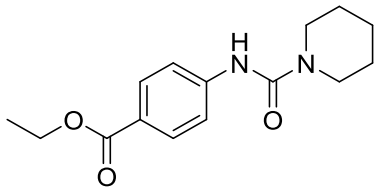


The title compound was obtained according to the general procedure **C** (0.5 *M*, 24 h, 50 °C, 0.25 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient 20 to 100% EtOAc/hexanes) to provide the desired compound as a white solid (29.5 mg, 50%). The product can additionally be recrystallized with toluene.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.19 (t, *J* = 8.5 Hz, 1H), 7.12-7.13 (m, 1H), 6.84-6.82 (m, 1H), 6.63-6.61 (m, 1H), 6.33 (br s, 1H), 3.81 (s, 3H), 3.75 (t, *J* = 4.5 Hz, 4H), 3.49 (t, *J* = 5 Hz, 4H).

Ref: Bolshon, Y.; Tomaszewski, M. J.; Santhakumar, V. *Tetrahedron Lett.* **2007**, *48*, 4925-4927.

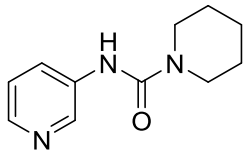
**Synthesis of Ethyl 4-(piperidine-1-carboxamido)benzoate**



The title compound was obtained according to the general procedure **C** (0.5 *M*, 24 h, 50 °C, 0.25 mmol), [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient 20 to 100% EtOAc/hexanes) to provide the desired compound as a white/yellow solid (47.5 mg, 69%). The product can additionally be recrystallized with toluene.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.98-7.95 (m, 2H), 7.46-7.43 (m, 2H), 6.65 (br s, 1H), 4.35 (q, *J* = 7 Hz, 2H), 3.47 (t, J = 5.5 Hz, 4H), 1.66-1.62 (m, 6H), 1.38 (t, *J* = 7.5 Hz, 3H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 166.6, 154.4, 143.9, 130.9, 124.5, 118.4, 60.8, 45.5, 25.9, 24.5, 14.5.
**IR (neat):** 3318, 3313, 2979, 2935, 1592, 1642, 1711, 1273, 852, 768 cm$^{-1}$.
**HRMS-ESI (*m/z*)** [M + Na]$^+$ calculated for $C_{15}H_{20}N_2O_3Na$ 399.1372, found 399.1366.

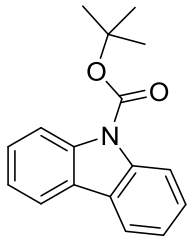
**Synthesis of *N*-(pyridin-3-yl)piperidine-1-carboxamide**



The title compound was obtained according to the general procedure **C** (0.5 *M*, 24 h, 50 °C, 0.25 mmol), [(π-allyl)PdCl]$_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv). The crude product was purified by silica gel column chromatography (eluent: gradient 20 to 100% EtOAc/hexanes followed by 5, 10% MeOH/DCM) to provide the desired compound as a white/yellow solid (18 mg, 35%). The product can additionally be recrystallized with toluene.

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$8.43 (br. s, 1H), 8.27 (br s, 1H), 7.25-7.23 (m, 1H), 6.43 (br s, 1H), 3.48 (t, J= 6 Hz, 4H), 1.68-1.61 (m, 6H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$154.7, 144.1, 141.2, **130.7, 128.5**, 127.3, 45.5, 25.9, 24.5.
The bolded peaks cannot be clearly determined, due to unknown inseparable impurity present. Nearby peaks could potentially be from the desired product.
**IR (neat):** 3286, 2924, 2853, 1641, 1534, 1424, 1394, 1255, 1023, 799, 708 cm$^{-1}$.
**HRMS-ESI (*m/z*)** [M + Na]$^+$ calculated for $C_{11}H_{15}N_3ONa$ 222.1113, found 222.1115.

### Synthesis of *t*-Butyl 9H-carbazole-9-carboxylate



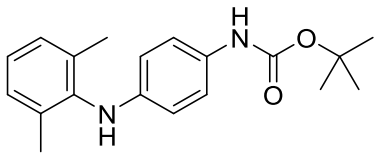
The title compound was obtained according to the general procedure **C** (0.5 *M*, 24 h, 50 °C, 0.25 mmol), $[(\pi\text{-allyl})PdCl]_2$ (2 mol %), cBRIDP (4 mol %), KOH (1.5 equiv), TIPSOH (1.5 equiv). The crude product was purified by silica gel column chromatography (eluent: EtOAc/hexanes) to provide the desired compound as a colorless/yellow oil (58.5 mg, 88% yield).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.33 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.48 (dt, *J* = 1, 7 Hz, 2H), 7.37 (m, 2H), 1.78 (s, 9H).

Ref: Tsang, W. C. P.; Munday, R. H.; Brasche, G.; Zheng, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *73*, 7603-7610.

## Tandem One-Pot Reactions

### Synthesis of *t*-butyl (4-((2,6-dimethylphenyl)amino)phenyl)carbamate

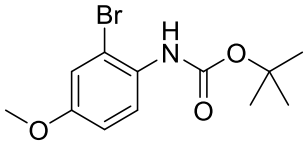


Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.05 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 M), and 1-bromo-4-iodobenzene (0.25 mmol). After being stirred vigorously at rt for 14 h $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), and KOH/TIPSOH (1.5 equiv) was quickly added to the vial. The vial was purged of oxygen with a positive flow of Ar. Via syringe, 2,6-dimethylaniline (1.2 equiv) was added and the reaction was then vigorously stirred in an oil bath at 50 °C until complete conversion was observed by TLC. The reaction mixture was diluted with $Et_2O$ and filtered through a pad of silica gel. The solvent was removed by rotary evaporation and purified by flash column chromatography (eluent: gradient 1

to 10% EtOAc/hexanes) to afford an off-white solid (50 mg, 65% yield). TLC: $R_f$ = 0.35 (20% EtOAc/hexanes).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.14-7.11 (m, 4H), 7.08-7.05(m, 1H), 6.48-6.45 (m, 2H), 6.25 (br. s, 1H), 5.11 (br s, 1H), 2.20 (s, 6H), 1.51 (s, 9H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 153.6, 142.7, 138.7, 135.7, 129.6, 128.7, 125.7, 121.3, 114.3, 28.6, 18.5.
**IR (neat):** 3363, 2976, 2926, 2862, 1698, 1513, 1225, 823, 731, 513 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{19}H_{24}N_2O_2Na$ 335.1735, found 335.1722.

## Synthesis of *t*-butyl (2-bromo-4-methoxyphenyl)carbamate

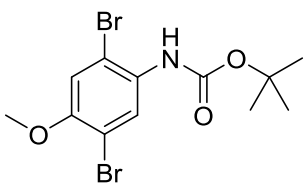



Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.05 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 M), and 1-bromo-4-iodobenzene (0.25 mmol). After being stirred vigorously at rt for 14 h, $Br_2$ (1.4 equiv) was added dropwise via syringe. The reaction was allowed to stir for 3.5 h and then quenched with $Na_2SO_3$ (sat. aq.). The reaction mixture was transferred to a sep. funnel with EtOAc, washed with water, and dried with brine and anhydrous $MgSO_4$. The solvent was removed via rotary evaporation. The crude mixture was purified by column chromatography (eluent: 2% EtOAc/hexanes) to afford a colorless to a slightly red oil (84 mg, 99% yield). The yield is based on the combination of both products.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.96 (br. d, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 6.86 (dd, *J* = 3.0, 9 Hz), 1H), 6.74 (br s, 1H) 3.78 (s, 3H), 1.53 (s, 9H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 155.8, 152.0, 129.9, 122.0 117.7, 115.6, 114.2, 81.0, 55.9, 28.5.

Ref: Jensen, T.; Pedersen, H.; Bang-Anderson, B.; Madsen, R.; Jørgensen, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 888-890.

## Synthesis of *t*-butyl (2,5-dibromo-4-methoxyphenyl)carbamate

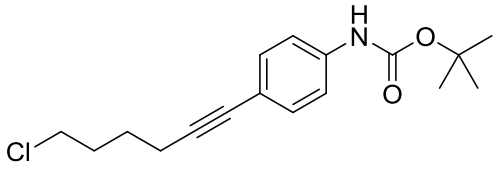


Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.05 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 M), and 1-bromo-4-iodobenzene (0.25 mmol). After being stirred vigorously at rt for 14 h, $Br_2$ (1.4 equiv) was added dropwise via syringe. The reaction was allowed to stir for 3.5 h and then quenched with $Na_2SO_3$ (sat. aq.). The reaction mixture was transferred to a sep. funnel with EtOAc, washed with water, and dried with brine and anhydrous $MgSO_4$. The solvent was removed via rotary evaporation. The crude mixture was purified by column chromatography (eluent: 2% EtOAc/hexanes) to afford a colorless to a slightly red oil (84 mg, 99% yield). The yield is based on the combination of both products.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 8.36 (br. s, 1H), 7.03 (s, 1H), 6.74 (br. s, 1H), 3.86 (s, 3H), 1.54 (s, 9H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 152.6, 151.1, 130.7, 124.1, 111.7, 111.5, 81.5, 56.9, 28.5.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{12}H_{15}Br_2NO_3Na$ 401.9316, found 401.9322.

Note: The bromination yielded two products that were inseparable by column chromatography. The isomers were distinguished by virtue of a previously reported spectrum of *t*-butyl (2-bromo-4-methoxyphenyl)carbamate. The $^1$H and $^{13}$C spectra contain both isomers. The yield of each was determined by the total mass of the isolated product and the ratio of the singlets in the $^1$H NMR spectrum at 3.86 and 3.78 ppm.

### Synthesis of *t*-butyl (4-(6-chlorohex-1-yn-1-yl)phenyl)carbamate

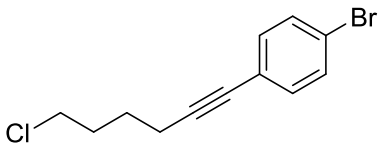



Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.05 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 M), and 1-bromo-4-iodobenzene (0.25 mmol). After being stirred vigorously at rt for 14 h, the crude reaction mixture was filtered through a pad of silica gel with $Et_2O$. The solvent was removed high vacuum pump. To the vial $Pd(OAc)_2$ (3 mol %), cBRIBP (6 mol %), $Et_3N$ (3 equiv), and 6-chloro-1-hexyne (1.1 equiv) was added to the vial, dissolved in 2 wt % TPGS-750-M and stirred for 16 h at 50 °C . The mixture was diluted with EtOAc and filtered through a pad of silica gel. The solvent was removed and the crude mixture was purified by flash column chromatography EtOAc/hex (gradient: 0% to 8%) to afford a colorless oil (65.4 mg, 85% yield).

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.29-7.23 (m, 4H), 6.47 (br. s, 1H), 3.57 (t, J = 6.5 Hz), 2.41 (t, J = 7.0 Hz, 2H), 1.92 (p, J = 7.0 Hz, 2H), 1.72 (t, J = 7.0 Hz, 2H), 1.48 (s, 9H);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 152.6, 138.0, 132.5, 118.3, 118.2, 88.5, 81.1, 44.8, 31.8, 28.5, 26.1, 18.9;
**IR (neat):** 3404, 3331, 2978, 2933, 1699, 1728, 1517, 1153, 1053, 835, 770, 533 521 $cm^{-1}$.
**HRMS-ESI (*m/z*)** $[M + Na]^+$ calculated for $C_{17}H_{22}ClNO_2Na$ 330.1237, found 330.1234.

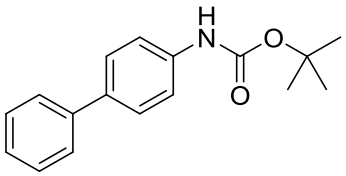
*Note: Reversing the order works as well (Sonogashira then amination). NaO-t-Bu can be used as the base for the amination setup, but leads to a lower extent of conversion. TIPSOH is difficult to separate from the desired final product, so using NaO-t-Bu might be preferred.*

**Intermediate:**



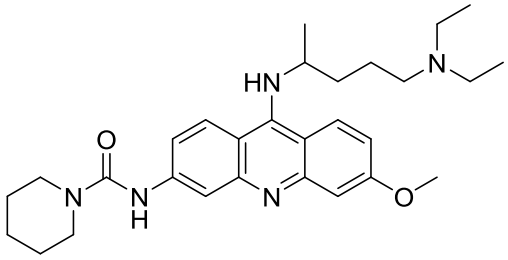

**$^1$H NMR (600 MHz, $CDCl_3$):** $\delta$ 7.42 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.46 (t, *J* = 6.6 Hz, 2H), 1.97 (p, *J* = 6.6 Hz, 2H), 1.77 (p, *J* = 7.2 Hz, 2H).
**$^{13}$C NMR (150 MHz, $CDCl_3$):** $\delta$ 133.2, 131.6, 122.9, 122.0, 90.8, 80.4, 44.7, 31.8, 26.0, 18.9.
**IR (neat):** 2928, 2866, 2236, 1485, 1071, 1011, 724, 521 $cm^{-1}$.
**HRMS-EI (*m/z*)** $[M]^+$ calculated for $C_{12}H_{12}BrCl$ 269.9811, found 269.9823.

**Synthesis of *t*-butyl [1,1'-biphenyl]-4-ylcarbamate**




Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $Pd(dtbpf)Cl_2$ (2 mol %), phenylboronic acid (1.1 equiv), and KOH (3 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 *M*), and 1-bromo-4-iodobenzene (0.25 mmol). After being stirred vigorously at rt for 20 h, $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.2 equiv) was added to the vial. The mixture was stirred for 20 h at 50 °C. This afforded the desired product (42 mg, 63% yield). See page 9 for work up and purification details.

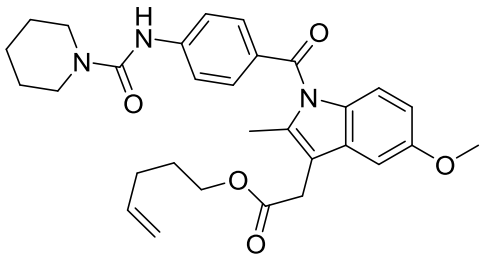
**Synthesis of *N*-(9-((5-(diethylamino)pentan-2-yl)amino)-6-methoxyacridin-3-yl)piperidine-1-carboxamide**




Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (3.5 equiv), and the urea (1.2 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 *M*), and quinacrine hydrochloride (0.25 mmol). The reaction mixture was then vigorously stirred in an oil bath at 50 °C for 24 h. The vial was then removed from the oil bath and allowed to cool to room temperature. The mixture was diluted with brine (~3 mL), washed with $NaHCO_3$ (~5 mL, sat. aq.), and extracted with EtOAc (~25 mL, each, 5 times). The solvent was removed via rotary evaporation. The crude mixture was purified by column chromatography affording a bright yellow oil (102 mg, 96% yield). Occasional peak broadening was observed on the $^1$H NMR spectrum after column chromatography which can be fixed by a $NaHCO_3$ (sat. aq.) wash.

**TLC:** 10% MeOH/DCM, with 2% $Et_3N$, $R_f$ = 0.5, bright yellow spot
**Purification (eluent):** gradient of 0.5% to 10% MeOH/DCM, with 2% $Et_3N$
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.92 (br t, *J* = 9.0 Hz, 2H), 7.85 (br d, *J* = 8.0 Hz, 1H), 7.68 (br s, 1H), 7.31 (br d, *J* = 8.5 Hz, 1H), 7.30-7.26 (m, 2H), 4.61 (br s, 0.5 H), 4.03 (br d, *J* = 5.5 Hz, 1H), 3.95 (s, 3H), 3.48 (br s, 4H), 3.1 (br s, 0.5H), 2.46 (q, *J* = 7.5 Hz, 4H), 2.38 (t, *J* = 6.0 Hz, 2H), 1.75-1.50 (m, 10 H), 1.28 (d, *J* = 6.5 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 6H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 155.4, 155.2, 149.3, 146.4, 148.6, 141.4, 130.6, 124.0, 122.9, 120.3, 118.6, 115.8, 114.7, 100.1 55.9, 55.6, 52.9, 47.0, 45.8, 37.1, 25.8, 24.5, 24.2, 22.3, 11.7.
**IR (neat):** 3320, 2965, 2932, 2854, 1643, 1477, 1643, 1423, 1227, 1186, 1031, 816 cm$^{-1}$.
**HRMS-EI (*m/z*)** $[M]^+$ calculated for $C_{29}H_{41}N_5O_2$ 491.3260, found 491.326

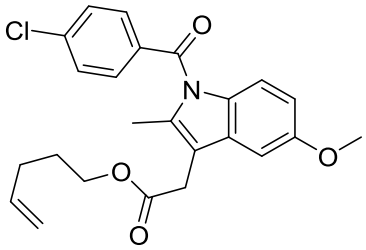
**Synthesis of pent-4-en-1-yl 2-(5-methoxy-2-methyl-1-(4-(piperidine-1-carboxamido)benzoyl)-1*H*-indol-3-yl)acetate**



Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol %), cBRIDP (2 mol %), KOH/TIPSOH (3.5 equiv), and the urea (1.2 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 *M*), and pentenyl ester of indomethacine (0.25 mmol). The reaction mixture was then vigorously stirred in an oil bath at 50 °C for 24 h. The vial was then removed from the oil bath and allowed to cool to rt. The reaction mixture was diluted with EtOAc and filtered through a plug of silica gel. The solvent was removed via rotary evaporation. The crude mixture was purified by column chromatography affording a colorless semi-solid (85 mg, 66% yield). Starting material (10 mg, 73% brsm) was also recovered.

**TLC:** 30% EtOAc/hexanes, $R_f$ = 0.2, UV active, stains purple with ninhydrin
**Purification (eluent):** gradient 20 to 100% EtOAc/hexanes
**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.65 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 1.8 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.82 (br s, 1H), 6.64 (dd, *J* = 2.4, 7.5 Hz, 1H), 5.79-5.72(m, 1H), 4.98-4.95 (m, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.67 (s, 2H), 3.48 (t, *J* = 5.4 Hz, 4H), 2.40 (s, 3H), 2.07 (q, *J* = 6.6 Hz, 2H), 1.72 (p, *J* = 6.6 Hz, 2H), 1.70-1.60 (m, 6H).
**$^{13}$C NMR (125 MHz, $CDCl_3$):** $\delta$ 171.3, 169.1, 155.9, 154.3, 144.3, 137.5, 136.2, 131.6, 131.3, 130.5, 129.0, 118.7, 115.5, 115.0, 112.0, 111.6, 101.2, 64.5, 55.9, 45.5, 30.64, 30.1, 28.0, 25.9, 24.4, 13.3.
**IR (neat):** 3354, 2939, 2855, 1731, 1641, 1592, 1477, 1422, 1324, 1225, 1037, 922, 850, 761, 684, 532 $cm^{-1}$.
**HRMS-EI (*m/z*)** $[M]^+$ calculated for $C_{30}H_{35}N_3O_5$ 517.2577, found 517.2580.

**Synthesis of pent-4-en-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate**




A 25 mL round-bottom flask containing a magnetic stir bar was charged with indomethacin (1.07 g, 2.98 mmol), EDCI (952 mg, 4.97 mmol), and DMAP (138 mg, 1.13 mmol). Under a positive flow of Ar, $Et_3N$ (0.50 mL, 3.6 mmol), $CH_2Cl_2$ (20 mL), and finally 4-pentenol (0.80 mL, 7.7 mmol) were each introduced via syringe and the reaction was allowed to stir at rt for ~48 h. The mixture was diluted with $Et_2O$ and transferred to a separatory funnel. The mixture was washed water, $NH_4Cl$ (sat. aq., twice), $NaHCO_3$ (sat. aq., twice), followed by brine. The solution was dried over anhydrous $MgSO_4$, filtered, and concentrated via rotary evaporation. The oily residue was purified by flash chromatography eluting with 15% EtOAc/hexanes to afford the ester (1.07 g, 84%) as a yellow oil. The $^1$H NMR matched that previously reported in the literature.

**$^1$H NMR (500 MHz, $CDCl_3$):** $\delta$ 7.68-7.65 (m, 2H), 7.49-7.47 (m, 2H), 6.98 (d, J = 2.5 Hz, 1H), 6.88 (d, J = 9.5 Hz, 1H), 6.68 (dd, J = 2.5, 9.0 Hz, 1H), 5.89-5.72 (m, 1H), 5.09-4.96 (m, 2H), 4.12 (t, J = 7.0 Hz, 2H), 3.85 (s, 3H), 3.67 (s, 2H), 2.40 (s, 3H), 2.08 (q, J = 7.0 Hz, 2H), 1.73 (p, J = 6.5 Hz, 2H).

Ref: Lipshutz, B. H.; Peterson, T. B.; Abela, A. *Org. Lett.* **2008**, *10*, 1333-1336.

# IV. E Factor and Recycle Study

Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (2.0 mol %), cBRIDP (4 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.2 equiv). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (1.0 mL, 1.0 *M*), and 2-bromo-1-methyl-4-nitrobenzene (1.00 mmol). The reaction was allowed to stir at rt for 20 h. The product was extracted with EtOAc: 350 μL + 350 μL. To ease separation a centrifuge can be used. The organic solvent was evaporated via rotary evaporation. The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (232 mg, 96% yield).

*Re-use of surfactant solution*:

Additional $[(\pi\text{-allyl})PdCl]_2$ (2.0 mol %), cBRIDP (4 mol %), TIPSOH (1.5 equiv), carbamate (1.2 equiv), and 2-bromo-1-methyl-4-nitrobenzene (1.00 mmol) were added to the flask. KOH (2 equiv) was added portion-wise over the course of the reaction (0.5 equiv at 3 h intervals) to achieve full conversion. The reaction was allowed to stir at rt for 20 h. The product was extracted with EtOAc: 350 μL + 350 μL. The organic solvent was evaporated via rotary evaporation The crude product was purified by silica gel column chromatography (eluent: gradient from 1 to 10% EtOAc/hexanes) to provide the desired compound as a white powder (218 mg, 94% yield).

**E Factor calculations:**

Note: Density of each liquid at 25 °C; ethyl acetate 0.897 g/mL; water = 1.00 g/mL.

*Water NOT included as waste*

Solvents:
700 μL EtOAc (628 mg)

first-cycle: $\frac{0.628 \text{ g waste}}{0.232 \text{ g product}} = 2.7$ E Factor

second-cycle: $\frac{0.628 \text{ g waste}}{0.218 \text{ g product}} = 2.9$ E Factor

*Water included as waste*

Solvents:
1 mL $H_2O$ (1 g)
700 μL EtOAc (628 mg)

first-cycle: $\frac{1.628 \text{ g waste}}{0.232 \text{ g product}} = 7.0$ E Factor

second-cycle: $\frac{1.628 \text{ g waste}}{0.218 \text{ g product}} = 7.5$ E Factor

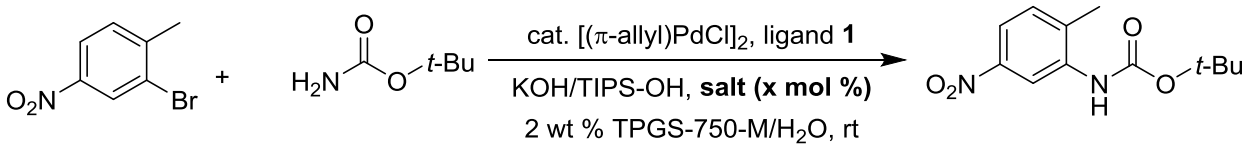
# V. Salt Additive Procedure and Additional Experimental Data

General Procedure:

Inside a dry box, a flame-dried 5 mL microwave vial equipped with a stir bar, fitted with a rubber septum and cooled under an Ar atmosphere was sequentially charged with $[(\pi\text{-allyl})PdCl]_2$ (2.0 mol %), cBRIDP (4 mol %), KOH/TIPSOH (1.5 equiv), and the carbamate (1.2 equiv). ). Outside the dry box, under a positive flow of Ar were sequentially added *via* syringe the 2 wt % TPGS-750-M/$H_2O$ solution (0.5 mL, 0.5 *M*), KOH (5-100 mol %), and the aryl bromide (0.25 mmol). The reaction was allowed to stir at rt or elevated temperatures until complete. The mixture was diluted with EtOAc and filtered through a pad of silica gel. The solvent was removed and the crude mixture was purified by column chromatography (eluent: EtOAc/hexanes) to afford the desired product.

*Note: The observed acceleration happened with a range of KBr loading (5-100 mol %). With some substrates, however, reaction rates were reduced when exposed to these conditions.*

Additional experiments:




| salt | mol % | % conv. (time, h) |
|---|---|---|
| NaBr | 50 | 55% (7.5 h) |
| LiBr | 50 | 80% (7.5 h) |
| CsF | 50 | 69% (7.5 h) |
| KF | 5 | 92% (6 h) |
| KBr | 5 | 95% (6 h) |
| KBr | 50 | >99% (4 h) |
| KBr | 100 | >99% (4 h) |

# VI. DLS Measurement

Sample Preparation:

Each sample was prepared in a 1 dram vial equipped with a stir bar. The amount of KOH and KBr is based on the amount employed on a 0.5 mmol reaction. A total of 42 mg of KOH was added to each vial, aside from the blank, along with 1 mL of 2 wt % TPGS-750-M/ $H_2O$. The respective amount (mol %) of KBr was added to each vial and stirred for several hours. Before analysis each solution was filtered through a Whatman 0.2 μm PTFE filter to remove trace dust particles.

Diameter of micelle:
Containing KOH and 0 mol % KBr: 55 and 212 nm
Containing KOH and 5 mol % KBr: 142 nm
Containing KOH and 20 mol % KBr: 220 nm
Containing KOH and 35 mol % KBr: 142 nm
Containing KOH and 50 mol % KBr: 79 and 295 nm
Containing KOH and 100 mol % KBr: 106 nm

# Size Distribution Report by Intensity

*v2.0*



## Sample Details

**Sample Name:** TPGS-750-M_and_KOH 3

**SOP Name:** micelles.sop

**General Notes:**

| | | | |
|---|---|---|---|
| **File Name:** | micelles.dts | **Dispersant Name:** | Water |
| **Record Number:** | 248 | **Dispersant RI:** | 1.330 |
| **Material RI:** | 1.33 | **Viscosity (cP):** | 1.0031 |
| **Material Absorbtion:** | 0.00 | **Measurement Date and Time:** | Thursday, March 14, 2013 1:... |

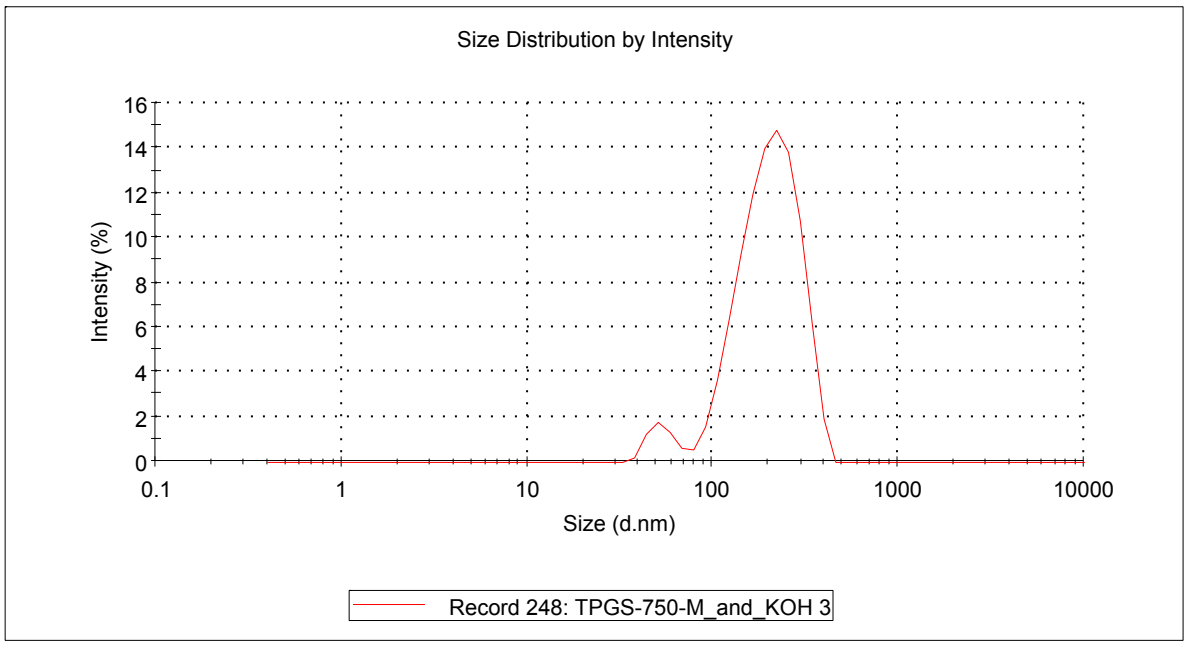
## System

| | | | |
|---|---|---|---|
| **Temperature (°C):** | 20.0 | **Duration Used (s):** | 10 |
| **Count Rate (kcps):** | 104.7 | **Measurement Position (mm):** | 1.25 |
| **Cell Description:** | Low volume disposable sizing ... | **Attenuator:** | 3 |

## Results

| | | | Diam. (nm) | % Intensity | Width (nm) |
|---|---|---|---|---|---|
| **Z-Average (d.nm):** | 309.5 | **Peak 1:** | 212.2 | 94.3 | 70.89 |
| **PdI:** | 0.639 | **Peak 2:** | 55.24 | 5.7 | 10.92 |
| **Intercept:** | 0.967 | **Peak 3:** | 0.000 | 0.0 | 0.000 |

**Result quality :** **Refer to quality report**



# Size Distribution Report by Intensity

*v2.0*



## Sample Details

**Sample Name:** TPGS-750-M_and_KOH_100mol_per_KBr 2

**SOP Name:** micelles.sop

**General Notes:**

| | | | |
|---|---|---|---|
| **File Name:** | micelles.dts | **Dispersant Name:** | Water |
| **Record Number:** | 271 | **Dispersant RI:** | 1.330 |
| **Material RI:** | 1.33 | **Viscosity (cP):** | 1.0031 |
| **Material Absorbtion:** | 0.00 | **Measurement Date and Time:** | Thursday, March 14, 2013 3:... |

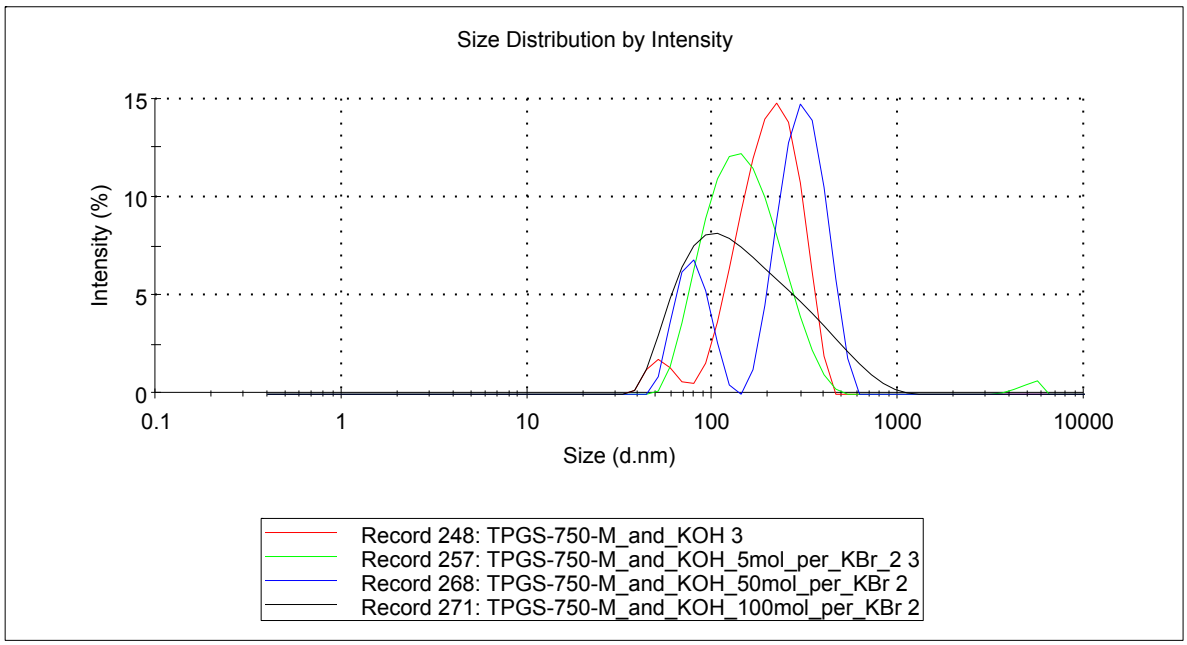
## System

| | | | |
|---|---|---|---|
| **Temperature (°C):** | 20.0 | **Duration Used (s):** | 60 |
| **Count Rate (kcps):** | 294.8 | **Measurement Position (mm):** | 4.65 |
| **Cell Description:** | Low volume disposable sizing ... | **Attenuator:** | 8 |

## Results

| | | | Diam. (nm) | % Intensity | Width (nm) |
|---|---|---|---|---|---|
| **Z-Average (d.nm):** | 124.6 | **Peak 1:** | 191.5 | 100.0 | 151.4 |
| **PdI:** | 0.258 | **Peak 2:** | 0.000 | 0.0 | 0.000 |
| **Intercept:** | 0.969 | **Peak 3:** | 0.000 | 0.0 | 0.000 |

**Result quality :** Good



# Size Distribution Report by Intensity

*v2.0*



## Sample Details

**Sample Name:** TPGS-750-M_and_KOH_35mol_per_KBr2 3

**SOP Name:** micelles.sop

**General Notes:**

| | | | |
|---|---|---|---|
| **File Name:** | micelles.dts | **Dispersant Name:** | Water |
| **Record Number:** | 275 | **Dispersant RI:** | 1.330 |
| **Material RI:** | 1.33 | **Viscosity (cP):** | 1.0031 |
| **Material Absorbtion:** | 0.00 | **Measurement Date and Time:** | Thursday, March 14, 2013 3:... |

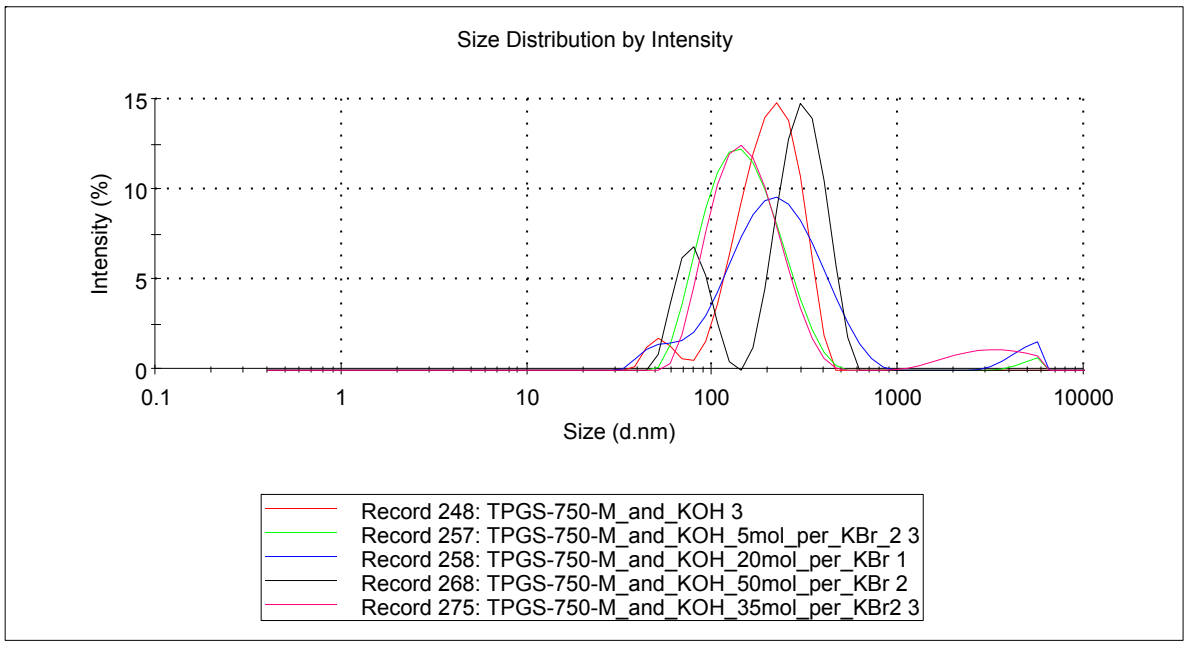
## System

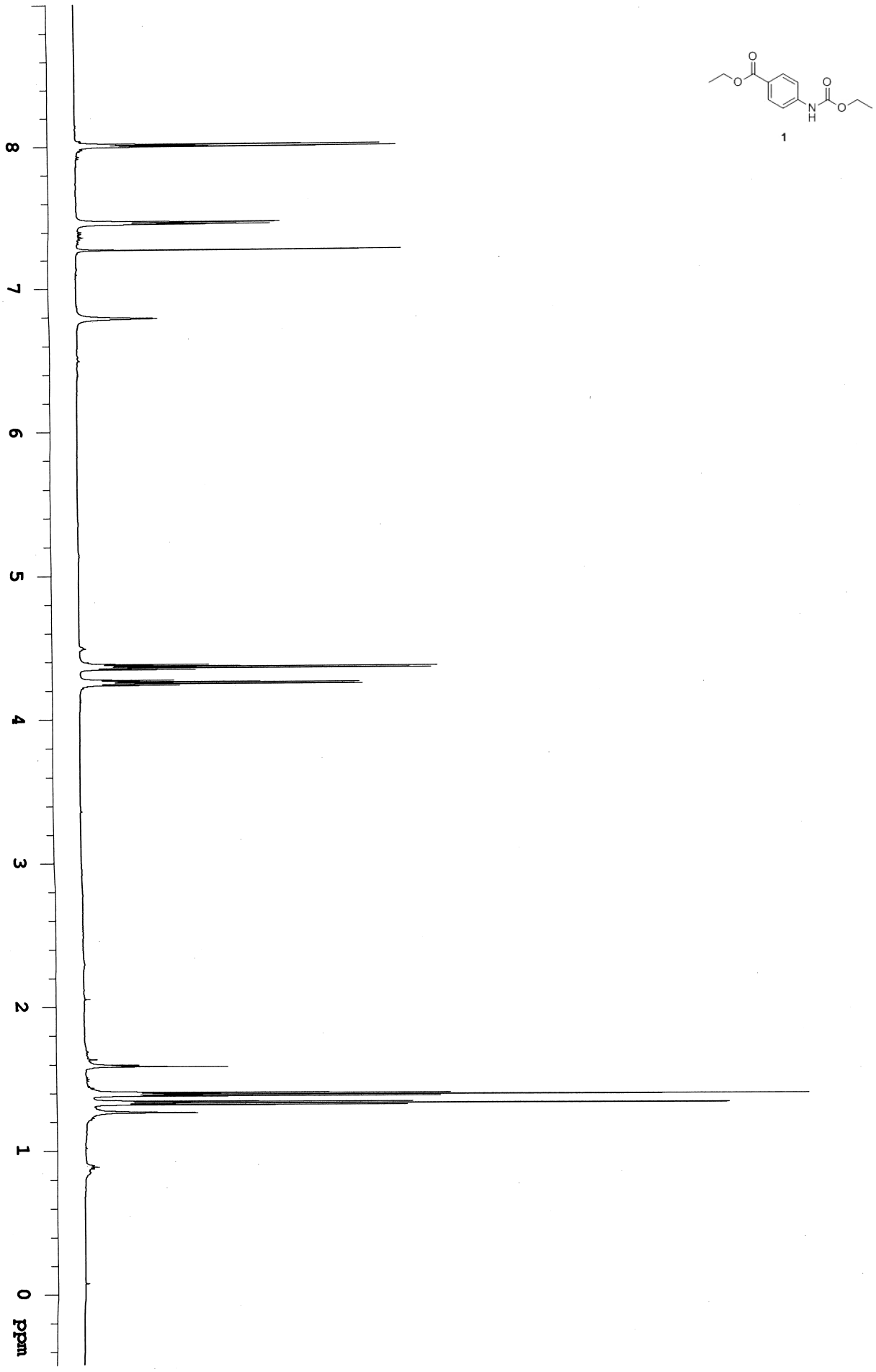
| | | | |
|---|---|---|---|
| **Temperature (°C):** | 20.0 | **Duration Used (s):** | 60 |
| **Count Rate (kcps):** | 307.3 | **Measurement Position (mm):** | 4.65 |
| **Cell Description:** | Low volume disposable sizing ... | **Attenuator:** | 9 |

## Results

| | | | Diam. (nm) | % Intensity | Width (nm) |
|---|---|---|---|---|---|
| **Z-Average (d.nm):** | 149.7 | **Peak 1:** | 160.0 | 90.6 | 66.13 |
| **PdI:** | 0.264 | **Peak 2:** | 3174 | 9.4 | 1241 |
| **Intercept:** | 0.951 | **Peak 3:** | 0.000 | 0.0 | 0.000 |

**Result quality :** Good









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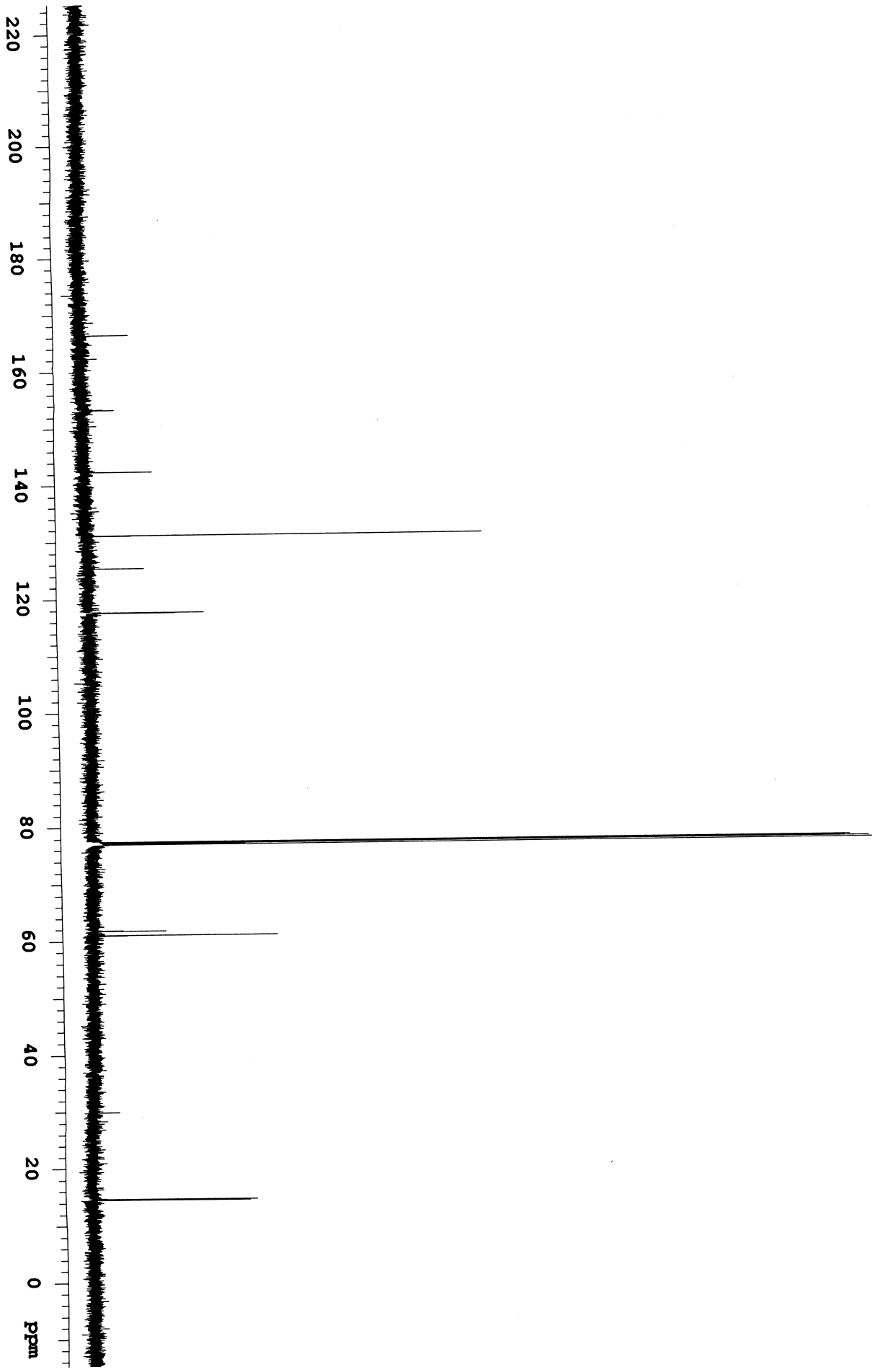

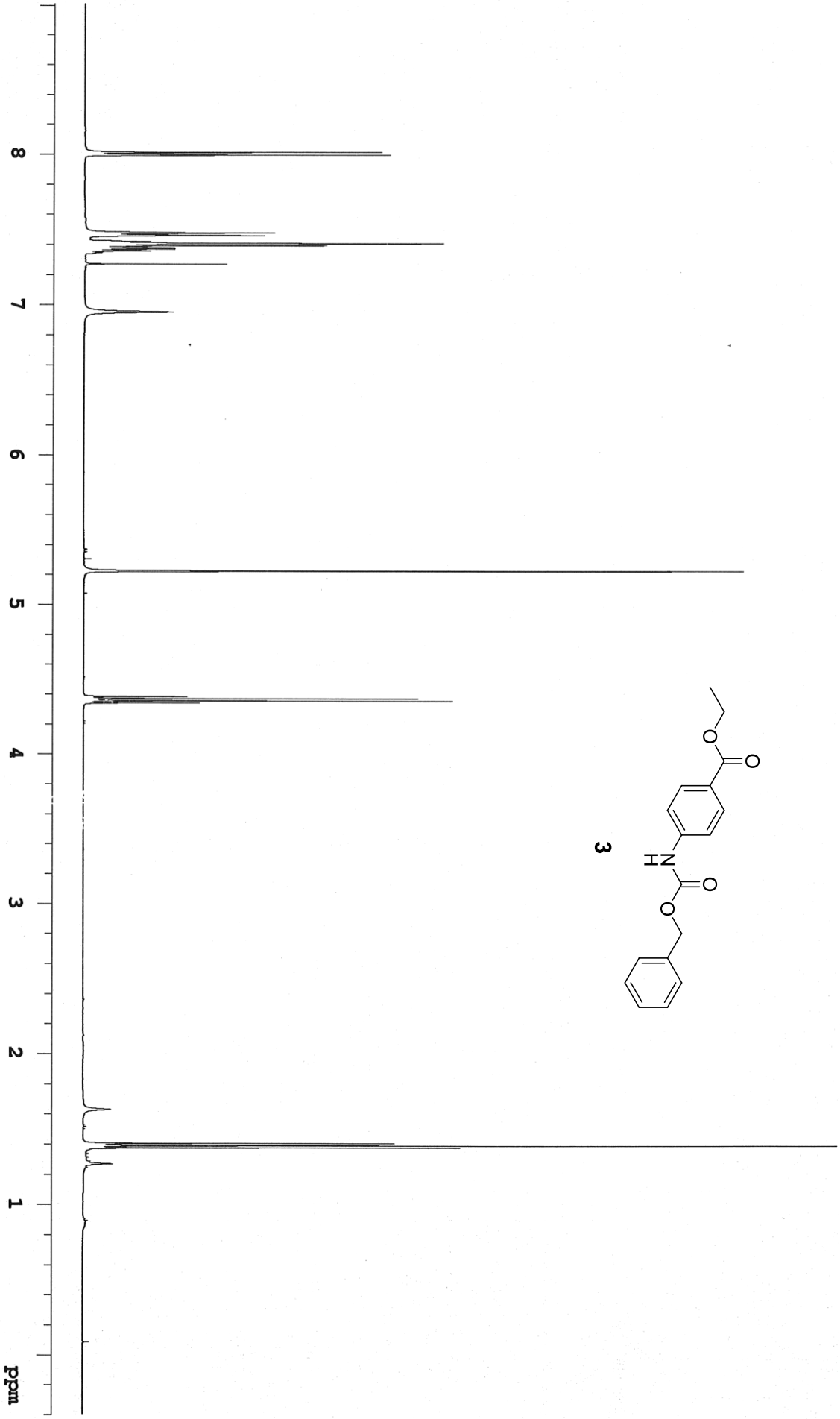

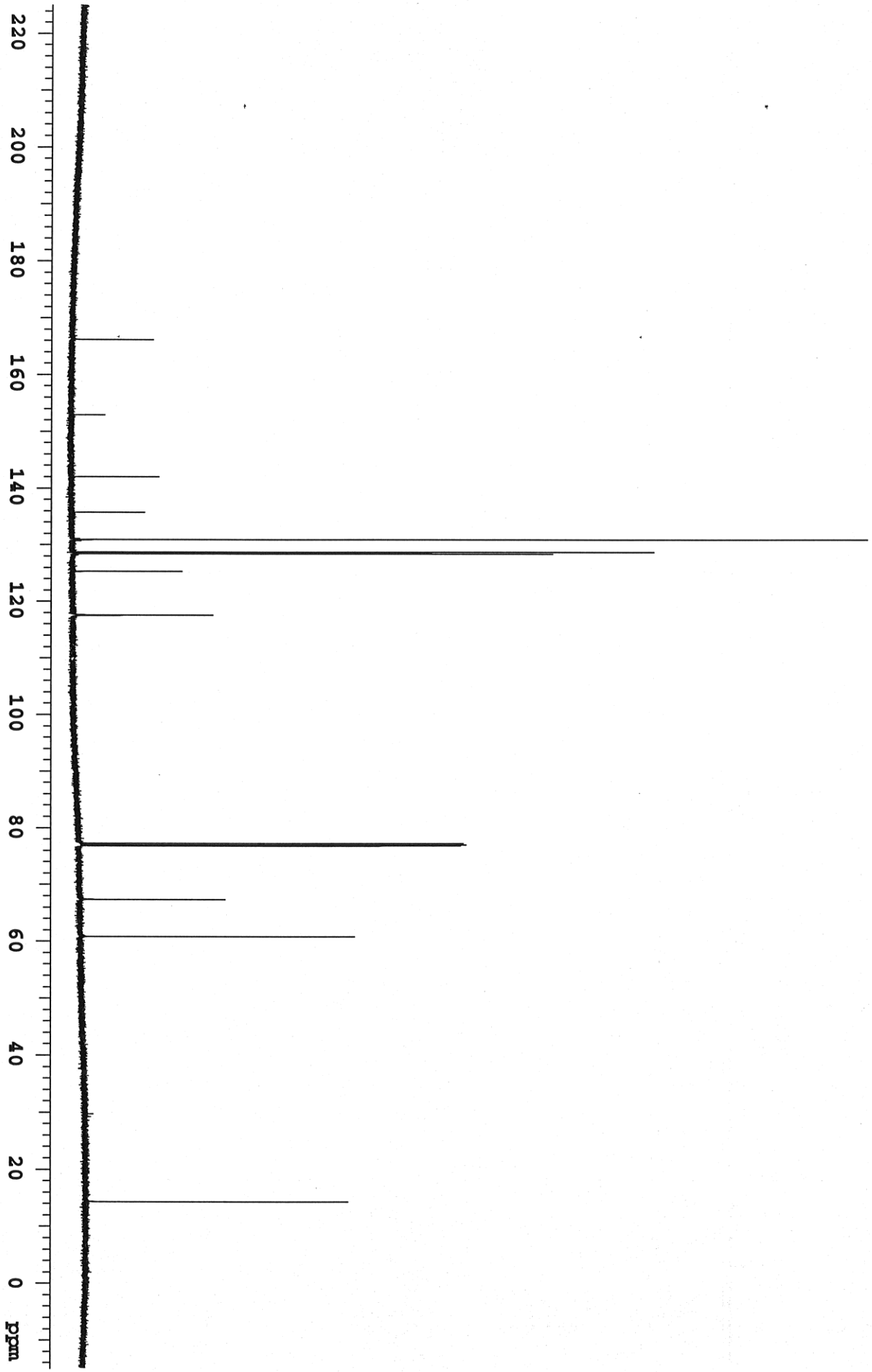

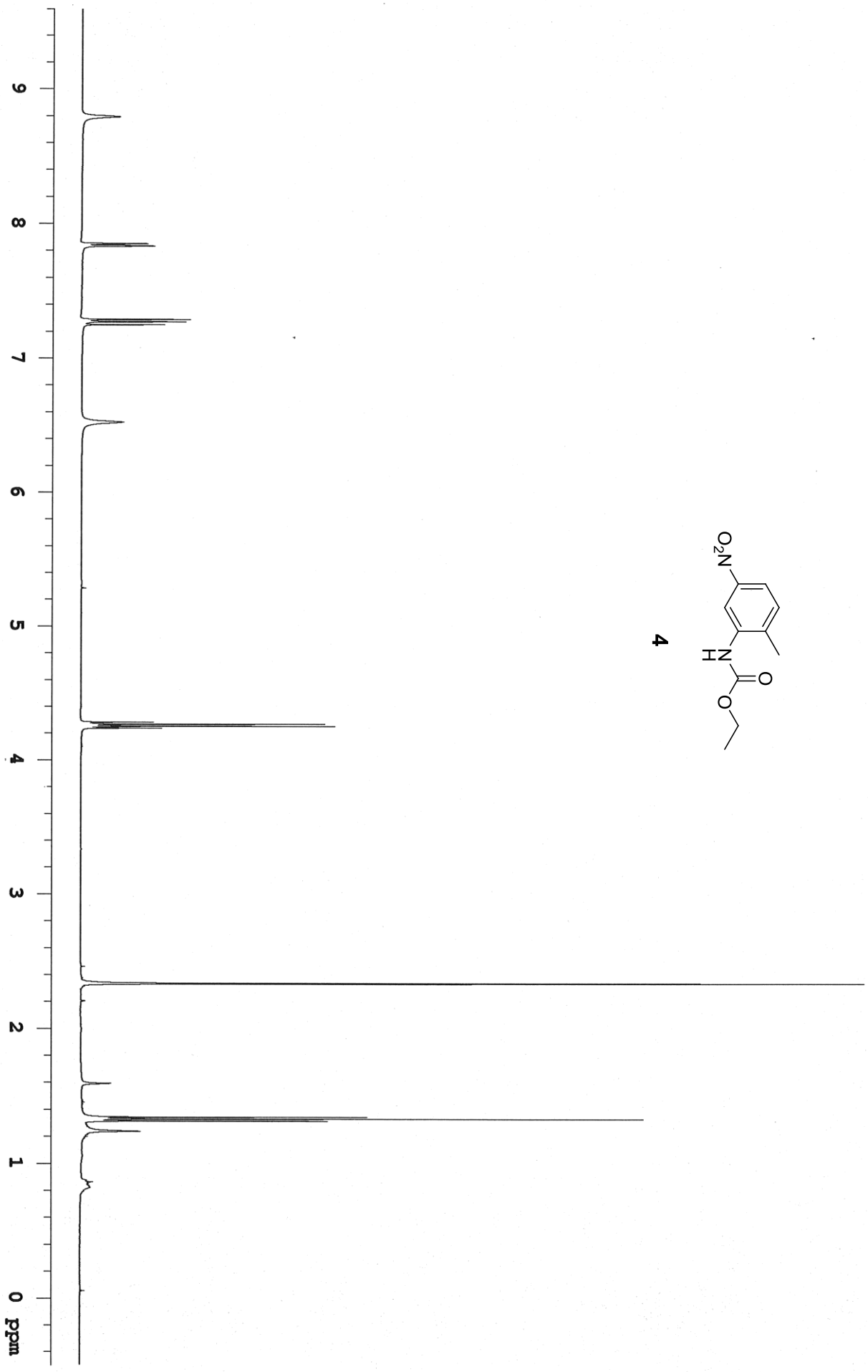


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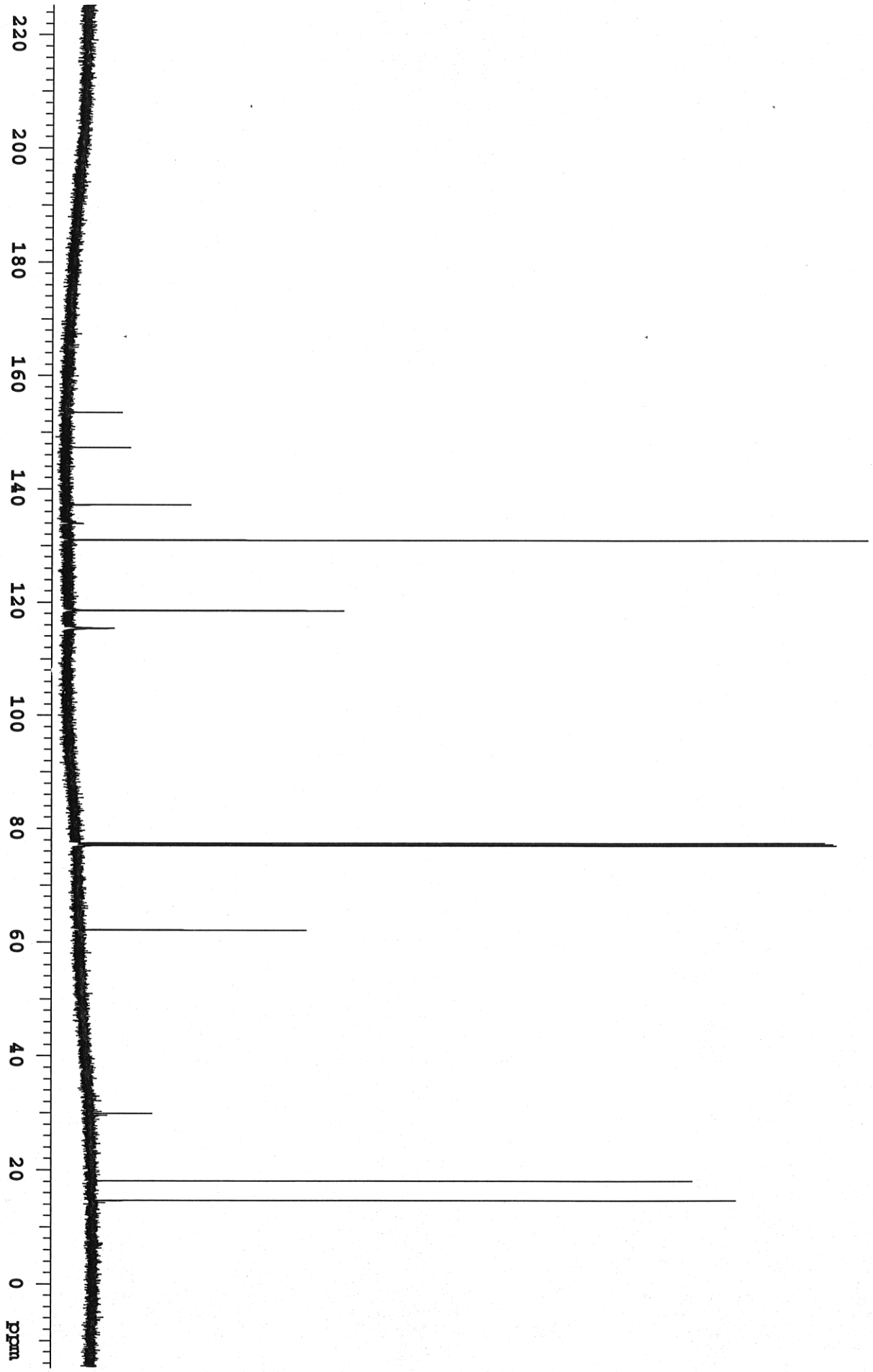

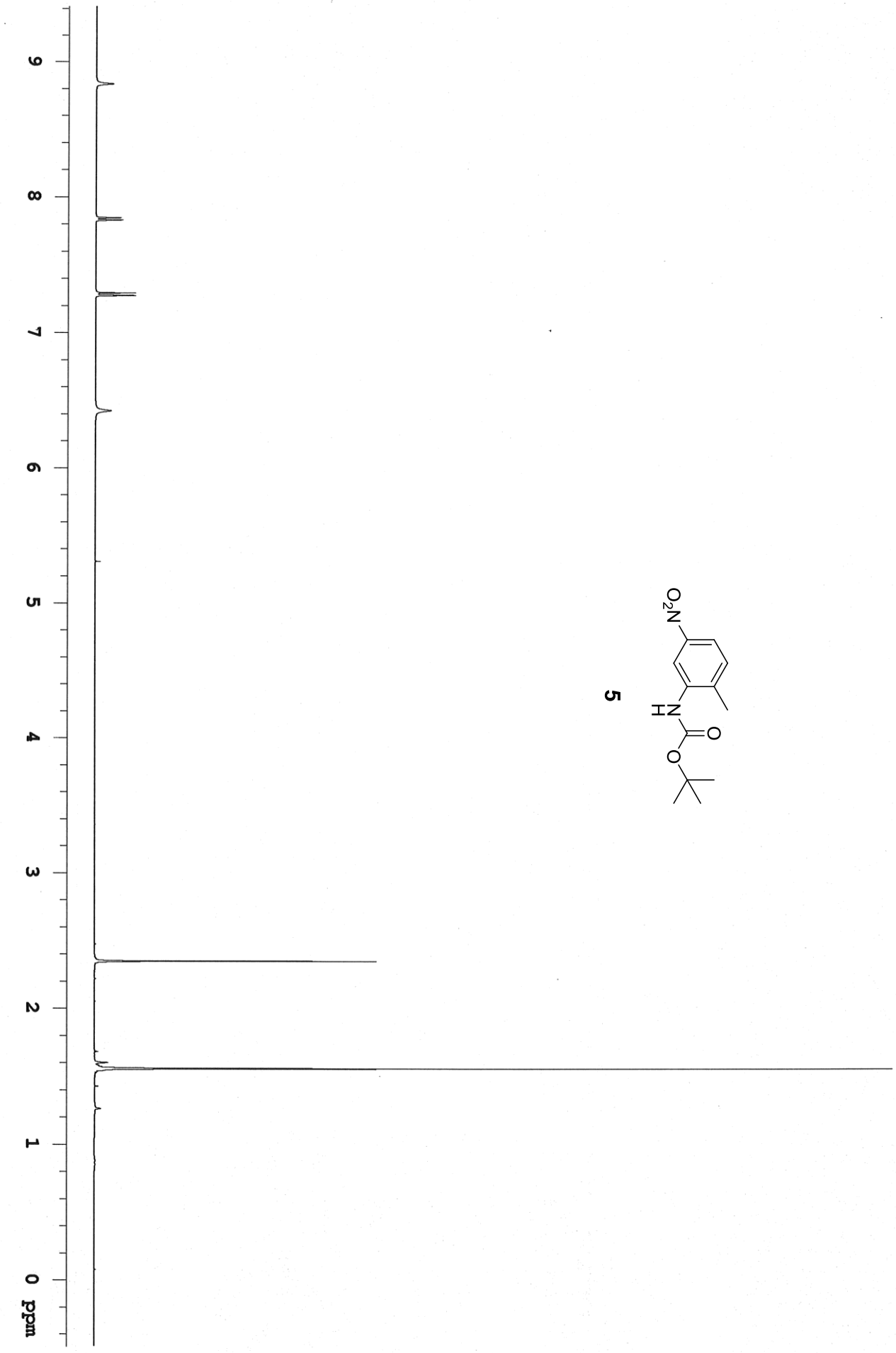





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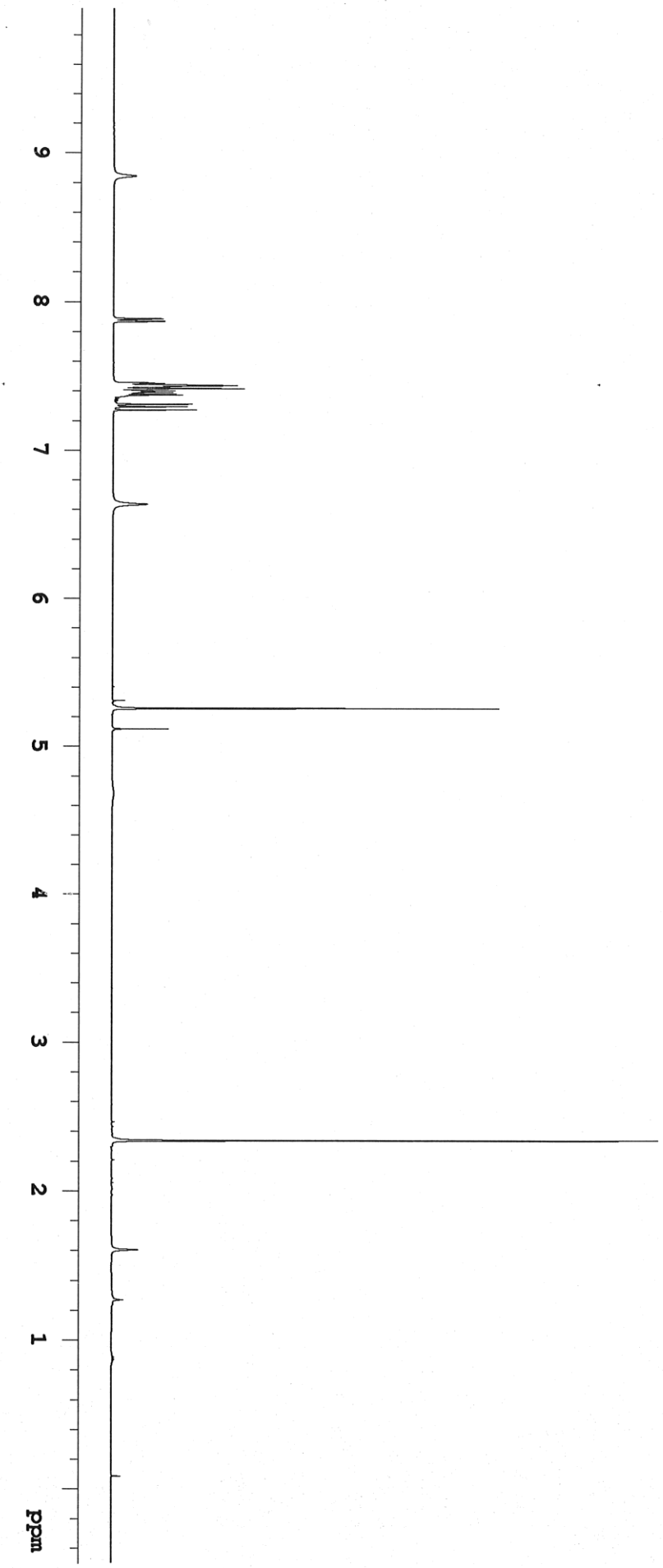


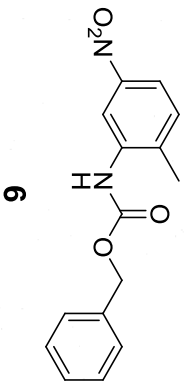


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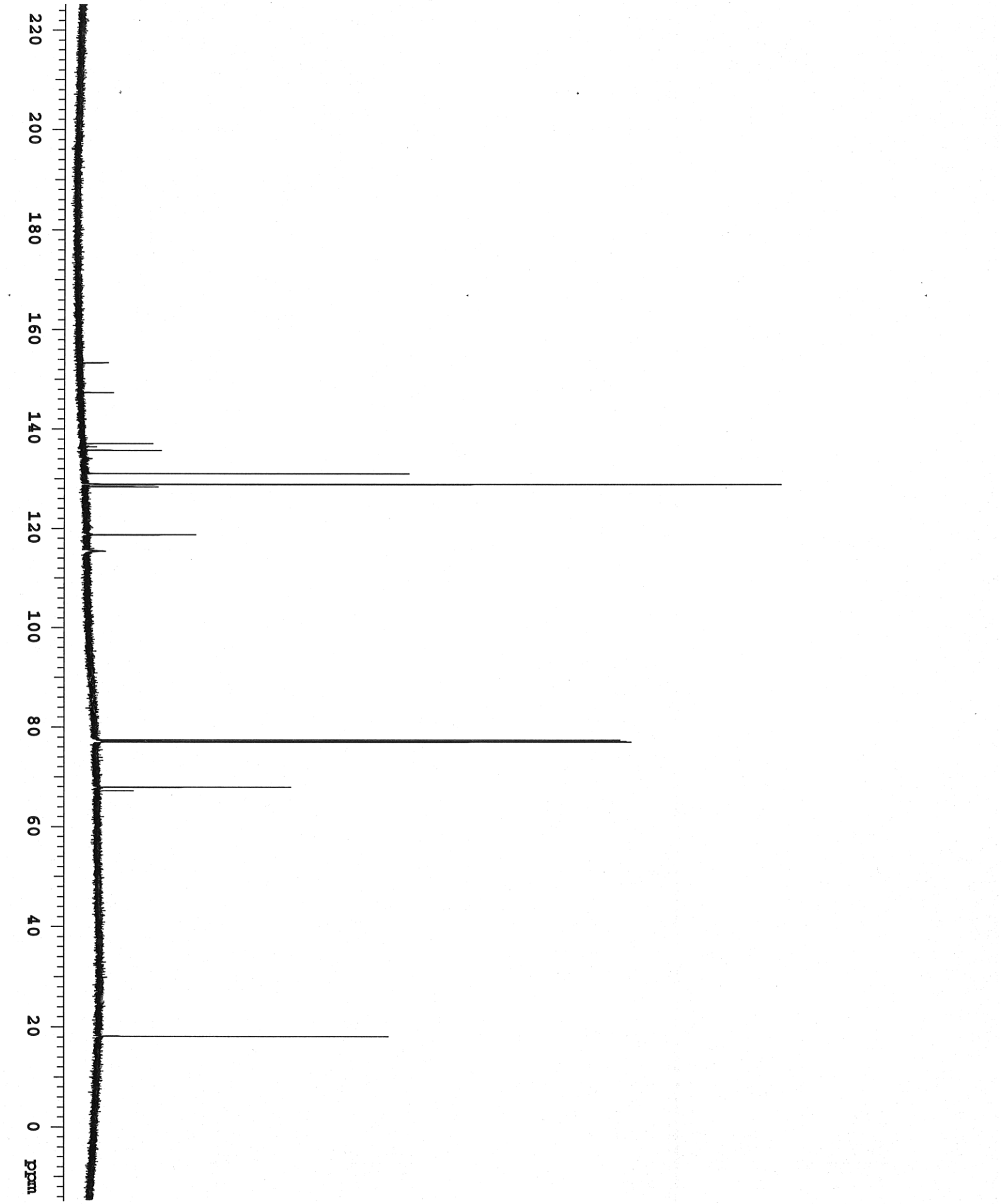

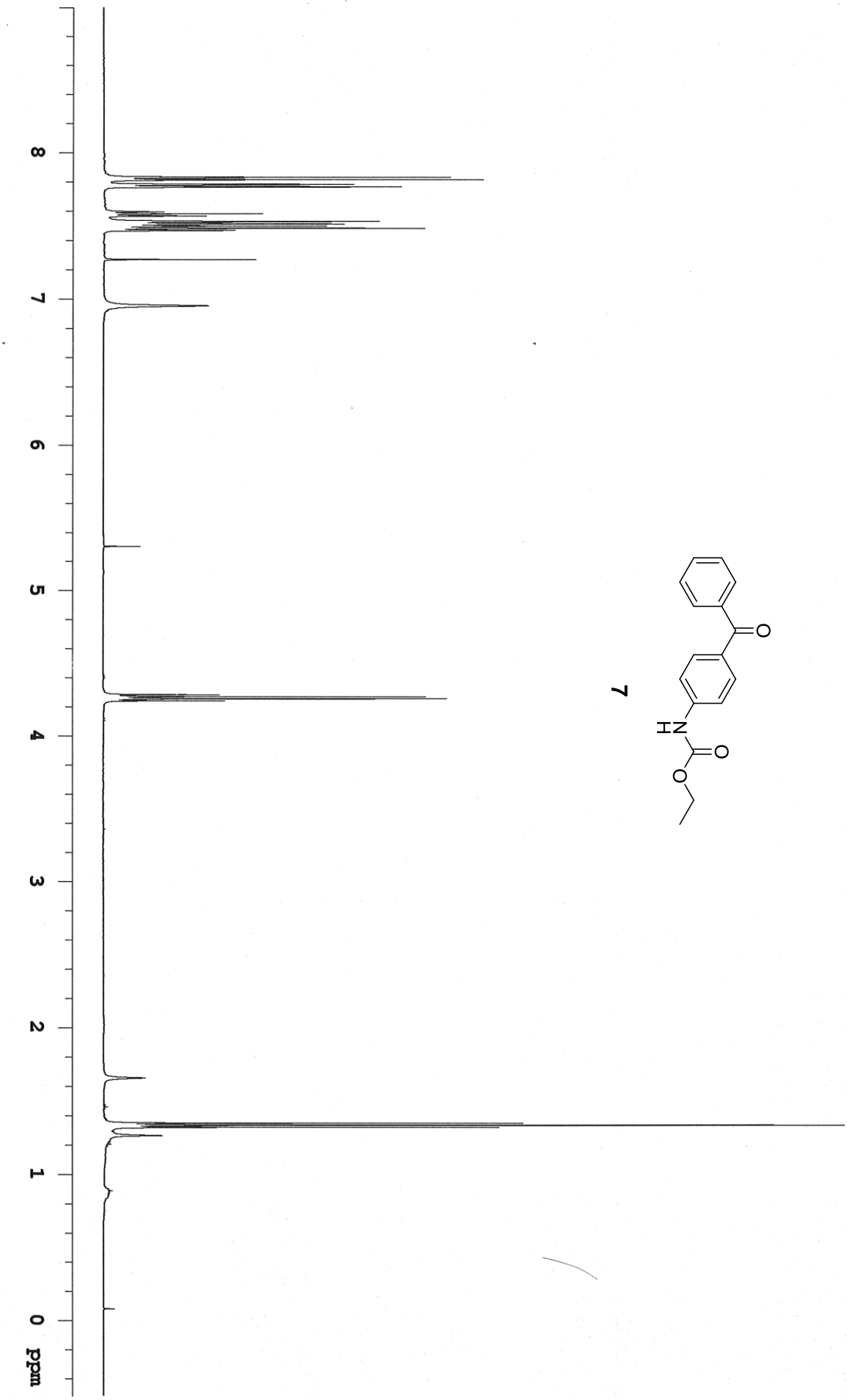

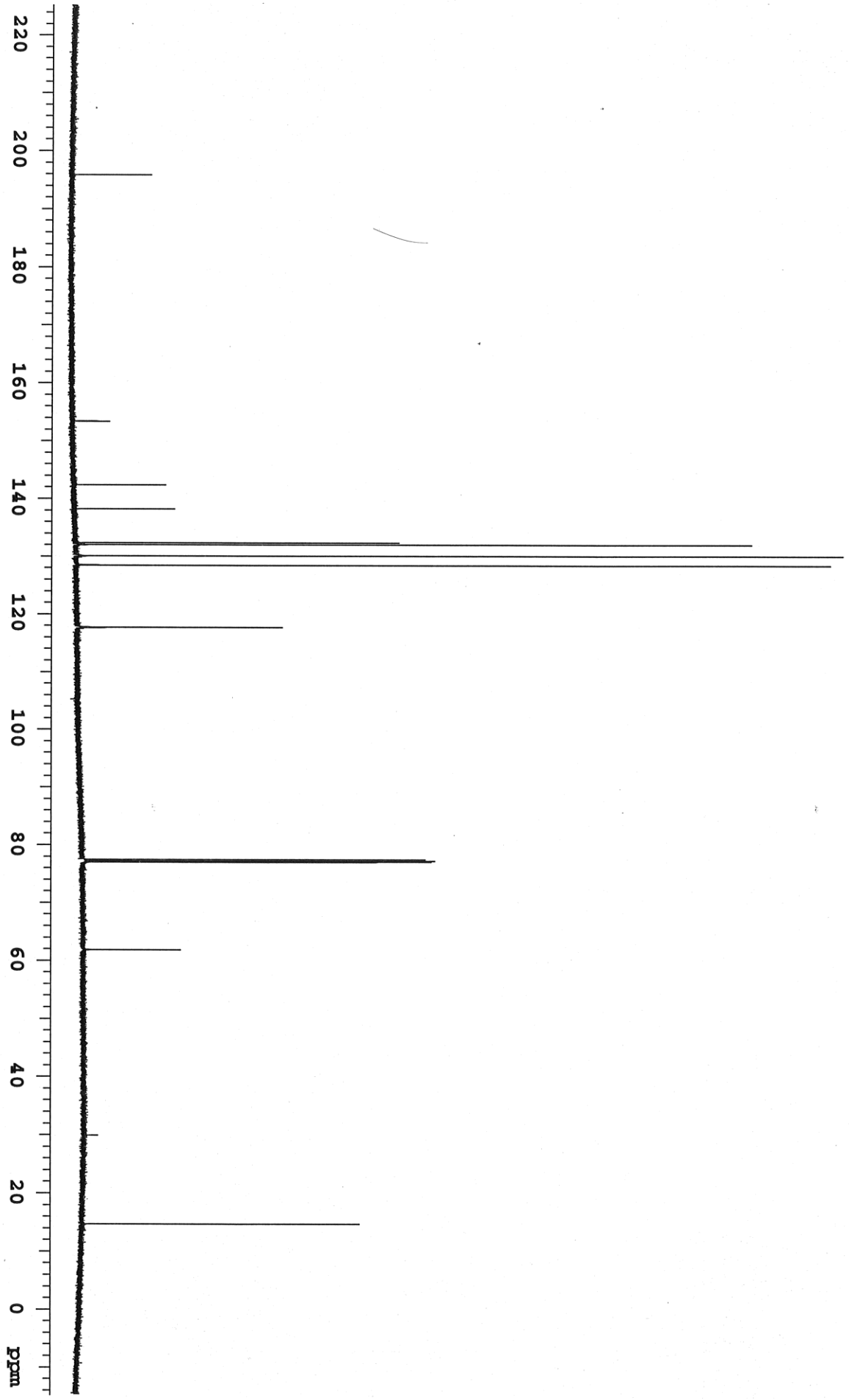

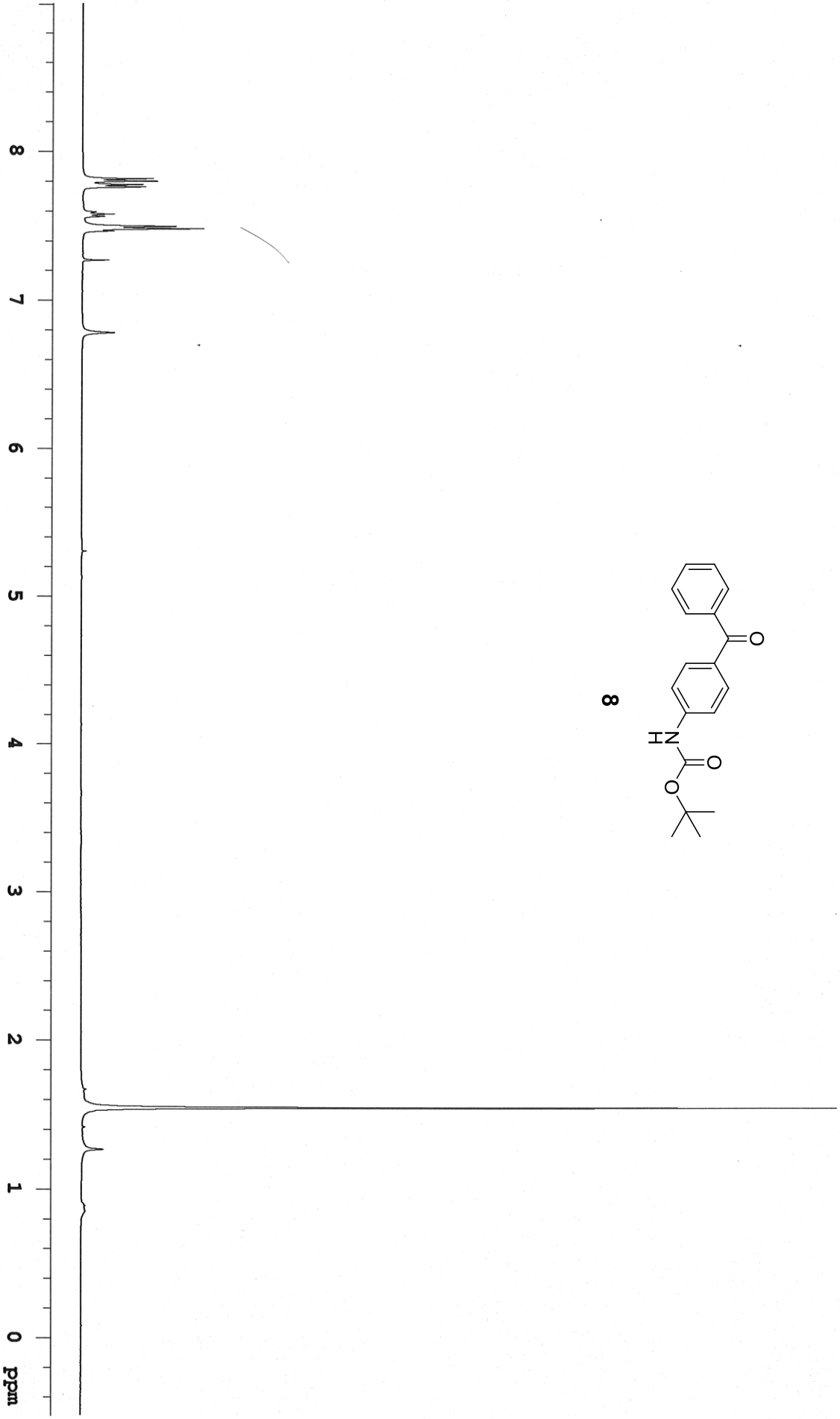

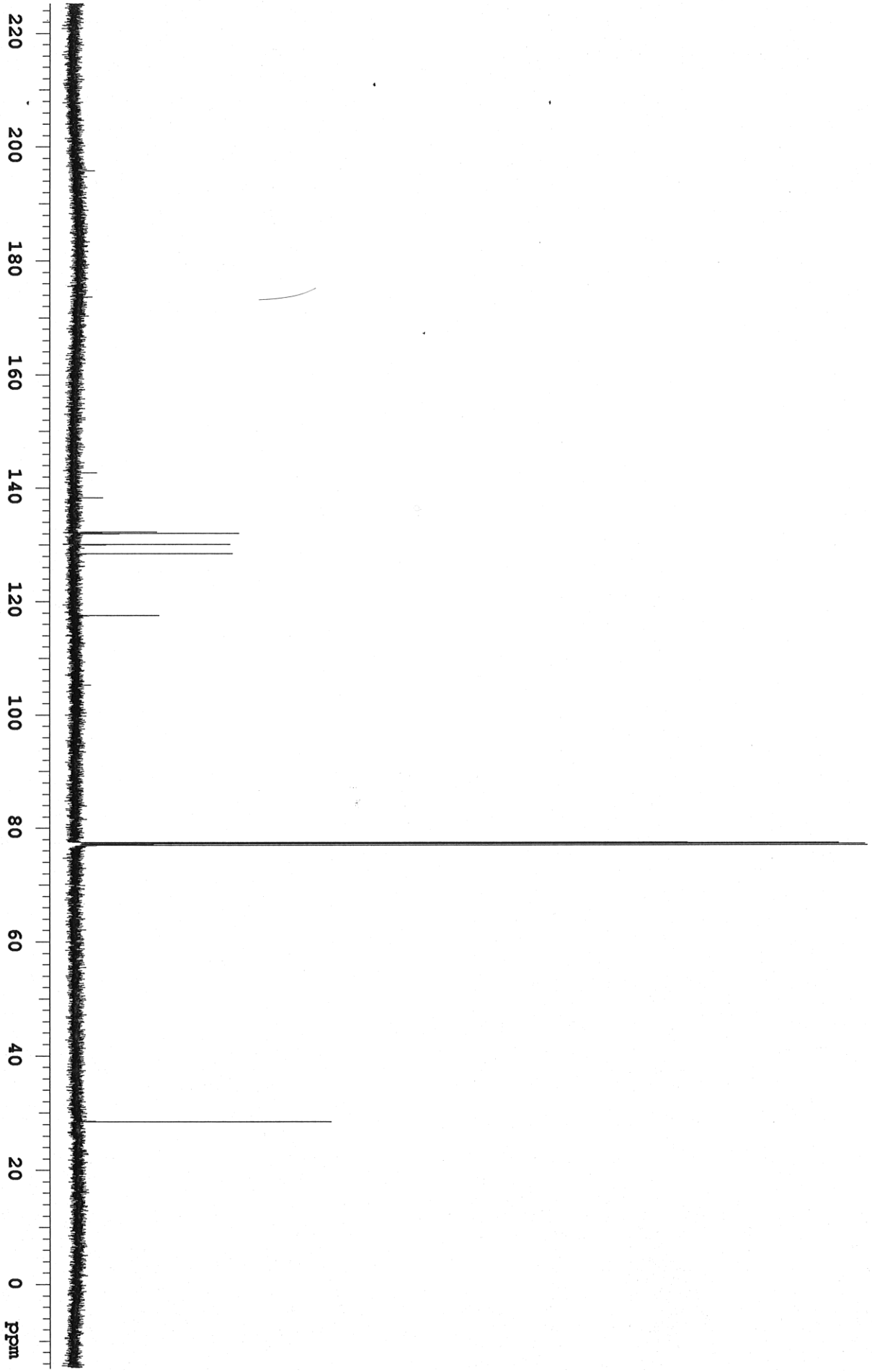

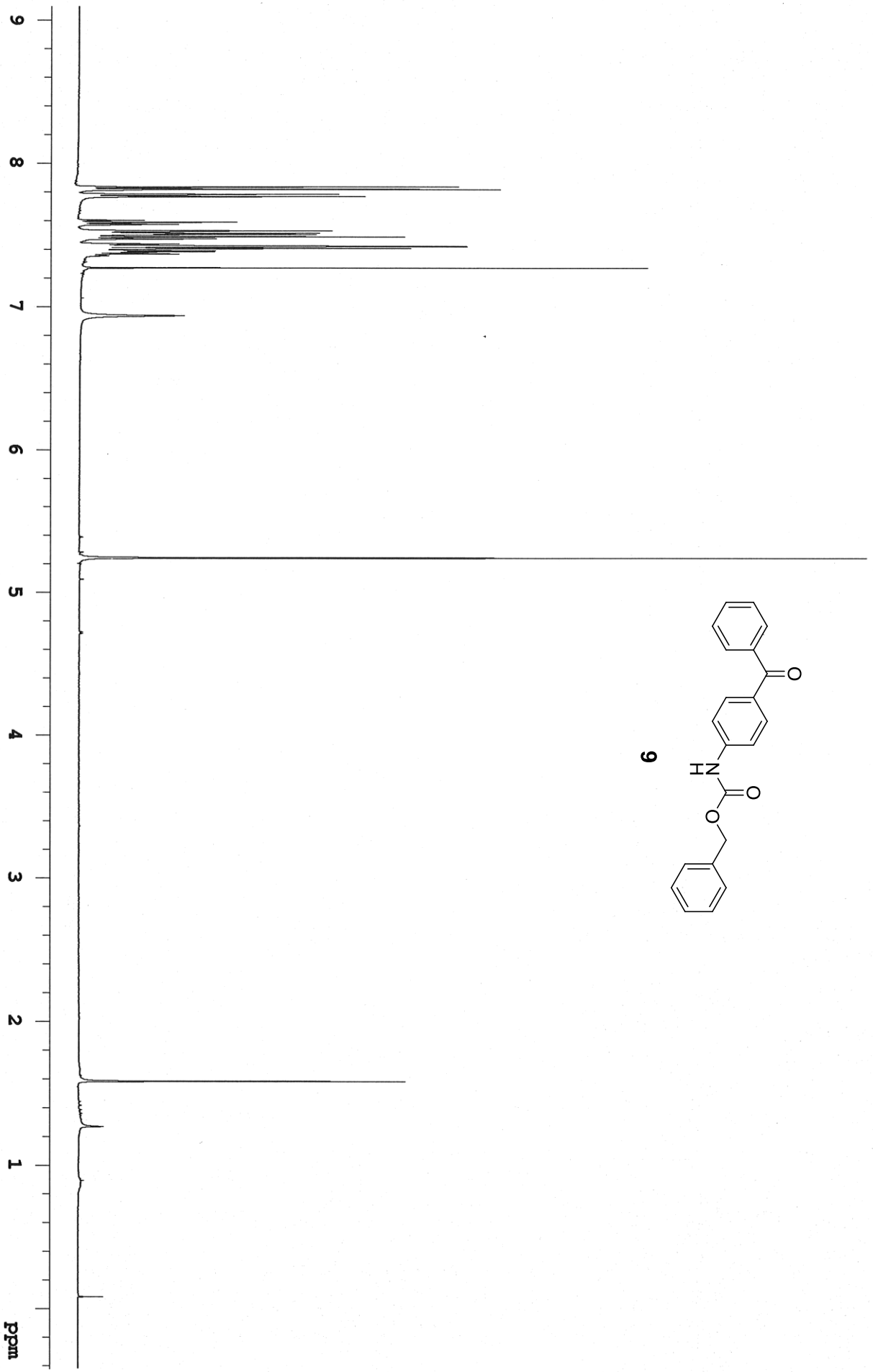

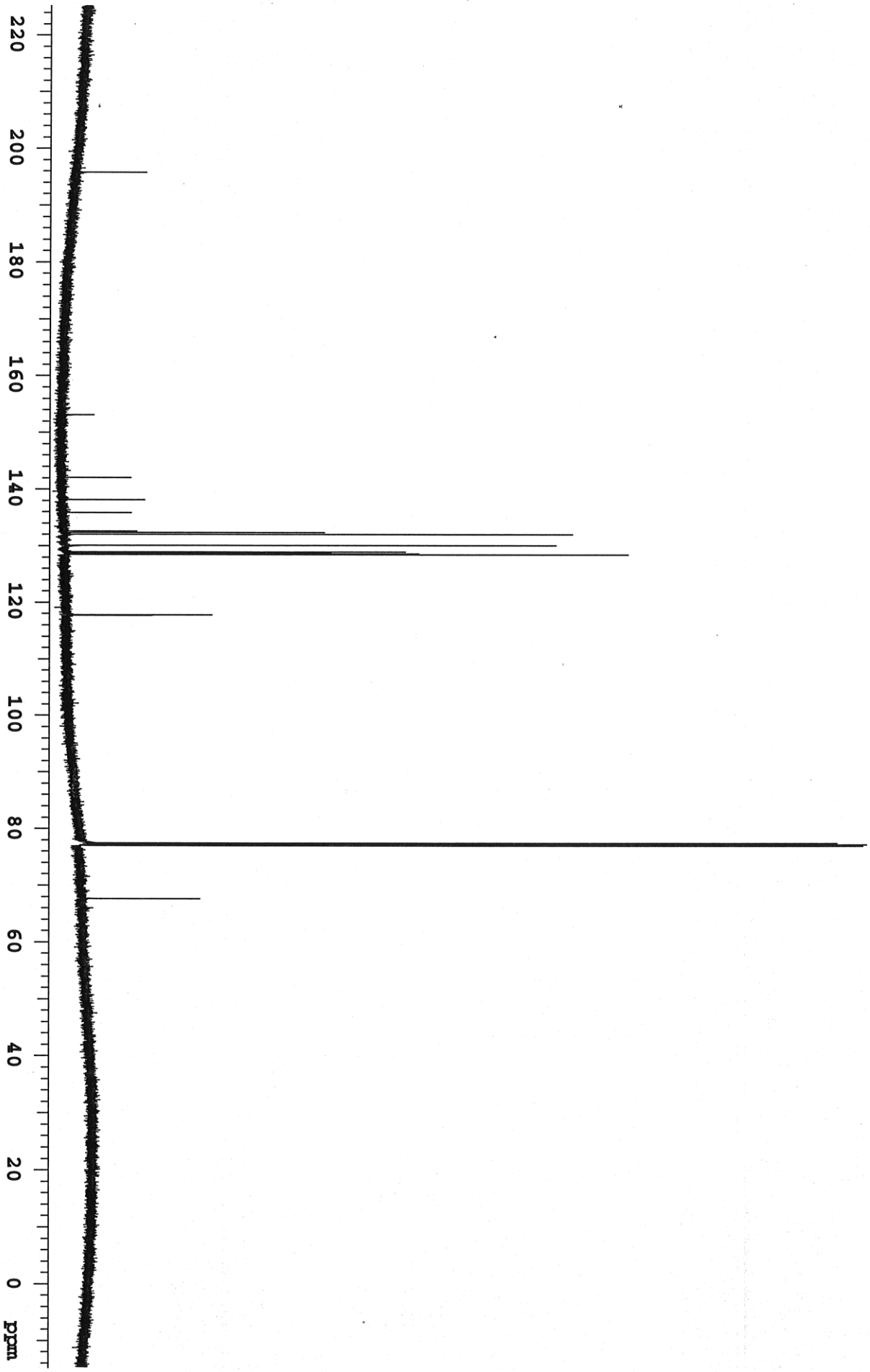

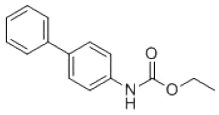


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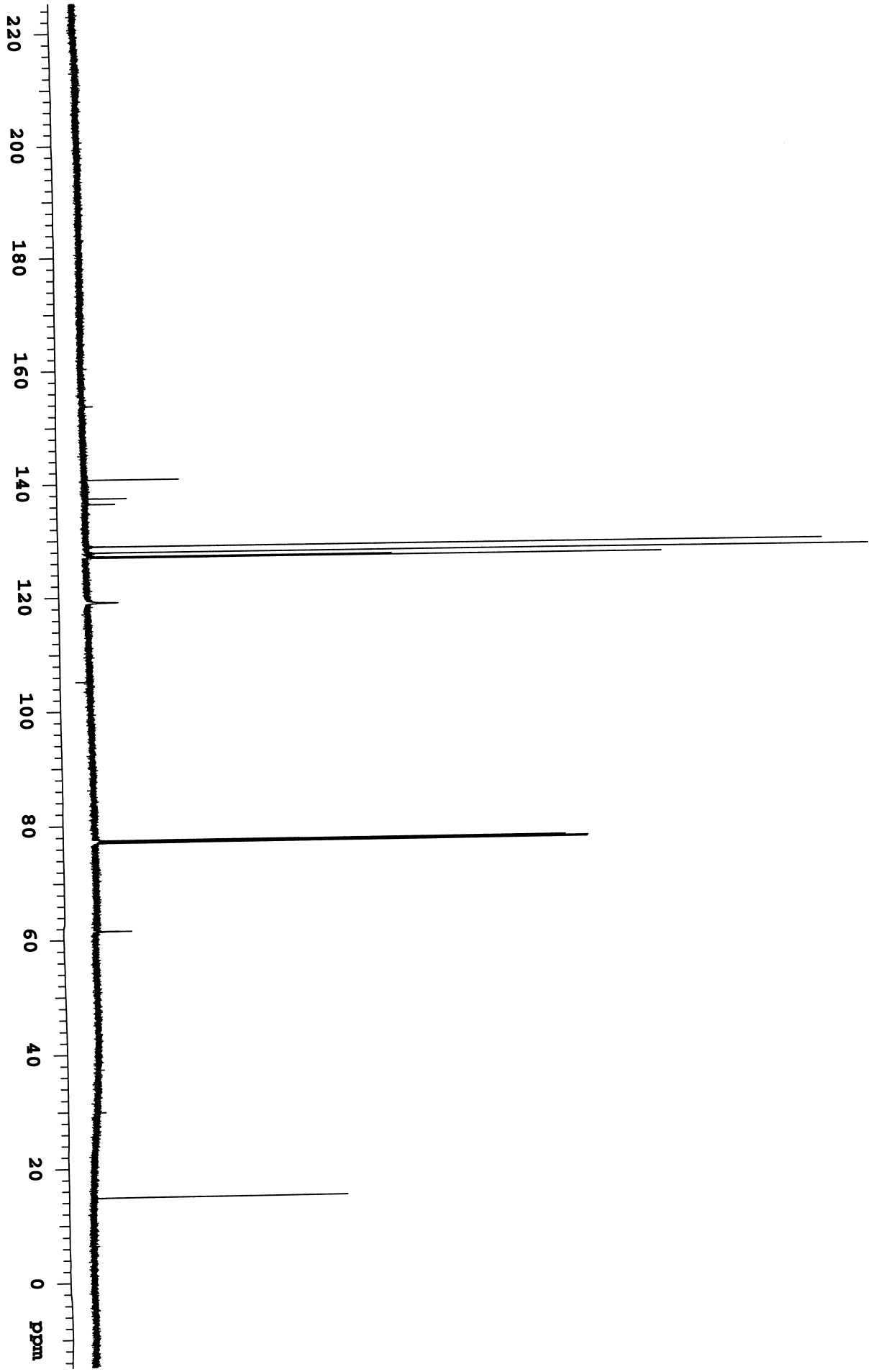

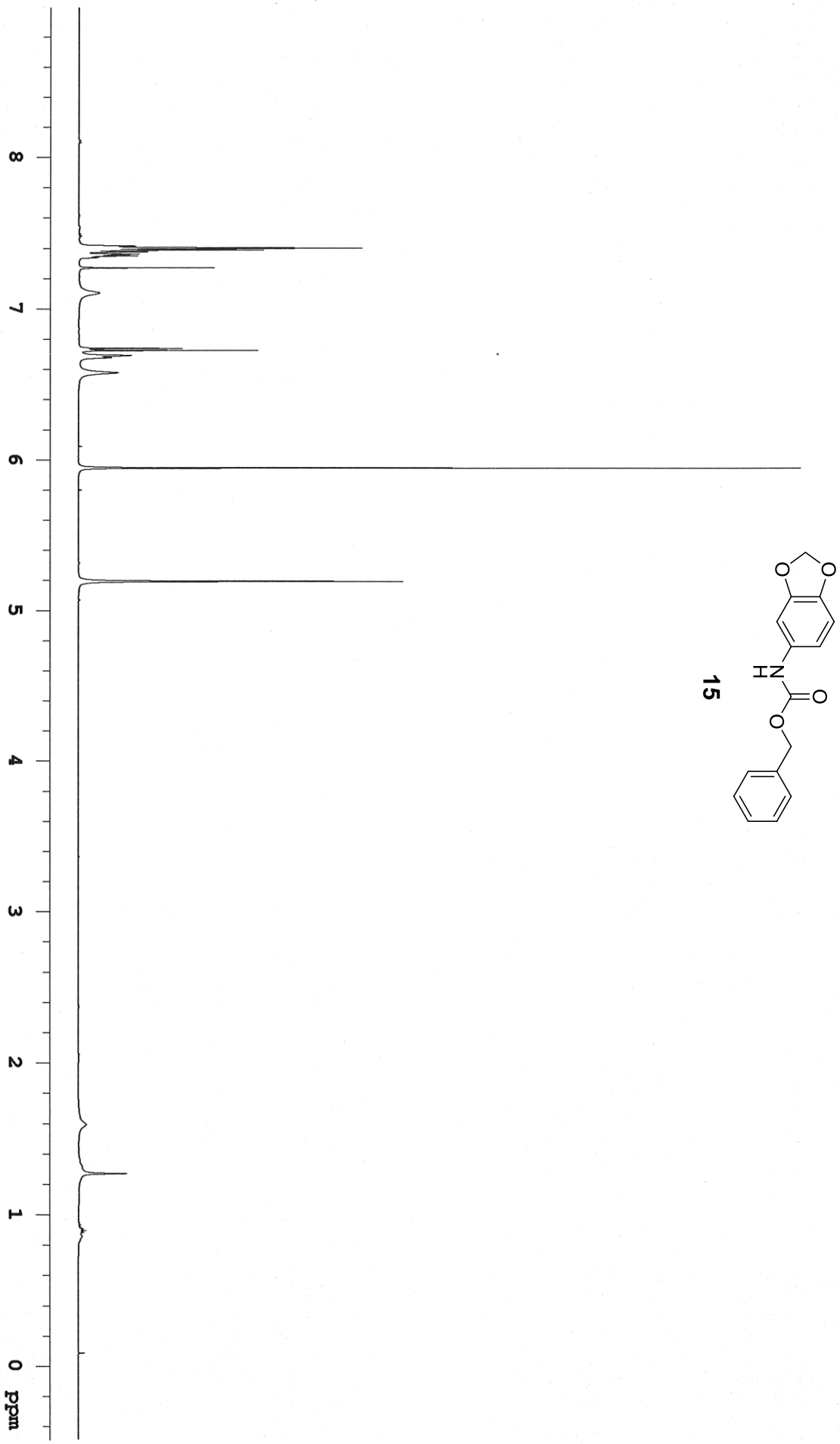





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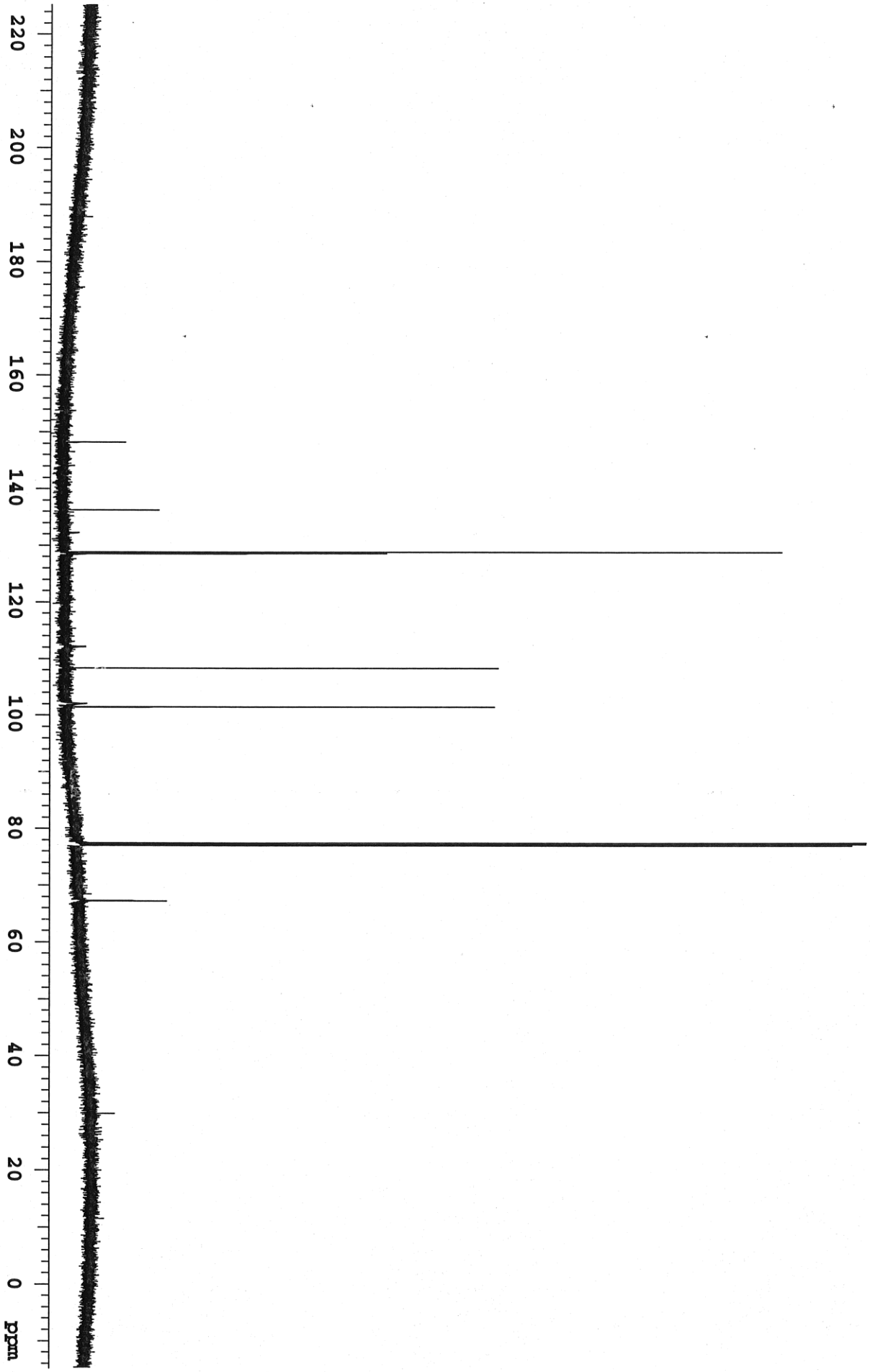

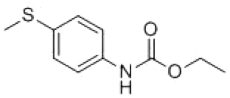


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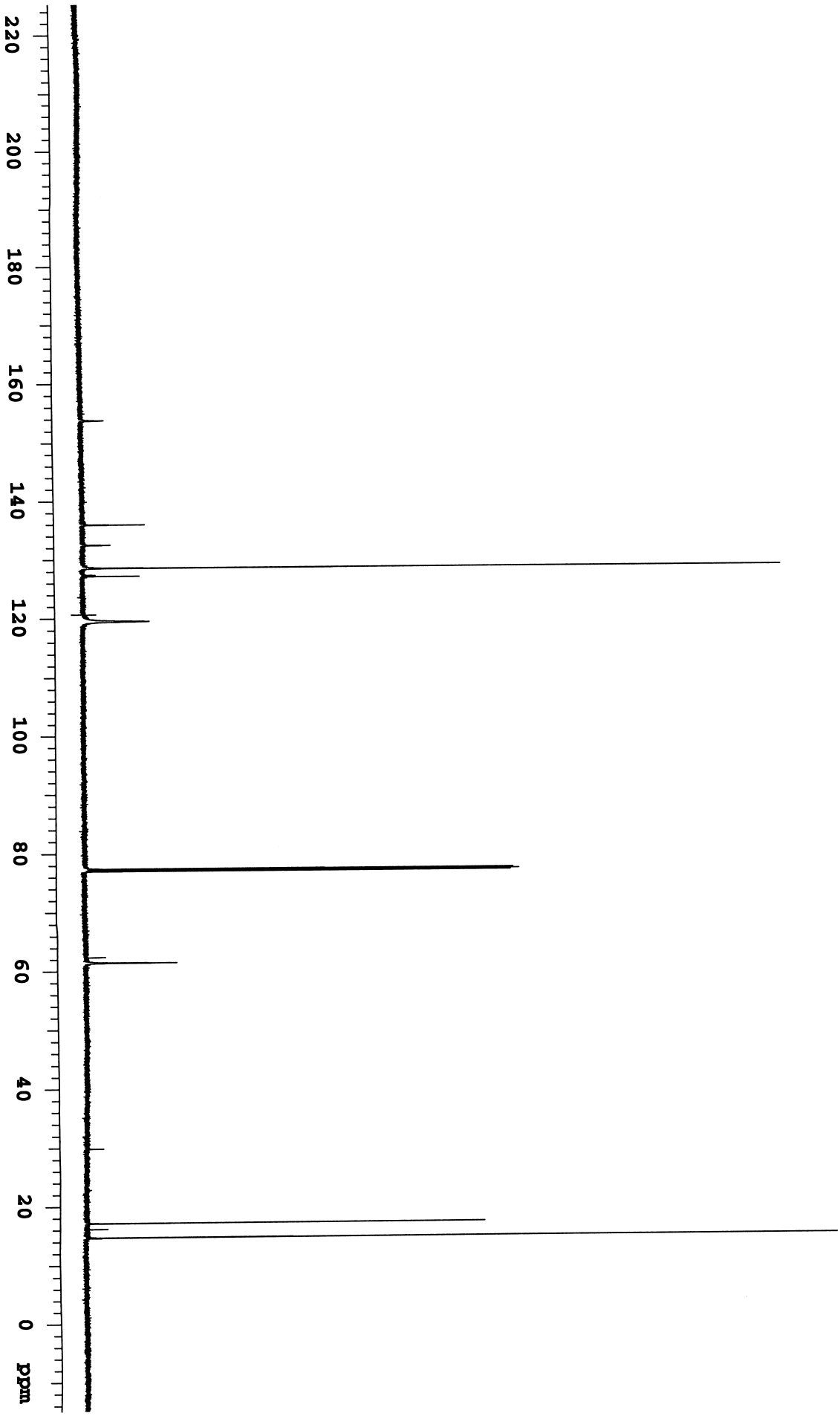

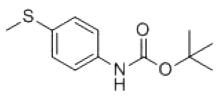


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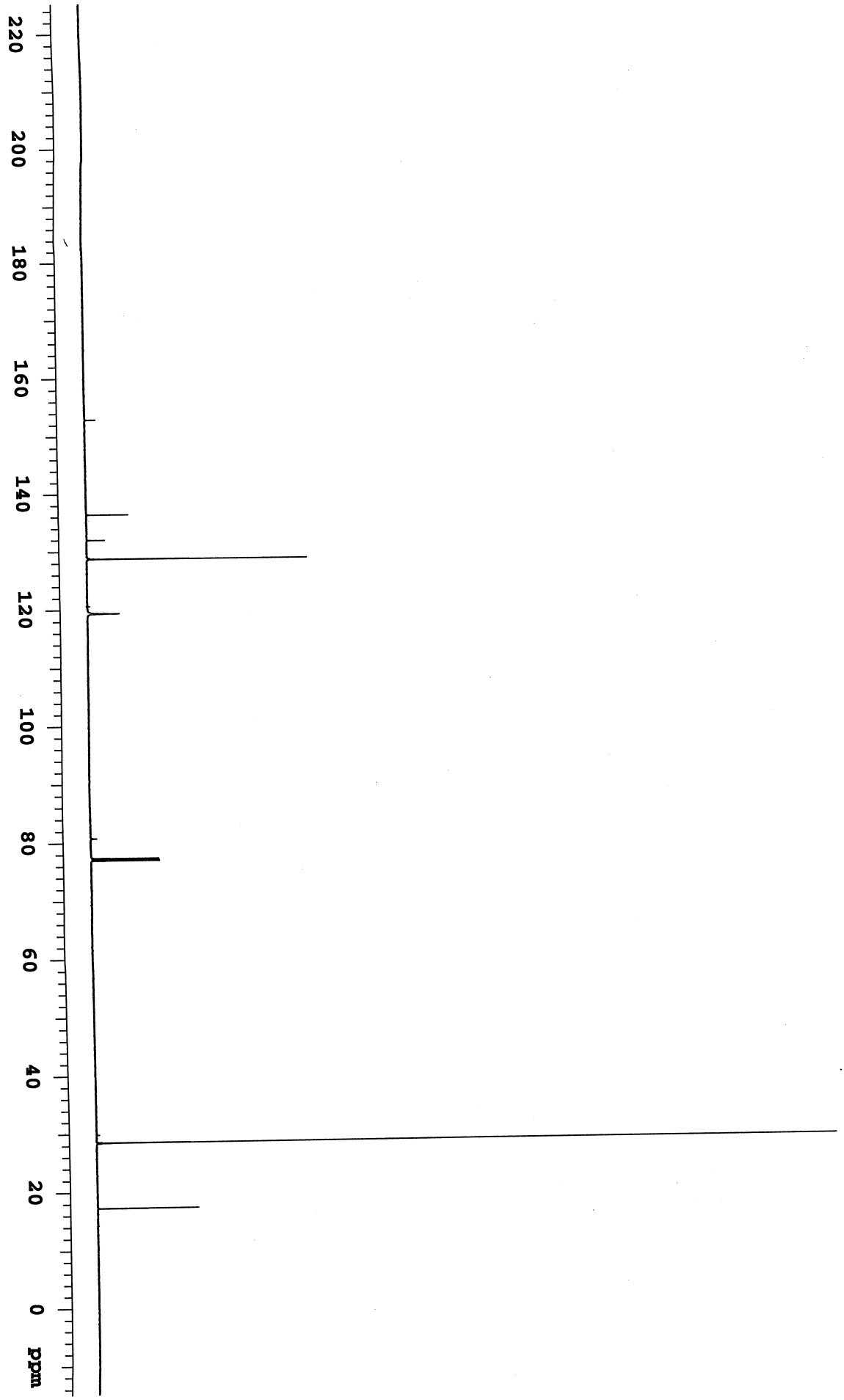

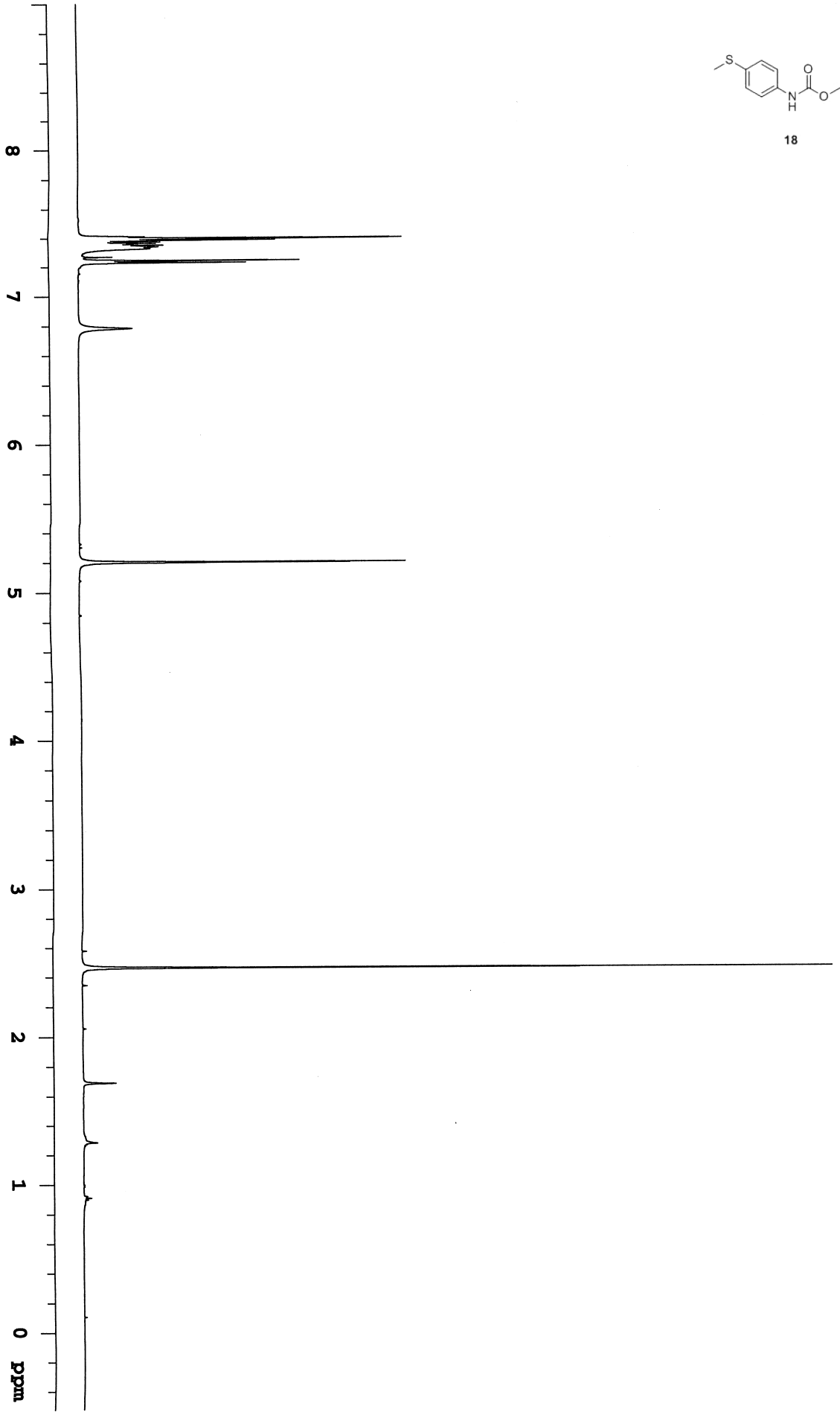





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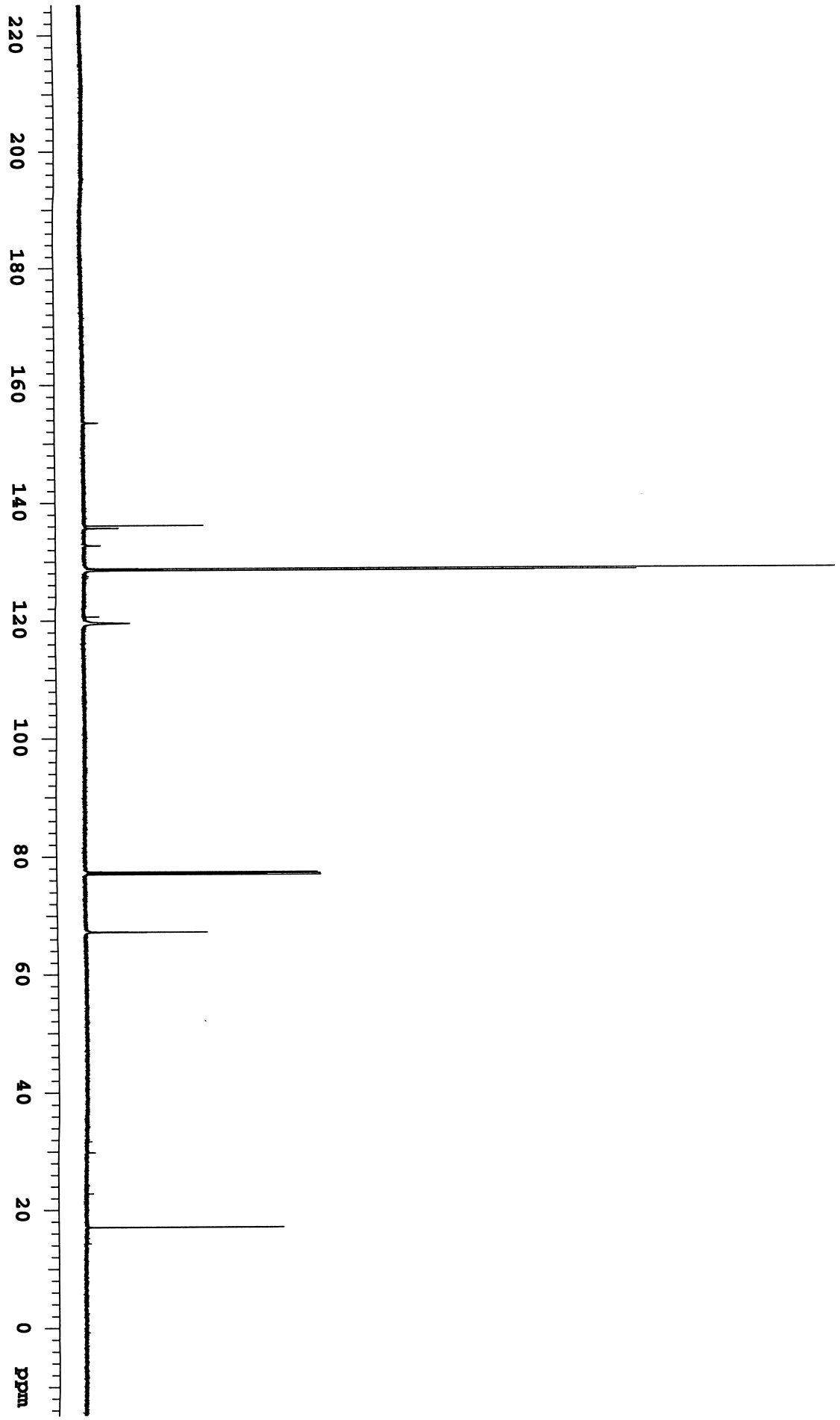

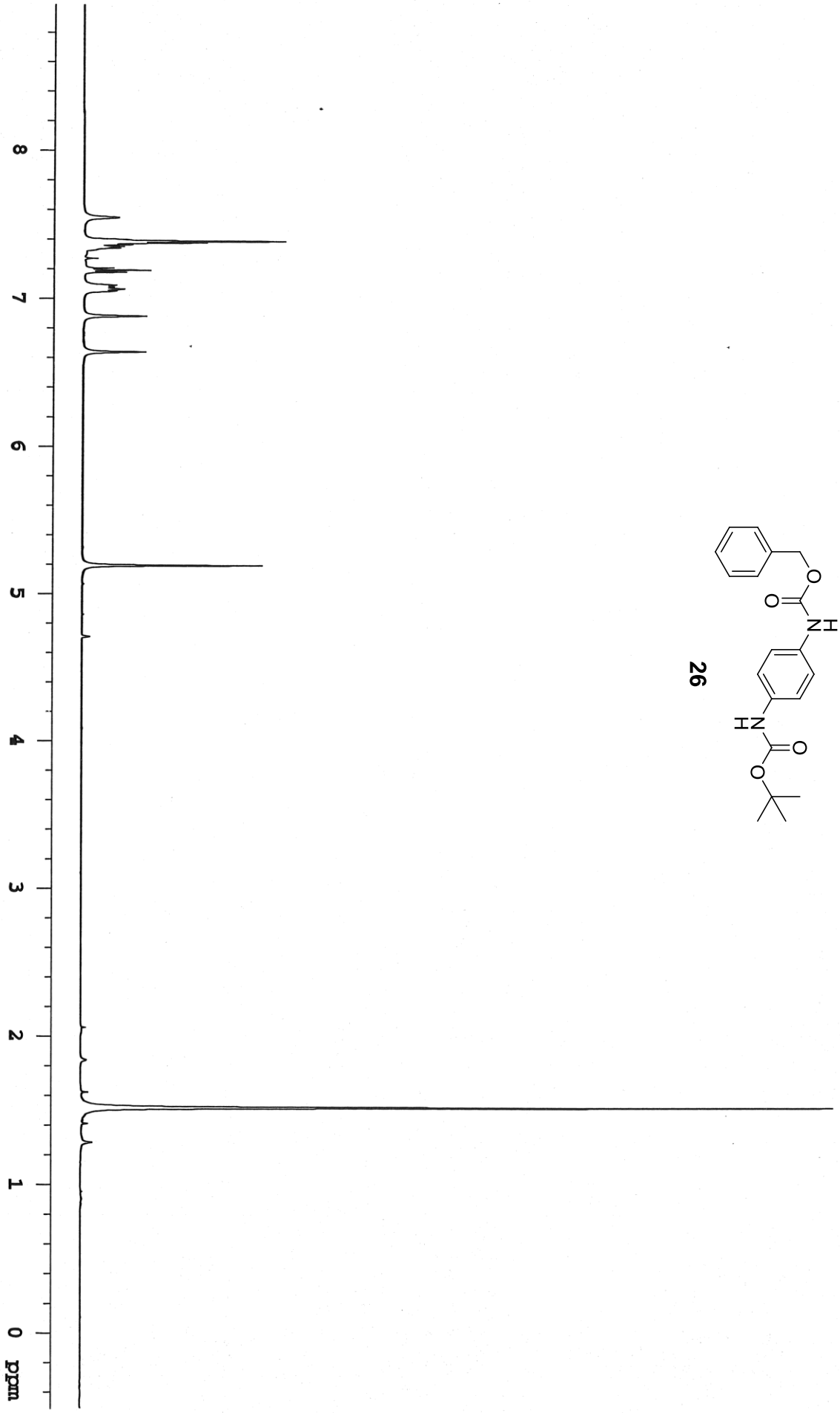




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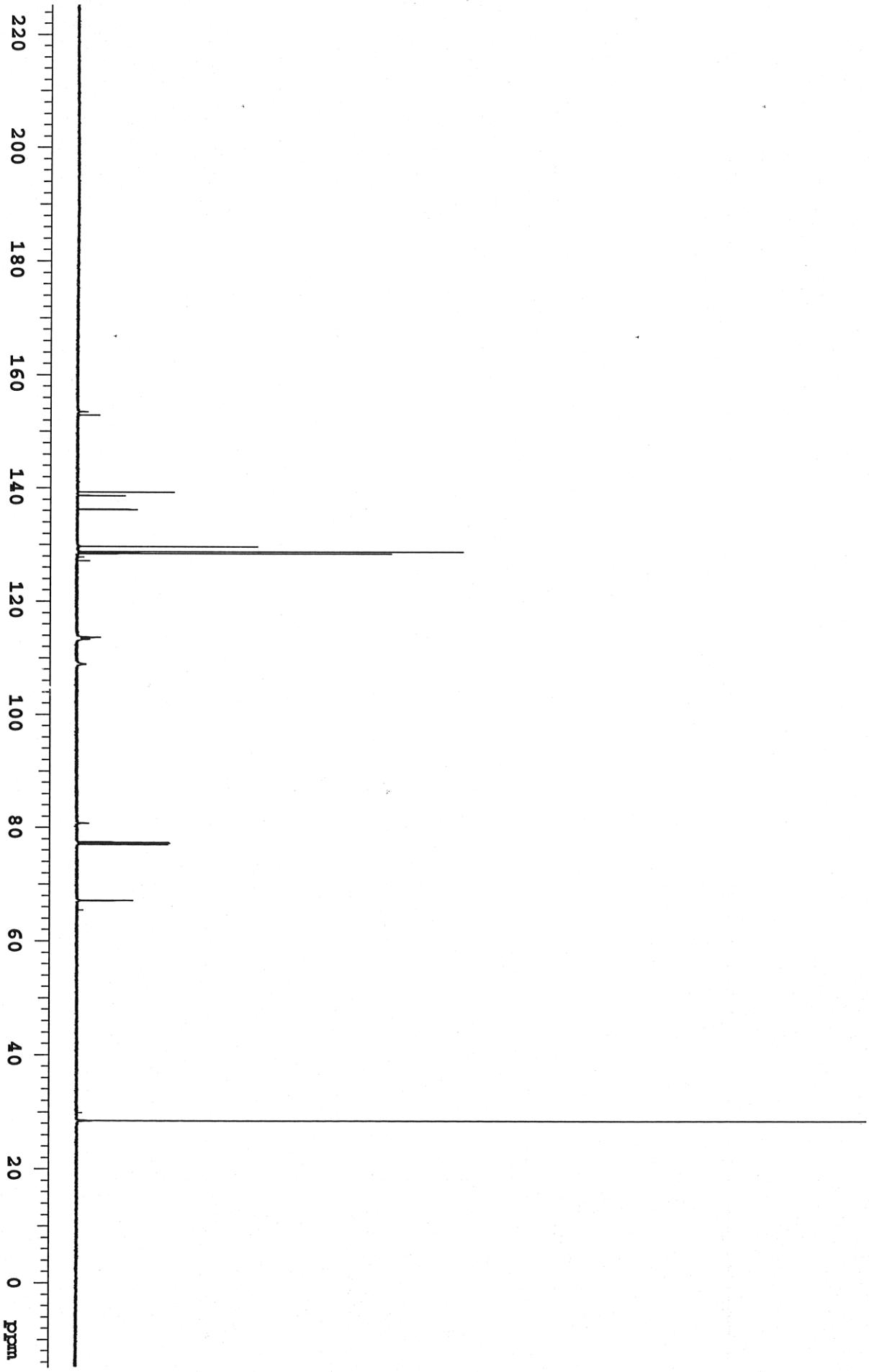

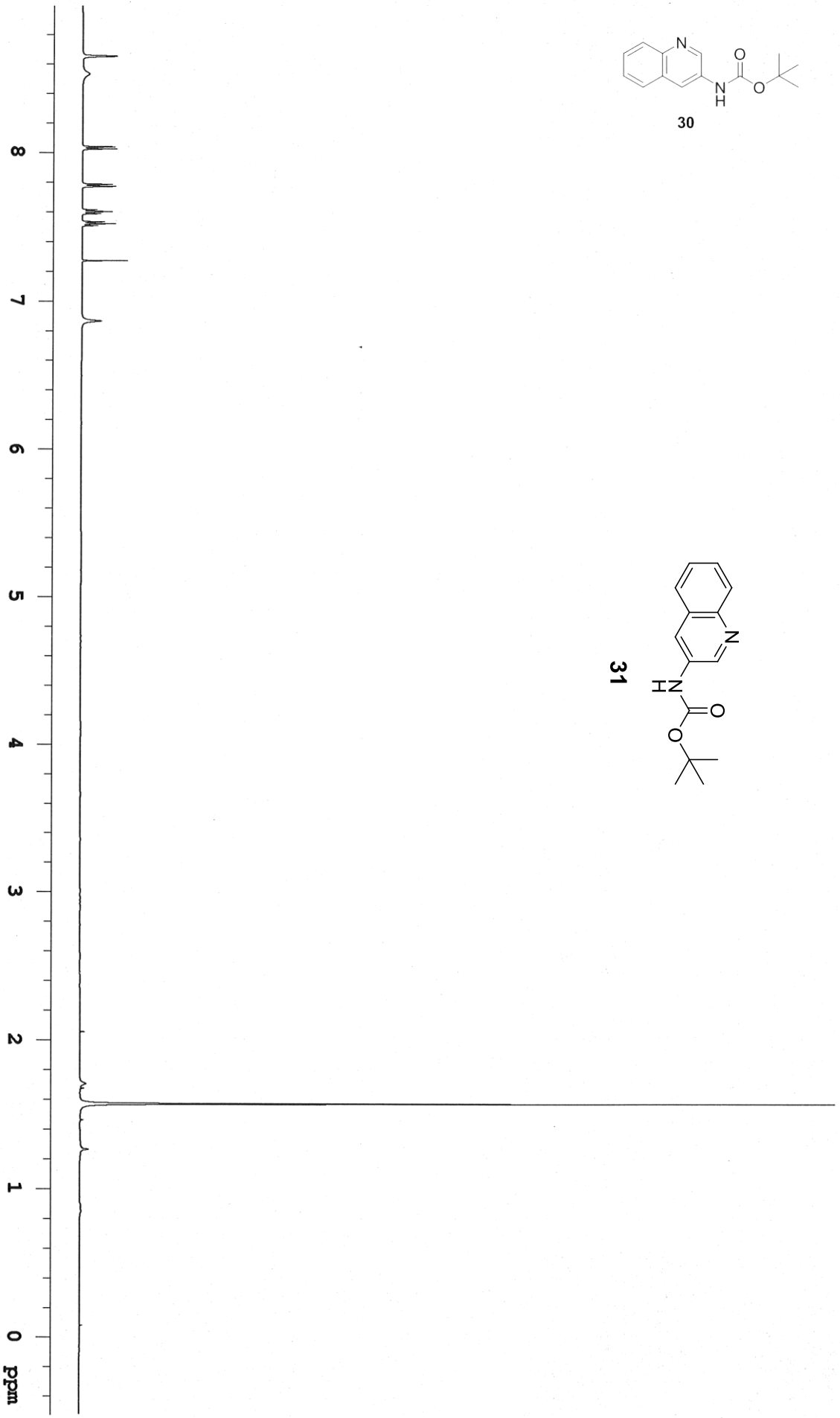




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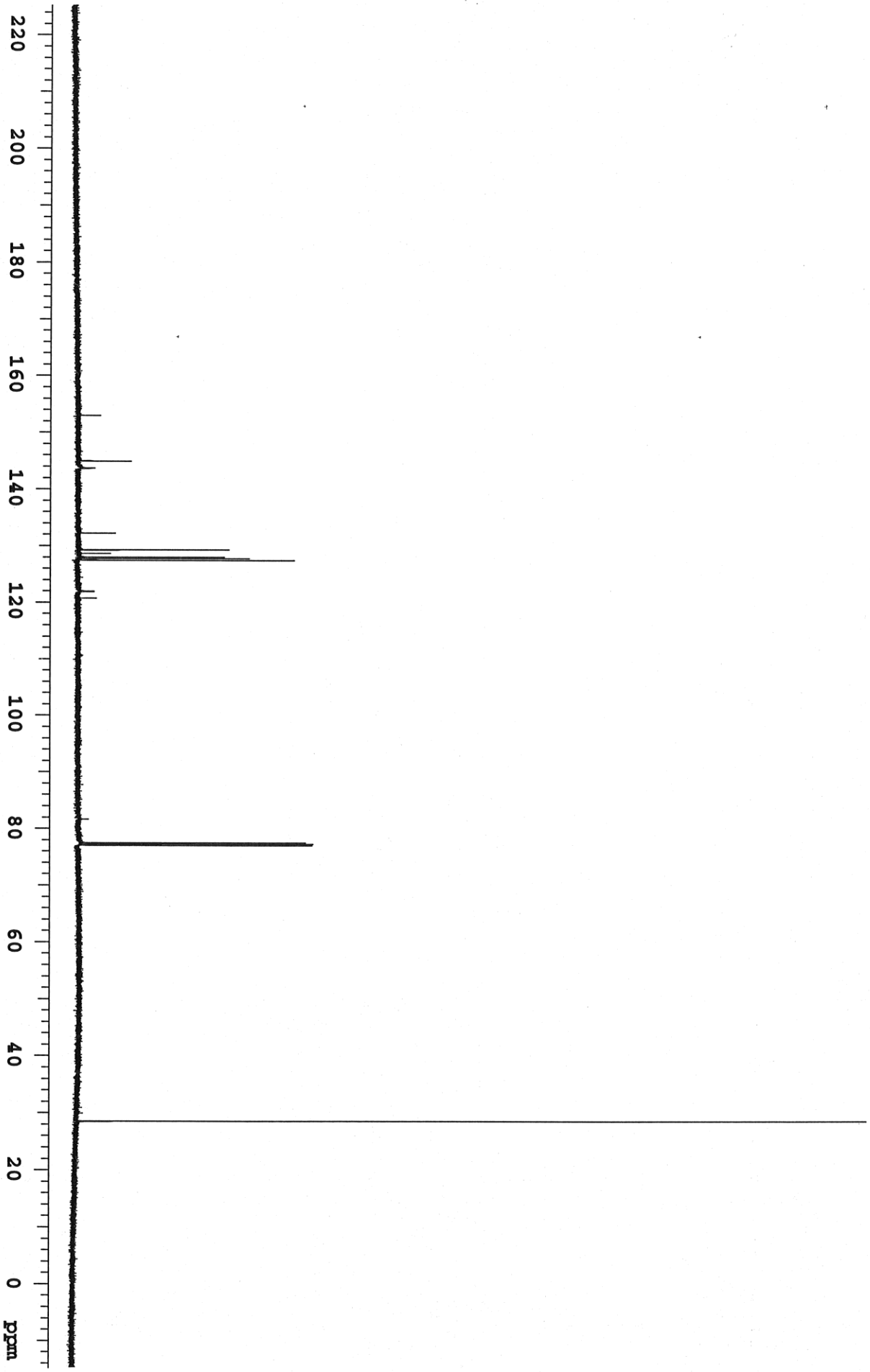

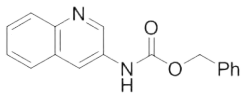


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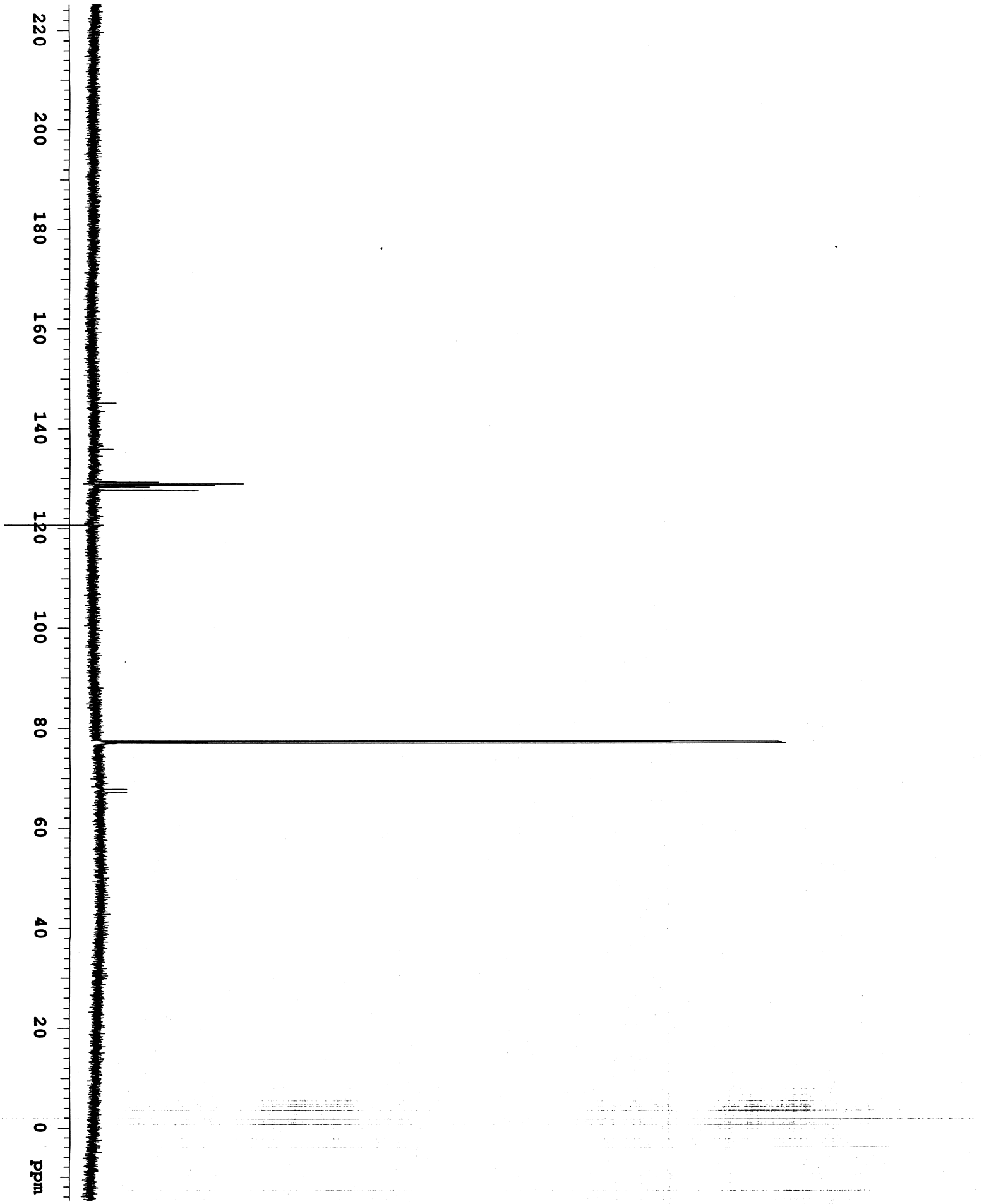

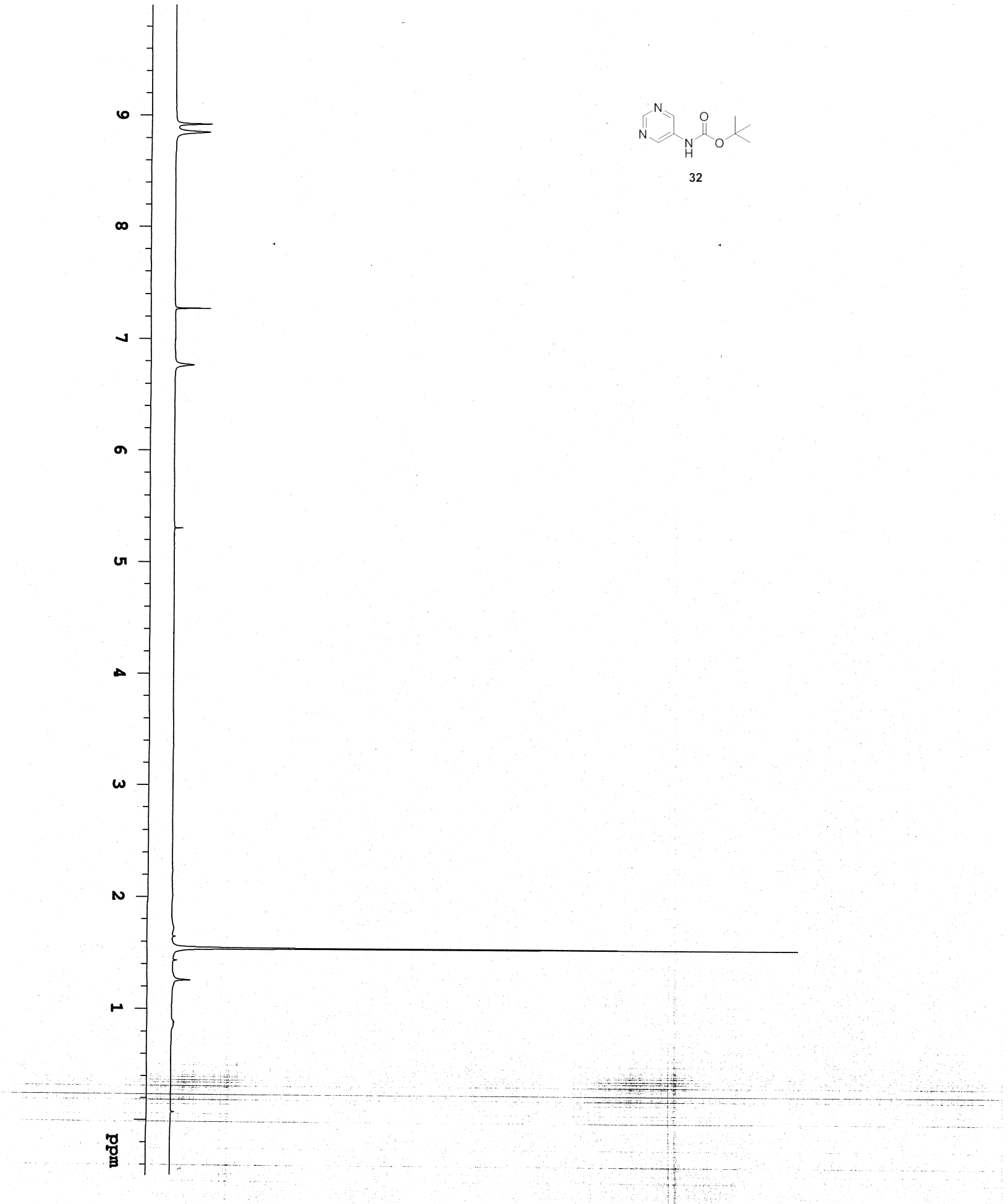




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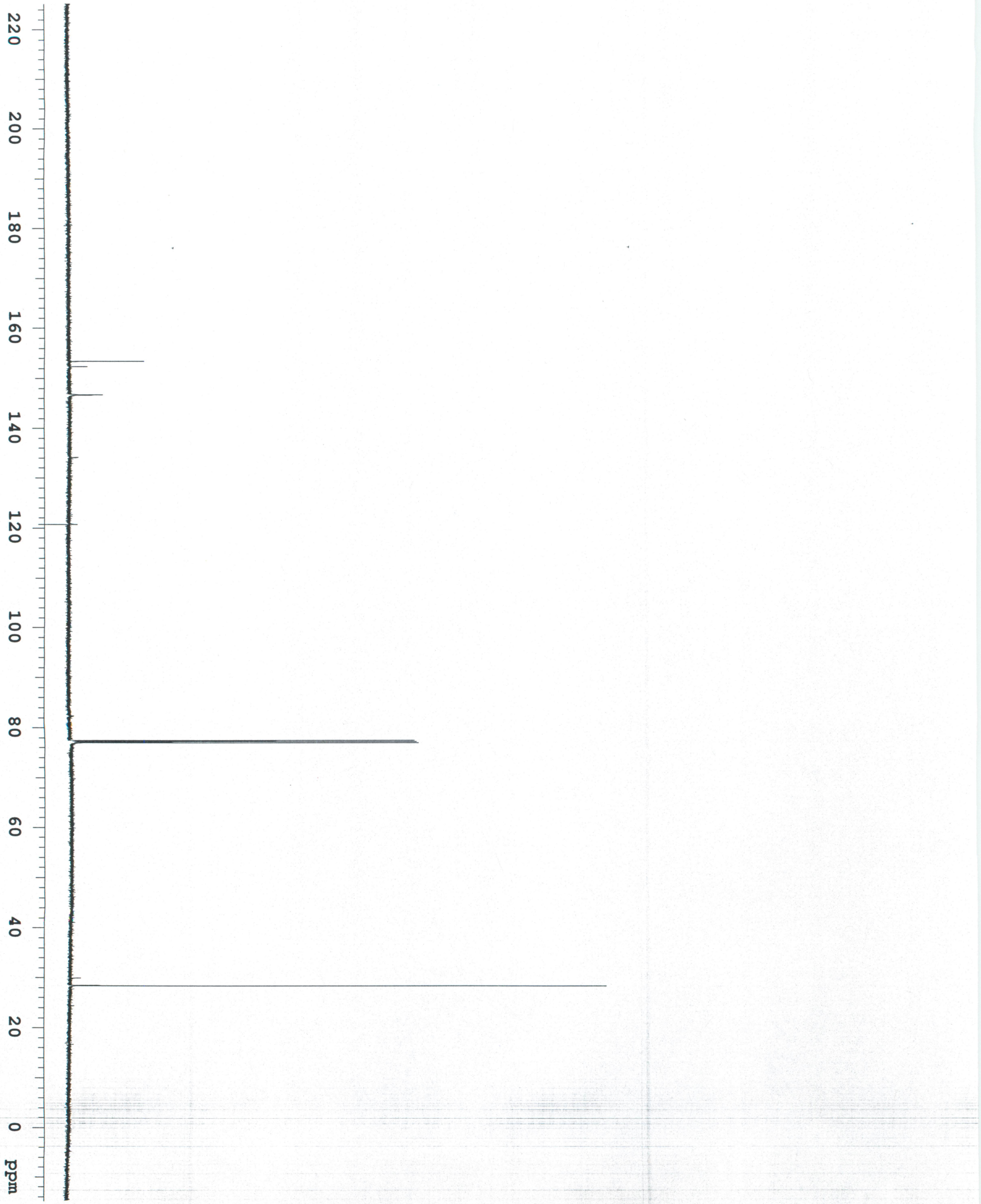

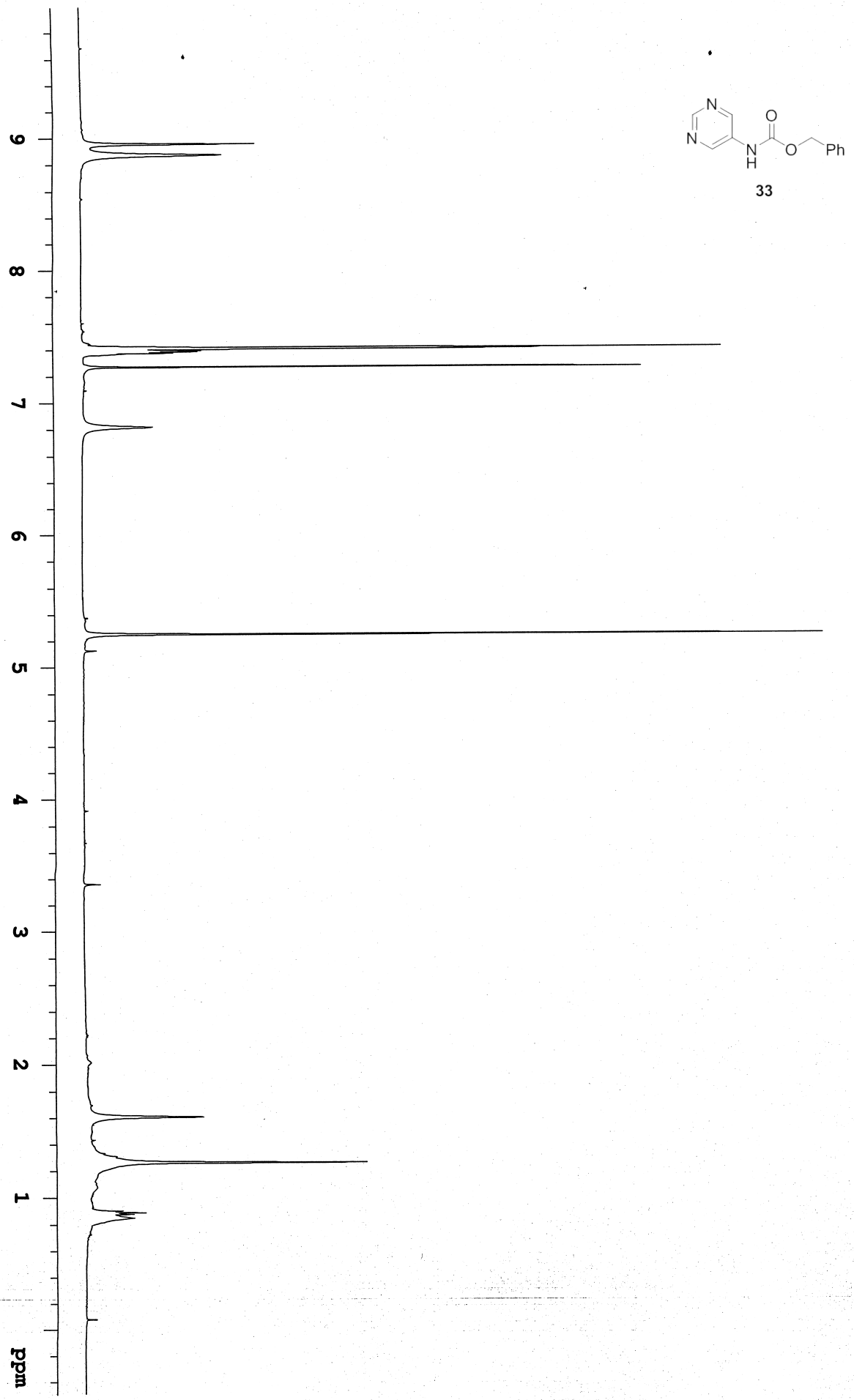

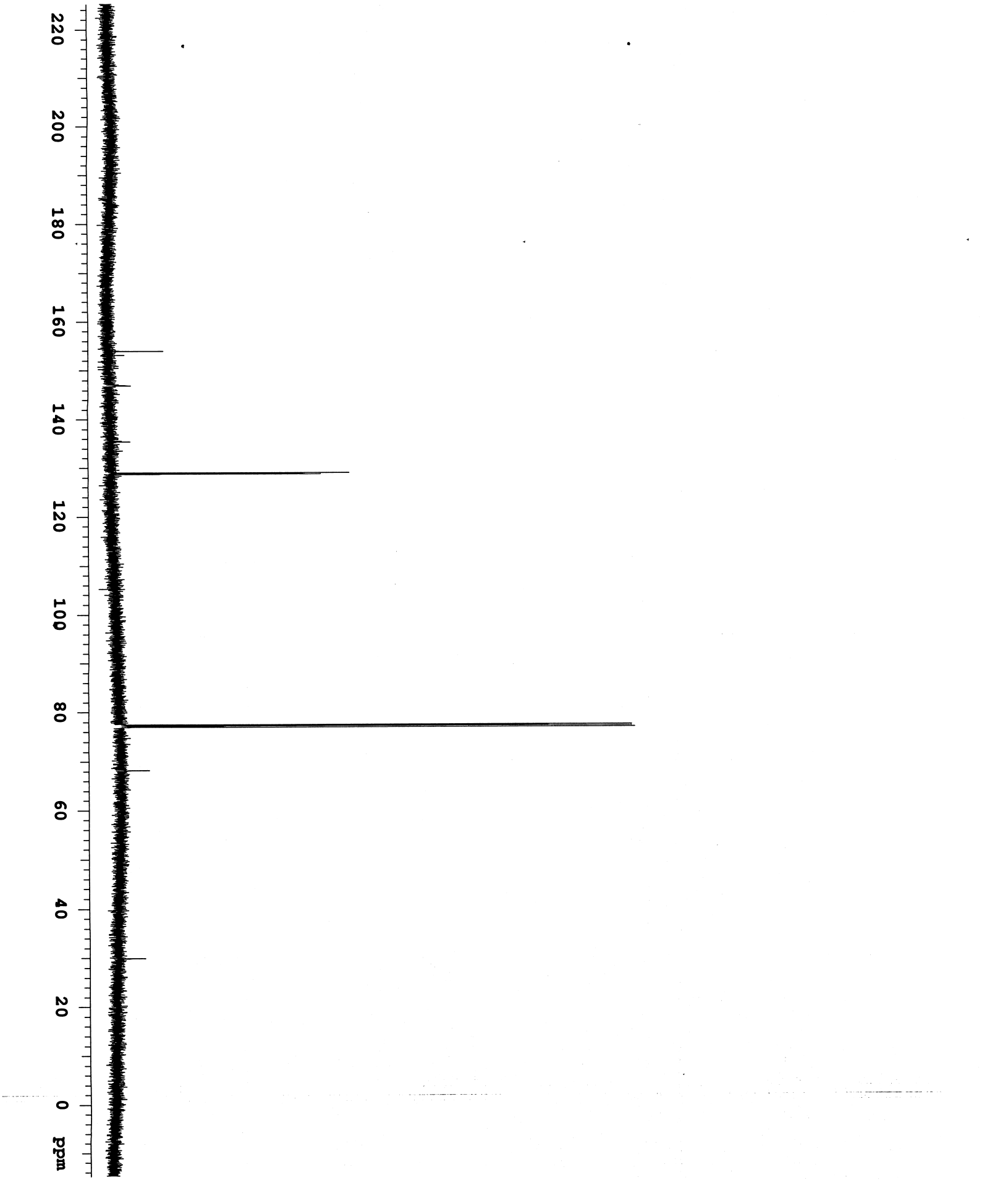

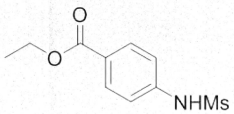


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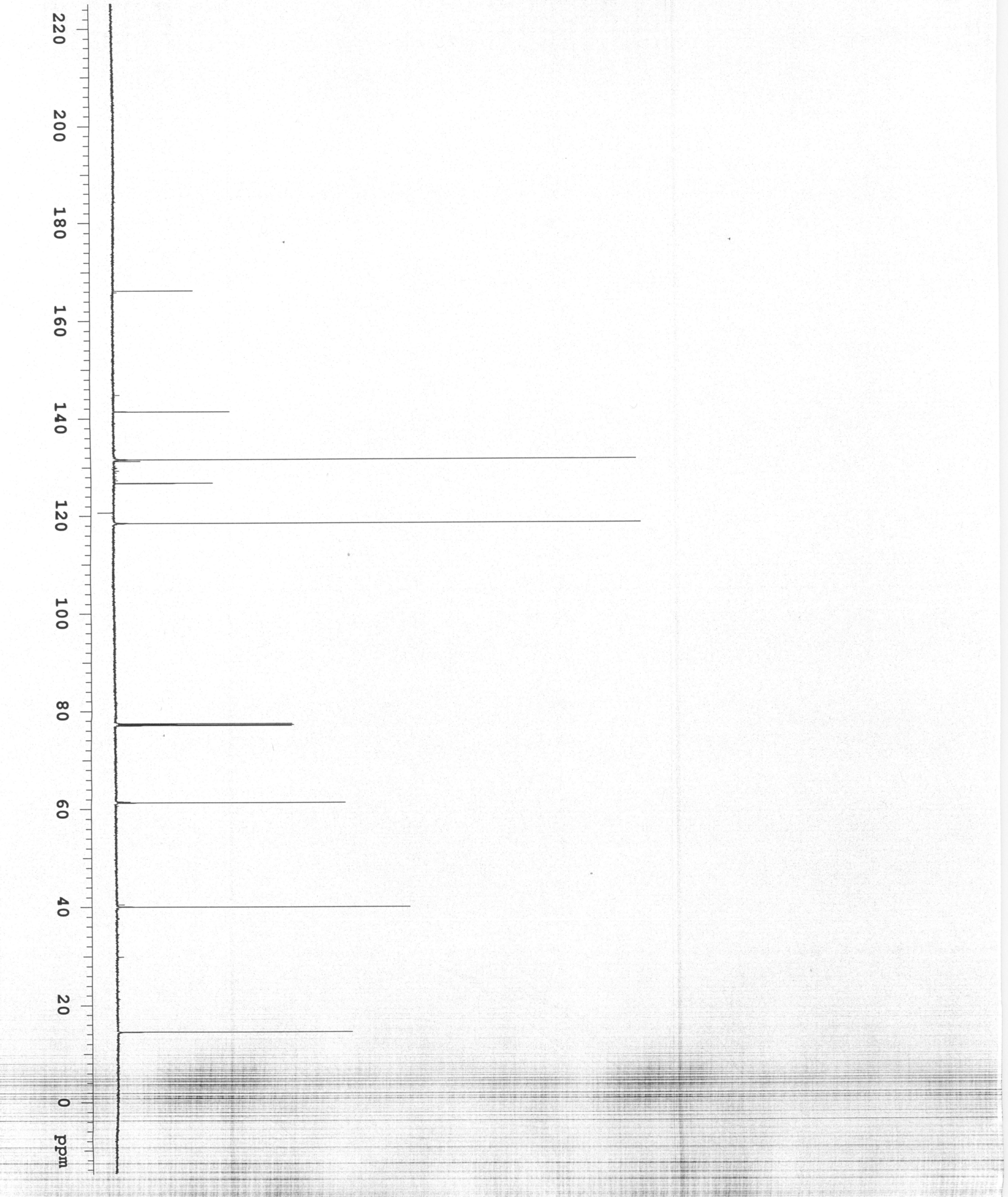

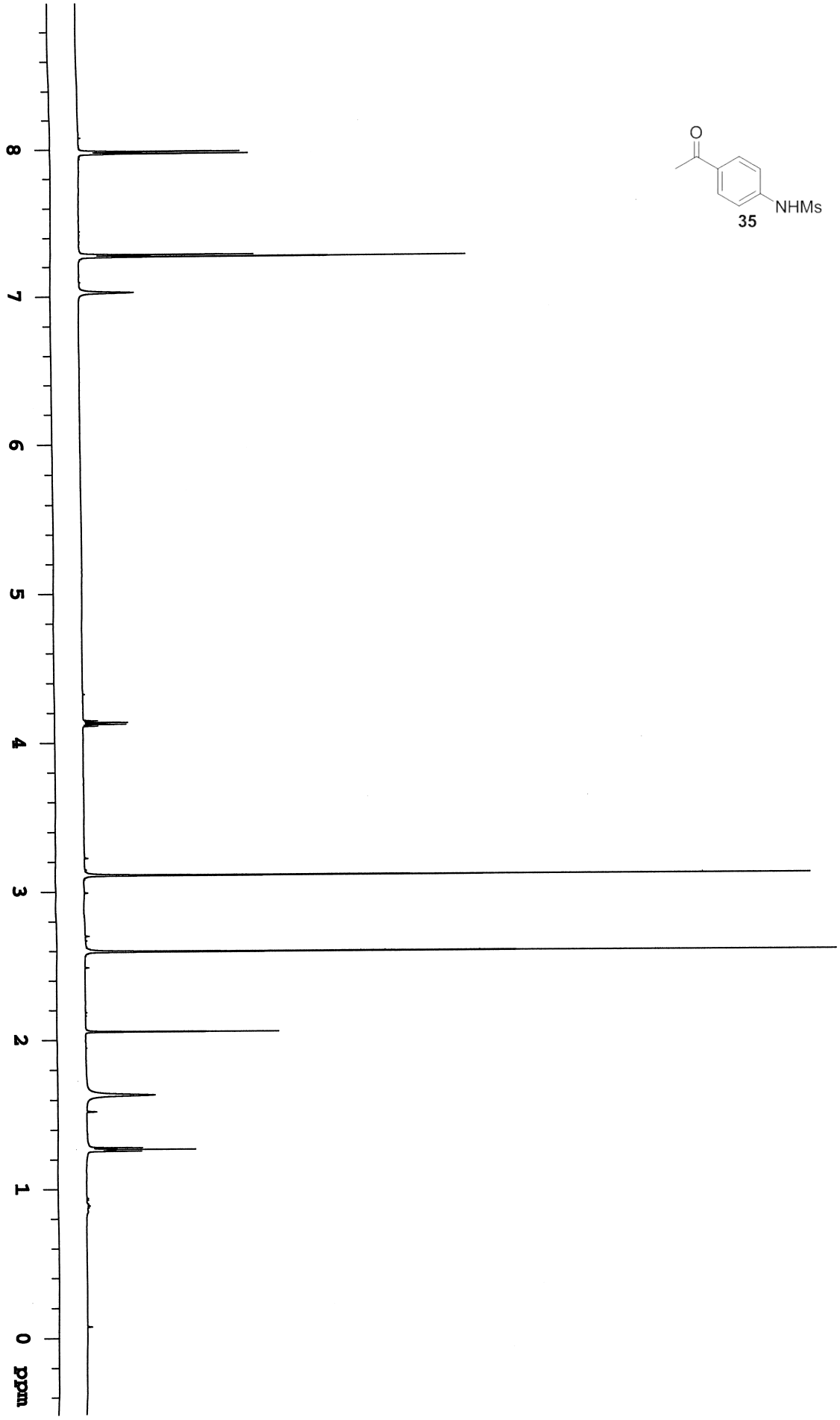

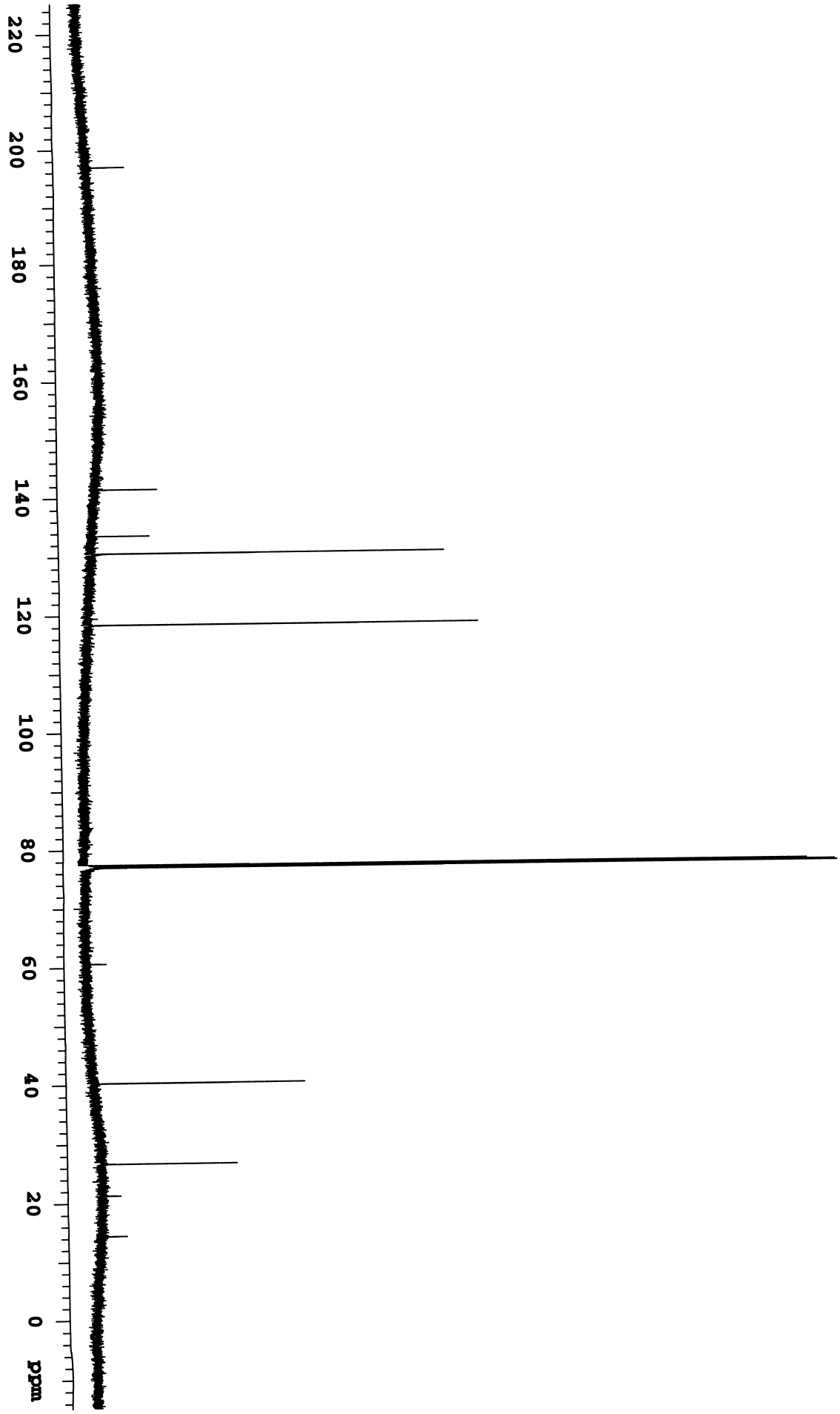

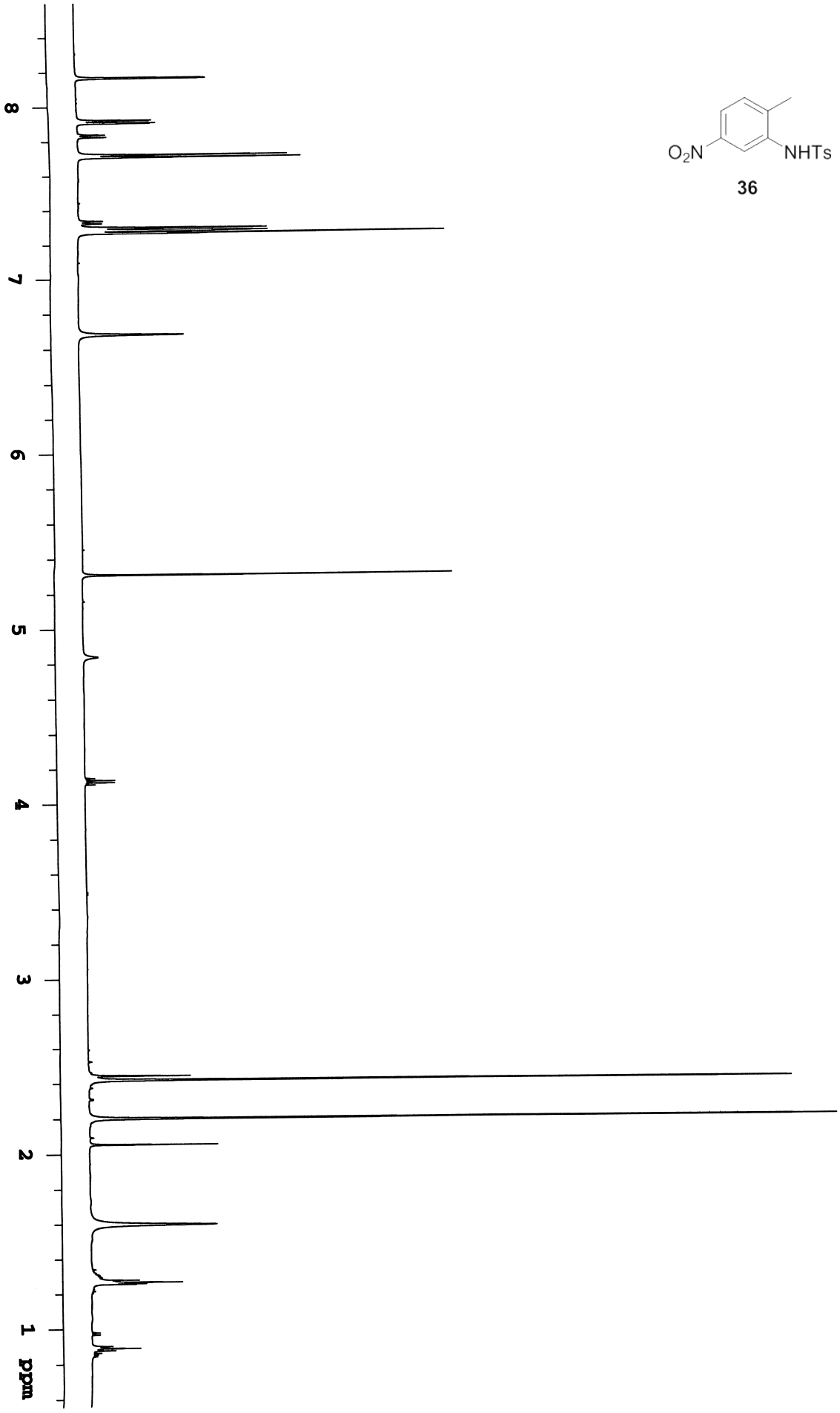





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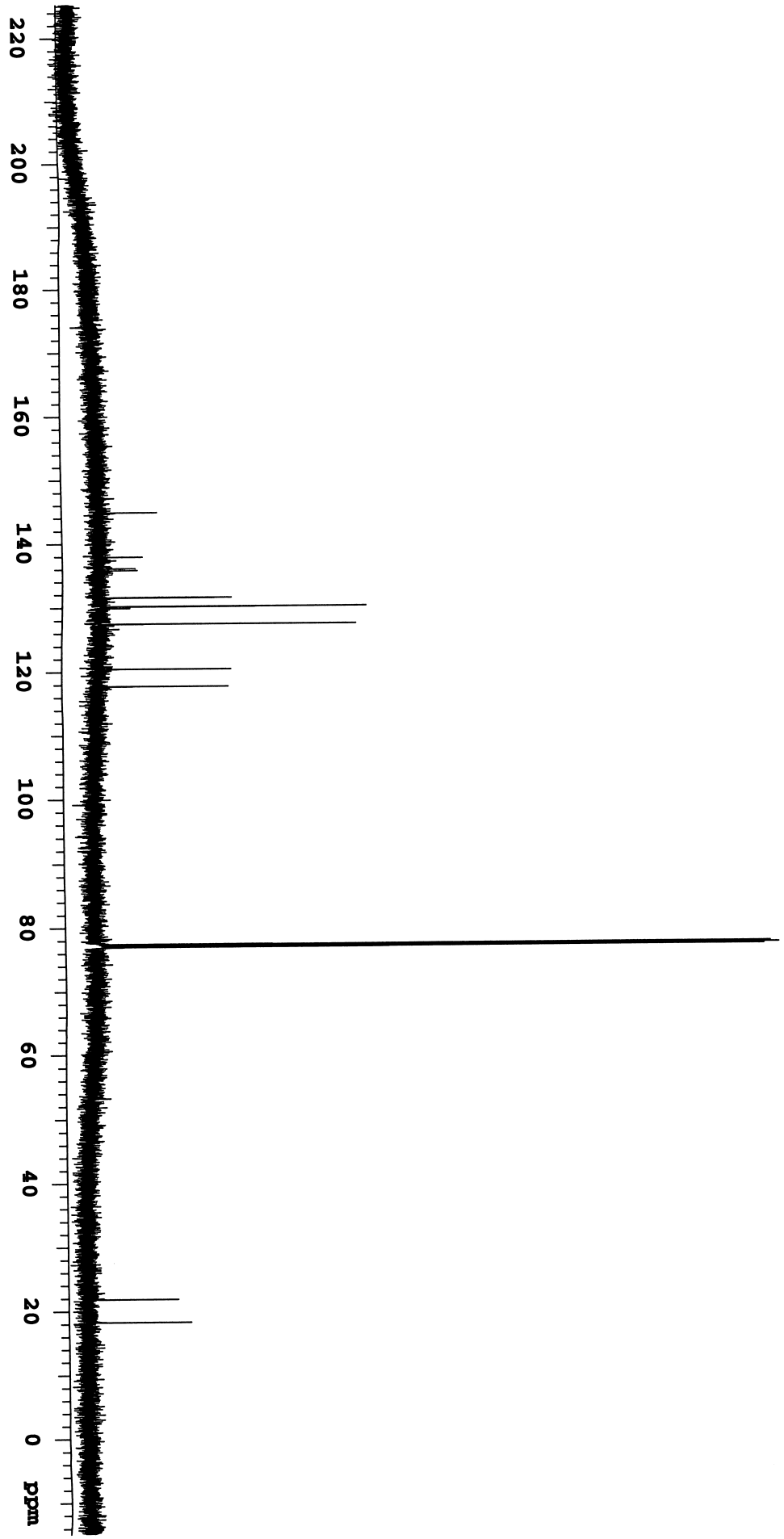

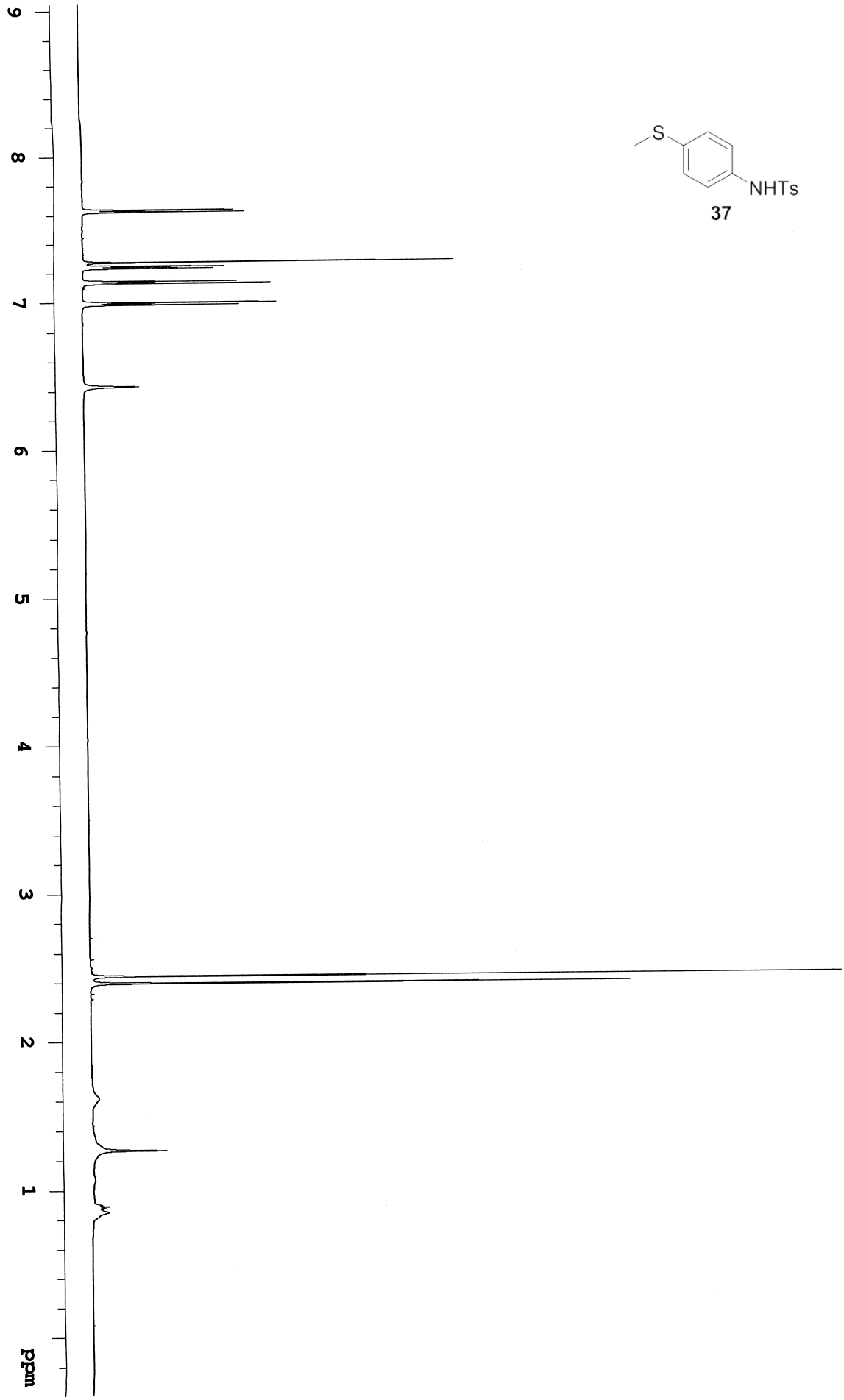





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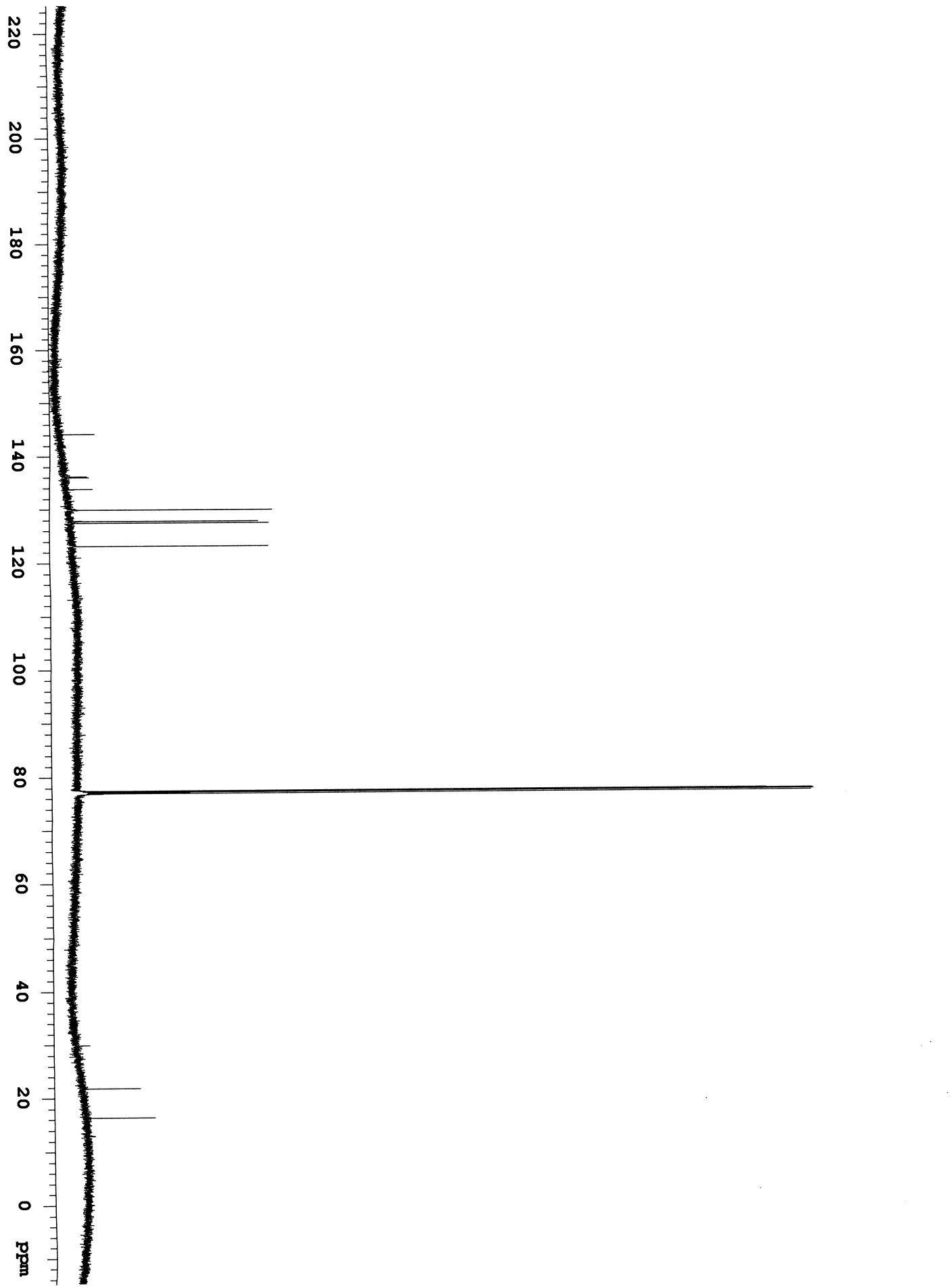

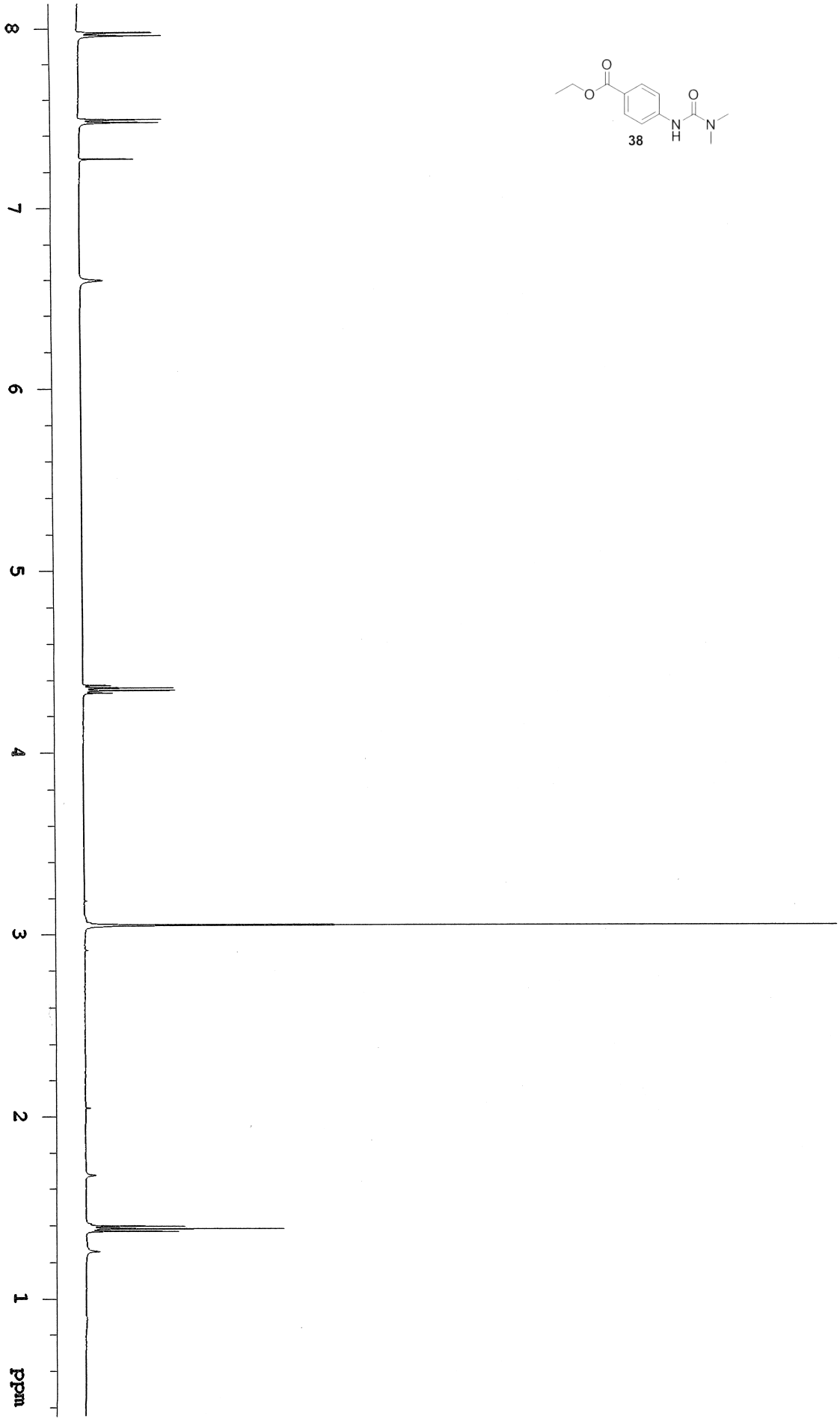





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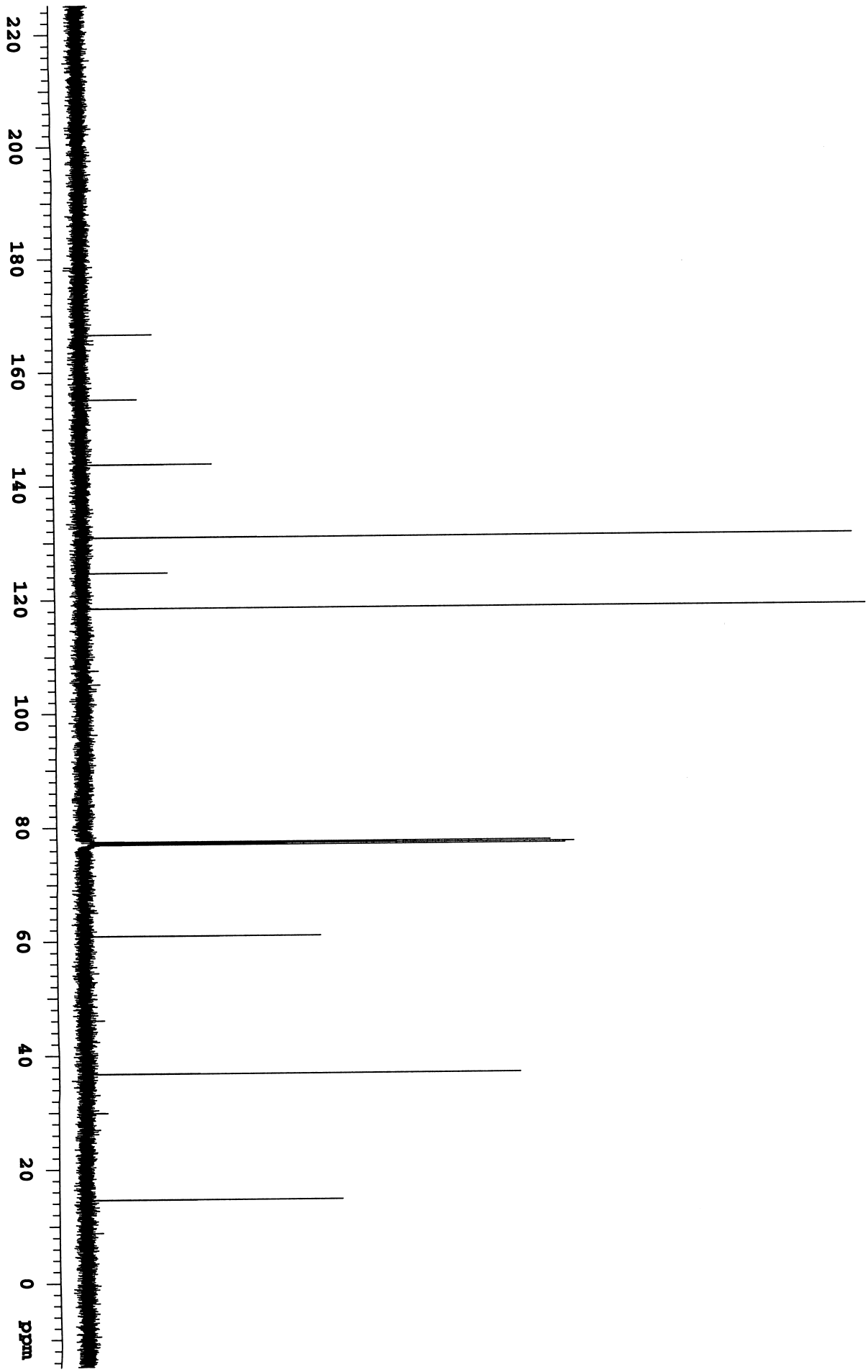

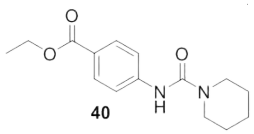


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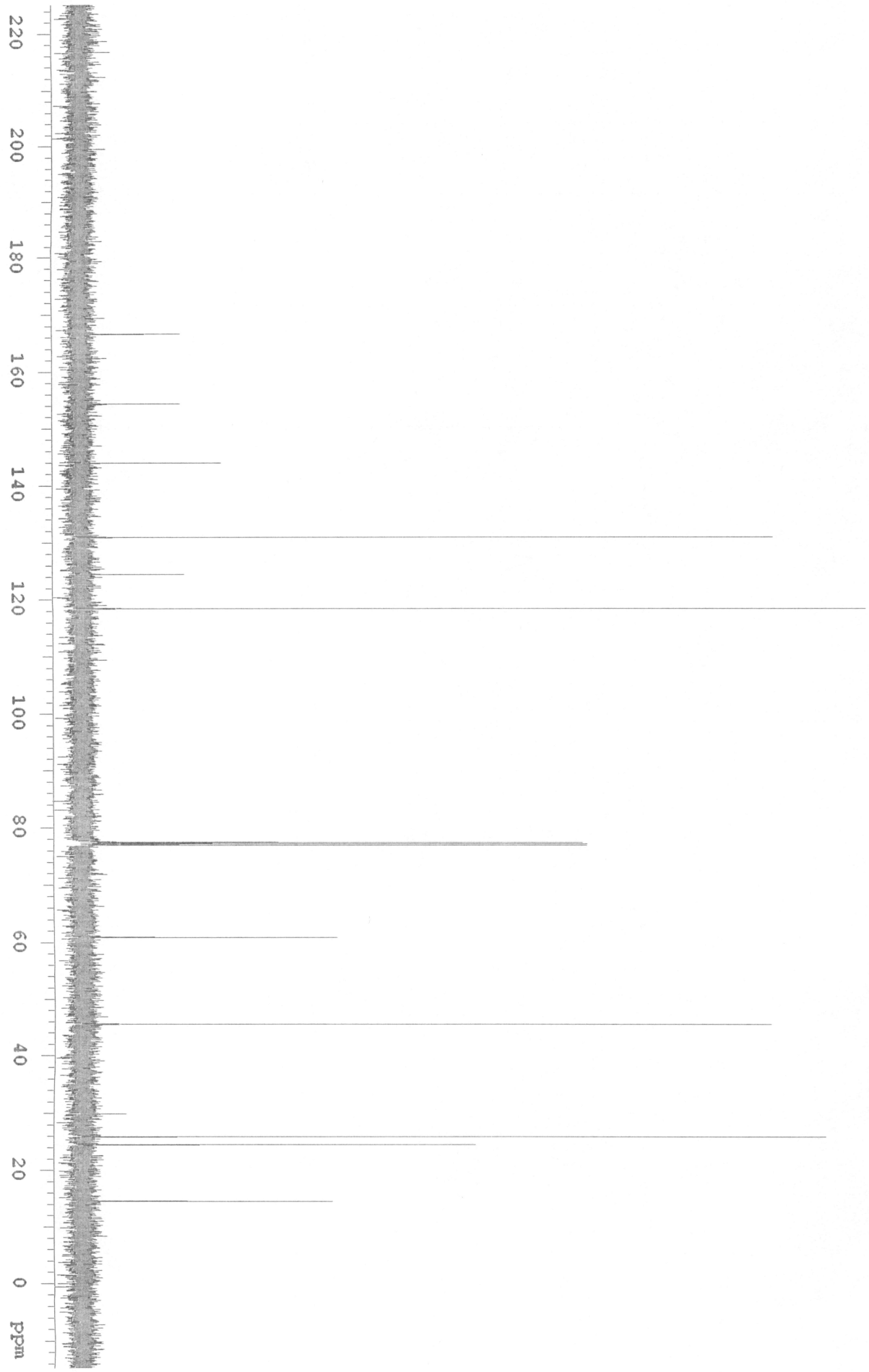

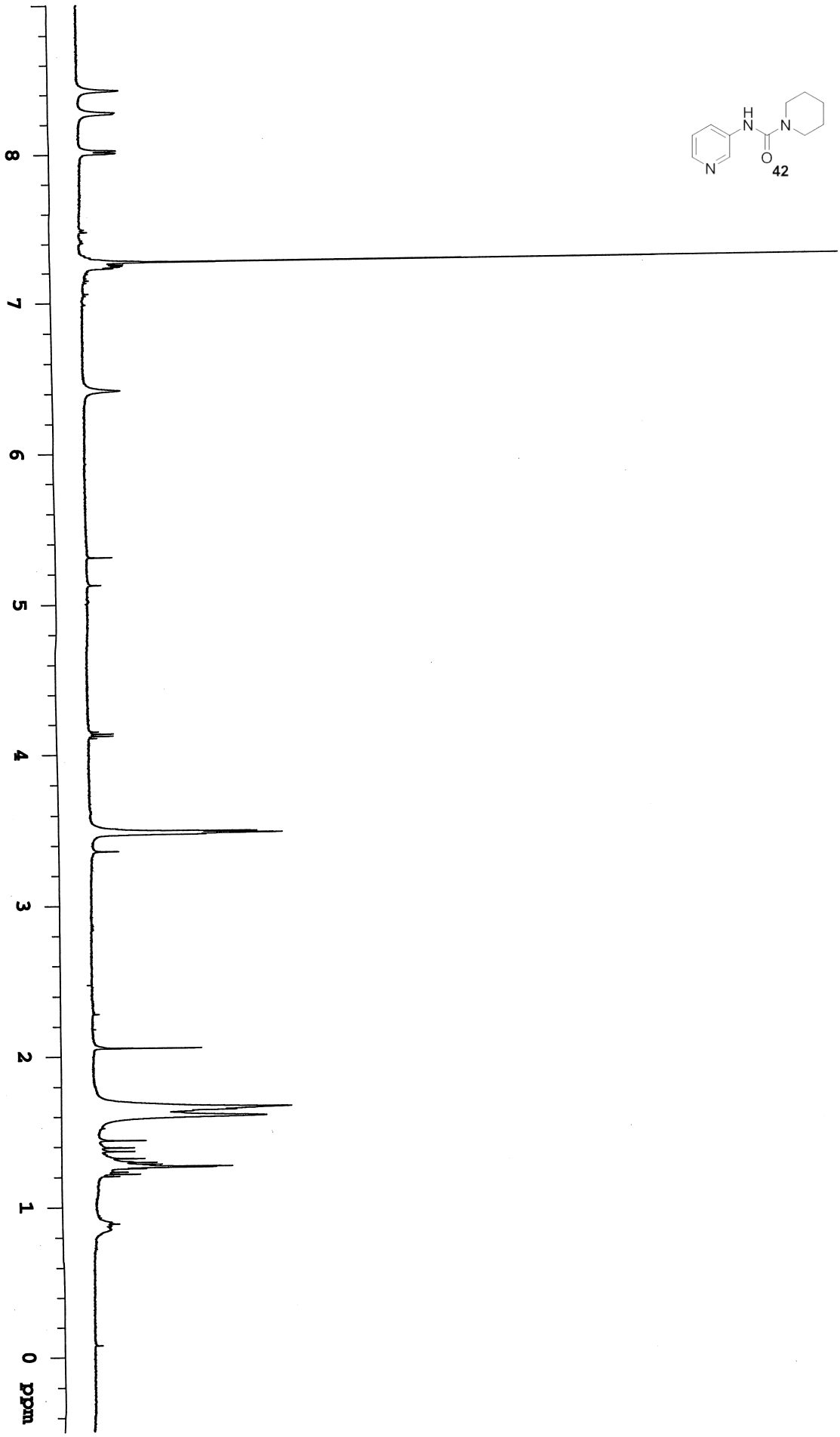





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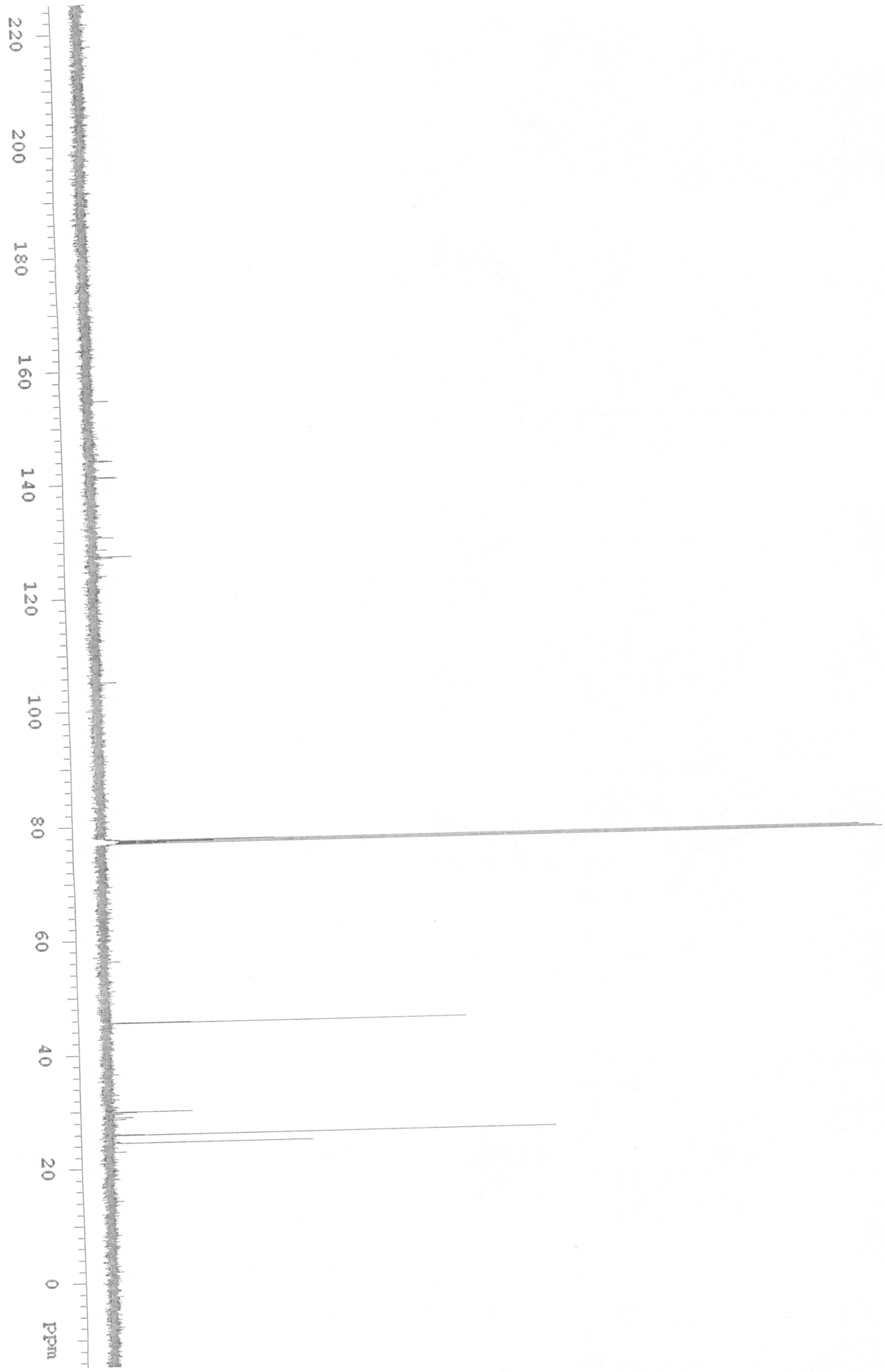

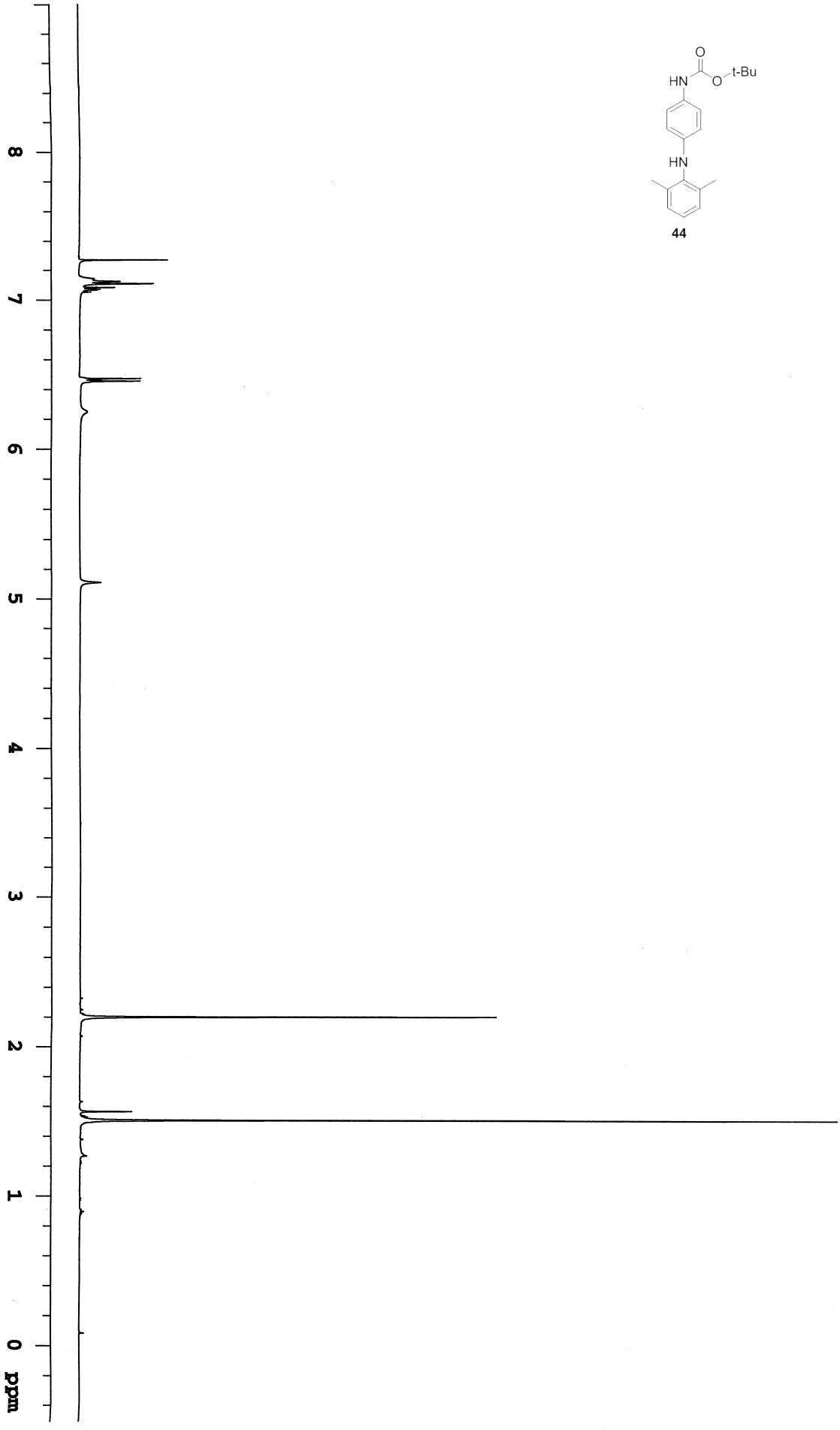





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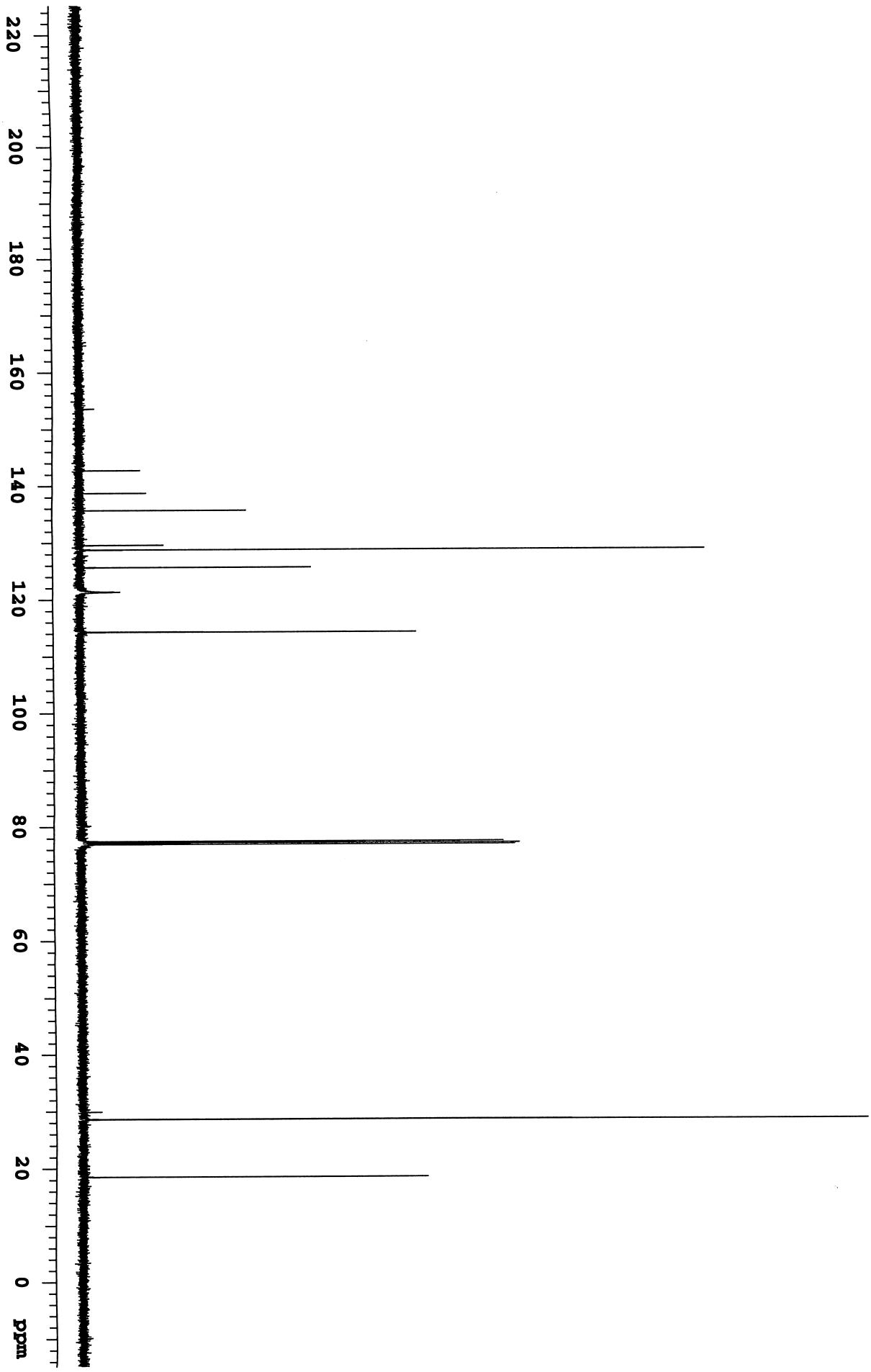
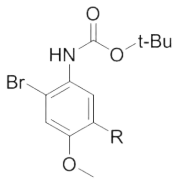
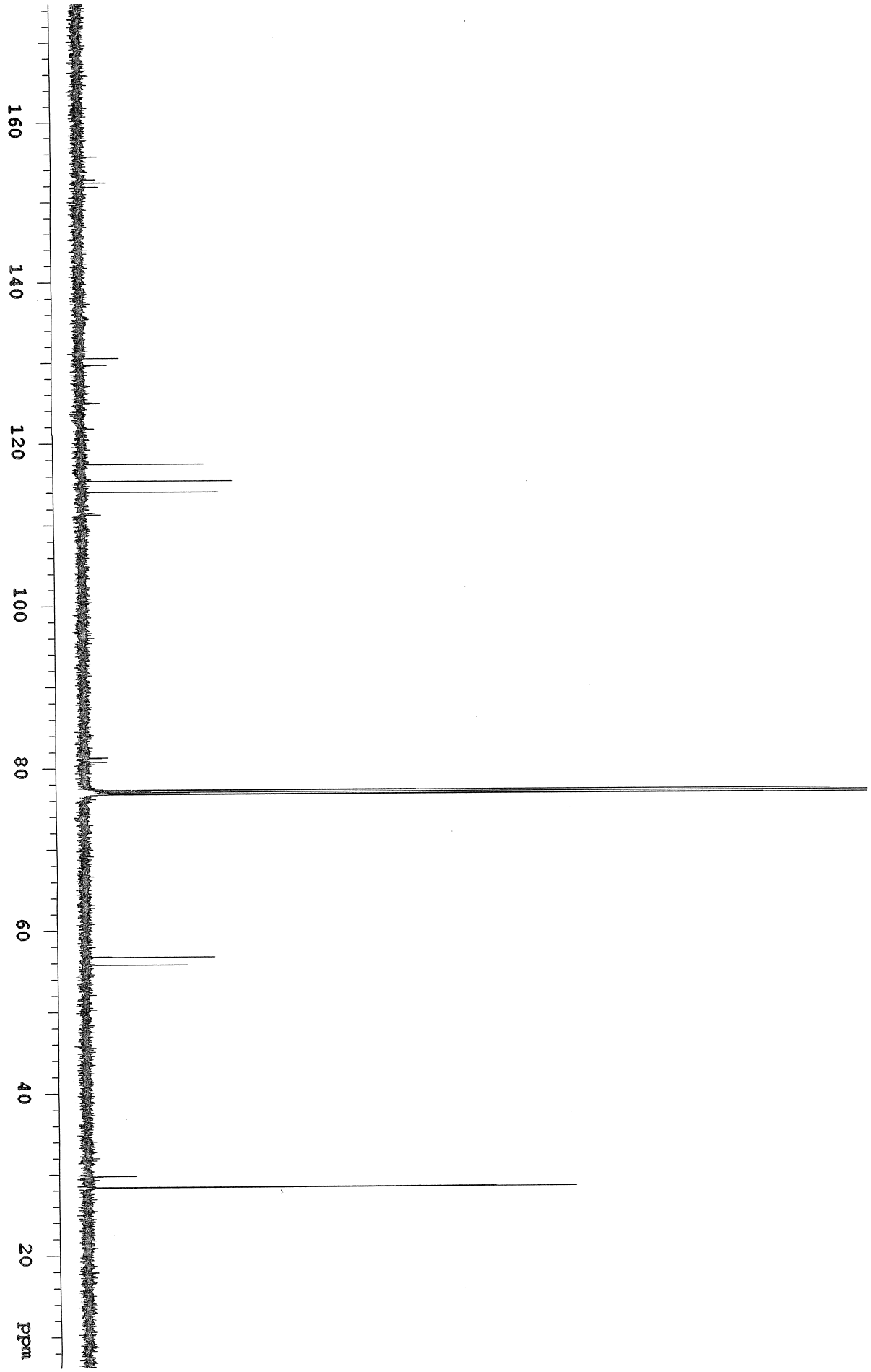
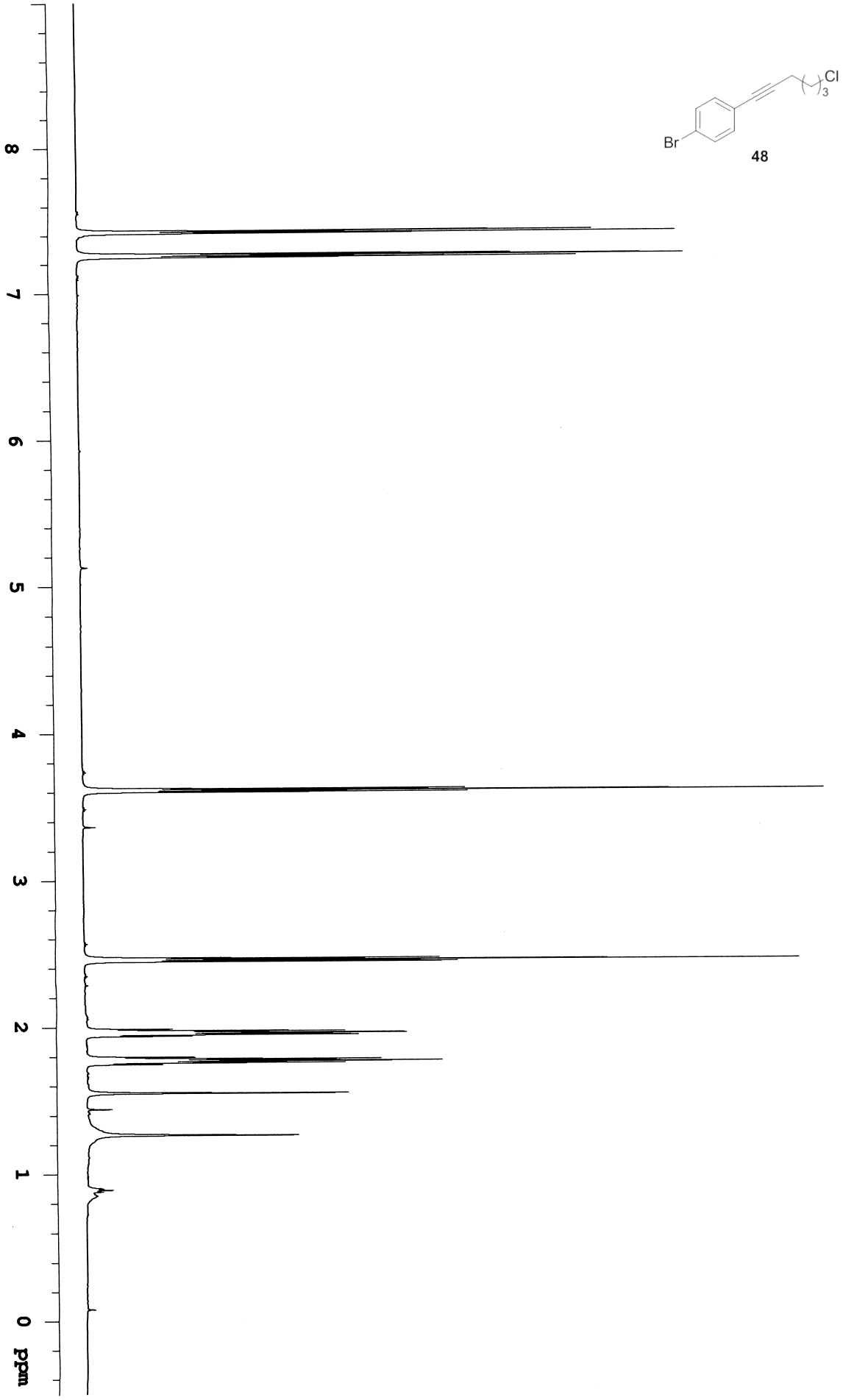
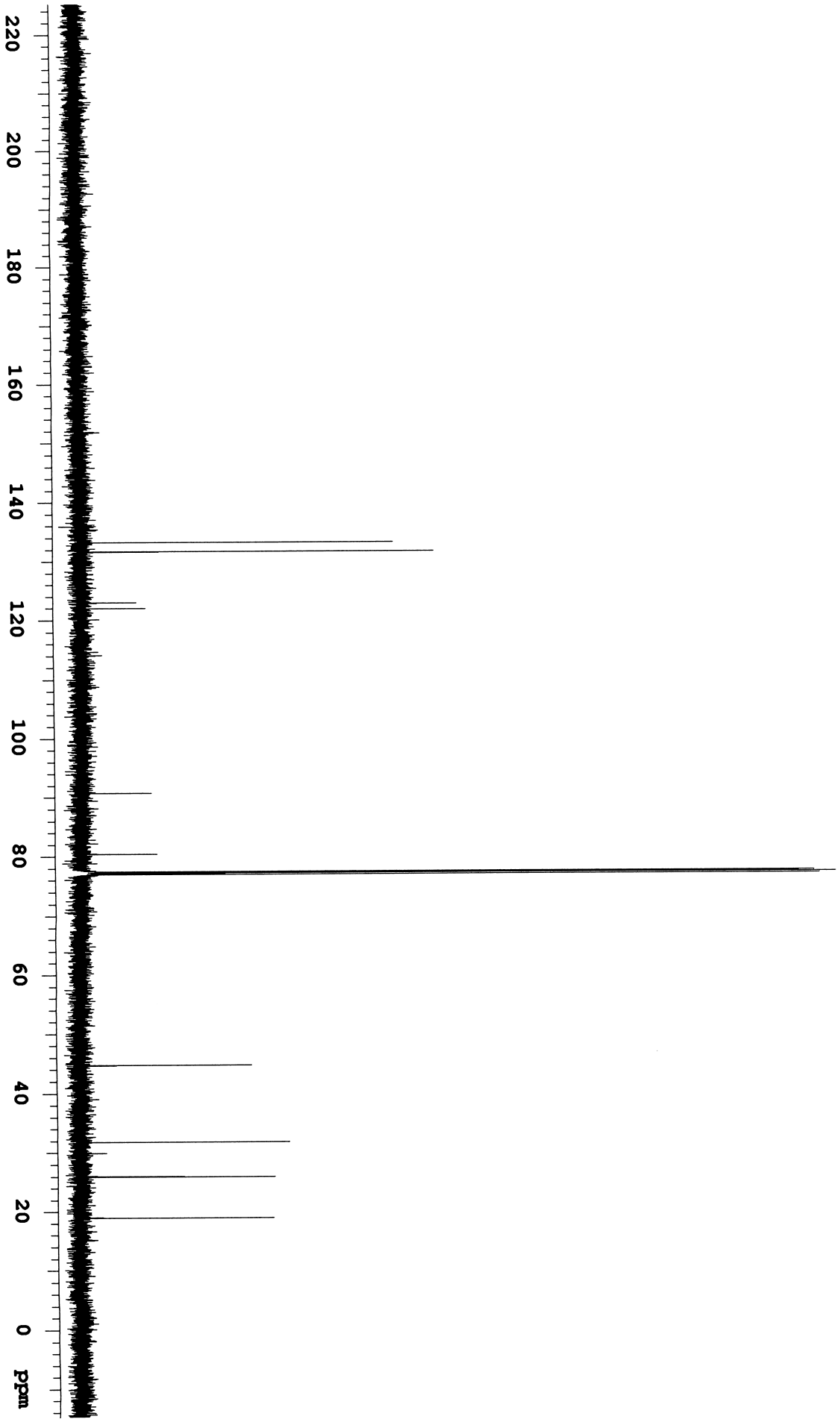


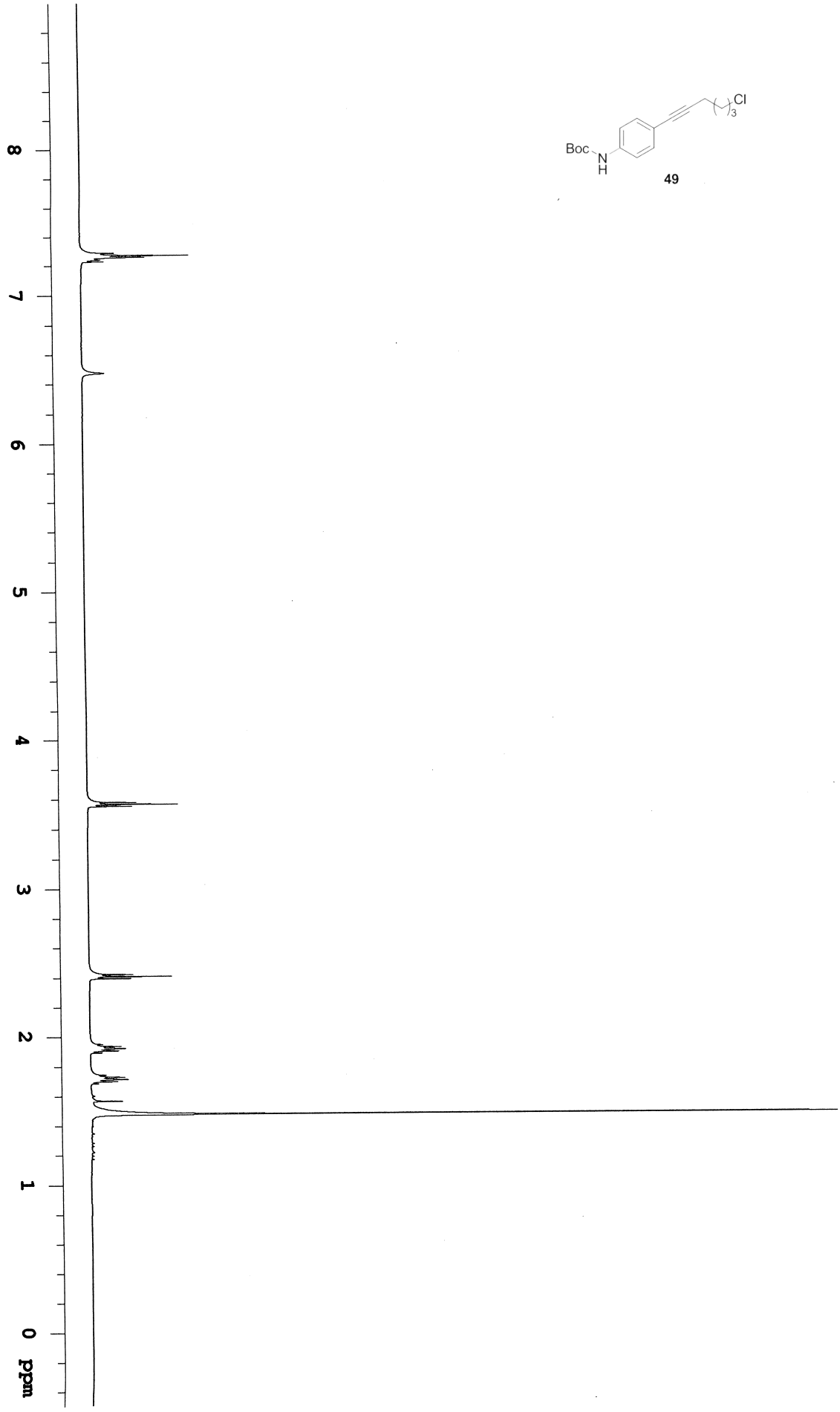



R = H, **46**
R = Br, **47**
spectrum of combined













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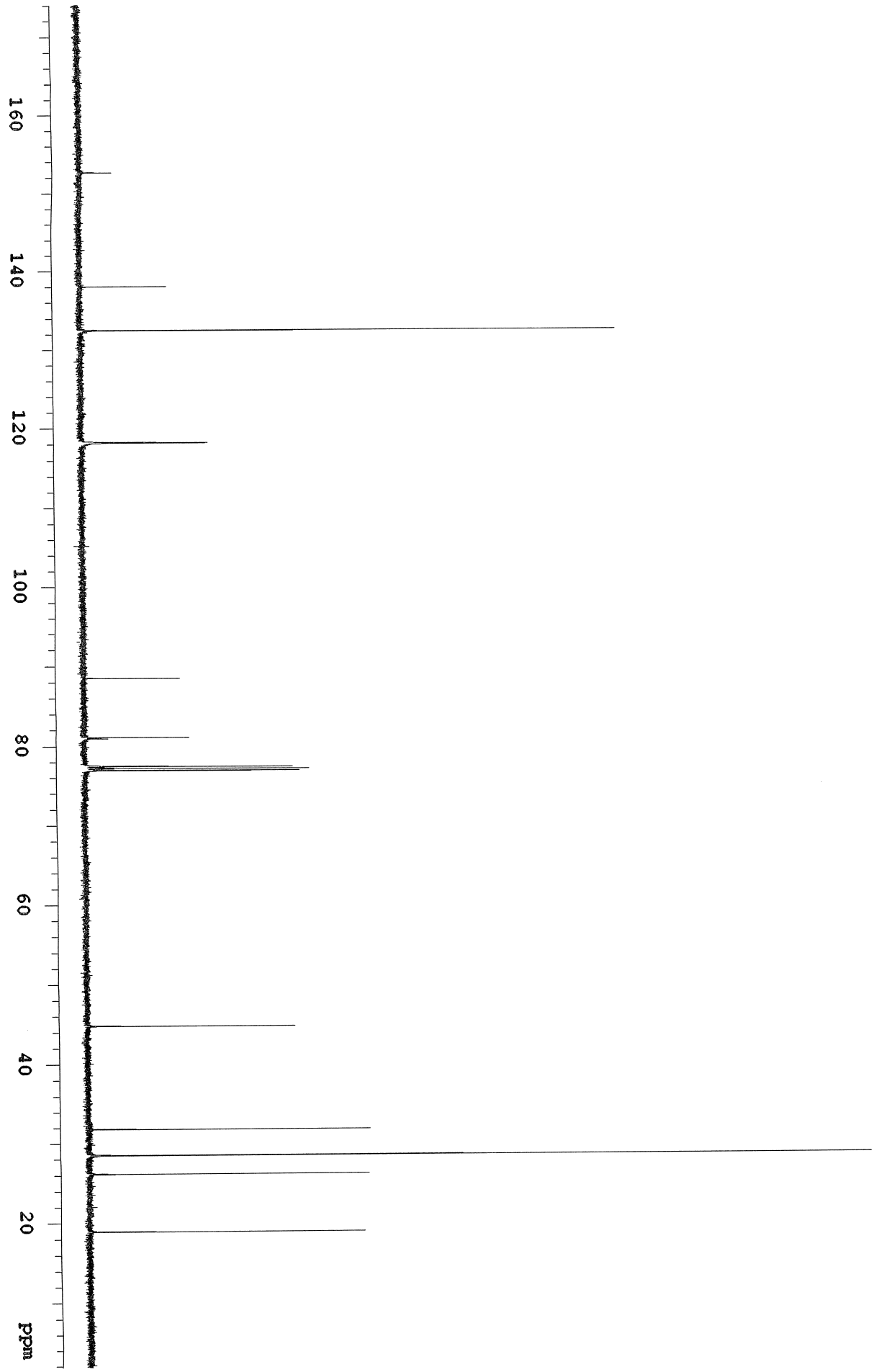

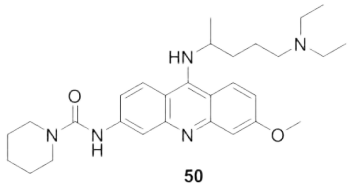


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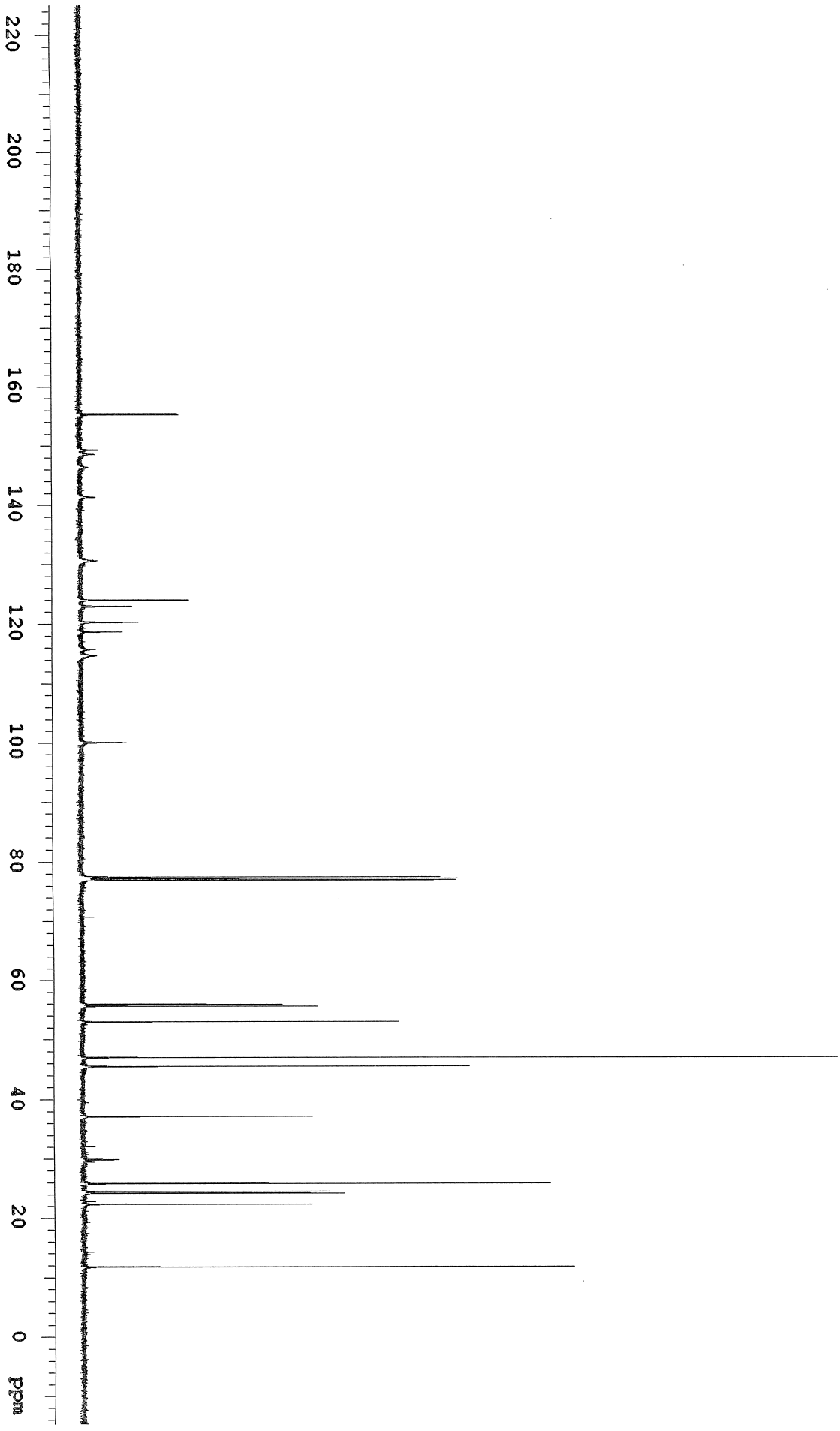

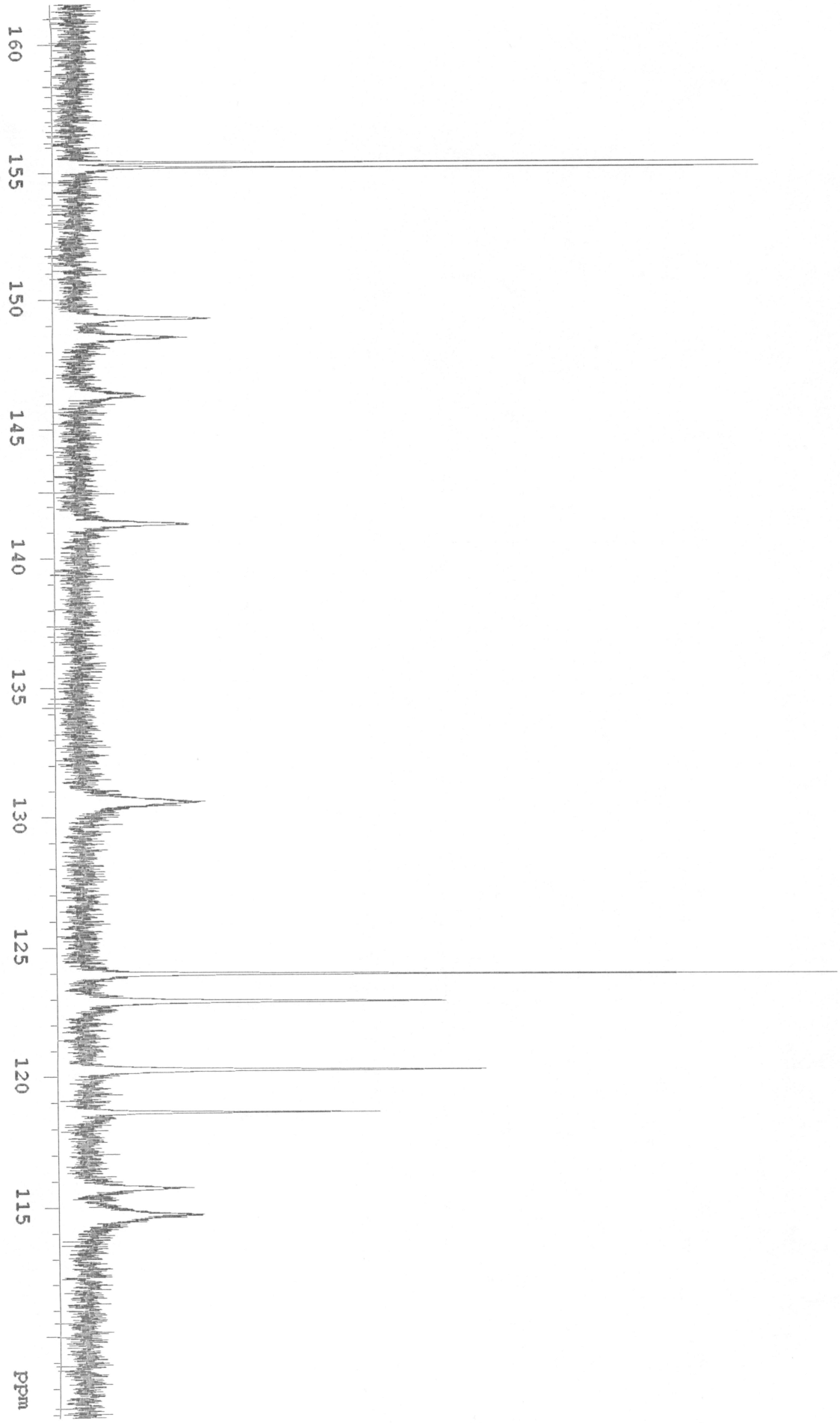

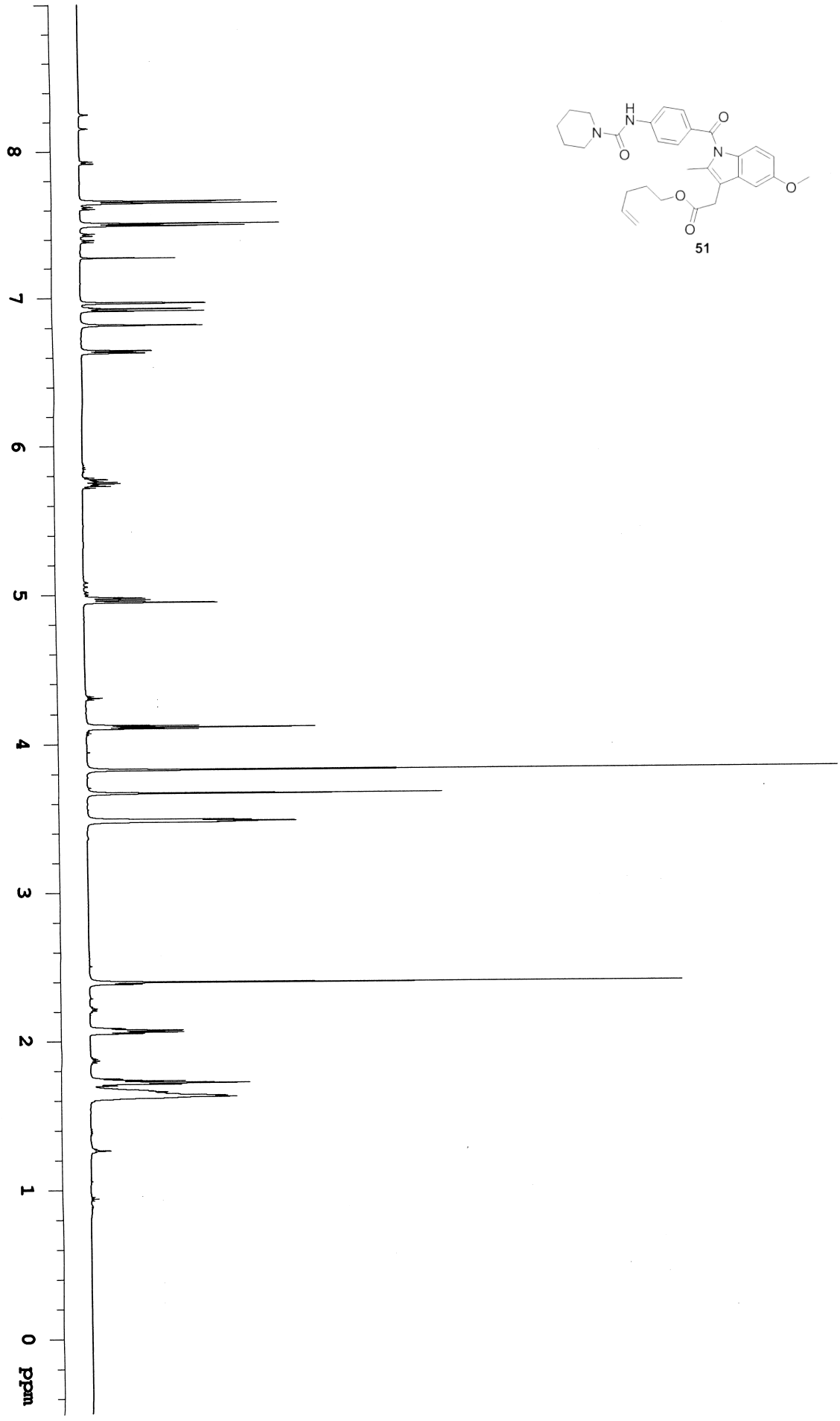





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