Supporting Information

Carbenoid-mediated N-O Bond Insertion and its Application in the Synthesis of Pyridines

Xinxin Qi, Lu Dai and Cheol-Min Park*

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General methods: All reactions were carried out in flame or oven dried glasswares under nitrogen atmosphere with freshly distilled solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel 60 (230 – 400 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using base solution of potassium permanganate and molybdate. NMR spectra were recorded at room temperature on 400 MHz Bruker DPX 400 and 400 MHz *J*EOL ECA 400 NMR spectrometers. The residual solvent signals were taken as the reference (0.00 ppm or 7.26 ppm for ^{1}H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, q = quartet and br = broad signal. HRMS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer.

Materials: All solvents were distilled under nitrogen from the following drying agents immediately before use: acetonitrile and dichloroethane were distilled from P_2O_5. Anhydrous pyridine and DBU were purchased from commercial suppliers and used without further purification.

Preparation of *α*-halo ketones:

α-Halo ketones were prepared by the literature procedures. References are listed below.

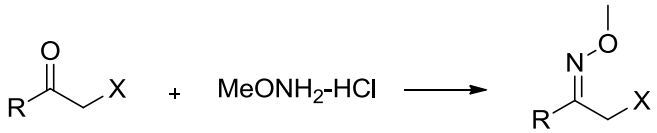
2-bromo-1-(*o*-tolyl)ethanone,[1] 2-chloro-1-(2-chlorophenyl)ethanone,[2]

2-bromo-1-(3-chlorophenyl)ethanone,[1] 2-chloro-1-(naphthalen-2-yl)ethanone,[3]

2-bromo-1-(thiophen-2-yl)ethanone,[4] 2-bromo-1-(furan-2-yl)ethanone,[5]

2-bromo-1-(1-bromocyclohexyl)ethanone.[6]

General procedure for compounds I:



I

α-Halo ketone (1 eq.) and methoxyamine hydrochloride (1.5 eq.) were dissolved in ethanol containing one drop of concentrated sulfuric acid. The mixture was stirred at ambient temperature for 2-12 h. The solvent was evaporated in *vacuo* to near dryness. The crude material was taken in ether and washed with 1 M aqueous $KHSO_4$, saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated in *vacuo* to afford the product as a colorless liquid. The crude material was used directly for the next step without further purification.

References for the known compounds are listed below.

2-chloro-1-phenylethanone *O*-methyl oxime,[7] 2-bromo-1-(*o*-tolyl)ethanone *O*-methyl oxime,[8] 2-chloro-1-(2-chlorophenyl)ethanone *O*-methyl oxime,[9]

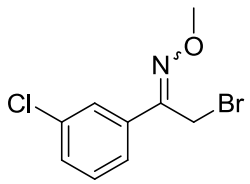
2-bromo-1-(4-chlorophenyl)ethanone *O*-methyl oxime,[10]

2-bromo-1-(4-methoxyphenyl)ethanone *O*-methyl oxime,[10]

2-chloro-1-(naphthalen-2-yl)ethanone *O*-methyl oxime,[11] 2-bromo-1-(thiophen-2-yl)ethanone *O*-methyl oxime,[12] 2-bromo-1-(furan-2-yl)ethanone *O*-methyl oxime,[13]

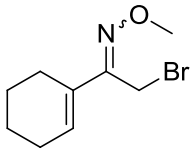
1-chloro-3,3-dimethylbutan-2-one *O*-methyl oxime.[11]

2-bromo-1-(3-chlorophenyl)ethanone *O*-methyl oxime:



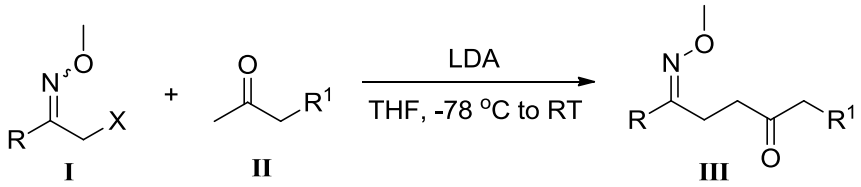
The *cis:trans* ratio was 13:87. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.57-7.54 (m, 1H), 7.33-7.28 (m, 2H), 4.78 & 4.63 (s, 2H), 4.13 & 4.11 (s, 3H).

2-bromo-1-(cyclohex-1-en-1-yl)ethanone *O*-methyl oxime:



The *cis:trans* ratio was 51:49. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23-6.22 & 6.13-6.11 (m, 1H), 3.96 & 3.88 (s, 3H), 2.28 (br, 2H), 2.23-.2.21 & 2.17-2.16 (m, 2H), 1.93 (s, 2H), 1.67-1.60 (m, 4H).

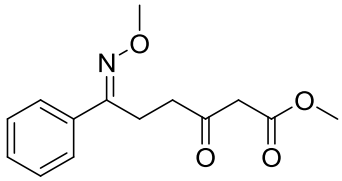
General procedure for compounds III:



I **II** **III**

To a solution of LDA (2.1 eq.) in dry THF at -78 °C was added a solution of **II** (1.0 eq.) in dry THF dropwise under nitrogen, after 30 min a solution of **I** (1.0 eq.) in dry THF was added and the reaction mixture was stirred for a further 30 min. Then rise the temperature to RT and stirred overnight. Upon completion of the reaction as indicated by TLC, the reaction mixture was quenched with saturated aq. NH_4Cl solution, extracted with ethyl acetate for 3 times, dried over anhydrous Na_2SO_4. The crude material was concentrated under vacuo and purified by column chromatography using hexane : ethyl acetate (9 : 1).

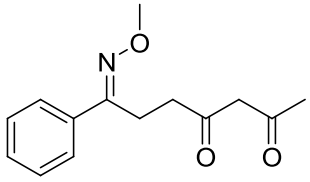
(*E*)-methyl 6-(methoxyimino)-3-oxo-6-phenylhexanoate:



The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 93 : 7). Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.38-7.35 (m, 3H), 3.98 (s, 3H), 3.73 (s, 3H), 3.46 (s, 2H), 3.02-2.99 (m, 2H), 2.81-2.77 (m, 2H); ^{13}C NMR (100 MHz,

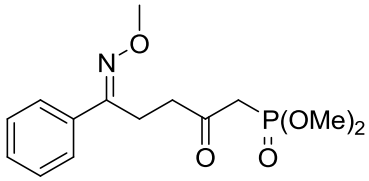
$CDCl_3$) δ 201.2, 167.4, 156.9, 135.0, 129.3, 128.6, 126.2, 62.0, 52.4, 48.8, 39.3, 20.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}NO_4$: 264.1236. Found: 264.1236.

(*E*)-7-(methoxyimino)-7-phenylheptane-2,4-dione:



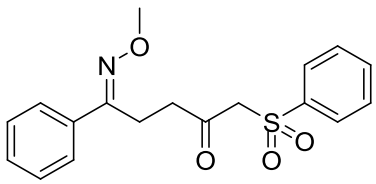
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 70: 30). Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.38-7.36 (m, 3H), 3.99 (s, 3H), 3.05-2.97 (m, 2H), 2.55-2.51 (m, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 190.2, 157.0, 135.1, 129.3, 129.2, 128.6, 128.5, 126.2, 99.8, 62.0, 57.6, 40.0, 34.9, 30.9, 24.6, 22.6, 20.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{17}NO_3$: 248.1287. Found: 248.1287.

(*E*)-dimethyl 5-(methoxyimino)-2-oxo-5-phenylpentylphosphonate:



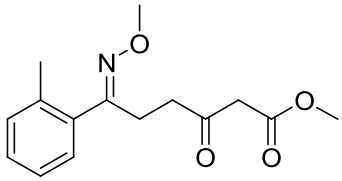
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil. Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.37-7.36 (m, 3H), 3.98 (s, 3H), 3.79 (s, 3H), 3.76 (s, 3H), 3.12 (s, 1H), 3.06 (s, 1H), 3.01-2.98 (m, 2H), 2.88-2.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 157.0, 135.1, 129.3, 128.6, 126.2, 62.0, 53.1, 53.0, 41.8, 40.5, 40.4, 40.4, 21.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{20}NO_5P$: 314.1157. Found: 314.1159.

(*E*)-5-(methoxyimino)-5-phenyl-1-(phenylsulfonyl)pentan-2-one:



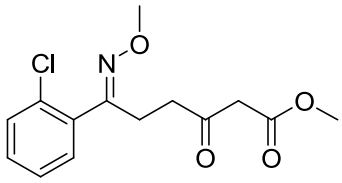
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.70-7.65 (m, 1H), 7.60-7.54 (m, 4H), 7.38-7.35 (m, 3H), 4.15 (s, 2H), 3.97 (s, 3H), 2.95 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 156.5, 138.5, 134.9, 134.3, 129.3, 128.6, 128.2, 126.2, 66.7, 62.0, 40.7, 20.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{19}NO_4S$: 346.1113. Found: 346.1119.

(*E*)-methyl 6-(methoxyimino)-3-oxo-6-(*o*-tolyl)hexanoate:



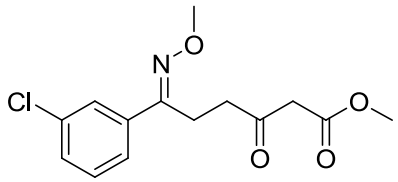
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 90 : 10). Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.11 (m, 4H), 3.93 (s, 3H), 3.68 (s, 3H), 3.34 (s, 2H), 2.94-2.90 (m, 2H), 2.70-2.66 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 167.4, 158.9, 136.1, 135.6, 130.7, 128.7, 128.6, 125.8, 89.0, 61.8, 52.3, 51.2, 49.4, 48.7, 38.6, 38.2, 26.4, 23.9, 19.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{19}NO_4$: 278.1392. Found: 278.1397.

(*E*)-methyl 6-(2-chlorophenyl)-6-(methoxyimino)-3-oxohexanoate:



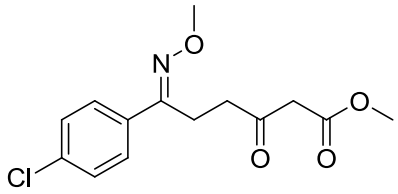
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 91 : 9). Yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.32-7.25 (m, 3H), 3.95 (s, 3H), 3.68 (s, 3H), 3.36 (s, 2H), 2.99-2.95 (m, 2H), 2.77-2.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 167.3, 157.9, 135.3, 132.8, 130.9, 130.1, 129.8, 126.9, 89.0, 62.1, 52.3, 48.7, 38.7, 23.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}ClNO_4$: 298.0846. Found: 298.0845.

(*E*)-methyl 6-(3-chlorophenyl)-6-(methoxyimino)-3-oxohexanoate:



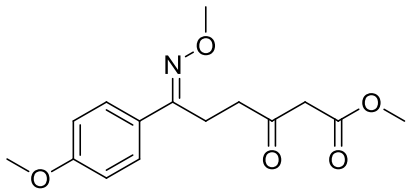
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 91 : 9). Yield: 21%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.48-7.47 (m, 1H), 7.35-7.27 (m, 2H), 3.98 (s, 3H), 3.73 (s, 3H), 3.46 (s, 2H), 2.98-2.94 (m, 2H), 2.80-2.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 167.4, 155.7, 136.9, 134.7, 129.8, 129.3, 126.3, 124.3, 62.3, 52.4, 48.8, 39.2, 20.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}ClNO_4$: 298.0846. Found: 298.0839.

(*E*)-methyl 6-(4-chlorophenyl)-6-(methoxyimino)-3-oxohexanoate:



The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 91 : 9). Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.35-7.32 (m, 2H), 3.97 (s, 3H), 3.73 (s, 3H), 3.46 (s, 2H), 2.99-2.95 (m, 2H), 2.80-2.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 167.4, 155.9, 135.3, 133.5, 128.8, 128.7, 127.8, 127.5, 62.2, 52.4, 48.8, 39.2, 20.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{16}ClNO_4$: 298.0846. Found: 298.0858.

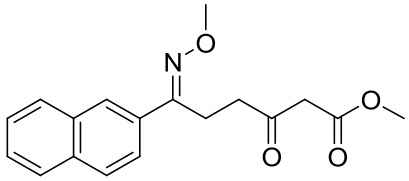
(*E*)-methyl 6-(methoxyimino)-6-(4-methoxyphenyl)-3-oxohexanoate:



The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 90 : 10). Yield: 44%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 6.90-6.88 (m, 2H), 3.95 (s, 3H), 3.82 (s, 3H), 3.73 (s, 3H), 3.46 (s, 2H), 3.00-2.96 (m, 2H), 2.80-2.76 (m, 2H); ^{13}C NMR

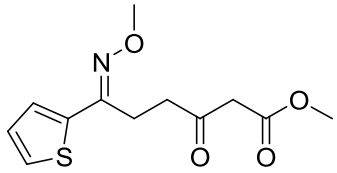
(100 MHz, $CDCl_3$) δ 201.4, 167.5, 160.6, 156.5, 127.6, 127.5, 114.0, 61.9, 55.3, 52.4, 48.8, 39.5, 20.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{19}NO_5$: 294.1341. Found: 294.1350

(*E*)-methyl 6-(methoxyimino)-6-(naphthalen-2-yl)-3-oxohexanoate:



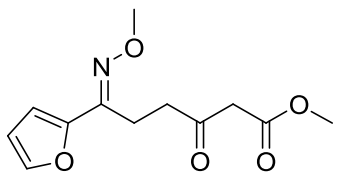
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 88 : 12). Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.95 (m, 1H), 7.88-7.77 (m, 4H), 7.52-7.47 (m, 2H), 4.03 (s, 3H), 3.72 (s, 3H), 3.48 (s, 2H), 3.15-3.11 (m, 2H), 2.87-2.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 167.5, 156.7, 133.7, 133.1, 132.3, 128.5, 128.3, 127.6, 126.7, 126.4, 125.8, 123.6, 62.2, 52.4, 48.9, 39.5, 20.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{19}NO_4$: 314.1392. Found: 314.1385.

(*E*)-methyl 6-(methoxyimino)-3-oxo-6-(thiophen-2-yl)hexanoate:



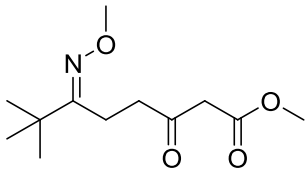
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as pale yellow oil (ketone ester : enol form = 92 : 8). Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 1H), 7.22-7.21 (m, 1H), 7.01-6.98 (m, 1H), 3.93 (s, 3H), 3.72 (s, 3H), 3.46 (s, 2H), 2.98-2.94 (m, 2H), 2.84-2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 167.4, 153.0, 138.9, 127.3, 127.2, 126.5, 89.3, 62.2, 52.4, 51.2, 48.8, 39.5, 31.9, 24.4, 21.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{15}NO_4S$: 270.0800. Found: 270.0799.

(*E*)-methyl 6-(furan-2-yl)-6-(methoxyimino)-3-oxohexanoate:



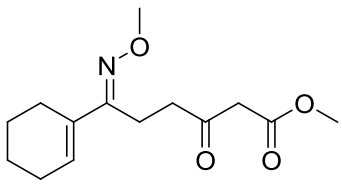
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as pale yellow oil (ketone ester : enol form = 92 : 8). Yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.45 (m, 1H), 6.65-6.65 (m, 1H), 6.43-6.42 (m, 1H), 3.97 (s, 3H), 3.72 (s, 3H), 3.46 (s, 2H), 2.89-2.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 167.4, 149.3, 149.0, 143.9, 111.4, 110.7, 62.4, 52.4, 48.8, 39.5, 20.6; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{15}NO_5$: 254.1028. Found: 254.1030.

(*E*)-methyl 6-(methoxyimino)-7,7-dimethyl-3-oxooctanoate:



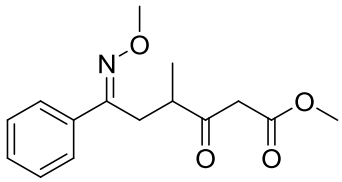
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 93 : 7). Yield: 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.73 (s, 3H), 3.46 (s, 2H), 2.76-2.72 (m, 2H), 2.50-2.46 (m, 2H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 167.6, 165.0, 61.2, 52.4, 48.8, 39.8, 37.3, 27.5, 20.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{21}NO_4$: 244.1549. Found: 244.1558.

(*E*)-methyl 6-(cyclohex-1-en-1-yl)-6-(methoxyimino)-3-oxohexanoate:



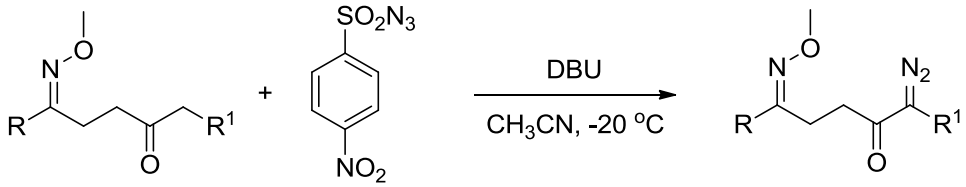
The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 92 : 8). Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08-6.06 (m, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 3.44 (s, 2H), 2.72-2.62 (m, 4H), 2.23-2.21 (m, 2H), 2.15-2.12 (m, 2H), 1.64-1.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 167.5, 158.2, 133.3, 129.3, 62.0, 61.6, 52.3, 51.1, 48.8, 40.0, 38.0, 26.0, 25.2, 24.5, 23.1, 22.3, 22.1, 21.4, 18.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{21}NO_4$: 268.1549. Found: 268.1550.

(*E*)-methyl 6-(methoxyimino)-4-methyl-3-oxo-6-phenylhexanoate:



The title compound was prepared according to the general procedure. The product was mixture with ketone ester and enol form as colorless oil (ketone ester : enol form = 83 : 17). Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.38-7.35 (m, 3H), 3.98 (s, 3H), 3.71 (s, 3H), 3.53-3.45 (m, 2H), 3.06-2.97 (m, 2H), 2.92-2.86 (m, 1H), 1.10 (d, J =6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 167.6, 156.3, 135.4, 129.3, 128.6, 128.5, 126.4, 87.9, 62.0, 61.9, 52.3, 51.1, 47.5, 43.9, 30.8, 29.1, 16.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{19}NO_4$: 278.1392. Found: 278.1394.

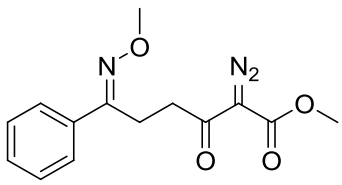
General procedure for compounds 1 (1a-o):



III **1**

To a solution of **III** (1.0 eq.) and 4-nitrobenzenesulfonyl azide (1.1 eq.) in CH_3CN at -20 °C was added DBU (1.1 eq.) dropwise under nitrogen. The resulting orange color solution was stirred at -20 °C overnight. Upon completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure, and the crude material was purified by column chromatography using hexane : ethyl acetate (9 : 1).

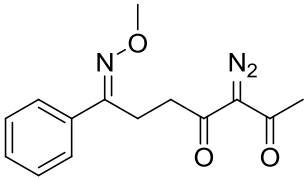
(*E*)-methyl 2-diazo-6-(methoxyimino)-3-oxo-6-phenylhexanoate (1a):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2H), 7.38-7.35 (m, 3H), 3.98 (s, 3H), 3.81 (s, 3H), 3.10-3.05 (m, 4H); ^{13}C NMR (100 MHz,

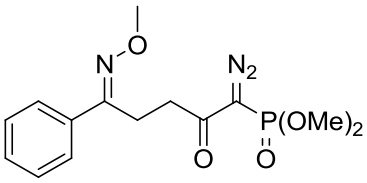
$CDCl_3$) δ 191.3, 161.7, 157.1, 135.3, 129.2, 128.5, 126.3, 62.0, 52.2, 36.8, 21.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{15}N_3O_4$: 290.1141. Found: 290.1145.

(*E*)-3-diazo-7-(methoxyimino)-7-phenylheptane-2,4-dione (1b):



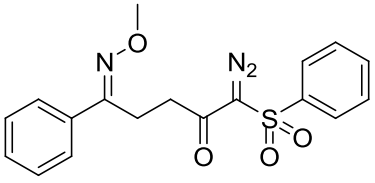
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.61 (m, 2H), 7.38-7.35 (m, 3H), 3.98 (s, 3H), 3.09-3.05 (m, 2H), 2.97-2.93 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 188.4, 156.6, 135.0, 129.3, 128.5, 126.1, 84.0, 62.0, 36.9, 28.5, 21.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{15}N_3O_3$: 274.1192. Found: 274.1194.

(*E*)-dimethyl 1-diazo-5-(methoxyimino)-2-oxo-5-phenylpentylphosphonate (1c):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 2H), 7.38-7.36 (m, 3H), 3.99 (s, 3H), 3.80 (s, 3H), 3.77 (s, 3H), 3.07-3.03 (m, 2H), 2.81-2.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 191.2, 156.8, 135.1, 129.3, 128.6, 126.2, 62.1, 53.7, 53.6, 35.7, 21.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{18}N_3O_5P$: 340.1062. Found: 340.1060.

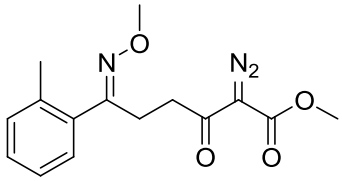
(*E*)-1-diazo-5-(methoxyimino)-5-phenyl-1-(phenylsulfonyl)pentan-2-one (1d):



The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 80-81 °C. Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.93 (m, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 4H), 7.36-7.32 (m, 3H), 3.93 (s, 3H),

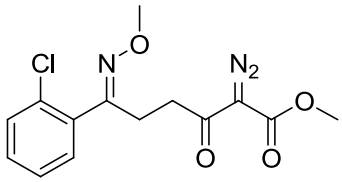
2.99-2.95 (m, 2H), 2.83-2.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 156.3, 141.8, 134.8, 134.1, 129.4, 129.3, 128.5, 127.3, 126.1, 62.0, 35.6, 21.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{17}N_3O_4S$: 372.1018. Found: 372.1019.

(*E*)-methyl 2-diazo-6-(methoxyimino)-3-oxo-6-(*o*-tolyl)hexanoate (1e):



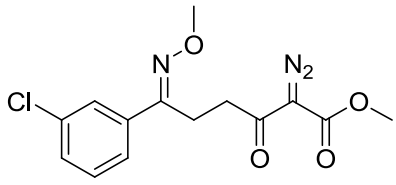
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 4H), 3.93 (s, 3H), 3.77 (s, 3H), 2.98 (s, 4H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 161.6, 159.2, 136.2, 135.7, 130.6, 128.7, 128.6, 125.7, 61.8, 52.1, 35.9, 24.4, 19.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{17}N_3O_4$: 304.1297. Found: 304.1301.

(*E*)-methyl 6-(2-chlorophenyl)-2-diazo-6-(methoxyimino)-3-oxohexanoate (1f):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 1H), 7.32-7.26 (m, 3H), 3.96 (s, 3H), 3.80 (s, 3H), 3.05 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 161.6, 158.2, 135.4, 132.9, 131.0, 130.0, 129.8, 126.8, 62.0, 52.2, 36.0, 24.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{14}ClN_3O_4$: 324.0751. Found: 324.0747.

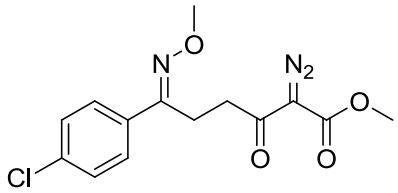
(*E*)-methyl 6-(3-chlorophenyl)-2-diazo-6-(methoxyimino)-3-oxohexanoate (1g):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.52-7.50 (m, 1H), 7.34-7.27 (m, 2H), 3.98 (s, 3H), 3.82 (s, 3H), 3.10-3.06 (m, 2H), 3.03-2.99 (m, 2H);

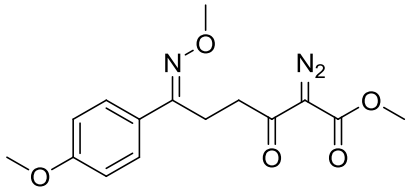
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 161.7, 155.9, 137.1, 134.6, 129.7, 129.2, 126.4, 124.4, 62.2, 52.2, 36.6, 21.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{14}ClN_3O_4$: 324.0751. Found: 324.0760.

(*E*)-methyl 6-(4-chlorophenyl)-2-diazo-6-(methoxyimino)-3-oxohexanoate (1h):



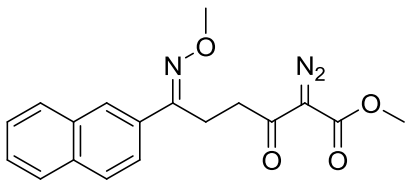
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 77-79 °C. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.58 (m, 2H), 7.34-7.30 (m, 2H), 3.97 (s, 3H), 3.80 (s, 3H), 3.10-3.06 (m, 2H), 3.03-2.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 161.6, 156.0, 135.1, 133.7, 128.7, 127.6, 75.8, 62.1, 52.2, 36.7, 21.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{14}ClN_3O_4$: 324.0751. Found: 324.0758.

(*E*)-methyl 2-diazo-6-(methoxyimino)-6-(4-methoxyphenyl)-3-oxohexanoate (1i):



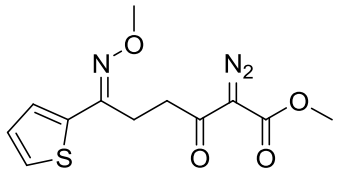
The title compound was prepared according to the general procedure. The product was obtained as pale yellow solid. mp: 85-86 °C Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 6.90-6.86 (m, 2H), 3.95 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.11-3.06 (m, 2H), 3.04-3.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 161.7, 160.5, 156.7, 127.8, 127.6, 113.9, 61.9, 55.3, 52.2, 36.9, 21.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{17}N_3O_5$: 320.1246. Found: 320.1243

(*E*)-methyl 2-diazo-6-(methoxyimino)-6-(naphthalen-2-yl)-3-oxohexanoate (1j):



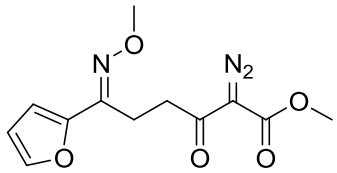
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.91-7.80 (m, 4H), 7.50-7.46 (m, 2H), 4.03 (s, 3H), 3.79 (s, 3H), 3.20-3.13 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 161.7, 156.9, 133.7, 133.2, 132.6, 128.5, 128.2, 127.6, 126.6, 126.3, 125.9, 123.7, 62.2, 52.2, 37.0, 21.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{18}H_{17}N_3O_4$: 340.1297. Found: 340.1305.

(*E*)-methyl 2-diazo-6-(methoxyimino)-3-oxo-6-(thiophen-2-yl)hexanoate (1k):



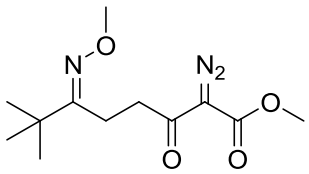
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 97-98 °C. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.26 (m, 2H), 7.02-6.99 (m, 1H), 3.95 (s, 3H), 3.82 (s, 3H), 3.16-3.09 (m, 2H), 3.06-3.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 161.7, 153.1, 139.2, 127.1, 127.1, 126.4, 62.2, 52.3, 37.0, 21.9; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_3O_4S$: 296.0705. Found: 296.0704.

(*E*)-methyl 2-diazo-6-(furan-2-yl)-6-(methoxyimino)-3-oxohexanoate (1l):



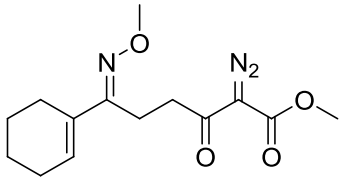
The title compound was prepared according to the general procedure. The product was obtained as yellow solid. mp: 66-68 °C. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.42 (m, 1H), 6.66-6.65 (m, 1H), 6.40-6.39 (m, 1H), 3.94 (s, 3H), 3.78 (s, 3H), 3.11-3.07 (m, 2H), 2.91-2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 161.6, 149.4, 149.2, 143.8, 111.4, 110.6, 62.3, 52.2, 37.0, 21.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{13}N_3O_5$: 280.0933. Found: 280.0937.

(*E*)-methyl 2-diazo-6-(methoxyimino)-7,7-dimethyl-3-oxooctanoate (1m):



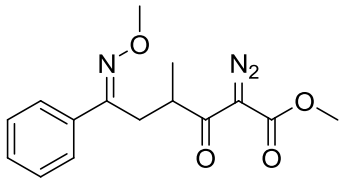
The title compound was prepared according to the general procedure. The product was obtained as pale yellow solid. mp: 59-62 °C. Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 3.78 (s, 3H), 3.07-3.03 (m, 2H), 2.56-2.52 (m, 2H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 165.0, 161.8, 61.2, 52.2, 37.3, 37.1, 27.6, 20.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{19}N_3O_4$: 270.1454. Found: 270.1460.

(*E*)-methyl 6-(cyclohex-1-en-1-yl)-2-diazo-6-(methoxyimino)-3-oxohexanoate (1n):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11-6.09 (m, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.98-2.94 (m, 2H), 2.77-2.73 (m, 2H), 2.24 (br, 2H), 2.15-2.14 (m, 2H), 1.63-1.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 161.8, 158.3, 133.5, 129.1, 61.6, 52.2, 37.4, 26.0, 24.6, 22.4, 22.1, 19.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{19}N_3O_4$: 294.1454. Found: 294.1458.

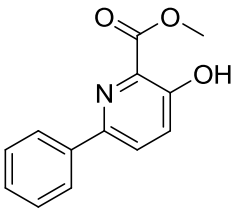
(*E*)-methyl 2-diazo-6-(methoxyimino)-4-methyl-3-oxo-6-phenylhexanoate (1o):



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield: 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.36-7.34 (m, 3H), 3.97 (s, 3H), 3.92 (q, J = 7.2Hz, 1H), 3.78 (s, 3H), 3.07-2.95 (m, 2H), 1.10 (d, J = 6.8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 161.3, 156.6, 135.8, 129.1, 128.4, 126.6, 61.9, 52.2, 39.3, 29.4, 17.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{15}H_{17}N_3O_4$: 304.1297. Found: 304.1300.

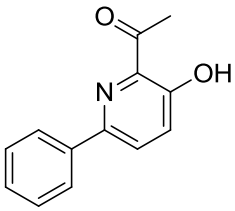
General procedure for pyridines: To a stirred suspension of $Rh_2(tfacam)_4$ (2 mol%) in dichloroethane was added a solution of diazo compound in dichloroethane under nitrogen, and the reaction mixture was stirred under reflux until the diazo compound was completely consumed (detected by TLC). The solvent was evaporated under reduced pressure to give crude compound which was purified by flash column chromatography using hexane : ethyl acetate (9 : 1) to give desired products.

Methyl 3-hydroxy-6-phenylpicolinate (2a):



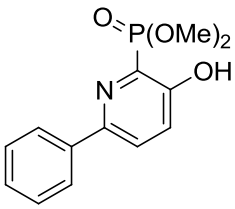
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 91-93°C. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.95-7.93 (m, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.49-7.44 (m, 3H), 7.41-7.37 (m, 1H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 157.8, 149.5, 138.3, 129.3, 128.8, 128.7, 127.0, 126.9, 126.6, 53.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{11}NO_3$: 230.0817. Found: 230.0816.

1-(3-hydroxy-6-phenylpyridin-2-yl)ethanone (2b):



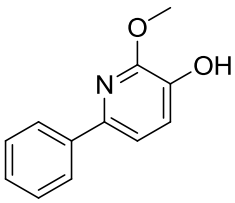
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 45-47 °C. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.8 (s, 1H), 8.01-7.99 (m, 2H), 7.89 (d, J = 9.2 Hz, 1H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 2H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 157.6, 148.2, 138.1, 135.3, 128.8, 128.7, 127.1, 127.0, 126.3, 25.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{11}NO_2$: 214.0868. Found: 214.0872.

Dimethyl (3-hydroxy-6-phenylpyridin-2-yl)phosphonate (2c):



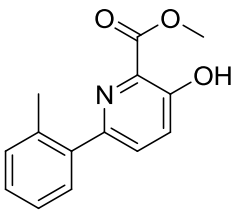
The title compound was prepared according to the general procedure. The product was obtained as pale yellow oil. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.2 (s, 1H), 7.95-7.93 (m, 2H), 7.85-7.83 (m, 1H), 7.48-7.44 (m, 2H), 7.41-7.37 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.2, 150.1, 149.9, 138.2, 131.9, 129.7, 128.8, 128.7, 126.3, 126.1, 126.0, 125.5, 125.5, 54.5, 54.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{14}NO_4P$: 280.0739. Found: 280.0737.

2-methoxy-6-phenylpyridin-3-ol (2d):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 92-93 °C. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.44-7.41 (m, 2H), 7.35-7.25 (m, 2H), 7.18 (d, J = 7.6 Hz, 1H), 5.40 (s, 1H), 4.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 145.4, 139.6, 138.9, 128.6, 127.9, 126.1, 121.4, 113.9, 53.5; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{12}H_{11}NO_2$: 202.0868. Found: 202.0862.

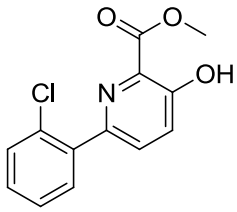
Methyl 3-hydroxy-6-(*o*-tolyl)picolinate (2e):



The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.54 (d, J = 8.8Hz, 1H), 7.43 (d, J = 8.8Hz, 1H), 7.38-7.36 (m, 1H), 7.28-7.24 (m, 3H), 4.04 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 157.4, 151.9, 139.3, 136.0, 130.9, 130.4,

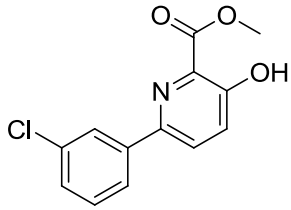
129.6, 129.0, 128.4, 126.4, 126.0, 53.1, 20.4; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{13}NO_3$: 244.0974. Found: 244.0973.

Methyl 6-(2-chlorophenyl)-3-hydroxypicolinate (2f):



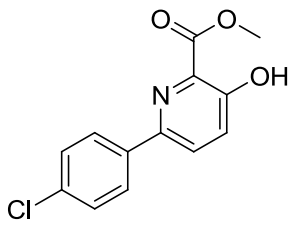
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 142-144 °C Yield: 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.8 (s, 1H), 7.78 (d, J = 8.8Hz, 1H), 7.60-7.57 (m, 1H), 7.46-7.43 (m, 2H), 7.38-7.30 (m, 2H), 4.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 158.0, 148.8, 138.2, 132.3, 131.7, 131.2, 130.0, 129.7, 129.5, 127.2, 126.0, 53.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{10}ClNO_3$: 264.0427. Found: 264.0422.

Methyl 6-(3-chlorophenyl)-3-hydroxypicolinate (2g):



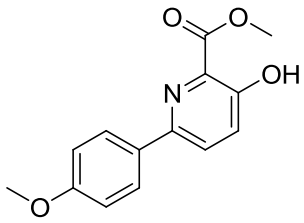
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 132-134 °C. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.8 (s, 1H), 7.97-7.96 (m, 1H), 7.85 (d, J = 8.8Hz, 1H), 7.81-7.79 (m, 1H), 7.46 (d, J = 8.8Hz, 1H), 7.41-7.35 (m, 2H), 4.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 158.2, 148.0, 140.1, 135.0, 130.1, 129.6, 128.8, 127.2, 126.9, 126.8, 124.7, 53.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{10}ClNO_3$: 264.0427. Found: 264.0424.

Methyl 6-(4-chlorophenyl)-3-hydroxypicolinate (2h):



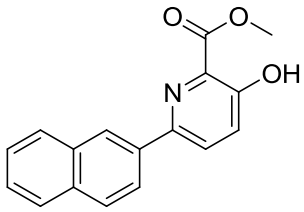
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 143-145 °C Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.90-7.87 (m, 2H), 7.83 (d, J = 8.8Hz, 1H), 7.46-7.41 (m, 3H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 158.0, 148.2, 136.8, 134.9, 129.5, 129.0, 127.9, 127.1, 126.6, 53.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{10}ClNO_3$: 264.0427. Found: 264.0427.

Methyl 3-hydroxy-6-(4-methoxyphenyl)picolinate (2i):



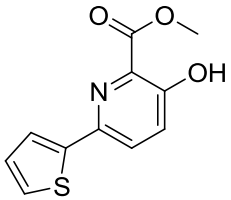
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 83-85 °C. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.90-7.88 (m, 2H), 7.81 (d, J = 8.7Hz, 1H), 7.41 (d, J = 8.7Hz, 1H), 6.99-6.97 (m, 2H), 4.06 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 160.2, 157.4, 149.3, 131.1, 129.1, 127.8, 127.0, 126.3, 114.2, 55.3, 53.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{13}NO_4$: 260.0923. Found: 260.0921.

Methyl 3-hydroxy-6-(naphthalen-2-yl)picolinate (2j):



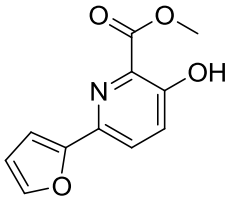
The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 103-105 °C. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.8 (s, 1H), 8.39-8.39 (m, 1H), 8.14-8.12 (m, 1H), 8.03 (d, J = 8.8Hz, 1H), 7.95-7.93 (m, 2H), 7.88-7.85 (m, 1H), 7.53-7.48 (m, 3H), 4.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 157.9, 149.4, 135.6, 133.5, 133.5, 129.5, 128.6, 128.6, 127.7, 127.2, 127.1, 126.5, 126.4, 125.8, 124.4, 53.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{17}H_{13}NO_3$: 280.0974. Found: 280.0968.

Methyl 3-hydroxy-6-(thiophen-2-yl)picolinate (2k):



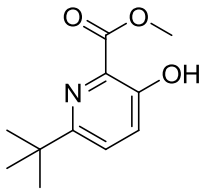
The title compound was prepared according to the general procedure. The product was obtained as pale yellow solid. mp: 135-137 °C. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.78 (d, J = 8.7Hz, 1H), 7.50-7.49 (m, 1H), 7.40-7.36 (m, 2H), 7.10-7.08 (m, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 157.6, 145.0, 143.6, 129.0, 128.0, 127.2, 127.1, 125.6, 124.3, 53.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_9NO_3S$: 236.0381. Found: 236.0382.

Methyl 6-(furan-2-yl)-3-hydroxypicolinate (2l):



The title compound was prepared according to the general procedure. The product was obtained as pale yellow solid. mp: 126-128 °C. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.7 (s, 1H), 7.82 (d, J = 9.2Hz, 1H), 7.52-7.52 (m, 1H), 7.41 (d, J = 8.8Hz, 1H), 6.96-6.96 (m, 1H), 6.52-6.51 (m, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 157.6, 152.5, 143.2, 141.9, 129.2, 127.0, 125.5, 112.0, 108.1, 53.2; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_9NO_4$: 220.0610. Found: 220.0610.

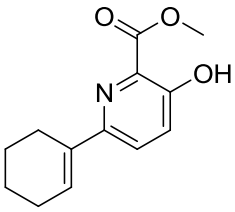
Methyl 6-(*tert*-butyl)-3-hydroxypicolinate (2m):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 63-65 °C. Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.6 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 4.02 (s, 3H), 1.35 (s, 9H); ^{13}C NMR

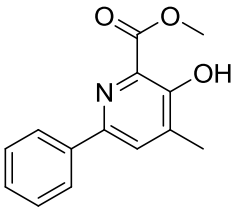
(100 MHz, $CDCl_3$) δ 170.5, 160.7, 156.7, 128.1, 126.2, 126.0, 52.9, 37.1, 30.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{11}H_{15}NO_3$: 210.1130. Found: 210.1130.

Methyl 6-(cyclohex-1-en-1-yl)-3-hydroxypicolinate (2n):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 75-77 °C. Yield: 60%. ^1H NMR (400 MHz, $CDCl_3$) δ 10.6 (s, 1H), 7.53 (d, J = 8.8Hz, 1H), 7.31 (d, J = 8.8Hz, 1H), 6.56-6.54 (m, 1H), 4.03 (s, 3H), 2.52-2.48 (m, 2H), 2.27-2.22 (m, 2H), 1.82-1.76 (m, 2H), 1.70-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 157.3, 151.5, 135.8, 128.4, 128.1, 126.3, 125.7, 53.0, 26.0, 25.8, 22.7, 22.0; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{13}H_{15}NO_3$: 234.1130. Found: 234.1133.

M ethyl 3-hydroxy-4-methyl-6-phenylpicolinate (2o):



The title compound was prepared according to the general procedure. The product was obtained as white solid. mp: 92-94 °C. Yield: 91%. ^1H NMR (400 MHz, $CDCl_3$) δ 10.9 (s, 1H), 7.93-7.91 (m, 2H), 7.72 (s, 1H), 7.47-7.43 (m, 2H), 7.39-7.35 (m, 1H), 4.06 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 157.1, 148.9, 138.6, 137.5, 128.7, 128.5, 128.3, 127.7, 126.6, 53.0, 15.7; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{14}H_{13}NO_3$: 244.0974. Found: 244.0972.

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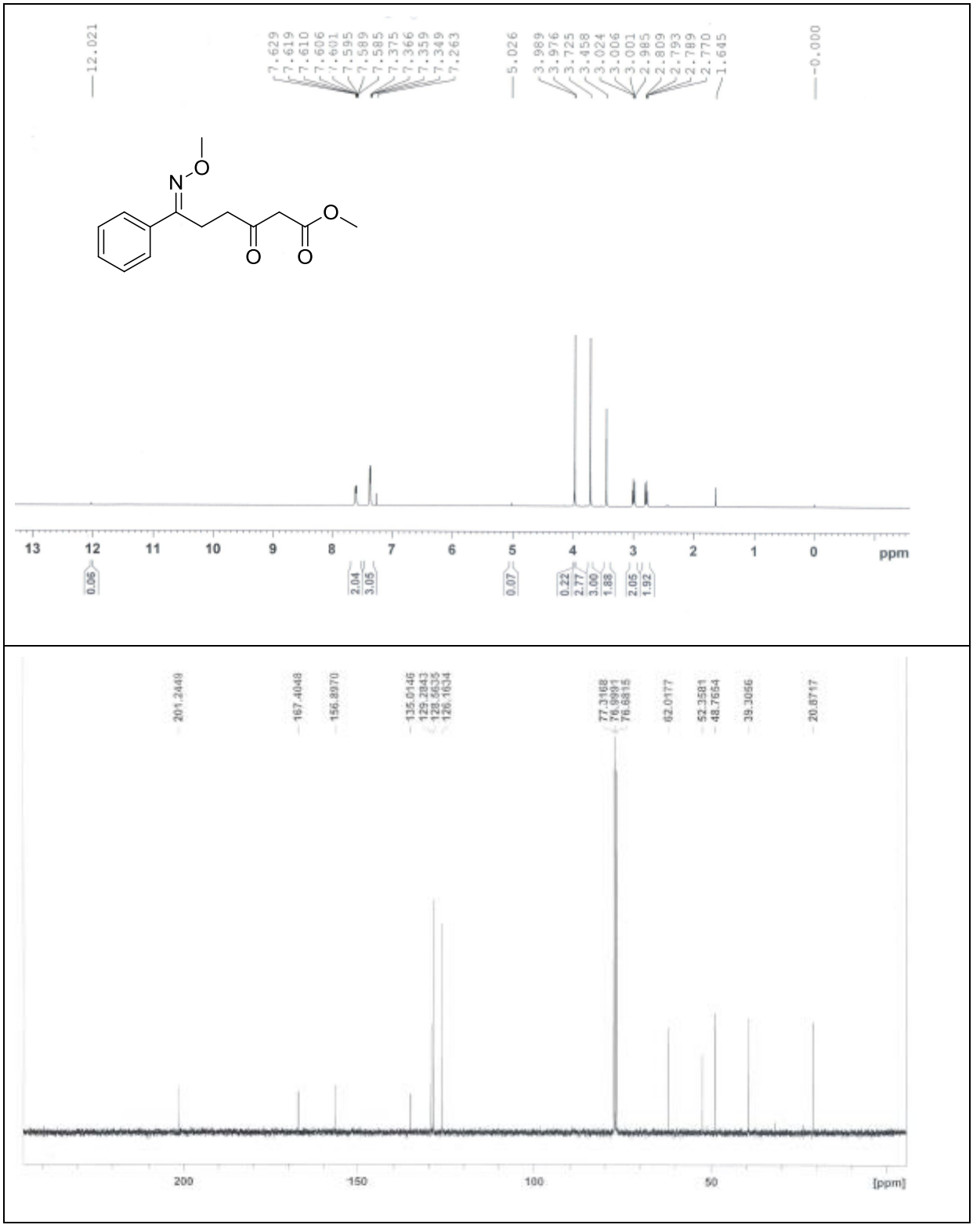
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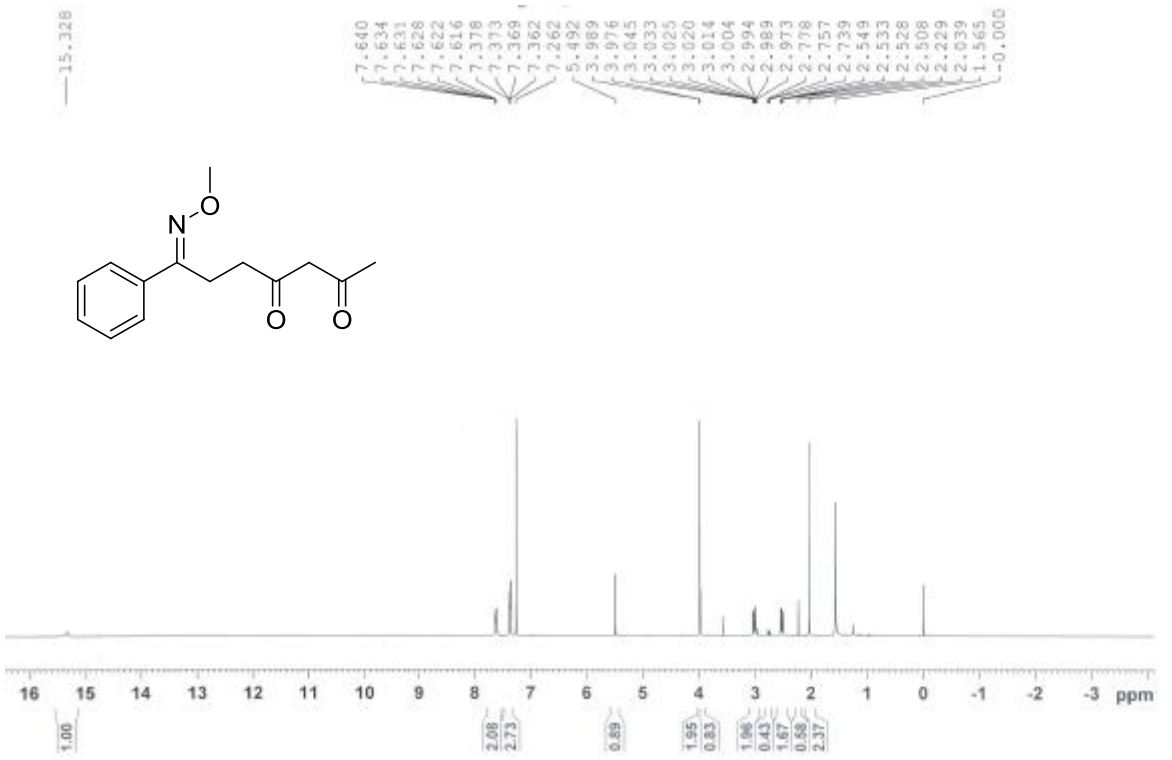
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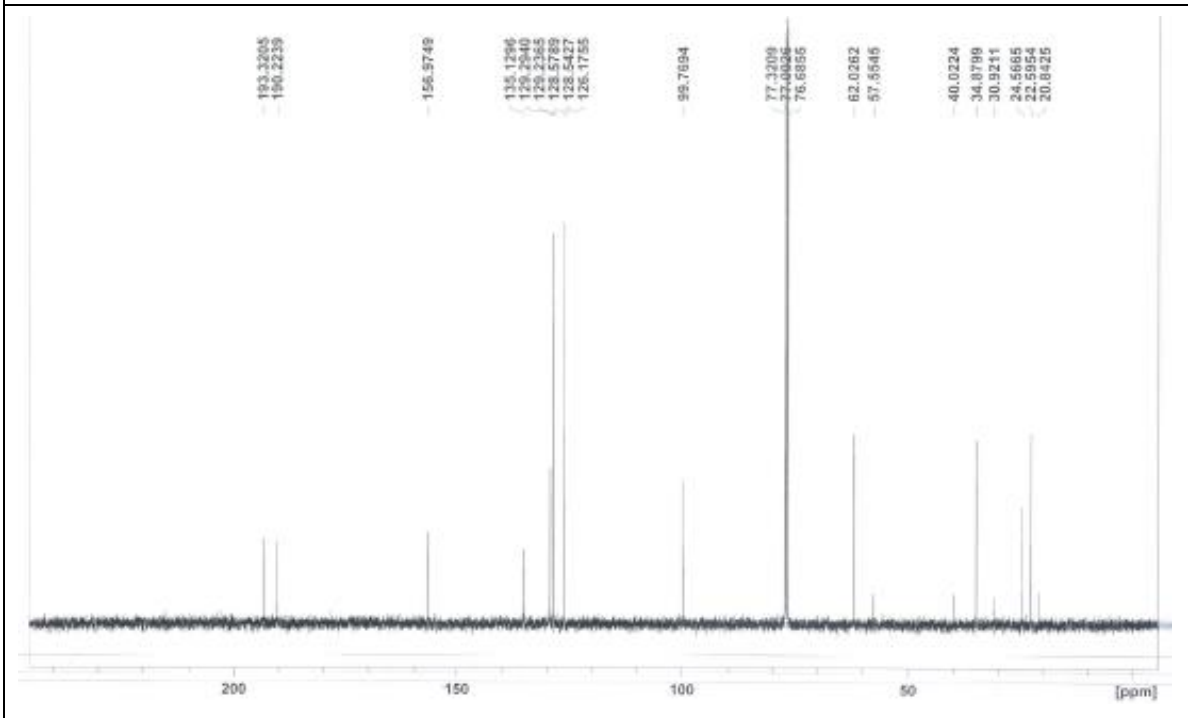
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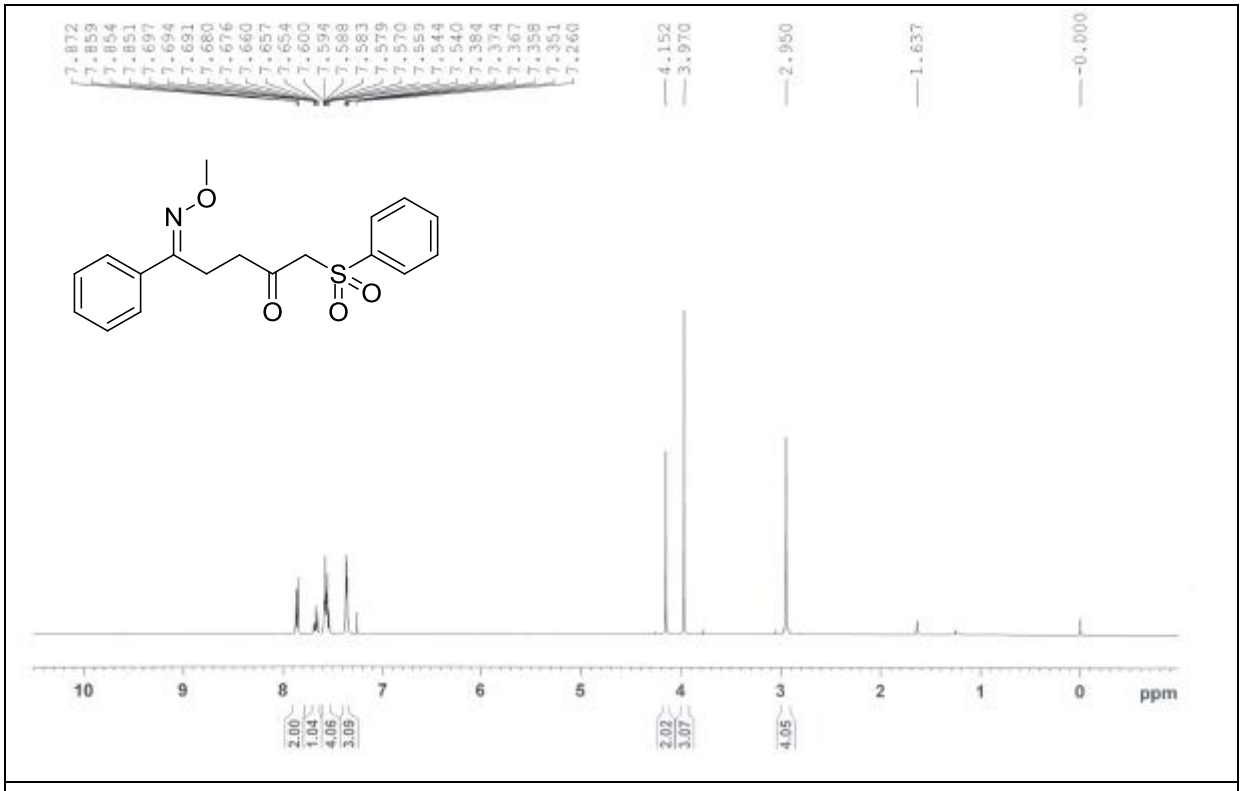

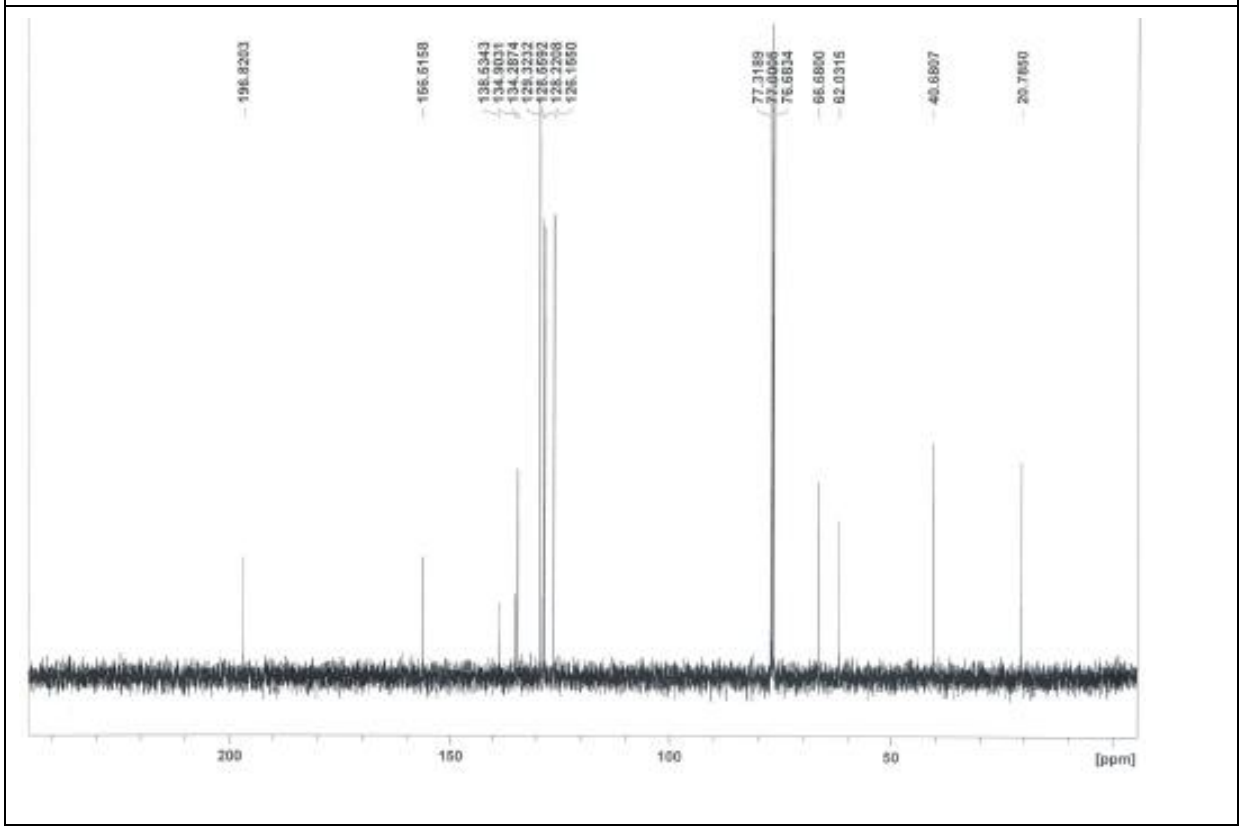

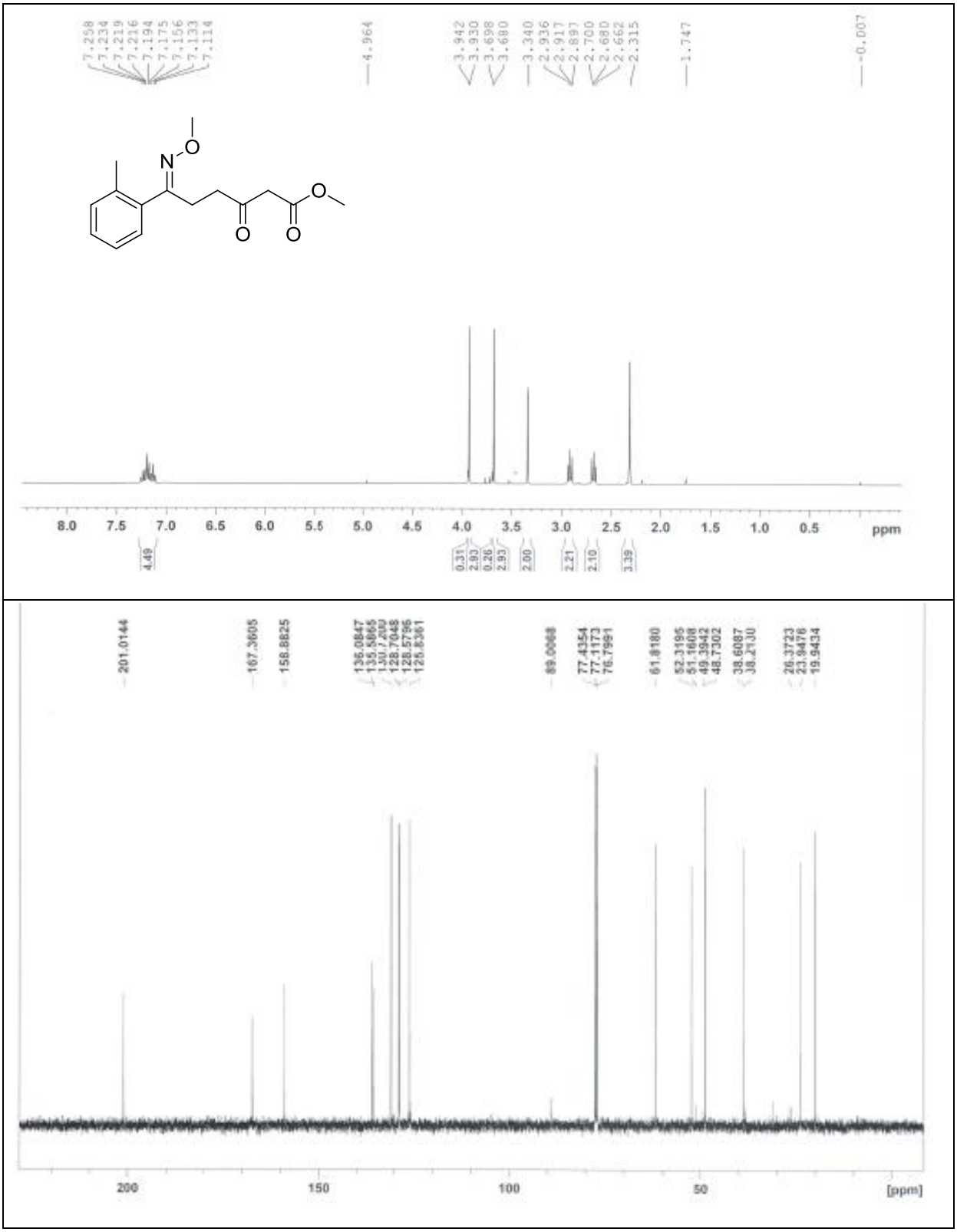
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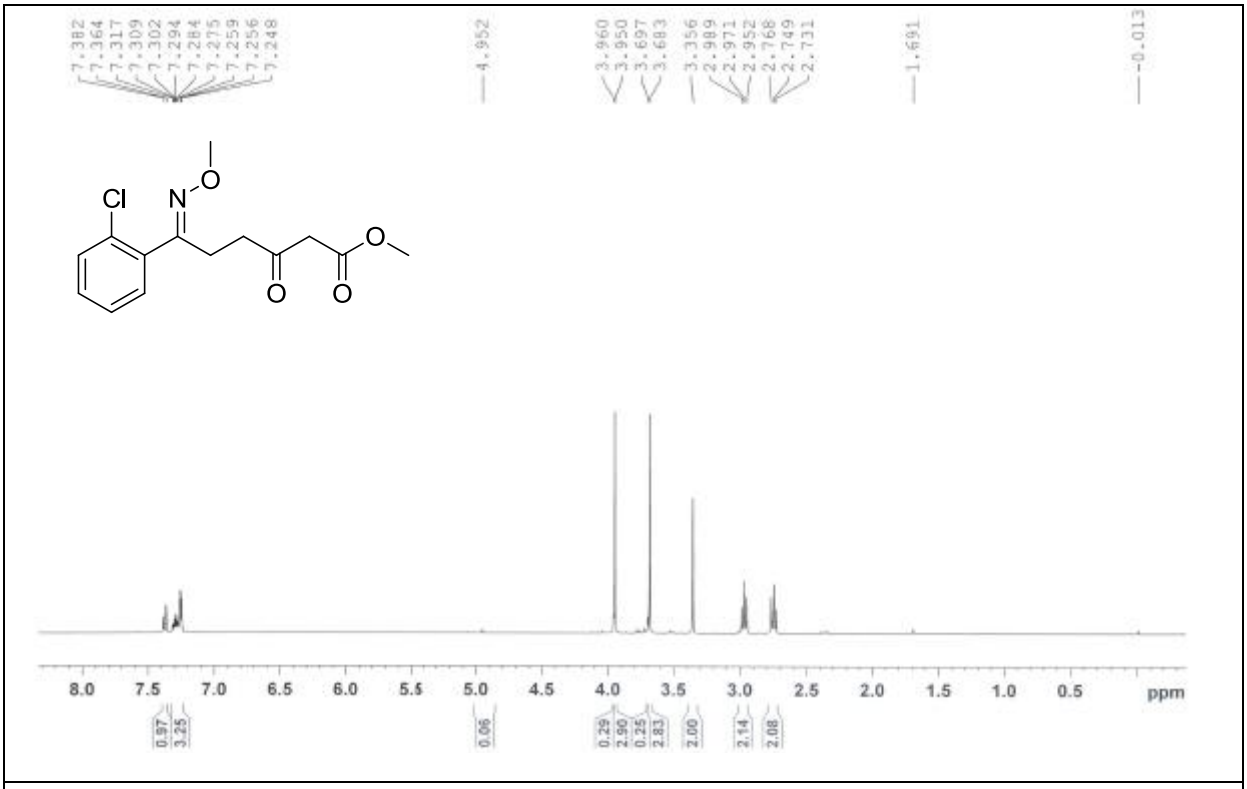
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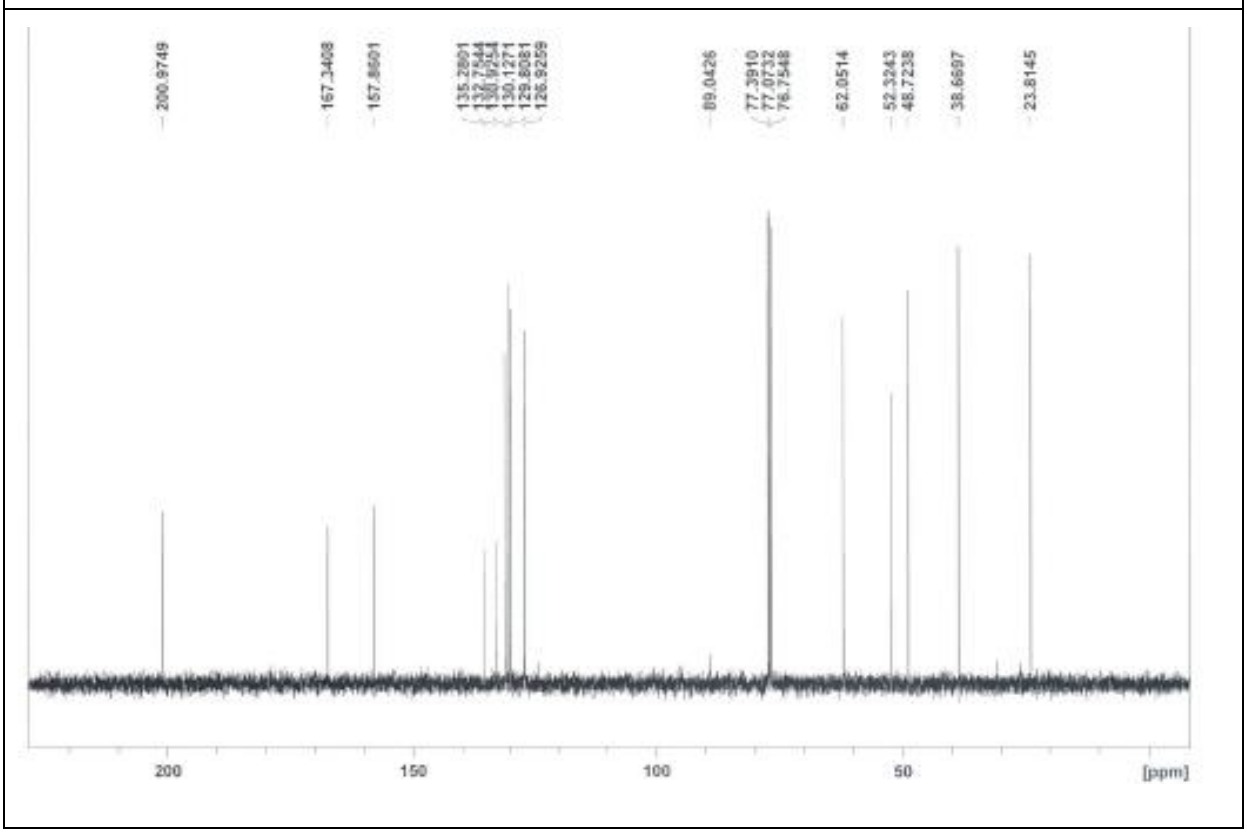
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157.8601
135.2801
132.7544
130.9254
130.1271
129.8081
126.9259
89.0426
77.3910
77.0732
76.7548
62.0514
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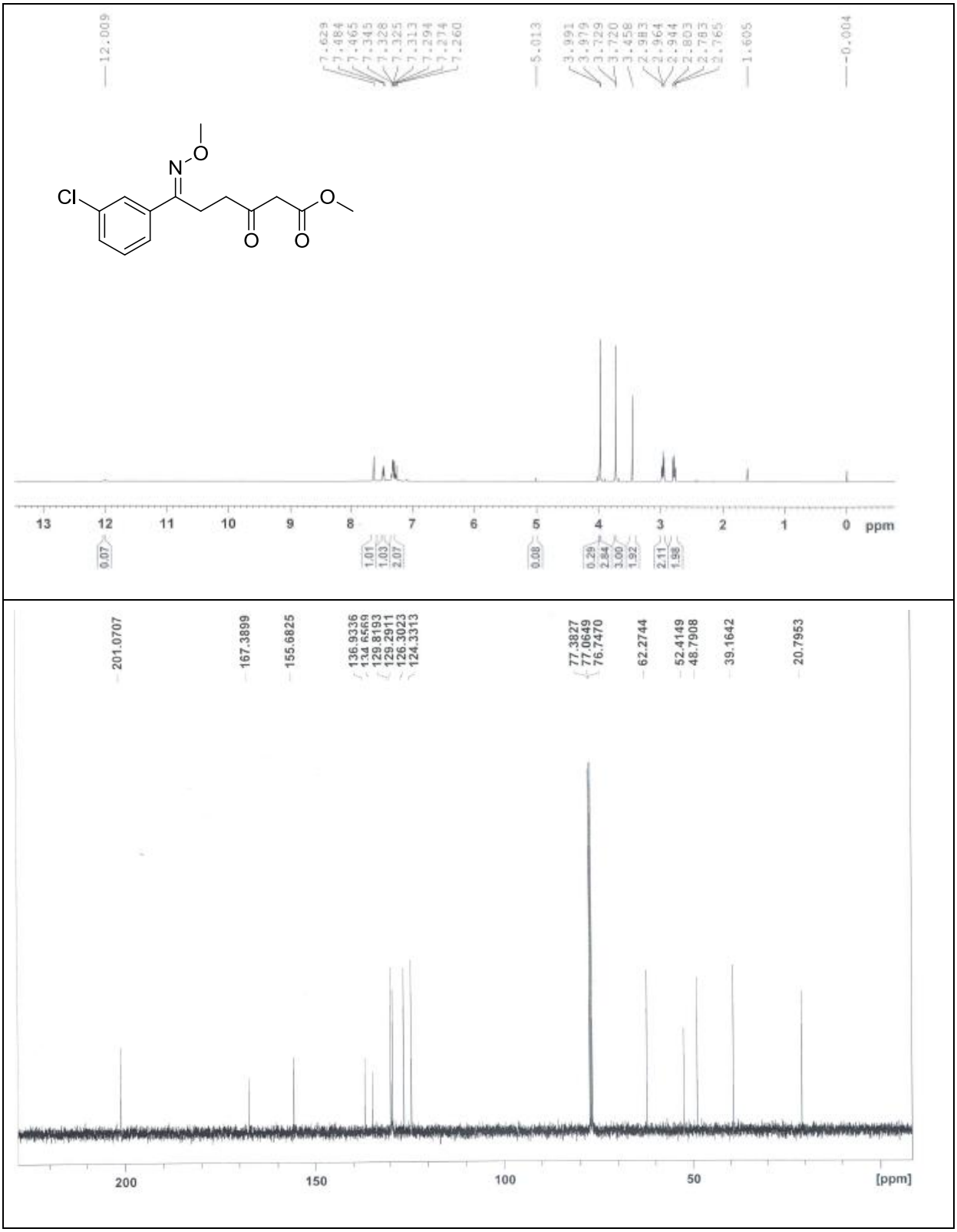
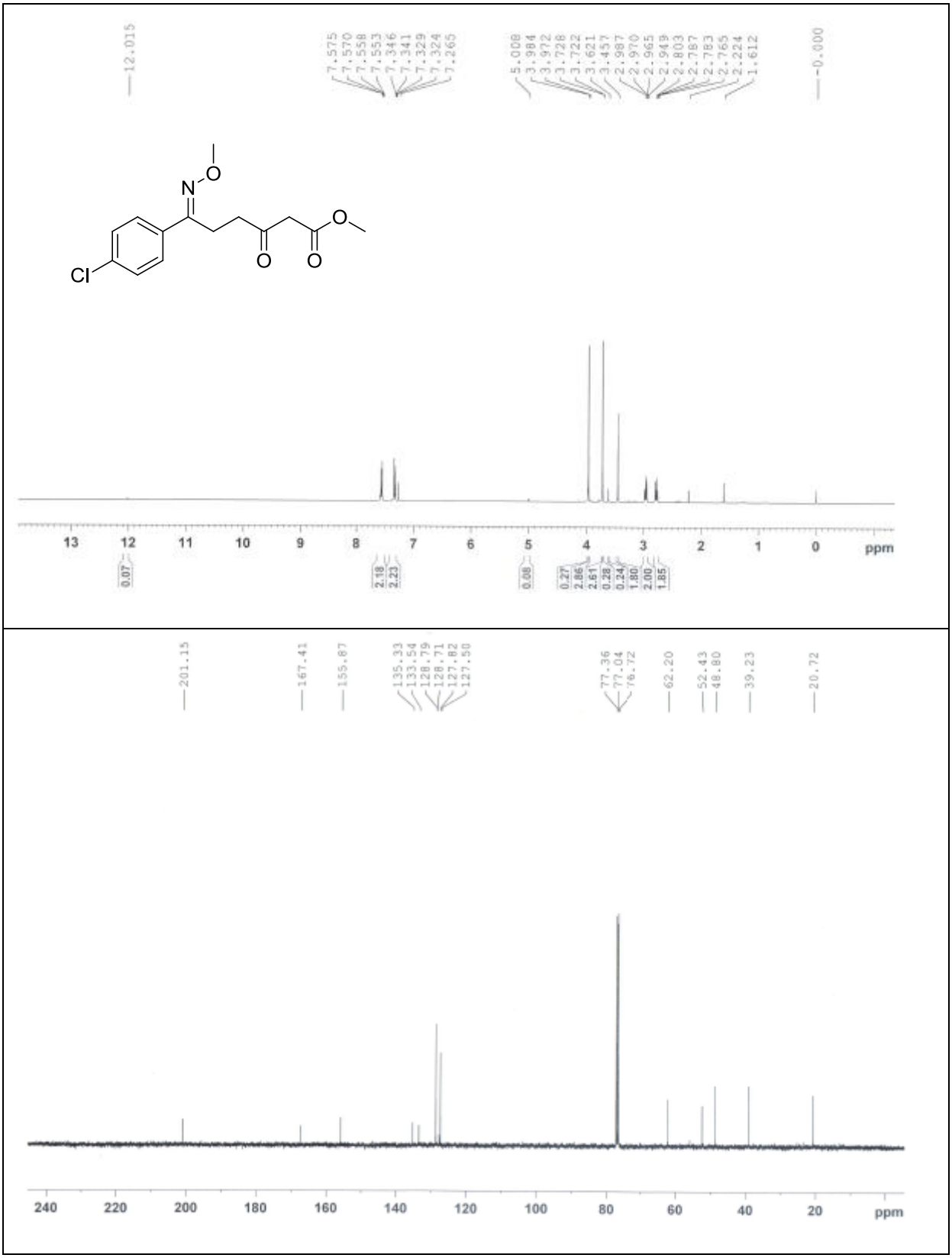
38.6697
23.8145
200
150
100
50
[ppm]

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7.570
7.558
7.553
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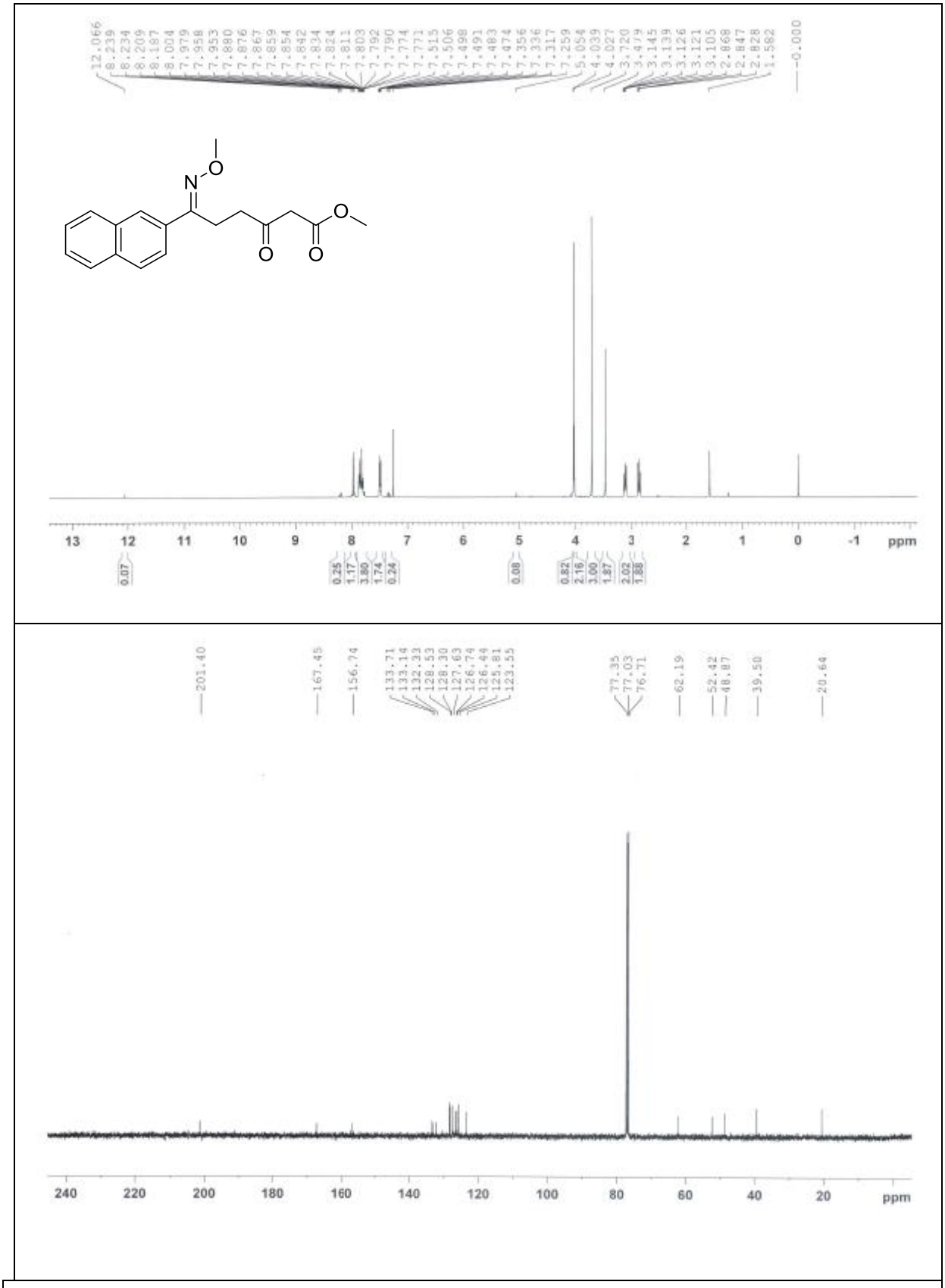
7.341
7.329
7.324
7.265
5.008
3.984
3.972
3.728
3.722
3.621
3.457
2.987
2.970
2.965
2.949
2.803
2.787
2.783
2.765
2.224
1.612
0.000
N
O
O
O
O
Cl
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.07
2.18
2.23
0.08
0.27
2.86
2.61
0.28
0.24
1.80
2.00
1.85
201.15
167.41
155.67
135.33
133.54
128.79
128.71
127.82
127.50
77.36
77.04
76.72
62.20
52.43
48.80
39.23
20.72
240
220
200
180
160
140
120
100
80
60
40
20
ppm


12.018
7.572
7.567
7.555
7.550
7.261
6.898
6.893
6.880
6.875
5.024
3.963
3.951
3.822
3.729
3.724
3.458
2.995
2.977
2.972
2.956
2.796
2.780
2.775
2.757
1.563
0.000
N
O
O
O
O
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.06
2.10
2.09
0.06
0.31
2.68
3.15
3.00
1.91
2.06
1.93
201.38
167.47
160.59
156.54
127.58
127.52
113.99
77.34
77.02
76.71
61.92
55.34
52.40
40.84
39.49
20.85
0.00
240
220
200
180
160
140
120
100
80
60
40
20
ppm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8.234
8.209
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8.004
7.979
7.958
7.953
7.880
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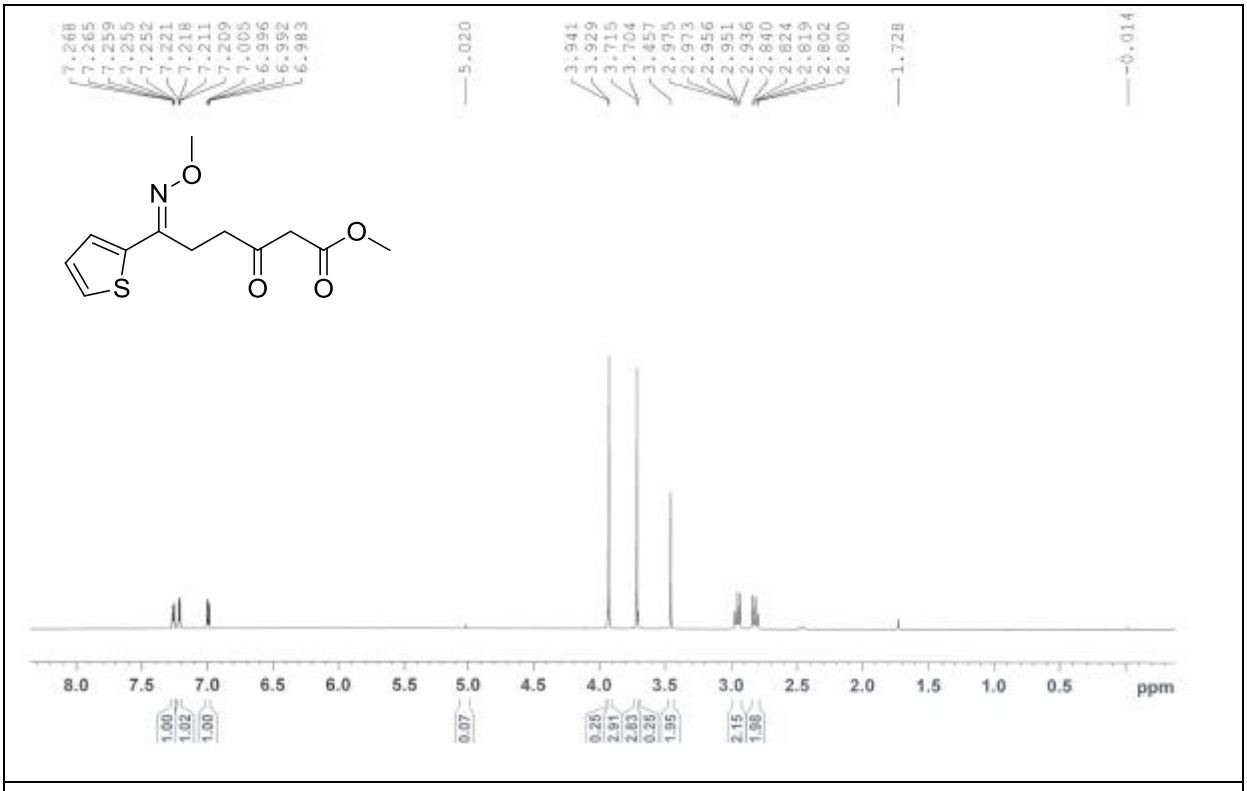
7.867
7.859
7.854
7.842
7.834
7.824
7.811
7.803
7.792
7.790
7.774
7.771
7.515
7.506
7.498
7.491
7.483
7.474
7.356
7.336
7.317
7.259
5.054
4.039
4.027
3.720
3.479
3.145
3.139
3.126
3.121
3.105
2.868
2.847
2.828
1.582
0.000
N
O
O
O
O
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
0.07
0.25
1.17
3.80
1.74
0.24
0.08
0.82
2.16
3.00
1.87
2.02
1.88
201.40
167.45
156.74
133.71
133.14
132.33
128.53
128.30
127.63
126.74
126.44
125.81
123.55
77.35
77.03
76.71
62.19
52.42
48.87
39.50
20.64
240 220 200 180 160 140 120 100 80 60 40 20 ppm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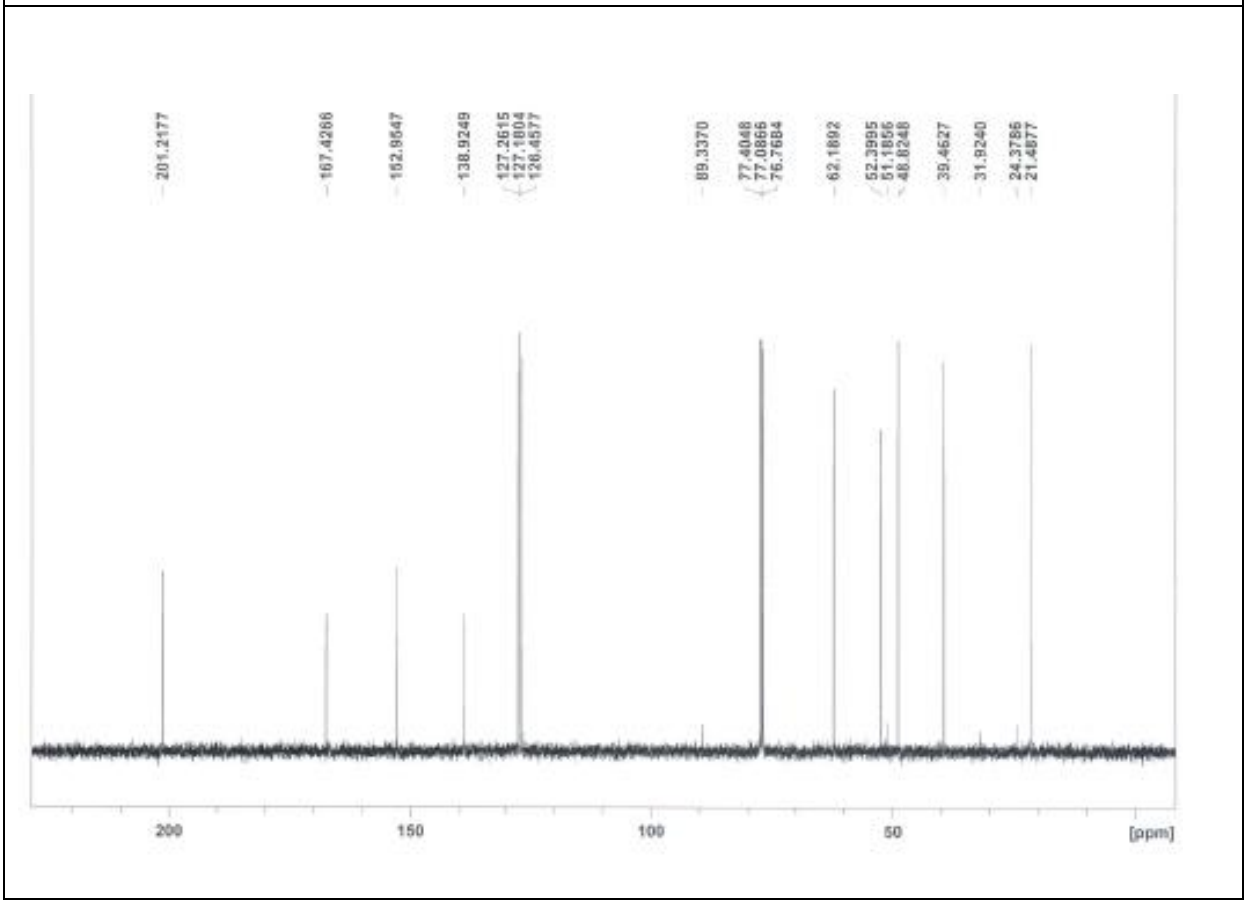
7.265
7.259
7.255
7.252
7.221
7.218
7.211
7.209
7.005
6.996
6.992
6.983
5.020
3.941
3.929
3.715
3.704
3.457
2.975
2.973
2.956
2.951
2.936
2.840
2.824
2.819
2.802
2.800
1.728
0.014
N
O
S
O
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.02
1.00
0.07
0.25
2.91
2.83
0.25
1.95
2.15
1.98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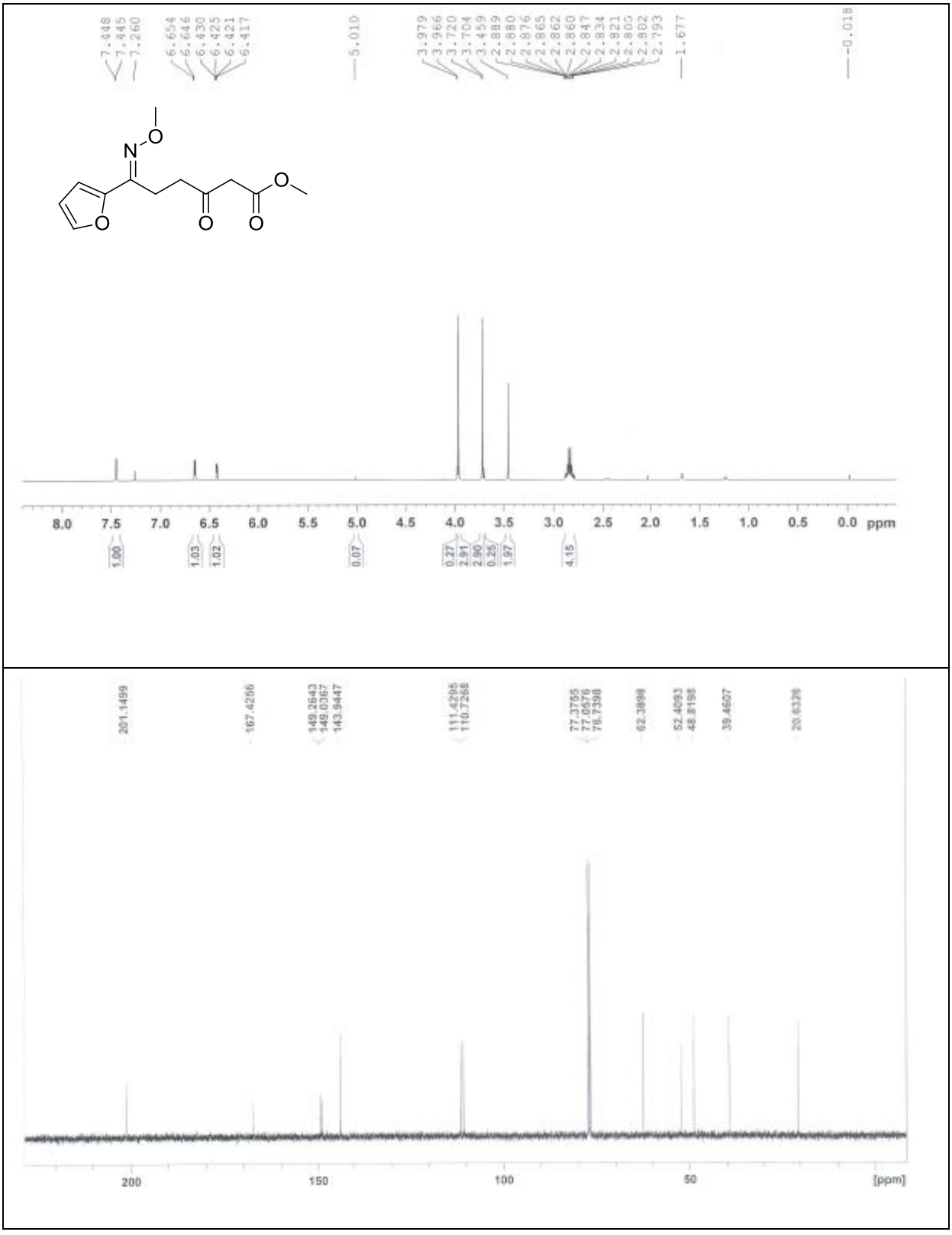
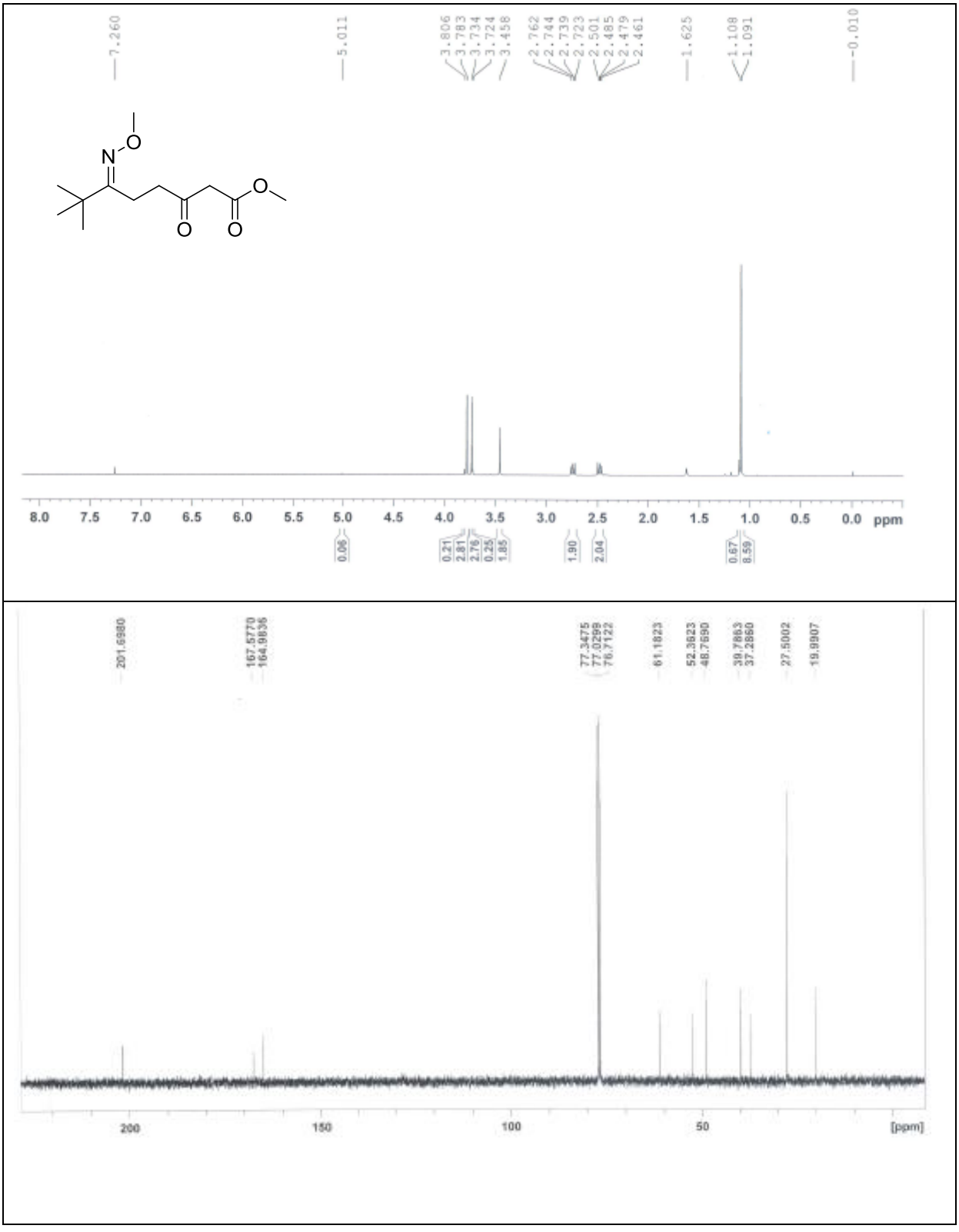
167.4266
162.9547
138.9249
127.2615
127.1804
126.4577
89.3370
77.4048
77.0866
76.7684
62.1692
52.3995
51.1856
48.8248
39.4627
31.9240
24.3786
21.4877
200
150
100
50
[ppm]


7.448
7.445
7.260
6.654
6.646
6.430
6.425
6.421
6.417
5.010
3.979
3.966
3.720
3.704
3.459
2.889
2.880
2.876
2.865
2.862
2.860
2.847
2.834
2.821
2.805
2.802
2.793
1.677
0.018
N
O
O
O
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.03
1.02
0.07
0.27
2.91
2.90
0.25
1.97
4.15
201.1499
167.4256
149.2643
149.0367
143.9447
111.4295
110.7268
77.3765
77.0676
76.7598
62.3898
52.4093
48.8198
39.4607
20.6328
200
150
100
50
[ppm]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5.011
3.806
3.783
3.734
3.724
3.458
2.762
2.744
2.739
2.723
2.501
2.485
2.479
2.461
1.625
1.108
1.091
0.010
N
O
O
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.06
0.21
2.81
2.76
0.25
1.85
1.90
2.04
0.67
8.59
201.6980
167.5770
164.9836
77.3475
77.0299
76.7122
61.1823
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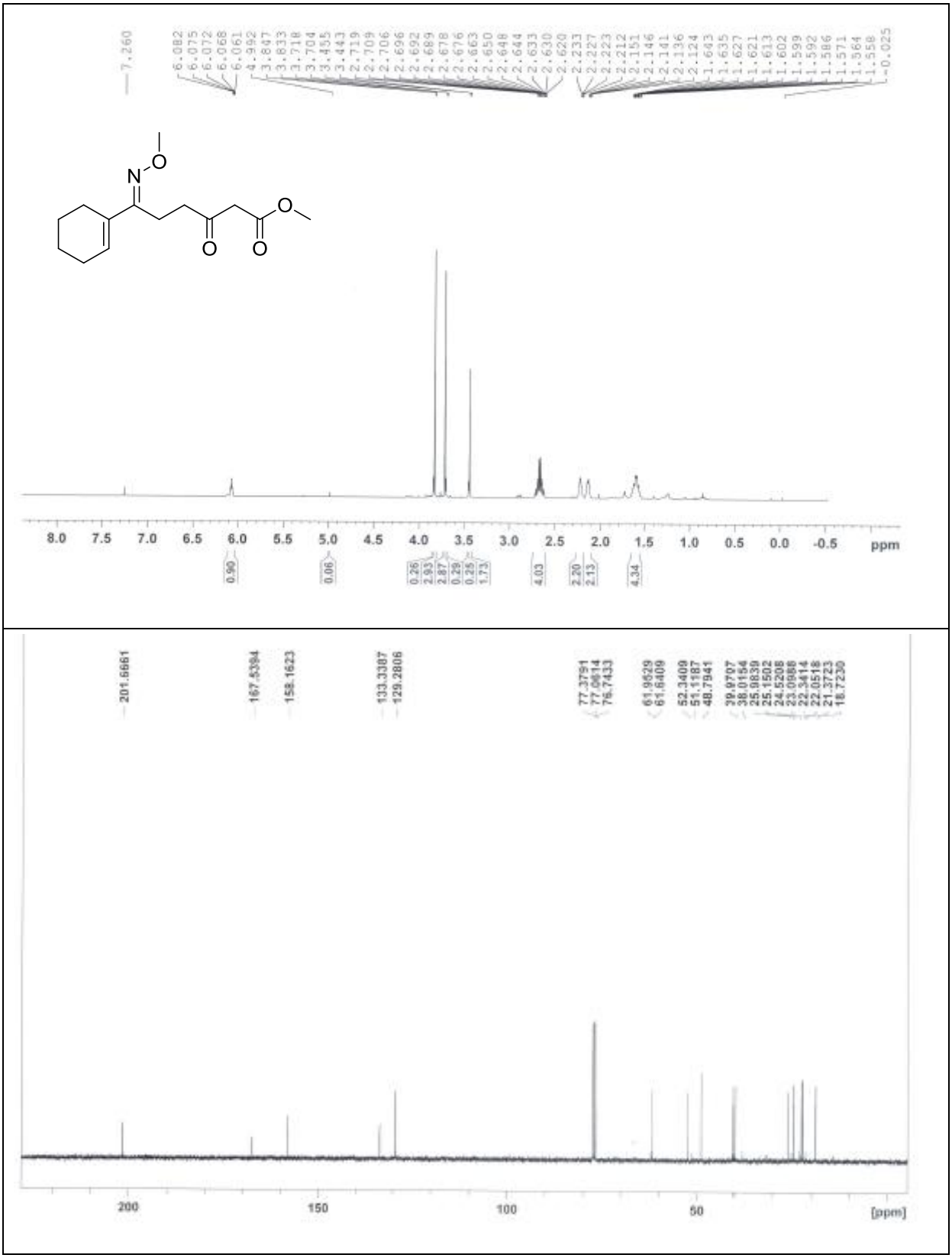
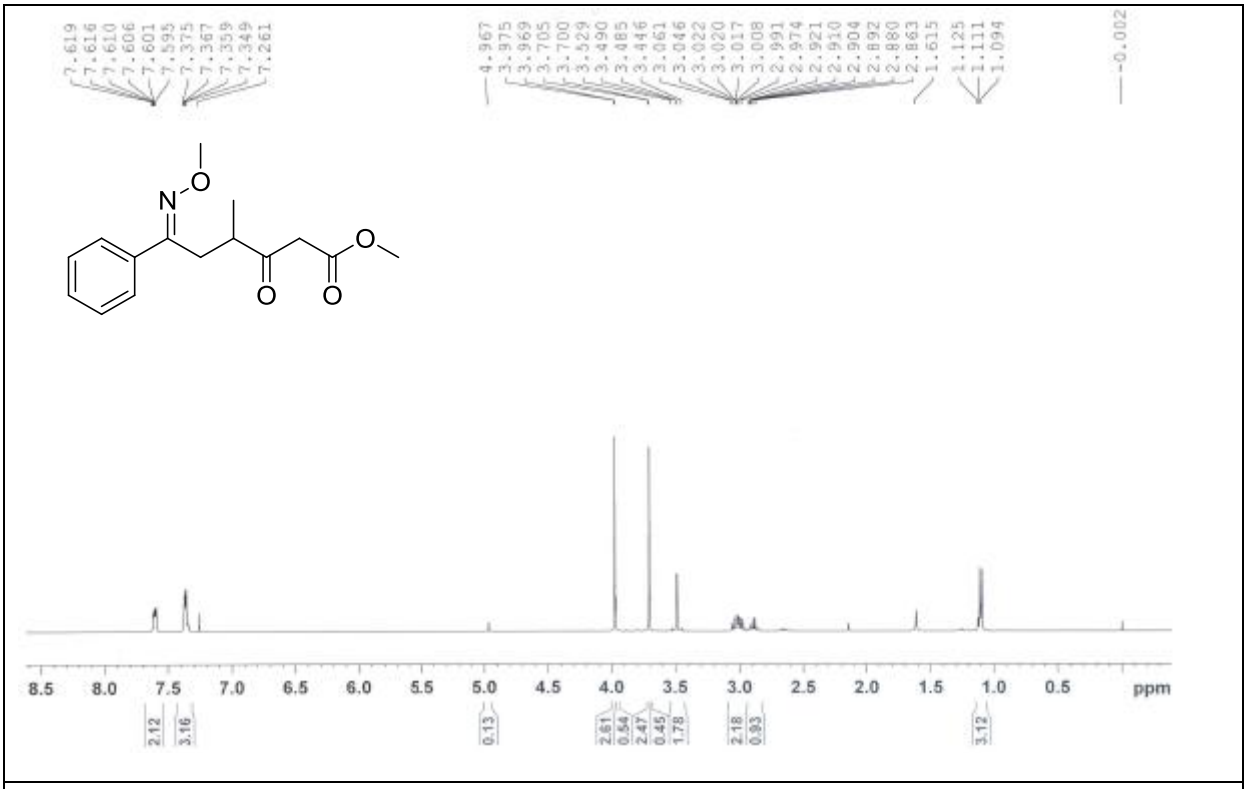
48.7690
39.7863
37.2860
27.5002
19.9907
200
150
100
50
[ppm]

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7.610
7.606
7.601
7.595
7.375
7.367
7.359
7.349
7.261
4.367
3.975
3.969
3.705
3.700
3.529
3.490
3.485
3.446
3.061
3.046
3.022
3.020
3.017
3.008
2.991
2.974
2.921
2.910
2.904
2.892
2.880
2.863
1.635
1.125
1.111
1.094
-0.002
N
O
O
O
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
ppm
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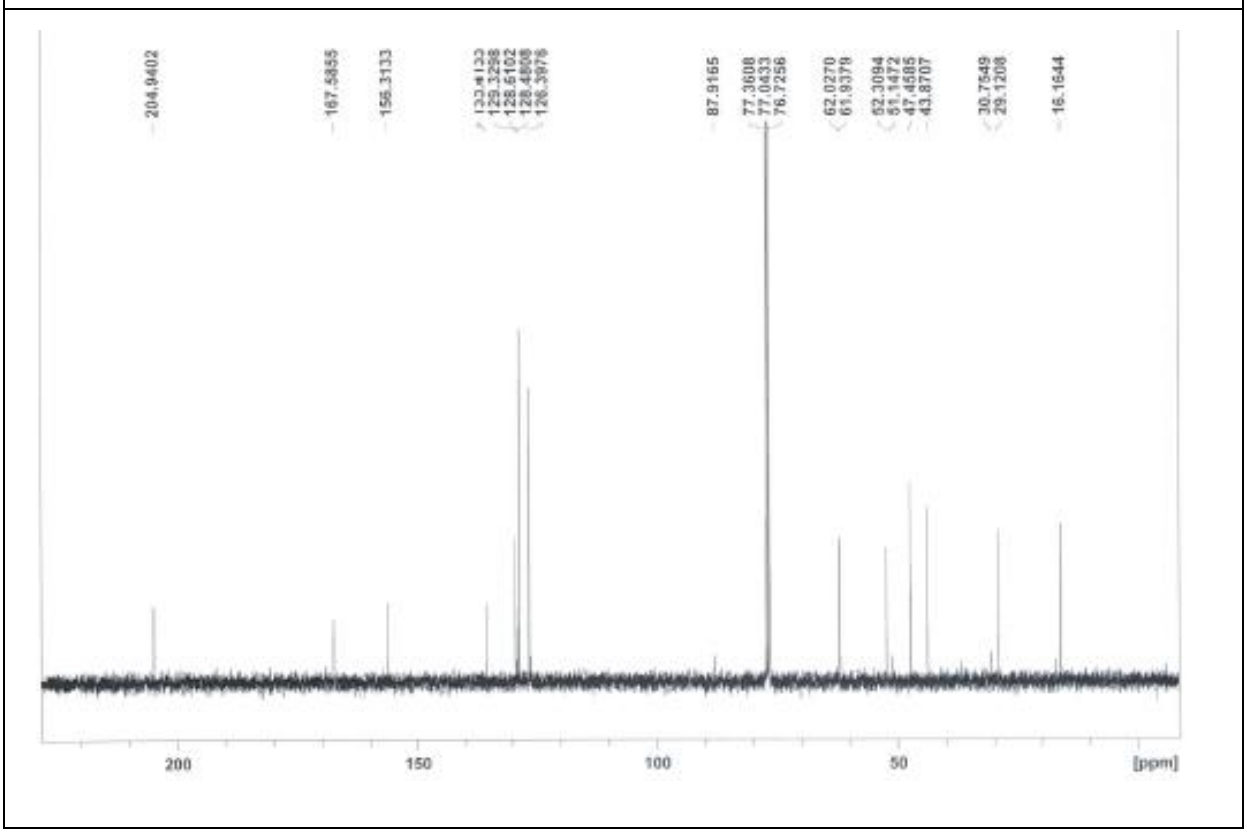
3.16
0.13
2.61
0.54
2.47
0.45
1.78
2.18
0.93
3.12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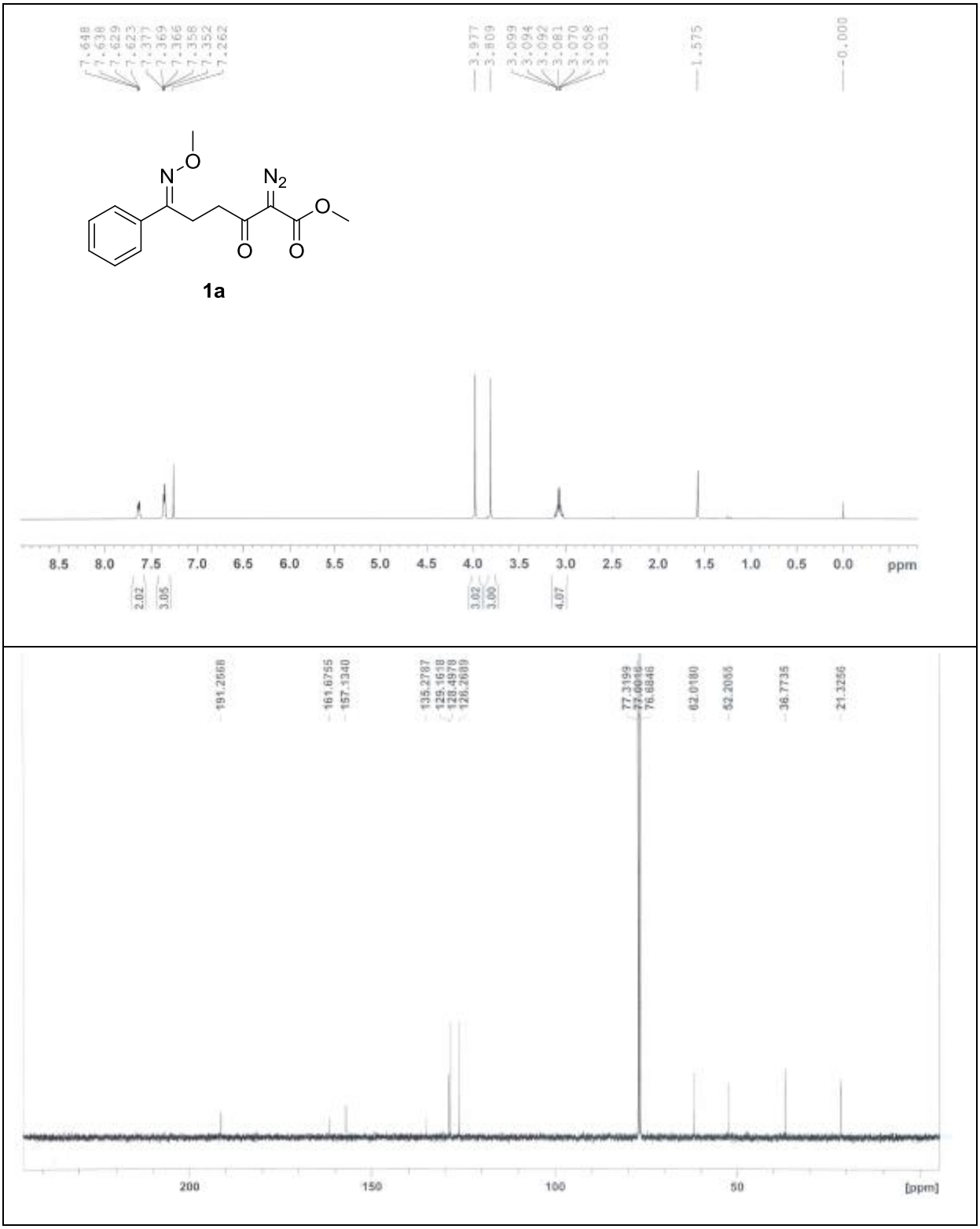
129.3298
128.6102
128.4808
126.3976
87.9165
77.3608
77.0433
76.7256
62.0270
61.9379
52.3094
51.1472
47.4585
43.8707
30.7549
29.1208
16.1644
200
150
100
50
[ppm]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7.629
7.623
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7.369
7.366
7.358
7.352
7.262
3.977
3.809
3.099
3.094
3.092
3.081
3.070
3.058
3.051
1.575
0.000
N
O
N2
O
O
O
1a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
3.05
3.02
3.00
4.07
191.2668
161.6755
157.1340
135.2787
129.1618
128.4978
126.2689
77.3199
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76.6846
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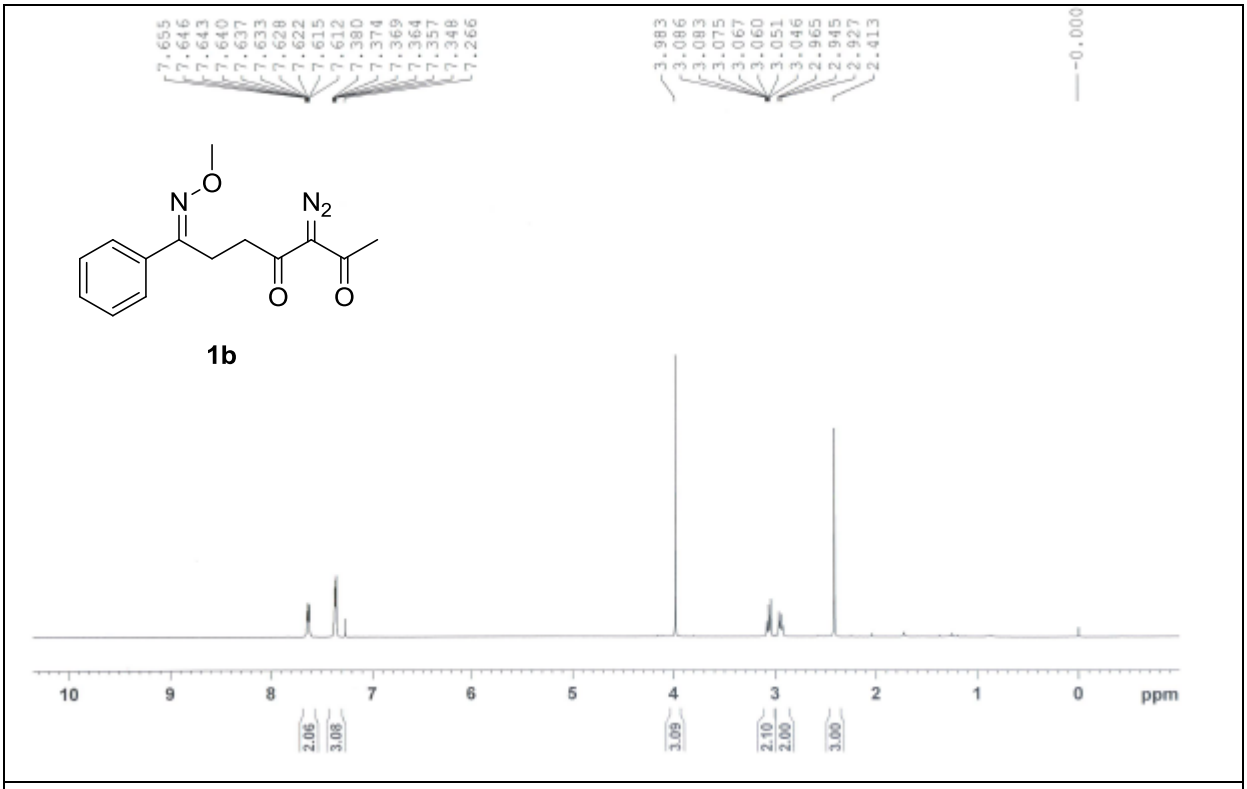
52.2055
36.7735
21.3256
200
150
100
50
[ppm]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7.637
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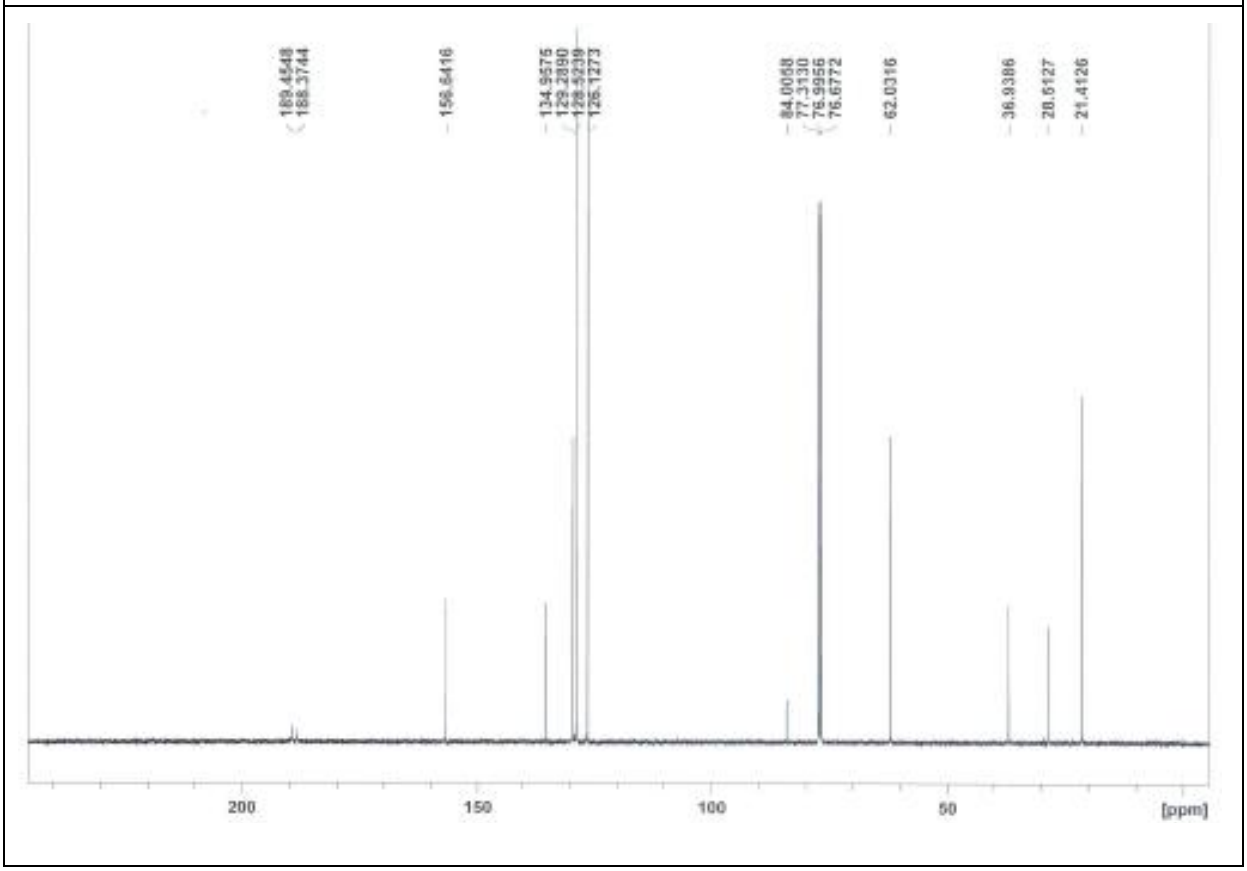
7.628
7.622
7.615
7.612
7.380
7.374
7.369
7.364
7.357
7.348
7.266
3.983
3.086
3.083
3.075
3.067
3.060
3.051
3.046
2.965
2.945
2.927
2.413
0.000
N
O
N2
O
O
1b
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
3.08
3.09
2.10
2.00
3.00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129.2890
128.5239
126.1273
84.0068
77.3130
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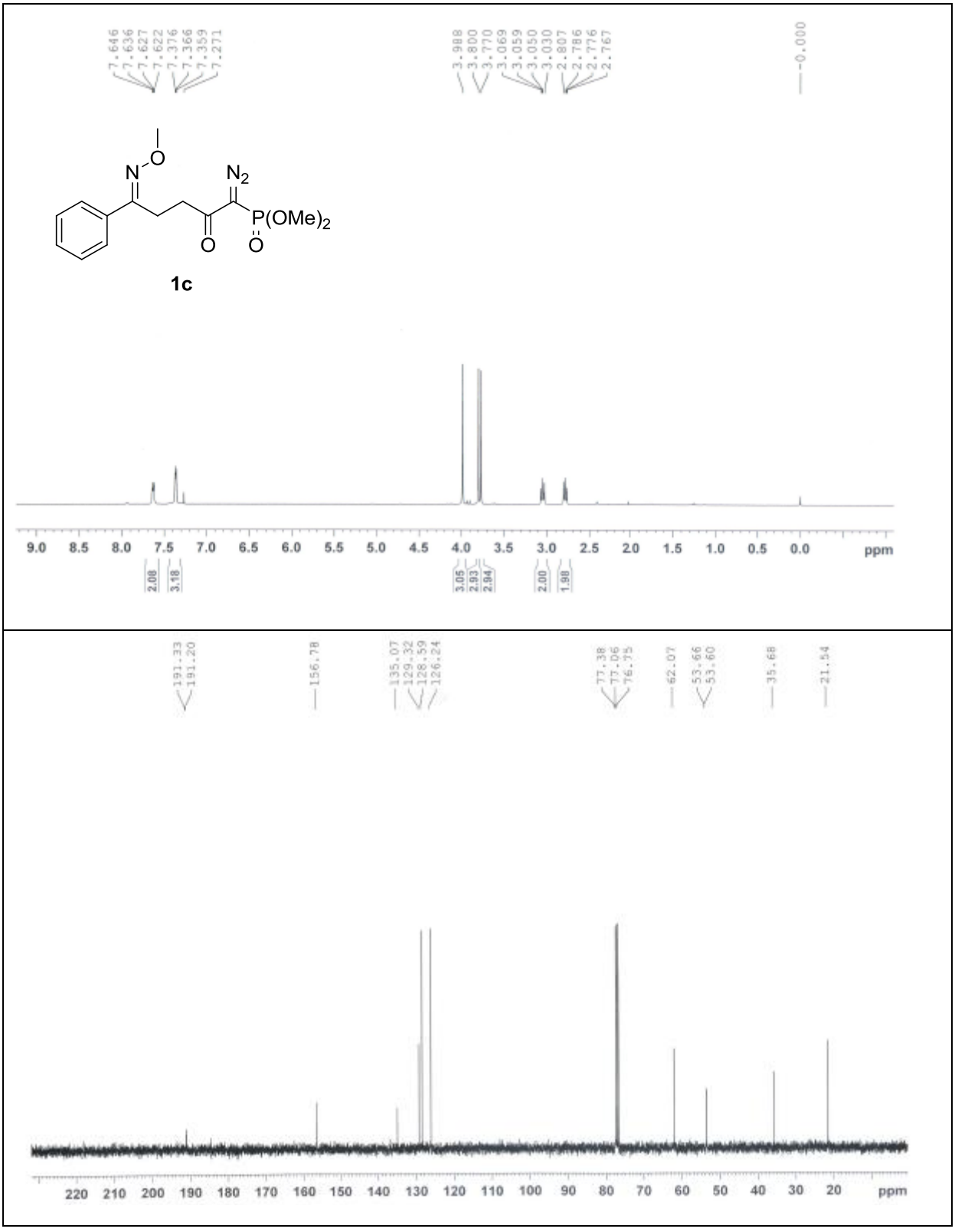
76.6772
62.0316
36.9386
28.6127
21.4126
200
150
100
50
[ppm]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7.627
7.622
7.376
7.366
7.359
7.271
3.988
3.800
3.770
3.069
3.059
3.050
3.030
2.807
2.786
2.776
2.767
0.000
N
O
N2
P(OMe)2
O
O
1c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.08
3.18
3.05
2.93
2.94
2.00
1.98
191.33
191.20
156.78
135.07
129.32
128.59
126.24
77.38
77.06
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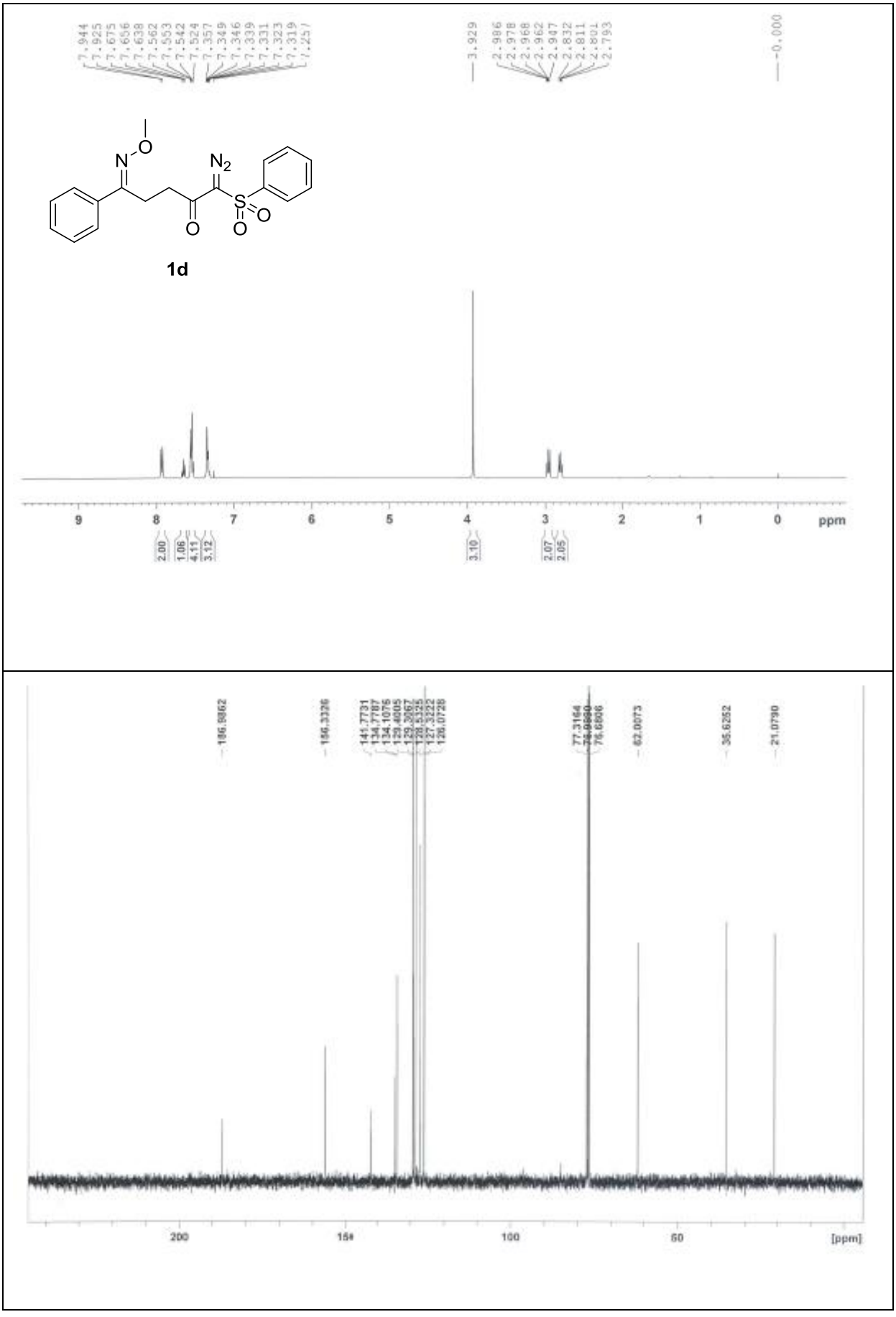
62.07
53.66
53.60
35.68
21.54
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.553
7.542
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7.346
7.339
7.331
7.323
7.319
7.257
3.929
2.986
2.978
2.968
2.962
2.947
2.832
2.811
2.801
2.793
0.000
N
O
N2
S
O
O
O
1d
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.06
4.11
3.12
3.10
2.07
2.05
166.8862
156.3326
141.7731
134.7787
134.1076
129.4005
129.3067
128.5335
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200
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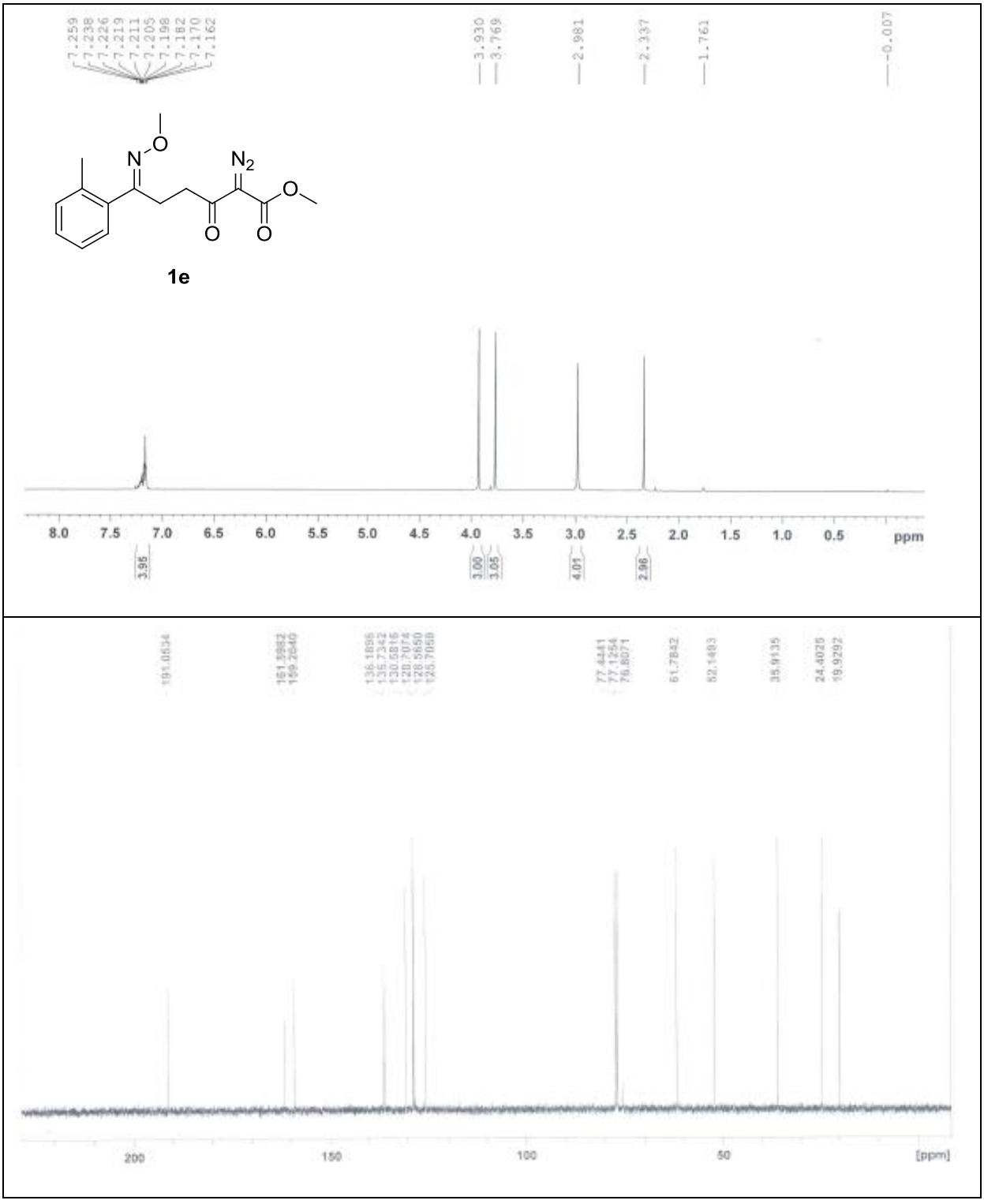
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7.205
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7.162
3.930
3.769
2.981
2.337
1.761
0.007
N
O
N2
O
O
O
1e
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.96
3.00
3.05
4.01
2.96
191.0634
161.5982
159.2640
136.1896
135.7342
130.6816
120.7074
120.5660
128.5660
125.7059
77.4441
77.1254
76.8071
61.7842
52.1493
35.9135
24.4025
19.9292
200
150
100
50
[ppm]


7.391
7.388
7.380
7.376
7.372
7.368
7.317
7.310
7.304
7.302
7.295
7.290
7.286
7.279
7.274
7.270
7.260
3.964
3.795
3.047
1.569
0.002
Cl
N
O
N2
O
O
O
1f
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
ppm
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3.55
3.00
2.98
4.00
191.0322
161.4176
158.2158
135.3518
134.8164
131.0077
130.0027
129.7503
126.7987
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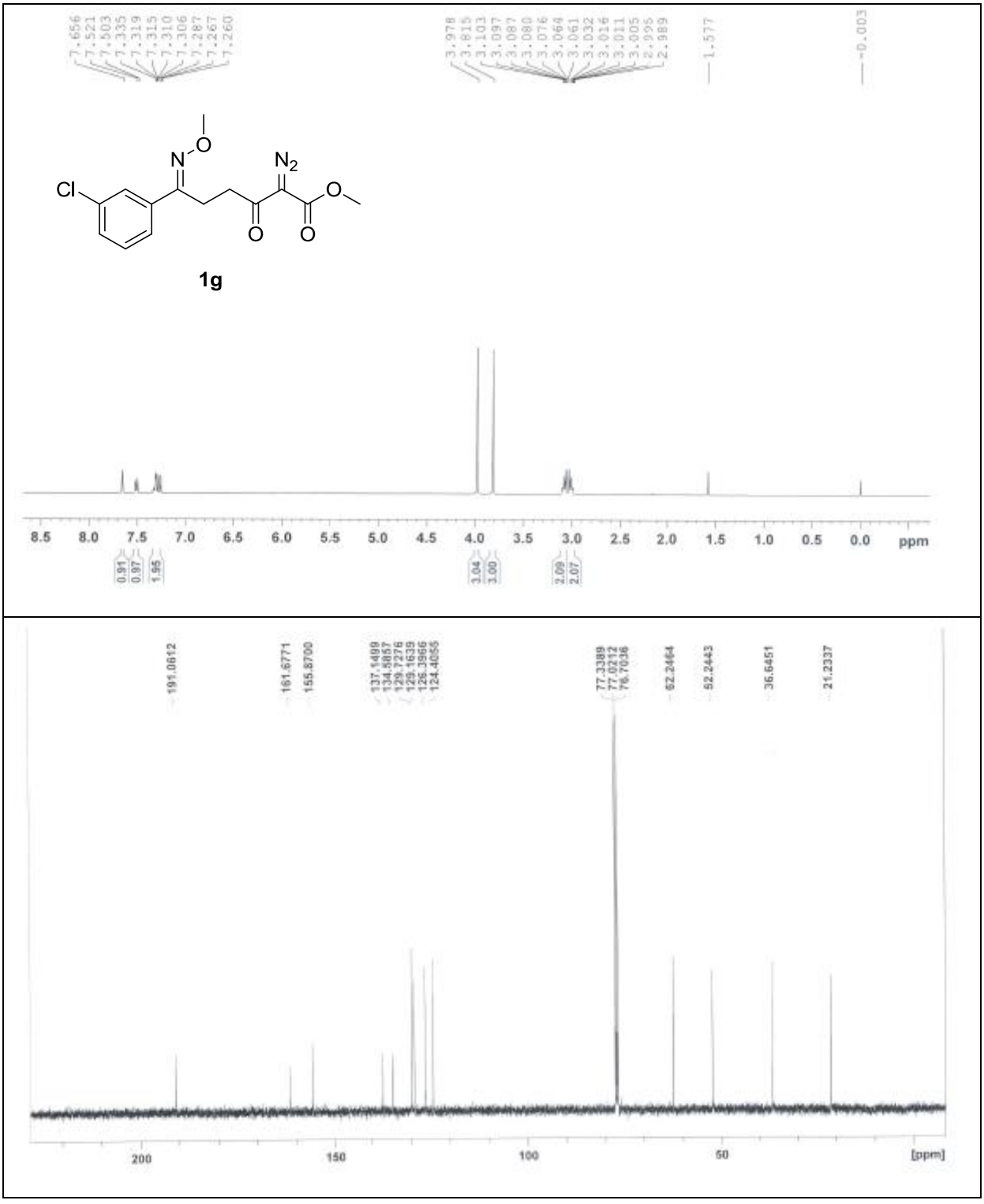
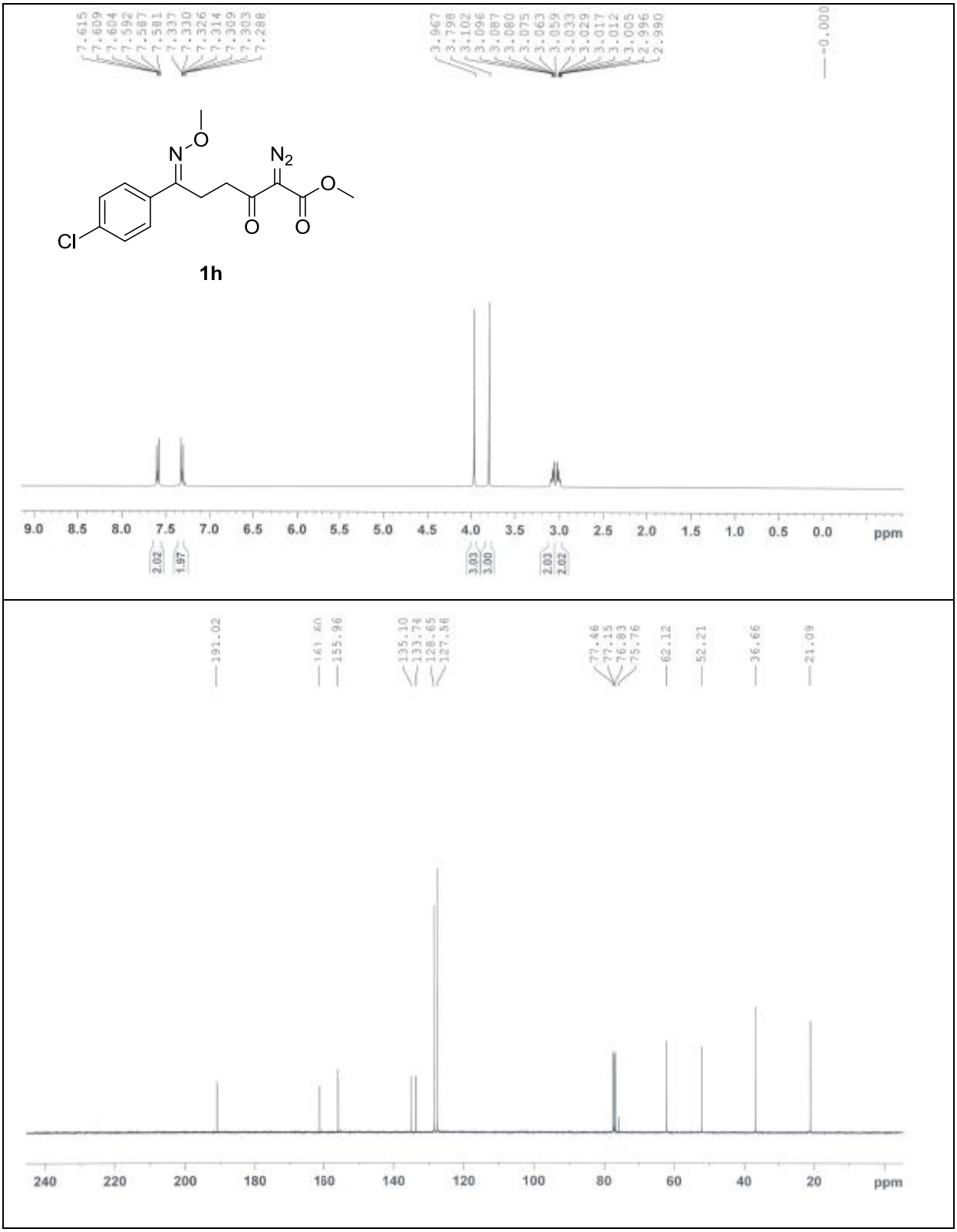
24.1762
200
150
100
50
[ppm]

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7.330
7.326
7.314
7.309
7.303
7.288
3.967
3.798
3.102
3.096
3.087
3.080
3.075
3.063
3.059
3.033
3.029
3.017
3.012
3.005
2.996
2.990
0.000
N
O
N2
O
O
O
Cl
1h
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
1.97
3.03
3.00
2.03
2.02
191.02
161.60
155.96
135.10
133.74
128.65
127.56
77.46
77.15
76.83
75.76
62.12
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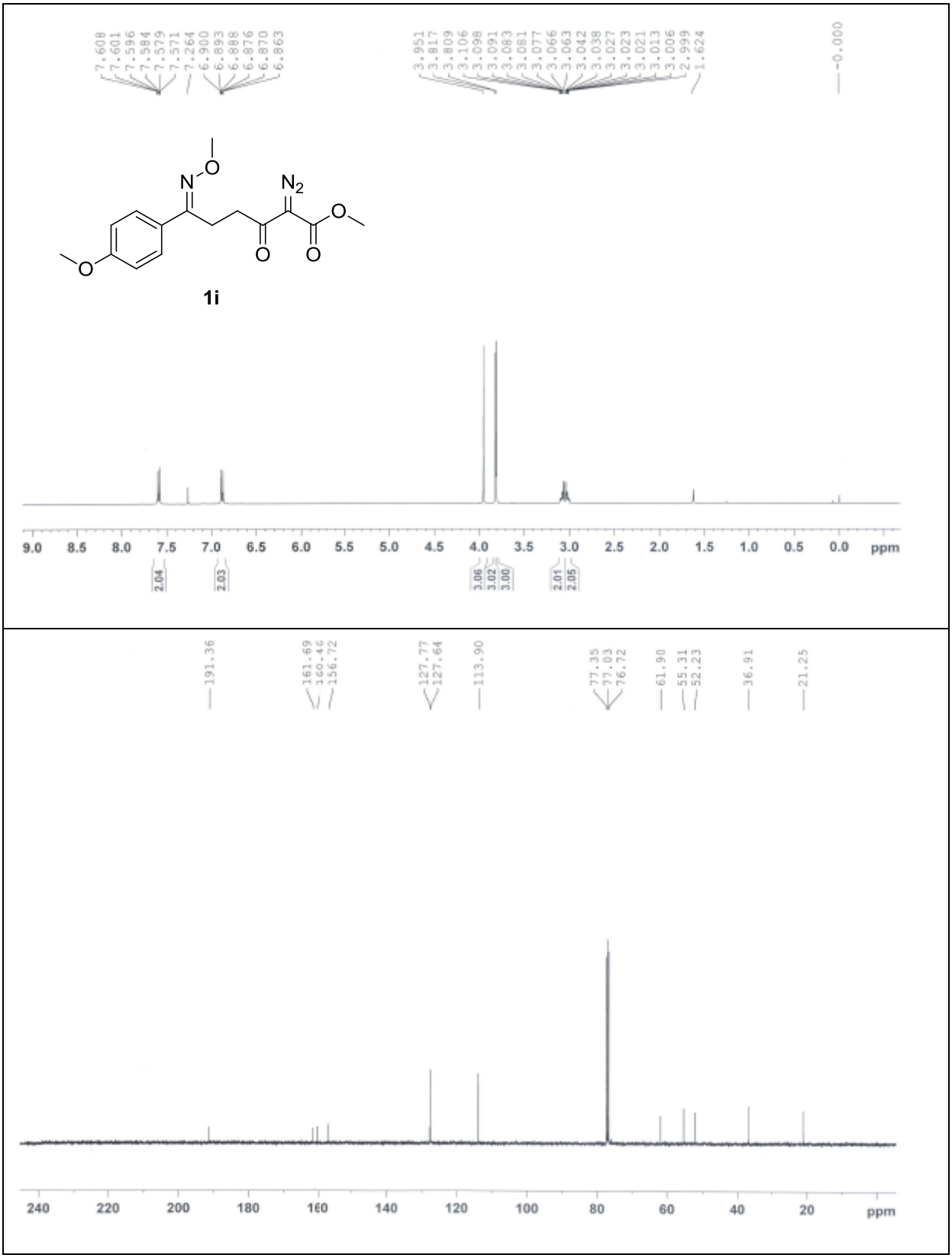
36.66
21.09
240
220
200
180
160
140
120
100
80
60
40
20
ppm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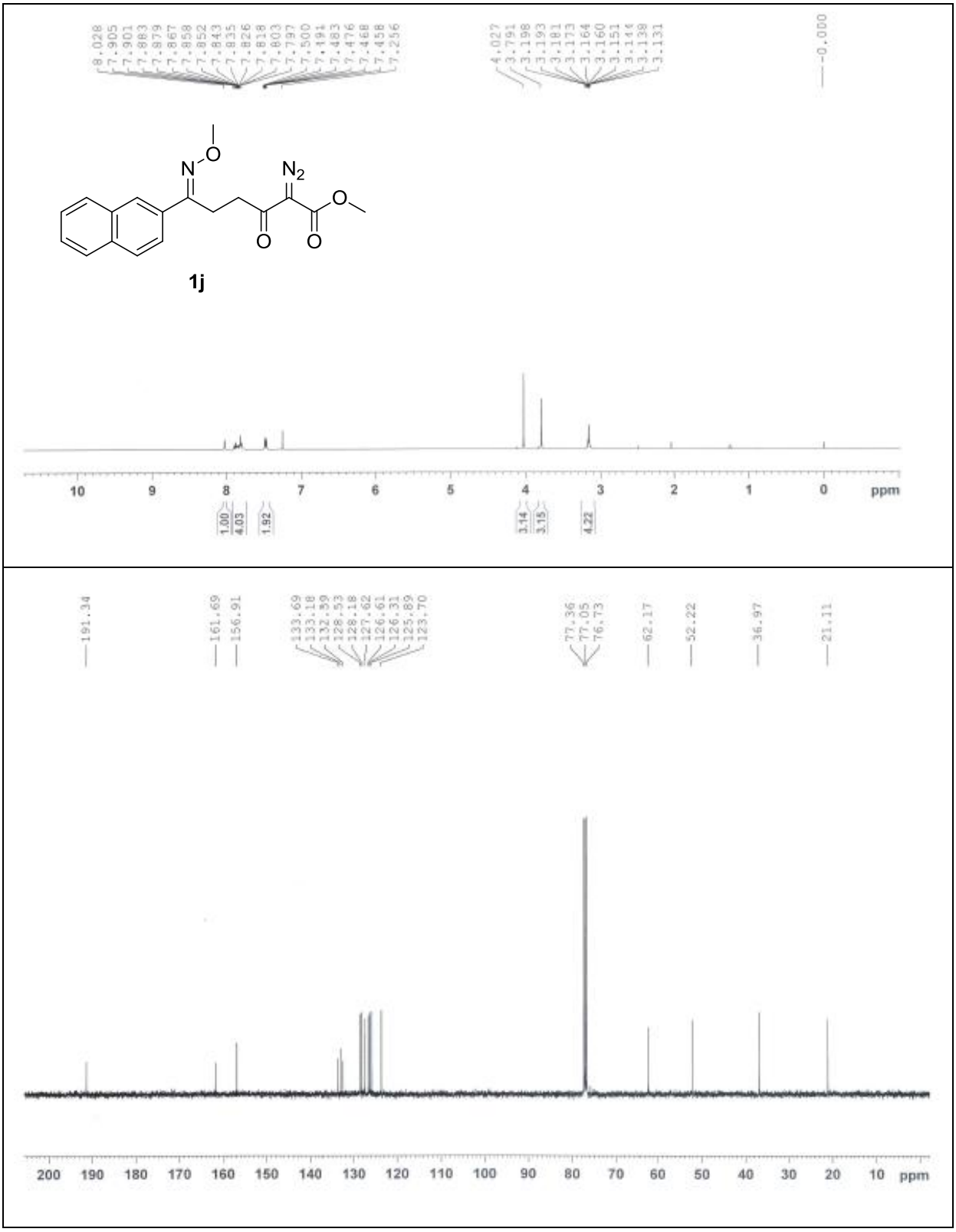
7.571
7.264
6.900
6.893
6.888
6.876
6.870
6.863
3.951
3.817
3.809
3.106
3.098
3.091
3.083
3.081
3.077
3.066
3.063
3.042
3.038
3.027
3.023
3.021
3.013
3.006
2.999
1.624
0.000
N
O
N2
O
O
O
O
1i
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.04
2.03
3.06
3.02
3.00
2.01
2.05
191.36
161.69
160.46
156.72
127.77
127.64
113.90
77.35
77.03
76.72
61.90
55.31
52.23
36.91
21.25
240 220 200 180 160 140 120 100 80 60 40 20 ppm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7.901
7.883
7.879
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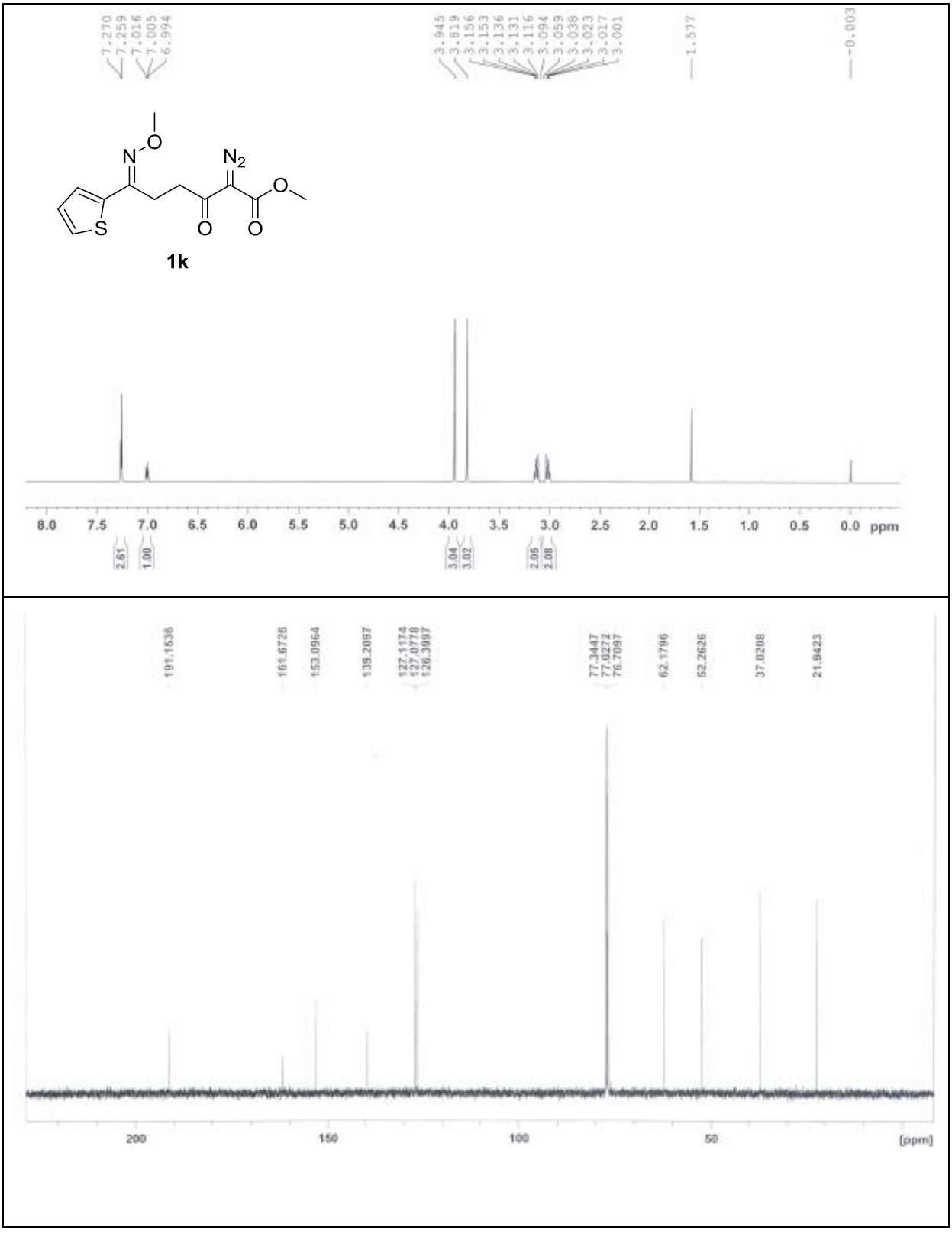
7.852
7.843
7.835
7.826
7.818
7.803
7.797
7.500
7.491
7.483
7.476
7.468
7.458
7.256
4.027
3.791
3.198
3.193
3.181
3.173
3.164
3.160
3.151
3.144
3.138
3.131
0.000
N
O
N2
O
O
O
1j
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.03
1.92
3.14
3.15
4.22
191.34
161.69
156.91
133.69
133.18
132.59
128.53
128.18
127.62
126.61
126.31
125.89
123.70
77.36
77.05
76.73
62.17
52.22
36.97
21.11
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.259
7.016
7.005
6.994
3.945
3.819
3.156
3.153
3.136
3.131
3.116
3.094
3.059
3.038
3.023
3.017
3.001
1.577
0.003
N
O
N2
O
S
O
O
1k
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.61
1.00
3.04
3.02
2.05
2.08
191.1536
161.6726
153.0964
139.2097
127.1174
127.0778
126.3997
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77.0272
76.7097
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21.9423
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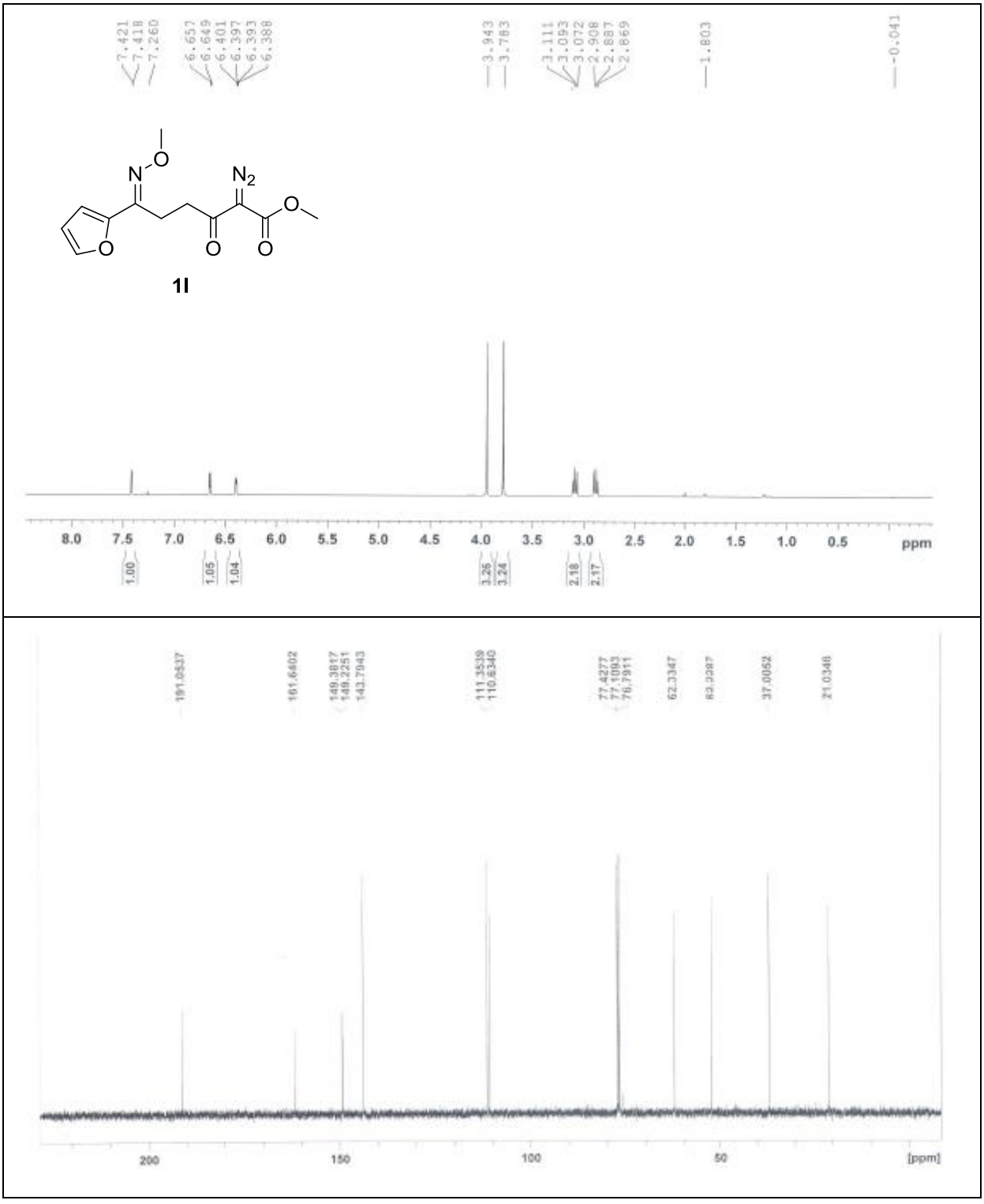
150
100
50
[ppm]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7.260
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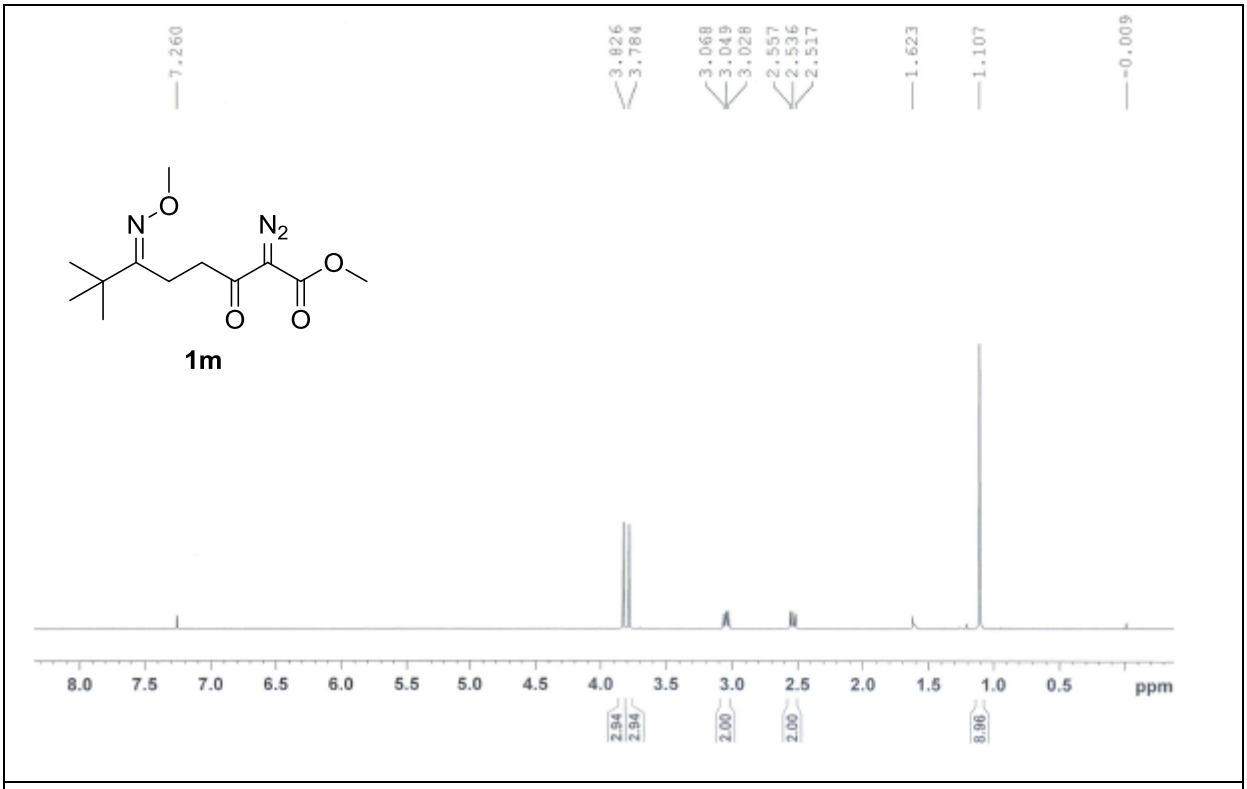
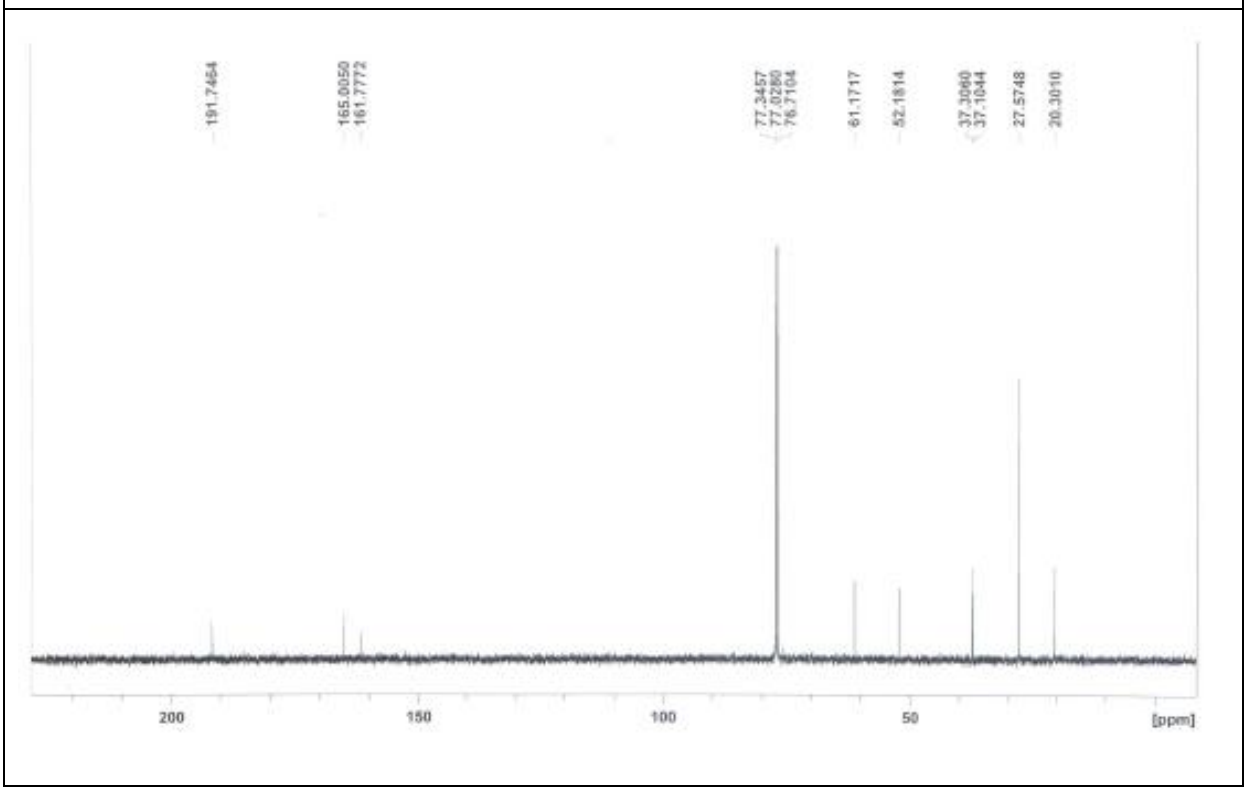
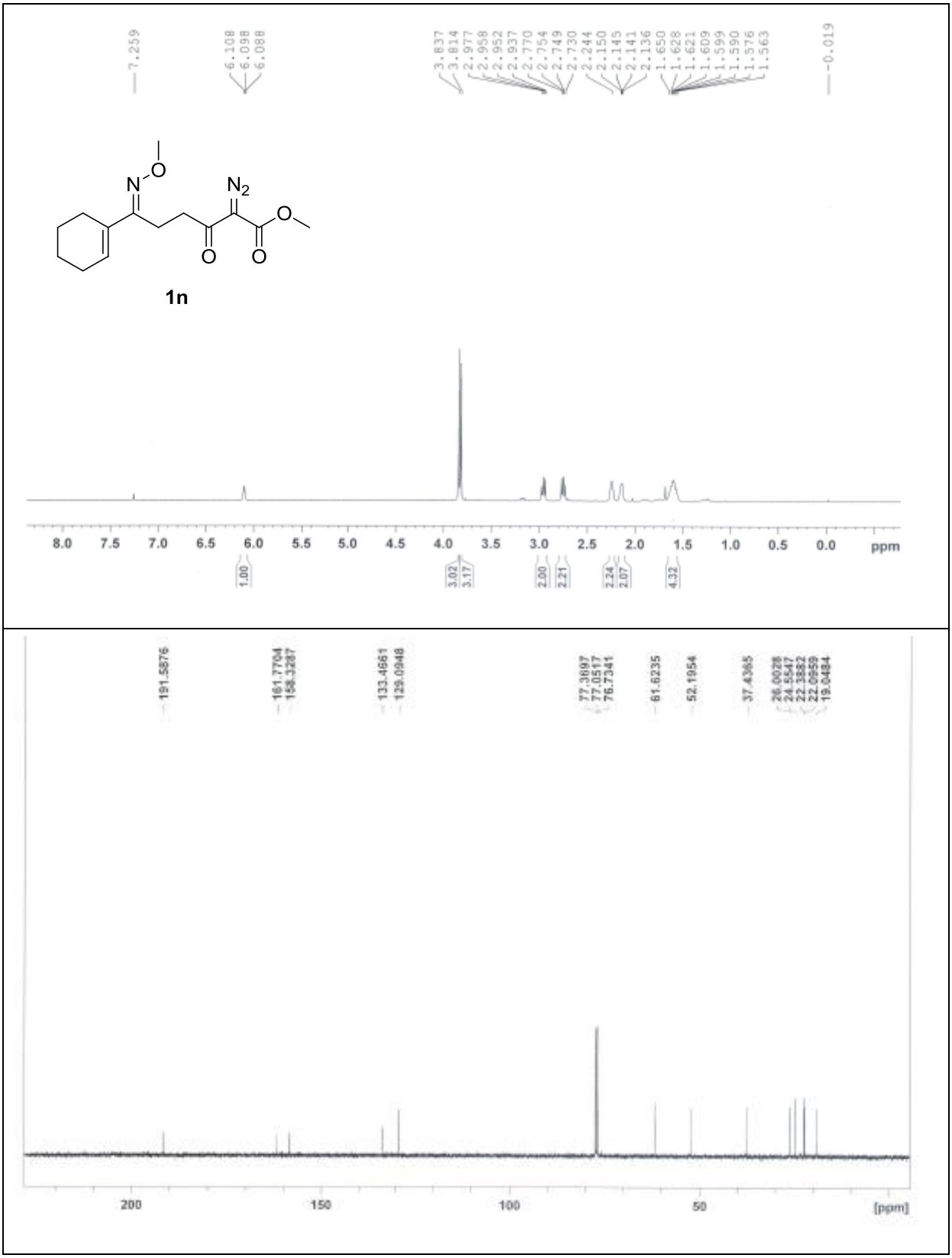
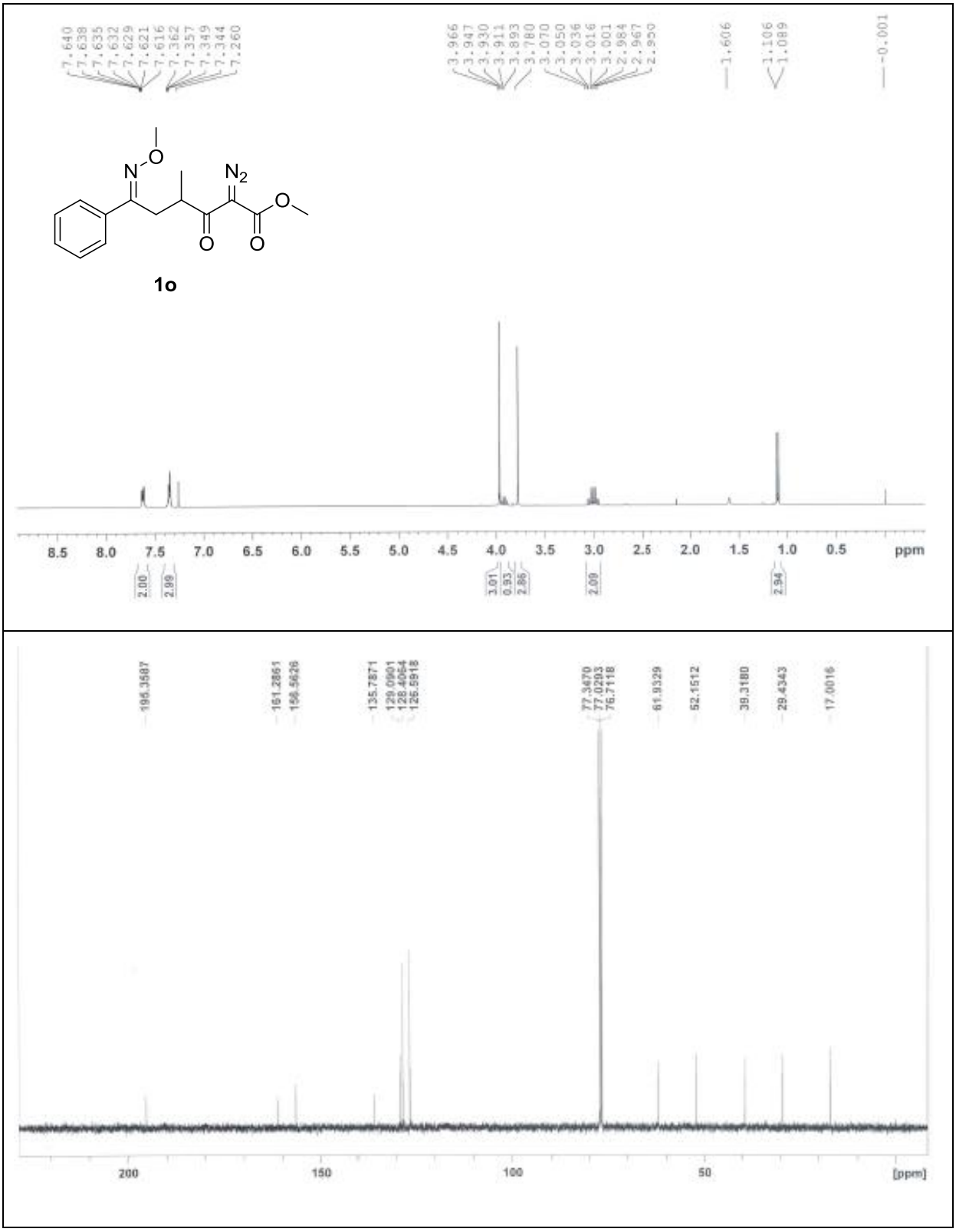
6.401
6.397
6.393
6.388
3.943
3.783
3.111
3.093
3.072
2.908
2.887
2.869
1.803
0.041
N
O
N2
O
O
O
O
1l
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.05
1.04
3.25
3.24
2.18
2.17
191.0437
161.6602
149.3817
149.2251
143.7943
111.3539
110.6340
77.4277
77.1093
76.7911
62.3347
53.9287
37.0052
21.0346
200
150
100
50
[ppm]


7.260
3.826
3.784
3.068
3.049
3.028
2.557
2.536
2.517
1.623
1.107
0.009
N
O
N2
O
O
O
1m
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
ppm
2.94
2.94
2.00
2.00
8.96


191.7464
165.0050
161.7772
77.3457
77.0280
76.7104
61.1717
52.1814
37.3060
37.1044
27.5748
20.3010
200
150
100
50
[ppm]


7.259
6.108
6.098
6.088
3.837
3.814
2.977
2.958
2.952
2.937
2.770
2.754
2.749
2.730
2.244
2.150
2.145
2.141
2.136
1.650
1.628
1.621
1.609
1.599
1.590
1.576
1.563
0.019
N
O
N2
O
O
O
1n
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
3.02
3.17
2.00
2.21
2.24
2.07
4.32
191.5876
161.7704
158.3287
133.4661
129.0948
77.3697
77.0517
76.7341
61.6235
52.1954
37.4365
26.0028
24.5547
22.3852
22.0959
19.0484
200
150
100
50
[ppm]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7.638
7.635
7.632
7.629
7.621
7.616
7.362
7.357
7.349
7.344
7.260
3.966
3.947
3.930
3.911
3.893
3.780
3.070
3.050
3.036
3.016
3.001
2.984
2.967
2.950
1.606
1.106
1.089
0.001
N
O
N2
O
O
O
1o
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
ppm
2.00
2.99
3.01
0.93
2.86
2.09
2.94
195.3587
161.2861
158.5626
135.7871
129.0901
128.4064
126.5918
77.3670
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61.9329
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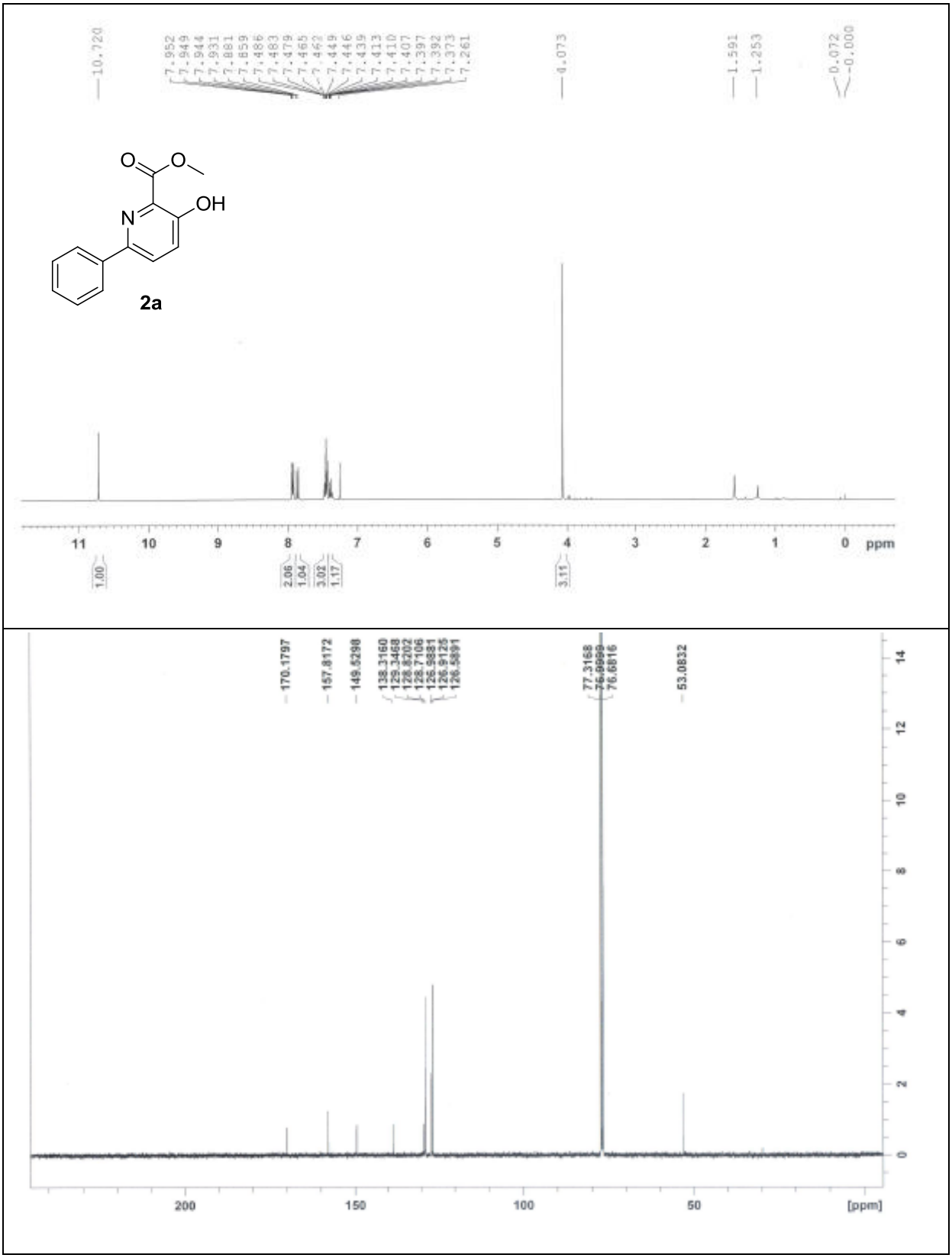
39.3180
29.4343
17.0016
200
150
100
50
[ppm]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7.949
7.944
7.931
7.881
7.859
7.486
7.483
7.479
7.465
7.462
7.449
7.446
7.439
7.413
7.410
7.407
7.397
7.392
7.373
7.261
0.073
1.591
1.253
0.072
0.000
O
O
OH
N
2a
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.06
1.04
3.02
1.17
3.11
170.1797
157.8172
149.5298
138.3160
129.3468
128.8202
128.7106
126.9831
126.9125
126.5891
77.3168
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53.0832
14
12
10
8
6
4
2
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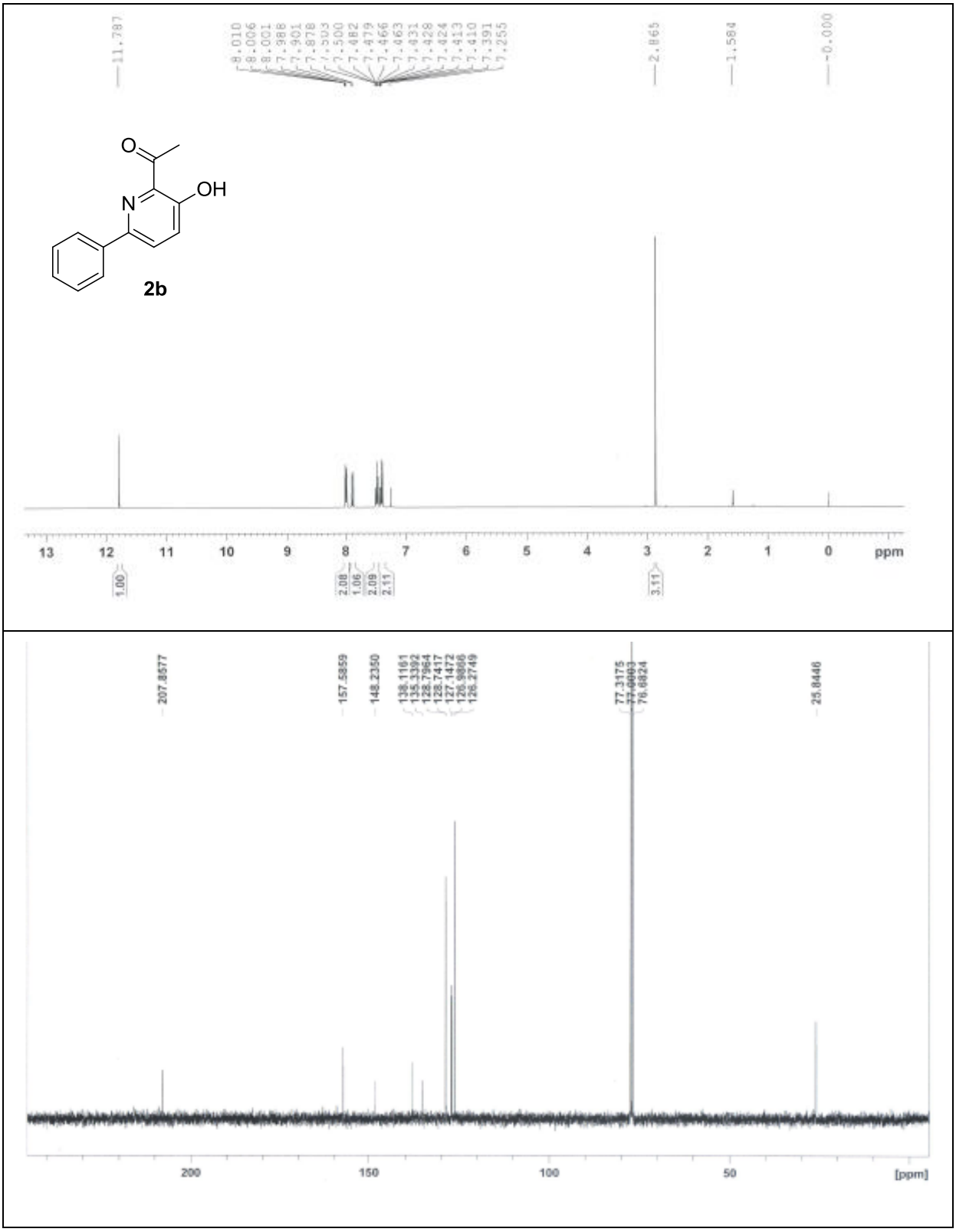
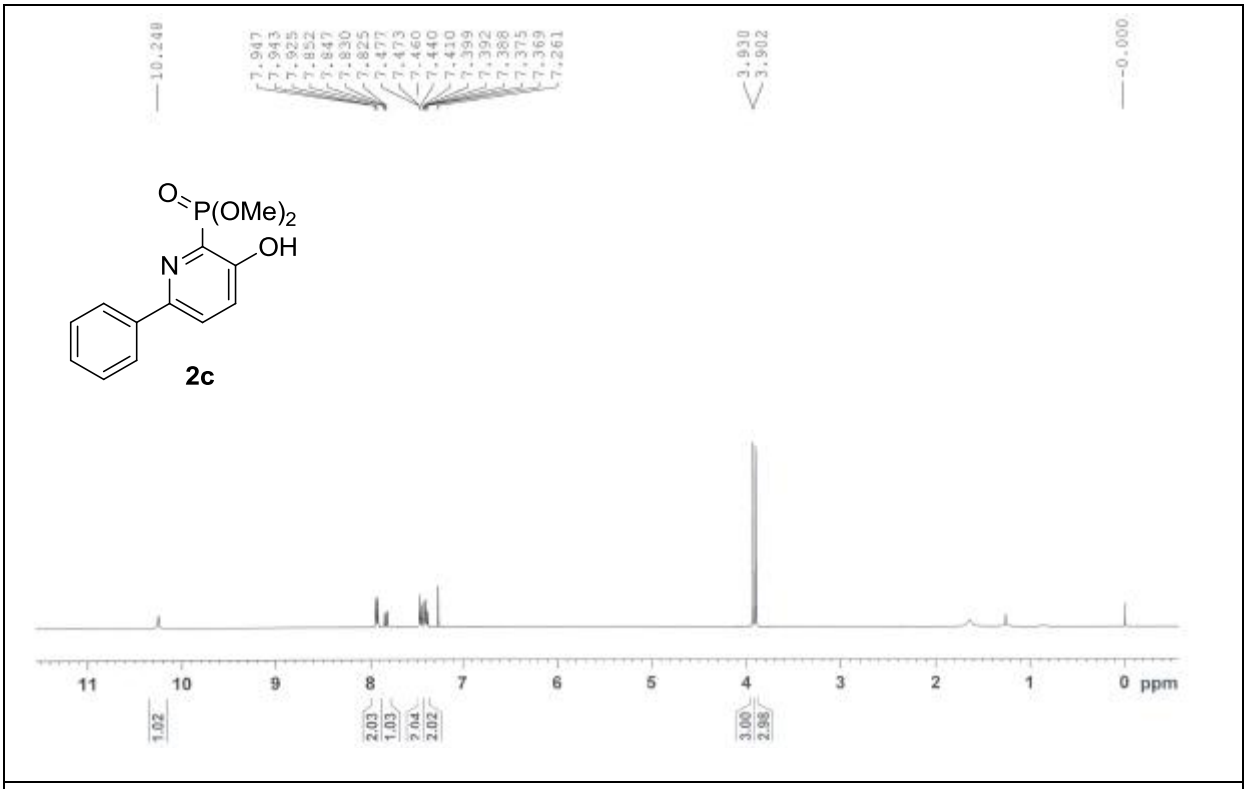
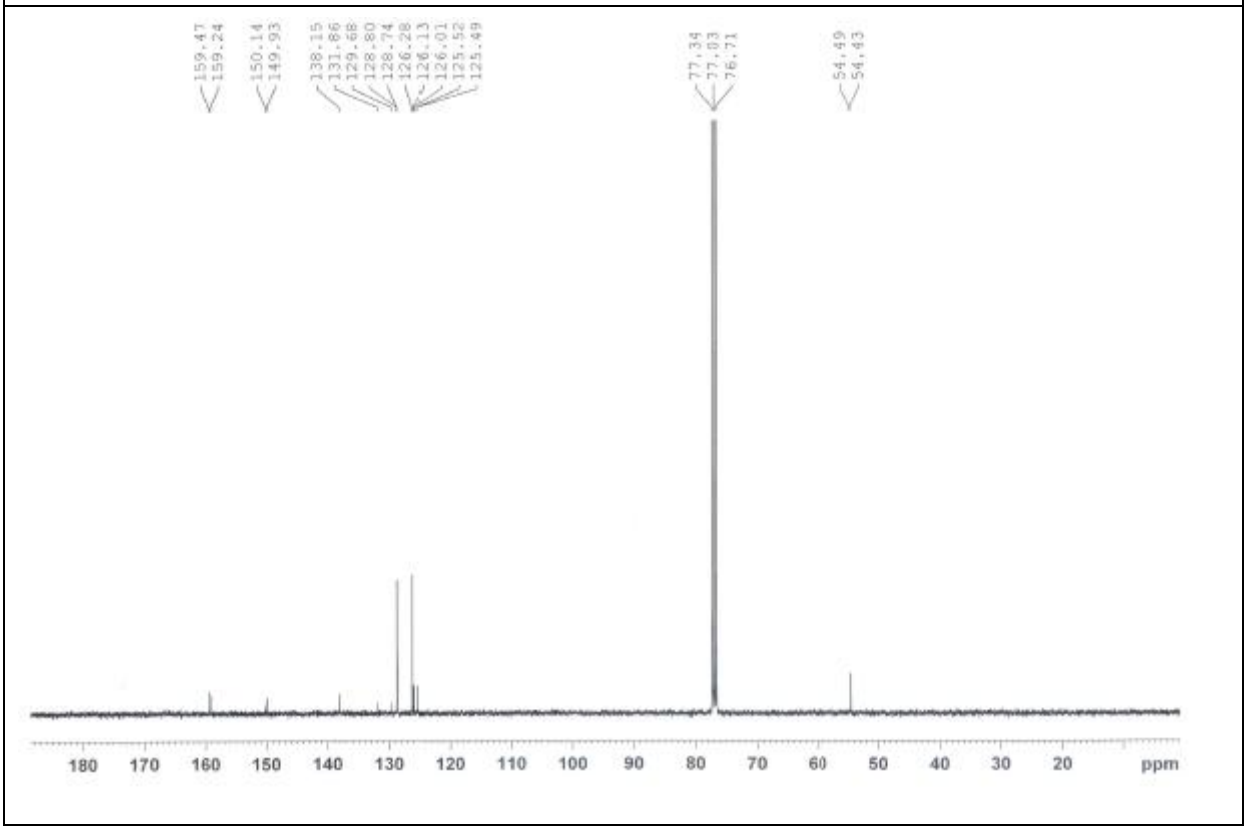
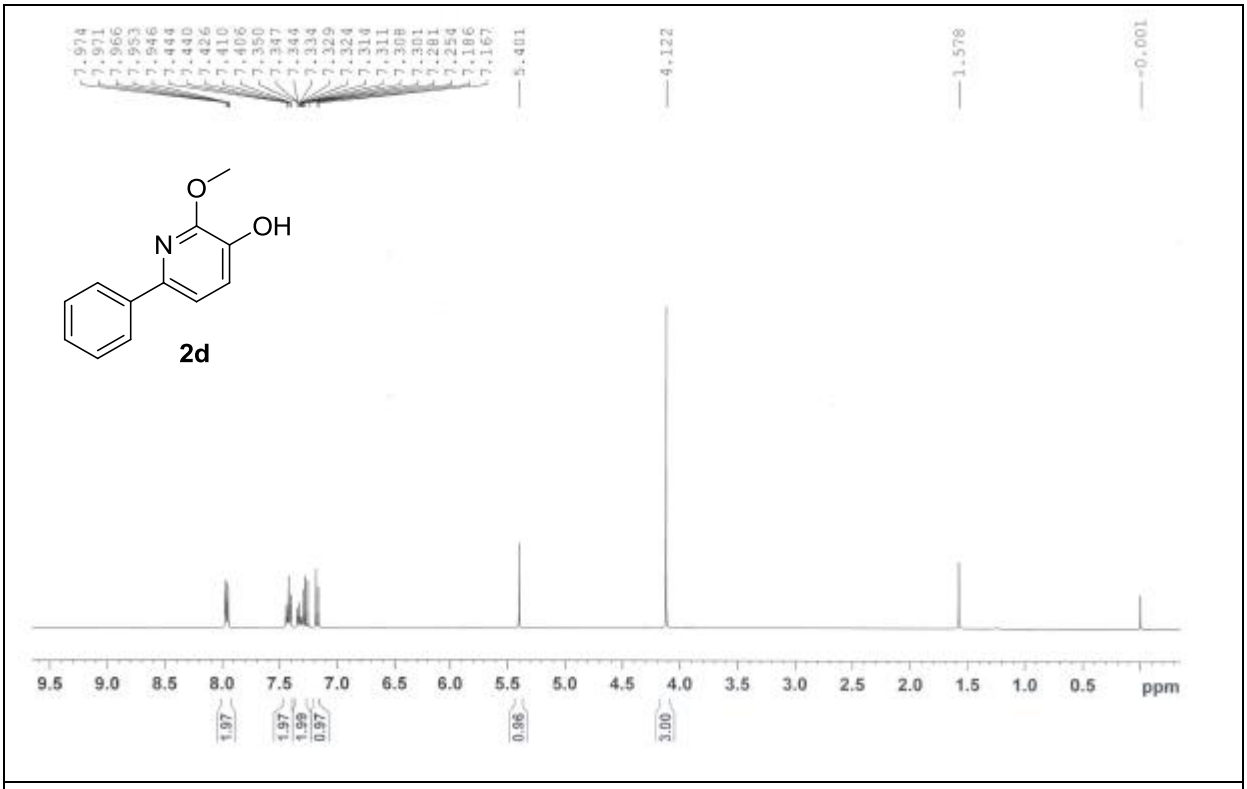
200
150
100
50
[ppm]




10.248
7.947
7.943
7.925
7.852
7.847
7.830
7.825
7.477
7.473
7.460
7.440
7.410
7.399
7.392
7.388
7.375
7.369
7.261
3.930
3.902
0.000
O
P(OMe)2
OH
N
2c
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.02
2.03
1.03
2.04
2.02
3.00
2.98


159.47
159.24
150.14
149.93
138.15
131.86
129.68
128.80
128.74
126.28
126.13
126.01
125.52
125.49
77.34
77.03
76.71
54.49
54.43
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.974
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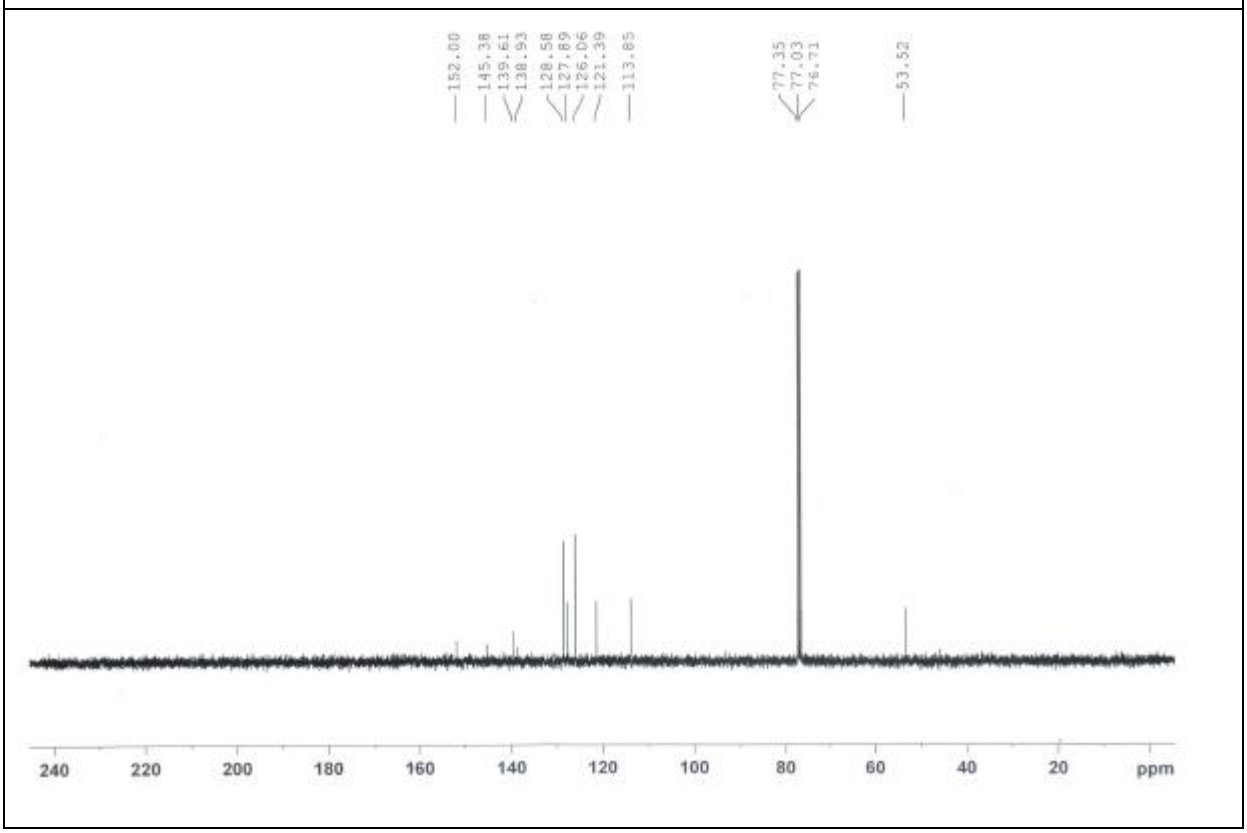
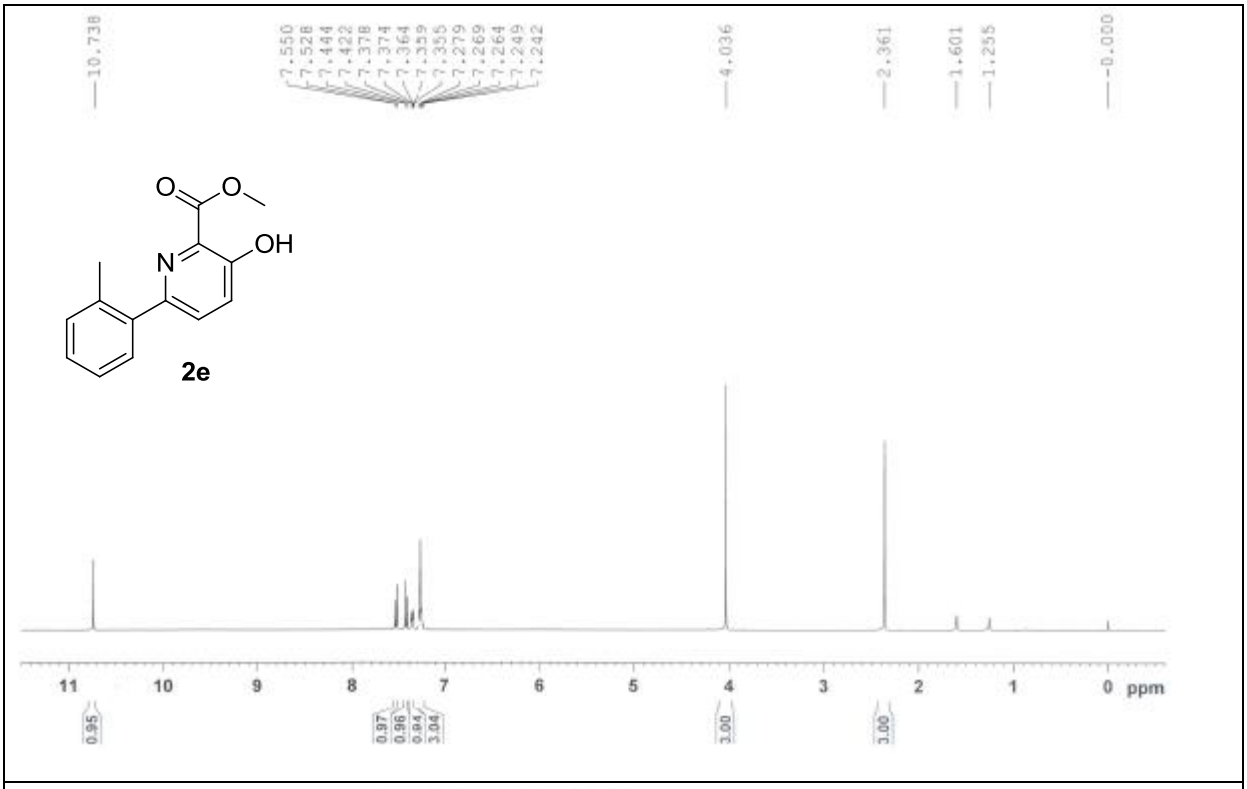
7.966
7.953
7.946
7.444
7.440
7.426
7.410
7.406
7.350
7.347
7.344
7.334
7.329
7.324
7.314
7.311
7.308
7.301
7.281
7.254
7.186
7.167
5.401
4.122
1.578
0.001
O
N
OH
2d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.97
1.97
1.99
0.97
0.96
3.00


152.00
145.38
139.61
138.93
128.58
127.89
126.06
121.39
113.85
77.35
77.03
76.71
53.52
240 220 200 180 160 140 120 100 80 60 40 20 ppm


10.738
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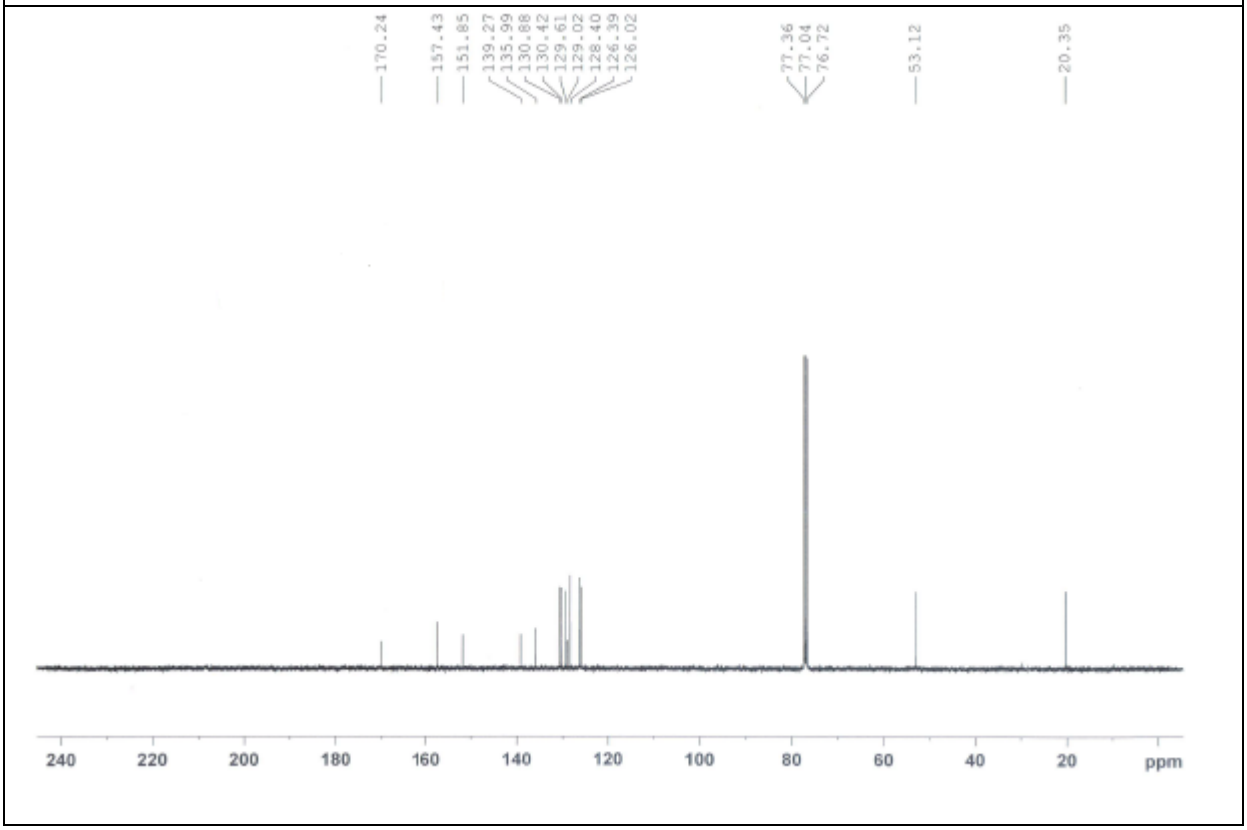
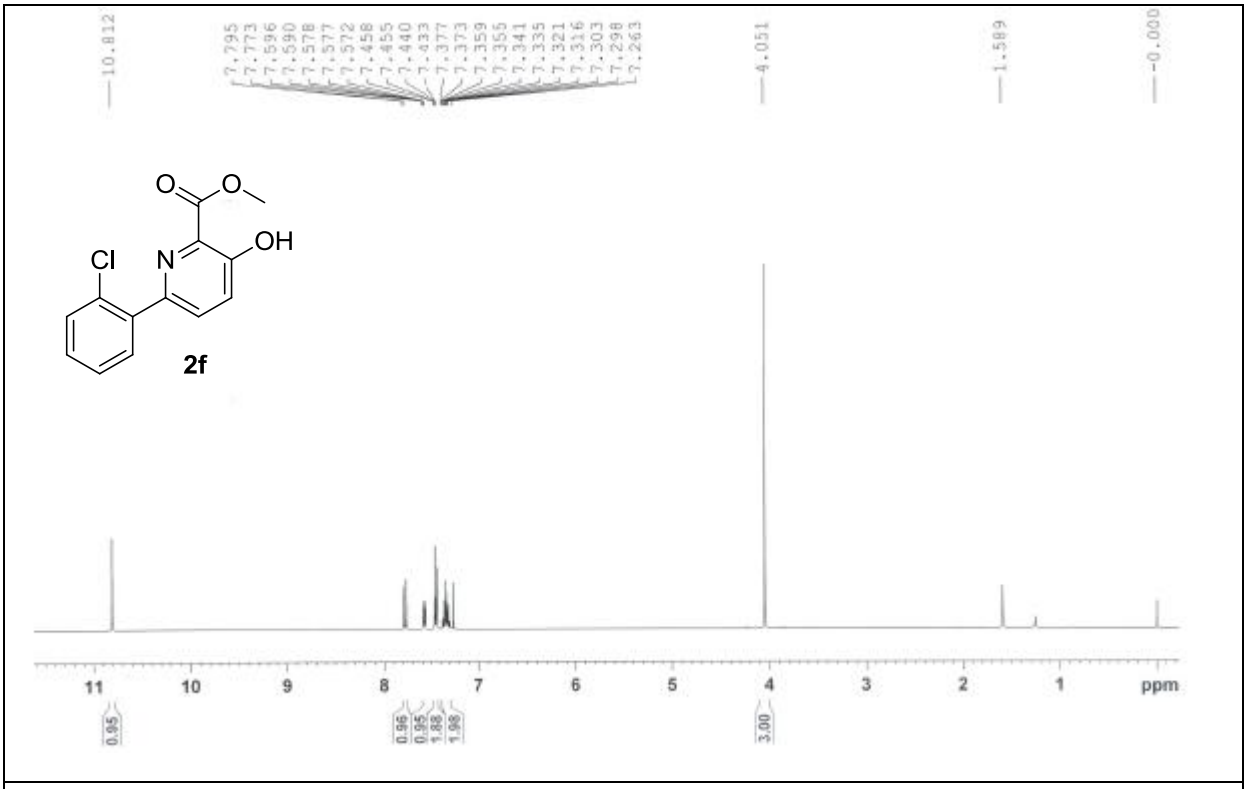
7.528
7.444
7.422
7.378
7.374
7.364
7.359
7.355
7.279
7.269
7.264
7.249
7.242
4.036
2.361
1.601
1.255
0.000
O
O
OH
N
2e
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.95
0.97
0.96
0.84
3.04
3.00
3.00


170.24
157.43
151.85
139.27
135.99
130.88
130.42
129.61
129.02
128.40
126.39
126.02
77.36
77.04
76.72
53.12
20.35
240
220
200
180
160
140
120
100
80
60
40
20
ppm


10.812
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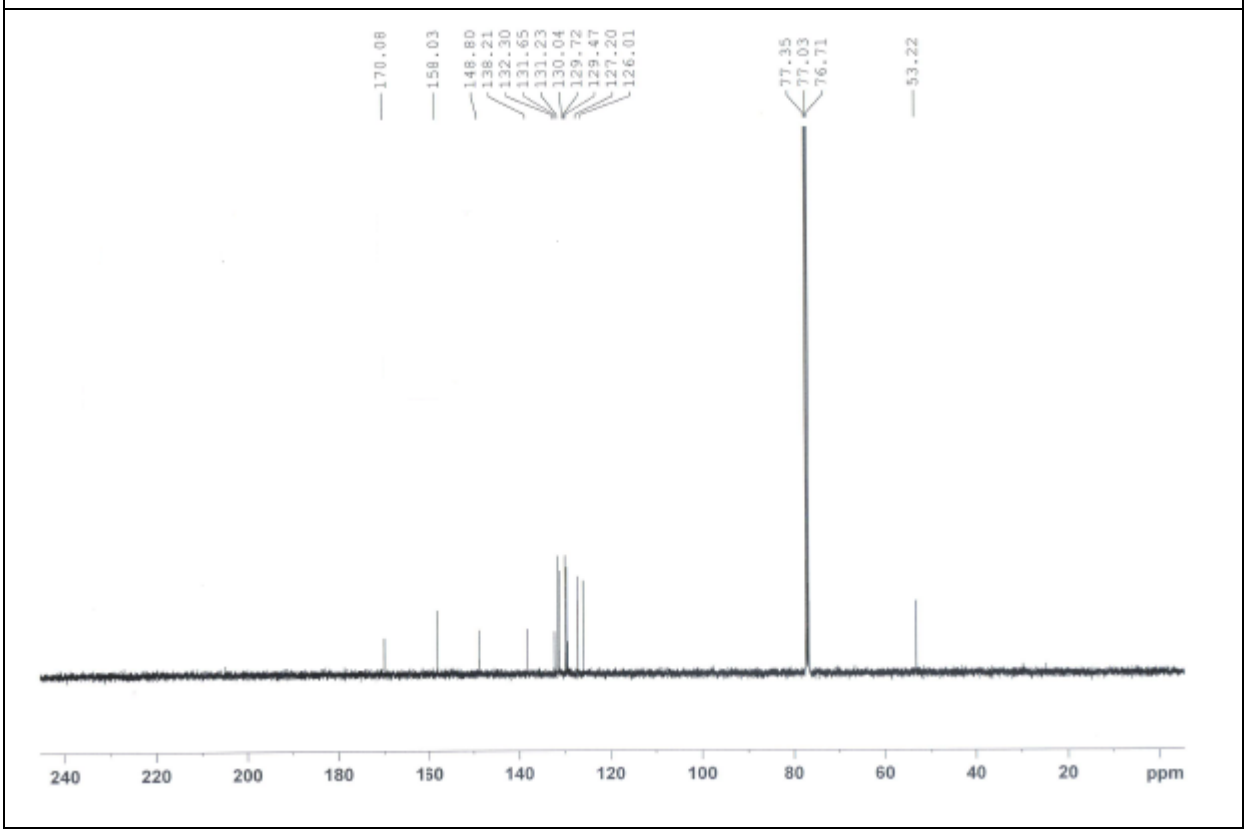
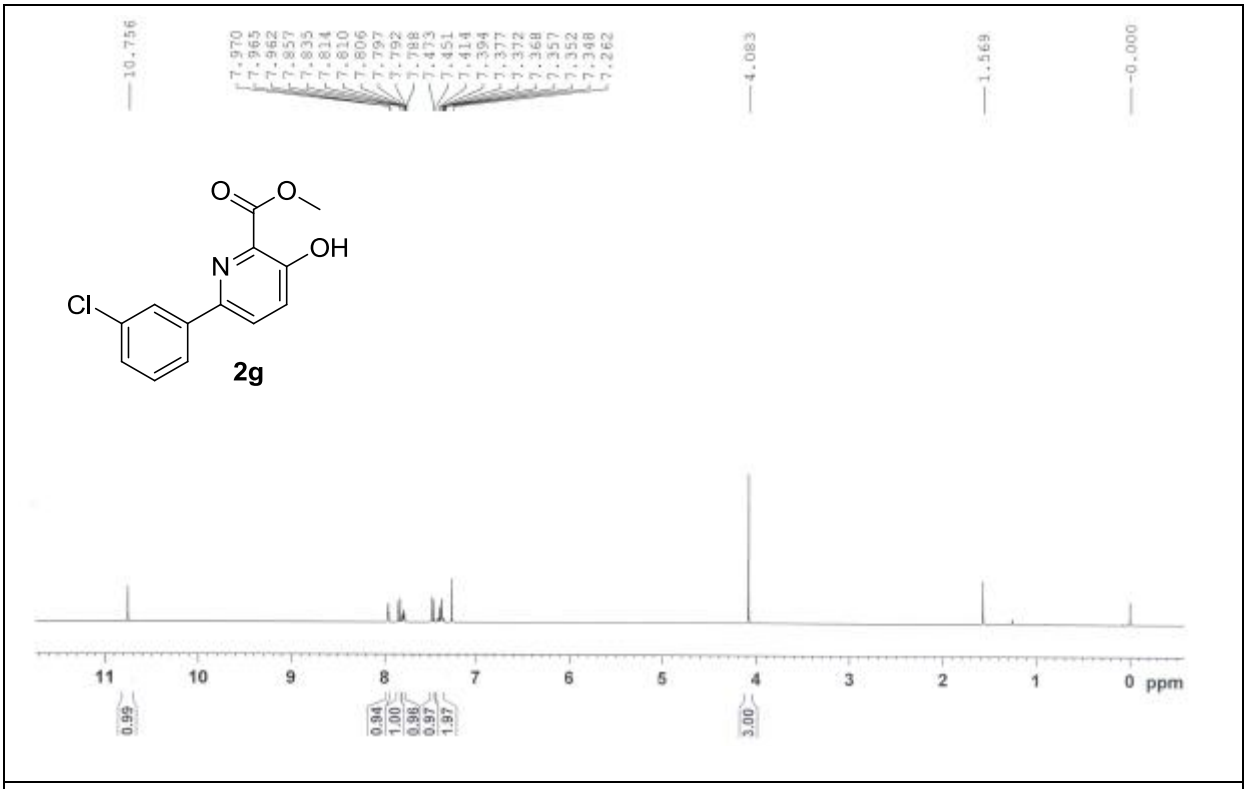
7.596
7.590
7.578
7.577
7.572
7.458
7.455
7.440
7.433
7.377
7.373
7.359
7.355
7.341
7.335
7.321
7.316
7.303
7.298
7.263
4.051
1.589
0.000
O
O
OH
Cl
N
2f
11
10
9
8
7
6
5
4
3
2
1
ppm
0.95
0.96
0.95
1.88
1.98
3.00


170.08
158.03
148.80
138.21
132.30
131.65
131.23
130.04
129.72
129.47
127.20
126.01
77.35
77.03
76.71
53.22
240
220
200
180
150
140
120
100
80
60
40
20
ppm


10.756
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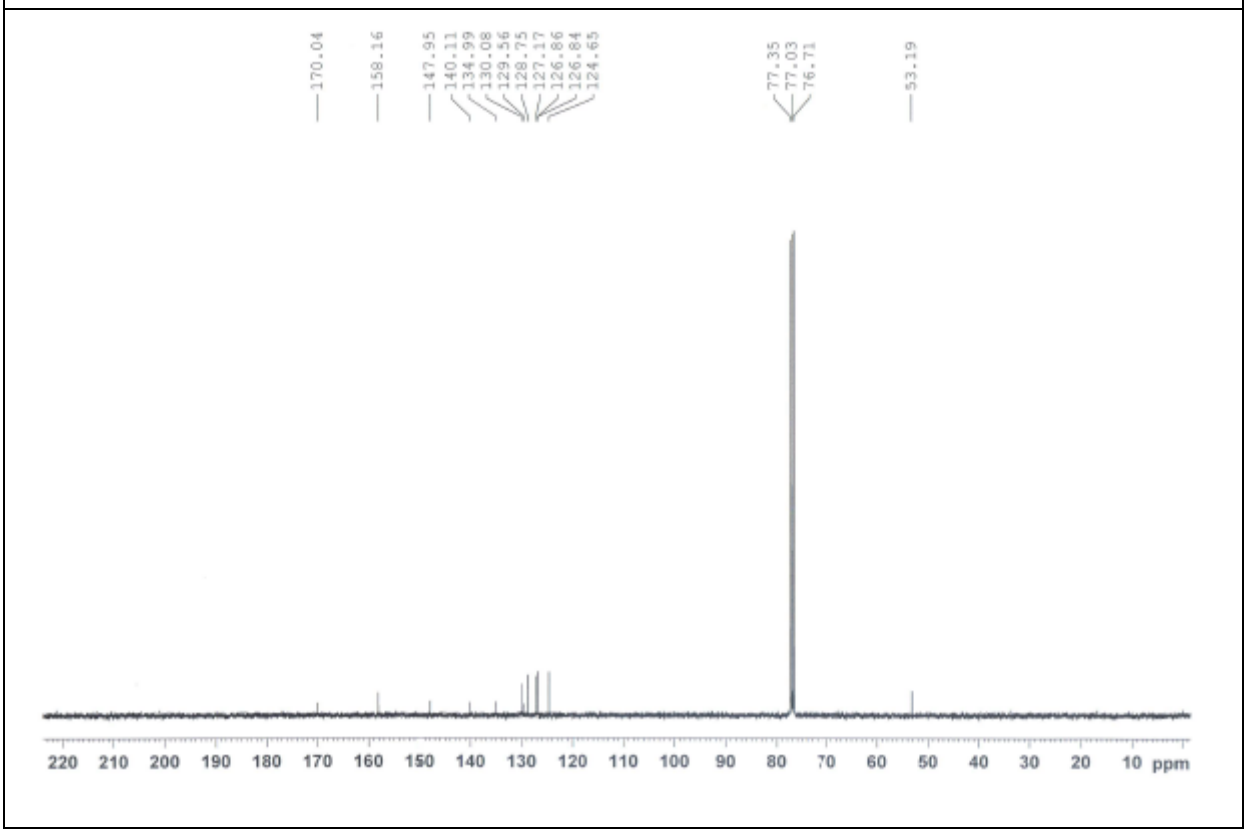
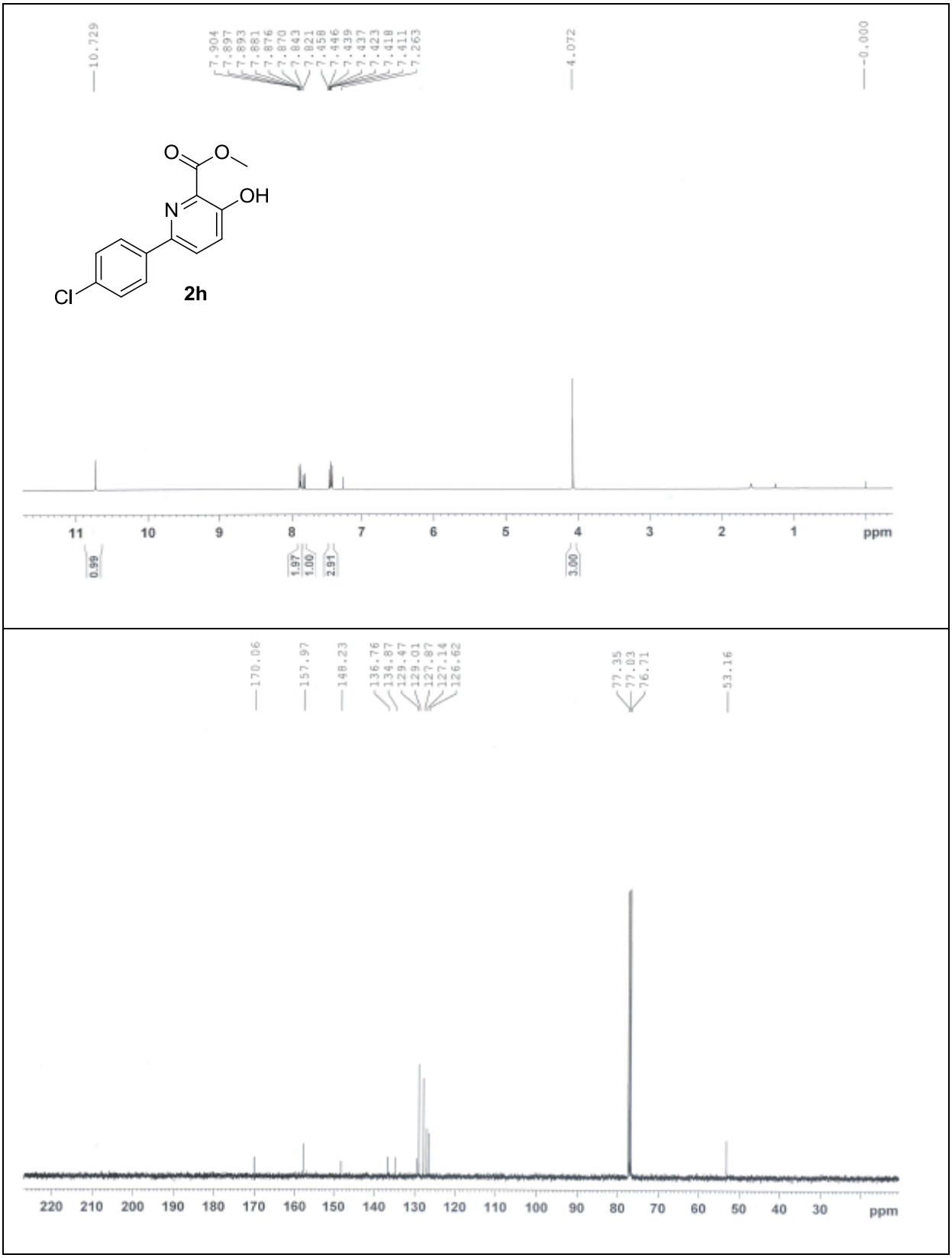
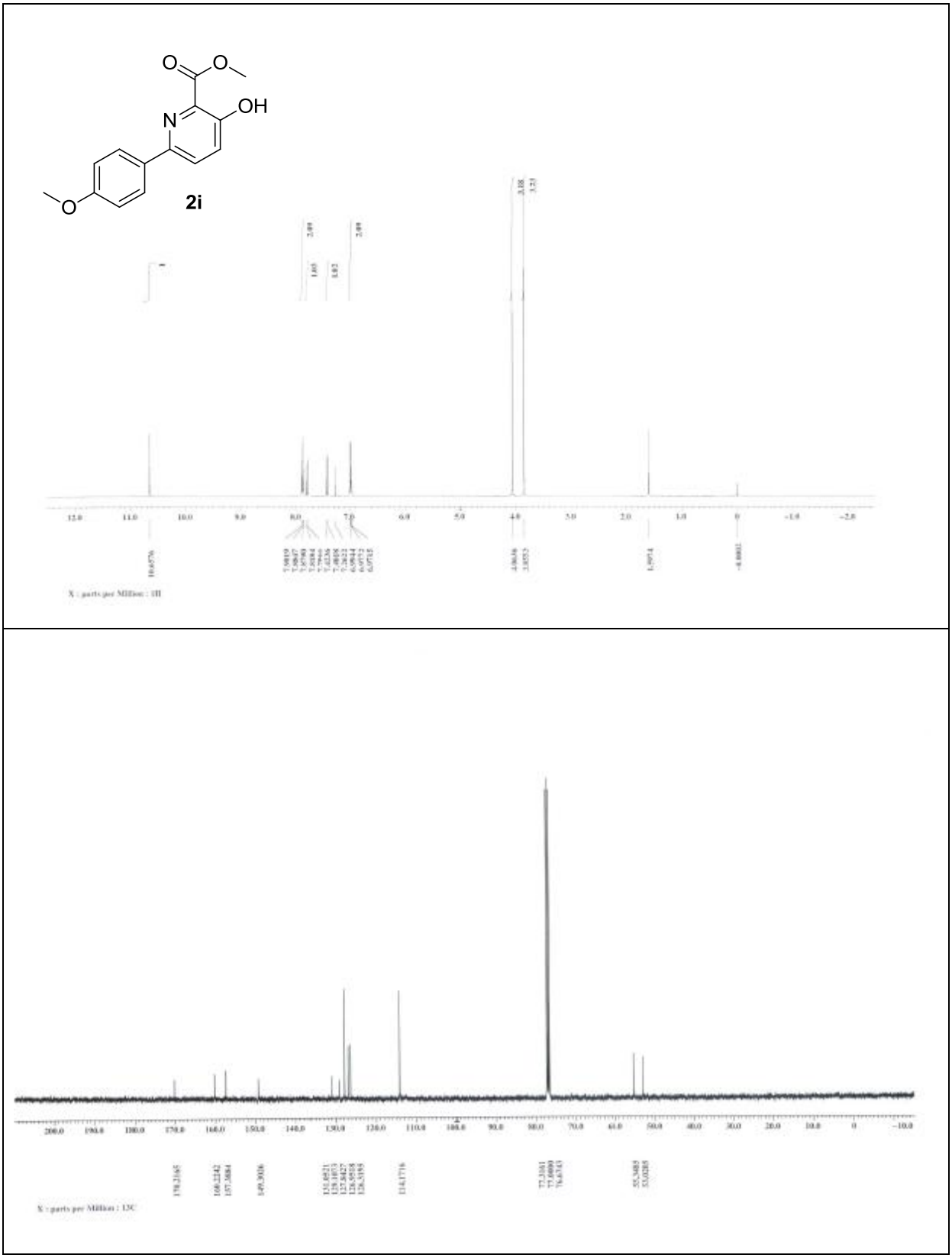
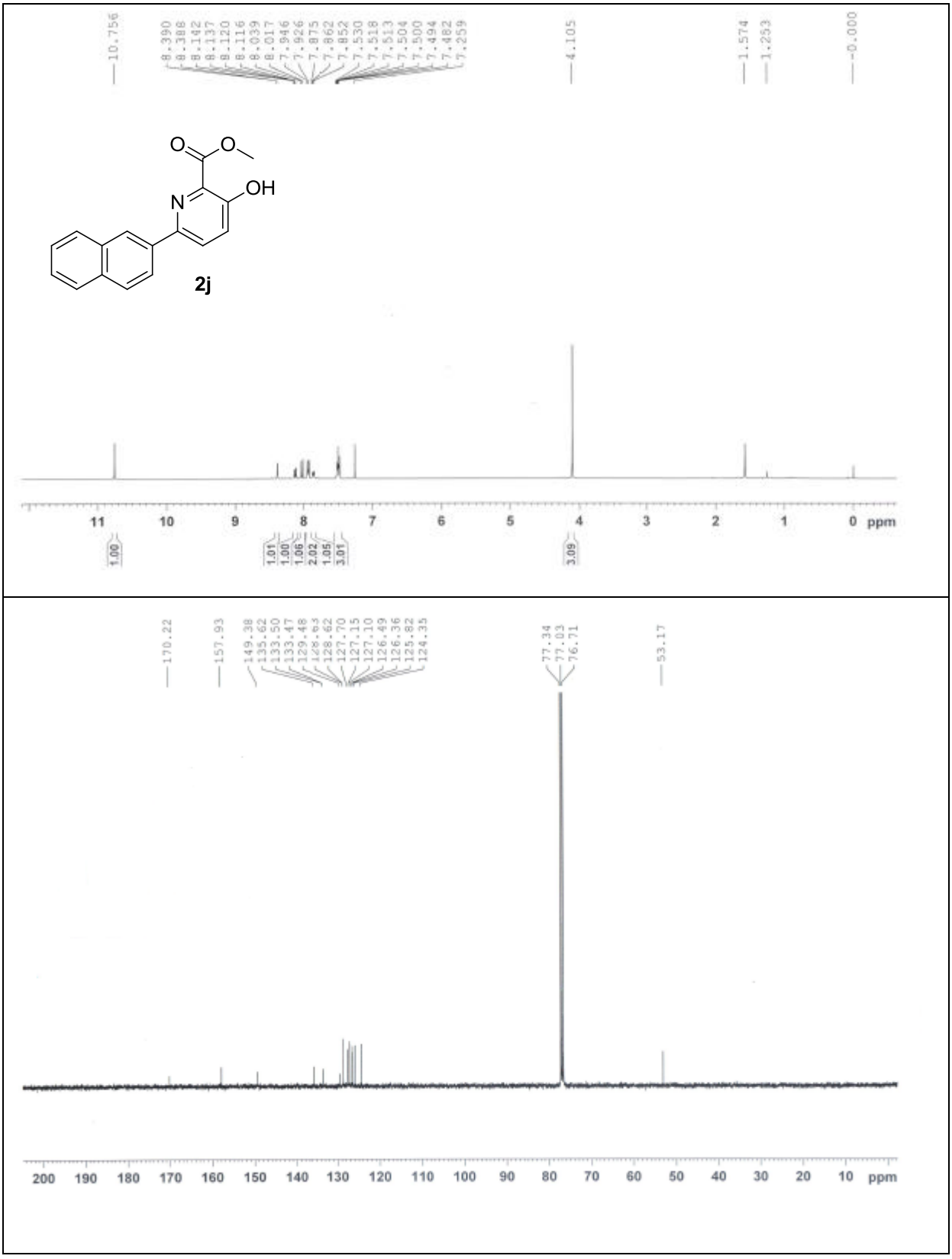
7.965
7.962
7.857
7.835
7.814
7.810
7.806
7.797
7.792
7.788
7.473
7.451
7.414
7.394
7.377
7.372
7.368
7.357
7.352
7.348
7.262
4.083
1.569
0.000
O
O
OH
N
Cl
2g
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.99
0.94
1.00
0.98
0.97
1.97
3.00


170.04
158.16
147.95
140.11
134.99
130.08
129.56
128.75
127.17
126.86
126.84
124.65
77.35
77.03
76.71
53.19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


10.729
7.904
7.897
7.893
7.881
7.876
7.870
7.863
7.821
7.458
7.446
7.439
7.437
7.423
7.418
7.411
7.263
4.072
0.000
O
O
OH
N
Cl
2h
11
10
9
8
7
6
5
4
3
2
1
ppm
0.99
1.97
1.00
2.91
3.00
170.06
157.97
148.23
136.76
134.87
129.47
129.01
127.87
127.14
126.62
77.35
77.03
76.71
53.16
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


O
O
OH
N
O
2i


10.756
8.390
8.388
8.142
8.137
8.120
8.116
8.039
8.017
7.946
7.926
7.875
7.862
7.852
7.530
7.518
7.513
7.504
7.500
7.494
7.482
7.259
4.105
1.574
1.253
0.000
O
O
OH
N
2j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.01
1.00
1.06
2.02
1.05
3.01
3.09
170.22
157.93
149.38
135.62
133.50
133.47
129.48
128.63
128.62
127.70
127.15
127.10
126.49
126.36
125.82
124.35
77.34
77.03
76.71
53.17
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110
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70
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30
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10
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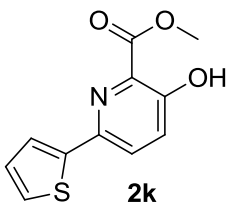

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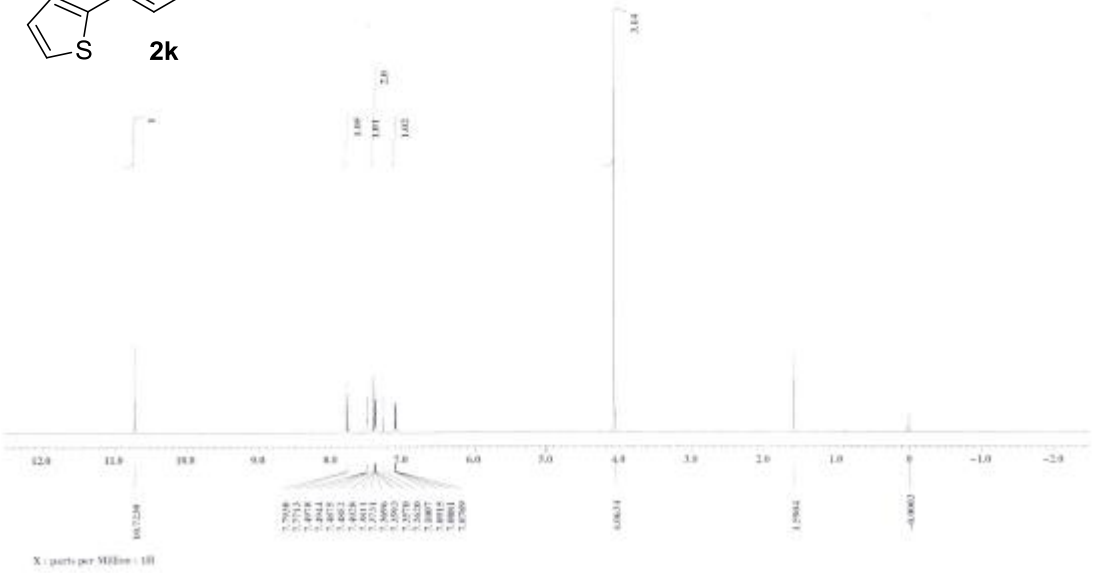

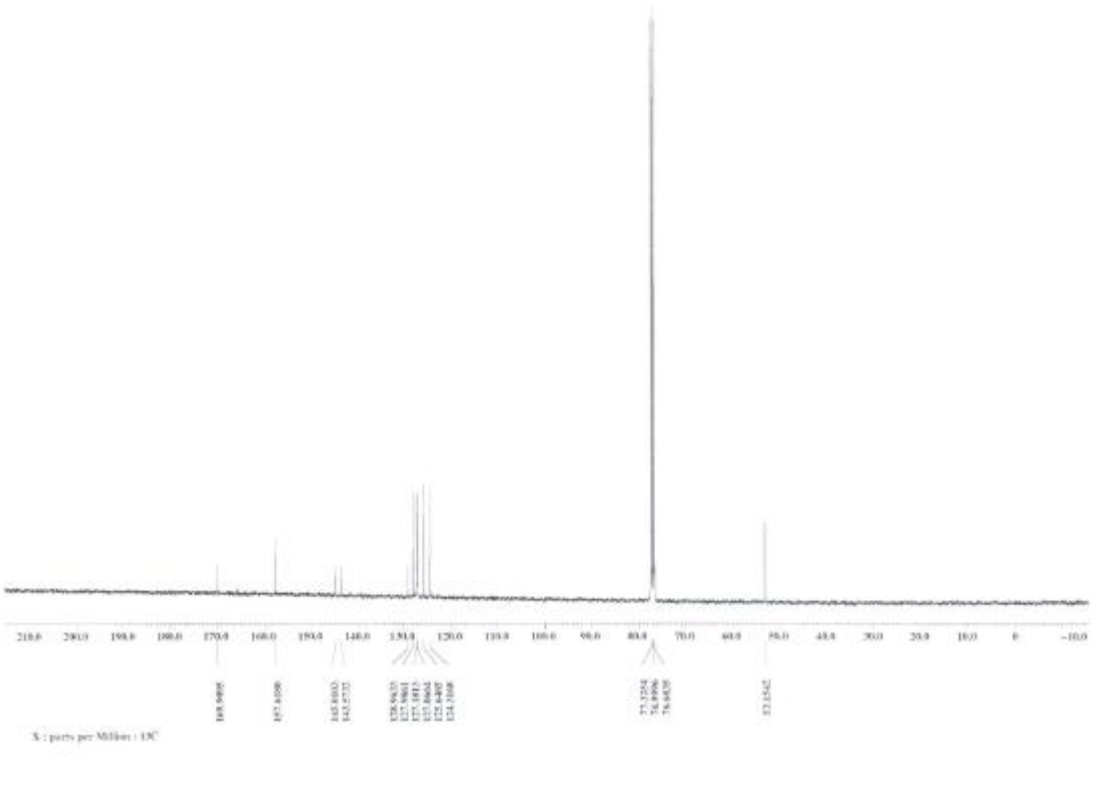

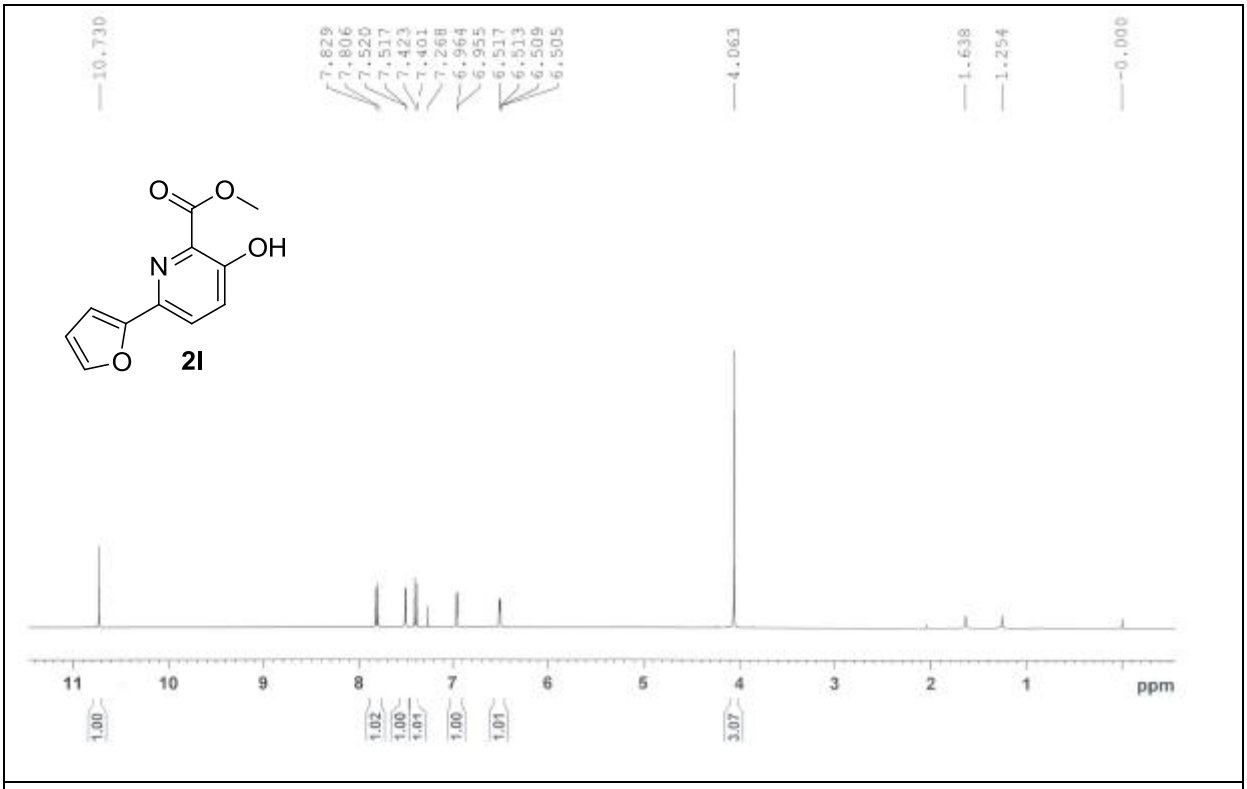
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6.955
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6.509
6.505
4.063
1.638
1.254
0.000
O
O
OH
N
O
2l
11
10
9
8
7
6
5
4
3
2
1
ppm
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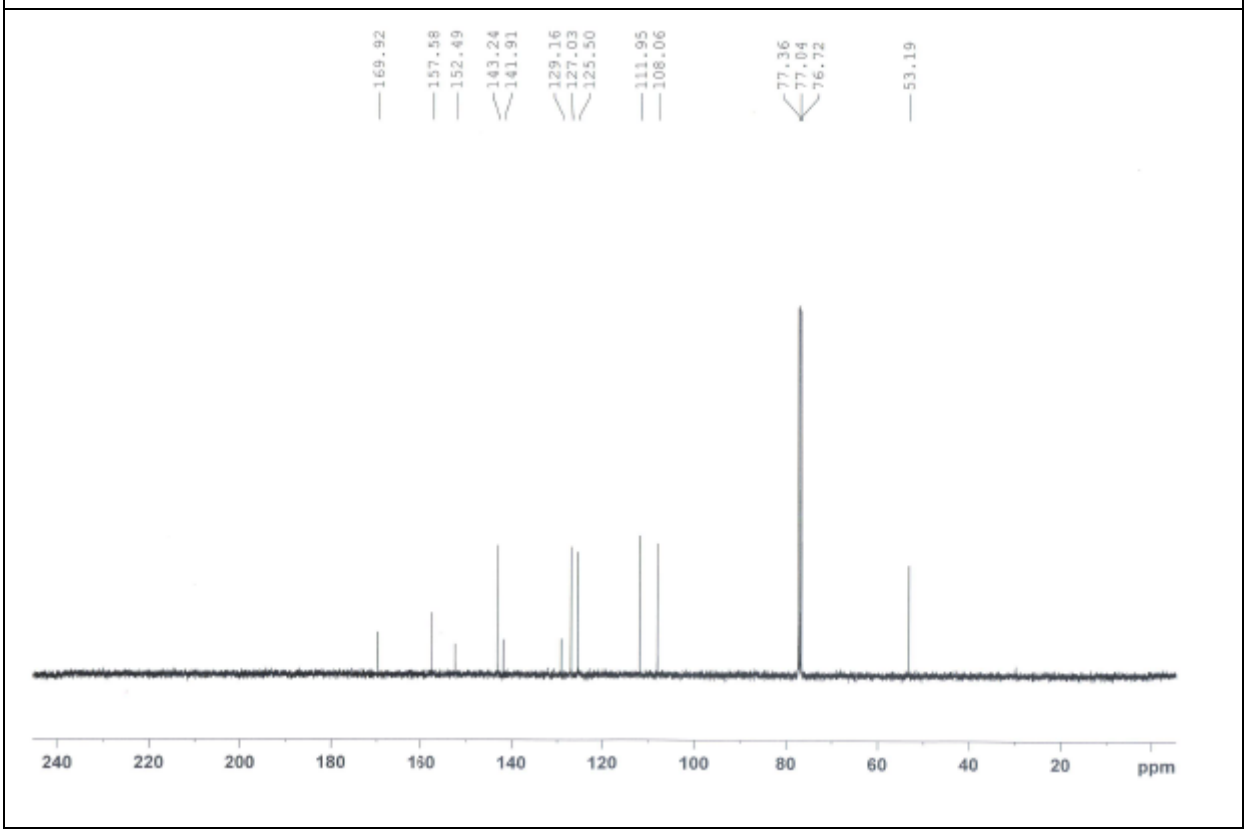
1.02
1.00
1.01
1.00
1.01
3.07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129.16
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125.50
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108.06
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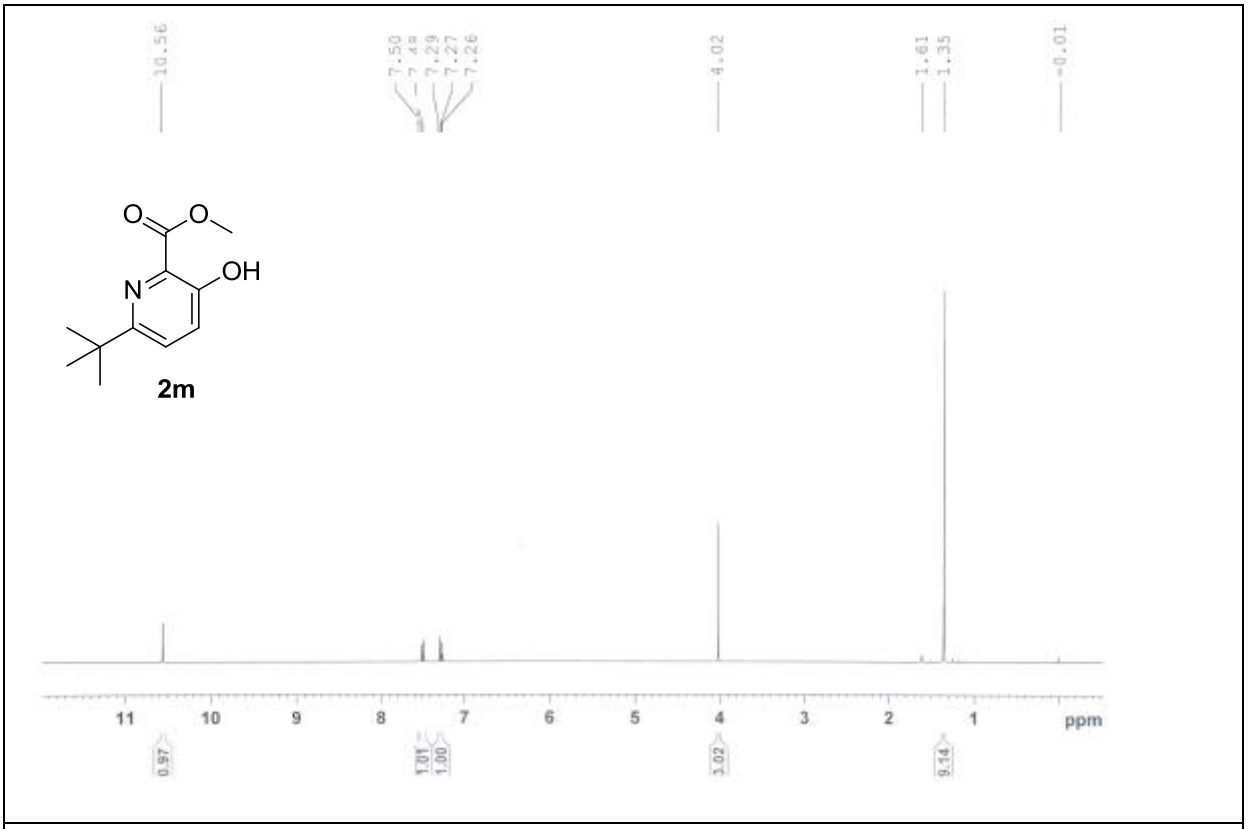
76.72
53.19
240
220
200
180
160
140
120
100
80
60
40
20
ppm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0.01
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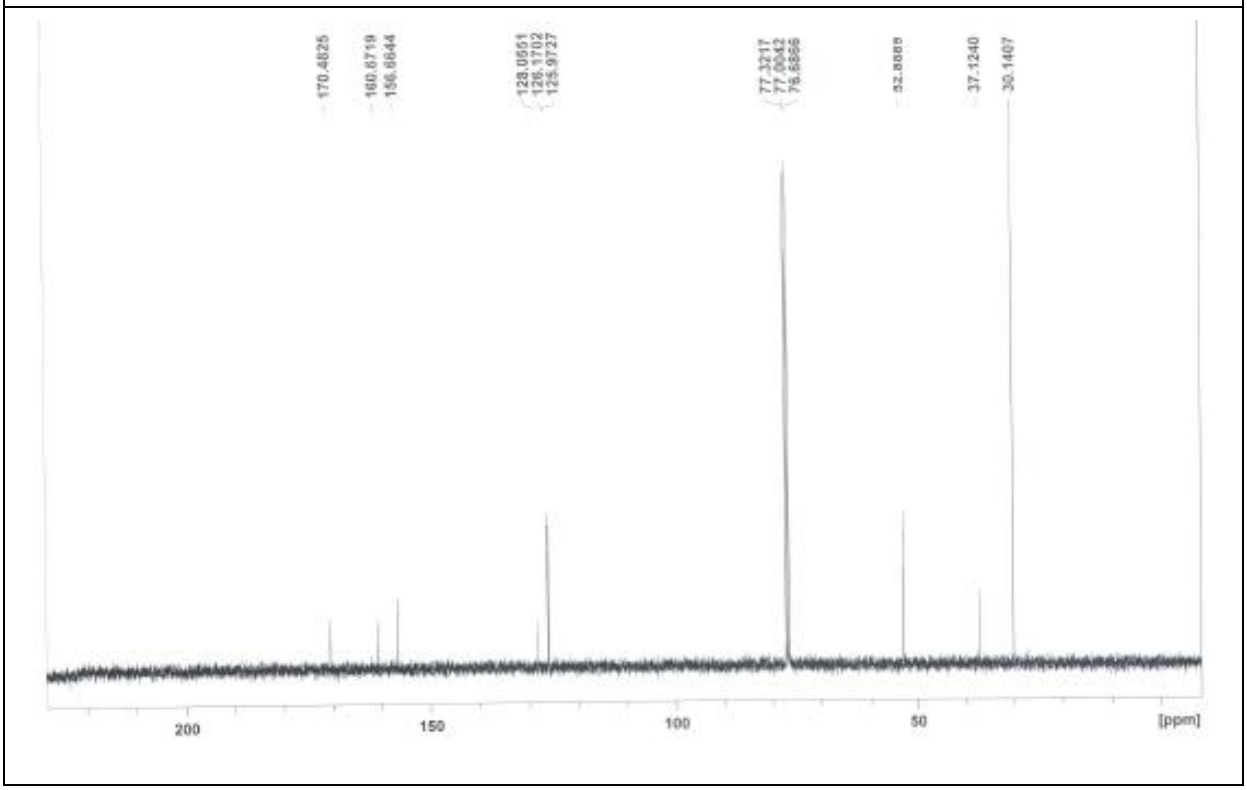
O
OH
N
2m
11
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.01
1.00
3.02
9.14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30.1407
200
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100
50
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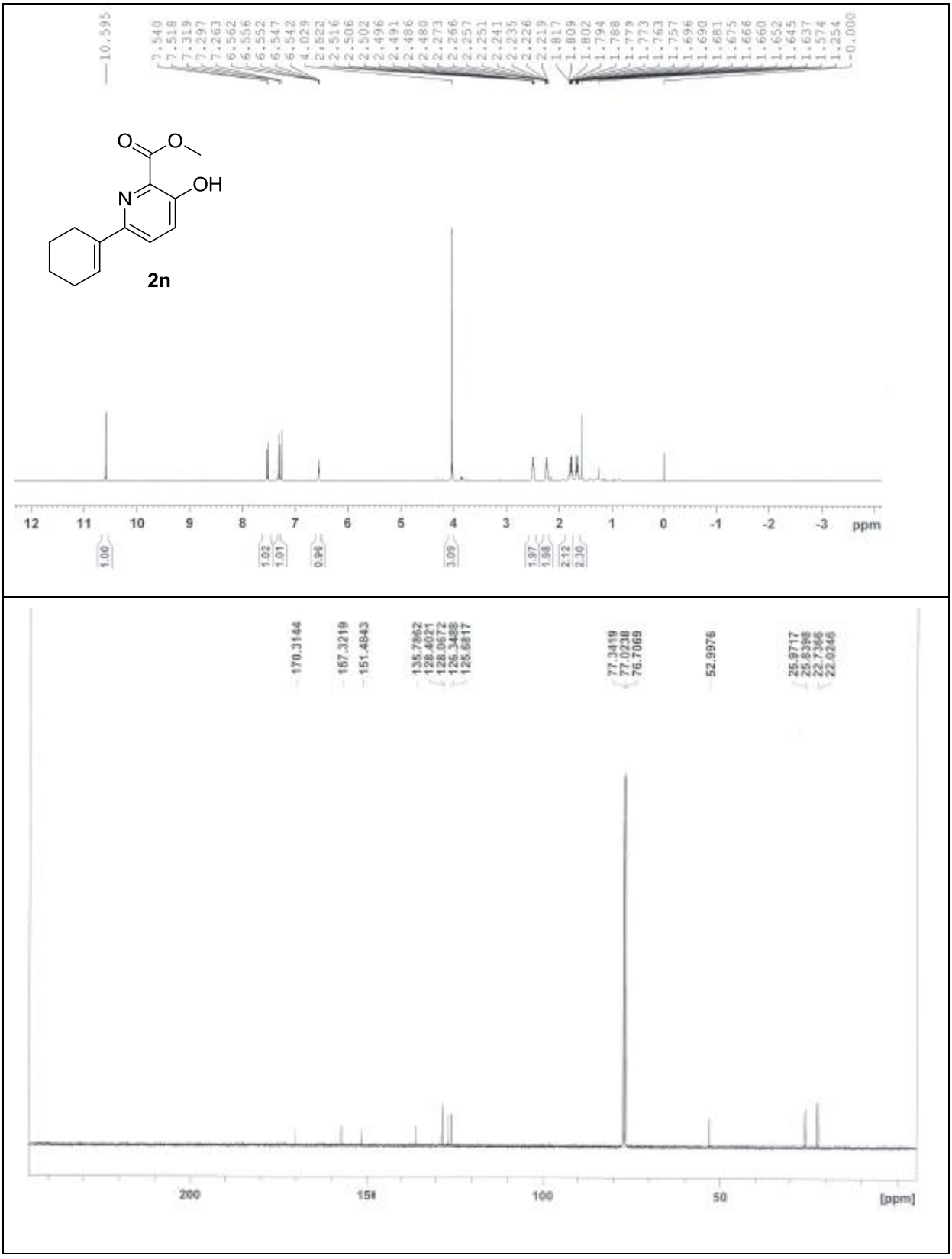
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6.547
6.542
4.029
2.522
2.516
2.506
2.502
2.496
2.491
2.486
2.480
2.273
2.266
2.257
2.251
2.241
2.235
2.226
2.219
1.817
1.809
1.802
1.794
1.788
1.779
1.773
1.763
1.757
1.696
1.690
1.681
1.675
1.666
1.660
1.652
1.645
1.637
1.574
1.254
0.000
O
O
OH
N
2n
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
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1.02
1.01
0.96
3.09
1.97
1.98
2.12
2.30
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135.7862
128.4021
128.0672
126.3488
125.6817
77.3419
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100
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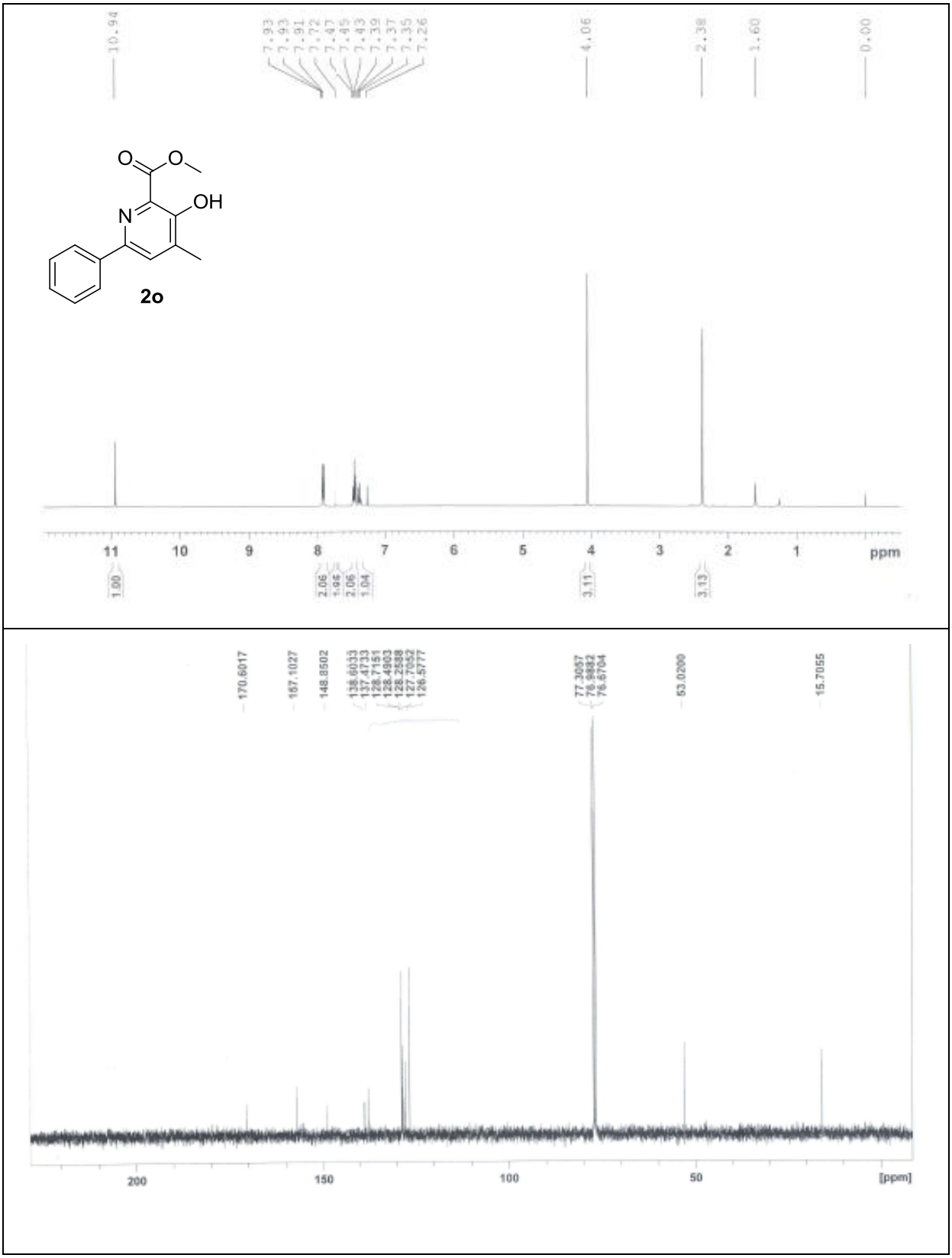
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7.91
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7.47
7.45
7.43
7.39
7.37
7.35
7.26
4.06
2.38
1.60
0.00
O
O
OH
N
2o
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.06
1.96
2.06
1.04
3.11
3.13
170.6017
157.1027
148.8502
138.6033
137.4733
128.7151
128.4903
128.2588
127.7052
126.5777
77.3057
76.9832
76.6704
53.0200
15.7055
200
150
100
50
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