Copper-Catalyzed Cross Dehydrogenative Coupling Reactions of Tertiary Amines with Ketones or Indoles

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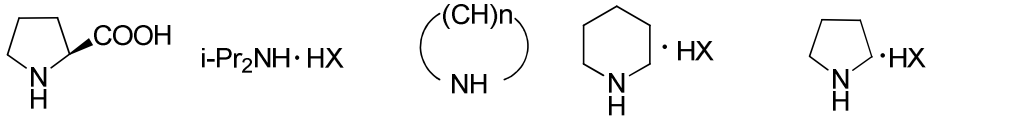
Supporting Information

Content

General Information

^{1}H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ on a Brucker ARX-300 (300 MHz) with TMS as internal standard. MS spectra was measured on ThermoFisher Scientific LCQ FLEET mass spectrometer. Ketones were dried over $CaSO_4$ and distilled. *N,N*-Dimethylaniline compounds were prepared from anilines according to the literature procedure.[1]

1. Optimizations of the CDC Reactions of *N,N*-Dimethylanilines with Ketones or Indoles



1

2a: HX = HOAc
2b: HX = PhCOOH

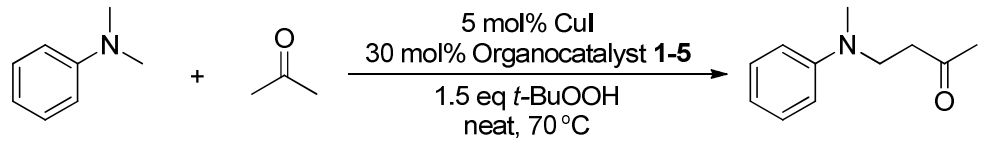
3a: n = 4
3b: n = 5

4a: HX = HOAc
4b: HX = PhCOOH

5a: HX = HOAc
5b: HX = PhCOOH
5c: HX = HBF4

Figure 1. Organocatalysts **1-5**

Table 1. Screening of Organocatalysts for the CDC Reaction of *N,N*-Dimethylaniline with Acetone.[a]

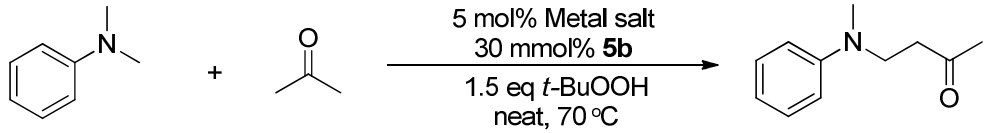


6a **7a** **8a**

entry	organocatalyst	t (h)	yield (%)[b]
1	**1**	8	0
2	**2a**	8	12
3	**2b**	8	15
4	**3a**	8	17
5	**3b**	8	trace
6	**4a**	8	8
7	**4b**	8	11
8	**5a**	4	23
9	**5b**	4	36
10	**5c**	4	18

[a] Reaction conditions: *N,N*-dimethylaniline (0.5 mmol), acetone (5.0 mmol), CuI (0.025 mmol), organocatalyst **1-5** (0.15 mmol), TBHP-decane (0.75 mmol), 70 °C. [b] Isolated yields.

Table 2. Screening of Metal Catalysts.[a]

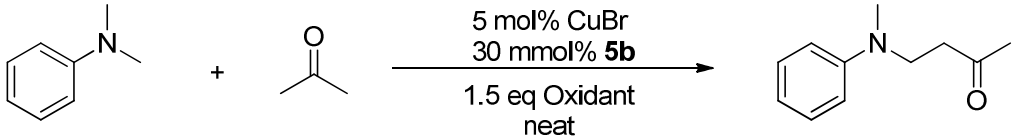


6a **7a** **8a**

entry	metal salt	t (h)	yield (%)[b]
1	CuCl	4	42
2	$CuCl_2$	4	35
3	$CuCl_2·2H_2O$	4	32
4	CuBr	4	53
5	CuI	4	36
6	$CuSO_4$	4	28
7	$Cu(OAc)_2$	4	40
8	$Cu(OAc)_2·2H_2O$	4	38
9	$Cu(acac)_2$	8	27
10	$FeCl_2$	4	28
11	$FeCl_3$	4	23
12	$Fe(acac)_2$	8	18
13	$CoCl_2·6H_2O$	4	26
14	$Co(OAc)_2·4H_2O$	4	22
15	$Co(acac)_2$	8	16
16	$Pd(OAc)_2$	8	11
17	$Fe(acac)_2$	8	18

[a] Reaction conditions: *N,N*-dimethylaniline (0.5 mmol), acetone (5.0 mmol), metal salt (0.025 mmol), organocatalyst **5b** (0.15 mmol), TBHP-decane (0.75 mmol), 70 °C. [b] Isolated yields.

Table 3. Screening of Oxidants.[a]

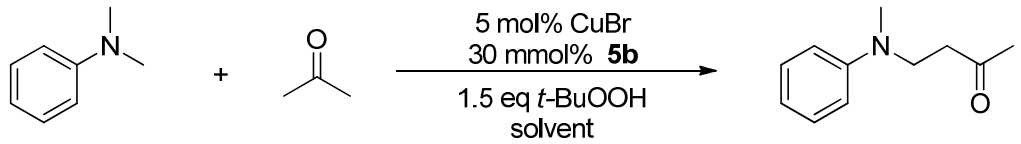


6a **7a** **8a**

entry	oxidant	temp (°C)	t (h)	yield (%)[b]
1	TBHB	70	4	53
2	TBP	70	8	0
3	O_2	50	8	14
4	H_2O_2	50	4	27
5	T-HYDRO	70	4	48

[a] Reaction conditions: *N,N*-dimethylaniline (0.5 mmol), acetone (5.0 mmol), CuBr (0.025 mmol), organocatalyst **5b** (0.15 mmol), oxidant (0.75 mmol), 70 °C. [b] Isolated yields.

Table 4. Screening of Solvents and Reaction Temperature.[a]

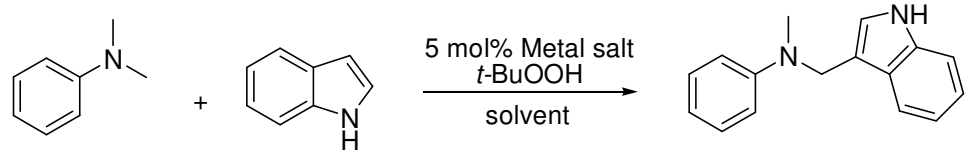


6a **7a** **8a**

entry	solvent	temp (°C)	t (h)	yield (%)[b]
1	DCE	rt	36	22
2	DCM	rt	36	14
3	$CHCl_3$	rt	36	trace
4	MeOH	rt	36	17
5	toluene	70	8	23
6	hexane	70	8	16
7	neat	50	8	38
8	neat	70	4	53
9[c]	MeOH	70	4	64

[a] Reaction conditions: *N,N*-dimethylaniline (0.5 mmol), acetone (5.0 mmol), CuBr (0.025 mmol), organocatalyst **5b** (0.15 mmol), TBHP-decane (0.75 mmol), solvent (1.0 mL). [b] Isolated yields. [c] MeOH (0.2 mL).

Table 5. Screening of Reaction Conditions for the CDC Reaction of *N,N*-Dimethylaniline with Indole .[a]



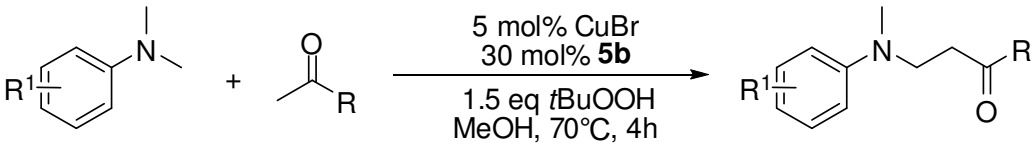
6a **9a** **10a**

entry	metal salt	TBHP (equiv)	temp (°C)	t (h)	solvent	yield (%)[b]
1	CuBr	1.0	40	3	neat	38
2	CuCl	1.0	40	3	neat	26
3	$CuCl_2$	1.0	40	3	neat	16
4	CuI	1.0	40	3	neat	25
5	$Cu(OAc)_2$	1.0	40	3	neat	18
6	CuBr	1.5	40	3	neat	52
7	CuBr	1.5	rt	12	neat	17
8	CuBr	1.5	50	3	neat	22
9	CuBr	1.5	40	12	CH_3CN	9
10	CuBr	1.5	40	12	hexane	18
11	CuBr	1.5	40	12	toluene	25

[a] Reaction conditions: *N,N*-dimethylaniline (1.0 mmol), indole (0.5 mmol), metal catalyst (0.025mmol), indicated amount of TBHP. [b] Isolated yields.

2. The CDC Reactions of *N*,*N*-dimethylanilines with ketones or indoles

(1) The CDC reaction by cooperative copper and aminocatalysis for the synthesis of β-arylamino ketones **8a-k**.

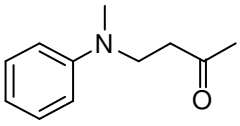


6a-g **7a-c** **8a-k**

6a: R^1 = H
6b: R^1 = 4-Me
6c: R^1 = 4-Cl
6d; R^1 = 4-OMe
6e: R^1 = 4-Br
6f : R^1 = 3-Me
6g: *N,N*-dimetyl-2-naphthylamine
7a: R^2 = Me
7b: R^2 = Et
7c: R^2 = n-Pr

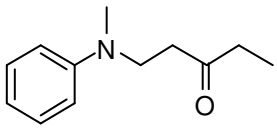
General procedure: A solution of ketone **7a-c** (5.0 mmol), pyrrolidine benzoate **5b** (29.0 mg, 0.15 mmol, 30 mol%) in MeOH (0.2 mL) was stired at room temperature for 15 min. To the mixture were added *N*,*N*-dimethylaniline **6a-g** (0.5 mmol) and CuBr (3.6 mg, 0.025 mmol), and then the solution of 5.5 M TBHP in decane (136 μL, 0.75 mmol) was added dropwise. The reaction mixture was stirred in a sealed vial at 70℃ for 4 -8 h. After the reaction was completed, the mixture was purified by preparative TLC (petroleum ether/ethyl acetate = 20:1 as eluent) to afford the desired β-arylamino ketones **8a-k**.

4-(*N*-Methyl-*N*-phenylamino)butan-2-one **8a**[2]



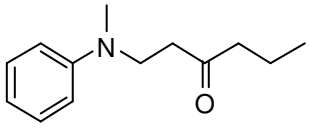
Yield: 64%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.30-7.20 (m, 2 H), 6.78-6.67 (m, 3 H), 3.64 (t, *J* = 6.9 Hz, 2 H), 2.92 (s, 3 H), 2.71 (t, *J* = 6.9 Hz, 2 H), 2.15 (s, 3 H).

1-(*N*-Methyl-*N*-phenylamino)pentan-3-one **8b**[3]



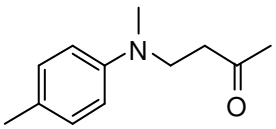
Yield: 53%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.27-7.17 (m, 2 H), 6.75-6.63 (m, 3 H), 3.62 (t, *J* = 6.9 Hz, 2 H), 2.89 (s, 3 H), 2.64 (t, *J* = 6.9 Hz, 2 H), 2.39 (q, *J* = 7.2 Hz, 2 H), 1.02 (t, *J* = 7.2 Hz, 3 H).

1-(*N*-Methyl-*N*-phenylamino)hexan-3-one **8c**



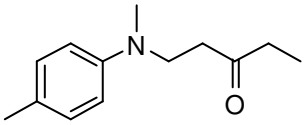
Yield: 42%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.28-7.18 (m, 2 H), 6.77-6.65 (m, 3 H), 3.62 (t, *J* = 6.9 Hz, 2 H), 2.89 (s, 3 H), 2.64 (t, *J* = 6.9 Hz, 2 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 1.65-1.50 (m, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 210.3, 148.7, 129.3, 116.7, 112.5, 47.5, 45.5, 39.4, 38.5, 17.2, 13.7; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{19}NO$: 206.15, found: 206.25.

4-(*N*-Methyl- *N*-(4-methylphenyl)amino)butan-2-one **8d**[4]



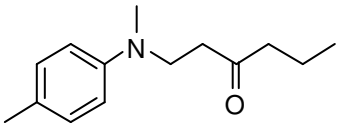
Yield: 73%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.05 (d, *J* = 8.1, 2 H), 6.65 (d, *J* = 8.1, 2 H), 3.59 (t, *J* = 6.9 Hz, 2 H), 2.88 (s, 3 H), 2.69 (t, *J* = 6.9 Hz, 2 H), 2.25 (s, 3 H), 2.14 (s, 3 H).

1-(*N*-Methyl-*N*-(4-methylphenyl)amino)pentan-3-one **8e**



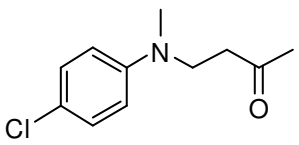
Yield: 56%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.02 (d, *J* = 8.1 Hz, 2 H), 6.61 (d, *J* = 8.1 Hz, 2 H), 3.59 (t, *J* = 6.9 Hz, 2 H), 2.85 (s, 3 H), 2.62 (t, *J* = 6.9 Hz, 2 H), 2.39 (q, *J* = 7.2 Hz, 2 H), 2.24 (s, 3 H), 1.02 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 210.7, 146.6, 129.7, 125.9, 112.9, 47.8, 38.8, 38.6, 36.6, 20.2, 7.6; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{19}NO$: 206.15, found: 206.17.

1-(*N*-Methyl-*N*-(4-methylphenyl)amino)hexan-3-one **8f**



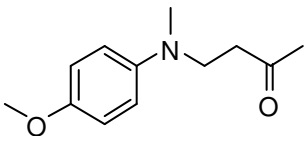
Yield: 44%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.03 (d, *J* = 8.7 Hz, 2 H), 6.62 (d, *J* = 8.7 Hz, 2 H), 3.58 (t, *J* = 6.9 Hz, 2 H), 2.85 (s, 3 H), 2.60 (t, *J* = 6.9 Hz, 2 H), 2.34 (t, *J* = 7.5 Hz, 2 H), 2.24 (s, 3 H), 1.63-1.48 (m, 2 H), 0.88 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 210.3, 146.6, 129.7, 125.8, 112.9, 47.7, 45.4, 39.1, 38.6, 20.2,17.1, 13.7; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{21}NO$: 220.17, found: 220.17.

4-(*N*-(4-chlorophenyl)-*N*-methyl)amino)butan-2-one **8g**[5]



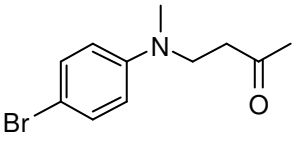
Yield: 57%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.16 (d, *J* = 9.0 Hz, 2 H), 6.61 (d, *J* = 9.0 Hz, 2 H), 3.61 (t, *J* = 6.9 Hz, 2 H), 2.90 (s, 3 H), 2.69 (t, *J* = 6.9 Hz, 2 H), 2.16 (s, 3 H).

4-(*N*-(4-Methoxyphenyl)-*N*-methylamino)butan-2-one **8h**



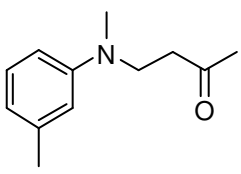
Yield: 58%. ^{1}H NMR ($CDCl_3$) δ (ppm): 6.88-6.80 (m, 2 H), 6.76-6.68 (m, 2 H), 3.76 (s, 3 H), 3.54 (t, *J* = 6.9 Hz, 2 H), 2.84 (s, 3 H), 2.66 (t, *J* = 6.9 Hz, 2 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 208.1, 152.0, 143.6, 115.0, 114.7, 55.6, 48.5, 40.1, 39.1, 30.5; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{17}NO_2$: 208.13, found: 208.17.

4-(*N*-(4-Bromophenyl)-*N*-methylamino)butan-2-one **8i**



Yield: 52%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.29 (d, *J* = 9.0 Hz, 2 H), 6.56 (d, *J* = 9.0 Hz, 2 H), 3.60 (t, *J* = 6.9 Hz, 2 H), 2.89 (s, 3 H), 2.68 (t, *J* = 6.9 Hz, 2 H), 2.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 207.6, 147.6, 131.9, 114.0, 108.4, 47.2, 40.1, 38.5, 30.6; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{11}H_{14}BrNO$ (M+H): 256.03, found: 256.17.

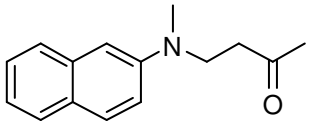
4-(*N*-Methyl-*N*-(3-methylphenyl)amino)butan-2-one **8j**



Yield: 68%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.17-7.08 (m, 1 H), 6.59-6.47 (m,

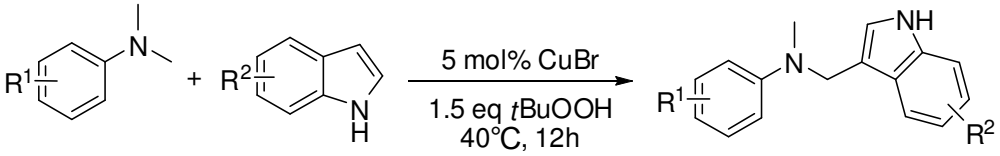
3 H), 3.62 (t, *J* = 6.9 Hz, 2 H), 2.90 (s, 3 H), 2.69 (t, *J* = 6.9 Hz, 2 H), 2.31 (s, 3 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 208.1, 148.8, 139.0, 129.2, 117.7, 113.3, 109.7, 47.3, 40.4, 38.6, 30.6, 22.0; MS (ESI) *m/z* Calcd for $C_{12}H_{17}NO$ (M+H): 192.14, found: 192.17.

4-(*N*-Methyl-*N*-(naphthalen-2-yl)amino)butan-2-one **8k**



Yield: 55%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.72-7.58 (m, 3 H), 7.38-7.30 (m, 1 H), 7.23-7.15 (m, 1 H), 7.13-7.07 (m, 1 H), 6.86 (d, *J* = 2.7 Hz, 1 H), 3.70 (t, *J* = 6.9 Hz, 2 H), 2.97 (s, 3 H), 2.68 (t, *J* = 6.9 Hz, 2 H), 2.10 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 208.0, 146.7, 135.0, 129.0, 127.5, 126.9, 126.3, 126.2, 122.2, 116.2, 106.6, 47.6, 40.4, 38.7, 30.6; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{17}NO$: 228.14, found: 228.17.

(2) The CDC reaction of *N*,*N*-dimethylanilines with indoles for the synthesis of alkyated indole derivatives **10a-g**.



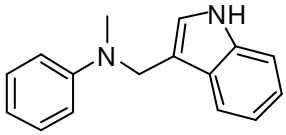
6a-c **9a-d** **10a-g**

6a: R^1 = H
6b: R^1 = 4-Me
6c: R^1 = 4-Cl

9a: R^2 = H
9b: R^2 = 5-Br
9c: R^2 = 5-NO_2
9d: R^2 = 6-$COOCH_3$

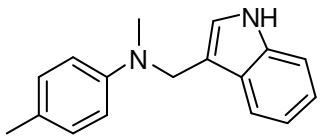
General procedure: To the mixture of *N*,*N*-dimethylanilines **6a-c** (1.0 mmol), indoles **9a-d** (0.50 mmol) and CuBr (3.6 mg, 0.025 mmol) was added the solution of 5.5 M TBHP in decane (136 μL, 0.75 mmol) dropwise at room temperature. The reaction mixture was stirred at 40 ℃ for 3 h. After the reaction was finished, the mixture was purified by preparative TLC (petroleum ether/ethyl acetate = 8:1 as eluent) to afford the alkylated indole derivatives **10a-g**.

N-((1H-Indol-3-yl)methyl)-*N*-methylbenzenamine **10a**[6]



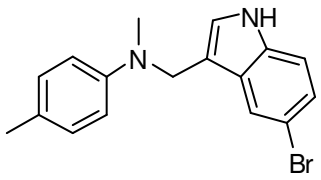
Yield: 52%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.82 (s, 1 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 7.32-7.05 (m, 5 H), 6.92-6.83 (m, 3 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 4.64 (s, 2 H), 2.94 (s, 3 H).

N-((1H-Indol-3-yl)methyl)-*N*,4-dimethylbenzenamine **10b**



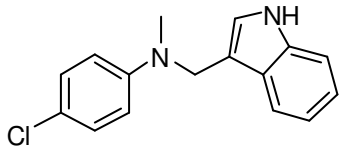
Yield: 72%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.84 (s, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H), 7.28-7.02 (m, 5 H), 6.90-6.85 (m, 1 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 4.58 (s, 2 H), 2.89 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 148.3, 136.4, 129.8, 126.9, 126.1, 122.8, 122.0, 119.5, 119.1, 113.8, 113.0, 111.3, 49.1, 38.2, 20.4; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{18}N_2$: 251.15, found: 251.25.

N-((5-Bromo-1*H*-indol-3-yl)methyl)-*N*, 4-menthylbenzenamine **10c**



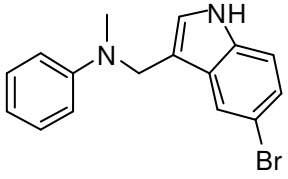
Yield: 76%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.91 (s, 1 H), 7.65 (d, *J* = 1.8 Hz, 1 H), 7.25-7.18 (m, 1 H), 7.12-6.98 (m, 3 H), 6.87-6.82 (m, 1 H), 6.77 (d, *J* = 8.7 Hz, 2 H), 4.49 (s, 2 H), 2.85 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 148.2, 138.0, 129.8, 128.7, 126.6, 125.0, 124.0, 121.7, 114.1, 113.0, 112.8, 112.7, 49.2, 38.4, 20.4; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{17}BrN_2$: 329.06, found: 329.00.

N-((1H-Indol-3-yl)methyl)-4-chloro-*N*-methylbenzenamine **10d**



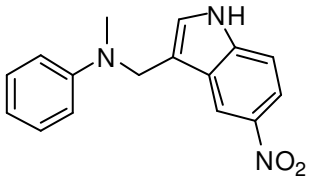
Yield: 67%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.87 (s, 1 H), 7.52 (d, *J* = 7.8 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 1 H), 7.23-7.05 (m, 4 H), 6.90-6.85 (m, 1 H), 6.72 (d, *J* = 8.7 Hz, 2 H), 4.60 (s, 2 H), 2.91 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 148.6, 136.5, 129.0, 126.8, 122.7, 122.4, 119.8, 119.0, 114.3, 113.5, 112.7, 111.4, 48.9, 38.3; MS (EI) *m/z* $[M]^+$ Calcd for $C_{16}H_{15}ClN_2$: 270.1, found: 270.1.

N-((5-Bromo-1*H*-indol-3-yl)methyl)-*N*-methylbenzenamine **10e**



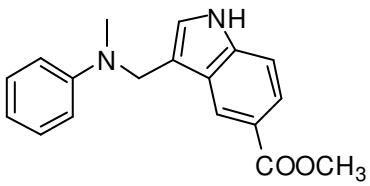
Yield: 69%. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.82 (s, 1 H), 7.69 (d, *J* = 1.2 Hz, 1 H), 7.28-7.18 (m, 3 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 6.87-6.78 (m, 3 H), 6.74 (t, *J* = 7.2 Hz, 1 H), 4.53 (s, 2 H), 2.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 150.1, 135.1, 129.3, 128.6, 125.0, 123.9, 121.7, 117.1, 113.4, 113.0, 112.9, 112.8, 48.7, 38.2; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{15}BrN_2$: 315.05, found: 315.00.

N-Methyl-*N*-((5-nitro-1*H*-indol-3-yl)methyl)benzenamine **10f**



Yield: 78%. ^{1}H NMR (DMSO) δ (ppm): 11.66 (s, 1 H), 8.50 (d, *J* = 1.8 Hz, 1 H), 7.97 (dd, *J* = 9.0 Hz, 2.1 Hz, 1 H), 7.51 (d, *J* = 9.0 Hz, 1 H), 7.41 (d, *J* = 2.1 Hz, 1 H), 7.22-7.10 (m, 2 H), 6.85 (d, *J* = 7.8 Hz, 2 H), 6.63 (t, *J* = 7.2 Hz, 1 H), 4.69 (s, 2 H), 2.90 (s, 3 H); ^{13}C NMR (DMSO) δ (ppm): 150.3, 141.2, 140.4, 129.8 (2 C), 128.4, 126.8, 117.4, 117.2, 117.0, 115.5, 113.9, 112.8, 48.1, 38.7; MS (ESI) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{15}N_3O_2$: 282.12, found: 282.08.

Methyl 3-((*N*-methyl-*N*-phenylamino)methyl)-1*H*-indole-5-carboxylate **10g**



Yield: 64%. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.53 (s, 1 H), 8.09 (d, *J* = 0.6 Hz, 1 H), 7.78 (dd, *J* = 8.1 Hz, 1.2 Hz, 1 H), 7.56 (d, *J* = 8.1 Hz, 1 H), 7.30-7.20 (m, 2 H), 7.12-7.06 (m, 1 H), 6.85 (d, *J* = 8.1 Hz, 2 H), 6.74 (t, *J* = 6.9 Hz, 1 H), 4.63 (s, 2 H), 3.91 (s, 3 H), 2.93 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ (ppm): 168.4, 150.0, 135.9, 130.5, 129.3, 126.3, 123.7, 120.6, 118.7, 117.1, 113.8, 113.6, 113.4, 52.1, 48.7, 38.2; MS

(EI) *m/z* $[M]^+$ Calcd for $C_{18}H_{18}N_2O_2$: 294.1, found: 294.1.

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(2) Bartoli, G.; Bartolacci, M.; Giuliani, A.; Marcantoni, E.; Massaccesi, M.; Torregiani, E. *J. Org. Chem*. **2005**, *70*, 169.

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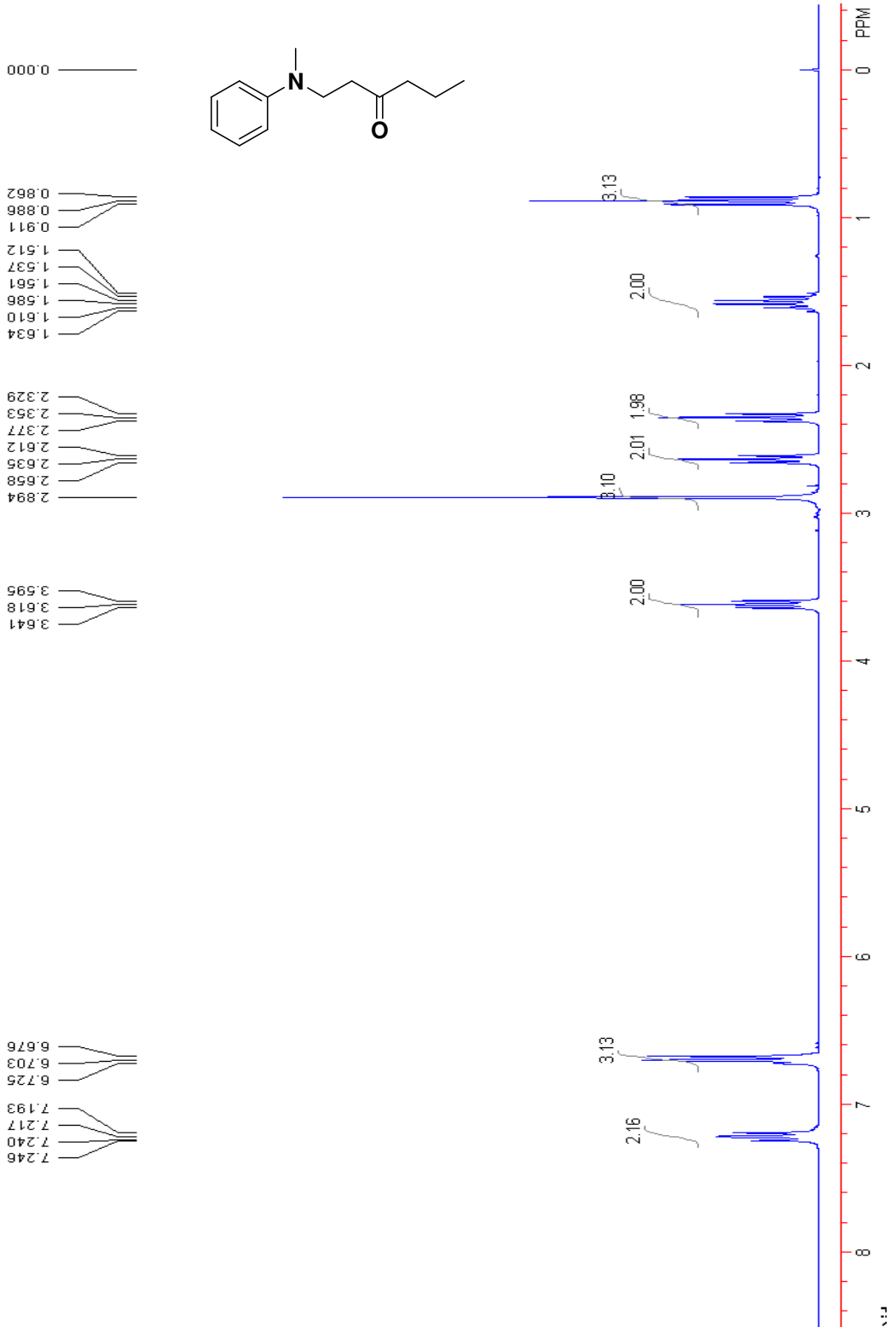
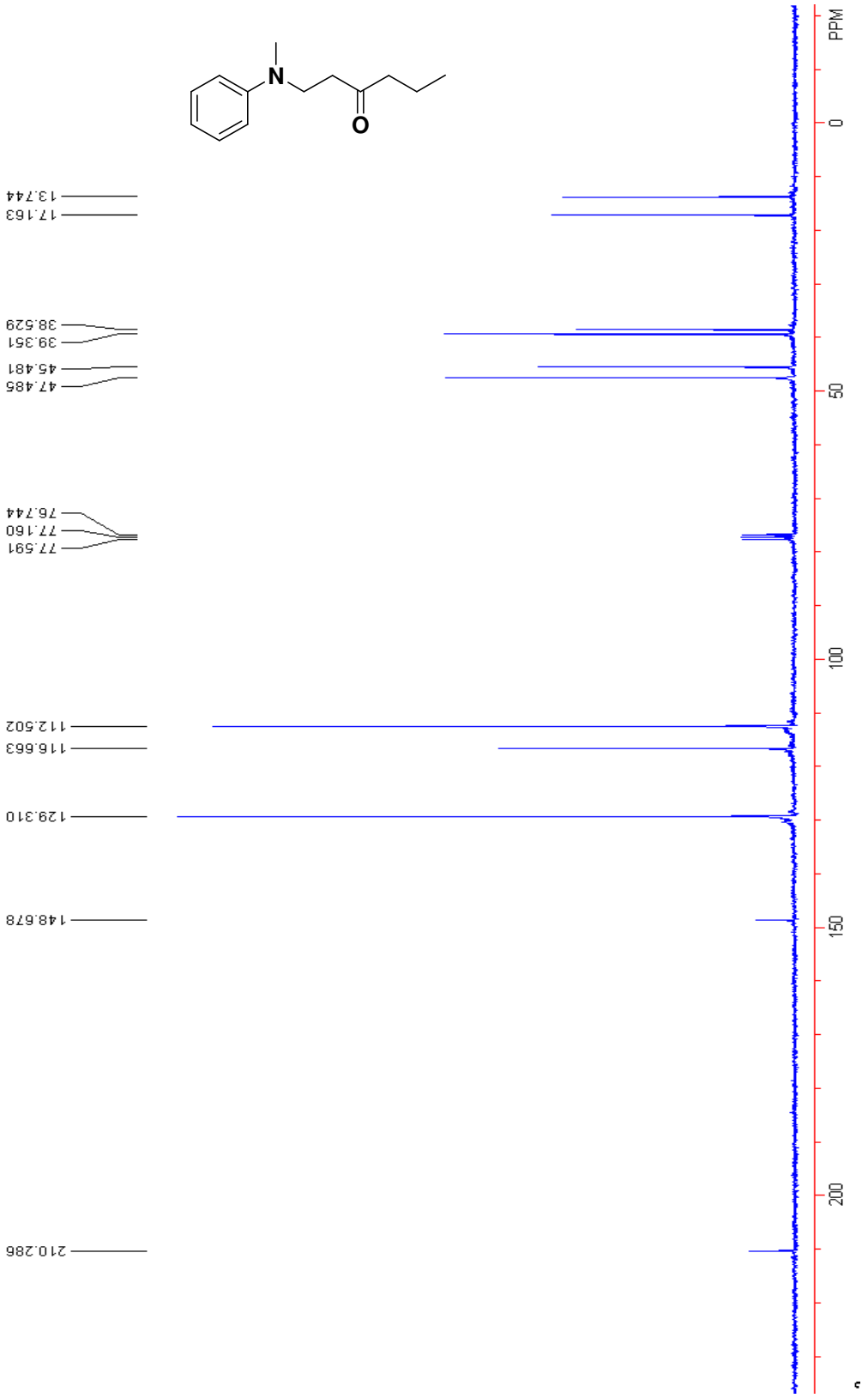
3. Spectra of ^{1}H NMR, ^{13}C NMR and MS

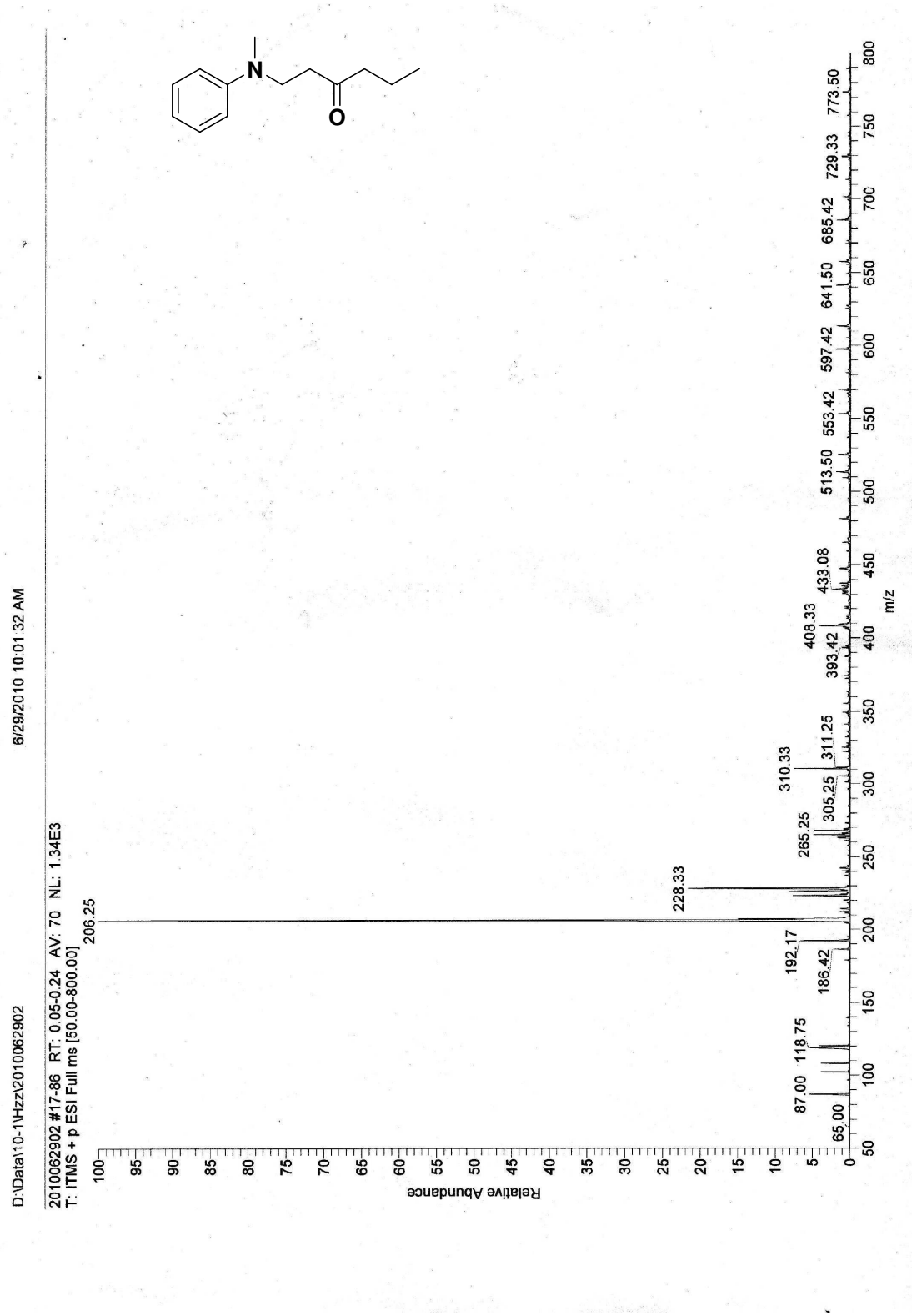
^{1}H NMR of 1-(*N*-methyl-*N*-phenylamino)-hexan-3-one **8c**



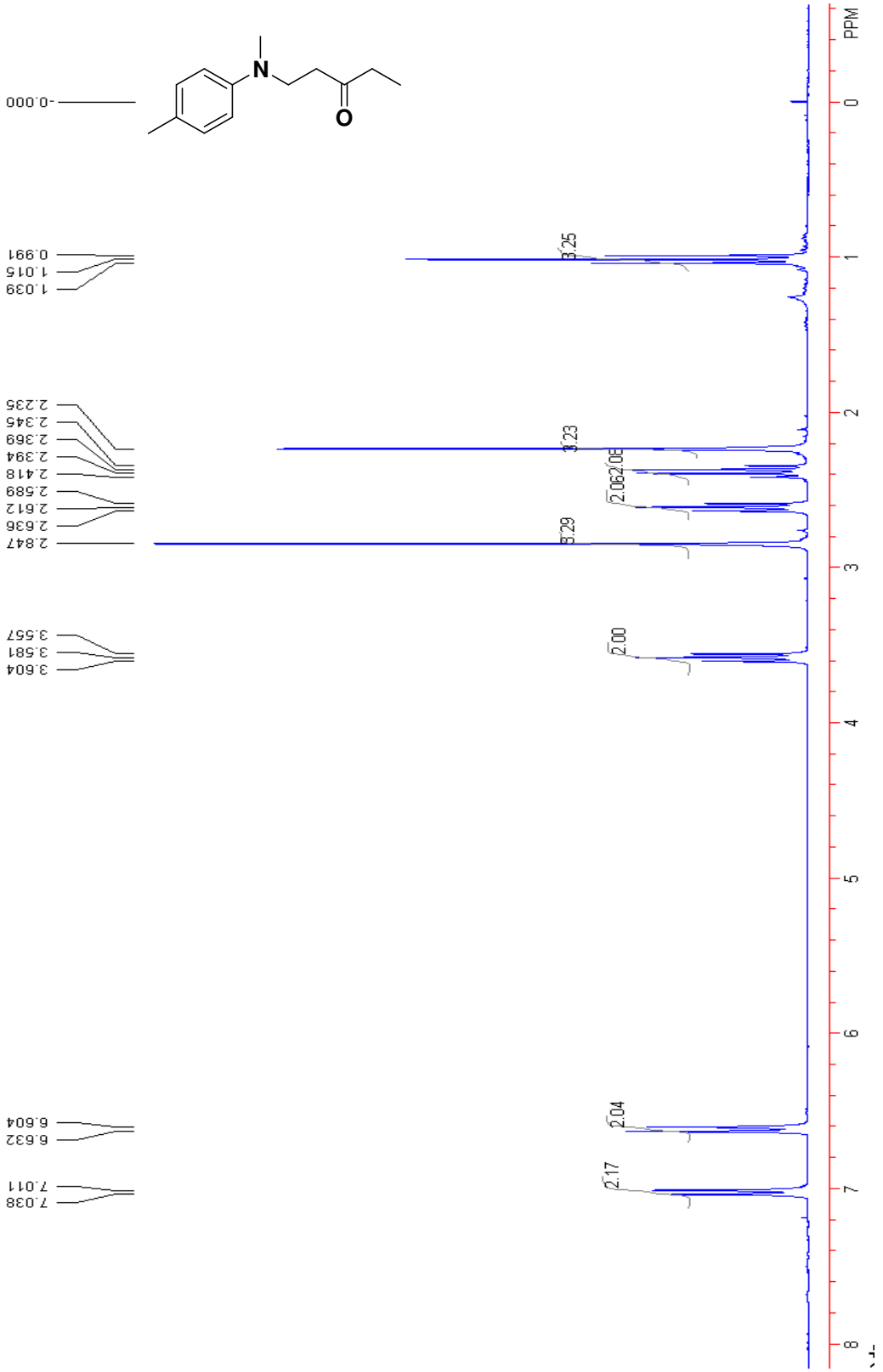
^{13}C NMR of 1-(*N*-methyl-*N*-phenylamino)-hexan-3-one **8c**



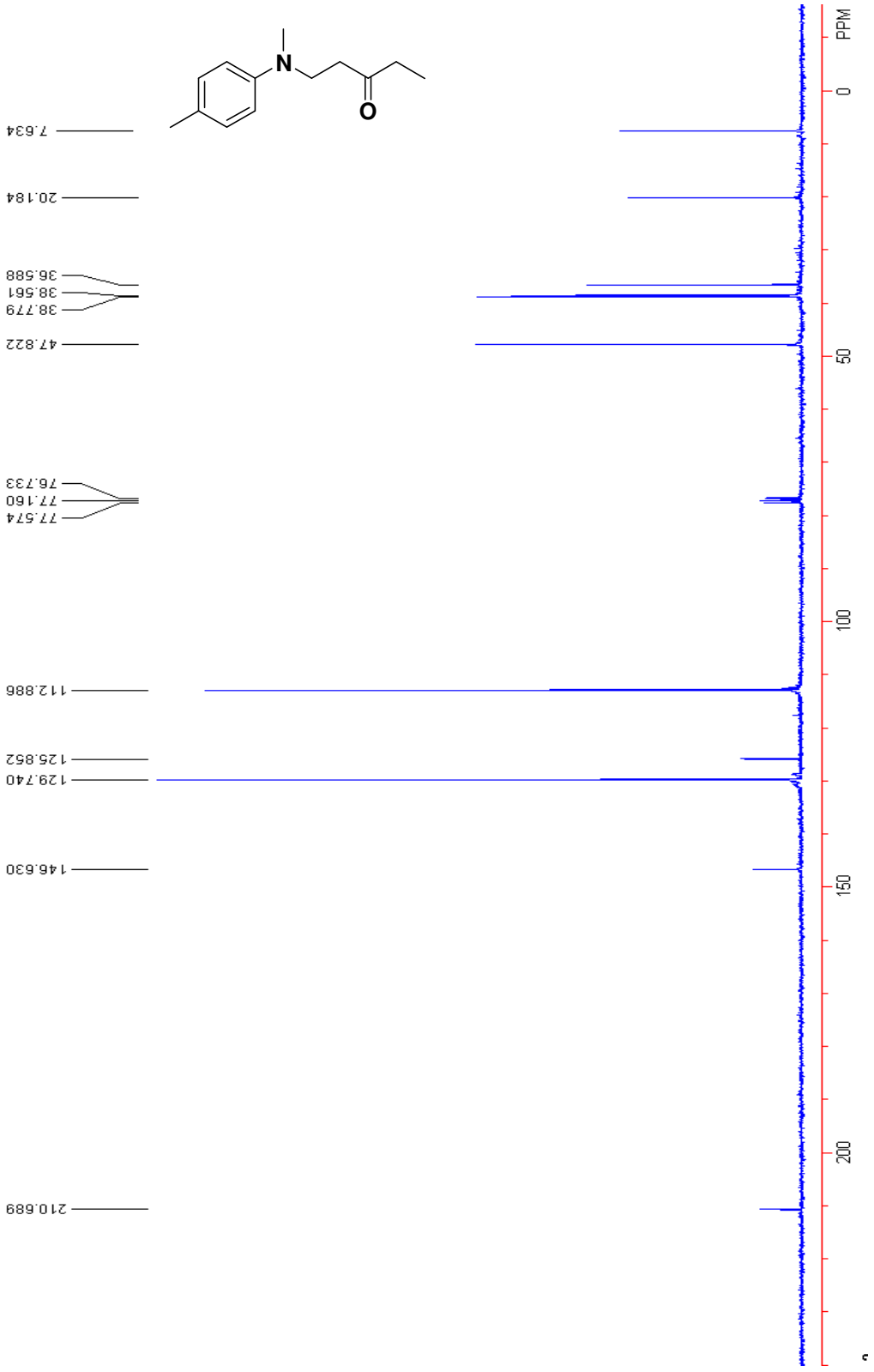
MS (ESI) of 1-(*N*-methyl-*N*-phenylamino)-hexan-3-one **8c**



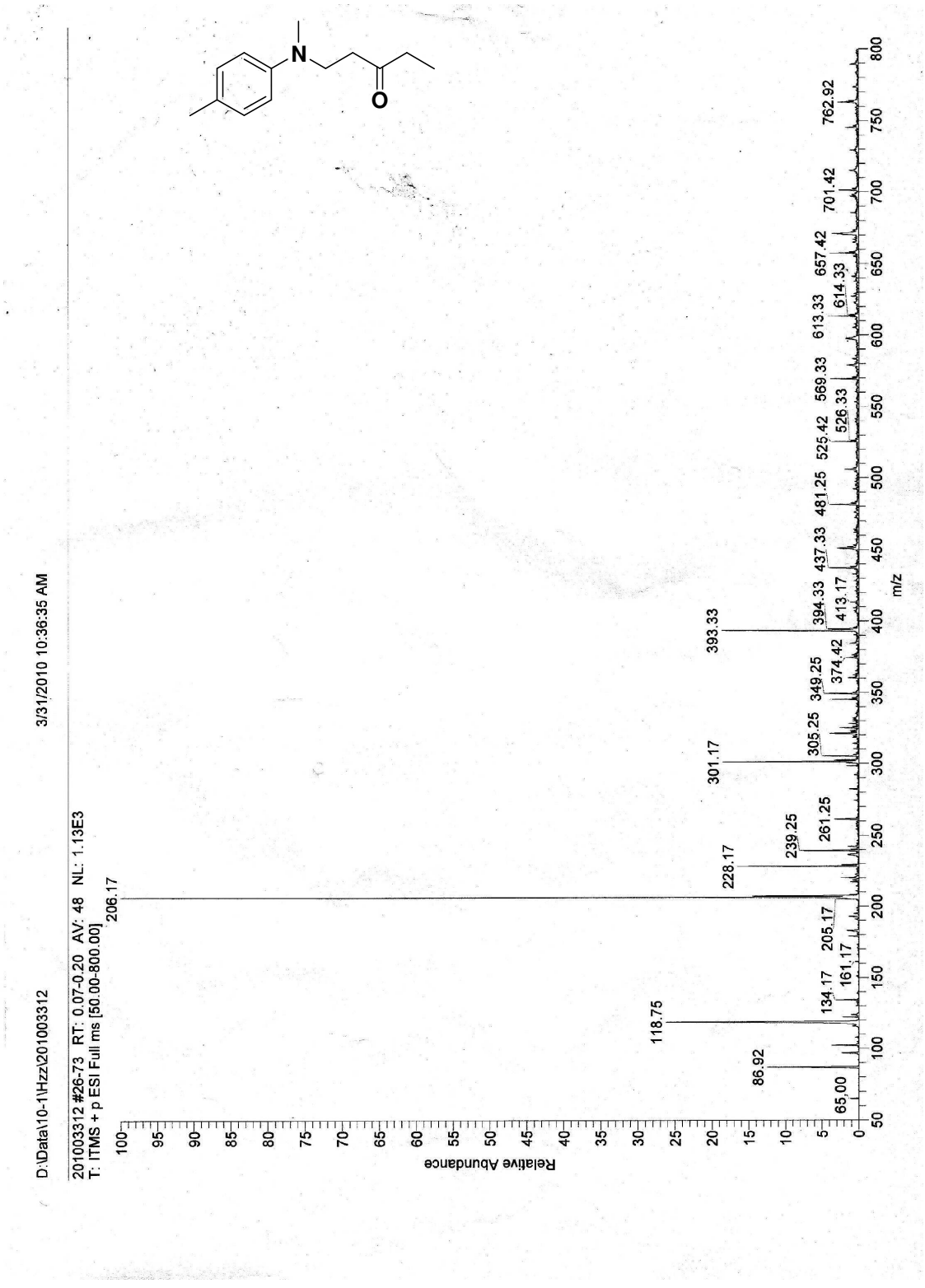
[1]HNMR of 1-(*N*-methyl-*N*-(4-methylphenyl)amino)-pentan-3-one **8e**



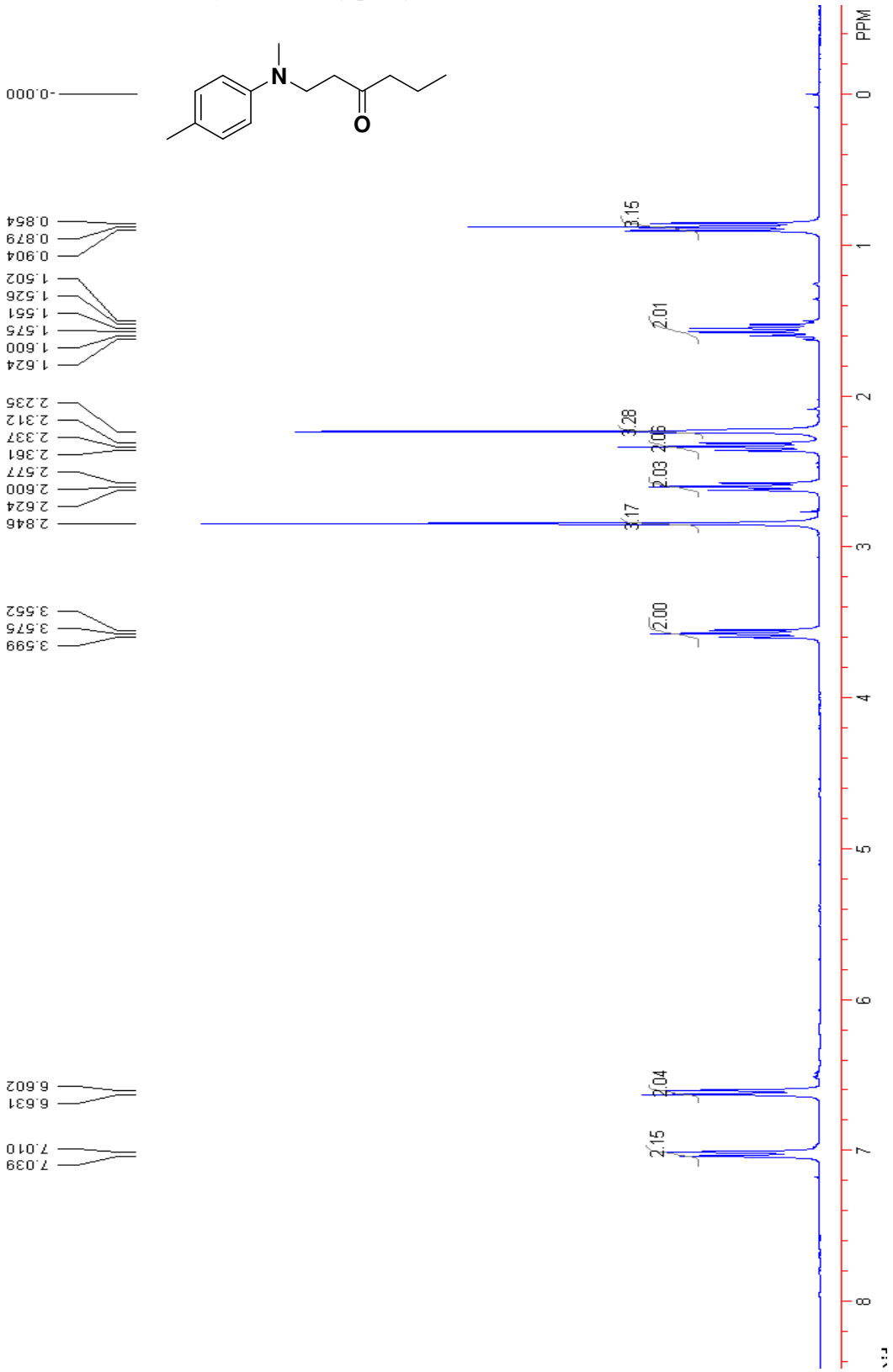
^{13}C NMR of 1-(*N*-methyl-*N*-(4-methylphenyl)amino)-pentan-3-one **8e**



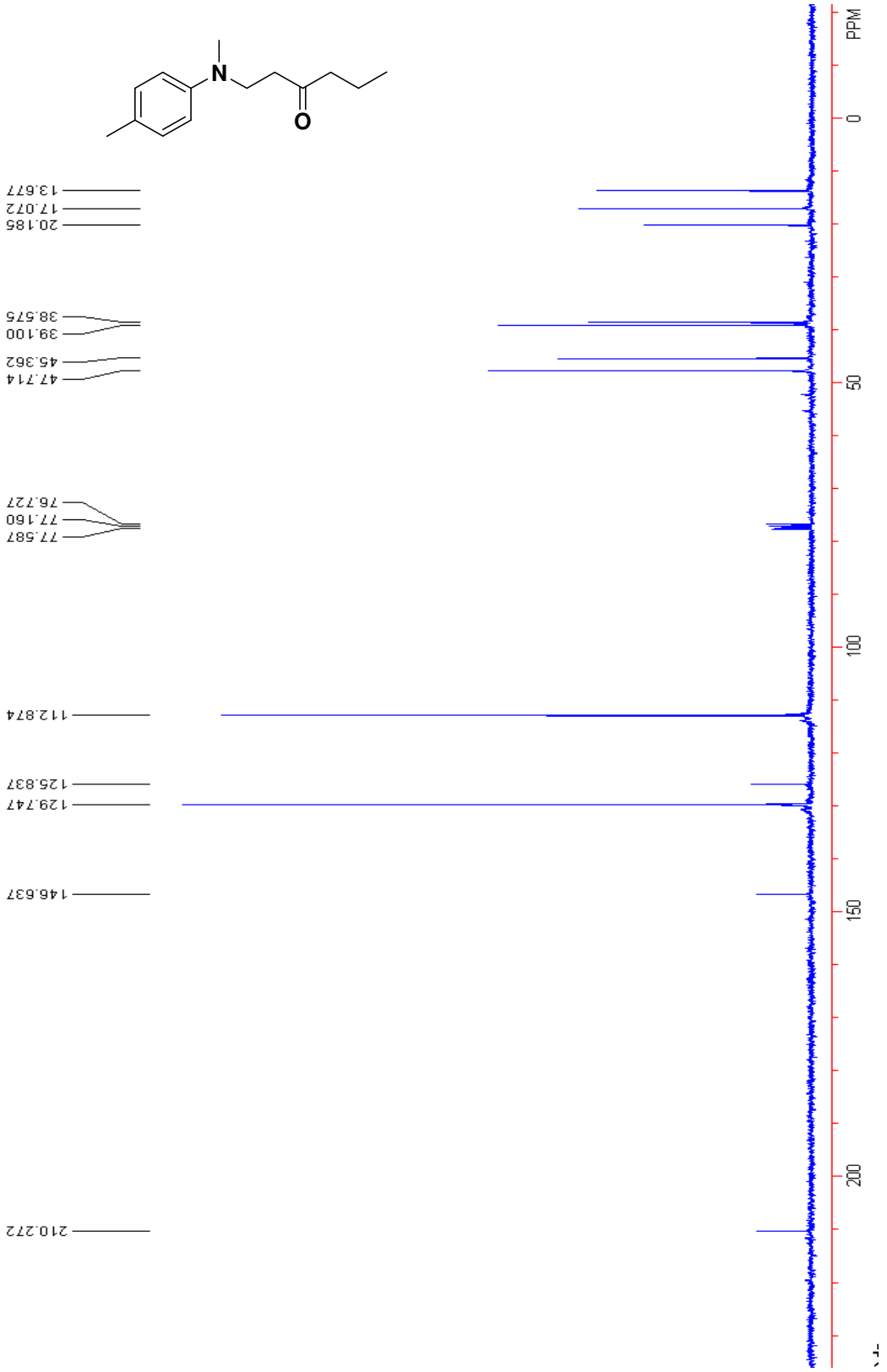
MS (ESI) of 1-(*N*-methyl-*N*-(4-methylphenyl)amino)-pentan-3-one **8e**



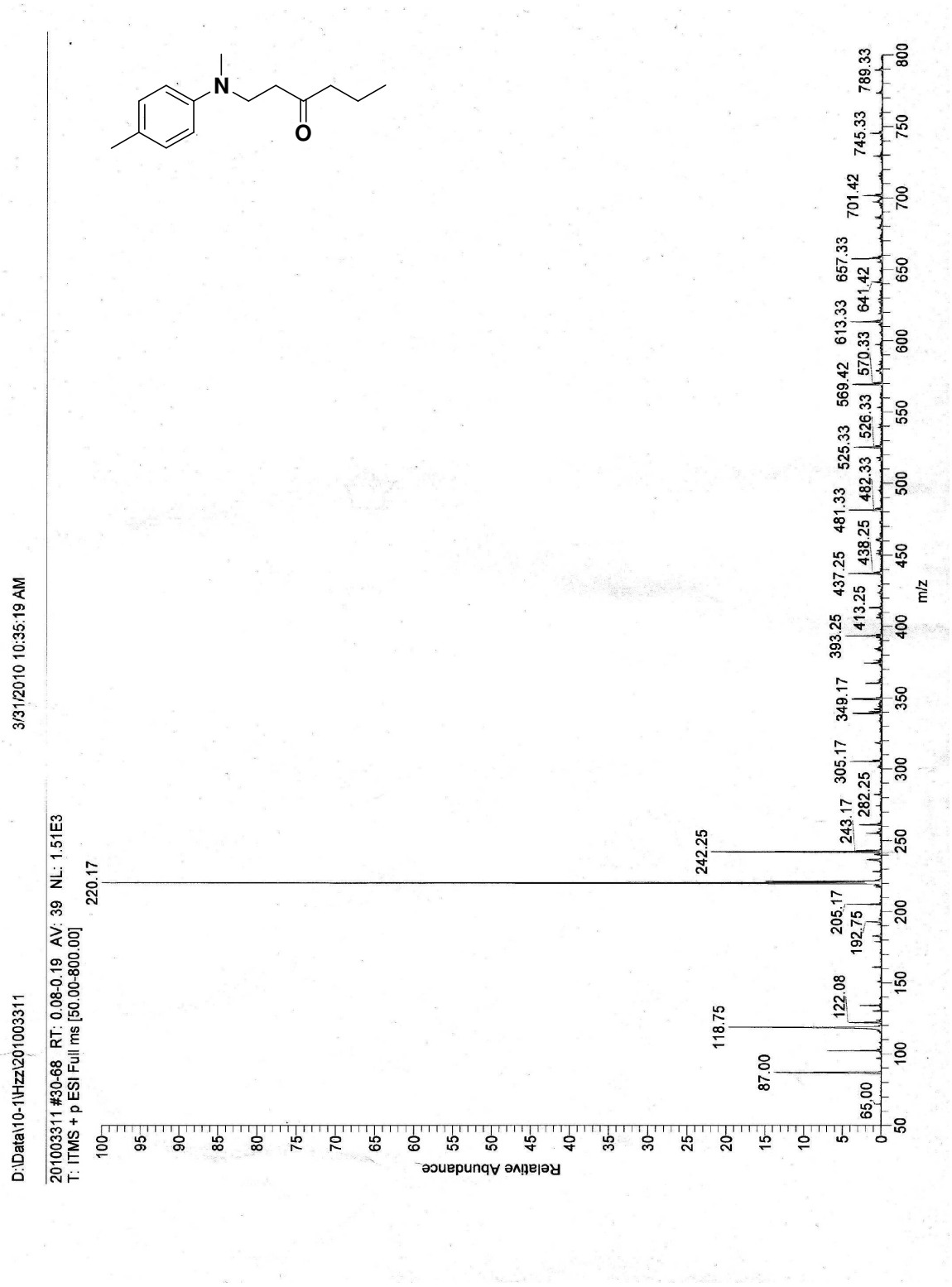
[1]H NMR of 1-(*N*-methyl-*N*-(4-methylphenyl)amino)-hexan-3-one **8f**



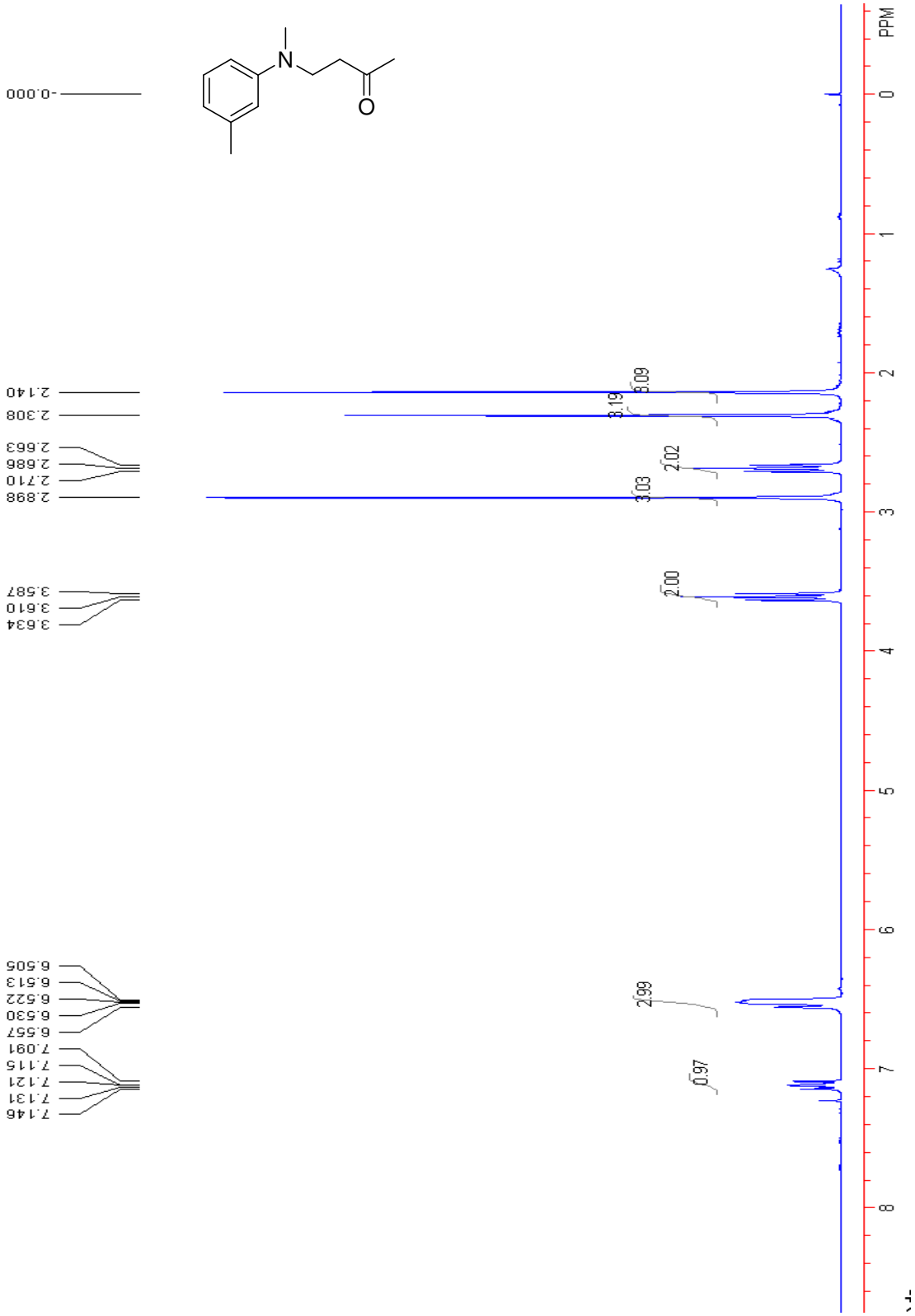
^{13}C NMR of 1-(*N*-methyl-*N*-(4-methylphenyl)amino)-hexan-3-one **8f**



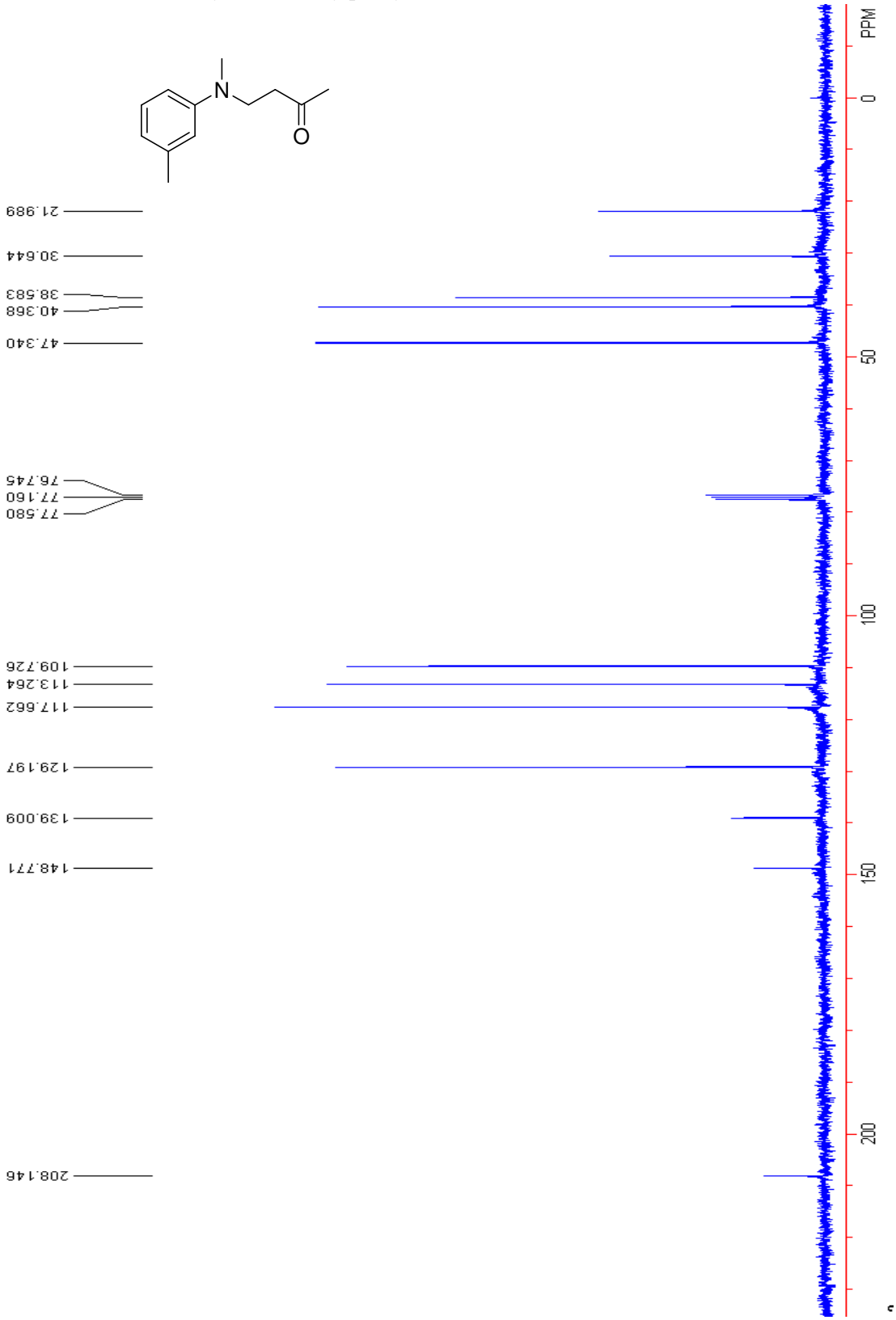
MS (ESI) of 1-(*N*-methyl-*N*-(4-methylphenyl)amino)-hexan-3-one **8f**



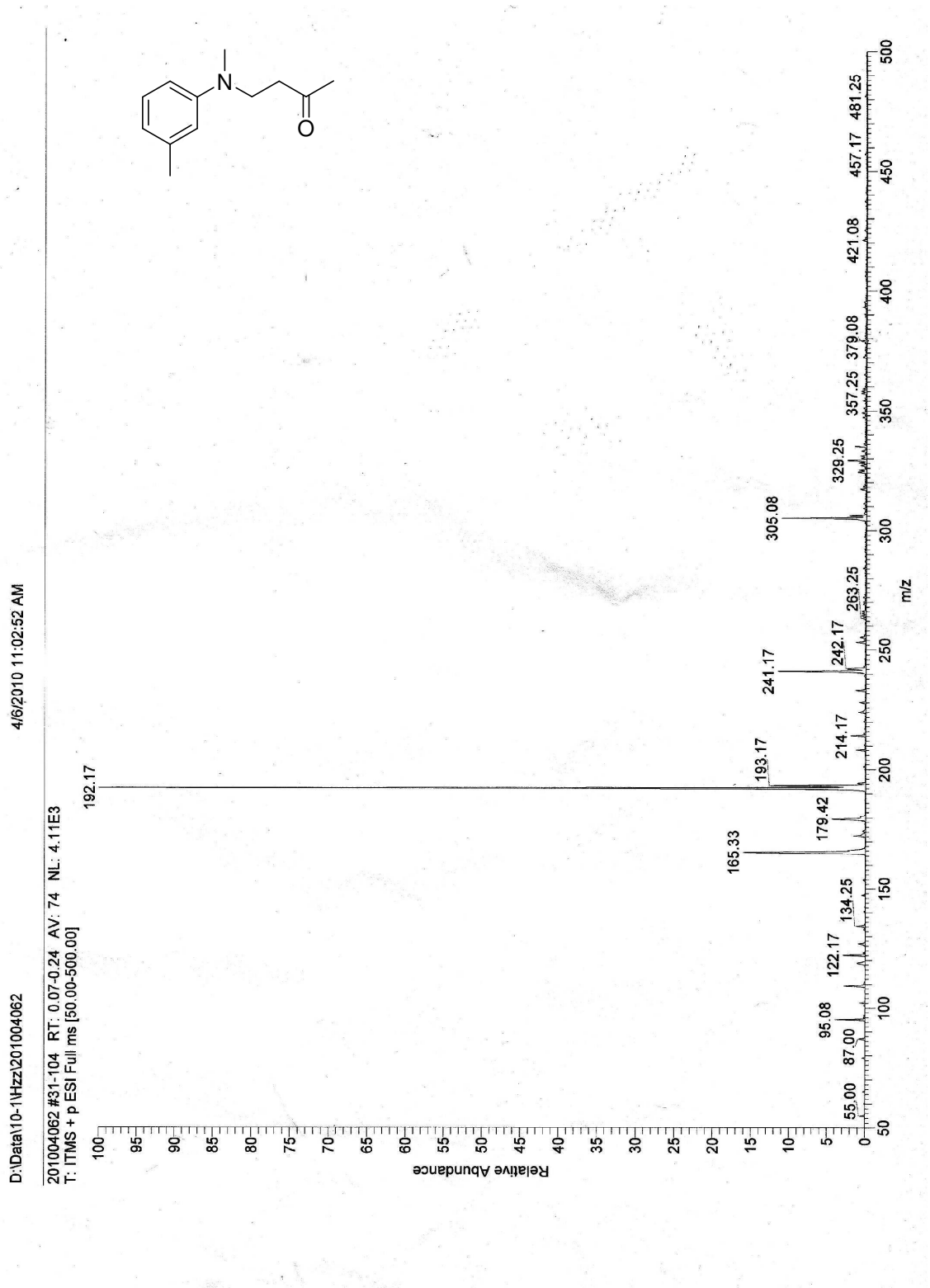
[1]H NMR of 4-(*N*-methyl-*N*-(3-methylphenyl)amino)-butan-2-one **8j**



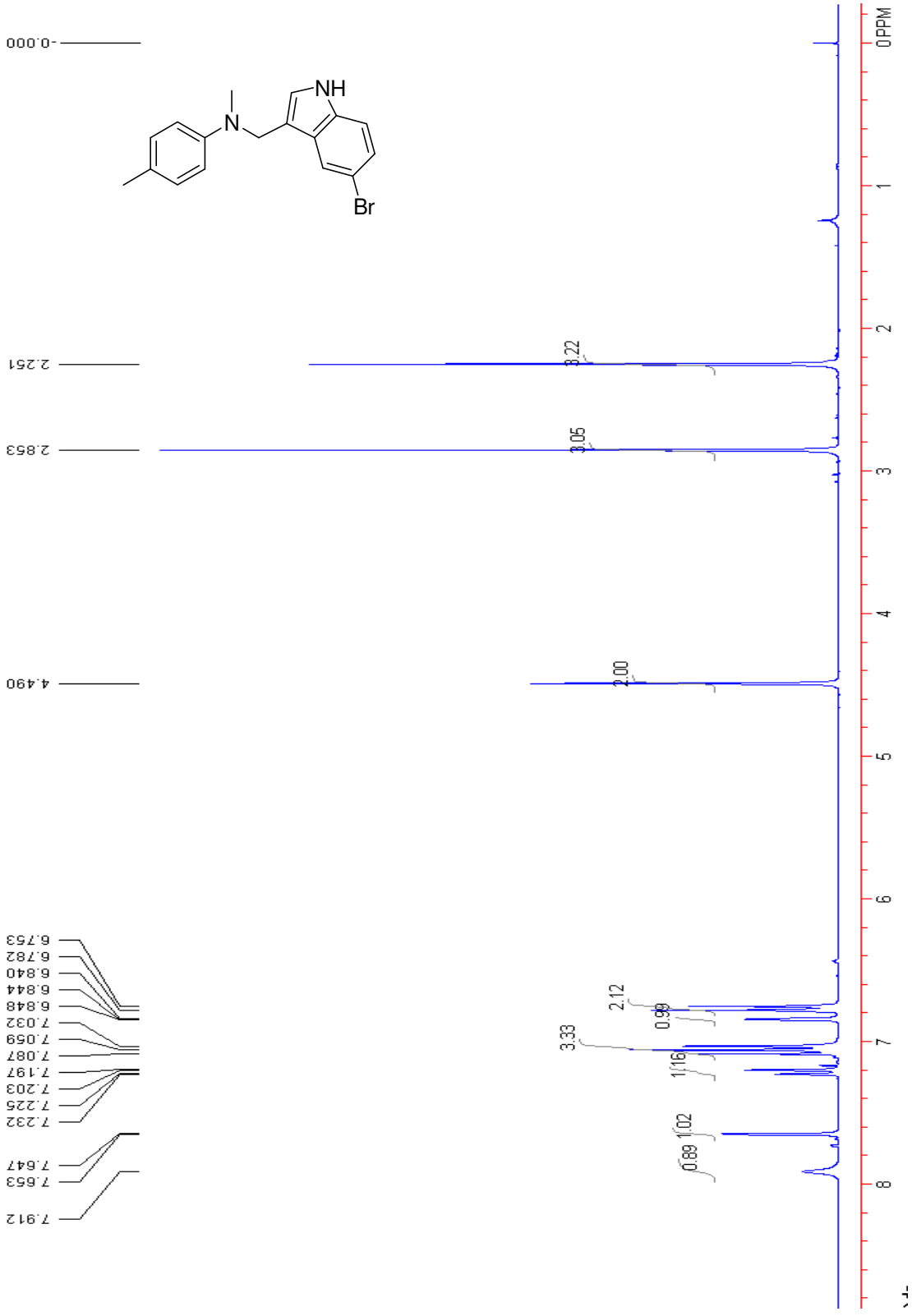
^{13}C NMR of 4-(*N*-methyl-*N*-(3-methylphenyl)amino)-butan-2-one **8j**



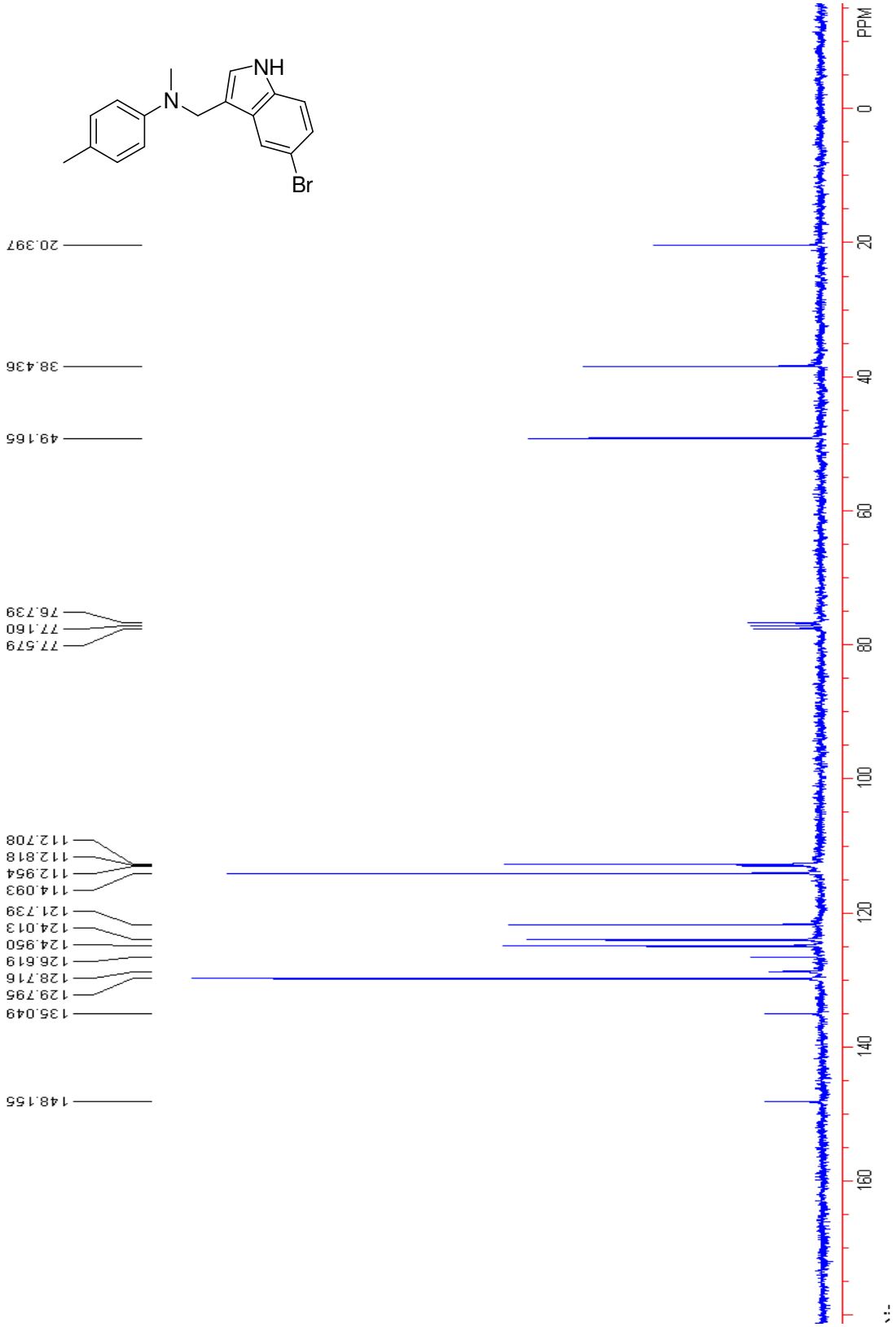
MS (ESI) of 4-(*N*-methyl-*N*-(3-methylphenyl)amino)-butan-2-one **8j**



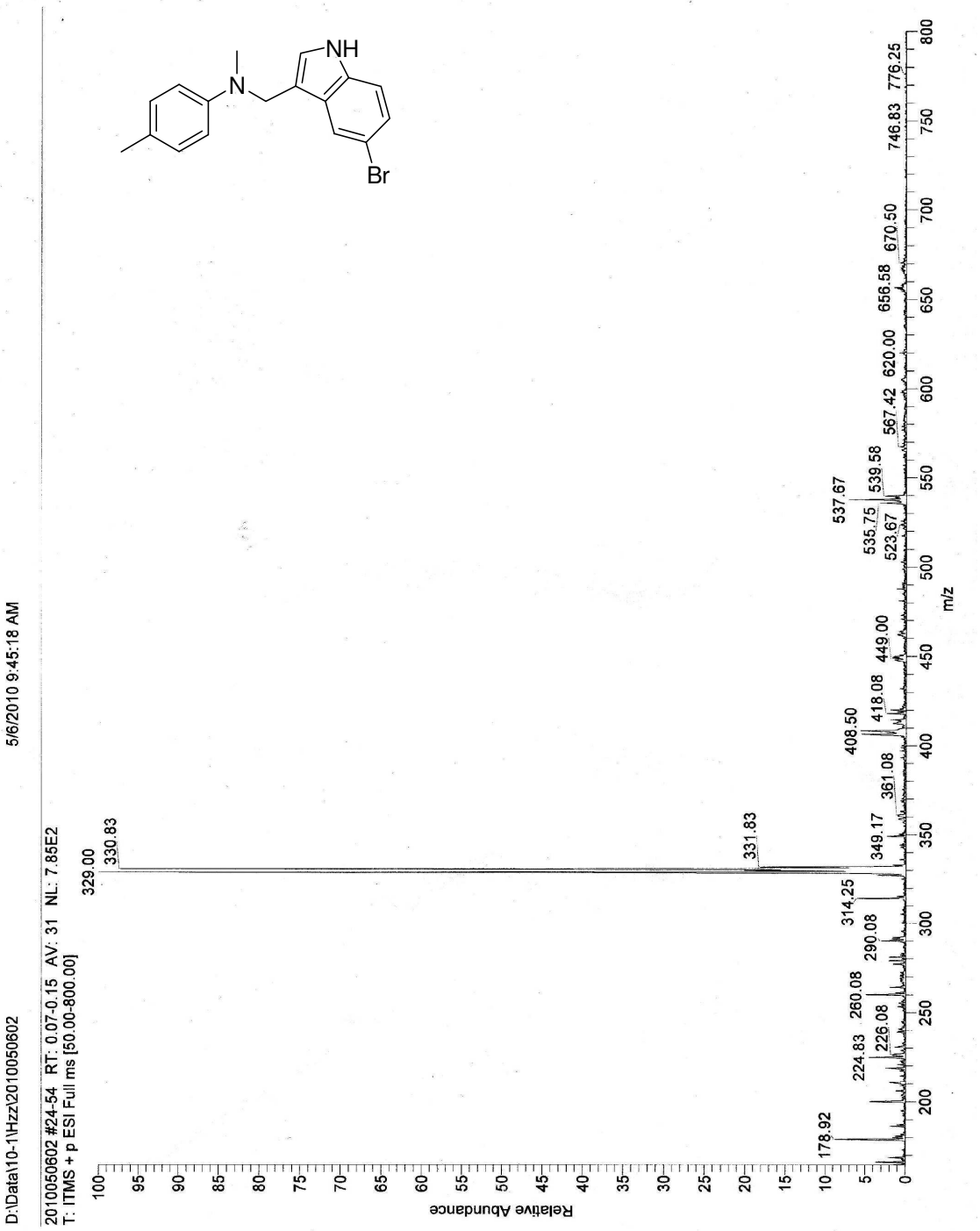
[1]H NMR of *N*-((5-bromol-1*H*-indol-3-yl)methyl)-*N*, 4-menthylbenzenamine **10c**



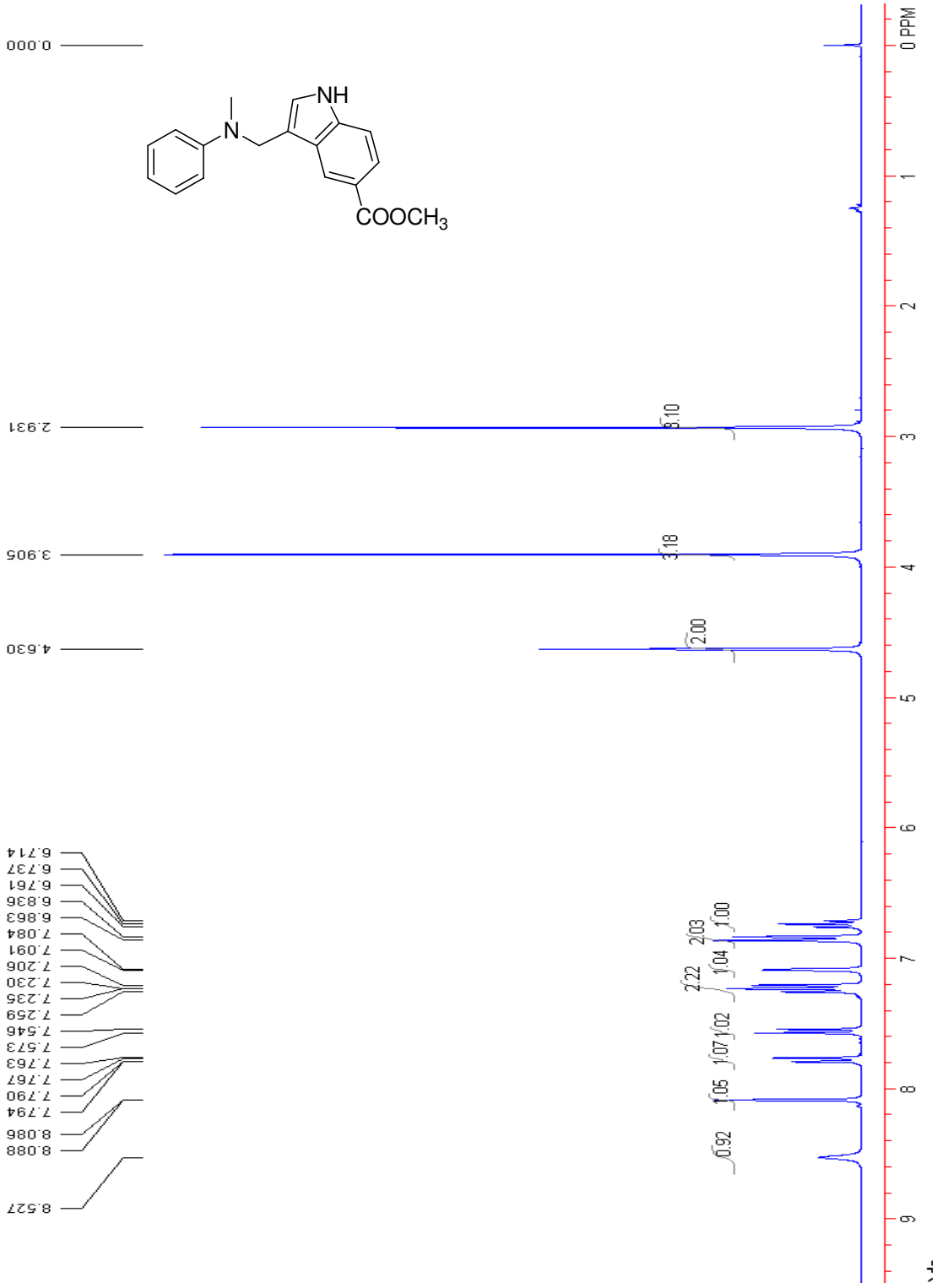
^{13}C NMR of *N*-((5-bromol-1*H*-indol-3-yl)methyl)-*N*, 4-menthylbenzenamine **10c**



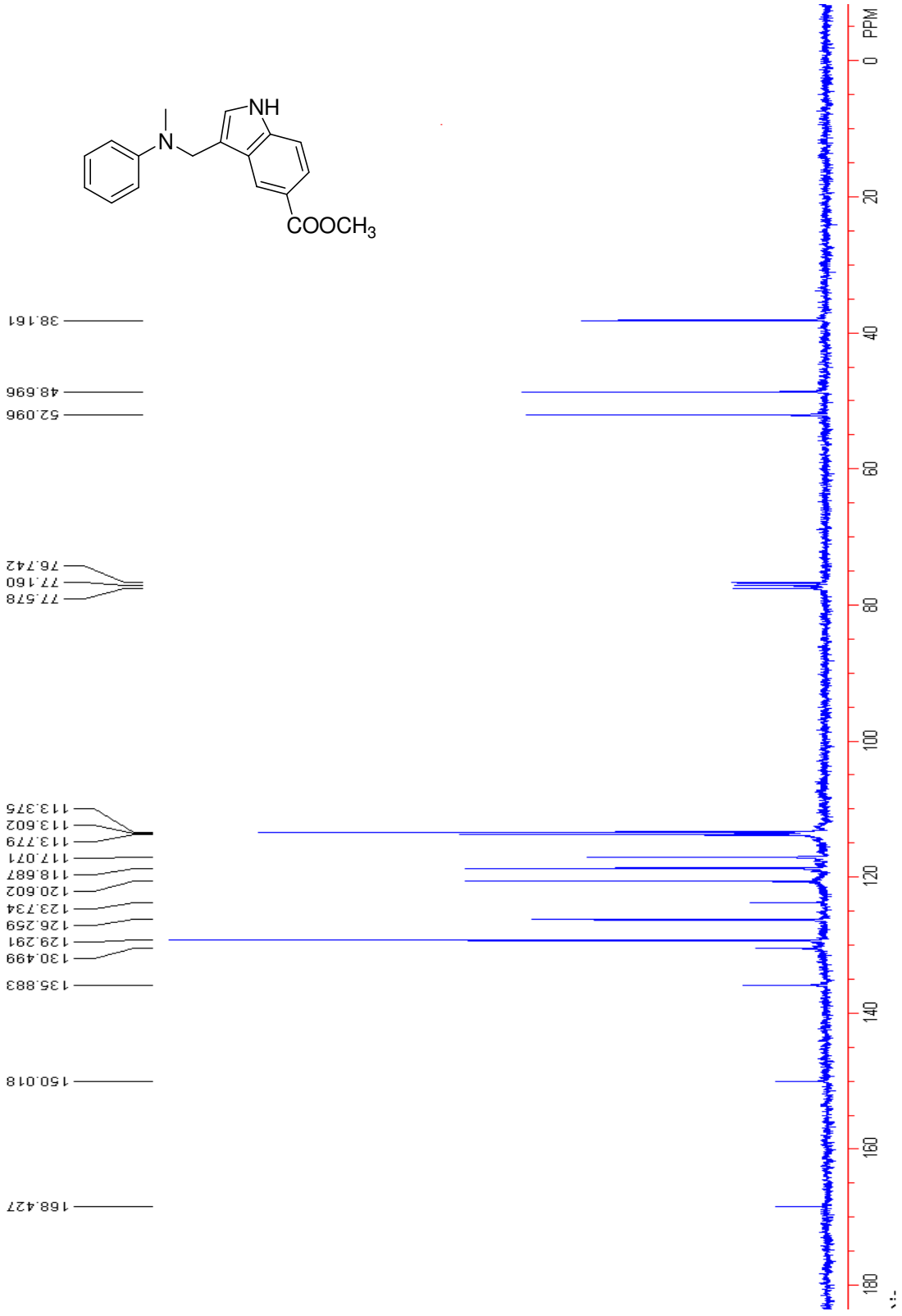
MS (ESI) of *N*-((5-bromol-1*H*-indol-3-yl)methyl)-*N*, 4-menthylbenzenamine **10c**



^{1}H NMR of 3-((*N*-methyl-*N*-phenylamino)methyl)-1*H*-indole-5-carboxylic acid methyl ester **10g**



^{13}C NMR of 3-((*N*-methyl-*N*-phenylamino)methyl)-1*H*-indole-5-carboxylic acid methyl ester **10g**



MS (EI) of 3-((*N*-methyl-*N*-phenylamino)methyl)-1*H*-indole-5-carboxylic acid methyl ester **10g**