Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information For:

Coupling of Enamides with Alkynes or Arynes for Synthesis of Substituted Pyridines and Isoquinolines *via* Amide Activation

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CONTENTS

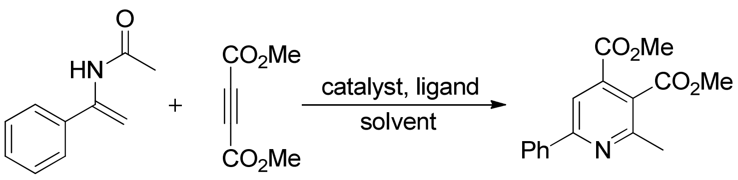
1. General Information

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All new products were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. The ketoximes were in all cases prepared from the corresponding ketones according to following literature:

Zhao, H.; Vandenbossche, C. P.; Koenig, S. G.; Singh, S. P.; Bakale, R. P. *Org. Lett.* **2008**, *10*, 505-507.

2. Optimization of Reaction Conditions

Table S1. Optimization of reaction conditions.[a]

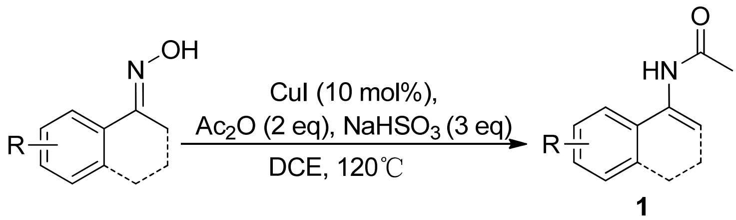


1a **2a** **3a**

entry	catalyst	ligand	solvent	T (°C)[b]	yield (%)
1	CuI		DMSO	120	23
2	CuI		DMF	120	31
3	CuI		DCE	120	40
4	CuI		THF	120	68
5	CuI		1,4-dioxane	120	70
6	CuBr		1,4-dioxane	120	54
7	CuCl		1,4-dioxane	120	38
8	Cu_2O		1,4-dioxane	120	25
9	CuI		1,4-dioxane	140	76
10	CuI	glycine	1,4-dioxane	140	88
11	CuI	N-methyl glycine	1,4-dioxane	140	70
12	CuI	N,N-dimethyl glycine	1,4-dioxane	140	66
13	CuI	Phenanthroline	1,4-dioxane	140	67
14	CuI	L-proline	1,4-dioxane	140	62
15	CuI	2,2'-dipyridine	1,4-dioxane	140	68

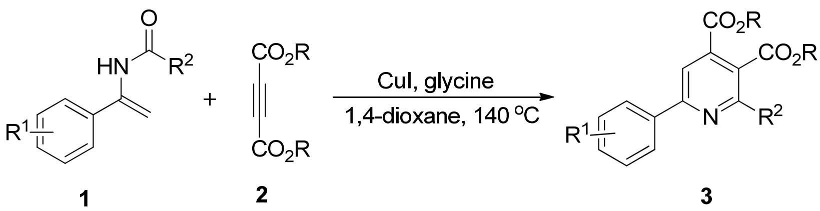
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalysts (10 mol%), and ligand (20 mol%) in solvent (3 mL) for 30 h. Isolated yields. [b] oil bath temperature.

3. Typical procedure for preparation of Enamides



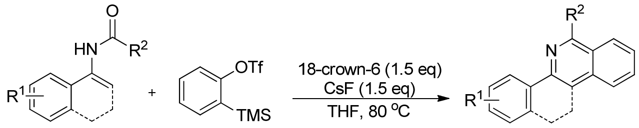
The mixture of ketoxime (5 mmol), acetic anhydride (10 mmol, 1.02 g), $NaHSO_3$ (1.5 mmol, 780.5 mg) and CuI (10 mol%, 95.5 mg) was stirred in 1,2-dichloroethane (DCE, 20 mL) at 120 °C (oil bath temperature) under Ar. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (30 mL) and washed with NaOH (2N, 20 mL) and brine (20 mL). The organic layer was dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired enamide **1** was obtained after purification by flash chromatography on silica gel with hexane/ethyl acetate as the eluent.

4. Typical procedure for the synthesis of pyridines



In a 25 mL round bottom flask, the enamide **1** (0.3 mmol), alkyne **2** (0.45 mmol), CuI (10 mol%, 5.7 mg) and glycine (20 mol%, 4.5 mg) was stirred in 1,4-dioxane (3 mL) at 140 °C (oil bath temperature) for 30 h. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, extracted with ethyl acetate (20 mL) and washed with dilute $NH_3 \cdot H_2O$ (5 mL) and brine (20 mL). The organic layer was dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired pyridine was obtained after purification by flash chromatography on silica gel with hexane/ethyl acetate (10/1) as the eluent.

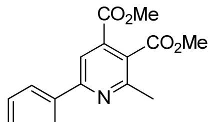
5. Typical procedure for the synthesis of isoquinolines



1 2 4

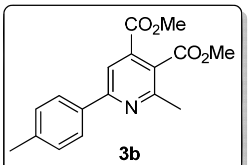
In a 25 mL round bottom flask, the enamide **1** (0.2 mmol), benzyne **2c** (0.3 mmol), CsF (0.3 mmol, 45.6 mg) and 18-crown-6 (0.3 mmol, 79.2 mg) was stirred in THF (3 mL) at 80 °C (oil bath temperature) under argon atmosphere for 24 h. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, extracted with ethyl acetate (20 mL) and washed with brine (20 mL). The organic layers were dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired isoquinoline was obtained after purification by flash chromatography on silica gel with hexane/ethyl acetate (40/1) as the eluent.

6. Spectroscopic data for pyridines and isoquinolines



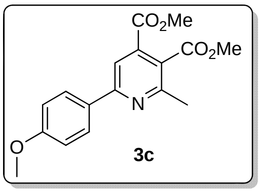
3a

3a: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 3H), 7.48-7.45 (m, 3H), 3.96 (s, 3H), 3.94 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 165.4, 158.2, 156.4, 137.8, 136.7, 129.8, 128.8, 127.1, 126.4, 116.9, 53.0, 52.8, 22.8. HRMS Calcd (ESI) m/z for $C_{16}H_{15}NNaO_4$: $[M+Na]^+$ 308.0893. Found: 308.0901.



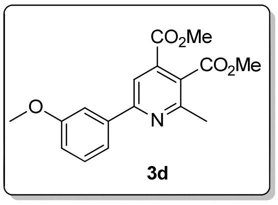
3b

3b: pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.66 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.5, 158.1, 156.3, 140.0, 136.7, 135.0, 129.6, 127.0, 126.0, 116.5, 53.0, 52.8, 22.8, 21.3. HRMS Calcd (ESI) m/z for $C_{17}H_{17}NNaO_4$: $[M+Na]^+$ 322.1050. Found: 322.1053.



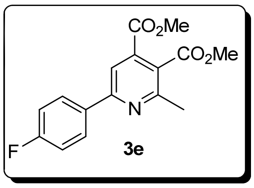
3c

3c: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 9.2 Hz, 2H), 7.97 (s, 1H), 7.00 (d, J = 8.4 Hz, 2H), 3.97 (s, 3H), 3.95 (s, 3H), 3.87 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.6, 161.1, 157.8, 156.2, 136.8, 130.4, 128.5, 125.5, 116.0, 114.2, 55.3, 53.0, 52.8, 22.8. HRMS Calcd (ESI) m/z for $C_{17}H_{18}NO_5$: $[M+H]^+$ 316.1179. Found: 316.1180.



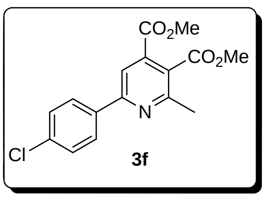
3d

3d: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.63-7.59 (m, 2H), 7.42-7.38 (t, J = 8.0 Hz, 1H), 7.02-6.99 (m, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 165.4, 160.1, 157.9, 156.3, 139.3, 136.7, 129.8, 126.5, 119.5, 117.0, 115.6, 112.4, 55.4, 53.0, 52.8, 22.8. HRMS Calcd (ESI) m/z for $C_{17}H_{18}NO_5$: $[M+H]^+$ 316.1179. Found: 316.1177.



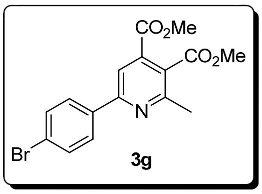
3e

3e: white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.00 (m, 2H), 7.96 (s, 1H), 7.16-7.12 (t, J = 8.4 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 165.3, 163.9 (d, J_{CF} = 248.6 Hz), 157.0, 156.4, 136.8, 134.0, 129.0 (d, J_{CF} = 8.6 Hz), 126.4, 116.5, 115.8 (d, J_{CF} = 21.9 Hz), 53.0, 52.8, 22.8. HRMS Calcd (ESI) m/z for $C_{16}H_{14}FNNaO_4$: $[M+Na]^+$ 326.0799. Found: 326.0792.

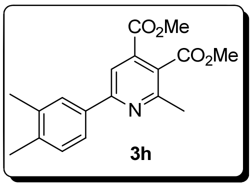


3f

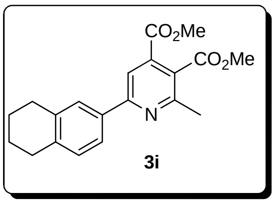
3f: white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.96 (m, 3H), 7.43 (d, J = 8.4 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 165.2, 156.8, 156.5, 136.8, 136.2, 136.0, 129.0, 128.4, 126.7, 116.6, 53.1, 52.9, 22.8. HRMS Calcd (ESI) m/z for $C_{16}H_{14}ClNNaO_4$: $[M+Na]^+$ 342.0504. Found: 342.0505.



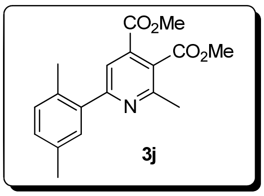
3g: white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 165.2, 156.8, 156.5, 136.8, 136.6, 132.0, 128.6, 126.8, 124.4, 116.5, 53.1, 52.9, 22.8. HRMS Calcd (ESI) m/z for $C_{16}H_{14}BrNNaO_4$: $[M+Na]^+$ 385.9998. Found: 385.9988.



3h: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.83 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 2.66 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.6, 158.3, 156.2, 138.7, 137.1, 136.7, 135.4, 130.1, 128.2, 125.9, 124.5, 116.5, 53.0, 52.8, 22.8, 19.9, 19.7. HRMS Calcd (ESI) m/z for $C_{18}H_{19}NNaO_4$: $[M+Na]^+$ 336.1206. Found: 336.1195.

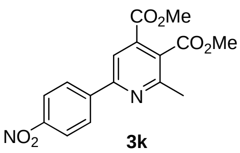


3i: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.74 (d, *J* = 10.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.85-2.80 (m, 4H), 2.66 (s, 3H), 1.83-1.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.6, 158.4, 156.2, 139.3, 137.7, 136.7, 135.0, 129.6, 127.7, 125.9, 124.1, 116.5, 53.0, 52.8, 29.5, 29.3, 23.1, 23.0, 22.8. HRMS Calcd (ESI) m/z for $C_{20}H_{21}NNaO_4$: $[M+Na]^+$ 362.1363. Found: 362.1364.



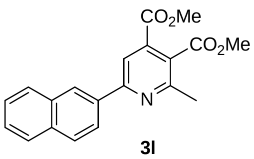
3j: brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.19-7.12 (m, 3H), 3.97 (s, 3H), 3.91 (s, 3H), 2.65 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 165.3, 161.2, 155.8, 138.7, 135.9, 135.5, 132.6, 130.9, 130.1, 129.6, 126.1, 120.5, 53.0, 52.9, 22.6, 20.9, 19.7. HRMS Calcd (ESI) m/z for $C_{18}H_{20}NO_4$: $[M+H]^+$

314.1387. Found: 314.1381.



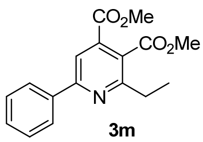
3k

3k: yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, *J* = 8.0 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.12 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.2, 164.8, 157.0, 155.3, 148.5, 143.5, 136.9, 128.0, 127.9, 124.0, 117.5, 53.2, 53.0, 22.7. HRMS Calcd (ESI) m/z for $C_{16}H_{14}N_2NaO_6$: [M+Na]$^+$ 353.0744. Found: 353.0738.



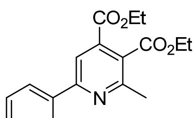
3l

3l: yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.52 (s, 1H), 8.18-8.16 (m, 2H), 7.96-7.92 (m, 2H), 7.87-7.85 (m, 1H), 7.52-7.50 (m, 2H), 3.98 (s, 3H), 3.96 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.7, 165.4, 158.0, 156.5, 136.8, 135.1, 134.0, 133.3, 128.8, 128.6, 127.7, 126.9, 126.9, 126.4, 126.4, 124.3, 117.0, 53.0, 52.8, 22.9. HRMS Calcd (ESI) m/z for $C_{20}H_{17}NNaO_4$: [M+Na]$^+$ 358.1050. Found: 358.1051.



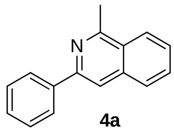
3m

3m: yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08-8.04 (m, 3H), 7.47-7.45 (m, 3H), 3.95 (s, 3H), 3.93 (s, 3H), 2.92-2.90 (m, 2H), 1.39-1.35 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.8, 165.4, 160.8, 158.1, 138.0, 136.5, 129.7, 128.8, 127.1, 126.1, 116.7, 53.0, 52.8, 29.3, 13.5. HRMS Calcd (ESI) m/z for $C_{17}H_{17}NNaO_4$: [M+Na]$^+$ 322.1050. Found: 322.1045.



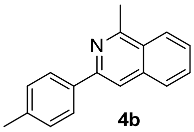
3n

3n: yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 9.2 Hz, 3H), 7.49 (d, *J* = 7.6 Hz, 3H), 4.46-4.41 (m, 4H), 2.70 (s, 3H), 1.43-1.39 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.2, 165.0, 158.0, 156.2, 137.9, 137.1, 129.6, 128.8, 127.1, 126.6, 116.9, 62.1, 61.8, 22.7, 14.0, 14.0. HRMS Calcd (ESI) m/z for $C_{18}H_{19}NNaO_4$: $[M+Na]^+$ 336.1206. Found: 336.1211.



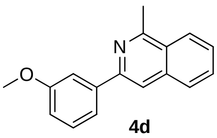
4a

4a: pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 1H), 7.50-7.44 (m, 3H), 7.36 (d, *J* = 6.8 Hz, 1H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 149.8, 139.7, 136.6, 129.9, 128.6, 128.2, 127.5, 126.9, 126.7, 126.4, 125.5, 115.1, 22.6. HRMS Calcd (ESI) m/z for $C_{16}H_{14}N$: $[M+H]^+$ 220.1121. Found: 220.1122.



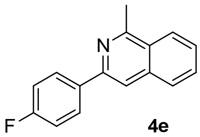
4b

4b: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.87 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.65-7.61 (m, 1H), 7.54-7.50 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.02 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 149.9, 138.1, 136.9, 136.7, 129.9, 129.4, 127.5, 126.8, 126.5, 126.4, 125.6, 114.7, 22.6, 21.2. HRMS Calcd (ESI) m/z for $C_{17}H_{16}N$: $[M+H]^+$ 234.1277. Found: 234.1276.



4d

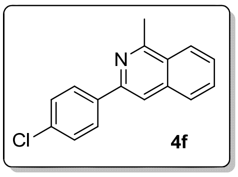
4d: pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.88 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.69-7.61 (m, 2H), 7.55-7.53 (m, 1H), 7.40-7.37 (m, 1H), 6.94 (d, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 158.5, 149.7, 141.3, 136.6, 130.0, 129.6, 127.6, 126.8, 126.6, 125.6, 119.3, 115.3, 114.1, 112.2, 55.3, 22.6. HRMS Calcd (ESI) m/z for $C_{17}H_{16}NO$: $[M+H]^+$ 250.1226. Found: 250.1230.



4e

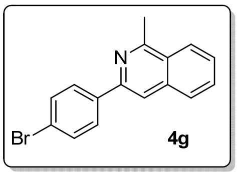
4e: white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-8.08 (m, 3H), 7.83 (s, 1H), 7.80

(s, 1H), 7.66-7.63 (m, 1H), 7.56-7.53 (m, 1H), 7.19-7.14 (m, 2H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, J_{CF} = 245.9 Hz), 158.6, 148.9, 136.6, 135.9, 130.1, 128.6 (d, J_{CF} = 7.6 Hz), 127.5, 126.8, 126.4, 125.6, 115.5 (d, J_{CF} = 21.3 Hz), 114.8, 22.6. HRMS Calcd (ESI) m/z for $C_{16}H_{13}NF$: $[M+H]^+$ 238.1027. Found: 238.1029.



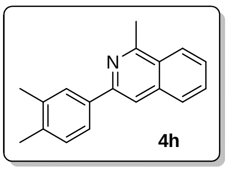
4f

4f: pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.06 (m, 3H), 7.86 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.67-7.63 (m, 1H), 7.57-7.56 (m, 1H), 7.44 (d, J = 8.4 Hz, 2H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.6, 138.2, 136.6, 134.2, 130.1, 128.8, 128.1, 127.6, 127.0, 126.6, 125.6, 115.1, 22.6. HRMS Calcd (ESI) m/z for $C_{16}H_{13}NCl$: $[M+H]^+$ 254.0731. Found: 254.0731.



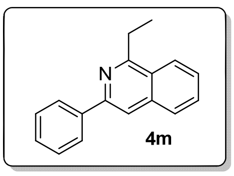
4g

4g: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.84 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.65-7.61 (m, 1H), 7.59-7.54 (m, 3H), 2.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.6, 138.6, 136.5, 131.7, 130.1, 128.4, 127.6, 127.0, 126.6, 125.6, 122.6, 115.0, 22.6. HRMS Calcd (ESI) m/z for $C_{16}H_{13}NBr$: $[M+H]^+$ 298.0226. Found: 298.0226.



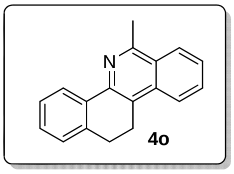
4h

4h: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.88-7.81 (m, 3H), 7.65-7.62 (m, 1H), 7.55-7.51 (m, 1H), 7.26 (d, J = 8.0 Hz, 1H), 3.03 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 150.1, 137.3, 136.8, 136.7, 130.0, 129.9, 128.1, 127.5, 126.4, 126.4, 125.6, 124.2, 114.7, 22.6, 20.0, 19.6. HRMS Calcd (ESI) m/z for $C_{18}H_{18}N$: $[M+H]^+$ 248.1434. Found: 248.1439.



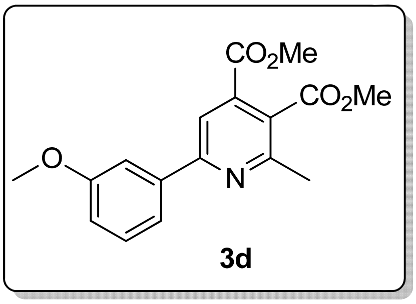
4m

4m: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.13 (m, 3H), 7.90 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.64-7.61 (t, *J* = 7.2 Hz, 1H), 7.55-7.48 (m, 3H), 7.41-7.39 (m, 1H), 3.42-3.36 (m, 2H), 1.54-1.51 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 149.7, 139.9, 137.0, 129.7, 128.7, 128.2, 127.8, 126.9, 126.6, 125.8, 125.1, 114.9, 28.5, 13.3. HRMS Calcd (ESI) m/z for $C_{17}H_{16}N$: $[M+H]^+$ 234.1277. Found: 234.1278.



4o: white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.73-7.70 (m, 1H), 7.59-7.55 (t, *J* = 7.6 Hz, 1H), 7.46-7.43 (m, 1H), 7.36-7.28 (m, 2H), 3.32-3.28 (t, *J* = 7.2 Hz, 2H), 3.09-3.06 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 144.2, 136.9, 135.4, 134.6, 129.7, 128.0, 127.3, 127.0, 126.6, 126.2, 125.9, 125.0, 123.1, 123.0, 27.8, 22.7, 22.7. HRMS Calcd (ESI) m/z for $C_{18}H_{16}N$: $[M+H]^+$ 246.1277. Found: 246.1284.

7. The X-ray data and crystal structure of pyridine 3d

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N1 C12 C16 115.9(2) . . ?
C13 C12 C16 121.5(2) . . ?
C3 C13 C12 118.0(2) . . ?
C3 C13 C14 124.4(2) . . ?
C12 C13 C14 117.5(2) . . ?
O4 C14 O3 124.8(2) . . ?
O4 C14 C13 124.7(2) . . ?
O3 C14 C13 110.42(19) . . ?
O3 C15 H15A 109.5 . . ?
O3 C15 H15B 109.5 . . ?
H15A C15 H15B 109.5 . . ?
O3 C15 H15C 109.5 . . ?
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H15B C15 H15C 109.5 . . ?
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H16A C16 H16C 109.5 . . ?
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H17A C17 H17B 109.5 . . ?
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O1 C2 C3 C4 3.1(4) . . . . ?
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O1 C2 C3 C13 -177.8(2) . . . . ?
O2 C2 C3 C13 3.5(3) . . . . ?
C13 C3 C4 C5 -0.1(3) . . . . ?
C2 C3 C4 C5 179.05(19) . . . . ?
C12 N1 C5 C4 0.6(3) . . . . ?
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C3 C4 C5 N1 -0.6(3) . . . . ?
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N1 C5 C6 C7 177.8(2) . . . . ?
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O5 C10 C11 C6 -179.8(2) . . . . ?
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C7 C6 C11 C10 -0.2(3) . . . . ?
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C5 N1 C12 C16 -179.3(2) . . . . ?
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C2 C3 C13 C14 0.4(4) . . . . ?
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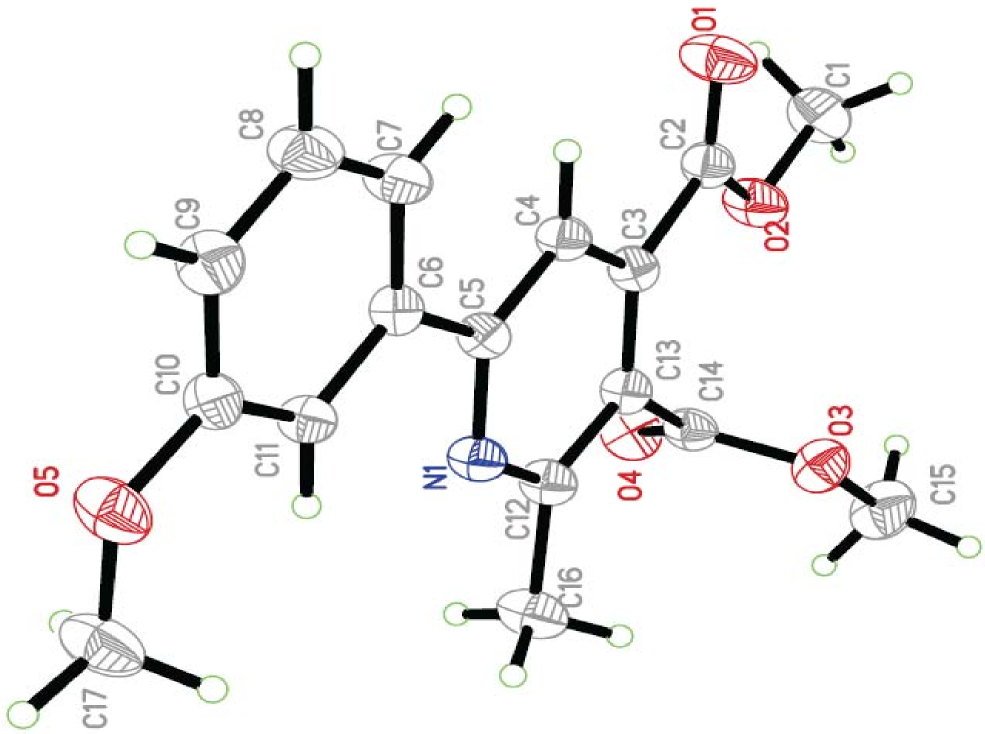
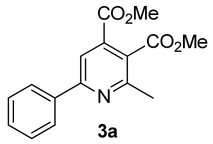


8. Appendix (copies of [1]H and [13]C NMR spectra)



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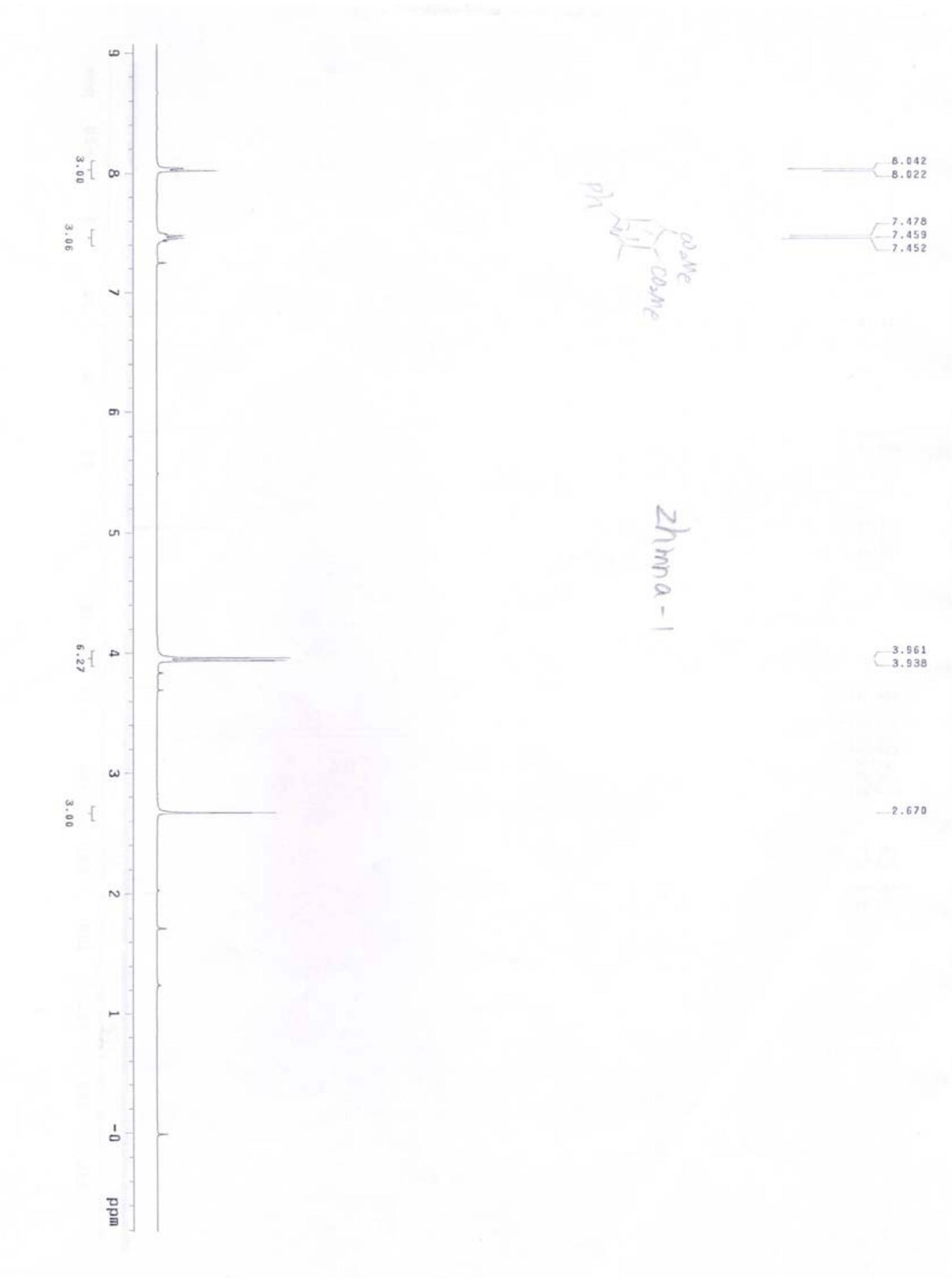

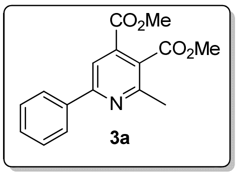
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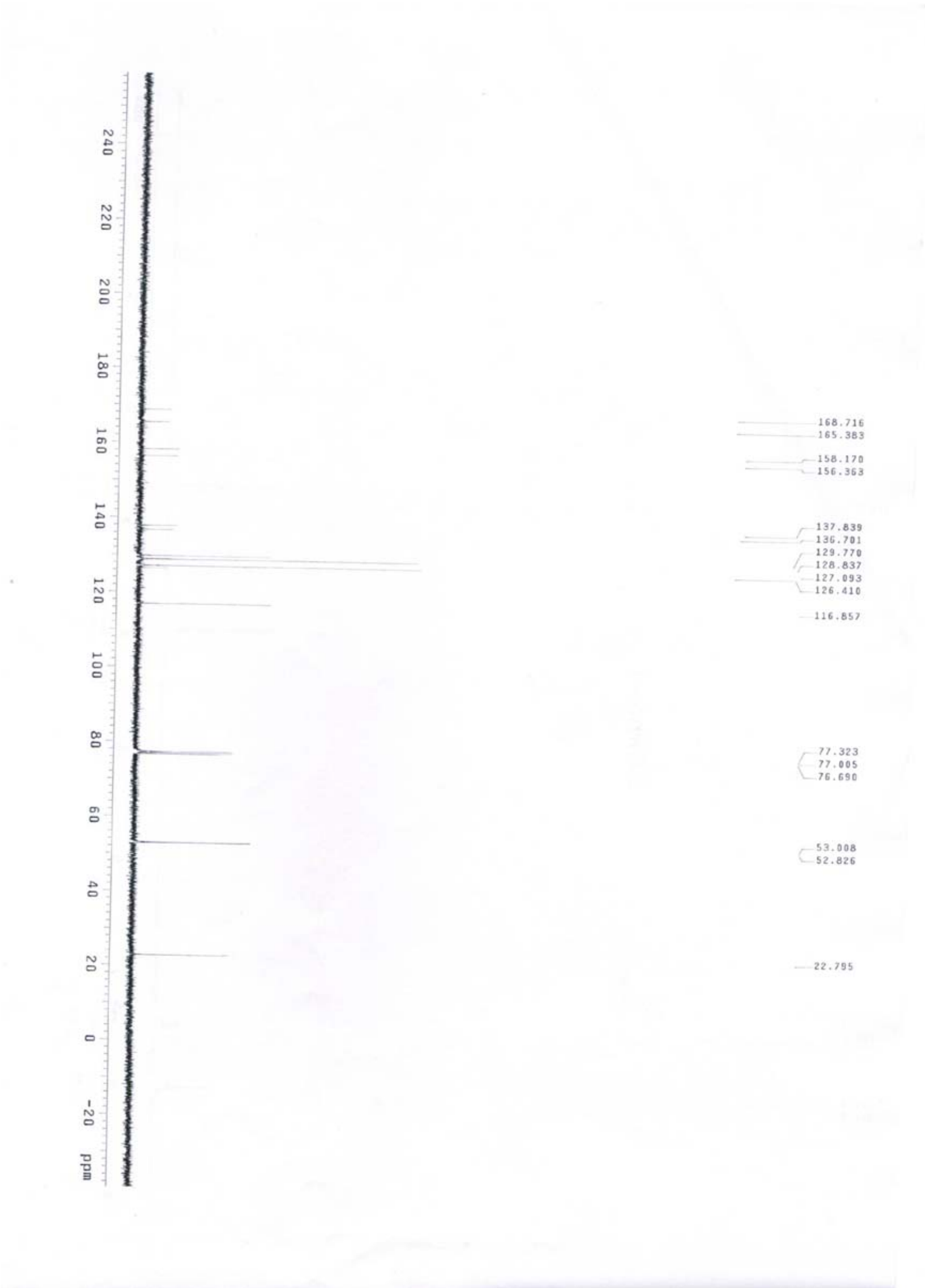
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76.690
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100
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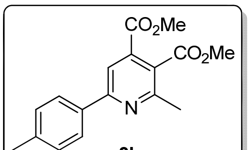
-20
ppm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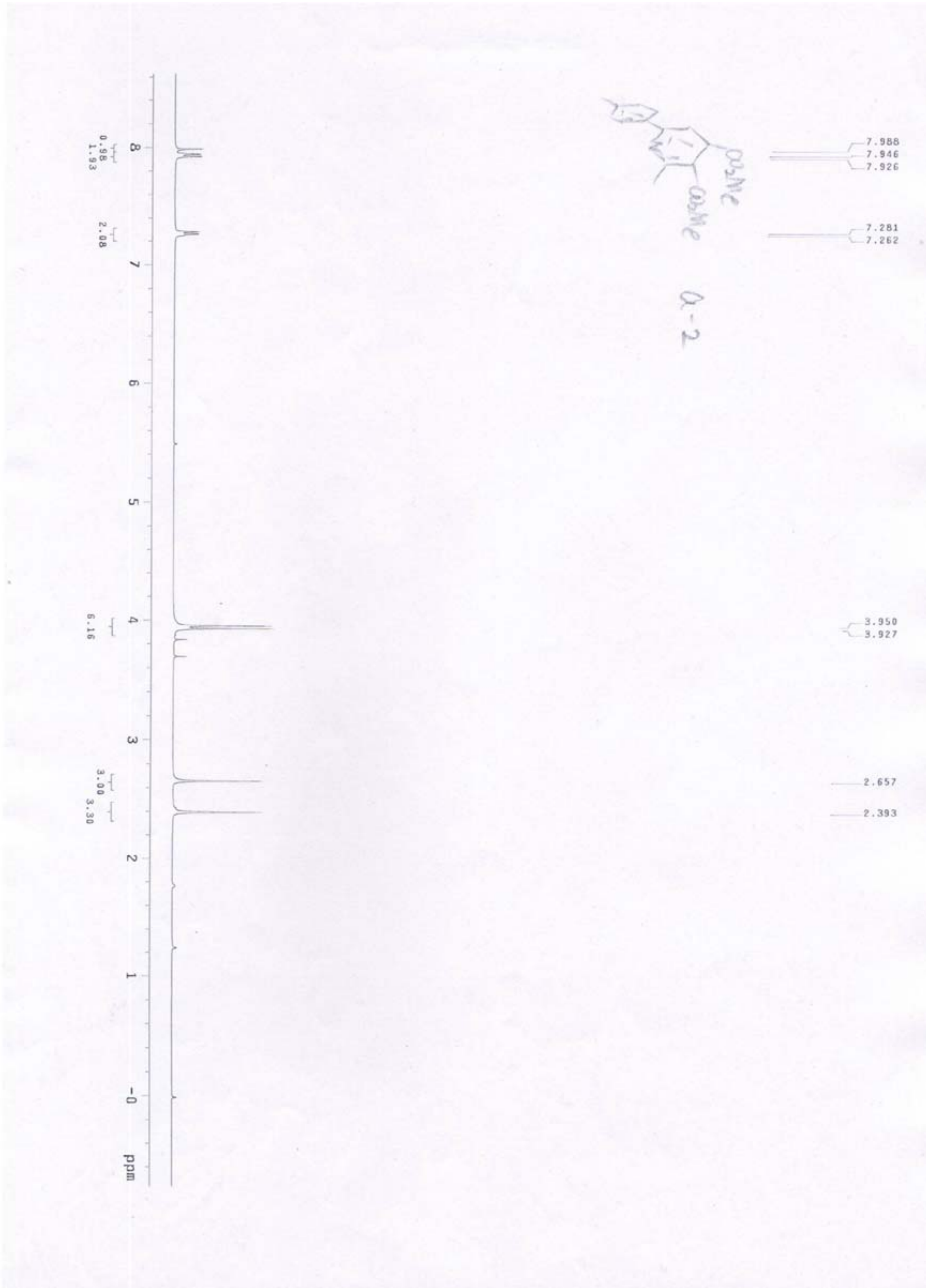
CO2Me
N

3b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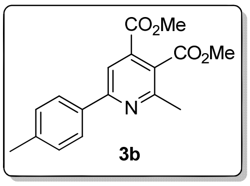
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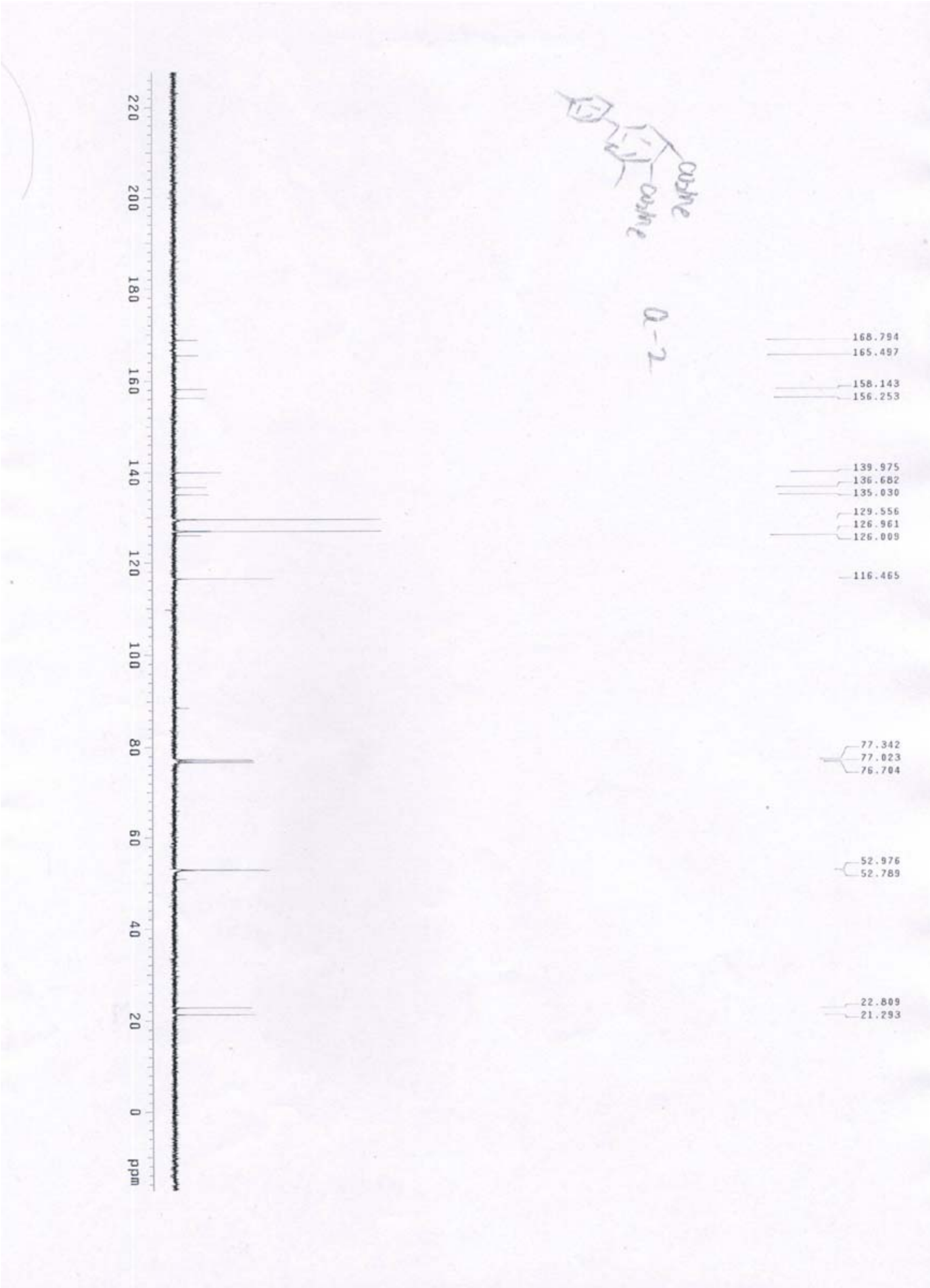

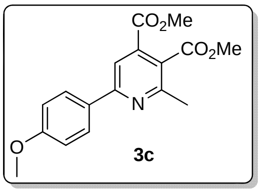
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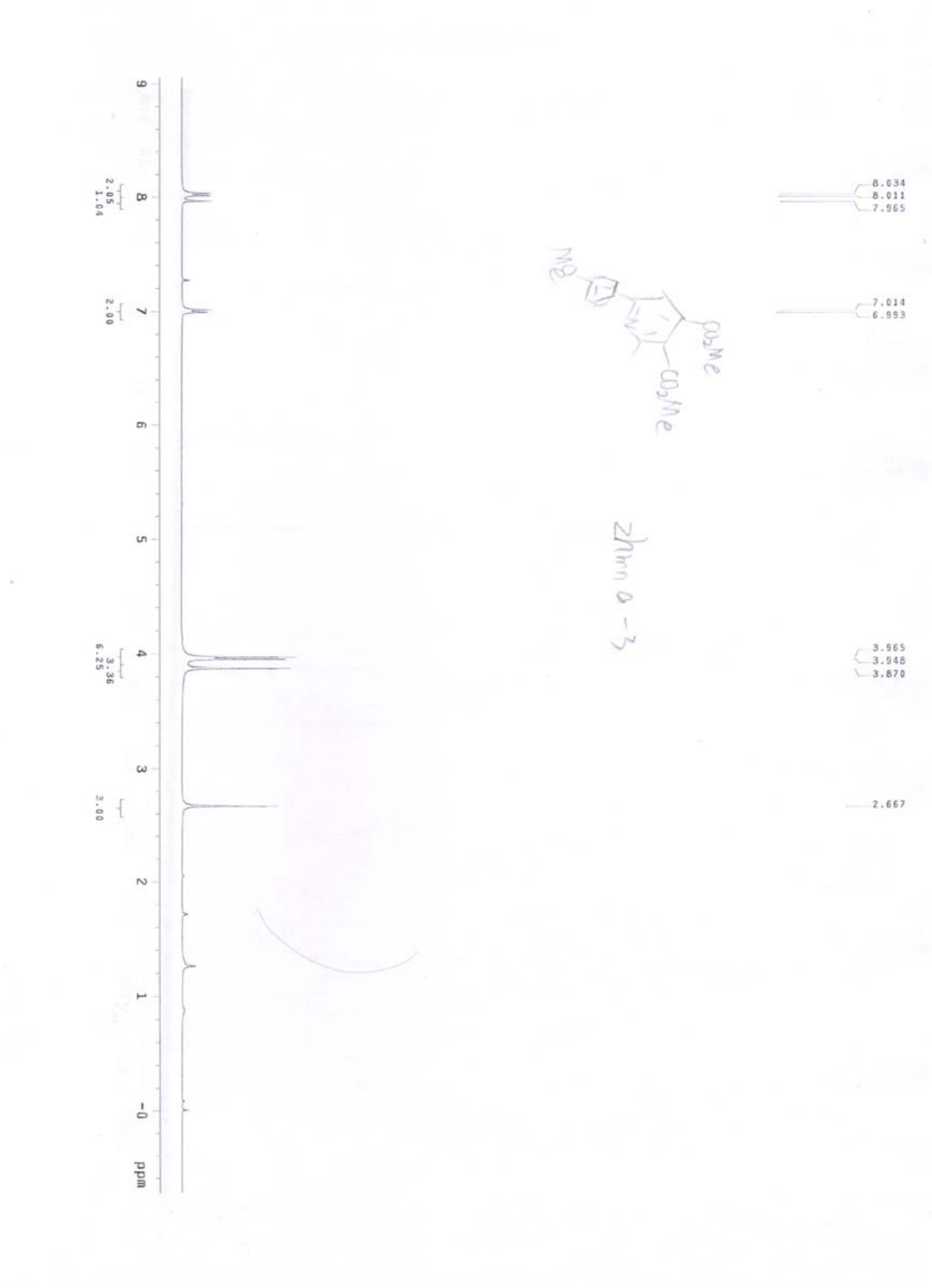
O

3c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3.00
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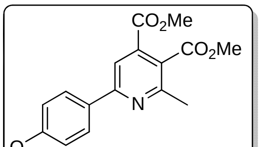
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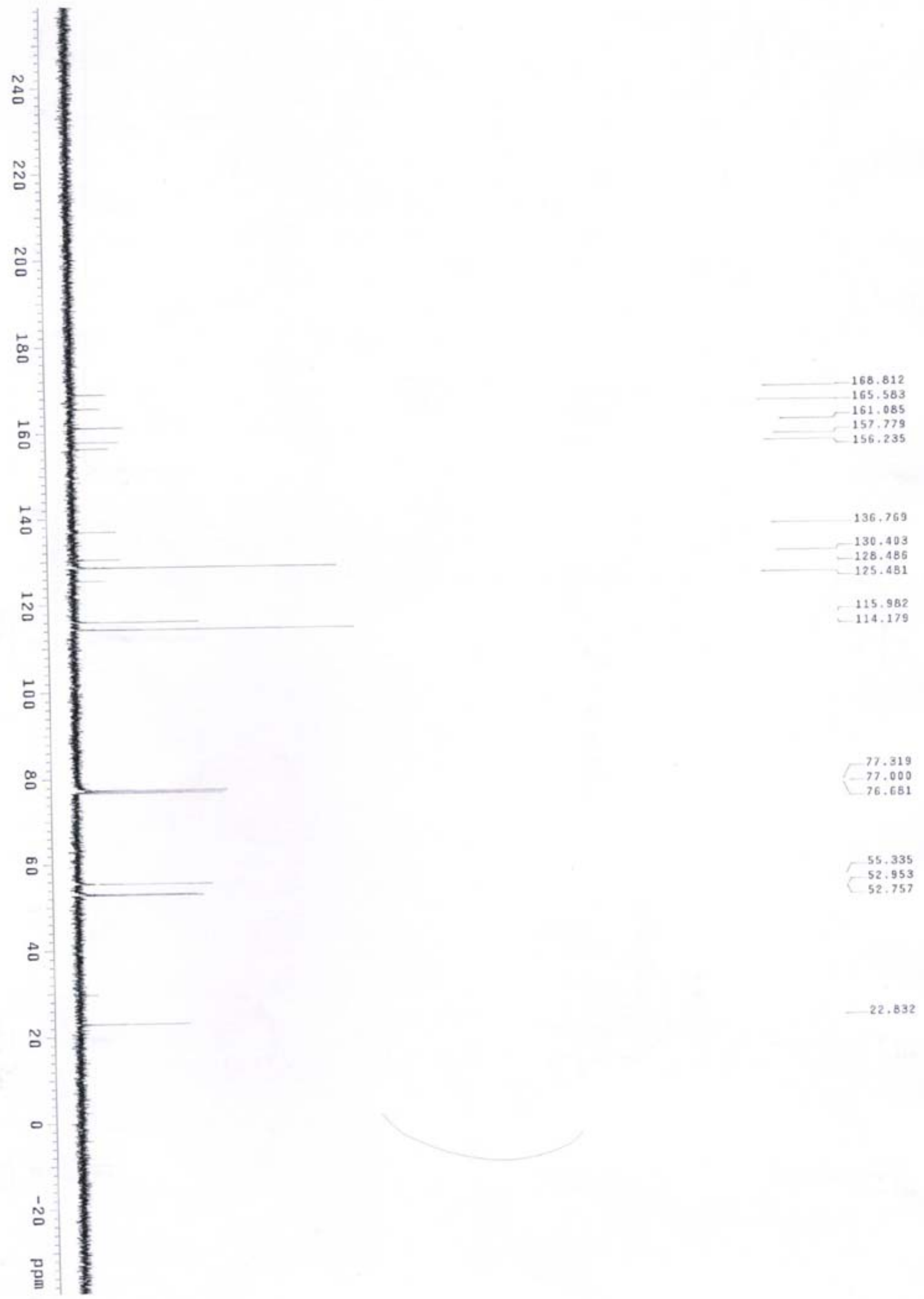
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115.982
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77.000
76.681
55.335
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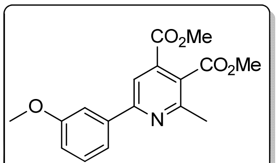

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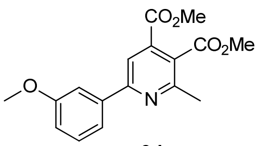
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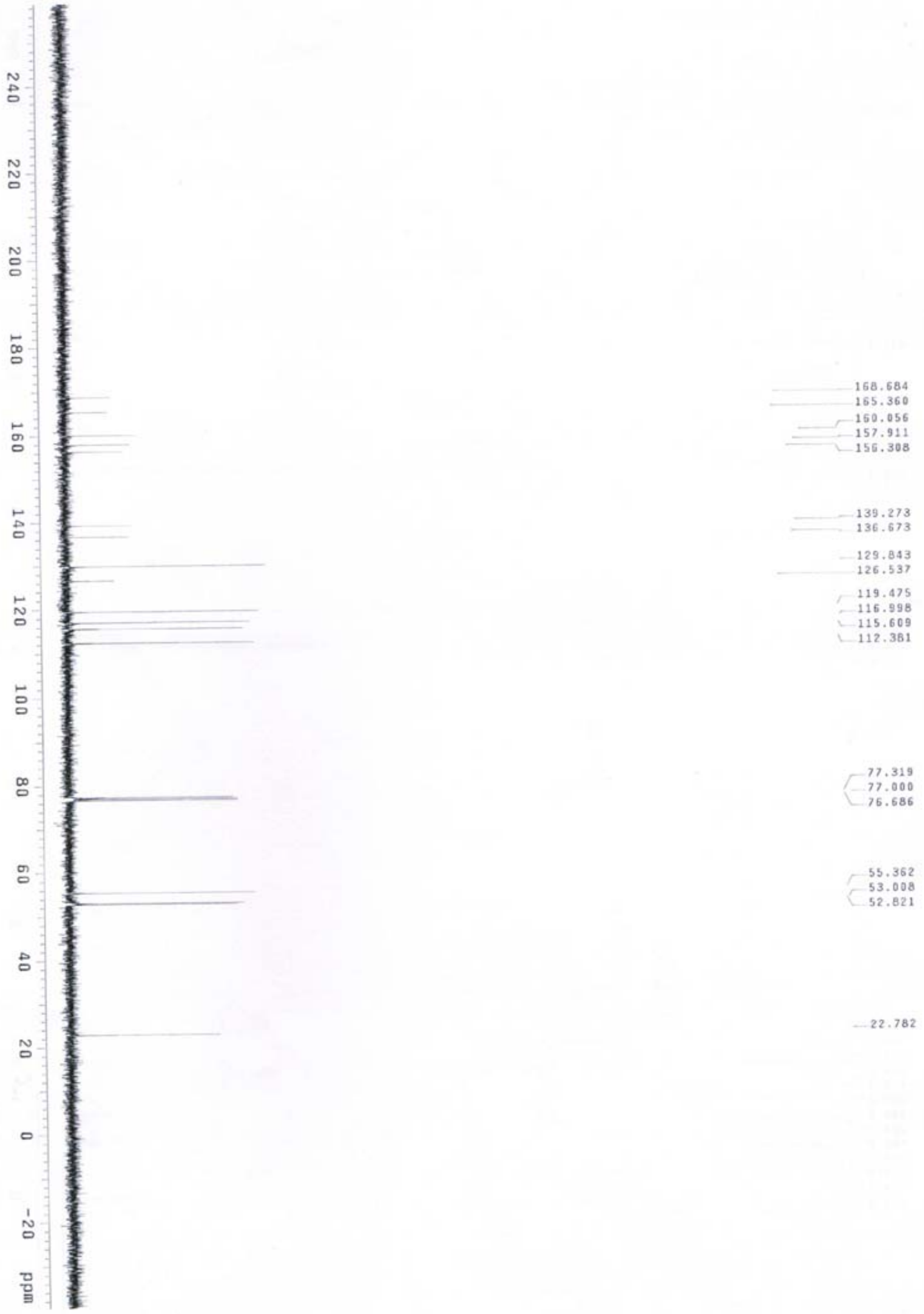
O
N

3d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77.319
77.000
76.686
55.362
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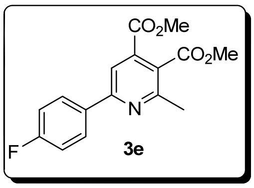
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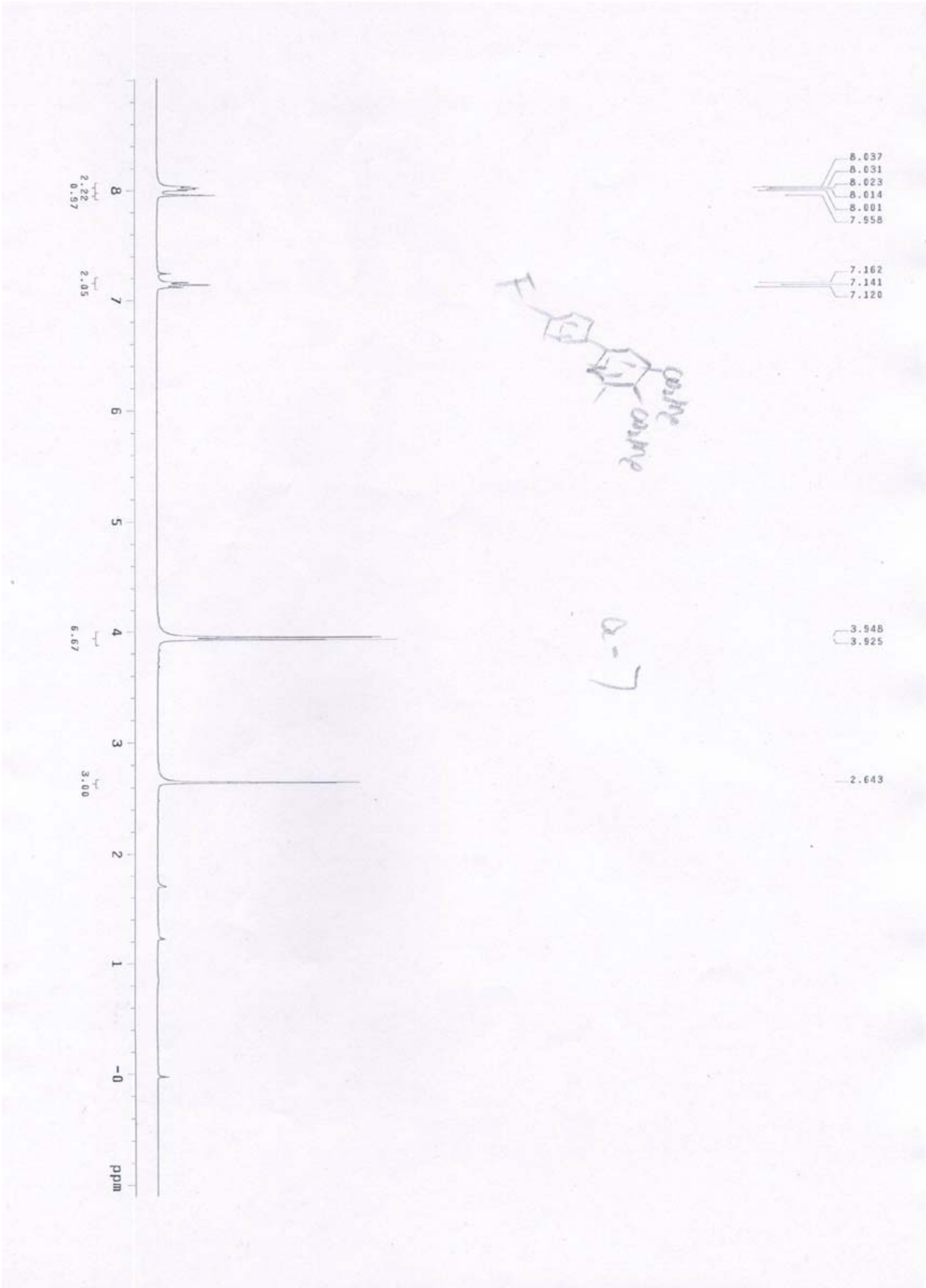
F

3e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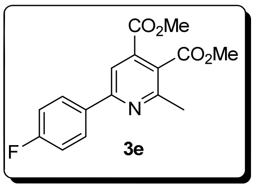
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CO2Me
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F
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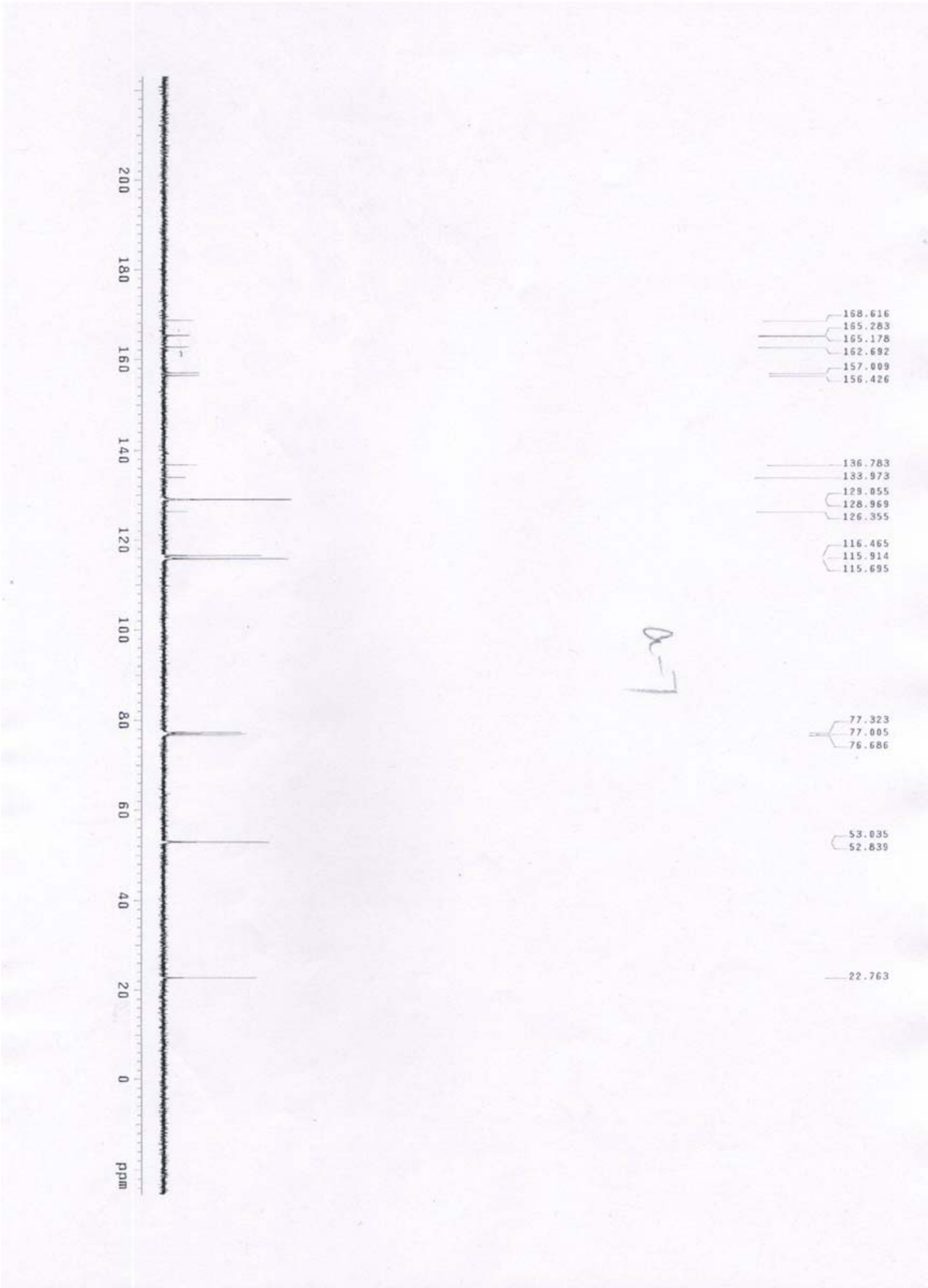
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115.695
77.323
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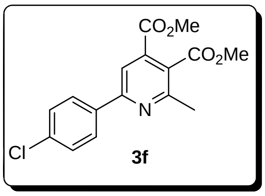
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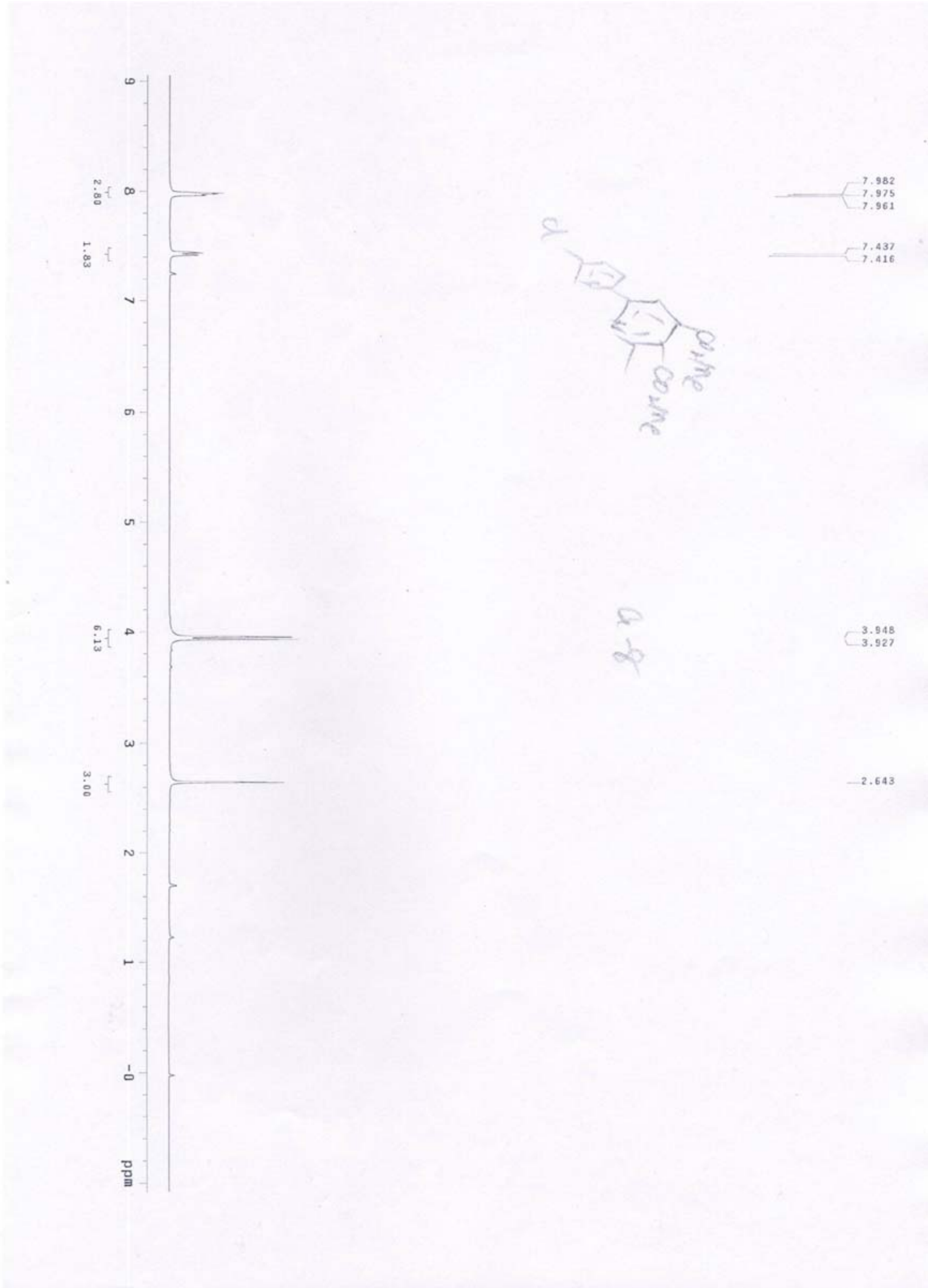
Cl
3f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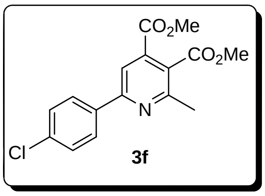
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Cl
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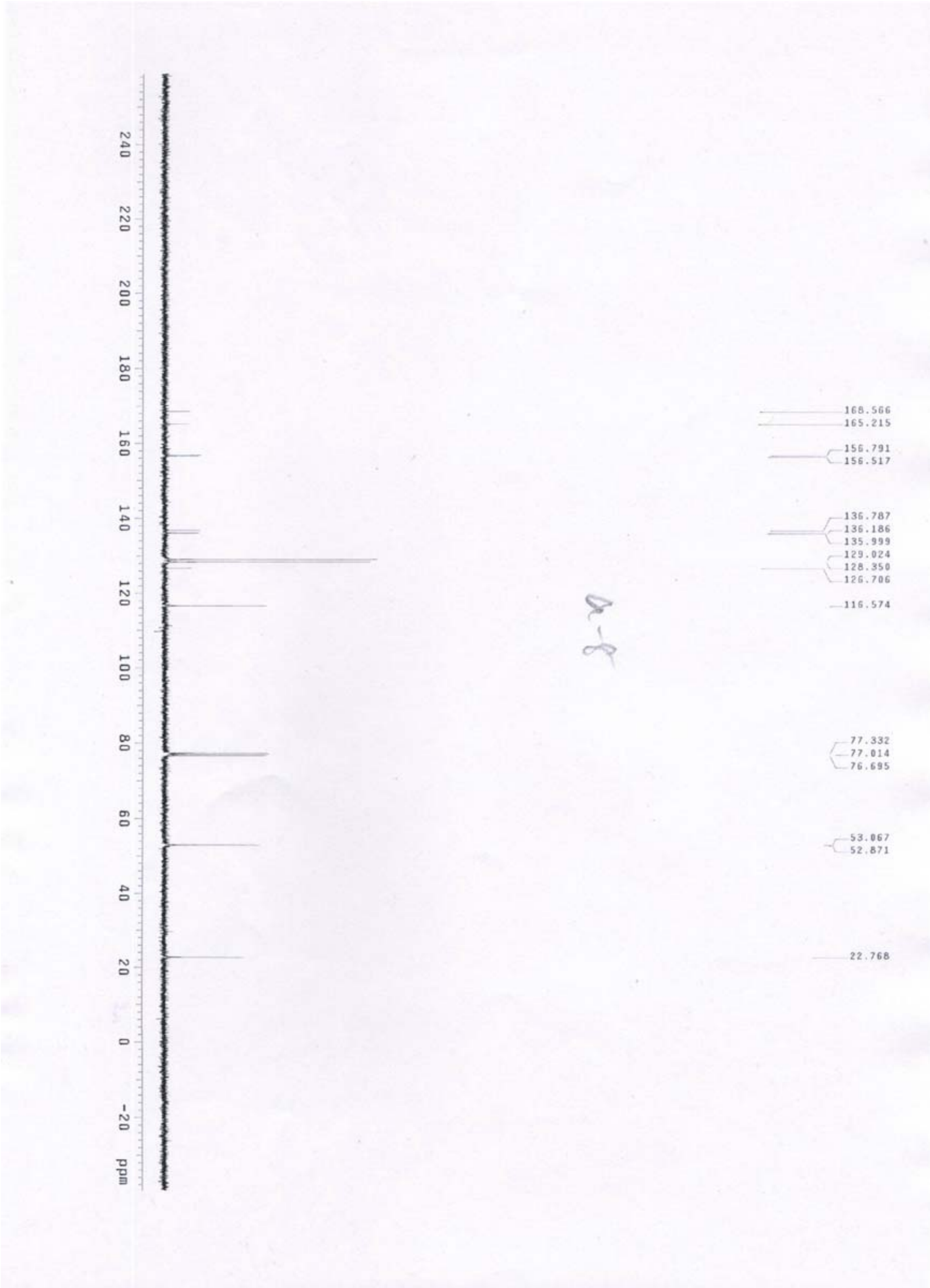
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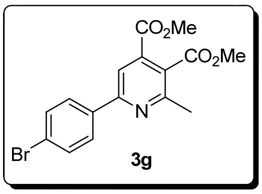
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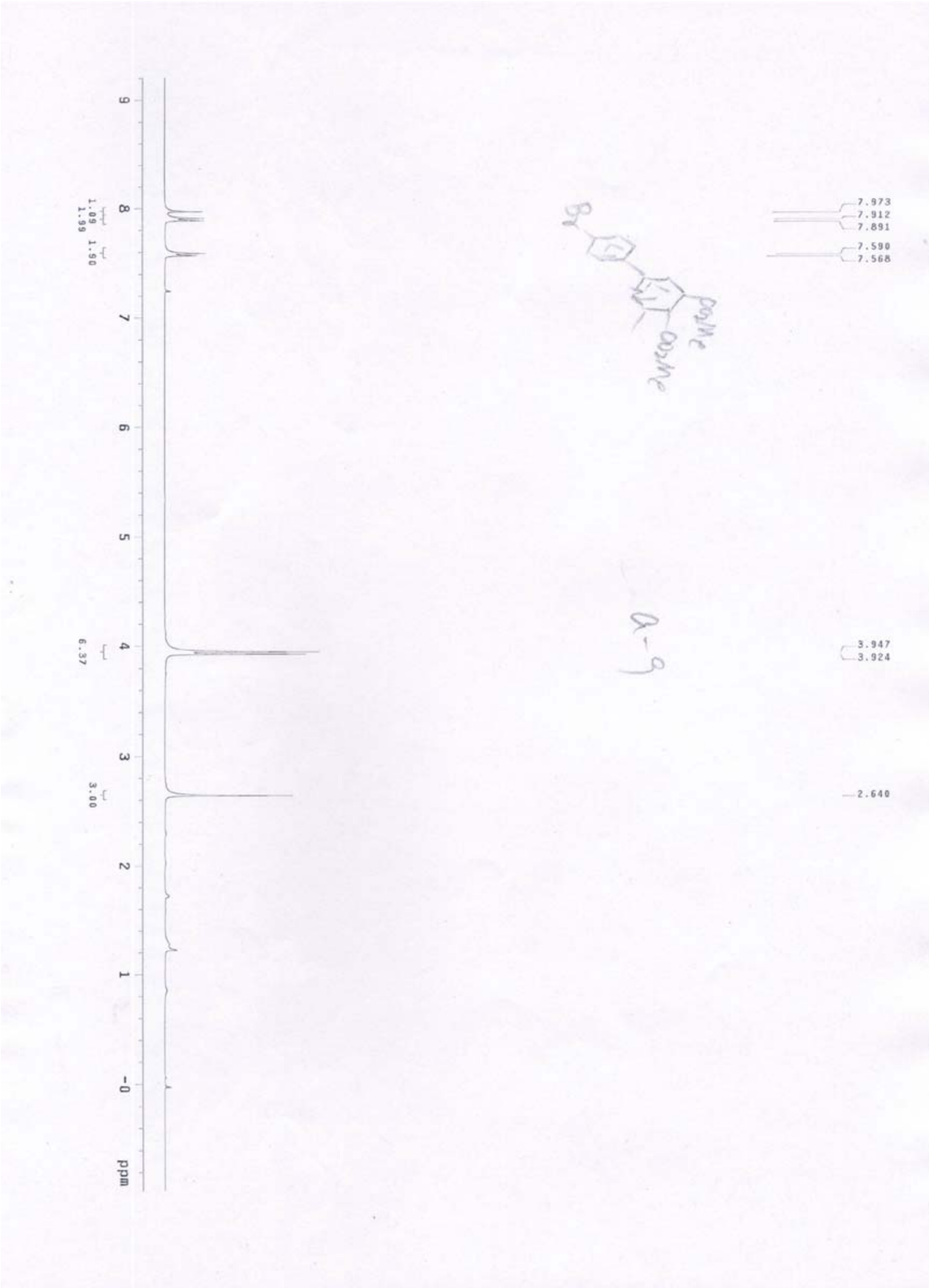
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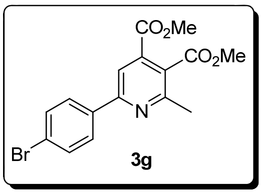
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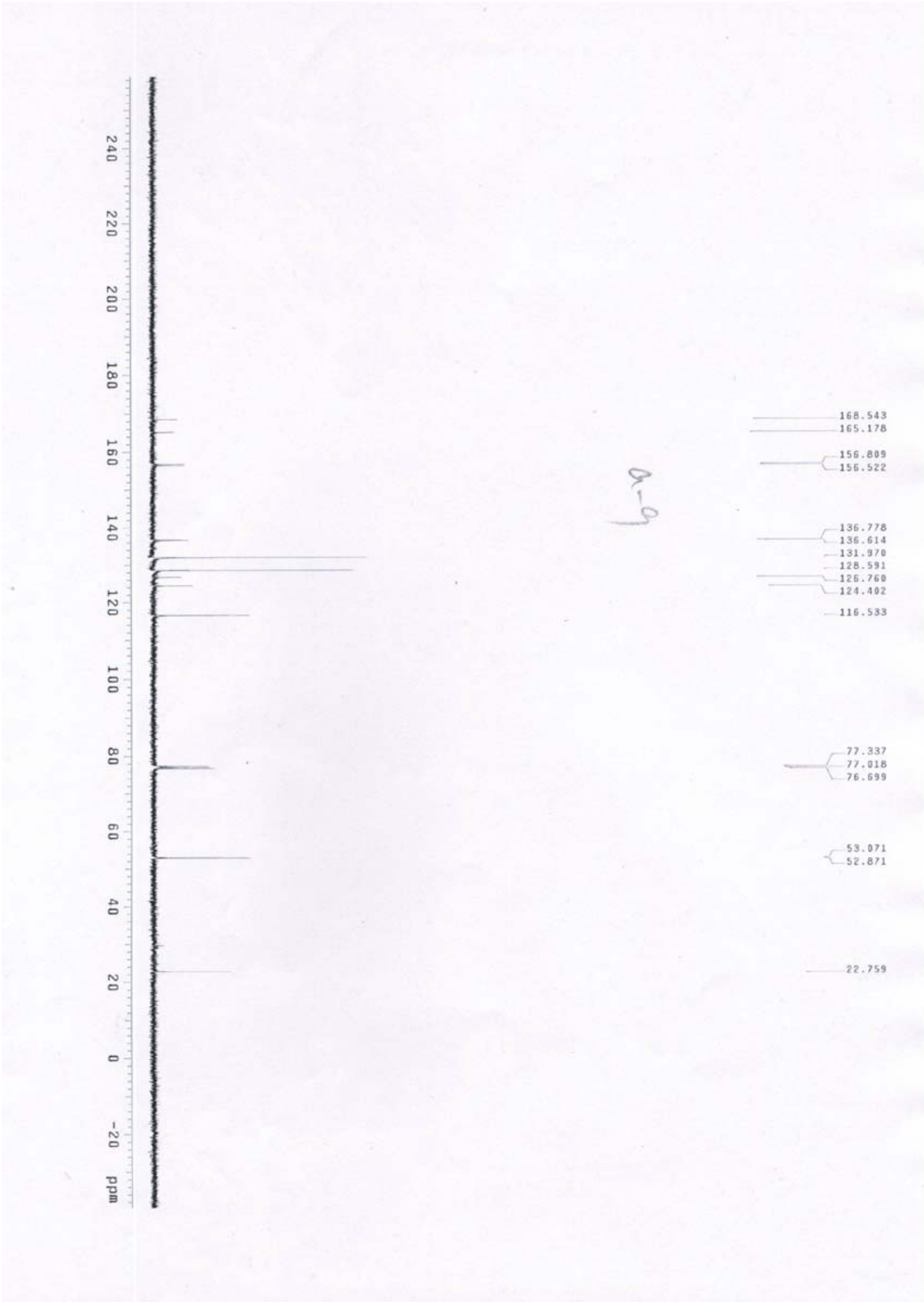
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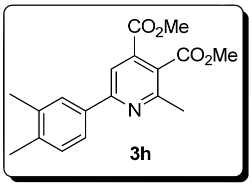
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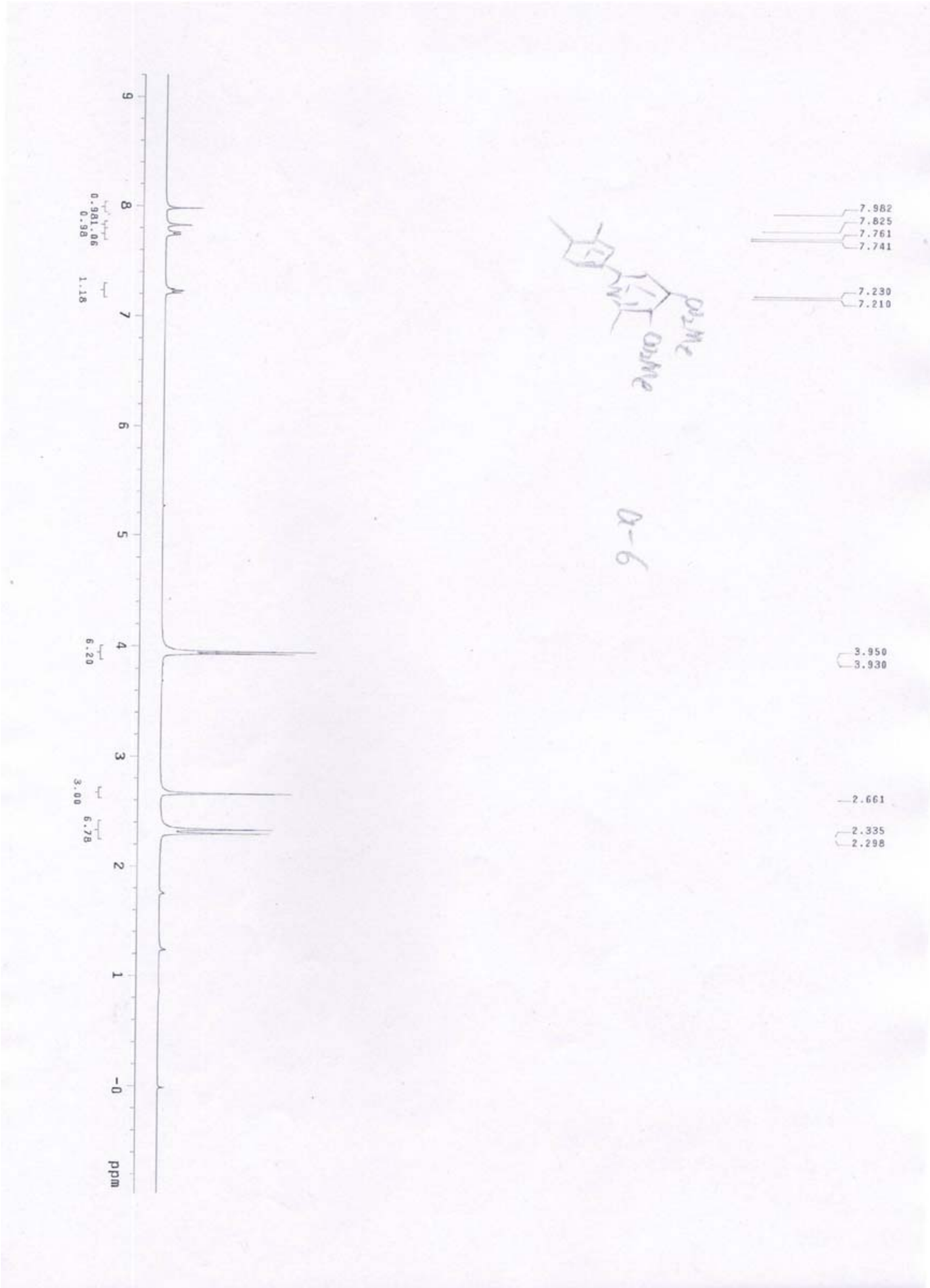
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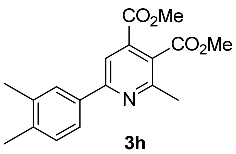
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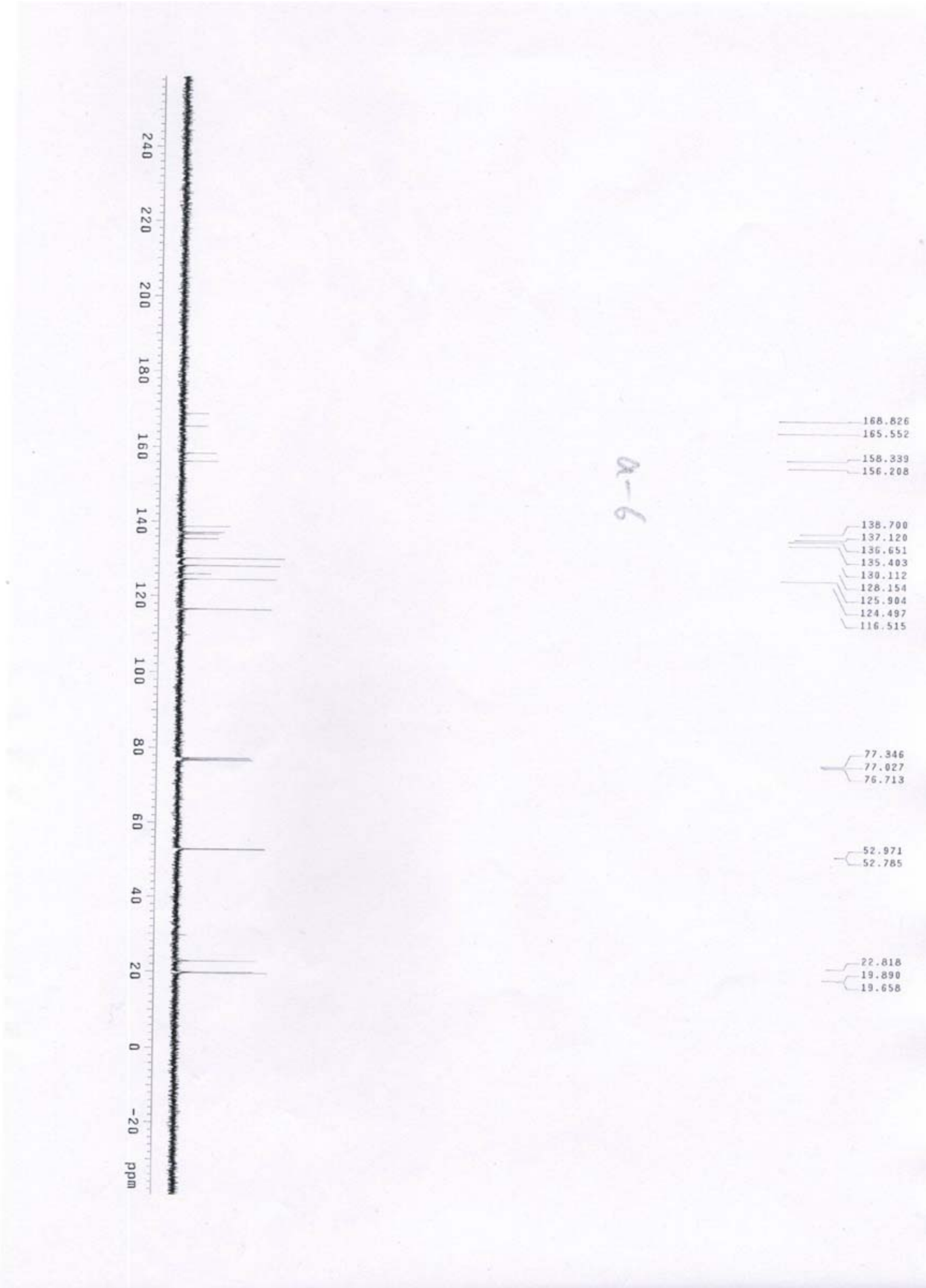
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52.785
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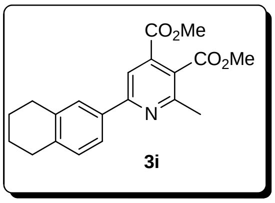

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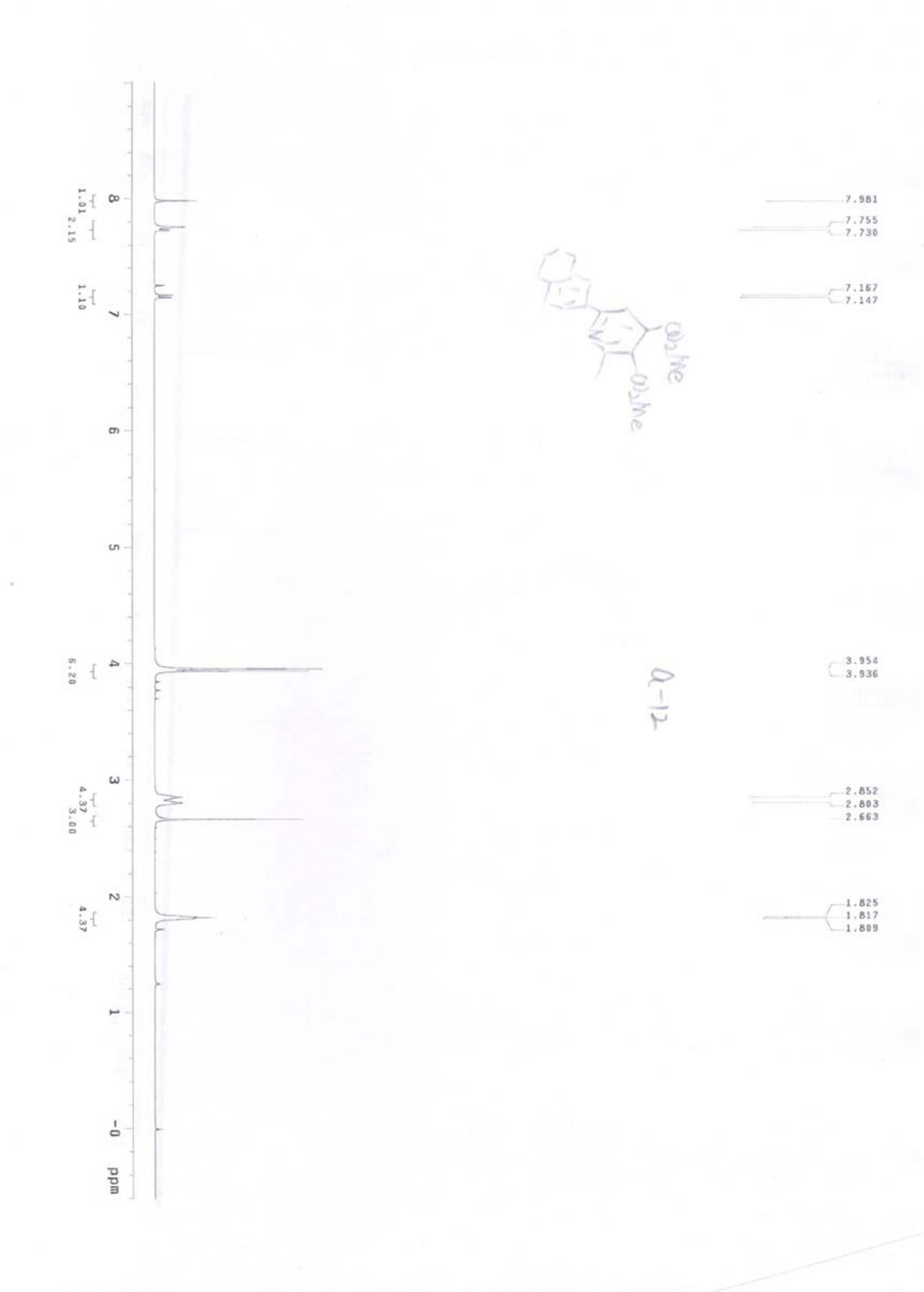

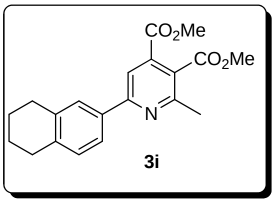
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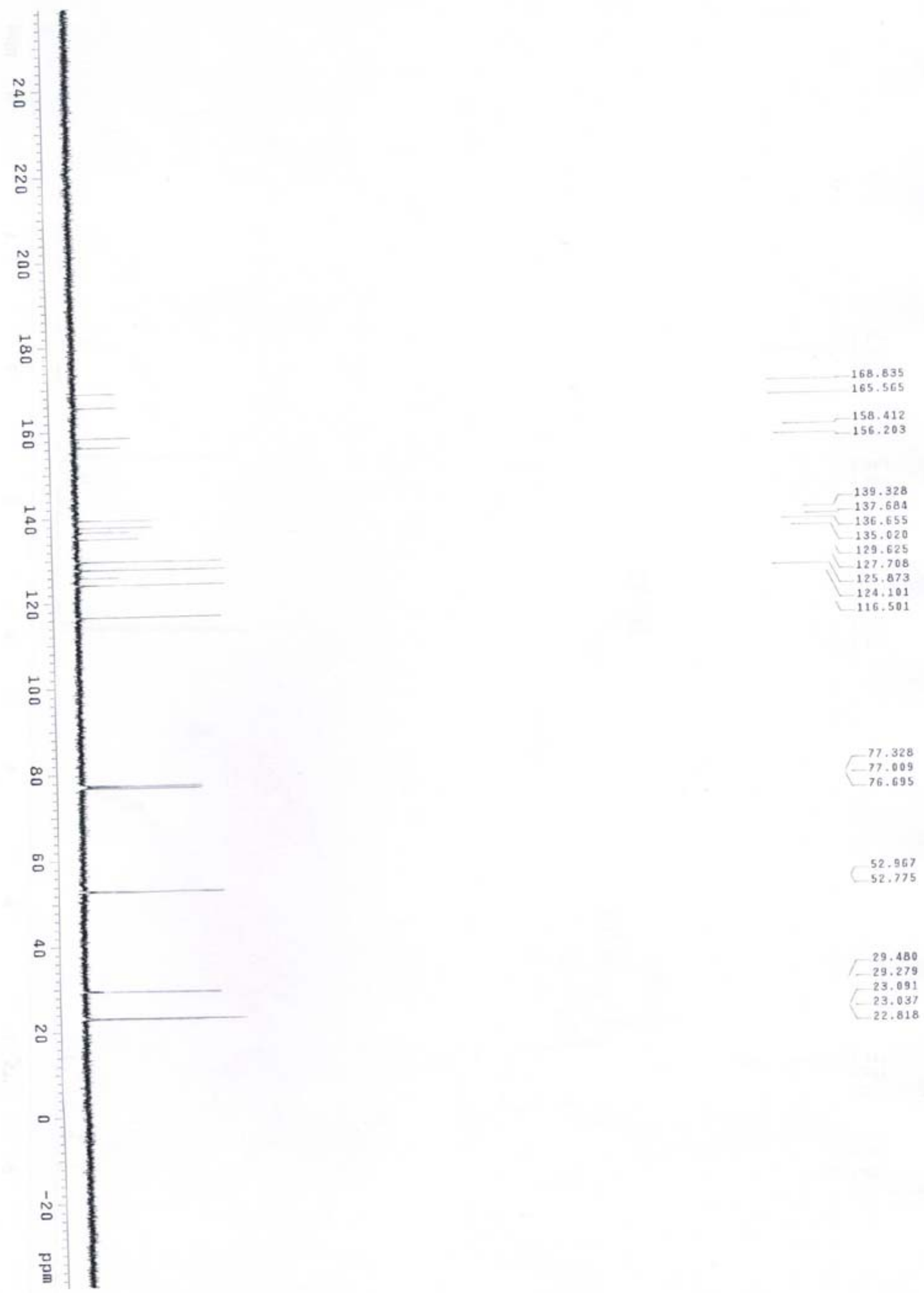
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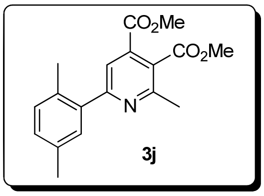
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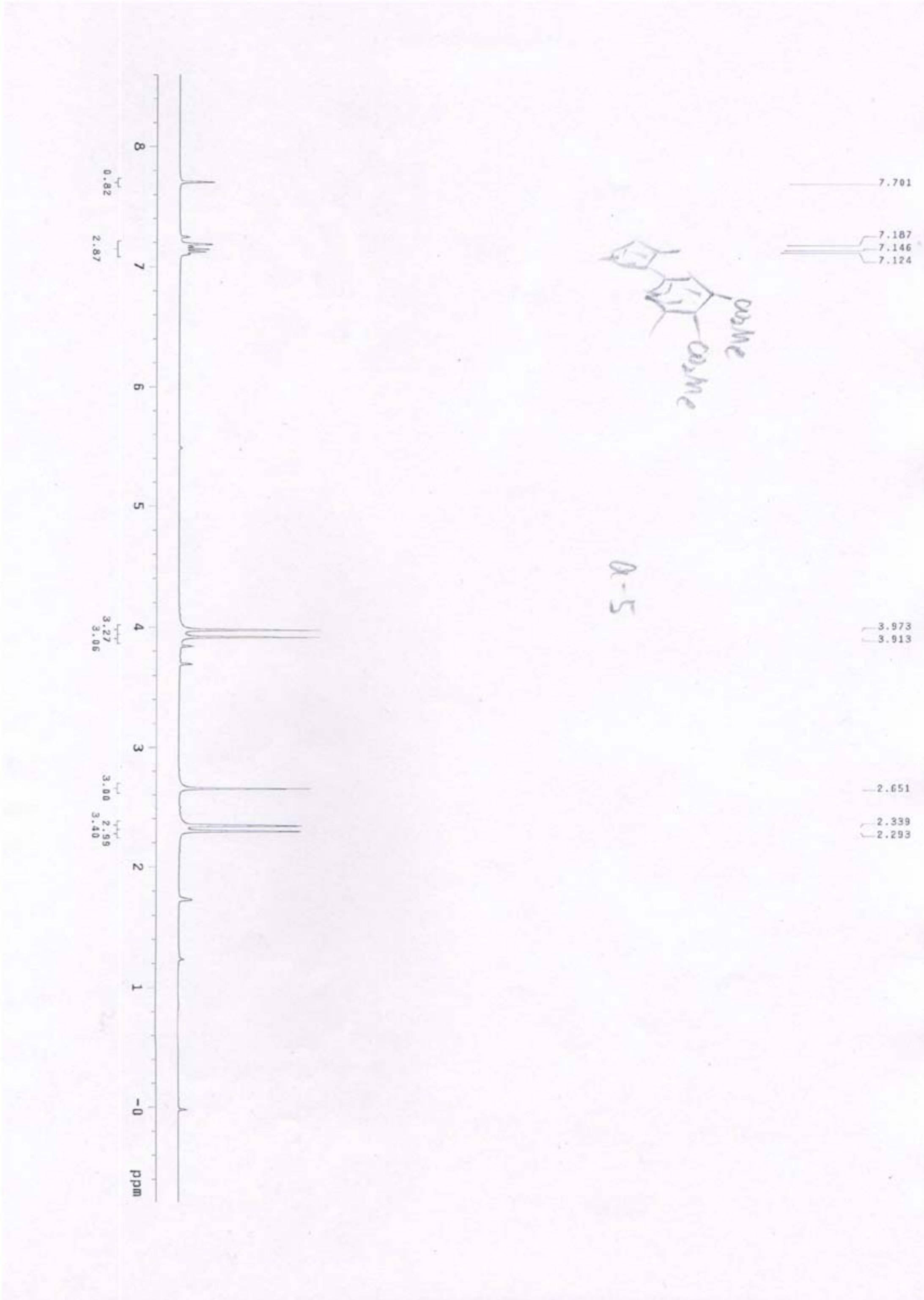
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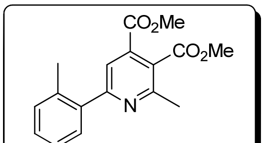
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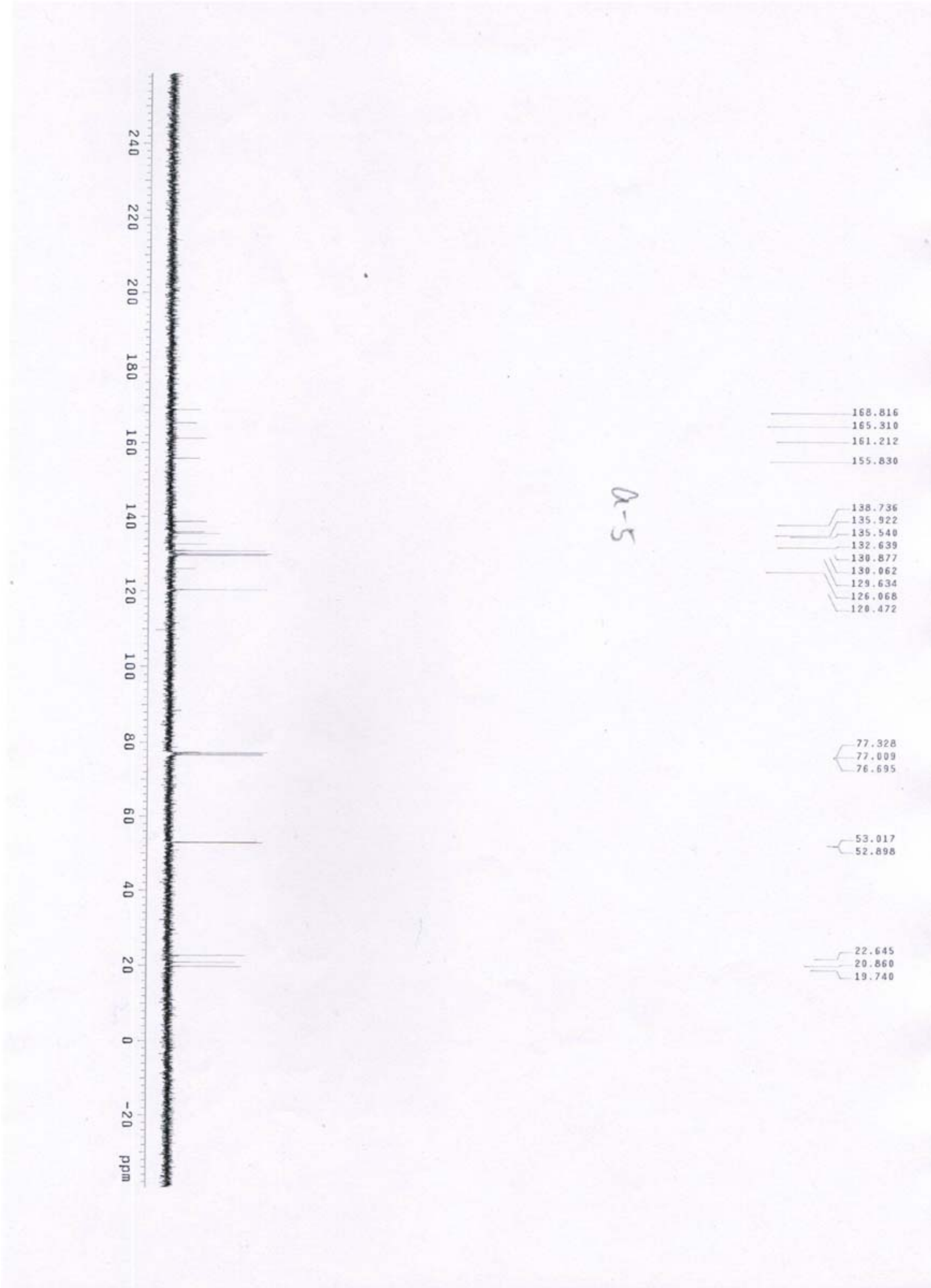
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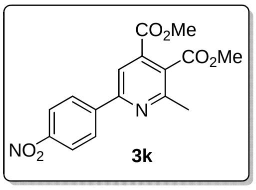
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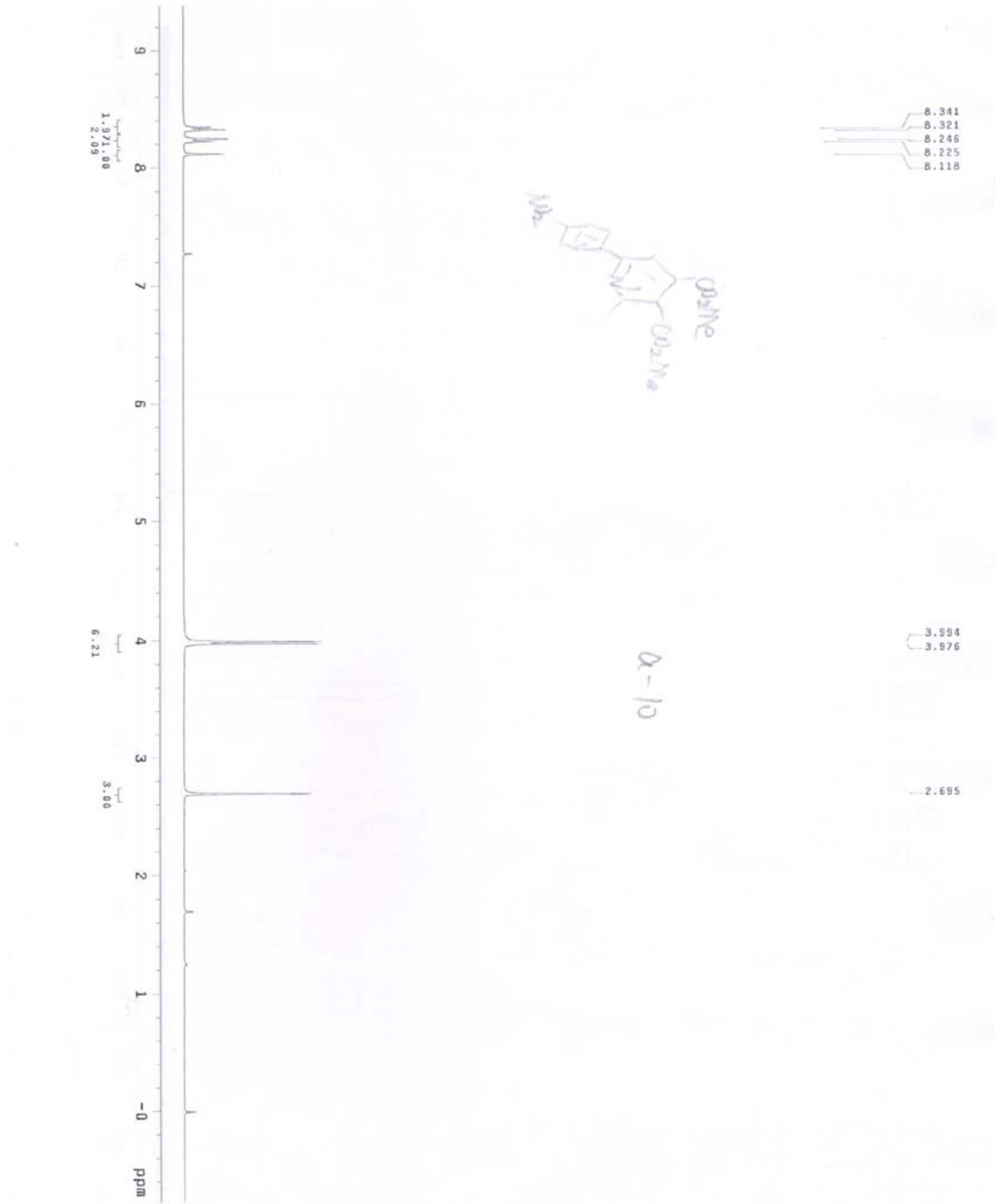
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8.118
3.994
3.976
2.695
1.97
1.00
2.09
6.21
3.00
9
8
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6
5
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-0
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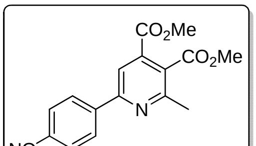
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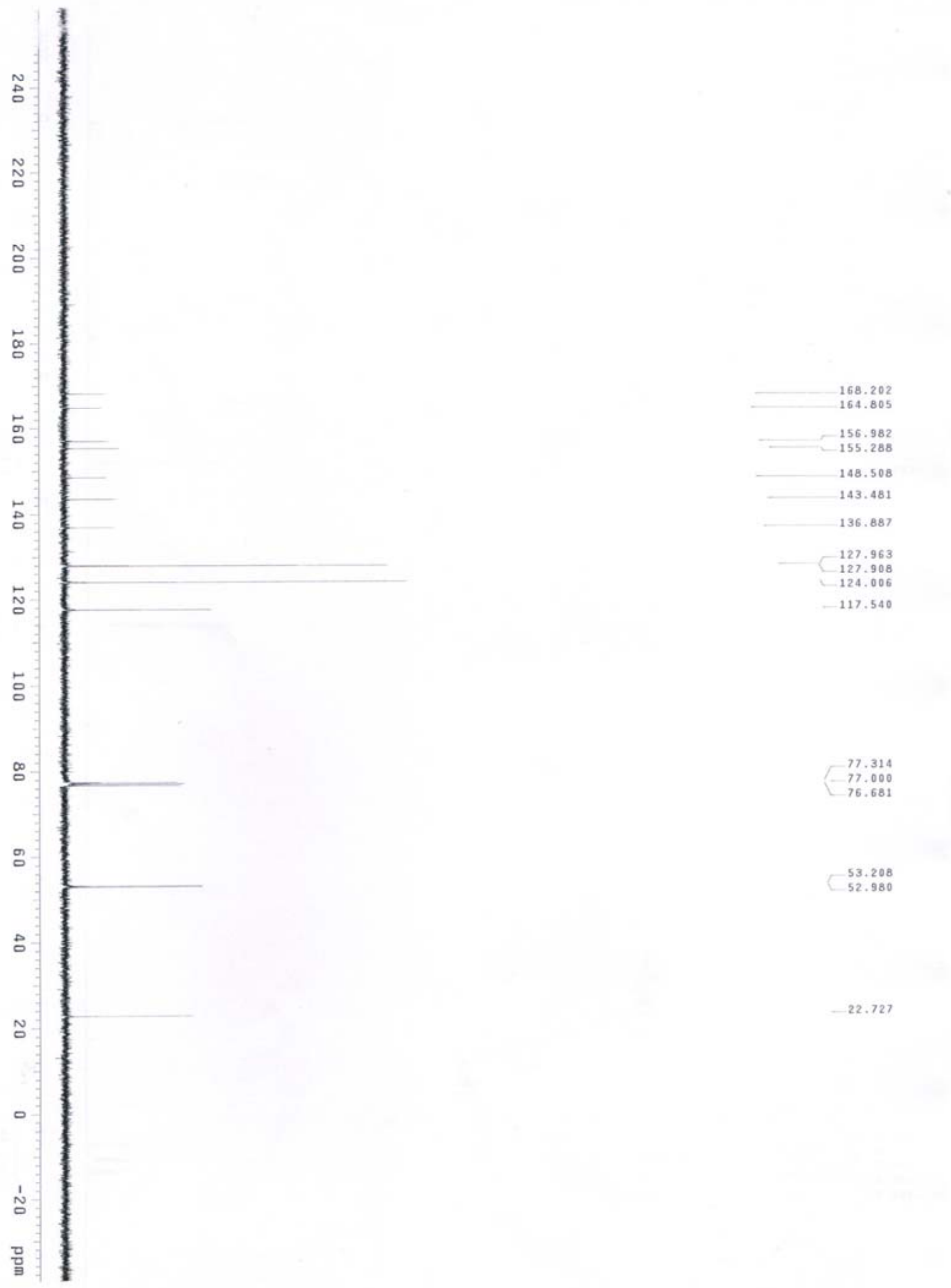
CO2Me
N
NO2

3k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136.887
127.963
127.908
124.006
117.540
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77.000
76.681
53.208
52.980
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180
160
140
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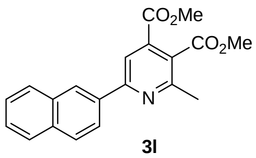
ppm


CO2Me
CO2Me
N

3l


8.524
8.182
8.179
8.156
7.959
7.941
7.920
7.868
7.860
7.854
7.845
7.523
7.515
7.507
7.498
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3.961
2.718
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1.08
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6.05
3.00
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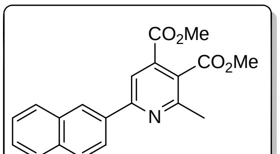
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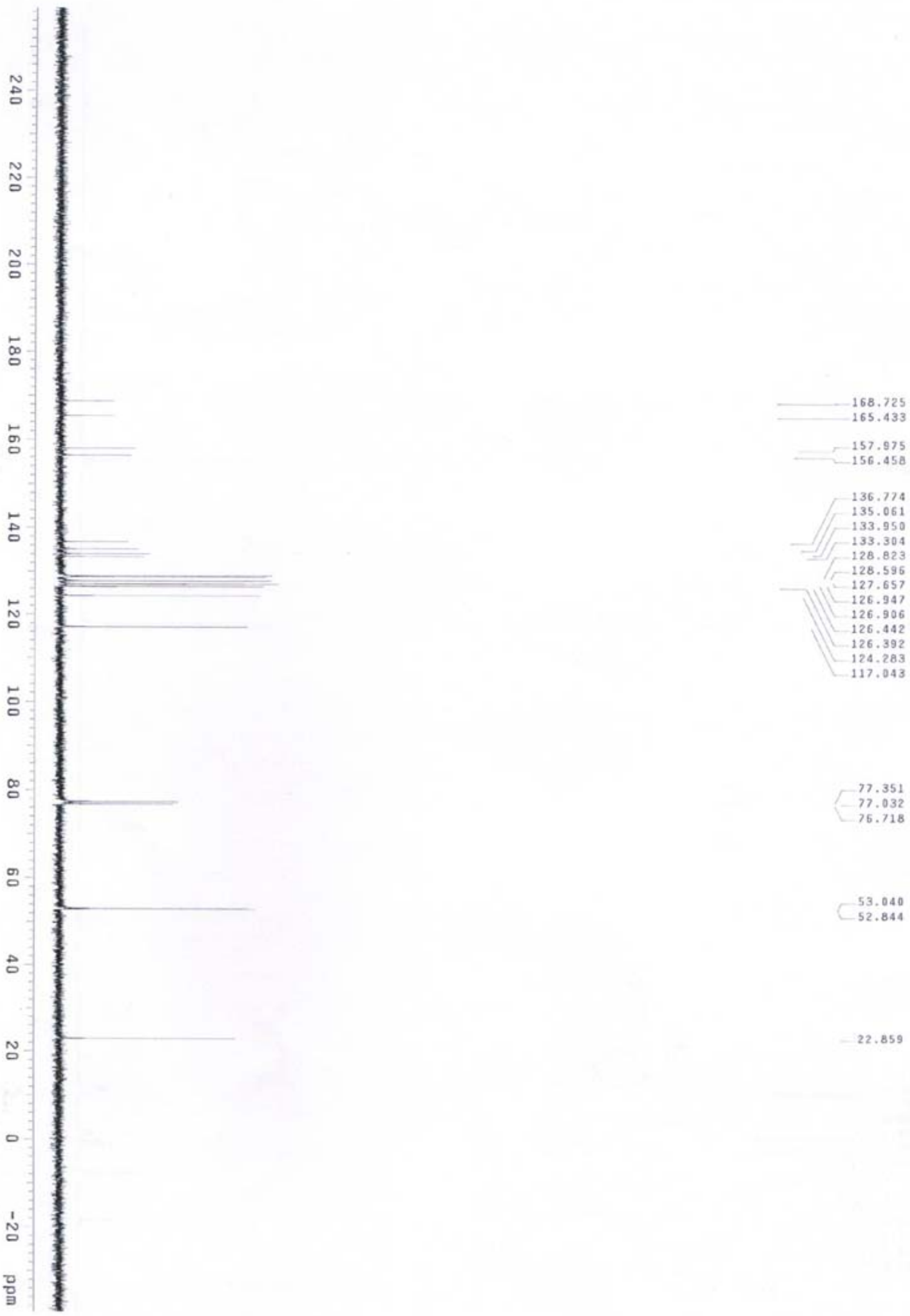
CO2Me
N

3l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133.304
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128.596
127.657
126.947
126.906
126.442
126.392
124.283
117.043
77.351
77.032
76.718
53.040
52.844
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220
200
180
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140
120
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80
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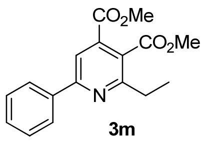
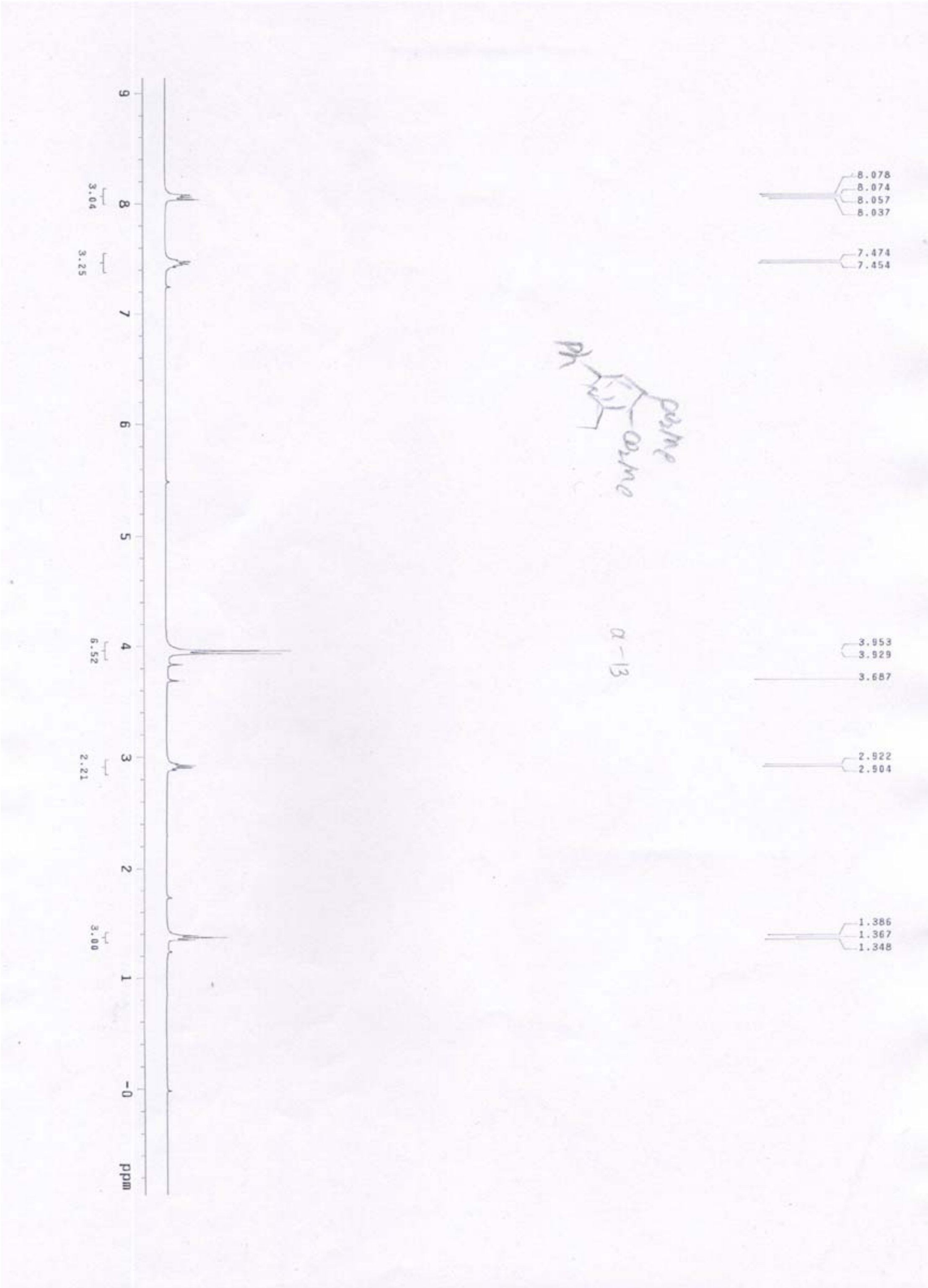
40
20
0
-20
ppm



3m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8.074
8.057
8.037
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3.929
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2.904
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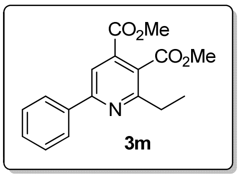
1.367
1.348
ppm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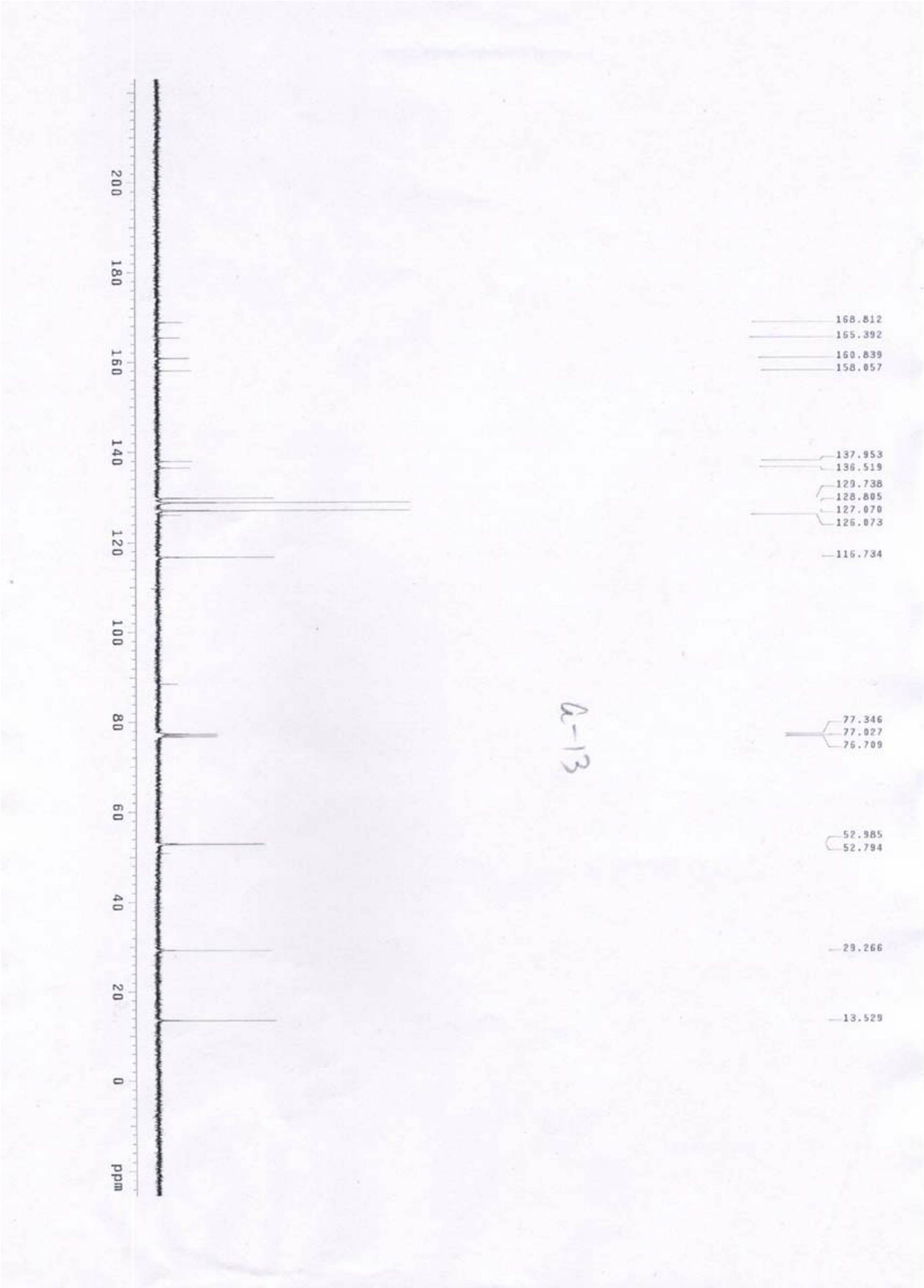
CO2Me
N

3m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137.953
136.519
129.738
128.805
127.070
126.073
116.734
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77.027
76.709
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52.794
29.266
13.529
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180
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140
120
100
80
60
40
20
0
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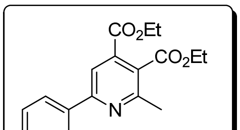
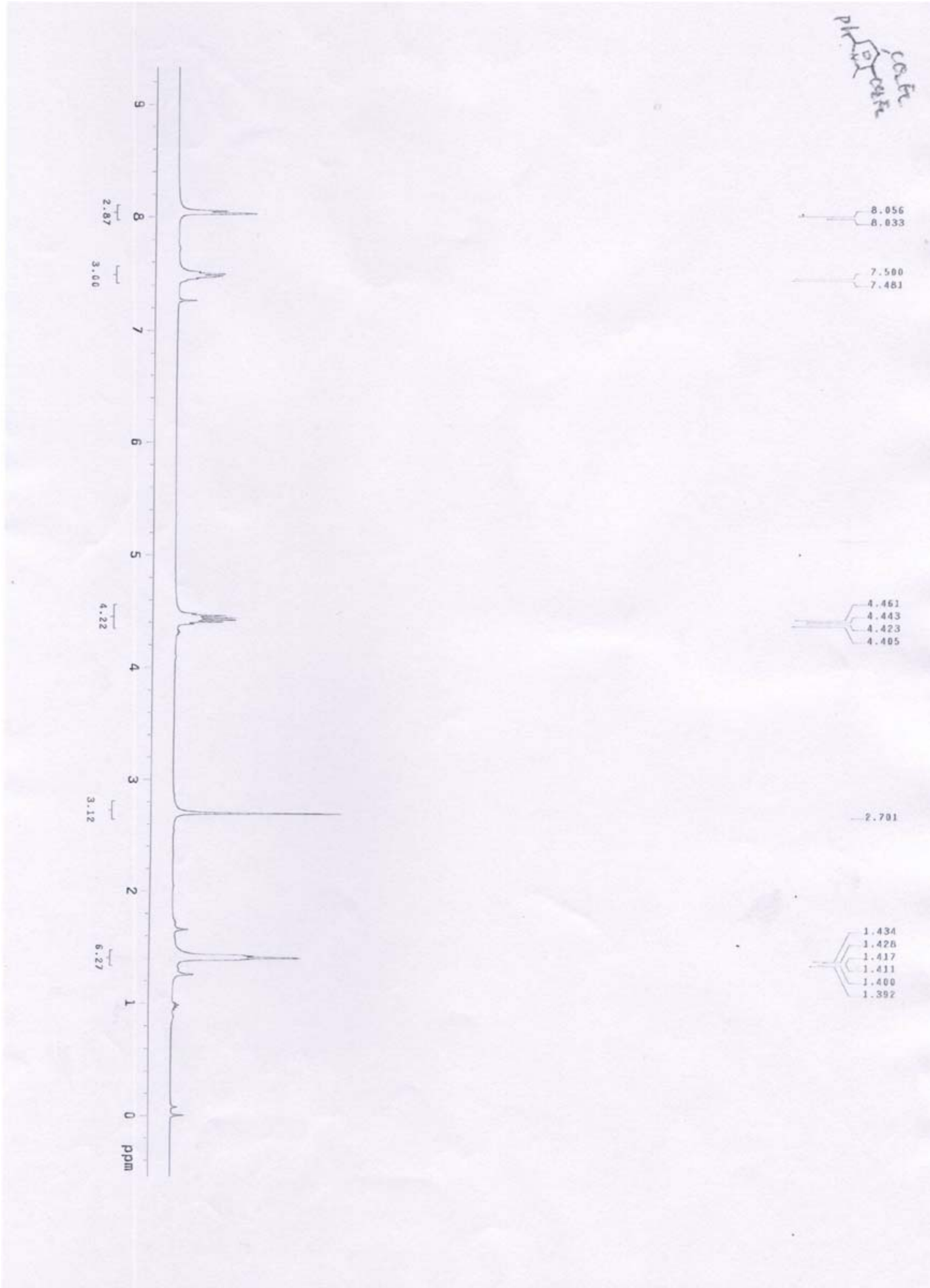

CO2Et
CO2Et
N

3n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8.033
7.500
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4.423
4.405
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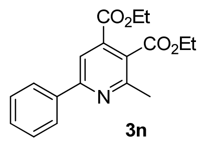
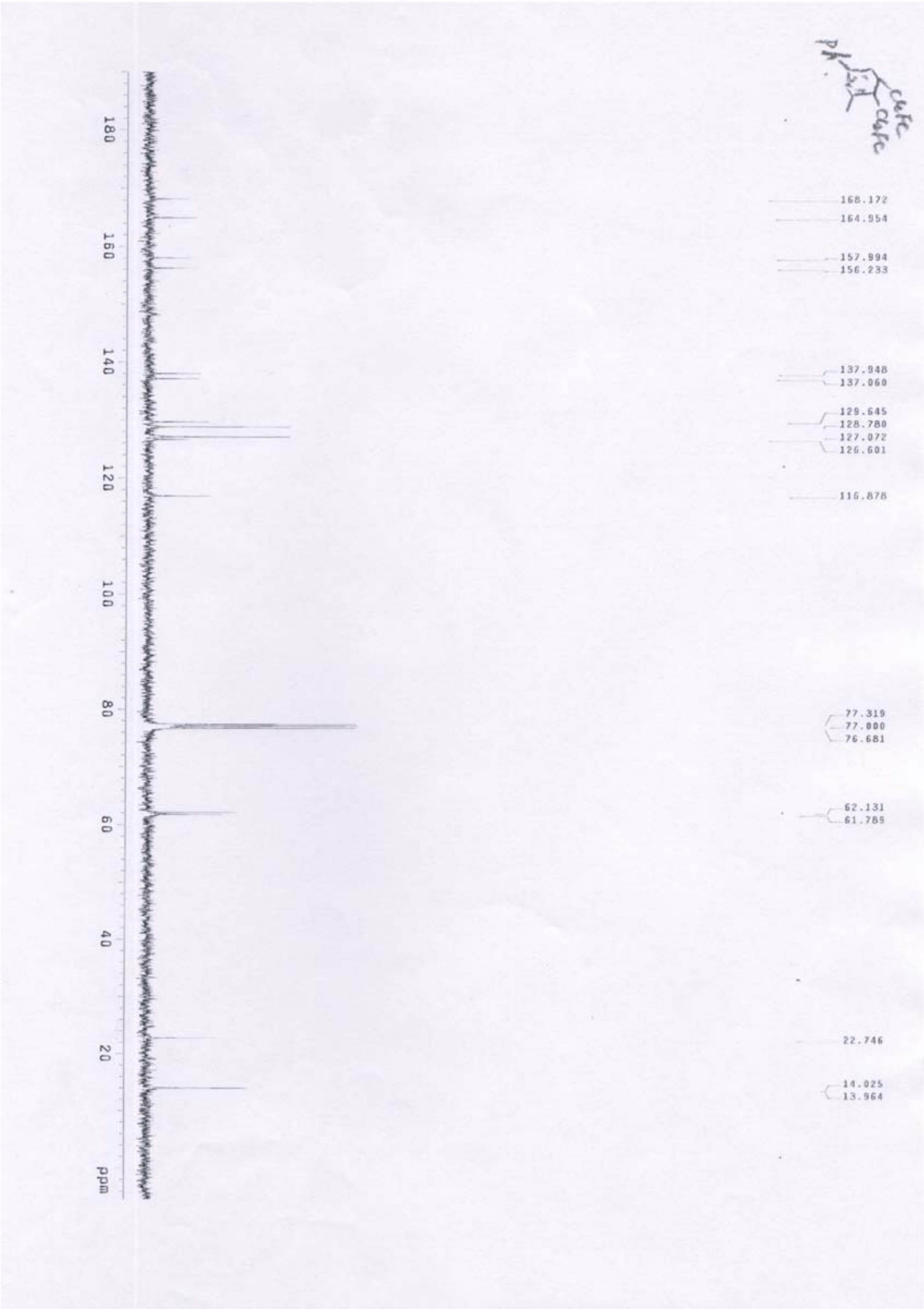
1.428
1.417
1.411
1.400
1.392
ppm


CO2Et
CO2Et
N

3n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137.060
129.645
128.780
127.072
126.601
116.878
77.319
77.000
76.681
62.131
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22.746
14.025
13.964
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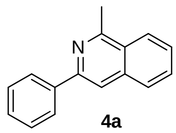
140
120
100
80
60
40
20
ppm



4a


8.107
8.089
8.045
8.025
7.845
7.775
7.755
7.602
7.584
7.564
7.501
7.477
7.457
7.437
7.373
7.356
2.977
11
10
9
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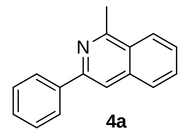
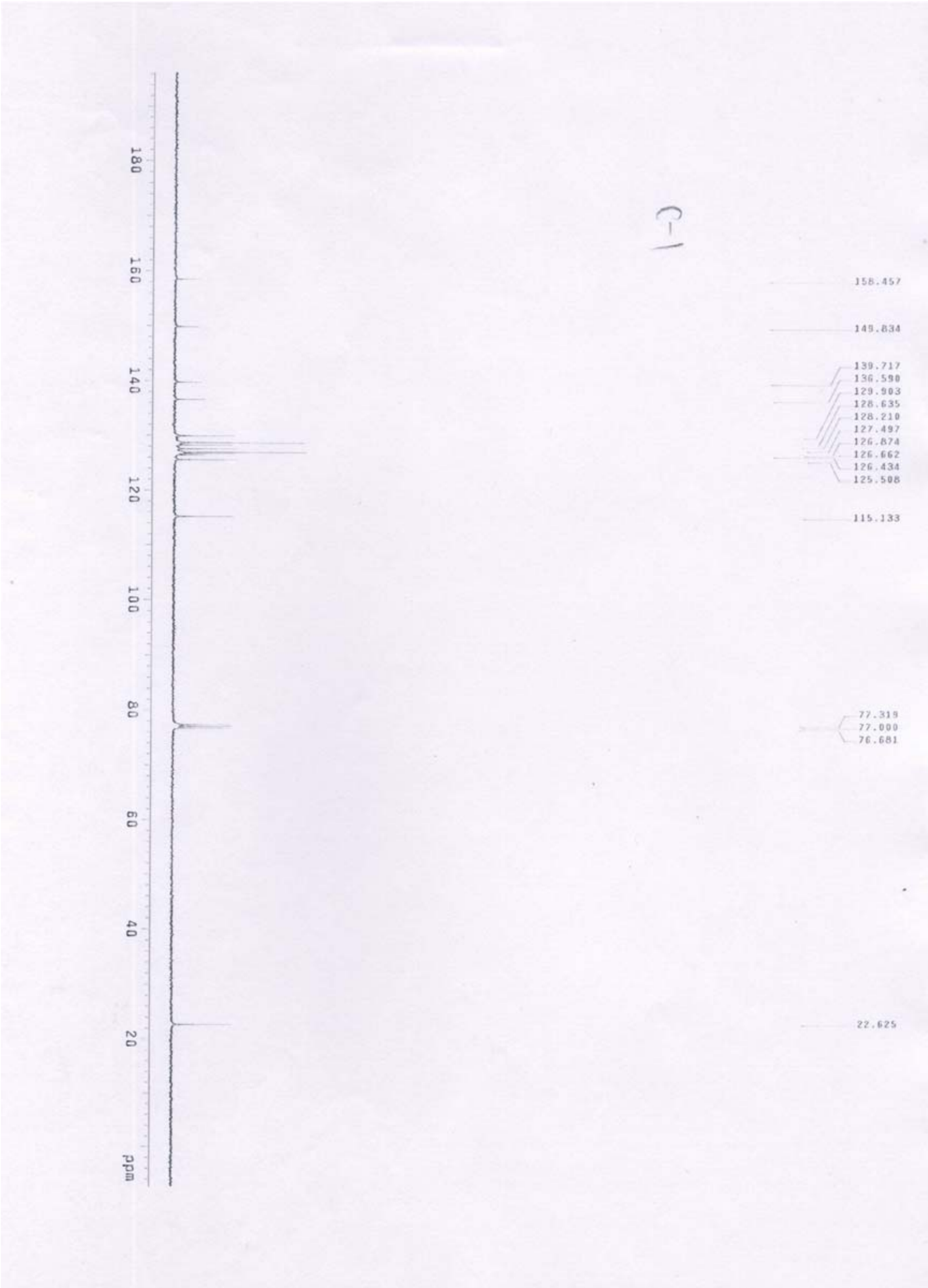
7
6
5
4
3
2
1
-0
ppm



4a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136.590
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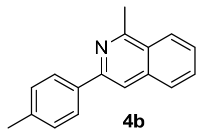
128.210
127.497
126.874
126.662
126.434
125.508
115.133
77.319
77.000
76.681
22.625
180
160
140
120
100
80
60
40
20
ppm
C-1



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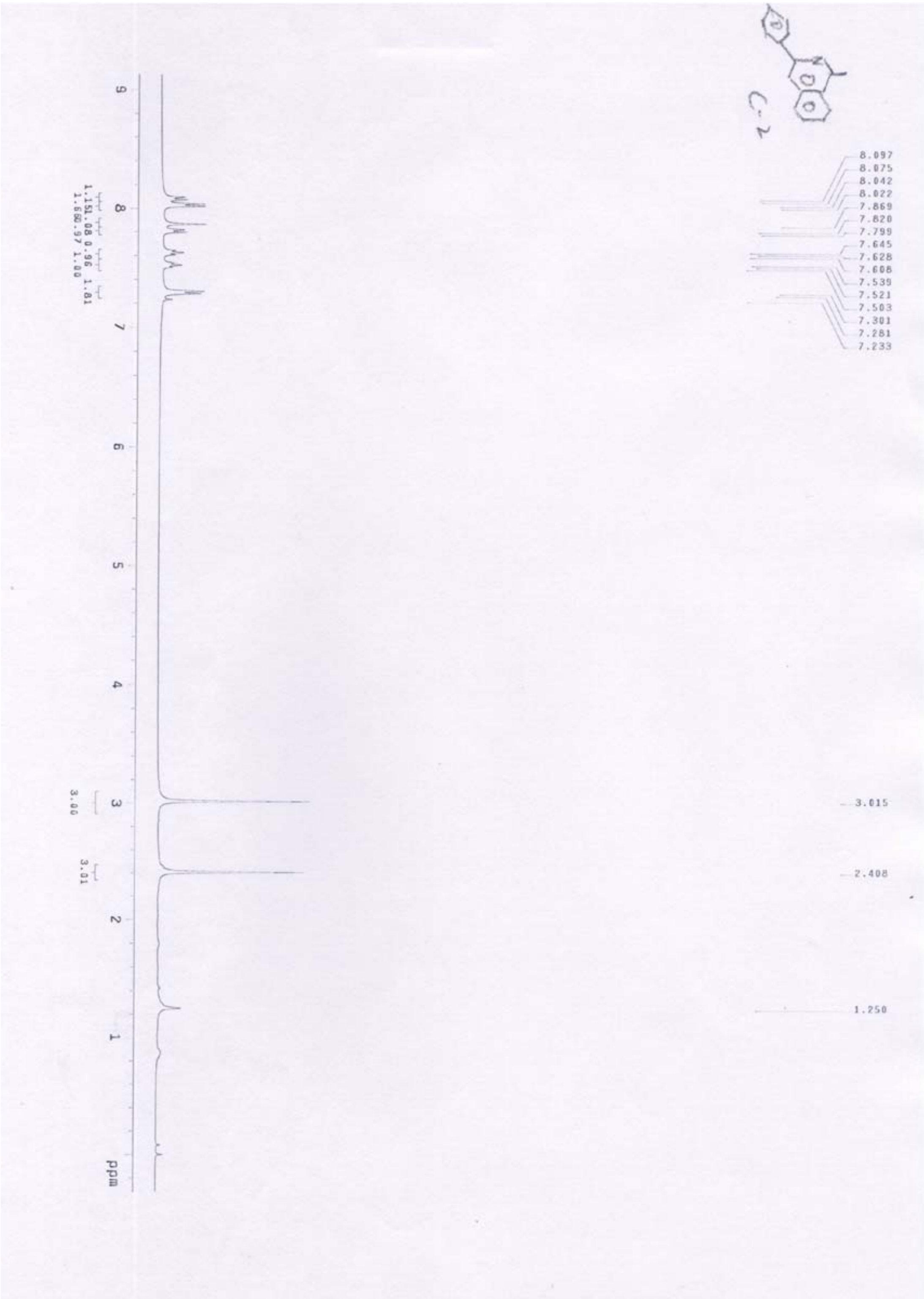
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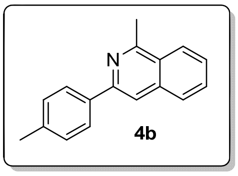
8.075
8.042
8.022
7.869
7.820
7.799
7.645
7.628
7.608
7.539
7.521
7.503
7.301
7.281
7.233
3.015
2.408
1.250
ppm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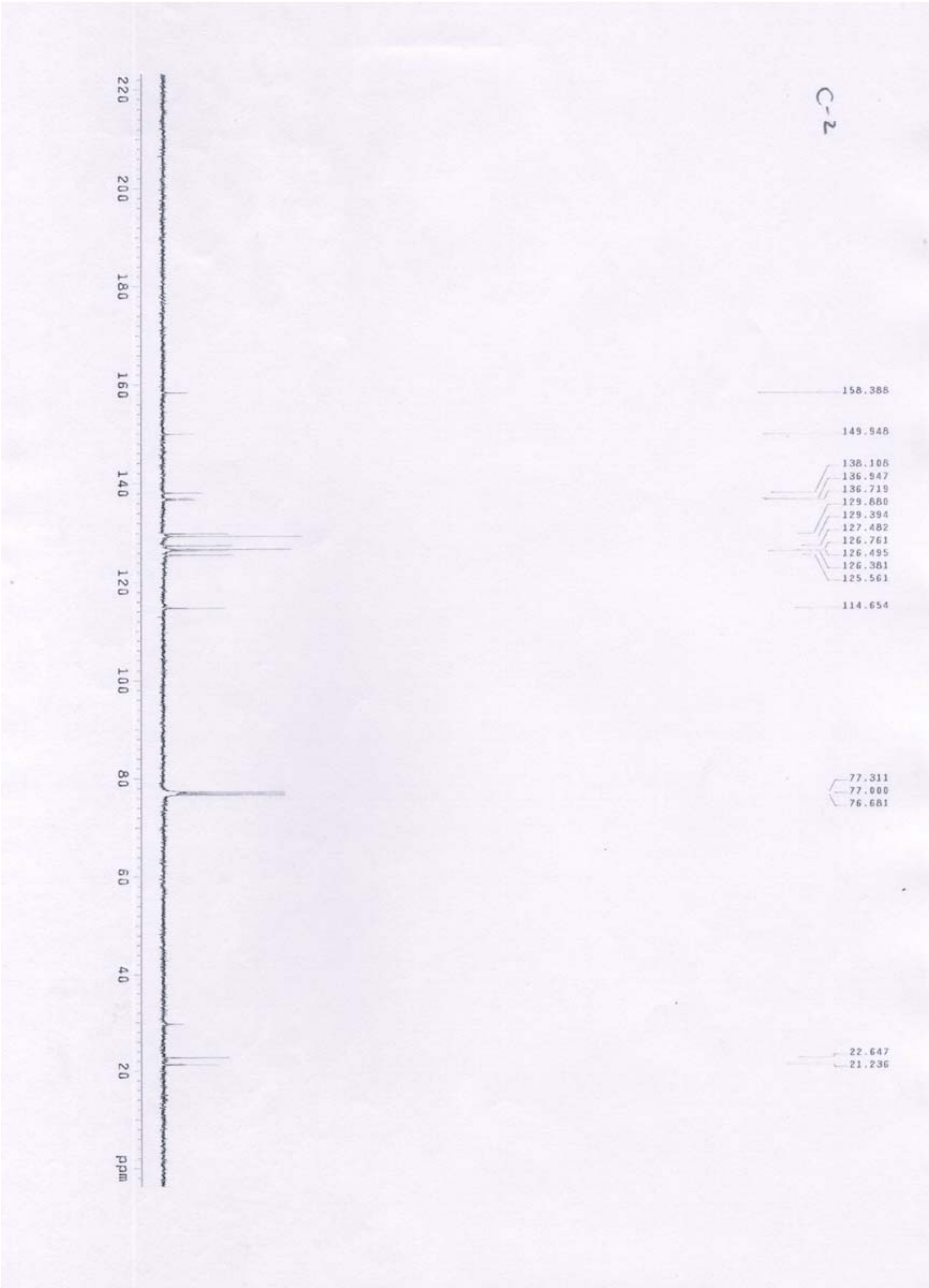
4b


C-2
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138.108
136.947
136.719
129.880
129.394
127.482
126.761
126.495
126.381
125.561
114.654
77.311
77.000
76.681
22.647
21.236
220
200
180
160
140
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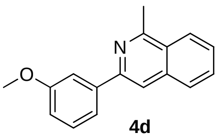
100
80
60
40
20
ppm



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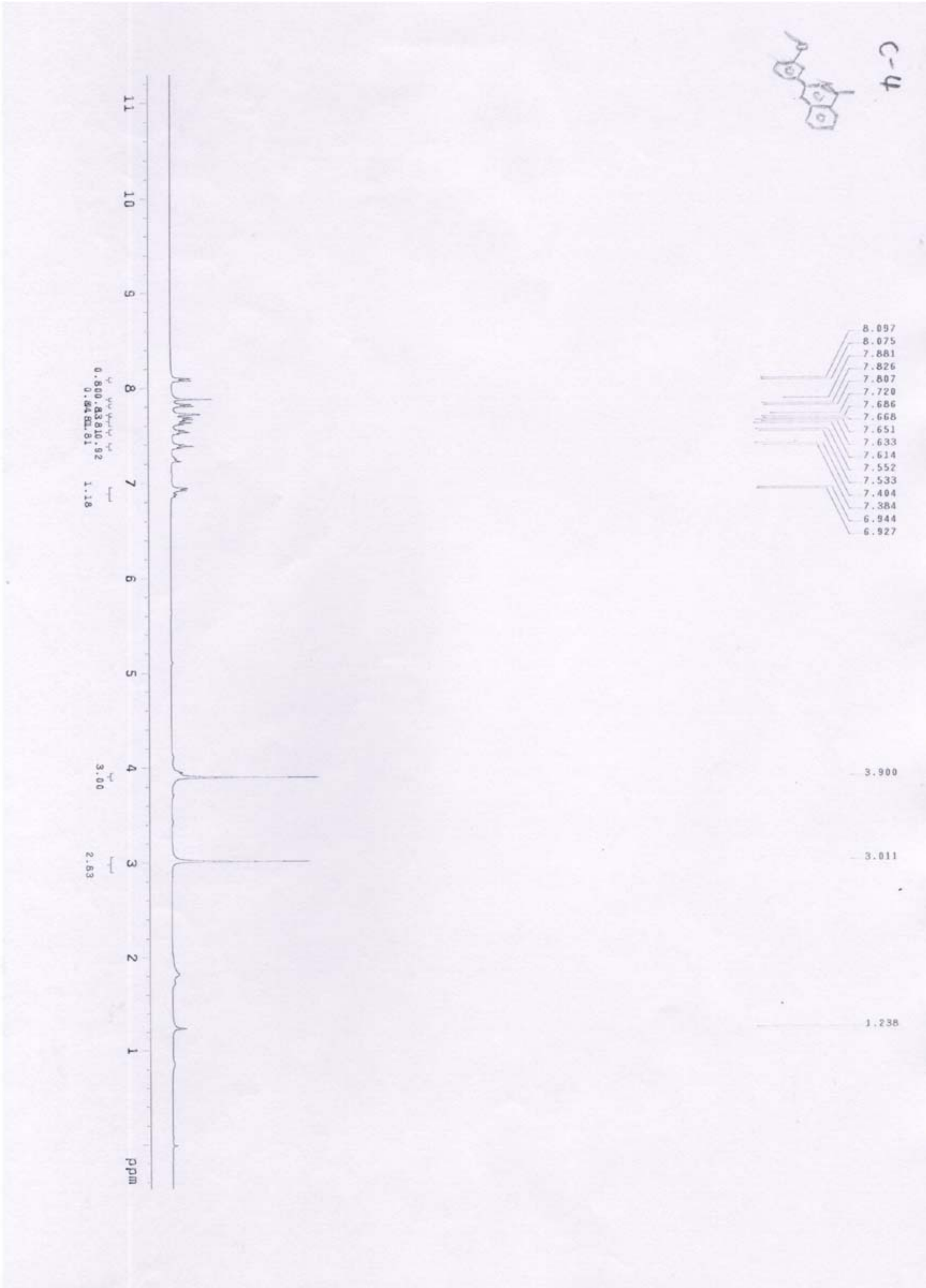
8.097
8.075
7.881
7.826
7.807
7.720
7.686
7.668
7.651
7.633
7.614
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7.533
7.404
7.384
6.944
6.927
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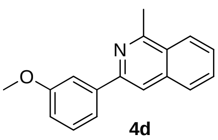
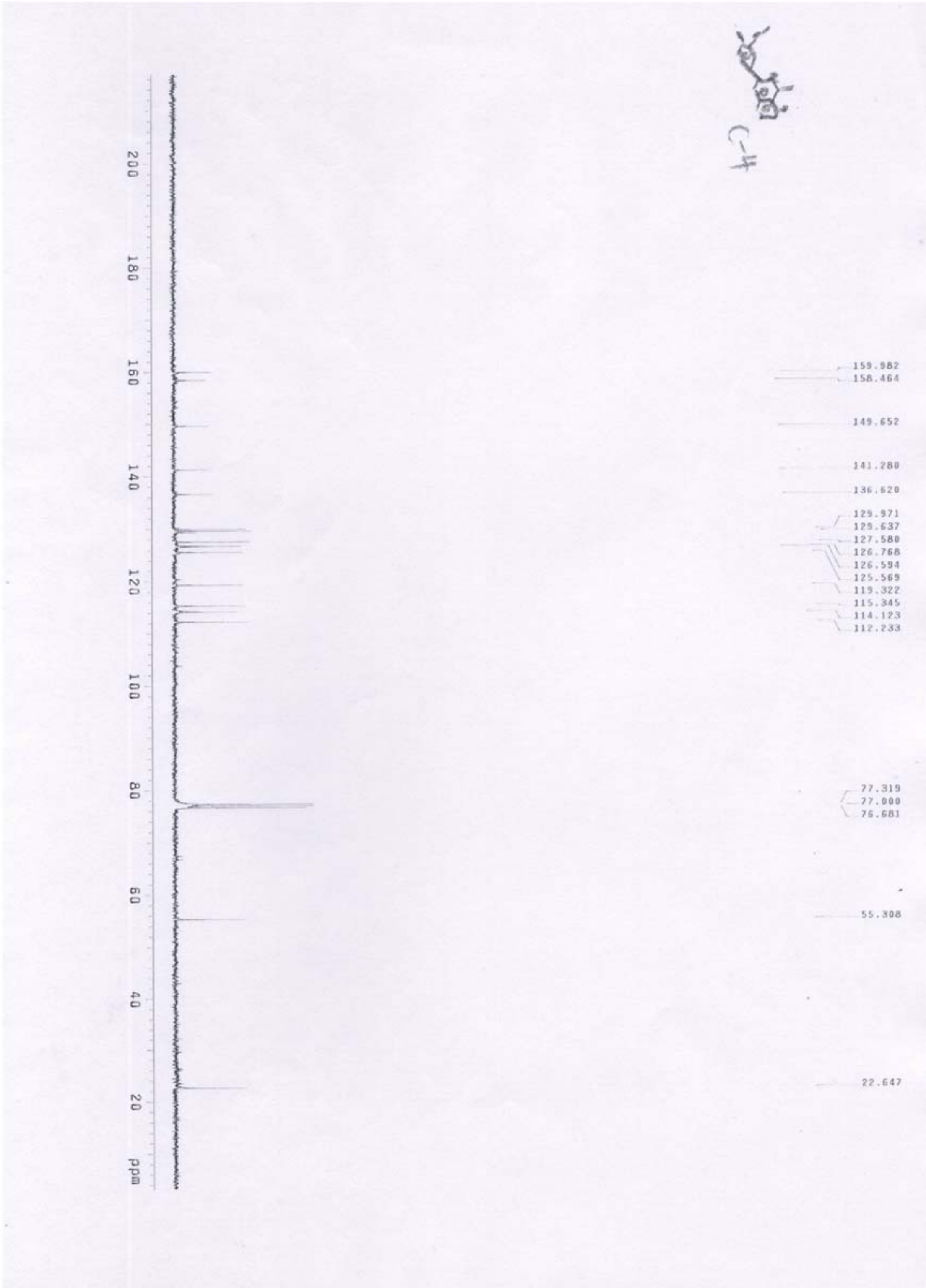
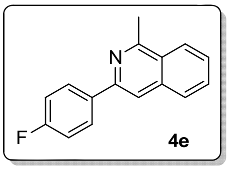
3.011
1.238
ppm


N
O

4d


159.982
158.464
149.652
141.280
136.620
129.971
129.637
127.580
126.768
126.594
125.569
119.322
115.345
114.123
112.233
77.319
77.000
76.681
55.308
22.647
200
180
160
140
120
100
80
60
40
20
ppm
C-4



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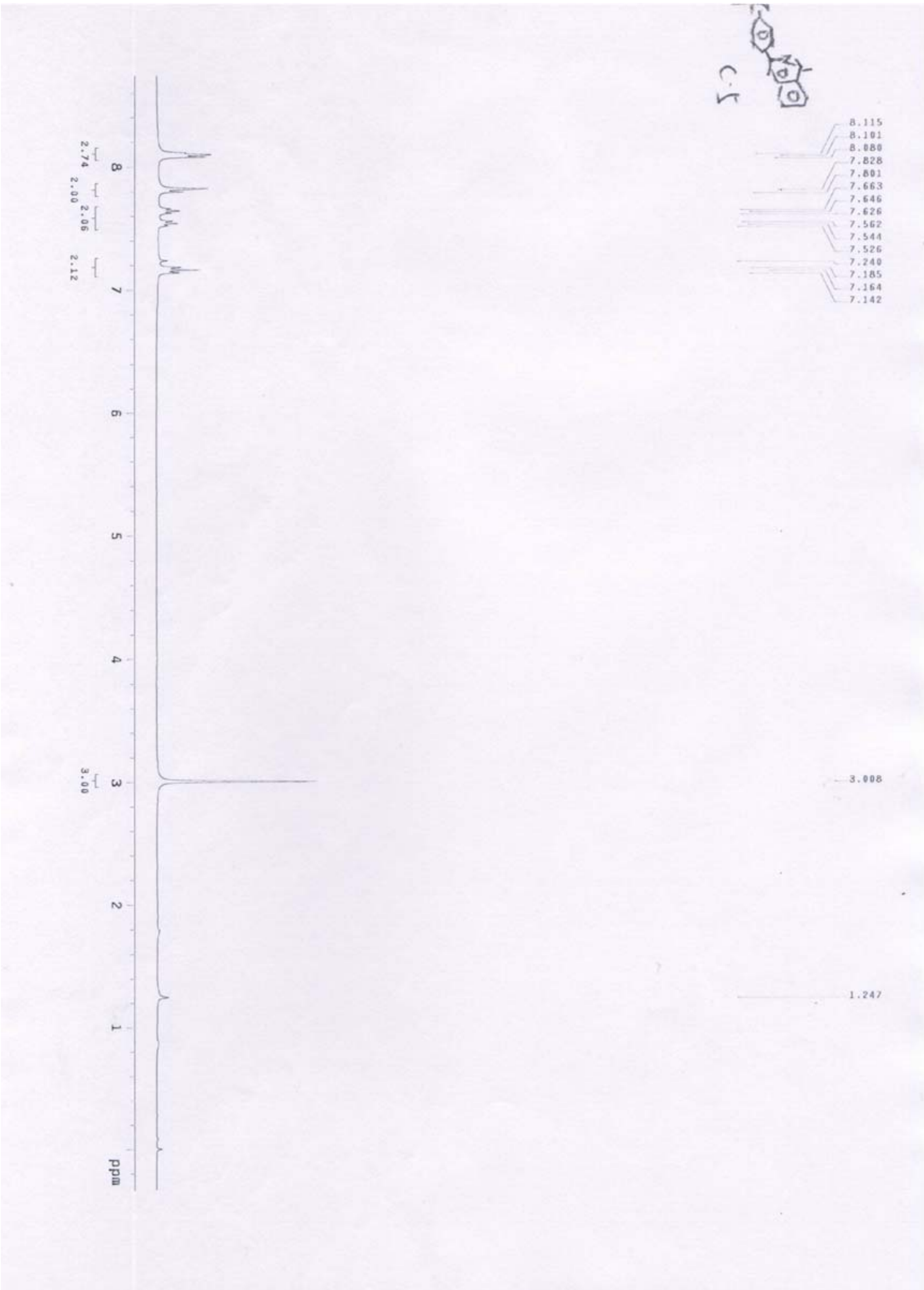
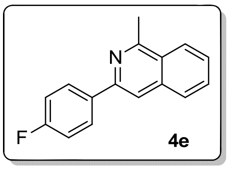
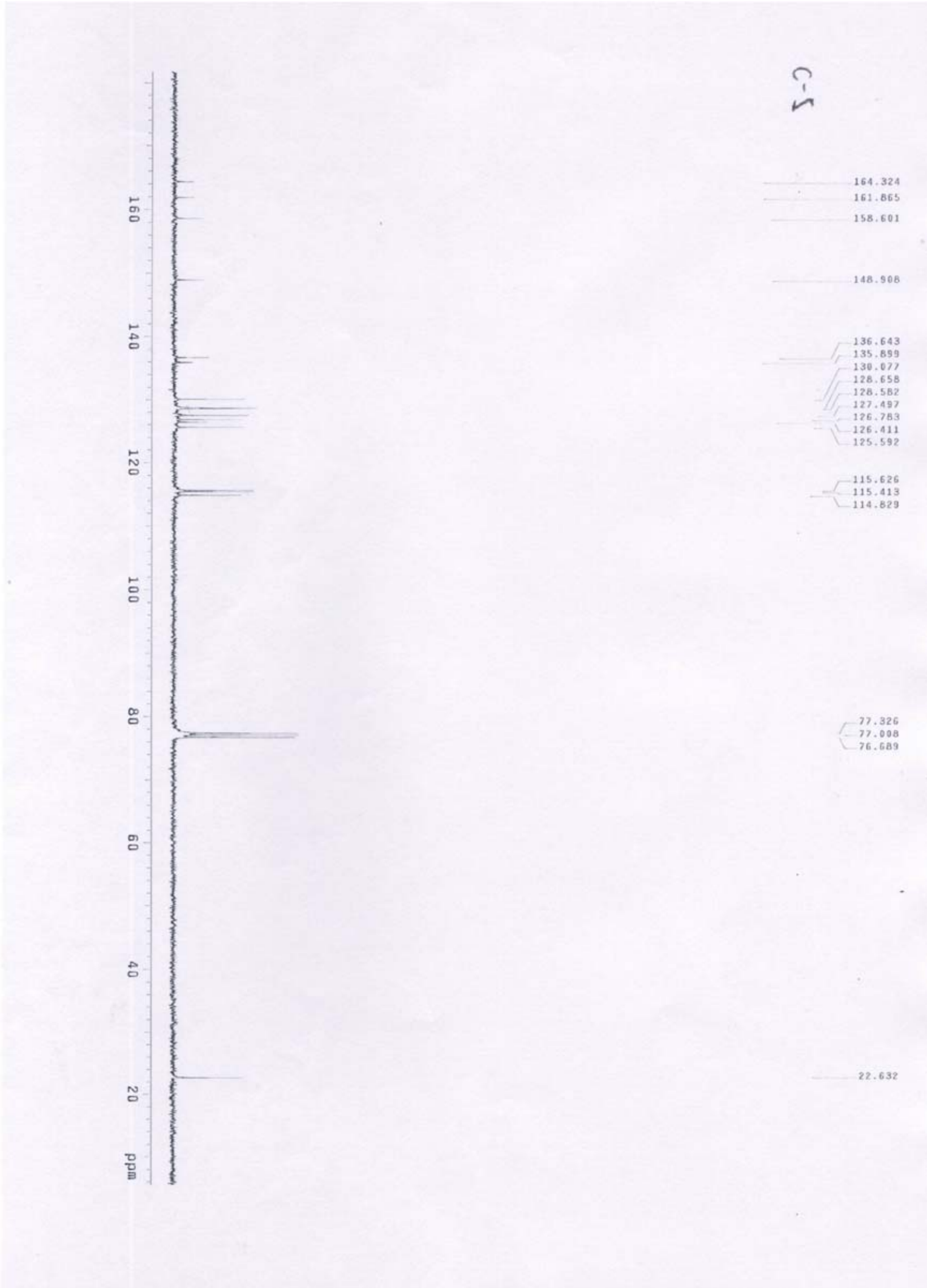



N
F

4e


C-5
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158.601
148.908
136.643
135.899
130.077
128.658
128.582
127.497
126.783
126.411
125.592
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115.413
114.829
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77.008
76.689
22.632
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140
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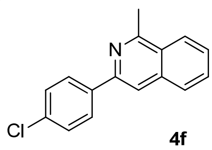
60
40
20
ppm



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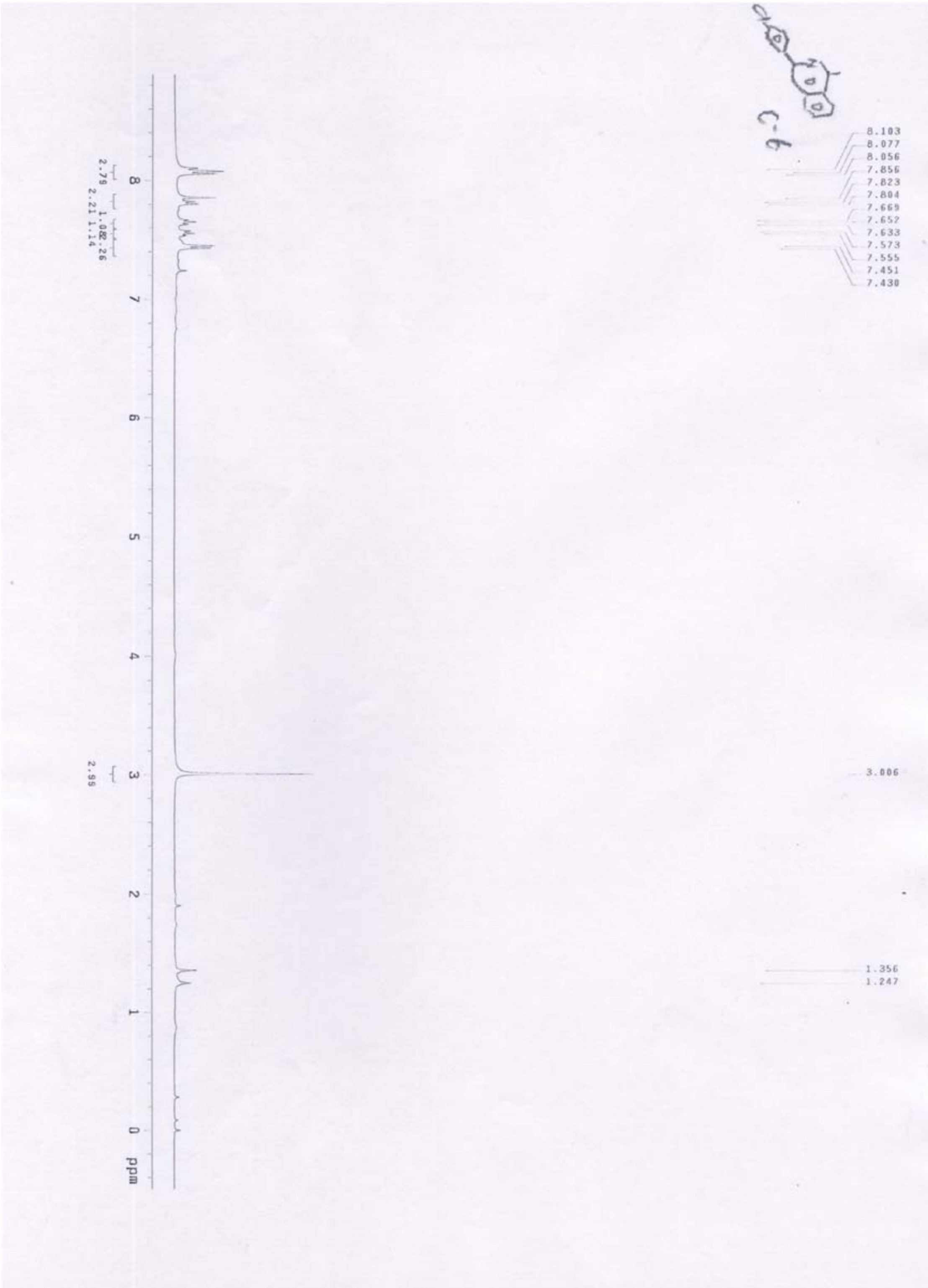

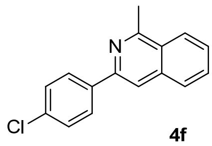
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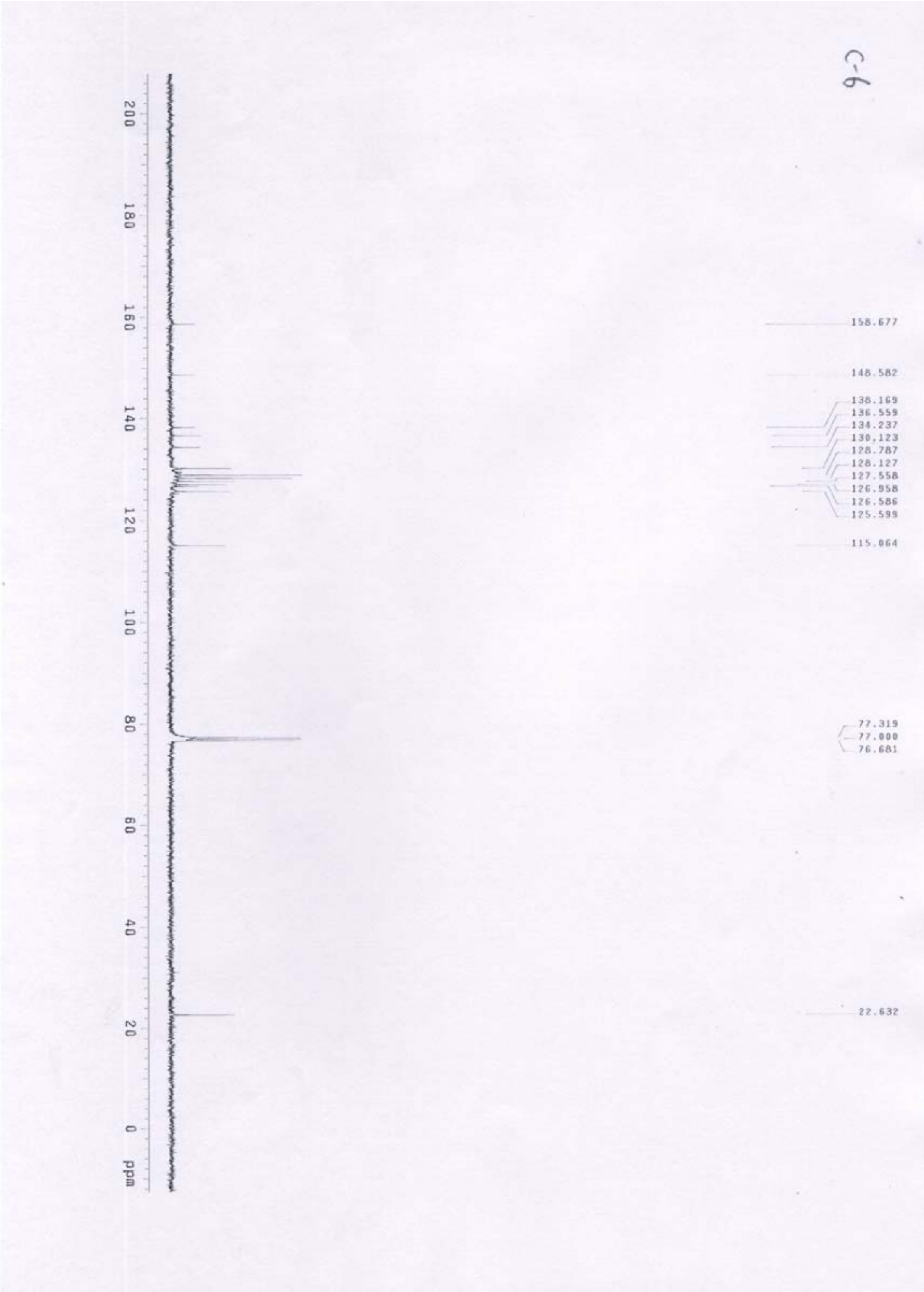
Cl

4f


C-6
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127.558
126.958
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125.599
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77.000
76.681
22.632
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120
100
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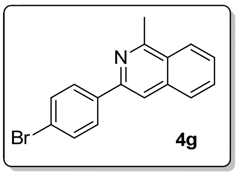
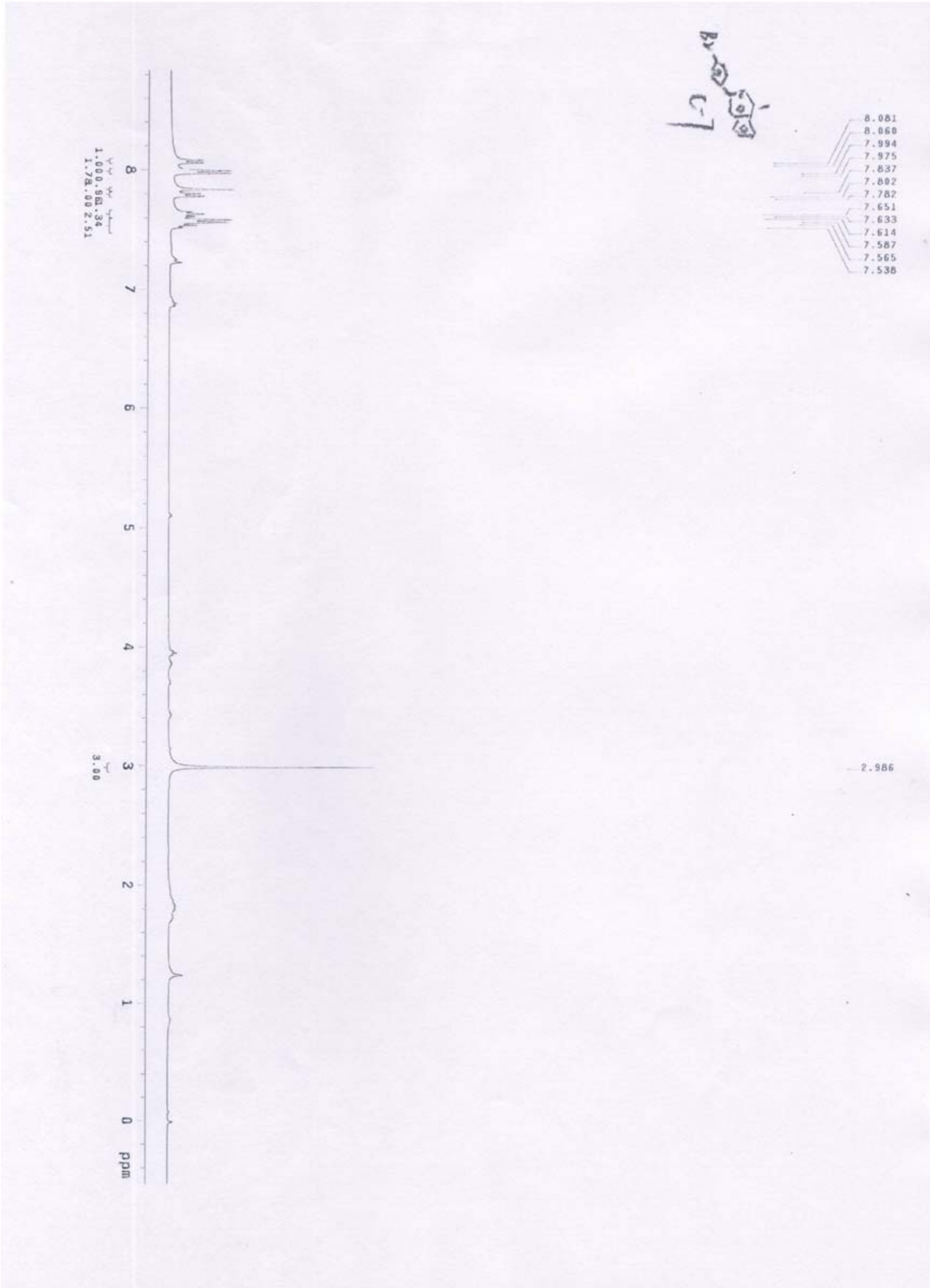

Br
N

4g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8.060
7.994
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7.802
7.782
7.651
7.633
7.614
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7.565
7.538
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6
5
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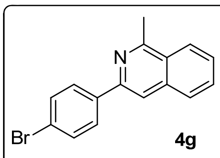
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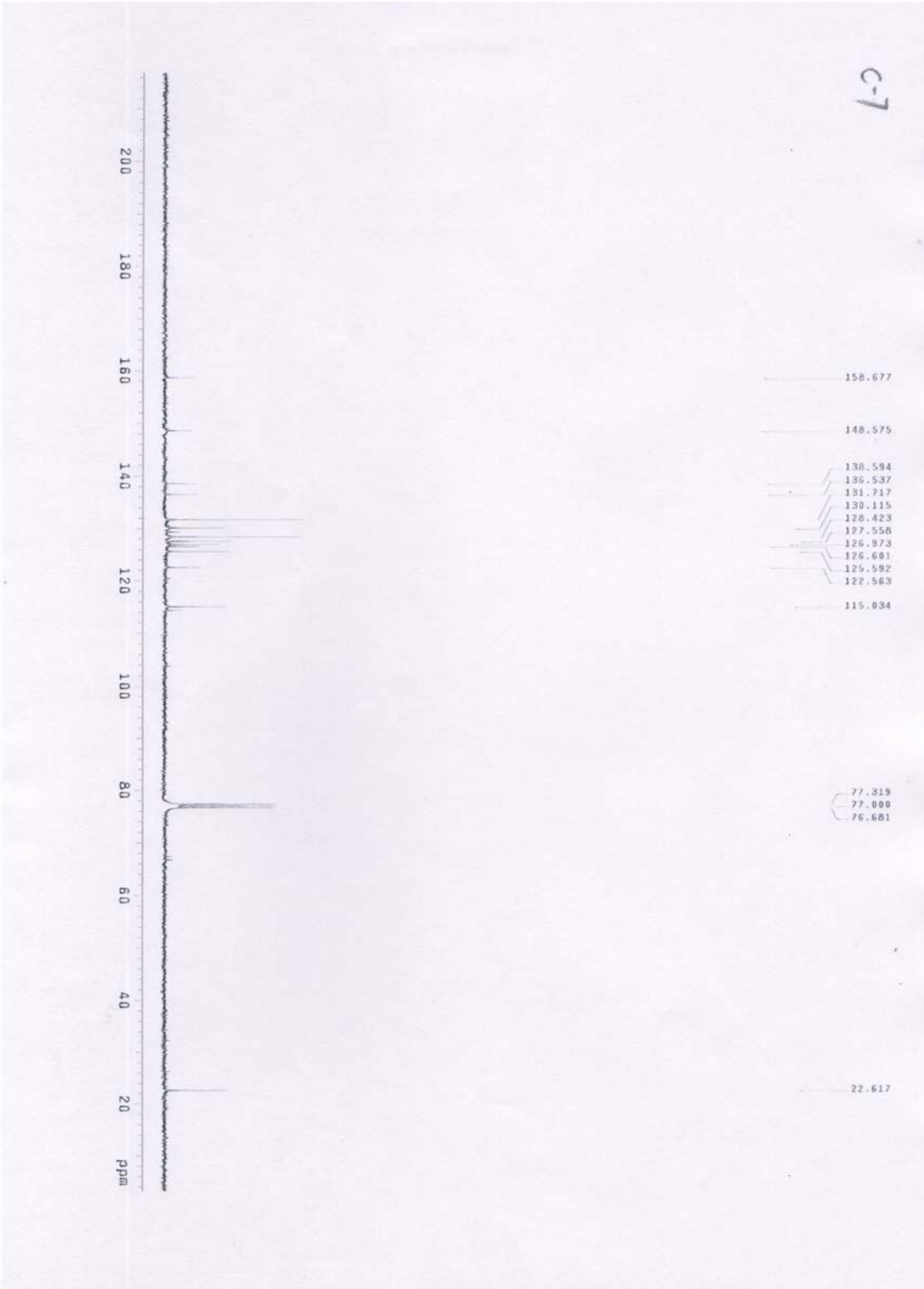
Br

4g


C-7
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136.537
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128.423
127.558
126.973
126.601
125.592
122.563
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77.000
76.681
22.617
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140
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60
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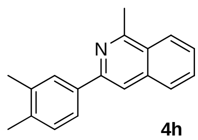
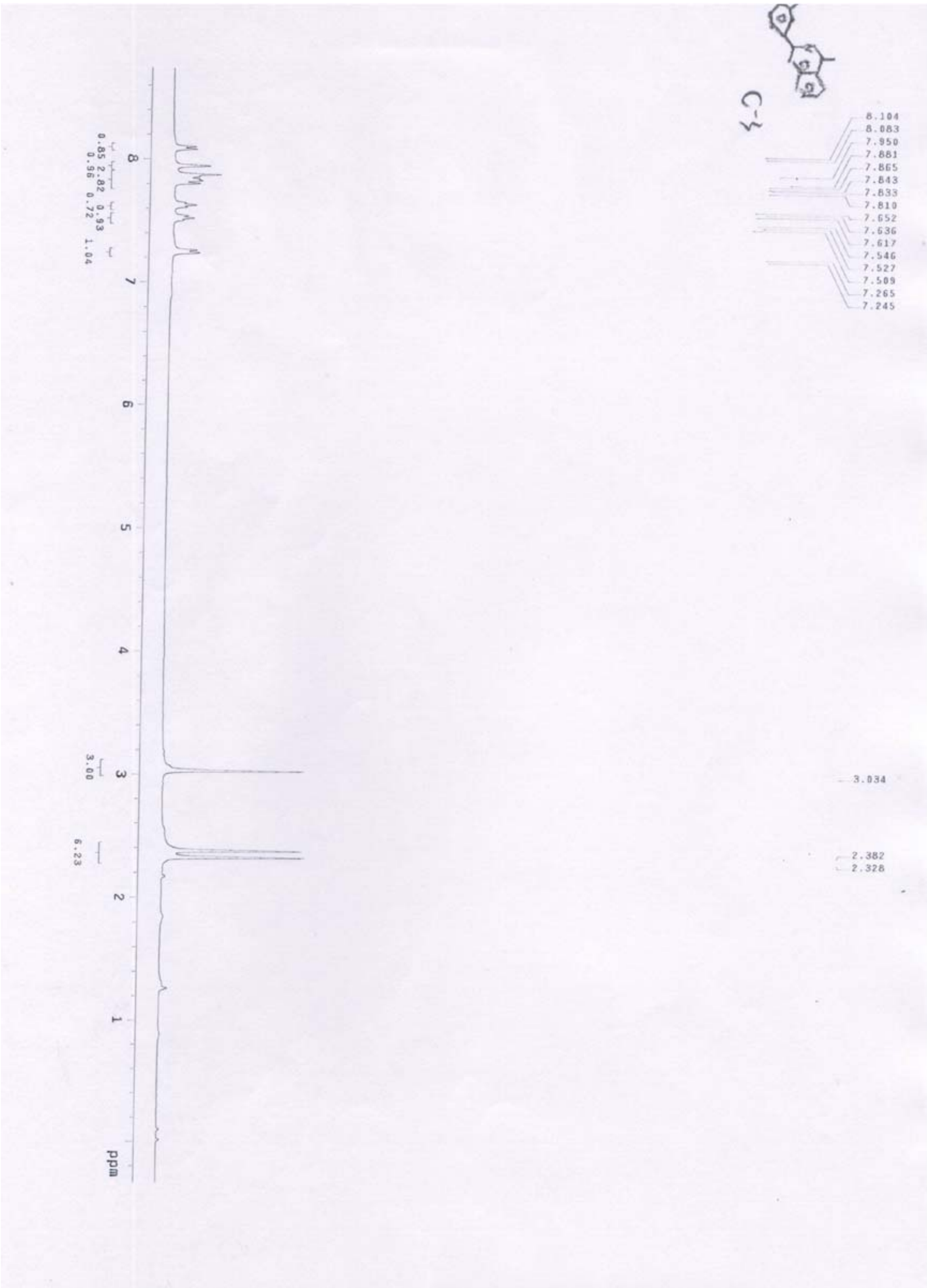
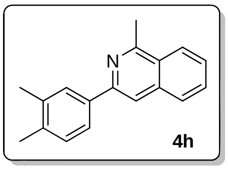
20
ppm



4h

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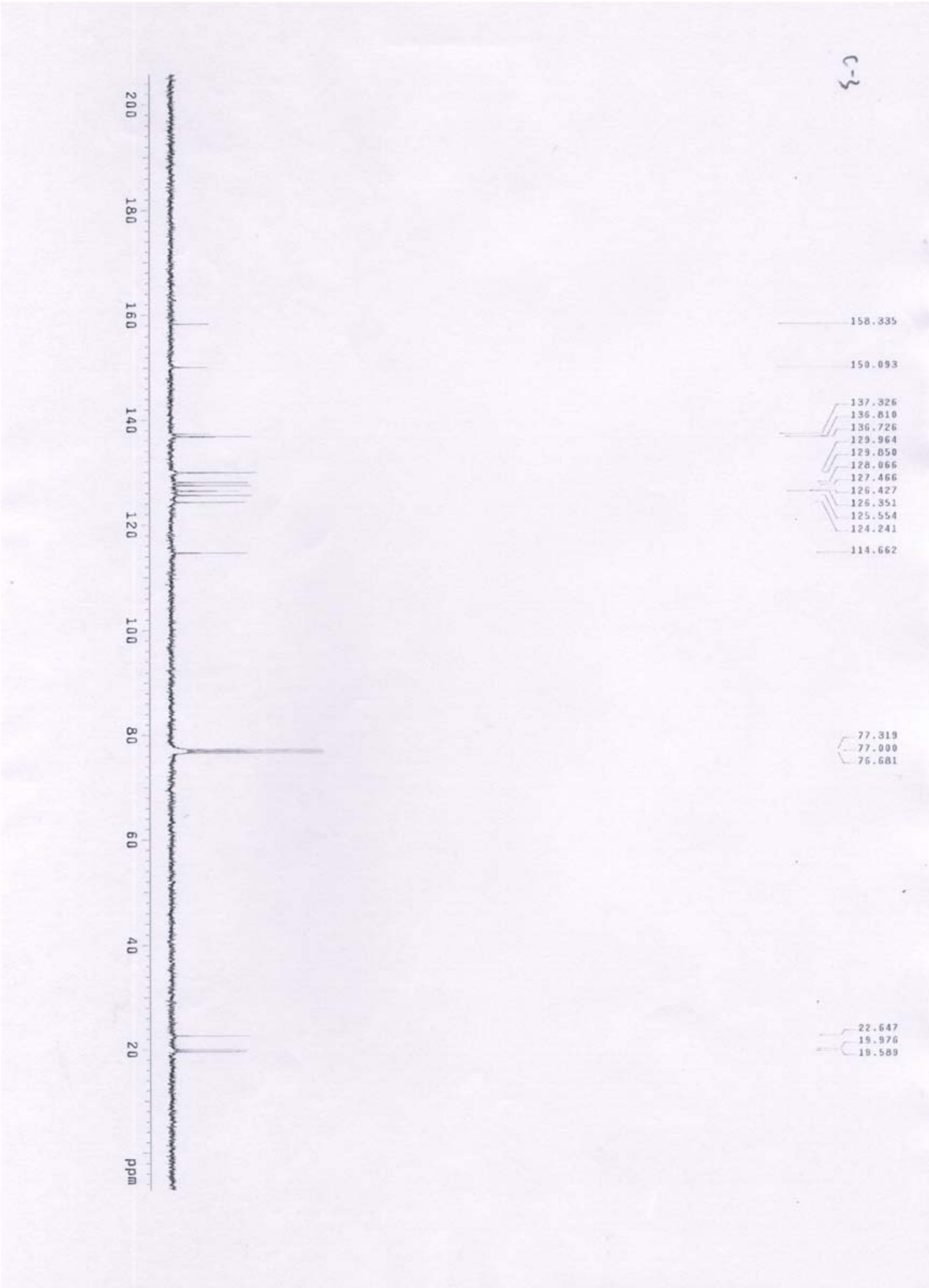
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128.066
127.466
126.427
126.351
125.554
124.241
114.662
77.319
77.000
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22.647
19.976
19.589
200
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140
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20
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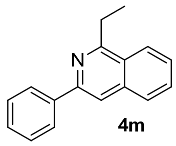
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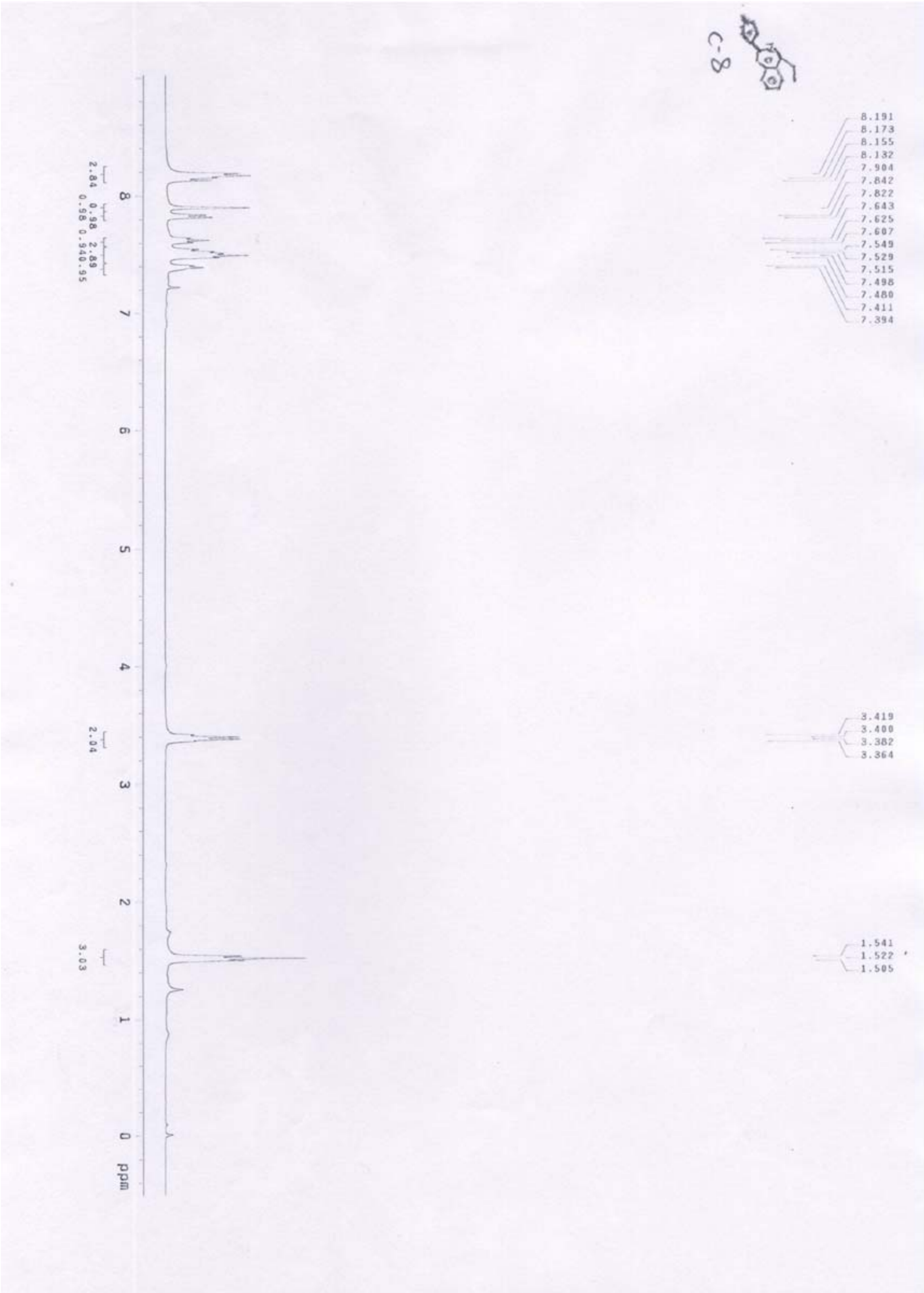
C-8
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7.822
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7.529
7.515
7.498
7.480
7.411
7.394
3.419
3.400
3.382
3.364
1.541
1.522
1.505
2.84
0.98
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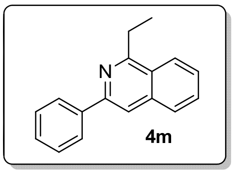
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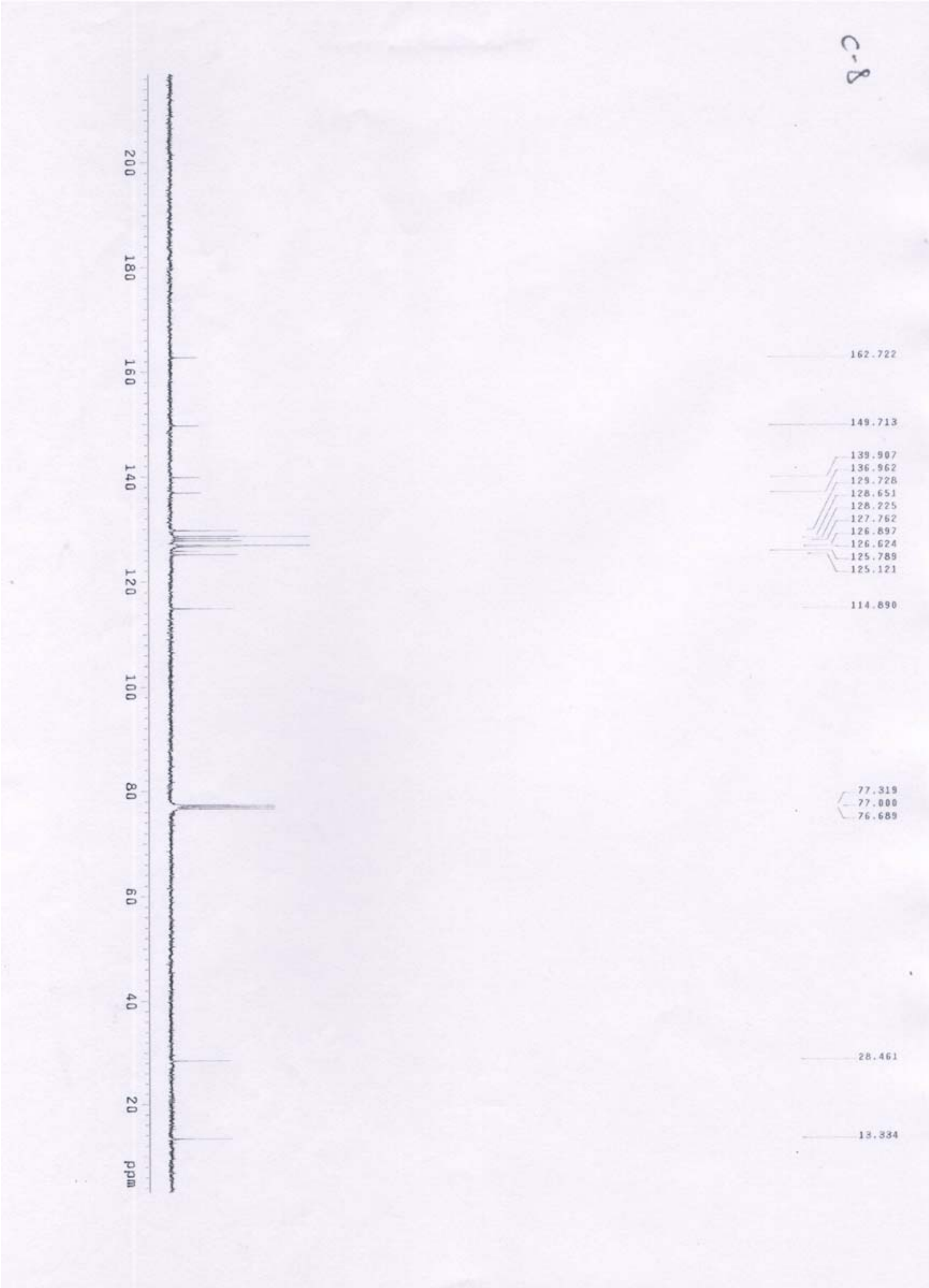
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129.728
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128.225
127.762
126.897
126.624
125.789
125.121
114.890
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77.000
76.689
28.461
13.334
200
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140
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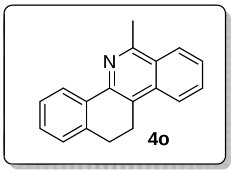
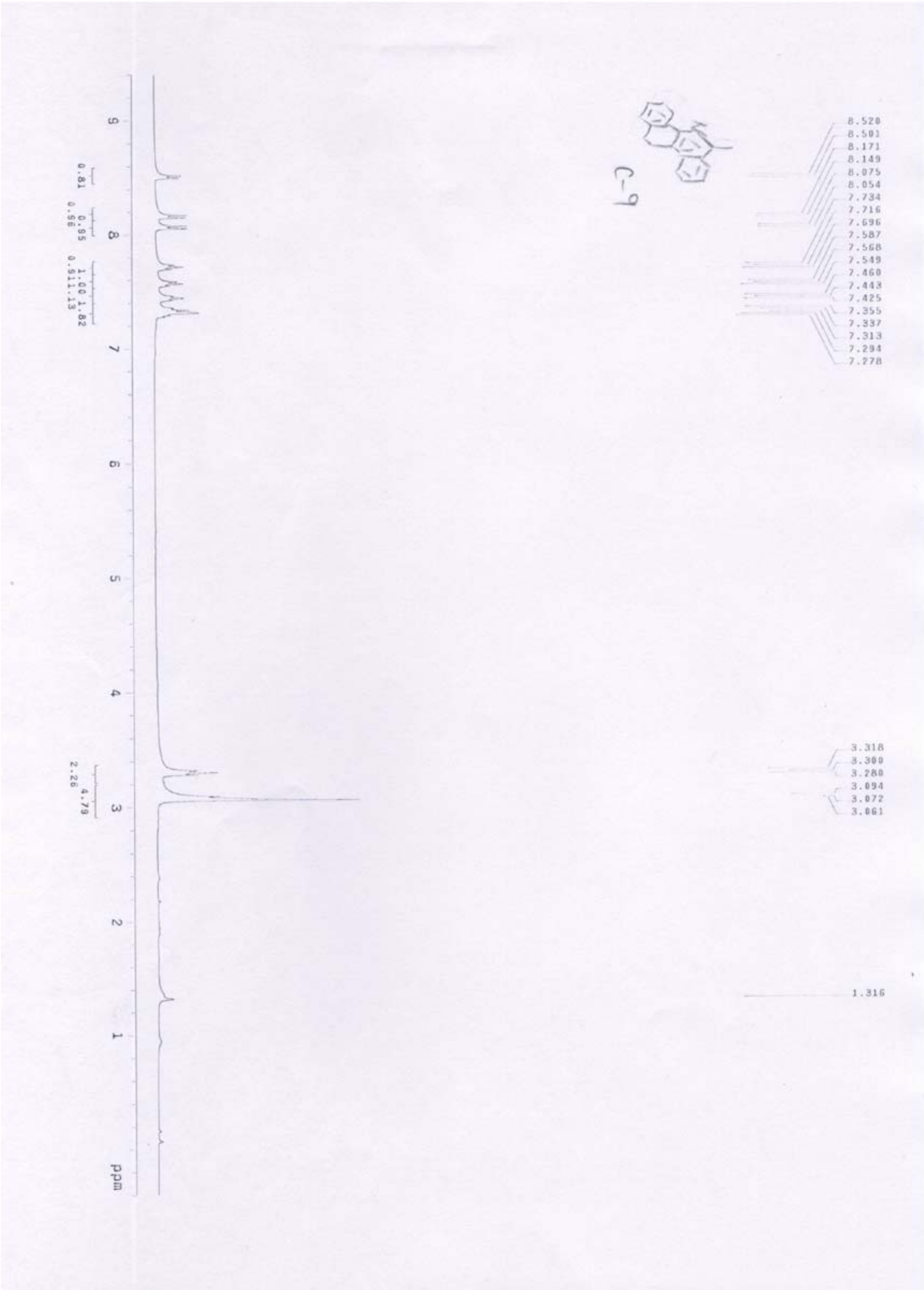
20
ppm


N
4o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8.149
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8.054
7.734
7.716
7.696
7.587
7.568
7.549
7.460
7.443
7.425
7.355
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7.278
3.318
3.300
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3.072
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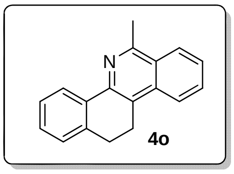
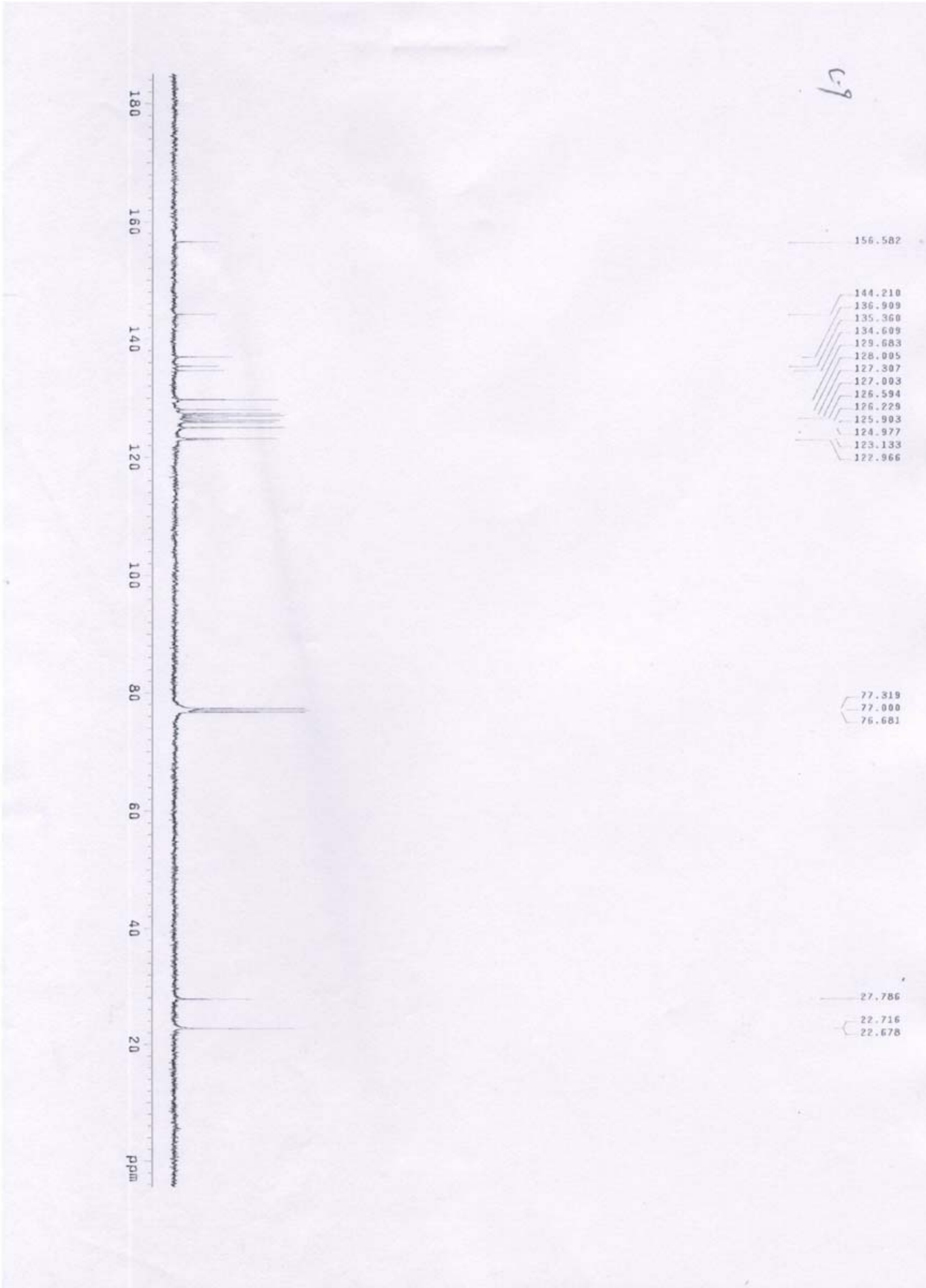
C-9
ppm


N
4o


C-9
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134.609
129.683
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127.003
126.594
126.229
125.903
124.977
123.133
122.966
77.319
77.000
76.681
27.786
22.716
22.678
180
160
140
120
100
80
60
40
20
ppm