Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Green and Practical Transition Metal-Free One Pot Conversion of Substituted Benzoic Acids to Anilines Using Tosyl Azide

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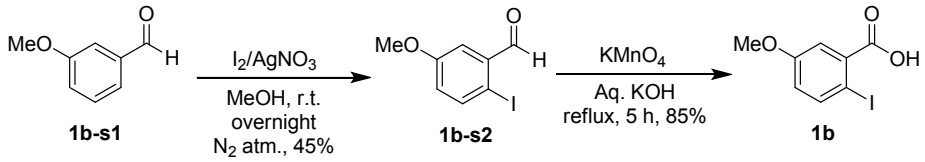
General Remarks

Melting points were determined by the open capillary tube method using a Toshniwal melting point apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 400 (400 MHz) NMR spectrometer. Chemical shifts are reported in ppm (δ) relative to internal standard tetramethylsilane (TMS, δ 0.00 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad resonance (br)], coupling constants [Hz], integration). All the NMR spectra were acquired at ambient temperature. ESI-MS was recorded on Agilent 1100 LC/MSD (70 ev) spectrometer. High resolution mass spectra (HRMS) were recorded on a Waters Q-Tof micro mass spectrometer. Elemental analyses were performed on a CHN analyser. Thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60F plates and visualized by exposure to UV light. ACME silica gel (100-200 mesh) was used for column chromatography. All commercially available reagents were used without purification unless otherwise indicated and were purchased from standard chemical supplier. Tosyl Azide was prepared according to literature procedure.[1]

Preparation of Carboxylic Acid Substrates

Preparation of *ortho*-iodobenzoic acids:

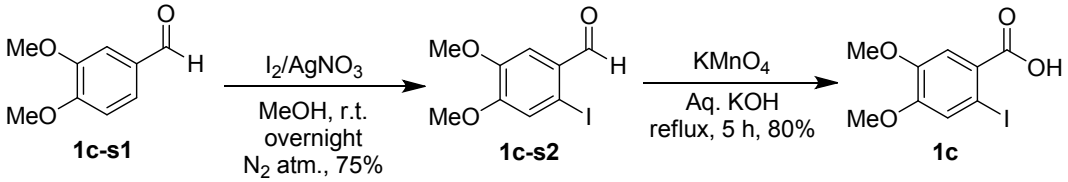
2-Iodo-5-methoxybenzoic acid (1b)[2]: The synthesis of **1b-s2** starting from **1b-s1** was carried out according to the literature procedure.[3] White solid. mp 104−106 °C (lit., mp 105−106 °C).



Next, a mixture of **1b-s2** (262 mg, 1.0 mmol) and $KMnO_4$ (632 mg, 4.0 mmol) in water (6 mL) was heated to reflux for 5 h and then cooled to room temperature. After reducing the unreacted $KMnO_4$ with $NaHSO_3$ and then the pH of the mixture was adjusted to greater than 12 using KOH. The mixture was then filtered through a celite bed, and the filtrate was slowly acidified to a pH of 2 using HC1 (18 M). Then white precipitate was obtained by filtration and washed with dilute HCl solution to afford **1b** (236 mg, 85%). M.p. 131-133 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 3.2 Hz,

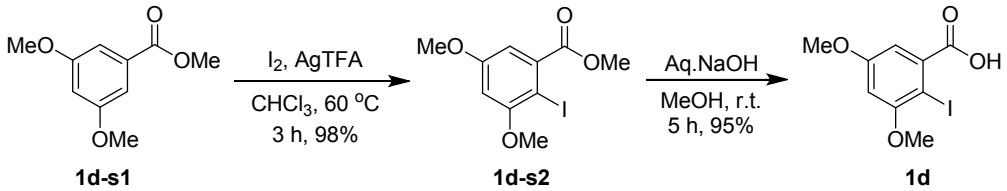
1H), 6.80 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 159.5, 142.5, 133.8, 120.5, 117.2, 83.1, 55.6 ppm.

2-Iodo-4,5-dimethoxybenzoic acid (1c)[4]: The synthesis of **1c-s2** starting from **1c-s1** was carried out according to the literature procedure.[3] White solid. mp 135−137 °C (lit., mp 137−139 °C).



Next, the reaction was carried out similar to compound **1b** using **1c-s2** (292 mg, 1.0 mmol) and $KMnO_4$ (632 mg, 4.0 mmol) in water (6 mL) at reflux for 5 h. The product **1c** (246 mg, 80%) was obtained as a pale white solid. M.p. 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.43 (s, 1H), 3.93 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 152.6, 148.7, 124.2, 114.7, 85.6, 56.3, 56.0 ppm.

2-Iodo-3,5-dimethoxybenzoic acid (1d)[5]: The synthesis of **1d-s2** starting from **1d-s1** was carried out according to the literature procedure.[6] Colorless solid. mp 67−69 °C (lit., mp 68−72 °C).



Next, to a stirred solution of compound **1d-s2** (322 mg, 1.0 mmol) in methanol (5 mL) was added 10% aq. NaOH (44 mg, 1.1 mmol) at room temperature and then allowed to stir at the same temperature for 5 h. The progress of the reaction was monitored by TLC (hexane - EtOAc = 7:3). The reaction mixture was evaporated and quenched into the ice water and then extracted by EtOAc (2 x 10 mL). EtOAc layer was separated out and then aqueous layer was acidified by slow addition of dil. HCl till pH-5. The precipitated solid was filtered, washed well with ice cold water and then dried. The product **1d** (293 mg, 95%) obtained as a white solid. M.p. 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-*d6*): δ 6.77 (d, *J* = 2.8 Hz, 1H), 6.40 (d, *J* = 2.8 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-*d6*): δ 169.3, 160.8, 159.2, 139.7, 106.5, 100.9, 75.4, 56.6, 55.6 ppm.

In the same manner, acids **6b**, **6c** and **6d** were prepared from its corresponding esters **6b-s2**, **6c-s6** and **6d-s2**.

2-Iodo-3,4,5-trimethoxybenzoic acid (1e): The synthesis of **1e** was carried out according to the literature procedure.[7] Colorless solid. mp 148−150 °C (lit., mp 151−152 °C).

5-Bromo-2-iodobenzoic acid (1f): The synthesis of **1f** was carried out according to the literature procedure.[8] Pale yellow solid. mp 160−162 °C (lit., mp 161−163 °C).[9]

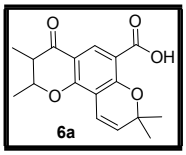
2-Iodo-5-nitrobenzoic acid (1g): The synthesis of **1g** was carried out according to the literature procedure.[10] Pale yellow solid. mp 198−200 °C (lit., mp 200−202 °C).

Source of *ortho*-Nitrobenzoic acids (4):

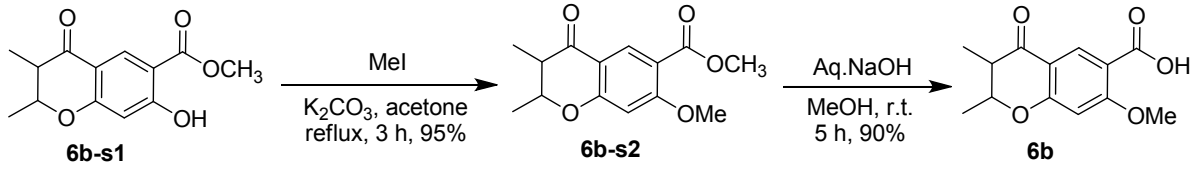
Substituted *ortho*-nitrobenzoic acids (**4a-4j**) were purchased from TCI chemicals (India) Pvt. Ltd.

Preparation of dihydropyranone fused benzoic acids (6):

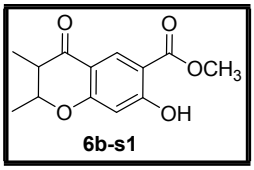
2,3,8,8-Tetramethyl-4-oxo-2,3,4,8-tetrahydropyrano[2,3-f]chromene-6-carboxylic acid (6a): The synthesis of **6a** was carried out according to our previous literature procedure[11] as an inseparable diastereomeric mixture (*trans*/*cis* = 65:35) as a white solid. mp 159−163 °C.



7-Methoxy-2,3-dimethyl-4-oxochroman-6-carboxylic acid (6b):

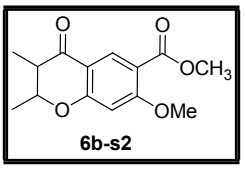


The synthesis of compound **6b-s1** was carried out according to our previous literature procedure[11] as an diastereomeric mixture (*trans*/*cis* = 50:50) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.28 (s, 1H), 8.48, 8.47 (2s, $1H_{trans+cis}$), 6.46, 6.45 (2s, $1H_{trans+cis}$), 4.69-4.64 (m, $1H_{cis}$), 4.31-4.24 (m, $1H_{trans}$), 3.94 (2s, $3H_{trans+cis}$), 2.70-2.63 (m, $1H_{cis}$), 2.57-2.49 (m, $1H_{trans}$), 1.52 (d, J = 6.0 Hz, $3H_{trans}$), 1.39 (d, J = 6.8 Hz, $3H_{cis}$), 1.21 (d, J = 6.8 Hz, $3H_{trans}$), 1.14 (d, J = 7.2 Hz, $3H_{cis}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 192.7, 170.2, 170.1, 167.1, 166.9, 166.1, 165.8, 131.9, 131.8, 113.8, 113.8, 113.3, 107.8, 107.7, 104.2, 104.1, 79.6, 52.4, 46.5, 45.0, 19.7,



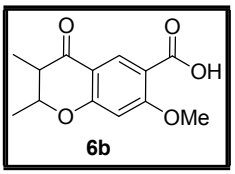
16.1, 10.3, 9.2 ppm, two signals are superimposed; MS (ESI): m/z 251 $[M+1]^+$. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.55; H, 5.69.

To a stirred solution of **6b-s1** (500 mg, 2.0 mmol) in acetone (10 mL) was added K_2CO_3 (304 mg, 2.2 mmol) followed by dropwise addition of MeI (150 µL, 2.4 mmol) at room temperature. After the completion of addition allowed to stir at reflux for 3 h. The reaction mixture was evaporated and quenched into the water and extracted by EtOAc (3 x 20 mL). The combined EtOAc layer was washed with water followed by brine to give the crude which was purified by silica gel column chromatography (hexane -EtOAc = 9:1) to afford the title compound **6b-s2** (502 mg, 95%) as an inseparable diastereomeric mixture (*trans*/*cis* = 80:20) as white solid. M.p. 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36, 8.35 (2s, $1H_{major+minor}$), 6.41, 6.39 (2s, $1H_{major+minor}$), 4.65-4.60 (m, $1H_{minor}$), 4.27-4.19 (m, $1H_{major}$), 3.86 (s, 3H), 3.80 (s, 3H), 2.61-2.55 (m, $1H_{minor}$), 2.52-2.44 (m, $1H_{major}$), 1.47 (d, J = 6.4 Hz, $3H_{major}$), 1.35 (d, J = 6.8 Hz, $3H_{minor}$), 1.15 (d, J = 6.8 Hz, $3H_{major}$), 1.08 (d, J = 7.2 Hz, $3H_{minor}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.1, 192.4, 165.2, 165.2, 165.1, 165.0, 164.9, 132.7, 132.6, 114.3, 114.2, 113.1, 112.6, 99.9, 99.8, 79.8, 56.3, 51.8, 46.3, 44.8, 19.6, 16.1, 10.2, 9.1 ppm, four signals are superimposed; HRMS (ESI): $[M + H]^+$ Calcd for $C_{14}H_{17}O_5$ 265.1076, found 265.1066. In the same manner, compound **6c-s6** was prepared from **6c-s5**.



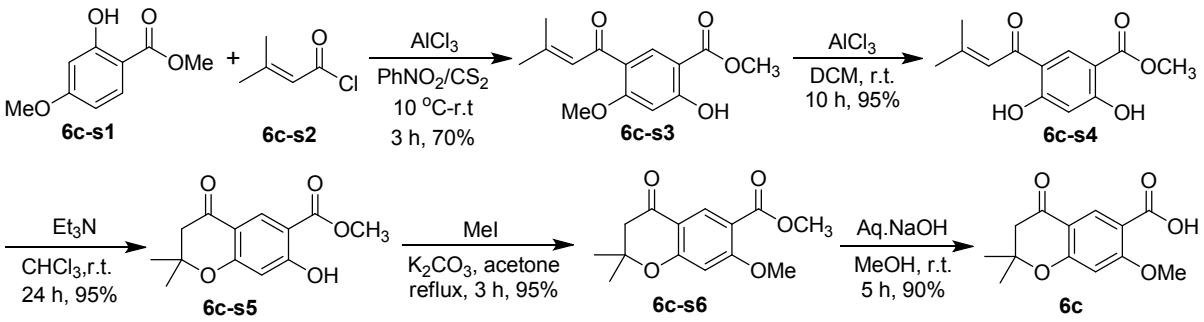
6b-s2

The reaction was carried out similar to compound **1d** using **6b-s2** (264 mg, 1.0 mmol) and 10% aq. NaOH (44 mg, 1.1 mmol) in methanol (5 mL) at room temperature for 5 h. The title compounds **6b** (225 mg, 90%) was obtained as an inseparable diastereomeric mixture (*trans*/*cis* = 80:20) as a white solid which is pure enough for further step. M.p. 197-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68, 8.67 (2s, $1H_{major+minor}$), 6.53 (s, $1H_{major+minor}$), 4.72-4.70 (m, $1H_{minor}$), 4.35-4.28 (m, $1H_{major}$), 4.04 (s, 3H), 2.70-2.68 (m, $1H_{minor}$), 2.59-2.51 (m, $1H_{major}$), 1.54 (d, J = 6.4 Hz, $3H_{major}$), 1.41 (d, J = 6.8 Hz, $3H_{minor}$), 1.21 (d, J = 7.2 Hz, $3H_{major}$), 1.14 (d, J = 7.6 Hz, $3H_{minor}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 192.0, 165.8, 165.6, 165.3, 163.7, 163.6, 134.9, 134.8, 114.7, 114.2, 112.4, 112.3, 100.0, 80.1, 77.8, 57.0, 46.4, 44.9, 19.6, 16.0, 10.1, 9.1 ppm, three signals are superimposed; HRMS (ESI): $[M + H]^+$ Calcd for $C_{13}H_{15}O_5$, 251.0919; found 251.0916. In the same manner, compound **6c** was prepared from **6c-s6**.

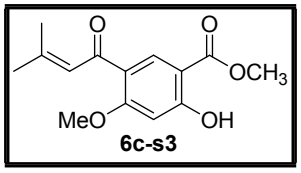


6b

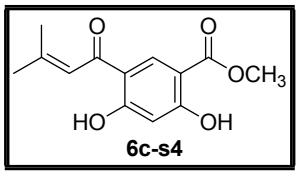
7-Methoxy-2,2-dimethyl-4-oxochroman-6-carboxylic acid (6c):



To a stirred solution of methyl 2-hydroxy-4-methoxybenzoate (**6c-s1**, 5.0 g, 27.47 mmol) in CS_2 (70 mL) was added $AlCl_3$ (10.96 g, 82.40 mmol) and then nitrobenzene (20 mL) was added dropwise in 30 min and stirred for additional 15 min at room temperature to get a homogeneous mixture. 3-Methylbut-2-enoyl chloride (**6c-s2**, 3.38 mL g, 30.22 mmol) in nitrobenzene (7 mL) was added dropwise in 30 min at room temperature and stirred for additional 3 h. The reaction mixture was quenched into the crushed ice and 1N HCl. The semi precipitated product was taken into EtOAc, and the aqueous solution was extracted with the same solvent (100 mL x 3). The combined EtOAc solutions were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo* (use high vacuum pump to remove the nitrobenzene). The residue was purified by silica gel column chromatography (hexane -EtOAc = 8:2) to afford the title compound **6c-s3** (5.01 g, 70%) as white solid. M.p. 82-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.21 (s, 1H), 8.19 (s, 1H), 6.59 (s, 1H), 6.46 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.20 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 170.2, 165.7, 163.8, 155.0, 133.8, 125.1, 123.4, 105.4, 99.5, 55.9, 52.1, 27.9, 21.2 ppm; HRMS (ESI): $[M + Na]^+$ Calcd for $C_{14}H_{16}NaO_5$, 287.0895; found 287.0883.

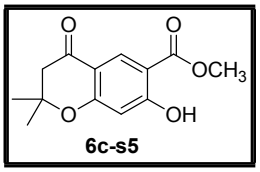


To a stirred solution of **6c-s3** (5.0 g, 18.94 mmol) in DCM (75 mL) was added $AlCl_3$ (12.59 g, 94.66 mmol) at room temperature and then allowed to stir for a period of 10 h. The reaction mixture was quenched into the crushed ice and 1N HCl. The aqueous solution was extracted with DCM (50 mL x 2). The combined DCM layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane-EtOAc = 9:1) to afford the title compound **6c-s4** (4.49 g, 95%) as a yellow solid. M.p. 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.51 (s, 1H), 11.28 (s, 1H), 8.34 (s, 1H), 6.71 (s, 1H), 6.44 (s, 1H), 3.96 (s, 3H), 2.21 (d, J = 0.8 Hz,



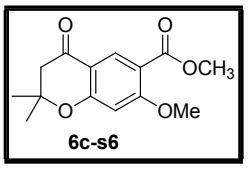
3H), 2.07 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 169.7, 169.5, 166.9, 158.7, 134.1, 119.2, 114.6, 104.9, 104.6, 52.3, 28.3, 21.5 ppm; MS (ESI): m/z 251 $[M+1]^+$. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.59; H, 5.71.

To a stirred solution of **6c-s4** (4.0 g, 16.0 mmol) in $CHCl_3$ (40 mL) was added triethylamine (6.7 mL, 48.0 mmol) and then allowed to stir at room temperature for 24 h. The reaction mixture was quenched into ice water and then neutralised by 1N HCl. The aqueous solution was extracted with $CHCl_3$ (2 x 30 mL). The combined $CHCl_3$ layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane-EtOAc = 9:1) to afford the title compound **6c-s5** (3.8 g, 95%) as a white solid. M.p. 128-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.27 (s, 1H), 8.47 (s, 1H), 6.43 (s, 1H), 3.93 (s, 3H), 2.69 (s, 2H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 170.1, 167.3, 165.1, 131.0, 113.8, 107.3, 104.7, 80.3, 52.4, 52.3, 48.5, 26.8 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{13}H_{15}O_5$, 251.0919; found 251.0913.



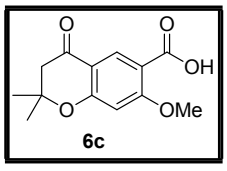
6c-s5

The reaction was carried out similar to compound **6b-s2** using compound **6c-s5** (3.0 g, 12.0 mmol), K_2CO_3 (1.76 g, 13.2 mmol) and MeI (896 µL, 14.4 mmol) in acetone (30 mL) at reflux for 3 h. The title compounds **6c-s6** (3.01 g, 95%) was obtained as a white solid after passing through a silica gel column chromatography (hexane–EtOAc = 8 : 2). M.p. 82-84 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 6.41 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.67 (s, 2H), 1.44 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 165.5, 165.1, 164.3, 132.0, 113.8, 113.1, 100.4, 80.5, 56.3, 51.8, 48.4, 26.7 ppm; MS (ESI): m/z 265 $[M+1]^+$. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.84; H, 6.18.



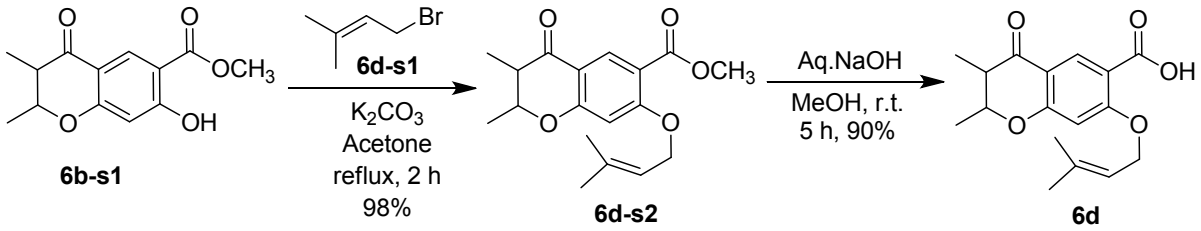
6c-s6

The reaction was carried out similar to compound **1d** using **6c-s6** (3.0 g, 11.36 mmol) and 10% aq. NaOH (0.5 g, 1.1 mmol) in methanol (30 mL) at room temperature for 5 h. The title compounds **6c** (2.55 g, 90%) was obtained as a white solid. M.p. 162-164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.93 (br, 1H), 8.57 (s, 1H), 6.45 (s, 1H), 3.97 (s, 3H), 2.68 (s, 2H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 167.1, 164.9, 164.8, 133.7, 114.0, 112.1, 100.6, 80.9, 56.8, 48.3, 26.7 ppm; HRMS (ESI): $[M + H]^+$ Calcd for $C_{13}H_{15}O_5$, 251.0919; found 251.0919.

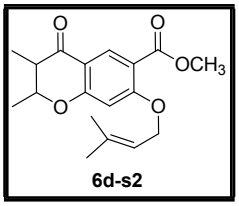


6c

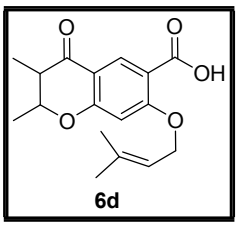
2,3-Dimethyl-7-((3-methylbut-2-en-1-yl)oxy)-4-oxochroman-6-carboxylic acid (6d):



To a stirred solution of **6b-s1** (2.0 g, 8.0 mmol) in acetone (40 mL) was added K_2CO_3 (1.43 g, 10.4 mmol) followed by dropwise addition of prenyl bromide **6d-s1** (1.31 g, 8.8 mmol) at room temperature. After the completion of addition allowed to stir at reflux for 2 h. The reaction mixture was evaporated and quenched into the water and extracted by EtOAc (3 x 30 mL). The combined EtOAc layer was layer was washed with water followed by brine to give the crude which was purified by silica gel column chromatography (hexane -EtOAc = 8:2) to afford the title compound **6d-s2** (2.49 g, 98%) as an inseparable diastereomeric mixture (*trans*/*cis* = 50:50) as a white solid as white solid. M.p. 87-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42, 8.41 (2s, $1H_{cis+trans}$), 6.44, 6.43 (2s, $1H_{cis+trans}$), 5.50 (t, J = 6.2 Hz, $1H_{cis+trans}$), 4.69-4.66 (m, $1H_{cis}$), 4.63 (d, J = 6.4 Hz, $2H_{cis+trans}$), 4.32-4.25 (m, $1H_{trans}$), 3.85 (s, $3H_{cis+trans}$), 2.66-2.60 (m, $1H_{cis}$), 2.57-2.49 (m, $1H_{trans}$), 1.79 (s, $3H_{cis+trans}$), 1.75 (s, $3H_{cis+trans}$), 1.53 (d, J = 6.4 Hz, $3H_{trans}$), 1.41 (d, J = 6.4 Hz, $3H_{cis}$), 1.21 (d, J = 7.2 Hz, $3H_{trans}$), 1.14 (d, J = 7.2 Hz, $3H_{cis}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 192.5, 165.2, 165.1, 165.0, 164.8, 164.5, 164.4, 138.6, 138.5, 132.7, 132.6, 118.6, 114.8, 114.7, 113.1, 112.5, 100.8, 100.7, 79.8, 66.3, 51.8, 46.4, 44.9, 25.7, 19.7, 18.3, 16.2, 10.3, 9.2 ppm, six signals are superimposed; HRMS (ESI): $[M + H]^+$ Calcd for $C_{18}H_{22}NaO_5$, 341.1365; found 341.1359.



The reaction was carried out similar to compound **1d** using **6c-s6** (3.0 g, 11.36 mmol) and 10% aq. NaOH (0.5 g, 1.1 mmol) in methanol (30 mL) at room temperature for 5 h. The title compounds **6c** (2.55 g, 90%) was obtained as an inseparable diastereomeric mixture (*trans*/*cis* = 60:40) as a white solid. M.p. 122-124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64, 8.61 (2s, $1H_{major+minor}$), 6.51, 6.50 (2s, $1H_{major+minor}$), 5.49-5.47 (m, $1H_{major+minor}$), 4.70 (d, J = 6.8 Hz, $2H_{major+minor}$+$1H_{minor}$), 4.32-4.25 (m, $1H_{major}$), 2.67-2.62 (m, $1H_{minor}$), 2.55-2.47 (m, $1H_{major}$), 1.80 (s, $3H_{major+minor}$), 1.75 (s, $3H_{major+minor}$), 1.51 (d, J = 6.8 Hz, $3H_{major}$), 1.38 (d, J = 6.8 Hz, $3H_{minor}$), 1.17 (d, J = 6.8 Hz, $3H_{major}$), 1.10 (d, J = 7.2 Hz, $3H_{minor}$); ^{13}C NMR (100 MHz,



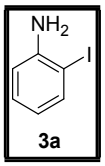
$CDCl_3$): δ 193.8, 192.2, 165.7, 165.4, 165.3, 162.9, 162.7, 142.0, 134.8, 134.7, 116.8, 116.6, 114.6, 114.1, 112.3, 101.0, 100.9, 80.1, 77.7, 67.2, 46.4, 44.8, 25.8, 19.6, 18.3, 16.0, 10.1, 9.1 ppm, six signals are superimposed; HRMS (ESI): $[M + Na]^+$ Calcd for $C_{17}H_{20}NaO_5$, 327.1208; found 327.1238.

General Experimental Procedure for the Synthesis of Substituted Anilines (3, 5 or 7)

To a stirred suspension of substituted benzoic acid **1**, **4** or **6** (1.0 mmol), K_2CO_3 (2.0 mmol) in 4 mL of DMF was added tosyl azide (1.2 mmol) dropwise at room temperature. After completion of the addition the reaction mixture was allowed to stir at 80 °C for 2-4 h. The reaction mixture was quenched with water and extracted with EtOAc (3 x 20 mL) and washed with brine. The EtOAc layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane/EtOAc) to afford corresponding pure substituted anilines **3**, **5** or **7**.

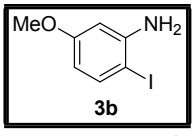
2-Iodoaniline (3a)[12]

The reaction was carried out according to general procedure using 2-iodobenzoic acid (**1a**, 248 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 µL, 1.2 mmol) in DMF (4 mL) for 2 h gave **3a** (193 mg, 88%) as a brownish solid after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). M.p. 54-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.16-7.11 (m, 1H), 6.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.49-6.45 (m, 1H), 4.08 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 139.0, 129.3, 119.9, 114.7, 84.1 ppm.



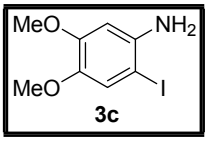
2-Iodo-5-methoxyaniline (3b)[13]

The reaction was carried out according to general procedure using 2-iodo-5-methoxybenzoic acid (**1b**, 278 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 µL, 1.2 mmol) in DMF (4 mL) for 1.5 h gave **3b** (209 mg, 84%) as a pale yellow paste after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 1H), 6.32 (d, *J* = 2.8 Hz, H), 6.13 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.91 (br, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 147.6, 139.1, 106.5, 100.5, 73.4, 55.3 ppm.



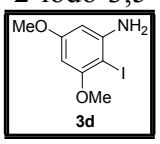
2-Iodo-4,5-dimethoxyaniline (3c)[14]

The reaction was carried out according to general procedure using 2-iodo-4,5-dimethoxybenzoic acid (**1c,** 308 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2 h gave **3c** (237 mg, 85%) as a brown paste after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). The product is easily decomposed after column and must be stored at 4 °C under inert atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 1H), 6.31 (s, 1H), 3.73 (s, 6H), 3.69 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 142.6, 141.3, 121.7, 99.7, 71.2, 56.8, 55.8 ppm.



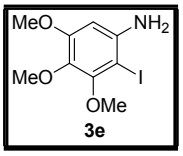
2-Iodo-3,5-dimethoxyaniline (3d)[15]

The reaction was carried out according to general procedure using 2-iodo-3,5-dimethoxybenzoic acid (**1d**, 308 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2,** 180 μL, 1.2 mmol) in DMF (4 mL) for 1.5 h gave **3d** (230 mg, 82%) as a brownish solid after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). The product is easily decomposed after column and must be stored at 4 °C under inert atmosphere. M.p. 65-67 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (d, J = 2.8 Hz, 1H), 5.89 (d, J = 2.4 Hz, 1H), 4.23 (br, 2H), 3.81 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 159.4, 148.4, 92.4, 89.5, 65.4, 56.3, 55.3 ppm.



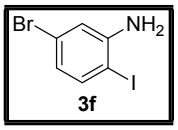
2-Iodo-3,4,5-trimethoxyaniline (1e)

The reaction was carried out according to general procedure using 2-iodo-3,4,5-dimethoxybenzoic acid (**1e**, 338 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 1.5 h gave **3e** (252 mg, 82%) as a brownish paste after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). The product is easily decomposed after column and must be stored at 4 °C under inert atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (s, 1H), 3.86-3.76 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 153.3, 143.6, 134.4, 94.6, 71.5, 61.2, 60.7, 56.0 ppm. MS (ESI): m/z 310 $[M+1]^+$. Anal. Calcd for $C_9H_{12}INO_3$: C, 34.97; H, 3.91; N, 4.53. Found: C, 35.13; H, 3.98; N, 4.68.



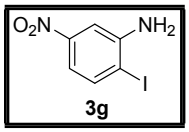
5-Bromo-2-iodoaniline (3f)[16]

The reaction was carried out according to general procedure using 5-bromo-2-iodobenzoic acid (**1f**, 327 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 3 h gave **3f** (237 mg, 80%) as pale white solid after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). The product is easily decomposed after column and must be stored at 4 °C under inert atmosphere. M.p.56-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 1H), 6.83 (d, J = 2.4 Hz, 1H), 6.57 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.12 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 139.9, 123.1, 122.8, 117.1, 82.0 ppm.



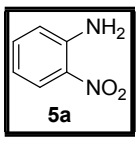
2-Iodo-5-nitroaniline (3g)[17]

The reaction was carried out according to general procedure using 2-iodo-5-nitrobenzoic acid (**1g**, 293 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2.5 h gave **3g** (219 mg, 83%) as a pale yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 9 : 1). M.p.157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79, (d, *J* = 8.8 Hz, 1H), 7.52 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 4.15 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 147.7, 139.7, 113.7, 108.0, 91.1 ppm



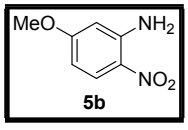
2-Nitroaniline (5a)[18]

The reaction was carried out according to general procedure using 2-nitrobenzoic acid (**4a**, 167 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2 h gave **5a** (124 mg, 90%) as a orange solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 70-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.34-7.31 (m, 1H), 6.81 (dd, *J* = 8.4, 0.4 Hz, 1H), 6.68-6.64 (m, 1H), 6.14 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 135.7, 132.1, 126.1, 118.9, 116.9 ppm.



5-Methoxy-2-nitroaniline (5b)[18]

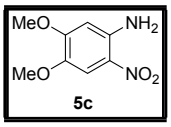
The reaction was carried out according to general procedure using 5-methoxy-2-nitrobenzoic acid (**4b**, 197 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2.5 h gave **5b** (126 mg, 75%) as a yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 128-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 9.6 Hz, 1H), 6.27-6.24 (m, 3H), 6.15



(d, J = 2.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 147.2, 128.4, 126.8, 106.7, 99.4, 55.7 ppm.

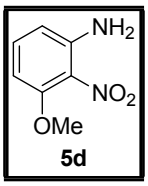
4,5-Dimethoxy-2-nitroaniline (5c)[18]

The reaction was carried out according to general procedure using 4,5-dimethoxy-2-nitrobenzoic acid (**4c**, 227 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 3 h gave **5c** (158 mg, 80%) as a orange red solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 172-174 ^{o} C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 6.22 (br, 2H), 6.17 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 142.7, 141.5, 124.4, 106.4, 99.0, 56.2 ppm.



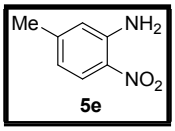
3-Methoxy-2-nitroaniline (5d)[19]

The reaction was carried out according to general procedure using 3-methoxy-2-nitrobenzoic acid (**4d**, 197 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2.5 h gave **5d** (129 mg, 77%) as a yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 124-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, *J* = 8.2 Hz, 1H), 6.36 (d, J = 8.0 Hz, 1H), 6.30 (d, J = 8.4 Hz, 1H), 4.97 (br, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 143.2, 133.1, 109.7, 100.8, 56.4 ppm.



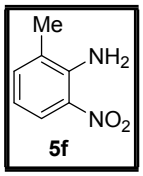
5-Methyl-2-nitroaniline (5e)[18]

The reaction was carried out according to general procedure using 5-methyl-2-nitrobenzoic acid (**4e**, 181 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 3 h gave **5e** (114 mg, 75%) as a yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 106-108 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 1H), 6.58 (s, 1H), 6.48 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.07 (br, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 144.8, 130.4, 126.0, 118.6, 118.3, 21.6 ppm



2-Methyl-6-nitroaniline (5f)[20]

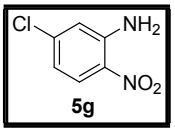
The reaction was carried out according to general procedure using 2-methyl-6-nitrobenzoic acid (**4f**, 181 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL,



1.2 mmol) in DMF (4 mL) for 2 h gave **5f** (144 mg, 95%) as orange solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 94-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 8.4 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 6.62 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.15 (br, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 136.1, 125.2, 124.3, 116.0, 17.5 ppm.

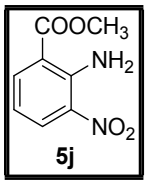
5-Chloro-2-nitroaniline (5g)[21]

The reaction was carried out according to general procedure using 5-chloro-2-nitrobenzoic acid (**4g**, 201 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 4 h gave **5g** (43 mg, 25%) as a yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 128-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 9.2 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.66 (dd, *J* = 9.2, 2.0 Hz, 1H), 6.15 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 141.9, 130.9, 127.7, 117.8, 117.6 ppm.



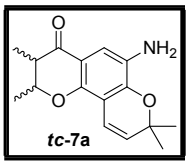
Methyl 2-amino-3-nitrobenzoate (5j)[22]

The reaction was carried out according to general procedure using 5-chloro-2-nitrobenzoic acid (**4j,** 255 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2 h gave **5j** (118 mg, 60%) as a yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 8:2). M.p. 96-98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39-8.37 (br, 2H), 8.38 (dd, *J* = 8.6, 1.4 Hz, 1H), 8.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.65 (t, *J* = 8.2, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 147.3, 139.4, 133.2, 132.3, 114.4, 113.9, 52.3 ppm.



6-Amino-2,3,8,8-tetramethyl-2,3-dihydropyrano[2,3-*f*]chromen-4(8*H*)-one (*tc*-7a)

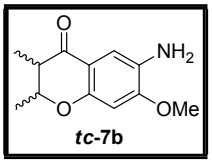
The reaction was carried out according to general procedure using 2,3,8,8-tetramethyl-4-oxo-2,3,4,8-tetrahydropyrano[2,3-*f*]chromene-6-carboxylic acid (**2a**, 302 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 2.5 h gave ***tc*-7a** (232 mg, 85%) as an inseparable diastereomeric mixture (*trans*/*cis* = 55:45) as a yellow solid after passing through silica gel column chromatography (hexane/EtOAc = 7:3). M.p. 120-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 5.56 (d, *J* = 10.4 Hz, 1H), 4.56-4.50 (m, $1H_{minor}$), 4.18-4.10 (m, $1H_{major}$), 3.50 (br, 2H), 2.50-2.39 (m, 1H), 1.48-1.44 (m, $9H_{major+minor}$),



1.36 (d, J = 6.4 Hz, $3H_{minor}$), 1.17 (d, J = 7.2 Hz, $3H_{major}$), 1.11 (d, J = 7.2 Hz, $3H_{minor}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 193.7, 151.2, 151.1, 147.5, 147.4, 129.7, 129.6, 128.3, 128.3, 116.3, 116.2, 113.3, 112.5, 111.5, 111.4, 109.0, 79.5, 77.7, 77.6, 76.7, 46.6, 45.2, 28.4, 28.4, 28.2, 28.1, 19.7, 16.5, 10.4, 9.3 ppm, one signal is superimposed; HRMS (ESI): $[M + H]^+$ Calcd for $C_{16}H_{20}NO_3$, 274.1443; found 274.1426.

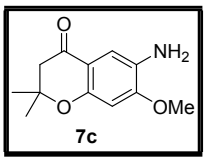
6-Amino-7-methoxy-2,3-dimethylchroman-4-one (*tc*-7b)

The reaction was carried out according to general procedure using 7-methoxy-2,3-dimethyl-4-oxochroman-6-carboxylic acid (**6b**, 250 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 3 h gave ***tc*-7b** (166 mg, 75%) as an inseparable diastereomeric mixture (*trans*/*cis* = 87:13) as a yellow paste after passing through silica gel column chromatography (hexane/EtOAc = 7:3). ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 1H), 6.34, 6.33 (2s, $1H_{major+minor}$), 4.56-4.50 (m, $1H_{minor}$), 4.19-4.11 (m, $1H_{major}$), 3.85 (s, $3H1H_{major+minor}$), 3.44 (br, $2H1H_{major+minor}$), 2.50-2.39 (m, $1H_{major+minor}$), 1.46 (d, J = 6.0 Hz, $3H_{major}$), 1.36 (d, J = 6.8 Hz, $3H_{minor}$), 1.17 (d, J = 6.8, $3H_{major}$), 1.11 (d, J = 7.2, $3H_{minor}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 193.6, 156.0, 154.5, 131.1, 131.0, 129.4, 126.2, 113.2, 112.5, 110.5, 110.46, 98.8, 79.5, 76.7, 55.7, 46.5, 45.1, 19.7, 16.5, 10.4, 9.2 ppm, two signals are superimposed. HRMS (ESI): $[M + Na]^+$ Calcd for $C_{12}H_{15}NNaO_3$, 244.0950; found 244.0967.



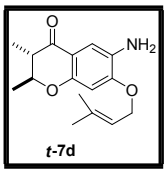
6-Amino-7-methoxy-2,2-dimethylchroman-4-one (7c)

The reaction was carried out according to general procedure using 7-methoxy-2,2-dimethyl-4-oxochroman-6-carboxylic acid (**6c**, 250 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 180 μL, 1.2 mmol) in DMF (4 mL) for 3 h gave **7c** (172 mg, 78%) as a yellow paste after passing through silica gel column chromatography (hexane/EtOAc = 7:3). ^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 1H), 6.32 (s, 1H), 3.85 (s, 3H), 3.26 (br, 2H), 2.62 (s, 2H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 191.4, 155.1, 154.9, 130.5, 113.2, 110.0, 99.5, 79.2, 55.8, 48.6, 26.6 ppm. MS (ESI): m/z 222 $[M+1]^+$. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.33; H, 6.91; N, 6.44.



6-Amino-2,3-dimethyl-7-((3-methylbut-2-en-1-yl)oxy)chroman-4-one (*t*-7d)

The reaction was carried out according to general procedure using 2,3-dimethyl-7-((3-methylbut-2-en-1-yl)oxy)-4-oxochroman-6-carboxylic acid (**6d**, 304 mg, 1.0 mmol), K_2CO_3 (276 mg, 2.0 mmol), tosyl azide (**2**, 184 μL, 1.0 mmol) in DMF (4 mL) for 2.5 h gave ***t*-7d** (220 mg, 80%) as a pure *trans* diastereomer as a yellow paste after passing through silica gel column chromatography (hexane/EtOAc = 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 1H), 6.35 (s, 1H), 5.49-5.46 (m, 1H), 4.55 (d, *J* = 6.8Hz, 2H), 4.20-4.12 (m, 1H), 2.51-2.40 (m, 1H), 1.79 (s, 3H), 1.73 (s, 3H), 1.47 (d, *J* = 6.0 Hz, 3H), 1.18 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 156.2, 153.8, 138.7, 131.1, 118.8, 113.7, 110.5, 99.6, 79.5, 65.5, 46.5, 25.8, 19.8, 18.2, 10.5 ppm. MS (ESI): m/z 276 $[M+1]^+$. Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.97; H, 7.78; N, 5.21.



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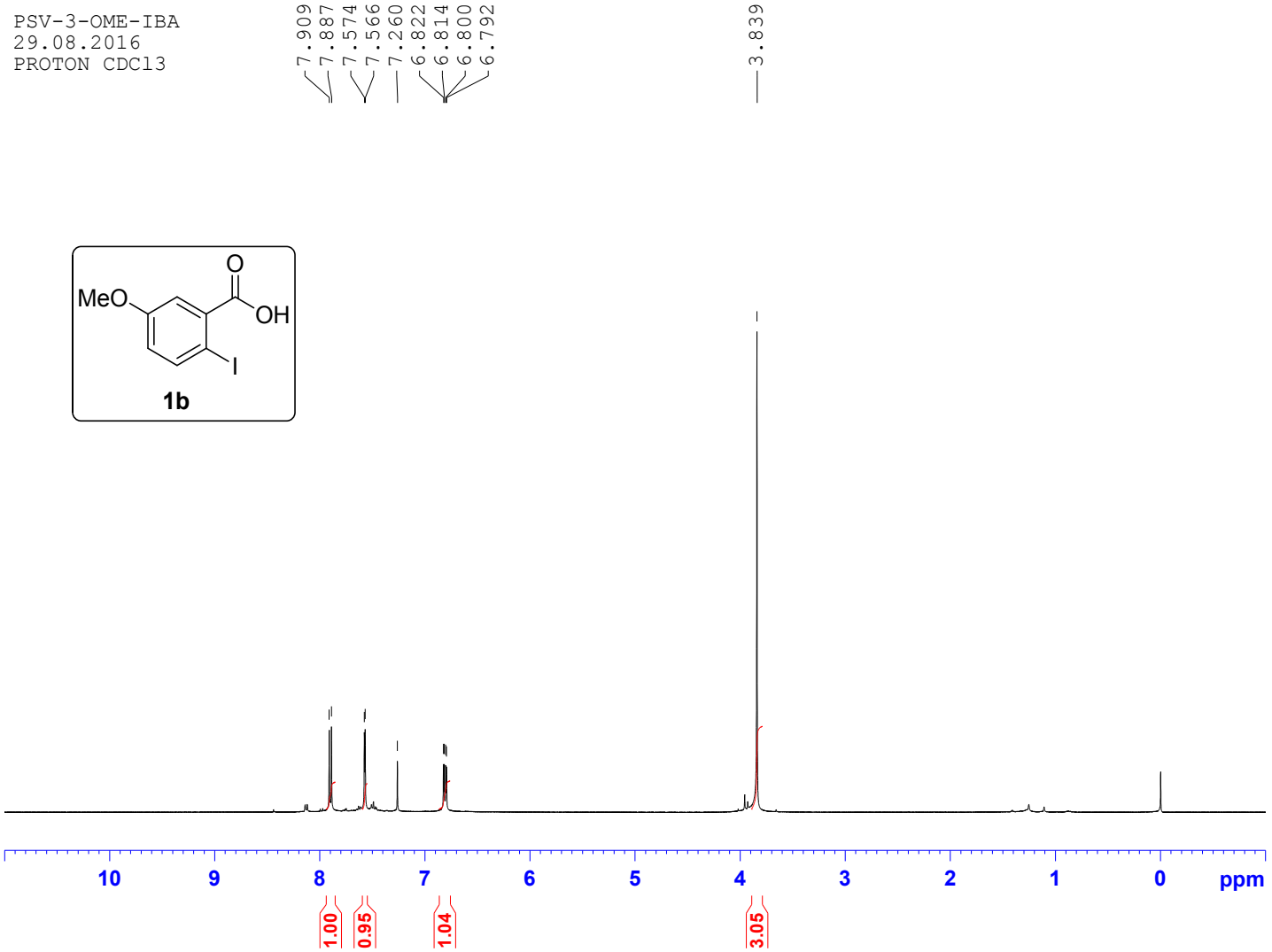

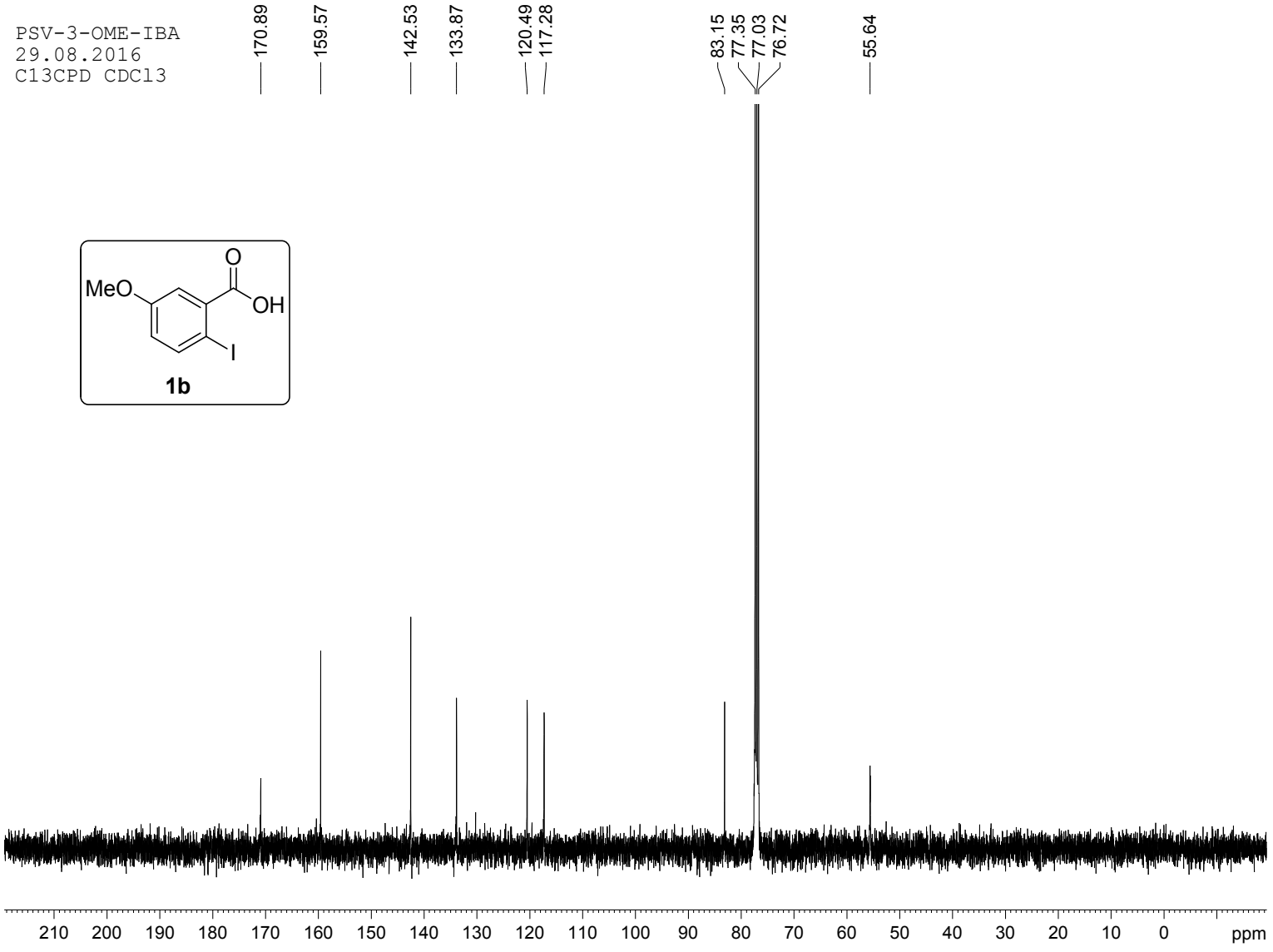
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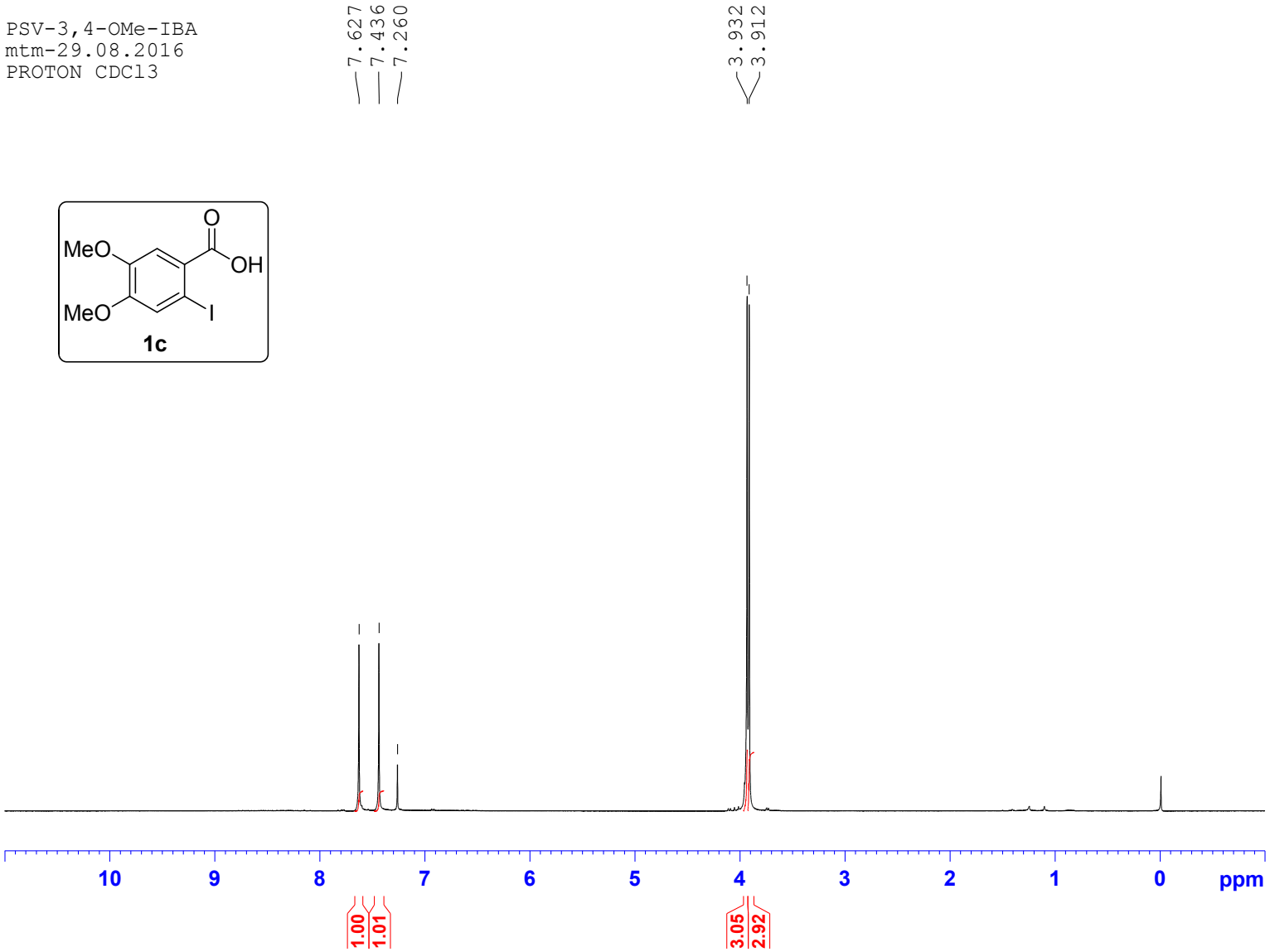

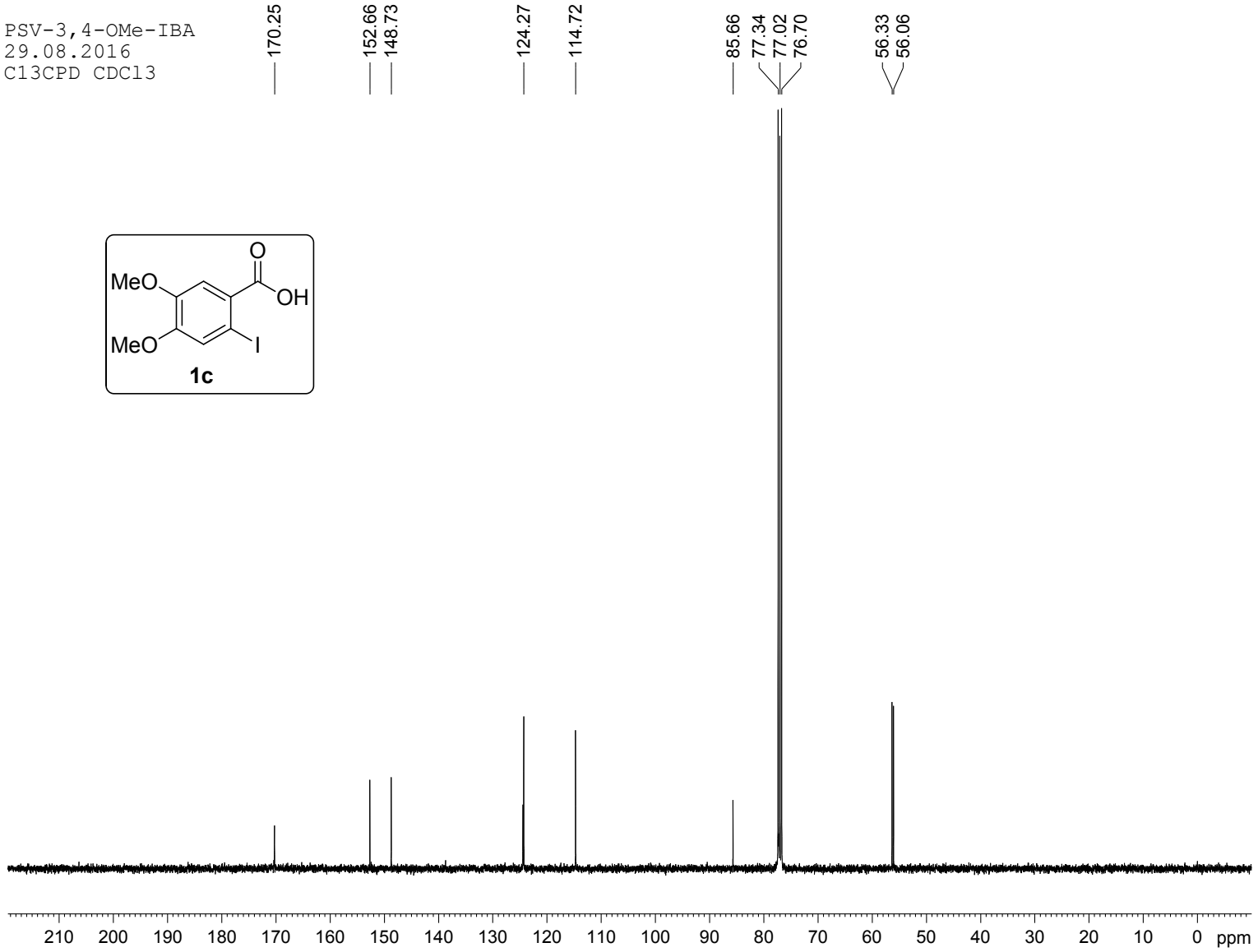
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I
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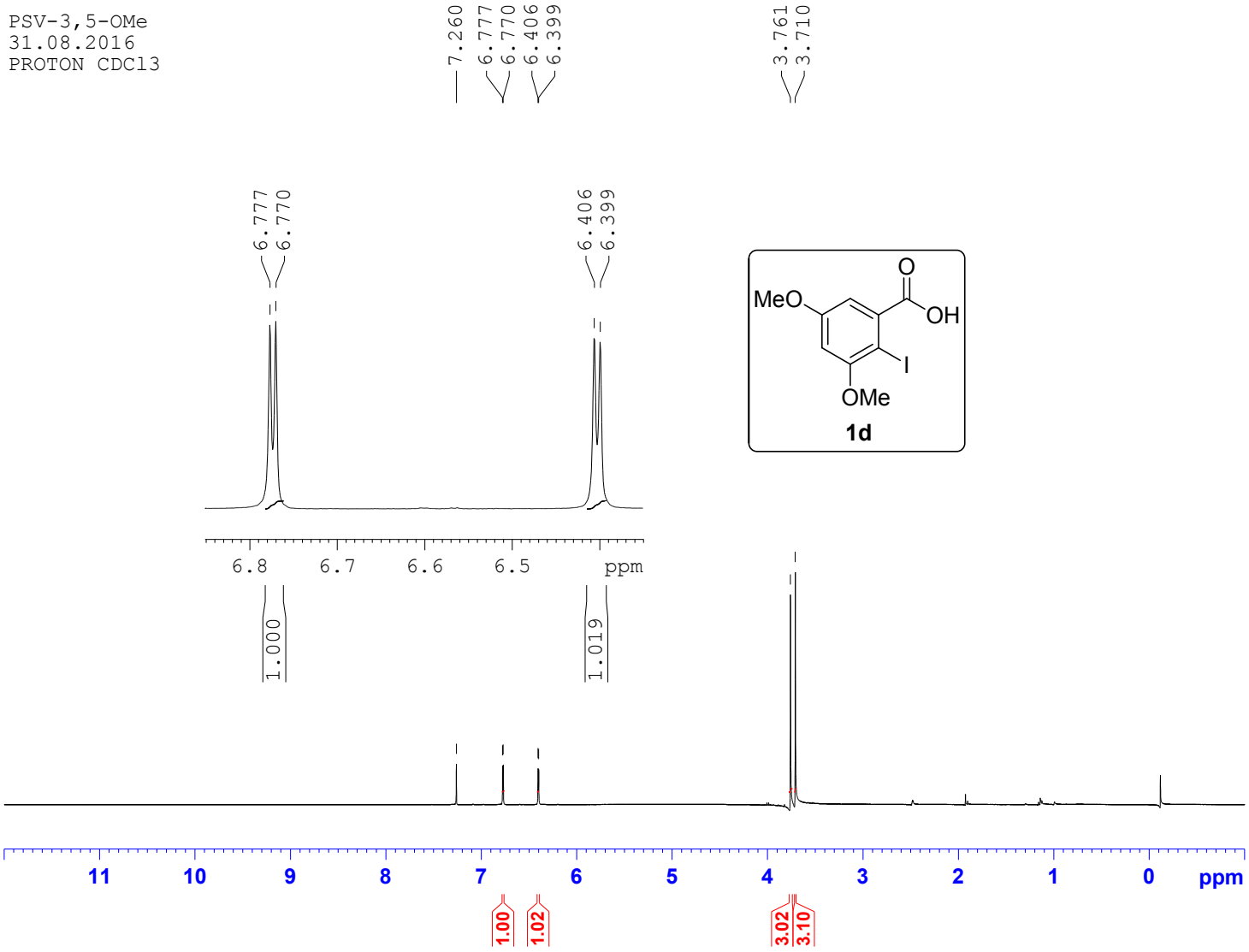
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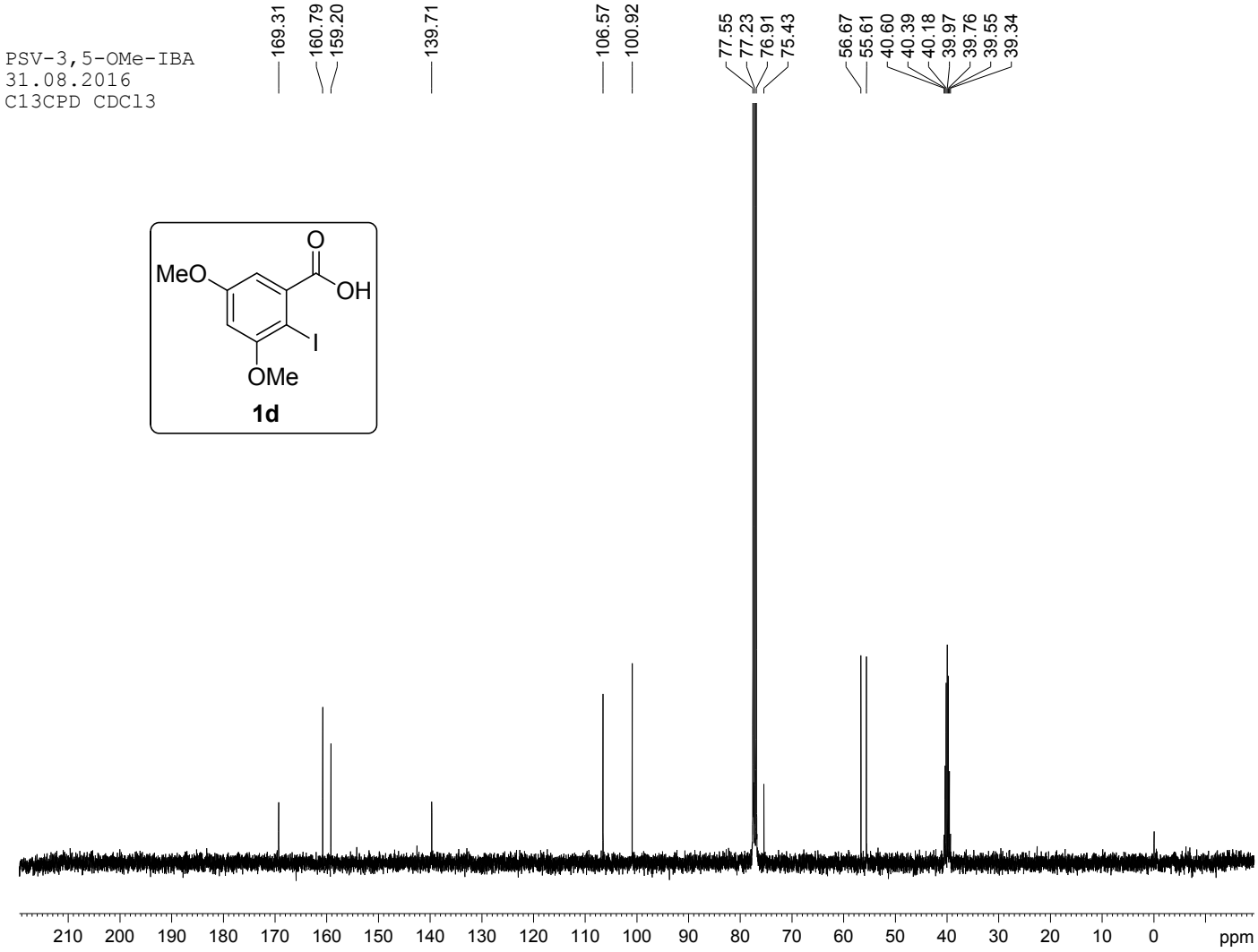
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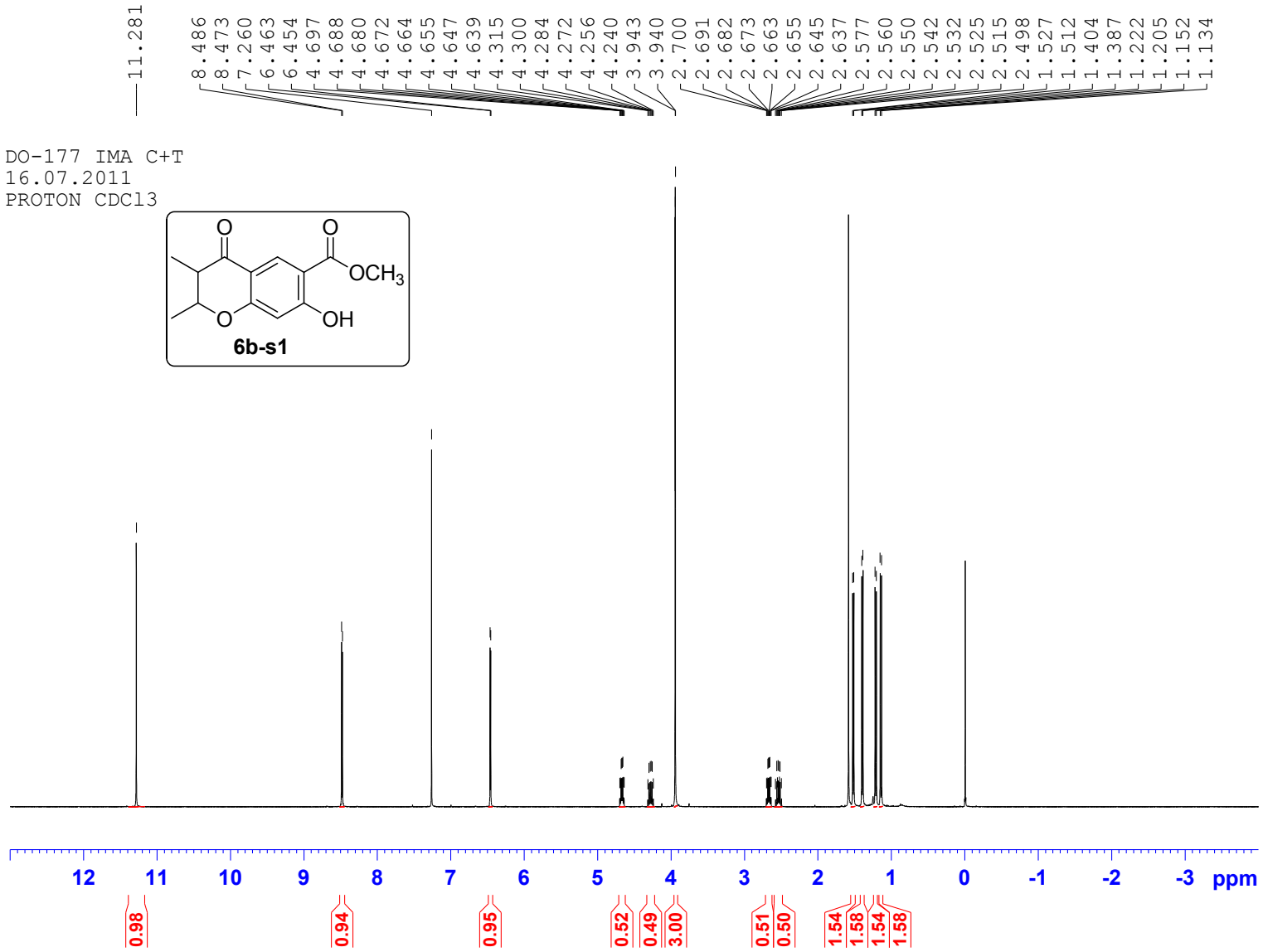
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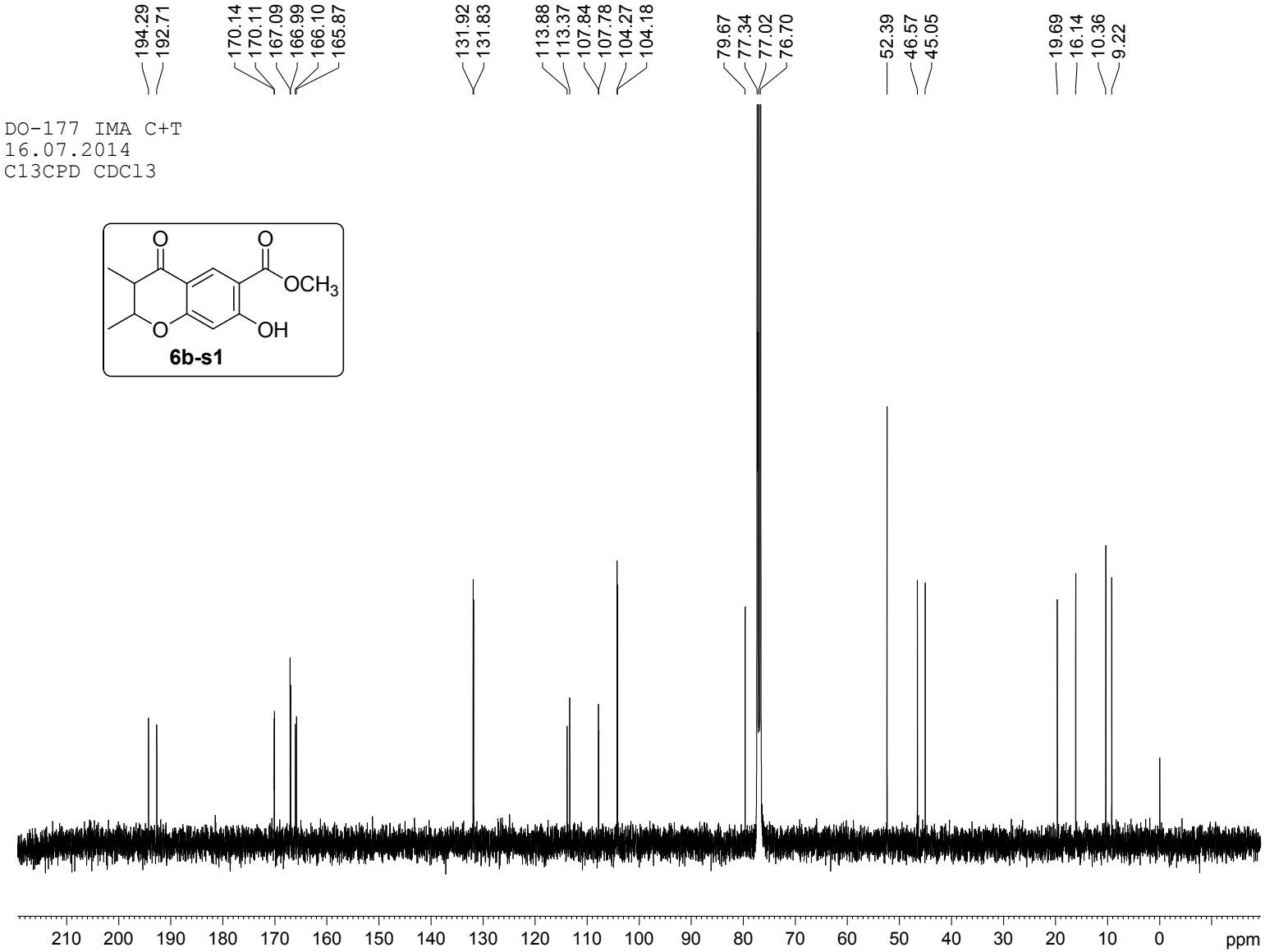
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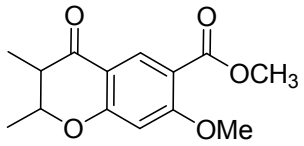

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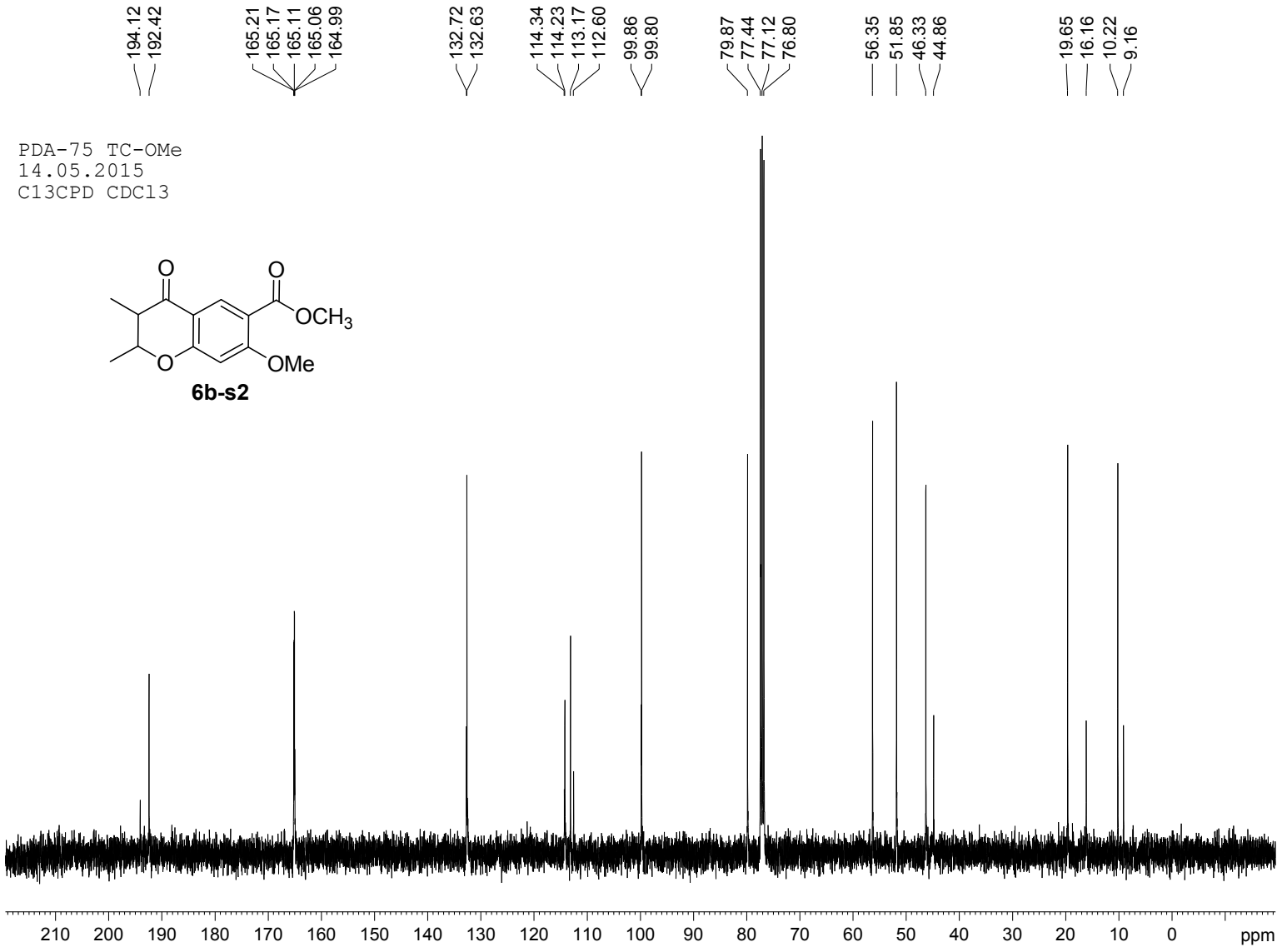
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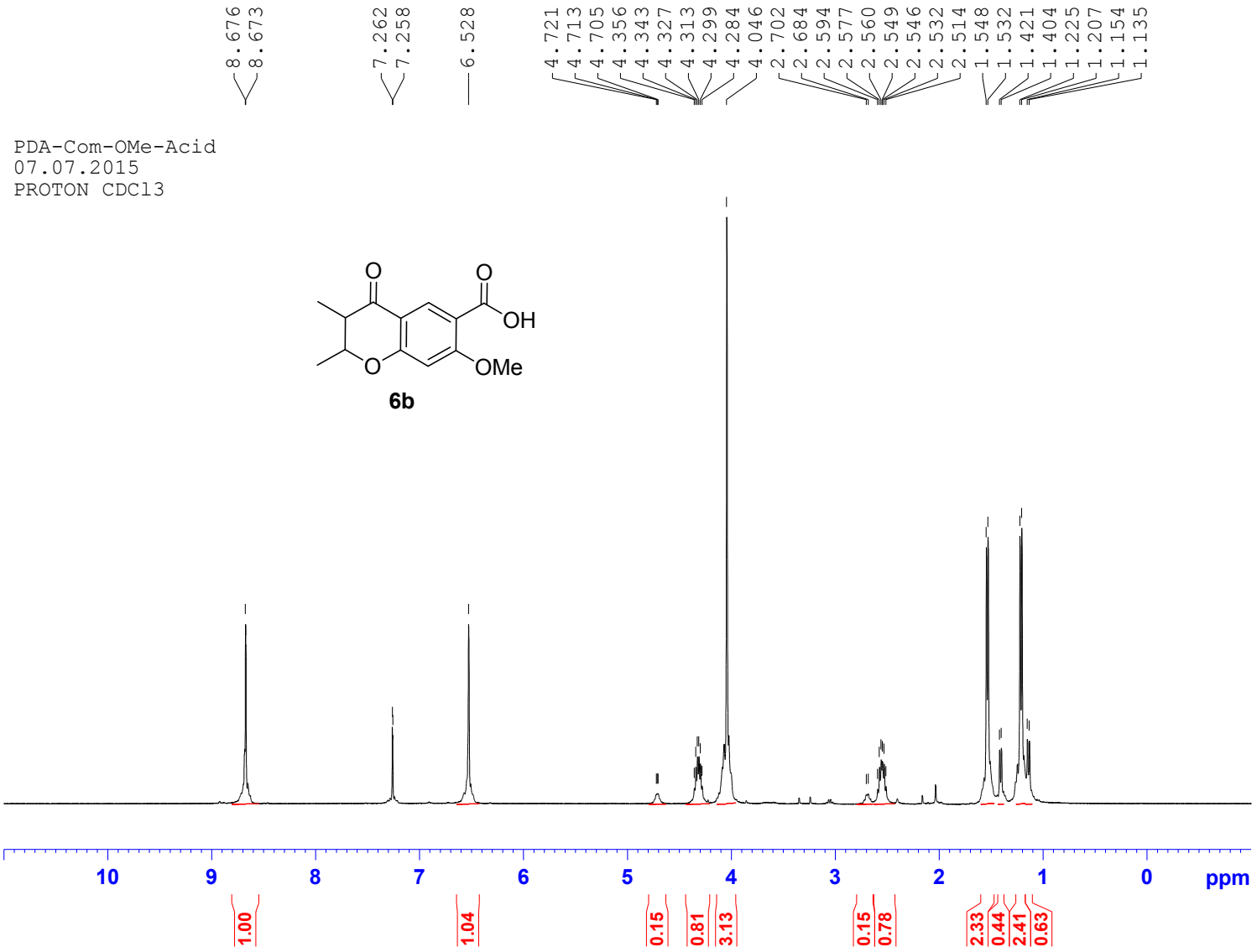
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07.07.2015
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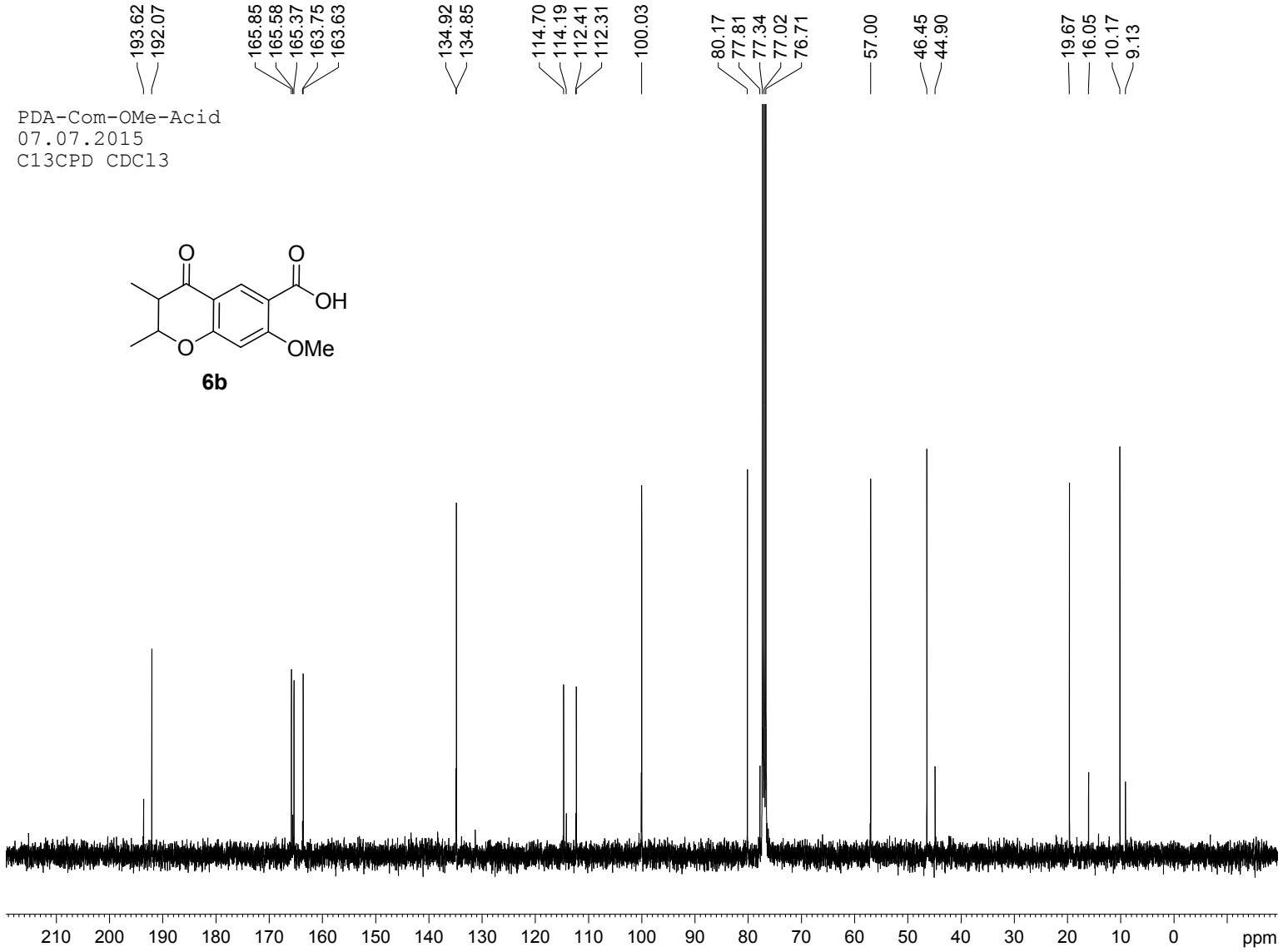
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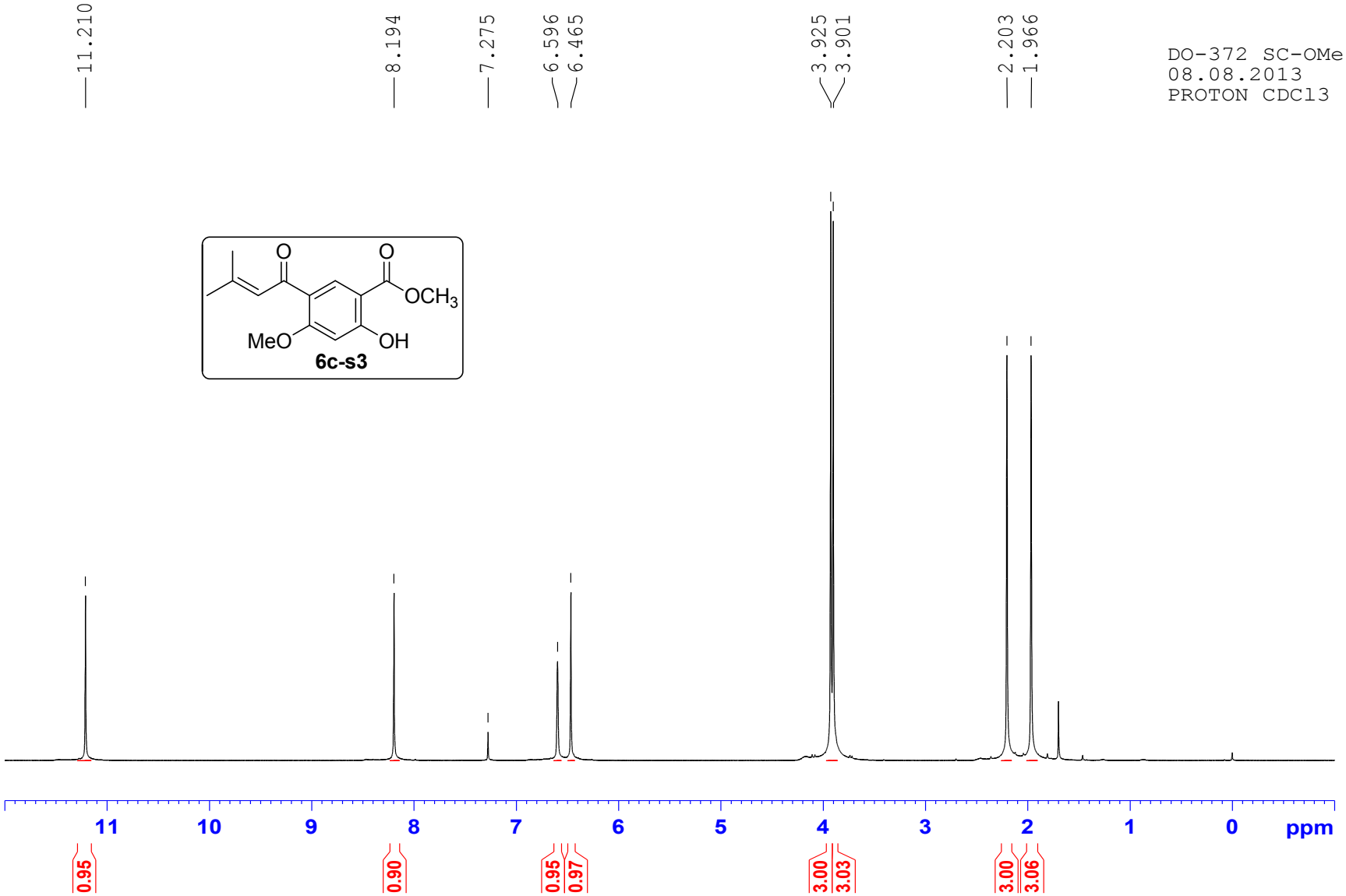
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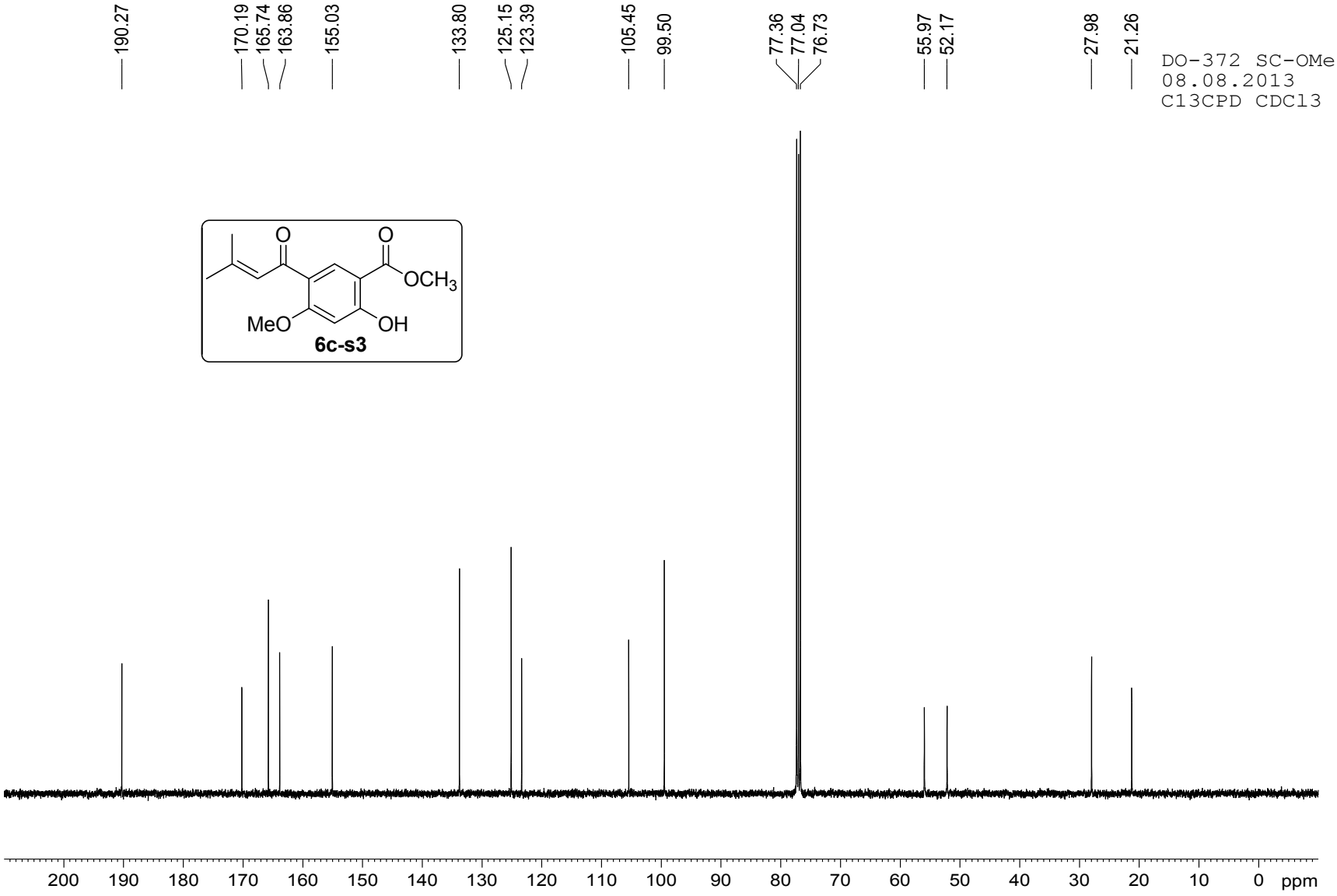
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08.08.2013
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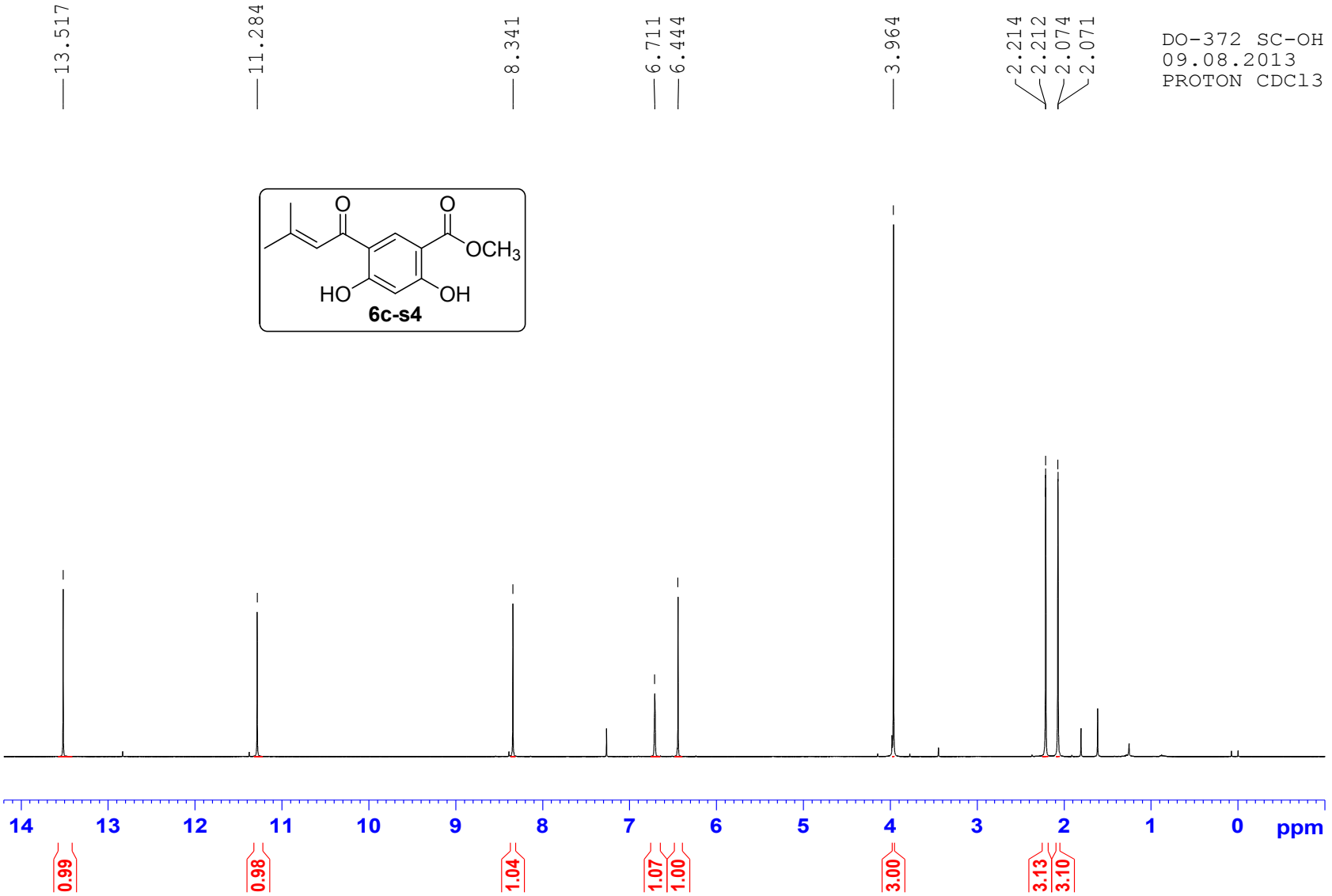
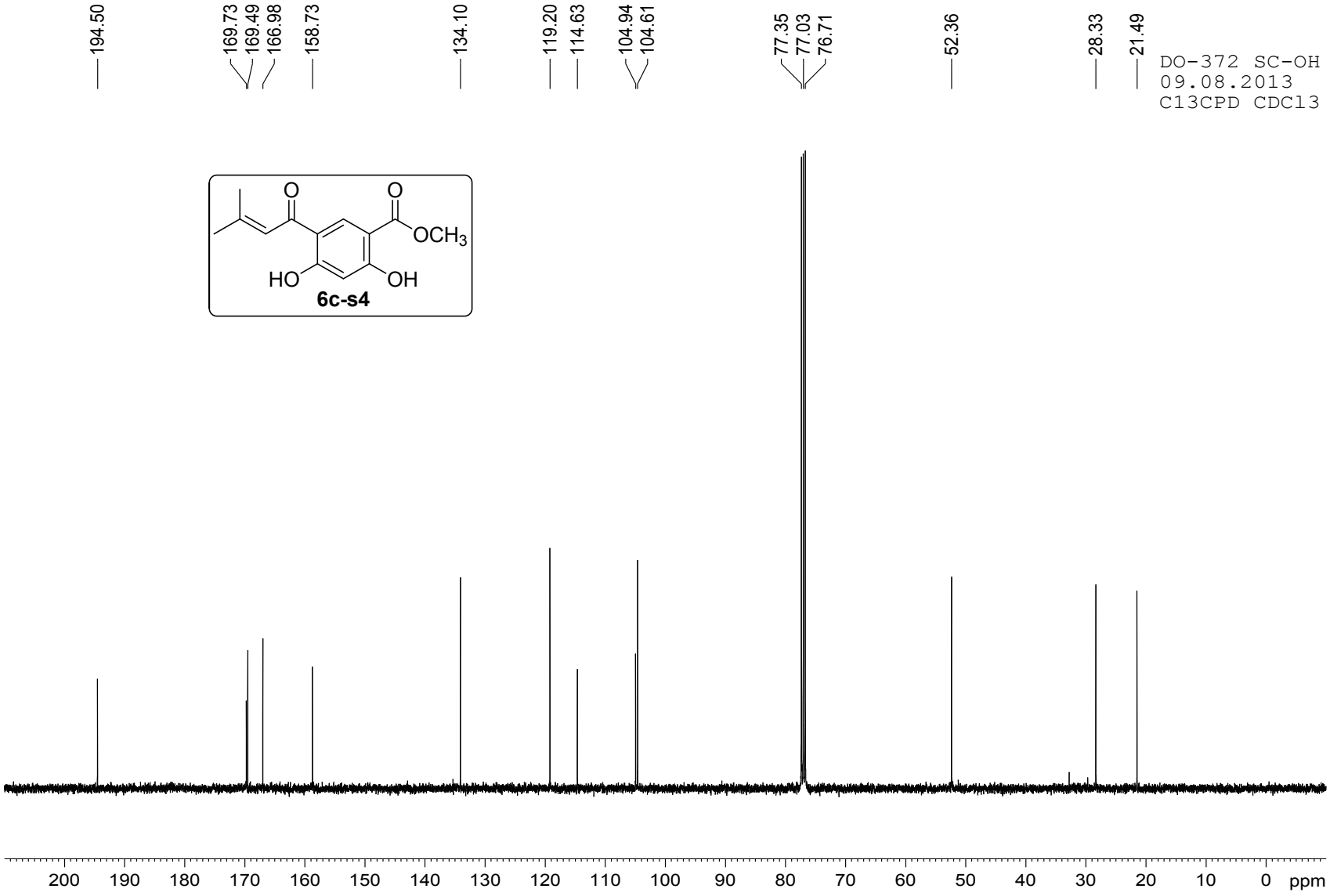
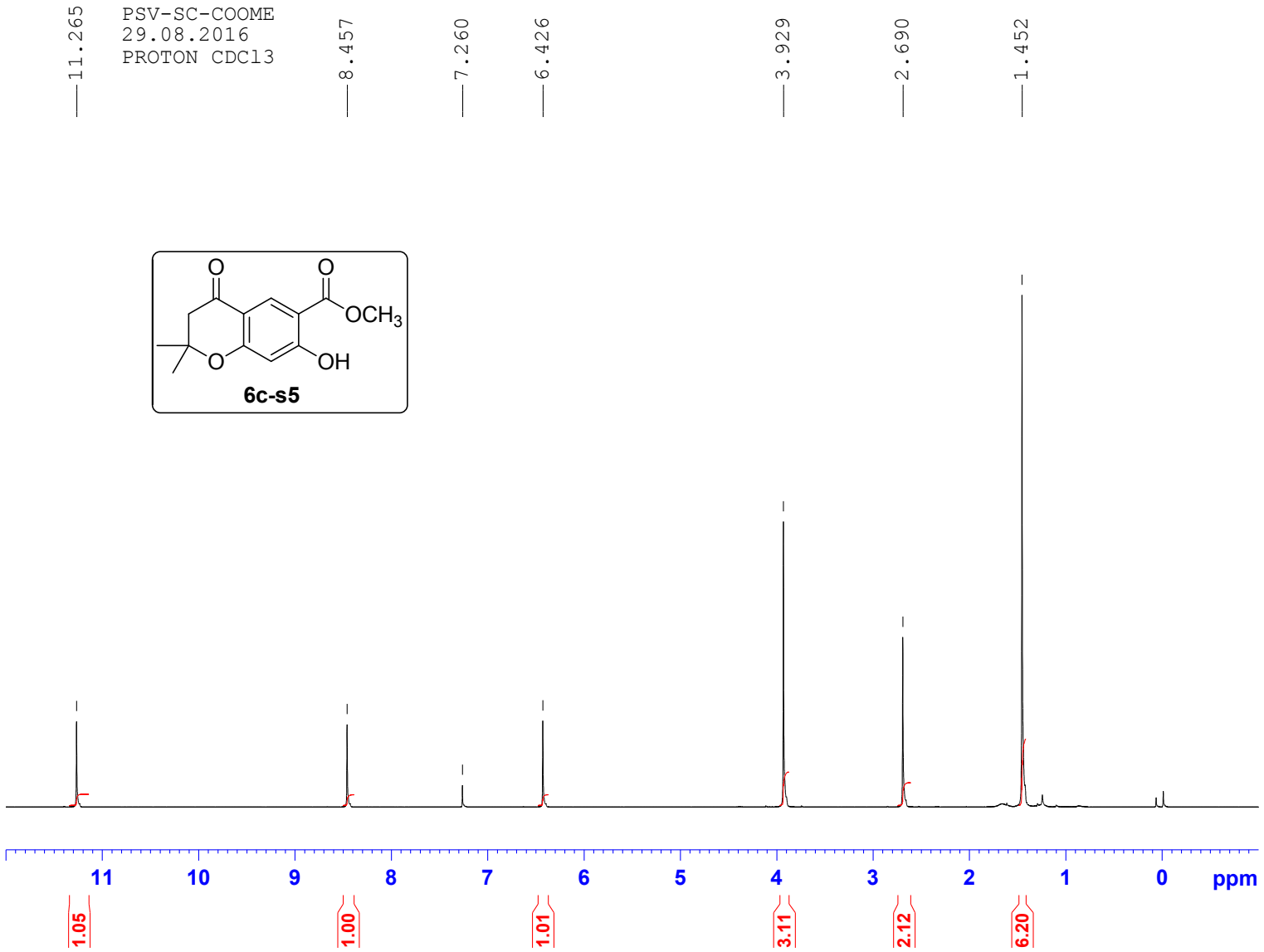
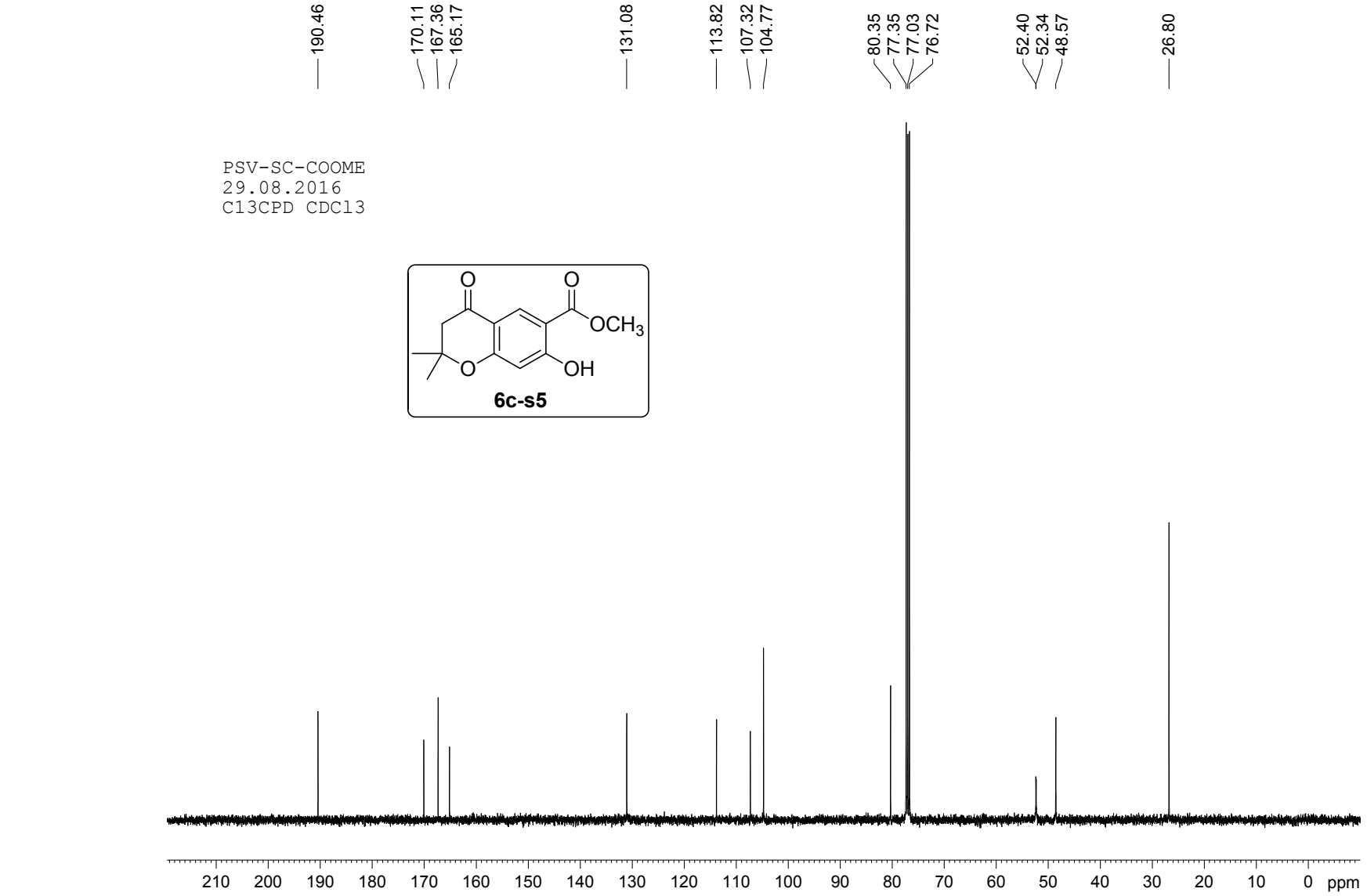
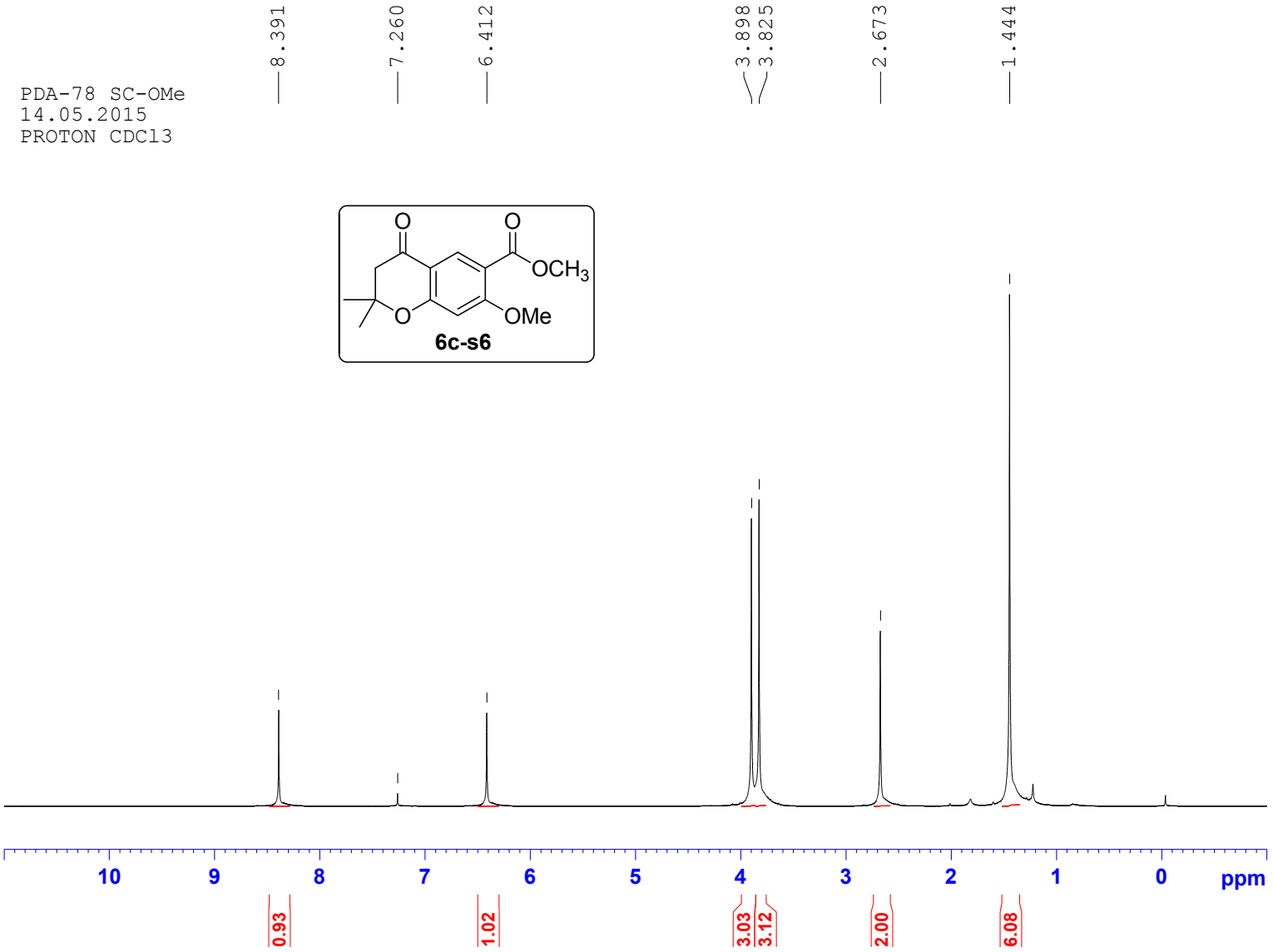
0
ppm

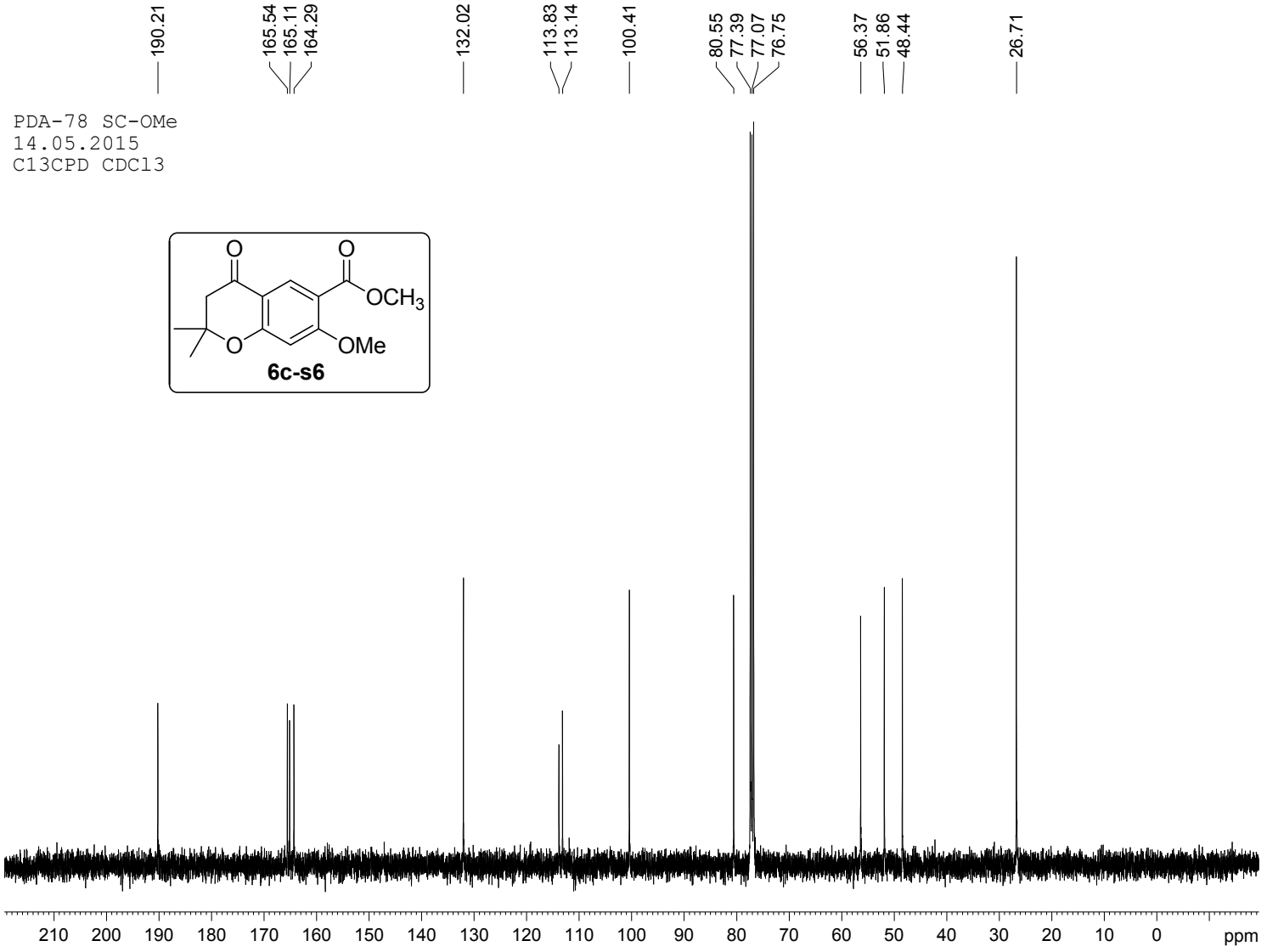

13.517
11.284
8.341
6.711
6.444
3.964
2.214
2.212
2.074
2.071
DO-372 SC-OH
09.08.2013
PROTON CDCl3
O
O
OCH3
HO
OH
6c-s4
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.98
1.04
1.07
1.00
3.00
3.13
3.10

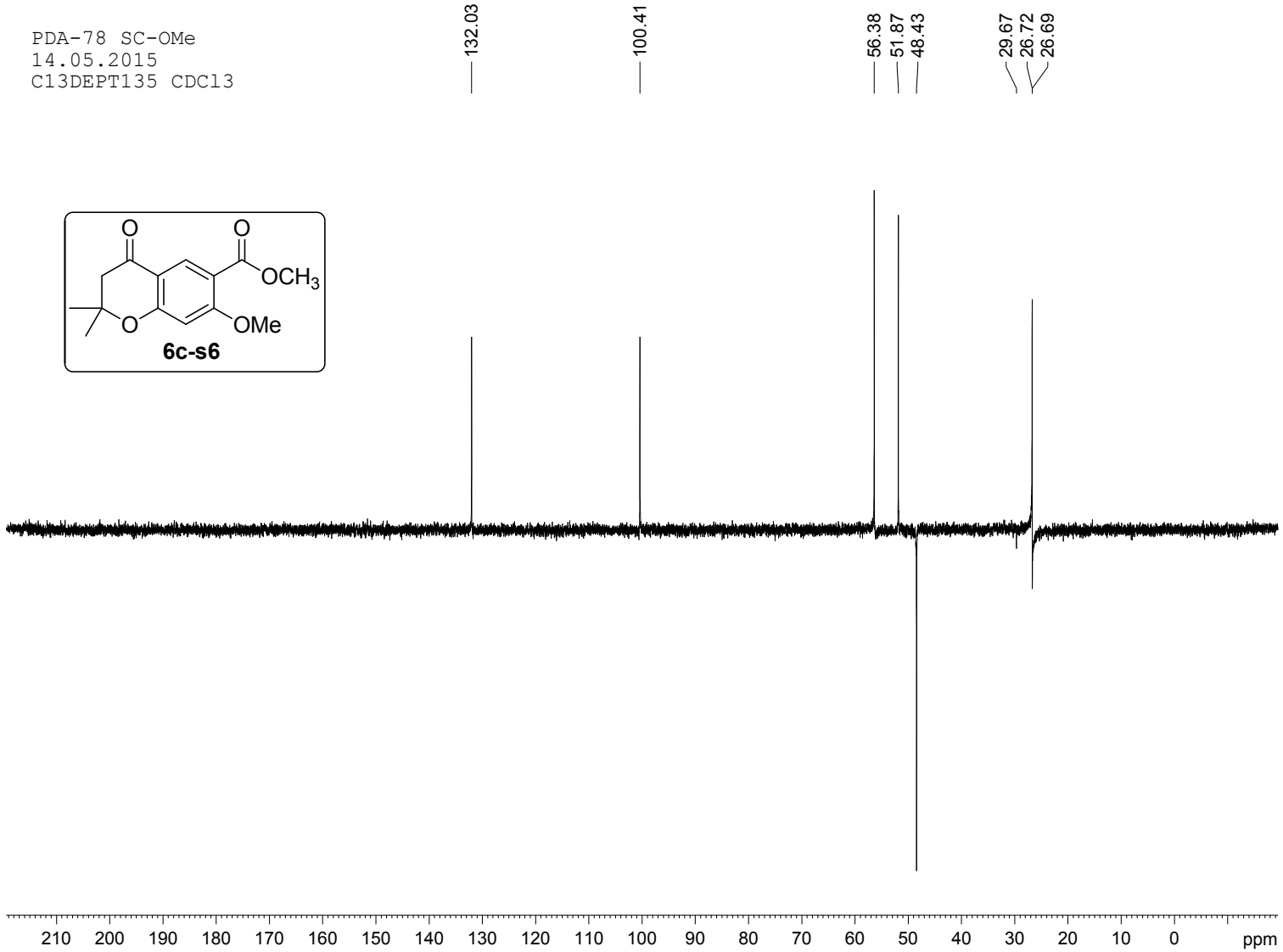

194.50
169.73
169.49
166.98
158.73
134.10
119.20
114.63
104.94
104.61
77.35
77.03
76.71
52.36
28.33
21.49
DO-372 SC-OH
09.08.2013
C13CPD CDCl3
O
O
OCH3
HO
OH
6c-s4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


PSV-SC-COOME
29.08.2016
PROTON CDCl3
11.265
8.457
7.260
6.426
3.929
2.690
1.452
6c-s5
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.00
1.01
3.11
2.12
6.20


190.46
170.11
167.36
165.17
131.08
113.82
107.32
104.77
80.35
77.35
77.03
76.72
52.40
52.34
48.57
26.80
PSV-SC-COOME
29.08.2016
C13CPD CDCl3
O
O
OCH3
O
OH
6c-s5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

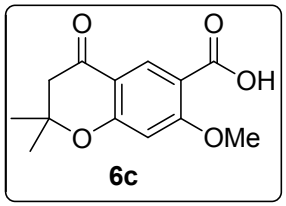

PDA-78 SC-OMe
14.05.2015
PROTON CDCl3
8.391
7.260
6.412
3.898
3.825
2.673
1.444
O
O
OCH3
O
OMe
6c-s6
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.02
3.03
3.12
2.00
6.08


190.21
165.54
165.11
164.29
132.02
113.83
113.14
100.41
80.55
77.39
77.07
76.75
56.37
51.86
48.44
26.71
PDA-78 SC-OMe
14.05.2015
C13CPD CDCl3
O
O
OCH3
O
OMe
6c-s6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

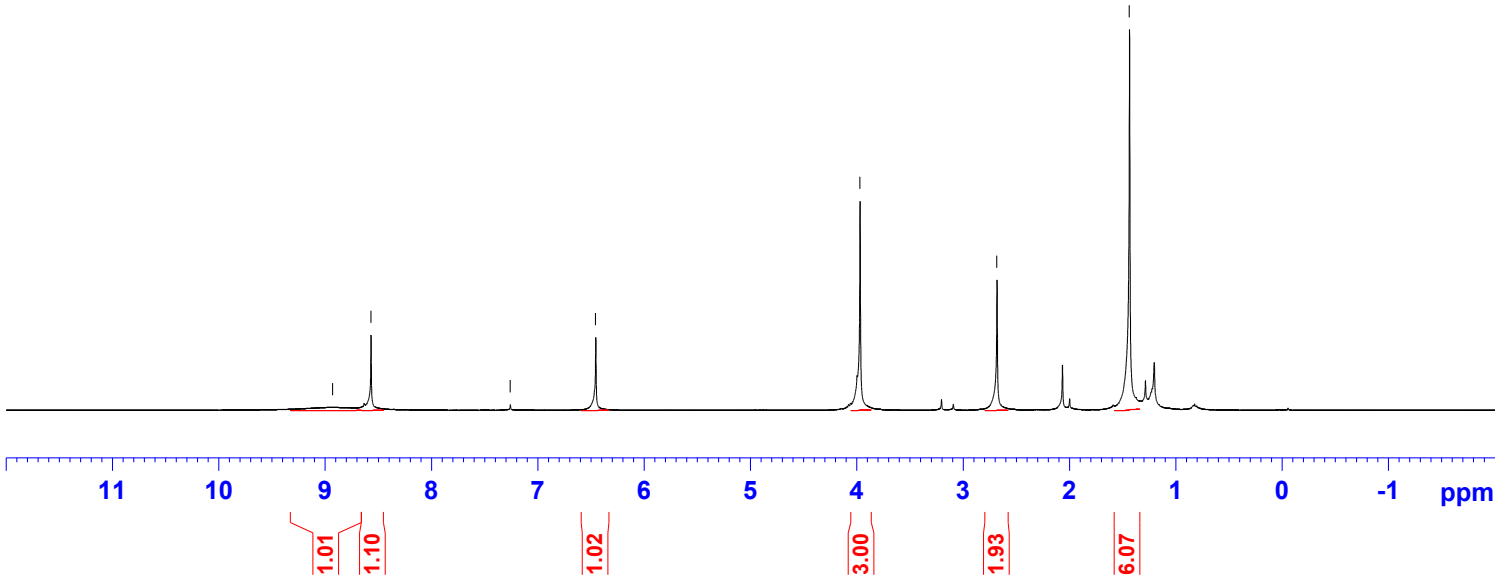

PDA-78 SC-OMe
14.05.2015
C13DEPT135 CDCl3
132.03
100.41
56.38
51.87
48.43
29.67
26.72
26.69
O
O
OCH3
O
OMe
6c-s6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

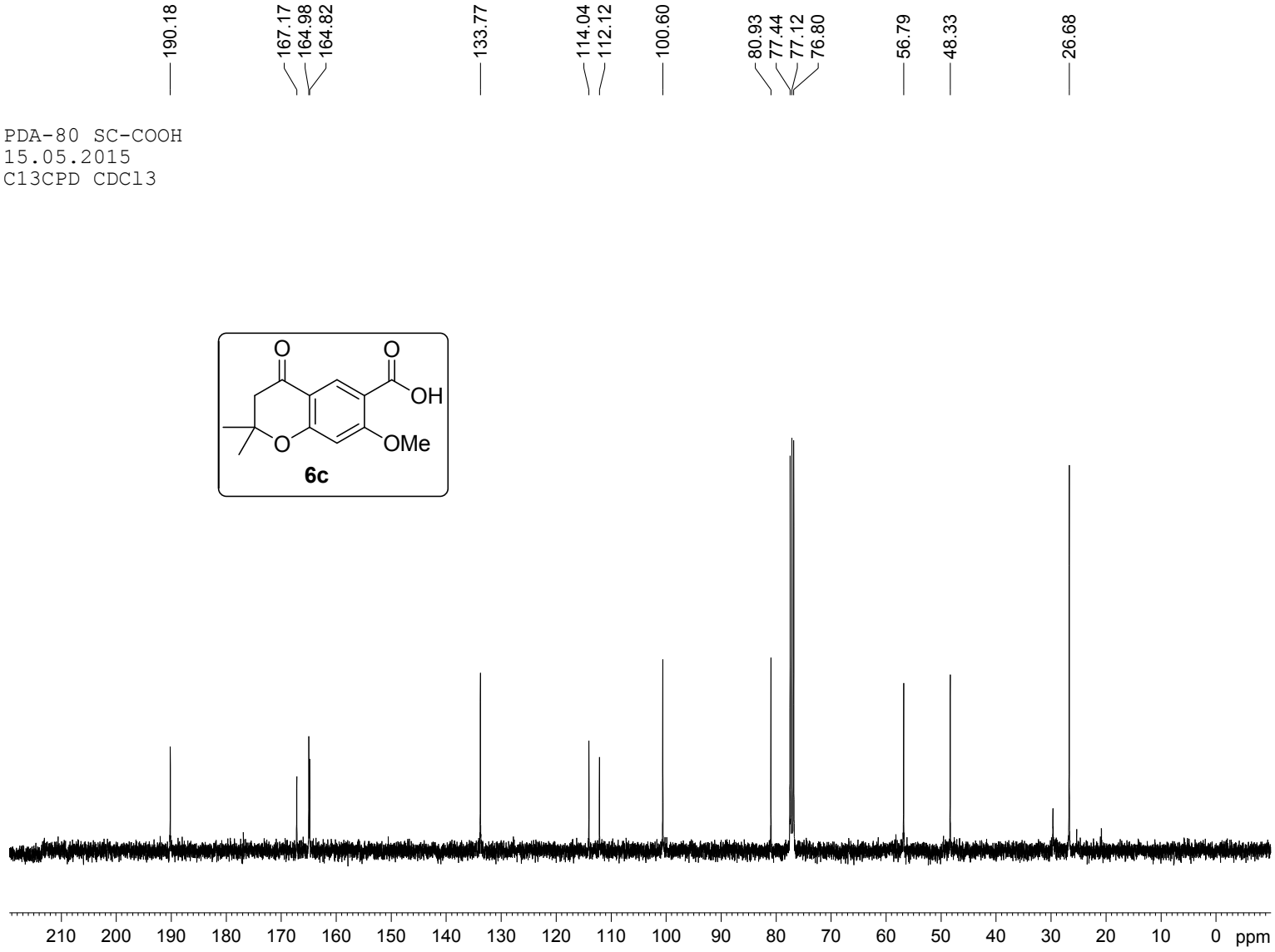
8.930
8.568
7.260
6.457
3.971
2.683
1.437

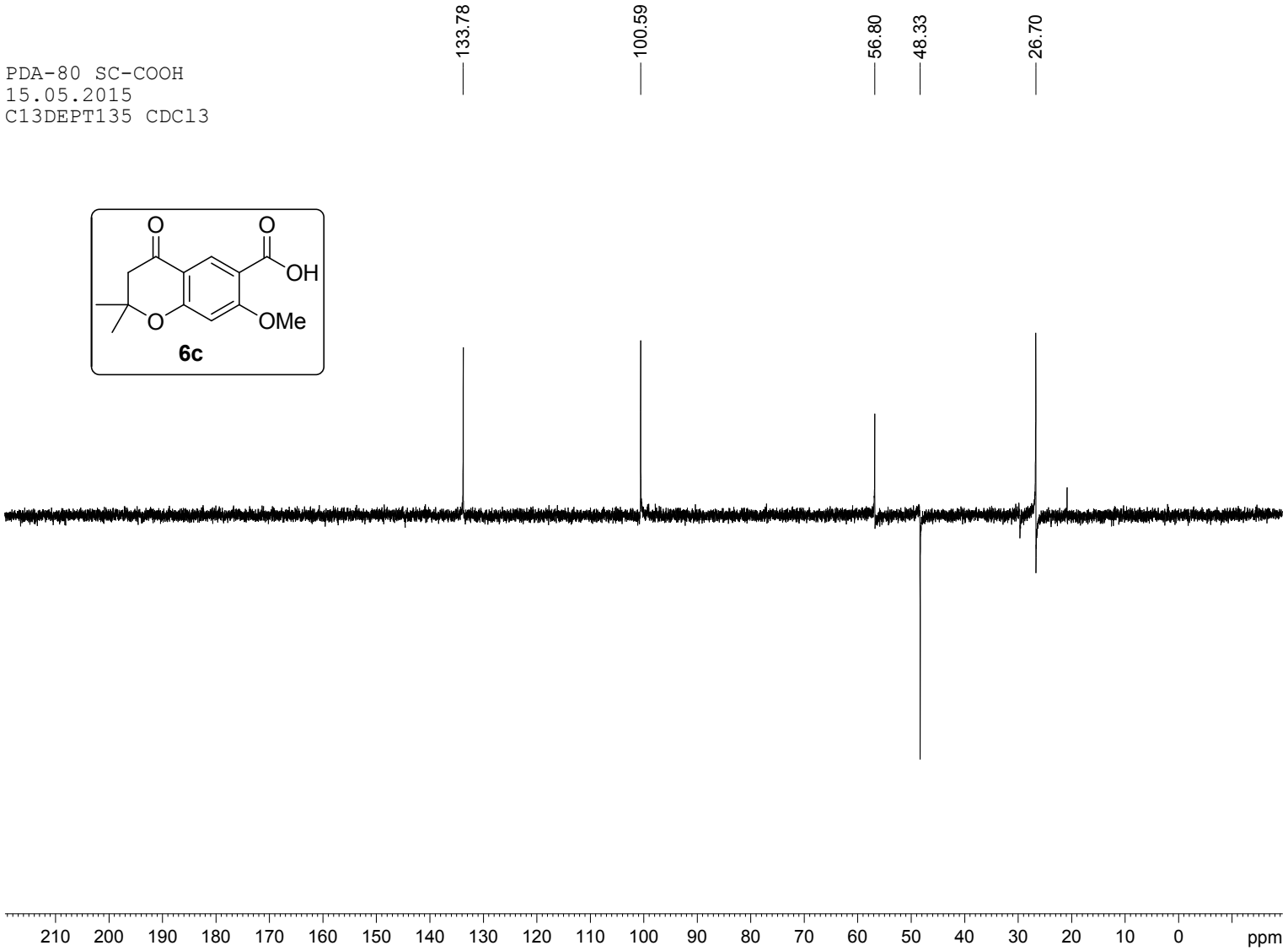
PDA-80 SC-COOH
15.05.2015
PROTON CDCl3

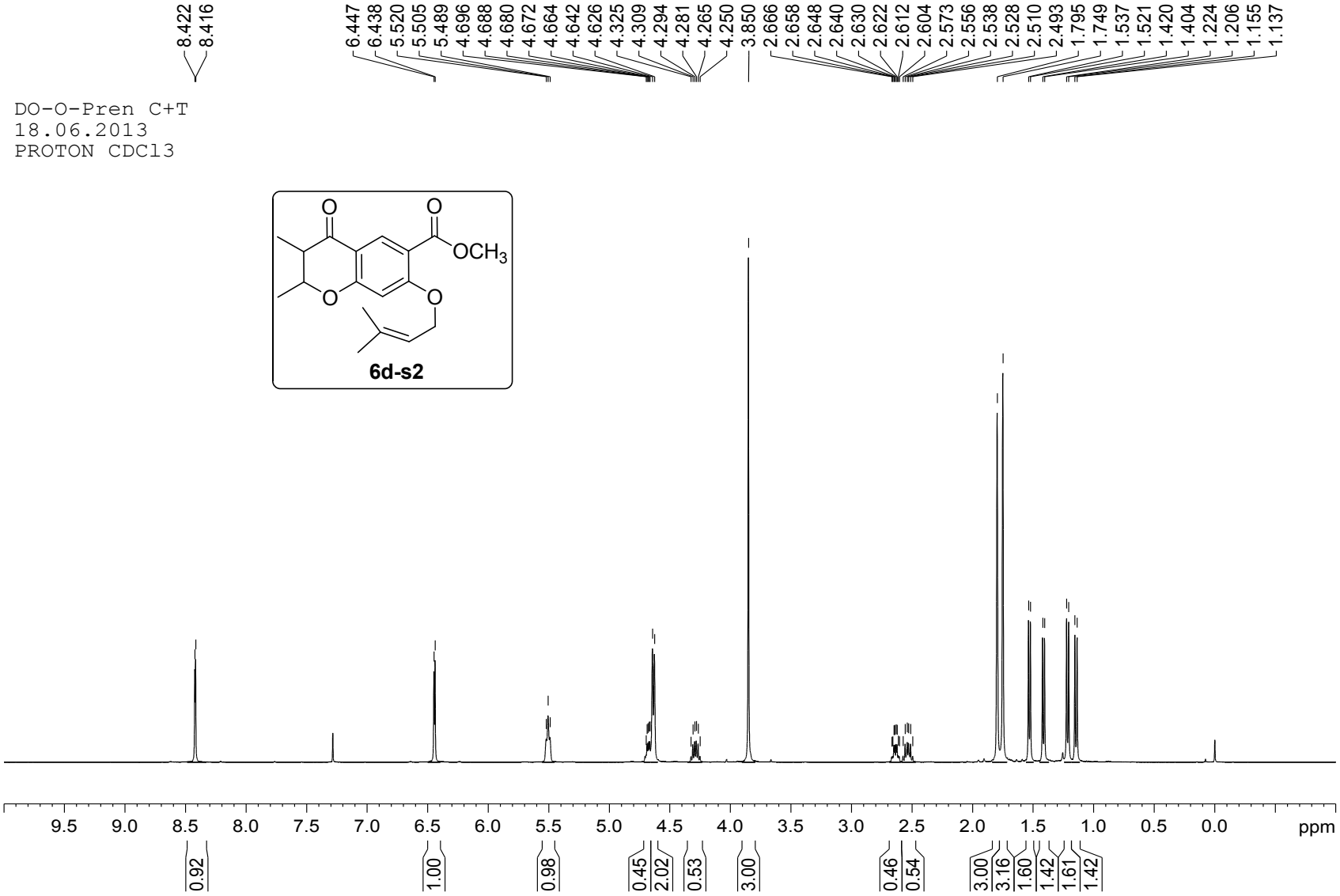


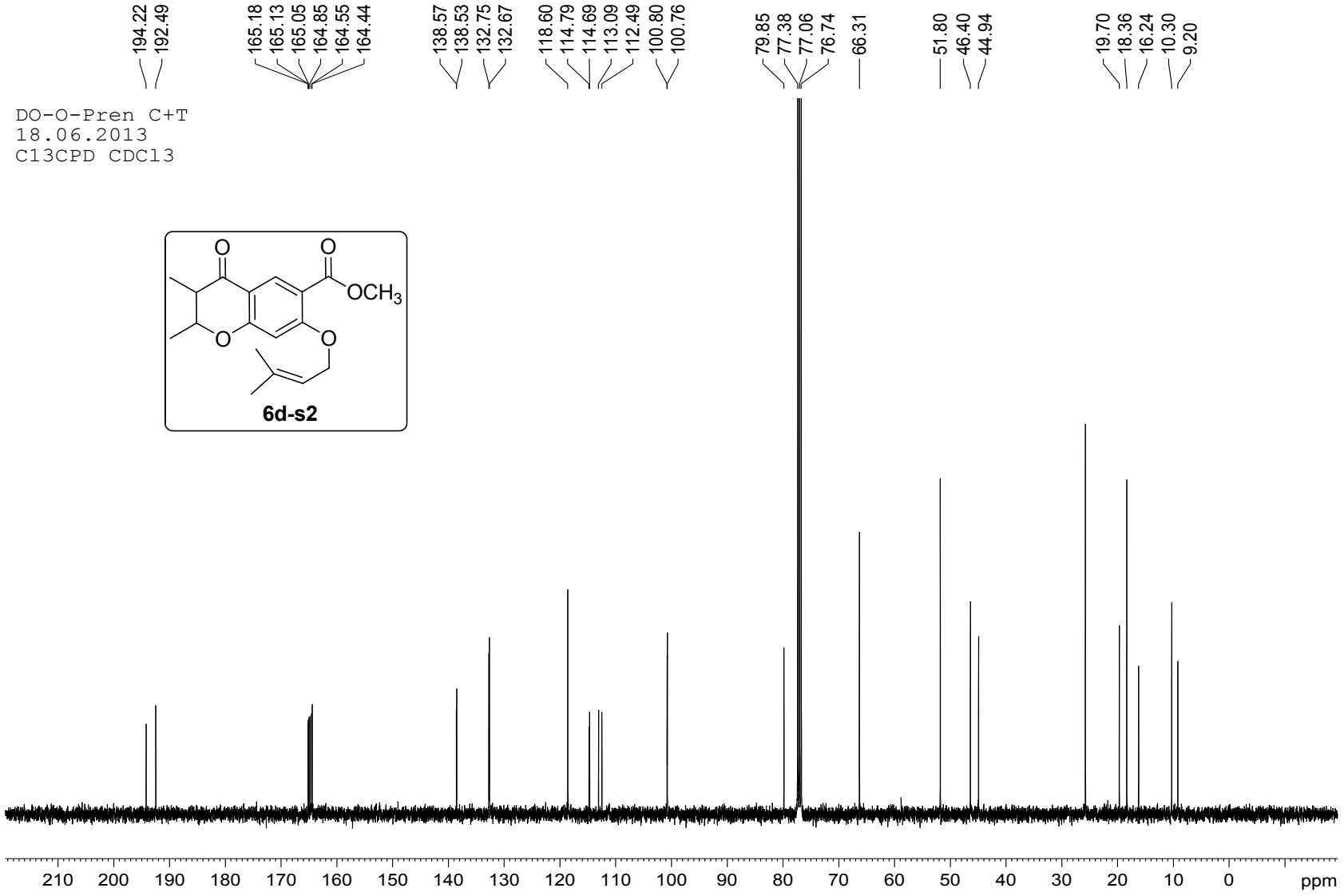
6c

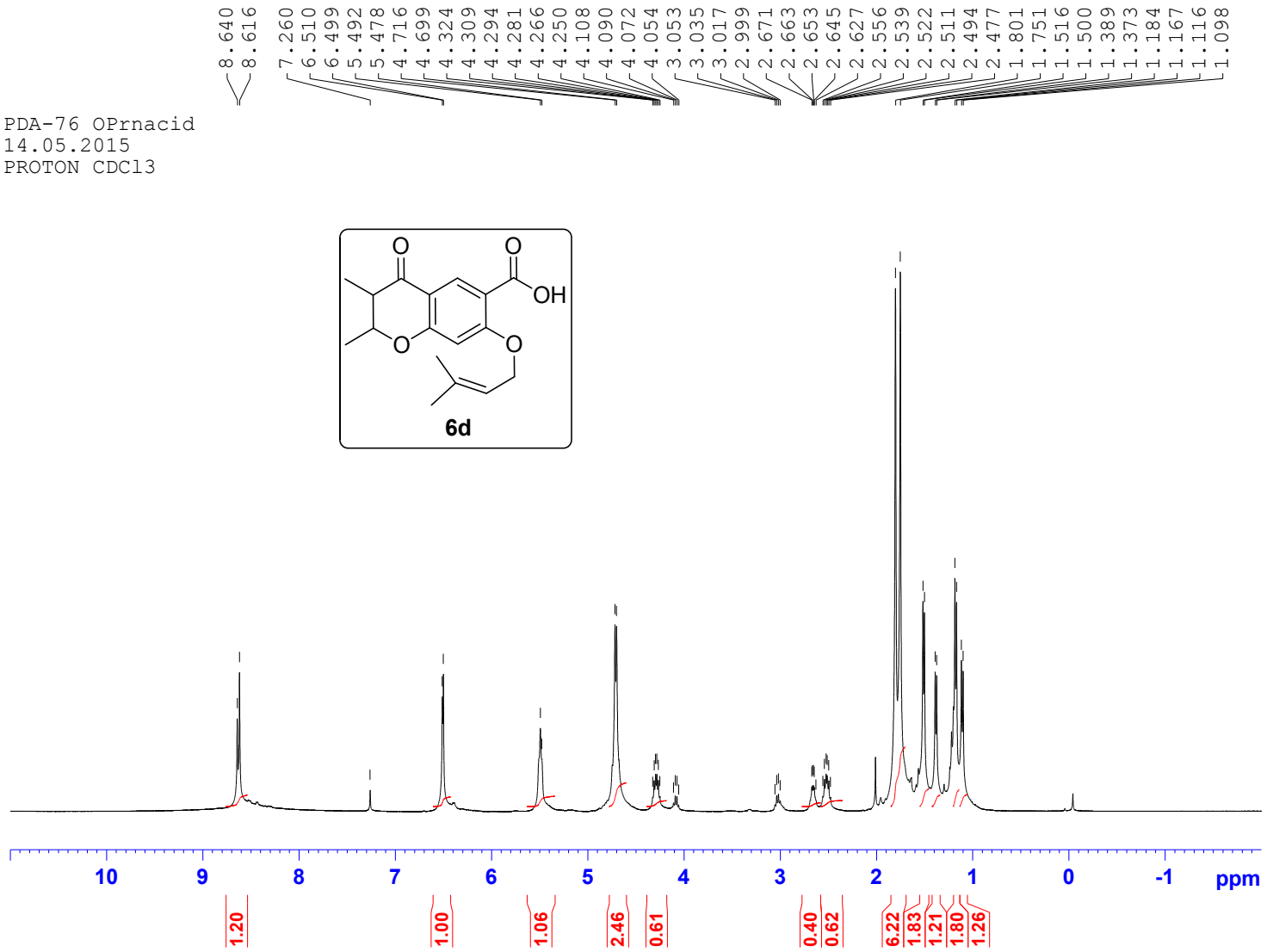


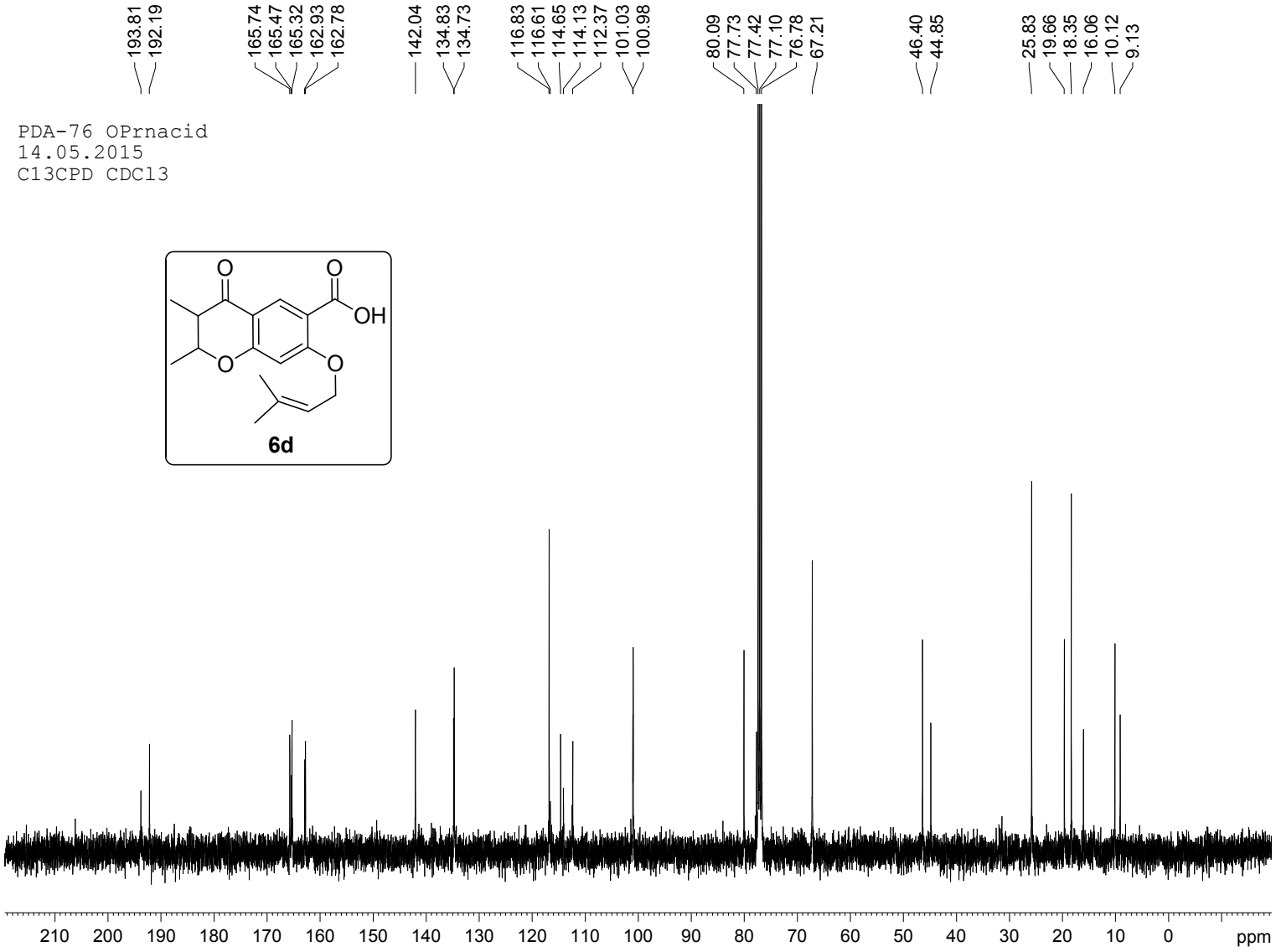

190.18
167.17
164.98
164.82
133.77
114.04
112.12
100.60
80.93
77.44
77.12
76.80
56.79
48.33
26.68
PDA-80 SC-COOH
15.05.2015
C13CPD CDCl3
O
O
OH
O
OMe
6c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


133.78
100.59
56.80
48.33
26.70
PDA-80 SC-COOH
15.05.2015
C13DEPT135 CDCl3
O
O
OH
O
OMe
6c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

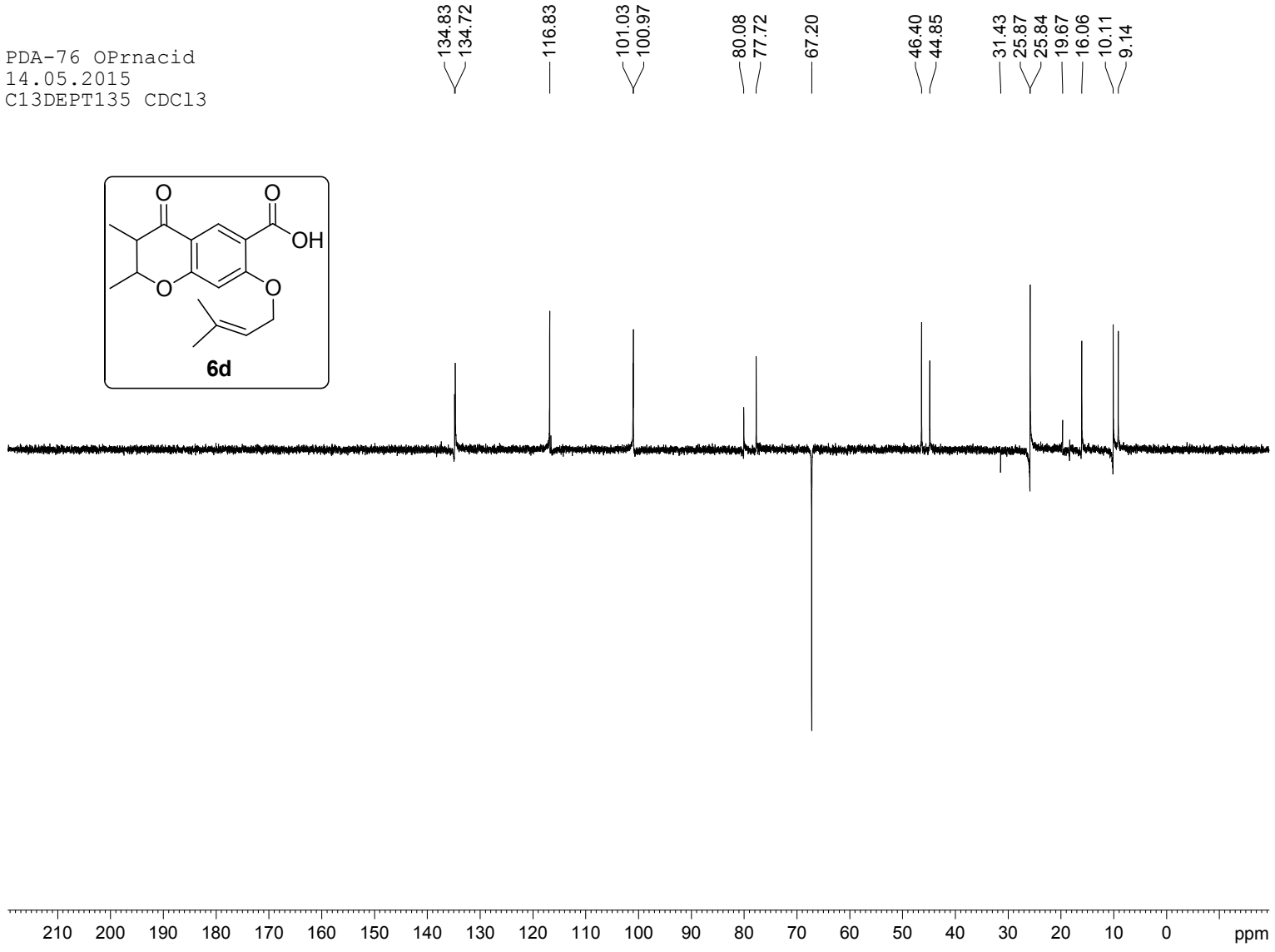

8.422
8.416
6.447
6.438
5.520
5.505
5.489
4.696
4.688
4.680
4.672
4.664
4.642
4.626
4.325
4.309
4.294
4.281
4.265
4.250
3.850
2.666
2.658
2.648
2.640
2.630
2.622
2.612
2.604
2.573
2.556
2.538
2.528
2.510
2.493
1.795
1.749
1.537
1.521
1.420
1.404
1.224
1.206
1.155
1.137
DO-O-Pren C+T
18.06.2013
PROTON CDCl3
O
O
OCH3
O
O
6d-s2
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
ppm
0.92
1.00
0.98
0.45
2.02
0.53
3.00
0.46
0.54
3.00
3.16
1.60
1.42
1.61
1.42

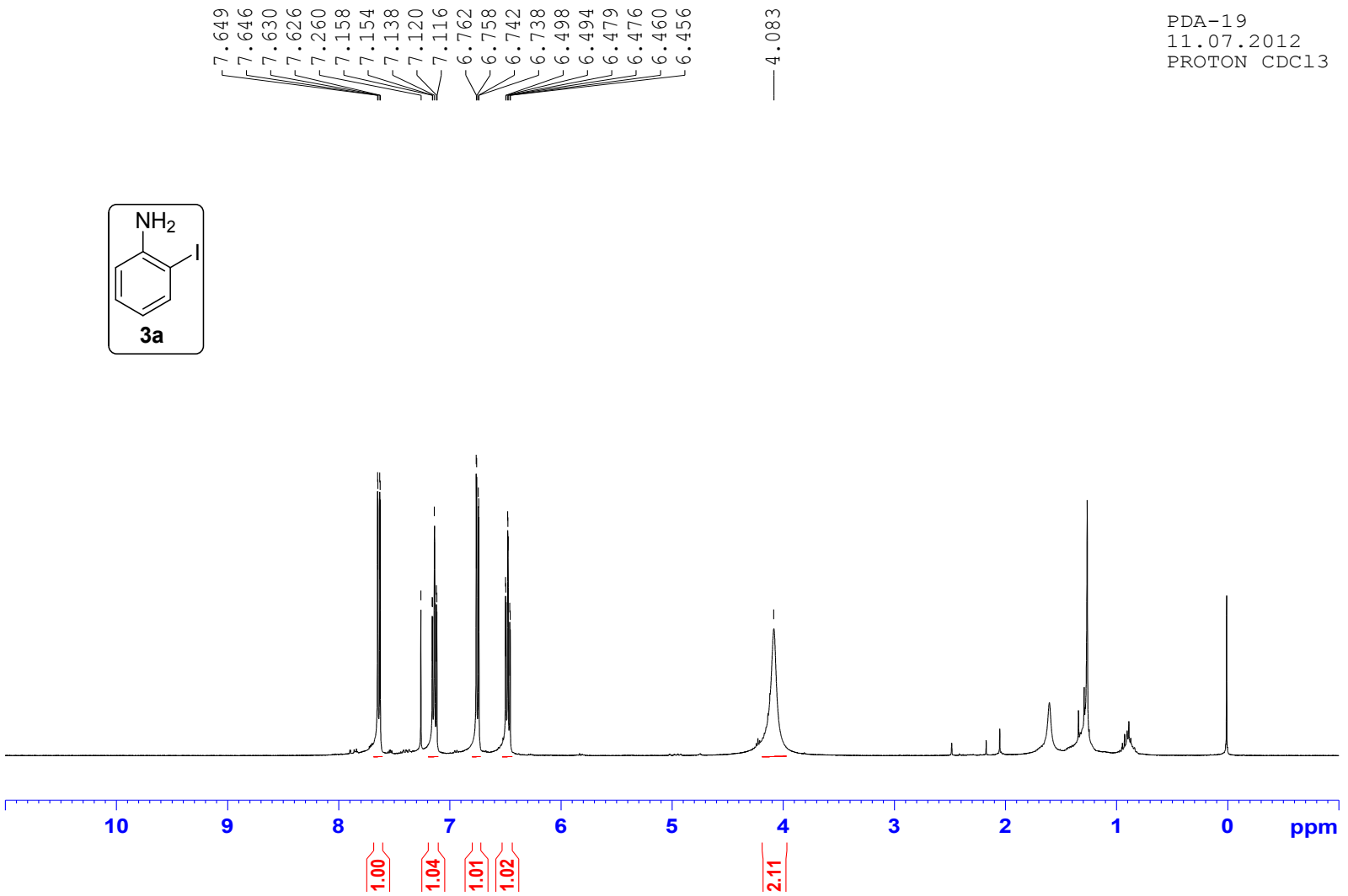

194.22
192.49
165.18
165.13
165.05
164.85
164.55
164.44
138.57
138.53
132.75
132.67
118.60
114.79
114.69
113.09
112.49
100.80
100.76
79.85
77.38
77.06
76.74
66.31
51.80
46.40
44.94
19.70
18.36
16.24
10.30
9.20
DO-O-Pren C+T
18.06.2013
C13CPD CDCl3
O
O
OCH3
O
O
6d-s2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

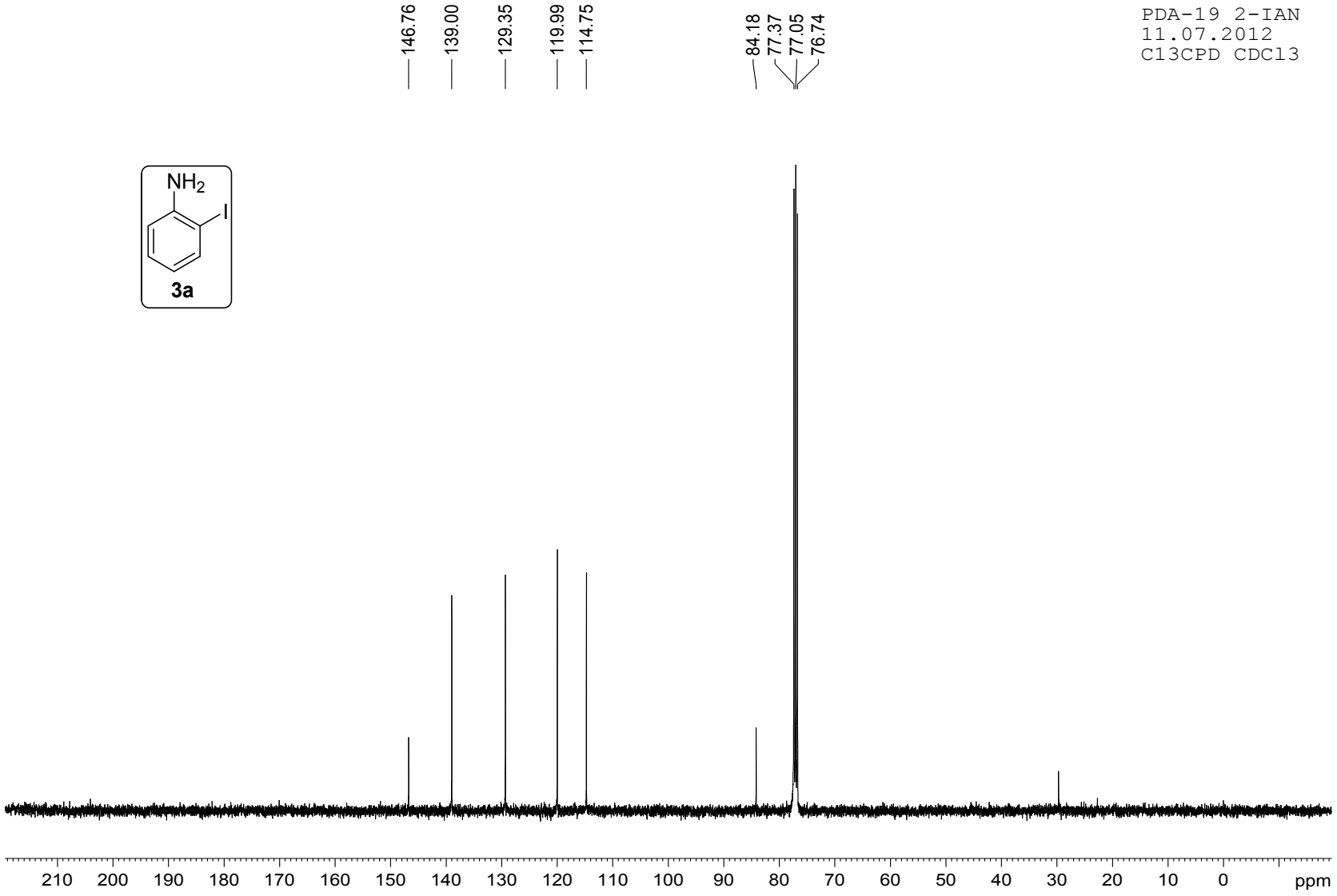

8.640
8.616
7.260
6.510
6.499
5.492
5.478
4.716
4.699
4.324
4.309
4.294
4.281
4.266
4.250
4.108
4.090
4.072
4.054
3.053
3.035
3.017
2.999
2.671
2.663
2.653
2.645
2.627
2.556
2.539
2.522
2.511
2.494
2.477
1.801
1.751
1.516
1.500
1.389
1.373
1.184
1.167
1.116
1.098
PDA-76 OPrnacid
14.05.2015
PROTON CDCl3
O
O
OH
O
O
6d
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.20
1.00
1.06
2.46
0.61
0.40
0.62
6.22
1.83
1.21
1.80
1.26


193.81
192.19
165.74
165.47
165.32
162.93
162.78
142.04
134.83
134.73
116.83
116.61
114.65
114.13
112.37
101.03
100.98
80.09
77.73
77.42
77.10
76.78
67.21
46.40
44.85
25.83
19.66
18.35
16.06
10.12
9.13
PDA-76 OPrnacid
14.05.2015
C13CPD CDCl3
O
O
OH
O
O
6d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

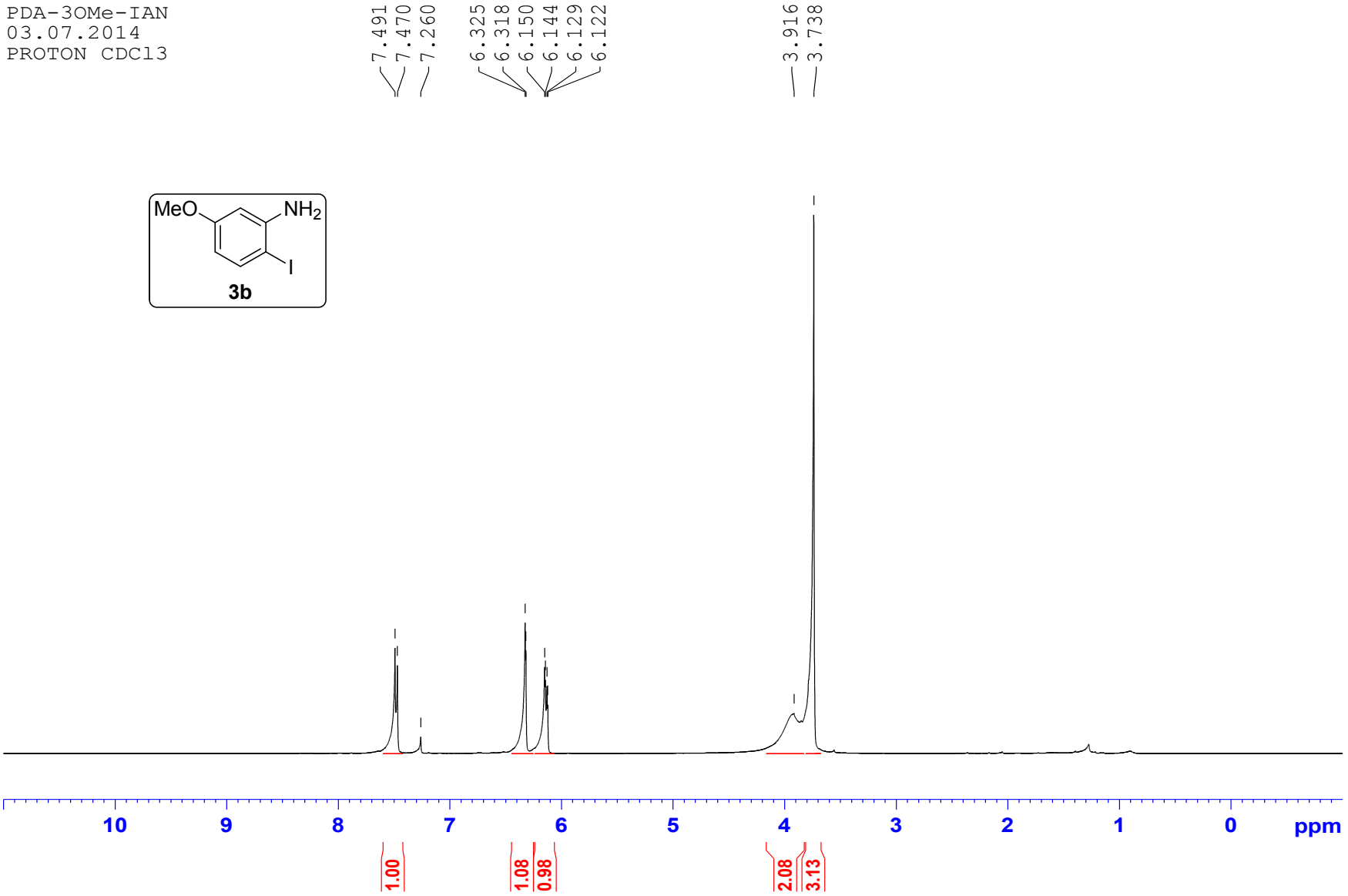
PDA-76 OPrnacid
14.05.2015
C13DEPT135 CDCl3




7.649
7.646
7.630
7.626
7.260
7.158
7.154
7.138
7.120
7.116
6.762
6.758
6.742
6.738
6.498
6.494
6.479
6.476
6.460
6.456
4.083
PDA-19
11.07.2012
PROTON CDCl3
NH2
I
3a
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.01
1.02
2.11

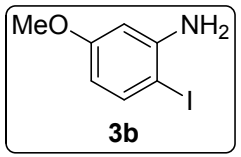

146.76
139.00
129.35
119.99
114.75
84.18
77.37
77.05
76.74
PDA-19 2-IAN
11.07.2012
C13CPD CDCl3
NH2
I
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

PDA-3OMe-IAN
03.07.2014
PROTON CDCl3

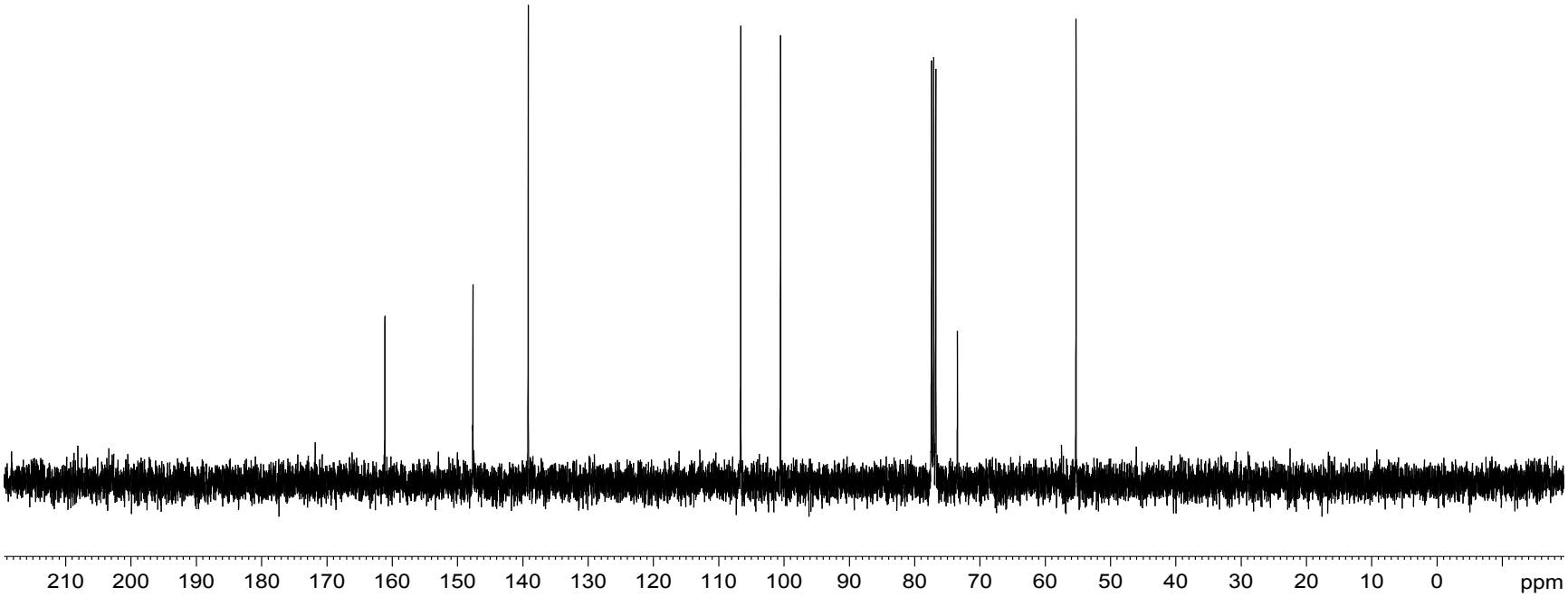


PDA-3OMe-IAN
03.07.2014
C13CPD CDCl3

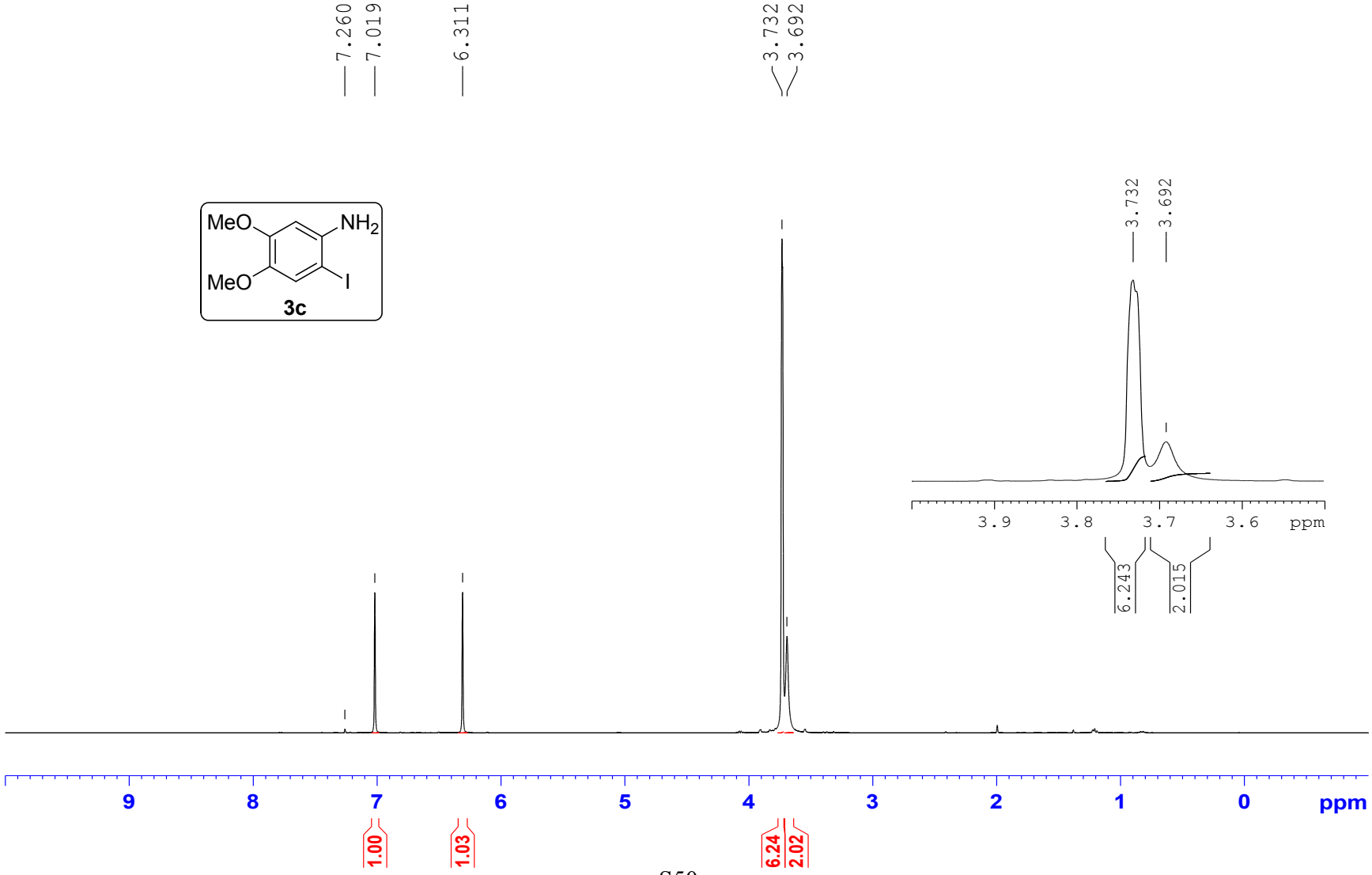
161.15
147.65
139.19
106.65
100.55
77.42
77.10
76.78
73.47
55.30



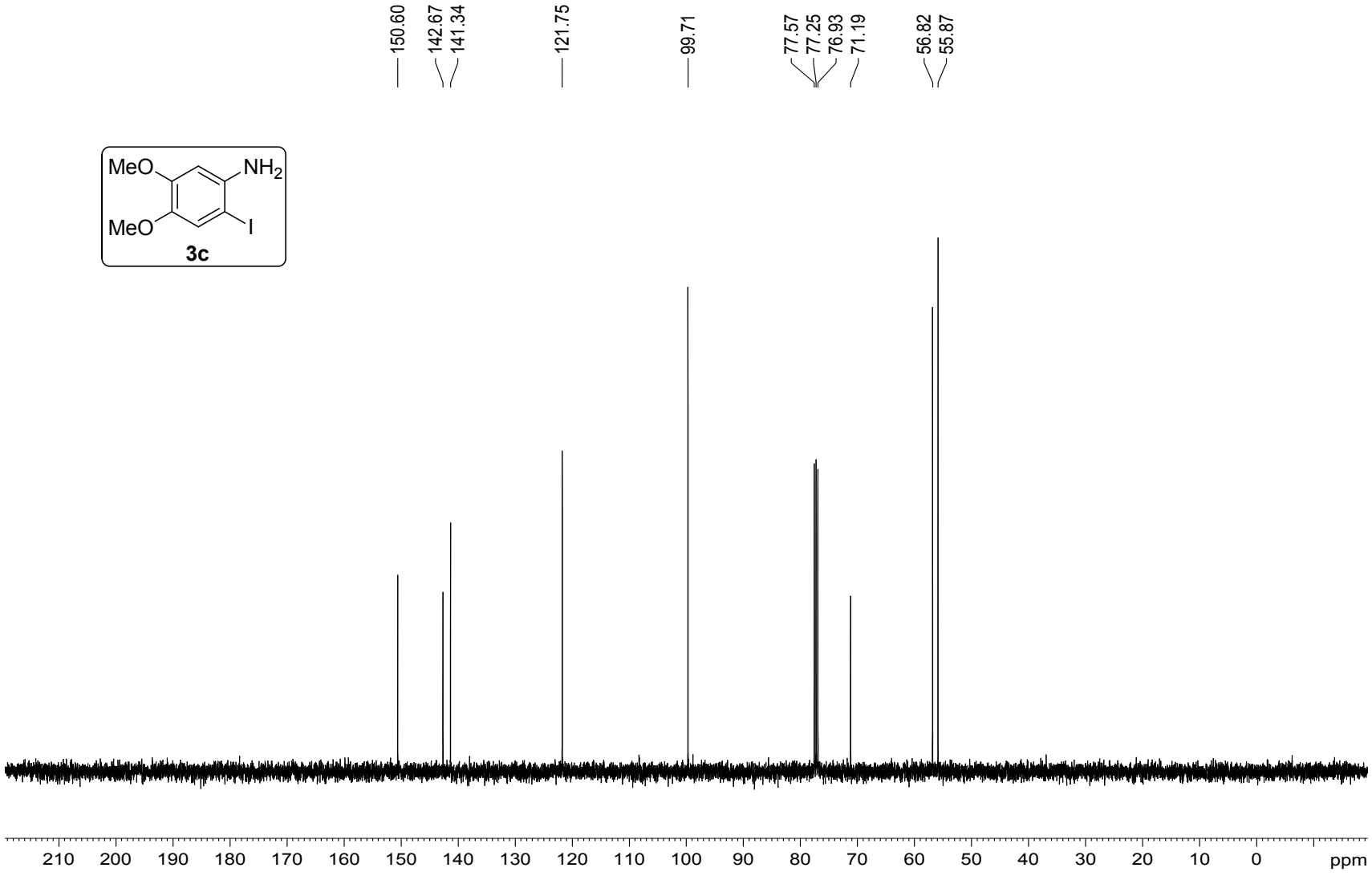
3b



PSV-28 Ver-I-Am 21/05/2014
PROTON CDCl3

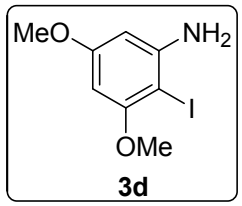


PSV-28 ver-I-Am 21/05/2014
C13CPD CDCl3

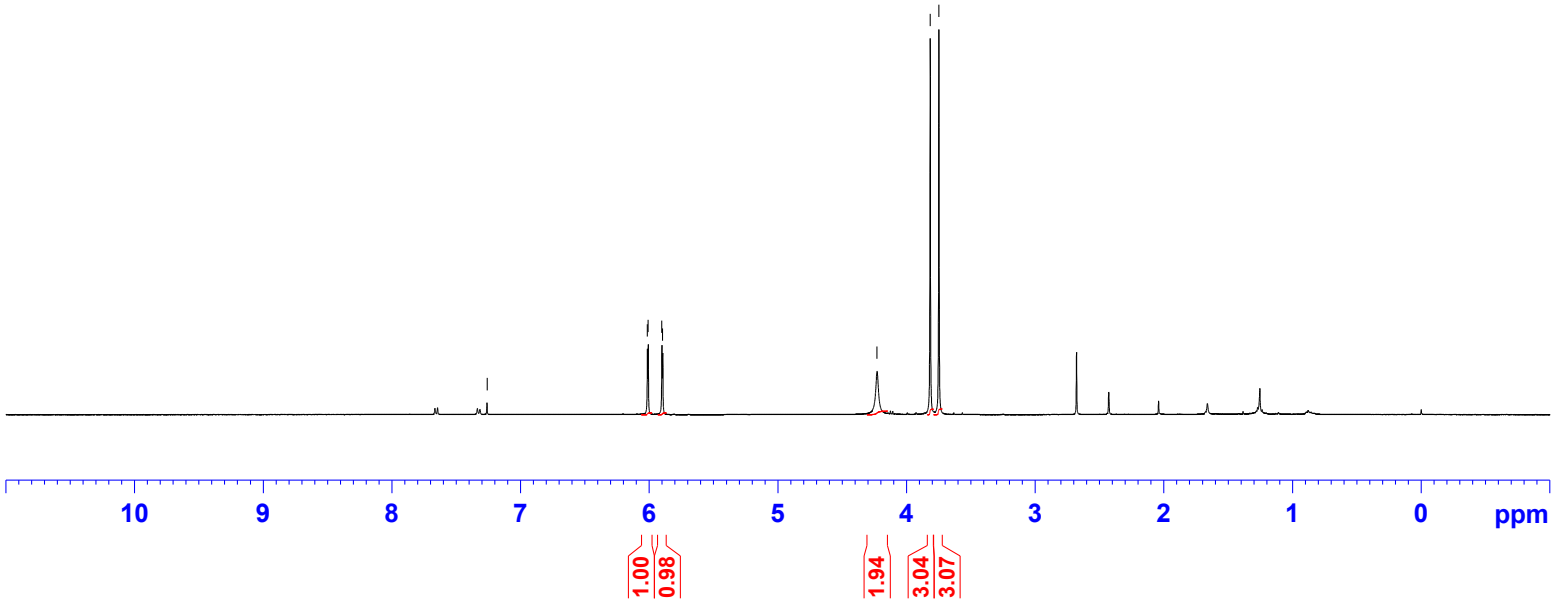


psv-3,5-OMe NH2
09.09.2016
PROTON CDCl3

7.260
6.015
6.008
5.902
5.896
4.230
3.817
3.749

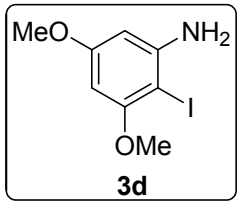


3d

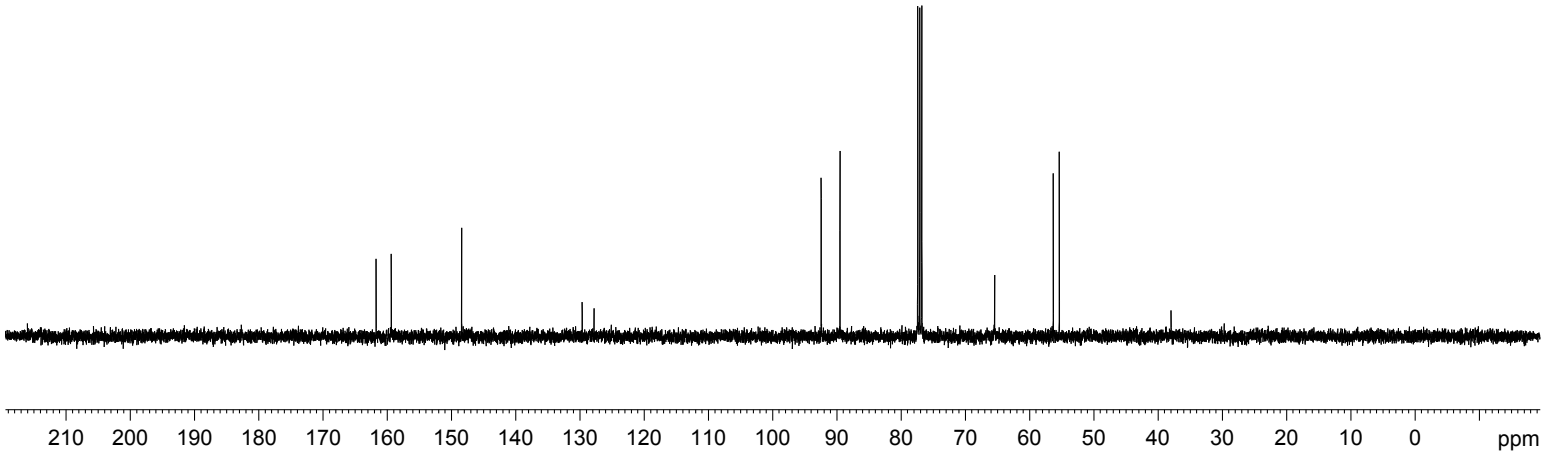


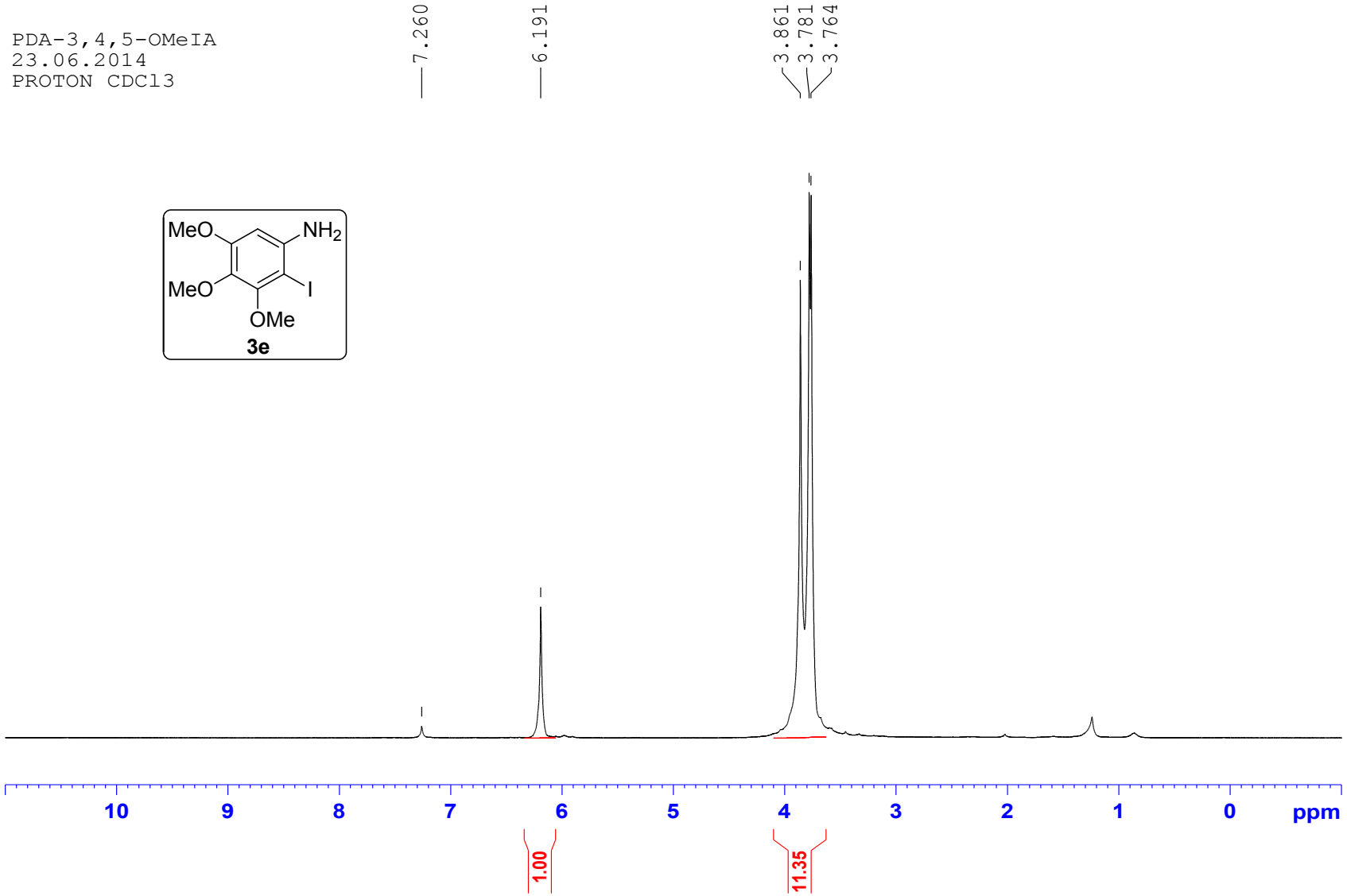
psv-3,5-OMe NH2
09.09.2016
C13CPD CDCl3

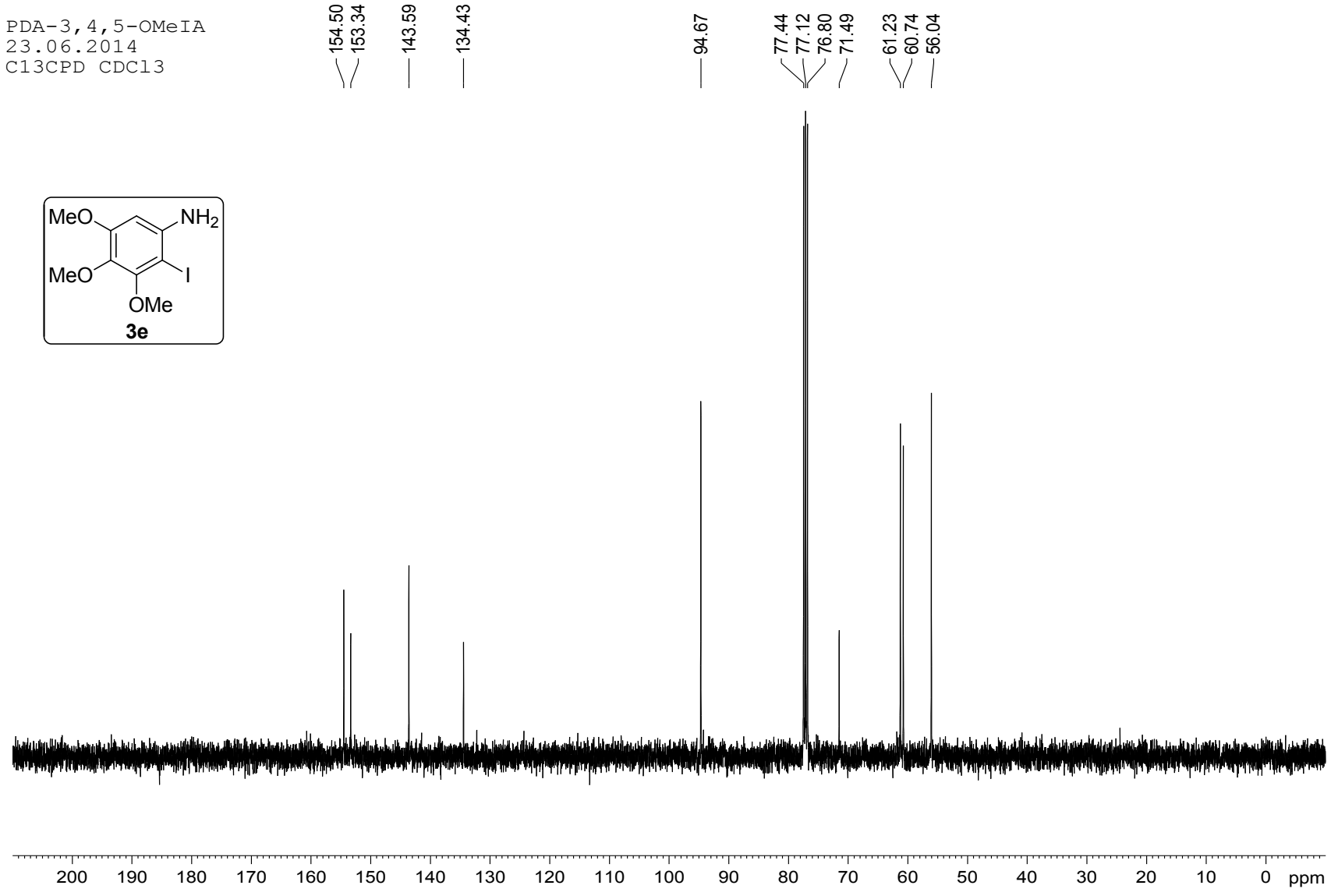
161.79
159.42
148.46
92.45
89.52
77.42
77.10
76.78
65.44
56.32
55.38



3d



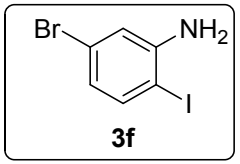

PDA-3,4,5-OMeIA
23.06.2014
PROTON CDCl3
7.260
6.191
3.861
3.781
3.764
MeO
NH2
MeO
I
OMe
3e
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
11.35


PDA-3,4,5-OMeIA
23.06.2014
C13CPD CDCl3
154.50
153.34
143.59
134.43
94.67
77.44
77.12
76.80
71.49
61.23
60.74
56.04
MeO
NH2
MeO
I
OMe
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

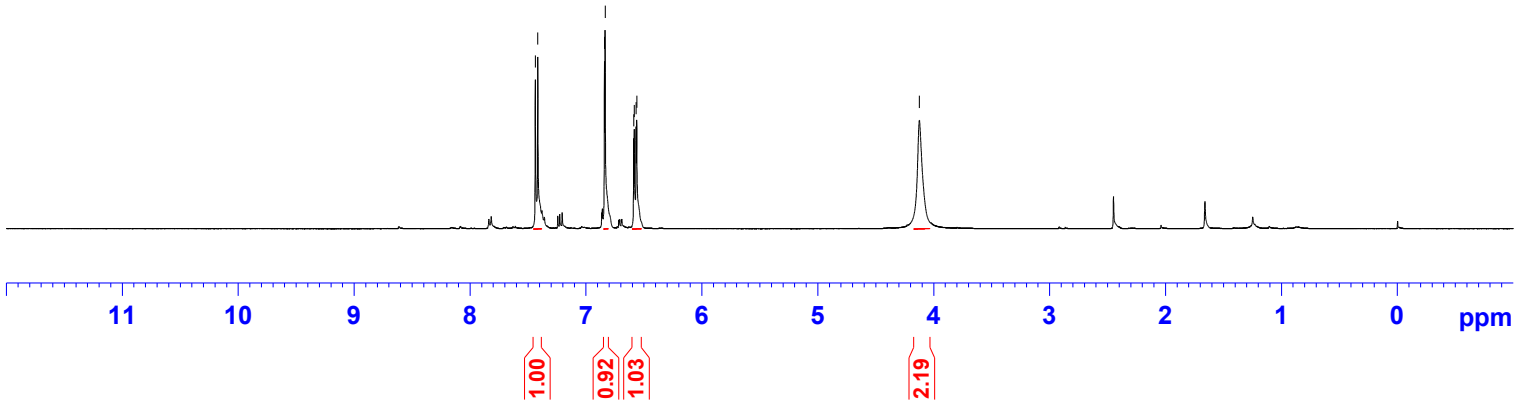
Br-IB-NH2-1
mtm-10.09.2016
PROTON CDCl3

7.436
7.415
6.840
6.834
6.588
6.583
6.567
6.562

4.123

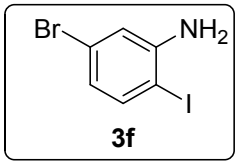


3f

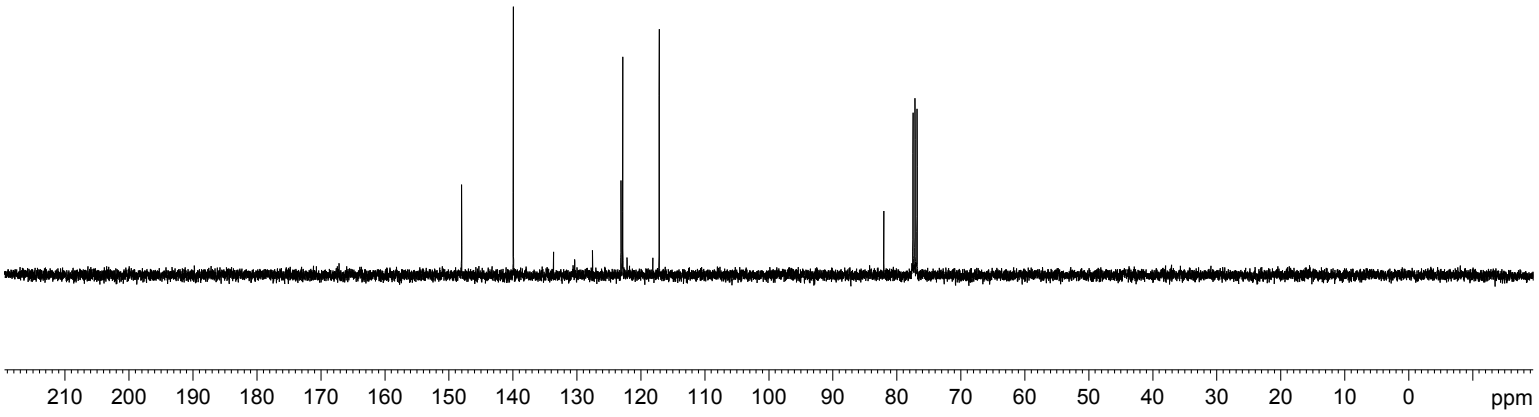


Br-IB-NH2-1
mtm-10.09.2016
C13CPD CDCl3

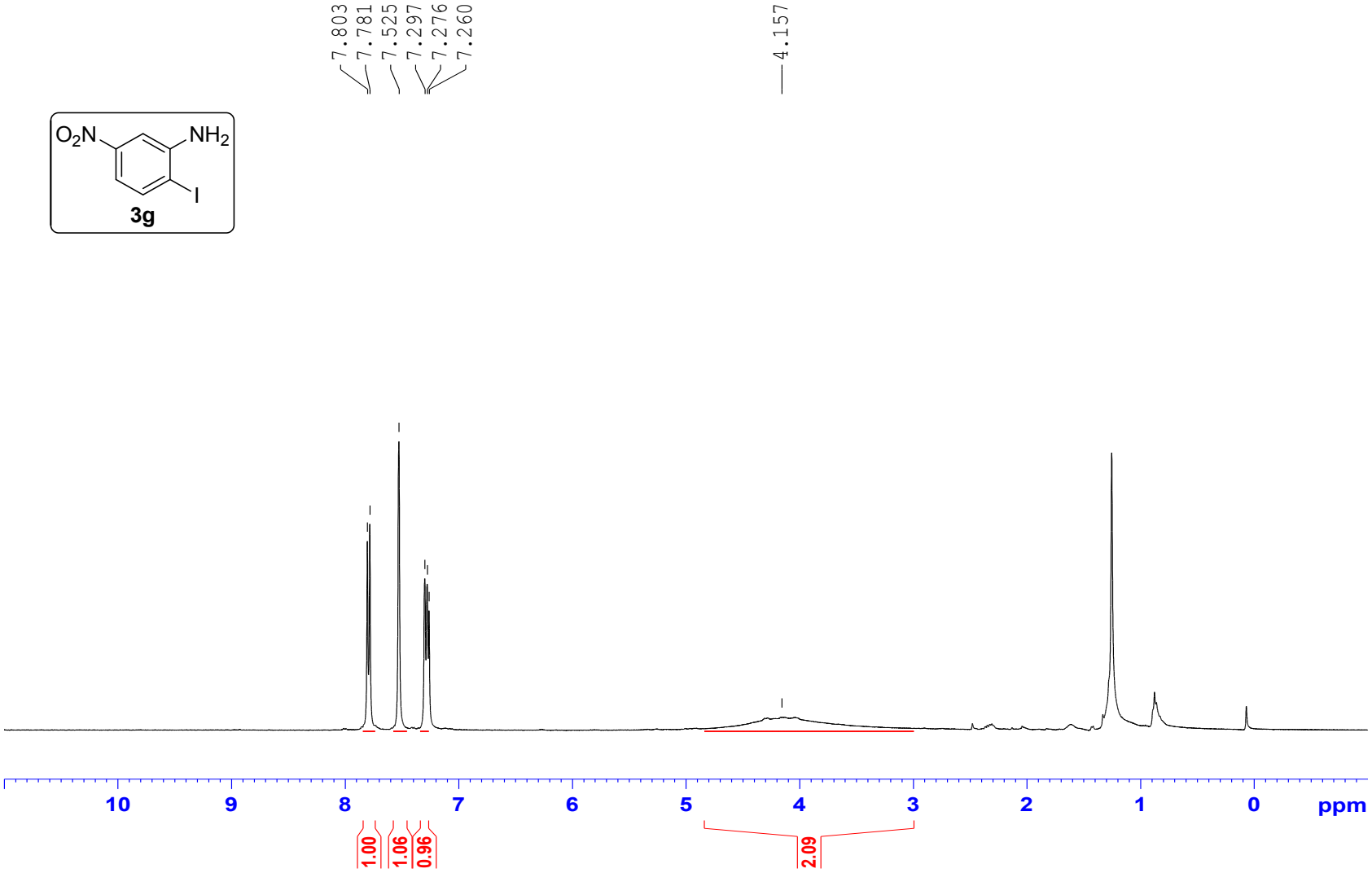
148.03
139.95
123.12
122.85
117.15
82.04
77.48
77.16
76.85



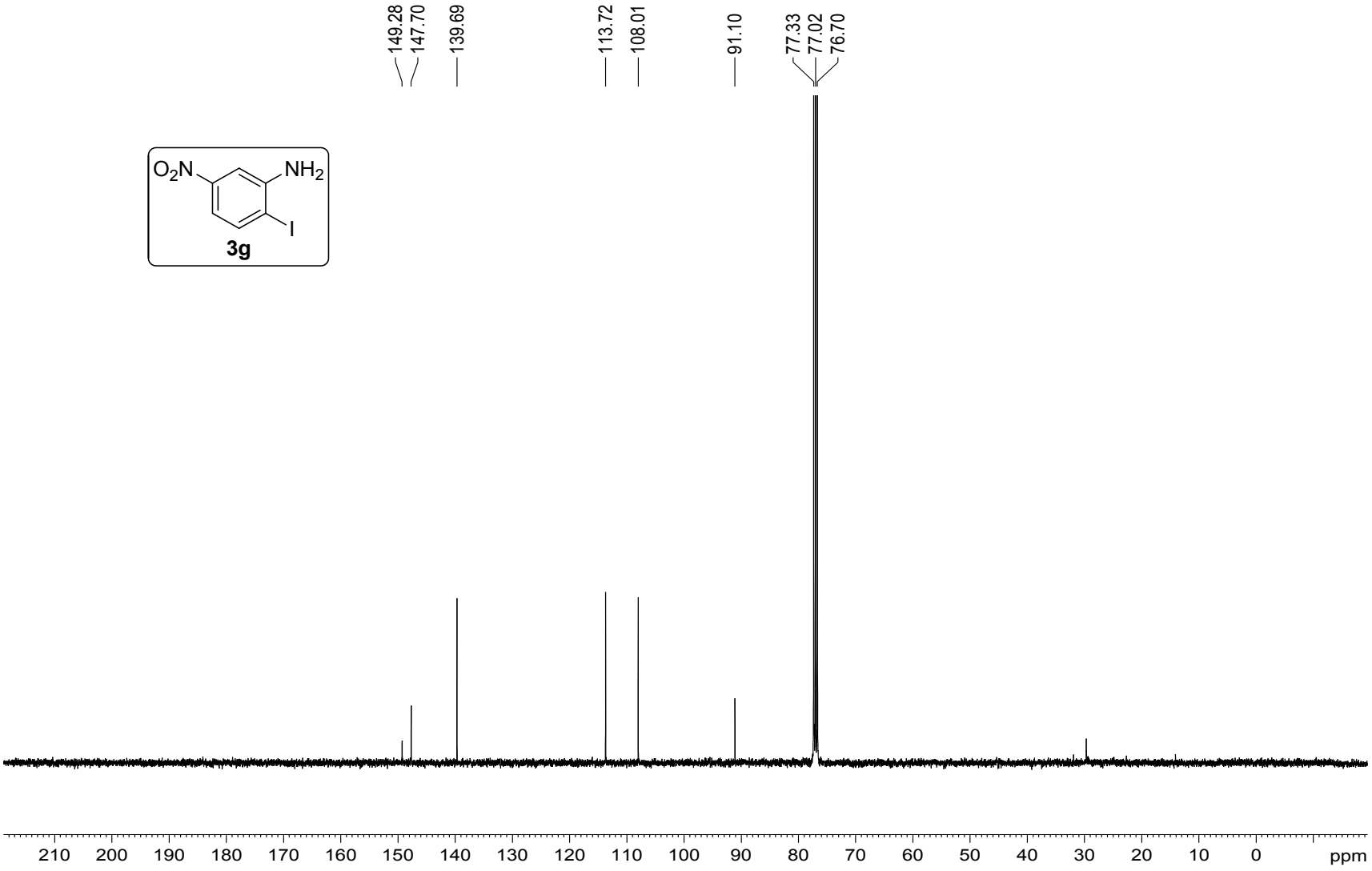
3f



PDA-56 5N-2I 12/06/2014
PROTON CDCl3

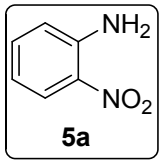


PDA-56 5N-2I 12/06/2014
C13CPD CDCl3

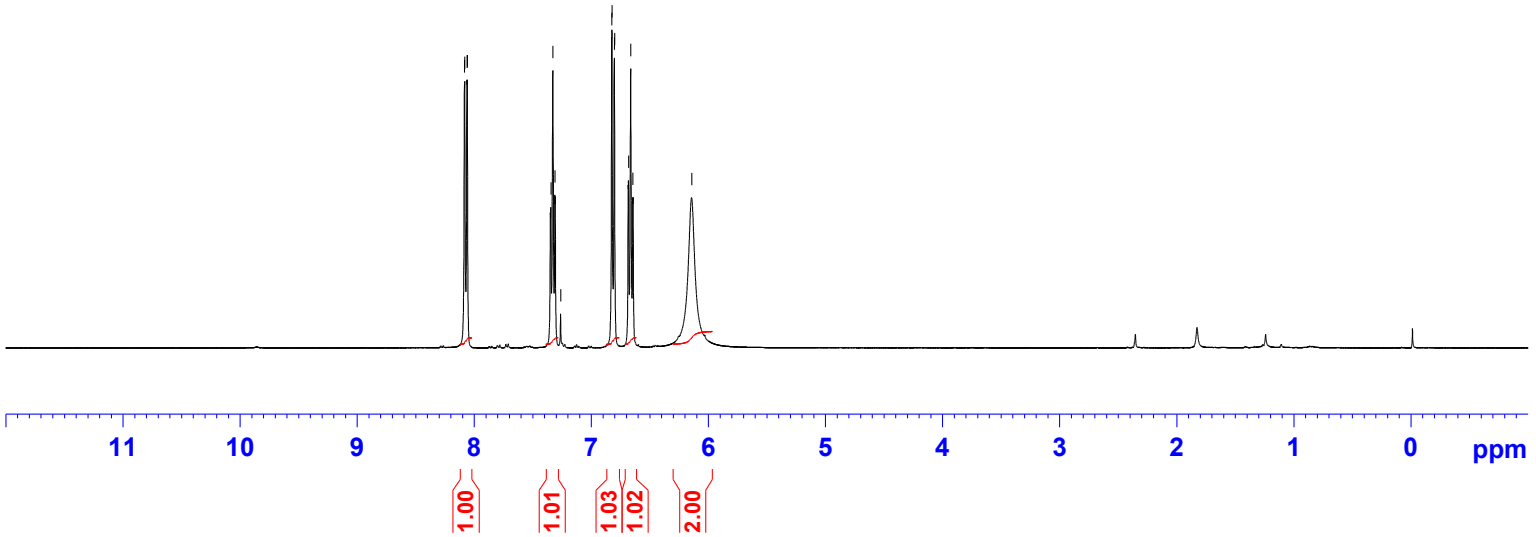


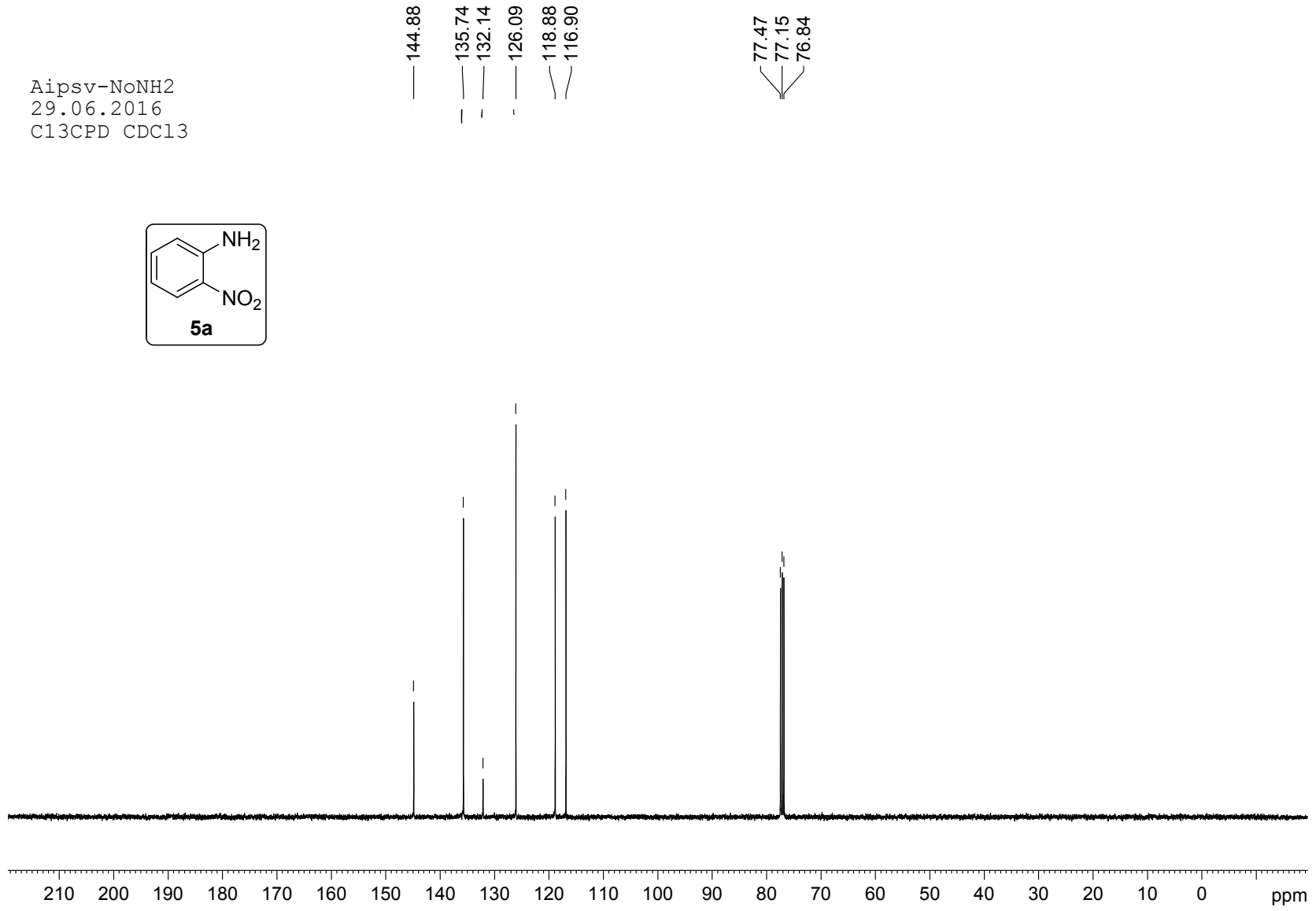
Aipsv-NoNH2
29.06.2016
PROTON CDCl3

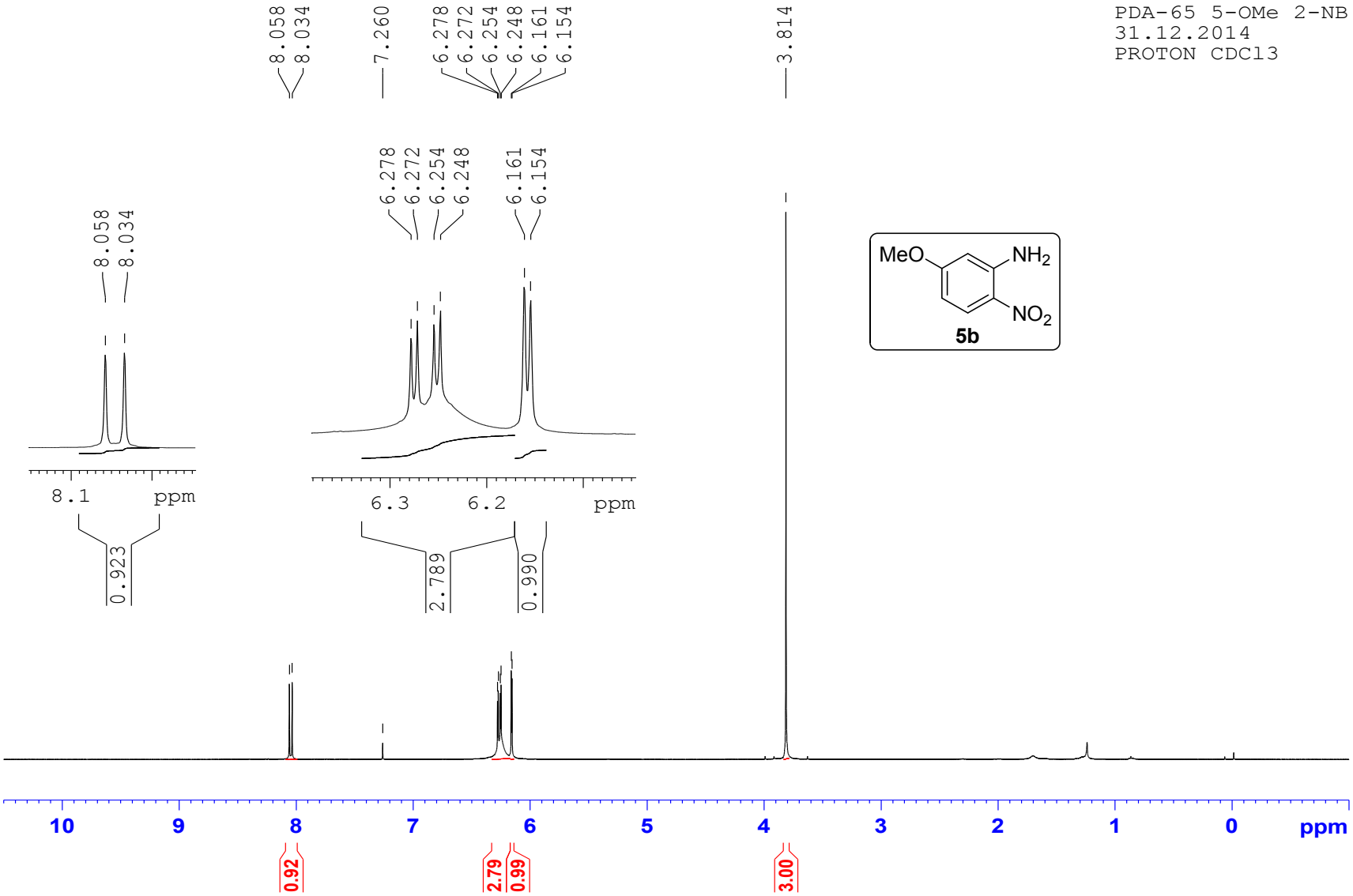
8.081
8.079
8.060
8.057
7.344
7.327
7.309
7.260
6.823
6.822
6.802
6.801
6.680
6.662
6.644
6.141

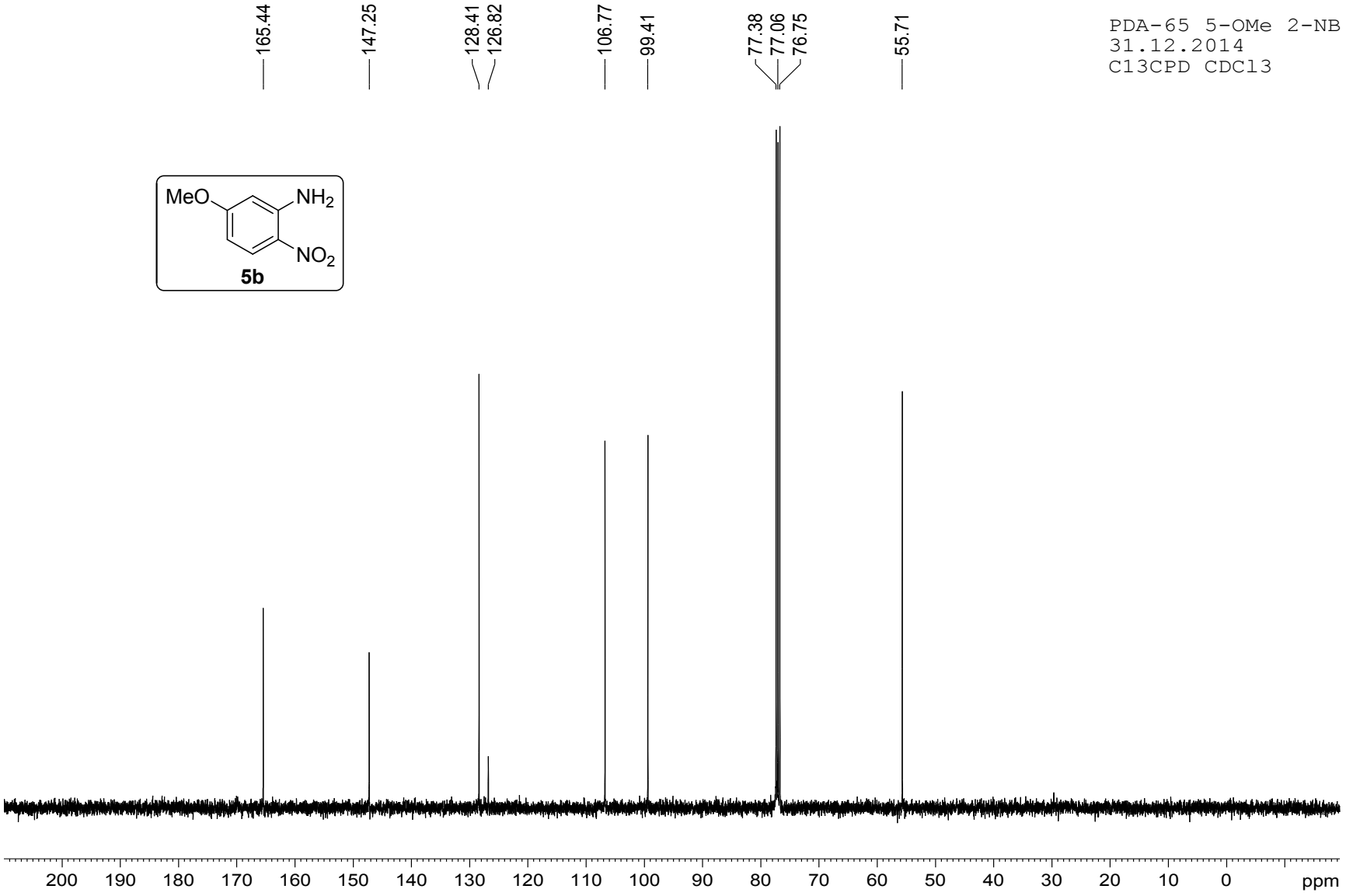


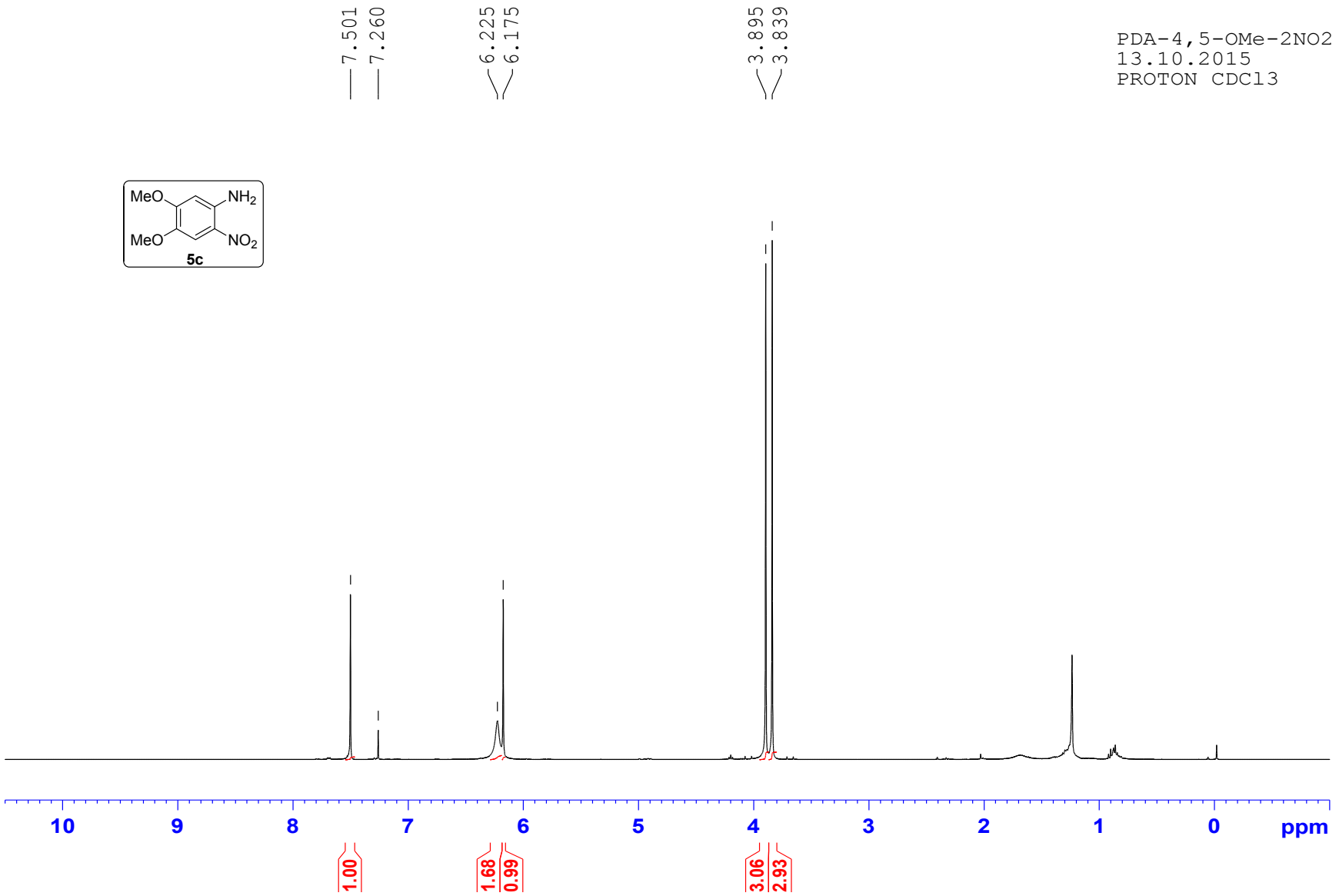
5a

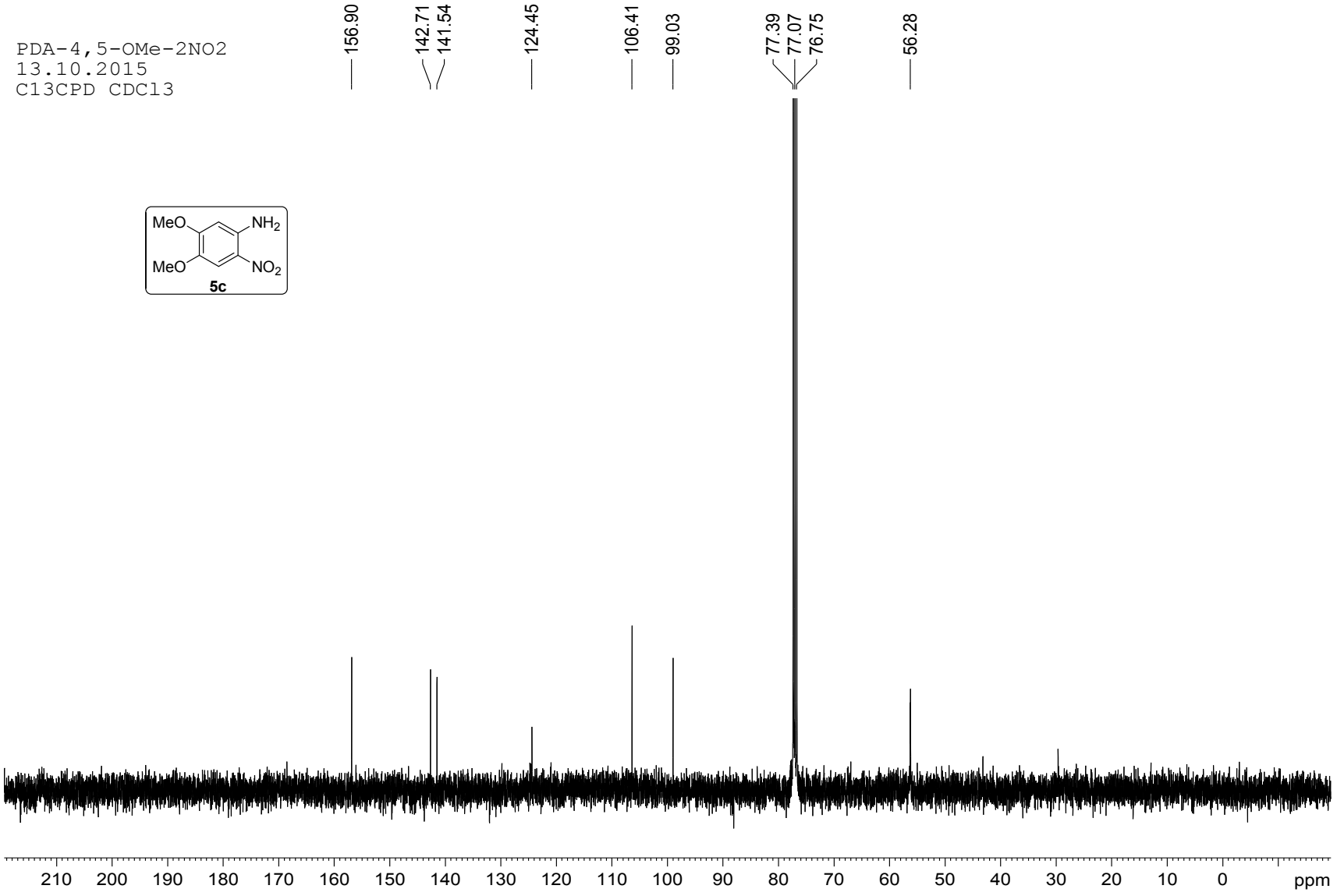


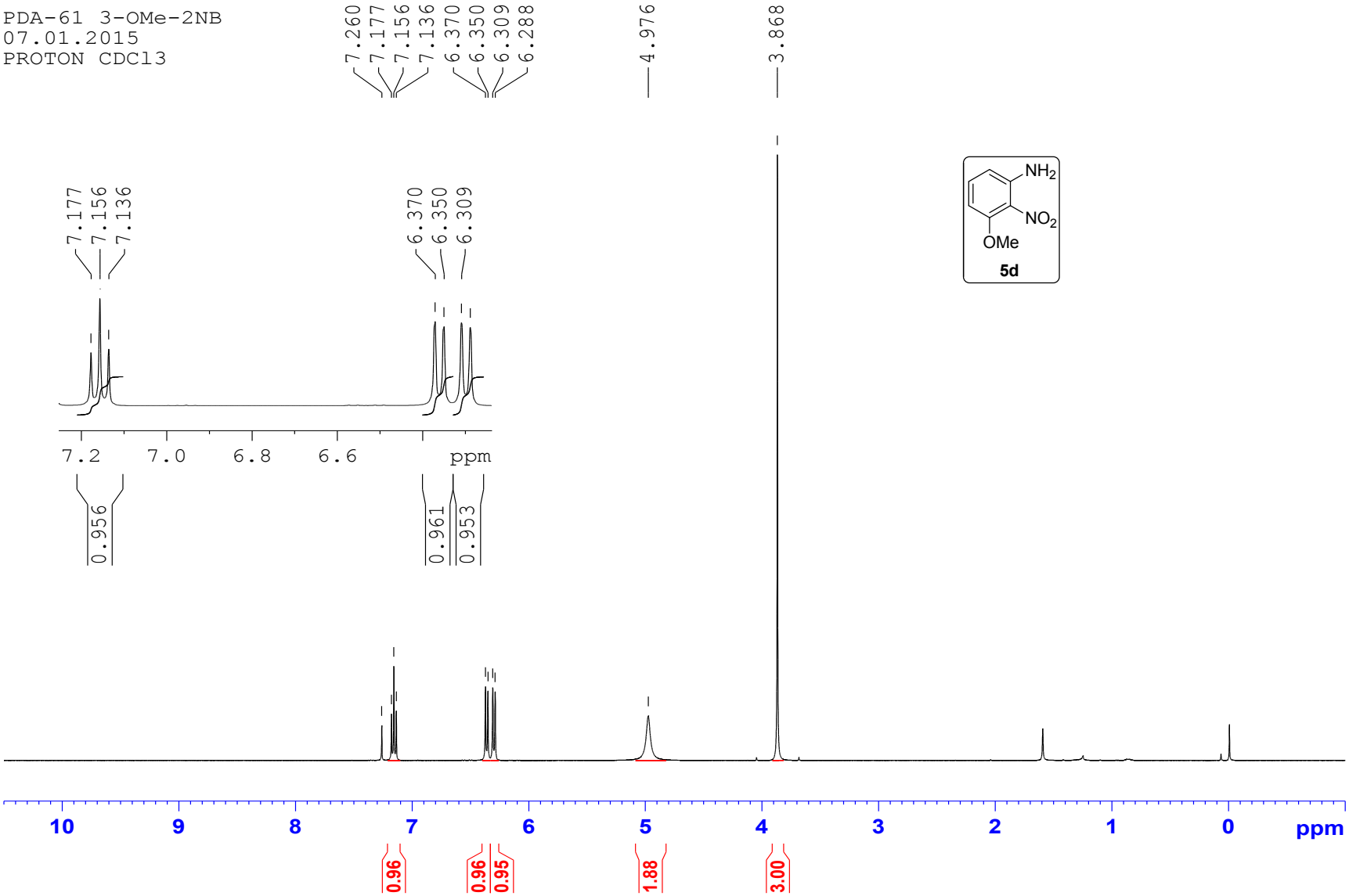

144.88
135.74
132.14
126.09
118.88
116.90
77.47
77.15
76.84
Aipsv-NoNH2
29.06.2016
C13CPD CDCl3
NH2
NO2
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

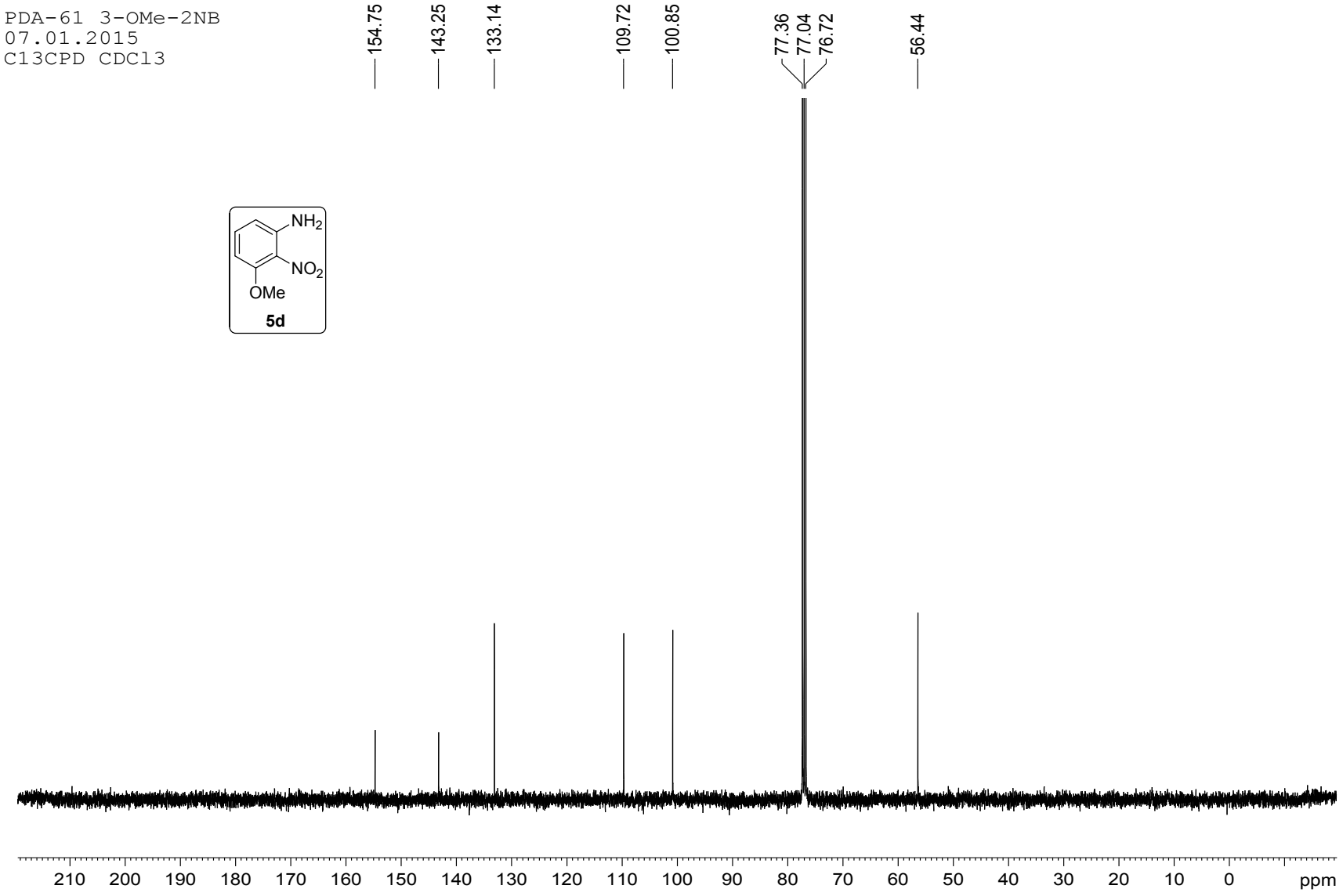

PDA-65 5-OMe 2-NB
31.12.2014
PROTON CDCl3
8.058
8.034
7.260
6.278
6.272
6.254
6.248
6.161
6.154
3.814
MeO
NH2
NO2
5b
8.1
ppm
6.3
6.2
ppm
0.923
2.789
0.990
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
2.79
0.99
3.00

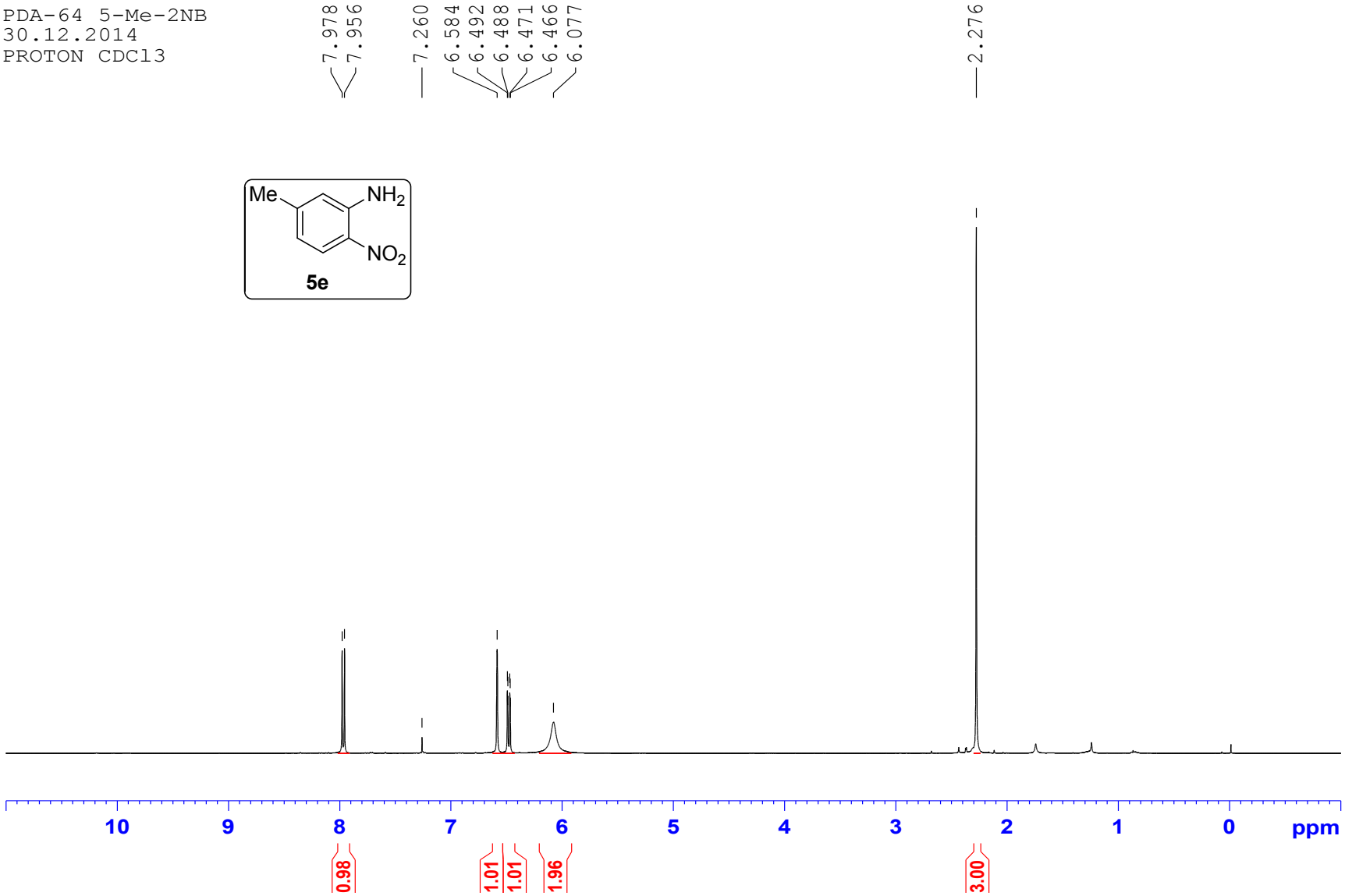

165.44
147.25
128.41
126.82
106.77
99.41
77.38
77.06
76.75
55.71
PDA-65 5-OMe 2-NB
31.12.2014
C13CPD CDCl3
MeO
NH2
NO2
5b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.501
7.260
6.225
6.175
3.895
3.839
PDA-4,5-OMe-2NO2
13.10.2015
PROTON CDCl3
MeO
NH2
MeO
NO2
5c
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.68
0.99
3.06
2.93

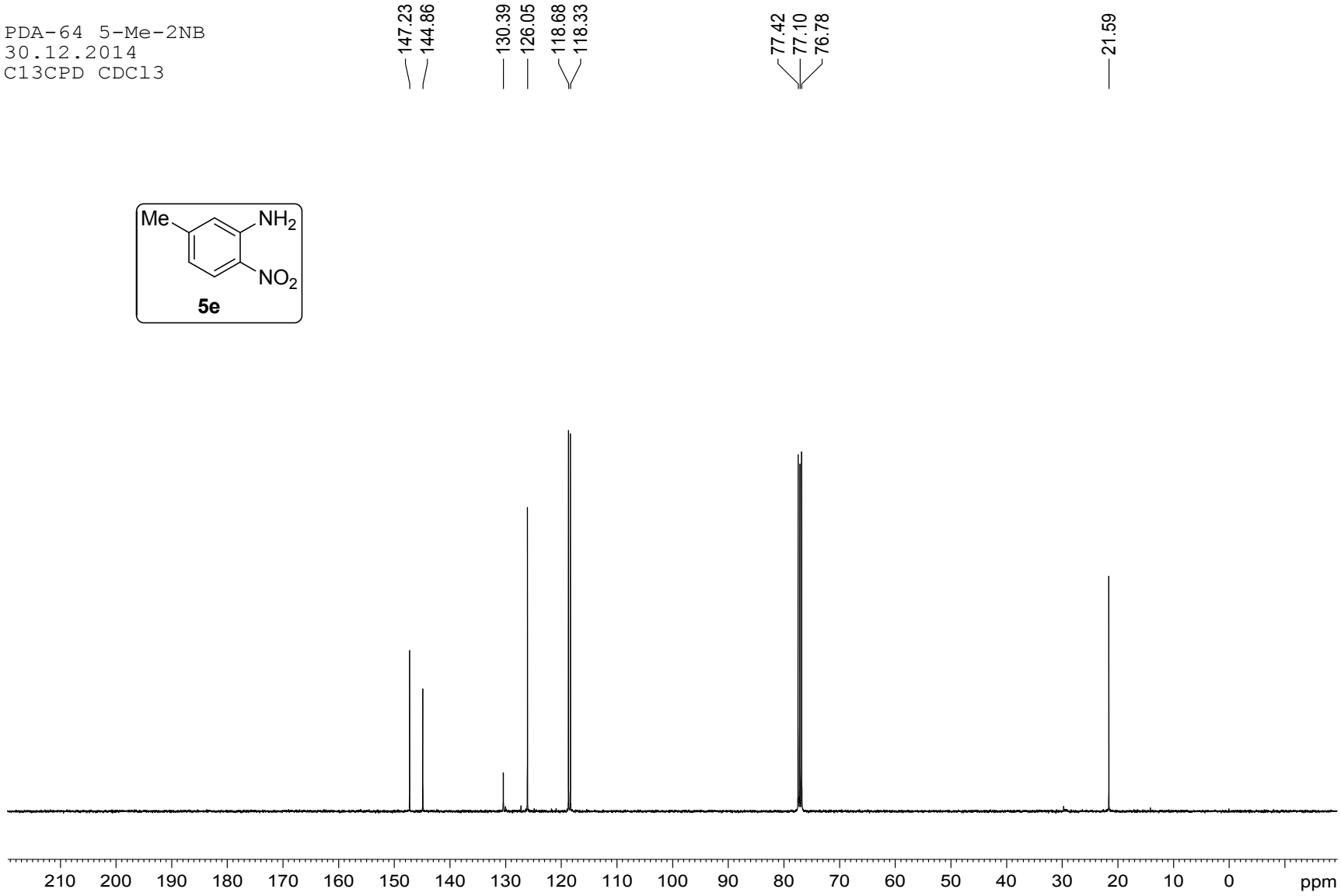

PDA-4,5-OMe-2NO2
13.10.2015
C13CPD CDCl3
156.90
142.71
141.54
124.45
106.41
99.03
77.39
77.07
76.75
56.28
MeO
NH2
MeO
NO2
5c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

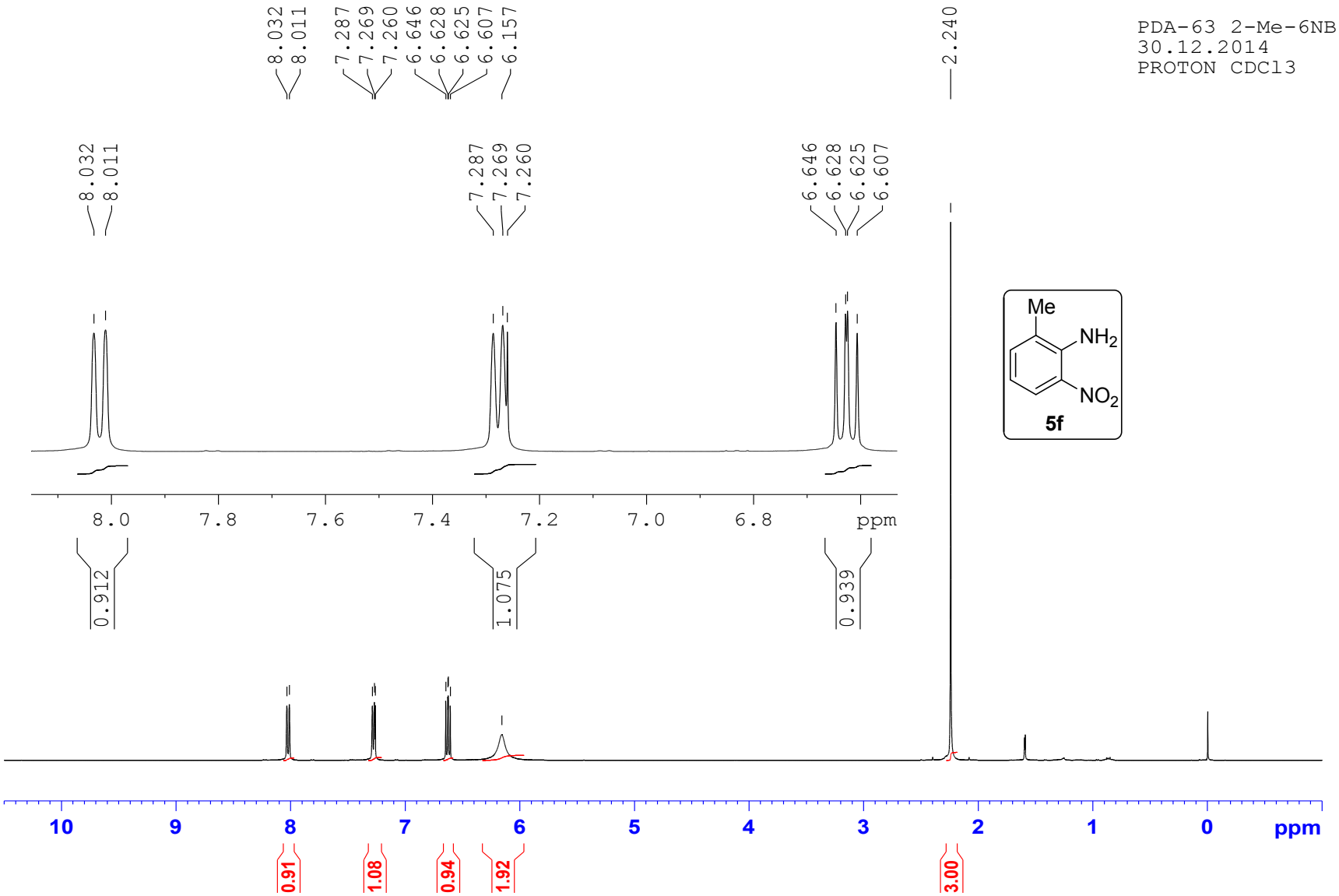

PDA-61 3-OMe-2NB
07.01.2015
PROTON CDCl3
7.260
7.177
7.156
7.136
6.370
6.350
6.309
6.288
4.976
3.868
NH2
NO2
OMe
5d
7.2
7.0
6.8
6.6
ppm
0.956
0.961
0.953
10
9
8
7
6
5
4
3
2
1
0
ppm
0.96
0.96
0.95
1.88
3.00

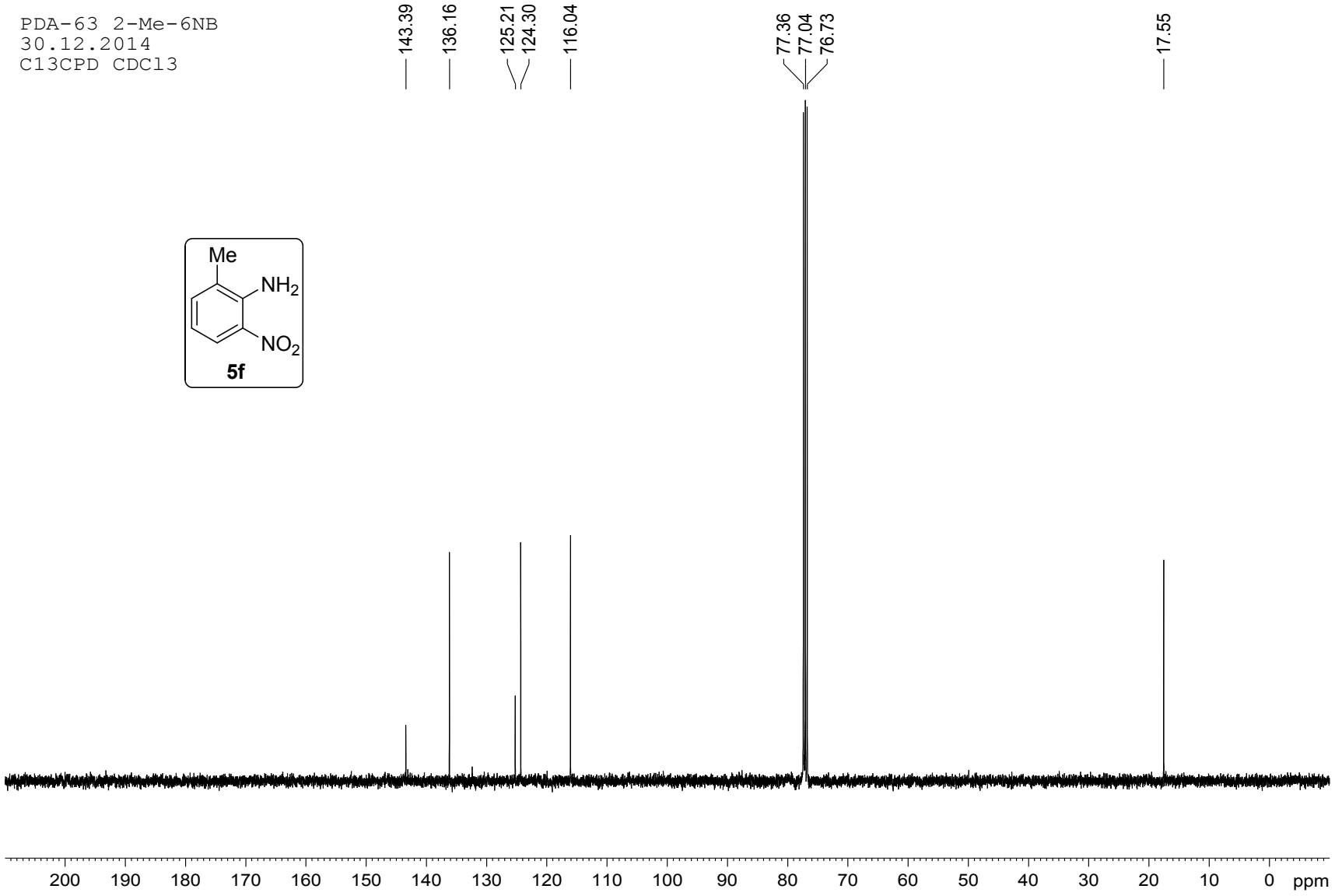

PDA-61 3-OMe-2NB
07.01.2015
C13CPD CDCl3
154.75
143.25
133.14
109.72
100.85
77.36
77.04
76.72
56.44
NH2
NO2
OMe
5d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


PDA-64 5-Me-2NB
30.12.2014
PROTON CDCl3
7.978
7.956
7.260
6.584
6.492
6.488
6.471
6.466
6.077
2.276
Me
NH2
NO2
5e
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.01
1.01
1.96
3.00

PDA-64 5-Me-2NB
30.12.2014
C13CPD CDCl3

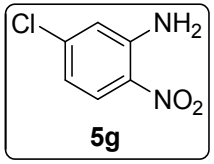



PDA-63 2-Me-6NB
30.12.2014
PROTON CDCl3
8.032
8.011
7.287
7.269
7.260
6.646
6.628
6.625
6.607
6.157
2.240
Me
NH2
NO2
5f
0.912
1.075
0.939
ppm
0.91
1.08
0.94
1.92
3.00

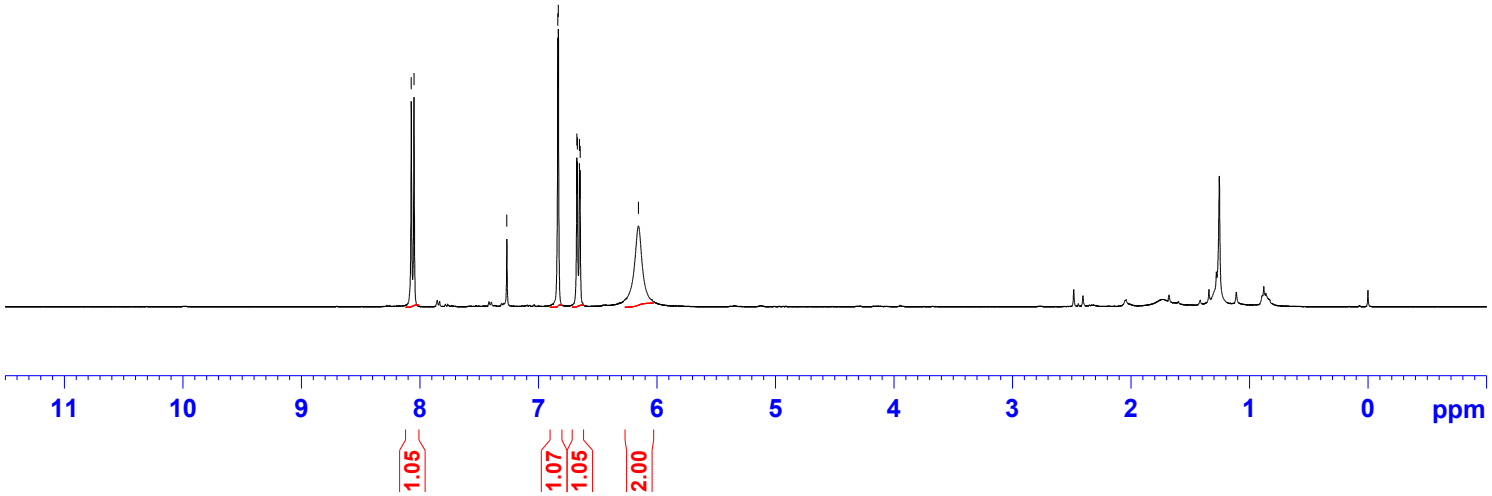

PDA-63 2-Me-6NB
30.12.2014
C13CPD CDCl3
143.39
136.16
125.21
124.30
116.04
77.36
77.04
76.73
17.55
Me
NH2
NO2
5f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

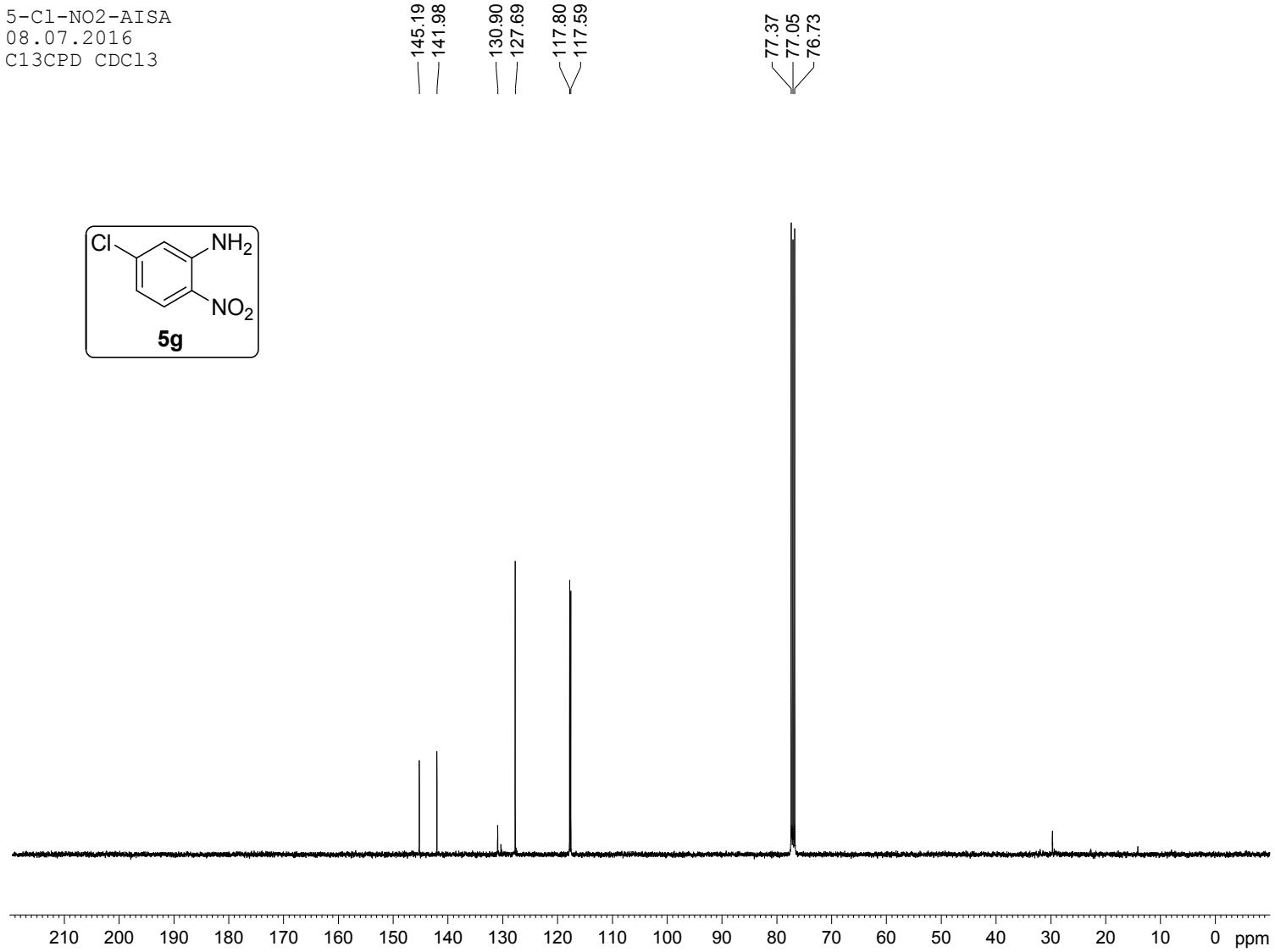
5-Cl-NO2-AISA
08.07.2016
PROTON CDCl3

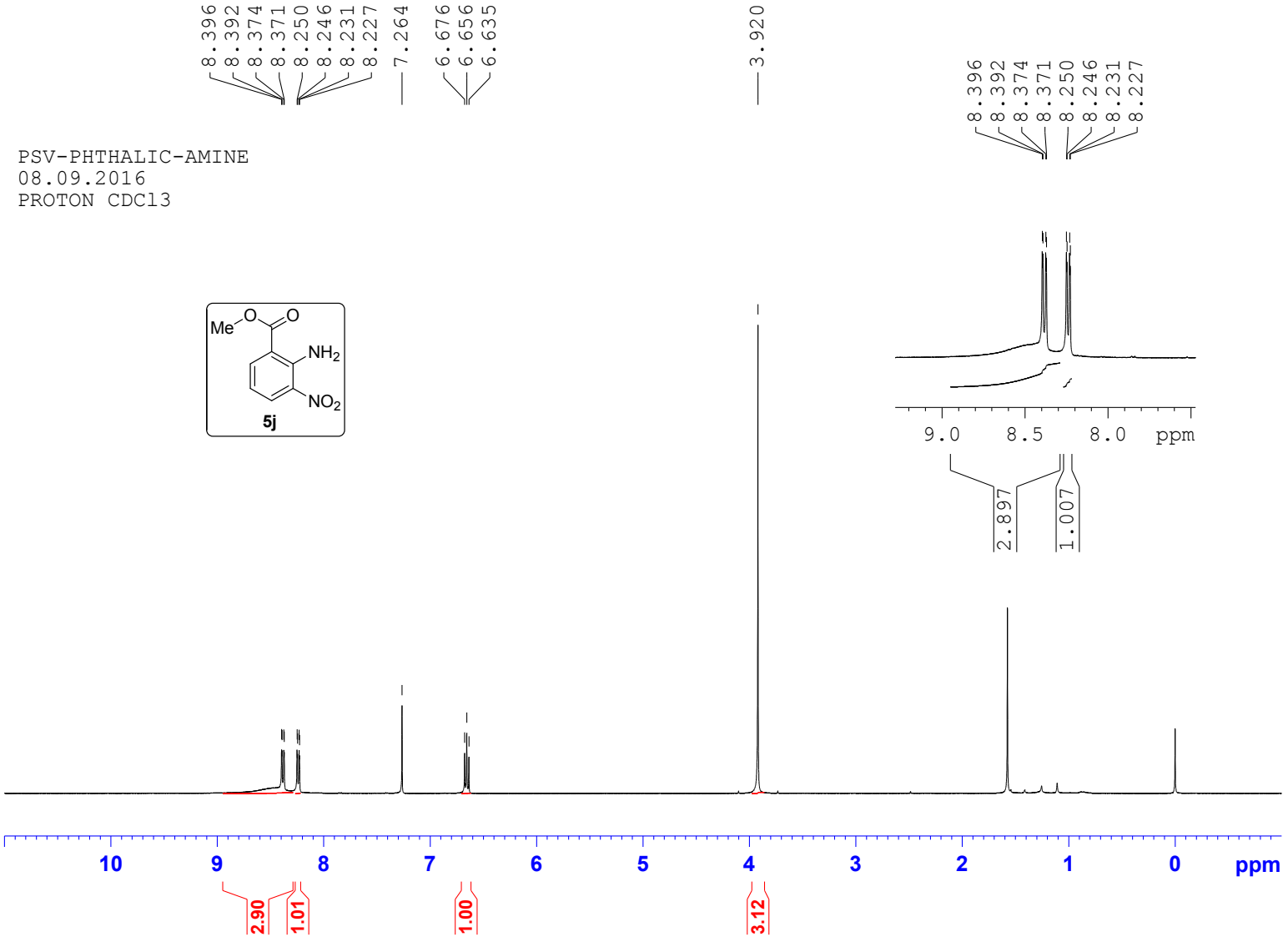
8.074
8.051
7.267
6.837
6.832
6.677
6.672
6.654
6.649
6.157

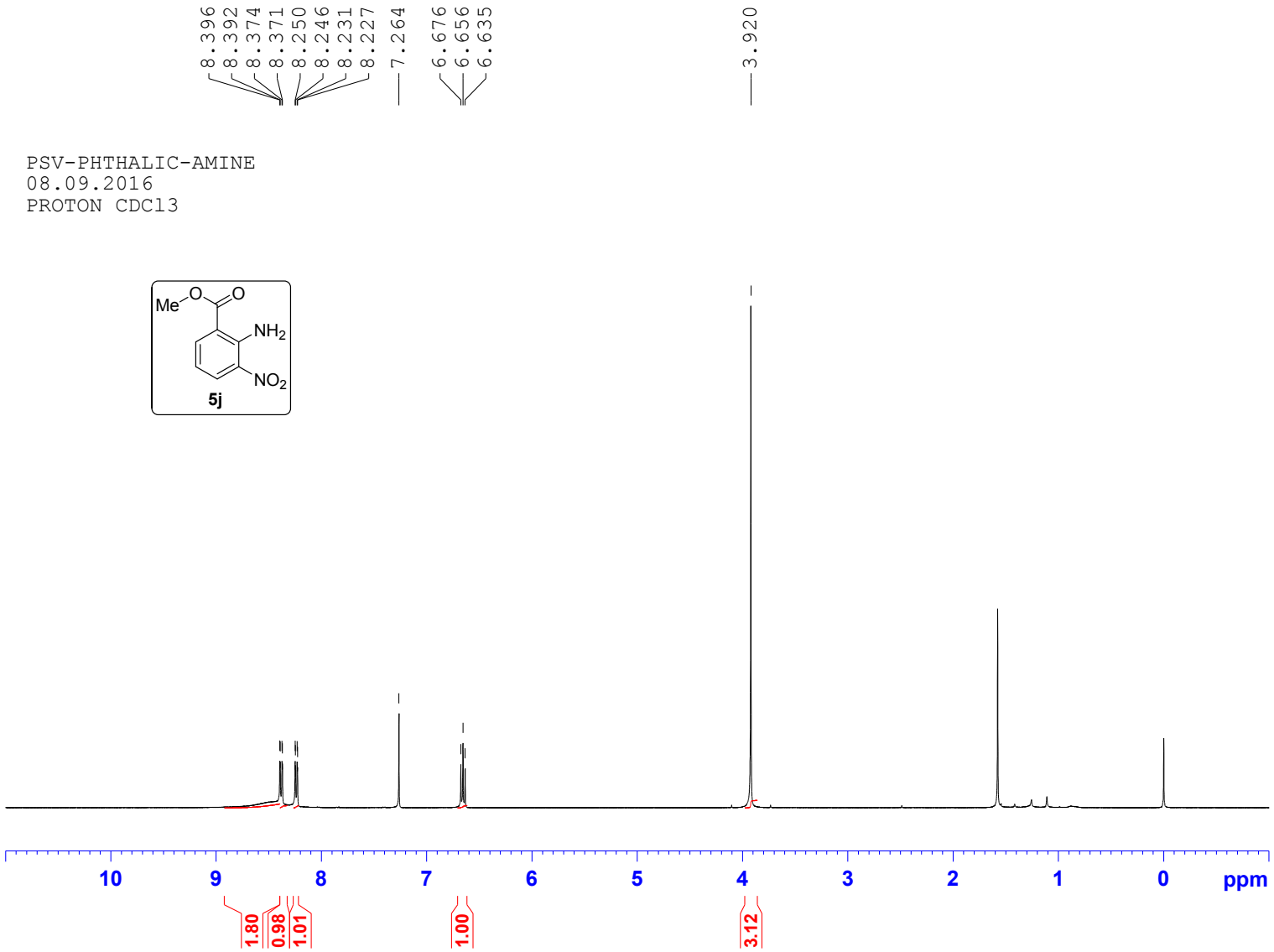


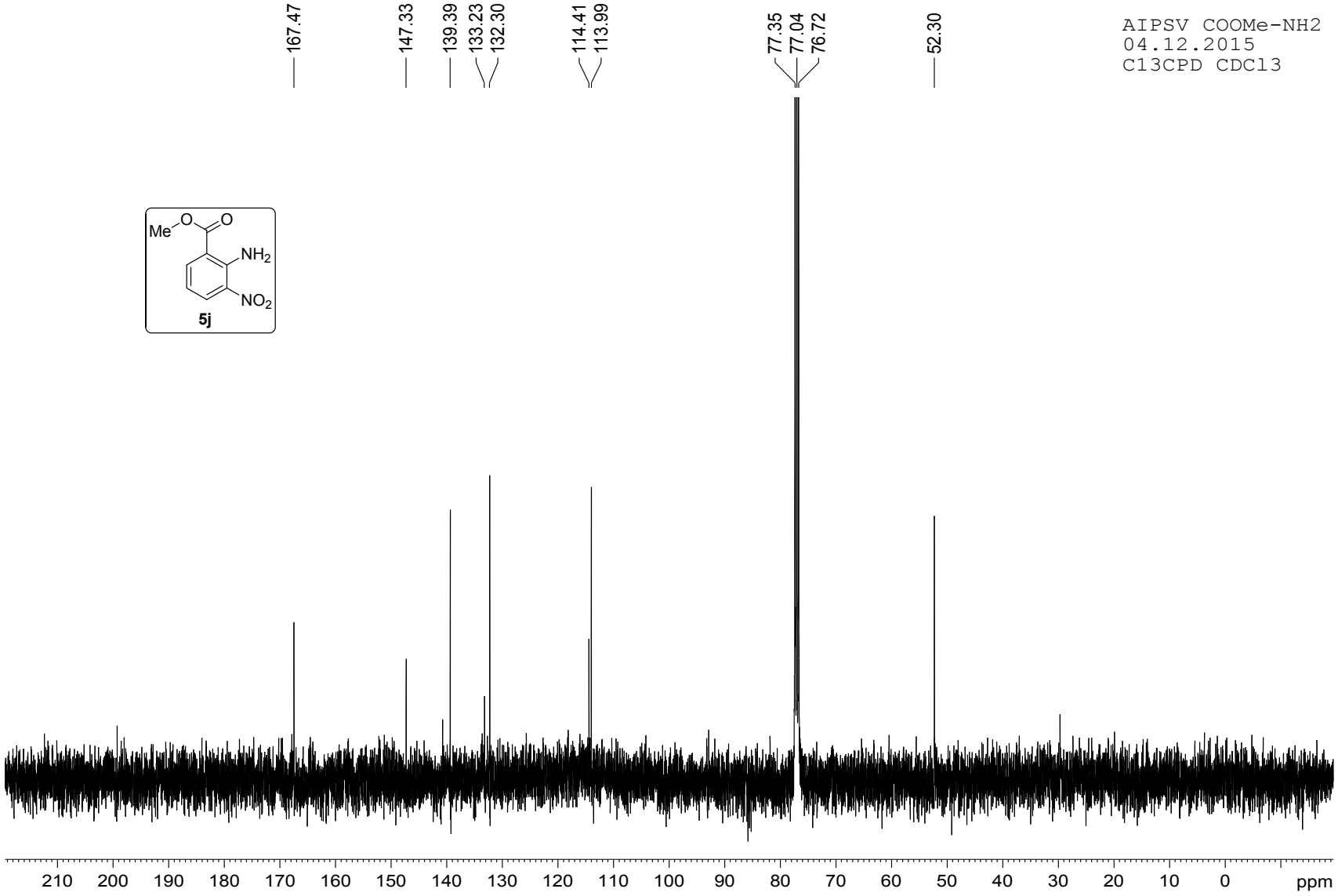
5g



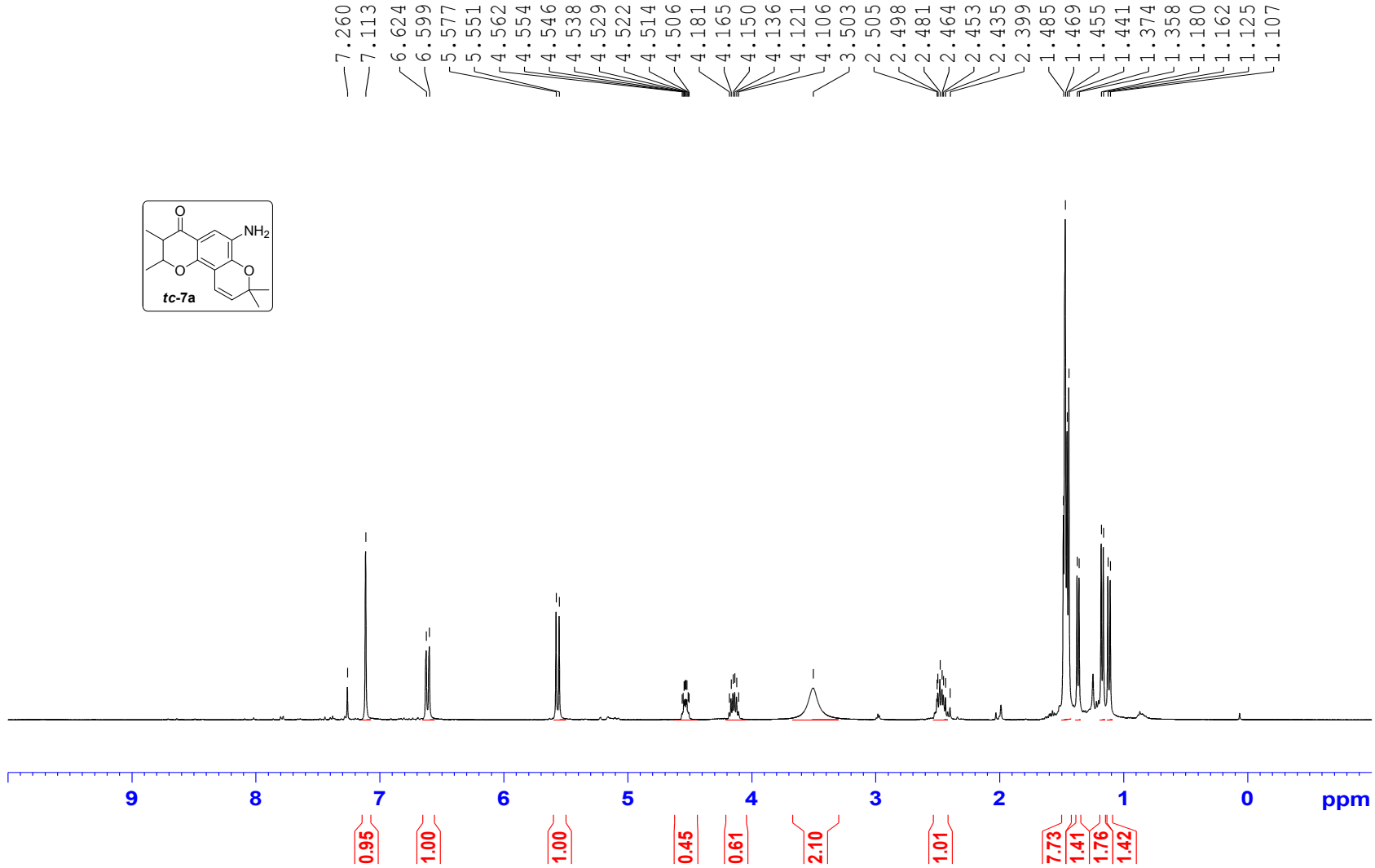

5-Cl-NO2-AISA
08.07.2016
C13CPD CDCl3
145.19
141.98
130.90
127.69
117.80
117.59
77.37
77.05
76.73
Cl
NH2
NO2
5g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

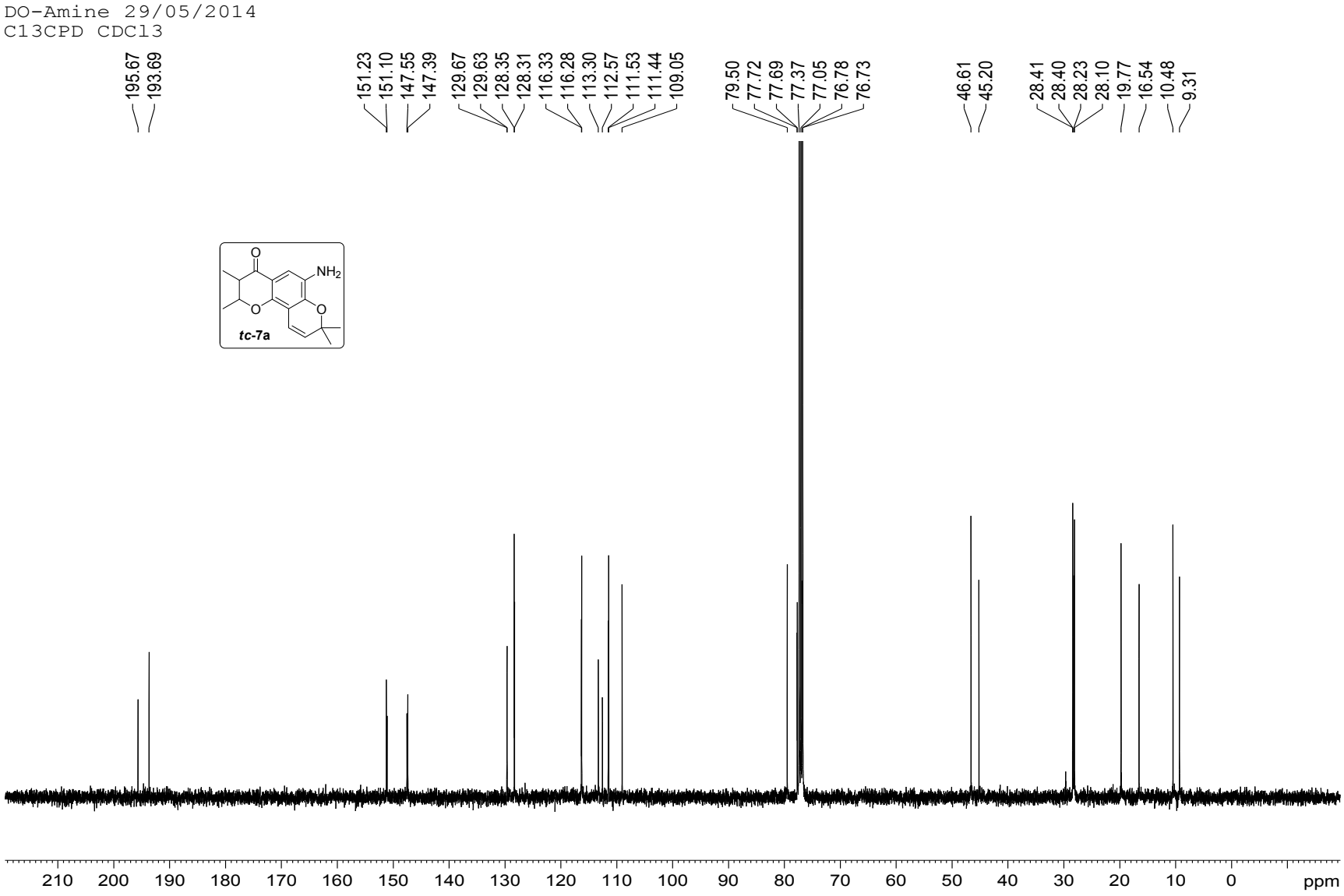

8.396
8.392
8.374
8.371
8.250
8.246
8.231
8.227
7.264
6.676
6.656
6.635
3.920
PSV-PHTHALIC-AMINE
08.09.2016
PROTON CDCl3
Me
O
O
NH2
NO2
5j
9.0
8.5
8.0
ppm
2.897
1.007
10
9
8
7
6
5
4
3
2
1
0
ppm
2.90
1.01
1.00
3.12

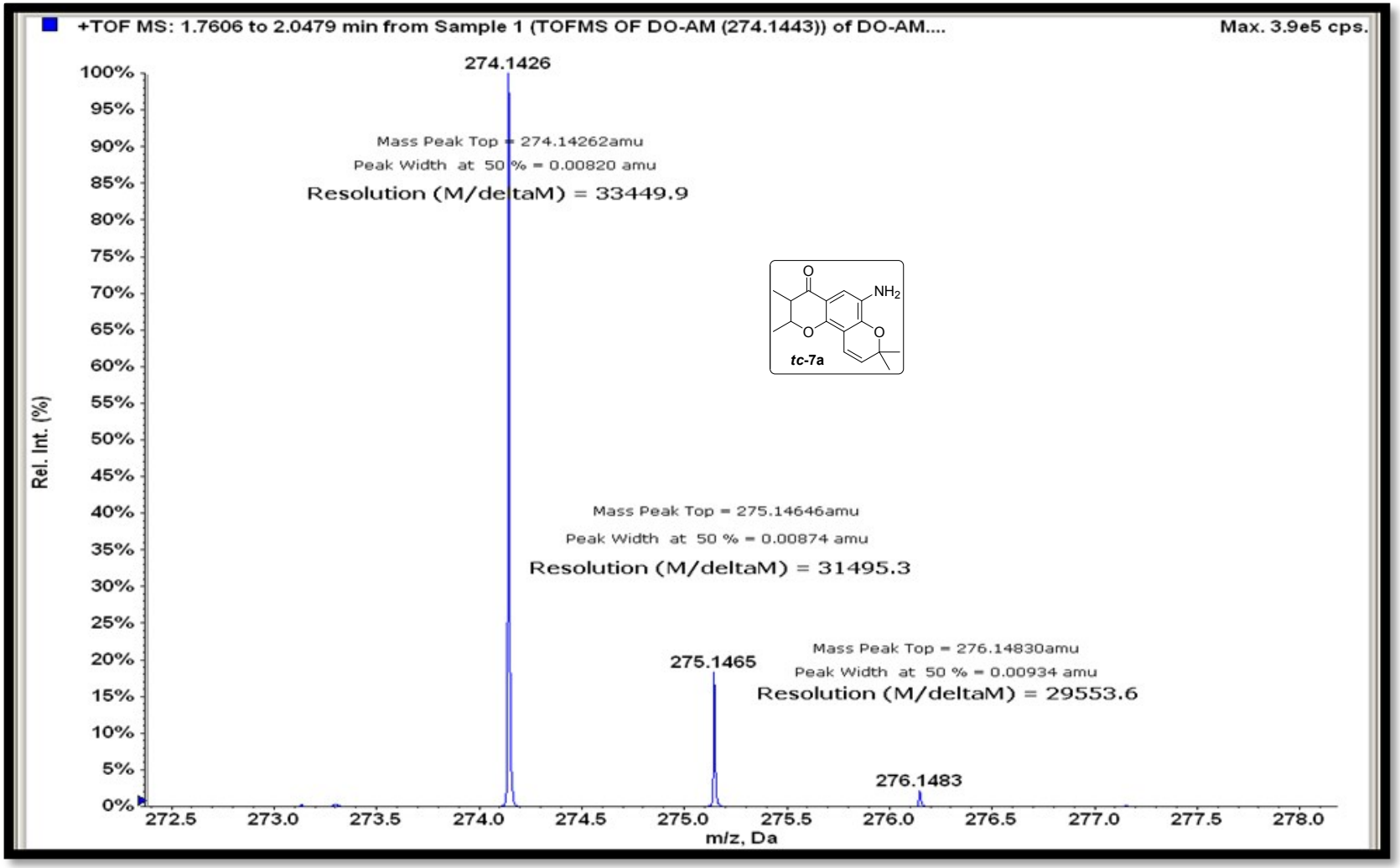

8.396
8.392
8.374
8.371
8.250
8.246
8.231
8.227
7.264
6.676
6.656
6.635
3.920
PSV-PHTHALIC-AMINE
08.09.2016
PROTON CDCl3
Me
O
O
NH2
NO2
5j
10
9
8
7
6
5
4
3
2
1
0
ppm
1.80
0.98
1.01
1.00
3.12


167.47
147.33
139.39
133.23
132.30
114.41
113.99
77.35
77.04
76.72
52.30
AIPSV COOMe-NH2
04.12.2015
C13CPD CDCl3
Me
O
O
NH2
NO2
5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

DO-Amine 29/05/2014
PROTON CDCl3

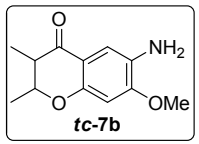



DO-Amine 29/05/2014
C13CPD CDCl3
195.67
193.69
151.23
151.10
147.55
147.39
129.67
129.63
128.35
128.31
116.33
116.28
113.30
112.57
111.53
111.44
109.05
79.50
77.72
77.69
77.37
77.05
76.78
76.73
46.61
45.20
28.41
28.40
28.23
28.10
19.77
16.54
10.48
9.31
O
NH2
O
O
tc-7a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

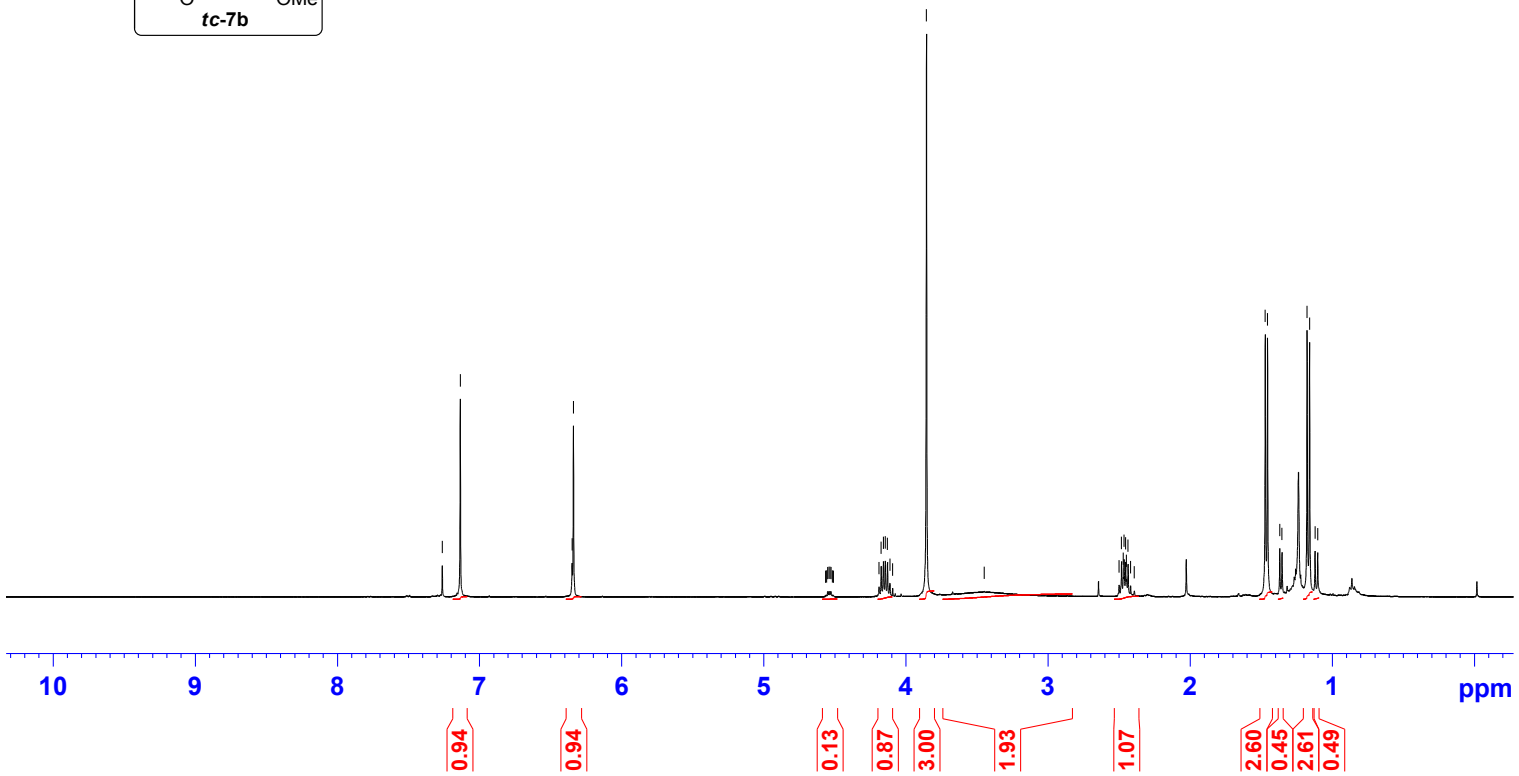

+TOF MS: 1.7606 to 2.0479 min from Sample 1 (TOFMS OF DO-AM (274.1443)) of DO-AM....
Max. 3.9e5 cps.
274.1426
Mass Peak Top = 274.14262amu
Peak Width at 50 % = 0.00820 amu
Resolution (M/deltaM) = 33449.9
tc-7a
Mass Peak Top = 275.14646amu
Peak Width at 50 % = 0.00874 amu
Resolution (M/deltaM) = 31495.3
275.1465
Mass Peak Top = 276.14830amu
Peak Width at 50 % = 0.00934 amu
Resolution (M/deltaM) = 29553.6
276.1483
Rel. Int. (%)
m/z, Da

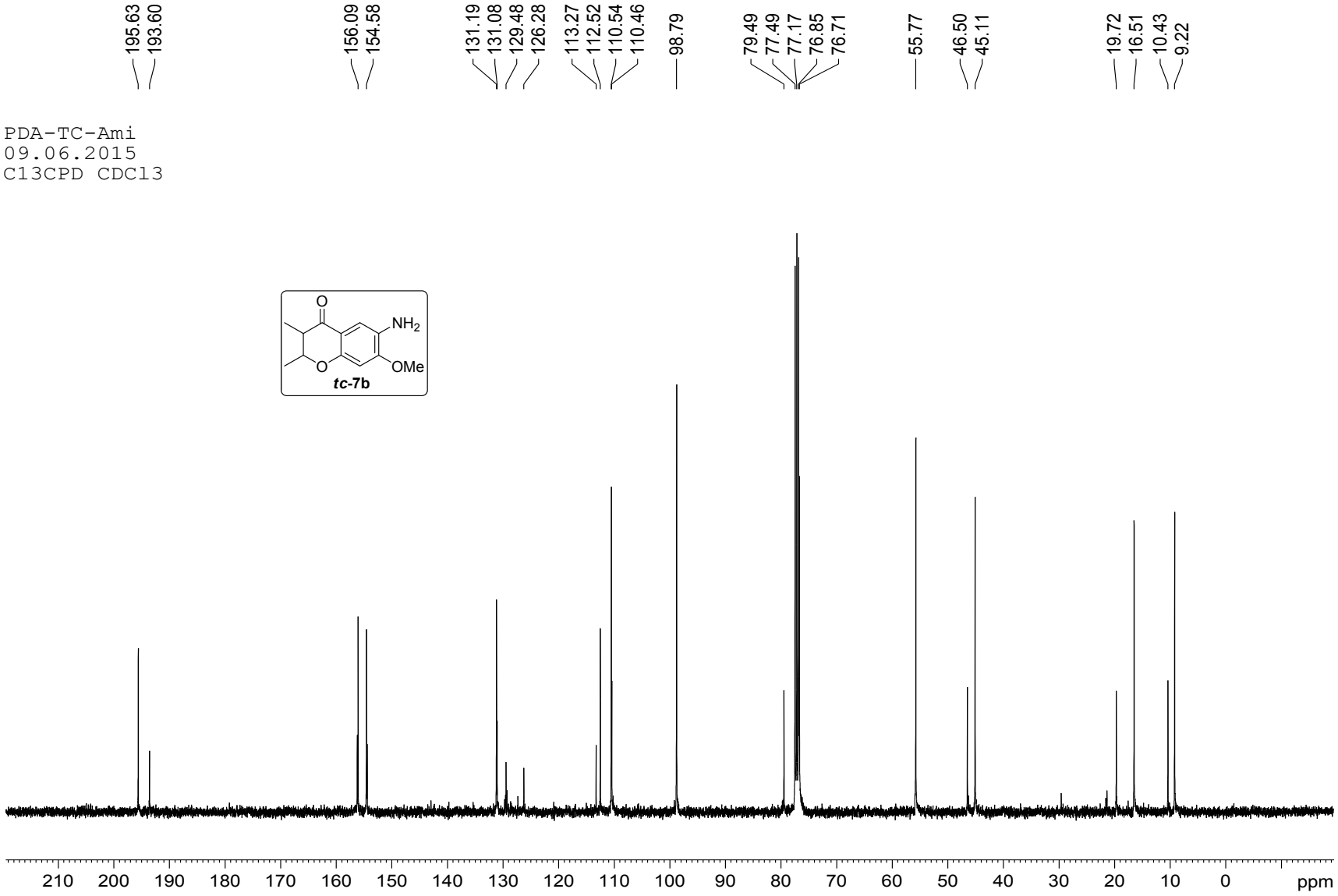
psv-chrome-NH2
mtm 02.09.2016
PROTON CDCl3

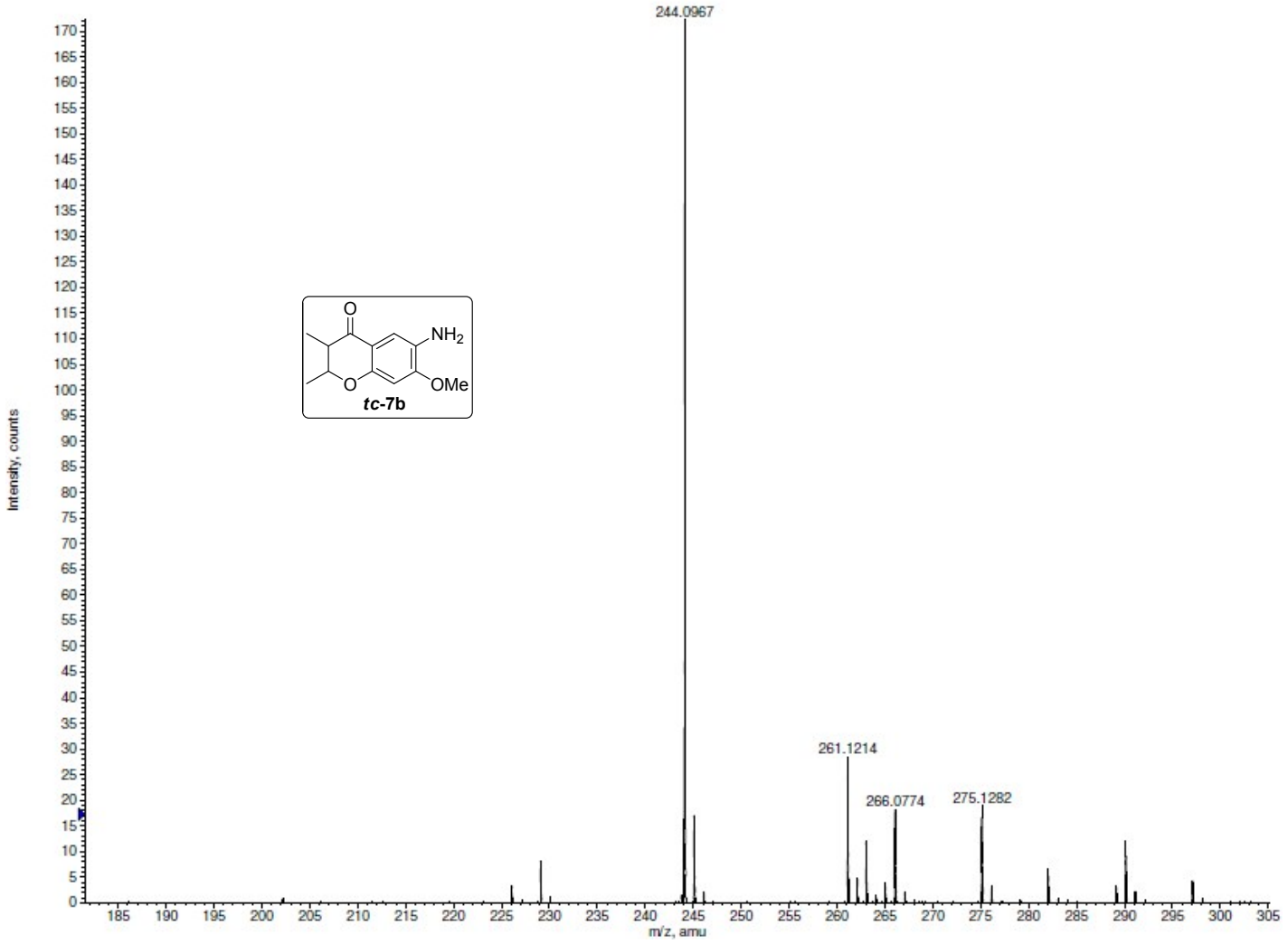
7.260
7.133
6.347
6.337
4.564
4.557
4.548
4.541
4.532
4.524
4.516
4.508
4.189
4.173
4.158
4.144
4.129
4.112
4.093
3.854
3.448
2.499
2.482
2.470
2.464
2.453
2.447
2.436
2.418
2.392
1.470
1.455
1.369
1.352
1.176
1.159
1.120
1.102

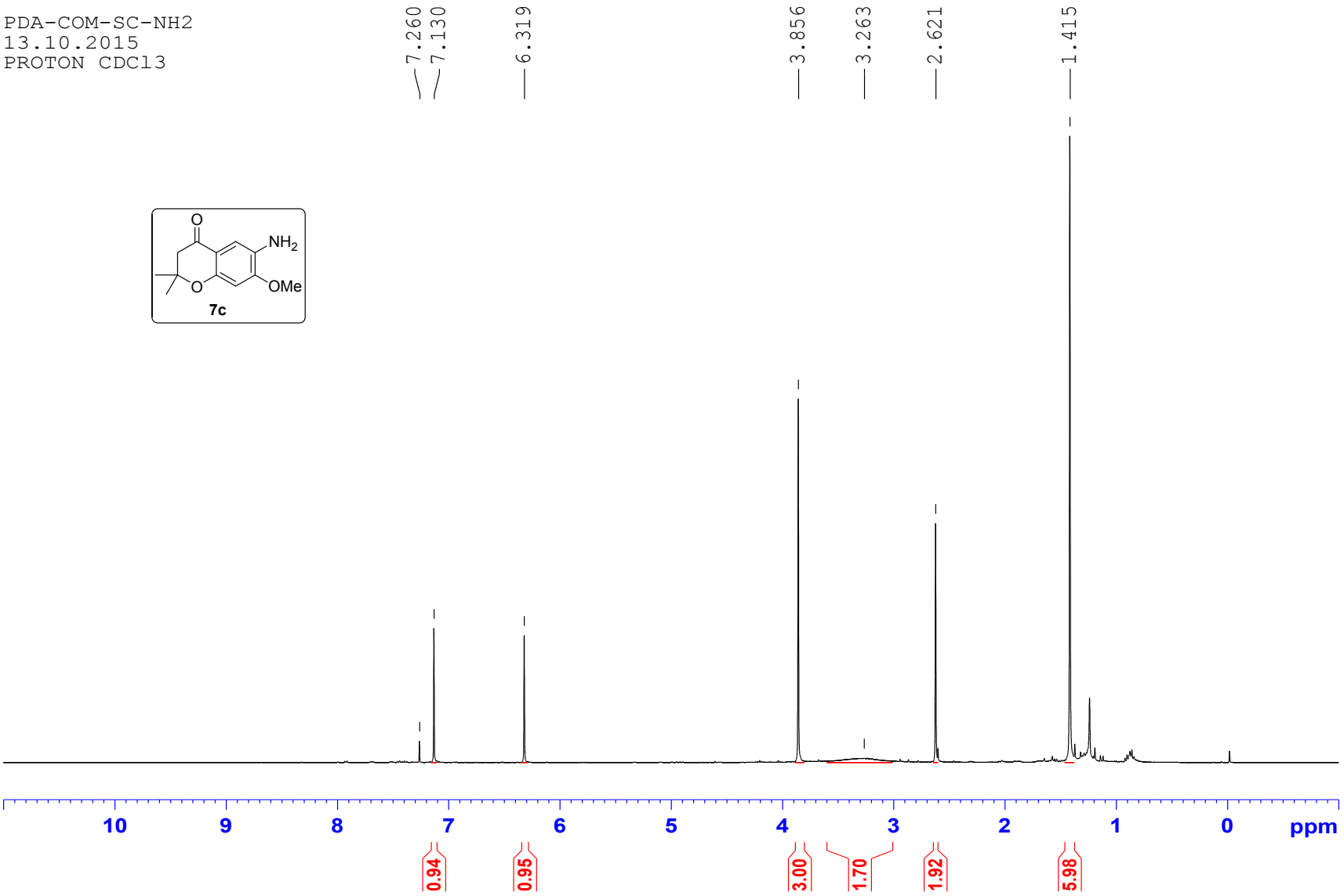


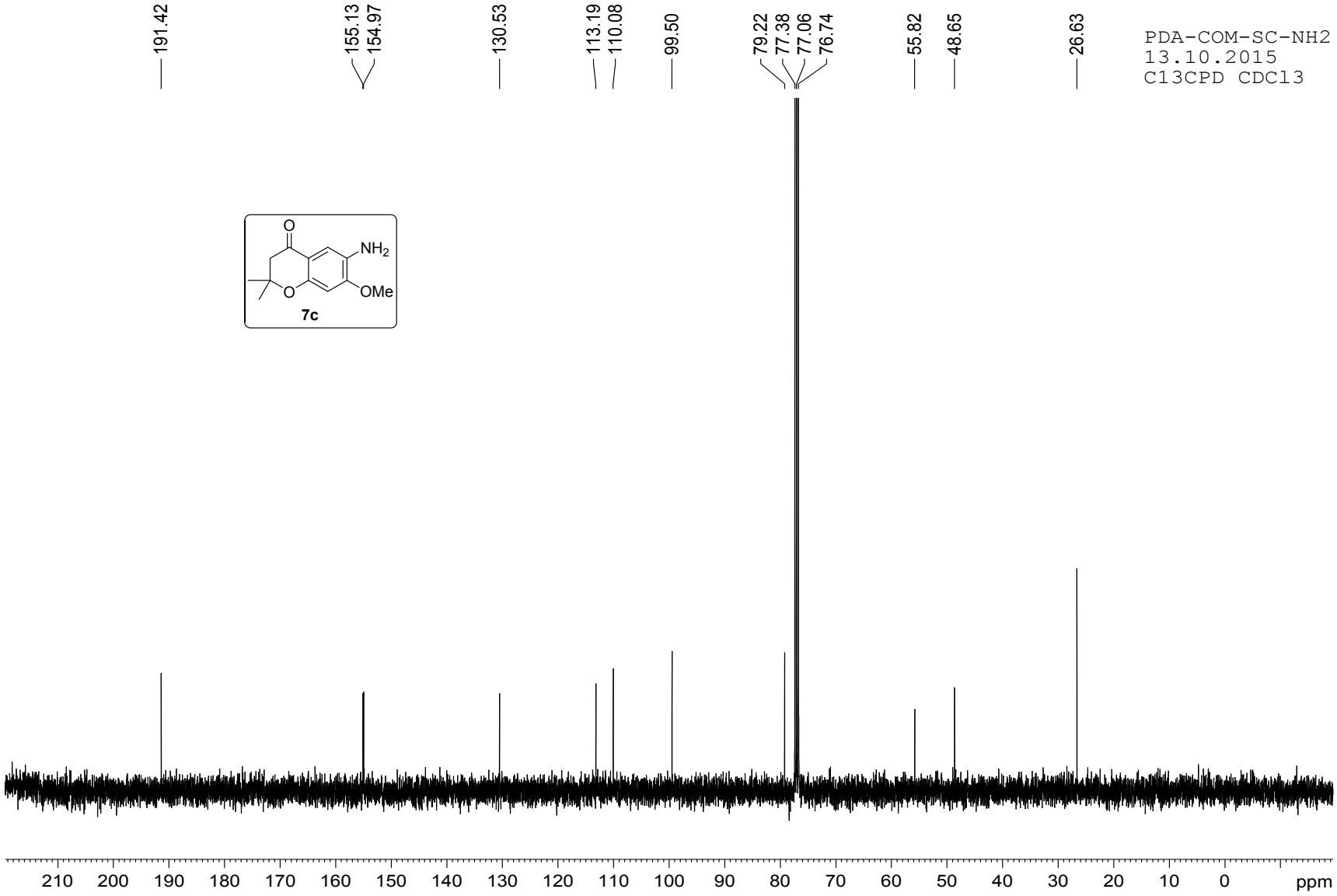
tc-7b




195.63
193.60
156.09
154.58
131.19
131.08
129.48
126.28
113.27
112.52
110.54
110.46
98.79
79.49
77.49
77.17
76.85
76.71
55.77
46.50
45.11
19.72
16.51
10.43
9.22
PDA-TC-Ami
09.06.2015
C13CPD CDCl3
O
NH2
O
OMe
tc-7b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

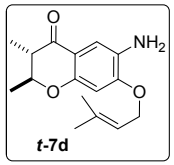

244.0967
261.1214
266.0774
275.1282
Intensity, counts
m/z, amu
NH2
OMe
O
O
tc-7b


PDA-COM-SC-NH2
13.10.2015
PROTON CDCl3
7.260
7.130
6.319
3.856
3.263
2.621
1.415
O
NH2
O
OMe
7c
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
0.95
3.00
1.70
1.92
5.98

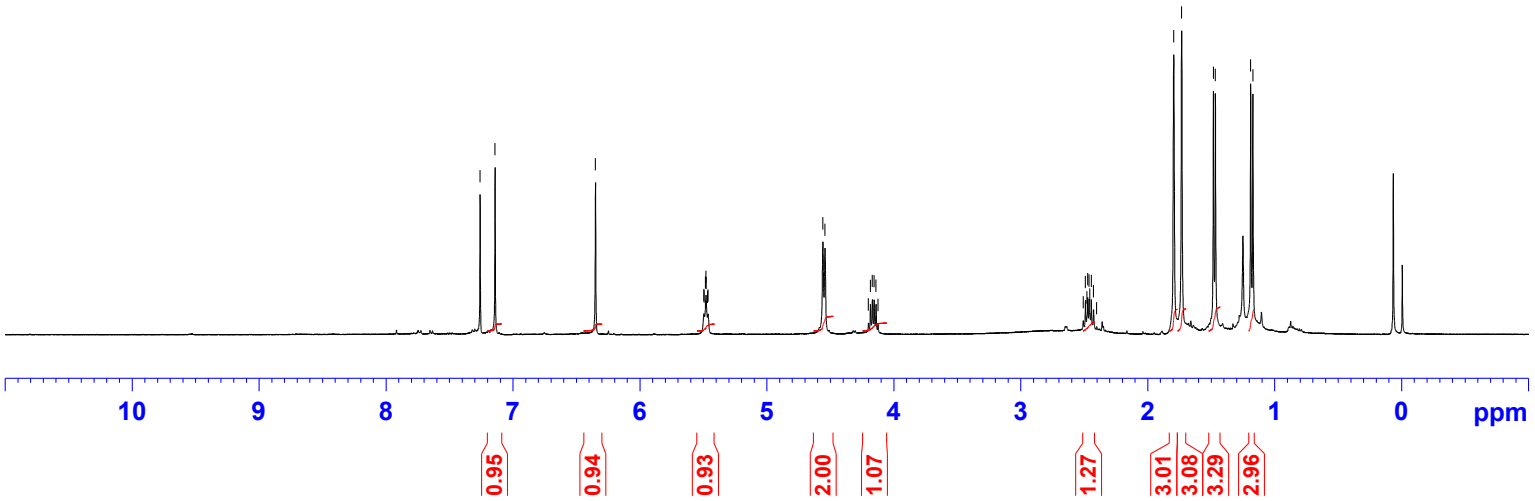

191.42
155.13
154.97
130.53
113.19
110.08
99.50
79.22
77.38
77.06
76.74
55.82
48.65
26.63
PDA-COM-SC-NH2
13.10.2015
C13CPD CDCl3
O
NH2
O
OMe
7c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

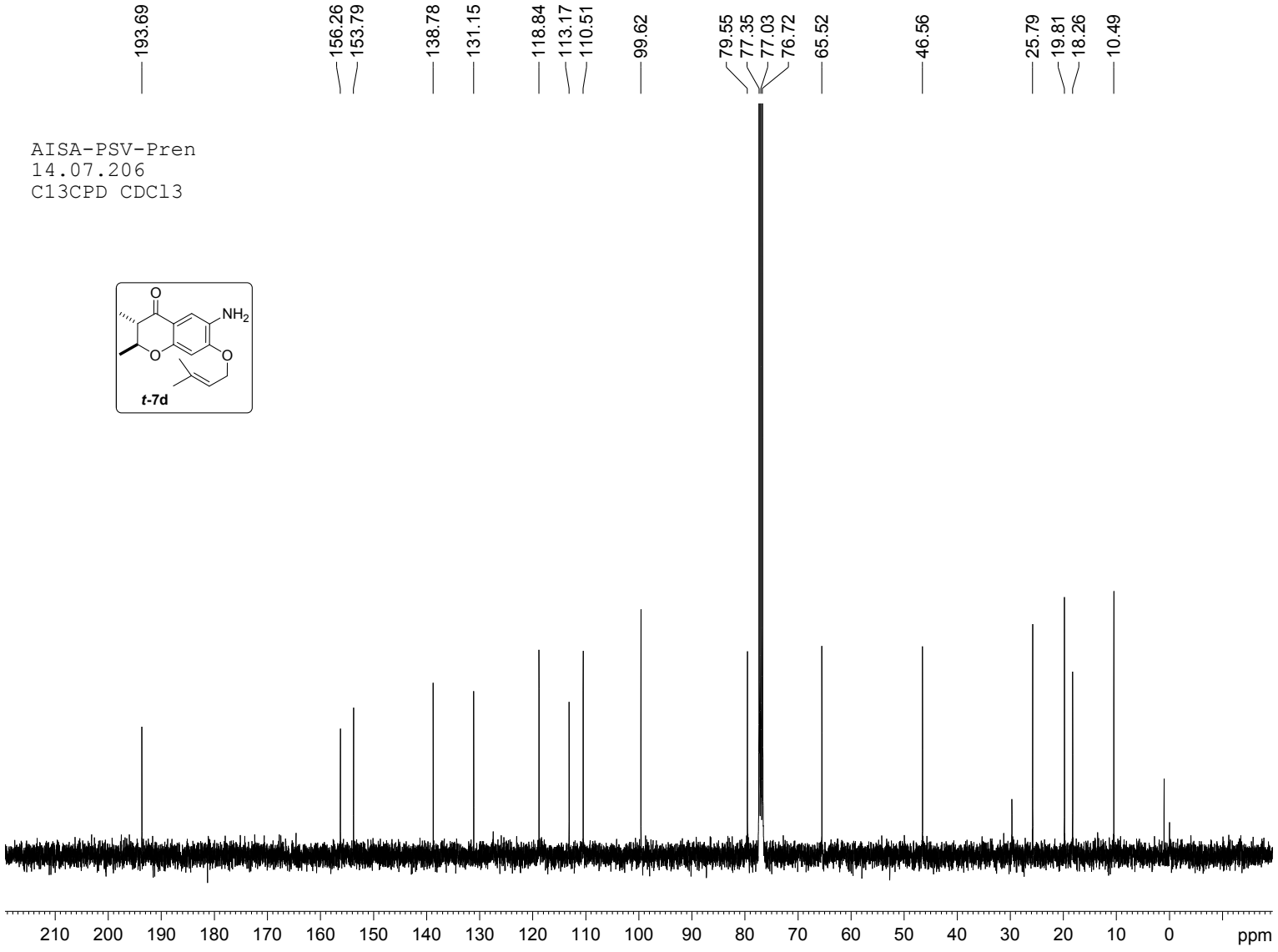
PSV-DO-Pren-NH2
23.06.2016
PROTON CDCl3

7.260
7.142
6.351
5.497
5.494
5.484
5.481
5.478
5.467
5.464
4.560
4.543
4.200
4.185
4.170
4.156
4.141
4.125
2.509
2.491
2.480
2.474
2.463
2.457
2.445
2.427
2.403
1.796
1.733
1.483
1.468
1.190
1.172



t-7d




193.69
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138.78
131.15
118.84
113.17
110.51
99.62
79.55
77.35
77.03
76.72
65.52
46.56
25.79
19.81
18.26
10.49
AISA-PSV-Pren
14.07.206
C13CPD CDCl3
O
NH2
O
O
t-7d
210
200
190
180
170
160
150
140
130
120
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90
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30
20
10
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ppm