C–H Chlorination of (hetero)anilines via photo-redox/organo co-catalysis

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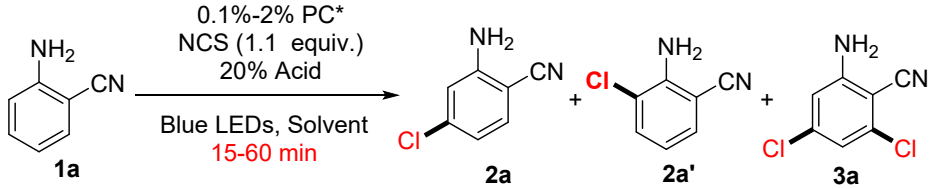
Supporting Information

1. General information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. All the reactions were conducted using reaction tube (25 mL). The reactions were performed under argon atmosphere. Blue LEDs (10W, equipped with a thermotank) was used as light source. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F25 plates. Column chromatograph was performed on silica gel 200~300 mesh. An Edinburgh Instruments Spectrofluorometer FS5 was used in the emission measurement. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ or DMSO using 300 MHz, 400 MHz Varian NMR spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual $CDCl_3$ (7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant in Hertz (Hz). Chemical shifts in ^{13}C NMR spectra are reported in ppm on the δ scale from the central peak of residual $CDCl_3$ (77.16 ppm).

2. Optimization of the reaction parameters

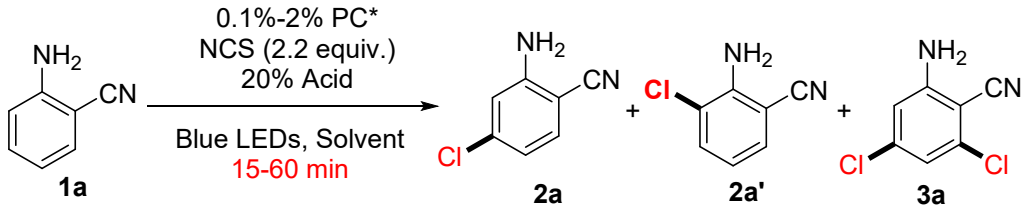
Table S1. Condition evaluations for chlorination of aniline **1a** with NCS (1.1 equivalents)



Entry	PC*/light (LEDs)	Acid	Solvent	Time/ min	Yield of **2a/2a'/3a**
1	-/-	20% $BrCF_2COOH$	CH_3CN	30	15/1.1/1.2
2	-/Blue	20% $BrCF_2COOH$	CH_3CN	30	43/3.2/2.6
3	0.1% 4CzIPN/Blue	-	CH_3CN	30	80/6/7
4	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	CH_3CN	30	68/5/0.9
5	0.1% 4CzIPN/Blue	20% $Br(CH_{2)2}CCOOH$	CH_3CN	30	83/6/2.7
6	0.1% 4CzIPN/Blue	20% $BrCH_2COOH$	CH_3CN	30	78/6/1.5
7	0.1% 4CzIPN/Blue	20% CH_3COOH	CH_3CN	30	83/6/4

8	0.1% 4CzIPN/Blue	5% $BrCF_2COOH$	CH_3CN	30	74/5/2.6
9	0.1% 4CzIPN/Blue	10% $BrCF_2COOH$	CH_3CN	30	70/5/1.6
10	0.1% 4CzIPN/Blue	50% $BrCF_2COOH$	CH_3CN	30	50/3/0.5
11	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	THF	60	95/4/0.9
12	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	CH_3CN	60	86/6/1.4
13	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	DMSO	60	84/4/0.8
14	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	DMF	60	78/7/2
15	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	H_2O	60	78/4/1.1
16	2% Eosin Y/Green	20% $BrCF_2COOH$	CH_3CN	30	58/4/2.4
17	2% Acr-Mes/Blue	20% $BrCF_2COOH$	CH_3CN	30	10/-/-
18	2% R6G/Blue	20% $BrCF_2COOH$	CH_3CN	30	62/5/1.8
19	0.1% 4CzIPN/Blue	20% $Br(CH_2)_2CCOOH$	CH_3CN	15	79/6/5
20	0.1% 4CzIPN/Blue	20% $Br(CH_2)_2CCOOH$	CH_3CN	45	82/6.5/5.2
21	0.1% 4CzIPN/Blue	20% $Br(CH_2)_2CCOOH$	CH_3CN	60	81/6.5/5.1
22	0.1% 4CzIPN/Blue	20% $BrCH_2COOH$	CH_3CN	15	57/5/2.2
23	0.1% 4CzIPN/Blue	20% $BrCH_2COOH$	CH_3CN	45	81/6.1/2.9
24	0.1% 4CzIPN/Blue	20% $BrCH_2COOH$	CH_3CN	60	81/6/3
25	0.1% 4CzIPN/Blue	20% CH_3COOH	CH_3CN	15	75/5.8/5
26	0.1% 4CzIPN/Blue	20% CH_3COOH	CH_3CN	45	76/6/5.3
27	0.1% 4CzIPN/Blue	20% CH_3COOH	CH_3CN	60	74/6/5.8
28	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	THF	30	89/4/0.9
29	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	THF	15	75/2.4/0.6
30	0.1% 4CzIPN/Solar light (14:00 pm)	20% $BrCF_2COOH$	THF	30	88/3.7/0.8
31	0.1% 4CzIPN/solar light (10:00 am)	20% $BrCF_2COOH$	THF	30	60/2.9/1.1

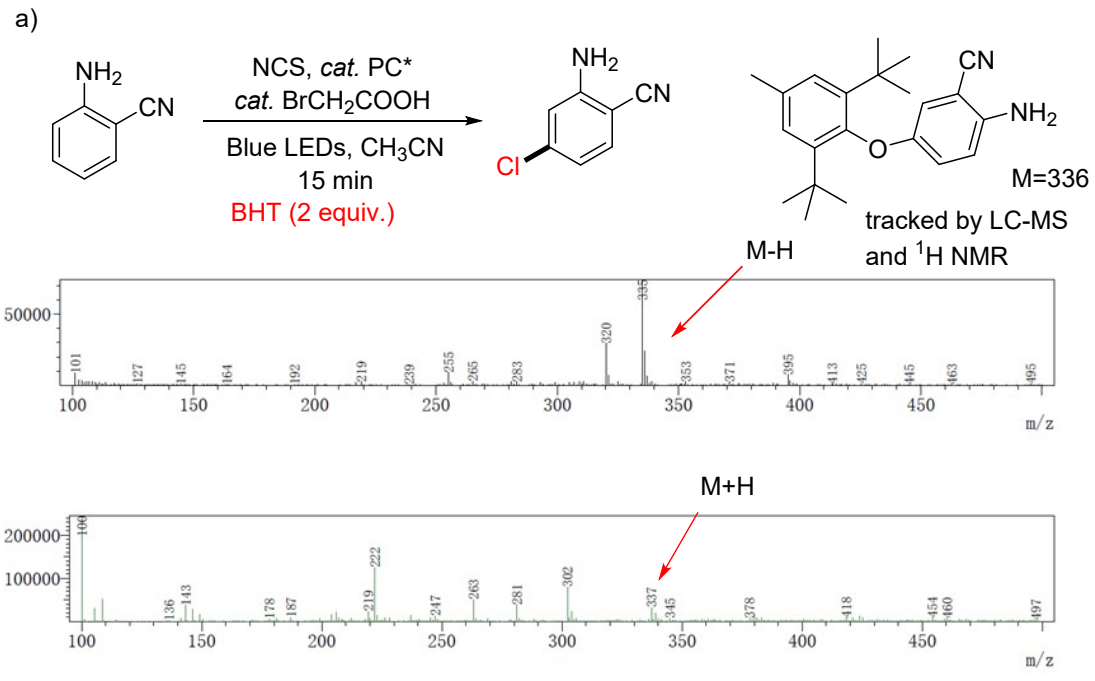
Table S2. Condition evaluations for chlorination of aniline **1a** with NCS (2 equivalents)



Entry	PC*/light (LEDs)	Acid	Solvent	Time/ min	Yield of **2a/2a'/3a**
1	-/-	20% $BrCF_2COOH$	CH_3CN	30	24/2.3/2.6
2	-/Blue	20% $BrCF_2COOH$	CH_3CN	30	45/4/2.9
3	0.1% 4CzIPN/Blue	-	CH_3CN	30	7/4.2/88
4	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	CH_3CN	30	70/5/25
5	0.1% 4CzIPN/Blue	20% $Br(CH_{2)2}CCOOH$	CH_3CN	30	15/5/80
6	0.1% 4CzIPN/Blue	20% $BrCH_2COOH$	CH_3CN	30	19/5.5/76
7	0.1% 4CzIPN/Blue	20% CH_3COOH	CH_3CN	30	16/5.5/74
8[a]	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	CH_3CN	30	93/4/1.3
9[b]	0.1% 4CzIPN/Blue	20% $BrCF_2COOH$	CH_3CN	30	85/3.9/10

[a] NCS (1.2 equivalents); [b] NCS (1.5 equivalents)

3. LC-Ms for radical capture experiments



4. General Experimental Procedures and Characterization Data

General procedure for selective chlorination

Condition A (for substrates **2a**-**2ad**, **4a**-**4h**) A 10 mL quartz tube was charged with amine (0.2 mmol), 2-bromo-2,2-difluoroacetic acid (0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL) and THF (2 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.22 mmol, 1.1 equivalents, pre-dissolved in THF) was added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). Upon completion of the reaction, the mixture was diluted with ethyl acetate (3 mL) and washed with saturated $NaHCO_3$ aqueous solution (5 mL). The organic layer was concentrated and purified via a flash column (PE/EA from 10/1 to 3/1) or recrystallization (Ethanol/Water). Note: specific solvent was used for products **4c**-**4h**. The purified of **4d**, **4g** and **4h** was taken via a flash column (DCM/Methanol from 30/1 to 10/1)

Condition B (for substrates **3a**-**3c**, **3e**, **3t**) A 10 mL quartz tube was charged with amine (0.2 mmol), 2-bromo-2,2-difluoroacetic acid (0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL) and THF (2 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.44 mmol, 2.2 equivalents, pre-dissolved in THF) was added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). Upon completion of the reaction, the mixture was diluted with ethyl acetate (3 mL) and washed with saturated $NaHCO_3$ aqueous solution (5 mL). The organic layer was concentrated and purified via a flash column (PE/EA from 10/1 to 3/1) or recrystallization (Methanol/Water).

2-amino-5-chlorobenzonitrile **2a**. The title compound was obtained according to general condition A using the following amounts and conditions: 2-aminobenzonitrile (23.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a white solid (27.1 mg, 89% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 2.5 Hz, 1H), 7.35 – 7.25 (m, 1H), 6.71 (d, J = 8.9 Hz, 1H), 4.47 (s, 2H). GC-MS(EI):152 m/z. The reported data was identical to the literature.[1]

4-amino-3-chlorobenzonitrile **2b.** The title compound was obtained according to general condition A using the following amounts and conditions: 4-aminobenzonitrile (23.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a white solid (29.0 mg, 95% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 1.9 Hz, 1H), 7.35 (dd, J = 8.4, 1.9 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 4.57 (s, 2H). GC-MS(EI):152 m/z.
The ^{1}H NMR shifts are identical to the literature.[2]

4-amino-5-chloro-2-(trifluoromethyl)benzonitrile **2c.** The title compound was obtained according to general condition A using the following amounts and conditions: 4-amino-2-(trifluoromethyl)benzonitrile (37.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a white solid (35.2 mg, 79% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.10 (s, 1H), 4.99 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 135.5, 132.7 ($^2J_{C-F}$=33 Hz), 120.3, 118.6 ($^1J_{C-F}$=270 Hz), 115.8, 112.6 ($^3J_{C-F}$=4.5 Hz), 97.3.
HRMS Calcd. For $C_8H_5ClF_3N_2$ $[M+H]^+$: 221.0088; found 221.0095.

4-chloro-2,5-difluoroaniline **2d.** The title compound was obtained according to general condition A using the following amounts and conditions: 2,5-difluoroaniline (25.8 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a white solid (26.4 mg, 81% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (dd, J = 10.2, 6.6 Hz, 1H), 6.58 (dd, J = 10.0, 7.8 Hz, 1H), 3.85 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7 (dd, $^1J_{C-F}$=240 Hz, $^3J_{C-F}$=3 Hz), 145.2, 139.0, 134.4 (dd, $^2J_{C-F}$=10.5 Hz), 116.7 ($^2J_{C-F}$=23.3 Hz), 104.0 ($^3J_{C-F}$=4.5 Hz).
HRMS Calcd. For $C_6H_5ClF_2N$ $[M+H]^-$: 164.0073; found 164.0075.

2-amino-3,5-dichlorobenzamide **2e.** The title compound was obtained according to general condition A using the following amounts and conditions: 2-amino-3-chlorobenzamide (34 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/5) to provide the desired compound as an off-white solid (32.2 mg, 78% yield).
^{1}H NMR (300 MHz, DMSO) δ 8.04 (s, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.51 (d, J = 2.4 Hz, 1H), 7.47 (s, 1H), 6.83 (s, 2H).
^{13}C NMR (75 MHz, DMSO) δ 169.8, 145.3, 131.6, 127.8, 120.2, 118.0, 116.6.
HRMS Calcd. For $C_7H_6Cl_2N_2O$ $[M+H]^+$: 204.9935; found 204.9940.

methyl 4-amino-3-chloro-5-methoxybenzoate **2f.** The title compound was obtained according to general condition A using the following amounts and conditions: methyl 4-amino-3-methoxybenzoate (36.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS

(29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/5) to provide the desired compound as as a brown solid (37.0 mg, 86% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.7 Hz, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 146.4, 138.1, 124.0, 118.7, 117.2, 109.3, 56.0, 51.9.
HRMS Calcd. For $C_9H_{10}ClNO_3$ $[M+H]^+$: 216.0427; found 216.0425.

methyl 3-amino-5-bromo-6-chloro-2-methylbenzoate **2g.** The title compound was obtained according to general condition A using the following amounts and conditions: methyl 3-amino-5-bromo-2-methylbenzoate (48.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/5) to provide the desired compound as a yellow solid (43.9 mg, 79% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (s, 1H), 4.38 (s, 2H), 3.90 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 143.6, 130.3, 123.3, 122.9, 122.2, 119.5, 52.3, 14.6.
HRMS Calcd. For $C_9H_9BrClNO_2$ $[M+H]^+$: 277.9583; found 277.9585.

3,4-dichloro-5-fluoroaniline **2h.** The title compound was obtained according to general condition A using the following amounts and conditions: 3-chloro-5-fluoroaniline (29.0 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/5) to provide the desired compound as a yellow oil (23.9 mg, 67% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.41 (dd, *J* = 10.3, 2.6 Hz, 1H), 3.86 (s, 2H).
GC-MS(EI):179 m/z.
The reported data was identical to the literature.[3]

4-chloro-2-nitroaniline **2i.** The title compound was obtained according to general condition A using the following amounts and conditions: 2-nitroaniline (27.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/5) to provide the desired compound as a yellow solid (26.1 mg, 76% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.5 Hz, 1H), 7.32 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 1H), 6.07 (s, 2H).
GC-MS(EI):172 m/z.
The ^{1}H NMR shifts are identical to the literature.[4]

4-bromo-2-chloroaniline **2j.** The title compound was obtained according to general condition A using the following amounts and conditions: 4-bromoaniline (34.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a white solid (26.2 mg, 63% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.2 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.66 (d, *J* = 8.6 Hz, 1H), 4.06 (s, 2H).
GC-MS(EI):205 m/z.
The ^{1}H NMR shifts are identical to the literature.[5]

2,4,6-trichloro-3,5-dimethoxyaniline **2k.** The title compound was obtained according to general condition A using the following amounts and conditions: 2,6-dichloro-3,5-dimethoxyaniline (44.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow solid (38.8 mg, 76% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.58 (s, 2H), 3.90 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 140.2, 112.0, 110.1, 60.7.
HRMS Calcd. For $C_8H_8Cl_3NO_2$ $[M+H]^+$: 255.9699; found 255.9705.

5-chloro-7-nitro-3,4-dihydro-2H-benzo[b][1,4]oxazine **2l** The title compound was obtained according to general condition A using the following amounts and conditions: 7-nitro-3,4-dihydro-2H-benzo[b][1,4]oxazine (36.0 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/3) to provide the desired compound as a yellow oil (34.0 mg, 79% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 5.08 (s, 1H), 4.33 – 4.23 (m, 2H), 3.64 (td, *J* = 4.5, 2.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 137.3, 137.0, 118.7, 117.0, 111.3, 64.1, 40.3.
HRMS Calcd. For $C_8H_8ClN_2O_3$ $[M+H]^+$: 215.0223; found 215.0219.

4-bromo-2-chloro-N,N-dimethylaniline **2m** The title compound was obtained according to general condition A using the following amounts and conditions: 4-bromo-N,N-dimethylaniline (39.9 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/3) to provide the desired compound as a yellow oil (39.6 mg, 85% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.3 Hz, 1H), 7.33 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 2.81 (s, 6H).
GC-MS(EI):233 m/z.

The ^{1}H NMR shifts are identical to the literature.[6]

2-chloro-3-(4-methylpiperazin-1-yl)-6-nitroaniline **2n** The title compound was obtained according to general condition A using the following amounts and conditions: 5-(4-methylpiperazin-1-yl)-2-nitroaniline (47.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/3) to provide the desired compound as a brown solid (42.3 mg, 78% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 9.5 Hz, 1H), 6.69 (s, 2H), 6.42 (d, J = 9.5 Hz, 1H), 3.38 – 3.07 (m, 4H), 2.60 (t, J = 4.8 Hz, 4H), 2.36 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 143.2, 128.3, 125.7, 112.3, 108.2, 55.0, 50.5, 46.1.
HRMS Calcd. For $C_{11}H_{15}ClN_4O_2$ $[M+H]^+$: 271.0962; found 271.0961.

N-(4-chlorophenyl)acetamide **2o** The title compound was obtained according to general condition A using the following amounts and conditions: N-phenylacetamide (27.0 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by recrystallization (ethanol/water =1/3) to provide the desired compound as a as a colorless solid (25.1 mg, 74% yield).
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.08 (s, 1H), 8.08 – 7.50 (m, 2H), 7.50 – 6.94 (m, 2H), 2.07 (s, 3H).
GC-MS(EI):169 m/z.
The ^{1}H NMR shifts are identical to the literature.[4]

4-chloro-N-phenylaniline **2p** The title compound was obtained according to general condition A using the following amounts and conditions: diphenylamine (33.8 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow solid (23 mg, 56% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.21 (m, 4H), 7.20 – 6.98 (m, 5H), 5.72 (s, 1H).
GC-MS(EI):203 m/z.
The ^{1}H NMR shifts are identical to the literature.[7]

N-(4-chlorophenyl)pyrimidin-2-amine **2q.** The title compound was obtained according to general condition A using the following amounts and conditions: N-phenylpyrimidin-2-amine (34.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a yellow solid (25 mg, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.8 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.35 – 7.29 (m, 2H), 6.77 (t, *J* = 4.8 Hz, 1H).
GC-MS(EI):205m/z.
The ^{1}H NMR shifts are identical to the literature.[7]

methyl 3-chloro-1H-indazole-6-carboxylate **2r** The title compound was obtained according to general condition A using the following amounts and conditions: methyl 1H-indazole-6-carboxylate (35.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/3) to provide the desired compound as a yellow oil (28.3 mg, 67% yield).
^{1}H NMR (300 MHz, DMSO) δ 13.68 (s, 1H), 8.12 (m, 1H), 7.72 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, DMSO) δ 166.6, 140.9, 132.9, 129.0, 122.3, 121.7, 119.5, 113.4, 52.9.
HRMS Calcd. For $C_9H_8ClN_2O_2$ $[M+H]^+$: 211.0269; found 211.0260.

6-bromo-3-chloro-1H-indole **2s** The title compound was obtained according to general condition A using the following amounts and conditions: 6-bromo-1H-indole (39.0 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/3) to provide the desired compound as a yellow oil (41.9 mg, 91% yield).
^{1}H NMR (300 MHz, DMSO) δ 11.53 (s, 1H), 7.63 (m, 1H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.24 (dd, *J* = 8.5, 1.7 Hz, 1H).
^{13}C NMR (75 MHz, DMSO) δ 136.2, 124.1, 124.0, 123.2, 119.4, 115.5, 115.2, 103.9.
HRMS Calcd. For C_8H_6BrClN $[M+H]^+$: 229.9367; found 229.9372.

5-chloro-1H-indole-3-carbonitrile **2u** The title compound was obtained according to general condition A using the following amounts and conditions: 1H-indole-3-carbonitrile (28.4 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/3) to provide the desired compound as a yellow oil (11.0 mg, 31% yield).
^{1}H NMR (300 MHz, DMSO) δ 12.41 (s, 1H), 8.35 (s, 1H), 7.71 – 7.64 (m, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.31 (dd, *J* = 8.7, 2.1 Hz, 1H).
GC-MS(EI):176 m/z.
The ^{1}H NMR shifts are identical to the literature.[8]

ethyl 5-amino-4-chloro-1H-pyrazole-3-carboxylate **2v** The title compound was obtained according to general condition A using the following amounts and conditions: ethyl 3-amino-1H-pyrazole-5-carboxylate (31.0 mg, 0.2 mmol), 2-bromo-2,2-

difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a yellow oil (23.2 mg, 61% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.43 (q, *J* = 7.1 Hz, 2H), 4.35 (s, 2H), 1.43 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 148.9, 134.4, 95.9, 61.7, 14.2.
HRMS Calcd. For $C_6H_8ClN_3O_2$ $[M+H]^+$: 190.0383; found 190.0379.

3-(tert-butyl)-4-chloroisoxazol-5-amine **2w** The title compound was obtained according to general condition A using the following amounts and conditions: 3-(tert-butyl)isoxazol-5-amine (28.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a yellow oil (21.1 mg, 60% yield).
^{1}H NMR (300 MHz, DMSO-d_6) δ 5.79 (s, 2H), 1.32 (s, 9H).
^{13}C NMR (75 MHz, DMSO) δ 171.2, 162.0, 95.6, 33.6, 27.7.
HRMS Calcd. For $C_7H_{11}ClN_2O$ $[M+H]^+$: 175.0638; found 175.0643.

5-chloropyridin-2-amine **2x** The title compound was obtained according to general condition A using the following amounts and conditions: pyridin-2-amine (18.8 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (14.0 mg, 54% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 2.6, 0.7 Hz, 1H), 7.38 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.45 (dd, *J* = 8.7, 0.7 Hz, 1H), 4.51 (s, 2H).
GC-MS(EI):128 m/z.
The ^{1}H NMR shifts are identical to the literature.[8]

5,6-dichloro-N-methylpyrimidin-4-amine **2y** The title compound was obtained according to general condition A using the following amounts and conditions: 6-chloro-N-methylpyrimidin-4-amine (28.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (22.2 mg, 62% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 5.61 (s, 1H), 3.12 (d, *J* = 4.9 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 155.1, 155.1, 111.2, 28.5.
HRMS Calcd. For $C_5H_5Cl_2N_3$ $[M+H]^+$: 177.9939; found 177.9937.

2,4,7-trichlorothieno[3,2-d]pyrimidine **2z** The title compound was obtained according to general condition A using the following amounts and conditions: 2,4-

dichlorothieno[3,2-d]pyrimidine (40.8 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/6) to provide the desired compound as an off-white solid (25.0 mg, 53% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 157.3, 156.4, 133.0, 128.4, 123.1.
HRMS Calcd. For $C_6HCl_3N_2S$ $[M+H]^+$: 238.9004; found 238.9007

2-amino-3,5-dichlorobenzonitrile **3a** The title compound was obtained according to general condition B using the following amounts and conditions: 2-aminobenzonitrile (23.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (58.8 mg, 0.44 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as an off-white solid (26.8 mg, 72% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 2.3 Hz, 1H), 7.32 (d, J = 2.3 Hz, 1H), 4.89 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 133.8, 130.1, 121.9, 120.2, 115.7, 97.6.
HRMS Calcd. For $C_7H_4Cl_2N_2$ $[M+H]^+$: 186.9830; found 186.9832.

4-amino-3,5-dichlorobenzonitrile **3b** The title compound was obtained according to general condition B using the following amounts and conditions: 4-aminobenzonitrile (23.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (58.8 mg, 0.44 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (30.3 mg, 80% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 2H), 5.03 (s, 2H).
GC-MS(EI):186m/z.
The reported data was identical to the literature.[9]

4-amino-3,5-dichloro-2-(trifluoromethyl)benzonitrile **3c** The title compound was obtained according to general condition B using the following amounts and conditions: 4-amino-2-(trifluoromethyl)benzonitrile (37.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (58.8 mg, 0.44 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a brown solid (39.8 mg, 78% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1H), 5.36 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 133.5, 129.4 ($^2J_{C-F}$=30.3Hz), 127.0, 121.5($^1J_{C-F}$=274.5 Hz), 121.4, 115.5, 98.8.
HRMS Calcd. For $C_8H_3Cl_2F_3N_2$ $[M+H]^+$: 254.9704; found 254.9711.

5-chloro-N-(2,4-dichlorophenyl)pyrimidin-2-amine **3q** The title compound was obtained according to general condition B using the following amounts and conditions: N-phenylpyrimidin-2-amine (34.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (88.2 mg, 0.66 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/10) to provide the desired compound as a white solid (44 mg, 81% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, J = 9.0 Hz, 1H), 8.42 (s, 2H), 7.63 (s, 1H), 7.42 (d, J = 2.5 Hz, 1H), 7.28 (dd, J = 9.0, 2.4 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 156.3, 134.5, 128.8, 127.6, 127.4, 123.1, 122.1, 120.9.
HRMS Calcd. For $C_{10}H_6Cl_3N_3$ $[M+H]^+$: 273.9706; found 273.9722.

tert-butyl(2-chloro-5-((4-cyano-1-methyl-1H-pyrazol-5-yl)amino)-4-methylphenyl)carbamate **4a** The title compound was obtained according to general condition A using the following amounts and conditions: tert-butyl (3-((4-cyano-1-methyl-1H-pyrazol-5-yl)amino)-4-methylphenyl)carbamate (65.4 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a yellow solid (53.2 mg, 73% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.45 (s, 1H), 7.30 (s, 1H), 6.86 (s, 1H), 6.15 (s, 1H), 3.65 (s, 3H), 2.19 (s, 3H), 1.48 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 146.3, 141.1, 139.4, 134.9, 133.9, 123.9, 113.5, 110.4, 106.2, 82.9, 81.2, 36.3, 28.3, 17.0.
HRMS Calcd. For $C_{17}H_{20}ClN_5O_2$ $[M+H]^+$: 362.1384; found 362.1276.

2,6-dichloro-4-((6,7-dimethoxyquinazolin-4-yl)oxy)aniline **4b** The title compound was obtained according to general condition A using the following amounts and conditions: 2-chloro-4-((6,7-dimethoxyquinazolin-4-yl)oxy)aniline (66.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a yellow solid (46.2 mg, 63% yield).
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.58 (s, 1H), 7.51 (s, 1H), 7.37 (s, 3H), 5.55 (s, 2H), 4.01 (s, 3H), 3.99 (s, 3H).
^{13}C NMR (75 MHz, DMSO-d_6) δ 165.3, 156.1, 152.5, 150.4, 149.2, 141.8, 139.8, 122.7, 118.1, 109.9, 107.0, 101.0, 56.5, 56.4.
HRMS Calcd. For $C_{16}H_{13}Cl_2N_3O_3$ $[M+H]^+$: 366.0412; found 366.0413.

tert-butyl (2-((5-bromopyrimidin-2-yl)amino)-5-chloro-3-methylphenyl)carbamate **4c** The title compound was obtained according to general condition A using the following amounts and conditions: tert-butyl (2-((5-bromopyrimidin-2-yl)amino)-3-methylphenyl)carbamate (75.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg,

0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (59.0 mg, 71% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 2H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 2.24 (s, 3H), 1.50 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 159.0, 152.9, 135.0, 134.7, 129.4, 128.7, 127.6, 119.3, 109.0, 81.1, 28.3, 16.0.
HRMS Calcd. For $C_{16}H_{18}BrClN_4O_2$ $[M+H]^+$: 413.0380; found 413.0374.

2-(5-chloro-2-((2,6-dichlorophenyl)amino)phenyl)acetic acid **4d** The title compound was obtained according to general condition A using the following amounts and conditions: 2-(2-((2,6-dichlorophenyl)amino)phenyl)acetic acid (59.0 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and THF (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (50.0 mg, 76% yield).
^{1}H NMR (300 MHz, Methanol-d4) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.15 – 7.05 (m, 2H), 6.40 (d, *J* = 8.6 Hz, 1H), 3.77 (s, 2H).
GC-MS(EI):329 m/z.
The ^{1}H NMR shifts are identical to the literature.[10]

N-(2-chloro-4-ethoxyphenyl)acetamide **4e** The title compound was obtained according to general condition A using the following amounts and conditions: N-(4-ethoxyphenyl)acetamide (35.8 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and CH_3CN (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (27.2 mg, 63% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.6 Hz, 1H), 7.35 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.16 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 151.3, 131.4, 122.9, 122.6, 119.8, 113.7, 65.1, 24.3, 14.7.
HRMS Calcd. For $C_{10}H_{12}ClNO_2$ $[M+H]^+$: 214.0635; found 214.0633.

N-(2,5-dichloro-4-ethoxyphenyl)acetamide **4e'** The title compound was obtained according to general condition B using the following amounts and conditions: N-(4-ethoxyphenyl)acetamide (35.8 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (58.8 mg, 0.44 mmol) and CH_3CN (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (38.2 mg, 77% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.42 (s, 1H), 6.93 (s, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 151.1, 128.1, 123.7, 122.0, 121.7, 113.7, 65.4, 24.6, 14.6.
HRMS Calcd. For $C_{10}H_{11}Cl_2NO_2$ $[M+H]^+$: 248.0245; found 248.0253.

2-(diethylamino)ethyl 4-amino-3,5-dichlorobenzoate **4f** The title compound was obtained according to general condition B using the following amounts and conditions: 2-(diethylamino)ethyl 4-aminobenzoate (47.2 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (58.8 mg, 0.44 mmol) and CH_3CN (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a brown solid (44.5 mg, 73% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 2H), 4.91 (s, 3H), 4.35 (t, *J* = 6.3 Hz, 2H), 2.83 (t, *J* = 6.3 Hz, 2H), 2.62 (q, *J* = 7.2 Hz, 4H), 1.07 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 133.4, 129.5, 118.5, 107.4, 50.6, 47.4, 29.6, 11.2.
HRMS Calcd. For $C_{13}H_{18}Cl_2N_2O_2$ $[M+H]^+$: 305.0824; found 305.0809.

5-(4-(2-((5-chloropyridin-2-yl)(methyl)amino)ethoxy)benzyl)thiazolidine-2,4-dione **4g** The title compound was obtained according to general condition A using the following amounts and conditions: 5-(4-(2-(methyl(pyridin-2-yl)amino)ethoxy)benzyl)thiazolidine-2,4-dione (71.4 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and CH_3CN (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a white solid (54.9 mg, 70% yield).
^{1}H NMR (300 MHz, DMSO) δ 8.13 (d, *J* = 2.6 Hz, 1H), 7.64 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.66 (d, *J* = 9.1 Hz, 1H), 4.84 (dd, *J* = 9.0, 4.3 Hz, 1H), 4.09 (t, *J* = 5.8 Hz, 2H), 3.86 (t, *J* = 5.8 Hz, 2H), 3.33 – 3.22 (m, 2H), 3.05 (s, 3H).
^{13}C NMR (75 MHz, DMSO) δ 176.5, 172.4, 158.5, 157.9, 148.0, 137.8, 130.8, 129.2, 114.7, 112.0, 106.2, 65.8, 53.6, 49.0, 37.5, 36.8.
HRMS Calcd. For $C_{18}H_{18}ClN_3O_3S$ $[M+H]^+$: 392.0836; found 392.0846

N-(2-chloro-4-methyl-5-((4-(pyridin-3-yl)pyrimidin-2-yl)amino)phenyl)-4-((4-methylpiperazin-1-yl)methyl)benzamide **4h** The title compound was obtained according to general condition A using the following amounts and conditions: N-(4-methyl-3-((4-(pyridin-3-yl)pyrimidin-2-yl)amino)phenyl)-4-((4-methylpiperazin-1-yl)methyl)benzamide (98.6 mg, 0.2 mmol), 2-bromo-2,2-difluoroacetic acid (7 mg, 0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL), NCS (29.4 mg, 0.22 mmol) and water (2 mL). The crude product was purified by silica gel filtration (eluent: petroleum ether/ ethyl acetate=1/2) to provide the desired compound as a yellow solid (51.7 mg, 49% yield)
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (s, 1H), 9.23 (d, *J* = 2.3 Hz, 1H), 8.75 – 8.61 (m, 2H), 8.52 (d, *J* = 5.2 Hz, 1H), 8.42 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.0

Hz, 2H), 7.42 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.25 (s, 1H), 7.23 – 7.17 (m, 2H), 3.59 (s, 2H), 2.53 (s, 8H), 2.33 (s, 3H), 2.32 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 162.8, 160.5, 159.2, 151.4, 148.5, 142.8, 136.9, 135.4, 133.6, 132.9, 132.7, 130.1, 129.5, 127.1, 125.5, 123.9, 117.2, 114.5, 108.5, 62.4, 55.0, 52.9, 45.8, 17.7.
HRMS Calcd. For $C_{29}H_{30}ClN_7O$ $[M+H]^+$: 528.2279; found 528.2293

Procedure for Radical capture experiments
A 10 mL quartz tube was charged with 2-aminobenzonitrile (0.2 mmol), 2-bromo-2,2-difluoroacetic acid (0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL) and THF (1 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.22 mmol, 1.1 equivalents, pre-dissolved in THF) and BHT (0.4 mmol) were added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). After 30 mins, the mixture was diluted with ethyl acetate (3 mL) and washed with saturated $NaHCO_3$ aqueous solution (5 mL). The organic layer was concentrated and monitored by LC-Ms.

Procedure for On-Off experiment
A 10 mL quartz tube was charged with 2-aminobenzonitrile (0.2 mmol), 2-bromo-2,2-difluoroacetic acid (0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL) and THF (1 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.22 mmol, 1.1 equivalents, pre-dissolved in THF) was added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank) for 10 minutes. The light was then removed for 10 minutes. After that, light was conducted or not with 10 minutes intervals. The rection was tracked with LC-Ms at each 10 minutes.

Procedure for chlorination of 2-amino-5-chlorobenzonitrile
A 10 mL quartz tube was charged with 2-amino-5-chlorobenzonitrile (0.2 mmol), 2-bromo-2,2-difluoroacetic acid (0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL) and THF (1 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.22 mmol, 1.1 equivalents, pre-dissolved in THF) was added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). Upon completion of the reaction, the mixture was diluted with ethyl acetate (3 mL) and washed with saturated $NaHCO_3$ aqueous solution (5 mL). The organic layer was concentrated and purified via a flash column (PE/EA from 10/1 to 3/1). Product **3a** was isolated in the yield of 15%. Using same reaction procedure without adding bromo-2,2-difluoroacetic acid, the yield was 80%.

Procedures for synthesis of product **6b**

A 10 mL quartz tube was charged with 2-aminobenzonitrile (0.2 mmol), 2-bromo-2,2-difluoroacetic acid (0.04 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.2 mL) and THF (1 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.22 mmol, 1.1 equivalents, pre-dissolved in THF) were added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). After 30 mins, the mixture was diluted with ethyl acetate (3 mL) and washed with saturated $NaHCO_3$ aqueous solution (5 mL). The organic extracts were concentrated and used without purification.

Another 10 mL reaction flask was charged with amine and DMF dimethyl acetal (0.4 mmol) in methanol (3 mL). The reaction mixture was stirred at 70 °C until completion as indicated by TLC. The mixture was concentrated and purified by column separation (CH_2Cl_2/MeOH = 20/1, v/v), to obtain the product **5a** Yellow oil (37 mg, 89% yield).

A mixture of (E)-N'-(4-chloro-2-cyanophenyl)-N,N-dimethylformimidamide (25 mg, 0.37 mmol), aniline (11.2 mg) and acetic acid (0. 5 mL) was stirred at 100 °C for 2 h. The reaction mixture was poured into ice water and extracted with ethyl acetate. The organic layer was concentrated and the residue was rinsed in a silica column with eluent (petroleum ether: ethyl acetate = 5: 1). Fractions were combined and dried under vacuum to afford the title compound as an off white solid (27.5 mg, 89% yield).

A 10 mL quartz tube was charged with 6-chloro-N-phenylquinazolin-4-amine **6a** (25.6 mg, 0.1 mmol), 2-bromo-2,2-difluoroacetic acid (0.02 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 0.1 mL) and THF (1 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (0.11 mmol, 1.1 equivalents, pre-dissolved in THF) were added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). After 30 mins, the mixture was diluted with ethyl acetate (3 mL) and washed with saturated $NaHCO_3$ aqueous solution (5 mL). The organic extracts were concentrated and purified via a flash column (PE/EA from 10/1 to 3/1) to yield product **6b** as a white solid (17.7 mg, 61% yield)

(E)-N'-(4-chloro-2-cyanophenyl)-N,N-dimethylformimidamide **5a.**

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.35 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 3.09 (d, *J* = 1.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 153.8, 133.6, 132.3, 126.7, 120.9, 117.5, 107.8, 40.4, 34.7.

HRMS Calcd. For $C_{10}H_{10}ClN_3$ $[M+H]^+$: 208.0641; found 208.0639.

6-chloro-N-phenylquinazolin-4-amine **6a**

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.74 (ddd, *J* = 8.4, 3.2, 1.6 Hz, 3H), 7.50 – 7.37 (m, 2H), 7.28 – 7.16 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 155.1, 148.4, 137.7, 133.8, 132.2, 130.6, 129.2, 125.1, 122.1, 119.9, 115.8.

HRMS Calcd. For $C_{14}H_{10}ClN_3$ $[M+H]^+$: 256.0641; found 256.0640.

6-chloro-N-(4-chlorophenyl)quinazolin-4-amine **6b**

The title compound was obtained according to general condition A as a white solid (35 mg, 61% yield).

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.86 (s, 1H), 8.74 (d, J = 2.2 Hz, 1H), 8.61 (s, 1H), 7.94 – 7.69 (m, 4H), 7.45 – 7.34 (m, 2H), 7.21 – 6.98 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 157.5, 155.4, 148.8, 139.3, 133.8, 130.9, 130.5, 129.0, 124.4, 122.9, 122.8, 116.5.

HRMS Calcd. For $C_{14}H_9Cl_2N_3$ $[M+H]^+$: 290.0252; found 290.0251.

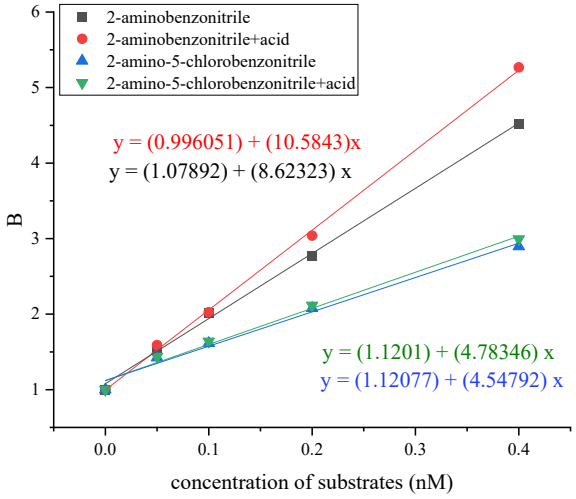
5. Gram-scale synthesis

A 50 mL quartz tube was charged with N-phenylacetamide (1.36g, 10 mmol), 2-bromo-2,2-difluoroacetic acid (69.6 mg, 0.4 mmol), photocatalyst (4CzIPN, 0.01 M, pre-dissolved in THF, 2 mL) and THF (20 mL) in sequence. The tube was seal with a rubber septum and protected with Nitrogen via bubbling using a springe. After that NCS (1.46 g, 11 mmol, 1.1 equivalents, pre-dissolved in 5 mL THF) was added. The mixture was then stirred with a Teflon® stir bar under the irritation of Blue LEDs (10W, equipped with a thermotank). Upon completion of the reaction, the solvent (THF) was vapored and recycled. The residue was diluted with ethyl acetate (10 mLx2) and washed with saturated $NaHCO_3$ aqueous solution (10 mLx2). The organic layer was concentrated and purified via recrystallization (Methanol/Water=1/3) to yield product (1.27g, 75%).

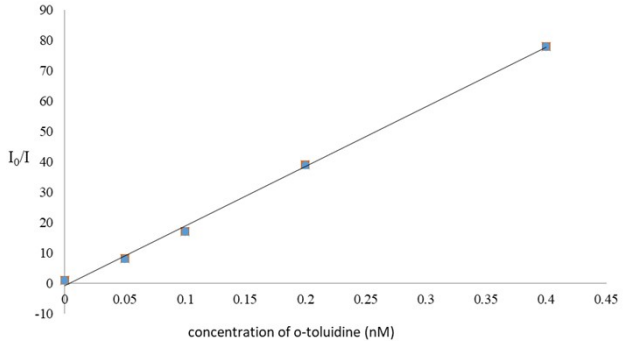
6. Stern Volmer Fluorescence Quenching

For the quenching of 4CzIPN with anilines or NCS, the emission of a 0.2 mM solution of 4CzIPN in THF excited at 455 nm (I_0 for 4CzIPN solution and I for solutions with anilines or NCS) was measured with varying concentrations at 20±0.5 ºC. [11] The ratio of I_0/I linearly increased along with the concentration of anilines, but remained almost constant at different NCS concentrations. Thus, the results showed emissions was quenched from anilines rather than NCS. The results were shown below:

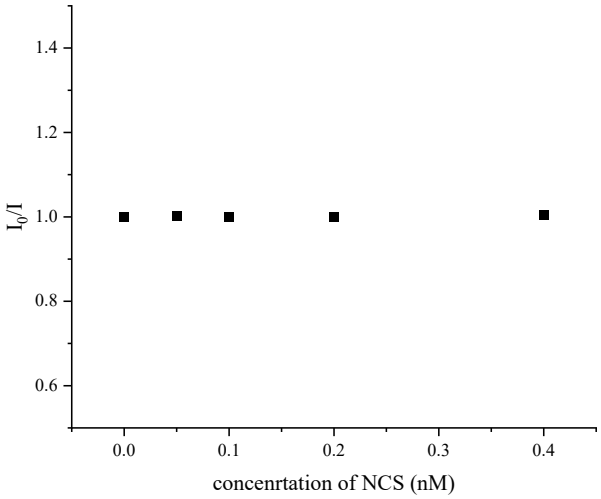
Fluorescence Quenching with 2-aminobenzonotrile, 2-amino-5-chlorobenzonotrile and acid catalyst (equal equivalents with aniline)



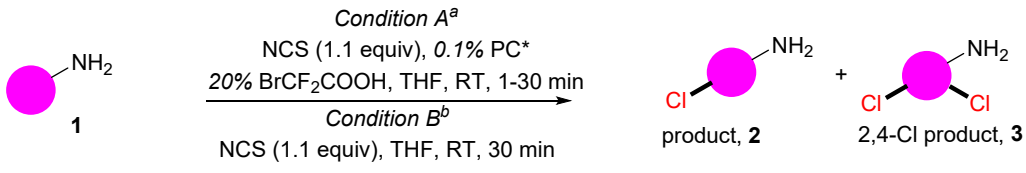
Fluorescence Quenching with o-toluidine.

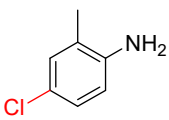


Fluorescence Quenching with NCS

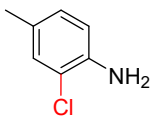


7. Other examples examined

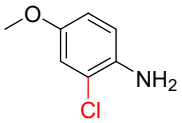




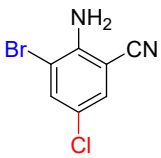
1 min, 75% (70%[b])



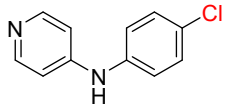
1 min, 85%(83%[b])



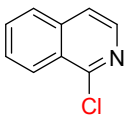
1 min, 80%(80[b])



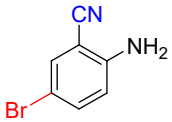
1st Cl 2nd Br
61% mixture of
product/byproduct
ratio=9/1



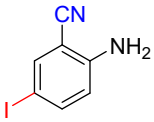
69% mixture of
4-Cl/2,4-Cl product (ratio=2/1)



<10%



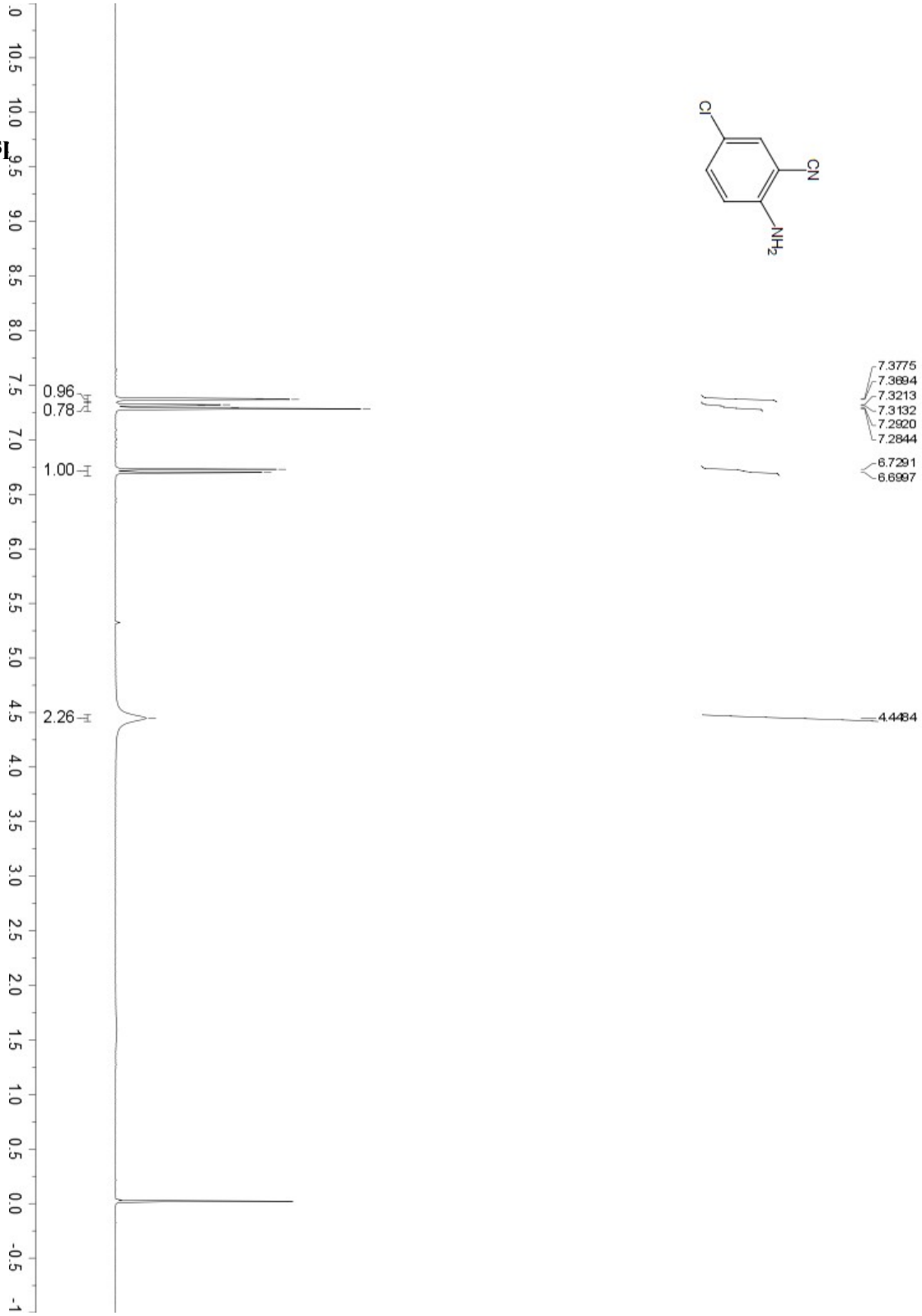
1 min, 95% (90%[b])



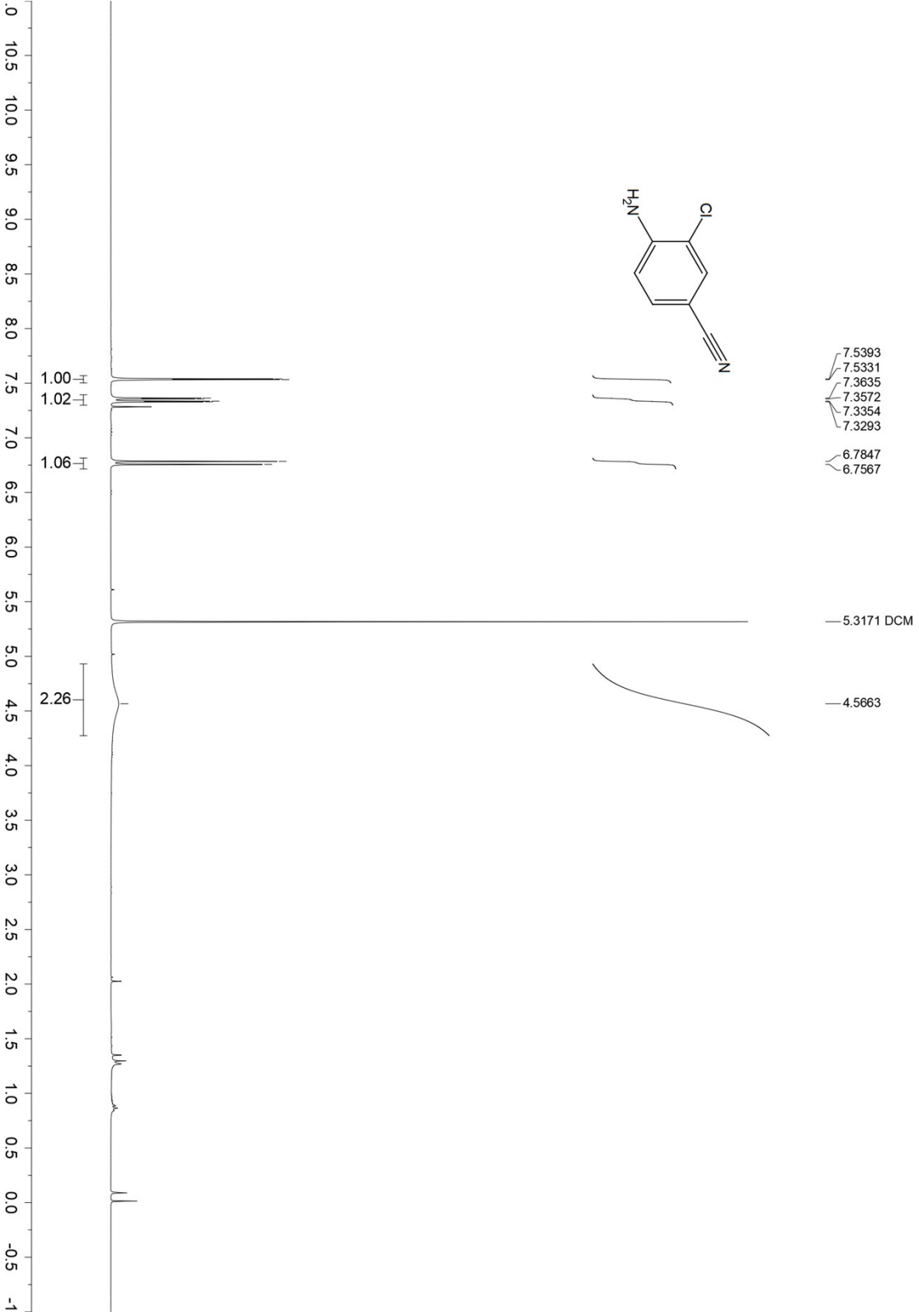
30 min, <5%

Copies of NMR sp

^{1}H NMR of 2a



^{1}H NMR of 2b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7.3572
7.3354
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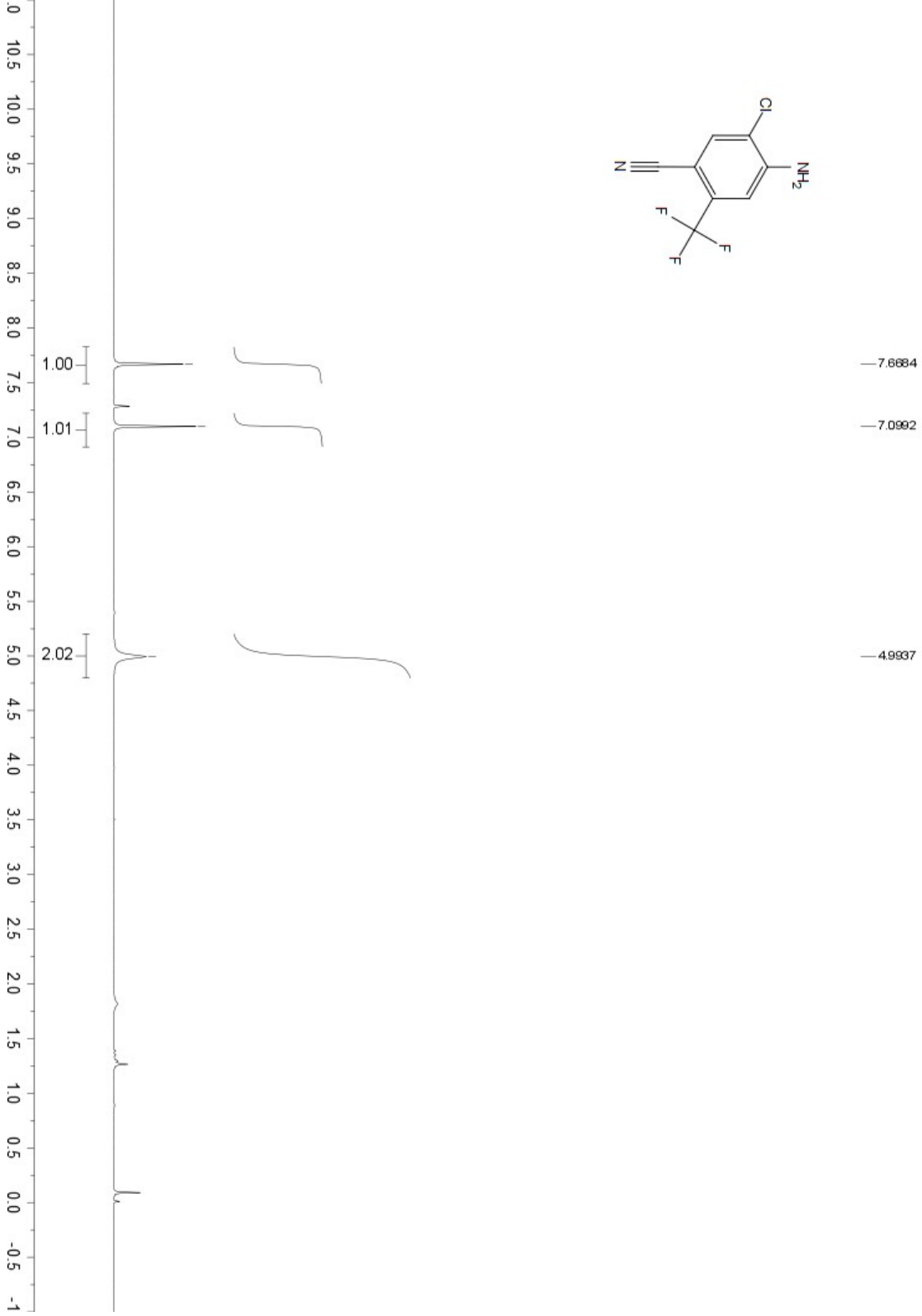
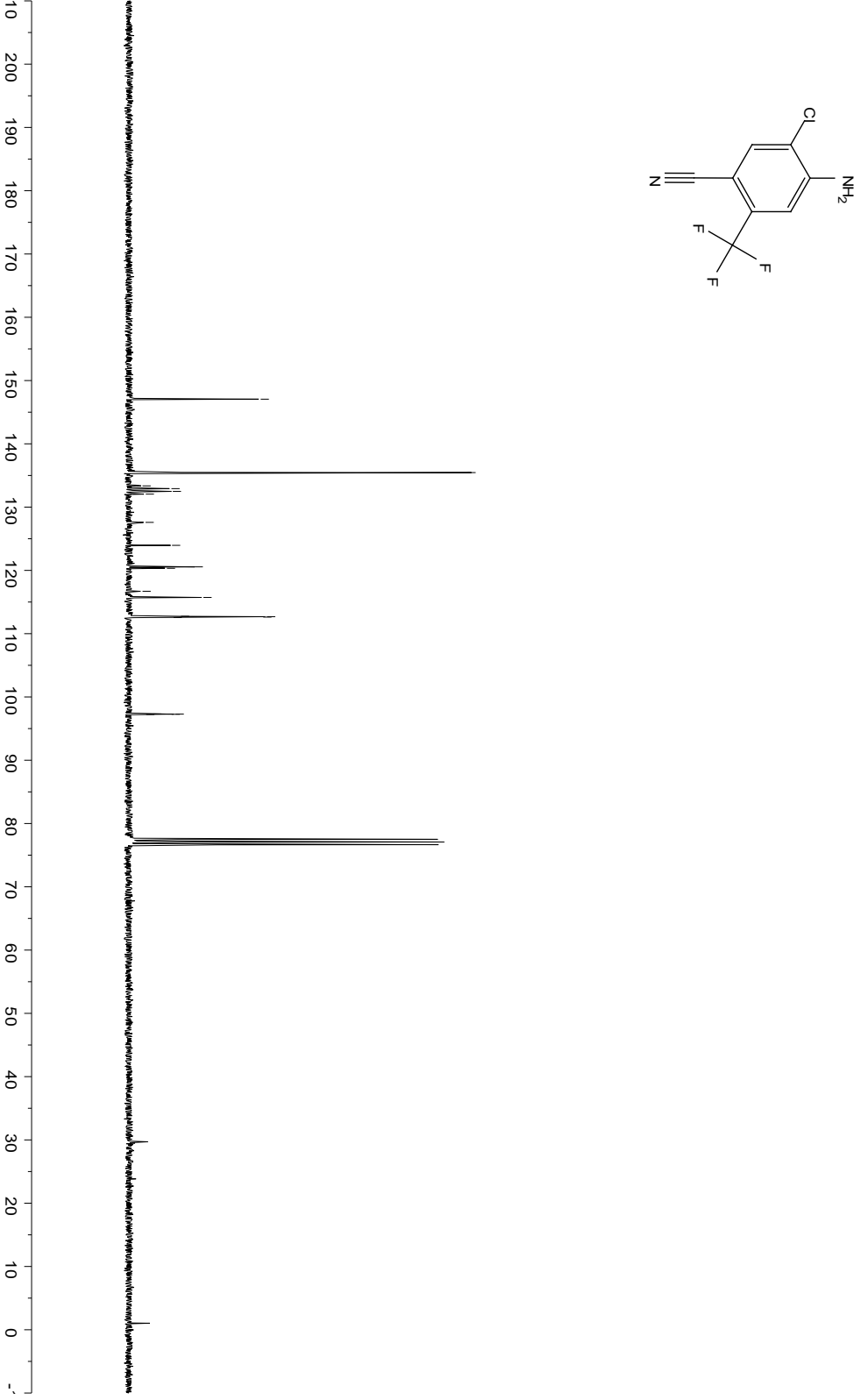
6.7567
5.3171 DCM
4.5663
H2N
Cl
N

^{1}H NMR of 2c



^{13}C NMR of 2c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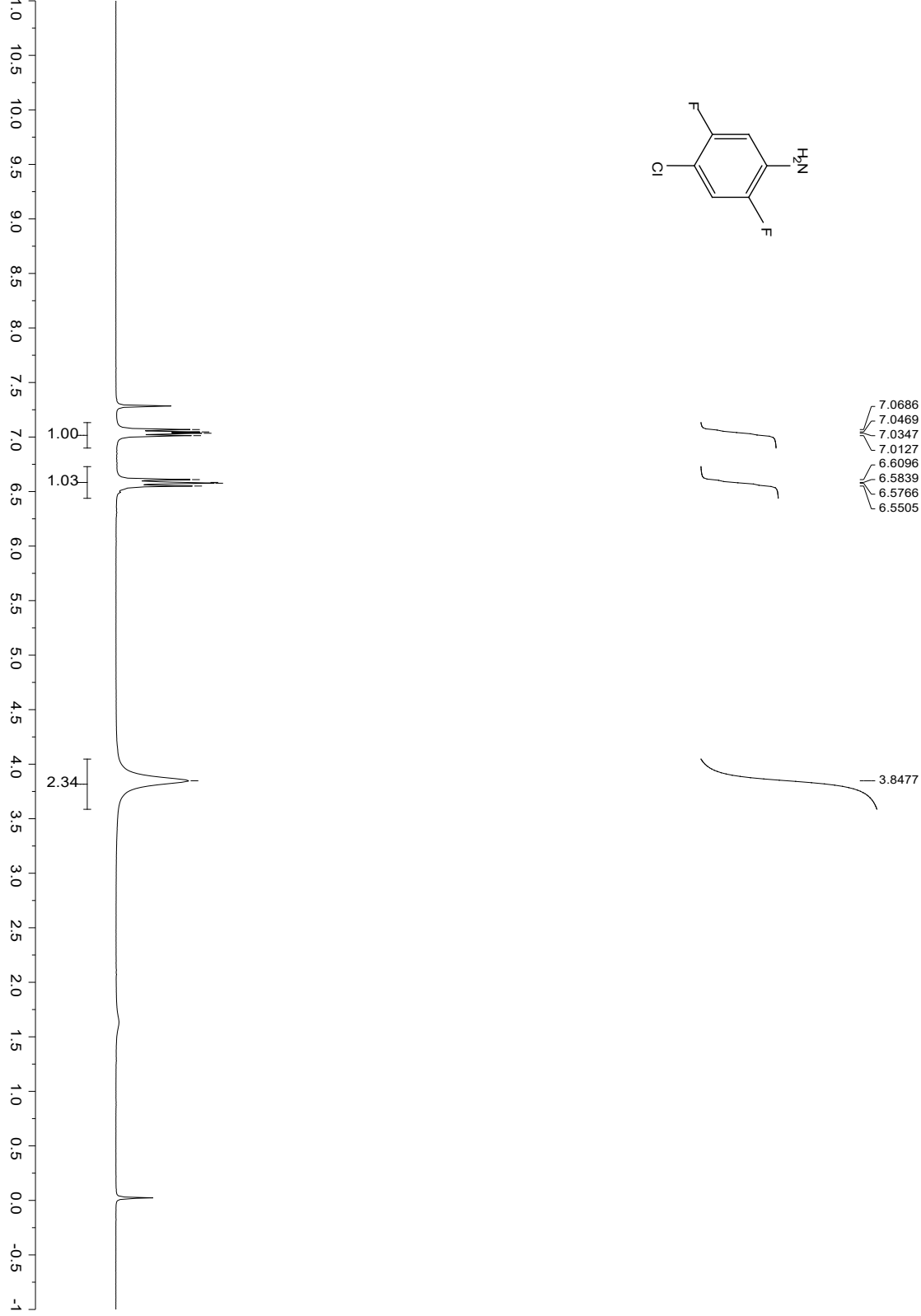
N
NH2
F
F
F
147.06
135.46
133.36
132.92
132.49
132.05
127.59
123.96
120.56
120.33
116.70
115.72
112.75
112.68
112.62
112.55
97.31
97.29
97.26
97.24

^{1}H NMR of 2d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Cl
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F
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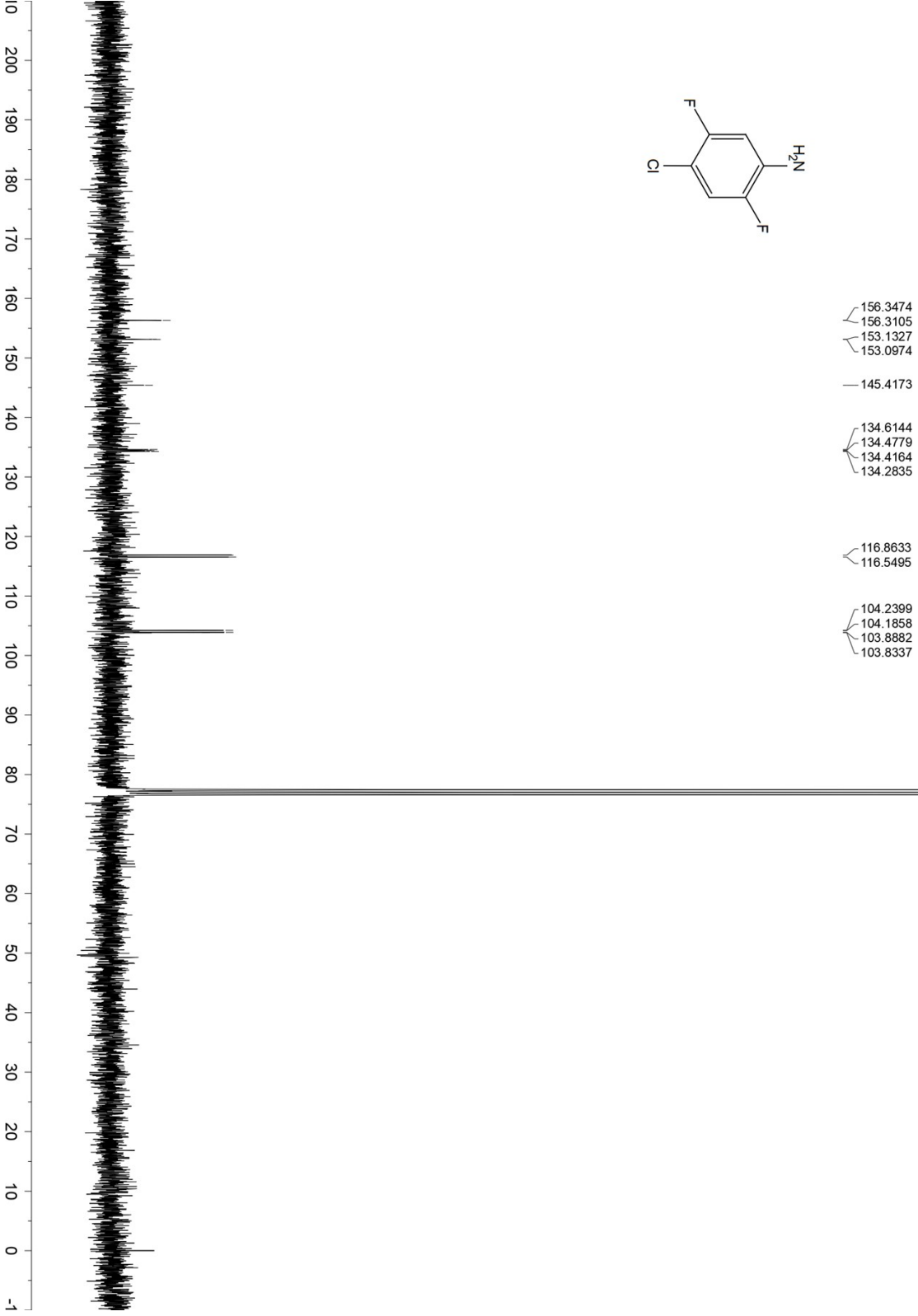
1.00
1.03
2.34

^{13}C NMR of 2d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Cl
H2N
F
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134.4779
134.4164
134.2835
116.8633
116.5495
104.2399
104.1858
103.8882
103.8337
210
200
190
180
170
160
150
140
130
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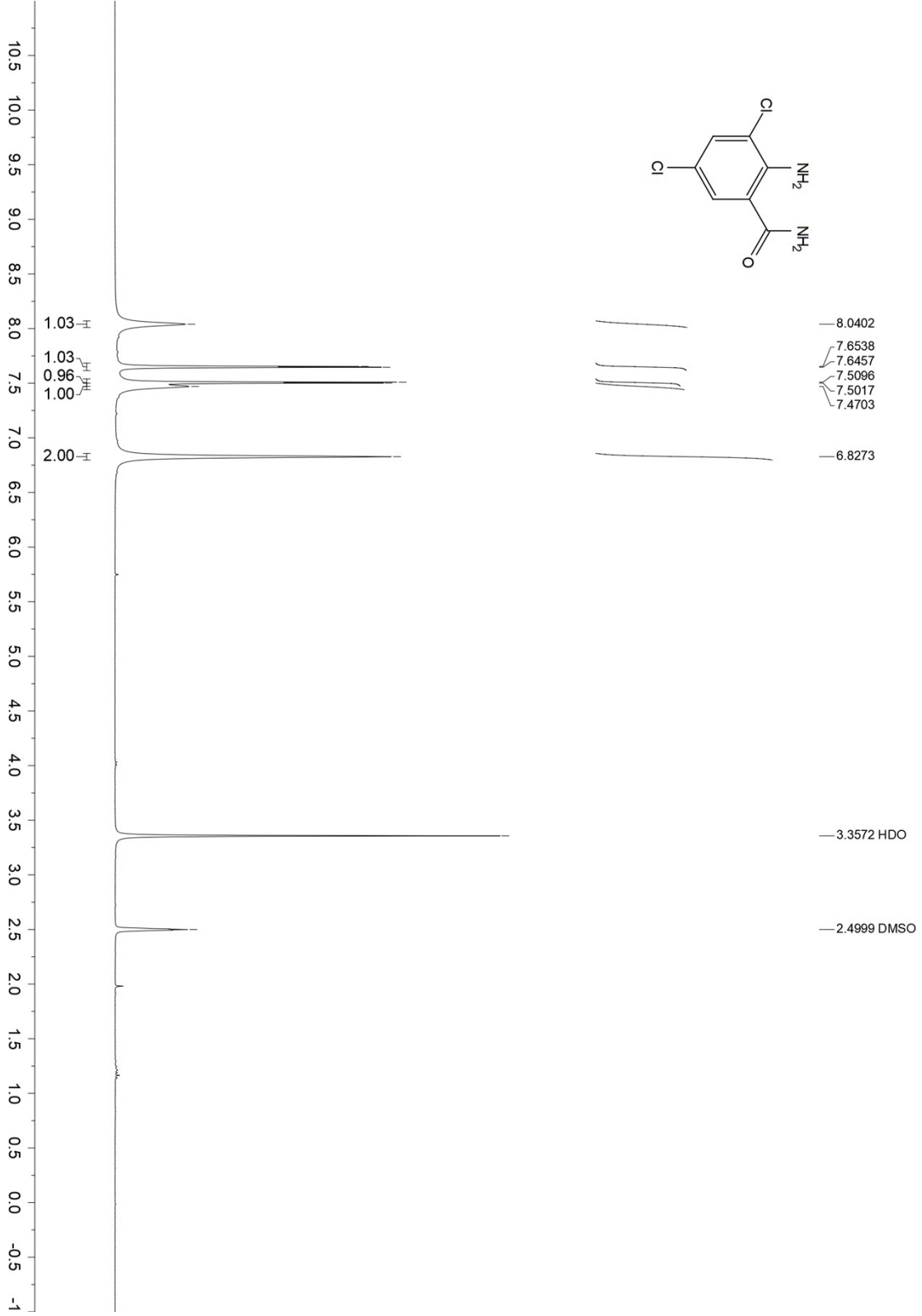
110
100
90
80
70
60
50
40
30
20
10
0
-1

^{1}H NMR of 2e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Cl
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NH2
O
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1.03
0.96
1.00
2.00
8.0402
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7.4703
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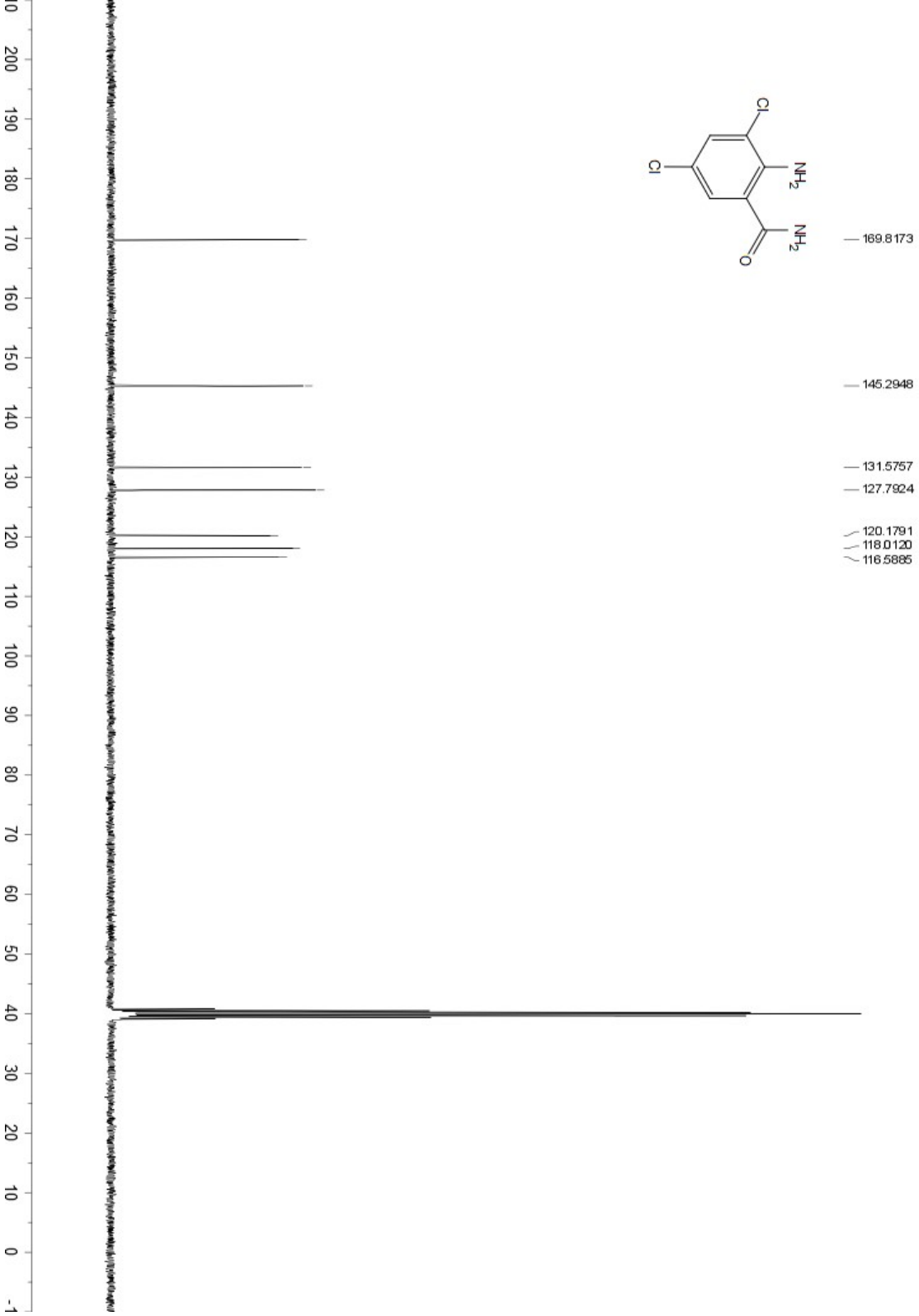
3.3572 HDO
2.4999 DMSO

^{13}C NMR of 2e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Cl
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O
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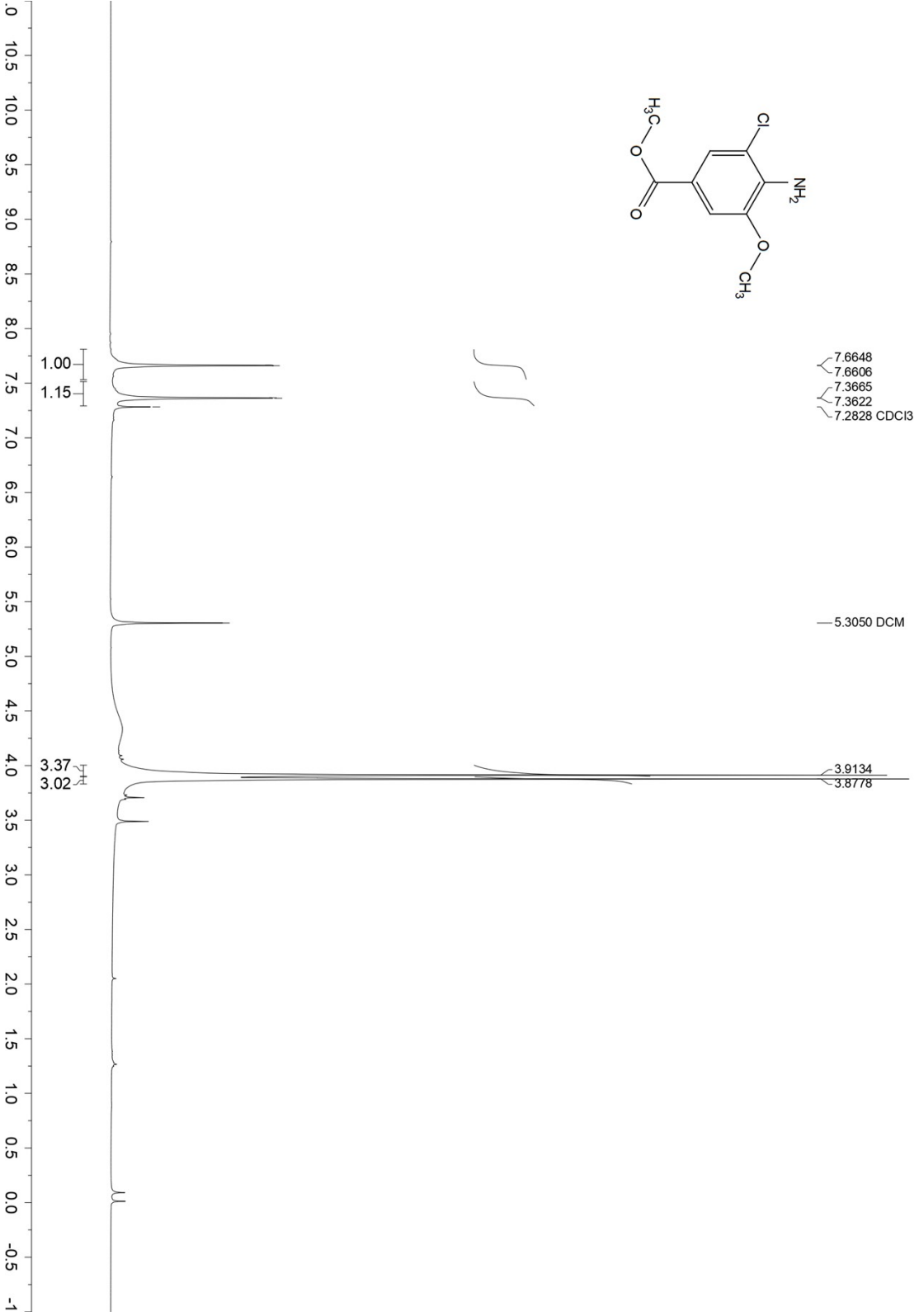
127.7924
120.1791
118.0120
116.5885

^{1}H NMR of 2f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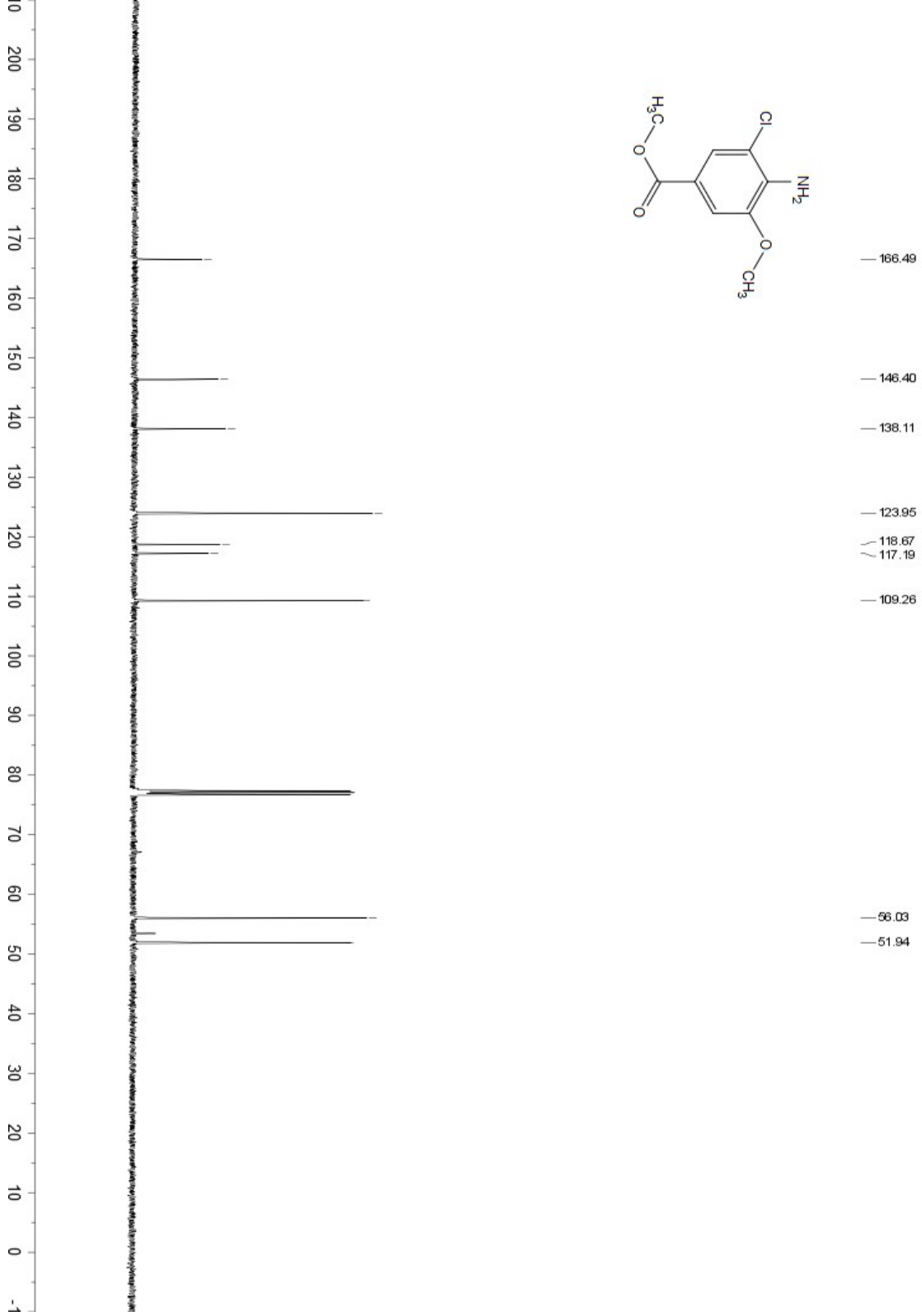
5.3050 DCM
3.9134
3.8778
Cl
NH2
O
CH3
H3C

^{13}C NMR of 2f


166.49
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138.11
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117.19
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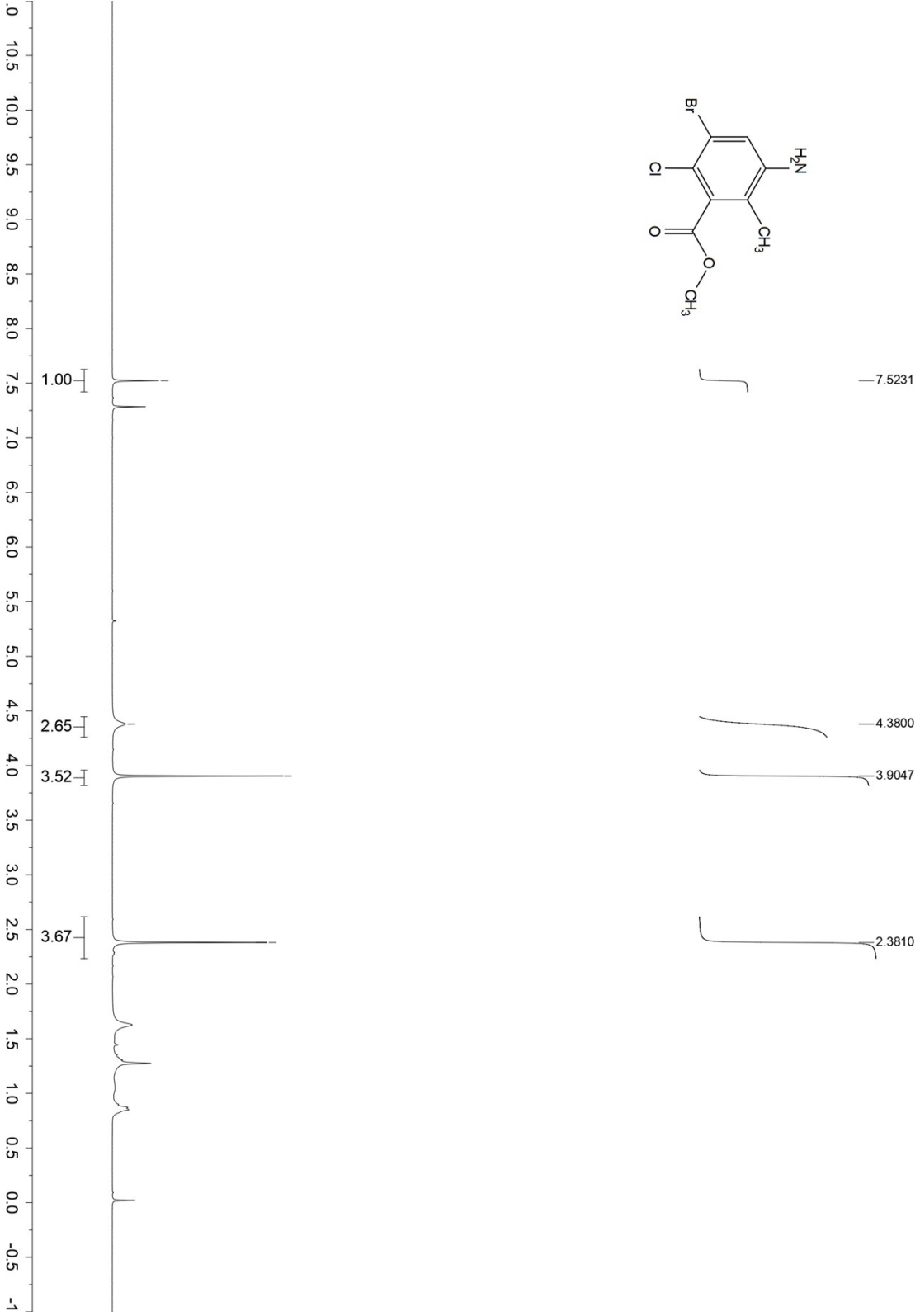
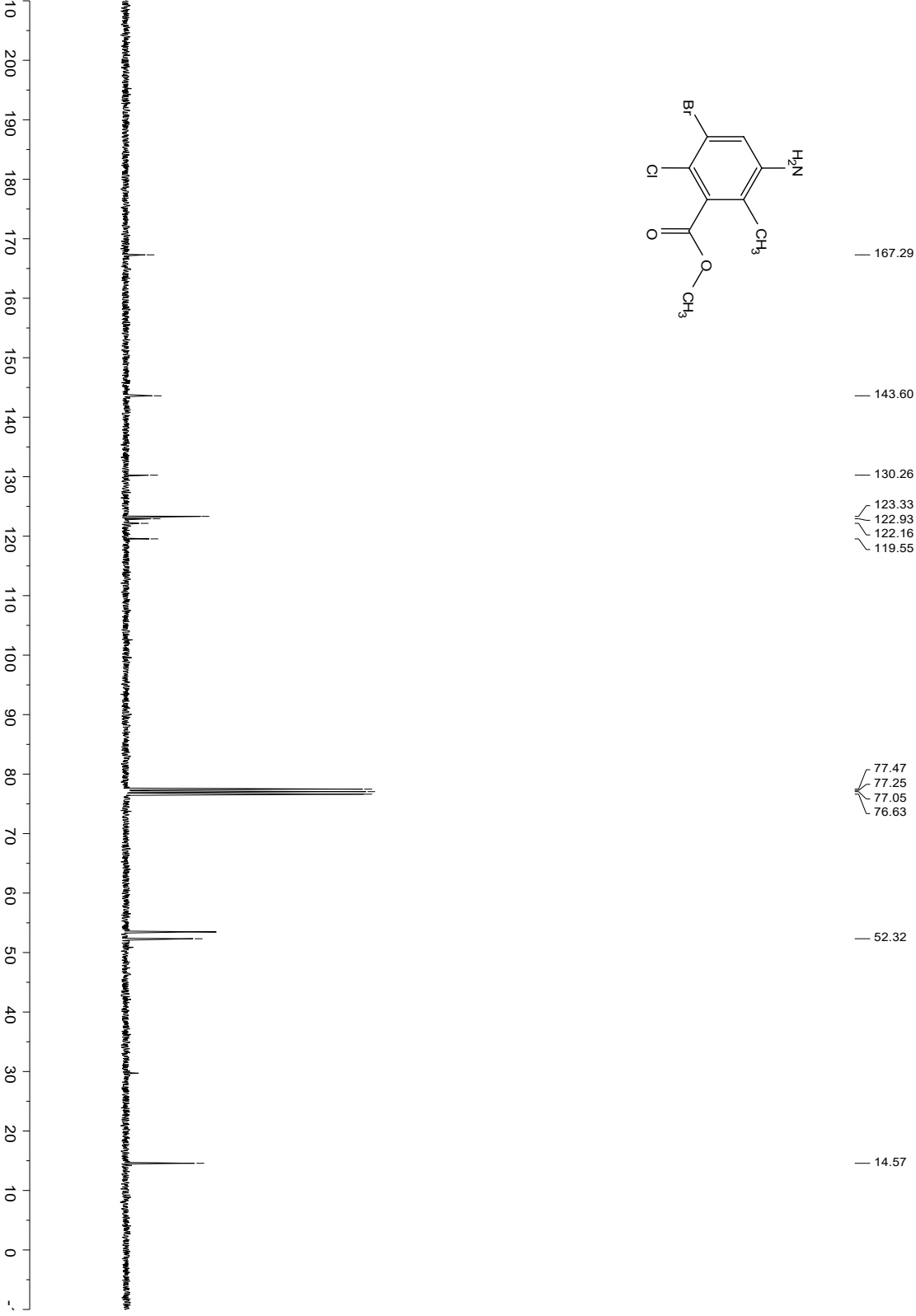
56.03
51.94
Cl
NH2
H3C
O
CH3

^{1}H NMR of 2g



^{13}C NMR of 2g


Br
Cl
O
O
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H2N
CH3
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130.26
123.33
122.93
122.16
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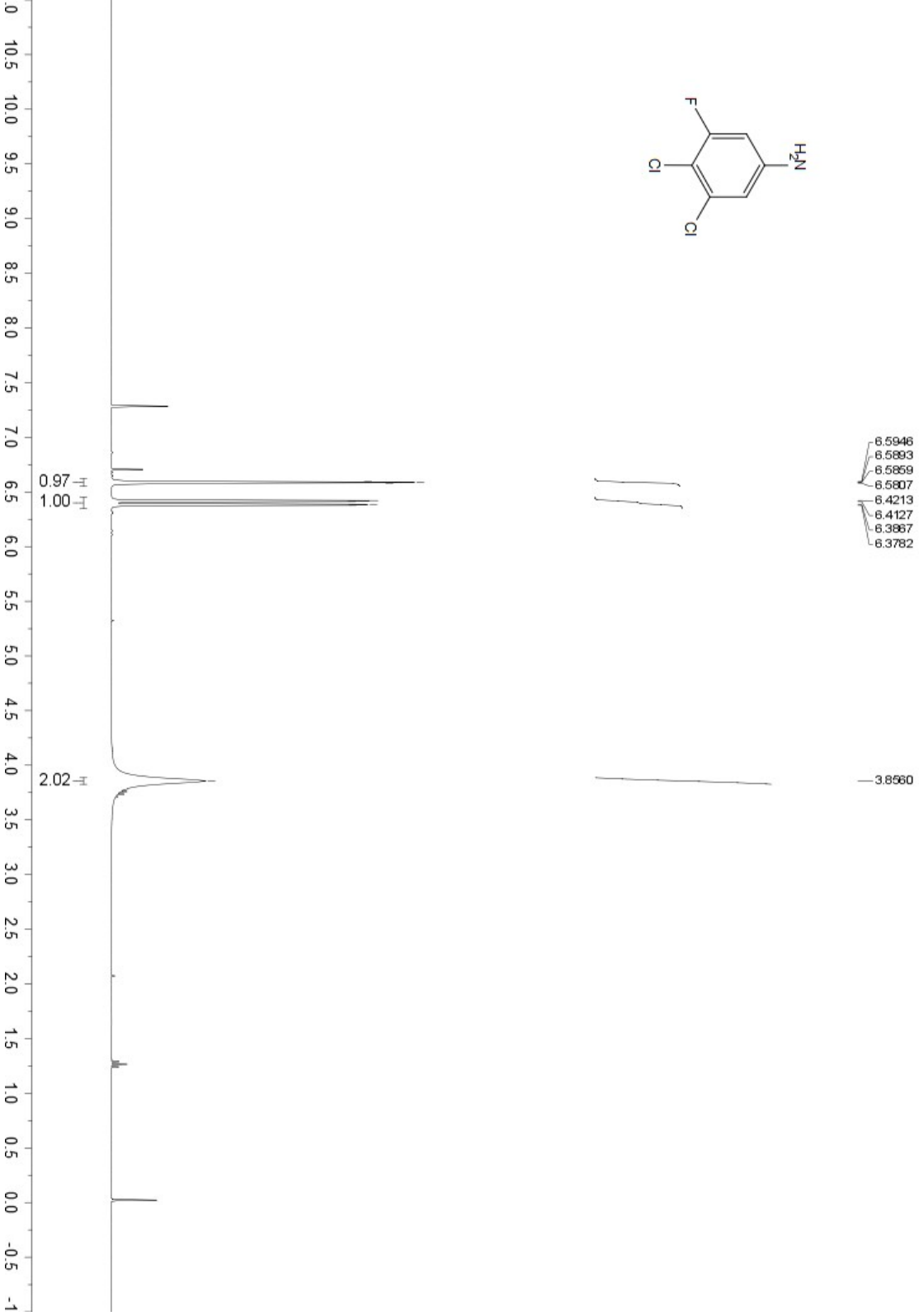
77.47
77.25
77.05
76.63
52.32
14.57

^{1}H NMR of 2h


F
Cl
Cl
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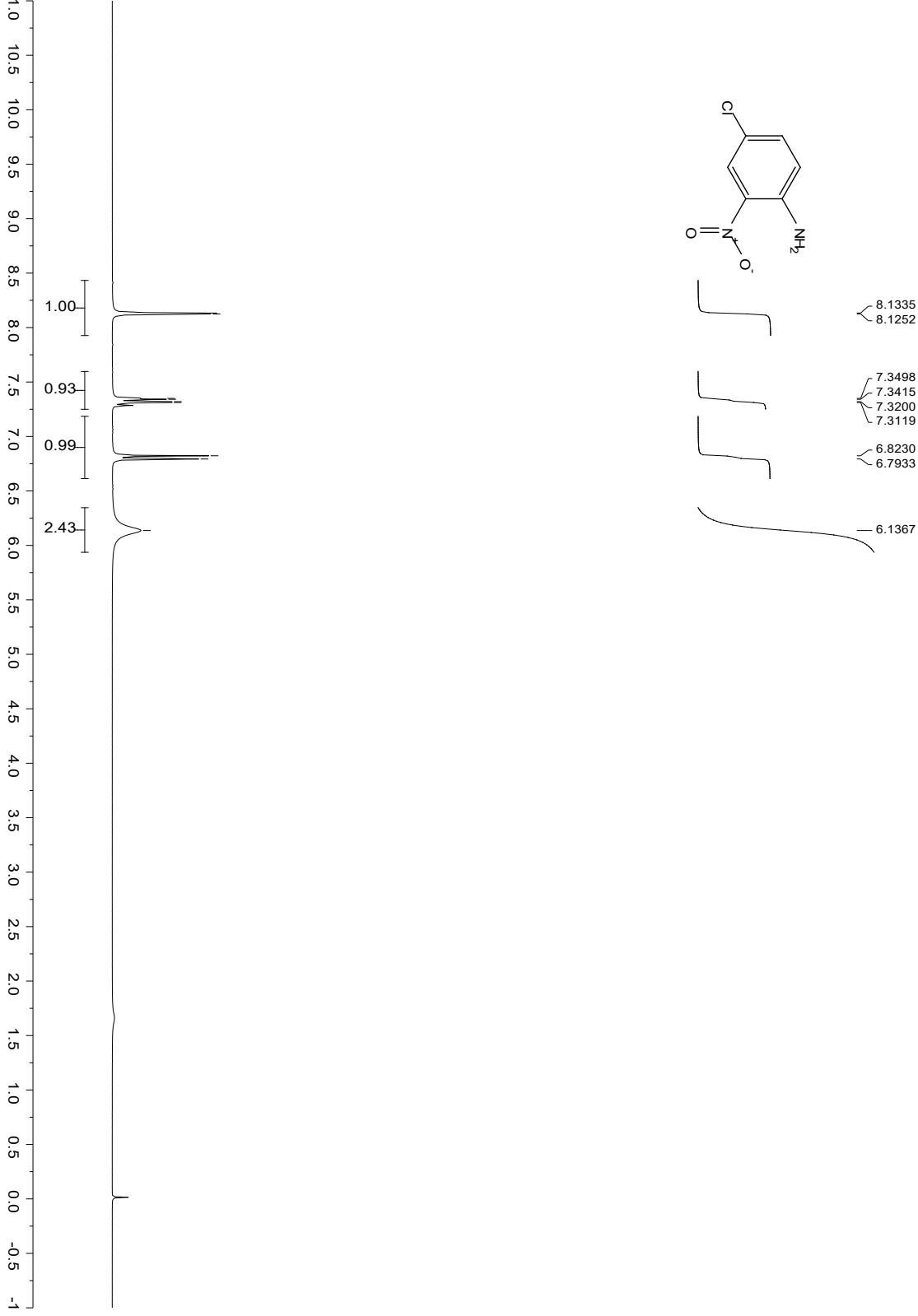
0.97
1.00
2.02

^{1}H NMR of 2i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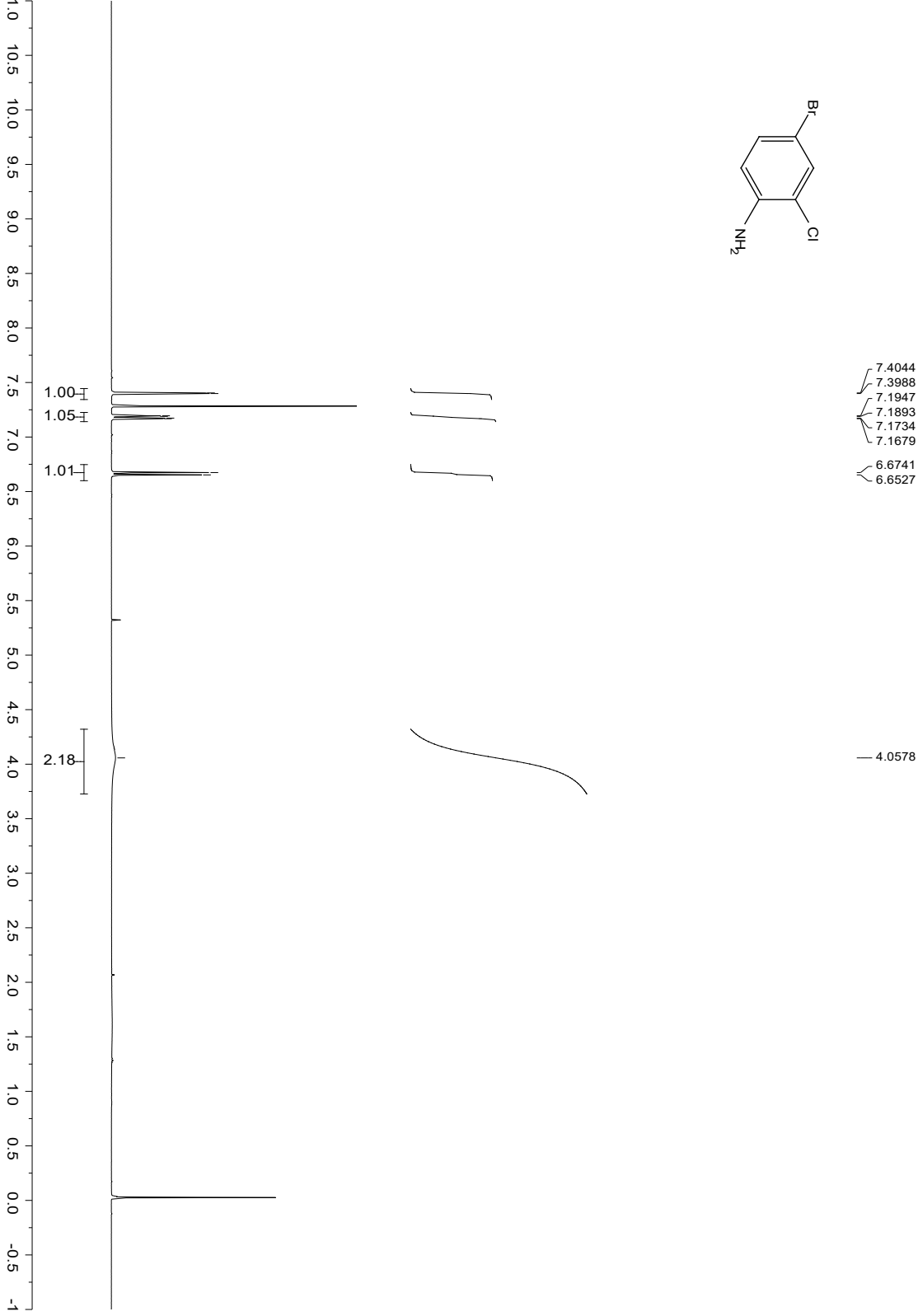
6.7933
6.1367

^{1}H NMR of 2j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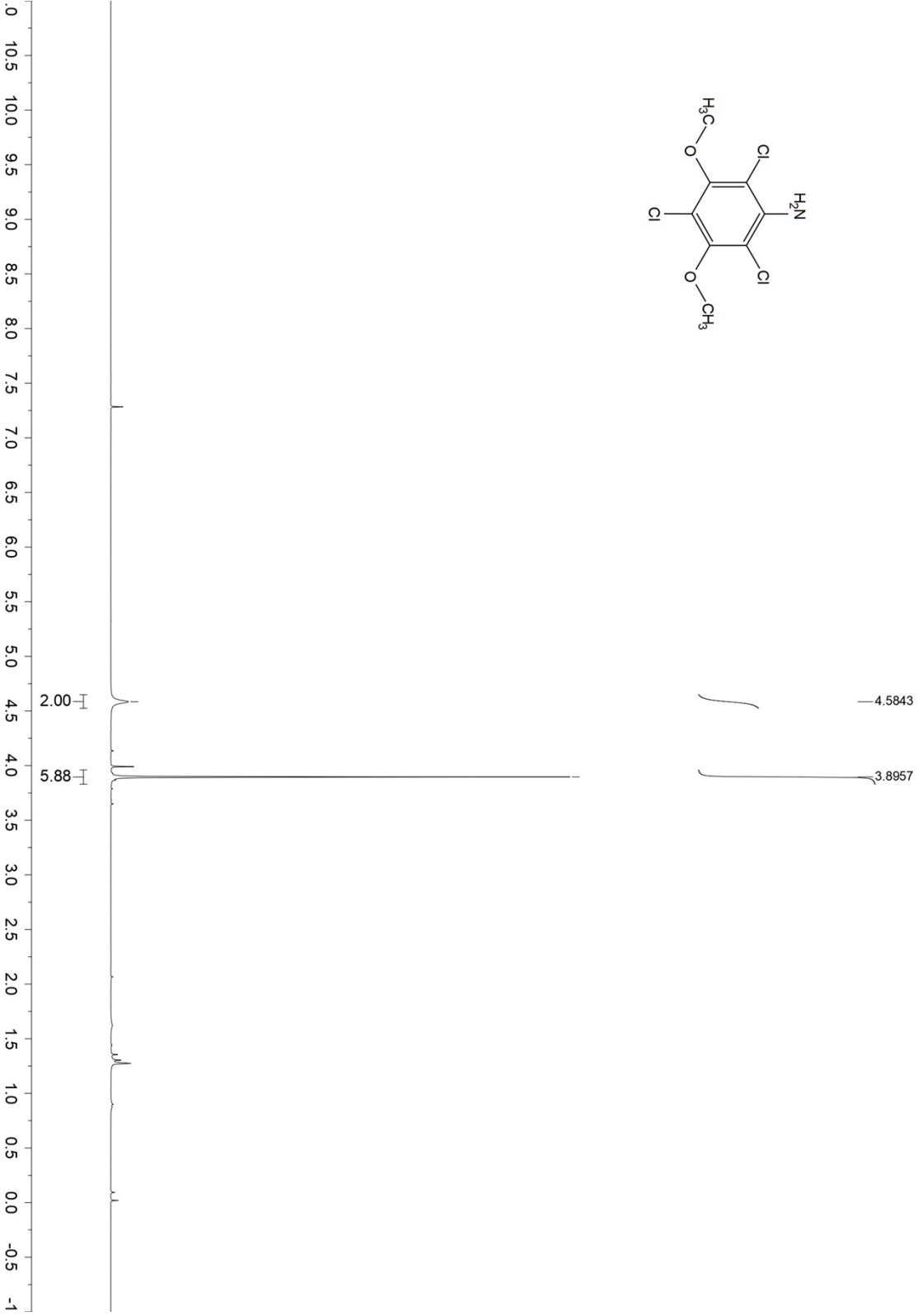
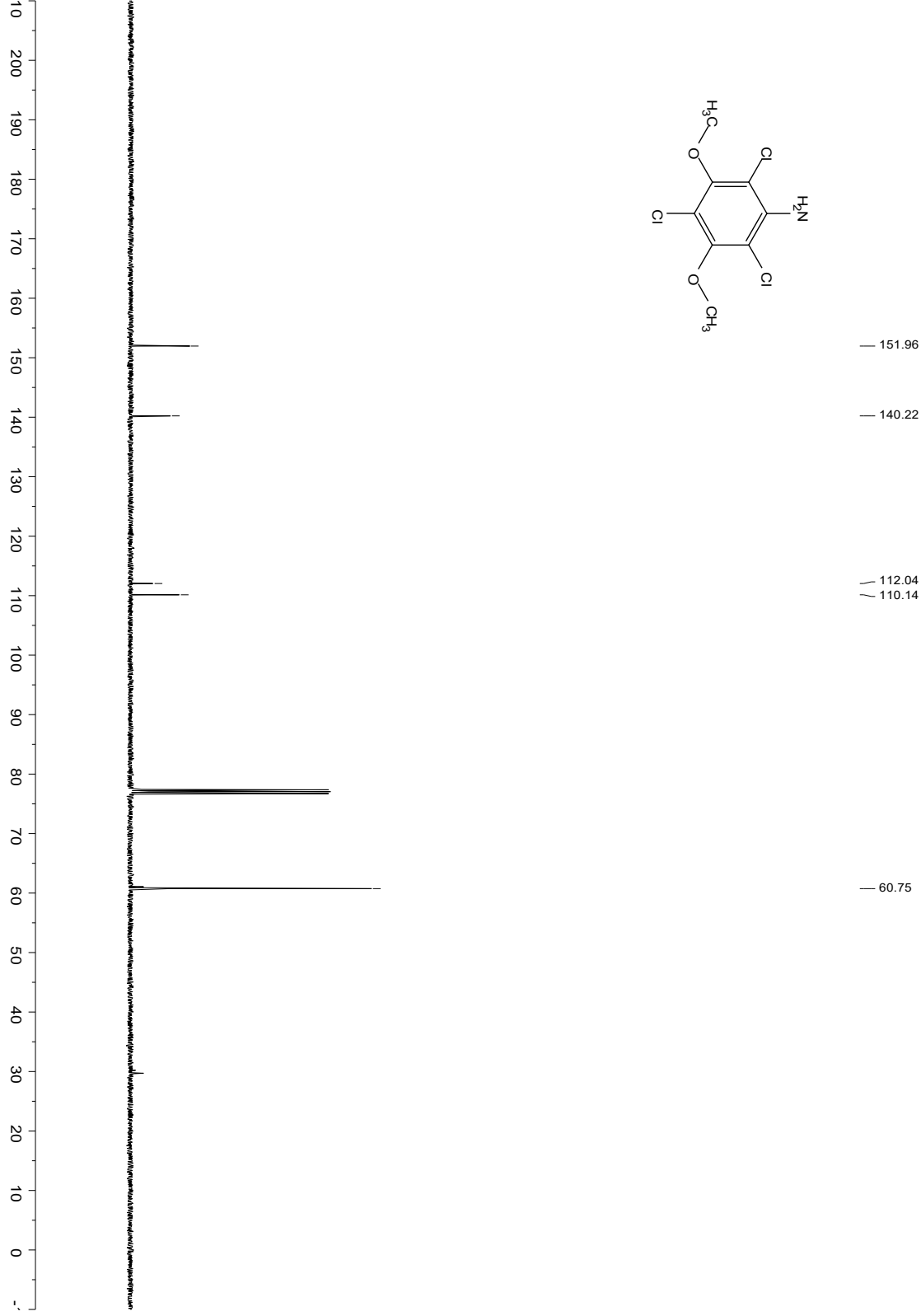
1.05
1.01
2.18

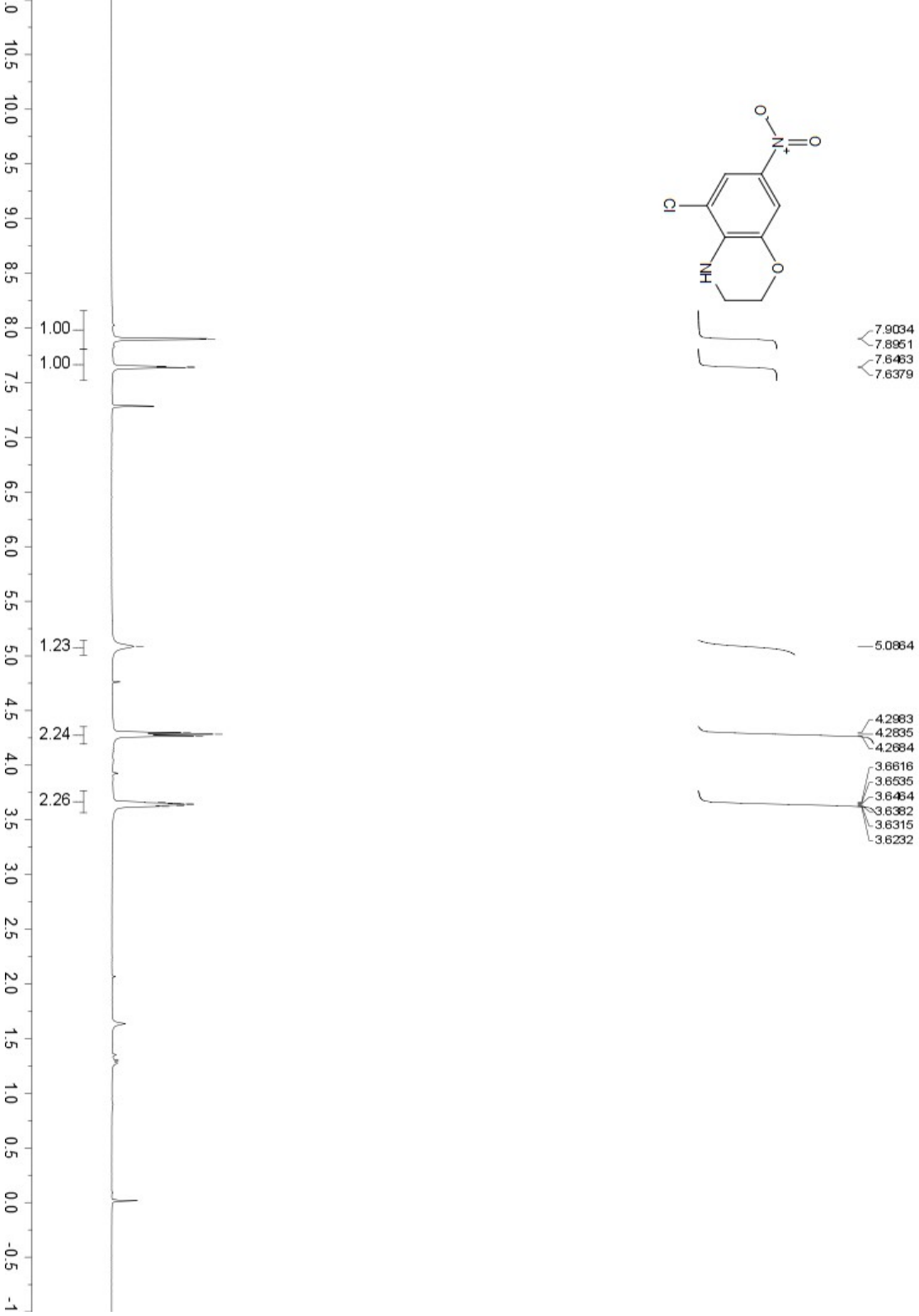
^{1}H NMR of 2k



^{13}C NMR of 2k



^{1}H NMR of 2l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2.26
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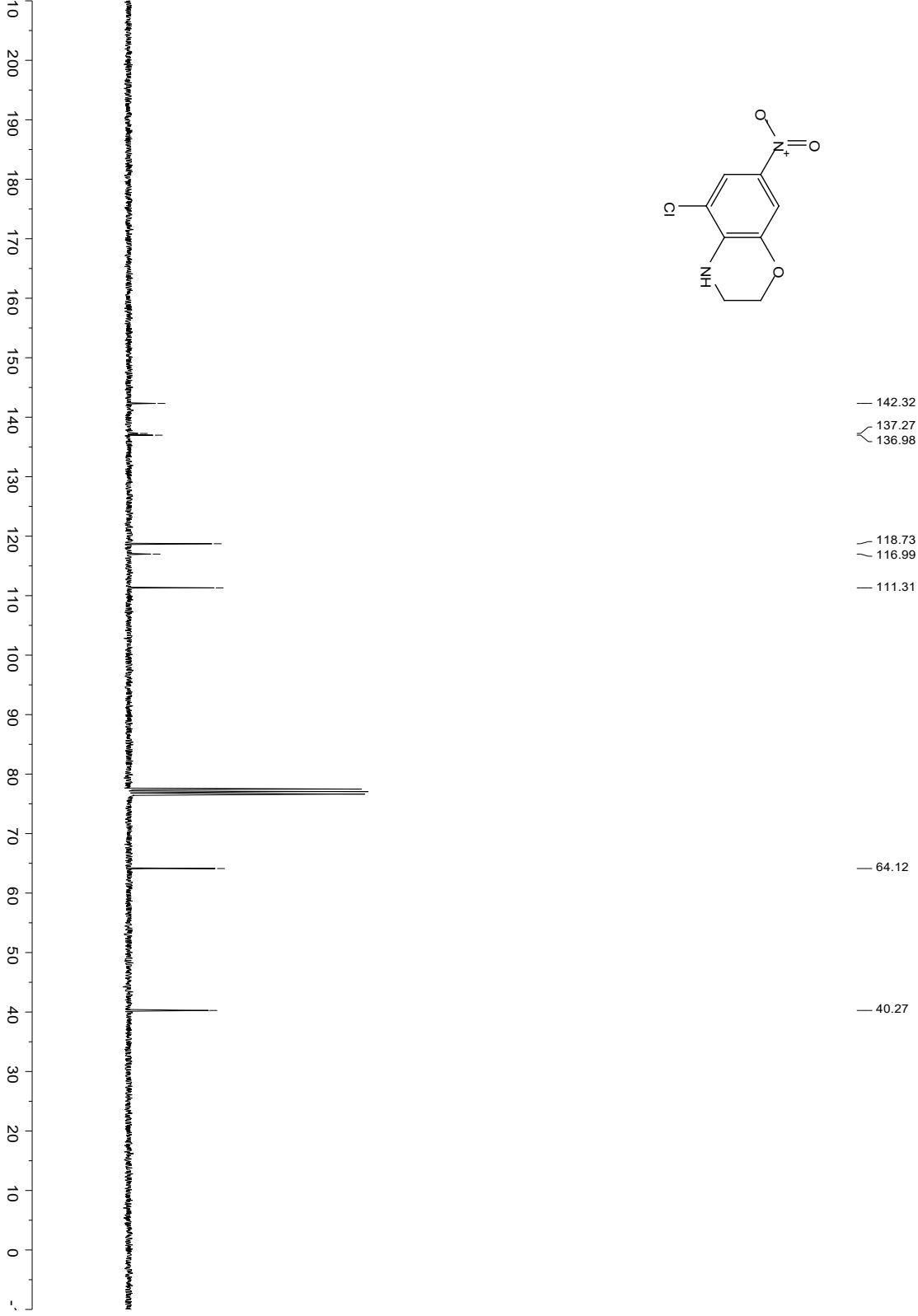
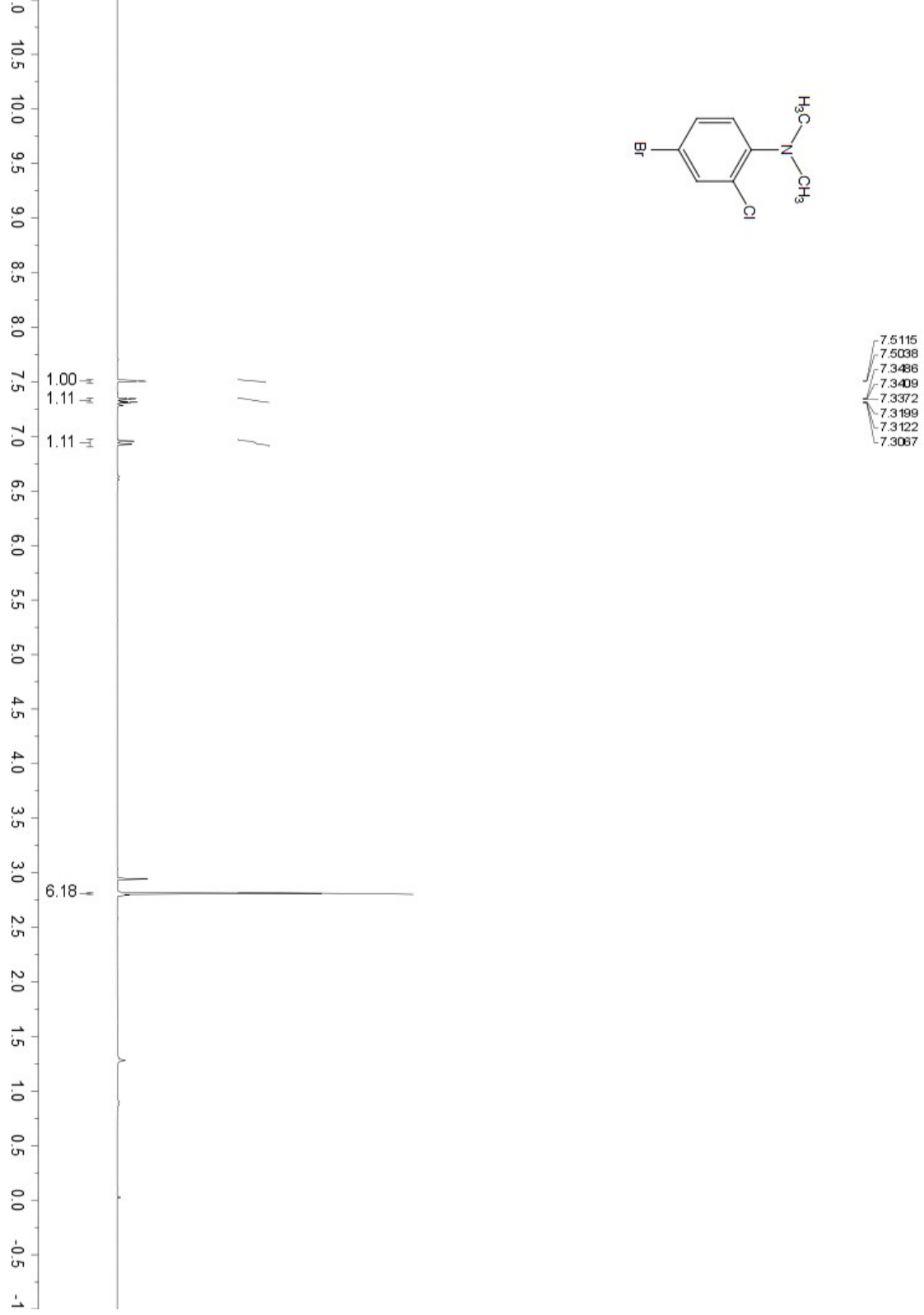
4.2835
4.2684
3.6616
3.6535
3.6464
3.6382
3.6315
3.6232
Cl
HN
O

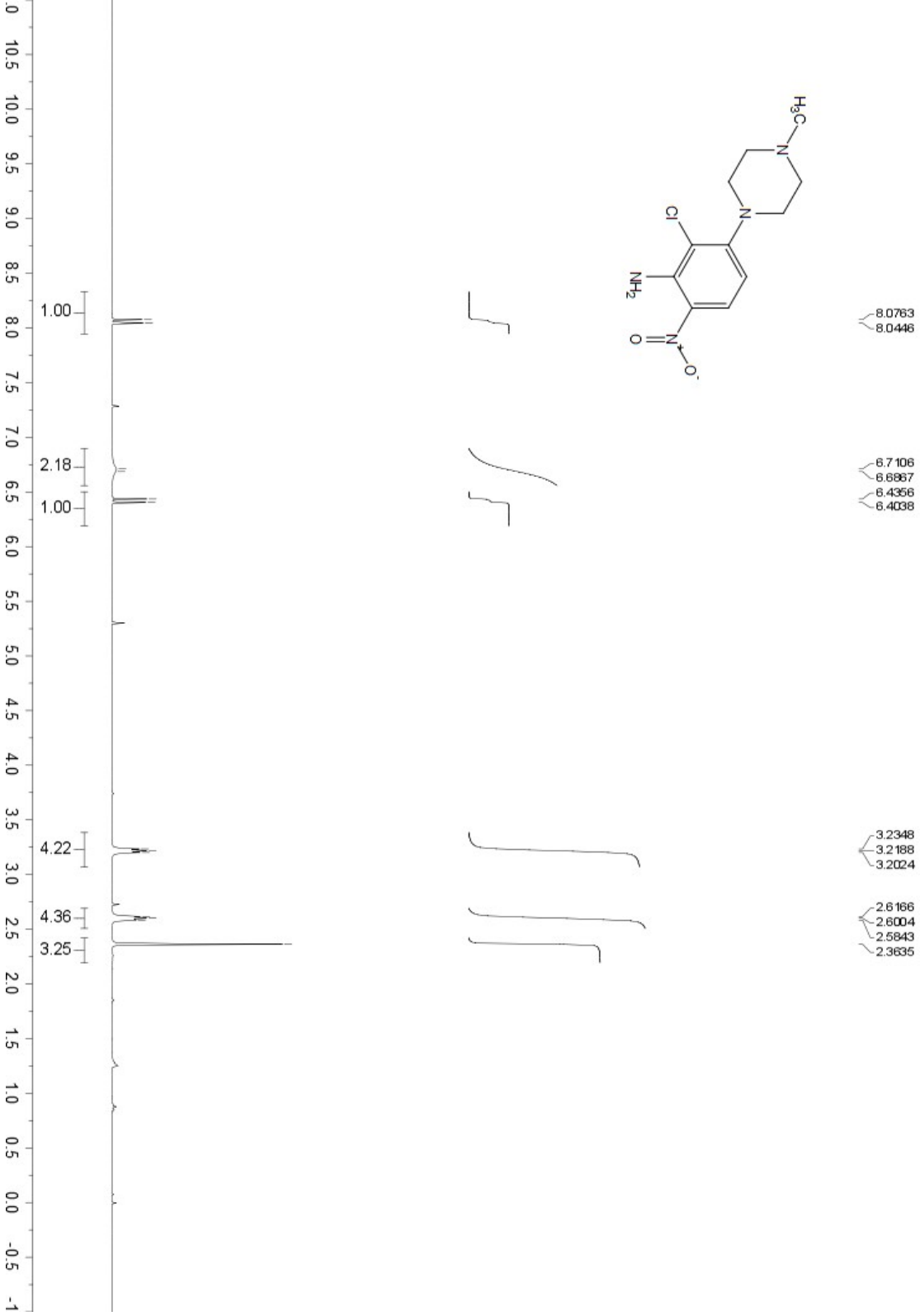
^{13}C NMR of 2l



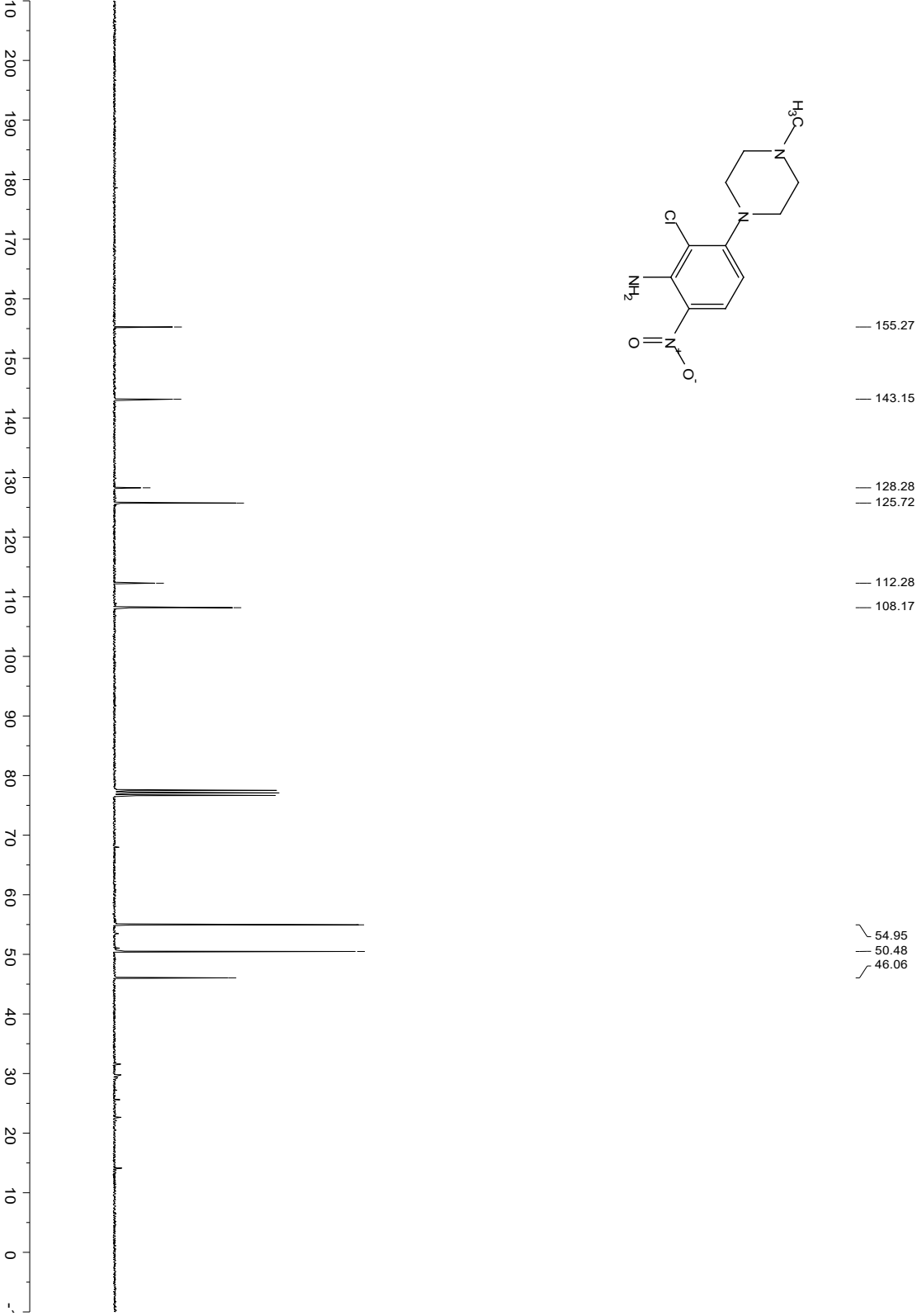
^{1}H NMR of 2m


Br
Cl
N
H3C
CH3
7.5115
7.5038
7.3486
7.3409
7.3372
7.3199
7.3122
7.3067
1.00
1.11
1.11
6.18

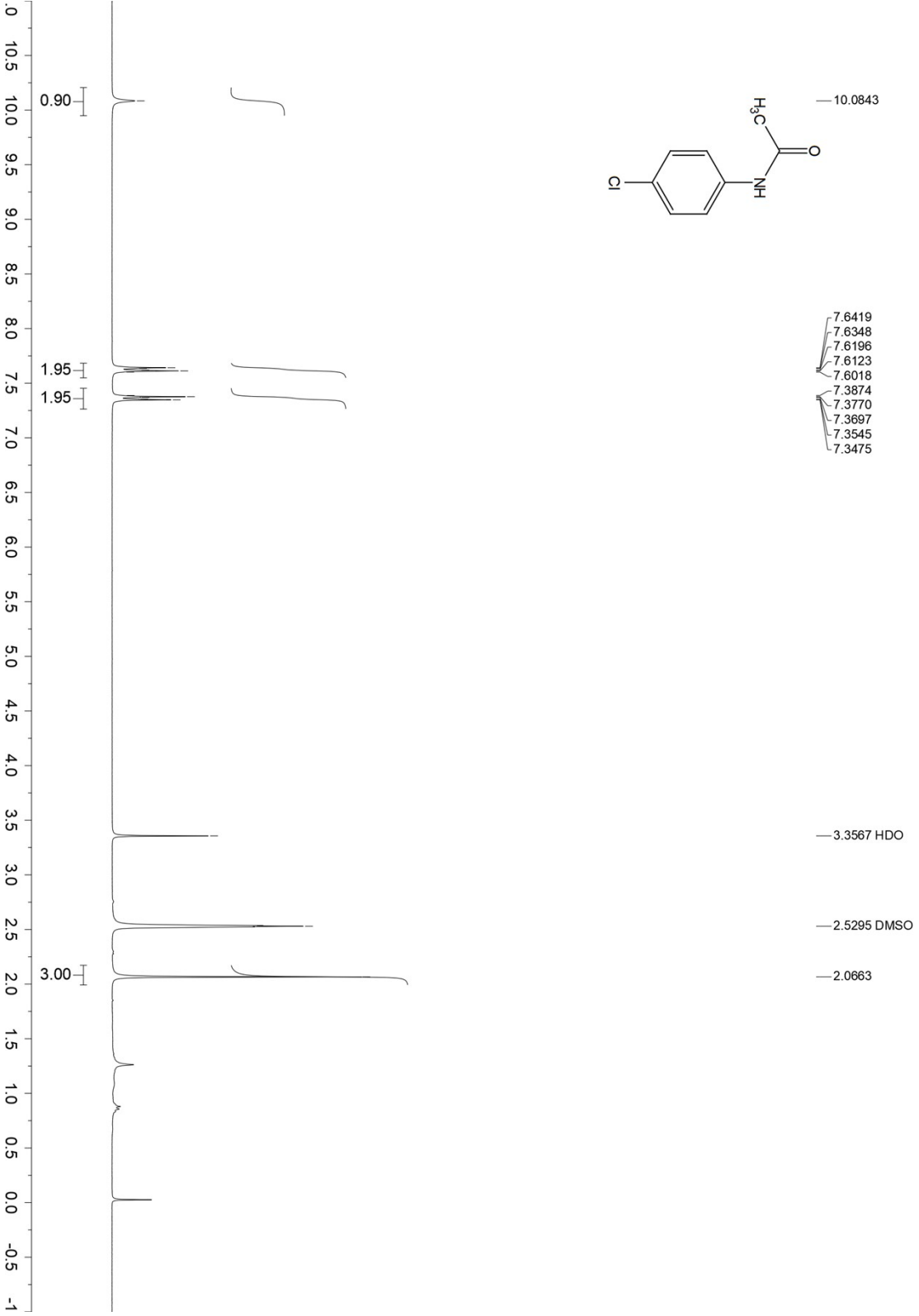
^{1}H NMR of 2n


1.00
2.18
1.00
4.22
4.36
3.25
8.0763
8.0446
6.7106
6.6867
6.4356
6.4038
3.2348
3.2188
3.2024
2.6166
2.6004
2.5843
2.3635

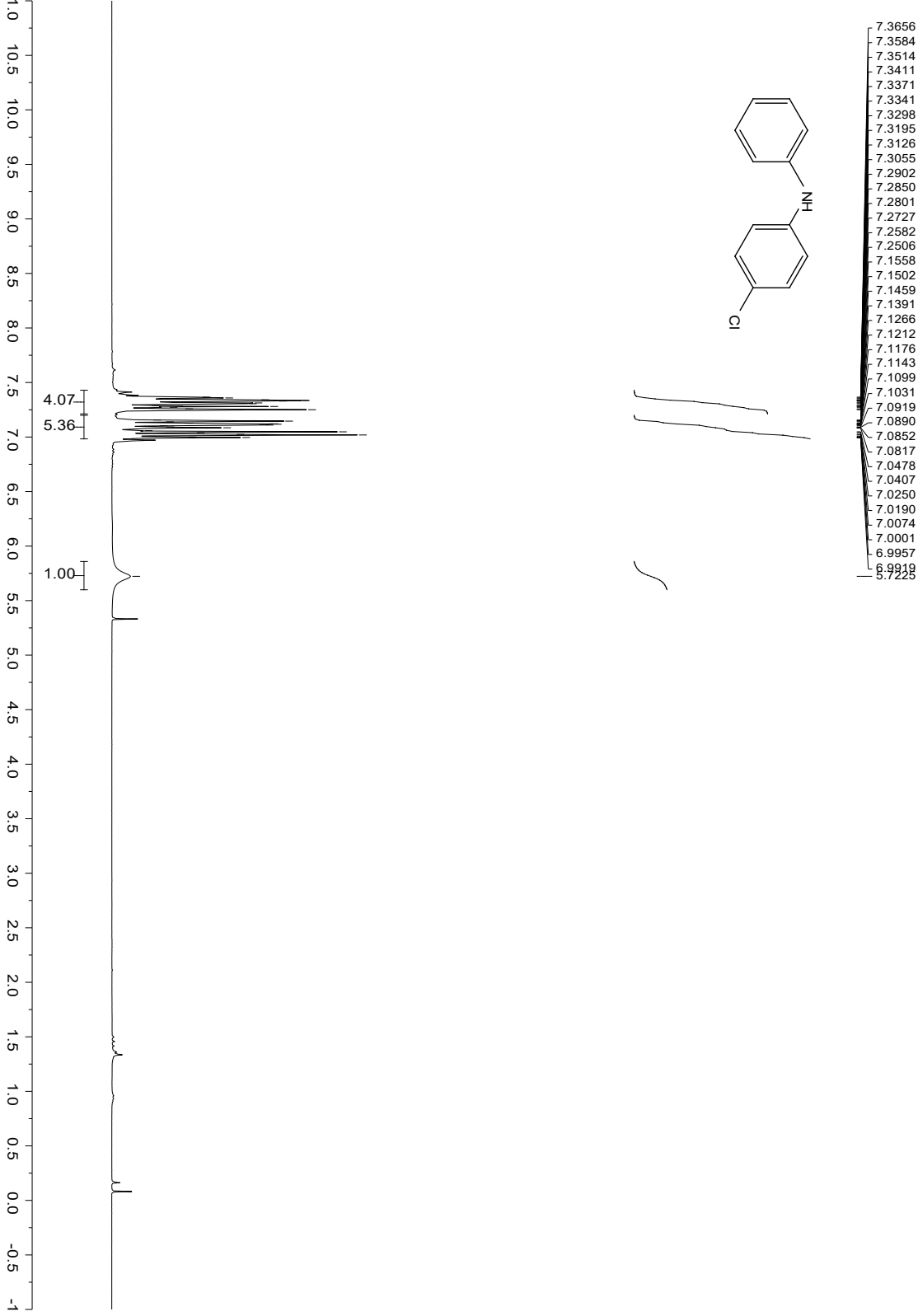
^{13}C NMR of 2n



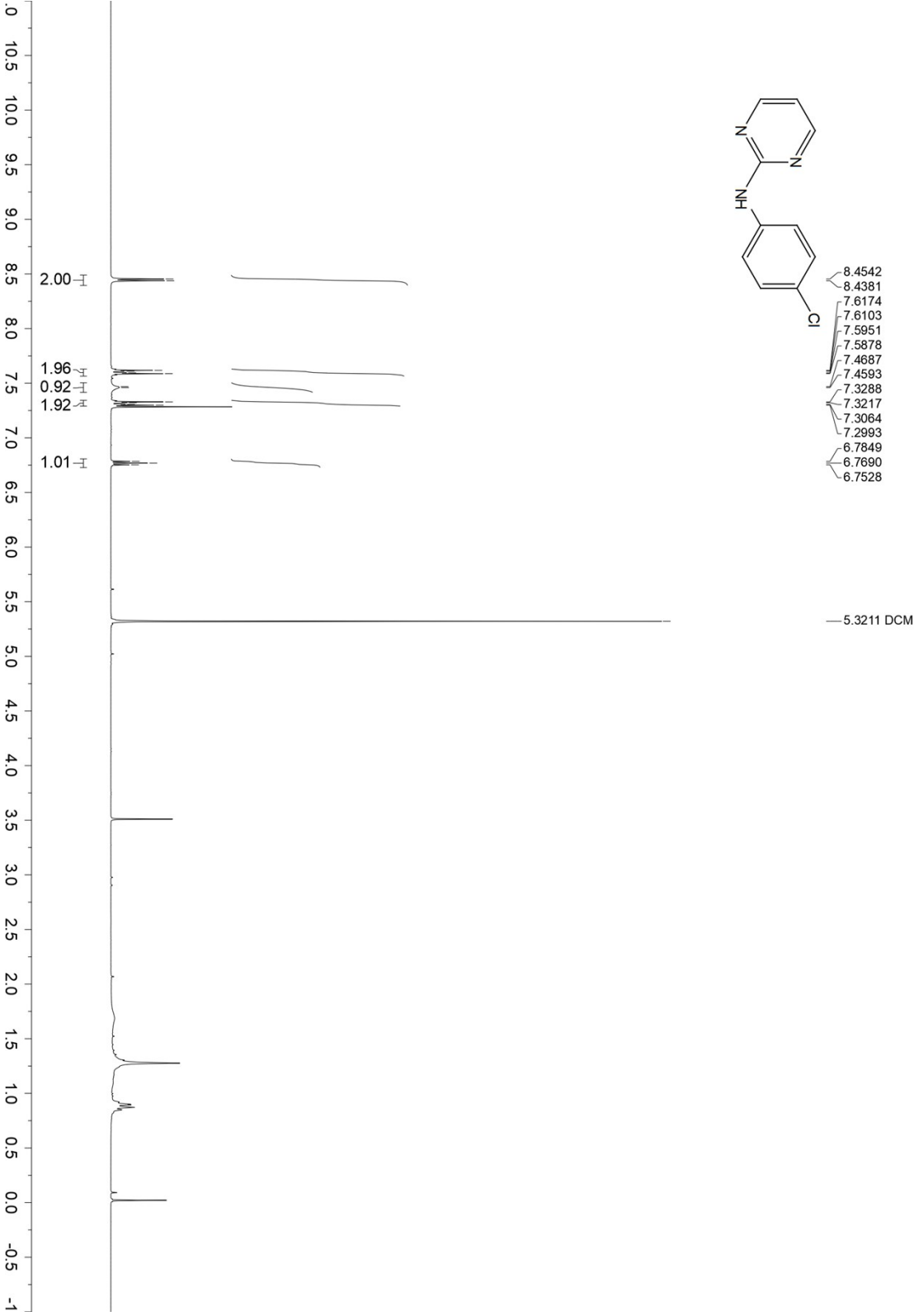
^{1}H NMR of 2o


0.90
1.95
1.95
3.00
10.0843
7.6419
7.6348
7.6196
7.6123
7.6018
7.3874
7.3770
7.3697
7.3545
7.3475
3.3567 HDO
2.5295 DMSO
2.0663
Cl
NH
O
H3C

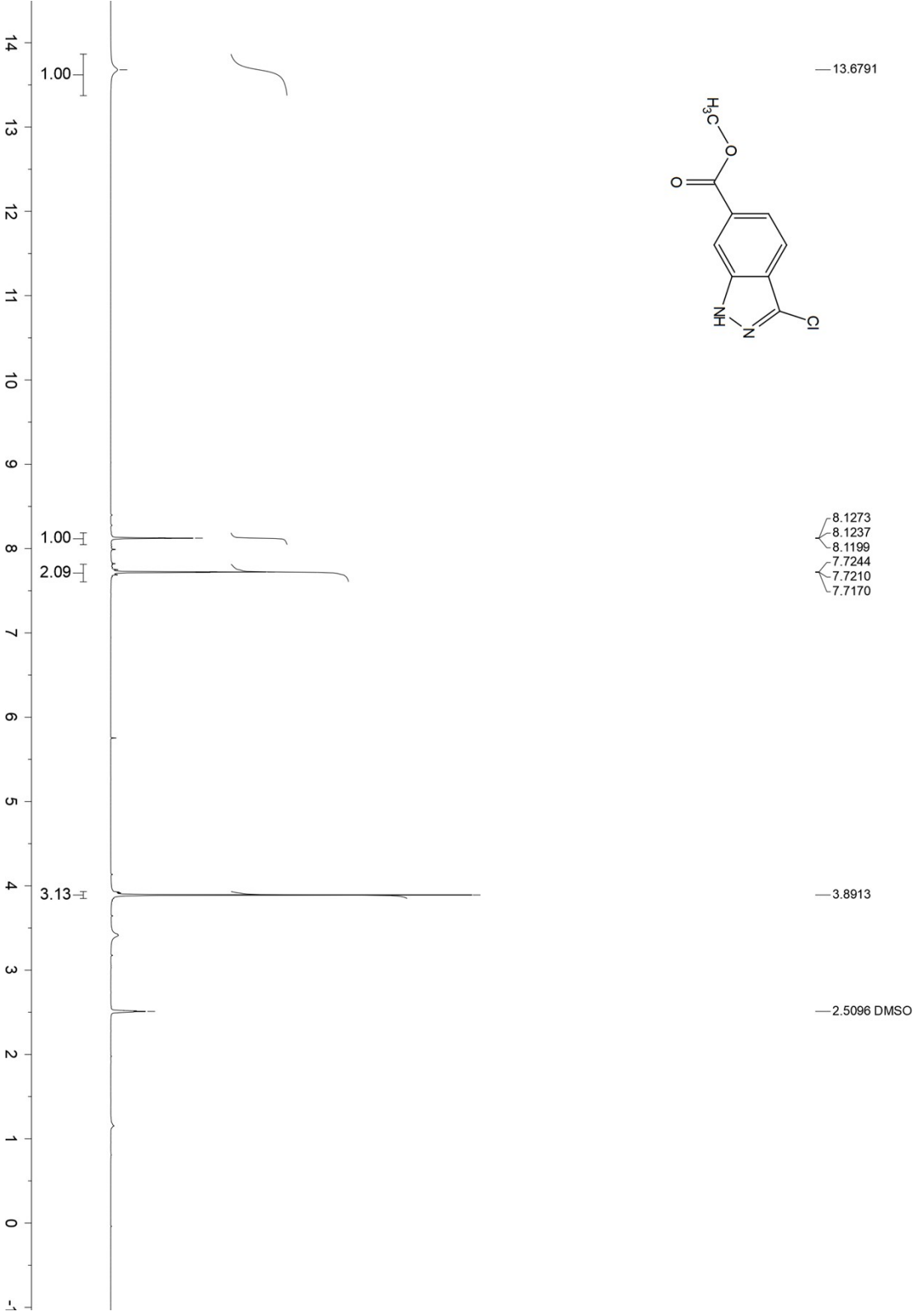
^{1}H NMR of 2p


NH
Cl
4.07
5.36
1.00
7.3656
7.3584
7.3514
7.3411
7.3371
7.3341
7.3298
7.3195
7.3126
7.3055
7.2902
7.2850
7.2801
7.2727
7.2582
7.2506
7.1558
7.1502
7.1459
7.1391
7.1266
7.1212
7.1176
7.1143
7.1099
7.1031
7.0919
7.0890
7.0852
7.0817
7.0478
7.0407
7.0250
7.0190
7.0074
7.0001
6.9957
6.9919
5.7225

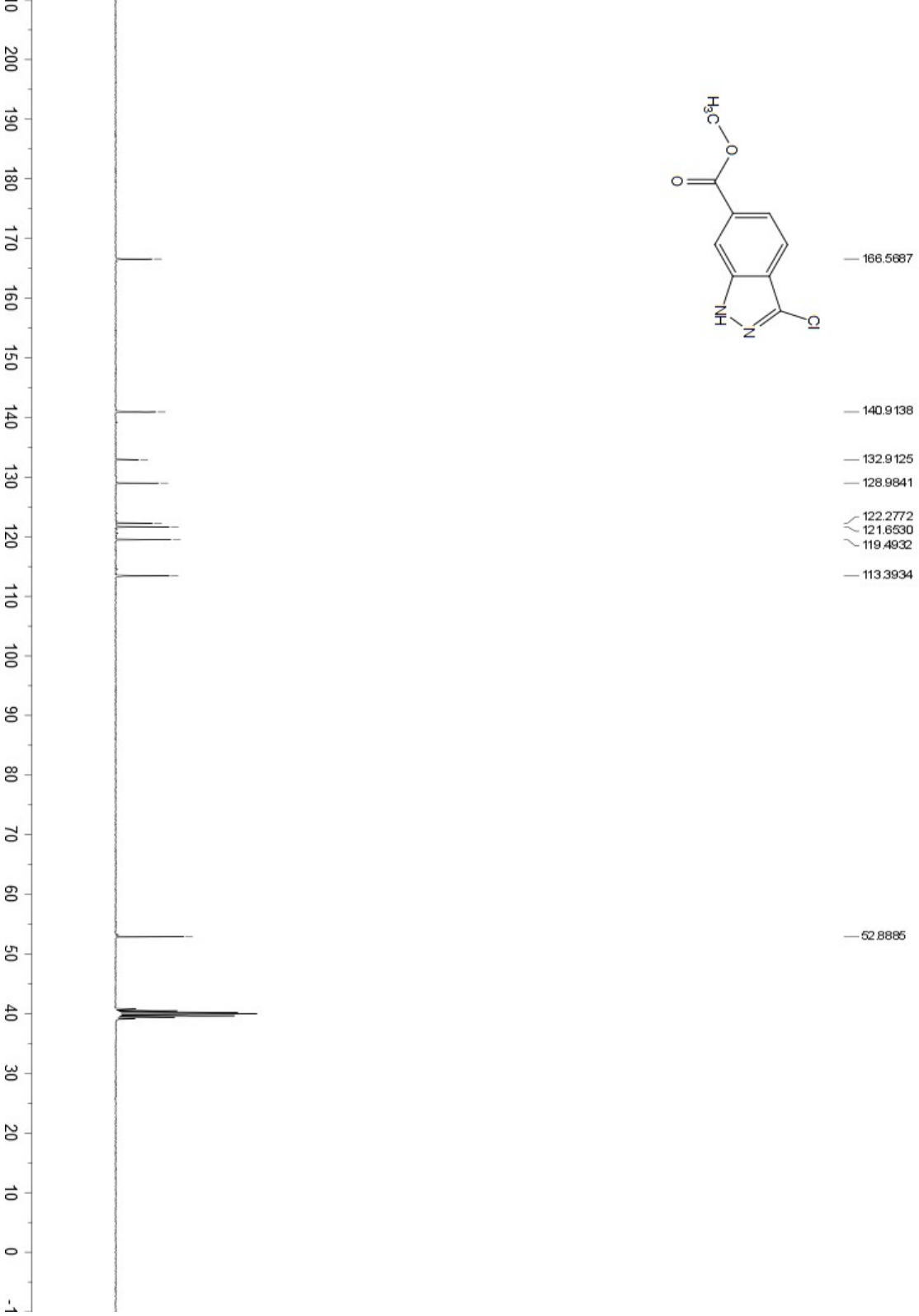
^{1}H NMR of 2q


2.00
1.96
0.92
1.92
1.01
8.4542
8.4381
7.6174
7.6103
7.5951
7.5878
7.4687
7.4593
7.3288
7.3217
7.3064
7.2993
6.7849
6.7690
6.7528
5.3211 DCM
N
N
HN
Cl

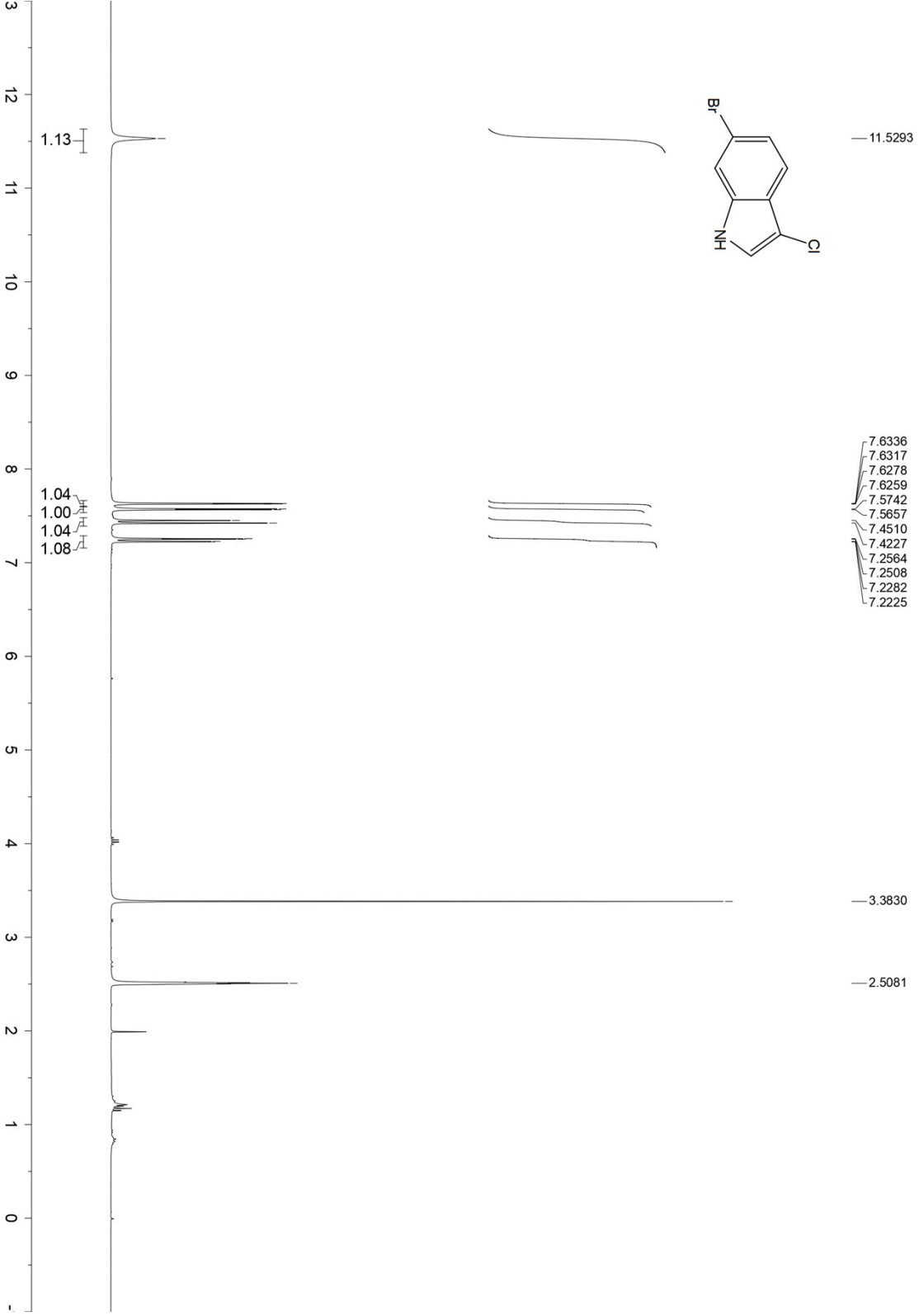
^{1}H NMR of 2r


1.00
1.00
2.09
3.13
13.6791
8.1273
8.1237
8.1199
7.7244
7.7210
7.7170
3.8913
2.5096 DMSO
H3C
O
O
NH
N
Cl

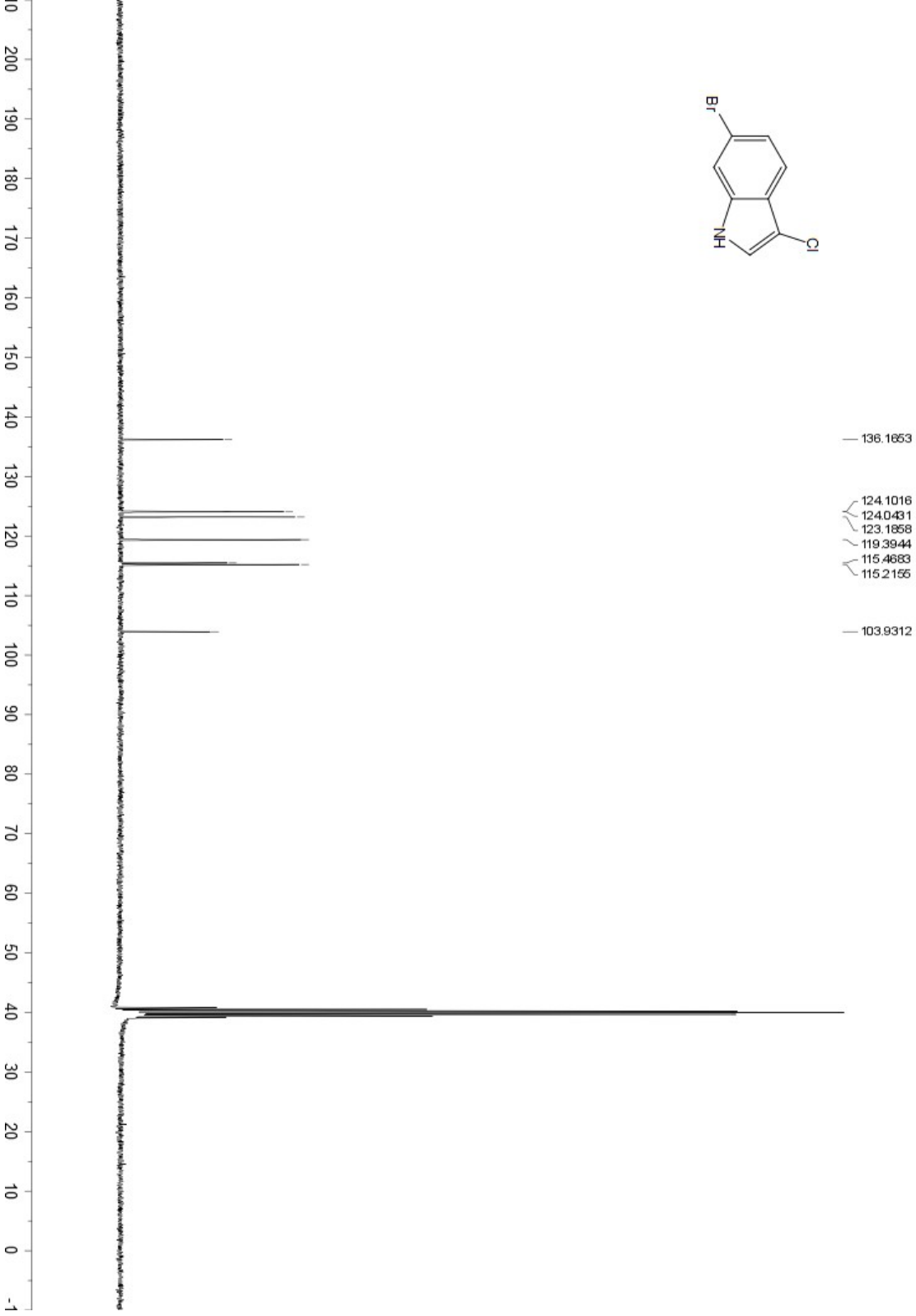
^{13}C NMR of 2r


166.5687
140.9138
132.9125
128.9841
122.2772
121.6530
119.4932
113.3934
52.8885

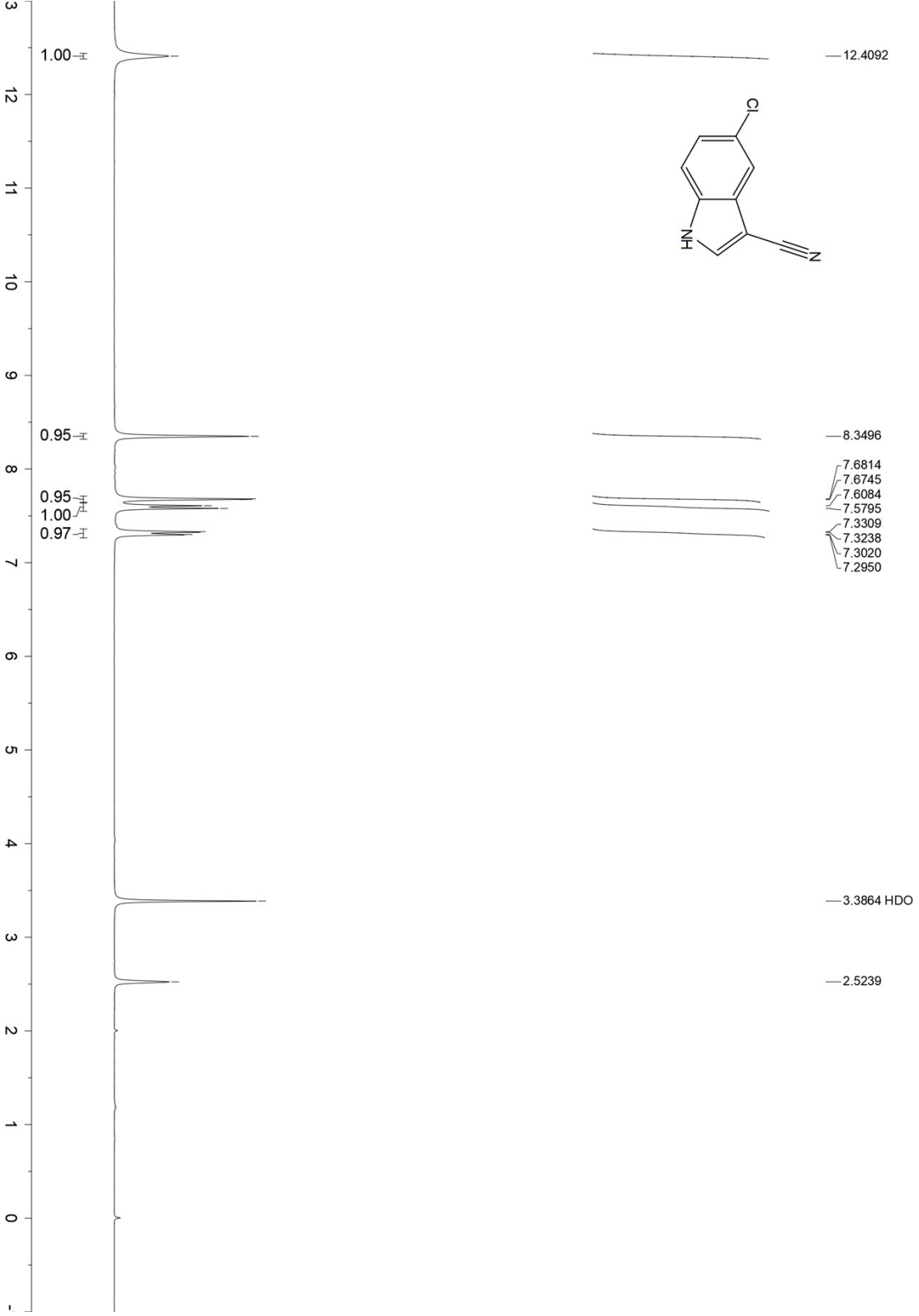
^{1}H NMR of 2s


1.13
1.04
1.00
1.04
1.08
11.5293
7.6336
7.6317
7.6278
7.6259
7.5742
7.5657
7.4510
7.4227
7.2564
7.2508
7.2282
7.2225
3.3830
2.5081
Br
NH
Cl

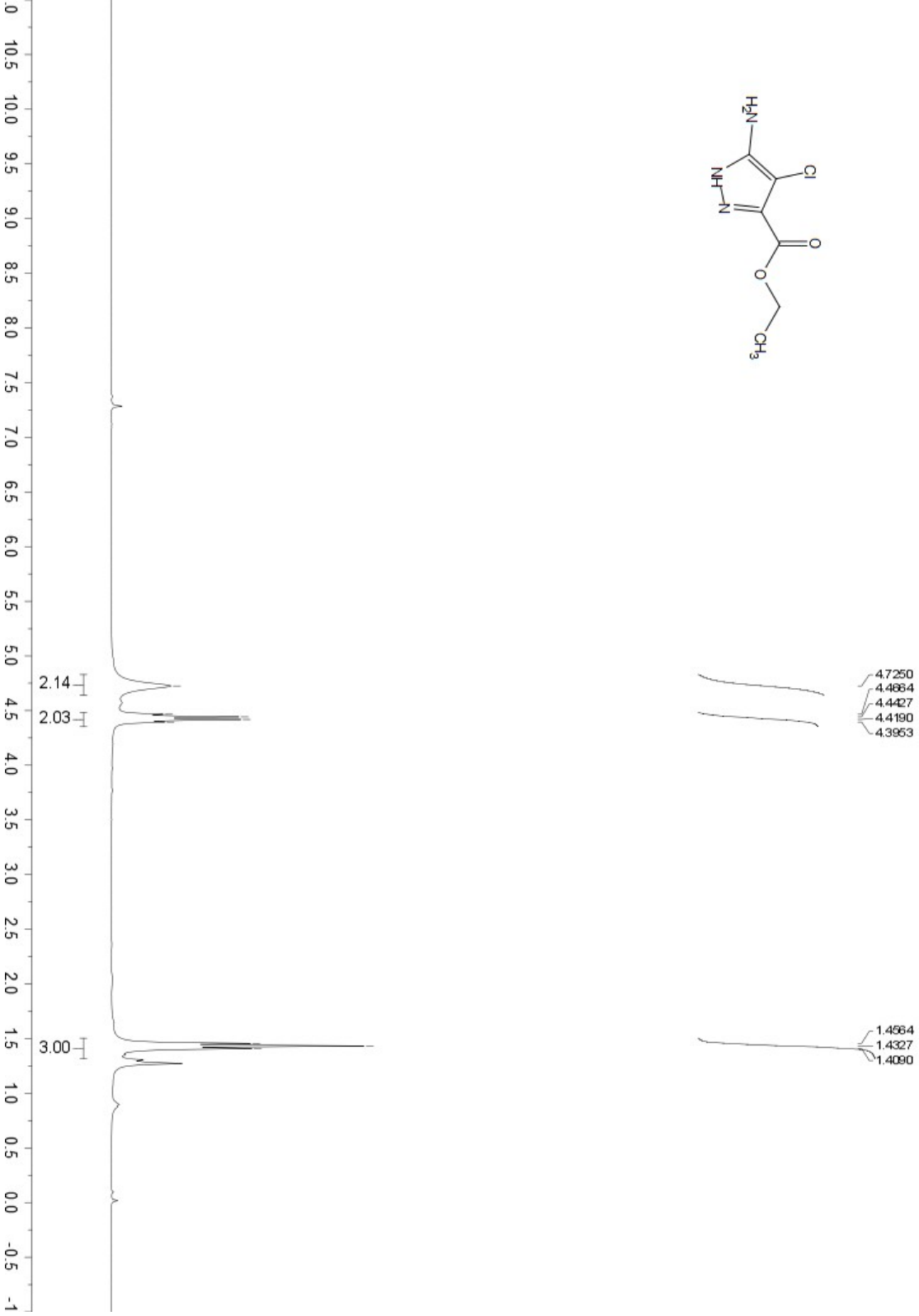
^{13}C NMR of 2s


Br
NH
Cl
136.1653
124.1016
124.0431
123.1858
119.3944
115.4683
115.2155
103.9312

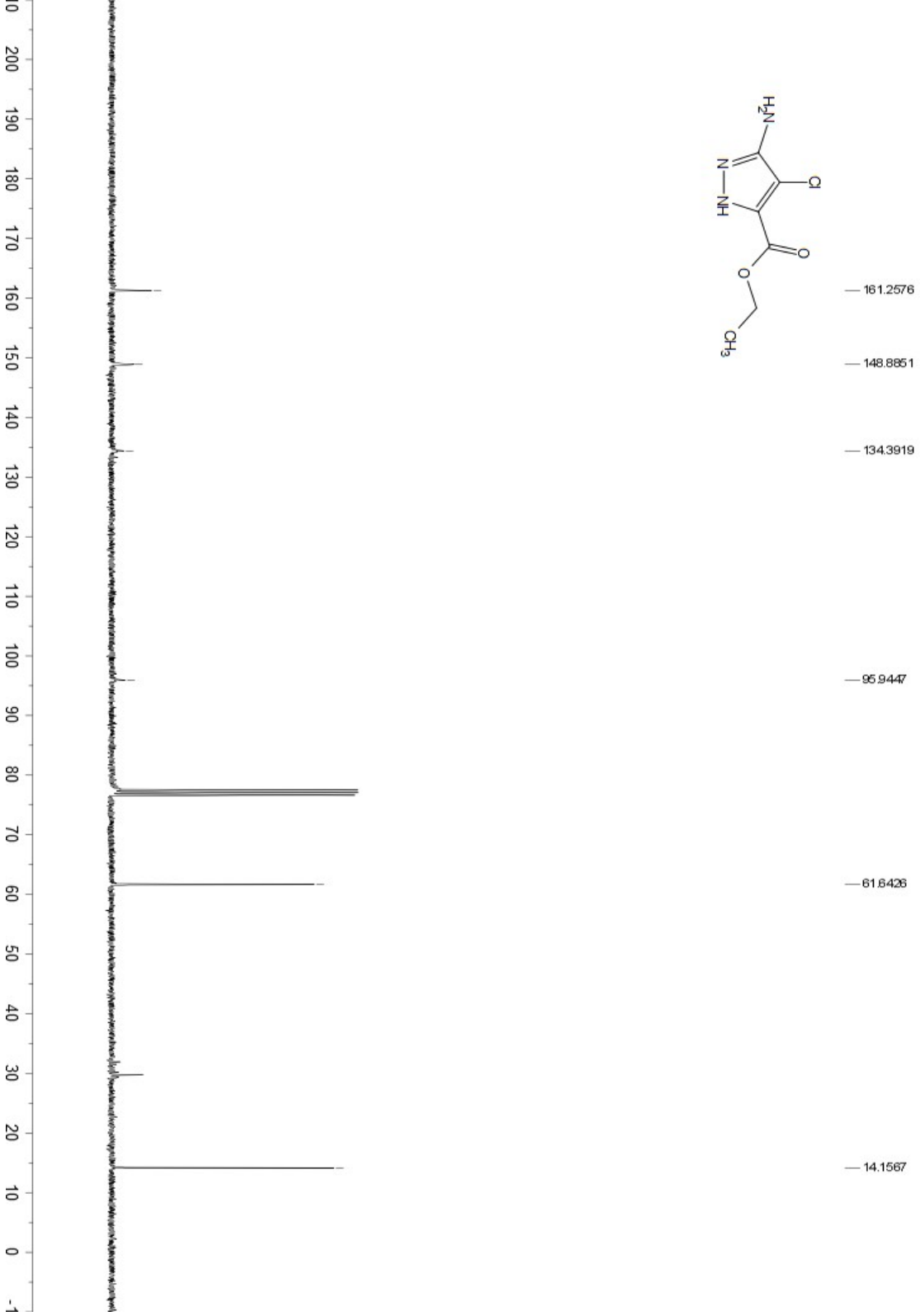
^{1}H NMR of 2u


1.00
0.95
0.95
1.00
0.97
12.4092
8.3496
7.6814
7.6745
7.6084
7.5795
7.3309
7.3238
7.3020
7.2950
3.3864 HDO
2.5239
Cl
NH
N

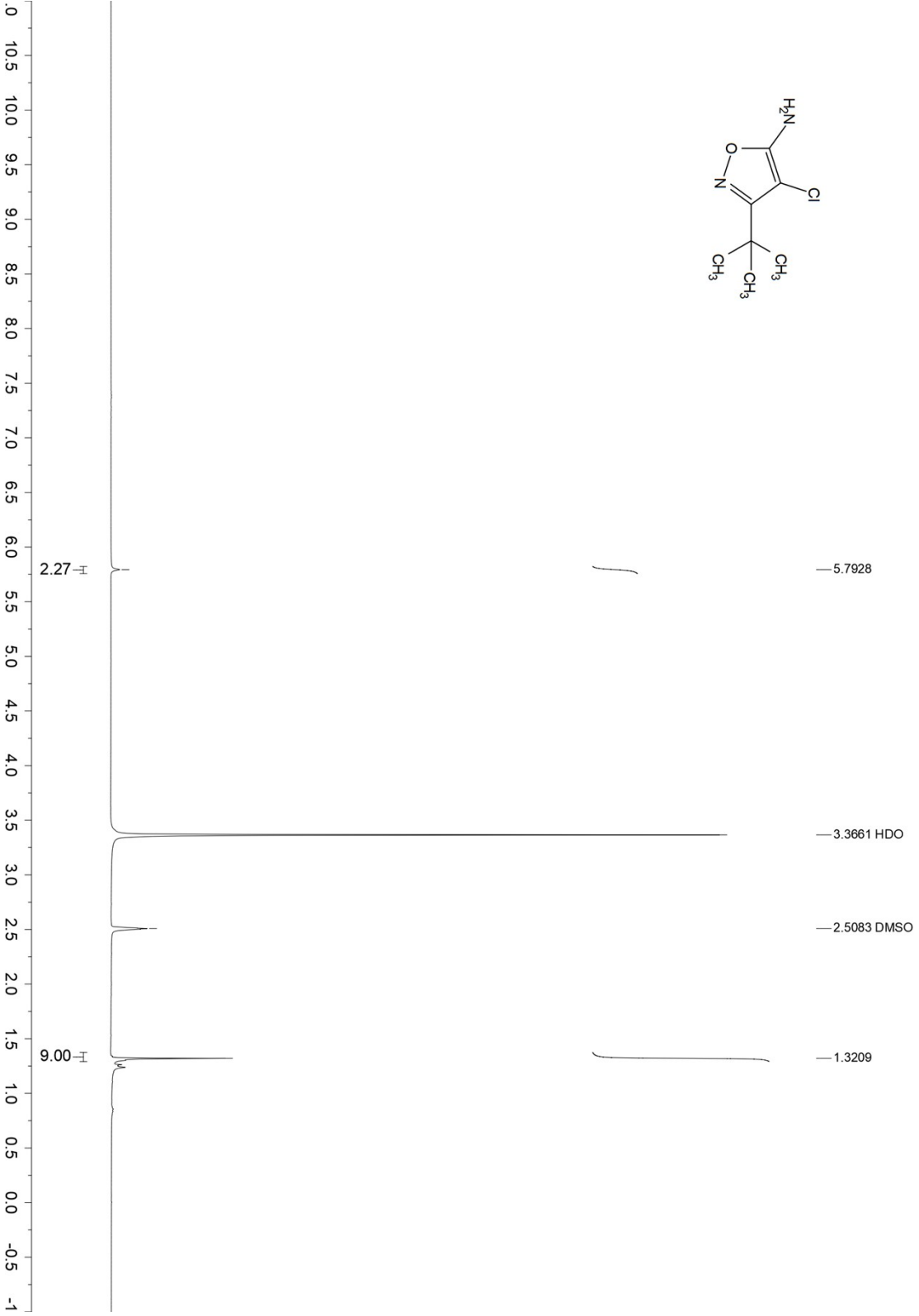
^{1}H NMR of 2v



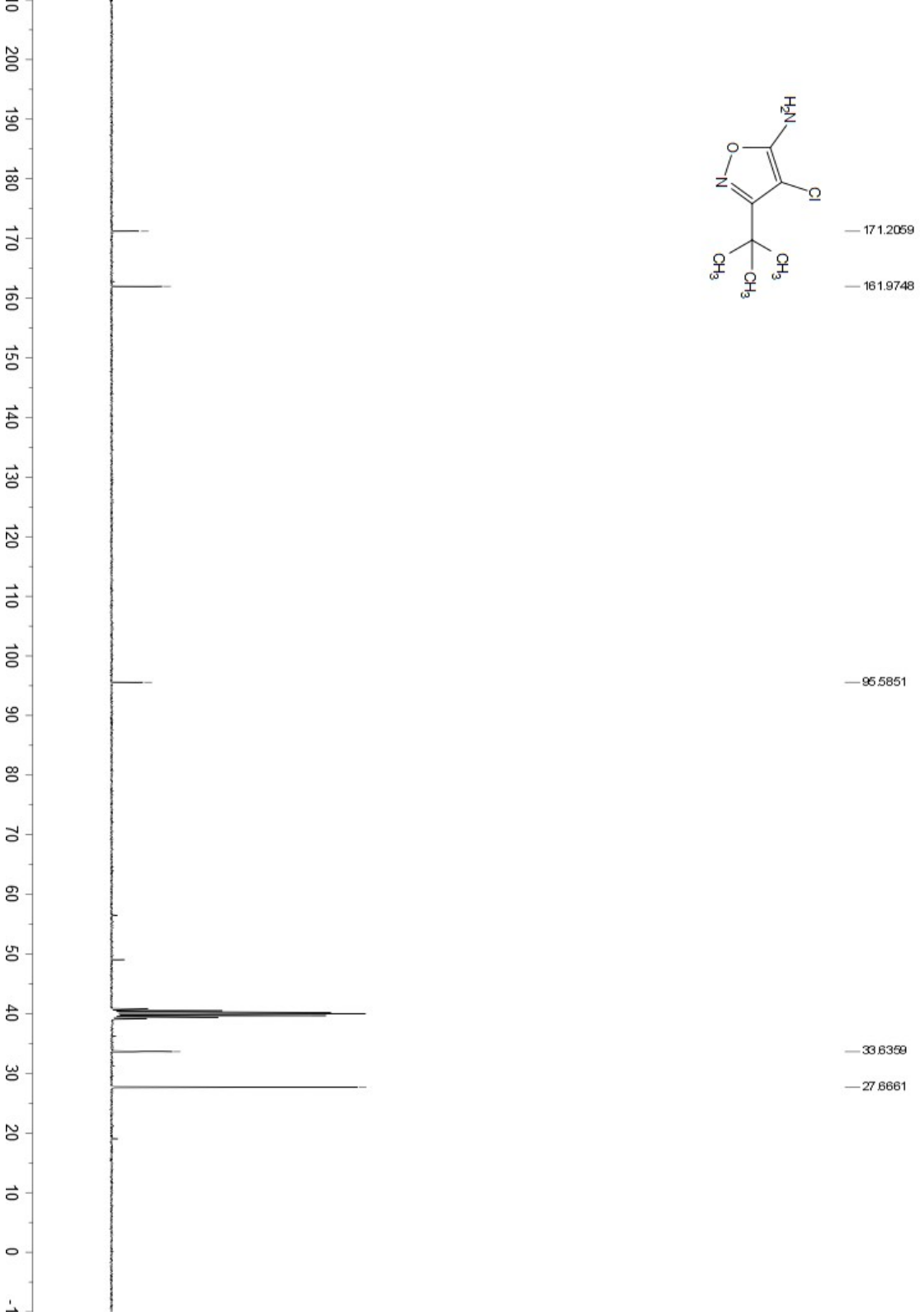
^{13}C NMR of 2v



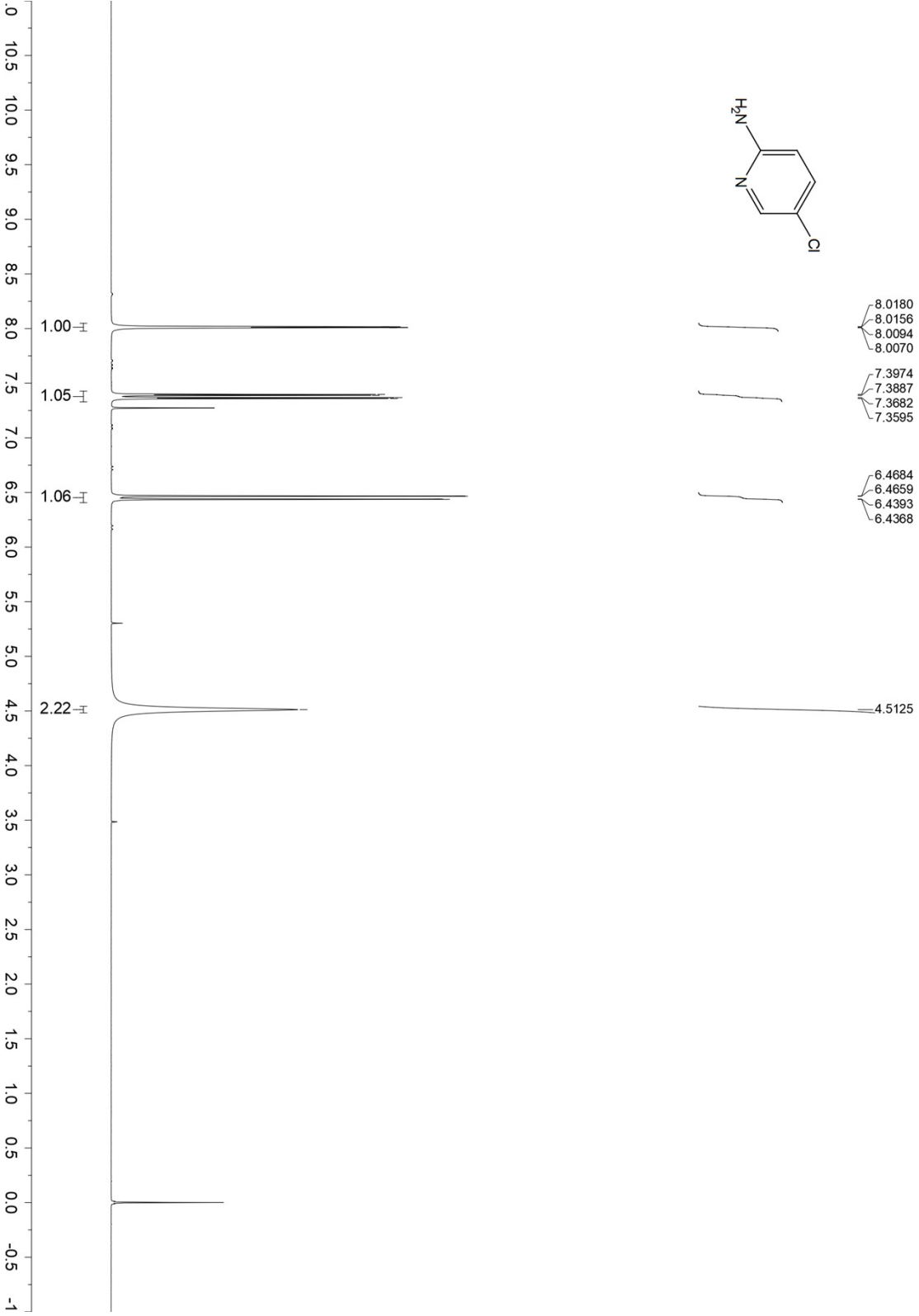
^{1}H NMR of 2w



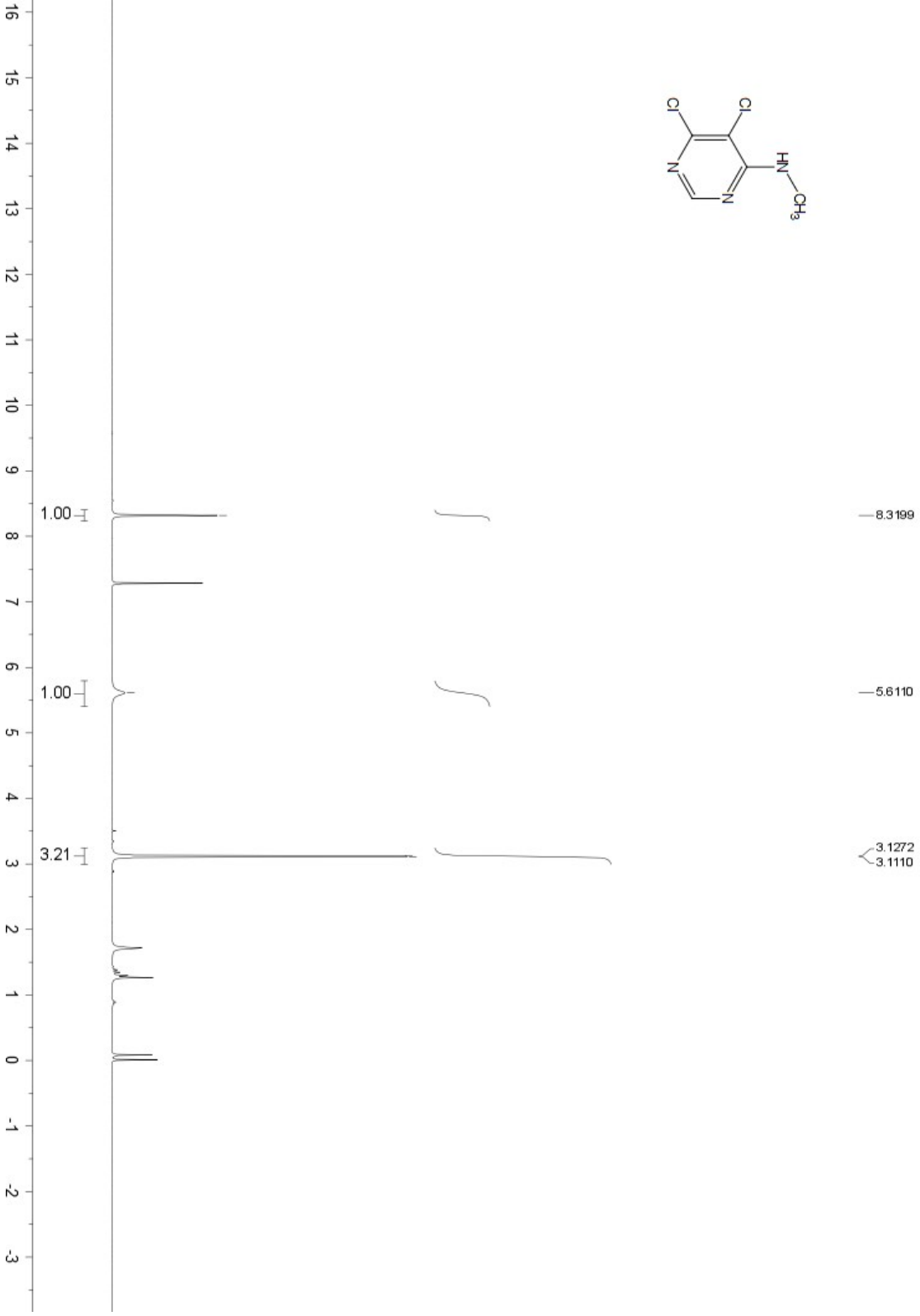
^{13}C NMR of 2w



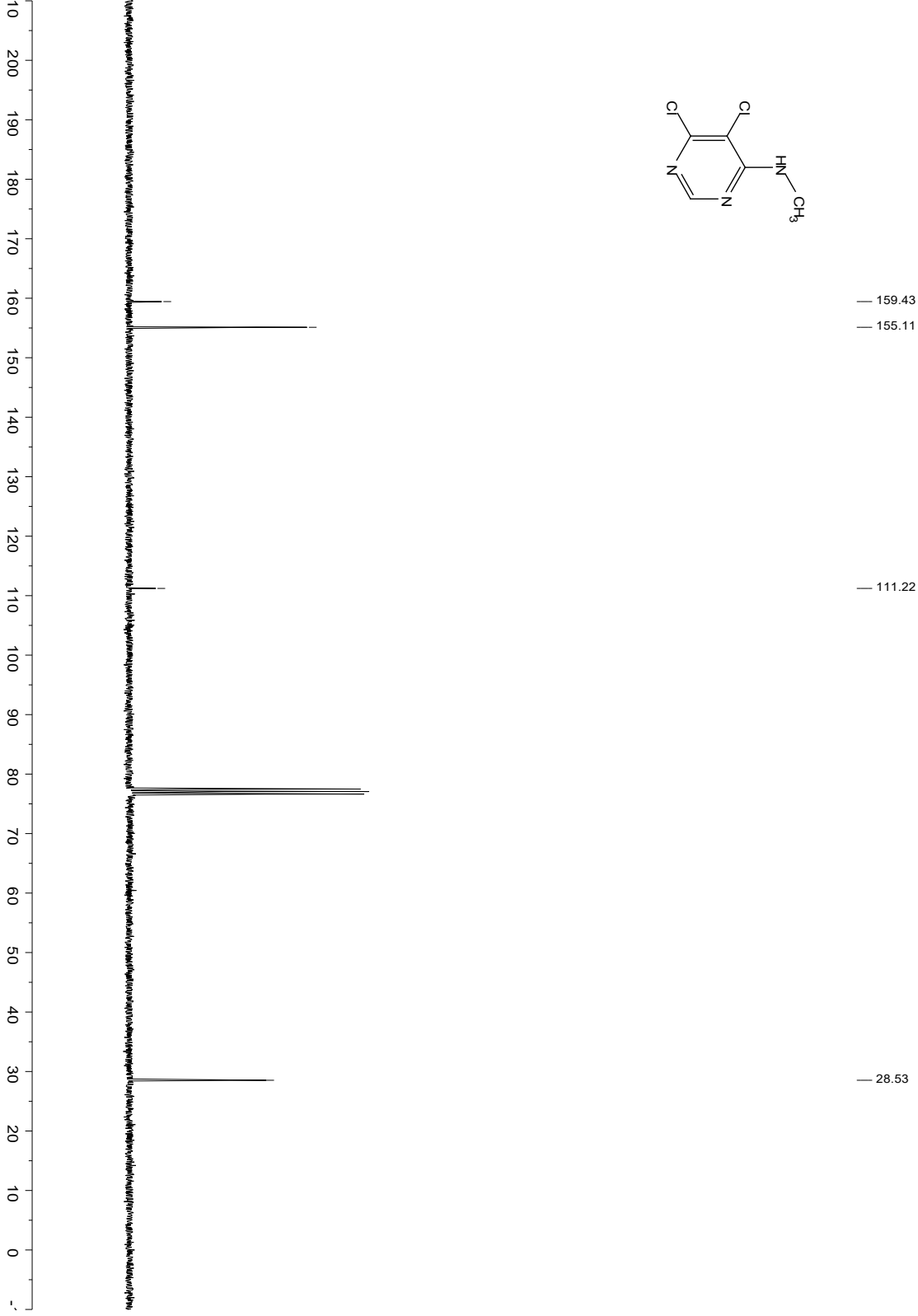
^{1}H NMR of 2x


H2N
N
Cl
8.0180
8.0156
8.0094
8.0070
7.3974
7.3887
7.3682
7.3595
6.4684
6.4659
6.4393
6.4368
4.5125
1.00
1.05
1.06
2.22

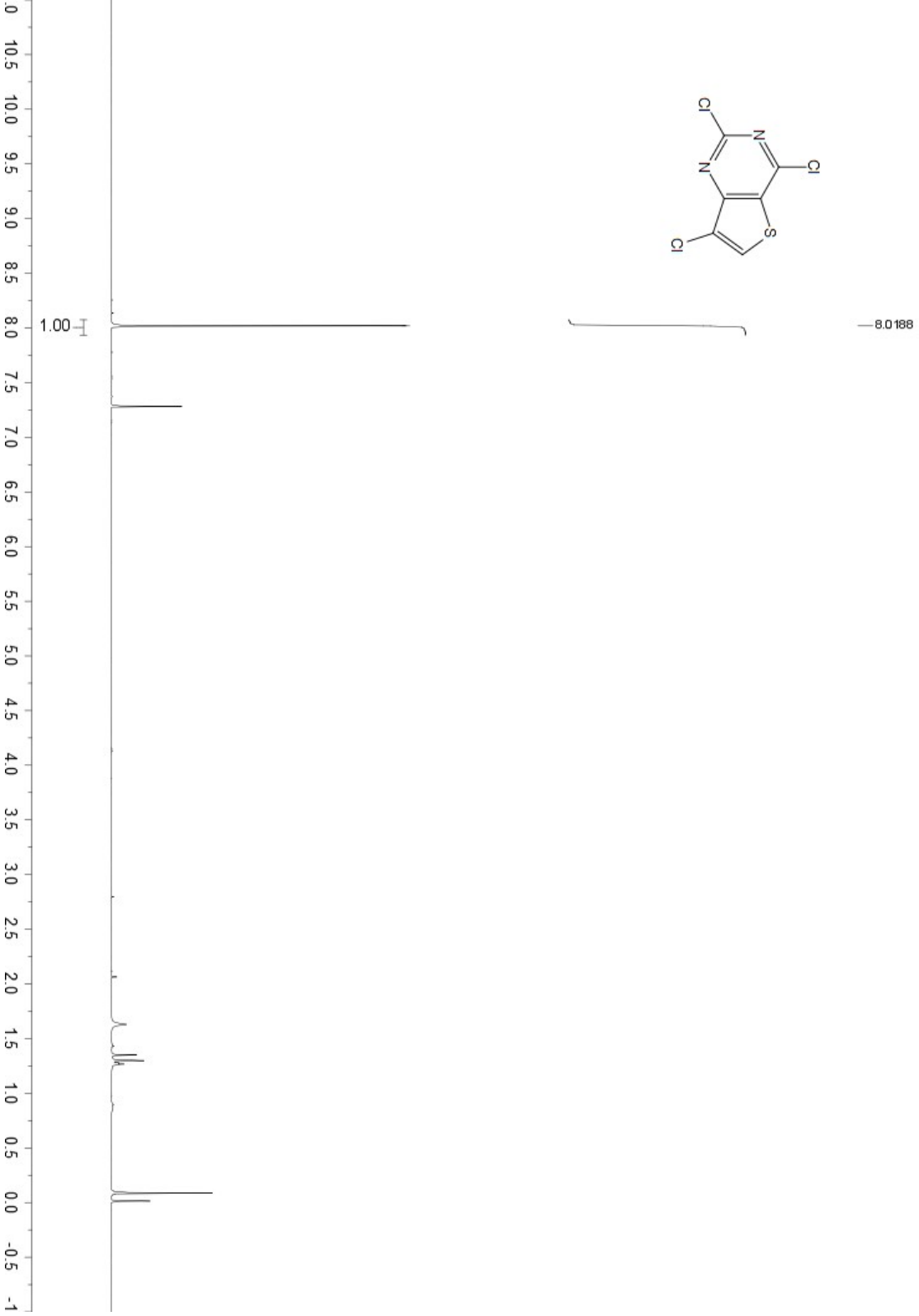
^{1}H NMR of 2y



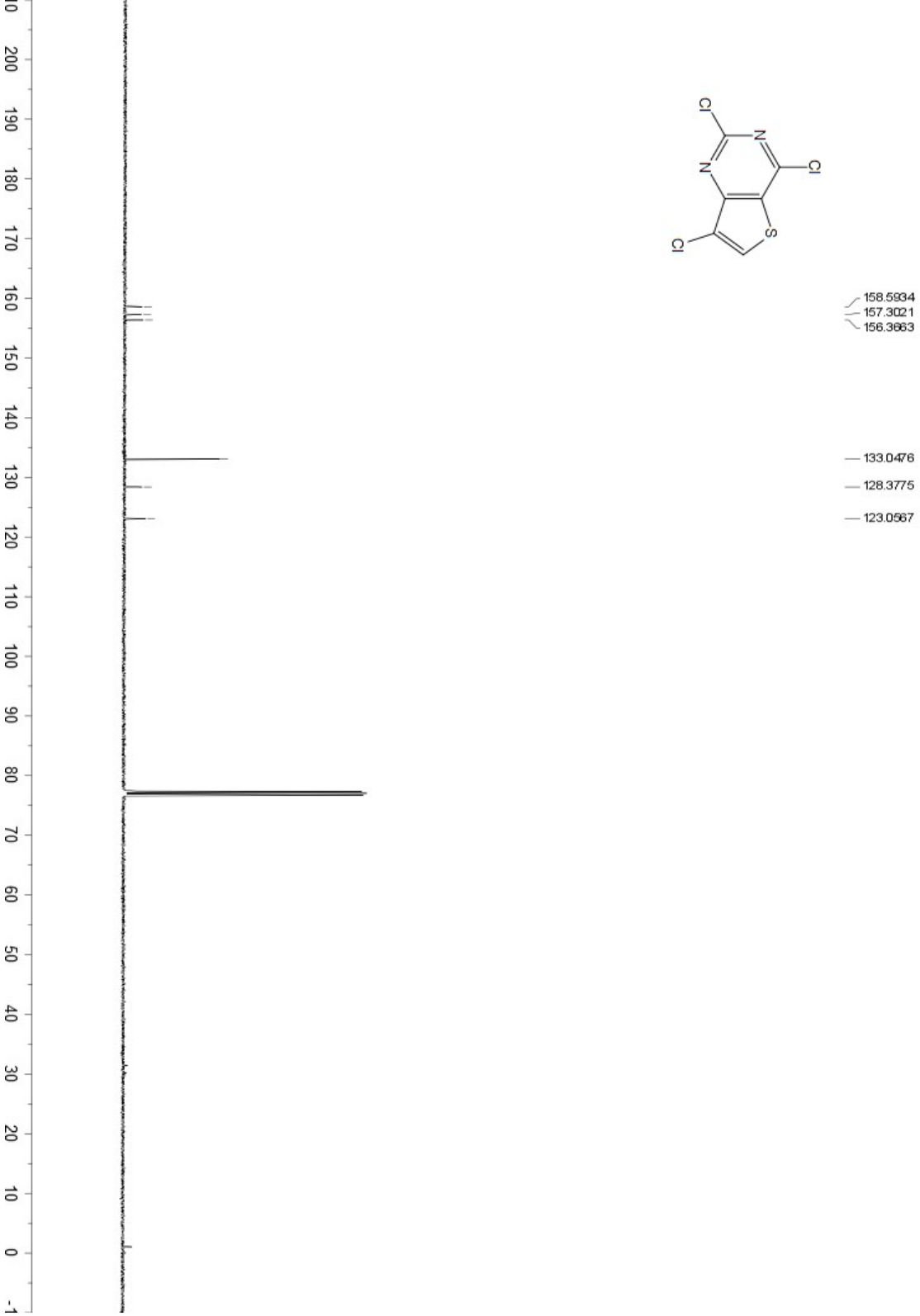
^{13}C NMR of 2y



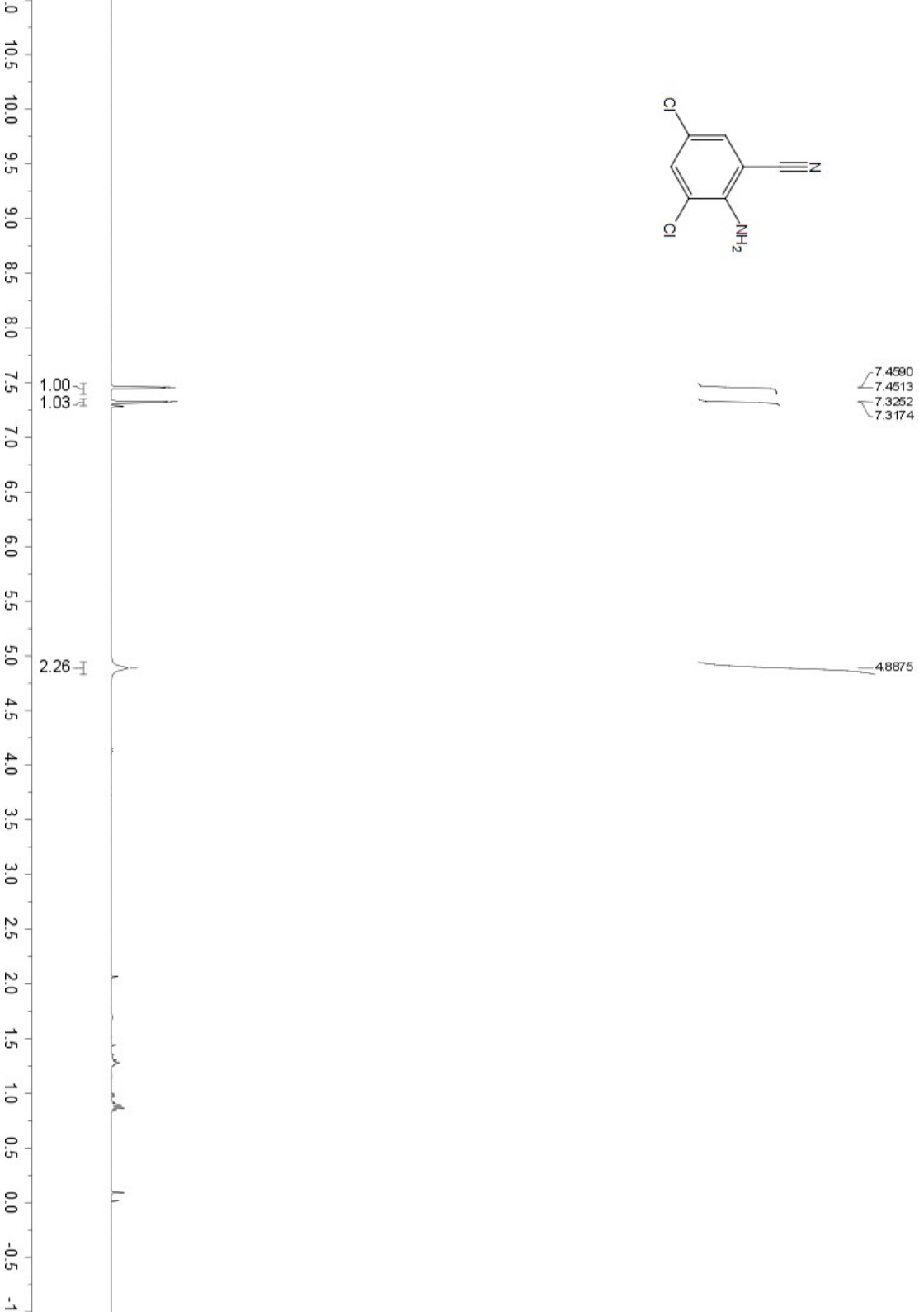
^{1}H NMR of 2z



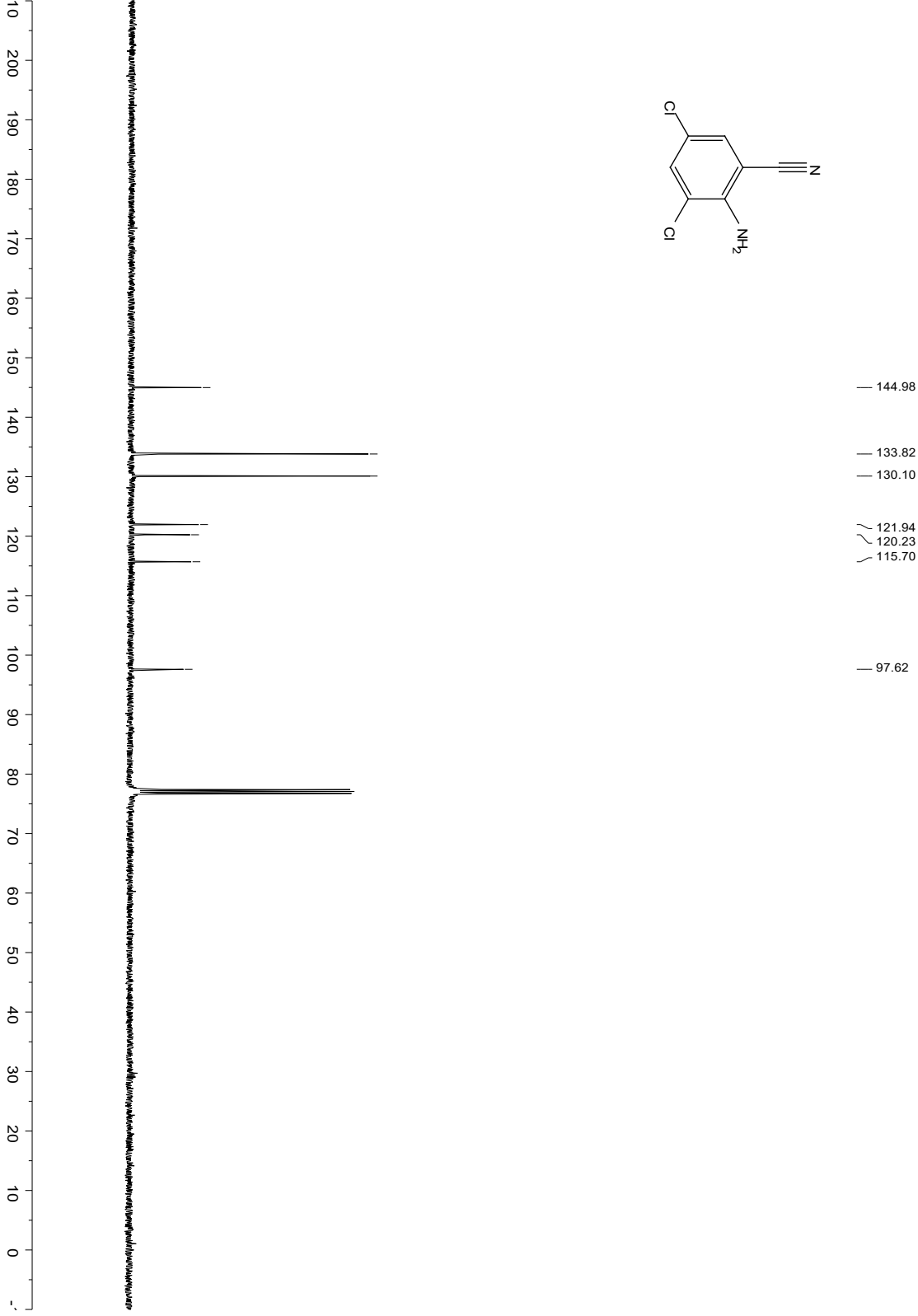
^{13}C NMR of 2z



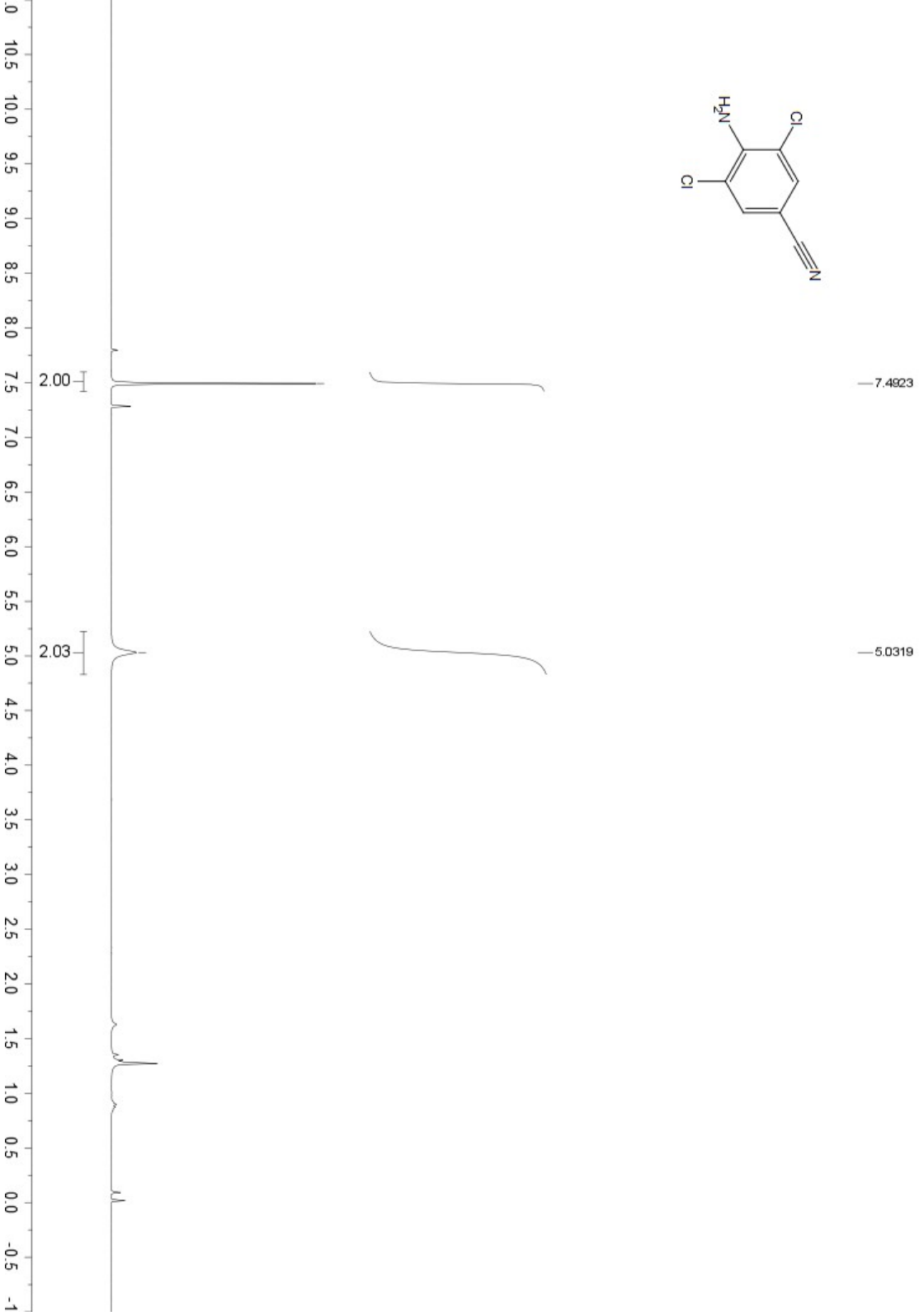
^{1}H NMR of 3a



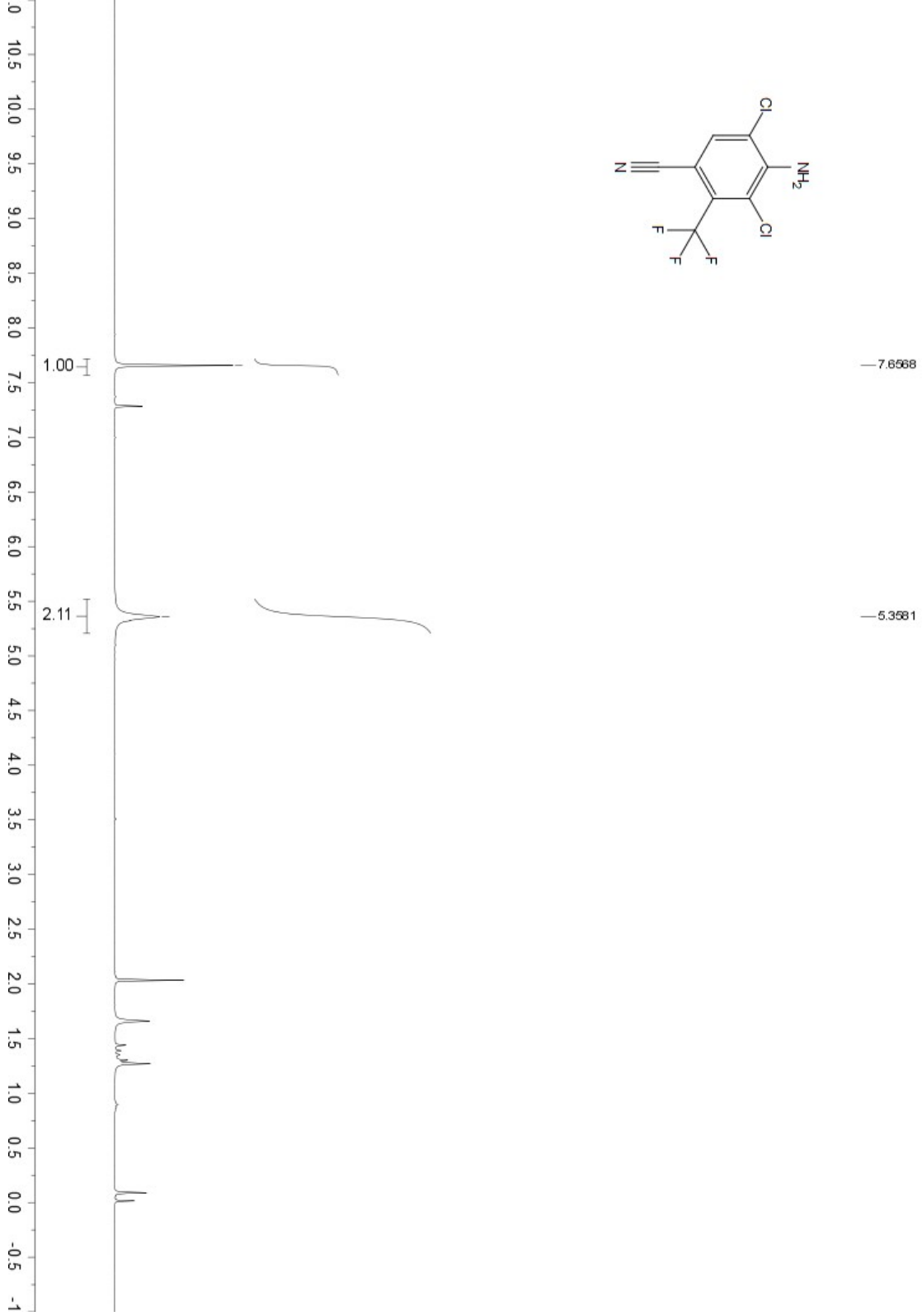
^{13}C NMR of 3a



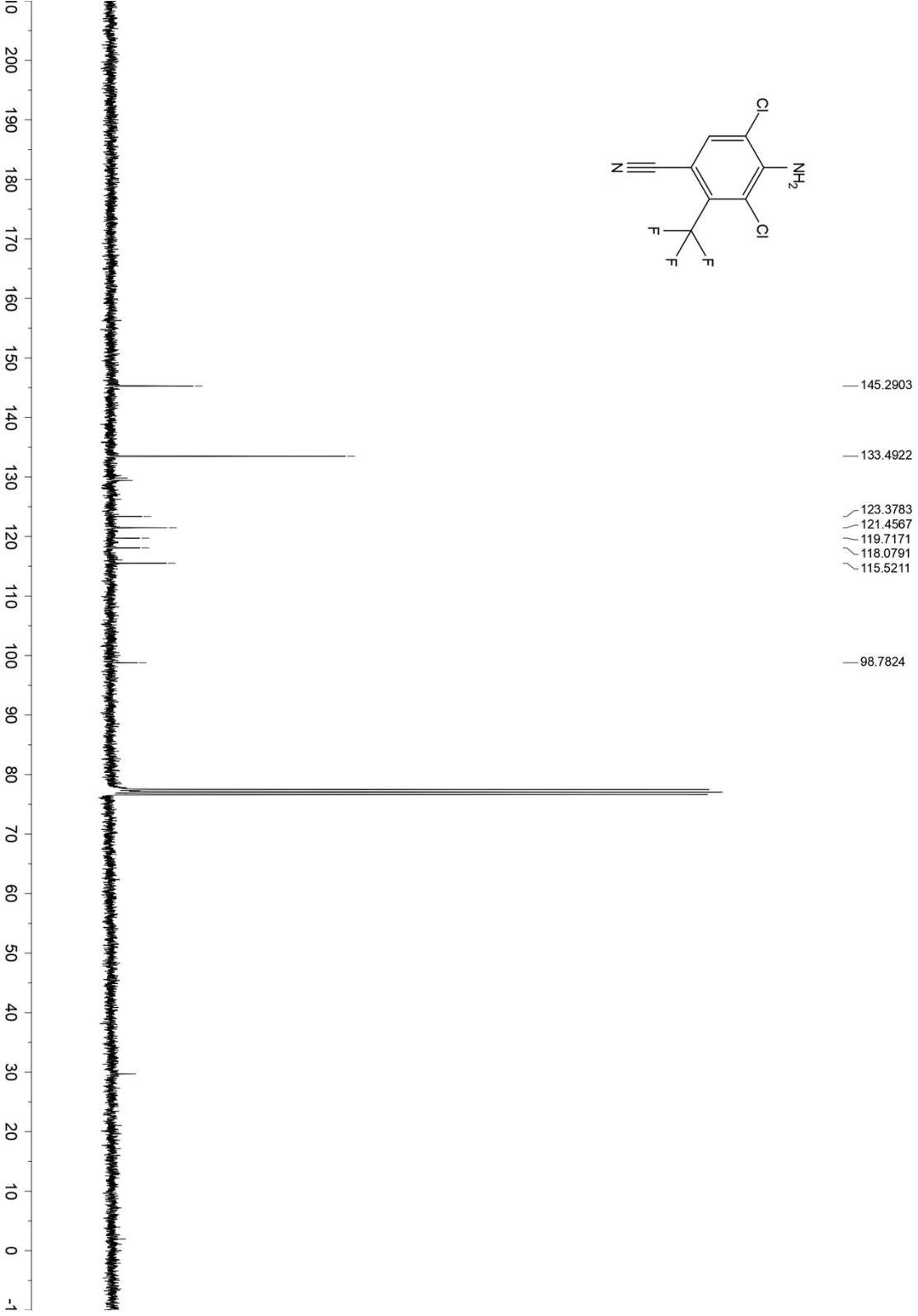
^{1}H NMR of 3b



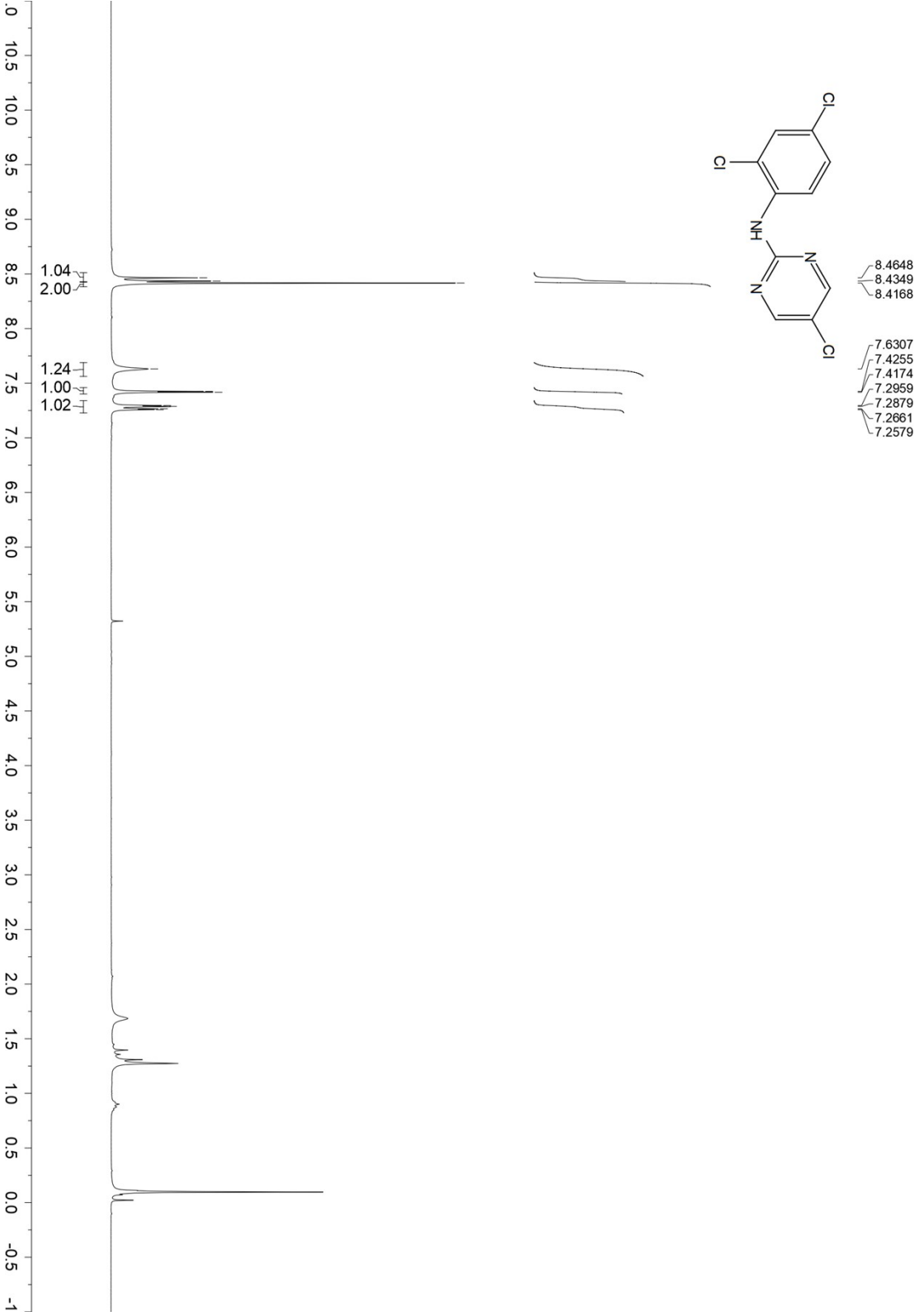
^{1}H NMR of 3c



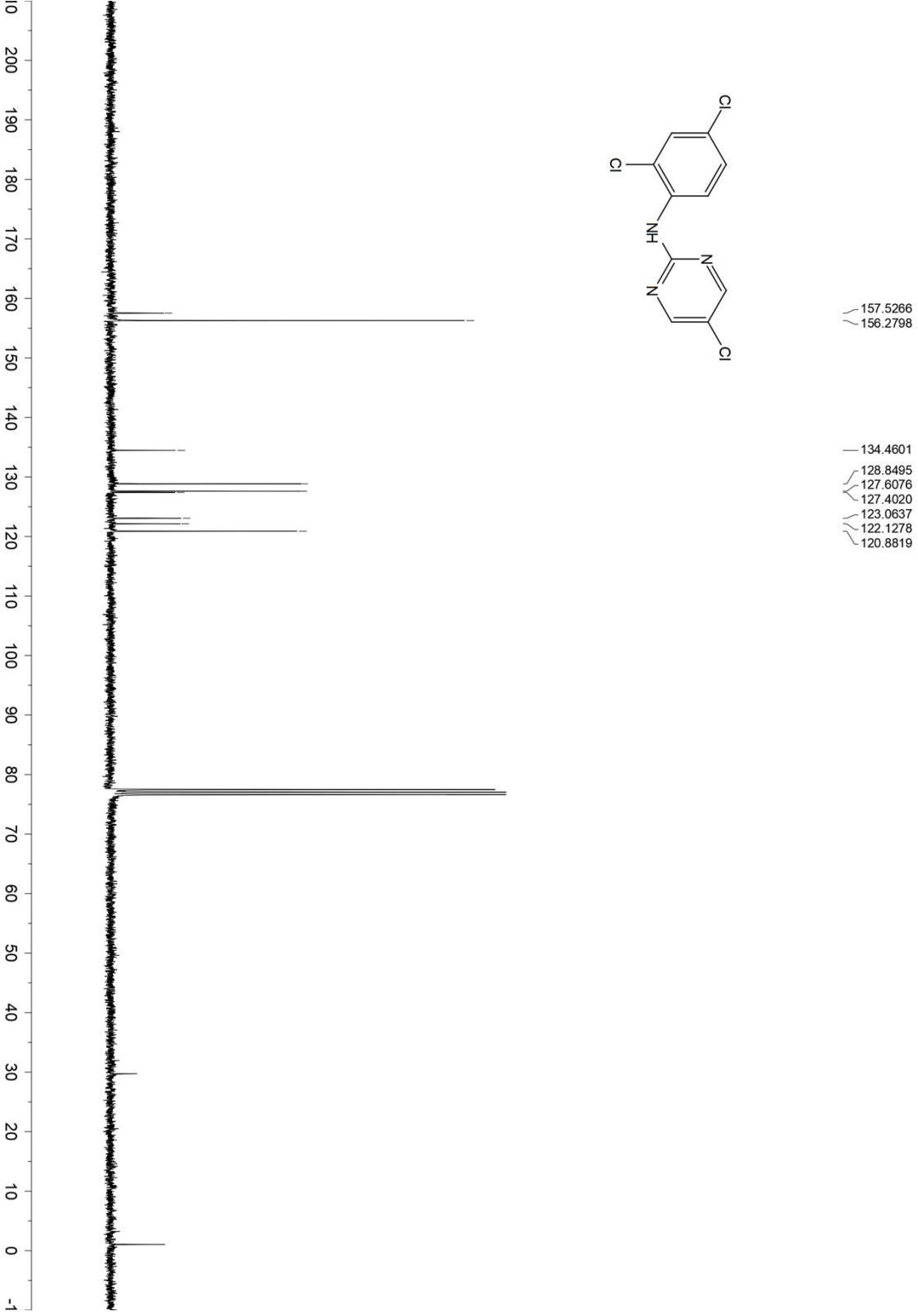
^{13}C NMR of 3c


145.2903
133.4922
123.3783
121.4567
119.7171
118.0791
115.5211
98.7824

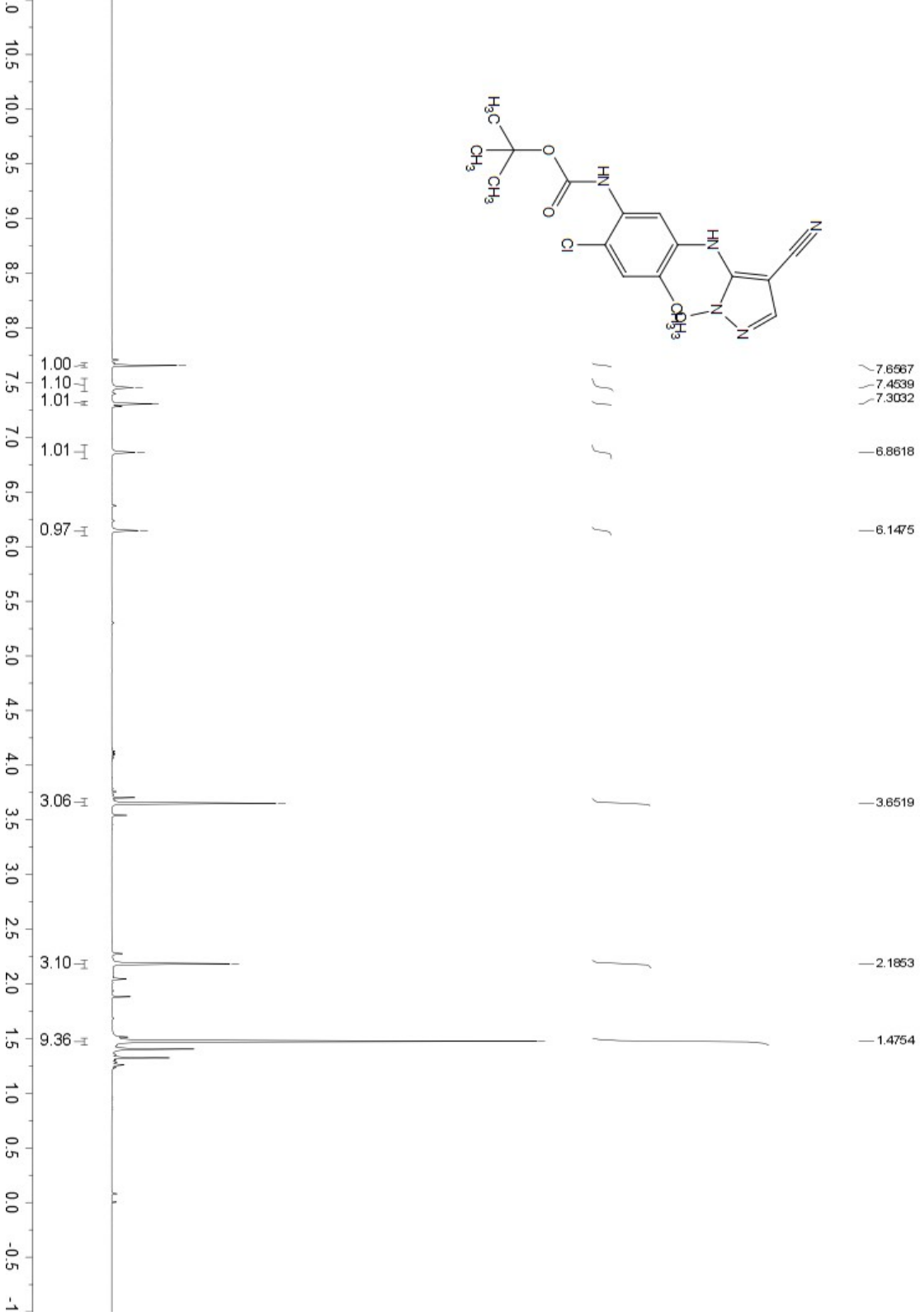
^{1}H NMR of 3q


Cl
Cl
HN
N
N
Cl
8.4648
8.4349
8.4168
7.6307
7.4255
7.4174
7.2959
7.2879
7.2661
7.2579
1.04
2.00
1.24
1.00
1.02

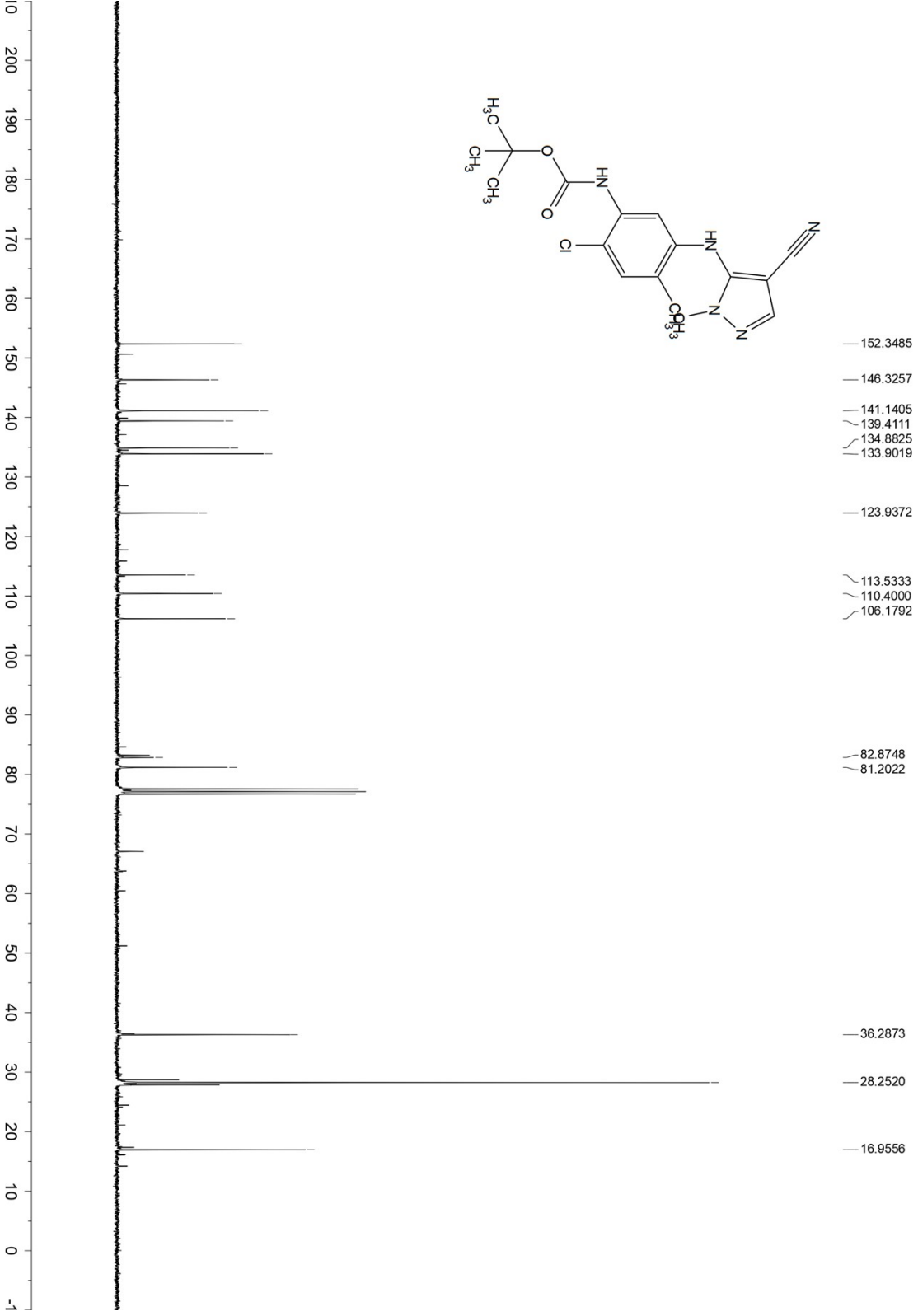
^{13}C NMR of 3q


Cl
Cl
NH
N
N
Cl
157.5266
156.2798
134.4601
128.8495
127.6076
127.4020
123.0637
122.1278
120.8819

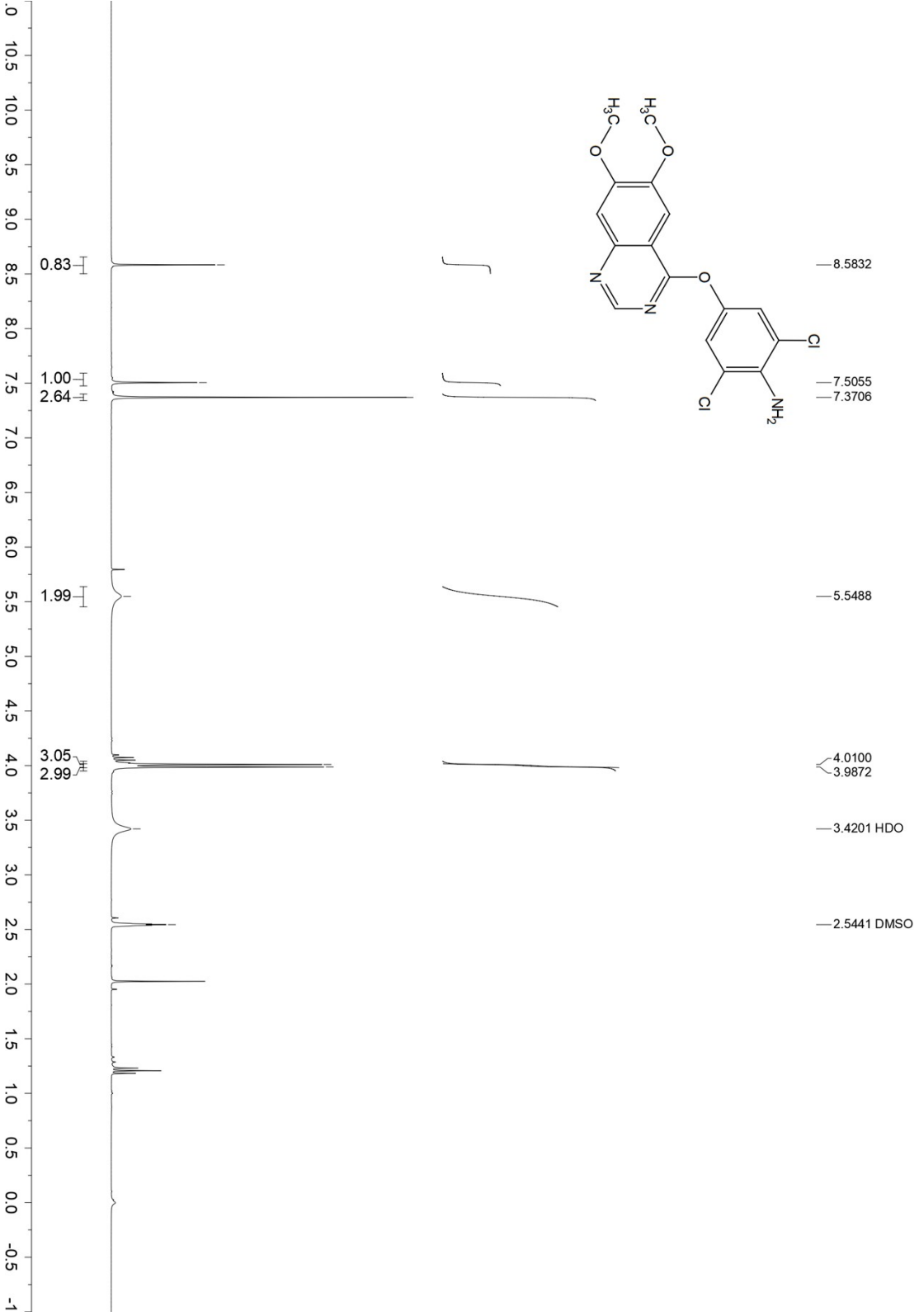
^{1}H NMR of 4a


1.00
1.10
1.01
1.01
0.97
3.06
3.10
9.36
7.8567
7.4539
7.3032
6.8618
6.1475
3.6519
2.1853
1.4754

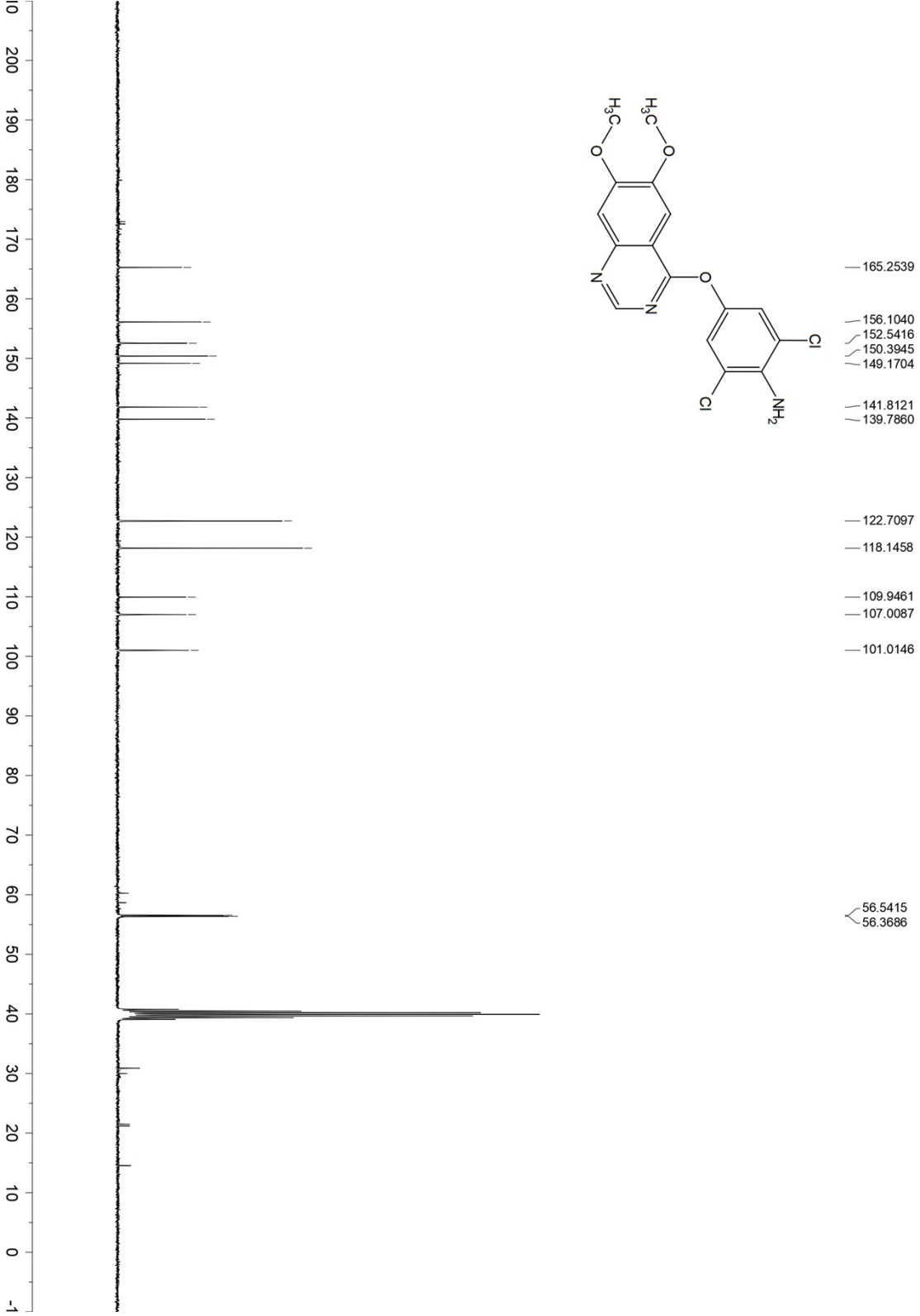
^{13}C NMR of 4a


H3C
CH3
CH3
O
O
HN
Cl
HN
N
N
N
CH3
152.3485
146.3257
141.1405
139.4111
134.8825
133.9019
123.9372
113.5333
110.4000
106.1792
82.8748
81.2022
36.2873
28.2520
16.9556

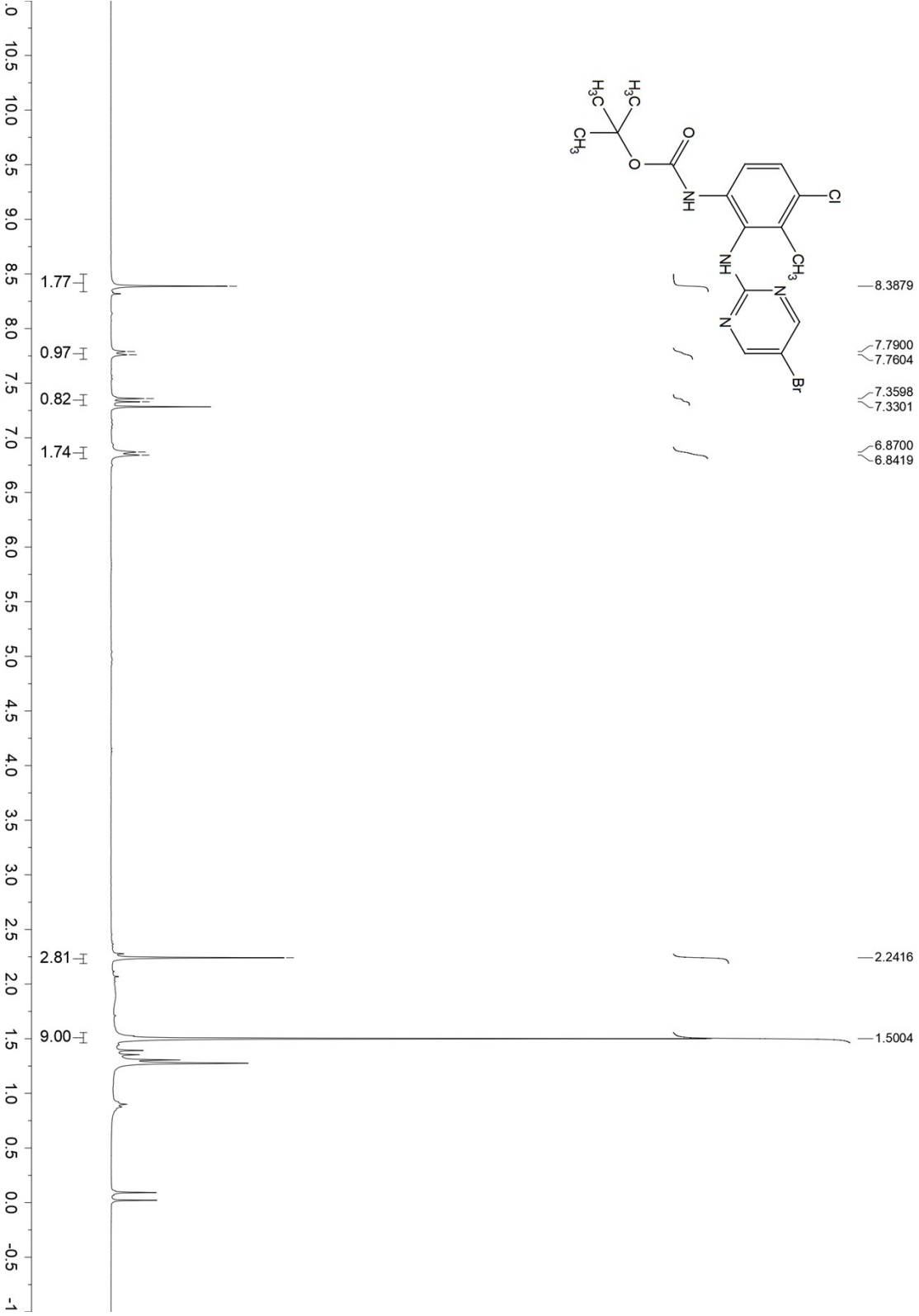
^{1}H NMR of 4b


0.83
1.00
2.64
1.99
3.05
2.99
8.5832
7.5055
7.3706
5.5488
4.0100
3.9872
3.4201 HDO
2.5441 DMSO

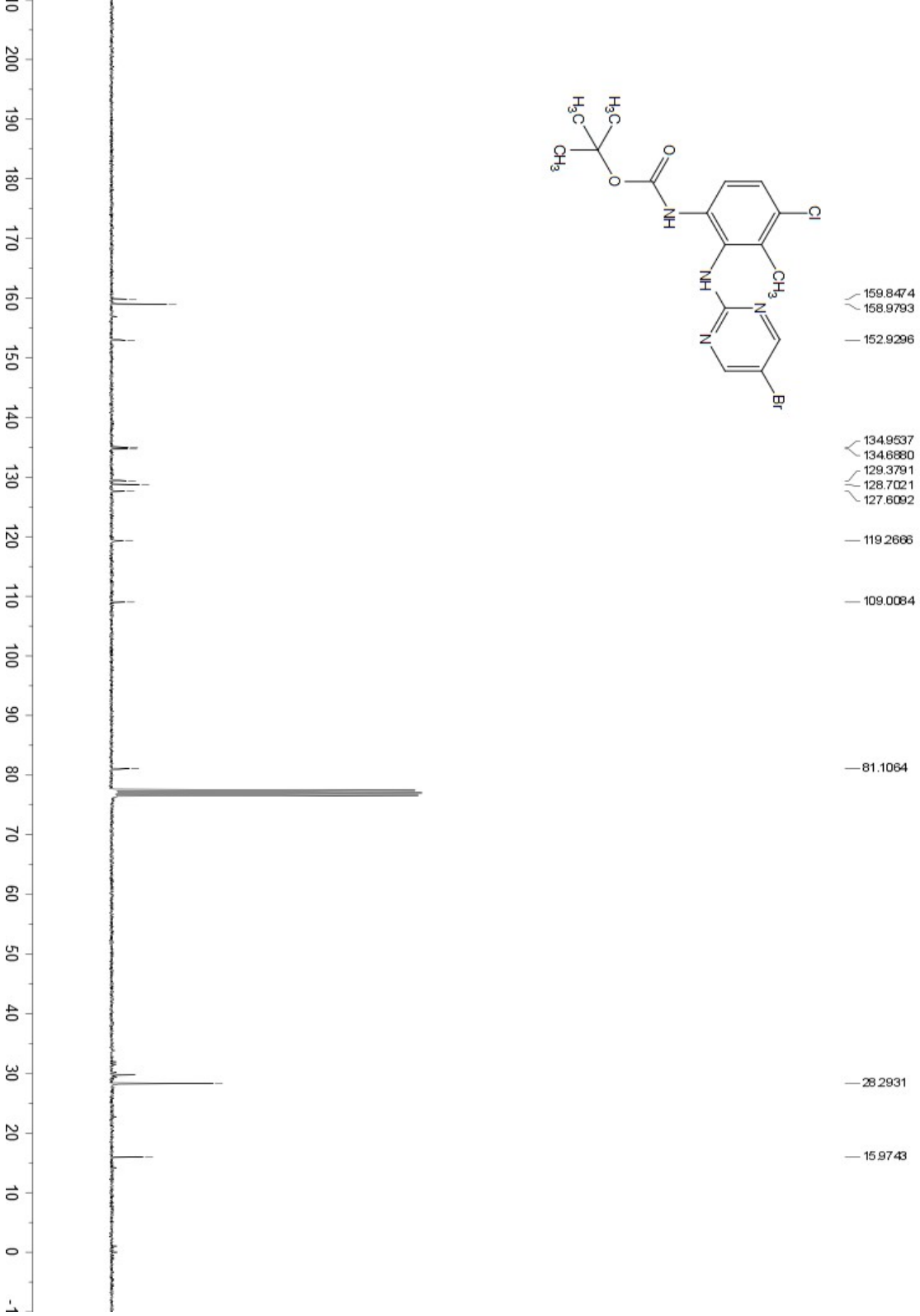
^{13}C NMR of 4b


165.2539
156.1040
152.5416
150.3945
149.1704
141.8121
139.7860
122.7097
118.1458
109.9461
107.0087
101.0146
56.5415
56.3686

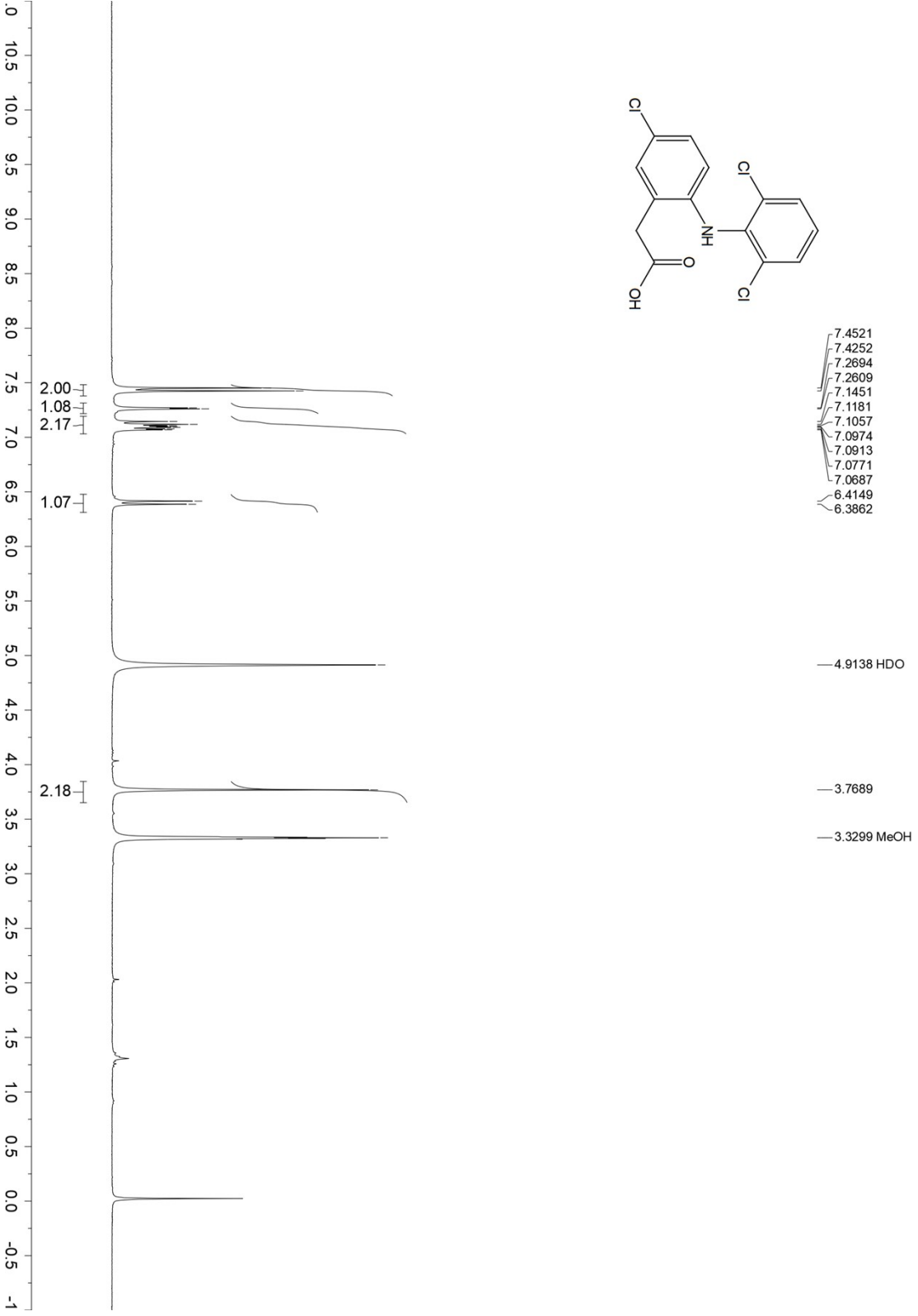
^{1}H NMR of 4c


1.77
0.97
0.82
1.74
2.81
9.00
8.3879
7.7900
7.7604
7.3598
7.3301
6.8700
6.8419
2.2416
1.5004
Cl
Br
NH
N
CH3
O

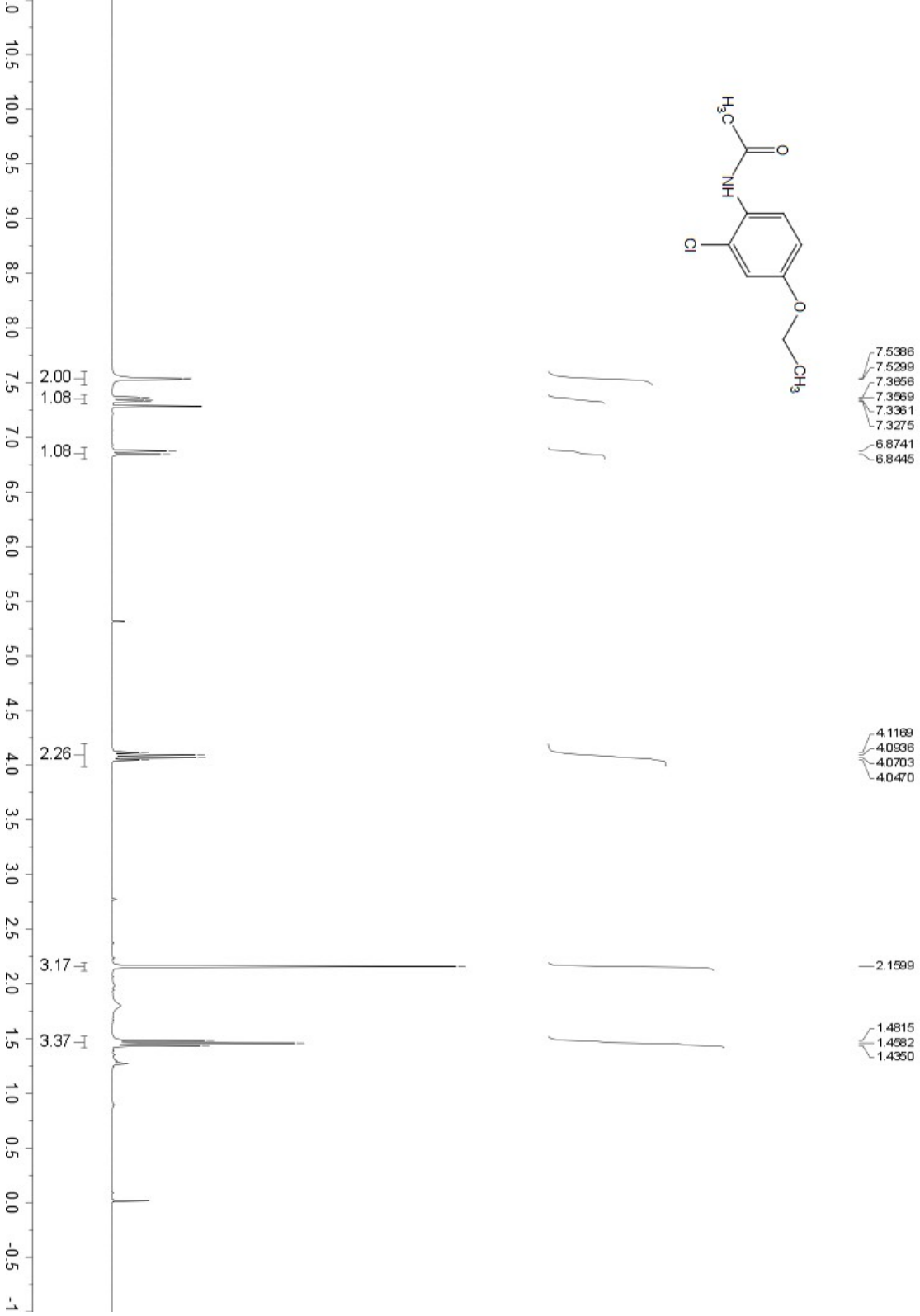
^{13}C NMR of 4c


159.8474
158.9793
152.9296
134.9537
134.6880
129.3791
128.7021
127.6092
119.2666
109.0084
81.1064
28.2931
15.9743

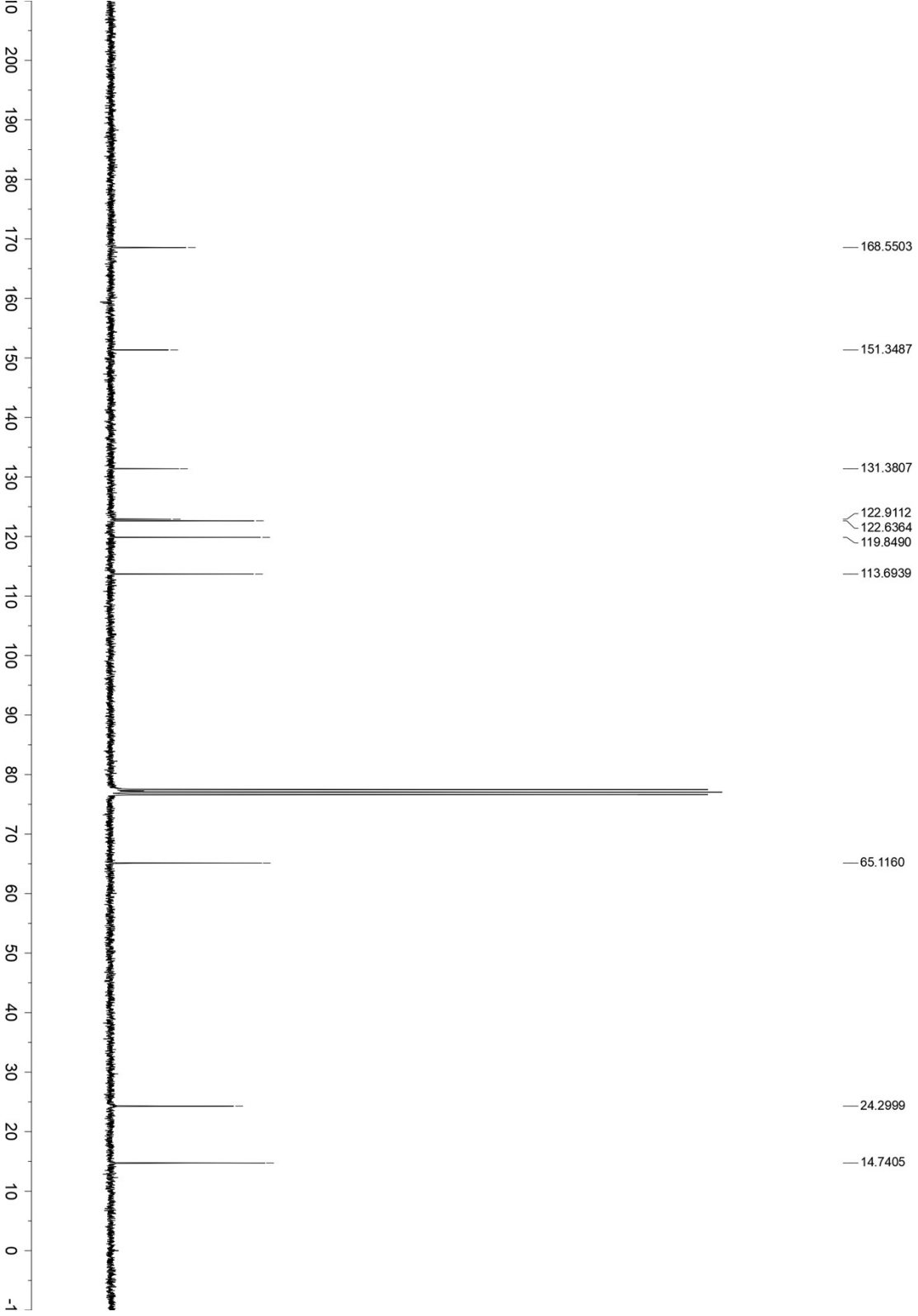
^{1}H NMR of 4d


Cl
Cl
NH
O
OH
Cl
7.4521
7.4252
7.2694
7.2609
7.1451
7.1181
7.1057
7.0974
7.0913
7.0771
7.0687
6.4149
6.3862
4.9138 HDO
3.7689
3.3299 MeOH
2.00
1.08
2.17
1.07
2.18

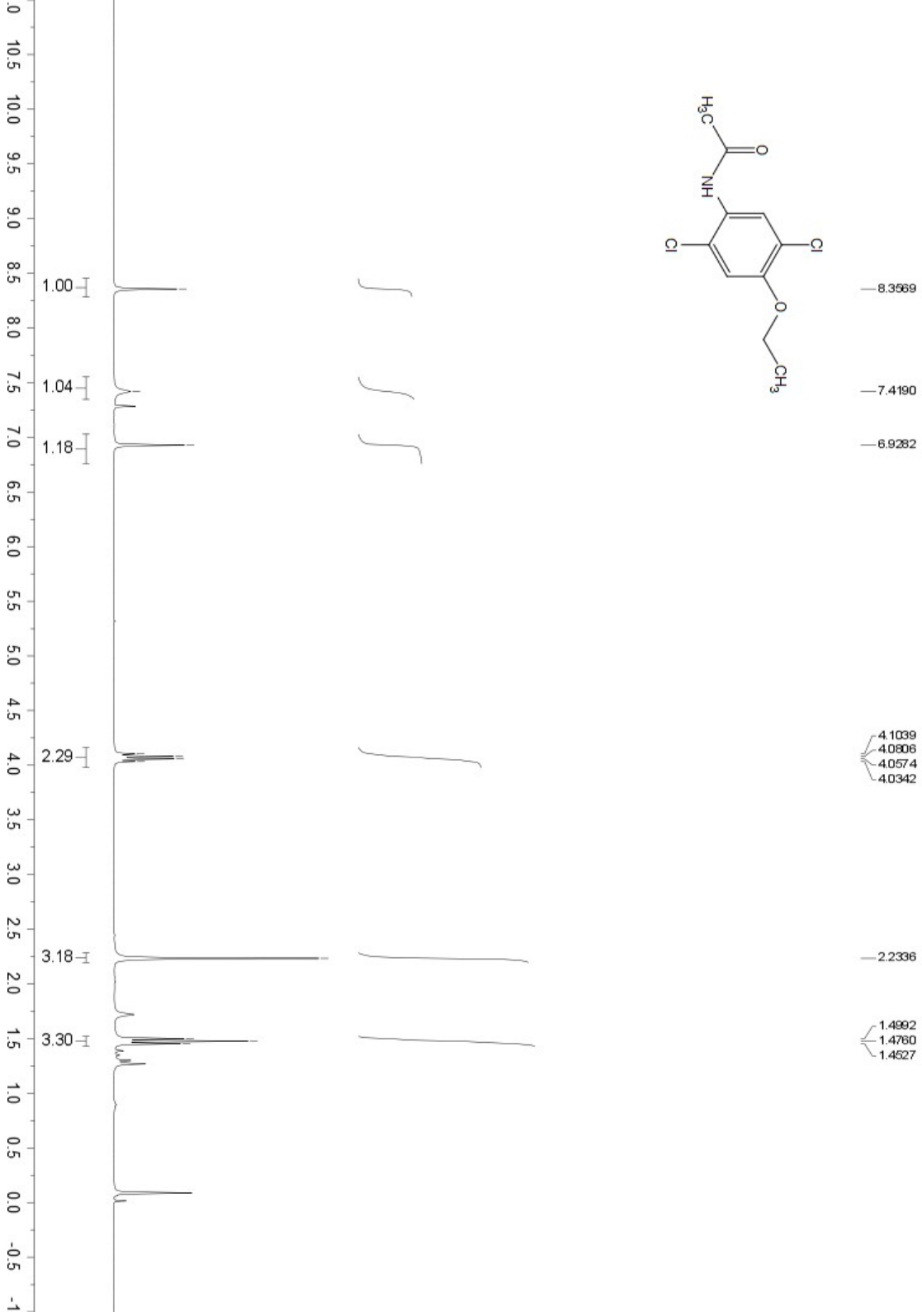
^{1}H NMR of 4e


H3C
O
NH
Cl
O
CH3
7.5386
7.5299
7.3656
7.3569
7.3361
7.3275
6.8741
6.8445
4.1189
4.0936
4.0703
4.0470
2.1599
1.4815
1.4582
1.4350
2.00
1.08
1.08
2.26
3.17
3.37

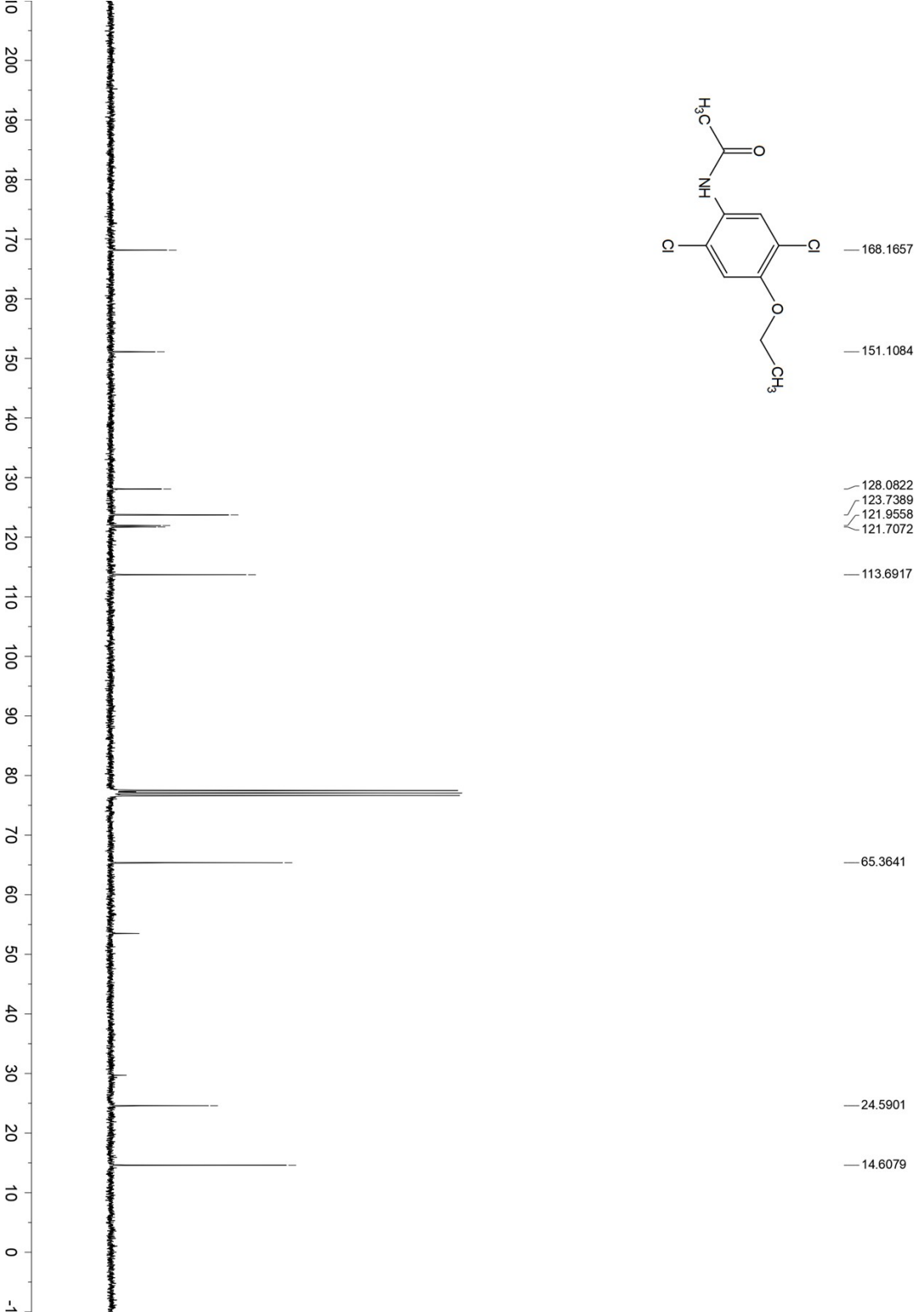
^{13}C NMR of 4e


168.5503
151.3487
131.3807
122.9112
122.6364
119.8490
113.6939
65.1160
24.2999
14.7405

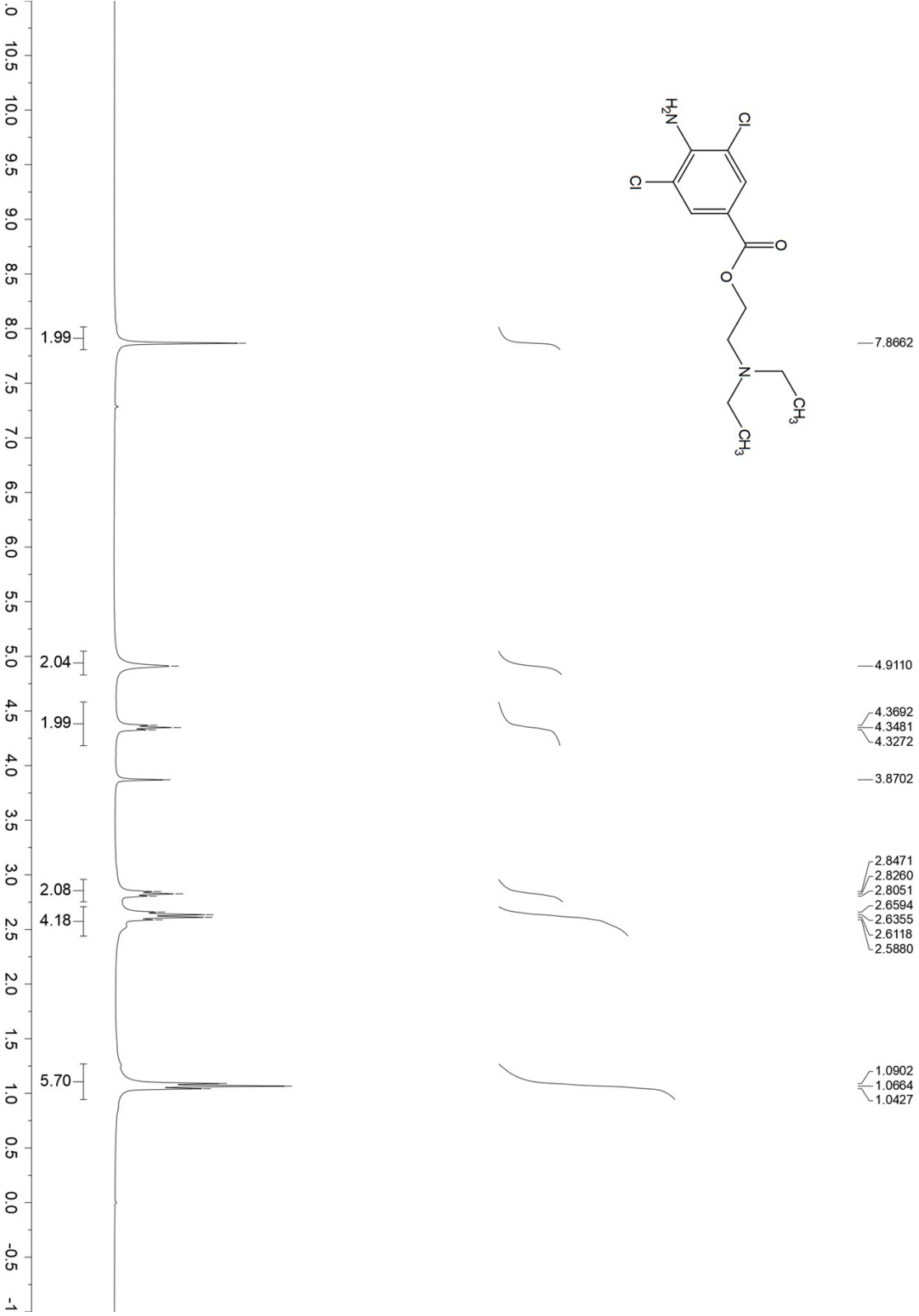
^{1}H NMR of 4e’


1.00
1.04
1.18
2.29
3.18
3.30
8.3569
7.4190
6.9282
4.1039
4.0806
4.0574
4.0342
2.2336
1.4992
1.4760
1.4527
H3C
O
NH
Cl
Cl
O
CH3

^{13}C NMR of 4e’


168.1657
151.1084
128.0822
123.7389
121.9558
121.7072
113.6917
65.3641
24.5901
14.6079

^{1}H NMR of 4f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4.3481
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3.8702
2.8471
2.8260
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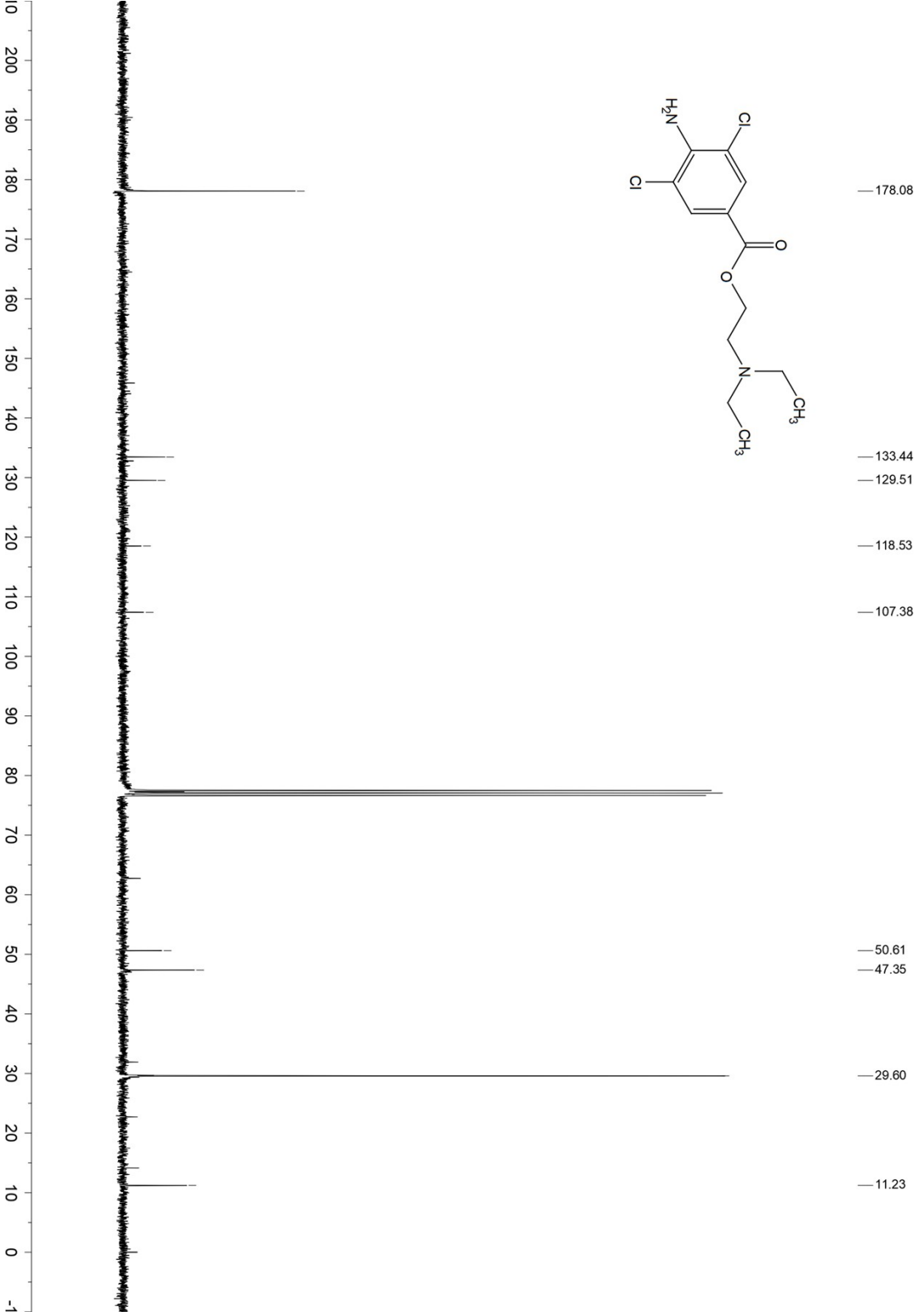
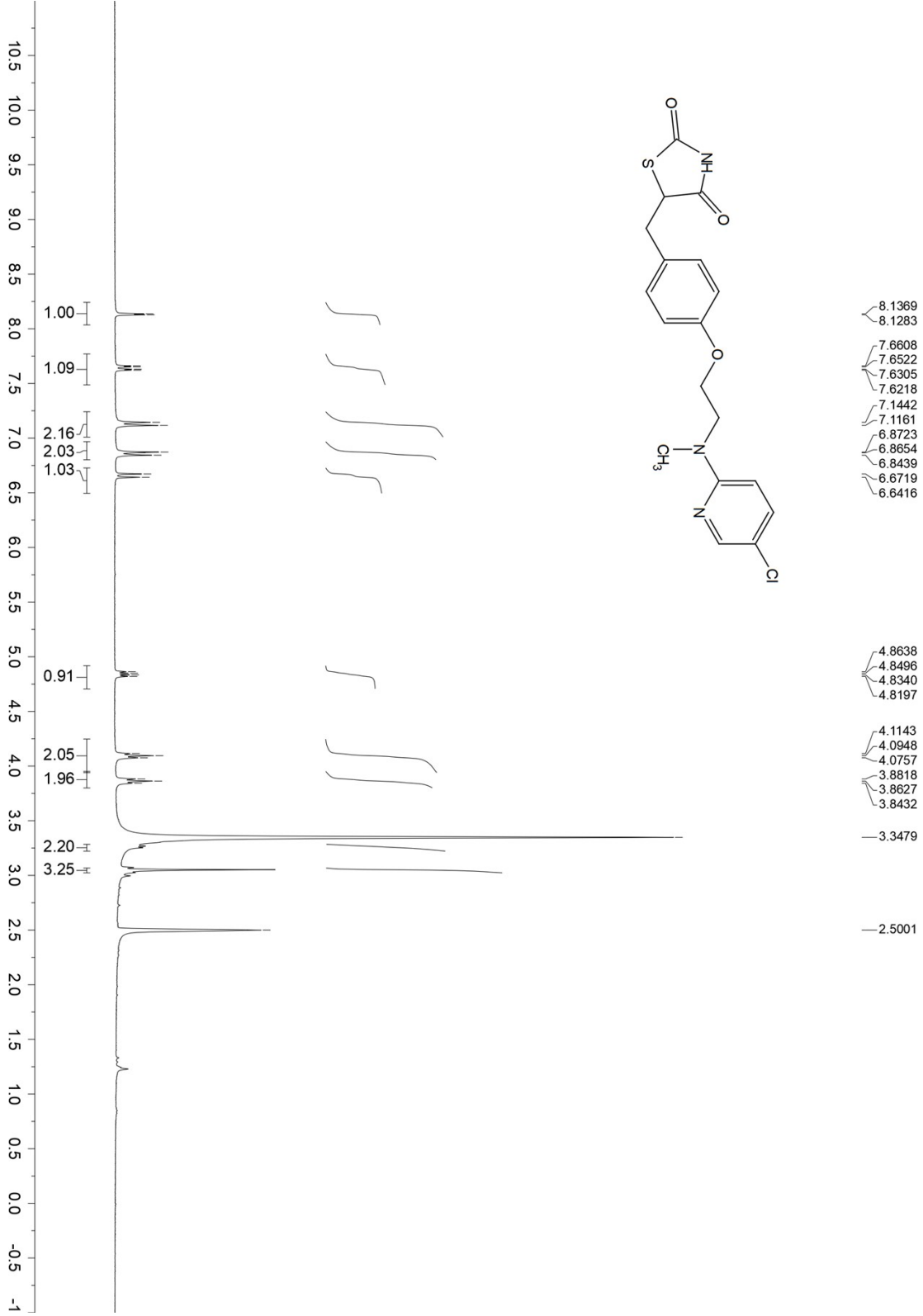
2.6355
2.6118
2.5880
1.0902
1.0664
1.0427

^{13}C NMR of 4f



^{1}H NMR of 4g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3.25
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8.1283
7.6608
7.6522
7.6305
7.6218
7.1442
7.1161
6.8723
6.8654
6.8439
6.6719
6.6416
4.8638
4.8496
4.8340
4.8197
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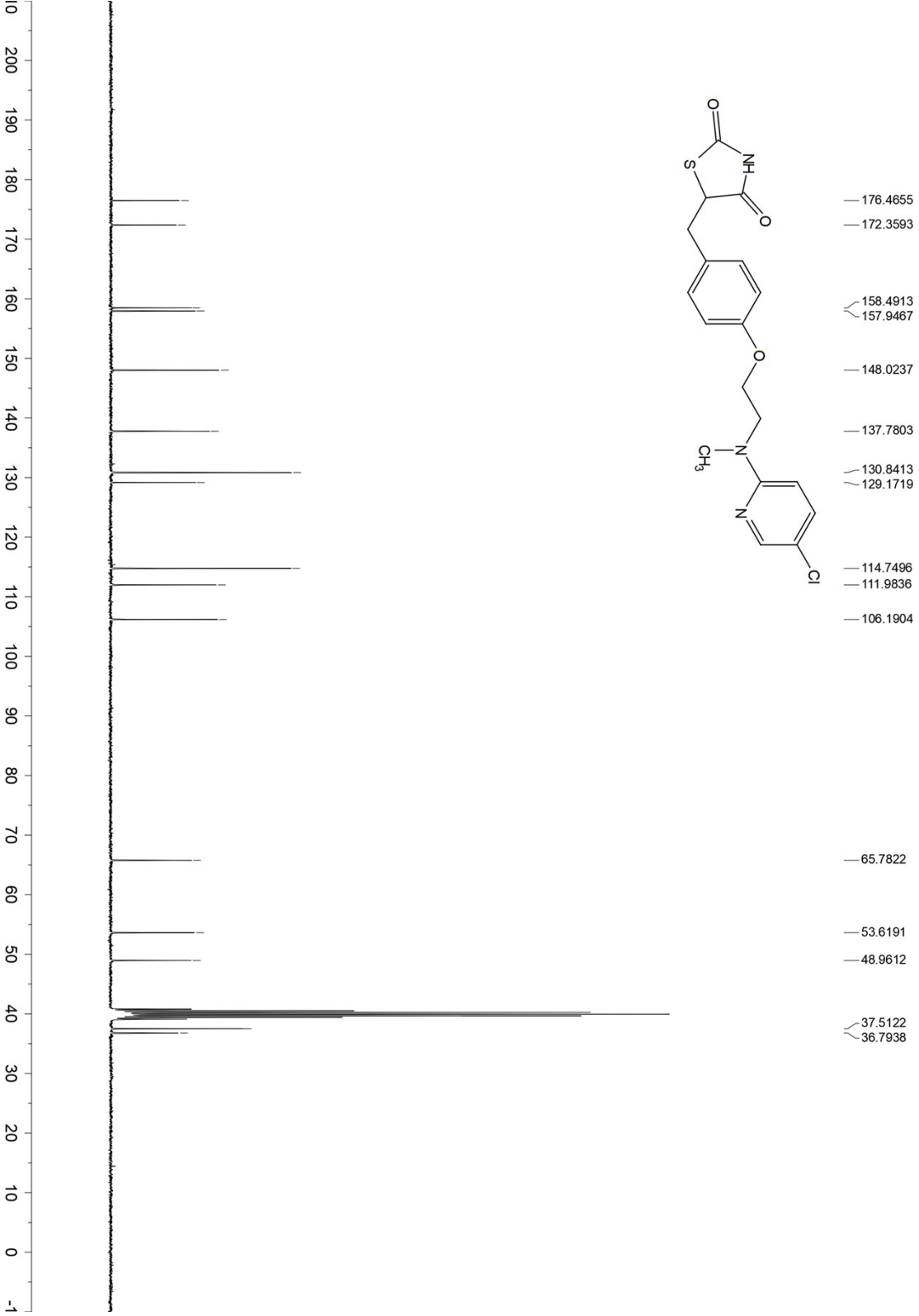
3.8432
3.3479
2.5001

^{13}C NMR of 4g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157.9467
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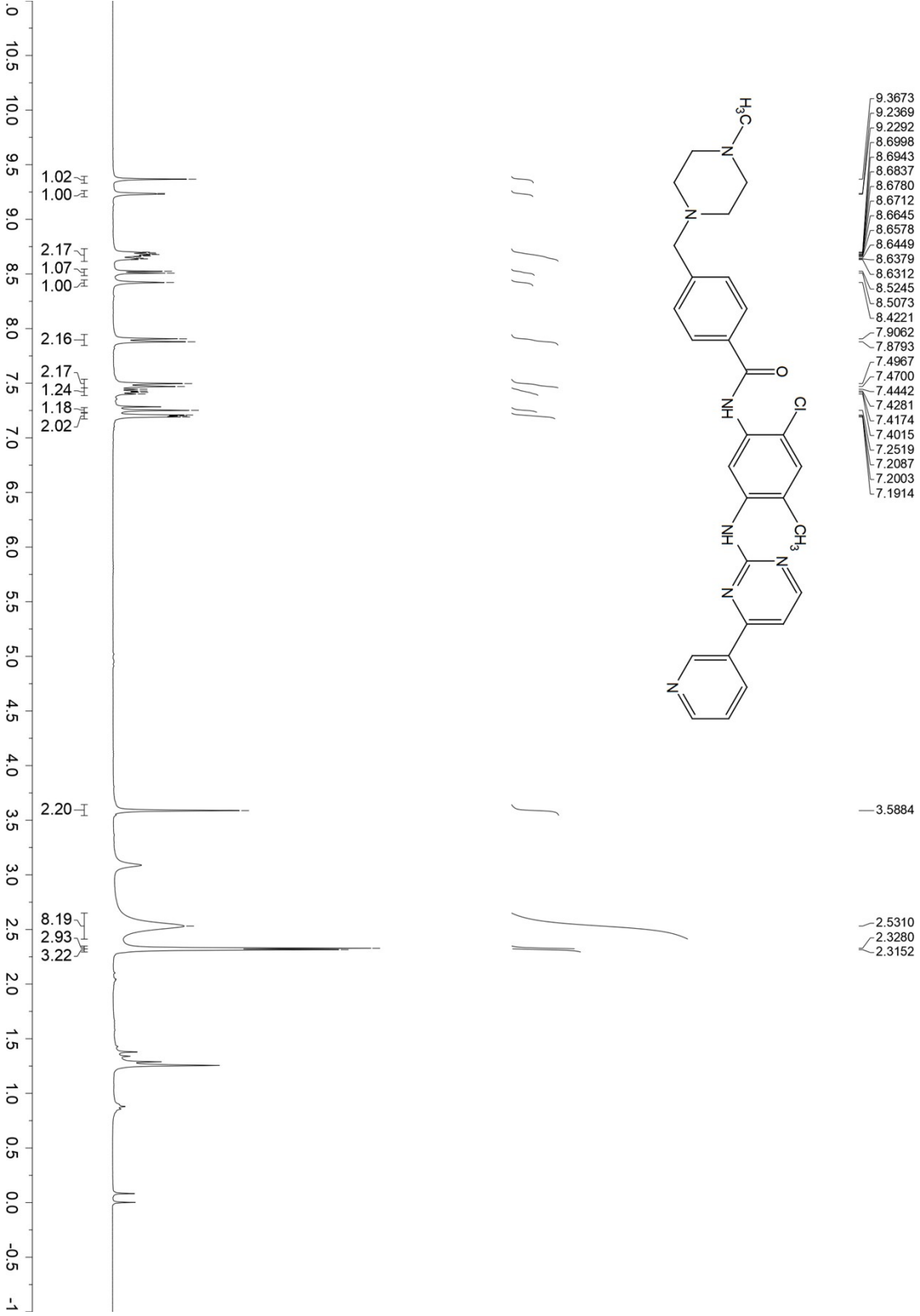
53.6191
48.9612
37.5122
36.7938

^{1}H NMR of 4h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2.17
1.07
1.00
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2.02
2.20
8.19
2.93
3.22
9.3673
9.2369
9.2292
8.6998
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8.6780
8.6712
8.6645
8.6578
8.6449
8.6379
8.6312
8.5245
8.5073
8.4221
7.9062
7.8793
7.4967
7.4700
7.4442
7.4281
7.4174
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7.2519
7.2087
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7.1914
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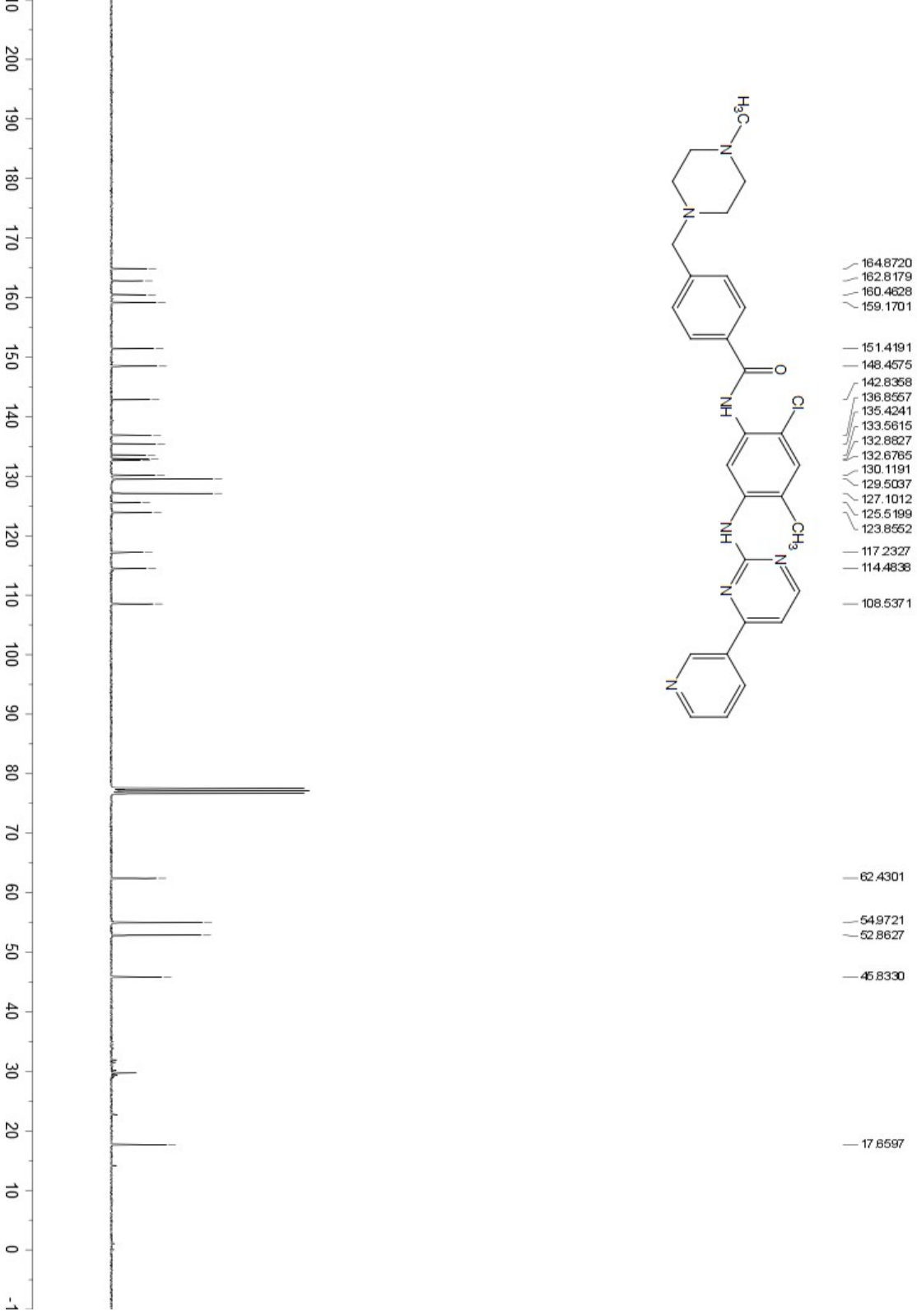
2.5310
2.3280
2.3152

^{13}C NMR of 4h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160.4628
159.1701
151.4191
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132.8827
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130.1191
129.5037
127.1012
125.5199
123.8552
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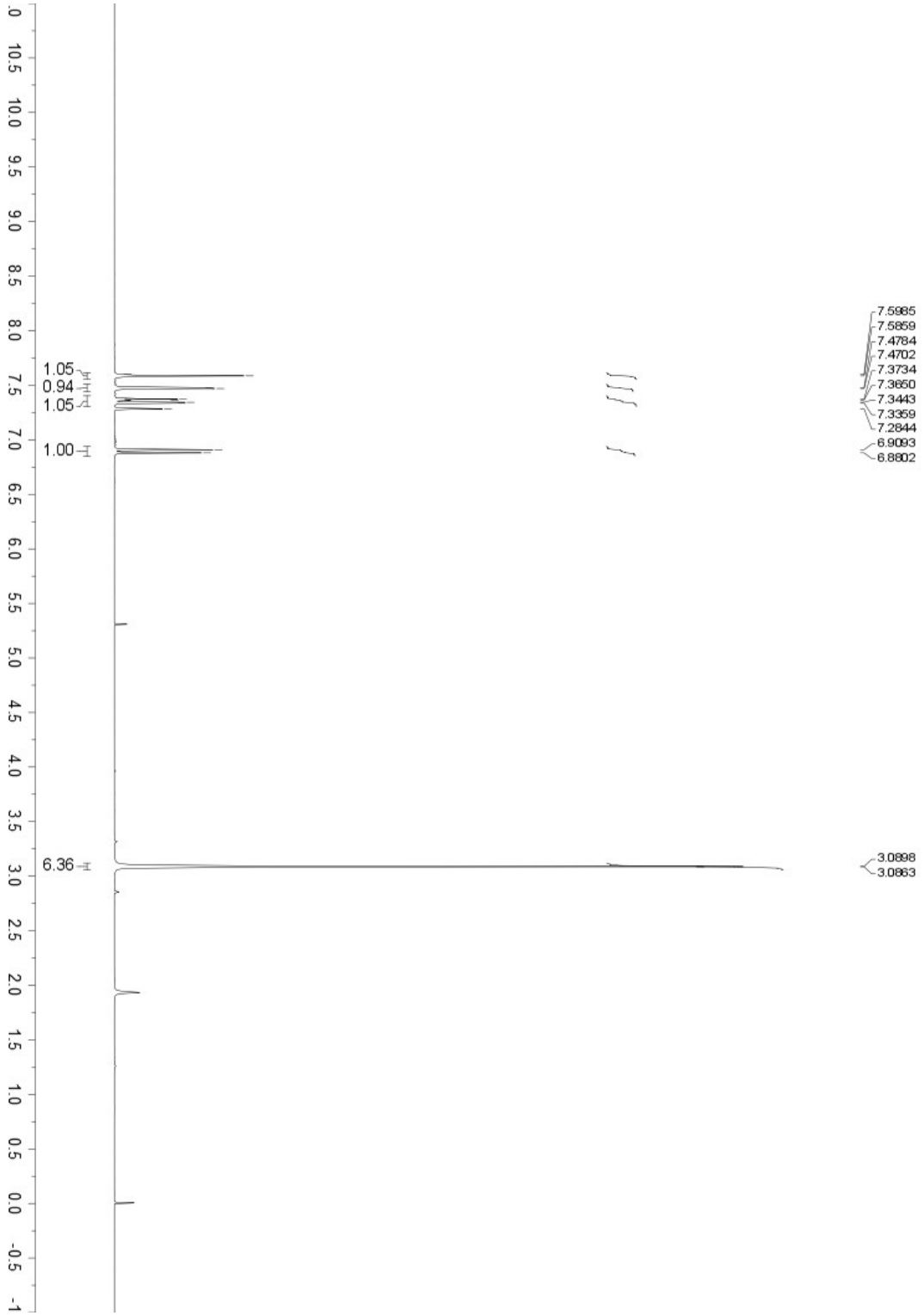
45.8330
17.8597

^{1}H NMR of 5a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1.05
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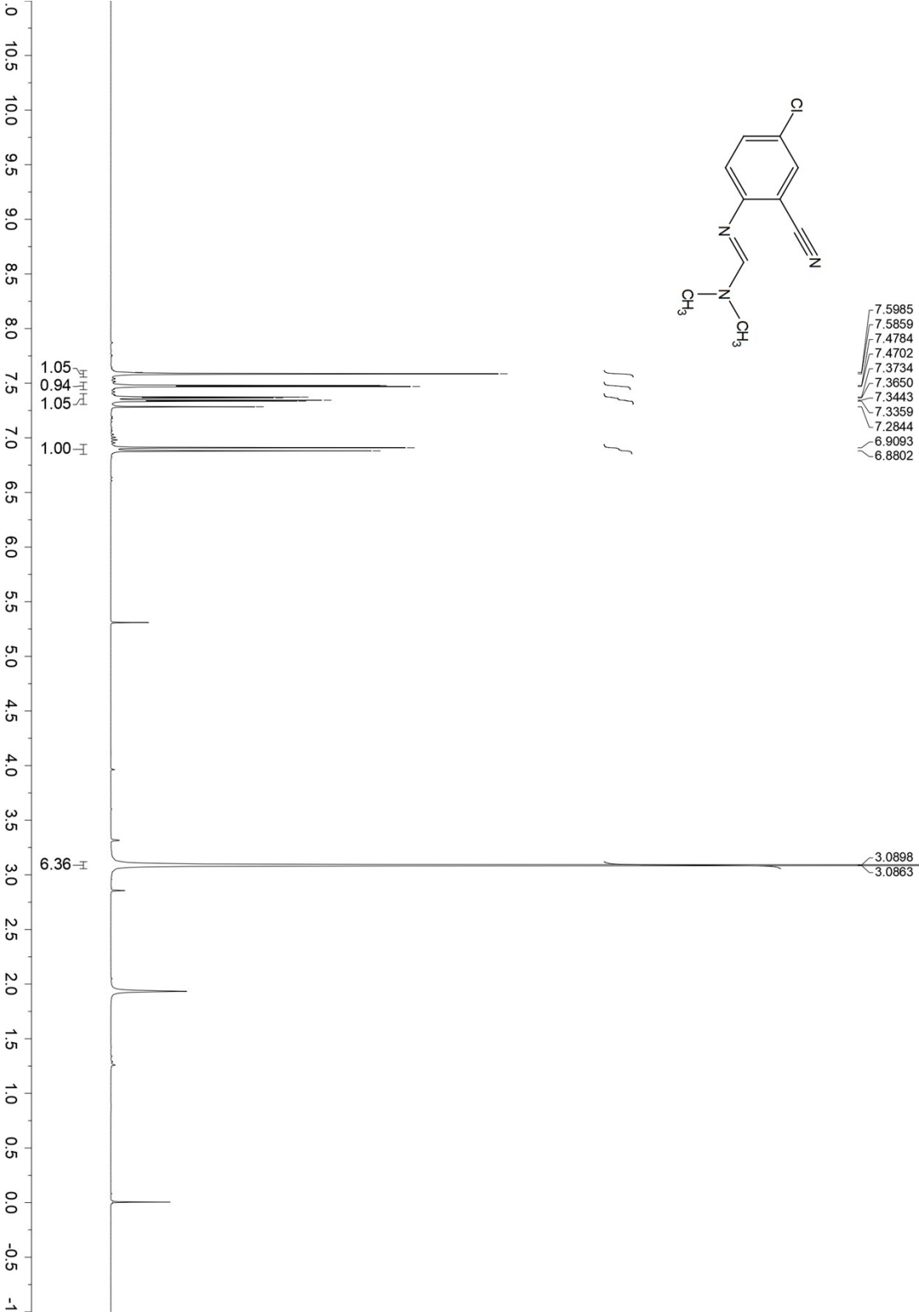
6.9093
6.8802
3.0898
3.0863

^{13}C NMR of 5a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CH3
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7.5859
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7.3734
7.3650
7.3443
7.3359
7.2844
6.9093
6.8802
3.0898
3.0863
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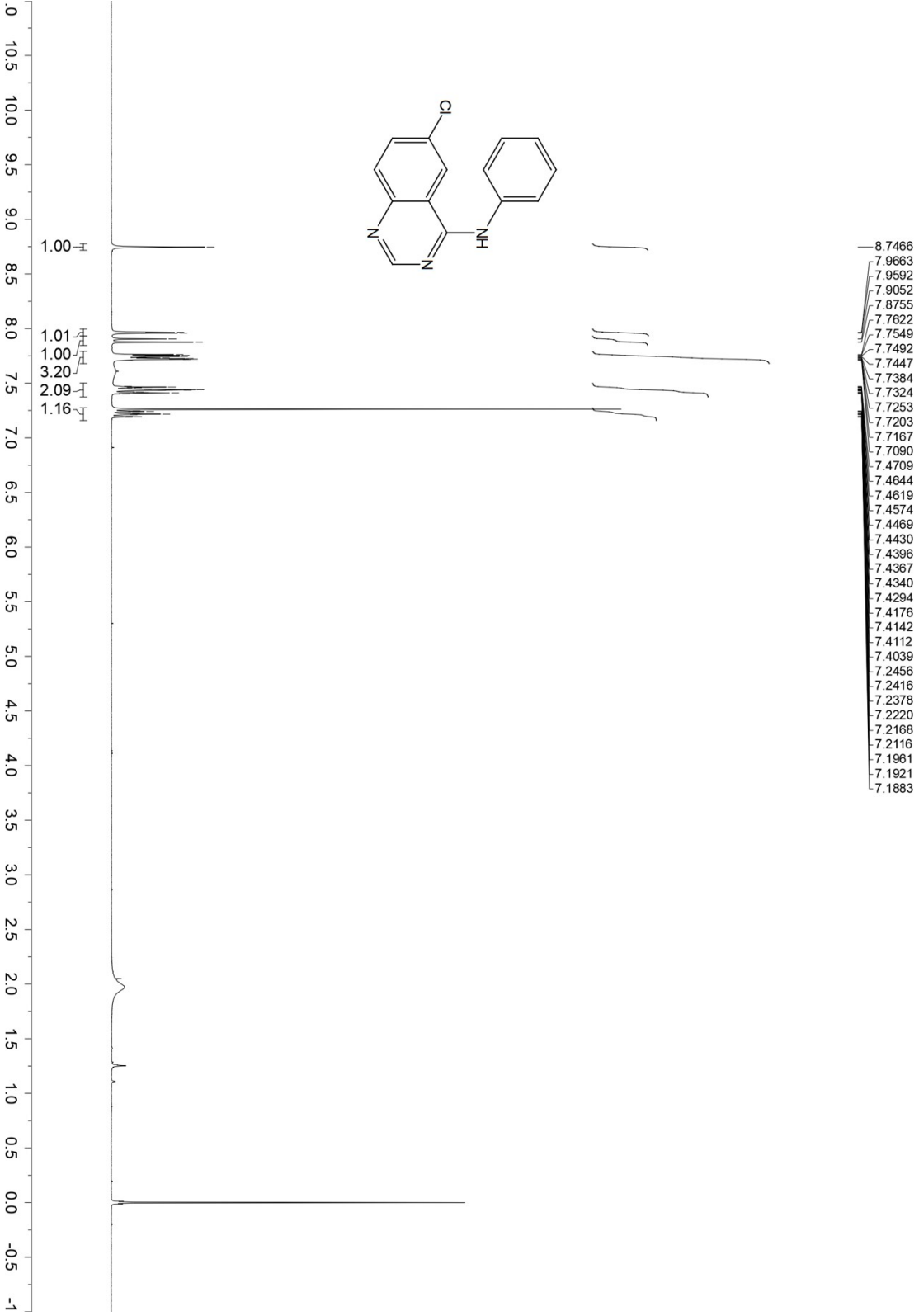
0.94
1.05
1.00
6.36

^{1}H NMR of 6a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NH
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1.00
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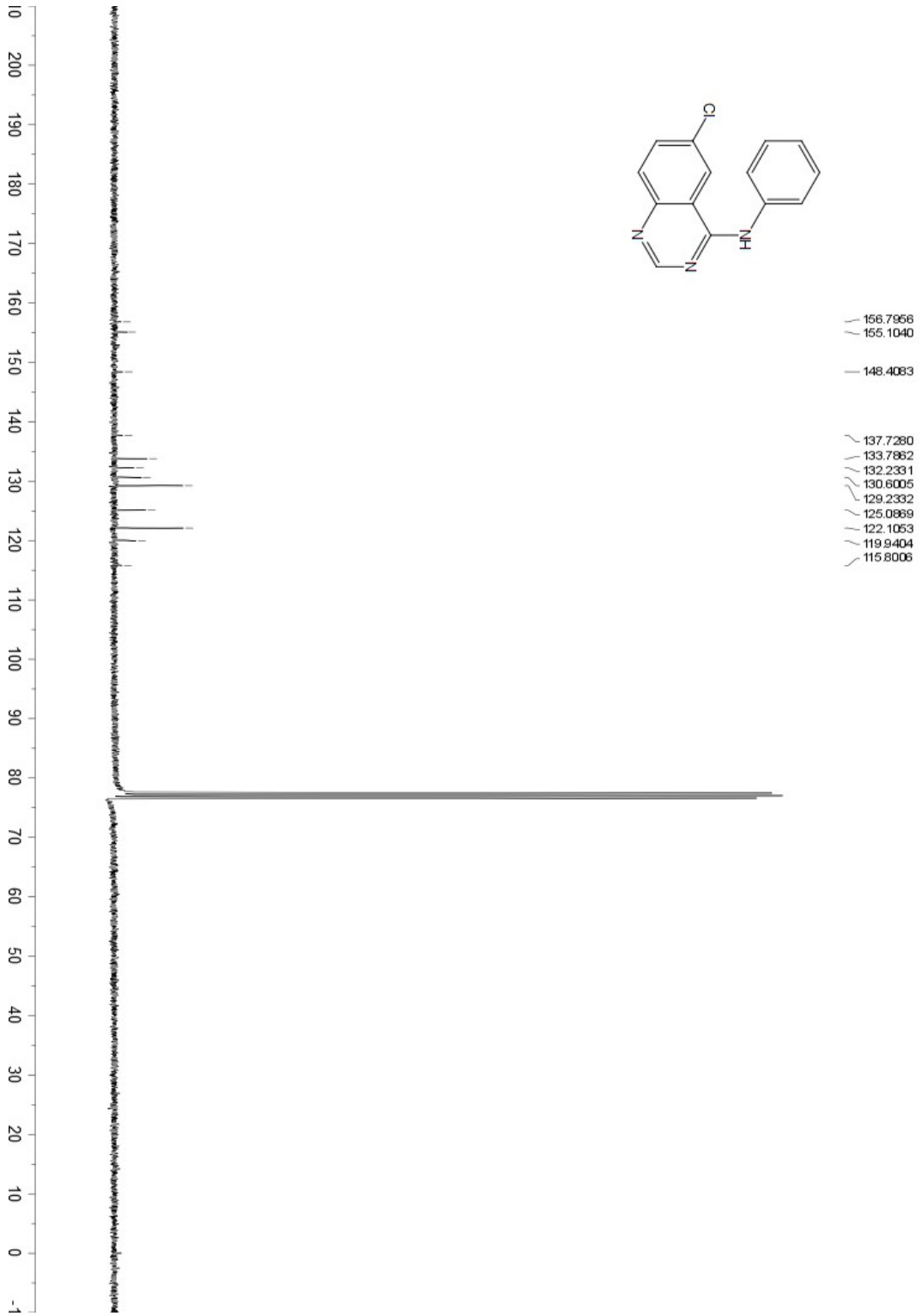
7.9052
7.8755
7.7622
7.7549
7.7492
7.7447
7.7384
7.7324
7.7253
7.7203
7.7167
7.7090
7.4709
7.4644
7.4619
7.4574
7.4469
7.4430
7.4396
7.4367
7.4340
7.4294
7.4176
7.4142
7.4112
7.4039
7.2456
7.2416
7.2378
7.2220
7.2168
7.2116
7.1961
7.1921
7.1883

^{13}C NMR of 6a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NH
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137.7280
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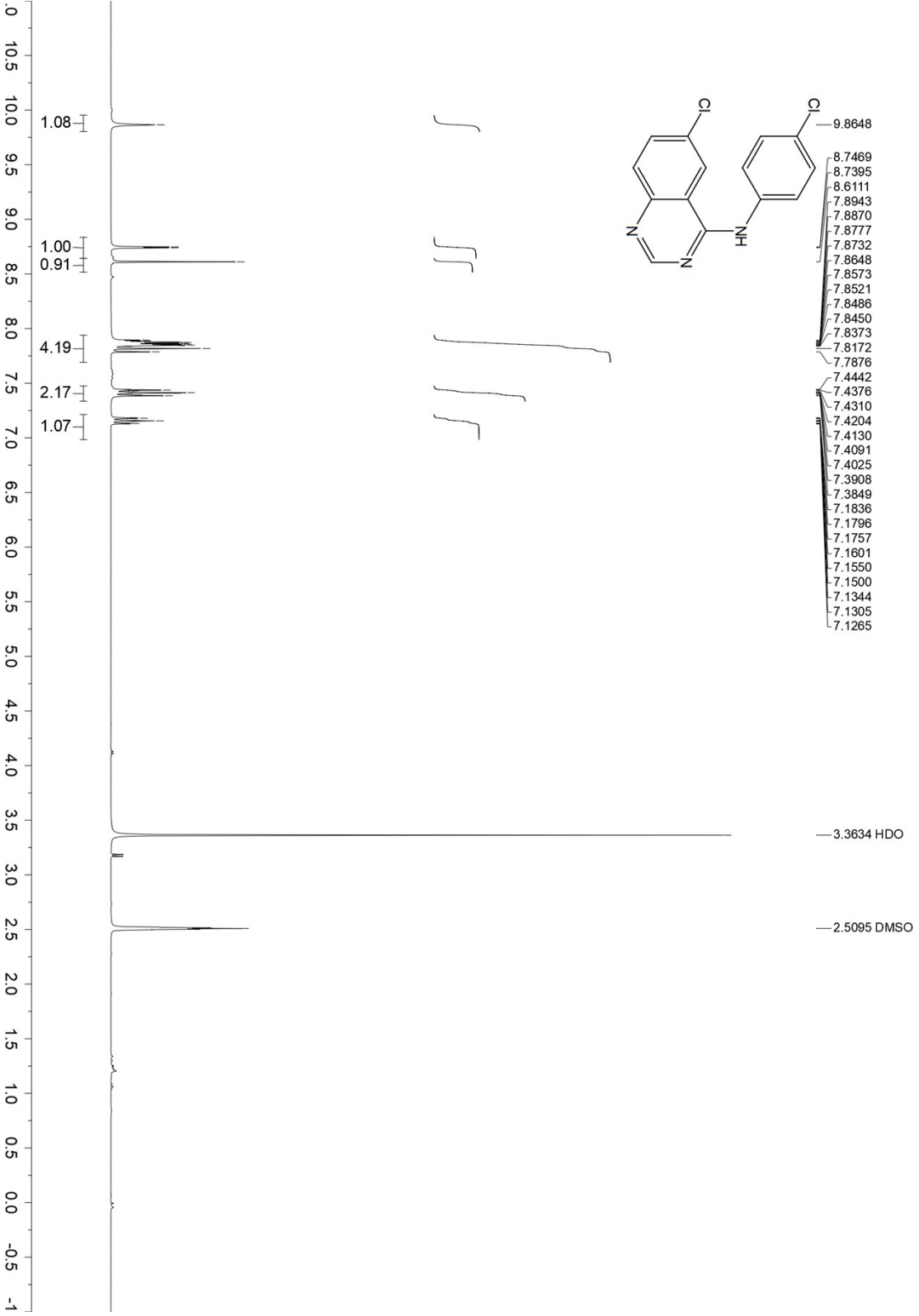
132.2331
130.6005
129.2332
125.0889
122.1053
119.9404
115.8006

^{1}H NMR of 6b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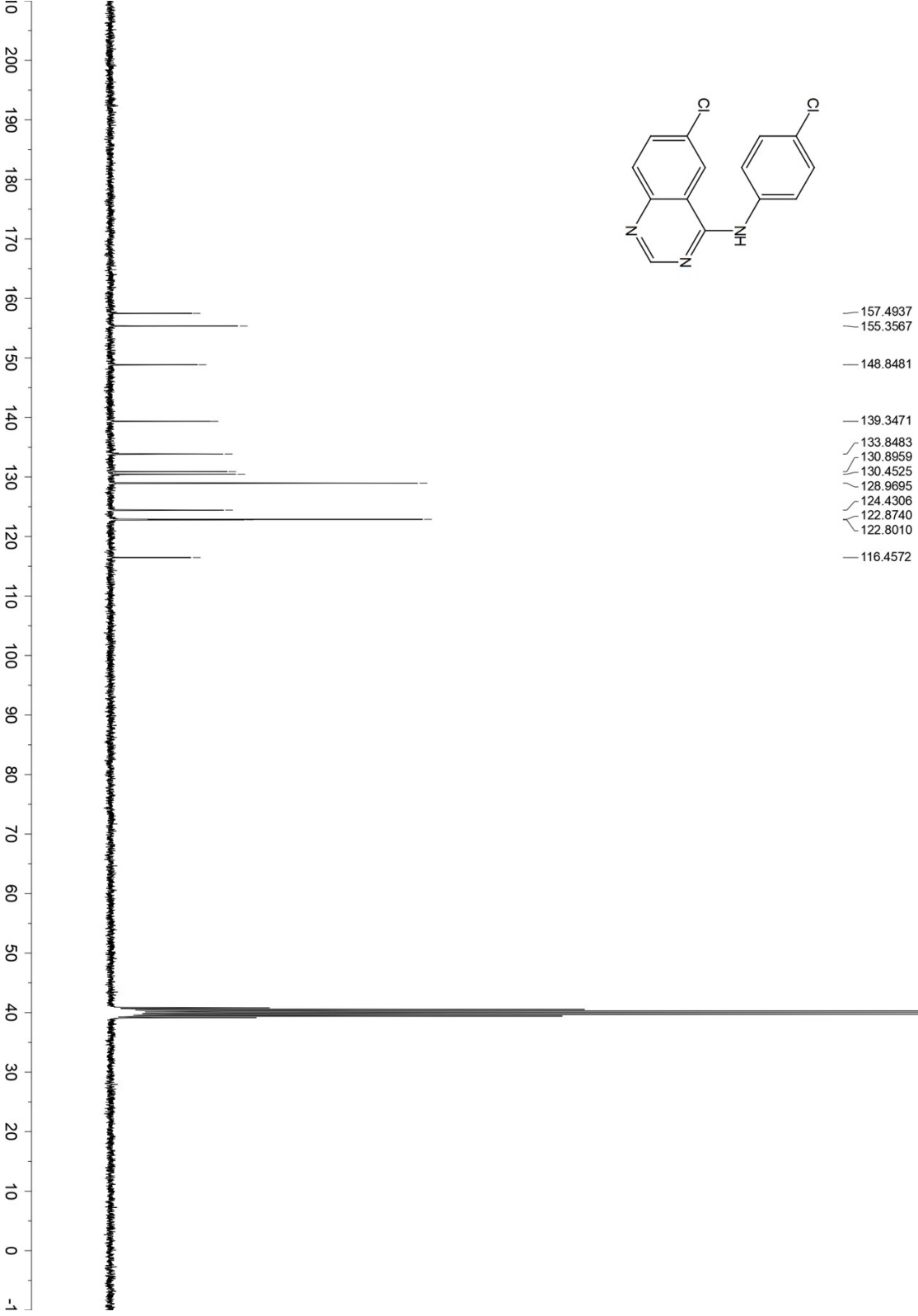
8.7395
8.6111
7.8943
7.8870
7.8777
7.8732
7.8648
7.8573
7.8521
7.8486
7.8450
7.8373
7.8172
7.7876
7.4442
7.4376
7.4310
7.4204
7.4130
7.4091
7.4025
7.3908
7.3849
7.1836
7.1796
7.1757
7.1601
7.1550
7.1500
7.1344
7.1305
7.1265
3.3634 HDO
2.5095 DMSO
Cl
Cl
N
NH
N

^{13}C NMR of 6b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148.8481
139.3471
133.8483
130.8959
130.4525
128.9695
124.4306
122.8740
122.8010
116.4572

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