Supporting Information

Cp*Co(III)-Catalyzed C-H Alkylation with Maleimides using Weakly Coordinating Carbonyl Directing Groups

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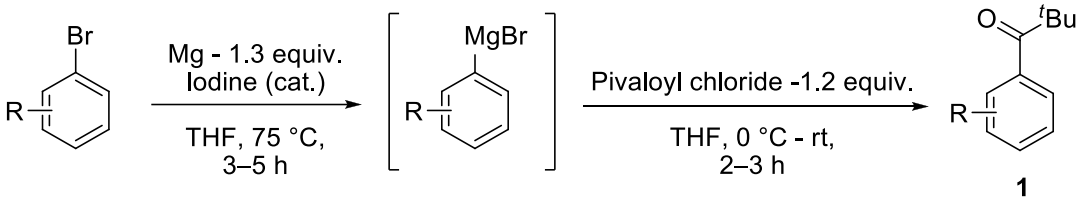
CONTENT

1. **General**: Unless otherwise mentioned, all reactions were carried out under argon atmosphere. 1,2-Dicholoroethane (1,2-DCE) was dried using calcium hydride under the established protocol. Reagent grade 2,2,2-trifluoroethanol (TFE) was used as such from the commercial sources. ^{1}H and ^{13}C NMR were recorded on JEOL (400 MHz) and JEOL (500 MHz) using $CDCl_3$ as a solvent. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals used as references and the chemicals shifts converted to TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminium sheets precoated with silica gel. Column chromatography was conducted on silica gel (Merck, 200-400 mesh). EI-MS/ESI-MS was recorded on a Waters Micromass Quattro Micro triplequadrupole mass spectrometer. LC-MS was recorded on an Agilent technologies 6120 Quadrupole LC/MS. Unless otherwise mentioned, all other chemicals were received and used as such from the commercial sources.

2. Experimental Section:

2.1. General Procedure (A) for the preparation Ketone:[1]



Comercially available magnesium was washed with 1(N) HCl followed by washing with distilled water and acetone. Magnesium was dried in oven for overnight. Magnesium (1.3 equiv.) was charged in an oven dried two necked round bottom flask equipped with a reflux condenser and a glass vacuum adapter. The flask was heated under vacuum two to three times to activate magnesium. After cooling to room temperature, a pinch of iodine followed by dry THF (4.0 mL per mmol) were added to the flask. The resultant suspension was heated to 75 °C, subsequently aryl bromide in dry THF (5.0 mL) solution was added

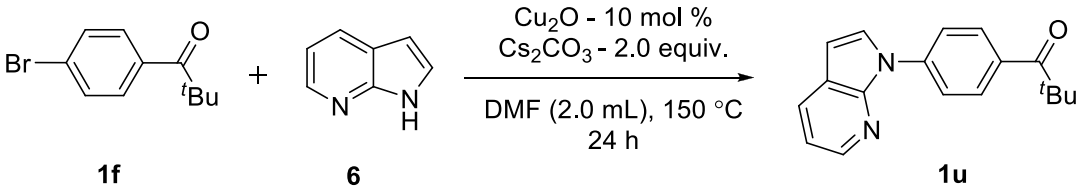
[1] Mo, F.; Trzepkowski, L. J.; Dong, G. *Angew. Chem. Int. Ed*. **2012**, *51*, 13075 –13079.

dropwise to the reaction flask. Disapperance of iodine colour was observed and slowly reaction mixture turned into the light black solution. The reaction was continued for additional 3-5 h and monitored by TLC. After that the reaction mixture was cooled down to room temperature. The corresponding Grignard solution was transferred to a solution of pivaloyl chloride (1.3 equiv.) in dry THF (4 mL per mmol) via cannula at 0 °C. After additional stirring for 2-3 hours at ambident temperature, the reaction was quenched by saturated NH_4Cl aqueous solution (20 mL), extracted with ethyl acetate (15 mL×3), combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (Hex/EA= 99/1 to 90/10) to give aryl *tert*-butyl ketone **1** in good yield (70 - 85 %).

Aryl ketone **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i** and **1j** were prepared according to the general procedure (**A**).

Ethyl benzoate **4a**, **4b**, **4c** and **4d** were prepared according to the literature procedure.[2]

2.2. Procedure (B) for the synthesis of ketone (1u):[3]

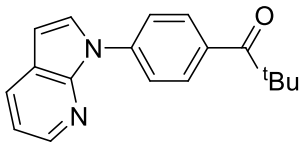


Ketone **1u** was prepared from it's bromo derivative **1f** using modified reported procedure mentioned below. An oven-dried Schlenk tube was charged with 1*H*-pyrrolo[2,3-*b*]pyridine **6** (0.200 g, 1.69 mmol, 1.0 equiv.), Cu_2O (0.024 g, 0.169 mmol) and Cs_2CO_3 (1.10 g, 3.38 mmol, 2.0 equiv.) under argon atmosphere. 1-(4-Bromophenyl)-2,2-dimethylpropan-1-one **1f** (0.611 g, 2.53 mmol, 1.5 equiv.), followed by dry DMF (2.0 mL) were added to the Schlenk tube. The Schlenk tube was sealed under argon, and then sealed tube was placed to a preheated oil bath at 150 °C (oil bath temperature). After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with

[2] Sun, L.; Xing, H.; Liang, Z.; Yu, J.; Xu, R. *Chem. Commun*., **2013**, *49*, 11155-11157.
[3] Correa, A.; Bolm, C. *Adv. Synth. Catal*. **2007**, *349*, 2673–2676.

dichloromethane. The resulting solution was directly filtered through a pad of silica gel and concentrated to yield the product, which was purified by silica gel chromatography (5:95 ethyl acetate/hexane) to yield (0.282 g, 1.01 mmol, 60 % yield) 1-(4-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-2,2-dimethylpropan-1-one **1u** as white solid.

1-(4-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)-2,2-dimethylpropan-1-one (1u):

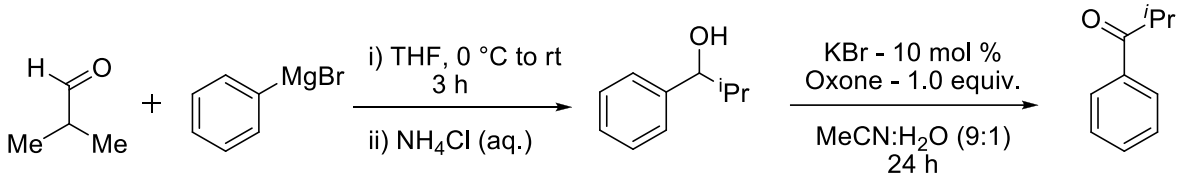


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.99-7.94 (m, 3H), 7.92-7.89 (m, 2H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.17 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.67 (d, *J* = 3.7 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 147.4, 143.7, 140.7, 135.1, 129.7, 129.2, 127.1, 122.4, 121.9, 117.1, 102.6, 44.1, 28.1.

HRMS calculated for $C_{18}H_{19}N_2O$ is $[M+H]^+$: 279.1497; found: 279.1490.

2.3. Procedure (C) for the synthesis of ketone (1k):[4]



7 **8** **1k**

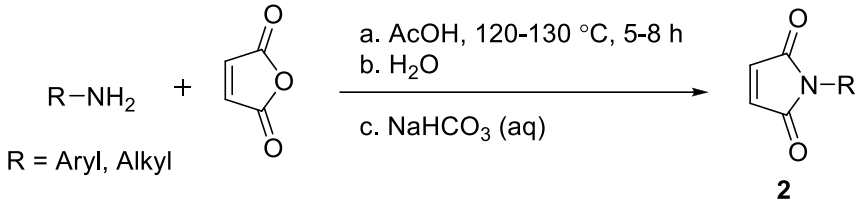
The phenyl magnesium bromide solution was prepared according to the procedure **A**. Grignard solution was added to a solution of isobutyraldehyde **7** (1.3 equiv.) in dry THF (4 mL per mmol) via cannula at 0 °C. After additional stirring for 3 h at ambident temperature, the reaction was quenched by saturated NH_4Cl aqueous solution (20 mL), extracted with ethyl acetate (15 mL × 3) and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate= 85/15) to give secondary alcohol **8**.

[4] Slagbrand, T.; Kivijärvi, T.; Adolfss, H. *ChemCatChem* **2015**, *7*, 3445 –3449.

Alcohol **8** was subjected for oxidation according to the literature procedure to furnish 2-methyl-1-phenylpropan-1-one (**1k**) in good yield.[5]

2.4. General Procedure (D) for the synthesis of N-aryl/N-alkyl maleimide derivatives:[6]

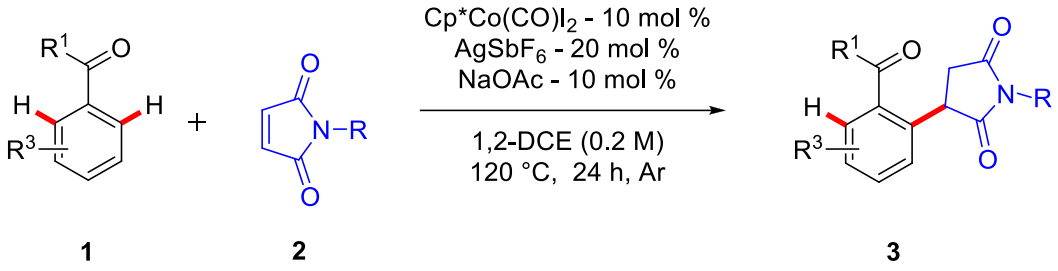
N-Aryl/Alkyl maleimides **2** were prepared using the modified reported procedure mentioned below from the corresponding primary amine.



Maleic anhydride (2.0 equiv.) and primary amine (1.0 equiv.) were stirred in acetic acid (1.5 ml per mmol of amine) until maleic anhydride dissolved completely. The reaction mixture was refluxed for 6-8 h at 125 °C (oil bath temperature). After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature and the whole reaction mixture was transferred to a 500 mL beaker. Saturated sodium bicarbonate aqueous solution was added to the beaker containing reaction mixture until effervescence stop. The aqueous mixture was extracted with ethyl acetate (3x20 mL). The organic layer was further washed with 1(N) HCl (2x50 mL) and brine solution (30 mL) respectively. The excess solvent was removed under reduced pressure and the residue was purified by flash column chromatography using ethyl acetate/ hexane (10/90-60/40) to get highly pure maleimide **2** in good yield (60-90 %).

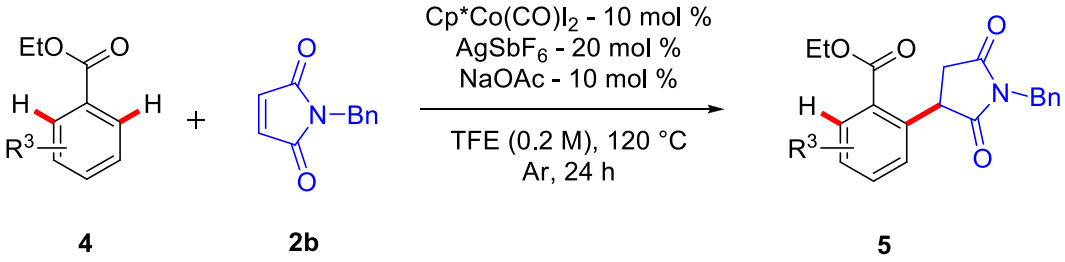
[5] Moriyama, K.; Takemura, M.; Togo, H. *J. Org. Chem*. **2014**, *79*, 6094−6104.
[6] Deshmukha, G. B.; Patila, N. S.; Gaikwada, V. B.; Bholeb, A. D.; Patil, S. V. *J. Chem. Pharm. Res*. **2014**, *6*, 393.

2.5. General catalytic procedure (E) of coupling of maleimide (2) with ketone (1):



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mol %), NaOAc (1.6 mg, 0.02 mmol, 10 mol %) under argon atmosphere. Small amount of 1,2-DCE (0.2 mL) was added to the Schlenk tube and stirred for few minutes. Ketone **1** (0.2 mmol, 1.0 equiv.), maleimide **2** (0.3 mmol, 1.5 equiv.) followed by 0.8 mL 1,2-DCE were successively added to the Schlenk. The closed tube was placed to a pre-heated oil bath at 120 °C for 24 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel afforded **3**.

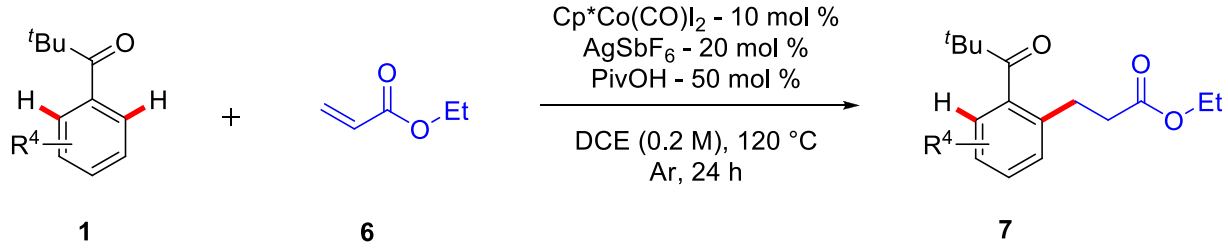
2.6. General catalytic procedure (F) of coupling of maleimide (2b) with ester (4):



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mol %), NaOAc (1.6 mg, 0.02 mmol, 10 mol %) under argon atmosphere. Small amount of 2,2,2-trifluoroethanol (TFE) (0.2 mL) was added to the Schlenk tube and stirred for few minutes. Ester **4** (0.2 mmol, 1.0

equiv.), 1-benzyl-1*H*-pyrrole-2,5-dione **2b** (56.1 mg, 0.3 mmol, 1.5 equiv.) followed by 0.8 mL TFE were successively added to the Schlenk tube. The closed Schlenk tube was placed to a pre-heated oil bath at 120 °C for 24 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel afforded **5.**

2.7. General catalytic procedure (G) of coupling of ethyl acrylate (6) with ketone (1):



1 **6** **7**

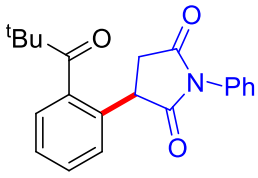
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mol %), PivOH (0.010 mg, 0.1 mmol, 50 mol %) under argon atmosphere. Small amount of 1,2-DCE (0.2 mL) was added to the Schlenk tube and stirred for few minutes. Ketone **1** (0.2 mmol, 1.0 equiv.), ethyl but-3-enoate **6** (0.4 mmol, 2.0 equiv.) followed by 0.8 mL 1,2-DCE were successively added to the Schlenk tube. The closed Schlenk tube was placed to a pre-heated oil bath at 120 °C for 24 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel afforded **7.**

2.8. Procedure for synthesis of the product (3nb) in (> 1.0 mmol scale):

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (197 mg, 0.416 mmol, 10 mol %), $AgSbF_6$ (286 mg, 0.832 mmol, 20 mol %), NaOAc (34 mg, 0.416 mmol, 10 mol %) under argon atmosphere. Small amount of 1,2-DCE (1.0 mL) was added to the Schlenk tube and stirred for few minutes. Acetophenone **1n** (0.5 g, 4.16 mmol, 1.0 equiv.), 1-benzyl-1*H*-pyrrole-2,5-dione **2b** (0.945 g, 6.24 mmol, 1.2 equiv.) followed by 9 mL 1,2-DCE were successively added to the Schlenk. The closed tube was placed to a pre-

heated oil bath at 120 °C for 36 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude mixture was purified by flash column chromatography (ethyl acetate/hexane) on silica gel afforded 0.752 g of **3nb** in 59 % yield.

1-Phenyl-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (**3aa**):



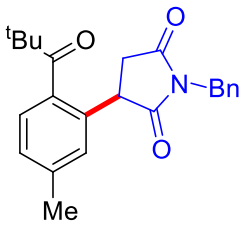
Compound **3aa** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 10 : 90) afforded 62.4 mg of **3aa** in 93 % yield as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (dd, J = 7.7, 1.2 Hz, 1H), 7.50-7.34 (m, 7H), 7.28 (dd, J = 7.7, 1.1 Hz, 1H), 4.15 (dd, J = 9.7, 6.0 Hz, 1H), 3.32 (dd, J = 18.3, 9.7 Hz, 1H), 3.02 (dd, J = 18.3, 6.0 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.3, 176.9, 175.0, 139.1, 135.6, 132.0, 130.5, 130.0, 129.1, 128.6, 126.9, 126.79, 126.75, 45.1, 44.7, 38.7, 28.1.

HRMS calculated for $C_{21}H_{22}NO_3$ is $[M+H]^+$: 336.1600; found: 336.1601.

1-Benzyl-3-(5-methyl-2-pivaloylphenyl)pyrrolidine-2,5-dione (3bb): Compound **3bb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 7 : 93) afforded 68.3 mg of **3bb** in 94 % yield as colourless liquid.

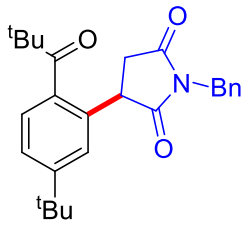


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.37 (d, J = 7.9 Hz, 1H), 7.35-7.28 (m, 3H), 7.09 (d, J = 7.9 Hz, 1H), 6.77 (brs, 1H), 4.75 (d, J = 14.1 Hz, 1H), 4.70 (d, J = 14.1 Hz, 1H), 3.89 (dd, J = 9.5, 5.2 Hz, 1H), 3.15 (dd, J = 18.4, 9.6 Hz, 1H), 2.76 (dd, J = 18.4, 5.2 Hz, 1H), 2.27 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.1, 177.7, 175.7, 140.5, 136.8, 135.84, 135.83, 129.3, 128.7, 128.5, 127.8, 127.3, 126.2, 44.7, 44.3, 42.5, 38.7, 27.8, 21.1.

HRMS calculated for $C_{23}H_{26}NO_3$ is $[M+H]^+$: 364.1913; found: 364.1911.

1-Benzyl-3-(5-*tert*-butyl-2-pivaloylphenyl)pyrrolidine-2,5-dione (**3cb**):



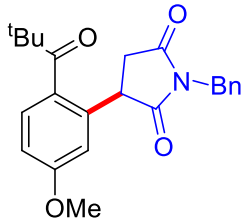
Compound **3cb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 3 : 97) afforded 77.0 mg of **3cb** in 95 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.42 (m, 3H), 7.34-7.28 (m, 4H), 6.94 (d, J = 1.8 Hz, 1H), 4.77 (d, J = 14.2 Hz, 1H), 4.73 (d, J = 14.2 Hz, 1H), 3.93 (dd, J = 9.6, 5.3 Hz, 1H), 3.17 (dd, J = 18.4, 9.5 Hz, 1H), 2.79 (dd, J = 18.5, 5.3 Hz, 1H), 1.30 (s, 9H), 1.20 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.2, 177.8, 175.8, 153.7, 136.6, 135.9, 135.7, 128.7, 128.6, 127.8, 126.2, 125.7, 123.8, 44.8, 44.7, 42.5, 38.8, 34.7, 30.9, 27.9.

HRMS calculated for $C_{26}H_{31}NNaO_3$ is $[M+Na]^+$: 428.2202; found: 428.2206.

1-Benzyl-3-(5-methoxy-2-pivaloylphenyl)pyrrolidine-2,5-dione (**3db**):



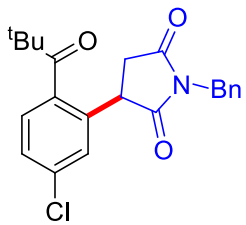
Compound **3db** was prepared according to the general procedure **E** and the was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 65.3 mg of **3db** in 86 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.6 Hz, 1H), 7.44-7.42 (m, 2H), 7.33-7.26 (m, 3H), 6.79 (dd, J = 8.6, 2.5 Hz, 1H), 6.50 (d, J = 2.5 Hz, 1H), 4.74 (d, J = 14.1 Hz, 1H), 4.69 (d, J = 14.1 Hz, 1H), 3.96 (dd, J = 9.4, 5.5 Hz, 1H), 3.69 (s, 3H), 3.16 (dd, J = 18.3, 9.6 Hz, 1H), 2.79 (dd, J = 18.3, 5.5 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.0, 177.5, 175.6, 160.7, 138.2, 135.8, 131.5, 128.7, 128.57, 128.50, 127.8, 114.7, 111.8, 55.1, 44.8, 44.6, 42.5, 38.5, 28.1.

HRMS calculated for $C_{23}H_{26}NO_4$ is $[M+H]^+$: 380.1862; found: 380.1858.

1-Benzyl-3-(5-chloro-2-pivaloylphenyl)pyrrolidine-2,5-dione (**3eb**):

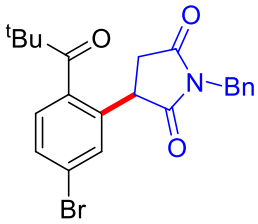


Compound **3eb** was prepared accoding to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane=7:83) afforded 68.3 mg of **3eb** in 89 % yield as colourless liquid.**^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 3H), 7.35-7.27 (m, 4H), 7.02 (d, J = 1.9 Hz, 1H), 4.74 (d, J = 14.1 Hz, 1H), 4.70 (d, J = 14.0 Hz, 1H), 3.89 (dd, J = 9.6, 5.5 Hz, 1H), 3.14 (dd, J = 18.4, 9.6 Hz, 1H), 2.76 (dd, J = 18.4, 5.5 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 176.8, 175.1, 137.8, 137.6, 136.0, 135.5, 129.1, 128.7, 128.6, 127.9, 127.5, 126.9, 44.7, 44.2, 42.6, 38.3, 27.8.

HRMS calculated for $C_{22}H_{23}ClNO_3$ is $[M+H]^+$: 384.1366; found: 384.1367.

1-Benzyl-3-(5-bromo-2-pivaloylphenyl)pyrrolidine-2,5-dione (**3fb**):



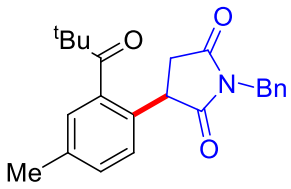
Compound **3fb** was prepared according to the general procedure **E** and the was purified by flash column chromatography (EtOAc : hexane = 7 : 83) afforded 68.5 mg of **3fb** in 80 % yield as dence colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, J = 8.4, 1.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.35-7.29 (m, 4H), 7.17 (d, J = 1.8 Hz, 1H), 4.75 (d, J = 14.1Hz, 1H), 4.69 (d, J = 14.1 Hz, 1H), 3.87 (dd, J = 9.5, 5.5 Hz, 1H), 3.15 (dd, J = 18.4, 9.6 Hz, 1H), 2.77 (dd, J = 18.4, 5.5 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4, 176.8, 175.1, 138.4, 137.8, 135.6, 132.0, 129.9, 128.8, 128.7, 128.0, 127.6, 124.3, 44.8, 44.2, 42.7, 38.4, 27.8.

HRMS calculated for $C_{22}H_{23}BrNO_3$ is $[M+H]^+$: 428.0861; found: 428.0860.

1-Benzyl-3-(4-methyl-2-pivaloylphenyl)pyrrolidine-2,5-dione (**3gb**):



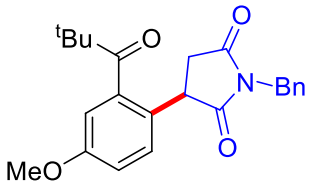
Compound **3gb** was prepared according to the general procedure **E** and the was purified by flash column chromatography (EtOAc : hexane = 8 : 92) afforded 65.4 mg of **3gb** in 90 % yield as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.34-7.27 (m, 3H), 7.22 (brs, 1H), 7.15 (dd, J = 8.0, 0.9 Hz, 1H), 6.89 (d, J = 7.9 Hz, 1H), 4.74 (d, J = 14.1 Hz, 1H), 4.69 (d, J= 14.1 Hz, 1H), 3.86 (dd, J = 9.5, 5.4 Hz, 1H), 3.14 (dd, J = 18.4, 9.5 Hz, 1H), 2.73 (dd, J = 18.4, 5.4 Hz, 1H), 2.35 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.5, 177.6, 175.6, 139.9, 136.6, 135.8, 132.4, 130.9, 128.7, 128.5, 128.3, 127.8, 126.4, 44.7, 43.9, 42.5, 38.7, 27.8, 21.0.

HRMS calculated for $C_{23}H_{26}NO_3$ is $[M+H]^+$: 364.1913; found: 364.1913.

1-Benzyl-3-(4-methyl-2-pivaloylphenyl)pyrrolidine-2,5-dione (**3hb**):



Compound **3hb** and **3hb'** were prepared accoding to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 37.2 mg of **3hb** (49 % yield) as white solid and 23.5 mg of **3hb'** (31 % yield) as red liquid.

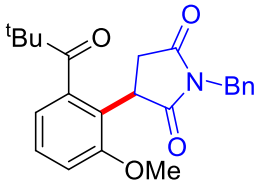
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.40 (m, 2H), 7.34-7.28 (m, 3H), 6.94 (d, J = 2.6 Hz, 1H), 6.93 (d, J = 8.6 Hz, 1H), 6.87 (dd, J = 8.6, 2.6 Hz, 1H), 4.74 (d, J = 14.1 Hz, 1H), 4.68 (d, J = 14.1 Hz, 1H), 3.83 (dd, J = 9.6, 5.4 Hz, 1H), 3.80 (s, 3H), 3.13 (dd, J = 18.4, 9.5 Hz, 1H), 2.72 (dd, J = 18.4, 5.4 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.0, 177.8, 175.7, 157.8, 140.9, 135.8, 129.6, 128.8, 128.6, 127.9, 127.3, 115.0, 112.4, 55.4, 44.8, 43.6, 42.6, 38.8, 27.8.

HRMS calculated for $C_{23}H_{26}NO_4$ is $[M+H]^+$: 380.1862; found: 380.1859.

1-Benzyl-3-(2-methoxy-6-pivaloylphenyl)pyrrolidine-2,5-dione (**3hb'**):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 6.9 Hz, 2H), 7.34-7.22 (m, 3H), 7.23 (d, J = 8.0 Hz,

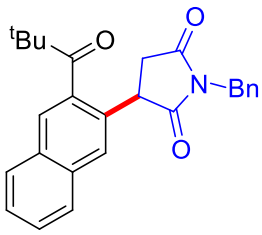


1H), 6.58 (d, J = 7.5 Hz, 1H), 6.78 (d, J = 8.2 Hz, 1H), 4.73 (d, J = 13.8 Hz, 1H), 4.66 (d, J = 13.8 Hz, 1H), 3.56 (dd, J = 8.6, 5.6 Hz, 1H), 3.13 (s, 3H), 3.00 (dd, J = 8.6, 5.6 Hz, 1H), 2.67 (dd, J = 18.2, 5.4 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.8, 178.1, 176.1, 157.1, 143.1, 136.1, 129.6, 128.5, 128.2, 127.8, 122.5, 117.2, 111.4, 54.8, 45.1, 42.5, 41.3, 36.4, 27.3.

HRMS calculated for $C_{23}H_{25}NNaO_4$ is $[M+Na]^+$: 402.1681; found: 402.1687.

1-Benzyl-3-(3-pivaloylnaphthalen-2-yl)pyrrolidine-2,5-dione (**3ib**):



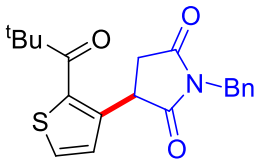
Compound **3ib** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 70.3 mg of **3ib** in 88 % yield as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.85-7.82 (m, 1H), 7.67-7.65 (m, 1H), 7.55-7.48 (m, 5H), 7.38-7.30 (m, 3H), 4.80 (d, J = 14.0 Hz, 1H), 4.76 (d, J = 14.0 Hz, 1H), 4.12 (dd, J = 9.5, 5.3 Hz, 1H), 3.22 (dd, J = 18.4, 9.6 Hz, 1H), 2.89 (dd, J = 18.4, 5.3 Hz, 1H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.0, 177.6, 175.7, 136.6, 135.8, 133.3, 133.1, 130.9, 128.8, 128.5, 128.3, 128.0, 127.9, 127.7, 127.4, 127.0, 126.3, 44.9, 44.6, 42.5, 38.8, 28.1.

HRMS calculated for $C_{26}H_{26}NO_3$ is $[M+H]^+$: 400.1913; found: 400.1913.

1-Benzyl-3-(2-pivaloylthiophen-3-yl)pyrrolidine-2,5-dione (**3jb**):



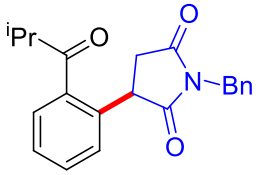
Compound **3jb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 60.4 mg of **3jb** in 85 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 3H), 7.34-7.27 (m, 3H), 6.86 (d, J = 5.2 Hz, 1H), 4.77 (d, J =14.2 Hz, 1H), 4.73 (d, J =14.2 Hz, 1H), 4.47 (dd, J = 9.5, 6.1 Hz, 1H), 3.18 (dd, J = 18.0, 9.4 Hz, 1H), 2.68 (dd, J = 17.9, 6.1 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 170.0, 175.7, 143.6, 135.8, 132.8, 129.3, 129.0, 128.7, 128.5, 127.7, 44.5, 42.5, 42.0, 36.9, 27.7.

HRMS calculated for $C_{20}H_{22}NO_3S$ is $[M+H]^+$: 356.1320; found: 356.1322.

1-Benzyl-3-(2-isobutyrylphenyl)pyrrolidine-2,5-dione (**3kb**):



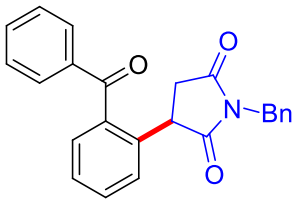
Compound **3kb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 43.6 mg of **3kb** in 65 % yield as colouless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (dd, J = 7.7, 1.1 Hz, 1H), 7.47-7.39 (m, 4H), 7.34-7.27 (m, 3H), 7.15 (dd, J = 7.5, 1.1 Hz, 1H), 4.77 (d, J = 14.1 Hz, 1H), 4.72 (d, J = 14.1 Hz, 1H), 4.26 (dd, J = 9.4, 6.1 Hz, 1H), 3.45 (sep, J = 6.9 Hz, 1H), 3.19 (dd, J = 18.1, 9.5 Hz, 1H), 2.79 (dd, J = 18.1, 6.1 Hz, 1H), 1.13 (t, J = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 207.8, 177.6, 175.8, 137.1, 136.5, 135.9, 132.2, 131.2, 129.2, 128.8, 128.5, 127.9, 127.7, 45.7, 42.5, 38.2, 37.4, 18.8, 18.6.

HRMS calculated for $C_{21}H_{22}NO_3$ is $[M+H]^+$: 336.1600; found: 336.1600.

3-(2-Benzoylphenyl)-1-benzylpyrrolidine-2,5-dione (**3lb**):

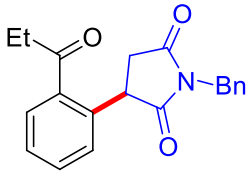


Compound **3lb** was prepared according to the general procedure **E** and the reaction was continued for 36 h. The crude reaction mixture was purified by flash column chromatography (EtOAc : hexane = 40 : 60) afforded 45.0 mg of **3lb** in 61 % yield as white solid. The NMR data of **3lb** is in accordance with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.77 (m, 2H), 7.62-7.58 (m, 1H), 7.51-7.34 (m, 7H), 7.31-7.26 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 1H), 4.72 (d, *J* = 14.1 Hz, 1H), 4.65 (d, *J* = 14.1 Hz, 1H), 4.31 (dd, *J* = 9.5, 5.8 Hz, 1H), 3.23 (dd, *J* = 18.3, 9.6 Hz, 1H), 2.90 (dd, *J* = 18.3, 5.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 177.6, 175.6, 137.6, 137.3, 137.2, 135.7, 133.2, 131.6, 130.6, 130.3, 129.6, 128.7, 128.5, 128.3, 127.7, 127.0, 44.5, 42.5, 38.3.

1-Benzyl-3-(2-propionylphenyl)pyrrolidine-2,5-dione (**3mb**):

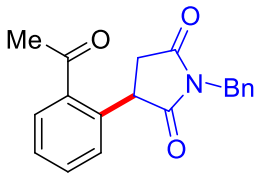


Compound **3mb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 35 : 75) afforded 54.0 mg of **3mb** in 84 % yield as colourless liquid. The NMR data of **3mb** is in accordance with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.48-7.38 (m, 4H), 7.35-7.27 (m, 3H), 7.16 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.78 (d, *J* = 14.1 Hz, 1H), 4.71 (d, *J* = 14.1 Hz, 1H), 4.34 (dd, *J* = 9.4, 6.2 Hz, 1H), 3.19 (dd, *J* = 18.0, 9.4 Hz, 1H), 2.95 (q, *J* = 7.2 Hz, 2H), 2.80 (dd, *J* = 18.0, 6.2 Hz, 1H), 1.11 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 204.3, 177.7, 175.8, 136.6, 136.2, 135.9, 132.2, 131.3, 129.6, 128.7, 128.4, 128.0, 127.7, 44.8, 42.5, 37.8, 33.8, 8.12.

3-(2-Acetylphenyl)-1-benzylpyrrolidine-2,5-dione (3nb):



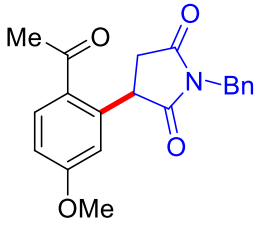
Compound **3nb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 40 : 60) afforded 43.6 mg of **3nb** in 71 % yield as red solid. The NMR data of **3nb** is in accordance with the literature.[7]

[7] Bettadapur, K. R.; Lanke, V.; Prabhu, K. R. *Org. Lett*. **2015**, *17*, 4658-4661.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, J = 7.6, 1.5 Hz, 1H), 7.51-7.41 (m, 4H), 7.35-7.28 (m, 3H), 7.17 (dd, J = 7.3, 1.2 Hz, 1H), 4.79 (dd, J = 14.0 Hz, 1H), 4.74 (dd, J = 14.0 Hz, 1H), 4.39 (dd, J = 9.4, 6.2 Hz, 1H), 3.19 (dd, J = 18.0, 9.5 Hz, 1H), 2.76 (dd, J = 17.9, 6.1 Hz, 1H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 177.6, 175.8, 136.5, 136.2, 135.9, 132.7, 131.5, 130.7, 128.8, 128.5, 128.1, 127.1, 45.9, 42.5, 37.6, 28.7.

3-(2-Acetyl-5-methoxyphenyl)-1-benzylpyrrolidine-2,5-dione (**3ob**):

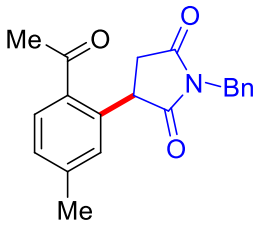


Compound **3ob** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 50 : 50) afforded 43.6 mg of **3ob** in 64 % yield (24 h) as red solid. 47.2 mg of **3ob** in 70 % yield obtained when the reaction was continued for 36 h. The NMR data of **3ob** is in accordance with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.6 Hz, 1H), 7.46-7.44 (m, 2H), 7.34-7.27 (m, 3H), 6.87 (dd, J = 8.7, 2.5 Hz, 1H), 6.63 (d, J = 2.5 Hz, 1H), 4.80 (d, J = 14.2 Hz, 1H), 4.73 (d, J = 14.2 Hz, 1H), 4.38 (m, 1H), 3.77 (s, 3H), 3.16 (dd, J = 18.0, 9.4 Hz, 1H), 2.68 (dd, J = 17.9, 6.1 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 177.5, 175.9, 162.6, 139.4, 136.1, 133.8, 128.8, 128.4, 128.2, 127.7, 117.7, 112.4, 55.3, 44.4, 42.4, 37.4, 28.3.

3-(2-Acetyl-5-methylphenyl)-1-benzylpyrrolidine-2,5-dione (**3pb**):

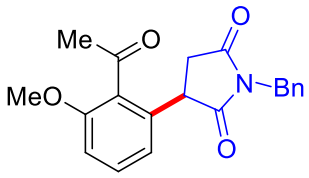


Compound **3pb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 50 : 50) afforded 39.2 mg of **3pb** in 61 % yield as dence colourless liquid. The NMR data of **3pb** is in accordance with the literature.[7]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1H), 7.46-7.44 (m, 2H), 7.34-7.27 (m, 3H), 7.21 (dd, J = 8.0, 1.0 Hz, 1H), 6.92 (bs, 1H), 4.79 (d, J = 14.1 Hz, 1H), 4.73 (d, J = 14.1 Hz, 1H), 4.36 (dd, J = 8.7, 6.2 Hz, 1H), 3.16 (dd, J =18.0, 9.4 Hz, 1H), 2.70 (dd, J = 18.0, 6.0 Hz, 1H), 2.53 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4, 177.8, 175.9, 143.5, 136.8, 136.0, 133.2, 132.3, 131.1, 128.8, 128.6, 128.4, 127.7, 45.9, 42.4, 37.6, 28.5, 21.3.

3-(2-Acetyl-3-methoxyphenyl)-1-benzylpyrrolidine-2,5-dione (**3qb**):



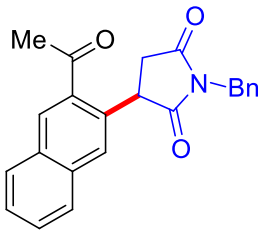
Compound **3qb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 45 : 55) afforded 31.0 mg of **3qb** in 46 % yield as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2H), 7.33-7.28 (m, 4H), 6.89 (d, J = 8.3 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 4.72 (d, J = 14.2 Hz, 1H), 4.70 (d, J = 14.2 Hz, 1H), 4.07 (dd, J = 9.5, 5.5 Hz, 1H), 3.85 (s, 3H), 3.15 (dd, J = 18.4, 9.6 Hz, 1H), 2.83 (dd, J = 18.4, 5.5 Hz, 1H), 2.51 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 205.2, 177.4, 175.6, 157.4, 135.79, 135.74, 131.3, 130.8, 128.7, 128.6, 127.9, 120.4, 110.6, 55.7, 43.9, 42.6, 38.1, 32.4.

HRMS calculated for $C_{28}H_{19}N_2O_2$ is $[M+H]^+$: 338.1392; found: 338.1391.

3-(3-Acetylnaphthalen-2-yl)-1-benzylpyrrolidine-2,5-dione (**3rb**):



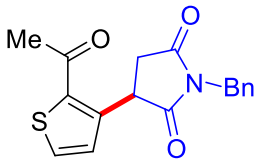
Compound **3rb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 40 : 60) afforded 46.5 mg of **3rb** in 65 % yield as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.63-7.54 (m, 3H), 7.50-7.48 (m, 2H), 7.37-7.29 (m, 3H), 4.83 (d, J = 14.2 Hz, 1H), 4.79 (d, J = 14.2 Hz, 1H), 4.52 (dd, J = 9.9, 6.1 Hz, 1H), 3.21 (dd, J = 18.0, 9.4 Hz, 1H), 2.84 (dd, J = 18.0, 6.0 Hz, 1H), 2.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.7, 178.0, 176.0, 136.0, 134.6, 133.5, 132.9, 132.4, 131.7, 131.2, 129.0, 128.9, 128.6, 128.5, 127.7, 127.3, 127.2, 46.3, 42.5, 37.6, 28.4.

HRMS calculated for $C_{23}H_{20}NO_3$ is $[M+H]^+$: 358.1443; found: 358.1441.

3-(2-Acetylthiophen-3-yl)-1-benzylpyrrolidine-2,5-dione (**3sb**):

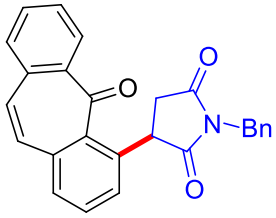


Compound **3sb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 30 : 70) afforded 47.0 mg of **3sb** in 75 % yield as colourless liquid. The NMR data of **3sb** is in accordance with the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 4.9 Hz, 1H), 7.44-7.41 (m, 2H), 7.34-7.27 (m, 3H), 6.93 (d, J = 5.0 Hz, 1H), 4.79 (d, J = 14.2 Hz, 1H), 4.72 (d, J = 14.2 Hz, 1H), 4.67 (dd, J = 9.5, 6.0 Hz, 1H), 3.18 (dd, J = 18.1, 9.6 Hz, 1H), 2.62 (dd, J = 17.9, 6.0 Hz, 1H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 176.7, 175.5, 142.4, 136.2, 135.8, 130.8, 130.6, 128.7, 128.5, 127.7, 42.5, 41.5, 36.4, 28.1.

Compound (3tb):



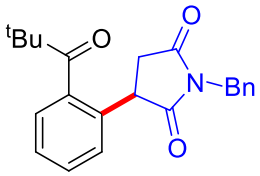
Compound **3tb** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 15 : 85) afforded 72.4 mg of **3tb** in 92 % yield as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.50(m, 4H), 7.48-7.43 (m, 4H), 7.40-7.30 (m, 3H), 7.24-7.19 (m, 1H), 7.05-6.98 (m, 2H), 4.88 (d, J = 14.1 Hz, 1H), 4.81 (d, J = 14.1 Hz, 1H), 4.31 (dd, J = 9.4, 6.1 Hz, 1H), 3.32 (dd, J = 18.2, 9.5 Hz, 1H), 3.03 (dd, J = 18.3, 5.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 196.9, 177.4, 175.8, 140.3, 136.9, 136.7, 135.9, 135.2, 133.4, 131.38, 131.33, 130.8, 130.7, 130.2, 129.1, 128.8, 128.5, 127.8, 46.0, 42.6, 38.7.

HRMS calculated for $C_{26}H_{20}NO_3$ is $[M+H]^+$: 394.1443; found: 394.1446.

1-Benzyl-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (**3ab**):



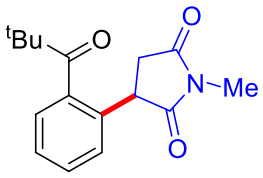
Compound **3ab** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 8 : 92) afforded 67.0 mg of **3ab** in 96 % yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, J = 8.8, 1.2 Hz, 1H), 7.43-7.41 (m, 2H), 7.36-7.28 (m, 5H), 7.02 (dd, J = 7.8, 0.9 Hz, 1H), 4.71 (d, J = 14.1 Hz, 1H), 4.71 (d, J = 14.1 Hz, 1H), 3.92 (dd, J = 9.5, 5.4 Hz, 1H), 3.15 (dd, J = 18.4, 9.6 Hz, 1H), 2.76 (dd, J = 18.4, 5.4 Hz, 1H), 1.30 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.2, 177.4, 175.4, 139.8, 135.7, 135.5 (overlapped), 130.2, 128.7, 128.5, 127.8, 126.7, 126.0, 44.7, 44.3, 42.5, 38.7, 27.7.

HRMS calculated for $C_{22}H_{23}NNaO_3$ is $[M+Na]^+$: 372.1576; found: 372.1573.

1-Methyl-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (3ac):



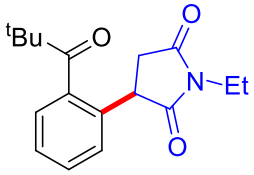
Compound **3ac** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 44.1 mg of **3ac** in 81 % yield as red solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46, (d, J = 7.7 Hz, 1H), 7.36 (td, J = 7.6, 1.3 Hz, 1H), 7.29 (td, J = 7.6, 1.2 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 3.92 (dd, J = 9.5, 5.6 Hz, 1H), 3.12 (dd, J = 18.3, 9.6 Hz, 1H), 3.02 (s, 3H), 2.77 (dd, J = 18.3, 5.6 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.3, 177.9, 175.9, 139.6, 135.4, 130.2, 129.2, 126.7, 126.1, 44.6 (overlapped with quaternary carbon of -CMe_3), 38.5, 27.8, 24.9.

HRMS calculated for $C_{16}H_{20}NO_3$ is $[M+H]^+$: 274.1443; found: 274.1443.

1-Ethyl-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (**3ad**):



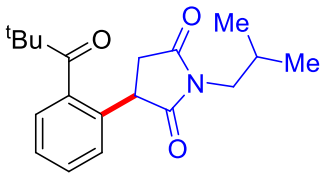
Compound **3ad** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 18 : 82) afforded 47.1 mg of **3ad** in 82 % yield as red solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46, (d, J = 7.7, 1.1 Hz, 1H), 7.38 (td, J = 7.6, 1.3 Hz, 1H), 7.30 (td, J = 7.6, 1.1 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 3.90 (dd, J = 9.5, 5.5 Hz, 1H), 3.66-3.56 (m, 2H), 3.12 (dd, J = 18.3, 9.5 Hz, 1H), 2.74 (dd, J = 18.3, 5.5 Hz, 1H), 1.31 (s, 9H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.2, 177.6, 175.7, 139.7, 135.6, 130.3, 128.8, 126.7, 126.1, 44.7, 44.4, 38.6, 33.9, 27.9, 13.0.

HRMS calculated for $C_{17}H_{22}NO_3$ is $[M+H]^+$: 288.1600; found: 288.1601.

1-Isobutyl-3-(2-pivaloylphenyl) pyrrolidine-2,5-dione (**3ae**):



Compound **3ae** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 13 : 87) afforded 61.2 mg of **3ae** in 97 % yield as colourless liquid.

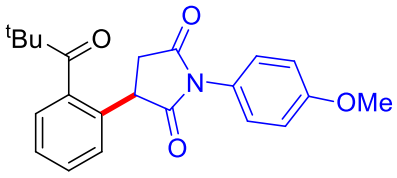
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, J = 7.7 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 7.8 Hz, 1H), 3.92 (dd, J = 9.6, 5.6 Hz, 1H), 3.41-3.33 (m, 2H), 3.14 (dd, J = 18.4,

9.6 Hz, 1H), 2.75 (dd, *J* = 18.4, 5.6 Hz, 1H), 2.07 (sep, *J* = 6.9 Hz, 1H), 1.30 (s, 9H), 0.91 (dd, *J* = 6.7, 2.2 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 213.3, 177.9, 176.0, 140.0, 135.5, 130.2, 128.5, 126.6, 126.0, 46.2, 44.7, 44.1, 38.5, 27.8, 27.0, 20.1, 20.0.

HRMS calculated for $C_{19}H_{26}NO_3$ is $[M+H]^+$: 316.1913; found: 316.1910.

1-(4-Methoxyphenyl)-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (**3af**):



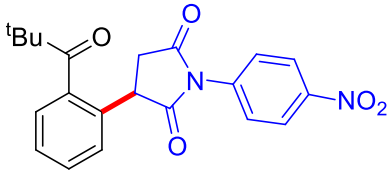
Compound **3af** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 15 : 85) afforded 64.9 mg of **3af** in 95 % yield as red solid.

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.57 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.34 (td, *J* = 7.6, 1.1 Hz, 1H), 7.29-7.26 (m, 3H), 7.00-6.97 (m, 2H), 4.13 (dd, *J* = 9.7, 5.9 Hz, 1H), 3.82 (s, 3H), 3.28 (dd, *J* = 18.3, 9.7 Hz, 1H), 2.99 (dd, *J* = 18.3, 5.9 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 213.3, 177.1, 175.2, 159.5, 139.1, 135.7, 130.4, 129.9, 127.9, 126.8, 126.6, 124.7, 114.4, 55.4, 45.0, 44.7, 38.6, 28.1.

HRMS calculated for $C_{22}H_{23}NNaO_4$ is $[M+Na]^+$: 388.1525; found: 388.1529.

1-(4-Nitrophenyl)-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (**3ag**):



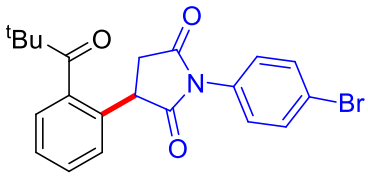
Compound **3ag** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 67.7 mg of **3ag** in 89 % yield as red solid.

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.34-8.31 (m, 2H), 7.68-7.65 (m, 3H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 4.20 (dd, *J* = 9.8, 6.2 Hz, 1H), 3.33 (dd, *J* = 18.4, 9.8 Hz, 1H), 3.05 (dd, *J* = 18.4, 6.2 Hz, 1H), 1.28 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): *δ* 213.2, 176.2, 174.1, 147.0, 138.2, 137.7, 135.3, 134.5, 131.0, 130.8, 127.3, 127.2, 124.2, 44.7, 44.6, 38.5, 28.2.

HRMS calculated for $C_{21}H_{20}N_2NaO_5$ is $[M+Na]^+$: 403.1270; found: 403.1270.

1-(4-Bromophenyl)-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (3ah):



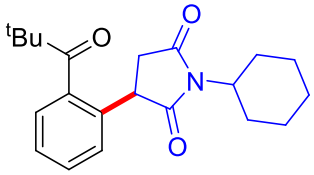
Compound **3ah** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc: hexane = 7 : 93) afforded 77.9 mg of **3ah** in 94 % yield as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62-7.59 (m, 3H), 7.47-7.43 (m, 1H), 7.38-7.35 (m, 1H), 7.29-7.27 (m, 3H), 4.15 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.29 (dd, *J* = 18.3, 9.7 Hz, 1H), 3.02 (dd, *J* = 18.3, 6.1 Hz, 1H), 1.29 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.3, 176.7, 174.6, 138.6, 135.4, 132.2, 131.0, 130.6, 130.5, 128.3, 127.08, 127.00, 122.5, 44.4, 44.6, 38.6, 28.1.

HRMS calculated for $C_{21}H_{20}BrNNaO_3$ is $[M+Na]^+$: 436.0524; found: 436.0522.

1-Cyclohexyl-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (3ai):



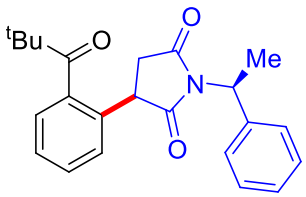
Compound **3ai** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 13 : 87) afforded 68.3 mg of **3ai** in 97 % yield as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 (td, *J* = 7.6, 1.1 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 4.01 (tt, *J* = 12.4, 3.8 Hz, 1H), 3.83 (dd, *J* = 9.6, 5.5 Hz, 1H), 3.07 (dd, *J* = 18.3, 9.6 Hz, 1H), 2.67 (dd, *J* = 18.3, 5.5 Hz, 1H), 2.17 (qd, *J* = 18.3, 3.5 Hz, 2H), 1.84-1.81 (m, *J* = 2.0 Hz, 2H), 1.68-1.63 (m, 3H), 1.33-1.31 (m, 10H), 1.27-1.18 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 213.2, 177.8, 176.0, 139.9, 135.9, 130.2, 128.3, 126.6, 126.0, 52.0, 44.7, 43.9, 38.5, 28.8, 28.7, 27.8, 25.8 (overlapped), 25.0.

HRMS calculated for $C_{21}H_{28}NO_3$ is $[M+H]^+$: 342.2069; found: 342.2065.

1-((S)-1-Phenylethyl)-3-(2-pivaloylphenyl)pyrrolidine-2,5-dione (3aj):

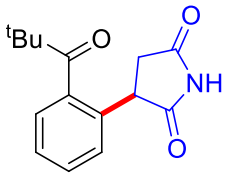


Compound **3aj** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 17 : 83) afforded 50.9 mg of **3aj** in 70 % yield (d.r. = 1.2:1.0) as colourless liquid.

Major Diastereomer: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50-7.43 (m, 3H), 7.38-7.28 (m, 5H), 7.02 (d, J =7.8 Hz, 1H), 5.52-5.48 (q, J =7.4 Hz, 1H), 3.83-3.81 (m, 1H), 3.09-3.04 (m, 1H), 2.67 (dd, J = 18.4, 5.4 Hz, 1H), 1.87 (d, J = 7.3 Hz, 3H), 1.31 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 213.22, 177.56, 175.64, 139.65, 139.53, 135.89, 130.29, 128.18, 128.39 (overlapped with minor), 127.75 (overlapped with minor), 127.52, 126.69, 126.01, 50.54, 44.81, 43.99, 38.64, 27.84, 16.60.

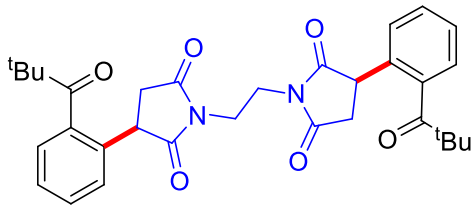
Minor Diastereomer: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50-7.43 (m, 3H), 7.38-7.28 (m, 5H), 6.96 (d, J =7.7 Hz, 1H), 5.49-5.45 (q, J = 7.4 Hz, 1H), 3.86-3.84 (m, 1H), 3.14-3.10 (m, 1H), 2.71 (dd, J = 18.4, 5.4 Hz, 1H), 1.89 (dd, J = 7.3 Hz, 3H), 1.31 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 213.25, 177.62, 175.67, 139.98, 139.73, 135.78, 130.27, 128.6, 128.39, 127.75, 127.55, 126.67, 126.08, 50.60, 44.76, 44.19, 38.65, 27.85, 16.53.
HRMS calculated for $C_{23}H_{26}NO_3$ is $[M+H]^+$: 364.1913; found: 364.1904.

3-(2-Pivaloylphenyl)pyrrolidine-2,5-dione (**3ak**):



Compound **3ak** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 20 : 80) afforded 32.1 mg of **3ak** in 62 % yield as colourless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (bs, 1H), 7.47 (dd, J = 7.4, 0.9 Hz, 1H), 7.41 (td, J = 7.7, 1.4 Hz, 1H), 7.32 (td, J = 7.6, 1.0 Hz, 1H), 7.23-7.21 (m, 1H), 4.00 (dd, J = 9.6, 5.8 Hz, 1H), 3.19 (dd, J = 18.5, 9.7 Hz, 1H), 2.83 (dd, J = 18.5, 5.8 Hz, 1H), 1.31 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 213.4, 178.3, 176.3, 139.7, 135.0, 130.3, 129.0, 126.9, 126.1, 45.8, 44.8, 39.8, 27.8.
HRMS calculated for $C_{15}H_{18}NO_3$ is $[M+H]^+$: 260.1287; found: 260.1284.

Catalytic Procedure for the synthesis of 1,1'-(ethane-1,2-diyl)bis(3-(2-pivaloylphenyl)pyrrolidine-2,5-dione) (3al):



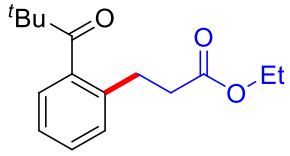
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mol %), NaOAc (1.6 mg, 0.02 mmol, 10 mol %) under argon atmosphere. Small amount of 1,2-DCE (0.2 mL) was added to the Schlenk tube and stirred for few minutes. 2,2-Dimethyl-1-phenylpropan-1-one **1a** (0.42 mmol, 2.1 equiv.), 1,1'-(ethane-1,2-diyl)bis(1*H*-pyrrole-2,5-dione) **2l** (37.4 mg, 0.2 mmol, 1.0 equiv.) followed by 0.8 mL 1,2-DCE were successively added to the Schlenk. The closed tube was placed to a pre-heated oil bath at 120 °C for 30 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude reaction mixture was purified by flash column chromatography (EtOAc : hexane = 30 : 70) afforded 70.9 mg of **3al** in 65 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 4H), 7.29-7.22 (m, 4H), 3.86-3.73 (m, 6H), 3.11-3.03 (m, 2H), 2.73-2.66 (m, 2H), 1.26 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.56, 213.54, 178.15, 178.12, 176.21 (overlapped), 140.1, 140.0, 134.76 (overlapped), 130.2 (overlapped), 129.18 (overlapped), 126.71 (overlapped), 125.79, 125.71, 44.7 (overlapped), 44.3, 44.2, 38.5 (overlapped), 37.5, 37.4, 27.79, 27.71.

HRMS calculated for $C_{32}H_{40}N_3O_6$ is $[M+NH_4]^+$: 562.2917; found: 562.2919.

Ethyl 3-(2-pivaloylphenyl)propanoate (3am):



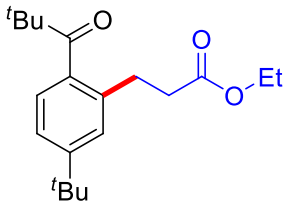
Compound **3am** was prepared according to the general procedure **G** and the was purified by flash column chromatography (EtOAc : hexane = 2 : 98) afforded 20.1 mg of **3am** in 38 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 1H), 7.26-7.16 (m, 2H), 4.12 (q, J = 7.2 Hz, 2H), 2.80-2.76 (m, 2H), 2.62-2.58 (m, 2H), 1.26 (s, 9H), 1.23 (t, J = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 214.5, 172.7, 140.6, 136.9, 129.5, 128.9, 125.4, 124.8, 60.4, 44.9, 35.9, 28.9, 27.4, 14.1.

LCMS calculated for $C_{16}H_{23}O_3$ is [M+H]: 263.1647; found: 263.2.

Ethyl 3-(5-*tert*-butyl-2-pivaloylphenyl)propanoate (**3an**):



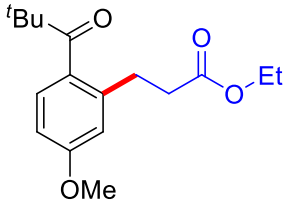
Compound **3an** was prepared according to the general procedure **G** and was purified by flash column chromatography (EtOAc : hexane = 2 : 98) afforded 18 mg of **3an** in 27 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 1.6 Hz, 1H), 7.20 (dd, J = 8.1, 1.8 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 2.81-2.77 (m, 2H), 2.63-2.59 (m, 2H), 1.30 (s, 9H), 1.26 (s, 9H), 1.24 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 214.6, 172.9, 152.0, 137.7, 136.9, 126.6, 124.8, 122.3, 60.3, 44.9, 36.3, 34.6, 31.1, 29.3, 27.5, 14.2.

LCMS calculated for $C_{20}H_{31}O_3$ is [M+H]: 319.2273; found: 319.2.

Ethyl 3-(5-methoxy-2-pivaloylphenyl)propanoate (**3ao**):



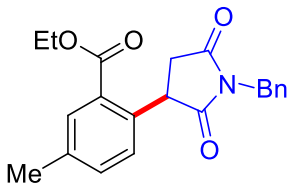
Compound **3ao** was prepared according to the general procedure **E** and was purified by flash column chromatography (EtOAc : hexane = 3 : 97) afforded 17.9 mg of **3ao** in 31 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.5 Hz, 1H), 6.78 (d, J = 2.5 Hz, 1H), 6.72 (dd, J = 8.5, 2.5 Hz, 1H), 4.12 (q, J = 7.2 Hz, 1H), 3.80 (s, 3H), 2.80-2.76 (m, 2H), 2.63-2.59 (m, 2H), 1.25 (s, 9H), 1.23 (t, J = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.6, 172.8, 159.8, 139.9, 132.9, 126.7, 115.2, 110.6, 60.4, 55.2, 44.9, 36.0, 29.1, 27.7, 14.1.

LCMS calculated for $C_{17}H_{25}O_4$ is [M+H]: 293.1753; found: 293.2.

Ethyl 2-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-5-methylbenzoate (**5ab**):



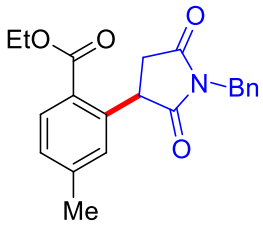
Compound **5ab** was prepared according to the general procedure **F** and was purified by flash column chromatography (EtOAc : hexane = 10 : 90) afforded 31.0 mg of **5ab** in 44 % yield as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 1.1 Hz, 1H), 7.45 (dd, J = 8.0, 1.2 Hz, 2H), 7.34-7.27 (m, 4H), 7.02 (d, J = 7.9 Hz, 1H), 4.75 (d, J = 14.1 Hz, 1H), 4.74 (d, J = 14.1 Hz, 1H), 4.54 (dd, J = 9.3, 6.2 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.19 (dd, J = 18.1, 9.5 Hz, 1H), 2.75 (dd, J = 17.9, 6.1 Hz, 1H), 2.37 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 176.0, 166.9, 138.1, 136.1, 135.4, 133.6, 132.1, 130.8, 129.0, 128.8, 128.6, 127.8, 61.3, 45.5, 42.6, 37.9, 21.0, 14.3.

HRMS calculated for $C_{21}H_{22}NO_4$ is $[M+H]^+$: 352.1549; found: 352.1542.

Ethyl 2-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-4-methylbenzoate (**5bb**):



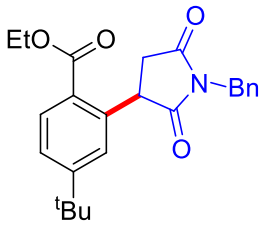
Compound **5bb** was prepared according to the general procedure **F** and was purified by flash column chromatography (EtOAc : hexane = 10 : 90) afforded 43.0 mg of **5bb** in 61 % yield as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J = 8.0 Hz, 1H), 7.47-7.46 (m, 2H), 7.34-7.27 (m, 3H), 7.16 (dd, J = 7.8, 0.9 Hz, 1H), 6.88 (bs, 1H), 4.77 (d, J = 14.1 Hz, 1H), 4.74 (d, J = 14.1 Hz, 1H), 4.61-4.58 (m, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.20 (dd, J = 18.1, 9.5 Hz, 1H), 2.74 (dd, J = 18.1, 5.9 Hz, 1H), 2.32 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.9, 176.0, 166.6, 143.5, 138.5, 136.0, 131.6, 131.4, 128.9, 128.6, 128.5, 127.7, 126.0, 61.0, 45.5, 42.5, 37.8, 21.3, 14.1.

HRMS calculated for $C_{21}H_{22}NO_4$ is $[M+H]^+$: 352.1549; found: 352.1549.

Ethyl 2-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-4-*tert*-butylbenzoate (5cb):



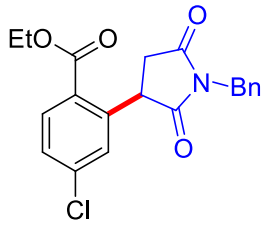
Compound **5cb** was prepared according to the general procedure **F** and was purified by flash column chromatography (EtOAc : hexane = 3 : 97) afforded 44.0 mg of **5cb** in 56 % yield as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.3 Hz, 1H), 7.48-7.46 (m, 2H), 7.38 (dd, J = 8.3, 2.0 Hz, 1H), 7.34 -7.27 (m, 3H), 7.08 (d, J = 1.9 Hz, 1H), 4.78 (d, J = 14.1 Hz, 1H), 4.75 (d, J = 14.1 Hz, 1H), 4.58 (dd, J = 8.8, 5.9 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.21 (dd, J = 18.1, 6.0 Hz, 1H), 2.78 (dd, J = 18.1, 6.0 Hz, 1H), 1.32 (t, J = 7.2 Hz, 3H), 1.25 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 176.1, 166.6, 156.5, 138.2, 136.1, 131.4, 129.1, 128.9, 128.5, 127.7, 125.8, 125.1, 61.0, 46.1, 42.5, 37.9, 34.9, 30.9, 14.2.

HRMS calculated for $C_{24}H_{28}NO_4$ is $[M+H]^+$: 394.2018; found: 394.2016.

Ethyl 2-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-4-chlorobenzoate (**5db**):



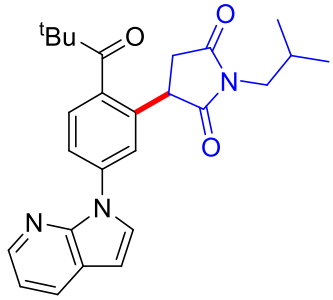
Compound **5db** was prepared according to the general procedure **F** and was purified by flash column chromatography (EtOAc : hexane = 8 : 92) afforded 26.0 mg of **5db** in 35 % yield as colourless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, J = 8.5 Hz, 1H), 7.45-7.43 (m, 2H), 7.36-7.28 (m, 4H), 7.12 (d, J = 2.0 Hz, 1H), 4.76 (d, J = 14.1 Hz, 1H), 4.72 (d, J = 14.1 Hz, 1H), 4.54 (dd, J = 9.3, 6.3 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.19 (dd, J = 18.1, 9.6 Hz, 1H), 2.75 (dd, J = 18.1, 6.1 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 175.5, 165.8, 140.2, 138.9, 135.8, 132.9, 131.0, 128.9, 128.5, 128.2, 127.9, 127.3, 61.5, 45.5, 42.7, 37.5, 14.1.

HRMS calculated for $C_{20}H_{19}NO_4$ is $[M+H]^+$: 372.1003; found: 372.1000.

1-Isobutyl-3-(2-pivaloyl-5-(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)phenyl)pyrrolidine-2,5-dione (3ue):



Compound **3ue** was prepared according to the general procedure **E** and the reaction was continued for 36 h. The crude reaction mixture was purified by flash column chromatography (EtOAc : hexane = 25 : 75) afforded 45.7 mg of **3ue** in 53 % yield as colourless liquid.

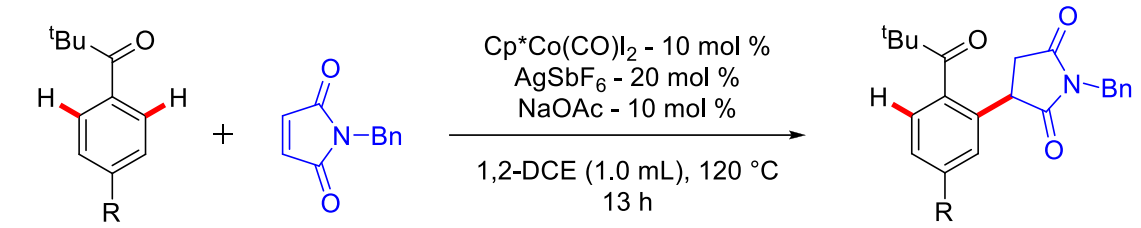
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, J = 4.7, 1.5 Hz, 1H), 7.96 (dd, J = 7.8, 1.5 Hz, 1H), 7.80 (dd, J = 8.4, 2.1 Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.51(d, J = 3.7 Hz, 1H), 7.15 (dd, J = 7.8 , 4.7 Hz, 1H), 6.65 (d, J = 3.7 Hz, 1H), 4.09 (dd, J = 9.5, 5.8 Hz, 1H), 3.44-3.36 (m, 2H), 3.22 (dd, J = 18.3, 9.6 Hz, 1H), 2.93 (dd, J = 18.3, 5.8 Hz, 1H), 2.14-2.06 (m, 1H), 1.36 (s, 9H), 0.93 (d, J = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 212.3, 177.8, 176.0, 147.4, 143.7, 140.0, 137.4, 136.7, 129.2, 127.6, 126.7, 123.7, 121.8, 120.9, 117.2, 102.8, 44.3, 44.8, 44.6, 38.4, 28.0, 27.0, 20.1, 20.0.

HRMS calculated for $C_{26}H_{30}N_3O_3$ is $[M+H]^+$: 432.2287; found: 432.2282.

3. Control Experiments:

3.1. Competitive experiment with *p*-substituted ketone:

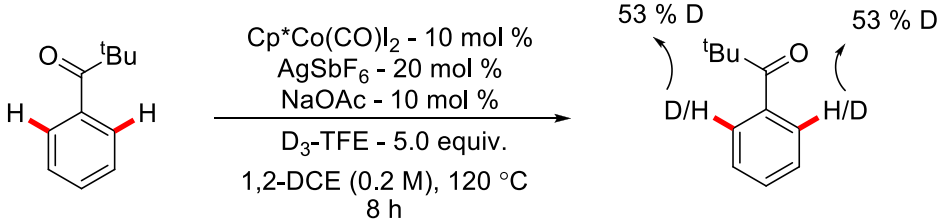


R = ^{t}Bu/Cl (**1c**/**1e**) **2b** **3cb**:**3eb** = 1.78:1.00 R = ^{t}Bu/Cl (**3cb**/**3eb**)

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (4.5 mg, 0.01 mmol, 10 mol %), $AgSbF_6$ (7.0 mg, 0.02 mmol, 20 mol %), NaOAc (0.8 mg, 0.01 mmol, 10 mol %) under argon atmosphere. Small amount of 1,2-DCE (0.2 mL) was added to the Schlenk tube and stirred for few minutes. 1-(4-*tert*-butylphenyl)-2,2-dimethylpropan-1-one **1c** (21.8 mg, 0.1 mmol, 1.0 equiv.), 1-(4-chlorophenyl)-2,2-dimethylpropan-1-one **1e** (19.6 mg, 0.1 mmol, 1.0 equiv) and 1-benzyl-1*H*-pyrrole-2,5-dione **2b** (28.0 mg, 0.15 mmol, 1.5 equiv.) followed by 0.8 mL 1,2-DCE were successively added to the Schlenk tube. The closed tube was placed to a pre-heated oil bath at 120 °C for 13 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude mixture was purified by flash column chromatography (10/90; EtOAc/Hexane) on silica gel afforded mixture of **3cb** and **3eb**. The ratio of **3cb** and **3eb** (**3cb**:**3eb** = 1.78:1.00) was calculated from **^{1}H NMR** analysis.

3.2. H/D exchange experiments:

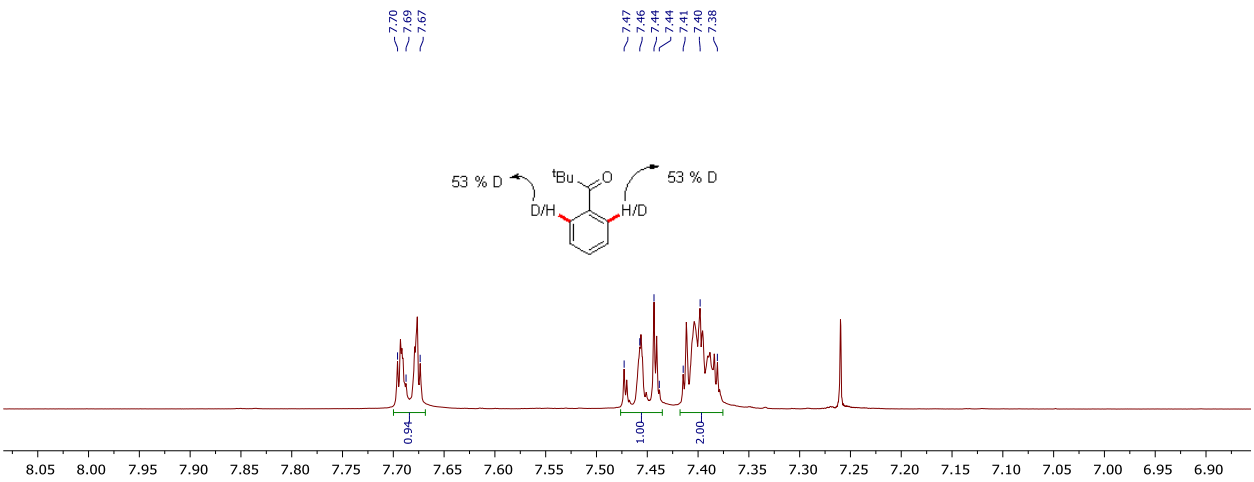
3.2.1. H/D exchange with ketone:



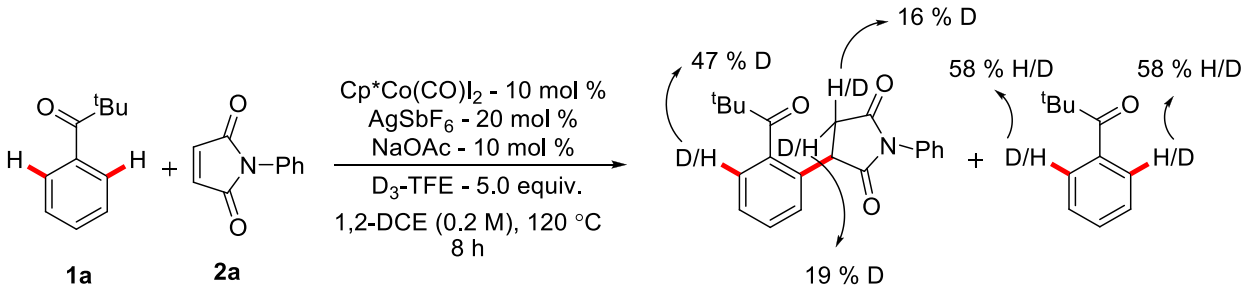
1a

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mol %), NaOAc (1.6 mg, 0.02 mmol, 10 mol %) under argon atmosphere. Small amount of 1,2-DCE (0.2 mL) was added to

the Schlenk tube and stirred for few minutes. 2,2-Dimethyl-1-phenylpropan-1-one **1a** (32.4 mg, 0.2 mmol, 1.0 equiv.) and D_3-TFE (0.073 mL, 1.0 mmol, 5.0 equiv.) followed by 0.8 mL 1,2-DCE were successively added to the Schlenk tube. The closed Schlenk tube was placed to a pre-heated oil bath at 120 °C for 8 h. After that, the reaction mixture was then allowed to cool down to room temperature. Then the reaction mixture was passed through a short pad of silica gel (eluent 5 % EtOAc/Hexane). The ^{1}H NMR of the isolated product shows deuterium incorporation of about 53 % in ortho position with respect to carbonyl of **1a**.

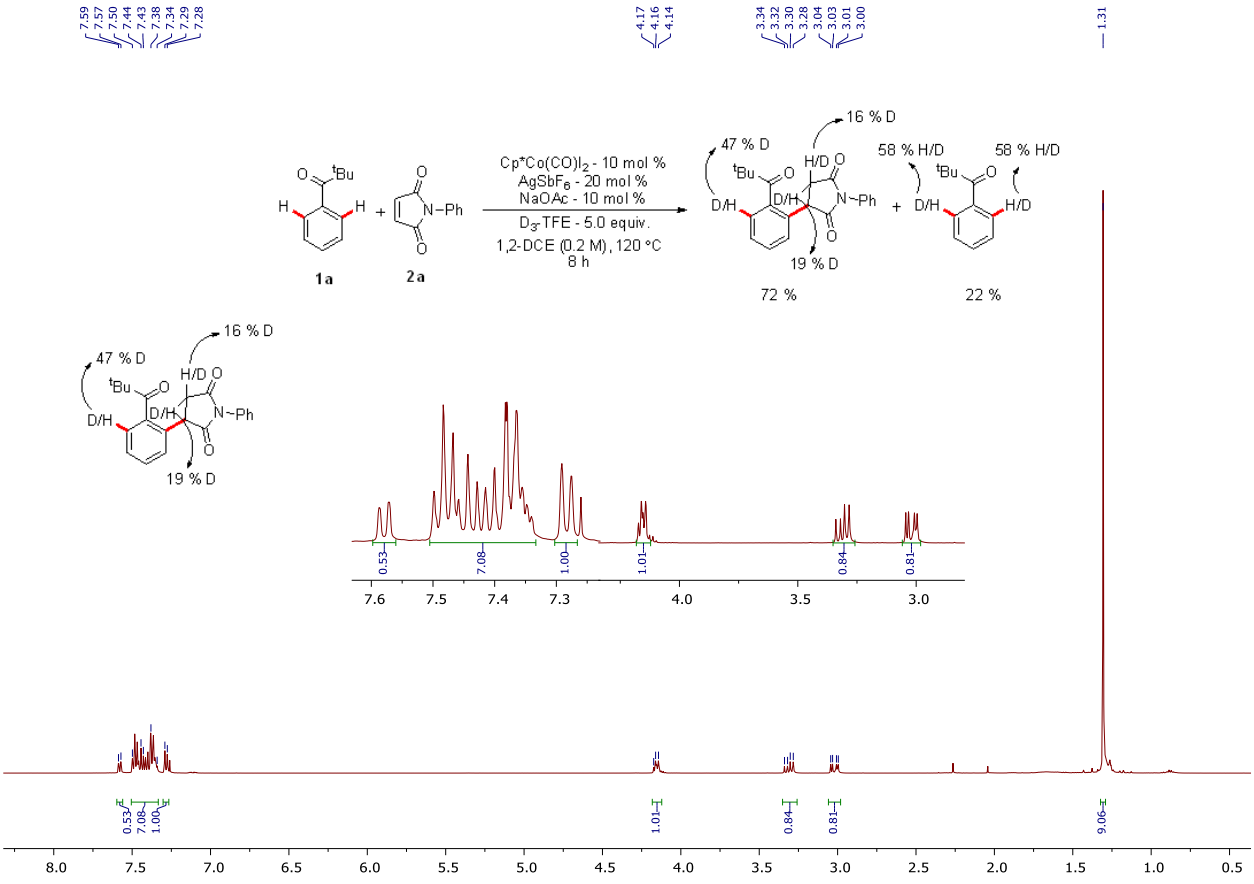


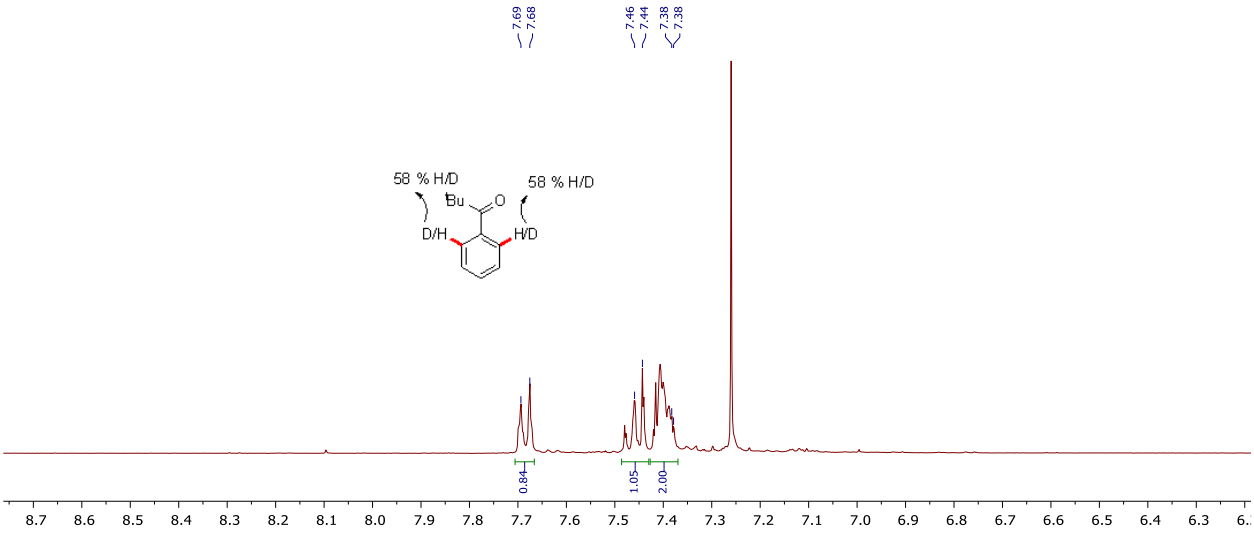
3.2.2. H/D exchange in the the product as well as with ketone (1a):



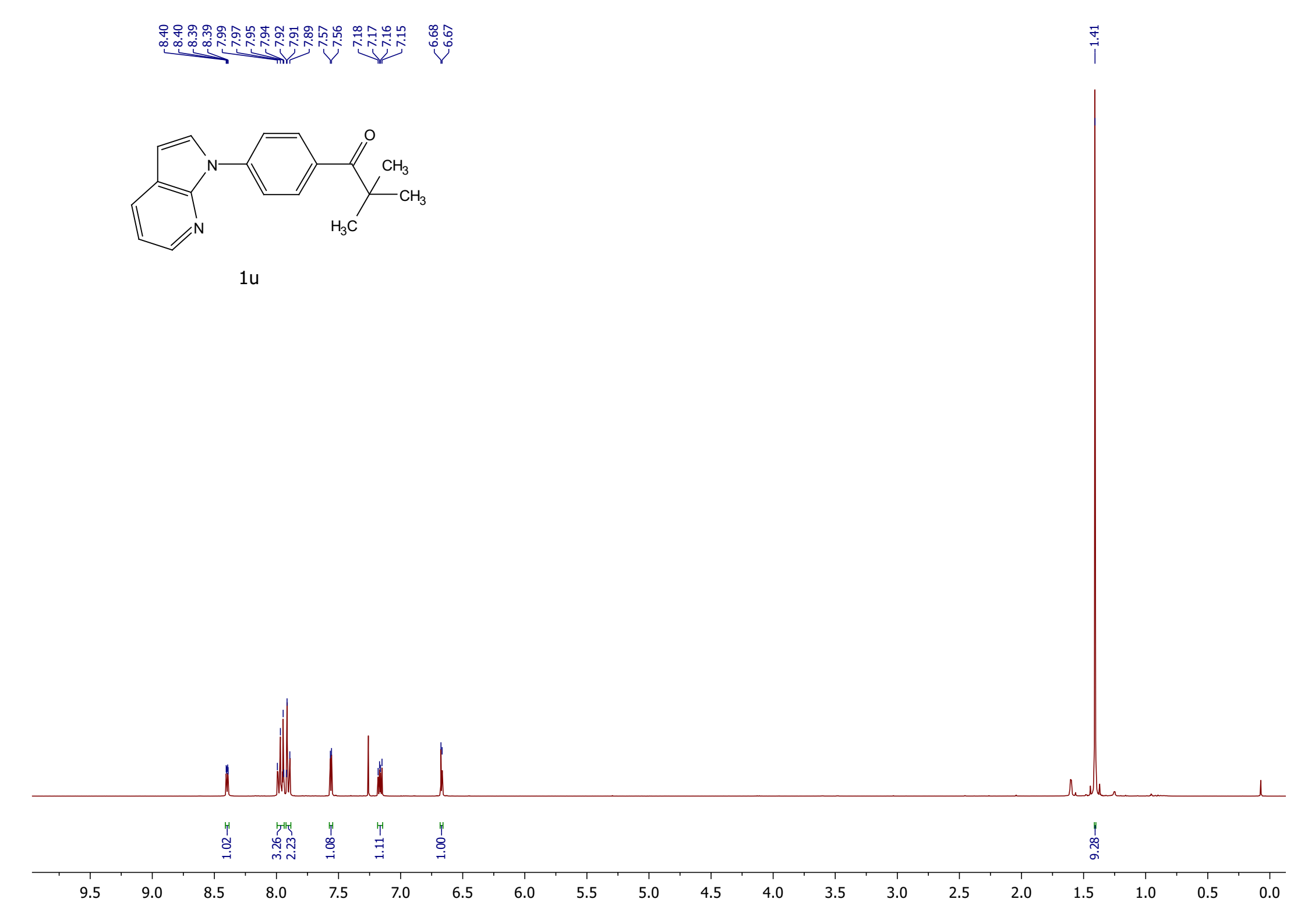
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), $AgSbF_6$ (14.0 mg, 0.04 mmol, 20 mol %), NaOAc (16.0 mg, 0.02 mmol, 10 mol %) under argon atmosphere. Small amount of 1,2-DCE (0.2 mL) was added to the Schlenk tube and stirred for few minutes. 2,2-Dimethyl-1-phenylpropan-1-one **1a** (32.4 mg, 0.2 mmol, 1.0 equiv.), 1-phenyl-1*H*-pyrrole-2,5-dione **2a** (51.9 mg, 0.3 mmol,

1.5 equiv.) and D_3-TFE (0.073 mL, 1.0 mmol, 5.0 equiv.) followed by 0.8 mL 1,2-DCE were successively added to the Schlenk. The closed tube was placed to a pre-heated oil bath at 120 °C for 8 h. After completion of the reaction, the reaction mixture was then allowed to cool down to room temperature. The crude mixture was purified by flash column chromatography (10/90; EtOAc/Hexane) on silica gel afforded 48.6 mg (72 % yield) of **3aa** and 7.2 mg (22 % yield) of **1a**.





The ^{1}H NMR of the isolated product **3aa** shows deuterium incorporation of about 47 % in ortho position with respect to ketone and 19 %, 16 % D incorporation occours to the methylene carbon of succinimide. Also 58 % D incorporation observed in the ortho position with respect to carbonyl of **1a.**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N
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CH3
H3C
1u
1.02
3.26
2.23
1.08
1.11
1.00
9.28
9.5
9.0
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8.0
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7.0
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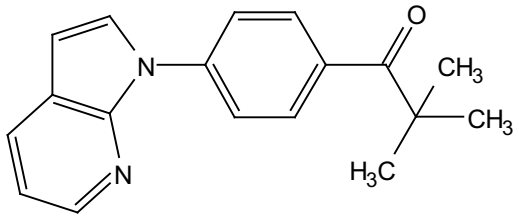

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121.95
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102.68
44.16
28.14

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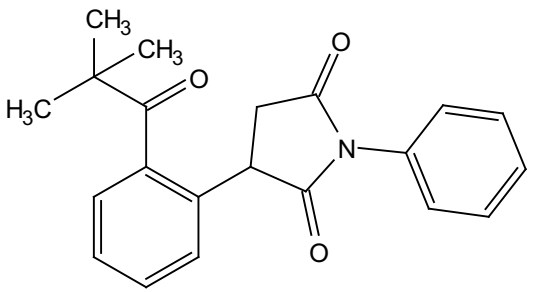
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N
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3aa

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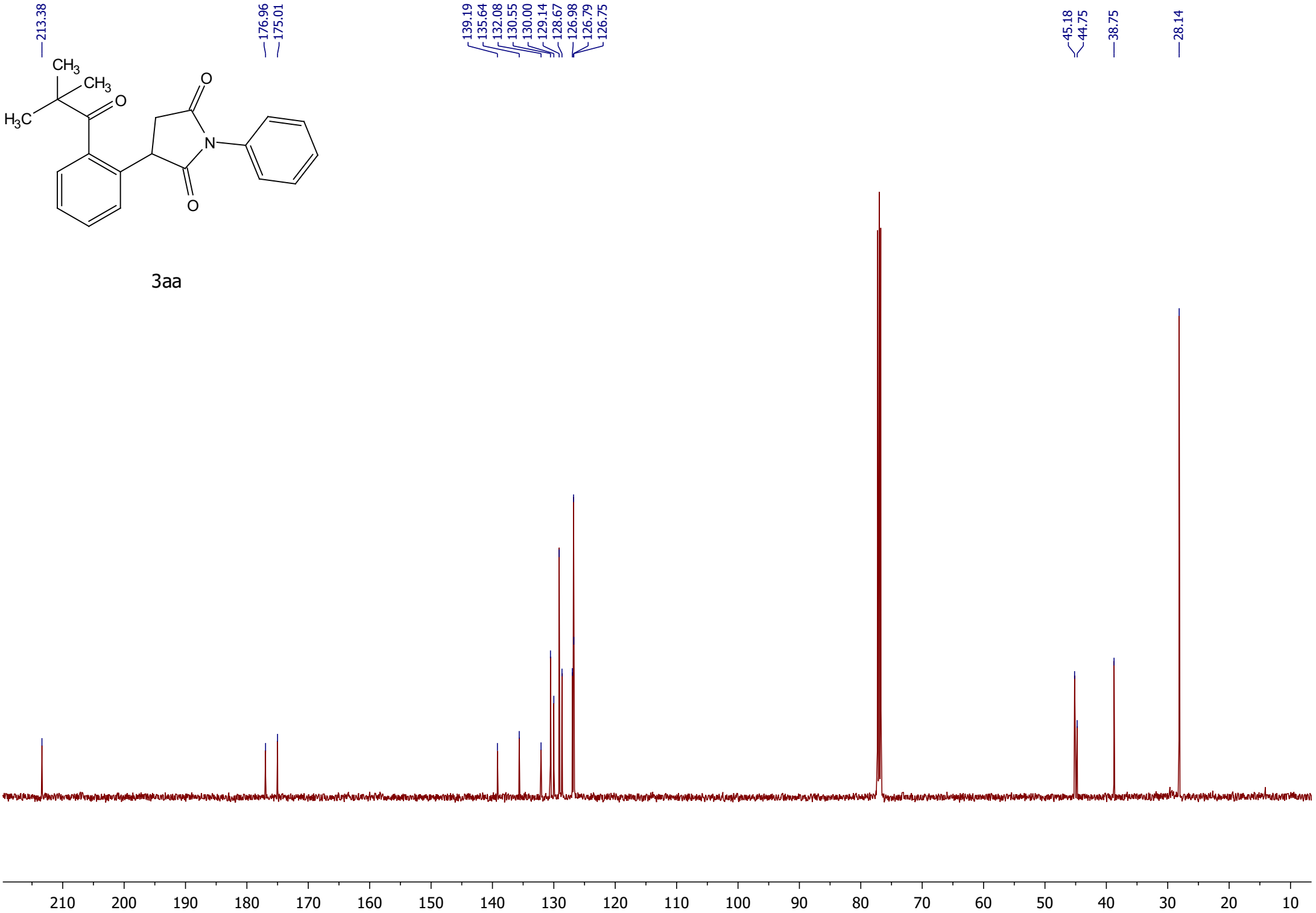
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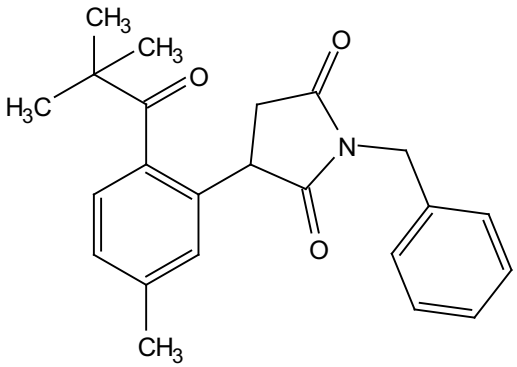
10

3aa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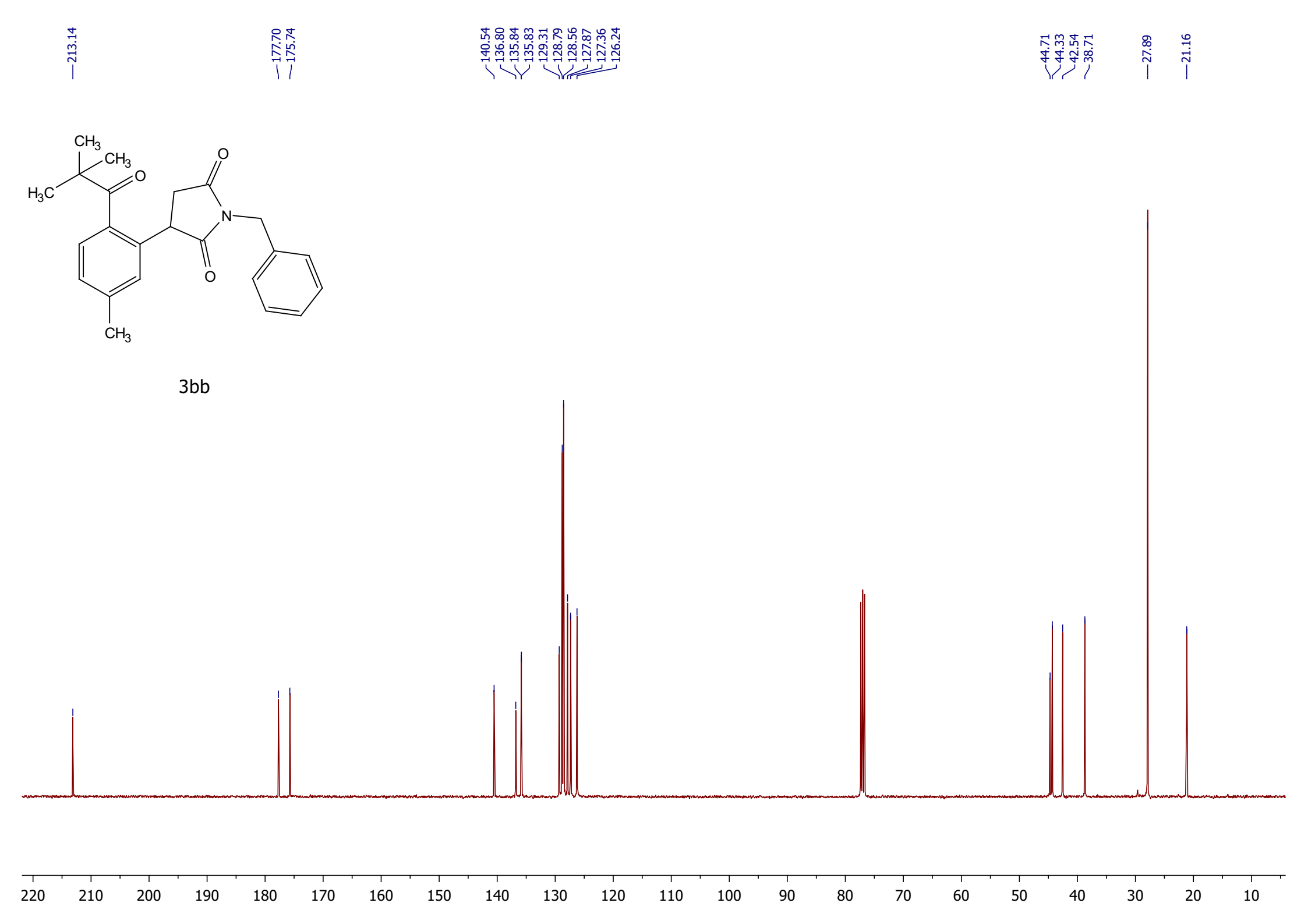
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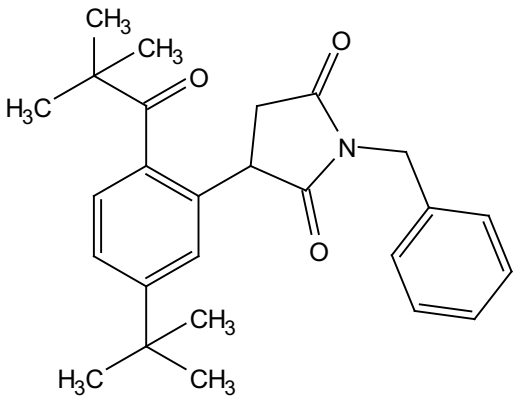
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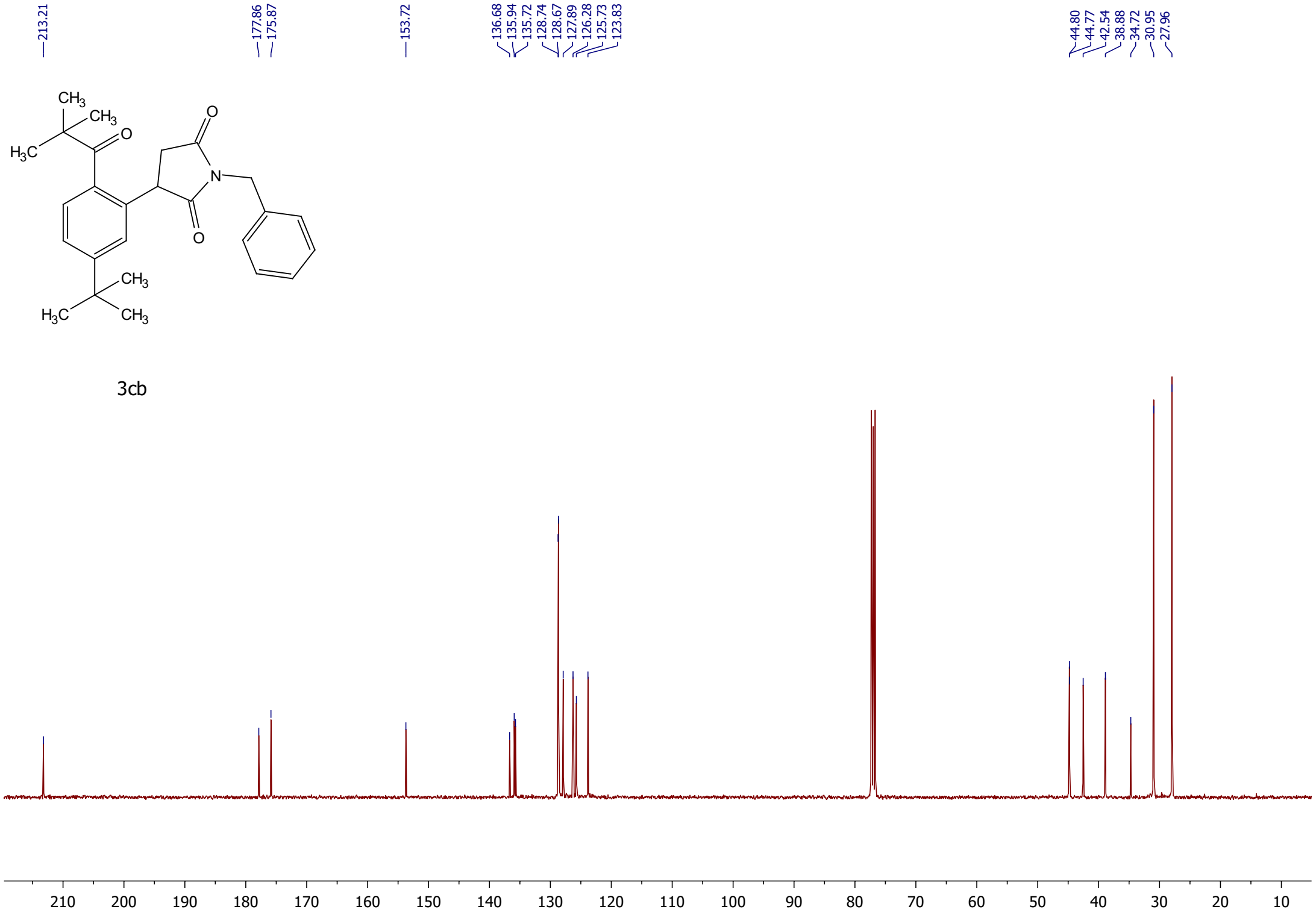
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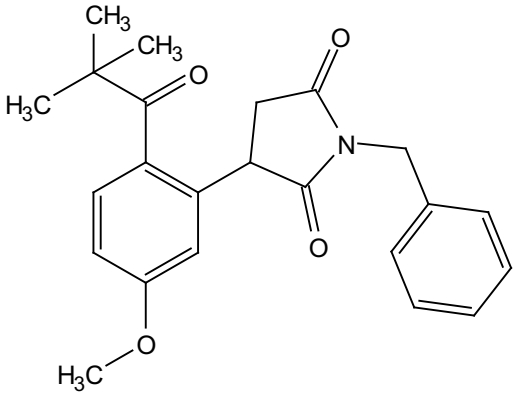
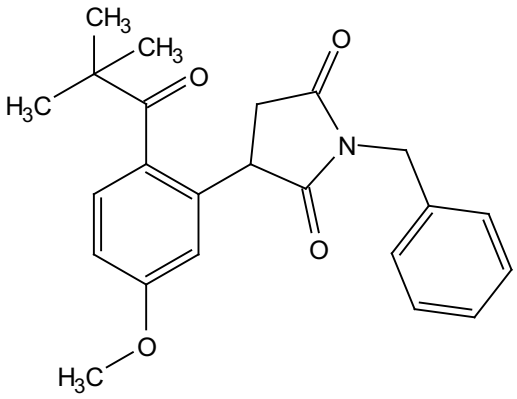


3db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H3C

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111.80
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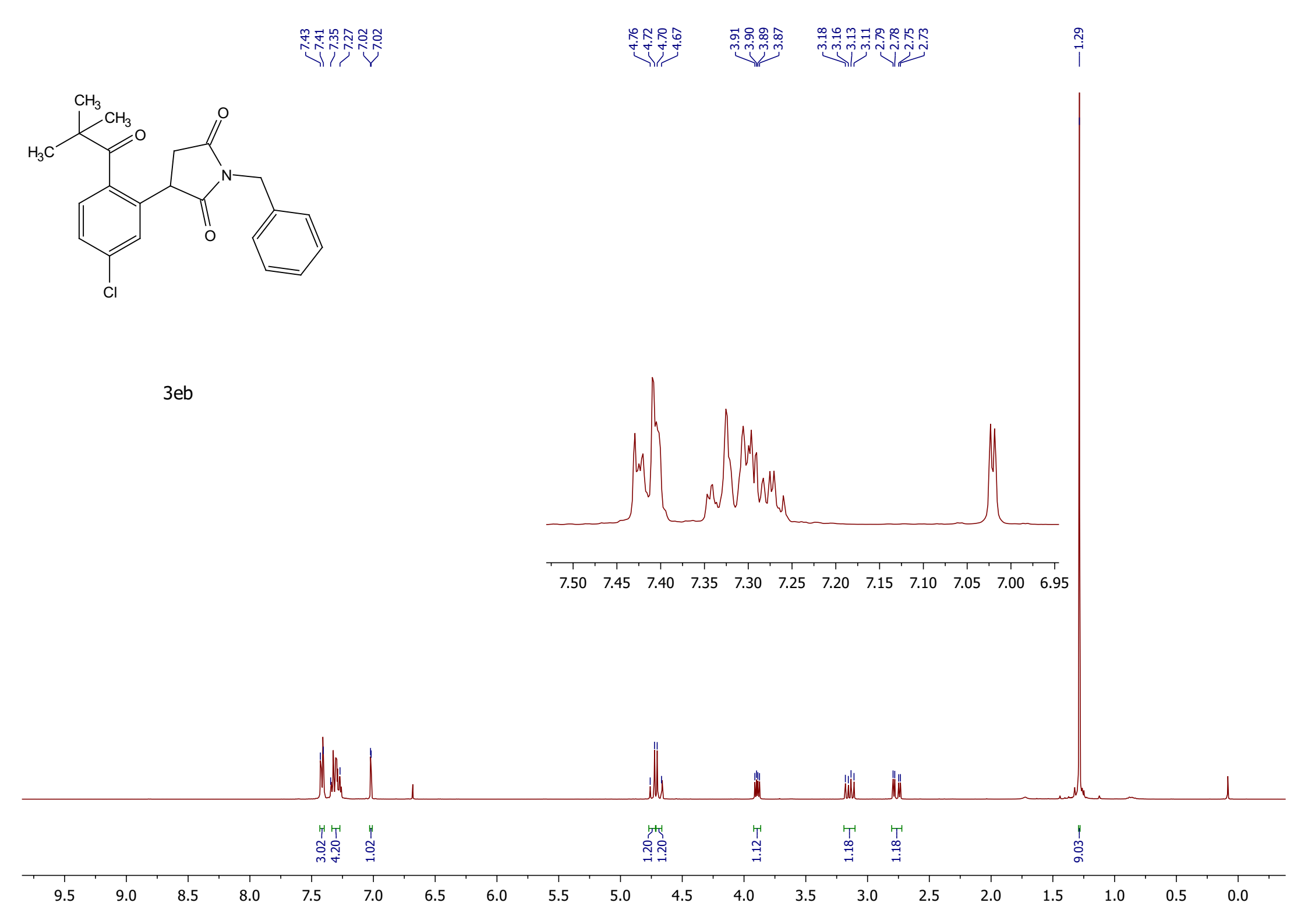
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2.75
2.73
1.29
CH3
CH3
H3C
O
O
N
O
Cl
3eb
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95
3.02
4.20
1.02
1.20
1.20
1.12
1.18
1.18
9.03
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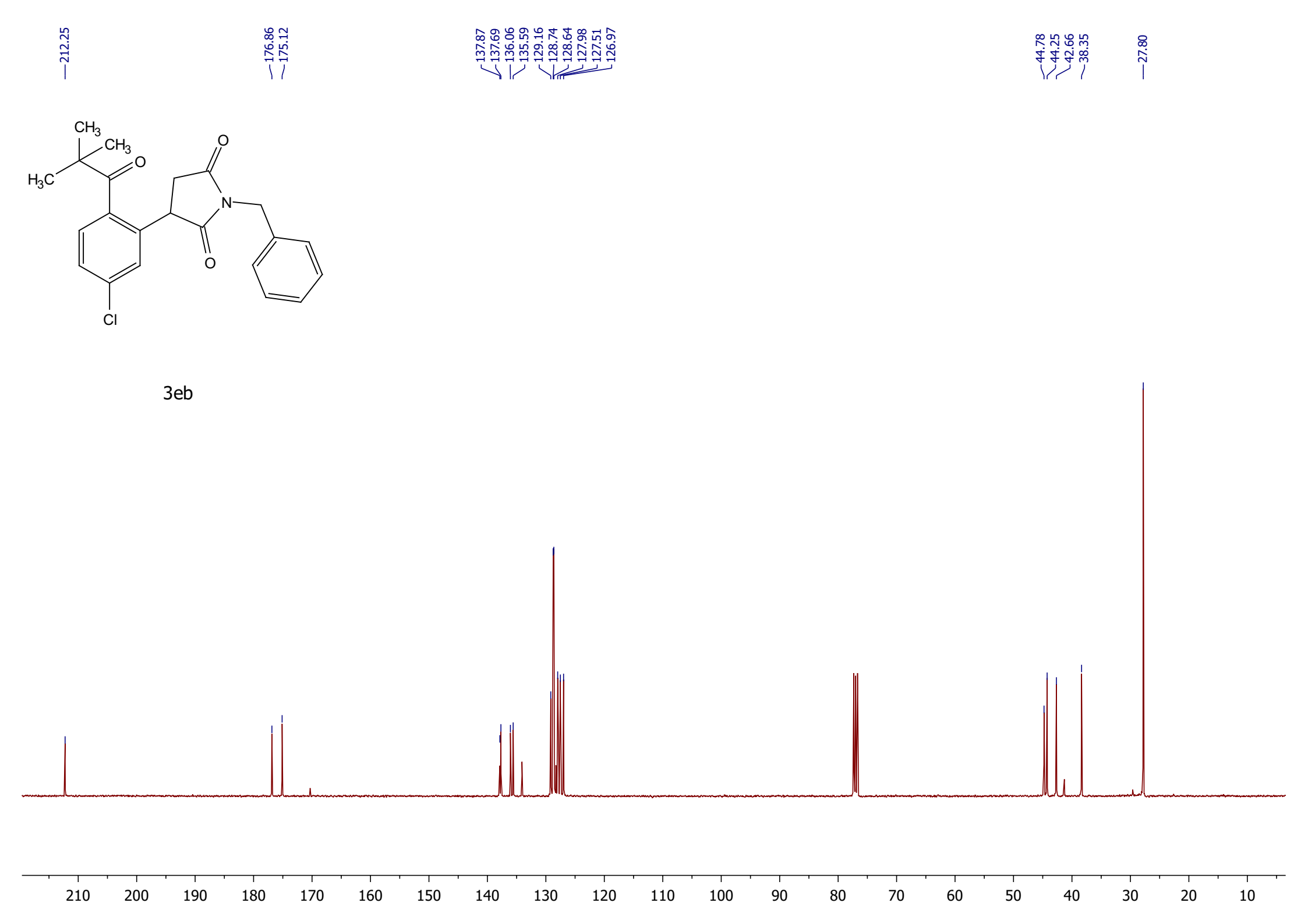
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27.80
CH3
CH3
H3C
O
O
N
O
Cl
3eb
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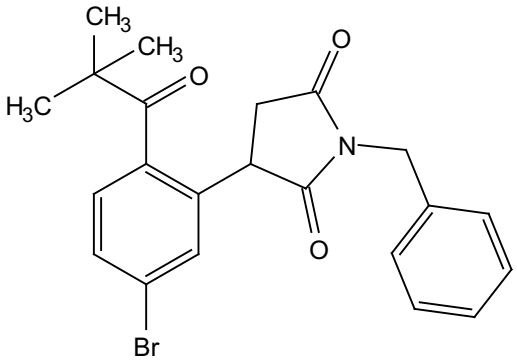
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Br

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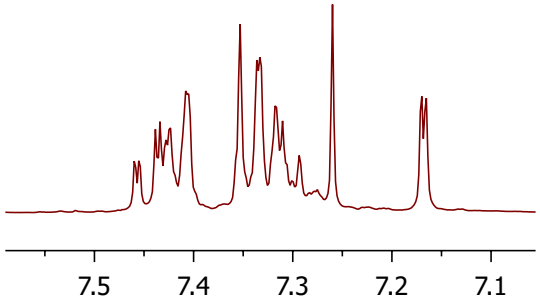
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7.29
7.17
7.17
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3.87
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3.19
3.17
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1.28
1.07
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1.15
1.19
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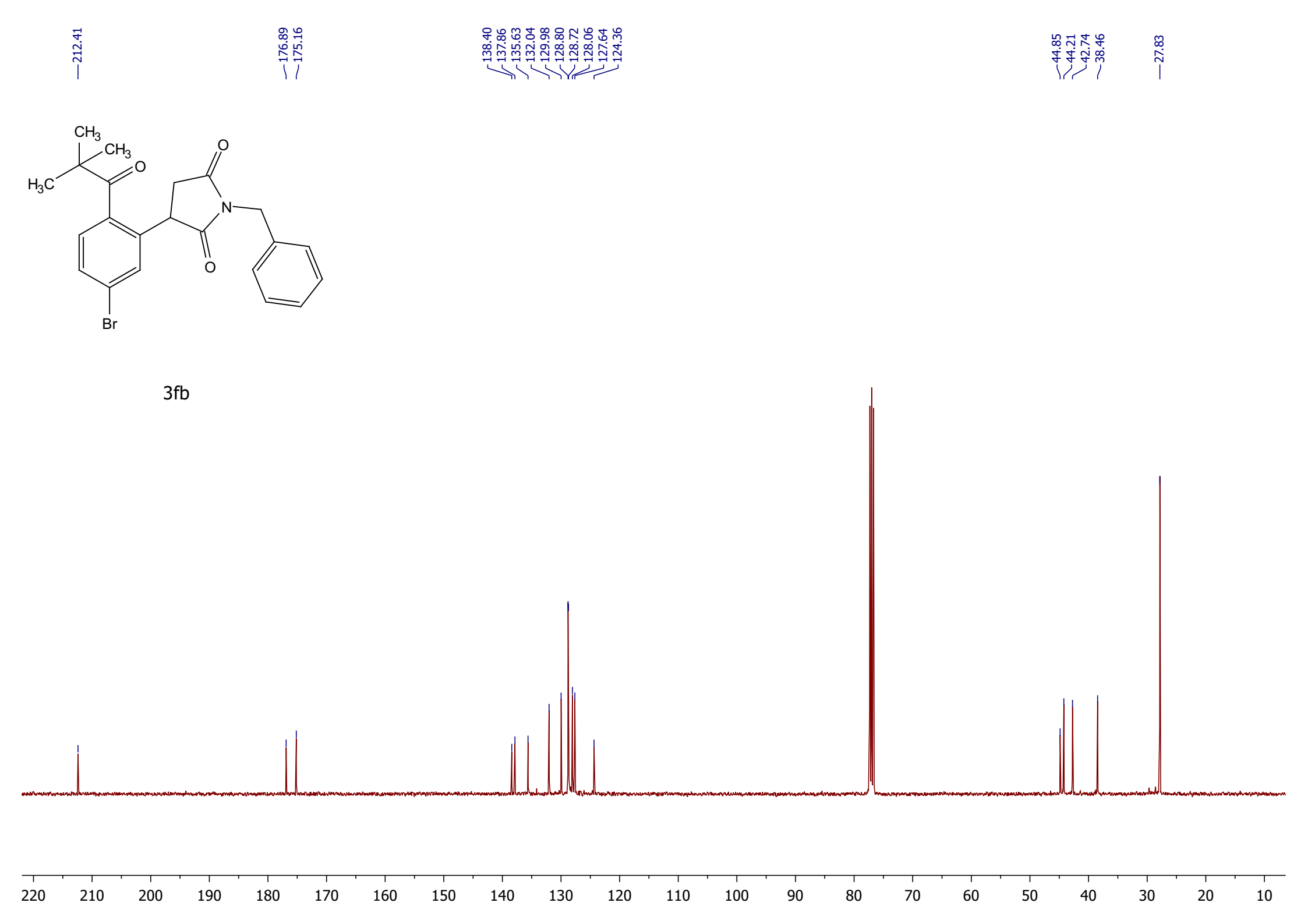
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O
N
O
Br
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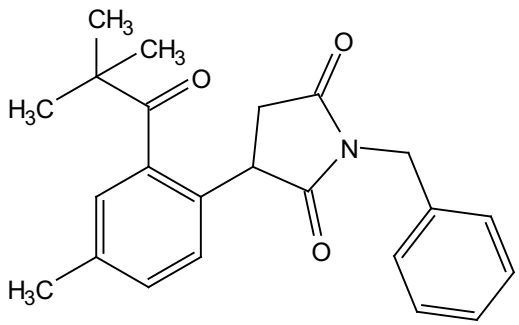
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O
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O
H3C

3gb

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7.16
7.14
7.14
6.90
6.89
4.75
4.73
4.70
4.68
3.88
3.87
3.86
3.85
3.17
3.15
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2.71
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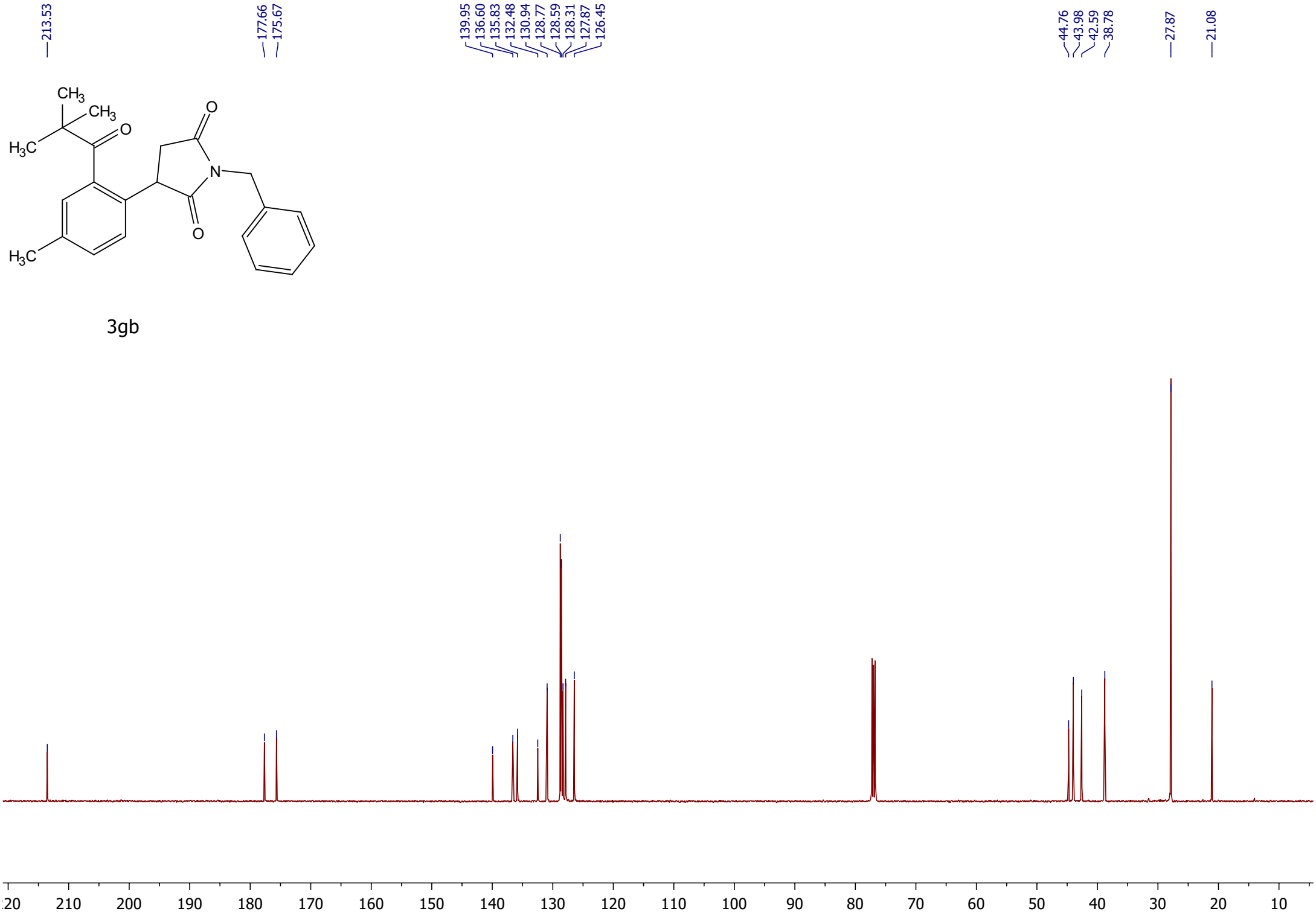
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21.08
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O
O
N
O
H3C
3gb
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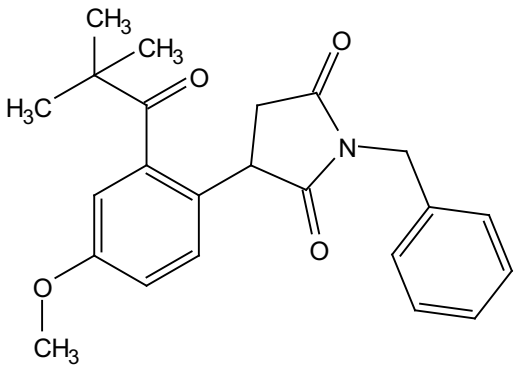
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CH3

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6.86
4.76
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4.67
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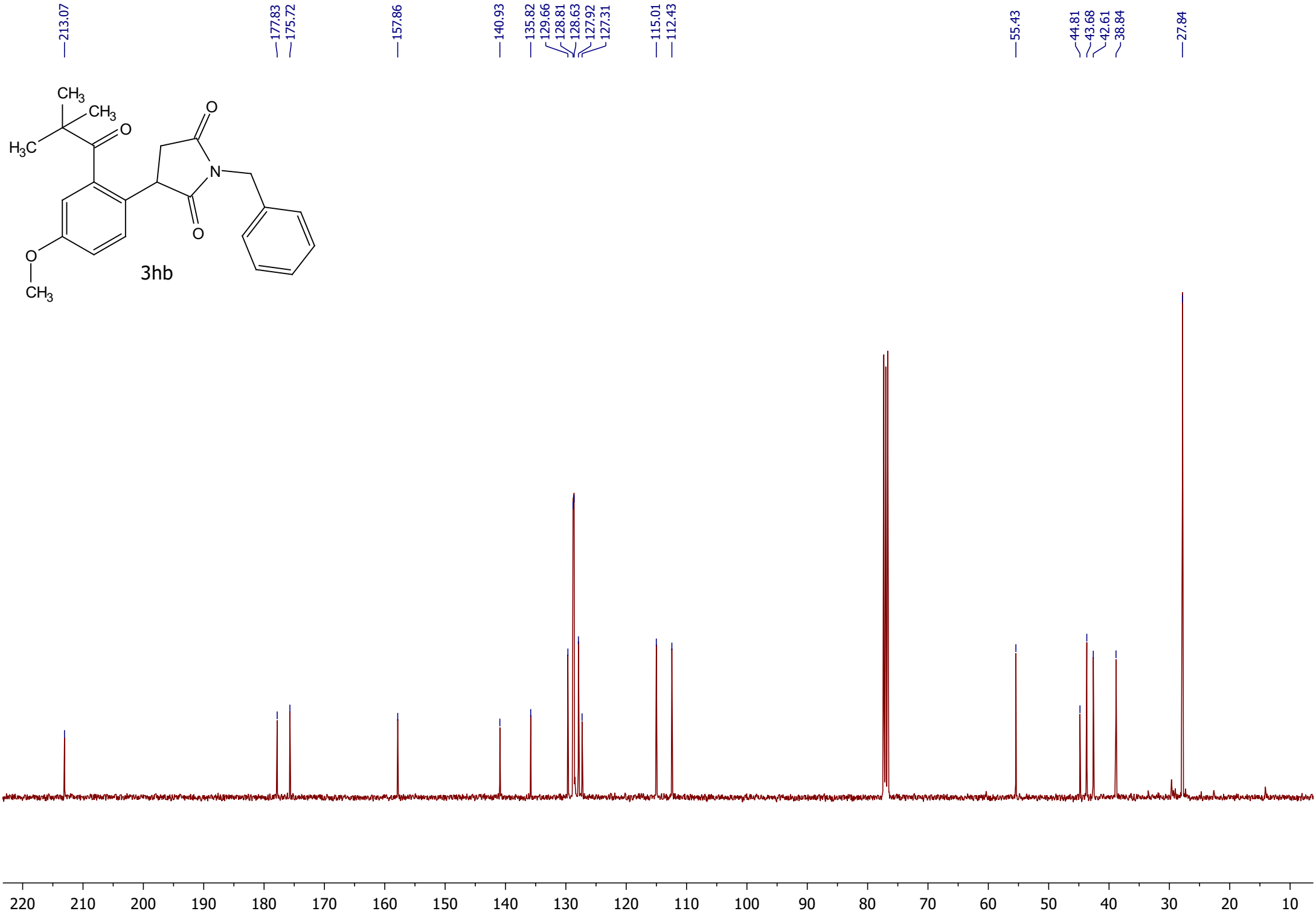
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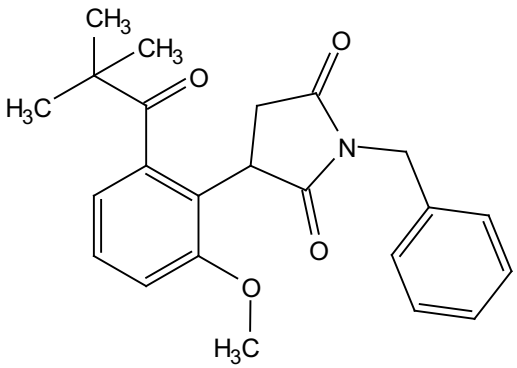
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O
H3C

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6.79
6.77
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3.13
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2.68
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2.64
1.29
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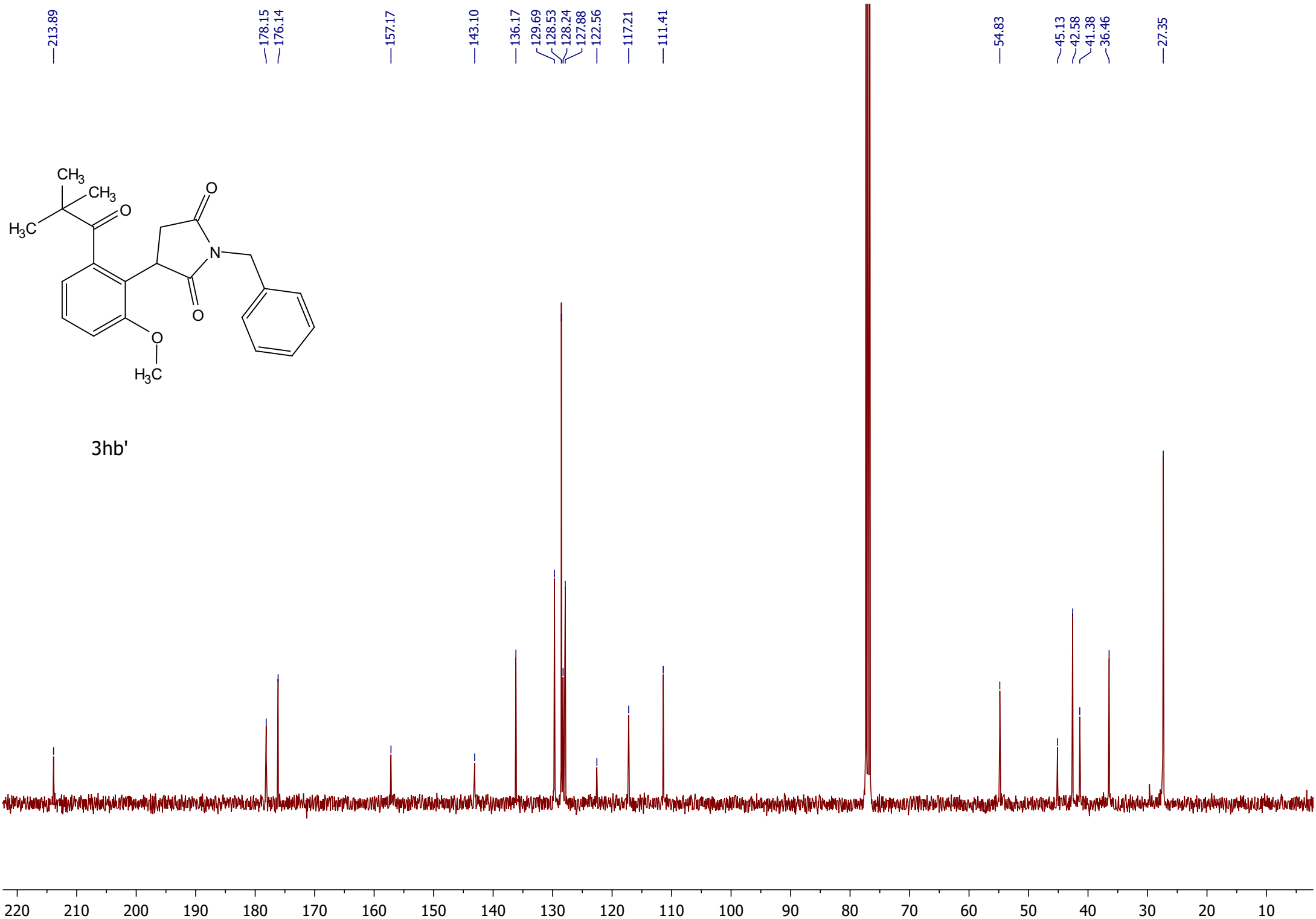
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45.13
42.58
41.38
36.46
27.35
CH3
CH3
H3C
O
O
N
O
O
H3C
3hb'
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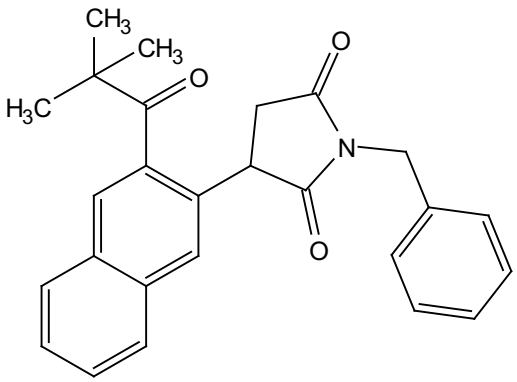

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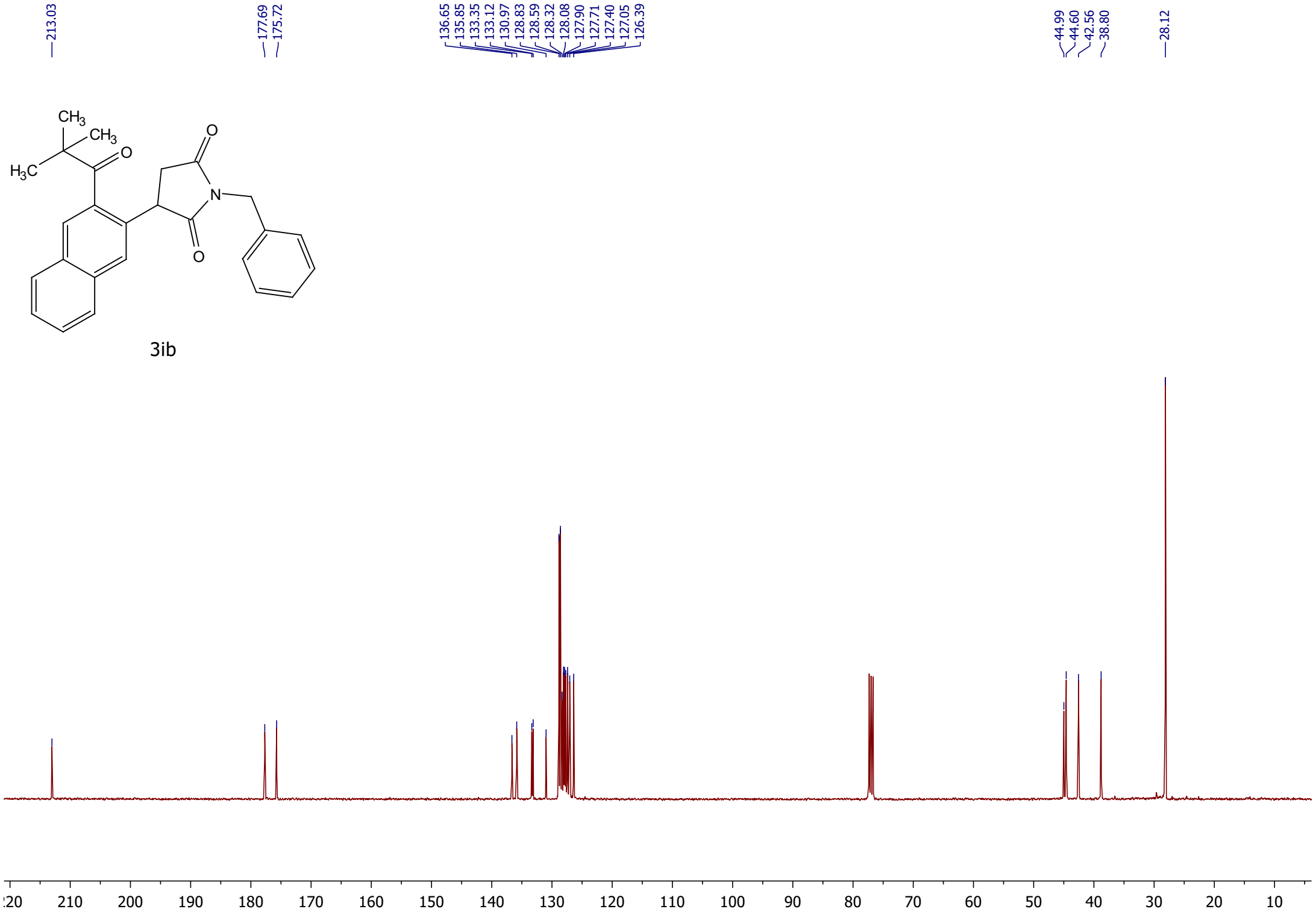
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127.40
127.05
126.39
44.99
44.60
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38.80
28.12
CH3
CH3
H3C
O
O
N
O
O
3ib
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20
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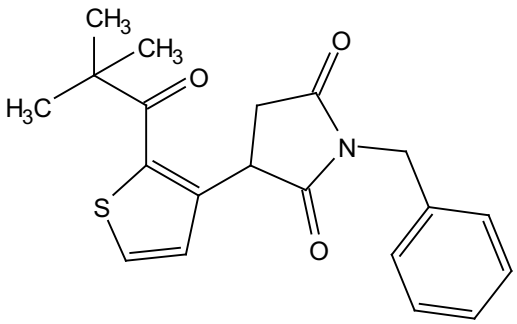
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3jb

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3.14
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7.2
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1.09
1.17
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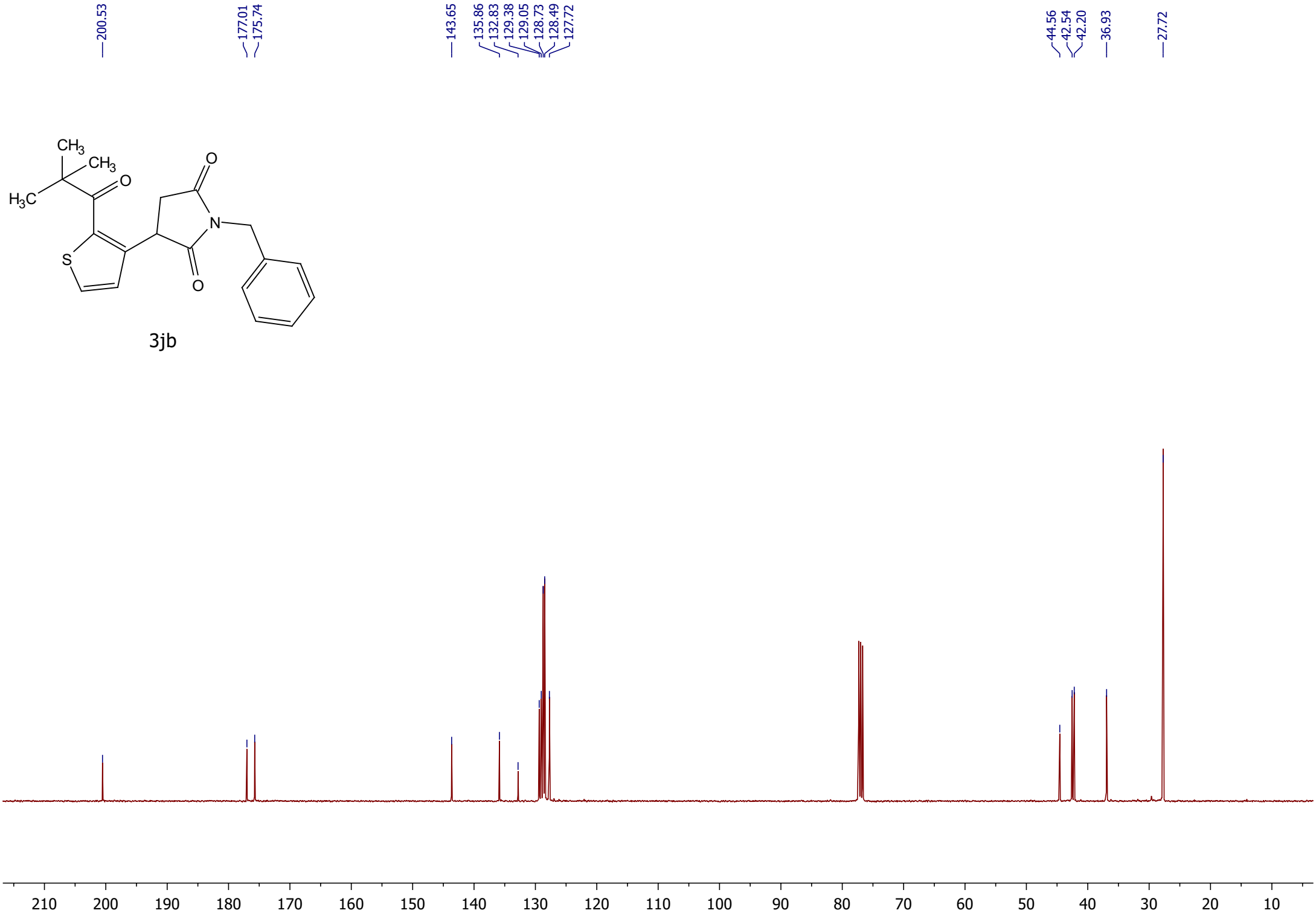
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128.49
127.72
44.56
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42.20
36.93
27.72
CH3
CH3
H3C
O
O
N
S
O
3jb
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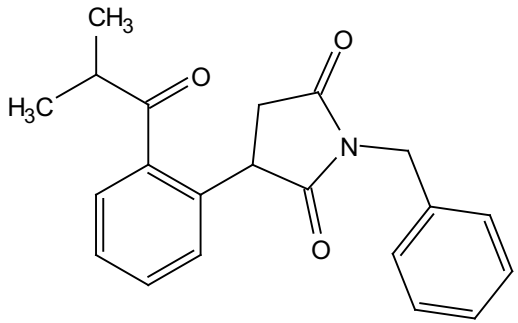
CH3
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O

3kb

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7.14
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3.48
3.47
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3.44
3.43
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7.5
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7.3
7.2
7.1
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4.14
3.12
1.02
1.03
1.09
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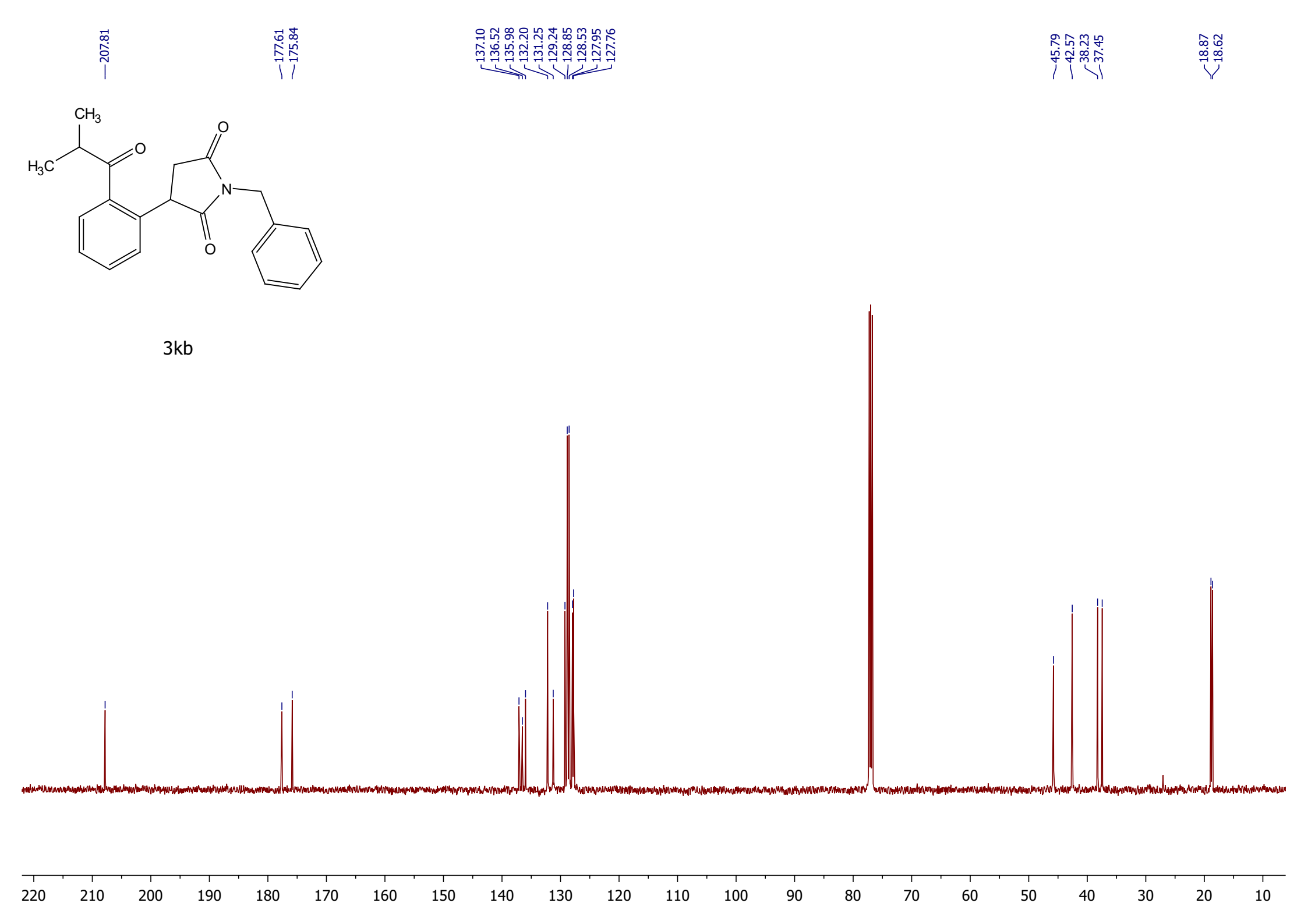
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18.62
CH3
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O
O
O
N
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220
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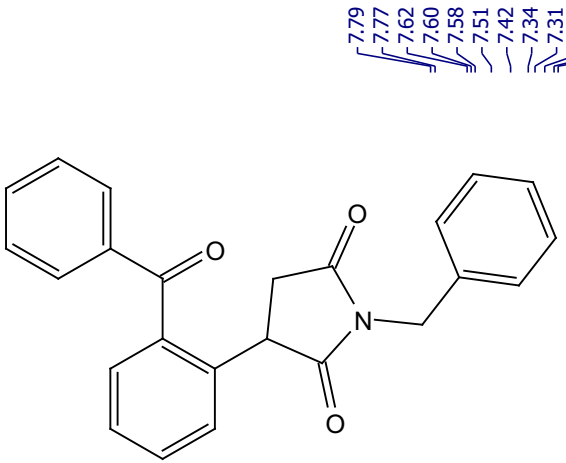
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3lb

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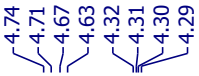
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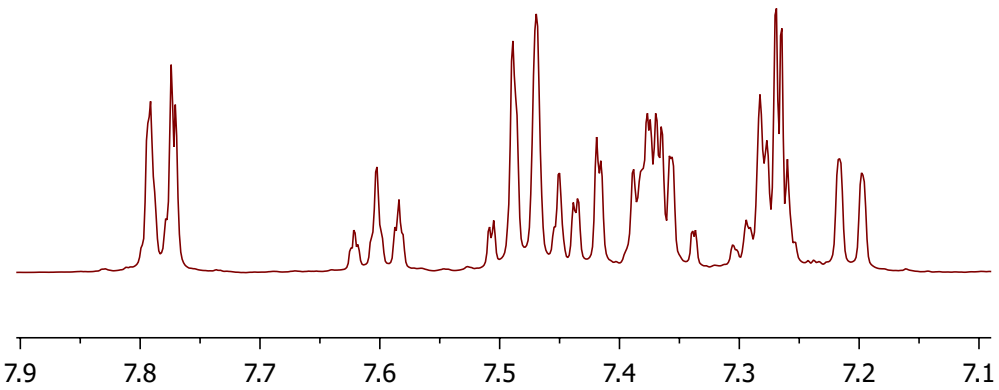
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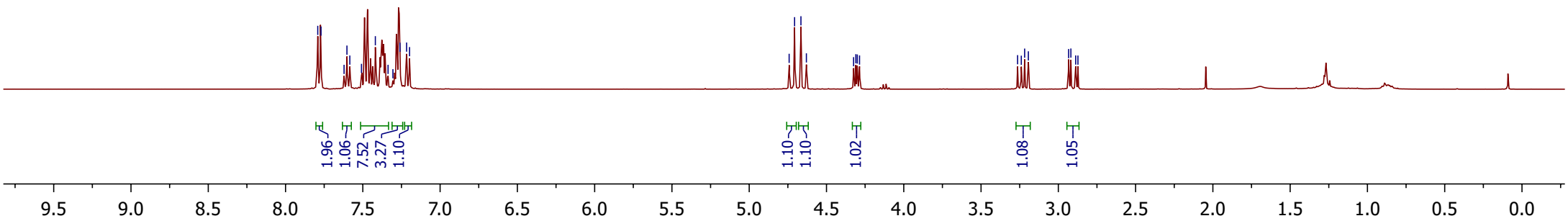
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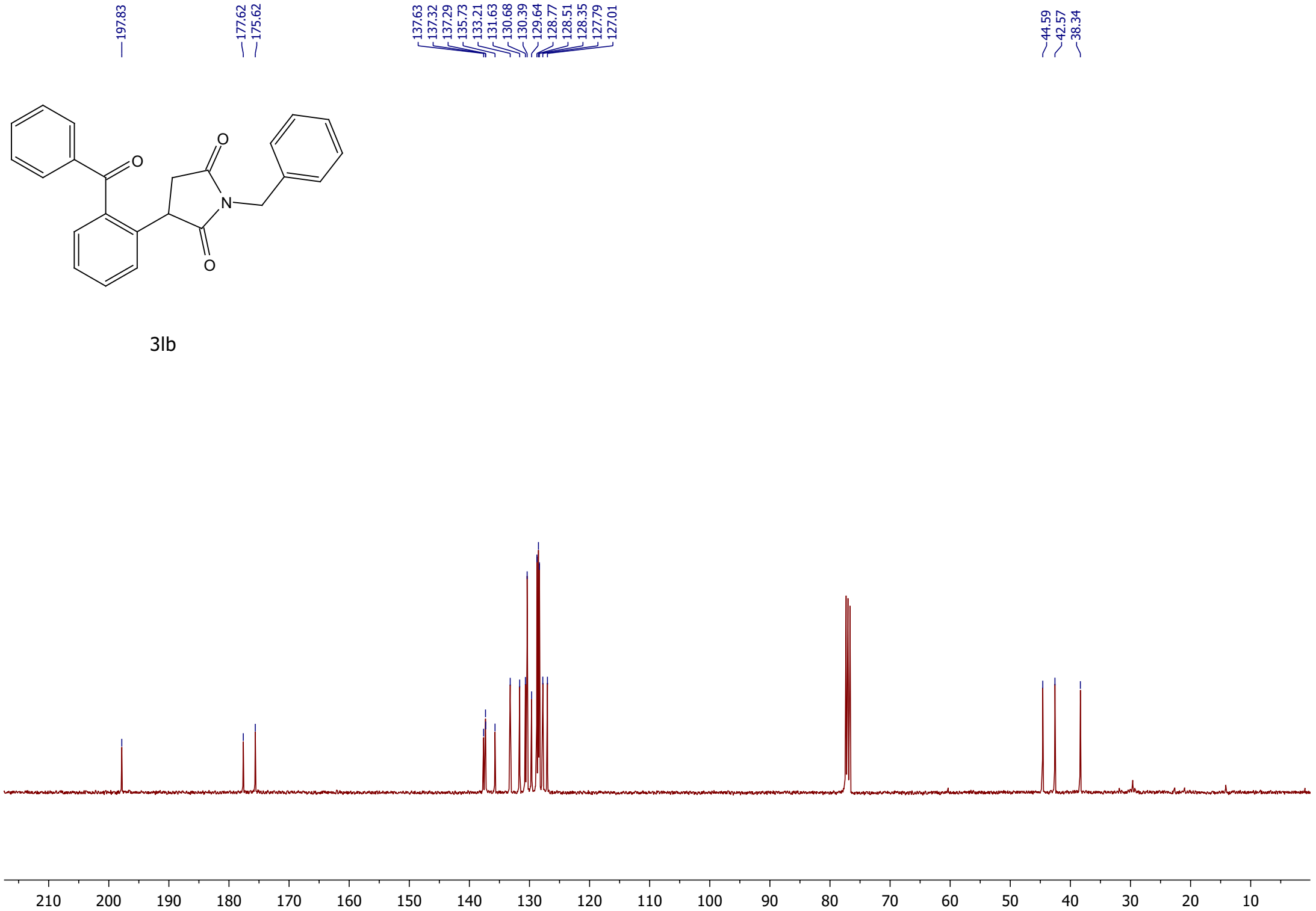
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O
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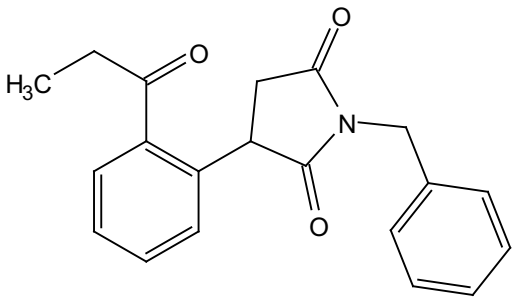
3lb


H3C
O
O
N
O
O

3mb

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3.08
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8.5
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6.5
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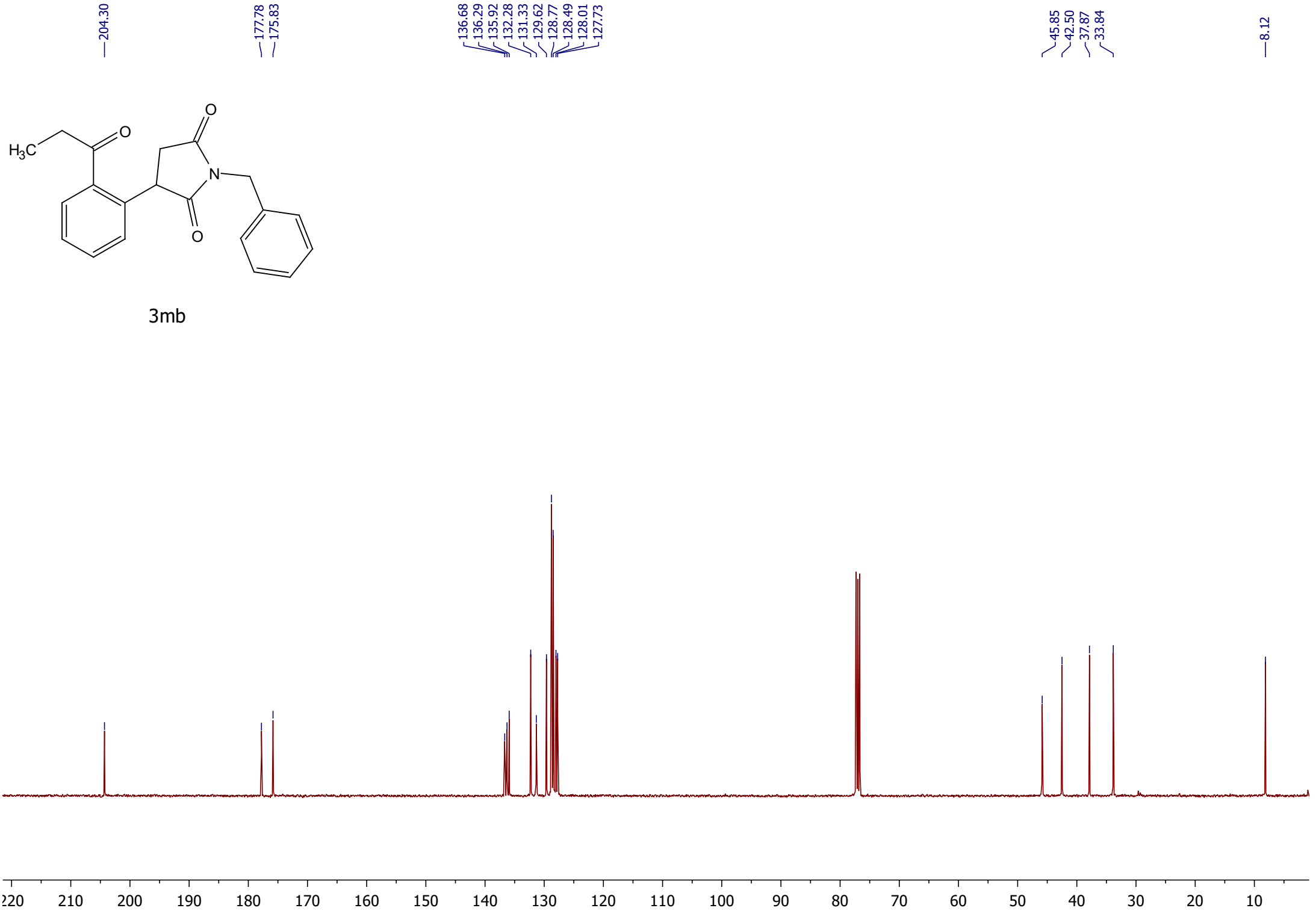
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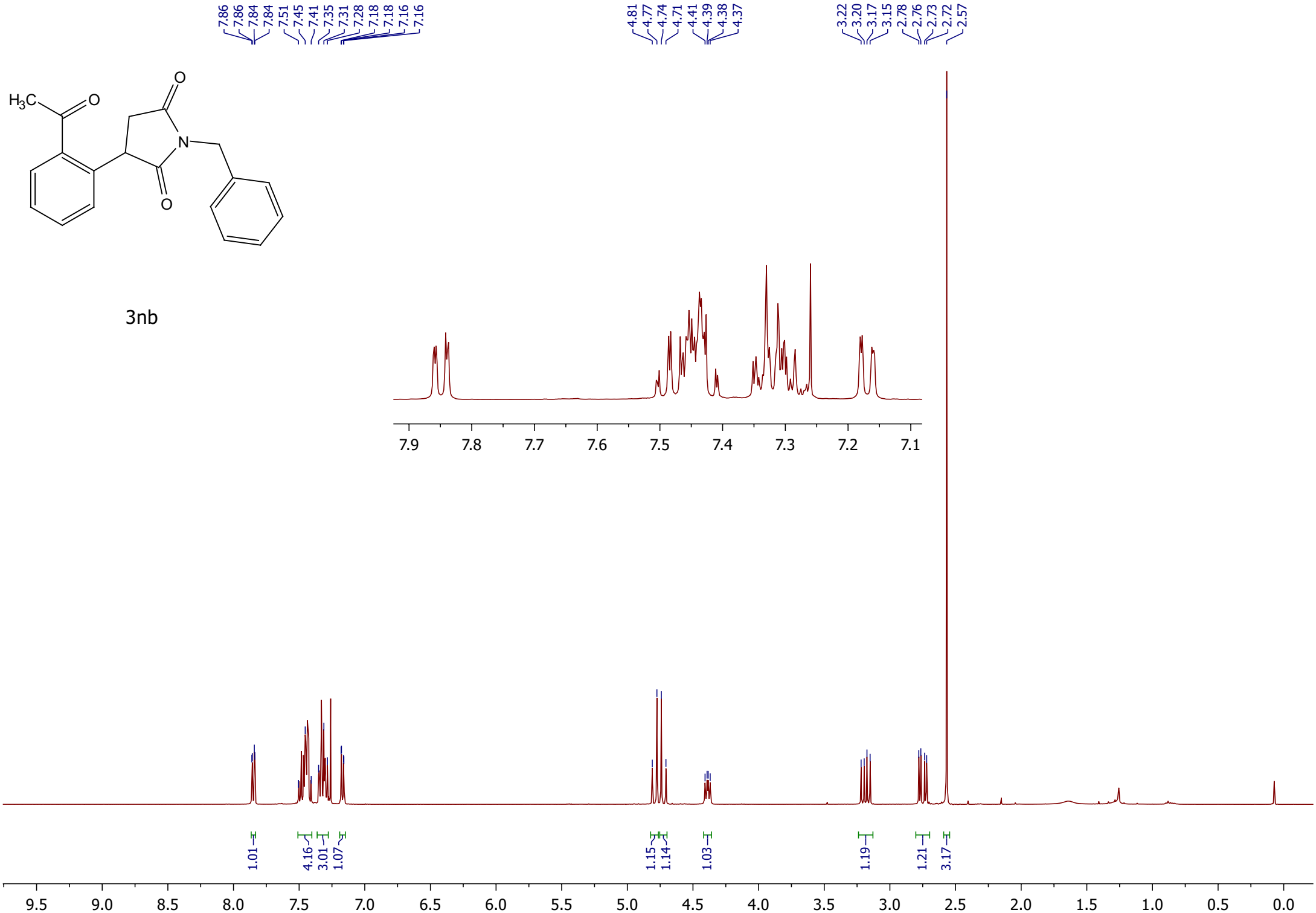
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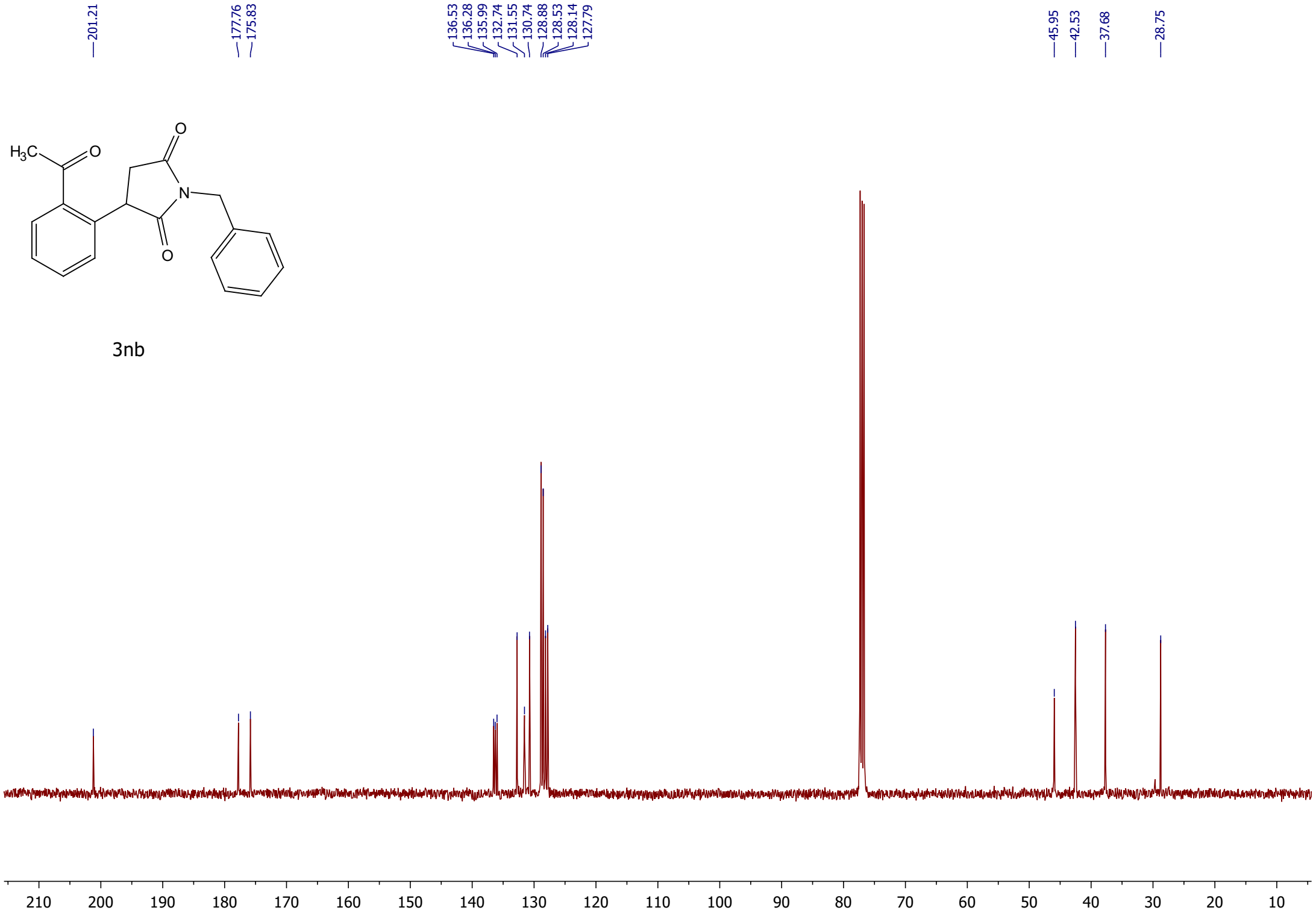
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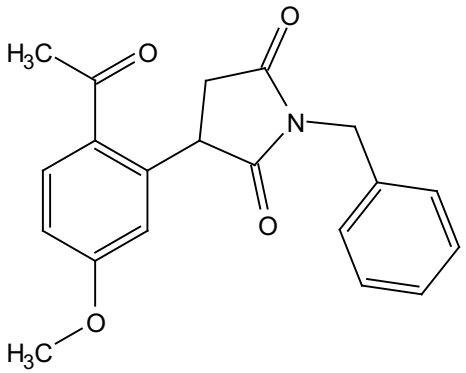
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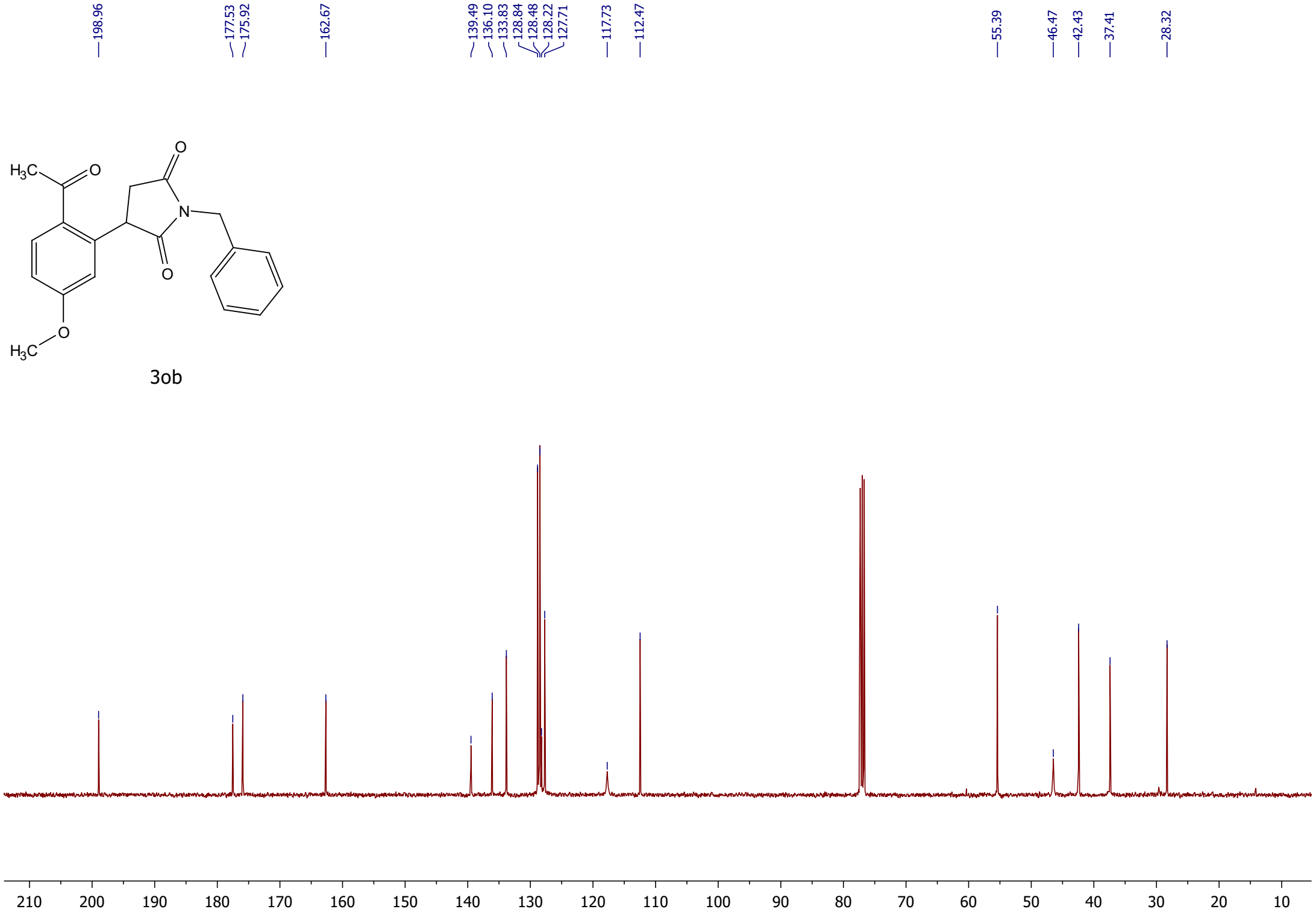
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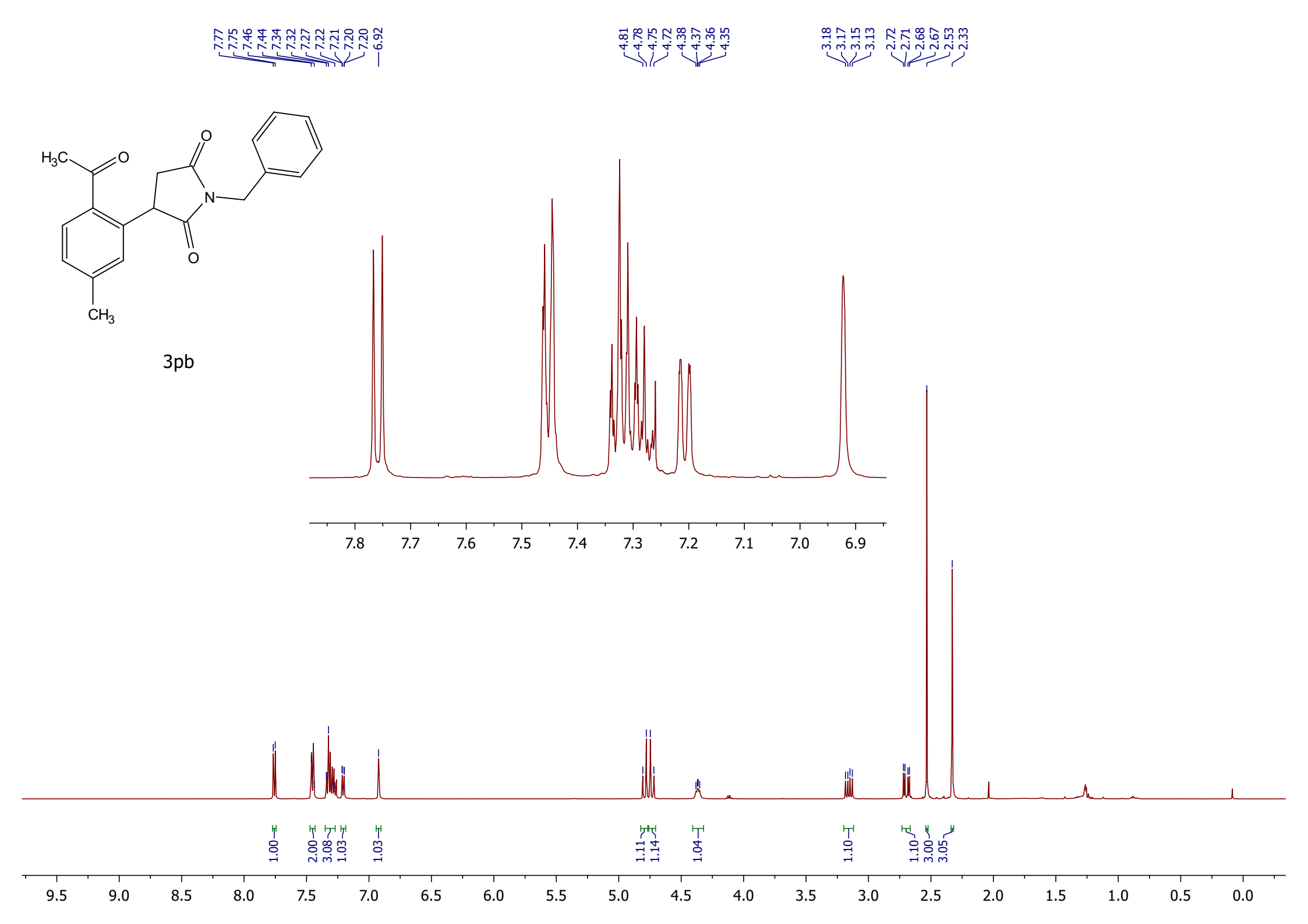
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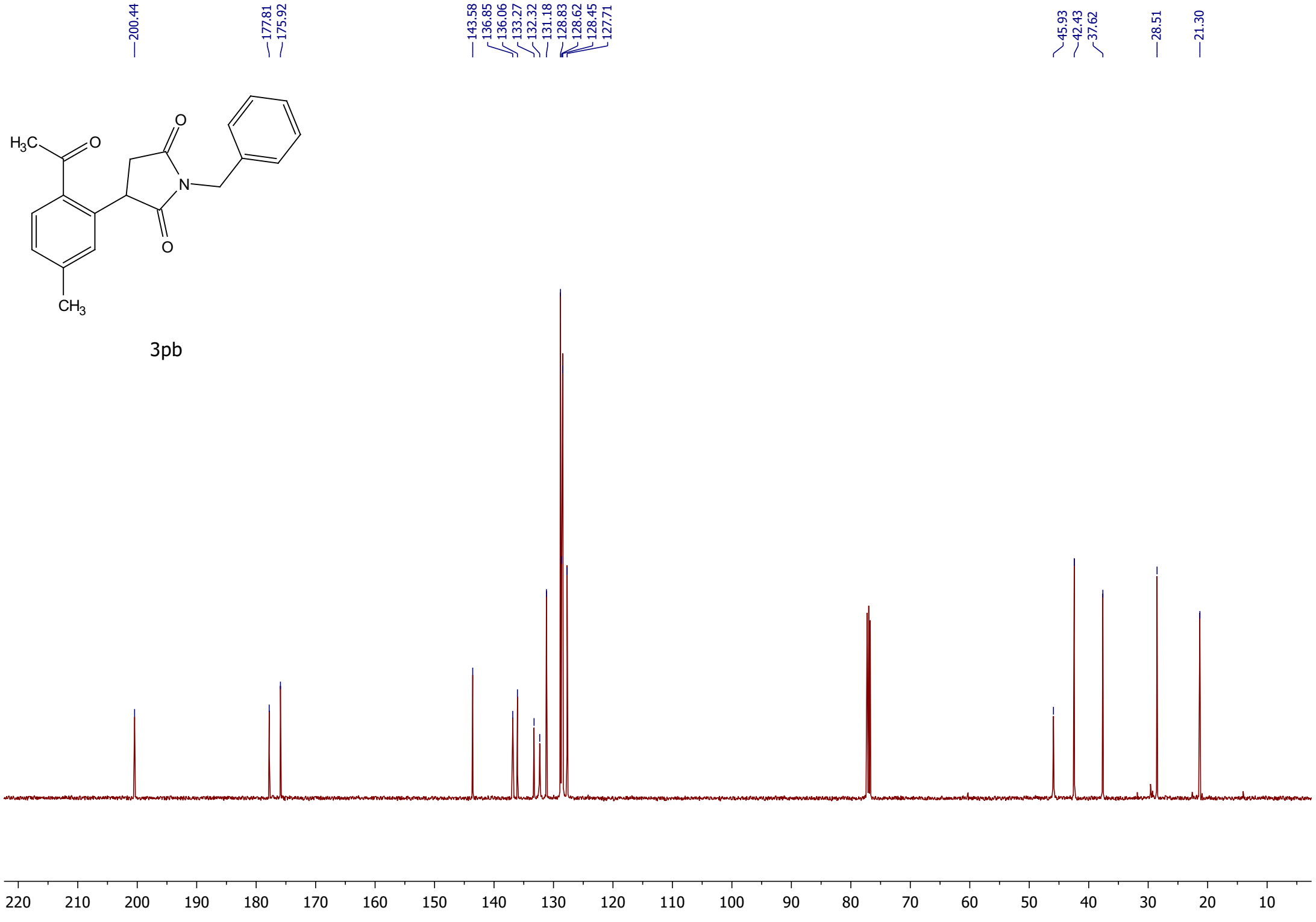
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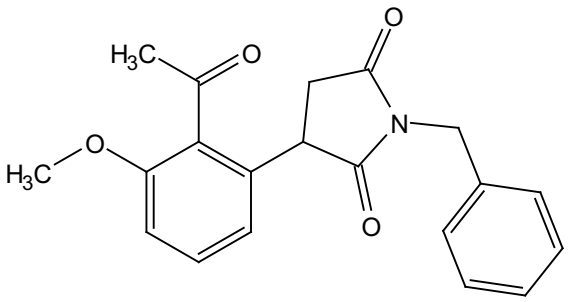
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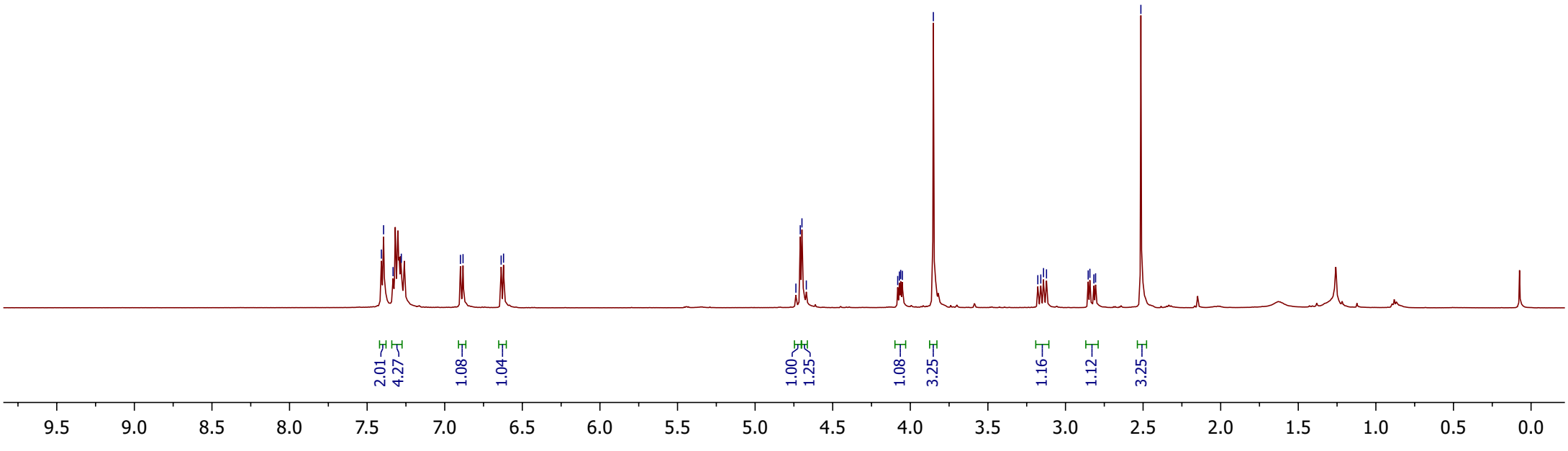
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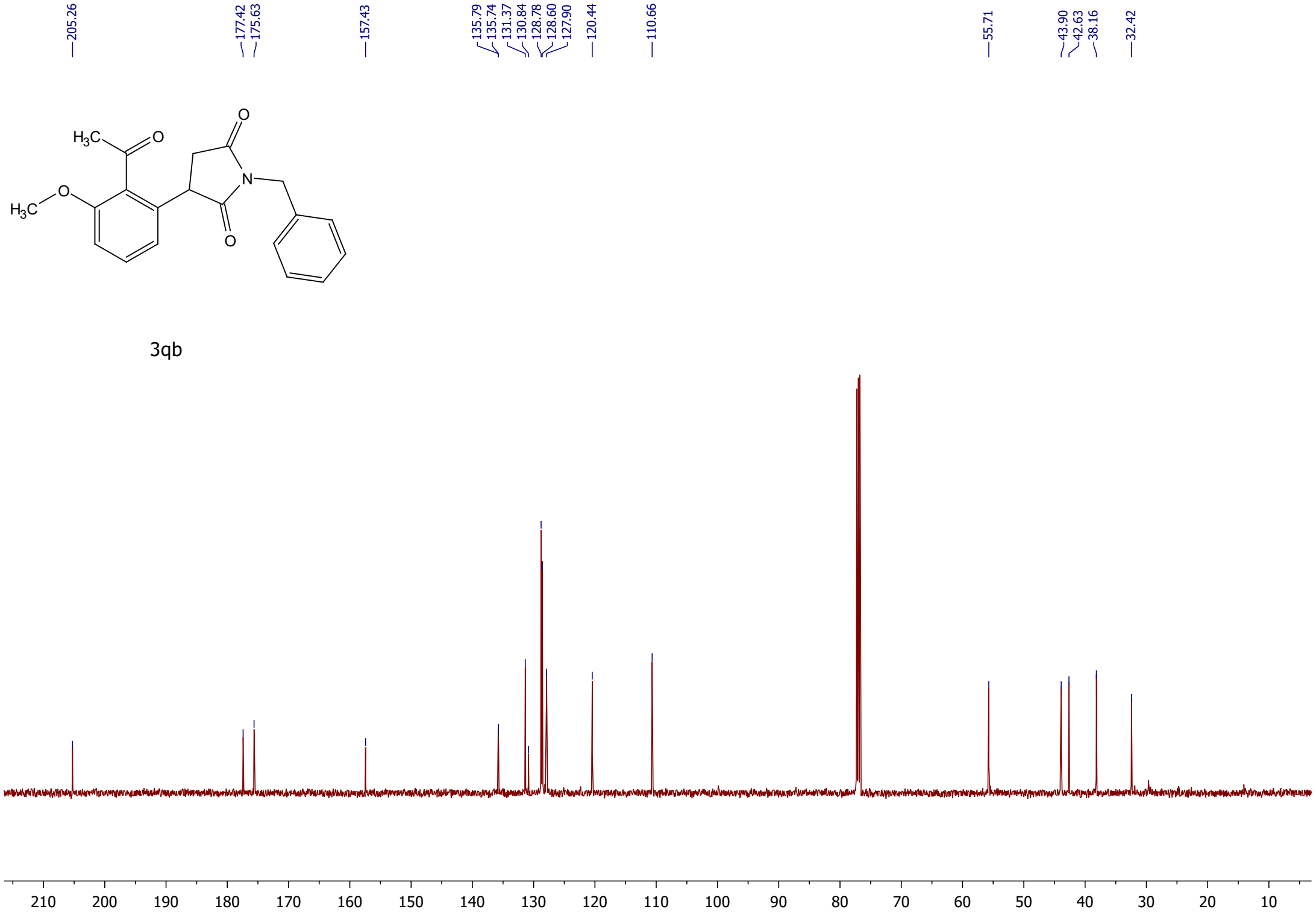
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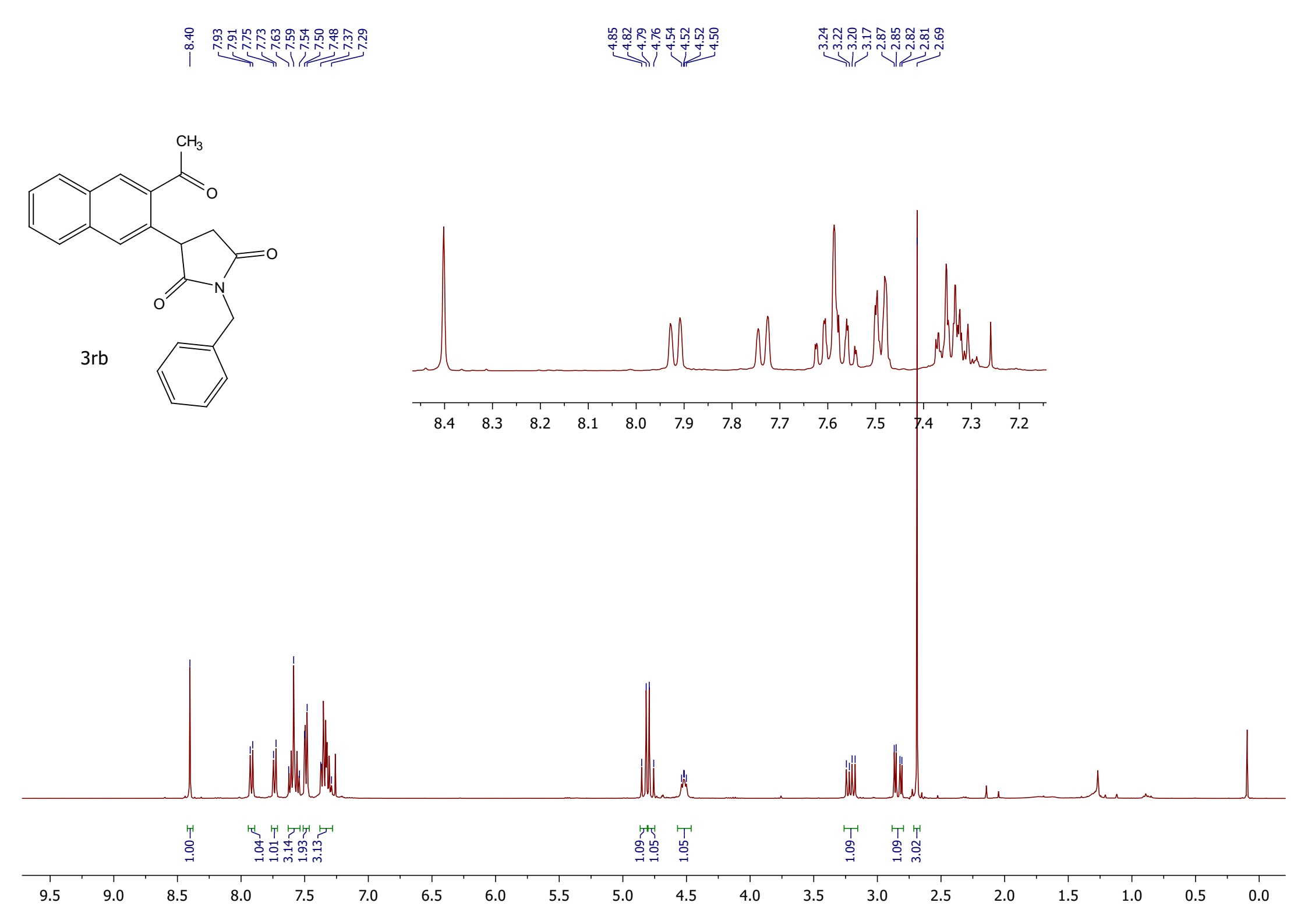
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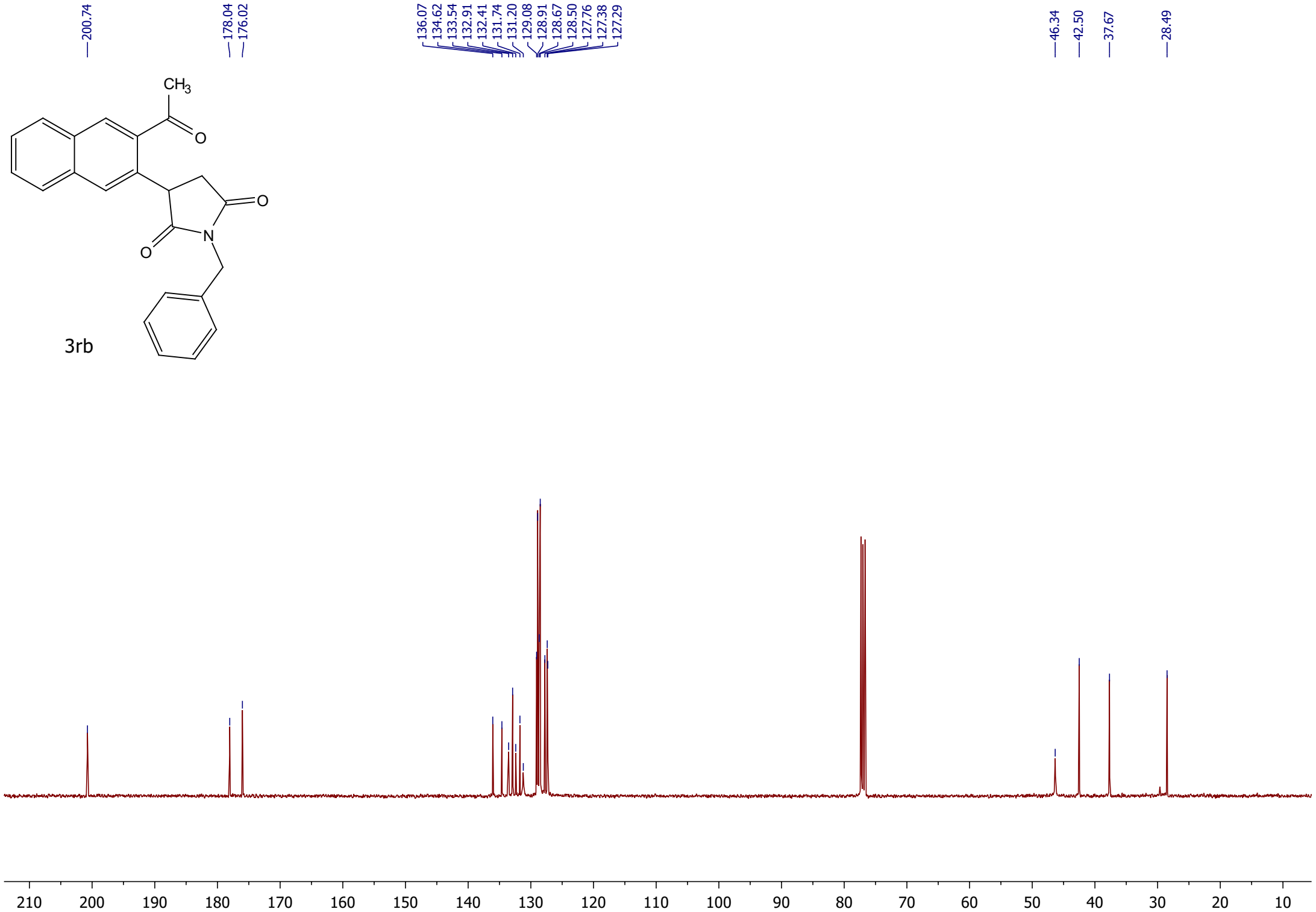
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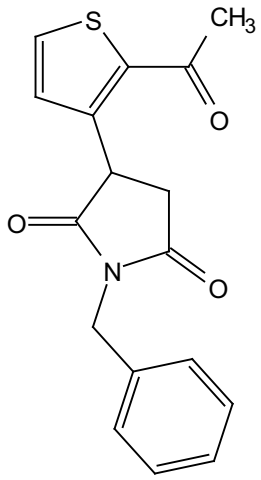
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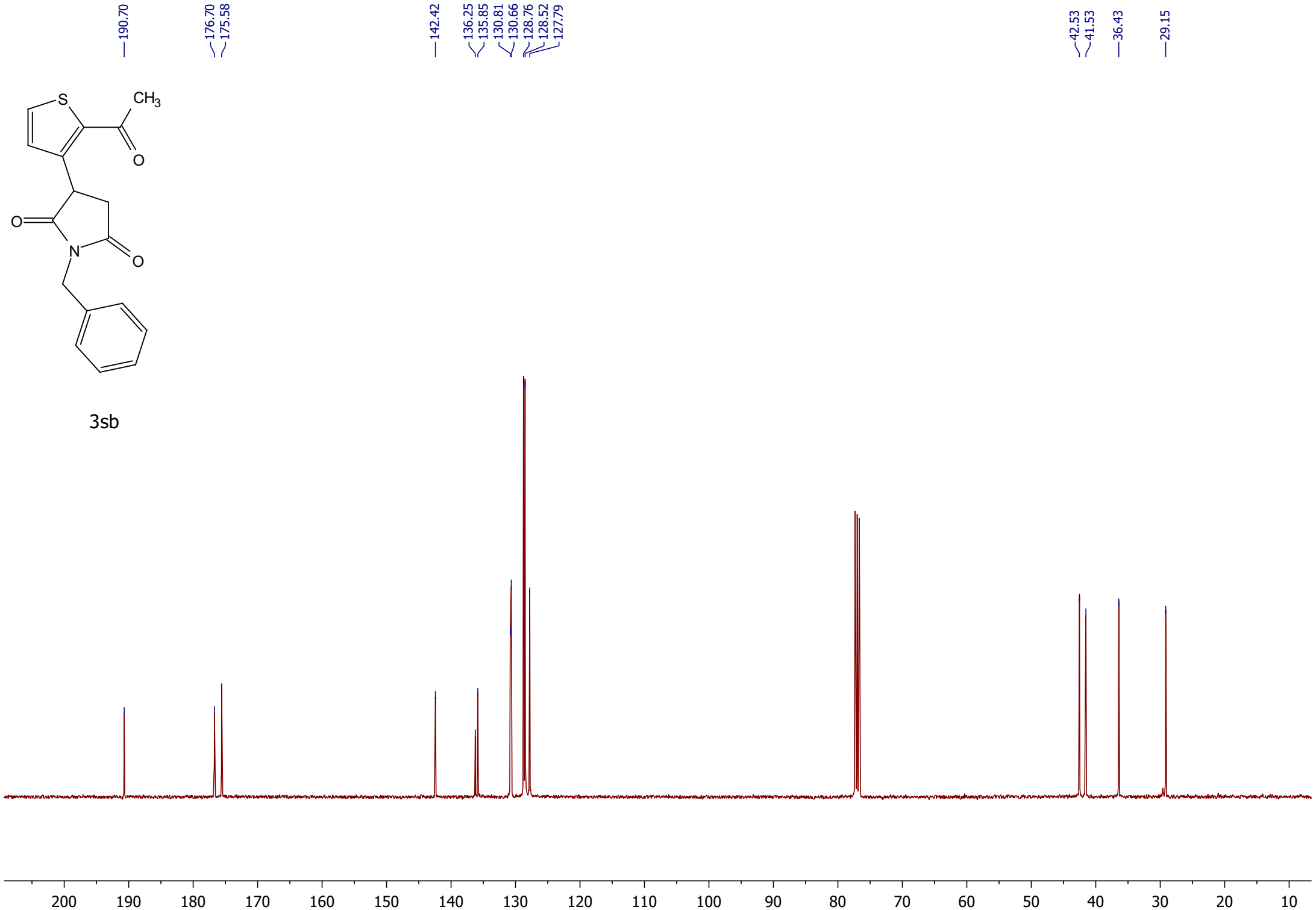
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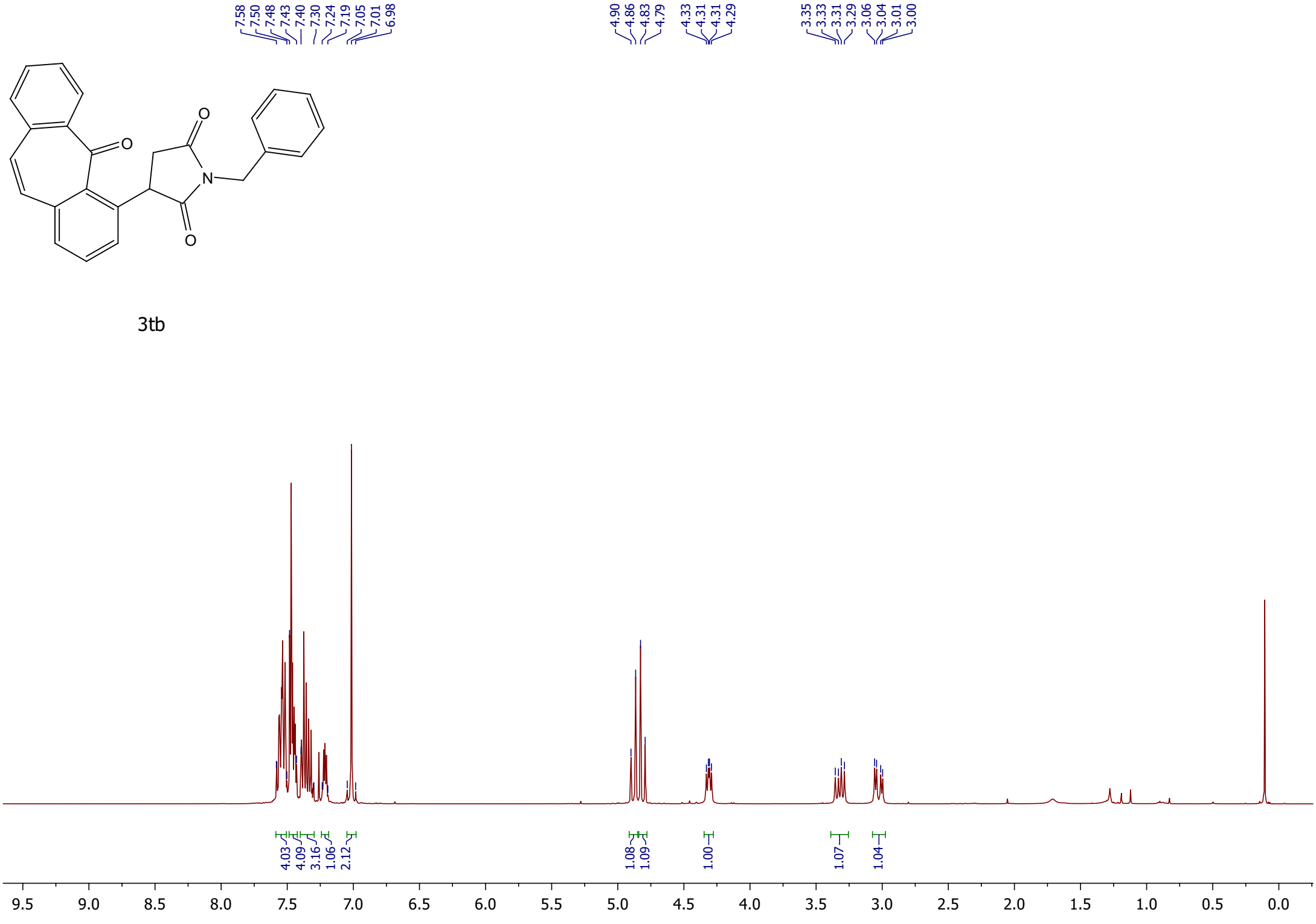
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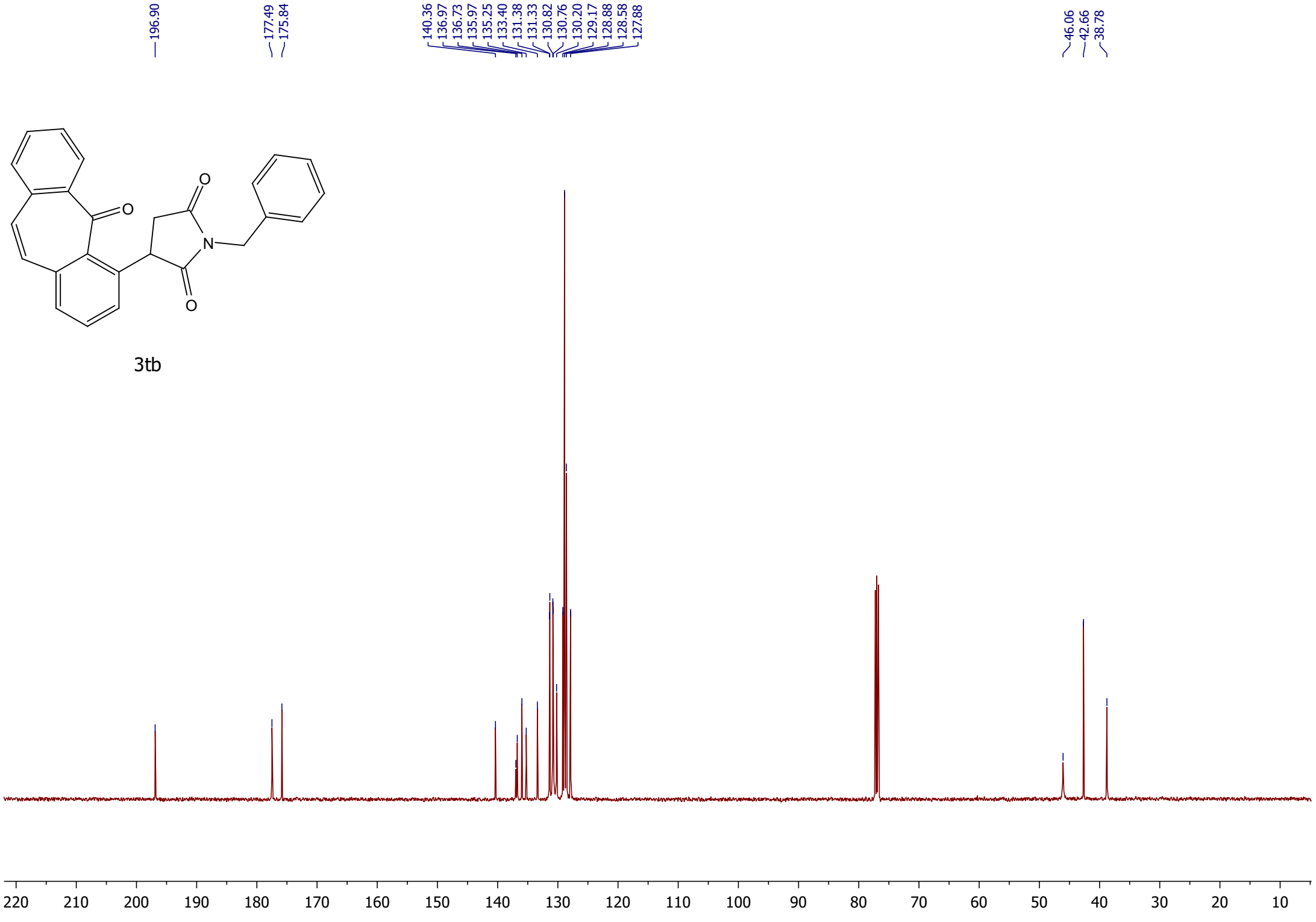
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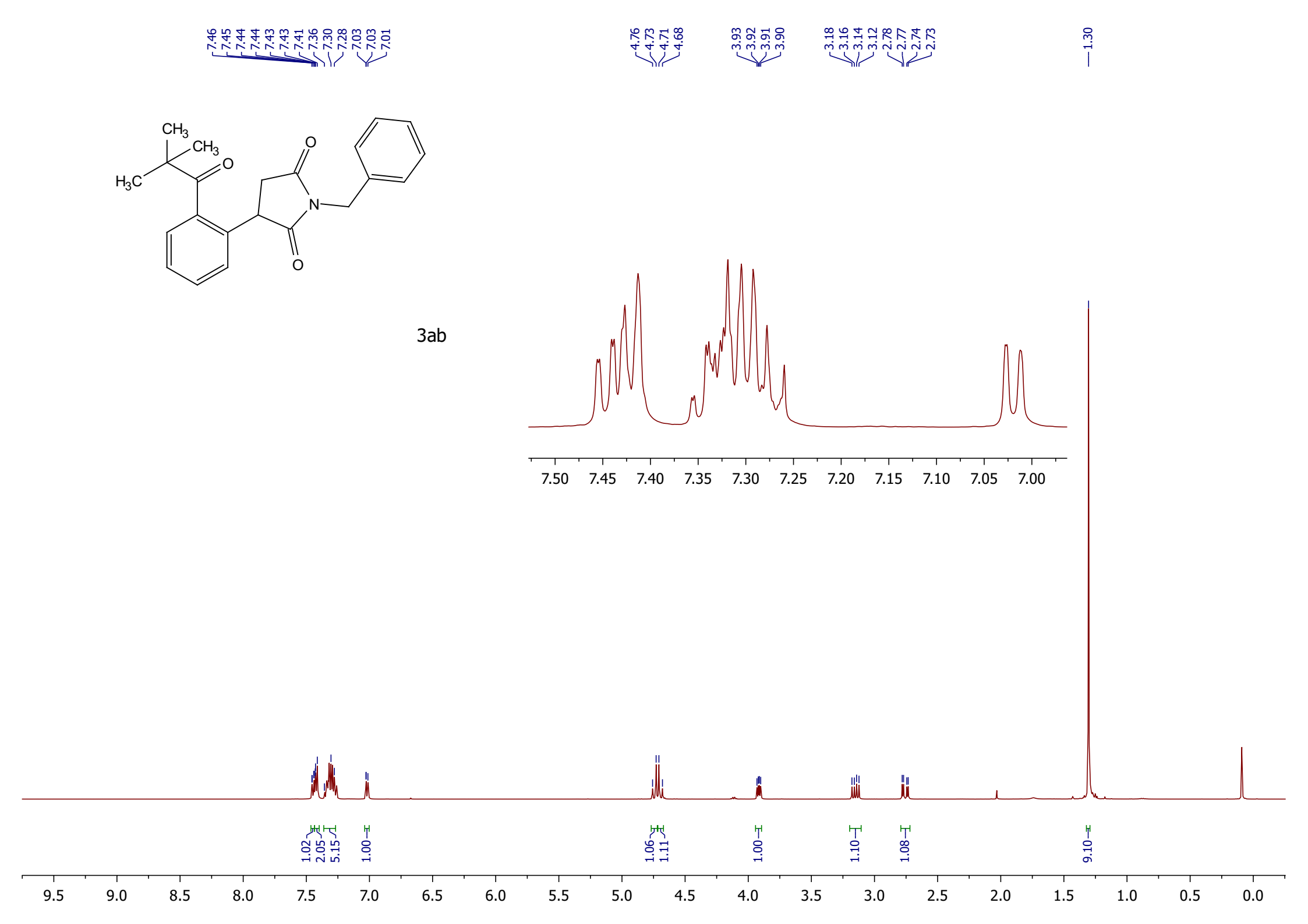
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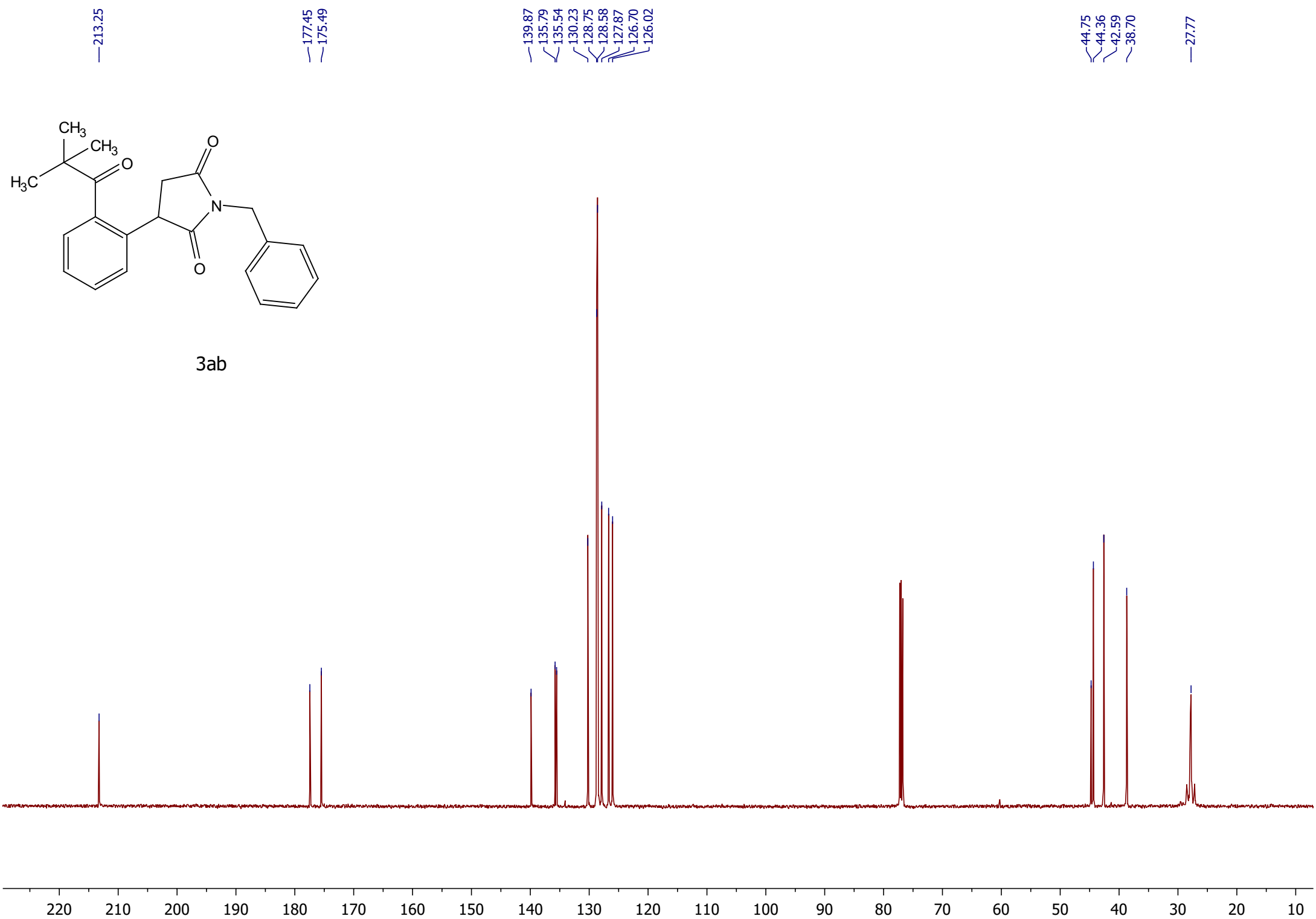
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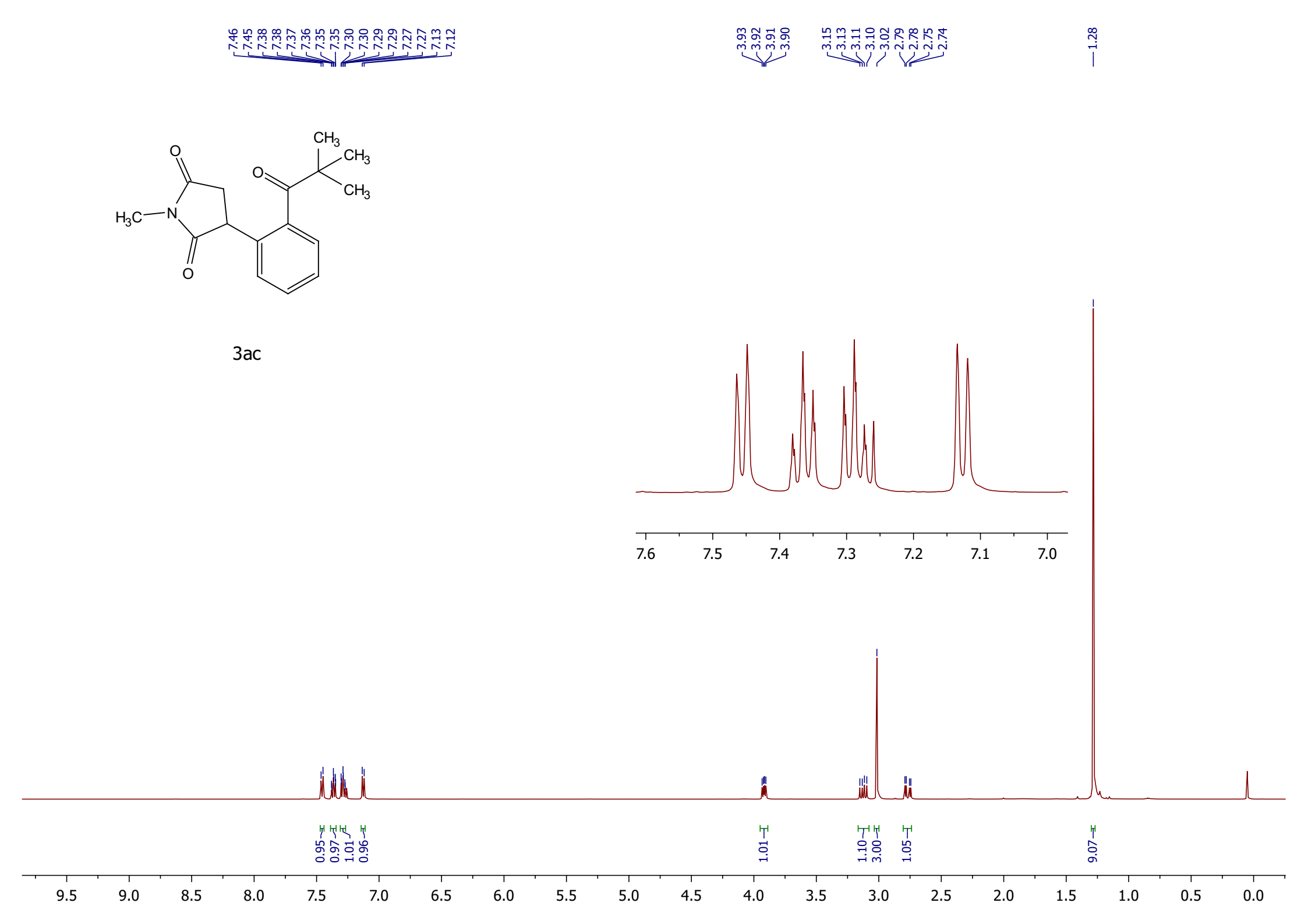
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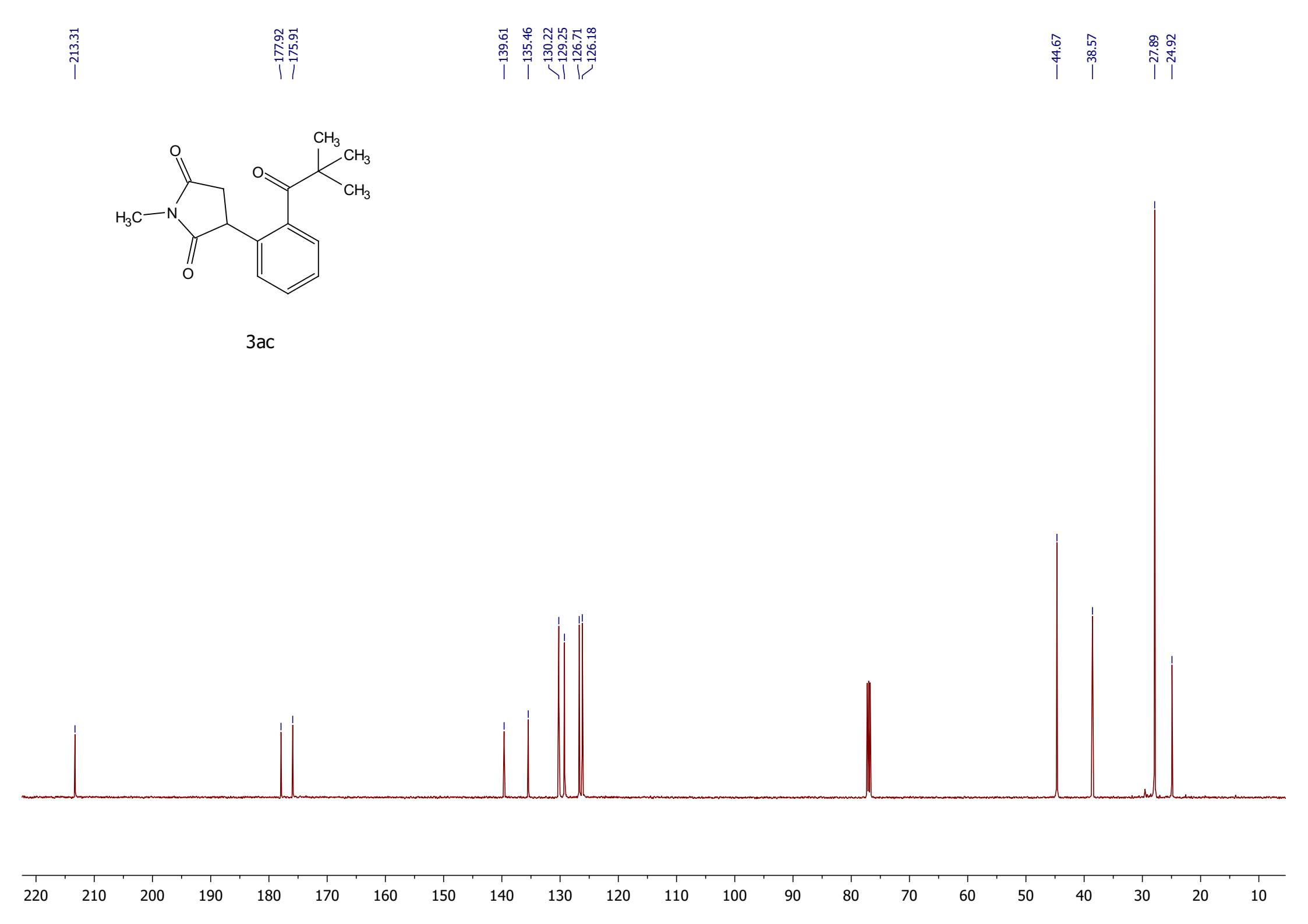
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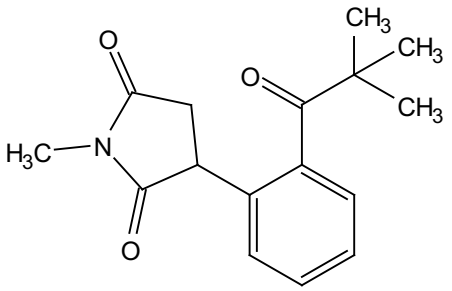
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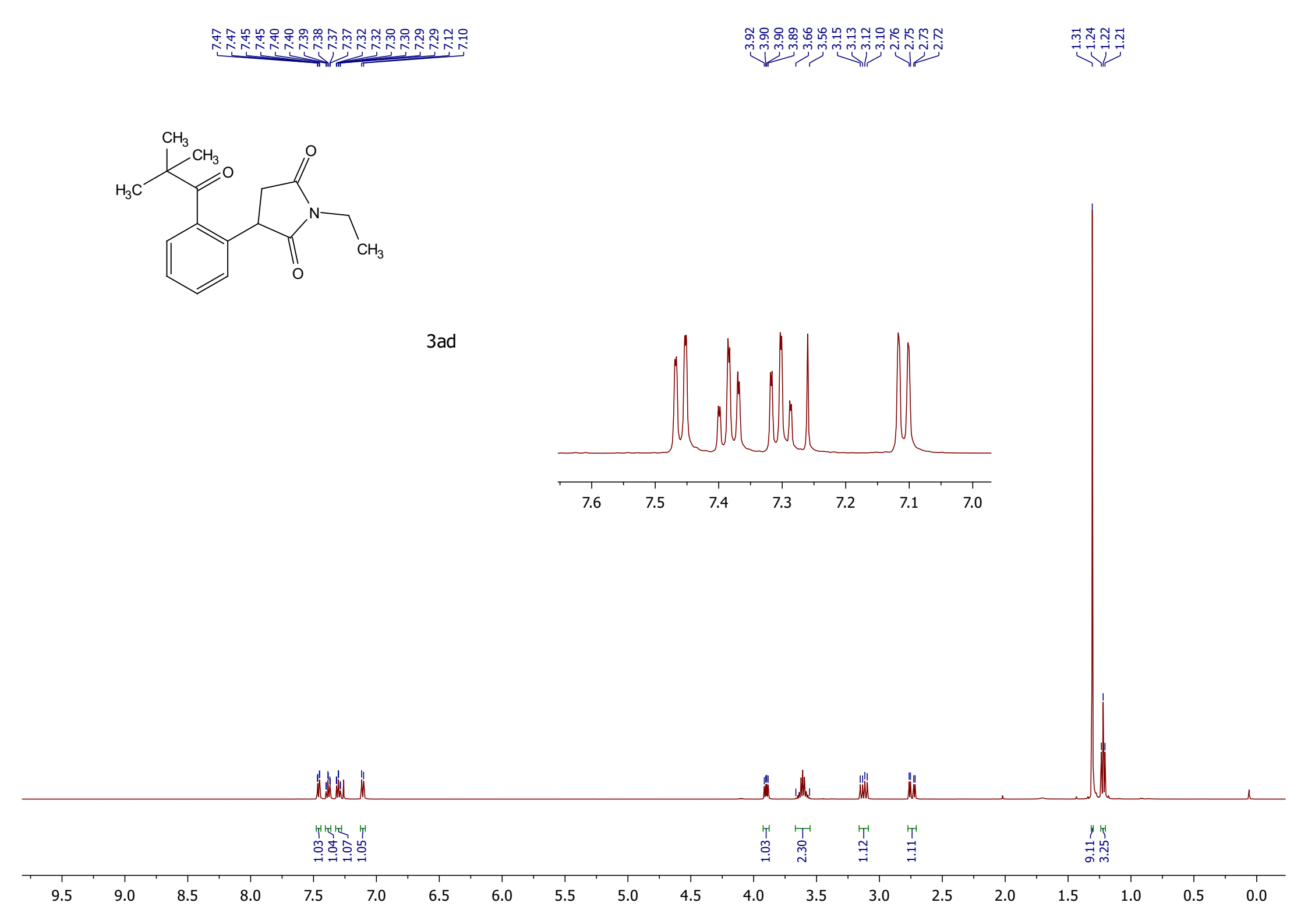
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CH3
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3ad
7.6
7.5
7.4
7.3
7.2
7.1
7.0
1.03
1.04
1.07
1.05
1.03
2.30
1.12
1.11
9.11
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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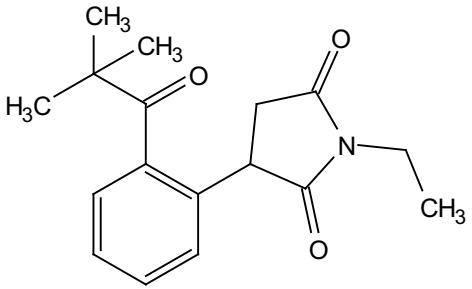
0.0


CH3
CH3
H3C
O
O
N
CH3
O

3ad

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139.79
135.63
130.30
128.81
126.74
126.17
44.76
44.45
38.69
33.96
27.91
13.00
220
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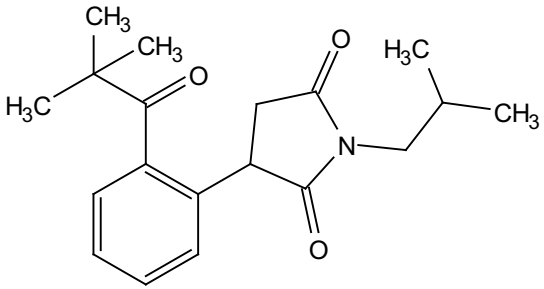
CH3
CH3
O
H3C
O
H3C
CH3
N
O

3ae

7.45
7.43
7.39
7.38
7.36
7.31
7.29
7.28
7.12
7.10
3.93
3.92
3.92
3.90
3.41
3.33
3.17
3.15
3.13
3.11
2.77
2.76
2.73
2.72
2.11
2.10
2.09
2.07
2.06
2.04
2.03
1.30
0.92
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0.90
0.90
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7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
1.00
1.05
1.05
0.99
1.05
2.27
1.10
1.09
1.09
9.27
6.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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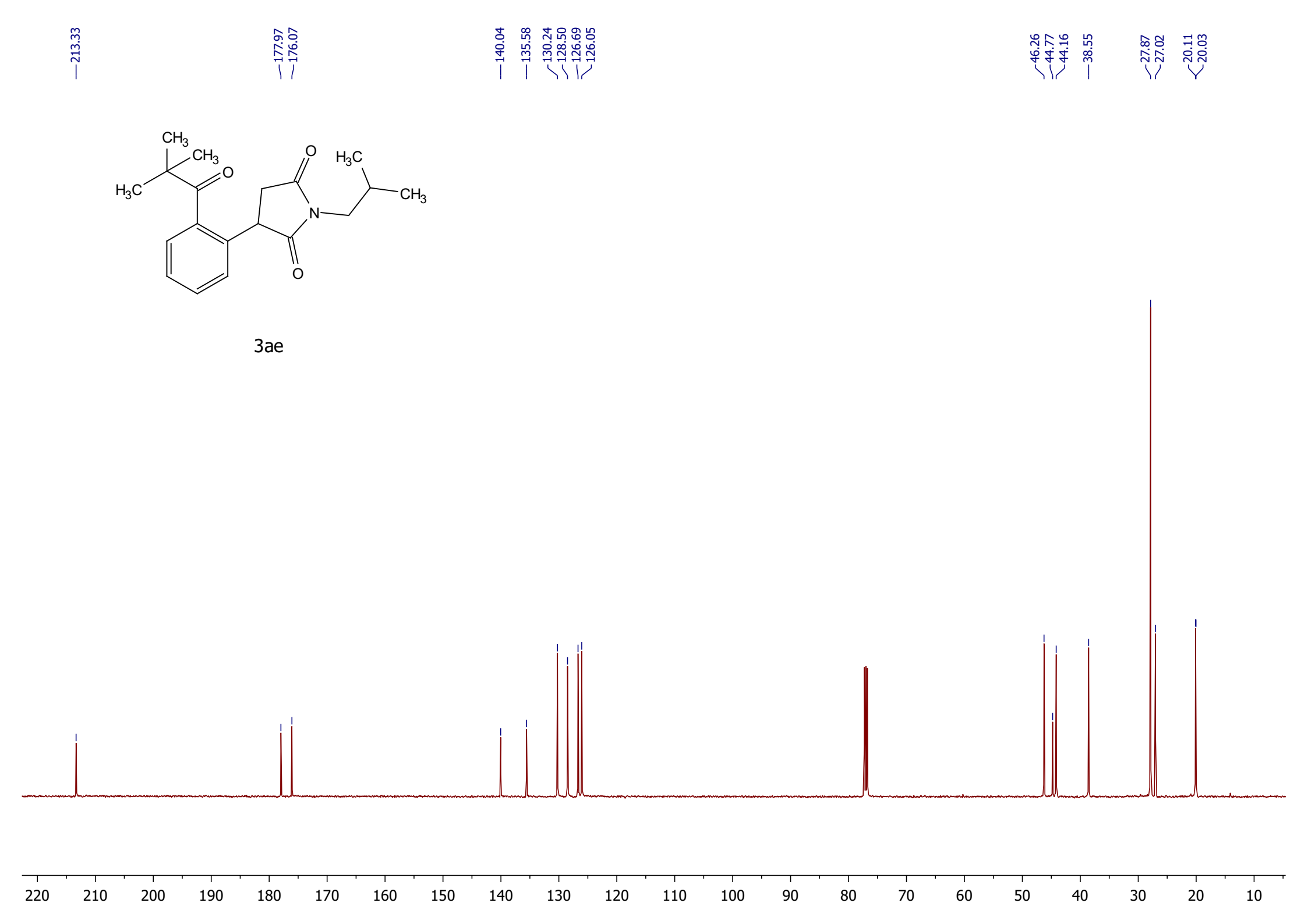
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126.05
46.26
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44.16
38.55
27.87
27.02
20.11
20.03
CH3
CH3
H3C
O
O
H3C
CH3
N
O
3ae
220
210
200
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160
150
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20
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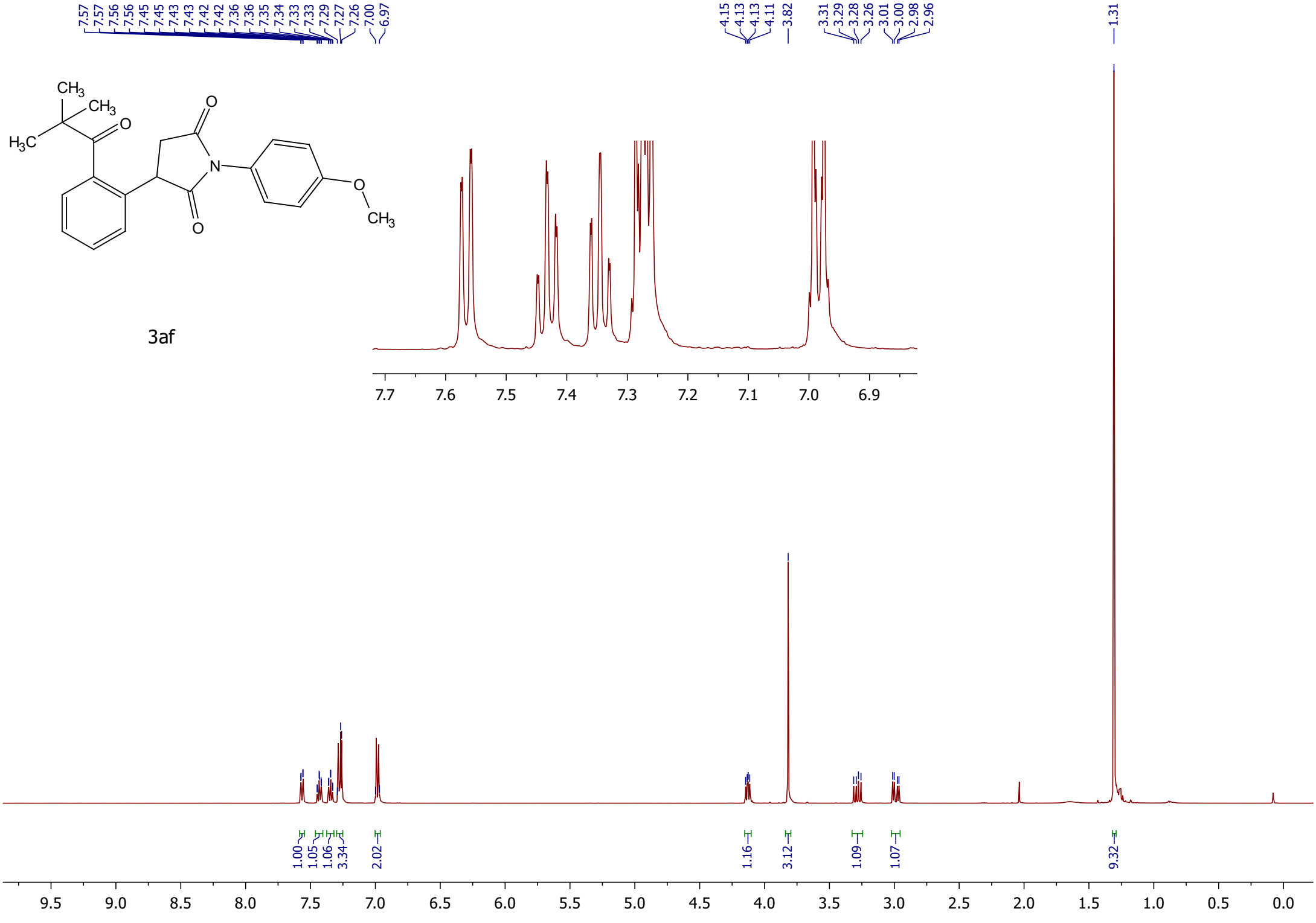
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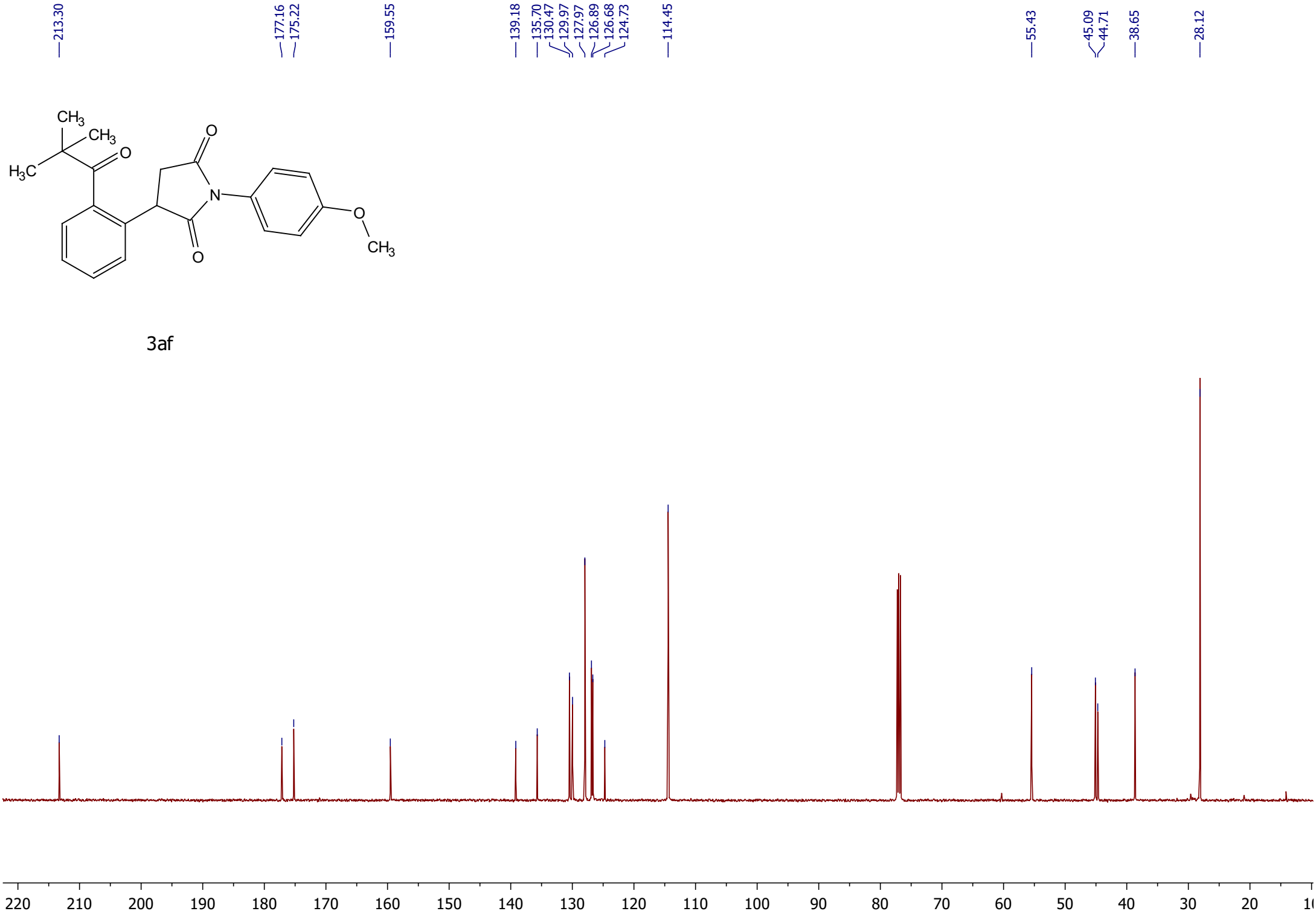
4.15 4.13 4.13 4.11 3.82 3.31 3.29 3.28 3.26 3.01 3.00 2.98 2.96 1.31
CH3 CH3 H3C O O N O CH3 O O
3af
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
1.00 1.05 1.06 3.34 2.02 1.16 3.12 1.09 1.07 9.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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129.97
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126.89
126.68
124.73
114.45
55.43
45.09
44.71
38.65
28.12
CH3
CH3
H3C
O
O
N
O
O
CH3
3af
220
210
200
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180
170
160
150
140
130
120
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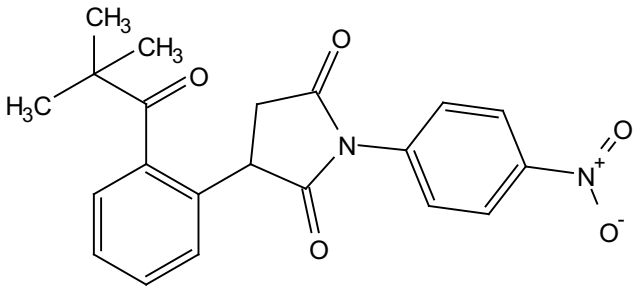
CH3
CH3
H3C
O
O
O
N
O
N+
O-

3ag

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8.31
7.68
7.65
7.48
7.47
7.46
7.46
7.45
7.44
7.40
7.40
7.38
7.38
7.37
7.37
7.30
7.28
4.22
4.21
4.20
4.19
3.35
3.33
3.32
3.30
3.08
3.06
3.04
3.03
1.28
2.18
3.22
1.00
1.00
0.99
1.03
1.06
1.05
9.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
2.5
2.0
1.5
1.0
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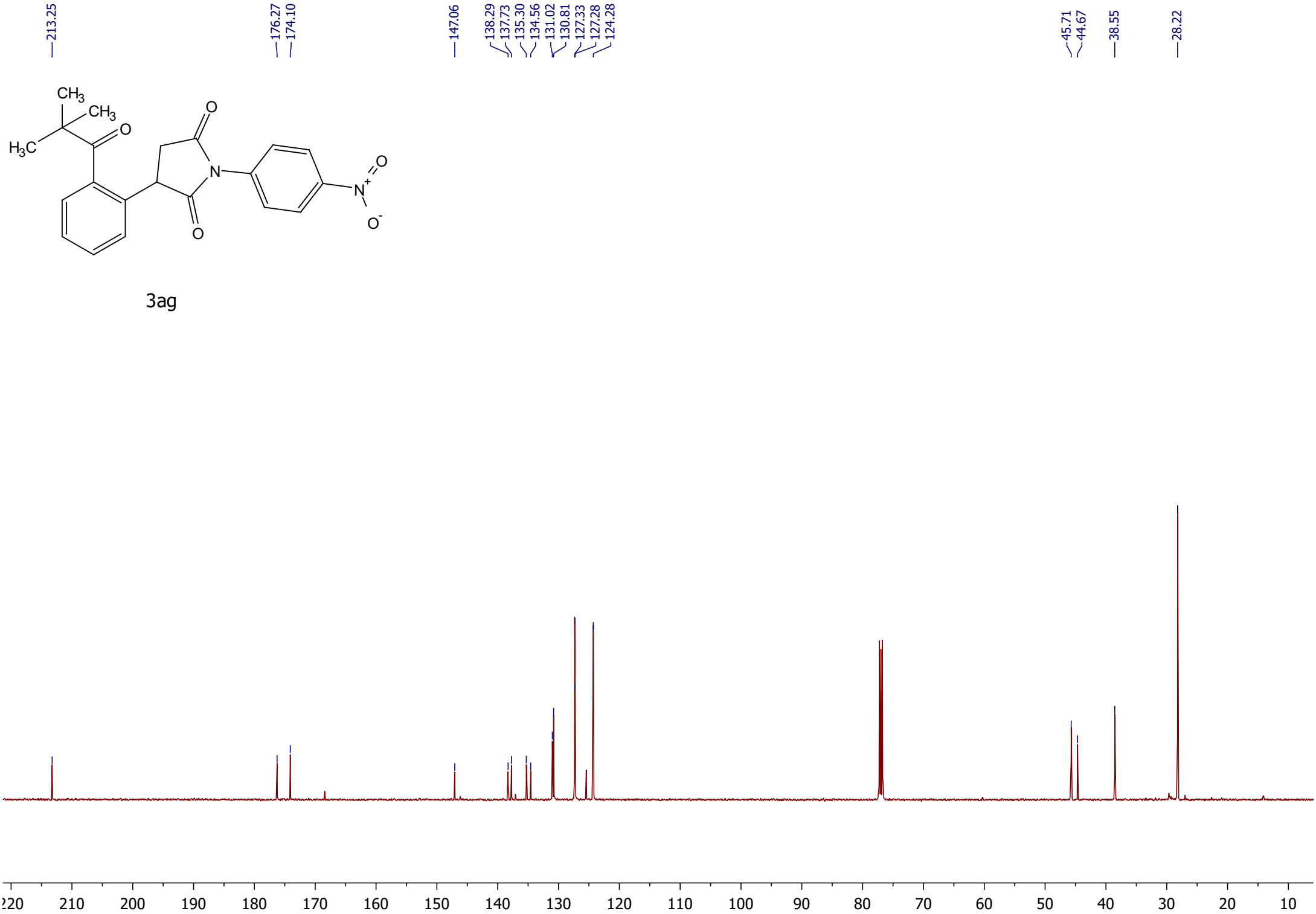
0.0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130.81
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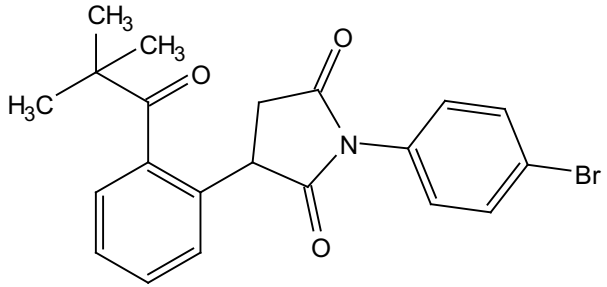
127.28
124.28
45.71
44.67
38.55
28.22
CH3
CH3
H3C
O
O
N
O
N+
O-
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

3ag


CH3
CH3
H3C
O
O
N
O
O
Br

3ah

7.62
7.59
7.47
7.45
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7.38
7.36
7.35
7.29
7.27
4.17
4.15
4.15
4.13
3.33
3.30
3.28
3.26
3.05
3.03
3.00
2.99
1.29
3.00
1.07
1.08
3.06
1.07
1.09
1.08
9.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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2.0
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1.0
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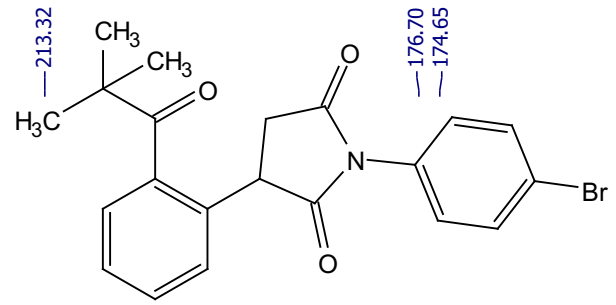
0.0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O
O
176.70
174.65
N
Br
O

3ah

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127.00
122.51
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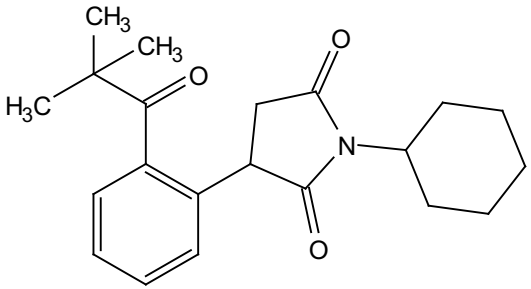
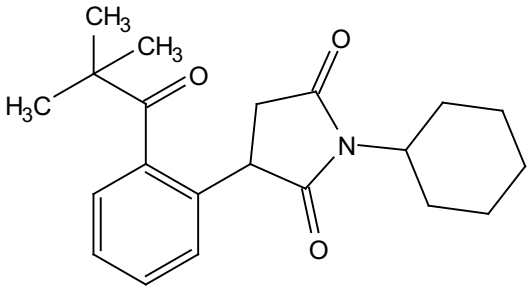
44.68
38.60
28.17



3ai


CH3
CH3
H3C
O
O
N
O
O

3ai

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128.39
126.63
126.03
52.01
44.76
43.95
38.57
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28.79
27.88
25.83
25.00
220
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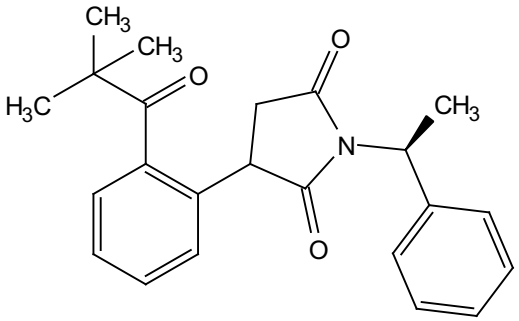

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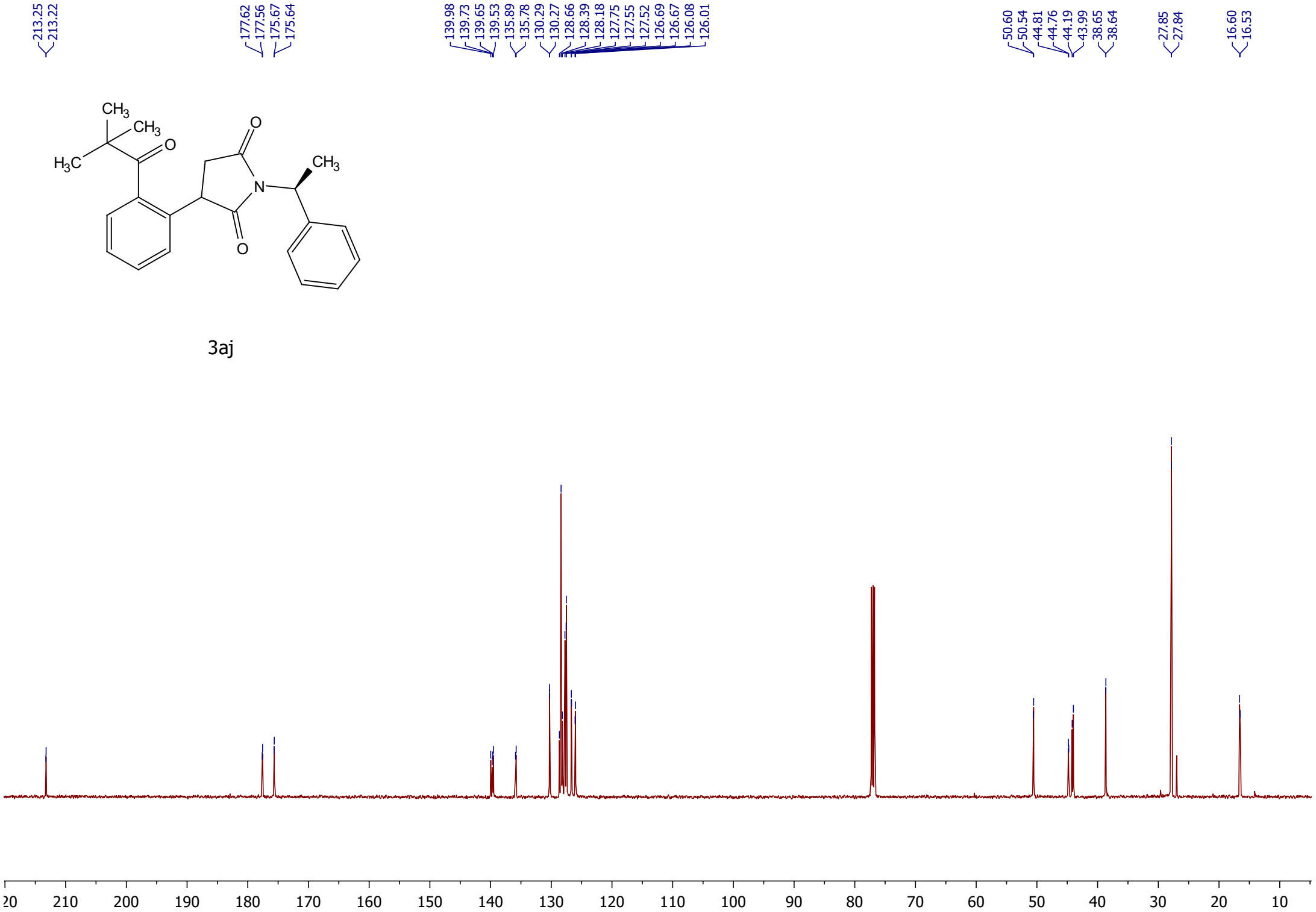
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127.52
126.69
126.67
126.08
126.01
50.60
50.54
44.81
44.76
44.19
43.99
38.65
38.64
27.85
27.84
16.60
16.53
CH3
CH3
H3C
O
O
N
CH3
O
3aj
220
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20
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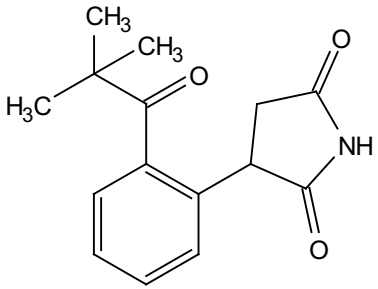
CH3
CH3
H3C
O
O
NH
O

3ak

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7.39
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7.31
7.30
7.23
7.21
7.21
4.02
4.00
3.99
3.98
3.23
3.20
3.18
3.16
2.86
2.84
2.81
2.80
1.31
1.00
1.00
1.07
1.06
1.04
1.01
1.10
1.09
9.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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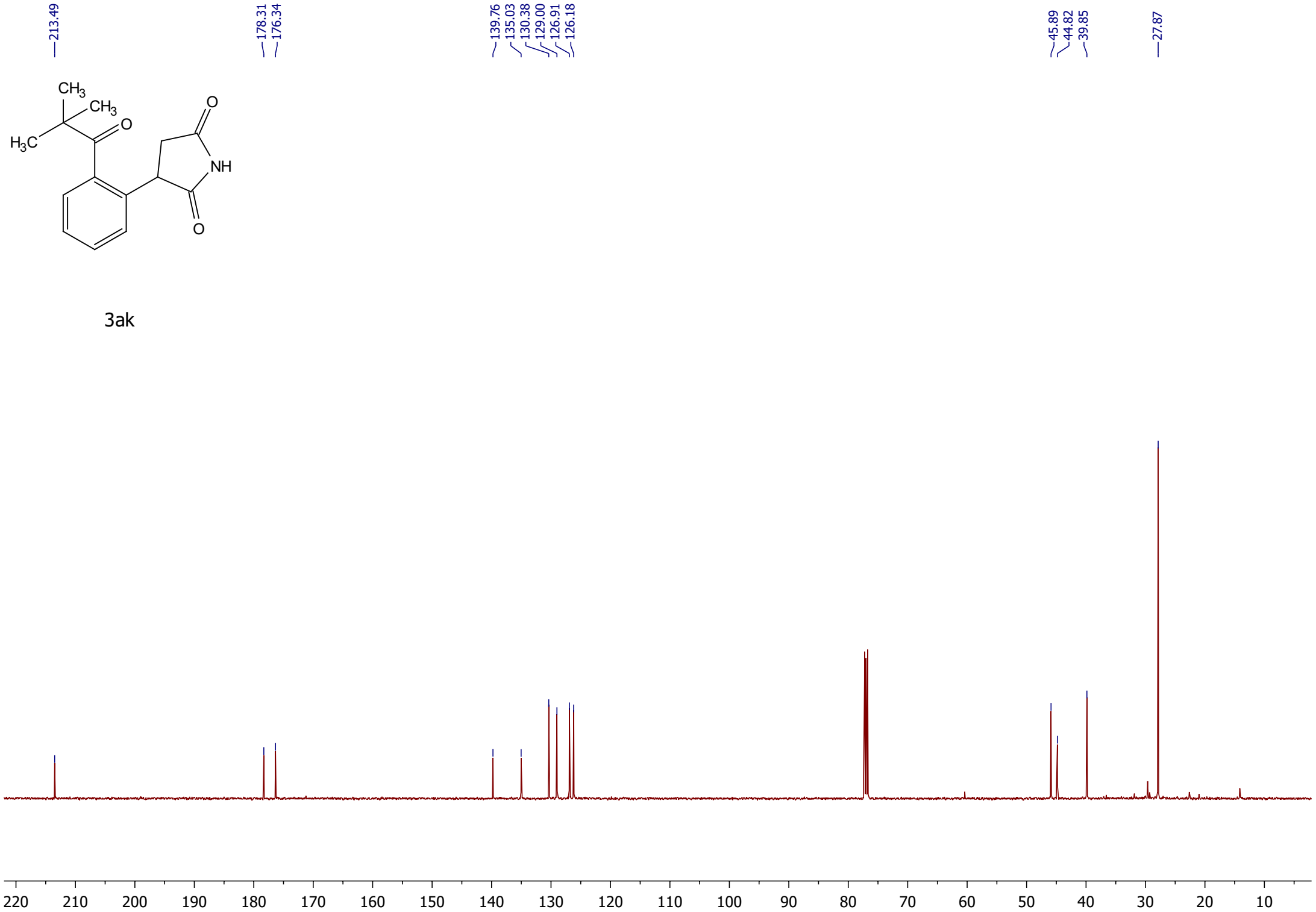
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44.82
39.85
27.87
CH3
CH3
H3C
O
O
NH
O
3ak
220
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20
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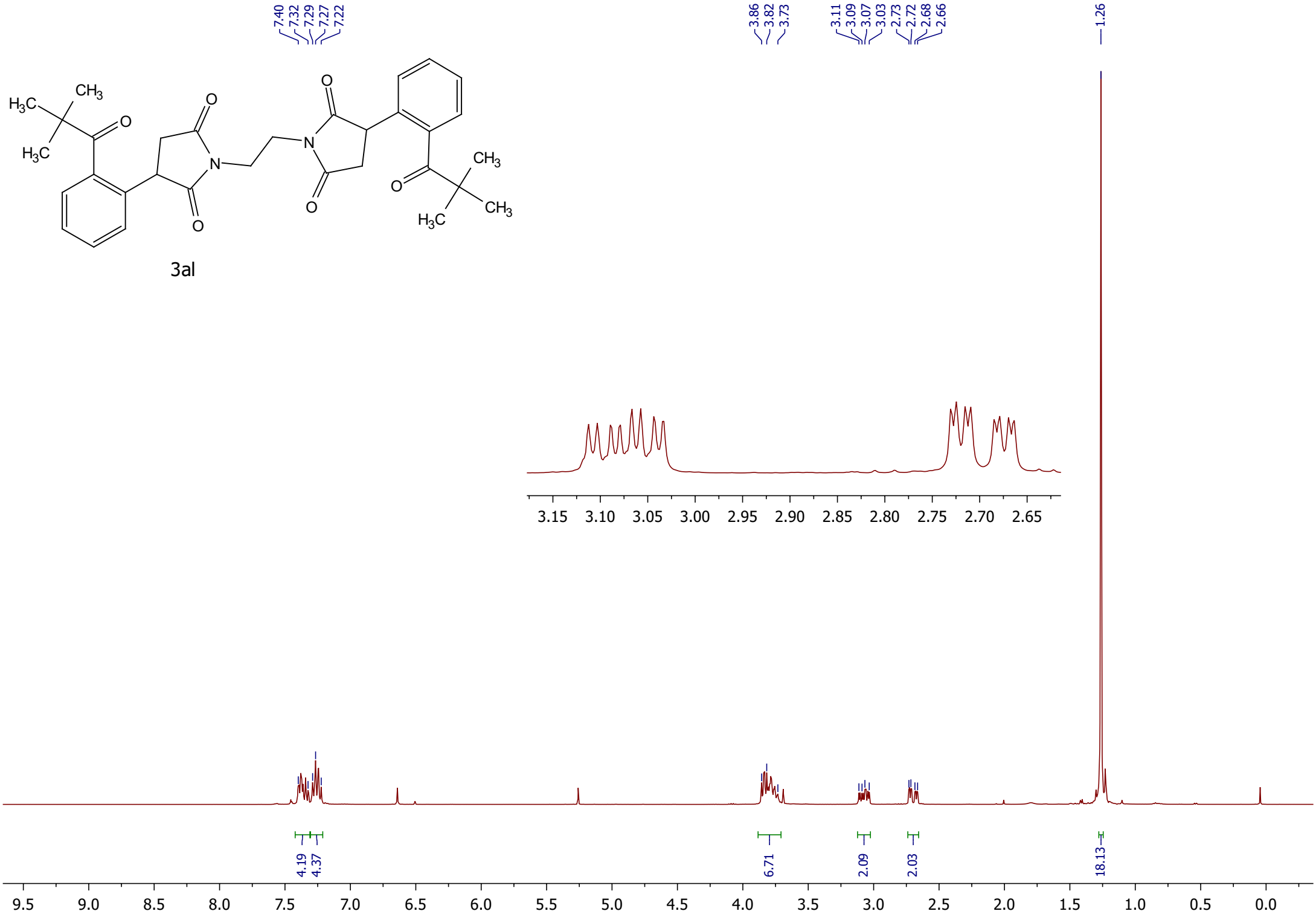
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3.82
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3.11
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3.07
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2.66
1.26
3.15
3.10
3.05
3.00
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2.85
2.80
2.75
2.70
2.65
4.19
4.37
6.71
2.09
2.03
18.13
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
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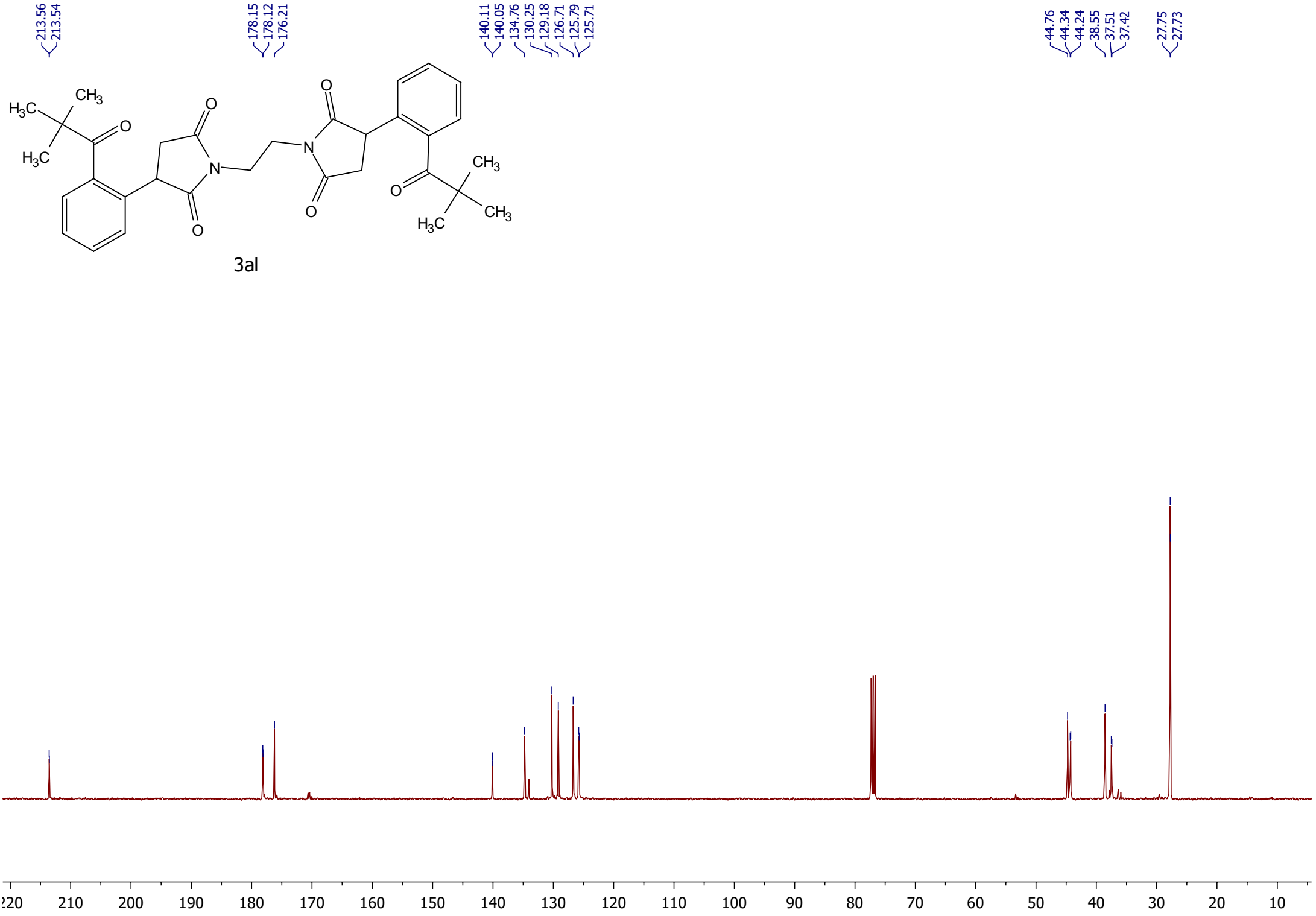
3al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125.79
125.71
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44.34
44.24
38.55
37.51
37.42
27.75
27.73
H3C
CH3
H3C
O
O
O
N
N
O
O
O
CH3
H3C
CH3
3al
220
210
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150
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130
120
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20
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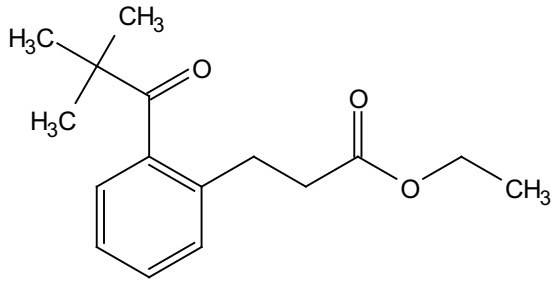
CH3
H3C
O
H3C
O
O
CH3

3am

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7.16
4.15
4.13
4.11
4.09
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2.77
2.76
2.62
2.61
2.58
1.26
1.25
1.23
1.21
1.00
3.19
2.07
2.20
2.21
9.40
3.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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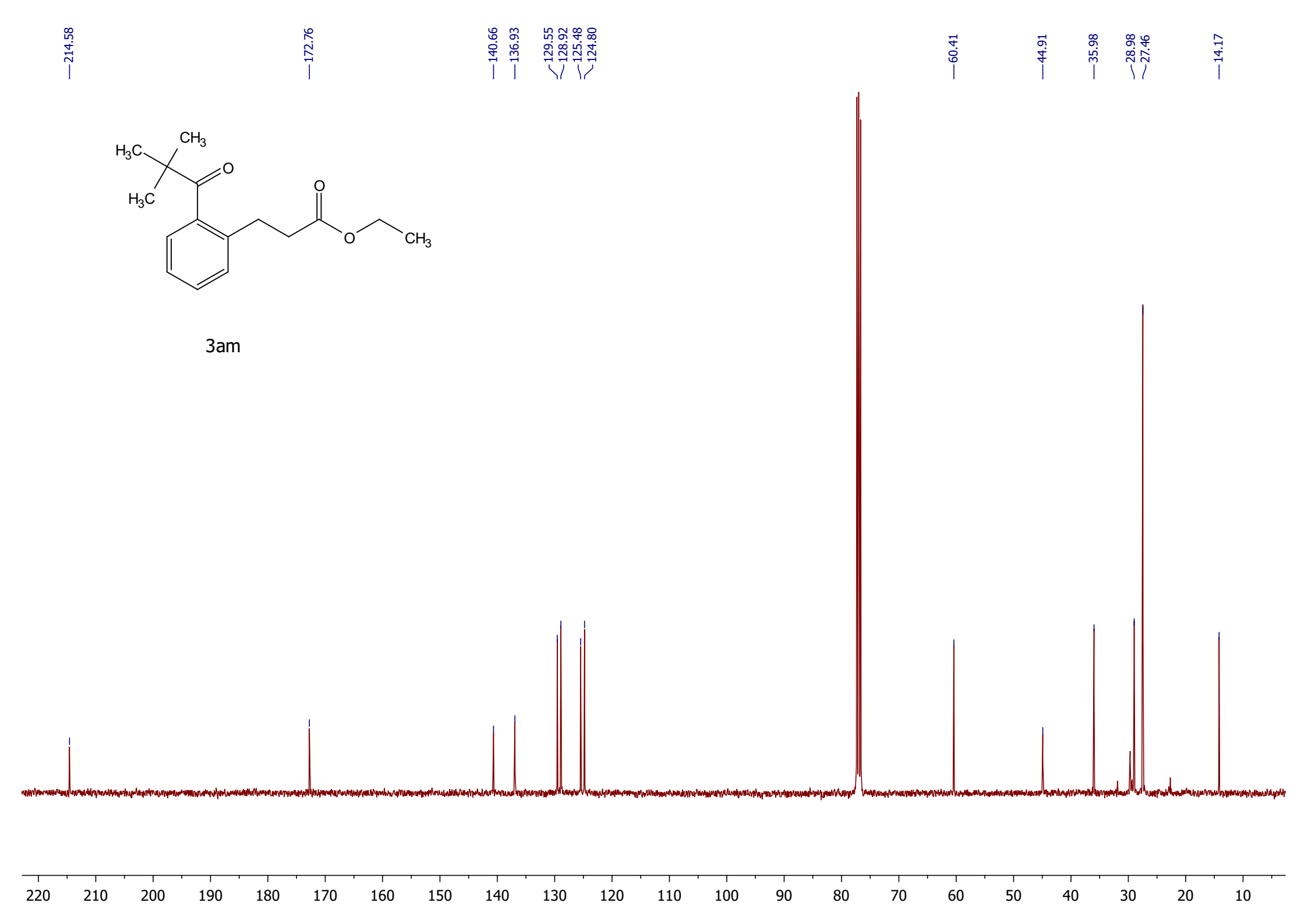
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44.91
35.98
28.98
27.46
14.17
CH3
H3C
O
H3C
O
O
CH3
3am
220
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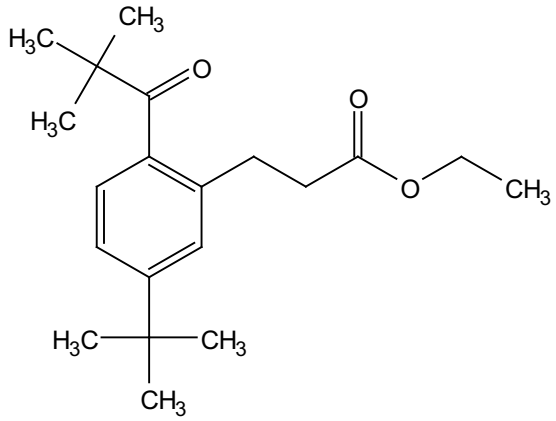
CH3
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O
H3C
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O
CH3
H3C
CH3
CH3

3an

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7.24
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4.15
4.13
4.11
4.09
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2.78
2.77
2.63
2.61
2.59
1.30
1.26
1.25
1.24
1.22
1.00
1.04
1.02
2.11
2.21
2.18
9.23
9.15
3.45
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8.0
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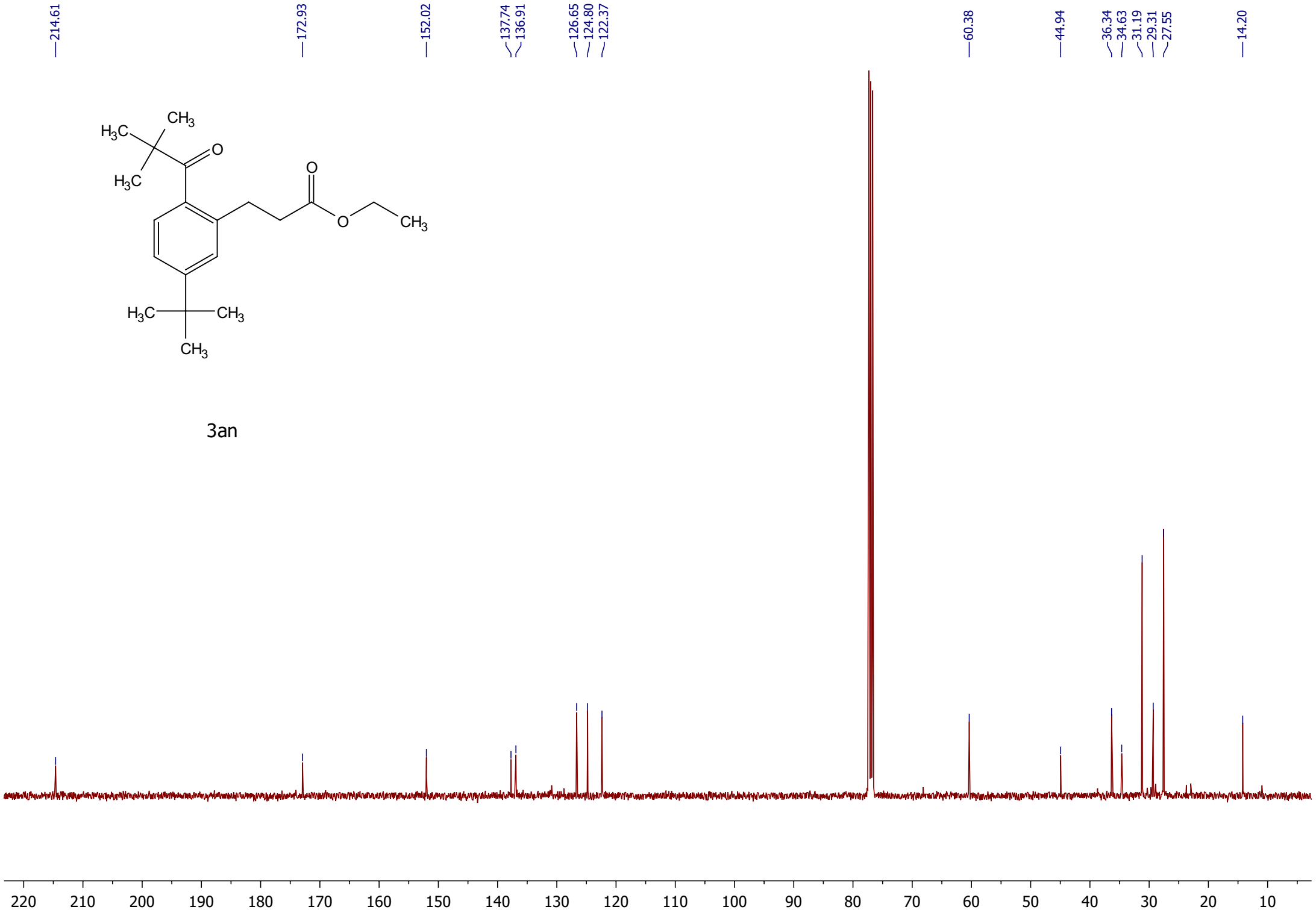
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29.31
27.55
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H3C
CH3
O
H3C
O
O
CH3
H3C
CH3
CH3
220
210
200
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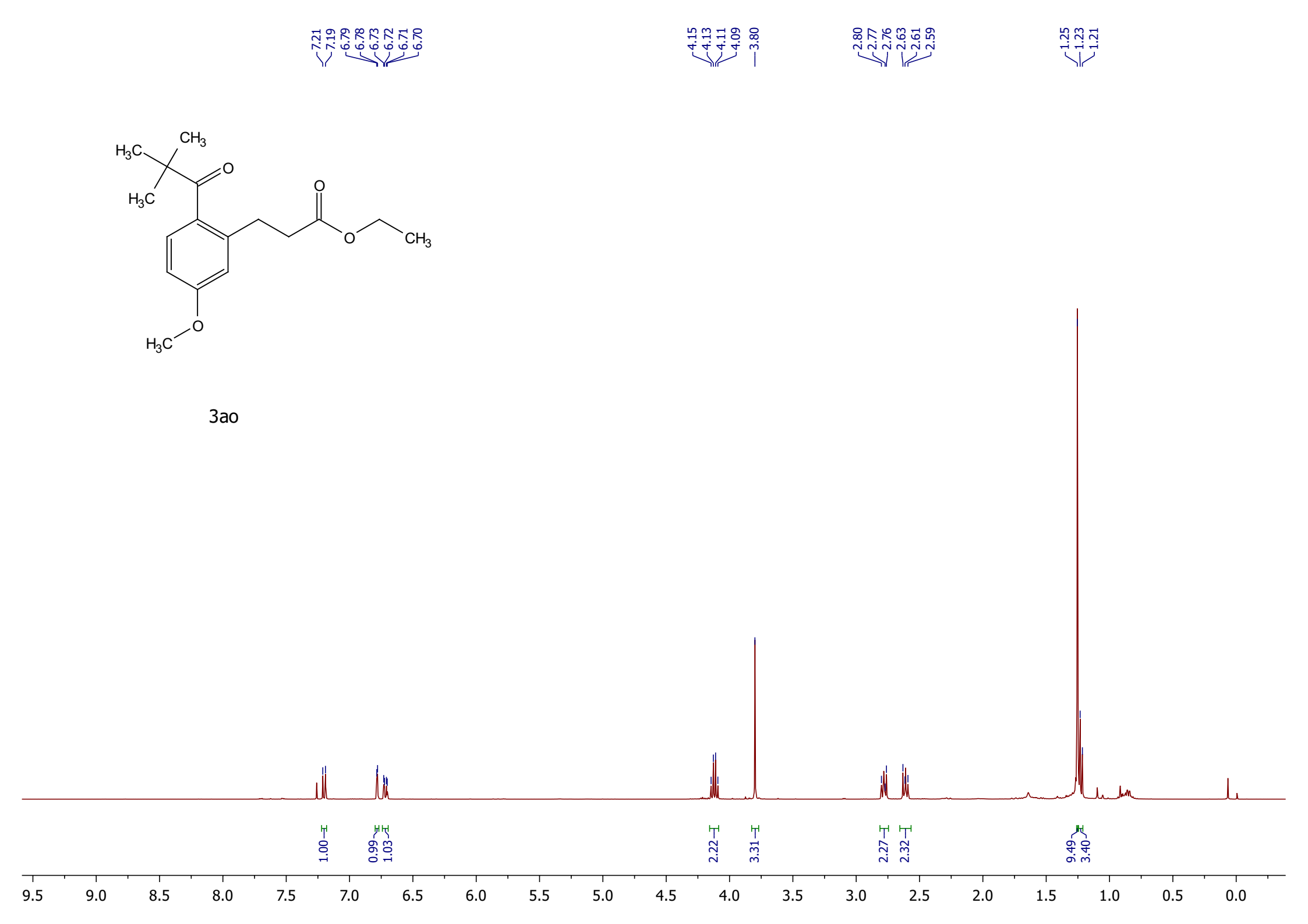
10

3an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4.09
3.80
2.80
2.77
2.76
2.63
2.61
2.59
1.25
1.23
1.21
CH3
H3C
O
H3C
O
O
CH3
O
H3C
1.00
0.99
1.03
2.22
3.31
2.27
2.32
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8.0
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6.0
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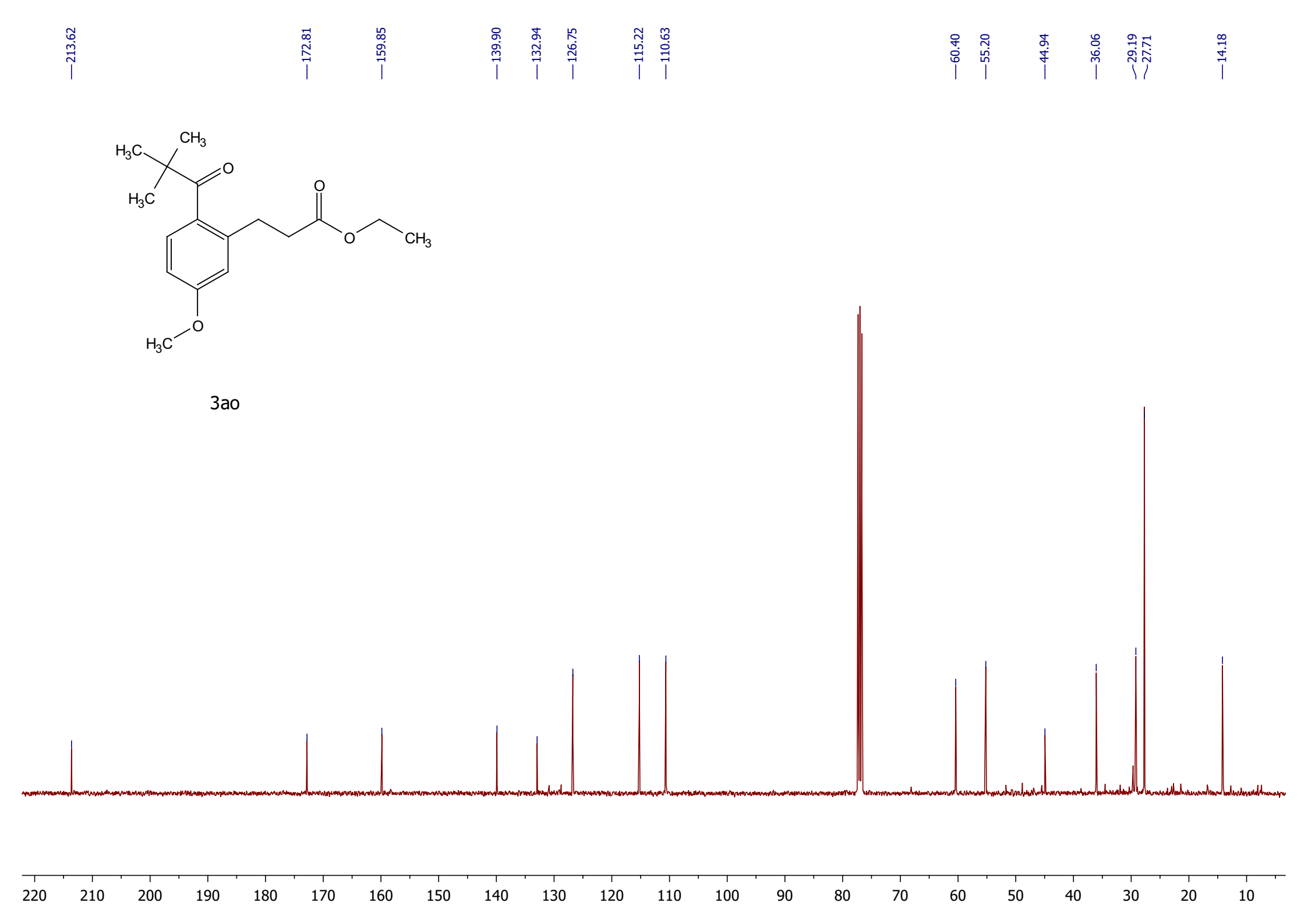
0.0

3ao


213.62
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44.94
36.06
29.19
27.71
14.18
CH3
H3C
O
H3C
O
O
CH3
O
H3C
3ao
220
210
200
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150
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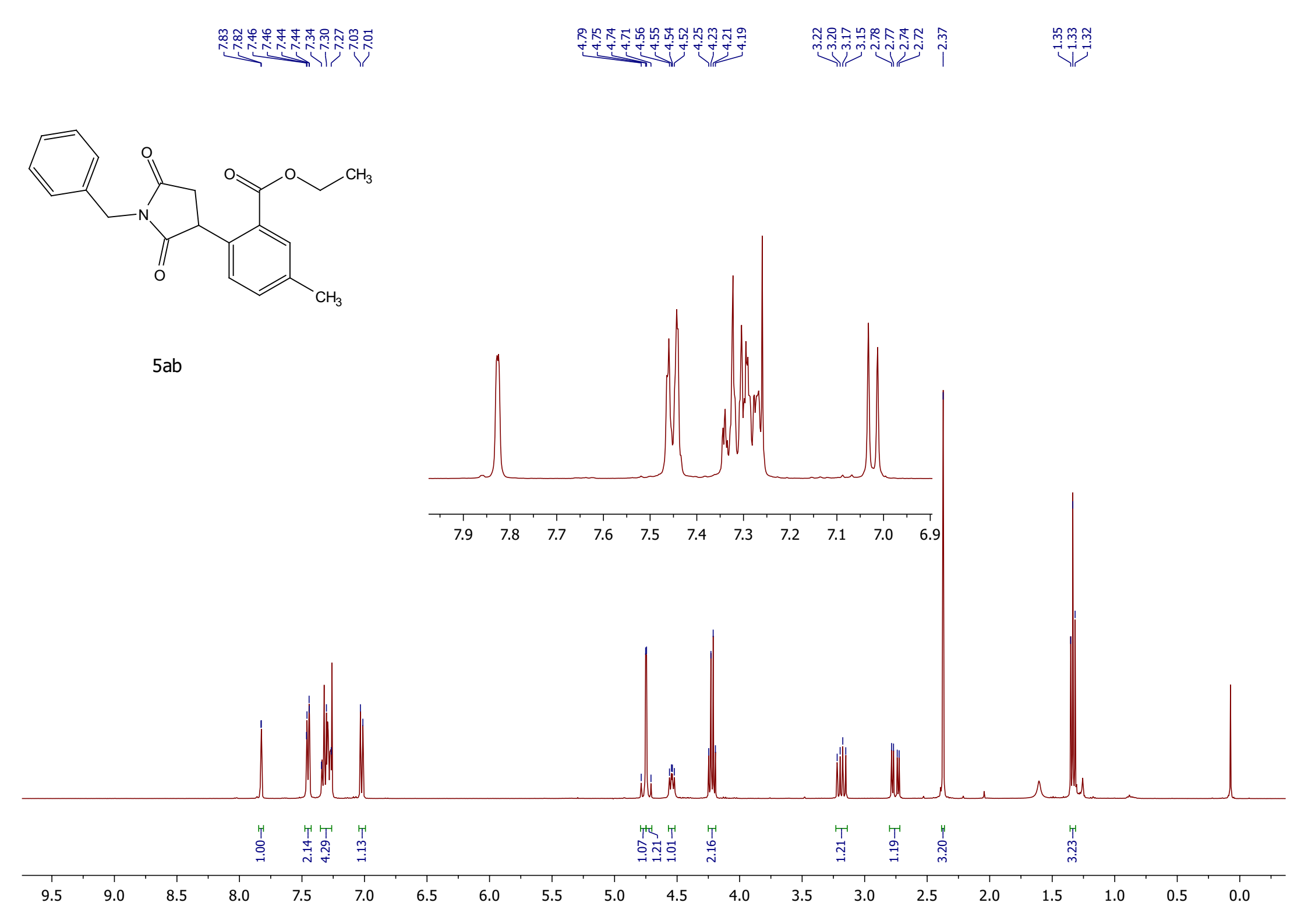
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7.82
7.46
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7.44
7.34
7.30
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7.01
4.79
4.75
4.74
4.71
4.56
4.55
4.54
4.52
4.25
4.23
4.21
4.19
3.22
3.20
3.17
3.15
2.78
2.77
2.74
2.72
2.37
1.35
1.33
1.32
O
O
O
O
N
O
CH3
CH3
5ab
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
1.00
2.14
4.29
1.13
1.07
1.21
1.01
2.16
1.21
1.19
3.20
3.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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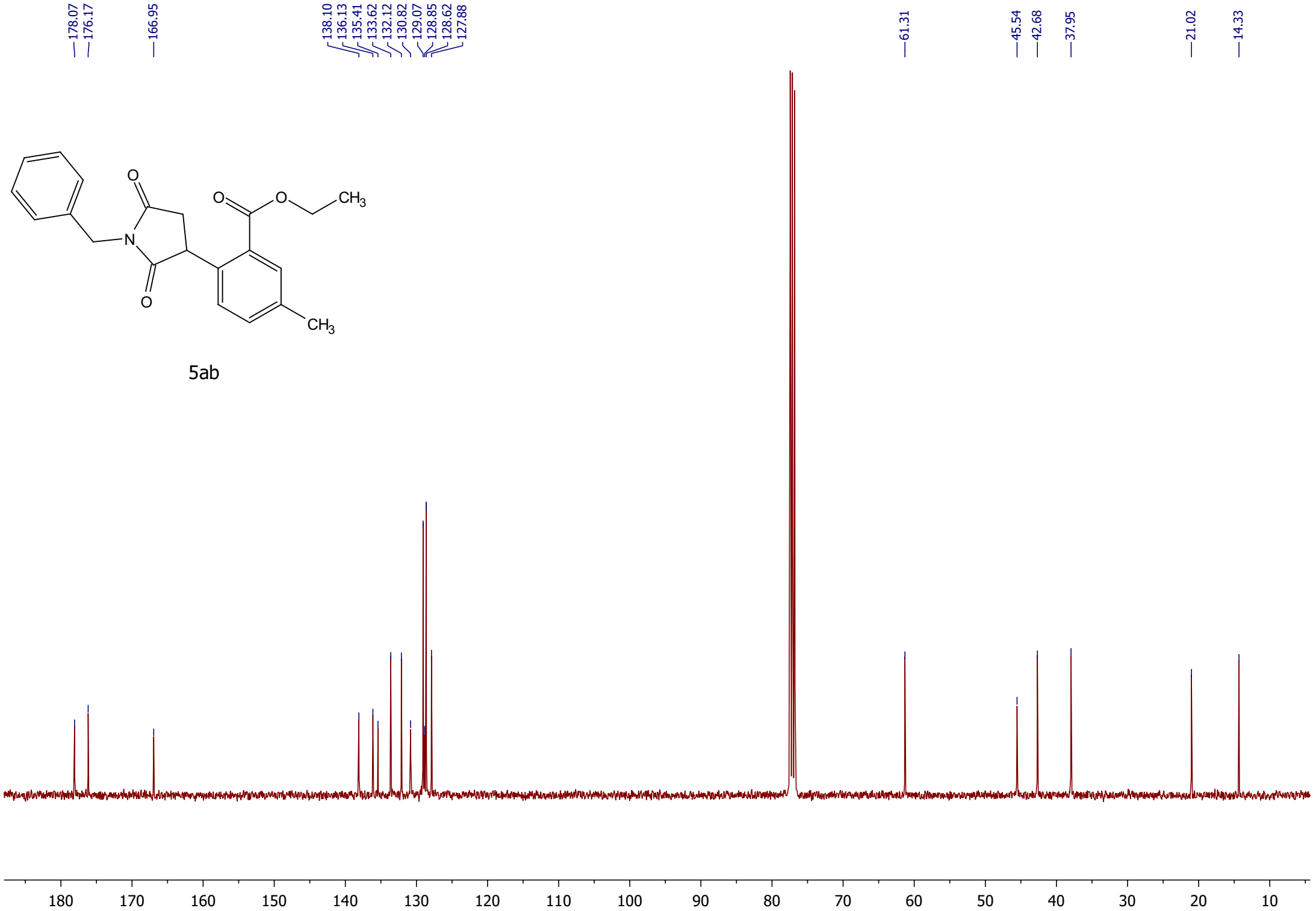
0.0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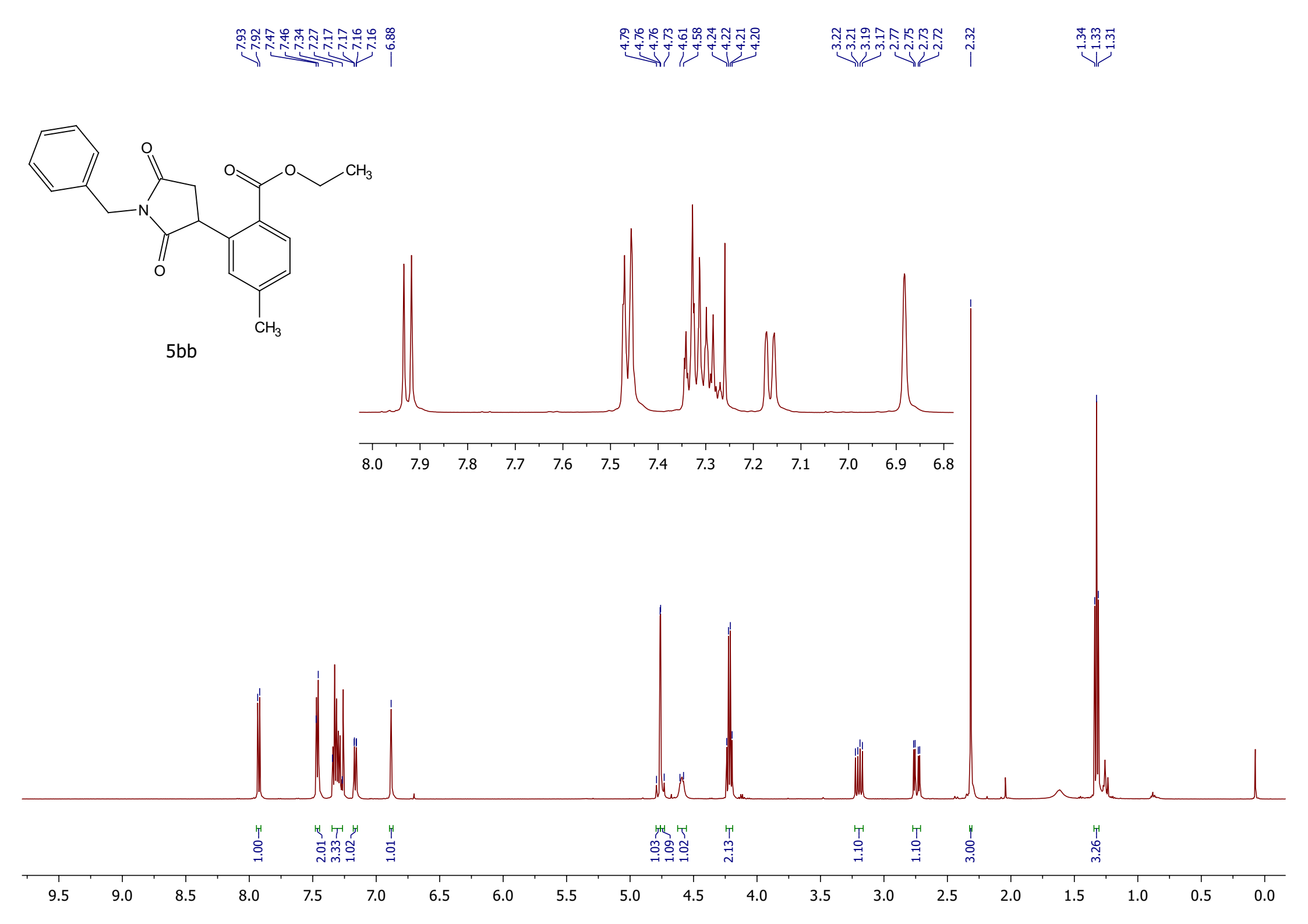
176.17
166.95
138.10
136.13
135.41
133.62
132.12
130.82
129.07
128.85
128.62
127.88
61.31
45.54
42.68
37.95
21.02
14.33
O
O
O
O
N
CH3
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

5ab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7.92
7.47
7.46
7.34
7.27
7.17
7.17
7.16
7.16
6.88
4.79
4.76
4.76
4.73
4.61
4.58
4.24
4.22
4.21
4.20
3.22
3.21
3.19
3.17
2.77
2.75
2.73
2.72
2.32
1.34
1.33
1.31
O
O
O
O
N
CH3
CH3
5bb
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
1.00
2.01
3.33
1.02
1.01
1.03
1.09
1.02
2.13
1.10
1.10
3.00
3.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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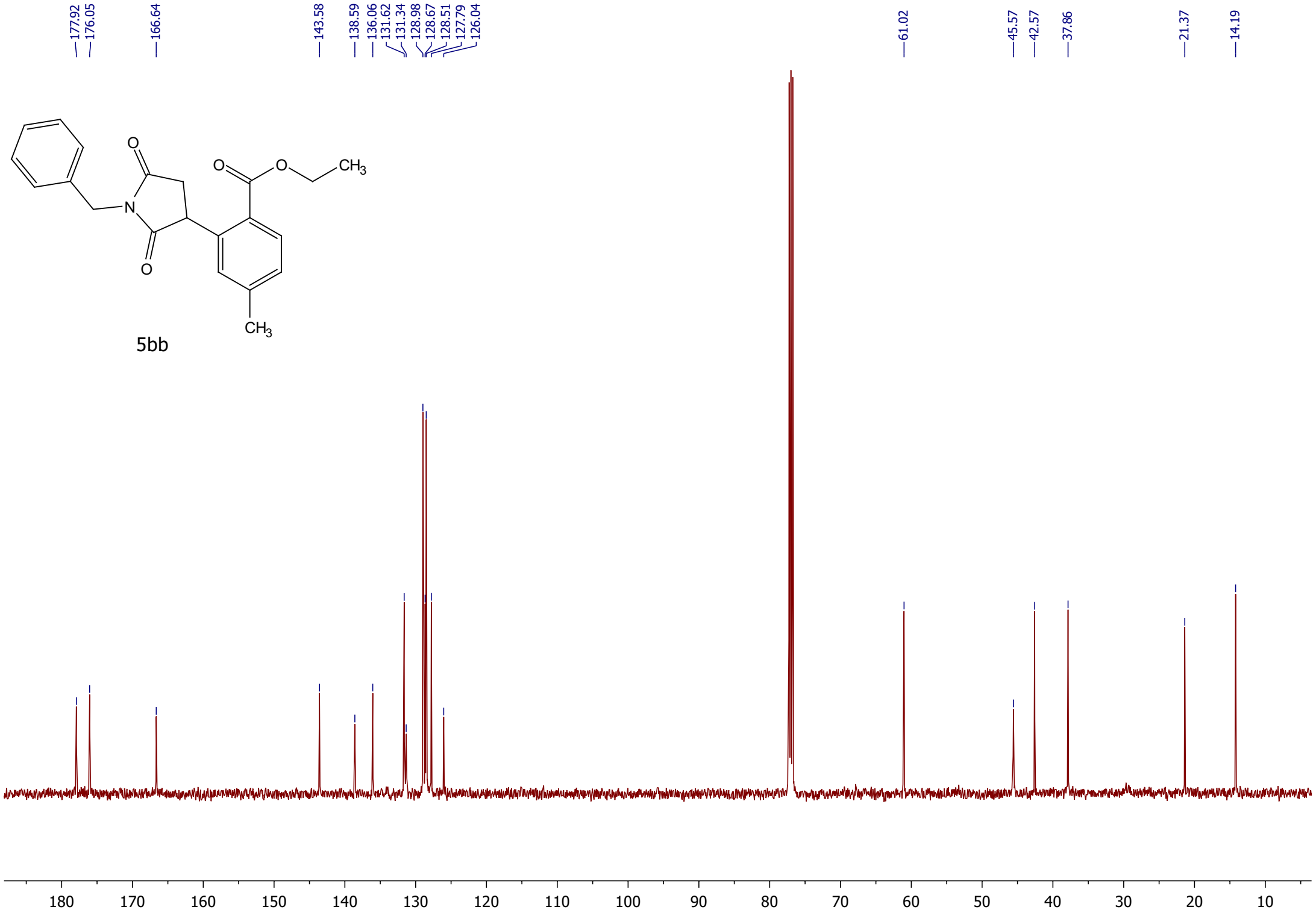
3.0
2.5
2.0
1.5
1.0
0.5
0.0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176.05
166.64
143.58
138.59
136.06
131.62
131.34
128.98
128.67
128.51
127.79
126.04
61.02
45.57
42.57
37.86
21.37
14.19
O
O
O
O
N
CH3
CH3
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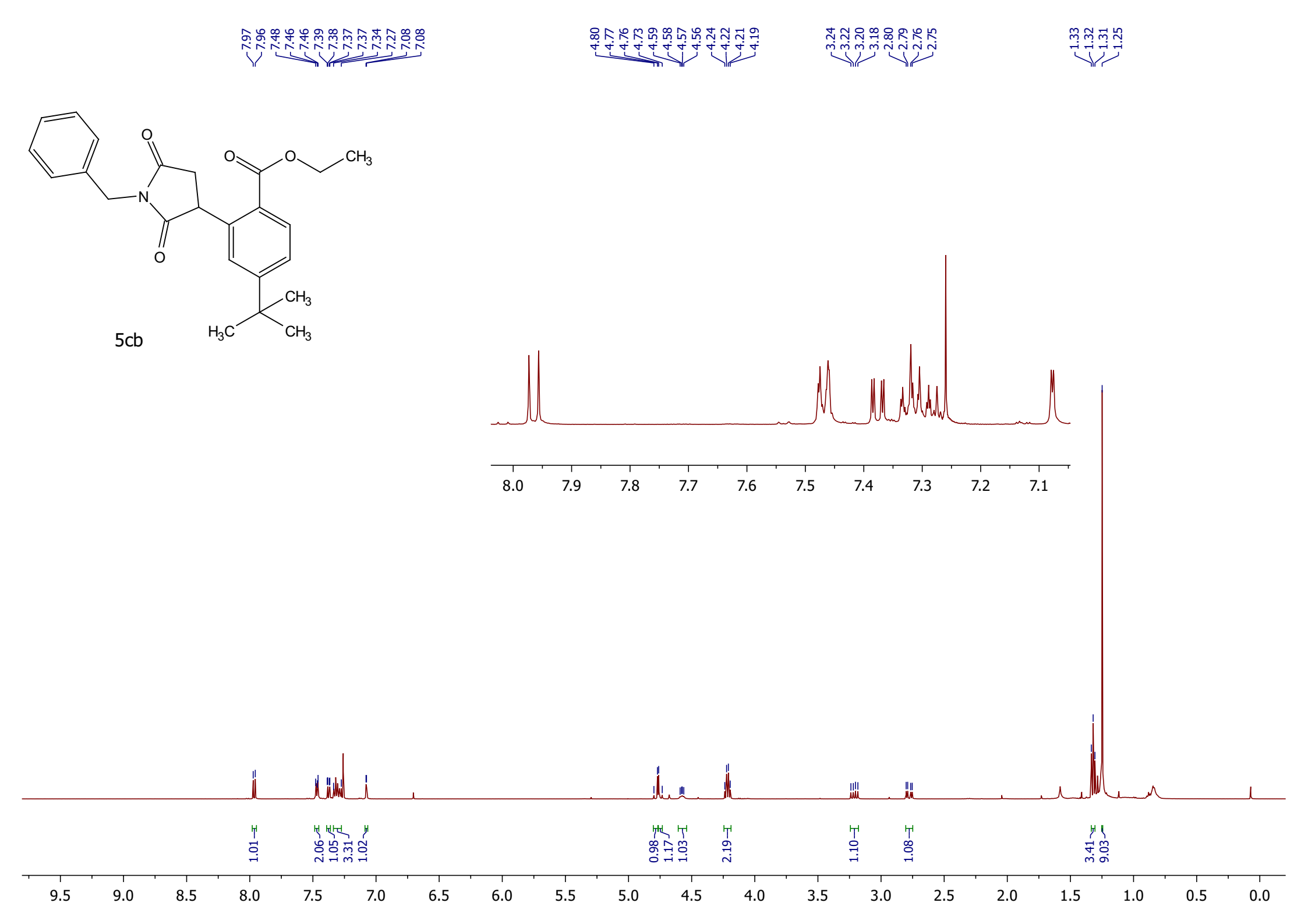
30
20
10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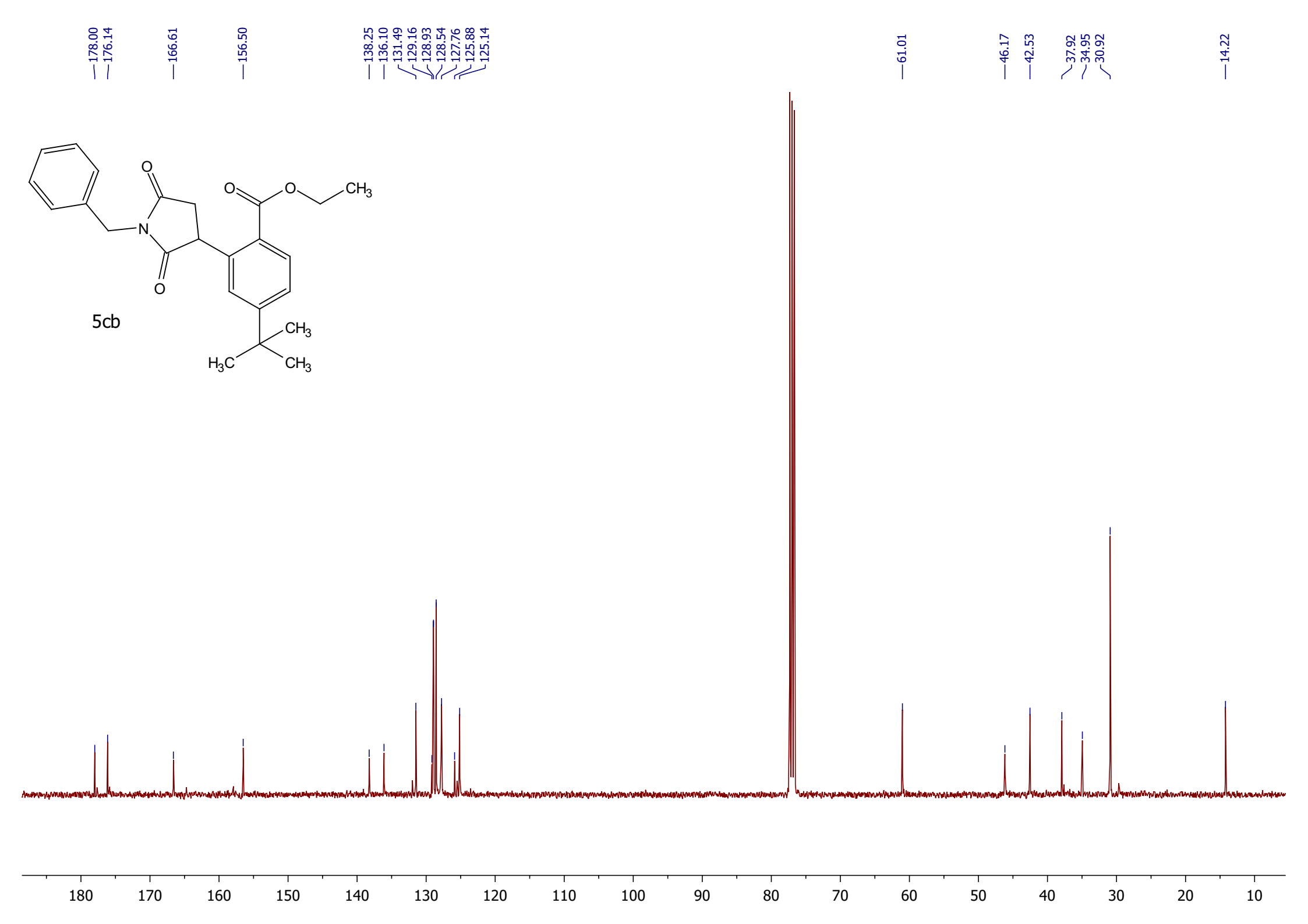
7.96
7.48
7.46
7.46
7.39
7.38
7.37
7.37
7.34
7.27
7.08
7.08
4.80
4.77
4.76
4.73
4.59
4.58
4.57
4.56
4.24
4.22
4.21
4.19
3.24
3.22
3.20
3.18
2.80
2.79
2.76
2.75
1.33
1.32
1.31
1.25
O
O
O
O
N
CH3
CH3
H3C
CH3
5cb
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
1.01
2.06
1.05
3.31
1.02
0.98
1.17
1.03
2.19
1.10
1.08
3.41
9.03
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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136.10
131.49
129.16
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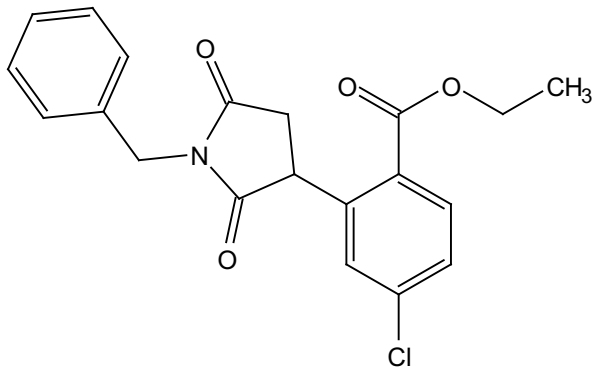
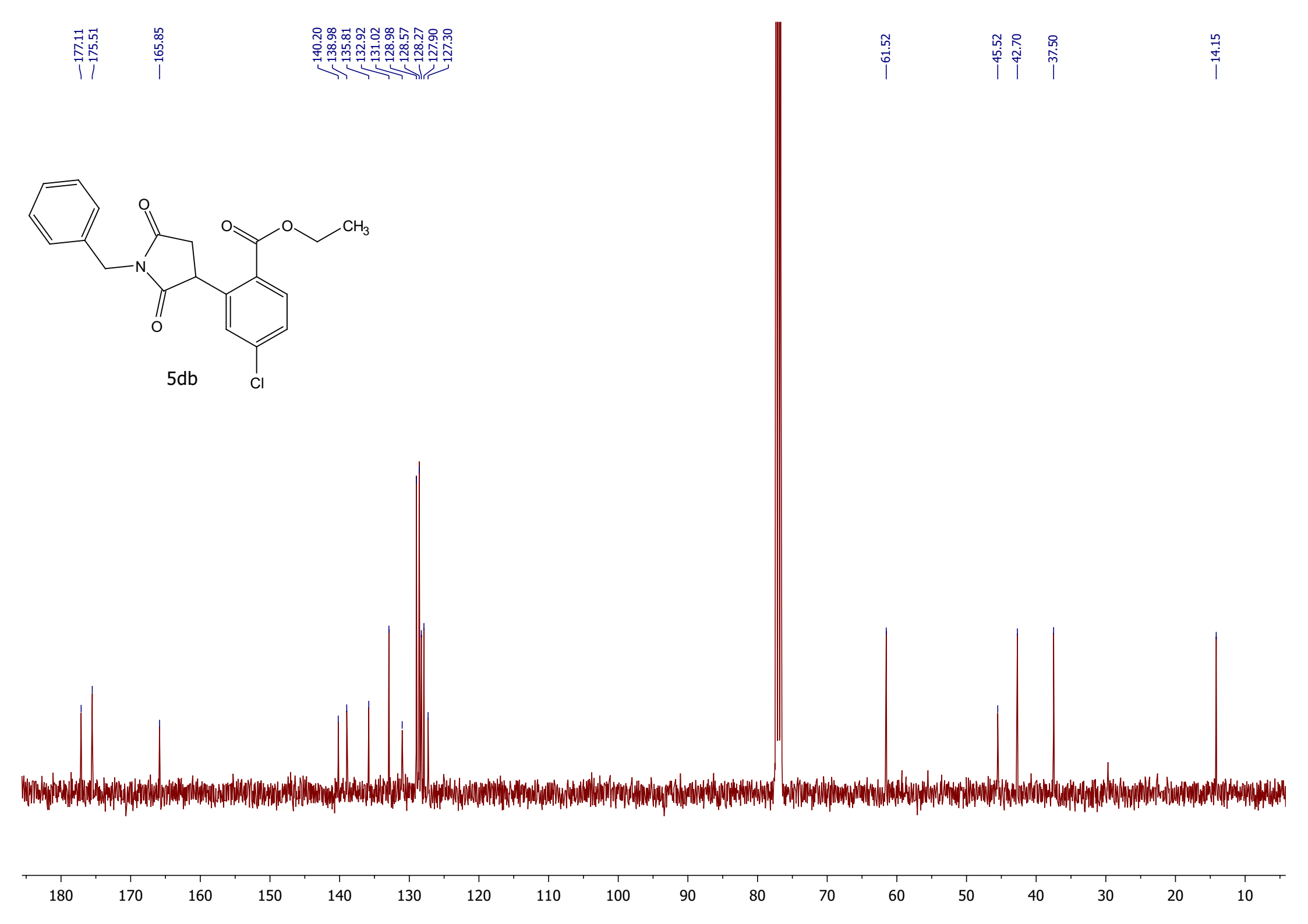
128.54
127.76
125.88
125.14
61.01
46.17
42.53
37.92
34.95
30.92
14.22
O
O
O
O
CH3
N
O
5cb
CH3
H3C
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


O
O
O
O
CH3
N
O
Cl

5db

7.97
7.95
7.45
7.43
7.36
7.32
7.28
7.13
7.12
4.78
4.74
4.74
4.70
4.56
4.54
4.54
4.52
4.23
4.21
4.19
4.18
3.23
3.20
3.18
3.16
2.78
2.76
2.73
2.72
1.33
1.31
1.29
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
1.00
2.13
4.33
1.08
1.13
1.06
1.14
2.20
1.14
1.20
3.19
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


177.11
175.51
165.85
140.20
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135.81
132.92
131.02
128.98
128.57
128.27
127.90
127.30
61.52
45.52
42.70
37.50
14.15
O
O
O
O
N
CH3
Cl
5db
180
170
160
150
140
130
120
110
100
90
80
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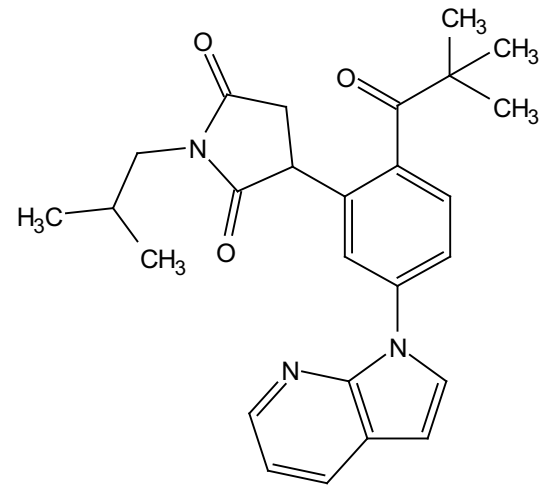
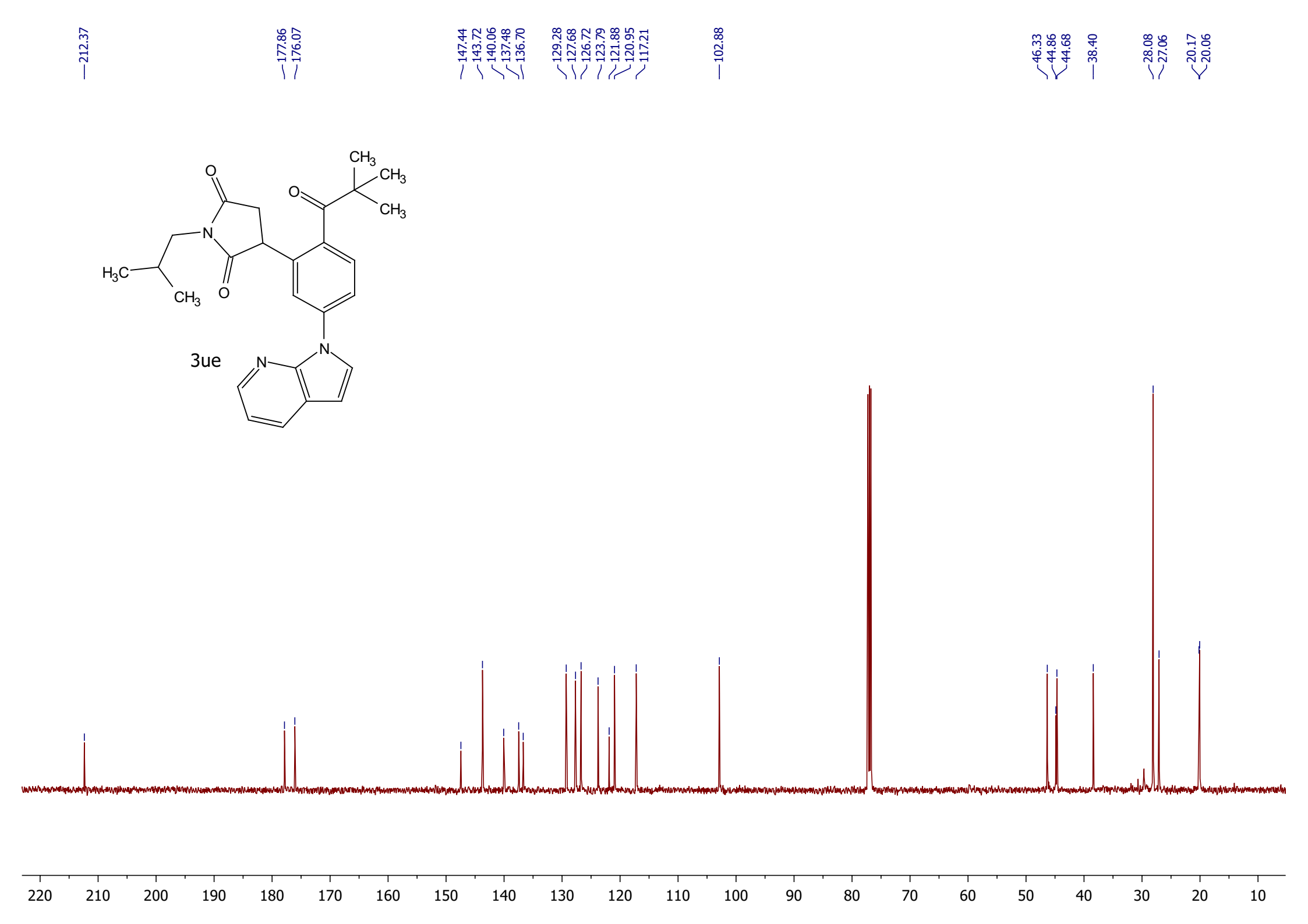
50
40
30
20
10



3ue


212.37
177.86
176.07
147.44
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140.06
137.48
136.70
129.28
127.68
126.72
123.79
121.88
120.95
117.21
102.88
46.33
44.86
44.68
38.40
28.08
27.06
20.17
20.06
3ue
220
210
200
190
180
170
160
150
140
130
120
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100
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80
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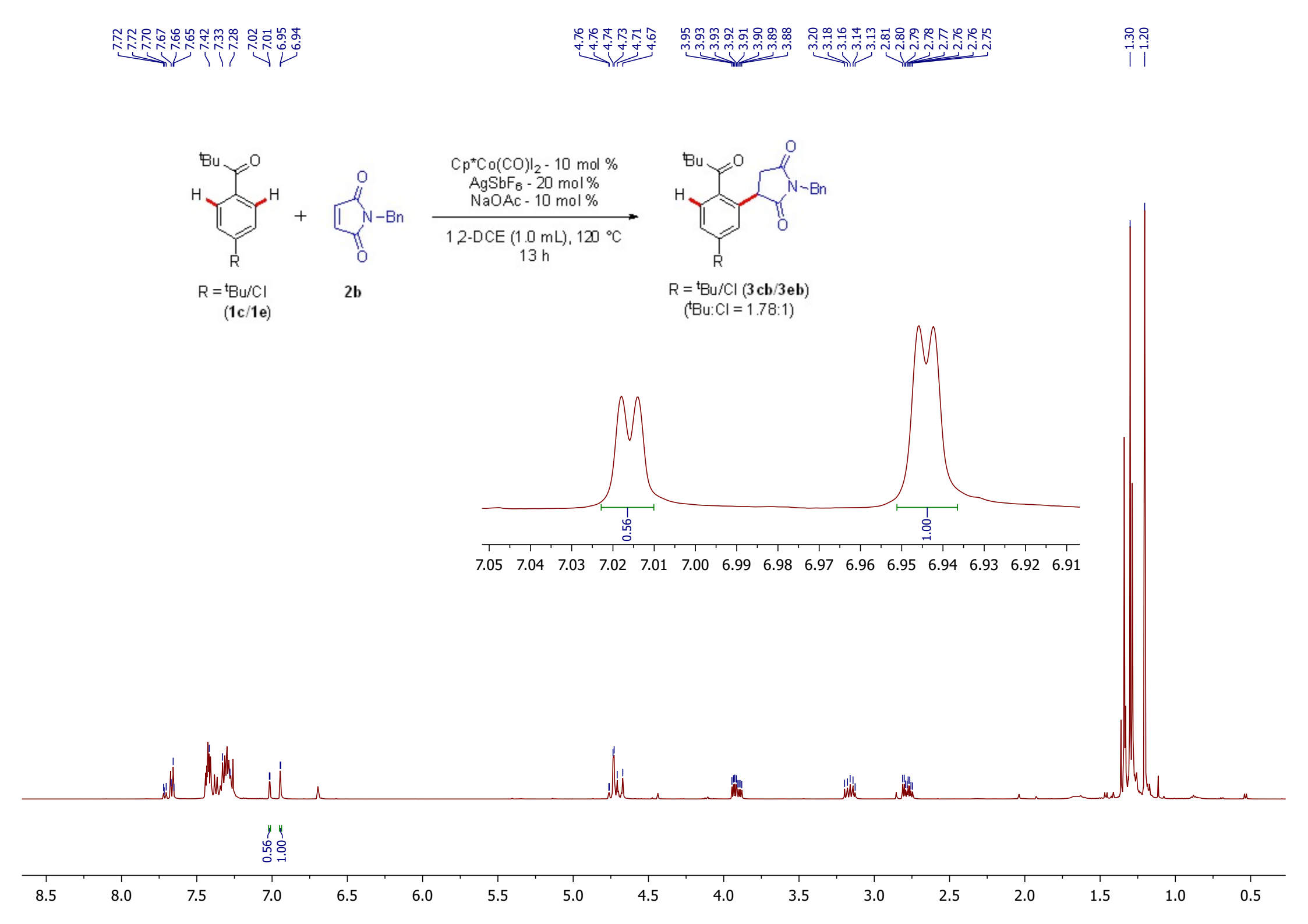
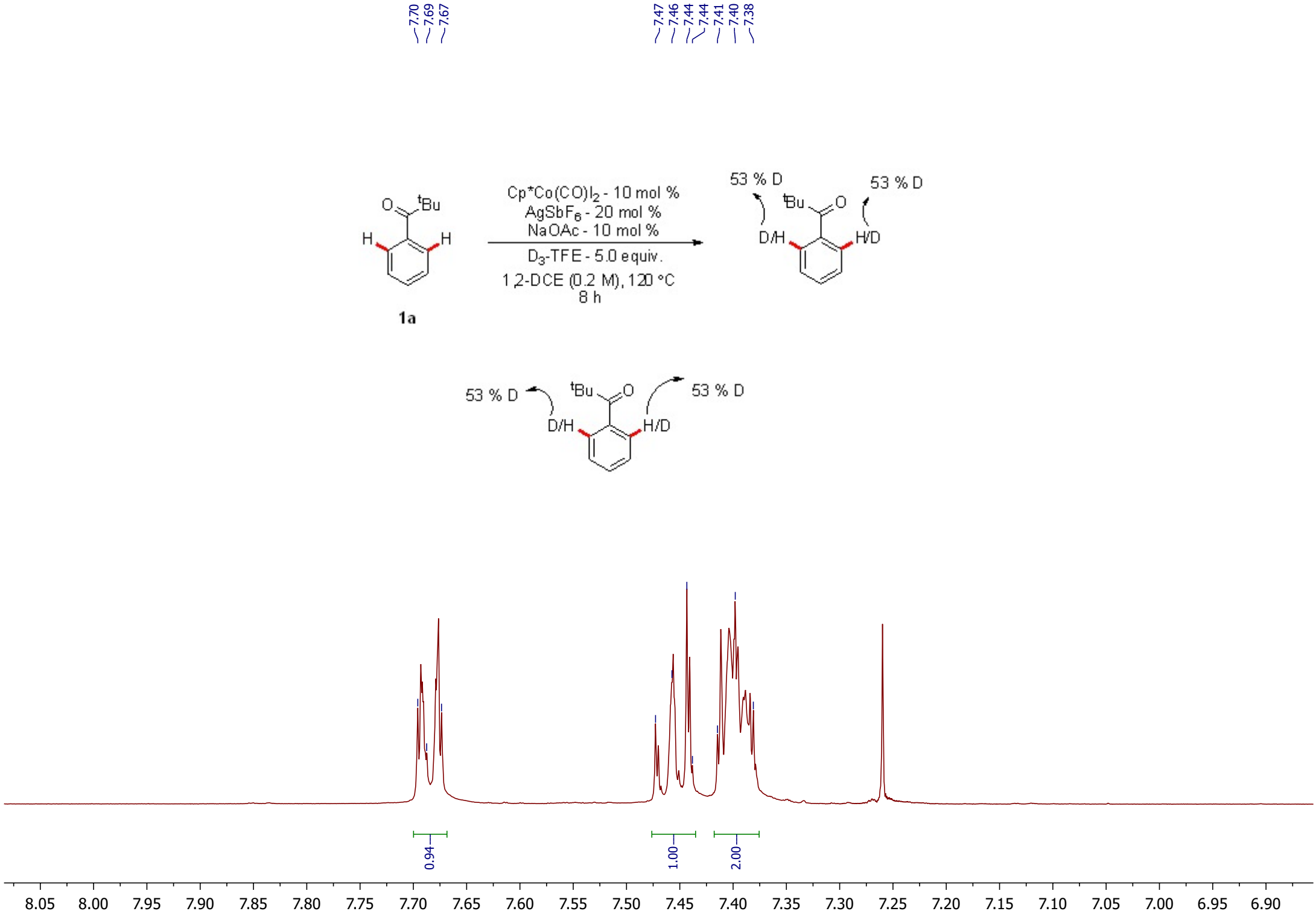
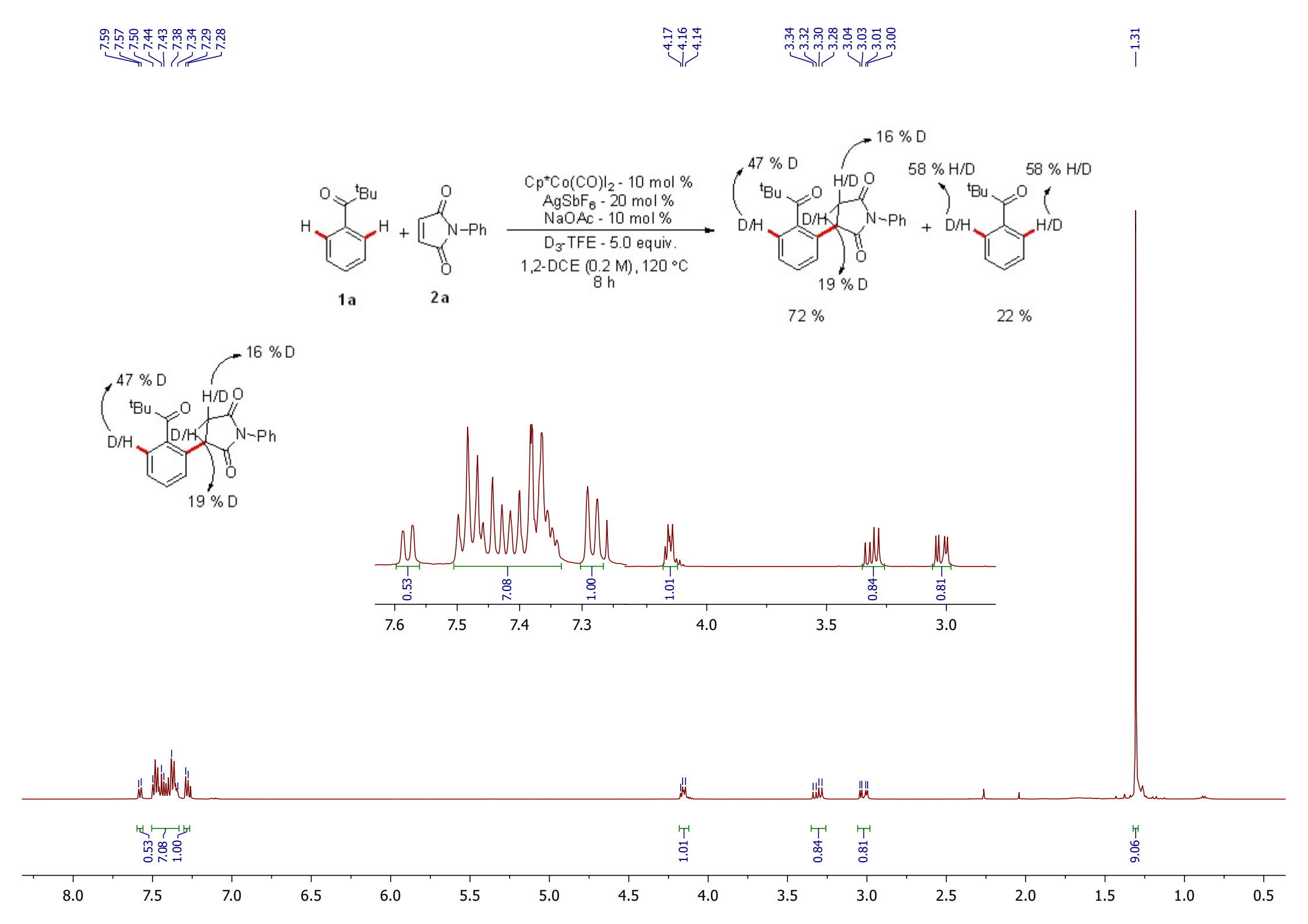
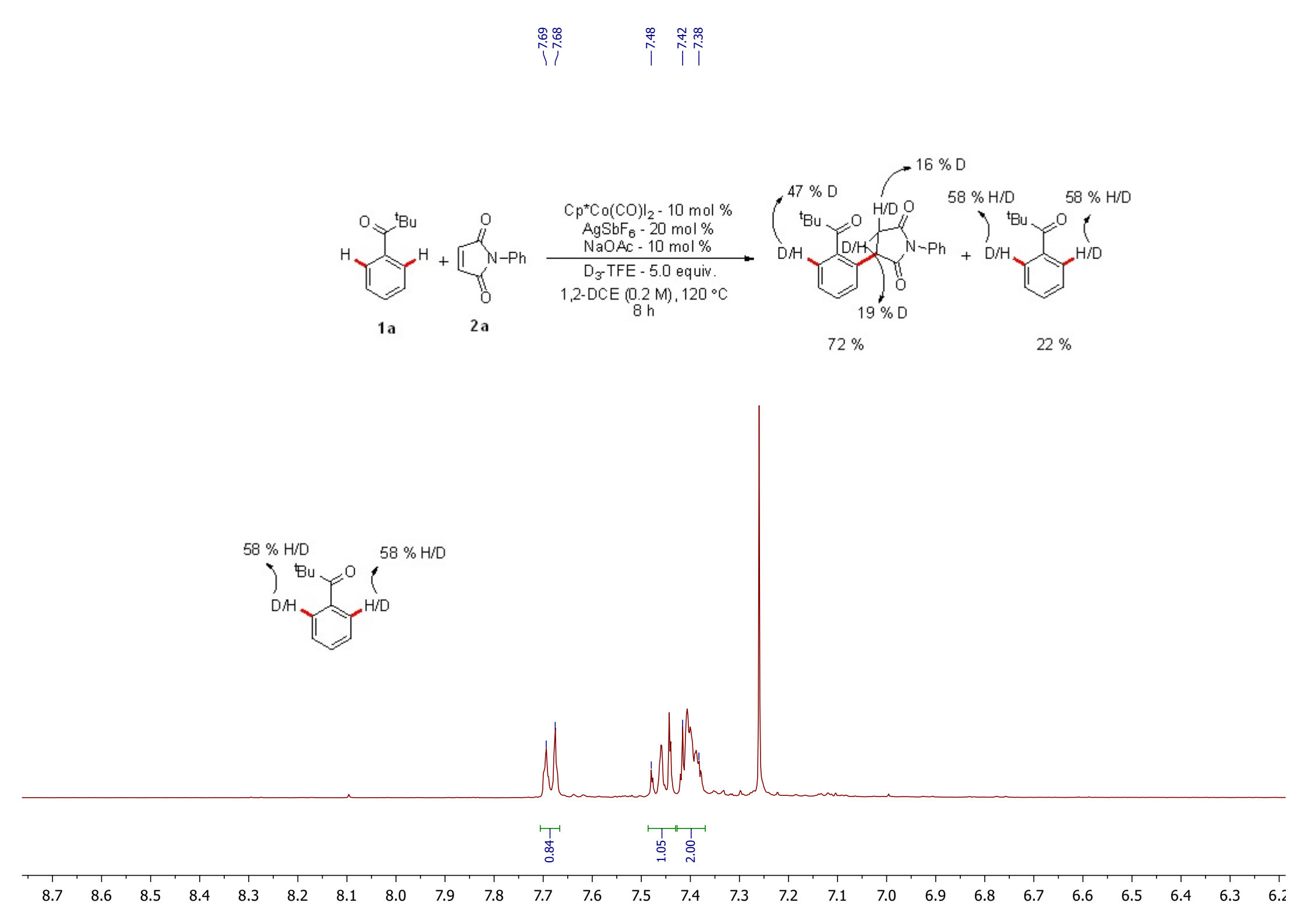
20
10


7.72 7.72 7.70 7.67 7.66 7.65 7.42 7.33 7.28 7.02 7.01 6.95 6.94
4.76 4.76 4.74 4.73 4.71 4.67
3.95 3.93 3.93 3.92 3.91 3.90 3.89 3.88
3.20 3.18 3.16 3.14 3.13
2.81 2.80 2.79 2.78 2.77 2.76 2.76 2.75
1.30 1.20
tBu
O
H
H
R
N–Bn
O
O
Cp*Co(CO)I2 - 10 mol %
AgSbF6 - 20 mol %
NaOAc - 10 mol %
1,2-DCE (1.0 mL), 120 °C
13 h
R = tBu/Cl
(1c/1e)
2b
R = tBu/Cl (3cb/3eb)
(tBu:Cl = 1.78:1)
0.56
1.00
7.05 7.04 7.03 7.02 7.01 7.00 6.99 6.98 6.97 6.96 6.95 6.94 6.93 6.92 6.91
0.56
1.00
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


7.70
7.69
7.67
7.47
7.46
7.44
7.44
7.41
7.40
7.38
O
tBu
H
H
1a
Cp*Co(CO)I2 - 10 mol %
AgSbF6 - 20 mol %
NaOAc - 10 mol %
D3-TFE - 5.0 equiv.
1,2-DCE (0.2 M), 120 °C
8 h
53 % D
53 % D
D/H
H/D
53 % D
53 % D
D/H
H/D
0.94
1.00
2.00
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90


7.59
7.57
7.50
7.44
7.43
7.38
7.34
7.29
7.28
4.17
4.16
4.14
3.34
3.32
3.30
3.28
3.04
3.03
3.01
3.00
1.31
1a
2a
Cp*Co(CO)I2 - 10 mol %
AgSbF6 - 20 mol %
NaOAc - 10 mol %
D3-TFE - 5.0 equiv.
1,2-DCE (0.2 M), 120 °C
8 h
47 % D
16 % D
19 % D
72 %
58 % H/D
58 % H/D
22 %
0.53
7.08
1.00
1.01
0.84
0.81
9.06


7.69
7.68
7.48
7.42
7.38
tBu
O
H
H
O
N–Ph
O
1a
2a
Cp*Co(CO)I2 - 10 mol %
AgSbF6 - 20 mol %
NaOAc - 10 mol %
D3-TFE - 5.0 equiv.
1,2-DCE (0.2 M), 120 °C
8 h
16 % D
47 % D
58 % H/D
58 % H/D
D/H
H/D
19 % D
72 %
22 %
58 % H/D
58 % H/D
0.84
1.05
2.00
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2