Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supplementary Information

Catalytic I_2-Moist DMSO Mediated Synthesis of Valuable *α*-Amidohydroxyketones and Unsymmetrical *gem*-Bisamides from Benzimidates

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1.	Materials and Methods	S-2
2.	General Procedure for the Synthesis of Benzimidates (**1a–i**)	S-3
3.	General Procedure for the Synthesis of α-amidohydroxyketone (**3aa–aj, 3ba–gd**)	S-4
4.	General Procedure for the Synthesis of Symmetric *gem*-Bisamides (**4aa–ii**)	S-4
5.	General Procedure for the Synthesis of Dissymmetric *gem*-Bisamide (**5ab, 5ac, 5ae, 5be, 5ce, 5bh, 5ch**)	S-5
6.	Plausible Mechanistic Cycle for the α-amidohydroxyketone Synthesis	S-6
7.	HRMS- Experimental Data for α-amidohydroxyketone	S-7
8.	Plausible Mechanistic Cycle for the bisamide Synthesis	S-12
9.	HRMS- Experimental Data for bisamide	S-13
10.	Spectroscopic Data of α-amidohydroxyketones (**3**), symmetric bisamides (**4**) and unsymmetrical bisamides (**5**)	S-18

11.	Spectroscopic Data of α-amidoketone	S-141
12.	Spectroscopic data of [**3aa (*d*)**] with labelling experiment	S-144
13.	Spectroscopic data of [4**aa (*d*)**] with labelling experiment	S-145
14.	HRMS data of **4aa**(*d*)	S-147
15.	NMR titration of compound (**3de**)	S-148
16.	NMR titration of compound (**3aa**)	S-184
17.	NMR titration of compound **(6)**	S-188
18.	Crystal structure of compound **3ea** (**CCDC 2152756**)	S-192
19.	Crystal summary data of compound **3ea** (**CCDC 2152756**)	S-193
20.	References	S-194

1. Materials and Methods:

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred through syringe using standard Schlenk techniques. All the solvents and reagents were used as received unless otherwise noted. Petroleum ether used in our experiments was in the boiling range of 60–80 ^{0}C. Reaction temperatures above 25 ^{0}C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F–254 precoated plates (0.25 mm) and visualized by UV irradiation. Silica gel of particle size 100–200 and 230–400 mesh was used for column chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. ^{1}H and

^{13}C NMR spectra were recorded 300 MHz and 400 MHz spectrometers with ^{13}C operating frequencies of 75 MHz and 100 MHz chemical shifts (δ) are reported in ppm relative to the residual solvent $CDCl_3$ signal (δ = 7.24 for 1H NMR and δ = 77.0 for ^{13}C NMR), DMSO-d_6 signal (δ = 2.47 for ^1H NMR and δ = 39.4–40.6 for ^{13}C NMR) and CD_3OD signal (δ = 49.0 for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, number of hydrogen and coupling constants). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT–IR system and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbance is reported. High-Resolution Mass Spectrometry (HRMS) data was recorded on Qtof-micro quadruple mass spectrophotometer using acetonitrile as a solvent.

2. General Procedure for the Synthesis of Benzimidates (1a–i)[1]**:** Ethanol (10 mmol) and aryl nitrile (1 mmol) were stirred in a round bottom flask. AcCl (10 mmol) was added to it drop wise for 15 minutes in an ice bath. The reaction mixture was stirred at room temperature for 6 h, solvent was removed under reduced pressure to afford the product as white solid. The white solid was washed with Et_2O, triturated with saturated $NaHCO_3$ solution until the gas evolution ceased and extracted three times with EtOAc (3x10mL). The organic layer was washed with water, dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the desired product **1a–i** as colorless oil.

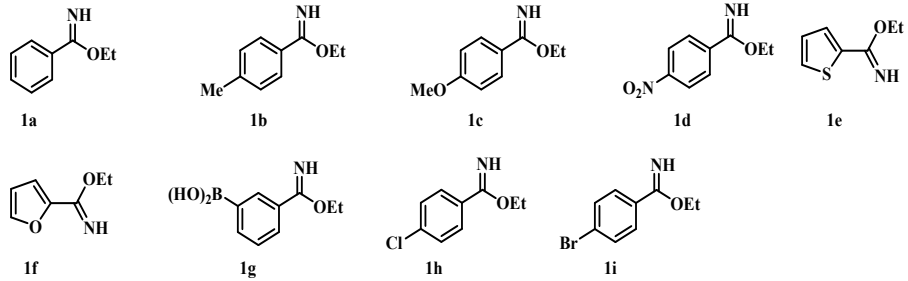
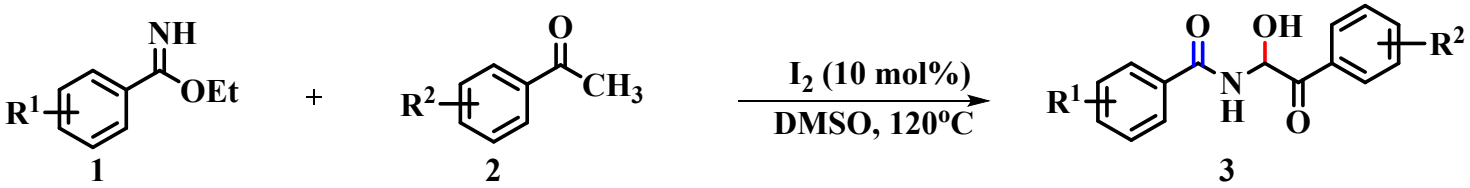


Figure S1. List of Synthesized Benzimidates Used in the Reactions

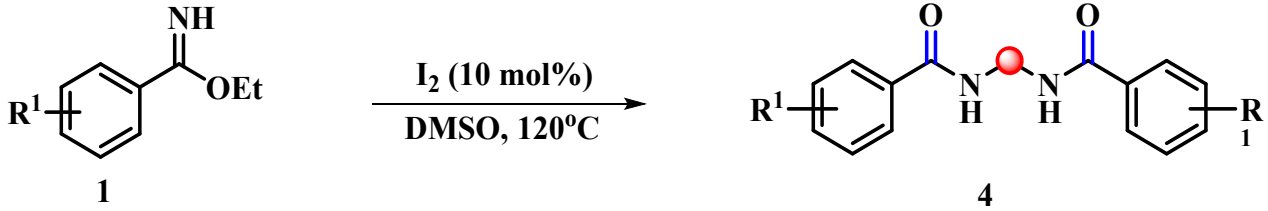
3. **General Procedure for the Synthesis of α-amidohydroxyketone (3aa–aj, 3ba–gd):** A mixture of ethyl benzimidate (**1**, 1 mmol), aryl ketone (**2**, 1 mmol) and I_2 (10 mol%, 25 mg) as a catalyst, was heated in dimethyl sulfoxide (2 ml) for 12-14 h in open air at 120 ^0C. After the completion of the reaction, the solvent was removed under reduced pressure to get a crude residue, which was purified by column chromatography over silica gel (100-200 mesh) using 20% ethyl acetate in petroleum ether as eluent to afford the desired

products (**3aa–3aj, 3ba–3gd**) with 70-85% yields. The compounds were characterized with the help of ^{1}H and ^{13}C NMR, FT-IR and mass spectroscopy data.



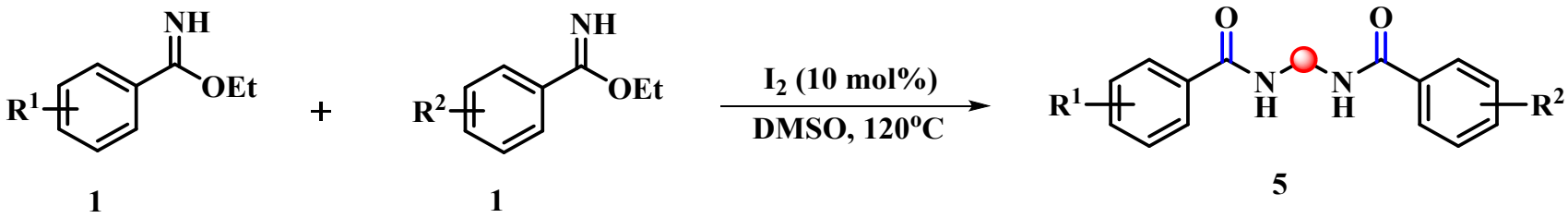
Scheme 1

4. **General Procedure for the Synthesis of Symmetric *gem*-Bisamides (4aa–ii):** A mixture of ethyl benzimidate (**1**, 2 mmol), I_2 (10 mol%, 25 mg) as a catalyst, was heated in dimethyl sulfoxide (2 ml, 12 mmol) for 12-14 h in open air at 120 ^{0}C. After the completion of the reaction, the solvent was removed under reduced pressure to get a crude residue, which was purified by column chromatography over silica gel (100-200 mesh) using 20% ethyl acetate in petroleum ether as eluent to afford the desired products (**4aa–ii**) with 88-94% yields. The compounds were characterized with the help of ^{1}H and ^{13}C NMR, FT-IR and mass spectroscopy data.



Scheme 2

5. General Procedure for the Synthesis of Dissymmetric *gem*-Bisamide (5ab, 5ac, 5ae, 5be, 5ce, 5bh, 5ch): To a mixture of ethyl benzimidate (**1a**, 1 mmol), substituted ethyl benzimidate (**1b–c**, **1e** and **1h**, 1 mmol) I_2 (10 mol%, 25 mg) as a catalyst, was heated in dimethyl sulfoxide (2 mL, 12 mmol) for 12-14 h in open air at 120 ^{0}C. After completion of the reaction, the solvent was removed under reduced pressure at room temperature to get a crude residue, which was purified by column chromatography over silica gel (100-200 mesh) using 20-25% ethyl acetate in petroleum ether as eluent to afford pure dissymmetric bisamide derivatives (**5ab, 5ac, 5ae, 5be, 5ce, 5bh, 5ch**) with 67-75% yields. The formation of the dissymmetrical bisamide was confirmed by the isolation and characterization of compounds with the help of spectroscopic analysis solid compounds.



Scheme 3

6. Plausible Mechanistic Cycle for the α-amidohydroxyketone

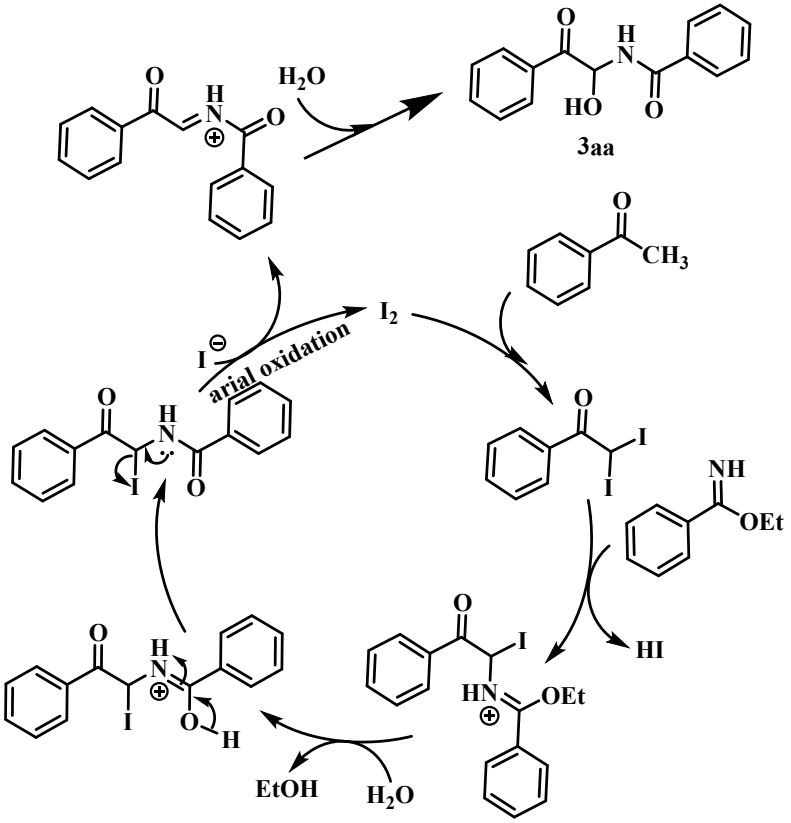
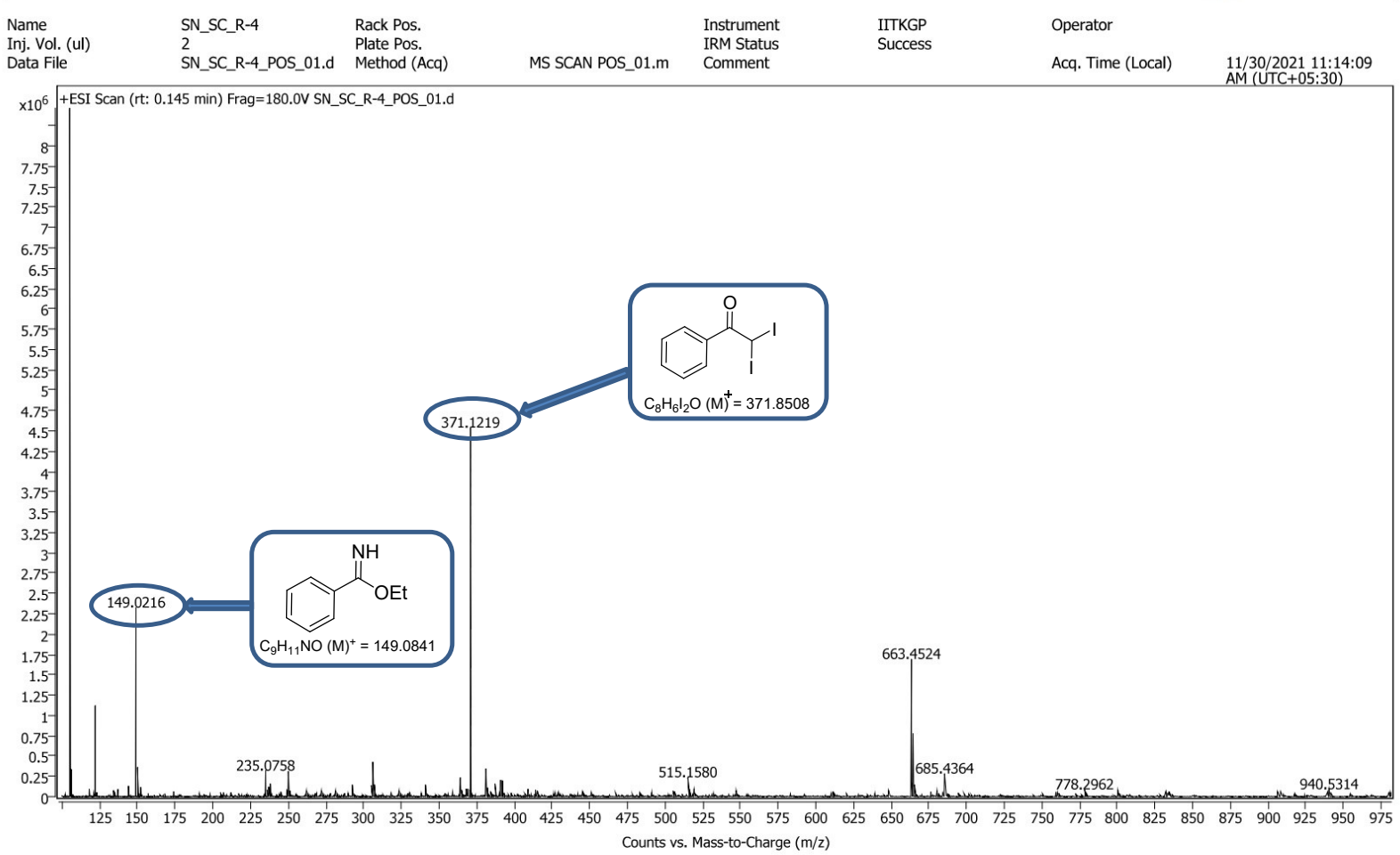


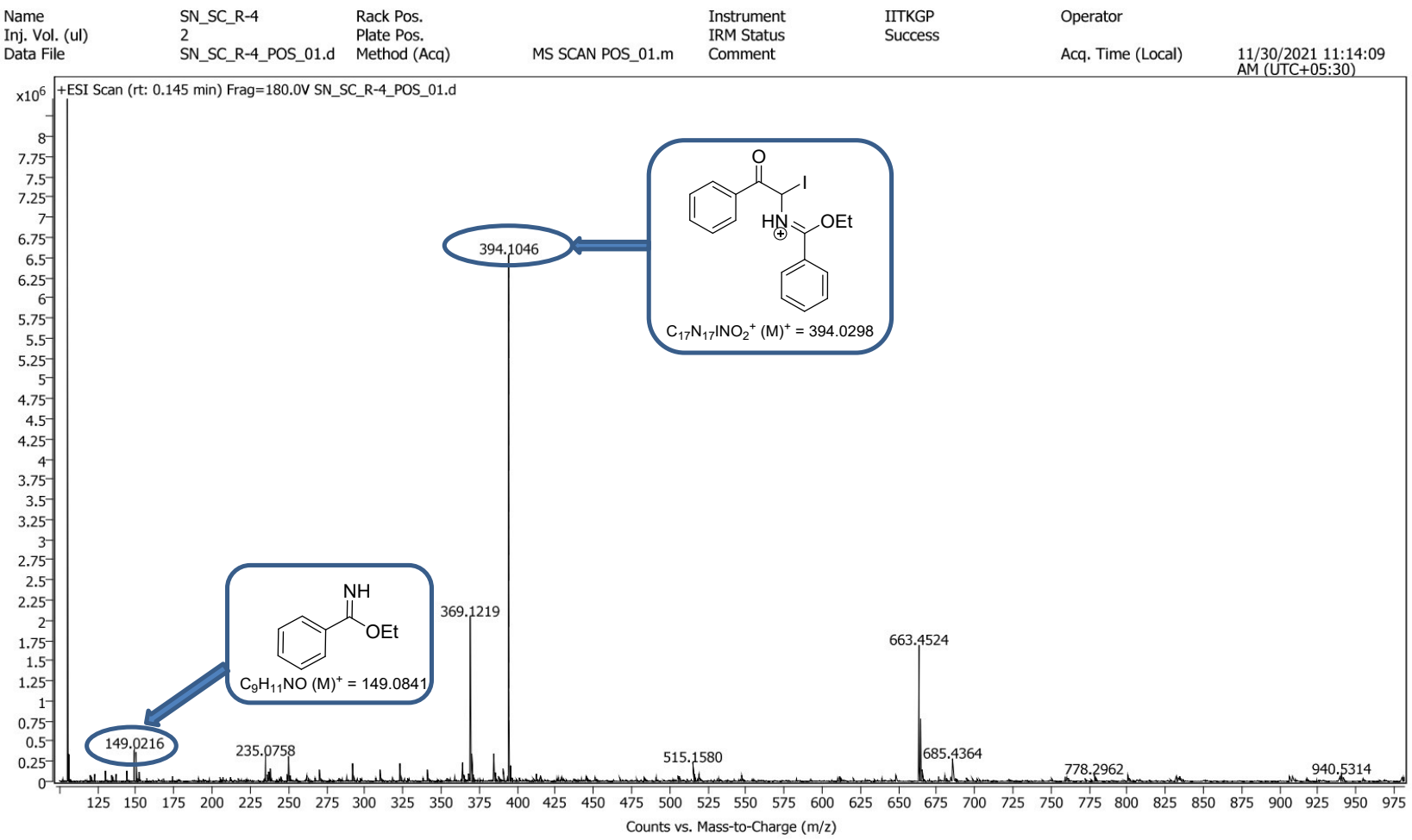
Figure S2: Plausible mechanistic cycle for the α-amidohydroxy ketone synthesis

7. HRMS- Experimental Data for α-amidohydroxyketone

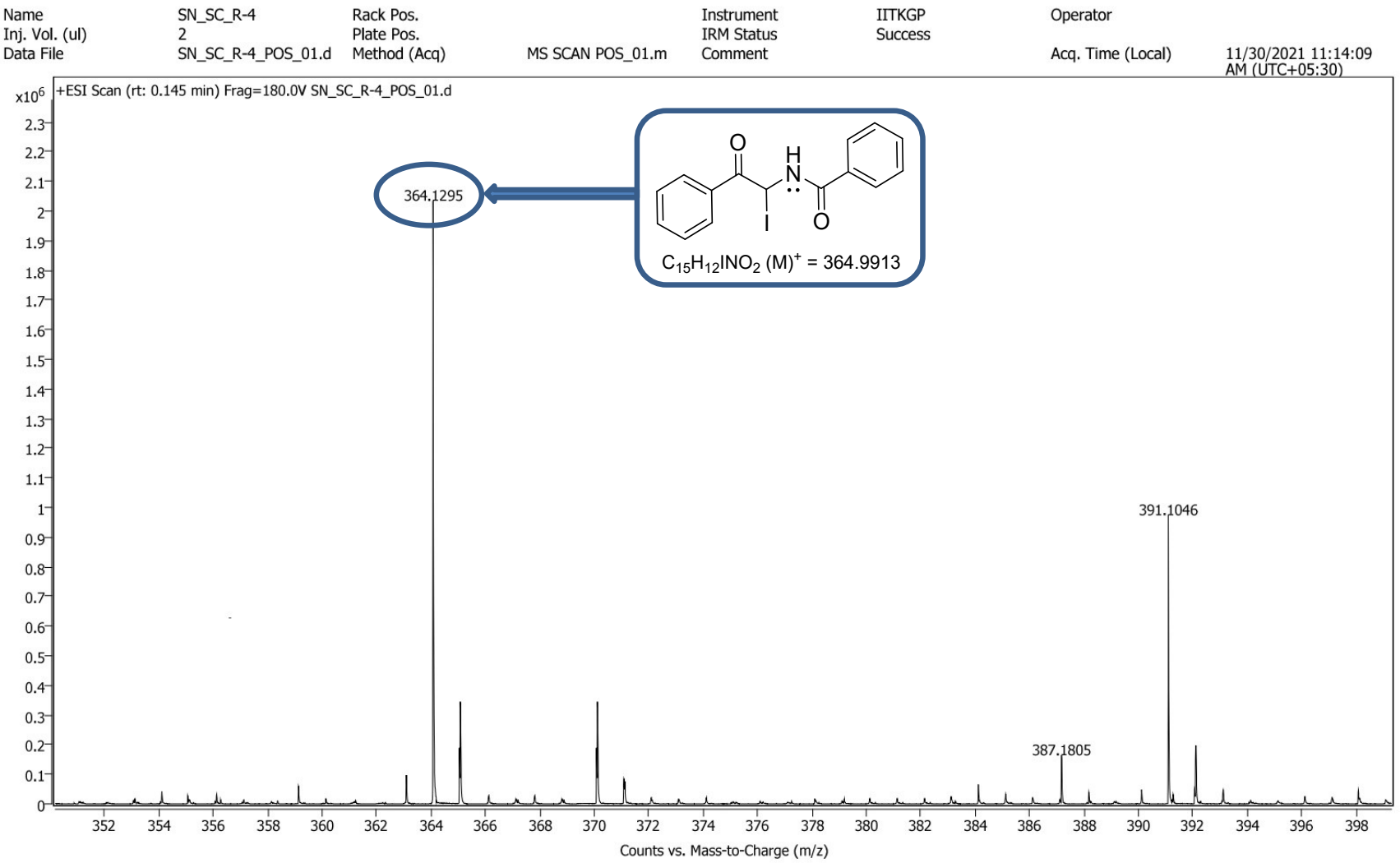
After 2 hours the mass data



After 4 hours the mass data



After 6 hours the mass data



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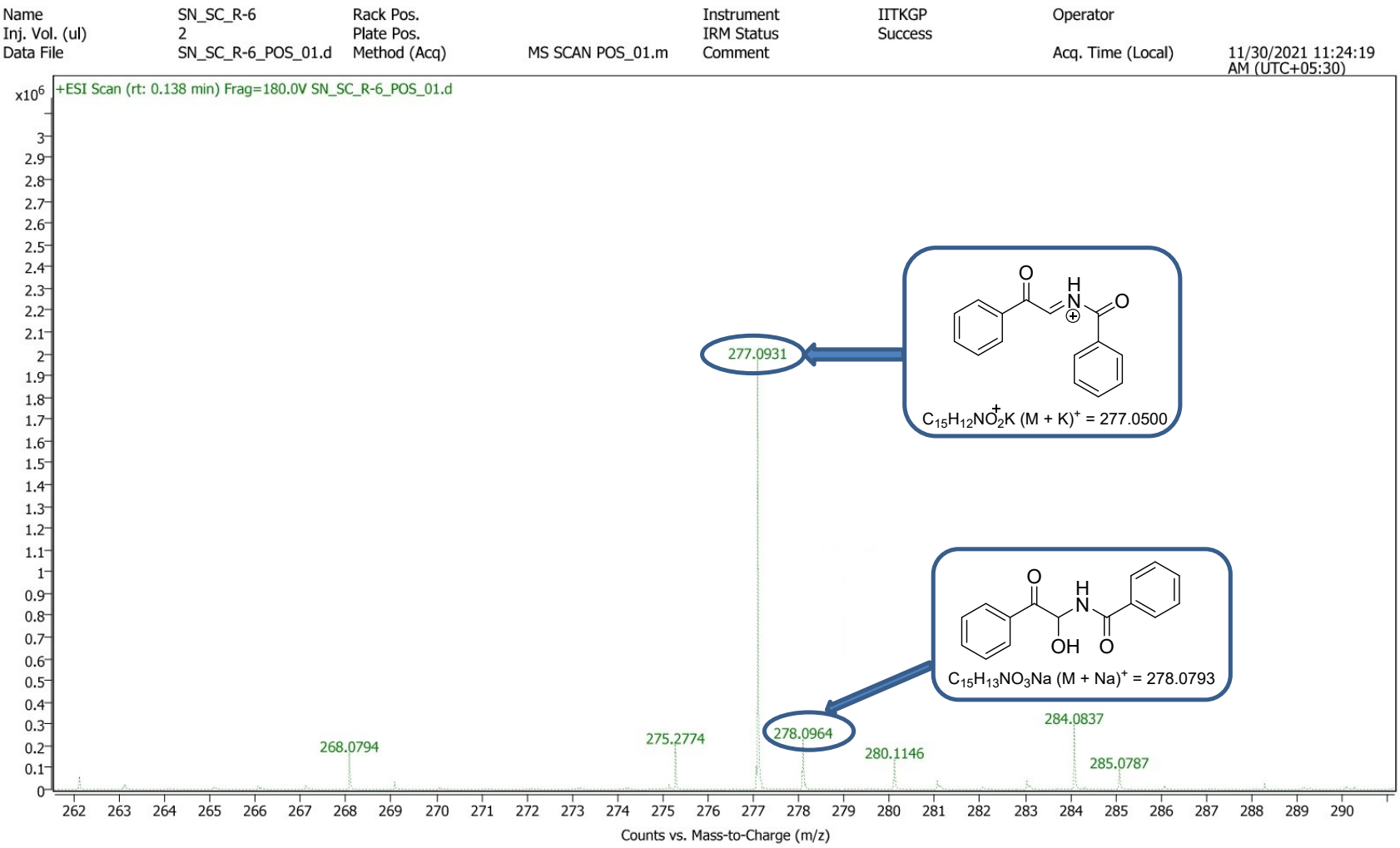

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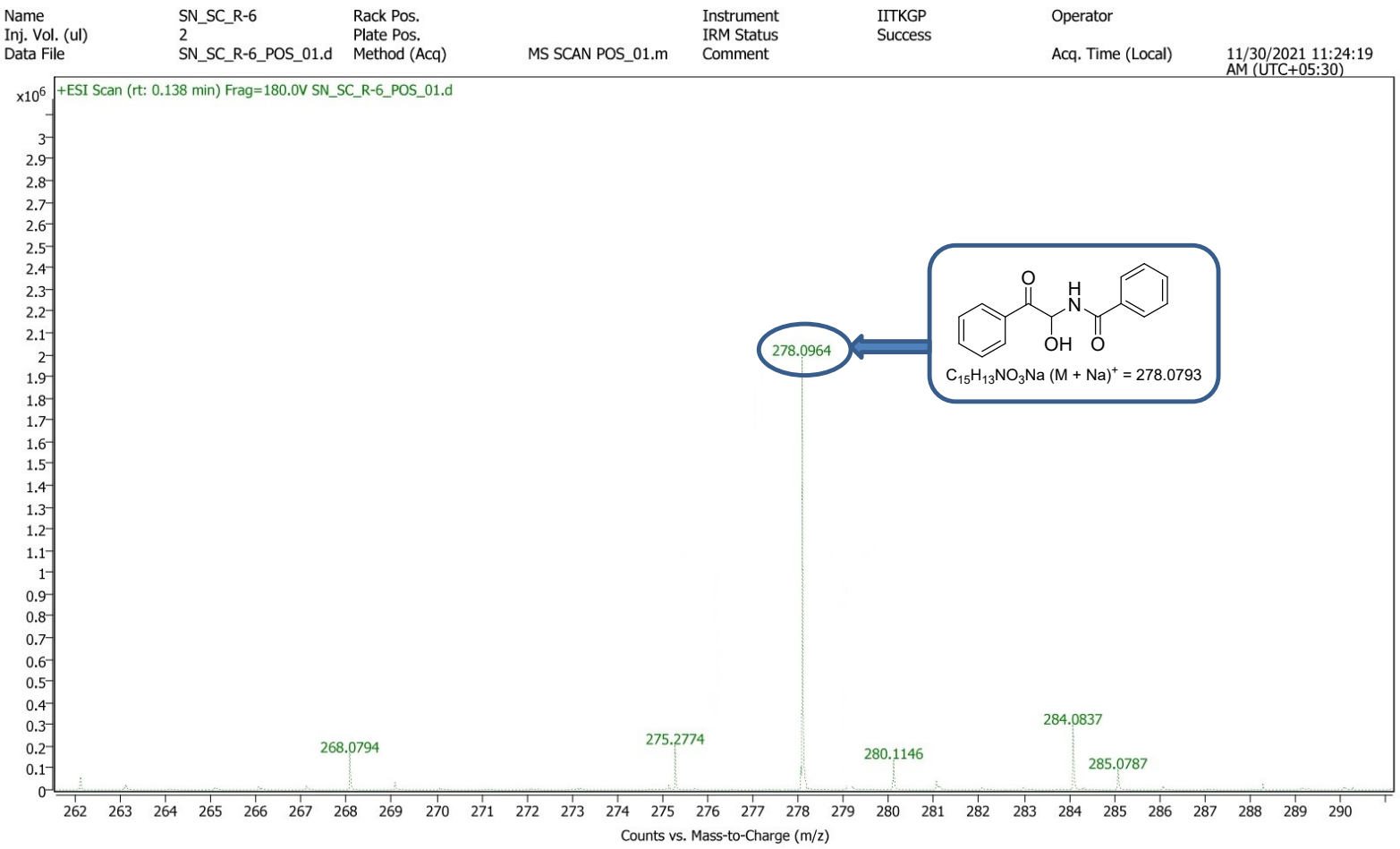


8. Plausible Mechanistic pathway for the bisamide

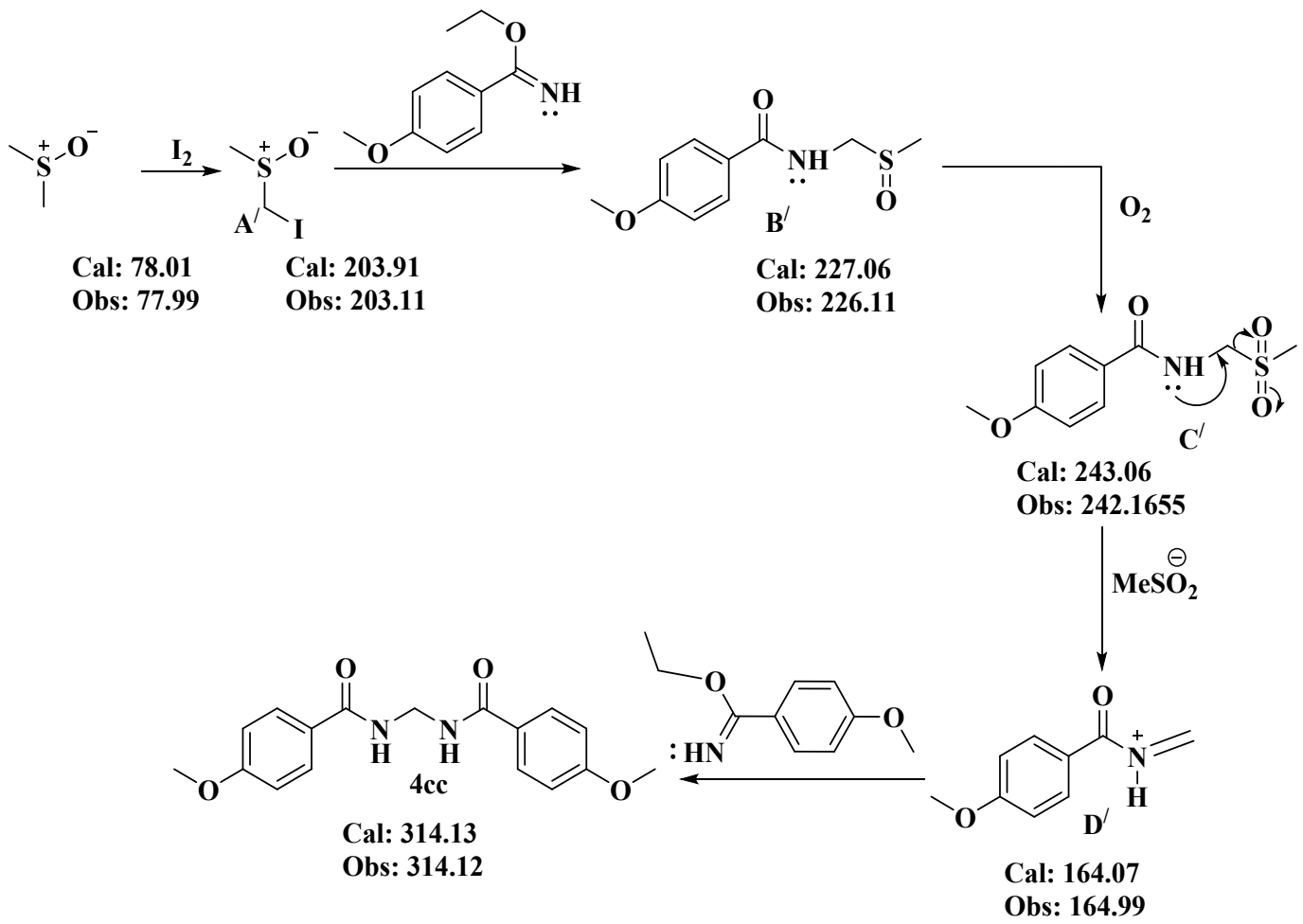
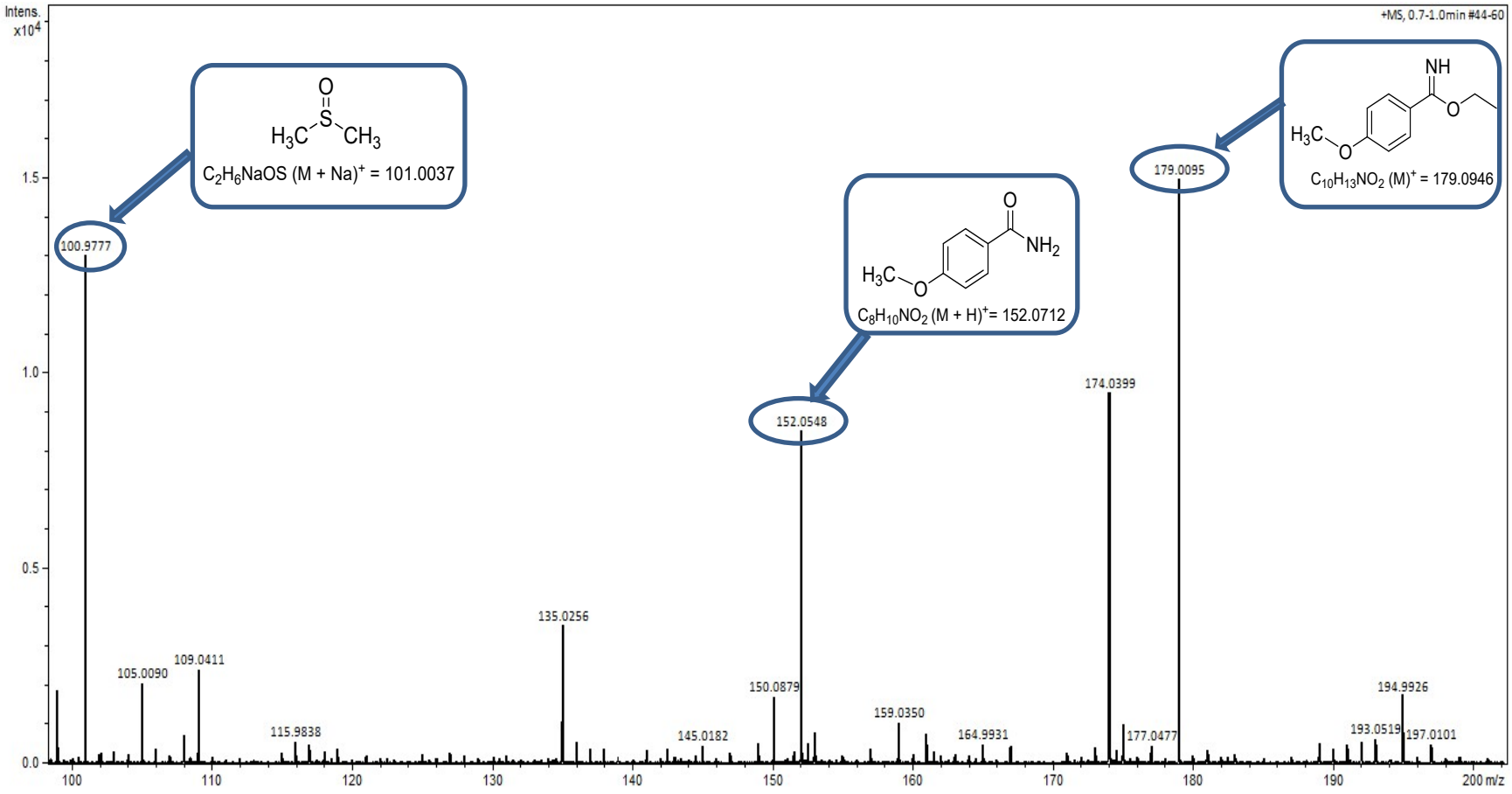


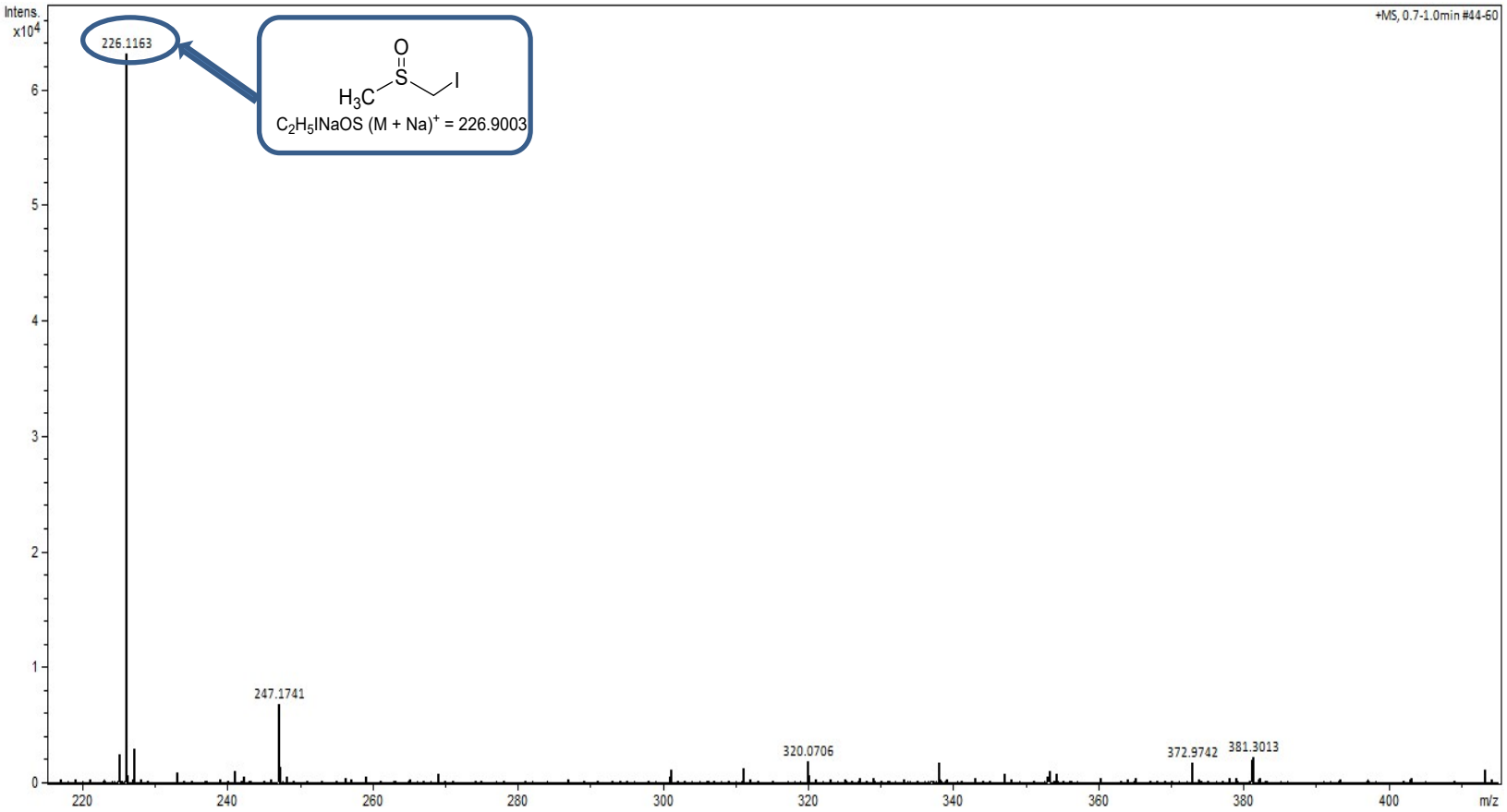
Figure S3: Plausible mechanistic pathway for the bisamide synthesis

9. HRMS- Experimental Data for Bisamide

After 2 hours the mass data



After 4 hours the mass data



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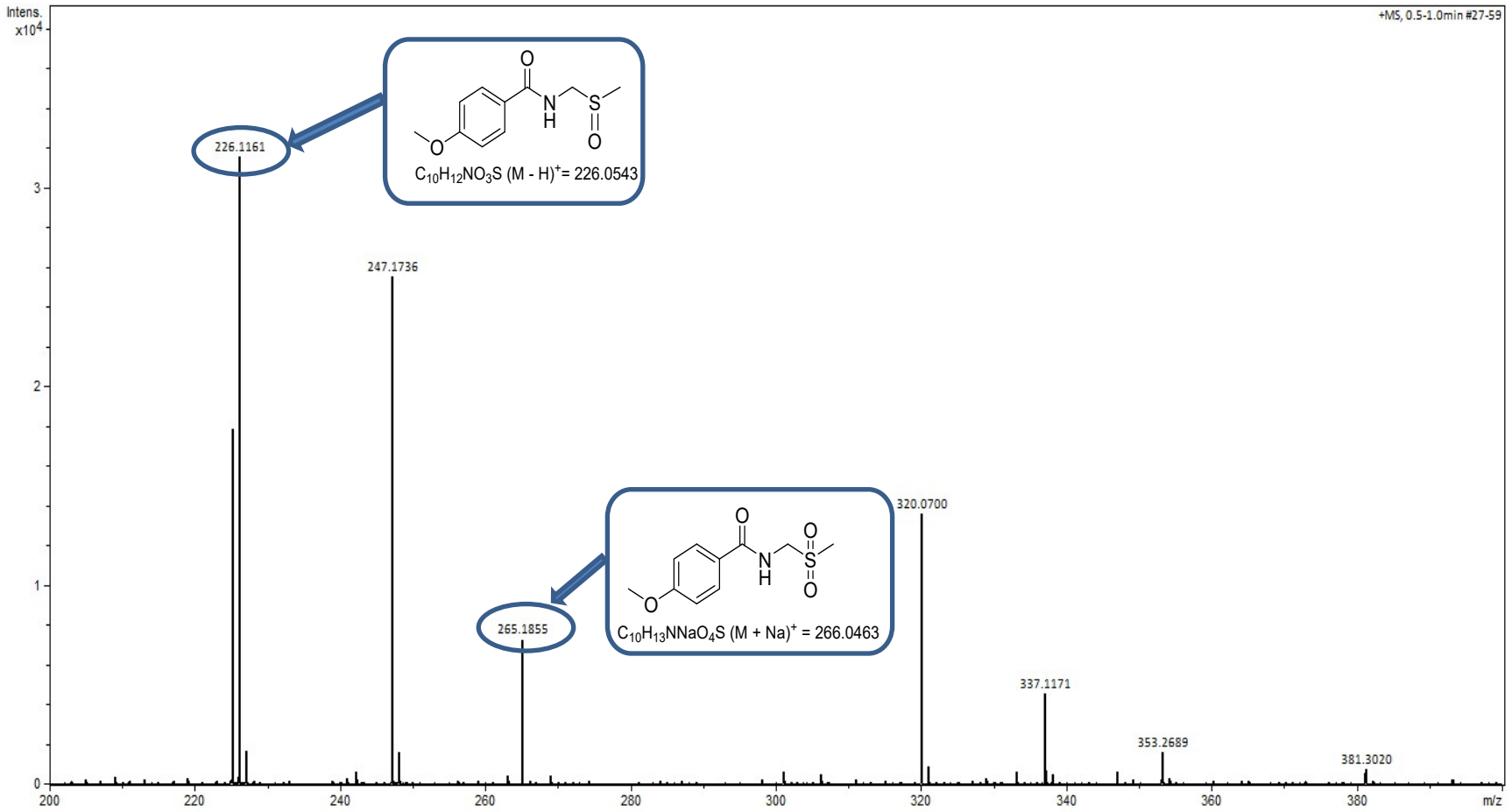
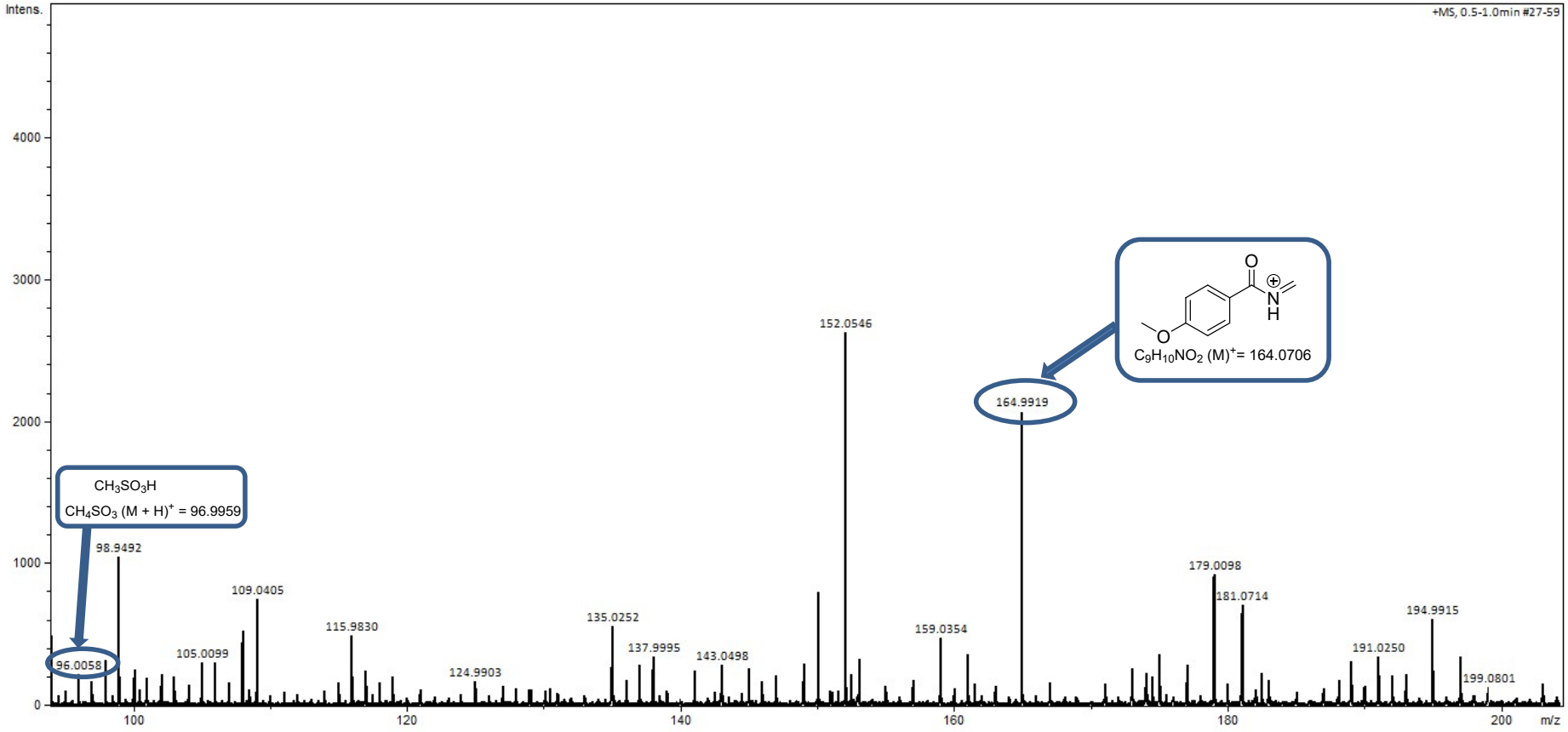
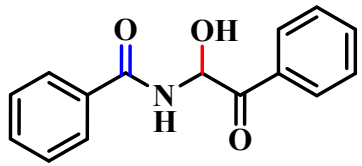


After 8 hours the mass data

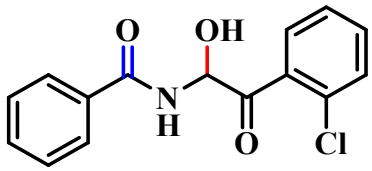


After 10 hours the mass data

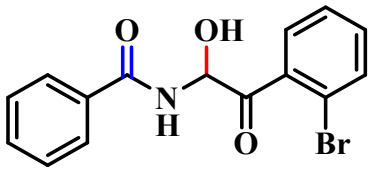
10. Spectroscopic Data of α-amidohydroxyketones (3), symmetric bisamides (4) and unsymmetrical bisamides (5)



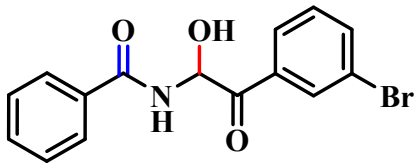
***N*-(1-Hydroxy-2-oxo-2-phenylethyl)benzamide (3aa)**: The compound **(3aa)** was prepared using ethyl benzimidate (1 mmol) and acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (192 mg, 0.75 mmol, 75% yield), **M.P.** 125-126 ^{0}C ; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.52 (d, *J*= 7.8 Hz, 2H), 7.46 – 7.55 (m, 5H), 7.62 (d, *J*= 7.5 Hz, 1H), 7.86 (d, *J*= 1.5 Hz, 2H), 7.89 – 8.01 (m, 2H), 9.37 (d, *J*= 7.5 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 73.6, 127.6, 128.4, 128.6, 128.7, 131.8, 133.5, 133.6, 134.3, 166.0, 195.2; **FT-IR** (KBr, cm^{-1}): υ_{max} 1062, 1093, 1384, 1483, 1509, 1584, 1641, 1696, 3381; ESI-MS (*m*/*z*) for $C_{15}H_{14}NO_3$ $[M+H]^+$: Calculated 256.0974, found 256.0978.



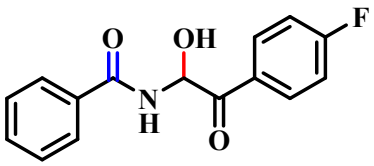
***N*-(2-(2-Chlorophenyl)-1-hydroxy-2-oxoethyl) benzamide (3ab)**: The compound **(3ab)** was prepared using ethyl benzimidate (1 mmol) and 2-chloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (25% ethyl acetate in petroleum ether) afforded the title compound as gummy colorless liquid (232 mg, 0.80 mmol, 80% yield); **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.27 (d, *J*= 8.1 Hz, 1H), 6.75 (s, 1H), 7.44 – 7.54 (m, 3H), 7.70 (d, *J*= 7.2 Hz, 2H), 7.84 – 7.90 (m, 3H), 8.04 (d, *J*= 7.2 Hz, 1H), 9.44 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 75.6, 118.5, 127.3, 127.5, 128.4, 129.6, 131.8, 132.0, 133.1, 133.5, 139.1, 166.3, 199.7; **FT-IR** (neat, cm^{-1}): υ_{max} 1064, 1094, 1386, 1482, 1510, 1586, 1643, 1695, 3380; ESI-MS (*m*/*z*) for $C_{15}H_{13}ClNO_3$ $[M+H]^+$: Calculated 290.0584, found 290.0588.



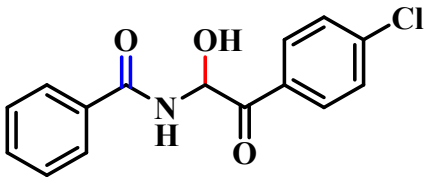
***N*-(2-(2-Bromophenyl)-1-hydroxy-2-oxoethyl) benzamide (3ac)**: The compound **(3ac)** was prepared using ethyl benzimidate (1 mmol) and 2-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as gummy liquid (265 mg, 0.80 mmol, 80% yield); **^{1}H NMR** (300MHz, d_6-DMSO): δ 6.26 (t, *J*= 6.9 Hz, 1H), 6.71 (d, *J*= 6.3 Hz, 1H), 7.44 – 7.55 (m, 6H), 7.68 (d, *J*= 1.5 Hz, 1H), 7.70 – 7.86 (m, 2H), 9.41 (d, *J*= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 75.5, 118.4, 127.3, 127.5, 128.4, 129.6, 131.8, 132.0, 133.1, 133.4, 139.1, 166.2, 199.6; **FT-IR** (Neat, cm^{-1}): u_{max} 1060, 1094, 1386, 1481, 1507, 1585, 1644, 1698, 3381; ESI-MS (*m*/*z*) for $C_{15}H_{12}BrNNaO_3$ $[M+Na]^+$: Calculated 355.9898, found 355.9894.



***N*-(2-(3-Bromophenyl)-1-hydroxy-2-oxoethyl) benzamide (3ad)**: The compound **(3ad)** was prepared using ethyl benzimidate (1 mmol) and 3-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (273 mg, 0.82 mmol, 82% yield), **M.P.** 129-130 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.42 (d, *J*= 7.5 Hz, 1H), 6.64 (s, 1H), 7.43 – 7.54 (m, 4H), 7.80 – 7.87 (m, 3H), 7.95 (d, *J*= 7.5 Hz, 1H), 8.10 (s, 1H), 9.43 (d, *J*= 7.5 Hz, 1H) ; **^{13}C NMR** (75 MHz, d_6-DMSO): δ 74.0, 121.8, 127.4, 127.5, 128.4, 130.8, 131.1, 131.8, 133.4, 135.8, 136.5, 166.0, 194.3; **FT-IR** (KBr, cm^{-1}): u_{max} 1061, 1094, 1382, 1484, 1510, 1586, 1643, 1697, 3378 ; ESI-MS (*m*/*z*) for $C_{15}H_{13}BrNO_3$ $[M+H]^+$: Calculated 334.0079, found 334.0084.

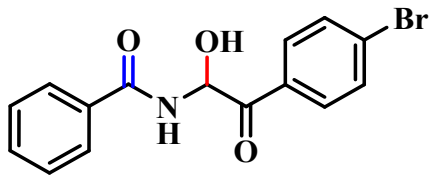


***N*-(2-(4-Fluorophenyl)-1-hydroxy-2-oxoethyl) benzamide (3ae)**: The compound **(3ae)** was prepared using ethyl benzimidate (1 mmol) and 4-fluoro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (232 mg, 0.85 mmol, 85% yield), **M.P.** 125-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.51 (d, J= 7.5 Hz, 1H), 6.59 (d, J= 6.9 Hz, 1H), 7.35 (t, J= 8.7 Hz, 2H), 7.45 – 7.54 (m, 3H), 7.88 (d, J= 7.2 Hz, 2H), 8.05 – 8.10 (m, 2H), 9.39 (d, J= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 73.7, 115.8 (C-F, $^2J_{C\text{-}F}$= 21.7 Hz), 127.6, 128.4, 131.0 (C-F, $^4J_{C\text{-}F}$= 3 Hz), 131.5 (C-F, $^3J_{C\text{-}F}$= 9.0 Hz), 131.8, 133.5, 165.0 (C-F, $^1J_{C\text{-}F}$= 250.5), 166.0, 193.8; **FT-IR** (KBr, cm^{-1}): υ_{max} 1065, 1092, 1381, 1484, 1508, 1585, 1640, 1697, 3383; ESI-MS (*m*/*z*) for $C_{15}H_{13}FNO_3$ $[M+H]^+$: Calculated 274.0879, found 274.0882.

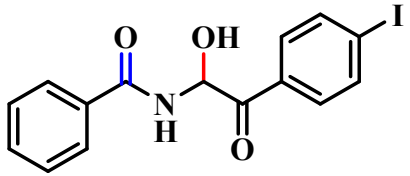


***N*-(2-(4-Chlorophenyl)-1-hydroxy-2-oxoethyl) benzamide (3af):** The compound **(3af)** was prepared using ethyl benzimidate (1 mmol), 4-chloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (243 mg, 0.84 mmol, 84% yield), **M.P.** 127-128 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.47 (d, J= 7.2 Hz, 1H), 6.60 (s, 1H), 7.43 – 7.47 (m, 2H), 7.51 – 7.60 (m, 3H), 7.86 – 7.98 (m, 2H), 8.01 – 8.11 (m, 2H), 9.41 (d, J= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 73.9, 127.6, 128.4, 128.8, 130.4, 131.8, 133.1, 133.4, 138.3, 166.0, 194.4; **FT-IR** (KBr, cm^{-1}):

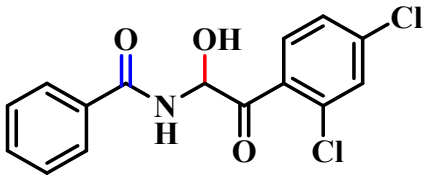
u_{max} 1062, 1093, 1384, 1483, 1509, 1584, 1641, 1696, 3381; ESI-MS (*m*/*z*) for $C_{15}H_{13}ClNO_3$ $[M+H]^+$: Calculated 290.0584, found 290.0586.



***N*-(2-(4-Bromophenyl)-1-hydroxy-2-oxoethyl) benzamide (3ag)**: The compound **(3ag)** was prepared using ethyl benzimidate (1 mmol) and 4-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (282 mg, 0.82 mmol, 82% yield), **M.P.** 126-128 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.43 (t, *J*= 7.5 Hz, 1H), 6.58 (d, *J*= 6.9 Hz, 1H), 7.45 (t, *J*= 7.5 Hz, 2H), 7.54 (t, *J*= 7.5 Hz, 1H), 7.74 (d, *J*= 8.4 Hz, 2H), 7.85 – 7.88 (m, 4H), 9.40 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 74.2, 127.9, 128.0, 128.8, 130.9, 131.8, 132.2, 132.3, 133.9, 166.4, 195.0; **FT-IR** (KBr, cm^{-1}): u_{max} 1061, 1095, 1380, 1480, 1511, 1585, 1640, 1699, 3387; ESI-MS (*m*/*z*) for $C_{15}H_{13}BrNO_3$ $[M+H]^+$: Calculated 334.0079, found 334.0075.

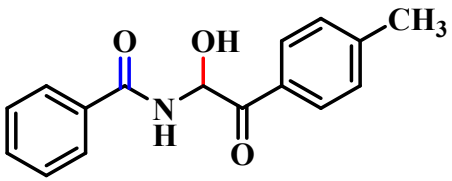


***N*-(1-Hydroxy-2-(4-iodophenyl)-2-oxoethyl) benzamide (3ah)**: The compound **(3ah)** was prepared using ethyl benzimidate (1 mmol), 4-iodo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (317 mg, 0.83 mmol, 83% yield), **M.P.** 125-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.43 (d, *J*= 7.5 Hz, 1H), 6.54 (d, *J*= 6.6 Hz, 1H), 7.43 – 7.48 (m, 2H), 7.53 (d, *J*= 7.2 Hz, 1H), 7.72 (d, *J*= 8.4 Hz, 2H), 7.86 (d, *J*= 7.2 Hz, 2H), 7.92 (d, *J*= 8.4 Hz, 2H), 9.37 (d, *J*= 7.8 Hz, 1H); **^{13}C NM**R (75 MHz, d_6-DMSO): δ 73.7, 102.0, 127.5, 128.4, 130.1, 131.8, 133.4, 133.7, 137.6, 166.0, 194.9; **FT-IR** (KBr, cm^{-1}): u_{max} 1060, 1096, 1383, 1481, 1507, 1585, 1640, 1697, 3385; ESI-MS (*m*/*z*) for $C_{15}H_{13}INO_3$ $[M+H]^+$: Calculated 381.9940, found 381.9938.

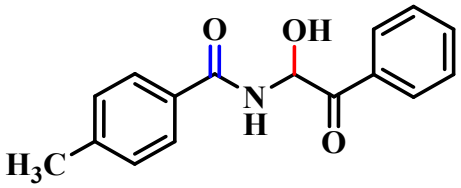


***N*-(2-(2,4-Dichlorophenyl)-1-hydroxy-2-oxoethyl) benzamide (3ai)**: The compound **(3ai)** was prepared using ethyl benzimidate (1 mmol) and 2,4-di chloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as gummy liquid (272 mg, 0.84 mmol, 84% yield); **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.20 (d, *J*= 6.3 Hz, 1H), 6.77 (s, 1H), 7.43 – 7.48 (m, 2H), 7.52 (d, *J*= 7.5 Hz, 2H), 7.67 (s, 1H), 7.74 (d, *J*= 8.4 Hz, 1H), 7.86 (d, *J*= 7.5 Hz, 2H), 9.46 (d, *J*= 7.5 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 75.9, 127.2, 127.5, 128.4, 129.6, 131.2, 131.4, 131.9, 133.3, 135.7,

135.9, 166.2, 198.1; **FT-IR** (neat, cm^{-1}): υ_{max} 1061, 1095, 1383, 1480, 1511, 1585, 1644, 1699, 3385; ESI-MS (*m*/*z*) for $C_{15}H_{12}Cl_2NO_3$ $[M+H]^+$: Calculated 324.0194, found 324.0190.

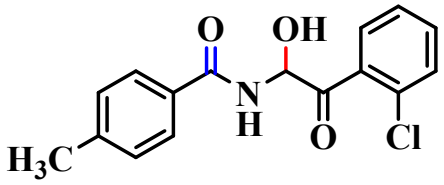


***N*-(1-Hydroxy-2-oxo-2-(p-tolyl) ethyl) benzamide (3aj)**: The compound **(3aj)** was prepared using ethyl benzimidate (1 mmol) and 4-methyl acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (194 mg, 0.72 mmol, 72% yield), **M.P.** 125-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.35 (s, 3H), 6.38 (s, 1H), 6.48 (s, 1H), 6.97 (d, *J*= 8.7 Hz, 2H), 7.31 (d, *J*= 7.8 Hz, 2H), 7.84 – 7.89 (m, 5H), 9.19 (d, *J*= 7.8 Hz, 1H);**^{13}C-NMR** (75 MHz, d_6-DMSO): δ 21.2, 73.3, 126.2, 127.5, 128.2, 129.5, 129.6, 131.0, 132.4, 141.5, 165.4, 194.8; **FT-IR** (KBr, cm^{-1}): υ_{max} 1062, 1094, 1385, 1484, 1511, 1585, 1646, 1699, 3380; ESI-MS (*m*/*z*) for $C_{16}H_{16}NO_3$ $[M+H]^+$: Calculated 270.1130, found 270.1128.

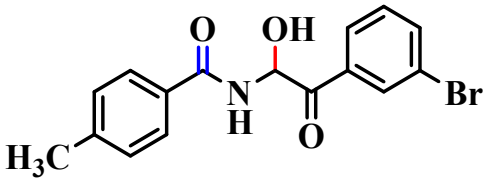


***N*-(1-Hydroxy-2-oxo-2-phenylethyl)-4-methylbenzamide (3ba)**: The compound **(3ba)** was prepared using 4-methyl ethyl benzimidate (1 mmol) and acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (216 mg, 0.80 mmol, 80% yield), **M.P.** 126-128 ^{0}C ; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.33 (s, 3H), 6.50 (d, *J*= 6.9 Hz, 2H), 7.25 (d, *J*= 8.1 Hz, 2H), 7.48 - 7.53 (m, 2H), 7.60 (d, *J*= 7.5 Hz, 1H), 7.78 (d, *J*= 8.1

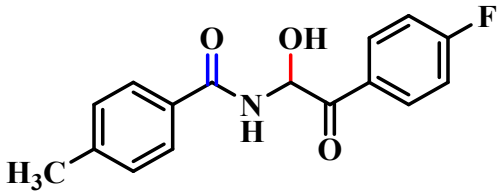
Hz, 2H), 7.97 – 8.00 (m, 2H), 9.28 (d, *J*= 6.9 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): *δ* 21.4, 73.9, 128.0, 128.9, 129.1, 129.3, 131.2, 133.9, 134.7, 142.2, 166.3, 195.7; **FT-IR** (KBr, cm^{-1}): u_{max} 1064, 1095, 1385, 1486, 1510, 1584, 1643, 1697, 3381; ESI-MS (*m*/*z*) for $C_{16}H_{16}NO_3$ $[M+H]^+$: Calculated 270.1130, found 270.1134.



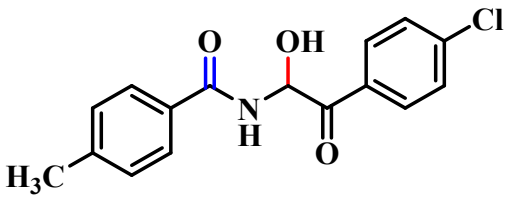
***N*-(2-(2-Chlorophenyl)-1-hydroxy-2-oxoethyl)-4-methylbenzamide (3bb)**: The compound **(3bb)** was prepared using 4 methyl ethyl benzimidate (1 mmol) and 2-chloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as grey liquid (224 mg, 0.74 mmol, 74% yield); **^{1}H NMR** (300 MHz, d_6-DMSO): *δ* 2.33 (s, 3H), 6.15 (d, *J*= 7.5 Hz, 1H), 6.71 (s, 1H), 7.25 (d, *J*= 7.8 Hz, 2H), 7.50 – 7.53 (m, 1H), 7.67 – 7.74 (m, 5H), 9.37 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR**(75MHz, d_6-DMSO): *δ* 21.0, 75.8, 127.1, 127.5, 128.7, 128.9, 129.5, 130.5, 131.2, 131.3, 135.8, 141.8, 166.0, 198.2; **FT-IR** (neat, cm^{-1}): u_{max} 1060, 1096, 1384, 1486, 1509, 1584, 1642, 1696, 3381; ESI-MS (*m*/*z*) for $C_{16}H_{15}ClNO_3$ $[M+H]^+$: Calculated 304.0740, found 304.0738.



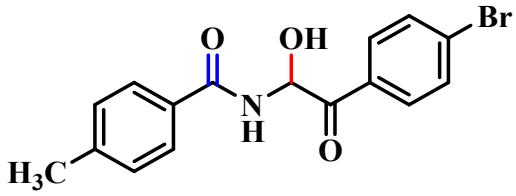
***N*-(2-(3-Bromophenyl)-1-hydroxy-2-oxoethyl)-4-methylbenzamide (3bd)**: The compound **(3bd)** was prepared using 4-methyl ethyl benzimidate (1 mmol) and 3-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (264 mg, 0.76 mmol, 76% yield), **M.P.** 126-128 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.33 (s, 3H), 6.41 (t, J= 7.5 Hz, 1H), 6.58 (d, J= 6.9 Hz, 1H), 7.25 (d, J= 8.1 Hz, 2H), 7.47 (t, J= 7.8 Hz, 1H), 7.76 – 7.82 (m, 3H), 7.95 (d, J= 7.8 Hz, 1H), 8.10 (s, 1H), 9.34 (d, J= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 21.0, 74.0, 121.8, 127.4, 127.6, 128.9, 130.6, 130.8, 131.0, 135.8, 136.5, 141.8, 165.9, 194.3; **FT-IR** (KBr, cm^{-1}): u_{max} 1061, 1093, 1386, 1482, 1508, 1586, 1643, 1697, 3382; ESI-MS (*m*/*z*) for $C_{16}H_{15}BrNO_3$ $[M+H]^+$: Calculated 348.0235, found 348.0239.



***N*-(2-(4-Fluorophenyl)-1-hydroxy-2-oxoethyl)-4-methylbenzamide (3be):** The compound **(3be)** was prepared using 4-methyl ethyl benzimidate (1 mmol), 4-fluoro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (224 mg, 0.78 mmol, 78% yield), **M.P.** 131-132 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.33 (s, 3H), 6.46 – 6.49 (m, 2H), 7.26 (d, J= 7.8 Hz, 2H), 7.36 (d, J= 9.0 Hz, 2H), 7.78 (d, J= 8.1 Hz, 2H), 8.04 – 8.08 (m, 2H), 9.26 (d, J= 7.5 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 21.0, 73.6, 115.7 (C-F, $^2J_{C\text{-}F}$ = 21.7 Hz), 127.6, 128.9, 130.7, 131.0 (C-F, $^4J_{C\text{-}F}$= 3 Hz), 131.5 (C-F, $^3J_{C\text{-}F}$= 9.7 Hz), 141.8, 165.0 (C-F, $^1J_{C\text{-}F}$= 250.5 Hz), 165.8, 193.9; **FT-IR** (KBr, cm^{-1}): u_{max} 1060, 1097, 1387, 1488, 1512, 1587, 1644, 1696, 3382; ESI-MS (*m*/*z*) for $C_{16}H_{15}FNO_3$ $[M+H]^+$: Calculated 288.1036, found 288.1034.

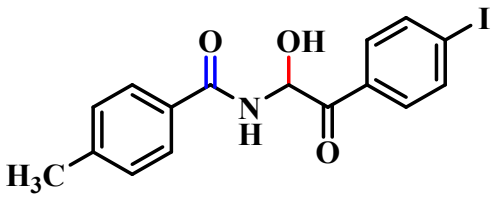


***N*-(2-(4-Chlorophenyl)-1-hydroxy-2-oxoethyl)-4-methylbenzamide (3bf)**: The compound **(3bf)** was prepared using 4-methyl ethyl benzimidate (1 mmol), 4-chloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (240 mg, 0.79 mmol, 79% yield), **M.P.** 125-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.33 (s, 3H), 6.44 (d, *J*= 7.8 Hz, 1H), 6.53 (s, 1H), 7.25 (d, *J*= 8.1 Hz, 2H), 7.58 (d, *J*= 8.4 Hz, 2H), 7.77 (d, *J*= 8.1 Hz, 2H), 7.98 (d, *J*= 8.4 Hz, 2H), 9.29 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 21.0, 73.8, 127.6, 128.8, 129.0, 130.4, 130.7, 133.1, 138.3, 141.9, 165.9, 194.5; **FT-IR** (KBr, cm^{-1}): υ_{max} 1061, 1096, 1387, 1485, 1511, 1586, 1647, 1697, 3381; ESI-MS (*m*/*z*) for $C_{16}H_{15}ClNO_3$ $[M+H]^+$: Calculated 304.0740, found 304.0735.

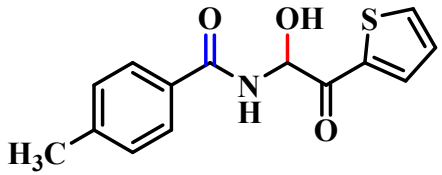


***N*-(2-(4-Bromophenyl)-1-hydroxy-2-oxoethyl)-4-methylbenzamide (3bg)** The compound **(3bg)** was prepared using 4-methyl ethyl benzimidate (1 mmol) and 4-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as reddish yellow solid (267 mg, 0.77 mmol, 77% yield), **M.P.** 128-130 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.33 (s, 3H), 6.43 (d, *J*= 6.9 Hz, 1H), 6.53 (d, *J*= 6.3 Hz, 1H), 7.25 (d, *J*= 7.8 Hz, 2H), 7.71 – 7.78 (m, 4H), 7.90 (d, *J*= 8.4 Hz, 2H), 9.30 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 21.0, 73.8, 127.5, 127.6, 129.0, 130.5, 130.6,

131.7, 133.5, 141.9, 166.0, 194.7; **FT-IR** (KBr, cm^{-1}): u_{max} 1063, 1095, 1386, 1485, 1507, 1587, 1647, 1696, 3383; ESI-MS (*m*/*z*) for $C_{16}H_{15}BrNO_3$ $[M+H]^+$: Calculated 348.0235, found 348.0239.

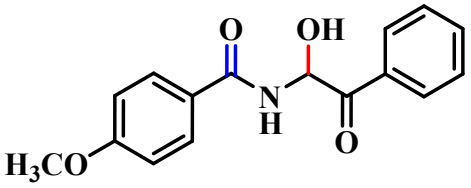


***N*-(1-Hydroxy-2-(4-iodophenyl)-2-oxoethyl)-4-methylbenzamide (3bh)**: The compound **(3bh)** was prepared using 4-methyl ethyl benzimidate (1 mmol) and 4-iodo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellowish solid (300 mg, 0.76 mmol, 76% yield), **M.P.** 124-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.34 (s, 3H), 6.41 (d, *J*= 7.5 Hz, 1H), 6.49 (d, *J*= 6.6 Hz, 1H), 7.25 (d, *J*= 8.1 Hz, 2H), 7.70 – 7.78 (m, 4H), 7.91 (d, *J*= 8.4 Hz, 2H), 9.27 (d, *J*= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 21.0, 73.6, 102.0, 127.6, 128.9, 130.1, 130.6, 133.7, 137.5, 141.8, 165.8, 194.9; **FT-IR** (KBr, cm^{-1}): u_{max} 1061, 1095, 1384, 1485, 1509, 1584, 1645, 1697, 3385; ESI-MS (*m*/*z*) for $C_{16}H_{15}INO_3$ $[M+H]^+$: Calculated 396.0097, found 396.0099.

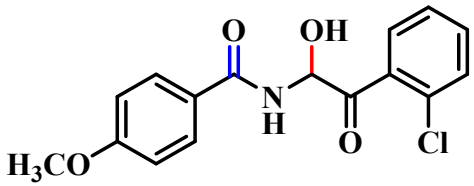


***N*-(1-Hydroxy-2-oxo-2-(thiophen-2-yl)ethyl)-4-methylbenzamide (3bk)**: The compound **(3bk)** was prepared using 4-methyl ethyl benzimidate (1 mmol) and 1-(thiophen-2-yl) ethan-1-one (1 mmol) as starting materials. Purification by column chromatography (25%

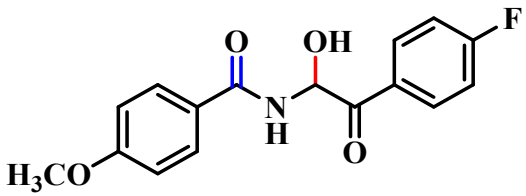
ethyl acetate in petroleum ether) afforded the title compound as white solid (193 mg, 0.70 mmol, 70% yield); **M.P.** 132-134 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 2.33 (s, 3H), 6.40 (t, J= 7.5 Hz, 1H), 6.62 (d, J= 6.9Hz, 1H), 7.25 (d, J= 7.8 Hz, 2H), 7.46 (d, J= 7.8 Hz, 2H), 7.79 – 7.91 (m, 3H), 8.95 (d, J= 6.9 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 21.4, 73.5, 127.9, 128.7, 129.2, 131.6, 131.9, 134.4, 141.7, 166.9, 194.3; **FT-IR** (KBr, cm^{-1}): υ_{max} 1064, 1098, 1384, 1486, 1512, 1583, 1643, 1697, 3383; ESI-MS (*m*/*z*) for $C_{14}H_{14}NO_3S$ $[M+H]^+$: Calculated 276.0694, found 276.0692.



***N*-(1-Hydroxy-2-oxo-2-phenylethyl)-4-methoxybenzamide (3ca)**: The compound **(3ca)** was prepared using 4-methoxy ethyl benzimidate (1 mmol) and acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (226 mg, 0.79 mmol, 79% yield), **M.P.** 125-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 3.79 (s, 3H), 6.44 (d, J= 6.6 Hz, 1H), 6.49 (d, J= 7.2 Hz, 1H), 6.98 (d, J= 9.0 Hz, 2H), 7.48 – 7.53 (m, 2H), 7.61 (d, J= 7.2 Hz, 1H), 7.86 (d, J= 8.7 Hz, 2H), 7.97 (d, J= 7.2 Hz, 2H), 9.21 (d, J= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 55.8, 73.9, 114.0, 126.1, 128.9, 129.1, 129.9, 133.9, 134.7, 162.4, 165.8, 195.7; **FT-IR** (KBr, cm^{-1}): υ_{max} 1060, 1096, 1388, 1485, 1509, 1586, 1648, 1697, 3383; ESI-MS (*m*/*z*) for $C_{16}H_{16}NO_4$ $[M+H]^+$: Calculated 286.1079, found 286.1074.

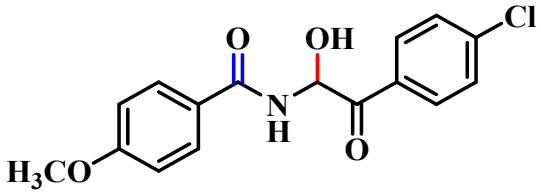


***N*-(2-(2-Chlorophenyl)-1-hydroxy-2-oxoethyl)-4-methoxybenzamide (3cb)**: The compound **(3cb)** was prepared using 4-methoxy ethyl benzimidate (1 mmol), 2-chloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (253 mg, 0.74 mmol, 74% yield), **M.P.** 130-132 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 3.79 (s, 3H), 6.23 (t, J= 6.9 Hz, 1H), 6.64 (d, J= 6.3 Hz, 1H), 6.99 (d, J= 8.7 Hz, 2H), 7.48 (d, J= 6.9 Hz, 2H), 7.68 (d, J= 6.9Hz, 1H), 7.84 (d, J= 8.7 Hz, 2H) 9.27 (d, J= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 55.8, 76.2, 113.8, 125.9, 127.3, 129.8, 129.9, 130.1, 130.4, 132.4, 137.4, 162.4, 166.1, 199.5; **FT-IR** (KBr, cm^{-1}): u_{max} 1061, 1095, 1386, 1486, 1508, 1588, 1641, 1695, 3381; ESI-MS (*m*/*z*) for $C_{16}H_{14}ClNNaO_4$ $[M+Na]^+$: Calculated 342.0509, found 342.0506.

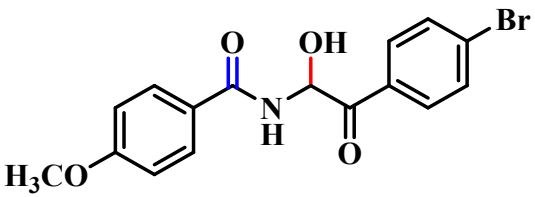


***N*-(2-(4-Fluorophenyl)-1-hydroxy-2-oxoethyl)-4-methoxybenzamide (3ce)**: The compound **(3ce)** was prepared using 4-methoxy ethyl benzimidate (1 mmol) and 4-fluoro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (243 mg, 0.80 mmol, 80% yield), **M.P.** 132-134 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 3.79 (s, 3H), 6.49 (s, 2H), 6.98 (d, J= 8.4 Hz, 2H), 7.35 (t, J= 8.7 Hz, 2H), 7.87 (d, J= 8.4 Hz, 2H), 8.04 – 8.08 (m, 2H), 9.23 (d, J= 6.3 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 55.4, 73.6, 113.6, 115.7 (C-F, $^2J_{C\text{-}F}$= 21.7 Hz), 125.6, 129.5,

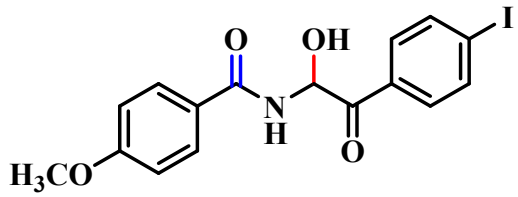
131.0 (C-F, $^{4}J_{C\text{-}F}$= 3 Hz), 131.5 (C-F, $^{3}J_{C\text{-}F}$= 9.7 Hz), 162.0, 165.0 (C-F, $^{1}J_{C\text{-}F}$= 250.5 Hz), 165.4, 193.9; **FT-IR** (KBr, cm^{-1}): u_{max} 1060, 1095, 1388, 1483, 1512, 1586, 1647, 1701, 3386; ESI-MS (*m*/*z*) for $C_{16}H_{15}FNO_4$ $[M+H]^+$: Calculated 304.0985, found 304.0984.



***N*-(1-Hydroxy-2-(4-iodophenyl)-2-oxoethyl)-4-methoxybenzamide (3cf)**: The compound **(3cf)** was prepared using 4-methoxy ethyl benzimidate (1 mmol) and 4-chloro acetophenone as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (320 mg, 0.70 mmol, 70% yield), **M.P.** 129-131 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 3.79 (s, 3H), 6.41 (d, *J*= 6.6 Hz, 1H), 6.49 (d, *J*= 6.6 Hz, 1H), 6.98 (d, *J*= 8.7 Hz, 2H), 7.57 – 7.60 (m, 2H), 7.84 – 7.87 (m, 2H), 7.96 – 7.99 (m, 2H), 9.23 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 55.4, 73.7, 113.6, 125.5, 128.7, 129.5, 130.3, 133.1, 138.2, 162.0, 165.4, 194.4; **FT-IR** (KBr, cm^{-1}): u_{max} 1065, 1096, 1384, 1488, 1509, 1583, 1644, 1697, 3381; ESI-MS (*m*/*z*) for $C_{16}H_{15}ClNO_4$ $[M+H]^+$: Calculated 320.0690, found 320.0682.

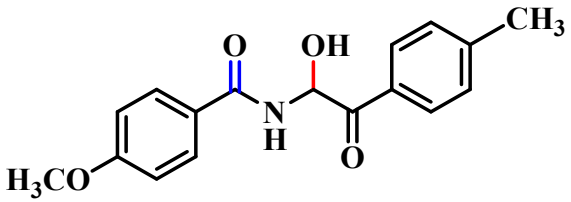


***N*-(2-(4-Bromophenyl)-1-hydroxy-2-oxoethyl)-4-methoxybenzamide(3cg):** The compound **(3cg)** was prepared using 4-methoxy ethyl benzimidate (1 mmol), 4-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (287 mg, 0.79 mmol, 79% yield), **M.P.** 133-134 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 3.80 (s, 3H), 6.41 (s, 1H), 6.48 (s, 1H), 6.98 (d, *J*= 7.8 Hz, 2H), 7.73 (d, *J*= 6.9 Hz, 2H), 7.84 – 7.90 (m, 4H), 9.24 (d, *J*= 7.2 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 55.4, 73.7, 113.6, 125.5, 127.3, 129.5, 130.4, 131.7, 133.5, 162.0, 165.4, 194.7; **FT-IR** (KBr, cm^{-1}): υ_{max} 1064, 1096, 1382, 1481, 1513, 1586, 1648, 1695, 3382; ESI-MS (*m*/*z*) for $C_{16}H_{15}BrNO_4$ $[M+H]^+$: Calculated 364.0184, found 364.0181.

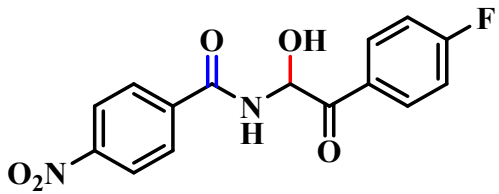


***N*-(1-Hydroxy-2-(4-iodophenyl)-2-oxoethyl)-4-methoxybenzamide (3ch)**: The compound **(3ch)** was prepared using 4-methoxy ethyl benzimidate (1 mmol), 4-iodo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellowish solid (329 mg, 0.80 mmol, 80% yield), **M.P.** 125-126 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 3.79 (s, 3H), 6.41 (s, 1H), 6.46 (s, 1H), 6.98 (d, *J*= 8.7 Hz, 2H), 7.71 (d, *J*= 7.8 Hz, 2H), 7.84 – 7.92 (m, 4H), 9.23

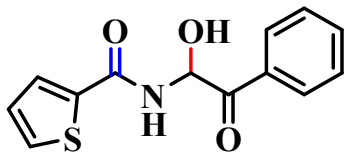
(d, *J*= 7.2 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): *δ* 55.4, 73.6, 102.0, 113.6, 125.5, 129.5, 130.1, 133.7, 137.5, 162.0, 165.3, 195.0; **FT-IR** (KBr, cm^{-1}): u_{max} 1063, 1096, 1388, 1482, 1517, 1582, 1643, 1701, 3385; ESI-MS (*m*/*z*) for $C_{16}H_{15}INO_4$ $[M+H]^+$: Calculated 412.0046, found 412.0042.



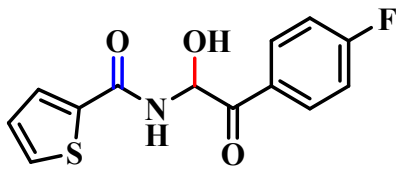
***N*-(1-Hydroxy-2-oxo-2-(p-tolyl)ethyl)-4-methoxybenzamide (3cj)**: The compound **(3cj)** was prepared using 4-methoxy ethyl benzimidate (1 mmol) and 4-methyl acetophenone as a starting material. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (222 mg, 0.74 mmol, 74% yield), **M.P.** 132-133 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): *δ* 2.34 (s, 3H), 3.79 (s, 3H), 6.39 (s, 1H), 6.47 (s, 1H), 6.97 (d, *J*= 8.7 Hz, 2H), 7.31 (d, *J*= 7.8 Hz, 2H), 7.84 – 7.89 (m, 4H), 9.19 (d, *J*= 7.8 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): *δ* 21.2, 55.4, 73.3, 113.6, 125.7, 128.6, 129.2, 129.5, 131.7, 144.0, 162.0, 165.4, 194.8; **FT-IR** (KBr, cm^{-1}): u_{max} 1065, 1097, 1382, 1487, 1515, 1588, 1643, 1695, 3382; ESI-MS (*m*/*z*) for $C_{17}H_{18}NO_4$ $[M+H]^+$: Calculated 300.1236, found 300.1234.



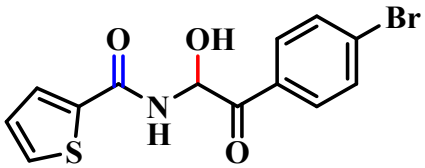
***N*-(2-(4-Fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de)**: The compound **(3de)** was prepared using 4-nitro ethyl benzimidate (1 mmol), 4-fluoro acetophenone (1 mmol) as a starting material. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (239 mg, 0.74 mmol, 74% yield), **M.P.** 132-134 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.51 (t, J= 7.2 Hz, 1H), 6.79 (d, J= 6.6 Hz, 1H), 7.37 (t, J= 9 Hz, 2H), 8.08 (t, J= 8.4 Hz, 4H), 8.31 (d, J= 8.7 Hz, 2H), 9.73 (d, J= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 74.0, 115.8 (C-F, $^2J_{C\text{-}F}$= 21.7 Hz), 123.6, 129.1, 130.9, 131.6 (C-F, $^3J_{C\text{-}F}$= 9.7 Hz), 139.1, 149.3, 165.1 (C-F, $^1J_{C\text{-}F}$= 251.2 Hz), 164.5, 193.5; **FT-IR** (KBr, cm^{-1}): υ_{max} 1064, 1096, 1388, 1488, 1509, 1582, 1645, 1693, 3384; ESI-MS (*m*/*z*) for $C_{15}H_{12}FN_2O_5$ [M+H]$^+$: Calculated 319.0730, found 319.0726.



***N*-(1-Hydroxy-2-oxo-2-phenylethyl) thiophene-2-carboxamide (3ea):** The compound **(3ea)** was prepared using thiophene-2-carbimidate (1 mmol), acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (198 mg, 0.76 mmol, 76% yield), **M.P.** 130-132 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.51 (d, J= 7.8 Hz, 1H), 6.58 (d, J= 6.6 Hz, 1H), 7.13 – 7.15 (m, 1H), 7.54 (d, J= 7.8 Hz, 2H), 7.63 (s, 1H), 7.78 – 7.80 (m, 1H), 7.88 – 7.90 (m, 1H), 7.97 – 8.00 (m, 2H), 9.37 (d, J= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 73.3, 128.1, 128.5, 128.7, 129.3, 131.8, 133.5, 134.2, 139.0, 160.9, 194.9; **FT-IR** (KBr, cm^{-1}): υ_{max} 1064, 1095, 1387, 1487, 1513, 1587, 1647, 1698, 3378; ESI-MS (*m*/*z*) for $C_{13}H_{12}NO_3S$ [M+H]$^+$: Calculated 262.0538, found 262.0536.

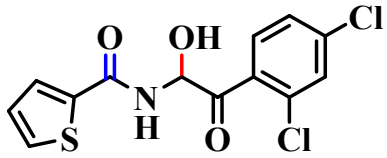


***N*-(2-(4-Fluorophenyl)-1-hydroxy-2-oxoethyl) thiophene-2-carboxamide (3ee)**: The compound **(3ee)** was prepared using ethyl thiophene-2-carbimidate (1 mmol) and 4-fluoro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as yellow solid (224 mg, 0.80 mmol, 80% yield), **M.P.** 130-132 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.49 – 6.53 (m, 1H), 6.66 (d, J= 6.6 Hz, 1H), 7.35 (t, J= 8.7 Hz, 2H), 7.78 (d, J= 4.8 Hz, 1H), 7.91 (d, J= 3.0 Hz, 1H), 8.01 – 8.11 (m , 2H), 9.40 (d, J= 8.1 Hz, 1H); **^{13}C NMR** (75MHz, d_6-DMSO): δ 73.5, 115.8 (C-F, $^2J_{C\text{-}F}$= 21.7 Hz), 128.2, 129.4, 130.9 (C-F, $^4J_{C\text{-}F}$= 3 Hz), 131.6 (C-F, $^3J_{C\text{-}F}$= 9.7 Hz), 131.9, 139.0, 160.9, 165.1 (C-F, $^1J_{C\text{-}F}$= 250.5), 193.6; **FT-IR** (KBr, cm^{-1}): υ_{max} 1066, 1097, 1388, 1488, 1512, 1587, 1647, 1696, 3383; ESI-MS (*m*/*z*) for $C_{13}H_{11}FNO_3S$ $[M+H]^+$: Calculated 280.0444, found 280.0448.

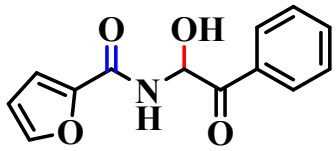


***N*-(2-(4-Bromophenyl)-1-hydroxy-2-oxoethyl) thiophene-2-carboxamide (3eg)**: The compound **(3eg)** was prepared using ethyl thiophene-2-carbimidate (1 mmol) and 4-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as reddish solid (264 mg, 0.78 mmol, 78% yield), **M.P.** 128-130 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.45 (d, J= 7.8 Hz, 1H), 6.53 (s, 1H), 7.12 – 7.15 (m, 1H), 7.74 (d, J= 8.4 Hz, 2H), 7.79 (d, J= 5.1 Hz, 1H), 7.91 (d, J= 8.4 Hz, 3 H), 9.40 (d, J= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 73.5, 127.6, 128.1, 129.3, 130.5, 131.8, 131.9,

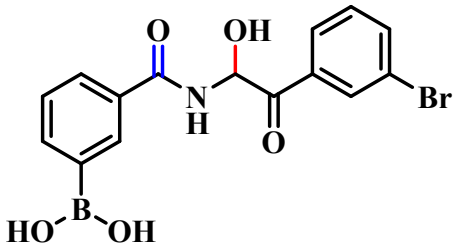
133.3, 138.9, 160.9, 194.3; **FT-IR** (KBr, cm^{-1}): u_{max} 1067, 1093, 1384, 1489, 1507, 1581, 1642, 1703, 3387; ESI-MS (*m*/*z*) for $C_{13}H_{11}BrNO_3S[M+H]^+$: Calculated 339.9643, found 339.9646.



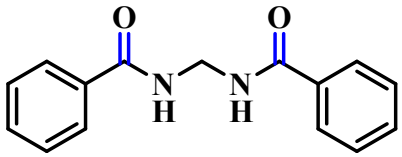
***N*-(2-(2,4-Dichlorophenyl)-1-hydroxy-2-oxoethyl) thiophene-2-carboxamide (3ei)**: The compound **(3ei)** was prepared using thiophene-2-carbimidate (1 mmol) and 2,4-dichloro acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (257 mg, 0.78 mmol, 78% yield), **M.P.** 132-134 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.14 – 6.18 (m, 1H) , 6.84 (d, *J*= 6.6 Hz, 1H), 7.14 – 7.17 (m, 1H), 7.56 (d, *J*= 2.1 Hz, 1H), 7.69 – 7.72 (m, 2H), 7.80 – 7.81 (m, 1H), 7.86 – 7.87 (m, 1H), 9.45 (d, *J*= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 75.6, 127.2, 128.1, 129.3, 129.6, 131.2, 131.4, 131.9, 135.6, 136.0, 138.7, 161.0, 197.8; **FT-IR** (KBr, cm^{-1}): u_{max} 1064, 1097, 1386, 1489, 1508, 1586, 1642, 1704, 3386; ESI-MS (*m*/*z*) for $C_{13}H_{10}Cl_2NO_3S$ $[M+H]^+$: Calculated 329.9758, found 329.9759.



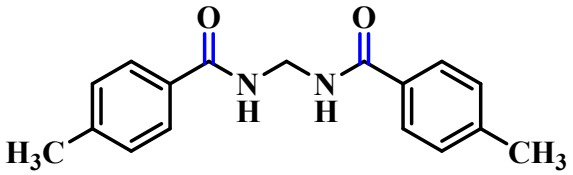
***N*-(1-Hydroxy-2-oxo-2-phenylethyl) furan-2-carboxamide (3fa)**: The compound **(3fa)** was prepared using furan-2-carbimidate (1 mmol) and acetophenone (1 mmol) as starting materials. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (196 mg, 0.80 mmol, 80% yield), **M.P.** 136-138 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.48 (d, *J*= 7.8 Hz, 1H), 6.56 – 6.63 (m, 2H), 7.26 (d, *J*= 3.6 Hz, 1H), 7.50 – 7.86 (m, 3H), 7.97 (s, 1H), 7.98 – 8.00 (m, 2H), 9.08 (d, *J*= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 73.0, 112.5, 115.1, 129.1, 129.1, 134.0, 134.5, 146.2, 147.4, 157.7, 195.2; **FT-IR** (KBr, cm^{-1}): υ_{max} 1066, 1098, 1385, 1490, 1510, 1587, 1640, 1710, 3380; ESI-MS (*m*/*z*) for $C_{13}H_{12}NO_4$ $[M+H]^+$: Calculated 246.0766, found 246.0768.



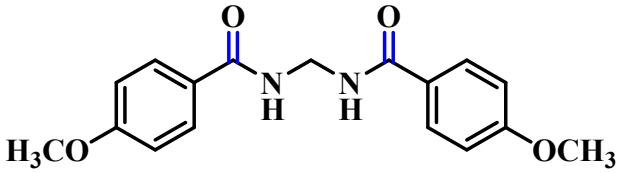
(3-((2-(3-Bromophenyl)-1-hydroxy-2-oxoethyl)carbamoyl)phenyl)boronic acid (3gd): The compound **(3gd)** was prepared using (3-(ethoxy(imino)methyl) phenyl) boronic acid (1 mmol) and 3-bromo acetophenone (1 mmol) as starting materials. Purification by column chromatography (50% ethyl acetate in petroleum ether) afforded the title compound as fluppy solid (272 mg, 0.72 mmol, 72% yield); **M.P.** 138-140 ^{0}C; **^{1}H NMR** (300 MHz, d_6-DMSO): δ 6.42 (t, *J*= 7.5 Hz, 1H), 6.63 (d, *J*= 6.9 Hz, 1H), 7.49 (t, *J*= 7.8 Hz, 1H), 7.79 – 7.86 (m, 5H), 7.95 (d, *J*= 8.1 Hz, 1H), 8.10 (s, 1H), 8.22 (d, *J*= 6.3 Hz, 2H), 9.43 (d, *J*= 8.1 Hz, 1H); **^{13}C NMR** (75 MHz, d_6-DMSO): δ 74.4, 115.1, 122.2, 126.8, 127.9, 129.9, 131.3, 131.5, 134.3, 134.4, 135.1, 136.3, 136.9, 166.6, 194.7; **FT-IR** (KBr, cm^{-1}): υ_{max} 1064, 1098, 1387, 1489, 1515, 1588, 1648, 1703, 3386, 3480; ESI-MS (*m*/*z*) for $C_{15}H_{14}BBrNO_5$ $[M+H]^+$: Calculated 378.0148, found 378.0153.



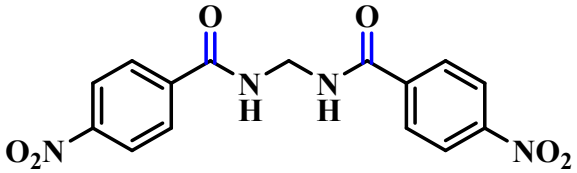
***N,N'*-Methylenedibenzamide (4aa)**[2]: The compound **(4aa)** was prepared using ethyl benzimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (229 mg, 0.90 mmol, 90% yield), **M.P.** 188-190 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.89 (t, J= 5.7 Hz, 2H), 7.44 – 7.54 (m, 6H), 7.91 – 7.94 (m, 4H), 9.07 (t, J= 5.7 Hz, 2H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 45.2, 127.4, 128.3, 131.4, 134.0, 166.5; **FT-IR** (KBr, cm^{-1}): υ_{max} 1053, 1110, 1152, 1183, 1249, 1282, 1402, 1472, 1503, 1536, 1580, 1609, 1633, 2840, 2963, 3326; ESI-MS (*m*/*z*) for $C_{15}H_{15}N_2O_2$ $[M+H]^+$: Calculated 255.1134, found 255.1130.



***N,N'*-Methylenebis(4-methylbenzamide) (4bb)**[2]: The compound **(4bb)** was prepared using 4-methyl ethyl benzimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (30% ethyl acetate in petroleum ether) afforded the title compound as white solid (260 mg, 0.92 mmol, 92% yield), **M.P.** 195-197 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.34 (s, 6H), 4.84 (t, J= 5.7 Hz, 2H), 7.25 (d, J= 8.1 Hz, 4H), 7.81 (d, J= 8.1 Hz, 4H), 8.94 (t, J= 5.4 Hz, 2H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 21.0, 45.1, 127.4, 128.8, 131.2, 141.3, 166.3; **FT-IR** (KBr, cm^{-1}): υ_{max} 1050, 1115, 1152, 1185, 1250, 1286, 1407, 1475, 1507, 1540, 1582, 1607, 1635, 2847, 2961, 3330; ESI-MS (*m*/*z*) for $C_{17}H_{19}N_2O_2$ $[M+H]^+$: Calculated 283.1447, found 283.1443.

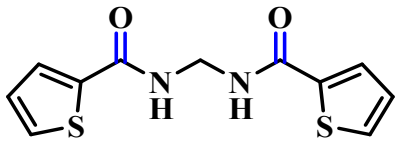


***N,N′*-Methylenebis(4-methoxybenzamide) (4cc)**[2]: The compound **(4cc)** was prepared using 4-methoxy ethyl benzimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (30% ethyl acetate in petroleum ether) afforded the title compound as white solid (295 mg, 0.94 mmol, 94% yield), **M.P.** 196-198 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.80 (s, 6H), 4.83 (t, J= 5.4 Hz, 2H), 6.98 (d, J= 8.7 Hz, 4H), 7.90 (d, J= 8.7 Hz, 4H), 8.90 (t, J= 5.4 Hz, 2H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 45.1, 55.3, 113.5, 126.2, 129.3, 161.7, 166.0; **FT-IR** (KBr, cm^{-1}): u_{max} 1058, 1118, 1153, 1186, 1248, 1285, 1407, 1476, 1508, 1539, 1587, 1610, 1634, 2845, 2964, 3327; ESI-MS (m/z) for $C_{17}H_{18}N_2NaO_4$ [M+Na]$^+$: Calculated 337.1164, found 337.1161.

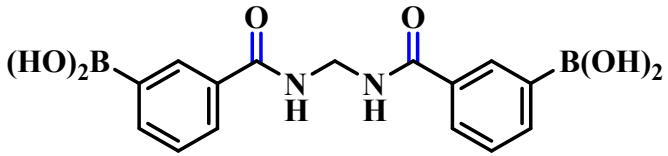


***N,N′*-Methylenebis(4-nitrobenzamide) (4dd)**[2]**:** The compound **(4dd)** was prepared using 4-nitro ethyl benzimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (40% ethyl acetate in petroleum ether) afforded the title compound as white solid (310 mg, 0.90 mmol, 90% yield), **M.P.** 218-220 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-

DMSO): δ 4.90 (t, *J*= 5.7 Hz, 2H), 8.12 (d, *J*= 8.7 Hz, 4H), 8.31 (d, *J*= 7.5 Hz, 4H), 9.49 (t, *J*= 5.1 Hz, 2H); **^{13}C-NMR** (100 MHz, d_6-DMSO): δ 45.4, 123.6, 129.1, 139.6, 149.2, 165.2; **FT-IR** (KBr, cm^{-1}): υ_{max} 1055, 1112, 1150, 1180, 1247, 1281, 1402, 1470, 1505, 1534, 1585, 1607, 1634, 2845, 2964, 3323; ESI-MS (*m*/*z*) for $C_{15}H_{13}N_4O_6$ $[M+H]^+$: Calculated 345.0835, found 345.0830.

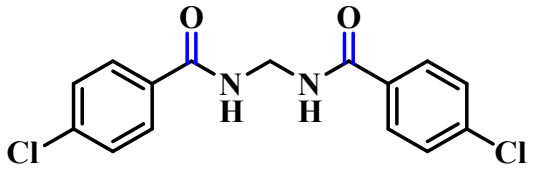


***N, N'*-Methylenebis(thiophene-2-carboxamide) (4ee)**[2]: The compound **(4ee)** was prepared using thiophene-2-carbimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (40% ethyl acetate in petroleum ether) afforded the title compound as white solid (245 mg, 0.92 mmol, 92% yield), **M.P.** 216-218 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.79 (t, *J*= 5.7 Hz, 2H), 7.14 (t, *J*= 4.5 Hz, 2H), 7.78 (d, *J*= 4.8 Hz, 2H), 7.88 (d, *J*= 3.3 Hz, 2H), 9.15 (t, *J*= 5.1 Hz, 2H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 44.5, 128.0, 128.7, 131.3, 139.5, 161.4; **FT-IR** (KBr, cm^{-1}): υ_{max} 1054, 1109, 1157, 1185, 1250, 1281, 1405, 1475, 1507, 1536, 1585, 1612, 1636, 2845, 2964, 3325; ESI-MS (*m*/*z*) for $C_{11}H_{11}N_2O_2S_2$ $[M+H]^+$: Calculated 267.0262, found 267.0266.

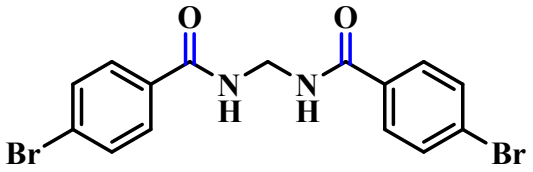


(((Methylenebis(azanediyl)) bis(carbonyl)) bis(3,1-phenylene)) diboronic acid (4gg): The compound **(4gg)** was prepared using (3-(ethoxy(imino)methyl) phenyl) boronic acid (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (40% ethyl acetate in petroleum ether) afforded the title compound as white solid (301 mg, 0.88 mmol, 88% yield), **M.P.** 223-225 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.86 (t, *J*= 5.1 Hz, 2H), 7.83 – 7.91 (m, 8H), 8.23 (d, *J*= 3.6 Hz, 4H), 9.06 (t, *J*= 5.1 Hz, 2H); **^{13}C-NMR** (100 MHz, d_6-DMSO): δ 45.8, 124.0, 126.8, 129.4, 134.3, 139.9, 149.6, 165.5; **FT-IR** (KBr,

cm^{-1}): υ_{max} 1057, 1112, 1153, 1184, 1244, 1284, 1409, 1475, 1505, 1534, 1585, 1613, 1635, 2844, 2964, 3324, 3456; ESI-MS (*m*/*z*) for $C_{15}H_{17}B_2N_2O_6$ $[M+H]^+$: Calculated 343.1273, found 343.1271.

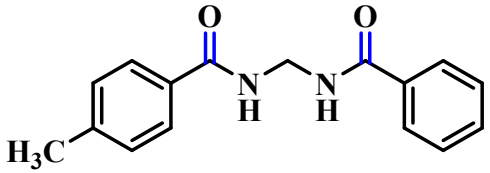


***N,N'*-Methylenebis(4-chlorobenzamide) (4hh)**[2]: The compound **(4hh)** was prepared using 4-chloro ethyl benzimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (35% ethyl acetate in petroleum ether) afforded the title compound as white solid (300 mg, 0.93 mmol, 93% yield), **M.P.** 210-212 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.84 (t, *J*= 5.4 Hz, 2H), 7.68 (d, *J*= 8.4 Hz, 4H), 7.85 (d, *J*= 8.7 Hz, 4H), 9.17 (t, *J*= 5.4 Hz, 2H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 45.2, 125.3, 129.6, 131.4, 133.0, 165.7; **FT-IR** (KBr, cm^{-1}): υ_{max} 1052, 1112, 1154, 1187, 1244, 1289, 1407, 1478, 1508, 1539, 1588, 1607, 1634, 2844, 2966, 3323; ESI-MS (*m*/*z*) for $C_{15}H_{13}N_2O_2Cl_2$ $[M+H]^+$: Calculated 323.0354, found 323.0359.

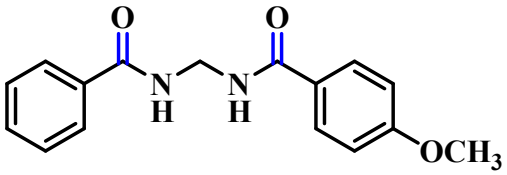


***N,N'*-Methylenebis(4-bromobenzamide) (4ii)**: The compound **(4ii)** was prepared using 4-bromo ethyl benzimidate (2 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (30% ethyl acetate in petroleum ether) afforded the title compound as white solid (373 mg, 0.91 mmol, 91% yield), **M.P.** 212-214 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 4.84 (t, *J*= 5.4 Hz, 2H), 7.67 (d, *J*= 8.4 Hz, 4H), 7.85 (d, *J*= 8.7 Hz, 4H), 9.17 (t, *J*= 5.4 Hz, 2H); **^{13}C-NMR** (75 MHz, d_6-

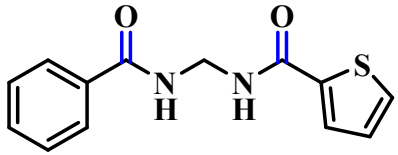
DMSO): *δ* 45.2, 125.2, 129.6, 131.3, 133.0, 165.6; **FT-IR** (KBr, cm^{-1}): υ_{max} 1057, 1112, 1154, 1184, 1247, 1281, 1405, 1473, 1504, 1534, 1578, 1607, 1635, 2845, 2964, 3330; ESI-MS (*m*/*z*) for $C_{15}H_{13}Br_2N_2O_2$ $[M+H]^+$: Calculated 410.9344, found 410.9340.



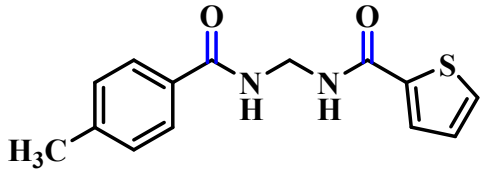
***N*-(Benzamidomethyl)-4-methylbenzamide (5ab)**: The compound **(5ab)** was prepared using 4-methyl ethyl benzimidate (1 mmol), ethyl benzimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (15% ethyl acetate in petroleum ether) afforded the title compound as white solid (182 mg, 0.68 mmol, 68% yield), **M.P.** 202-204 ^{0}C; **^{1}H-NMR** (300 MHz, $CDCl_3$): *δ* 2.39 (s, 3H), 5.04 – 5.11 (m, 2H), 7.19 – 7.28 (m, 2H), 7.41 (t, *J*= 7.5 Hz, 2H), 7.51 (t, *J*= 7.2 Hz, 1H), 7.74 (d, *J*= 8.1 Hz, 2H), 7.85 (d, *J*= 7.8 Hz, 2H), 7.96 (s, 1H), 8.06 (s, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): *δ* 21.5, 45.7, 127.4, 128.5, 129.2, 130.7, 131.9, 131.9, 133.6, 142.4, 168.6, 168.7; **FT-IR** (KBr, cm^{-1}): υ_{max} 1054, 1116, 1154, 1187, 1252, 1287, 1407, 1478, 1505, 1537, 1587, 1606, 1637, 2847, 2967, 3328; ESI-MS (*m*/*z*) for $C_{16}H_{17}N_2O_2$ $[M+H]^+$: Calculated 269.1290, found 269.1285.



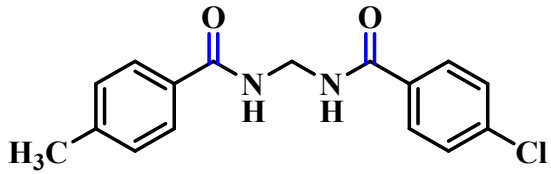
***N*-(Benzamidomethyl)-4-methoxybenzamide (5ac)**: The compound **(5ac)** was prepared using 4-methoxy ethyl benzimidate (1 mmol), ethyl benzimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (15% ethyl acetate in petroleum ether) afforded the title compound as white solid (199 mg, 0.70 mmol, 70% yield), **M.P.** 206-208 ^{0}C; **^{1}H-NMR** (300 MHz, $CDCl_3$): *δ* 3.89 (s, 3H), 5.06 – 5.12 (m, 2H), 7.19 – 7.28 (m, 2H), 7.40 (t, *J*= 7.5 Hz, 2H), 7.51 (t, *J*= 7.2 Hz, 1H), 7.74 (d, *J*= 8.4 Hz, 2H), 7.85 (d, *J*= 8.4 Hz, 2H), 7.97 (s, 1H), 8.07 (s, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$): *δ* 44.7, 55.9, 114.0, 126.3, 127.5, 128.2, 129.6, 131.0, 141.5, 162.3, 163.4, 166.6; **FT-IR** (KBr, cm^{-1}): u_{max} 1055, 1117, 1155, 1185, 1254, 1283, 1407, 1475, 1507, 1540, 1587, 1612, 1635, 2845, 2967, 3329; ESI-MS (*m*/*z*) for $C_{16}H_{17}N_2O_3$ $[M+H]^+$: Calculated 285.1239, found 285.1242.



***N*-(Benzamidomethyl)thiophene-2-carboxamide (5ae)**: The compound **(5ae)** was prepared using ethyl benzimidate (1 mmol), thiophene-2-carbimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (30% ethyl acetate in petroleum ether) afforded the title compound as white solid (174 mg, 0.67 mmol, 67% yield), **M.P.** 210-212 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): *δ* 4.81 (t, *J*= 5.7 Hz, 2H), 6.99 (d, *J*= 2.7 Hz, 1H), 7.13 – 7.15 (m, 2H), 7.73 – 7.75 (m, 2H), 7.90 (d, *J*= 8.7 Hz, 2H), 8.95 (t, *J*= 5.4 Hz, 1H), 9.06 – 9.10 (m, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): *δ* 45.2, 127.6, 128.1, 129.3, 130.5, 131.8, 131.9, 133.3, 138.9, 163.4, 168.3; **FT-IR** (KBr, cm^{-1}): u_{max} 1055, 1118, 1157, 1185, 1251, 1283, 1407, 1475, 1504, 1534, 1587, 1612, 1638, 2846, 2970, 3336; ESI-MS (*m*/*z*) for $C_{13}H_{13}N_2O_2S$ $[M+H]^+$: Calculated 261.0698, found 261.0692.

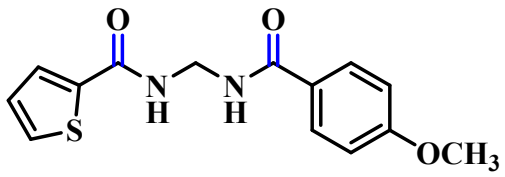


***N*-((4-Methylbenzamido)methyl)thiophene-2-carboxamide (5be)**: The compound **(5be)** was prepared using thiophene-2-carbimidate (1 mmol),4-methyl ethyl benzimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (350% ethyl acetate in petroleum ether) afforded the title compound as white solid (192 mg, 0.70 mmol, 70% yield), **M.P.** 218-220 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.40 (s, 3H), 4.82 (t, J= 5.7 Hz, 2H), 7.17 – 7.20 (m, 1H), 7.30 (d, J= 8.1 Hz, 2H), 7.79 – 7.84 (m, 2H), 7.94 – 8.02 (m, 2H), 8.95 (t, J= 5.4 Hz, 1H), 9.08 (t, J= 5.7 Hz, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 21.4, 45.2, 128.0, 128.3, 129.1, 129.2, 131.4, 131.9, 140.8, 141.5, 163.4, 168.3; **FT-IR** (KBr, cm^{-1}): υ_{max} 1054, 1117, 1157, 1184, 1248, 1283, 1406, 1475, 1505, 1540, 1587, 1602, 1635, 2845, 2965, 3336; ESI-MS (*m*/*z*) for $C_{14}H_{15}N_2O_2S$ $[M+H]^+$: Calculated 275.0854, found 275.0856.

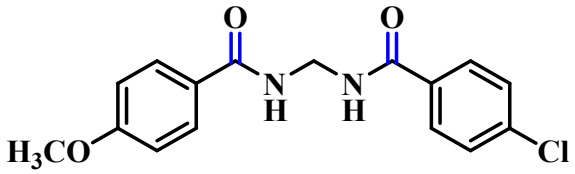


4-Chloro-*N*-((4-methylbenzamido)methyl)benzamide (5bh): The compound **(5bh)** was prepared using 4-chloro ethyl benzimidate (1 mmol),4-methyl ethyl benzimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (35% ethyl acetate in petroleum ether) afforded the title compound as white solid (217 mg, 0.72 mmol, 72% yield), **M.P.** 223-225 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 2.34 (s, 3H), 4.84 (t, J= 5.4 Hz, 2H), 7.26 (d, J= 7.8 Hz, 2H), 7.53 (d, J= 5.4

Hz, 2H), 7.80 (d, *J*= 8.1 Hz, 2H), 7.92 (d, *J*= 8.4 Hz, 2H), 8.95 (t, *J*= 5.7 Hz, 1H), 9.13 (d, *J*= 5.1 Hz, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): *δ* 21.4, 45.6, 127.9, 128.8, 129.3, 129.9, 131.6, 133.2, 136.7, 141.8, 165.9, 166.8; **FT-IR** (KBr, cm^{-1}): υ_{max} 1057, 1108, 1159, 1188, 1250, 1285, 1405, 1477, 1504, 1537, 1587, 1610, 1635, 2845, 2967, 3325; ESI-MS (*m*/*z*) for $C_{16}H_{15}ClN_2O_2$ [M]$^+$: Calculated 302.0822, found 302.0821.



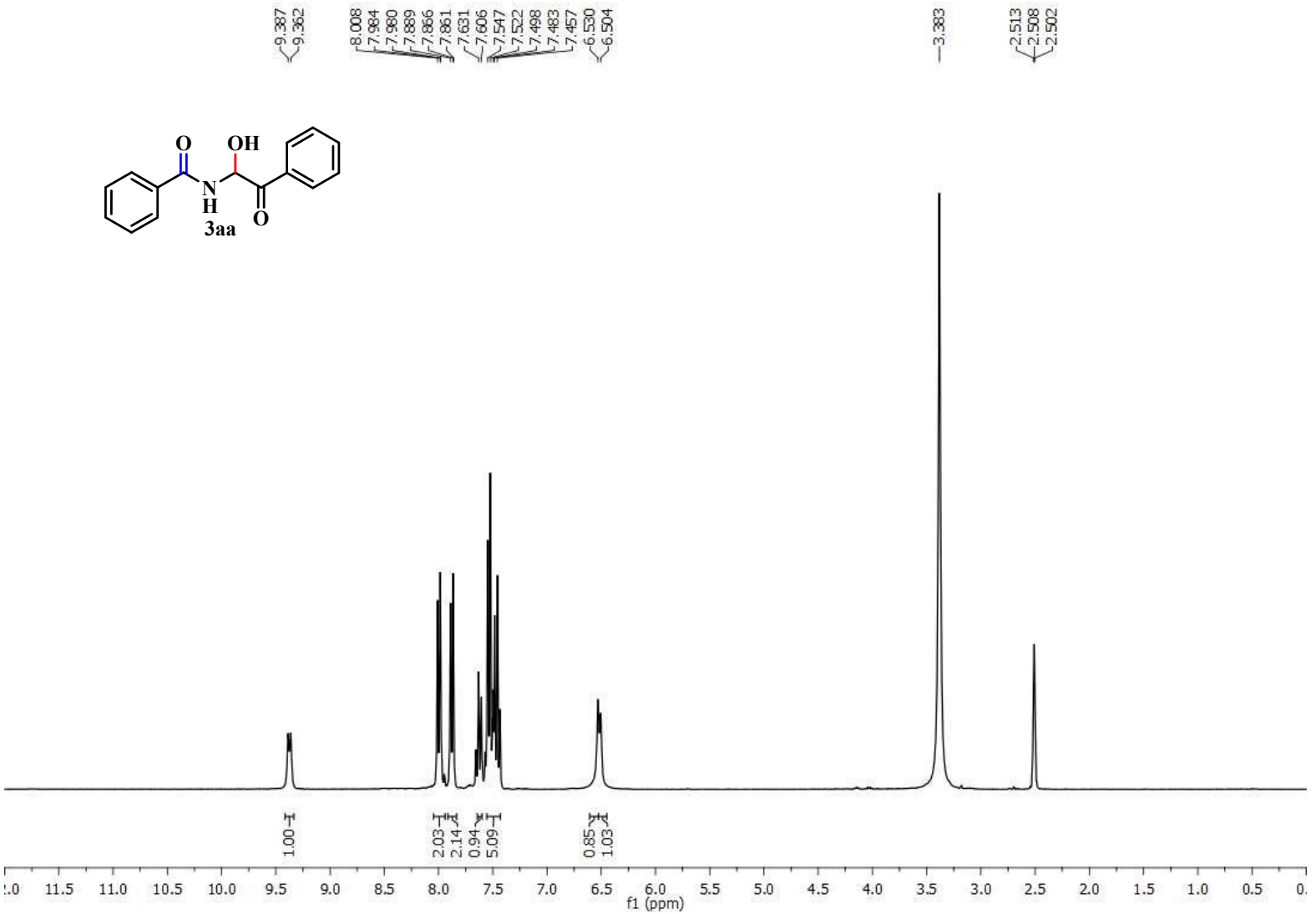
***N*-((4-Methoxybenzamido) methyl) thiophene-2-carboxamide (5ce)**: The compound **(5ce)** was prepared using 4-methoxy ethyl benzimidate (1 mmol), thiophene-2-carbimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (30% ethyl acetate in petroleum ether) afforded the title compound as white solid (206 mg, 0.71 mmol, 71% yield), **M.P.** 224-226 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): *δ* 3.81 (s, 3H), 4.81 (t, *J*= 5.7 Hz, 2H), 6.99 (d, *J*= 8.7 Hz, 1H), 7.11 – 7.15 (m, 2H), 7.73 – 7.75 (m, 2H), 7.89 – 7.91 (m, 2H), 8.95 (t, *J*= 5.4 Hz, 1H), 9.08 (t, *J*= 5.7 Hz, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): *δ* 45.2, 55.8, 113.9, 128.4, 129.1, 129.2, 129.8, 131.5, 140.7, 162.2, 163.4, 166.5; **FT-IR** (KBr, cm^{-1}): υ_{max} 1055, 1119, 1158, 1184, 1247, 1282, 1409, 1478, 1502, 1537, 1588, 1607, 1634, 2845, 2965, 3332; ESI-MS (*m*/*z*) for $C_{14}H_{15}N_2O_3S$ [M+H]$^+$: Calculated 291.0803, found 291.0799.

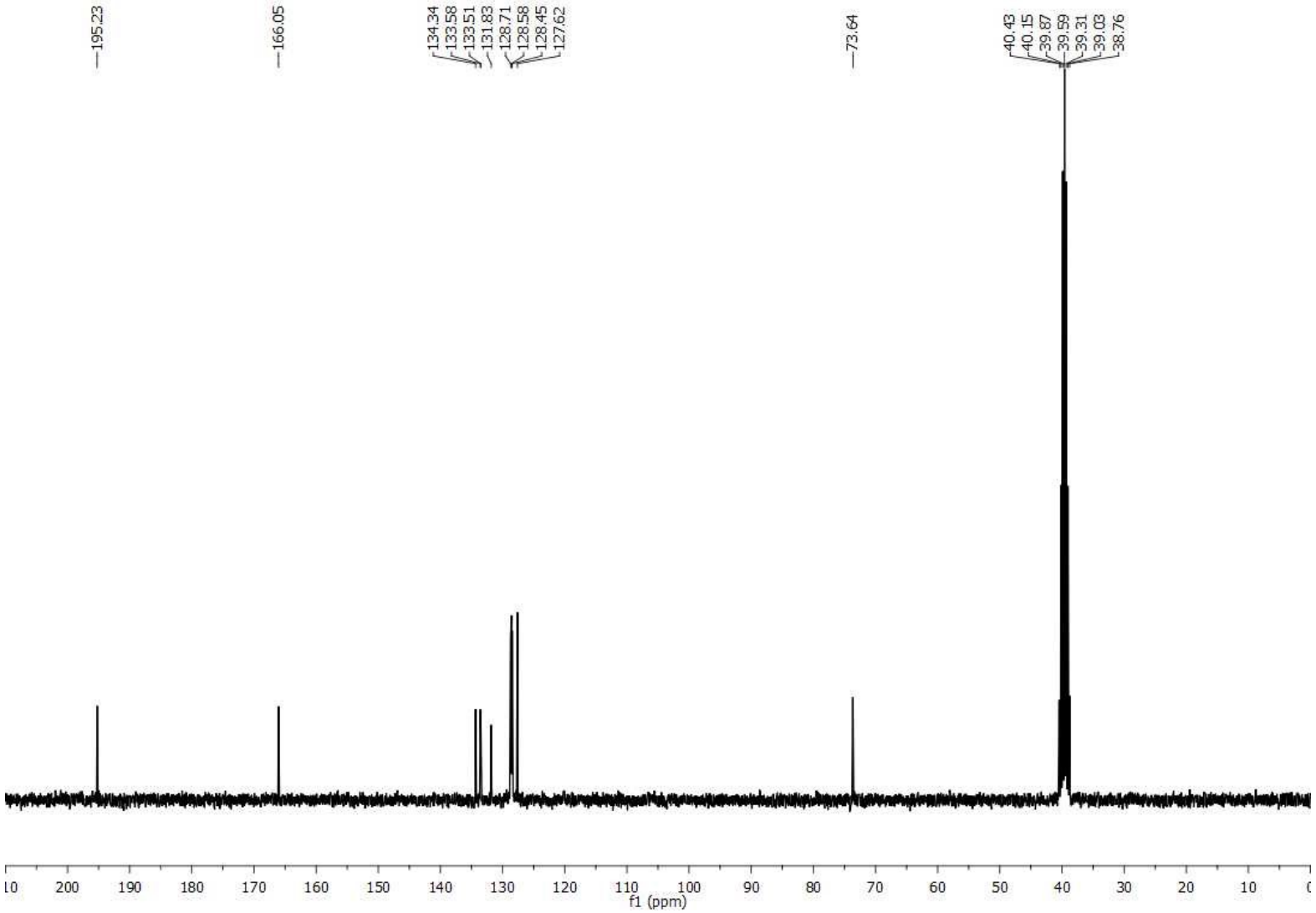


4-Chloro-*N*-((4-methoxybenzamido)methyl)benzamide (5ch): The compound **(5ch)** was prepared using 4-methoxy ethyl benzimidate (1 mmol), 4-chloro ethyl benzimidate (1 mmol), dimethyl sulfoxide (12 mmol) and iodine (10 mol %) as a starting material. Purification by column chromatography (30% ethyl acetate in petroleum ether) afforded the title compound as white solid (238 mg, 0.75 mmol, 75% yield), **M.P.** 225-227 ^{0}C; **^{1}H-NMR** (300 MHz, d_6-DMSO): δ 3.79 (s, 3H), 4.84 (t, J= 5.4 Hz, 2H), 7.25 (d, J= 8.4 Hz, 2H), 7.53 (d, J= 8.4 Hz, 2H), 7.80 (d, J= 8.7 Hz, 2H), 7.91 (d, J= 8.4 Hz, 2H), 8.95 (t, J= 5.7 Hz, 1H), 9.12 (d, J= 5.4 Hz, 1H); **^{13}C-NMR** (75 MHz, d_6-DMSO): δ 45.3, 55.8, 113.9, 128.4, 129.1, 129.2, 129.8, 131.5, 140.7, 162.2, 167.3, 168.2; **FT-IR** (KBr, cm^{-1}): υ_{max} 1058, 1112, 1153, 1187, 1258, 1283, 1407, 1475, 1509, 1540, 1589, 1615, 1635, 2845, 2967, 3337; ESI-MS (*m*/*z*) for $C_{16}H_{15}ClN_2O_3$ $[M]^+$: Calculated 318.0771, found 319.0774.

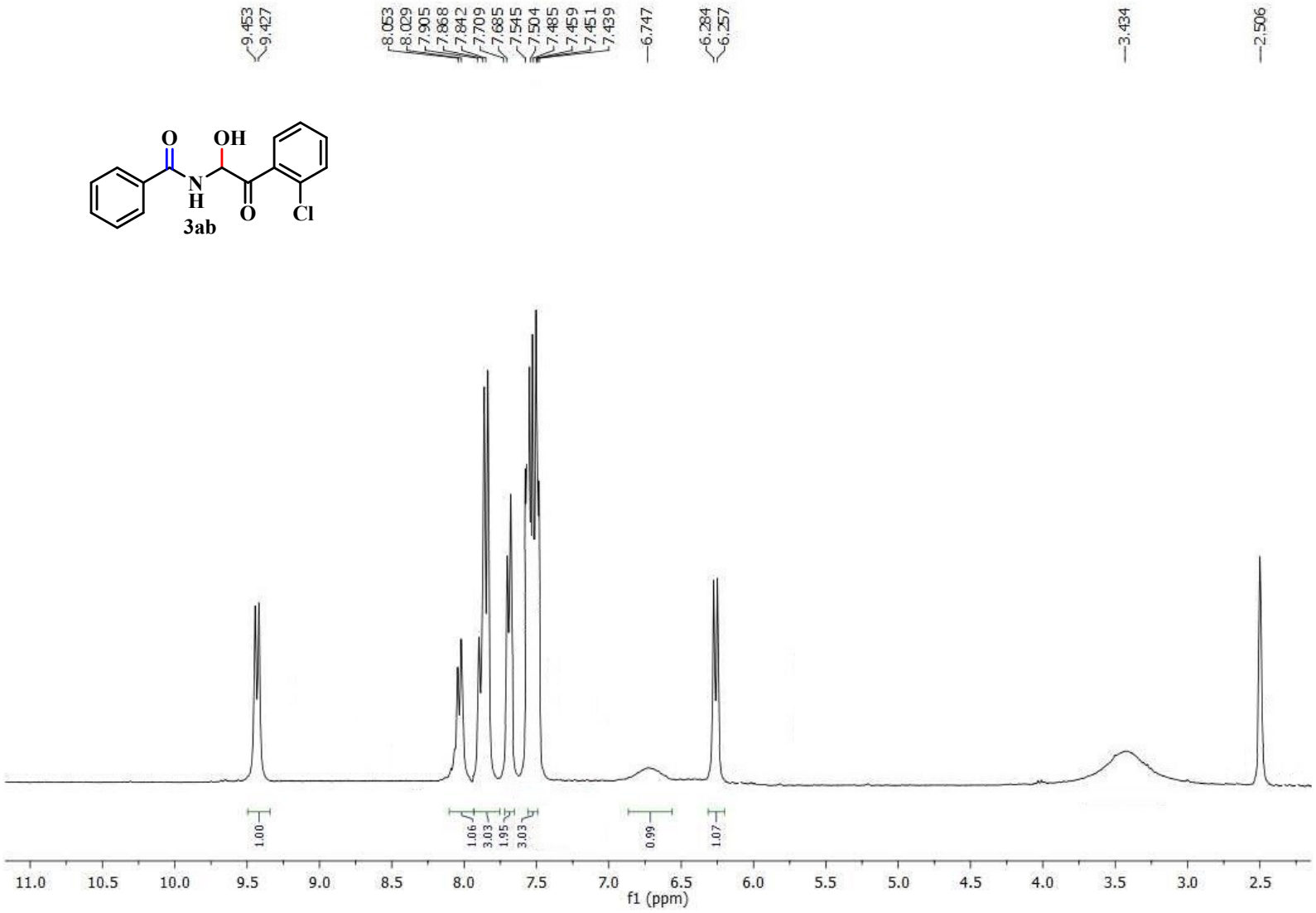
^{1}H and ^{13}C-NMR spectra of synthesized α-amidohydroxy ketones (3), symmetrical and un-symmetrical bisamide (4, 5)

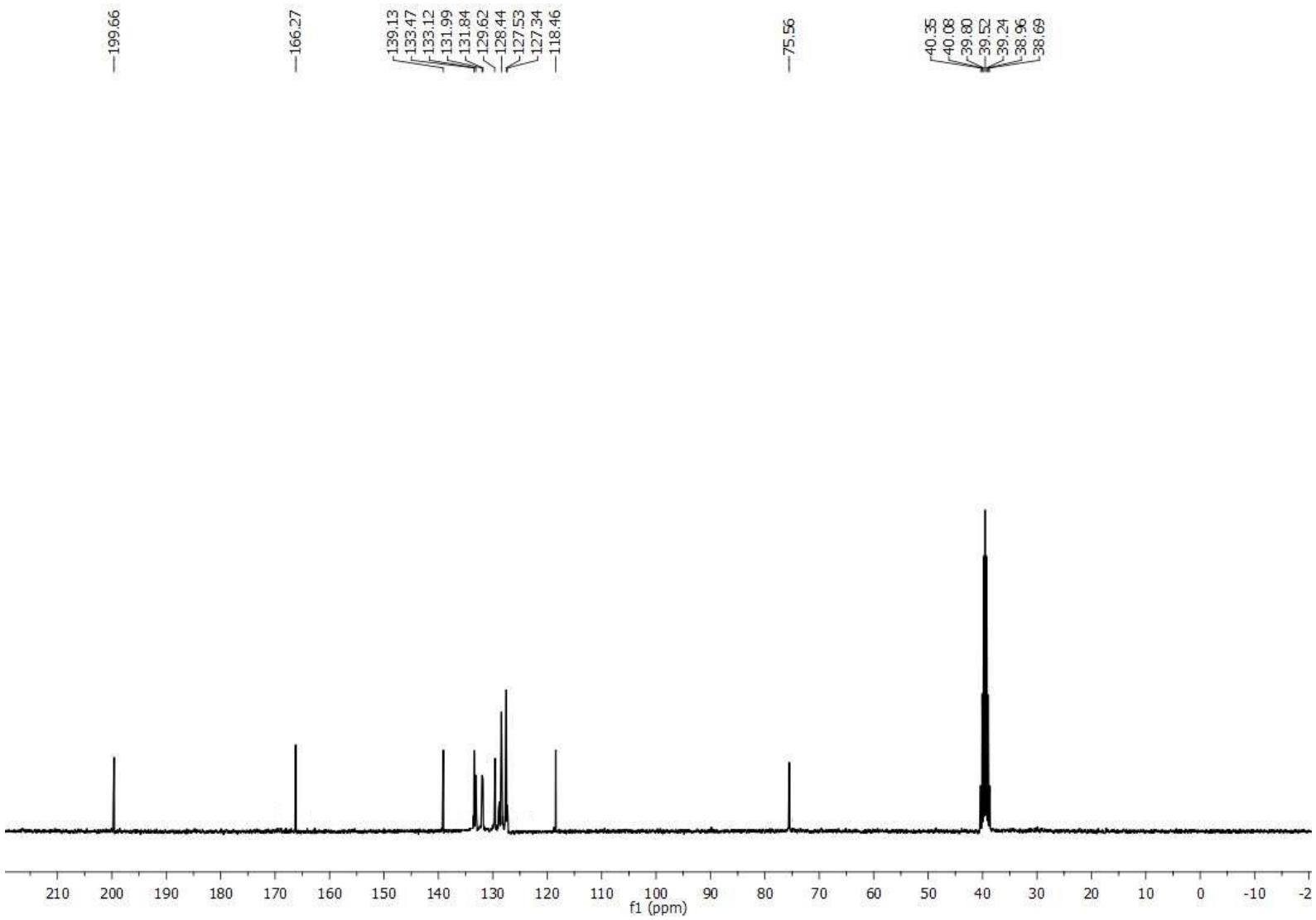
^{1}H NMR and ^{13}C NMR of Compound (3aa)




195.23
166.05
134.34
133.58
133.51
131.83
128.71
128.58
128.45
127.62
73.64
40.43
40.15
39.87
39.59
39.31
39.03
38.76
f1 (ppm)

^{1}H NMR and ^{13}C NMR of Compound (3ab)




199.66
166.27
139.13
133.47
133.12
131.99
131.84
129.62
128.44
127.53
127.34
118.46
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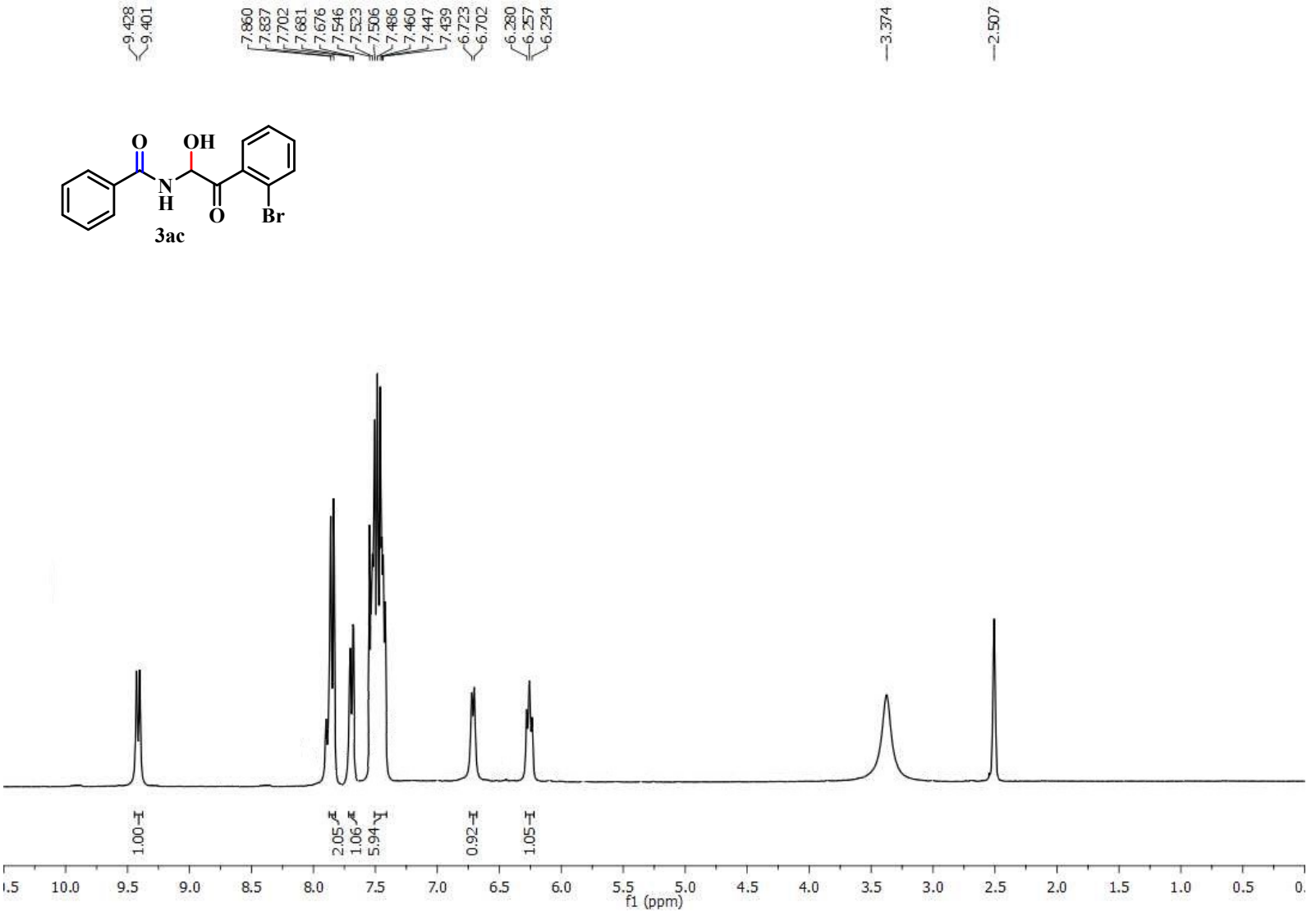
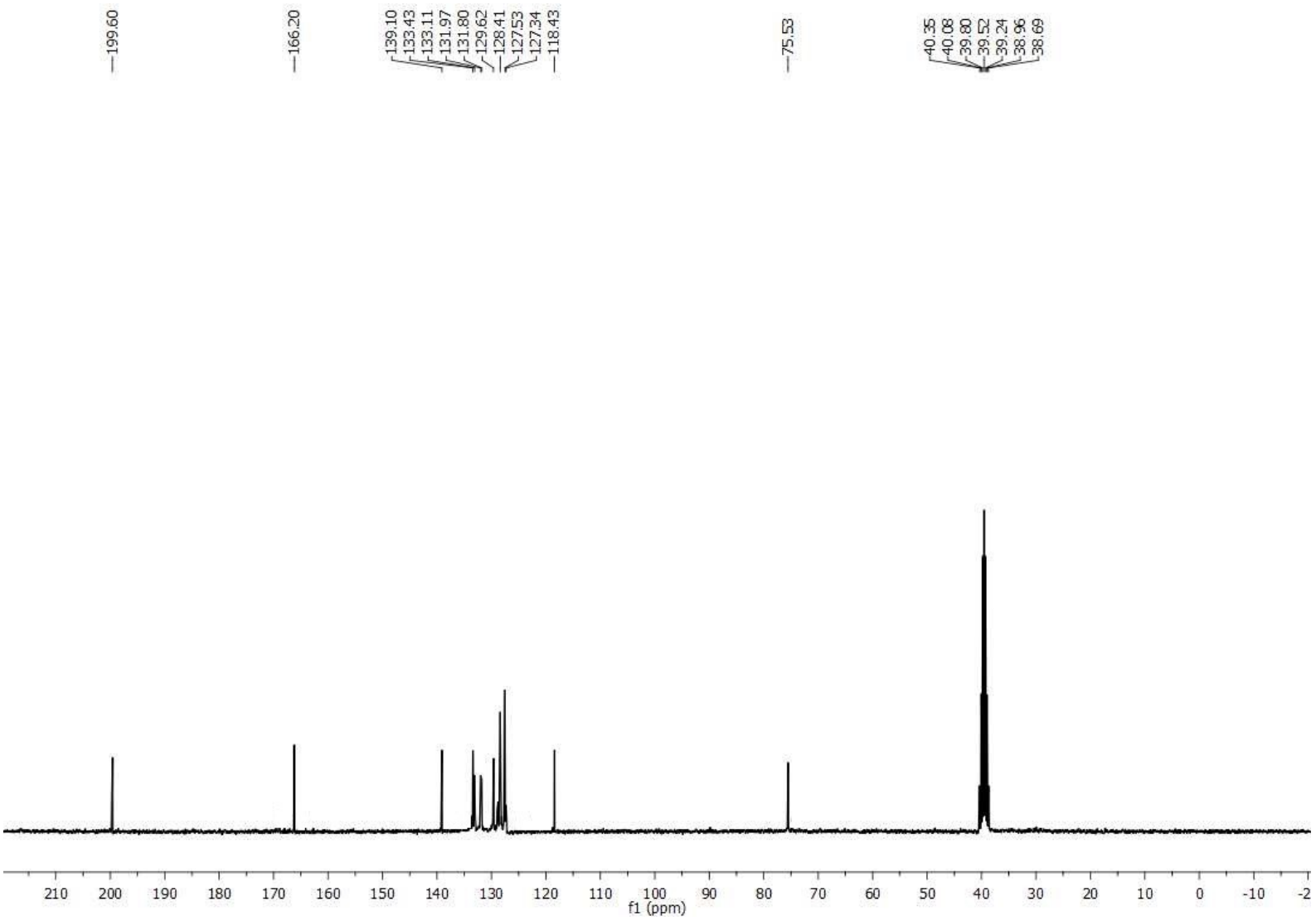
40.35
40.08
39.80
39.52
39.24
38.96
38.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

^{1}H NMR and ^{13}C NMR of Compound (3ac)




199.60
166.20
139.10
133.43
133.11
131.97
131.80
129.62
128.41
127.53
127.34
118.43
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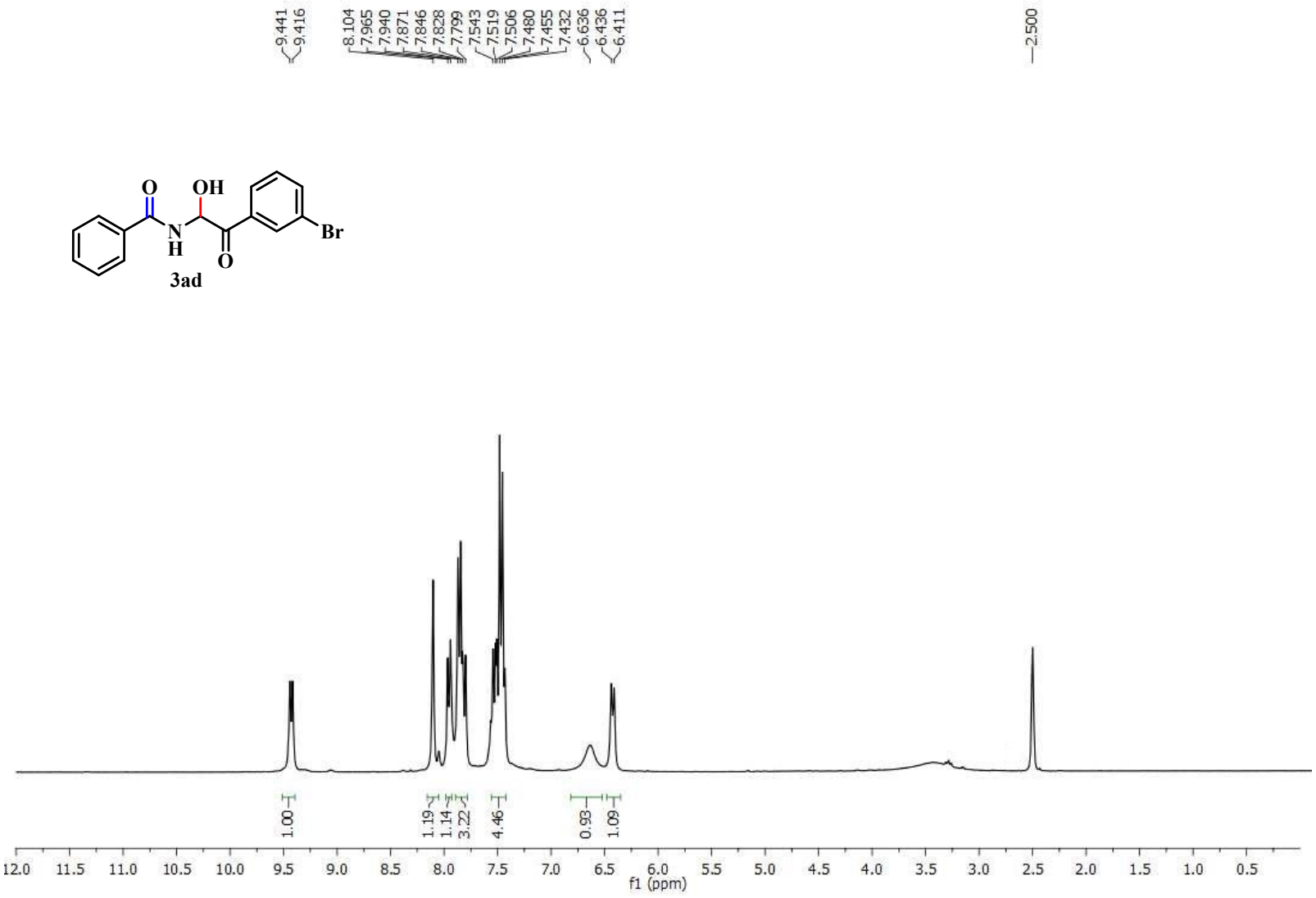
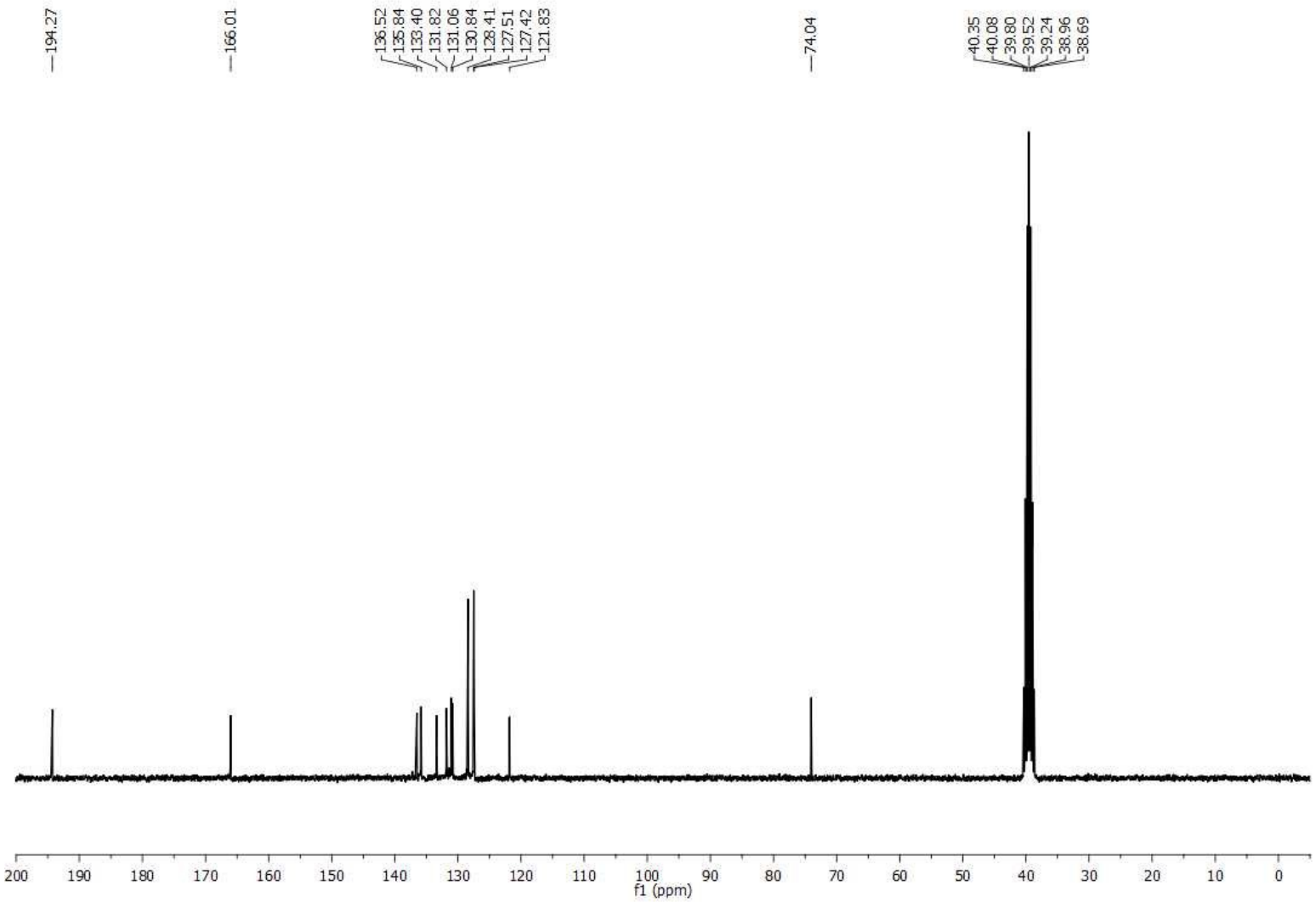
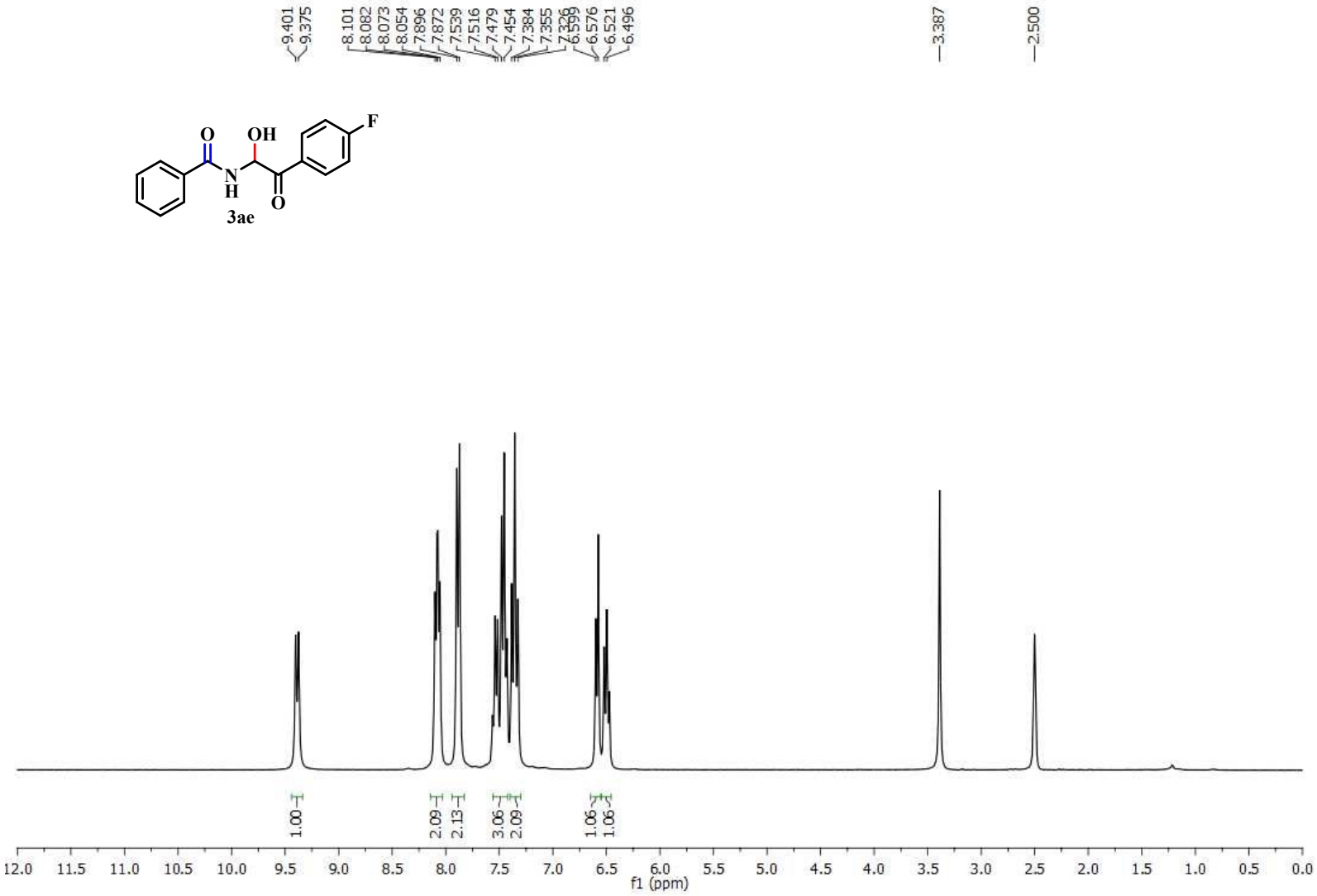
40.35
40.08
39.80
39.52
39.24
38.96
38.69
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

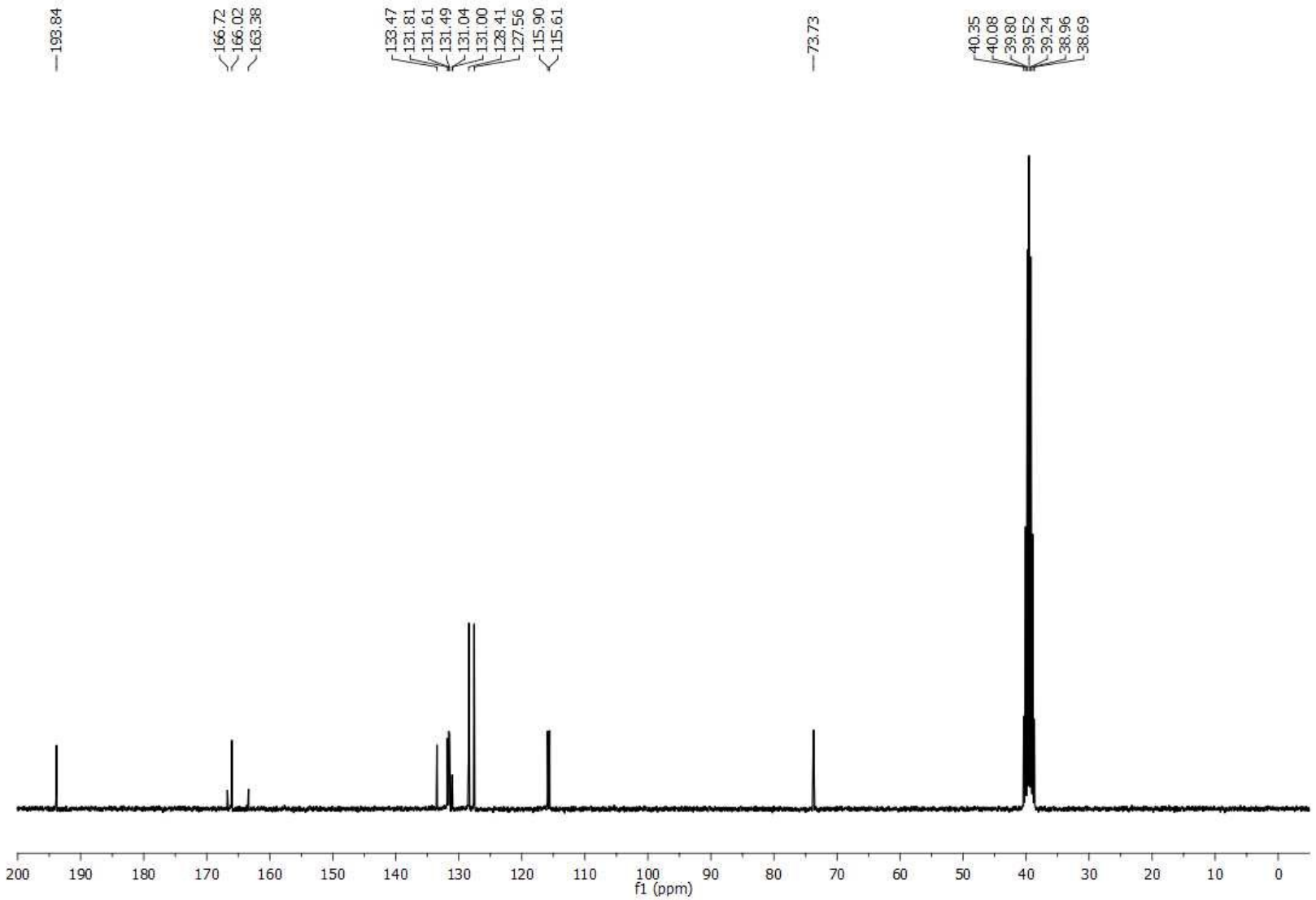
^{1}H NMR and ^{13}C NMR of Compound (3ad)



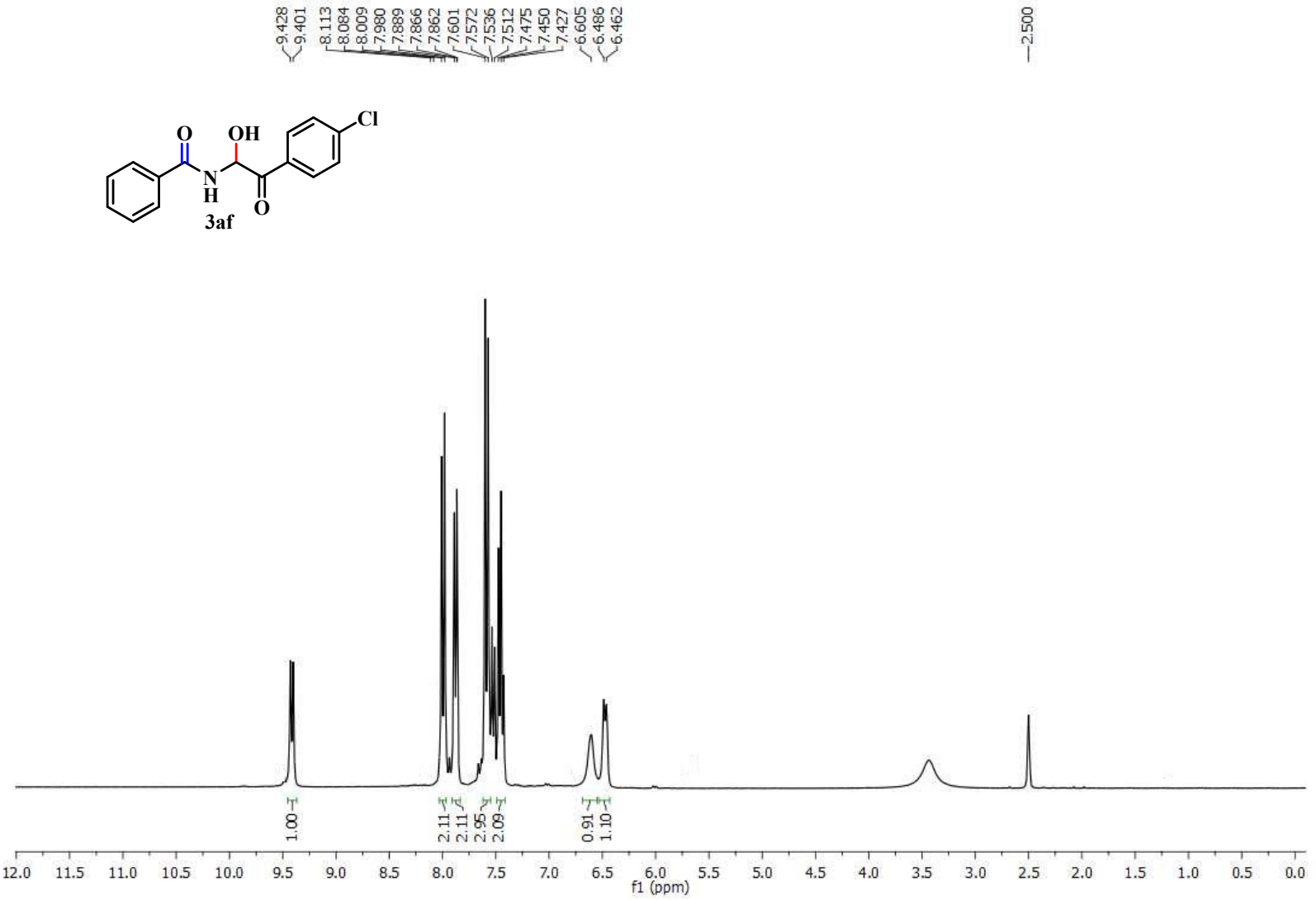

194.27
166.01
136.52
135.84
133.40
131.82
131.06
130.84
128.41
127.51
127.42
121.83
74.04
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

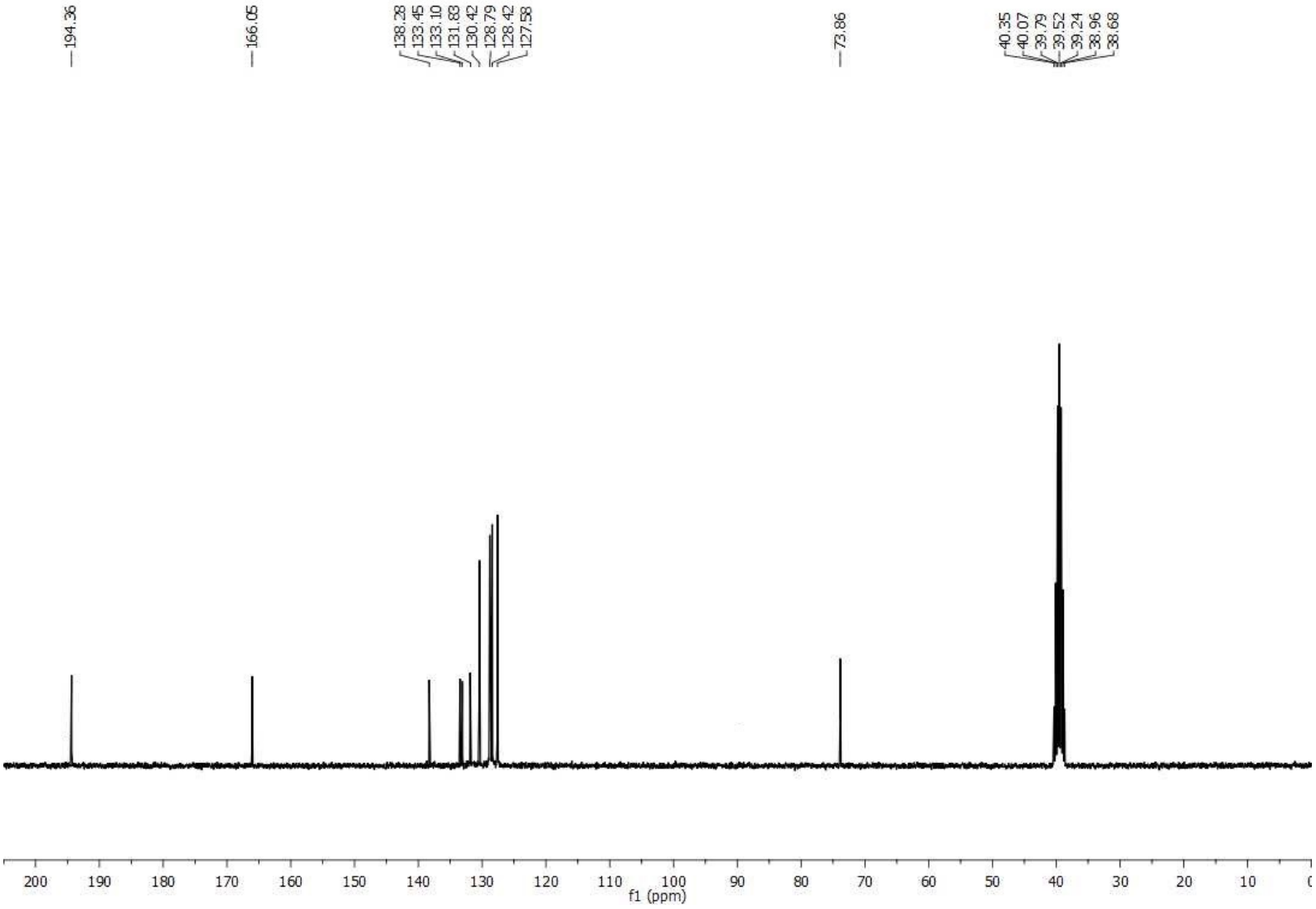
^{1}H NMR and ^{13}C NMR of Compound (3ae)



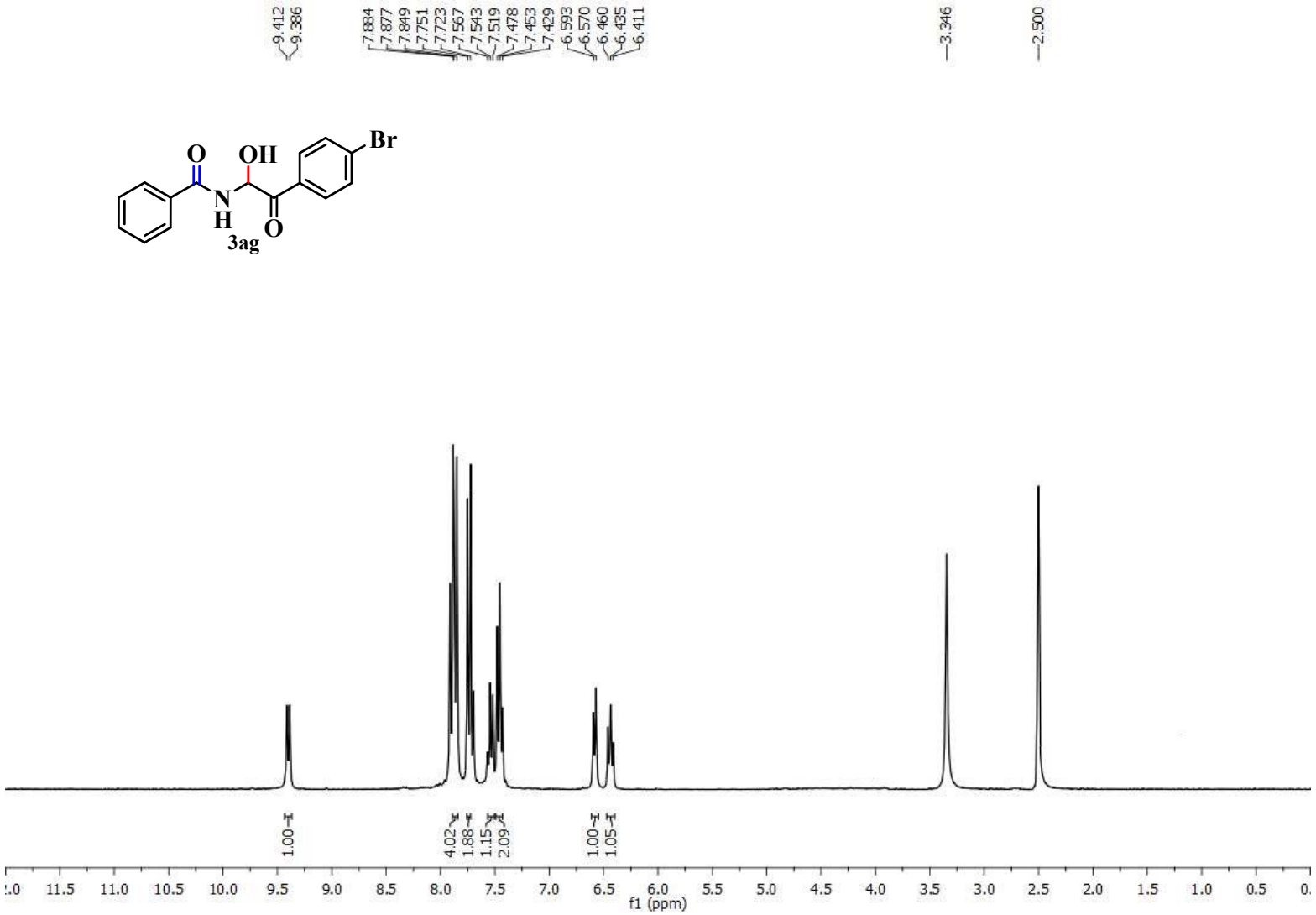

193.84
166.72
166.02
163.38
133.47
131.81
131.61
131.49
131.04
131.00
128.41
127.56
115.90
115.61
73.73
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

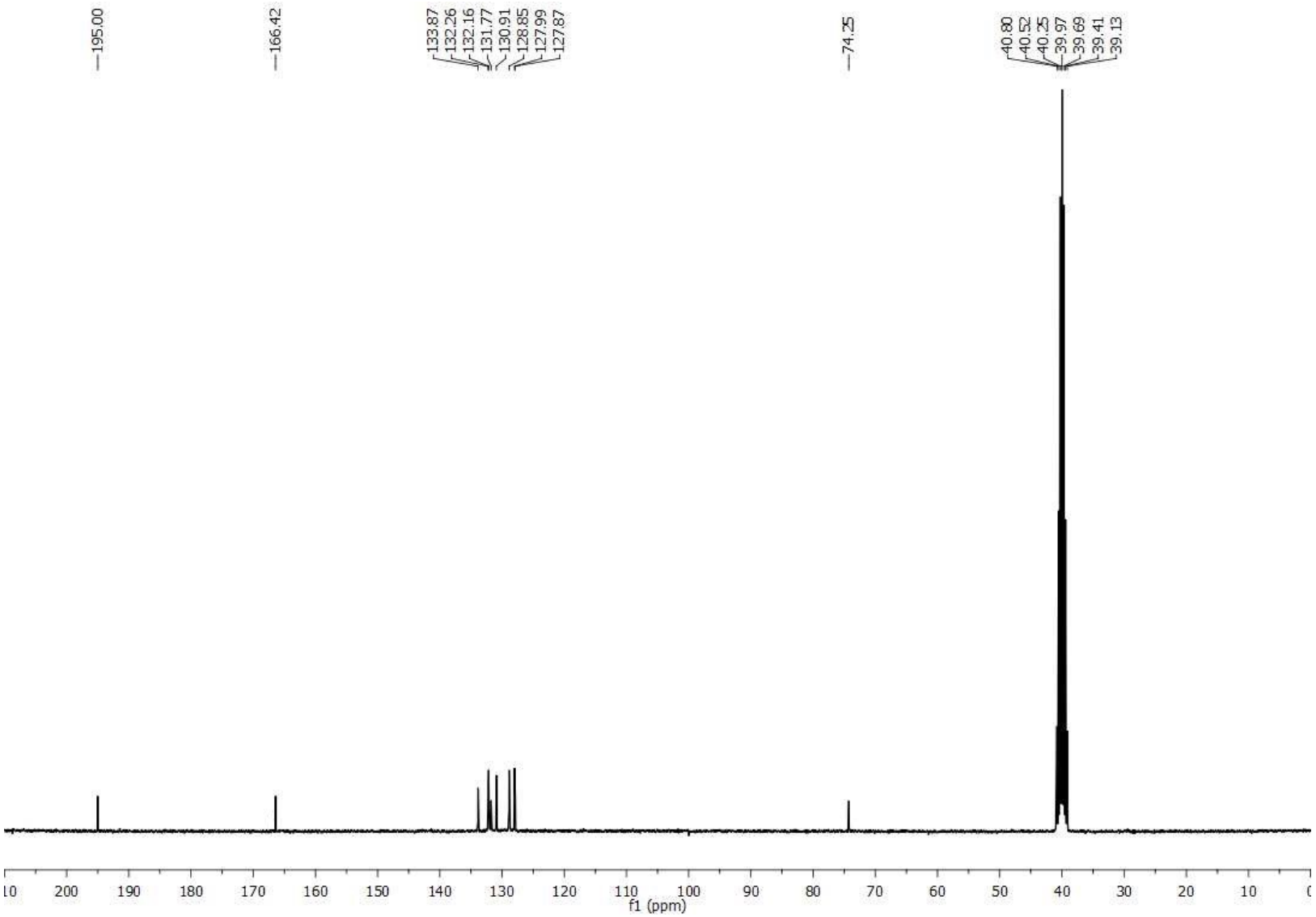
^{1}H NMR and ^{13}C NMR of Compound (3af)



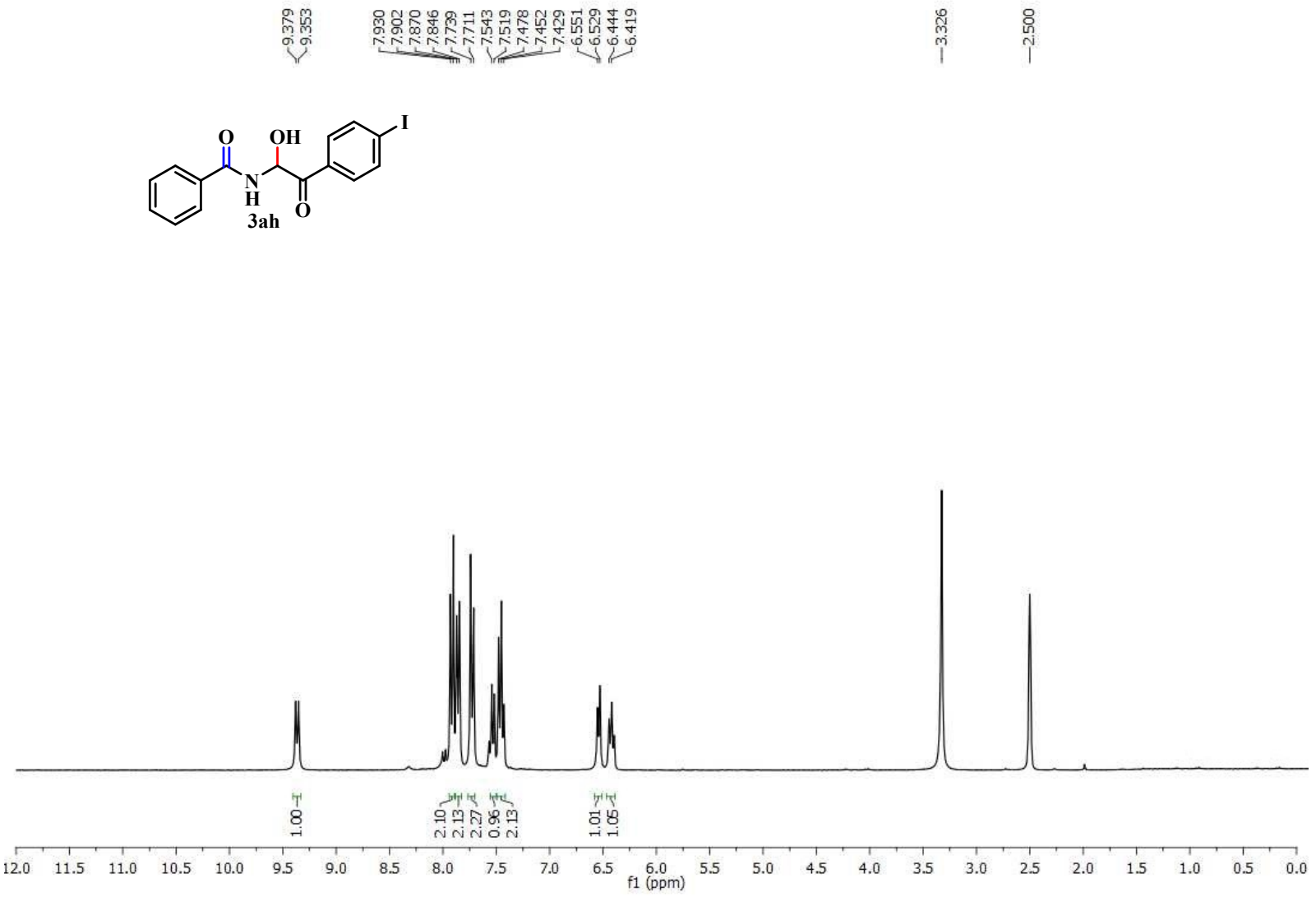

194.36
166.05
138.28
133.45
133.10
131.83
130.42
128.79
128.42
127.58
73.86
40.35
40.07
39.79
39.52
39.24
38.96
38.68
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

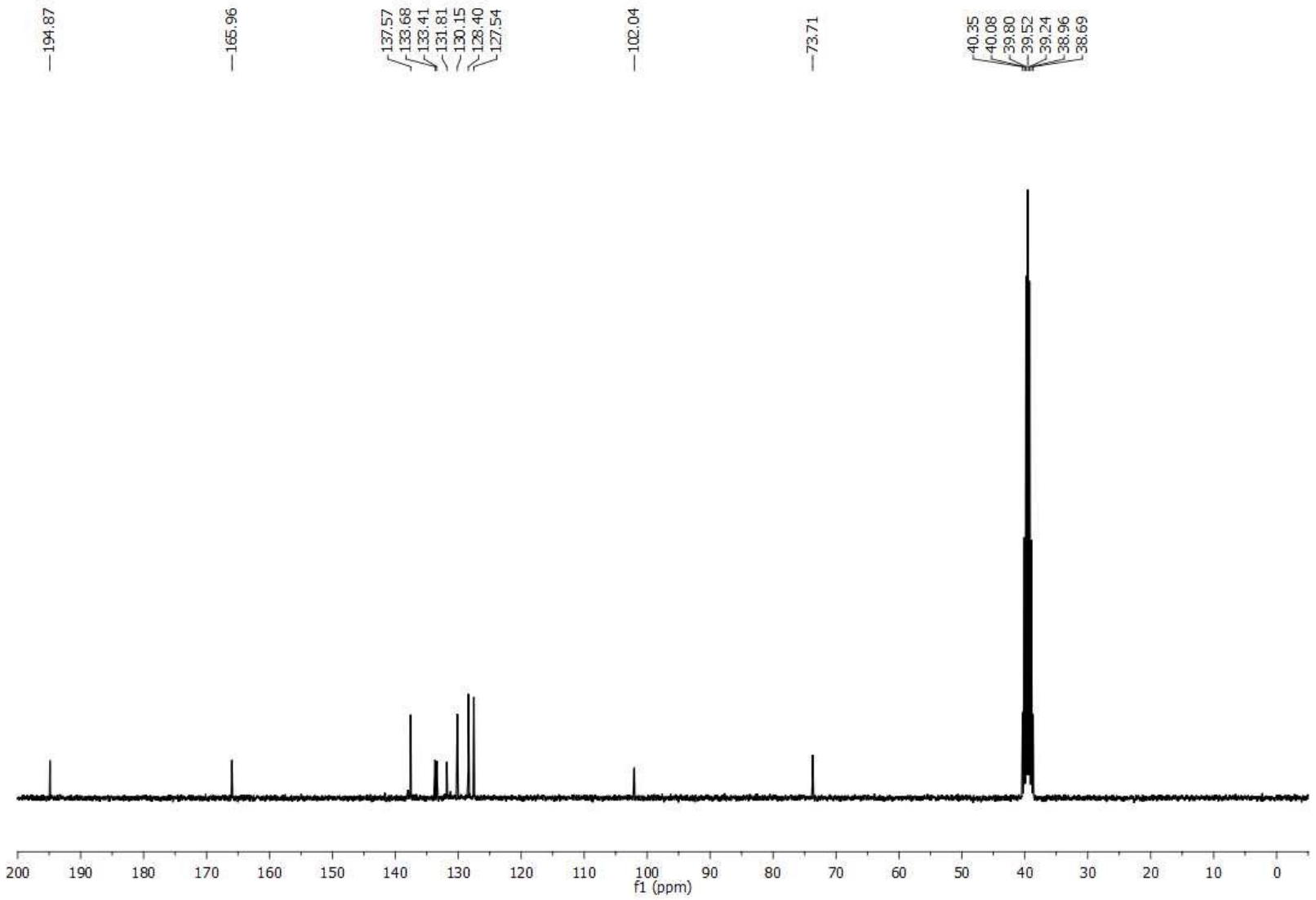
^{1}H NMR and ^{13}C NMR of Compound (3ag)



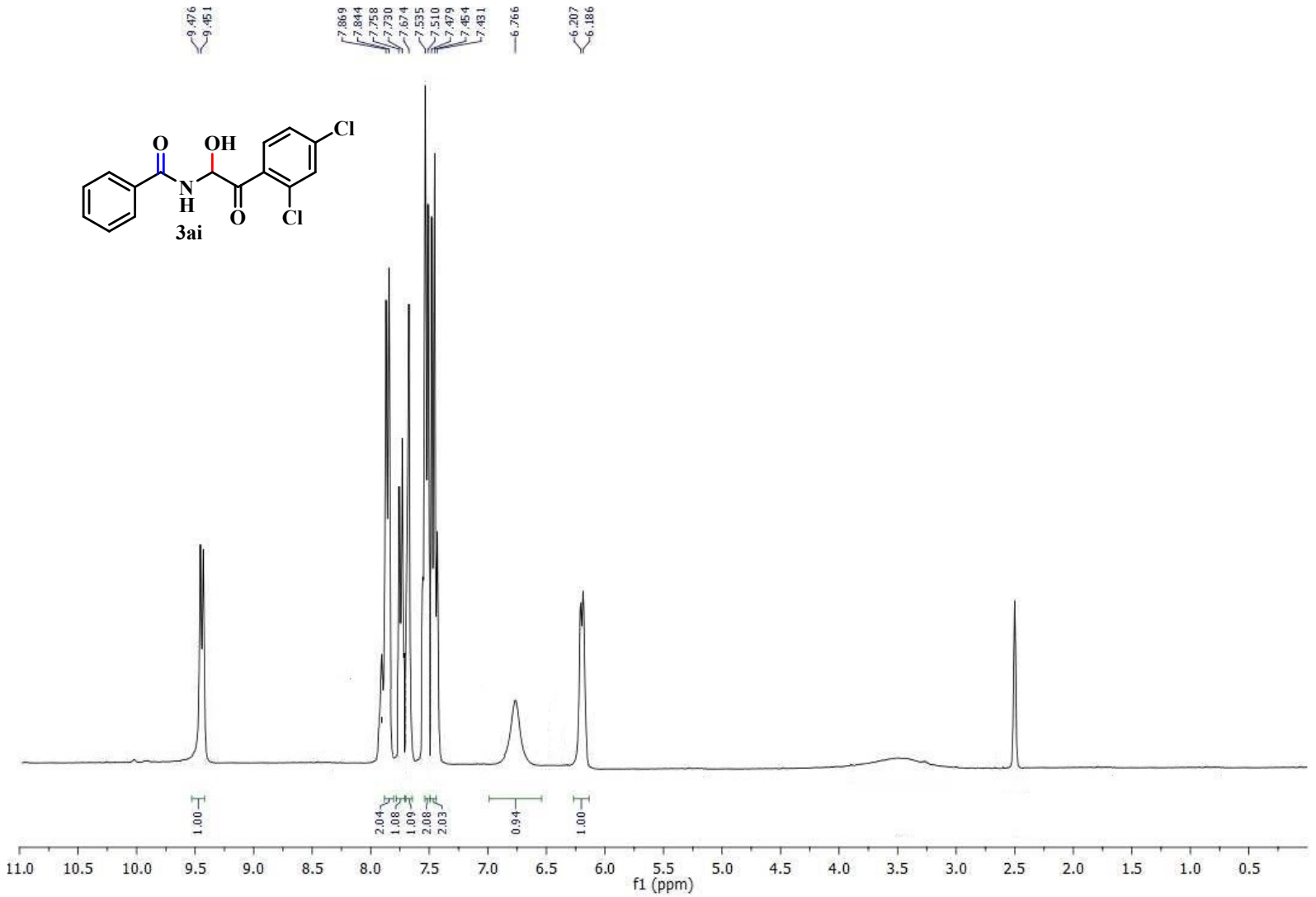

195.00
166.42
133.87
132.26
132.16
131.77
130.91
128.85
127.99
127.87
74.25
40.80
40.52
40.25
39.97
39.69
39.41
39.13
f1 (ppm)

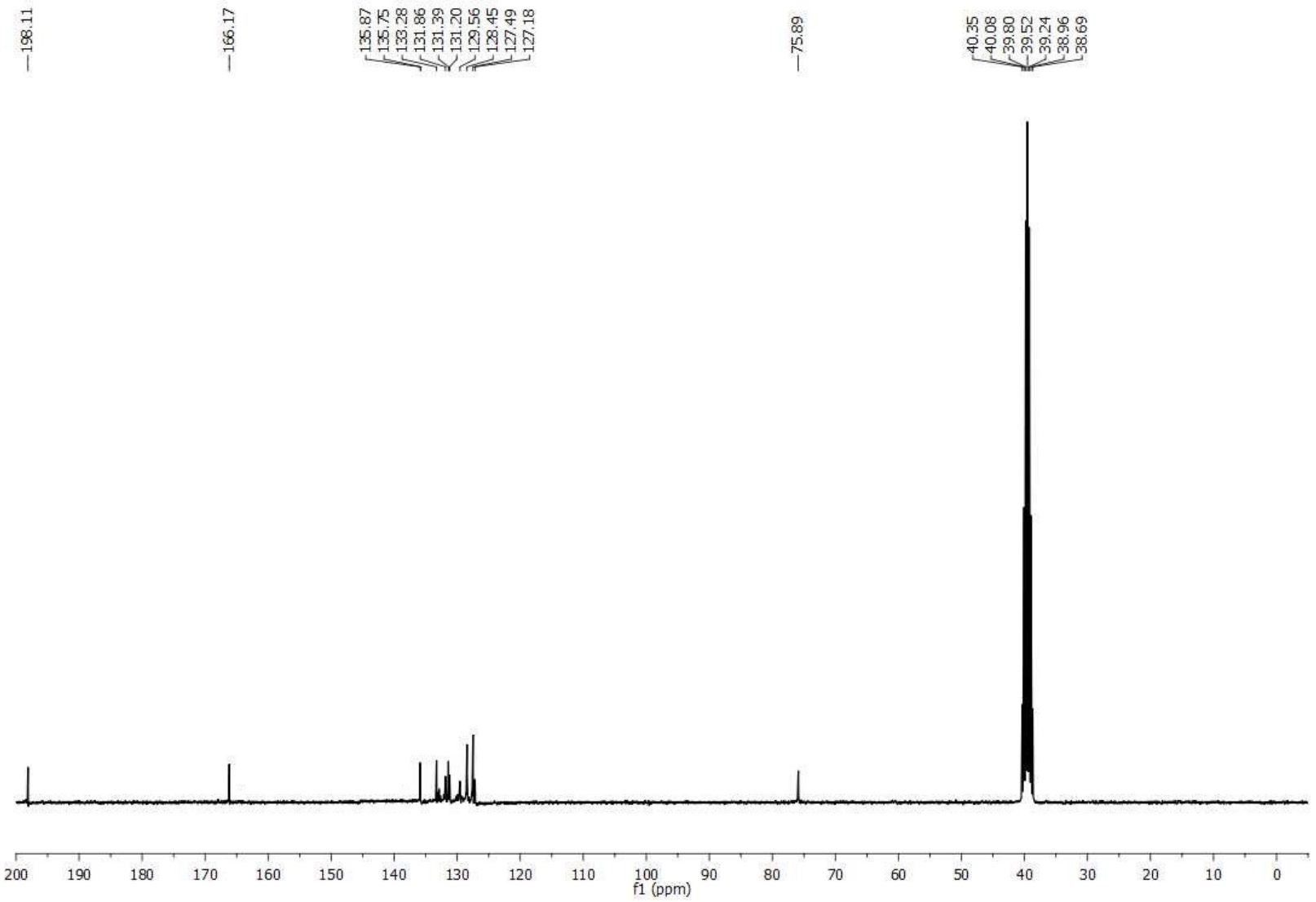
^{1}H NMR and ^{13}C NMR of Compound (3ah)



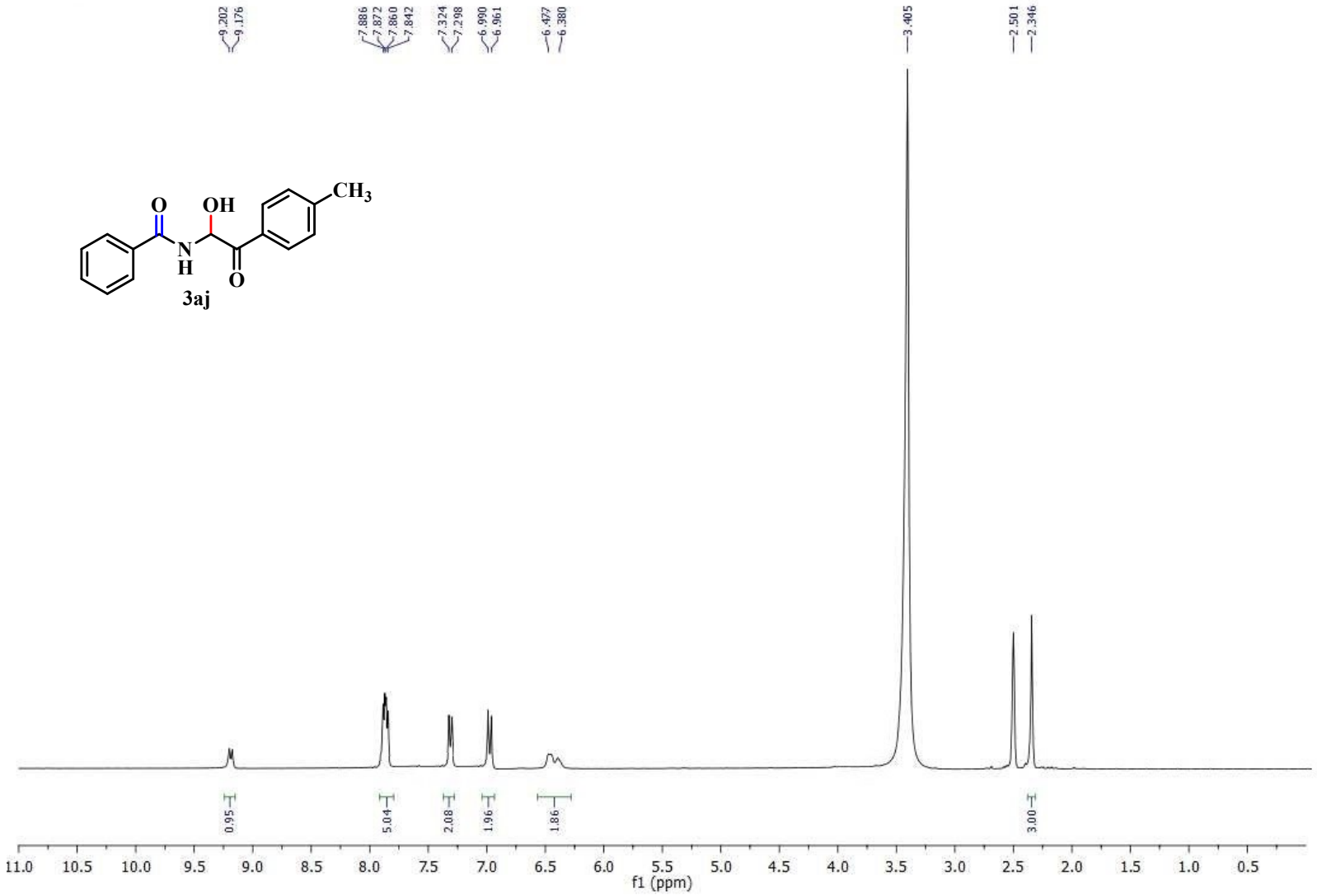

194.87
165.96
137.57
133.68
133.41
131.81
130.15
128.40
127.54
102.04
73.71
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

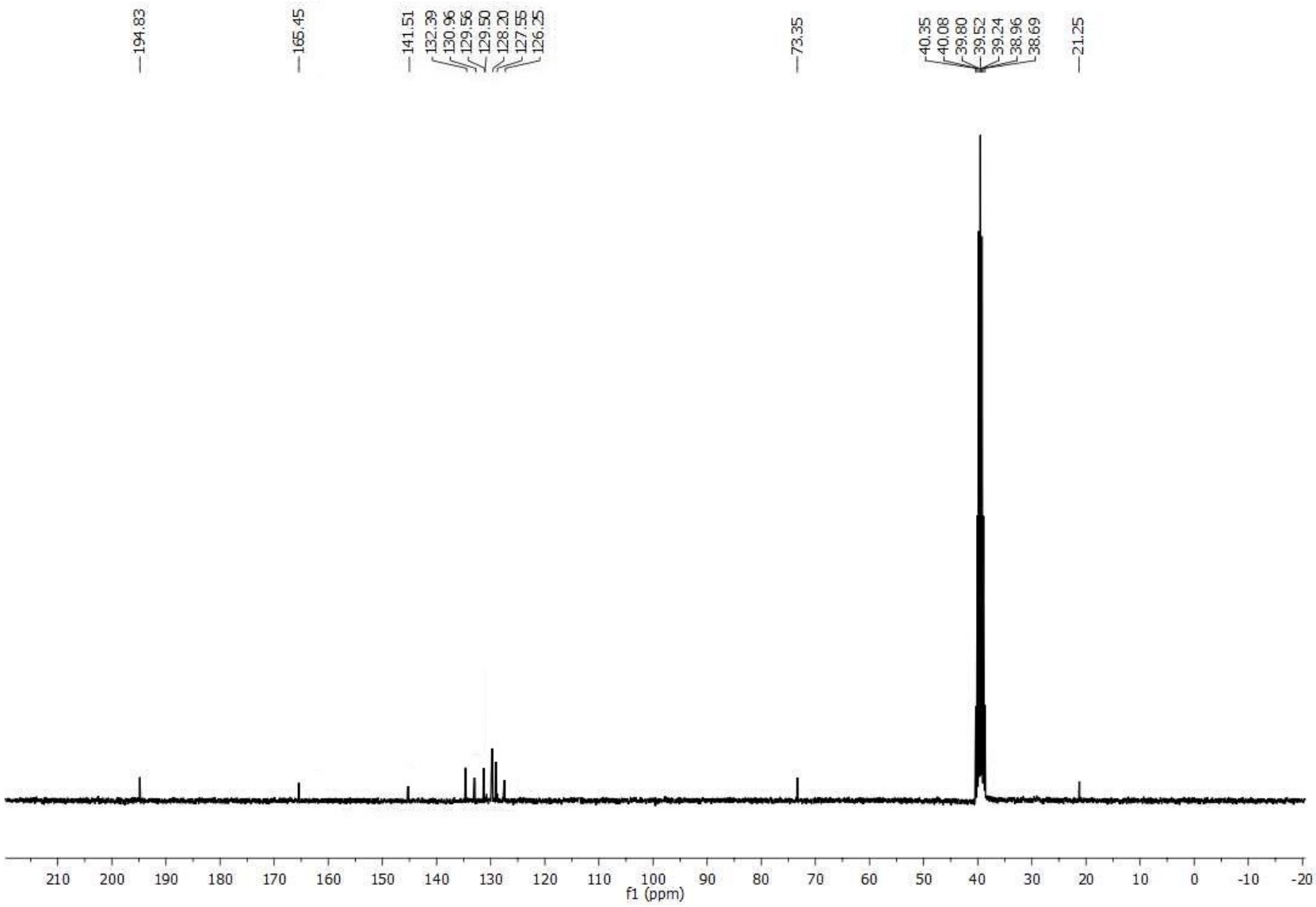
^{1}H NMR and ^{13}C NMR of Compound (3ai)



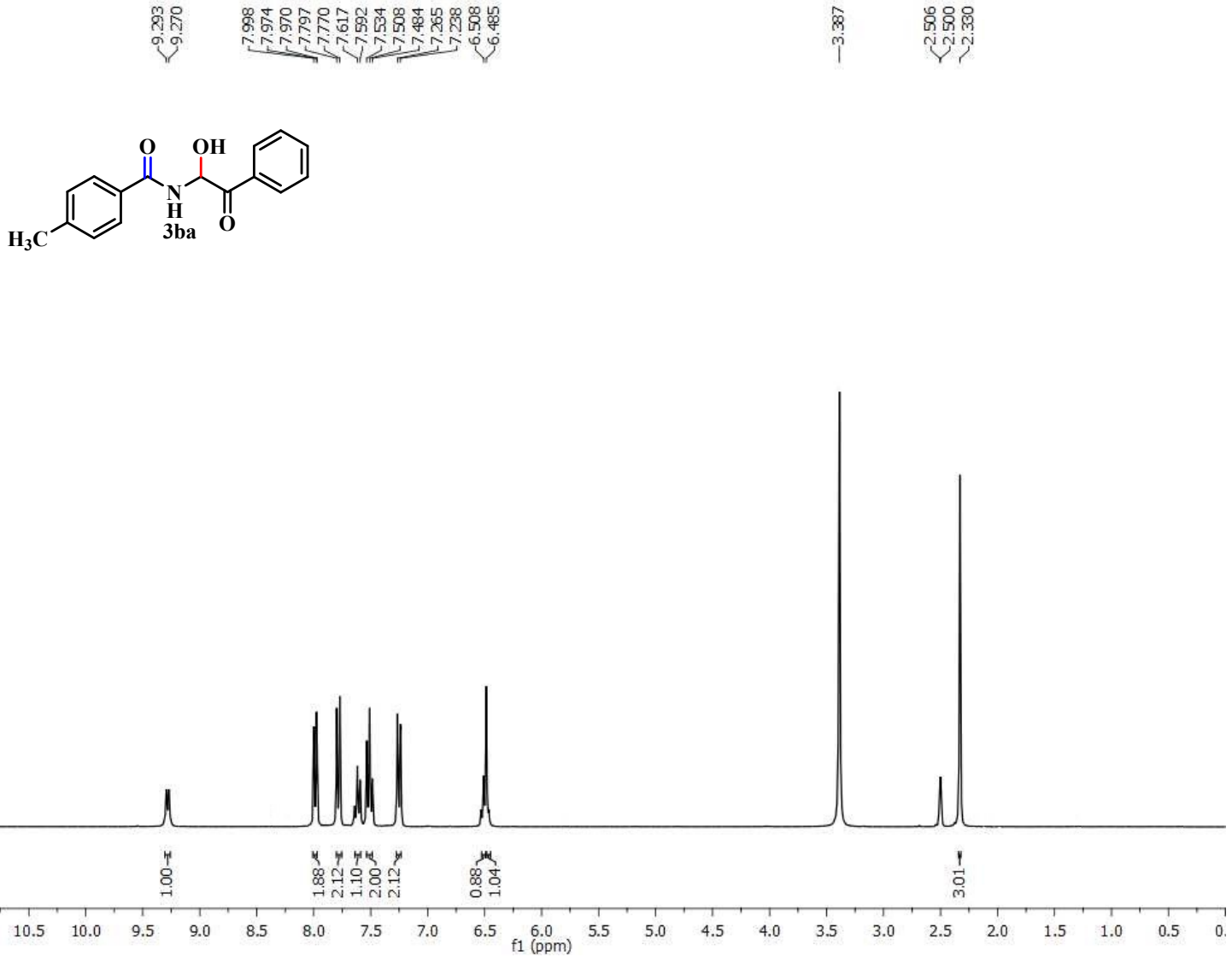

198.11
166.17
135.87
135.75
133.28
131.86
131.39
131.20
129.56
128.45
127.49
127.18
75.89
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

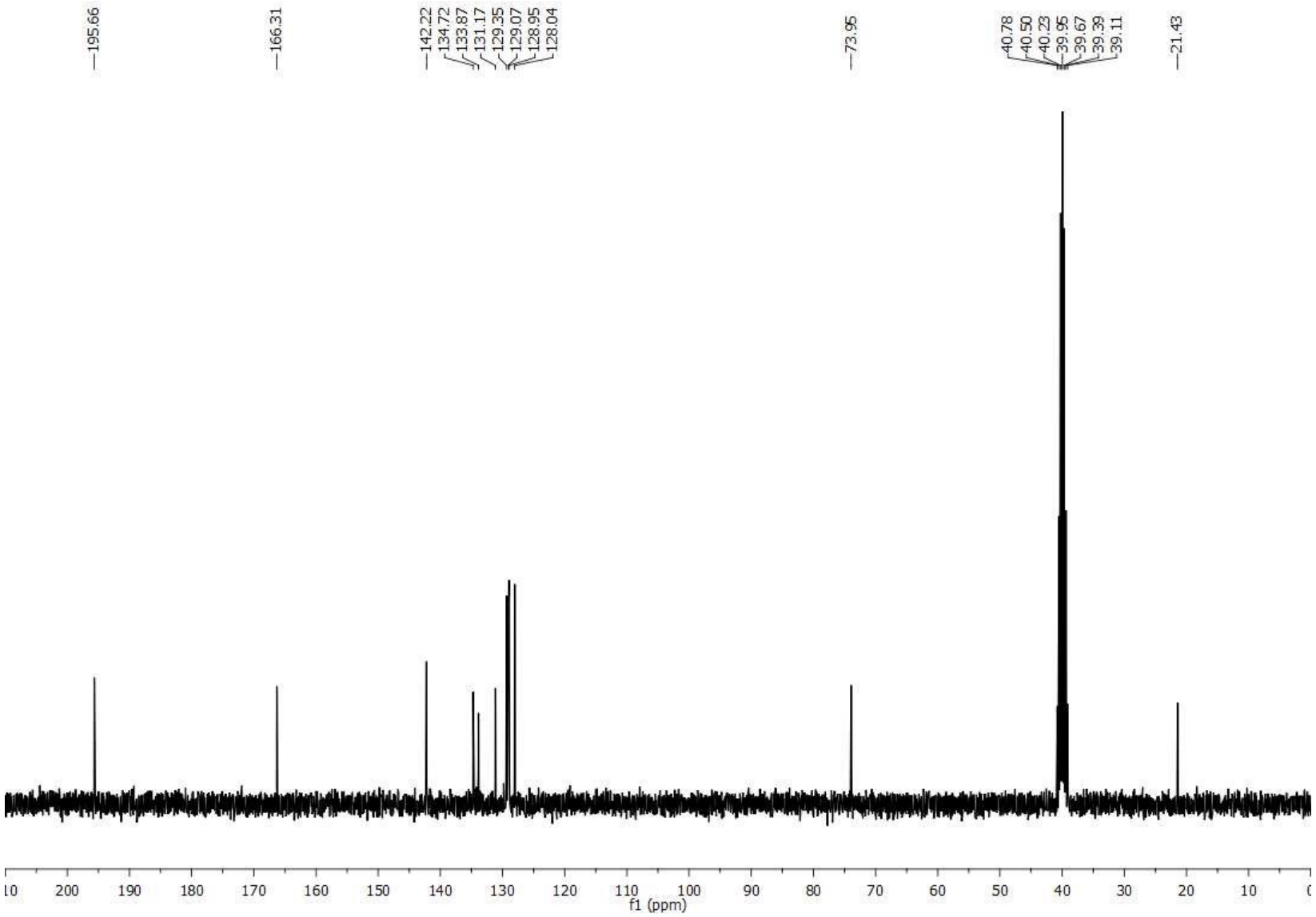
^{1}H NMR and ^{13}C NMR of Compound (3aj)



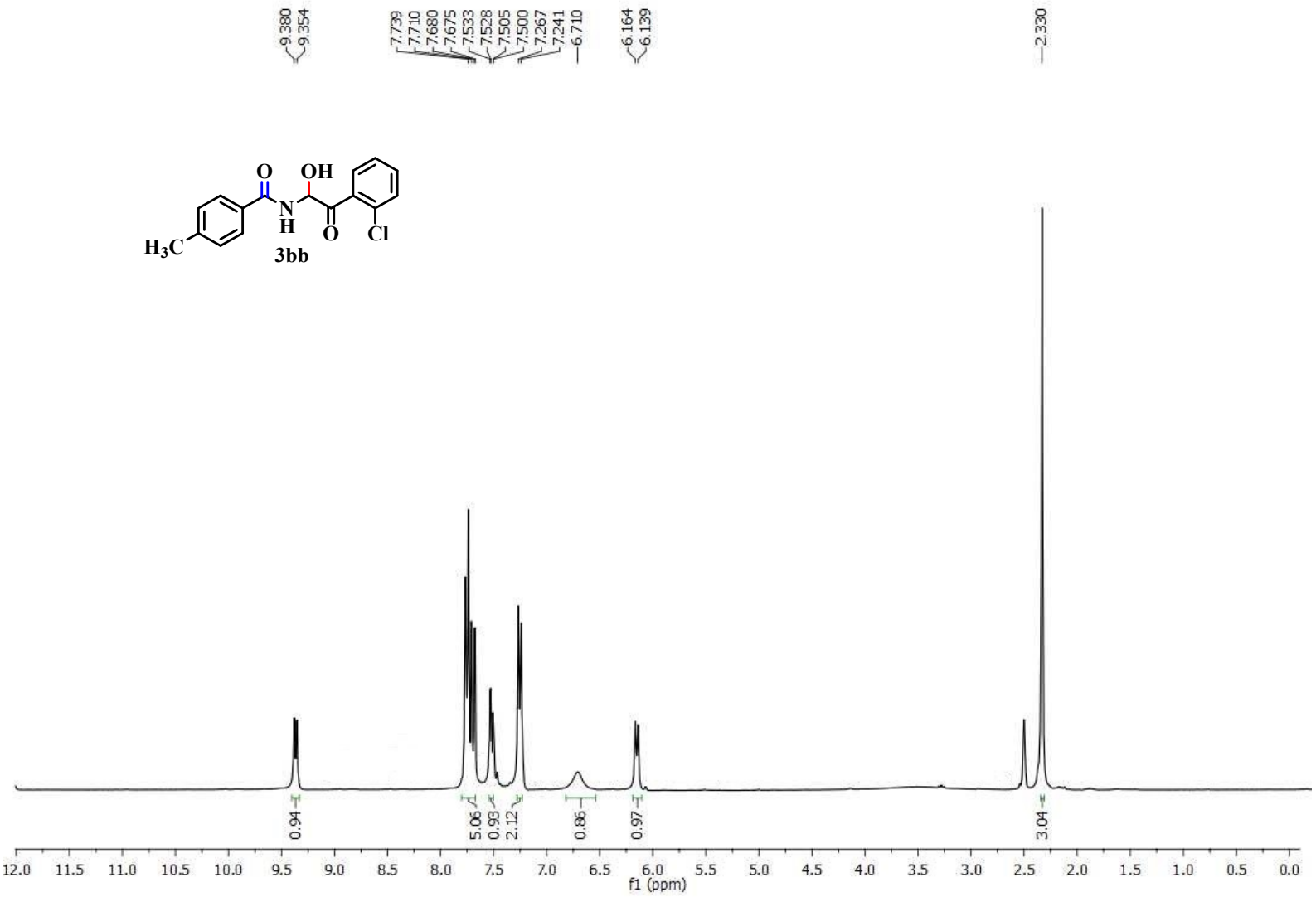

194.83
165.45
141.51
132.39
130.96
129.56
129.50
128.20
127.55
126.25
73.35
40.35
40.08
39.80
39.52
39.24
38.96
38.69
21.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

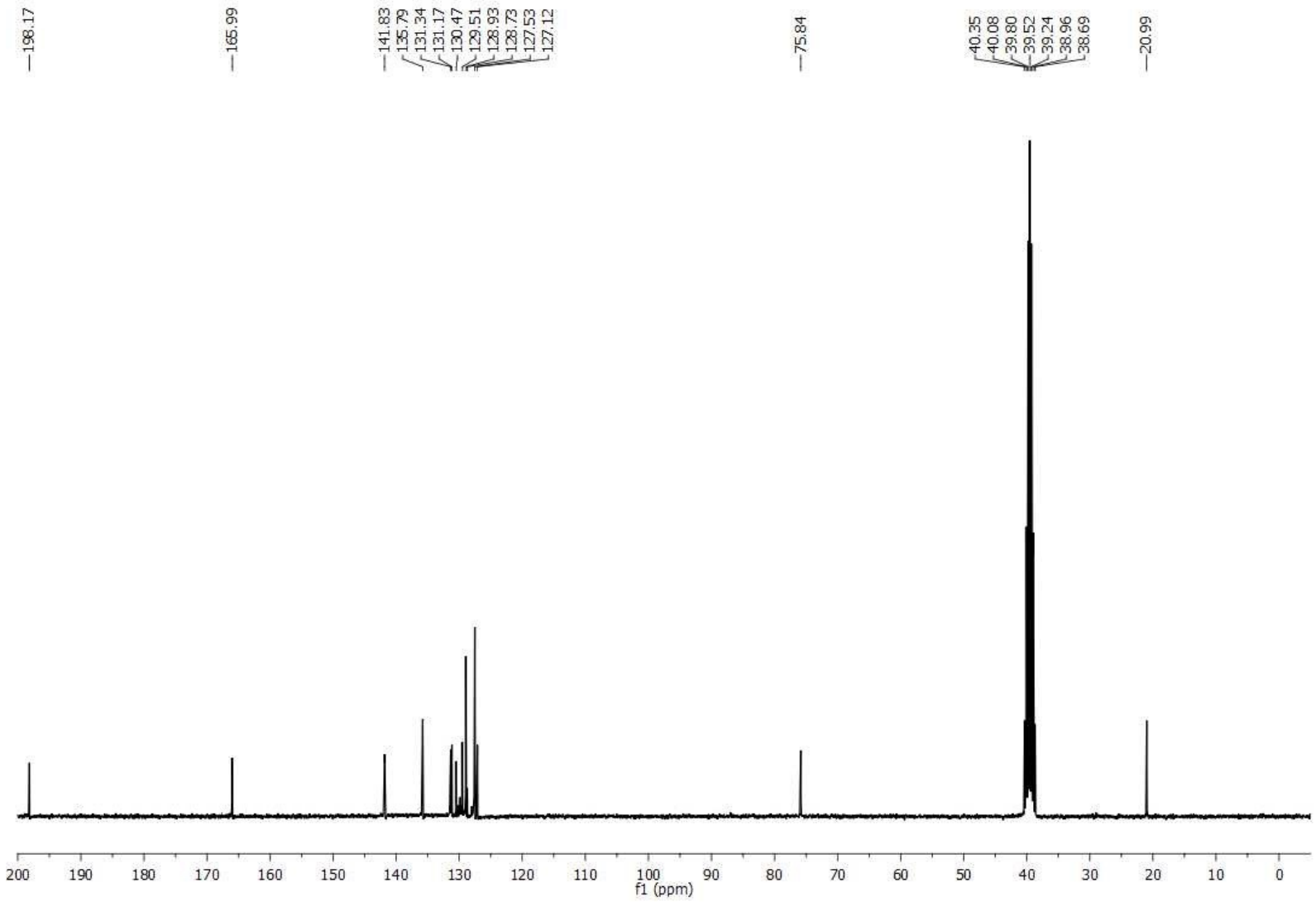
^{1}H NMR and ^{13}C NMR of Compound (3ba)



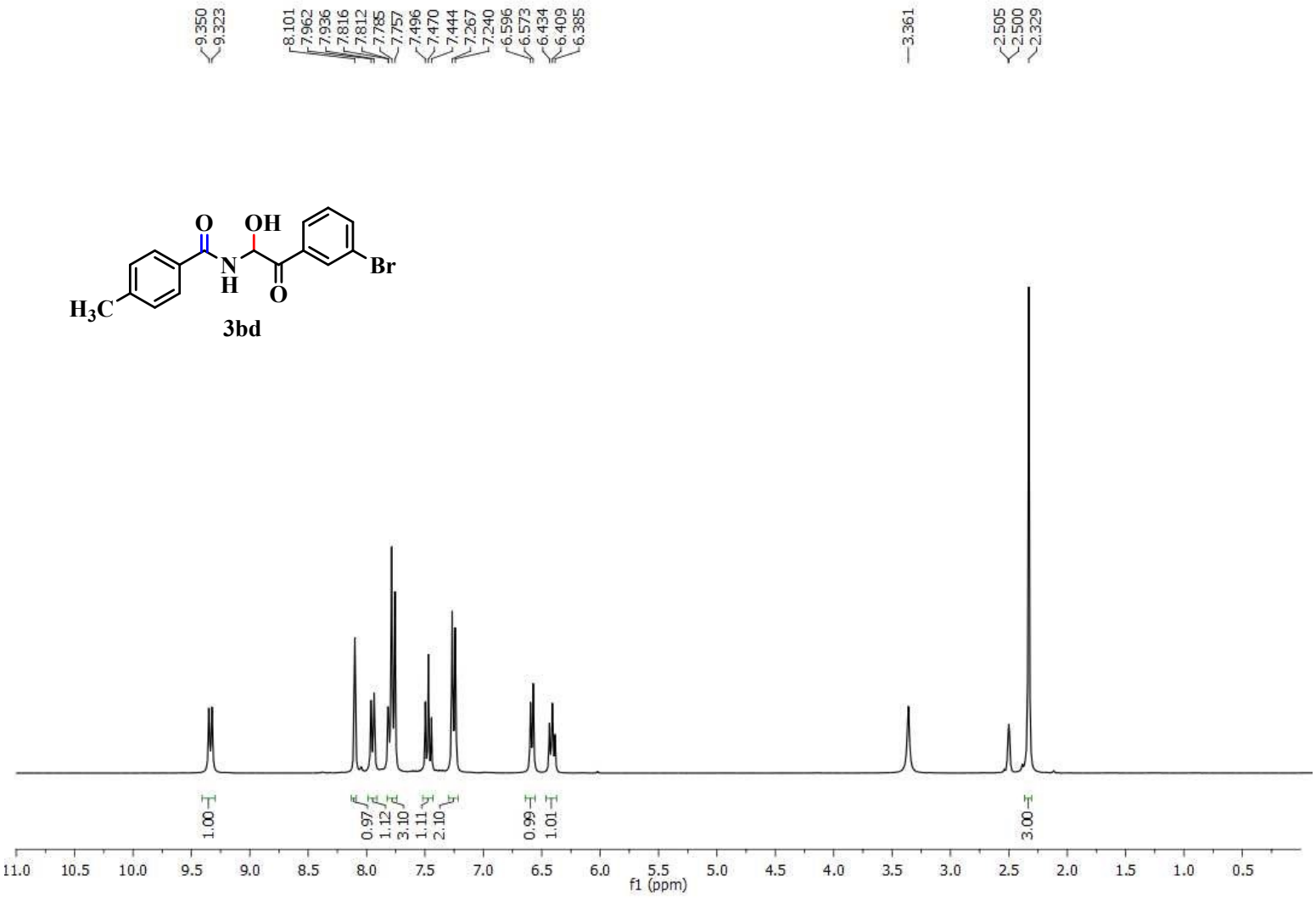

195.66
166.31
142.22
134.72
133.87
131.17
129.35
129.07
128.95
128.04
73.95
40.78
40.50
40.23
39.95
39.67
39.39
39.11
21.43
f1 (ppm)

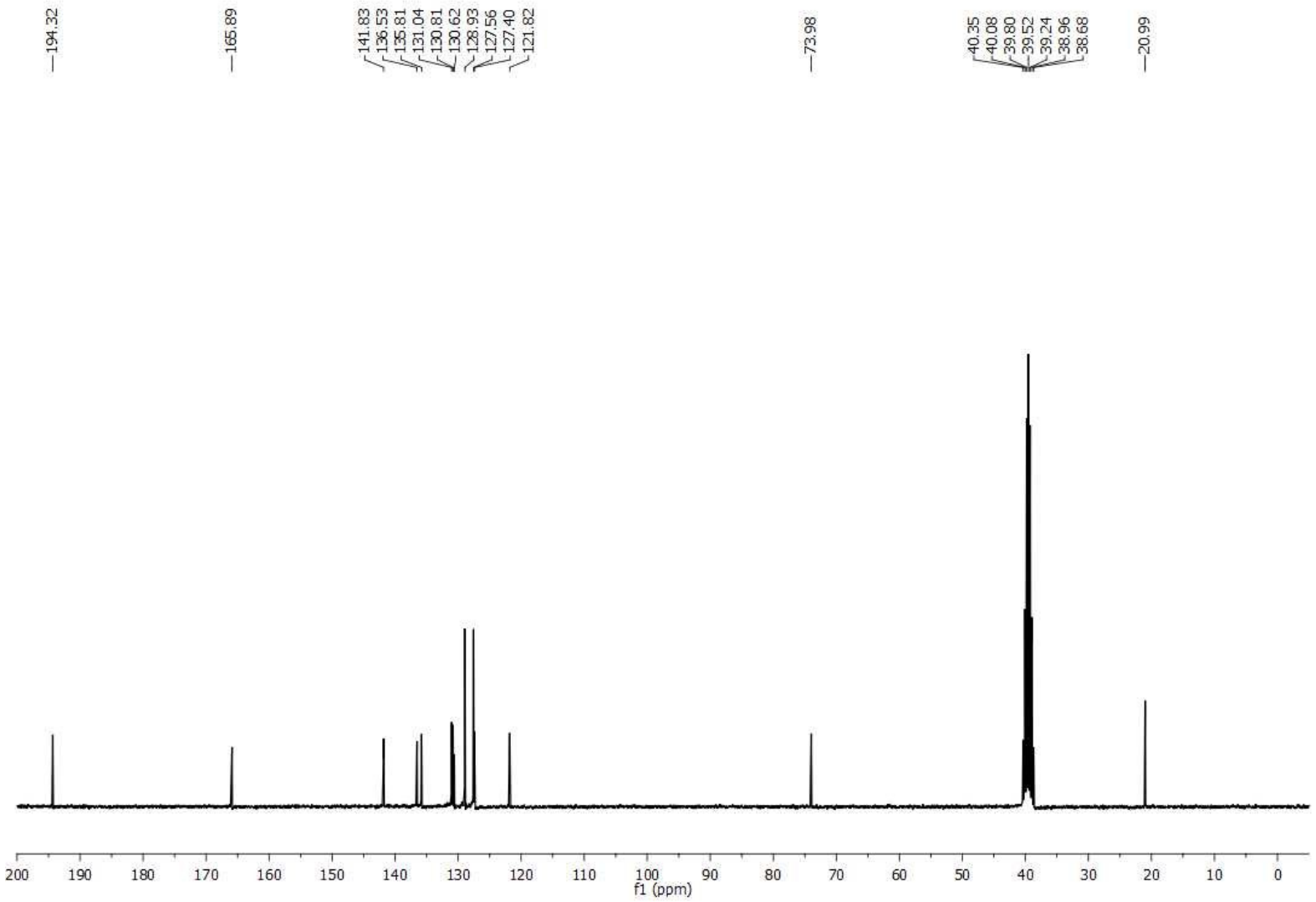
^{1}H NMR and ^{13}C NMR of Compound (3bb)



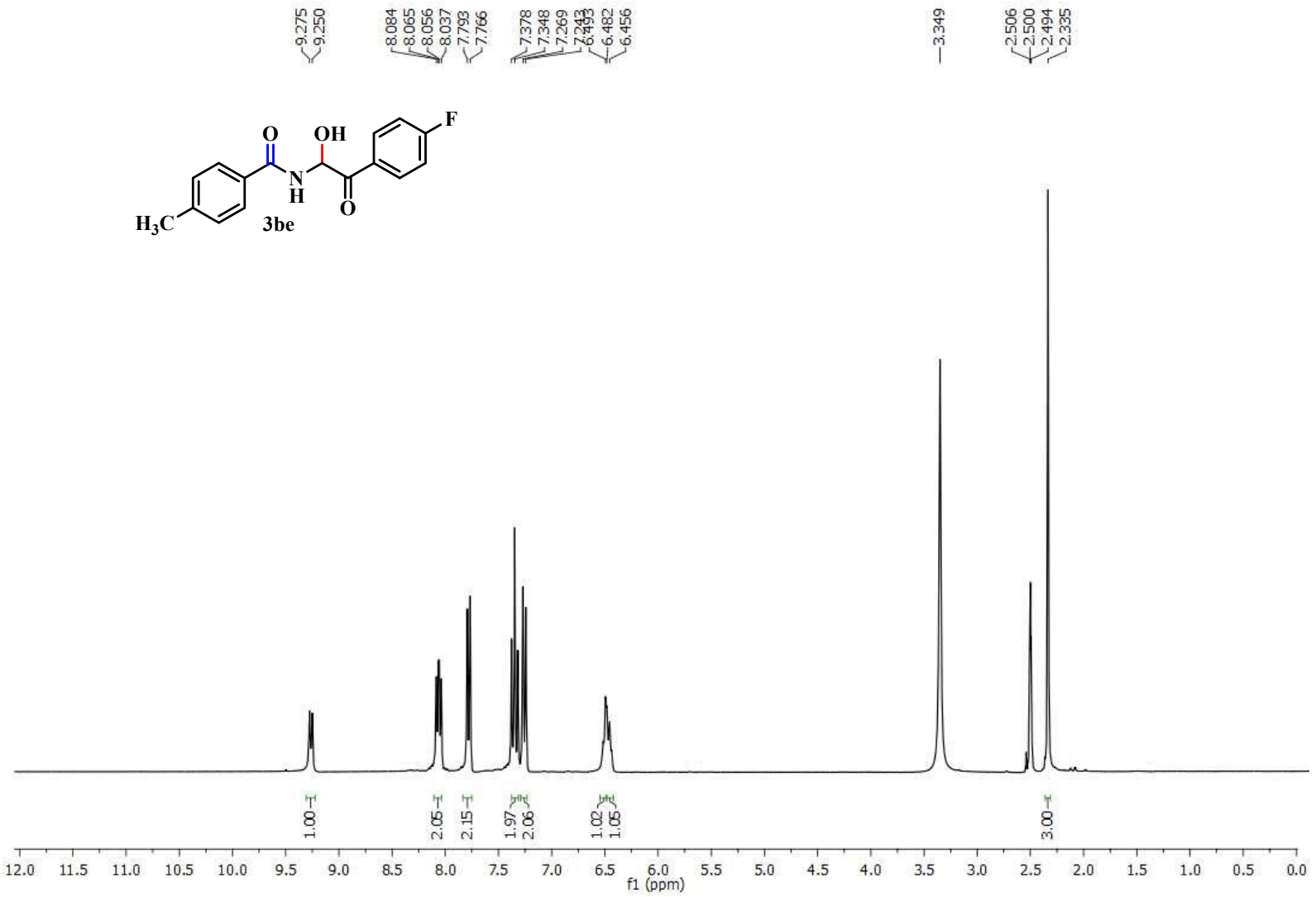

198.17
165.99
141.83
135.79
131.34
131.17
130.47
129.51
128.93
128.73
127.53
127.12
75.84
40.35
40.08
39.80
39.52
39.24
38.96
38.69
20.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

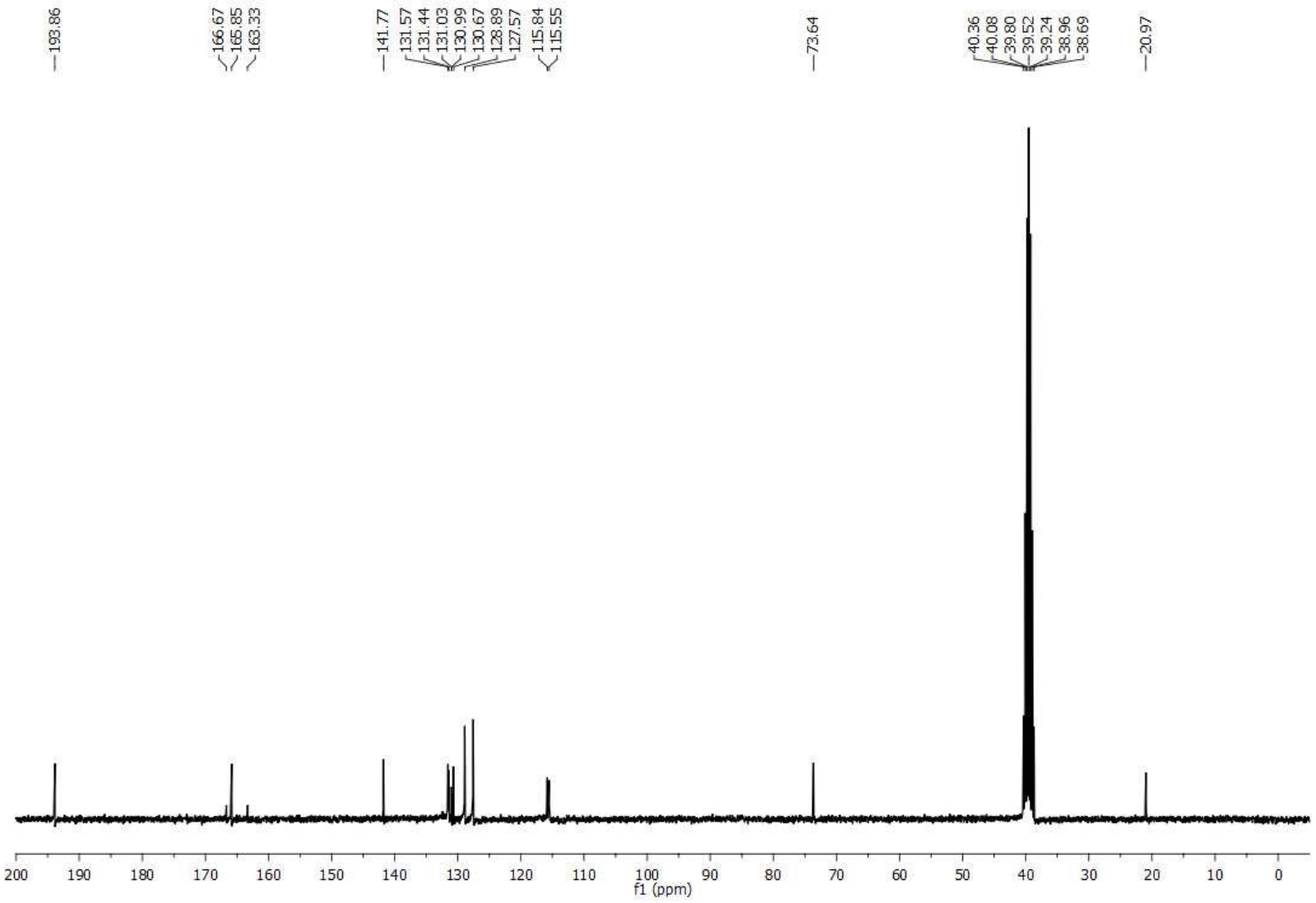
^{1}H NMR and ^{13}C NMR of Compound (3bd)



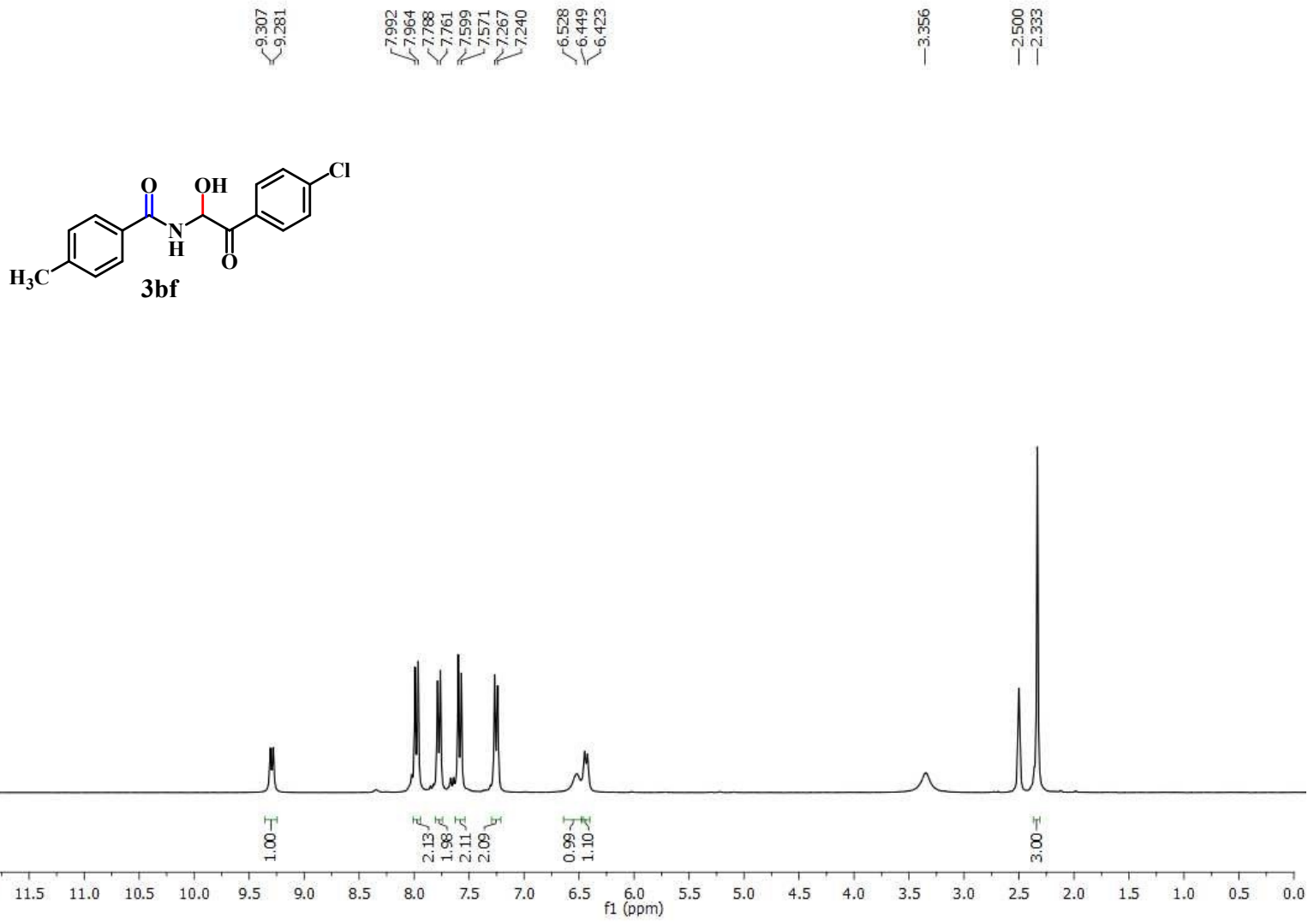

194.32
165.89
141.83
136.53
135.81
131.04
130.81
130.62
128.93
127.56
127.40
121.82
73.98
40.35
40.08
39.80
39.52
39.24
38.96
38.68
20.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

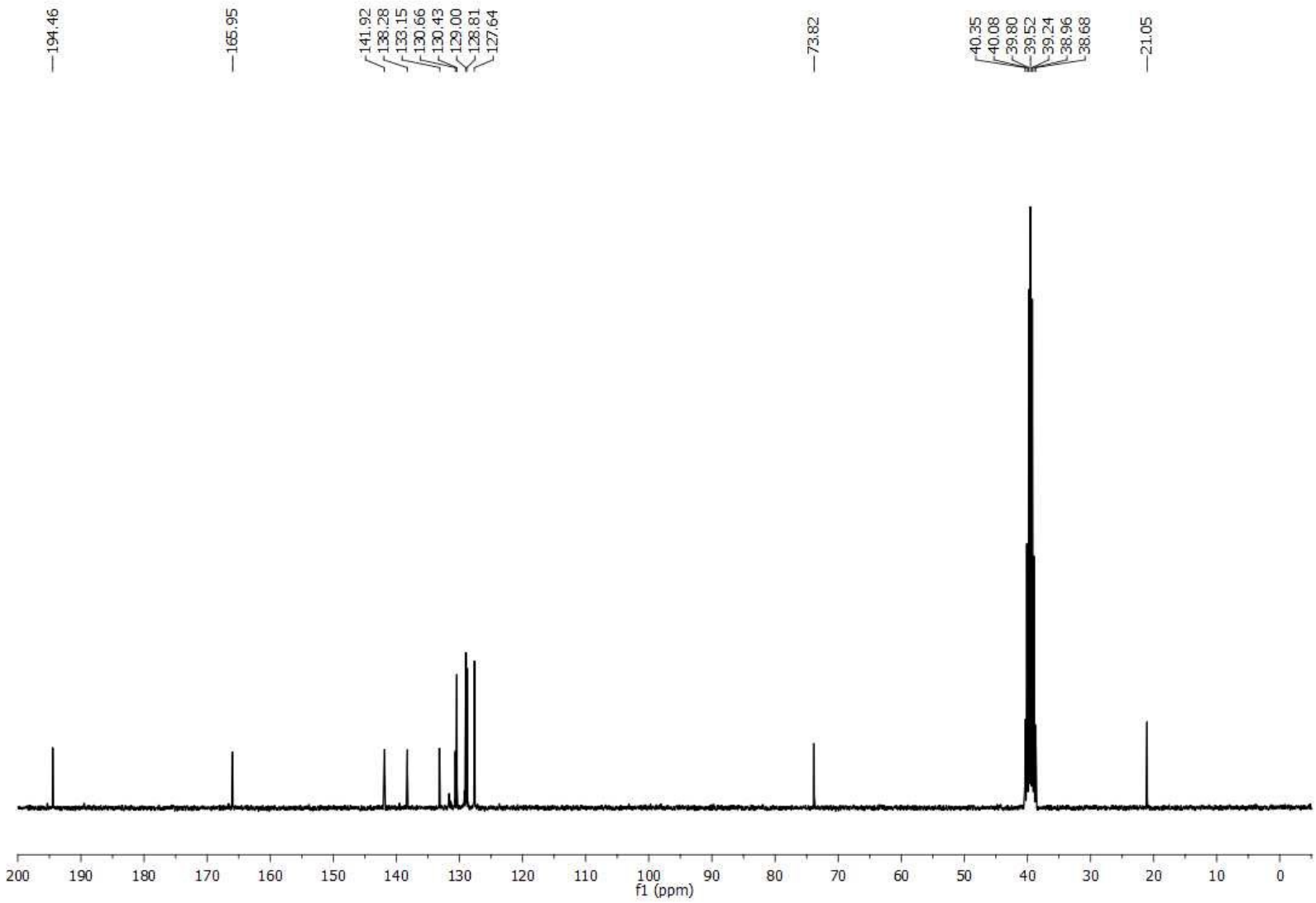
^{1}H NMR and ^{13}C NMR of Compound (3be)



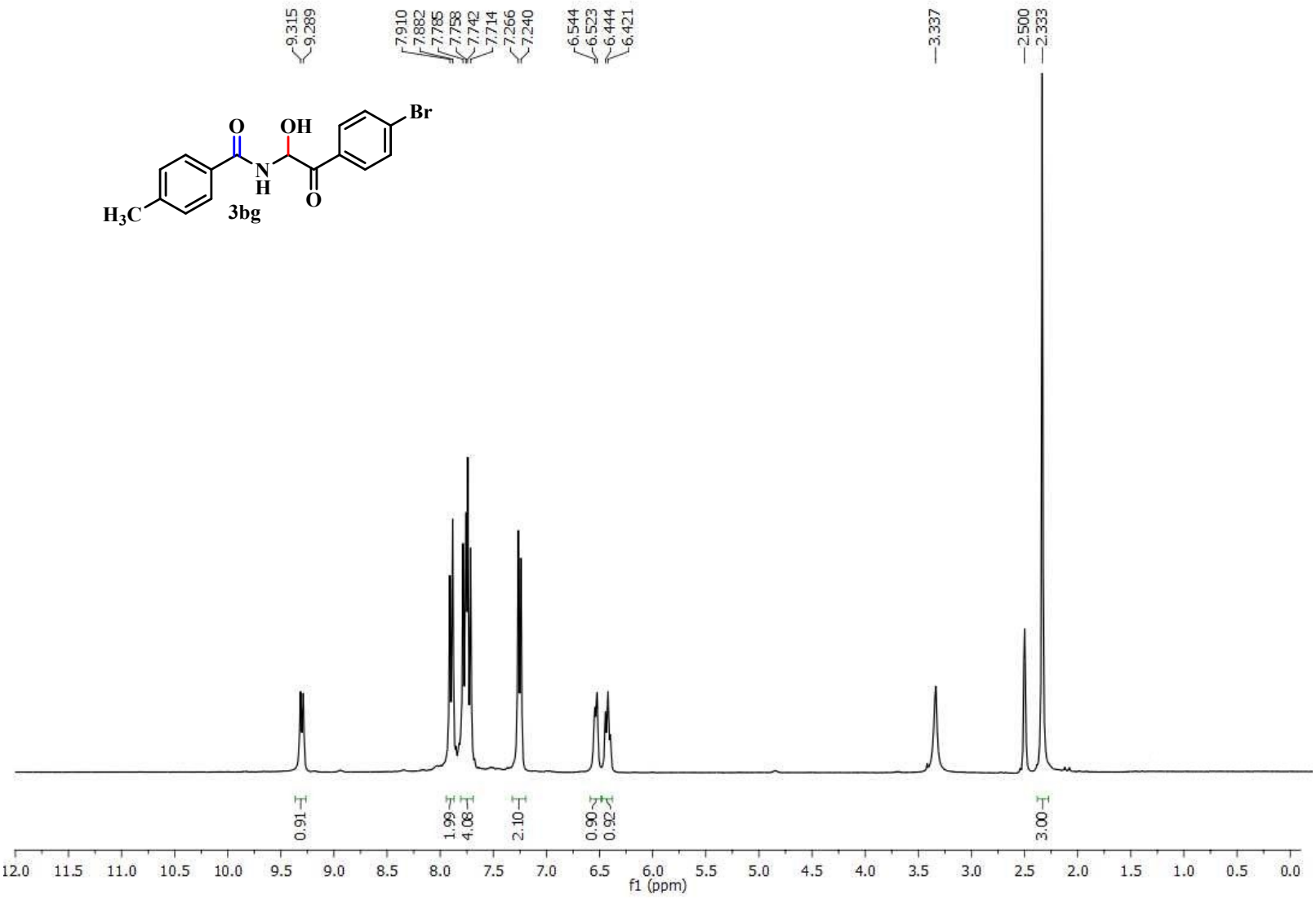

193.86
166.67
165.85
163.33
141.77
131.57
131.44
131.03
130.99
130.67
128.89
127.57
115.84
115.55
73.64
40.36
40.08
39.80
39.52
39.24
38.96
38.69
20.97
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

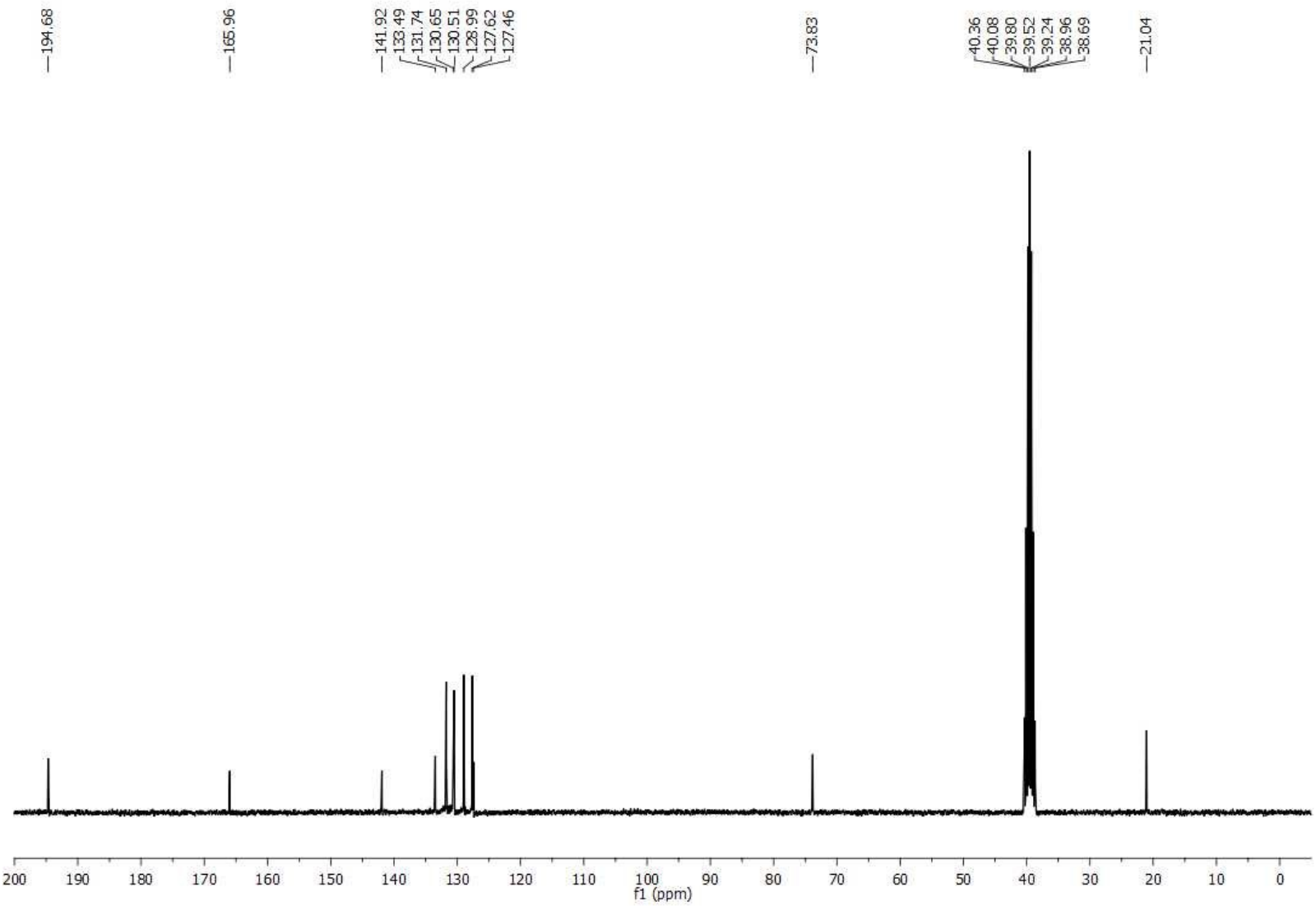
^{1}H NMR and ^{13}C NMR of Compound (3bf)



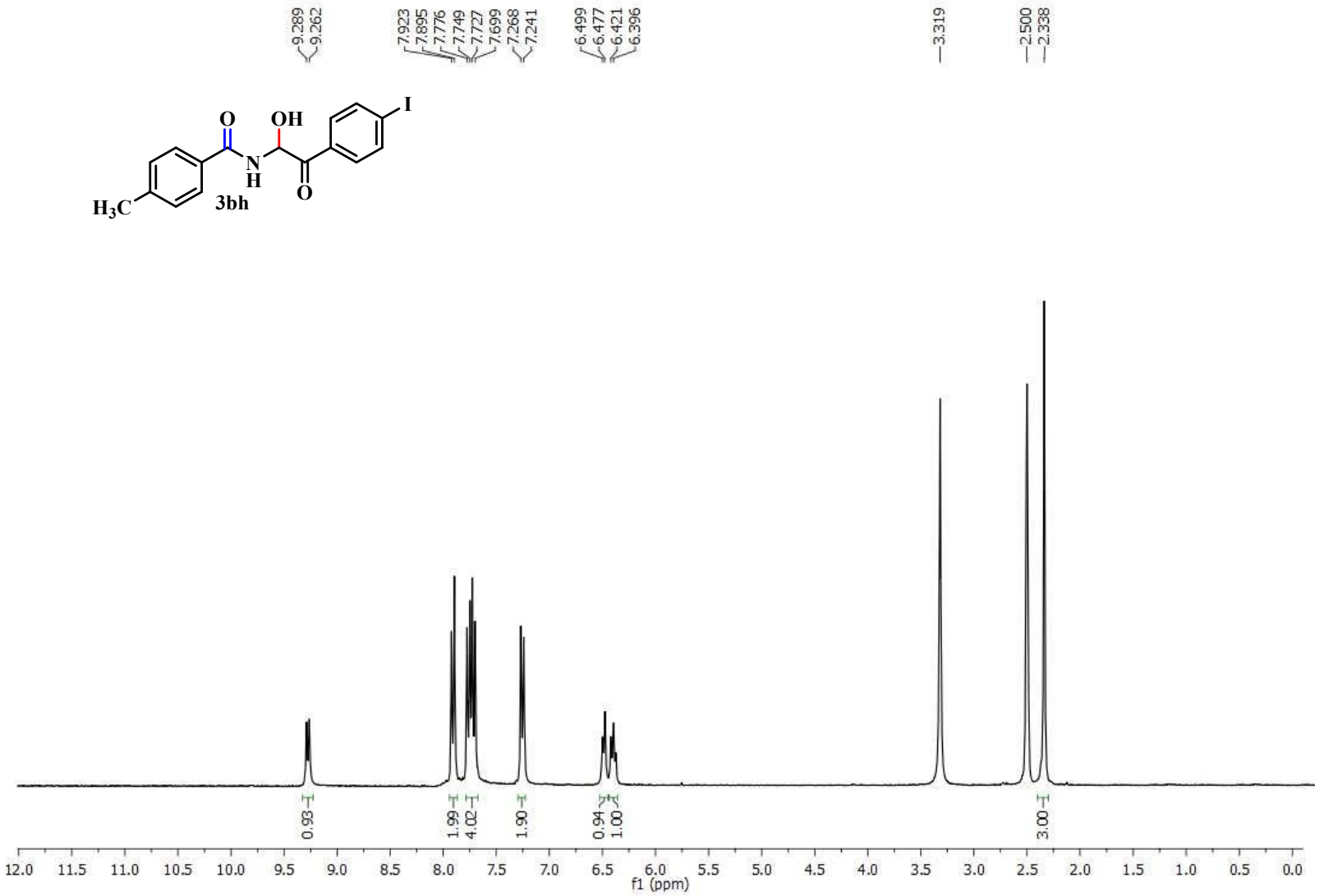

194.46
165.95
141.92
138.28
133.15
130.66
130.43
129.00
128.81
127.64
73.82
40.35
40.08
39.80
39.52
39.24
38.96
38.68
21.05
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

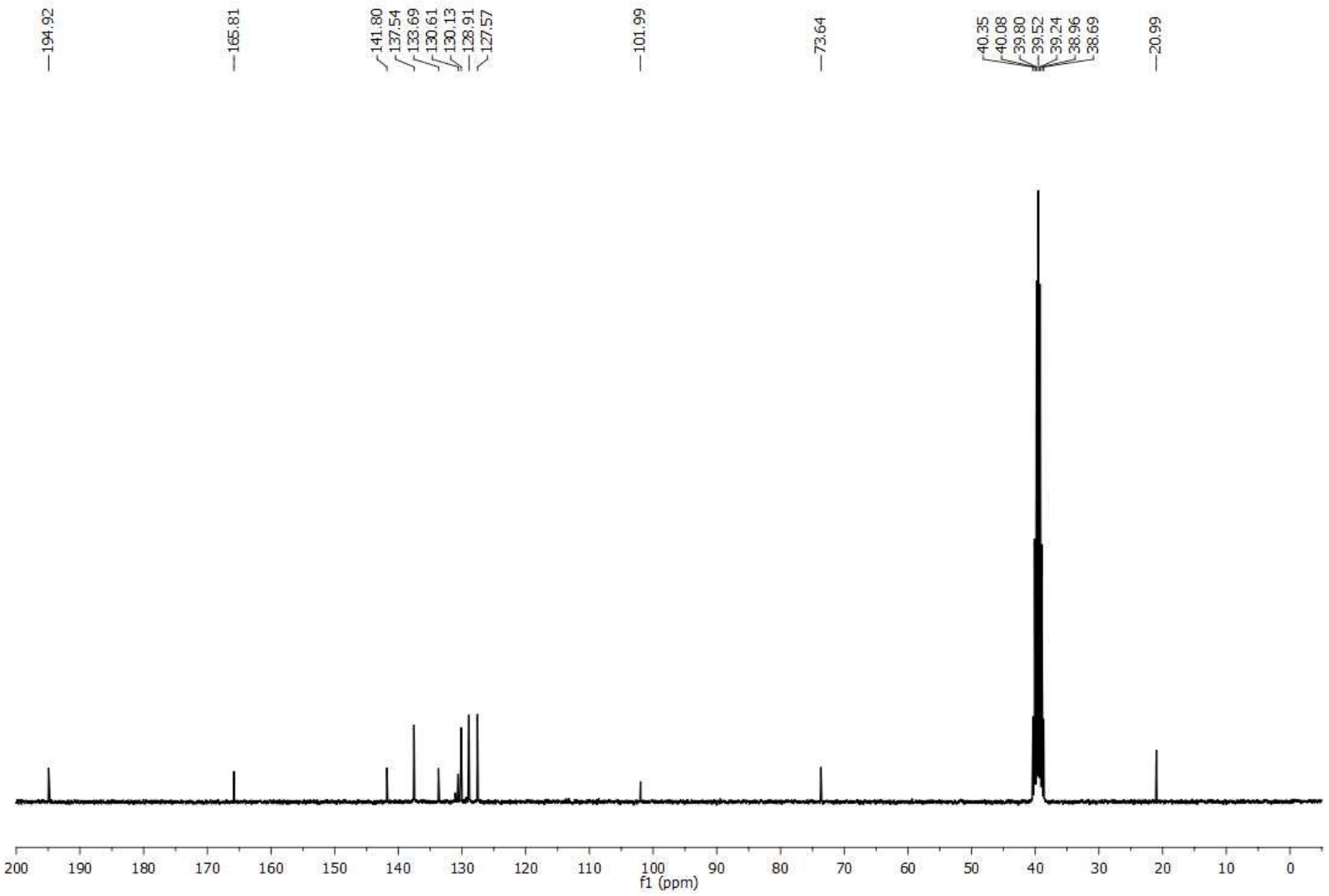
^{1}H NMR and ^{13}C NMR of Compound (3bg)


9.315
9.289
7.910
7.882
7.785
7.758
7.742
7.714
7.266
7.240
6.544
6.523
6.444
6.421
3.337
2.500
2.333
O
OH
Br
N
H
O
H3C
3bg
0.91
1.99
4.08
2.10
0.90
0.92
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

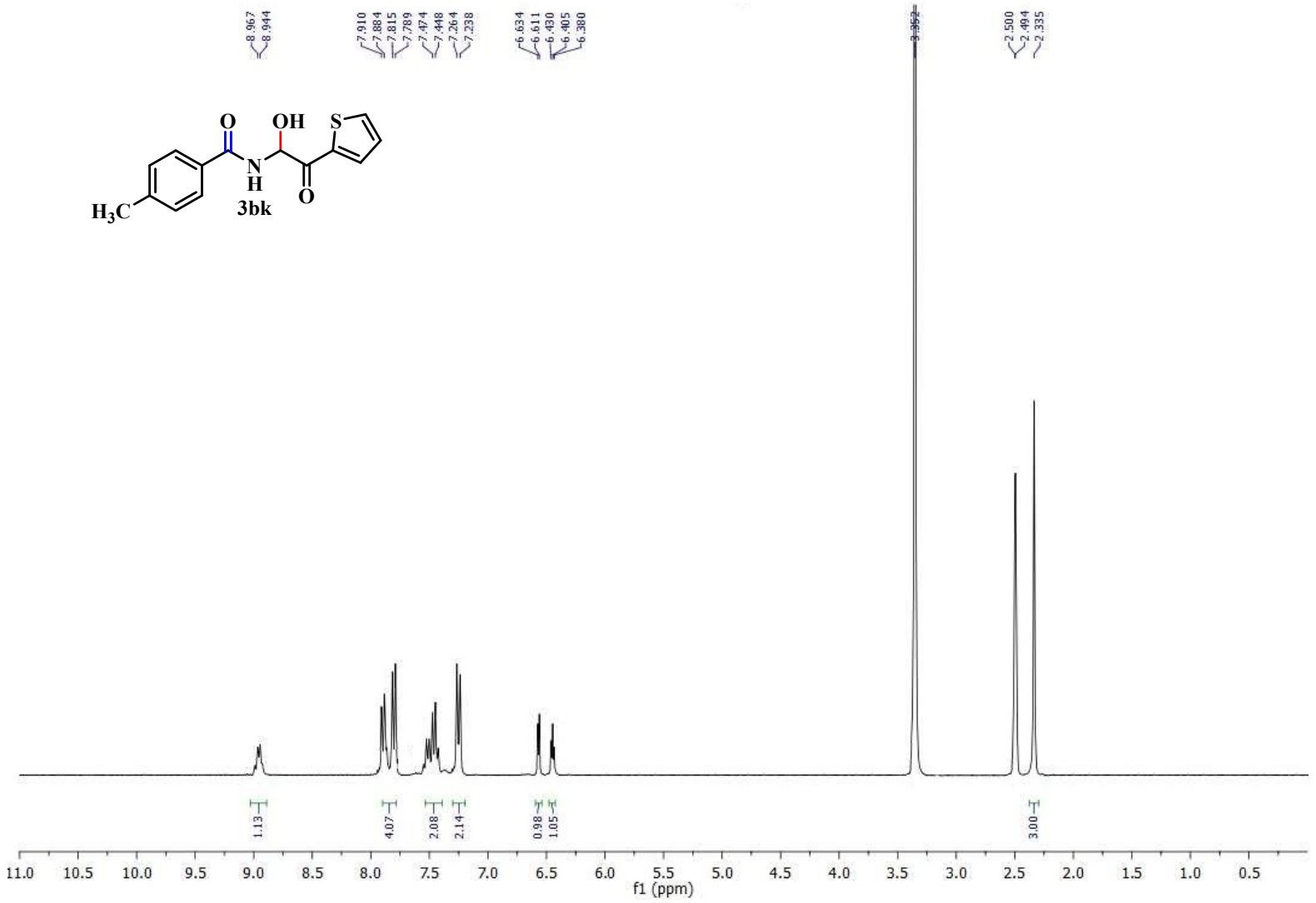


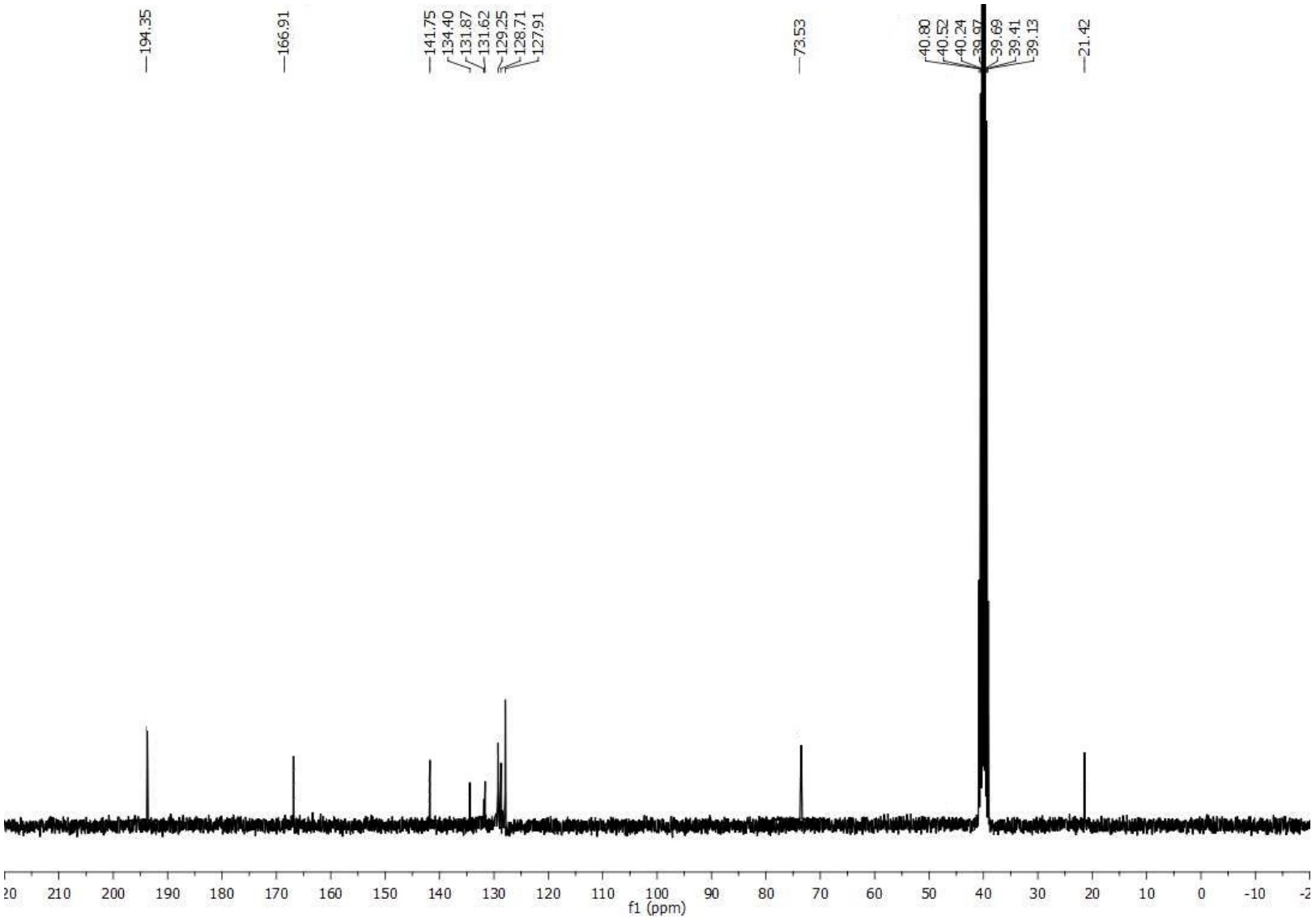
^{1}H NMR and ^{13}C NMR of Compound (3bh)


9.289
9.262
7.923
7.895
7.776
7.749
7.727
7.699
7.268
7.241
6.499
6.477
6.421
6.396
3.319
2.500
2.338
O
OH
N
H
O
I
H3C
3bh
0.93
1.99
4.02
1.90
0.94
1.00
3.00
f1 (ppm)

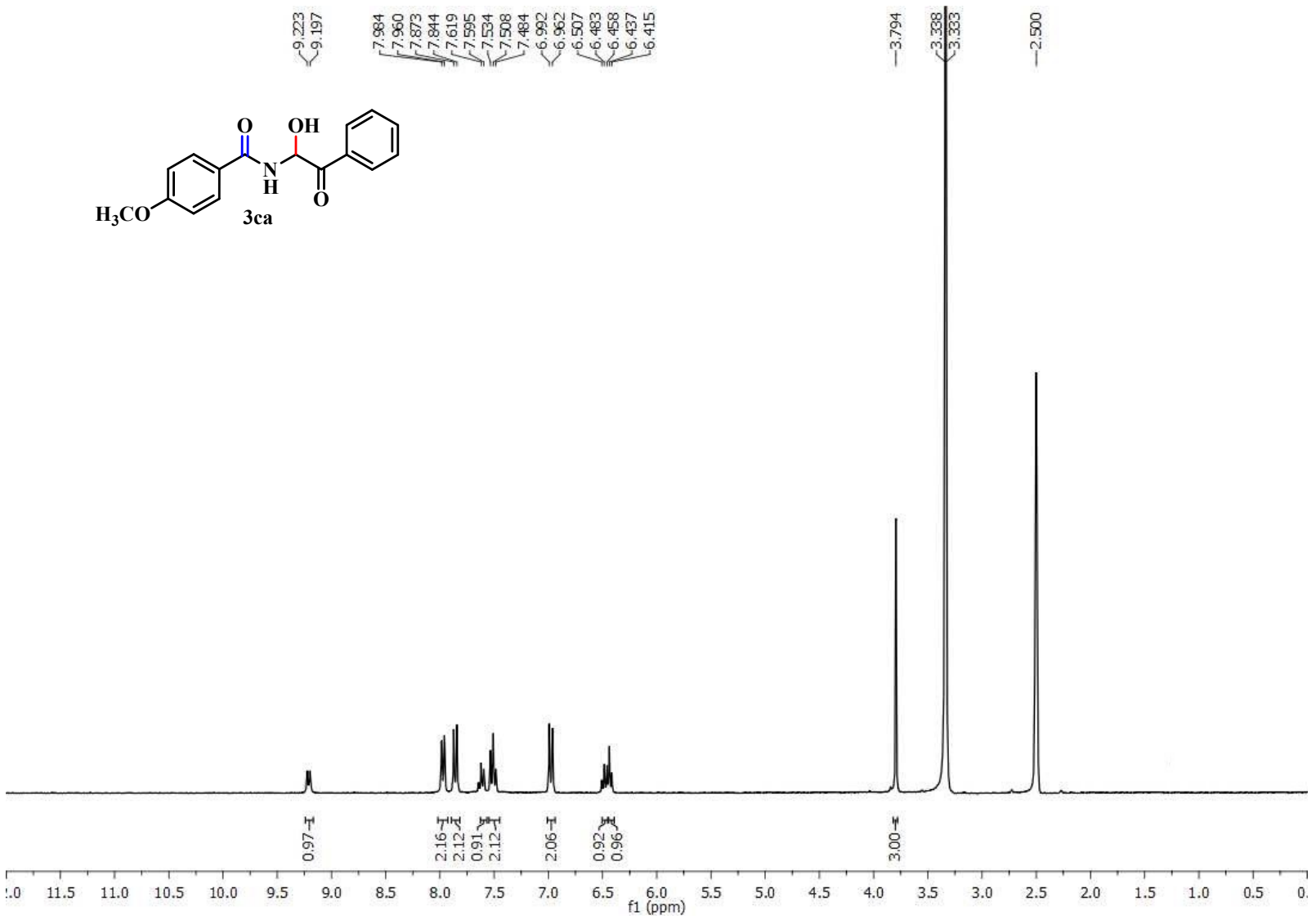


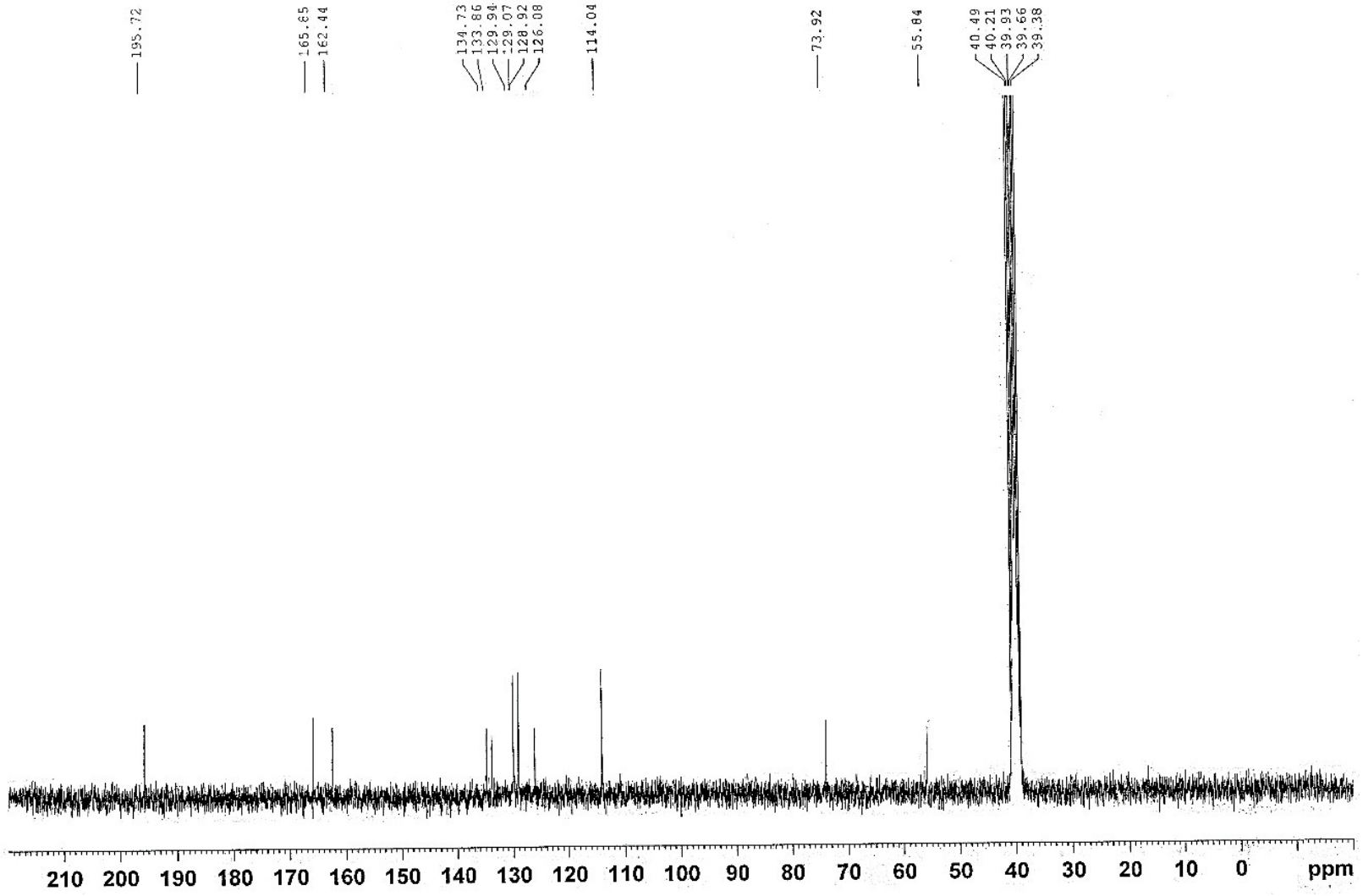
^{1}H NMR and ^{13}C NMR of Compound (3bk)


8.967
8.944
7.910
7.884
7.815
7.789
7.474
7.448
7.264
7.238
6.634
6.611
6.430
6.405
6.380
3.352
2.500
2.494
2.335
O
OH
S
N
H
O
H3C
3bk
1.13
4.07
2.08
2.14
0.98
1.05
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

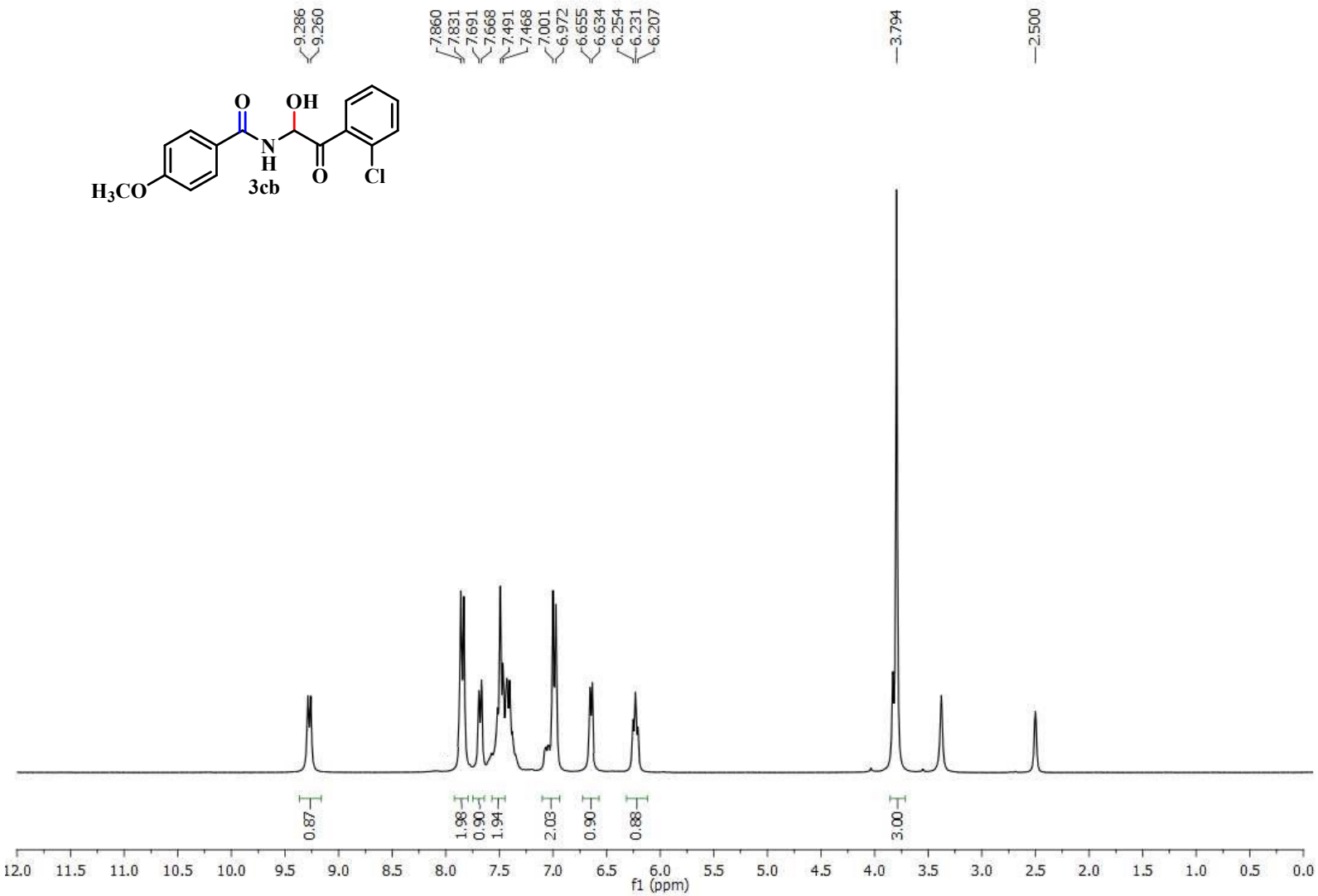


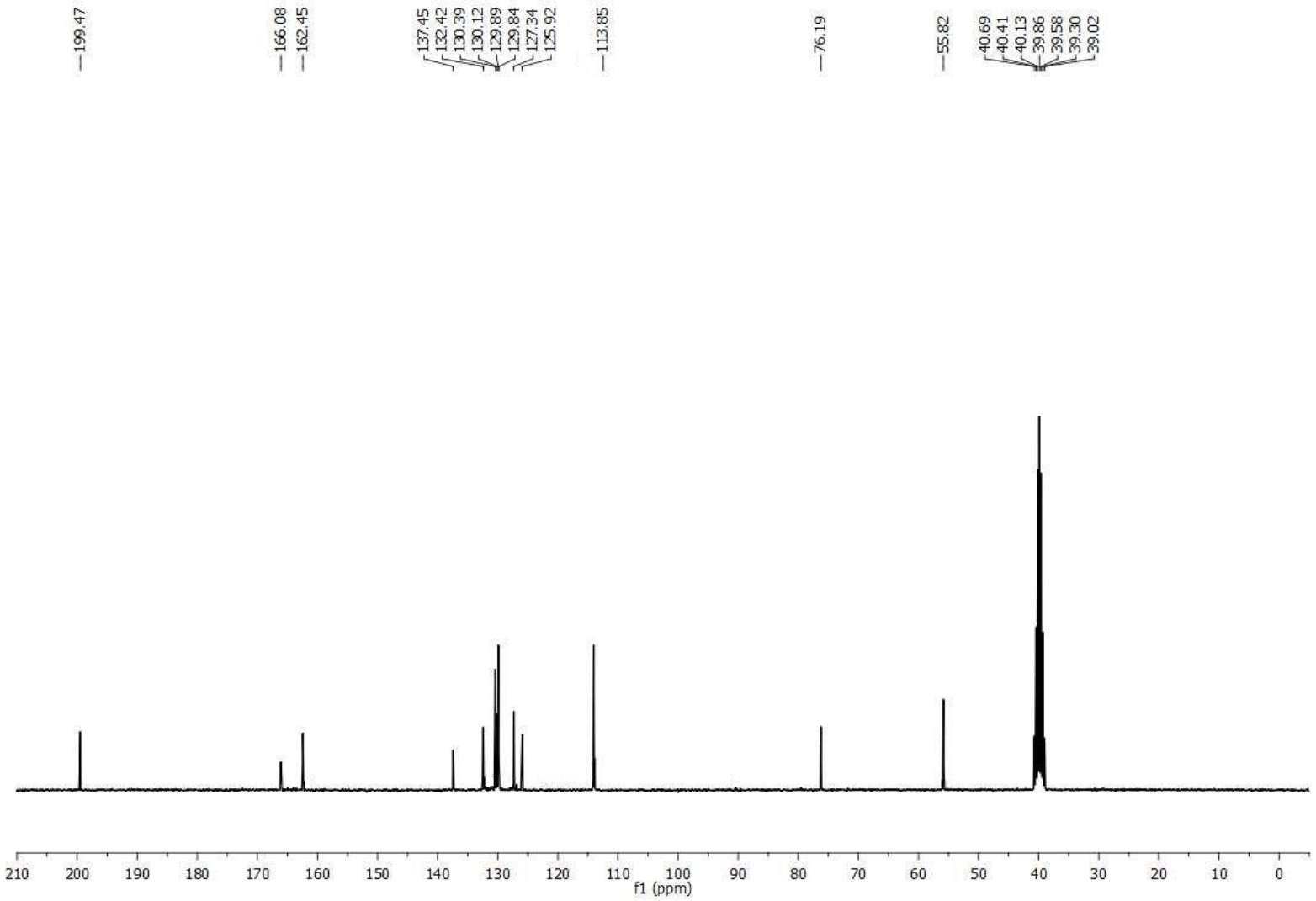
^{1}H NMR and ^{13}C NMR of Compound (3ca)


9.223
9.197
7.984
7.960
7.873
7.844
7.619
7.595
7.534
7.508
7.484
6.992
6.962
6.507
6.483
6.458
6.437
6.415
3.794
3.338
3.333
2.500
O
OH
N
H
O
H3CO
3ca
0.97
2.16
2.12
0.91
2.12
2.06
0.92
0.96
3.00
f1 (ppm)

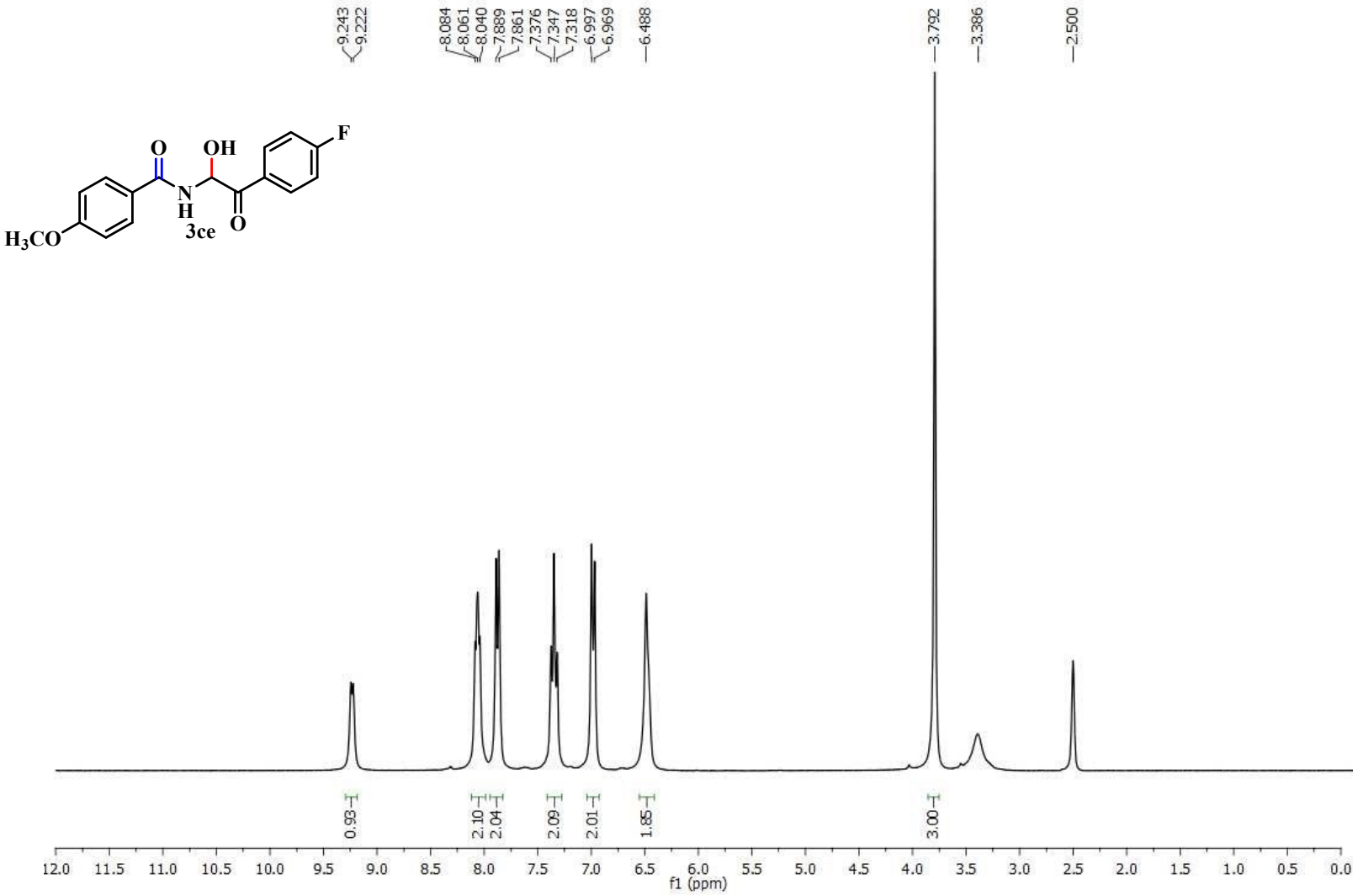

195.72
165.85
162.44
134.73
133.86
129.94
129.07
128.92
126.08
114.04
73.92
55.84
40.49
40.21
39.93
39.66
39.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

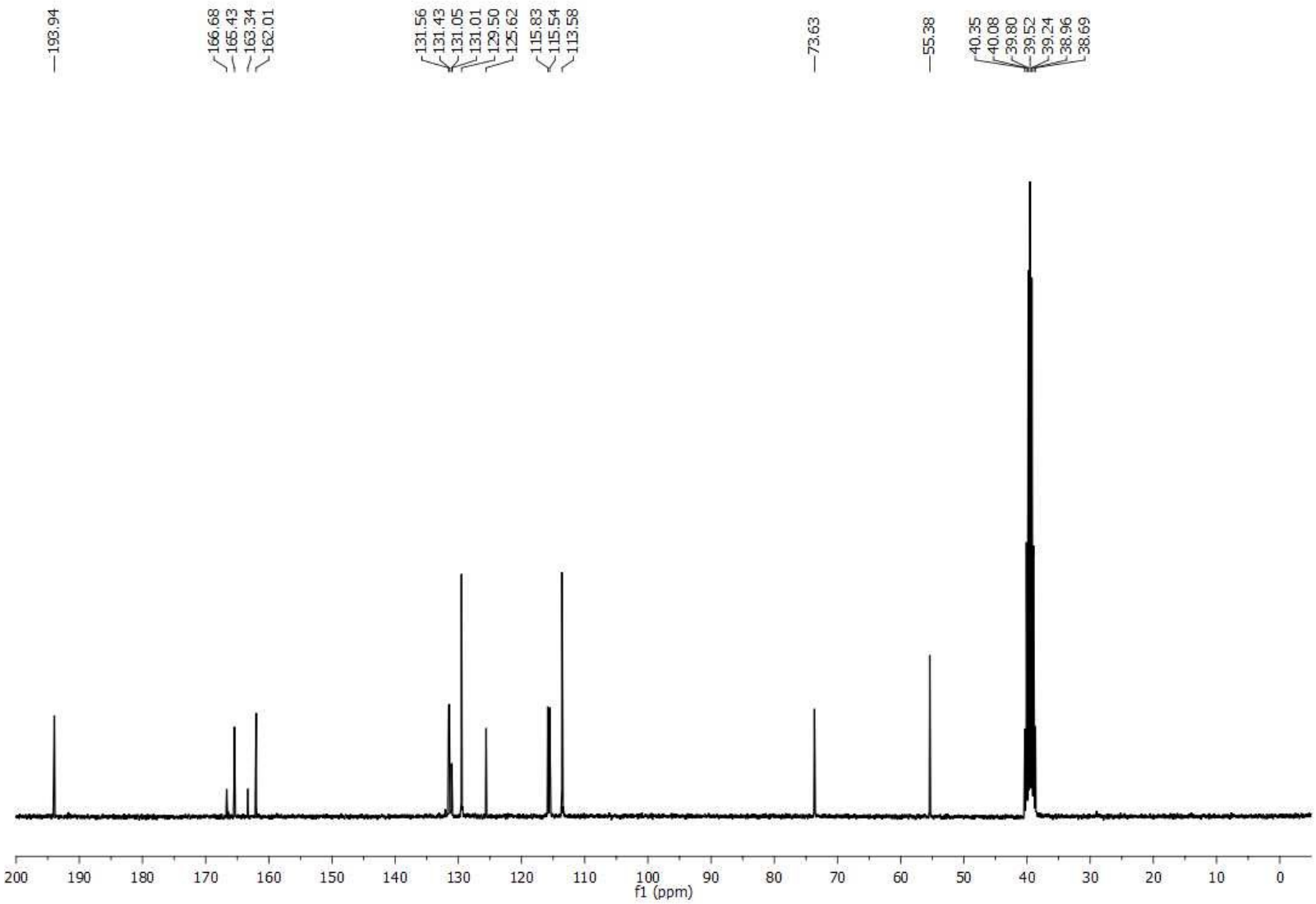
^{1}H NMR and ^{13}C NMR of Compound (3cb)



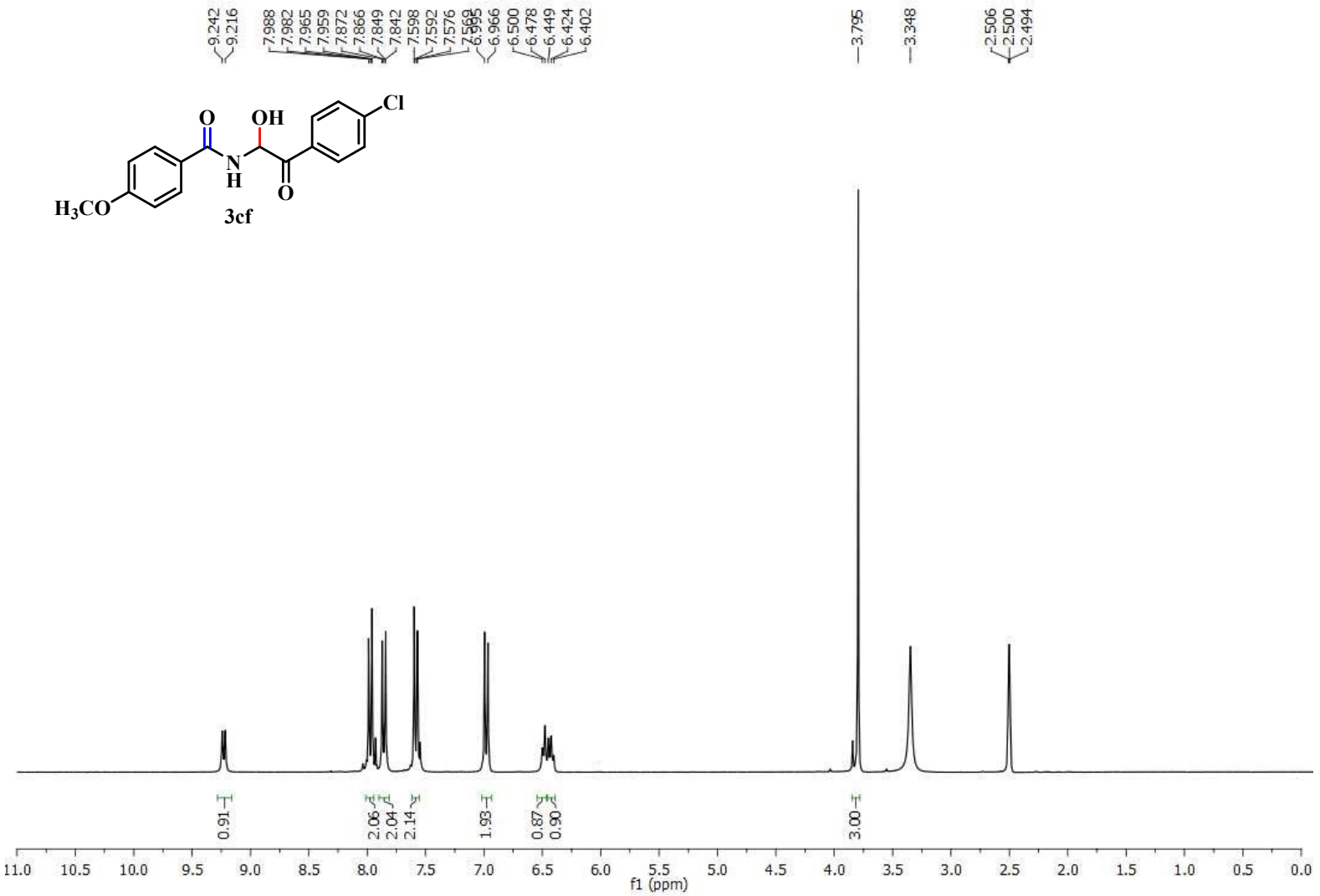

199.47
166.08
162.45
137.45
132.42
130.39
130.12
129.89
129.84
127.34
125.92
113.85
76.19
55.82
40.69
40.41
40.13
39.86
39.58
39.30
39.02
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

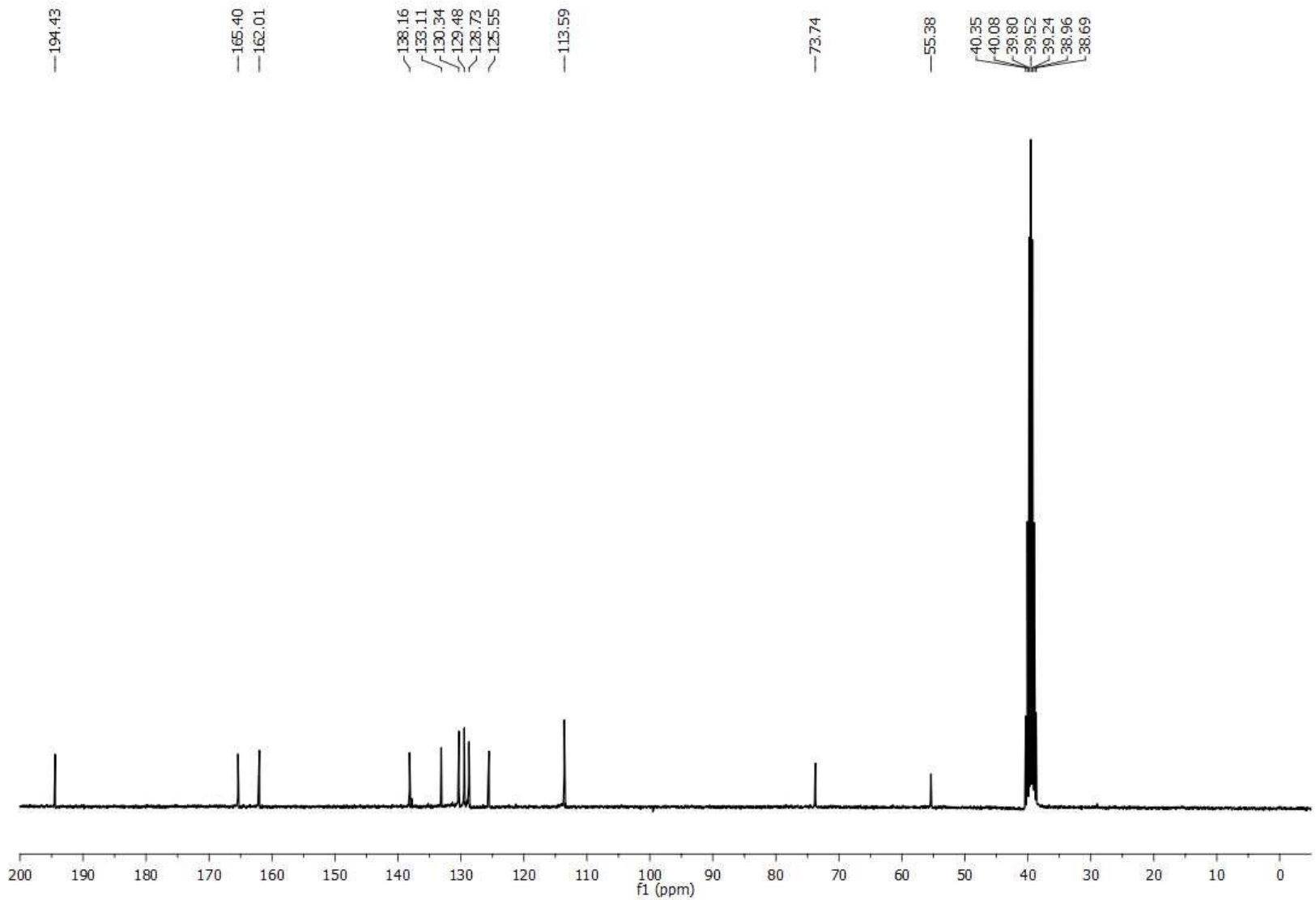
^{1}H NMR and ^{13}C NMR of Compound (3ce)



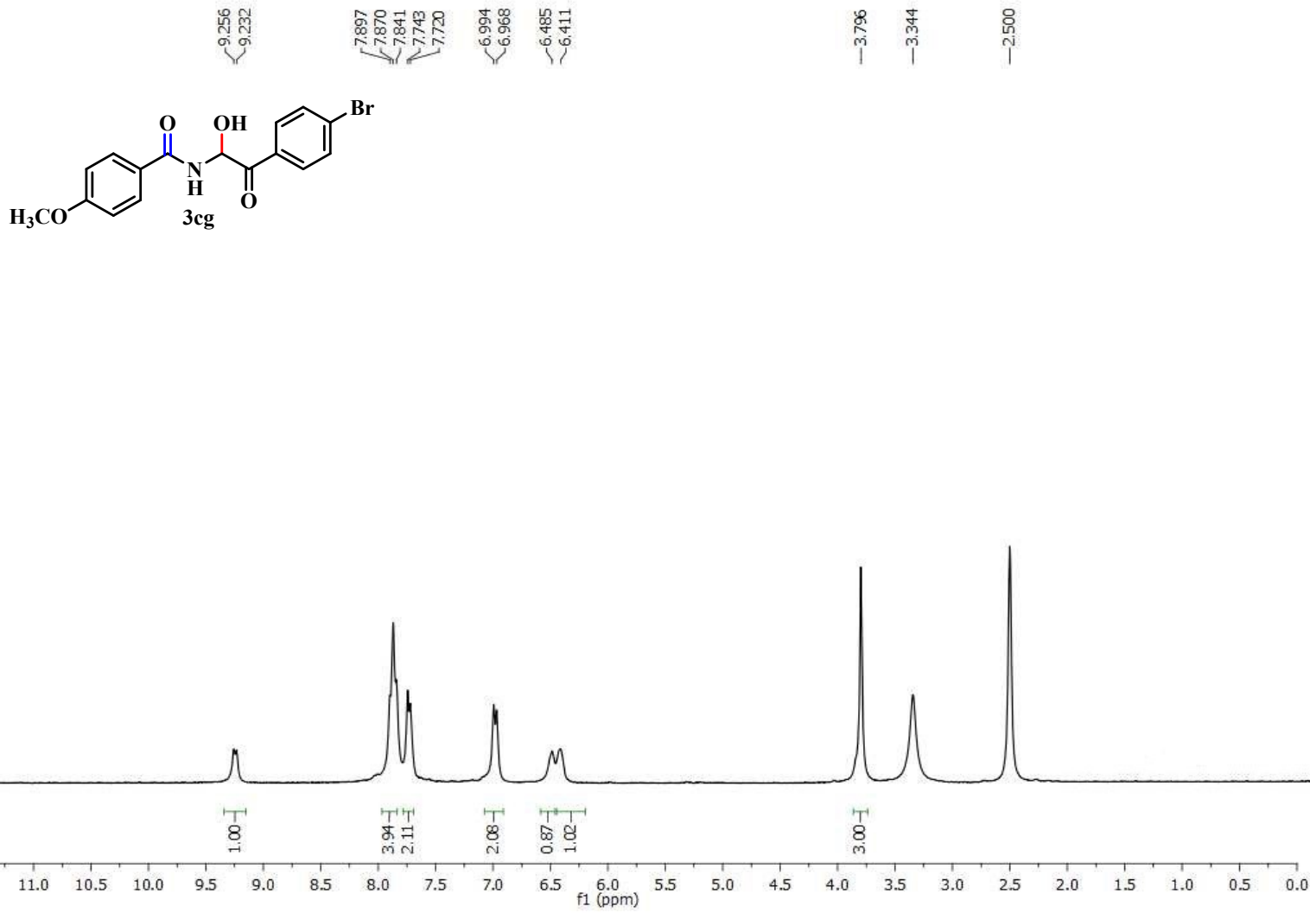

193.94
166.68
165.43
163.34
162.01
131.56
131.43
131.05
131.01
129.50
125.62
115.83
115.54
113.58
73.63
55.38
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

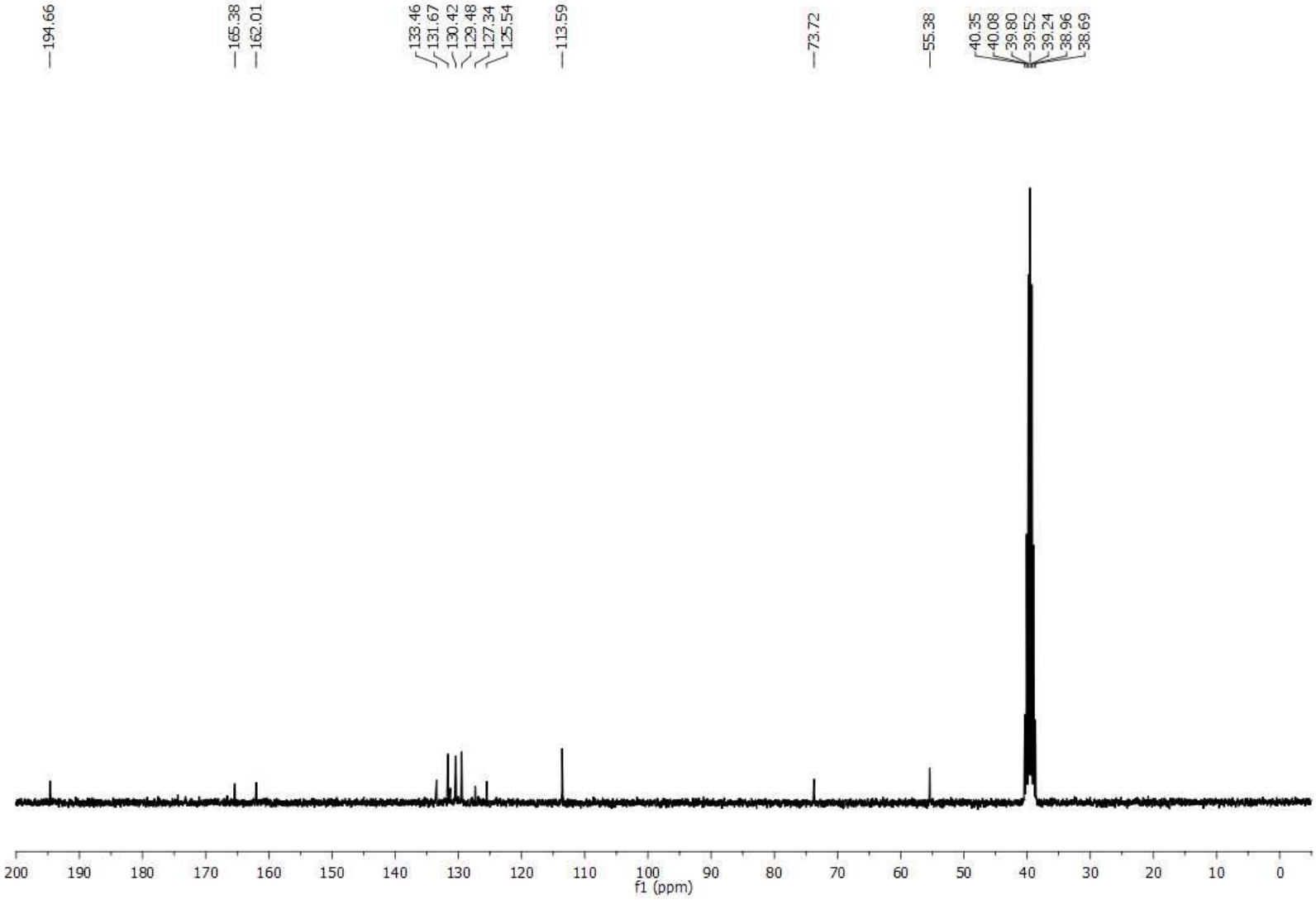
^{1}H NMR and ^{13}C NMR of Compound (3cf)



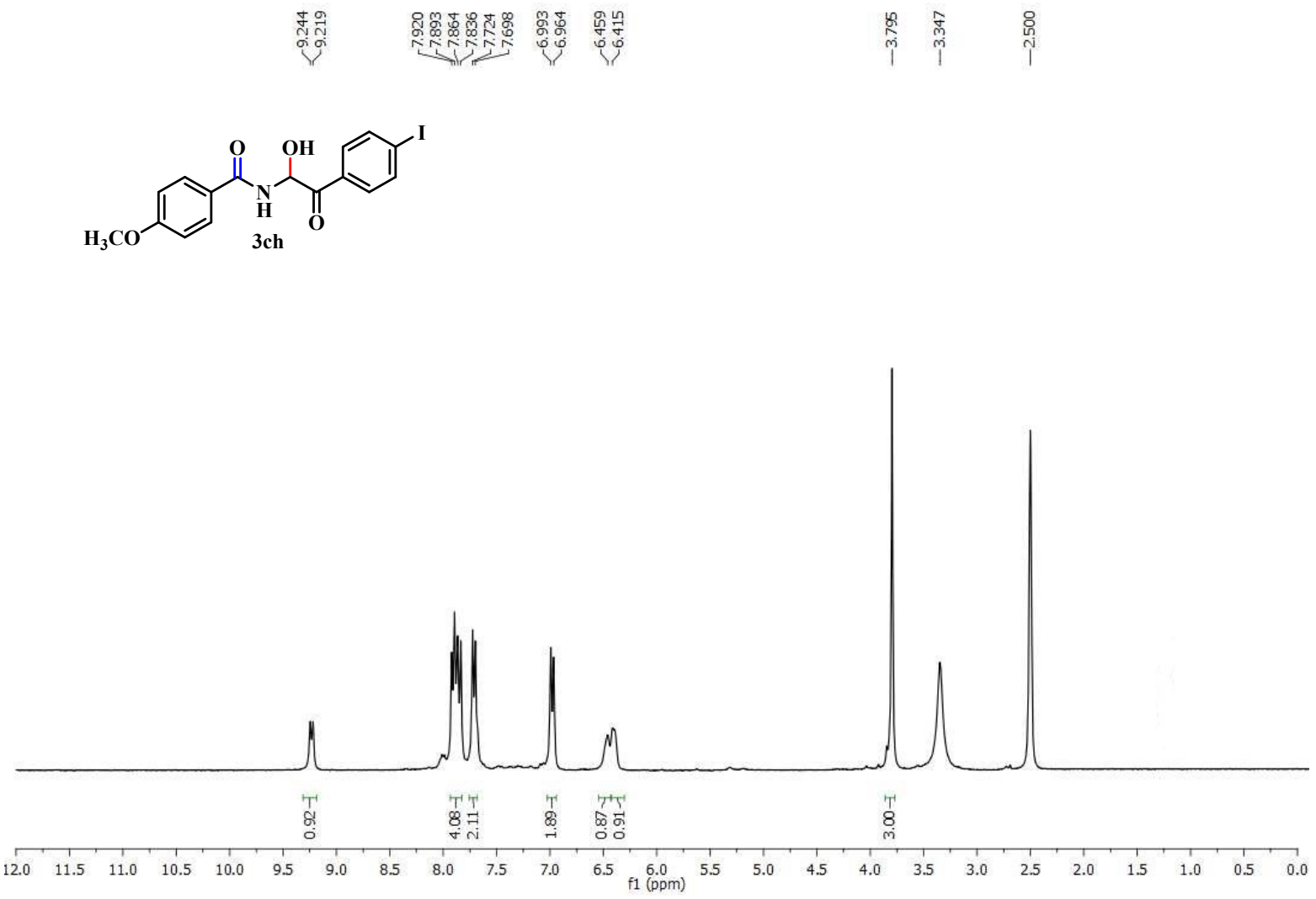

194.43
165.40
162.01
138.16
133.11
130.34
129.48
128.73
125.55
113.59
73.74
55.38
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

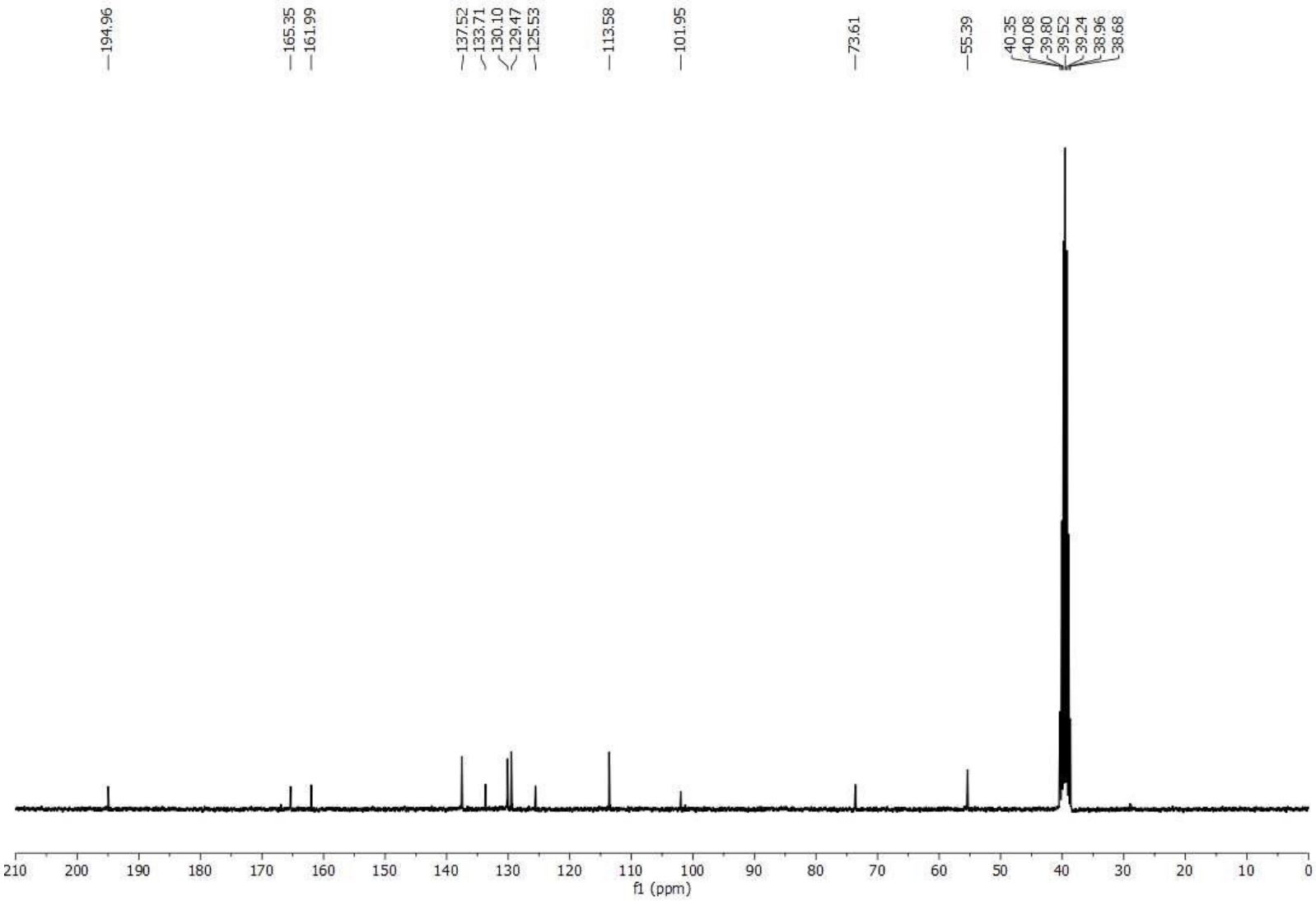
^{1}H NMR and ^{13}C NMR of Compound (3cg)



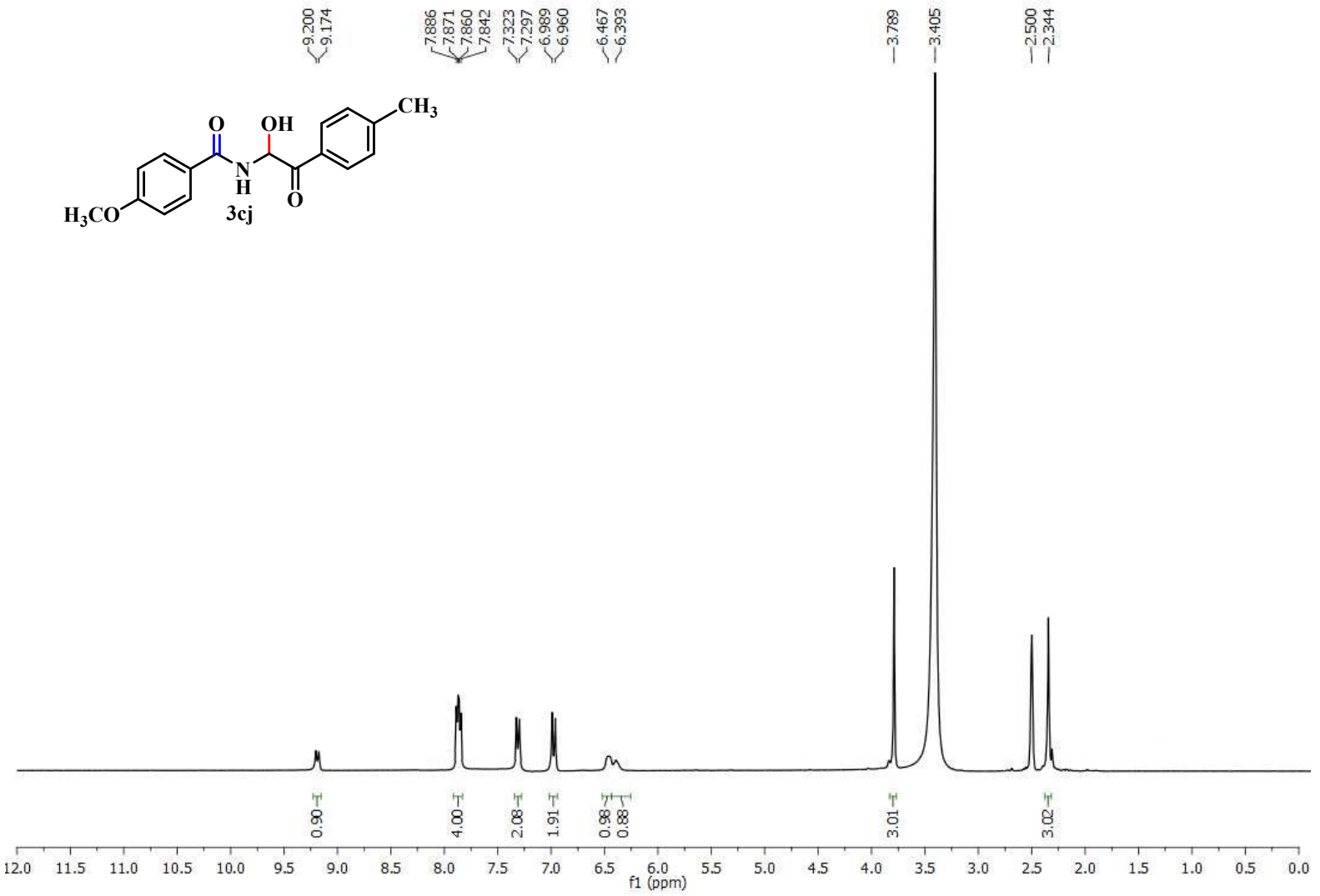

194.66
165.38
162.01
133.46
131.67
130.42
129.48
127.34
125.54
113.59
73.72
55.38
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

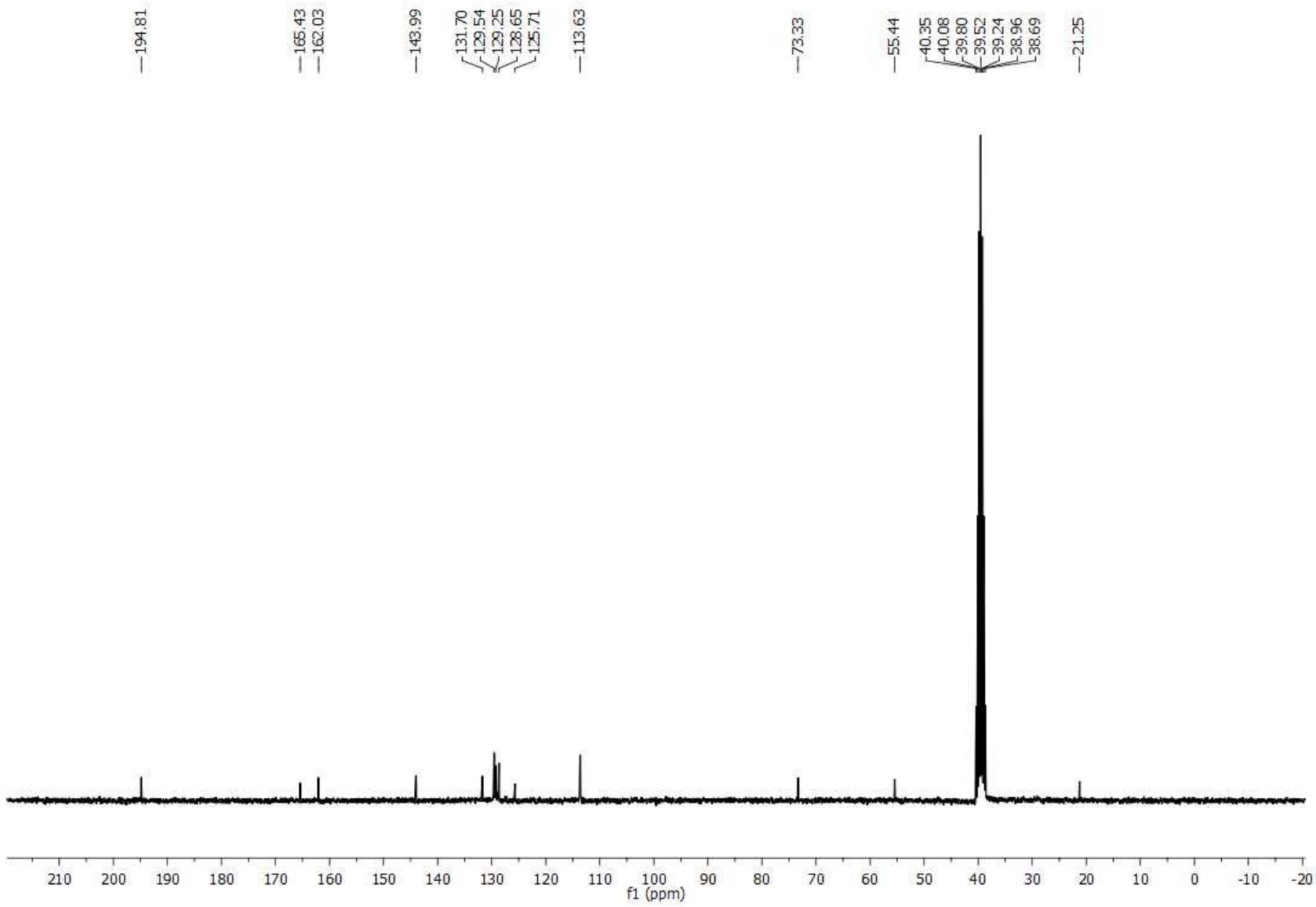
^{1}H NMR and ^{13}C NMR of Compound (3ch)



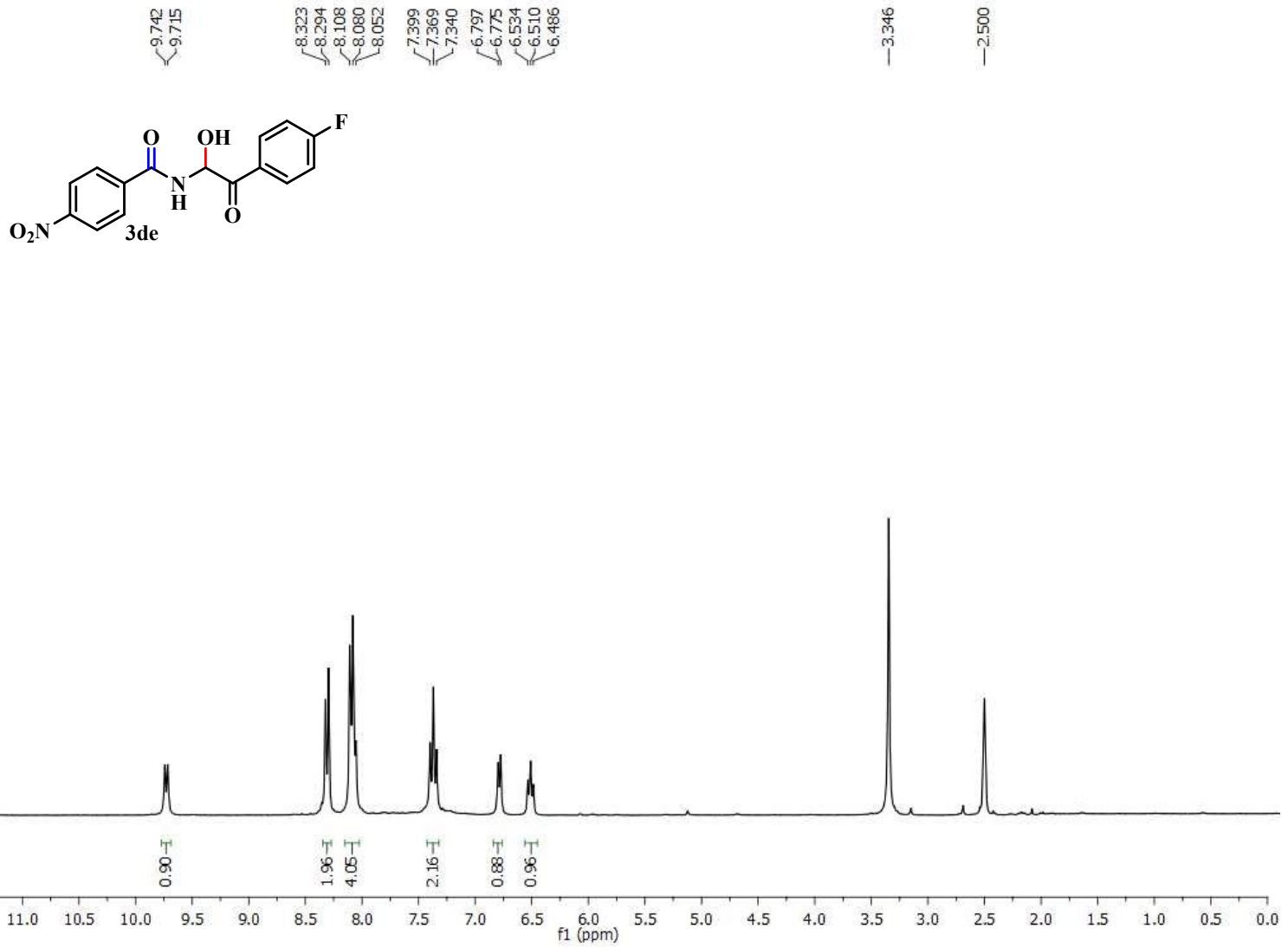

194.96
165.35
161.99
137.52
133.71
130.10
129.47
125.53
113.58
101.95
73.61
55.39
40.35
40.08
39.80
39.52
39.24
38.96
38.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

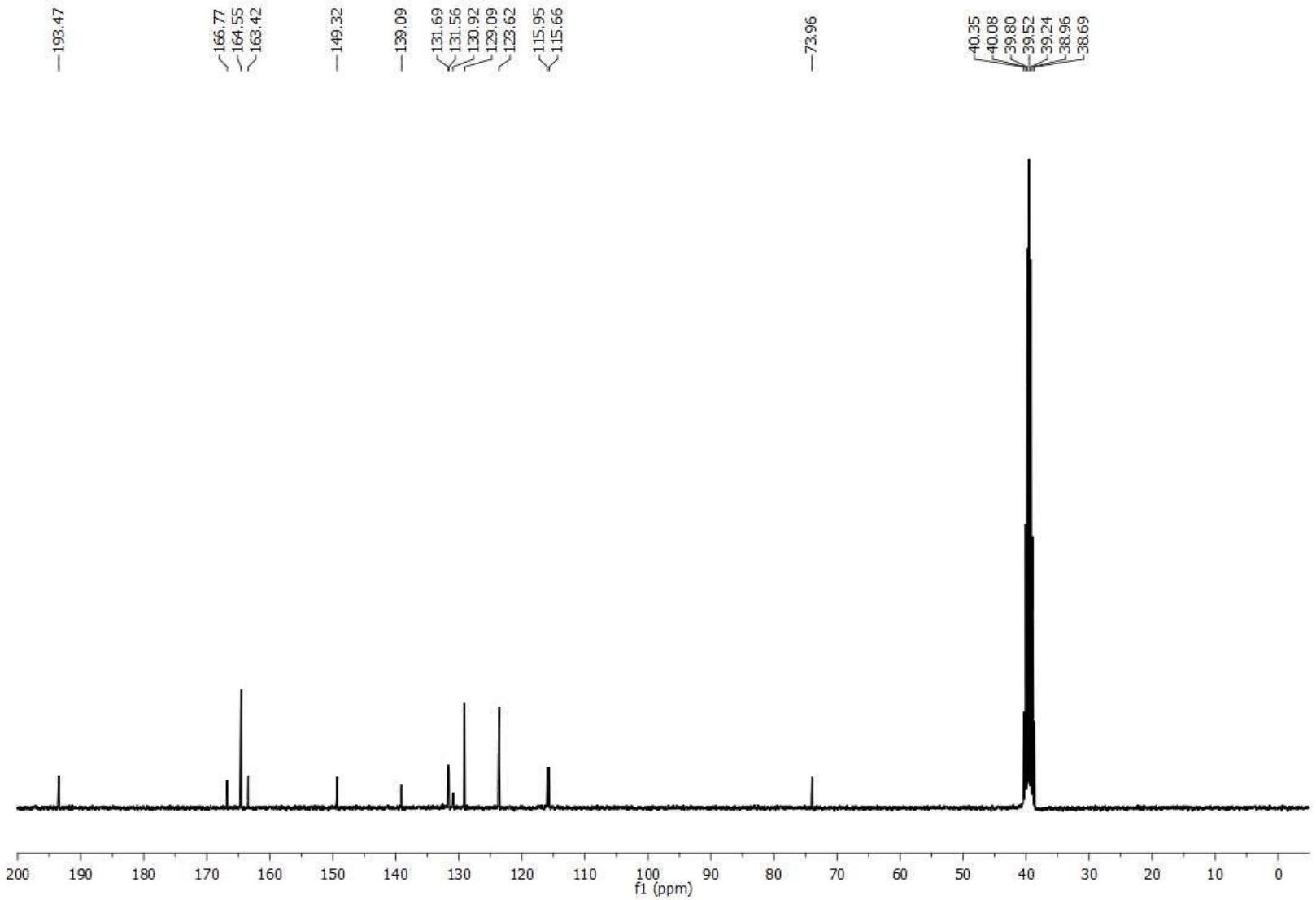
^{1}H NMR and ^{13}C NMR of Compound (3cj)


9.200
9.174
7.886
7.871
7.860
7.842
7.323
7.297
6.989
6.960
6.467
6.393
3.789
3.405
2.500
2.344
O
OH
CH3
N
H
O
H3CO
3cj
0.90
4.00
2.08
1.91
0.98
0.88
3.01
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

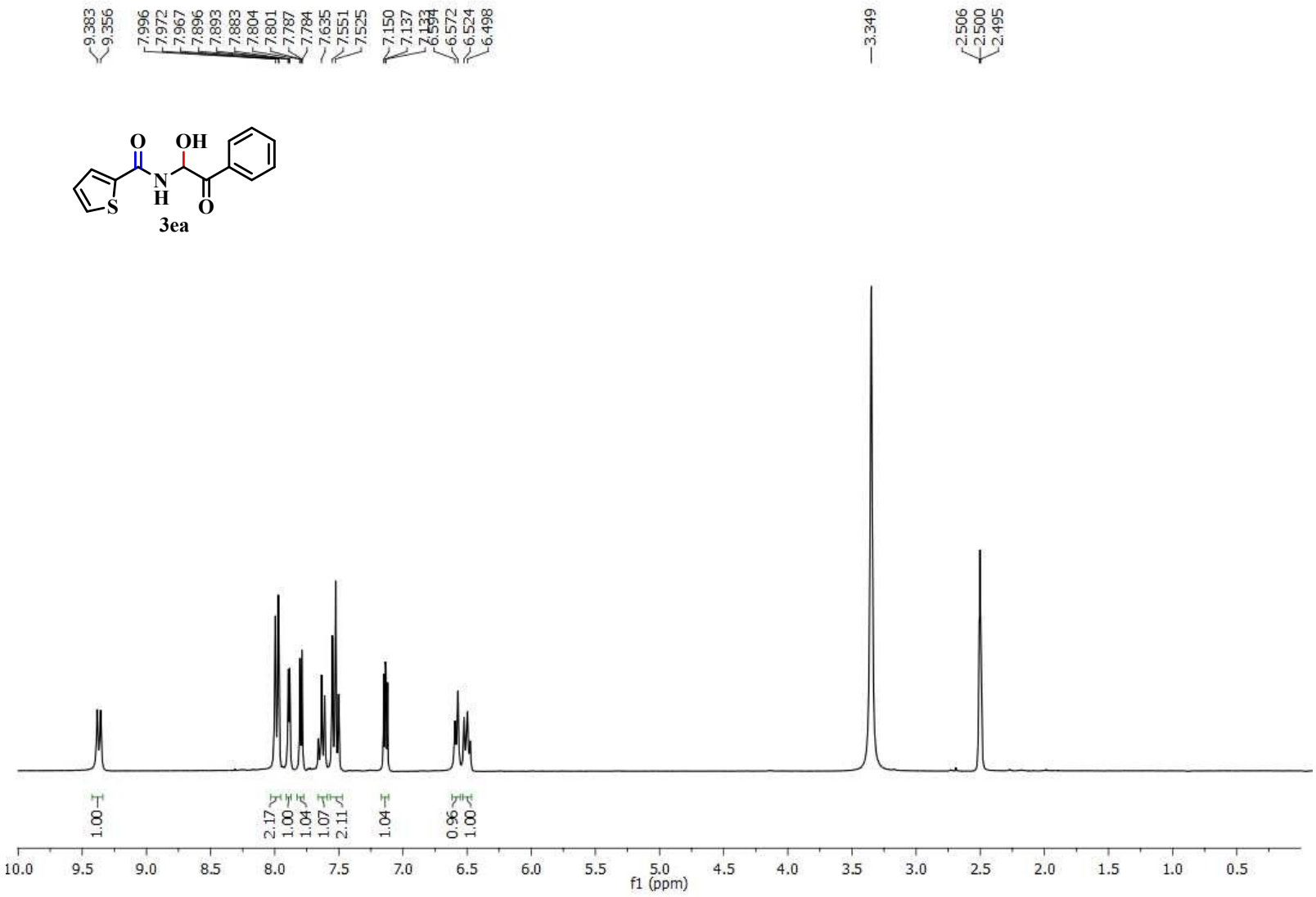

194.81
165.43
162.03
143.99
131.70
129.54
129.25
128.65
125.71
113.63
73.33
55.44
40.35
40.08
39.80
39.52
39.24
38.96
38.69
21.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

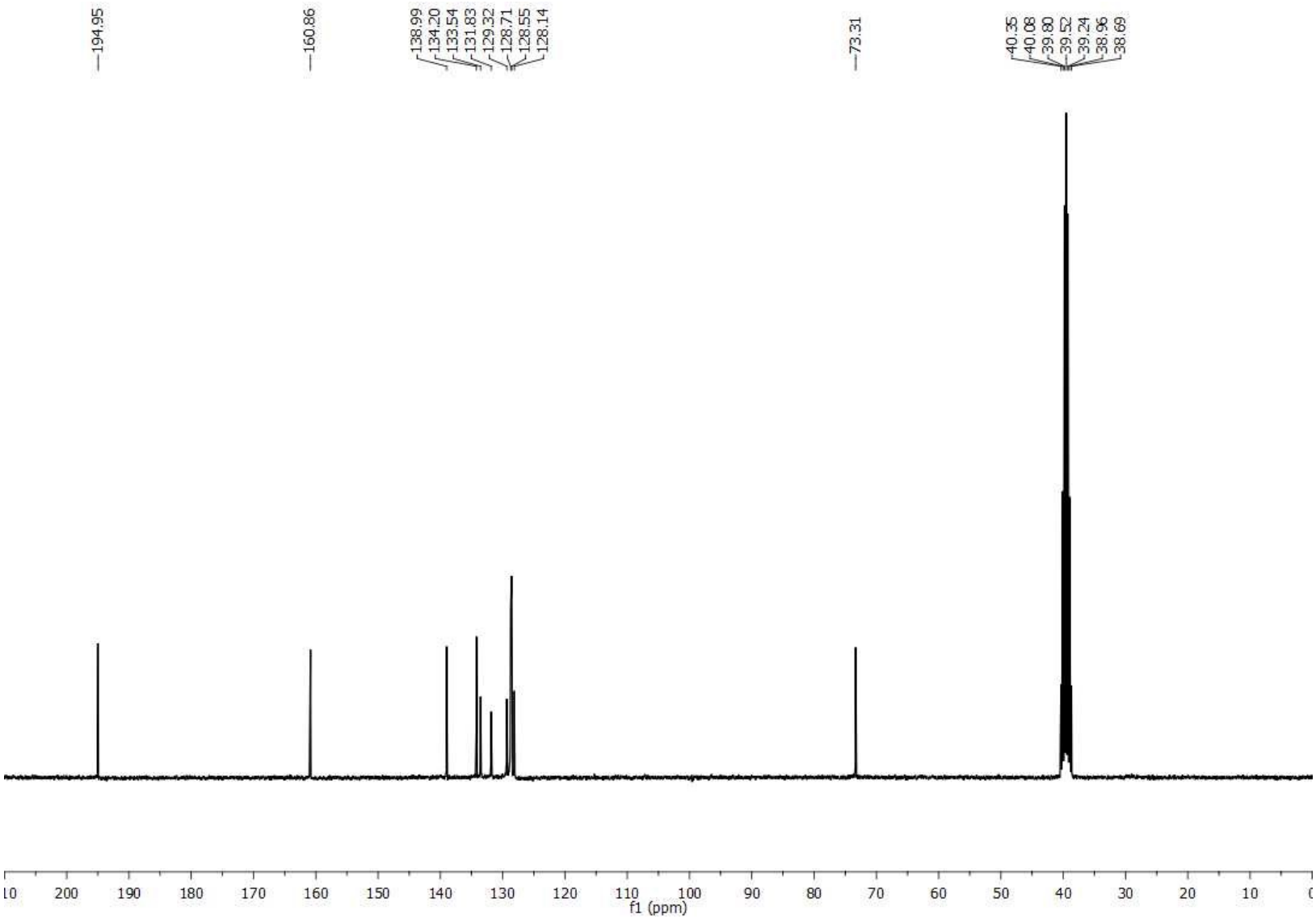
^{1}H NMR and ^{13}C NMR of Compound (3de)



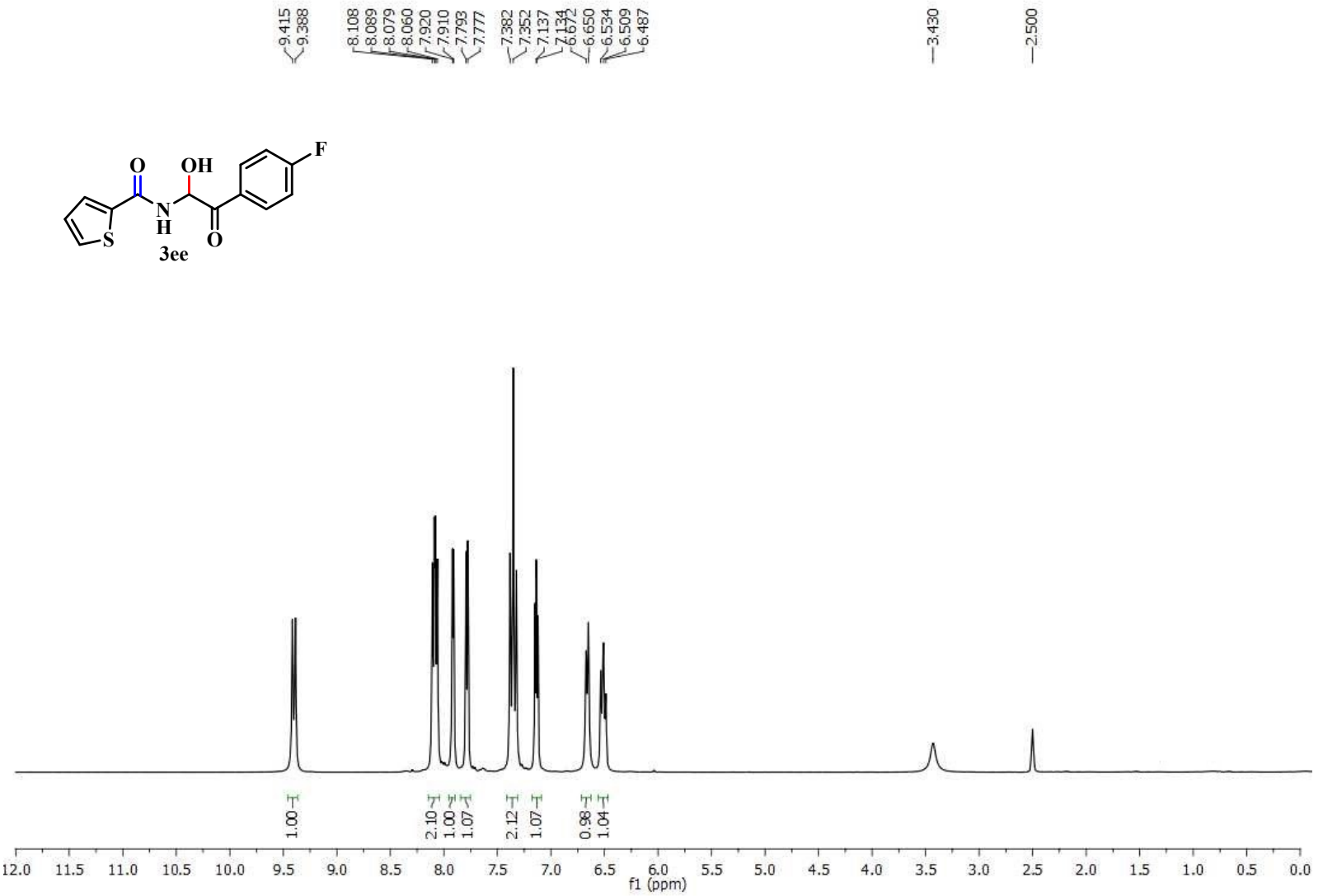

193.47
166.77
164.55
163.42
149.32
139.09
131.69
131.56
130.92
129.09
123.62
115.95
115.66
73.96
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

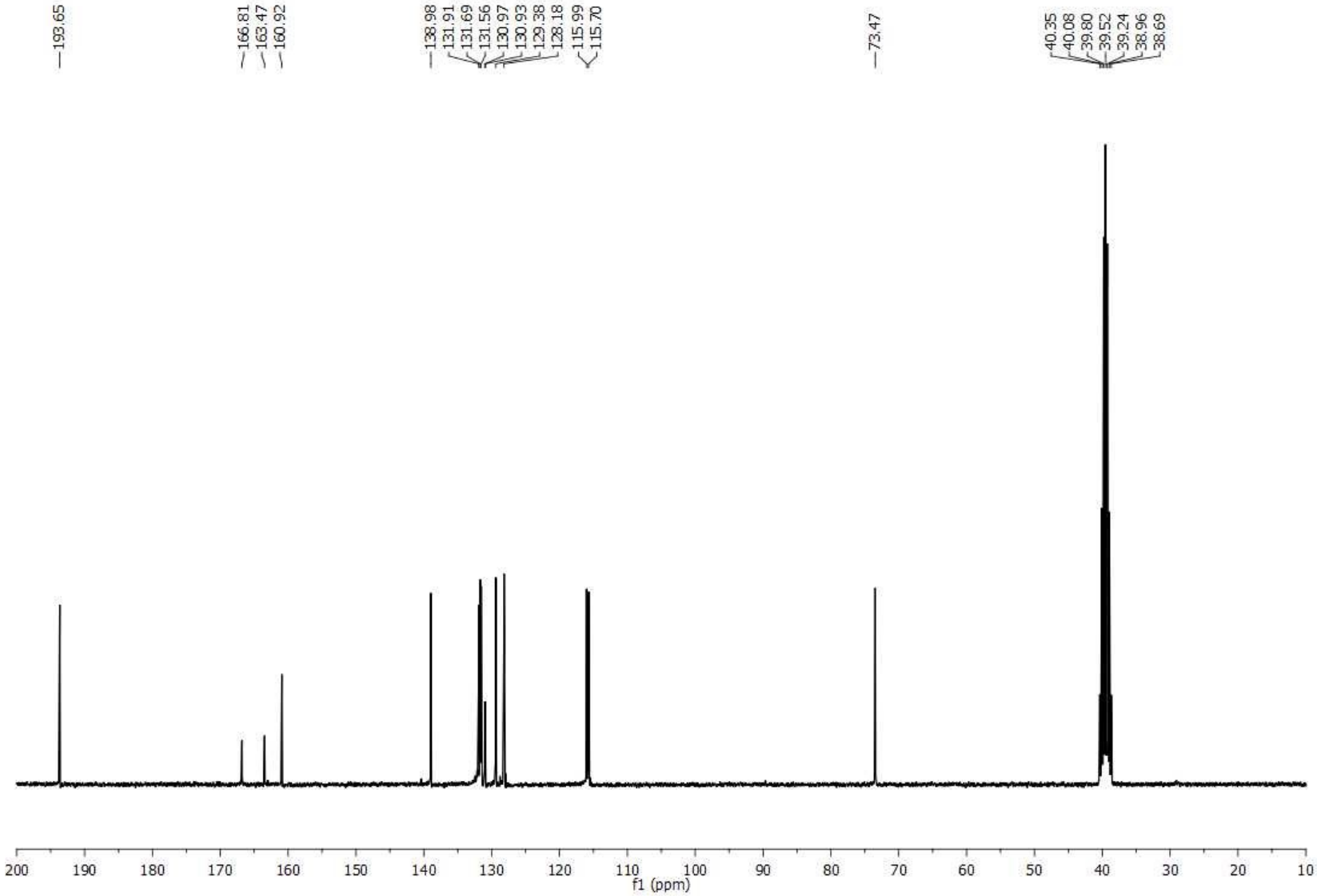
^{1}H NMR and ^{13}C NMR of Compound (3ea)



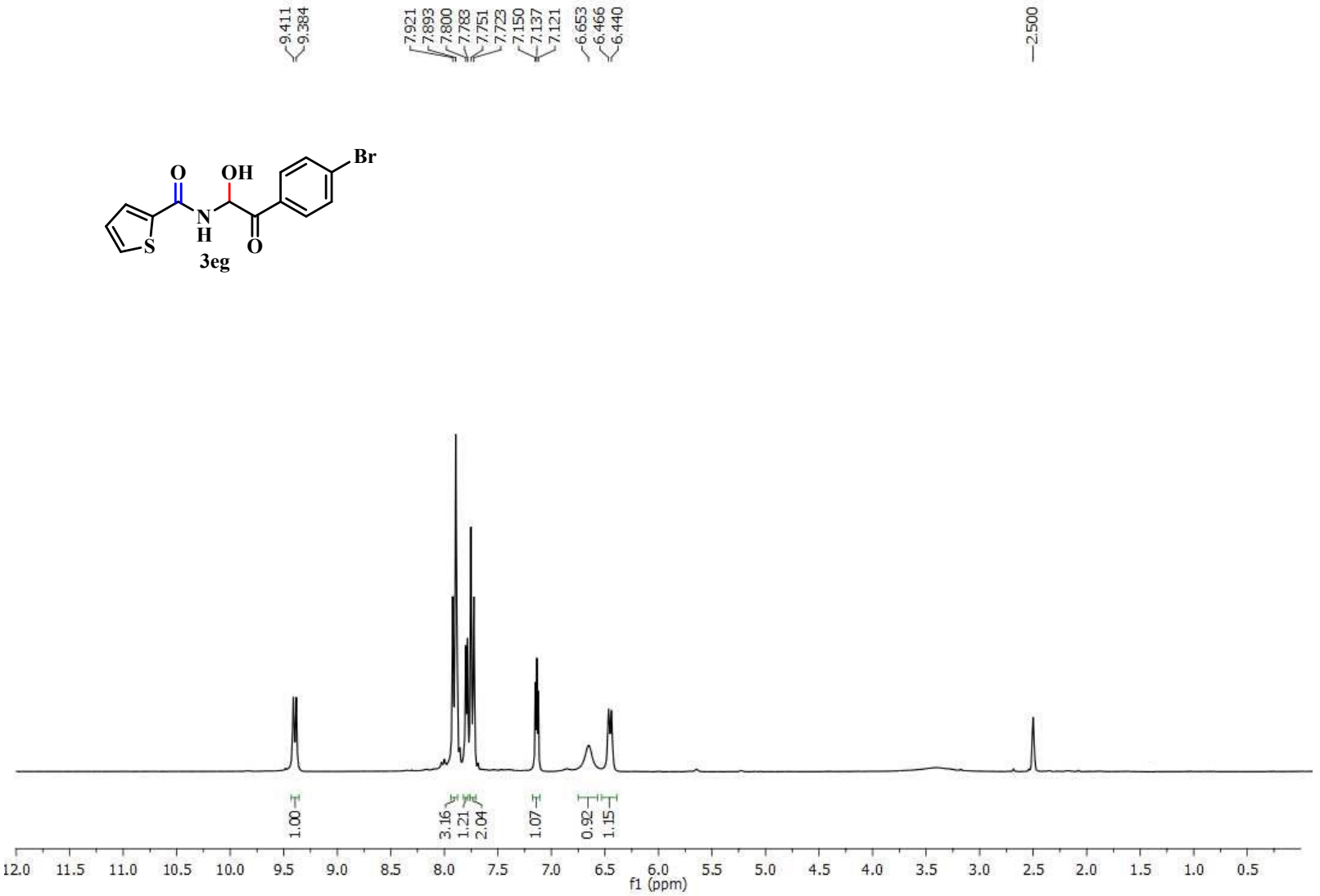

194.95
160.86
138.99
134.20
133.54
131.83
129.32
128.71
128.55
128.14
73.31
40.35
40.08
39.80
39.52
39.24
38.96
38.69
f1 (ppm)

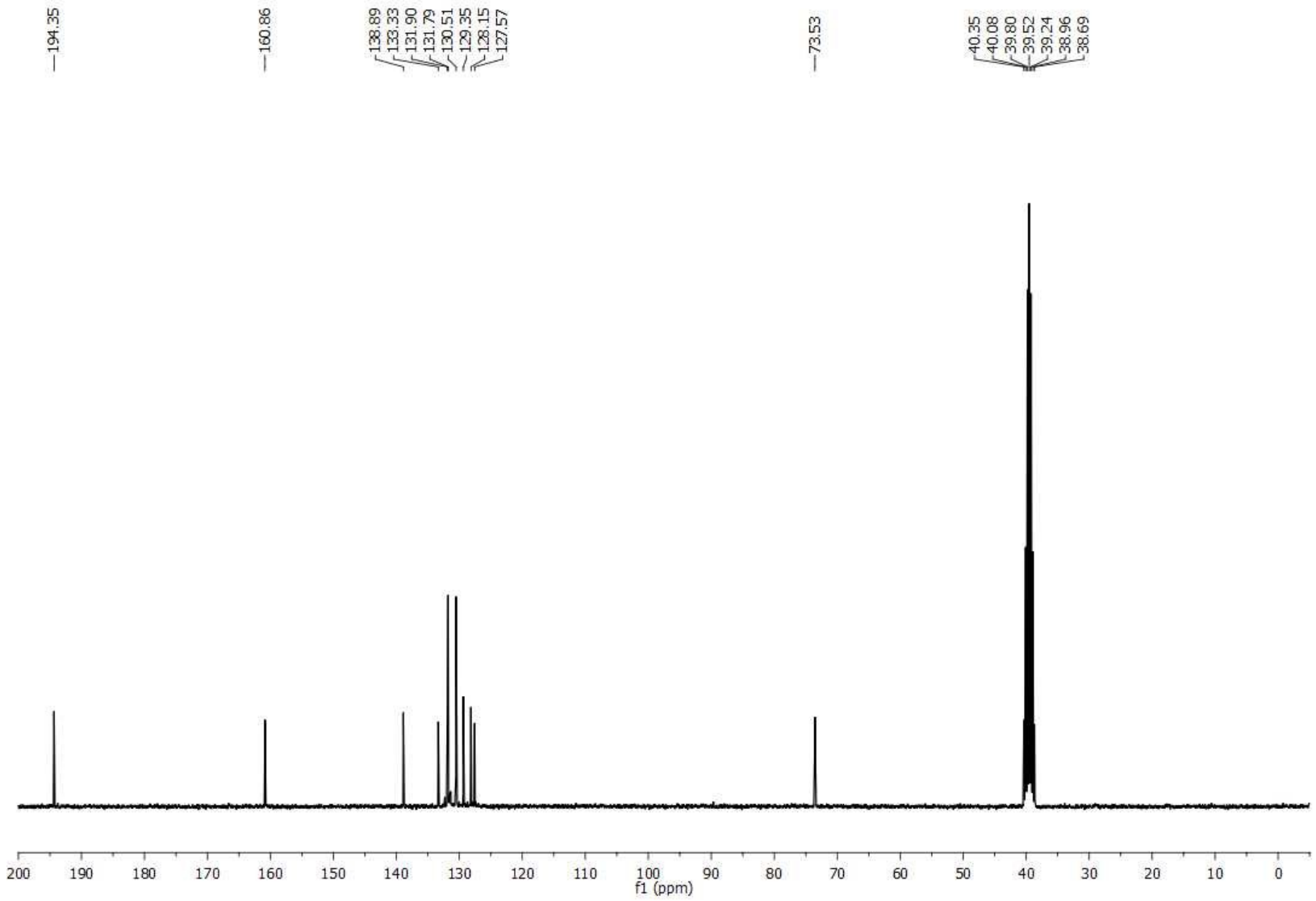
^{1}H NMR and ^{13}C NMR of Compound (3ee)



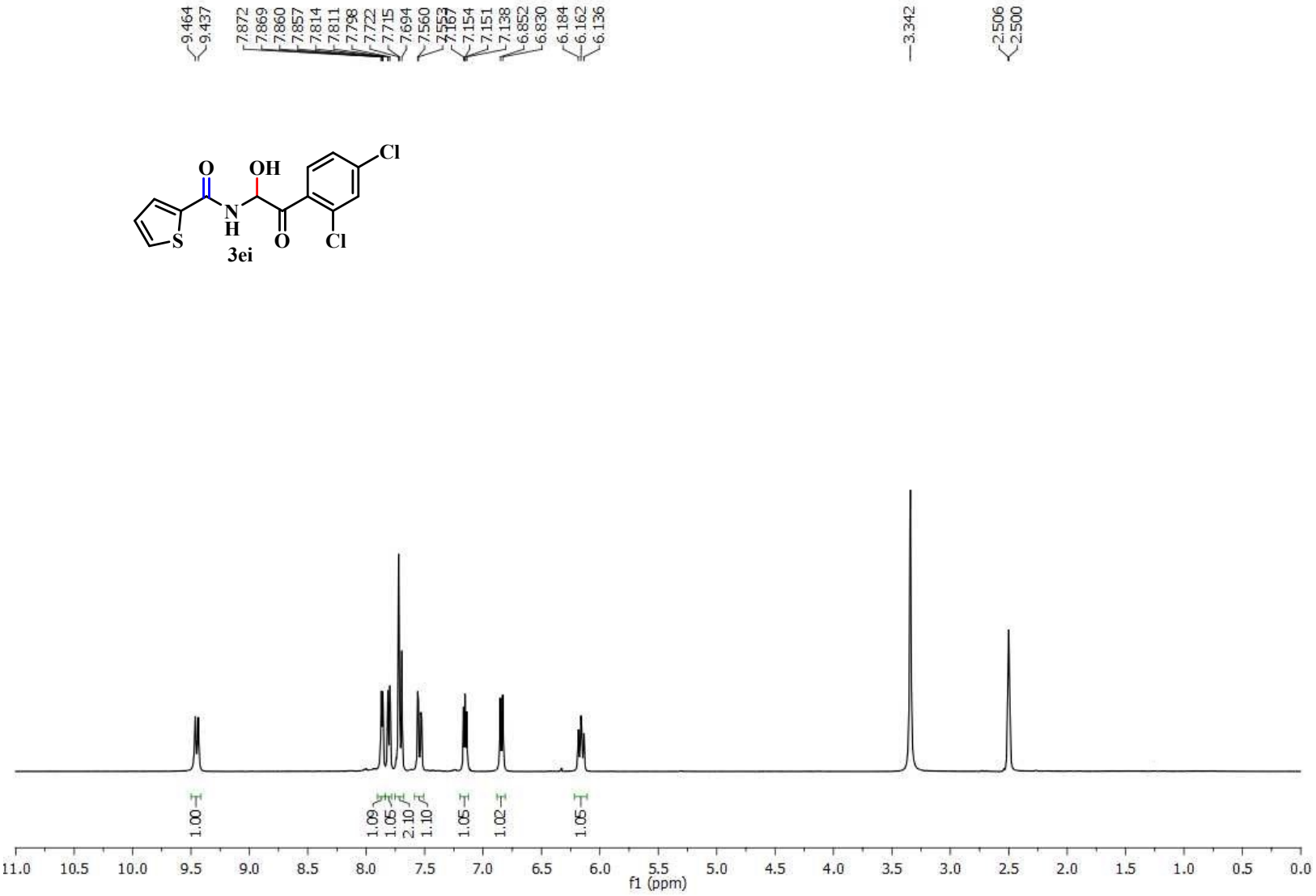

193.65
166.81
163.47
160.92
138.98
131.91
131.69
131.56
130.97
130.93
129.38
128.18
115.99
115.70
73.47
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

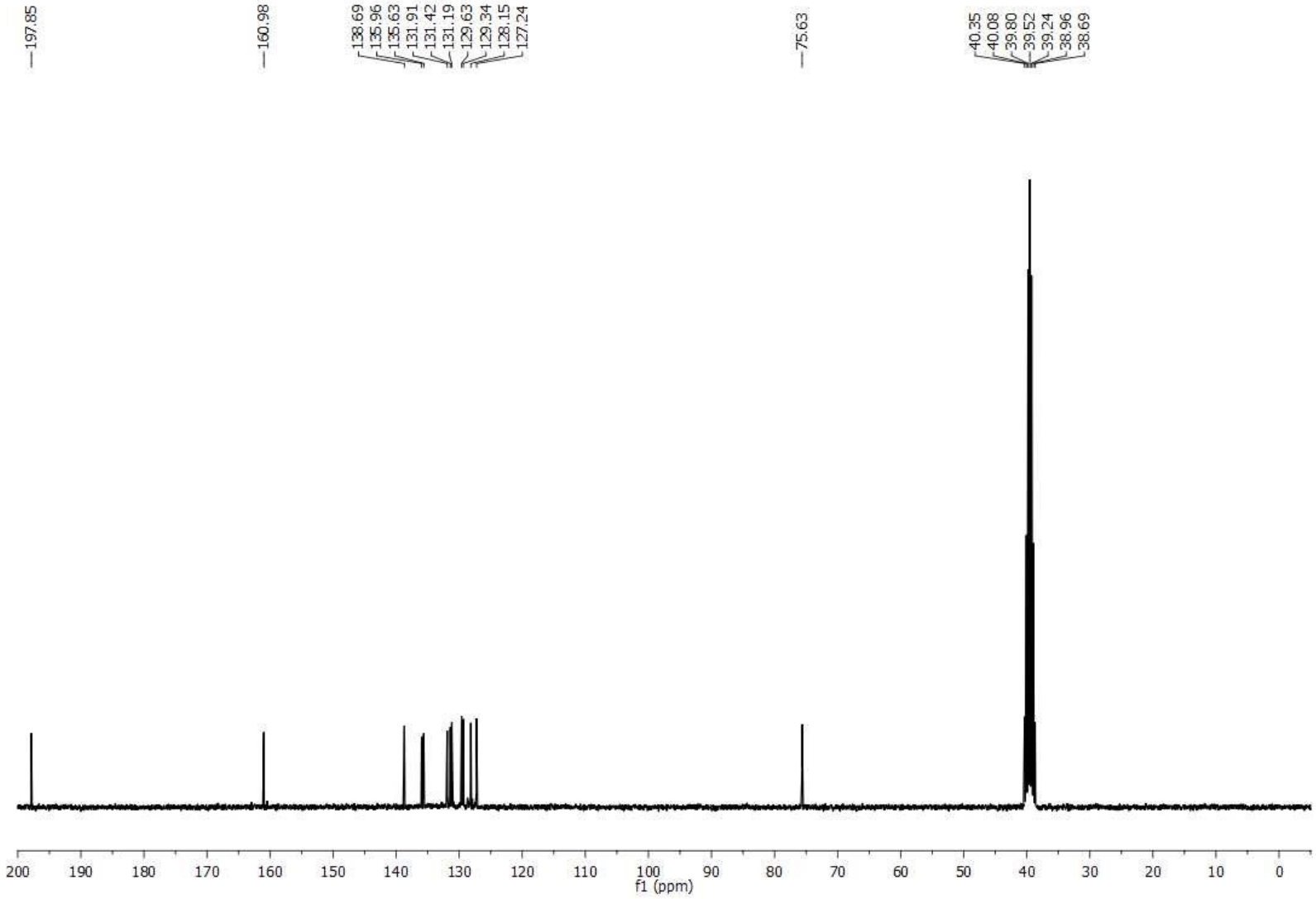
^{1}H NMR and ^{13}C NMR of Compound (3eg)



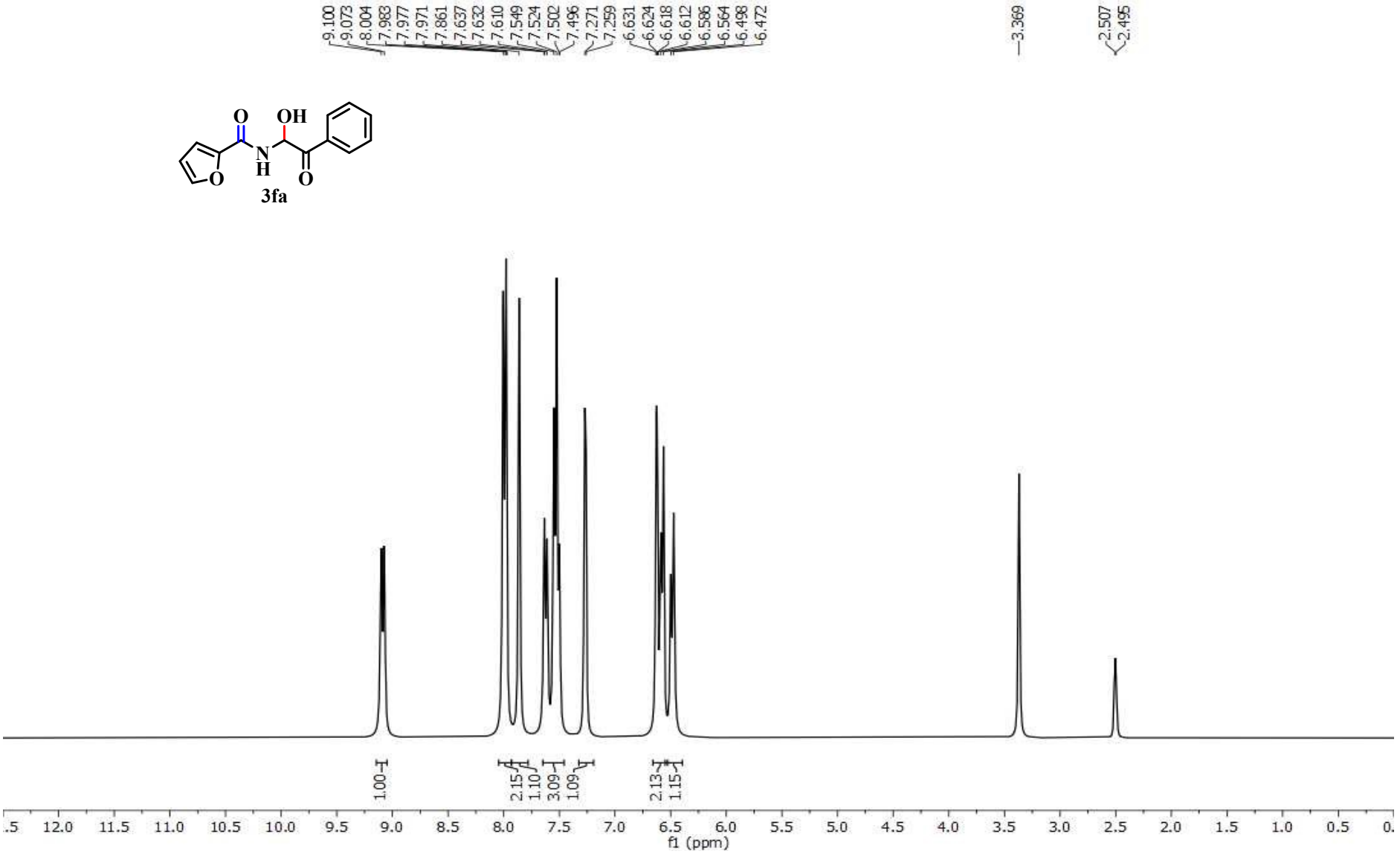

194.35
160.86
138.89
133.33
131.90
131.79
130.51
129.35
128.15
127.57
73.53
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

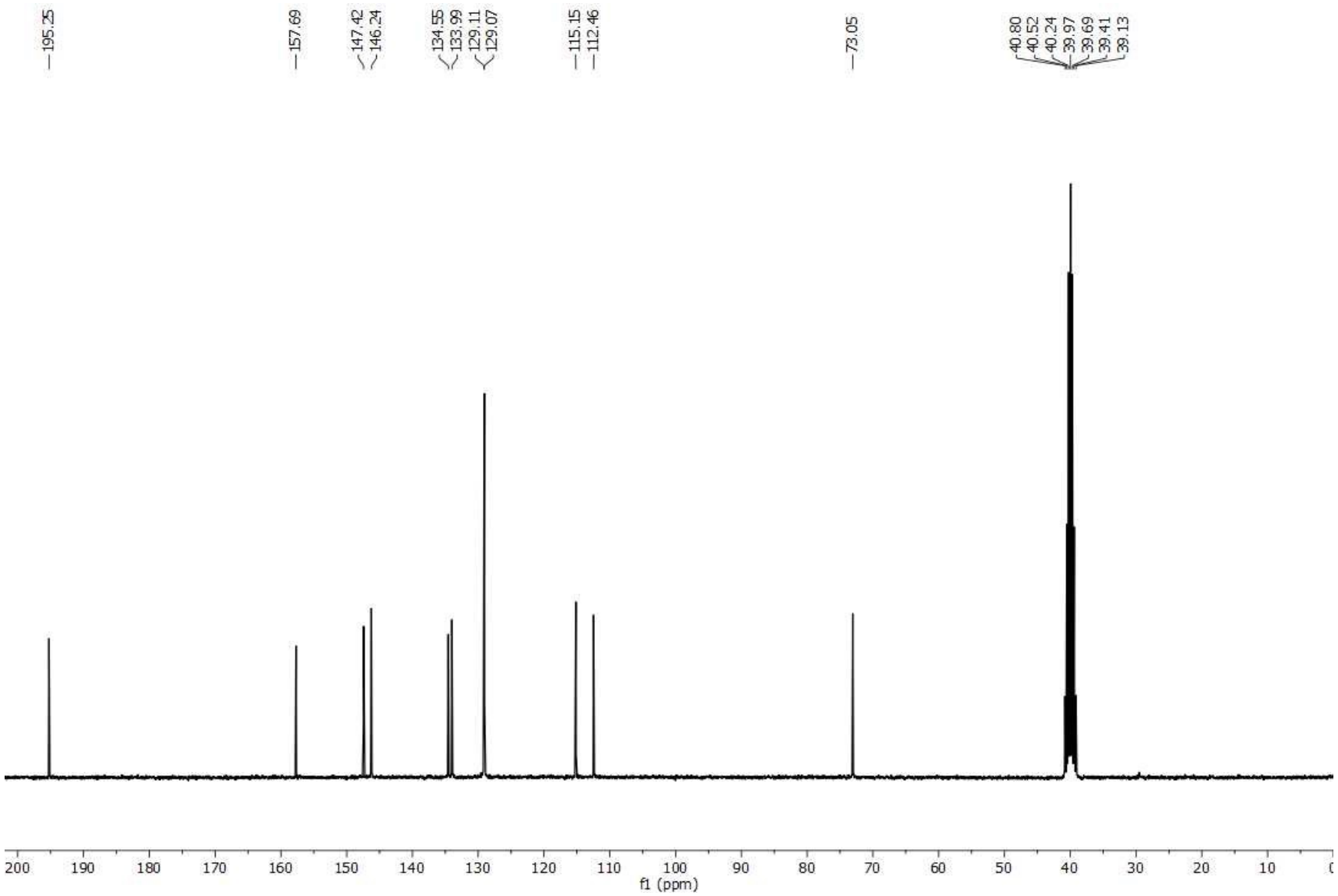
^{1}H NMR and ^{13}C NMR of Compound (3ei)



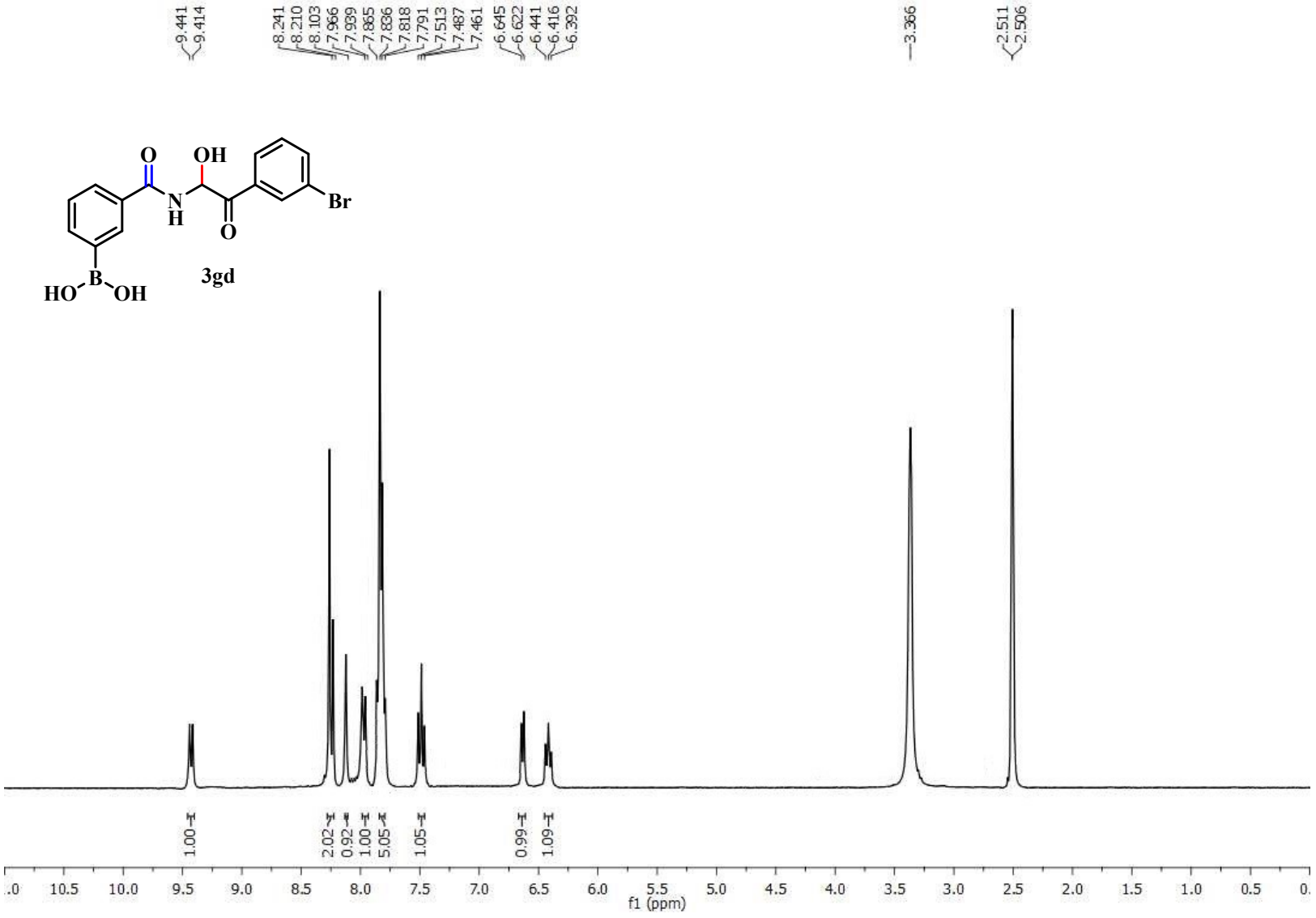

197.85
160.98
138.69
136.96
135.63
131.91
131.42
131.19
129.63
129.34
128.15
127.24
75.63
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

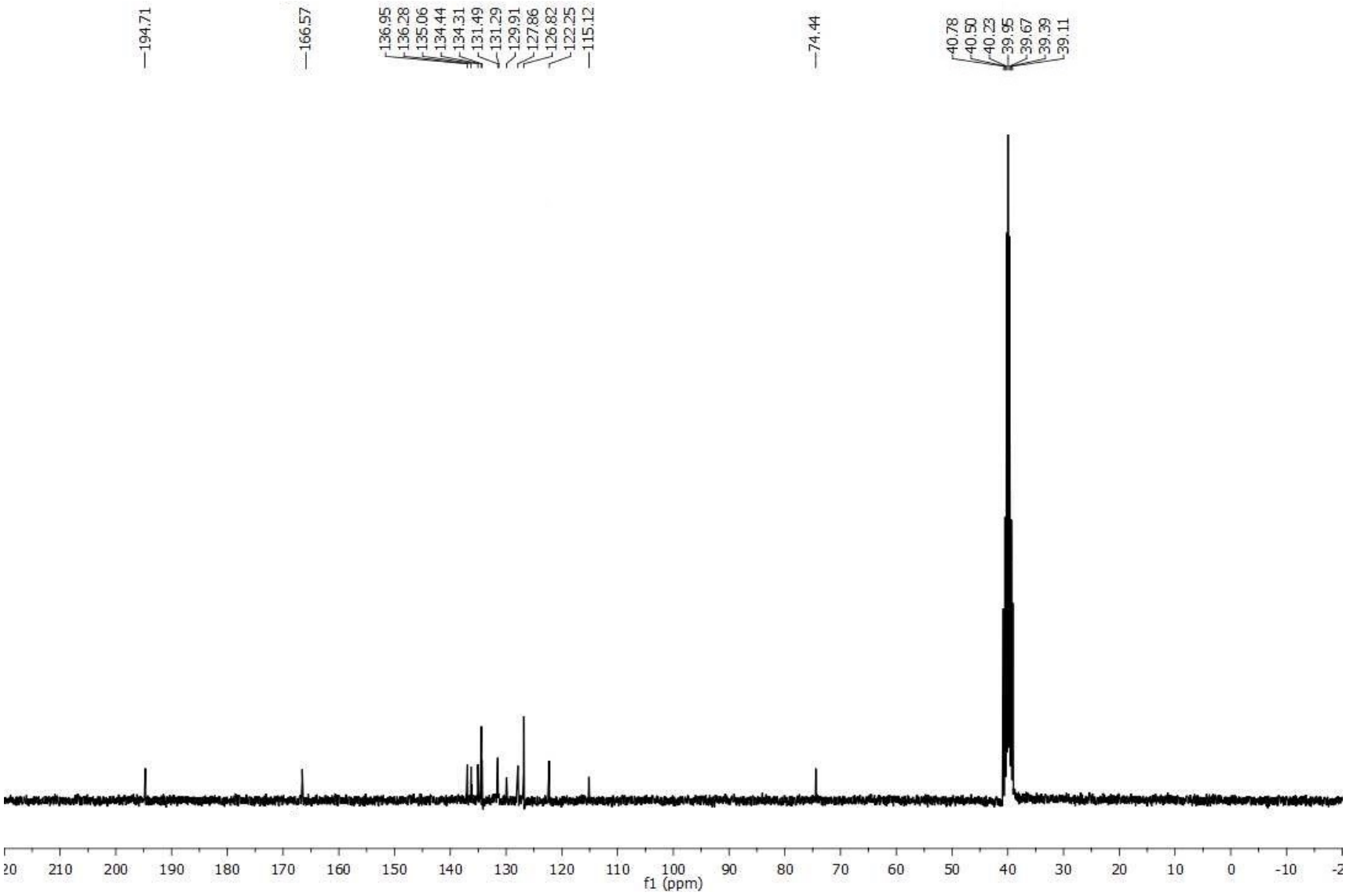
^{1}H NMR and ^{13}C NMR of Compound (3fa)



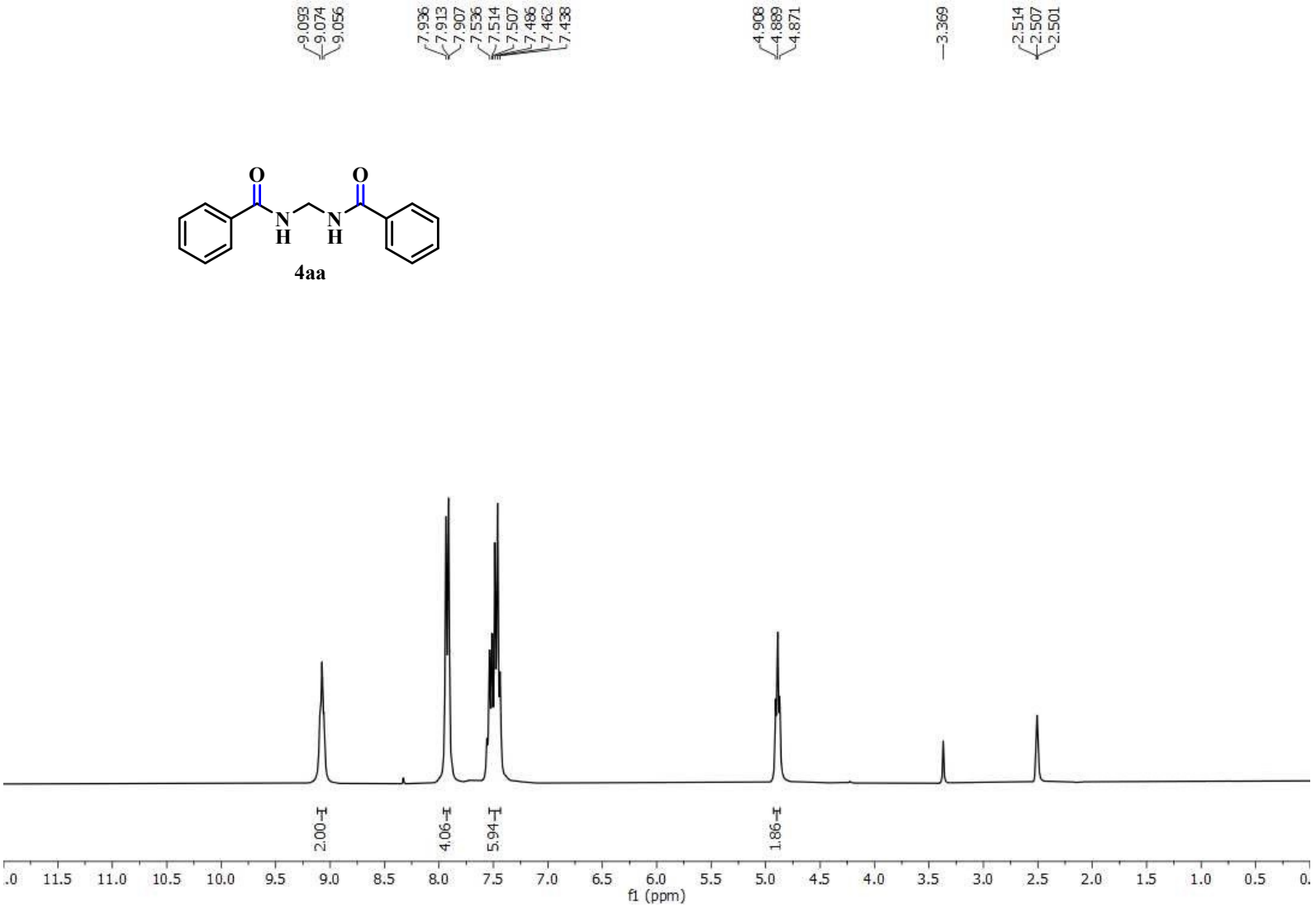

195.25
157.69
147.42
146.24
134.55
133.99
129.11
129.07
115.15
112.46
73.05
40.80
40.52
40.24
39.97
39.69
39.41
39.13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

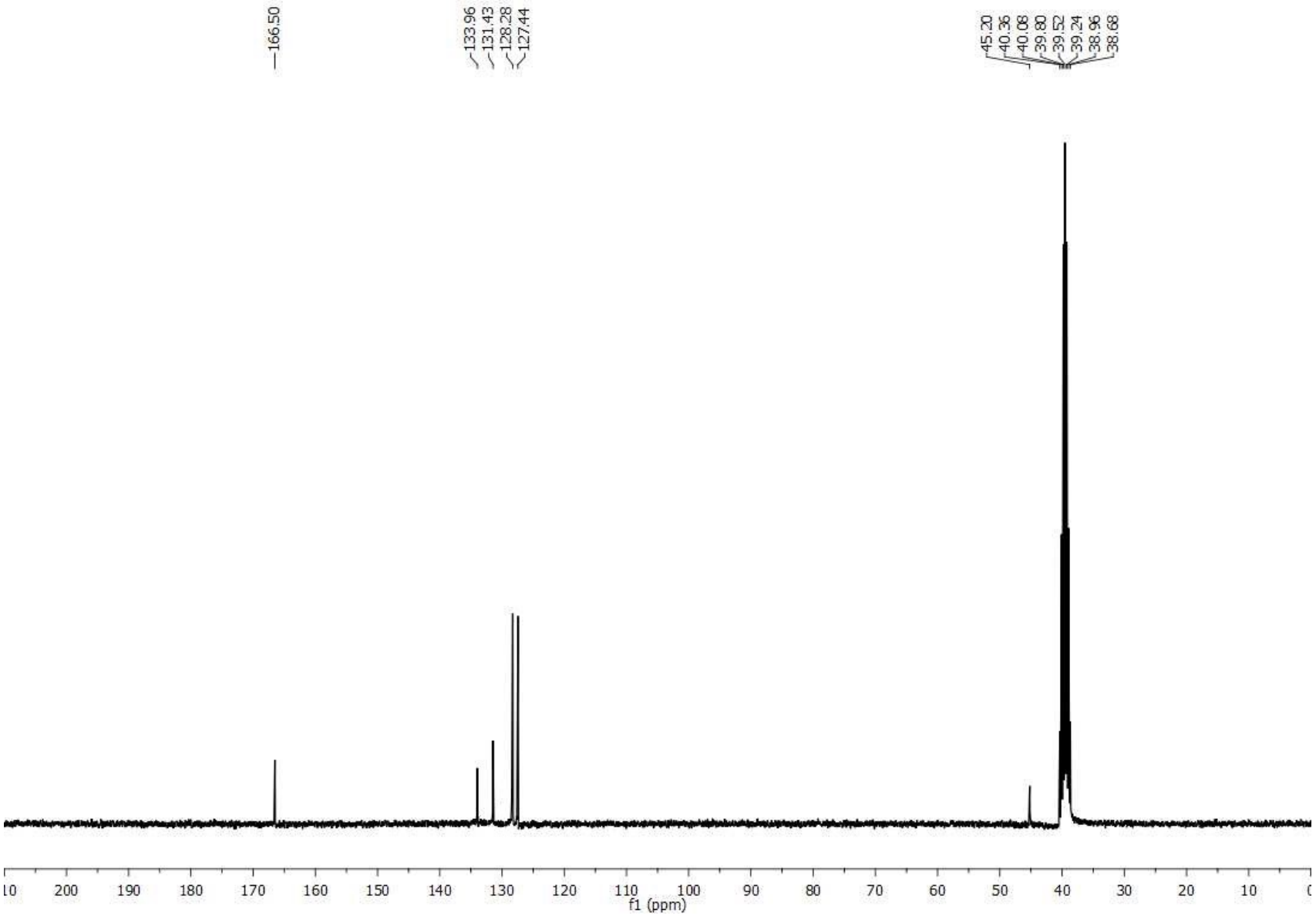
^{1}H NMR and ^{13}C NMR of Compound (3gd)



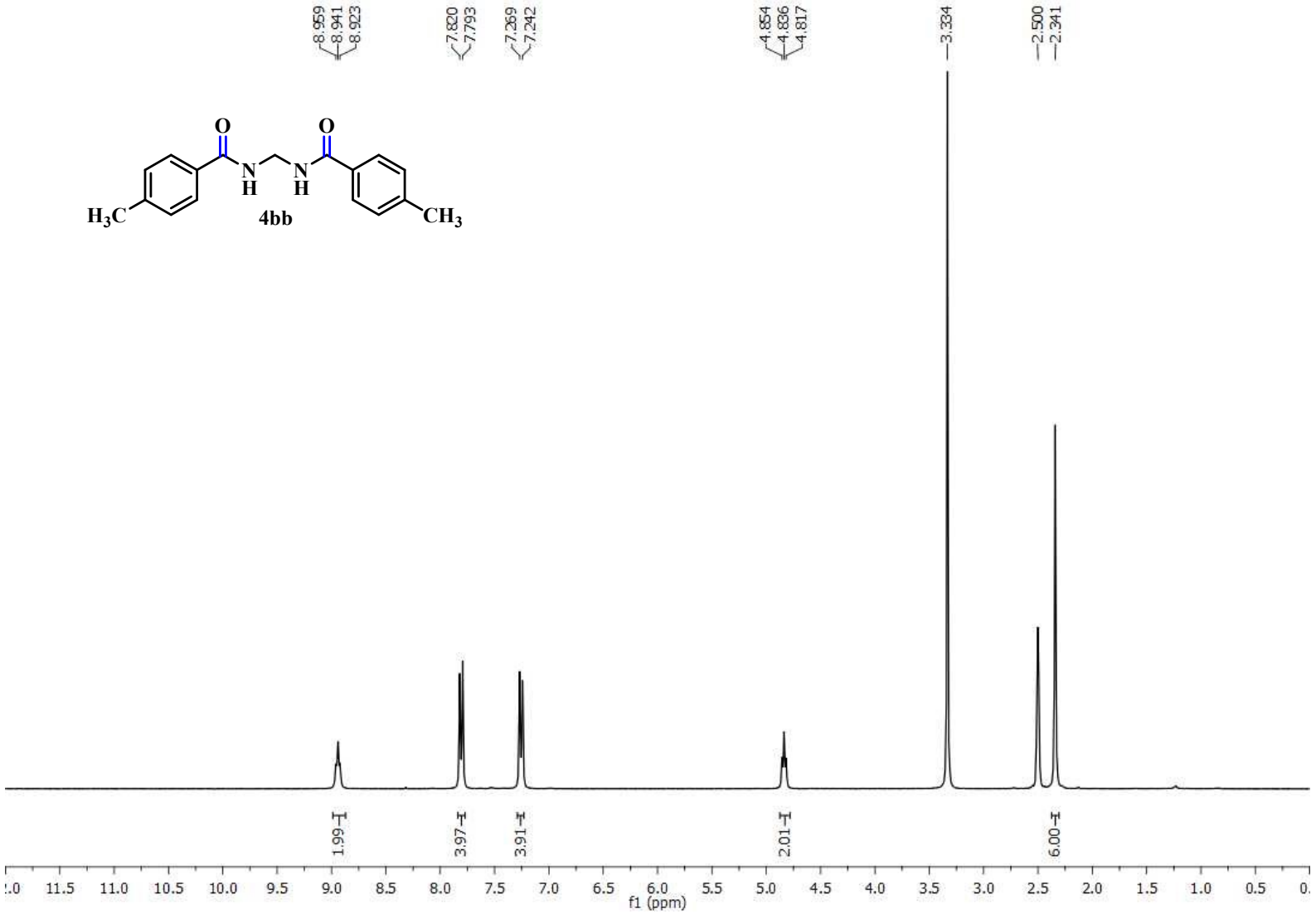

194.71
166.57
136.95
136.28
135.06
134.44
134.31
131.49
131.29
129.91
127.86
126.82
122.25
115.12
74.44
40.78
40.50
40.23
39.95
39.67
39.39
39.11
f1 (ppm)

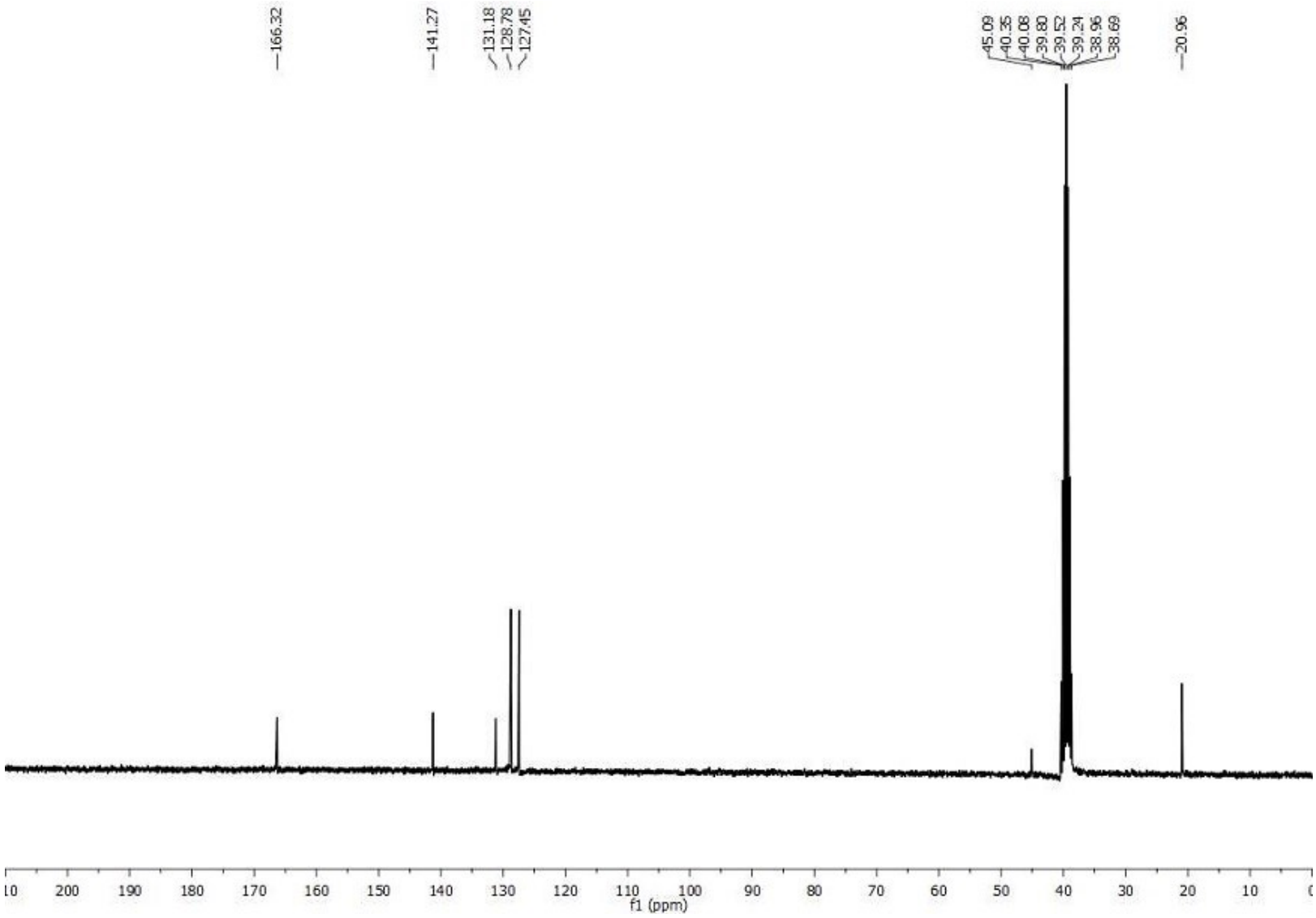
^{1}H NMR and ^{13}C NMR of Compound (4aa)



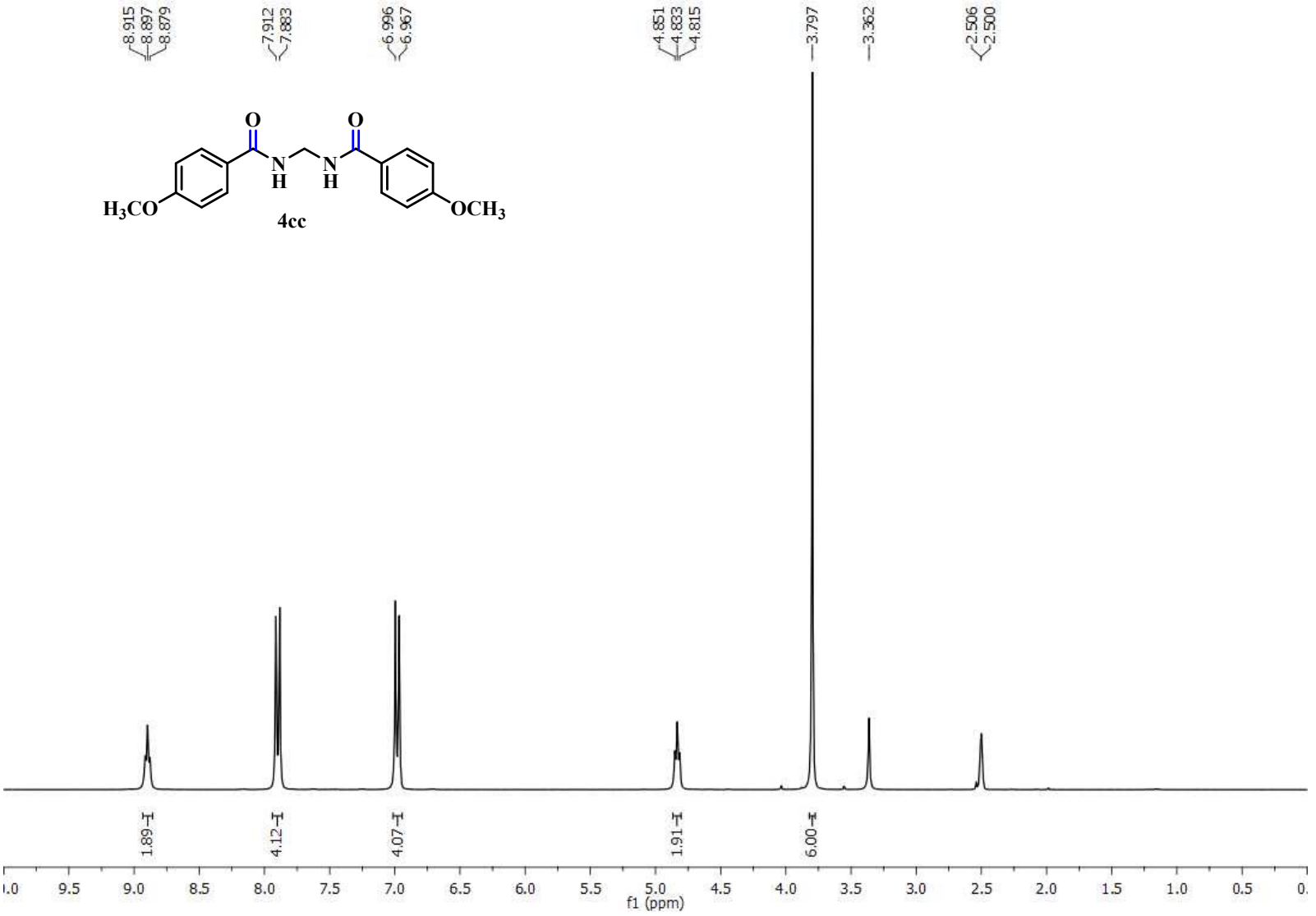

166.50
133.96
131.43
128.28
127.44
45.20
40.36
40.08
39.80
39.52
39.24
38.96
38.68
f1 (ppm)

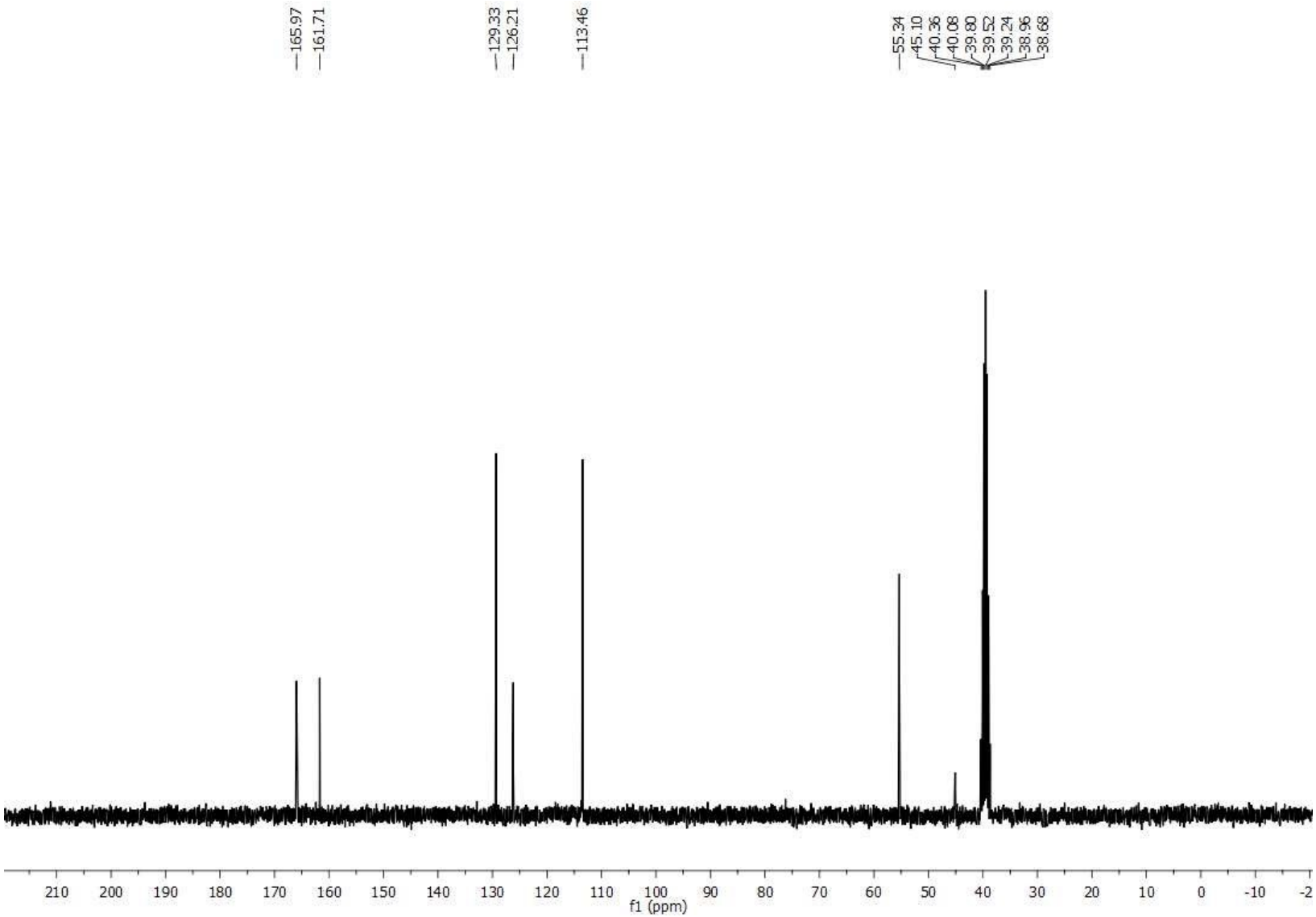
^{1}H NMR and ^{13}C NMR of Compound (4bb)



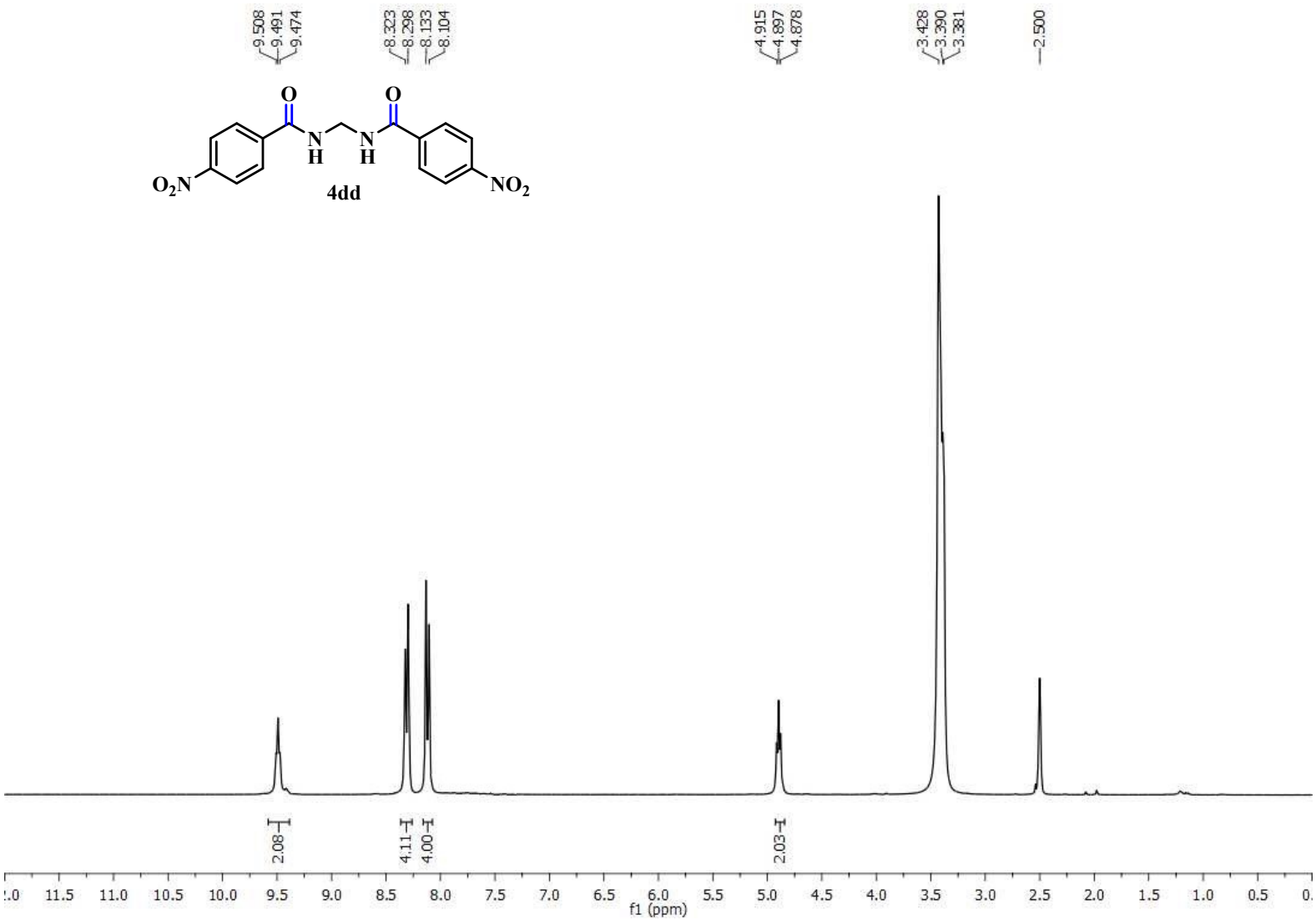

166.32
141.27
131.18
128.78
127.45
45.09
40.35
40.08
39.80
39.52
39.24
38.96
38.69
20.96
f1 (ppm)

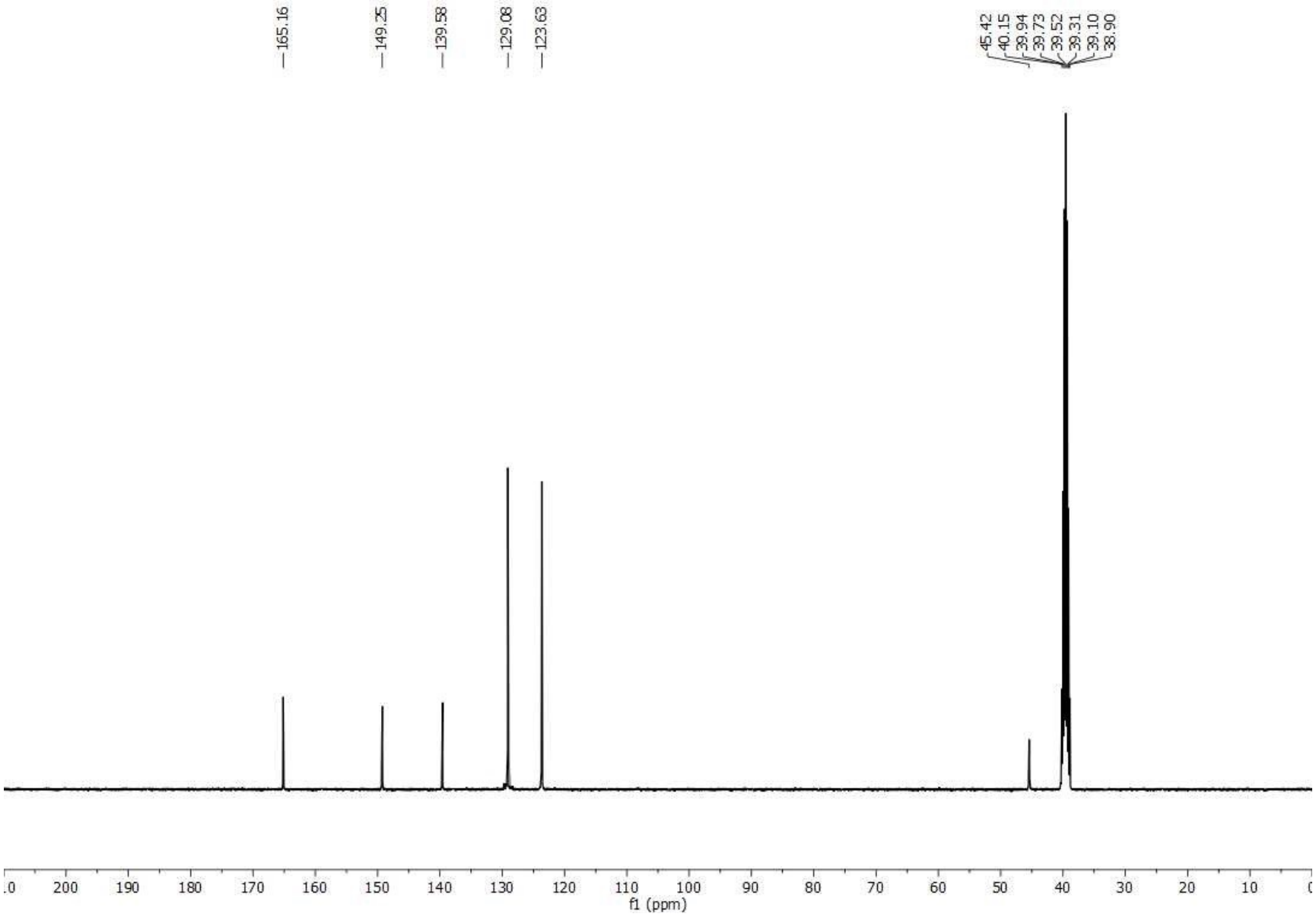
^{1}H NMR and ^{13}C NMR of Compound (4cc)



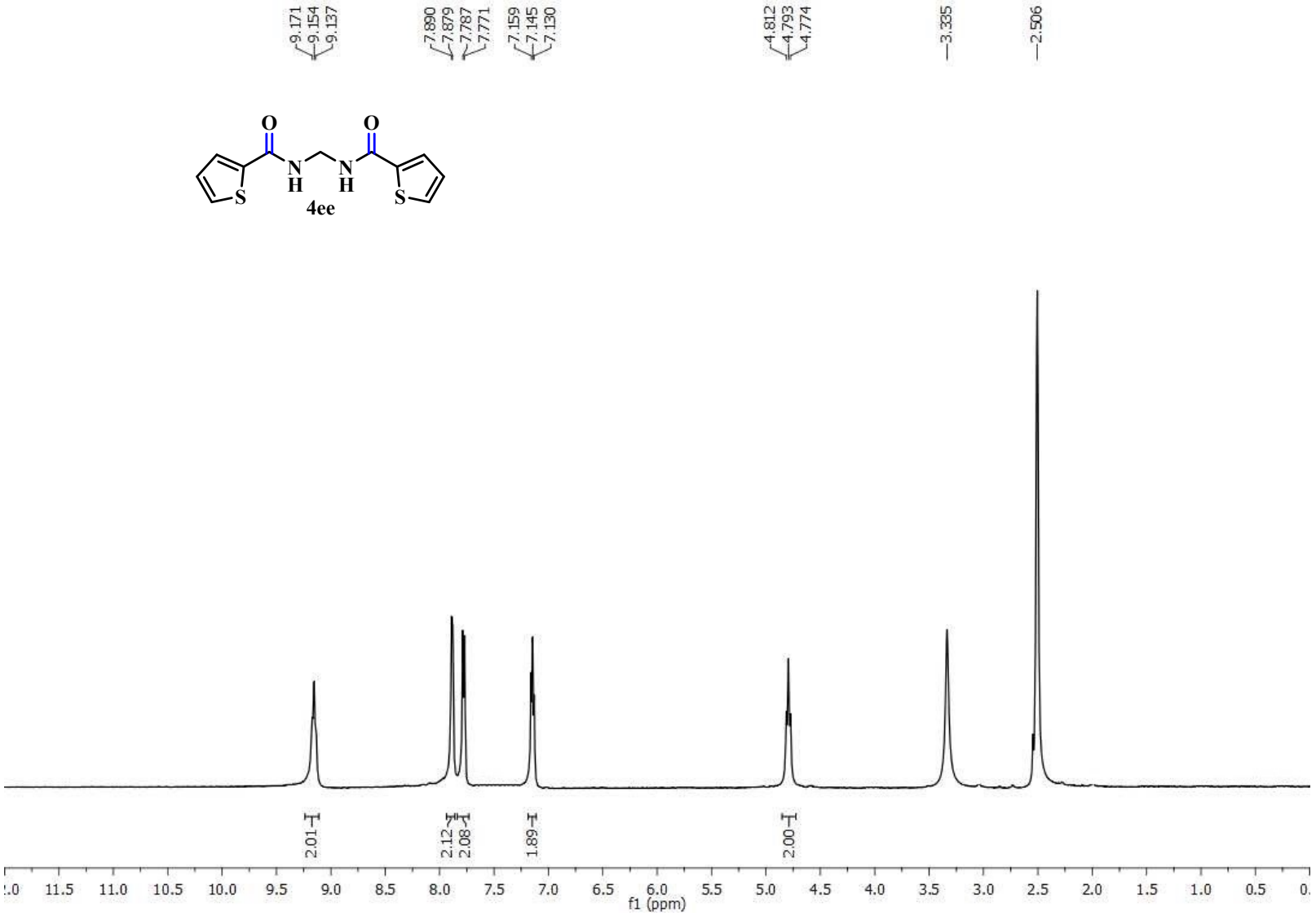

165.97
161.71
129.33
126.21
113.46
55.34
45.10
40.36
40.08
39.80
39.52
39.24
38.96
38.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

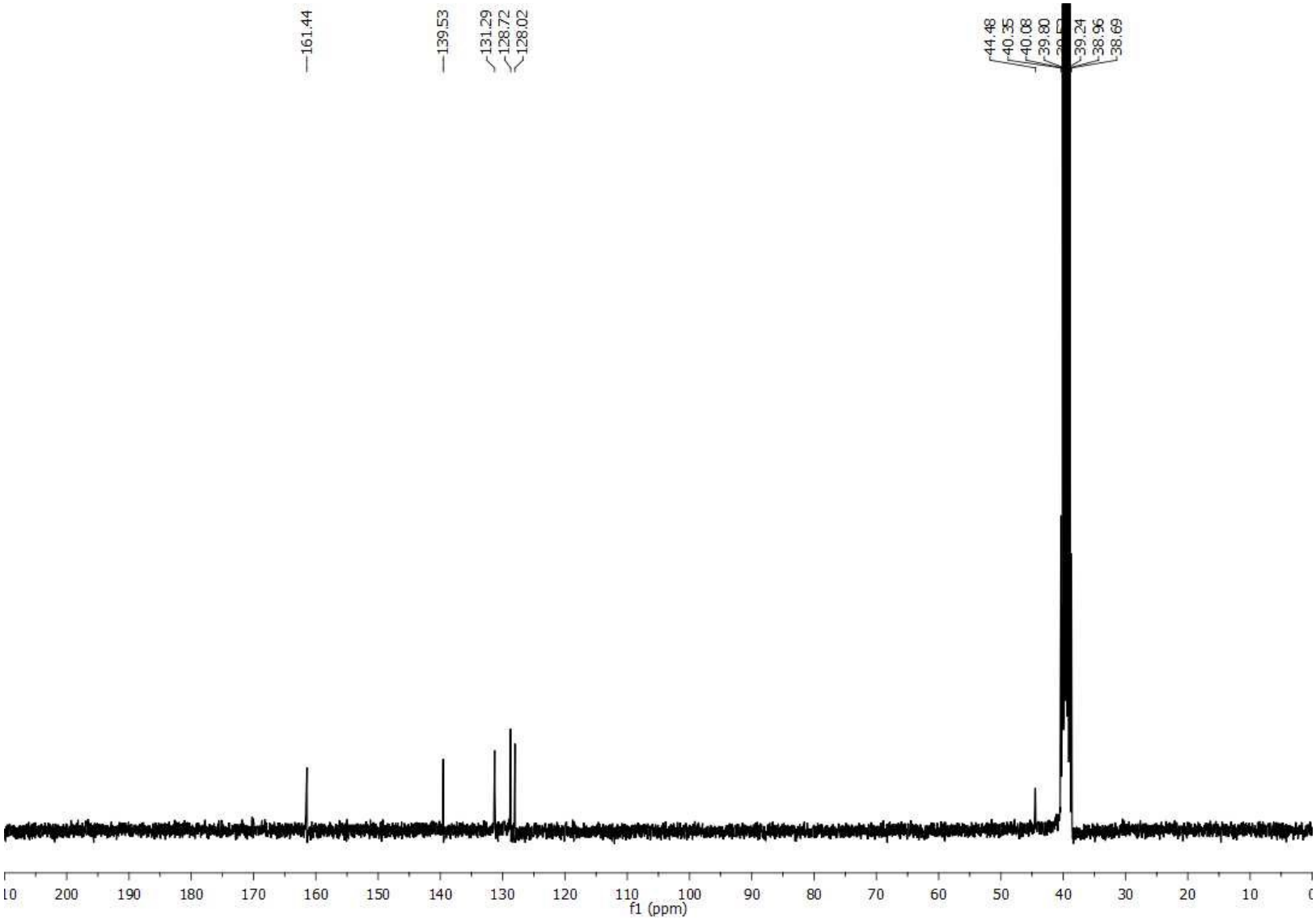
^{1}H NMR and ^{13}C NMR of Compound (4dd)



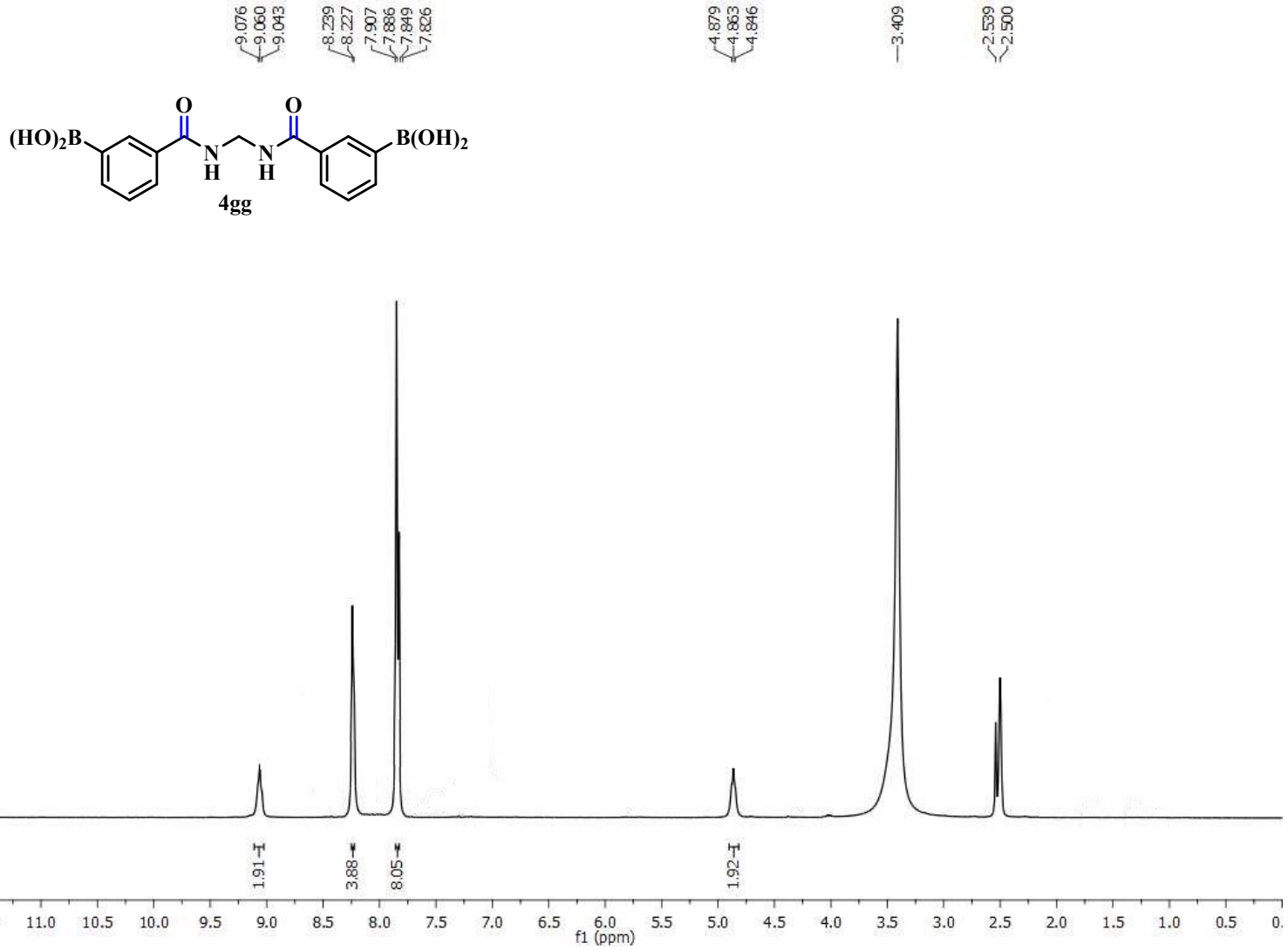

165.16
149.25
139.58
129.08
123.63
45.42
40.15
39.94
39.73
39.52
39.31
39.10
38.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

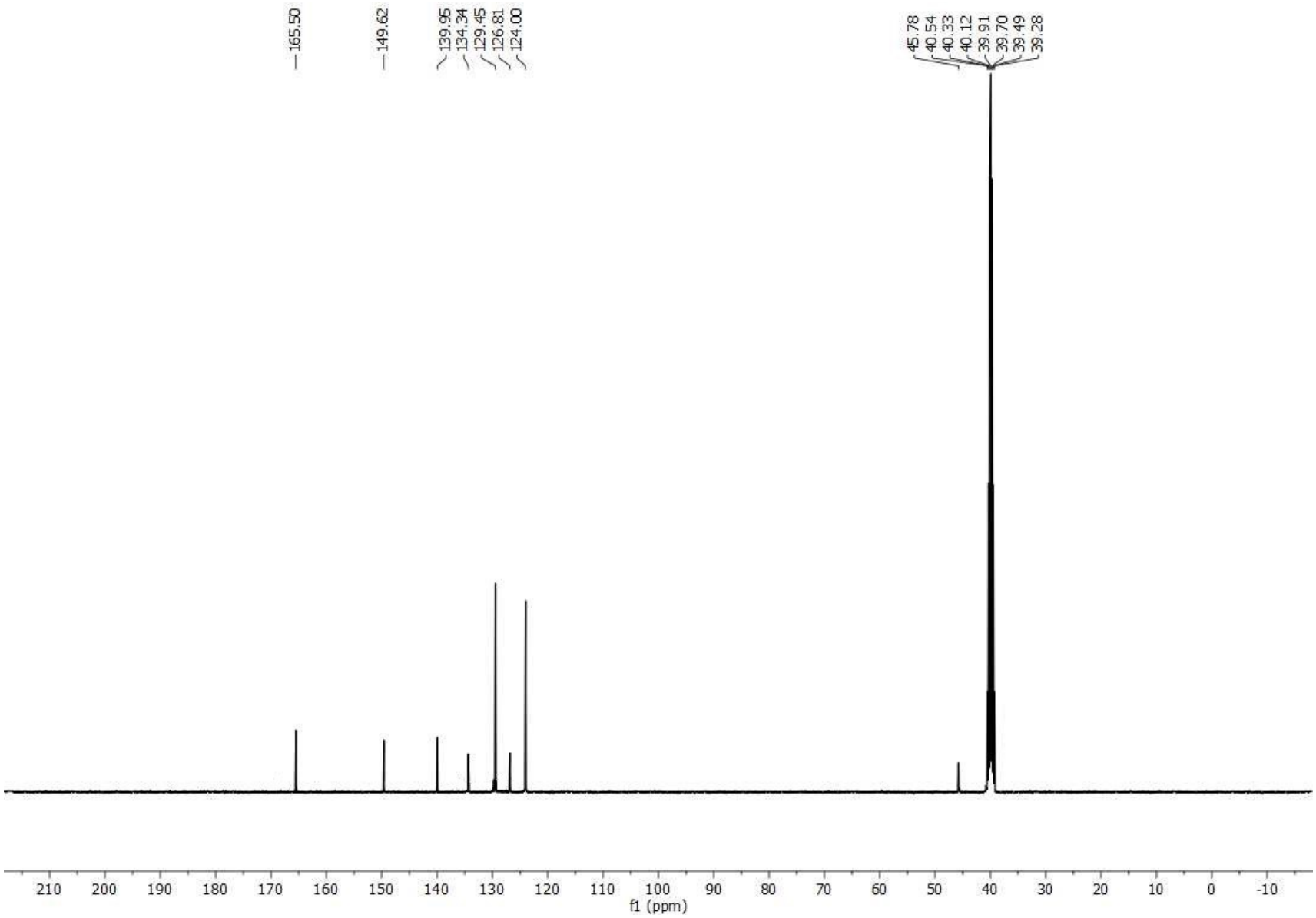
^{1}H NMR and ^{13}C NMR of Compound (4ee)



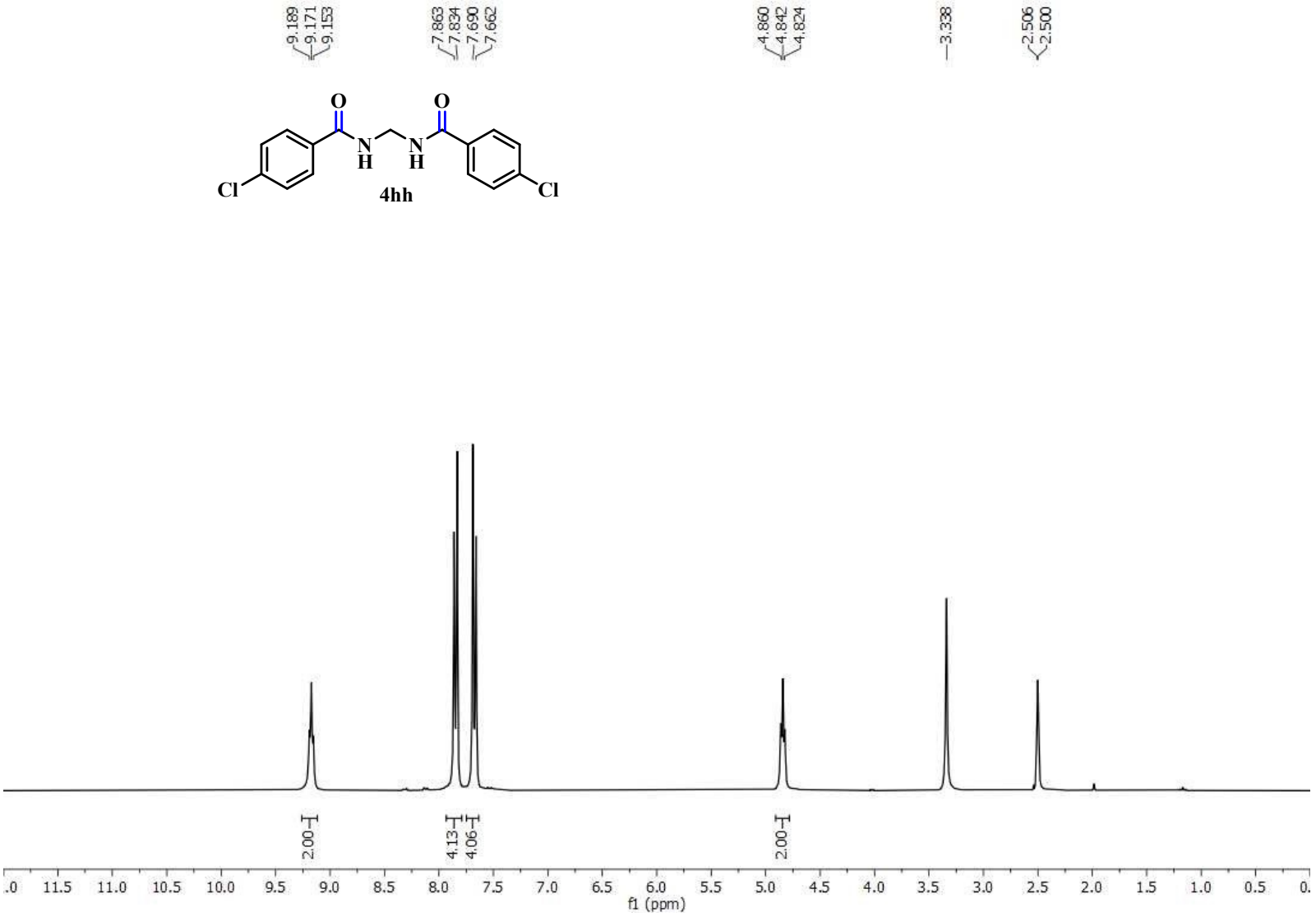

161.44
139.53
131.29
128.72
128.02
44.48
40.35
40.08
39.80
39.24
38.96
38.69
f1 (ppm)

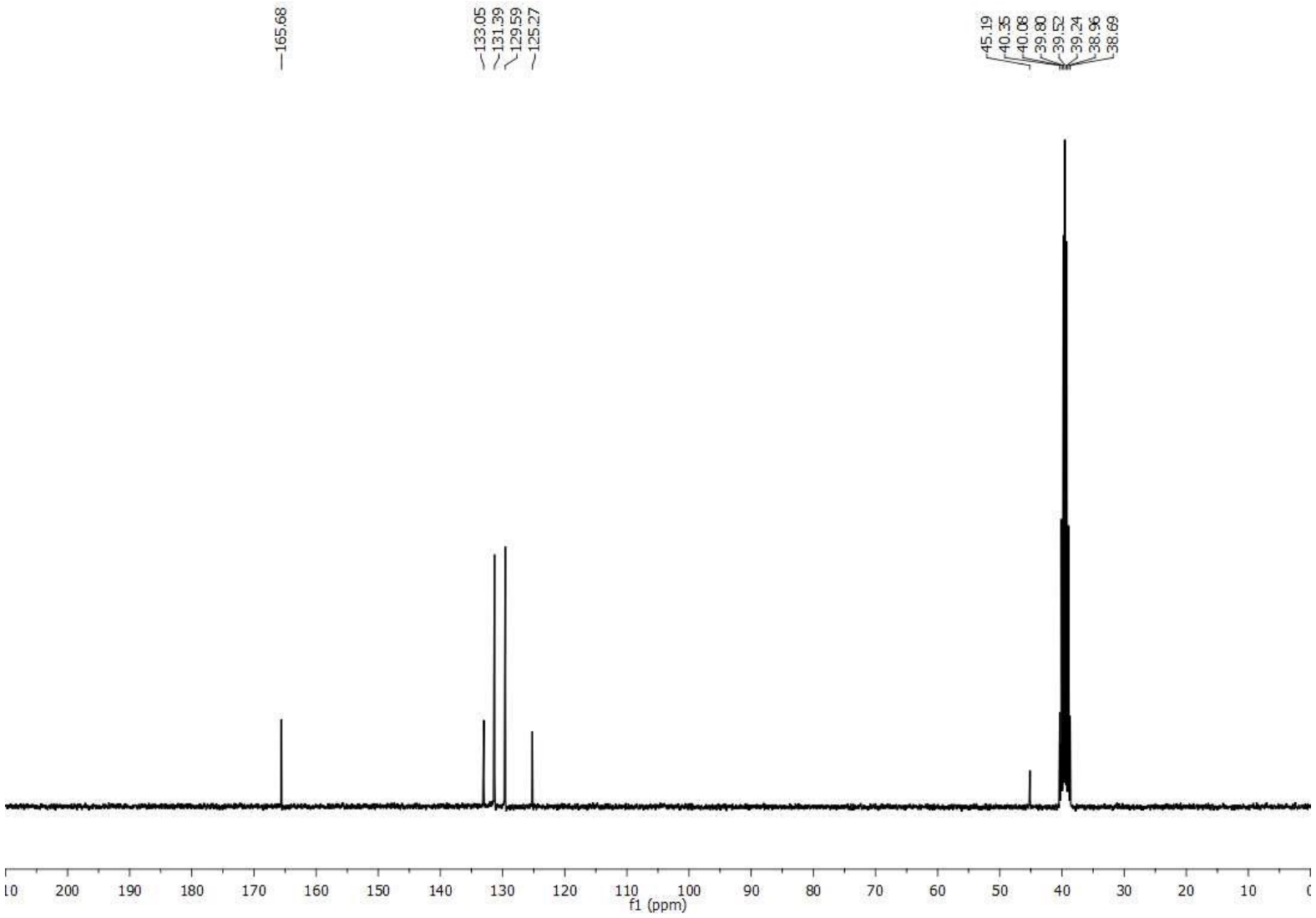
^{1}H NMR and ^{13}C NMR of Compound (4gg)



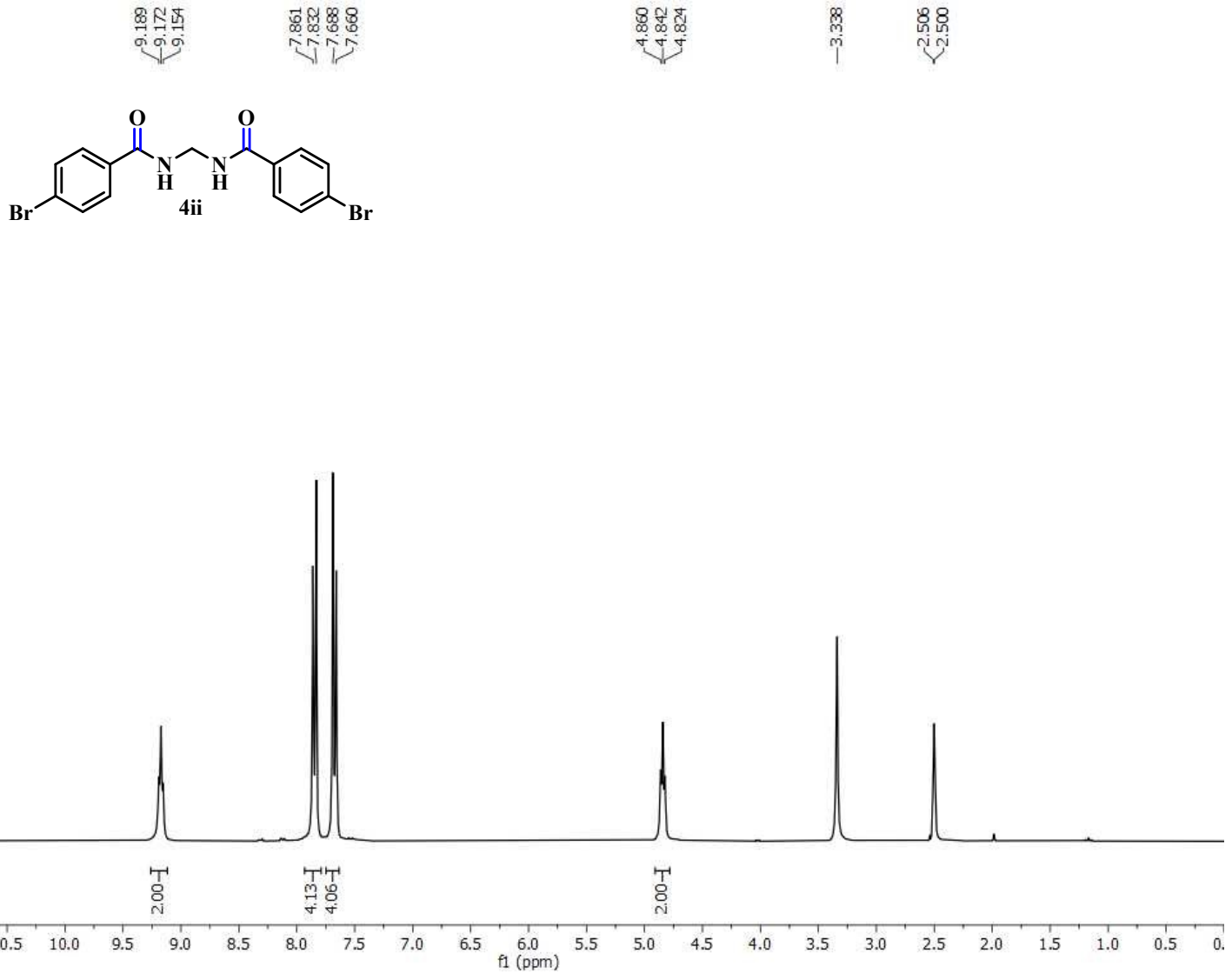

165.50
149.62
139.95
134.34
129.45
126.81
124.00
45.78
40.54
40.33
40.12
39.91
39.70
39.49
39.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

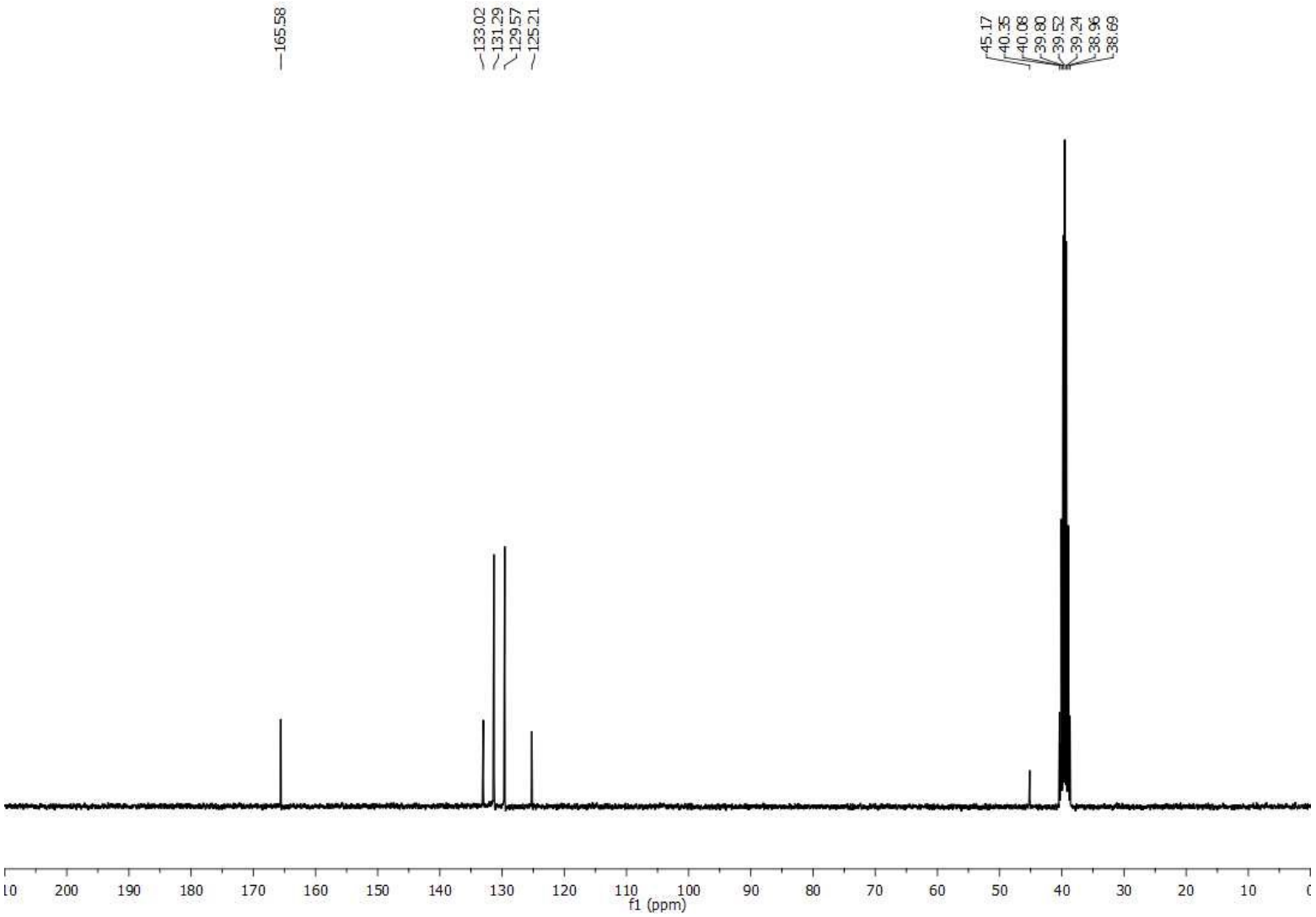
^{1}H NMR and ^{13}C NMR of Compound (4hh)



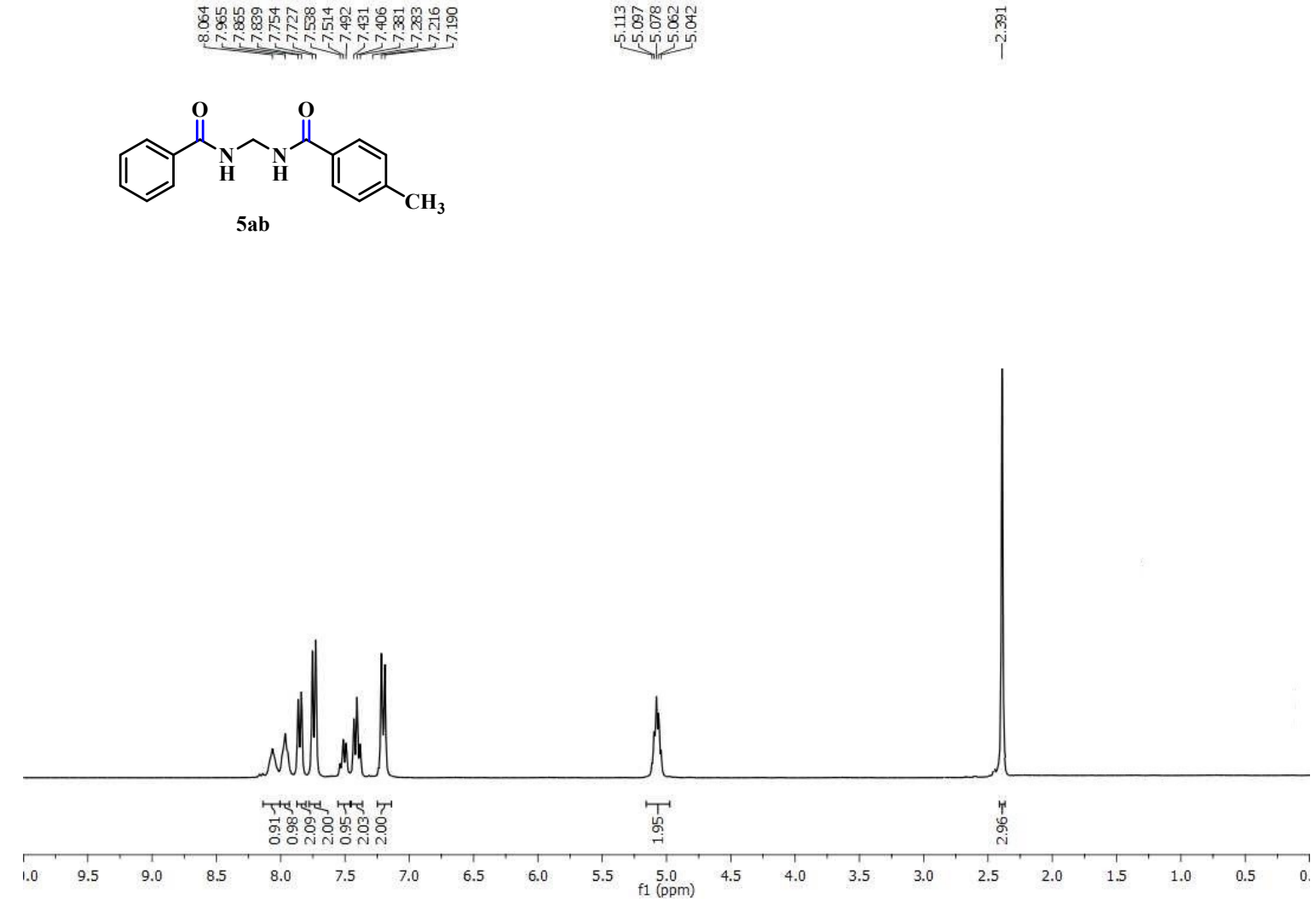

165.68
133.05
131.39
129.59
125.27
45.19
40.35
40.08
39.80
39.52
39.24
38.96
38.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

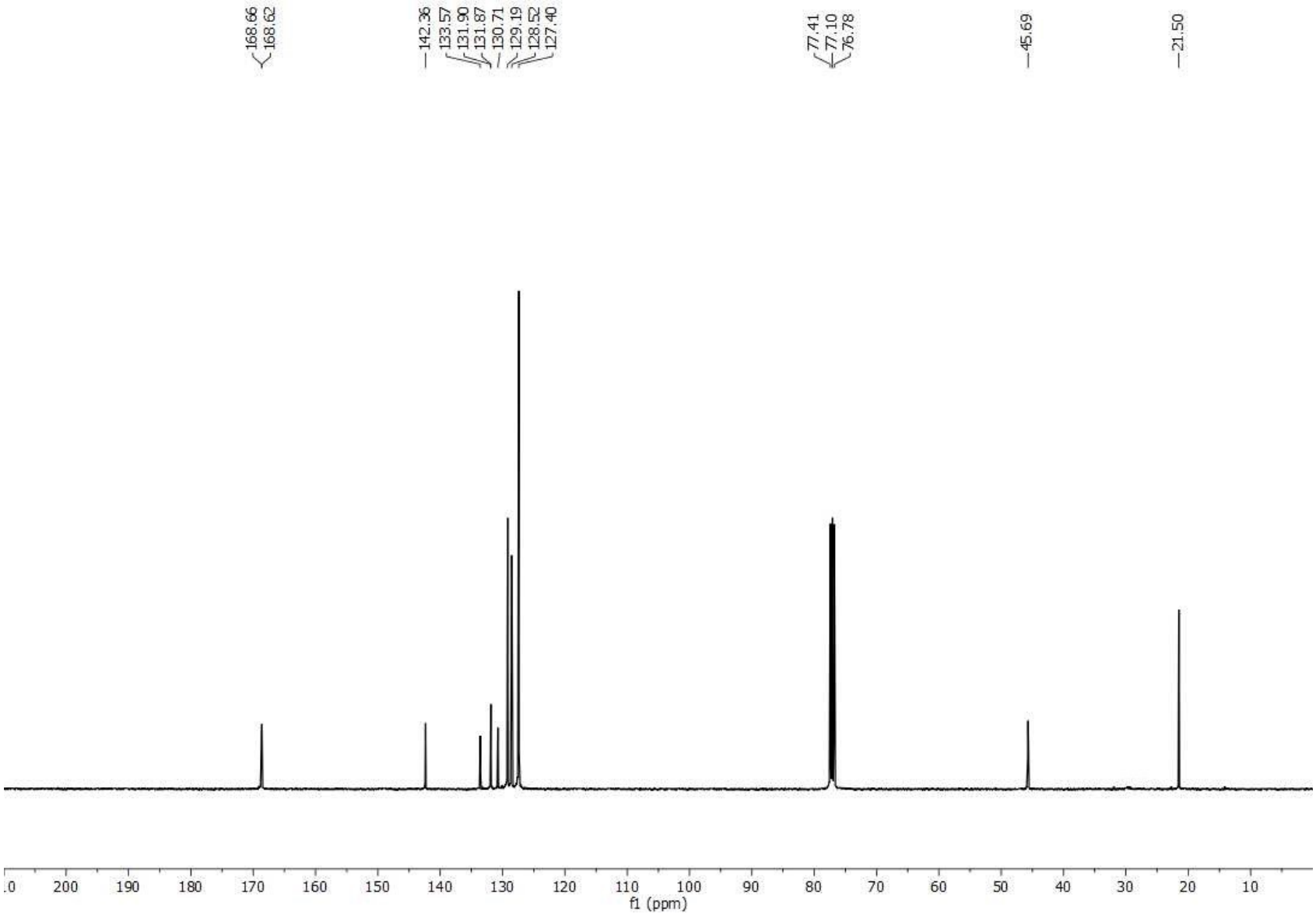
^{1}H NMR and ^{13}C NMR of Compound (4ii)



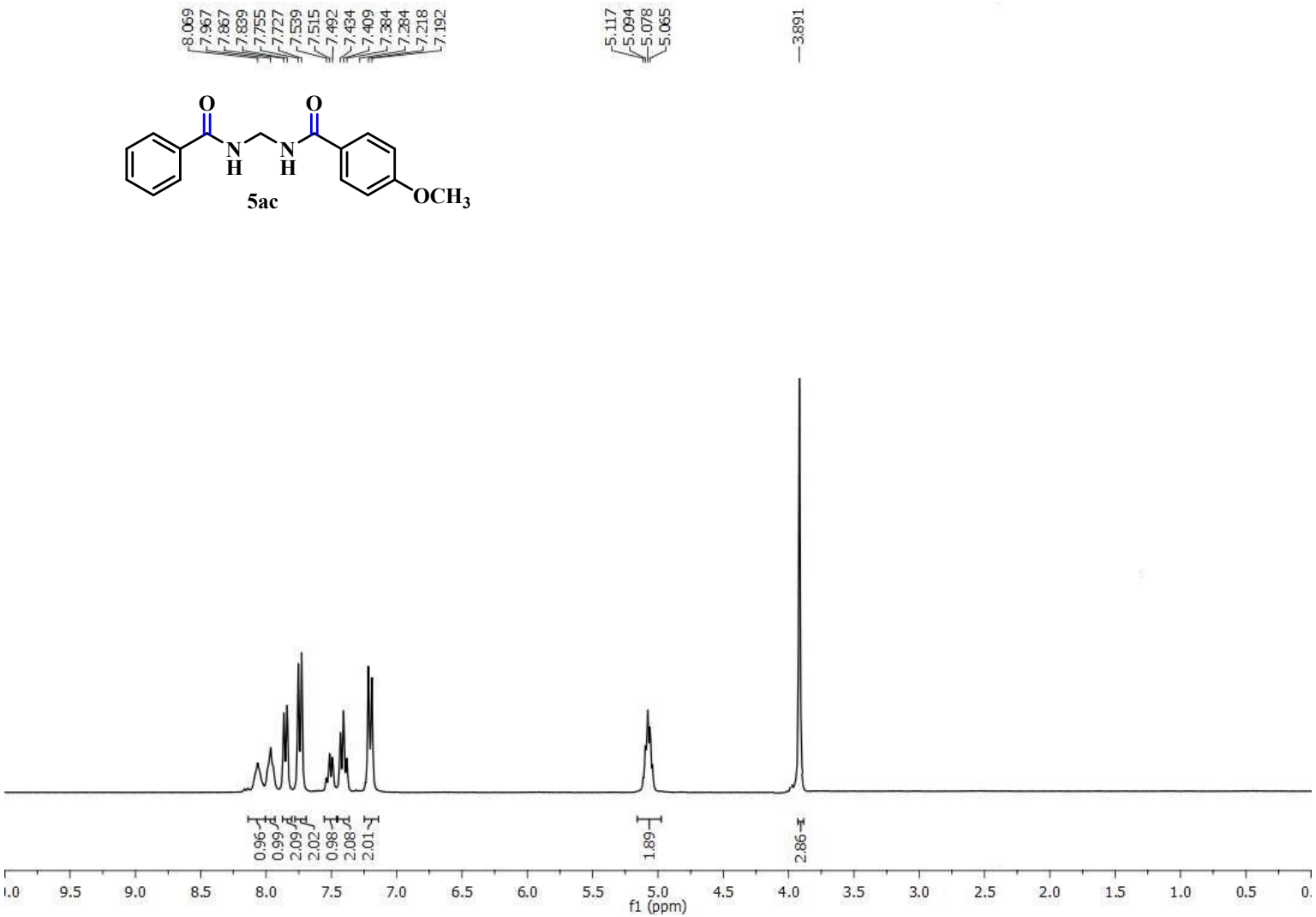

165.58
133.02
131.29
129.57
125.21
45.17
40.35
40.08
39.80
39.52
39.24
38.96
38.69
f1 (ppm)

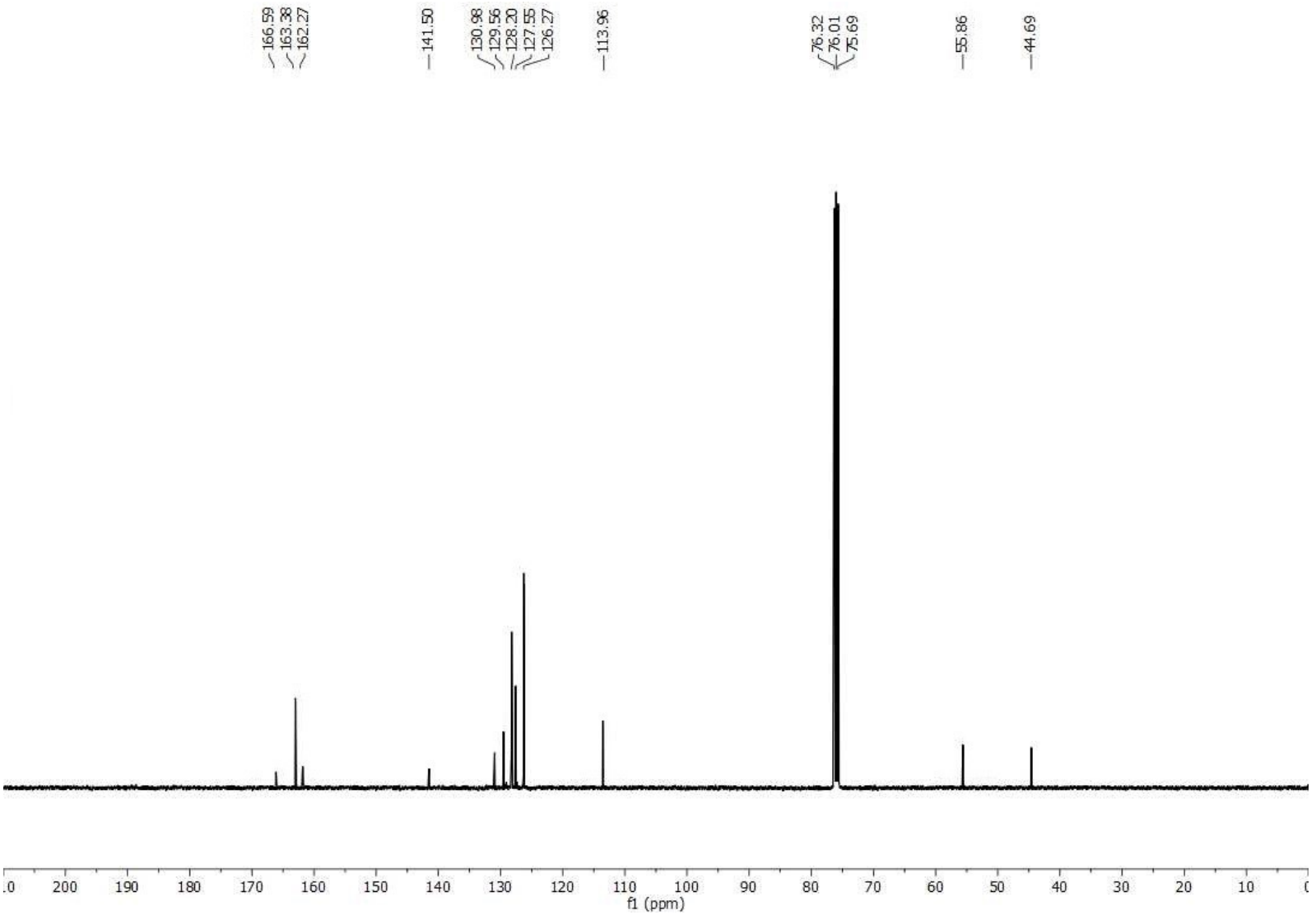
^{1}H NMR and ^{13}C NMR of Compound (5ab)



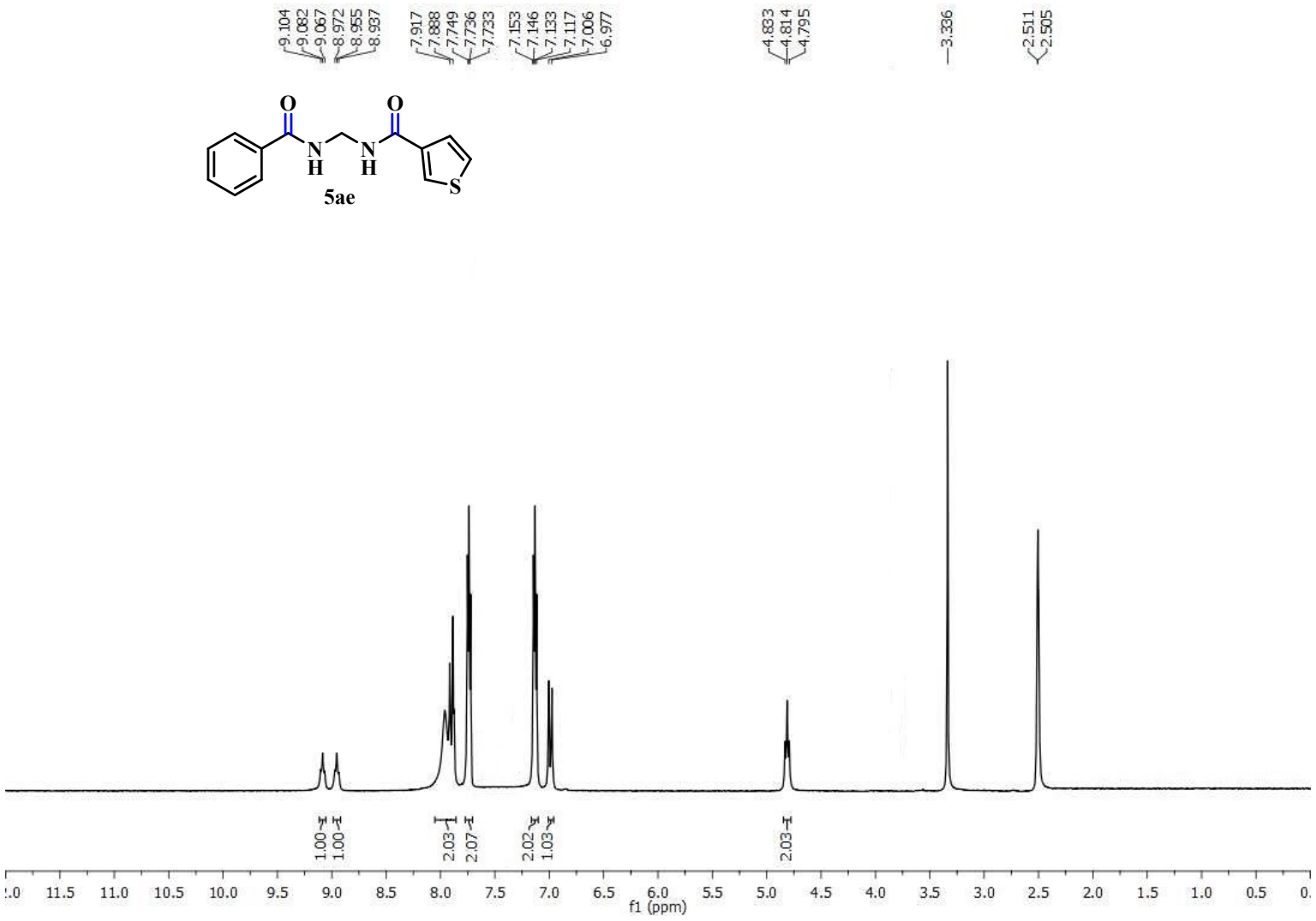

168.66
168.62
142.36
133.57
131.90
131.87
130.71
129.19
128.52
127.40
77.41
77.10
76.78
45.69
21.50
f1 (ppm)

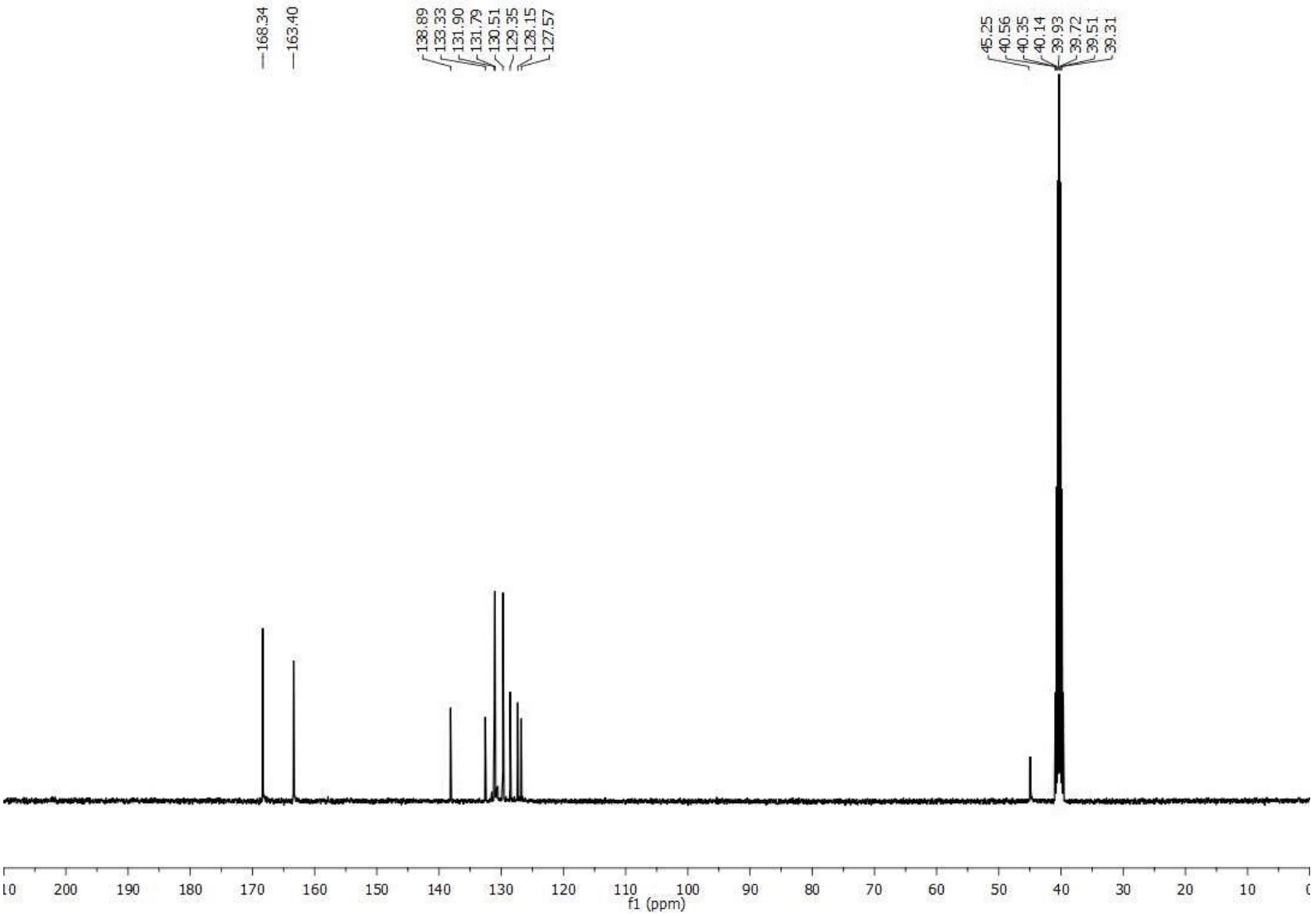
^{1}H NMR and ^{13}C NMR of Compound (5ac)



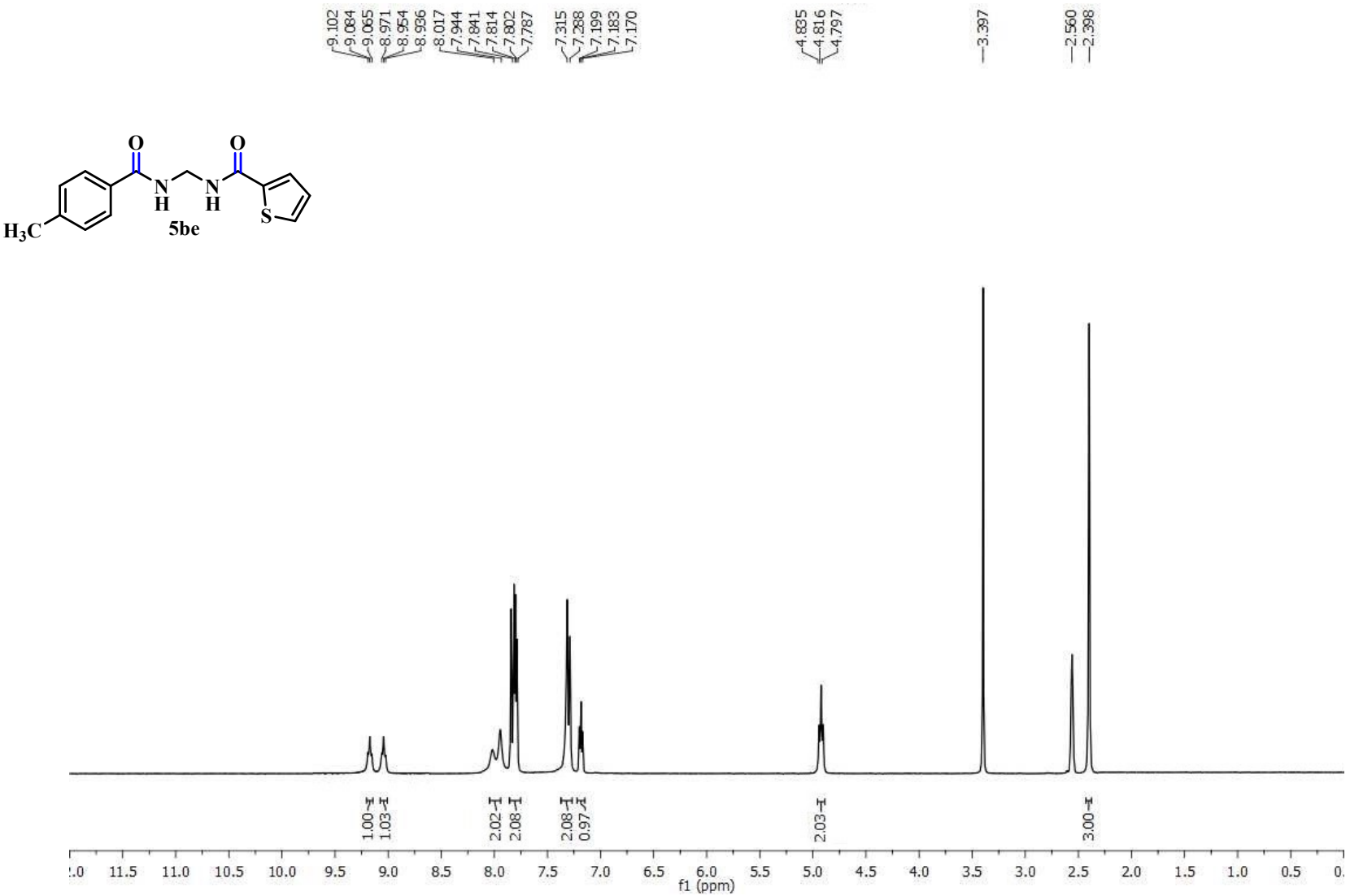

166.59
163.38
162.27
141.50
130.98
129.56
128.20
127.55
126.27
113.96
76.32
76.01
75.69
55.86
44.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

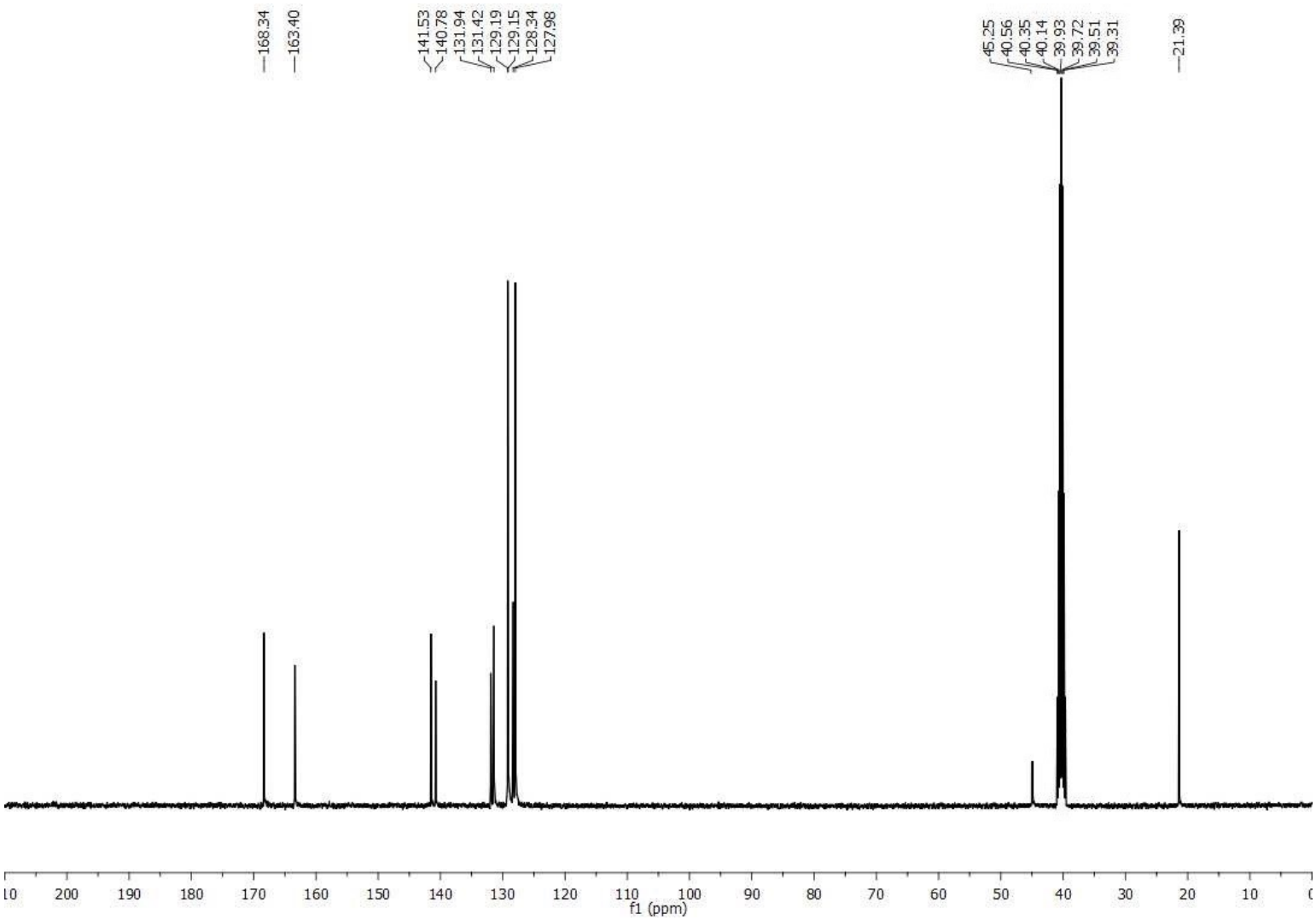
^{1}H NMR and ^{13}C NMR of Compound (5ae)



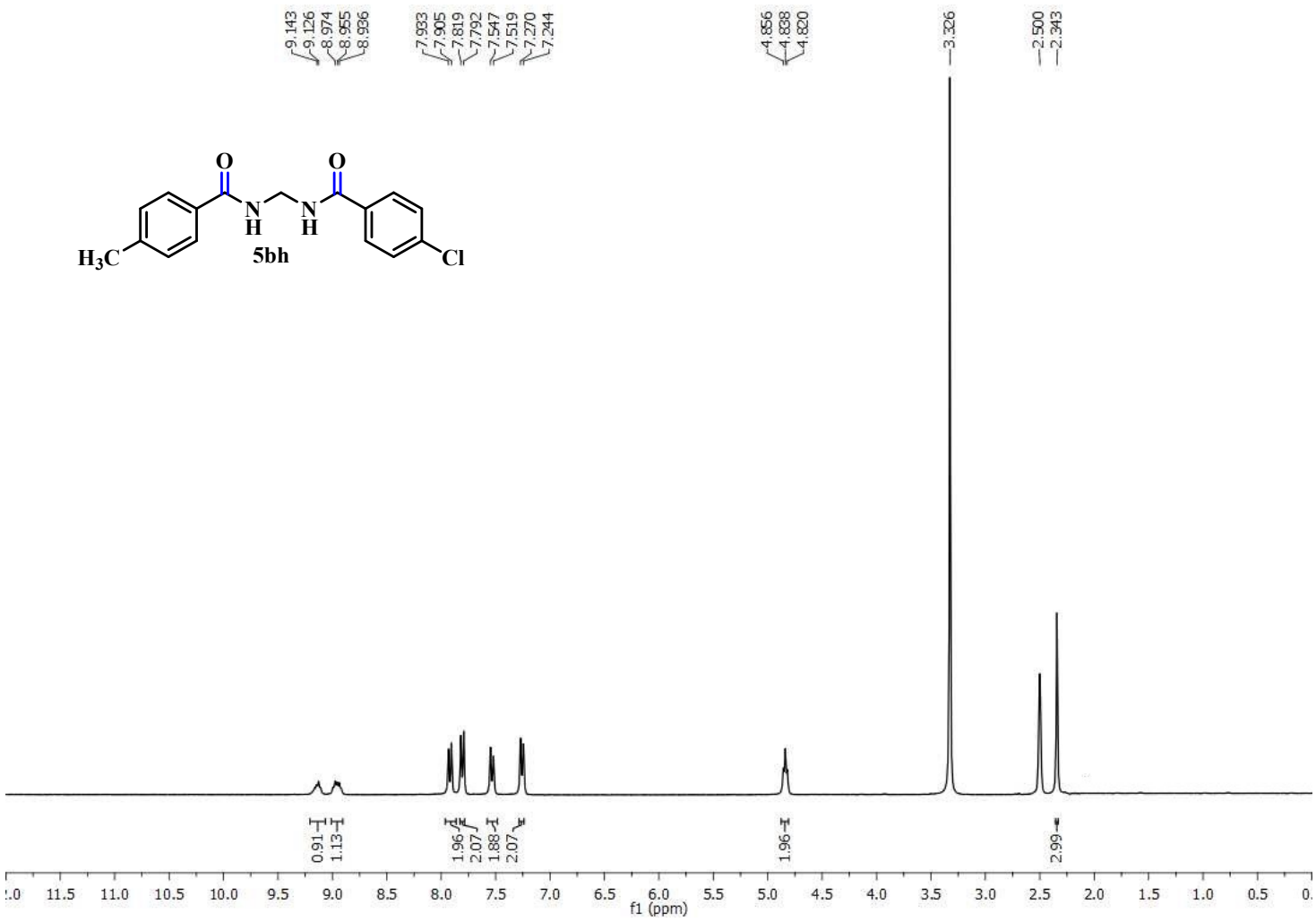

168.34
163.40
138.89
133.33
131.90
131.79
130.51
129.35
128.15
127.57
45.25
40.56
40.35
40.14
39.93
39.72
39.51
39.31
f1 (ppm)

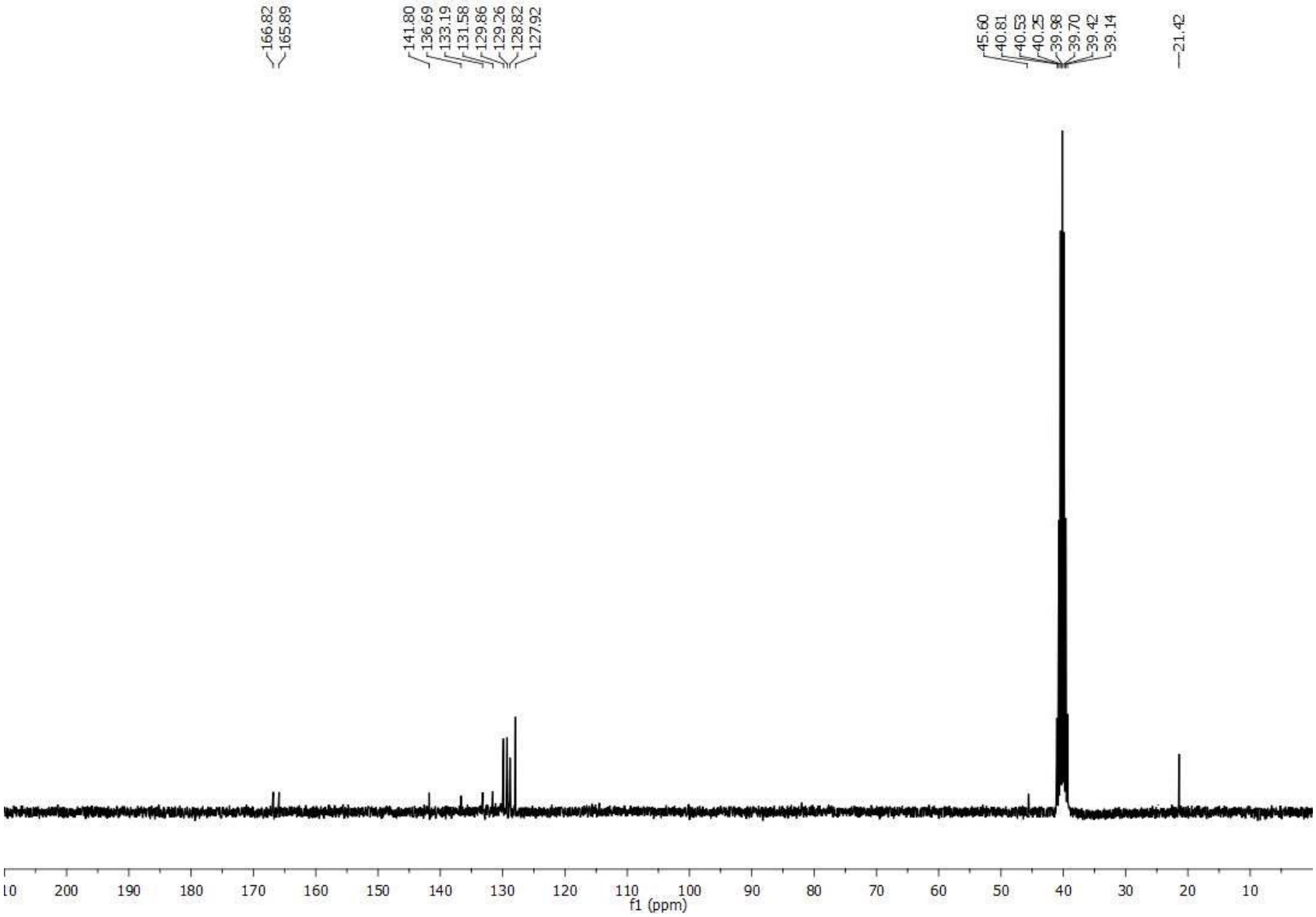
^{1}H NMR and ^{13}C NMR of Compound (5be)



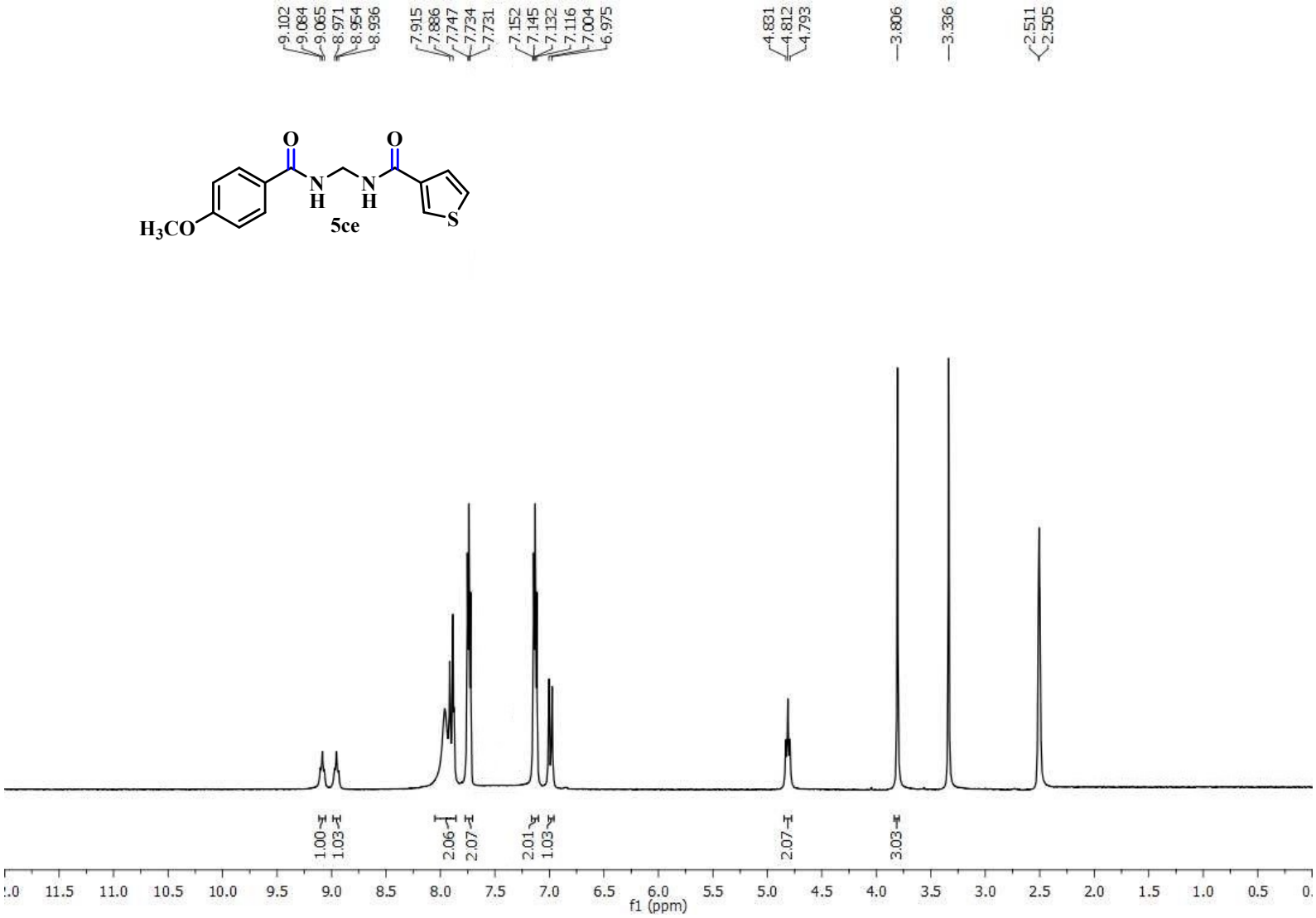

168.34
163.40
141.53
140.78
131.94
131.42
129.19
129.15
128.34
127.98
45.25
40.56
40.35
40.14
39.93
39.72
39.51
39.31
21.39
f1 (ppm)

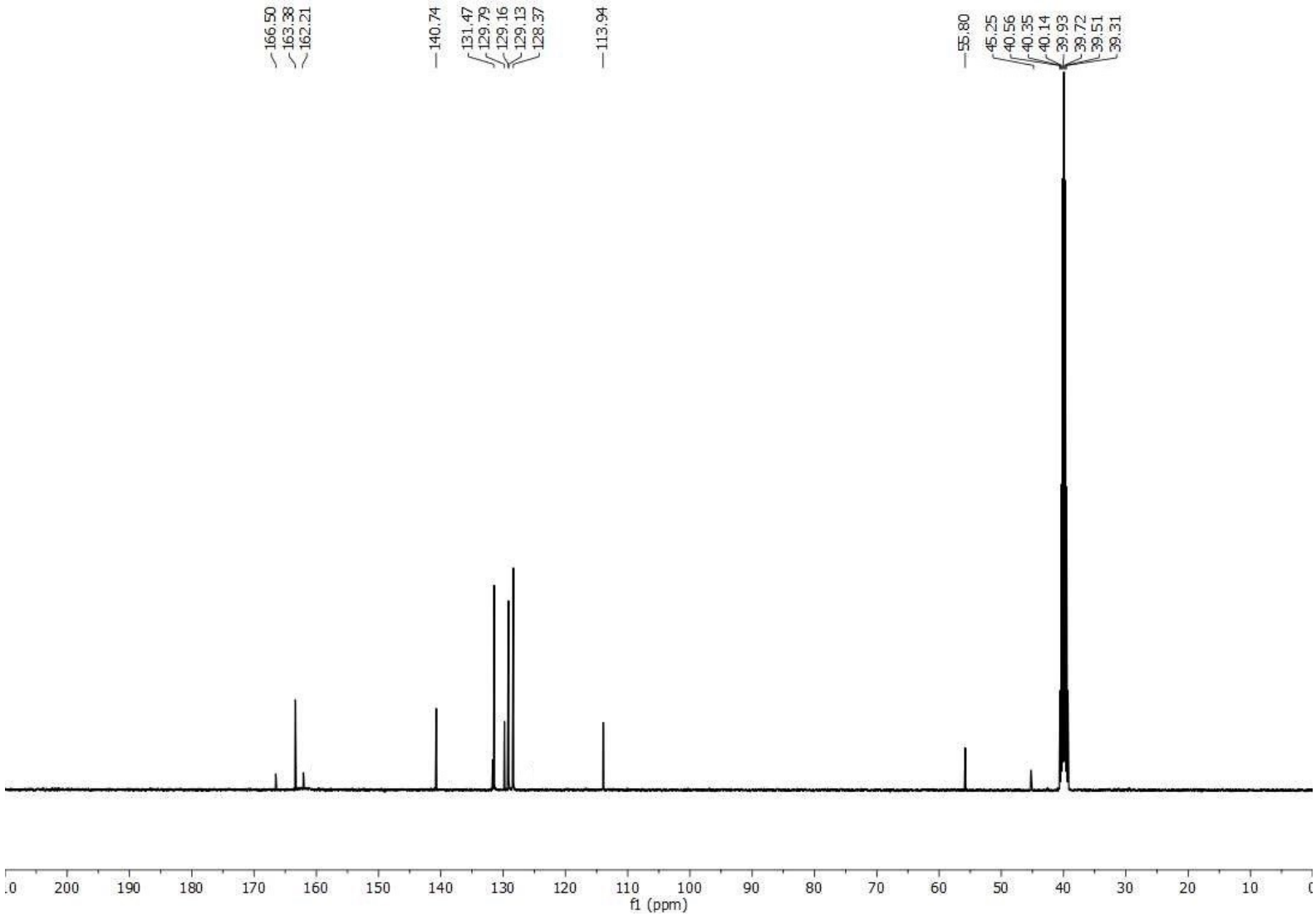
^{1}H NMR and ^{13}C NMR of Compound (5bh)



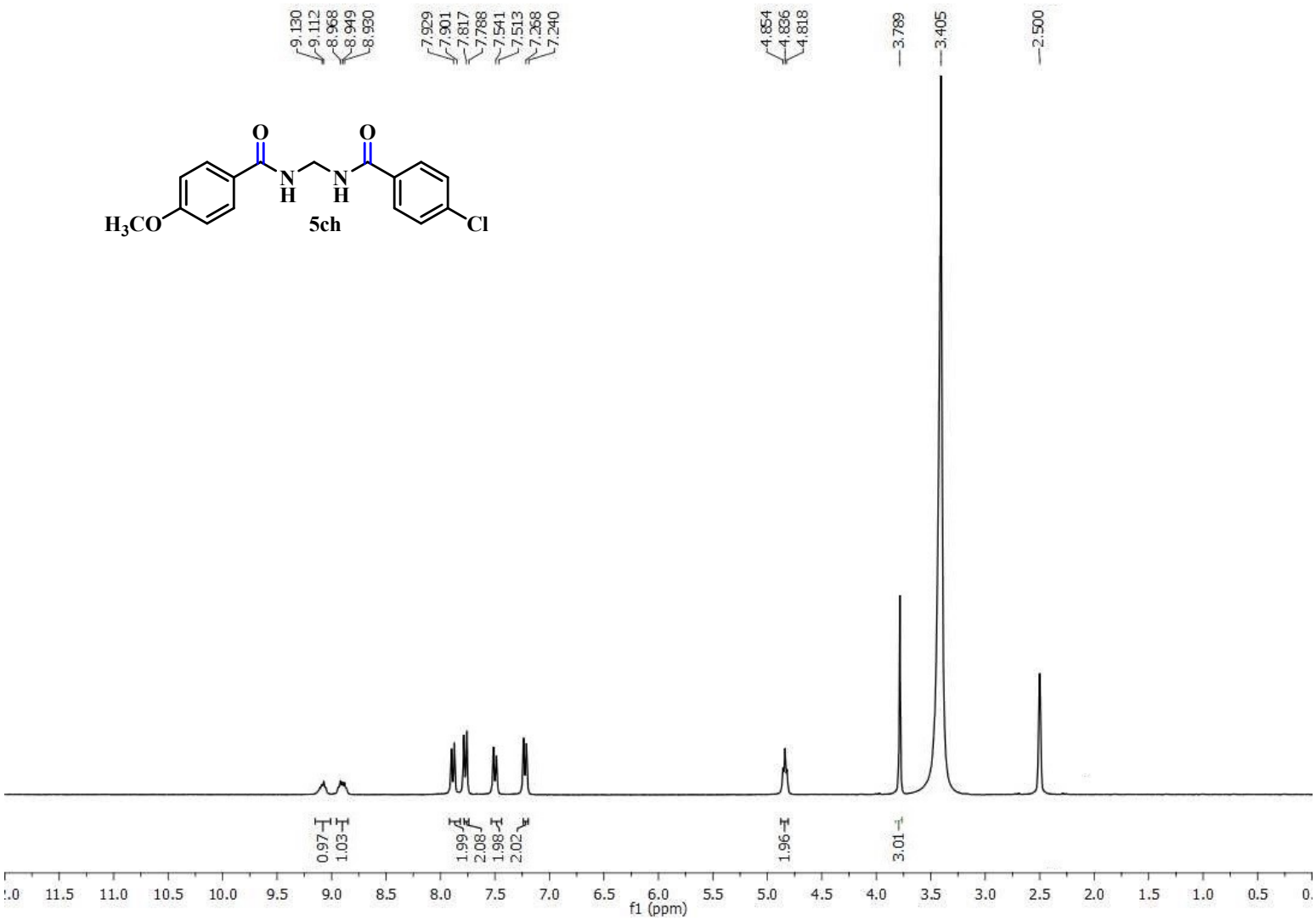

166.82
165.89
141.80
136.69
133.19
131.58
129.86
129.26
128.82
127.92
45.60
40.81
40.53
40.25
39.98
39.70
39.42
39.14
21.42
f1 (ppm)

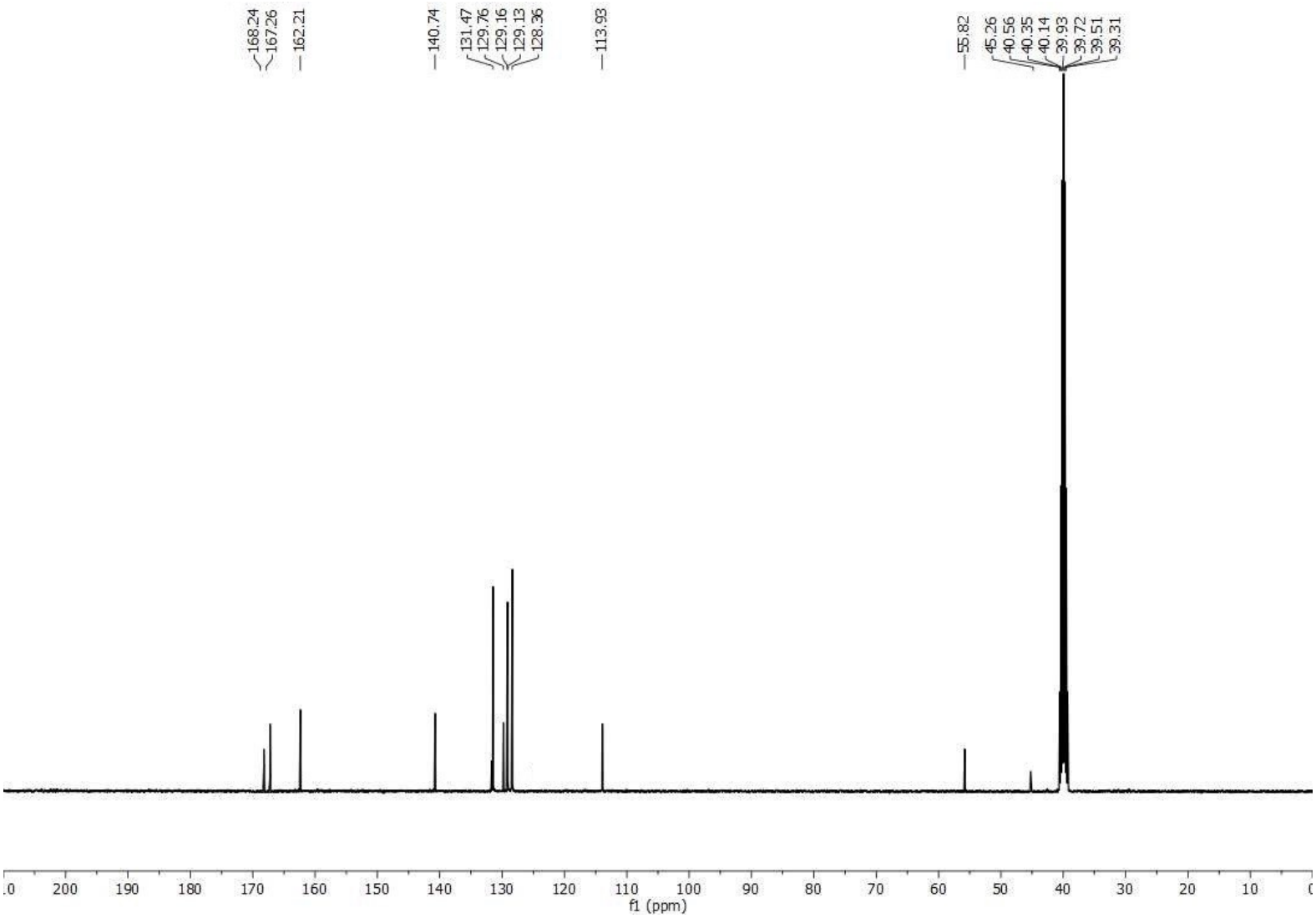
^{1}H NMR and ^{13}C NMR of Compound (5ce)


9.102
9.084
9.065
8.971
8.954
8.936
7.915
7.886
7.747
7.734
7.731
7.152
7.145
7.132
7.116
7.004
6.975
4.831
4.812
4.793
3.806
3.336
2.511
2.505
O
O
N
H
N
H
H3CO
S
5ce
1.00
1.03
2.06
2.07
2.01
1.03
2.07
3.03
f1 (ppm)

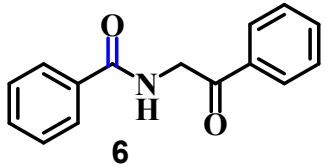

166.50
163.38
162.21
140.74
131.47
129.79
129.16
129.13
128.37
113.94
55.80
45.25
40.56
40.35
40.14
39.93
39.72
39.51
39.31
f1 (ppm)

^{1}H NMR and ^{13}C NMR of Compound (5ch)





11. <u>Spectroscopic Data of α-amidoketone</u>

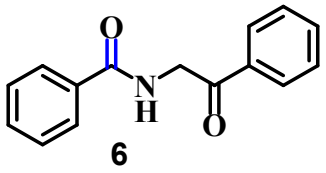


6

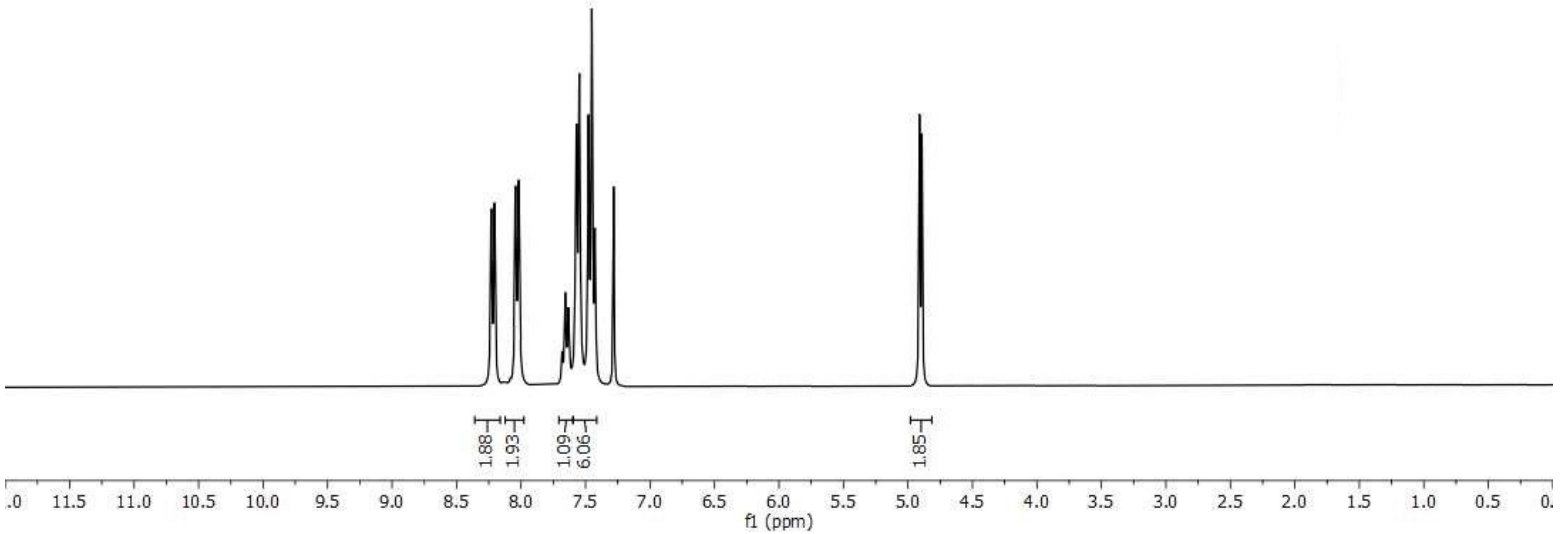
***N*-(2-oxo-2-phenylethyl)benzamide (6)**[3]: Et_3N (5 mmol, 2.5 equiv.) was added to a solution of 2- aminoacetophenone hydrochloride[4] (2 mmol) in DCM (5 mL). Benzoyl chloride (2.6 mmol, 1.3 equiv.) was added to this reaction mixture at 0 ℃ and the reaction mixture was allowed to warm to room temperature for 2 h. Water (5 mL) was added, the mixture extracted with DCM (3*5 mL), the combined organic layer washed with sat. $NaHCO_3$ (10 mL) and brine (10 mL). The solution was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product could be purified by silica gel chromatography (20% ethyl acetate in petroleum ether) afforded the title compound as white solid (191 mg, 0.80 mmol, 80% yield), **^{1}H-NMR** (300 MHz, $CDCl_3$): δ 4.93 (d, J= 3.3 Hz, 2H), 7.43 – 7.57 (m, 6H), 7.63 – 7.68 (m, 1H), 8.02 – 8.05 (m, 2H), 8.20 – 8.23 (m, 2H); **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 46.8, 127.6, 128.4, 128.6, 128.7, 131.8, 133.5, 134.3, 166.5, 196.0; ESI-MS (*m*/*z*) for $C_{15}H_{14}NO_2$ $[M+H]^+$: Calculated 240.1025, found 240.1028.

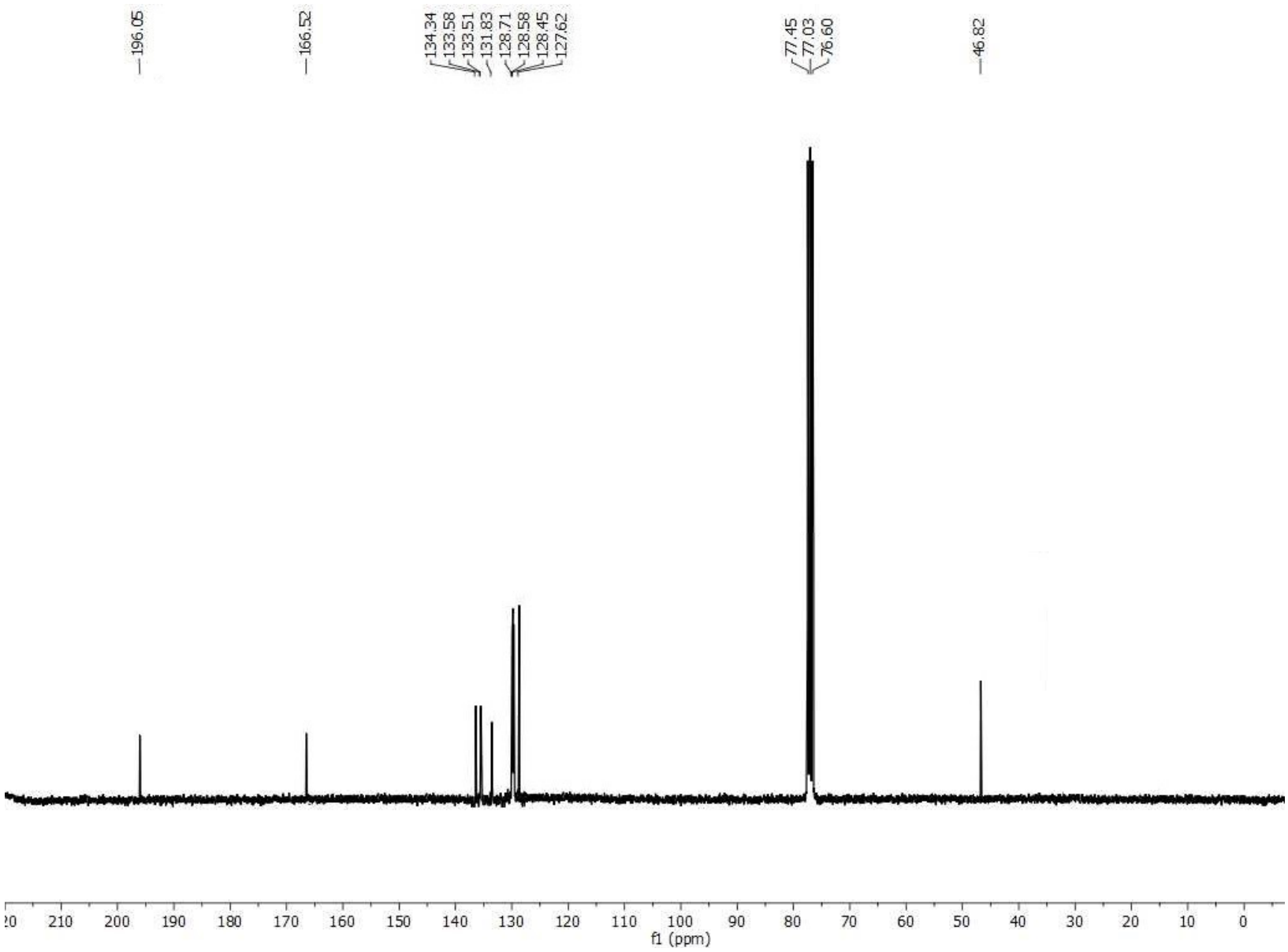
^{1}H NMR and ^{13}C NMR of Compound (6)


8.230
8.207
8.201
8.046
8.022
8.016
7.681
7.657
7.632
7.575
7.569
7.548
7.477
7.452
7.426
7.282
4.939
4.928


O
N
H
O

6

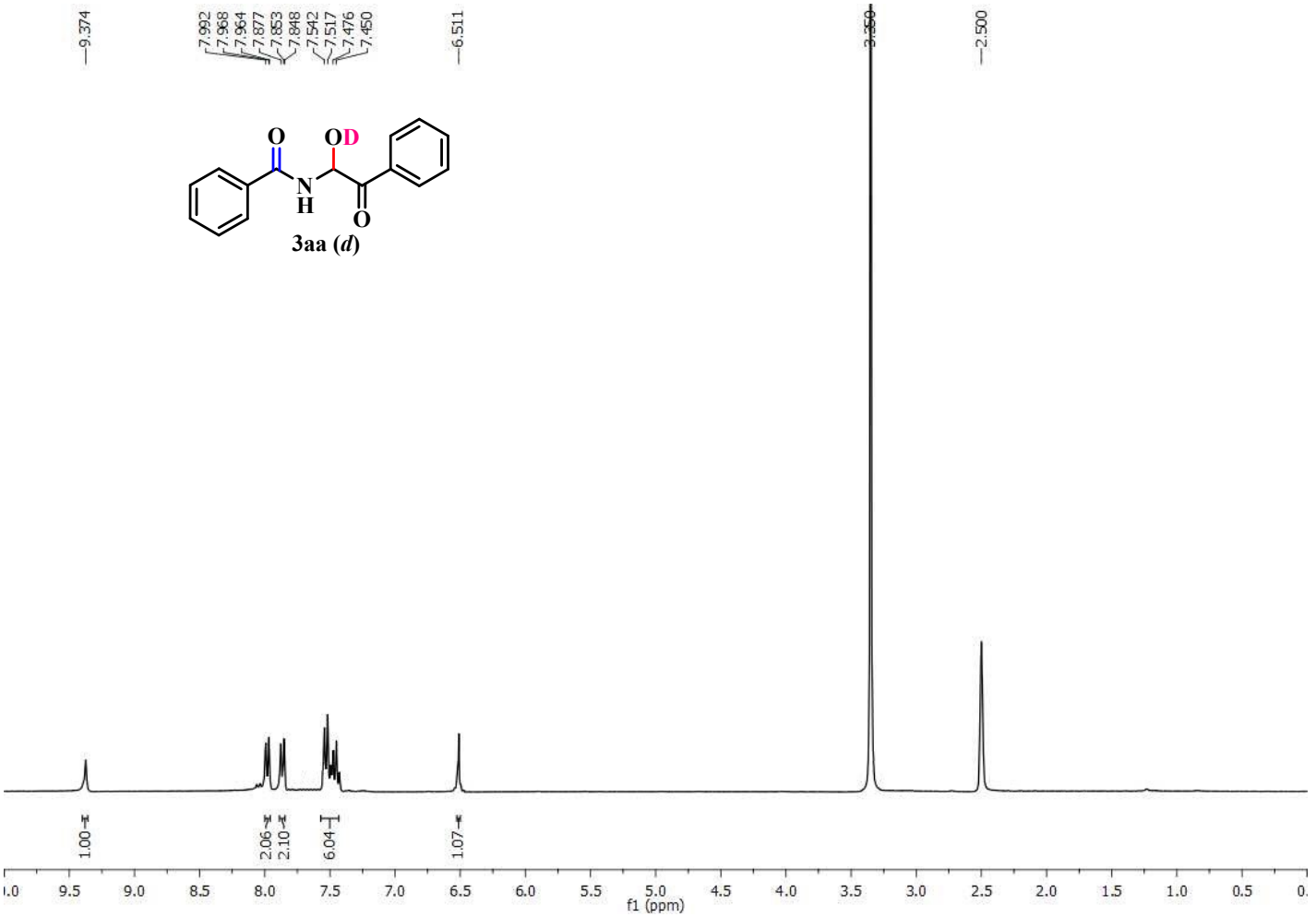

1.88
1.93
1.09
6.06
1.85
f1 (ppm)


196.05
166.52
134.34
133.58
133.51
131.83
128.71
128.58
128.45
127.62
77.45
77.03
76.60
46.82
f1 (ppm)

12. Spectroscopic data of [3aa (*d*)] with labelling experiment

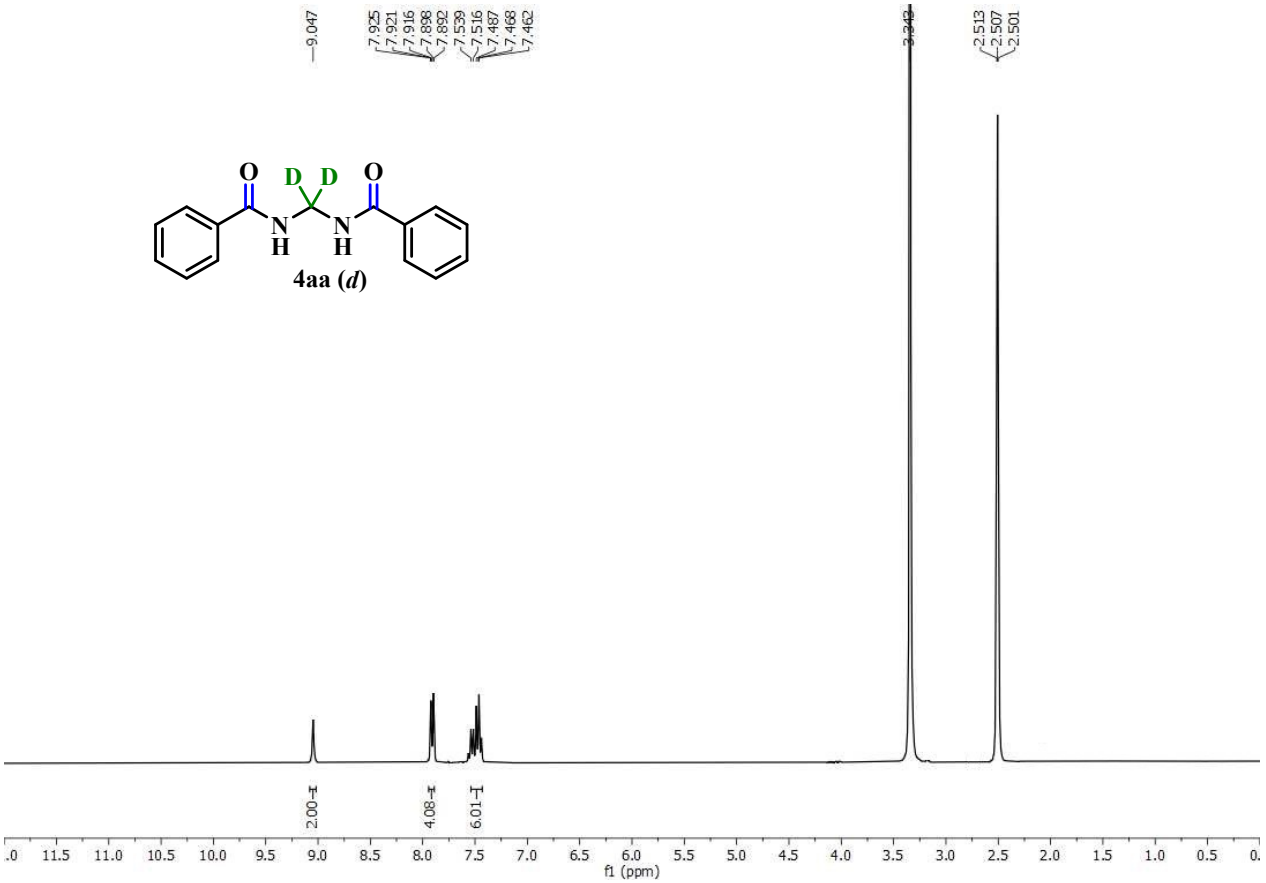
^{1}H NMR of 3aa (300 MHz, d_6-DMSO): δ 6.51 (s, 1H), 7.45 – 7.54 (m, 6H), 7.85 – 7.88 (m, 2H), 7.96 – 7.99 (m, 2H), 9.37 (s, 1H)

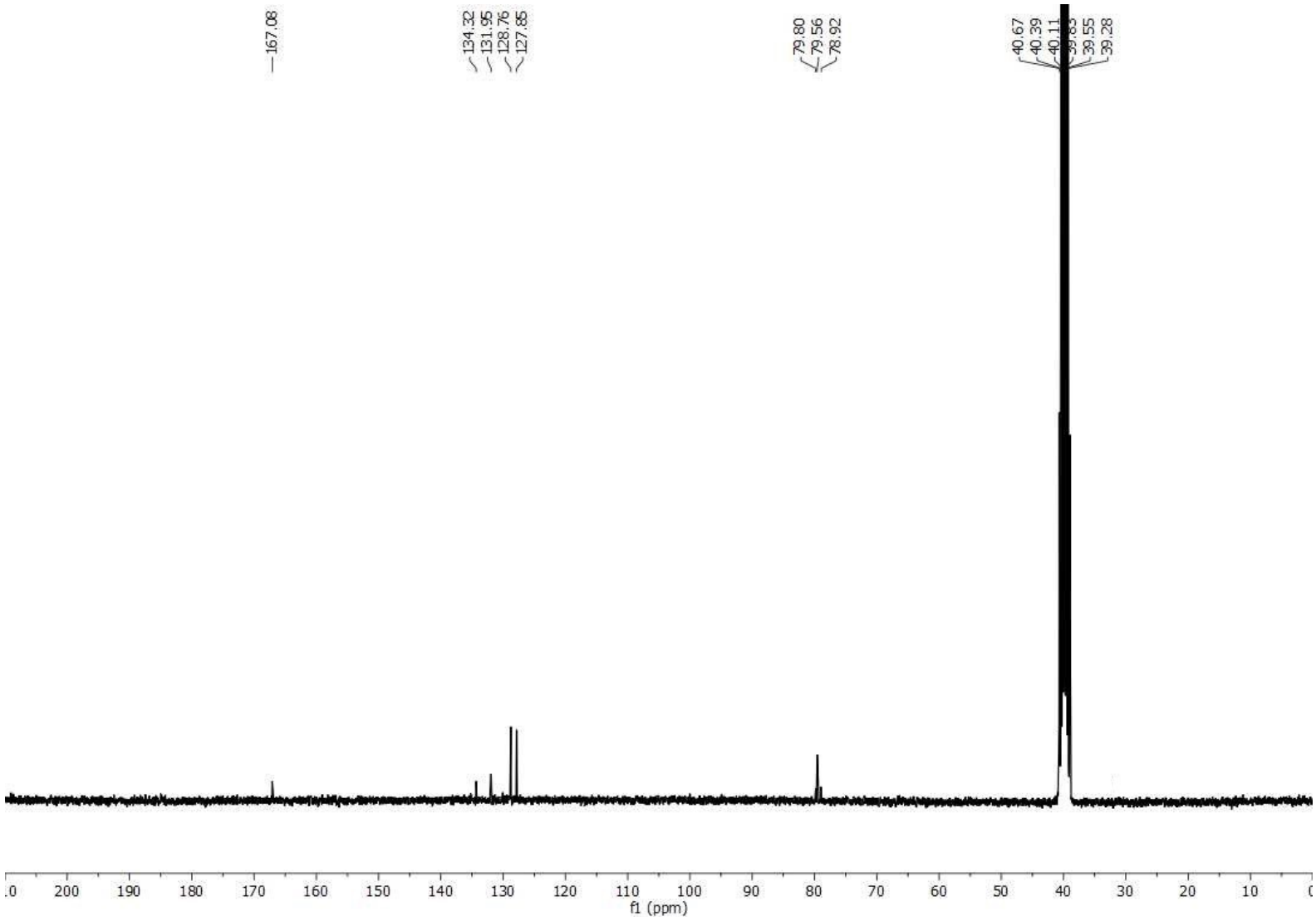
^{1}H NMR of Compound [3aa (*d*)] with deuterated (D_2O)



13. Spectroscopic data of [4aa (*d*)] with labelling experiment

^{1}H NMR of 4aa(*d*) (300 MHz, d_6-DMSO): δ 7.46 – 7.54 (m, 6H), 7.89 – 7.92 (m, 4H), 9.05 (s, 2H)
^{13}C-NMR of 4aa(*d*) (75 MHz, d_6-DMSO): δ 78.9, 79.6, 127.8, 128.8, 131.9, 134.3, 167.1
^{1}H NMR and ^{13}C-NMR of Compound [4aa (*d*)] with deuterated (DMSO-D_6)




167.08
134.32
131.95
128.76
127.85
79.80
79.56
78.92
40.67
40.39
40.11
39.83
39.55
39.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

14. HRMS data of 4aa(*d*)

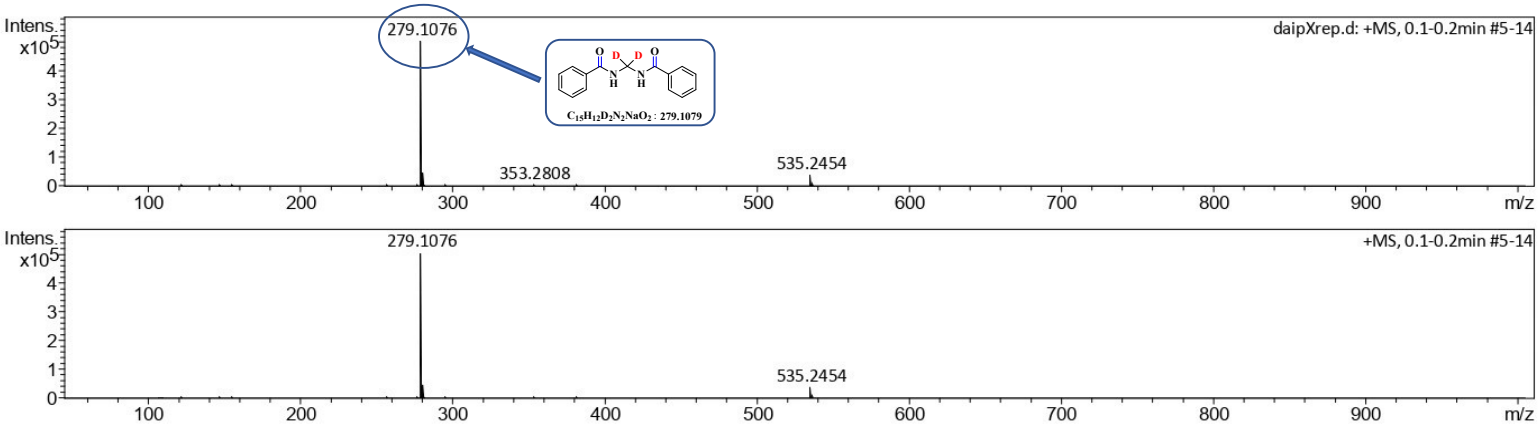
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2023\JAN\daipXrep.d	Acquisition Date	1/27/2023 4:52:23 PM
Method	Tune_pos_Standard_July2022.new.m	Operator	IISER Kolkata
Sample Name	daipX	Instrument	maXis impact 8282001.00127
Comment			

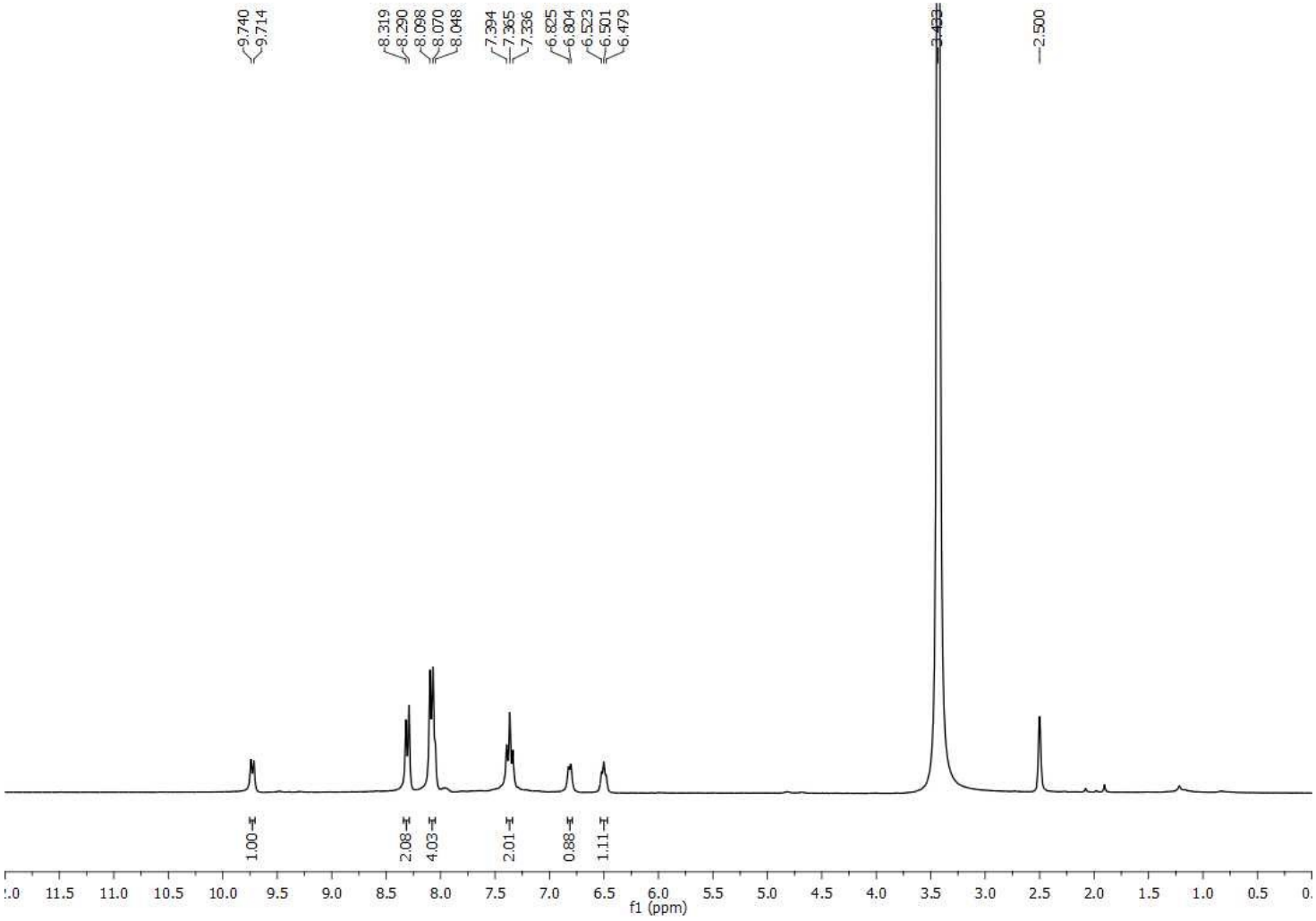
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

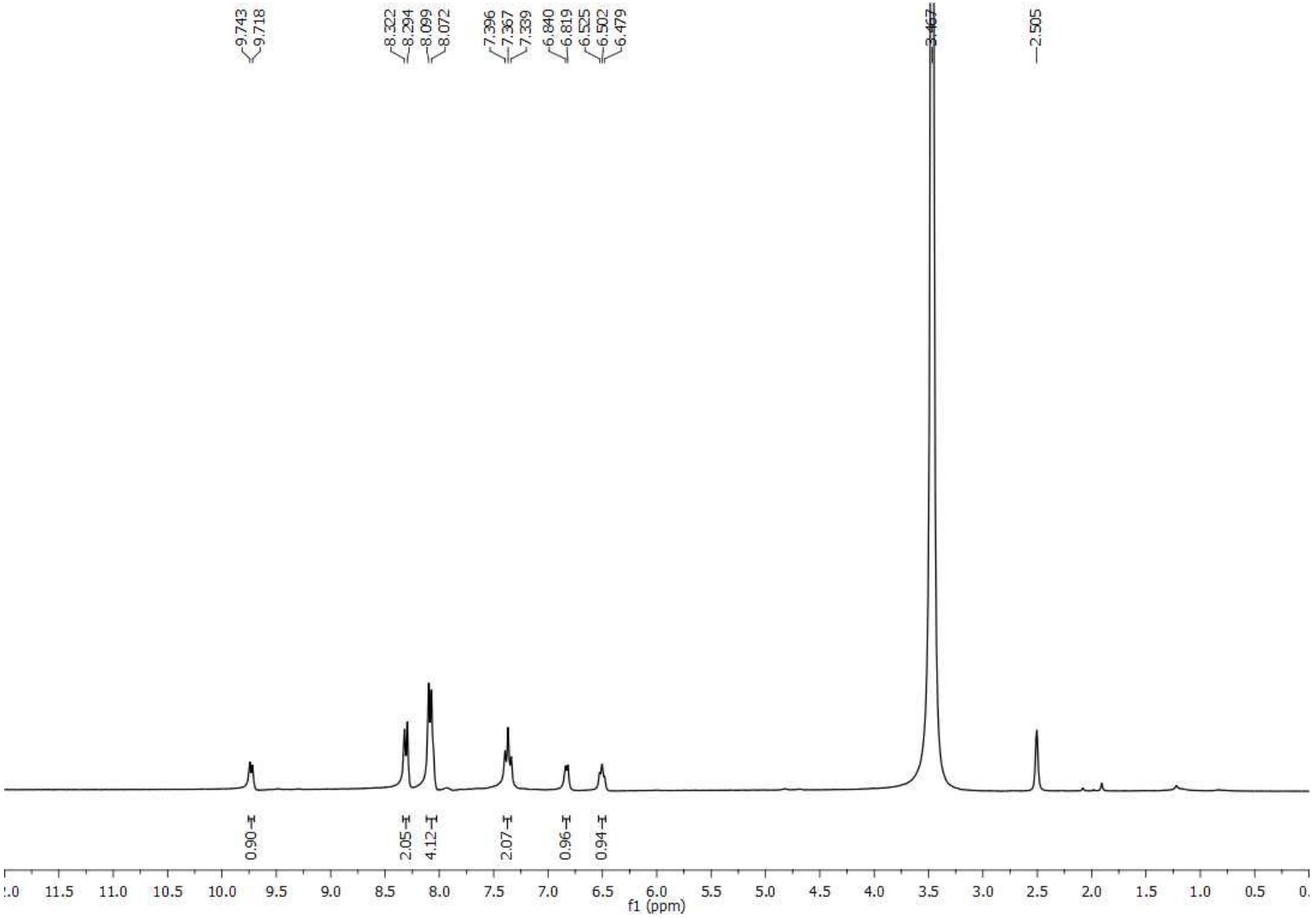


15. NMR titration of compound (3de)

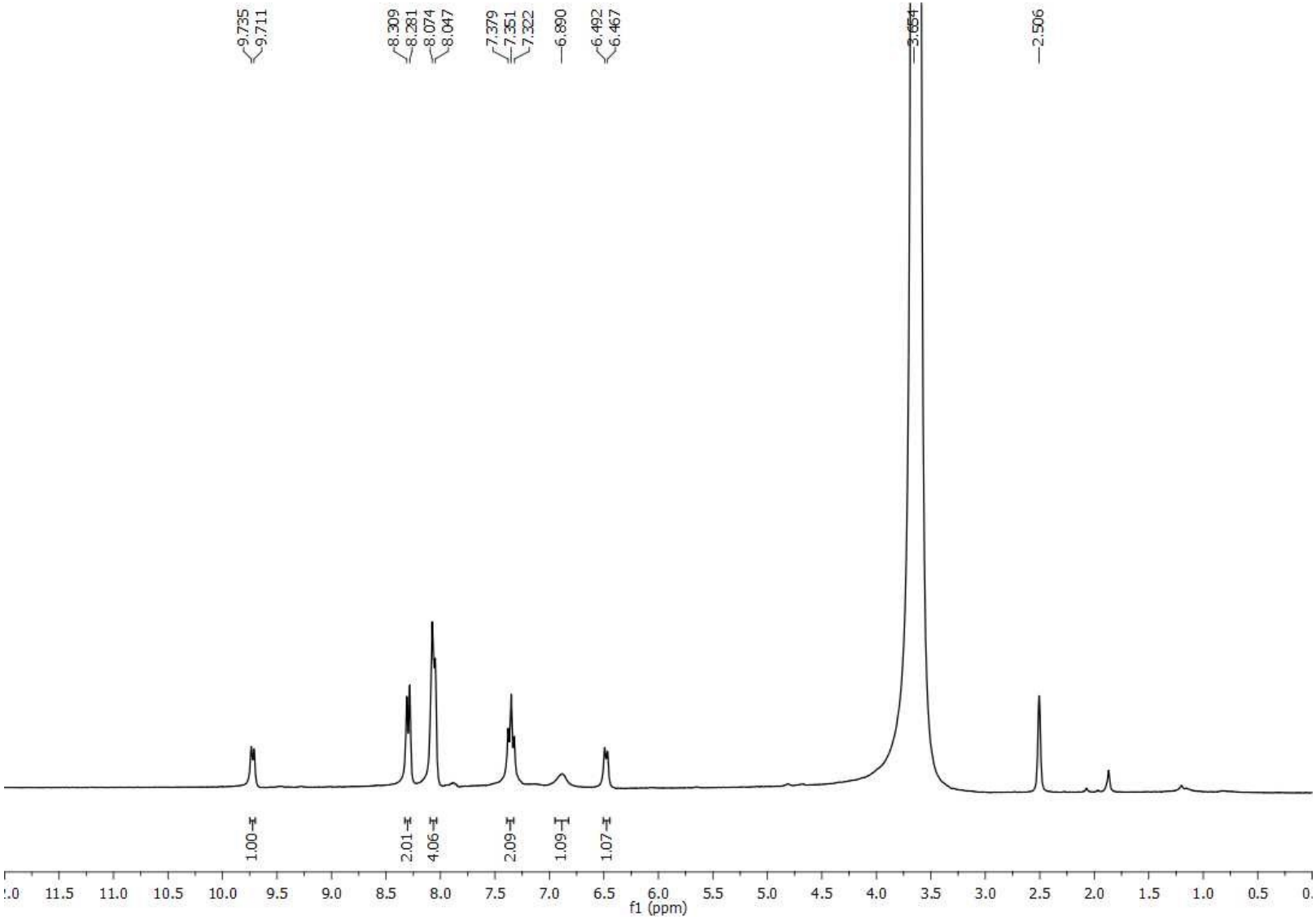
NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with acetate anion
After addition of 10 *µ*l of acetate anion



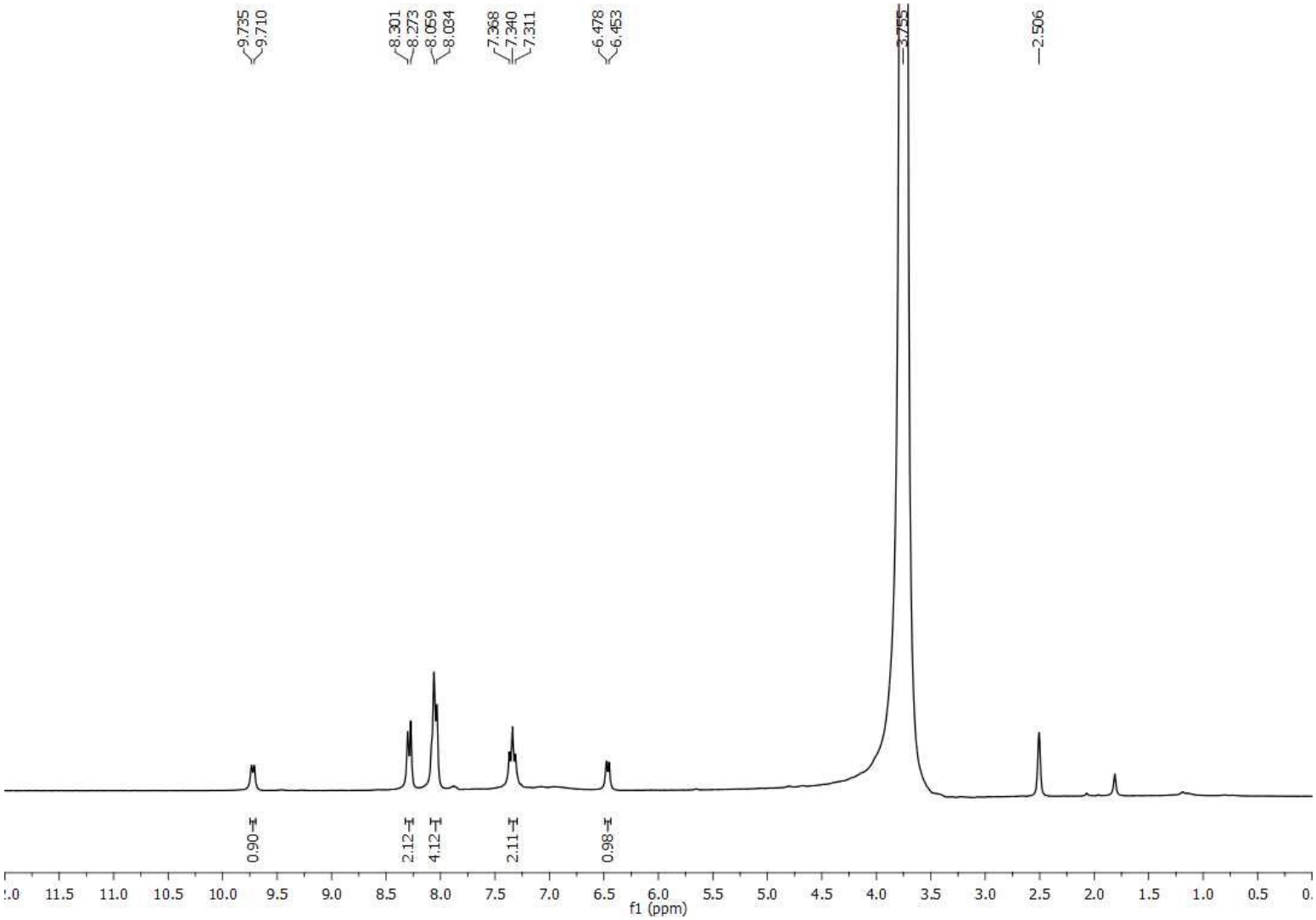
After addition of 20 *μ*l of acetate anion



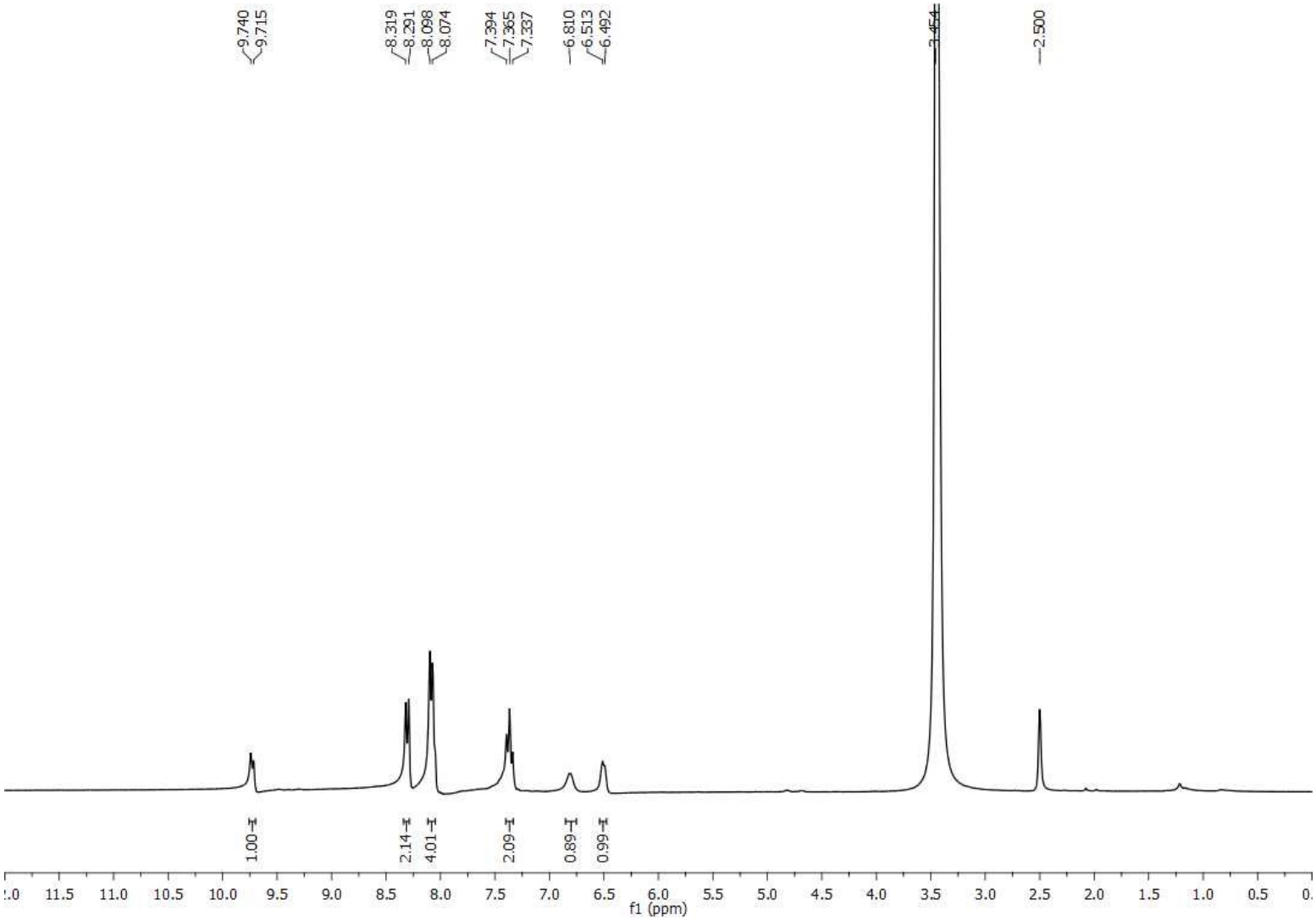
After addition of 30 *µ*l of acetate anion



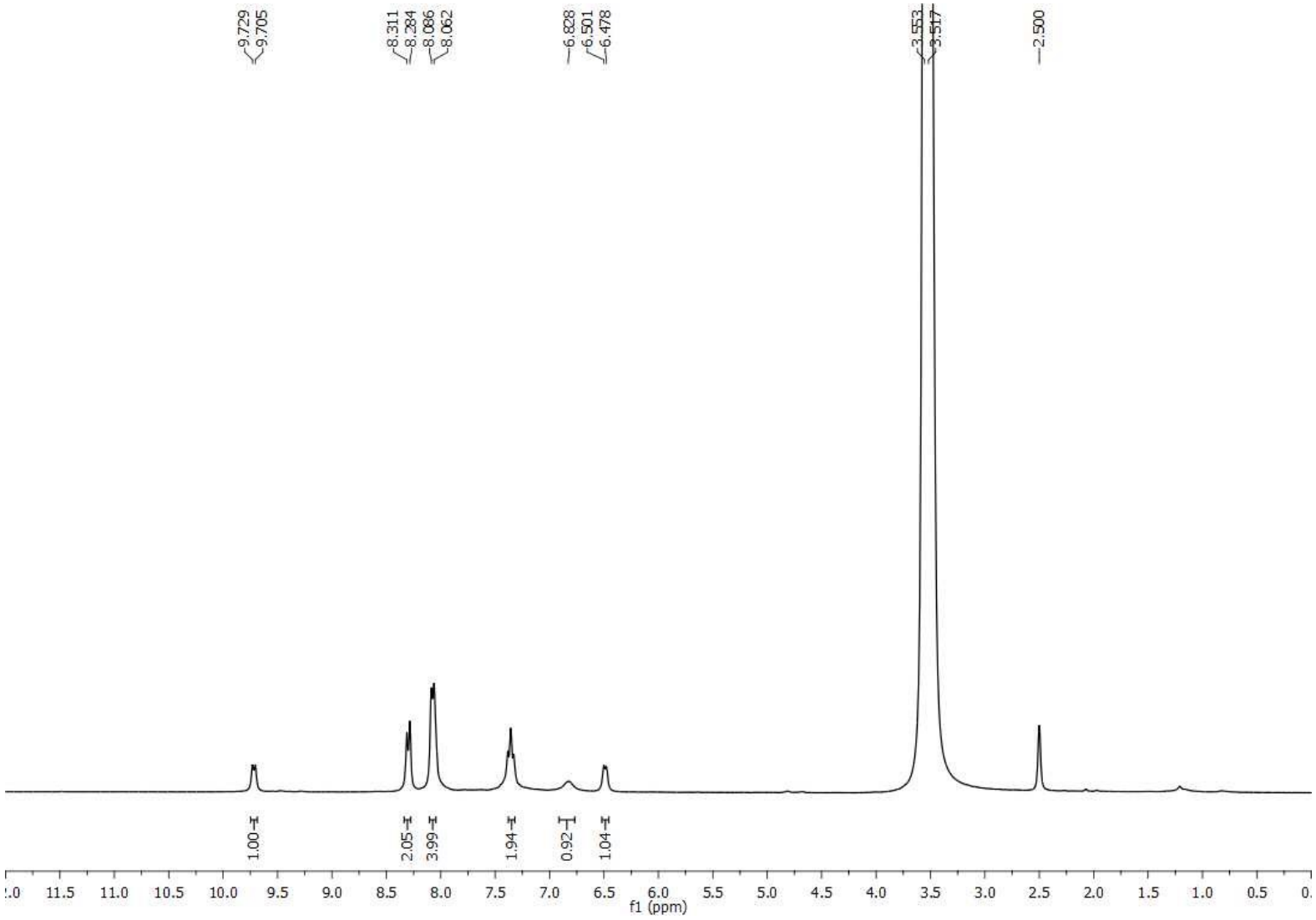
After addition of 40 *µ*l of acetate anion



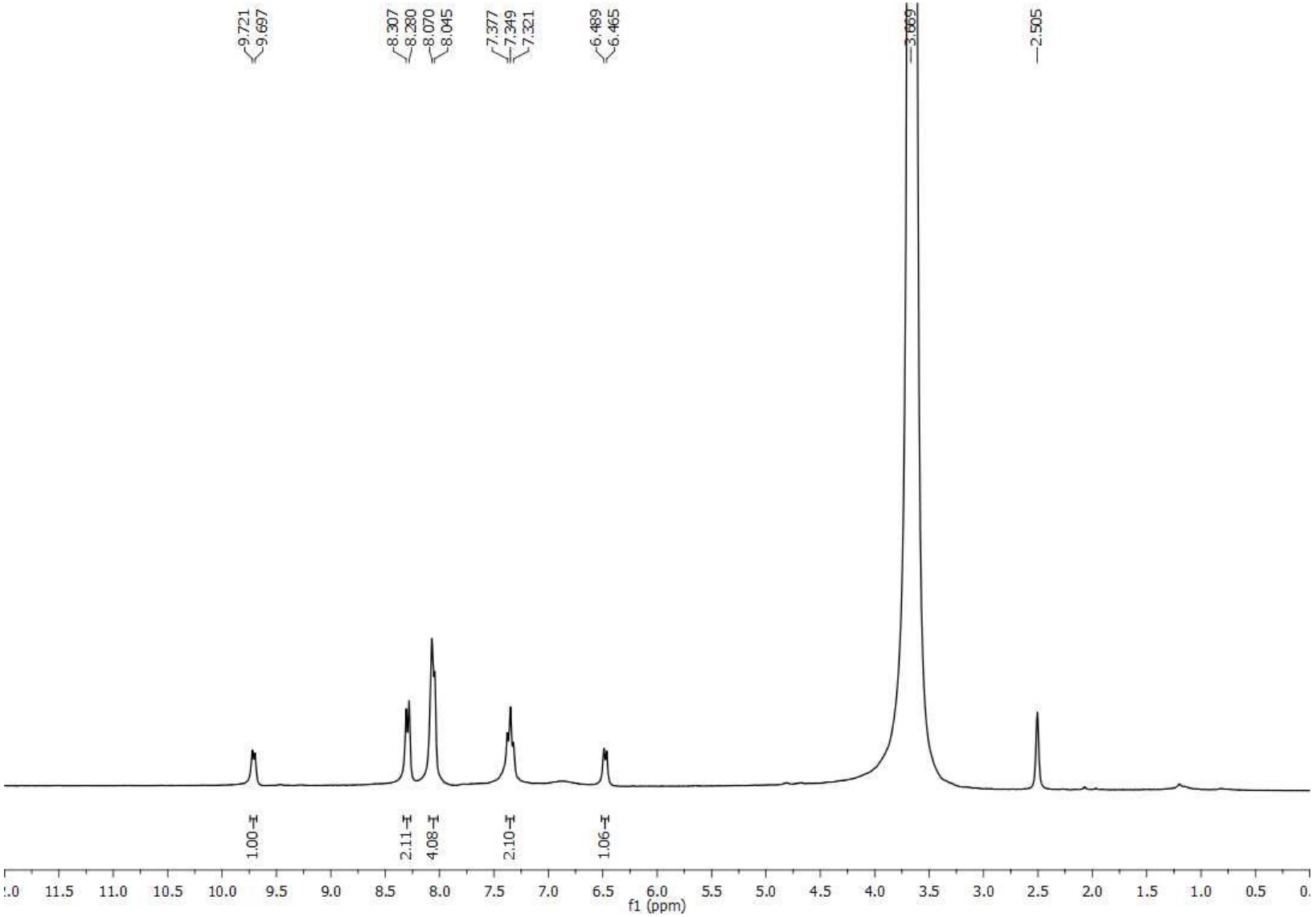
NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with chloride anion
After addition of 10 *µ*l of chloride anion



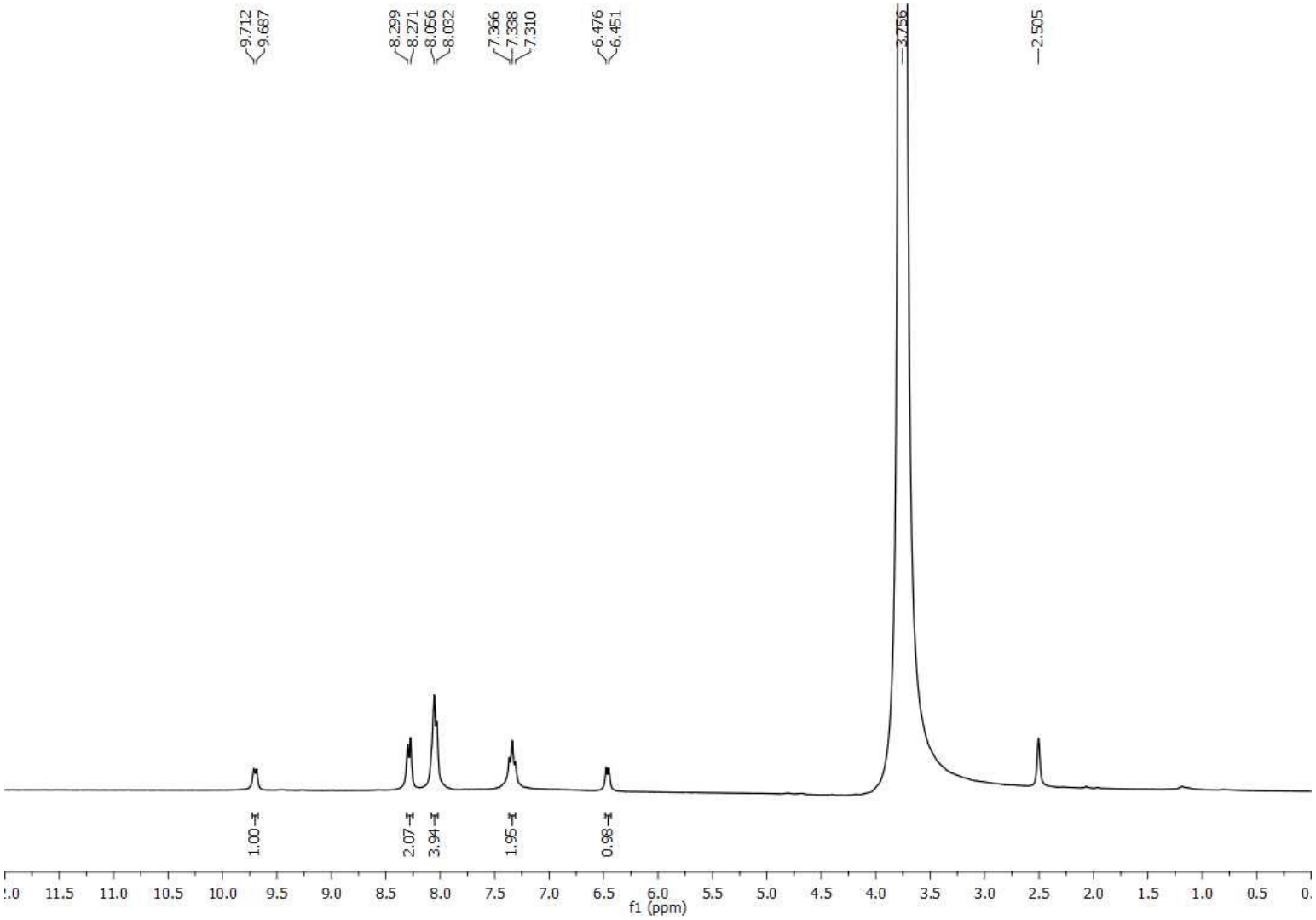
After addition of 20 *μ*l of chloride anion



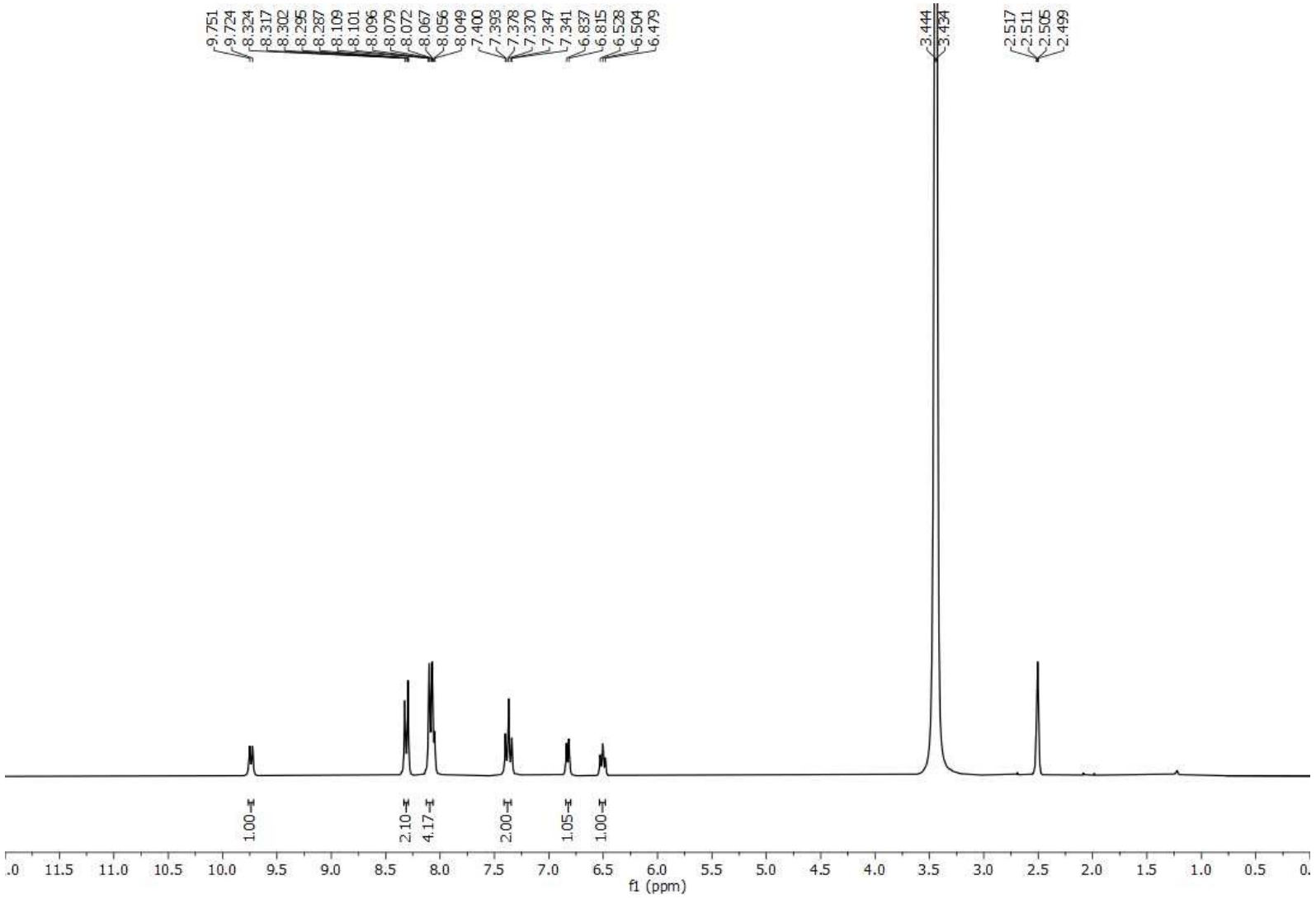
After addition of 30 *μ*l of chloride anion



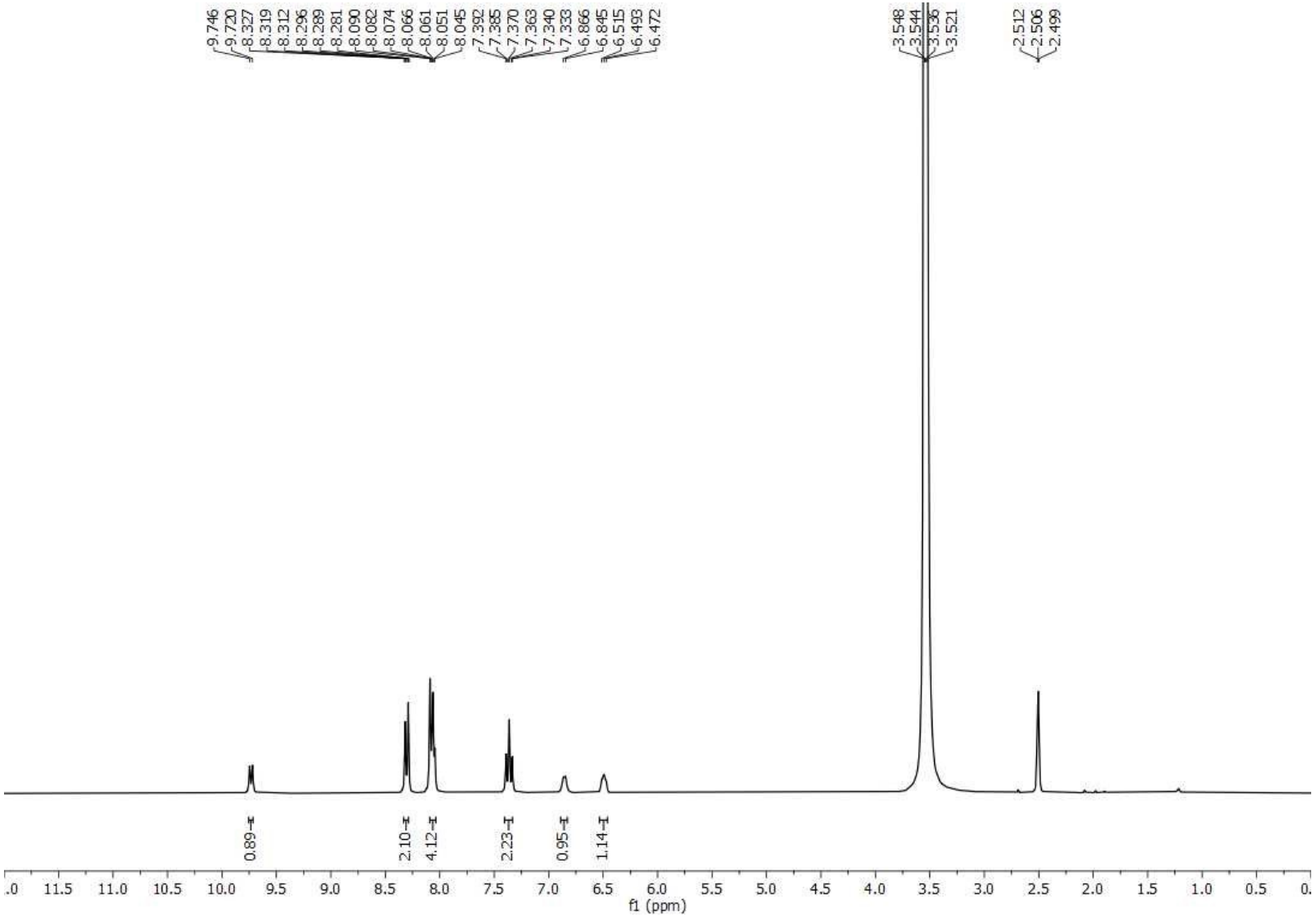
After addition of 40 *µ*l of chloride anion



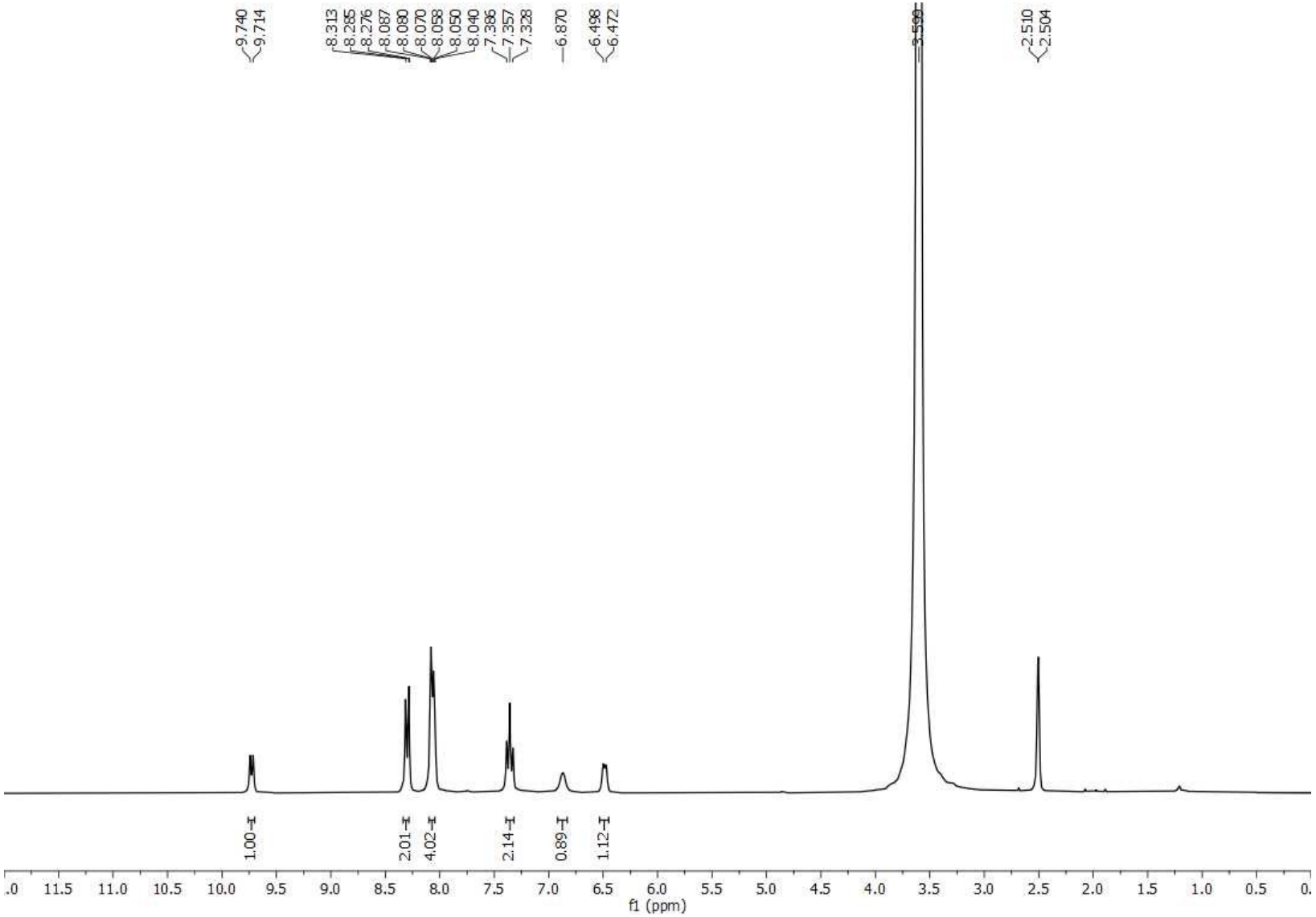
NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with cyanide anion
After addition of 10 *μ*l of cyanide anion



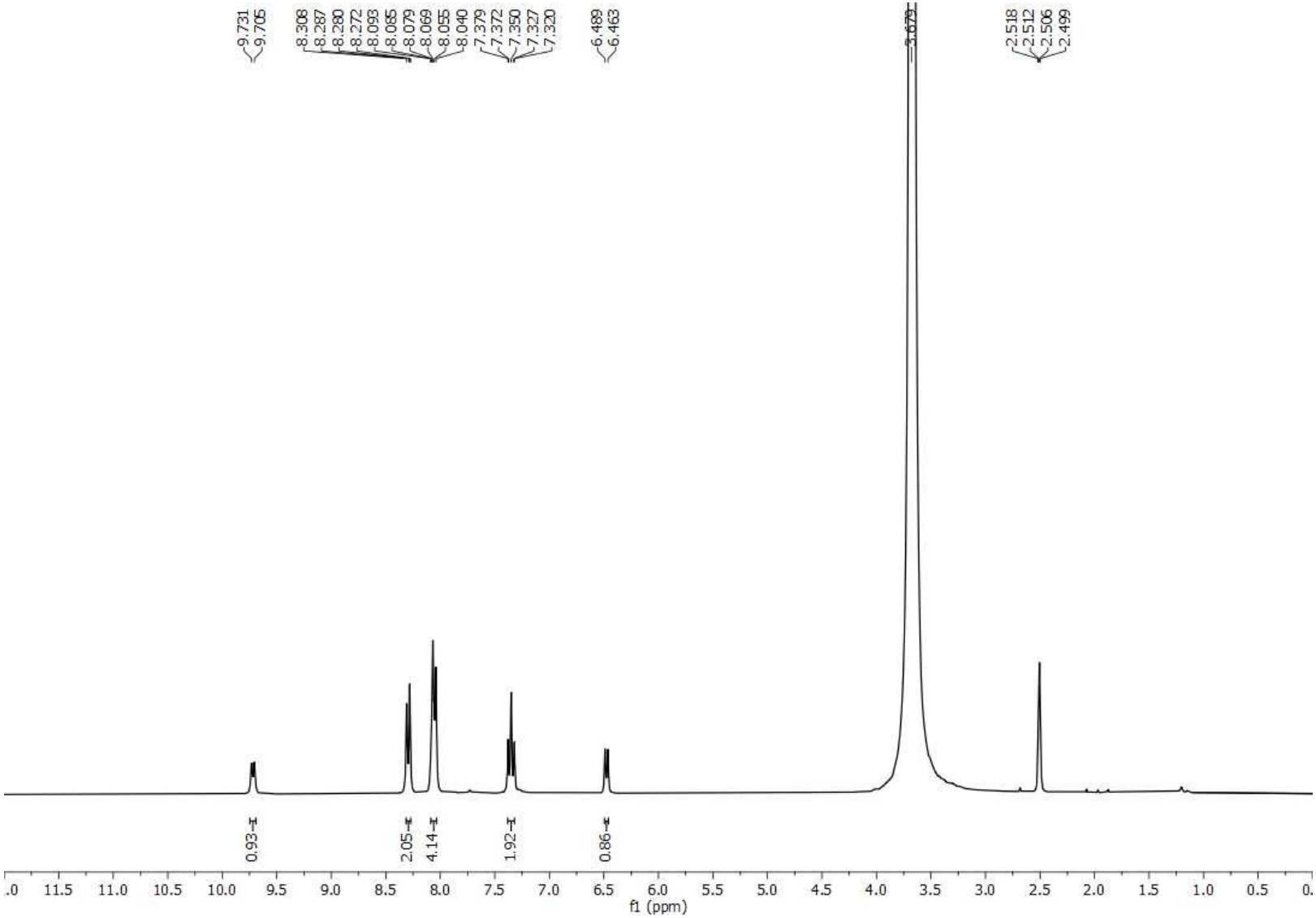
After addition of 20 *μ*l of cyanide anion



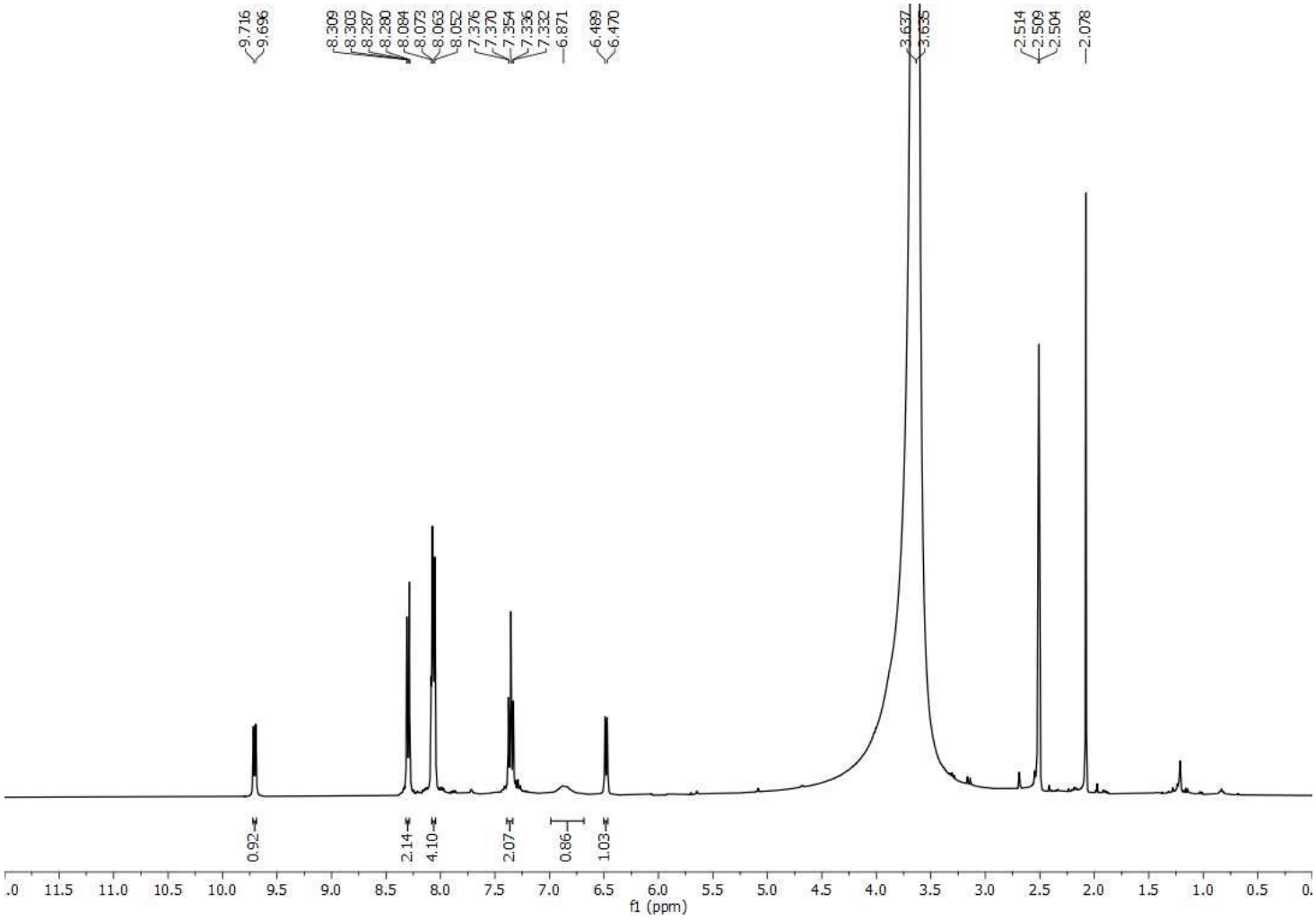
After addition of 30 *μ*l of cyanide anion



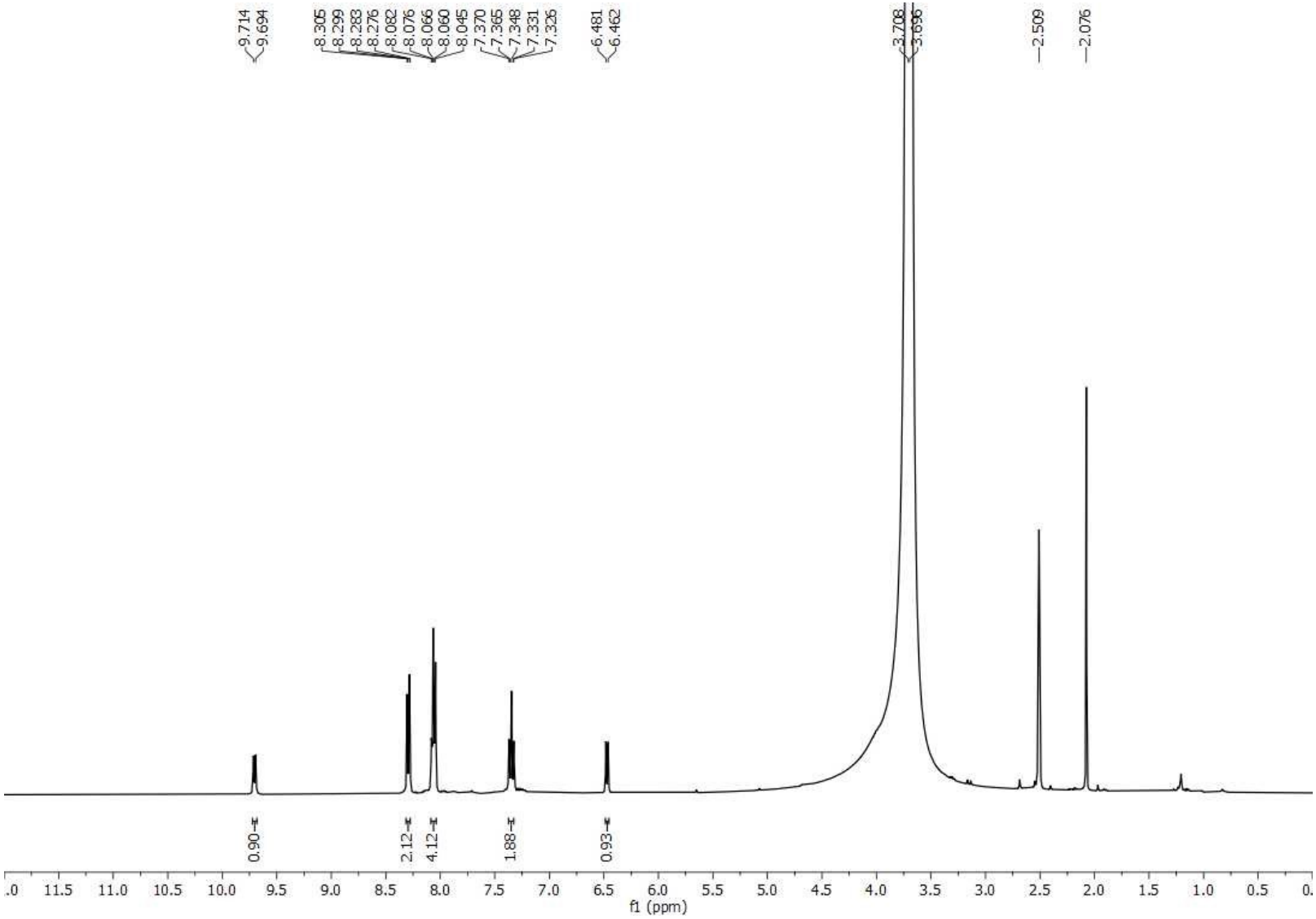
After addition of 40 *μ*l of cyanide anion



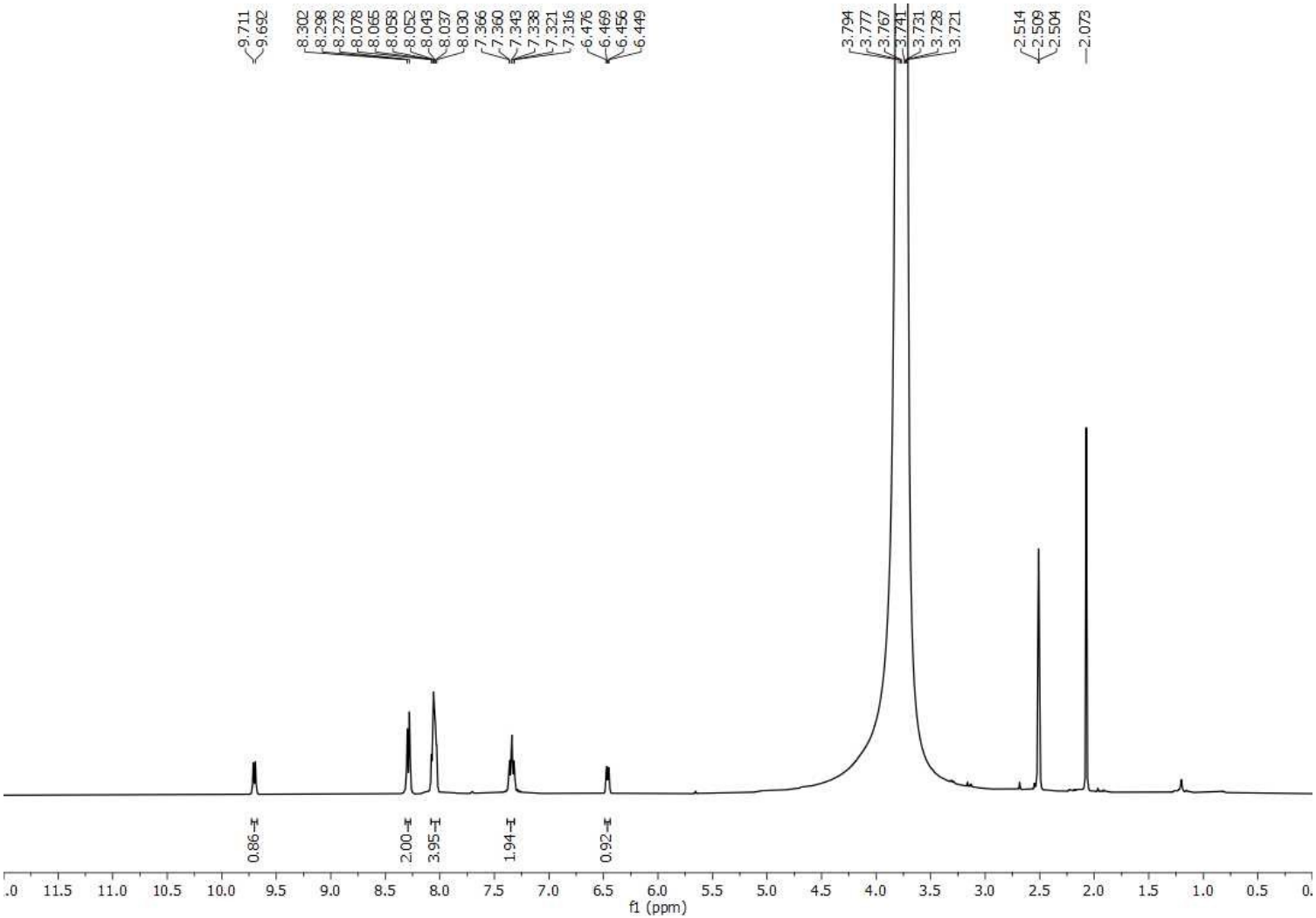
NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with dihydrogen phosphate anion
After addition of 10 *μ*l of dihydrogen phosphate anion



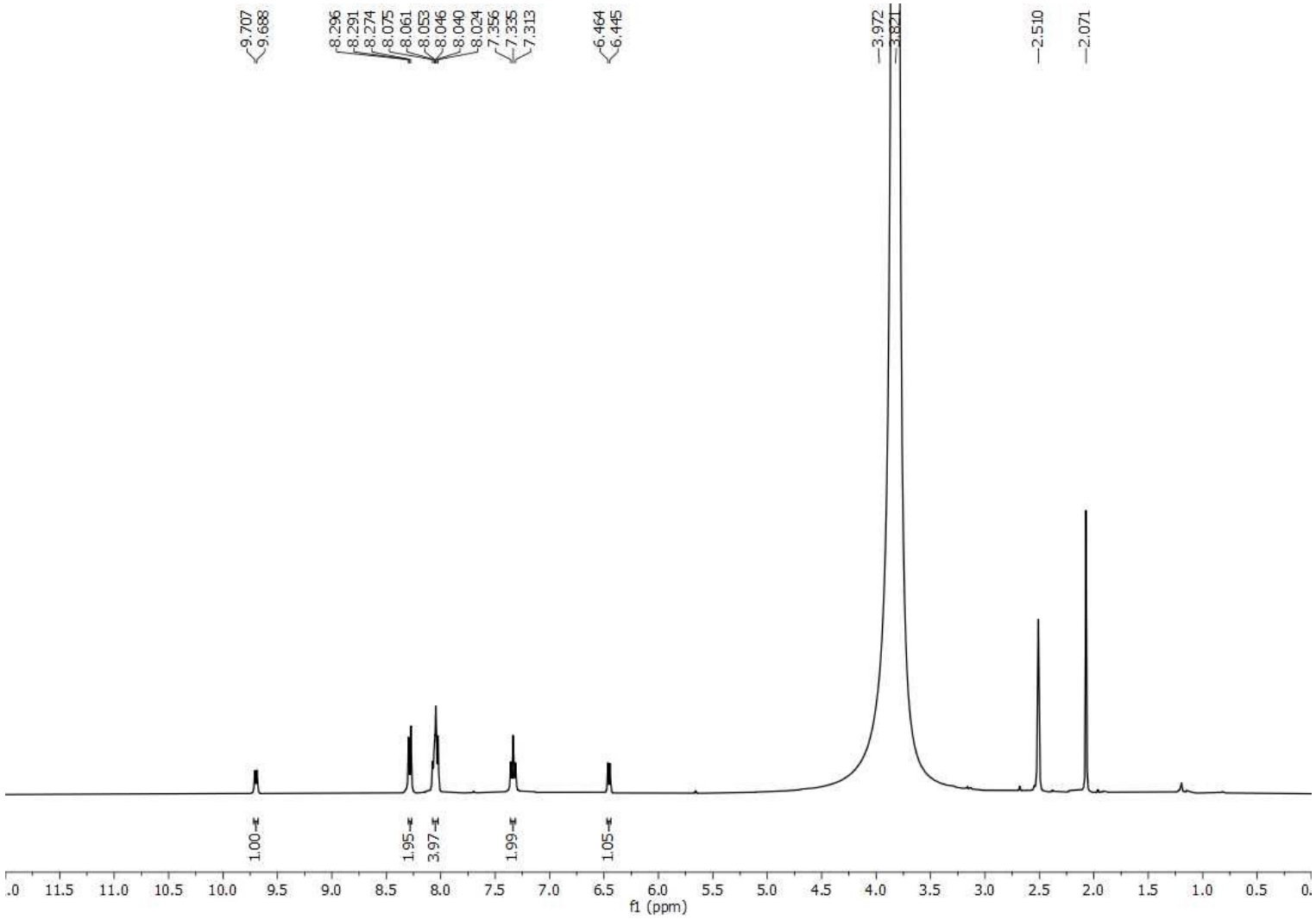
After addition of 20 *μ*l of dihydrogen phosphate anion



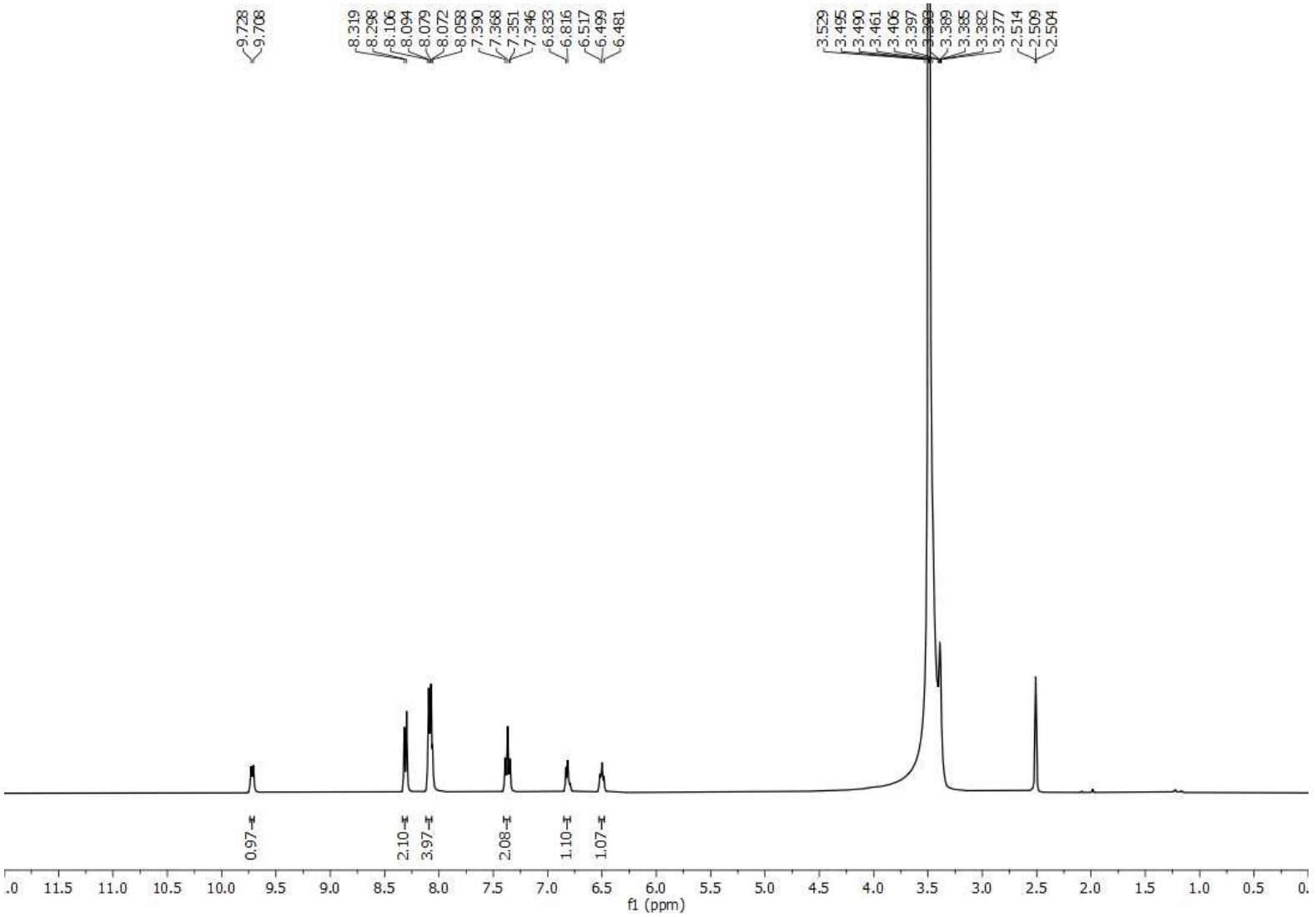
After addition of 30 *µ*l of dihydrogen phosphate anion



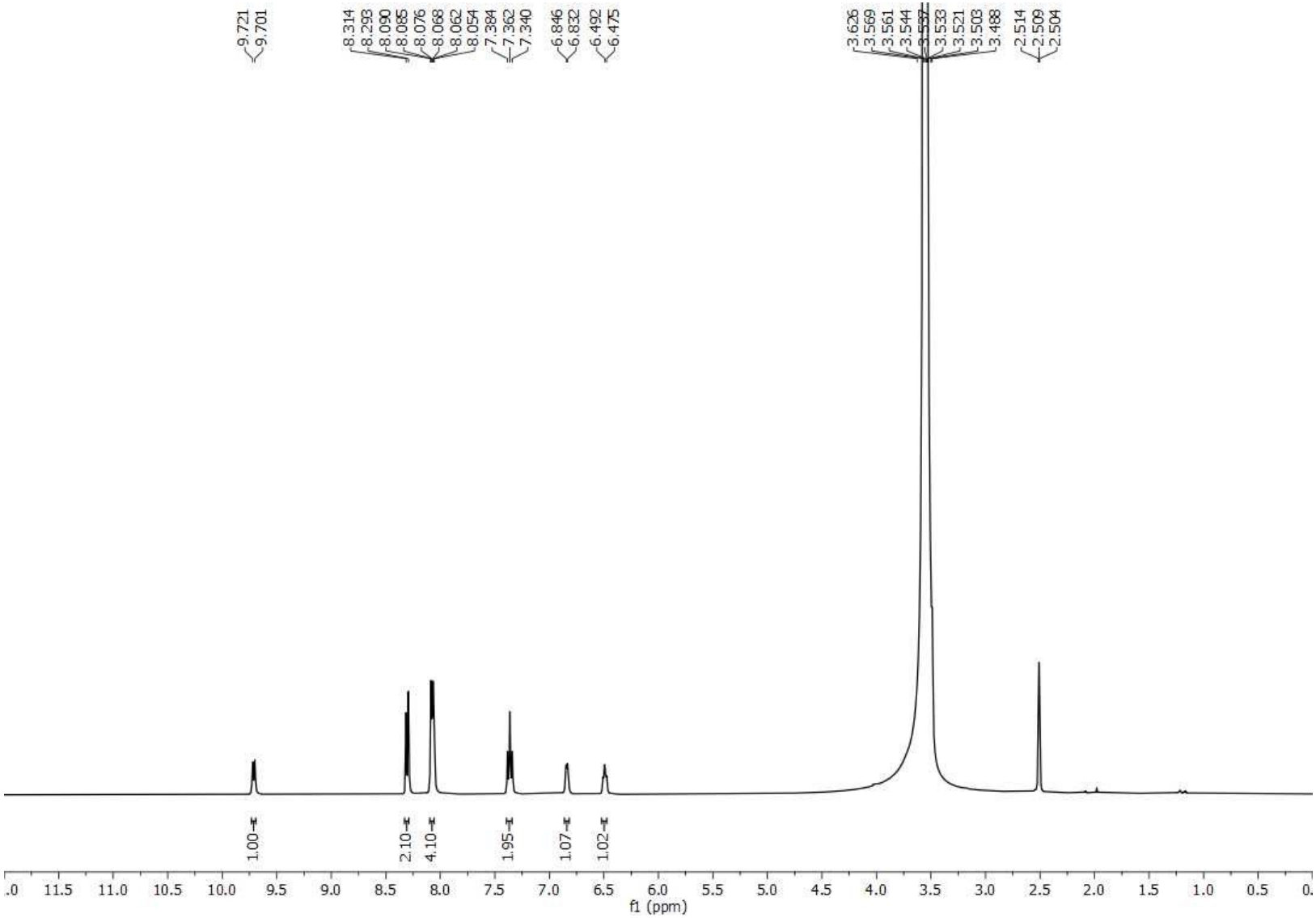
After addition of 40 *µ*l of dihydrogen phosphate anion



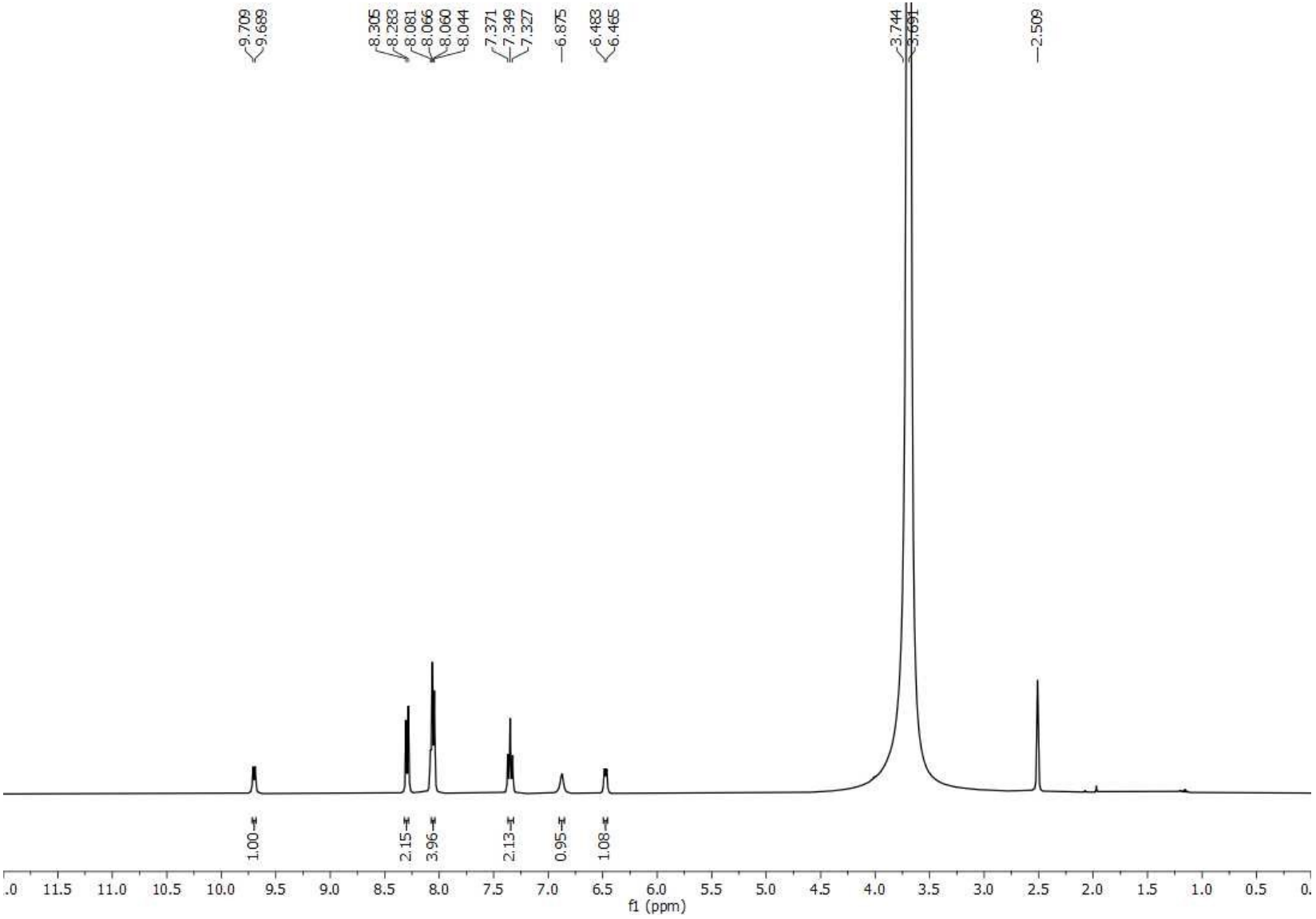
NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with fluoride anion
After addition of 10 *μ*l of fluoride anion



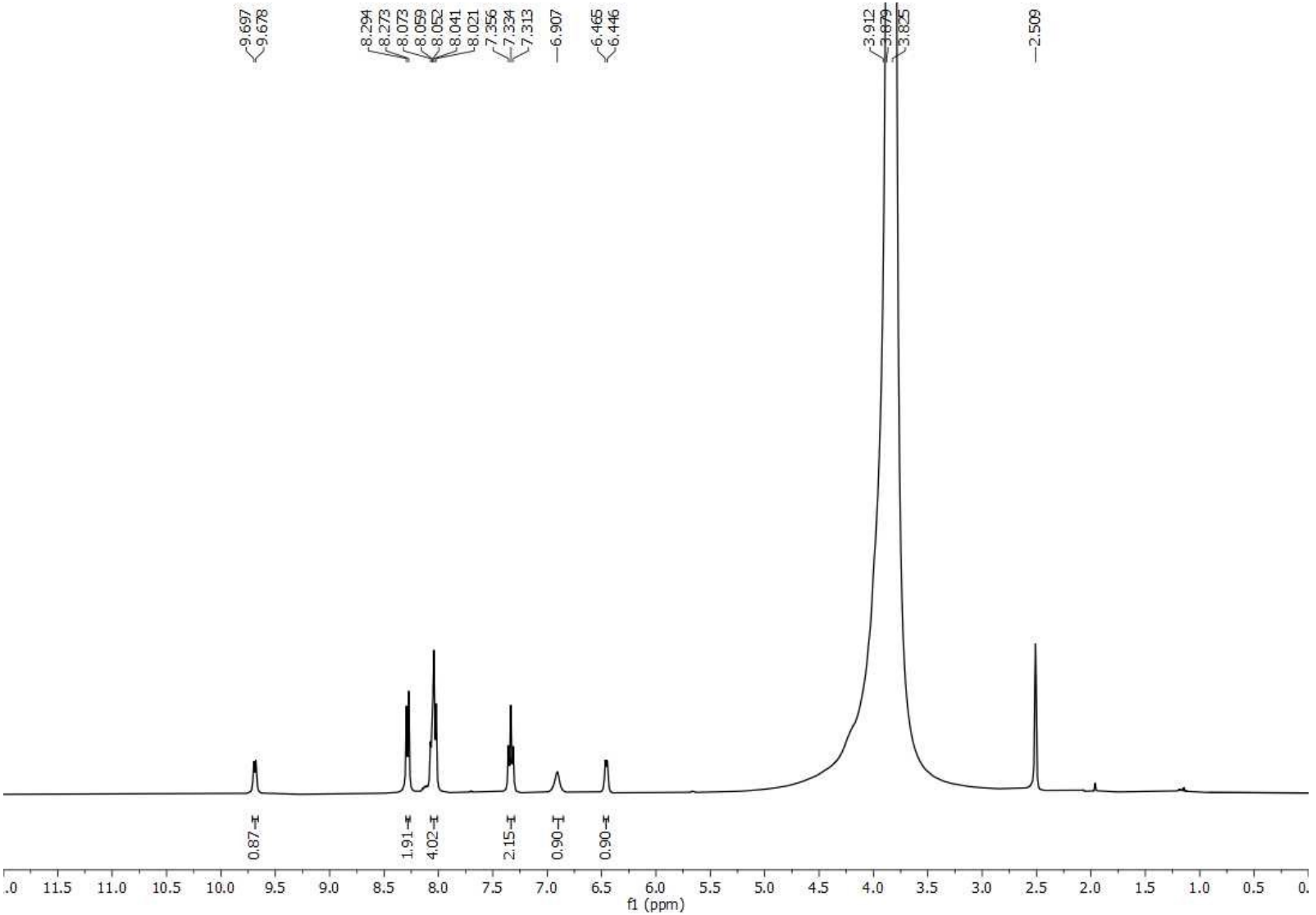
After addition of 20 *μ*l of fluoride anion



After addition of 30 *μ*l of fluoride anion

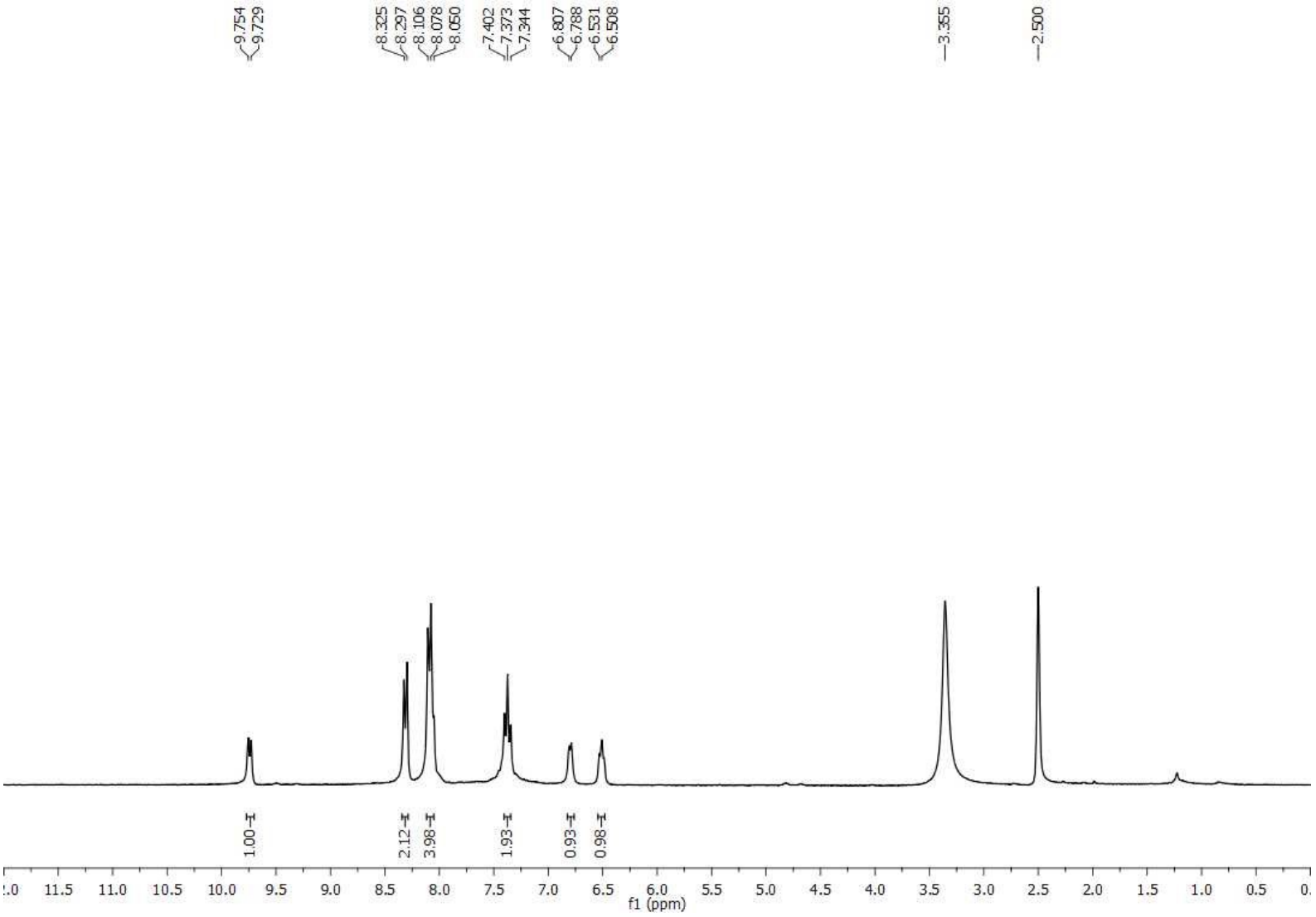


After addition of 40 *μ*l of fluoride anion

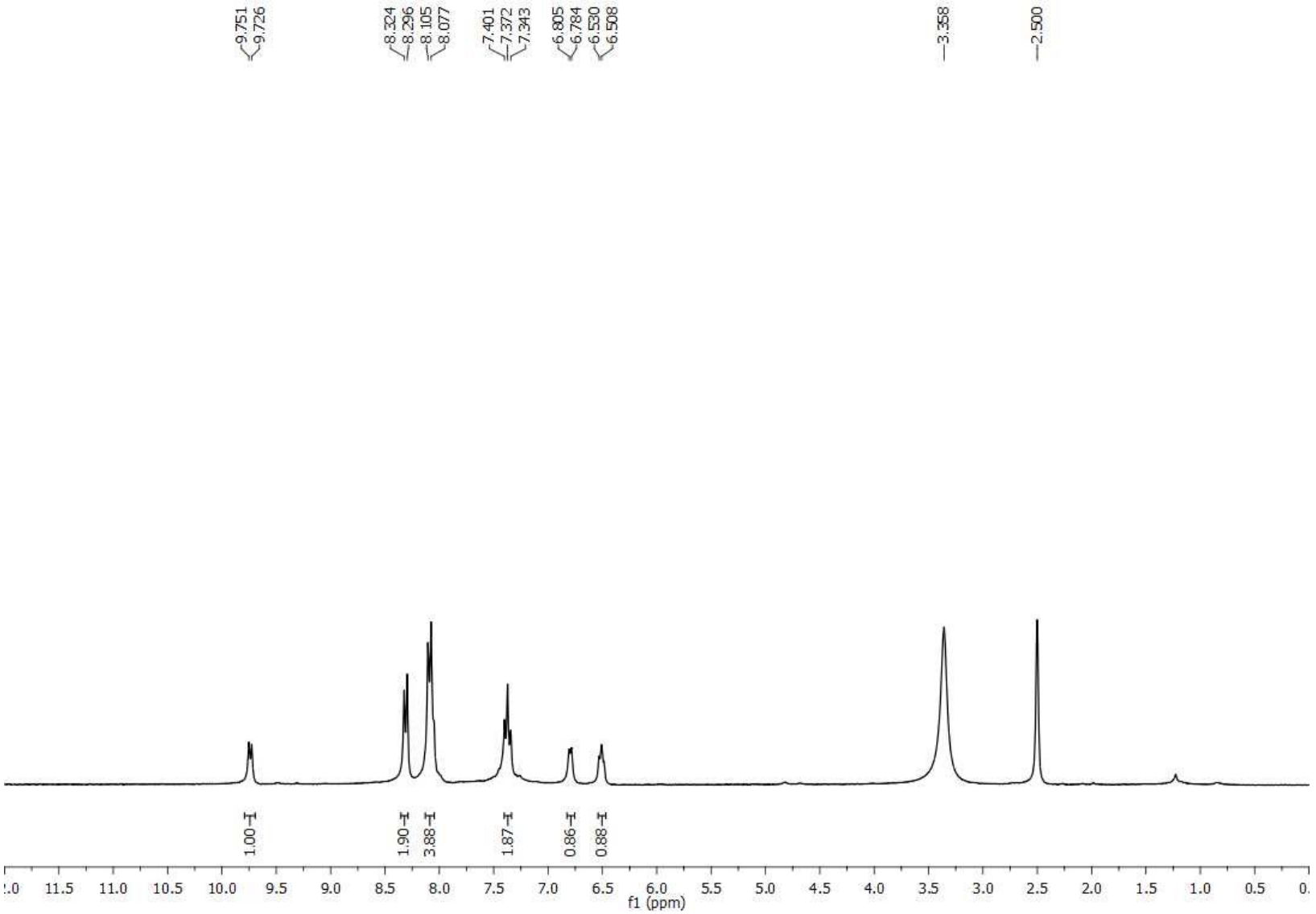


NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with adenine

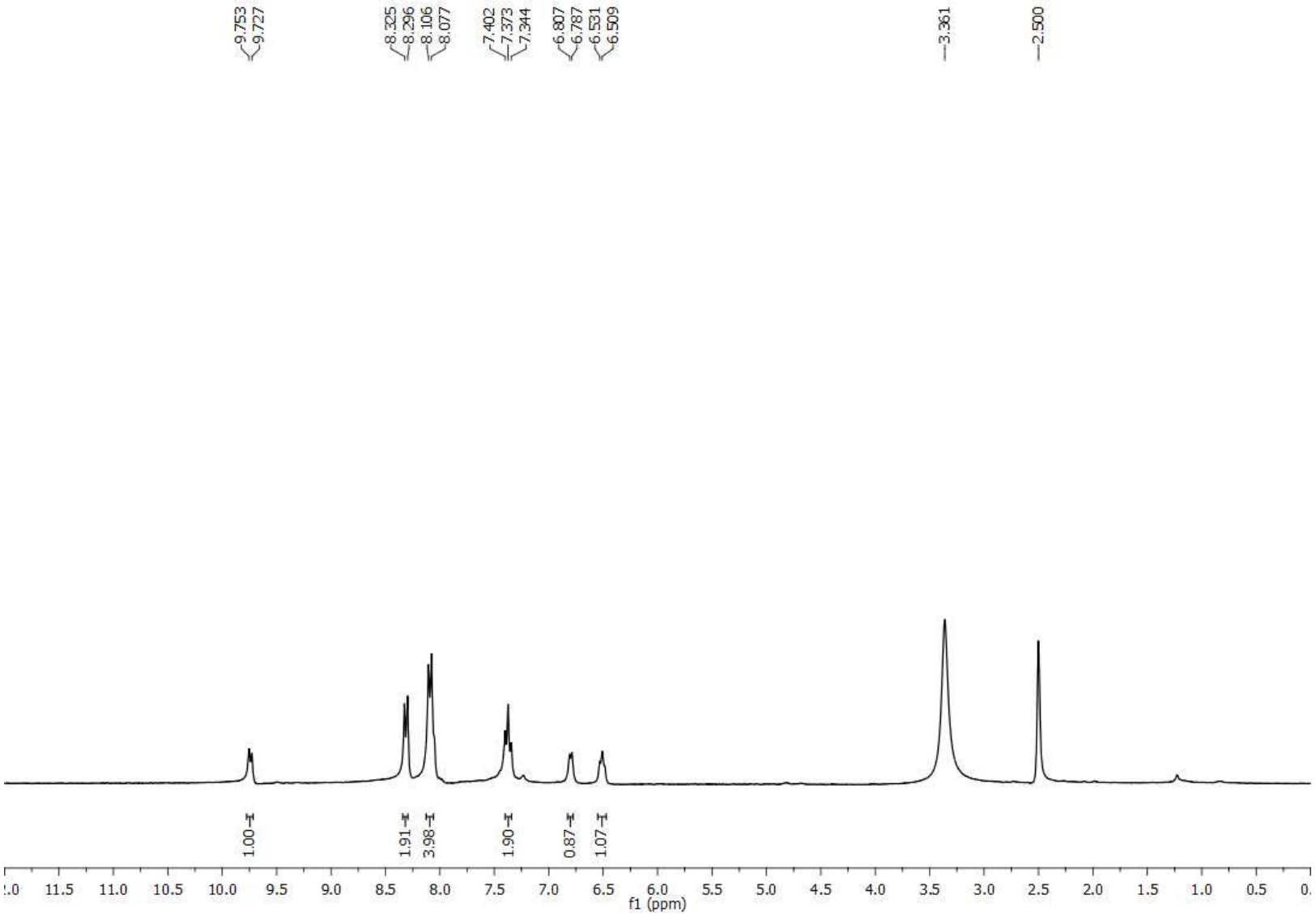
After addition of 10 *µ*l of adenine



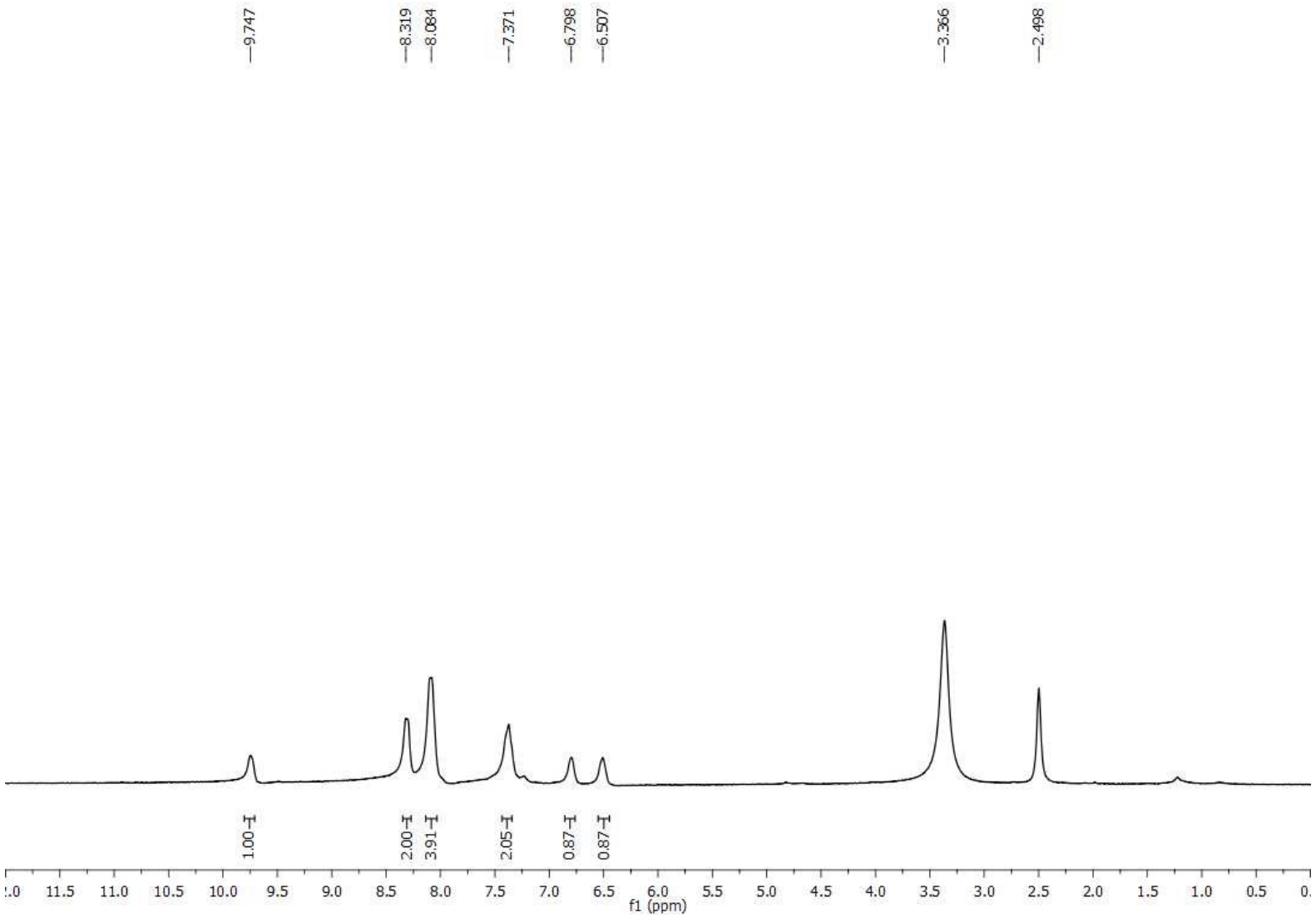
After addition of 20 *µ*l of adenine



After addition of 30 *µ*l of adenine

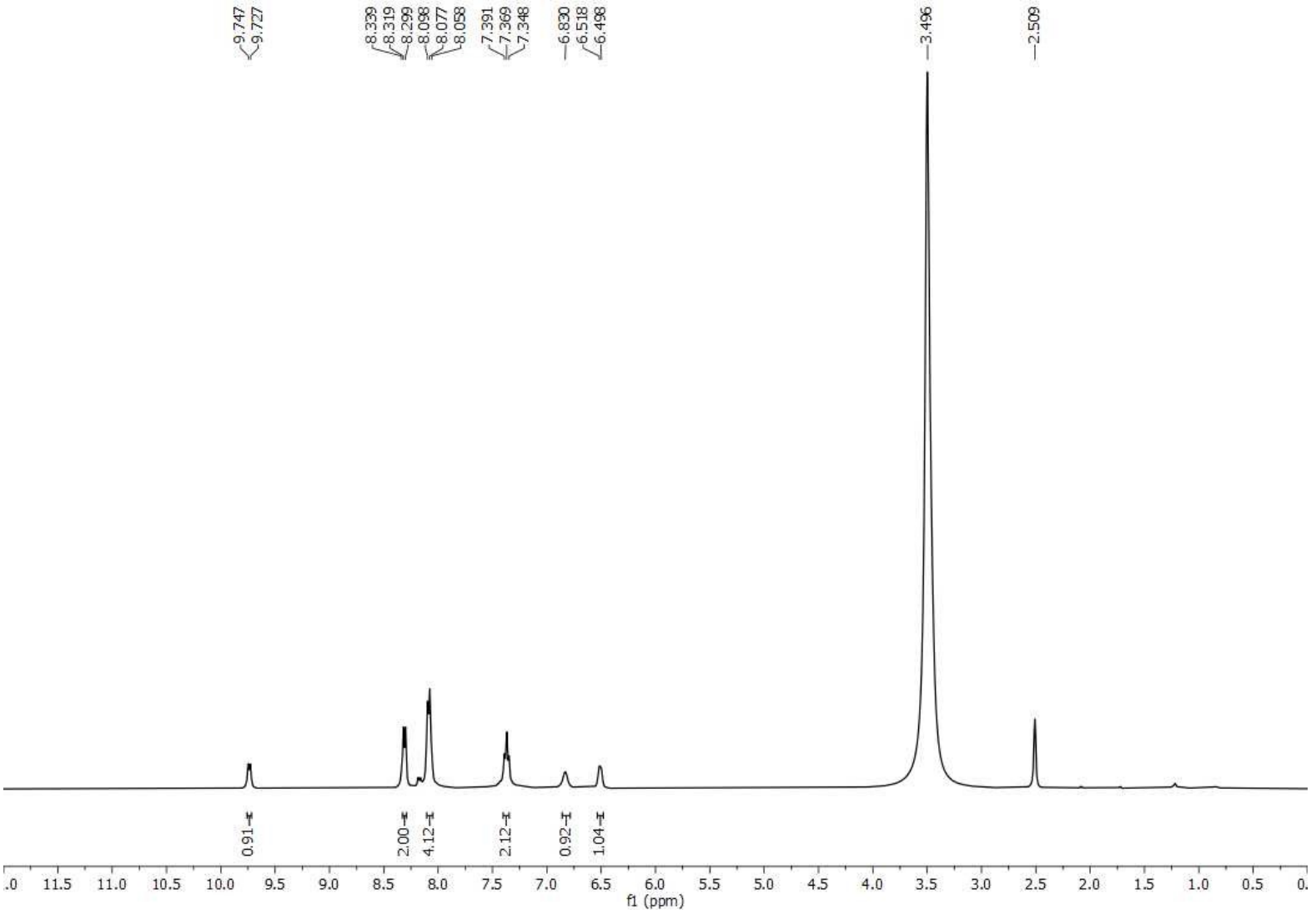


After addition of 40 *µ*l of adenine

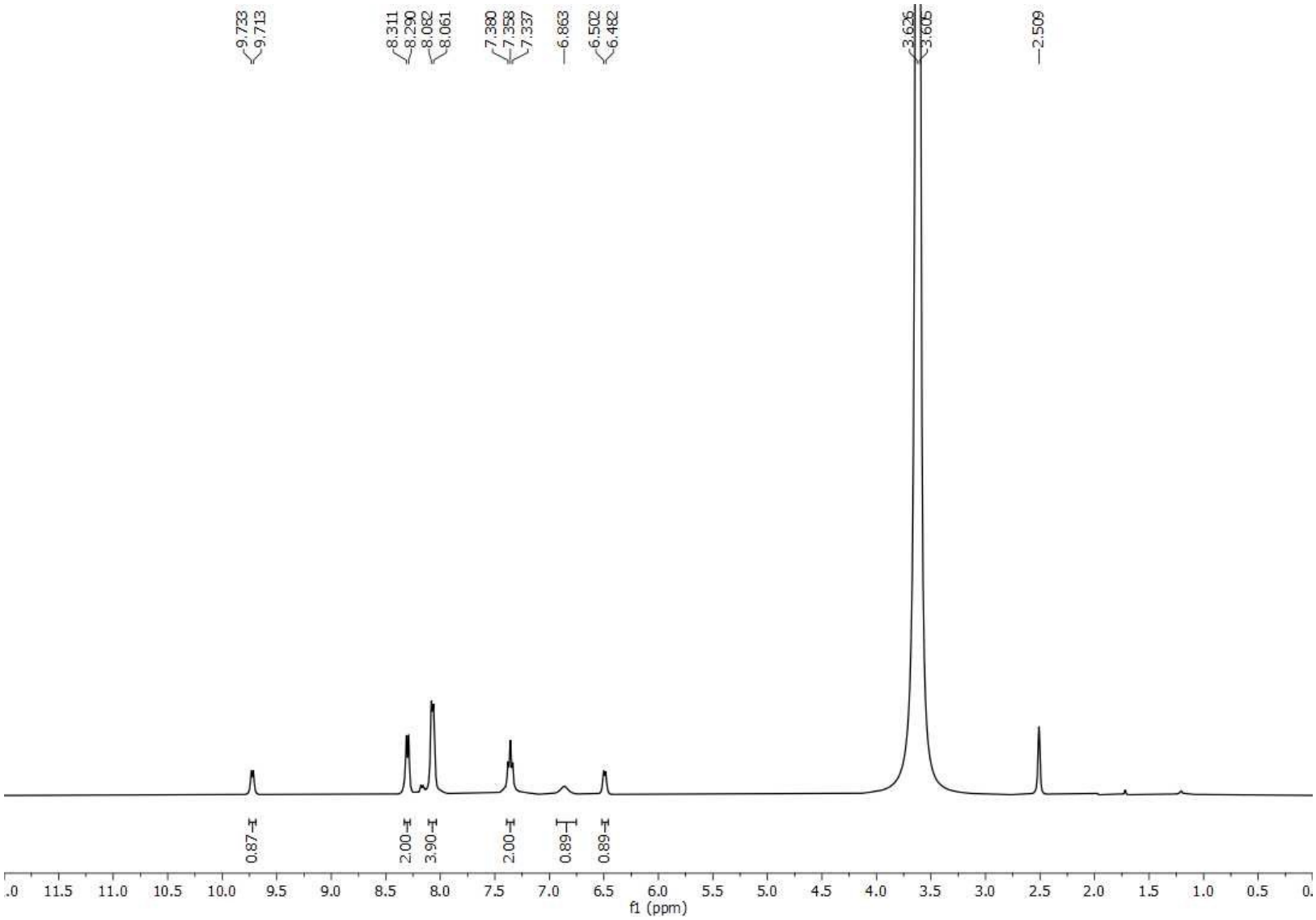


NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with thymine

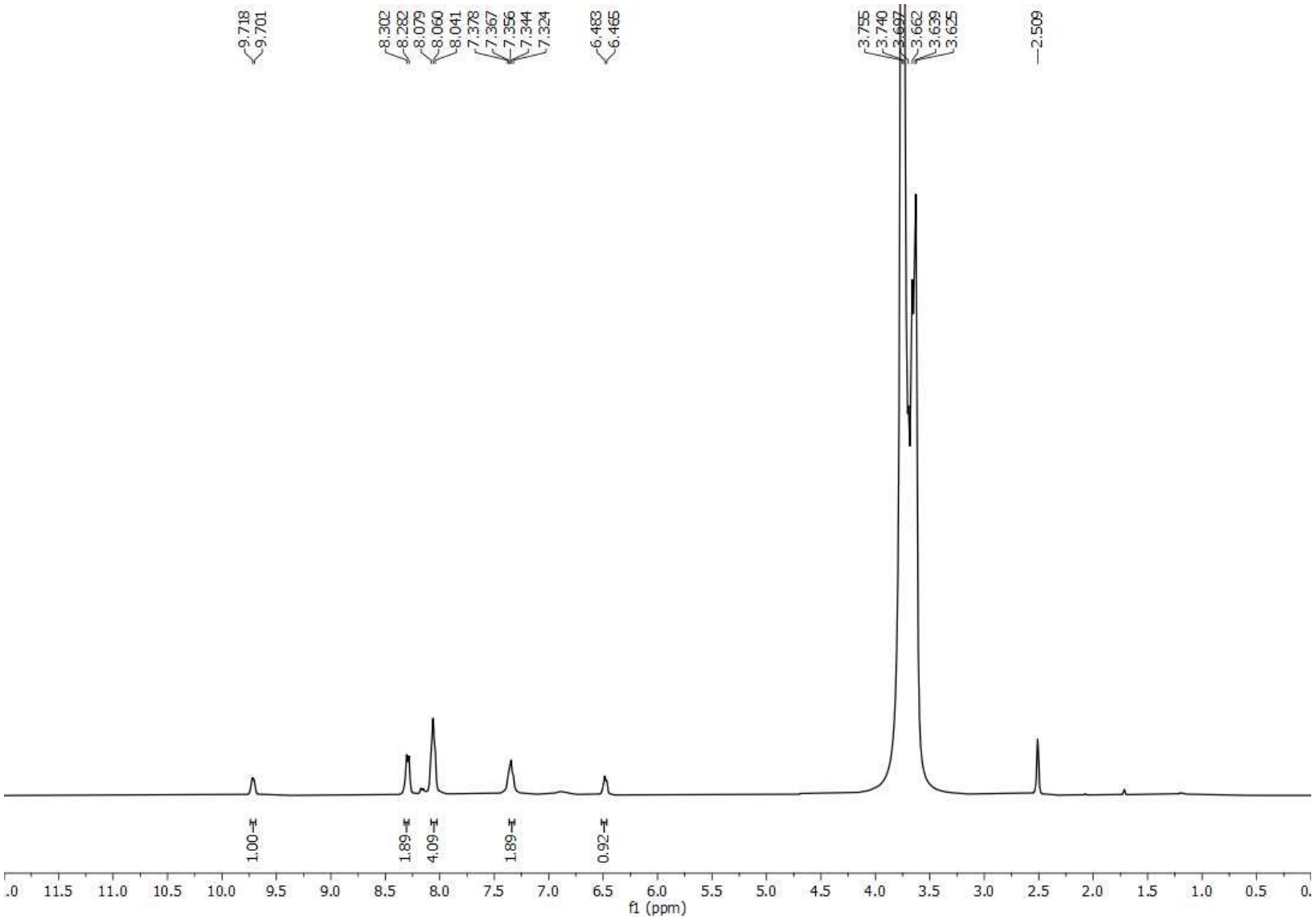
After addition of 10 *μ*l of thymine



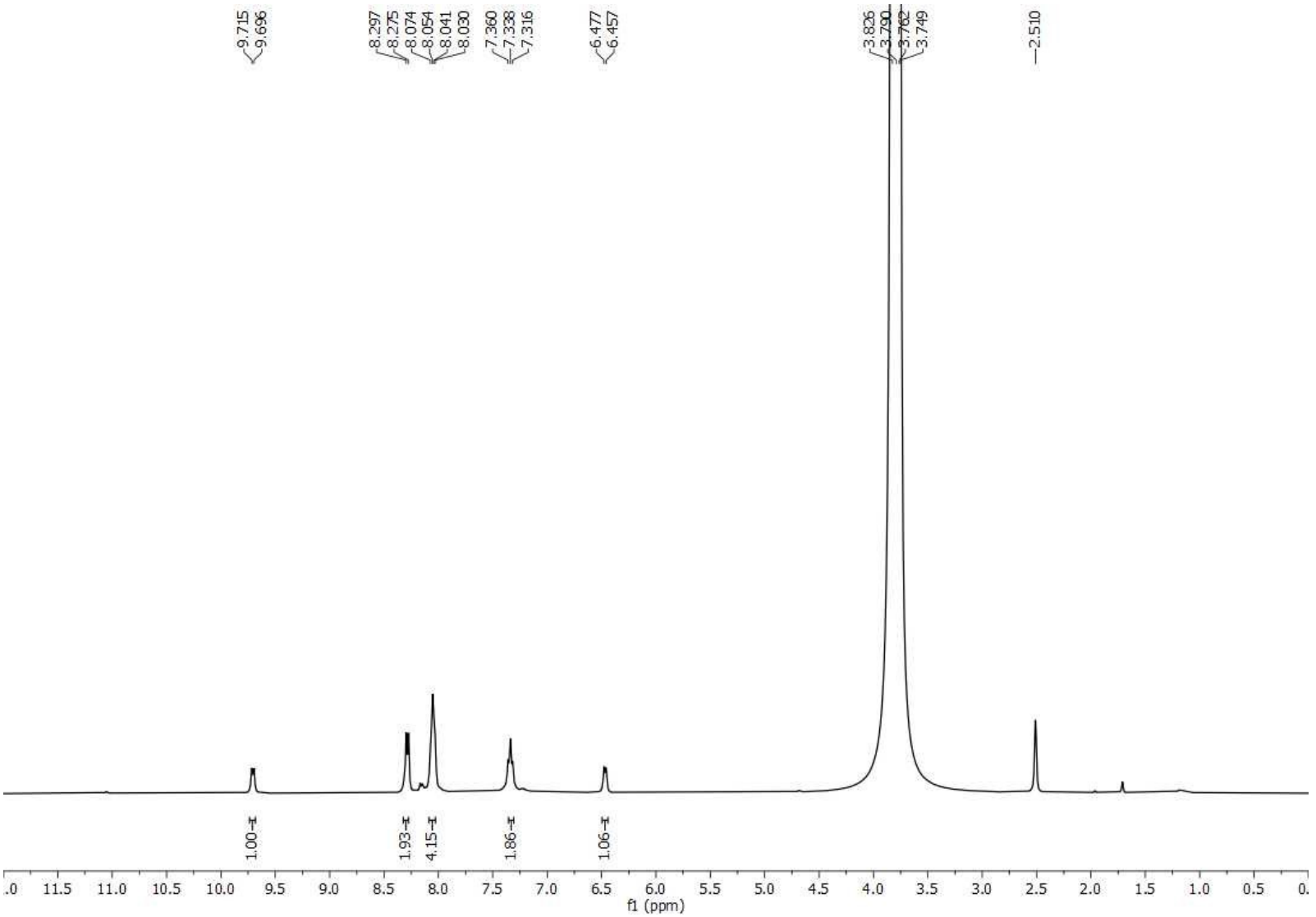
After addition of 20 *μ*l of thymine



After addition of 30 *μ*l of thymine

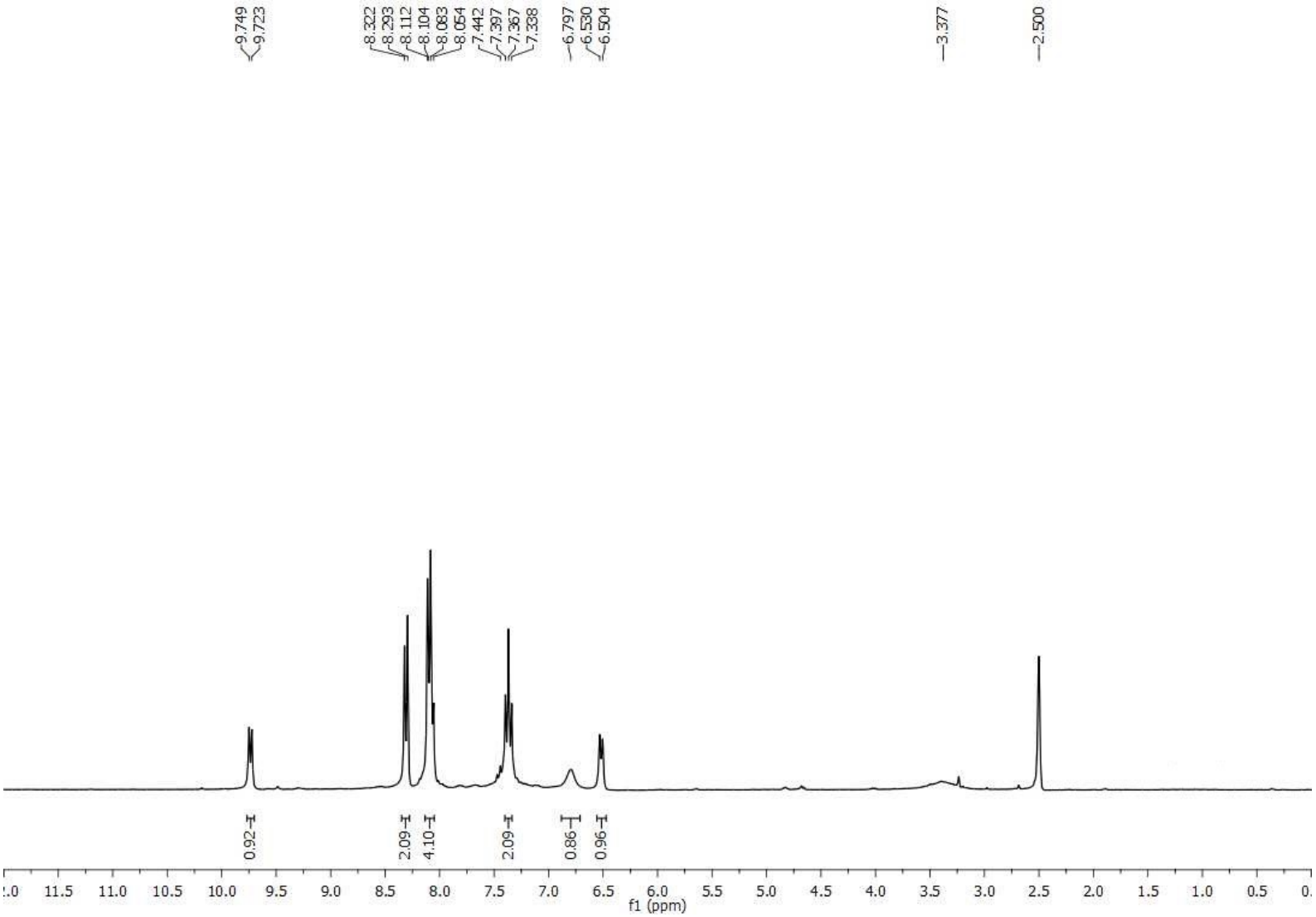


After addition of 40 *µ*l of thymine

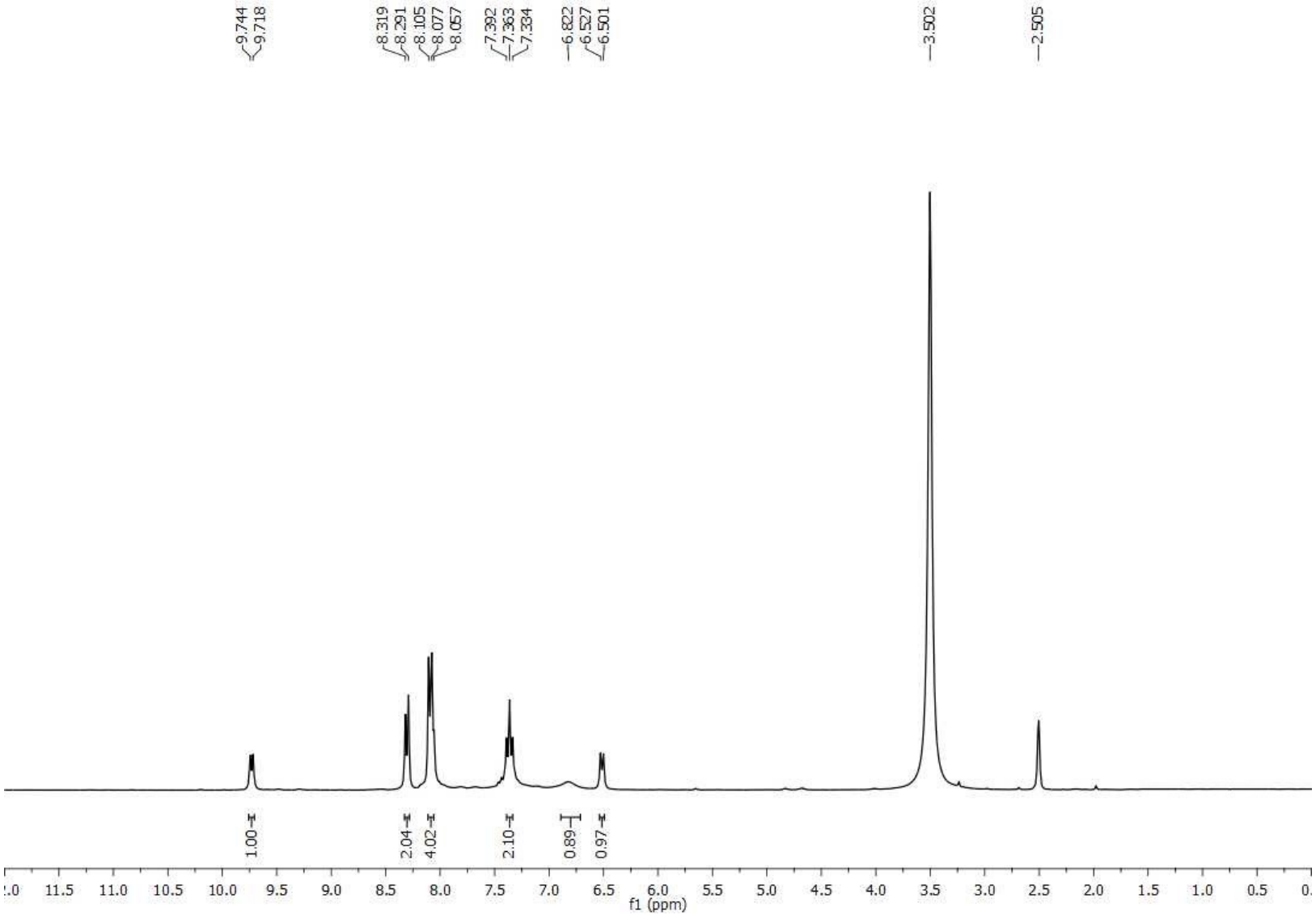


NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with uracil

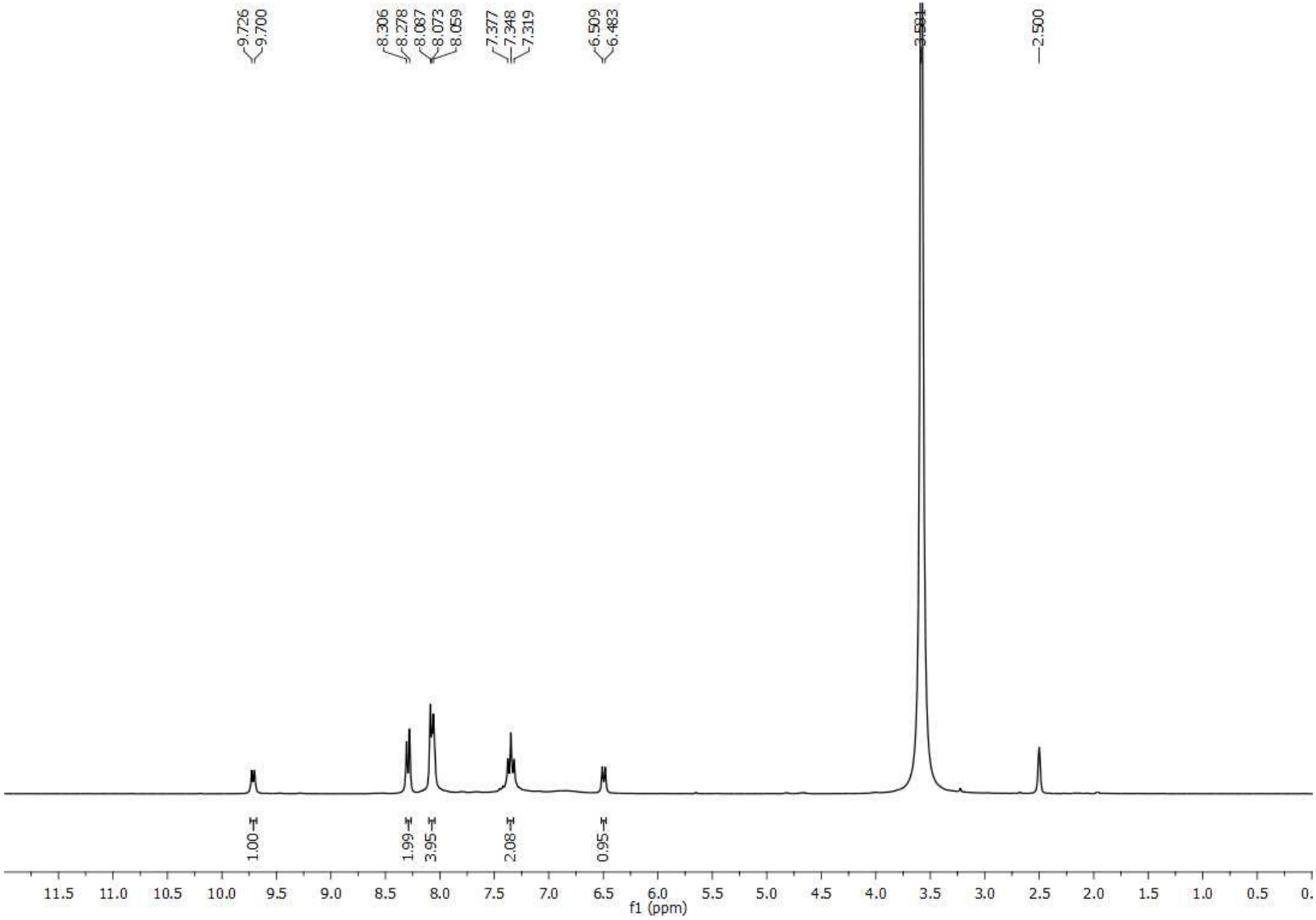
After addition of 10 *µ*l of uracil



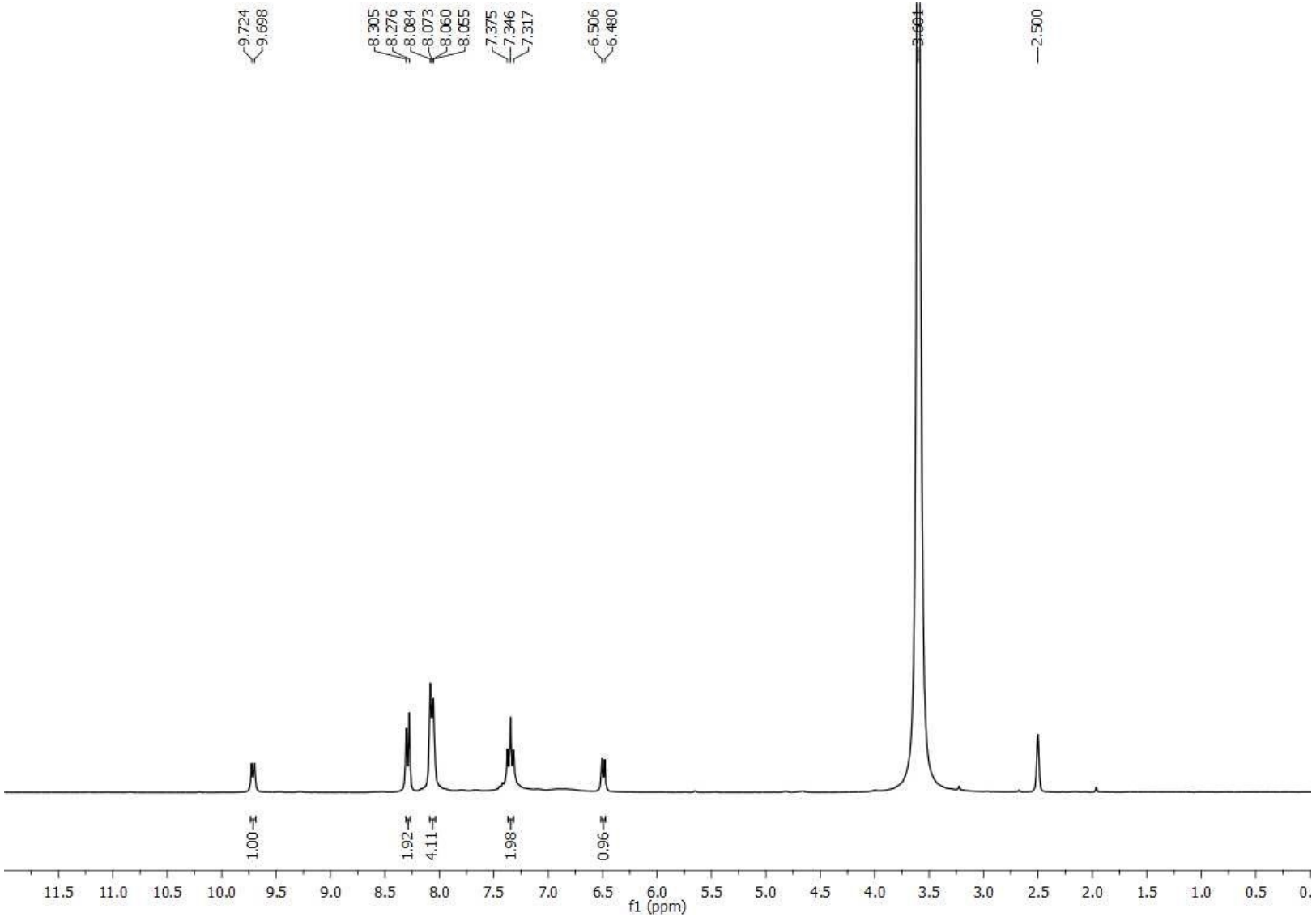
After addition of 20 *µ*l of uracil


9.744
9.718
8.319
8.291
8.105
8.077
8.057
7.392
7.363
7.334
6.822
6.527
6.501
3.502
2.505
1.00
2.04
4.02
2.10
0.89
0.97
f1 (ppm)

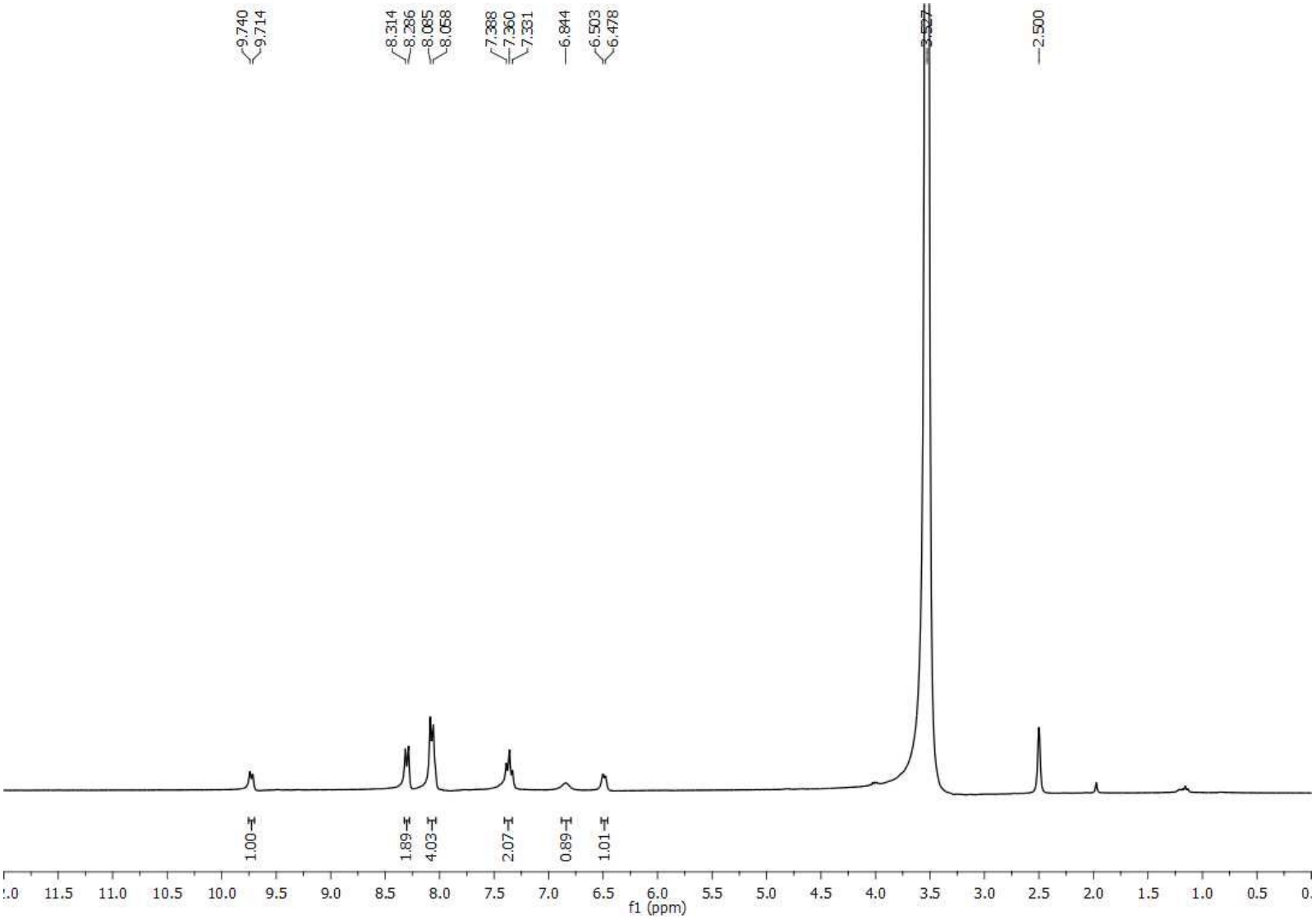
After addition of 30 *µ*l of uracil



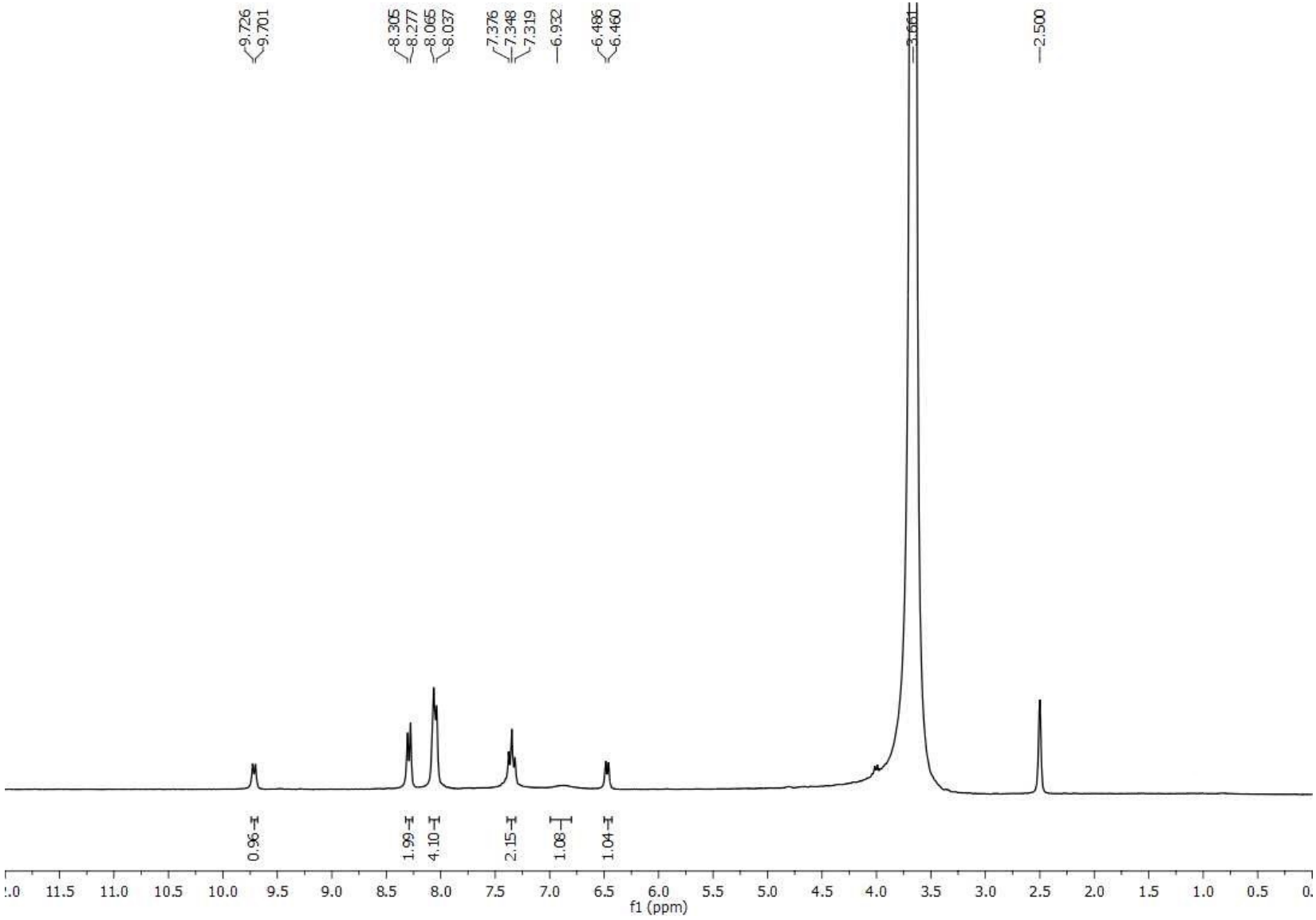
After addition of 40 *µ*l of uracil



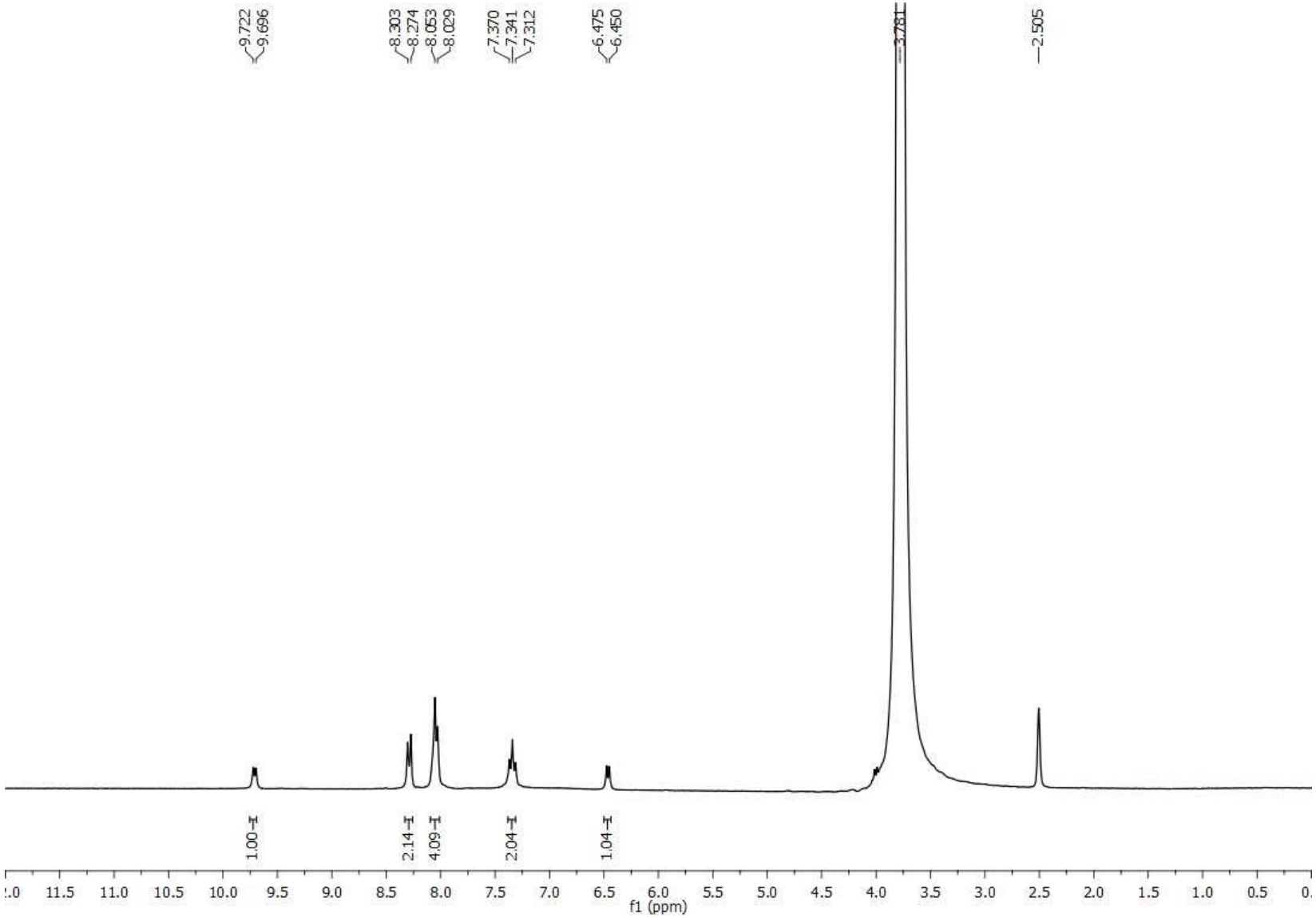
NMR titration of *N*-(2-(4-fluorophenyl)-1-hydroxy-2-oxoethyl)-4-nitrobenzamide (3de) with ATP
After addition of 10 *µ*l of ATP



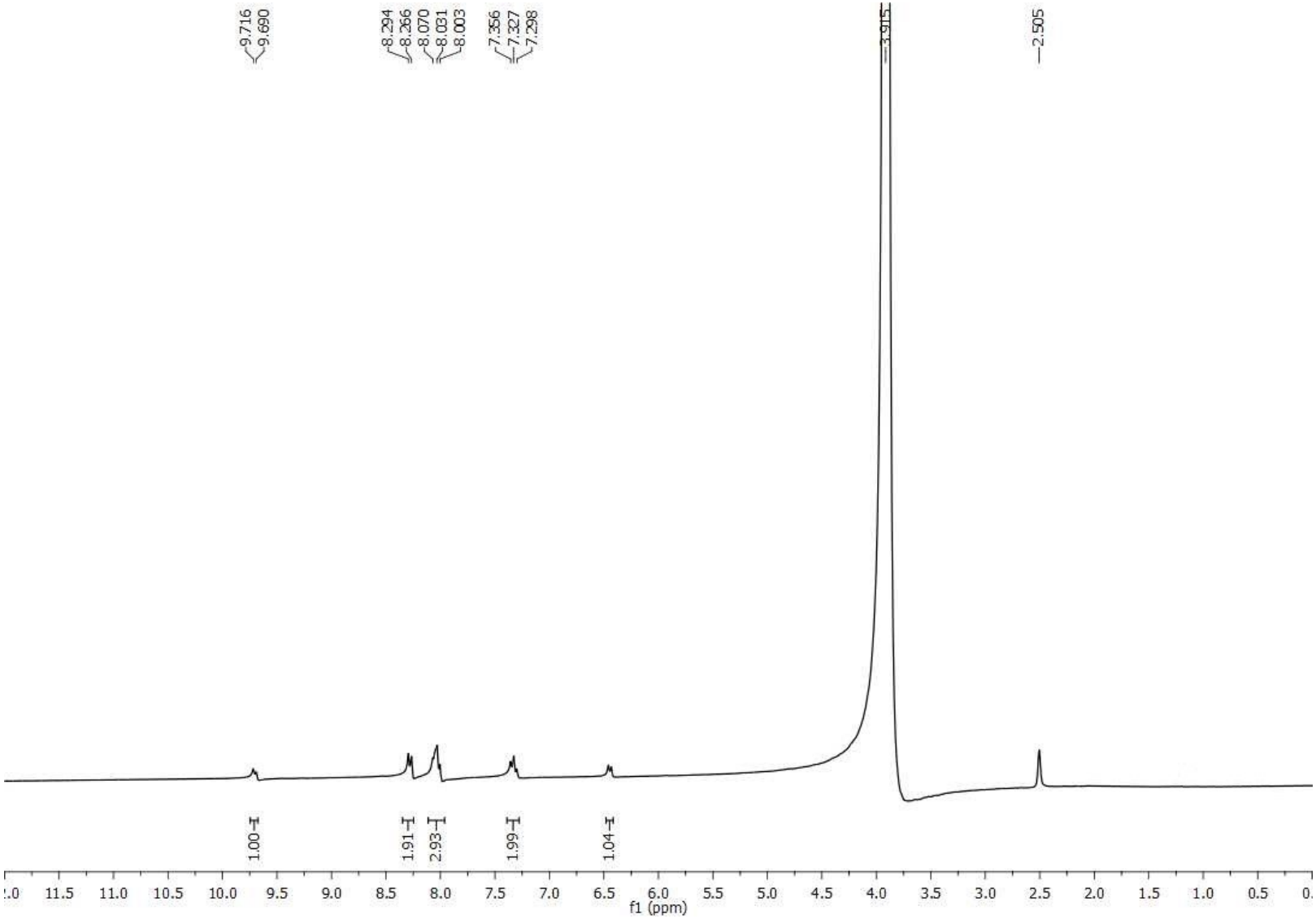
After addition of 20 *µ*l of ATP



After addition of 30 *µ*l of ATP

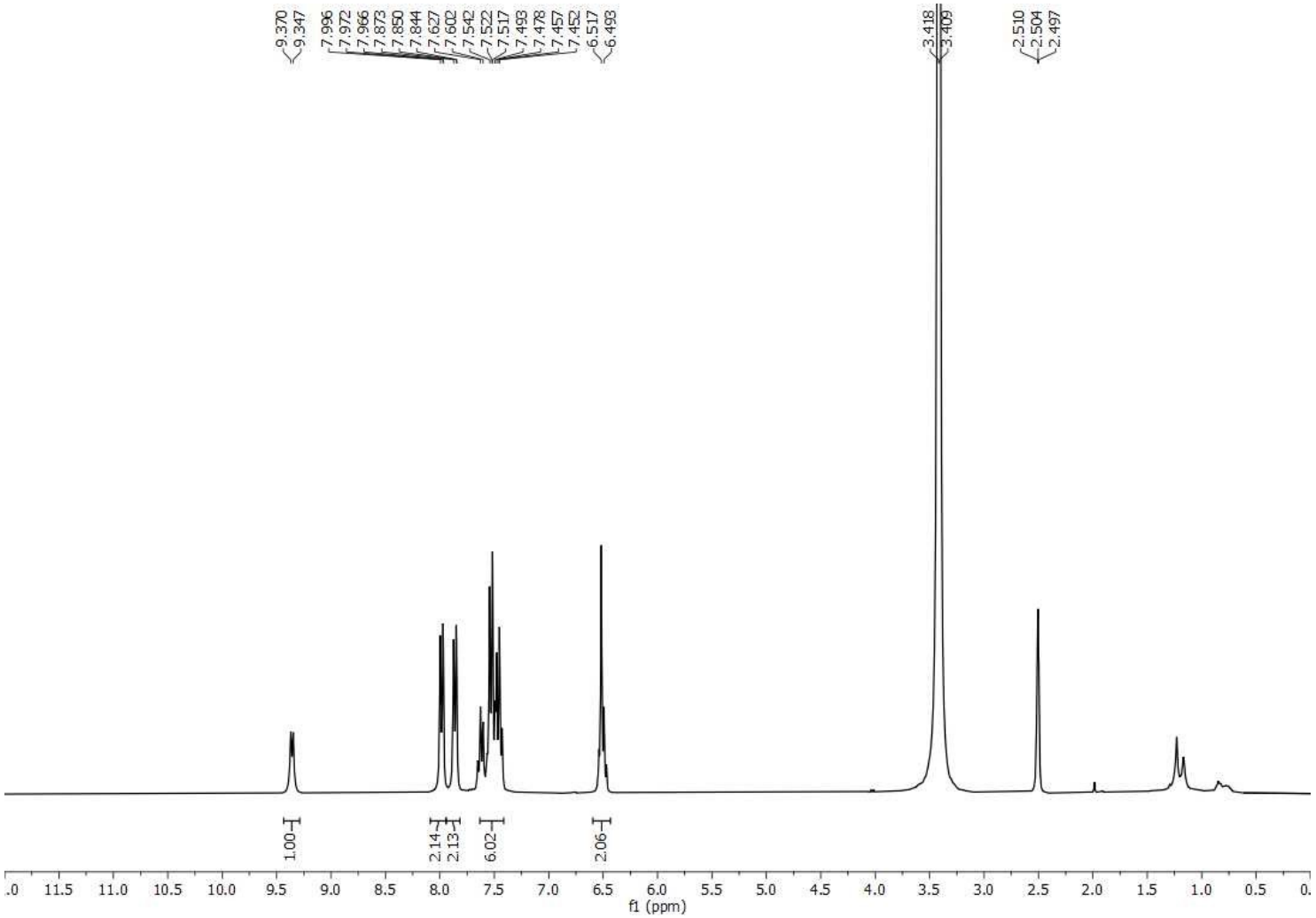


After addition of 40 *µ*l of ATP

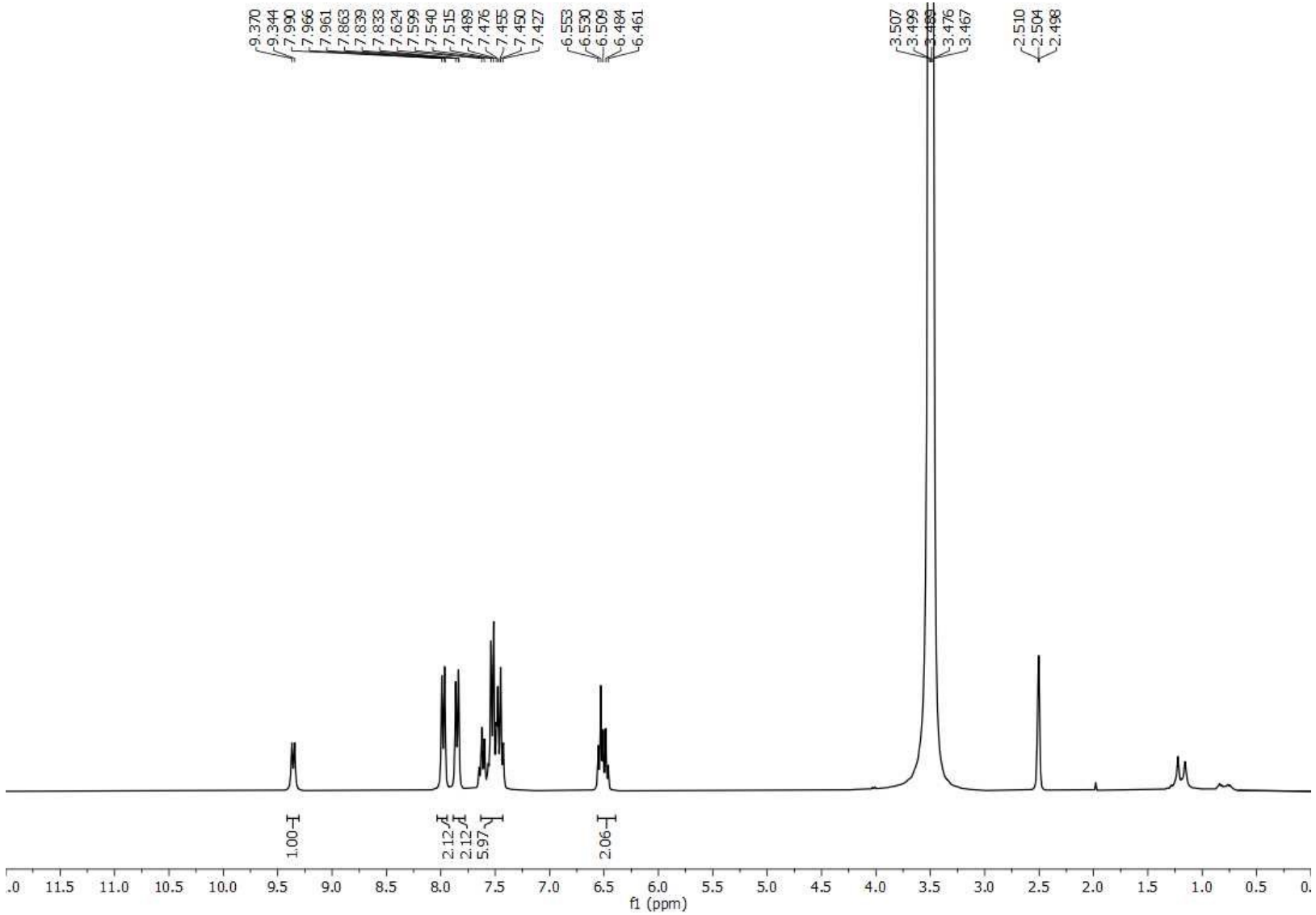


16. NMR titration of compound (3aa)

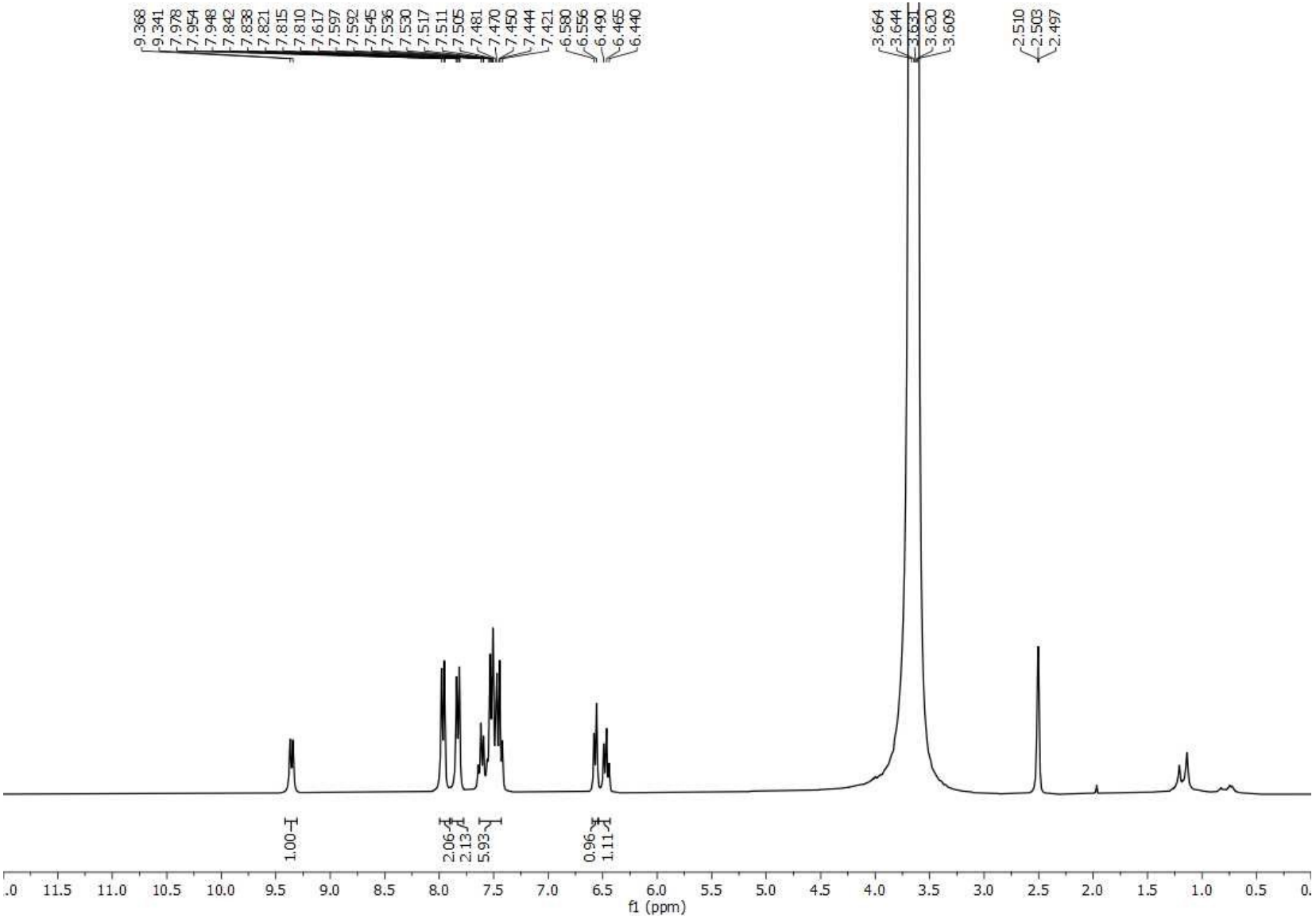
NMR titration of *N*-(1-hydroxy-2-oxo-2-phenylethyl)benzamide (3aa)with chloride anion
After addition of 10 *µ*l of chloride anion



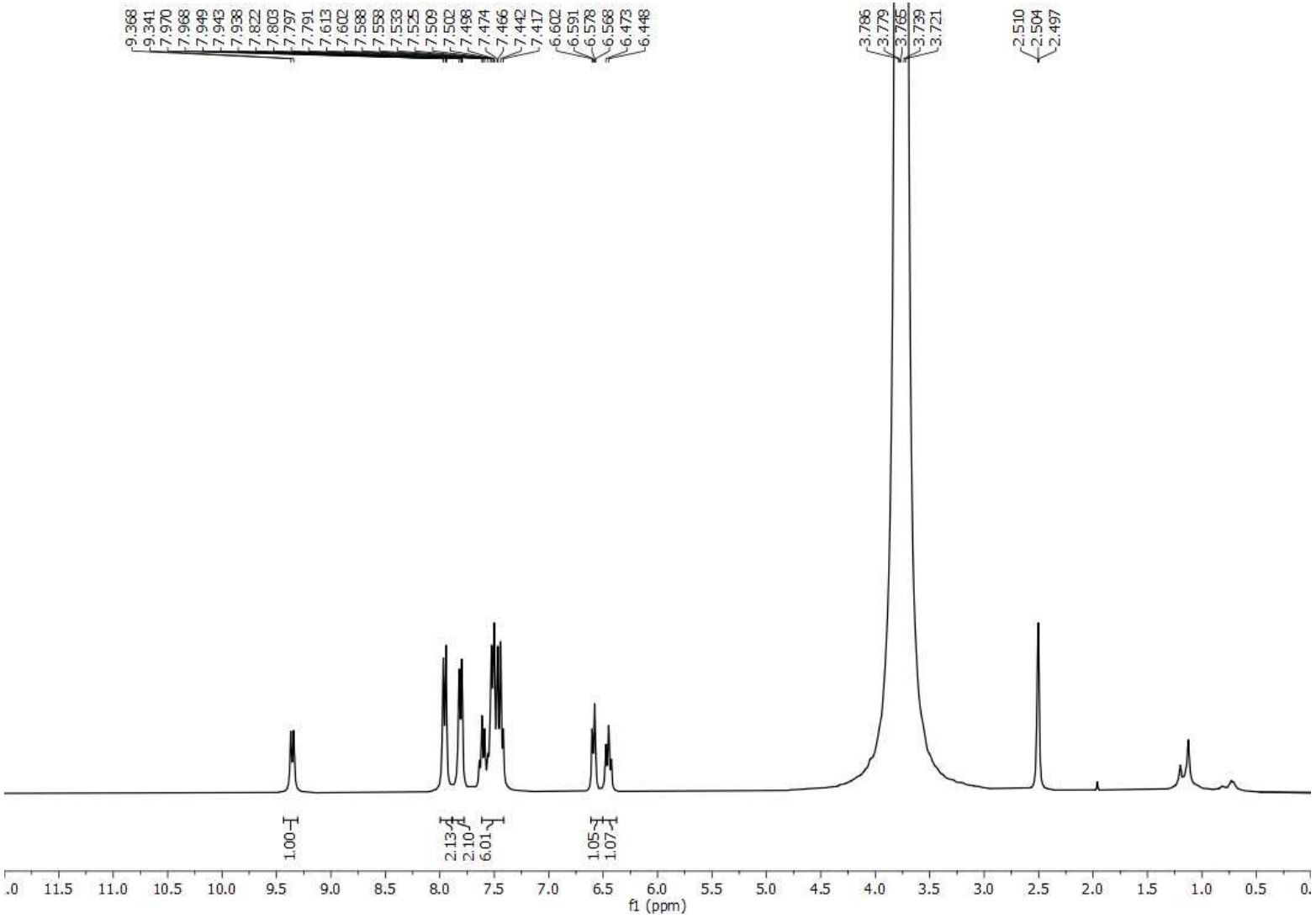
After addition of 20 *μ*l of chloride anion



After addition of 30 *μ*l of chloride anion



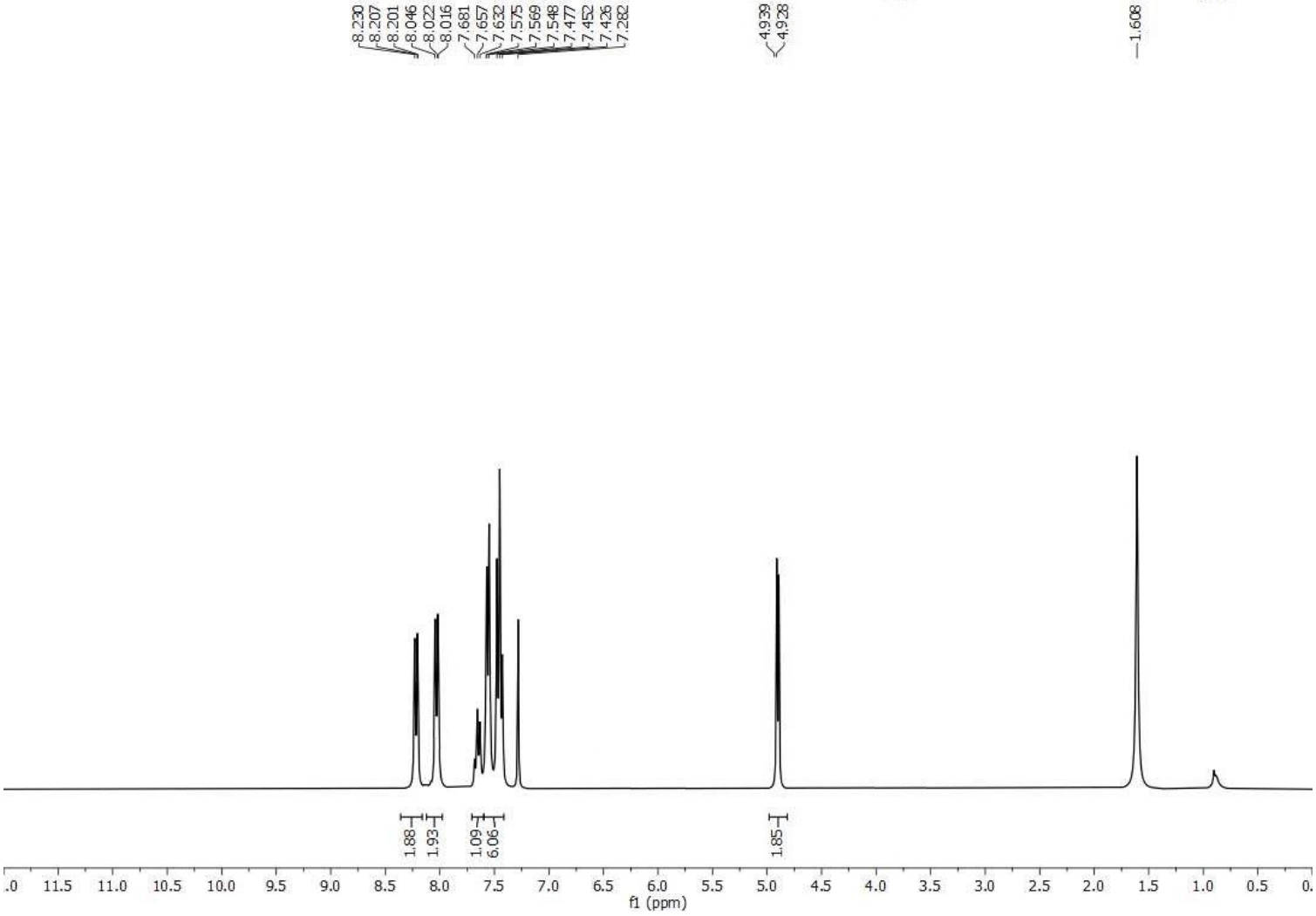
After addition of 40 *μ*l of chloride anion



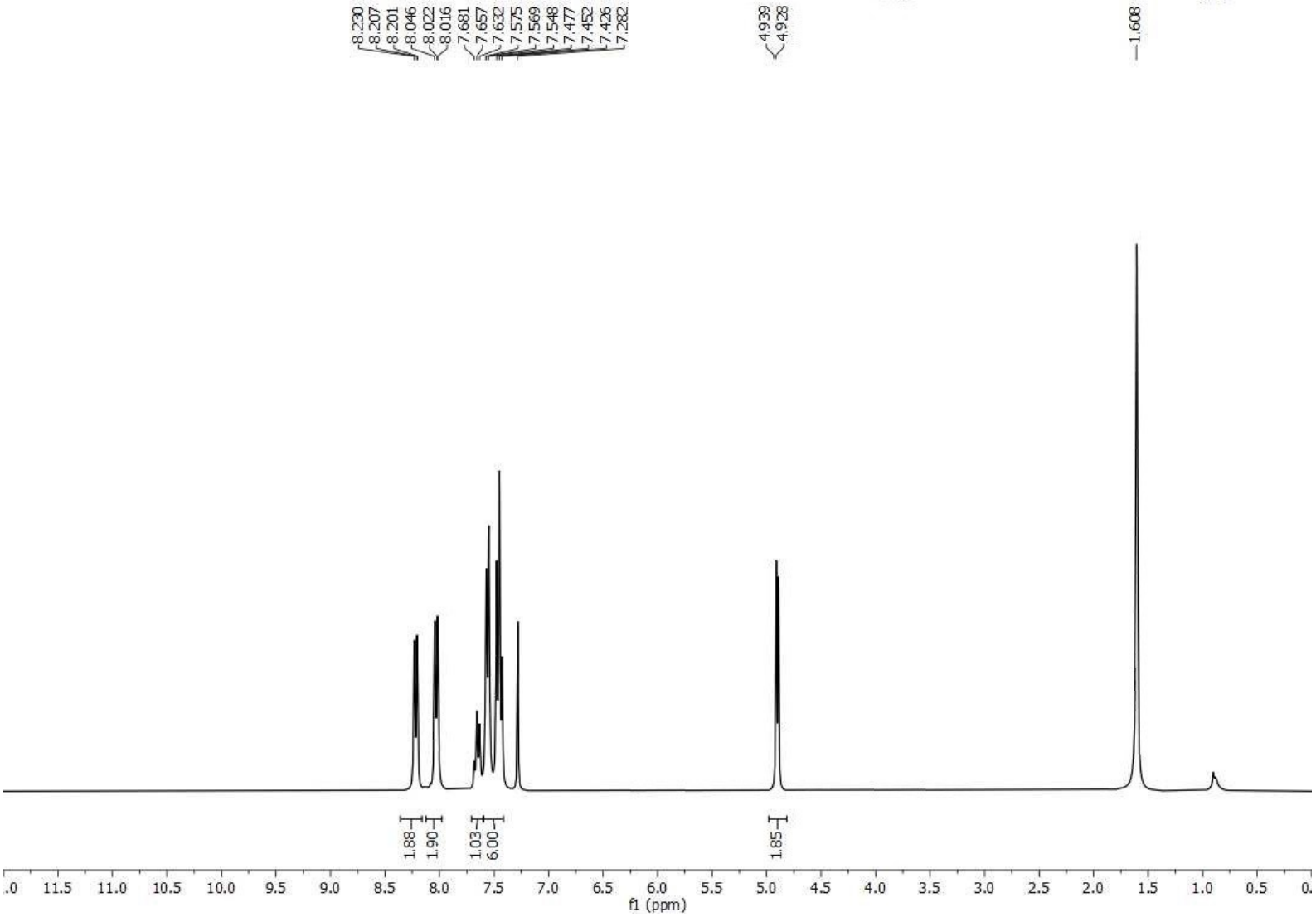
17. NMR titration of compound (6)

NMR titration of *N*-(2-oxo-2-phenylethyl)benzamide (6)with chloride anion

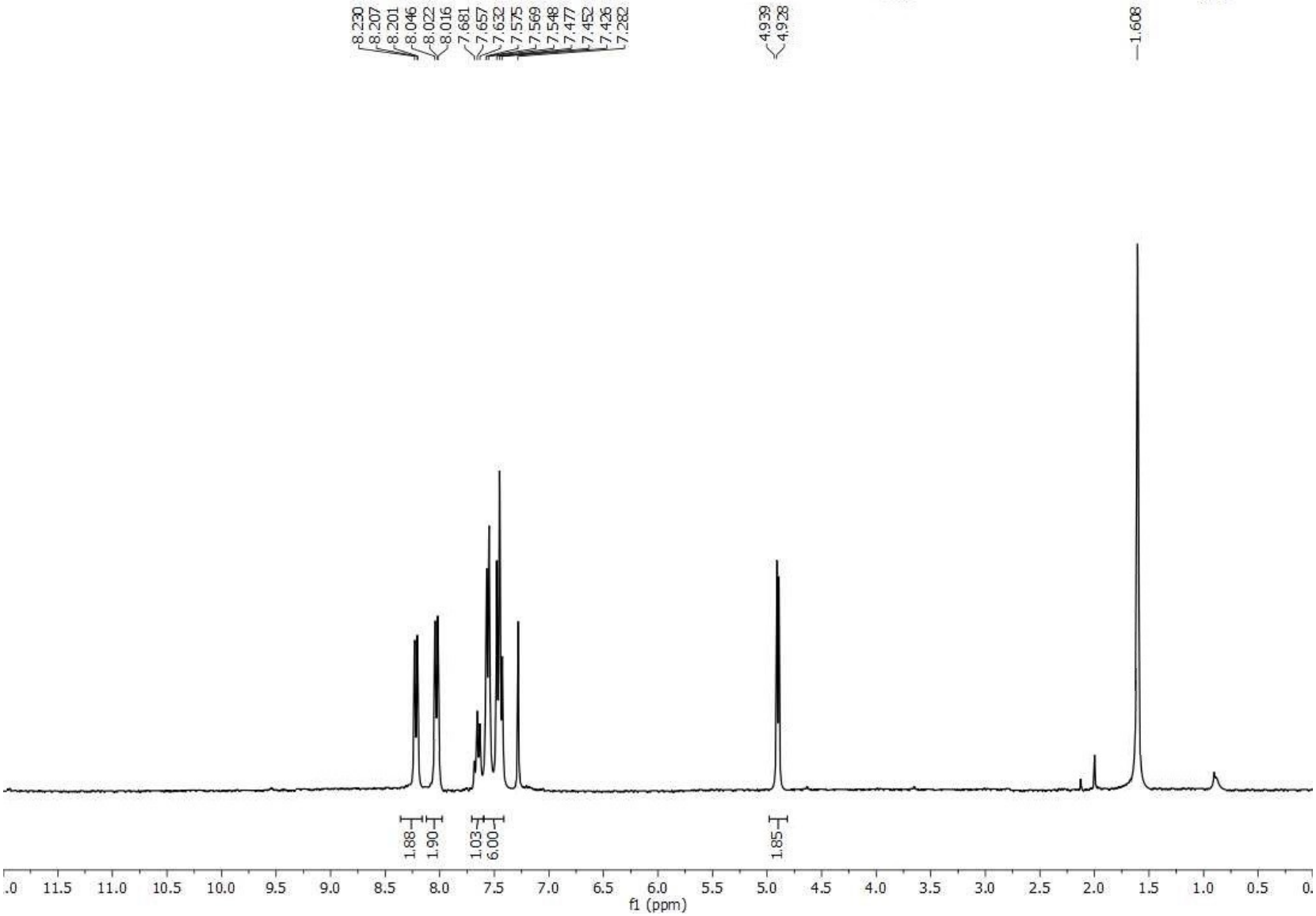
After addition of 10 *µ*l of chloride anion



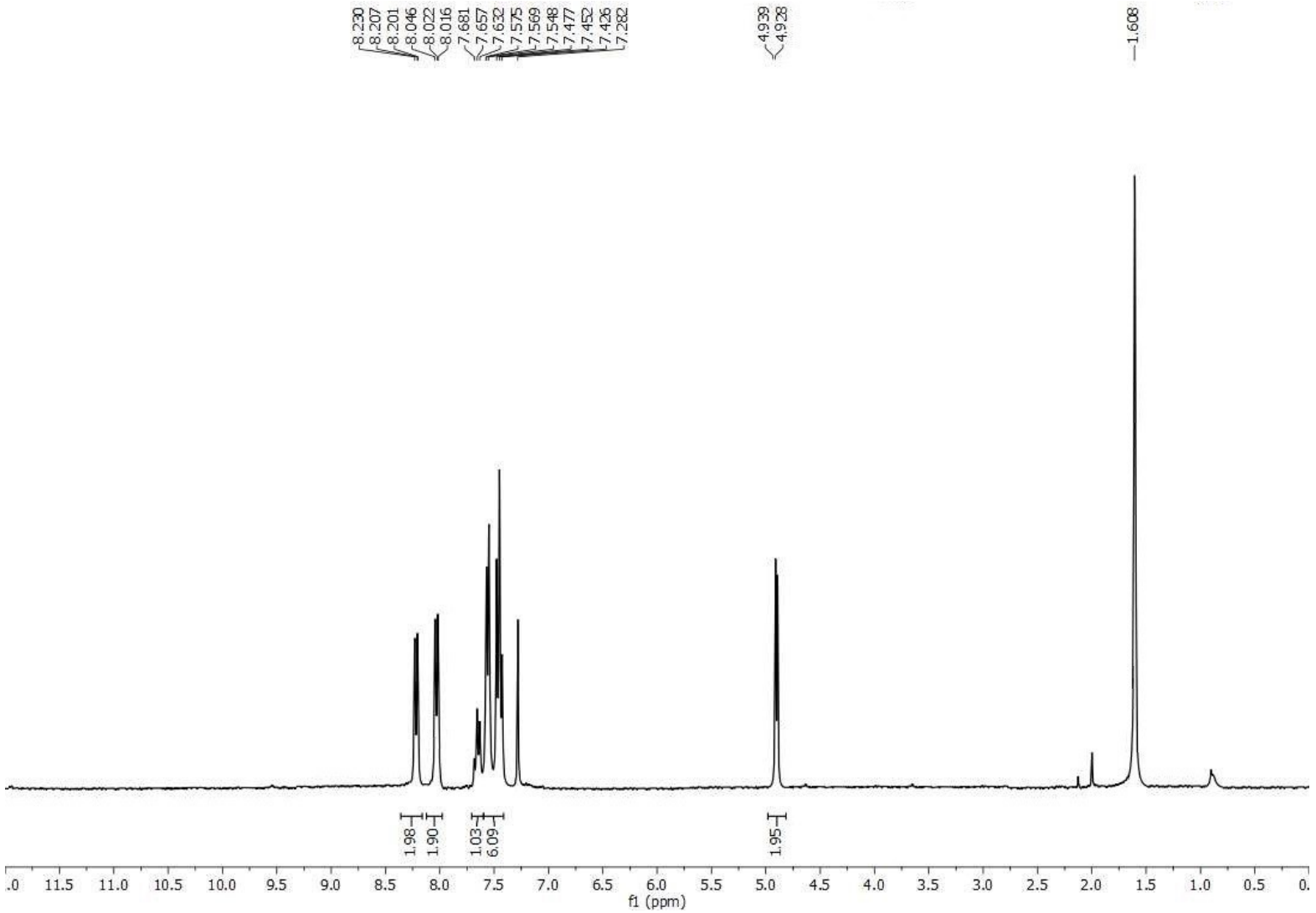
After addition of 20 *μ*l of chloride anion



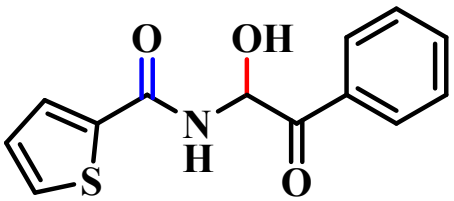
After addition of 30 *μ*l of chloride anion

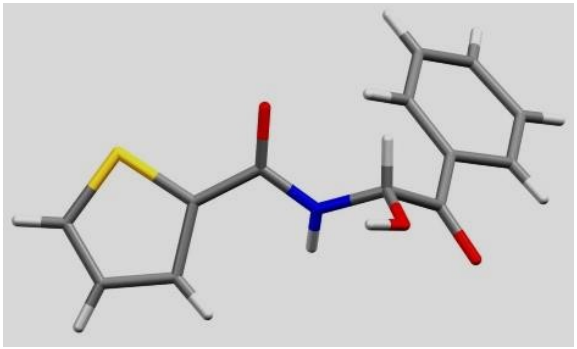


After addition of 40 *µ*l of chloride anion



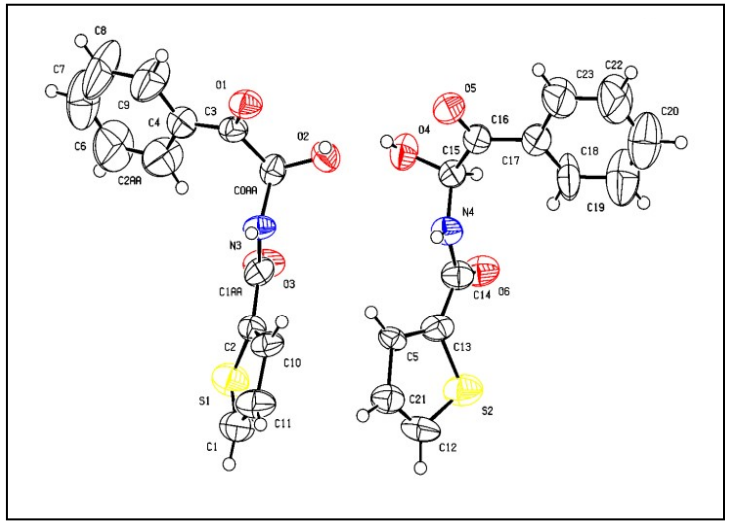
18. Crystal structure of compound 3ea (CCDC 2152756)





Single crystal XRD structure of **3ea**

19. Crystal summary data of compound 3ea (CCDC 2152756**)**



- Chemical formula and formula weight (M): $C_{13}H_{11}NO_3S$ and 261.29
- Crystal system: Monoclinic Unit-cell dimensions (angstrom, degrees) and volume, with edges: a 5.107(4) b 24.81(2) c 9.865(8), 90.00, 92.955(17), 90.00, 1248.2(17)
- Temperature: 296 K
- Space group symbol: P 21
- No. of formula units in unit cell (Z): 4
- Number of reflections measured and/or number of independent reflections, R_{int} = 0.0829
- Final R values (and whether quoted for all or obrserved data): 0.2395

20. References

(1) R. Manikandan, M. Tamizmani, M. Jeganmohan, *Org. Lett.* 2017, **19,** 6678 – 6682.

(2) P. S. Mahajan, S. D. Tanpure, N. A. More, J. M. Gajbhiye, S. B. Mhaske, *RSC Adv*. 2015, **5,** 101641 – 101646.

(3) Y. Wang, M. Yang, C. Laoa, Z. Jiang, *Org. Lett.* 2022, **24**, 2625–2629.

(4) M. Balti, S. A. Miller, M. L. Efrit, N. E. Leadbeater, *RSC Adv.*, 2016, **6**, 72165-72169.